

Anion-cation co-operative catalysis by artificial sweetener saccharine based ionic liquid for sustainable synthesis of 3,4-dihydropyrano[c]chromenes, 4,5-dihydropyrano[4,3-b]pyran and tetrahydrobenzo[b]pyrans in aqueous medium

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Experimental General Remarks: All chemicals were reagent grade and purchased from Aldrich, CDH, Spectrochem, and Fisher scientific and used without further purification. All reactions were monitored by TLC over silica gel plate. The spots on TLC plates were visualized under UV lamp or by iodine vapors. ^1H and ^{13}C NMR spectra were recorded on Jeol JNM ECX 500 MHz spectrometer in CDCl_3 and DMSO-d_6 . Data expresses the chemical shift values in δ ppm from upfield to downfield in both ^1H NMR and ^{13}C NMR spectra. For all compounds, ^1H NMR data is reported in the following order: Chemical shift (multiplicity, number of protons, J value, and nature of proton). IR spectra were recorded on a Bruker alpha FT-IR spectrometer. Melting points were determined by open glass capillary method and were uncorrected.

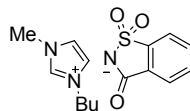
Typical experimental procedure for the [Bmim]Sac (3): Sodium Saccharinate (2) 27.0 g (0.112 mol) was added into a solution of 1-*n*-Butyl-3-methylimidazolium Bromide [Bmim]Br (1) 24.6 g (0.112 mol) in 100 mL acetone at rt. After stirring for 30h, the reaction mixture was filtered through a plug of Celite. The volatiles were removed under reduced pressure overnight and 31.0 g (96%) of viscous oil was obtained as pure product.

General Experimental Procedure for 3,4-dihydropyrano [c] chromenes, tetrahydrobenzo [b] pyrans, 4,5-dihydropyrano[4,3-b]pyran (7a-j, 9a-k, 12a-g, and 11a-d): A mixture of Aldehyde (1 mmol), (4) malononitrile (1.2 mmol), (5) 4-Hydroxy Coumarin (6)/4-hydroxy-6-methyl-2-pyrone (10) or 5,5-dimethyl-1,3-cyclohexanedione/1,3-cyclohexanedione (1 mmol) (8)/ and [Bmim]Sac (3) (5 mol%) in water (2 mL) was heated at 80°C for an appropriate period of time as indicated in Table 2 and 3 respectively. During the procedure, the reaction was monitored by TLC. Upon completion, the product was separated by simple filtration. Then, the resulting solid product was recrystallized from ethanol to afford pure product in high yields without any purification.

Reusability of the [Bmim] Sac: After completion of reaction, ice water was added to the reaction mixtures. The solid product was filtered and the filtrate (Bmim-Sac in water) was dried under vacuum to remove water and the dried IL was found to be identical (spectral data) with an authentic sample of (unused ionic liquid) then the organic reaction mixture was added to the IL to start next run. It is interesting to note that recovered IL was reused for 5 successive batches of reactions to afford pure product after crystallisation.

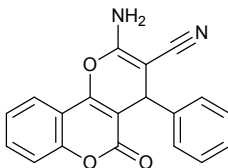
¹H and ¹³C data of 3,4-Dihydropyrano[c]chromene, 4,5-Dihydropyrano[4,3-b]pyran and Tetrahydrobenzo[b]pyran

[Bmim]Sac (3):



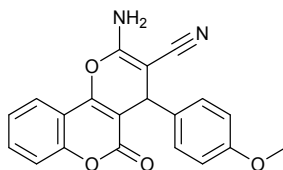
Colorless oil; ¹H NMR (DMSO-*d*₆, 300 MHz) δ = 0.90 (t, 3H, J = 7.3 Hz, CH₃), 1.28 (m, 2H, CH₂), 1.80 (m, 2H, CH₂), 3.85(s, 3H, CH₃), 4.18 (t, 2H, J = 7.2Hz, NCH₂), 7.71(s, 1H, ArH), 7.78 (d, J= 2.0Hz, 4H, ArH), 7.89 (d, J=5.4Hz, 1H, ArH), 9.17 (s, 1H, ArH); ¹³C NMR (DMSO-*d*₆, 50 MHz) δ = 13.2, 18.7, 31.3, 35.7, 48.4, 120.0, 122.2, 123.5, 131.5, 133.0, 136.5, 142.5, 164.7, IR (neat, cm⁻¹): 766, 951, 1148, 1166, 1260, 1332, 1458, 1580, 1633, 2873, 2961, 3097, 3147;

2-Amino-4-(phenyl)-4, 5-dihydro-5-oxopyrano[3,2-c]chromene-3-carbonitrile (7a)¹:



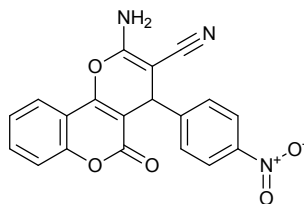
White solid, m. p. 262-263°C (reported m. p. 260-261); ¹H NMR (DMSO-*d*₆, 400 MHz) δ : 4.46 (s, 1H, CH), 7.25 (d, 2H, J= 7.80 Hz, Ar-H), 7.28 (m, 1H, Ar-H), 7.33 (t, 2H, J= 7.50 Hz, Ar-H), 7.42 (br s, 2H, NH₂), 7.45 (d, 1H, J= 8.40 Hz, Ar-H), 7.49 (t, 1H, J= 7.6 Hz, Ar-H), 7.71 (t, 1H, J= 7.50 Hz, Ar-H), 7.91 (d, 1H, J= 7.60 Hz, Ar-H); ¹³C NMR (DMSO-*d*₆, 100 MHz,) δ : 58.8, 104.9, 113.8, 117.4, 120.1, 123.3, 125.5, 128.0, 128.5, 129.4, 133.8, 144.2, 153.0, 154.3, 158.8, 160.4; IR (KBr, cm⁻¹): 1609, 1671, 1707, 2188, 3177, 3275, 3387.

2-Amino-4-(4-methoxyphenyl)-4, 5-dihydro-5-oxopyrano[3,2-c]chromene-3-carbonitrile (7b)¹:



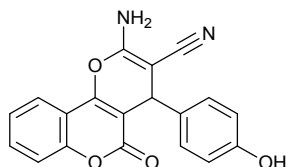
White solid, m.p. 252-253 °C (reported m. p. 250-251); ¹H NMR (DMSO-*d*₆, 400 MHz) δ: 3.72 (s, 3H, OCH₃), 4.40 (s, 1H, CH), 6.87 (d, 2H, J= 8.15 Hz, Ar-H), 7.18 (d, 2H, J= 8.15 Hz, Ar-H), 7.37 (br s, 2H, NH₂), 7.45 (d, 1H, J= 8.10 Hz, Ar-H), 7.49 (t, 1H, J= 7.85 Hz, Ar-H), 7.70 (t, 1H, J= 7.70 Hz, Ar-H), 7.89 (d, 1H, J= 7.7 Hz, ArH); ¹³C NMR (DMSO-*d*₆, 100 MHz,) δ: 55.9, 59.1, 105.1, 113.8, 114.7, 117.4, 120.2, 123.3, 125.5, 129.6, 133.66, 136.2, 152.9, 153.9, 158.8, 159.2, 160.4; IR (KBr, cm⁻¹): 1607, 1668, 1711, 2189, 3184, 3311, 3381.

2-Amino-4-(4-nitrophenyl)-5-oxo-4H, 5H-pyrano- [3,2-c]chromene-3-carbonitrile (7c)¹:



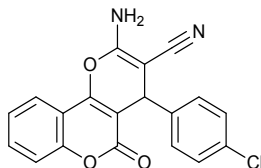
Pale yellow solid, m.p. 264-265°C (reported m. p. 261-263); ¹H NMR (DMSO-*d*₆, 400 MHz) δ: 4.68 (s, 1H, CH), 7.47 (d, 1H, J= 8.00 Hz, Ar-H), 7.52 (t, 1H, J= 7.80 Hz, Ar-H), 7.57 (br s, 2H, NH₂), 7.60 (d, 2H, J= 8.00 Hz, Ar-H), 7.74 (t, 1H, J= 7.80 Hz, Ar-H), 7.91 (d, 1H, J= 7.80 Hz, Ar-H), 8.18 (d, 2H, J= 8.00 Hz, Ar-H); ¹³C NMR (DMSO-*d*₆, 100 MHz,) δ: 57.6, 103.6, 113.7, 117.5, 119.8, 123.4, 124.6, 125.6, 130.0, 134.0, 147.4, 151.6, 153.1, 154.8, 158.9, 160.4; IR (KBr, cm⁻¹): 1292, 1379, 1518, 1609, 1666, 1711, 2190, 3323, 3369, 3422, 3477.

2-Amino-4-(4-hydroxyphenyl)-4,5-dihydro-5-oxopyrano[3,2-c]chromene-3-carbonitrile (7d)¹.



White solid; m. p. 266-267 °C (reported m. p. 267-269); ¹H NMR (DMSO-*d*₆, 400 MHz) δ: 4.34 (1H, s, CH); 6.72 (2H, s, Ar-H); 7.07 (2H, s, NH₂); 7.34-7.43 (4H, m, Ar-H); 7.66 (1H, s Ar-H); 7.88 (1H, s Ar-H); 9.38 (1H, s, OH); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ: 36.13, 58.4, 104.4, 112.9, 115.1, 116.4, 119.3, 122.3, 124.5, 128.6, 132.7, 133.6, 152.0, 152.9, 156.4, 157.8, 159.4. IR (KBr, cm⁻¹): 1182, 1580, 1723, 2340, 3428.

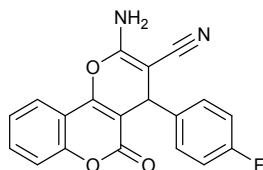
2-Amino-4-(4-chlorophenyl)-5-oxo-4H, 5H-pyrano[3,2-c]chromene- 3-carbonitrile (7e)¹:



White solid, m. p. 265-267°C (reported m. p. 266-268); ¹H NMR (DMSO-*d*₆, 400 MHz) δ: 4.50 (s, 1H, CH), 7.31 (d, 2H, J= 8.00 Hz, Ar-H), 7.36 (br s, 2H, NH₂), 7.38 (br s, 2H, Ar-H), 7.44 (d, 1H, J= 8.00

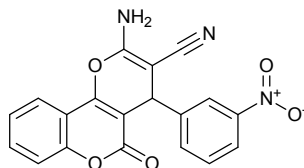
Hz, Ar-H), 7.49 (t, 1H, J= 7.6 Hz, Ar-H), 7.71 (t, 1H, J= 7.80 Hz, Ar-H), 7.92 (d, 1H, J= 7.80 Hz, Ar-H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ: 36.4, 58.8, 104.4, 113.9, 117.3, 119.3, 123.3, 129.2, 130.4, 132.6, 133.8, 143.1, 153.0, 154.4, 158.9, 160.3; IR (KBr, cm⁻¹): 763, 1059, 1374, 1609, 1672, 1717, 2139, 3385.

2-Amino-4-(4-fluorophenyl)-5-oxo-4H, 5H-pyrano[3,2-c]chromene-3-carbonitrile (7f)¹:



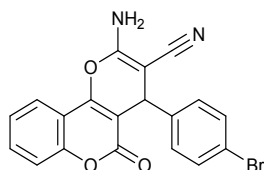
White solid, m.p. 257-258°C (reported m. p. 258-259); ¹H NMR (DMSO-*d*₆, 400 MHz) δ: 4.44 (s, 1H, CH), 7.09 (br.s, 2H, Ar-H), 7.28 (br.s, 2H, Ar-H), 7.41 (br s, 4H, Ar-H and NH₂), 7.65 (br.s, 1H, Ar-H), 7.95 (br.s, 1H, Ar-H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ: 36.6, 58.2, 104.2, 113.4, 115.6, 117.0, 119.7, 122.8, 125.1, 130.1, 133.4, 140.0, 152.6, 153.9, 158.4, 160.0, 160.7, 162.7; IR (KBr, cm⁻¹): 1501, 1603, 1668, 1711, 2186, 3281, 3386.

2-Amino-4-(3-nitrophenyl)-5-oxo-4H,5H-pyrano- [3,2-c]chromene-3-carbonitrile (7g)¹:



White solid, m.p. 255-256°C (reported m. p. 250-251); ¹H NMR (DMSO-*d*₆, 400 MHz) δ: 4.74 (s, 1H, CH), 7.44 (d, 1H, J= 6.50 Hz, Ar-H), 7.51 (t, 1H, J= 7.50 Hz, Ar-H), 7.55 (br s, 2H, NH₂), 7.64 (t, 1H, J= 7.50 Hz, Ar-H), 7.73 (dt, 1H, J= 7.50 Hz, 1.25 Hz, Ar-H), 7.82 (d, 1H, J= 6.75 Hz, Ar-H), 7.92 (dd, 1H, J= 6.50 Hz, 1.25 Hz, Ar-H), 8.12 (dd, 1H, J= 8.50 Hz, 1.40 Hz, Ar-H), 8.14 (s, 1H, Ar-H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ: 57.8, 103.7, 113.8, 117.4, 119.8, 123.1, 123.3, 123.5, 125.5, 130.9, 134.0, 135.6, 146.4, 148.7, 153.1, 154.7, 159.0, 160.5; IR (KBr, cm⁻¹): 1354, 1526, 1669, 1701, 2192, 3188, 3317, 3387.

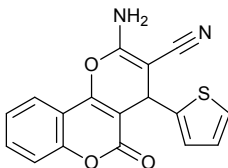
2-Amino-4-(4-bromophenyl)-4,5-dihydro-5-oxopyrano[3,2-c]chromene-3-carbonitrile (7h)¹:



White solid, m.p. 257-258°C (reported m. p. 255-258); ¹H NMR (DMSO-*d*₆, 400 MHz) δ: 4.48 (s, 1H, CH), 7.25 (d, 2H, J= 8.00 Hz, Ar-H), 7.47-7.52 (m, 4H, Ar-H), 7.73 (t, 1H, J= 7.20 Hz, Ar-H), 7.91 (d, 1H, J= 7.40 Hz, Ar-H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ: 57.8, 103.9, 113.4, 117.1, 119.5, 120.7,

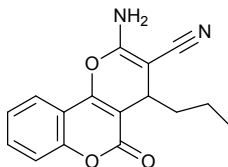
123.0, 125.2, 130.5, 131.8, 133.5, 143.2, 152.6, 154.0, 158.3, 160.0; IR (KBr, cm^{-1}): 1057, 1371, 1612, 1670, 1705, 2166, 3371.

2-Amino-5-oxo-4-(thiophen-2-yl)-4,5-dihydropyrano-[3,2-c]chromene-3-carbonitrile (7i) ¹.



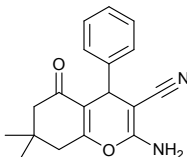
White Solid, m.p. 226-230°C (reported m. p. 228-230); ¹H NMR (DMSO-*d*₆, 400MHz) δ : 4.94 (s, 1H, CH), 6.54 (s, 2H, NH₂), 6.98 (m, 1H, thiophene ring), 7.20-7.22 (dd, 2H, J= 3.8Hz, 1.3Hz, thiophene ring), 7.65-7.67 (dd, 2H, J= 4.2Hz, 1.0Hz, ArH), 7.69-7.70 (dd, 2H, J = 2.6Hz, 1.1Hz, ArH); ¹³C NMR (DMSO-*d*₆, 100MHz) δ : 31.94, 57.84, 103.97, 116.22, 118.94, 122.51, 124.27, 124.58, 124.67, 127.72, 132.52, 138.41, 140.90, 152.95, 153.84, 158.40, 159.49. IR (KBr, cm^{-1}): 1383, 1535, 1606, 1670, 1699, 2200, 3319, 3403.

2-amino-5-oxo-4-propyl-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (7j) ¹:



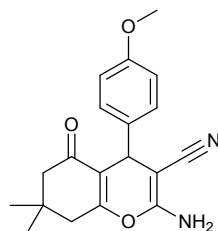
Light yellow colored solid; m.p. 195-200°C (reported m. p. 193-195); ¹H NMR (DMSO-*d*₆, 300MHz) δ : 0.73-0.91 (m, 3H, CH₃), 1.27-1.31 (m, 2H, CH₂), 1.44-1.53 (m, 1H, CH), 1.60-1.72 (m, 1H, CH), 3.36-3.39 (m, 1H, CH), 7.26 (s, 2H, NH₂), 7.33-7.44 (m, 2H, ArH), 7.65 (t, 1H, J = 7.2 Hz, ArH), 7.76 (d, 1H, J = 7.8 Hz, ArH); ¹³C NMR (DMSO-*d*₆, 75MHz) δ : 14.3, 18.1, 31.3, 36.7, 55.7, 104.8, 113.4, 117.0, 120.1, 122.6, 125.1, 133.2, 152.5, 154.6, 159.9, 160.4; IR (KBr) cm^{-1} : 473, 740, 813, 845, 955, 1169, 1214, 1277, 1403, 1460, 1509, 1591, 1629, 3051, 3246.

2-Amino-3-cyano-4-(phenyl)-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahydrobenzo[b]pyran (9a):



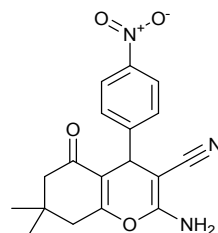
White solid, m.p. 238-240°C (reported m. p. 227-228); ¹H NMR (DMSO-*d*₆, 400 MHz) δ : 0.94 (s, 3H, CH₃), 1.04 (s, 3H, CH₃), 2.08 (d, 1H, J= 16.10 Hz, CH₂), 2.23 (d, 1H, J= 16.10 Hz, CH₂), 2.50 (m, 2H, CH₂), 4.11 (s, 1H, CH), 7.06 (s, 2H, NH₂), 7.19 (m, 3H, Ar-H), 7.33 (m, 2H, Ar-H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ : 26.3, 27.6, 31.2, 35.1, 39.1, 50.0, 59.7, 113.1, 118.4, 125.8, 126.6, 127.5, 142.7, 158.5, 162.3, 194.2; IR (KBr, cm^{-1}): 1358, 1655, 1678, 2191, 2951, 3179, 3321, 3390.

2-Amino-3-cyano-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahydrobenzo[b]pyran (9b):



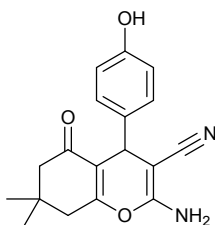
Pale yellow solid, m.p. 201-203°C (reported m. p. 194-196 °C); ¹H NMR (DMSO-d₆, 400 MHz) δ: 0.96 (s, 3H, CH₃), 1.04 (s, 3H, CH₃), 2.11 (d, 1H, J= 16.00 Hz, CH₂), 2.25 (d, 1H, J= 16.00 Hz, CH₂), 2.50 (s, 1H, J= 2.50 Hz, CH₂), 2.51 (s, 1H, J= 2.50 Hz, CH₂), 3.72 (s, 3H, OCH₃), 4.14 (s, 1H, CH), 6.85 (d, 2H, J= 8.60 Hz, Ar-H), 6.95 (s, 2H, NH₂), 7.07 (d, 2H, J= 8.60 Hz); ¹³C NMR (DMSO-d₆, 100 MHz) δ: 27.6, 29.3, 32.6, 35.6, 50.9, 55.8, 59.5, 113.9, 114.5, 120.6, 129.1, 137.7, 158.8, 159.3, 163.0, 196.5; IR (KBr, cm⁻¹): 1209, 1606, 1657, 1679, 2191, , 2960, 3321, 3371.

2-Amino-3-cyano-4-(4-nitrophenyl)-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahydrobenzo[b]pyran (9c):



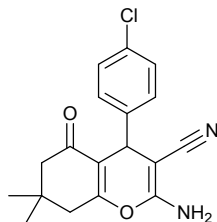
Yellow solid, m. p. 179-181°C (reported m. p. 178-180 °C); ¹H NMR (DMSO-d₆, 400 MHz) δ: 0.97 (s, 3H, CH₃), 1.05 (s, 3H, CH₃), 2.12 (d, 1H, J= 16.00 Hz, CH₂), 2.27 (d, 1H, J= 16.00 Hz, CH₂), 2.54 (brs, 2H, CH₂), 4.38 (s, 1H, CH), 7.18 (s, 2H, NH₂), 7.46 (d, 2H, J= 8.60 Hz, Ar-H), 8.18 (d, 2H, J= 8.60 Hz, Ar-H); ¹³C NMR (DMSO-d₆, 100 MHz) δ: 27.8, 29.1, 32.7, 36.5, 50.7, 57.9, 112.6, 120.2, 124.5, 129.5, 147.1, 153.1, 159.5, 163.9, 196.5; IR (KBr, cm⁻¹): 1212, 1518, 1591, 1628, 1653, 2189, 2967, 3320, 3408.

2-Amino-3-cyano-4-(4-hydroxyphenyl)-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahydrobenzo[b]pyran (9d):



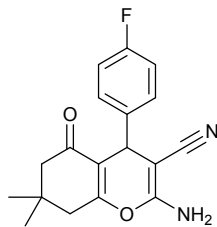
White solid, m. p. 269–270 °C (reported m. p. 265-266 °C); ¹H NMR (CDCl₃, 200 MHz) δ: 1.04 (s, 3H, CH₃), 1.25 (s, 3H, CH₃), 2.23 (s, 2H, CH₂), 2.44 (s, 2H, CH₂), 4.35 (s, 1H, CH), 4.49 (s, 2H, NH₂), 6.71-7.27 (m, 4H, Ar-H); IR (KBr, cm⁻¹): 1218, 1395, 1660, 2170, 2958, 3353.

2-Amino-3-cyano-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahydrobenzo[b]pyran (9e):



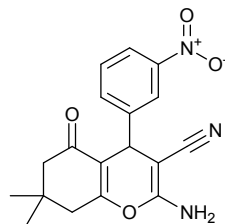
White solid, m.p. 212-213 °C (reported m. p. 207-209°C); ¹H NMR (DMSO-d₆, 400 MHz) δ: 0.96 (s, 3H, CH₃), 1.04 (s, 3H, CH₃), 2.12 (d, 1H, J= 16.00 Hz, CH₂), 2.26 (d, 1H, J= 16.00 Hz, CH₂), 2.51 (brs, 2H, CH₂), 4.22 (s, 1H, CH), 7.05 (s, 2H, NH₂), 7.19 (d, 2H, J= 8.40 Hz, Ar-H), 7.35 (d, 2H, J= 8.40 Hz, Ar-H); ¹³C NMR (DMSO-d₆, 100 MHz) δ: 27.7, 29.2, 32.6, 36.0, 50.8, 58.7, 113.2, 120.4, 129.2, 123.0, 132.0, 144.6, 159.4, 163.4, 196.5; IR (KBr, cm⁻¹): 1215, 1363, 1493, 1638, 1676, 2189, 2960, 3184, 3381.

2-Amino-3-cyano-4-(4-fluorophenyl)-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahydrobenzo[b]pyran (9f):



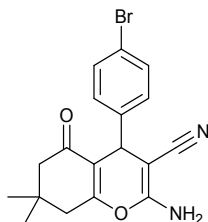
White solid, m.p. 195-197 °C (reported m. p. 191-193°C); ¹H NMR (DMSO-d₆, 400 MHz) δ: 0.90 (s, 3H, CH₃), 0.99 (s, 3H, CH₃), 2.08 (d, 1H, J=12.0 Hz, CH₂), 2.22 (d, 1H, J=12.0 Hz, CH₂), 2.51 (br,s, 2H, CH₂), 4.16 (s, 1H, CH), 7.01 (s, 2H, NH₂), 7.06-7.09 (m, 2H, Ar-H), 7.13-7.14 (m, 2H, Ar-H); ¹³C NMR (DMSO-d₆, 100 MHz,) δ: 27.3, 28.8, 32.3, 35.4, 36.7, 50.4, 58.5, 112.9, 115.6, 120.2, 129.4, 141.4, 158.9, 160.4, 162.3, 163.0, 196.1; IR (KBr, cm⁻¹): 1212, 1601, 1653, 1671, 2195, 2959, 3341.

2-Amino-3-cyano-4-(3-nitrophenyl)-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahydrobenzo[b]pyran (9g):



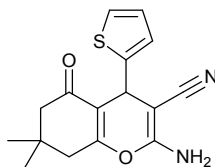
Yellow solid, m.p. 209-211 °C (reported m. p. 208-211°C); ¹H NMR (DMSO-d₆, 400 MHz) δ: 1.03 (s, 3H, CH₃), 1.11 (s, 3H, CH₃), 2.16-2.17 (m, 2H, CH₂), 2.44-2.53 (m, 2H, Hz, CH₂), 4.51 (s, 1H, CH), 4.73 (s, 2H, NH₂), 7.46-7.49 (m, 1H, Ar-H), 7.67 (d, 1H, Ar-H), 8.03-8.09 (m, 2H, Ar-H); ¹³C NMR (DMSO-d₆, 100 MHz) δ: 27.6, 28.8, 32.2, 35.5, 40.5, 50.4, 61.9, 112.9, 118.1, 122.2, 122.3, 129.4, 134.4, 145.3, 148.5, 157.7, 162.3, 195.8; IR (KBr, cm⁻¹): 1375, 1529, 1678, 2186, 2958, 3337, 3430.

2-Amino-3-cyano-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahydrobenzo[b]pyran (9h):



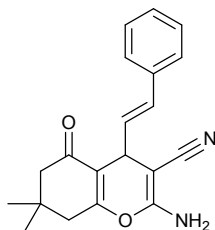
White solid, m.p. 200-201°C (reported m. p. 196-198°C); ¹H NMR (DMSO-d₆, 300 Hz) δ: 0.94 (s, 3H, CH₃), 1.04 (s, 3H, CH₃), 2.09 (d, 1H, J = 16.0 Hz, CH₂), 2.26 (d, 1H, J = 16.0 Hz, CH₂), 2.50 (brs, 2H, CH₂), 4.17 (s, 1H, CH), 7.08 (brs, 2H, NH₂), 7.10 (d, 2H, J = 8.3 Hz, Ar-H), 7.48 (2H, d, J = 8.3 Hz, Ar-H); IR (KBr, cm⁻¹): 1676, 2188, 2958, 3182, 3322, 3389.

2-Amino-3-cyano-4-(thiophen-2-yl)-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahydrobenzo[b]pyran (9i):



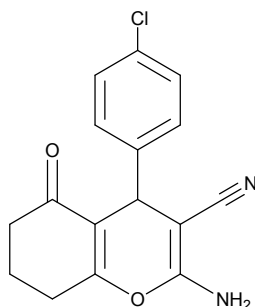
Yellow solid, m. p. 226-228 °C (reported m. p. 230-231°C); ¹H NMR (DMSO-d₆, 400 MHz) δ: 0.99 (s, 3H, CH₃), 1.05 (s, 3H, CH₃), 2.31 (m, 2H, CH₂), 2.49 (m, 2H, CH₂), 4.34 (s, 1H, CH), 6.33 (dd, 1H, J = 3.40 Hz, Ar-H), 6.15 (d, 1H, J = 3.40 Hz, Ar-H), 6.05 (d, 1H, J = 3.4 Hz, Ar-H), 7.08 (s, 2H, NH₂); ¹³C NMR (DMSO-d₆, 100 MHz) δ: 27.4, 29.6, 31.4, 32.7, 50.6, 58.4, 113.9, 121.1, 124.7, 125.7, 128.4, 151.5, 159.7, 163.4, 196.5; IR (KBr, cm⁻¹): 1201, 1664, 1686, 2202, 2973, 3211, 3401.

(E)-2-amino-7,7-dimethyl-5-oxo-4-styryl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (9k)



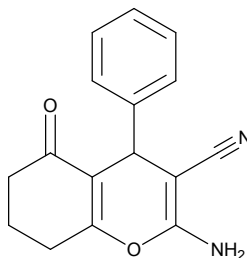
White solid, m.p. 200-202°C (reported m. p. 205-207°C); ¹H NMR (CDCl₃-d₆, 400 Hz,) δ: 1.08(s, 3H, CH₃), 1.11 (s, 3H, CH₃), 2.29 (s, 2H, CH₂), 2.38 (s, 2H, CH₂), 4.09 (d, 1H, J = 6.4 Hz, C-H), 4.59 (brs, 2H, NH₂), 6.11 (dd, 1H, J = 6.0, 12.0 Hz, =CH), 6.51 (d, 1H, J = 6.0Hz, =CH), 7.18-7.21 (m, 1H, Ar-H) 7.26-7.29 (m, 2H, Ar-H) 7.33-7.35 (m, 2H, Ar-H); ¹³C NMR (CDCl₃-d₆, 100 MHz,) δ: 27.4, 28.7, 29.6, 32.2, 32.3, 40.6, 50.7, 60.6, 113.3, 118.8, 126.5, 127.4, 128.3, 129.5, 131.0, 136.7, 158.2, 161.6, 196.1; IR (KBr, cm⁻¹): 1676, 2188, 2958, 3182, 3322, 3389

2-amino-4-(4-chlorophenyl)-5-oxo-5, 6, 7, 8-tetrahydro-4H-chromene-3-carbonitrile (12a):



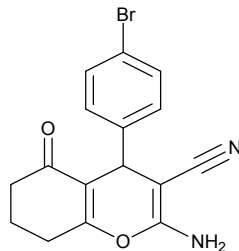
Yellow solid, m. p. 223-225 °C (reported m. p. 224-226°C); ¹H NMR (400 MHz, DMSO-d₆+CDCl₃) δ: 1.83-1.96 (m, 2H, CH₂), 2.14-2.25 (m, 2H, CH₂), 2.42-2.54 (m, 2H, CH₂), 4.26 (s, 1H, CH), 4.50 (s, 2H, NH₂), 7.05 (d, J=12.0Hz, 2H, Ar-H), 7.12 (d, J=12.0Hz, Ar-H).

2-amino-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (12b):



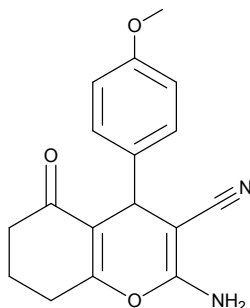
Yellow solid, m. p. 219-221°C (reported m. p. 220-222°C) ¹H NMR (400 MHz, CDCl₃) δ: 1.94-2.08 (m, 2H, CH₂), 2.28-2.38 (m, 2H, CH₂), 2.57-2.61 (m, 2H, CH₂), 4.42 (s, 1H, CH), 4.42 (br,s, 2H, NH₂), 7.18-7.30 (m, 5H, Ar-H).

2-amino-4-(4-bromophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (12c):



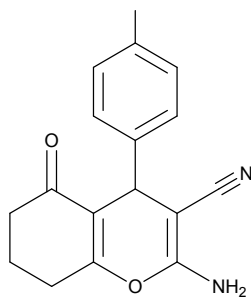
Yellow solid, m. p. 196-200 °C; ¹H NMR (400 MHz, CDCl₃) δ: 1.95-2.03 (m, 2H, CH₂), 2.37-2.41 (m, 2H, CH₂), 2.56-2.66 (m, 2H, CH₂), 4.39 (s, 1H, CH), 4.54 (s, 2H, NH₂), 7.15 (d, J=16.0Hz, 2H, Ar-H), 7.44 (d, J=16.0Hz, Ar-H) ppm

2-amino-4-(4-methoxyphenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (12d):

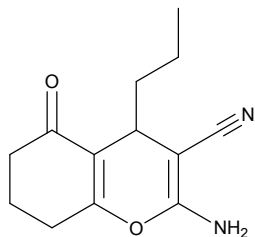


Yellow solid, m. p. 189-191 °C (reported m. p. 186-189°C); ¹H NMR (400 MHz, CDCl₃) δ: 1.69-2.06 (m, 2H, CH₂), 2.28-2.40 (m, 2H, CH₂), 2.51-2.63 (m, 2H, CH₂), 3.76(s, 3H, OCH₃), 4.38 (s, 1H, CH), 4.49 (s, 2H, NH₂), 6.80 (d, J=12.0Hz, 2H, Ar-H), 7.12 (d, J=8.0Hz, 2H Ar-H)

2-amino-5-oxo-4-(p-tolyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (12e):

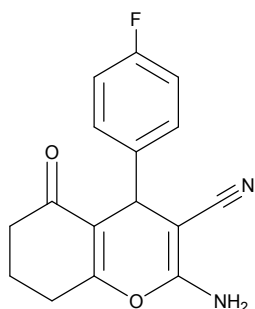


Yellow solid, m. p. 228-230 °C; ¹H NMR (400 MHz, CDCl₃) δ: 1.95-2.09 (m, 2H, CH₂), 2.29 (s, 3H, CH₃), 2.35-2.39 (m, 2H, CH₂), 2.54-2.64(m, 2H, CH₂), 4.38(s, 1H, CH), 4.48 (s, 2H, NH₂), 7.05-7.13 (m, 4H, Ar-H). **2-amino-5-oxo-4-propyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (12f):**

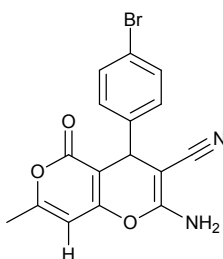


Yellow solid, m. p. 200-205 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 0.88 (t, 3H, CH_3), 0.95-1.07 (m, 2H, CH_2), 1.40-1.62 (m, 2H, CH_2), 1.93-2.06 (m, 1H, CHH), 2.31-2.53 (m, 3H, CH_2 CHH), 4.40 (t, 1H, CH), 4.48 (s, 2H, NH_2) .

2-amino-4-(4-fluorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (12g):

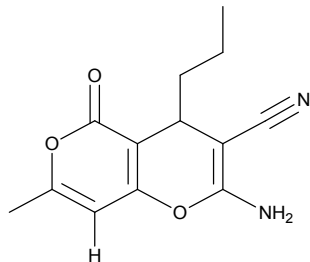


Yellow solid, m. p. 198-201°C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 1.94-2.07 (m, 2H, CH_2), 2.33-2.38 (m, 2H, CH_2), 2.51-2.63 (m, 2H, CH_2), 4.41 (s, 1H, CH), 4.57 (s, 2H, NH_2), 6.63-6.97 (m, 2H, Ar-H), 7.18-7.24 (m, 2H, Ar-H) ppm. **2-amino-4-(4-bromophenyl)-7-methyl-5-oxo-4,5-dihydropyrano[4,3-b]pyran-3-carbonitrile (11a);**



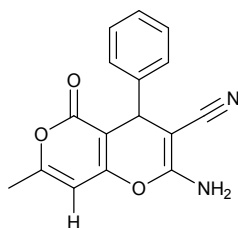
Yellow solid, m. p. 239-242°C (reported m. p. 240-242°C); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ : 2.23 (s, 3H, CH_3), 4.31 (s, 1H, CH), 4.57 (br.s, 2H, NH_2), 6.29 (s, 1H, =CH), 7.17 (d, 2H, $J = 8.4$ Hz, ArH), 7.51 (d, 2H, $J = 8.4$ Hz, ArH).

2-amino-7-methyl-5-oxo-4-propyl-4,5-dihydropyrano[4,3-b]pyran-3-carbonitrile (11b):



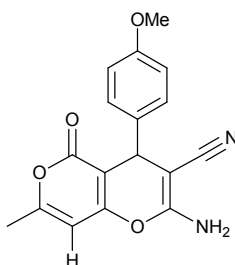
Yellow solid, m. p. 218-220°C (reported m. p. 220-222°C); ¹H NMR (400 MHz, CDCl₃) δ: 0.91(t, 3H, CH₃), 1.09-1.20 (m, 1H, CHH), 1.33-134 (m, 1H, CHH), 1.61-1.66 (m, 1H, CHH), 1.75-1.80 (m, 1H, CHH), 2.24 (s, 3H, CH₃), 3.50(s, 1H, CH), 4.67 (br.s, 2H, NH₂), 5.82 (s, 1H, =CH).

2-amino-7-methyl-5-oxo-4-phenyl-4,5-dihydropyrano[4,3-b]pyran-3-carbonitrile (11c):



White solid, m.p. 236-238 (reported m. p. 237-239°C); ¹H NMR (CDCl₃, 400 MHz,) δ: 2.08(s, 3H, CH₃), 4.27(s, 1H, CH), 5.61 (br.s, 2H, NH₂), 5.79 (s, 1H, =CH), 7.05-7.15 (m, 5H, Ar-H),.

2-amino-4-(4-methoxyphenyl)-7-methyl-5-oxo-4,5-dihydropyrano[4,3-b]pyran-3-carbonitrile (11d):



Colourless crystals, m.p. 222-224°C (reported m. p. 223-225°C). ¹H NMR (CDCl₃, 400 MHz) δ: 2.25(s, 3H, CH₃), 3.79 (s, 3H, OCH₃), 4.44 (s, 2H, CH), 5.91(s, 2H, NH₂), 5.79 (s, 1H, =CH), 6.83-6.87 (m, 2H, Ar-H), 7.01-7.28 (m, 2H, Ar-H).

Representative spectral data

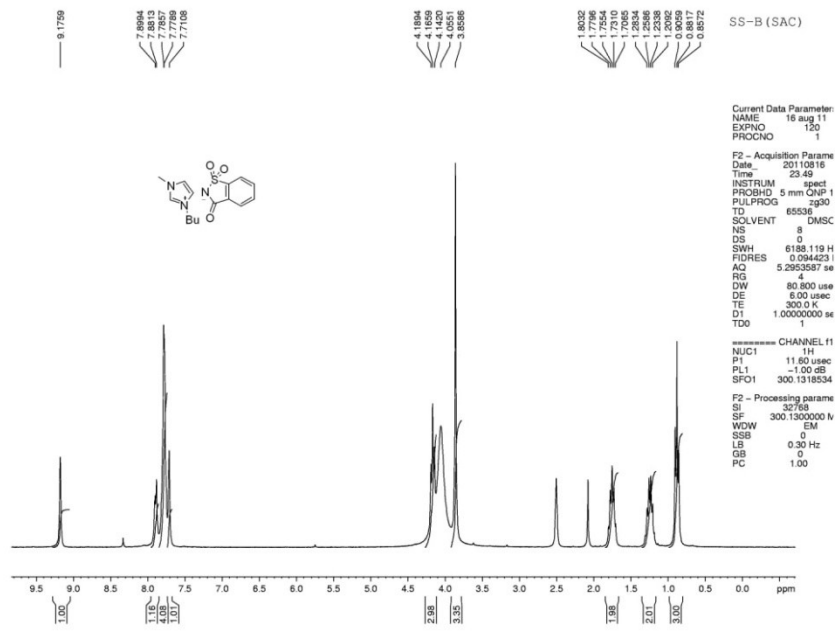


Figure 1. ^1H NMR of **3** in $\text{DMSO-}d_6$

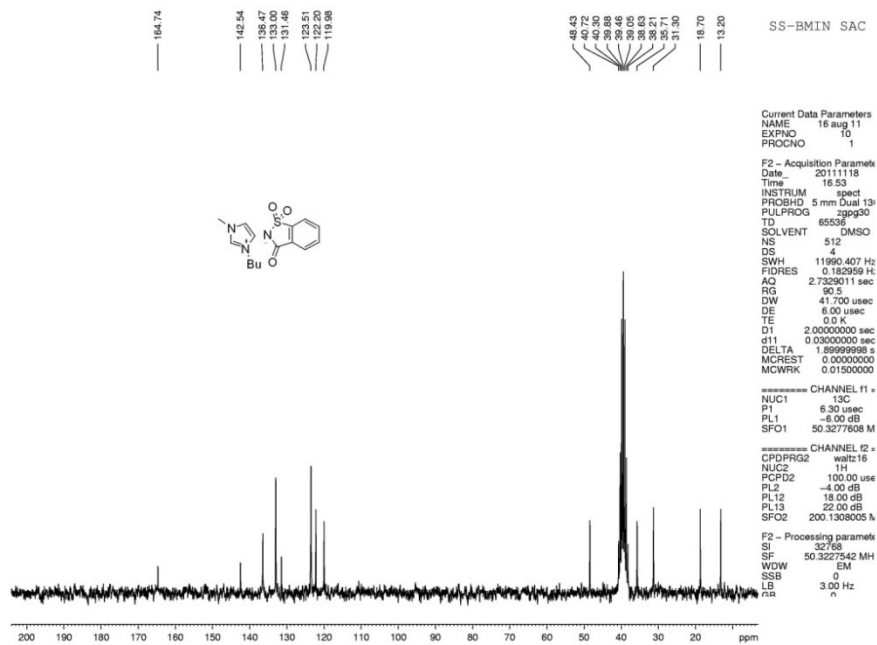


Figure 2. ^{13}C NMR of **3** in $\text{DMSO-}d_6$

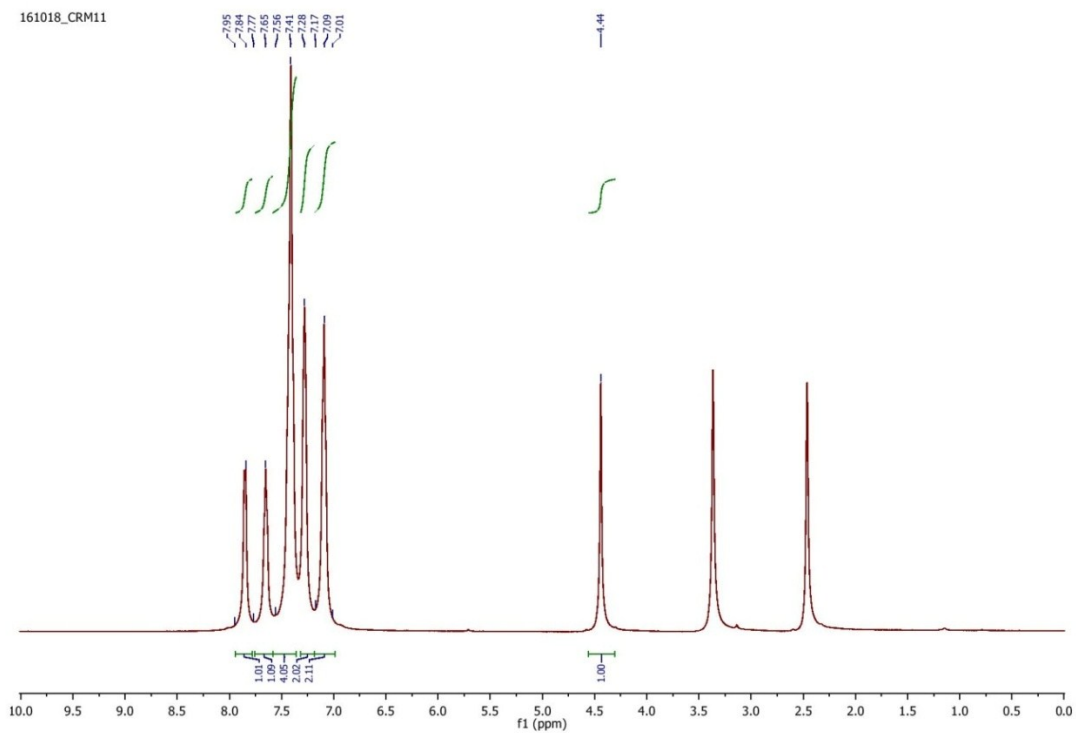


Figure 3. ^1H NMR of **7f** in $\text{DMSO-}d_6$

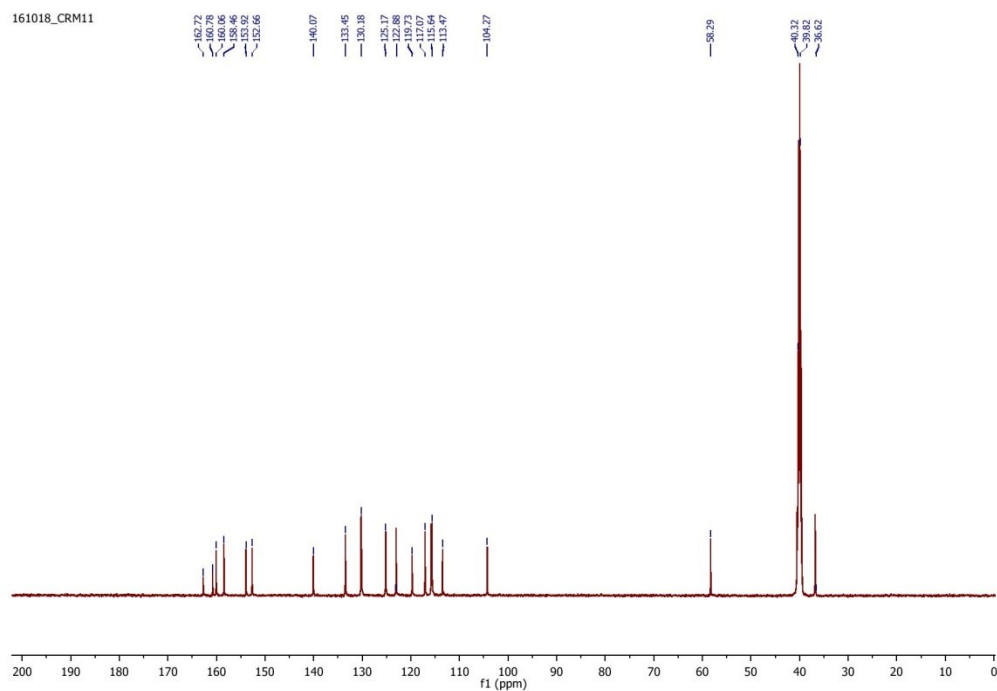


Figure 4. ^{13}C NMR of **7f** in $\text{DMSO-}d_6$

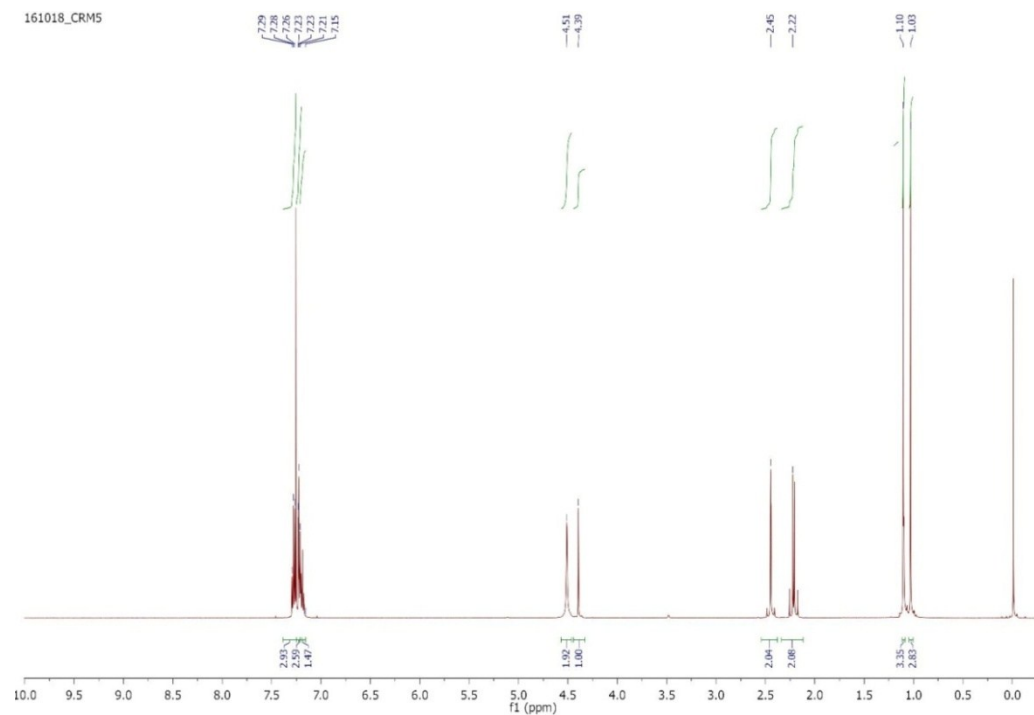


Figure 5. ^1H NMR of **9a** in $\text{DMSO-}d_6$

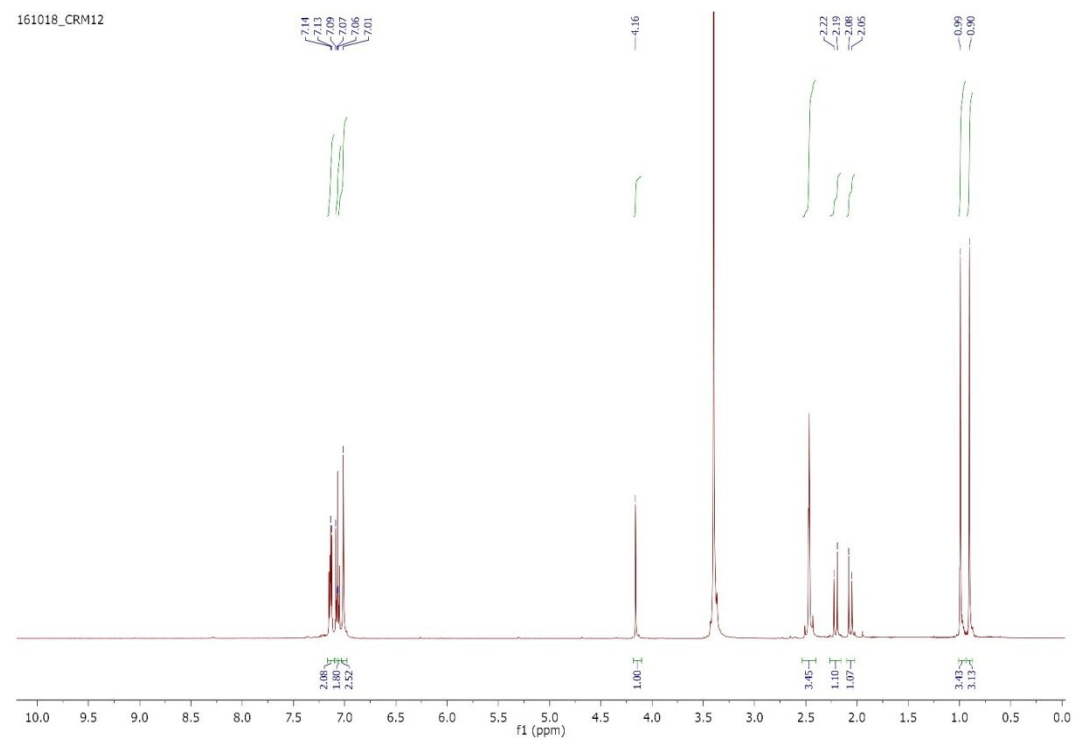


Figure 6. ^1H NMR of **9f** in $\text{DMSO-}d_6$

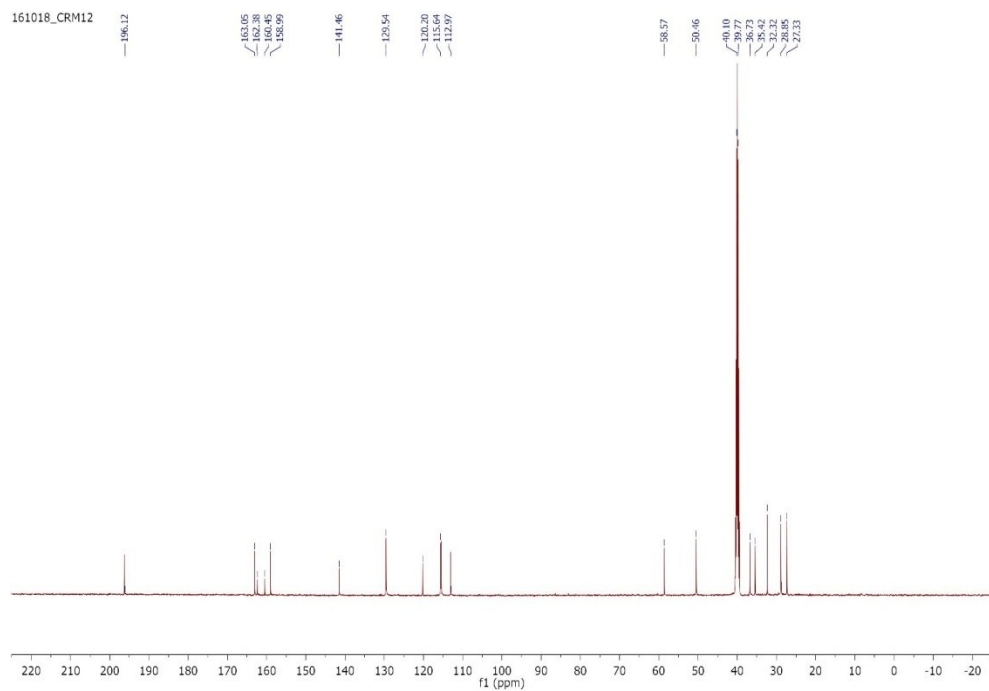


Figure 7. ^{13}C NMR of **9f** in $\text{DMSO-}d_6$

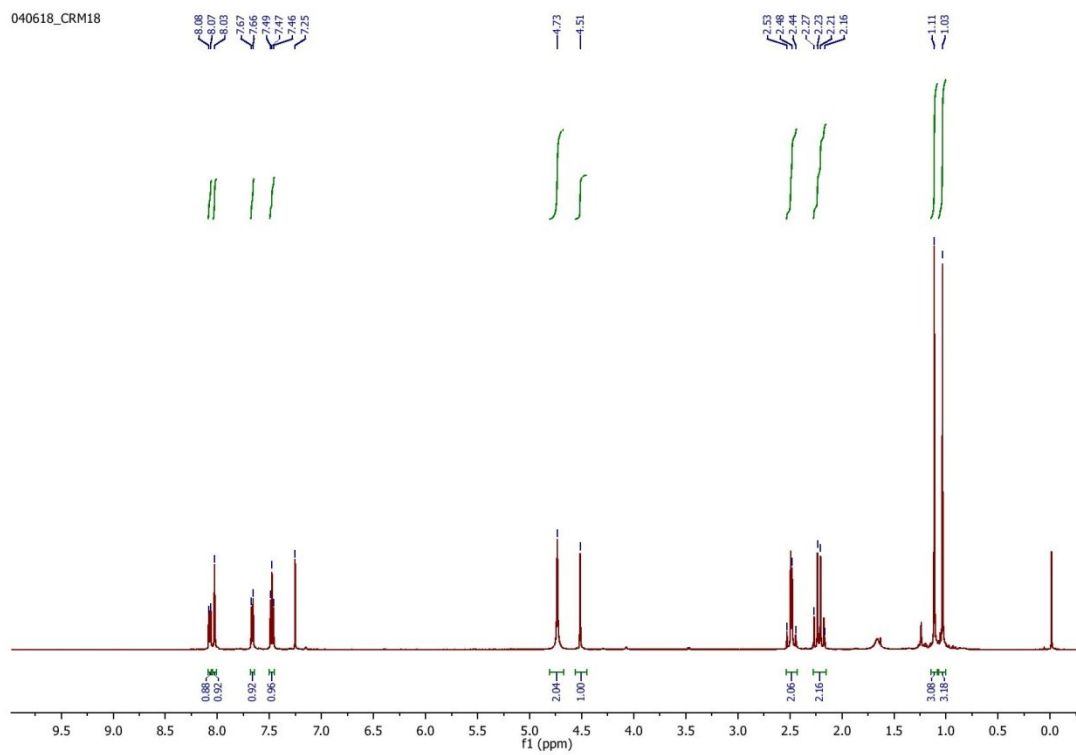


Figure 8. ^1H NMR of **9g** in $\text{DMSO-}d_6$

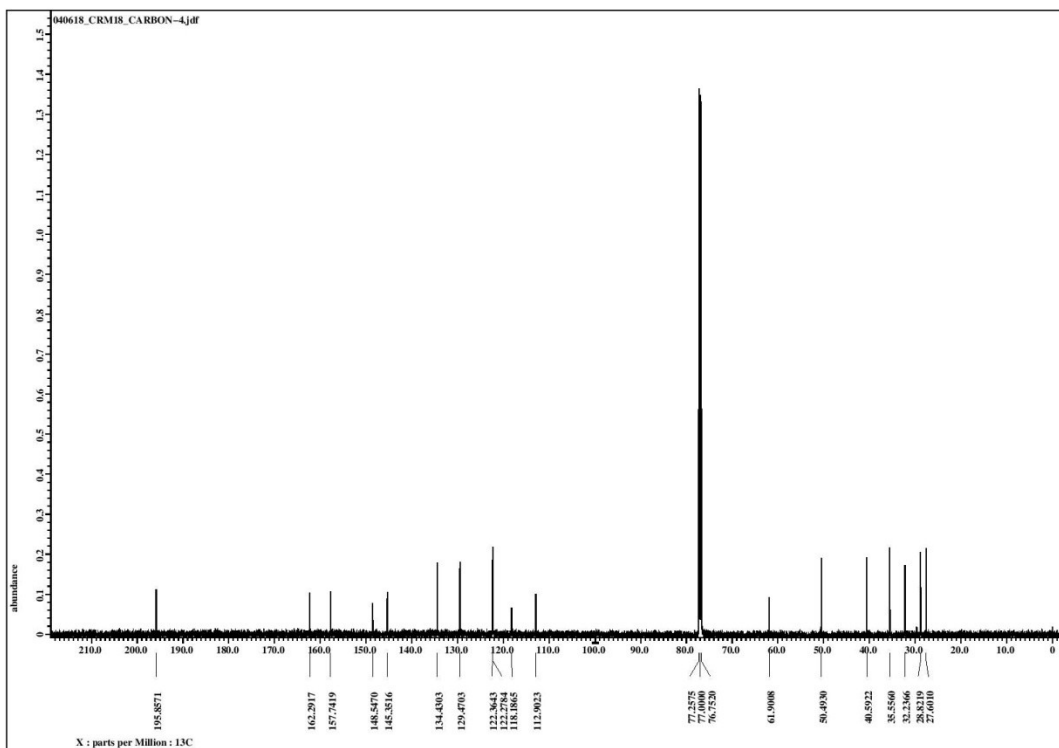


Figure 9. ¹H NMR of 9k in DMSO-d₆

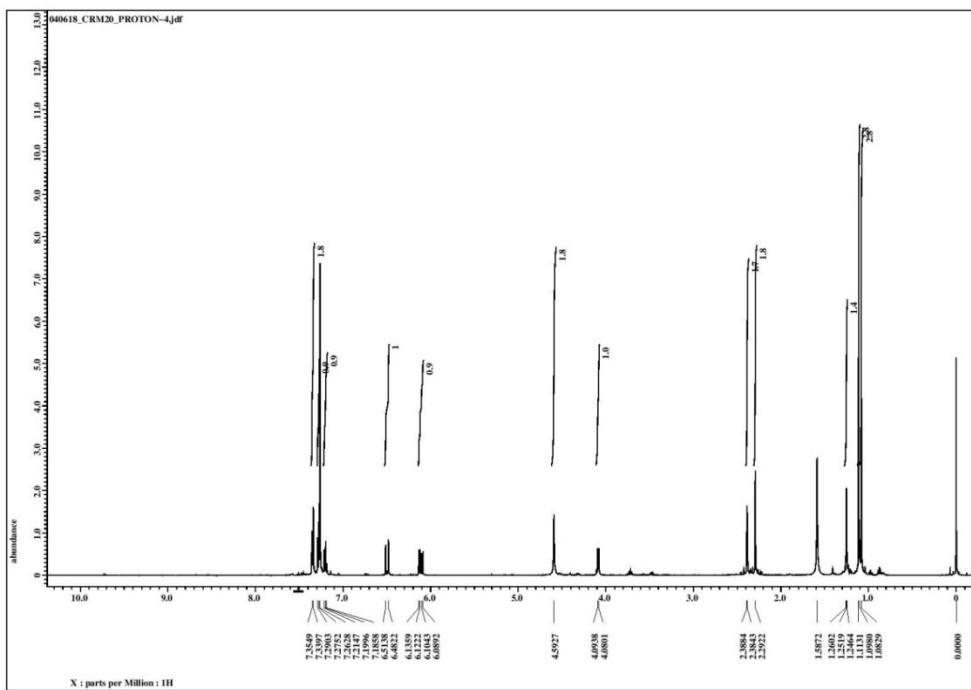


Figure 10. ¹H NMR of 9k in DMSO-d₆

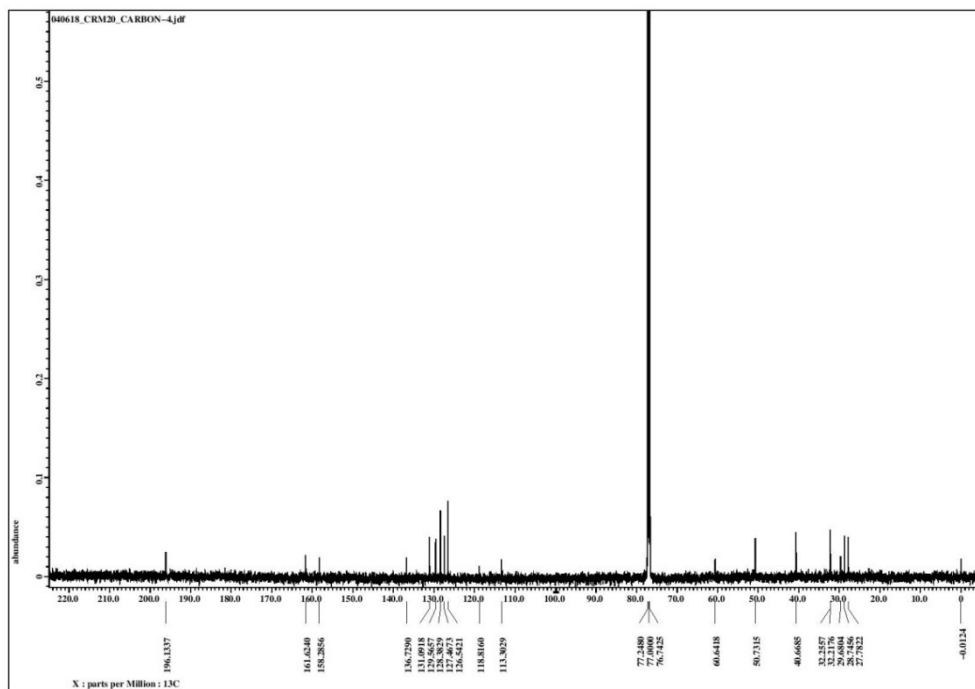


Figure 11. ^{13}C NMR of **9k** in $\text{DMSO-}d_6$

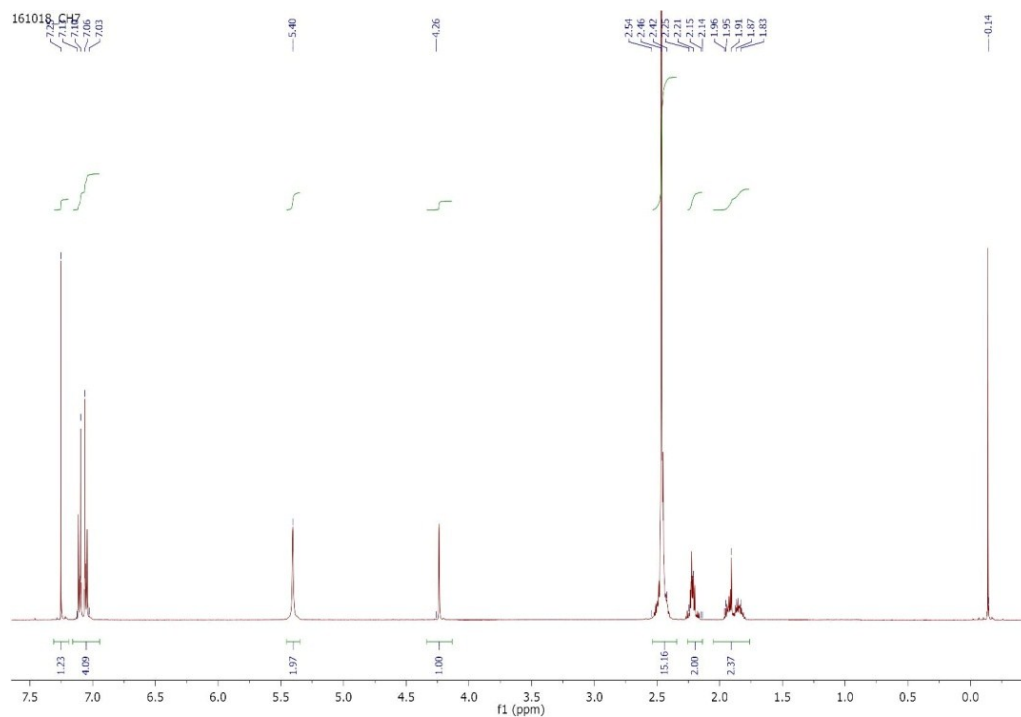


Figure 12 ^1H NMR of **12a** in CDCl_3

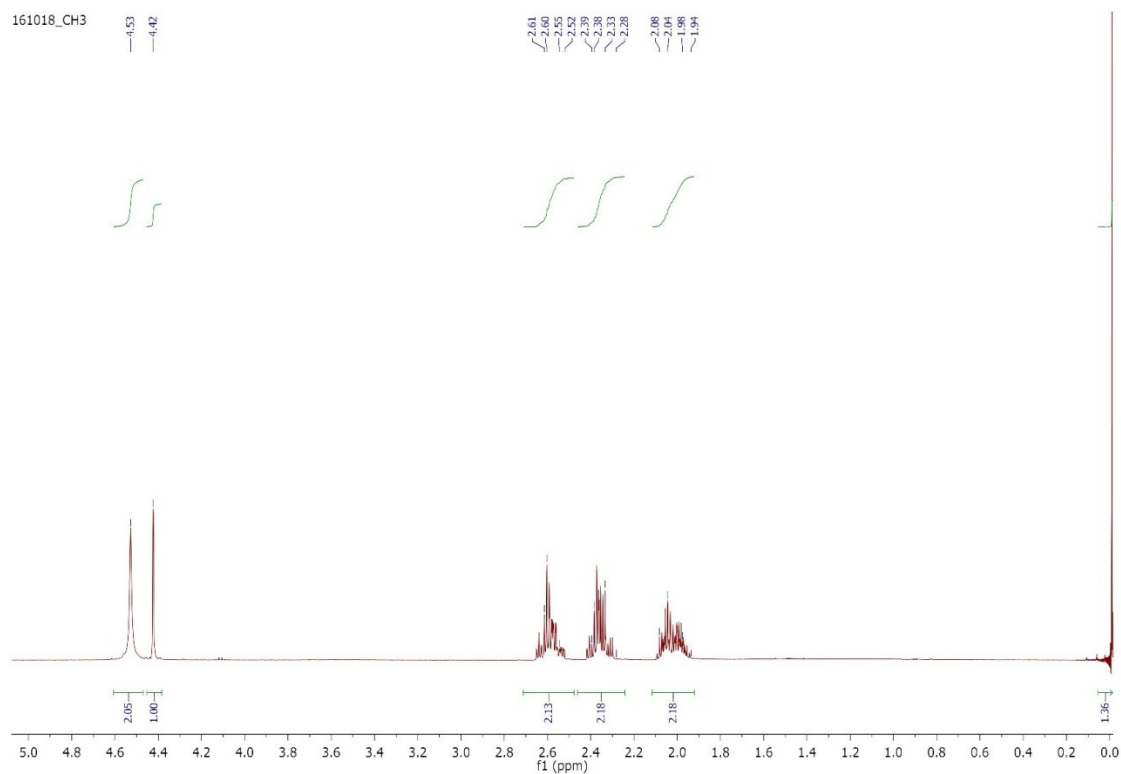


Figure 13 ^1H NMR of **12b** in CDCl_3

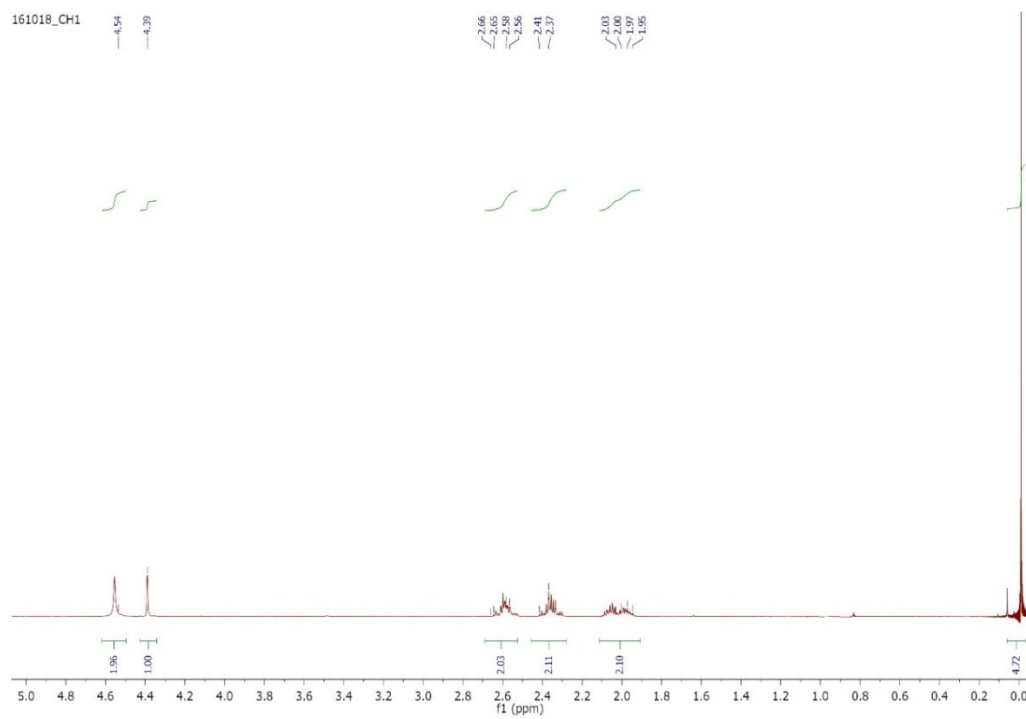


Figure 14 ^1H NMR of **12c(a)** in CDCl_3

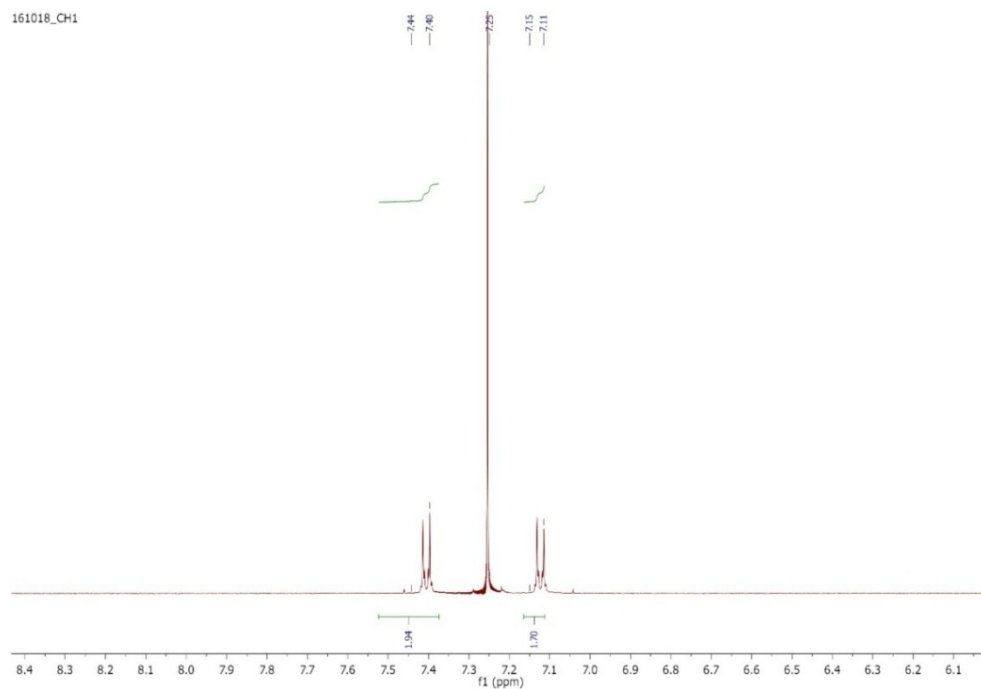


Figure 15 ^1H NMR of **12c(b)** in CDCl_3

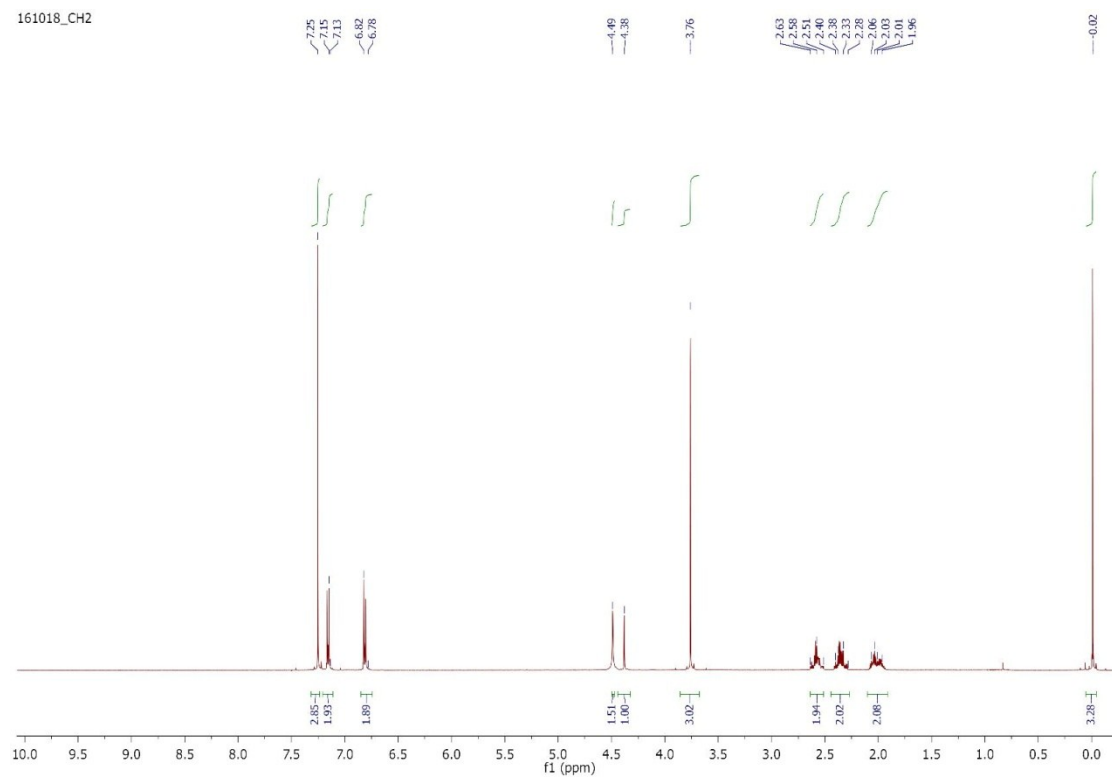


Figure 16. ^1H NMR of **12d** in CDCl_3

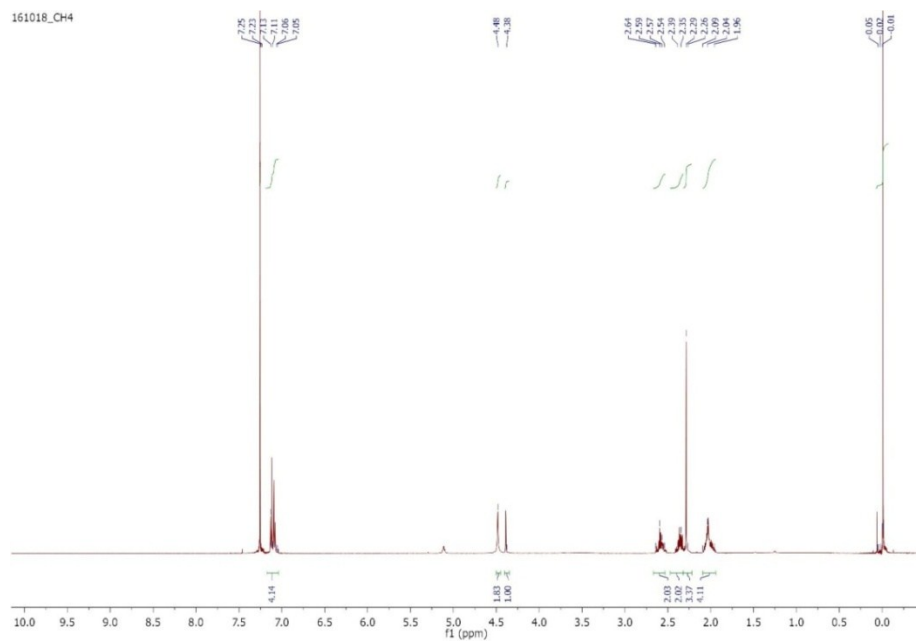


Figure 17. ^1H NMR of **12e** in CDCl_3

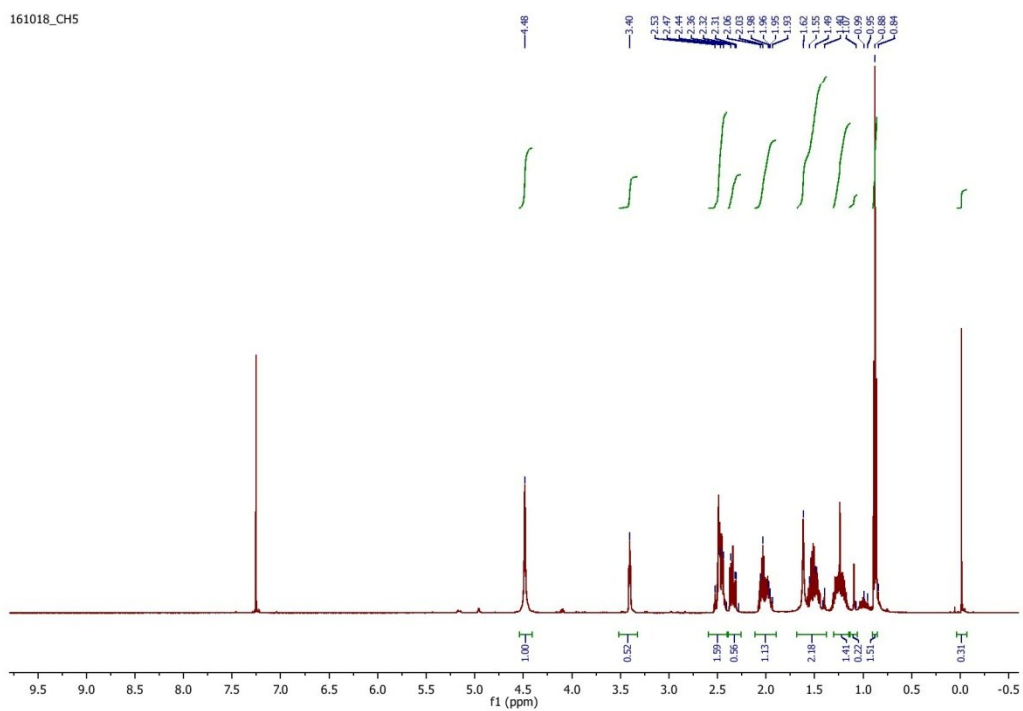


Figure 18. ^1H NMR of **12f** in CDCl_3

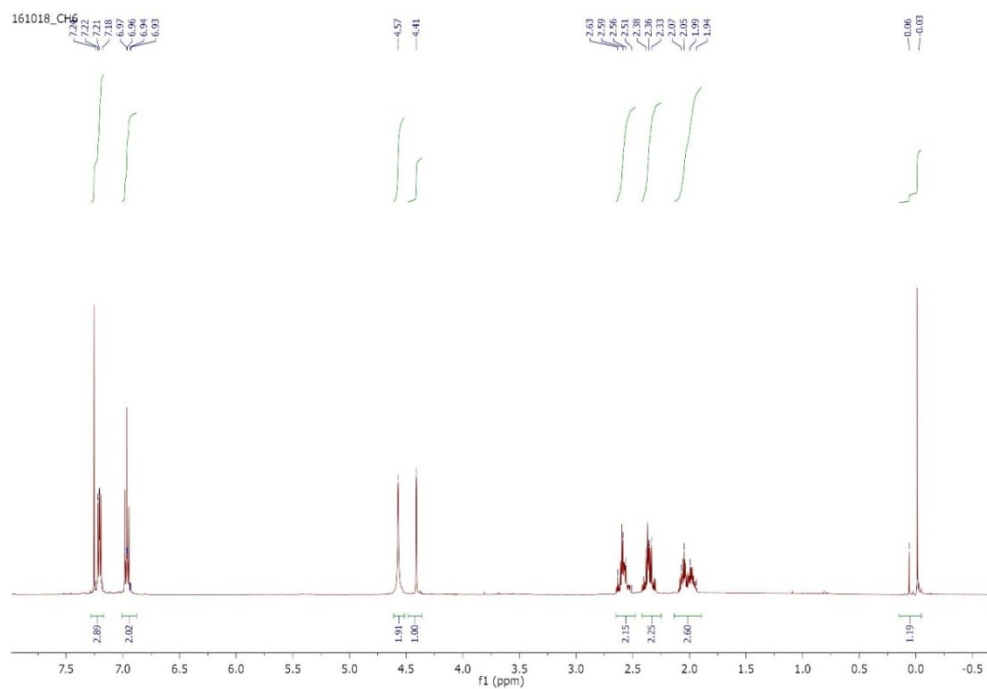


Figure 19. ^1H NMR of **12g** in CDCl_3

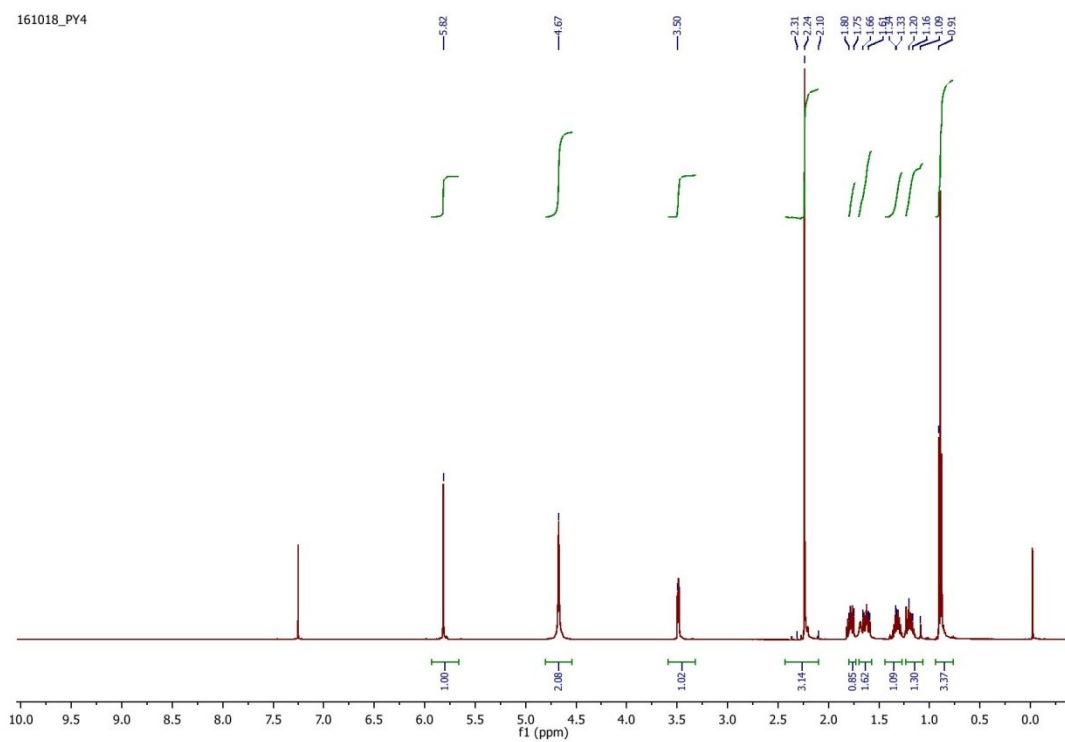


Figure 20. ^1H NMR of **11b** in CDCl_3

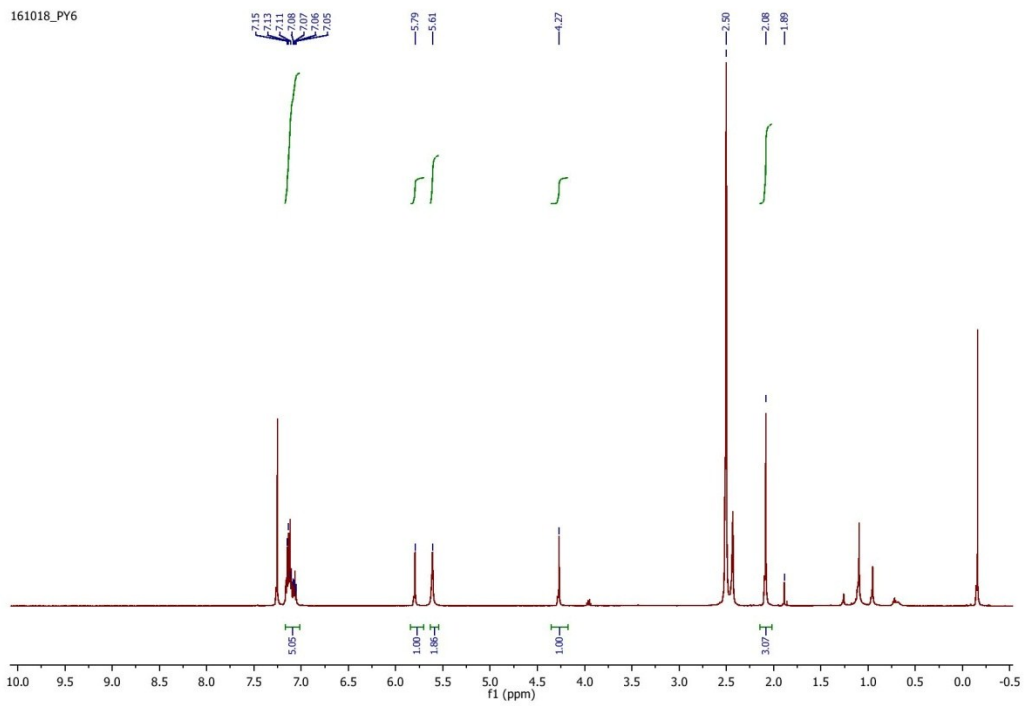


Figure 21. ^1H NMR of **11c** in CDCl_3

References

1. P. Das, A. Dutta, A. Bhaumik and C. Mukhopadhyay *Green Chem.*, **2014**, *16*, 1426-1435.