Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

A Practical Green Approach to Diversified Spirochromene/Spiropyran Scaffolds via a Glucose-Water Synergy Driven Organocatalytic System

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Experimental

General Remarks

All chemicals were reagent grade and purchased from Aldrich, Alfa Aesar, Merck, Spectrochem and Qualigens and were used without further purification. The reactions were monitored using pre-coated Aluminium TLC plates of silica gel G/UV-254 of 0.25 mm thickness (Merck 60 F-254). Column chromatography was performed using silica gel (60-120) and (100-200). NMR spectra were recorded on a Bruker Avance-II 400FT spectrometer at 400 MHz, 300 MHz (^{1}H) and 100 MHz. 75 MHz (^{13}C) in DMSO using TMS as an internal reference. Mass spectra (ESIMS) were obtained on a Waters UPLC-TQD mass spectrometer. Elemental analyses were carried out in a Thermo Scientific (FLASH 2000) CHN Elemental Analyser. Melting points were determined by open glass capillary method and were uncorrected.

General Experimental Procedure [ab]

Compound 4a-4k: To a 50 mL round bottom flask containing 40 mol% of glucose in 5 mL of water was added the respective isatins (1 mmol) and the respective CH-acids (1 mmol) and the resulting mixture was stirred at 45 °C. On completion of the reaction (TLC control), the reaction mixture was allowed to stand undisturbed for 15 minutes whence the solid product that settled down was filtered, washed with water and dried. The crude product was then recrystallized from ethanol to obtain the pure compound. The aqueous filtrate so obtained was then reused for the next cycle. Only a slight decrease in the yield of the product was observed even after reusing the glucose solution for three cycles, thereby amply demonstrating the recyclability of glucose as a catalyst.

Compound 6a-6d & 8a-8d: To a 50 mL round bottom flask containing 40 mol% of glucose in 5 mL of water was added ninhydrin/acenaphthelene (1 mmol) and the respective CH-acids (1 mmol) and the resulting mixture was stirred at 45 °C. On completion of the reaction (TLC control), the reaction mixture was allowed to stand undisturbed for 15 minutes whence the solid product which settled down was filtered, washed with water and dried. The crude product was then recrystallized from ethanol to obtain the pure compound. The aqueous filtrate so obtained was then reused for the next cycle. Only a slight decrease in the yield of the product was observed even after reusing the glucose solution for three cycles, thereby amply demonstrating the recyclability of glucose as a catalyst.

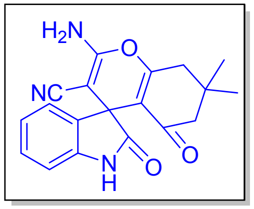
Compound 10a-10d: To a 50 mL round bottom flask containing 40 mol% of glucose in 5 mL of water was added the respective aldehydes (1 mmol) and respective CH-acids (1 mmol) and the resulting mixture was stirred at 55 °C. On completion of the reaction (TLC control), the reaction mixture was allowed to stand undisturbed for 15 minutes whence the solid product which settled down was filtered, washed with water and dried. The crude product was then recrystallized from ethanol to obtain the pure compound. The aqueous filtrate so obtained was then reused for the next cycle. Only a slight decrease in the yield of the product was observed even after reusing the glucose solution for three cycles, thereby amply demonstrating the recyclability of glucose as a catalyst.

[a] *In those instances where required purity could not be achieved through recrystallization, column chromatography (100-200 mesh silica gel; EtOAc/Hexane) was performed to obtain the pure molecules.*

[b] *In some cases the temperature required was 55 °C.*

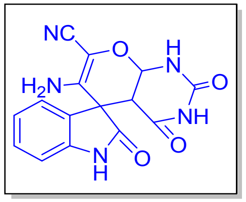
Figure S1. The phenomenon of the multicomponent reaction between Isatin, Malononitrile and Dimedone. (A) The reaction mixture at the completion of the reaction. (B) The product precipitated after allowed the reaction to stand.

Compound 4a



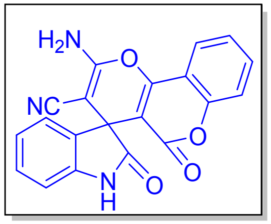
2-amino-7,7-dimethyl-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carbonitrile Yield: 96%, 321.6 mg; White solid; Mp: 290-293ºC[14k] ^{1}HNMR (300 MHz, DMSO-d6) (δ, ppm) 1.02-0.99 (6H, m), 2.14-2.11 (2H, m), 2.55-2.50 (2H, m), 6.80-6.77 (1H, m), 6.91-6.86 (1H, m), 6.99-6.96 (1H, m), 6.97-6.95 (2H, s), 7.25 (2H, m), 7.16-7.11 (1H, m), 10.42 (1H, s); ^{13}CNMR (400 MHz, DMSO-d6) (δ, ppm) 27.0, 27.6, 32.0, 40.3, 46.8, 50.0, 57.4, 109.3, 110.8, 117.4, 121.7, 123.0, 128.2, 134.4, 142.0, 158.3, 164.2, 178.1, 195.0; MS (ESI): *m/z* 335; found 336 $[M+H]^+$; Anal. calcd for $C_{19}H_{17}N_3O_3$: C 68.09; H 5.10; N 12.49; Found C 68.05, H 5.12, N 12.55%.

Compound 4c



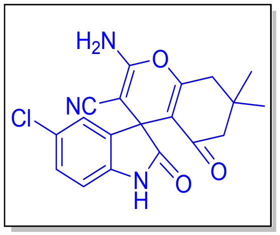
6'-amino-2,2',4'-trioxo-1',2',3',4',4a',8a'-hexahydrospiro[indoline-3,5'-pyrano[2,3-d]pyrimidine]-7'-carbonitrile Yield: 92%, 299.0 mg; Mp: 297-298ºC[14e] ^{1}HNMR (300 MHz, DMSO-d6) (δ, ppm) 6.8-6.78 (1H, m), 6.93-6.88 (1H, m), 7.18-7.12 (3H, m), 7.39 (2H, s), 10.50 (1H, s), 11.15 (1H, s), 12.29 (1H, brs); ^{13}CNMR (400 MHz, DMSO-d6) (δ, ppm) 40.34, 46.7, 57.8, 86.8, 109.4, 117.0, 121.9, 123.8, 133.6, 128.5, 142.1, 149.3, 153.4, 158.3, 161.5, 177.7; MS (ESI): *m/z* 325; found 326 $[M+H]^+$; Anal calcd for $C_{15}H_{11}N_5O_4$: C 55.35; H 3.45; N 21.50; Found C 55.39, H 3.41, N 21.53%.

Compound 4d



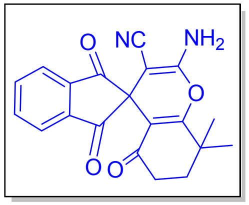
2'-amino-2,5'-dioxo-5'H-spiro[indoline-3,4'-pyrano[3,2-c] chromene]-3'-carbonitrile Yield: 90%, 321.3 mg; Mp: 289-290ºC^{14t} ^{1}HNMR (400 MHz, DMSO-d6) (δ, ppm) 1.05-1.04 (6H, d, J =13.84), 2.13 (2H, *q*, *J* = 16), 2.56-2.51 (2H, m), 6.81-6.79 (1H, m), 6.91-6.87 (1H, m), 6.97-6.95 (1H, m), 8.02 (1H, m), 10.49 (1H, m); MS (ESI): *m/z* 357; found 358 $[M+H]^+$; Anal calcd for $C_{20}H_{11}N_3O_4$: C 67.20; H 3.12; N 11.75; Found C 67.23, H 3.10, N 11.76%.

Compound 4k



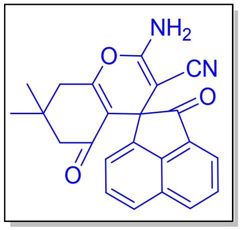
2-Amino-5'-chloro-7,7-dimethyl-2',5-dioxo-5,6,7,8-tetrahydrospiro [chromene-4,3 '-indoline]-3-carbonitrile Yield: 95%, 351.3 mg; Mp: 290-291ºC[14c] ^{1}H NMR (400MHz, DMSO-d6): δ = 1.02 (6H, s), 2.161-2.164 (2H, m), 2.51-2.57 (2H, m), 6.81 (1H, d, J = 8.2 Hz), 7.11 (1H, d, J = 2.1 Hz), 7.20 (1H, dd, J=8.3 & 2.2), 7.32 (2H, s), 10.55 (1H, s) ppm. MS (ESI):m/z 369; found 370 $[M+H]^+$; Anal. Calcd. for $C_{19}H_{16}ClN_3O_3$: C, 61.71; H, 4.36; N, 11.36; Found: C, 60.92; H, 4.41; N, 10.37.

Compound 6b



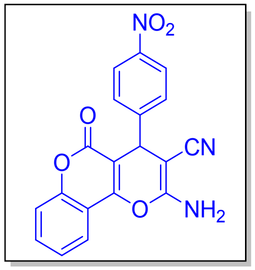
2-amino-8,8-dimethyl-1',3',5-trioxo-1',3',5,6,7,8-hexahydrospiro[chromene-4,2'-indene]-3-carbonitrile Yield: 88%, 306.5 mg; Mp: 291-294ºC[14s] 1 H-NMR (DMSO-d6, 400 MHz): d (ppm) = 1.04 (6H, s), 2.20 (2H, s), 2.62 (2H, s), 7.66 (2H, s), 8.00-8.06 (4H, m) ppm. 13C-NMR (DMSO-d6, 100 MHz): 27.1, 32.4, 48.9, 51.7, 53.0, 109.9, 116.8, 123.1, 136.6, 140.5, 159.8, 166.4, 196.0, 199.7 ppm. MS (ESI):m/z 348; found 349 $[M+H]^+$; Anal. Cacld for $C_{23}H_{18}N_2O_3$: C, 74.58; H, 4.90; N, 7.56. Found: C, 75.10; H, 4.79; N, 7.19

Compound 8a

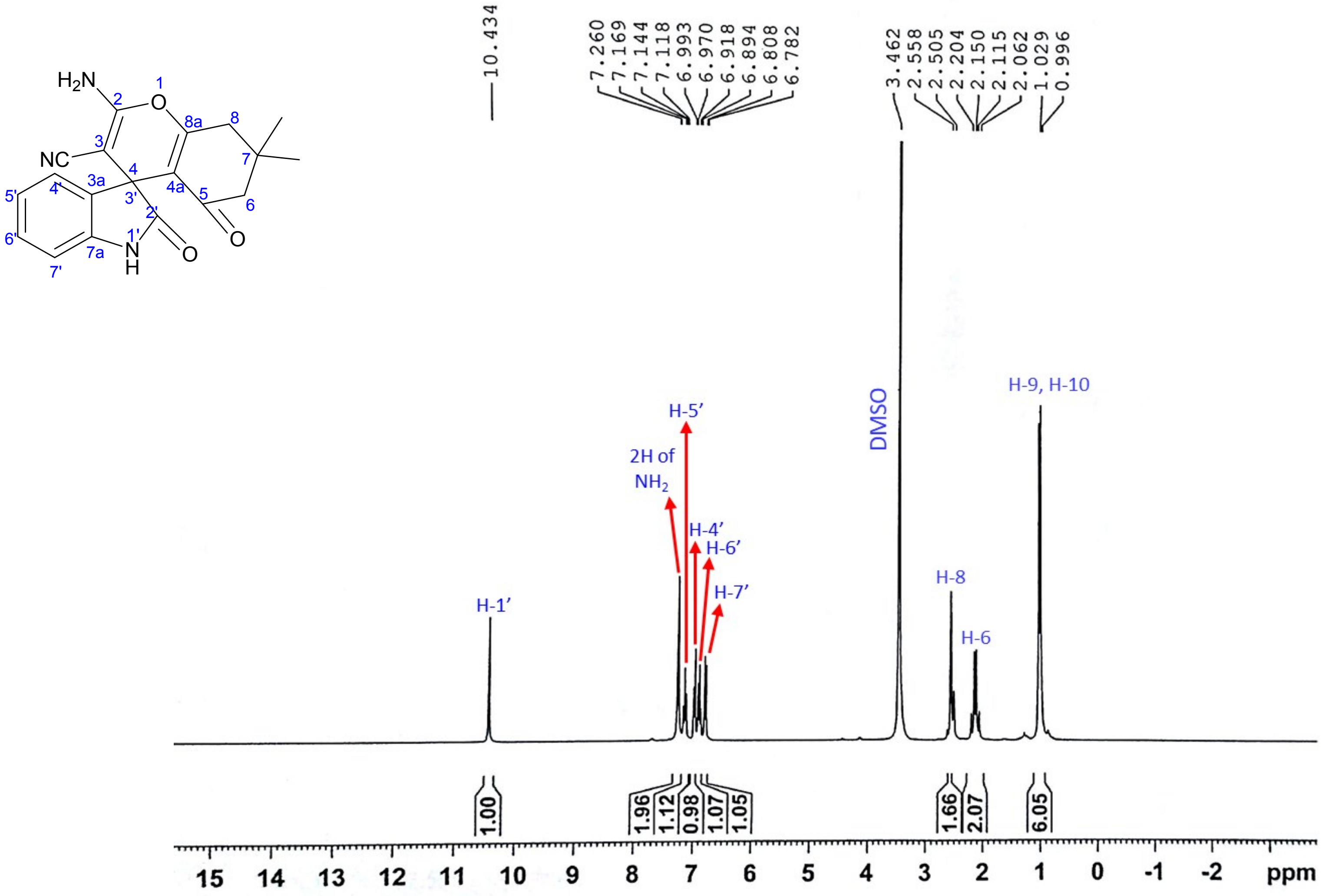


2'-amino-7',7'-dimethyl-2,5'-dioxo-5',6',7',8'-tetrahydro-2H-spiro[acenaphthylene-1,4'-chromene]-3'-carbonitrile Yield: 95%, 351.6 mg; Mp: 269-272ºC[14t] 1HNMR (DMSO-d6, 400 MHz): δ = 1.04 (6H, d, J=6.7 Hz), 2.09-2.10 (2H, m), 2.63 (2H, s), 7.34 (2H, s), 7.40 (1H, d, J = 6.5 Hz,), 7.66 (1H, t, J = 7.3 Hz), 7.84 (1H, t, J = 7.2 Hz), 7.95 (2H, d, J=7.2 Hz), 8.28 (1H, d, J = 7.8 Hz).13C NMR (DMSO-d6, 400 MHz): δ =27.1, 27.4, 32.0, 49.6, 50.9, 58.0, 112.0, 117.4, 119.8, 121.4, 124.5, 128.4, 128.8, 129.7, 131.4, 132.1, 140.5, 143.1, 158.7, 164.5, 195.2, 203.5 ppm. MS (ESI):m/z 370; found 371 $[M+H]^+$; Anal. Cacld for $C_{23}H_{18}N_2O_3$: C, 74.58; H, 4.90; N, 7.56. Found: C, 75.10; H, 4.79; N, 7.19

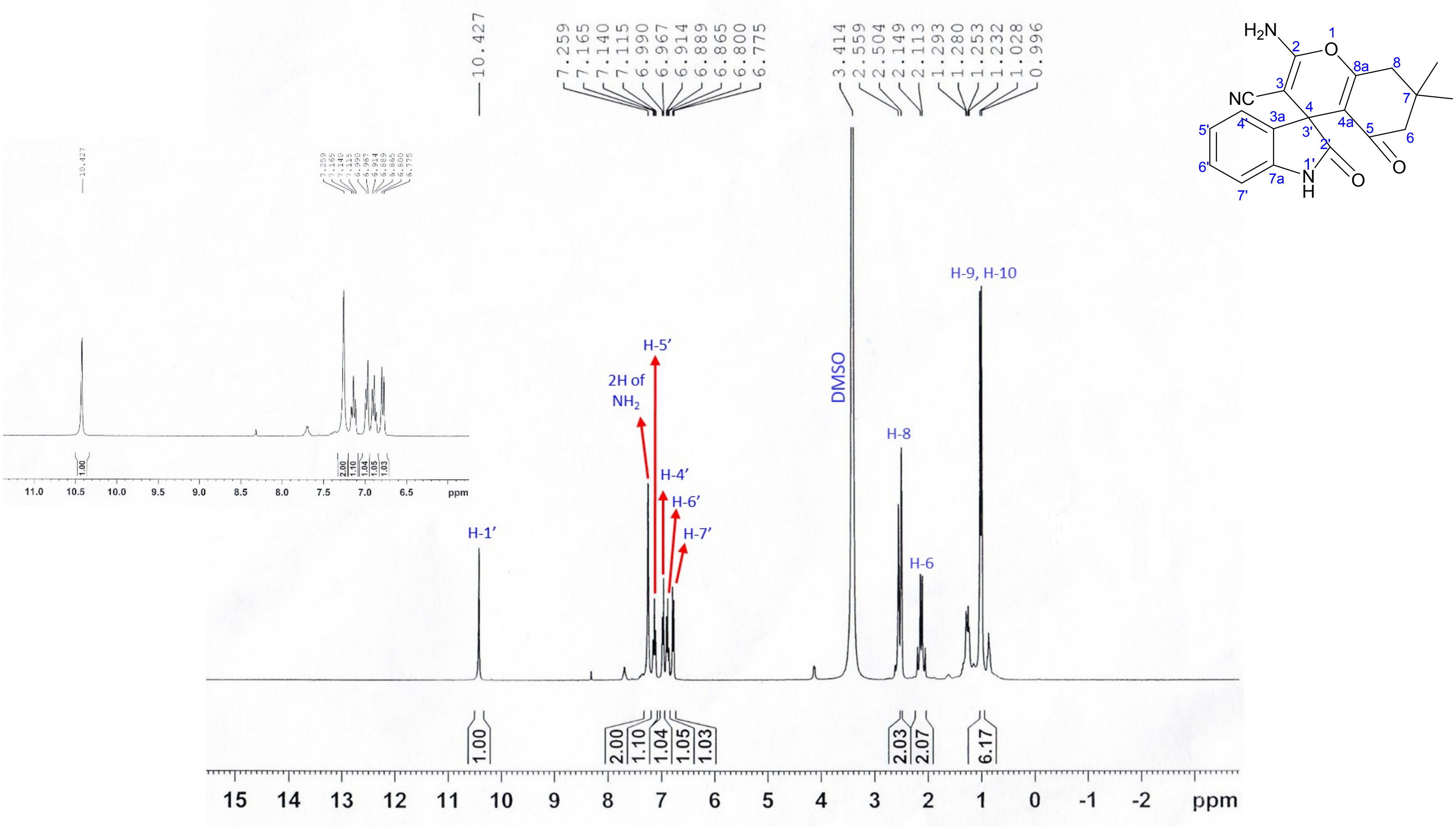
Compound 10c



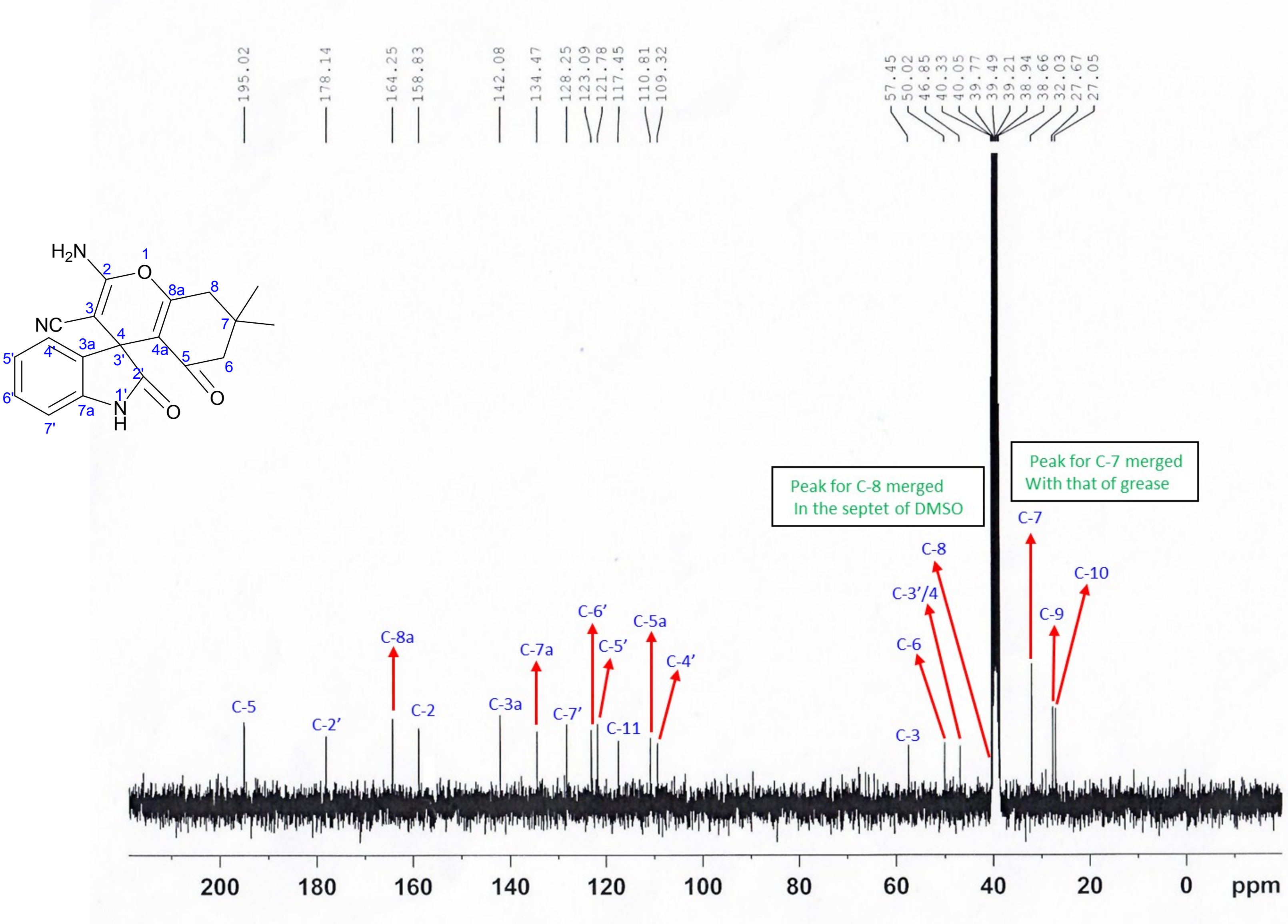
2-amino-4-(4-nitrophenyl)-5-oxo-4,5-dihydropyrano[3,2-c] chromene-3-carbonitrile Yield: 83%, 299.9 mg; Mp: 257-259 ºC[15d] 1H NMR (DMSO-d_6) (δ, ppm): 4.62 (1H, s), 7.36-7.44 (2H, m), 7.45 (2H, s), 7.52-7.54 (2H, m), 7.63-7.67 (1H, m) 7.90 (1H, dd, J=8.0 &1.6), 8.12-8.14 (2H, d, J=8.8 Hz) ppm. MS (ESI):m/z 361; found 362 $[M+H]^+$; Anal. calcd for $C_{19}H_{11}N_3O_5$: C 63.16, H 3.07, N 11.63; found C 63.71 H 3.10, N 11.21 %.



^{1}H NMR spectrum of compound 4a (crude product)



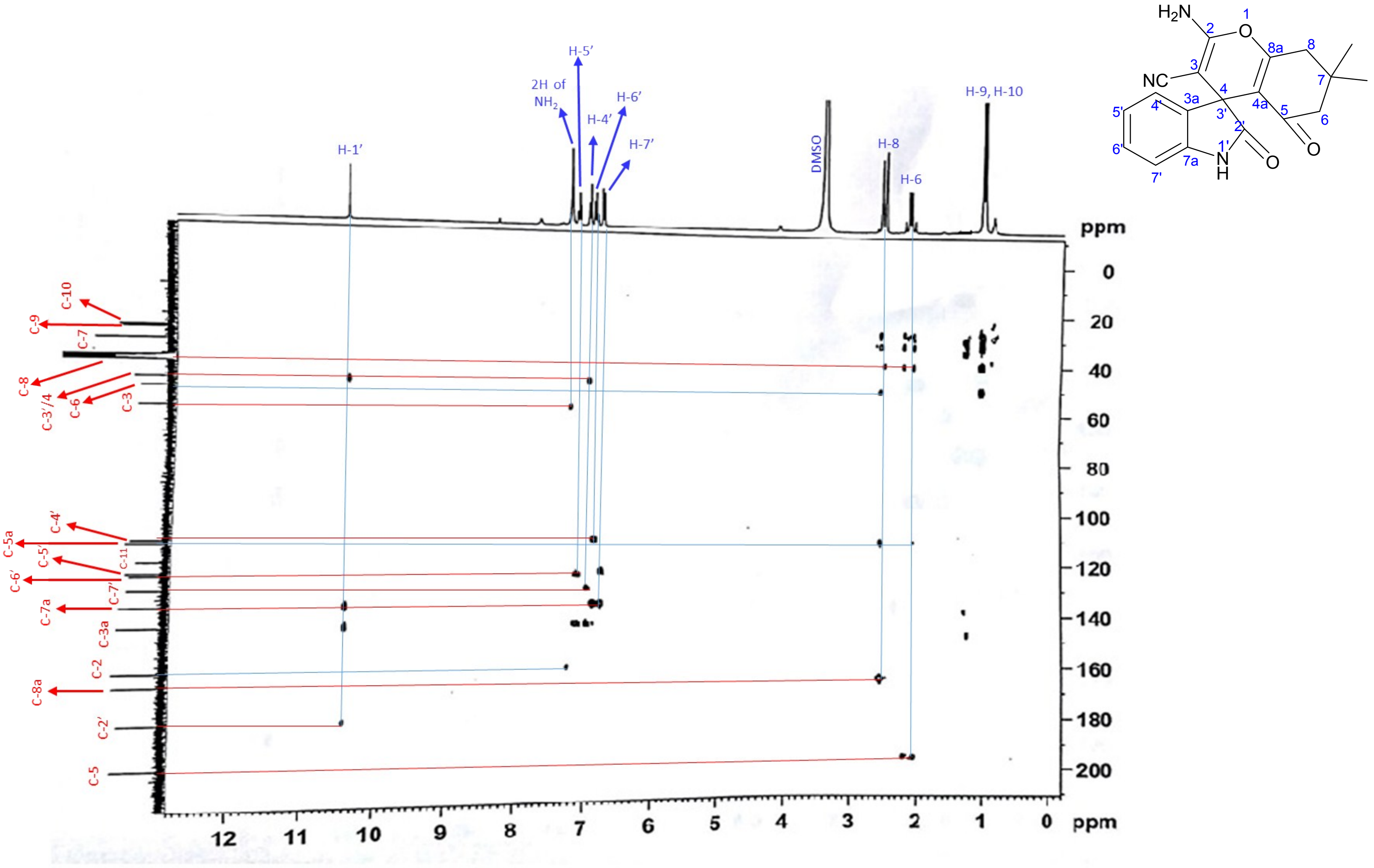
^{1}H NMR spectrum of compound 4a and its expansion (Column purified product)



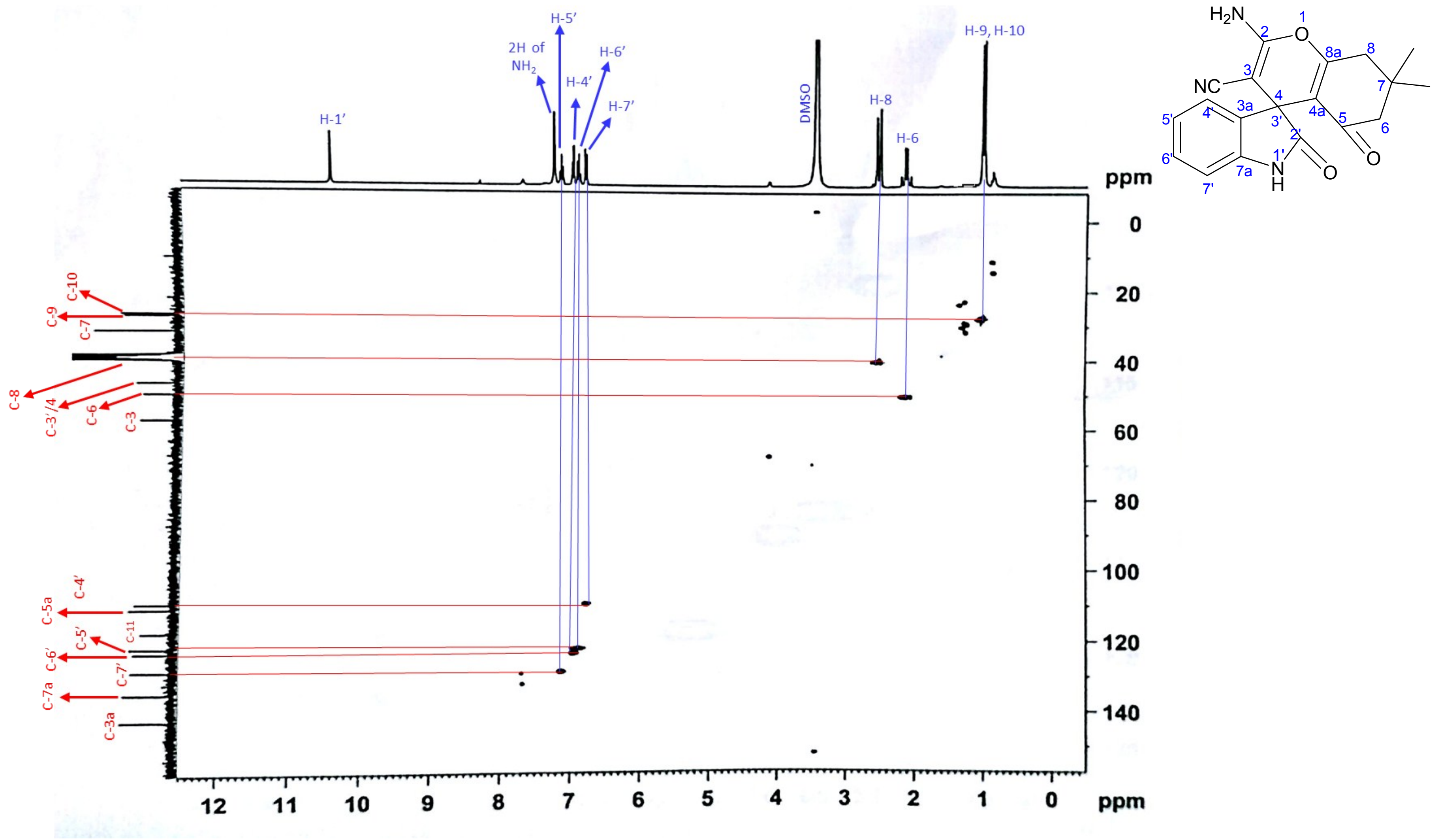
Peak for C-8 merged
In the septet of DMSO

Peak for C-7 merged
With that of grease

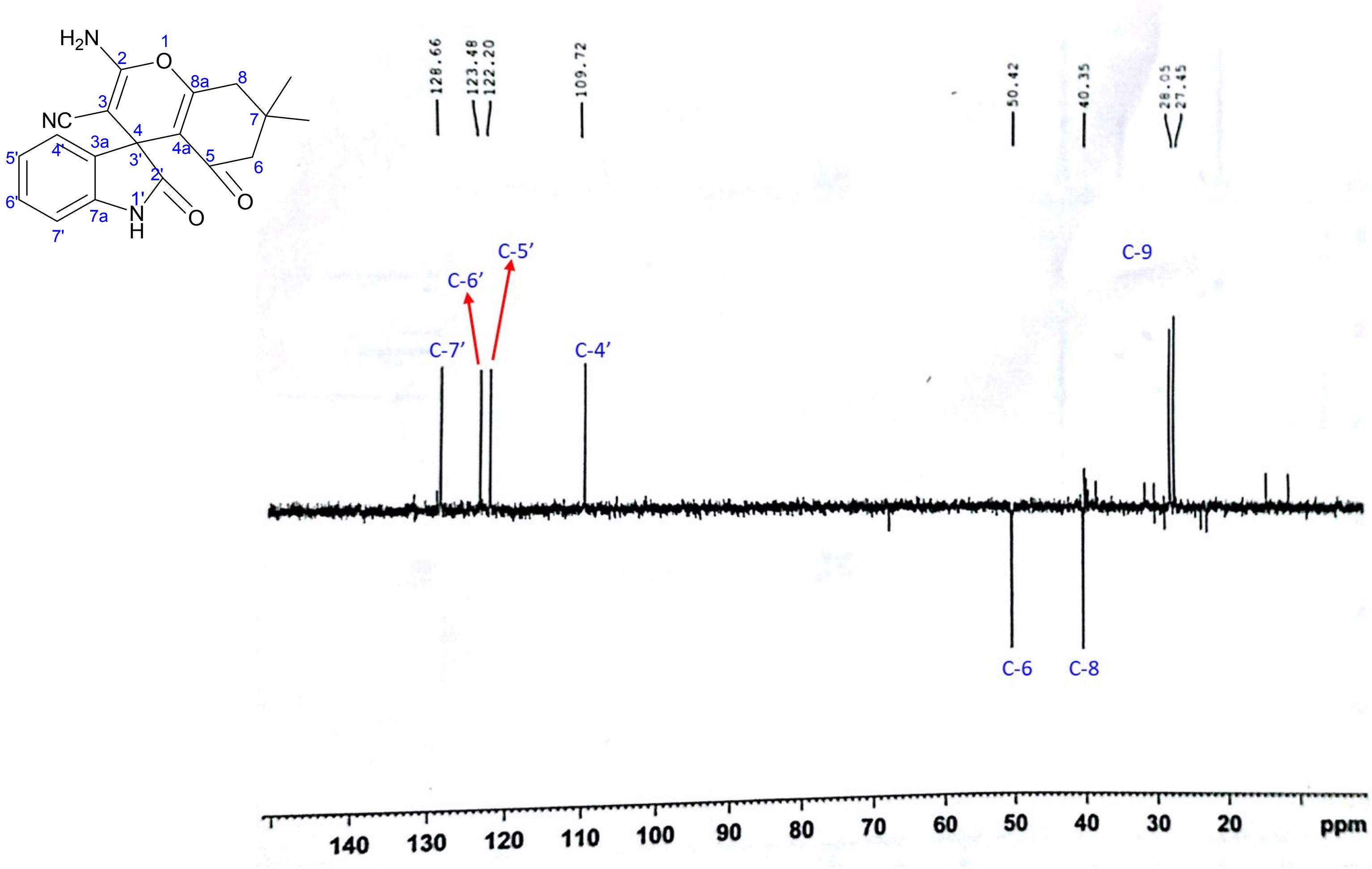
^{13}C NMR spectrum of compound 4a



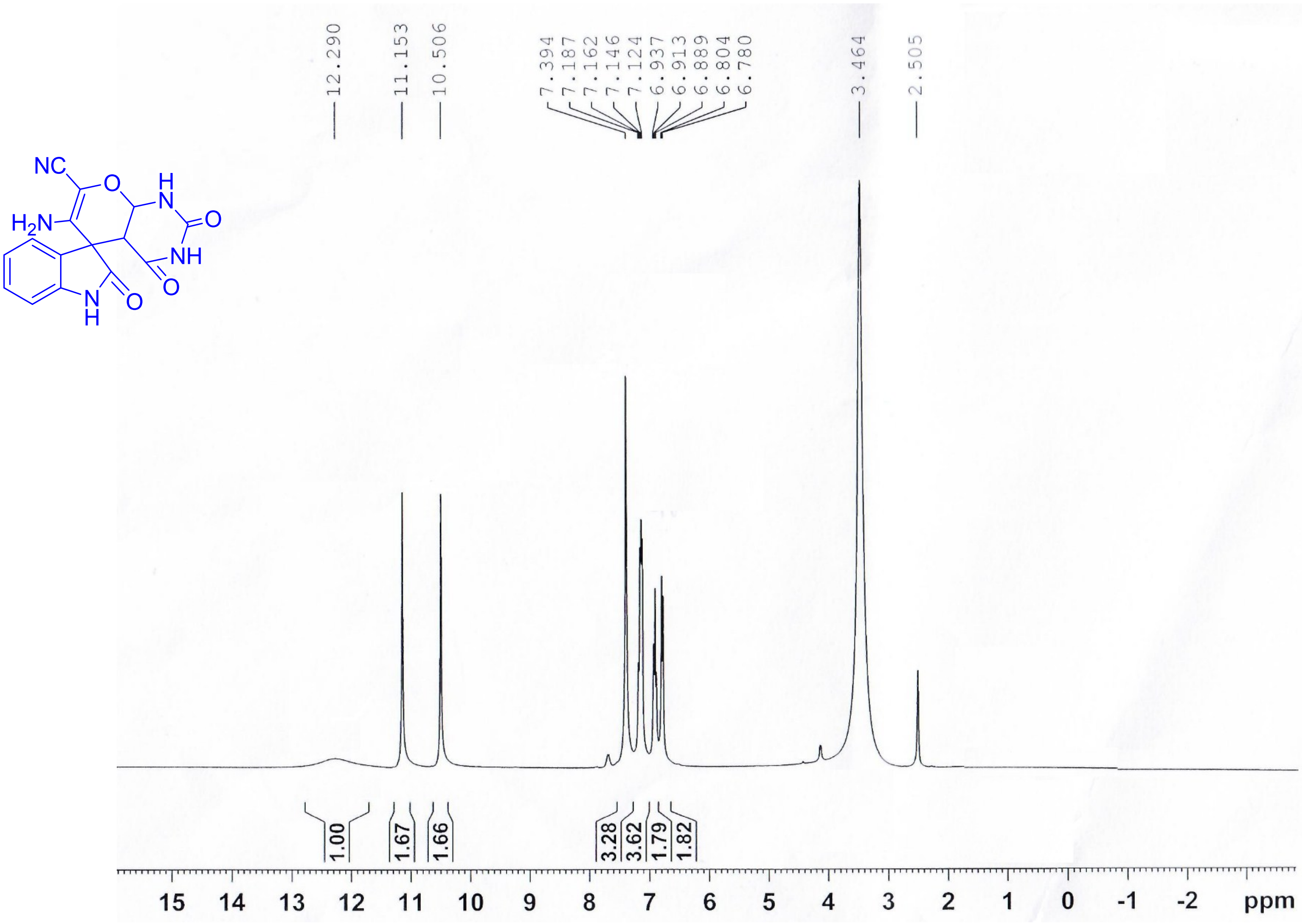
HMBC spectrum of compound 4a



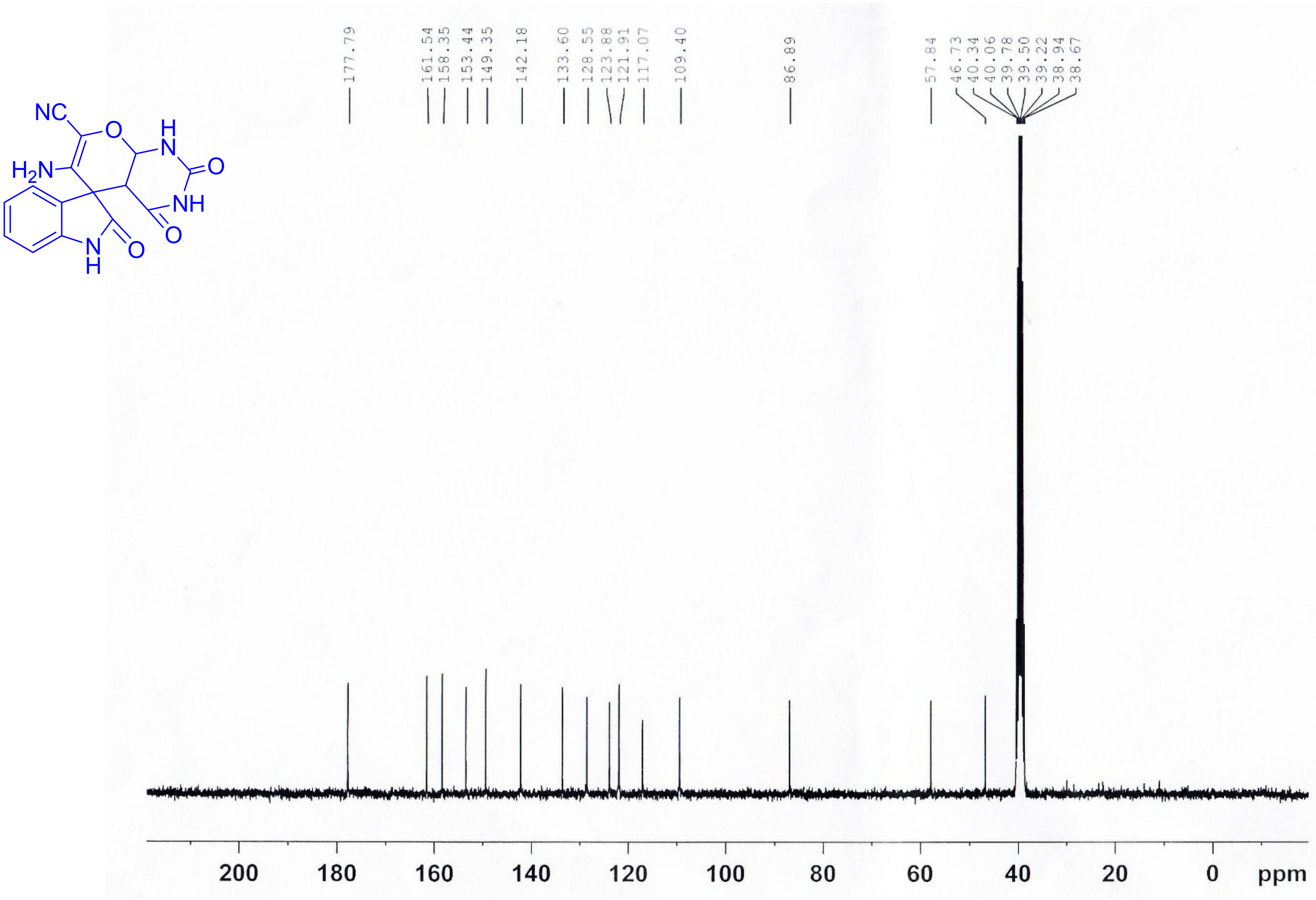
HSQC spectrum of compound 4a



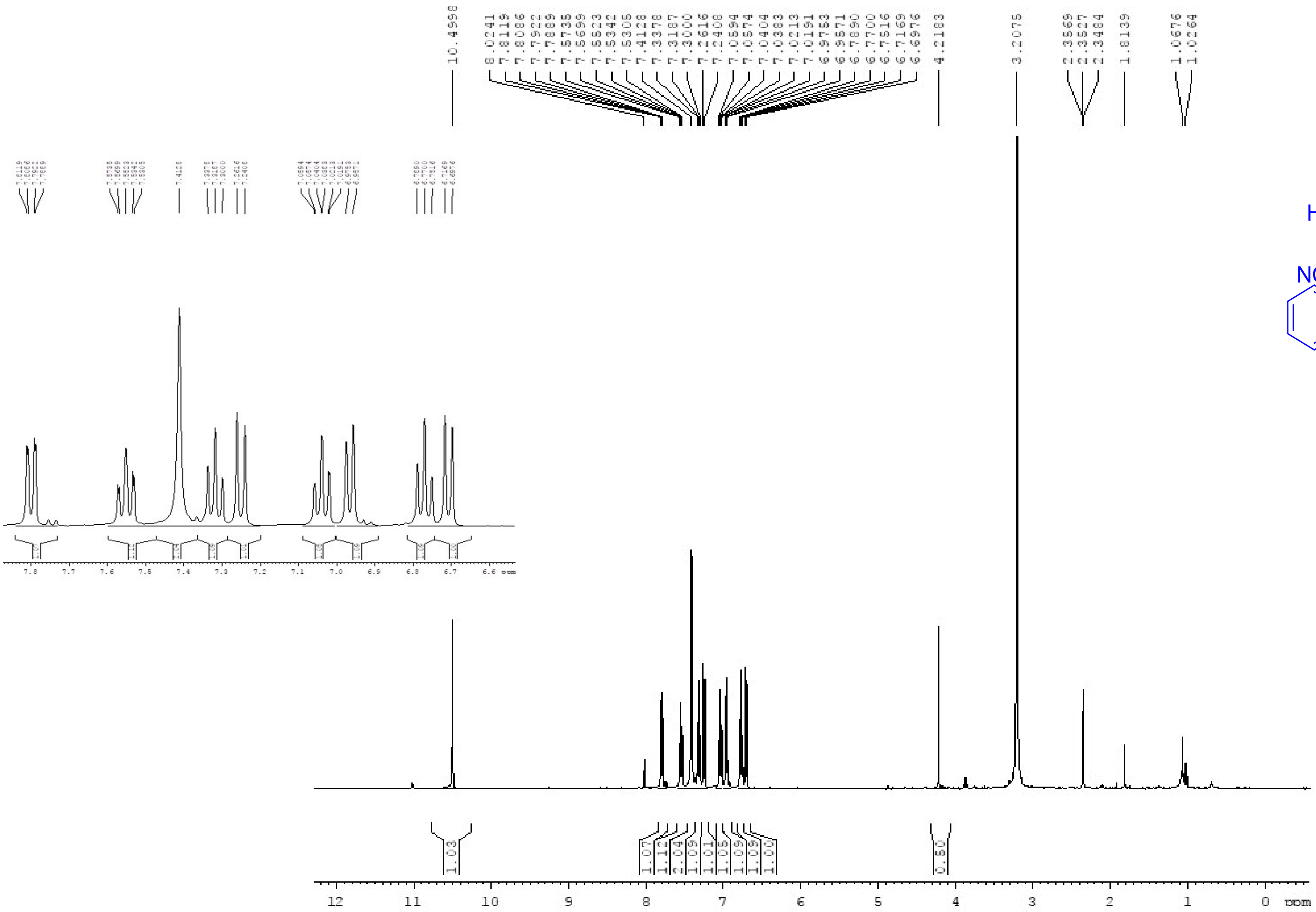
DEPT135 spectrum of compound 4a

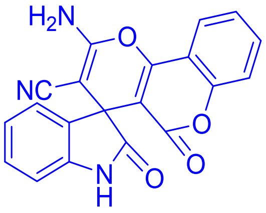


^{1}H NMR spectrum of compound 4c

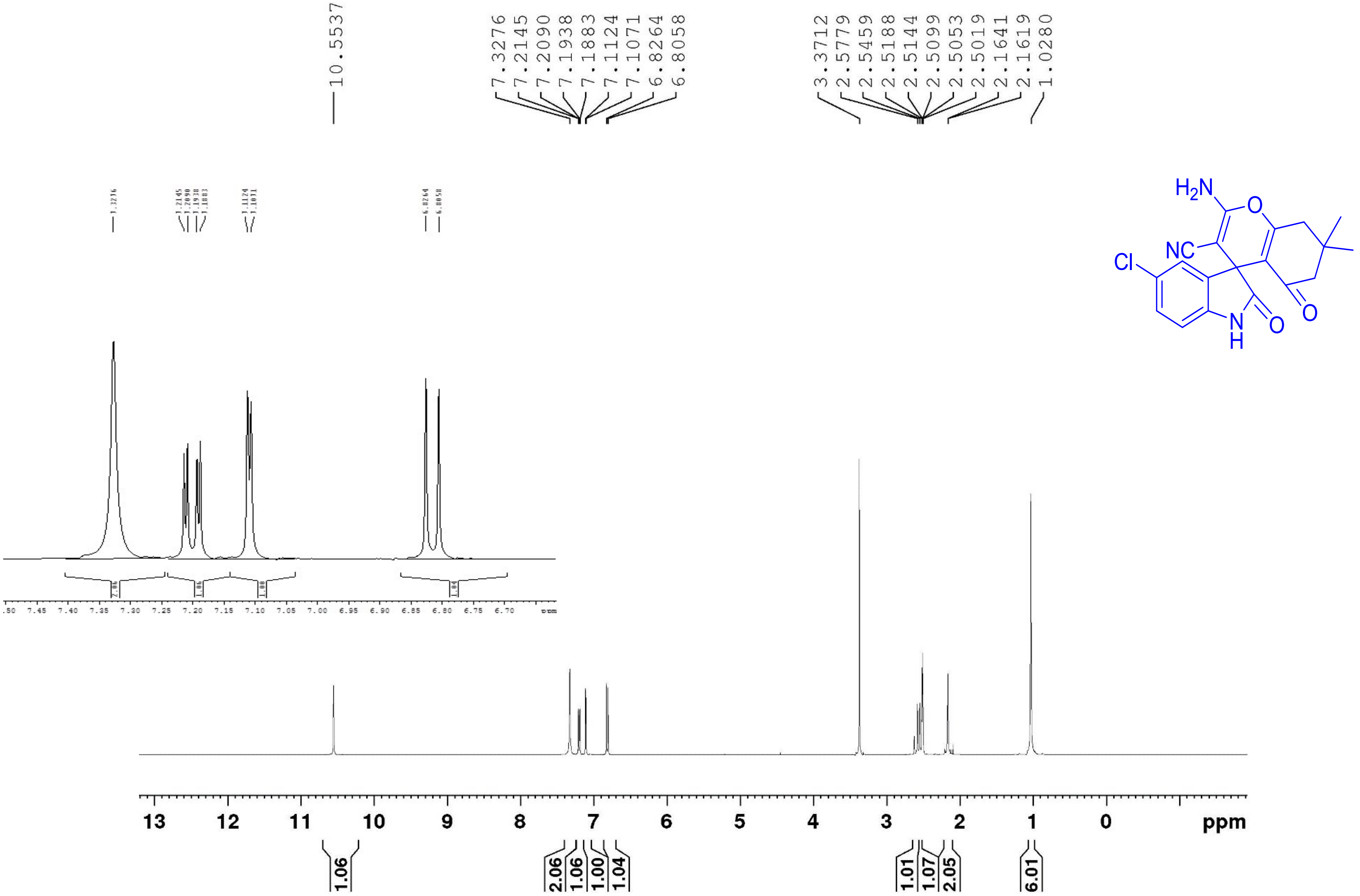


^{13}C NMR spectrum of compound 4c

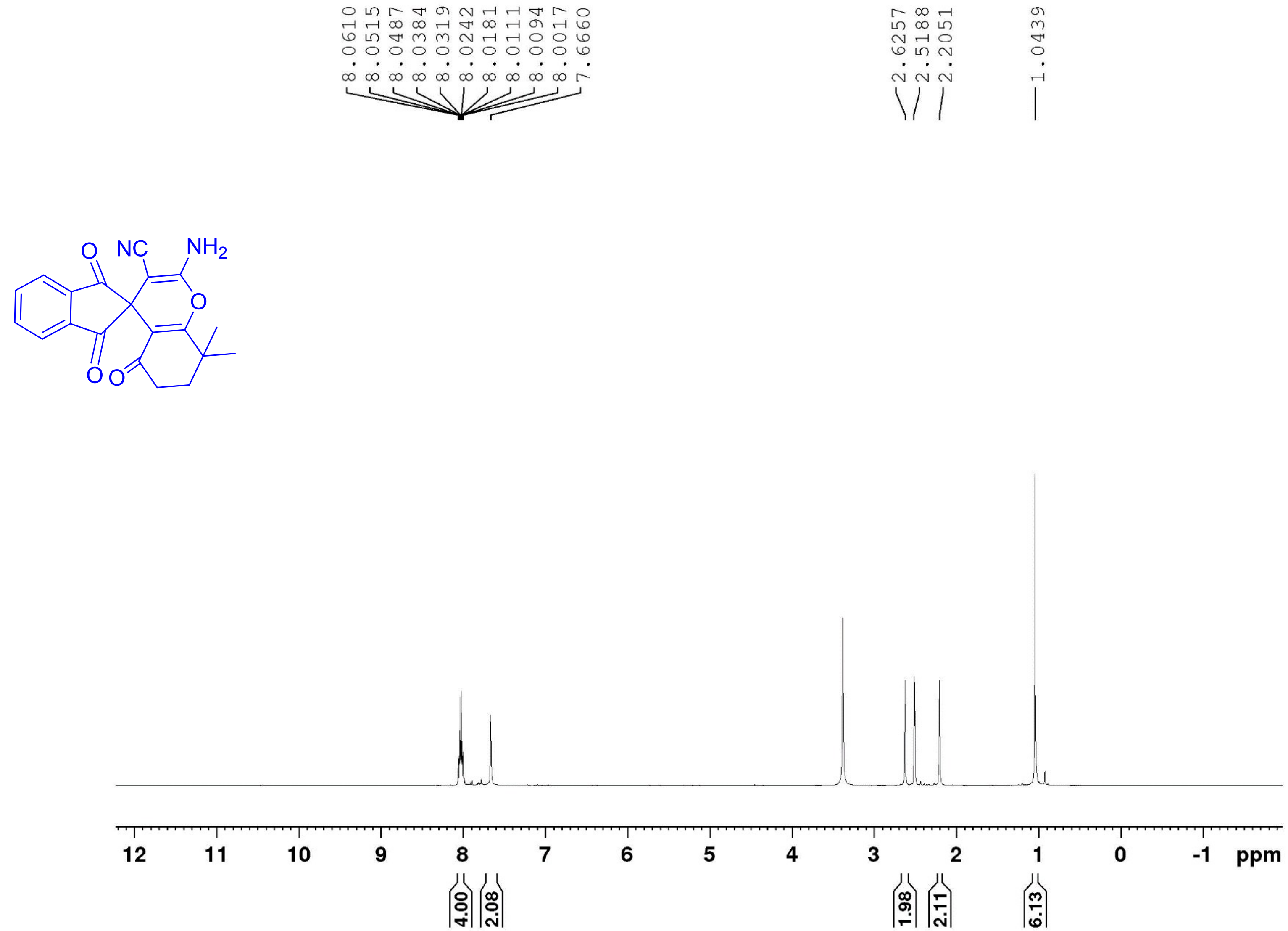




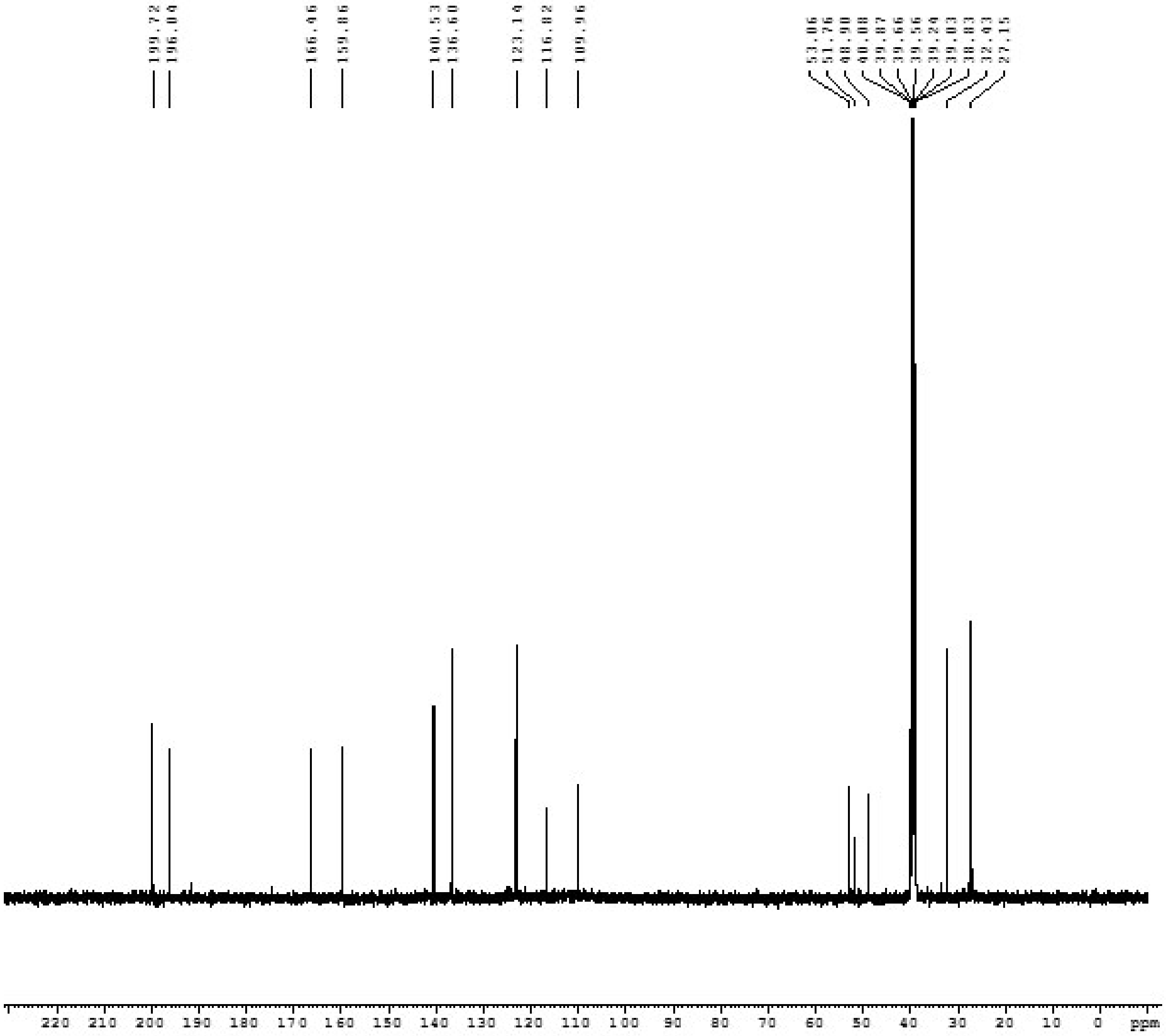
^{1}H NMR spectrum of compound 4d and its expansion



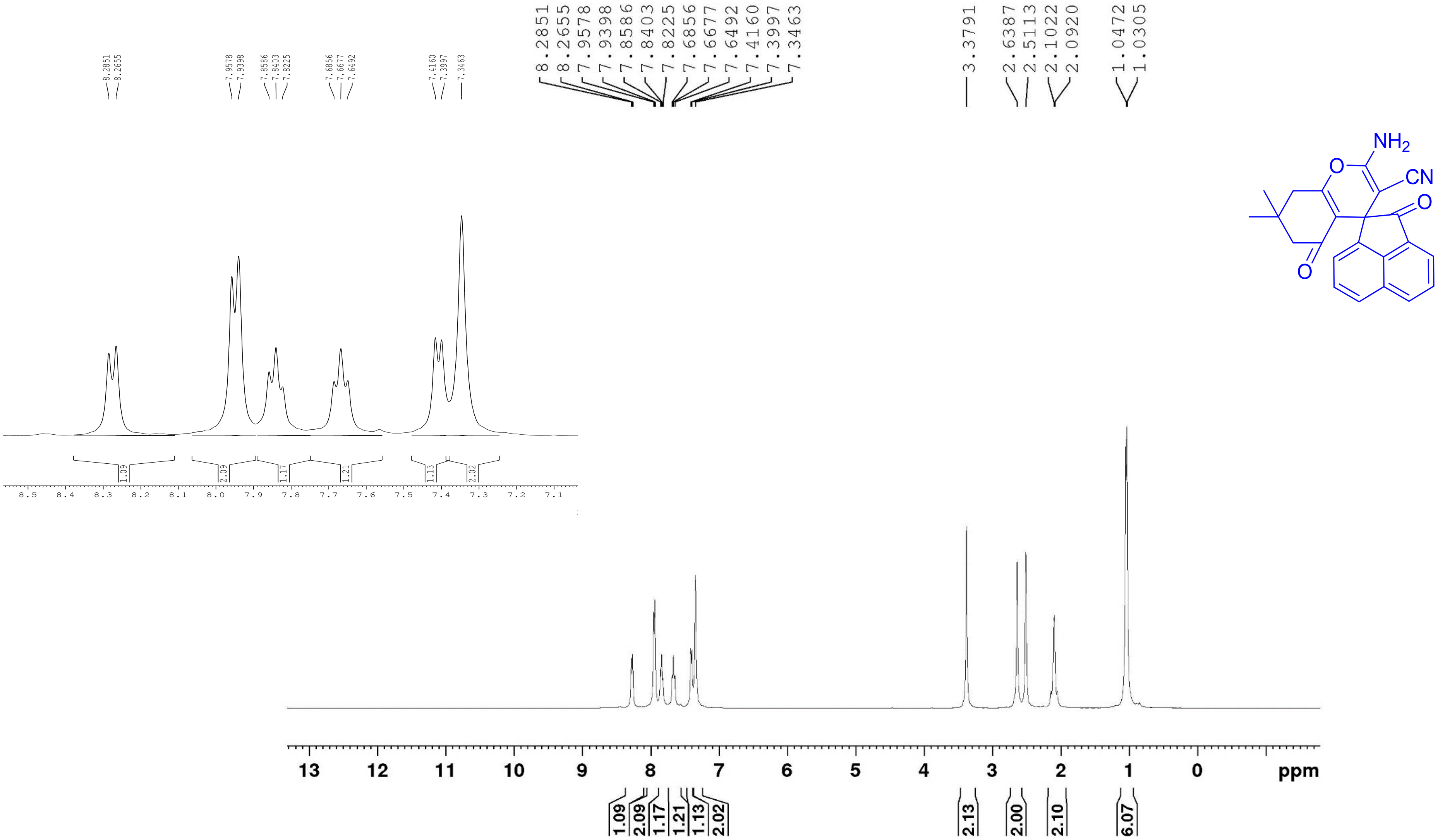
^{1}H NMR spectrum of compound 4k



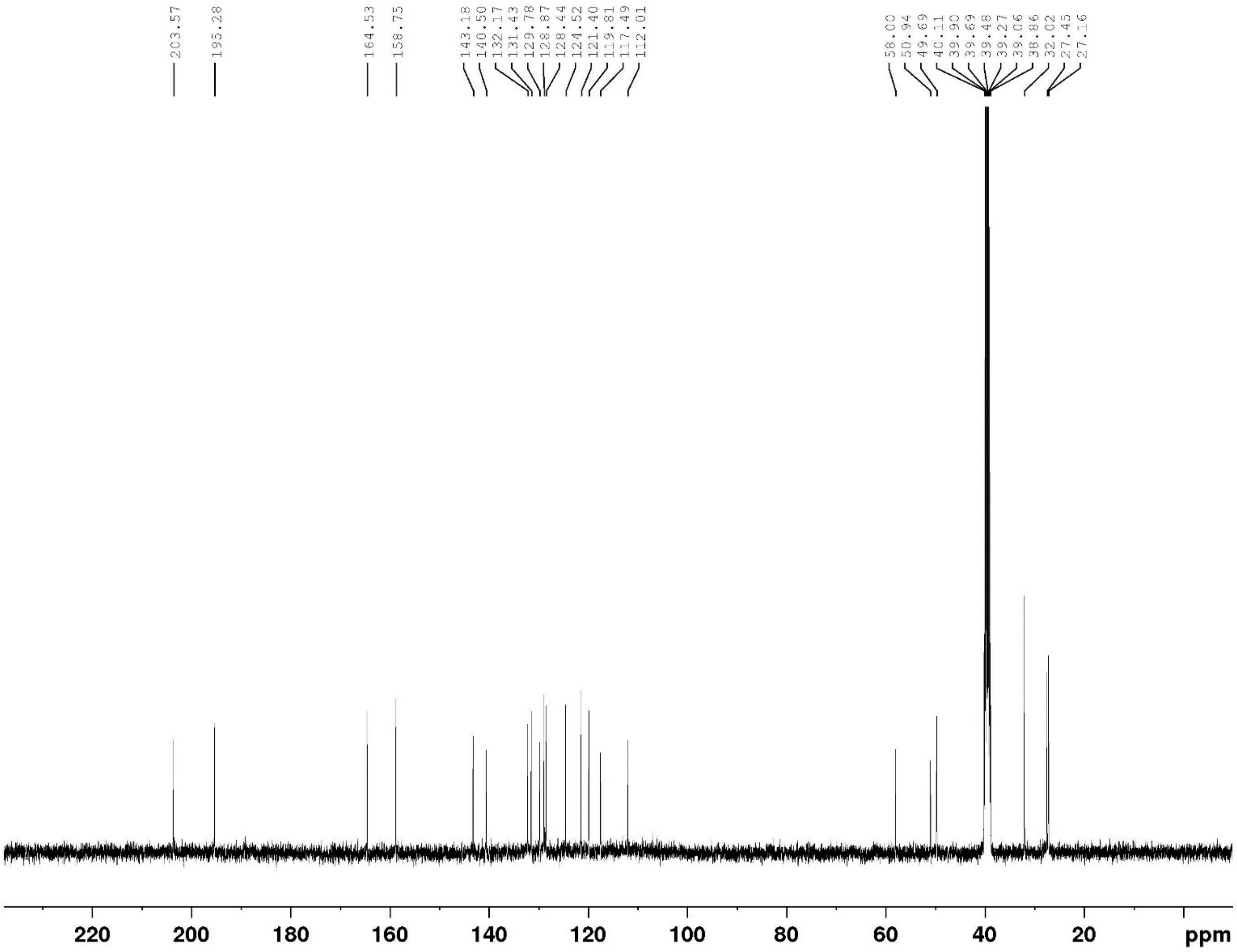
^{1}H NMR spectrum of compound 6b



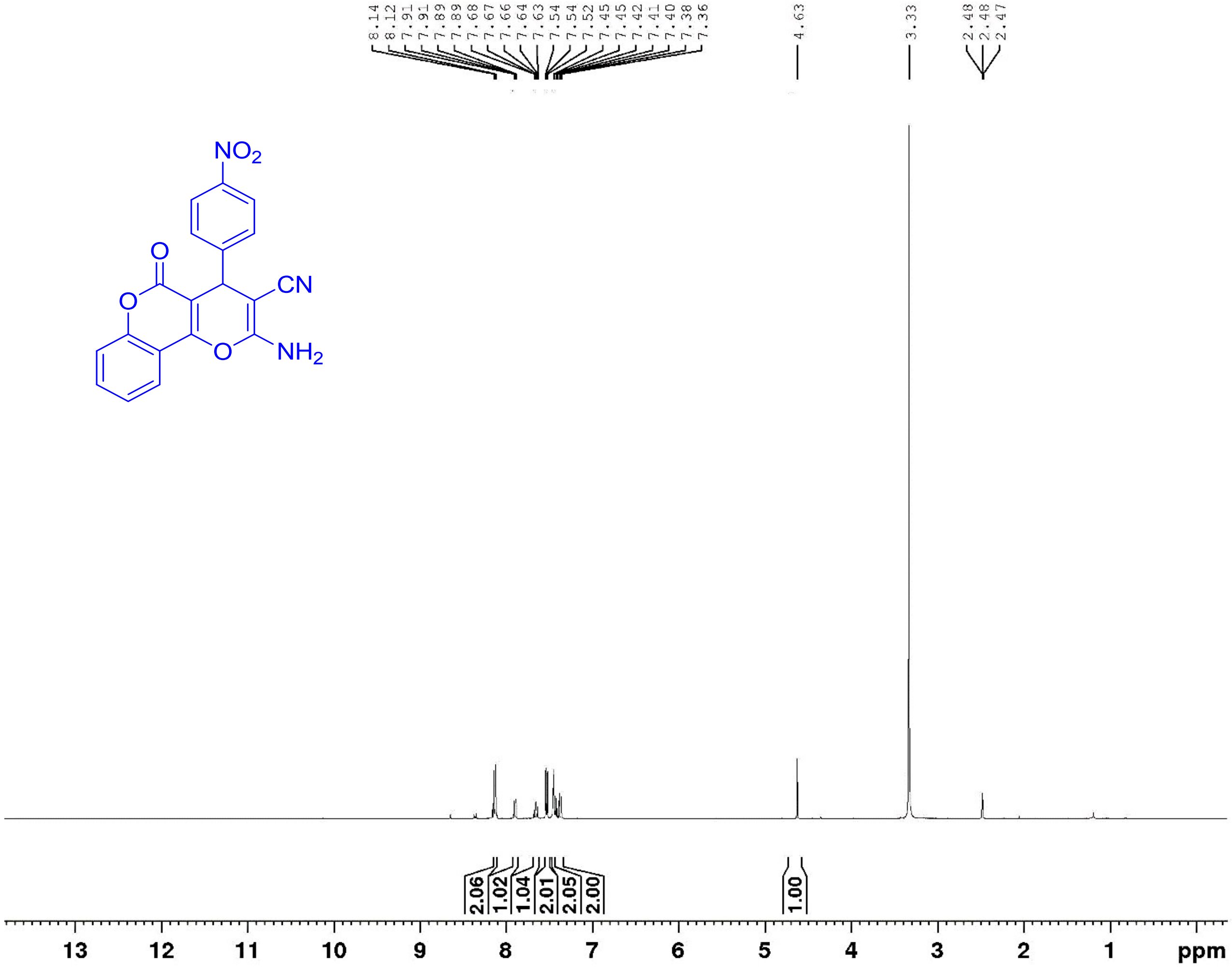
^{13}C NMR spectrum of compound 6b



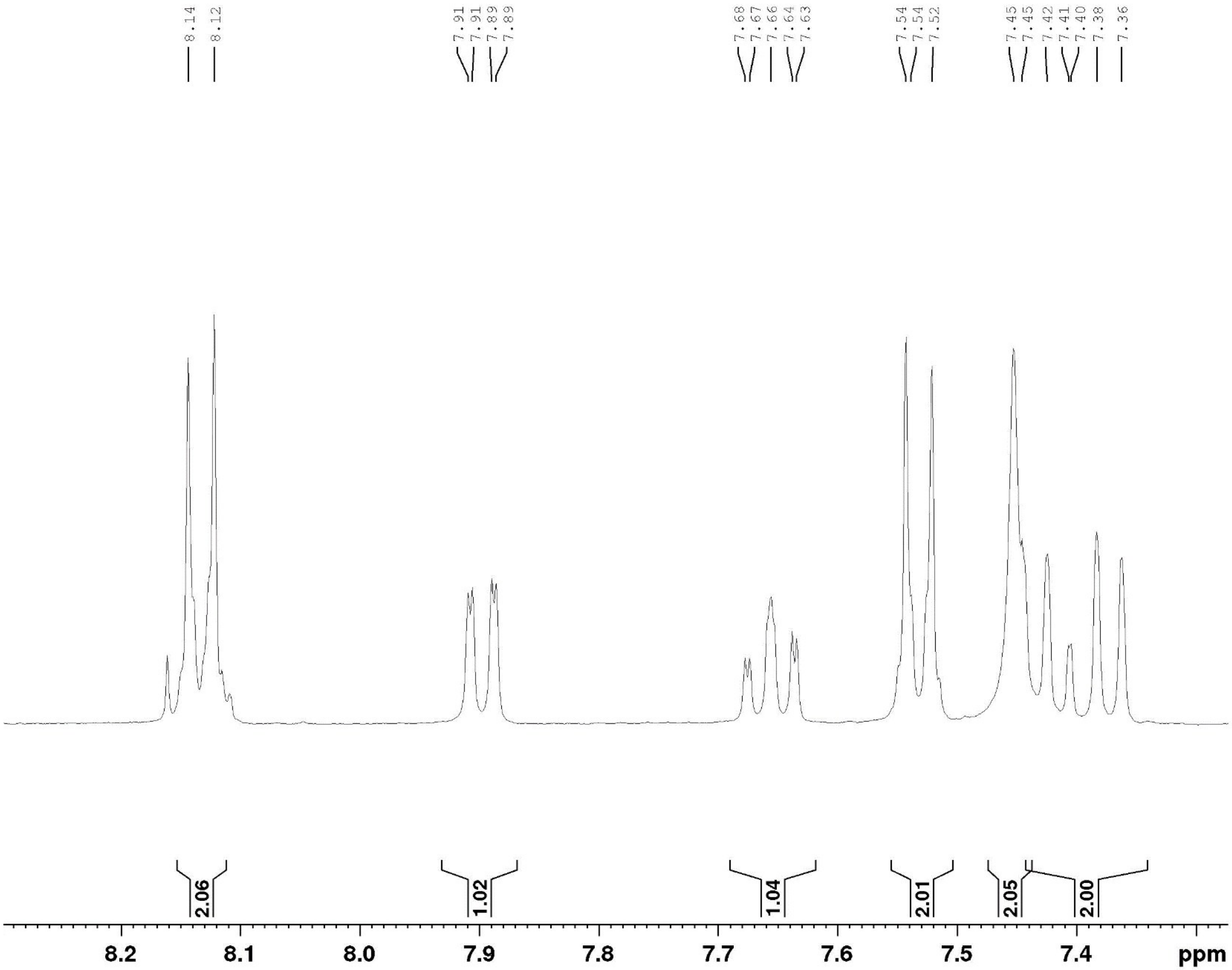
^{1}H NMR spectrum of compound 8a



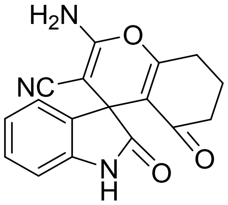
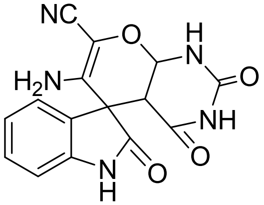
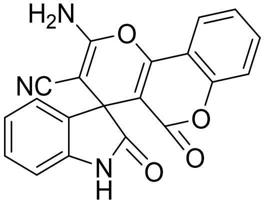
^{13}C NMR spectrum of compound 8a

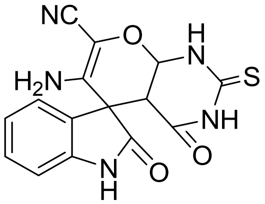
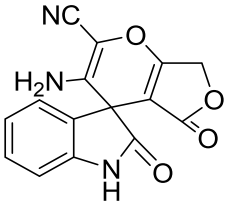
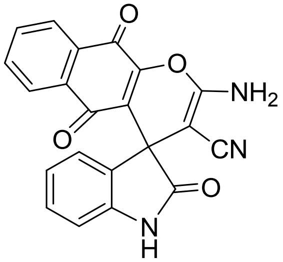
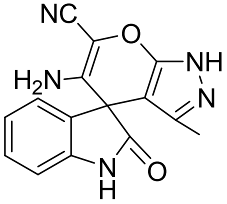


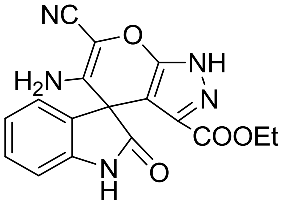
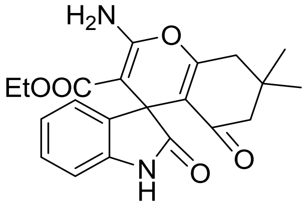
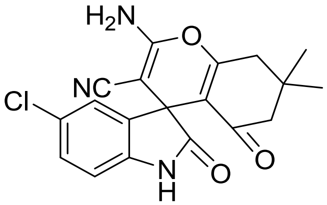
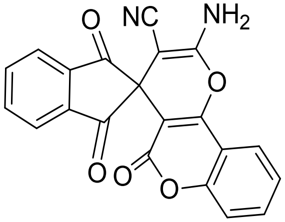
^{1}H NMR spectrum of compound 10c

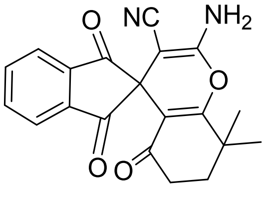
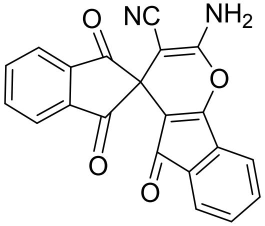
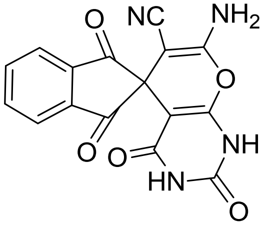
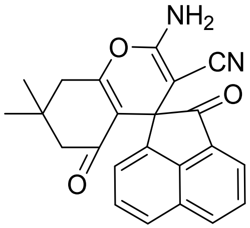


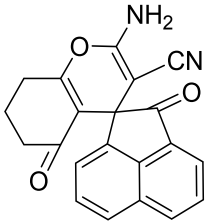
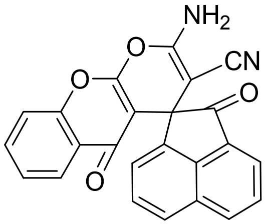
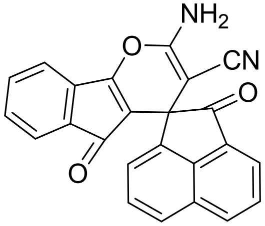
^{1}H NMR spectrum expansion of compound 10c

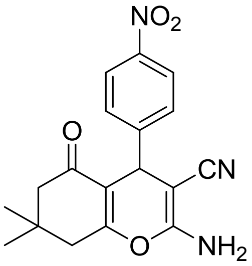
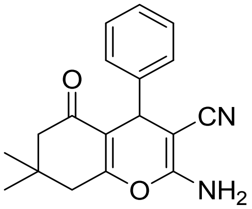
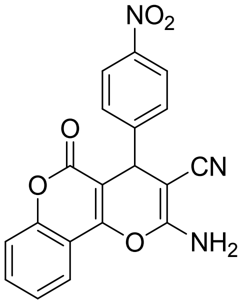
S. No.	Compound	M.P. (Obs.)	M.P. (Rep.)	Ref.
1.	 **4b**	296-297	298-299	14g
2.	 **4c**	297-298	296-298	14e
3.	 **4d**	289-290	288-292	14t

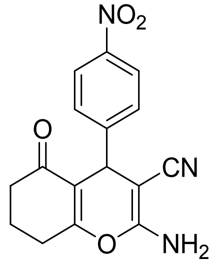
4.	 **4e**	239-241	243-245	14k
5.	 **4f**	238-241	238-240	14v
6.	 **4g**	247-248	250-252	14d
7.	 **4h**	180-184	180-182	14f

8.	 **4i**	282-284	281-284	14q
9.	 **4j**	238-23 449	238-239	14t
10.	 **4k**	290-291	290-292	14c
11.	 **6a**	290-293	288-292	14s

12.	 **6b**	291-294	292-294	14s
13.	 **6c**	258-262	255-260	14u
14.	 **6d**	275-279	275-277	14u
15.	 **8a**	269-272	268-270	14t

16.	 **8b**	246-248	245-246	14t
17.	 **8c**	>300	>300	14d
18.	 **8d**	278-280	270-272	14u

19.	 **10a**	176-179	175-177	14t
20.	 **10b**	224-226	224-226	14c
21.	 **10c**	257-259	258-261	15d

22.	 **10d**	241-243	241-243	15d

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