Supporting Information

Visible-light-induced Organophotocatalytic and Singlet Oxygen-initiated Domino construction of 1,4-Dihydropyridines, C-3 Functionalized Spiro[indoline-3,4'-pyridines] and C-11 functionalized Spiro[indeno-[1,2-*b*]quinoxalines-11,4'-pyridines]

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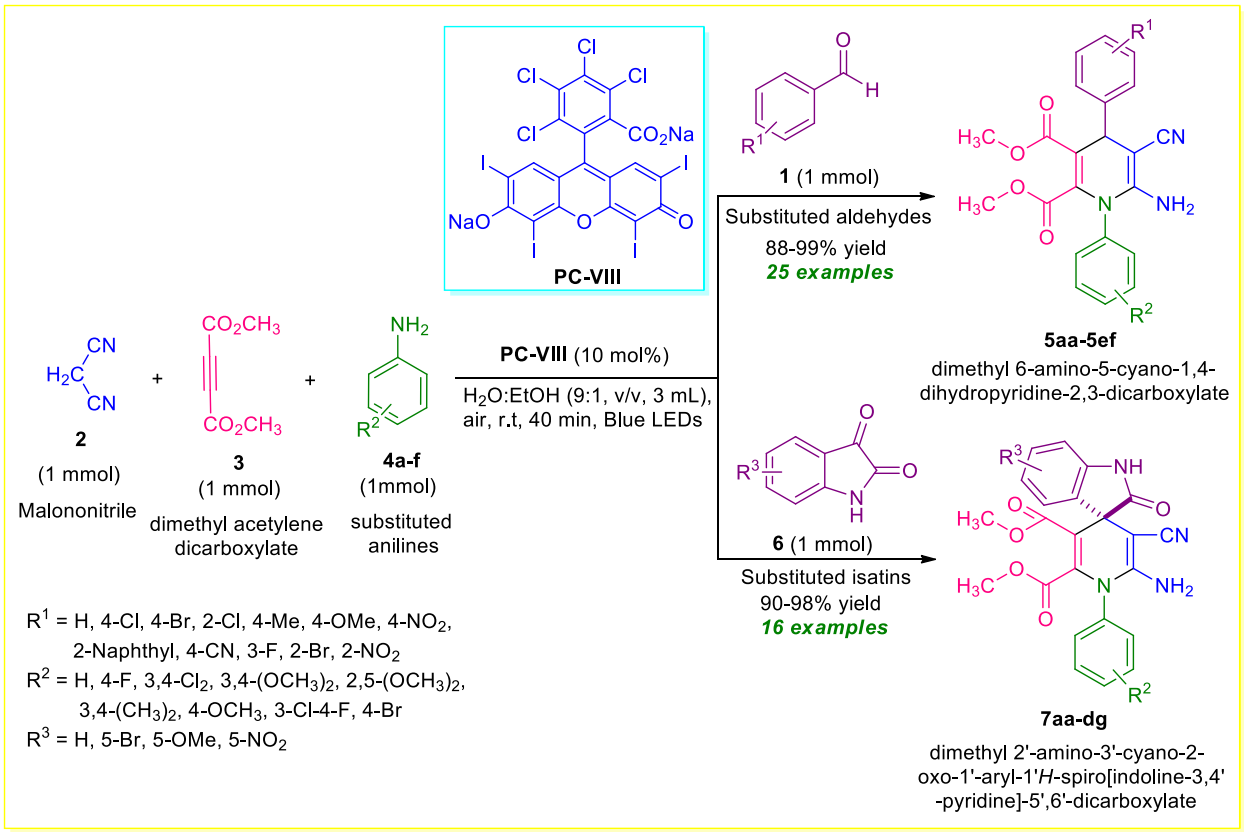
1. General Experimental Detail

All reagents and starting materials were purchased from commercially available suppliers (Alfa Aesar, Sigma Aldrich, or Avra Synthesis) and used without further purification. Thin Layer Chromatography (TLC) was executed utilizing silica gel 60 F_{254} (Merck) plates. The TLC spots were visualized with ultraviolet light using the Optima Ultraviolet Fluorescence Analysis Cabinet of model OSI-072 and/or *p*-anisaldehyde with heat as a revealing agent. Proton nuclear magnetic resonance spectra (^{1}H NMR spectra) were obtained on Bruker 500 MHz FT-NMR spectrometers and 400 MHz Bruker FT-NMR in $CDCl_3$ and DMSO-d_6 solvents. ^{13}C NMR spectra were recorded at 126 MHz and 101 MHz. ^{19}F NMR was recorded at 471 MHz. Chemical shifts (δ) are reported in parts per million (ppm) relative to the standard TMS signal and *J* values are given in Hz. Multiplicity is indicated as follows: s (singlet); bs (broad singlet); d (doublet); t (triplet); q (quartet); m (multiplet); dd (doublet of doublets), etc. TOF and quadrupole mass analyzer types are used for the HRMS measurements. IR spectra were recorded using a Perkin-Elmer Spectrum 65 FT-IR Spectrometer in KBR mode in the range of 400-4000 cm^{-1}.

2. General Procedure for the synthesis of amino-substituted 1,4-dihydropyridines (1,4-DHPs), (5aa-5ef) and 2-amino-3-cyano-spiro[indoline-3,4'-pyridines], (7aa-7dg):

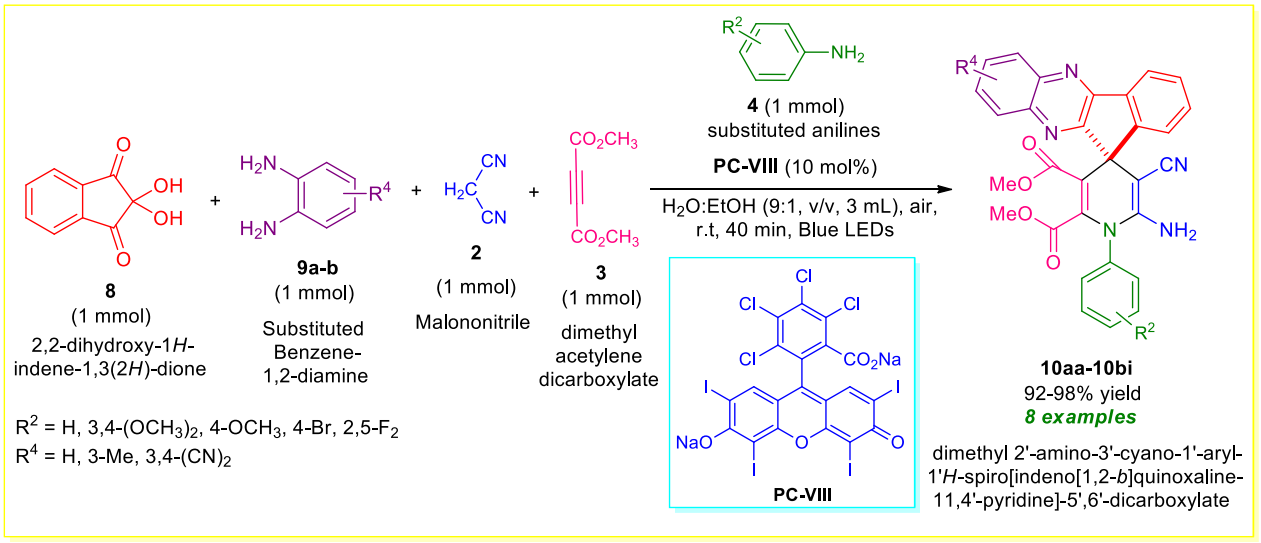
An oven-dried 10 mL round bottom flask charged with 1.0 mmol aldehydes **1**/1.0 mmol isatins **6**, 1.0 mmol malononitrile **2**, 1.0 mmol dimethyl acetylene dicarboxylate **3**, and 1.0 mmol aniline **4** in presence of 10 mol% of rose bengal (**PC-VIII**) in H_2O:EtOH (9:1, v/v, 3 mL) was stirred at room temperature under blue LEDs irradiation at room temperature in air conditions for the indicated time. The progress of the reaction was monitored by visualization of thin-layer chromatography (TLC) on the ultraviolet cabinet. After the complete consumption of starting material as indicated by TLC, EtOH was removed under reduced pressure, and then the reaction mixture was poured onto the ice water. The precipitation was filtered off and the crude solid product was washed with 3 × 5 mL distilled water and 2 × 3 mL cold ethanol to obtain the pure products amino-substituted 1,4-dihydropyridines (**5aa-5ef**) and 2-amino-3-cyano-spiro[indoline-3,4-pyridines] (**7aa-7dg**). All the synthesized compounds were subjected to spectroscopic analysis including ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, HRMS, and FT-IR without further purifications. The pictorial representation of the general procedure for the synthesis of compounds **5** and **7** is depicted in **Scheme S1**.



Scheme S1: Visible light-induced organophotocatalytic and singlet oxygen promoted one-pot domino four-component reactions of malononitrile **2**, dimethyl acetylene dicarboxylate **3**, substituted anilines **4**, and aldehydes **1**/isatins **6**

3. General Procedure for the synthesis of amino-substituted dimethyl 2'-amino-3'-cyano-1'-aryl-1'*H*-spiro[indeno[1,2-*b*]quinoxaline- 11,4'-pyridine]-5',6'-dicarboxylate, 10:

A mixture of 2,2-dihydroxy-1*H*-indene-1,3(2*H*)-dione **8** (1.0 mmol), substituted benzene-1,2-diamine **9** (1.0 mmol), malononitrile **2** (1.0 mmol), dimethyl acetylene dicarboxylate **3** (1.0 mmol), anilines **4** (1.0 mmol) and 10 mol% rose bengal (**PC-VIII**) in H_2O:EtOH (9:1, v/v, 3 mL) was subjected to blue LEDs irradiation with constant stirring at room temperature under air conditions for the indicated time (**Scheme S2**). The formation of the products was confirmed by visualizing the complete conversion of the starting material with the help of thin layer chromatography (TLC). Once the starting material was found to be consumed, EtOH was removed under reduced pressure and the reaction mixture was transferred into a 20 mL beaker filled with ice water up to 10 mL. The precipitate was filtered off, washed with 4 × 5 mL distilled water and 2 × 2 mL cold ethanol, and dried. Furthermore, the product was washed by using a 10% EtOAc/petroleum ether mixture to get the pure products.

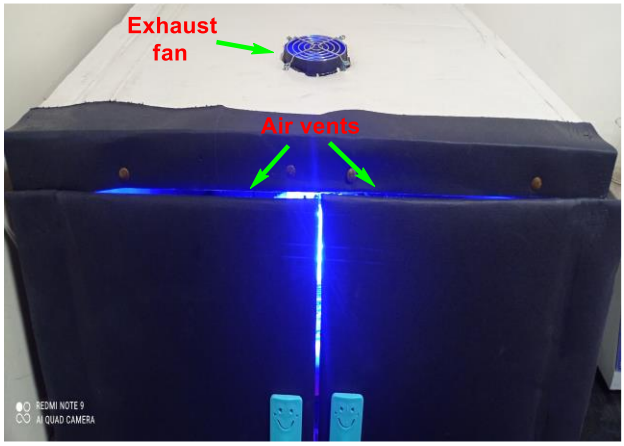


Scheme S2: Rose-Bengal catalyzed one-pot five-component reaction of 2,2-dihydroxy-1*H*-indene-1,3(2*H*)-dione **8**, substituted benzene-1,2-diamine **9**, malononitrile **2**, dimethyl acetylene dicarboxylate **3**, and substituted anilines **4** in presence of blue LEDs irradiation.

4. Photochemical reaction setup

A typical photochemical reactor was self-constructed (**Figure S1**) by utilizing a cuboid wooden box, black and white craft papers, crystallizing dish with a diameter of 150 mm, 12 volts (V) DC 3-inch CPU cooling fan of brand ERH, India, commercially available 4 meters blue LED belt with separable LED elements purchased from e-commerce hub, India, burette condenser stand with three finger clamp boss head & rod, Tarson magnetic stirrer, and golden color push pins. The outside and inside of the cuboid wooden box were glued with black craft papers and the top outside of the box was glued with white craft paper. On the center of the upper side of the setup, the CPU cooling fan was installed in such a way that the reaction mixture was underneath of the fan to maintain the temperature of the reaction. The inside of the crystallizing dish was glued with 4 meters blue LED strip with an entire power of 40 watts and the light was dimmed at maximum 50% with a total power of 20 watts with broadband source (λ) 450-460 nm. The electrical configuration of the photochemical setup was executed by the electrician of Central University of Gujarat. Furthermore, the distance of the reaction mixture from the blue LED strip was kept at 7 cm. The temperature of the reaction mixture, particularly in the inside of the crystallizing dish was initially found to be 27 °C, which was slightly increased to 30 °C after 5 minutes, and remained constant until the completion of the reaction.

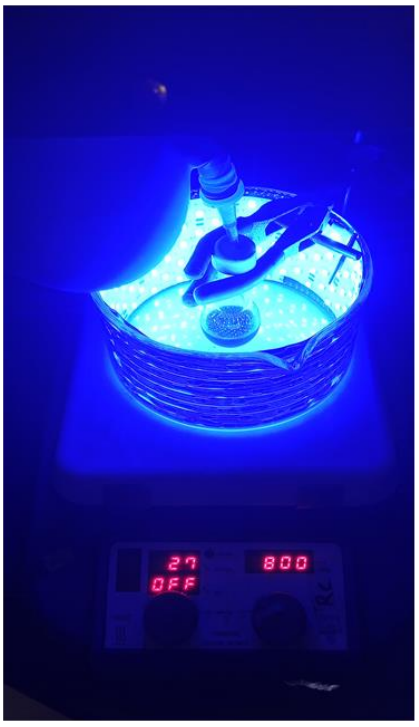
a) Front view of the photochemical set up when the light was off



b) Different parts of the photochemical set up and light was turn on

c) The reaction carried out under the blue LEDs irradiation in air atmosphere

d) The installation of exhaust fan on the top of the reaction mixture



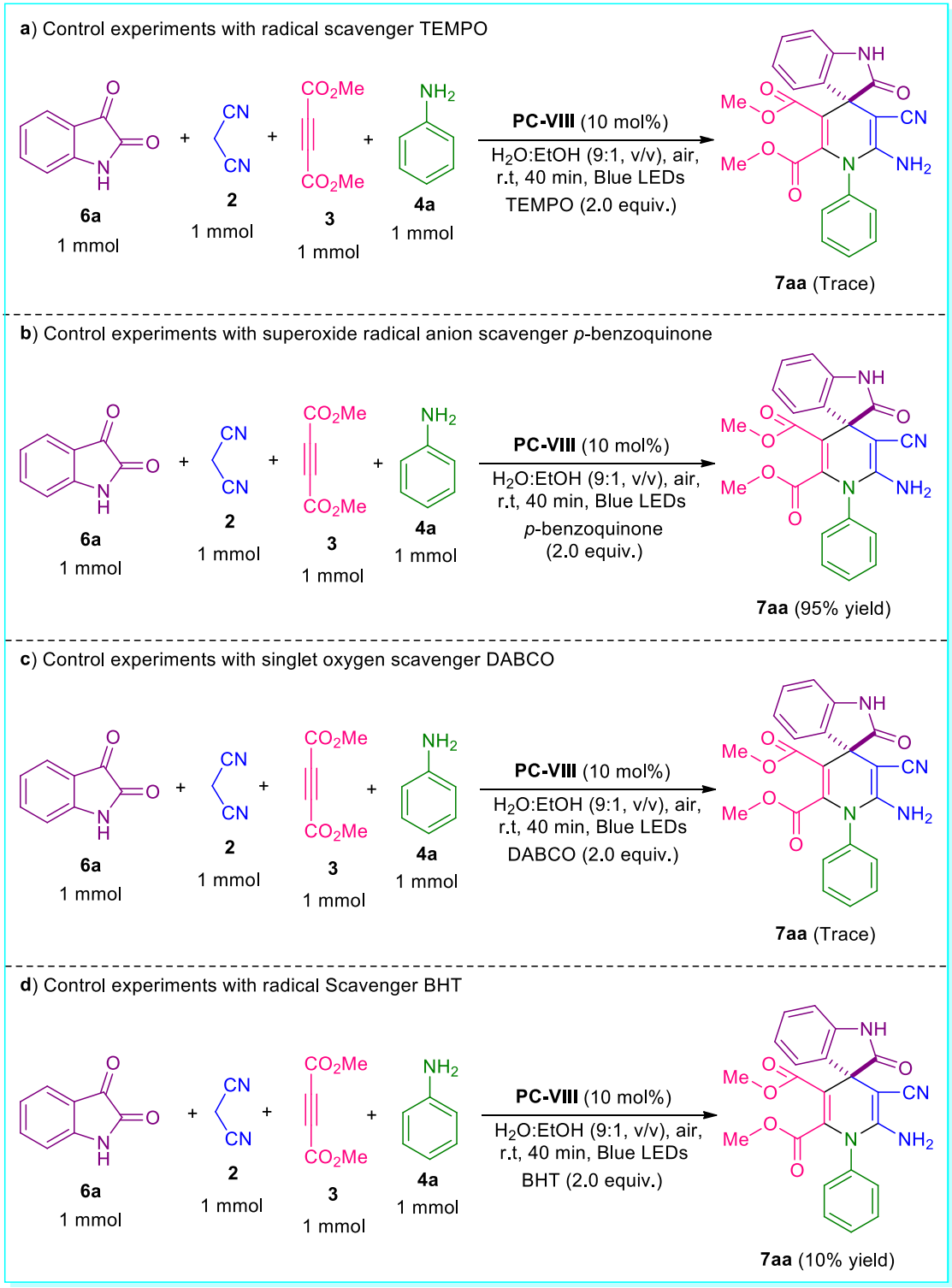
e) The reaction carried out under the blue LEDs irradiation using oxygen ballon

Figure S1: A pictorial demonstration of the photochemical setup made up for the present study

5. Control experiments

To established the reaction mechanism involved for this rose bengal catalyzed domino multicomponent synthesis of diverse amino-substituted 1,4-dihydropyridines (**5**), 2-amino-3-cyano-spiro[indoline-3,4'-pyridines] (**7**), and spiro[indeno[1,2-*b*]quinoxaline-11,4'-pyridines] (**10**) various control experiments was performed. To executing the control experiments, the

three-component reaction of isatin **6a**, malononitrile **2**, dimethyl acetylene dicarboxylate **3**, and aniline **4a** was chosen as the model reaction and conducted in presence of TEMPO, *p*-benzoquinone, DABCO, and BHT under the standard reaction conditions (**Scheme S3**).



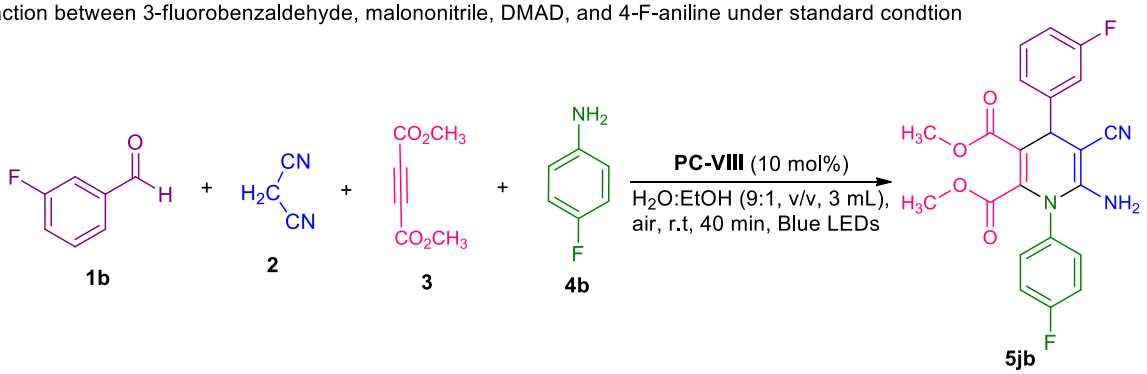
Scheme S3: Control experiments for the domino multicomponent reactions

6. Green Chemistry Metrics calculation

In order to formulate realistic improvements of chemical synthesis and chemical processes in both industry and academia in the direction toward greater environmental sustainability, it is imperative that the greenness of various chemical processes be evaluated. The evaluation of the sustainability of chemical processes or reactions to quantify their environmental impact, several mathematical parameters have been introduced over the past decades. The commonly employed green metrics such as atom Economy (AE), atom efficiency (AEf), the environmental impact factor (*E*-factor), Reaction Mass Efficiency (RME), Carbon Efficiency (CE) are evaluated for the synthesized compounds **5jb**, **7ac,** and **10aa** (**Table S1**). The schematic representation of the obtained value for the synthesis of compounds **5jb**, **7ac**, and **10aj** to calculate the above-mentioned green chemistry parameters are presented in **Scheme S4**. For the synthesis of compound **5jb**, the reaction of 0.124 gm of 3-fluorobenzaldehyde **1b**, 0.066 gm of malononitrile **2**, 0.142 gm of dimethyl acetylene dicarboxylate **3**, and 0.111 gm of 4-fluoroaniline **4a** was carried out and 0.421 gm of product was obtained (**Scheme S4a**). Similarly, the reaction of 0.147 gm of isatin **6a**, 0.066 gm of malononitrile **2**, 0.142 gm of dimethyl acetylene dicarboxylate **3**, and 0.162 gm of 3,4-dichloroaniline **4c** was performed and 0.489 gm of product **7ac** was achieved (**Scheme S4b**). Subsequently, almost 0.505 gm of product **10aa** has been accomplished from the reaction of 0.178 gm of 2,2-dihydroxy-1*H*-indene-1,3(2*H*)-dione **8**, 0.108 gm of benzene-1,2-diamine **9a**, 0.066 gm of malononitrile **2**, 0.142 gm of dimethyl acetylene dicarboxylate **3**, and 0.093 gm of aniline **4** (**Scheme S4c**).

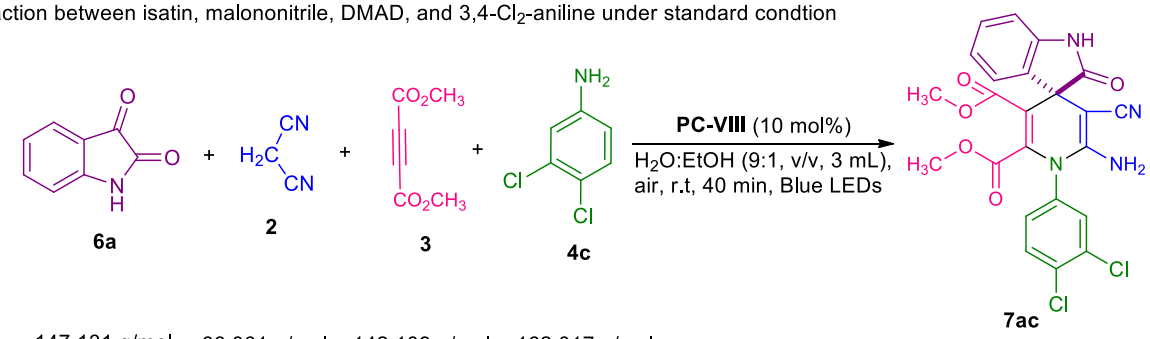
A quick survey of the results summarized in **Table S1**, revealed that the obtained value for the atom economy and atom efficiency for compounds **5jb**, **7ac**, and **10aa** have been found to be very close to the ideal value of AE and AEf, which demonstrated the occurrences of all starting material in the target product. The identical value of the environmental factor is 0 and the obtained E-factor for compounds **5jb**, **7ac,** and **10aa** resembled the ideal value which indicates the deduction of waste from the reaction. Similarly, the value of RME ranges from 0-100 %, and a large amount of RME signifies the “cleanness” of a chemical reaction. The obtained value of RME for compounds **5jb**, **7ac,** and **10aa** matched the ideal value, confirming the presented protocol's cleanness. Moreover, the estimated value of carbon efficiency for compounds **5jb**, **7ac,** and **10aa** matches the ideal value of CE.

a) Reaction between 3-fluorobenzaldehyde, malononitrile, DMAD, and 4-F-aniline under standard condtion



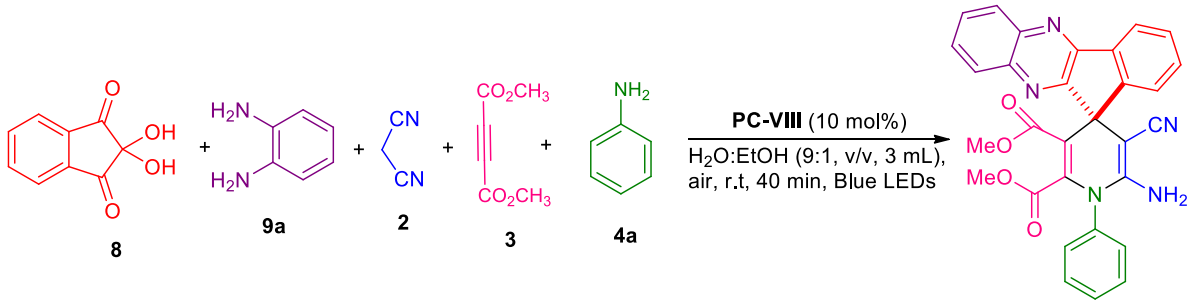
	1b	2	3	4b	5jb
FW	124.112 g/mol	66.061 g/mol	142.109 g/mol	111.117 g/mol	425.385 g/mol
mmol	1	1	1	1	0.99
weight	0.124 gm	0.066 gm	0.142 gm	0.111 gm	0.421 gm

b) Reaction between isatin, malononitrile, DMAD, and 3,4-Cl_2-aniline under standard condtion



	6a	2	3	4c	7ac
FW	147.131 g/mol	66.061 g/mol	142.109 g/mol	162.017 g/mol	499.303 g/mol
mmol	1	1	1	1	0.98
weight	0.147 gm	0.066 gm	0.142 gm	0.162 gm	0.489 gm

c) Reaction between ninhydrin, benzene-1,2-diamine, malononitrile, DMAD, and 2,5-F_2-aniline under standard condtion



	8	9a	2	3	4a	10aa
FW	178.142 g/mol	108.141 g/mol	66.061 g/mol	142.109 g/mol	93.126 g/mol	515.519 g/mol
mmol	1	1	1	1	1	0.98
weight	0.178 gm	0.108 gm	0.066 gm	0.142 gm	0.093 gm	0.505 gm

Scheme S4: Materials used in the synthetic purpose and the obtained value of their representative products

Table S1: Green chemistry metrics value for compounds **5jb**, **7ac**, and **10aa**

Sl No	Green Metrics	Compound 5jb	Compound 7ac	Compound 10aa
1	**Atom economy (AE) (%)** = Mol. Wt. of product ÷ Σ (MW of stoichiometric reactants) × 100%	425.385 g/mol ÷ (124.112 g/mol + 66.061 g/mol + 142.109 g/mol + 111.117 g/mol) × 100% = 95.93%	499.303 g/mol ÷ (147.131 g/mol + 66.061 g/mol + 142.109 g/mol + 162.017 g/mol) × 100% = 96.48%	515.519 g/mol ÷ (178.142 g/mol + 108.141 g/mol + 66.061 g/mol + 142.109 g/mol + 93.126 g/mol) × 100% = 87.74%
2	**Atom efficiency (%)** = (Yield × AE)/100	(99% × 95.93%)/ 100 = 94.97%	(98% × 96.48%)/ 100 = 94.55%	(98% × 87.74%)/100 = 85.98%
3	**E-factor** = [mass of waste]/mass of product Mass of waste = total mass of raw materials - Total mass of product	[(0.124 + 0.066 + 0.142 + 0.111) – 0.421]/0.421 = 0.05	[(0.147 + 0.066 + 0.142 + 0162) – 0.489]/0.489 = 0.05	[(0.178 + 0.108 + 0.066 + 0.142 + 0.093) – 0.505]/ 0.505 = 0.16
4	**Reaction mass efficiency (RME) (%)** = mass of product / Σ (mass of stoichiometric reactants) × 100%	0.421 ÷ (0.124 + 0.066 + 0.142 + 0.111) × 100% = 95.03%	0.489 ÷ (0.147 + 0.066 + 0.142 + 0.162) × 100% = 94.58%	0.505 ÷ (0.178 + 0.108 + 0.066 + 0.142 + 0.093) × 100% = 86.03%
5	**Process mass intensity (PMI)** = Σ (mass of stoichiometric reactants + solvent) / mass of product	[0.124 + 0.066 + 0.142 + 0.111 + 0.018 + 0.046] ÷ 0.421 = 1.20	[0.147 + 0.066 + 0.142 + 0.162 + 0.018 + 0.046] ÷ 0.489 = 1.18	[0.178 + 0.108 + 0.066 + 0.142 + 0.093 + 0.018 + 0.046] ÷ 0.505 = 1.28
6	**Carbon efficiency (CE) (%)** (Amount of carbon in product/Total carbon present in reactant) × 100%	[0.99 × 22/ (1 × 7 + 1 × 3 + 1 × 6 + 1 × 6)] × 100% = 99%	[0.98 × 23/ (1 × 8 + 1 × 3 + 1 × 6 + 1 × 6)] × 100% = 98%	[0.98 × 30/ (1 × 9 + 1 × 6 + 1 × 3 + 1 × 6 + 1 × 6)] × 100% = 98%

The estimated data for several metrics calculated above for the selected compounds **5jb**, **7ac**, and **10aa** were represented graphically in the form of a radial pentagon diagram (**Figure S2**), which clearly demonstrating/supports the greenness or sustainability of the current strategy.

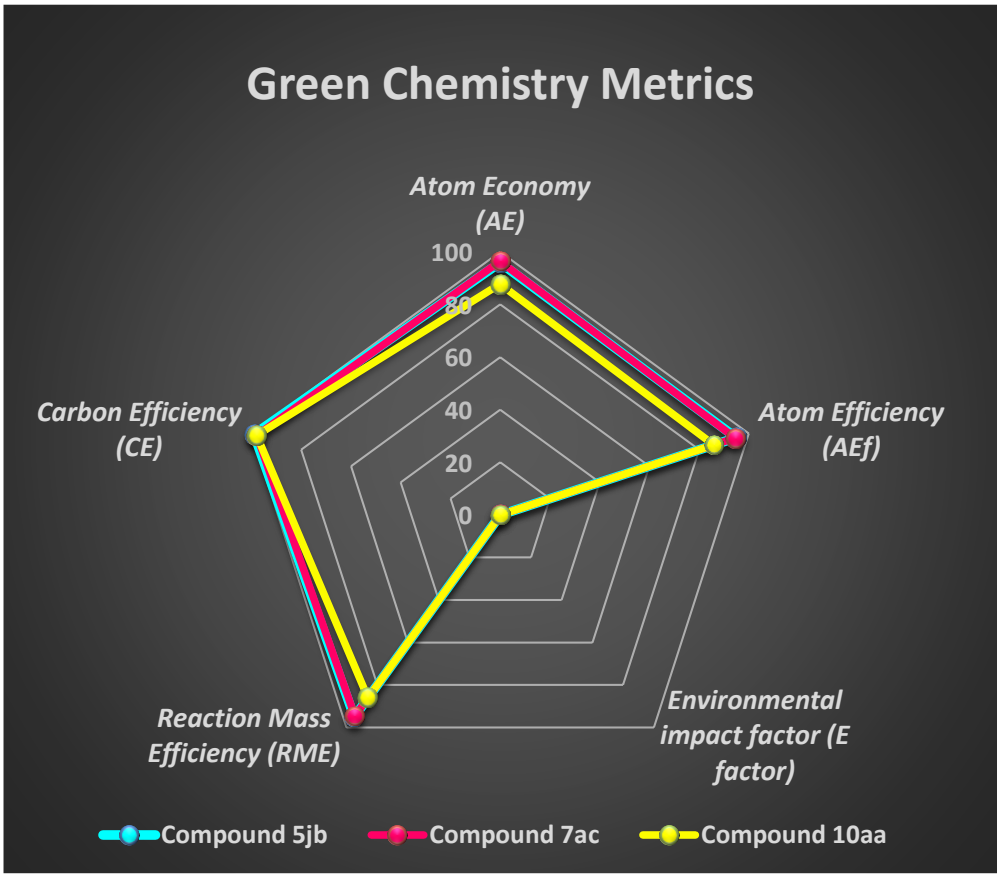
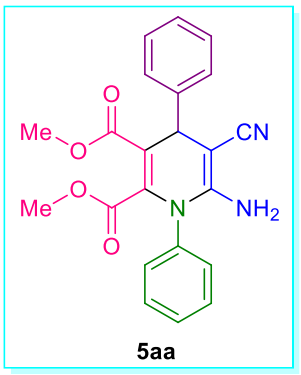


Figure S2: Radial pentagon diagram representing the cleanness of the present study for the synthesized compounds **5jb**, **7ac**, and **10aa**

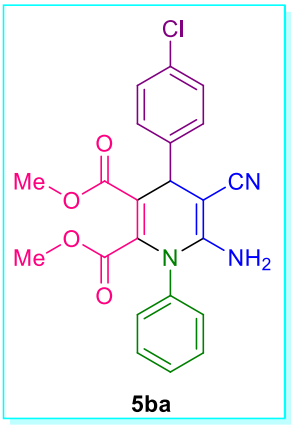
7. Characterization Data for the product (5aa-5ef), (7aa-7dg), (10aa-10bi):

Dimethyl 6-amino-5-cyano-1,4-diphenyl-1,4-dihydropyridine-2,3-dicarboxylate, 5aa:



95% yield; pale yellow solid. R_f = 0.45 (40% EtOAc/Hexane); M.P. 186-188 °C. IR (KBr) υ_{max} (cm^{-1}): 3460, 3325, 3220, 2951, 2190, 1748, 1707, 1650, 1580, 1490, 1420, 1350, 1251, 1115, 1045, 921, 856, 768, 538, 430. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.45 (m, 6H), 7.37 – 7.32 (m, 2H), 7.26 – 7.23 (m, 2H), 4.65 (s, 1H), 4.10 (s, 2H), 3.60 (s, 3H), 3.44 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.87, 163.65, 149.75, 144.84, 141.91, 135.22, 132.01, 130.63, 130.33, 130.04, 128.91, 127.26, 127.08, 120.63, 105.27, 62.85, 52.66, 52.11, 38.54. HRMS (ESI^+): m/z calculated for [$C_{22}H_{19}N_3O_4$ + H^+]: 390.1454; found 390.1448

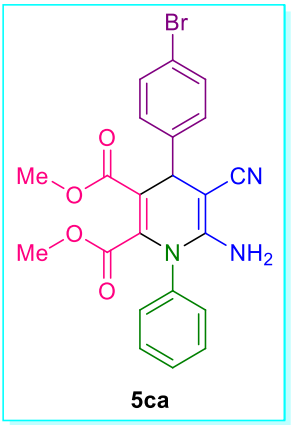
Dimethyl 6-amino-4-(4-chlorophenyl)-5-cyano-1-phenyl-1,4-dihydropyridine-2,3-dicarboxylate, 5ba:



96% yield, yellow solid. R_f = 0.4 (40% EtOAc/Hexane); M.P. 215-217 °C. IR (KBr) υ_{max} (cm^{-1}): 3465, 3371, 3241, 2940, 2196, 1752, 1710, 1655, 1590, 1481, 1421, 1310, 1265, 1121, 1049, 945, 830, 705, 532. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 3H), 7.37 – 7.32 (m, 4H), 7.13

– 7.02 (m, 2H), 4.68 (s, 1H), 4.09 (s, 2H), 3.60 (s, 3H), 3.44 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.81, 163.59, 149.62, 141.91, 140.79, 135.18, 130.80, 130.37, 130.17, 128.78, 128.72, 120.48, 115.90, 115.73, 105.27, 62.86, 52.77, 52.22, 38.03. HRMS (ESI$^+$): m/z calculated for [$C_{22}H_{18}ClN_3O_4$ + H^+]: 424.1064; found 424.1058

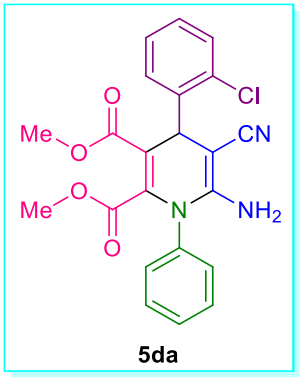
Dimethyl 6-amino-4-(4-bromophenyl)-5-cyano-1-phenyl-1,4-dihydropyridine-2,3-dicarboxylate, 5ca:



5ca

95% yield, yellow solid. R_f = 0.4 (40% EtOAc/Hexane); M.P. 218-220 °C. IR (KBr) υ_{max} (cm^{-1}): 3470, 3345, 3231, 2956, 2188, 1749, 1708, 1653, 1589, 1489, 1423, 1359, 1253, 1108, 1049, 949, 779, 711, 692, 541. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 – 8.20 (m, 2H), 7.62 – 7.50 (m, 5H), 7.38 – 7.35 (m, 1H), 4.81 (s, 1H), 4.19 (s, 2H), 3.60 (s, 3H), 3.46 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.28, 163.17, 151.87, 150.19, 147.14, 142.65, 134.73, 130.93, 130.27, 130.19, 128.01, 124.34, 120.10, 103.93, 61.20, 52.80, 52.29, 38.78. HRMS (ESI$^+$): m/z calculated for [$C_{22}H_{18}BrN_3O_4$ + H^+]: 468.0559; found 468.0547

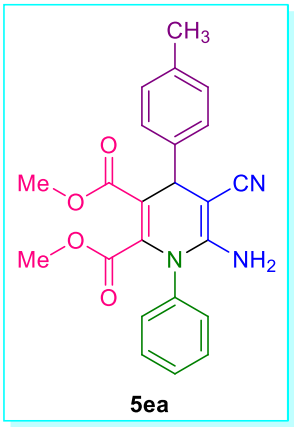
Dimethyl 6-amino-4-(2-chlorophenyl)-5-cyano-1-phenyl-1,4-dihydropyridine-2,3-dicarboxylate, 5da:



5da

94% yield, white solid. R_f = 0.42 (40% EtOAc/Hexane); M.P. 217-219 °C. IR (KBr) υ_{max} (cm^{-1}): 3462, 3326, 3218, 2949, 2187, 1745, 1705, 1649, 1579, 1491, 1417, 1354, 1324, 1249, 1109, 1034, 936, 821, 759, 701, 592, 421. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 3H), 7.46 – 7.40 (m, 1H), 7.40 – 7.37 (m, 3H), 7.33 – 7.29 (m, 1H), 7.23 – 7.16 (m, 1H), 5.29 (s, 1H), 4.08 (s, 2H), 3.56 (s, 3H), 3.44 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.67, 163.48, 150.05, 142.61, 142.27, 135.01, 132.69, 130.68, 130.43, 130.02, 129.99, 129.95, 128.39, 127.56, 120.26, 104.29, 61.57, 52.65, 52.05, 35.84. HRMS (ESI^+): m/z calculated for [$C_{22}H_{18}ClN_3O_4$ + H^+]: 424.1064; found 424.1058

Dimethyl 6-amino-5-cyano-1-phenyl-4-(*p*-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate, 5ea:

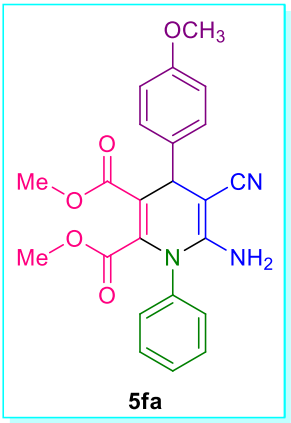


5ea

88% yield, pale yellow solid. R_f = 0.45 (40% EtOAc/Hexane); M.P. 210-212 °C. IR (KBr) υ_{max} (cm^{-1}): 3474, 3369, 3220, 2951, 2193, 1749, 1703, 1646, 1576, 1510, 1490, 1425, 1339, 1238, 1110, 1031, 971, 860, 759, 648, 530. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 3H), 7.38 – 7.33 (m, 2H), 7.27 (d, *J* = 2.5 Hz, 2H), 7.26 (s, 1H), 4.64 (s, 1H), 4.05 (s, 2H), 3.60 (s, 3H), 3.44 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.96, 163.74, 149.66, 141.99, 141.81,

136.87, 135.34, 130.62, 130.36, 130.05, 129.65, 126.97, 120.73, 105.49, 63.16, 52.66, 52.14, 38.13, 21.23. HRMS (ESI$^+$): m/z calculated for [$C_{23}H_{21}N_3O_4$ + H^+]: 404.1610; found 404.1602

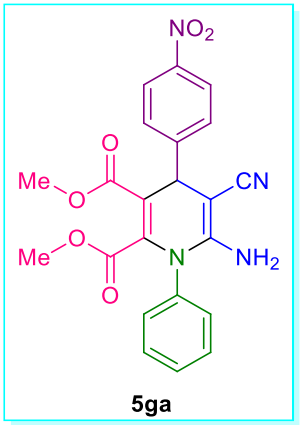
Dimethyl 6-amino-5-cyano-4-(4-methoxyphenyl)-1-phenyl-1,4-dihydropyridine-2,3-dicarboxylate, 5fa:



5fa

85% yield, yellow solid. R_f = 0.45 (40% EtOAc/Hexane); M.P. 216-218 °C. IR (KBr) υ_{max} (cm^{-1}): 3478, 3369, 3231, 3051, 2948, 2193, 1755, 1708, 1648, 1561, 1507, 1493, 1431, 1349, 1245, 1105, 1029, 975, 869, 765, 639, 529. ^{1}H NMR (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 7.41 (s, 1H), 7.38 – 7.34 (m, 2H), 7.30 (d, *J* = 2.2 Hz, 1H), 7.29 (d, *J* = 2.1 Hz, 1H), 6.94 – 6.89 (m, 2H), 4.63 (s, 1H), 4.05 (s, 2H), 3.82 (s, 3H), 3.60 (s, 3H), 3.44 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.71, 163.54, 158.95, 148.87, 140.83, 136.72, 135.53, 134.72, 134.15, 132.24, 131.64, 129.64, 128.19, 120.17, 114.41, 106.70, 64.59, 55.42, 53.04, 52.31, 37.79. HRMS (ESI$^+$): m/z calculated for [$C_{23}H_{21}N_3O_5$ + H^+]: 420.1559; found 424.1540

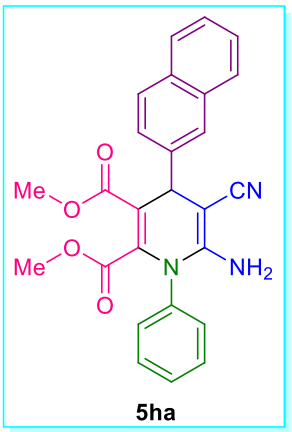
Dimethyl 6-amino-5-cyano-4-(4-nitrophenyl)-1-phenyl-1,4-dihydropyridine-2,3-dicarboxylate, 5ga:



5ga

95% yield, yellow solid. R_f = 0.42 (40% EtOAc/Hexane); M.P. 217-220 °C. IR (KBr) υ_{max} (cm^{-1}): 3470, 3375, 3214, 3046, 2953, 2191, 1750, 1702, 1652, 1566, 1518, 1488, 1421, 1344, 1241, 1116, 1022, 964, 862, 756, 636, 550. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 – 8.23 (m, 2H), 7.57 – 7.51 (m, 5H), 7.38 – 7.35 (m, 2H), 4.81 (s, 1H), 4.19 (s, 2H), 3.60 (s, 3H), 3.46 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.30, 163.19, 151.86, 150.12, 147.19, 142.67, 134.75, 130.99, 130.30, 130.24, 128.03, 124.40, 120.07, 103.97, 61.39, 52.84, 52.34, 38.79. HRMS (ESI^+): m/z calculated for [$C_{22}H_{18}N_4O_6$ + H^+]: 435.1305; found 435.1299

Dimethyl 6-amino-5-cyano-4-(naphthalen-1-yl)-1-phenyl-1,4-dihydropyridine-2,3-dicarboxylate, 5ha:

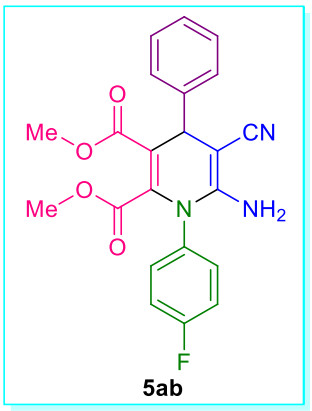


5ha

92% yield, pale yellow solid. R_f = 0.4 (40% EtOAc/Hexane); M.P. 206-208 °C. IR (KBr) υ_{max} (cm^{-1}): 3469, 3353, 3231, 3054, 2949, 2189, 1748, 1710, 1647, 1569, 1508, 1493, 1414, 1340, 1240, 1115, 1020, 953, 833, 746, 639, 595, 528. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (dd, J = 8.7, 1.1 Hz, 1H), 7.89 – 7.86 (m, 1H), 7.81 – 7.76 (m, 1H), 7.64 – 7.60 (m, 1H), 7.57 (dd, J = 7.2, 1.4 Hz, 1H), 7.56 – 7.48 (m, 5H), 7.44 – 7.41 (m, 2H), 5.61 (s, 1H), 4.03 (s, 2H), 3.48 (s, 3H), 3.43

(s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.88, 163.76, 149.86, 142.32, 141.74, 135.29, 134.06, 130.82, 130.66, 130.39, 130.09, 128.68, 127.90, 126.41, 125.91, 125.90, 125.49, 123.54, 120.67, 105.72, 63.24, 52.74, 52.09, 33.23. HRMS (ESI^+): m/z calculated for [$C_{26}H_{21}N_3O_4$ + H^+]: 440.1610; found 440.1605

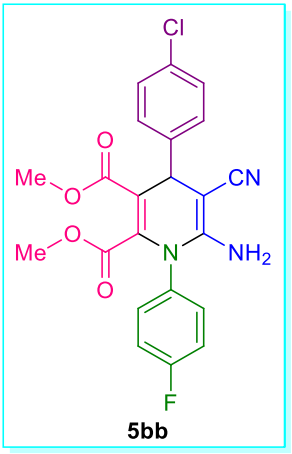
Dimethyl 6-amino-5-cyano-1-(4-fluorophenyl)-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate, 5ab:



5ab

96% yield, white solid. R_f = 0.45 (40% EtOAc/Hexane); M.P. 192-194 °C. IR (KBr) υ_{max} (cm^{-1}): 3470, 3320, 3225, 3070, 2949, 2190, 1749, 1703, 1649, 1580, 1510, 1486, 1415, 1357, 1331, 1249, 1219, 1110, 924, 831, 776, 729, 635, 542, 514, 487. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 7H), 7.21 – 7.17 (m, 2H), 4.67 (s, 1H), 4.04 (s, 2H), 3.60 (s, 3H), 3.50 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.80, 164.37, 163.67, 162.36, 149.56, 144.66, 141.81, 132.52, 132.45, 131.18, 131.15, 129.01, 127.39, 127.09, 120.39, 117.20 (d, $J_{C\text{-}F}$ = 22.9 Hz), 105.72, 63.57, 52.85, 52.21, 38.54. ^{19}F NMR (471 MHz, $CDCl_3$) δ -108.14 ppm. HRMS (ESI^+): m/z calculated for [$C_{22}H_{18}FN_3O_4$ + H^+]: 408.1360; found 408.1383

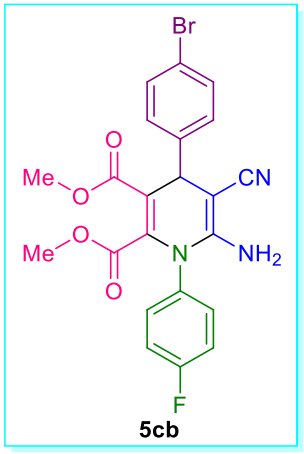
Dimethyl 6-amino-4-(4-chlorophenyl)-5-cyano-1-(4-fluorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate, 5bb:



5bb

97% yield, yellow solid. R_f = 0.45 (40% EtOAc/Hexane); M.P. 208-210 °C. IR (KBr) υ_{max} (cm^{-1}): 3467, 3340, 3210, 3015, 2970, 2910, 2282, 1672, 1606, 1508, 1422, 1385, 1270, 1221, 1174, 1055, 844, 589, 530, 431. ^1H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 4H), 7.29 (d, J = 2.1 Hz, 1H), 7.28 (d, J = 1.9 Hz, 1H), 7.22 – 7.18 (m, 2H), 4.66 (s, 1H), 4.07 (s, 2H), 3.60 (s, 3H), 3.49 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.58, 164.41, 163.48, 162.40, 149.66, 143.26, 141.94, 133.15, 132.49, 132.42, 130.97, 129.15, 128.49, 120.22, 117.25 (d, J_{C-F} = 23.0 Hz), 105.24, 62.92, 52.89, 52.26, 38.14. ^{19}F NMR (471 MHz, $CDCl_3$) δ -107.87 ppm. HRMS (ESI^+): m/z calculated for [$C_{22}H_{17}ClFN_3O_4$ + H^+]: 442.0970; found 442.0973

Dimethyl 6-amino-4-(4-bromophenyl)-5-cyano-1-(4-fluorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate, 5cb:

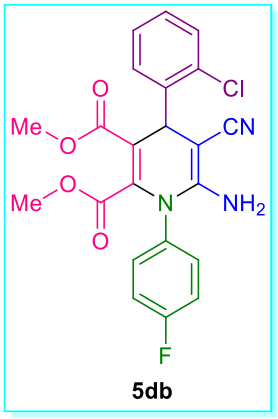


5cb

98% yield, white solid. R_f = 0.45 (40% EtOAc/Hexane); M.P. 242-244 °C. IR (KBr) υ_{max} (cm^{-1}): 3476, 3321, 3228, 3066, 2952, 2195, 1746, 1704, 1653, 1576, 1506, 1418, 1352, 1251, 1220, 1114, 1006, 930, 873, 821, 779, 638, 557, 540. ^1H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.48 (m,

2H), 7.37 – 7.33 (m, 2H), 7.25 – 7.17 (m, 4H), 4.64 (s, 1H), 4.09 (s, 2H), 3.60 (s, 3H), 3.49 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.32, 164.04, 163.22, 162.03, 149.87, 143.80, 141.83, 132.32, 132.25, 131.72, 130.78, 128.65, 120.83, 120.31, 116.83 (d, J_{C-F} = 22.9 Hz), 104.68, 61.62, 52.56, 51.95, 38.08. ^{19}F NMR (471 MHz, $CDCl_3$) δ -107.87 ppm. HRMS (ESI$^+$): m/z calculated for [$C_{22}H_{17}BrFN_3O_4$ + H^+]: 486.0465; found 486.0466

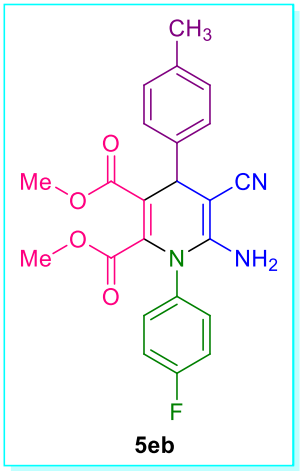
Dimethyl 6-amino-4-(2-chlorophenyl)-5-cyano-1-(4-fluorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate, 5db:



5db

96% yield, yellow solid. R_f = 0.42 (40% EtOAc/Hexane); M.P. 228-230 °C. IR (KBr) υ_{max} (cm^{-1}): 3470, 3331, 3215, 2953, 2192, 1746, 1703, 1651, 1508, 1420, 1351, 1254, 1114, 1037, 931, 847, 751, 551. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.36 (m, 4H), 7.31 (t, J = 7.3 Hz, 1H), 7.23-7.17 (m, 3H), 5.28 (s, 1H), 4.04 (s, 2H), 3.56 (s, 3H), 3.49 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 165.65, 164.43, 163.54, 162.42, 149.85, 142.52, 142.04, 132.92, 132.68, 130.98, 130.22, 130.03, 128.58, 127.62, 120.04, 117.24 (d, J_{C-F} = 23.1 Hz), 104.73, 62.37, 52.89, 52.19, 36.05. ^{19}F NMR (471 MHz, $CDCl_3$) δ -107.96. HRMS (ESI$^+$): m/z calculated for [$C_{22}H_{17}ClFN_3O_4$ + H^+]: 442.0970; found 442.0970

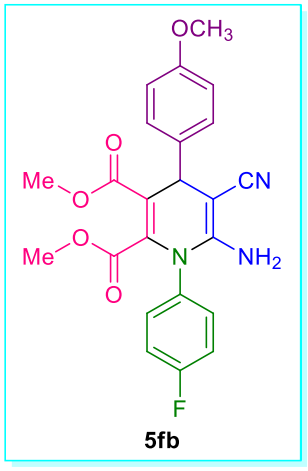
Dimethyl 6-amino-5-cyano-1-(4-fluorophenyl)-4-(*p*-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate, 5eb:



5eb

89% yield, yellow solid. R_f = 0.45 (40% EtOAc/Hexane); M.P. 185-187 °C. IR (KBr) υ_{max} (cm^{-1}): 3467, 3370, 3209, 3069, 2961, 2185, 1746, 1710, 1654, 1605, 1582, 1508, 1420, 1350, 1257, 1109, 1065, 930, 821, 642, 542. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 7.26 – 7.23 (m, 2H), 7.21 – 7.16 (m, 4H), 4.63 (s, 1H), 4.01 (s, 2H), 3.60 (s, 3H), 3.49 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.87, 164.35, 163.72, 162.34, 149.46, 141.81, 141.68, 136.99, 132.51, 132.44, 131.24, 129.70, 126.96, 120.46, 117.18 (d, J_{C-F} = 22.9 Hz), 105.84, 63.75, 52.83, 52.22, 38.10, 21.26. ^{19}F NMR (471 MHz, $CDCl_3$) δ -108.24 ppm. HRMS (ESI^+): m/z calculated for [$C_{23}H_{20}FN_3O_4$ + H^+]: 422.1516; found 422.1515

Dimethyl 6-amino-5-cyano-1-(4-fluorophenyl)-4-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate, 5fb:

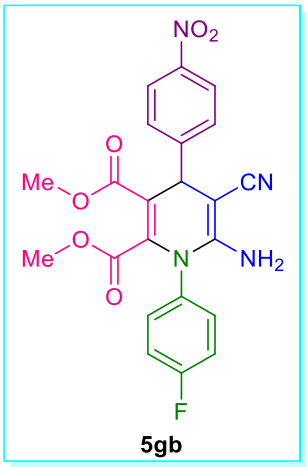


5fb

88% yield, yellow solid. R_f = 0.45 (40% EtOAc/Hexane); M.P. 190-192 °C. IR (KBr) υ_{max} (cm^{-1}): 3460, 3359, 2951, 2853, 2195, 1746, 1708, 1654, 1580, 1508, 1420, 1353, 1109, 977, 827,

658, 542. ^{1}H NMR (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 7.28 (d, *J* = 2.1 Hz, 1H), 7.27 (d, *J* = 1.4 Hz, 1H), 7.21 – 7.16 (m, 2H), 6.96 – 6.85 (m, 2H), 4.62 (s, 1H), 4.04 (s, 2H), 3.81 (s, 3H), 3.60 (s, 3H), 3.49 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.86, 164.28, 163.68, 162.27, 158.80, 149.47, 141.44, 137.12, 132.47, 132.40, 131.16, 131.13, 128.15, 120.56, 117.11 (d, J_{C-F} = 23.0 Hz), 114.28, 105.87, 63.48, 55.35, 52.78, 52.16, 37.73. ^{19}F NMR (471 MHz, $CDCl_3$) δ -108.20 ppm. HRMS (ESI^+): m/z calculated for [$C_{23}H_{20}FN_3O_5$ + H^+]: 438.1465; found 438.1466

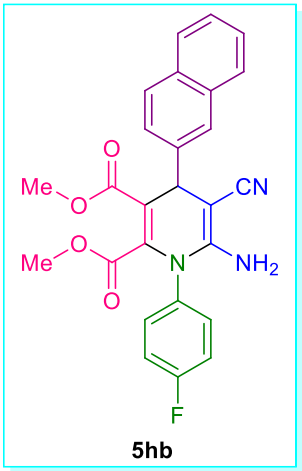
Dimethyl 6-amino-5-cyano-1-(4-fluorophenyl)-4-(4-nitrophenyl)-1,4-dihydropyridine-2,3-dicarboxylate, 5gb:



5gb

93% yield, yellow solid. R_f = 0.45 (40% EtOAc/Hexane); M.P. 218-220 °C. IR (KBr) υ_{max} (cm^{-1}): 3469, 3318, 3226, 3075, 2952, 2187, 1740, 1714, 1648, 1568, 1506, 1485, 1419, 1332, 1250, 1233, 1114, 1052, 969, 843, 783, 725, 684, 621, 549, 431. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 – 8.21 (m, 2H), 7.54 – 7.51 (m, 2H), 7.39 – 7.35 (m, 2H), 7.24 – 7.20 (m, 2H), 4.80 (s, 1H), 4.18 (s, 2H), 3.60 (s, 3H), 3.51 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$ + DMSO-d_6) δ 164.65, 163.67, 162.61, 161.65, 151.69, 150.16, 146.38, 142.16, 132.11, 132.04, 130.30, 127.50, 123.67, 123.59, 119.93, 116.43 (d, J_{C-F} = 23.0 Hz), 103.28, 59.53, 52.24, 51.65, 38.37. ^{19}F NMR (471 MHz, $CDCl_3$) δ -107.43. HRMS (ESI^+): m/z calculated for [$C_{22}H_{17}FN_4O_6$ + H^+]: 453.1210; found 453.1210

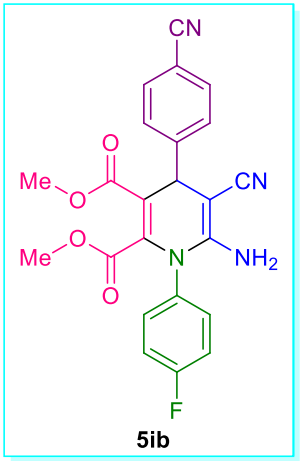
Dimethyl 6-amino-5-cyano-1-(4-fluorophenyl)-4-(naphthalen-1-yl)-1,4-dihydropyridine-2,3-dicarboxylate, 5hb:



5hb

95% yield, pale yellow solid. R_f = 0.4 (40% EtOAc/Hexane); M.P. 215-217 °C. IR (KBr) υ_{max} (cm^{-1}): 3477, 3380, 3071, 2956, 2188, 1751, 1705, 1654, 1579, 1506, 1491, 1418, 1259, 1211, 1157, 1109, 1056, 842, 689, 531. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.79 (dd, *J* = 6.7, 2.7 Hz, 1H), 7.62 (t, *J* = 8.4 Hz, 1H), 7.55 – 7.49 (m, 3H), 7.45 – 7.40 (m, 2H), 7.25 – 7.18 (m, 2H), 5.60 (s, 1H), 4.01 (s, 2H), 3.53 (s, 3H), 3.43 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.79, 164.38, 163.75, 162.37, 149.71, 142.20, 141.60, 134.10, 132.56, 132.49, 131.20, 130.84, 128.73, 128.02, 126.50, 125.90, 125.43, 123.52, 120.46, 117.22 (d, J_{C-F} = 22.9 Hz), 106.12, 63.79, 52.91, 52.16, 33.22. ^{19}F NMR (471 MHz, $CDCl_3$) δ -108.14 ppm. HRMS (ESI^+): m/z calculated for [$C_{26}H_{20}FN_3O_4$ + H^+]: 458.1516; found 458.1513

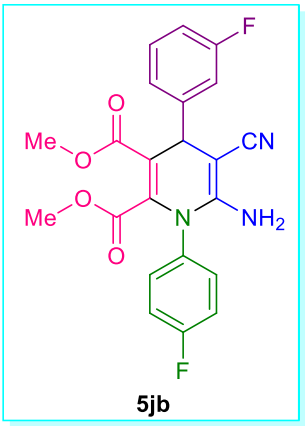
Dimethyl 6-amino-5-cyano-4-(4-cyanophenyl)-1-(4-fluorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate, 5ib:



5ib

90% yield, pale yellow solid. R_f = 0.35 (40% EtOAc/Hexane); M.P. 223-225 °C. IR (KBr) υ_{max} (cm^{-1}): 3468, 3370, 3231, 2960, 2195, 1754, 1710, 1647, 1610, 1592, 1483, 1419, 1356, 1248, 1218, 1108, 967, 868, 791, 702, 645, 587, 529. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.64 (m, 2H), 7.48 – 7.45 (m, 2H), 7.38 – 7.34 (m, 2H), 7.23 – 7.19 (m, 2H), 4.74 (s, 1H), 4.14 (s, 2H), 3.59 (s, 3H), 3.50 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.15, 164.38, 163.11, 162.36, 149.84, 149.66, 142.37, 132.85, 132.38, 132.31, 130.58, 130.55, 127.82, 119.82, 118.78, 117.33, 117.24 (d, J_{C-F} = 23.0 Hz), 104.25, 61.85, 52.87, 52.26, 38.82. ^{19}F NMR (471 MHz, $CDCl_3$) δ -107.51 ppm. HRMS (ESI^+): m/z calculated for [$C_{23}H_{17}FN_4O_4$ + H^+]: 433.1312; found 433.1313

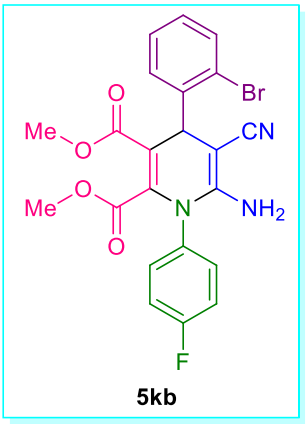
Dimethyl 6-amino-5-cyano-4-(3-fluorophenyl)-1-(4-fluorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate, 5jb:



5jb

99% yield, white solid. R_f = 0.42 (40% EtOAc/Hexane); M.P. 188-190 °C. IR (KBr) υ_{max} (cm^{-1}): 3460, 3315, 3225, 2958, 2179, 1743, 1712, 1653, 1615, 1572, 1509, 1421, 1354, 1245, 1223, 1110, 1055, 972, 871, 785, 727, 621, 536. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 3H), 7.22 – 7.18 (m, 2H), 7.15 (dd, J = 9.0, 1.4 Hz, 1H), 7.05 (dd, J = 9.8, 2.6 Hz, 1H), 6.97 (t, J = 0.9 Hz, 1H), 4.68 (s, 1H), 4.09 (s, 2H), 3.61 (s, 3H), 3.49 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.56, 164.41, 164.29, 163.46, 162.40, 162.33, 149.78, 147.27, 147.22, 142.00, 132.51, 132.44, 130.93, 130.50, 130.43, 122.82, 120.19, 117.26 (d, J_{C-F} = 23.0 Hz), 114.45, 114.29, 114.12, 113.94, 105.18, 62.79, 52.89, 52.28, 38.40. ^{19}F NMR (471 MHz, $CDCl_3$) δ -107.90, -112.42 ppm. HRMS (ESI^+): m/z calculated for [$C_{22}H_{17}F_2N_3O_4$ + H^+]: 426.1265; found 426.1265

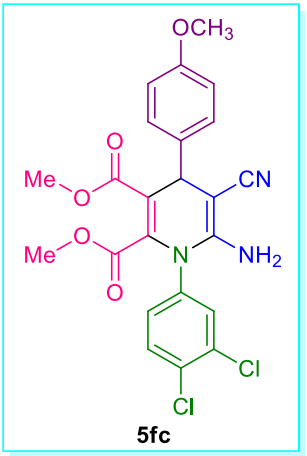
Dimethyl 6-amino-4-(2-bromophenyl)-5-cyano-1-(4-fluorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate, 5kb:



5kb

94% yield, pale yellow solid. R_f = 0.42 (40% EtOAc/Hexane); M.P. 190-192 °C. IR (KBr) υ_{max} (cm^{-1}): 3471, 3331, 3230, 3056, 2948, 2189, 1751, 1701, 1651, 1579, 1503, 1411, 1358, 1256, 1225, 1120, 1016, 941, 879, 819, 776, 641, 567, 533. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.42 – 7.38 (m, 3H), 7.38 – 7.34 (m, 1H), 7.23 – 7.18 (m, 2H), 7.13 – 7.09 (m, 1H), 5.32 (s, 1H), 4.04 (s, 2H), 3.56 (s, 3H), 3.50 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.60, 164.34, 163.46, 162.33, 149.78, 144.09, 142.35, 133.25, 132.60, 130.87, 129.97, 128.73, 128.34, 122.82, 119.99, 117.14 (d, J_{C-F} = 23.0 Hz), 105.04, 62.24, 52.82, 52.11, 37.96. ^{19}F NMR (471 MHz, $CDCl_3$) δ -107.97 ppm. HRMS (ESI^+): m/z calculated for [$C_{22}H_{17}BrFN_3O_4$ + H^+]: 486.0465; found 486.0461

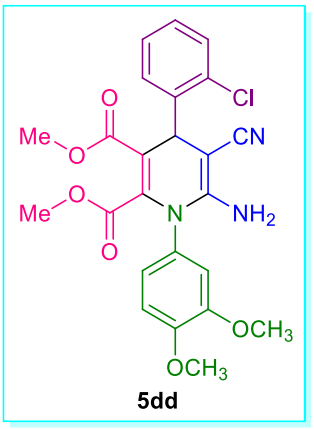
Dimethyl 6-amino-5-cyano-1-(3,4-dichlorophenyl)-4-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate, 5fc:



5fc

91% yield, pale yellow solid. R_f = 0.35 (60% EtOAc/Hexane); M.P. 240-242 °C. IR (KBr) υ_{max} (cm^{-1}): 3402, 3321, 3225, 2952, 2189, 1753, 1707, 1653, 1618, 1564, 1472, 1423, 1325, 1290, 1221, 1125, 1092, 982, 920, 901, 814, 763, 721, 682, 606, 586, 536. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.5 Hz, 1H), 7.48 (d, *J* = 2.5 Hz, 1H), 7.26 – 7.20 (m, 3H), 6.94 – 6.89 (m, 2H), 4.61 (s, 1H), 4.03 (s, 2H), 3.82 (s, 3H), 3.61 (s, 3H), 3.55 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.72, 163.55, 158.96, 148.88, 140.84, 136.73, 135.54, 134.73, 134.16, 132.25, 131.65, 129.65, 128.20, 120.18, 114.42, 106.71, 64.60, 55.43, 53.05, 52.32, 37.80. HRMS (ESI^+): m/z calculated for [$C_{23}H_{19}Cl_2N_3O_5$ + H^+]: 488.0780; found 488.0774

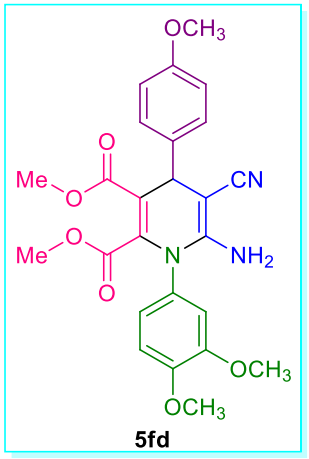
Dimethyl 6-amino-4-(2-chlorophenyl)-5-cyano-1-(3,4-dimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate, 5dd:



5dd

92% yield, green solid. R_f = 0.4 (60% EtOAc/Hexane); M.P. 248-250 °C. IR (KBr) υ_{max} (cm^{-1}): 3470, 3365, 3213, 3080, 3014, 2959, 2834, 2187, 1749, 1701, 1650, 1613, 1574, 1514, 1441, 1411, 1358, 1322, 1261, 1238, 1115, 1021, 928, 811, 767, 748, 670, 583, 545. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.38 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.30 (t, *J* = 1.3 Hz, 1H), 7.19 (t, *J* = 1.7 Hz, 1H), 6.96 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 1H), 6.83 (d, *J* = 2.4 Hz, 1H), 5.28 (s, 1H), 4.15 (s, 2H), 3.93 (s, 3H), 3.91 (s, 3H), 3.55 (s, 3H), 3.52 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.63, 163.52, 150.49, 150.38, 149.52, 142.89, 142.32, 132.64, 129.94, 129.93, 128.32, 127.47, 127.13, 122.95, 120.32, 113.04, 110.99, 104.07, 61.15, 56.27, 56.12, 52.73, 51.98, 35.83. HRMS (ESI^+): m/z calculated for [$C_{24}H_{22}ClN_3O_6$ + H^+]: 484.1275; found 484.1270

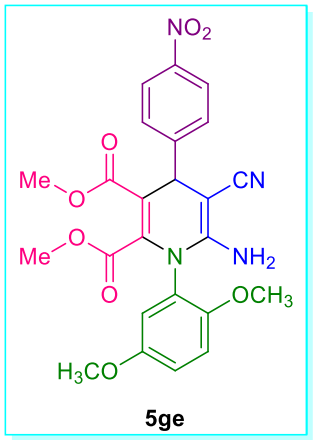
Dimethyl 6-amino-5-cyano-1-(3,4-dimethoxyphenyl)-4-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate, 5fd:



5fd

98% yield, green solid. R_f = 0.38 (60% EtOAc/Hexane). M.P. 262-264 °C. IR (KBr) υ_{max} (cm^{-1}): 3453, 3314, 3211, 3004, 2953, 2837, 2192, 1744, 1701, 1650, 1605, 1569, 1510, 1465, 1421, 1327, 1241, 1117, 1057, 1024, 975, 925, 851, 789, 767, 699, 674, 582, 528. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 2H), 6.94 – 6.88 (m, 4H), 6.80 (s, 1H), 4.63 (s, 1H), 4.12 (s, 2H), 3.93 (s, 3H), 3.90 (s, 3H), 3.81 (s, 3H), 3.60 (s, 3H), 3.51 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.99, 163.79, 158.75, 150.50, 149.95, 149.61, 141.90, 137.42, 128.20, 127.46, 122.87, 120.84, 114.23, 113.01, 111.05, 105.39, 62.79, 56.34, 56.18, 55.36, 52.78, 52.09, 37.79. HRMS (ESI^+): m/z calculated for [$C_{25}H_{25}N_3O_7$ + H^+]: 480.1771; found 424.1765

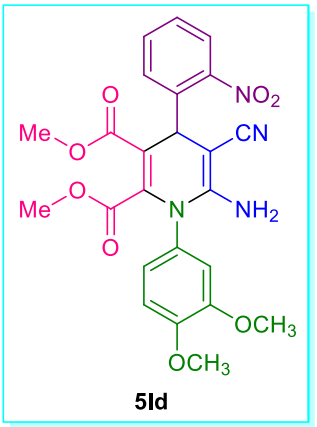
Dimethyl 6-amino-5-cyano-1-(2,5-dimethoxyphenyl)-4-(4-nitrophenyl)-1,4-dihydropyridine-2,3-dicarboxylate, 5ge:



5ge

89% yield, pale yellow solid. R_f = 0.4 (60% EtOAc/Hexane); M.P. 222-224 °C. IR (KBr) υ_{max} (cm^{-1}): 3468, 3361, 3215, 3075, 2956, 2190, 1751, 1703, 1649, 1610, 1576, 1519, 1448, 1415, 1368, 1331, 1269, 1221, 1114, 1023, 930, 819, 769, 676, 589, 539. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 – 8.19 (m, 2H), 7.74 – 7.65 (m, 2H), 7.04 (dd, *J* = 9.1, 3.1 Hz, 1H), 7.00 – 6.96 (m, 1H), 6.87 (d, *J* = 3.0 Hz, 1H), 4.74 (s, 1H), 4.22 (s, 2H), 3.91 (s, 3H), 3.79 (s, 3H), 3.60 (s, 3H), 3.51 (s, 3H). HRMS (ESI^+): m/z calculated for [$C_{24}H_{22}N_4O_8$ + H^+]: 495.1516; found 495.1505

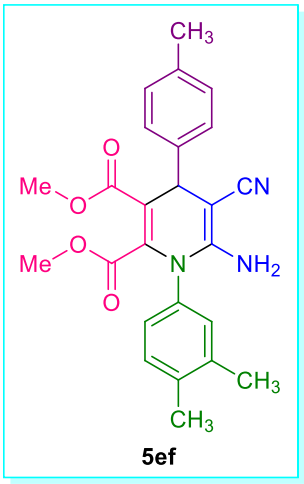
Dimethyl 6-amino-5-cyano-1-(3,4-dimethoxyphenyl)-4-(2-nitrophenyl)-1,4-dihydropyridine-2,3-dicarboxylate, 5ld:



5ld

97% yield, yellow solid. R_f = 0.45 (60% EtOAc/Hexane). M.P. 236-238 °C. IR (KBr) υ_{max} (cm^{-1}): 3465, 3363, 3214, 3065, 2953, 2189, 1750, 1701, 1650, 1611, 1578, 1521, 1443, 1411, 1378, 1321, 1271, 1221, 1115, 1033, 929, 820, 767, 675, 591, 534. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.7 Hz, 2H), 7.59 – 7.49 (m, 2H), 6.96 – 6.90 (m, 2H), 6.83 – 6.75 (m, 1H), 4.81 (s, 1H), 4.26 (s, 2H), 3.94 (s, 3H), 3.91 (s, 3H), 3.59 (s, 3H), 3.53 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.28, 163.23, 151.96, 150.71, 150.50, 149.70, 147.06, 142.94, 128.02, 126.78, 124.28, 122.84, 120.18, 112.87, 111.09, 103.66, 60.83, 56.36, 56.18, 52.90, 52.24, 38.79. HRMS (ESI^+): m/z calculated for [$C_{24}H_{22}N_4O_8$ + H^+]: 495.1516; found 495.1510

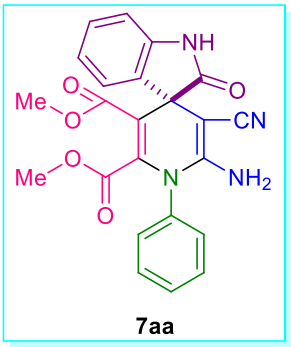
Dimethyl 6-amino-5-cyano-1-(3,4-dimethylphenyl)-4-(*p*-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate 5ef:



5ef

88% yield, brown solid. R_f = 0.4 (50% EtOAc/Hexane); M.P. 253-255 °C. IR (KBr) υ_{max} (cm^{-1}): 3476, 3371, 3221, 3085, 2949, 2186, 1746, 1701, 1653, 1618, 1586, 1521, 1451, 1411, 1365, 1321, 1271, 1219, 1121, 1031, 929, 825, 763, 671, 586, 533. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 4H), 7.10 – 7.03 (m, 3H), 4.63 (s, 1H), 4.09 (s, 2H), 3.59 (s, 3H), 3.48 (s, 3H), 2.35 (s, 3H), 2.29 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.08, 163.82, 149.89, 142.16, 139.63, 138.86, 136.83, 132.74, 131.00, 130.89, 129.65, 127.34, 127.02, 120.90, 105.14, 62.91, 52.67, 52.13, 38.13, 21.27, 19.91, 19.76. HRMS (ESI^+): m/z calculated for [$C_{25}H_{25}N_3O_4$ + H^+]: 432.1923; found 432.1918

Dimethyl 2'-amino-3'-cyano-2-oxo-1'-phenyl-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate, 7aa:

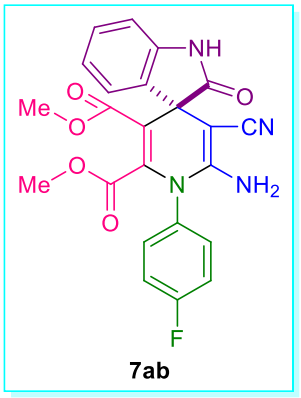


7aa

97% yield, yellow solid. R_f = 0.4 (70% EtOAc/Hexane). M.P. 225-227 °C. IR (KBr) υ_{max} (cm^{-1}): 3465, 3390, 3210, 2953, 2187, 1750, 1710, 1654, 1618, 1563, 1503, 1470, 1415, 1326, 1283, 1223, 1130, 1095, 982, 928, 866, 750, 722, 681, 585, 534. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.47 (s, 1H), 7.61 – 7.49 (m, 3H), 7.43 (m, 2H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.22 (t, *J* = 7.6 Hz,

1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 7.7 Hz, 1H), 5.81 (s, 2H), 3.33 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 178.83, 164.14, 162.59, 151.48, 143.46, 141.32, 135.66, 135.53, 130.24, 130.18, 129.67, 128.72, 123.85, 122.11, 118.54, 109.37, 103.77, 60.06, 52.47, 51.81, 49.72. HRMS (ESI$^+$): m/z calculated for [$C_{23}H_{18}N_4O_5$ + H^+]: 431.1355; found 431.1350

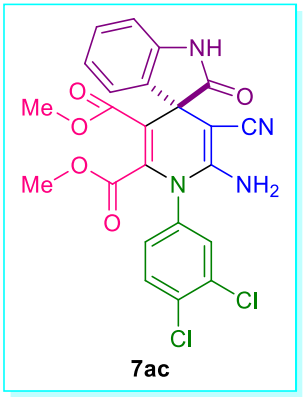
Dimethyl 2'-amino-3'-cyano-1'-(4-fluorophenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate, 7ab:



7ab

98% yield, yellow solid. R_f = 0.4 (70% EtOAc/Hexane). M.P. 250-252 °C. IR (KBr) υ_{max} (cm^{-1}): 3470, 3381, 3221, 2949, 2191, 1753, 1703, 1650, 1614, 1569, 1510, 1476, 1414, 1321, 1276, 1221, 1121, 1089, 986, 930, 867, 728, 687, 537. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.47 (s, 1H), 7.52 – 7.46 (m, 2H), 7.37 (t, *J* = 8.8 Hz, 2H), 7.29 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.21 (t, *J* = 8.3 Hz, 1H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 7.7 Hz, 1H), 5.94 (s, 2H), 3.39 (s, 3H), 3.33 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 178.86, 164.11, 163.82, 162.62, 161.37, 151.54, 143.52, 141.33, 135.68, 132.87, 131.69, 128.72, 123.93, 122.09, 118.56, 116.61 (d, J_{C-F} = 23.1 Hz), 109.37, 103.69, 59.87, 52.58, 51.83, 49.72. ^{19}F NMR (471 MHz, DMSO) δ -111.28 ppm. HRMS (ESI$^+$): m/z calculated for [$C_{23}H_{17}FN_4O_5$ + H^+]: 449.1261; found 449.1261

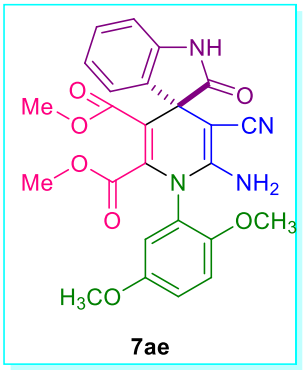
Dimethyl 2'-amino-3'-cyano-1'-(3,4-dichlorophenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate, 7ac:



7ac

98% yield, pale yellow solid. R_f = 0.45 (70% EtOAc/Hexane); M.P. 268-270 °C. IR (KBr) υ_{max} (cm^{-1}): 3404, 3322, 3227, 3028, 2953, 2190, 1751, 1710, 1653, 1615, 1564, 1503, 1469, 1422, 1325, 1290, 1221, 1126, 1093, 981, 920, 865, 814, 763, 723, 680, 585, 535. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.47 (s, 1H), 7.89 – 7.72 (m, 2H), 7.44 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.21 (t, *J* = 7.0 Hz, 1H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.13 (s, 2H), 3.42 (s, 3H), 3.33 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 178.71, 164.01, 162.52, 151.26, 142.79, 141.32, 135.42, 135.39, 133.27, 132.81, 131.87, 131.41, 130.74, 128.72, 124.15, 122.03, 118.41, 109.30, 104.38, 59.90, 52.74, 51.88, 49.67. HRMS (ESI+): m/z calculated for [$C_{23}H_{16}Cl_2N_4O_5$ + H^+]: 499.0576; found 499.0570

Dimethyl 2'-amino-3'-cyano-1'-(2,5-dimethoxyphenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate, 7ae:

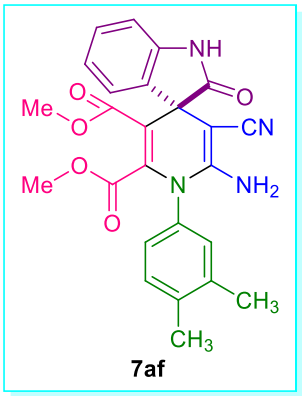


7ae

90% yield, green solid. R_f = 0.42 (70% EtOAc/Hexane); M.P. 275-277 °C. IR (KBr) υ_{max} (cm^{-1}): 3489, 3368, 3223, 3061, 2951, 2191, 1752, 1716, 1694, 1653, 1616, 1571, 1508, 1471, 1415, 1325, 1289, 1227, 1133, 1039, 987, 929, 861, 824, 761, 679, 591, 539. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.43 (s, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.14 – 7.05 (m,

2H), 6.88 (d, *J* = 2.9 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 5.80 (s, 2H), 3.88 (s, 3H), 3.76 (s, 6H), 3.33 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 179.53, 163.00, 153.07, 151.87, 144.62, 141.21, 136.87, 128.96, 124.27, 122.47, 118.02, 113.73, 109.74, 103.28, 60.22, 56.88, 56.15, 52.87, 52.21, 50.22. HRMS (ESI+): m/z calculated for [$C_{25}H_{22}N_4O_7$ + H^+]: 491.1567; found 491.1561

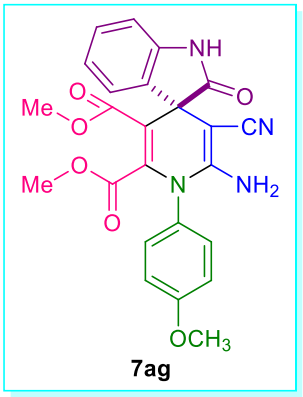
Dimethyl 2'-amino-3'-cyano-1'-(3,4-dimethoxyphenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate, 7af:



7af

95% yield, yellow solid. R_f = 0.42 (70% EtOAc/Hexane); M.P. 268-270 °C. IR (KBr) υ_{max} (cm^{-1}): 3476, 3321, 3223, 3031, 2949, 2189, 1753, 1716, 1655, 1618, 1569, 1501, 1476, 1421, 1329, 1287, 1223, 1121, 1089, 987, 921, 869, 821, 769, 721, 669, 587, 532. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.45 (s, 1H), 7.27 (t, *J* = 7.8 Hz, 2H), 7.23 – 7.18 (m, 2H), 7.11 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 5.73 (s, 2H), 3.36 (s, 6H), 2.28 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 178.87, 164.17, 162.56, 151.48, 143.62, 141.28, 138.56, 137.91, 135.79, 132.88, 130.66, 130.41, 128.65, 127.18, 123.83, 122.06, 118.60, 109.32, 103.29, 59.79, 52.43, 51.74, 49.70, 19.29, 19.22. HRMS (ESI+): m/z calculated for [$C_{25}H_{22}N_4O_5$ + H^+]: 459.1668; found 459.1668

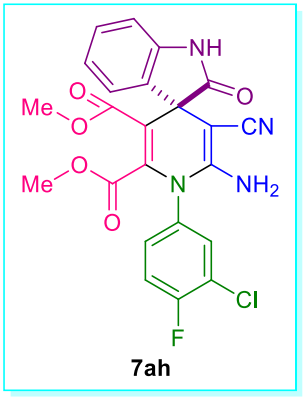
Dimethyl 2'-amino-3'-cyano-1'-(4-methoxyphenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate, 7ag:



7ag

97% yield, pale yellow solid. R_f = 0.4 (80% EtOAc/Hexane). M.P. 270-272 °C. IR (KBr) υ_{max} (cm^{-1}): 3502, 3406, 3313, 3211, 3092, 2952, 2181, 1741, 1716, 1644, 1617, 1559, 1513, 1470, 1411, 1331, 1283, 1222, 1134, 1030, 983, 927, 865, 835, 748, 670, 573, 539. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.44 (s, 1H), 7.34 – 7.30 (m, 2H), 7.26 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.20 (t, *J* = 8.3 Hz, 1H), 7.07 – 7.03 (m, 2H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 7.7 Hz, 1H), 5.78 (s, 2H), 3.81 (s, 3H), 3.36 (s, s6H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 178.92, 164.15, 162.61, 160.09, 151.67, 143.95, 141.28, 135.86, 131.54, 128.64, 127.56, 123.83, 122.05, 118.62, 114.73, 109.31, 103.07, 59.72, 55.53, 52.48, 51.73, 49.70. HRMS (ESI+): m/z calculated for [$C_{24}H_{20}N_4O_6$ + H^+]: 461.1461; found 461.1456

Dimethyl 2'-amino-1'-(3-chloro-4-fluorophenyl)-3'-cyano-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate, 7ah:

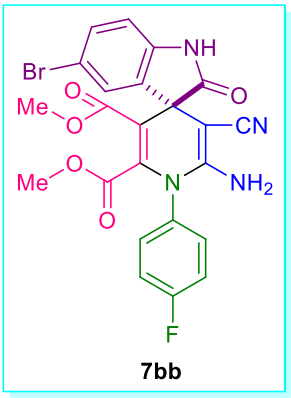


7ah

98% yield, yellow solid. R_f = 0.4 (70% EtOAc/Hexane); M.P. 239-241 °C. IR (KBr) υ_{max} (cm^{-1}): 3481, 3351, 3227, 3067, 2947, 1754, 1719, 1653, 1613, 1571, 1513, 1467, 1414, 1323, 1289, 1218, 1131, 1029, 987, 928, 866, 831, 778, 719, 673, 593, 533. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.47 (s, 1H), 7.81 (dd, *J* = 6.6, 2.6 Hz, 1H), 7.58 (t, *J* = 8.9 Hz, 1H), 7.48 (dd, *J* = 12.5, 3.2

Hz, 1H), 7.35 (d, *J* = 7.3 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.10 (s, 2H), 3.41 (s, 3H), 3.33 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 178.77, 164.03, 162.55, 159.37, 156.89, 151.38, 143.06, 141.31, 135.52, 133.23, 132.40, 131.66, 131.57, 128.72, 124.16, 122.04, 120.40, 120.21, 118.48, 117.68 (d, J_{C-F} = 22.4 Hz), 109.30, 104.10, 59.81, 52.69, 51.86, 49.69. ^{19}F NMR (471 MHz, DMSO) δ -113.45. HRMS (ESI+): m/z calculated for [$C_{23}H_{16}ClFN_4O_5$ + H^+]: 483.0872; found 483.0868

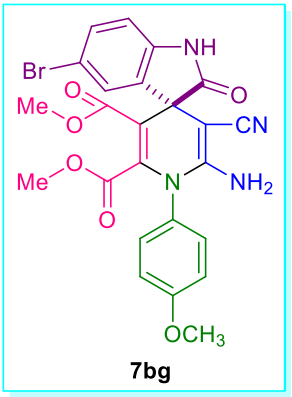
Dimethyl 2'-amino-5-bromo-3'-cyano-1'-(4-fluorophenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate, 7bb:



7bb

98% yield, white solid. R_f = 0.45 (60% EtOAc/Hexane). M.P. 280-282 °C. IR (KBr) υ_{max} (cm^{-1}): 3480, 3348, 3213, 3067, 2951, 1753, 1711, 1649, 1613, 1578, 1505, 1487, 1421, 1329, 1284, 1223, 1118, 1058, 986, 928, 869, 821, 786, 721, 676, 589, 537. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.60 (s, 1H), 7.54 (m, 3H), 7.43 – 7.30 (m, 3H), 6.79 (d, *J* = 8.2 Hz, 1H), 6.01 (s, 2H), 3.37 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 179.08, 164.44, 162.86, 161.90, 151.76, 144.67, 141.18, 138.71, 133.60, 133.51, 131.91, 131.66, 127.24, 118.91, 116.95 (d, J_{C-F} = 22.9 Hz), 114.11, 111.72, 102.18, 59.37, 52.98, 52.37, 50.60. ^{19}F NMR (471 MHz, DMSO) δ -110.40 ppm. HRMS (ESI+): m/z calculated for [$C_{23}H_{16}BrN_4O_5$ + H^+]: 527.0366; found 527.0361

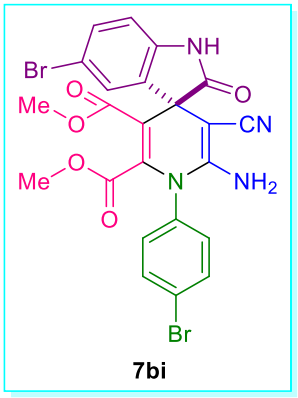
Dimethyl 2'-amino-5-bromo-3'-cyano-1'-(4-methoxyphenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate, 7bg:



7bg

90% yield, green solid. R_f = 0.4 (70% EtOAc/Hexane). M.P. 274-276 °C. IR (KBr) υ_{max} (cm^{-1}): 3457, 3310, 3206, 2954, 2188, 1748, 1705, 1652, 1616, 1570, 1508, 1474, 1418, 1331, 1245, 1223, 1133, 1028, 989, 938, 868, 811, 776, 734, 664, 543. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.59 (s, 1H), 7.50 (d, *J* = 2.1 Hz, 1H), 7.42 – 7.33 (m, 3H), 7.07 – 7.00 (m, 2H), 6.79 (d, *J* = 8.2 Hz, 1H), 5.85 (s, 2H), 3.81 (s, 3H), 3.36 (s, 6H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 178.72, 164.07, 162.46, 160.19, 151.55, 144.66, 140.75, 138.41, 131.80, 131.45, 127.17, 126.68, 118.54, 114.68, 113.66, 111.32, 101.38, 58.88, 55.54, 52.50, 51.88, 50.18. HRMS (ESI+): m/z calculated for [$C_{24}H_{19}BrN_4O_6$ + H^+]: 539.0566; found 539.0560

Dimethyl 2'-amino-5-bromo-1'-(4-bromophenyl)-3'-cyano-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate, 7bi:

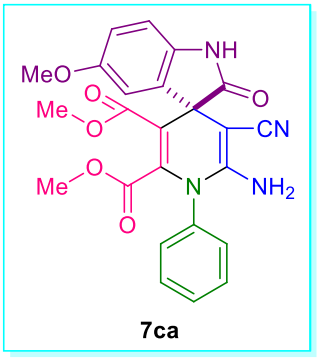


7bi

90% yield, yellow solid. R_f = 0.42 (70% EtOAc/Hexane). M.P. 278-280 °C. IR (KBr) υ_{max} (cm^{-1}): 3450, 3314, 3215, 2951, 2191, 1752, 1707, 1654, 1614, 1576, 1514, 1476, 1421, 1331, 1296, 1226, 1135, 1031, 985, 865, 810, 777, 689, 614, 538. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.61 (s, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.46 – 7.36 (m, 4H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.05 (s, 2H), 3.38 (s, 3H), 3.36 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 178.62, 164.00, 162.42, 151.17, 143.92,

140.79, 138.20, 134.46, 132.78, 132.67, 131.51, 131.36, 126.81, 123.84, 118.43, 115.82, 113.73, 111.34, 102.08, 59.12, 52.64, 51.97, 50.19. HRMS (ESI+): m/z calculated for [$C_{23}H_{26}Br_2N_4O_5$ + H^+]: 588.9545; found 588.9540

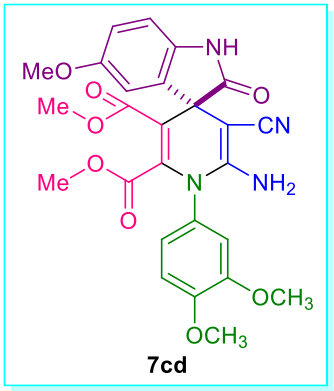
Dimethyl 2'-amino-3'-cyano-5-methoxy-2-oxo-1'-phenyl-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate, 7ca:



7ca

95% yield, green solid. R_f = 0.4 (80% EtOAc/Hexane). M.P. 226-228 °C. IR (KBr) υ_{max} (cm^{-1}): 3469, 3331, 3217, 2949, 2187, 1715, 1648, 1607, 1564, 1491, 1417, 1322, 1271, 1226, 1130, 1026, 956, 866, 793, 765, 699, 606, 527. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.30 (s, 1H), 7.54-7.51 (m, 3H), 7.43 – 7.40 (m, 2H), 6.83 (d, *J* = 2.5 Hz, 1H), 6.79 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 5.81 (s, 2H), 3.74 (s, 3H), 3.33 (s, 3H), 3.32 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 178.63, 164.12, 162.56, 155.16, 151.46, 143.44, 136.87, 135.54, 134.76, 130.20, 130.12, 129.62, 118.49, 112.83, 110.99, 109.69, 103.78, 60.14, 55.48, 52.42, 51.76, 50.16. HRMS (ESI+): m/z calculated for [$C_{24}H_{20}N_4O_6$ + H^+]: 461.1461; found 461.1455

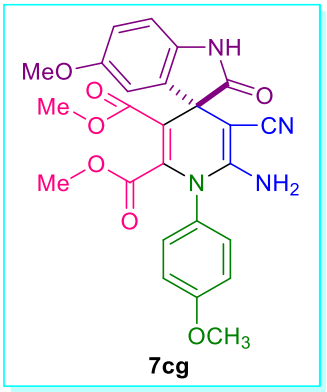
Dimethyl 2'-amino-3'-cyano-1'-(3,4-dimethoxyphenyl)-5-methoxy-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate, 7cd:



7cd

96% yield, green solid. R_f = 0.35 (70% EtOAc/Hexane); M.P. 235-237 °C. IR (KBr) υ_{max} (cm^{-1}): 3458, 3349, 3084, 2952, 2188, 1743, 1723, 1650, 1601, 1564, 1514, 1489, 1411, 1327, 1303, 1264, 1230, 1129, 1025, 987, 953, 929, 892, 868, 790, 765, 734, 687, 610, 540. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.26 (s, 1H), 7.06 (d, *J* = 8.5 Hz, 1H), 7.00 – 6.91 (m, 2H), 6.86 (d, *J* = 2.5 Hz, 1H), 6.79 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 5.82 (s, 2H), 3.81 (s, 3H), 3.80 (s, 3H), 3.74 (s, 3H), 3.39 (s, 3H), 3.33 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 178.80, 164.20, 162.59, 155.14, 151.66, 149.82, 148.83, 143.90, 137.16, 134.76, 127.53, 122.61, 118.70, 113.69, 112.65, 111.44, 111.22, 109.59, 102.98, 59.56, 55.74, 55.64, 55.48, 52.49, 51.73, 50.18. HRMS (ESI+): m/z calculated for [$C_{26}H_{24}N_4O_8$ + H^+]: 521.1672; found 521.1666

Dimethyl 2'-amino-3'-cyano-5-methoxy-1'-(4-methoxyphenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate, 7cg:

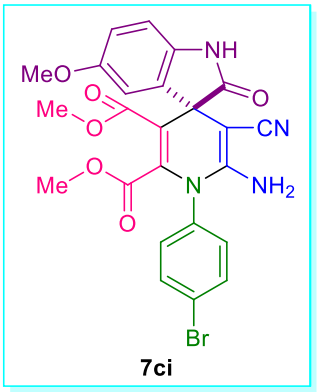


7cg

96% yield, green solid. R_f = 0.4 (80% EtOAc/Hexane). M.P. 228-230 °C. IR (KBr) υ_{max} (cm^{-1}): 3545, 3470, 3309, 3196, 2952, 2187, 1745, 1711, 1649, 1606, 1562, 1510, 1491, 1420, 1330, 1298, 1251, 1229, 1131, 1107, 1024, 981, 919, 893, 872, 819, 765, 730, 674, 623, 569, 545. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.27 (s, 1H), 7.35 – 7.30 (m, 2H), 7.07 – 7.02 (m, 2H), 6.82 (d, *J*

= 2.5 Hz, 1H), 6.78 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 5.78 (s, 2H), 3.81 (s, 3H), 3.73 (s, 3H), 3.36 (s, 3H), 3.33 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 178.81, 164.19, 162.65, 160.11, 155.21, 151.70, 144.01, 137.16, 134.76, 131.56, 127.59, 118.66, 114.75, 112.75, 111.09, 109.68, 103.05, 59.82, 55.54, 55.51, 52.50, 51.76, 50.20. HRMS (ESI+): m/z calculated for [$C_{25}H_{22}N_4O_7$ + H^+]: 491.1567; found 491.1561

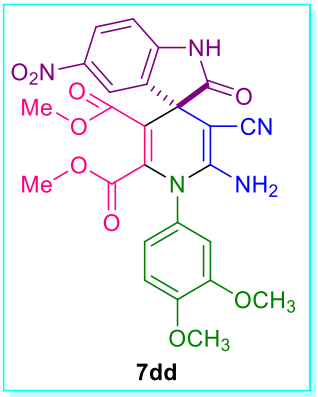
Dimethyl 2'-amino-1'-(4-bromophenyl)-3'-cyano-5-methoxy-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate, 7ci:



7ci

92% yield, pale yellow solid. R_f = 0.40 (80% EtOAc/Hexane). M.P. 240-242 °C. IR (KBr) υ_{max} (cm^{-1}): 3550, 3463, 3330, 3220, 3092, 2949, 2187, 1719, 1649, 1611, 1568, 1490, 1436, 1325, 1298, 1226, 1103, 1028, 916, 871, 791, 719, 688, 613, 527. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.30 (s, 1H), 7.74 – 7.71 (m, 2H), 7.39 – 7.35 (m, 2H), 6.85 (d, *J* = 2.5 Hz, 1H), 6.78 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 5.98 (s, 2H), 3.73 (s, 3H), 3.38 (s, 3H), 3.33 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 178.61, 164.08, 162.56, 155.19, 151.36, 143.15, 136.81, 134.95, 134.80, 132.68, 132.48, 123.58, 118.46, 112.83, 111.15, 109.69, 104.04, 60.11, 55.50, 52.62, 51.82, 50.17. HRMS (ESI+): m/z calculated for [$C_{24}H_{19}BrN_4O_6$ + H^+]: 539.0566; found 539.0560

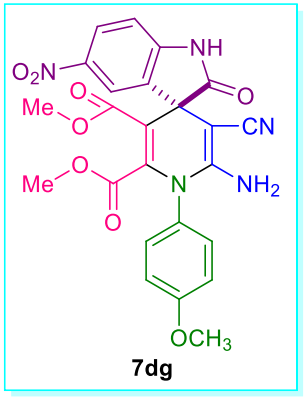
Dimethyl 2'-amino-3'-cyano-1'-(3,4-dimethoxyphenyl)-5-nitro-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate, 7dd:



7dd

91% yield, brown solid. R_f = 0.4 (70% EtOAc/Hexane); M.P. 251-253 °C. IR (KBr) υ_{max} (cm^{-1}): 3441, 3334, 3297, 2947, 2190, 1759, 1742, 1680, 1654, 1619, 1564, 1519, 1479, 1420, 1333, 1274, 1240, 1136, 1071, 1023, 986, 932, 850, 829, 782, 768, 737, 684, 614, 588, 555. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.20 (s, 1H), 8.33 – 8.13 (m, 2H), 7.19 – 6.90 (m, 4H), 6.03 (s, 2H), 3.82 (s, 3H), 3.81 (s, 3H), 3.41 (s, 3H), 3.36 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 179.62, 163.98, 162.26, 151.77, 149.99, 148.89, 148.03, 145.09, 142.61, 137.04, 126.91, 126.19, 122.87, 119.50, 118.44, 113.85, 111.42, 109.57, 100.55, 57.78, 55.79, 55.65, 52.58, 52.01, 50.18. HRMS (ESI+): m/z calculated for [$C_{25}H_{21}N_5O_9$ + H^+]: 536.1418; found 536.1414

Dimethyl 2'-amino-3'-cyano-1'-(4-methoxyphenyl)-5-nitro-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate, 7dg:

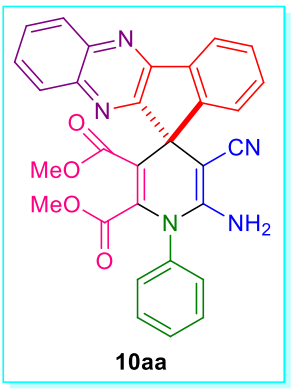


7dg

90% yield, brown solid. R_f = 0.42 (70% EtOAc/Hexane). M.P. 262-264 °C. IR (KBr) υ_{max} (cm^{-1}): 3441, 3317, 3223, 2950, 2189, 1757, 1743, 1679, 1652, 1619, 1562, 1510, 1478, 1419, 1335, 1251, 1223, 1182, 1132, 1071, 1017, 987, 942, 916, 877, 849, 826, 781, 734, 673, 617, 571, 550, 457. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.21 (s, 1H), 8.24 – 8.15 (m, 2H), 7.37 (s, 2H), 7.13 – 6.98 (m, 3H), 5.99 (s, 2H), 3.82 (s, 3H), 3.35 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 179.57,

163.93, 162.27, 160.24, 151.77, 147.99, 145.13, 142.62, 136.99, 131.76, 126.97, 126.18, 119.40, 118.35, 114.73, 109.57, 100.58, 57.98, 55.53, 52.55, 52.00, 50.14. HRMS (ESI+): m/z calculated for [$C_{24}H_{19}N_5O_8$ + H^+]: 506.1312; found 536.1306

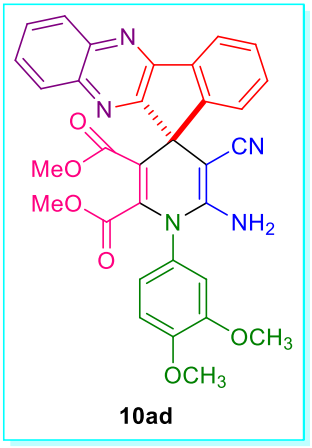
Dimethyl 2'-amino-3'-cyano-1'-phenyl-1'*H*-spiro[indeno[1,2-*b*]quinoxaline-11,4'-pyridine]-5',6'-dicarboxylate, 10aa:



10aa

98% yield, yellow solid. R_f = 0.40 (80% EtOAc/Hexane). M.P. 274-276 °C. IR (KBr) υ_{max} (cm^{-1}): 3480, 3381, 3211, 3060, 2945, 2180, 1744, 1707, 1649, 1617, 1593, 1566, 1510, 1491, 1416, 1327, 1281, 1218, 1137, 1112, 1093, 1037, 1024, 983, 933, 865, 767, 698, 610, 587, 528, 503. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.23 – 8.18 (m, 2H), 8.13 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.91 – 7.82 (m, 3H), 7.74 (t, *J* = 7.5, Hz, 1H), 7.63 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.61-7.57 (m, 5H), 5.93 (s, 2H), 3.34 (s, 3H), 3.02 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.18, 163.96, 162.66, 153.83, 152.66, 151.53, 144.01, 141.86, 141.04, 135.54, 135.37, 132.82, 130.39, 130.26, 129.99, 129.72, 129.32, 129.16, 128.95, 125.34, 121.53, 118.69, 104.76, 61.20, 52.50, 51.65, 49.52. HRMS (ESI+): m/z calculated for [$C_{30}H_{21}N_5O_4$ + H^+]: 516.1672; found 516.1666

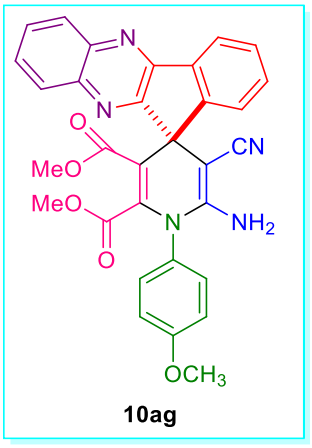
Dimethyl 2'-amino-3'-cyano-1'-(3,4-dimethoxyphenyl)-1'H-spiro[indeno[1,2-*b*]quinoxaline-11,4'-pyridine]-5',6'-dicarboxylate, 10ad:



10ad

94% yield, green solid. R_f = 0.35 (80% EtOAc/Hexane). M.P. 292-294 °C. IR (KBr) υ_{max} (cm^{-1}): 3471, 3398, 3327, 3229, 2948, 2185, 1745, 1701, 1651, 1622, 1562, 1513, 1465, 1416, 1333, 1290, 1235, 1216, 1138, 1113, 1027, 933,869, 765, 663, 587, 504. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.19 (dd, *J* = 7.8, 1.8 Hz, 2H), 8.12 (d, *J* = 7.5 Hz, 1H), 7.91-7.81 (m, 3H), 7.73 (t, *J* = 8.1 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 13.3 Hz, 3H), 5.95 (s, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 3.41 (s, 3H), 3.02 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.50, 164.12, 162.79, 153.96, 151.78, 150.05, 149.01, 144.55, 141.89, 141.10, 135.38, 132.92, 130.11, 129.46, 129.40, 129.19, 129.02, 127.54, 125.57, 122.91, 121.58, 118.98, 113.90, 111.64, 104.03, 60.64, 55.95, 55.78, 52.67, 51.71, 49.65. HRMS (ESI+): m/z calculated for [$C_{32}H_{25}N_5O_6$ + H^+]: 576.1883; found 576.1878

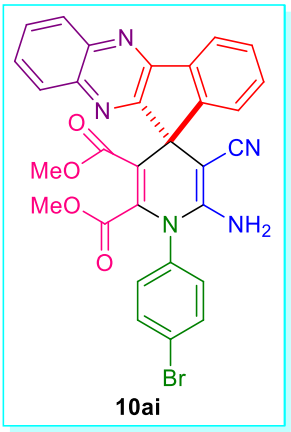
Dimethyl 2'-amino-3'-cyano-1'-(4-methoxyphenyl)-1'H-spiro[indeno[1,2-b]quinoxaline-11,4'-pyridine]-5',6'-dicarboxylate, 10ag:



10ag

95% yield, light green solid. R_f = 0.35 (80% EtOAc/Hexane); M.P. 262-264 °C. IR (KBr) υ_{max} (cm^{-1}): 3469, 3286, 3190, 3054, 2951, 2184, 1745, 1706, 1647, 1618, 1567, 1511, 1432, 1409, 1319, 1259, 1221, 1198, 1130, 1111, 1029, 973, 934, 865, 841, 763, 723, 631, 569, 544, 525. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.24-8.17 (m, 2H), 8.12 (d, *J* = 7.6 Hz, 1H), 7.90 – 7.81 (m, 3H), 7.73 (t, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 (d, *J* = 8.9 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 5.91 (s, 2H), 3.84 (s, 3H), 3.39 (s, 3H), 3.02 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 166.30, 163.96, 162.69, 160.16, 153.85, 152.82, 151.75, 144.48, 141.82, 141.02, 135.30, 132.78, 131.69, 129.93, 129.26, 129.13, 128.93, 127.61, 125.33, 121.48, 118.77, 114.78, 104.13, 60.83, 55.55, 52.52, 51.59, 49.49. HRMS (ESI+): m/z calculated for [$C_{31}H_{23}N_5O_5$ + H^+]: 546.1777; found 546.1772

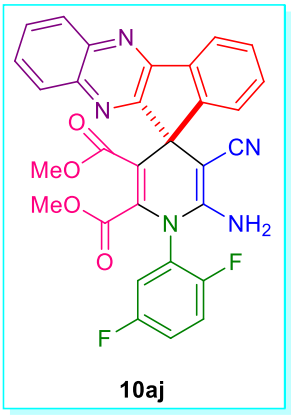
Dimethyl 2'-amino-1'-(4-bromophenyl)-3'-cyano-1'*H*-spiro[indeno[1,2-*b*]quinoxaline-11,4'-pyridine]-5',6'-dicarboxylate, 10ai:



10ai

98% yield, yellow solid. R_f = 0.38 (80% EtOAc/Hexane); M.P. 258-260 °C. IR (KBr) υ_{max} (cm^{-1}): 3476, 3389, 3291, 3068, 2951, 2191, 1748, 1703, 1649, 1618, 1569, 1519, 1469, 1421, 1329, 1269, 1223, 1133, 1031, 987, 929, 867, 781, 619, 587, 541, 515. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.25-8.17 (m, 2H), 8.12 (d, *J* = 7.5 Hz, 1H), 7.90 – 7.82 (m, 3H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 2H), 6.09 (s, 2H), 3.41 (s, 3H), 3.02 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 166.08, 163.87, 162.62, 153.78, 152.52, 151.43, 143.64, 141.85, 141.00, 135.38, 134.95, 132.76, 132.61, 129.99, 129.32, 129.15, 128.93, 125.38, 123.70, 121.50, 118.61, 105.08, 61.10, 52.68, 51.68, 49.47. HRMS (ESI+): m/z calculated for [$C_{30}H_{20}BrN_5O_6$ + H^+]: 594.0777; found 594.0773

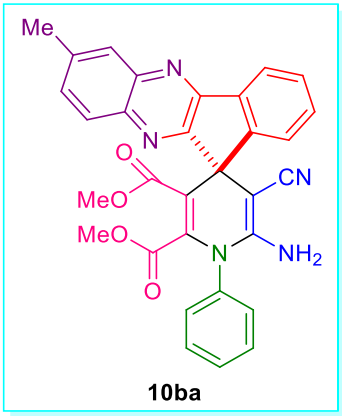
dimethyl 2'-amino-3'-cyano-1'-(2,5-difluorophenyl)-1'H-spiro[indeno[1,2-b]quinoxaline-11,4'-pyridine]-5',6'-dicarboxylate, 10aj:



10aj

92% yield, yellow solid. R_f = 0.4 (80% EtOAc/Hexane); M.P. 278-280 °C. IR (KBr) υ_{max} (cm^{-1}): 3481, 3384, 3227, 3088, 2948, 2856, 2181, 1741, 1715, 1652, 1613, 1574, 1509, 1462, 1415, 1341, 1299, 1248, 1221, 1130, 1039, 996, 932, 868, 771, 755, 712, 640, 588, 535, 503. ^{1}H NMR (500 MHz, DMSO) δ 8.27 (dd, *J* = 8.2, 1.6 Hz, 1H), 8.23-8.17 (m, 3H), 8.12 (d, *J* = 7.5 Hz, 1H), 7.97 – 7.93 (m, 2H), 7.86 (t, *J* = 9.0 Hz, 1H), 7.82-7.77 (m, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.54 – 7.50 (m, 1H), 6.25 (s, 2H), 3.46 (s, 3H), 3.03 (s, 3H). ^{19}F NMR (471 MHz, DMSO) δ -108.36, -108.37. HRMS (ESI+): m/z calculated for [$C_{30}H_{19}F_2N_5O_4$ + H^+]: 552.1483; found 552.1478

Dimethyl 2'-amino-3'-cyano-7-methyl-1'-phenyl-1'H-spiro[indeno[1,2-b]quinoxaline-11,4'-pyridine]-5',6'-dicarboxylate, 10ba:

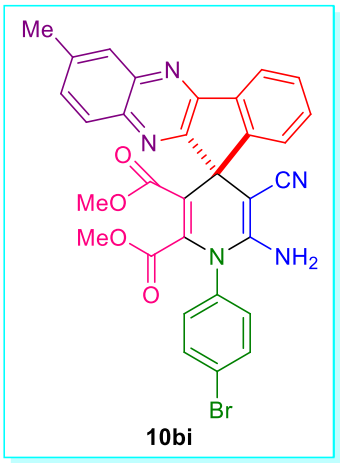


10ba

94% yield, pale yellow solid. R_f = 0.35 (80% EtOAc/Hexane); M.P. 256-258 °C. IR (KBr) υ_{max} (cm^{-1}): 3467, 3380, 3283, 3169, 3056, 2950, 2189, 1754, 1719, 1650, 1573, 1508, 1491, 1414,

1332, 1269, 1214, 1134, 1113, 1037, 972, 935, 875, 825, 767, 701, 659, 581, 527. ^{1}H NMR (500 MHz, DMSO) δ 8.14-8.06 (m, 2H), 8.00 (d, *J* = 10.4 Hz, 1H), 7.83 (dd, *J* = 7.5, 2.8 Hz, 1H), 7.76 – 7.65 (m, 2H), 7.64 – 7.57 (m, 6H), 5.92 (s, 2H), 3.35 (s, 3H), 3.01 (s, 3H), 2.59 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 166.06, 165.31, 164.00, 162.70, 153.67, 152.97, 151.55, 143.92, 141.96, 141.11, 140.07, 139.46, 135.63, 132.59, 131.20, 130.36, 130.22, 129.70, 129.23, 128.69, 127.95, 125.29, 121.45, 118.68, 105.01, 61.37, 52.46, 51.57, 49.43, 21.25. HRMS (ESI+): m/z calculated for [$C_{31}H_{23}N_5O_4$ + H^+]: 530.1828; found 530.1823

Dimethyl 2'-amino-1'-(4-bromophenyl)-3'-cyano-7-methyl-1'H-spiro[indeno[1,2-b]quinoxaline-11,4'-pyridine]-5',6'-dicarboxylate, 10bi:



10bi

92% yield, pale yellow solid. R_f = 0.4 (80% EtOAc/Hexane); M.P. 238-240 °C. IR (KBr) υ_{max} (cm^{-1}): 3471, 3399, 3321, 3229, 3192, 2949, 2187, 1745, 1718, 1651, 1572, 1509, 1486, 1417, 1333, 1282, 1204, 1134, 1116, 1039, 1011, 981, 940, 866, 829, 772, 717, 636, 582, 526. ^{1}H NMR (500 MHz, DMSO) δ 8.12 – 8.05 (m, 2H), 7.95 (t, *J* = 9.5 Hz, 1H), 7.84 – 7.78 (m, 3H), 7.72 – 7.65 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.57 – 7.52 (m, 2H), 6.07 (s, 1H), 3.40 (s, 3H), 3.01 (s, 3H), 2.59 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 165.20, 163.90, 162.65, 153.62, 152.91, 152.49, 151.43, 143.54, 141.92, 140.09, 139.40, 135.56, 135.01, 132.75, 132.58, 131.88, 131.21, 129.25, 128.69, 127.93, 125.34, 123.65, 121.40, 118.59, 106.33, 61.23, 52.65, 51.63, 43.63, 21.25. HRMS (ESI+): m/z calculated for [$C_{31}H_{22}BrN_5O_4$ + H^+]: 608.0933; found 608.0928

8. Copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra for products (5aa-5ef), (7aa-7dg), (10aa-10bi):

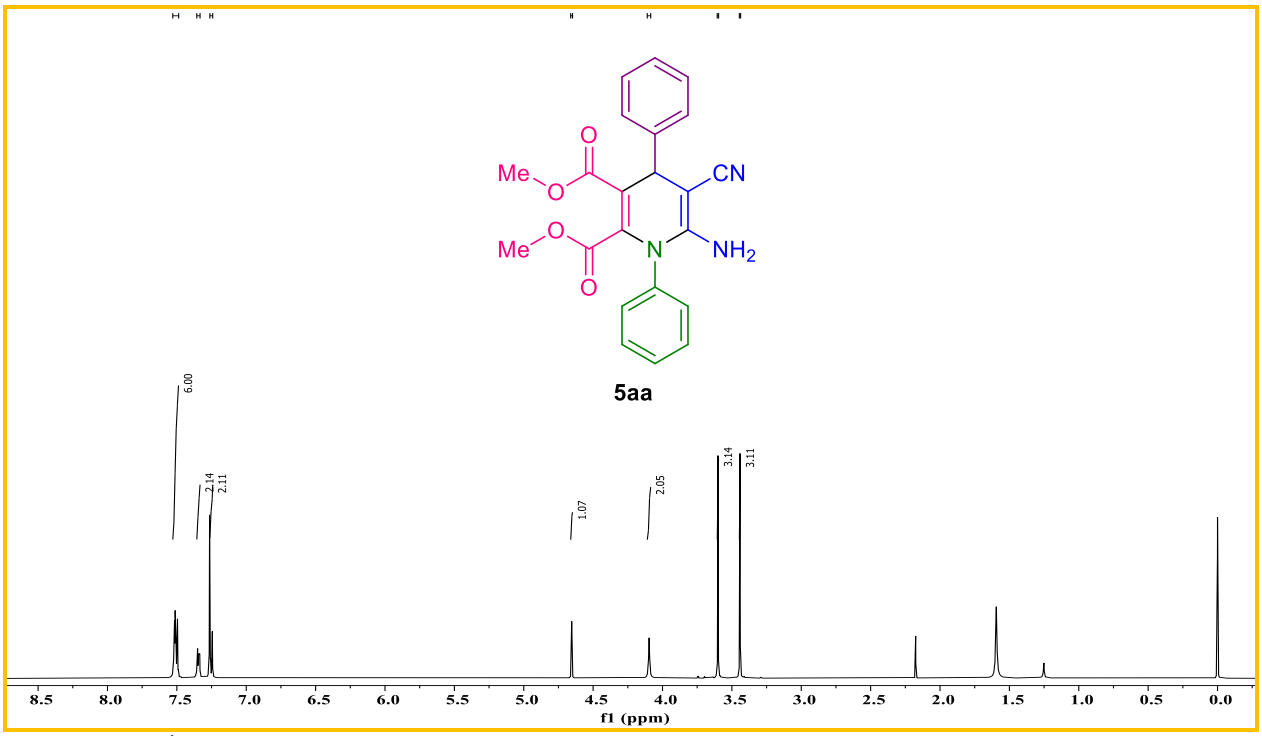


Figure S3: ^{1}H NMR spectra of dimethyl 6-amino-5-cyano-1,4-diphenyl-1,4-dihydropyridine-2,3-dicarboxylate **5aa**

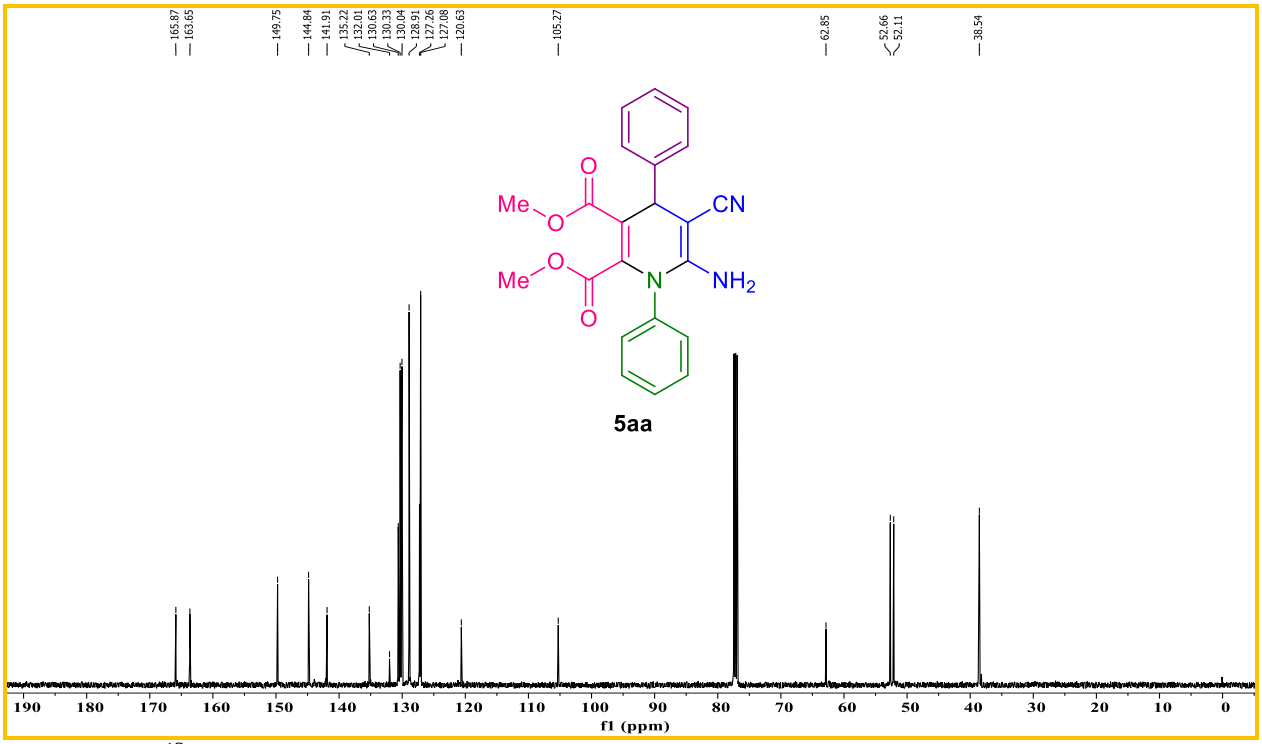


Figure S4: ^{13}C NMR spectra of dimethyl 6-amino-5-cyano-1,4-diphenyl-1,4-dihydropyridine-2,3-dicarboxylate **5aa**

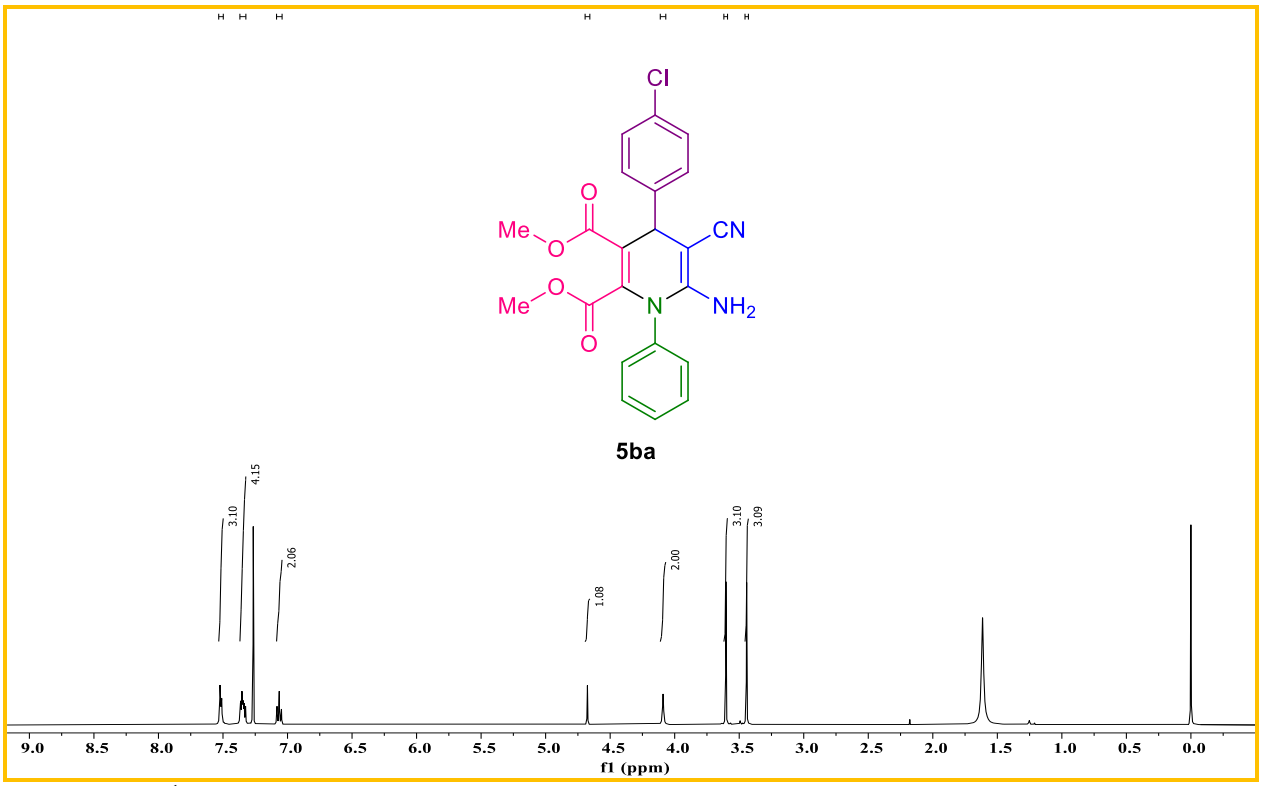


Figure S5: ^{1}H NMR spectra of dimethyl 6-amino-4-(4-chlorophenyl)-5-cyano-1-phenyl-1,4-dihydropyridine-2,3-dicarboxylate **5ba**

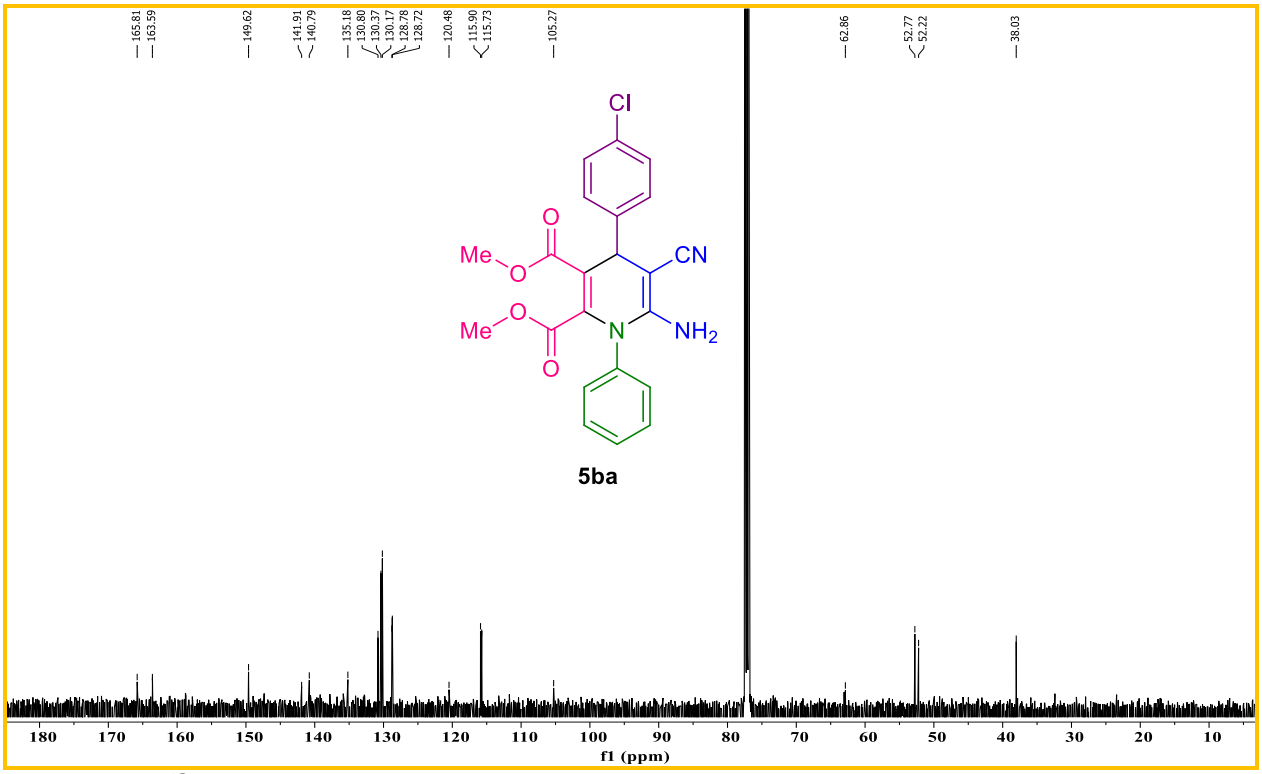


Figure S6: ^{13}C NMR spectra of dimethyl 6-amino-4-(4-chlorophenyl)-5-cyano-1-phenyl-1,4-dihydropyridine-2,3-dicarboxylate **5ba**

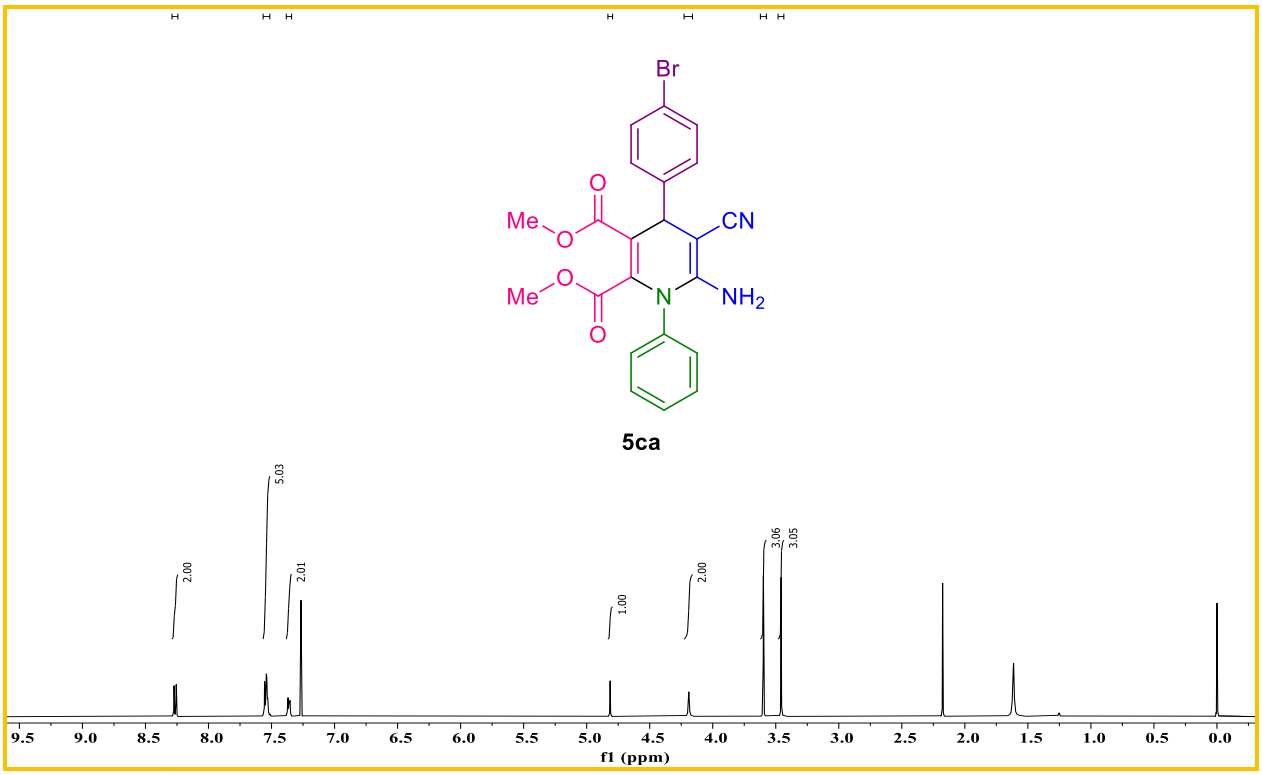


Figure S7: ^{1}H NMR spectra of dimethyl 6-amino-4-(4-bromophenyl)-5-cyano-1-phenyl-1,4-dihydropyridine-2,3-dicarboxylate **5ca**

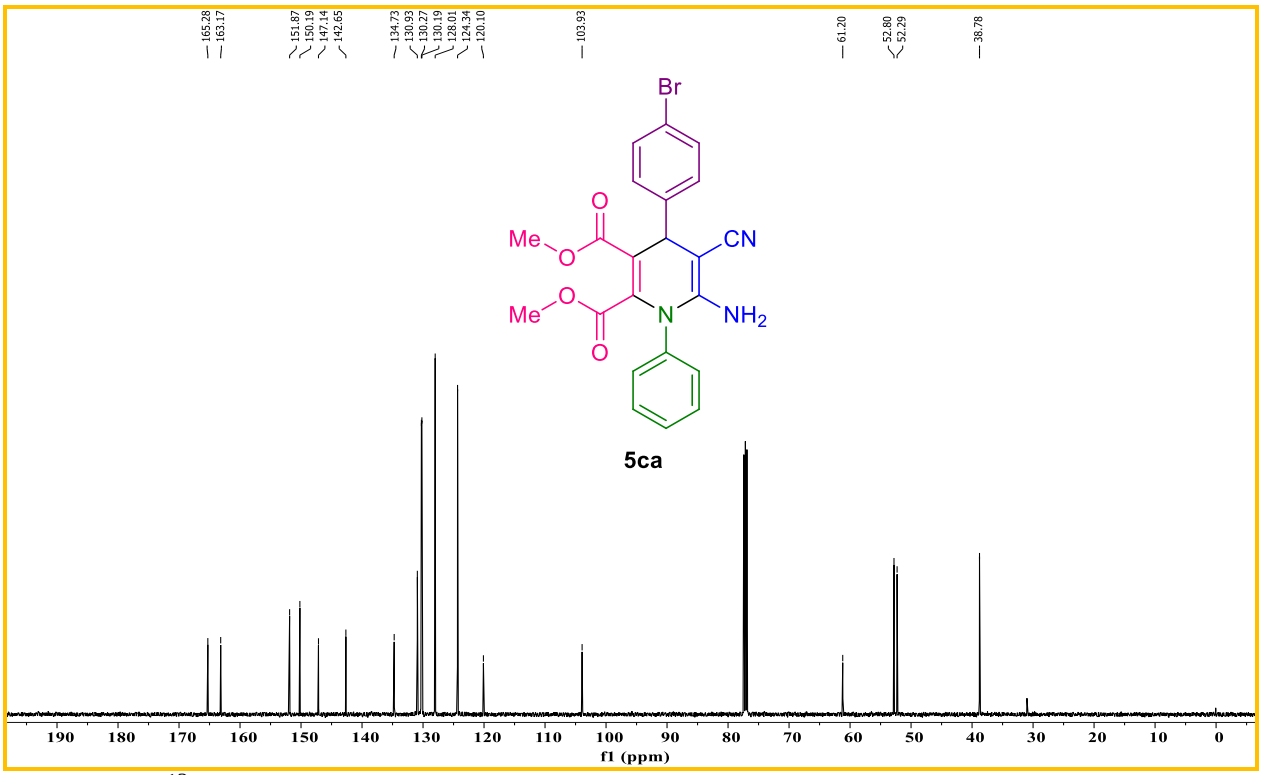


Figure S8: ^{13}C NMR spectra of dimethyl 6-amino-4-(4-bromophenyl)-5-cyano-1-phenyl-1,4-dihydropyridine-2,3-dicarboxylate **5ca**

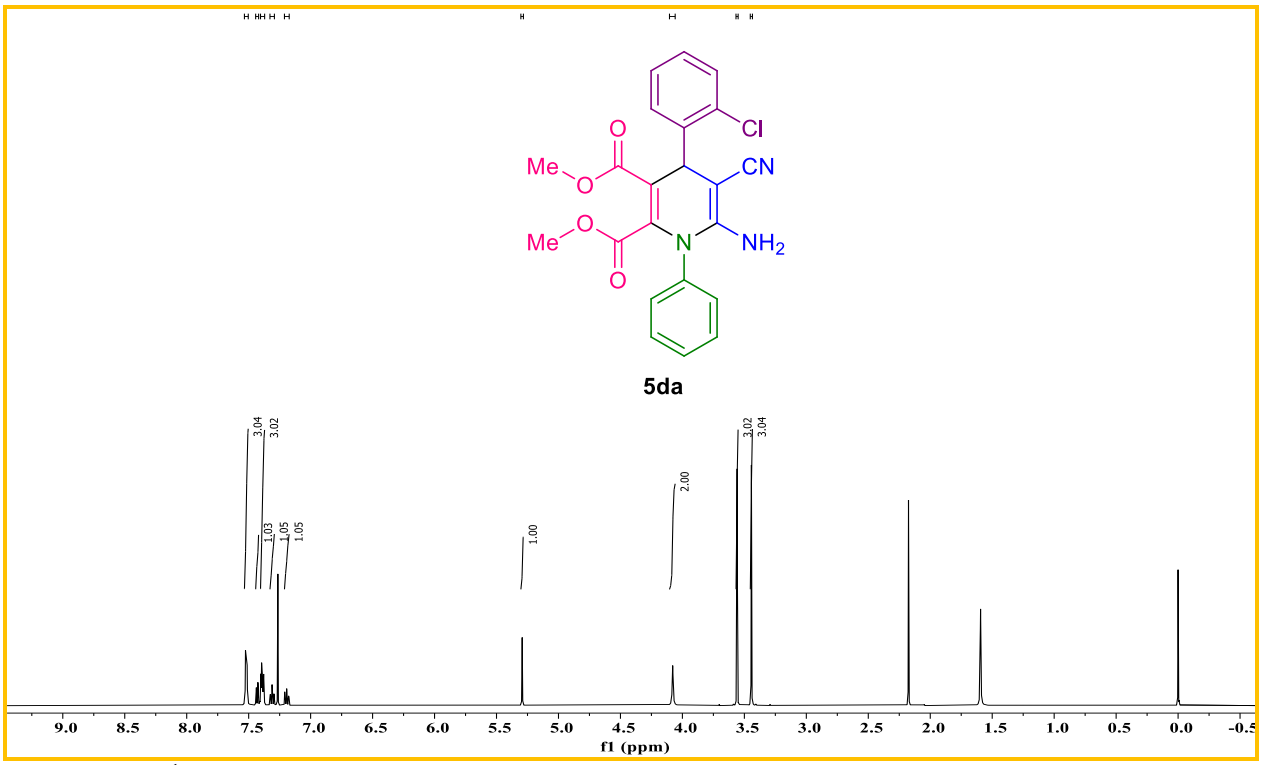


Figure S9: ^{1}H NMR spectra of dimethyl 6-amino-4-(2-chlorophenyl)-5-cyano-1-phenyl-1,4-dihydropyridine-2,3-dicarboxylate **5da**

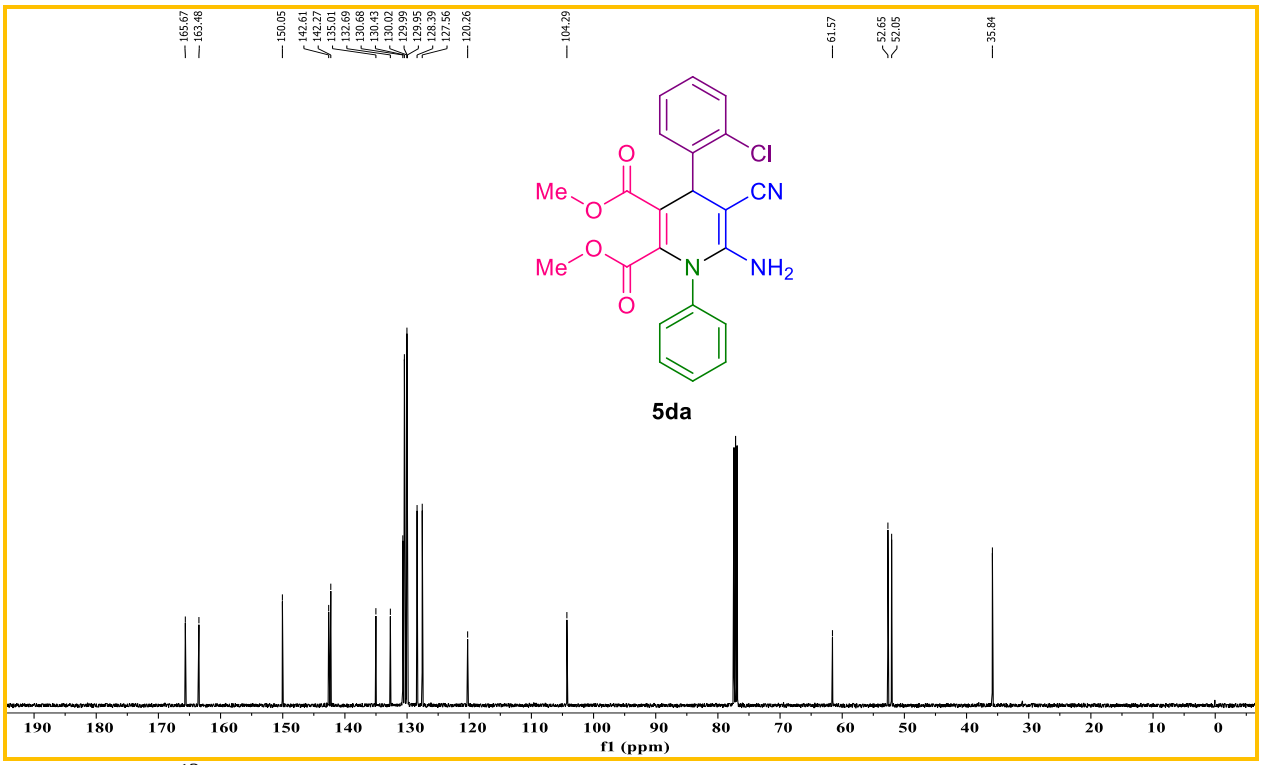


Figure S10: ^{13}C NMR spectra of dimethyl 6-amino-4-(2-chlorophenyl)-5-cyano-1-phenyl-1,4-dihydropyridine-2,3-dicarboxylate **5da**

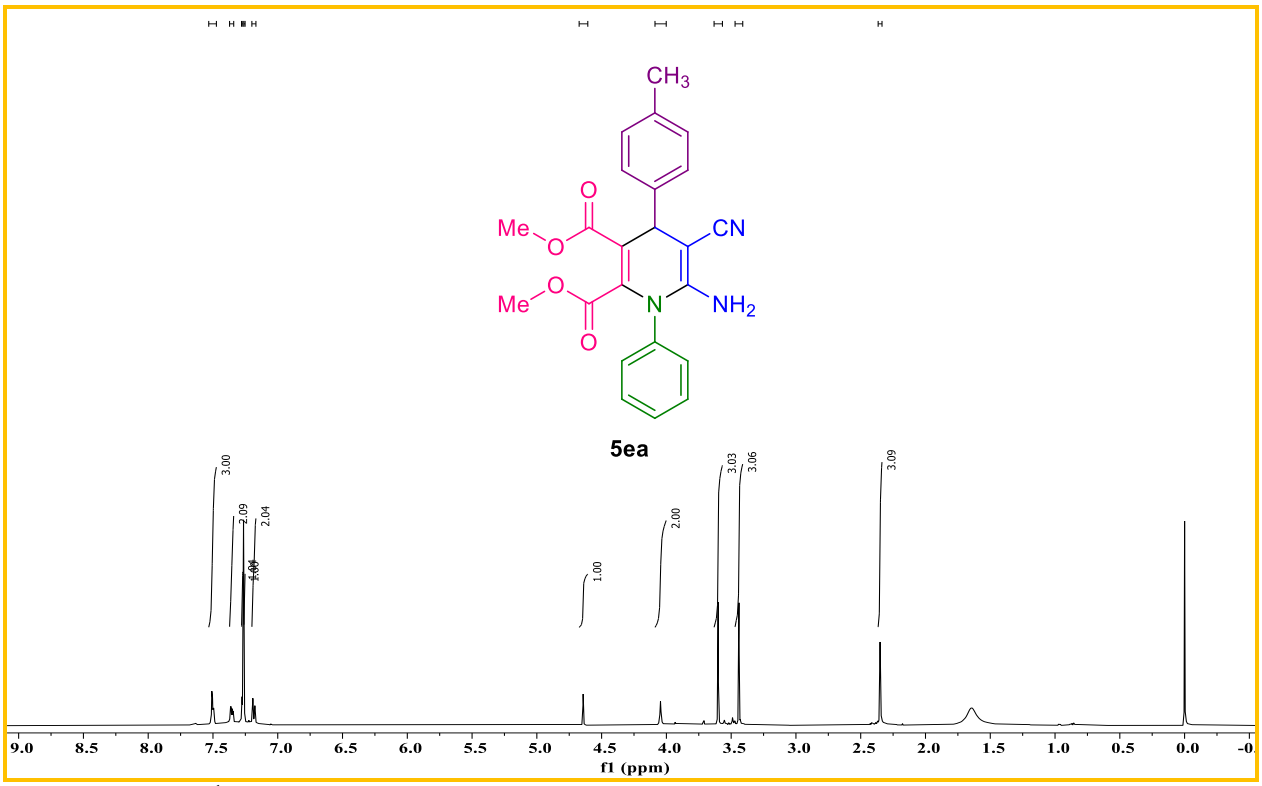


Figure S11: ^{1}H NMR spectra of dimethyl 6-amino-5-cyano-1-phenyl-4-(*p*-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate **5ea**

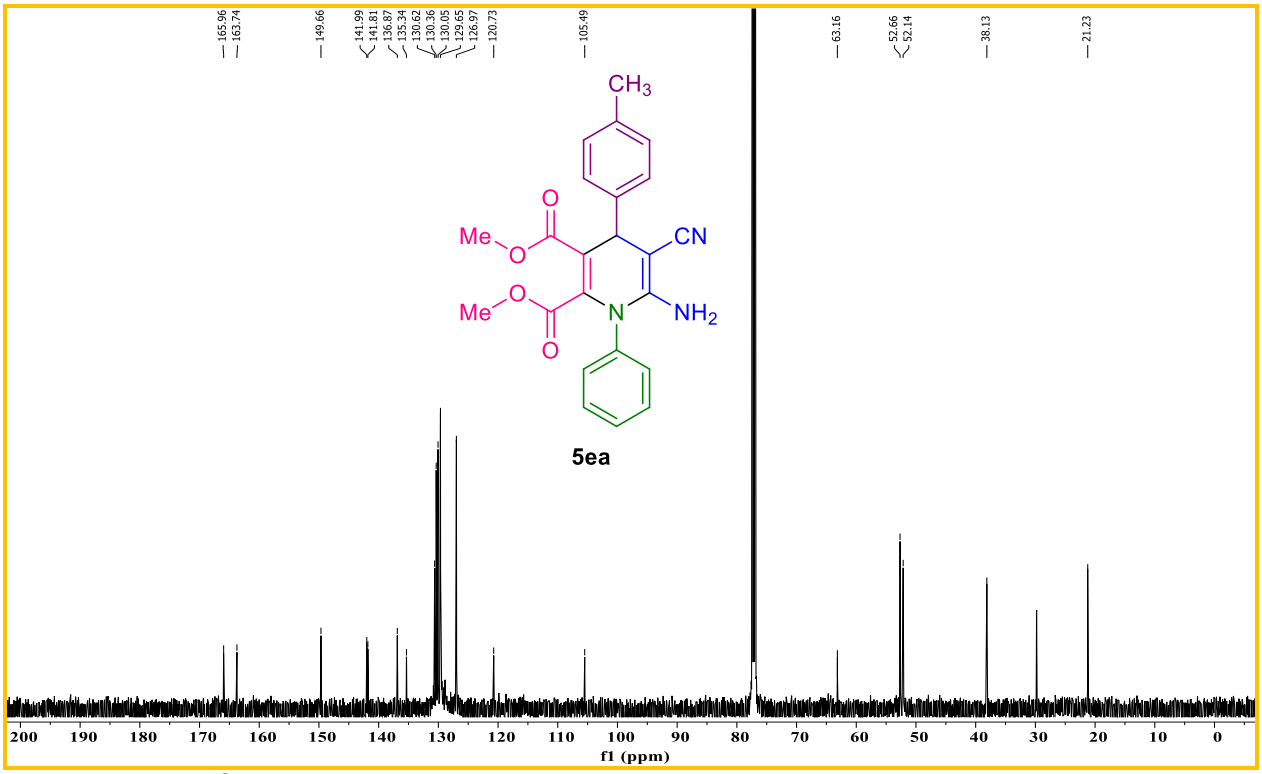


Figure S12: ^{13}C NMR spectra of dimethyl 6-amino-5-cyano-1-phenyl-4-(*p*-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate **5ea**

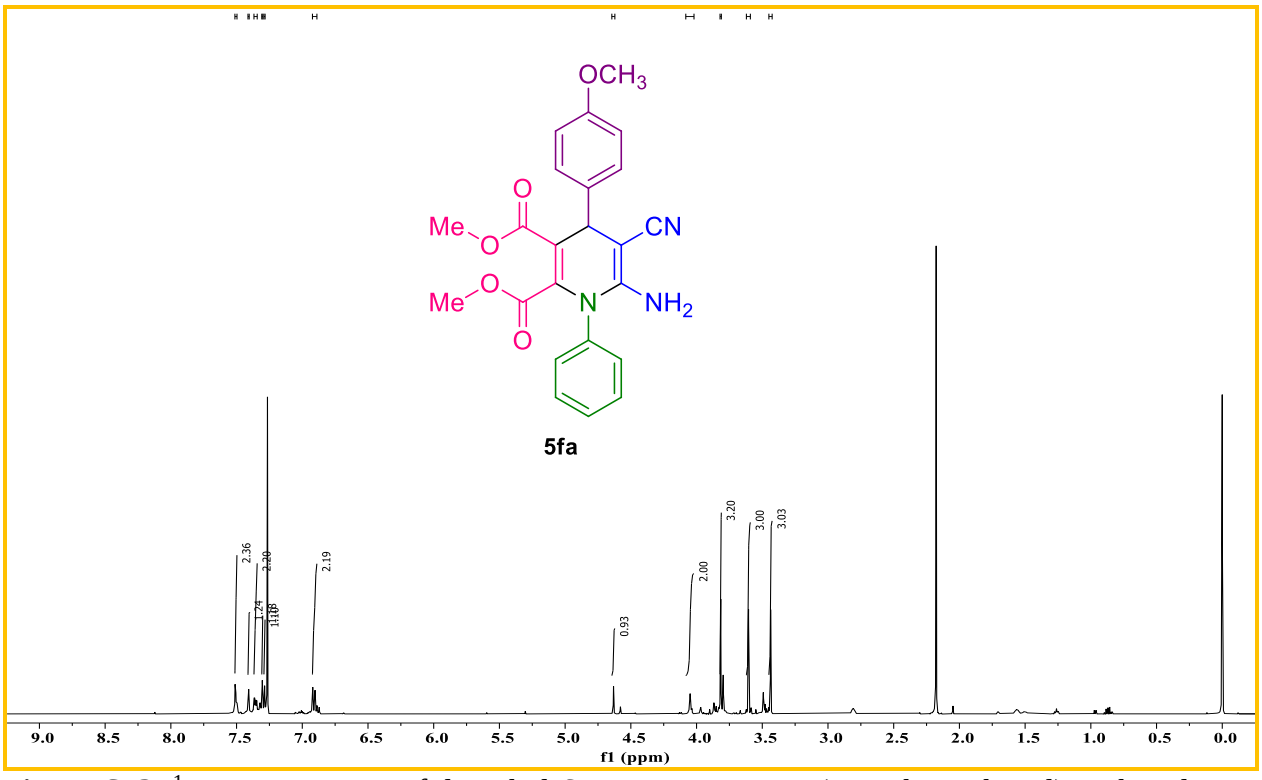


Figure S13: ^{1}H NMR spectra of dimethyl 6-amino-5-cyano-4-(4-methoxyphenyl)-1-phenyl-1,4-dihydropyridine-2,3-dicarboxylate **5fa**

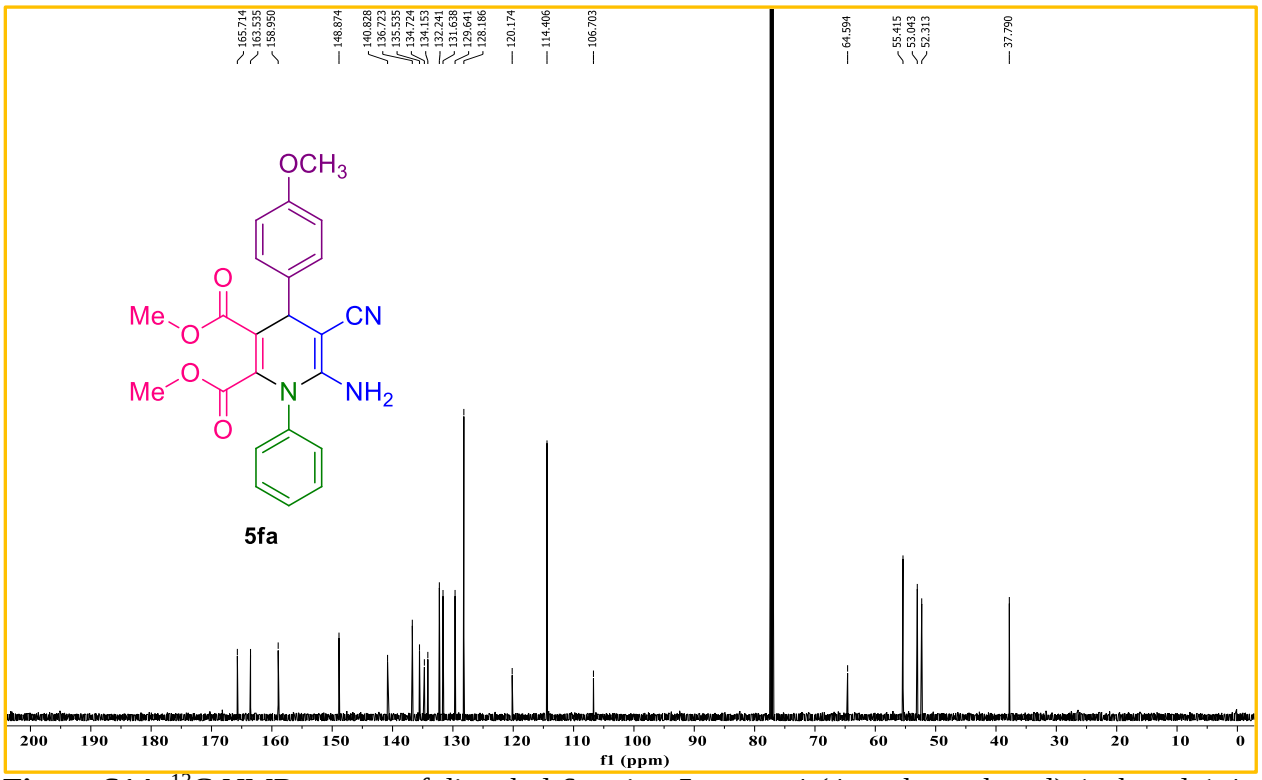


Figure S14: ^{13}C NMR spectra of dimethyl 6-amino-5-cyano-4-(4-methoxyphenyl)-1-phenyl-1,4-dihydropyridine-2,3-dicarboxylate **5fa**

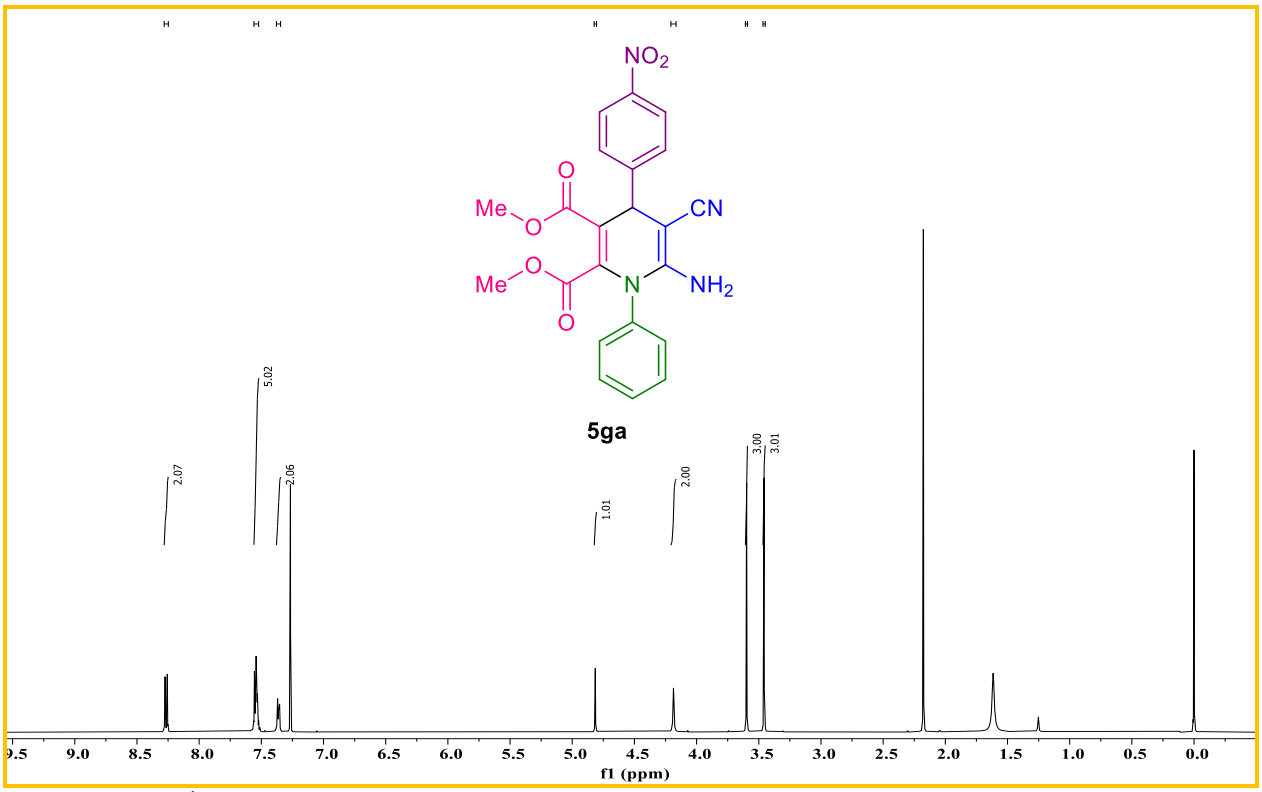


Figure S15: ^{1}H NMR spectra of dimethyl 6-amino-5-cyano-4-(4-nitrophenyl)-1-phenyl-1,4-dihydropyridine-2,3-dicarboxylate **5ga**

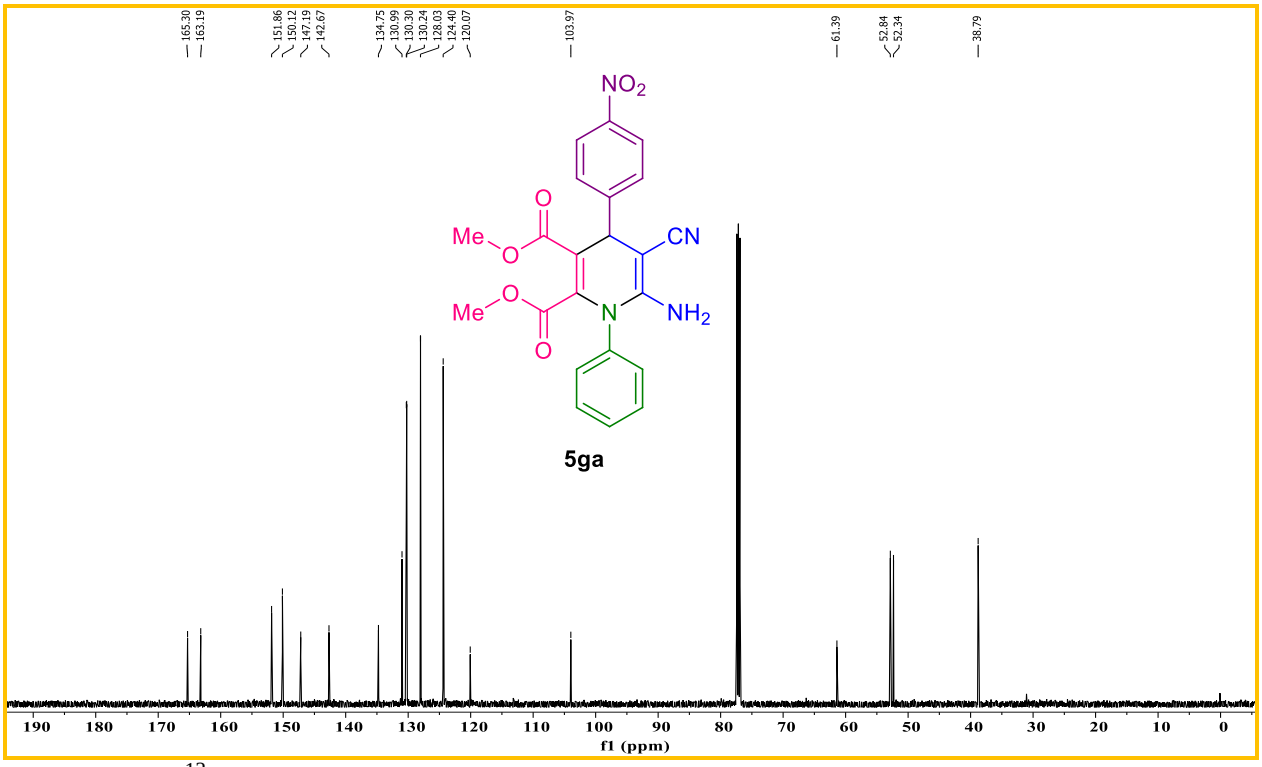


Figure S16: ^{13}C NMR spectra of dimethyl 6-amino-5-cyano-4-(4-nitrophenyl)-1-phenyl-1,4-dihydropyridine-2,3-dicarboxylate **5ga**

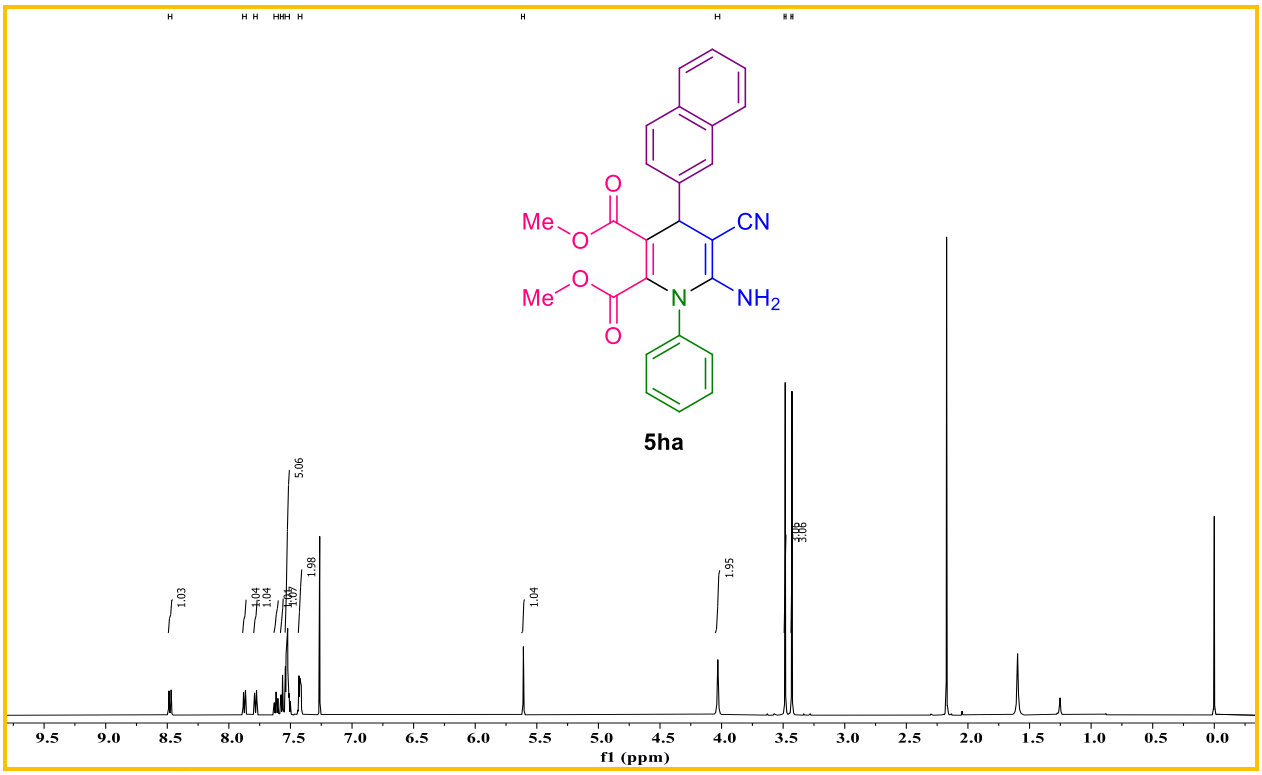


Figure S17: ^{1}H NMR spectra of dimethyl 6-amino-5-cyano-4-(naphthalen-1-yl)-1-phenyl-1,4-dihydropyridine-2,3-dicarboxylate **5ha**

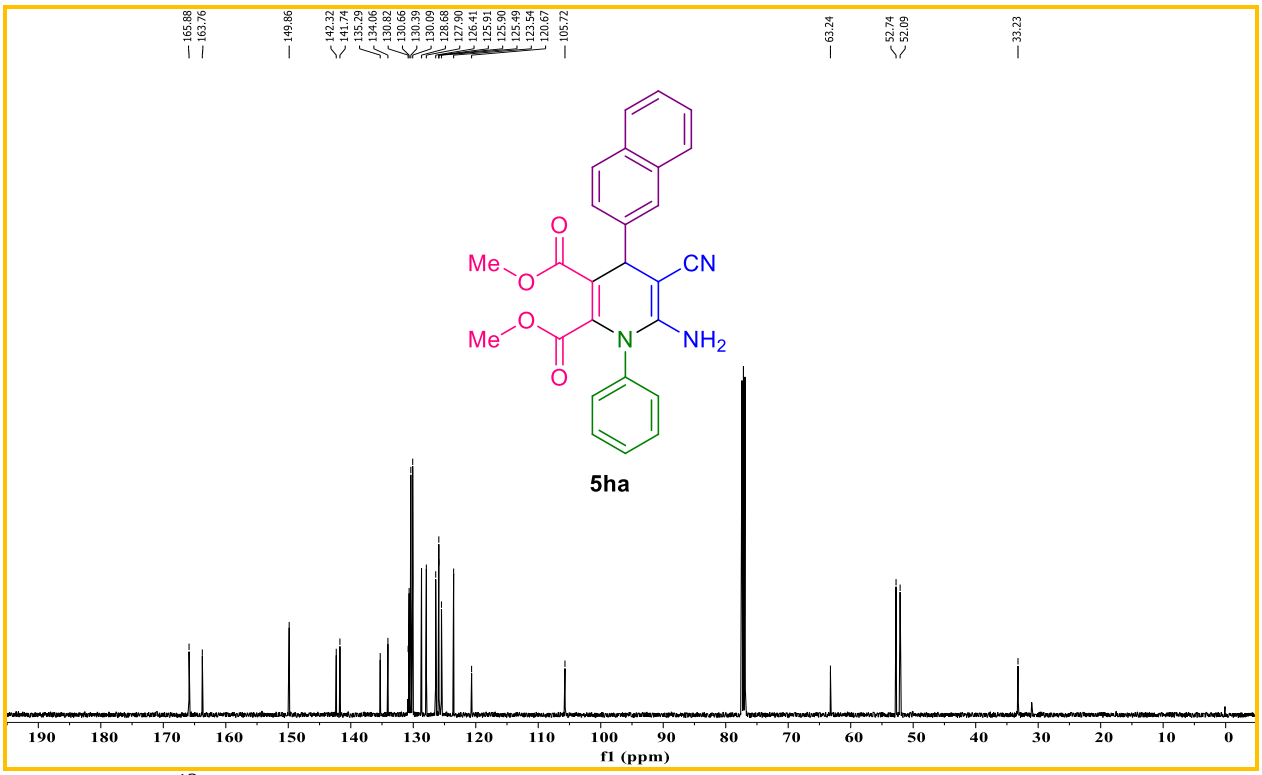


Figure S18: ^{13}C NMR spectra of dimethyl 6-amino-5-cyano-4-(naphthalen-1-yl)-1-phenyl-1,4-dihydropyridine-2,3-dicarboxylate **5ha**

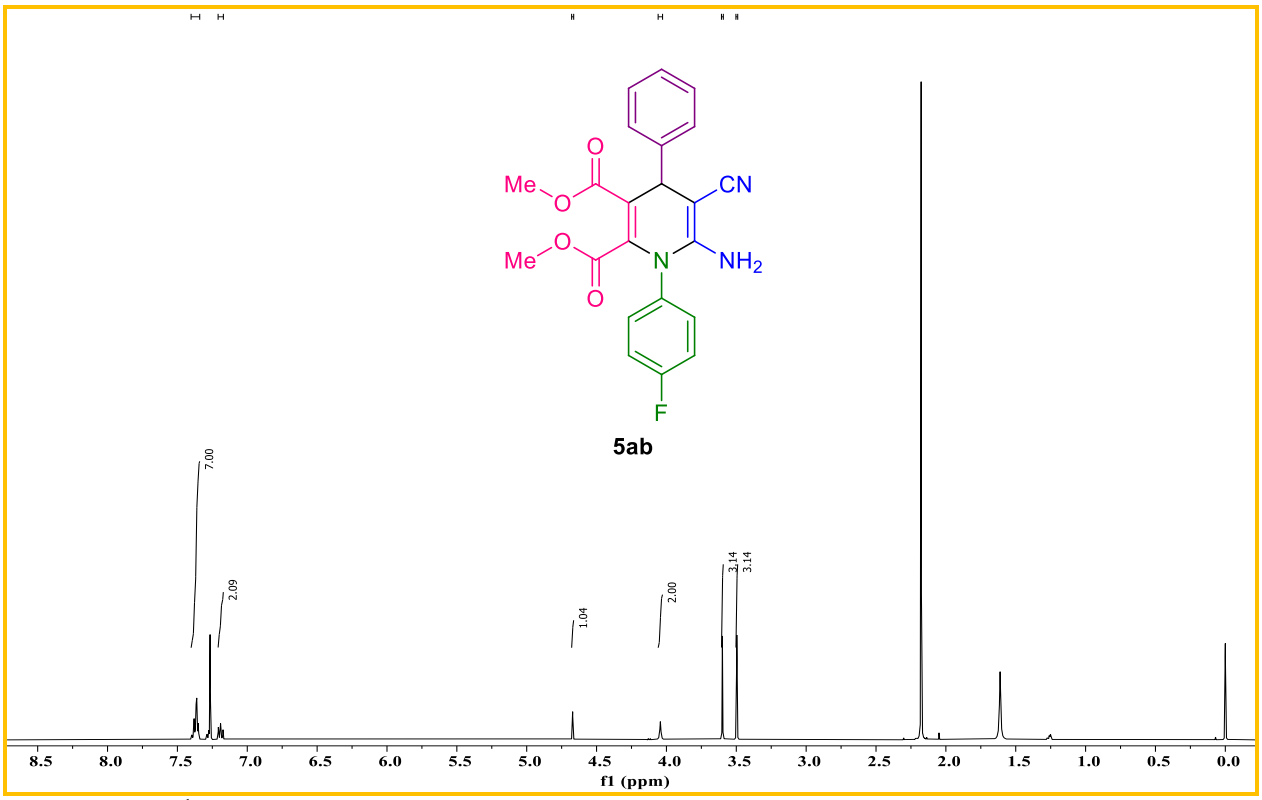


Figure S19: ^{1}H NMR spectra of dimethyl 6-amino-5-cyano-1-(4-fluorophenyl)-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate **5ab**

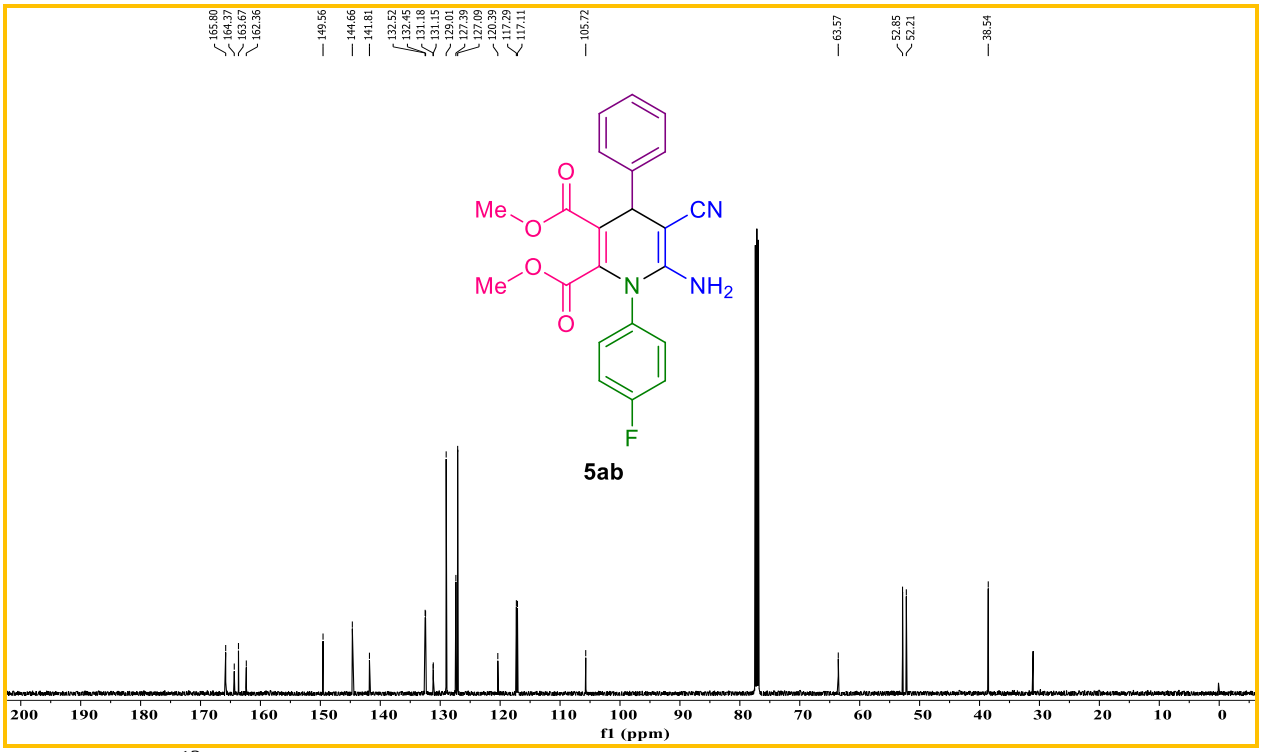


Figure S20: ^{13}C NMR spectra of dimethyl 6-amino-5-cyano-1-(4-fluorophenyl)-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate **5ab**

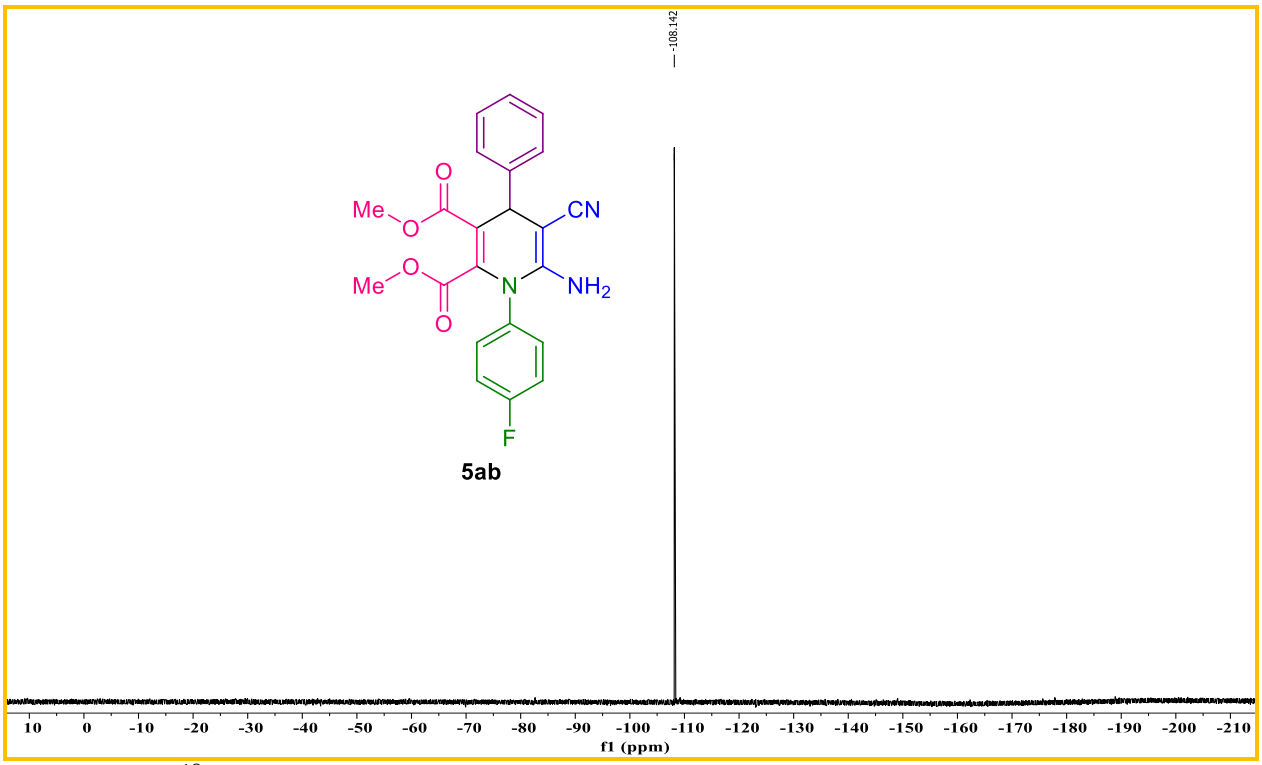


Figure S21: ^{19}F NMR spectra of dimethyl 6-amino-5-cyano-1-(4-fluorophenyl)-4-phenyl-1,4-dihydropyridine-2,3-dicarboxylate **5ab**

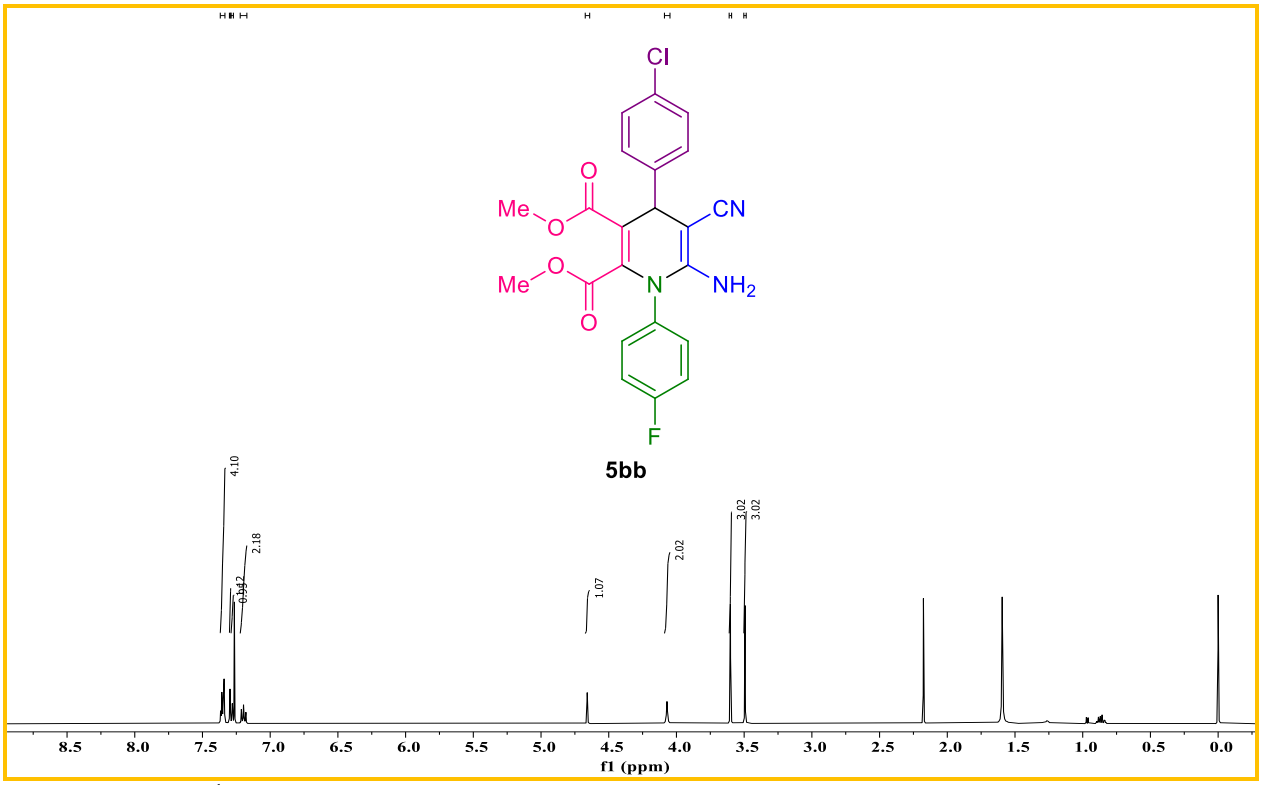


Figure S22: ^{1}H NMR spectra of dimethyl 6-amino-4-(4-chlorophenyl)-5-cyano-1-(4-fluorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5bb**

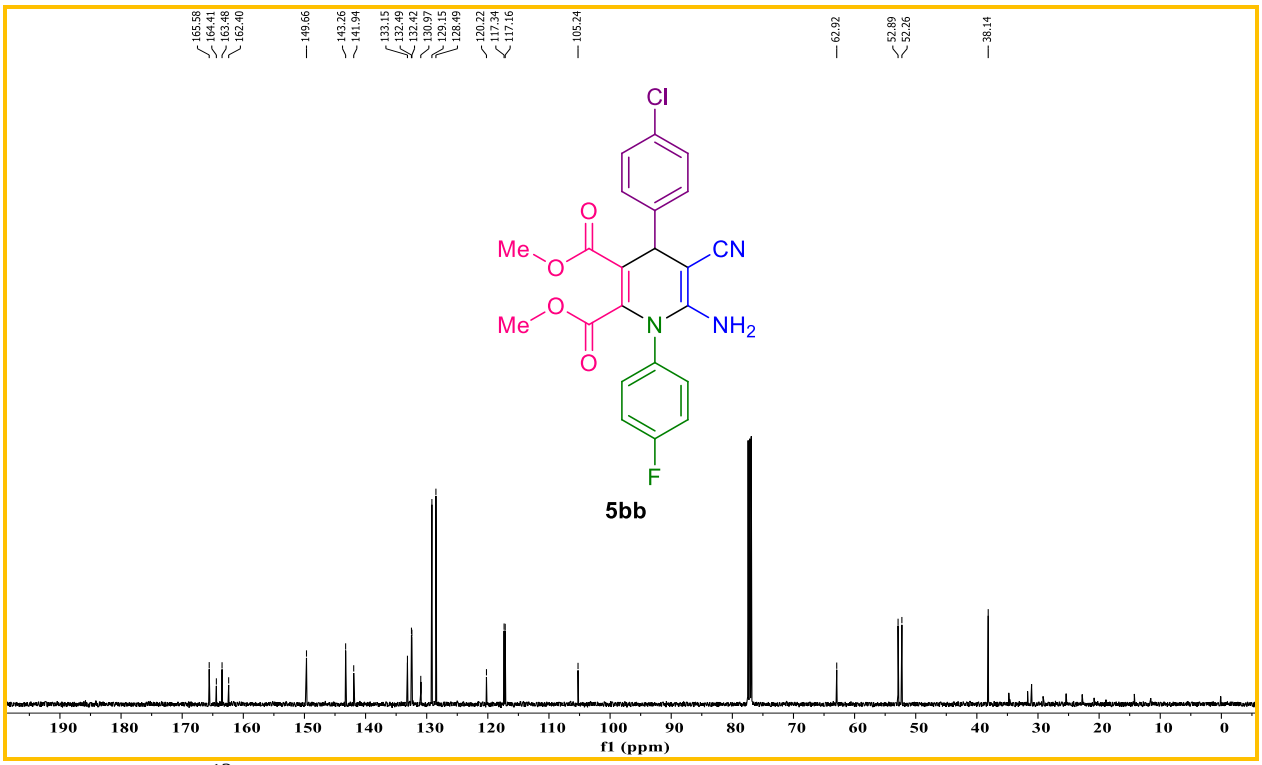


Figure S23: ^{13}C NMR spectra of dimethyl 6-amino-4-(4-chlorophenyl)-5-cyano-1-(4-fluorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5bb**

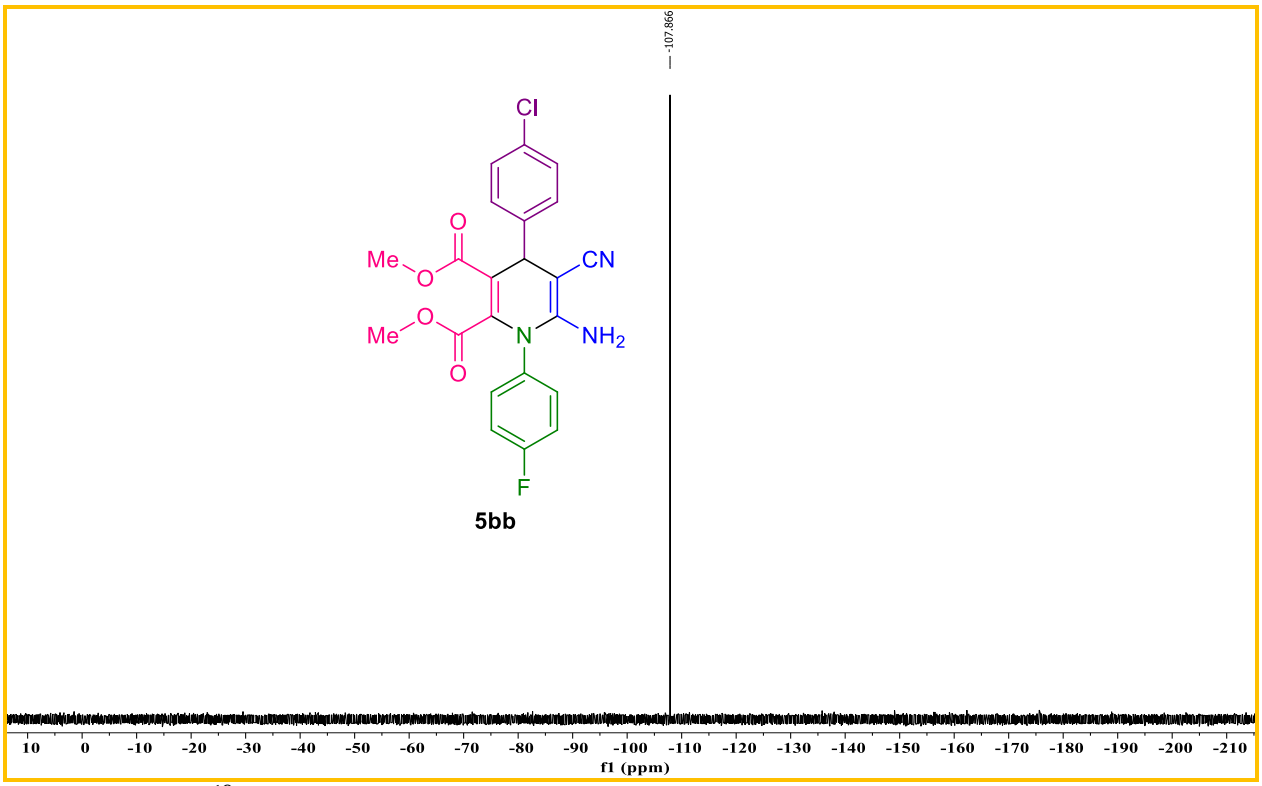


Figure S24: ^{19}F NMR spectra of dimethyl 6-amino-4-(4-chlorophenyl)-5-cyano-1-(4-fluorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5bb**

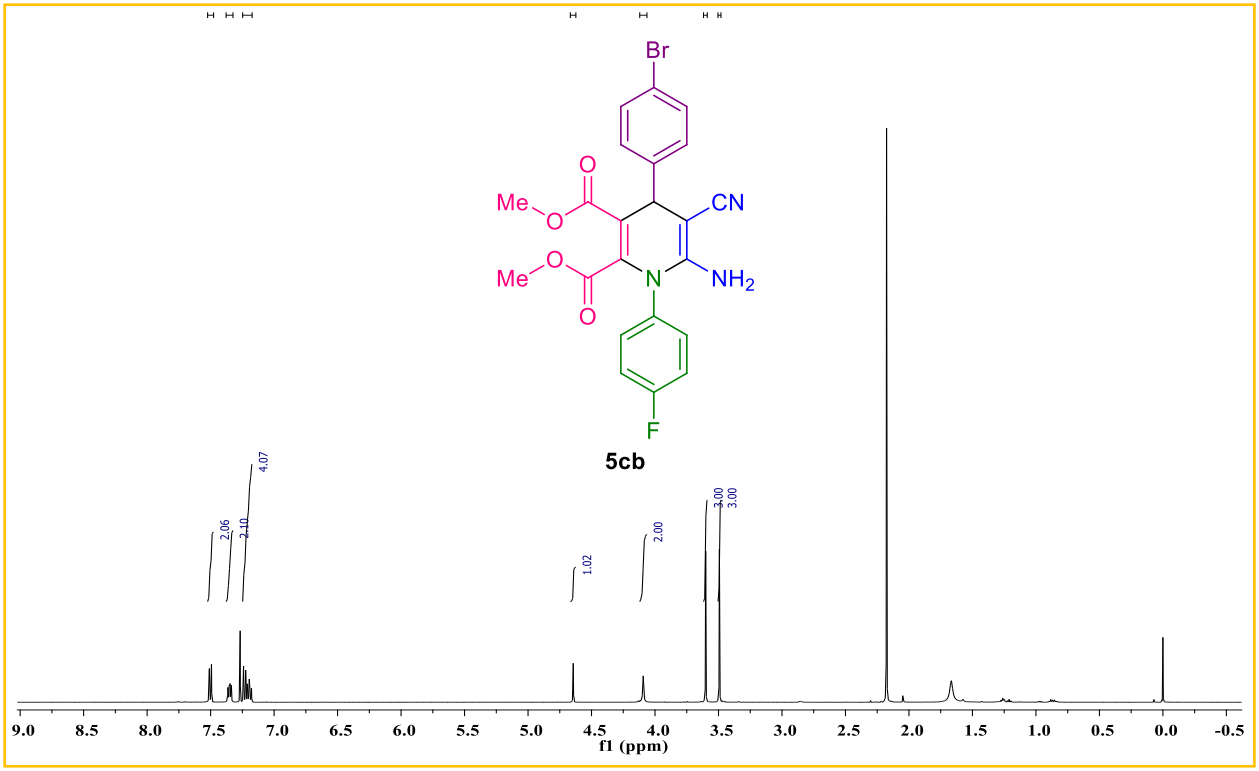


Figure S25: ^{1}H NMR spectra of dimethyl 6-amino-4-(4-bromophenyl)-5-cyano-1-(4-fluorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5cb**

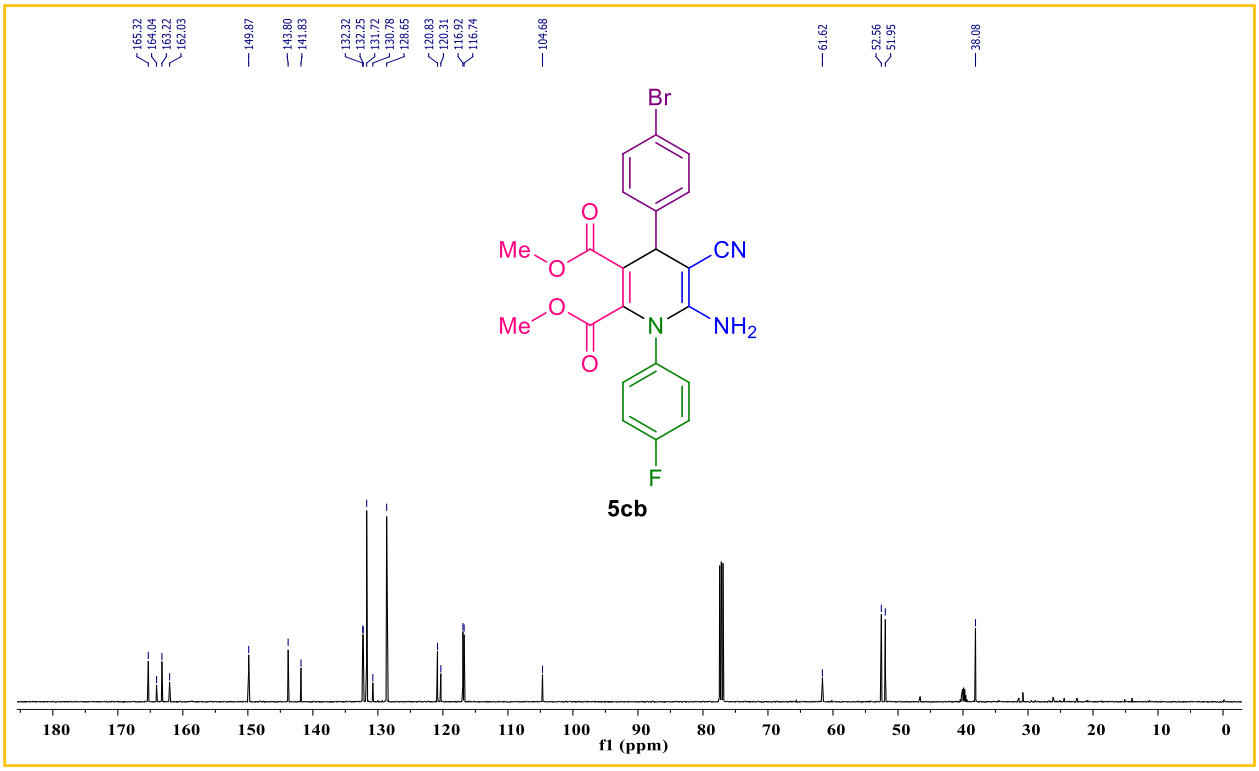


Figure S26: ^{13}C NMR spectra of dimethyl 6-amino-4-(4-bromophenyl)-5-cyano-1-(4-fluorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5cb**

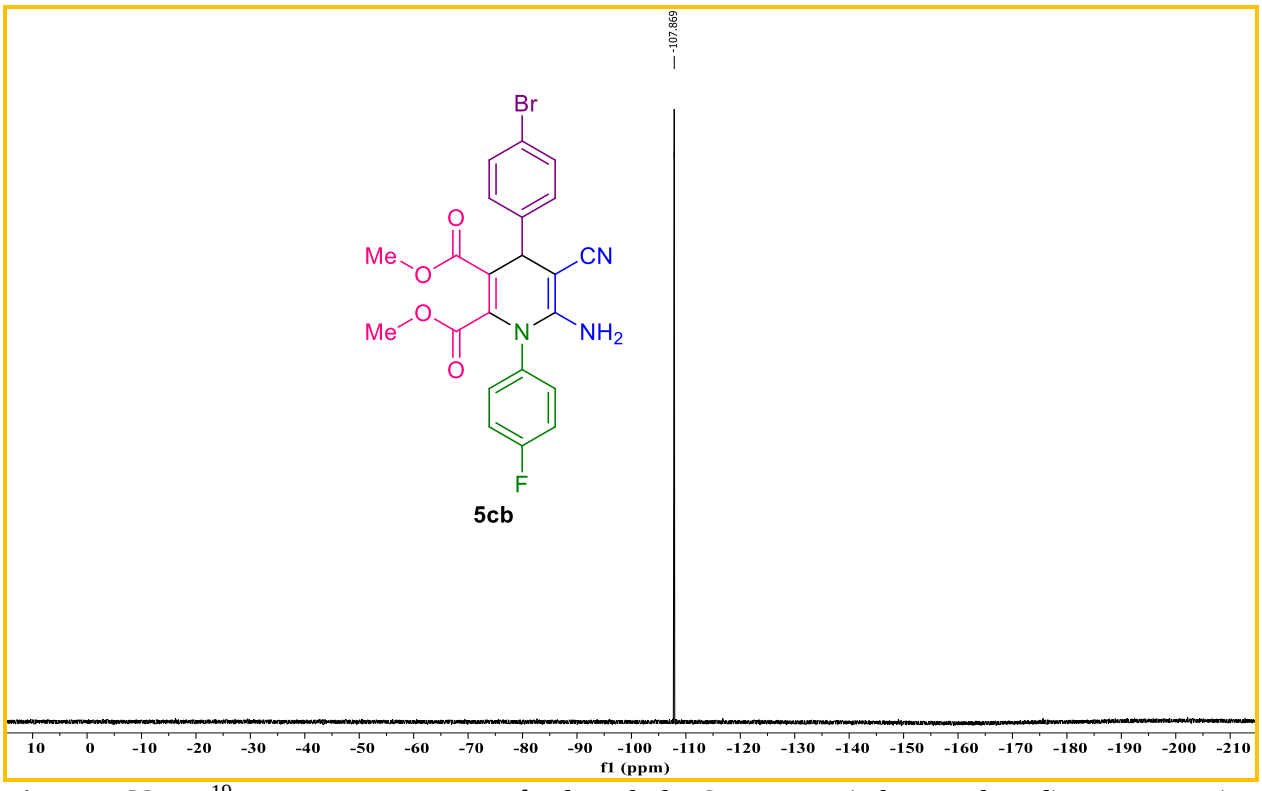


Figure S27: ^{19}F NMR spectra of dimethyl 6-amino-4-(4-bromophenyl)-5-cyano-1-(4-fluorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5cb**

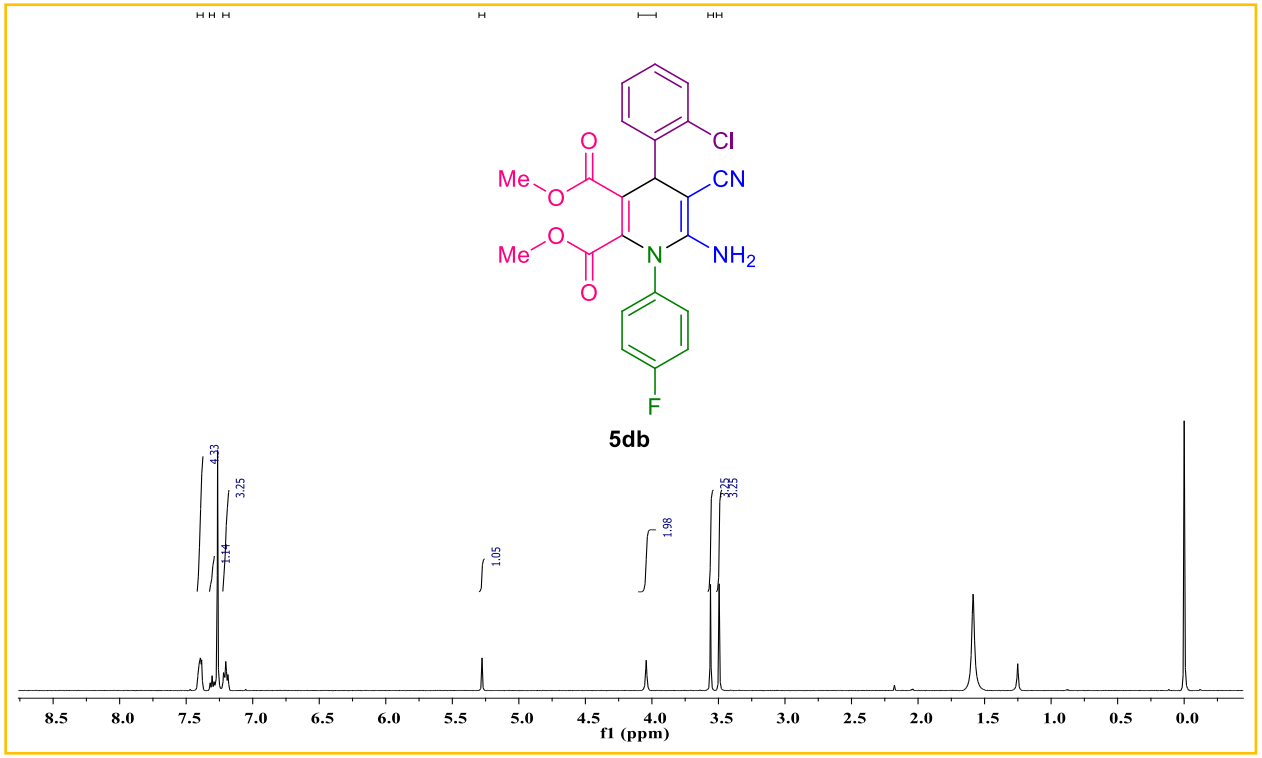


Figure S28: ^{1}H NMR spectra of dimethyl 6-amino-4-(2-chlorophenyl)-5-cyano-1-(4-fluorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5db**

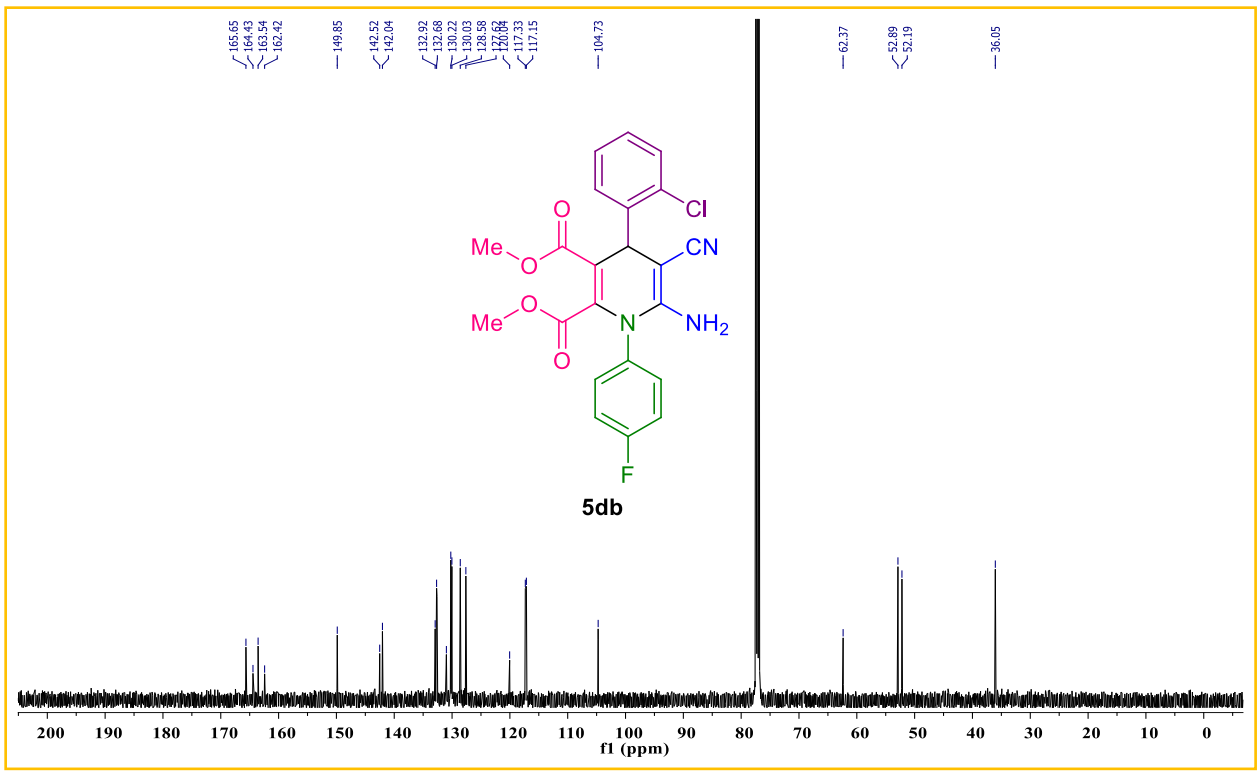


Figure S29: ^{13}C NMR spectra of dimethyl 6-amino-4-(2-chlorophenyl)-5-cyano-1-(4-fluorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5db**

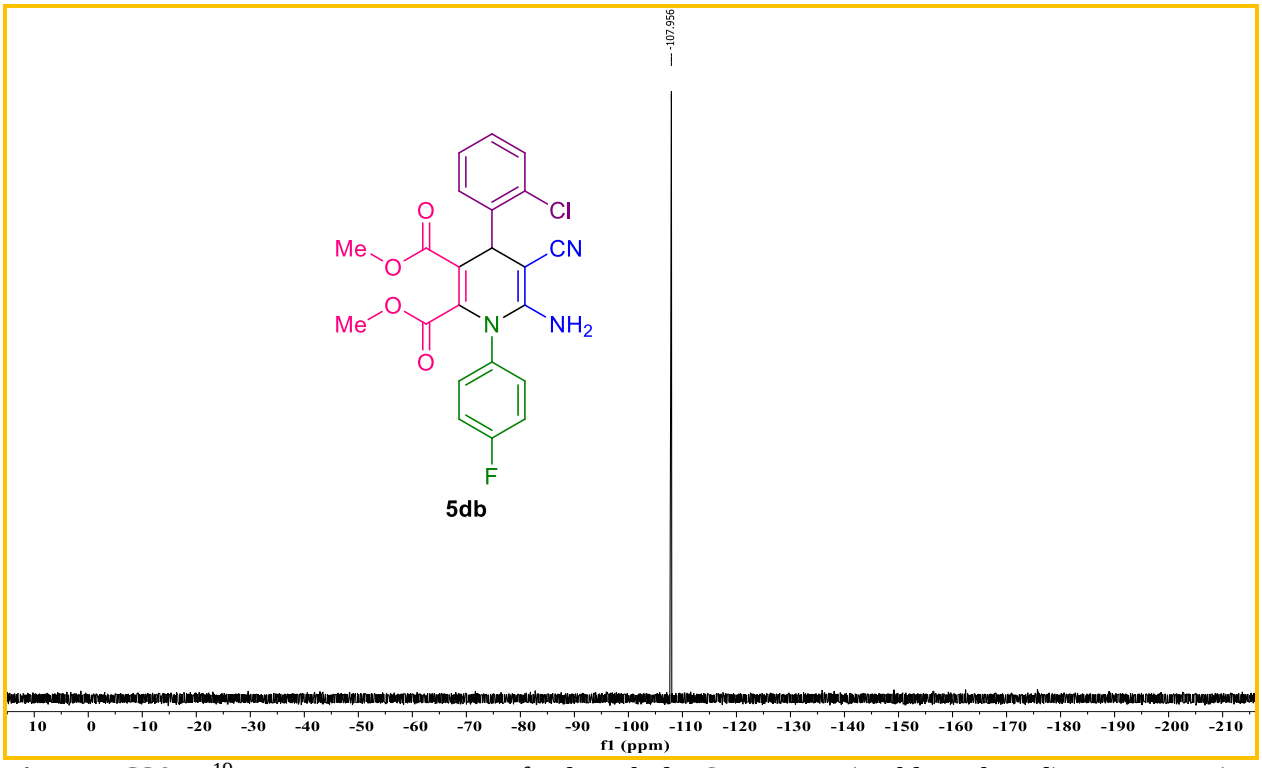


Figure S30: ^{19}F NMR spectra of dimethyl 6-amino-4-(2-chlorophenyl)-5-cyano-1-(4-fluorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5db**

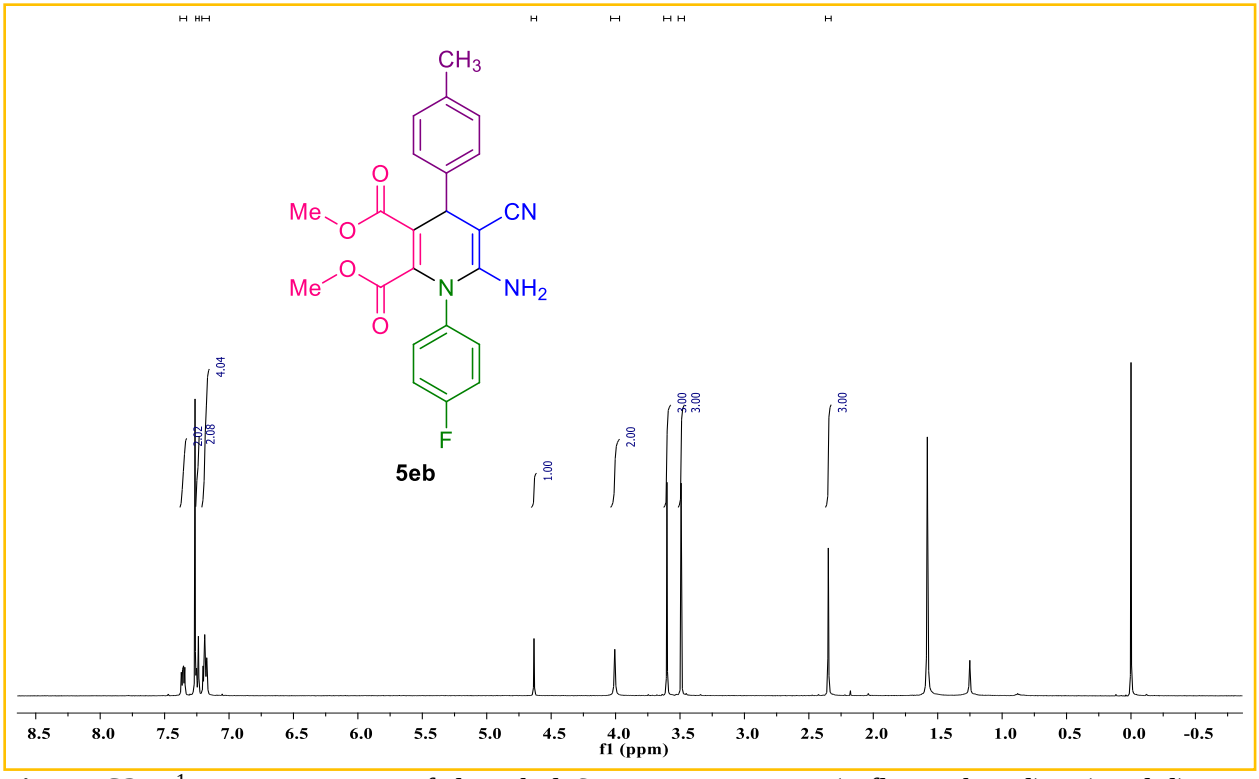


Figure S31: ^{1}H NMR spectra of dimethyl 6-amino-5-cyano-1-(4-fluorophenyl)-4-(*p*-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate **5eb**

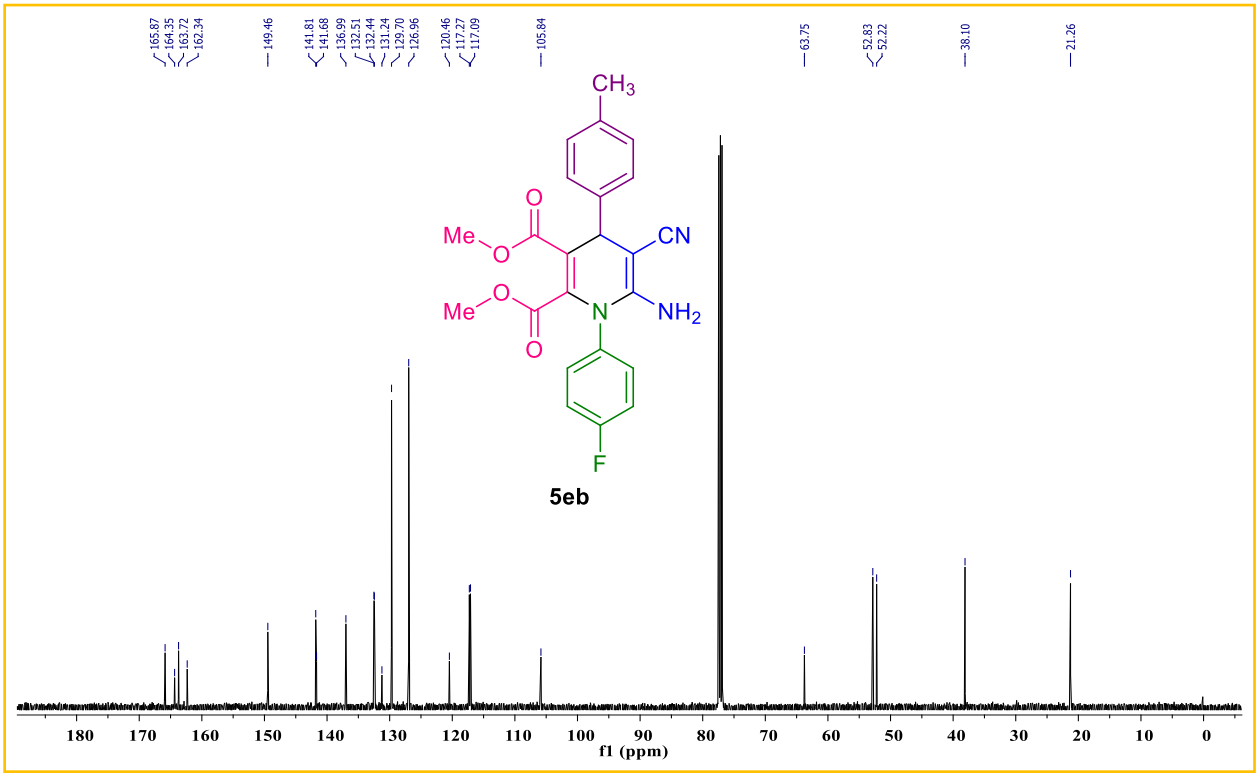


Figure S32: ^{13}C NMR spectra of dimethyl 6-amino-5-cyano-1-(4-fluorophenyl)-4-(*p*-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate **5eb**

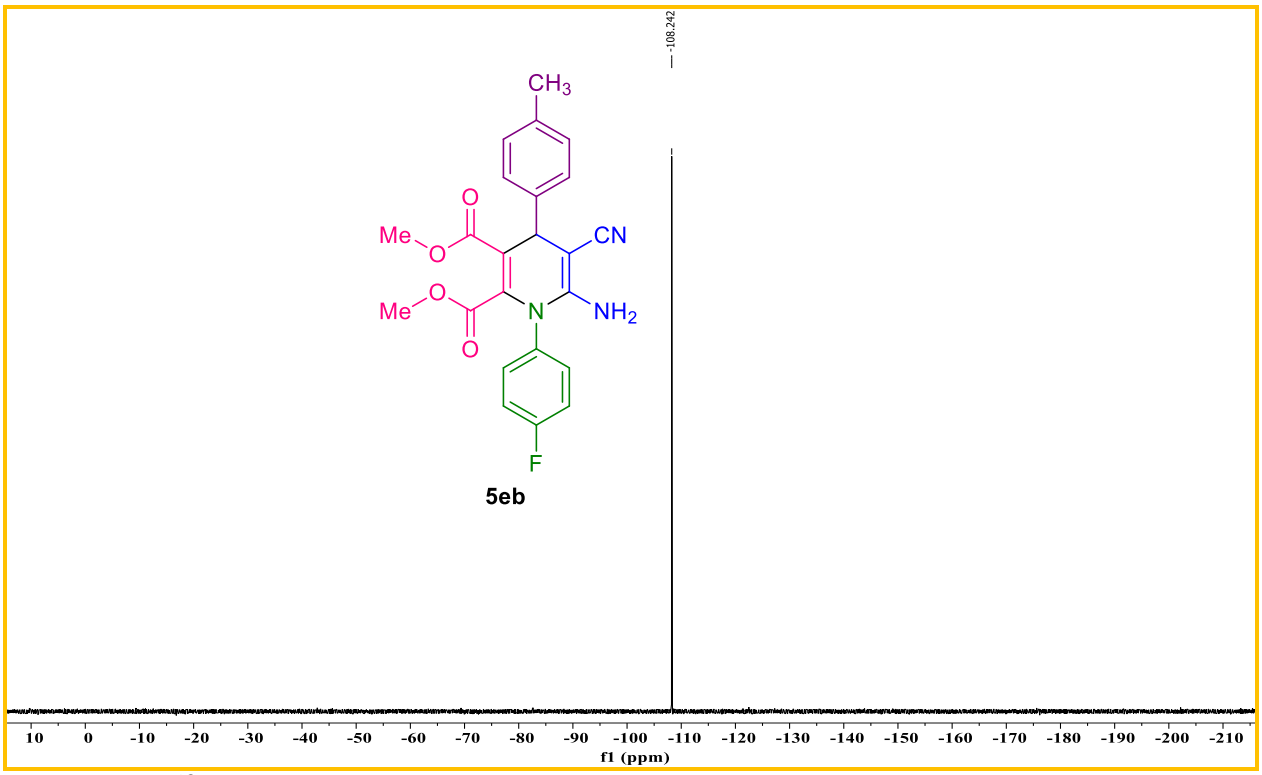


Figure S33: ^{19}F NMR spectra of dimethyl 6-amino-5-cyano-1-(4-fluorophenyl)-4-(*p*-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate **5eb**

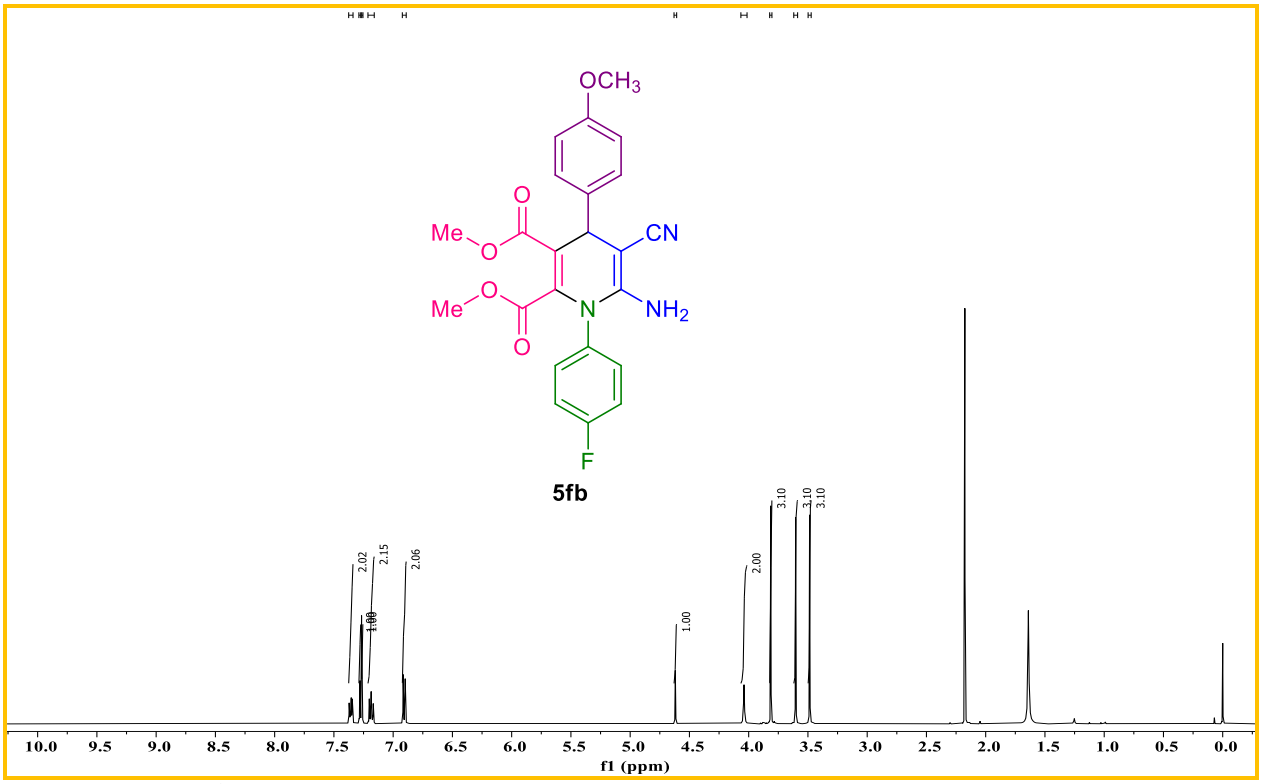


Figure S34: ^{1}H NMR spectra of dimethyl 6-amino-5-cyano-1-(4-fluorophenyl)-4-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5fb**

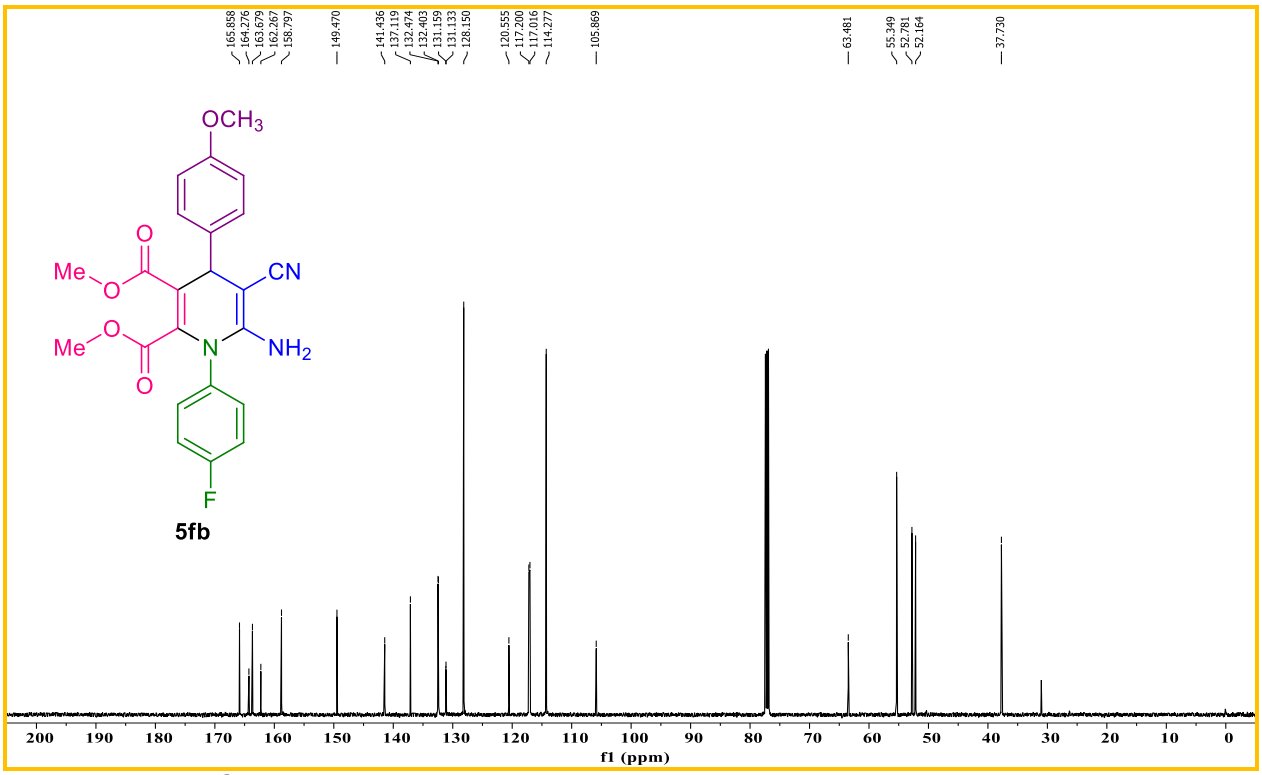


Figure S35: ^{13}C NMR spectra of dimethyl 6-amino-5-cyano-1-(4-fluorophenyl)-4-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5fb**

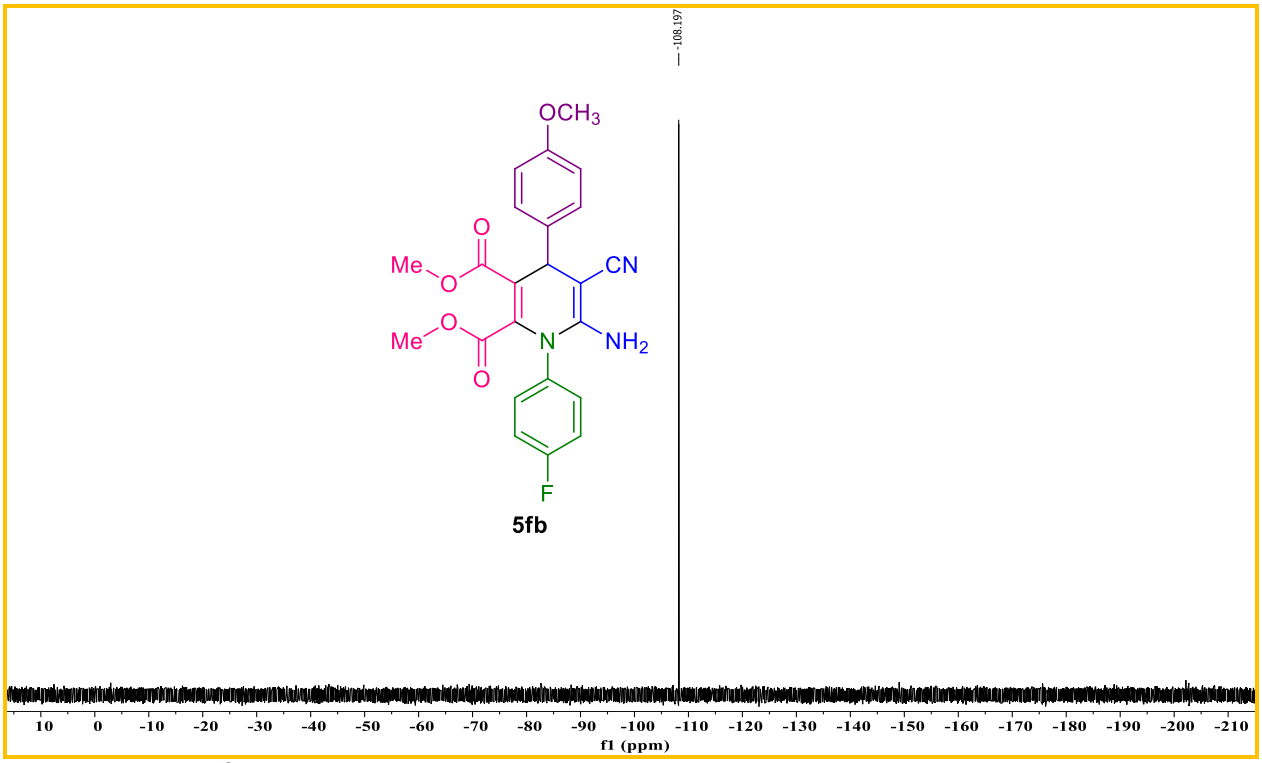


Figure S36: ^{19}F NMR spectra of dimethyl 6-amino-5-cyano-1-(4-fluorophenyl)-4-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5fb**

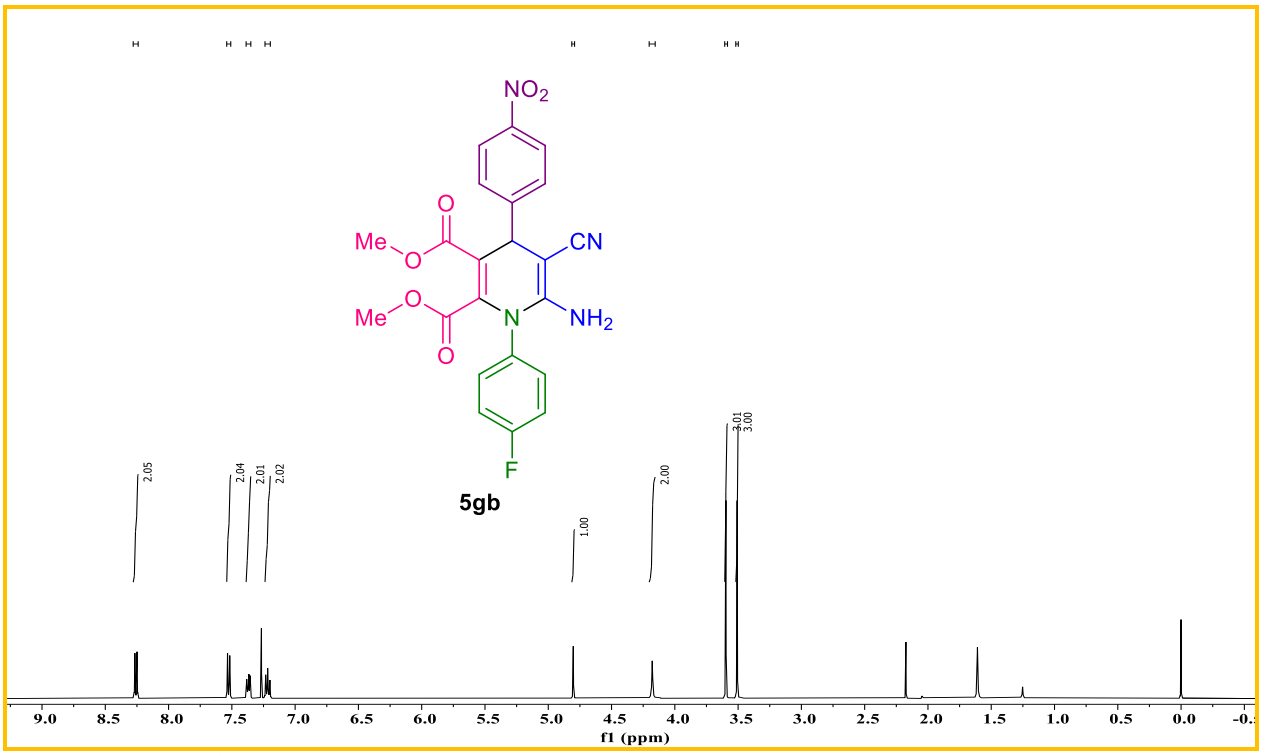


Figure S37: ^{1}H NMR spectra of dimethyl 6-amino-5-cyano-1-(4-fluorophenyl)-4-(4-nitrophenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5gb**

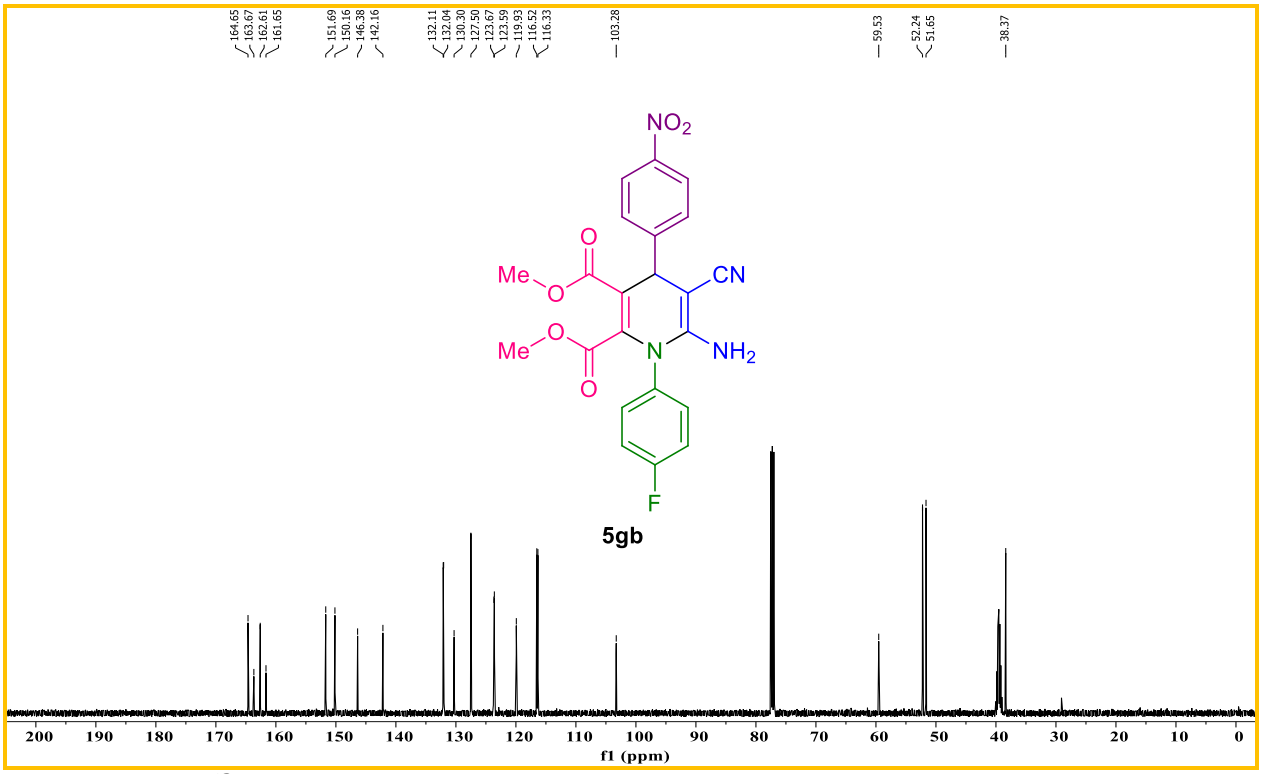


Figure S38: ^{13}C NMR spectra of dimethyl 6-amino-5-cyano-1-(4-fluorophenyl)-4-(4-nitrophenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5gb**

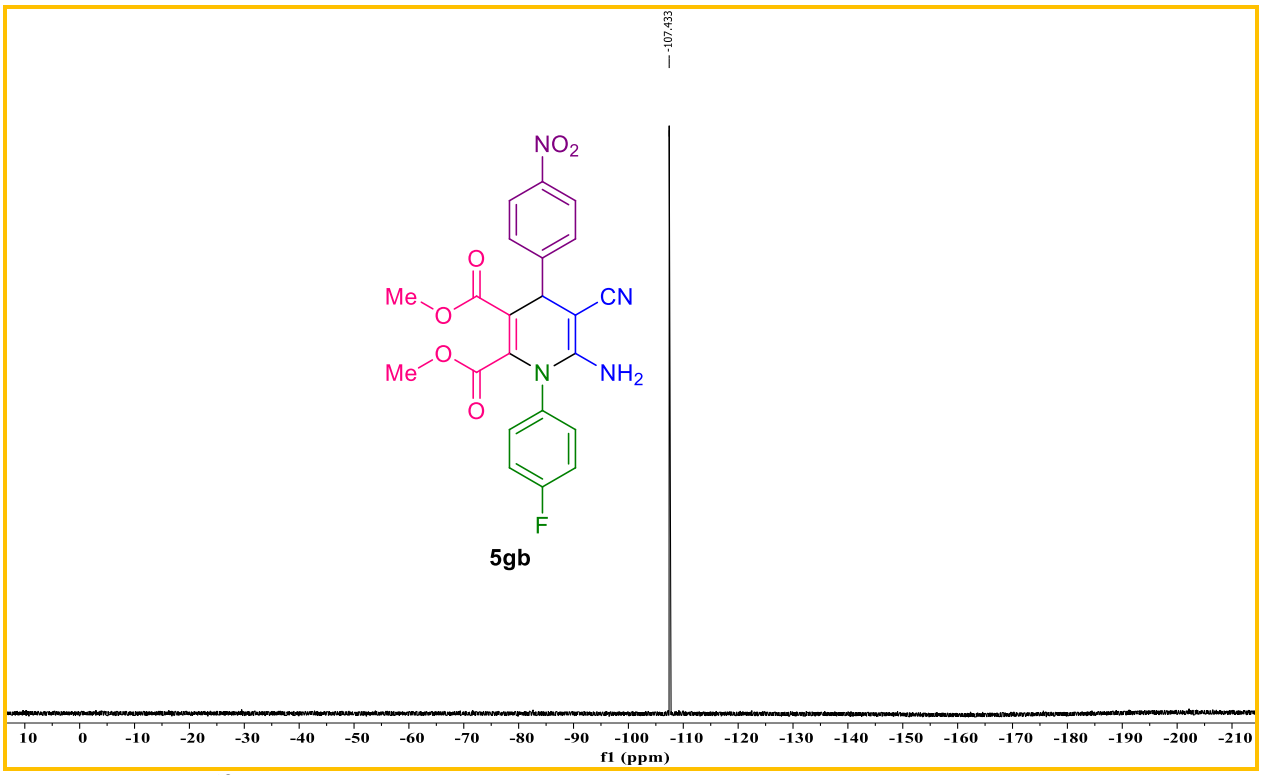


Figure S39: ^{19}F NMR spectra of dimethyl 6-amino-5-cyano-1-(4-fluorophenyl)-4-(4-nitrophenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5gb**

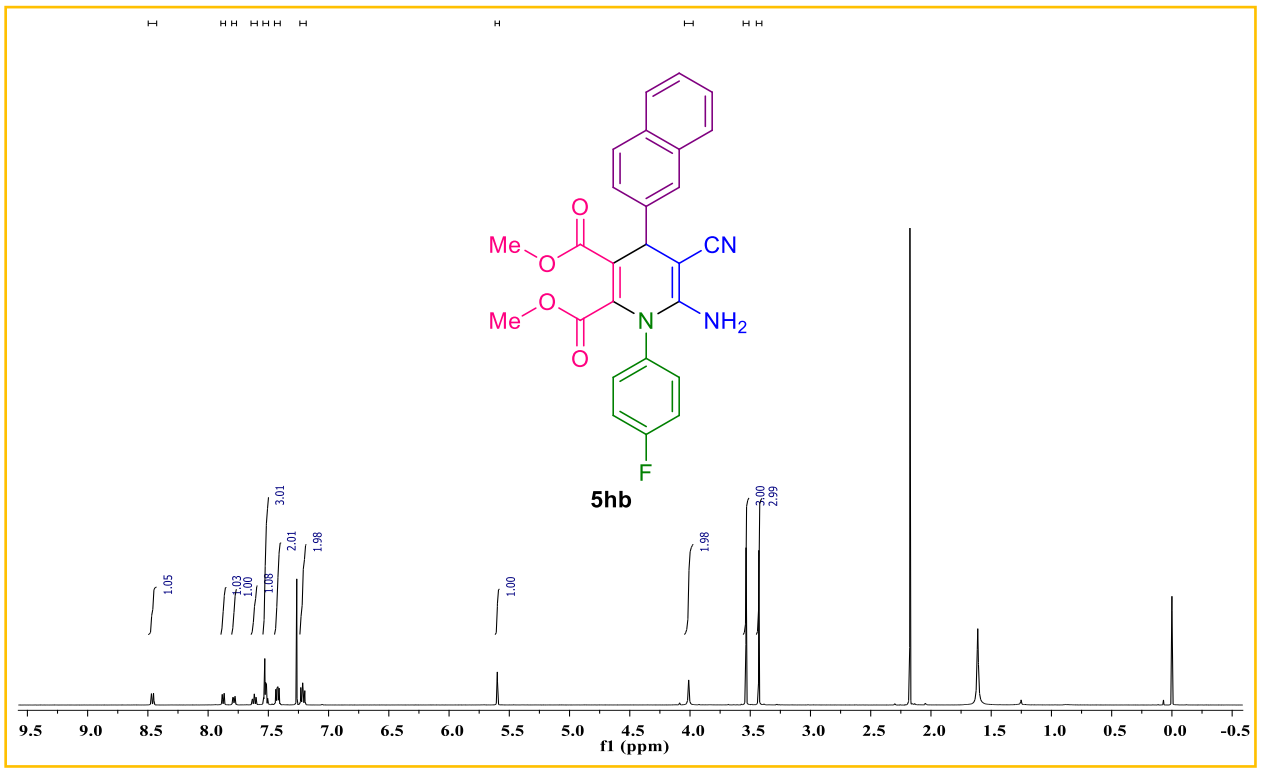


Figure S40: ^{1}H NMR spectra of dimethyl 6-amino-5-cyano-1-(4-fluorophenyl)-4-(naphthalen-1-yl)-1,4-dihydropyridine-2,3-dicarboxylate **5hb**

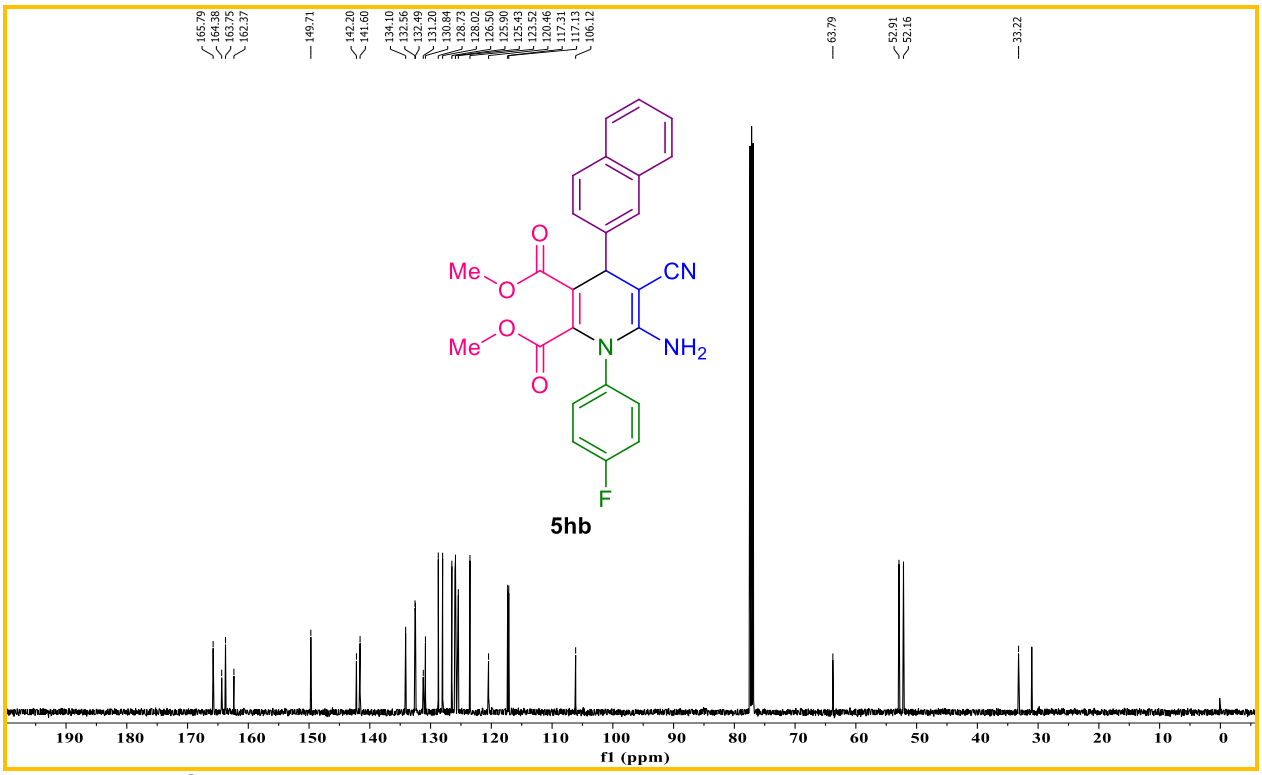


Figure S41: ^{13}C NMR spectra of dimethyl 6-amino-5-cyano-1-(4-fluorophenyl)-4-(naphthalen-1-yl)-1,4-dihydropyridine-2,3-dicarboxylate **5hb**

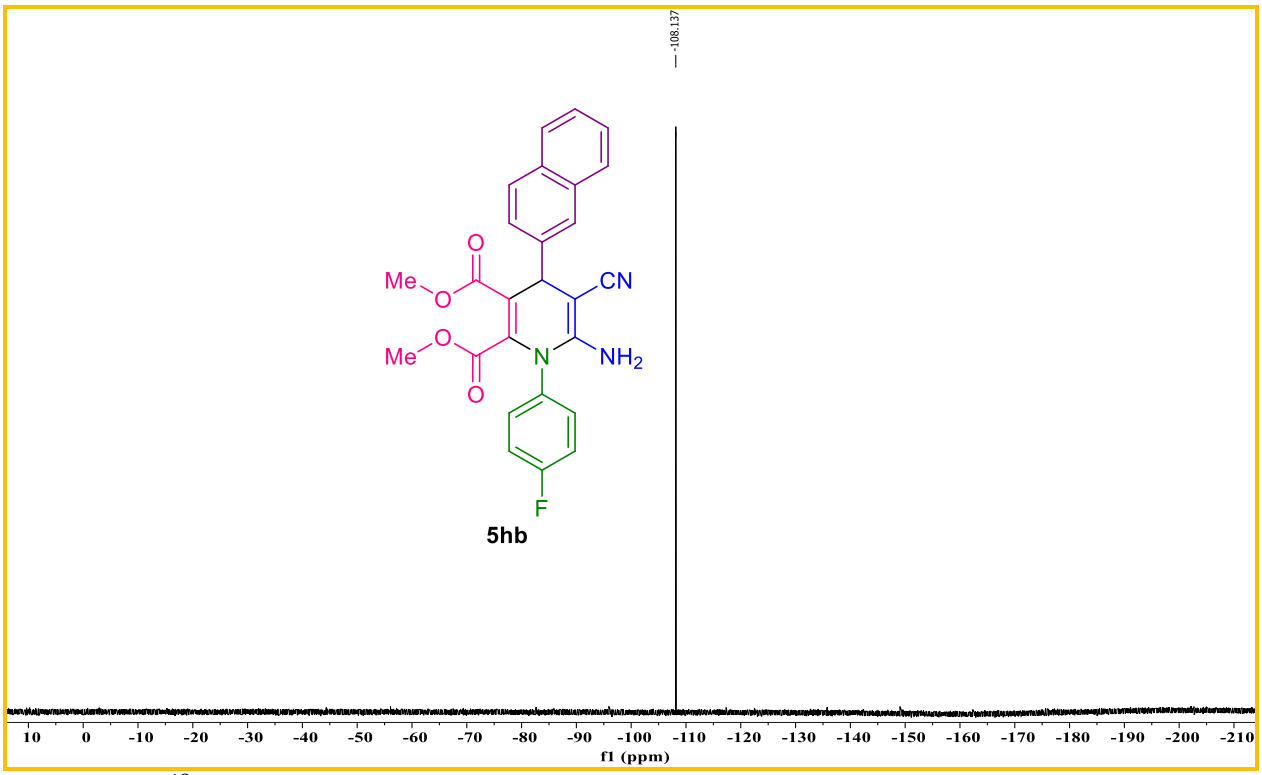


Figure S42: ^{19}F NMR spectra of dimethyl 6-amino-5-cyano-1-(4-fluorophenyl)-4-(naphthalen-1-yl)-1,4-dihydropyridine-2,3-dicarboxylate **5hb**

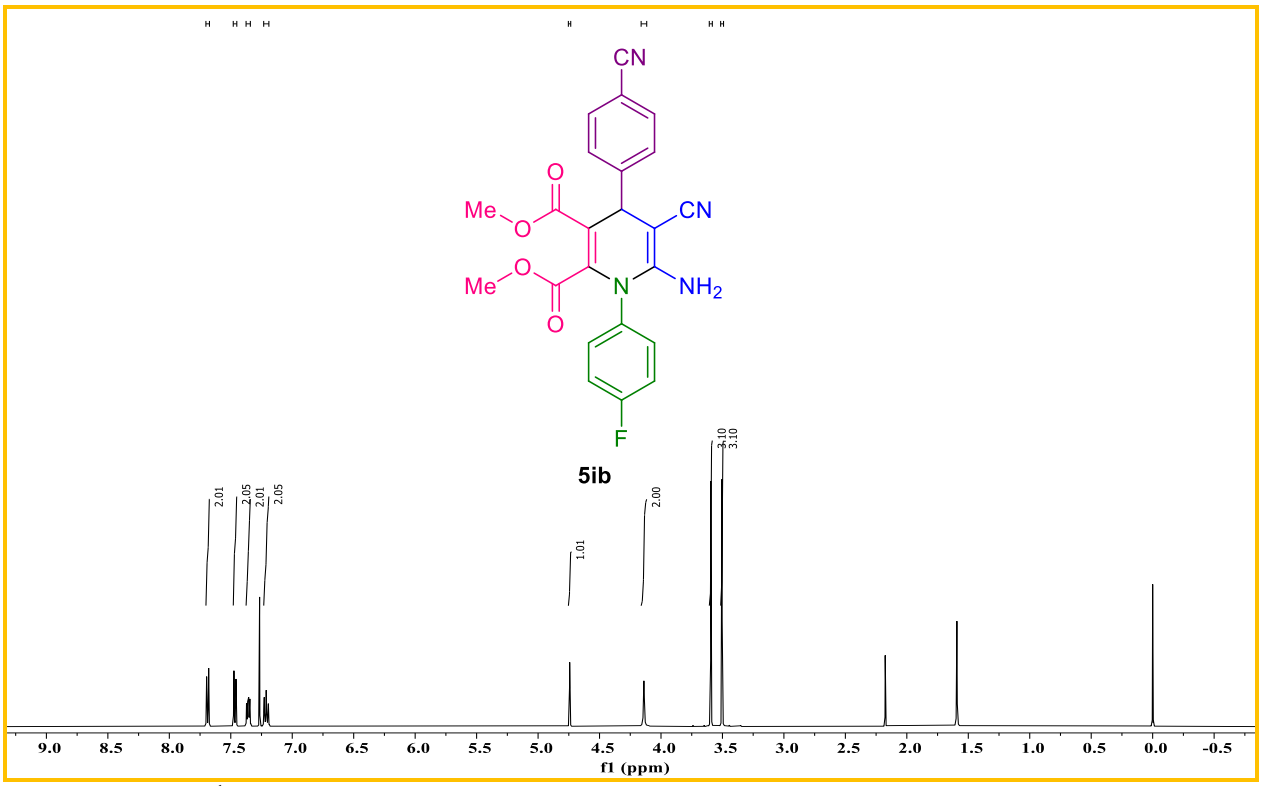


Figure S43: ^{1}H NMR spectra of dimethyl 6-amino-5-cyano-4-(4-cyanophenyl)-1-(4-fluorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5ib**

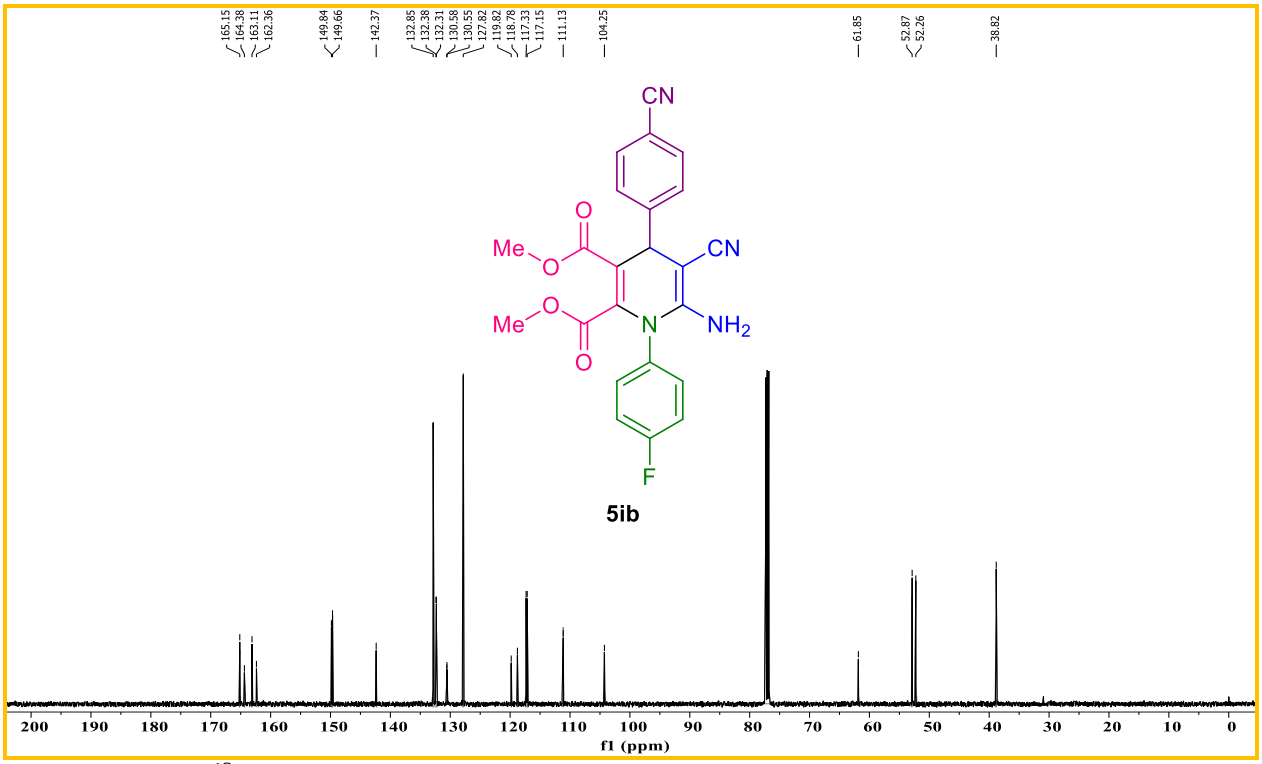


Figure S44: ^{13}C NMR spectra of dimethyl 6-amino-5-cyano-4-(4-cyanophenyl)-1-(4-fluorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5ib**

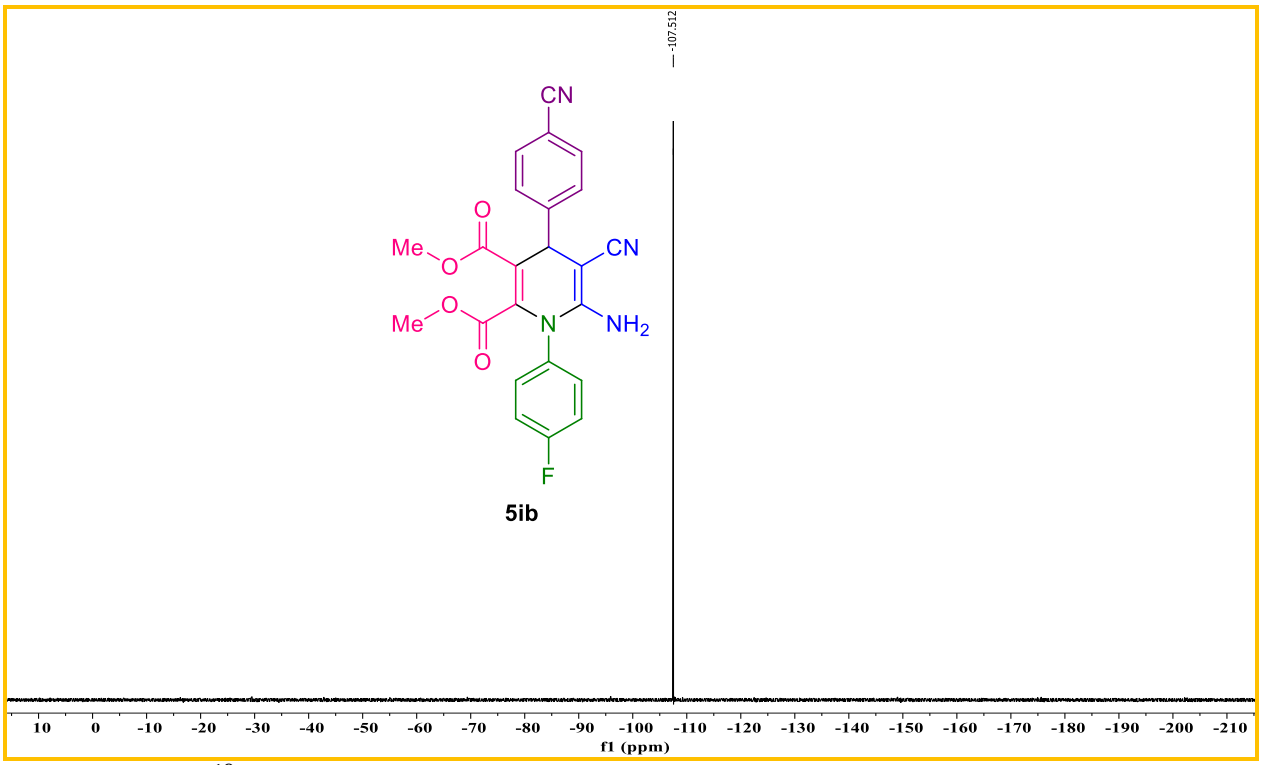


Figure S45: ^{19}F NMR spectra of dimethyl 6-amino-5-cyano-4-(4-cyanophenyl)-1-(4-fluorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5ib**

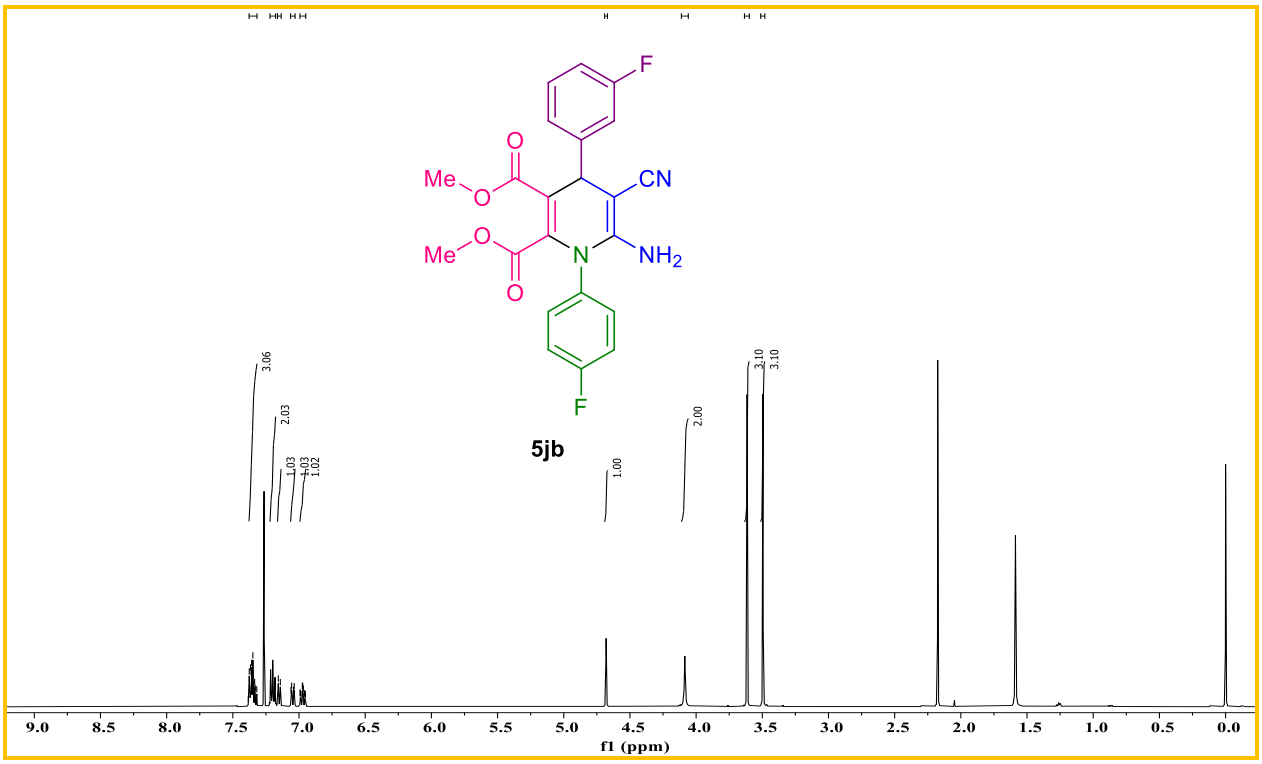


Figure S46: ^{1}H NMR spectra of dimethyl 6-amino-5-cyano-4-(3-fluorophenyl)-1-(4-fluorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5jb**

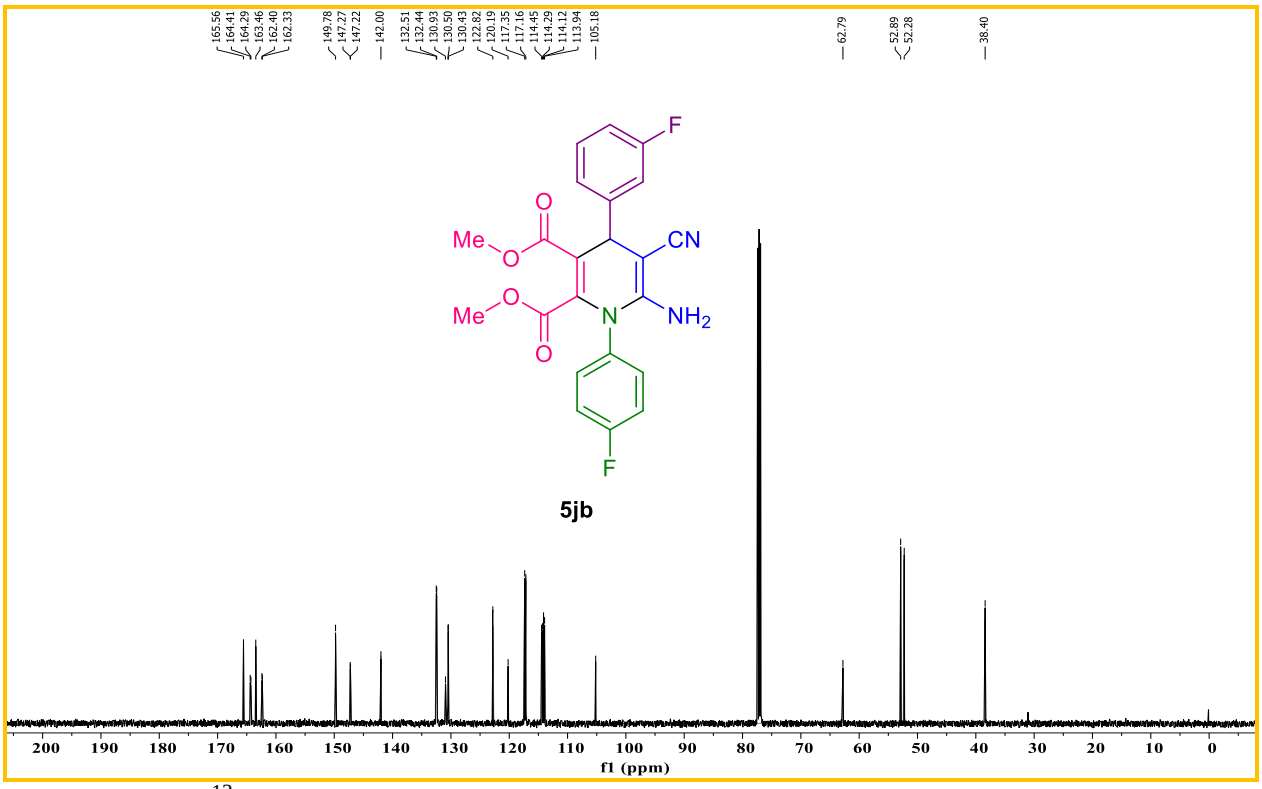


Figure S47: ^{13}C NMR spectra of dimethyl 6-amino-5-cyano-4-(3-fluorophenyl)-1-(4-fluorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5jb**

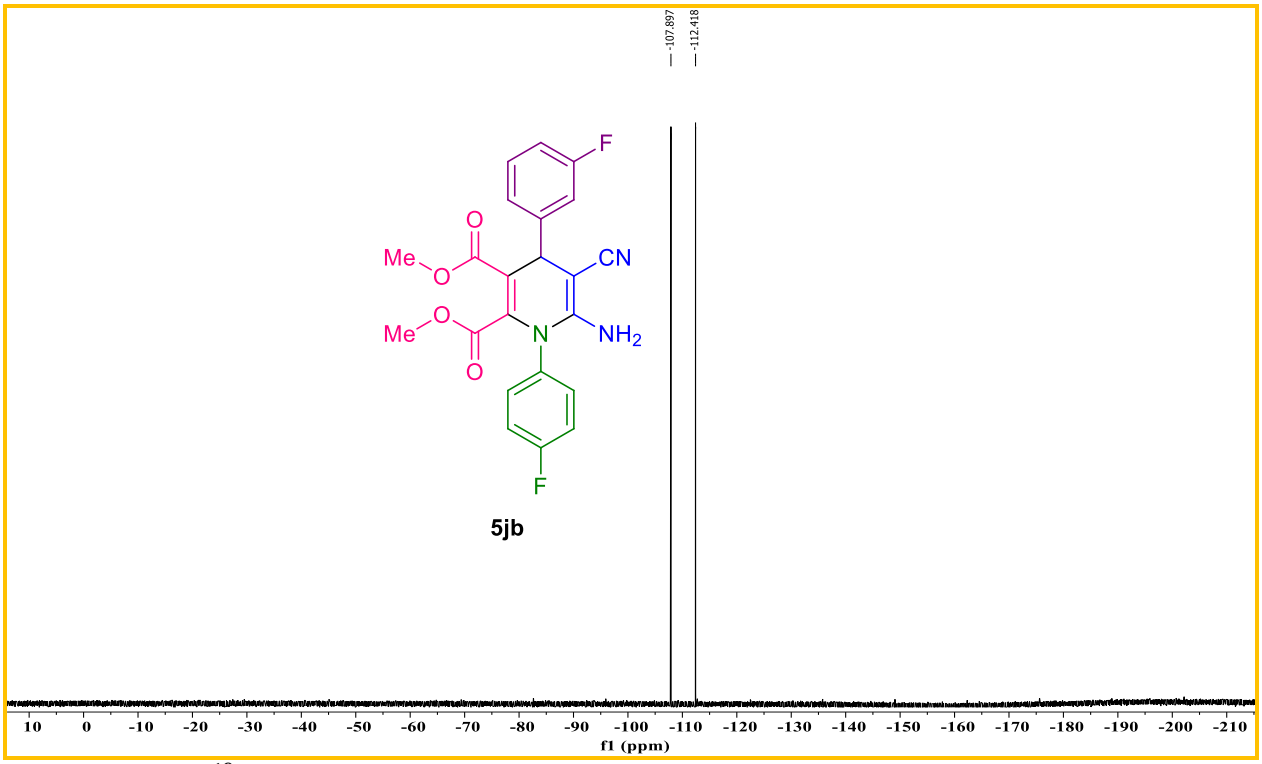


Figure S48: ^{19}F NMR spectra of dimethyl 6-amino-5-cyano-4-(3-fluorophenyl)-1-(4-fluorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5jb**

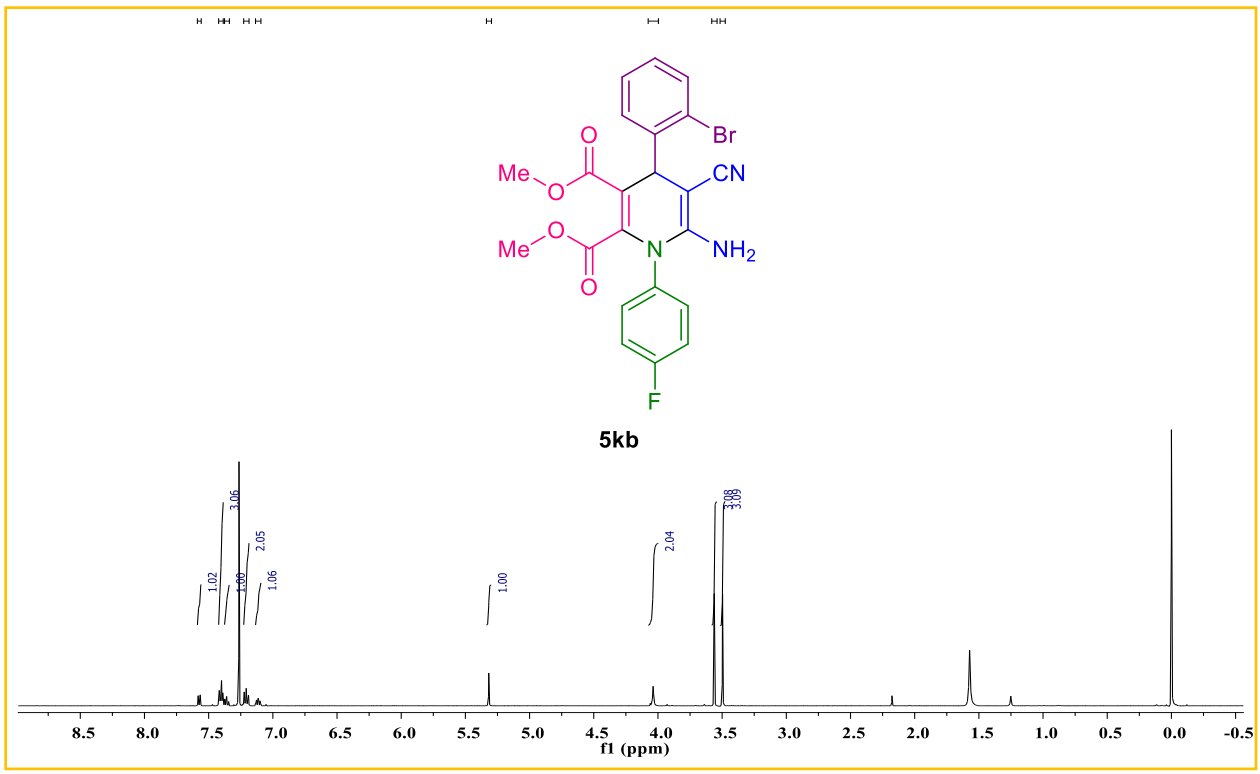


Figure S49: ^{1}H NMR spectra of dimethyl 6-amino-4-(2-bromophenyl)-5-cyano-1-(4-fluorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5kb**

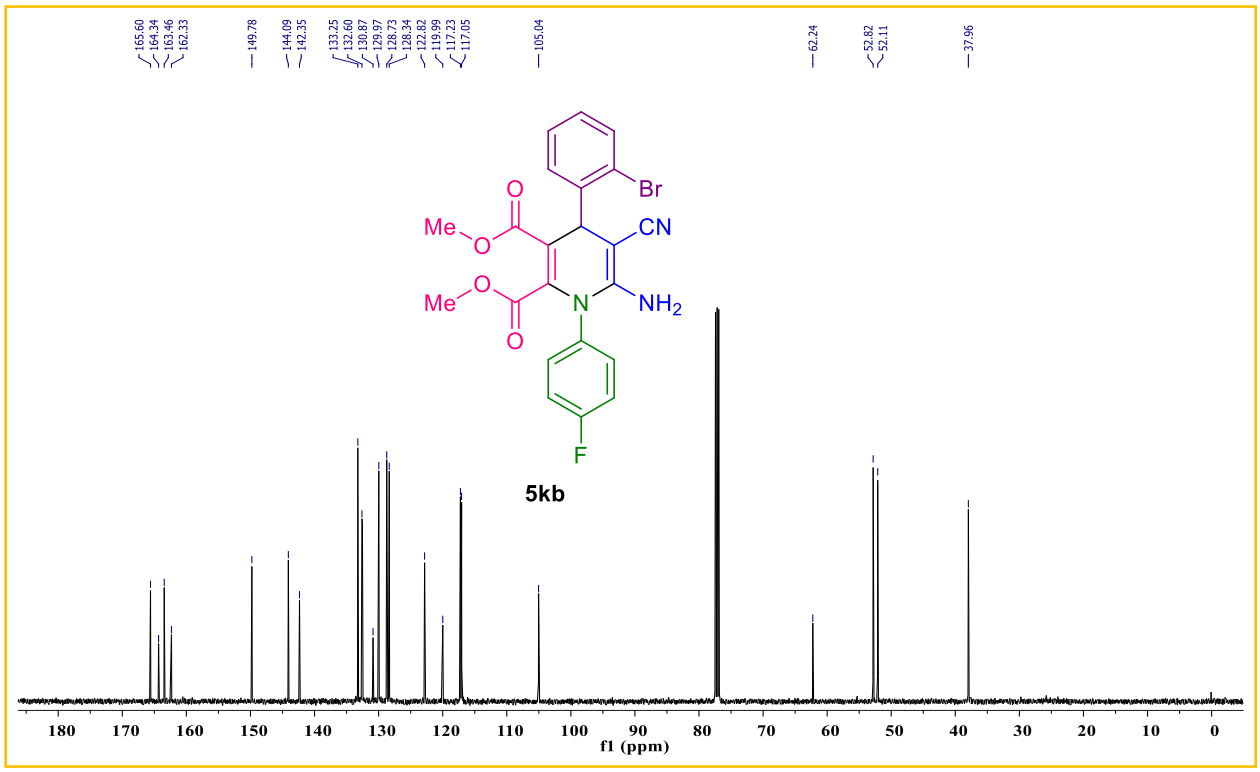


Figure S50: ^{13}C NMR spectra of dimethyl 6-amino-4-(2-bromophenyl)-5-cyano-1-(4-fluorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5kb**

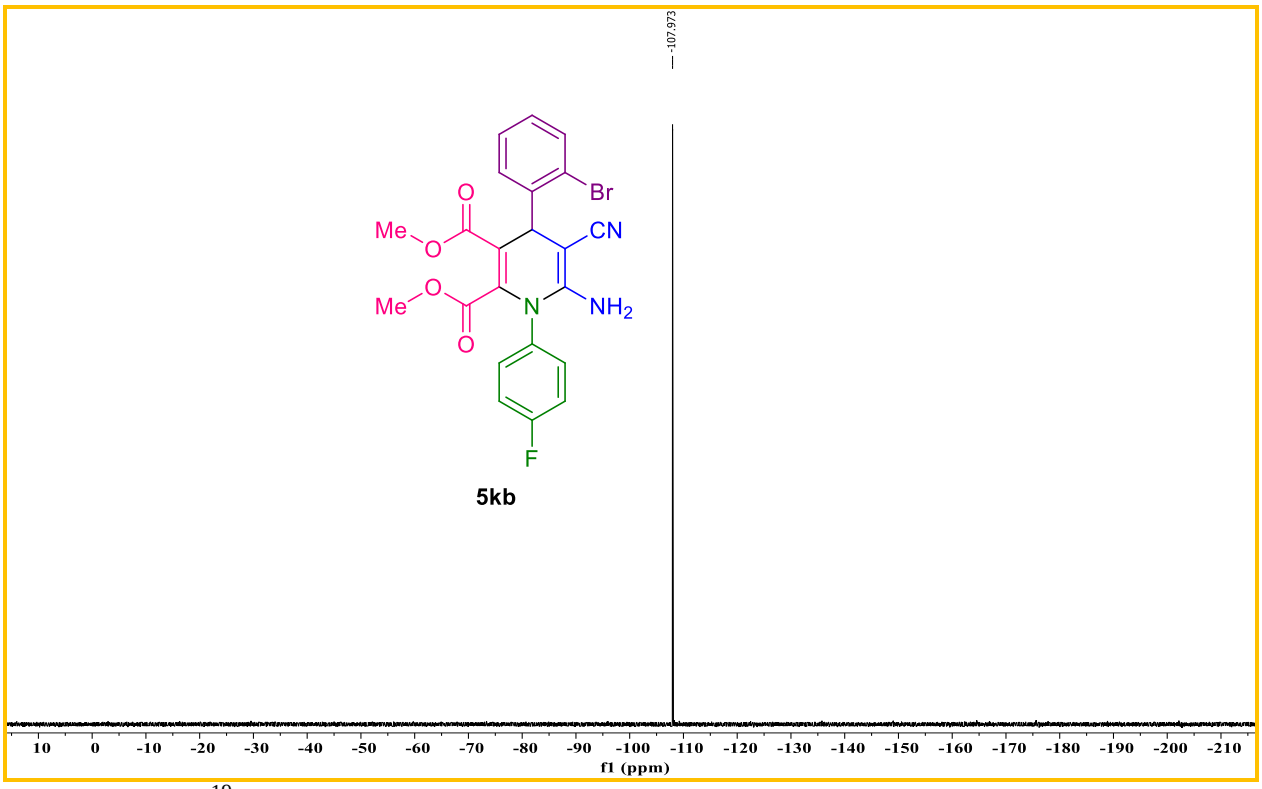


Figure S51: ^{19}F NMR spectra of dimethyl 6-amino-4-(2-bromophenyl)-5-cyano-1-(4-fluorophenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5kb**

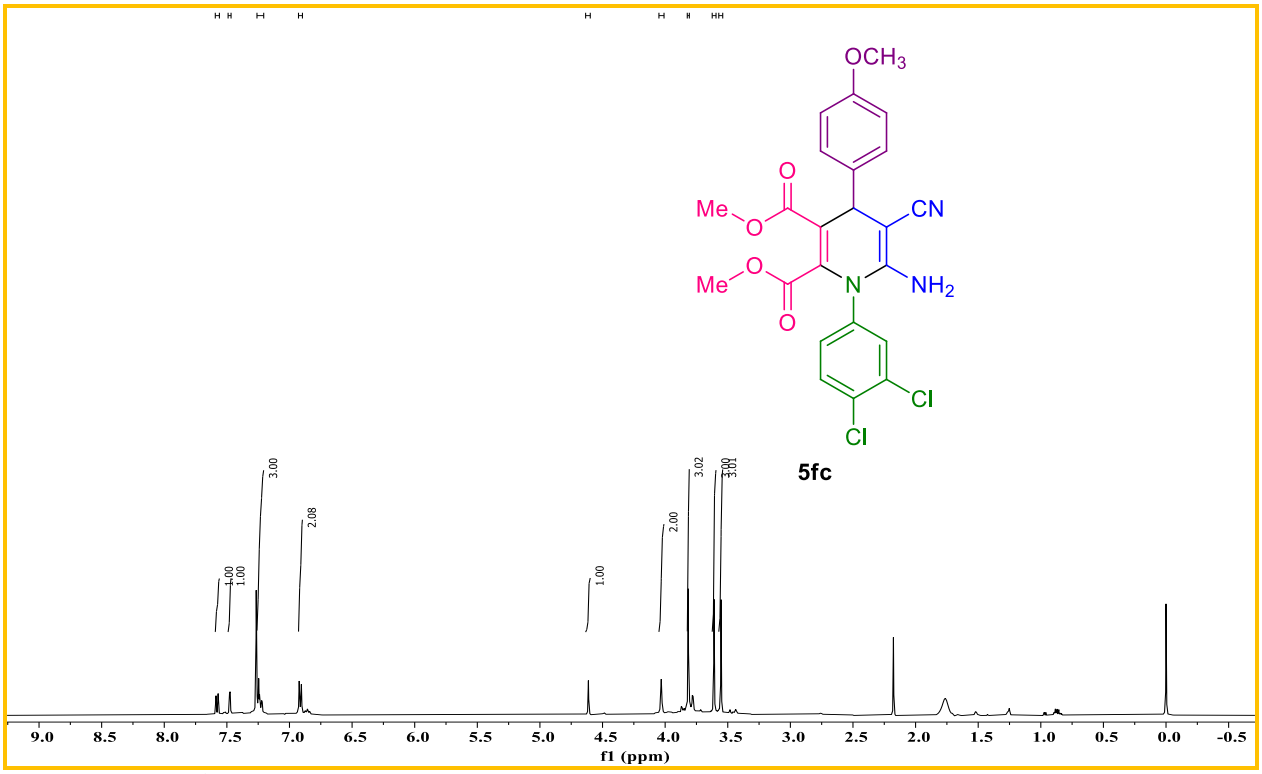


Figure S52: ^{1}H NMR spectra of dimethyl 6-amino-5-cyano-1-(3,4-dichlorophenyl)-4-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5fc**

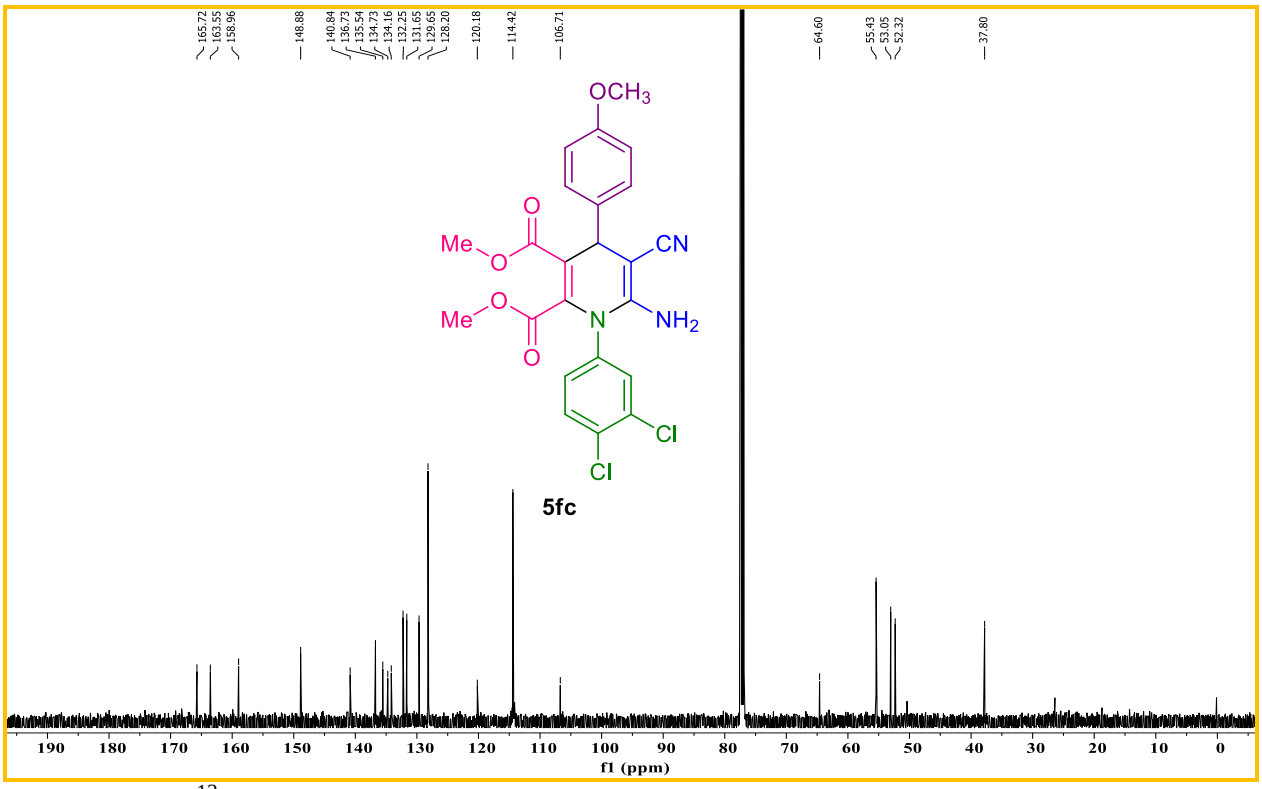


Figure S53: ^{13}C NMR spectra of dimethyl 6-amino-5-cyano-1-(3,4-dichlorophenyl)-4-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5fc**

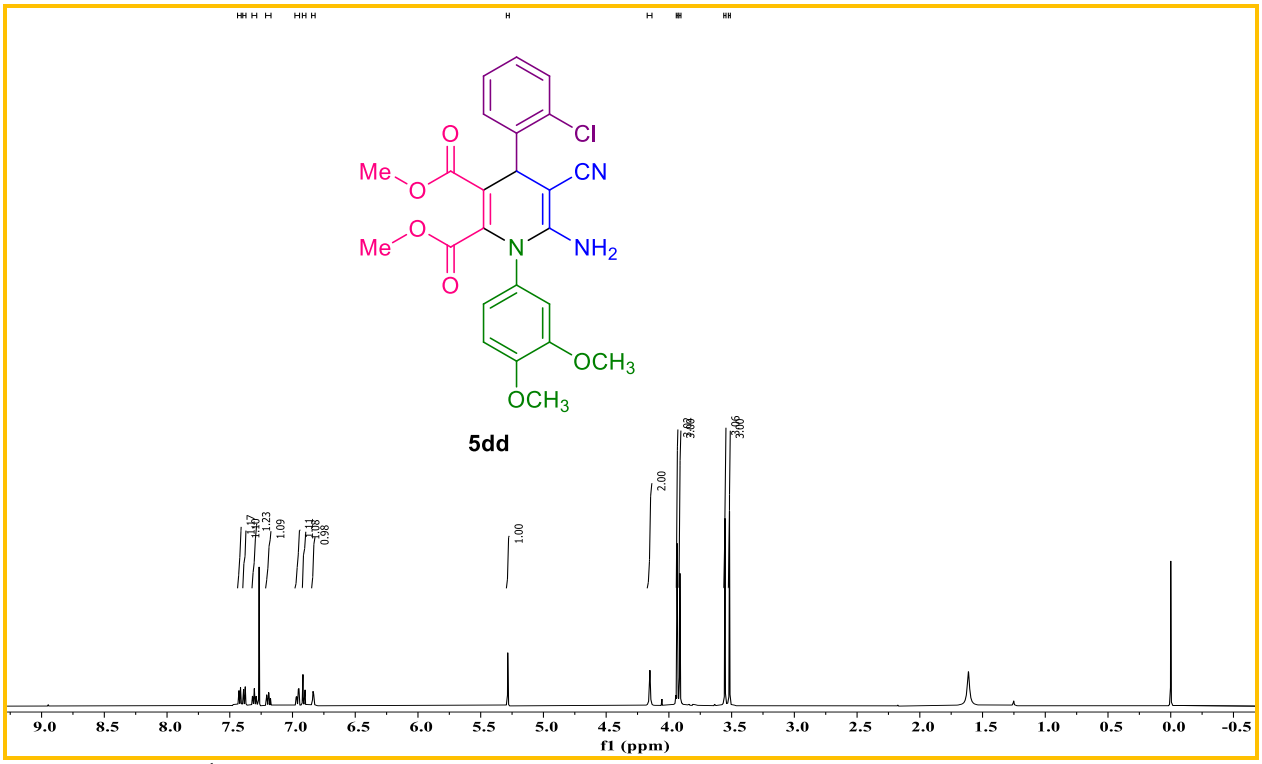


Figure S54: ^{1}H NMR spectra of dimethyl 6-amino-4-(2-chlorophenyl)-5-cyano-1-(3,4-dimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5dd**

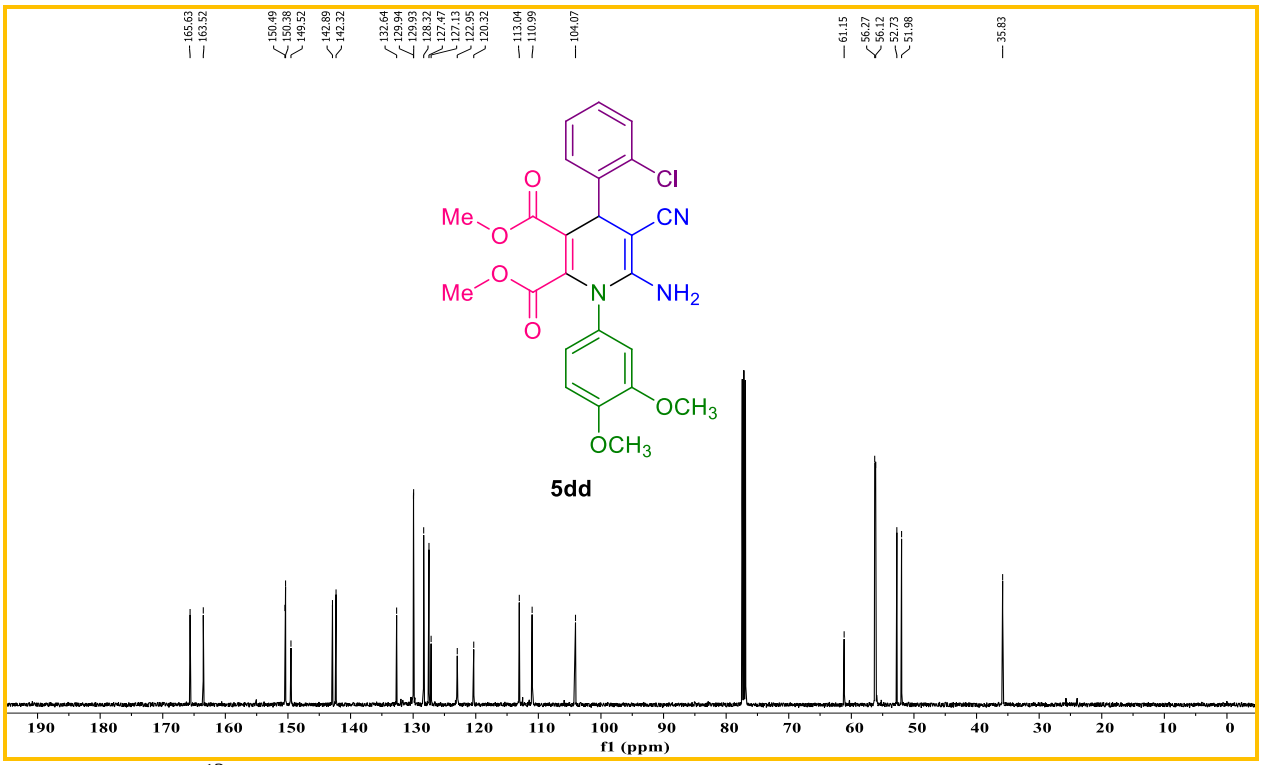


Figure S55: ^{13}C NMR spectra of dimethyl 6-amino-4-(2-chlorophenyl)-5-cyano-1-(3,4-dimethoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5dd**

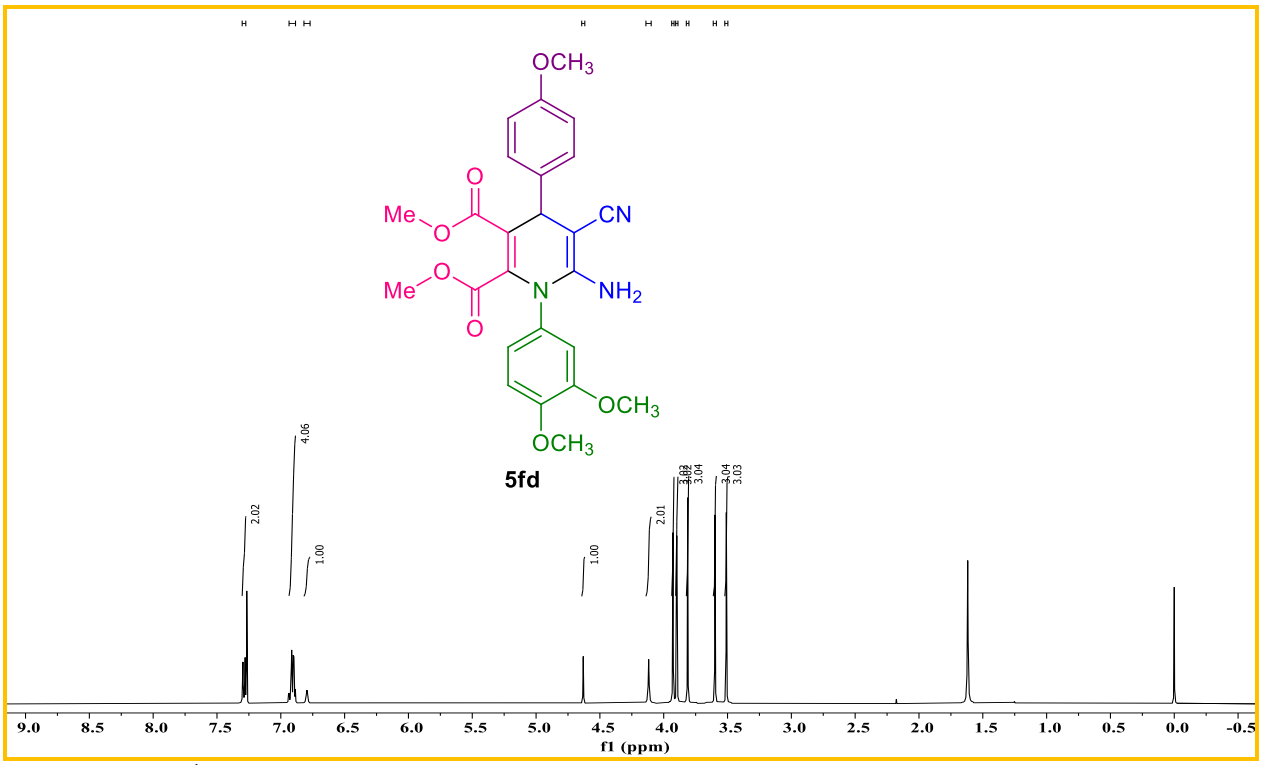


Figure S56: ^{1}H NMR spectra of dimethyl 6-amino-5-cyano-1-(3,4-dimethoxyphenyl)-4-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5fd**

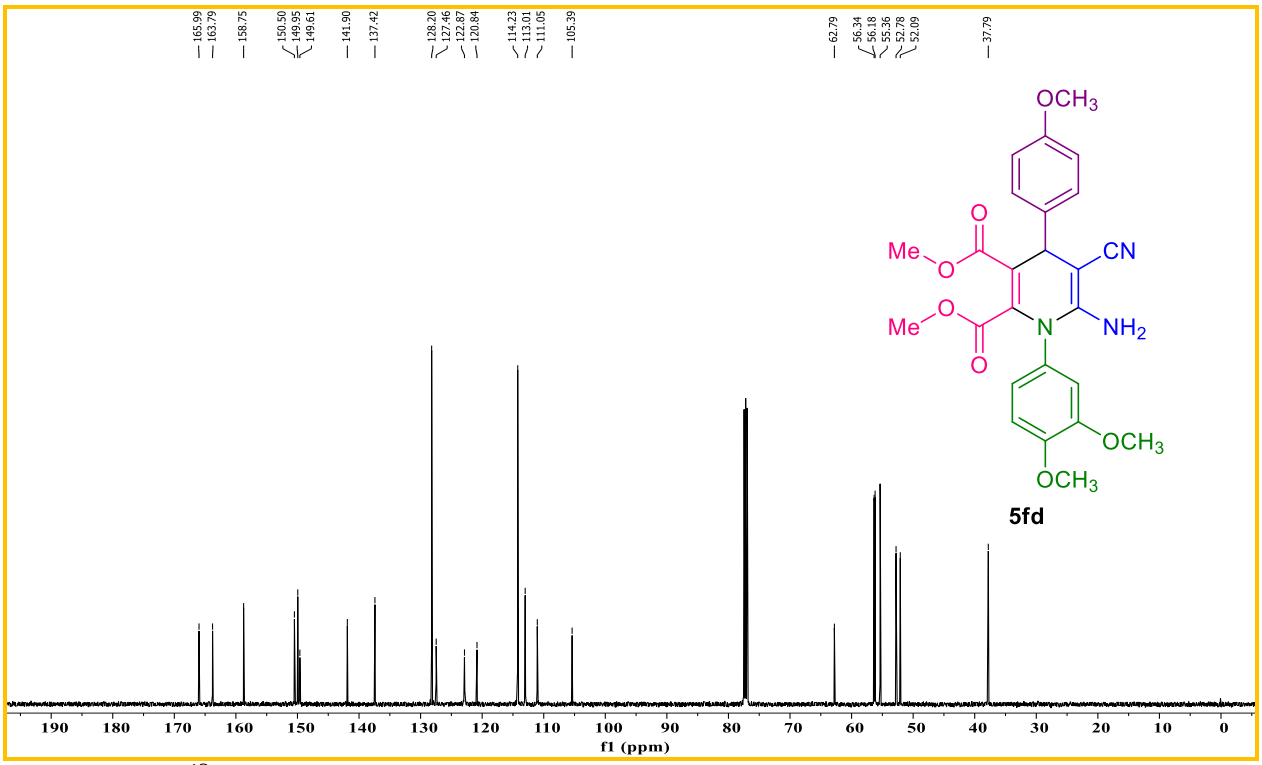


Figure S57: ^{13}C NMR spectra of dimethyl 6-amino-5-cyano-1-(3,4-dimethoxyphenyl)-4-(4-methoxyphenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5fd**

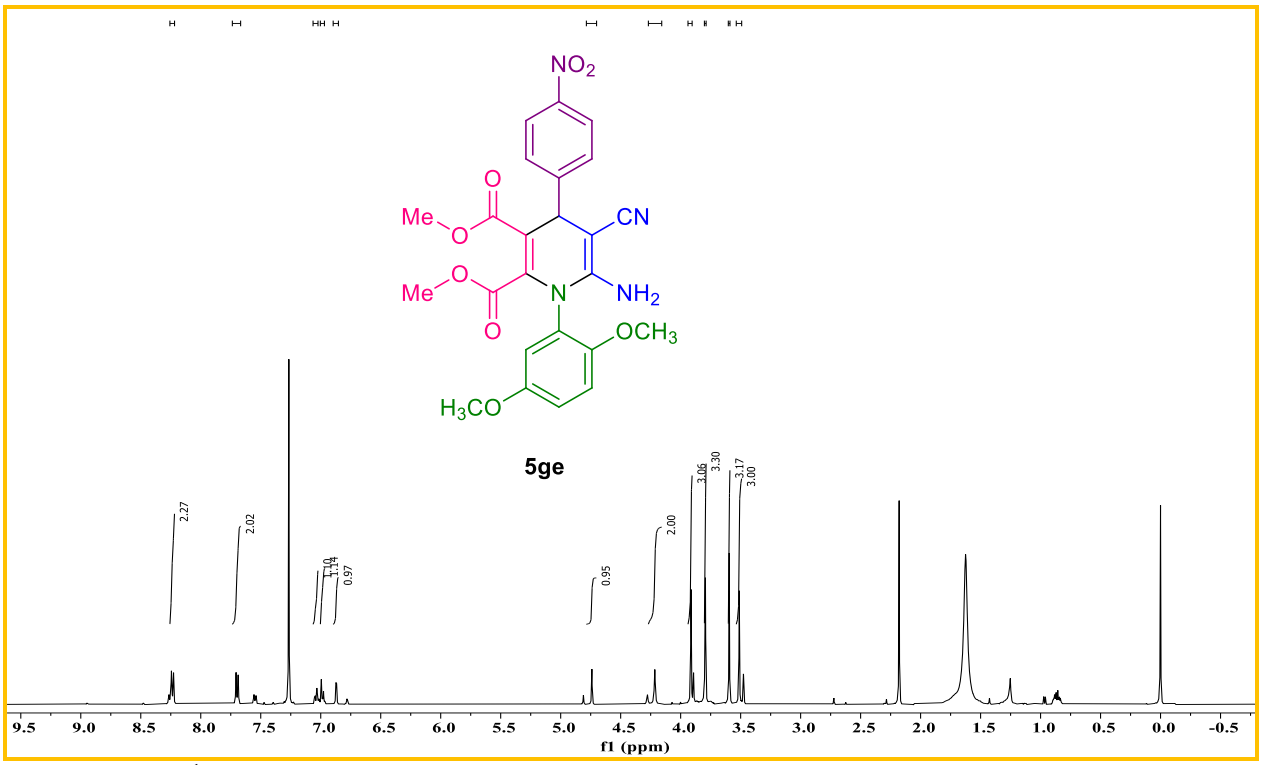


Figure S58: ^{1}H NMR spectra of dimethyl 6-amino-5-cyano-1-(2,5-dimethoxyphenyl)-4-(4-nitrophenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5ge**

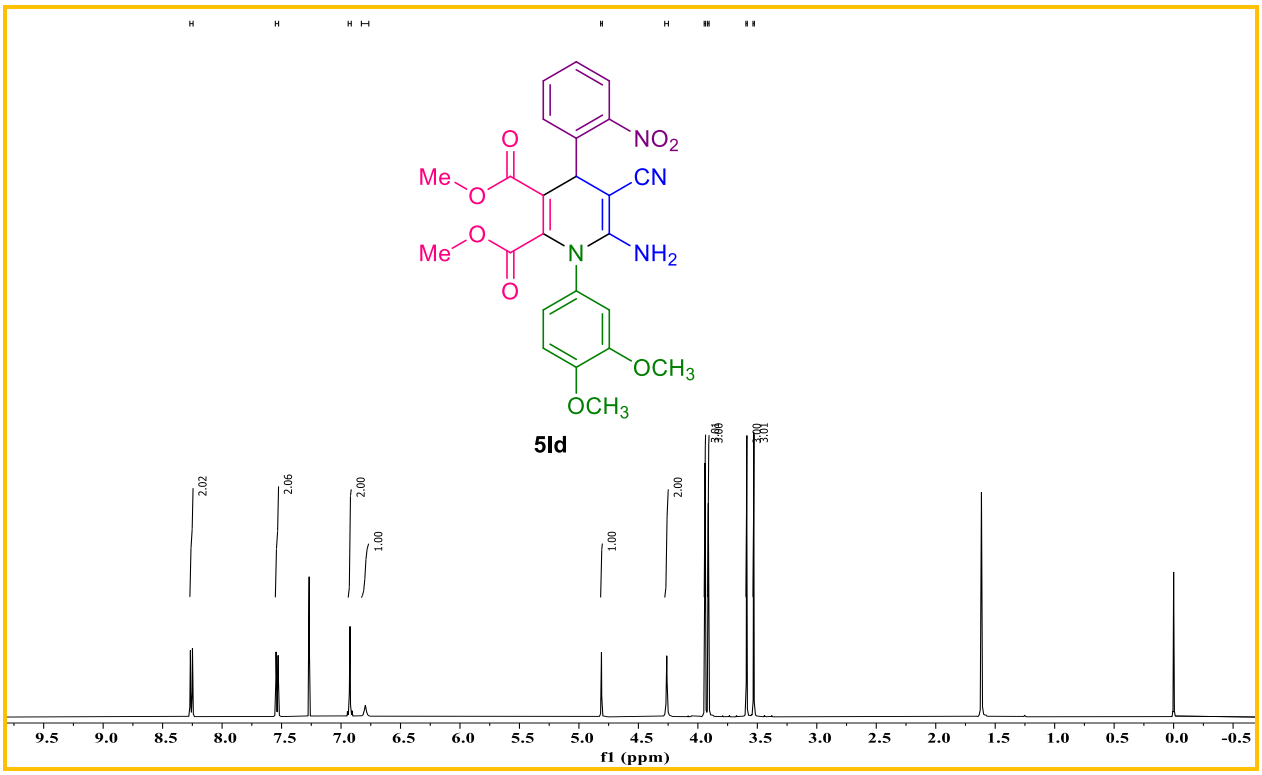


Figure S59: ^{1}H NMR spectra of dimethyl 6-amino-5-cyano-1-(3,4-dimethoxyphenyl)-4-(2-nitrophenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5ld**

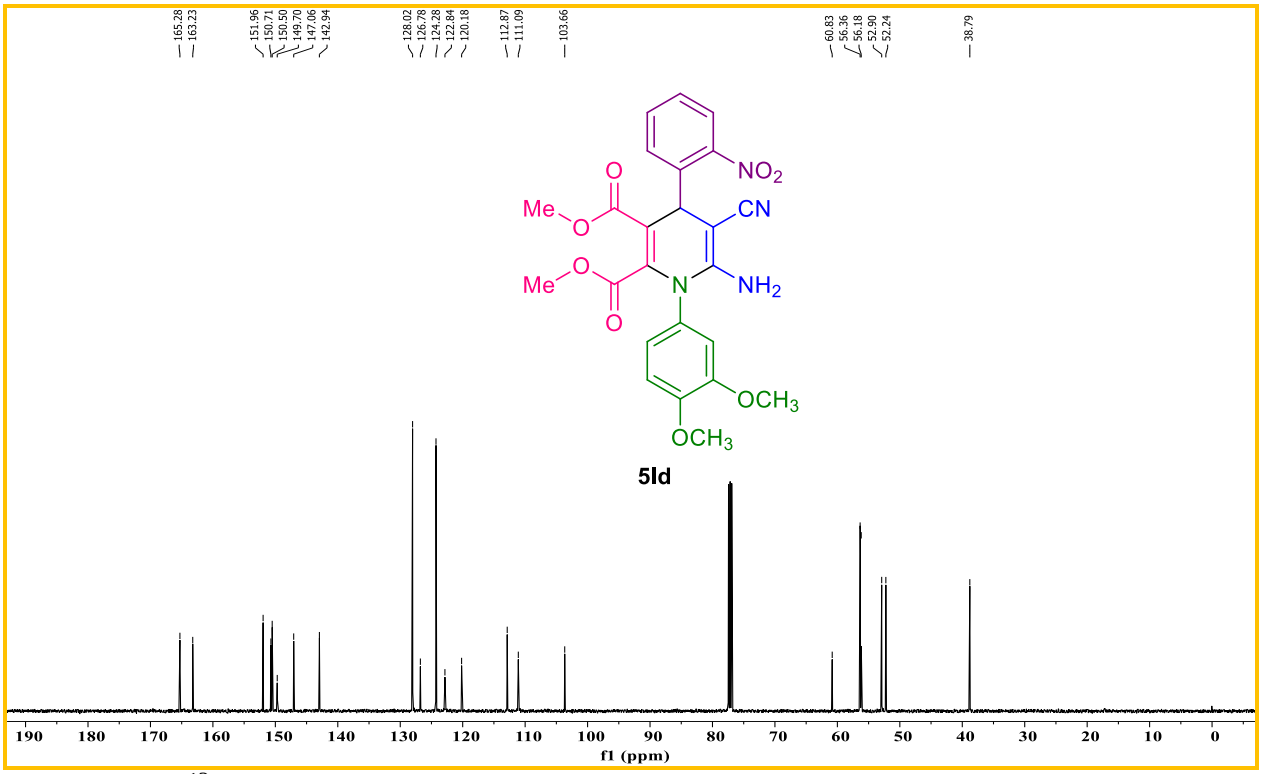


Figure S60: ^{13}C NMR spectra of dimethyl 6-amino-5-cyano-1-(3,4-dimethoxyphenyl)-4-(2-nitrophenyl)-1,4-dihydropyridine-2,3-dicarboxylate **5ld**

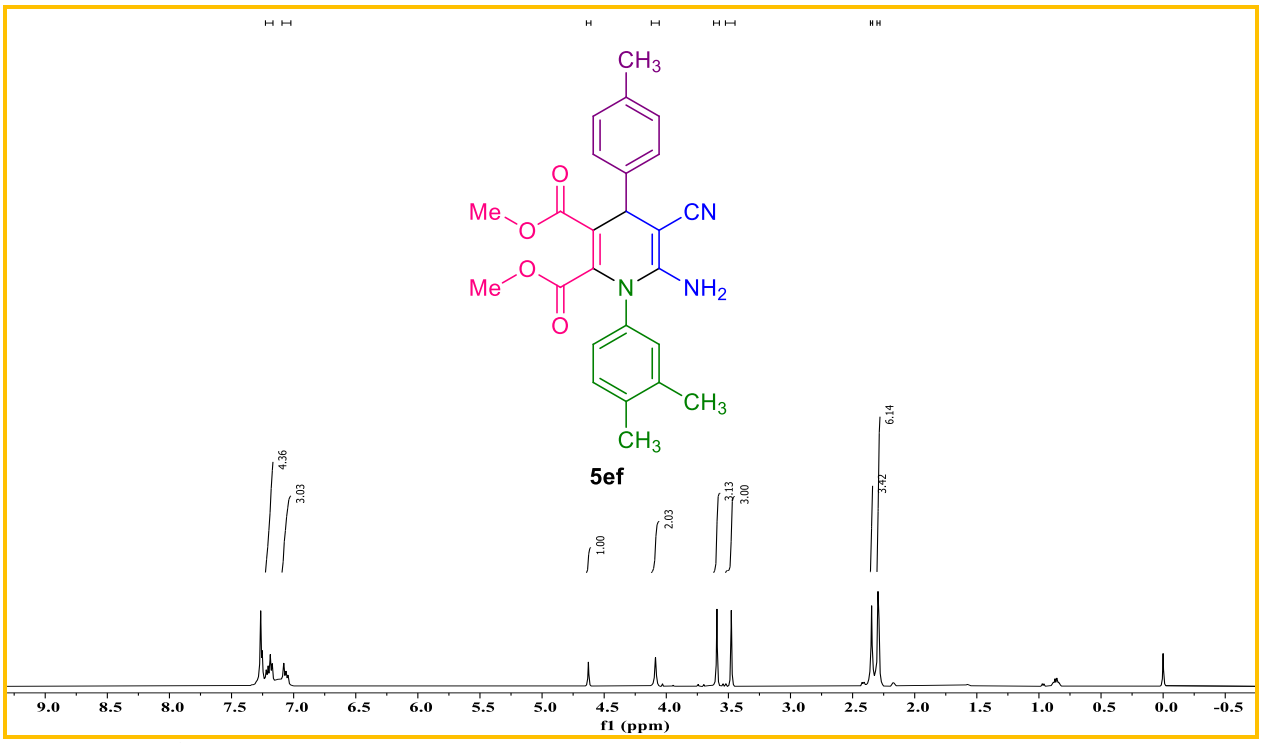


Figure S61: ^{1}H NMR spectra of dimethyl 6-amino-5-cyano-1-(3,4-dimethylphenyl)-4-(p-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate **5ef**

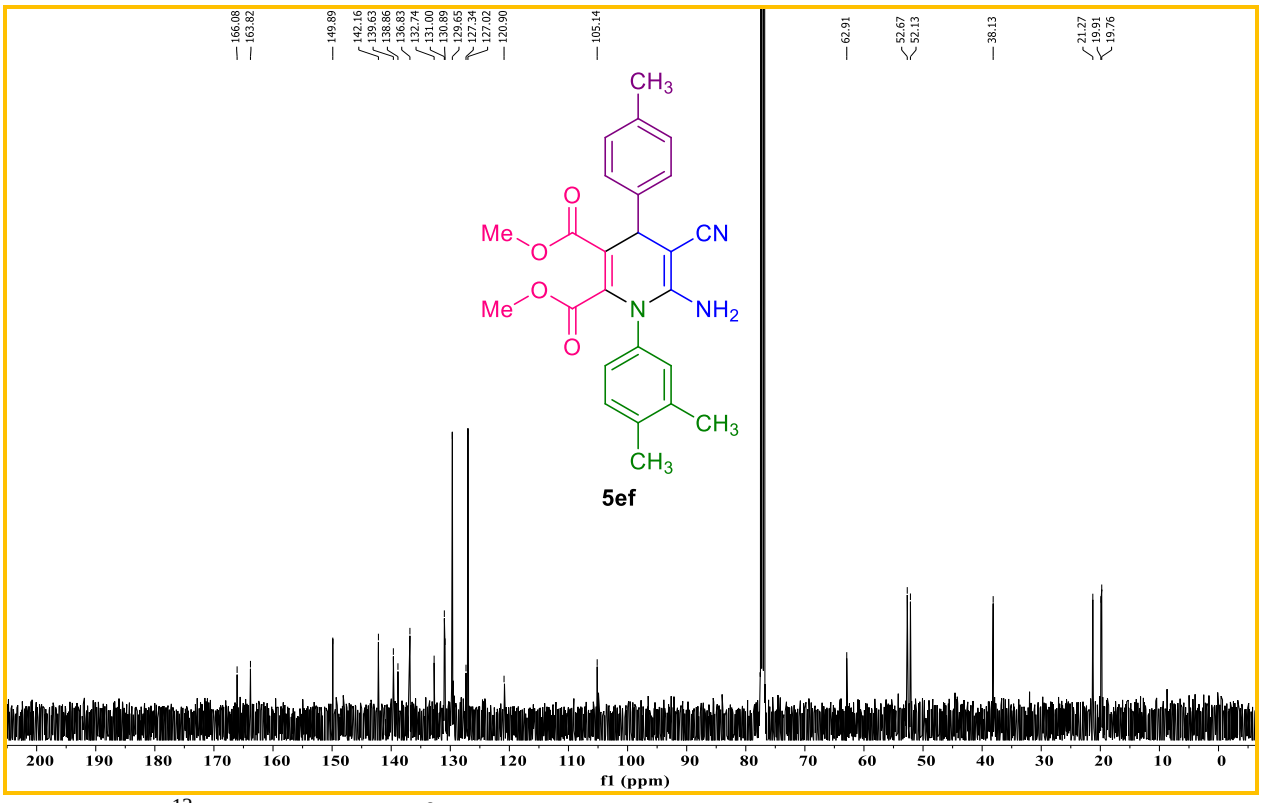


Figure S62: ^{13}C NMR spectra of dimethyl 6-amino-5-cyano-1-(3,4-dimethylphenyl)-4-(p-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate **5ef**

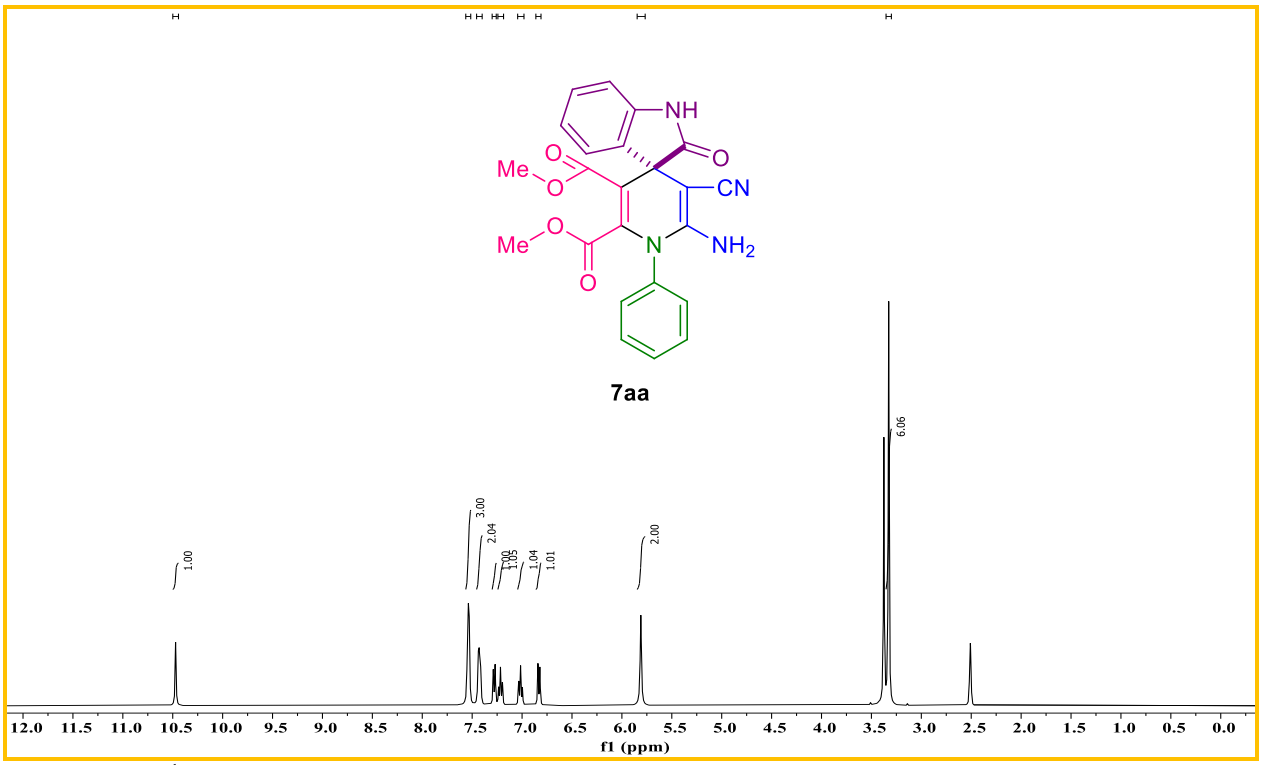


Figure S63: ^{1}H NMR spectra of dimethyl 2'-amino-3'-cyano-2-oxo-1'-phenyl-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7aa**

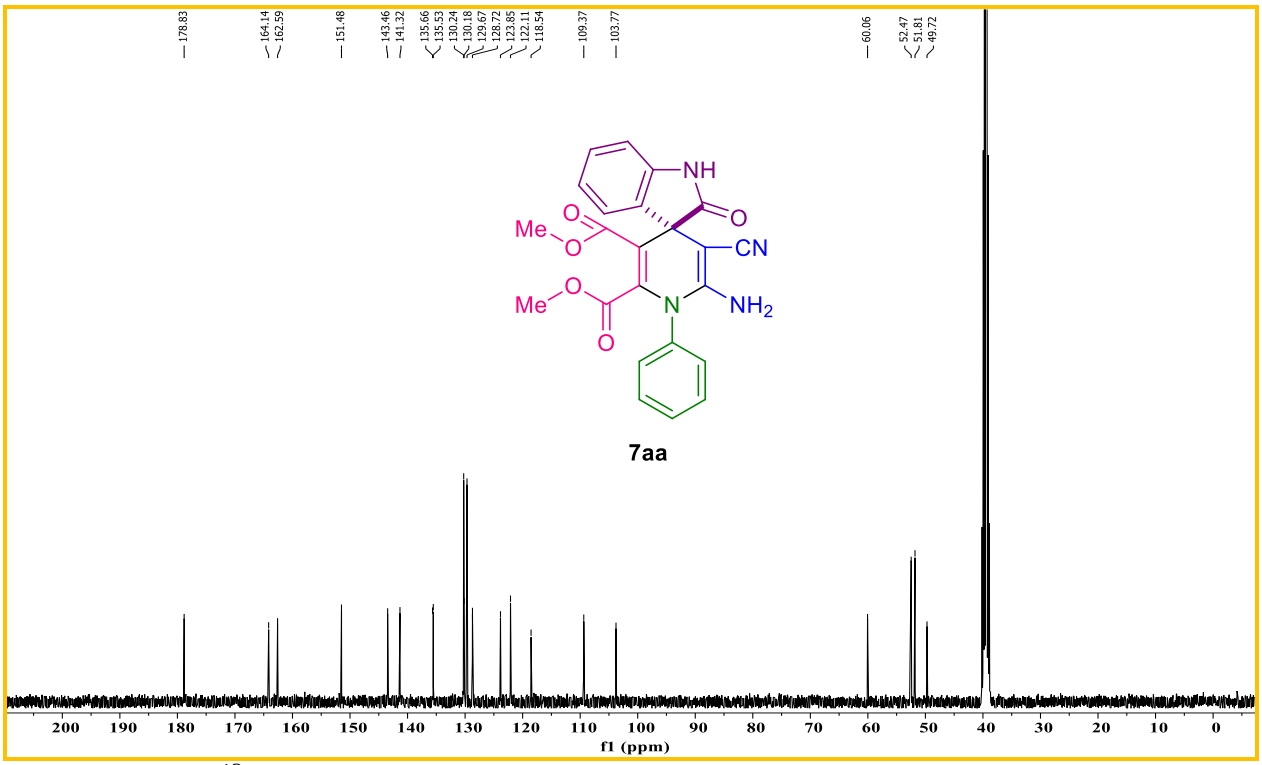


Figure S64: ^{13}C NMR spectra of dimethyl 2'-amino-3'-cyano-2-oxo-1'-phenyl-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7aa**

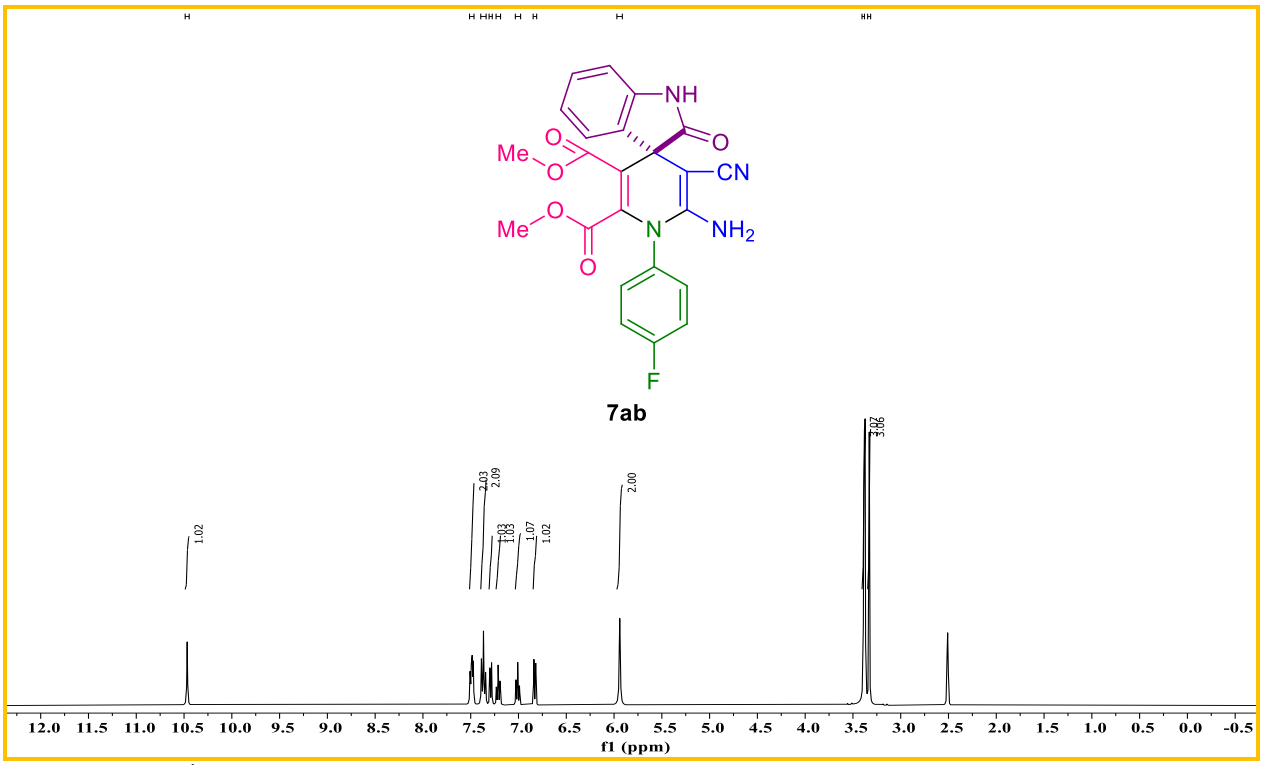


Figure S65: ^{1}H NMR spectra of dimethyl 2'-amino-3'-cyano-1'-(4-fluorophenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7ab**

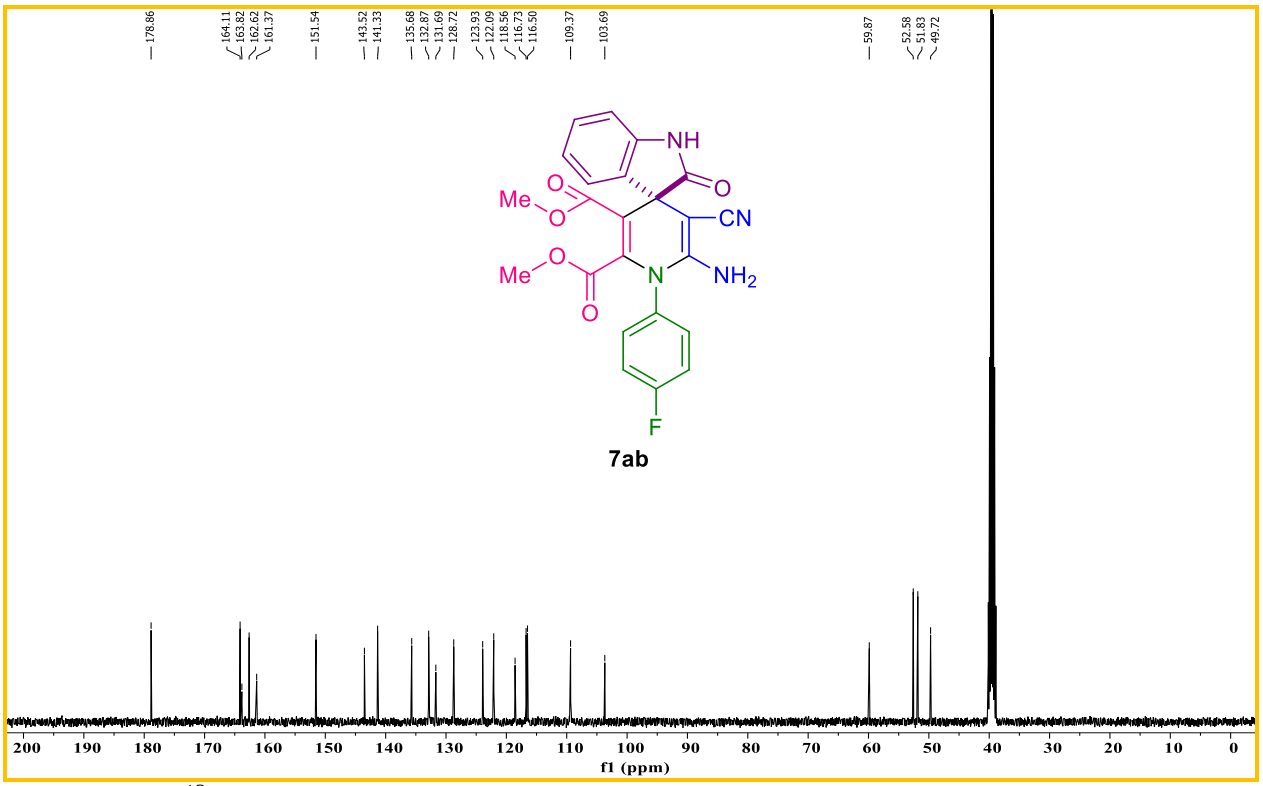


Figure S66: ^{13}C NMR spectra of dimethyl 2'-amino-3'-cyano-1'-(4-fluorophenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7ab**

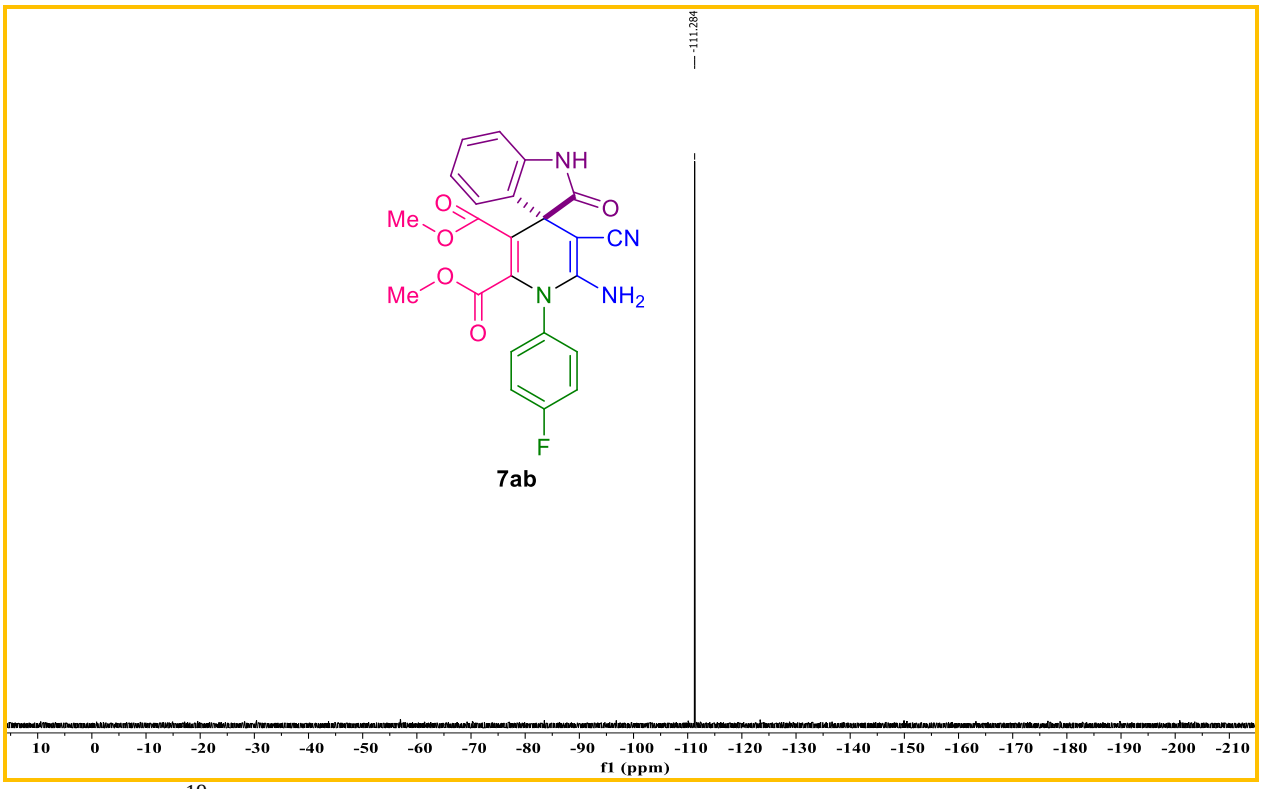


Figure S67: ^{19}F NMR spectra of dimethyl 2'-amino-3'-cyano-1'-(4-fluorophenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7ab**

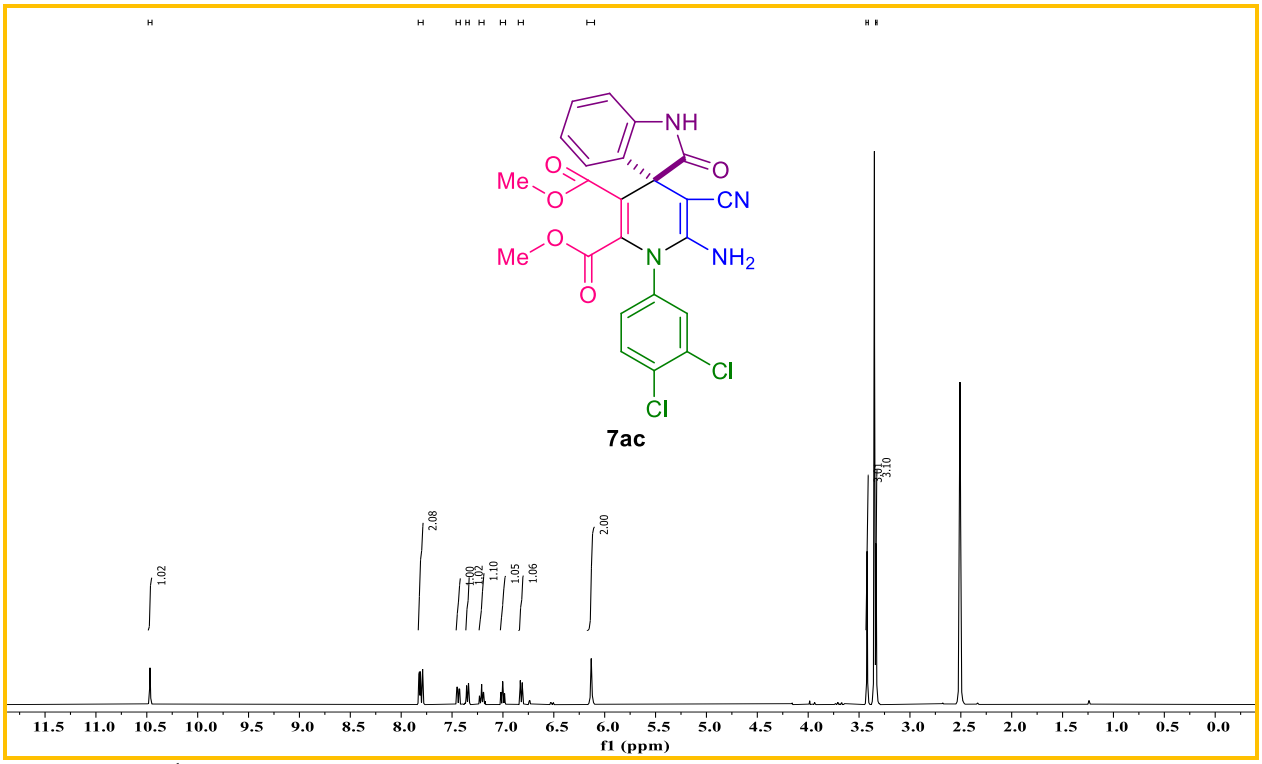


Figure S68: ^{1}H NMR spectra of dimethyl 2'-amino-3'-cyano-1'-(3,4-dichlorophenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7ac**

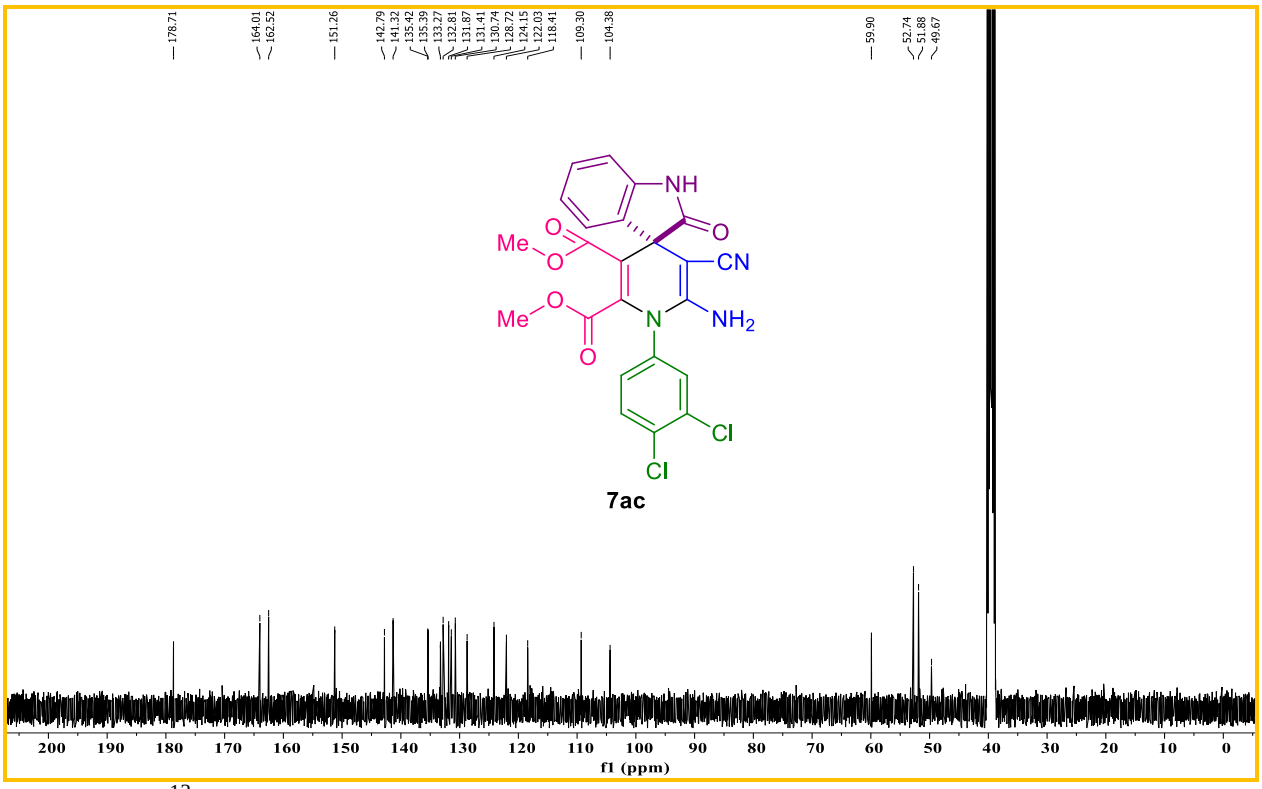


Figure S69: ^{13}C NMR spectra of dimethyl 2'-amino-3'-cyano-1'-(3,4-dichlorophenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7ac**

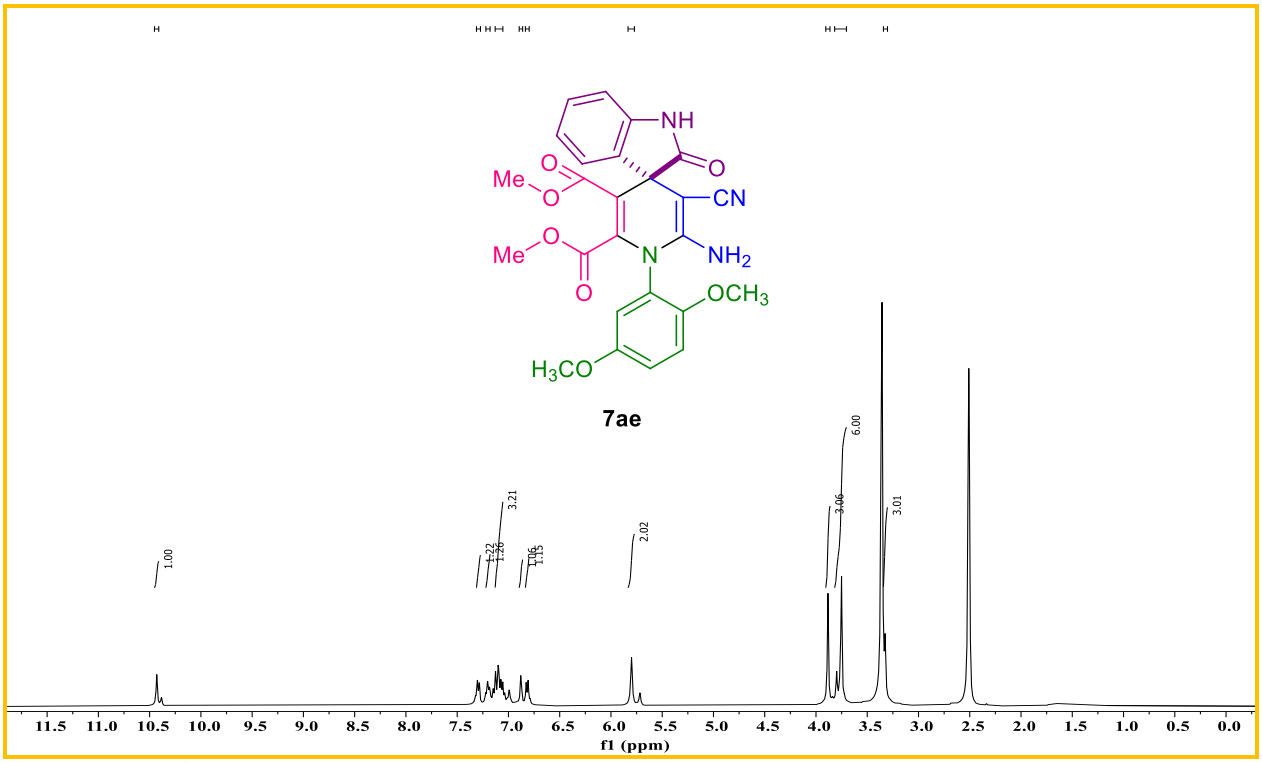


Figure S70: ^{1}H NMR spectra of dimethyl 2'-amino-3'-cyano-1'-(2,5-dimethoxyphenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate, **7ae**

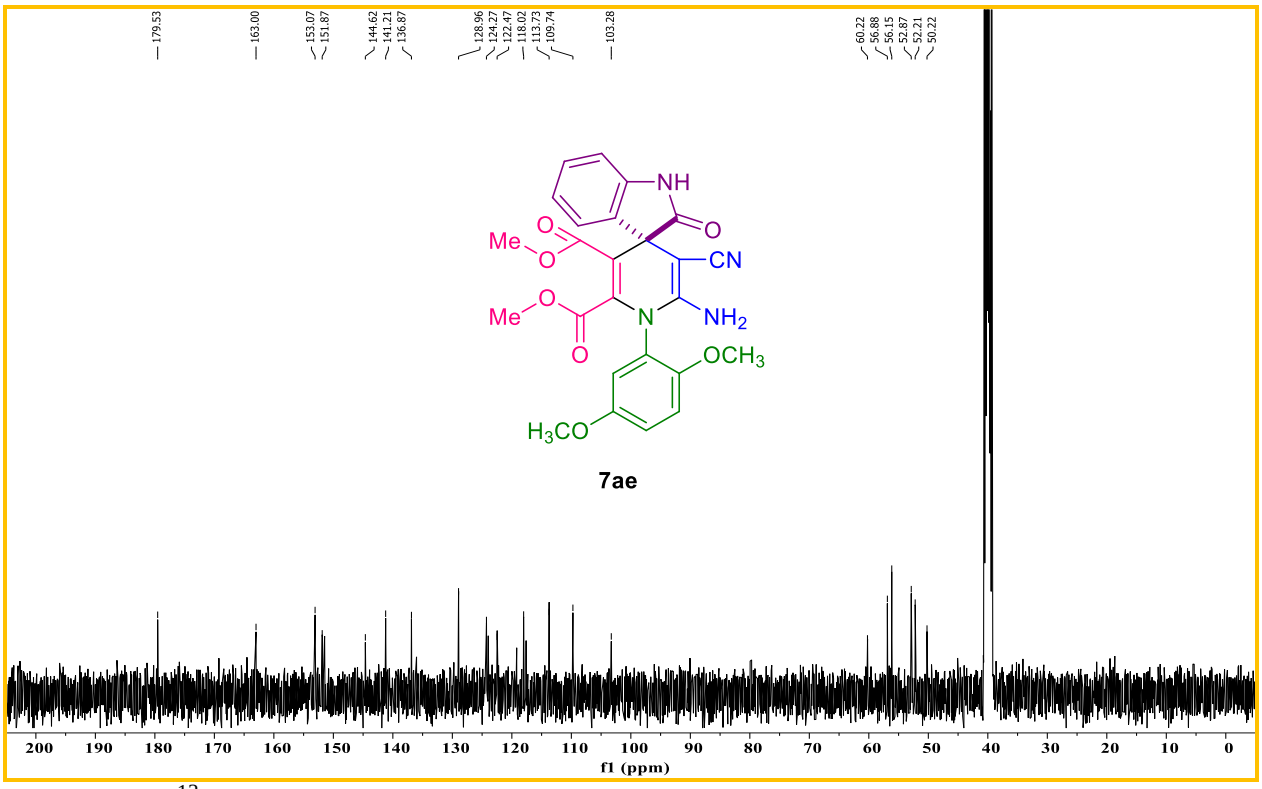


Figure S71: ^{13}C NMR spectra of dimethyl 2'-amino-3'-cyano-1'-(2,5-dimethoxyphenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate, **7ae**

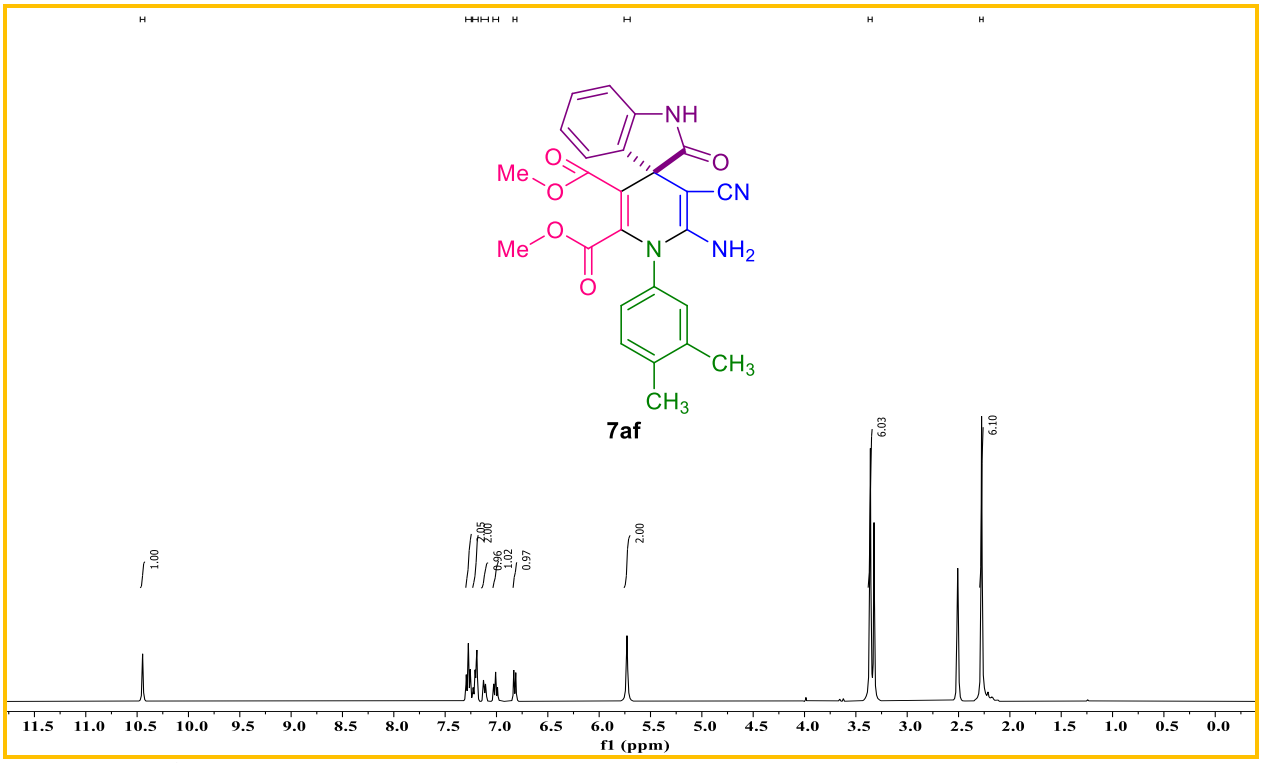


Figure S72: ^{1}H NMR spectra of dimethyl 2'-amino-3'-cyano-1'-(3,4-dimethylphenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7af**

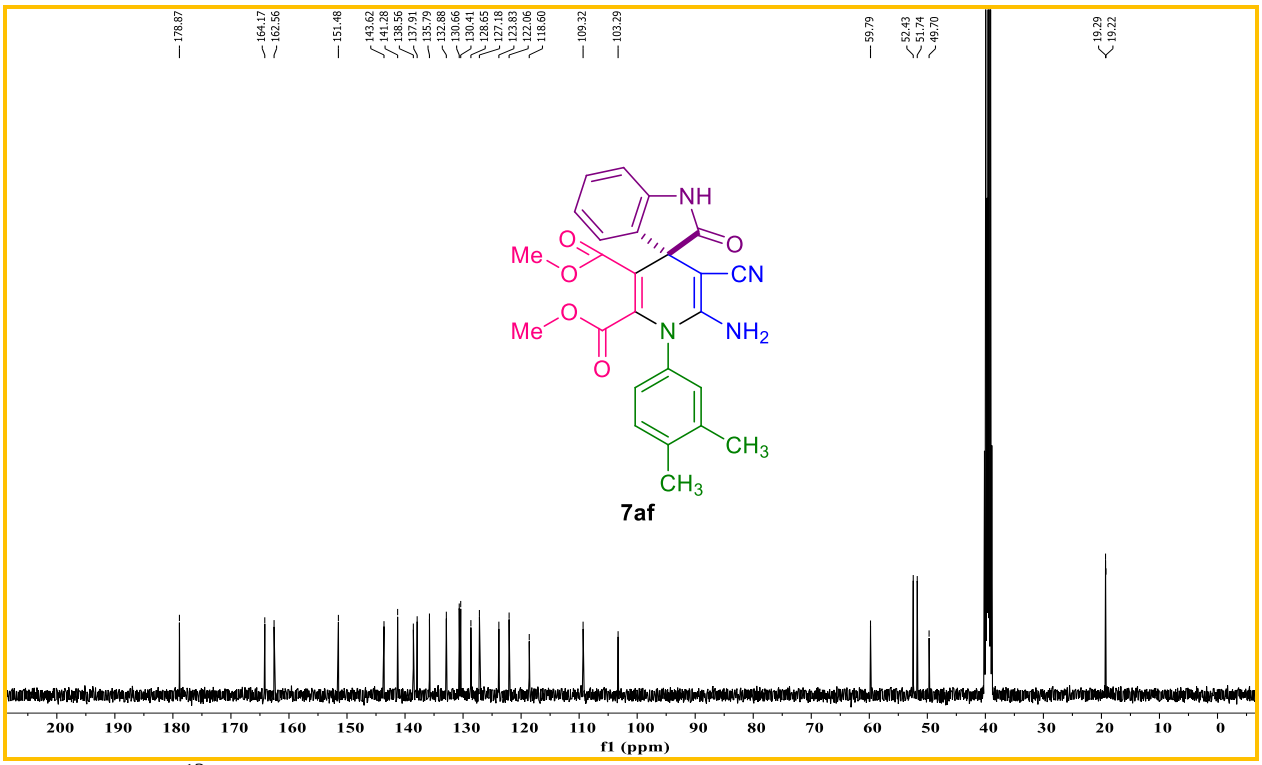


Figure S73: ^{13}C NMR spectra of dimethyl 2'-amino-3'-cyano-1'-(3,4-dimethylphenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7af**

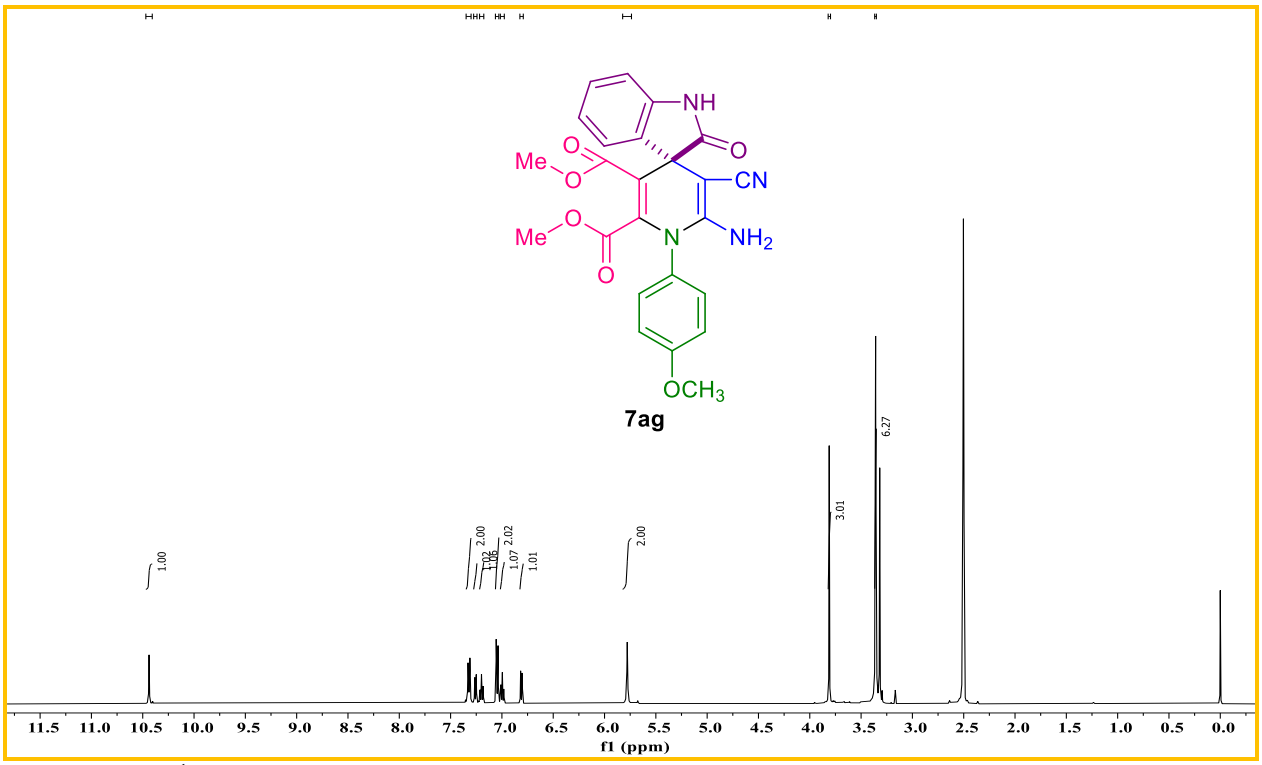


Figure S74: ^{1}H NMR spectra of dimethyl 2'-amino-3'-cyano-1'-(4-methoxyphenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7ag**

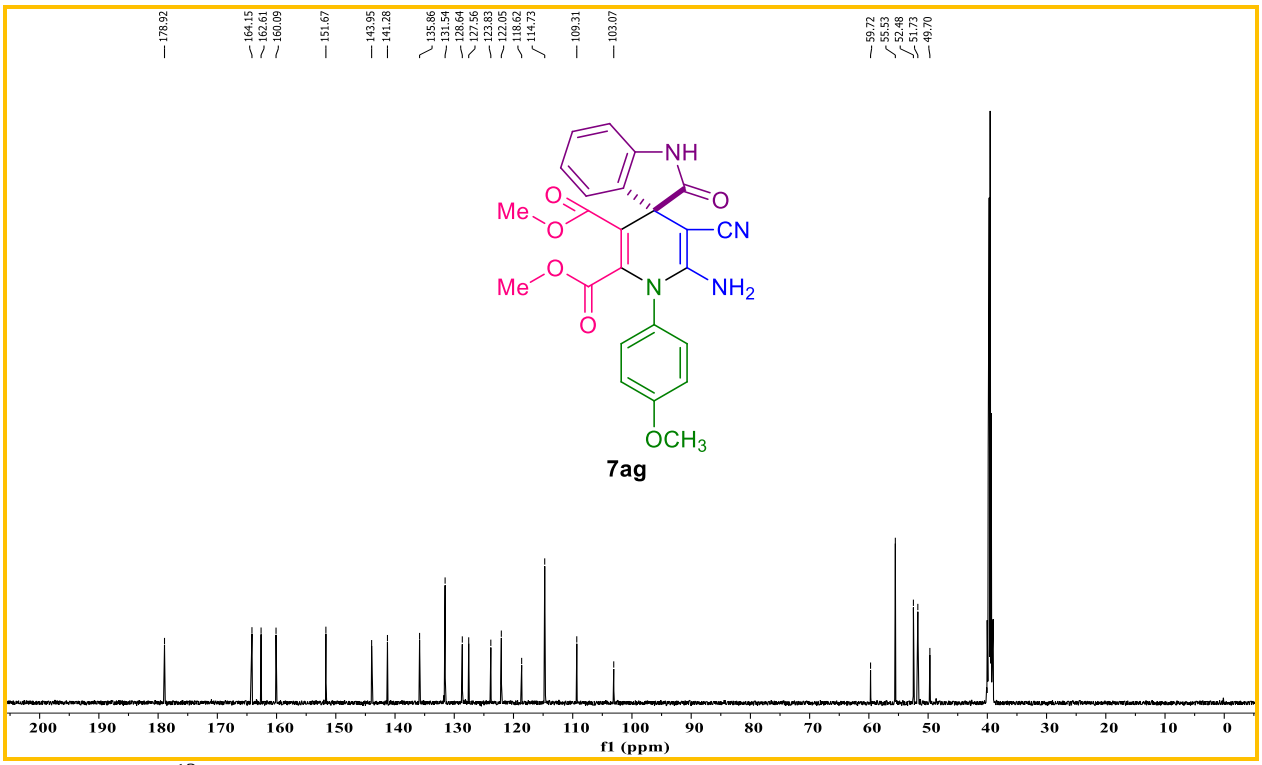


Figure S75: ^{13}C NMR spectra of dimethyl 2'-amino-3'-cyano-1'-(4-methoxyphenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7ag**

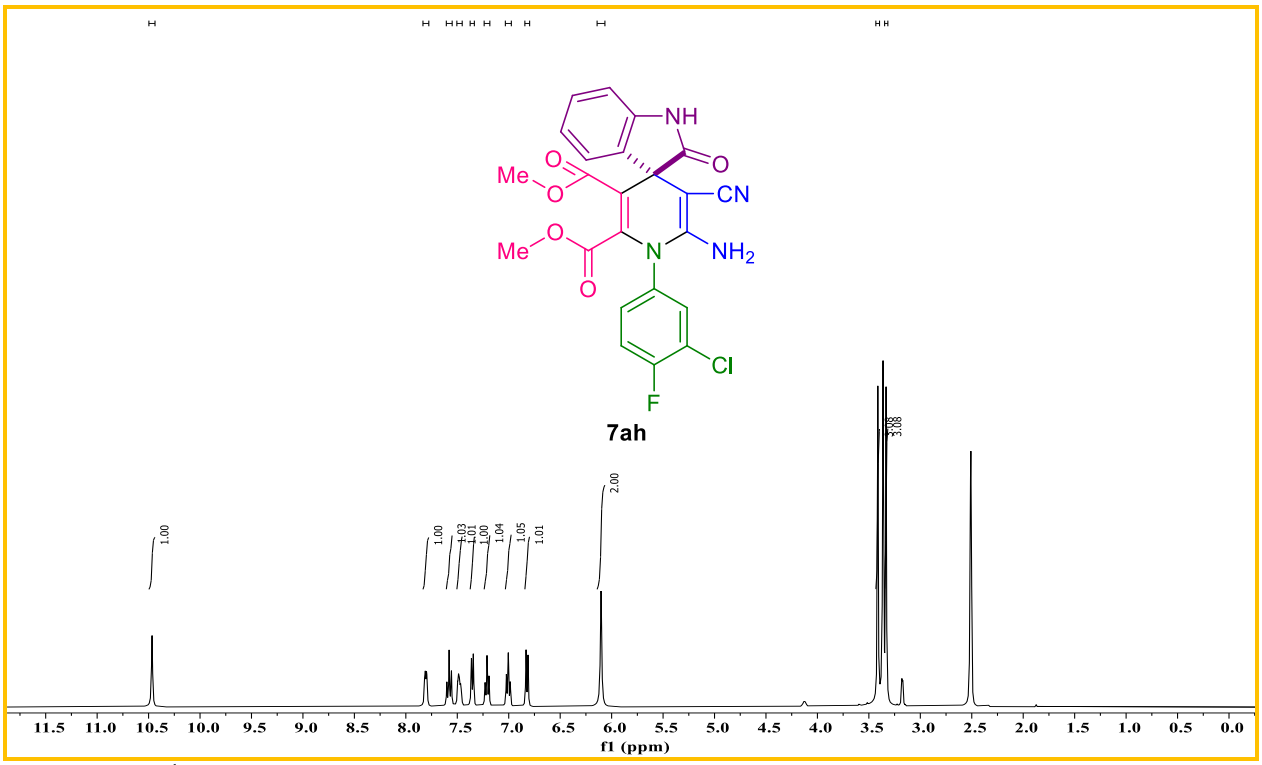


Figure S76: ^{1}H NMR spectra of dimethyl 2'-amino-1'-(3-chloro-4-fluorophenyl)-3'-cyano-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7ah**

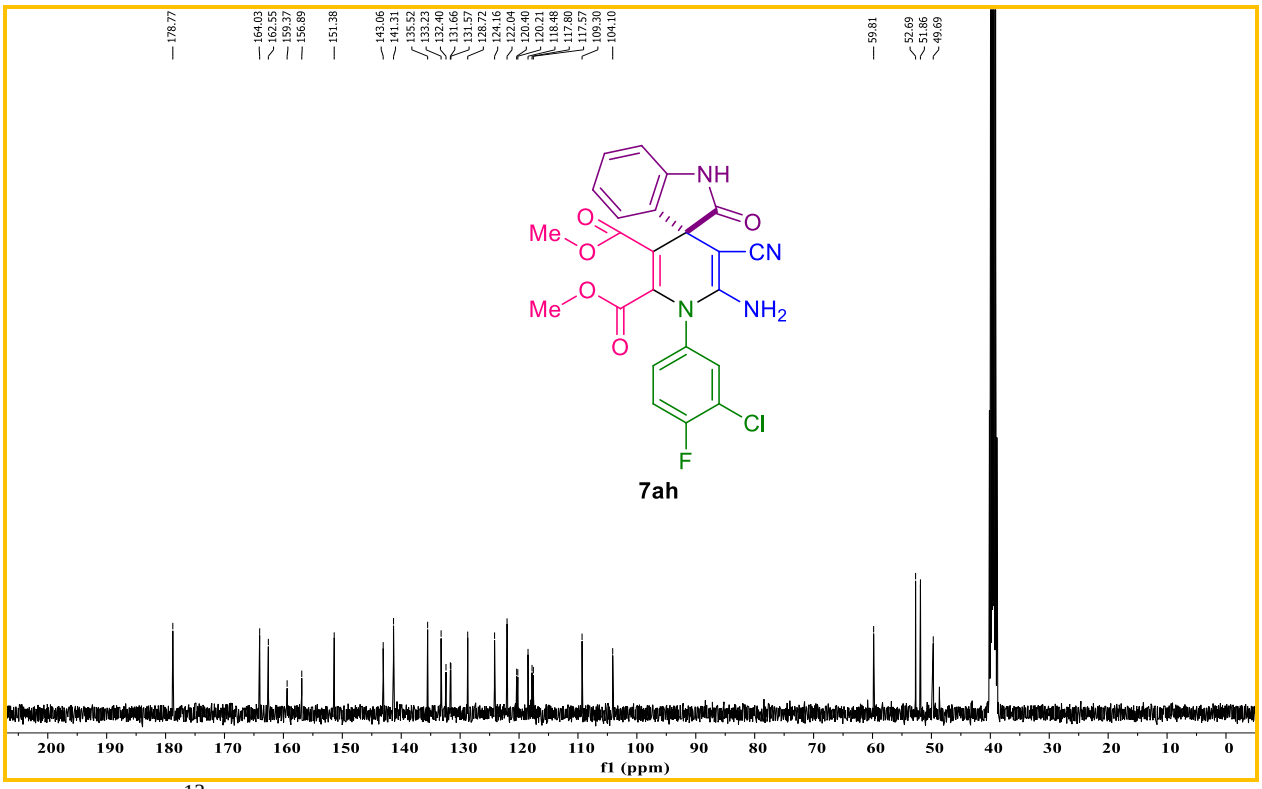


Figure S77: ^{13}C NMR spectra of dimethyl 2'-amino-1'-(3-chloro-4-fluorophenyl)-3'-cyano-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7ah**

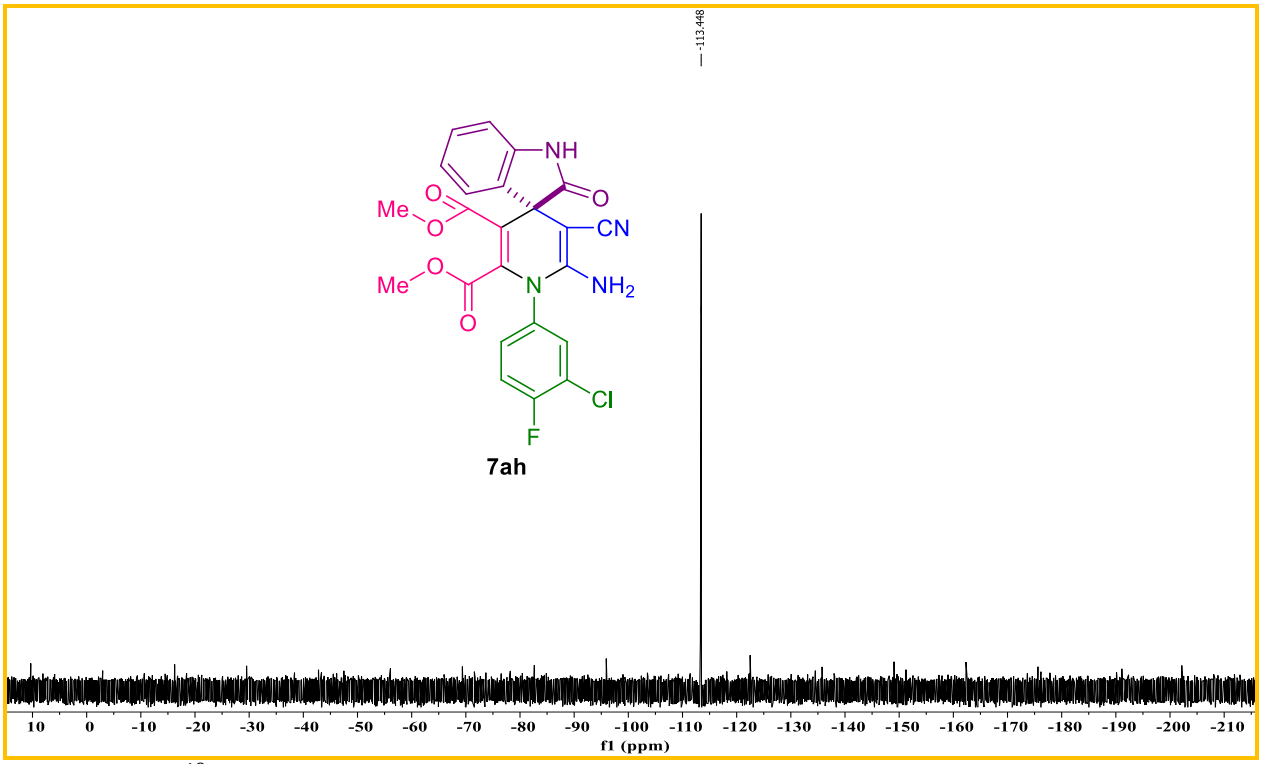


Figure S78: ^{19}F NMR spectra of dimethyl 2'-amino-1'-(3-chloro-4-fluorophenyl)-3'-cyano-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7ah**

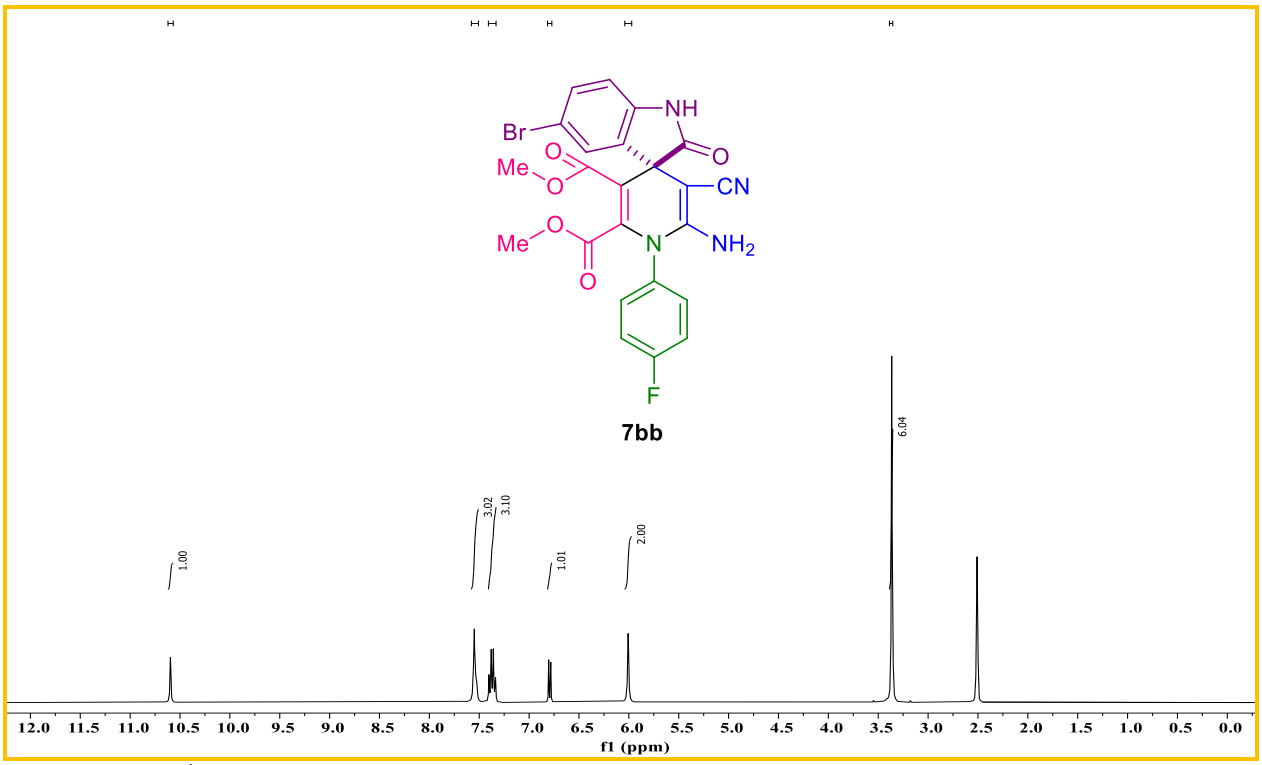


Figure S79: ^{1}H NMR spectra of dimethyl 2'-amino-5-bromo-3'-cyano-1'-(4-fluorophenyl)-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7bb**

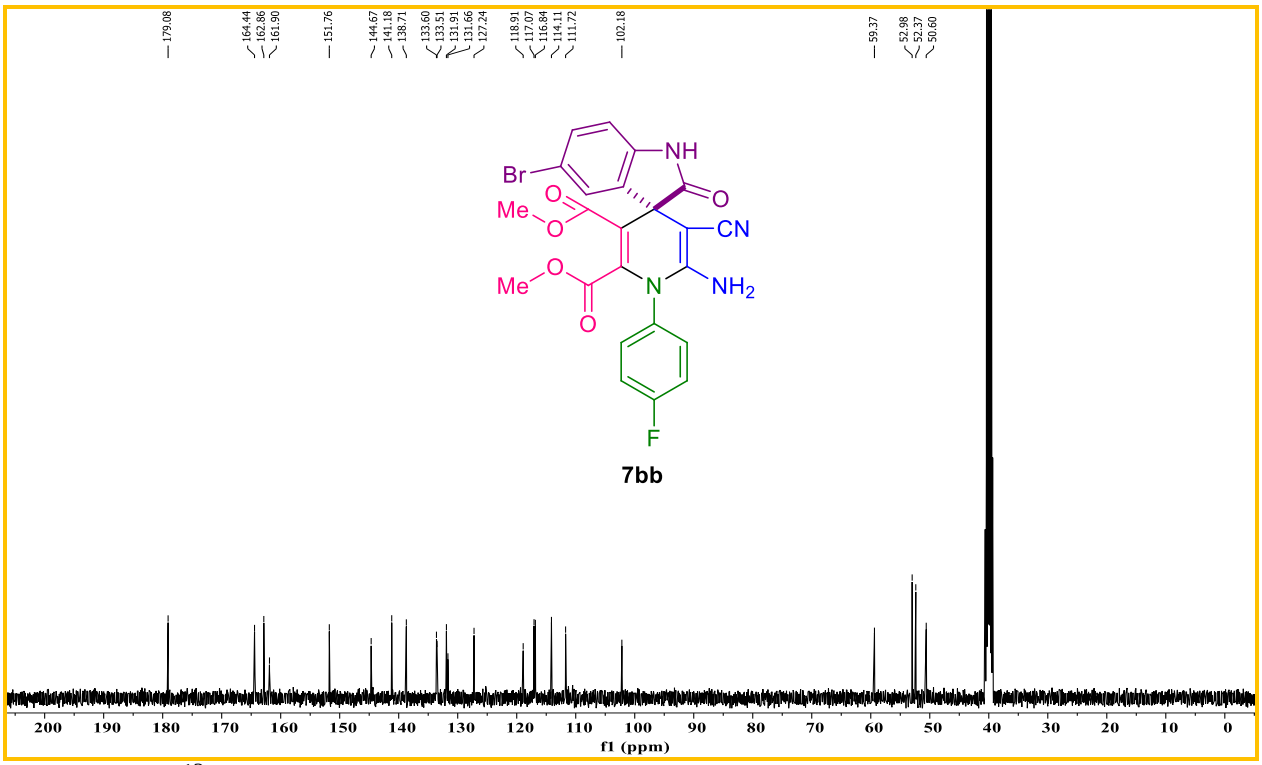


Figure S80: ^{13}C NMR spectra of dimethyl 2'-amino-5-bromo-3'-cyano-1'-(4-fluorophenyl)-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7bb**

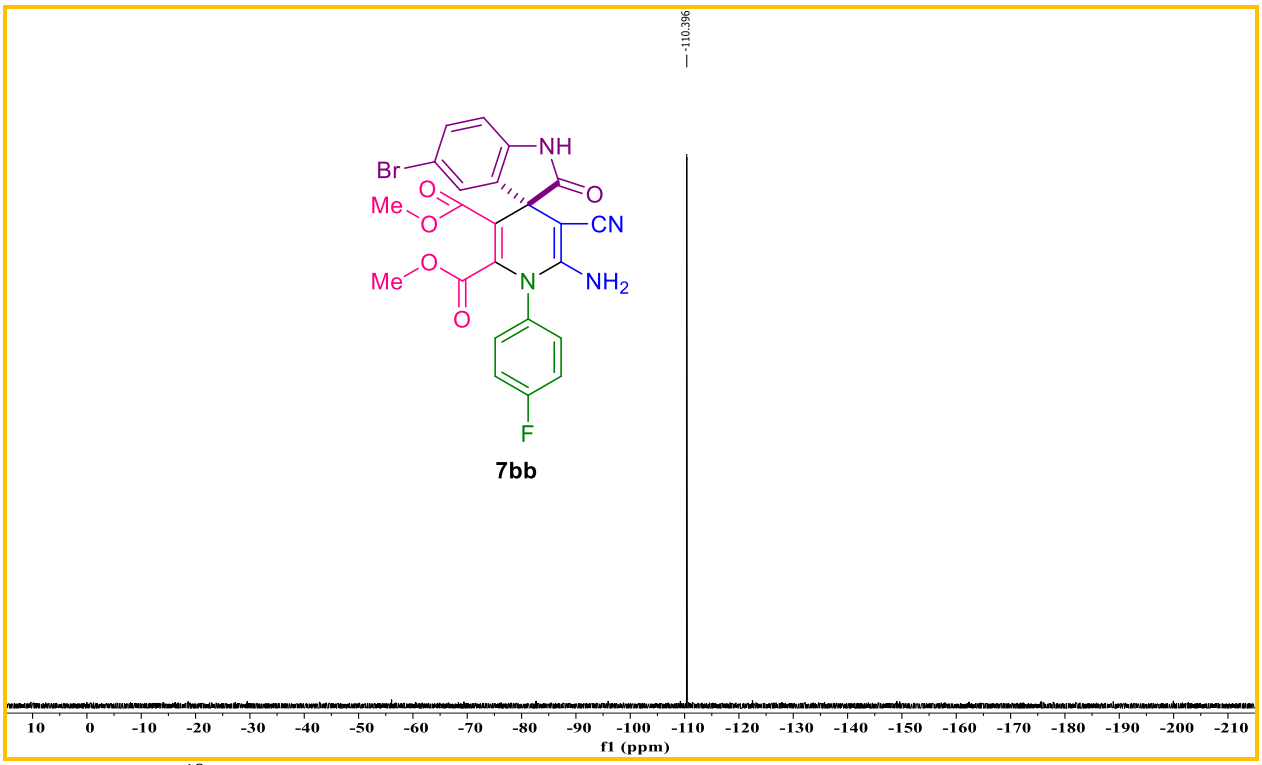


Figure S81: ^{19}F NMR spectra of dimethyl 2'-amino-5-bromo-3'-cyano-1'-(4-fluorophenyl)-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7bb**

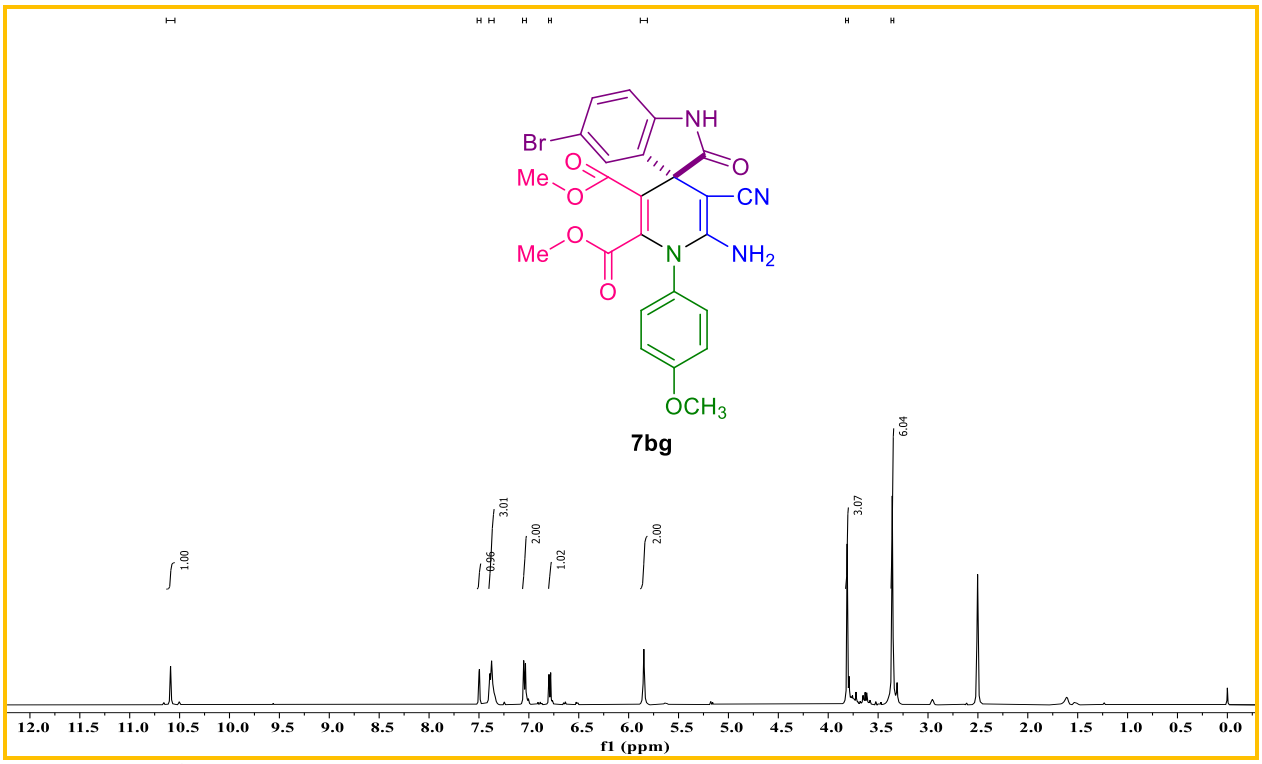


Figure S82: ^{1}H NMR spectra of dimethyl 2'-amino-5-bromo-3'-cyano-1'-(4-methoxyphenyl)-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7bg**

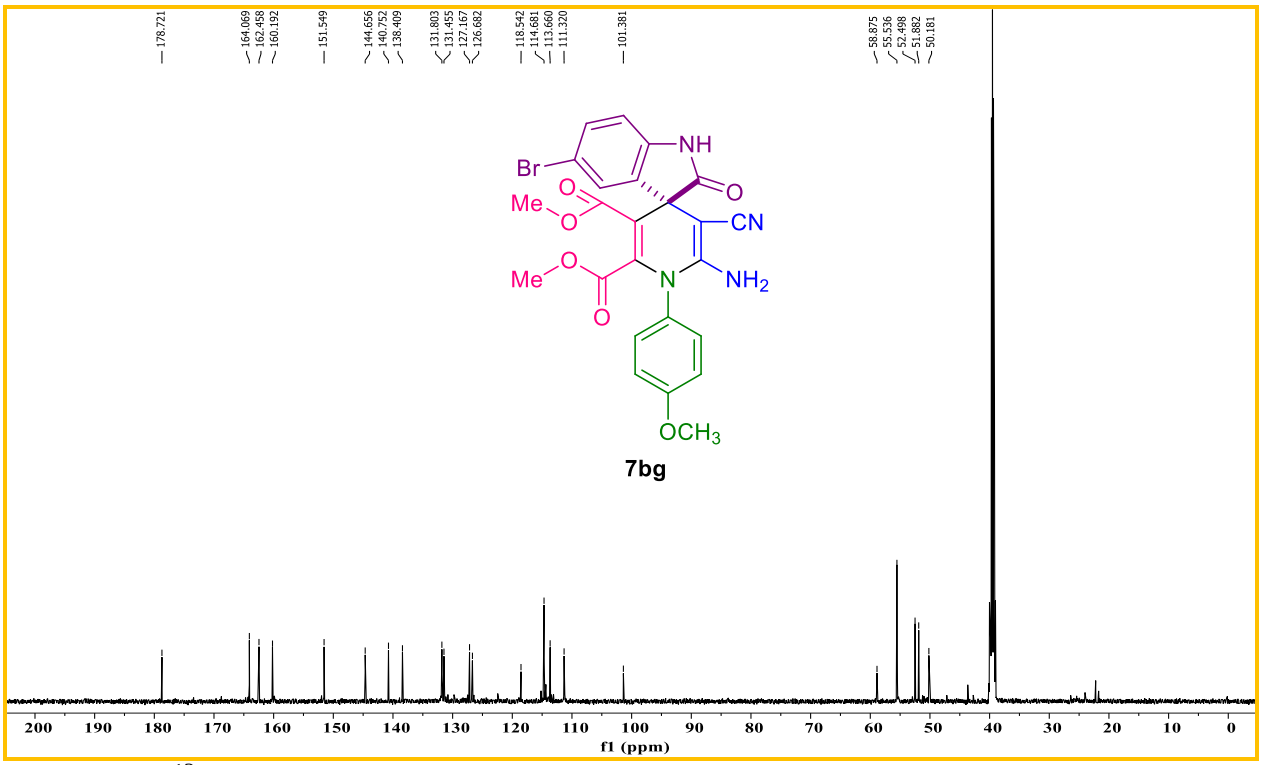


Figure S83: ^{13}C NMR spectra of dimethyl 2'-amino-5-bromo-3'-cyano-1'-(4-methoxyphenyl)-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7bg**

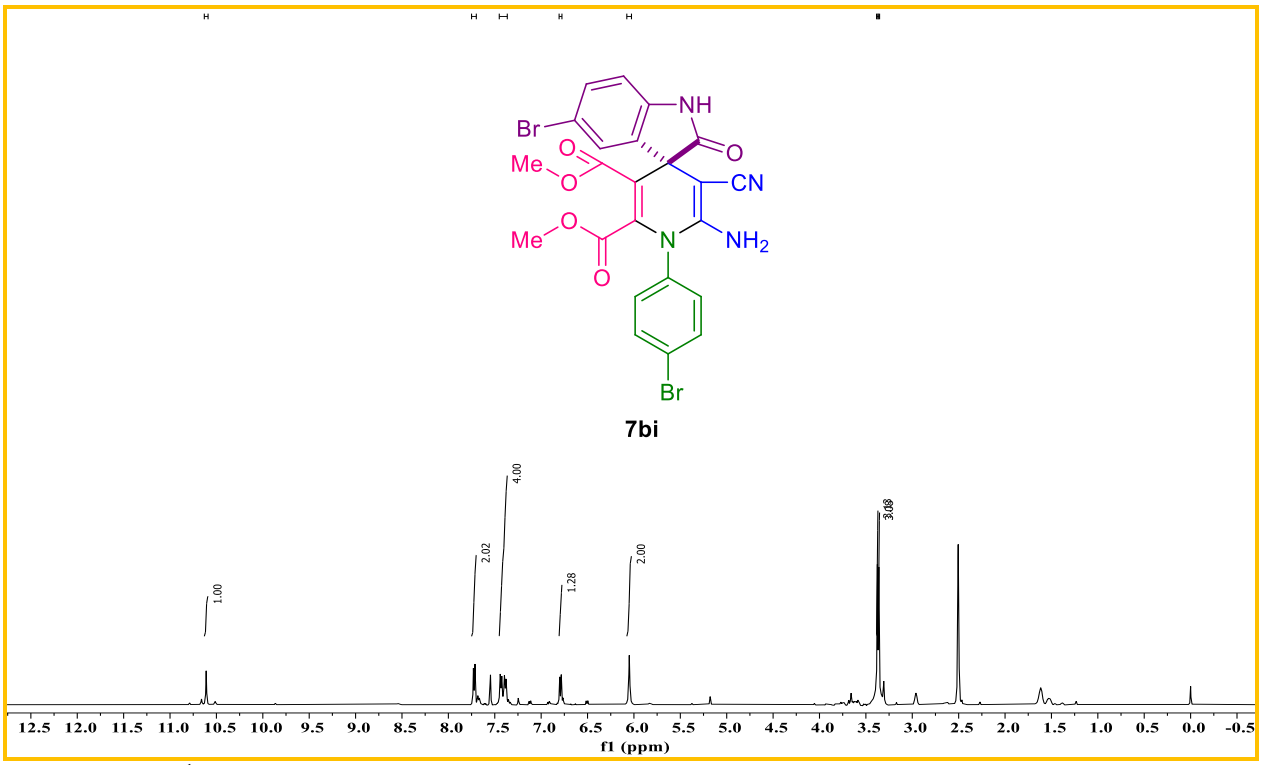


Figure S84: ^{1}H NMR spectra of dimethyl 2'-amino-5-bromo-1'-(4-bromophenyl)-3'-cyano-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7bi**

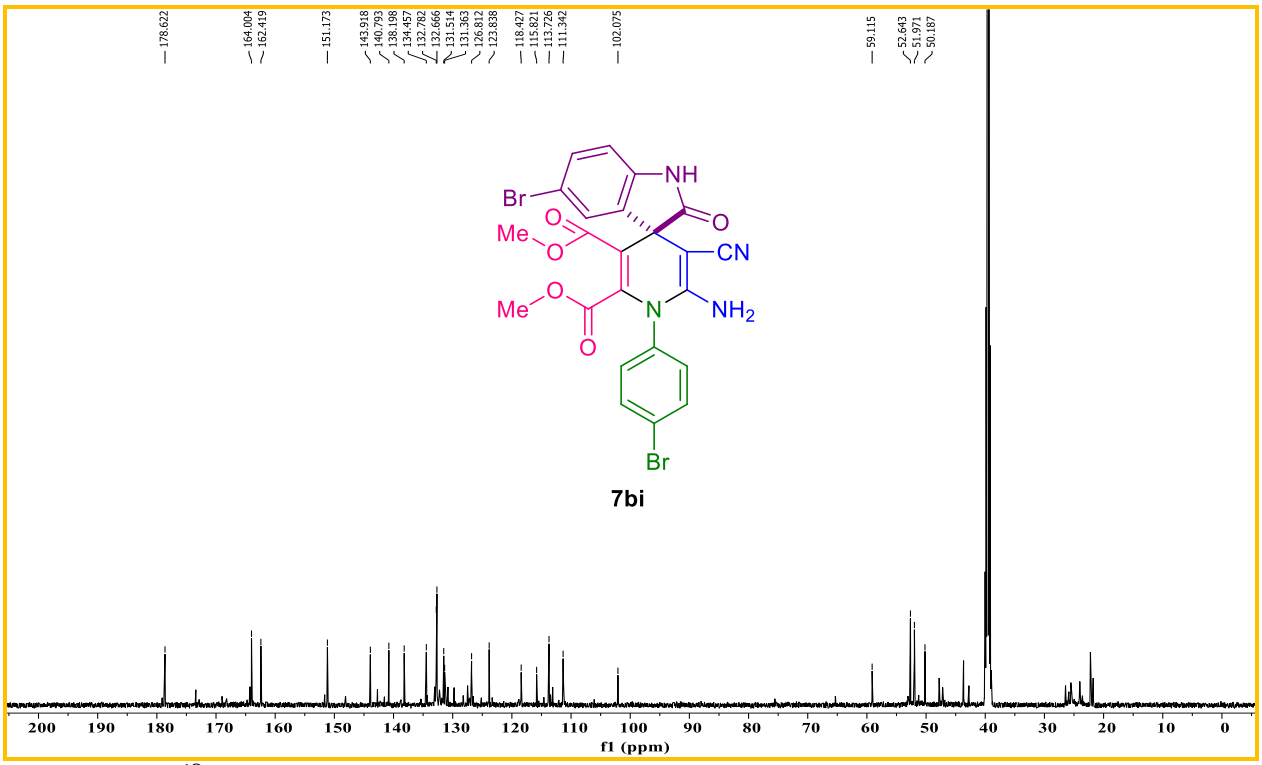


Figure S85: ^{13}C NMR spectra of dimethyl 2'-amino-5-bromo-1'-(4-bromophenyl)-3'-cyano-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7bi**

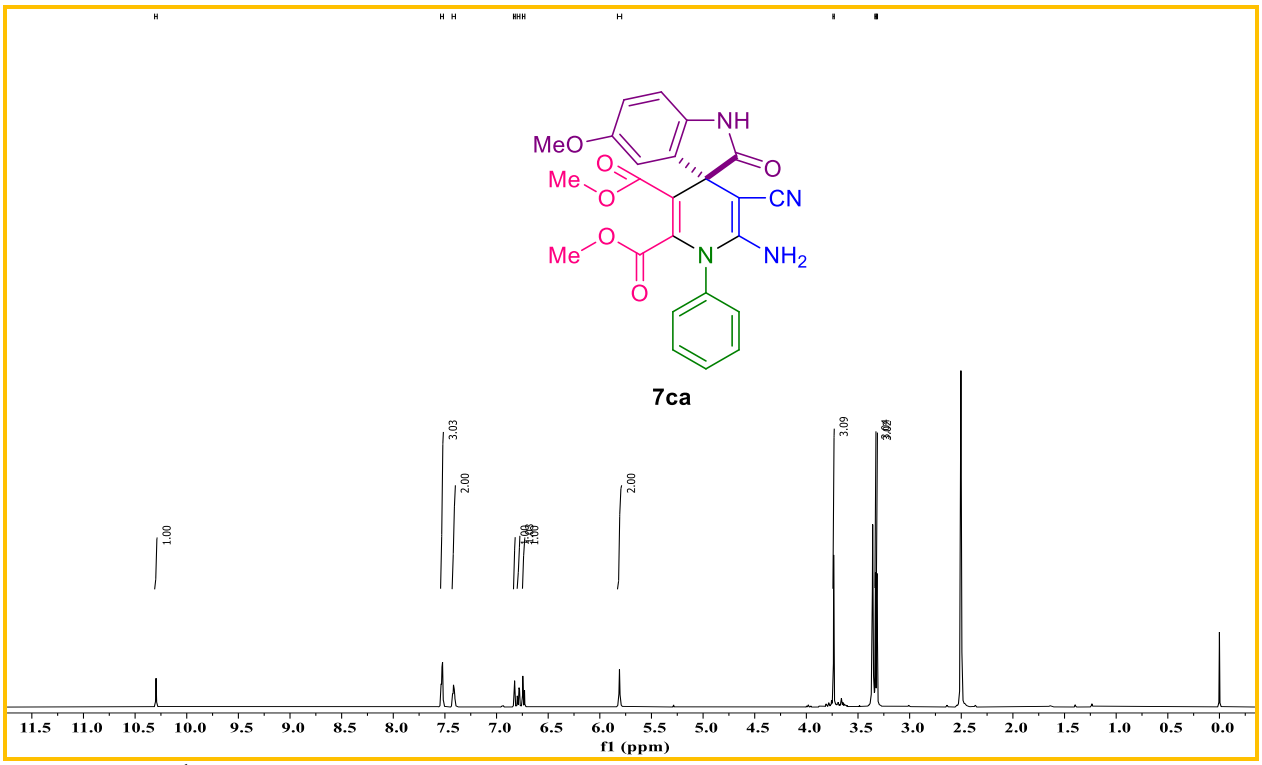


Figure S86: ^{1}H NMR spectra of dimethyl 2'-amino-3'-cyano-5-methoxy-2-oxo-1'-phenyl-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7ca**

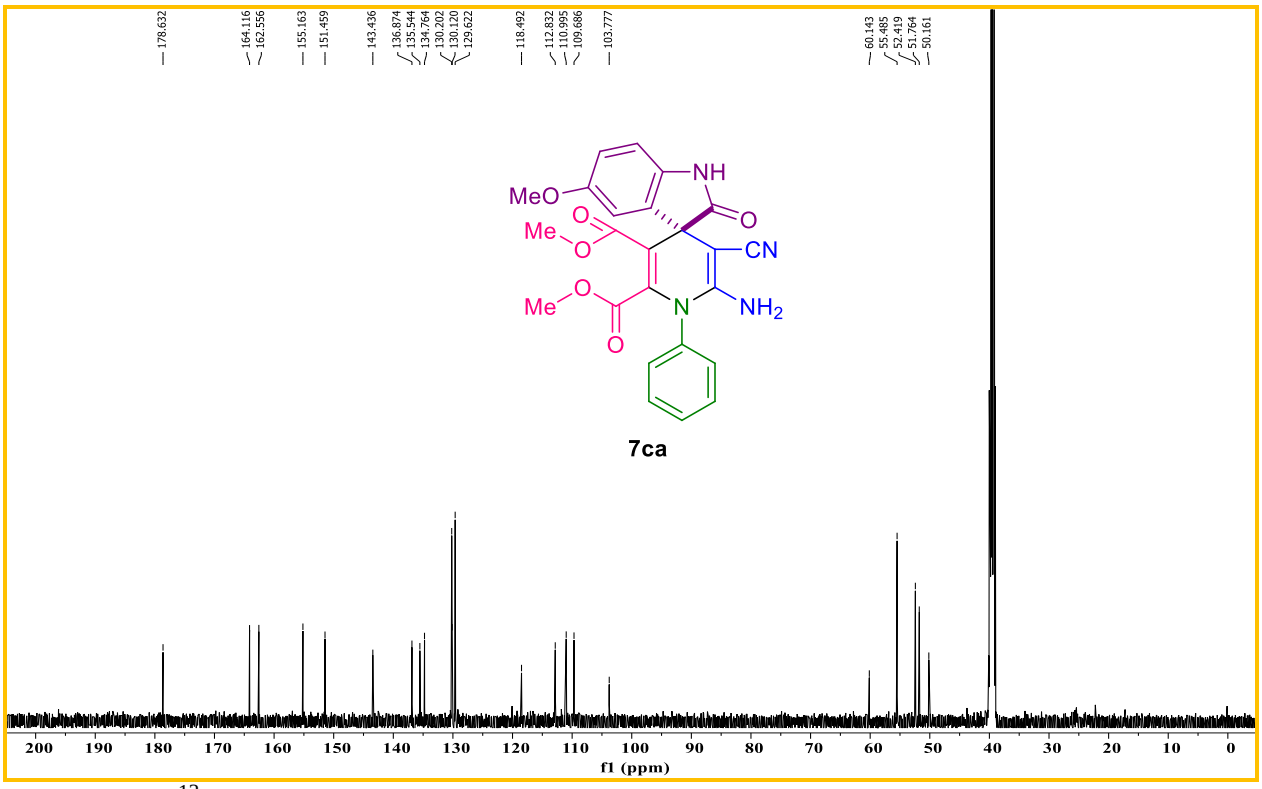


Figure S87: ^{13}C NMR spectra of dimethyl 2'-amino-3'-cyano-5-methoxy-2-oxo-1'-phenyl-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7ca**

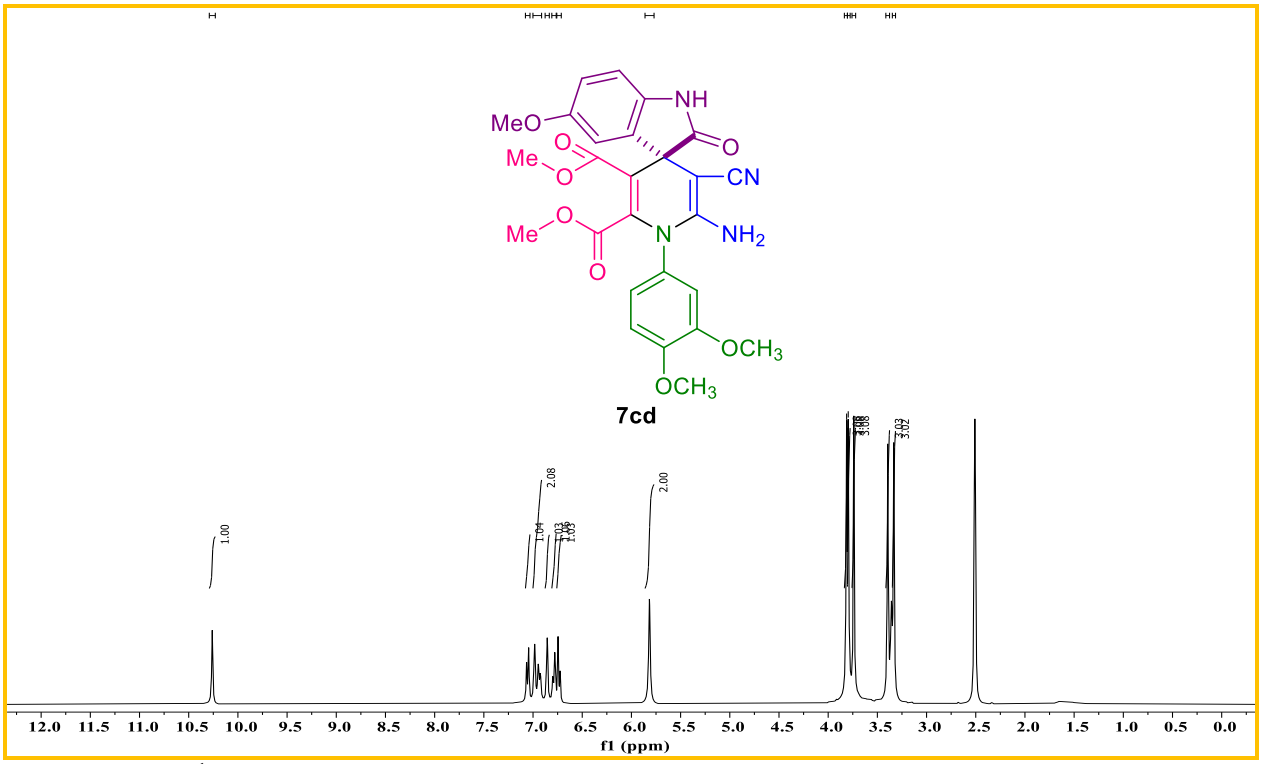


Figure S88: ^{1}H NMR spectra of dimethyl 2'-amino-3'-cyano-1'-(3,4-dimethoxyphenyl)-5-methoxy-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7cd**

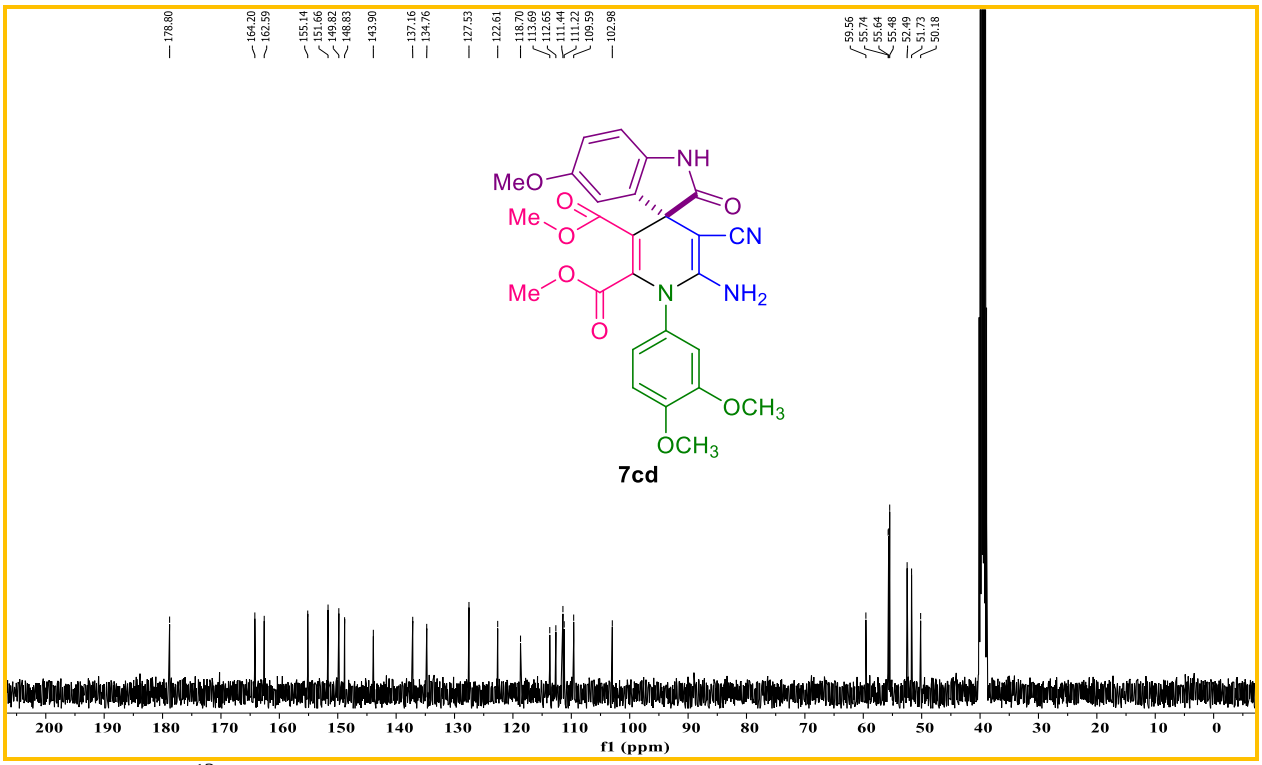


Figure S89: ^{13}C NMR spectra of dimethyl 2'-amino-3'-cyano-1'-(3,4-dimethoxyphenyl)-5-methoxy-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7cd**

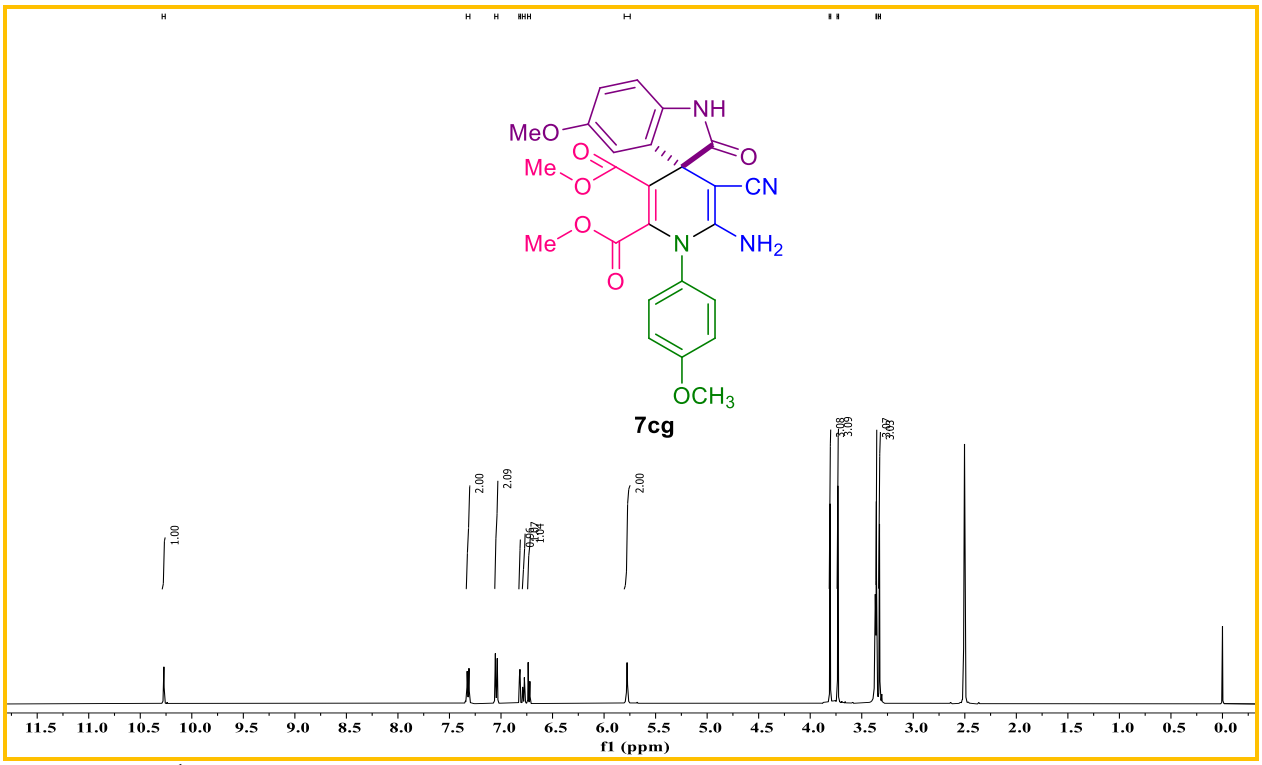


Figure S90: ^{1}H NMR spectra of dimethyl 2'-amino-3'-cyano-5-methoxy-1'-(4-methoxyphenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7cg**

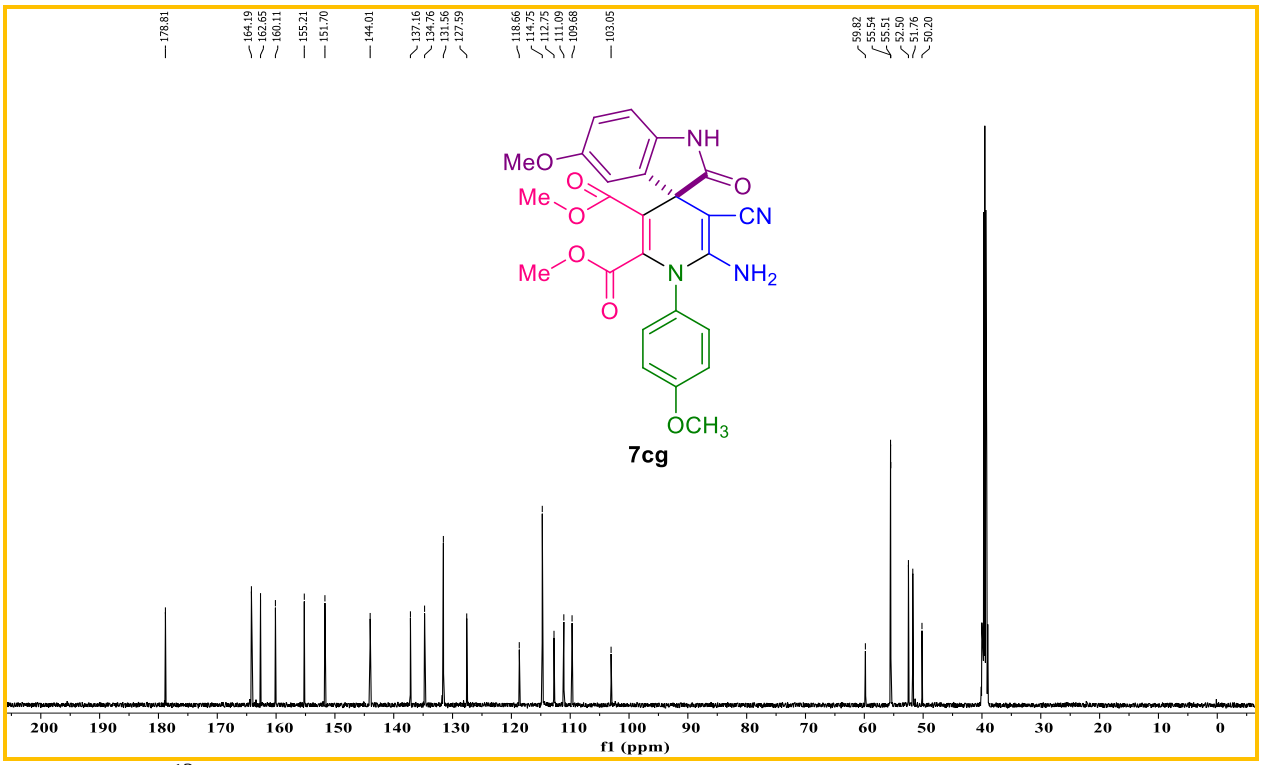


Figure S91: ^{13}C NMR spectra of dimethyl 2'-amino-3'-cyano-5-methoxy-1'-(4-methoxyphenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7cg**

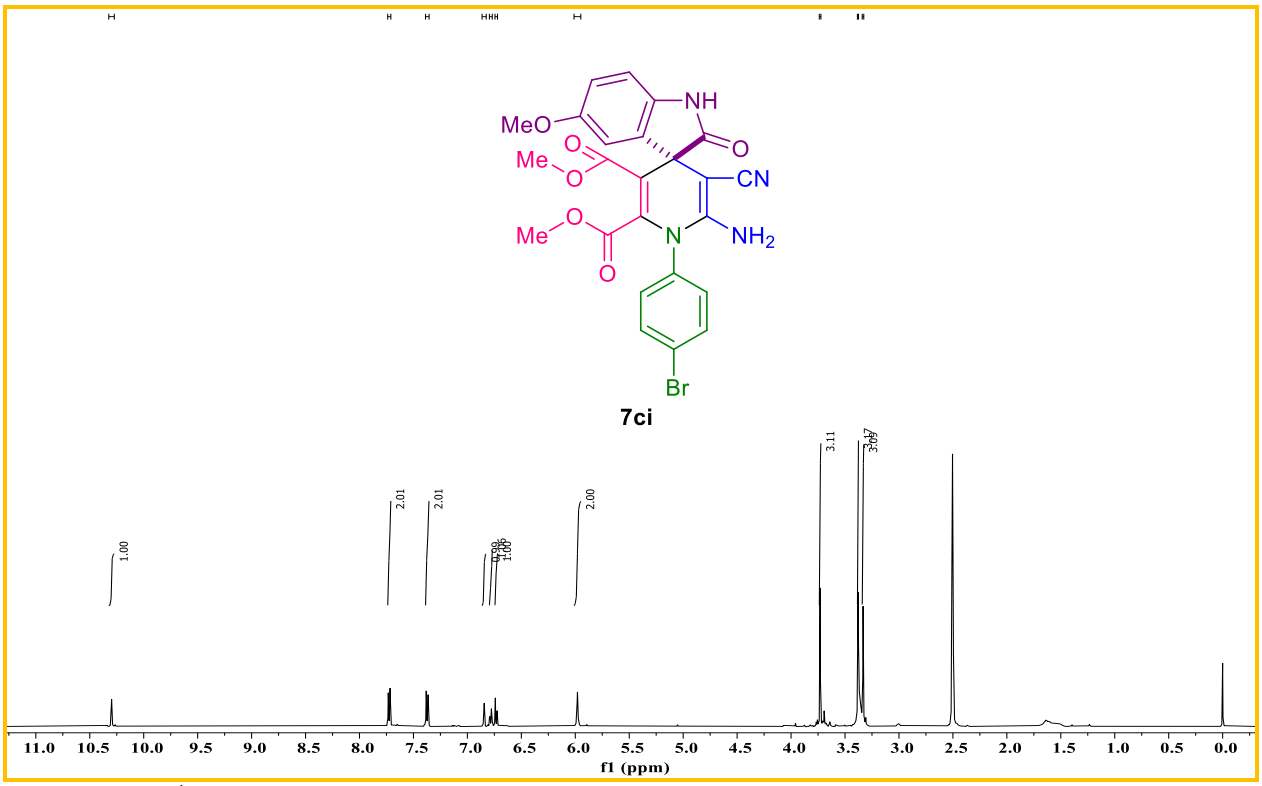


Figure S92: ^{1}H NMR spectra of dimethyl 2'-amino-1'-(4-bromophenyl)-3'-cyano-5-methoxy-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7ci**

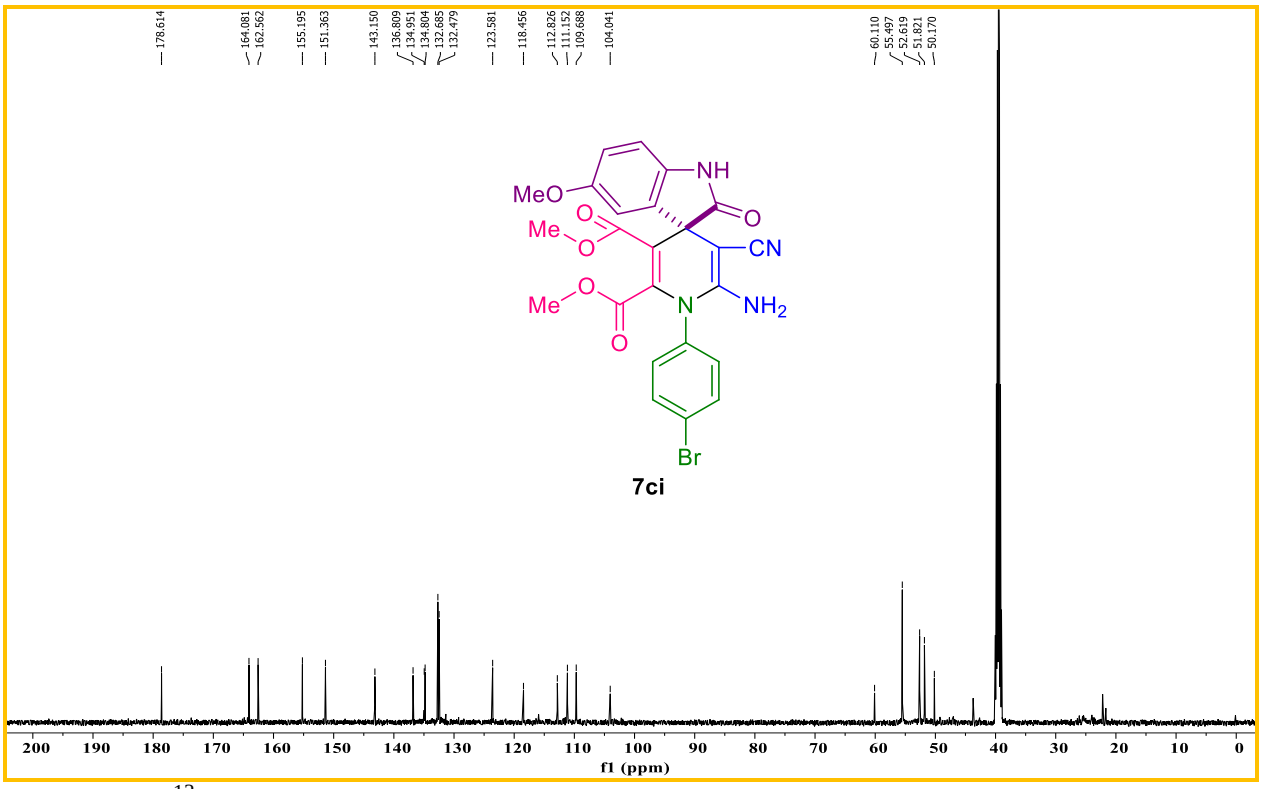


Figure S93: ^{13}C NMR spectra of dimethyl 2'-amino-1'-(4-bromophenyl)-3'-cyano-5-methoxy-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7ci**

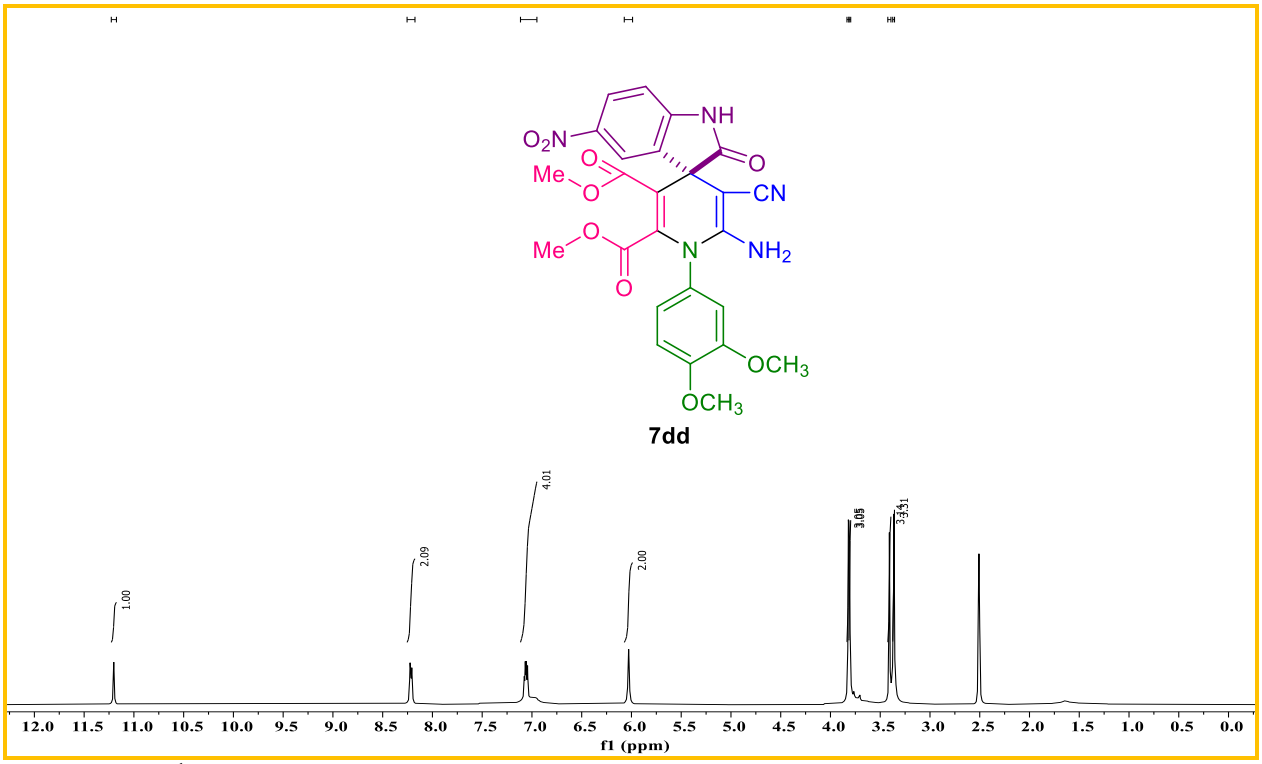


Figure S94: ^{1}H NMR spectra of dimethyl 2'-amino-3'-cyano-1'-(3,4-dimethoxyphenyl)-5-nitro-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7dd**

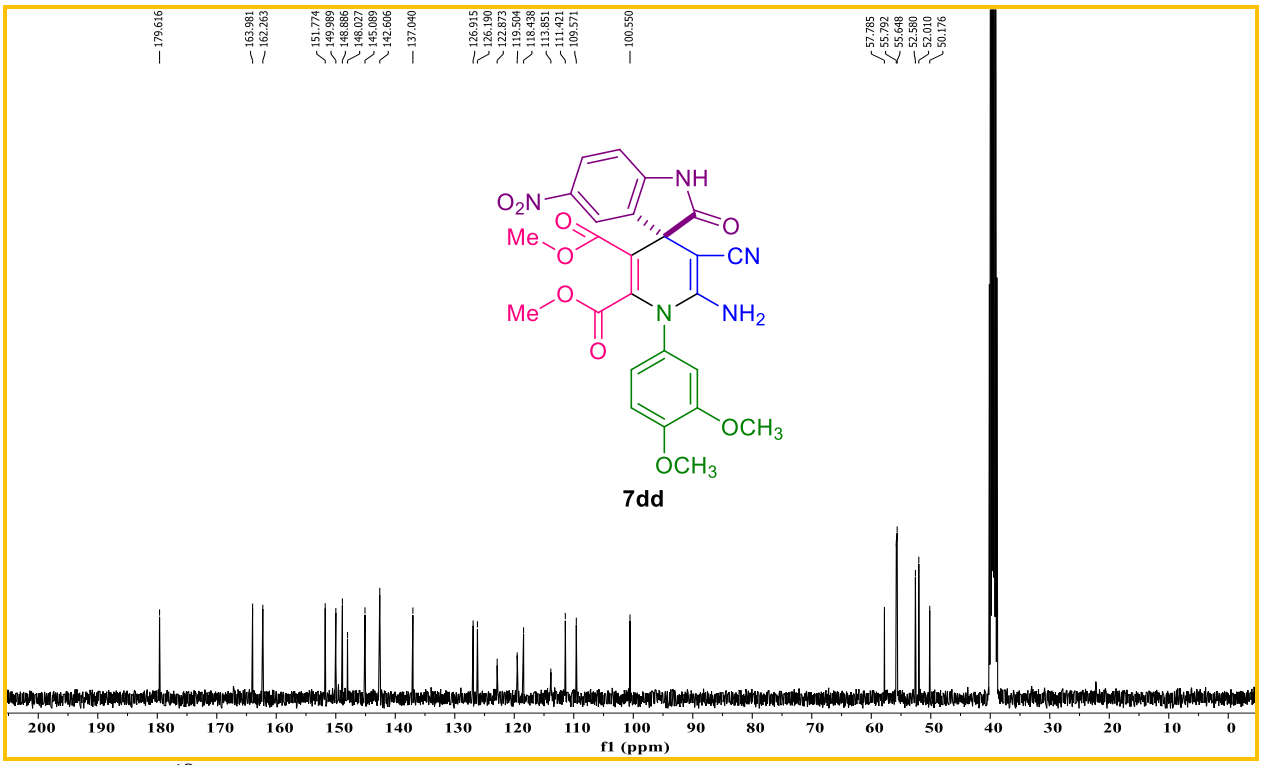


Figure S95: ^{13}C NMR spectra of dimethyl 2'-amino-3'-cyano-1'-(3,4-dimethoxyphenyl)-5-nitro-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7dd**

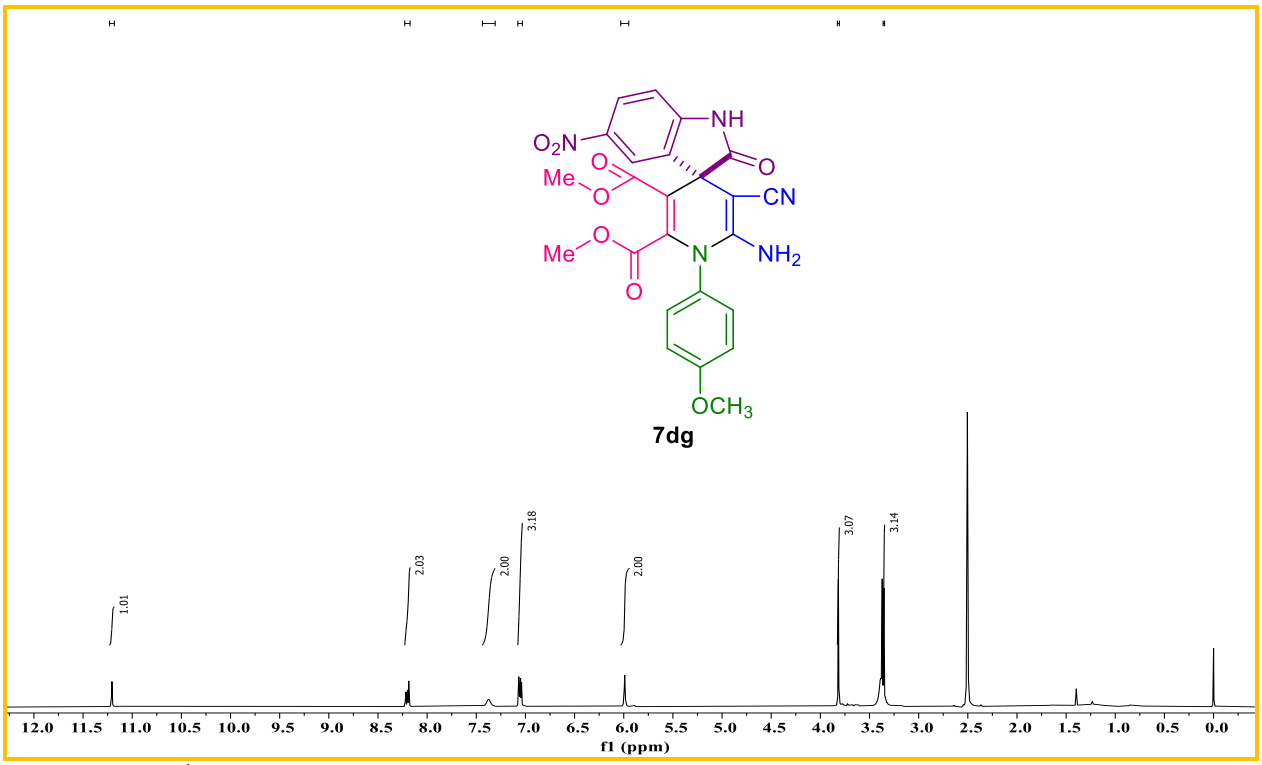


Figure S96: ^{1}H NMR spectra of dimethyl 2'-amino-3'-cyano-1'-(4-methoxyphenyl)-5-nitro-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7dg**

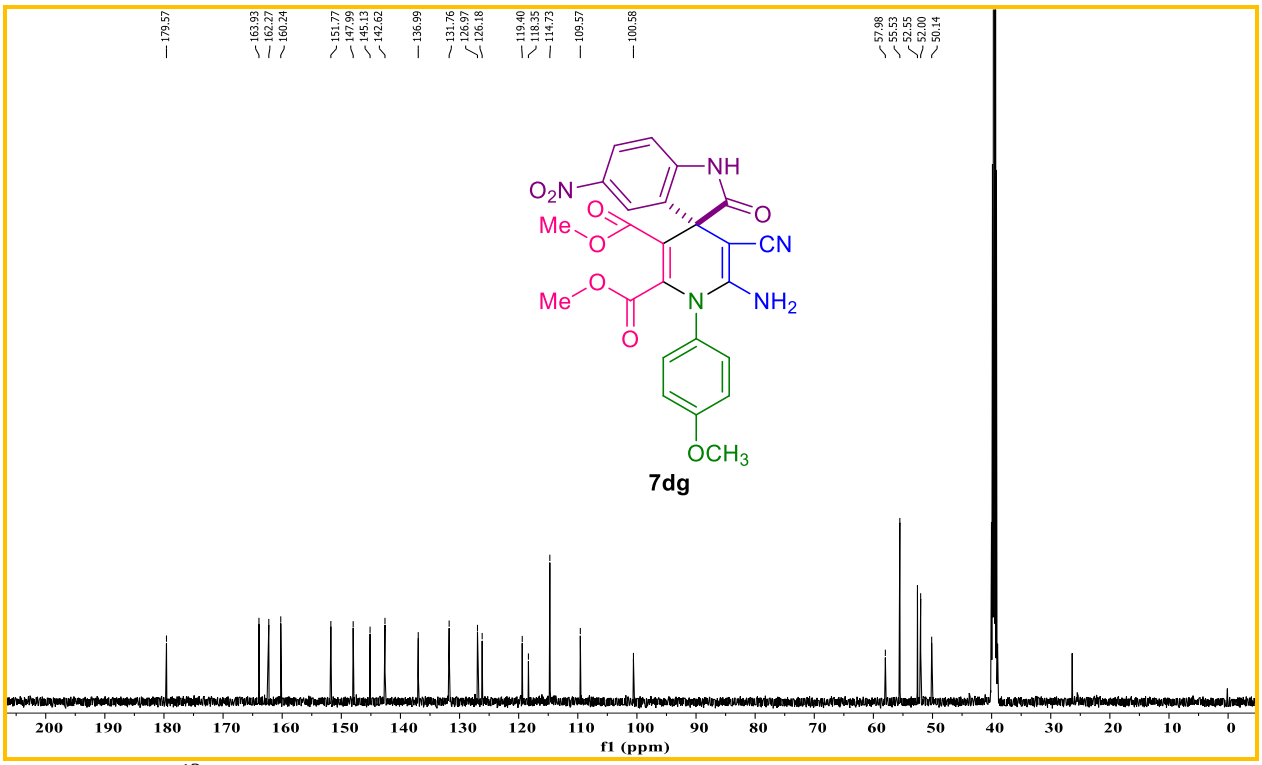


Figure S97: ^{13}C NMR spectra of dimethyl 2'-amino-3'-cyano-1'-(4-methoxyphenyl)-5-nitro-2-oxo-1'H-spiro[indoline-3,4'-pyridine]-5',6'-dicarboxylate **7dg**

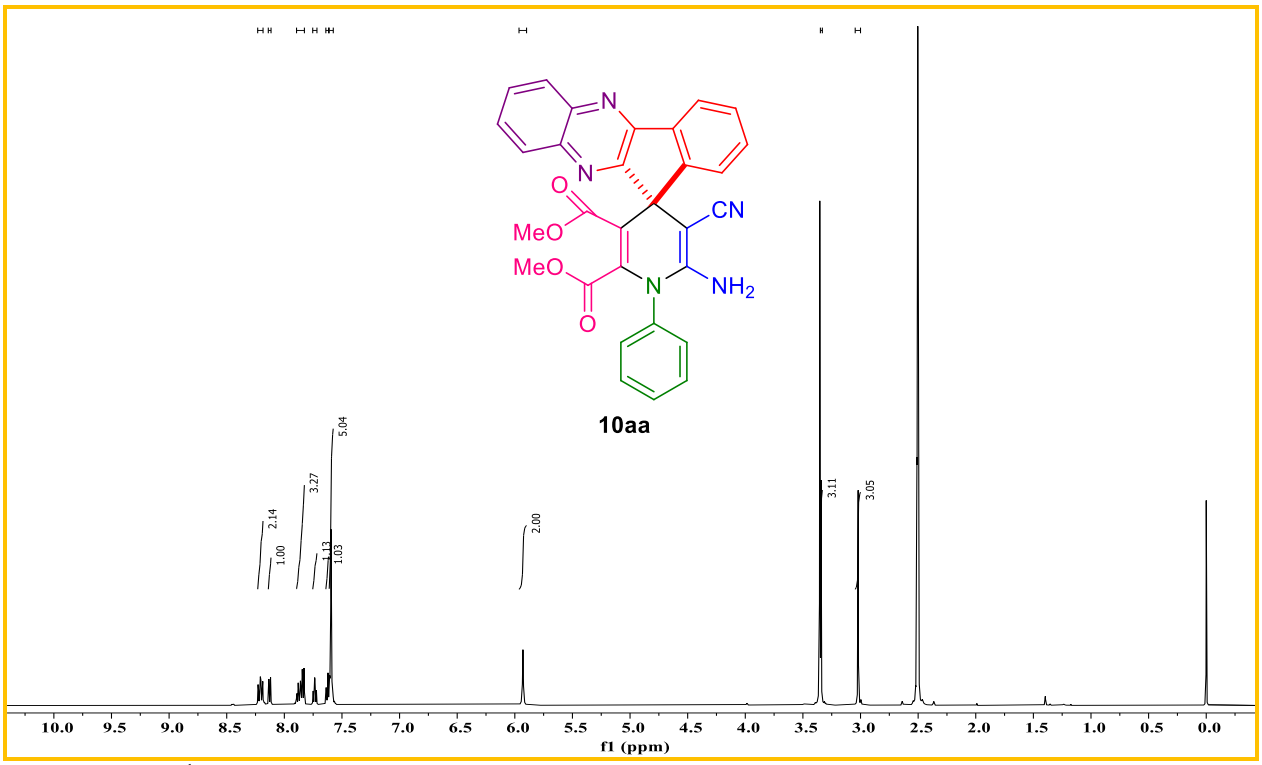


Figure S98: ^{1}H NMR spectra of dimethyl 2'-amino-3'-cyano-1'-phenyl-1'*H*-spiro[indeno[1,2-*b*]quinoxaline-11,4'-pyridine]-5',6'-dicarboxylate **10aa**

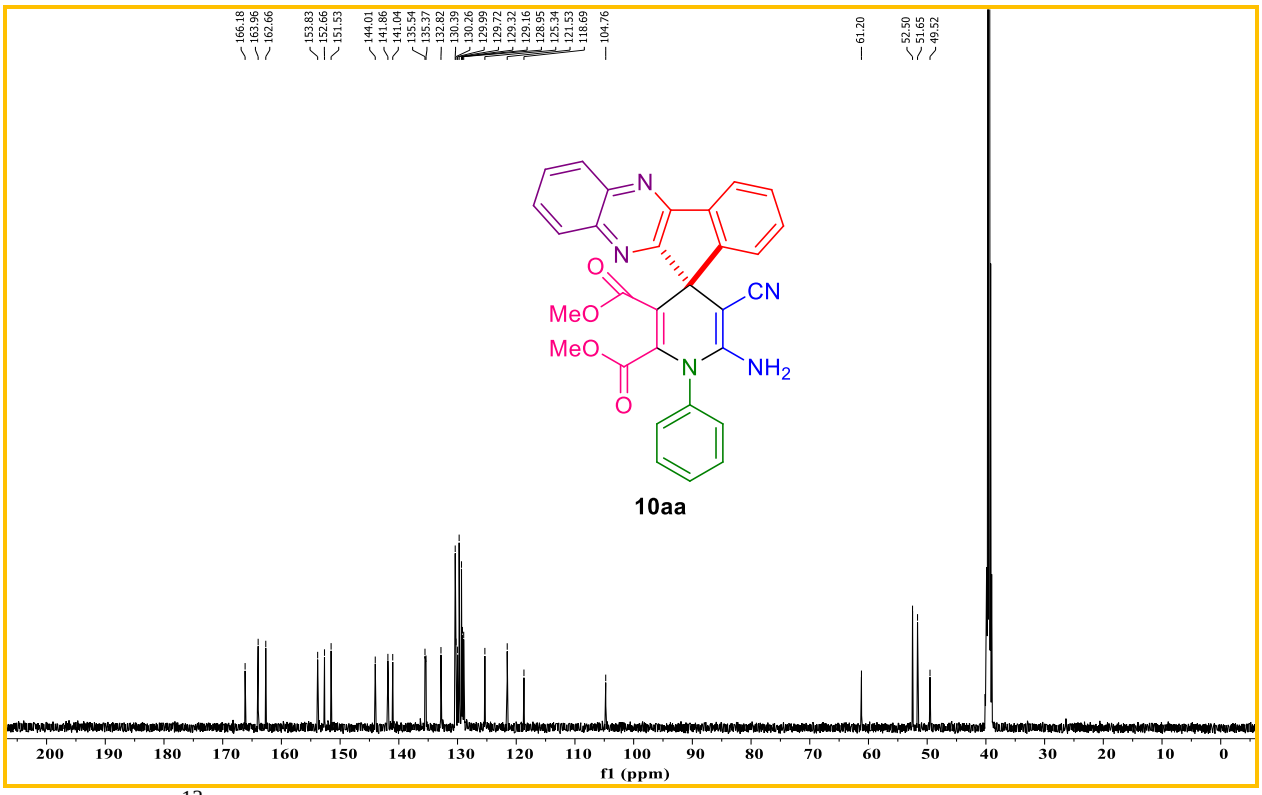


Figure S99: ^{13}C NMR spectra of dimethyl 2'-amino-3'-cyano-1'-phenyl-1'*H*-spiro[indeno[1,2-*b*]quinoxaline-11,4'-pyridine]-5',6'-dicarboxylate **10aa**

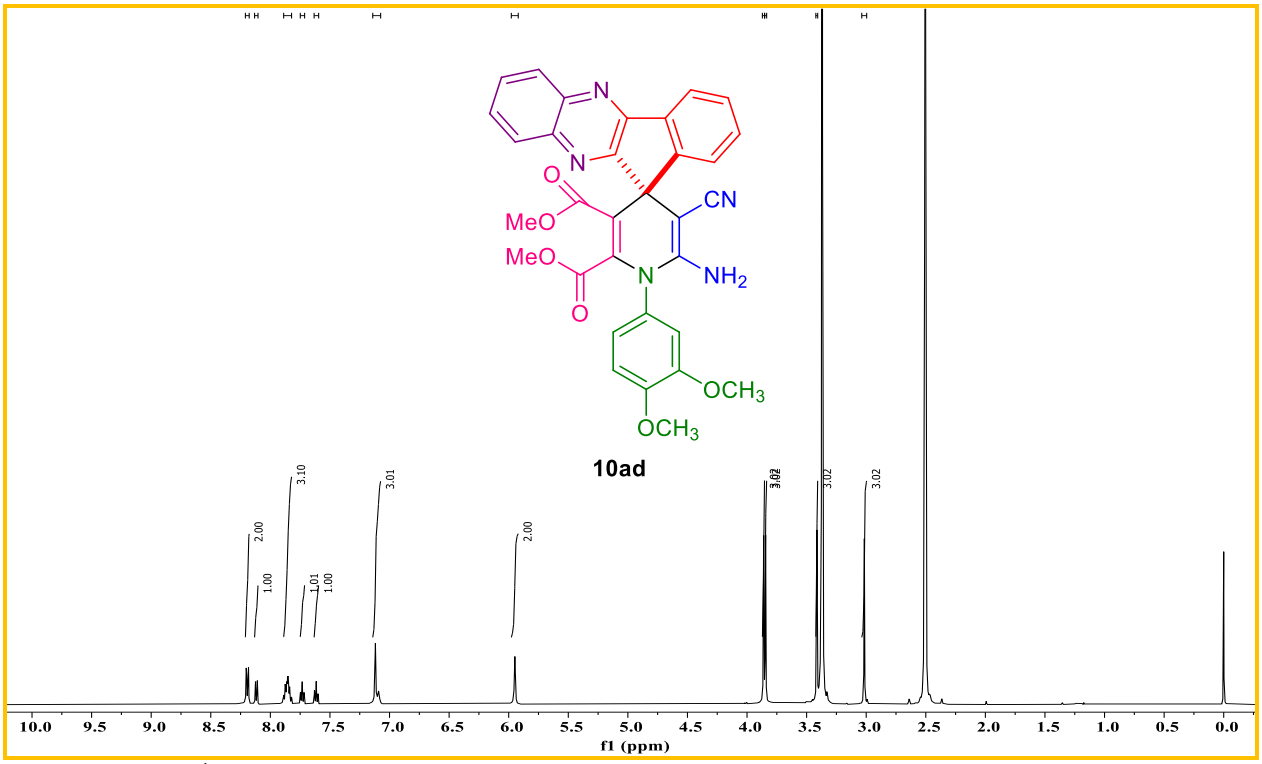


Figure S100: ^{1}H NMR spectra of dimethyl 2'-amino-3'-cyano-1'-(3,4-dimethoxyphenyl)-1'*H*-spiro[indeno[1,2-*b*]quinoxaline-11,4'-pyridine]-5',6'-dicarboxylate **10ad**

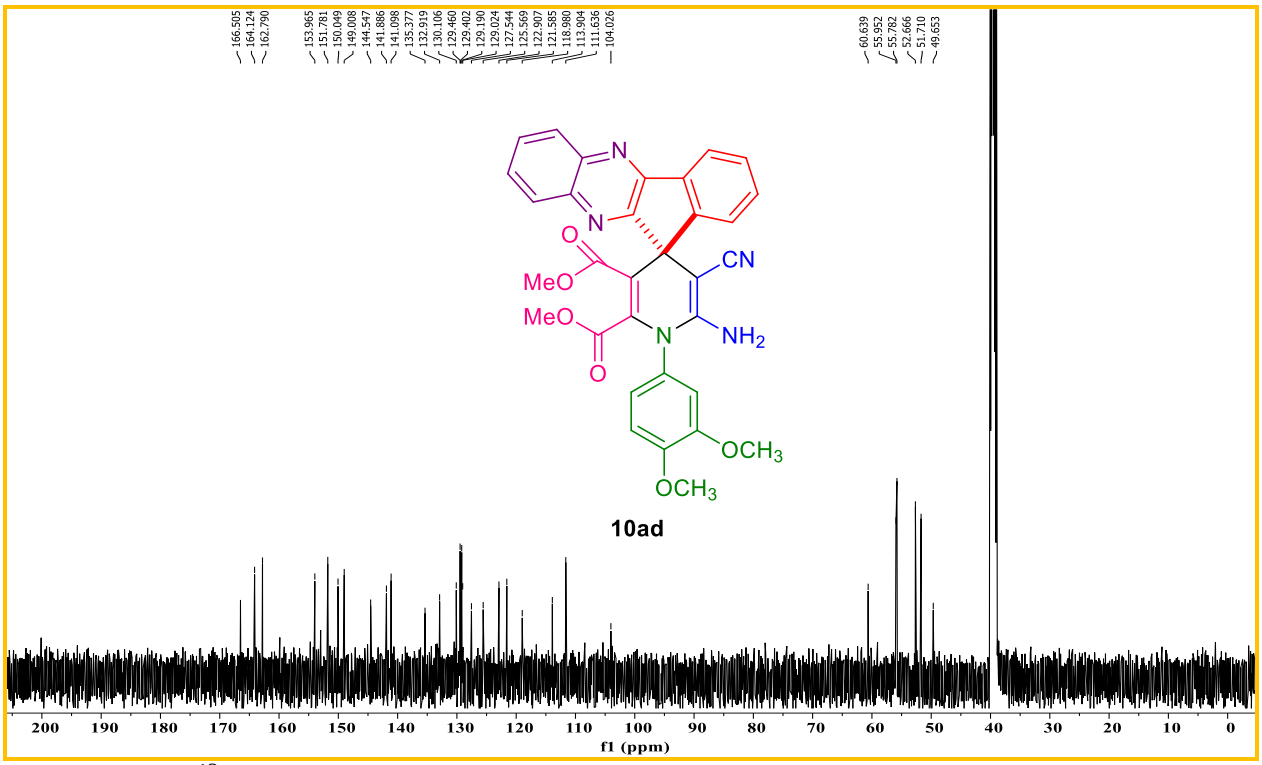


Figure S101: ^{13}C NMR spectra of dimethyl 2'-amino-3'-cyano-1'-(3,4-dimethoxyphenyl)-1'*H*-spiro[indeno[1,2-*b*]quinoxaline-11,4'-pyridine]-5',6'-dicarboxylate **10ad**

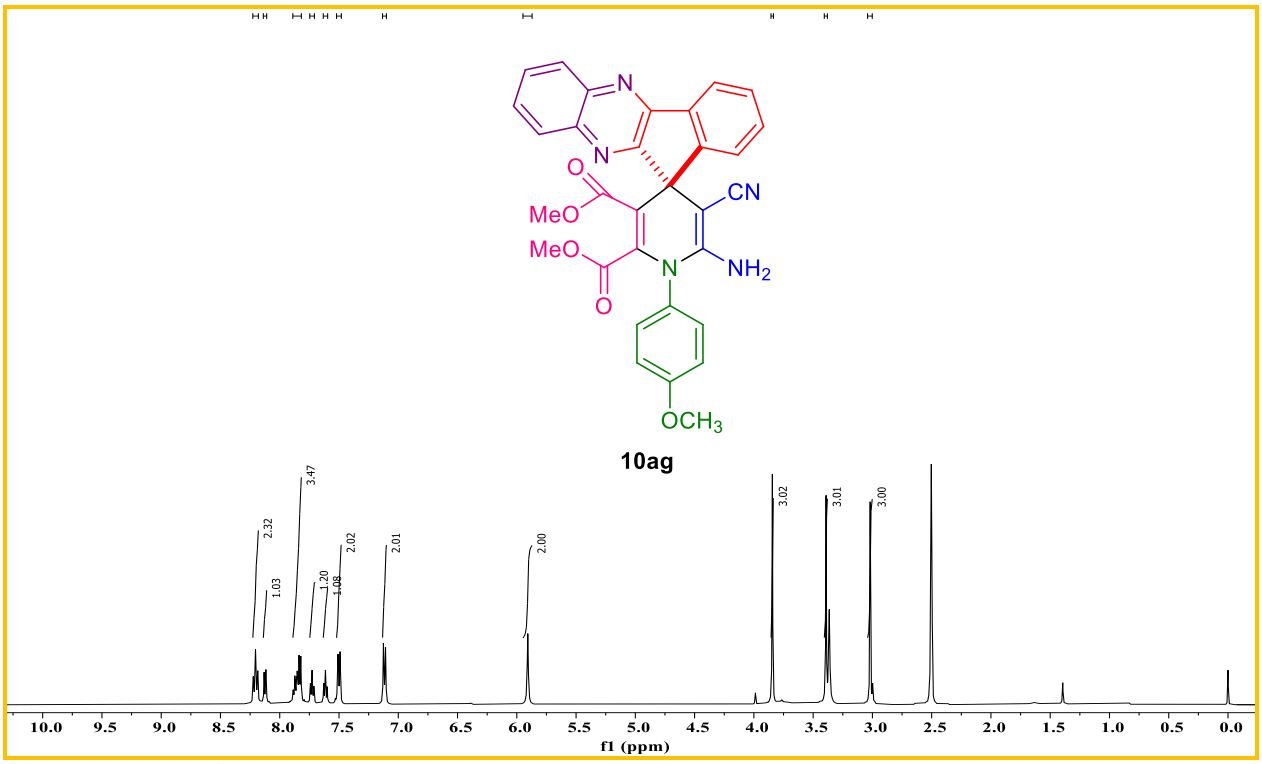


Figure S102: ^{1}H NMR spectra of dimethyl 2'-amino-3'-cyano-1'-(4-methoxyphenyl)-1'*H*-spiro[indeno[1,2-*b*]quinoxaline-11,4'-pyridine]-5',6'-dicarboxylate **10ag**

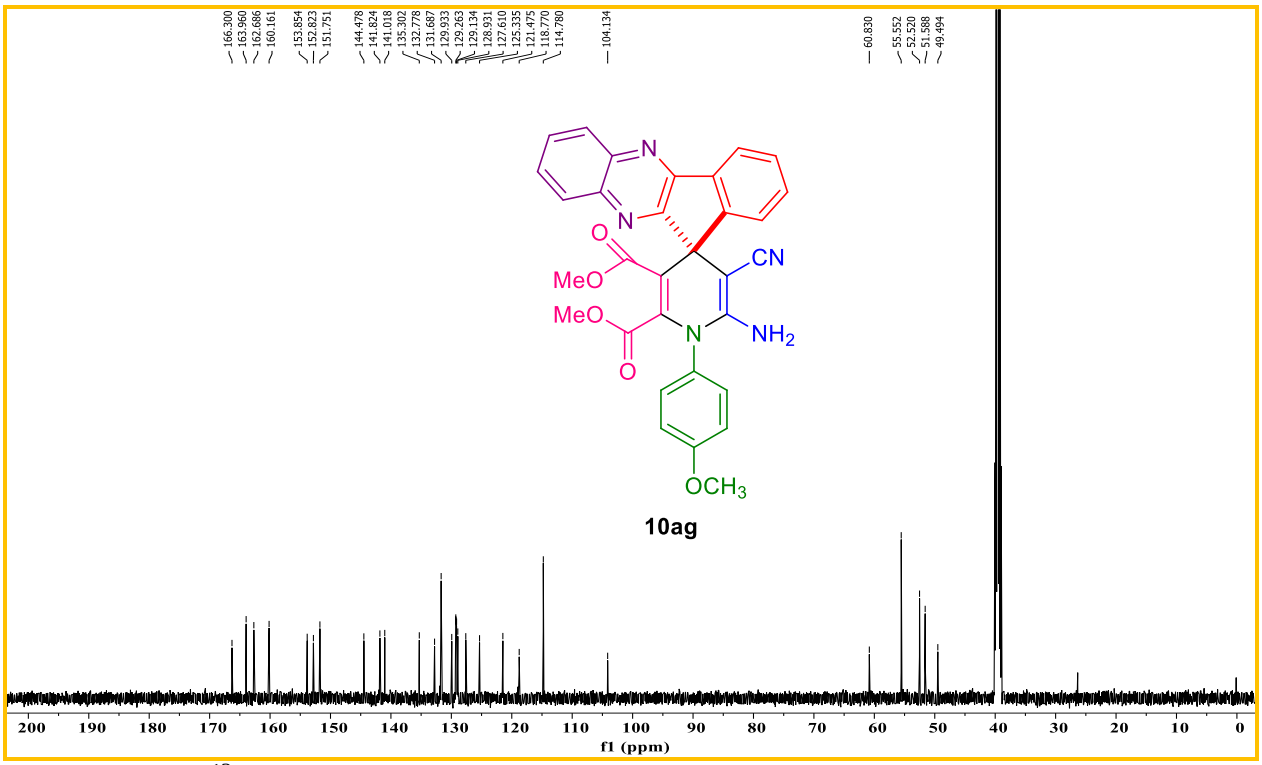


Figure S103: ^{13}C NMR spectra of dimethyl 2'-amino-3'-cyano-1'-(4-methoxyphenyl)-1'*H*-spiro[indeno[1,2-*b*]quinoxaline-11,4'-pyridine]-5',6'-dicarboxylate **10ag**

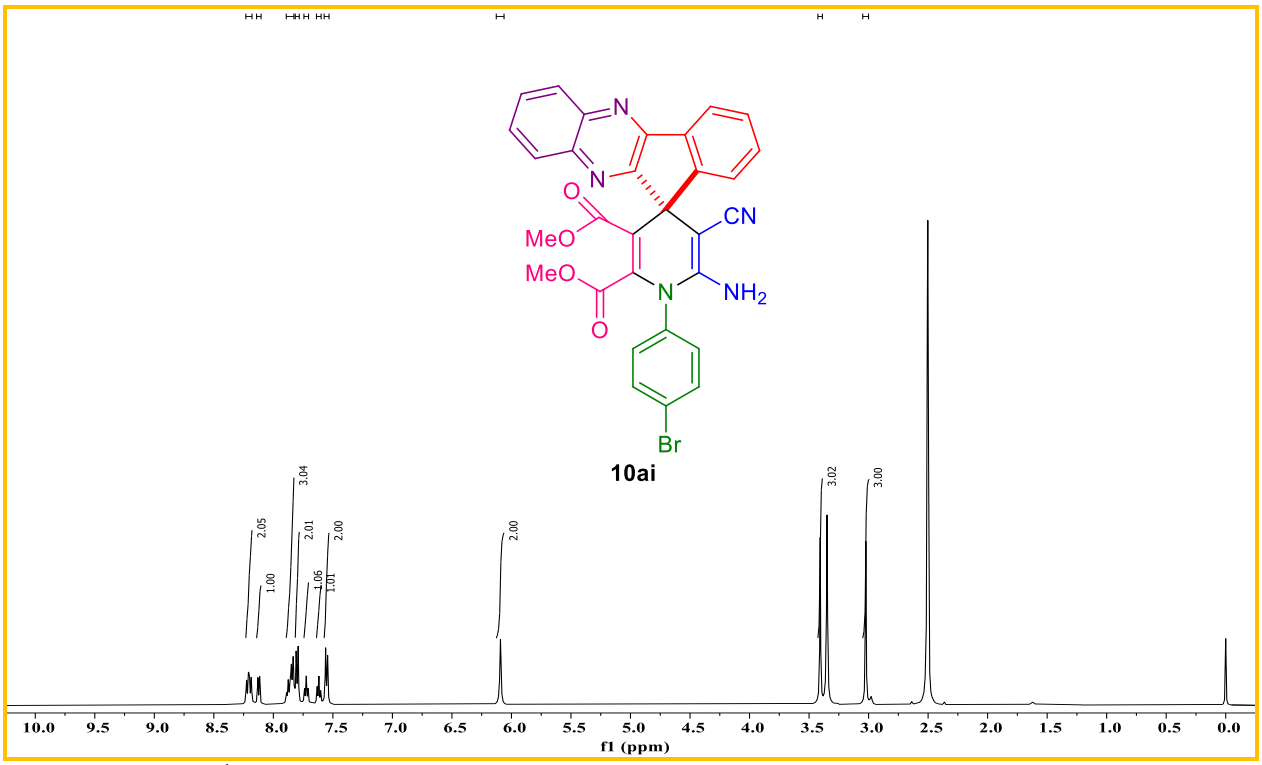


Figure S104: ^{1}H NMR spectra of dimethyl 2'-amino-1'-(4-bromophenyl)-3'-cyano-1'*H*-spiro[indeno[1,2-*b*]quinoxaline-11,4'-pyridine]-5',6'-dicarboxylate **10ai**

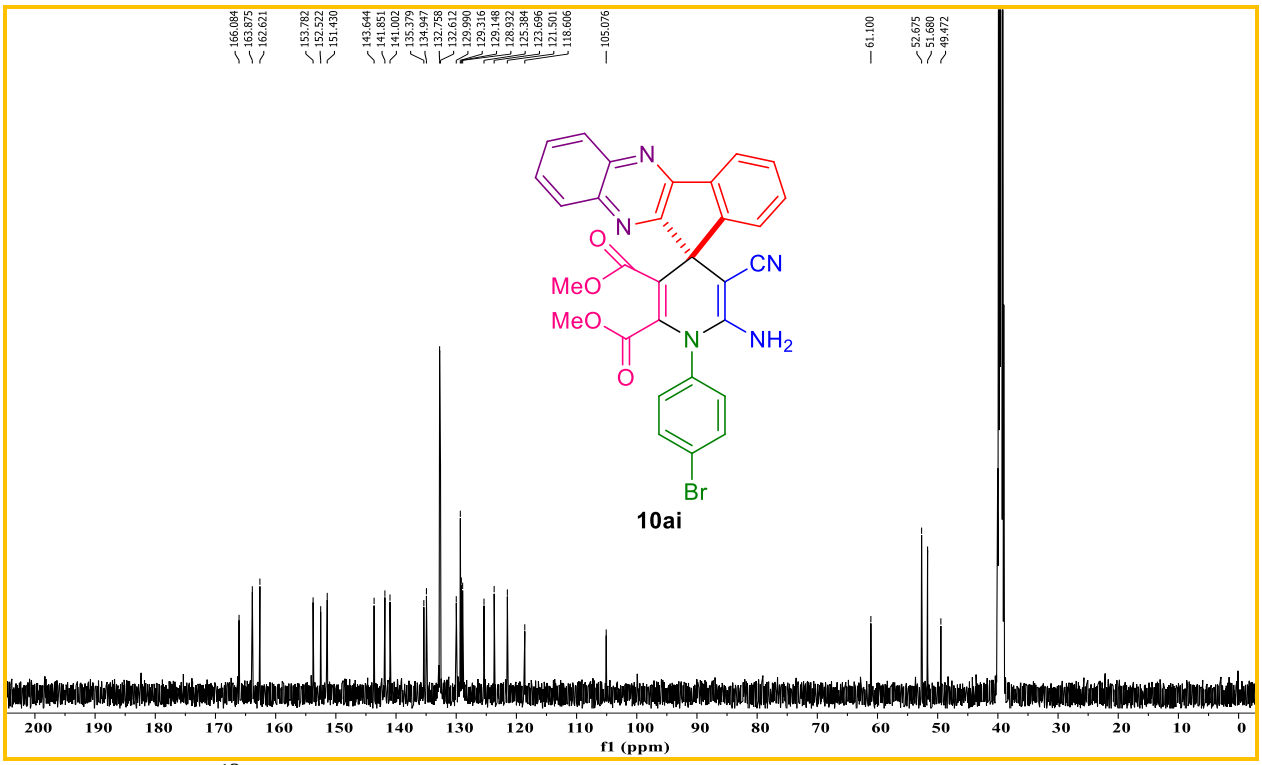


Figure S105: ^{13}C NMR spectra of dimethyl 2'-amino-1'-(4-bromophenyl)-3'-cyano-1'*H*-spiro[indeno[1,2-*b*]quinoxaline-11,4'-pyridine]-5',6'-dicarboxylate **10ai**

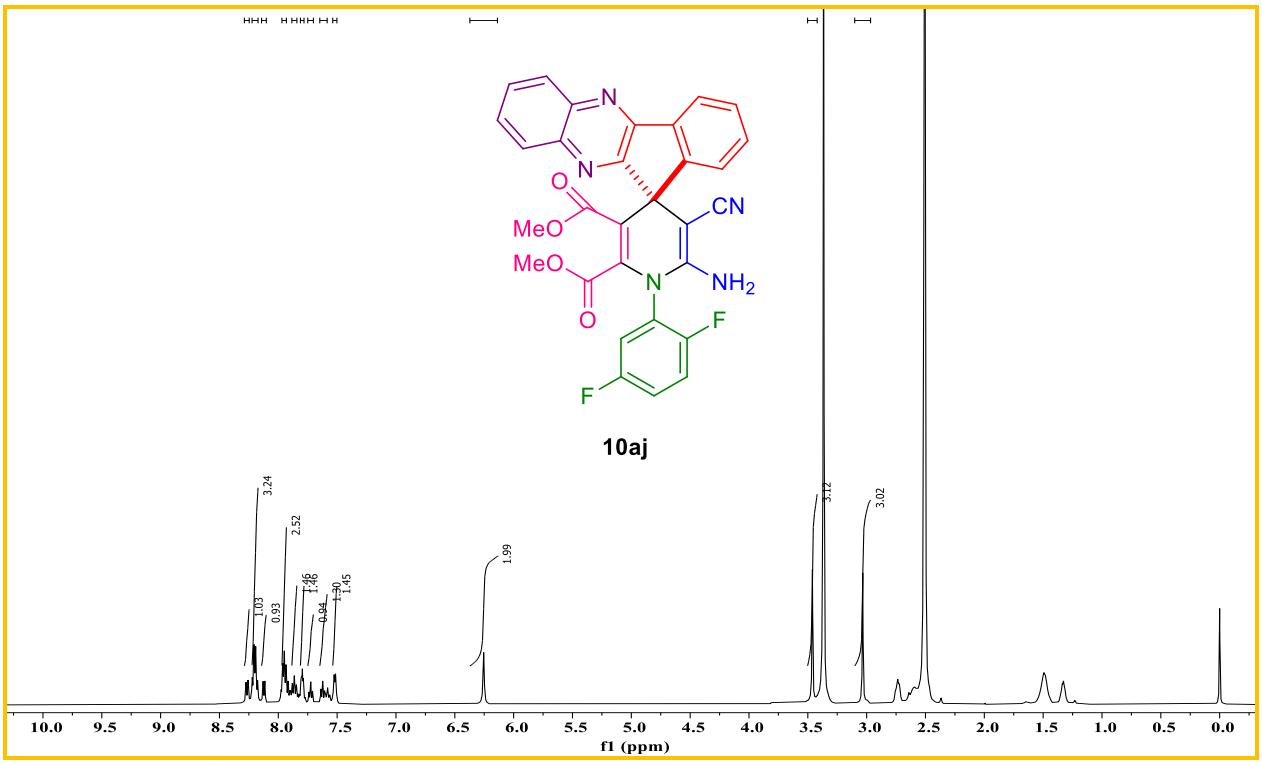


Figure S106: ^{1}H NMR spectra of dimethyl 2'-amino-3'-cyano-1'-(2,5-difluorophenyl)-1'*H*-spiro[indeno[1,2-*b*]quinoxaline-11,4'-pyridine]-5',6'-dicarboxylate **10aj**

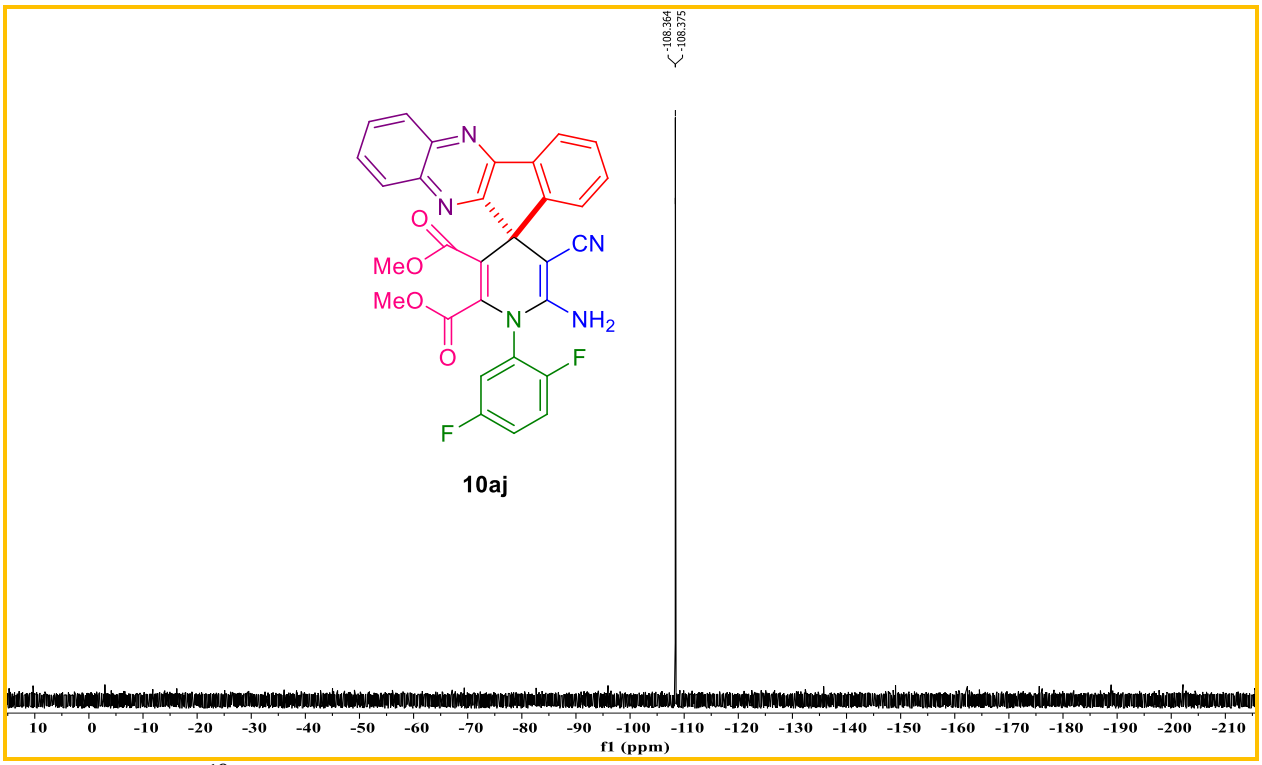


Figure S107: ^{19}F NMR spectra of dimethyl 2'-amino-3'-cyano-1'-(2,5-difluorophenyl)-1'*H*-spiro[indeno[1,2-*b*]quinoxaline-11,4'-pyridine]-5',6'-dicarboxylate **10aj**

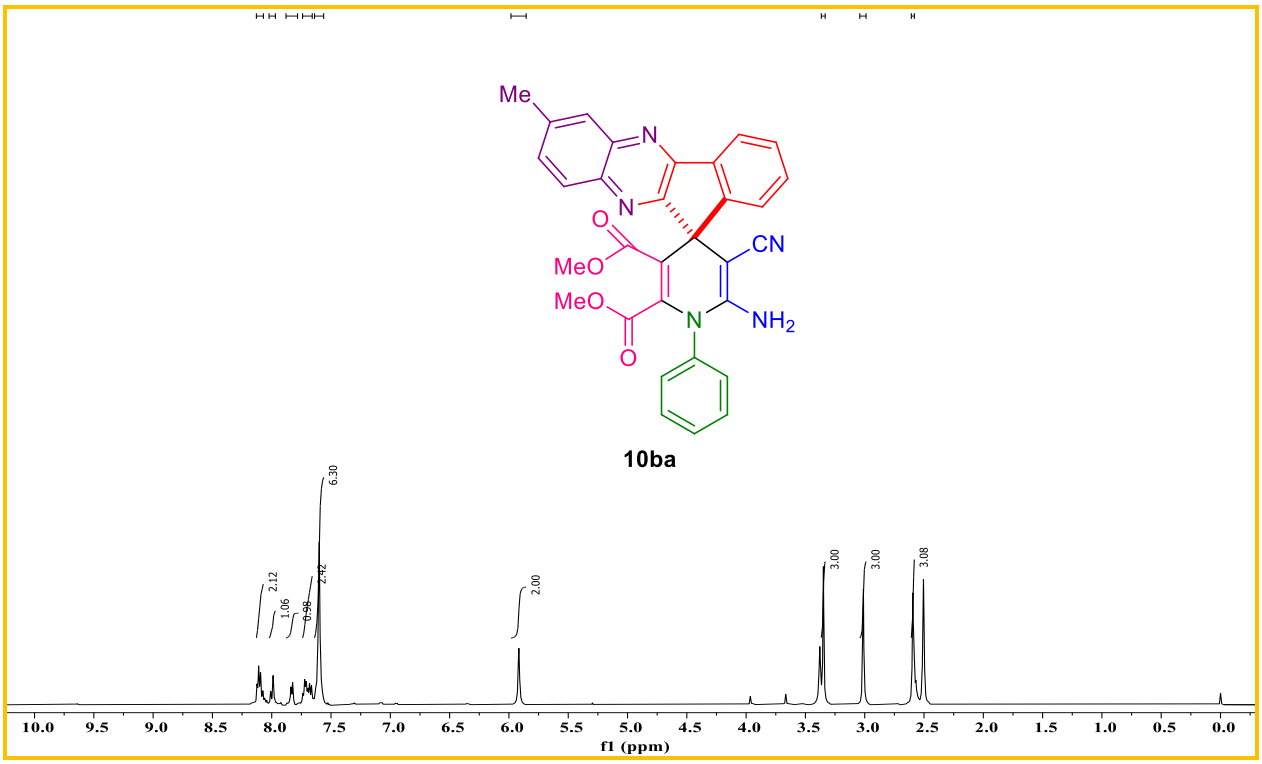


Figure S108: ^{1}H NMR spectra of dimethyl 2'-amino-3'-cyano-7-methyl-1'-phenyl-1'*H*-spiro[indeno[1,2-*b*]quinoxaline-11,4'-pyridine]-5',6'-dicarboxylate **10ba**

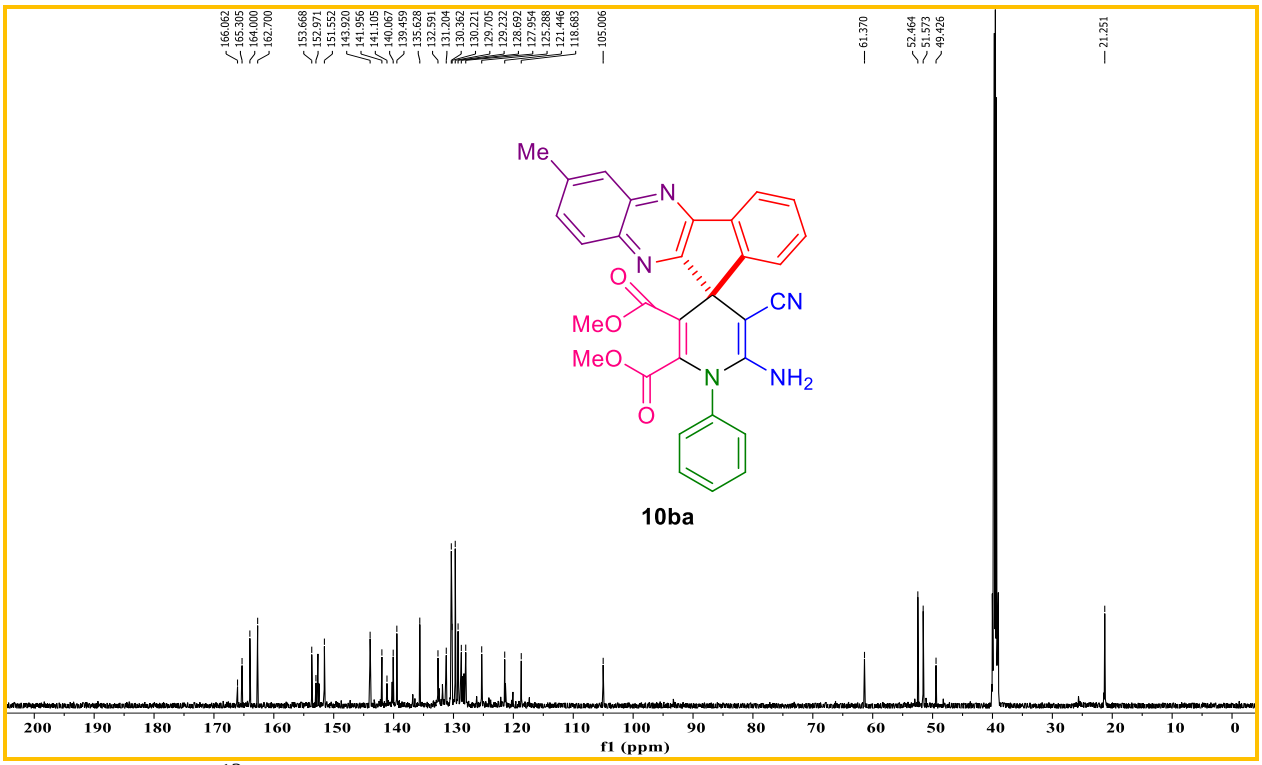


Figure S109: ^{13}C NMR spectra of dimethyl 2'-amino-3'-cyano-7-methyl-1'-phenyl-1'*H*-spiro[indeno[1,2-*b*]quinoxaline-11,4'-pyridine]-5',6'-dicarboxylate **10ba**

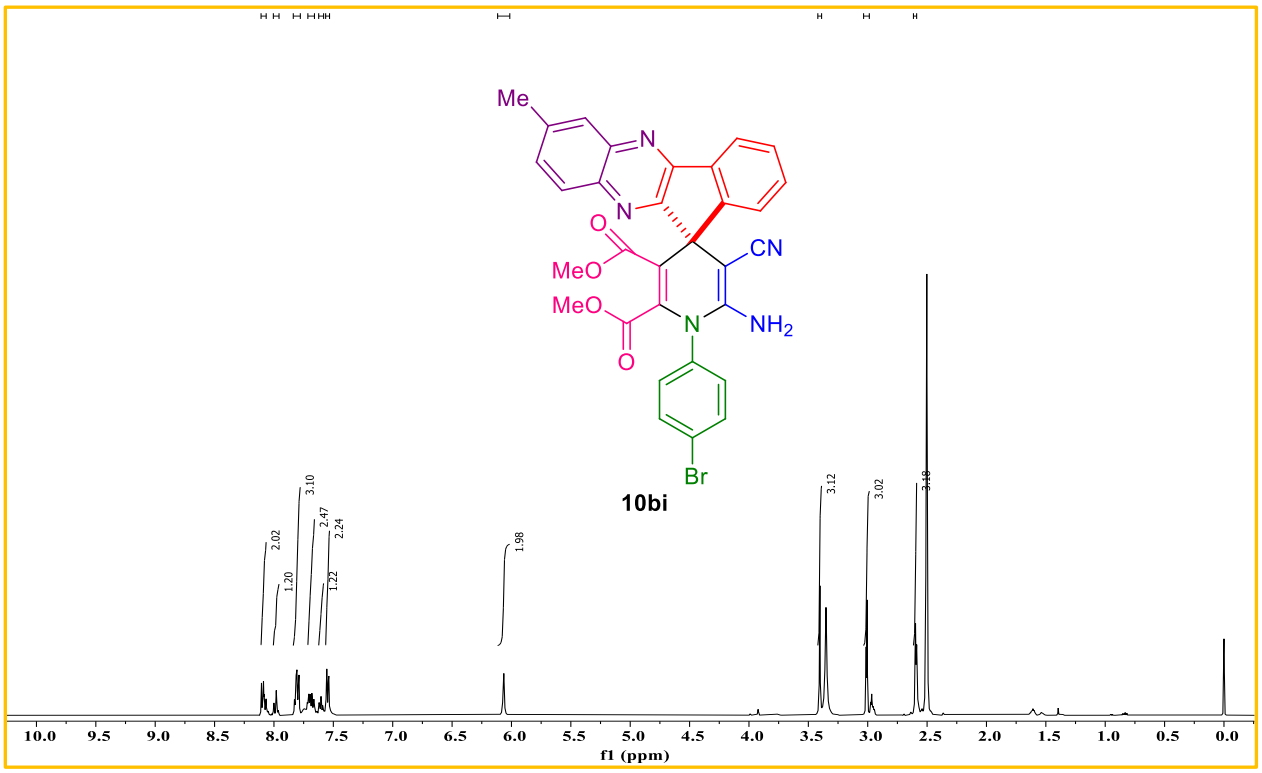


Figure S110: ^{1}H NMR spectra of dimethyl 2'-amino-1'-(4-bromophenyl)-3'-cyano-7-methyl-1'*H*-spiro[indeno[1,2-*b*]quinoxaline-11,4'-pyridine]-5',6'-dicarboxylate **10bi**

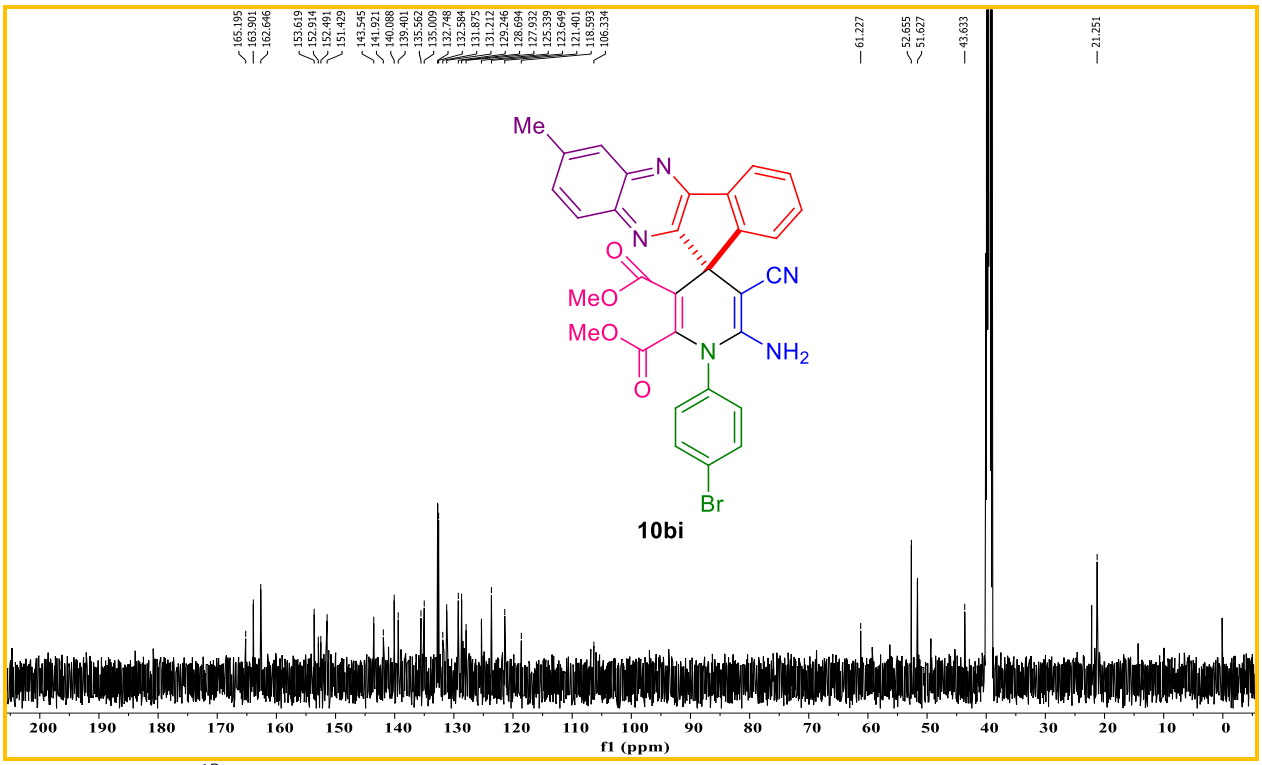


Figure S111: ^{13}C NMR spectra of dimethyl 2'-amino-1'-(4-bromophenyl)-3'-cyano-7-methyl-1'*H*-spiro[indeno[1,2-*b*]quinoxaline-11,4'-pyridine]-5',6'-dicarboxylate **10bi**

9. HRMS spectra of radical adduct **I**

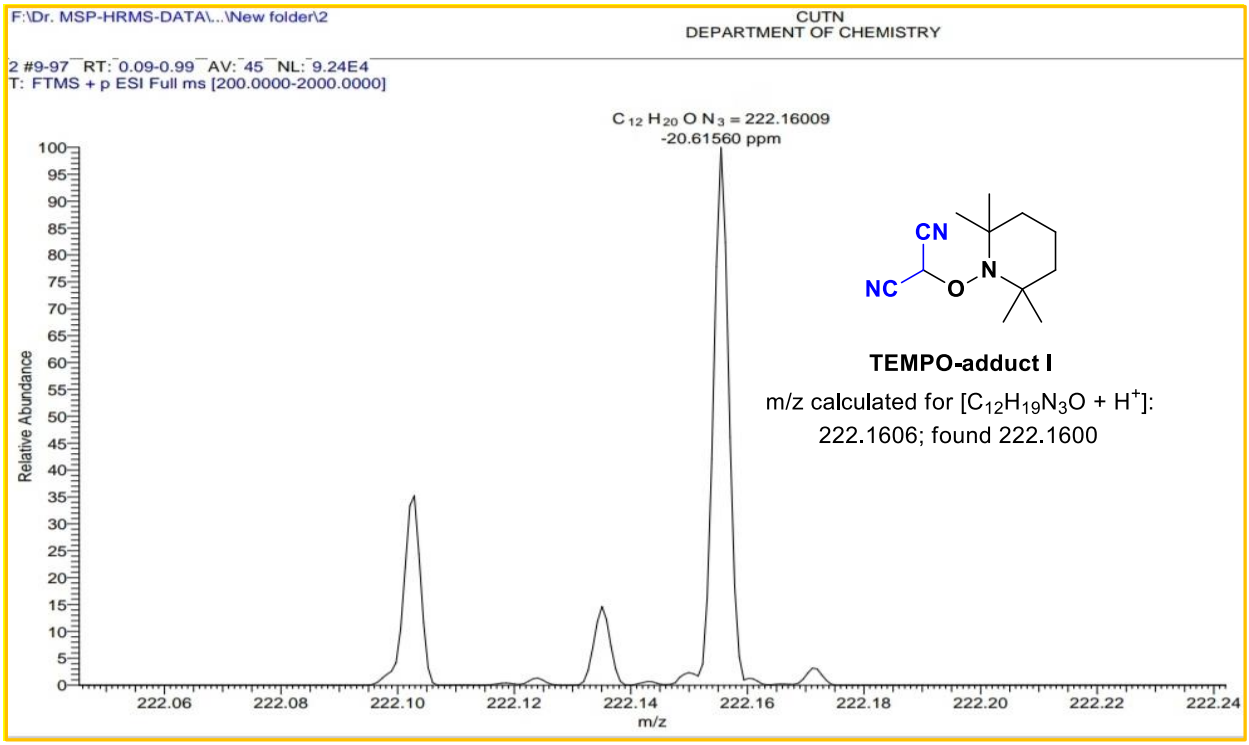


Figure S112: High Resolution Mass Spectrum of radical adduct **I** formed in this photocatalytic domino multicomponent reaction.