Supplementary information

Surface modified novel magnetically tuned halloysite functionalized sulfonic acid: Synthesis, characterization and catalytic activity

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^{1}H and ^{13}C data of some representative compounds

N,N′-(4-Chlorophenylmethylene)dibenzamide **(Figure S2, table 2, entry 1d):** White solid**,** ^{1}H NMR (400 MHz, DMSO) δ 9.10 (d, *J* = 7.6 Hz, 2H, NH, exchangeable with D_2O), 7.92 (d, *J* = 7.4 Hz, 4H, aromatic H), 7.57 (t, *J* = 7.3 Hz, 2H, aromatic H), 7.48 (dd, *J* = 18.4, 8.1 Hz, 8H, aromatic H), 6.99 (t, *J* = 7.4 Hz, 1H, CH).

N,N′-(4-Fluorophenylmethylene)dibenzamide **(Figure S3, table 2, entry 1f):** White solid, ^{1}H NMR (600 MHz,) δ 9.00 (d, *J* = 7.6 Hz, 2H, exchangeable with D_2O), 7.89 – 7.86 (m, 4H, aromatic H), 7.54 – 7.51 (m, 2H, aromatic H), 7.48 – 7.43 (m, 6H, aromatic H), 7.20 – 7.15 (m, 2H, aromatic H), 6.97 (t, *J* = 7.6 Hz, 1H, CH).

N,N′-(2-Nitrophenylmethylene)dibenzamide **(Figure S4, S5, table 2, entry 1g**): White solid, ^{1}H NMR (400 MHz, DMSO) δ 9.21 (d, *J* = 6.9 Hz, 2H, NH, exchangeable with D_2O), 8.00 (d, *J* = 7.9 Hz, 1H, aromatic H), 7.91 (d, *J* = 7.4 Hz, 4H, aromatic H), 7.84 – 7.73 (m, 2H, aromatic H), 7.62 (t, *J* = 7.1 Hz, 1H, aromatic H), 7.56 (t, *J* = 7.3 Hz, 2H, aromatic H), 7.48 (t, *J* = 7.5 Hz, 4H, aromatic H), 7.41 (t, *J* = 6.9 Hz, 1H, CH). ^{13}C NMR (101 MHz, DMSO) δ 166.46, 148.98, 134.23, 134.03, 132.09, 129.72, 129.29, 128.69, 128.17, 124.89, 56.56.

N,N′-(3-Nitrophenylmethylene)dibenzamide **(Figure S6, S7, table 2, entry 1h):** White solid, ^{1}H NMR (400 MHz, DMSO) δ 9.27 (d, *J* = 7.3 Hz, 2H, NH, exchangeable with D_2O), 8.34 (s, 1H, aromatic H), 8.22 (d, *J* = 8.1 Hz, 1H, aromatic H), 7.94 (t, *J* = 7.5 Hz, 5H, aromatic H), 7.71 (t, *J* = 7.9 Hz, 1H, aromatic H), 7.58 (t, *J* = 7.3 Hz, 2H, aromatic H), 7.50 (t, *J* = 7.5 Hz, 4H, aromatic H), 7.08 (t, *J* = 7.2 Hz, 1H, CH). ^{13}C NMR (101 MHz, DMSO) δ 166.39, 148.27, 134.27, 134.01, 132.24, 130.47, 128.83, 128.10, 123.28, 121.89, 59.08.

N,N′-(4-Nitrophenylmethylene)dibenzamide **(Figure S8, S9, table 2, entry 1i):** White solid, ^{1}H NMR (400 MHz, DMSO) δ 9.26 (d, *J* = 7.4 Hz, 2H, NH, exchangeable with D_2O), 8.30 – 8.24 (m, 2H, aromatic H), 7.93 (t, *J* = 8.9 Hz, 4H, aromatic H), 7.75 (d, *J* = 8.7 Hz, 2H, aromatic H), 7.58 (t, *J* = 7.3 Hz, 2H, aromatic H), 7.50 (t, *J* = 7.5 Hz, 4H, aromatic H), 7.08 (t, *J* = 7.2 Hz, 1H, CH). ^{13}C NMR (101 MHz, DMSO) δ 166.37, 148.03, 133.97, 132.25, 131.86, 128.82, 128.53, 128.09, 124.01, 59.01.

2-Amino-7,7-dimethyl-4-(4-Methylphenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile **(Figure S10, S11, table 5, entry 2b):** White solid ^{1}H NMR (400 MHz, DMSO) δ 7.29 (t, *J* = 7.5 Hz, 2H, aromatic H), 7.14 (d, *J* = 7.3 Hz, 2H, aromatic H), 7.03 (s, 2H, NH_2), 4.17 (s, 1H, CH,), 2.58 – 2.44 (m, 5H, CH_2, CH_3), 2.26 (d, *J* = 16.1 Hz, 1H, CH_2), 2.10 (d, *J* = 16.1 Hz, 1H, CH_2), 1.04 (s, 3H, CH_3), 0.96 (s, 3H, CH_3). ^{13}C NMR (101 MHz, DMSO) δ 196.17, 162.99, 158.94, 145.22, 128.81, 127.61, 127.05, 120.22, 113.17, 58.72, 50.42, 36.02, 32.29, 28.86, 27.25.

2-Amino-7,7-dimethyl-4-(4-Methoxy-phenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile **(Figure S12, S13, table 5, entry 2c):** White solid ^{1}H NMR (400 MHz, DMSO) δ 7.05 (d, *J* = 8.6 Hz, 2H, aromatic H), 6.99 (s, 2H,NH_2), 6.84 (d, *J* = 8.6 Hz, 2H, aromatic H), 4.12 (s, 1H, CH), 3.71 (s, 3H, OCH_3), 2.51 (d, *J* = 1.5 Hz, 2H, CH_2), 2.25 (d, *J* = 16.1 Hz, 1H, CH_2), 2.12 – 2.05 (m, 1H, CH_2), 1.01 (s, *J* = 17.8 Hz, 3H, CH_3), 0.95 (s, 3H, CH_3). ^{13}C NMR (101 MHz, DMSO) δ 196.17, 162.62, 158.86, 158.36, 137.32, 128.69, 120.31, 114.13, 113.43, 58.96, 55.45, 50.45, 35.20, 32.27, 28.89, 27.22.

2-Amino-7,7-dimethyl-4-(4-Fluorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile **(Figure S14, S15, table 5, entry 2h):** White solid, ^{1}H NMR (400 MHz, DMSO) δ 7.18 (dd, *J* = 8.6, 5.6 Hz, 2H, aromatic H), 7.11 (t, *J* = 8.8 Hz, 2H, aromatic H), 7.04 (s, 2H, NH_2), 4.20 (s, 1H, CH), 2.51 (s, 2H, CH_2), 2.25 (d, *J* = 16.1 Hz, 1H, CH_2), 2.11 (d, *J* = 16.1 Hz, 1H, CH_2), 1.04 (s, 3H, CH_3), 0.95 (s, 3H, CH_3).^{13}C NMR (101 MHz, DMSO) δ 196.19, 162.97, 162.56, 160.16, 159.78, 158.94, 141.42, 141.39, 129.55, 129.47, 120.11, 115.60, 115.39, 113.05, 58.54, 50.42, 35.37, 32.26, 28.79, 27.30.

2-Amino-7,7-dimethyl-4-(2-Nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile **(Figure S16, S17, table 5, entry 2i):** Yellow solid, ^{1}H NMR (400 MHz, DMSO) δ 7.85 – 7.79 (m, 1H, aromatic H), 7.66 (t, *J* = 7.2 Hz, 1H, aromatic H), 7.47 – 7.33 (m, 2H aromatic H), 7.22 (s, 2H, NH_2), 4.94 (s, 1H, CH), 2.50 (dd, *J* = 8.7, 6.8 Hz, 2H, CH_2), 2.21 (d, *J* = 16.1 Hz, 1H, CH_2), 2.02 (d, *J* = 16.1 Hz, 1H, CH_2), 1.04 (s, 3H, CH_3), 0.88 (s, 3H, CH_3). ^{13}C NMR (101 MHz, DMSO) δ 196.32, 163.20, 159.66, 149.43, 139.43, 133.85, 130.75, 128.34, 124.19, 119.56, 112.78, 56.75, 50.00, 32.32, 30.37, 28.76, 27.14.

2-Amino-7,7-dimethyl-4-(4-Furan)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile **(Figure S18, S19, table 5, entry 2l):** Orange solid, ^{1}H NMR (400 MHz, DMSO) δ 7.49 (d, *J* = 1.0 Hz, 1H, aromatic H), 7.11 (s, 2H, NH_2), 6.33 (dd, *J* = 3.0, 1.9 Hz, 1H, aromatic H), 6.06 (d, *J* = 3.1 Hz, 1H, aromatic), 4.33 (s, 1H, CH), 2.51 (s, 2H, CH_2), 2.29 (d, *J* = 16.1 Hz, 1H, CH_2), 2.17 (d, *J* = 16.1 Hz, 1H, CH_2), 1.05 (s, 3H, CH_3), 0.99 (s, 3H, CH_3).^{13}C NMR (101 MHz, DMSO) δ 195.94, 163.76, 159.77, 156.18, 142.25, 120.06, 118.74, 110.93, 110.79, 105.54, 55.79, 50.34, 32.30, 29.43, 28.90, 27.01.

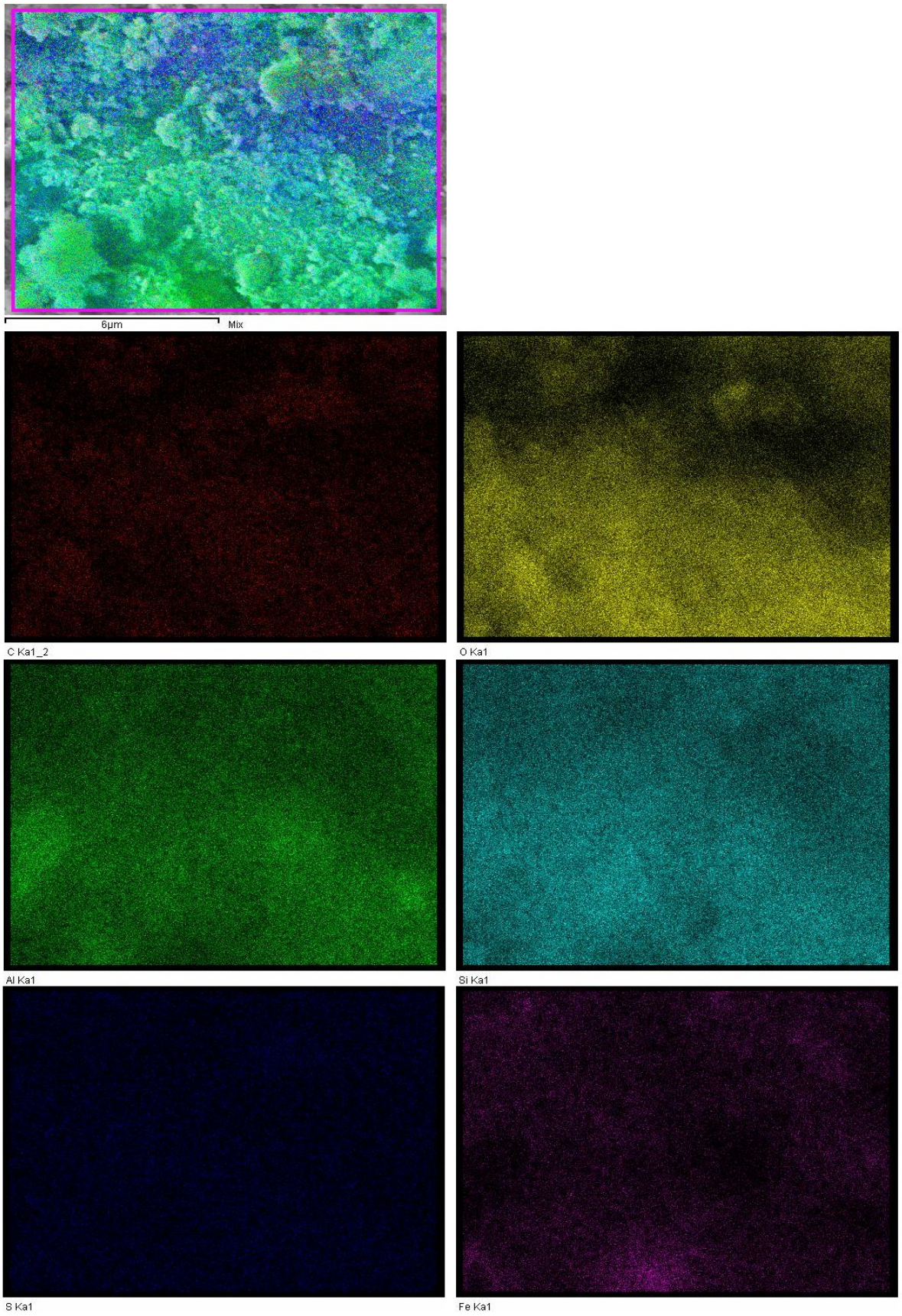


Figure S1. *STEM Elemental Mapping of M-Fe_3O_4@HAL-SO_3H*

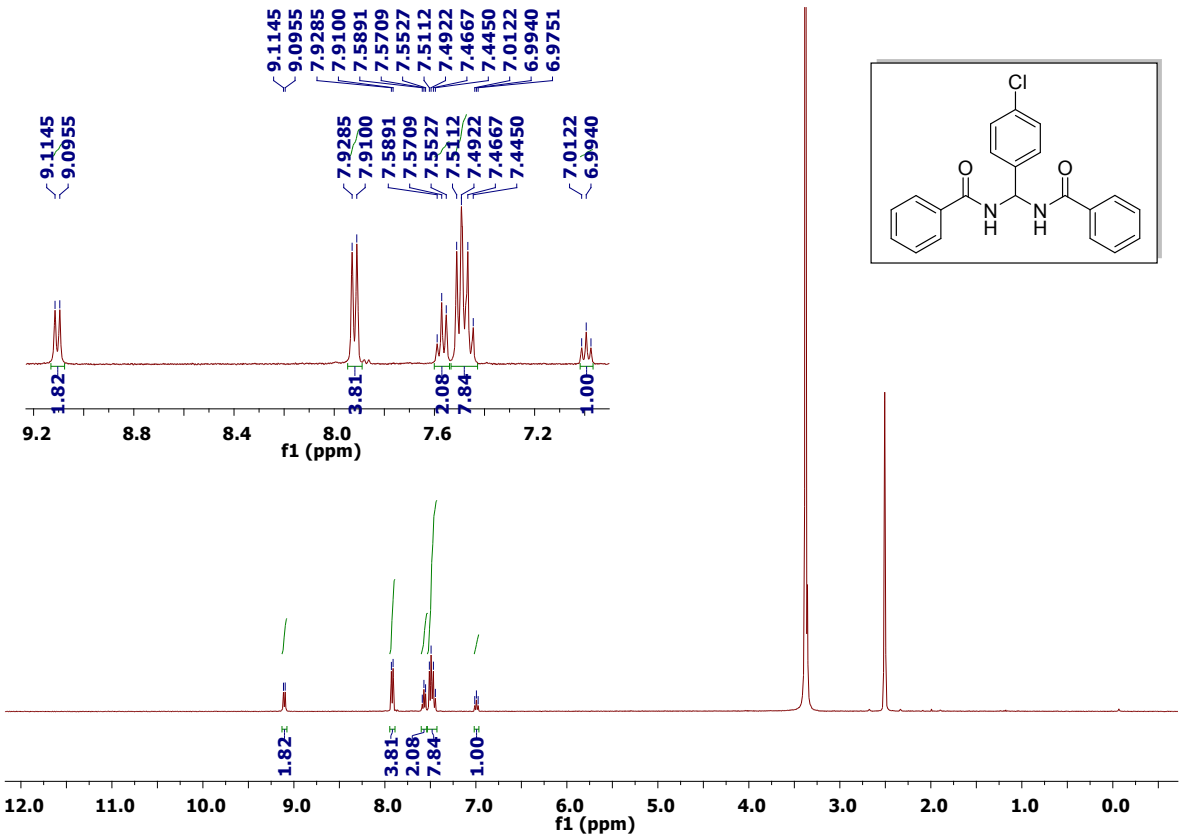


Figure S2. [1]H NMR spectra of N,N'-(4-Chlorophenylmethylene)dibenzamide (table 2, entry 1d)

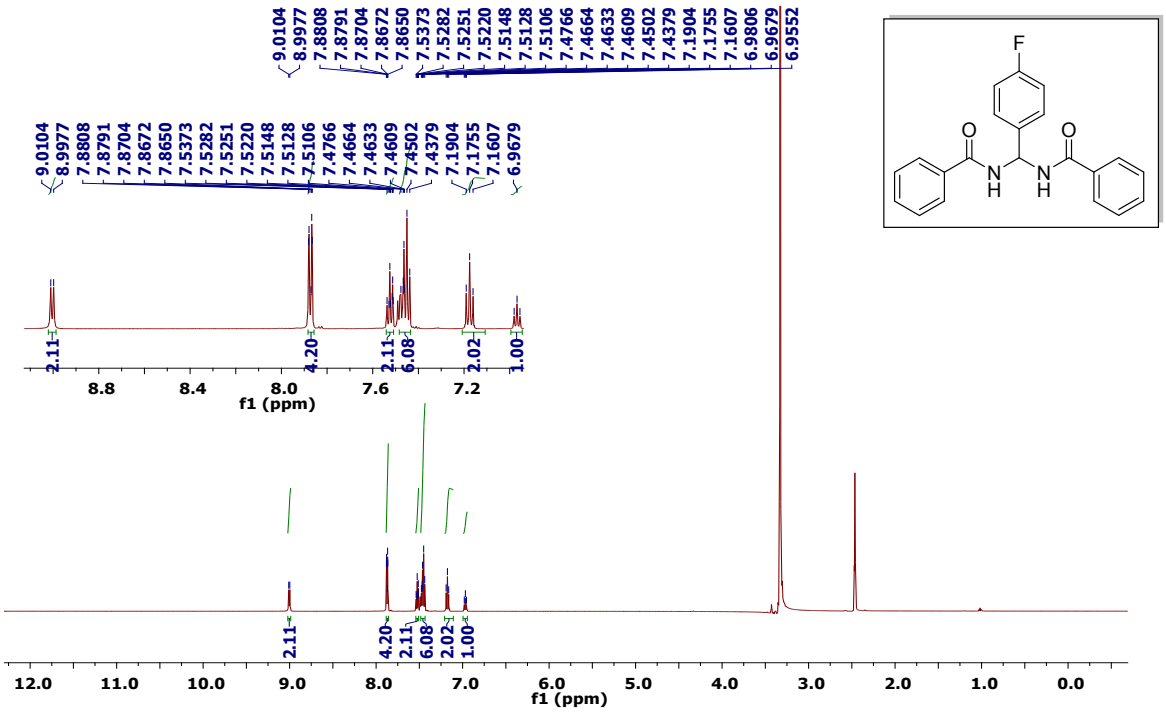


Figure S3 ^{1}H NMR spectra of N,N'-(4-Fluorophenylmethylene)dibenzamide (table 2, entry 1f)

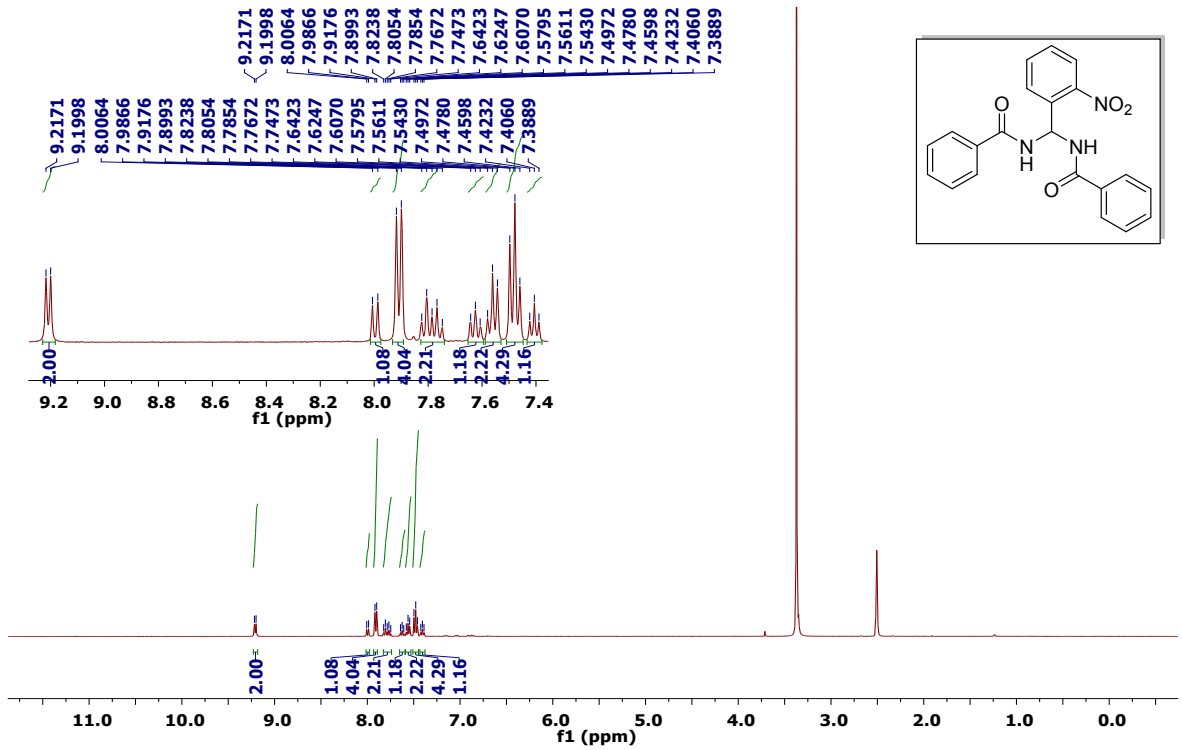


Figure S4 [1]H NMR spectra of N,N'-(2-Nirophenylmethylene)dibenzamide (table 2, entry 1g)

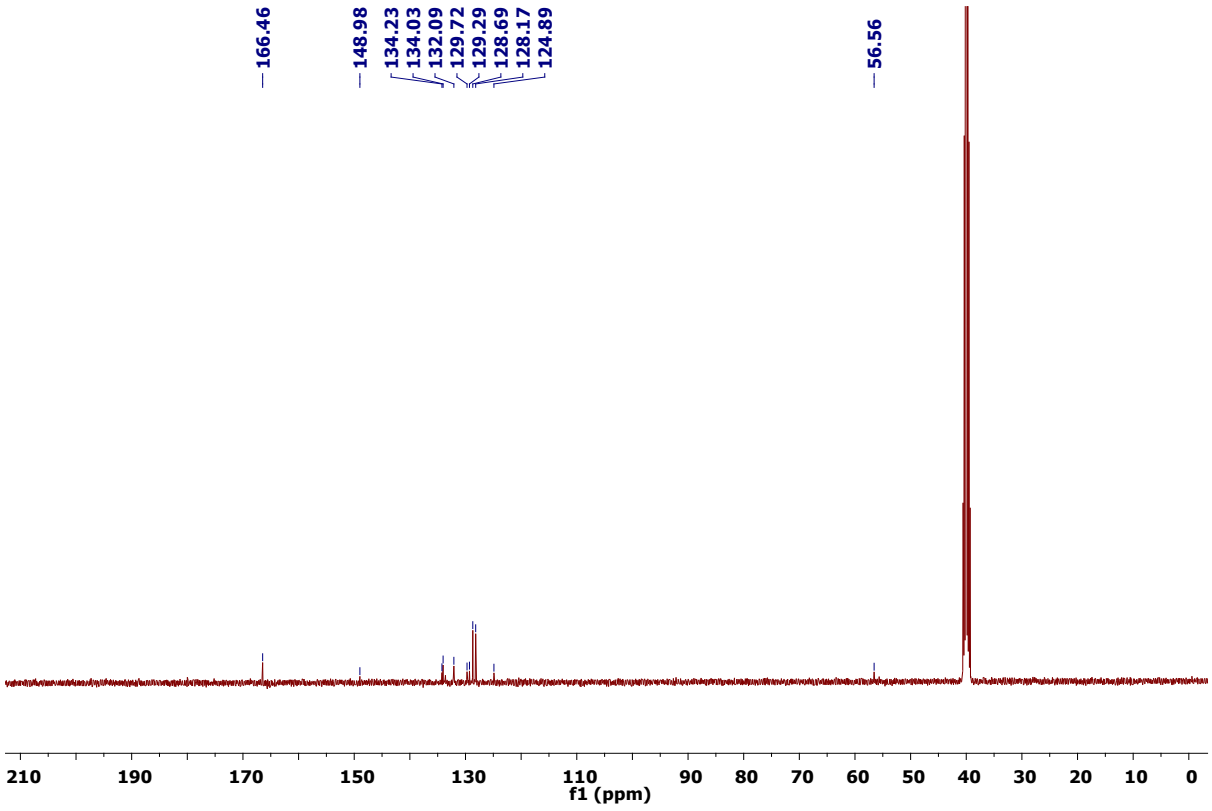


Figure S5 [13]C spectra of N,N'-(2-Nirophenylmethylene)dibenzamide (table 2, entry 1g)

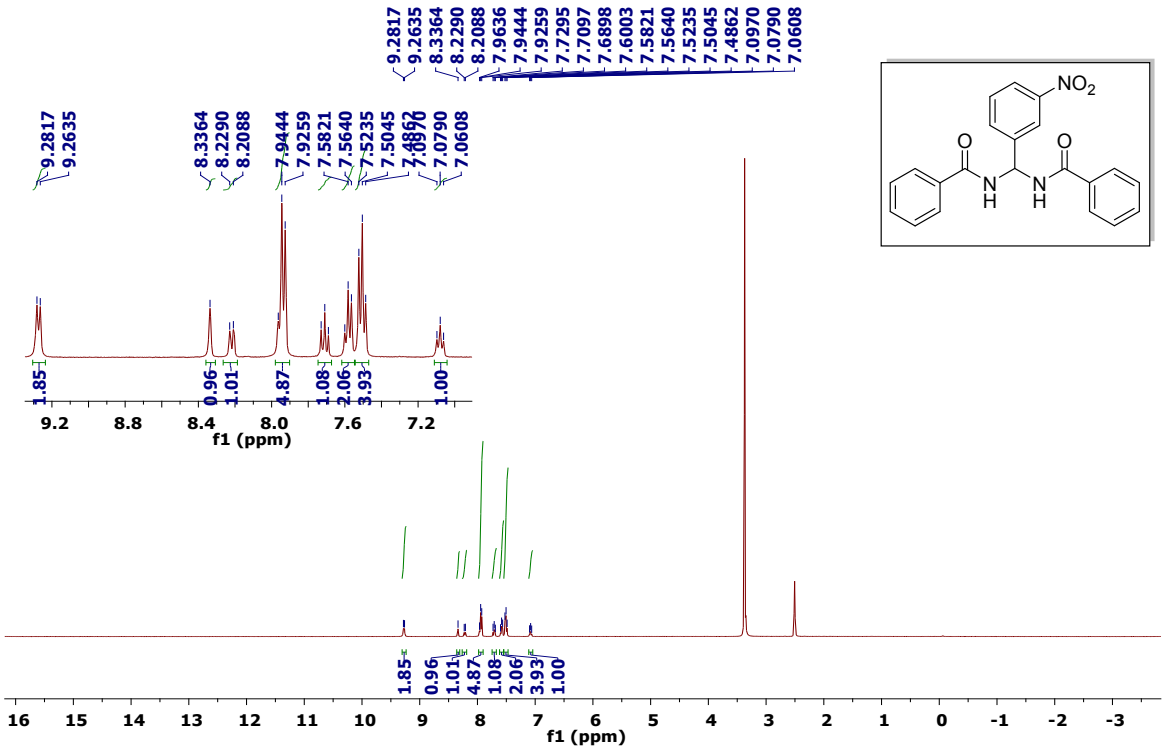
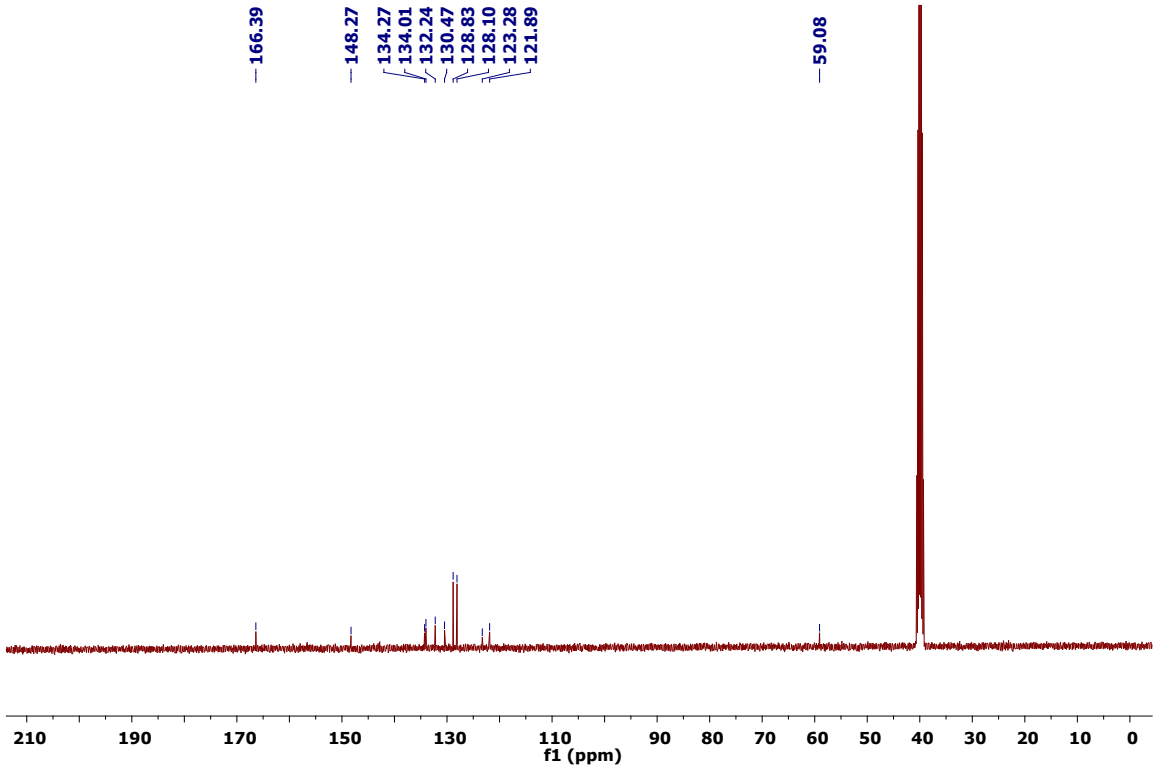


Figure S6 ^{1}H NMR spectra of N,N'-(3-Nirophenylmethylene)dibenzamide (table 2, entry 1h)



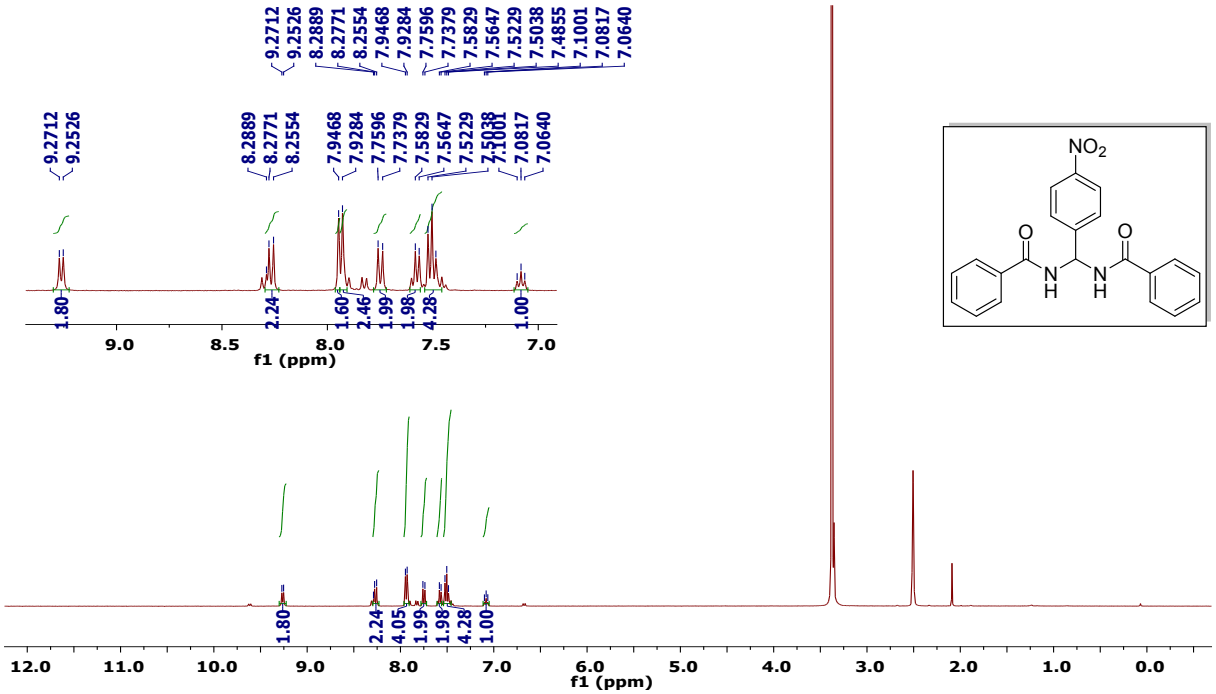
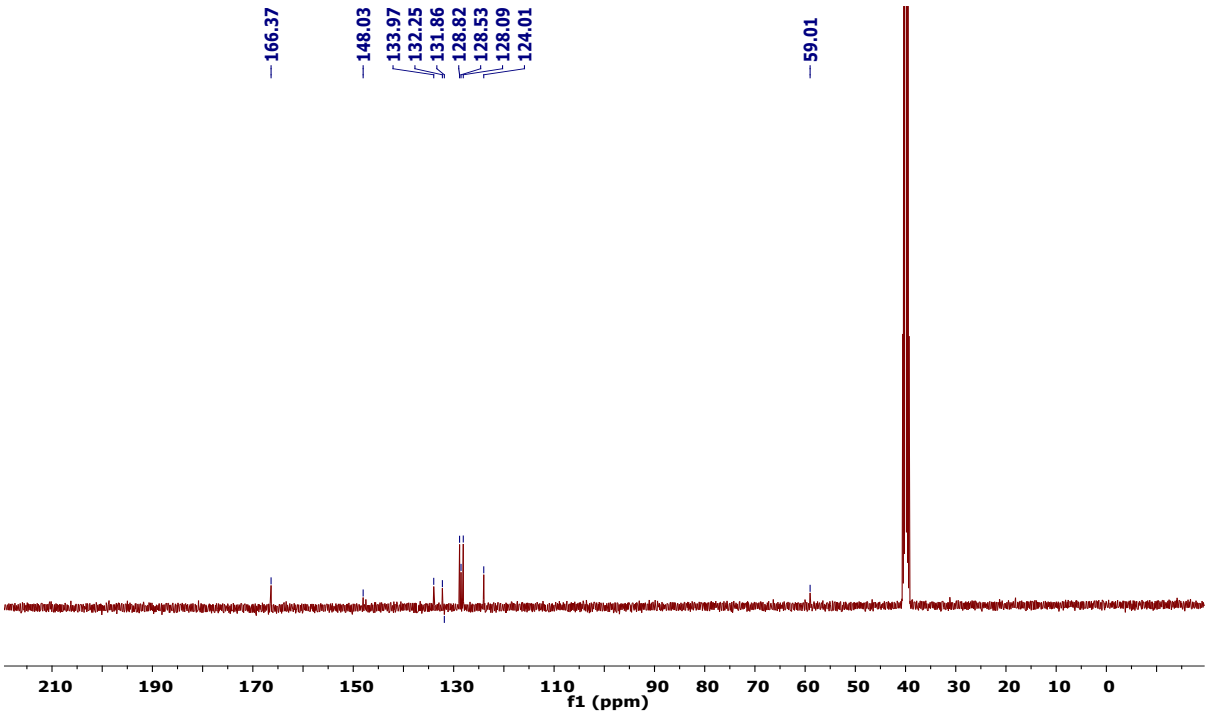


Figure S8 [1]H NMR spectra of N,N'-(4-Nirophenylmethylene)dibenzamide (table 2, entry 1i)

Figure S7 13C spectra of N,N'-(3-Nirophenylmethylene)dibenzamide (table 2, entry 1h)



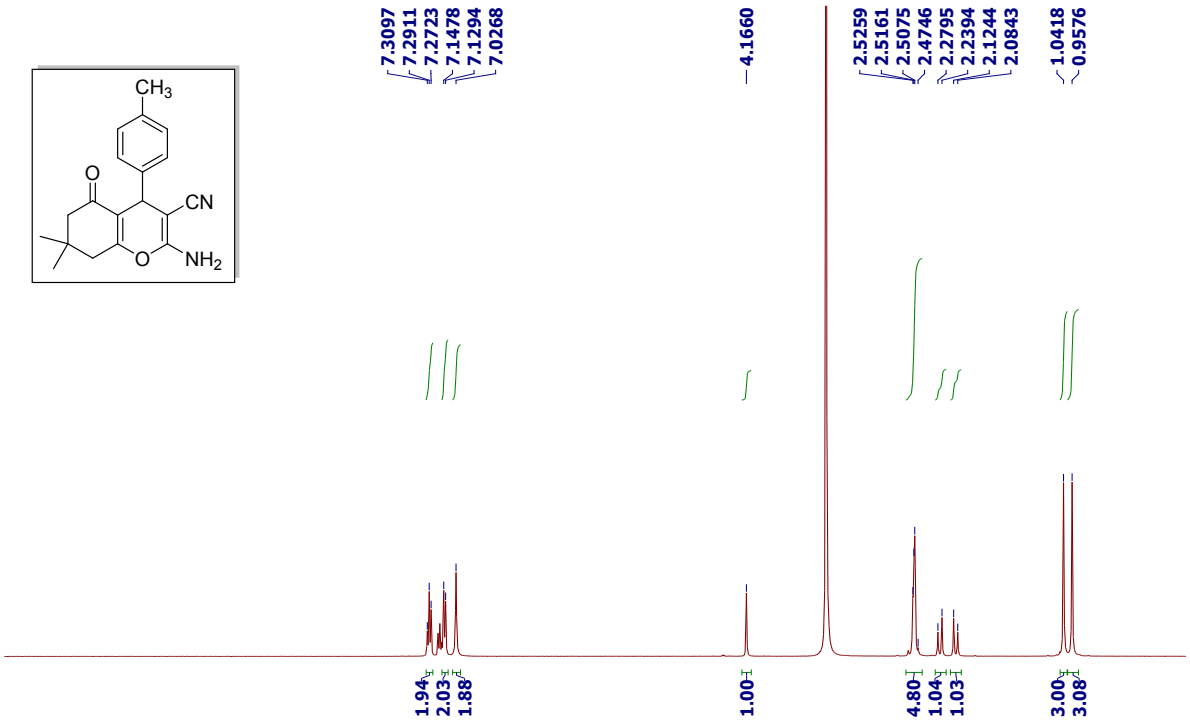


Figure S9 [13]C spectra of N,N'-(4-Nirophenylmethylene)dibenzamide (table 2, entry 1i)

Figure S10 [1]H NMR spectra of 2-Amino-7,7-dimethyl-4-(4-Methylphenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (table 5, entry 2b)

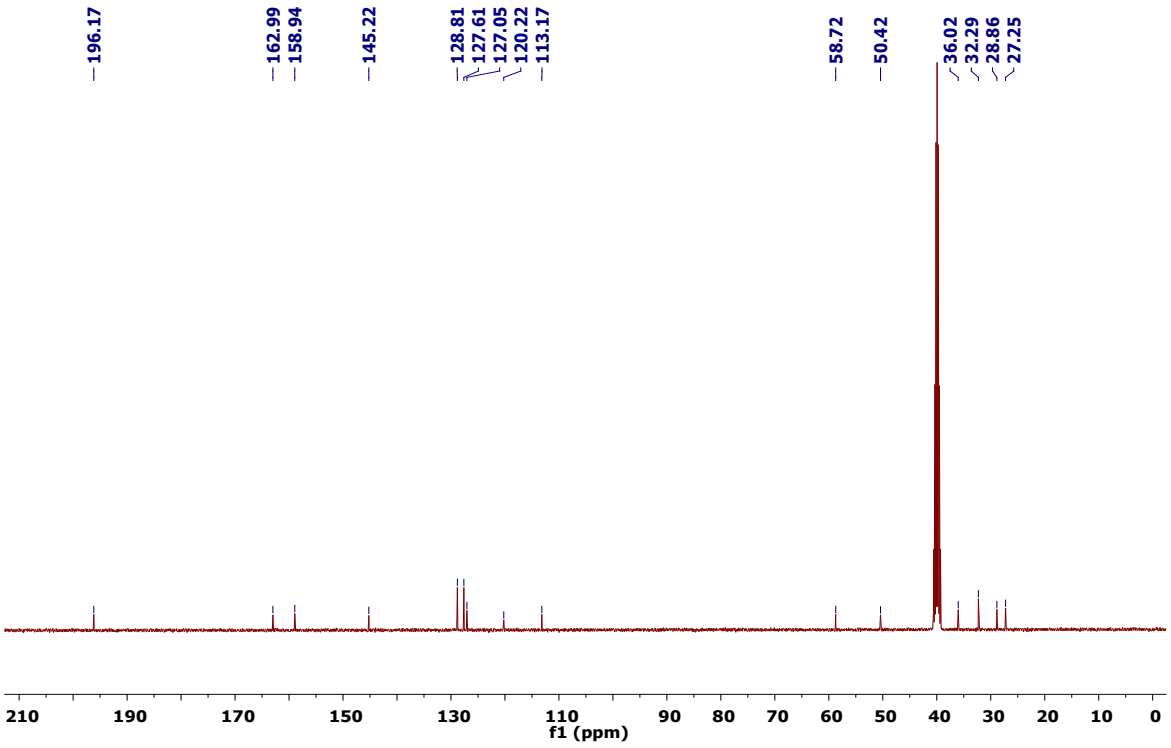


Figure S11 [13]C spectra of 2-Amino-7,7-dimethyl-4-(4-Methylphenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (table 5, entry 2b)

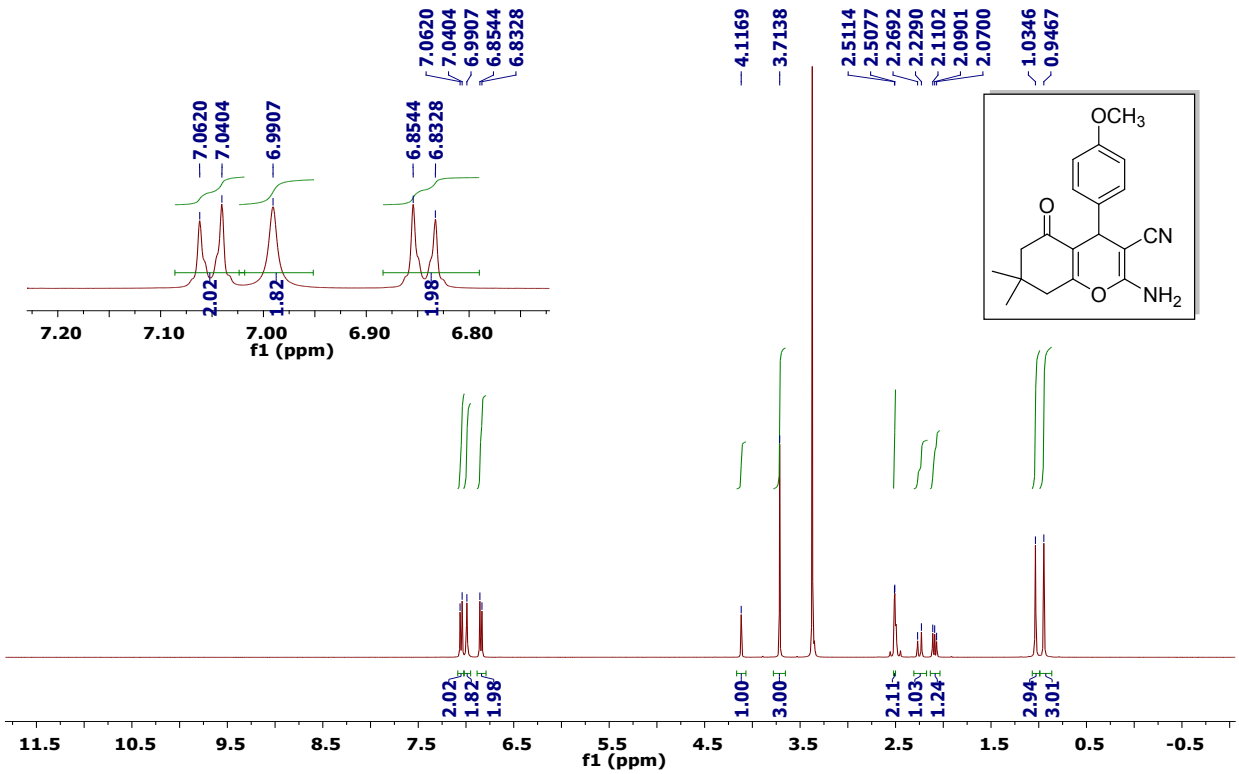


Figure 12 Figure [1]H NMR spectra of 2-Amino-7,7-dimethyl-4-(4-Methoxy-phenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (table 5, entry 2c)

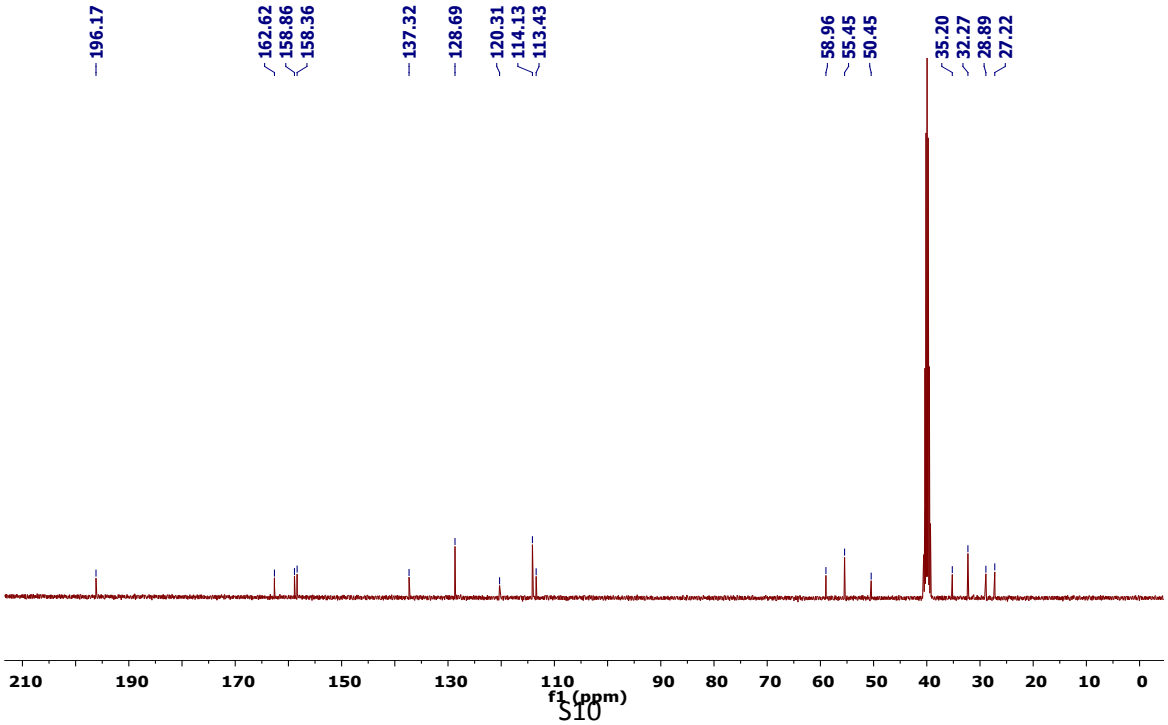


Figure 13 [13]C spectra of 2-Amino-7,7-dimethyl-4-(4-Methoxy-phenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (table 5, entry 2c)

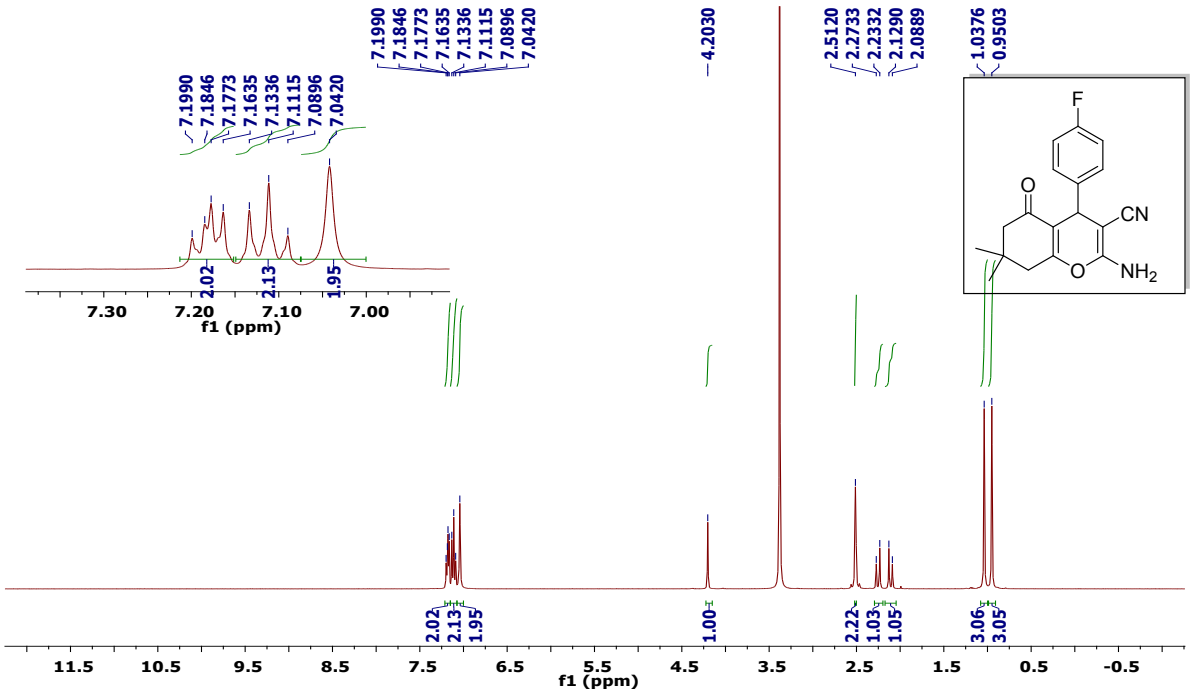


Figure S14 [1]H NMR spectra of 2-Amino-7,7-dimethyl-4-(4-Fluorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (table 5, entry 2h)

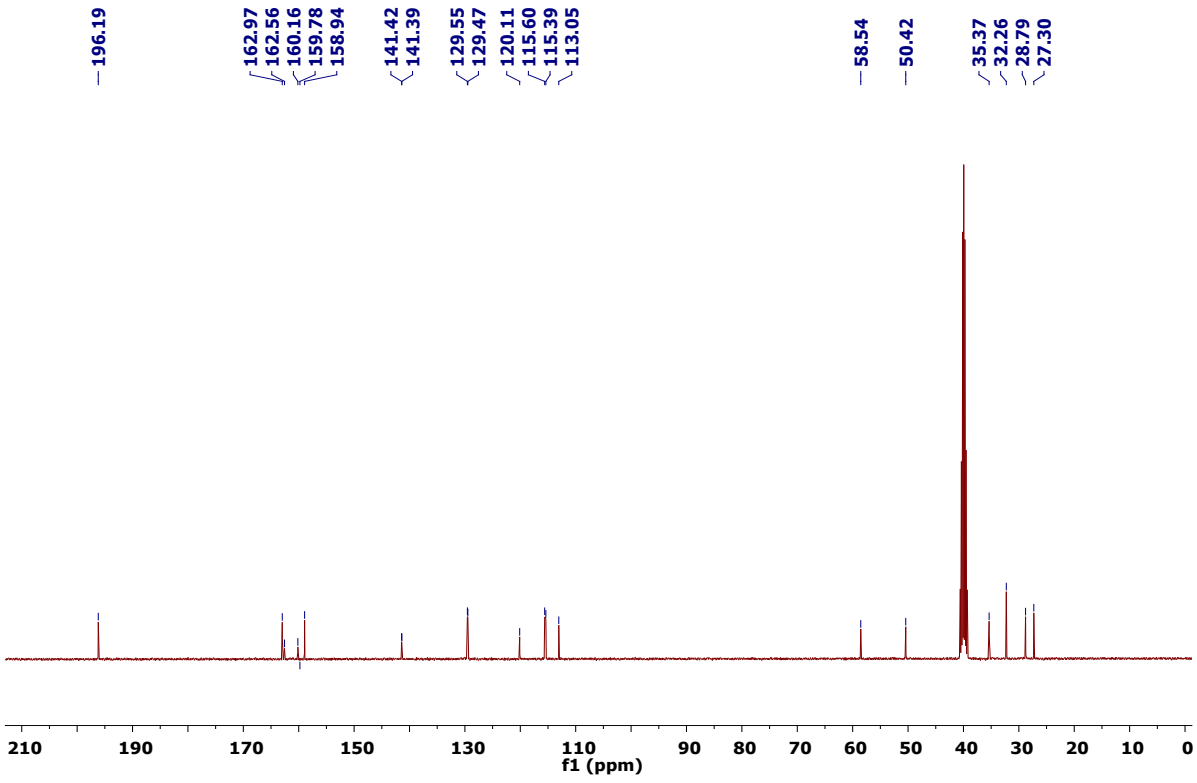


Figure 15 [13]C spectra of 2-Amino-7,7-dimethyl-4-(4-Fluorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (table 5, entry 2h)

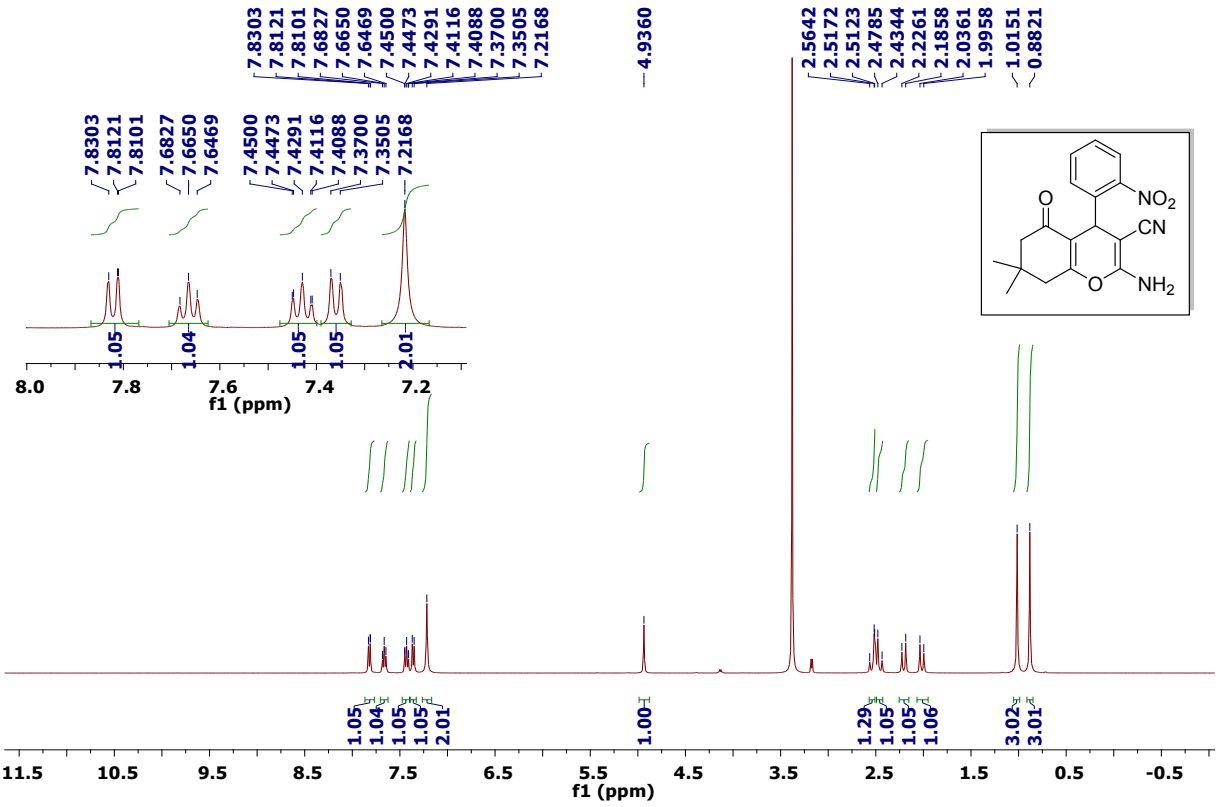


Figure S16 [1]H NMR spectra of 2-Amino-7,7-dimethyl-4-(2-Nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (table 5, entry 2i)

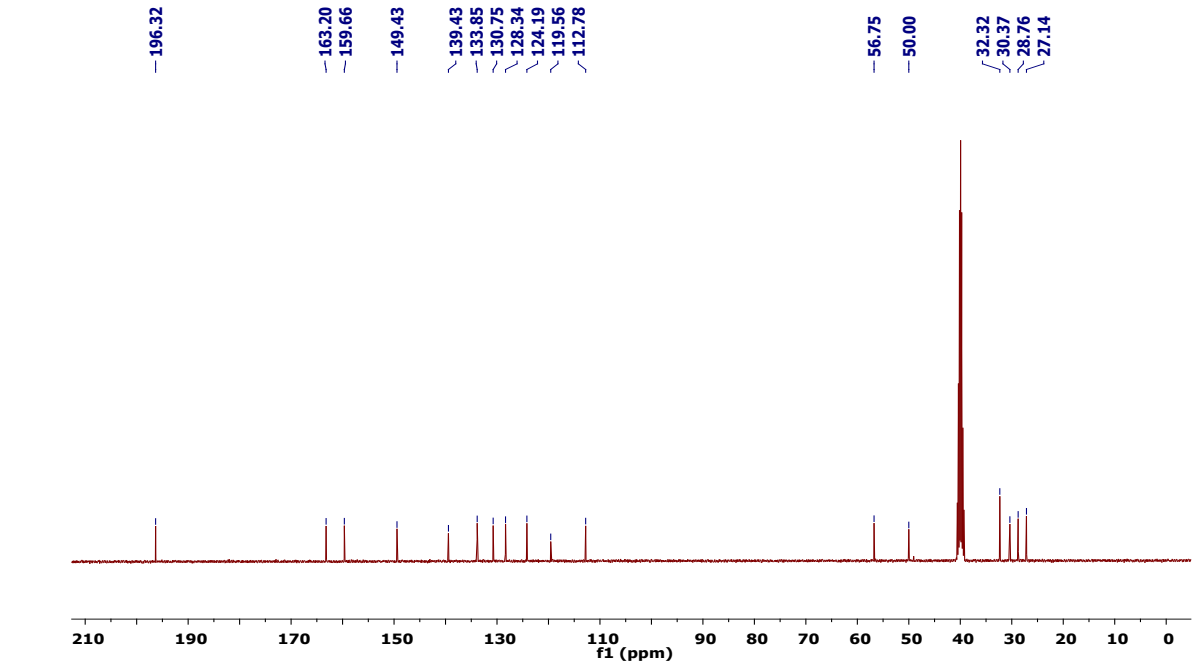


Figure S17 [13]C spectra of 2-Amino-7,7-dimethyl-4-(2-Nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (table 5, entry 2i)

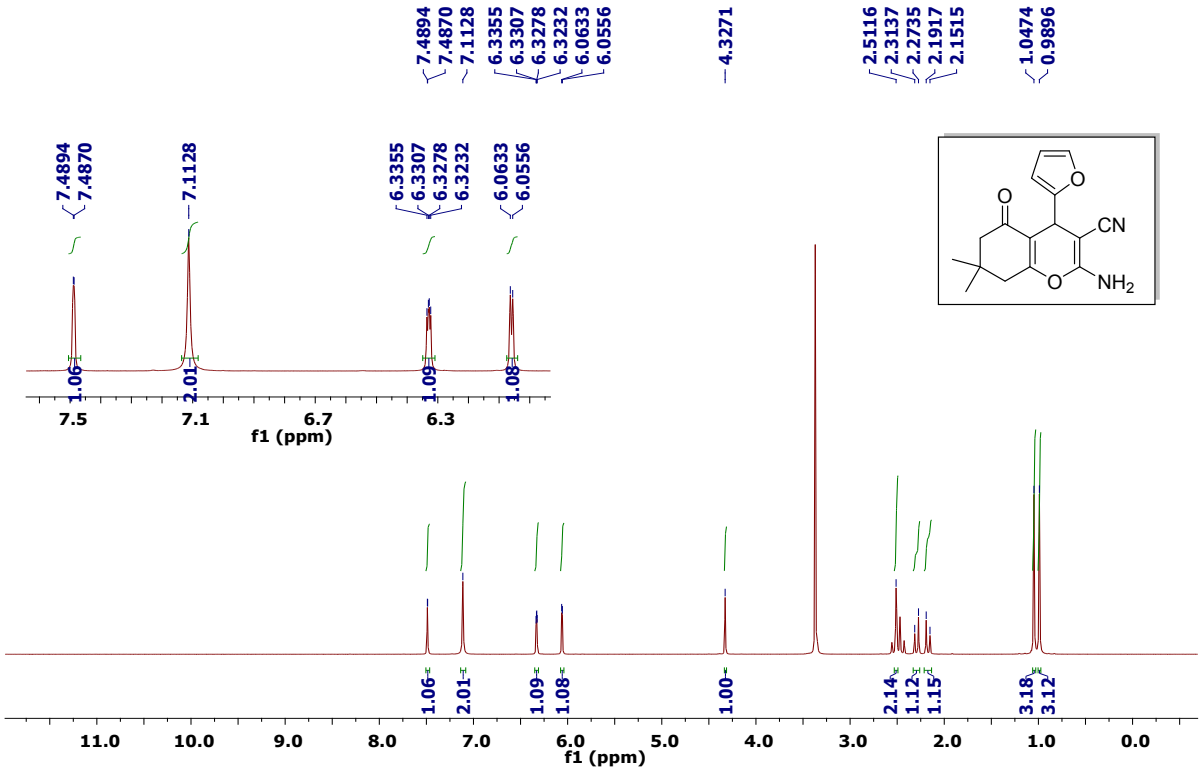


Figure S18 [1]H NMR of 2-Amino-7,7-dimethyl-4-(4-Furan)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (table 5, entry 2l)

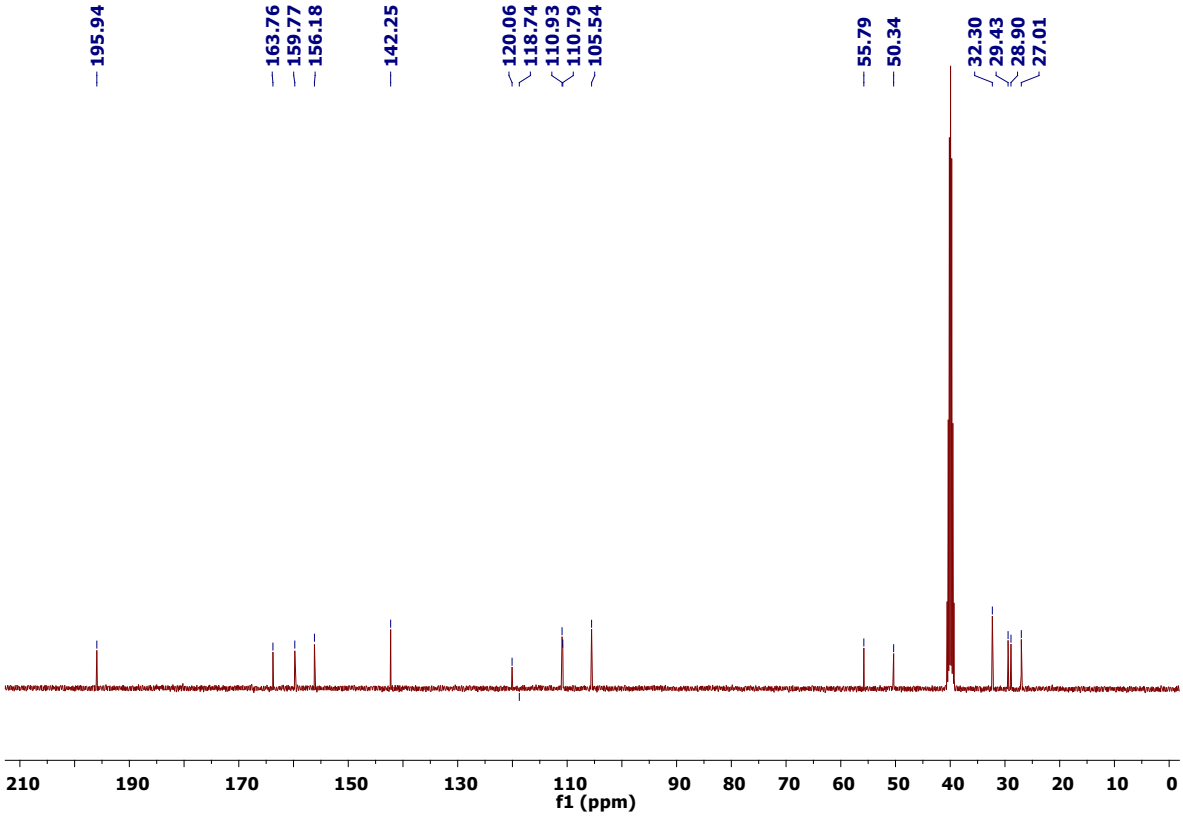


Figure S19 [13]C spectra of 2-Amino-7,7-dimethyl-4-(4-Furan)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (table 5, entry 2l)