Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

$POCl_3$ mediated One-pot deoxygenative aromatization and electrophilic chlorination of Dihydroxy-2-methyl-4-oxo-indeno[1,2-*b*]pyrroles

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1. General Information and Methods

All commercially available solvents and reagents were purchased from Merck, Fluka and Aldrich chemical companies. Solvents were dried by the general methods and degassed before use. Electrothermal MEL-TEMP apparatus (model 1202D) was applied to measure melting points without correction. FT-IR spectra (in KBr) were obtained using a Bruker Tensor 27 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded by a Bruker Spectrospin Avance 400 spectrometer (400 MHz and 100 MHz), and chemical shifts were reported relative to the solvent. Silica-precoated TLC plates (Merck Kieselgel 60 PF254 + 366) were utilized for Thin-layer chromatography (TLC). Elemental analyses were measured by the Vario ELIII apparatus (Elementar Co.). Preparative thin layer chromatographies (TLC) were performed with prepared glass-backed plates (20 × 20 cm^2, 500 μ) using silica gel (Merck Kieselgel 60 PF254 + 366). X-ray diffraction measurements were performed at 95 K using a four-circle diffractometer, SuperNova of Rigaku Oxford Diffraction, with a micro-focus sealed tube, mirror-collimated Cu Kα radiation (λ = 1.54184 Å), and a CCD detector, Atlas S2. The single crystal was twinned by a rotation of 2.2° around [0.11 0.6 0.79] which corresponds to a randomly orientated second domain. The data reduction and absorption correction were carried out with CrysAlisPro software[1]. The structure was solved with the deconvoluted data set of the main domain (63%) using a dual-space algorithm in SHELXT software[2] and refined by full-matrix least squares on F2 value using Jana2020 (not yet published successor of Jana2006[3]) and the same data set. Non-hydrogen atoms were refined with harmonic atomic displacement parameters (displacement ellipsoids), and the hydrogen atoms on carbon atoms were placed at calculated positions derived from the parent atoms with Uiso (H) equal to 1.2 times Ueq of C. The structure was deposited on the CCDC database under the number 2227028.

2. General experimental procedure

2.1. General Experimental Procedure for the synthesis of compounds 2a-c

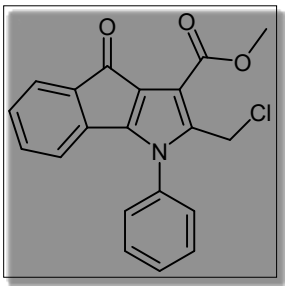
A mixture of substrates **1a-c** (1.0 mmol) and $POCl_3$ (1.3 mmol, 0.12 cc) in DMF (2 mL) was heated at 60 °C for 3-7 h (TLC monitoring). After completion of the reaction, the precipitates were filtered and washed with *n*-hexane (10 mL) and then with diethyl ether (10 mL) to afford pure products **2a-c.**

2.2. General Experimental Procedure for the synthesis of compounds 3a, 3b, and 3d-h

A mixture of substrates **1a**, **1b**, **1d** and **1f-i** (1.0 mmol) and $POCl_3$ (1.3 mmol, 0.12 cc) in DMF (2 mL) was heated at 60 °C for 0.25-7 h (TLC monitoring). After completion of the reaction, water (50 mL) was added, and the mixture was stirred at 60 °C for 24 h. Finally, the precipitate was filtered and purified by preparative thin-layer chromatography to get **3a**, **3b**, and **3d-h.**

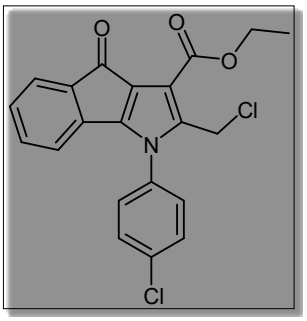
3. Characterization of compounds

Methyl 2-(chloromethyl)-4-oxo-1-phenyl-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (2a).



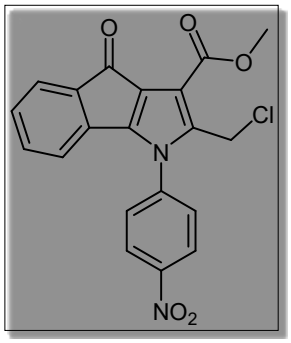
Orange solid (0.26 g, 74%); mp 224 °C (decomp.). **FT-IR (KBr, ν, cm^{-1})**: 3055, 2918, 2848, 1704, 1603, 1447. **^{1}H NMR (CDCl$_3$, 400 MHz)**: *δ* 7.66-7.61 (m, 3H, Ph), 7.60-7.56 (m, 2H, Ph), 7.44 (d, *J* = 6.9 Hz, 1H, Ph), 7.12-7.08 (m, 1H, Ph), 7.05-7.01 (m, 1H, Ph), 6.17 (d, *J* = 7.1 Hz, 1H, Ph), 4.77 (s, 2H, CH_2), 3.96 (s, 3H, Me). **^{13}C NMR (CDCl$_3$, 100 MHz)**: *δ* 183.1, 162.7, 151.4, 139.2, 137.7, 134.0, 133.1, 131.5, 129.4, 129.0, 127.9, 126.4, 122.9, 120.2, 116.5, 110.8, 50.9, 33.9. **^{13}C/DEPT-135 (CDCl$_3$, 100 MHz)**: *δ* 131.5, 129.4, 129.0, 127.9, 126.4, 122.9, 116.6, 50.9, 34.0 (negative peak). **Anal. Calcd for $C_{20}H_{14}ClNO_3$**: C, 68.29; H, 4.01; N, 3.98. **Found**: C, 68.33; H, 4.06; N, 3.92.

Ethyl 2-(chloromethyl)-1-(4-chlorophenyl)-4-oxo-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (2b)



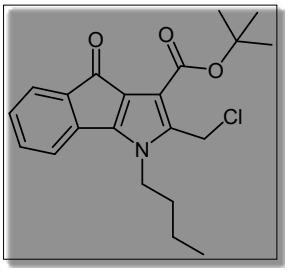
Orange solid (0.27 g, 67%); mp 210 °C (decomp.). **FT-IR (KBr, ν, cm^{-1})**: 3064, 2954, 2920, 2854, 1703, 1607, 1452. **^{1}H NMR (CDCl$_3$, 400 MHz)**: *δ* 7.62 (d, *J* = 8.6 Hz, 2H, Ph), 7.53 (d, *J* = 8.6 Hz, 2H, Ph), 7.45 (d, *J* = 6.8 Hz, 1H, Ph), 7.14-7.05 (m, 2H, Ph), 6.22 (d, *J* = 7.0 Hz, 1H, Ph), 4.77 (s, 2H, CH_2-Cl), 4.40 (q, *J* = 7.1 Hz, 2H, CH_2-OCO), 1.46 (t, *J* = 7.1 Hz, 3H, Me). **^{13}C NMR (CDCl$_3$, 100 MHz)**: *δ* 182.9, 162.0, 151.3, 138.8, 137.7, 135.6, 132.9, 132.5, 131.6, 129.3, 128.0, 127.8, 123.0, 120.6, 116.4, 111.8, 59.9, 33.9, 13.2. **Anal. Calcd for $C_{21}H_{15}Cl_2NO_3$**: C, 63.02; H, 3.78; N, 3.50. **Found**: C, 63.06; H, 3.72; N, 3.55.

Methyl 2-(chloromethyl)-1-(4-nitrophenyl)-4-oxo-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (2c).



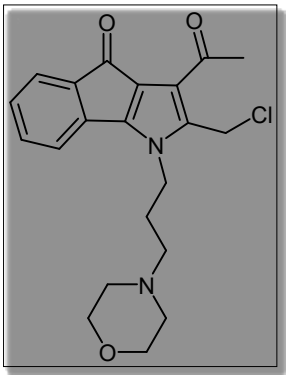
Orange solid (0.21 g, 53%); mp 260 °C (decomp.). **FT-IR (KBr, ν, cm^{-1})**: 3068, 2924, 2854, 1708, 1523, 1606, 1446, 1350. **^{1}H NMR (DMSO-d$_6$, 400 MHz)**: *δ* 8.53 (d, *J* = 8.8 Hz, 2H, Ph), 7.83 (d, *J* = 8.8 Hz, 2H, Ph), 7.49 (d, *J*= 7.0 Hz, 1H, Ph), 7.18-7.14 (m, 1H, Ph), 7.11-7.07 (m, 1H, Ph), 6.22 (d, *J*= 7.1 Hz, 1H, Ph), 4.81 (s, 2H, CH_2-Cl), 3.97 (s, 3H, Me). **^{13}C NMR (DMSO-d$_6$, 100 MHz)**: *δ* 148.5, 140.1, 139.8, 137.8, 133.4, 129.3, 129.2, 125.4, 123.6, 118.0, 51.8, 35.1. **Anal. Calcd for $C_{20}H_{13}ClN_2O_5$**: C, 60.54; H, 3.30; N, 7.06. **Found**: C, 60.61; H, 3.38; N, 7.11.

***tert*-Butyl 1-butyl-2-(chloromethyl)-4-oxo-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (2d)**



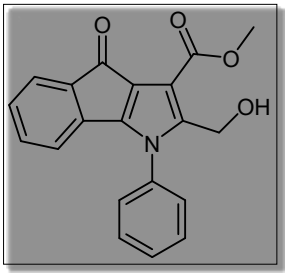
A mixture of substrate **1d** (1.0 mmol, 0.37 g) and $POCl_3$ (1.3 mmol, 0.12 cc) in DMF (2 mL) was heated at 60 °C for 0.25 h. Water (50 mL) was then added to the reaction solution. Finally, the obtained precipitate was quickly filtered and purified by preparative thin-layer chromatography (*n*-hexane/ethyl acetate = 5:1) to give product **2d**. Orange solid (0.24 g, 68%); mp 202 °C (decomp.). **FT-IR (KBr, ν, cm^{-1})**: 3067, 2926, 2861, 1705, 1609, 1452. **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.41 (d, J = 7.1 Hz, 1H, Ph), 7.24-7.22 (m, 1H, Ph), 7.14-7.10 (m, 1H, Ph), 6.94 (d, J = 7.2 Hz, 1H, Ph), 4.93 (s, 2H, CH_2-Cl), 4.04 (t, J = 7.7 Hz, 2H, CH_2-N), 1.80-1.72 (m, 2H, CH_2-C$\underline{H}_2$-CH_2), 1.61 (s, 9H, $C(CH_3)_3$), 1.45-1.35 (m, 2H, C$\underline{H}_2$-CH_3), 0.92 (t, J = 7.3 Hz, 3H, C$\underline{H}_3$-CH_2). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 183.2, 162.0, 150.2, 138.5, 138.4, 133.6, 131.4, 127.4, 122.6, 120.2, 116.2, 112.9, 80.1, 59.7, 45.0, 32.2, 27.5, 27.3, 19.0, 18.9, 12.7. **Anal. Calcd for $C_{21}H_{24}ClNO_3$**: C, 67.46; H, 6.47; N, 3.75. **Found**: C, 67.42; H, 6.51; N, 3.78.

3-Acetyl-2-(chloromethyl)-1-(3-morpholinopropyl)indeno[1,2-*b*]pyrrol-4-one (2e)



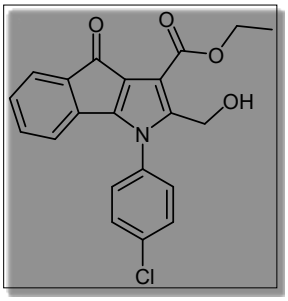
A mixture of substrate **1e** (1.0 mmol, 0.39 g) and $POCl_3$ (1.3 mmol, 0.12 cc) in DMF (2 mL) was heated at 60 °C for 1.5 h. Water (20 mL) was then added and extracted with chloroform (3 × 20 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under vacuum to afford product **2e** as orange solid (0.25 g, 65%); mp 120 °C (decomp.). **FT-IR (KBr, ν, cm^{-1})**: 2923, 2856, 1702, 1656, 1609, 1456, 1105. **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.43 (d, J = 6.9 Hz, 1H, Ph), 7.28-7.25 (m, 1H, Ph), 7.17- 7.13 (m, 2H, Ph), 4.65 (s, 2H, CH_2-Cl), 4.23 (t, J = 6.8 Hz, 2H, CH_2), 3.69 (t, J = 4.1 Hz, 4H, CH_2), 2.76 (s, 3H, Me), 2.40- 2.37 (m, 6H, CH_2), 2.00 (quin, J = 6.4 Hz, 2H, CH_2). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 196.7, 184.3, 149.8, 143.7, 137.2, 133.6, 131.7, 127.6, 123.0, 119.7, 118.9, 116.5, 65.8, 53.8, 53.3, 52.6, 42.7, 30.3, 26.4. **Anal. Calcd for $C_{21}H_{23}ClN_2O_3$**: C, 65.20; H, 5.99; N, 7.24. **Found**: C, 65.24; H, 5.94; N, 7.30.

Methyl 2-(hydroxymethyl)-4-oxo-1-phenyl-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (3a).



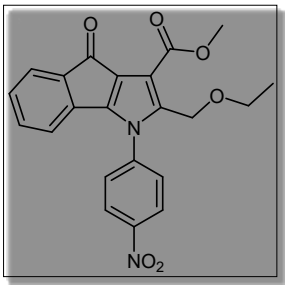
Purified by preparative thin-layer chromatography (*n*-hexane/acetone = 4:1). Orange solid (0.27 g, 81%); mp 264 °C (decomp.). **FT-IR (KBr, ν, cm^{-1})**: 3514, 3062, 3010, 2946, 1706, 1605, 1447. **^{1}H NMR (CDCl$_3$, 400 MHz)**: *δ* 7.62-7.58 (m, 3H, Ph), 7.54-7.48 (m, 2H, Ph), 7.40 (d, *J* = 6.7 Hz, 1H, Ph), 7.08-7.00 (m, 2H, Ph), 6.25 (d, *J* = 7.1 Hz, 1H, Ph), 4.49 (d, *J* =6.4 Hz, 2H, CH_2-O), 3.96 (s, 3H, Me), 3.86 (t, *J* =7 Hz, 1H, exchangeable with D_2O, OH). **^{13}C NMR (CDCl$_3$, 100 MHz)**: *δ* 183.4, 164.6, 150.3, 145.0, 137.6, 134.3, 133.4, 131.3, 129.0, 128.9, 127.5, 126.2, 122.7, 120.0, 116.3, 110.1, 53.7, 51.2. **Anal. Calcd for $C_{20}H_{15}NO_4$**: C, 72.06; H, 4.54; N, 4.20. **Found**: C, 72.09; H, 4.51; N, 4.24.

Ethyl 1-(4-chlorophenyl)-2-(hydroxymethyl)-4-oxo-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (3b).



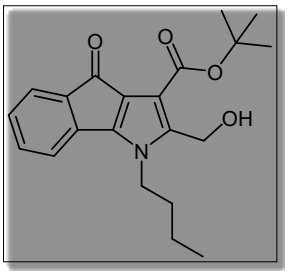
Purified by preparative thin-layer chromatography (*n*-hexane/ethyl acetate = 2:1). Pale orange solid (0.31 g, 81%); mp 206-208 °C. **FT-IR (KBr, ν, cm^{-1})**: 3436, 2924, 2855, 1707, 1671, 1635, 1455. **^{1}H NMR (CDCl$_3$, 400 MHz)**: *δ* 7.59 (d, *J* = 8.6 Hz, 2H, Ph), 7.47-7.42 (m, 3H, Ph), 7.12- 7.05 (m, 2H, Ph), 6.31 (d, *J* = 6.4 Hz, 1H, Ph), 4.49 (d, *J* = 7.2 Hz, 2H, C$\underline{H_2}$-OH), 4.41 (q, *J* = 7.1 Hz, 2H, CH_2-OCO), 3.76 (t, *J* = 7.2 Hz, 1H, OH), 1.48 (t, *J* = 7.2 Hz, 3H, Me). **^{13}C NMR (CDCl$_3$, 100 MHz)**: *δ* 183.2, 164.1, 150.6, 144.6, 137.6, 135.2, 133.3, 132.8, 131.5, 129.2, 127.7, 127.5, 122.9, 116.3, 111.2, 60.3, 53.6, 13.3. **Anal. Calcd for $C_{21}H_{16}ClNO_4$**: C, 66.06; H, 4.22; N, 3.67. **Found**: C, 66.09; H, 4.19; N, 3.69.

Methyl 2-(ethoxymethyl)-1-(4-nitrophenyl)-4-oxo-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (3c)



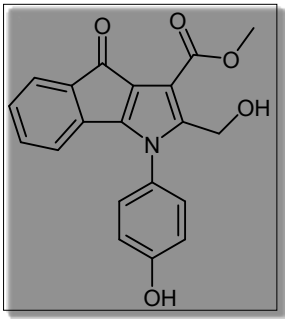
Compound **2c** (1.0 mmol, 0.4 g) in EtOH (10 mL) was heated at 60 °C for 24 h. Then EtOH was removed using a rotary evaporator. Finally, the precipitate was purified by preparative thin-layer chromatography (n-hexane/ethyl acetate = 4:1) to give product **3c** as a pale orange solid (0.24 g, 58%); mp 188-190 °C. **FT-IR (KBr, ν, cm^{-1})**: 3072, 2953, 2919, 2854, 1699, 1600, 1519 (NO_2), 1447, 1343 (NO_2), 1085. **^{1}H NMR (CDCl$_3$, 400 MHz)**: *δ* 8.47 (d, *J* = 8.9 Hz, 2H, Ph), 7.82 (d, *J* = 8.9 Hz, 2H, Ph), 7.46 (d, *J* = 6.7 Hz, 1H, Ph), 7.15-7.11 (m, 1H, Ph), 7.09- 7.05 (m, 1H, Ph), 6.27 (d, *J* = 7.1 Hz, 1H, Ph), 4.59 (s, 2H, CH_2-O), 3.94 (s, 3H, CH_3-O), 3.47 (q, *J* = 7.0 Hz, 2H, O-C$\underline{H_2}$-CH_3), 1.13 (t, *J* = 7.0 Hz, 3H, C$\underline{H_3}$-CH_2). **^{13}C NMR (CDCl3, 100 MHz)**: *δ* 183.0, 162.8, 150.6, 147.2, 140.5, 140.4, 137.6, 132.9, 131.6, 128.1, 127.5, 123.9, 123.1, 120.9, 116.3, 112.0, 64.7, 59.5, 50.9, 14.1. **Anal. Calcd for $C_{22}H_{18}N_2O_6$**: C, 65.02; H, 4.46; N, 6.89. **Found**: C, 65.07; H, 4.49; N, 6.84.

***tert*-Butyl 1-butyl-2-(hydroxymethyl)-4-oxo-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (3d).**



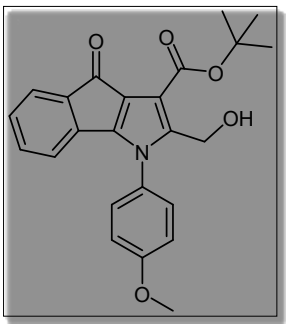
Purified by preparative thin-layer chromatography (*n*-hexane/ethyl acetate = 5:1) to give product **3d**. Pale orange solid (0.15 g, 76%); mp 60-62 °C. **FT-IR (KBr, ν, cm^{-1})**: 3433, 3065, 2925, 2860, 1704, 1606, 1452. **^{1}H NMR (CDCl$_3$, 400 MHz)**: δ 7.41 (d, *J* = 7.1 Hz, 1H, Ph), 7.24-7.22 (m, 1H, Ph), 7.14-7.10 (m, 1H, Ph), 6.96 (d, *J* = 7.3 Hz, 1H, Ph), 4.70 (s, 2H, C$\underline{H}_2$-OH), 4.07 (t, *J* = 7.5 Hz, 2H, CH_2-N), 3.88 (br. 1H, OH), 1.83-1.75 (m, 2H, CH_2-C$\underline{H}_2$-CH_2), 1.63 (s, 9H, C$(CH_3)_3$), 1.46-1.38 (m, 2H, C$\underline{H}_2$-CH_3), 0.98 (t, *J* = 7.3 Hz, 3H, C$\underline{H}_3$-CH_2). **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 183.2, 163.5, 149.6, 143.3, 138.2, 133.7, 131.5, 127.3, 122.7, 120.1, 116.0, 112.2, 80.9, 53.3, 44.9, 32.3, 27.3, 18.9, 12.7. **Anal. Calcd for $C_{21}H_{25}NO_4$**: C, 70.96; H, 7.09; N, 3.94. **Found**: C, 70.92; H, 7.11; N, 3.97.

Methyl 2-(hydroxymethyl)-1-(4-hydroxyphenyl)-4-oxo-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (3e).



A mixture of substrates **1f** (1.0 mmol, 0.37 g) and $POCl_3$ (1.3 mmol, 0.12 cc) in DMF (2 mL) was heated at 60 °C for 3 h. Water (50 mL) was then added and the mixture was stirred at 60 °C for 24 h. Finally, the precipitate was filtered and after drying was washed diethyl ether (10 mL) to give product **3e**. Orange solid (0.33 g, 93%); mp 228-230 °C. **FT-IR (KBr, ν, cm^{-1})**: 3421, 3160, 2924, 2855, 1706, 1677, 1606, 1443. **^{1}H NMR (DMSO-d$_6$, 400 MHz)**: δ 10.2 (s, 1H, O$\underline{H}$-Ph), 7.40 (d, *J* = 8.6 Hz, 2H, Ph), 7.30 (d, *J* = 6.4 Hz, 1H, Ph), 7.17-7.10 (m, 2H, Ph), 6.96 (d, *J* = 8.6 Hz, 2H, Ph), 6.17 (d, *J* = 6.8 Hz, 1H, Ph), 5.05 (t, *J* = 5.1 Hz, 1H, exchangeable with D_2O, CH_2-O$\underline{H}$), 4.44 (d, *J* = 4.9 Hz, 2H, C$\underline{H}_2$-OH), 3.76 (s, 3H, Me). **^{13}C NMR (DMSO-d$_6$, 100 MHz)**: δ 183.9, 163.6, 158.7, 151.9, 146.0, 138.4, 134.3, 133.3, 128.9, 128.7, 126.6, 123.5, 117.5, 116.2, 110.1, 52.2, 51.6. **^{13}C/DEPT-135 (DMSO-d$_6$, 100 MHz)**: δ 133.4, 129.2, 128.9, 123.7, 117.6, 116.4, 52.3 (negative peak), 52.2 (negative peak), 51.8. **Anal. Calcd for $C_{20}H_{15}NO_5$**: C, 68.76; H, 4.33; N, 4.01. **Found**: C, 68.72; H, 4.37; N, 3.97.

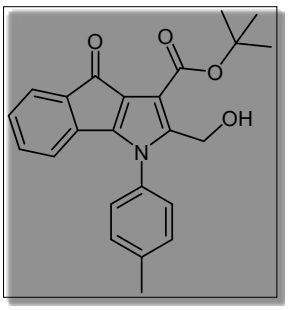
***tert*-Butyl 2-(hydroxymethyl)-1-(4-methoxyphenyl)-4-oxo-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (3f)**



Purified by preparative thin-layer chromatography (*n*-hexane/ethyl acetate = 5:1). Orange solid (0.36 g, 87%); mp 194-196 °C. **FT-IR (KBr, ν, cm^{-1})**: 3490, 3070, 2974, 2924, 2873, 1707, 1681, 1605, 1445, 1252, 1136. **^{1}H NMR (CDCl$_3$, 400 MHz)**: δ 7.40-7.35 (m, 3H, Ph), 7.07-7.02 (m, 4H, Ph), 6.26 (d, *J* = 6.8 Hz, 1H, Ph), 4.46 (d, *J* = 6.0 Hz, 2H, C$\underline{H}_2$-OH), 4.05 (t, *J* =6.3 Hz, 1H, OH), 3.91 (s, 3H, CH_3-O-Ph), 1.66 (s, 9H, C$(CH_3)_3$). **^{13}C NMR (CDCl$_3$, 100 MHz)**: δ 183.4, 163.7, 159.4, 150.2,

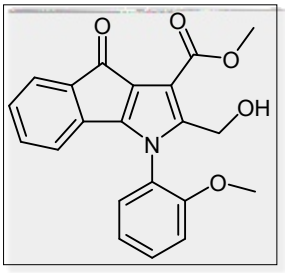
144.7, 137.9, 133.6, 131.3, 127.3, 127.0, 122.5, 120.0, 116.2, 113.9, 112.5, 81.0, 54.7, 53.8, 27.3. **Anal. Calcd for $C_{24}H_{23}NO_5$**: C, 71.10; H, 5.72; N, 3.45. **Found**: C, 71.13; H, 5.76; N, 3.40.

***tert*-Butyl 2-(hydroxymethyl)-4-oxo-1-(p-tolyl)-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (3g).**



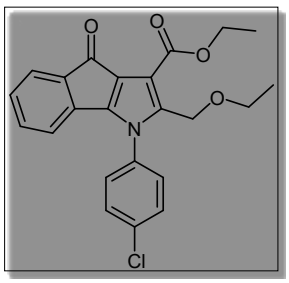
Purified by preparative-thin layer chromatography (*n*-hexane/acetone = 7:1). Pale orange, (0.32 g, 83%); mp 160-162 °C. **FT-IR (KBr, ν, cm^{-1})**: 3434, 2957, 2923, 2858, 1710, 1606, 1451. **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.40-7.31 (m, 5H, Ph), 7.07- 6.99 (m, 2H, Ph), 6.26 (d, *J*=7.3 Hz, 1H, Ph), 4.46 (d, *J* = 7.0 Hz, 2H, C$\underline{H}_2$-OH), 4.06 (t, *J* = 7.1 Hz, 1H, OH), 2.48 (s, 3H, C$\underline{H}_3$-Ph), 1.66 (s, 9H, $C(CH_3)_3$). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 183.4, 163.7, 150.0, 144.6, 139.2, 137.9, 133.6, 131.8, 131.3, 129.4, 127.4, 125.9, 122.5, 120.1, 116.2, 112.6, 81.0, 53.8, 27.3, 20.3. **Anal. Calcd for $C_{24}H_{23}NO_4$**: C, 74.02; H, 5.95; N, 3.60. **Found**: C, 74.05; H, 5.92; N, 3.54.

Methyl 2-(hydroxymethyl)-1-(2-methoxyphenyl)-4-oxo-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (3h)



Purified by preparative thin layer chromatography (*n*-hexane/acetone = 3:1). Orange solid (0.29 g, 80%); mp 172-174 °C. **FT-IR (KBr, ν, cm^{-1})**: 3440, 3065, 2921, 2853, 1708, 1607, 1514, 1451, 1291, 1019. **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.58-7.54 (m, 1H, Ph), 7.43-7.40 (m, 2H, Ph), 7.17-7.12 (m, 2H, Ph), 7.08-6.99 (m, 2H, Ph), 6.14 (d, *J* = 7.0 Hz, 1H, Ph), 4.61 (d, *J* = 14.0 Hz, 1H, C$\underline{H}$-OH), 4.28 (d, *J* = 14.0 Hz, 1H, C$\underline{H}$-OH), 3.97 (s, 3H, Me), 3.80 (s, 3H, Me), 3.24 (br. 1H). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 183.5,165.0, 153.8, 151.1, 146.0, 137.8, 133.7, 131.4, 130.7, 128.0, 127.4, 122.9, 122.6, 120.2, 115.9, 111.3, 109.7, 54.9, 54.1, 51.2. **Anal. Calcd for $C_{21}H_{17}NO_5$**: C, 69.41; H,4.72; N, 3.85. **Found**: C, 69.37; H, 4.78; N, 3.87.

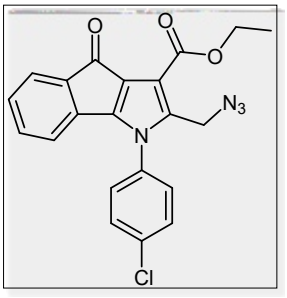
Ethyl 1-(4-chlorophenyl)-2-(ethoxymethyl)-4-oxo-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (3i).



Compound **2b** (1.0 mmol, 0.4 g) in EtOH (10 mL) was heated at 60 °C for 24 h. Then EtOH was removed using a rotary evaporator. Finally, the precipitate was purified by preparative thin-layer chromatography (*n*-hexane/ethyl acetate = 2:1) to give product **3i**. Pale orange solid (0.31 g, 75%); mp 150-152 °C. **FT-IR (KBr, ν, cm^{-1})**: 3068, 2972, 2925, 2866, 1719, 1609, 1445, 1090. **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.57-7.49 (m, 4H, Ph), 7.42 (d, *J* = 6.6 Hz, 1H, Ph), 7.11-7.02 (m, 2H,

Ph), 6.25 (d, *J* = 6.6 Hz, 1H, Ph), 4.54 (s, 2H, pyrrole-CH_2-O-), 4.37 (q, *J* = 7.1 Hz, 2H, CH_3-C<u>H</u>$_2$-OCO), 3.45 (q, *J* = 7.0 Hz, 2H, O-C<u>H</u>$_2$-CH_3), 1.45 (t, *J*= 7.1 Hz, 3H,C<u>H</u>$_3$-CH_2-OCO), 1.13 (t, *J*= 7.0 Hz, 3H, O-CH_2-C<u>H</u>$_3$). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 183.2, 162.5, 150.9, 140.4, 137.8, 134.9, 133.4, 133.2, 131.4, 129.3, 128.7, 127.7, 122.8, 120.4, 116.3, 112.0, 64.5, 59.7, 59.6, 14.1, 13.3. **^{13}C/DEPT-135 ($CDCl_3$, 100 MHz,)**: δ 131.2, 129.1, 128.5, 127.5, 122.6, 116.1, 64.3, 59.5 (negative peak), 59.3 (negative peak), 13.9, 13.1. **Anal. Calcd for $C_{23}H_{20}ClNO_4$**: C, 67.40; H, 4.92; N, 3.42. **Found**: C, 67.44; H, 4.96; N, 3.38.

Ethyl 2-(azidomethyl)-1-(4-chlorophenyl)-4-oxo-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (3j)



A mixture of substrate **2b** (1.0 mmol, 0.4 g) and NaN_3 (1.5 mmol, 0.1 g) in DMF (2 mL) was heated at 60 °C for 3 h. Water was then added to the reaction solution. The obtained precipitate was filtered and washed with water (10 mL) to give product **3j**. Orange solid (0.29 g, 70%); mp 202 °C (decomp.). **FT-IR (KBr, ν, cm^{-1})**: 3062, 2977, 2925, 2089, 1705, 1607, 1447. **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.60 (d, *J* = 8.6 Hz, 2H, Ph), 7.49 (d, *J* = 8.6 Hz, 2H, Ph), 7.43 (d, *J* = 6.7 Hz, 1H, Ph), 7.12-7.04 (m, 2H, Ph), 6.26 (d, *J* = 6.8 Hz, 1H, Ph), 4.43 (s, 2H, CH_2-N_3), 4.37 (q, *J* = 7.1 Hz, 2H, C<u>H</u>$_2$-CH_3), 1.45 (t, *J* = 7.1 Hz, 3H, Me). **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 182.9, 162.2, 151.1, 137.6, 137.4, 135.5, 132.9, 132.6, 131.5, 129.3, 127.9, 127.6, 122.9, 120.4, 116.4, 112.1, 59.9, 42.4, 13.2. **Anal. Calcd for $C_{21}H_{15}ClN_4O_3$**: C, 62.00; H, 3.72; N, 13.77. **Found**: C, 62. 04; H, 3.77; N, 13.71.

4. IR, ^{1}H NMR and ^{13}C NMR Spectra

Methyl 2-(chloromethyl)-4-oxo-1-phenyl-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (2a)

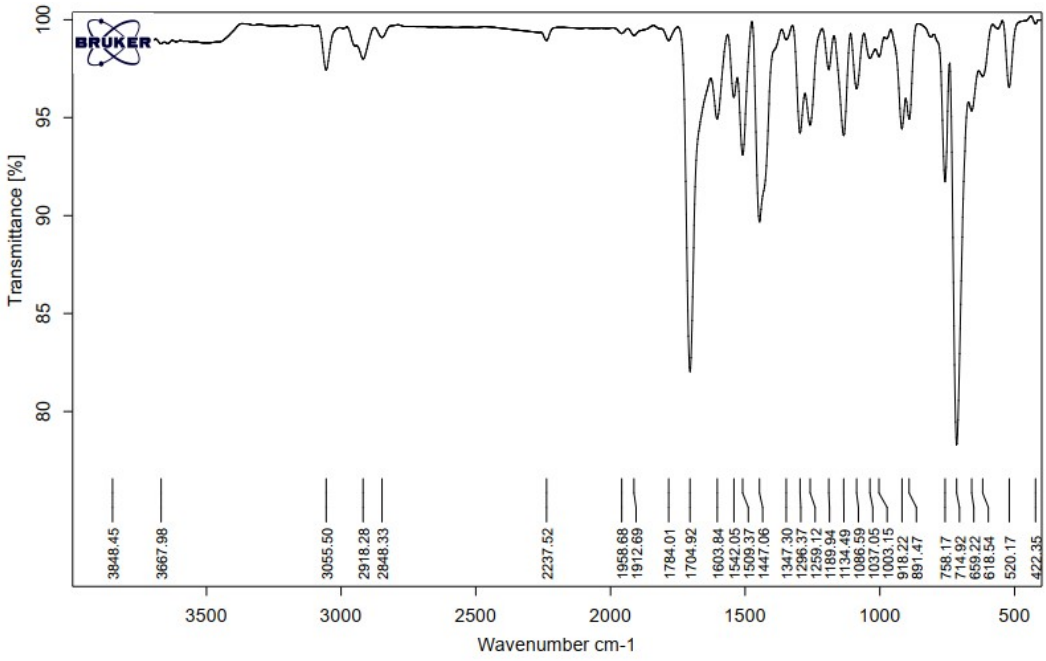


Figure 1: FT-IR (KBr) spectrum of **2a**.

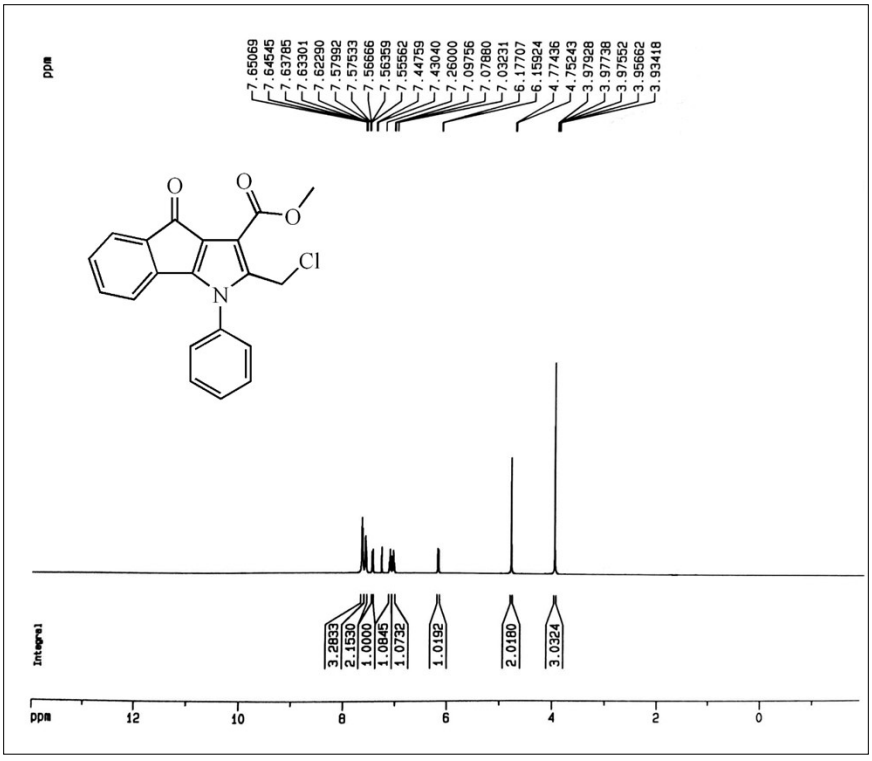


Figure 2: ^{1}H NMR spectrum (400 MHz) of compound **2a** in $CDCl_3$.

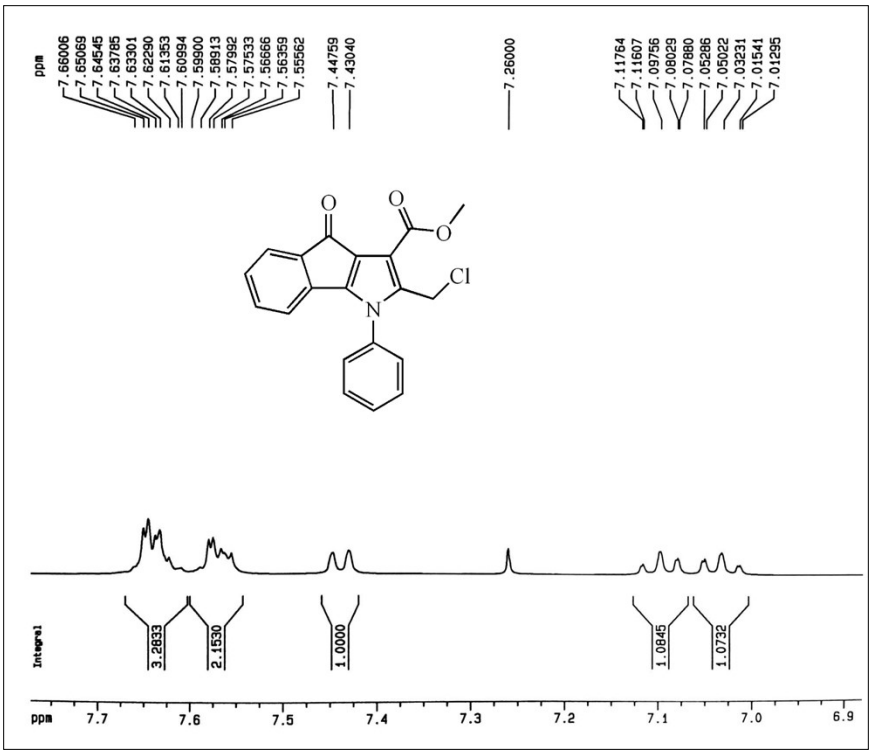


Figure 3: Expanded ^{1}H NMR spectrum (400 MHz) of compound **2a** in $CDCl_3$.

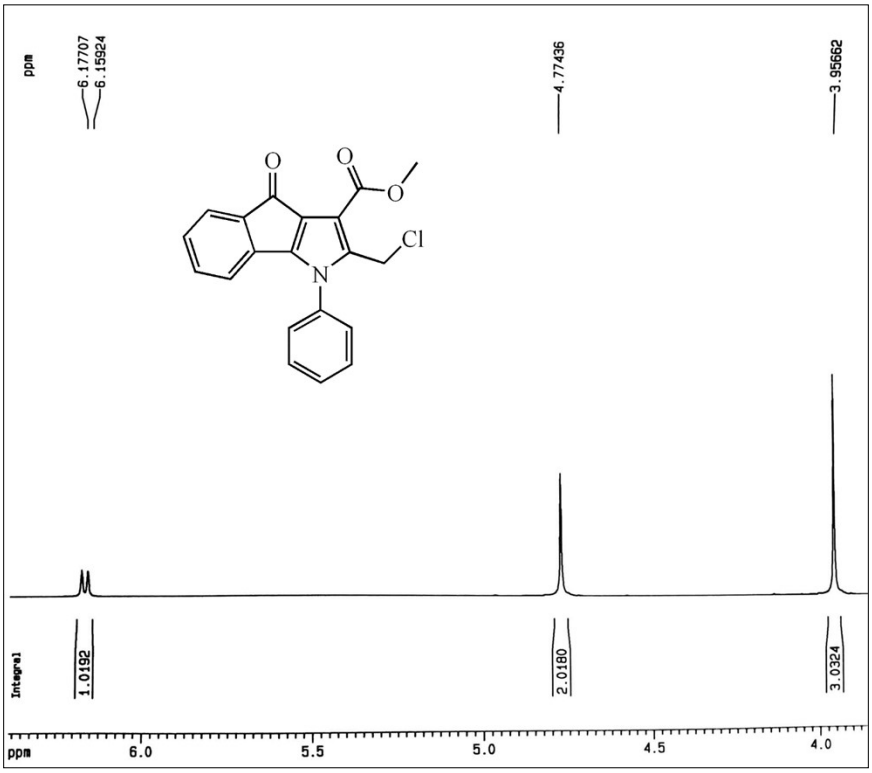


Figure 4: Expanded ^{1}H NMR spectrum (400 MHz) of compound **2a** in $CDCl_3$.

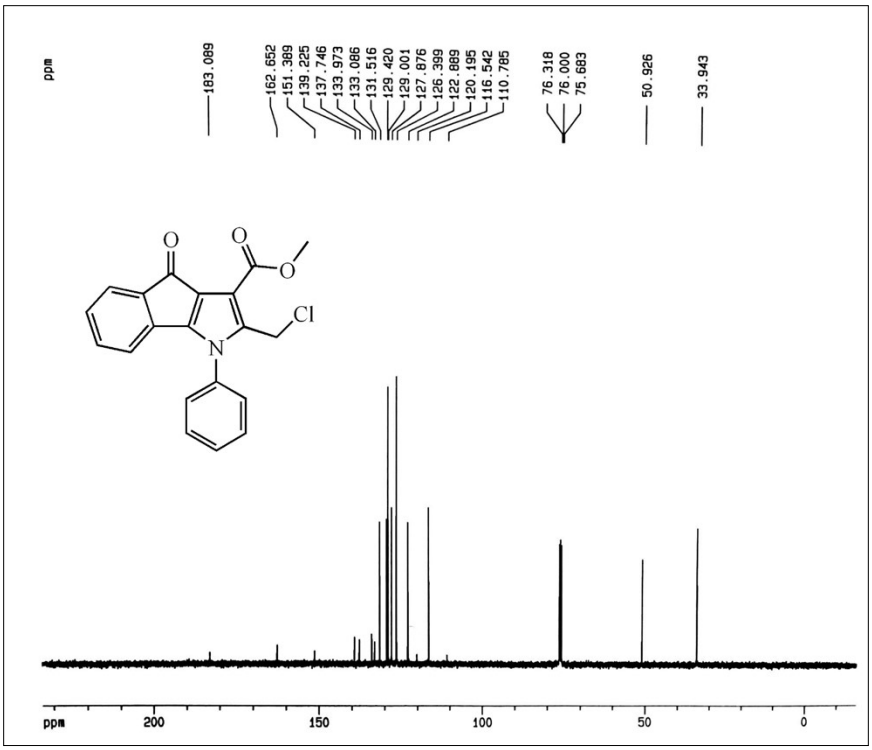


Figure 5: ^{13}C NMR spectrum (100 MHz) of compound **2a** in $CDCl_3$.

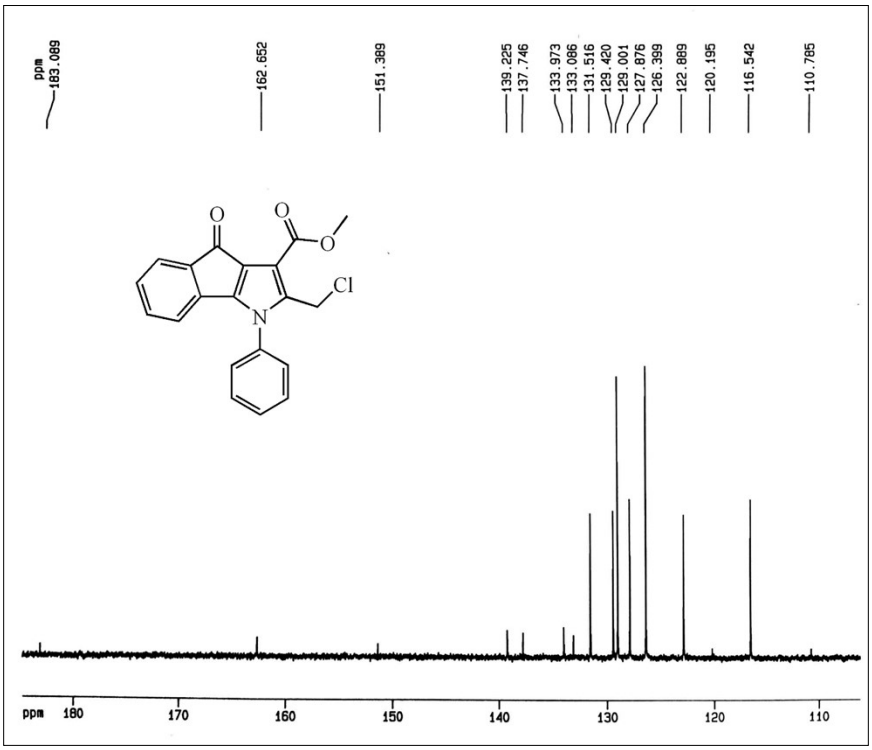


Figure 6: Expanded ^{13}C NMR spectrum (100 MHz) of compound **2a** in $CDCl_3$.

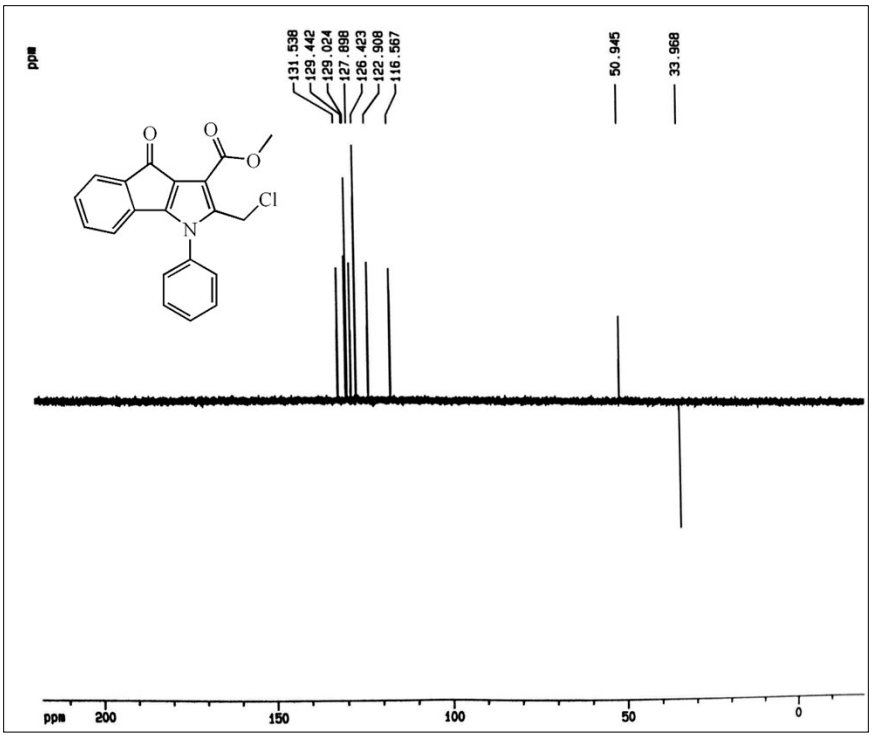


Figure 7: ^{13}C/DEPT-135 spectrum (100 MHz) of compound **2a** in $CDCl_3$.

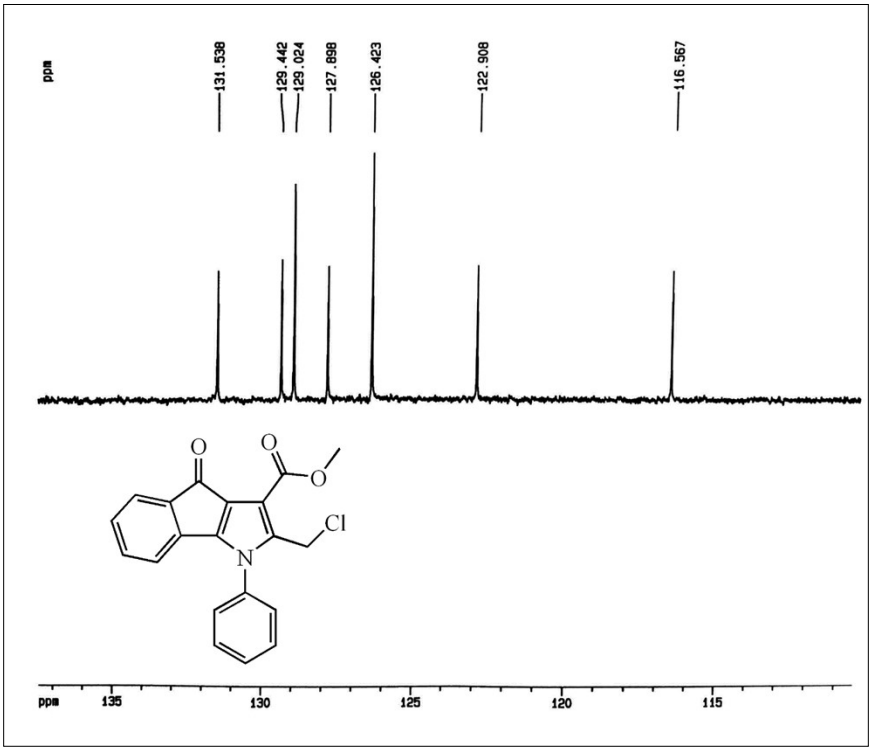


Figure 8: Expanded ^{13}C/DEPT-135 spectrum (100 MHz) of compound **2a** in $CDCl_3$.

Ethyl 2-(chloromethyl)-1-(4-chlorophenyl)-4-oxo-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (2b)

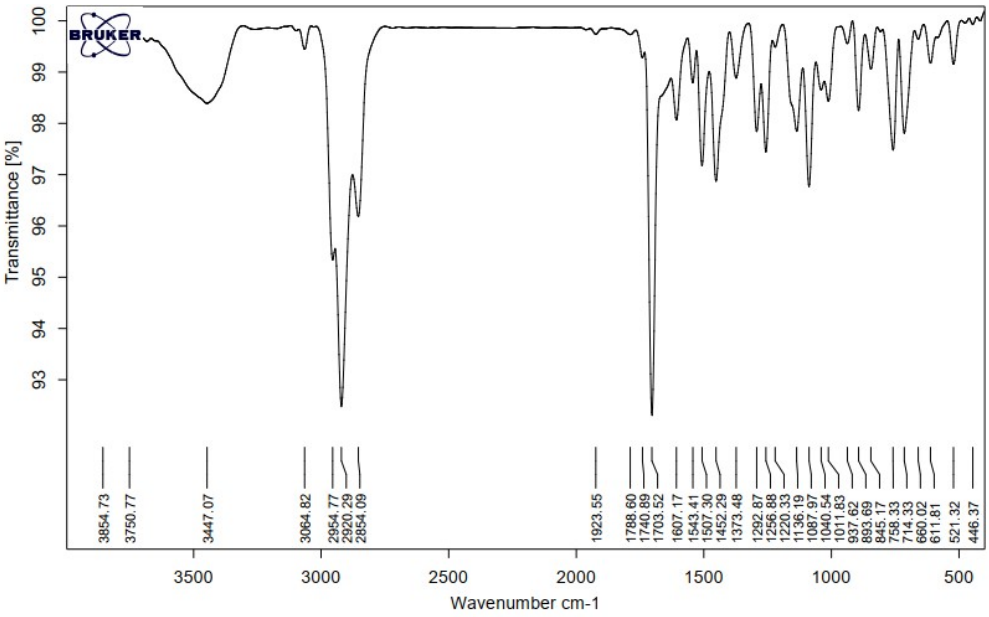


Figure 9: FT-IR (KBr) spectrum of **2b**.

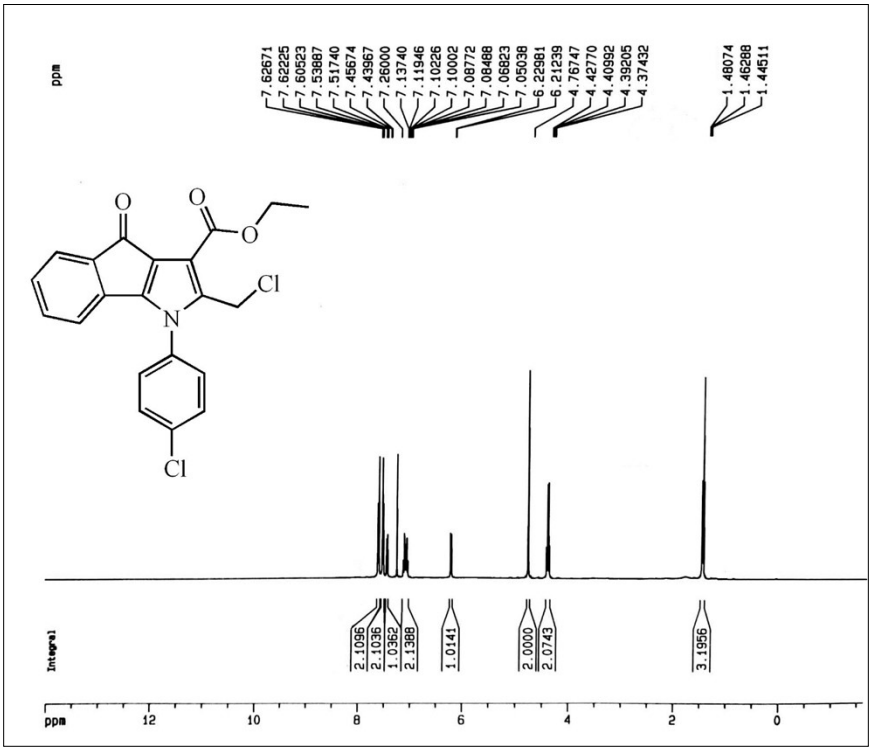


Figure 10: ^{1}H NMR spectrum (400 MHz) of compound **2b** in $CDCl_3$.

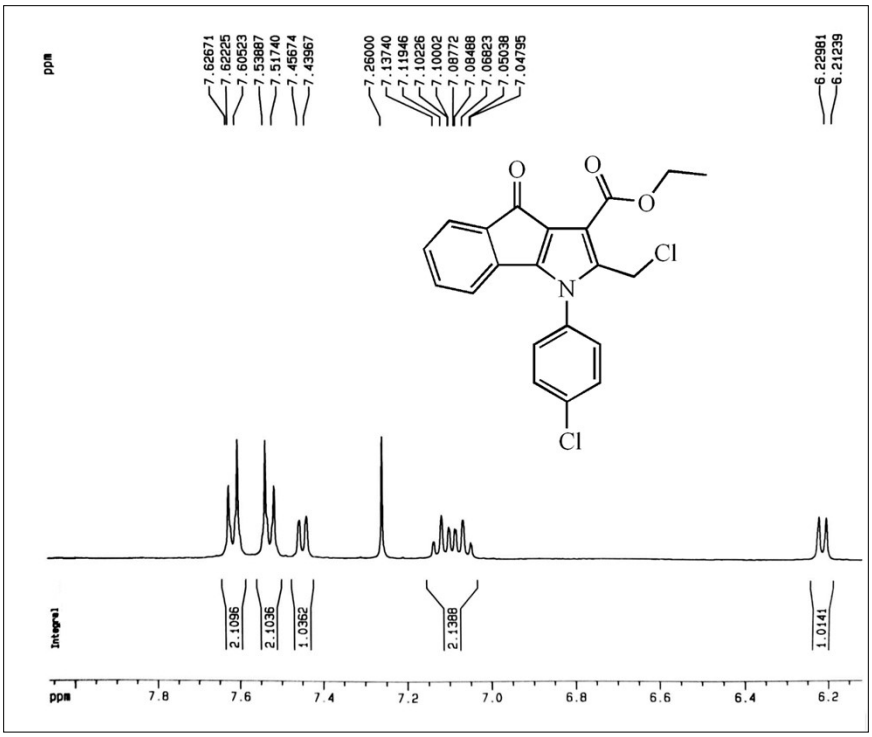


Figure 11: Expanded ^{1}H NMR spectrum (400 MHz) of compound **2b** in $CDCl_3$.

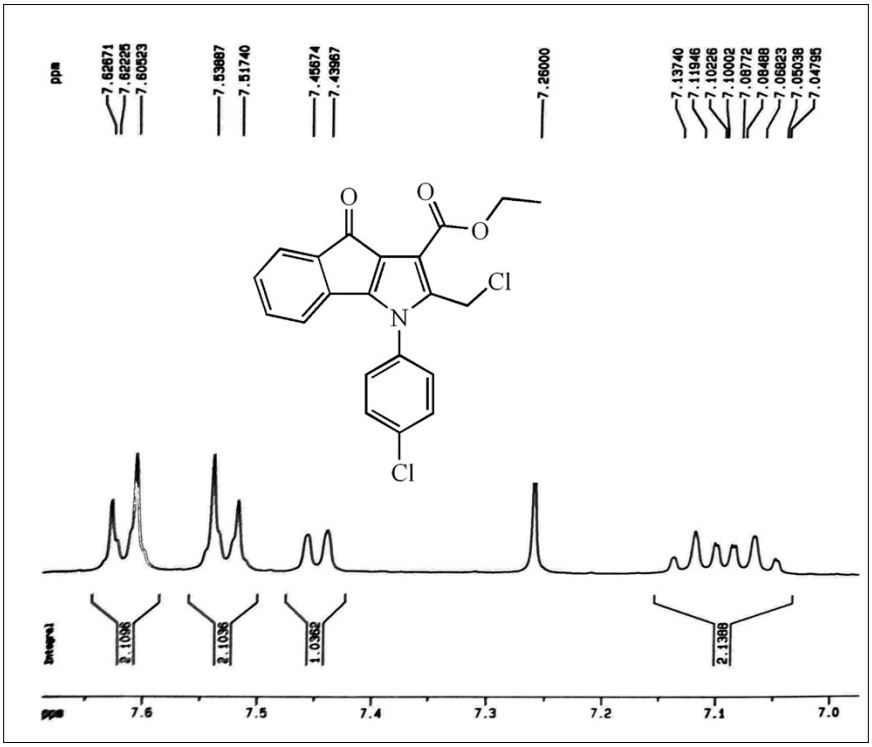


Figure 12: Expanded ^{1}H NMR spectrum (400 MHz) of compound **2b** in $CDCl_3$.

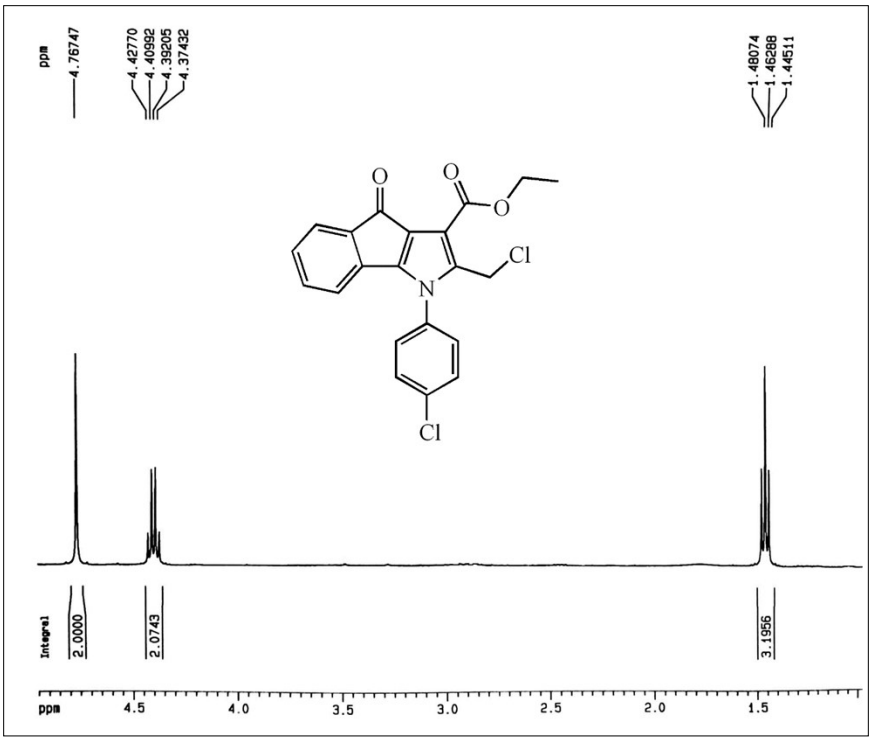


Figure 13: Expanded ^{1}H NMR spectrum (400 MHz) of compound **2b** in $CDCl_3$.

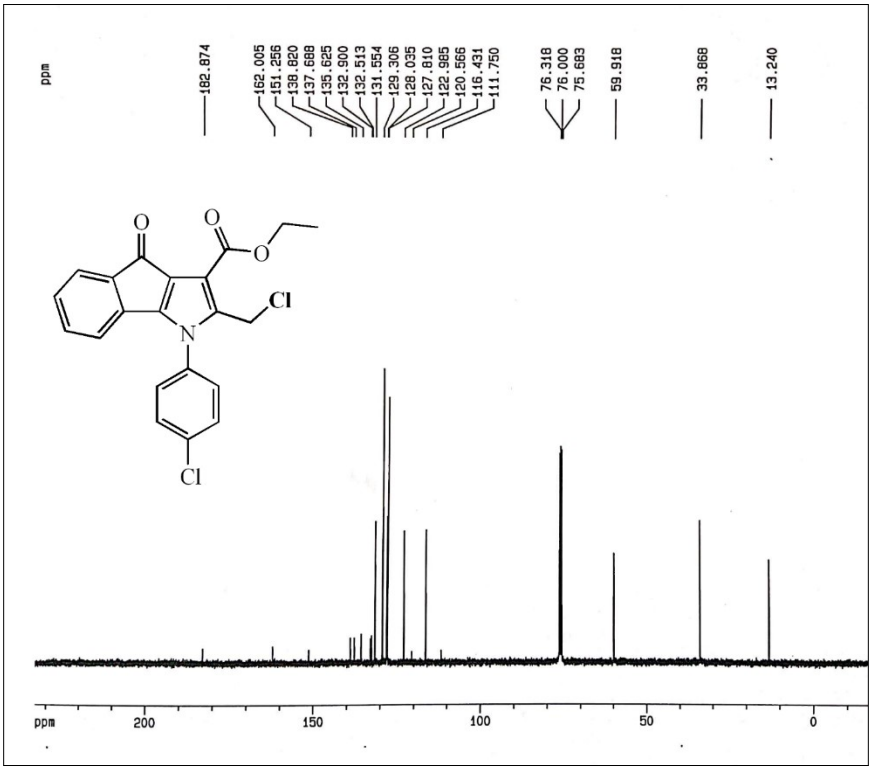


Figure 14: ^{13}C NMR spectrum (100 MHz) of compound **2b** in $CDCl_3$**.**

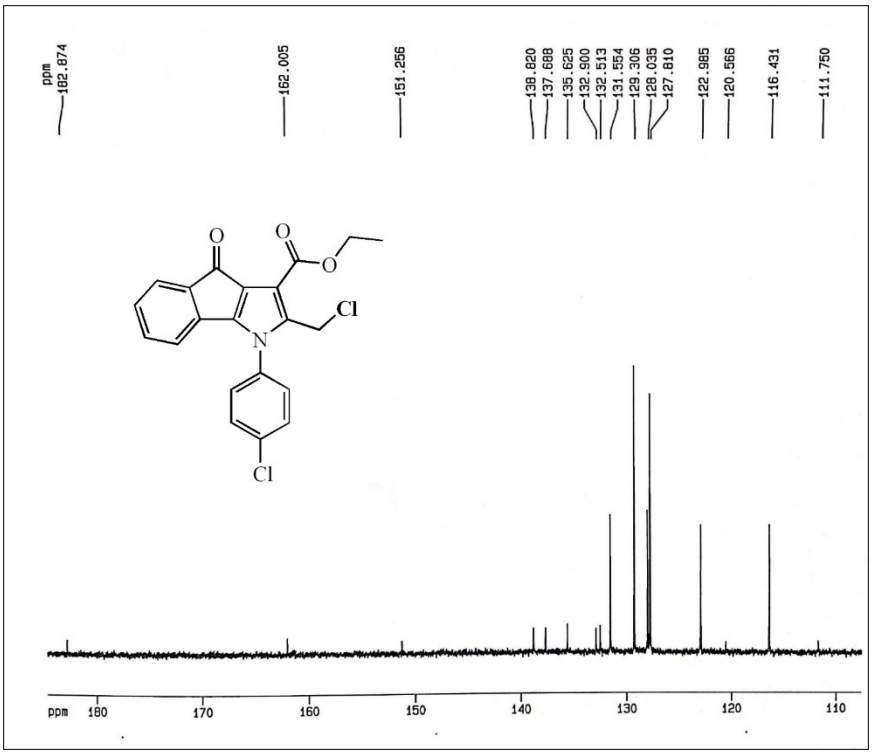


Figure 15: Expanded ^{13}C NMR spectrum (100 MHz) of compound **2b** in $CDCl_3$.

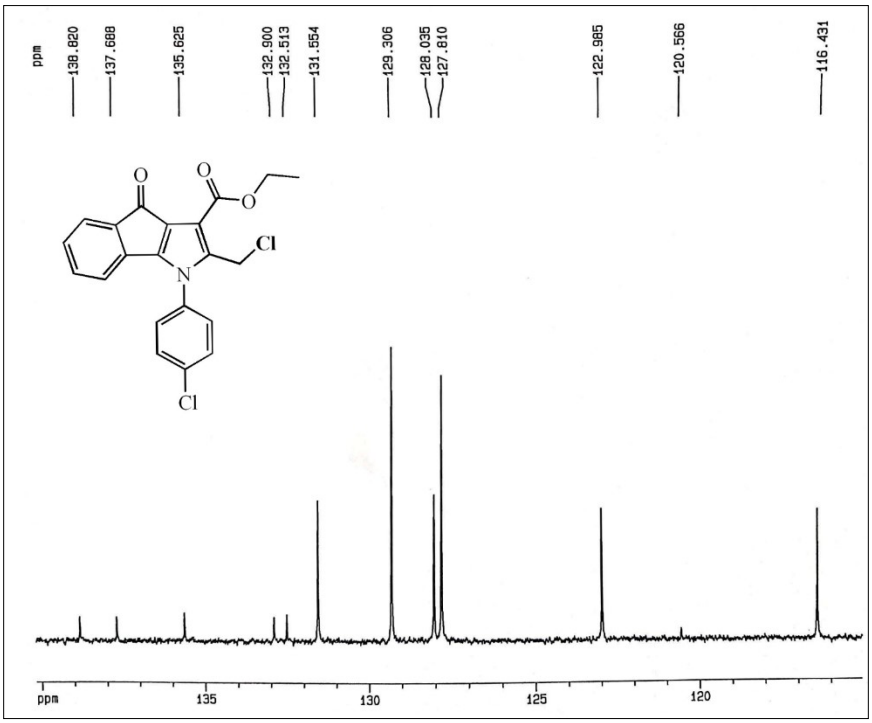


Figure 16: Expanded ^{13}C NMR spectrum (100 MHz) of compound **2b** in $CDCl_3$.

Methyl 2-(chloromethyl)-1-(4-nitrophenyl)-4-oxo-1,4-dihydroindeno[1,2-b]pyrrole-3-carboxylate (2c)

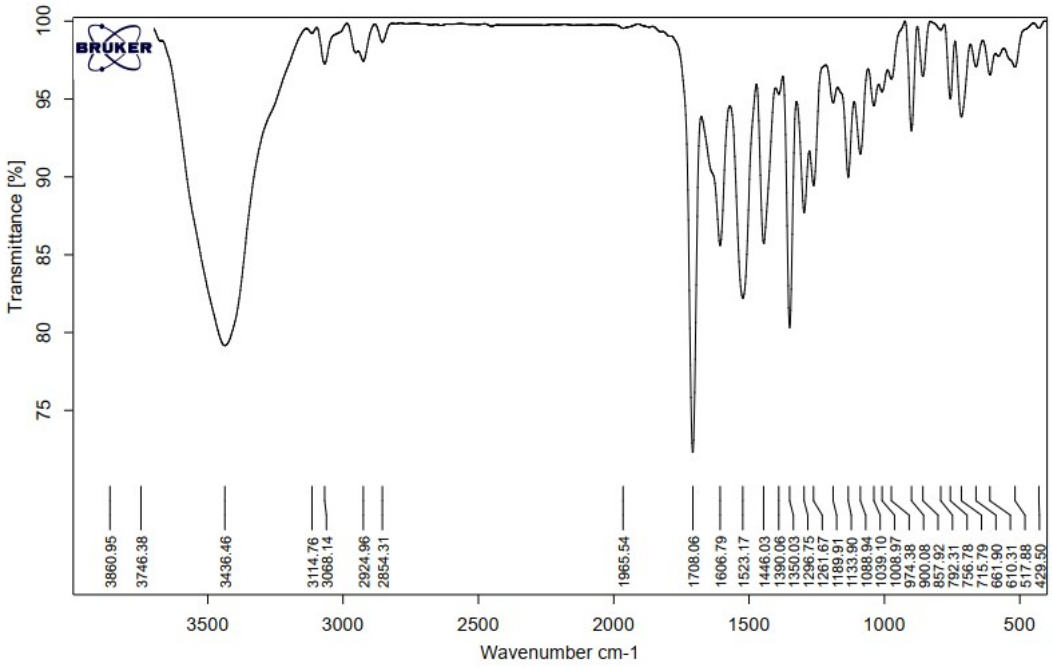


Figure 17: FT-IR (KBr) spectrum of **2c**.

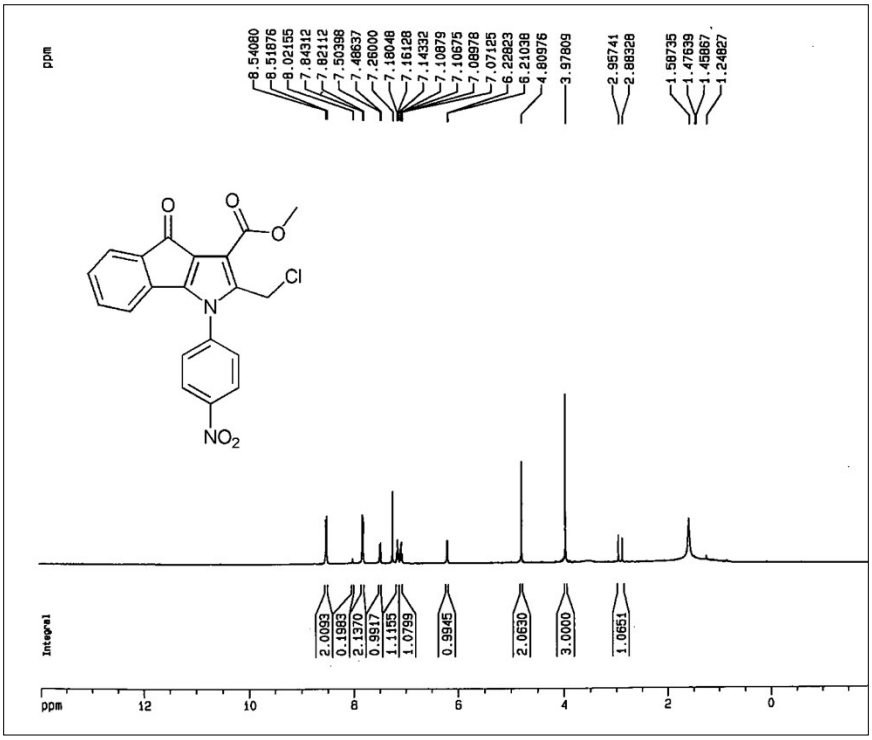


Figure 18: ^{1}H NMR spectrum (400 MHz) of compound **2c** in $CDCl_3$.

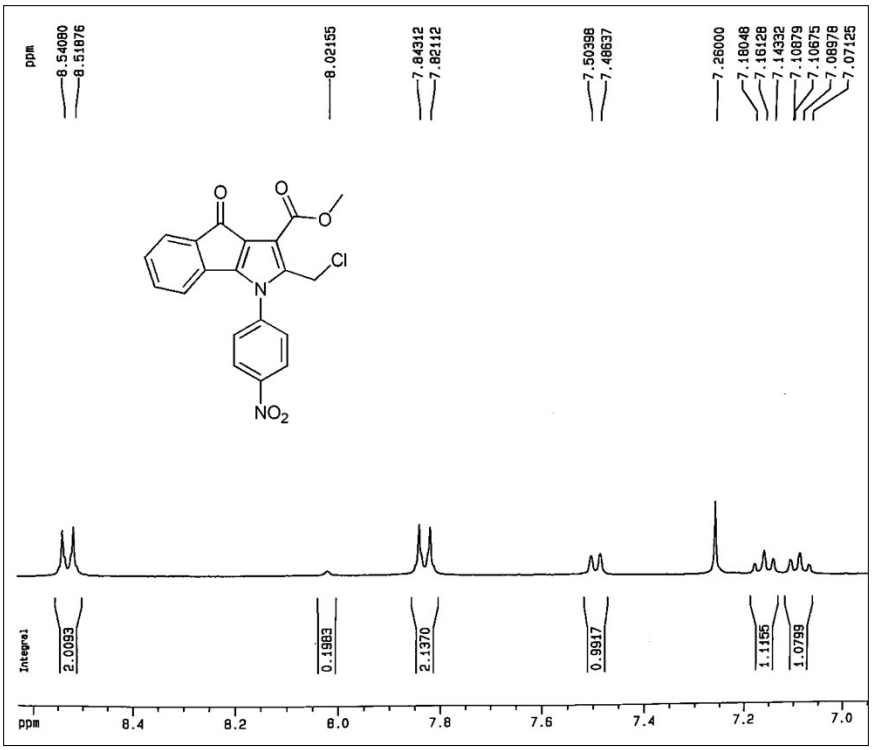


Figure 19: Expanded ^{1}H NMR spectrum (400 MHz) of compound **2c** in $CDCl_3$.

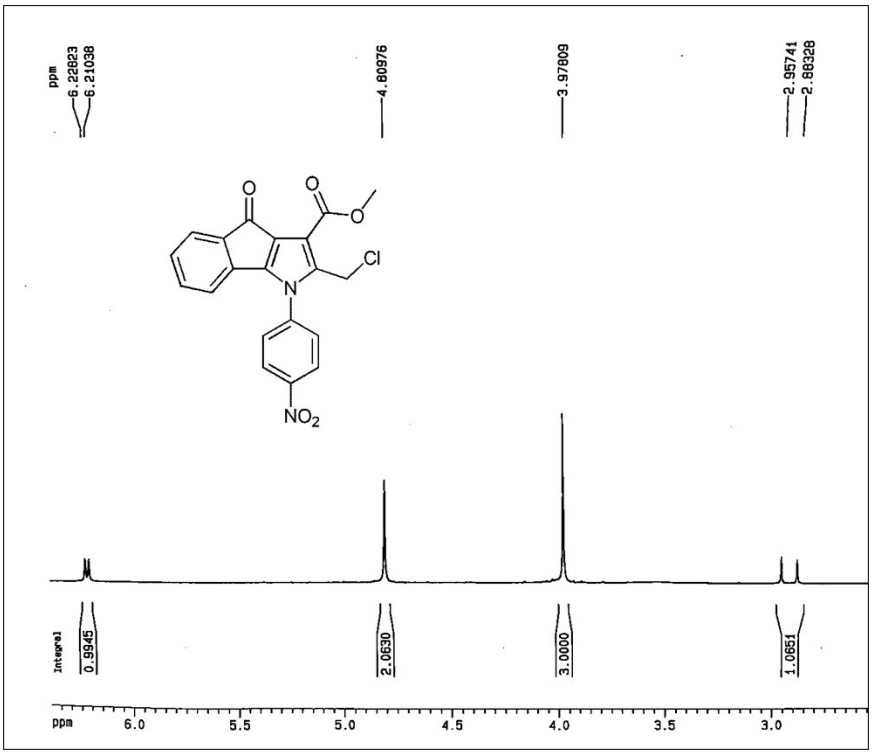


Figure 20: Expanded ^{1}H NMR spectrum (400 MHz) of compound **2c** in $CDCl_3$.

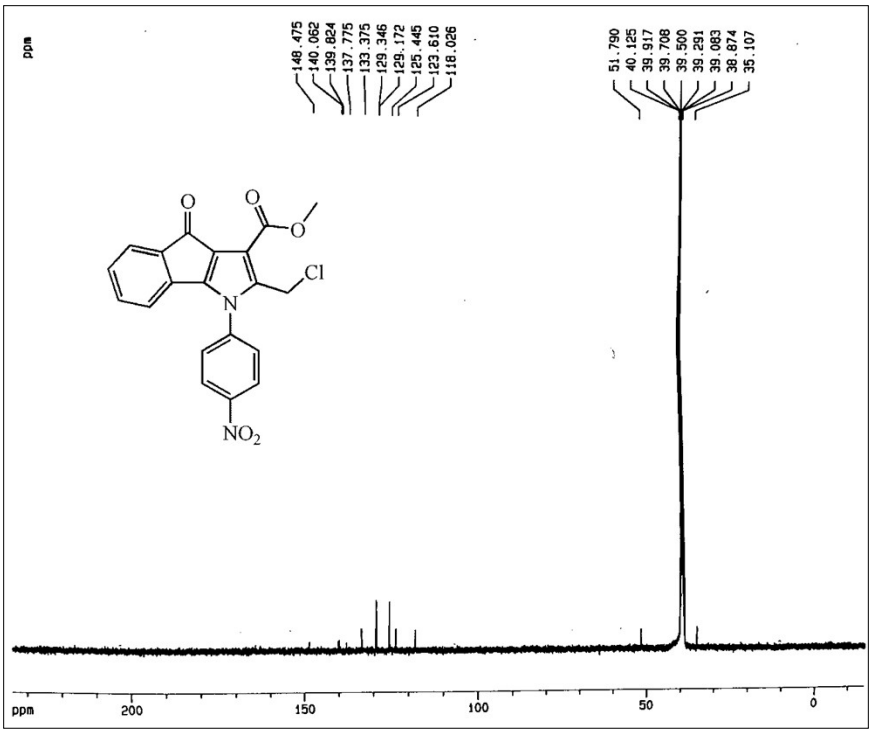


Figure 21: ^{13}C NMR spectrum (100 MHz) of compound **2c** in DMSO-d_6. The low solubility of this compound even in DMSO-d_6 caused that some of peaks were not observed.

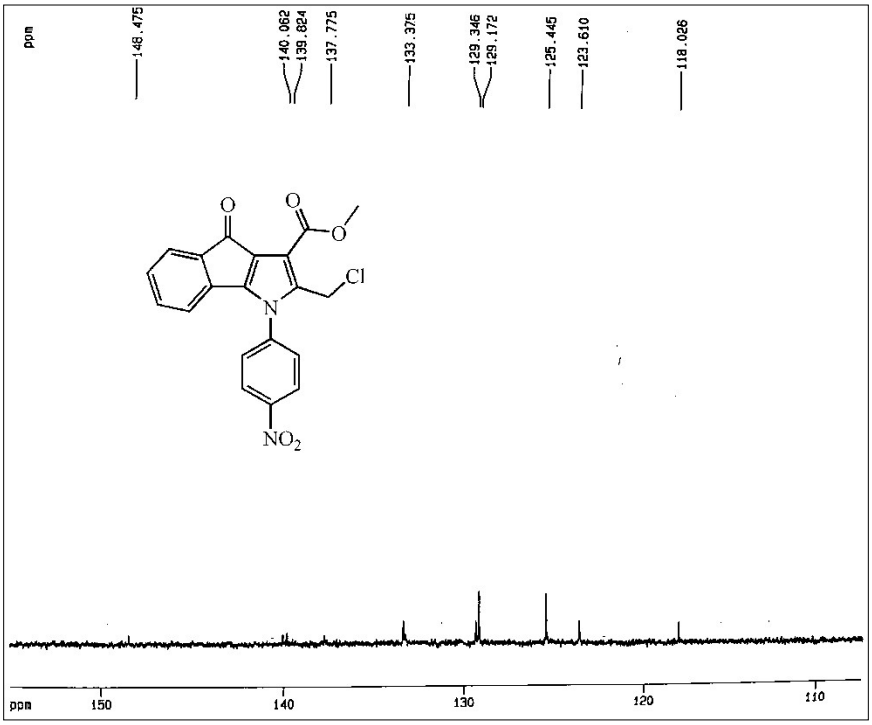


Figure 22: Expanded ^{13}C NMR spectrum (100 MHz) of compound **2c** in DMSO-d_6.

***tert*-Butyl 1-butyl-2-(chloromethyl)-4-oxo-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (2d)**

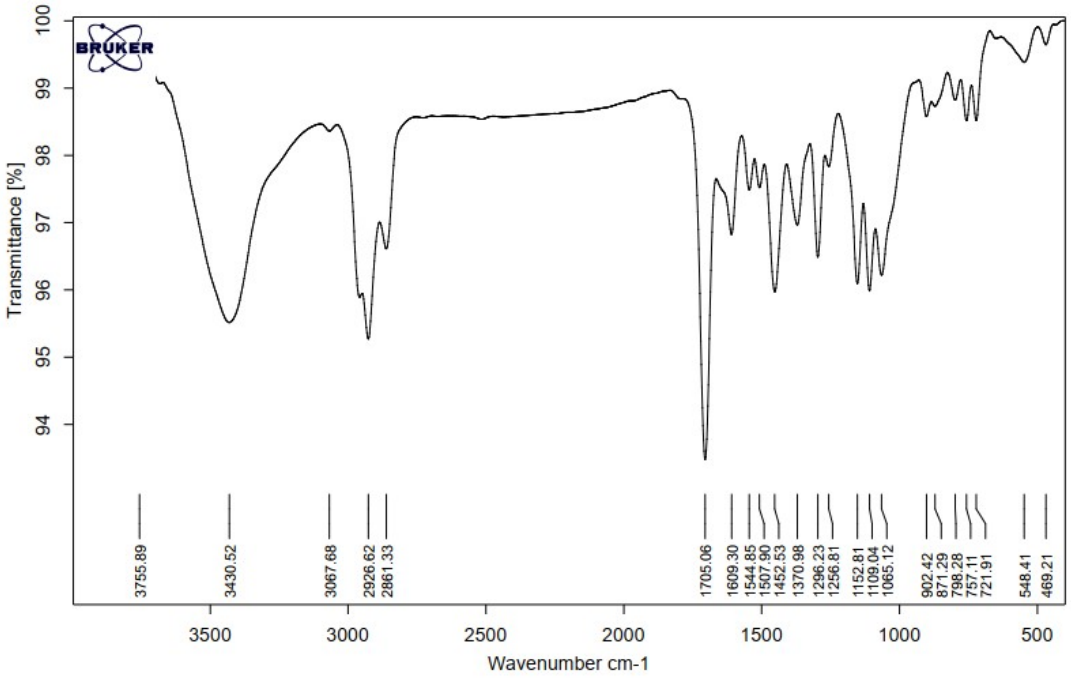


Figure 23: FT-IR (KBr) spectrum of **2d**.

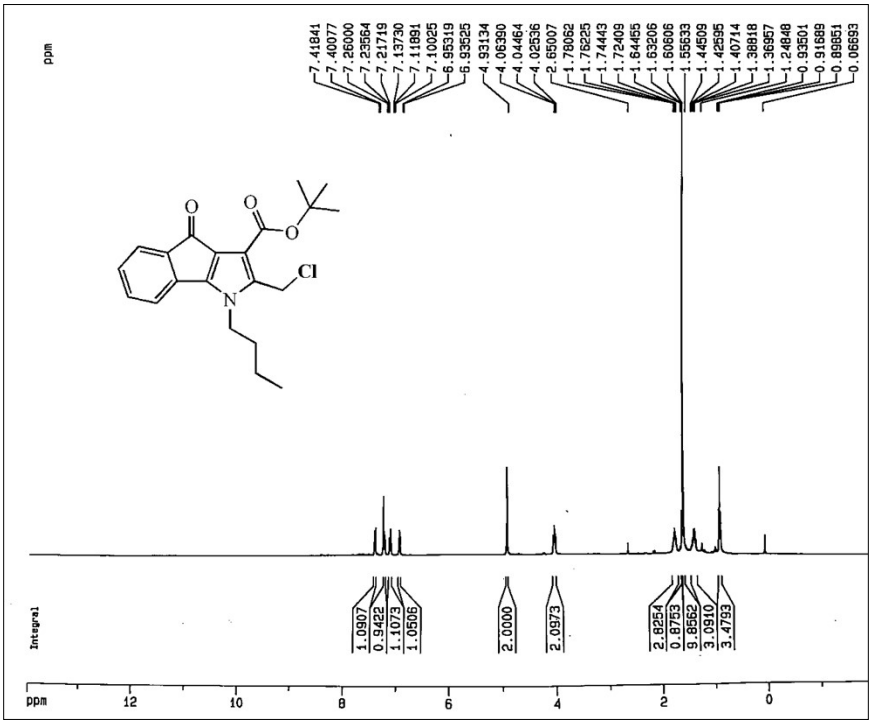


Figure 24: ^{1}H NMR spectrum (400 MHz) of compound **2d** in $CDCl_3$.

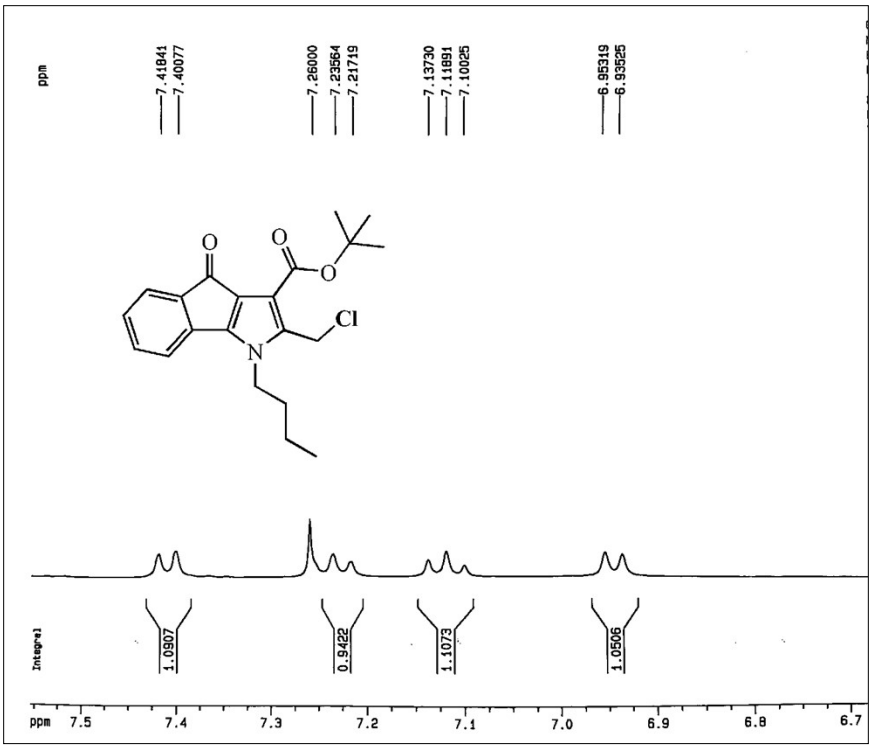


Figure 25: Expanded ^{1}H NMR spectrum (400 MHz) of compound **2d** in $CDCl_3$.

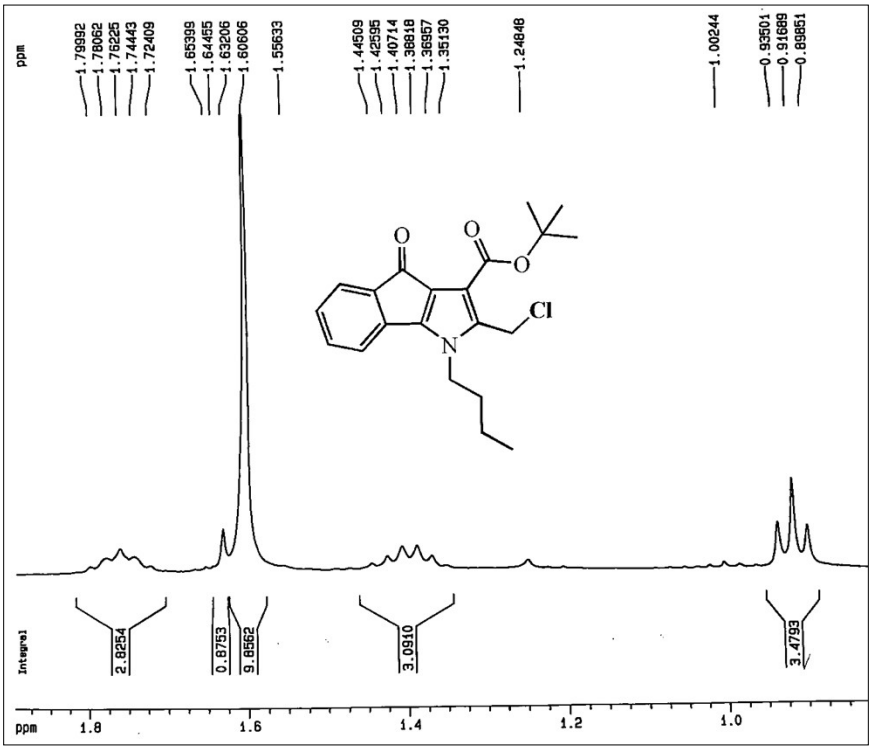


Figure 26: Expanded ^{1}H NMR spectrum (400 MHz) of compound **2d** in $CDCl_3$.

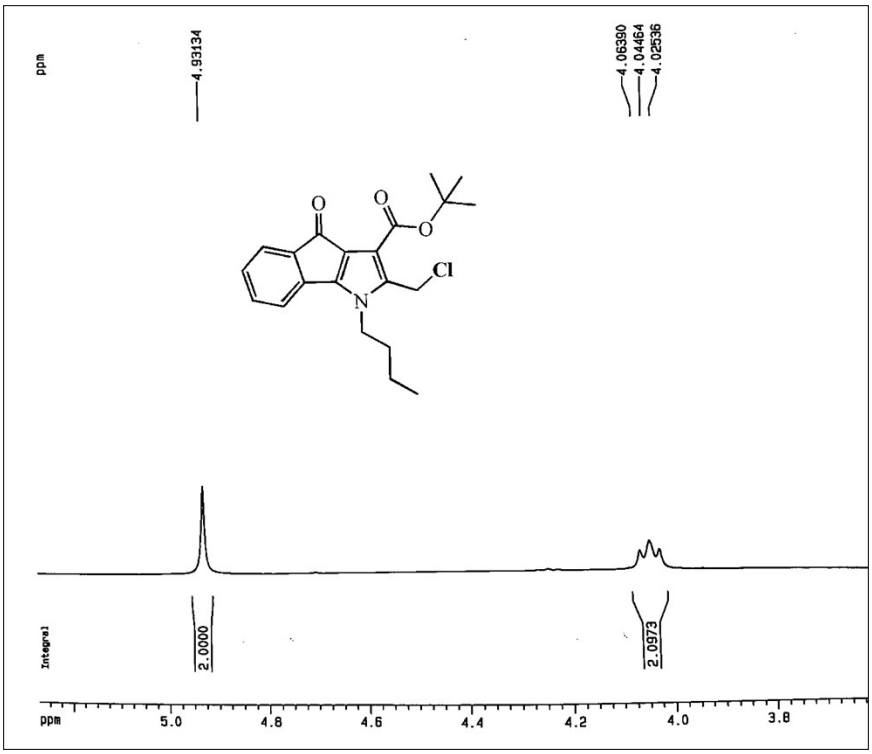


Figure 27: Expanded ^{1}H NMR spectrum (400 MHz) of compound **2d** in $CDCl_3$.

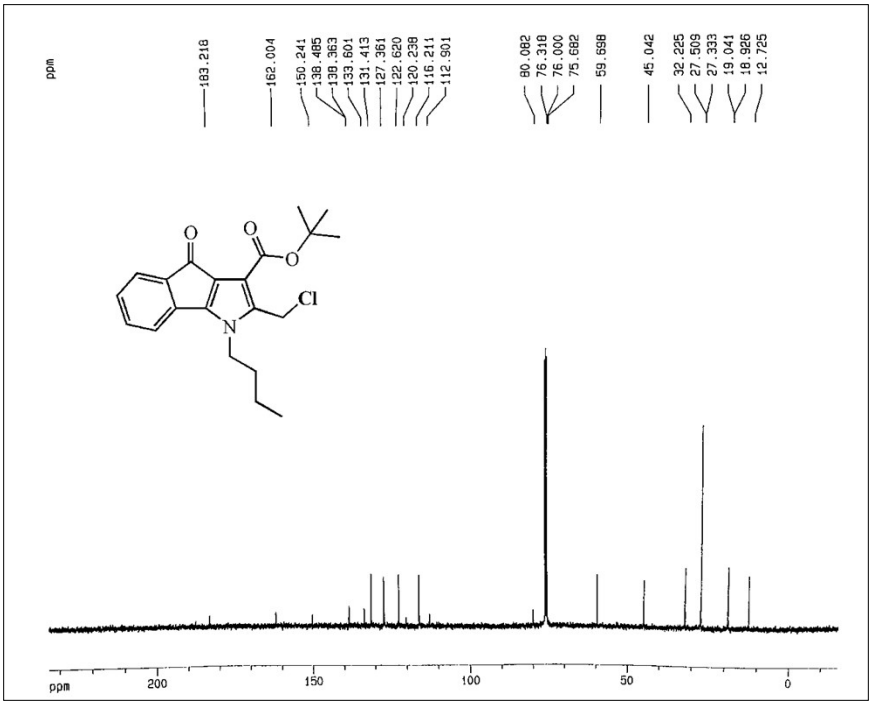


Figure 28: ^{13}C NMR spectrum (100 MHz) of compound **2d** in $CDCl_3$.

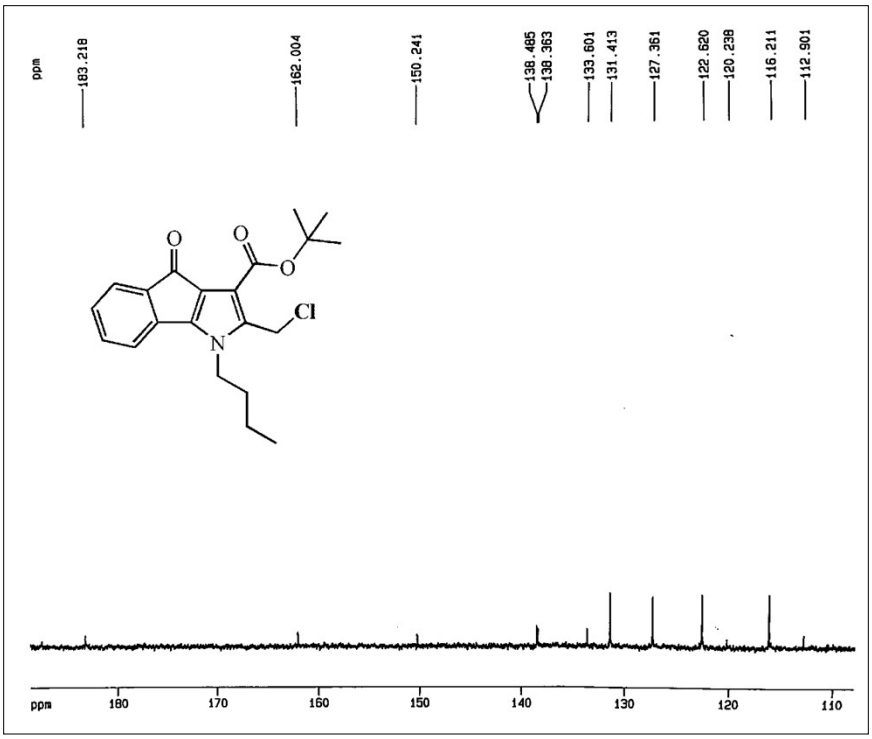


Figure 29: Expanded ^{13}C NMR spectrum (100 MHz) of compound **2d** in $CDCl_3$.

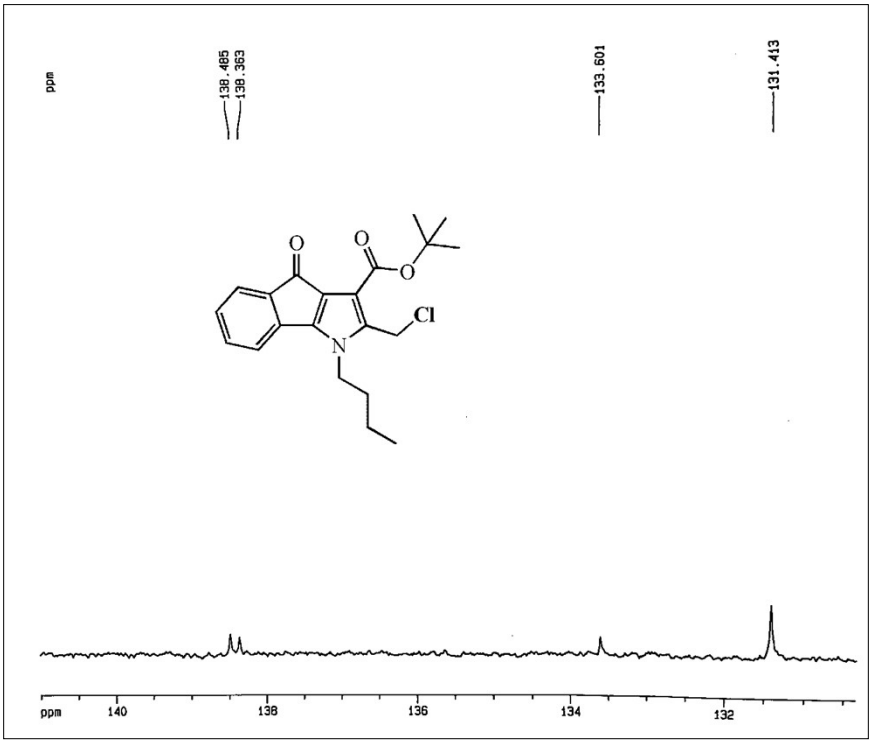


Figure 30: Expanded ^{13}C NMR spectrum (100 MHz) of compound **2d** in $CDCl_3$.

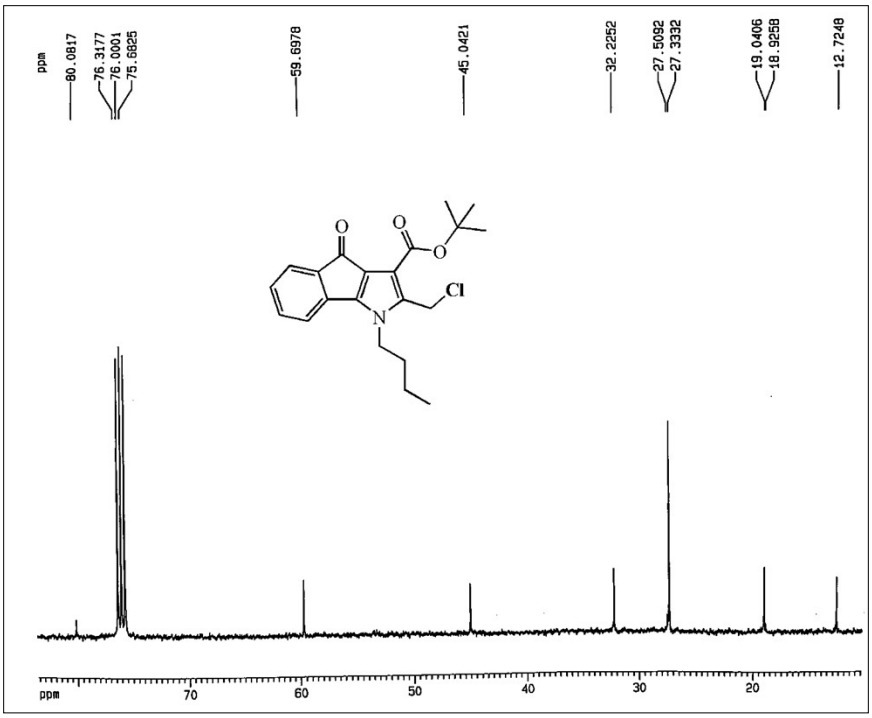


Figure 31: Expanded ^{13}C NMR spectrum (100 MHz) of compound **2d** in $CDCl_3$.

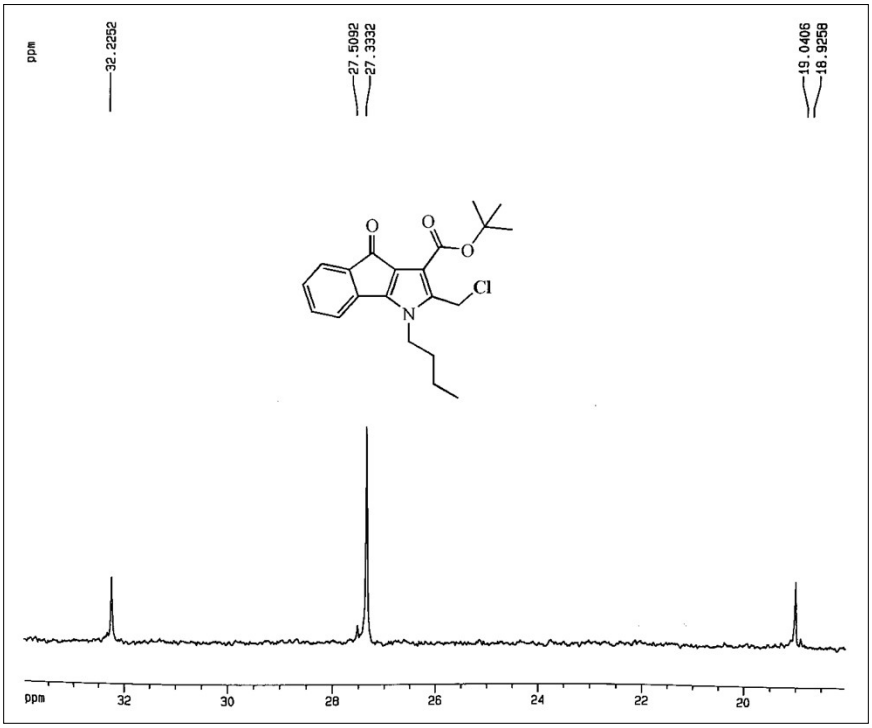


Figure 32: Expanded ^{13}C NMR spectrum (100 MHz) of compound **2d** in $CDCl_3$.

3-Acetyl-2-(chloromethyl)-1-(3-morpholinopropyl)indeno[1,2-*b*]pyrrol-4-one (2e)

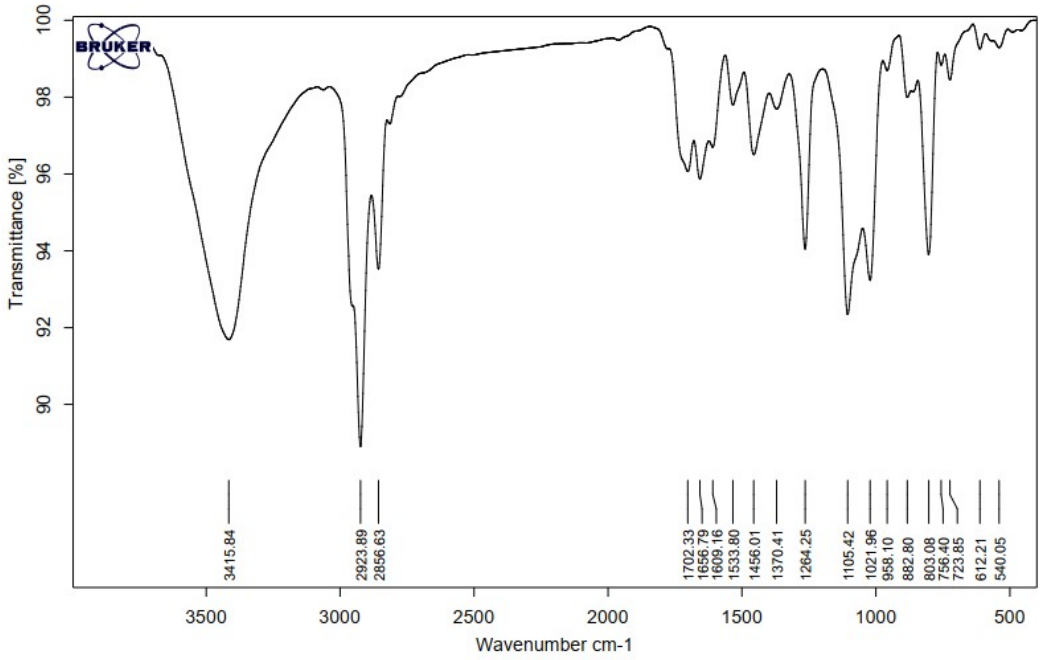


Figure 33: FT-IR (KBr) spectrum of **2e**.

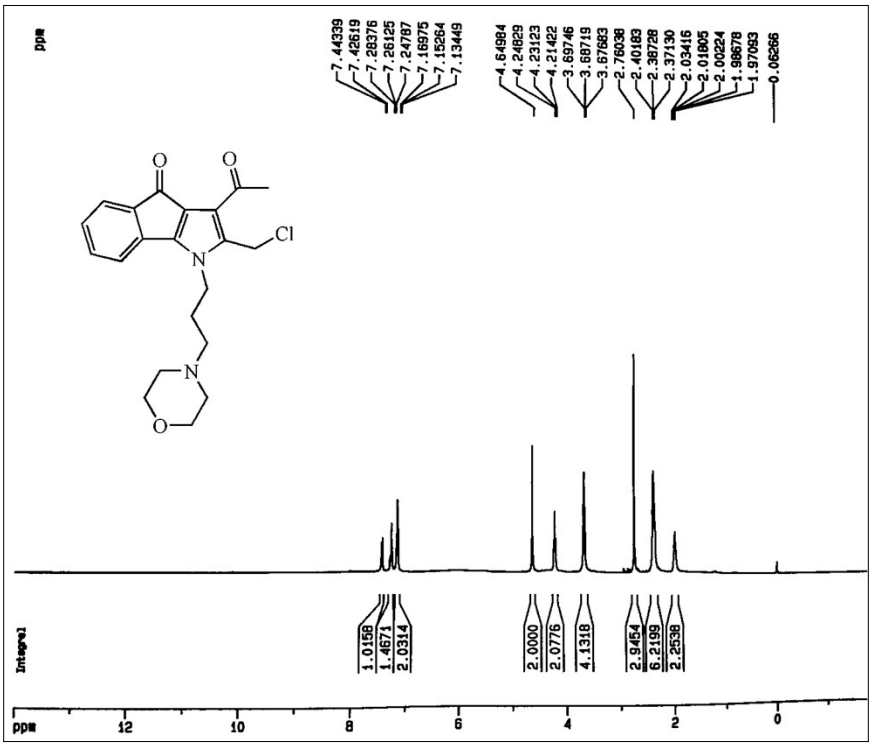


Figure 34: ^{1}H NMR spectrum (400 MHz) of compound **2e** in $CDCl_3$.

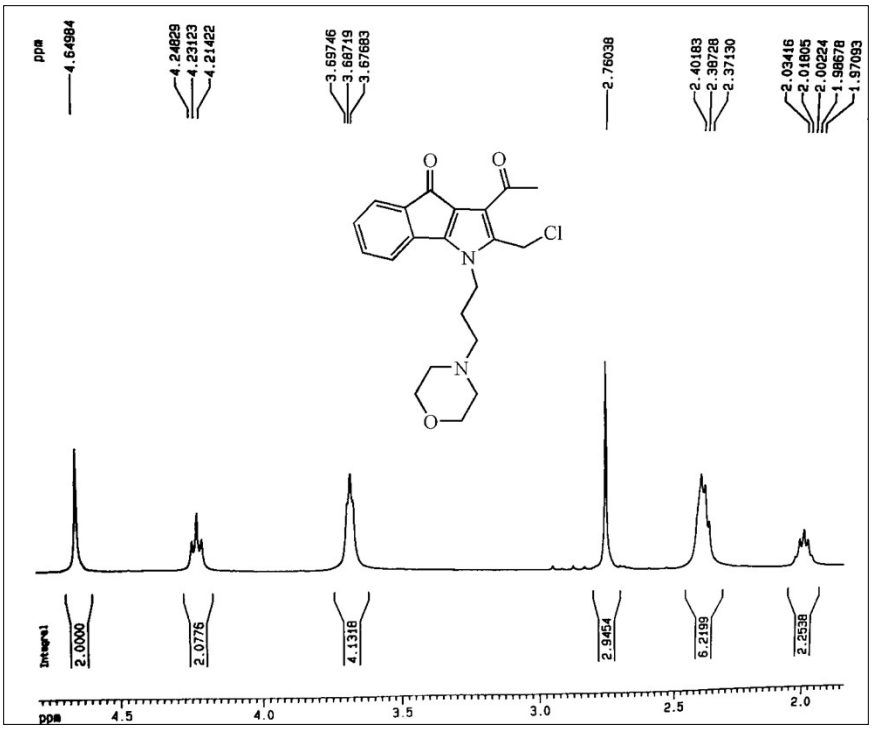


Figure 35: Expanded ^{1}H NMR spectrum (400 MHz) of compound **2e** in $CDCl_3$.

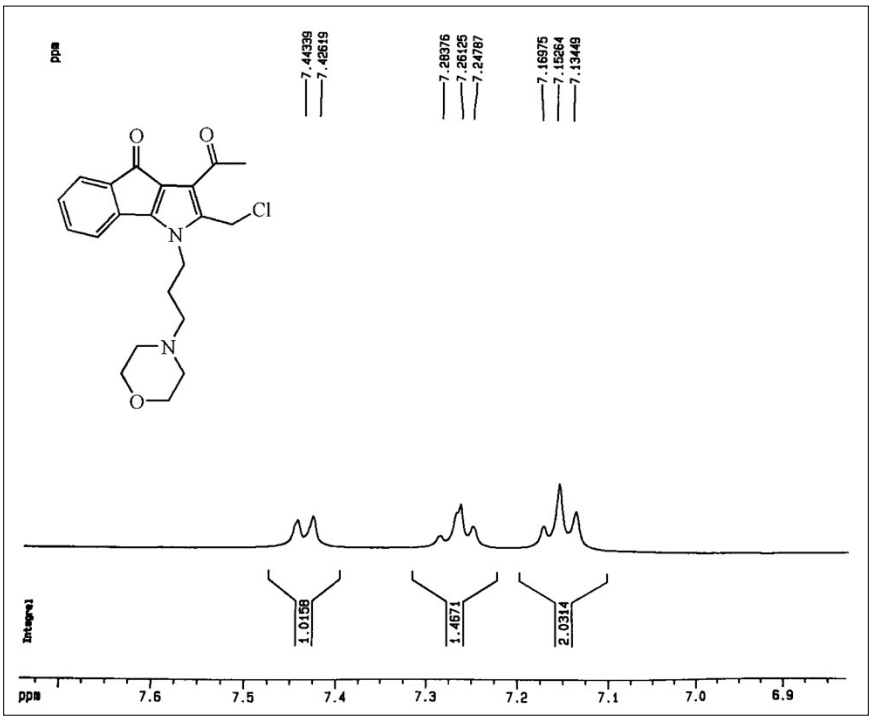


Figure 36: Expanded ^{1}H NMR spectrum (400 MHz) of compound **2e** in $CDCl_3$.

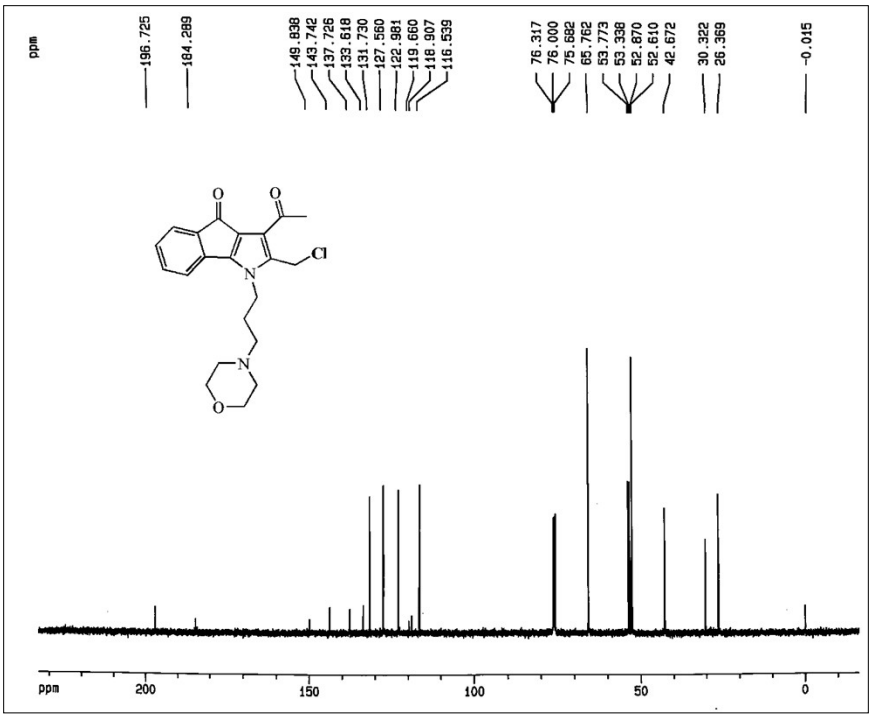


Figure 37: ^{13}C NMR spectrum (100 MHz) of compound **2e** in $CDCl_3$**.**

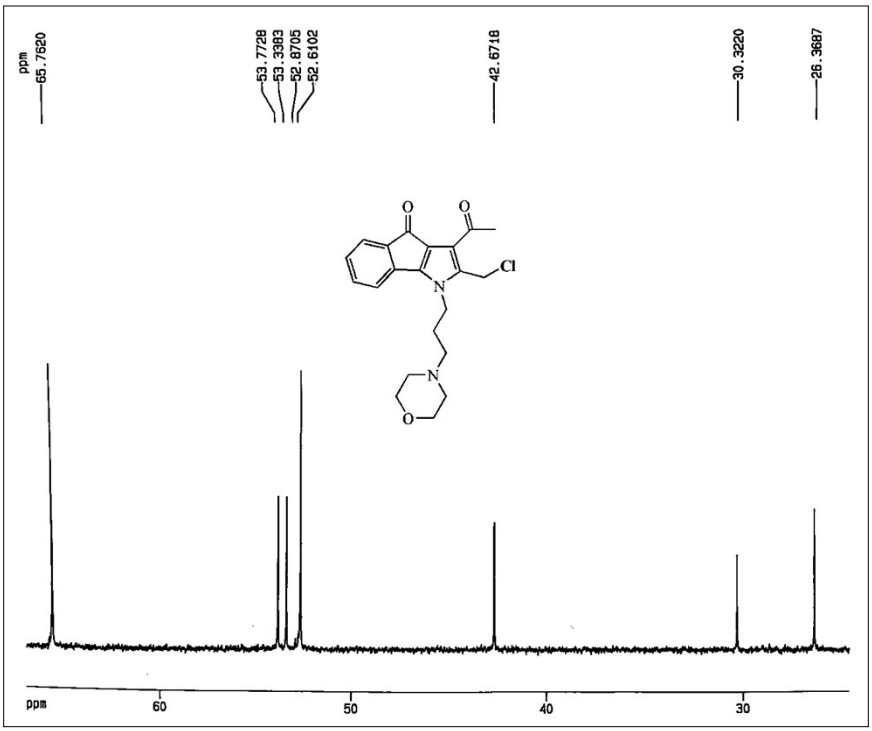


Figure 38: Expanded ^{13}C NMR spectrum (100 MHz) of compound **2e** in $CDCl_3$**.**

Methyl 2-(hydroxymethyl)-4-oxo-1-phenyl-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (3a)

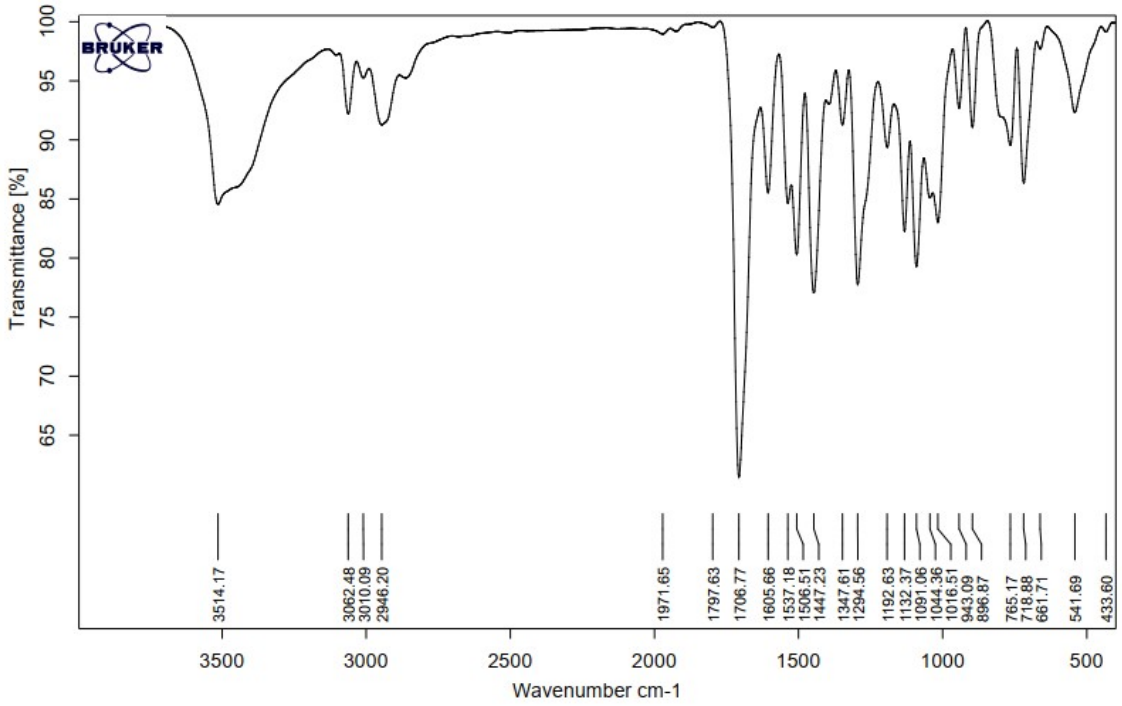


Figure 39: FT-IR (KBr) spectrum of **3a**.

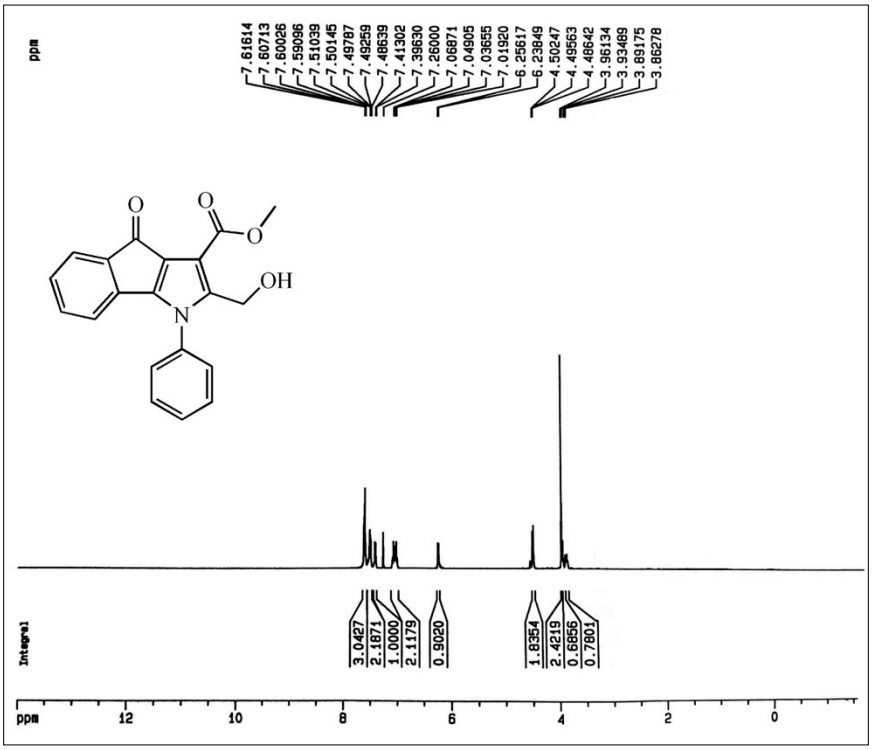


Figure 40: ^{1}H NMR spectrum (400 MHz) of compound **3a** in $CDCl_3$.

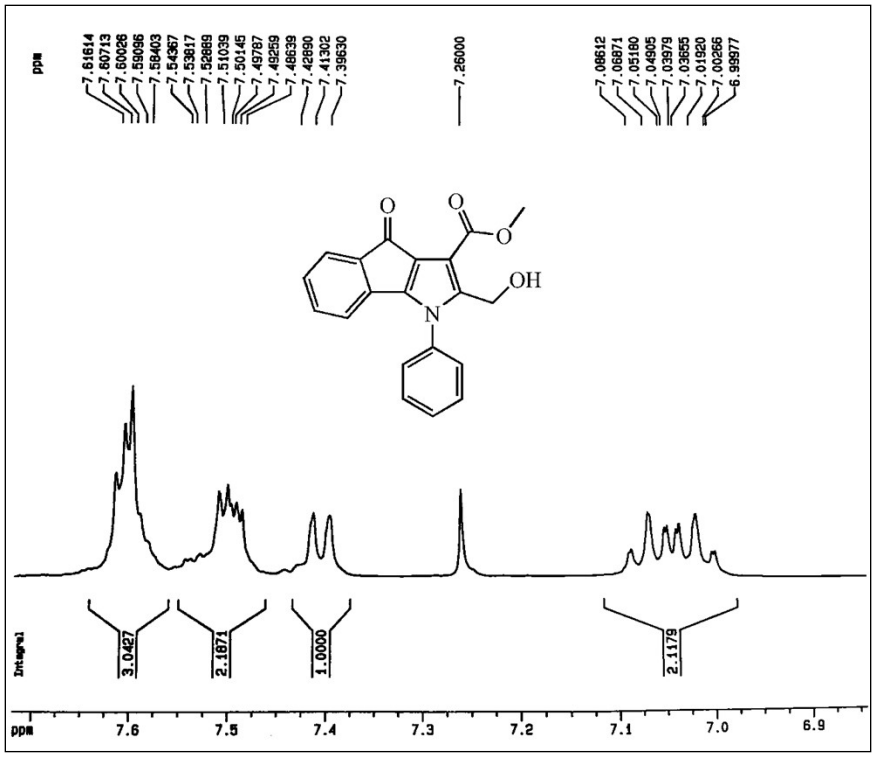


Figure 41: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3a** in $CDCl_3$.

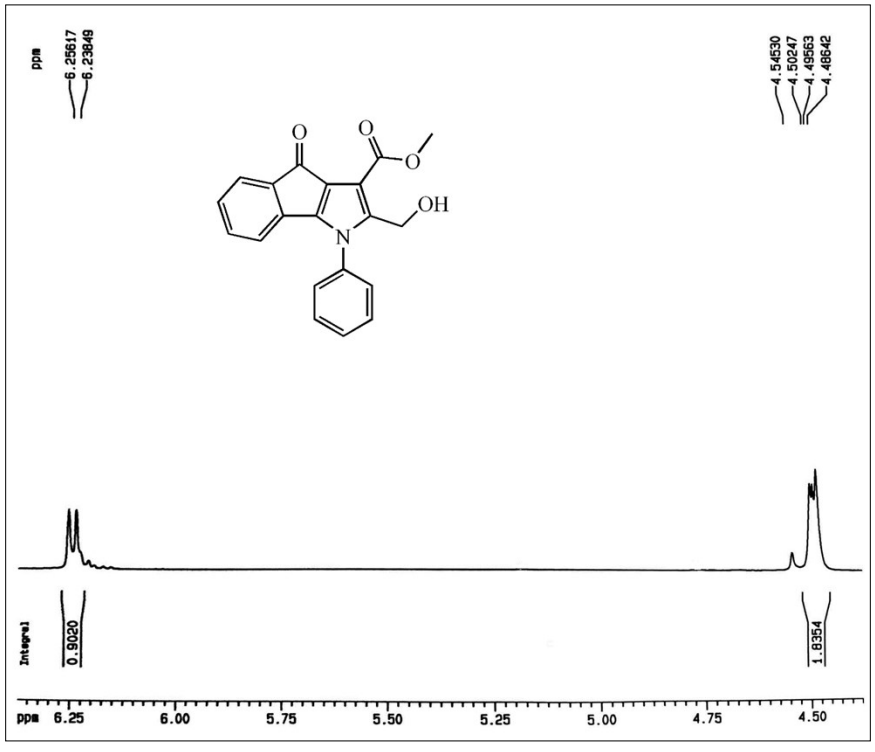


Figure 42: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3a** in $CDCl_3$.

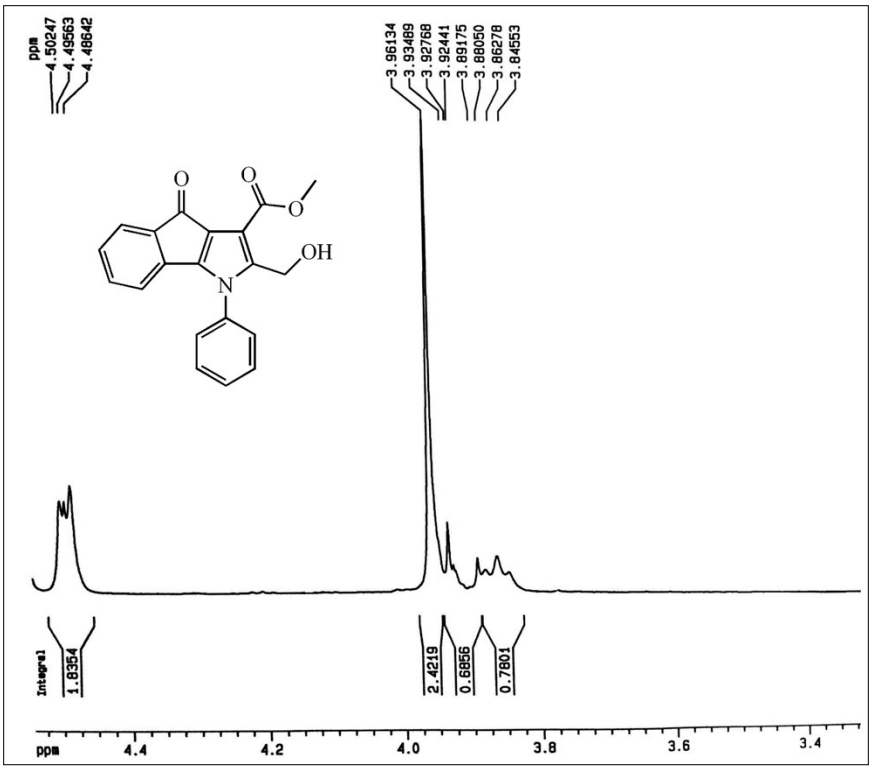


Figure 43: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3a** in $CDCl_3$.

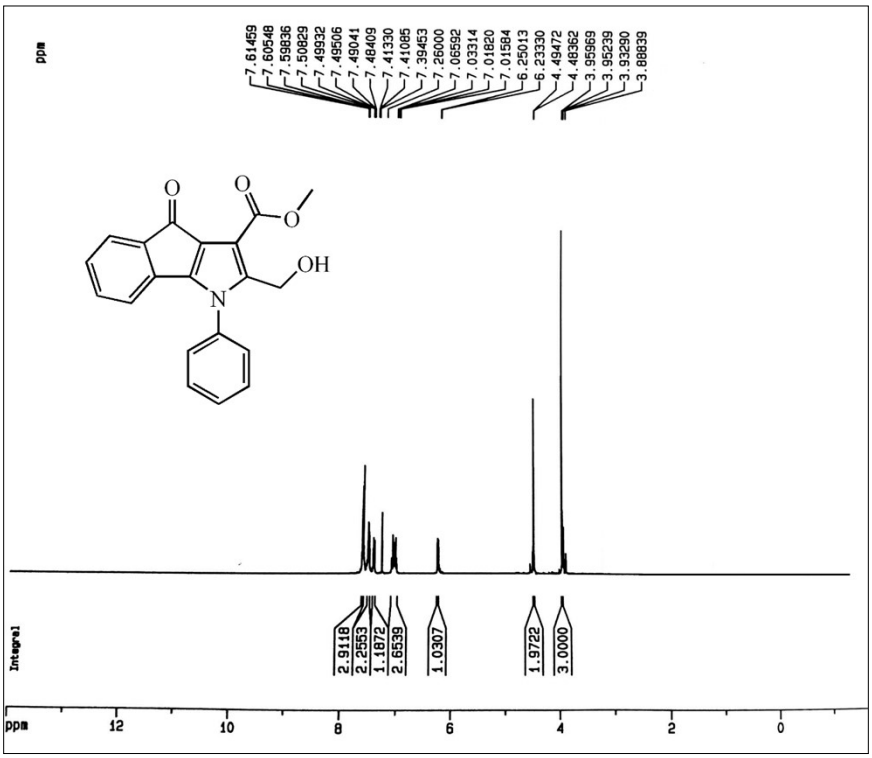


Figure 44: ^{1}H NMR spectrum (400 MHz) of compound **3a** in $CDCl_3/D_2O$.

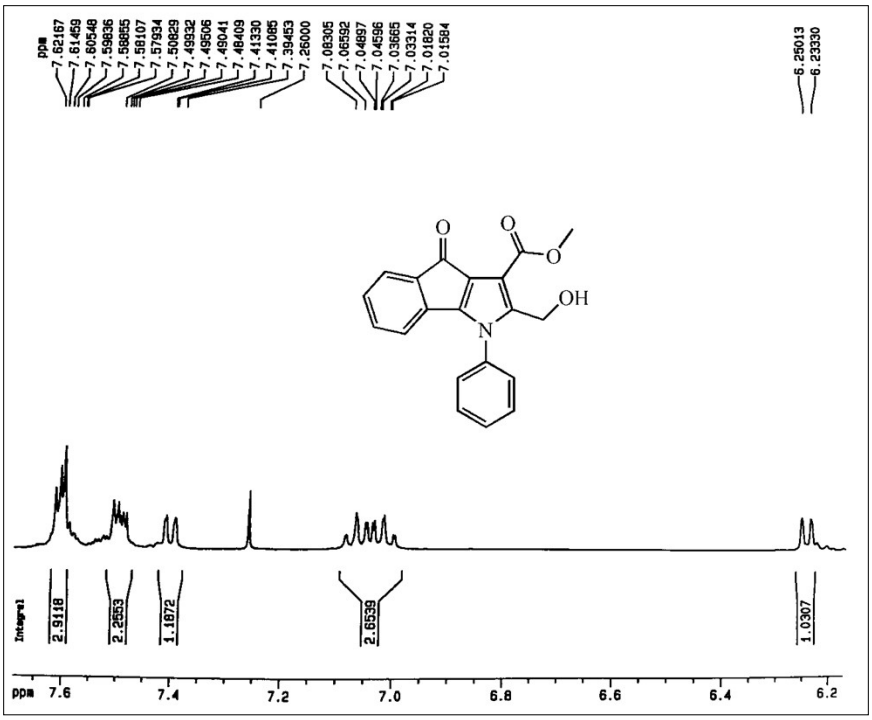


Figure 45: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3a** in $CDCl_3/D_2O$.

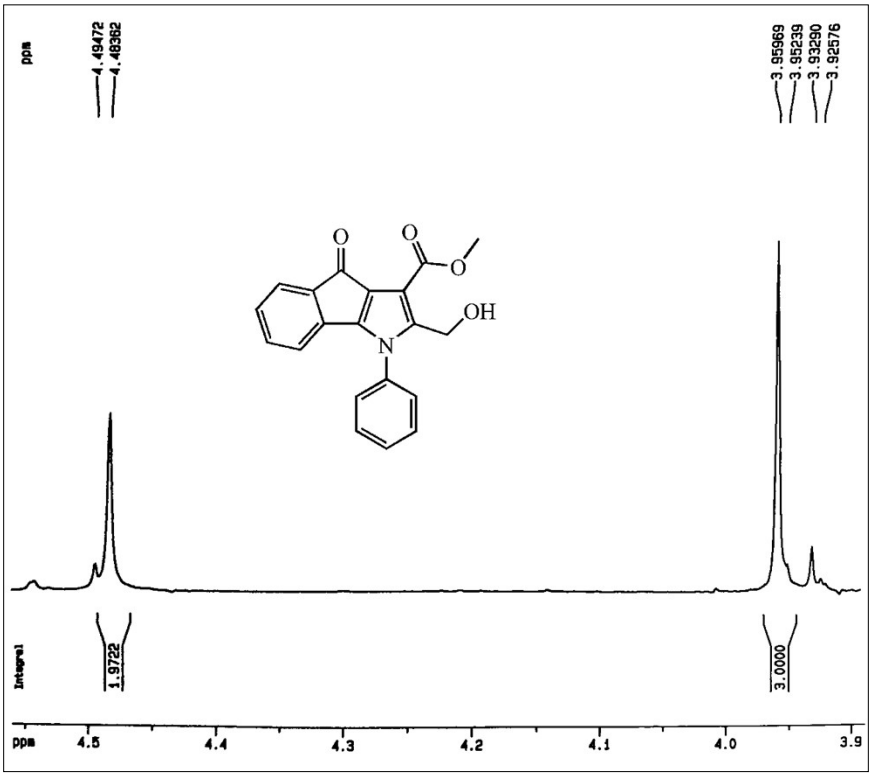


Figure 46: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3a** in $CDCl_3/D_2O$.

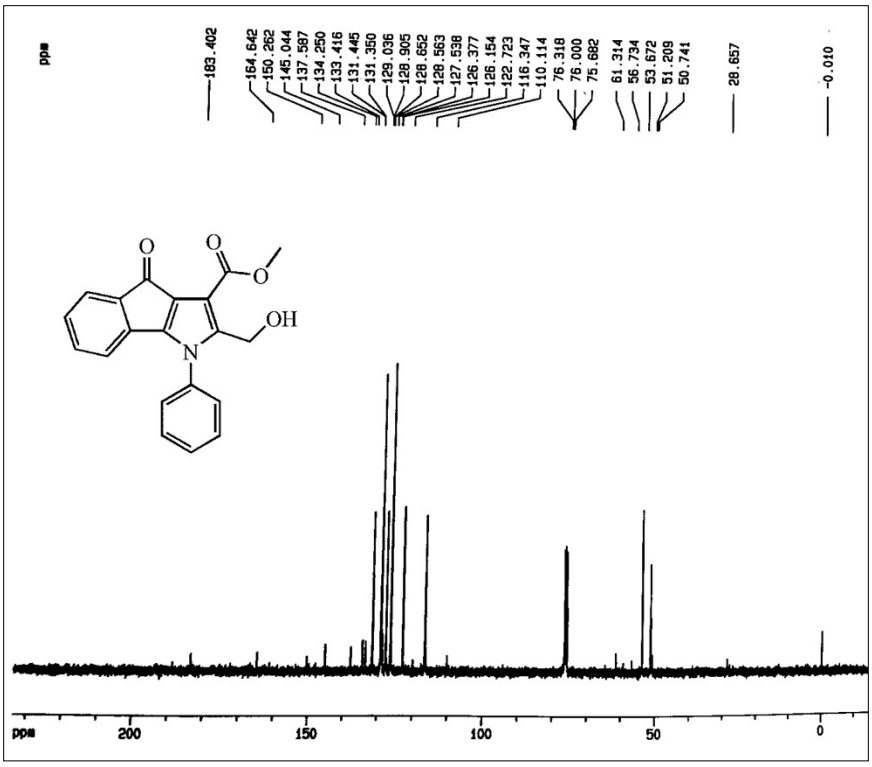


Figure 47: ^{13}C NMR spectrum (100 MHz) of compound **3a** in $CDCl_3$.

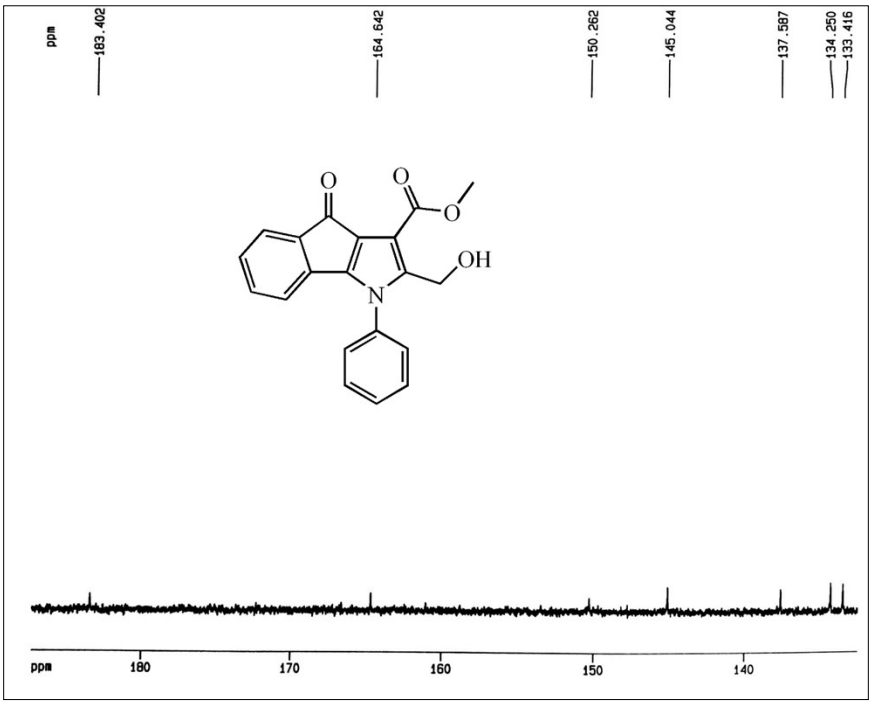


Figure 48: Expanded ^{13}C NMR spectrum (100 MHz) of compound **3a** in $CDCl_3$.

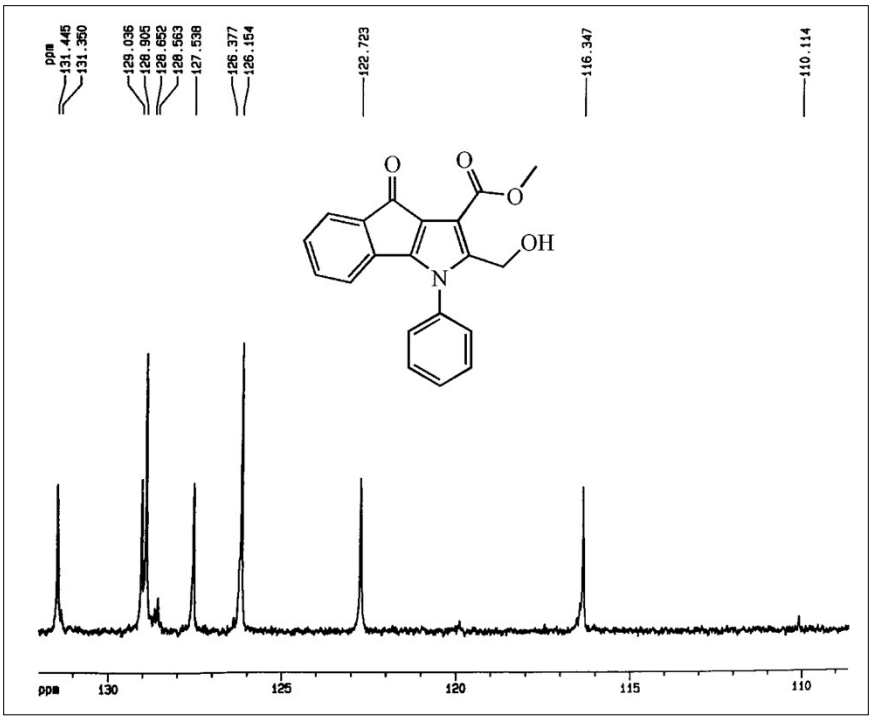


Figure 49: Expanded ^{13}C NMR spectrum (100 MHz) of compound **3a** in $CDCl_3$.

Ethyl 1-(4-chlorophenyl)-2-(hydroxymethyl)-4-oxo-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (3b)

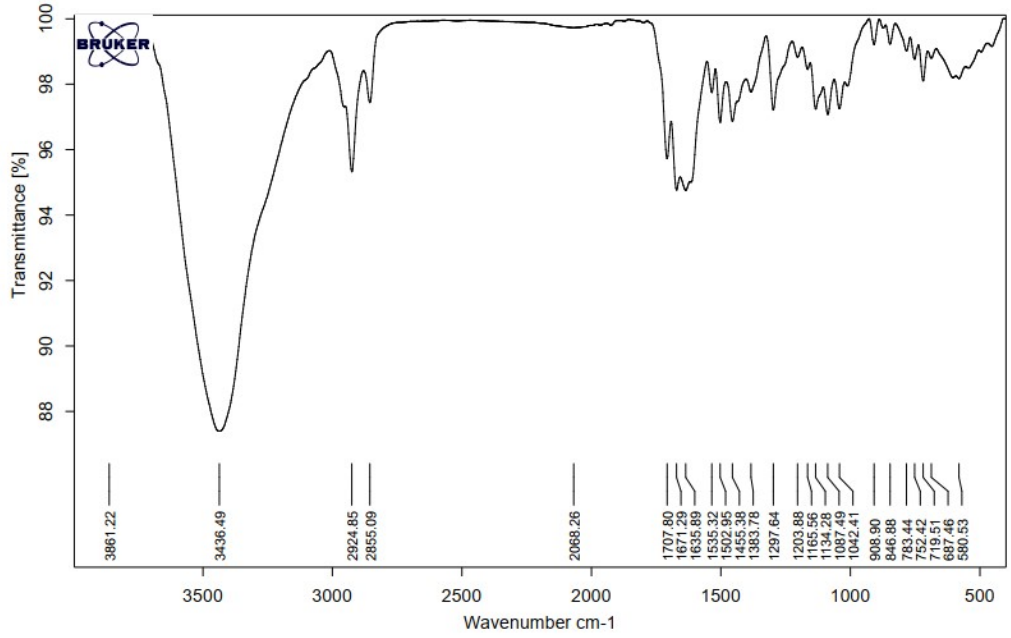


Figure 50: FT-IR (KBr) spectrum of **3b**.

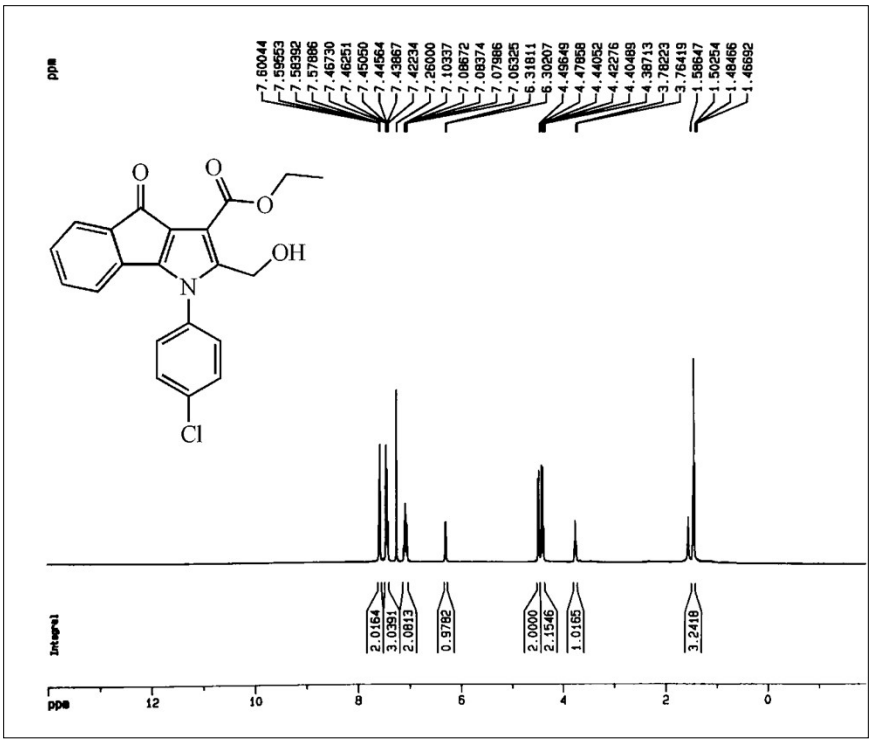


Figure 51: ^{1}HNMR spectrum (400 MHz) of compound **3b** in $CDCl_3$.

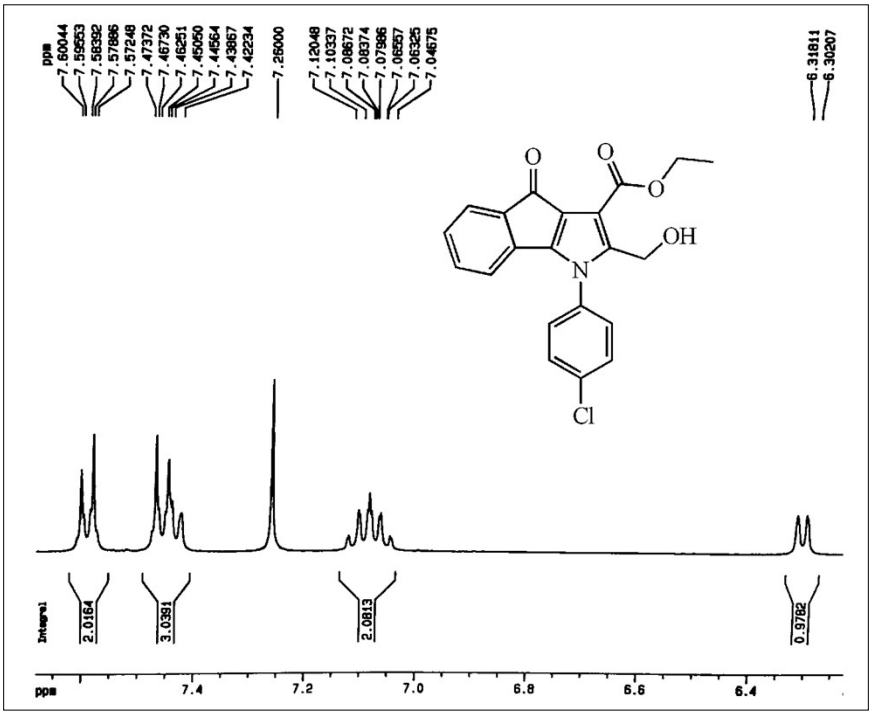


Figure 52: Expanded ^{1}HNMR spectrum (400 MHz) of compound **3b** in $CDCl_3$.

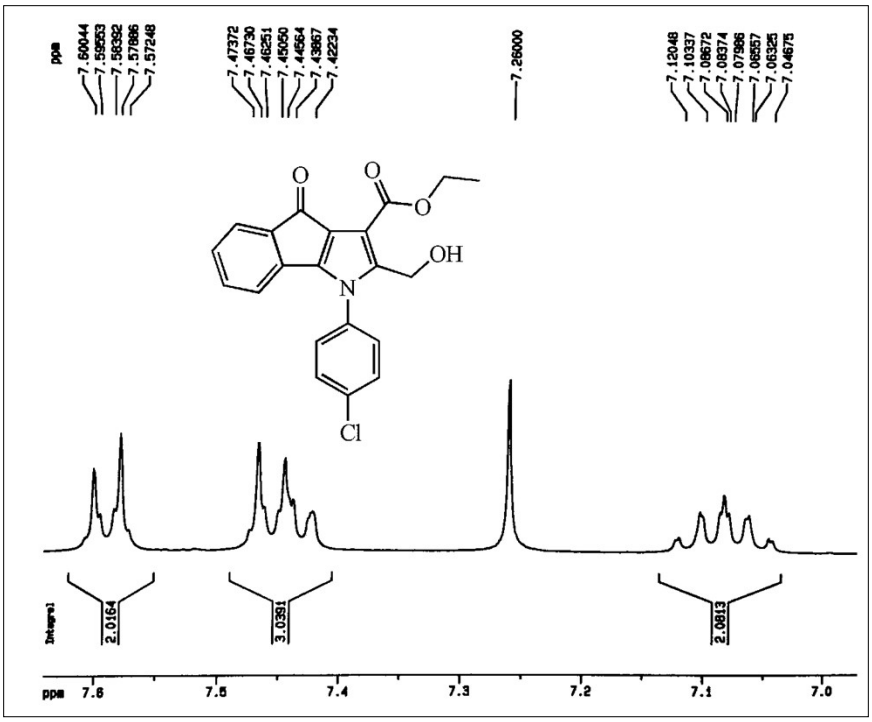


Figure 53: Expanded ^{1}HNMR spectrum (400 MHz) of compound **3b** in $CDCl_3$.

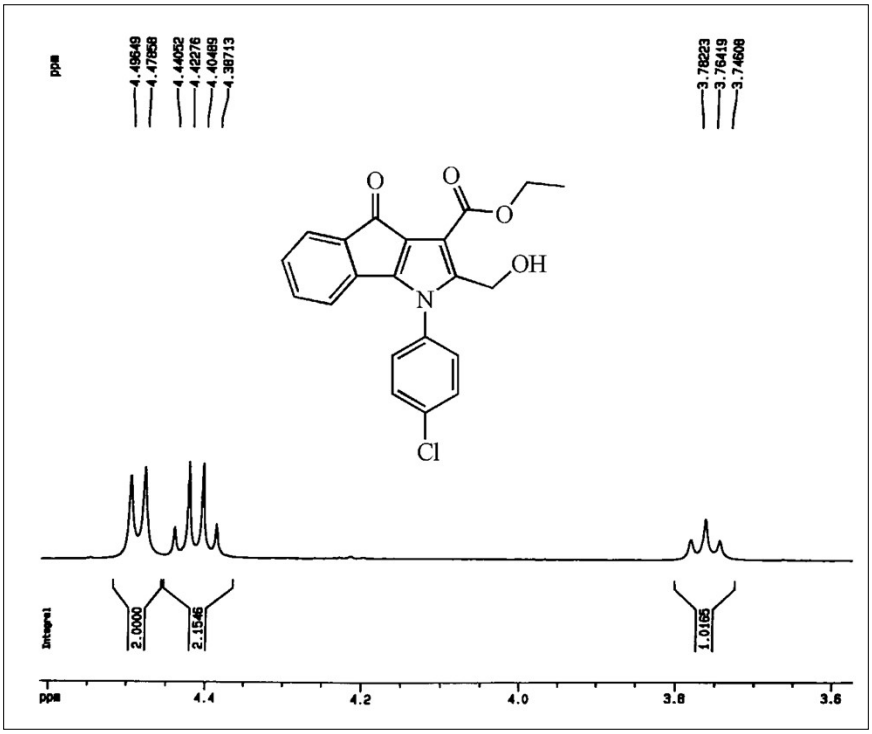


Figure 54: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3b** in $CDCl_3$.

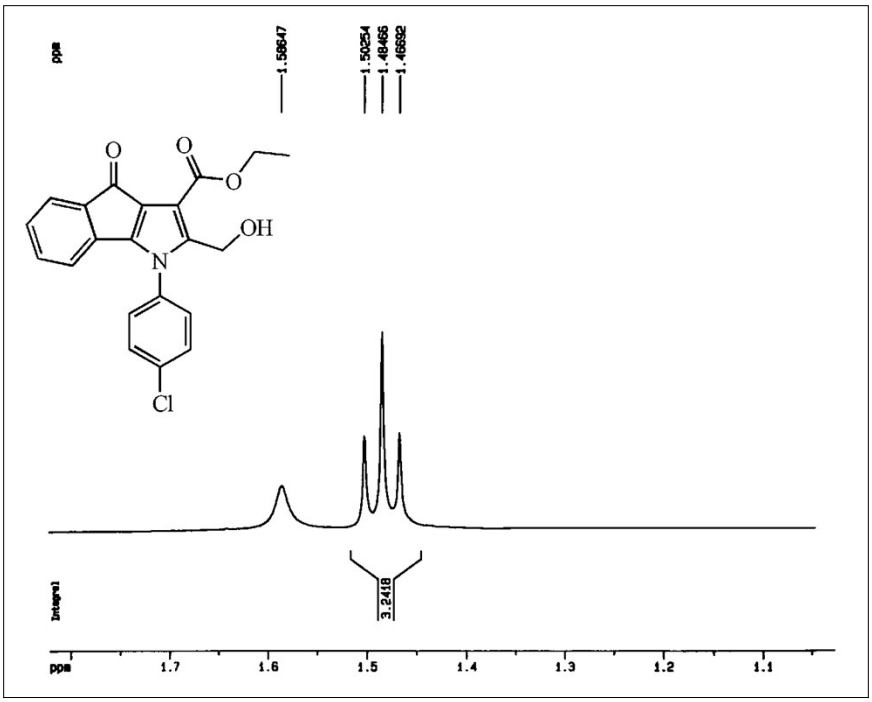


Figure 55: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3b** in $CDCl_3$.

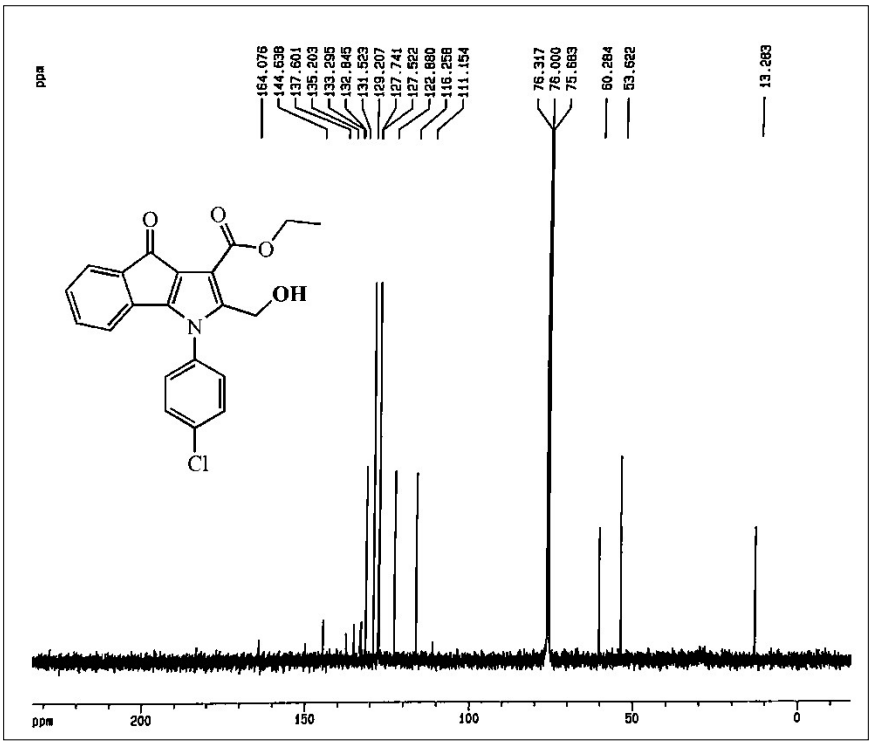


Figure 56: ^{13}C NMR spectrum (100 MHz) of compound **3b** in $CDCl_3$.

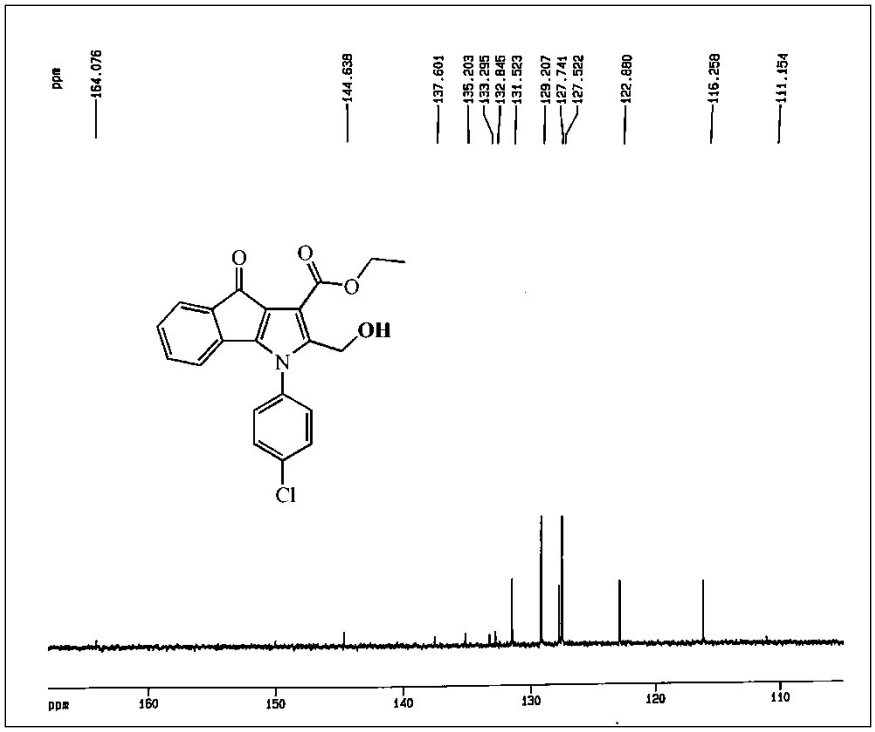


Figure 57: Expanded ^{13}C NMR spectrum (100 MHz) of compound **3b** in $CDCl_3$.

Methyl 2-(ethoxymethyl)-1-(4-nitrophenyl)-4-oxo-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (3c)

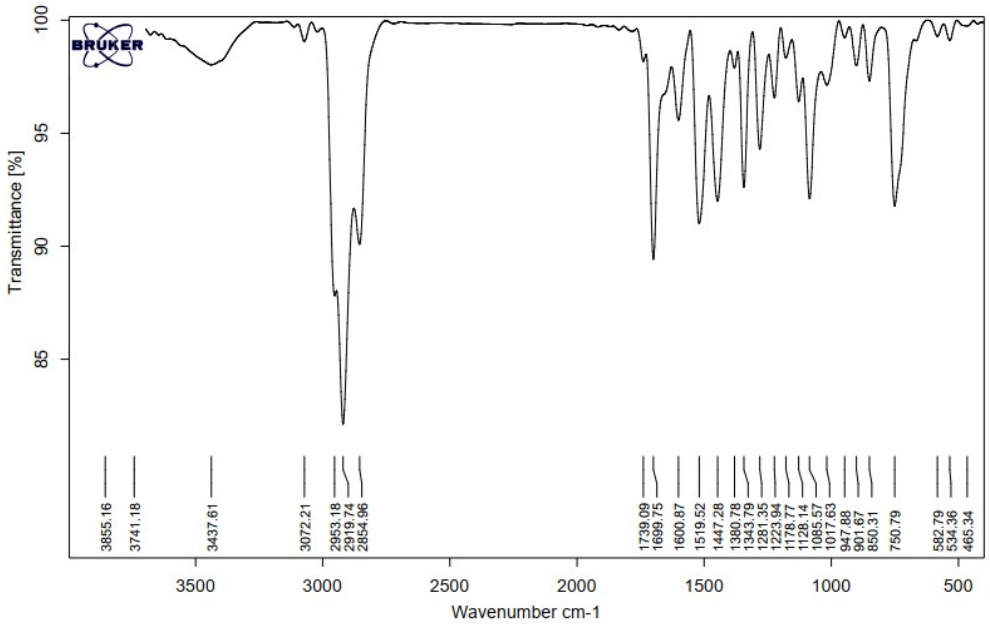


Figure 58: FTIR (KBr) spectrum of **3c**.

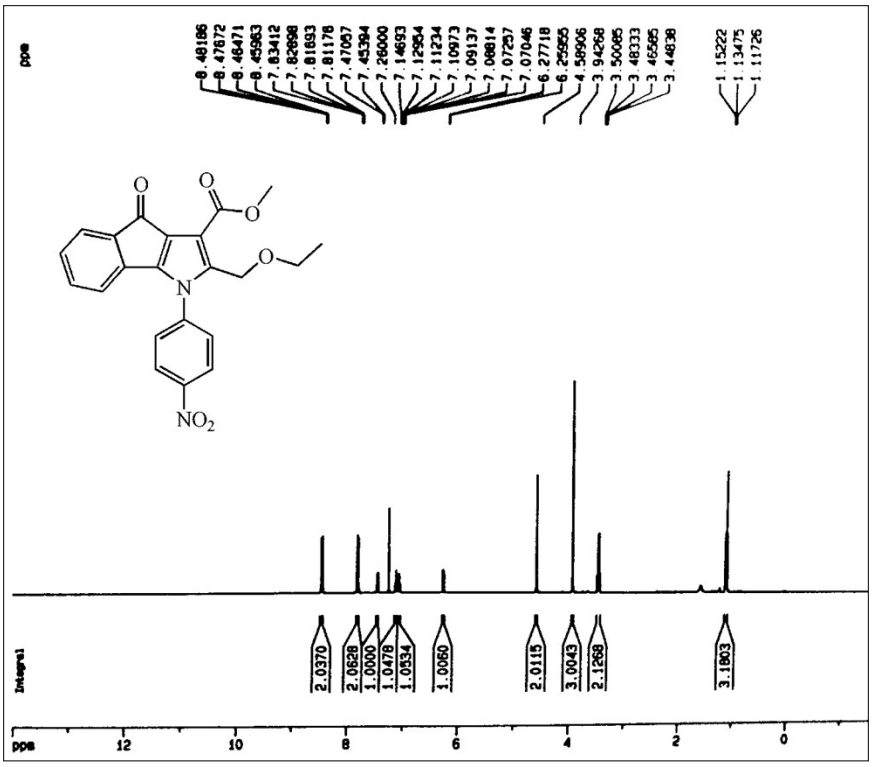


Figure 59: ^{1}H NMR spectrum (400 MHz) of compound **3c** in $CDCl_3$.

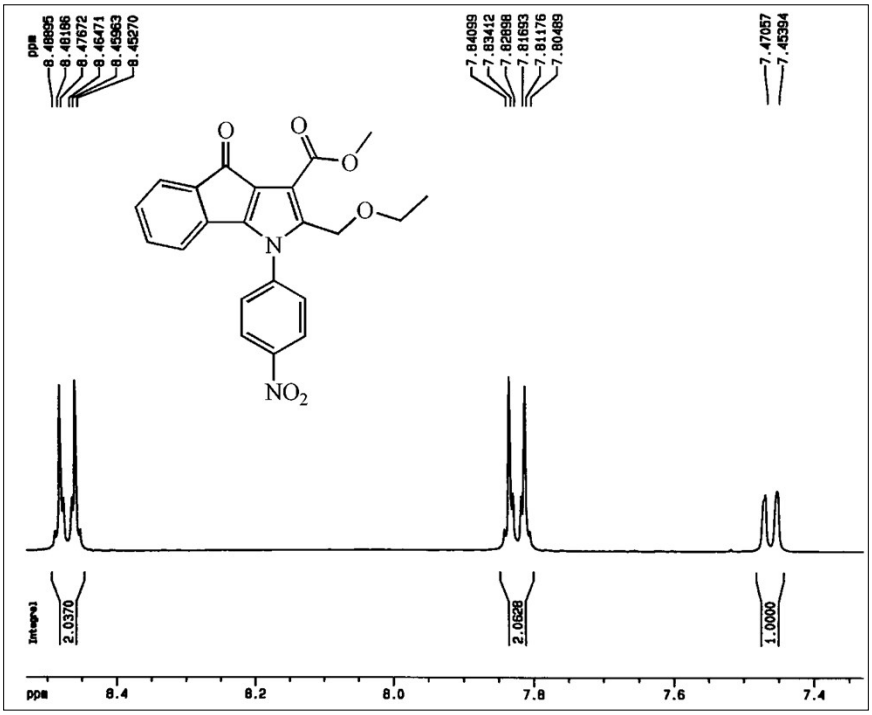


Figure 60: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3c** in $CDCl_3$.

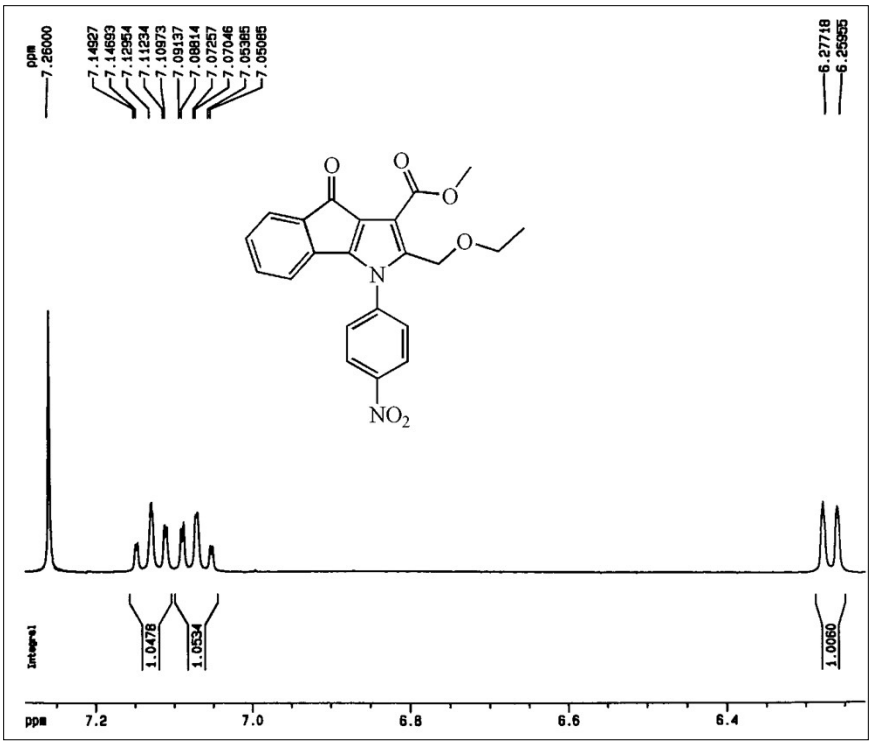


Figure 61: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3c** in $CDCl_3$.

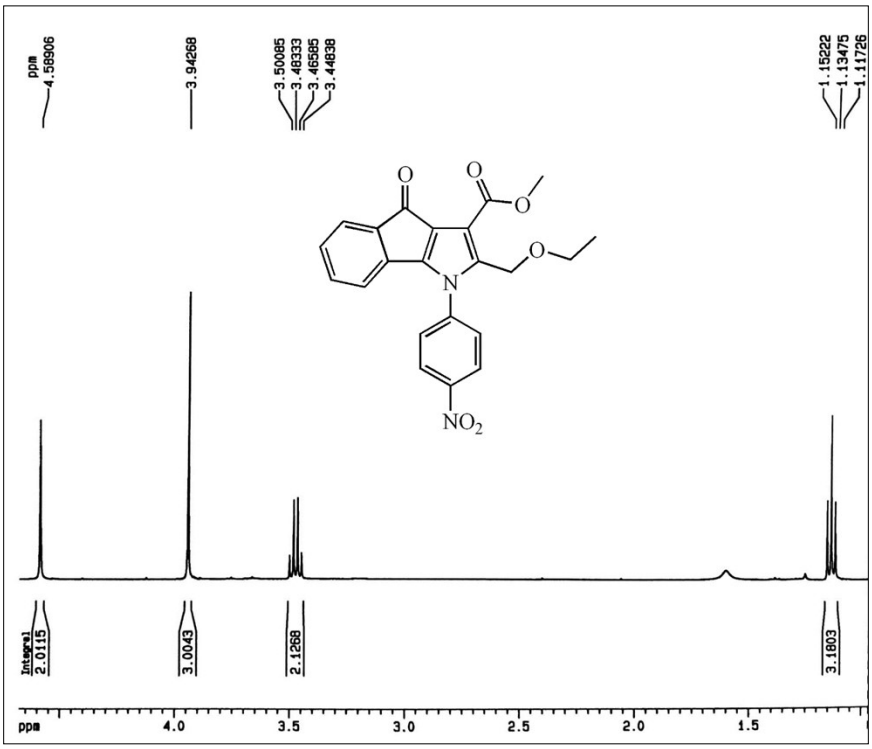


Figure 62: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3c** in $CDCl_3$.

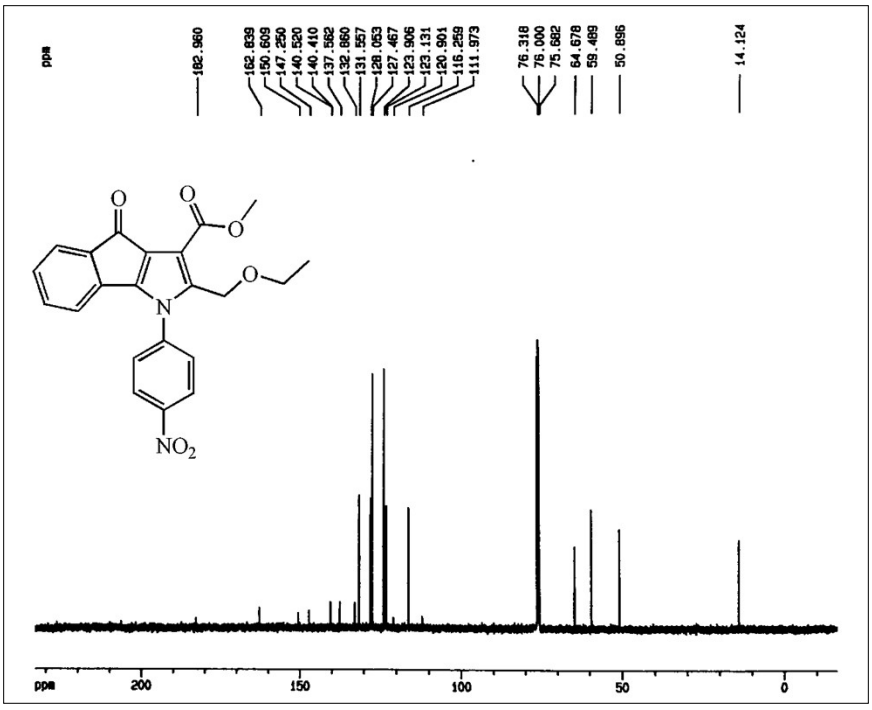


Figure 63: ^{13}C NMR spectrum (100 MHz) of compound **3c** in $CDCl_3$.

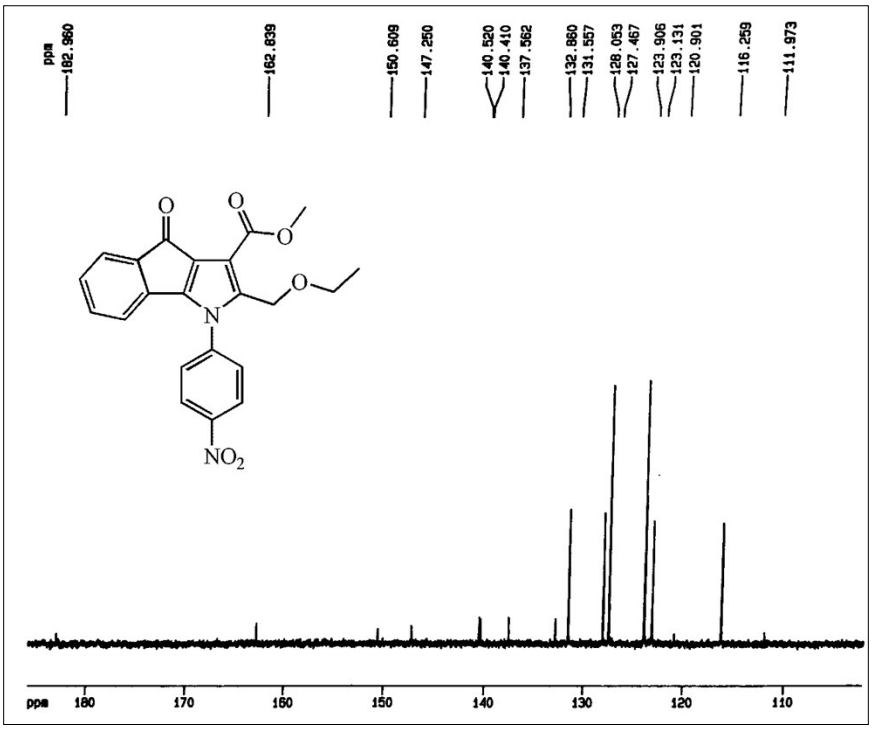


Figure 64: Expanded ^{13}C NMR spectrum (100 MHz) of compound **3c** in $CDCl_3$.

***tert*-Butyl 1-butyl-2-(hydroxymethyl)-4-oxo-1,4-dihydroindeno[1,2-b]pyrrole-3-carboxylate (3d)**

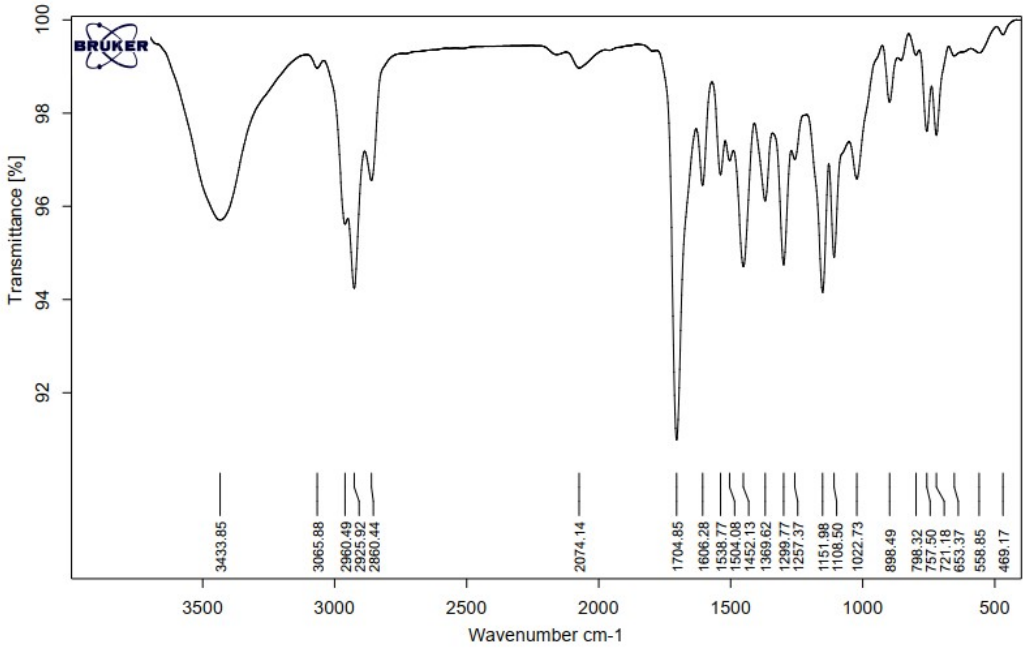


Figure 65: FT-IR (KBr) spectrum of **3d**.

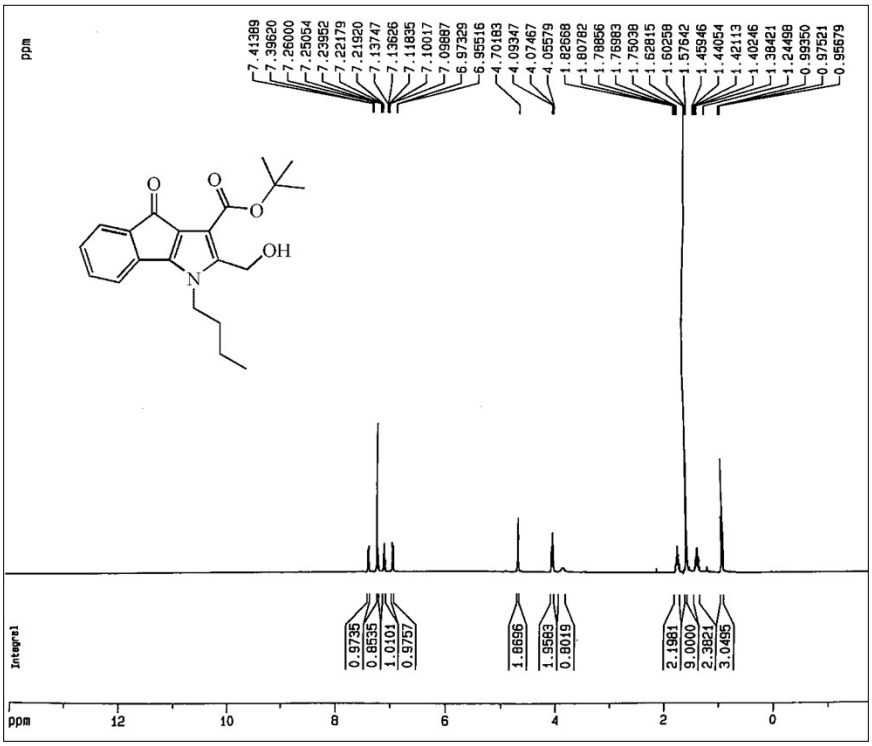


Figure 66: ^{1}H NMR spectrum (400 MHz) of compound **3d** in $CDCl_3$.

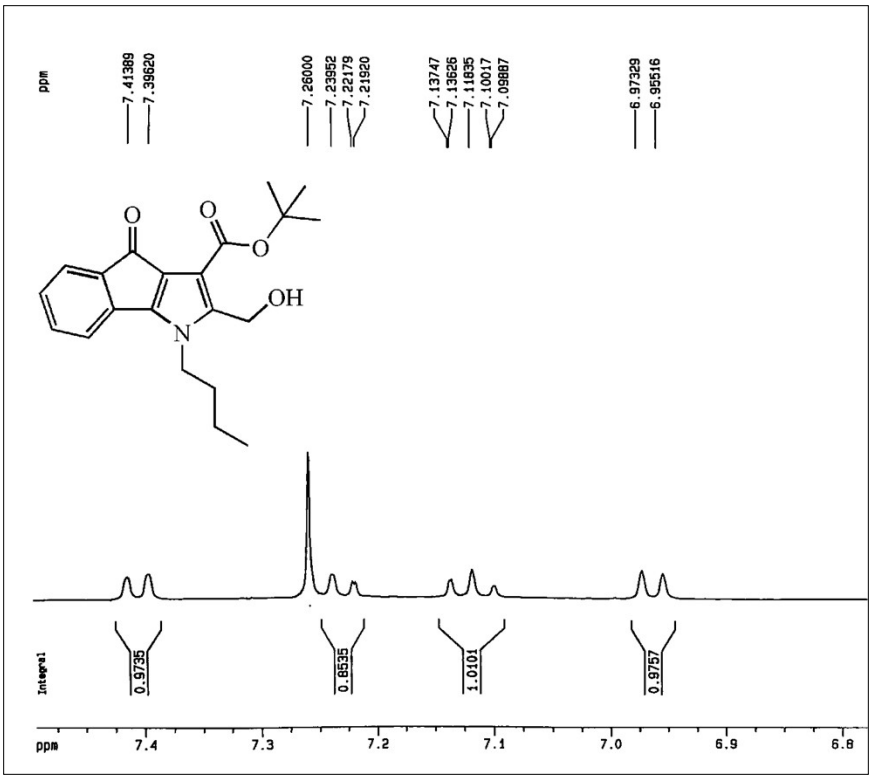


Figure 67: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3d** in $CDCl_3$.

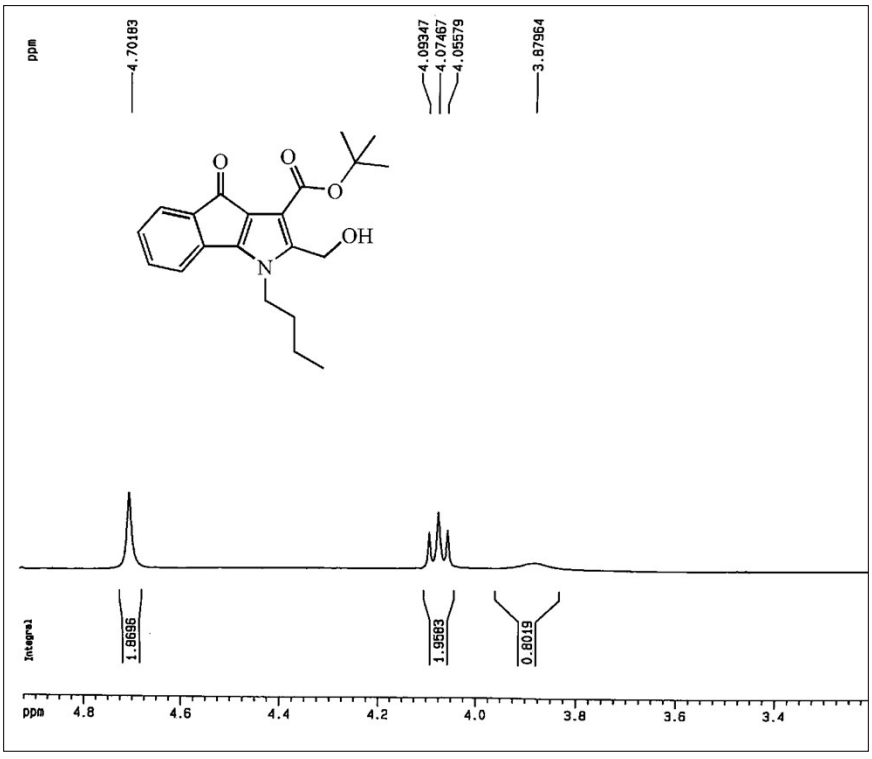


Figure 68: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3d** in $CDCl_3$.

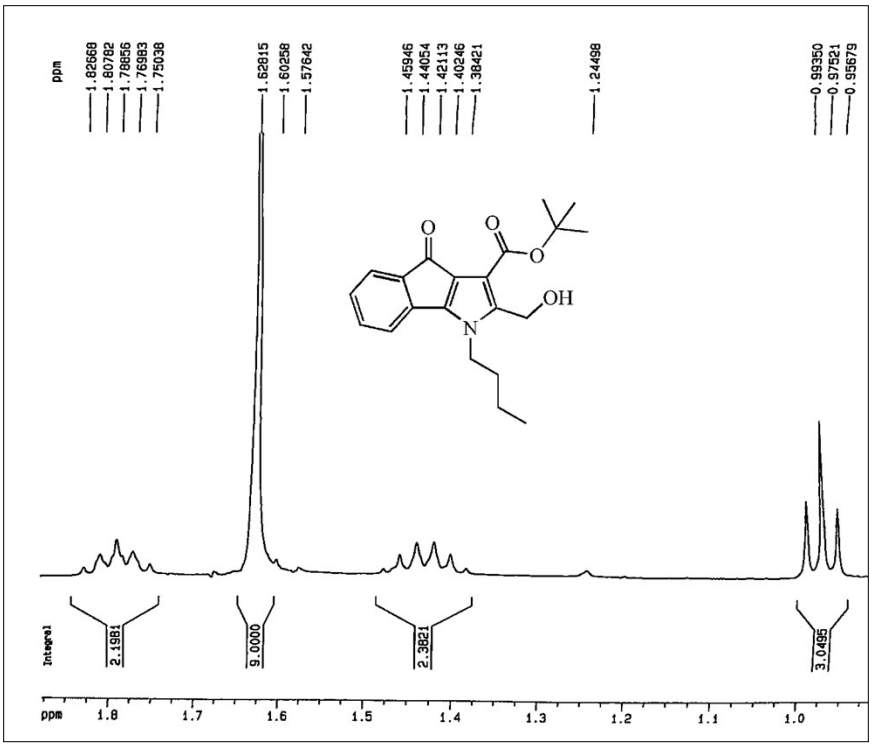


Figure 69: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3d** in $CDCl_3$.

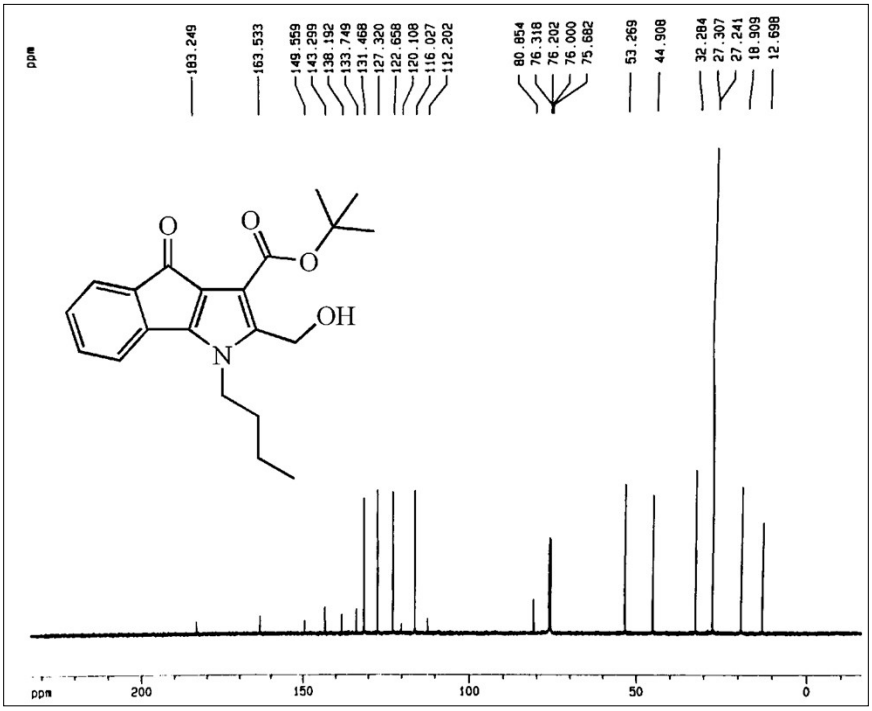


Figure 70: ^{13}C NMR spectrum (100 MHz) of compound **3d** in $CDCl_3$.

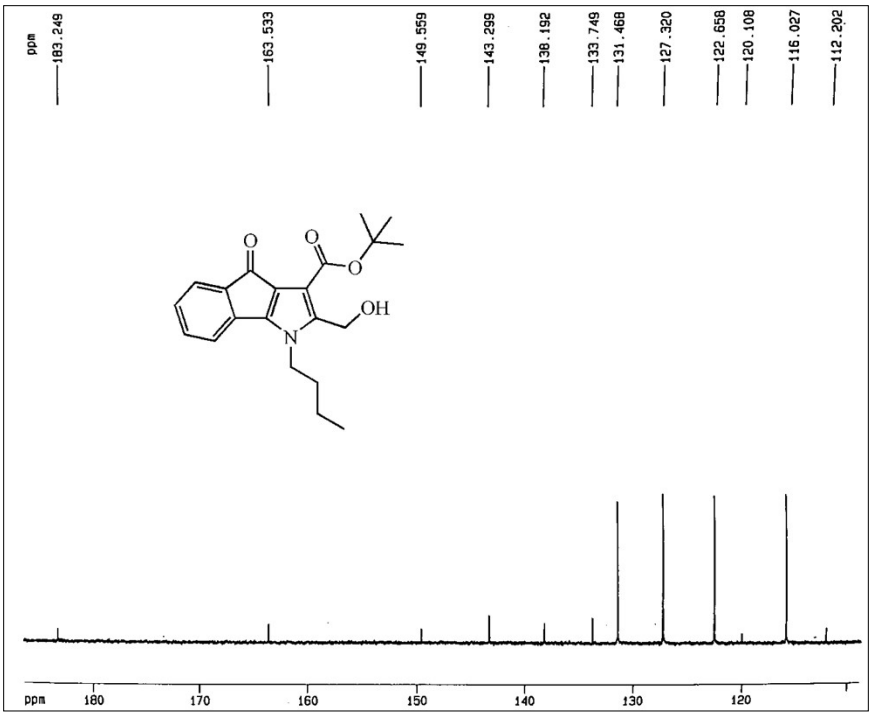


Figure 71: Expanded ^{13}C NMR spectrum (100 MHz) of compound **3d** in $CDCl_3$.

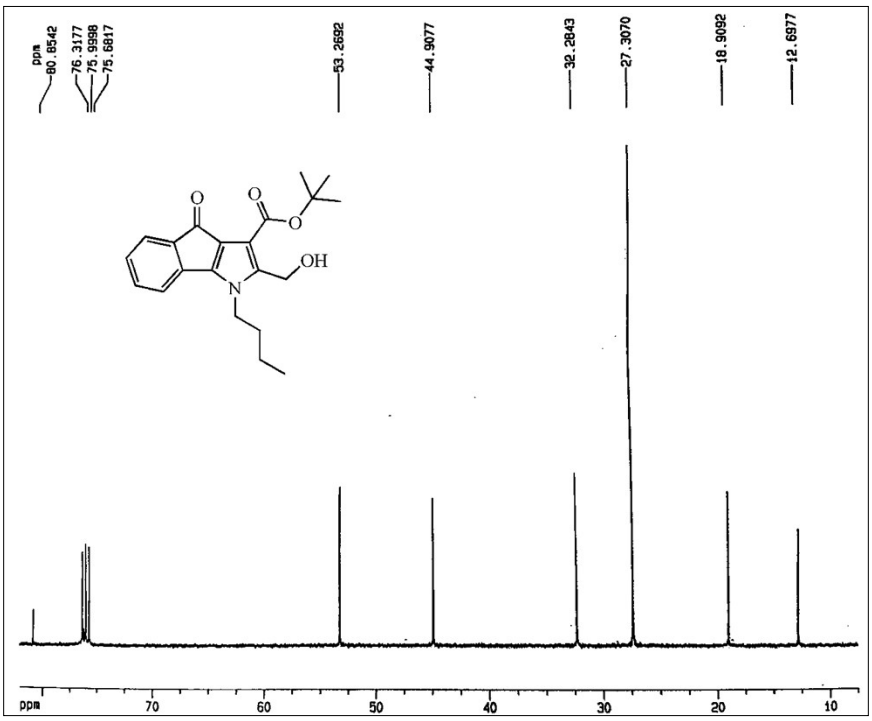


Figure 72: Expanded ^{13}C NMR spectrum (100 MHz) of compound **3d** in $CDCl_3$.

Methyl 2-(hydroxymethyl)-1-(4-hydroxyphenyl)-4-oxo-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (3e)

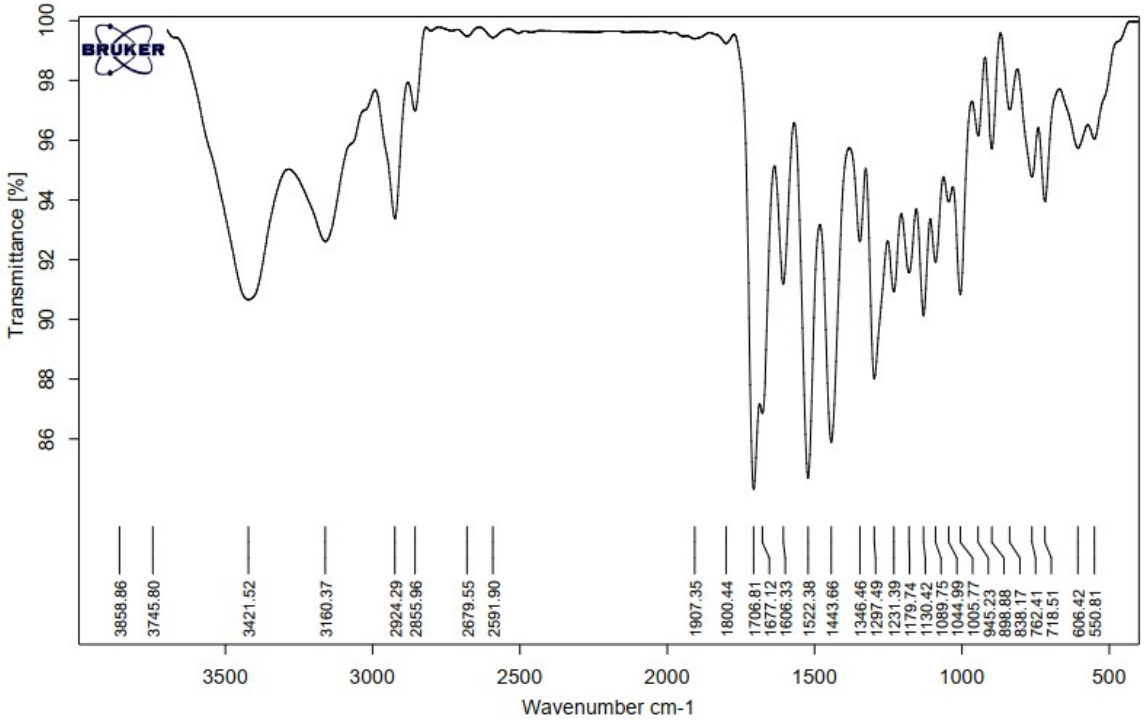


Figure 73: FT-IR (KBr) spectrum of **3e**.

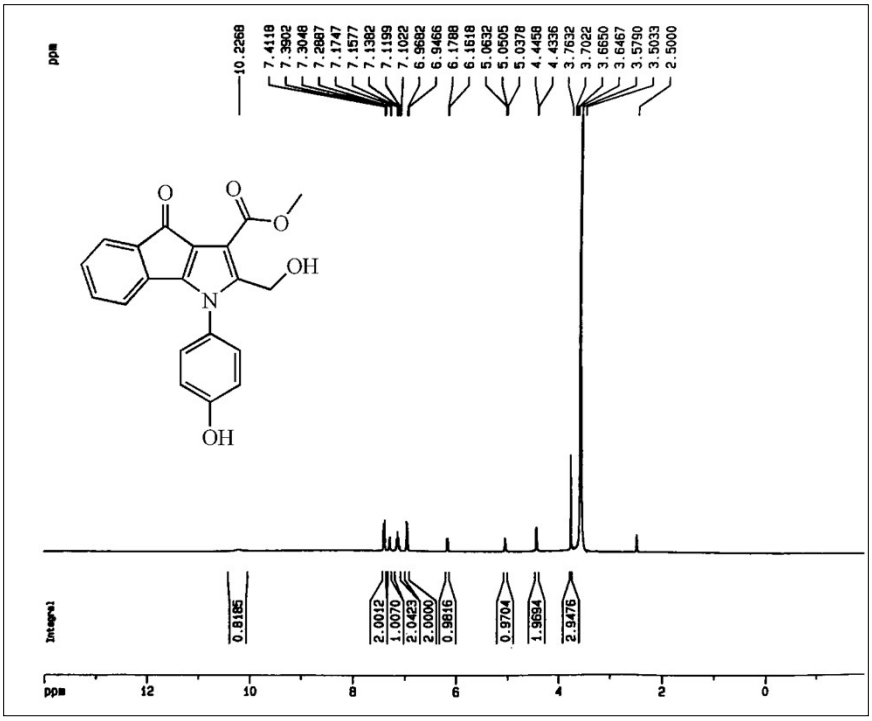


Figure 74: ^{1}H NMR spectrum (400 MHz) of compound **3e** in DMSO.

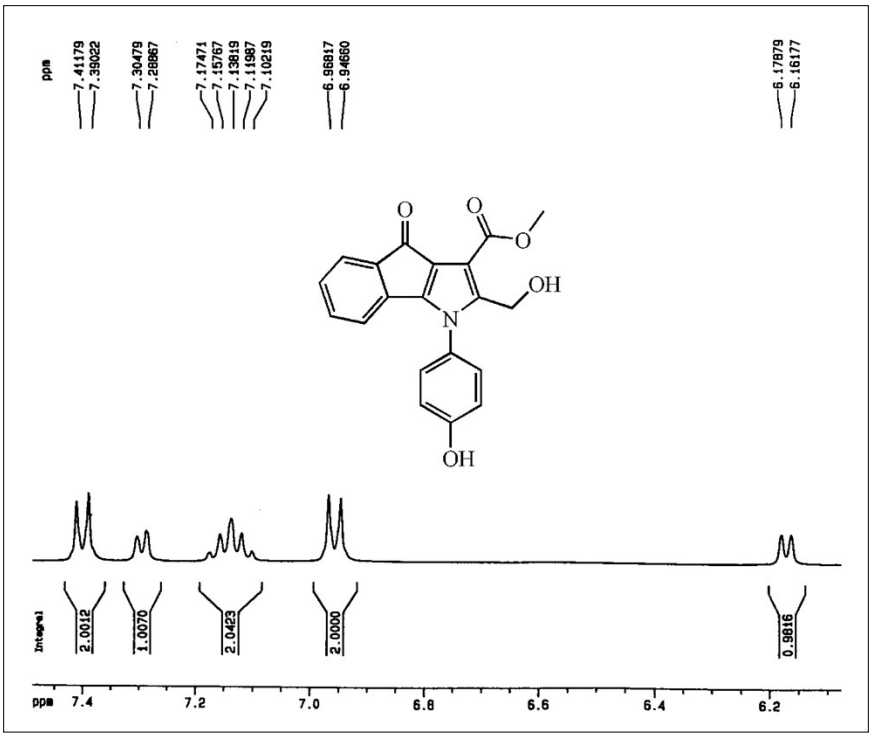


Figure 75: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3e** in DMSO**.**

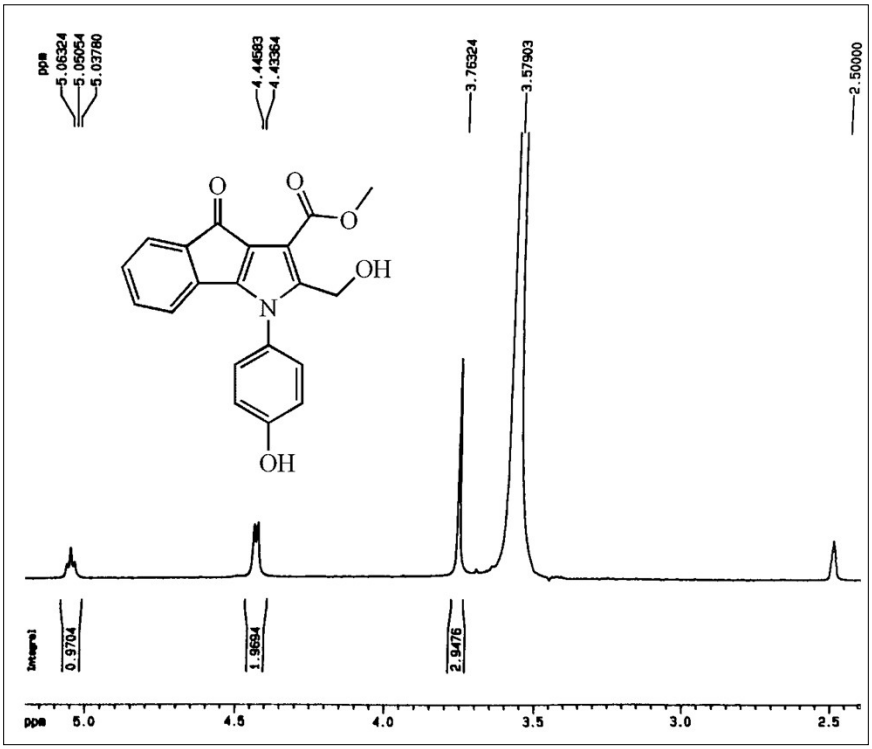


Figure 76: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3e** in DMSO**.**

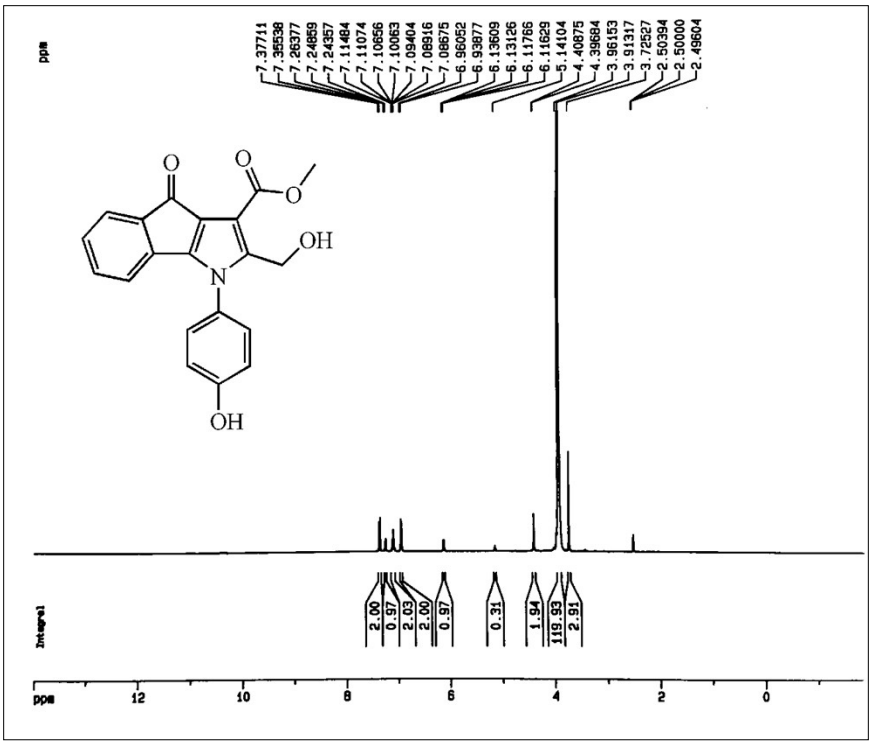


Figure 77: ^{1}H NMR spectrum (400 MHz) of compound **3e** in DMSO+ D_2O**.**

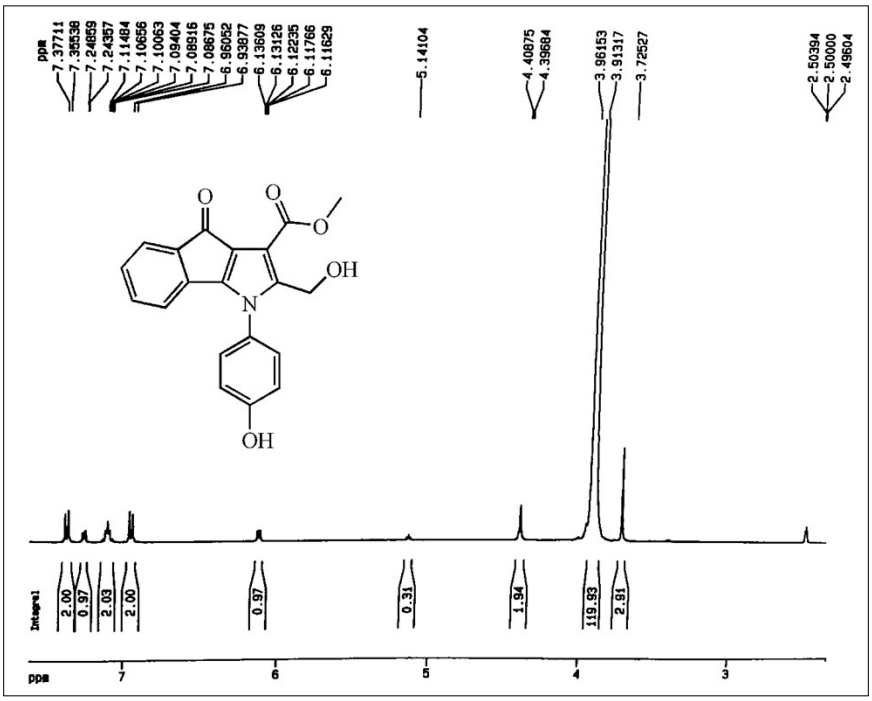


Figure 78: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3e** in DMSO+ D_2O**.**

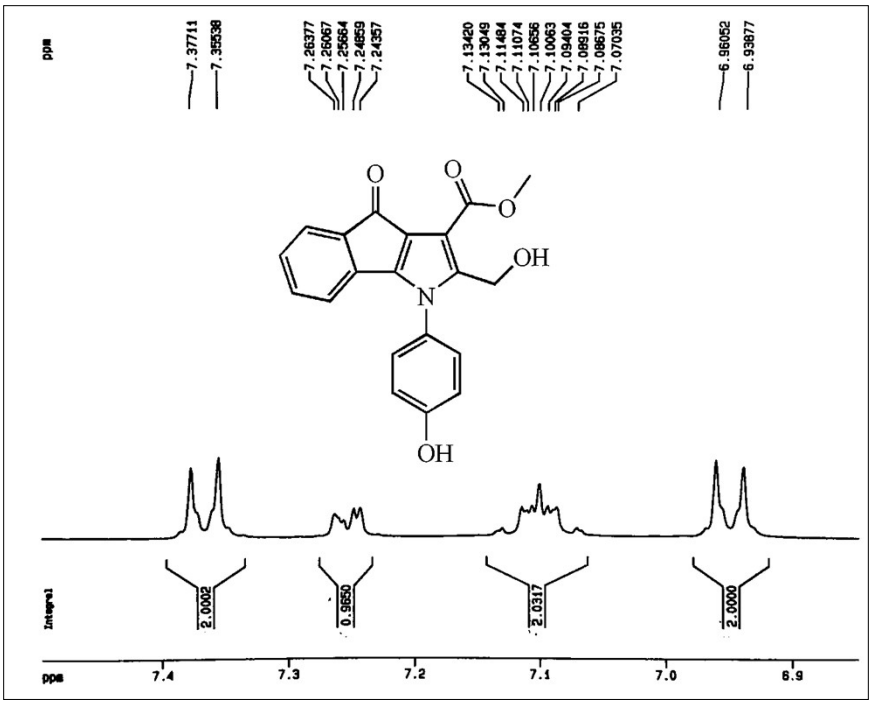


Figure 79: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3e** in DMSO+ D_2O**.**

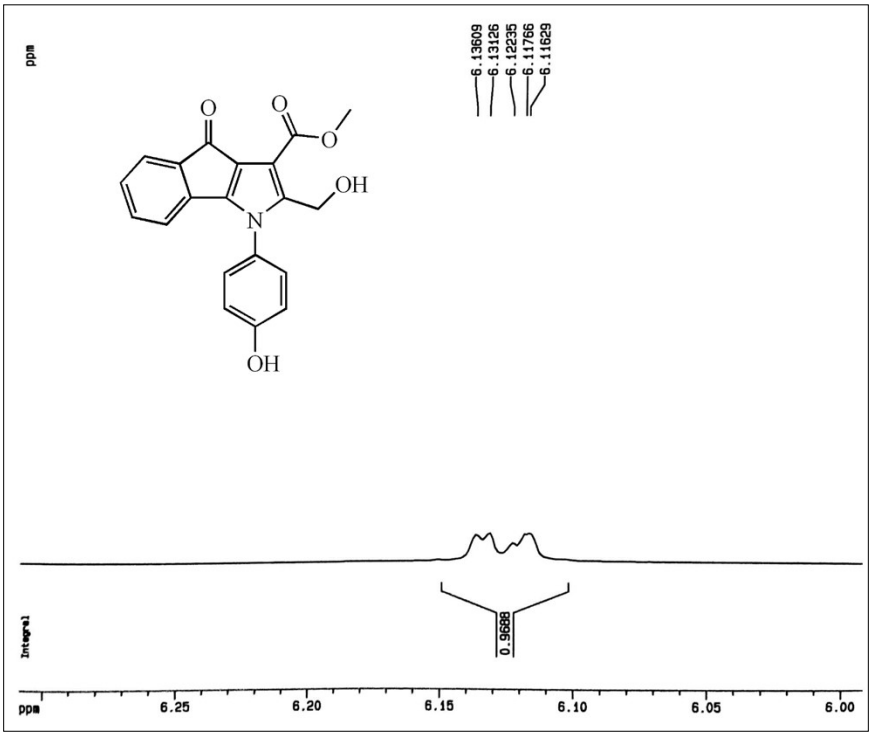


Figure 80: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3e** in DMSO+ D_2O**.**

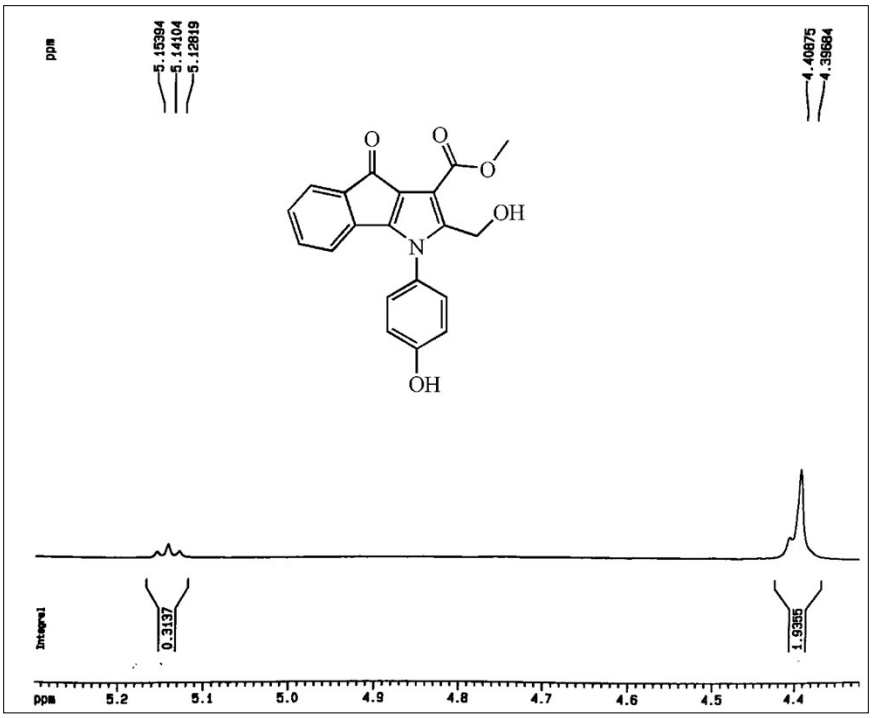


Figure 81: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3e** in DMSO+ D_2O**.**

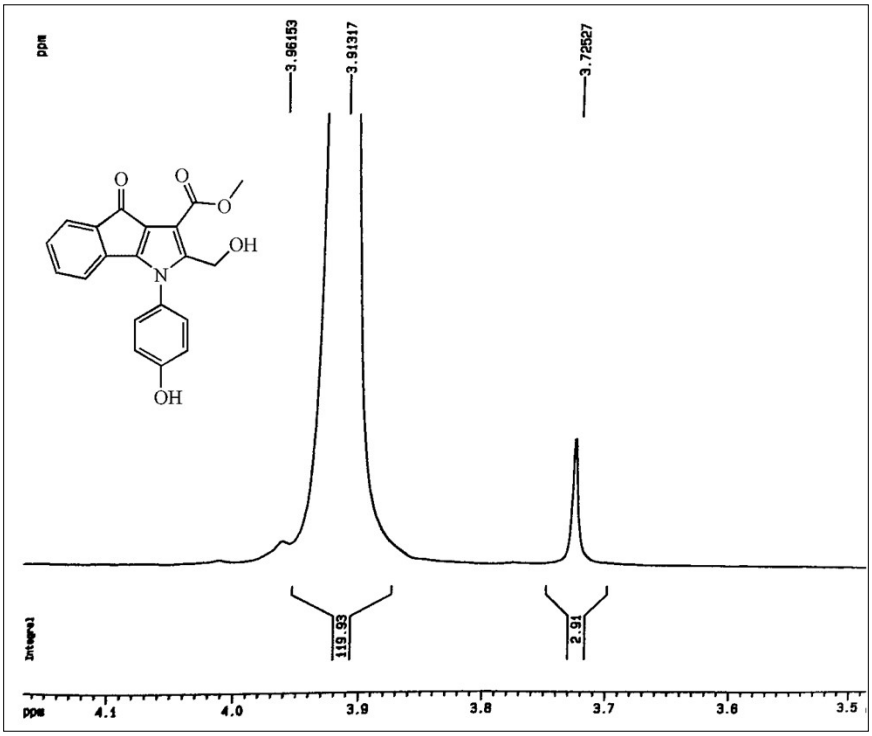


Figure 82: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3e** in DMSO+ D_2O.

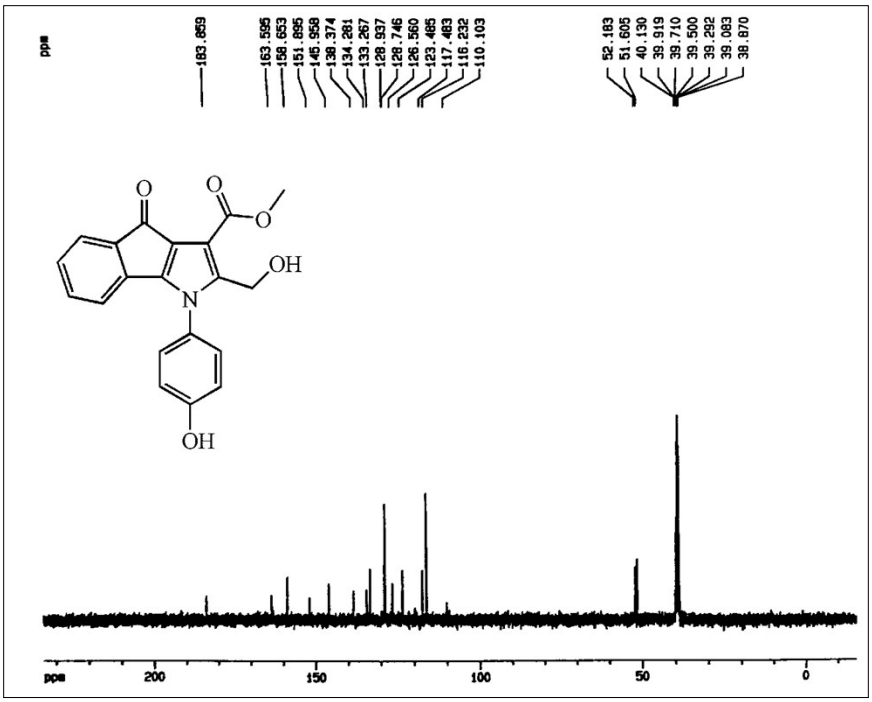


Figure 83: ^{13}C NMR spectrum (100 MHz) of compound **3e** in DMSO.

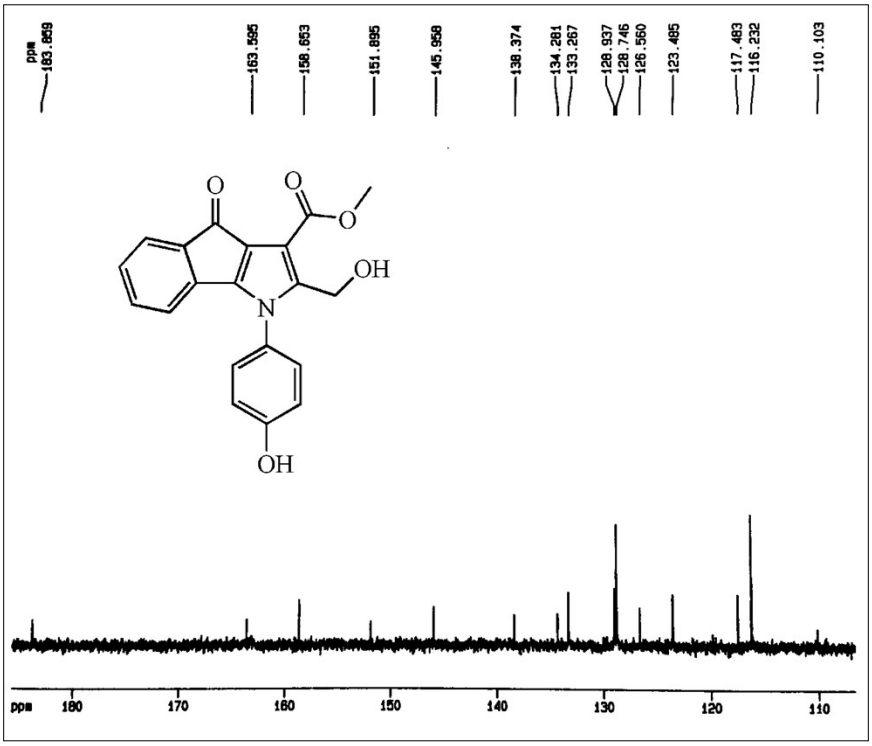


Figure 84: Expanded ^{13}C NMR spectrum (100 MHz) of compound **3e** in DMSO.

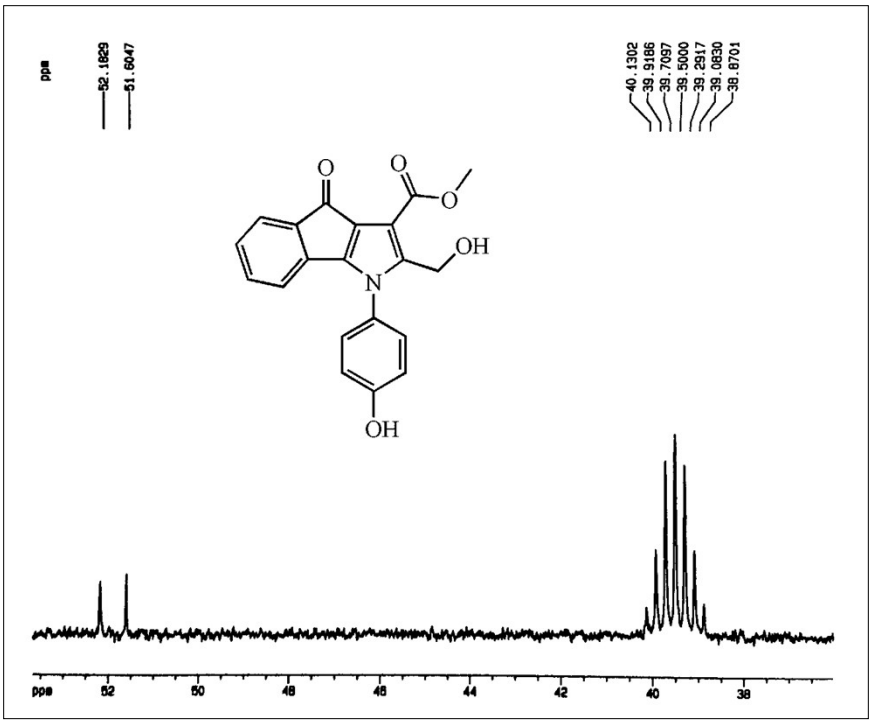


Figure 85: Expanded ^{13}C NMR spectrum (100 MHz) of compound **3e** in DMSO.

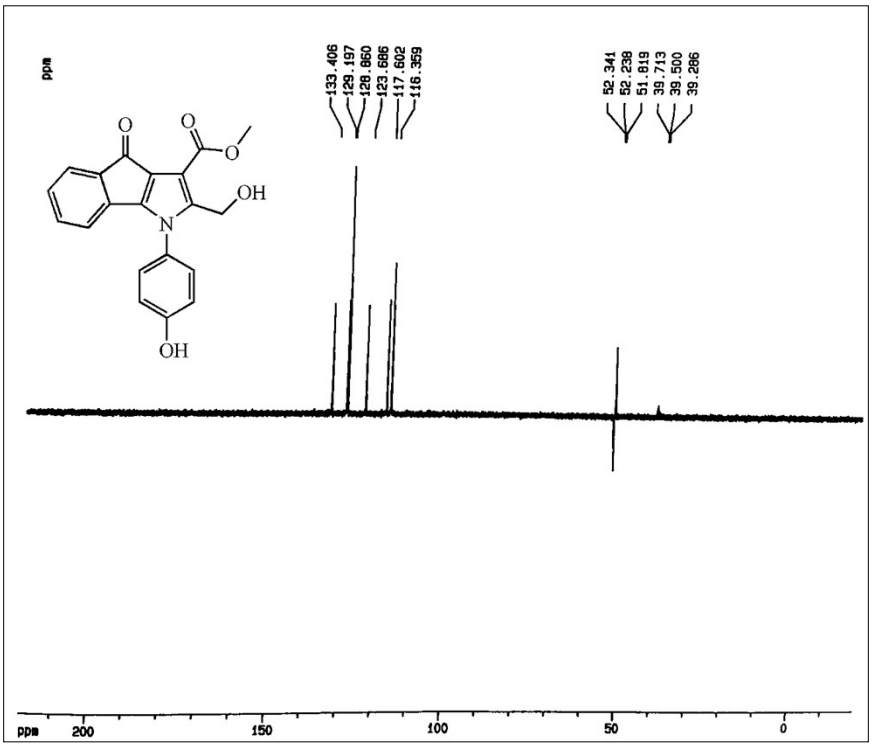


Figure 86: ^{13}C/DEPT-135 spectrum (100 MHz) of compound **3e** in DMSO.

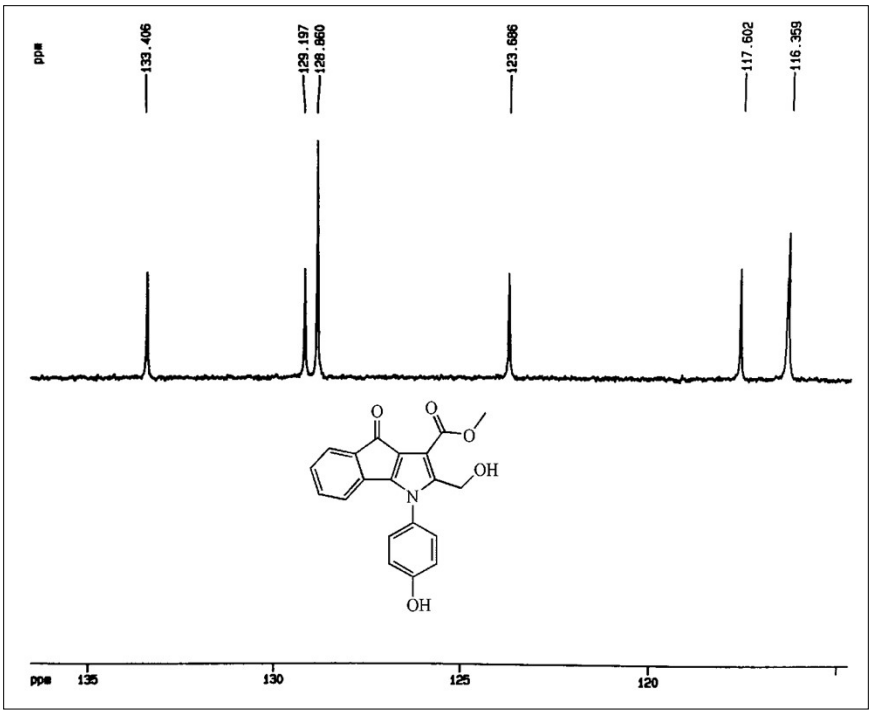


Figure 87: Expanded ^{13}C/DEPT-135 spectrum (100 MHz) of compound **3e** in DMSO**.**

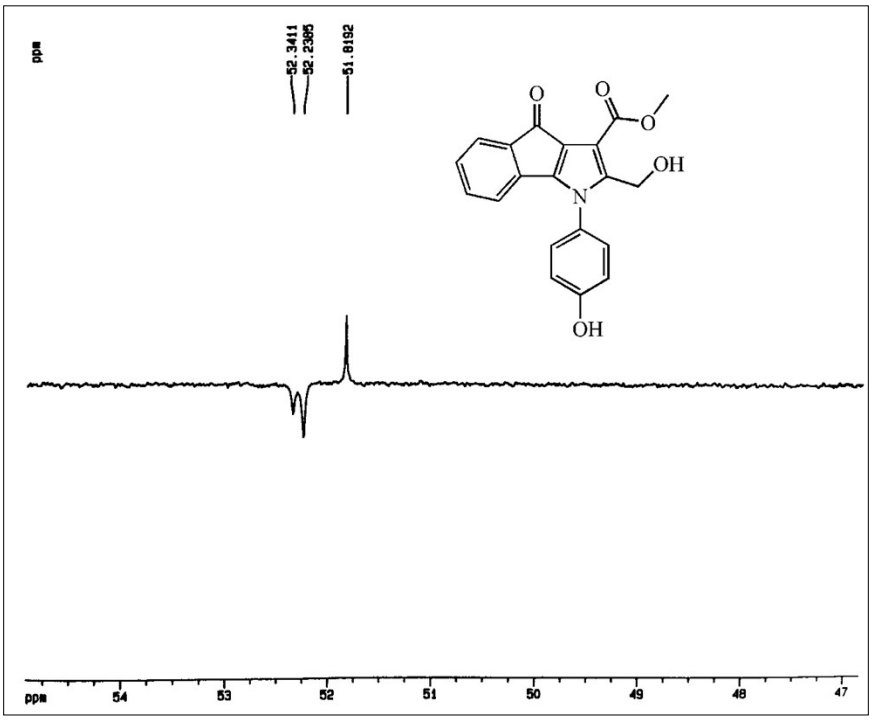


Figure 88: Expanded ^{13}C/DEPT-135 spectrum (100 MHz) of compound **3e** in DMSO.

***tert*-Butyl 2-(hydroxymethyl)-1-(4-methoxyphenyl)-4-oxo-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (3f)**

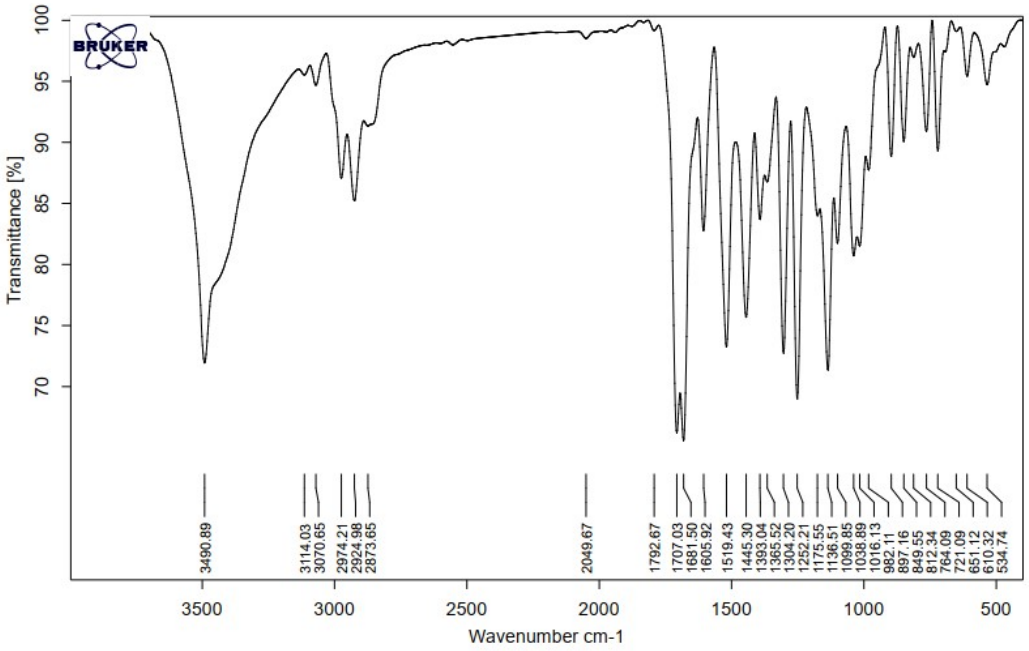


Figure 89: FT-IR (KBr) spectrum of **3f**.

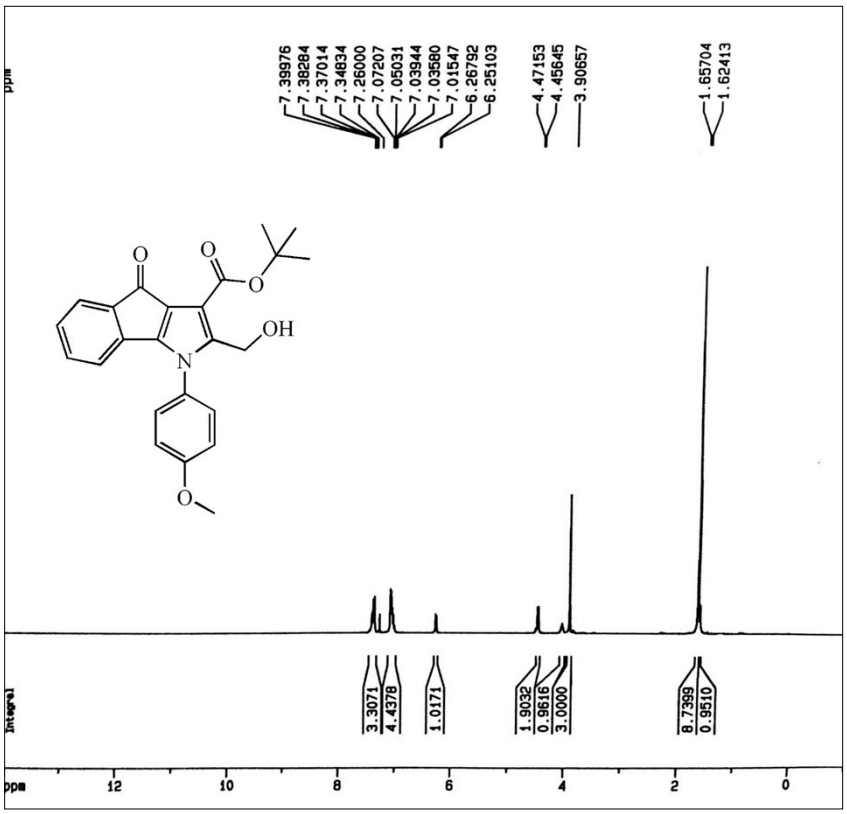


Figure 90: ^{1}H NMR spectrum (400 MHz) of compound **3f** in $CDCl_3$.

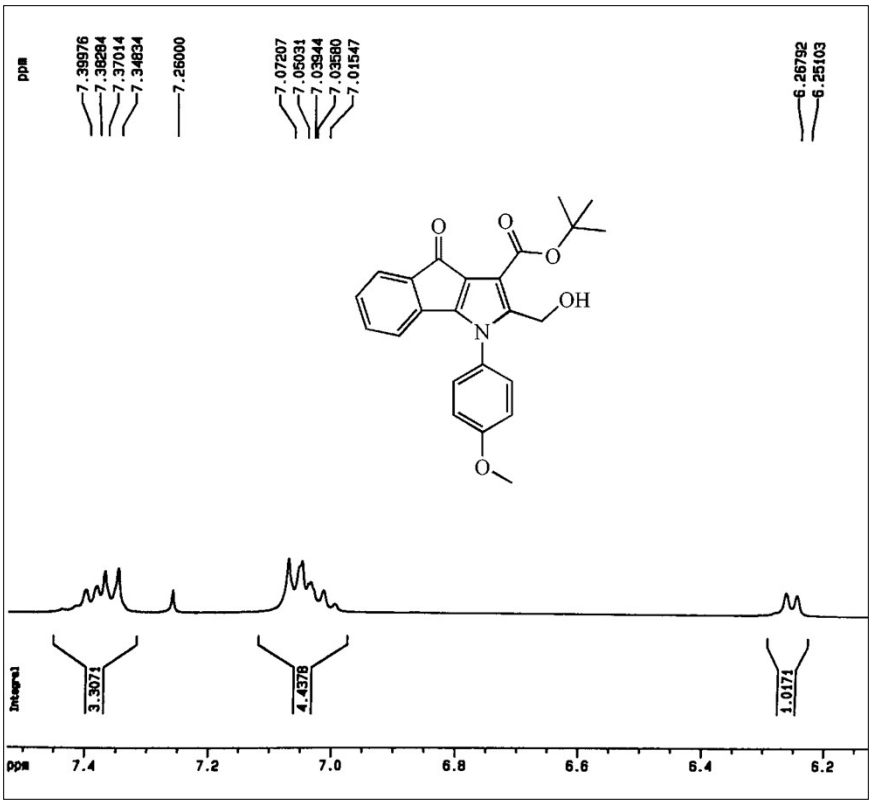


Figure 91: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3f** in $CDCl_3$.

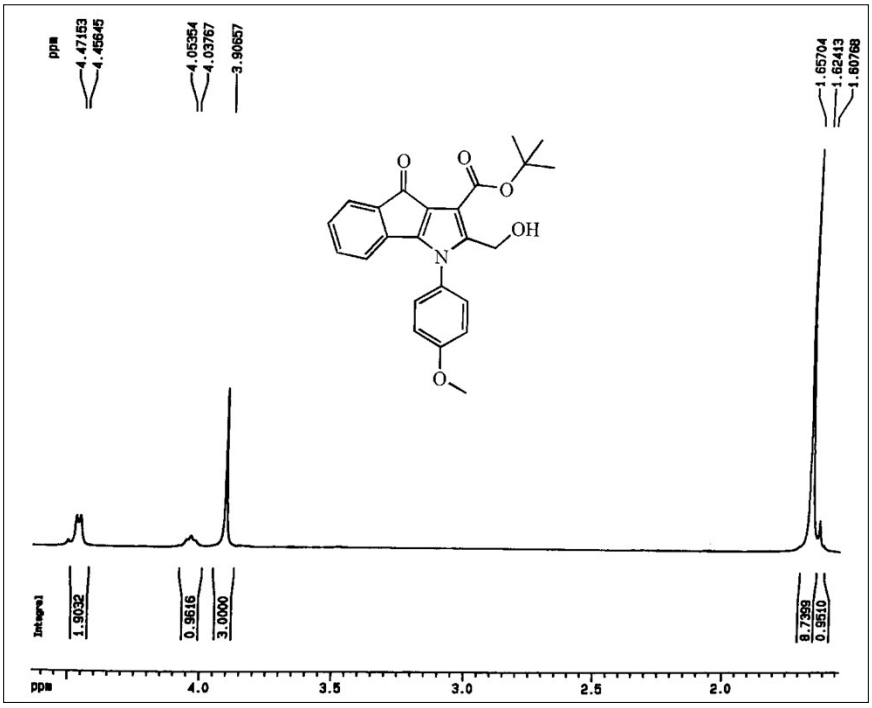


Figure 92: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3f** in $CDCl_3$.

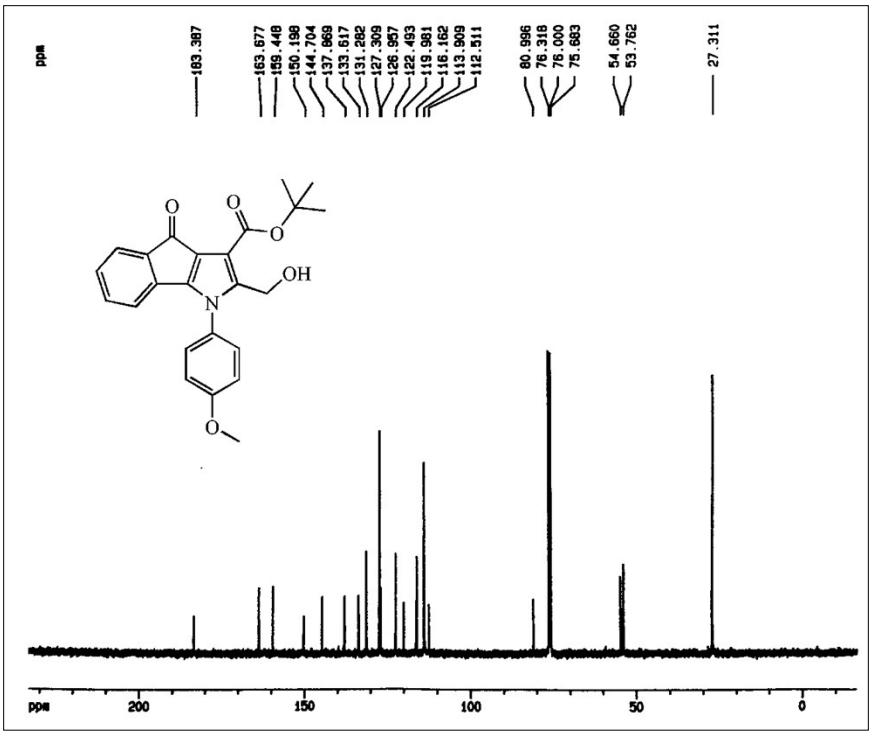


Figure 93: ^{13}C NMR spectrum (100 MHz) of compound **3f** in $CDCl_3$.

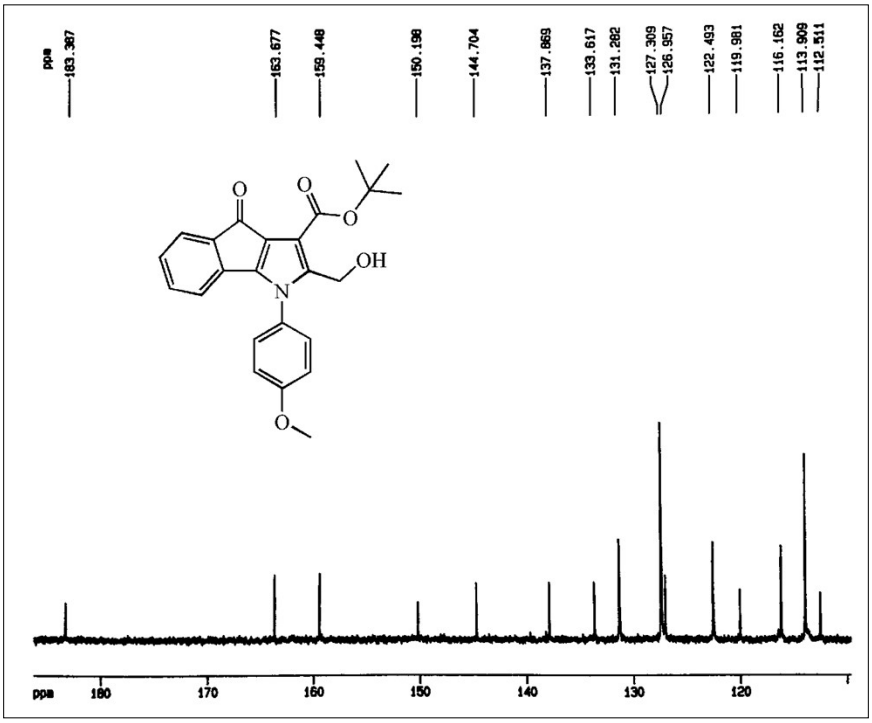


Figure 94: Expanded ^{13}C NMR spectrum (100 MHz) of compound **3f** in $CDCl_3$.

***tert*-Butyl 2-(hydroxymethyl)-4-oxo-1-(p-tolyl)-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (3g)**

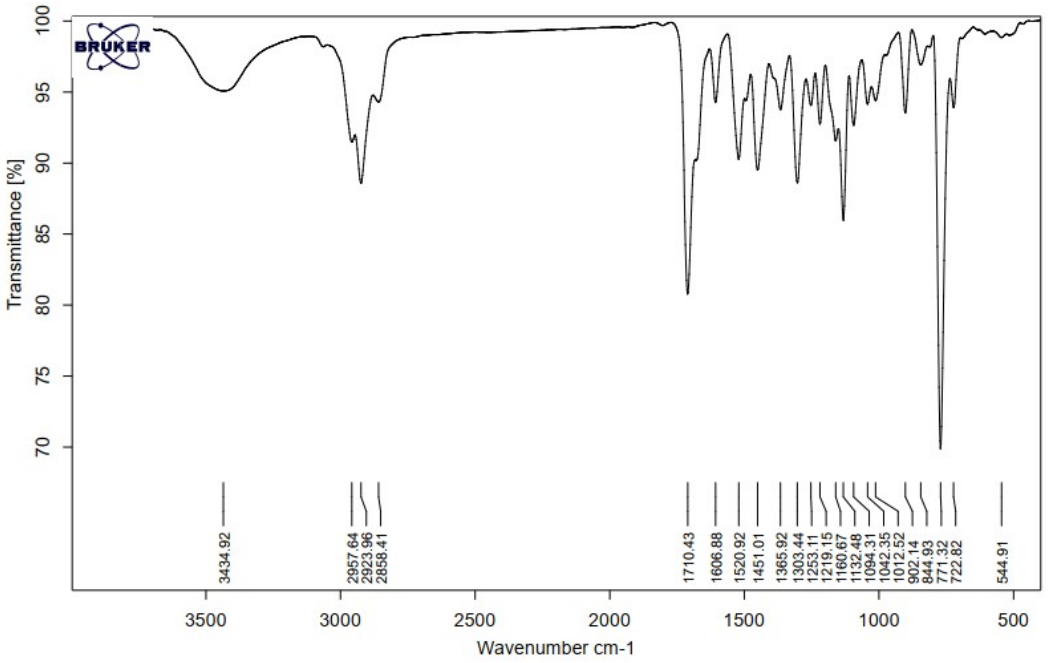


Figure 95: FT-IR (KBr) spectrum of **3g**.

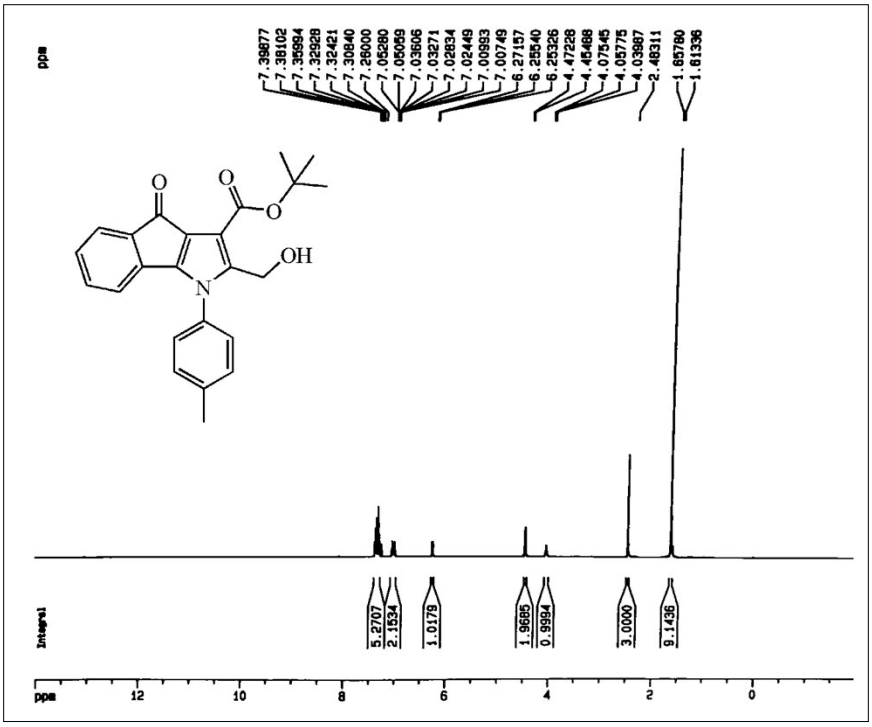


Figure 96: ^{1}H NMR spectrum (400 MHz) of compound **3g** in $CDCl_3$.

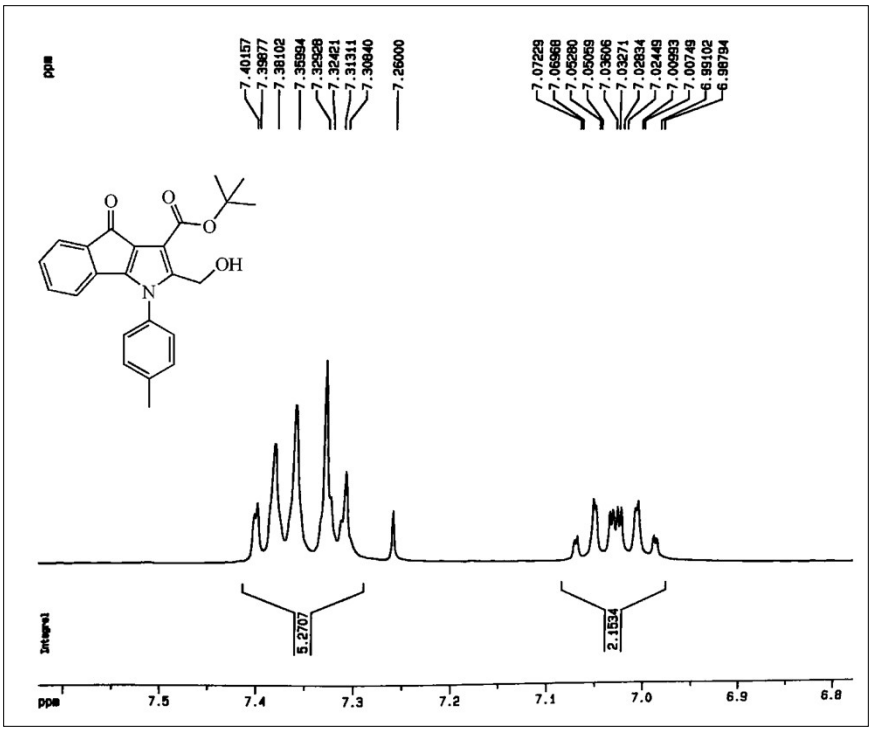


Figure 97: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3g** in $CDCl_3$.

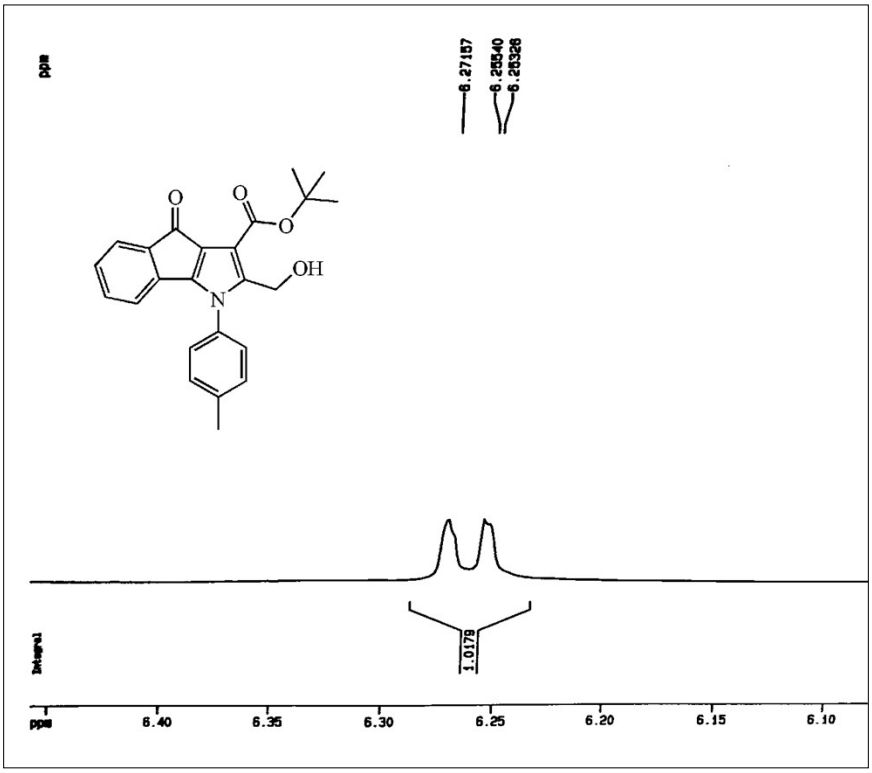


Figure 98: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3g** in $CDCl_3$.

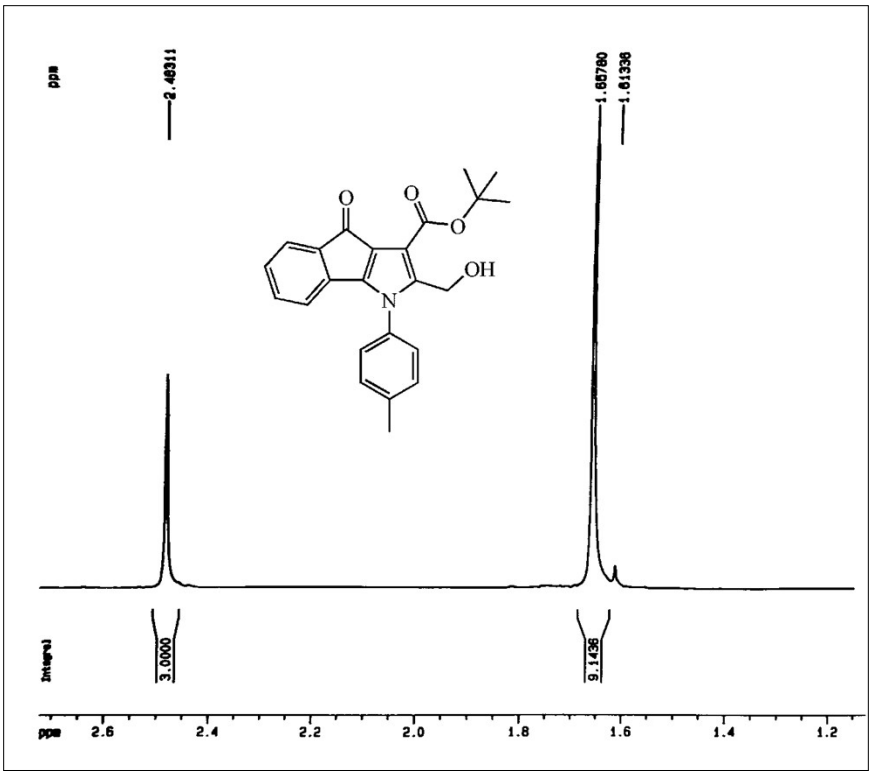


Figure 99: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3g** in $CDCl_3$.

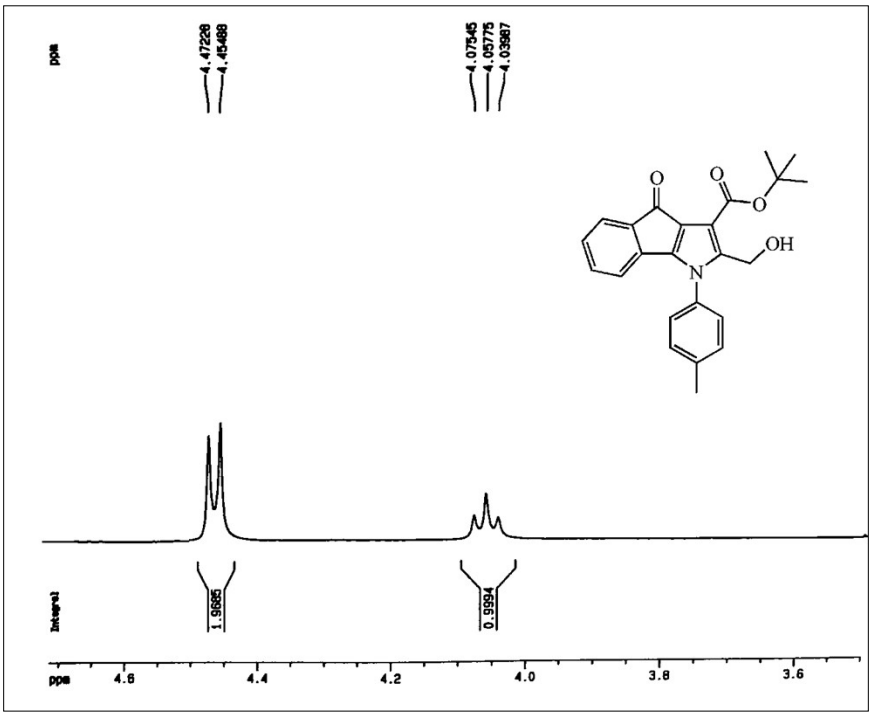


Figure 100: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3g** in $CDCl_3$.

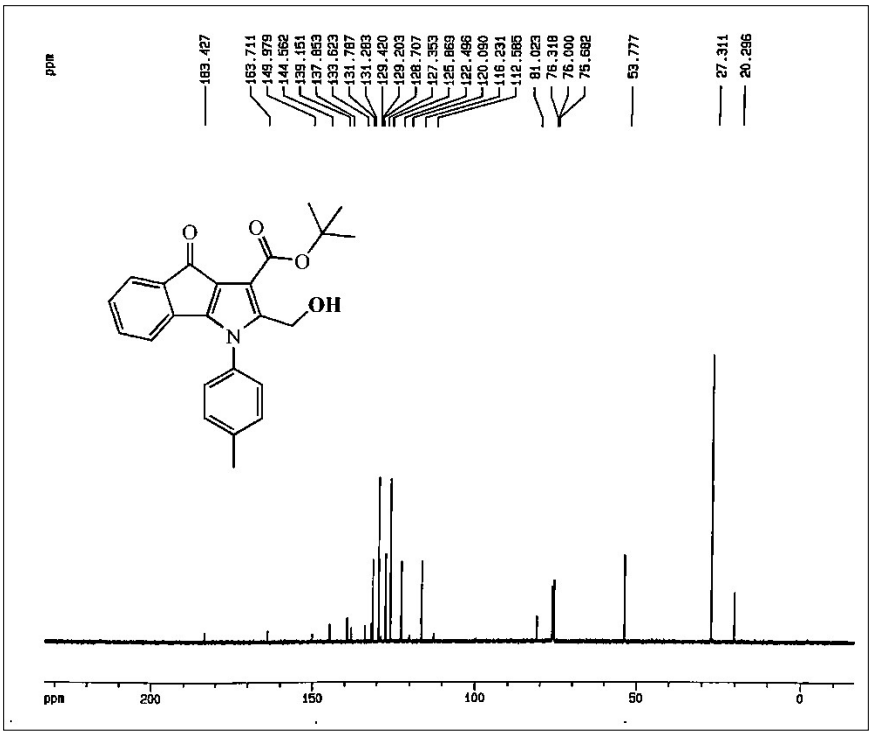


Figure 101: ^{13}C NMR spectrum (100 MHz) of compound **3g** in $CDCl_3$.

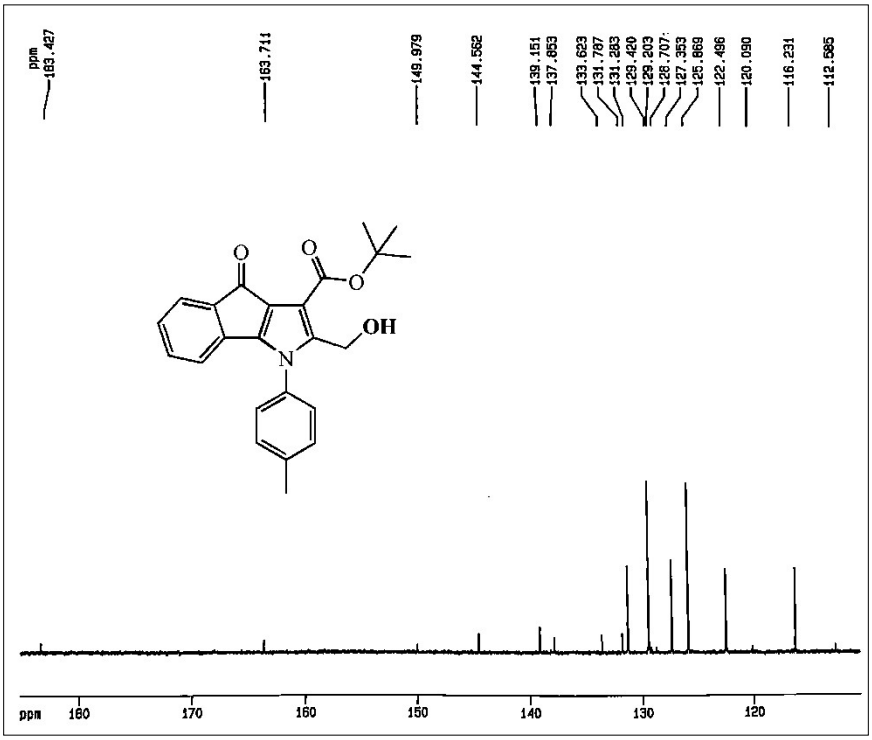


Figure 102: Expanded ^{13}C NMR spectrum (100 MHz) of compound **3g** in $CDCl_3$.

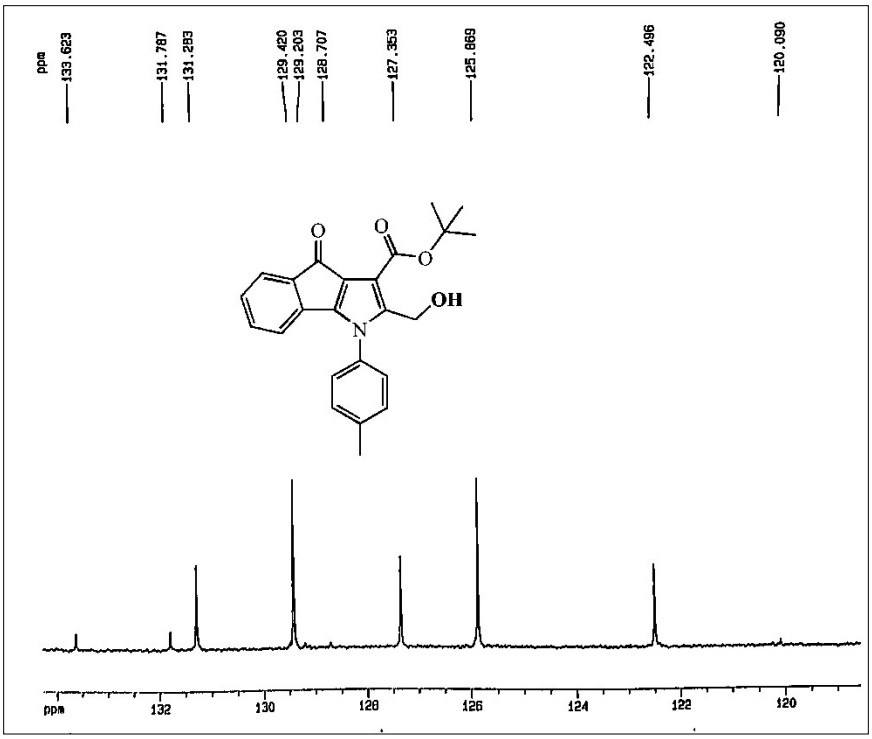


Figure 103: Expanded ^{13}C NMR spectrum (100 MHz) of compound **3g** in $CDCl_3$.

Methyl 2-(hydroxymethyl)-1-(2-methoxyphenyl)-4-oxo-1,4-dihydroindeno[1,2-b]pyrrole-3-carboxylate (3h)

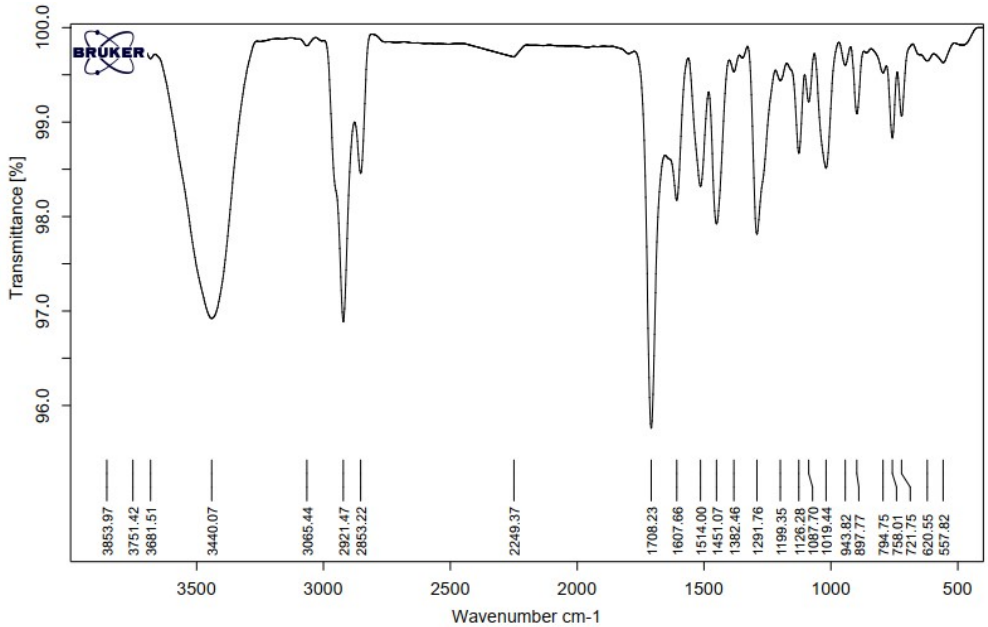


Figure 104: FT-IR (KBr) spectrum of **3h**.

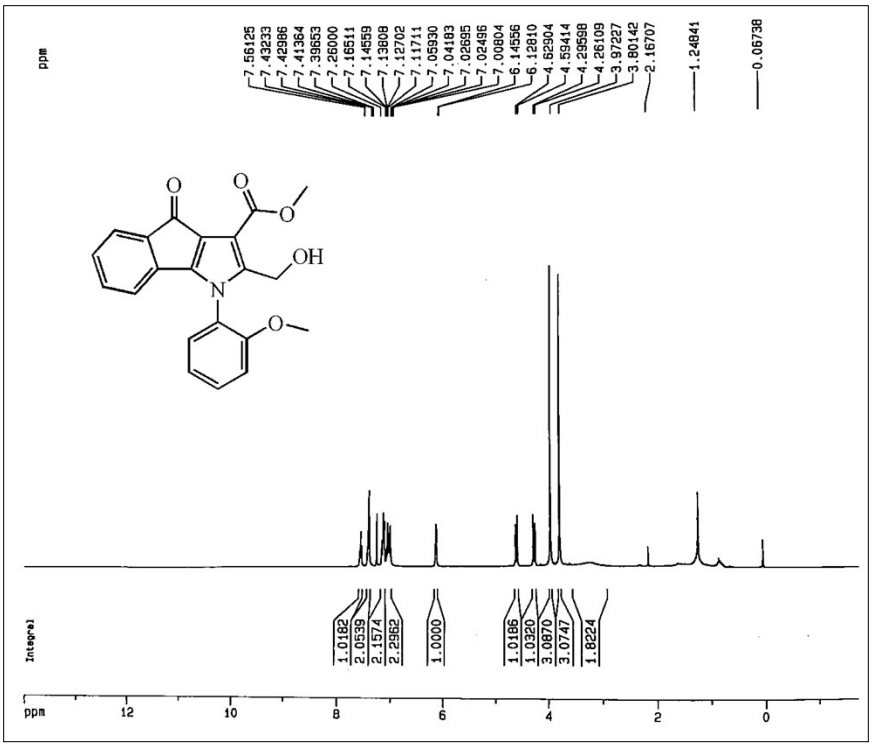


Figure 105: ^{1}H NMR spectrum (400 MHz) of compound **3h** in $CDCl_3$.

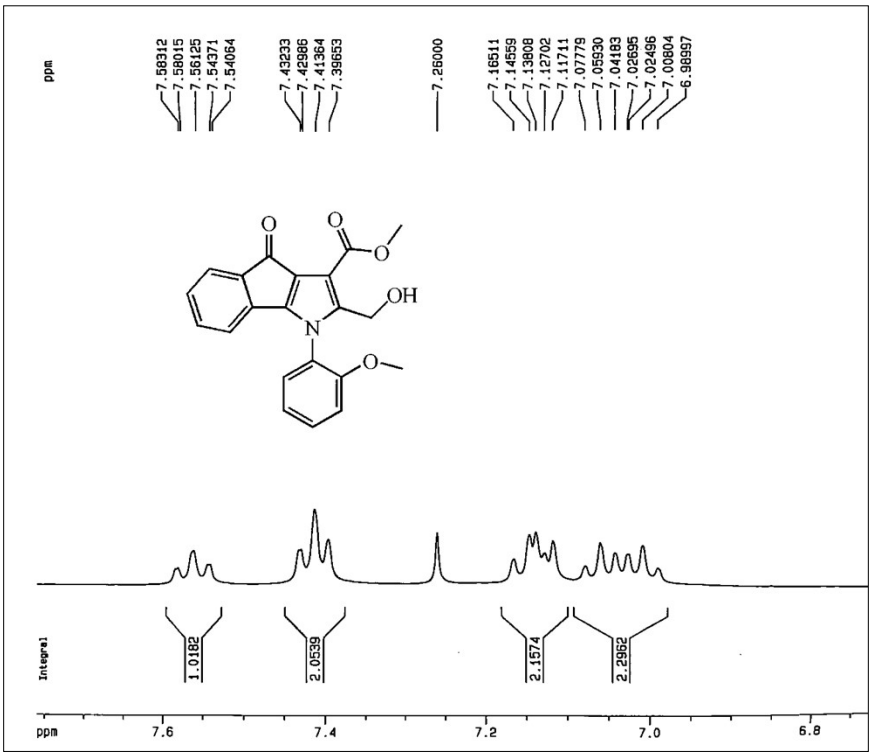


Figure 106: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3h** in $CDCl_3$.

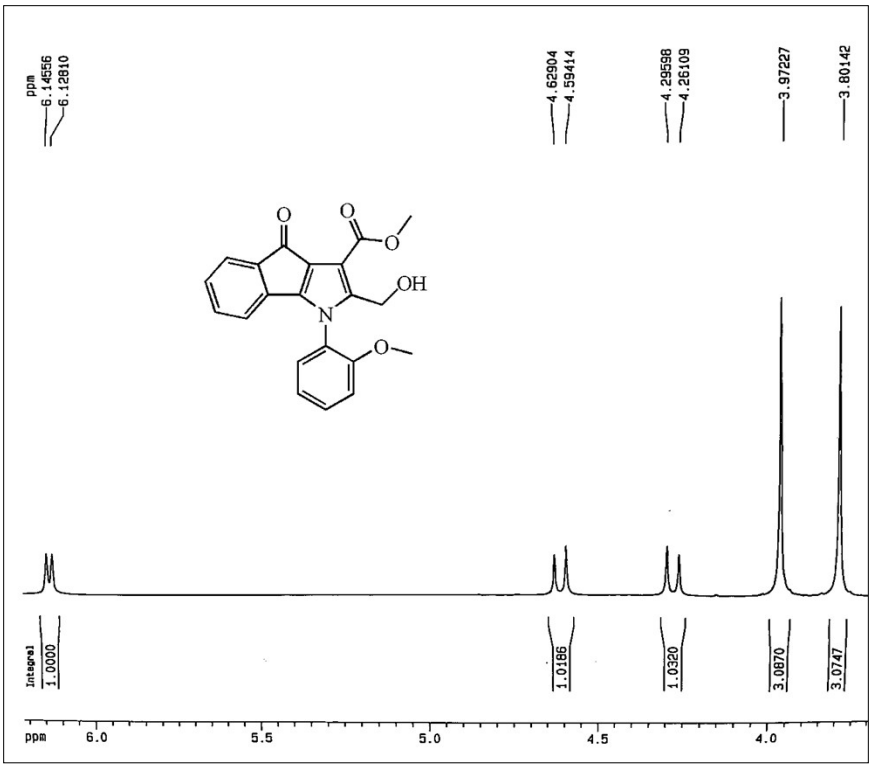


Figure 107: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3h** in $CDCl_3$.

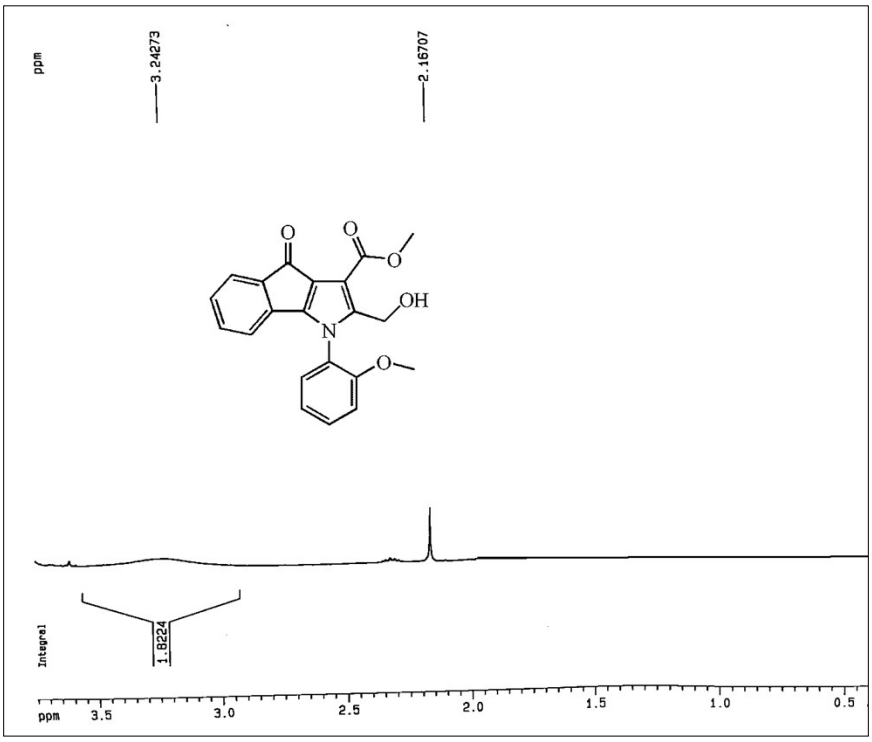


Figure 108: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3h** in $CDCl_3$.

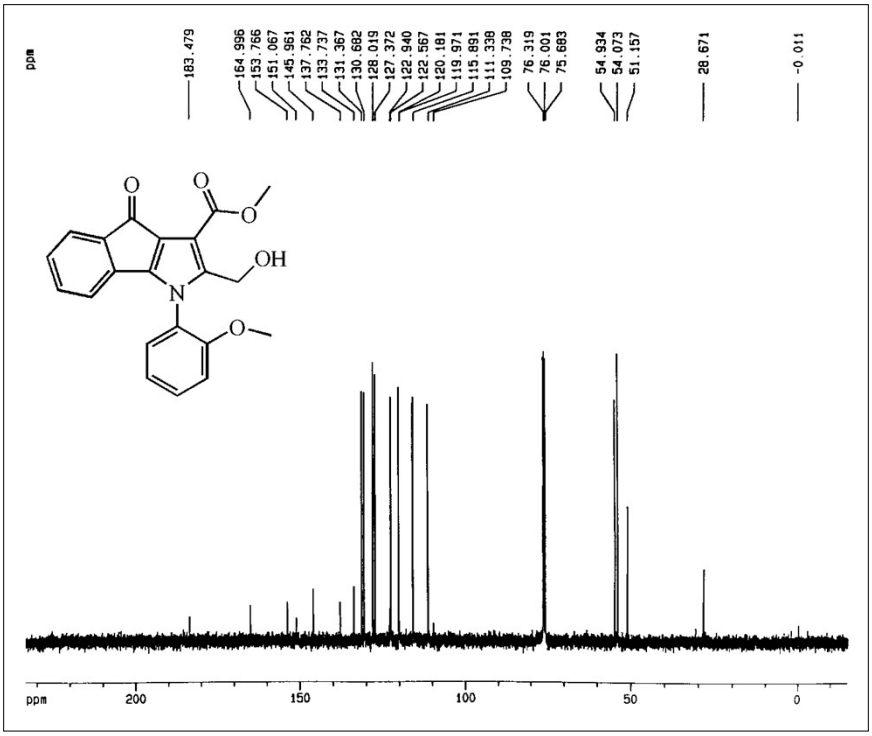


Figure 109: ^{13}C NMR spectrum (100 MHz) of compound **3h** in $CDCl_3$.

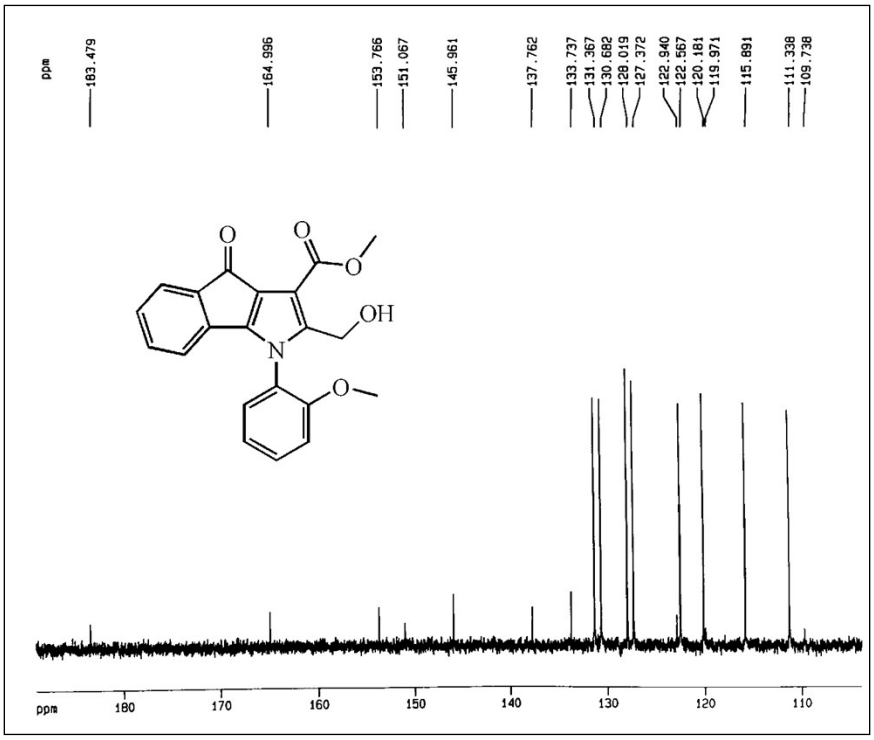


Figure 110: Expanded ^{13}C NMR spectrum (100 MHz) of compound **3h** in $CDCl_3$.

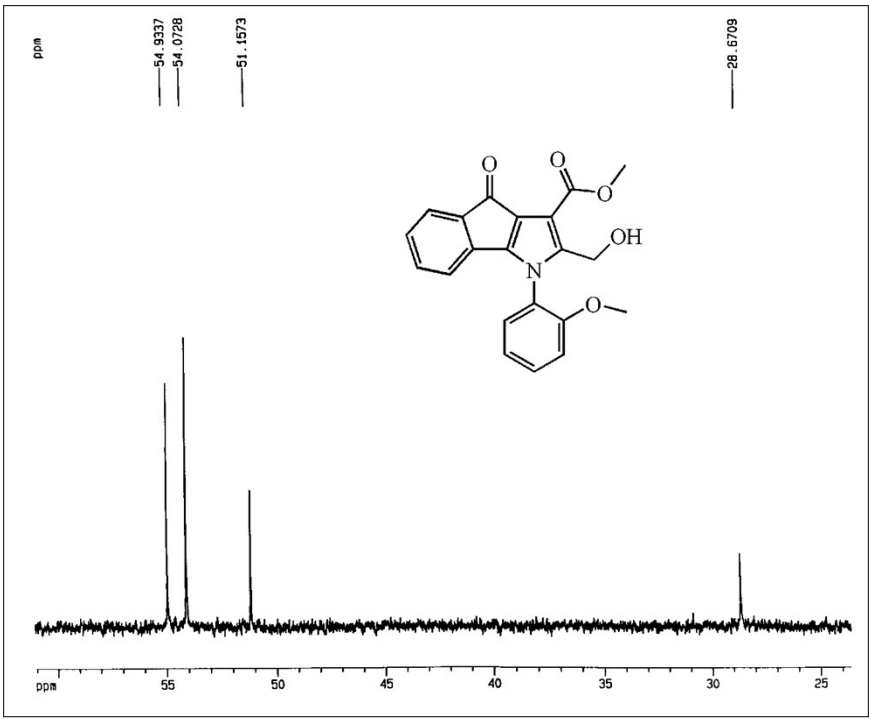


Figure 111: Expanded ^{13}C NMR spectrum (100 MHz) of compound **3h** in $CDCl_3$.

Ethyl 1-(4-chlorophenyl)-2-(ethoxymethyl)-4-oxo-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (3i)

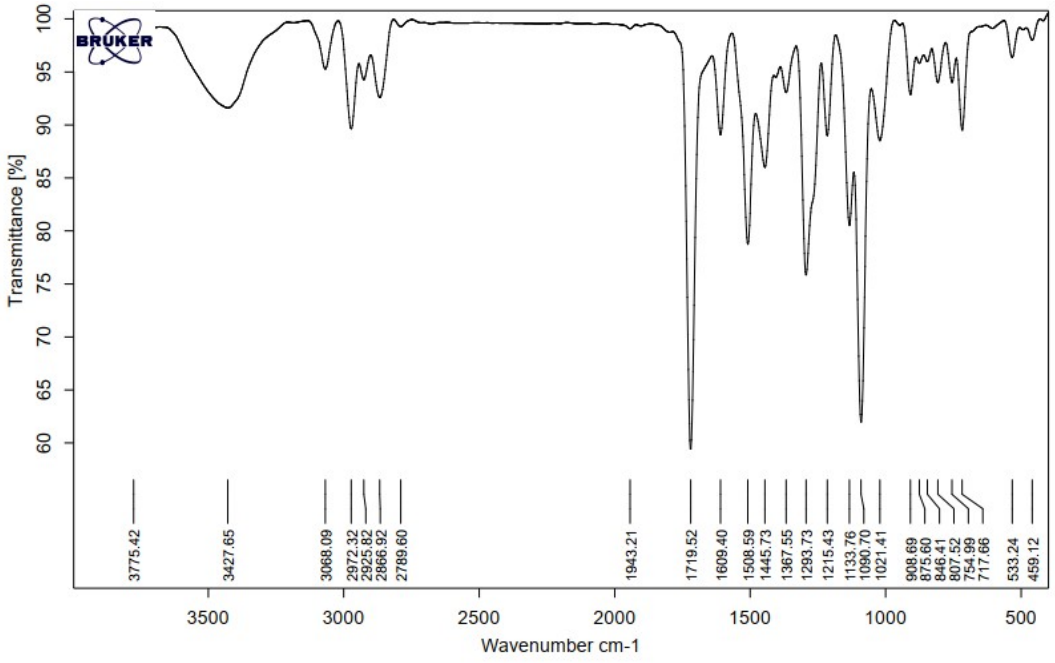


Figure 112: FT-IR (KBr) spectrum of **3i**.

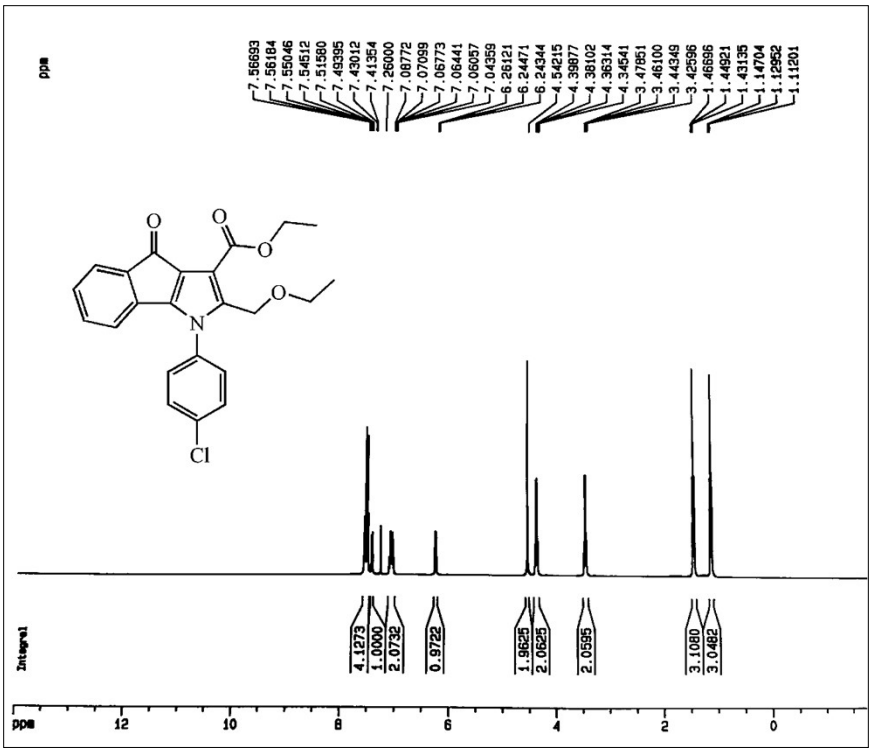


Figure 113: ^{1}H NMR spectrum (400 MHz) of compound **3i** in $CDCl_3$.

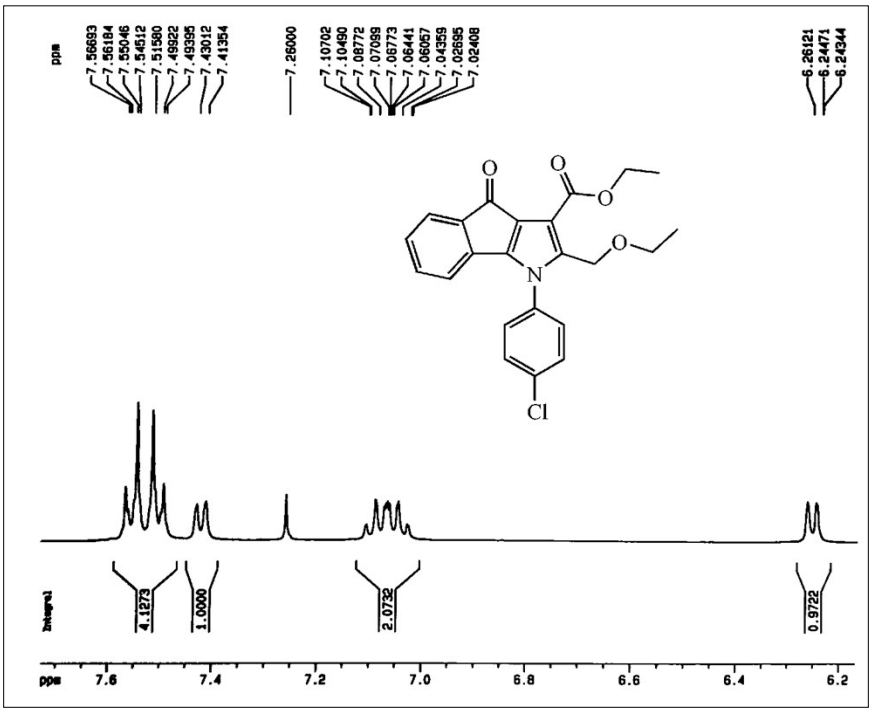


Figure 114: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3i** in $CDCl_3$.

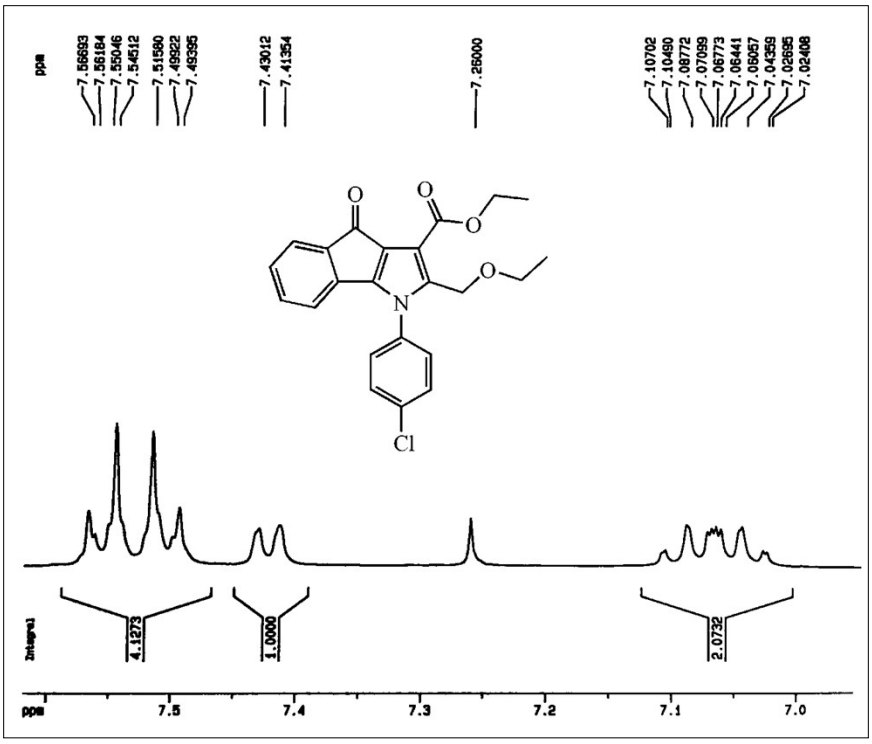


Figure 115: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3i** in $CDCl_3$.

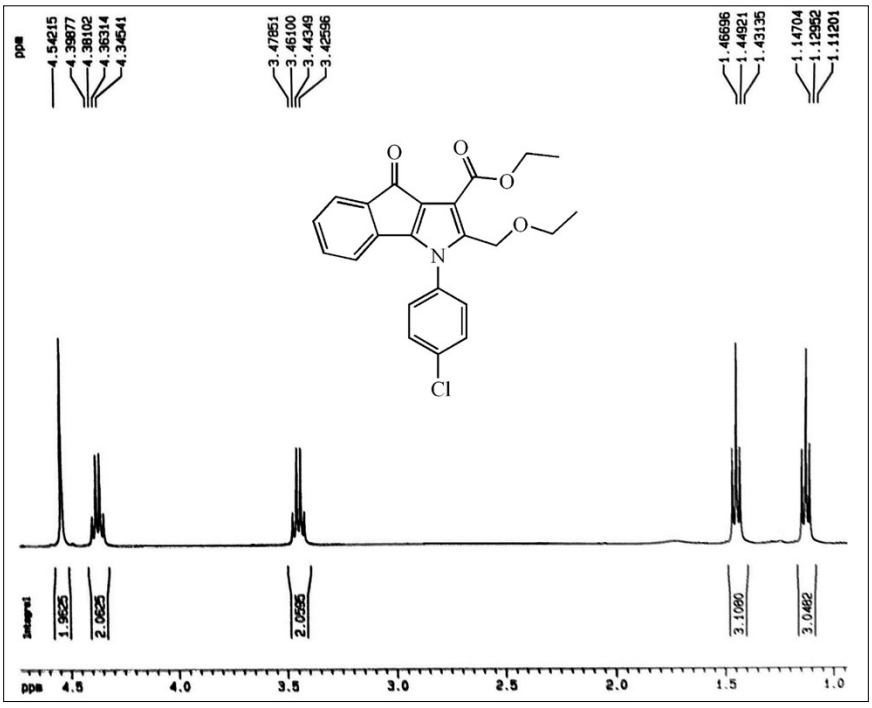


Figure 116: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3i** in $CDCl_3$.

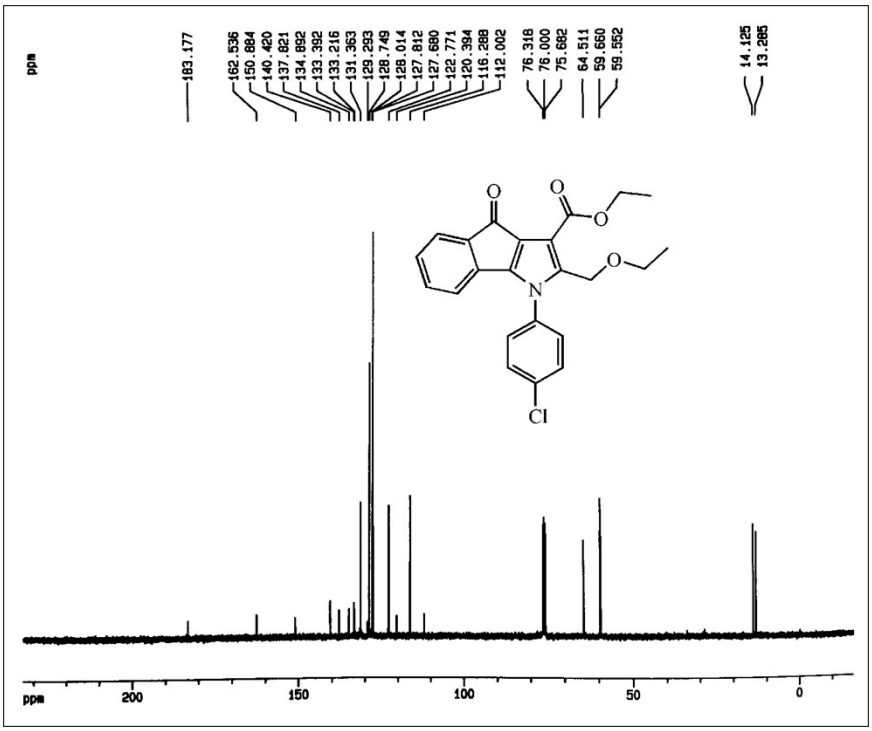


Figure 117: ^{13}C NMR spectrum (100 MHz) of compound **3i** in $CDCl_3$.

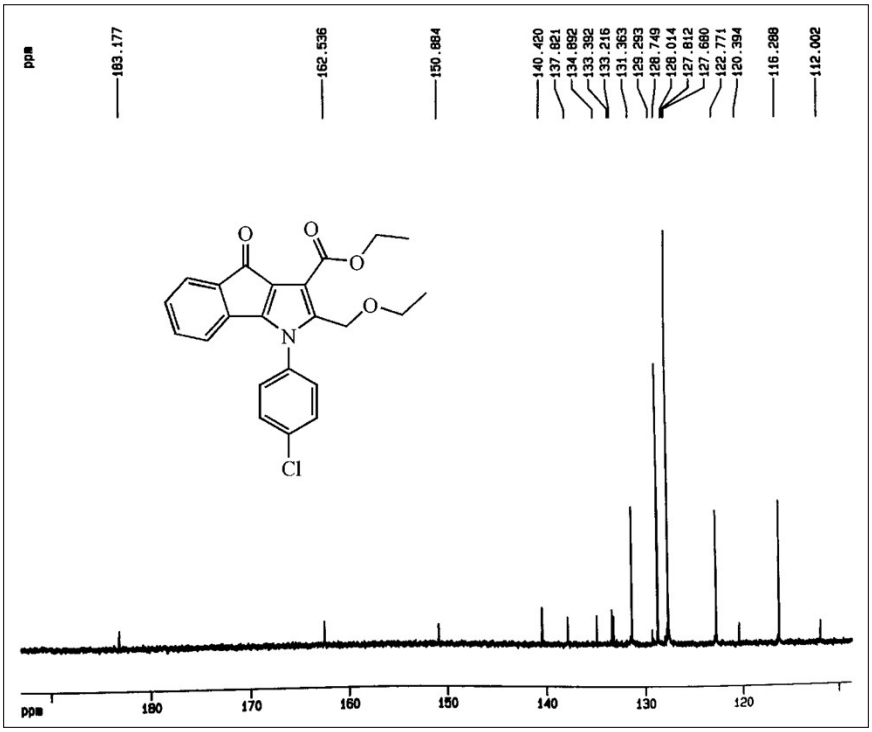


Figure 118: Expanded ^{13}C NMR spectrum (100 MHz) of compound **3i** in $CDCl_3$.

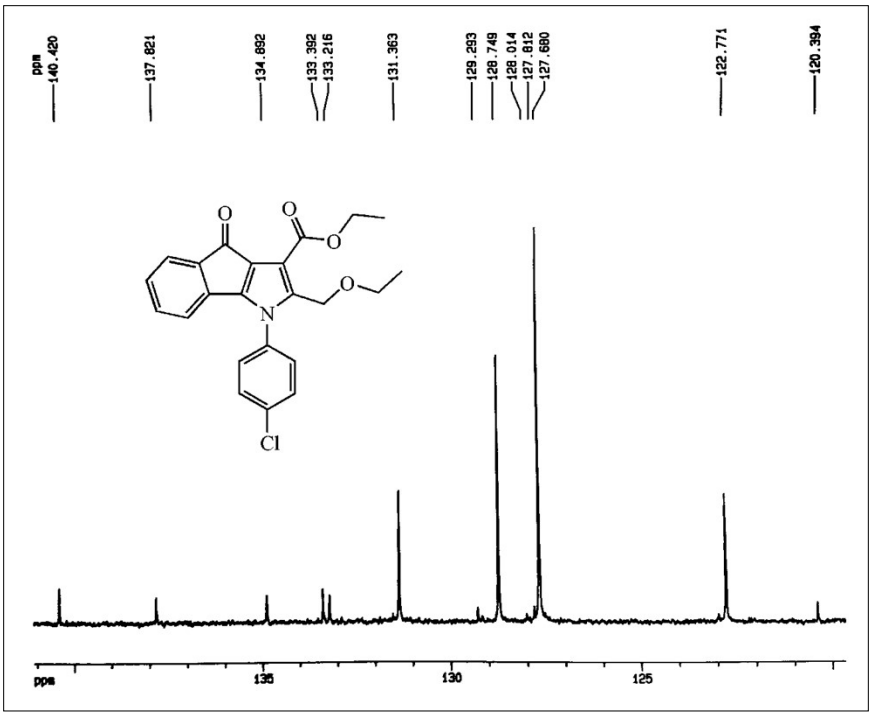


Figure 119: Expanded ^{13}C NMR spectrum (100 MHz) of compound **3i** in $CDCl_3$.

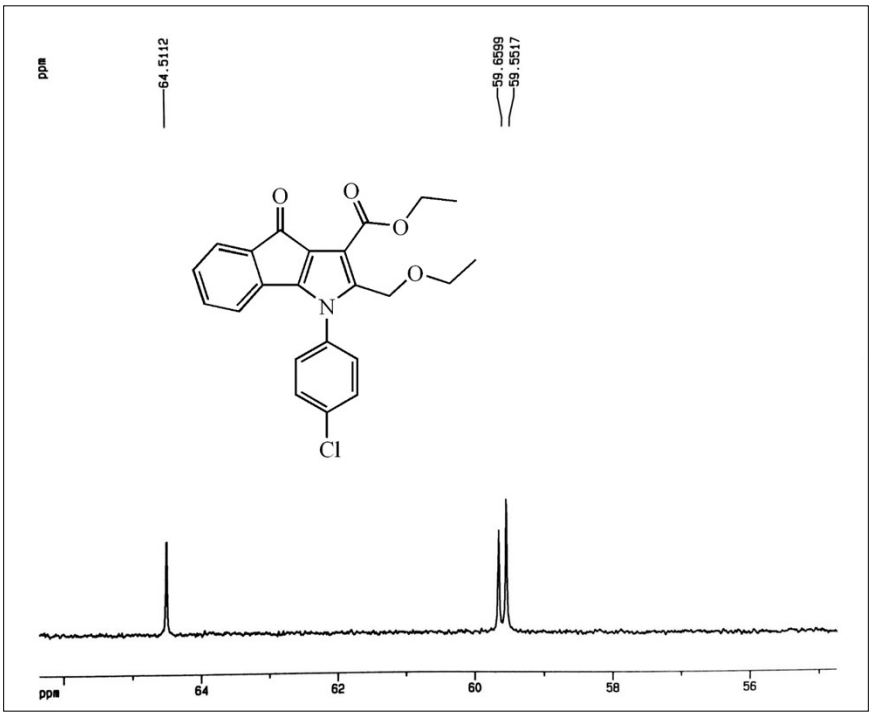


Figure 120: Expanded ^{13}C NMR spectrum (100 MHz) of compound **3i** in $CDCl_3$.

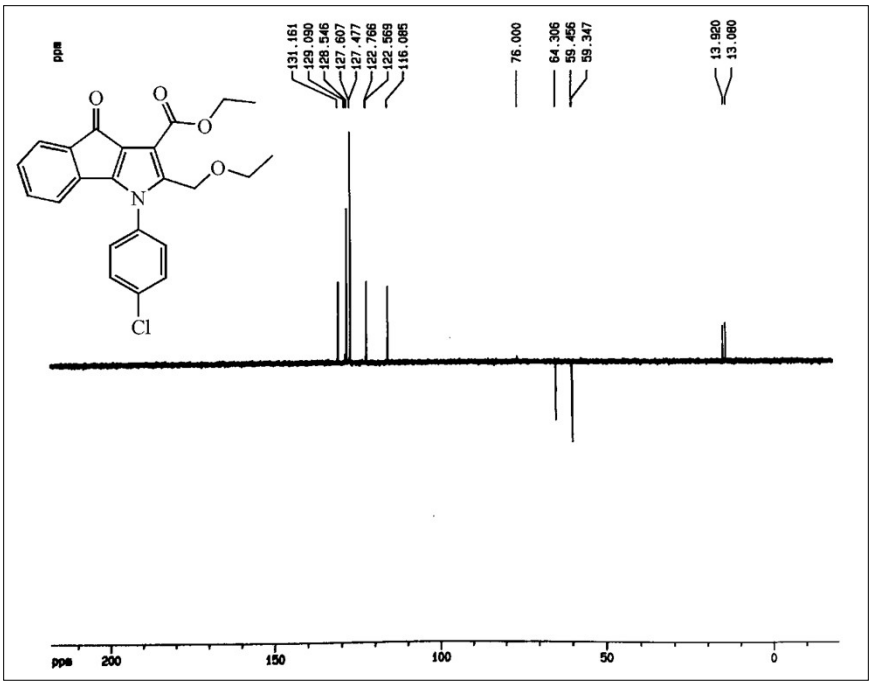


Figure 121: ^{13}C/DEPT-135 spectrum (100 MHz) of compound **3i** in $CDCl_3$.

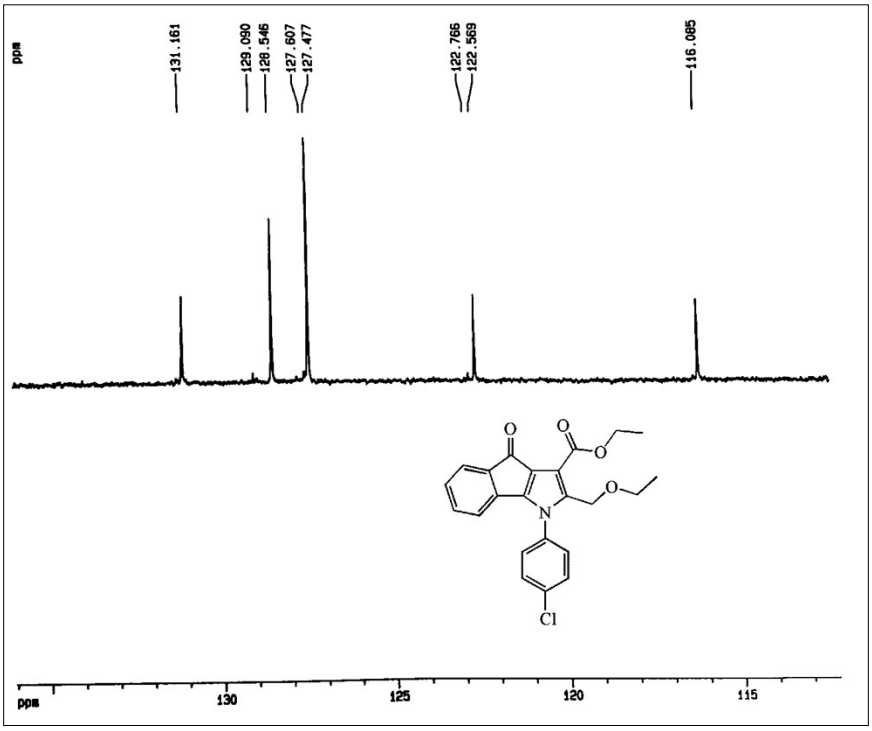


Figure 123: Expanded ^{13}C/DEPT-135 spectrum (100 MHz) of compound **3i** in $CDCl_3$.

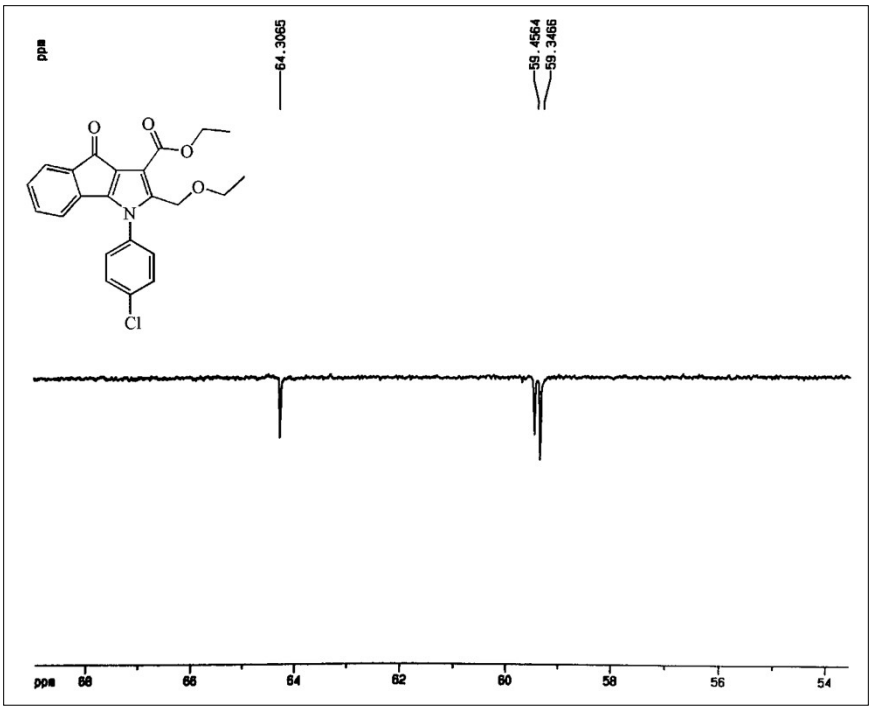


Figure 124: Expanded ^{13}C/DEPT-135 spectrum (100 MHz) of compound **3i** in $CDCl_3$.

Ethyl 2-(azidomethyl)-1-(4-chlorophenyl)-4-oxo-1,4-dihydroindeno[1,2-*b*]pyrrole-3-carboxylate (3j)

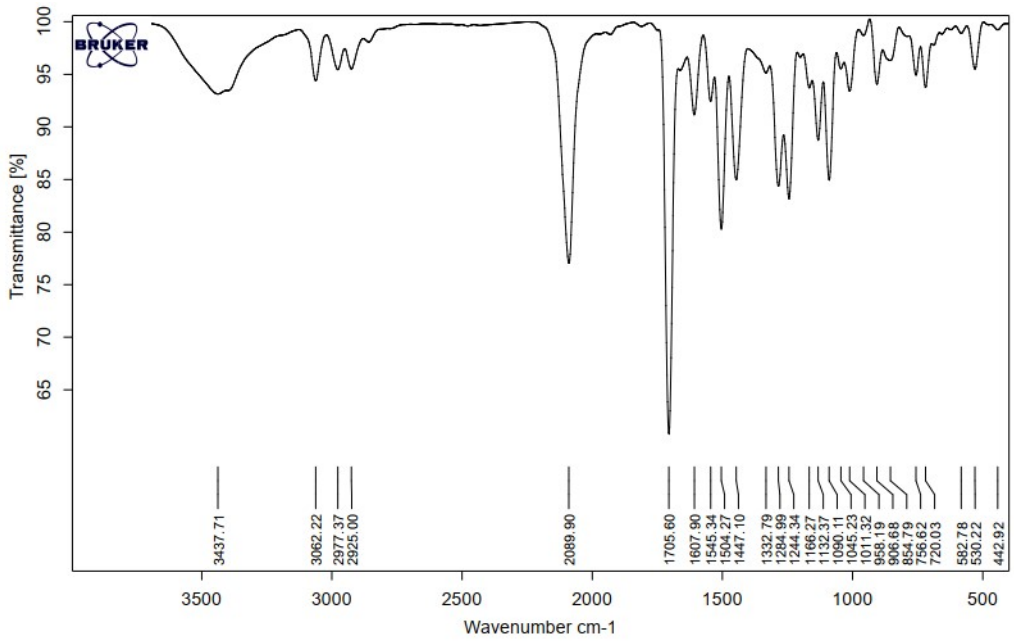


Figure 125: FT-IR (KBr) spectrum of **3j**.

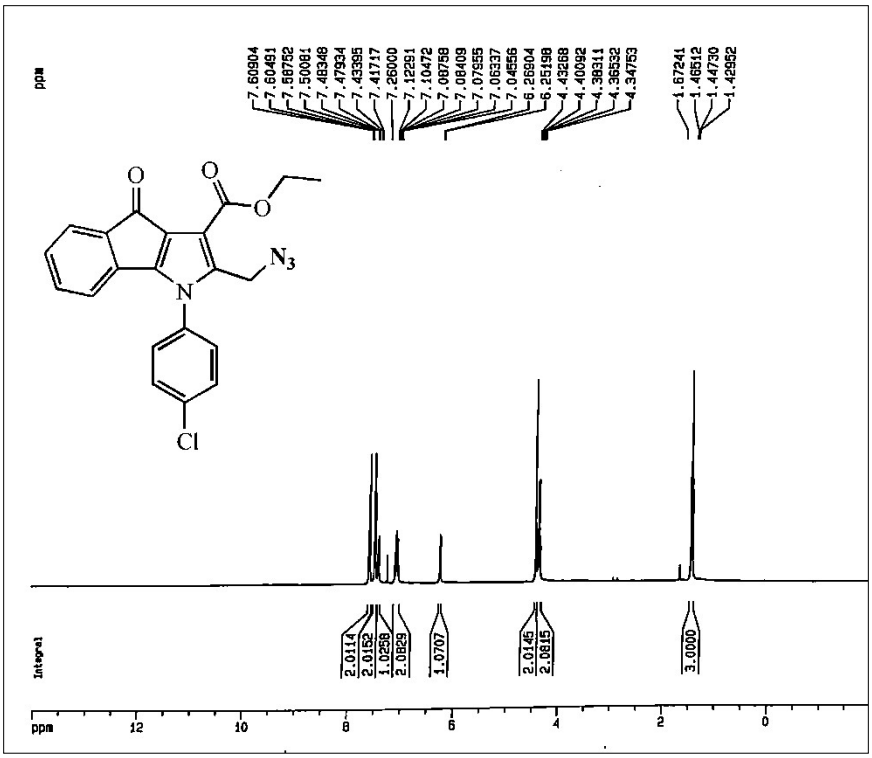


Figure 126: ^{1}H NMR spectrum (400 MHz) of compound **3j** in $CDCl_3$.

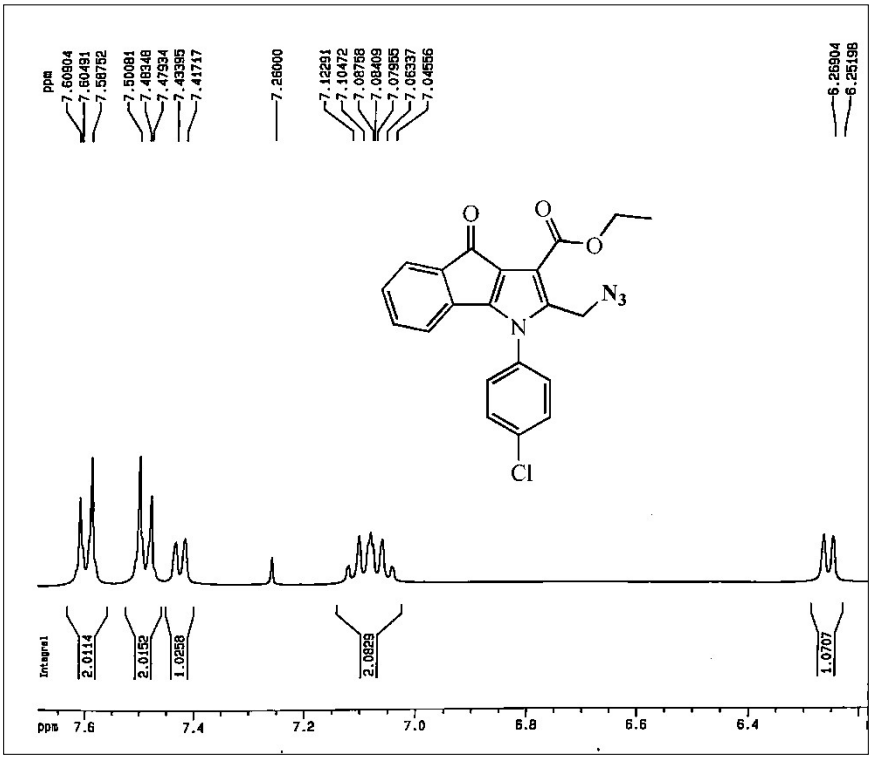


Figure 127: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3j** in $CDCl_3$.

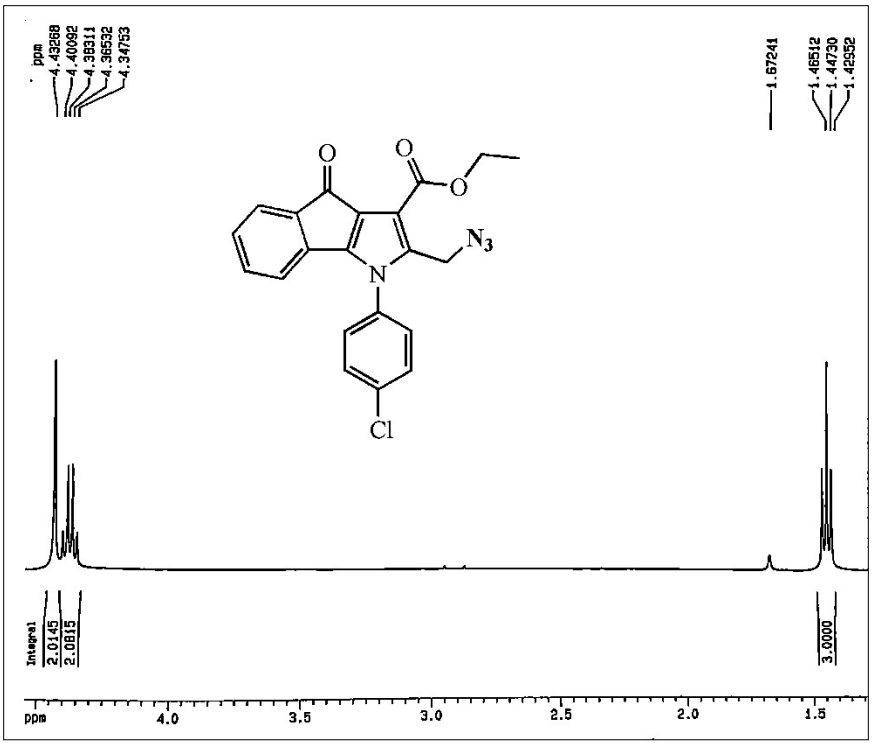


Figure 128: Expanded ^{1}H NMR spectrum (400 MHz) of compound **3j** in $CDCl_3$.

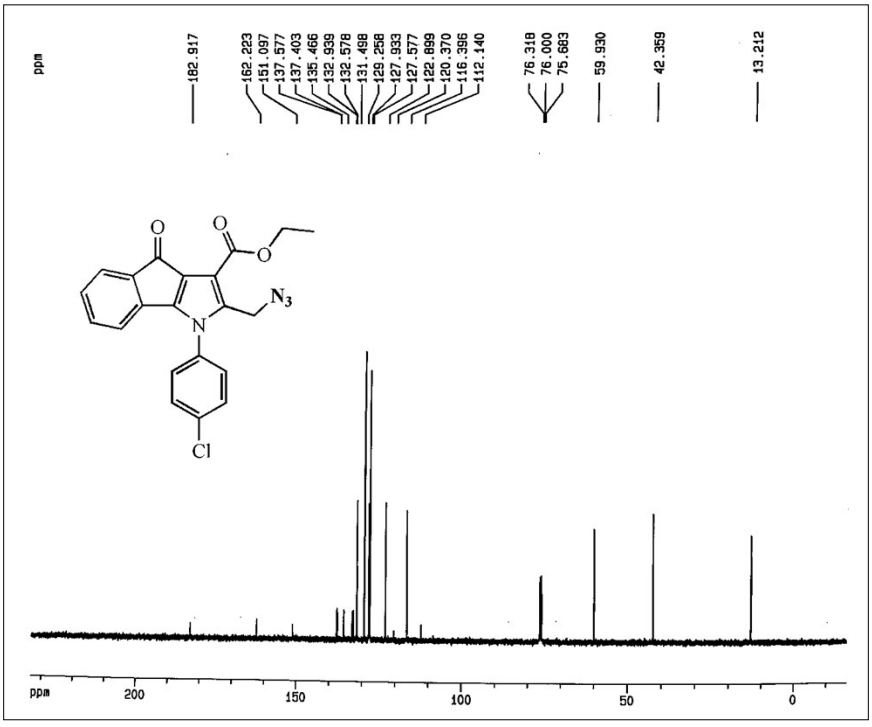


Figure 129: ^{13}C NMR spectrum (100 MHz) of compound **3j** in $CDCl_3$.

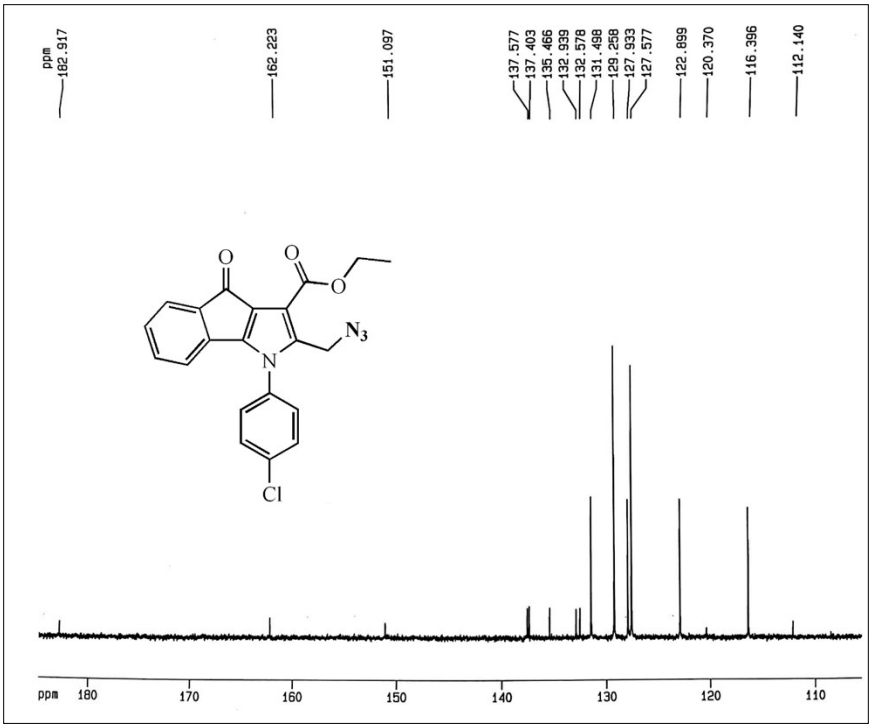


Figure 130: Expanded ^{13}C NMR spectrum (100 MHz) of compound **3j** in $CDCl_3$.

5. NaI in acetone test

The NaI in acetone test was carried out on Cl-products **2a-e**. Nucleophilic substitution of chlorine atom with iodine atom followed by the formation of NaCl precipitate in acetone proved the existence of chlorine atoms in these structures.

Figure 131. a) **2a-e** solutions in acetone, b) after adding of NaI in acetone to **2a-e** solutions and formation of NaCl precipitation

6. Crystallographic Data of 3f

Additional information crystallographic data of **3f** is available in the supplementary material Table 1.

Table 1 Crystal data and structure refinement parameters for **3f**

	3f
Formula	$C_{24}H_{22}NO_5$
M_r	404.4
Crystal description	Orange, block
Crystal size (mm)	0.28 × 0.23 × 0.21
Crystal system	Monoclinic
Space group	*P*21/*c*
T (K)	95
a (Å)	8.8388 (3)
b (Å)	21.2913 (5)
c (Å)	10.8389 (4)
α(°)	90
β (°)	91.297 (3)
γ(°)	90
V (Å^3)	2039.24 (11)
Z	4
F(000)	852
D_x(g cm^{-3})	1.317
Radiation type (λ, Å)	Cu *K*α (1.54184)
μ (mm^{-1})	0.76
ϑ range (°)	4.6 - 73.2
Index ranges	− 9 ≤ *h* ≤ 10
	− 25 ≤ *k* ≤ 26
	− 13 ≤ *l* ≤ 13
Diffractometer	SuperNova, Dual, Cu at home/near, AtlasS2
Absorption correction	Multi-scan

	CrysAlis PRO 1.171.40.53 (Rigaku Oxford Diffraction, 2019) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.811-1
Reflections collected	17655
Independent reflections	4016
[$I > 3\sigma(I)$] reflections	3120
R_{int}	0.105
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.621
No. reflections, constraints, parameters, restraints	4016, 88, 272, 0
H-atom treatment	H-atom parameters constrained
R [$I > 3\sigma(I)$]	0.076
R (all data)	0.247
S	3.78
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.55; -0.54
CCDC number	2227028

7. References

1 Computer program: CrysAlis PRO 1.171.41.117a, Rigaku OD (2021).

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3 V. Petříček, M. Dušek and L. Palatinus, Crystallographic Computing System JANA2006: General Features. Z. Kristallogr. - Cryst. Mater. 2014, **229**, 345– 352, DOI: 10.1515/zkri-2014-1737.