

A new application of polymer supported, homogeneous and reusable catalyst PEG–SO₃H in the synthesis of coumarin and uracil fused pyrrole derivatives

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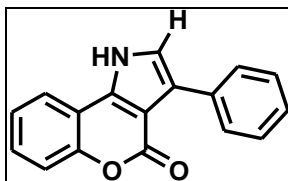
ardchem@caluniv.ac.in, ardas66@rediffmail.com (A R Das)

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1. Materials and Methods

^1H -NMR and ^{13}C -NMR spectral analysis were carried out on Bruker-Advance Digital 300 MHz and 75.5 MHz instruments; tetramethylsilane (TMS) was used as internal standard. Infrared spectra were recorded in KBr pellets in reflection mode on a Perkin Elmer RX-1 FTIR spectrophotometer. Melting points were determined on a Köfler Block apparatus. Merck aluminum-blocked silica gel plates coated with silica gel G were used for analytical TLC and monitored under UV light and also by exposure to iodine vapor. Synthetic grade chemicals from Sigma-Aldrich, Spectrochem and E-Merck were used for carrying out the organic reactions. All the solvents used in the reaction were distilled and dried over Na_2SO_4 .

1. 3-Phenyl-1*H*-5-oxa-1-azacyclopenta[*a*]naphthalene-4-one (4a):



Yield: 81%

Characteristic: Grey amorphous solid

Mp: 295 °C (dec);

IR (KBr): 3109, 1679, 1574, 1462 cm⁻¹;

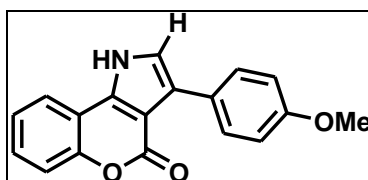
¹H NMR (300 MHz, DMSO-*d*₆): δ 7.21-7.44 (6H, m), 7.55 (1H, s), 7.73 (2H, d, *J* = 7.5Hz), 8.05 (1H, d, *J* = 7.5Hz), 12.83 (1H, s);

¹³C NMR (75 MHz, DMSO-*d*₆): δ 104.6, 113.7, 116.7, 121.3, 122.5, 124.1, 124.5, 126.6, 128.0, 128.6, 128.9, 133.3, 136.5, 151.2, 157.9, 161.9;

Anal. calcd for C₁₇H₁₁NO₂: C 78.15, H 4.24, N 5.36 %. Found: C 78.14, H 4.29, N 5.38 %.

HRMS Calcd for C₁₇H₁₁NO₂ ([M+H]⁺) 262.0869 found : 262.0861

2. 3-(4-Methoxyphenyl)-1*H*-5-oxa-1-azacyclopenta[*a*]naphthalene-4-one (4b):



Yield: 85%

Characteristic: Grey amorphous solid

Mp: >300 °C

IR (KBr): 3219, 1685 cm⁻¹;

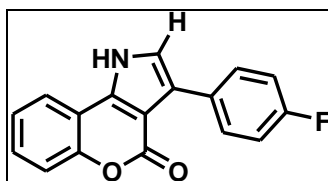
¹H NMR (300 MHz, DMSO-d₆): δ 3.74 (3H, s), 6.92 (2H, d, J= 7.8Hz), 7.32-7.46 (4H, m), 7.66 (2H, d, J= 7.8Hz), 8.03 (1H, d, J= 7.2Hz), 12.74 (1H, s);

¹³C NMR (75 MHz, DMSO-d₆): δ 55.6, 104.9, 113.9, 114.2, 117.0, 121.7, 122.0, 124.5, 124.6, 126.2, 129.2, 130.1, 136.6, 142.5, 151.6, 158.4, 158.6, 162.3;

Anal. calcd for C₁₈H₁₃NO₃: C 74.22, H 4.50, N 4.81 %. Found: C 74.26, H 4.48, N 4.78 %.

HRMS Calcd for C₁₈H₁₃NO₃ ([M+H]⁺) 292.0974 found : 292.0970

3. 3-(4-Fluorophenyl)-1H-5-oxa-1-azacyclopenta[a]naphthalene-4-one (4c):



Yield: 73%

Characteristic: Grey amorphous solid

Mp: >300 °C;

IR (KBr): 3113, 1678 cm⁻¹;

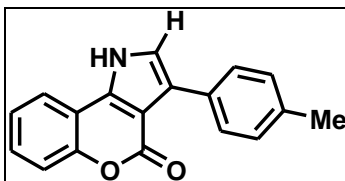
¹H NMR (300 MHz, DMSO-d₆): δ 7.13-7.37 (5H, m), 7.52 (1H, s), 7.75 (2H, s), 8.02 (1H, d, J= 6.9 Hz), 12.79 (1H, s);

¹³C NMR (75 MHz, DMSO-d₆): δ 104.6, 113.8, 114.7, 114.9, 116.7, 121.4, 122.4, 123.4, 124.2, 128.9, 129.8, 130.4, 130.5, 136.5, 151.2, 158.0, 159.7, 162.9;

Anal. calcd for C₁₇H₁₀FNO₂: C 73.11, H 3.61, N 5.02 %. Found: C 73.18, H 3.64 N 5.00 %.

HRMS Calcd for $C_{17}H_{10}FNO_2$ ($[M+H]^+$) 280.0775 found : 280.0778

4. 3-*p*-Tolyl-1*H*-5-oxa-1-azacyclopenta[*a*]naphthalene-4-one(4d) :



Yield: 82%

Characteristic: Yellow amorphous solid

Mp: >300 °C;

IR (KBr): 3185, 1690 cm^{-1} ;

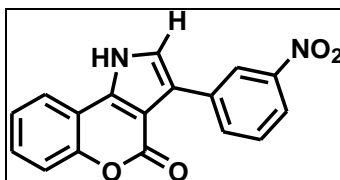
1H NMR (300 MHz, DMSO- d_6): δ 2.28 (3H, s), 7.15 (2H, d, $J=7.8Hz$), 7.30-7.45 (3H, m), 7.49 (1H, s), 7.62 (2H, d, $J=7.5 Hz$), 8.03 (1H, d, $J=7.5 Hz$), 12.76 (1H, s);

^{13}C NMR (75 MHz, DMSO- d_6): δ 20.8, 104.6, 113.8, 116.7, 121.3, 122.0, 124.1, 124.5, 128.5, 128.8, 130.5, 135.6, 136.3, 151.2, 157.9;

Anal. calcd for $C_{18}H_{13}NO_2$: C 78.53, H 4.76, N 5.09 %. Found: C 78.59, H 4.73, N 5.05 %.

HRMS Calcd for $C_{18}H_{13}NO_2$ ($[M+H]^+$) 276.1025 found : 276.1019

5. 3-(3-Nitrophenyl)-1*H*-5-oxa-1-azacyclopenta[*a*]naphthalene-4-one (4e):



Yield: 79%

Characteristic: Yellow amorphous solid

Mp: 290 °C (dec);

IR (KBr): 3117, 1678 cm^{-1} ;

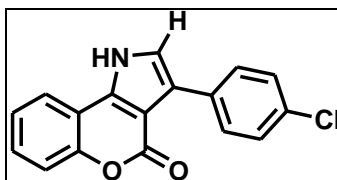
^1H NMR (300 MHz, DMSO-d_6): δ 7.36-7.64 (4H, m), 7.83 (1H, s), 8.05-8.22 (3H, m), 8.69 (1H, s), 13.03 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 113.5, 116.8, 117.8, 121.2, 121.9, 122.7, 123.9, 124.3, 129.5, 134.7, 135.0, 137.1, 147.9, 151.2, 158.0, 161.9;

Anal. calcd for $\text{C}_{17}\text{H}_{10}\text{N}_2\text{O}_4$: C 66.67, H 3.29, N 9.15 %. Found: C 66.63, H 3.30, N 9.19 %.

HRMS Calcd for $\text{C}_{17}\text{H}_{10}\text{N}_2\text{O}_4$ ($[\text{M}+\text{H}]^+$) 307.0720 found : 307.0728

6. 3-(4-Chlorophenyl)-1H-5-oxa-1-azacyclopenta[*a*]naphthalene-4-one (4f):



Yield: 77%

Characteristic: Yellow amorphous solid

Mp: 296 $^{\circ}\text{C}$ (dec);

IR (KBr): 3114, 1684 cm^{-1} ;

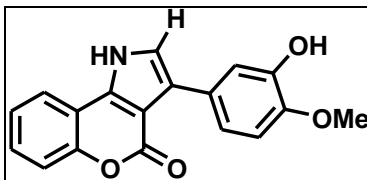
^1H NMR (300 MHz, DMSO-d_6): δ 7.31-7.41 (5H, m), 7.60 (1H, s), 7.77 (2H, d, $J= 8.1\text{Hz}$), 8.03 (1H, d, $J= 7.5\text{ Hz}$), 12.86 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 104.5, 113.6, 116.7, 121.3, 122.8, 122.9, 124.1, 127.9, 129.0, 130.1, 131.1, 132.2, 136.7, 151.2, 157.9;

Anal. Calcd for $\text{C}_{17}\text{H}_{10}\text{ClNO}_2$: C 69.05, H 3.41, N 4.74%. Found: C 69.02, H 3.48, N 4.77%.

HRMS Calcd for $\text{C}_{17}\text{H}_{10}\text{ClNO}_2$ ($[\text{M}+\text{H}]^+$) 296.0479 found : 296.0471

7. 3-(3-Hydroxy-4-methoxyphenyl)-1H-5-oxa-1-azacyclopenta[*a*]naphthalene-4-one (4g):



Yield: 78%

Characteristic: Yellow amorphous solid

Mp: >300 °C;

IR (KBr): 3134, 1657 cm⁻¹;

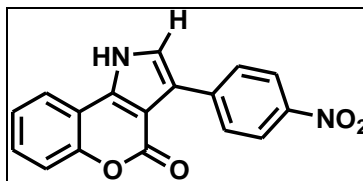
¹H NMR (300 MHz, DMSO-*d*₆): δ 3.75 (3H, s), 6.89 (1H, d, J=8.1Hz), 7.11-7.55 (6H, m), 8.03 (1H, d, J=7.5Hz), 8.85 (1H, s), 12.71 (1H, s);

¹³C NMR (75 MHz, DMSO-*d*₆): δ 56.2, 104.7, 112.4, 114.2, 116.7, 117.0, 120.0, 121.7, 122.1, 124.5, 125.0, 126.7, 129.2, 136.5, 146.4, 147.2, 151.5, 158.3, 162.3;

Anal. calcd for C₁₈H₁₃NO₄: C 70.35, H 4.26, N 4.56 %. Found: C 70.38, H 4.28, N 4.59 %.

HRMS Calcd for C₁₈H₁₃NO₄ ([M+H]⁺) 308.0924 found : 308.0928

8. 3-(4-Nitrophenyl)-1H-5-oxa-1-azacyclopenta[*a*]naphthalene-4-one (4h)



Yield: 72%

Characteristic: Yellow amorphous solid

Mp: 290 °C (dec);

IR (KBr): 3158, 1680 cm^{-1} ;

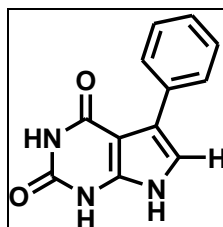
^1H NMR (300 MHz, DMSO-d_6): δ 7.30-7.37 (4H, m) 7.73 (1H, s), 8.03-8.15 (4H, m), 12.98 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 104.7, 113.8, 116.8, 118.8, 121.2, 121.4, 121.9, 122.7, 123.9, 124.9, 129.3, 129.5, 134.7, 135.0, 137.1, 147.9, 151.5, 157.7, 161.7;

Anal. calcd for $\text{C}_{17}\text{H}_{10}\text{N}_2\text{O}_4$: C 66.67, H 3.29, N 9.15 %. Found: C 66.63, H 3.30, N 9.19 %.

HRMS Calcd for $\text{C}_{17}\text{H}_{10}\text{N}_2\text{O}_4$ ($[\text{M}+\text{H}]^+$) 307.072 found : 307.0719

9. 5-Phenyl-1,7-dihydropyrrolo[2,3-*d*]pyrimidine-2,4-dione(4i):



Yield: 71%

Characteristic: Pink powder

Mp: 250 $^{\circ}\text{C}$ (dec);

IR (KBr): 3131, 1738, 1663, cm^{-1} ;

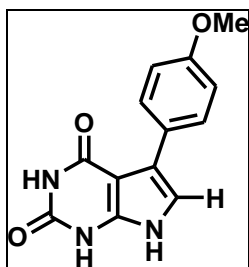
^1H NMR (300 MHz, DMSO-d_6): δ 6.84 (1H, s) 7.15-7.78 (5H, m), 10.46 (1H, s), 11.24 (1H, s), 11.49 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 96.2, 115.2, 121.4, 126.3, 128.2, 128.3, 134.3, 140.9, 151.1, 160.5;

Anal. calcd for $\text{C}_{12}\text{H}_9\text{N}_3\text{O}_2$: C 63.43, H 3.99, N 18.49 %. Found: C 63.41, H 3.96, N 18.51 %.

HRMS Calcd for $\text{C}_{12}\text{H}_9\text{N}_3\text{O}_2$ ($[\text{M}+\text{H}]^+$) 228.0774 found : 228.0771

10. 5-(4-Methoxyphenyl)-1,7-dihydropyrrolo[2,3-*d*]pyrimidine-2,4-dione(4j):



Yield: 75%

Characteristic: Pink powder

Mp: 270 °C (dec);

IR (KBr): 3135, 1736, 1663, 1601 cm⁻¹;

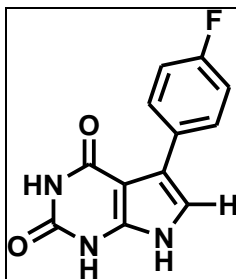
¹H NMR (300 MHz, DMSO-d₆): δ 3.70 (3H, s), 6.74 (1H, s), 6.83 (2H, d, J=8.4 Hz), 7.70(2H, d, J=8.4Hz), 10.42 (1H, s), 11.14 (1H, s), 11.43 (1H, s);

¹³C NMR (75 MHz, DMSO-d₆): δ 56.7, 96.1, 113.3, 114.1, 117.8, 120.7, 128.9, 142.6, 150.9, 161.9;

Anal. calcd for C₁₃H₁₁N₃O₃: C 60.70, H 4.31, N 16.33 %. Found: C 60.73, H 4.30, N 16.35 %.

HRMS Calcd for C₁₃H₁₁N₃O₃ ([M+H]⁺) 258.0879 found : 258.0870

11. 5-(4-Fluorophenyl)-1,7-dihydropyrrolo[2,3-d]pyrimidine-2,4-dione(4j):



Yield: 68%

Characteristic: Pink powder

Mp: 281 °C (dec);

IR (KBr): 3138, 1734, 1604 cm⁻¹;

¹H NMR (300 MHz, DMSO-d₆): δ 6.85 (1H, s), 7.09 (2H, d, J=7.5Hz), 7.82 (2H, d, J=7.5Hz), 10.48 (1H, s), 11.26 (1H, s), 11.50 (1H, s);

¹³C NMR (75 MHz, DMSO-d₆): δ 95.7, 114.5, 114.7, 119.8, 129.5, 129.6, 130.4, 140.5, 150.7, 160.1;

Anal. calcd for C₁₂H₈FN₃O₂: C 58.78, H 3.29, N 17.14 %. Found: C 58.80, H 3.27, N 17.18 %.

HRMS Calcd for C₁₂H₈FN₃O₂ ([M+H]⁺) 246.068 found : 246.0678

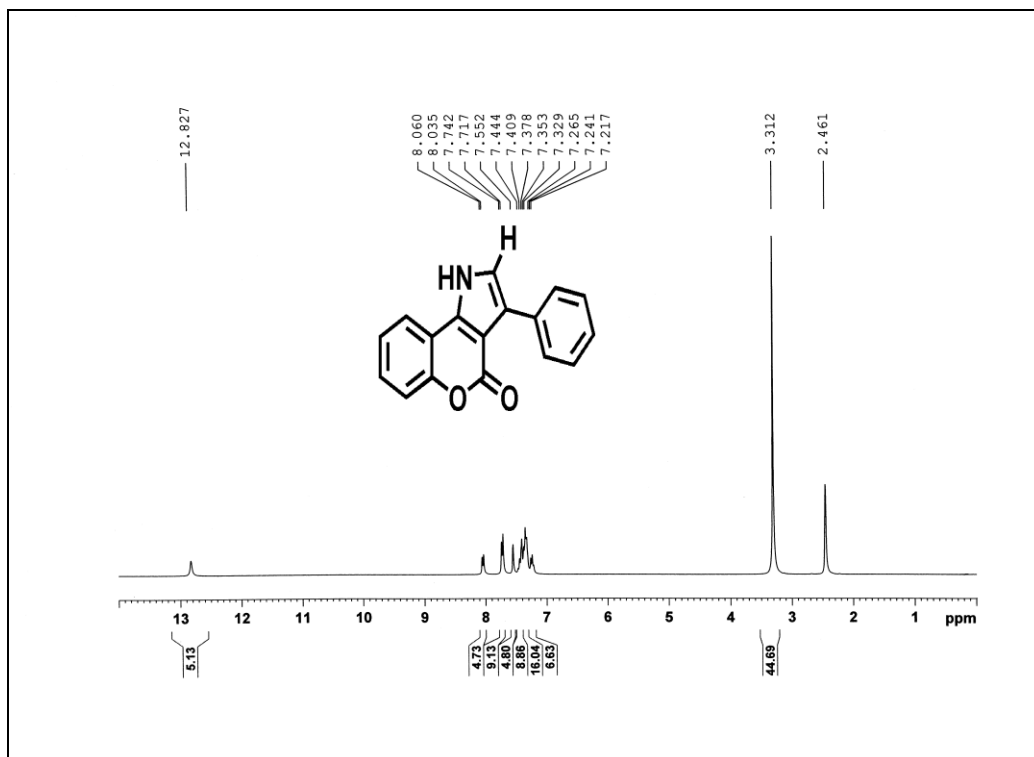


Figure 1a ¹H NMR spectrum of the product (4a)

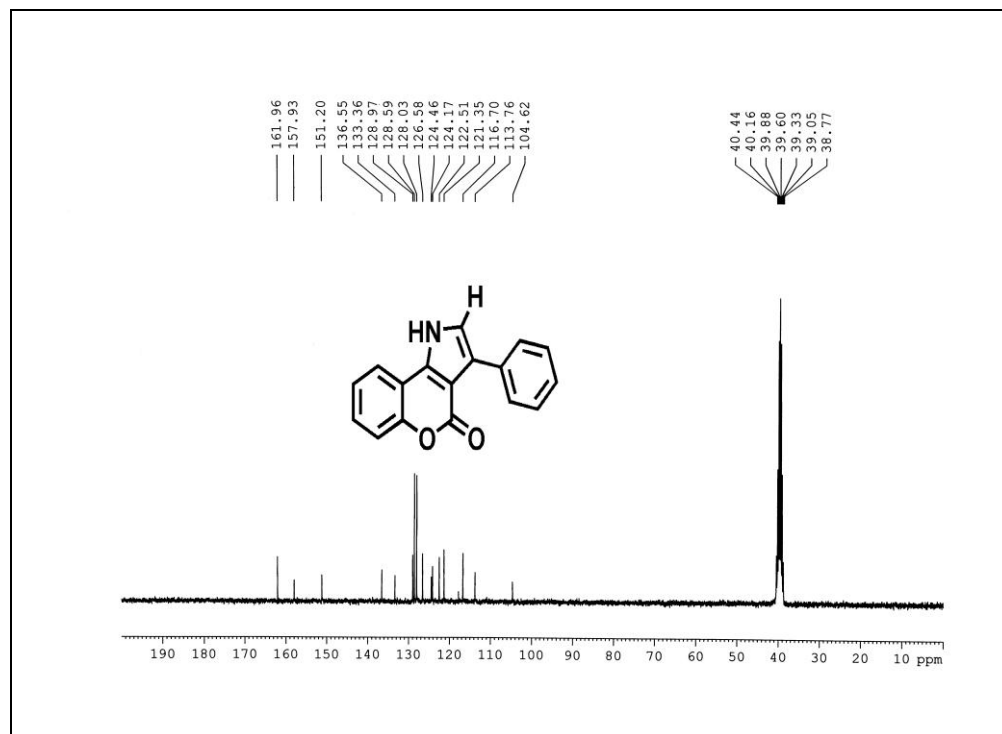


Figure 1b ¹³C NMR spectrum of the product (4a)

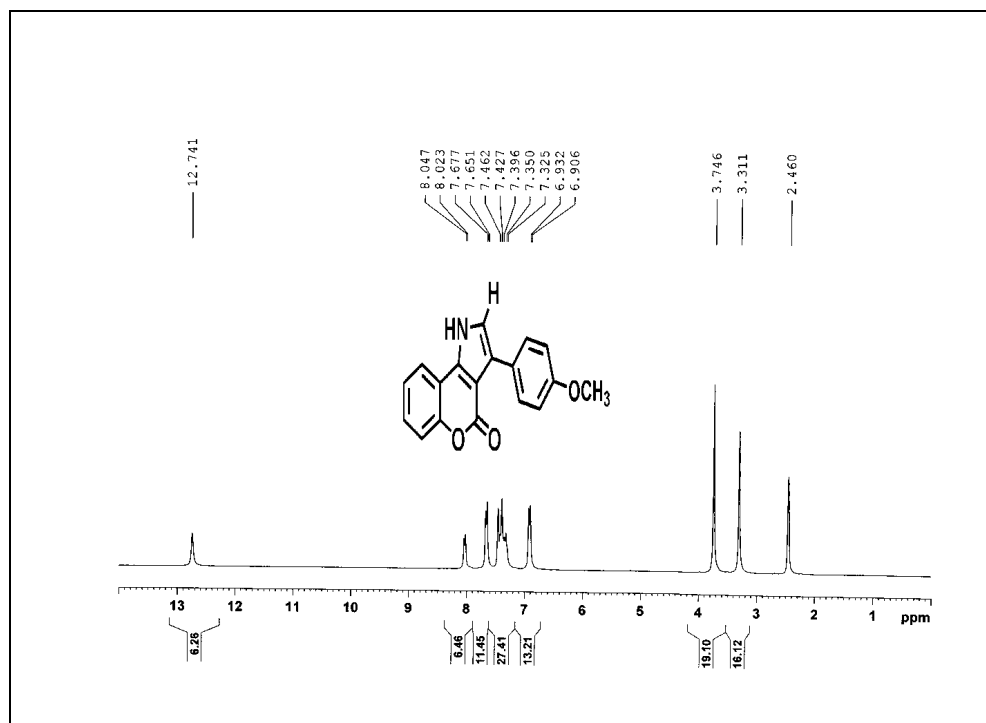


Figure2a ¹H NMR spectrum of the product (4b)

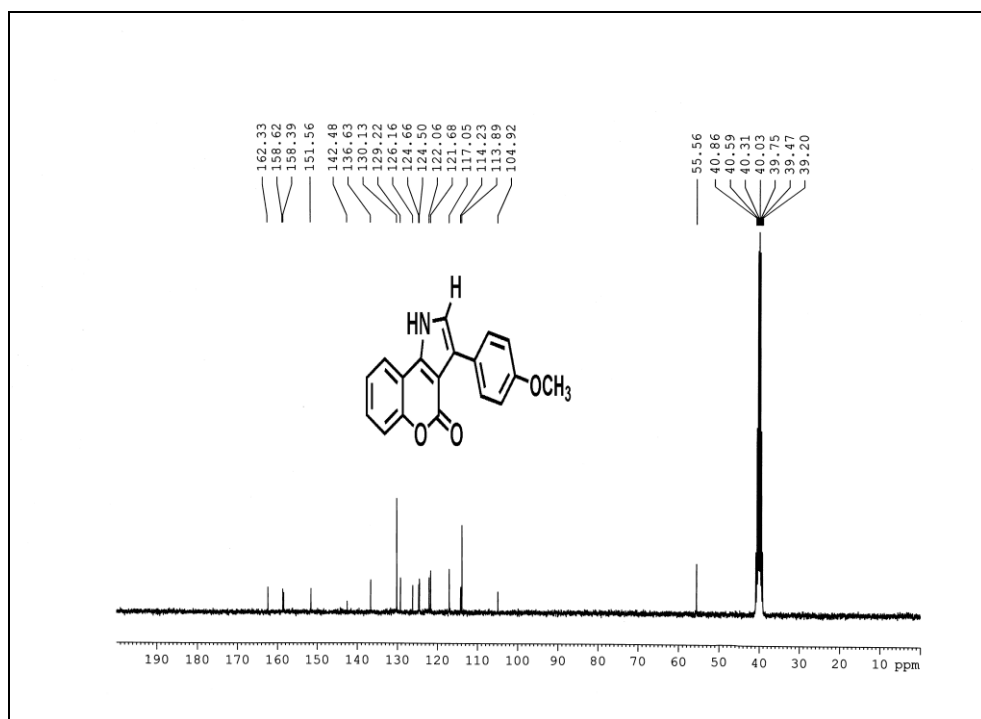


Figure2b ¹³C NMR spectrum of the product (4b)

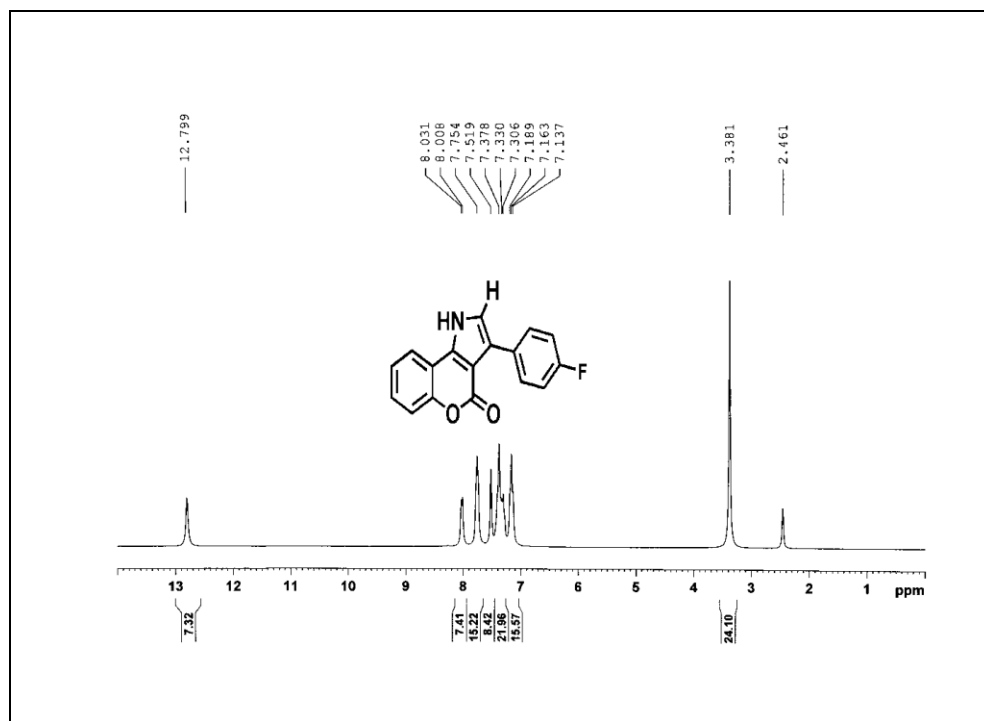


Figure3a ¹H NMR spectrum of the product (4c)

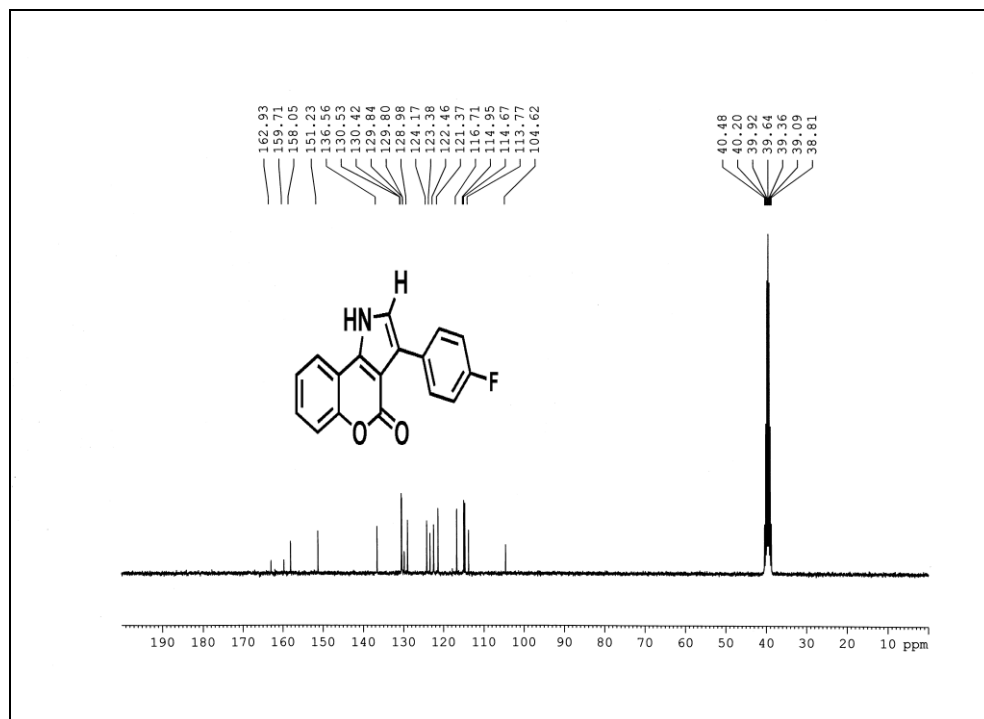


Figure3b ¹³C NMR spectrum of the product (4c)

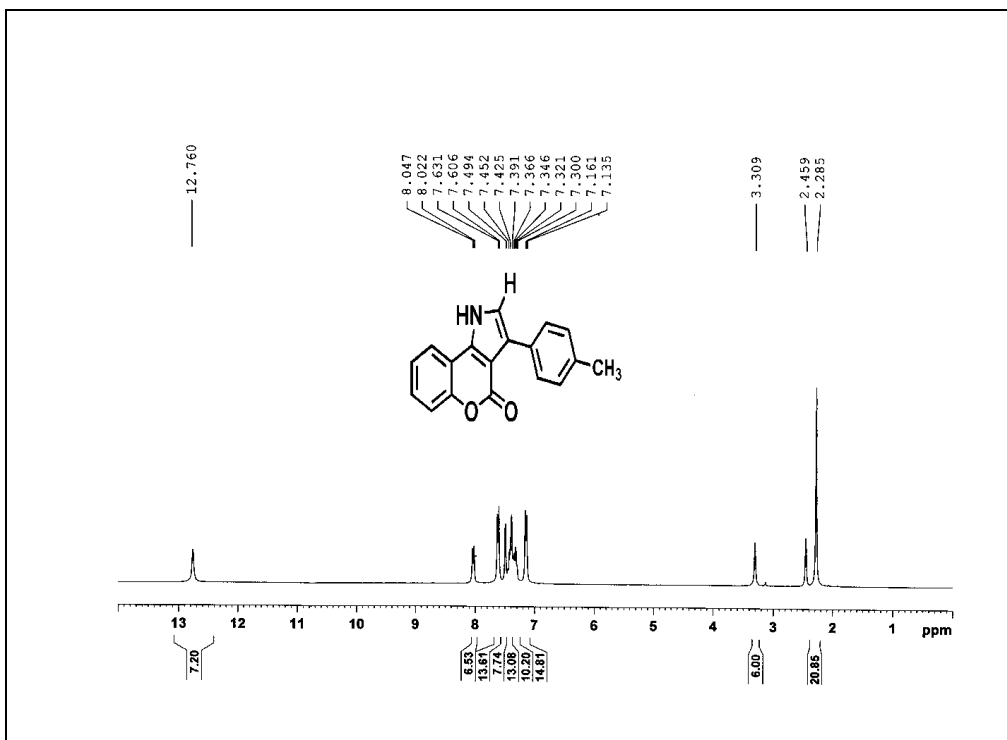


Figure 4a ^1H NMR spectrum of the product (4d)

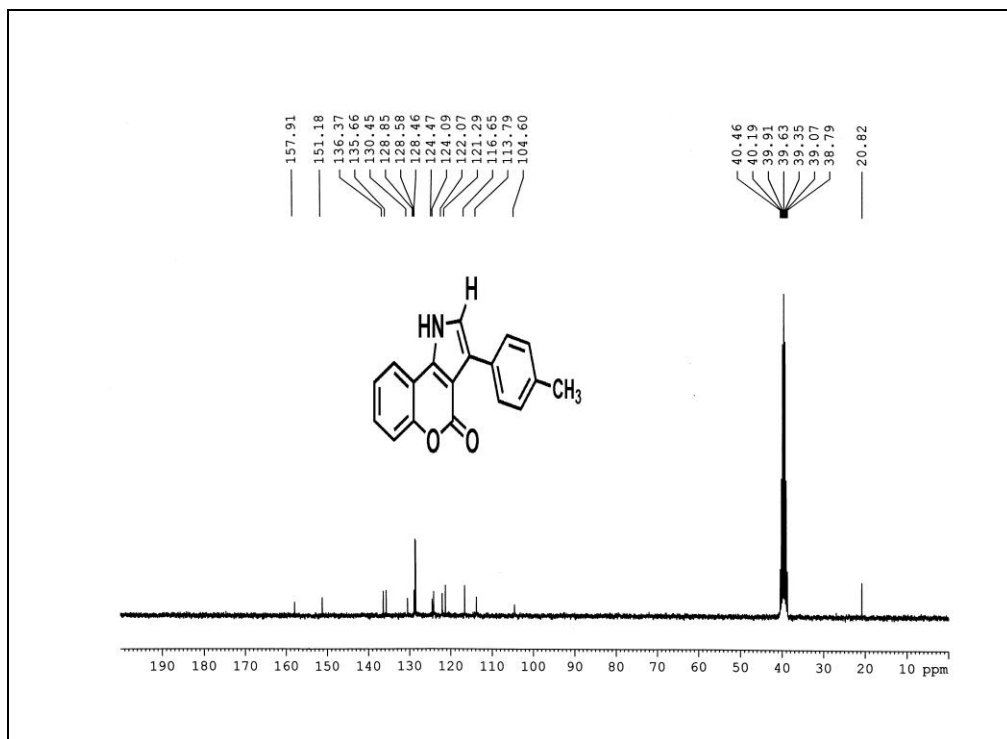


Figure 4b ^{13}C NMR spectrum of the product (4d)

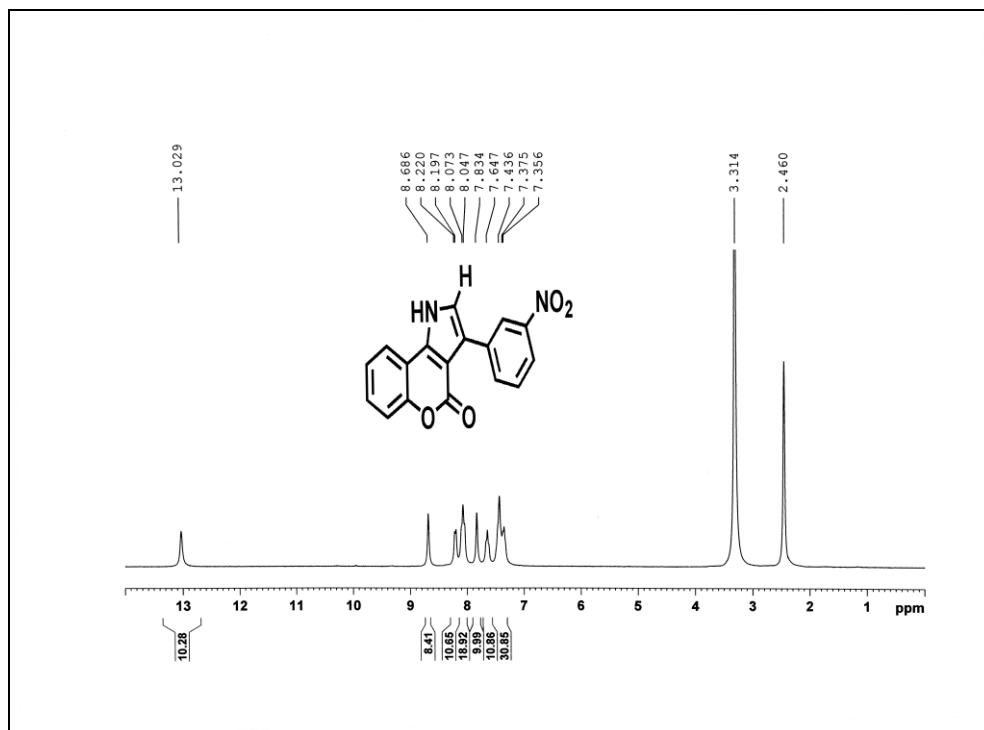


Figure 5a ^1H NMR spectrum of the product (4e)

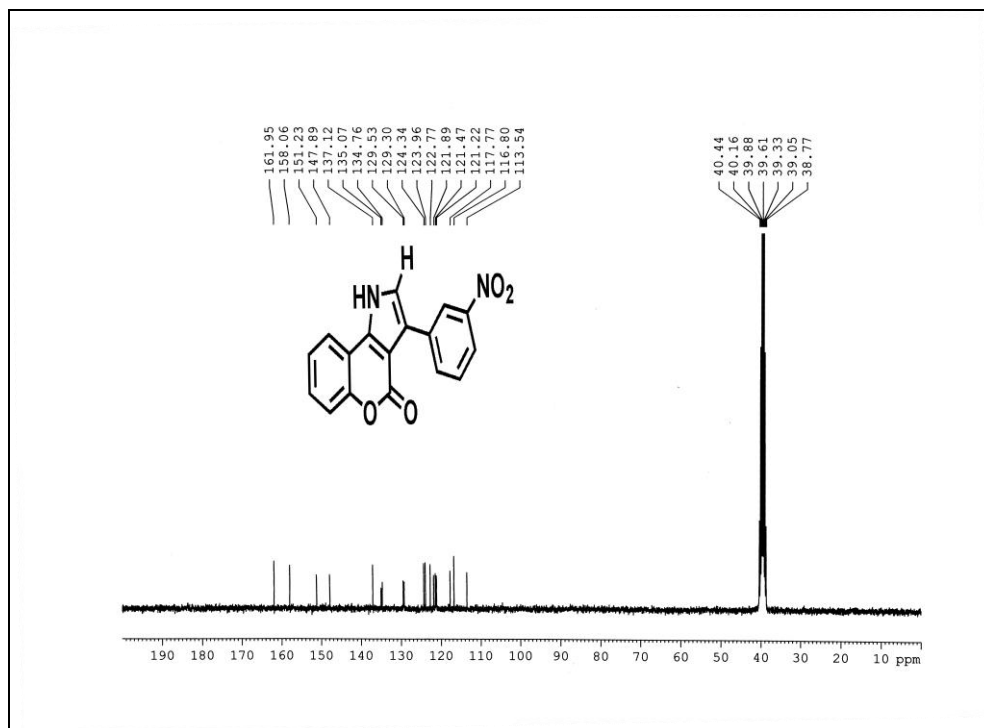


Figure 5b ^{13}C NMR spectrum of the product (4e)

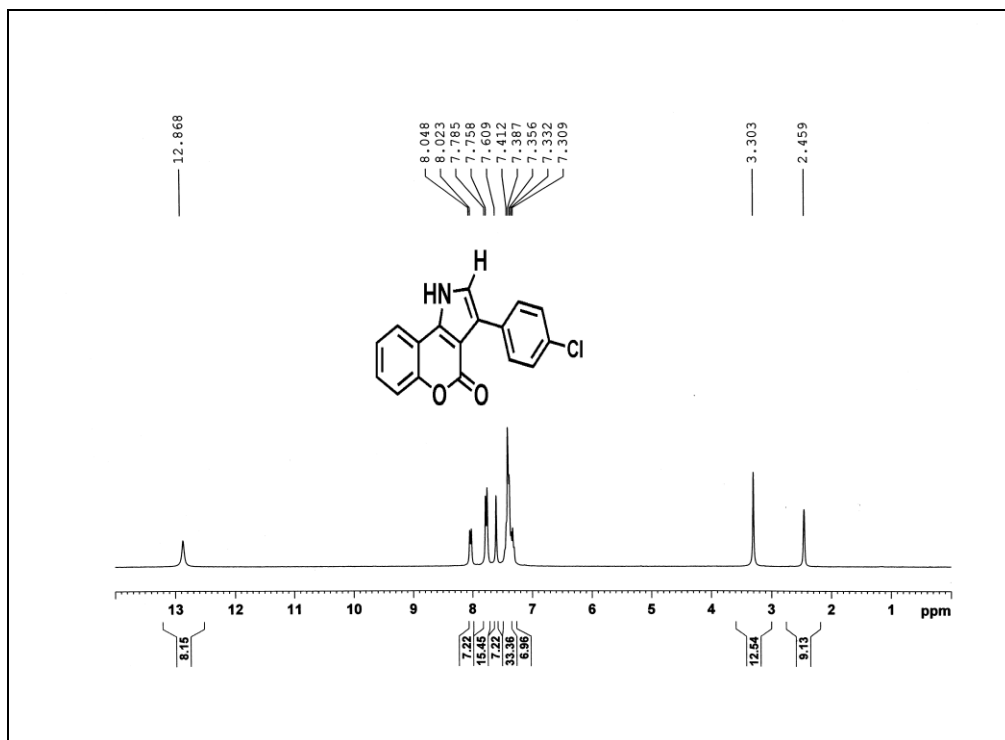


Figure 6a ^1H NMR spectrum of the product (4f)

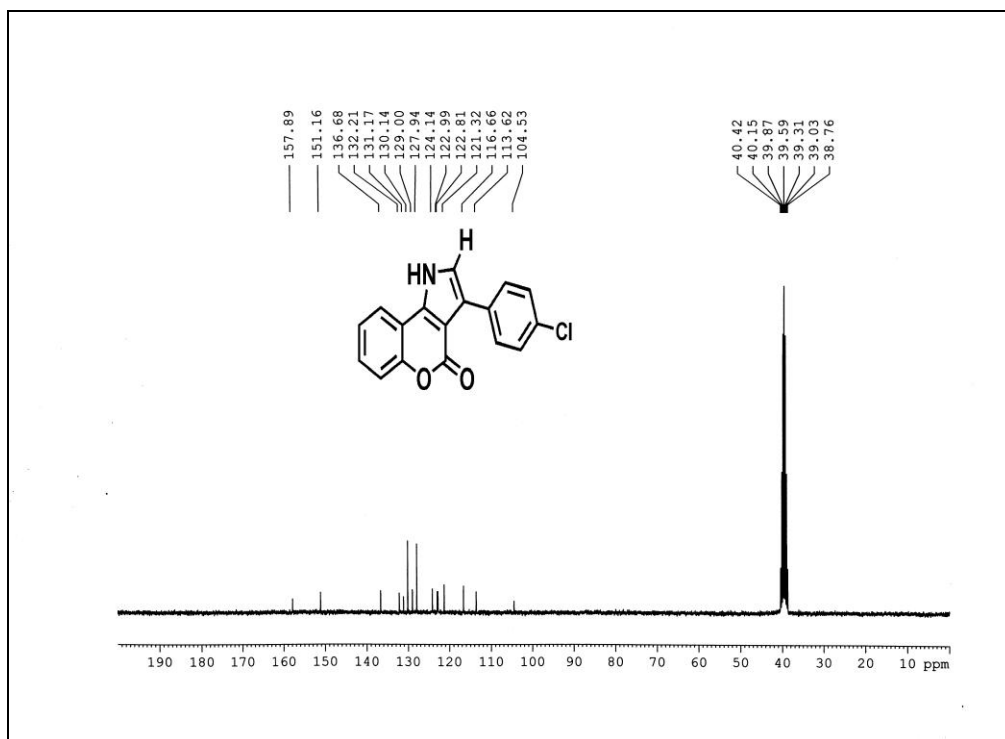


Figure 6b ^{13}C NMR spectrum of the product (4f)

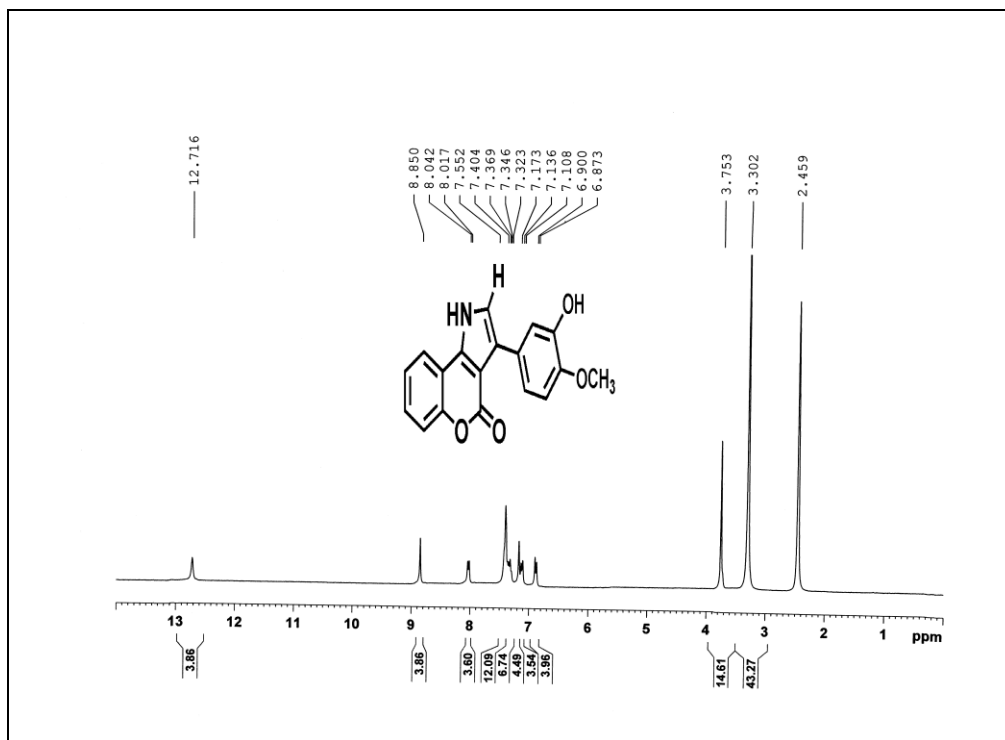


Figure7a ¹H NMR spectrum of the product (4g)

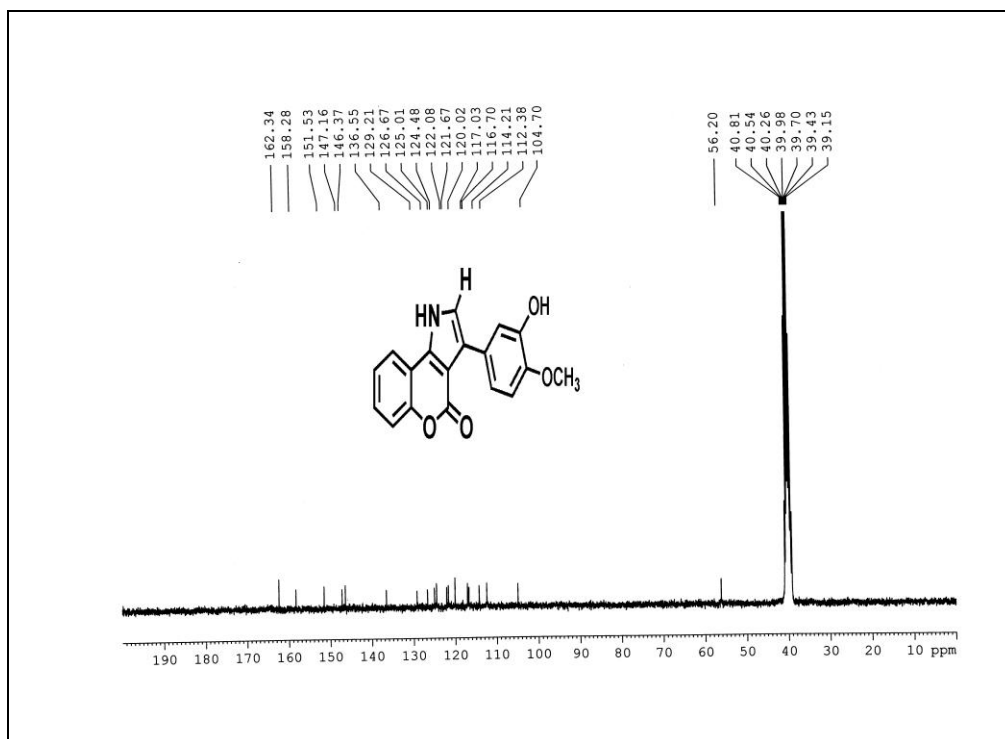


Figure7b ¹³C NMR spectrum of the product (4g)

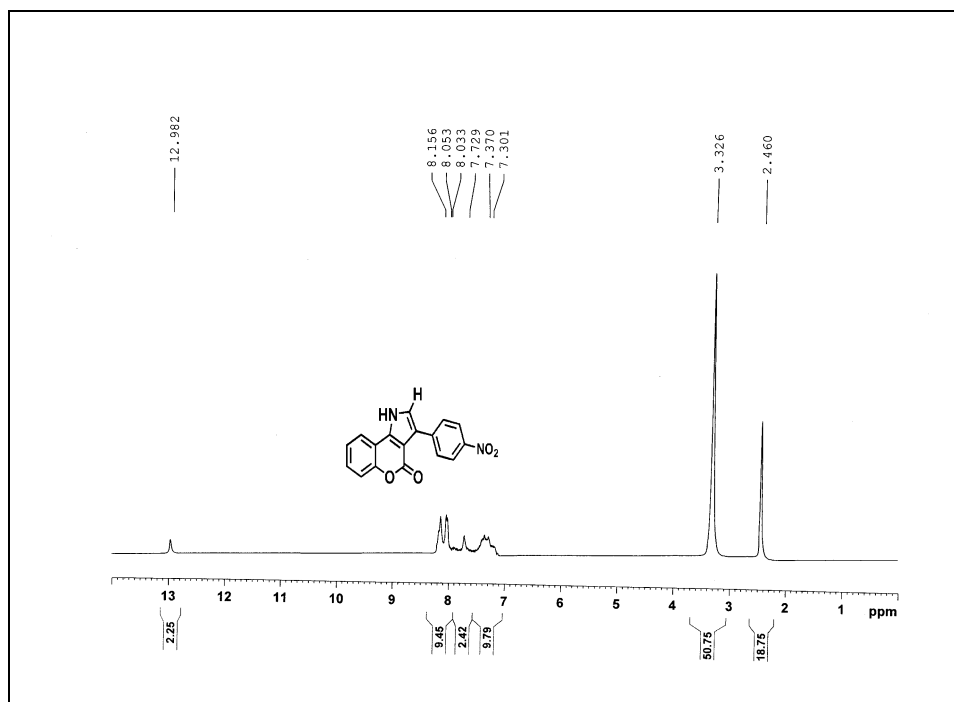


Figure8a ¹H NMR spectrum of the product (4h)

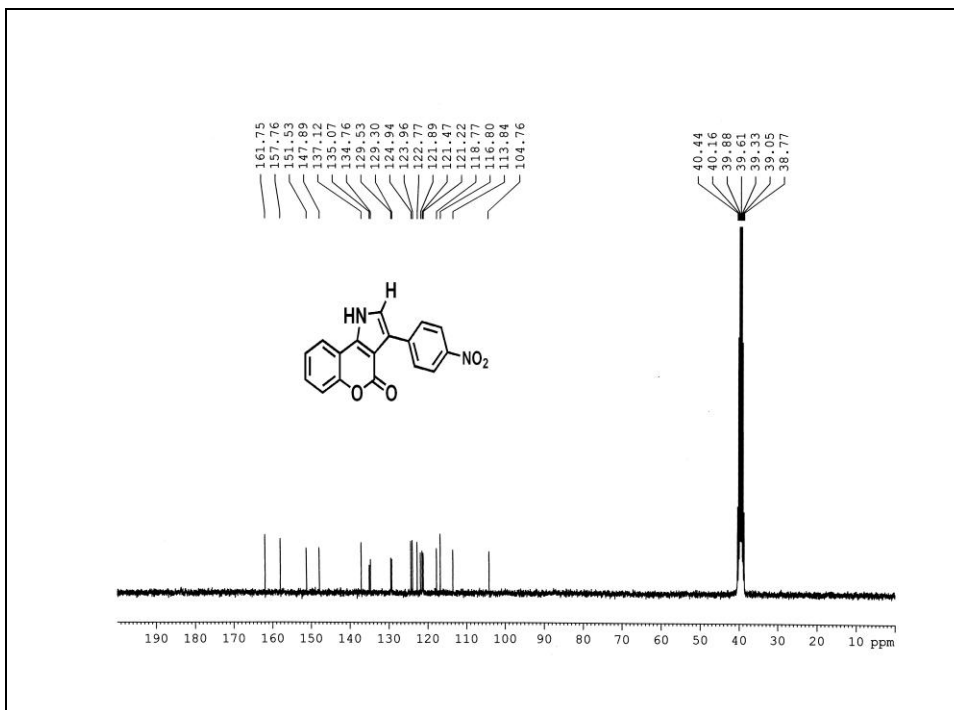


Figure8b ¹³C NMR spectrum of the product (4h)

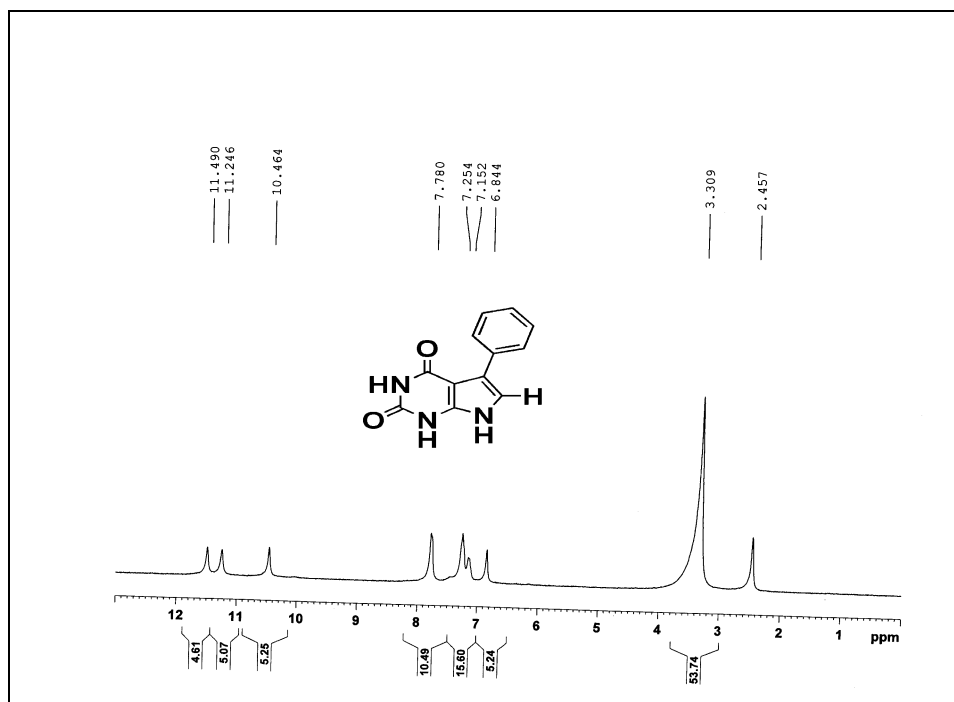


Figure9a ¹H NMR spectrum of the product (4i)

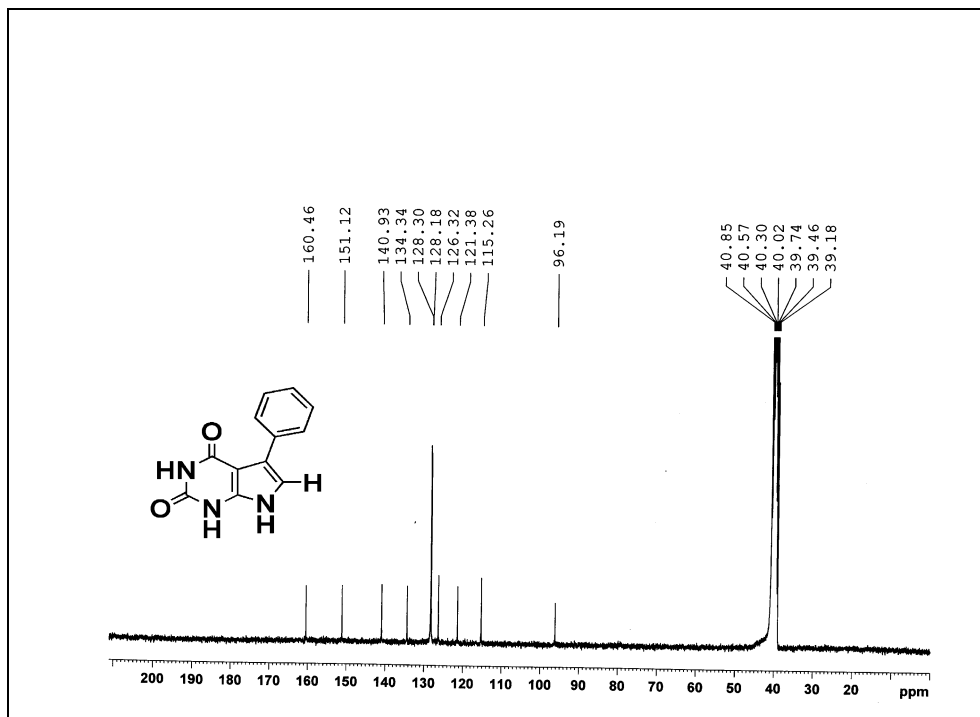


Figure9b ¹³C NMR spectrum of the product (4i)

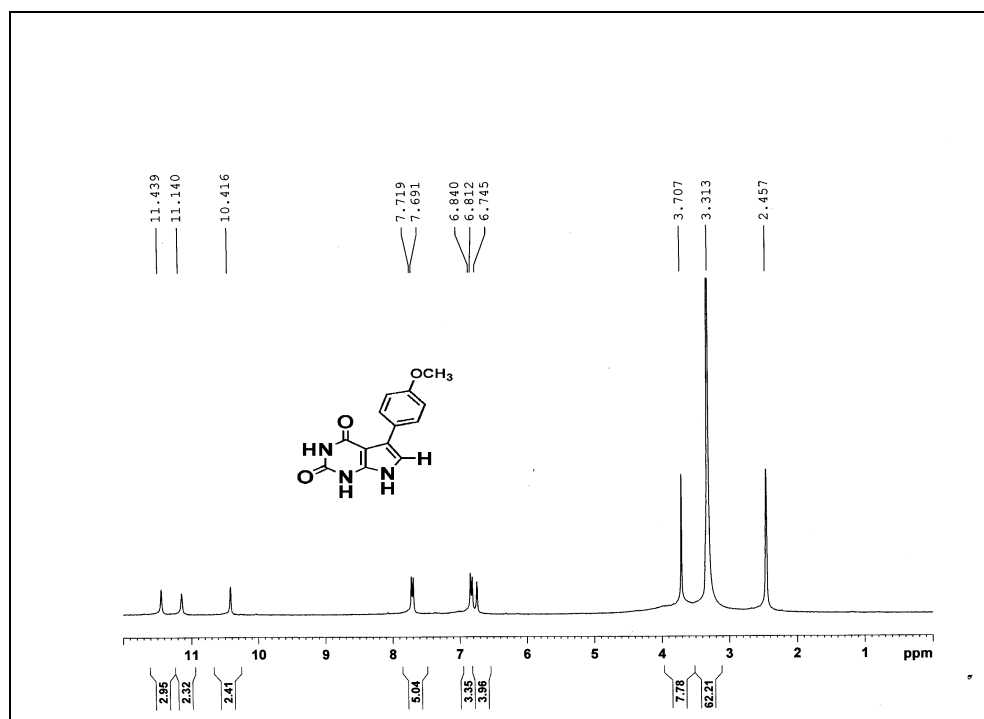


Figure10a ¹H NMR spectrum of the product (4j)

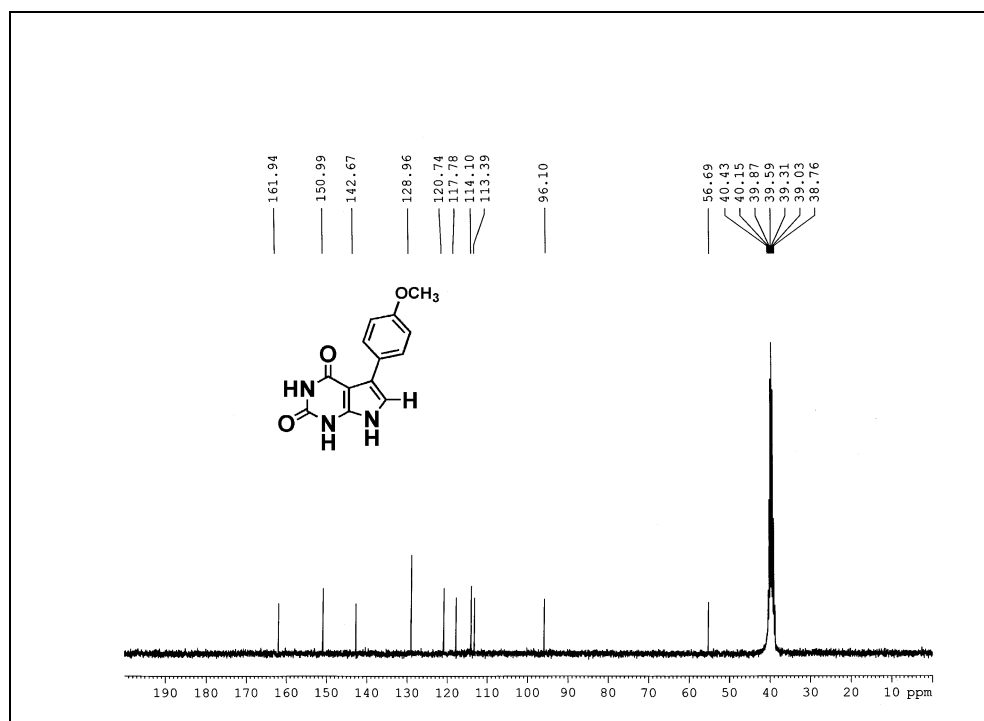


Figure10b ¹³C NMR spectrum of the product (4j)

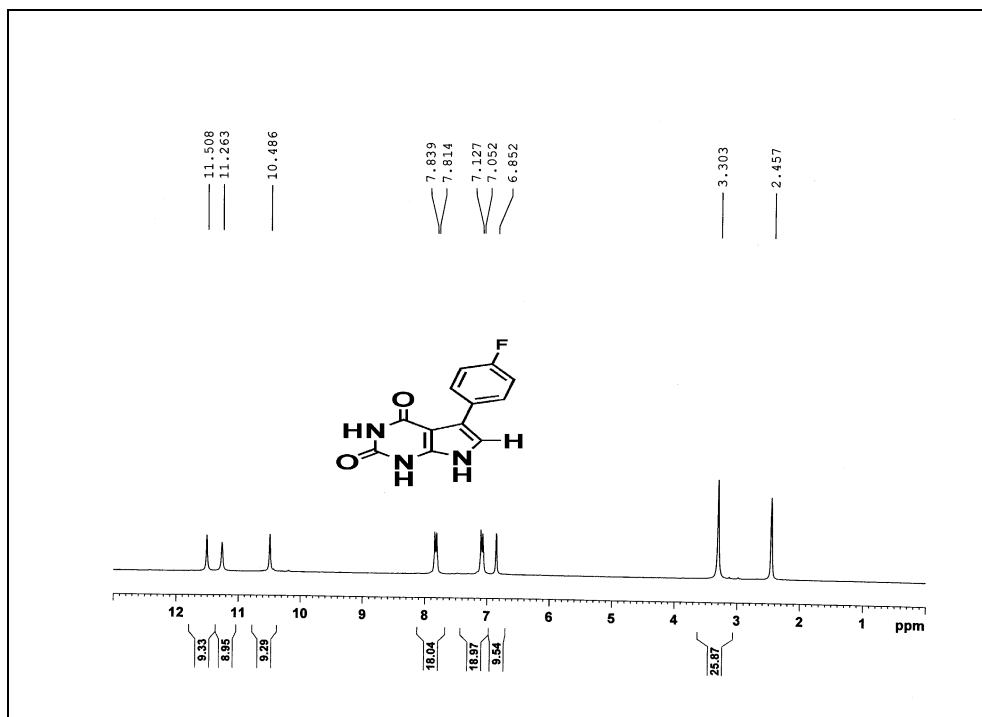


Figure 11a ¹H NMR spectrum of the product (4k)

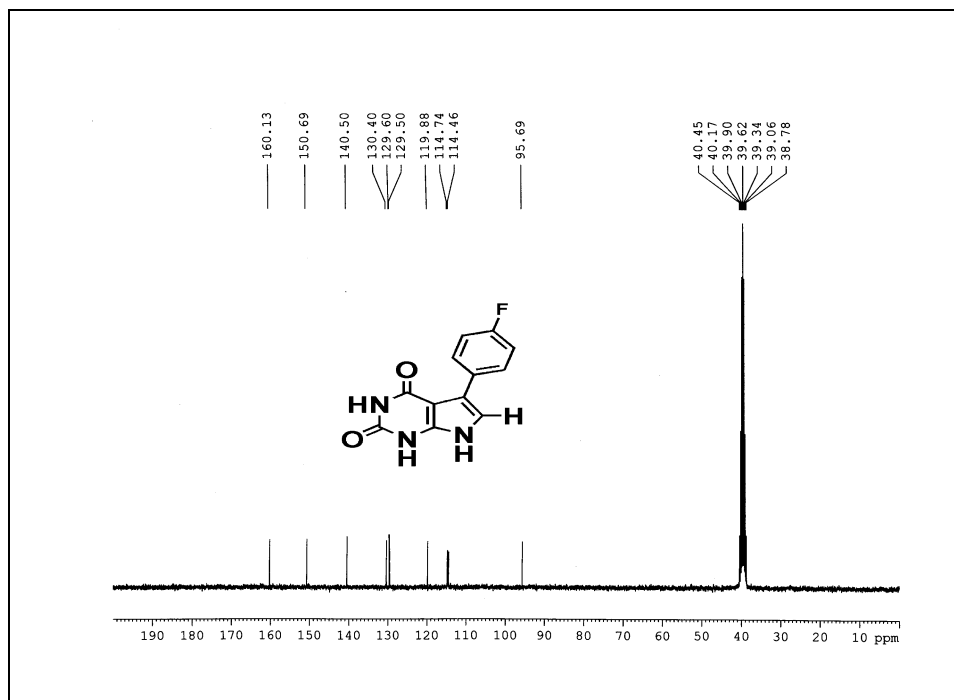


Figure 11b ¹³C NMR spectrum of the product (4k)