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

Supporting Information

3D Mesoporous Polycalix-functionalized Dual Bronsted-Lewis Acidic Double-charged DABCO-based Ionic Liquid: as a Powerful and Recyclable Supramolecular Polymeric Catalyst for Spiro-fused[4H-pyran] Synthesis in Green Solvent

Zahra Karimi, Bahador Karami*, Aref Mahmoudi Asl

Supporting information

3D Mesoporous Polycalix-functionalized Dual Bronsted-Lewis Acidic Double-charged DABCO-based Ionic Liquid: as a Powerful and Recyclable Supramolecular Polymeric Catalyst for Spiro-fused[4H-pyran] Synthesis in Green Solvent

Zahra Karimi, Bahador Karami, Aref Mahmoudi Asl*

Department of Chemistry, Yasouj University, P. O. Box 353, Yasouj, 75918-74831, Iran. Phone number: +987431004000, Fax number: + 987433223822, E-mail: karami@yu.ac.ir

Table of Contents

1. Preparing Cis-C4RA (1)

Cis-calix[4]resorcinarene macromolecule, Cis-C4RA (1), was produced via a condensation reaction of resorcinol with acetaldehyde. Synthesizing Cis confirmation was based on a formerly documented approach (also mentioned in the main article). The structure correctness was approved using FT-IR, ^{1}H NMR, and ^{13}C NMR analysis.

2. Characterization of Cis-C4RA (1)

White powder, Yield >75%, Mp.: > 360 °C; FT-IR (KBr, cm^{-1}): ν_{max} = 3000–3400 (OH); ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.30–1.32 (12H, CH_3, d), 4.43–4.501 (4H, CH, q), 6.16 (4H, ArH, s), 6.78 (4H, ArH, s), 8.57 (8H, OH, s) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 22.10 (CH_3), 29.05 (C-H), 102.57, 123.57, 125.78, 152.36 ppm.

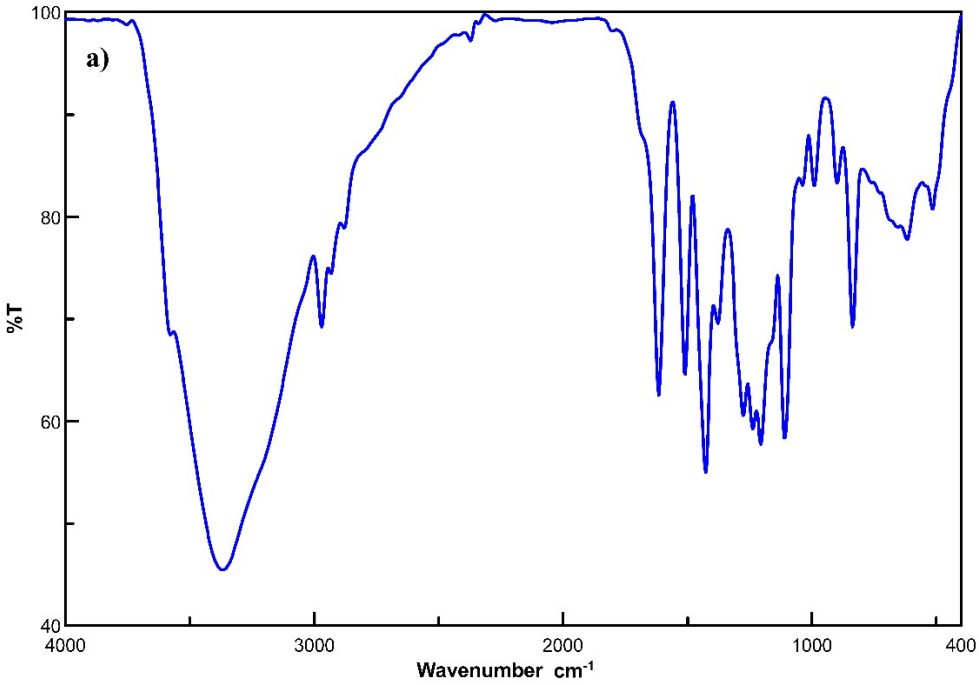


Fig. 1S. FT-IR (a) of synthesized Cis-C4RA

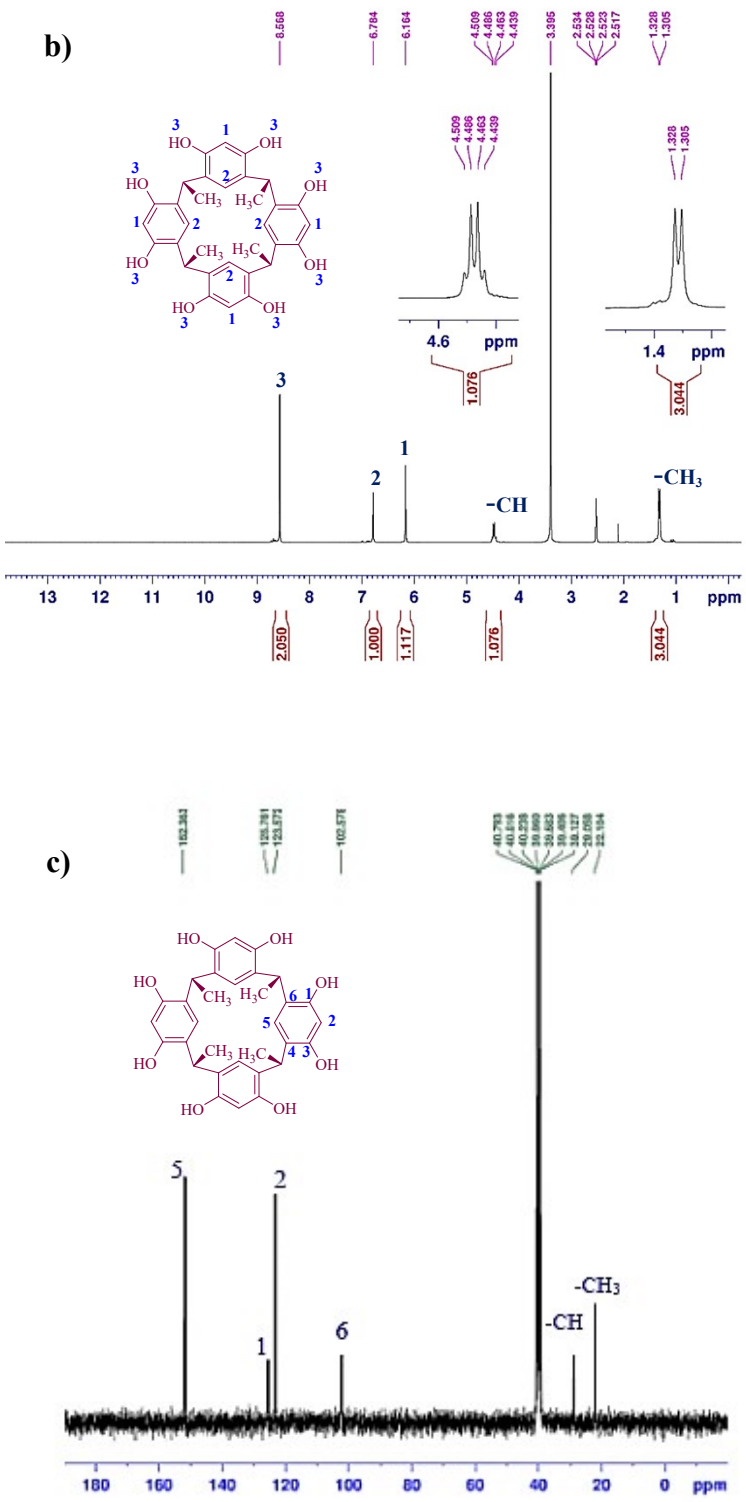
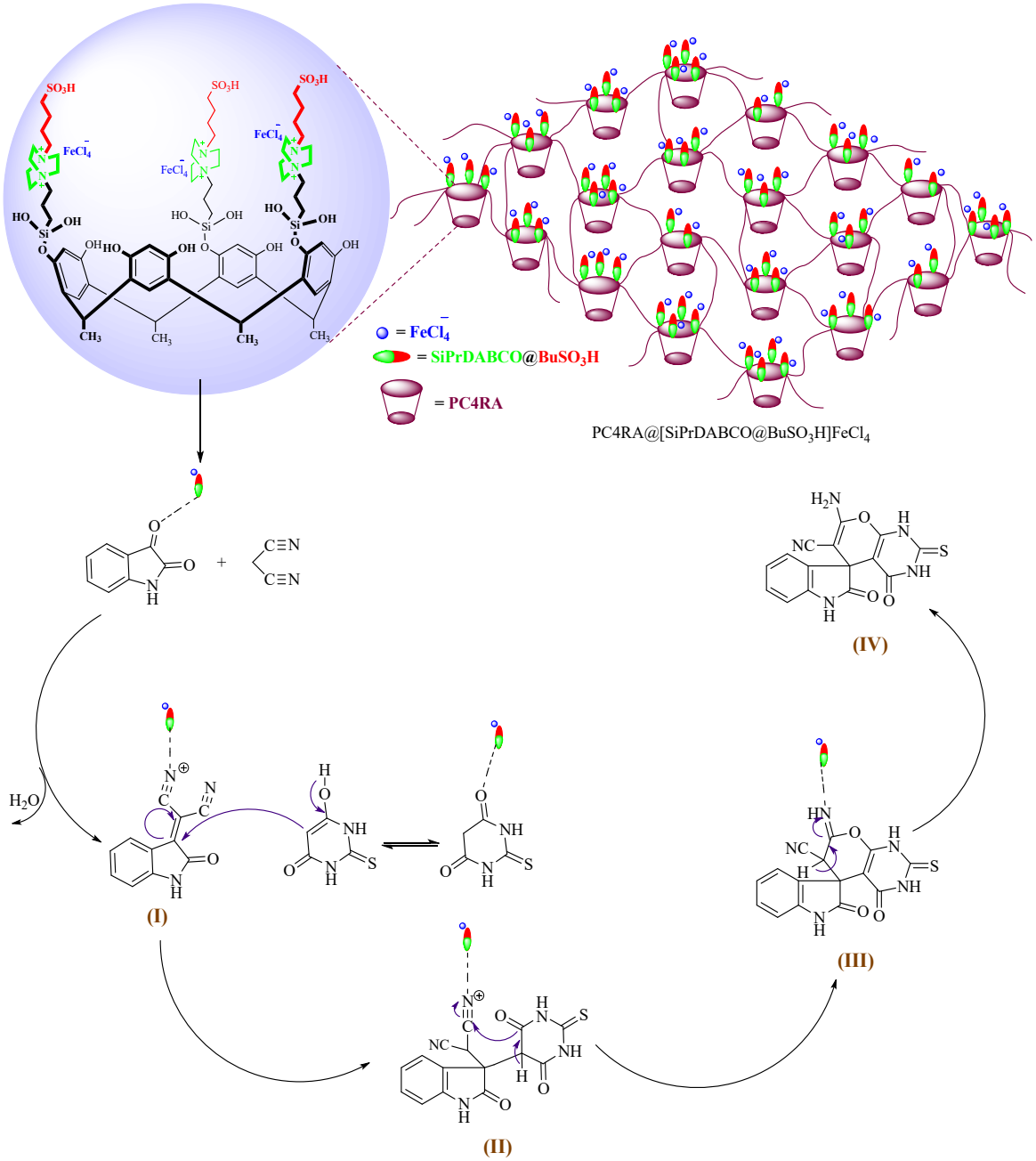


Fig. 2S. ^{1}H NMR (b) and ^{13}C NMR (c) of synthesized Cis-C4RA

3. The general mechanism for preparing spiro heterocycles

As depicted in scheme 1S, the mechanism of spirooxindole synthesis is composed of 3 cascade reactions, namely: the Knoevenagel condensation, Michael addition, and Cyclo-addition to produce isatylidene malononitrile (I), intermediate (II), and intramolecular cyclo-condensation between hydroxyl and the cyano groups (III), respectively. Eventually, compound (III) is converted to the target molecule (IV) by the tautomerization process (Note that Bronsted acid SO_3H acts as the active site with the most contribution in activation of compounds. Lewis acid $FeCl_3$ in the form of $FeCl_4$ with less contribution has a synergistic effect).

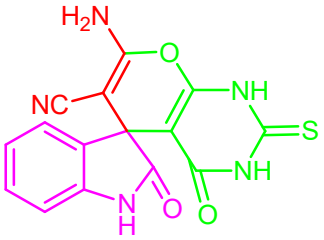


Scheme 1S. A designed mechanism for the preparation of spirooxindole heterocycles by using PC4RA@[SiPrDABCO@BuSO$_3$H](FeCl$_4$)

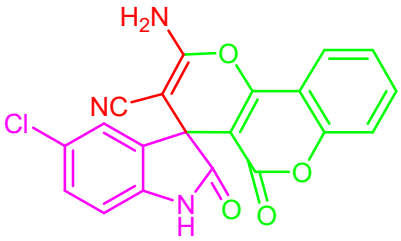
4. General experimental procedure for one-pot synthesis of spiro-fused[4H-pyran] heterocycles including spirooxindoles (3a-3d) and spiro-2-amino-4H-pyrans (4e-4h):

A combination of equal ratio (1 mmol) of ninhydrin/isatin, 1,3-dicarbonyl compound, malononitrile, by using PC4RA@[SiPrDABCO@BuSO$_3$H](FeCl$_4$) (0.01 g), as the acidic catalyst, was stirred and refluxed in H_2O (5 mL) for the needed time presented in Table 2. The reaction completion was followed by using TLC. After completing, the crude mixture was cooled, isolated, and then washed with hot EtOH to separate the catalyst. A 2:1 ratio of hot EtOH/H_2O was applied to recrystallize the remaining powder to afford the purified product (3a-4h), leading to an 85-95% yield. Characterization of spiro products was studied using IR and nuclear magnetic resonance spectroscopy analyses (NMR, 400 and 300 MHz spectrometers in DMSO solvent).

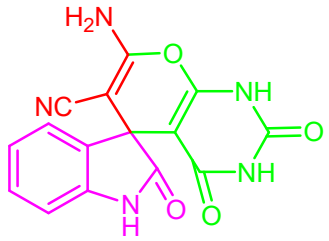
5. Product Characterization (3a-4h)



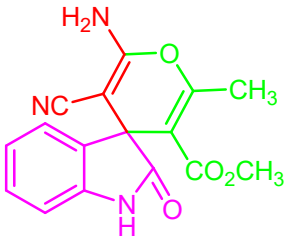
7'-amino-2,4'-dioxo-2'-thioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-d]pyrimidine]-6'-carbonitrile (3a): White powder, IR (KBr): ν_{max} = 3509, 3421, 3319, 3207, 3122, 3159, 2212, 1657, 1620, 1469 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.78 (1H, ArH, d, J = 7.8 Hz), 6.92 (1H, ArH, t, J = 7.6 Hz), 7.16-7.21 (2H, ArH, m), 7.43 (2H, NH_2, s), 10.55 (1H, NH, s), 12.51 (1H, NH, s), 13.90 (1H, NH, brs) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 46.59, 57.46, 91.53, 109.26, 116.76, 121.79, 123.97, 128.57, 132.93, 142.11, 152.85, 158.08, 159.12, 173.90, 177.14 ppm.



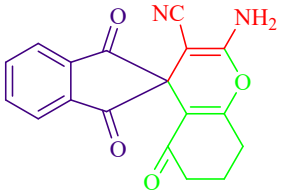
2'-amino-5-chloro-2,5'-dioxo-5'H-spiro[indoline-3,4'-pyrano[3,2-c]chromene]-3'carbonitrile (3b): White powder, IR (KBr): ν_{max} = 3317, 3248, 3204, 3053, 2197, 1736, 1671, 1476, 1165, 617 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.88 (1H, ArH, d, J = 6.6 Hz), 7.27 (1H, ArH, dd, J_1 = 6.6 Hz, J_2 = 1.7 Hz), 7.45 (1H, ArH, d, J = 1.7 Hz), 7.52 (1H, d, ArH, J = 6.8 Hz), 7.56 (1H, ArH, dt, J_1 = 6.2 Hz, J2 = 0.8 Hz), 7.74 (2H, NH_2, s), 7.77-7.81 (1H, ArH, m), 7.95 (1H, ArH, dd, J_1 = 6.5 Hz, J_2 = 1.1 Hz), 10.81 (1H, NH, s) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 47.85, 56.37, 100.74, 110.85, 112.58, 116.66, 116.87, 122.72, 124.57, 124.99, 126.05, 128.77, 133.68, 135.00, 141.11, 152.09, 155.39, 158.44, 158.54, 176.98 ppm.



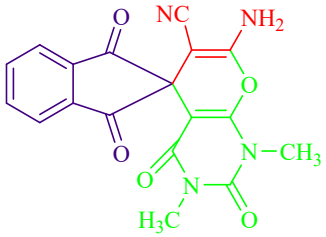
7'-amino-2,2',4'-trioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-d]pyrimidine]-6'-carbonitrile (3c): White powder**,** IR (KBr): ν_{max} = 3400, 3308, 3253, 2204, 1673, 1614, 1531, 1486, 1331 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.69 (1H, d, ArH, J = 7.6 Hz), 6.82 (1H, ArH, t, J = 7.7 Hz), 7.04-7.09 (2H, ArH, m), 7.28 (2H, NH_2, s), 10.40 (1H, NH, s), 11.04 (1H, NH, s), 12.22 (1H, NH, brs) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 46.61, 57.76, 86.79, 109.25, 116.93, 121.76, 123.75, 128.40, 133.48, 142.08, 149.22, 153.32, 158.23, 161.41, 177.63 ppm.



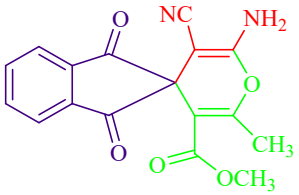
Methyl 2'-amino-3'-cyano-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (3d): White powder**,** IR (KBr): ν_{max} = 3355, 3305, 3150, 2202, 1716,1670, 1608, 1469 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.33 (3H, CH_3, s), 3.35 (3H, CH_3, s), 6.80 (1, ArH, d, J = 7.8 Hz), 6.92 (1H, ArH, m), 7.06 (1H, ArH, m), 7.16-7.21 (1H, ArH, m), 7.18 (2H, NH_2, s), 10.42 (1H, NH, s) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 19.28, 49.51, 51.89, 56.94, 105.34, 109.77, 117.94, 122.34, 123.83, 129.05, 134.89, 142.42, 158.91, 159.40, 165.57, 178.96 ppm.



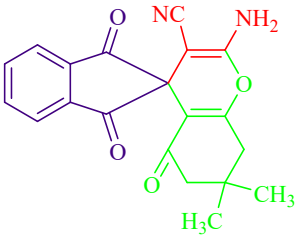
2-amino-1',3',5-trioxo-1',3',5,6,7,8-hexahydrospiro[chromene-4,2'-indene]-3-carbonitrile (4e): Yellow crystal, FT-IR (KBr): ν_{max} = 3402, 3317, 3198, 2191, 1706, 1672, 1644, 1591 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.93-1.99 (2H, CH_2, m), 2.29 (2H, CH_2, t, J = 6.6 Hz), 2.72 (2H, CH_2, t, J = 5.9 Hz), 7.66 (2H, NH_2, s), 7.99-8.05 (4H, ArH, m) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 19.77, 26.31, 35.21, 51.85, 53.09, 110.90, 116.81, 123.10 (2C, ArC), 136.58 (2C, ArC), 140.47 (2C, ArC), 159.71, 168.29, 196.08 (2C, C=O), 199.72.



7'-amino-1',3'-dimethyl-1,2',3,4'-tetraoxo-1,1',2',3,3',4'-hexahydrospiro[indene-2,5'-pyrano [2,3-d]pyrimidine]-6'-carbonitrile (4f): Yellow crystal, FT-IR (KBr): ν_{max} = 3378, 3293, 3189, 2194, 1704, 1643, 1496 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ = 3.02 (3H, CH_3, s), 3.40 (3H, CH_3, s), 8.02 (2H, NH_2, s), 8.04–8.12 (4H, ArH, m). ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 28.26, 29.97, 52.39, 53.67, 86.06, 116.81, 123.75, 137.44, 140.88, 149.97, 153.50, 159.88, 160.89, 200.15 ppm.

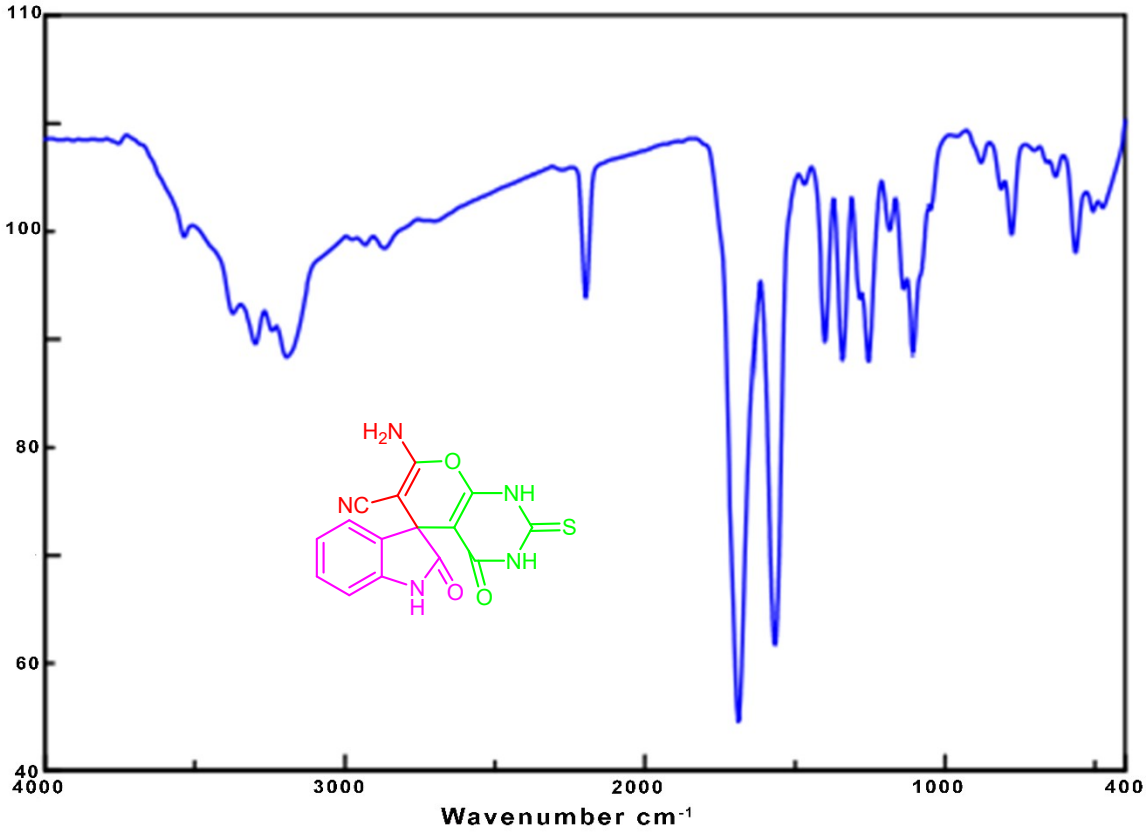


methyl 2'-amino-3'-cyano-6'-methyl-1,3-dioxo-1,3-dihydrospiro[indene-2,4'-pyran]-5'-carboxylate (4g): Yellow crystal, FT-IR (KBr): ν_{max} = 3386, 3250, 2198, 1724, 1654, 1592, 1434 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ = 2.25 (3H, CH_3, s), 3.73 (3H, CH_3, s), 7.80 (2H, NH_2, brs), 7.82-7.84 (1H, ArH, m), 7.89-7.92 (1H, ArH, m), 7.98-8.00 (2H, ArH, m) ppm; ^{13}C-NMR (75 MHz, DMSO-d_6): δ = 14.32, 51.25, 53.77, 68.21, 106.11, 117.31, 119.86, 125.02, 133.21, 136.11, 137.62, 142.99, 164.13, 167.08, 168.51, 194.00 ppm.

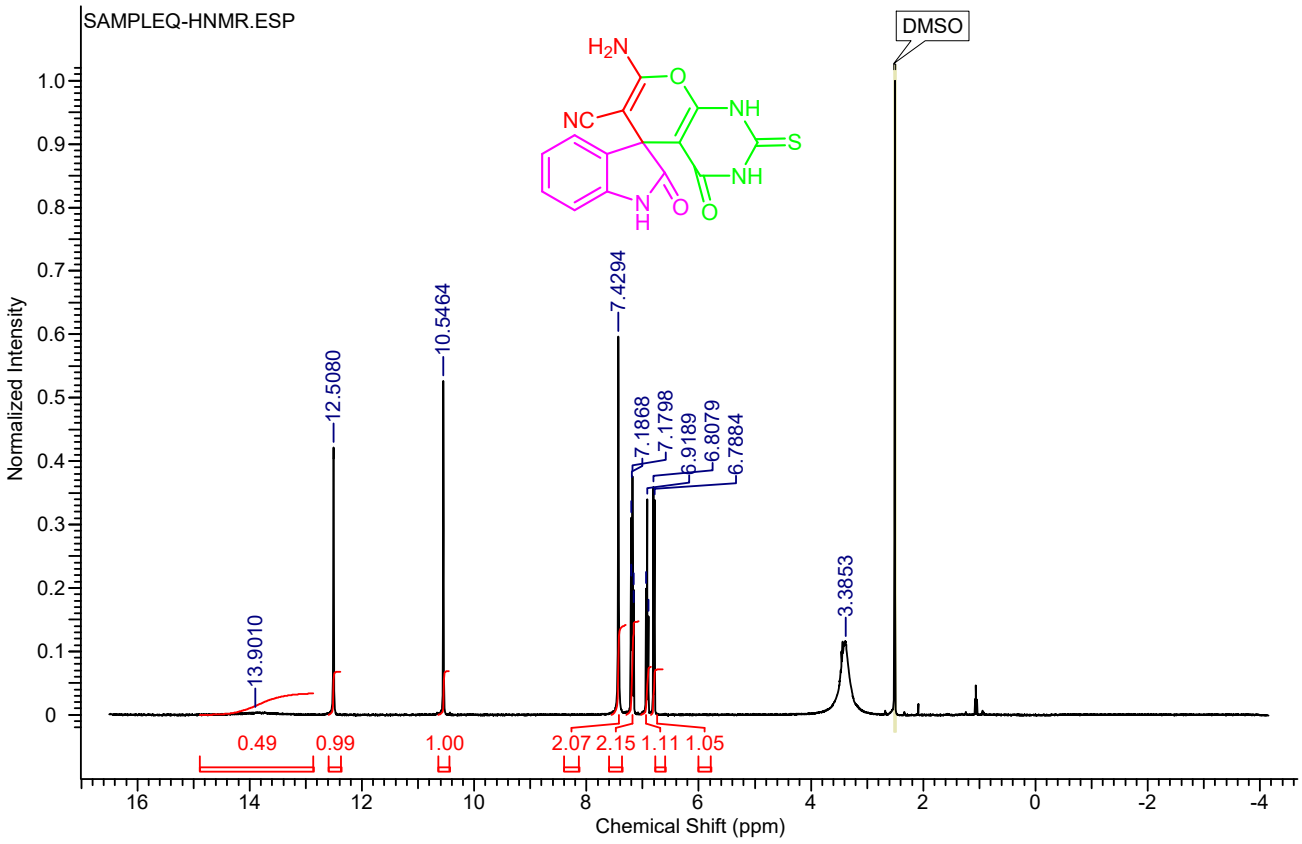


2-amino-7,7-dimethyl-1',3',5-trioxo-1',3',5,6,7,8-hexahydrospiro[chromene-4,2'-indene]-3-carbonitrile (4h): Yellow crystal, FT-IR (KBr): ν_{max} = 3374, 3309, 3193, 2190, 1716, 1658, 1592, 1461 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ = 1.06 (6H, CH_3, s), 2.22 (2H, CH_2, s), 2.64 (2H, CH_2, s), 7.70 (2H, NH_2, s), 8.01 (4H, ArH, m) ppm; ^{13}C-NMR (75 MHz, DMSO-d_6): δ = 27.65, 32.95, 40,75, 49.39, 52.25, 53.52, 110.44, 117.33, 123.66, 137.14, 141.01, 160.35, 167.00, 196.58, 200.26 ppm.

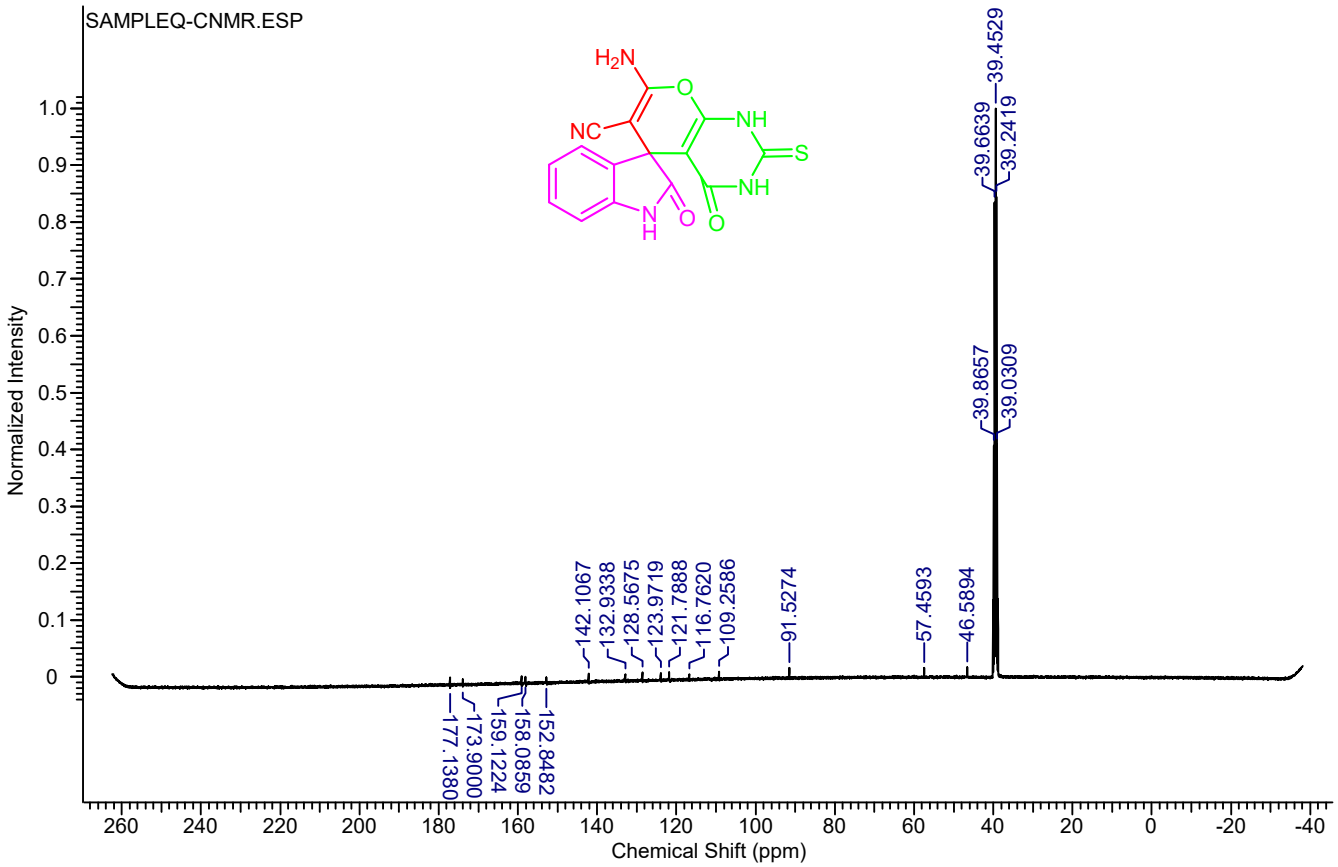
6. Spectral data for compounds 3a-4h



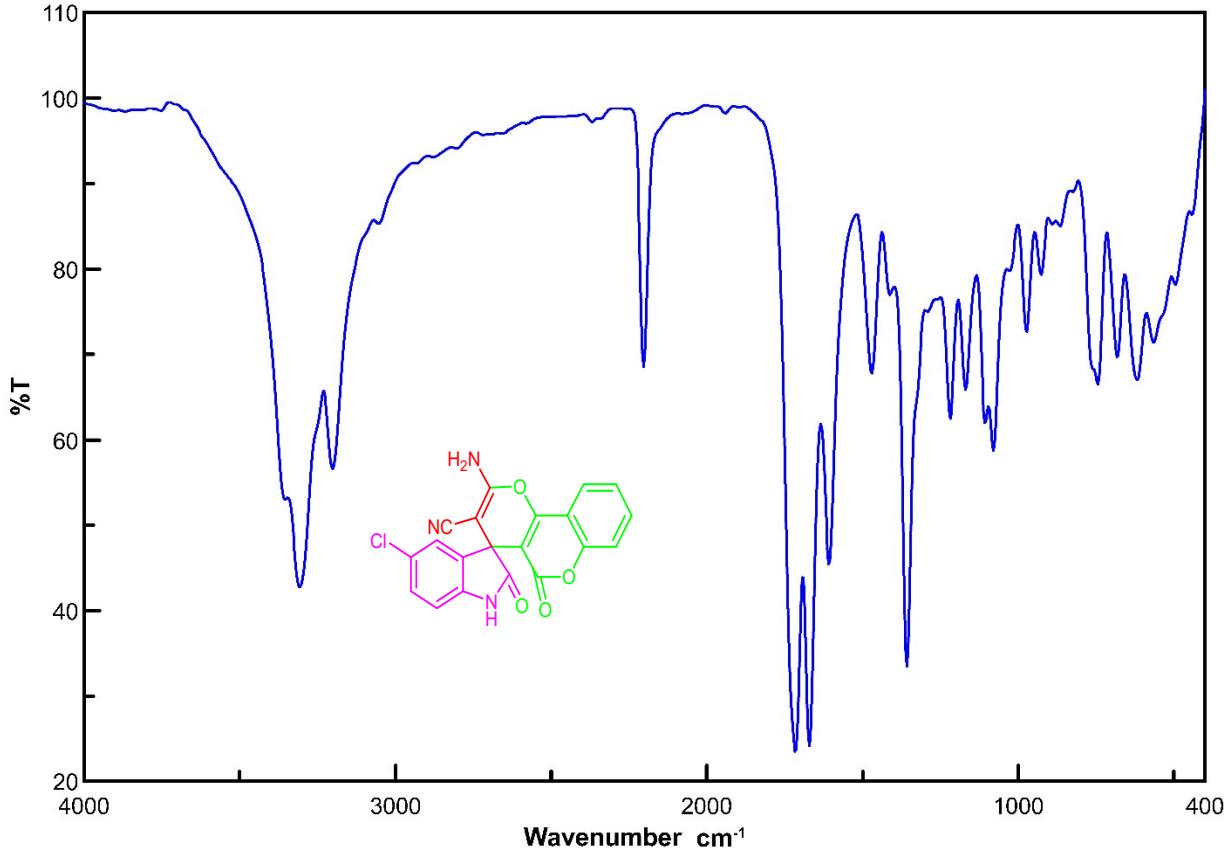
FT-IR spectrum of the product **3a**



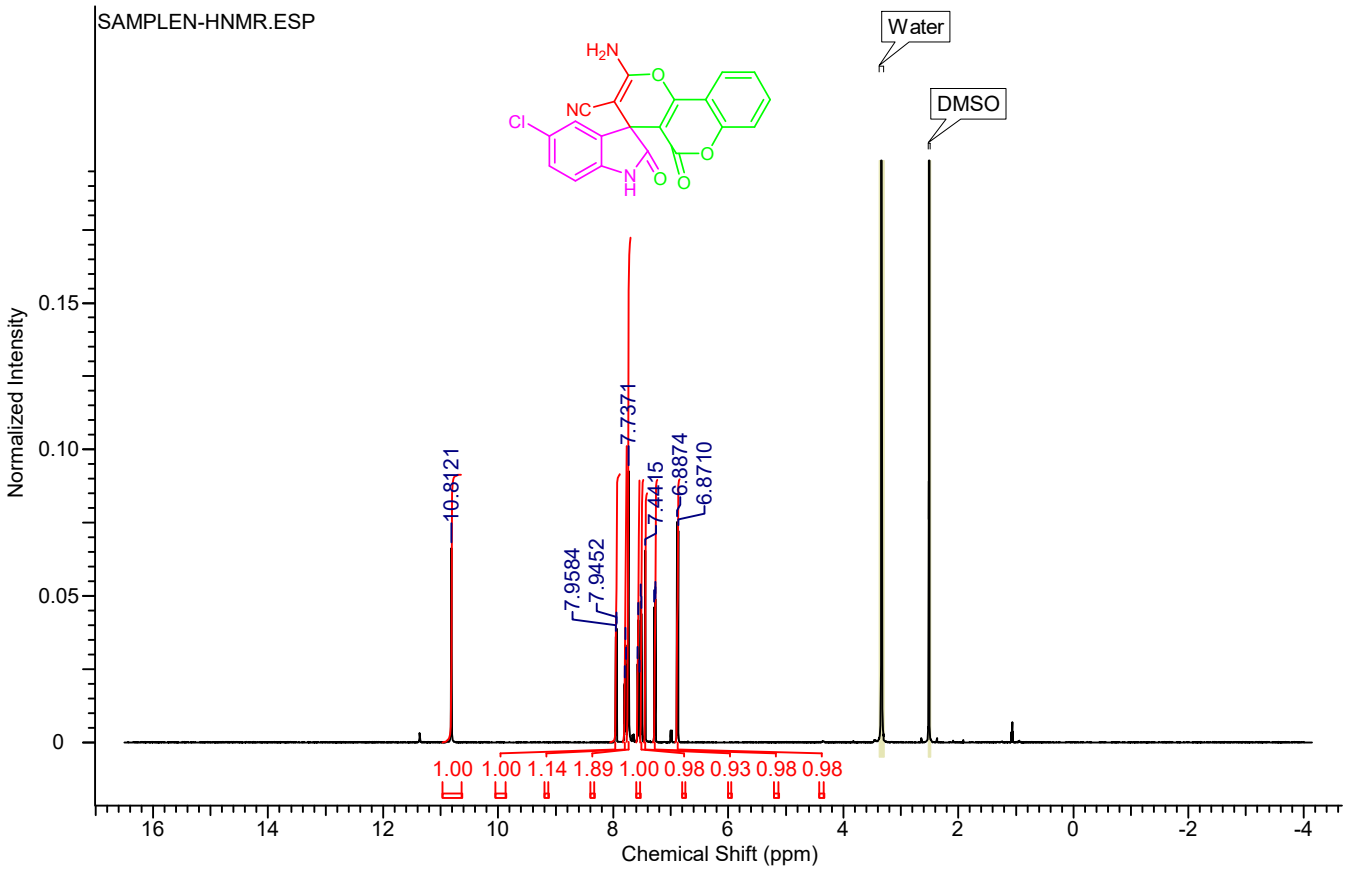
^{1}H NMR spectrum of the product **3a**



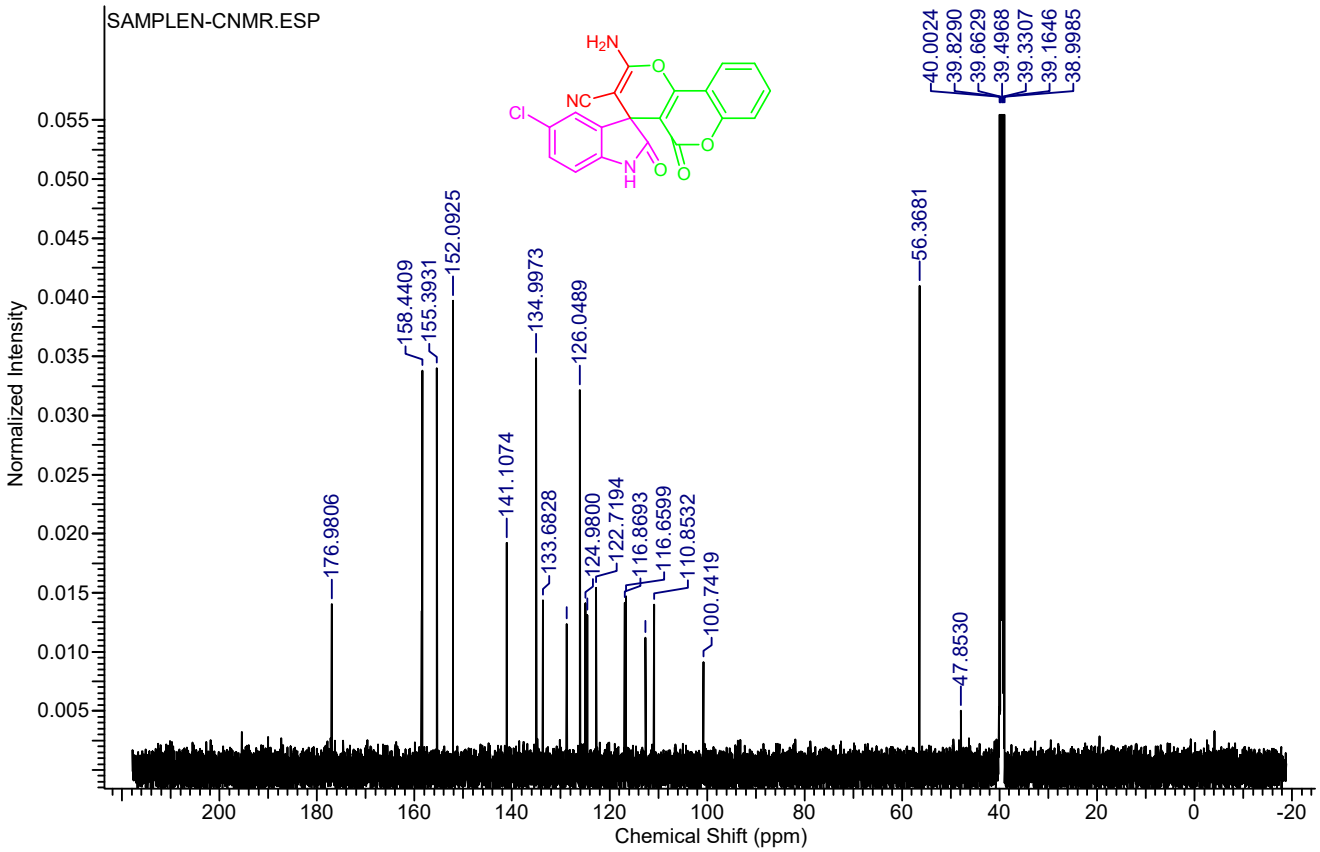
^{13}C NMR spectrum of the product **3a**



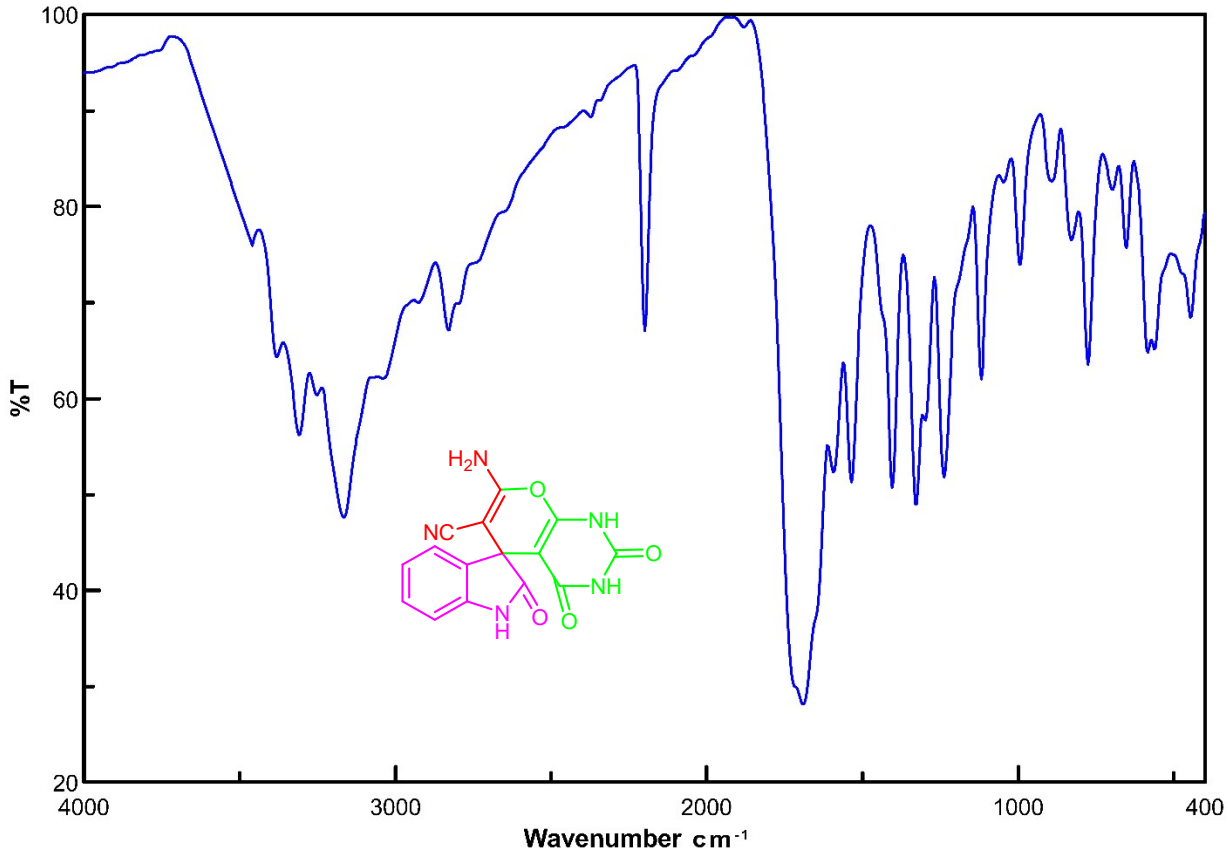
FT-IR spectrum of the product **3b**



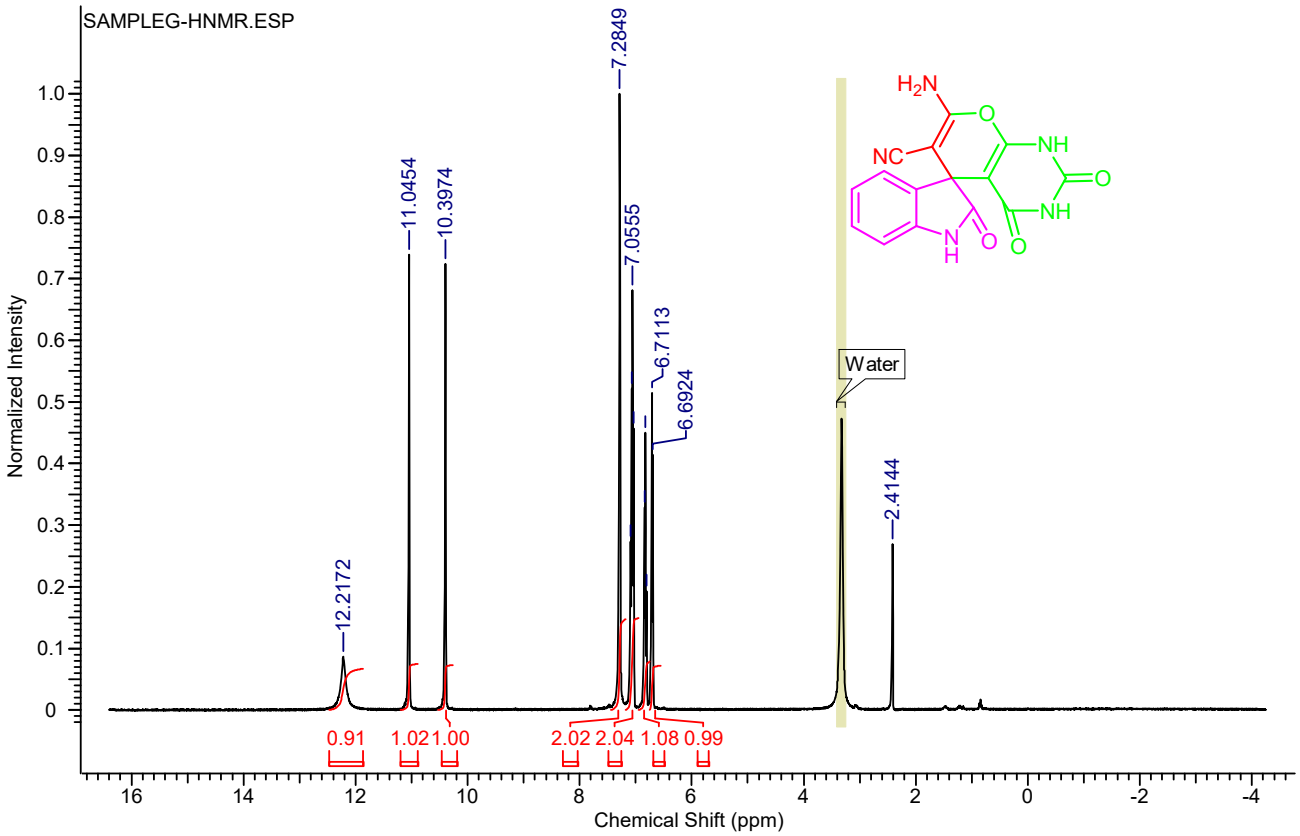
^{1}H NMR spectrum of the product **3b**



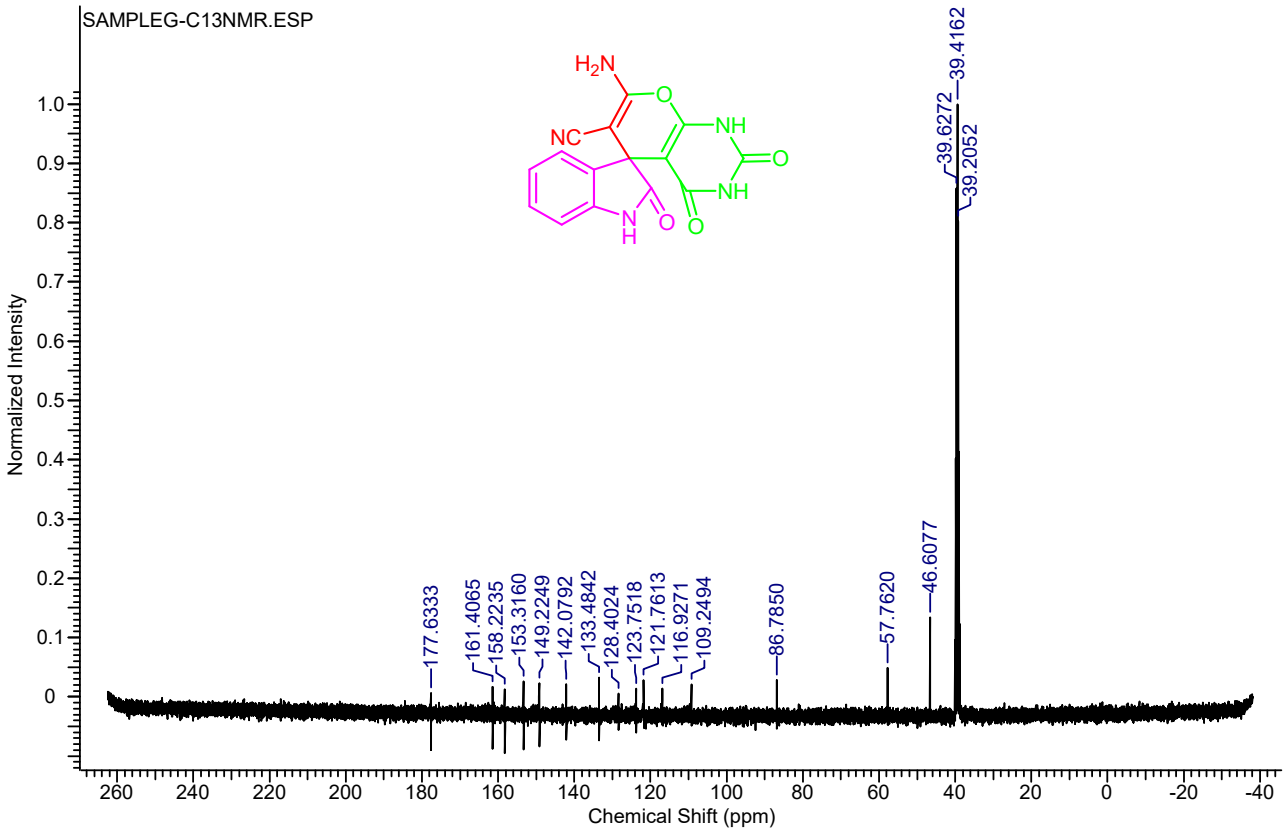
^{13}C NMR spectrum of the product **3b**



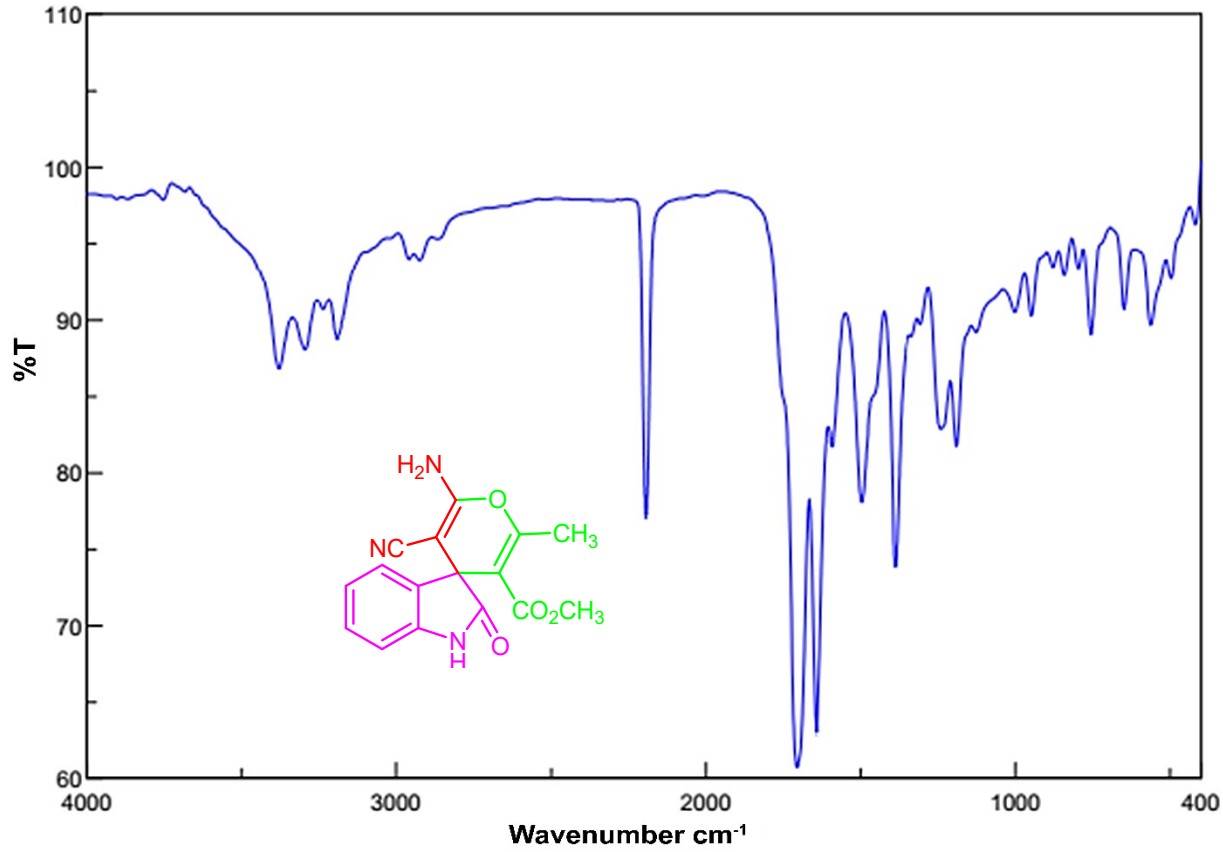
FT-IR spectrum of the product **3c**



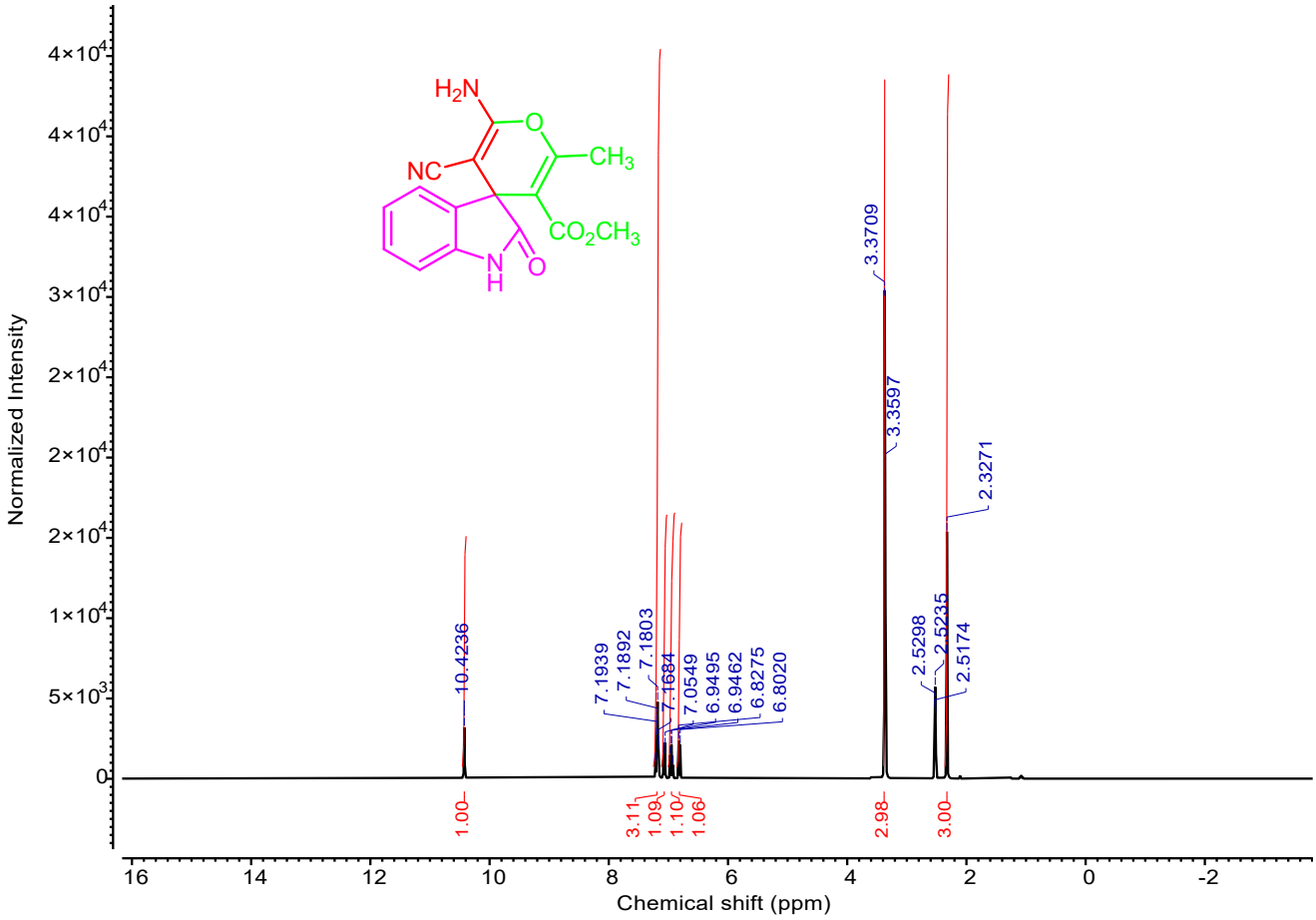
^{1}H NMR spectrum of the product **3c**



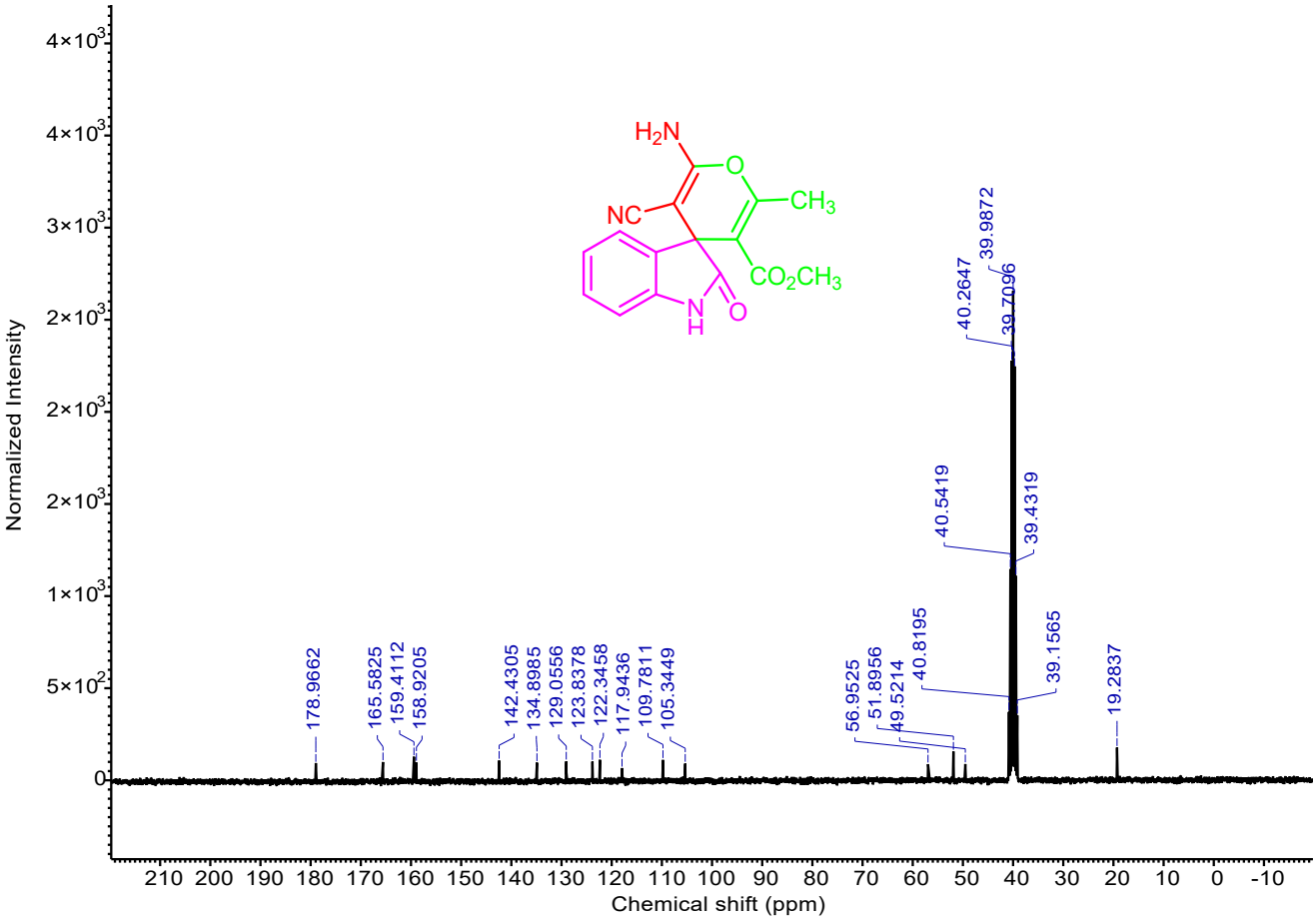
^{13}C NMR spectrum of the product **3c**



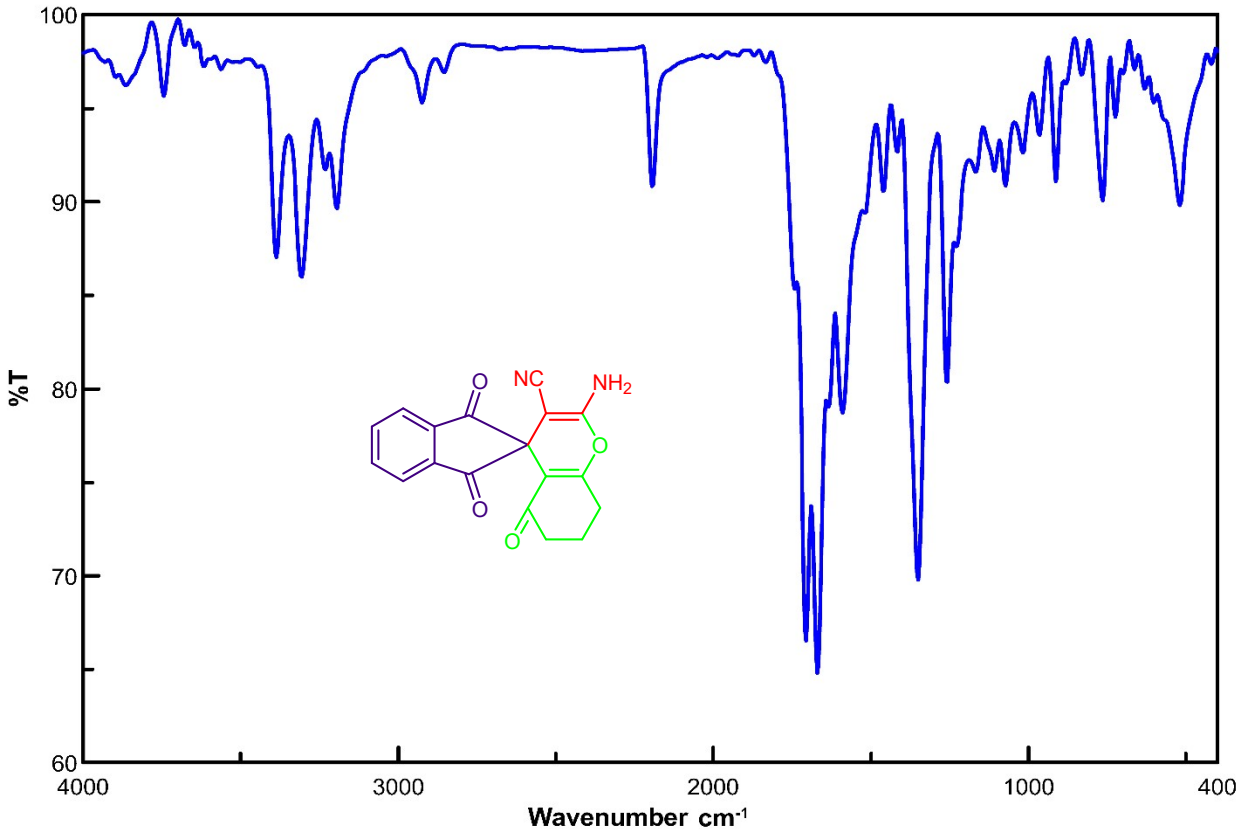
FT-IR spectrum of the product **3d**



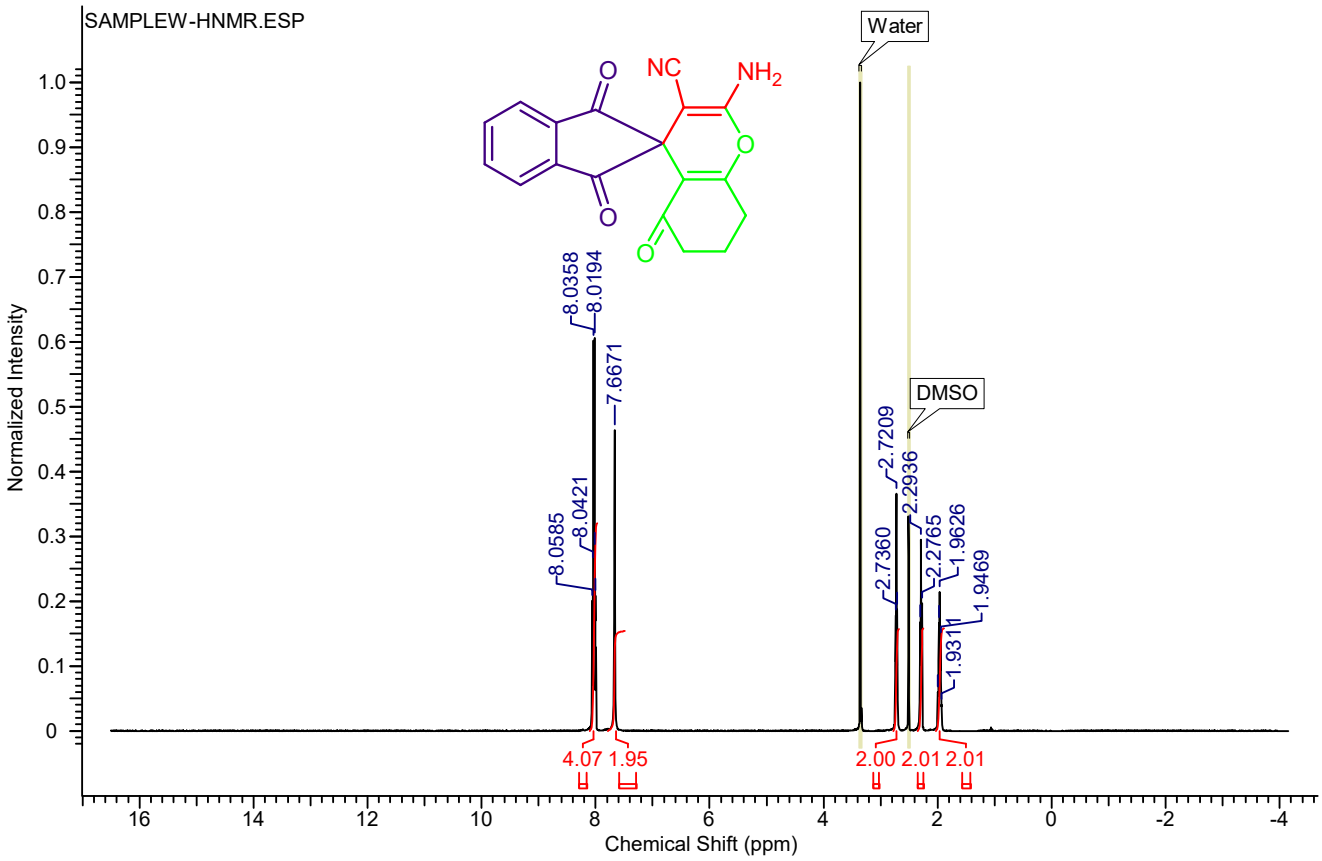
^{1}H NMR spectrum of the product **3d**



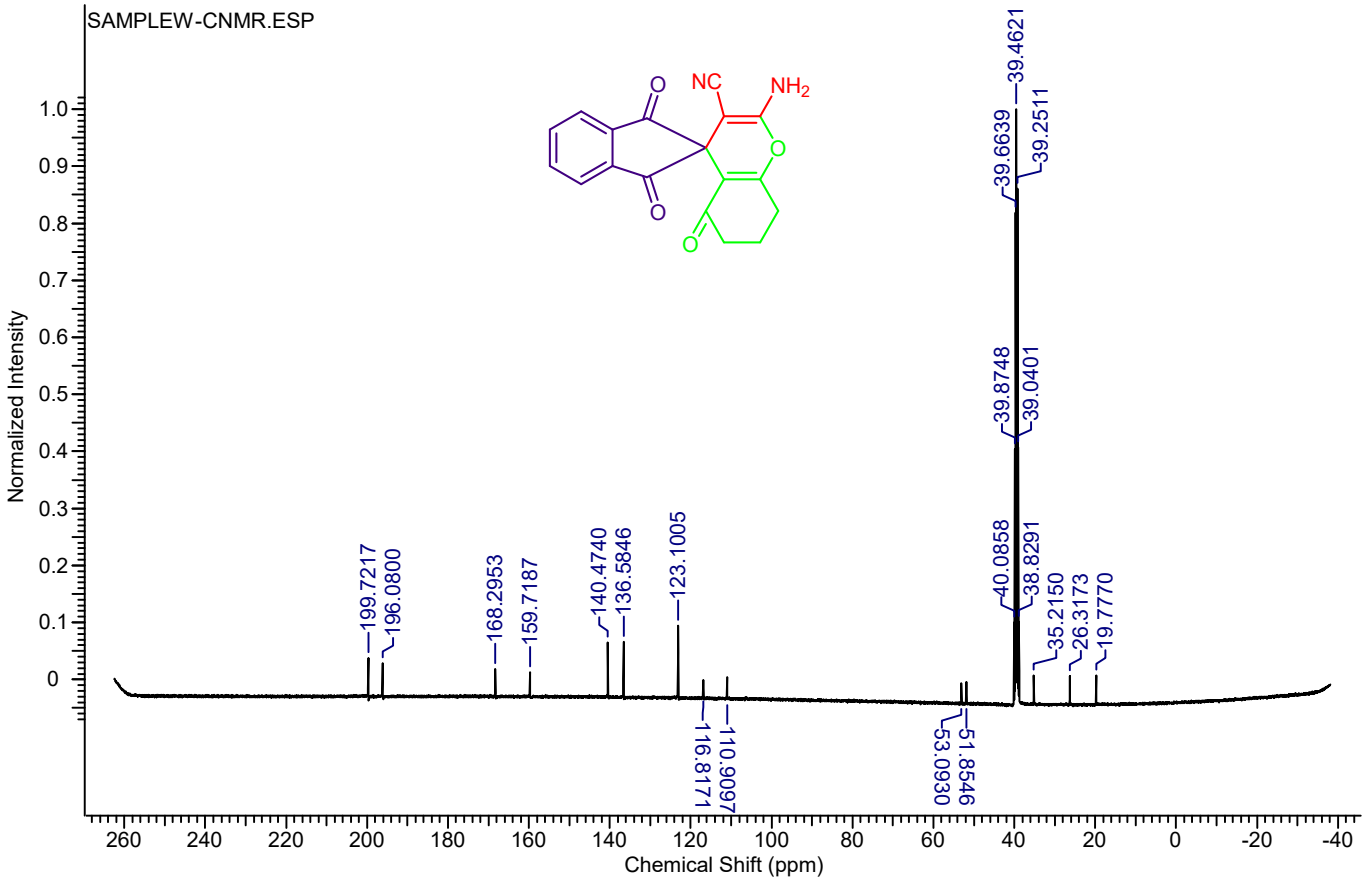
^{13}C NMR spectrum of the product **3d**



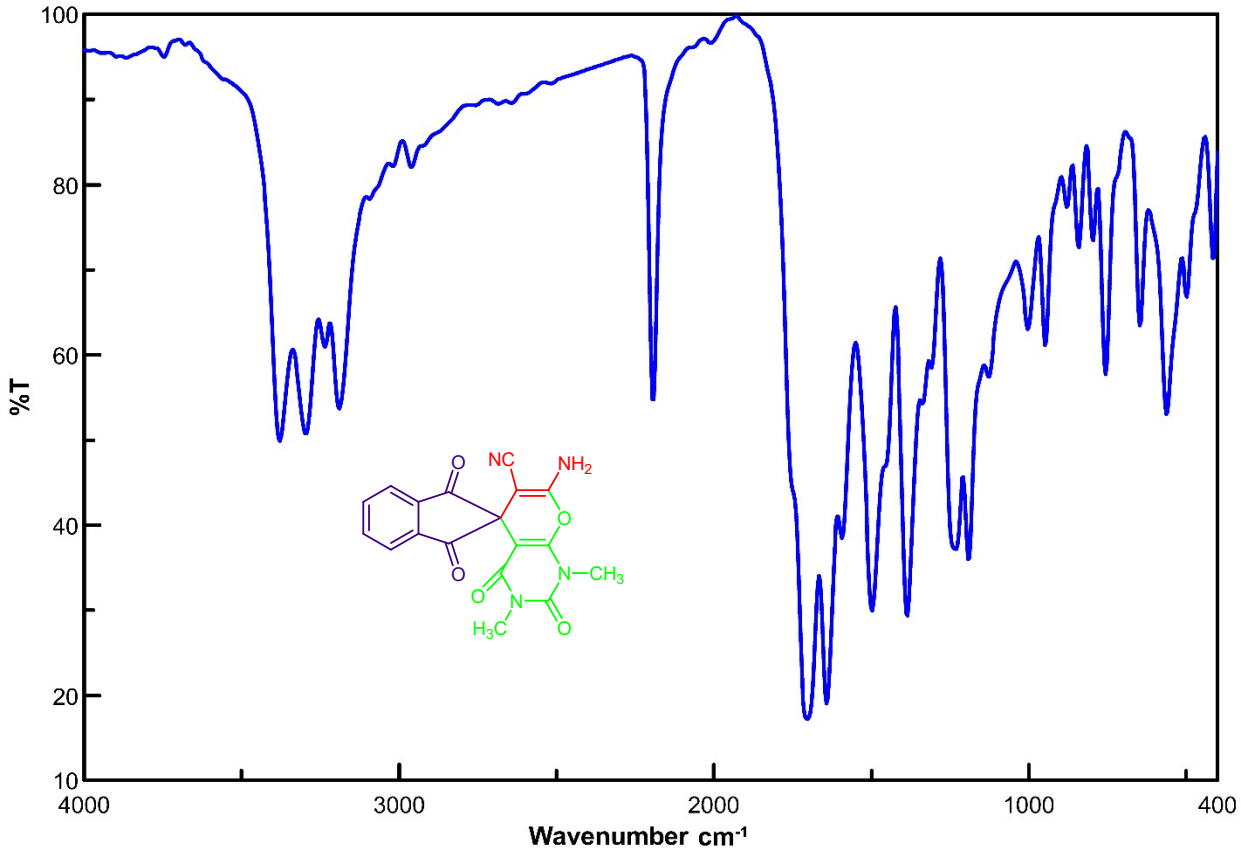
FT-IR spectrum of the product **4e**



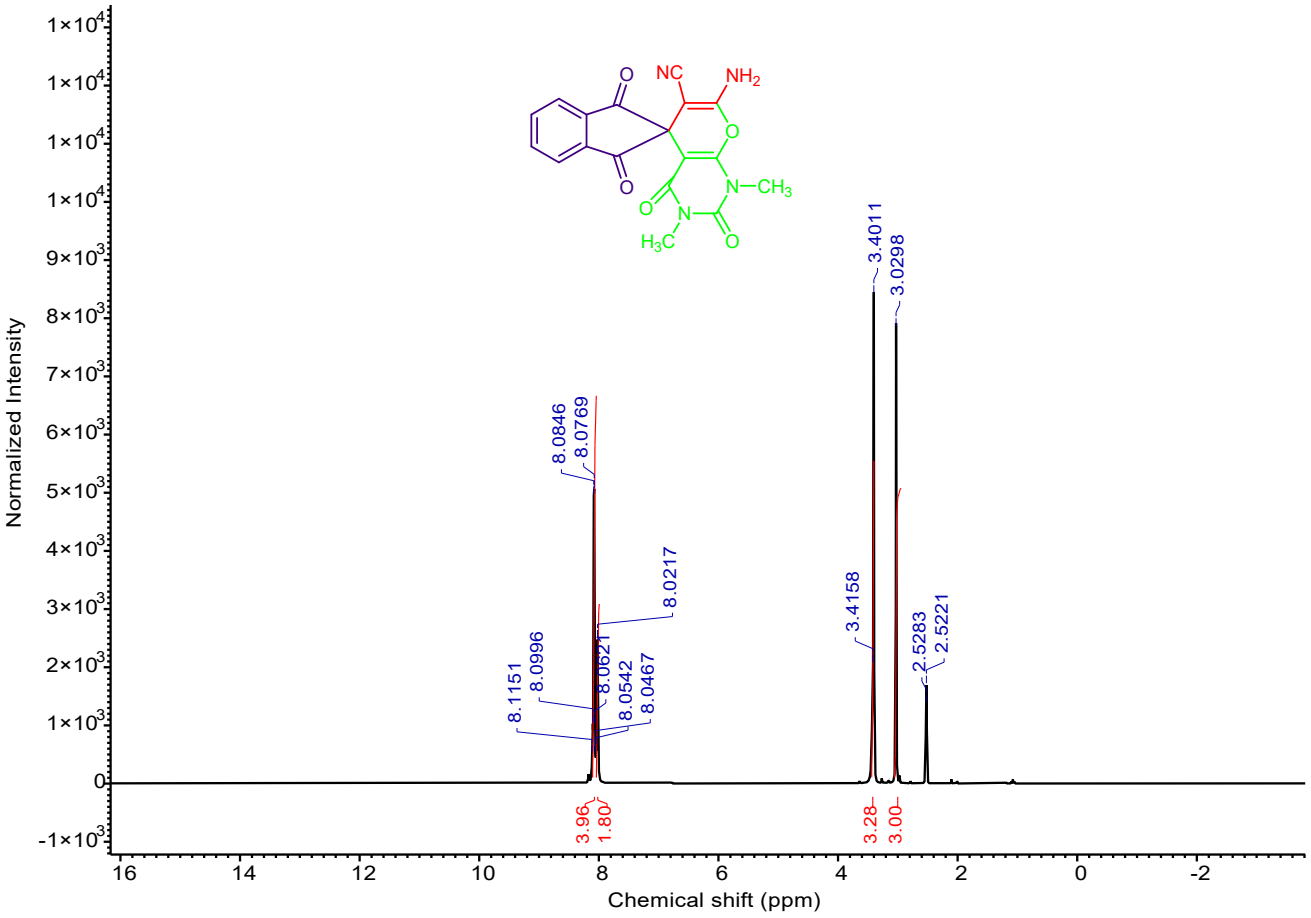
^{1}H NMR spectrum of the product **4e**



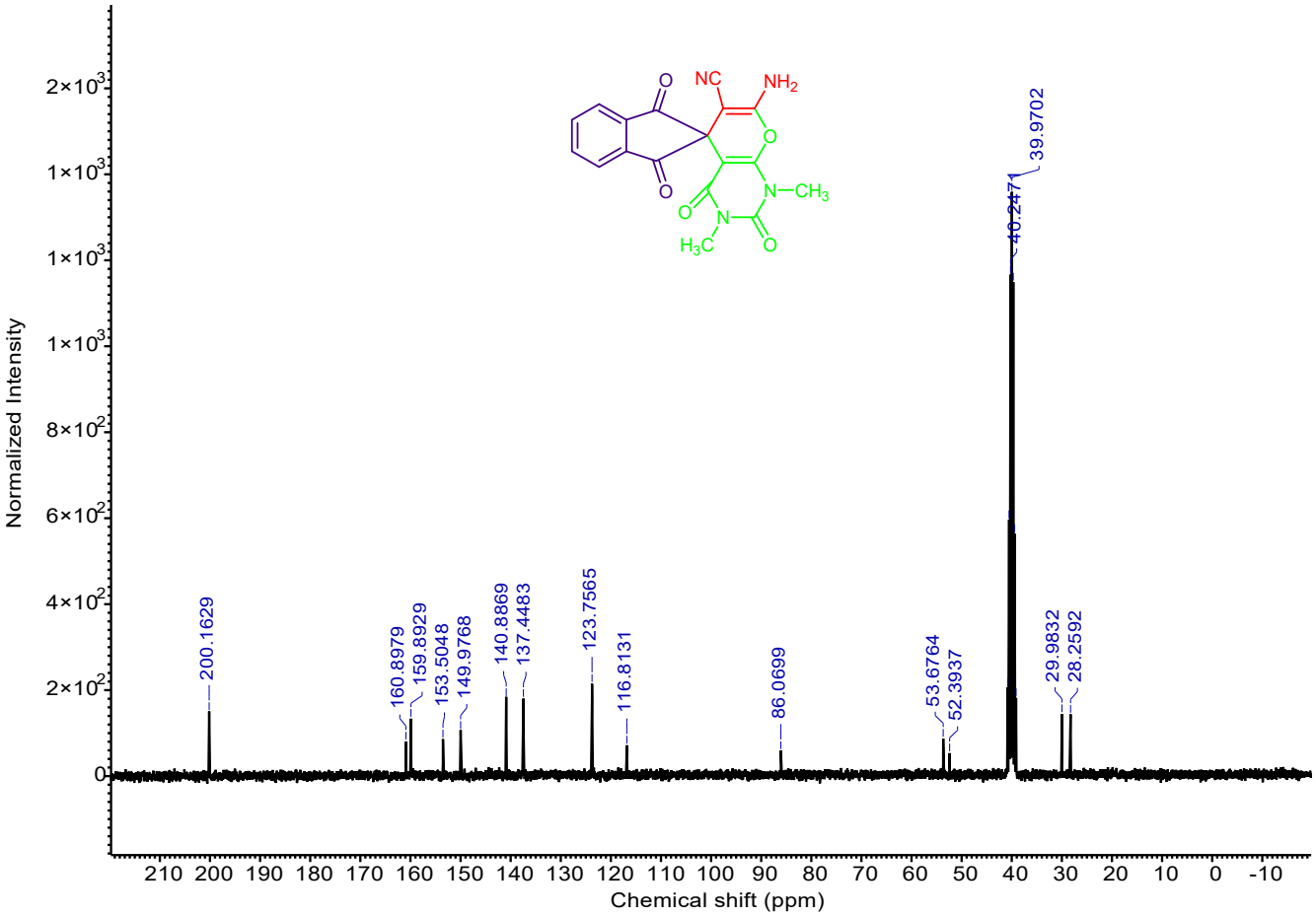
^{13}C NMR spectrum of the product **4e**



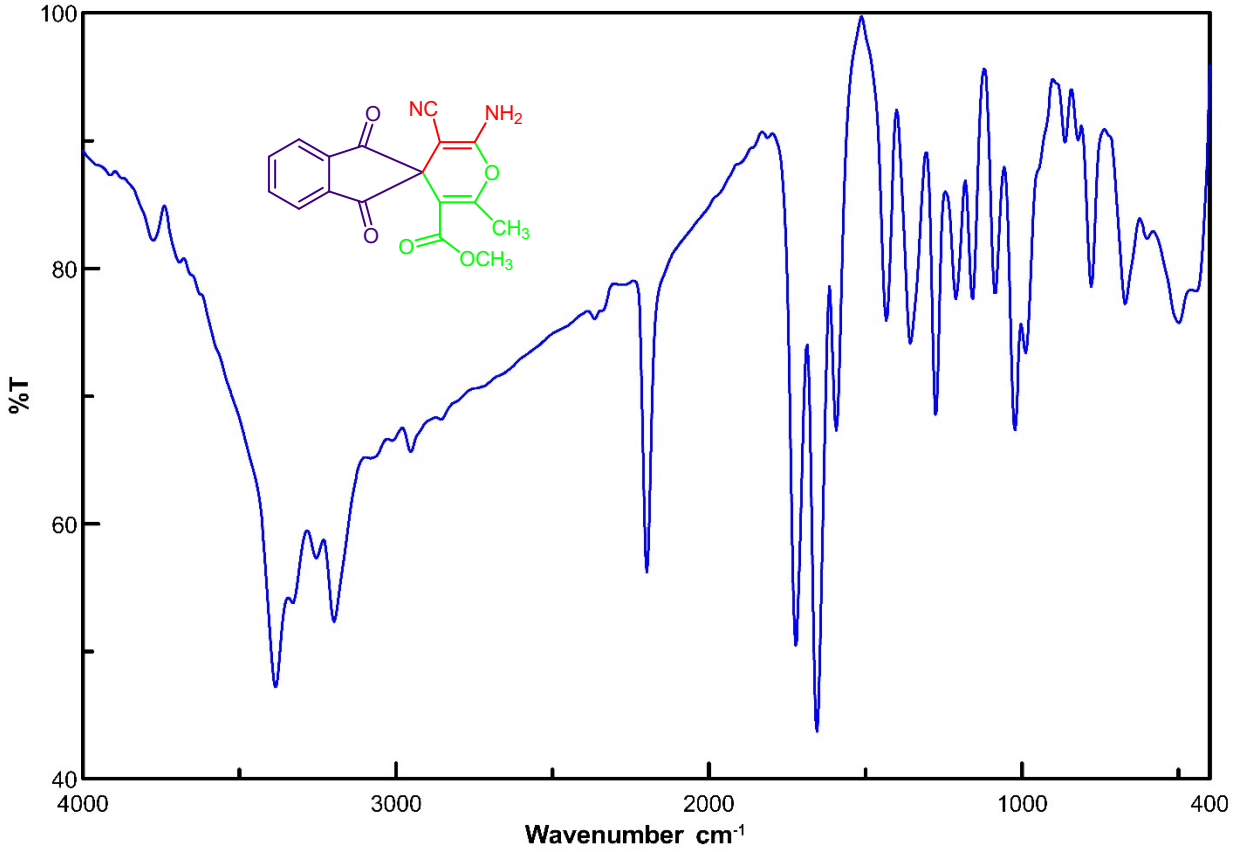
FT-IR spectrum of the product **4f**



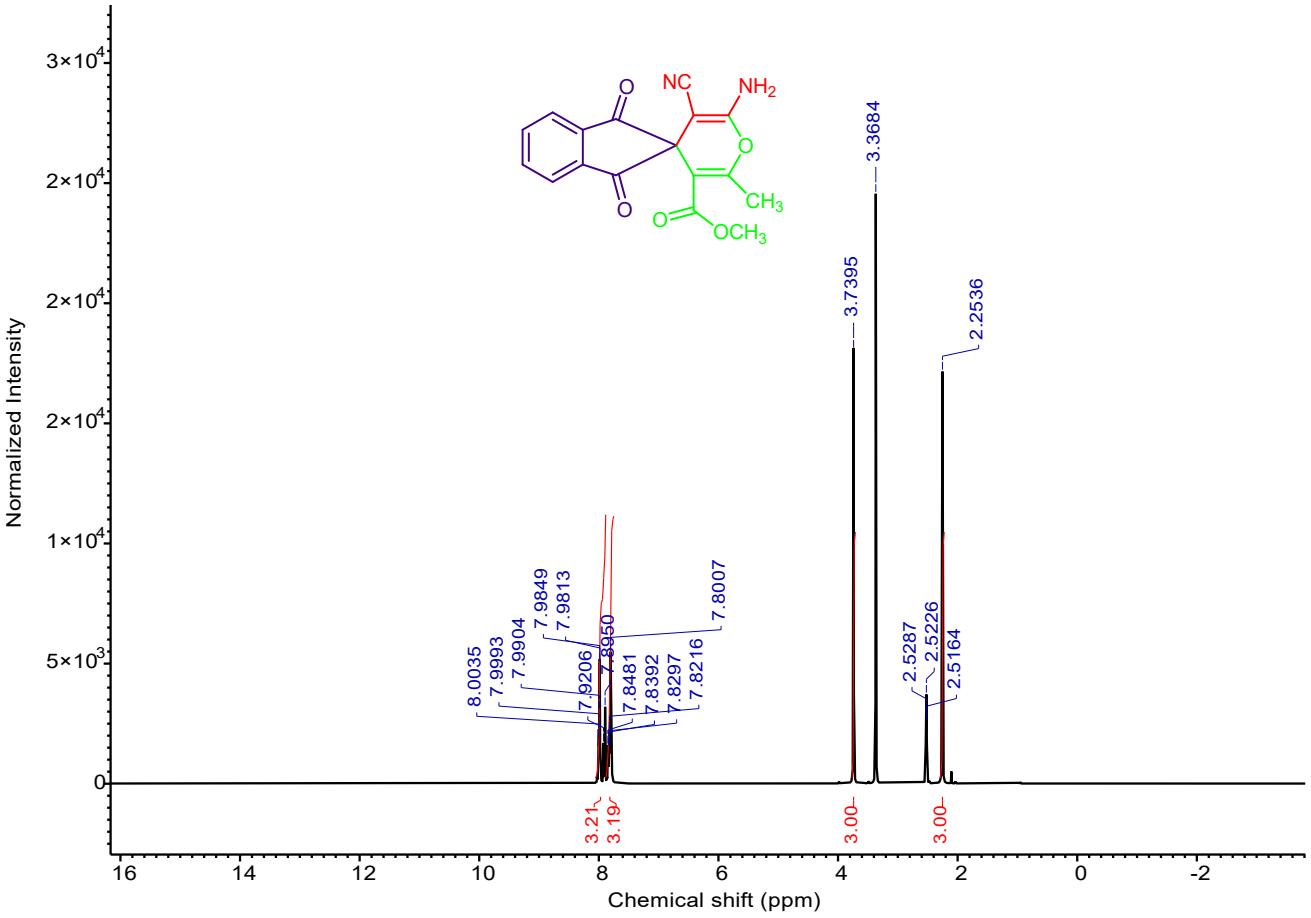
^{1}H NMR spectrum of the product **4f**



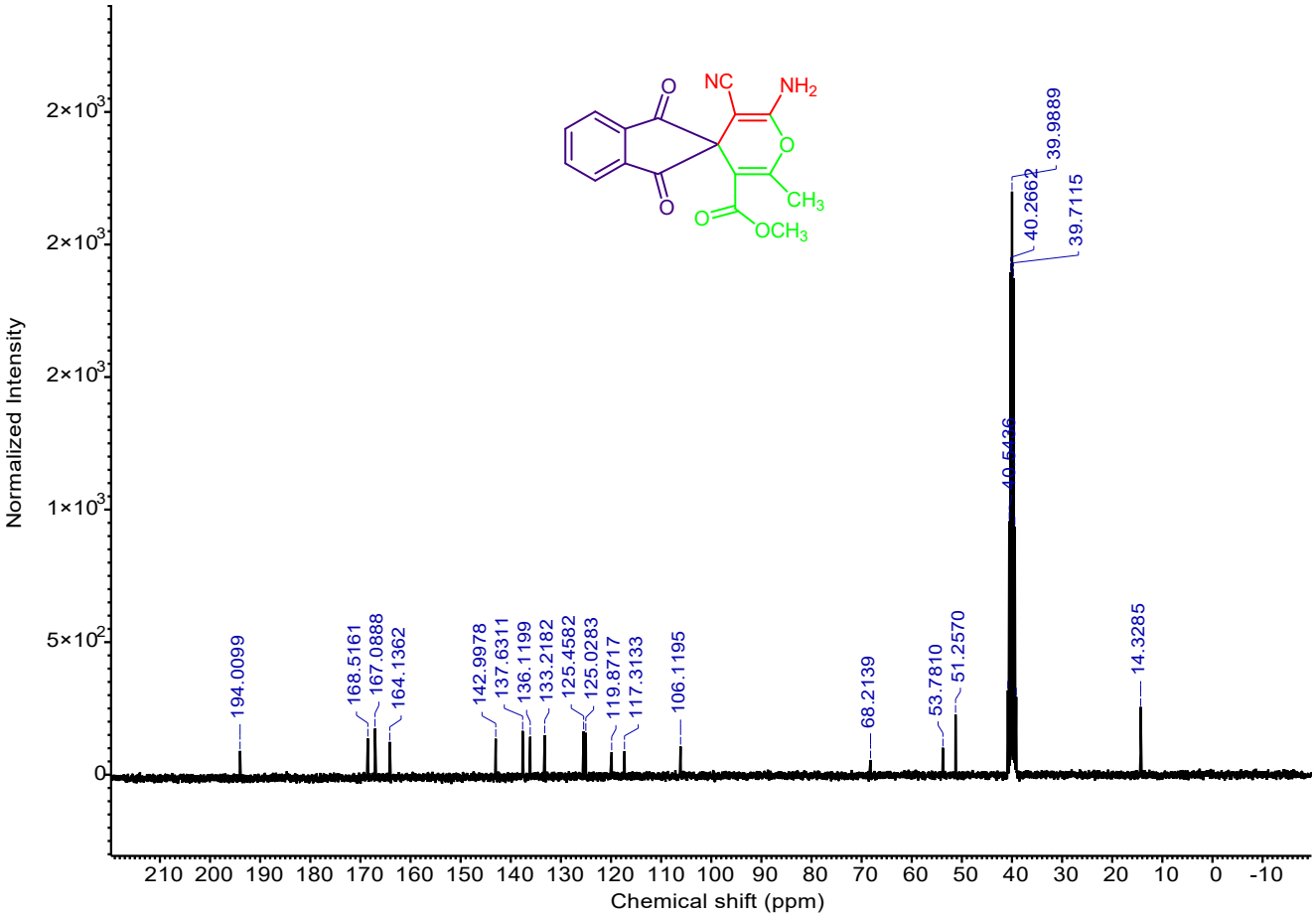
^{13}C NMR spectrum of the product **4f**



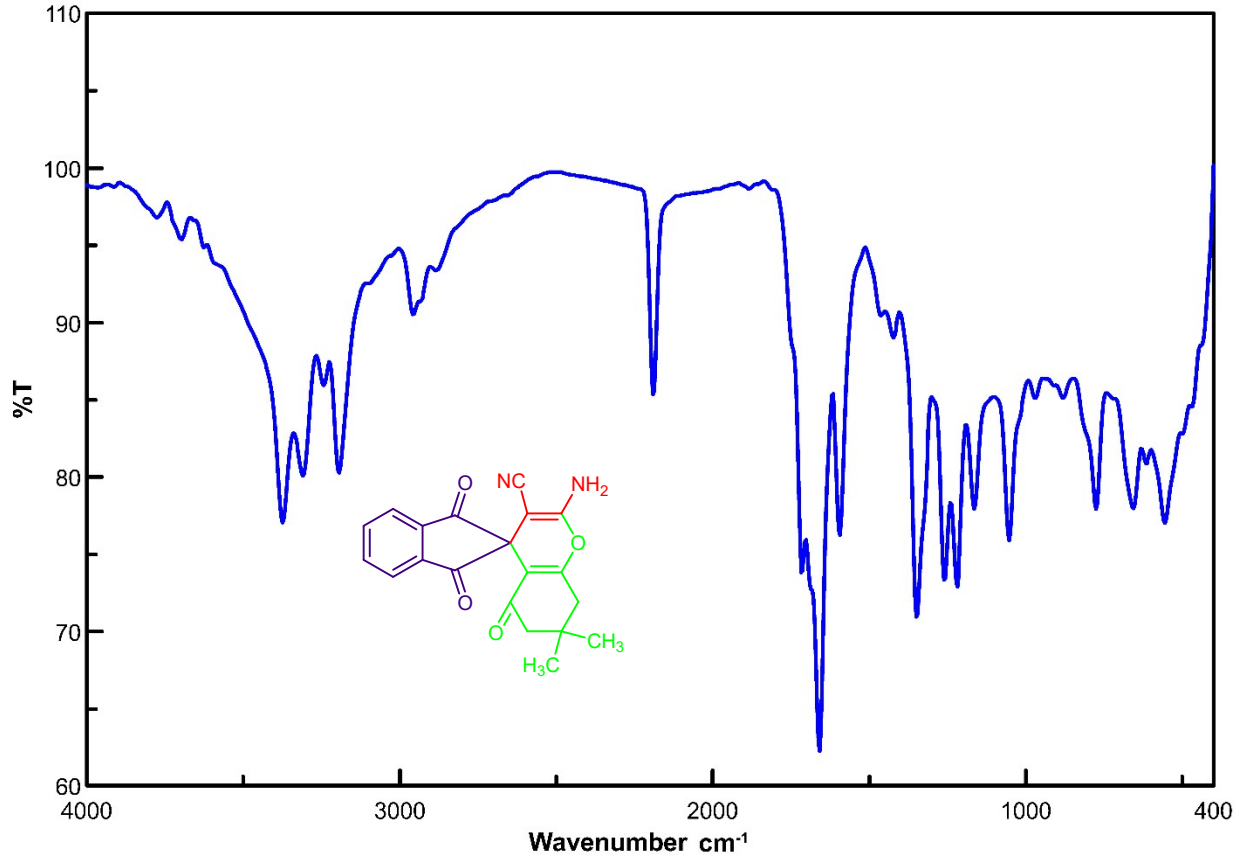
FT-IR spectrum of the product **4g**



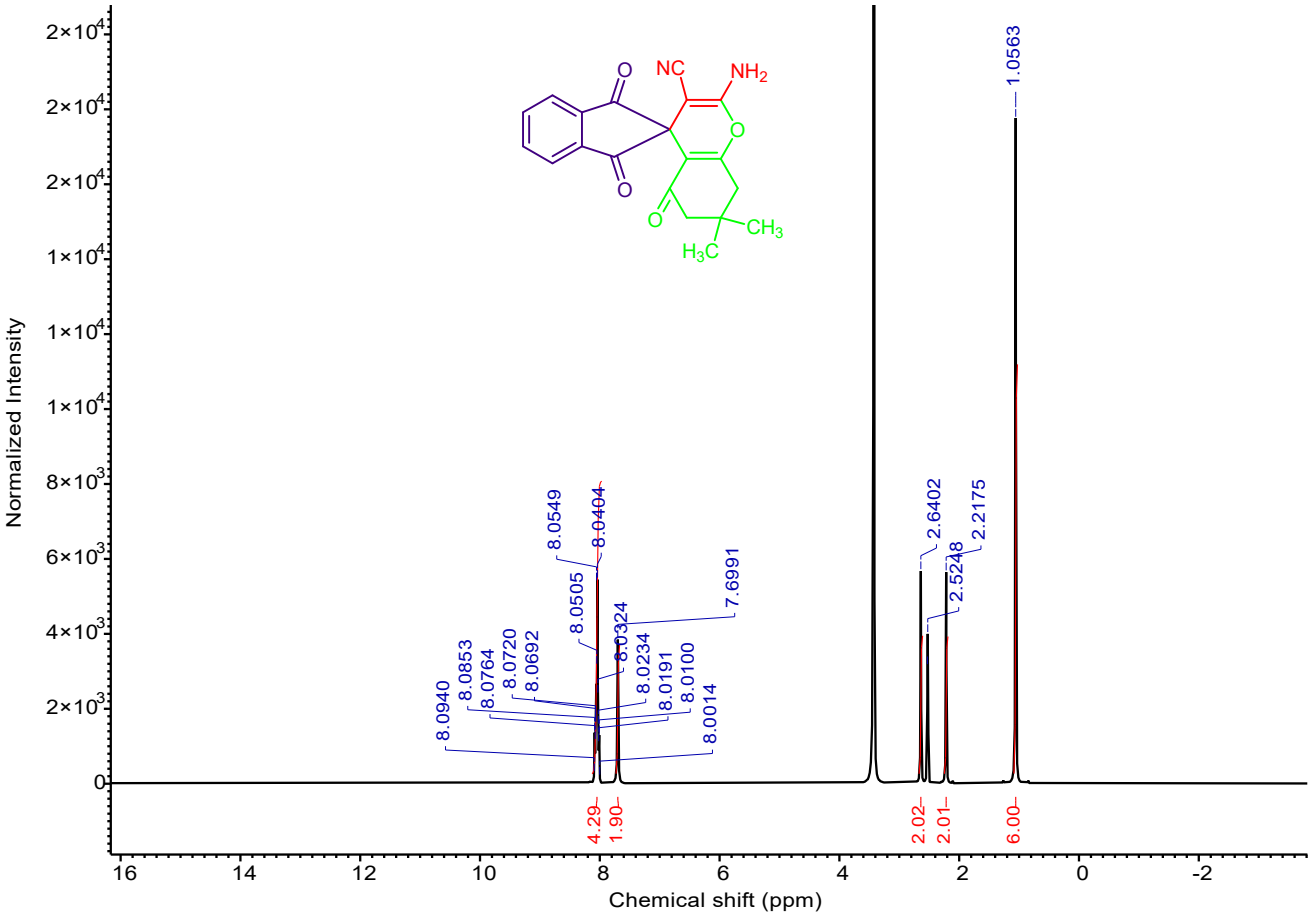
^{1}H NMR spectrum of the product **4g**



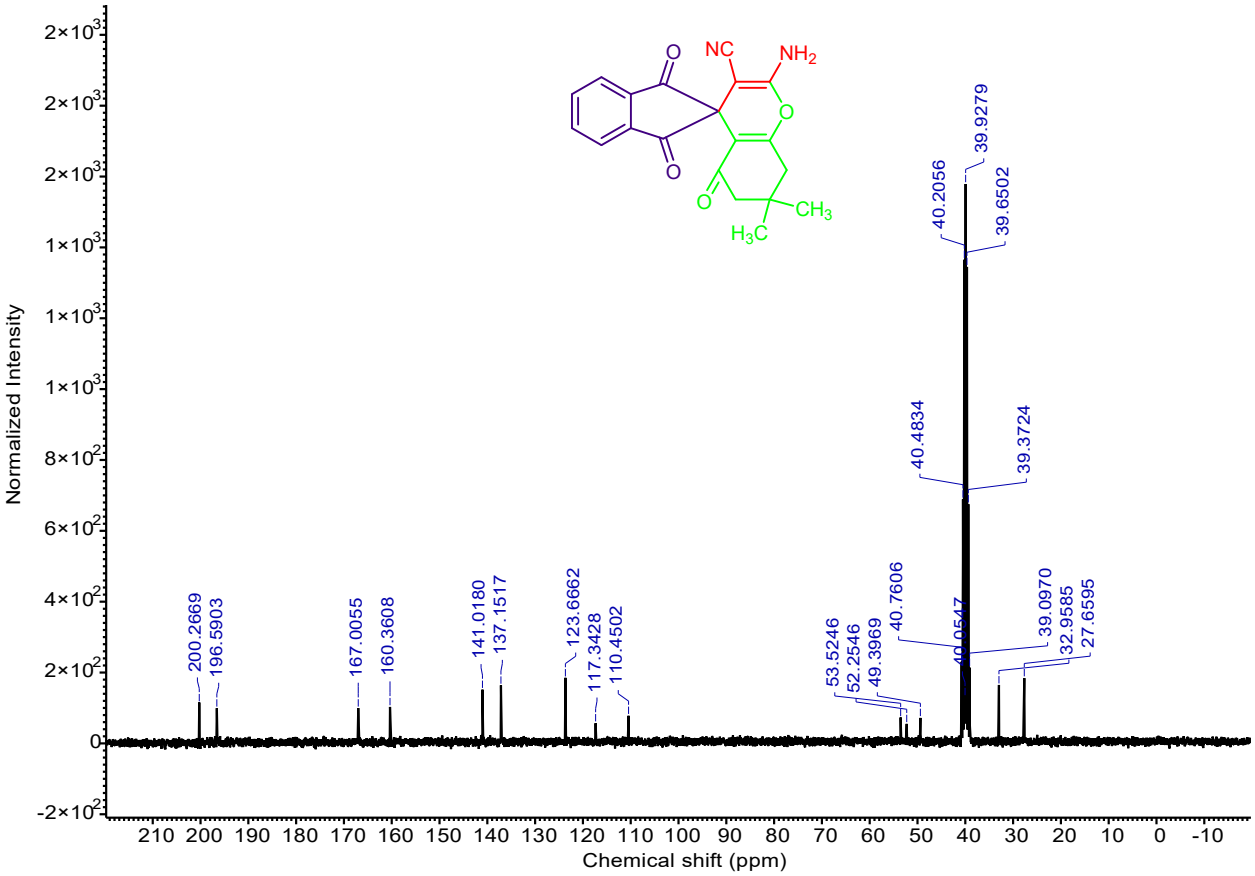
^{13}C NMR spectrum of the product **4g**



FT-IR spectrum of the product **4h**



^{1}H NMR spectrum of the product **4h**



^{13}C NMR spectrum of the product **4h**