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

A facile and efficient synthesis of functionalized 4-oxo-2-(phenylimino)thiazolidin-5-ylideneacetate derivatives *via* $CuFe_2O_4$ magnetic nanoparticles catalyzed regioselective pathway

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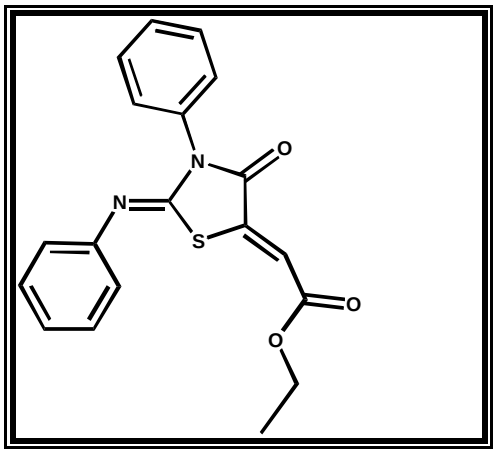
Materials and Methods

^{1}H-NMR and ^{13}C-NMR spectral analysis were carried out on Bruker-Advance Digital 300 MHz and 75 MHz instruments where tetramethylsilane (TMS) was used as internal standard. Infrared spectra were recorded in KBr pallets in reflection mode on a Perkin Elmer RX-1 FTIR spectrophotometer. High Resolution Mass Spectra was obtained using a QTOFMICRO YA263 mass spectrometer. Suitable single crystals of compound **4f** and **4e** were mounted on a Bruker-AXS SMART APEX II diffractometer equipped with a graphite monochromator. All the reactions were monitored by thin layer chromatography carried out on Merck aluminum-blocked silica gel plates coated with silica gel G under UV light and also by exposure to iodine vapor for detection. Melting points were determined on a Köfler Block apparatus and are uncorrected. Synthetic grade chemicals from Sigma-Aldrich, Spectrochem and E-Merck were used for carrying out the organic reactions. For column chromatography Spectrochem 100-200 mesh silica gel was used. All the solvents used in the reaction were distilled and dried over Na_2SO_4.

General Procedure for the synthesis of 4-oxo-2-(phenylimino)thiazolidin-5-ylideneacetate Derivatives:

A solution of phenyl isothiocyanate (1mmol), aniline (1mmol), acetylenicester (1mmol) and nano $CuFe_2O_4$ (10 mol%) in ethanol (5ml) was stirred at room temperature. After completion of the reaction (analyzed by TLC), catalyst was deposited on the magnetic bar and then easily removed by using an external magnet, leaving the clear reaction mixture. Then the solvent was removed from the reaction mixture under reduced pressure to get the crude product which was purified by column chromatography (silica gel 100-200 mesh). All compounds were well characterized by ^{1}H ,^{13}C NMR, FT-IR and HRMS analysis.

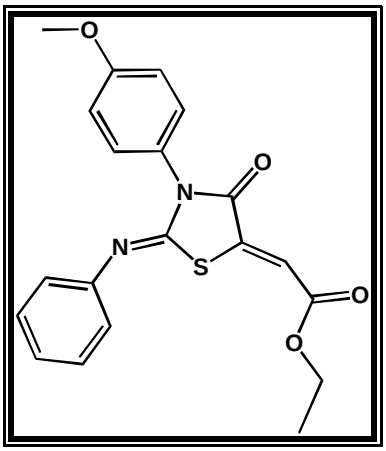
(*Z*)-methyl 2-((*Z*)-4-oxo-3-phenyl-2-(phenylimino)thiazolidin-5-ylidene)acetate (4a)



Yield: 94%, (0.330 g); M.p. 85 ^{0}C; Characteristics: Yellow crystalline solid;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57-7.27 (m, 7H), 7.15 (t, 1H, *J*=7.5 Hz), 6.99-6.93 (m, 3H), 4.28 (q, 2H, *J*= 7.1 Hz), 1.32 (t, 3H, *J*= 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.9, 164.6, 151.8, 147.3, 141.1, 133.9, 129.5, 129.2, 128.8, 127.7, 125.2, 120.9, 116.9, 62.9, 13.9; HRMS (ESI-TOF) m/z Calculated for $[C_{19}H_{16}N_2O_3S+H]^+$: 353.0954, found: 353.0955; IR (KBr) cm^{-1}: 1266.3, 1324.5, 1614.7, 1644.5, 1723.6, 2953.8, 3033.2.

((*Z*)-ethyl 2-((*Z*)-3-(4-methoxyphenyl)-4-oxo-2-(phenylimino)thiazolidin-5-ylidene)acetate (4b)

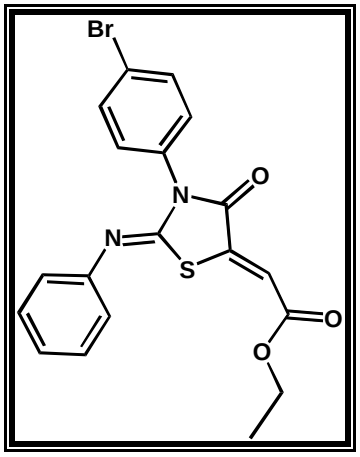


Yield: 93%, (0.355 g); M.p. 92 ^{0}C; Characteristics: Yellow crystalline solid;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28-7.17 (m, 3H), 7.08-7.03 (m, 1H), 6.96-6.76 (m, 6H), 4.17 (q, 2H, *J*= 7.2 Hz), 3.74 (s, 3H), 1.20 (t, 3H, *J*= 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.8, 164.6, 159.8, 147.4, 141.1, 129.2, 129.0, 127.8, 127.4, 126.4, 125.1, 122.1, 120.9, 120.8, 116.8, 114.6, 61.6, 55.4, 13.8; HRMS (ESI-TOF) m/z Calculated for $[C_{20}H_{18}N_2O_4S+H]^+$: 383.1061, found: 383.1062; IR (KBr) cm^{-1}: 1267.1, 1324.4, 1371.3, 1614.7, 1645.0, 1727.4, 2953.8, 3032.3.

(*Z*)-ethyl-2-((*Z*)-3-(4-bromophenyl)-4-oxo-2-(phenylimino)thiazolidin-5-ylidene)acetate (4c)

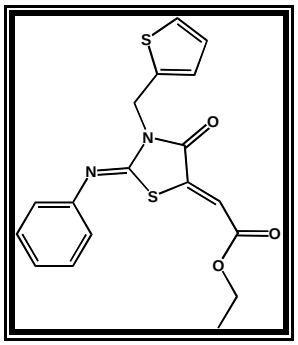
(4c)



Yield: 92%, (0.396 g); M.p. 81 ^{0}C; Characteristics: Yellow crystalline solid;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62-7.58 (m, 1H), 7.50-7.24 (m, 6H), 6.93-6.91 (m, 1H), 6.86 (d, 1H, *J*=8.1 Hz), 6.75 (d, 1H, *J* =8.1 Hz), 4.21 (q, 2H, *J*= 7.8 Hz), 1.26 (t, 3H, *J*= 7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.7, 152.0, 146.2, 140.6, 140.4, 137.3, 132.2. 130.1, 129.3, 129.2, 127.6, 127.3, 125.2, 122.6, 120.7, 118.3, 117.3, 61.7, 13.9; HRMS (ESI-TOF) m/z Calculated for $[C_{19}H_{15}BrN_2O_3S+H]^+$: 431.0060, found: 431.0061; IR (KBr) cm^{-1}: 1266.9, 1325.0, 1370.6, 1614.2, 1644.8, 1724.6, 2952.0, 3033.0.

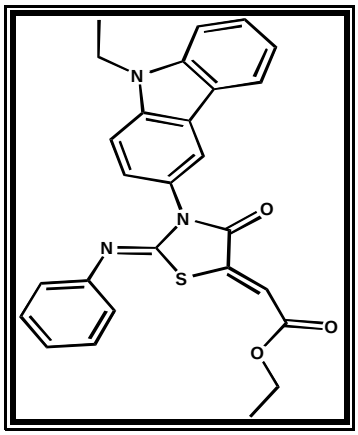
(*Z*)-ethyl 2-((*Z*)-4-oxo-2-(phenylimino)-3-(thiophen-2-ylmethyl)thiazolidin-5-ylidene)acetate (4d)



Yield: 98%, (0.364 g); M.p. 93 ^{0}C; Characteristics: Yellow crystalline solid;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62-7.59 (m, 1H), 7.31-6.82 (m, 8H), 5.20 (s, 2H), 4.18 (q, 2H, *J*= 7.2 Hz), 1.21 (t, 3H, *J*= 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.8, 164.3, 151.8, 147.1, 141.3, 137.5, 130.2, 129.4, 128.7, 127.5, 126.6, 126.5, 125.3, 121.2, 116.8, 63.0, 40.4, 13.9; HRMS (ESI-TOF) m/z Calculated for $[C_{18}H_{16}N_2O_3S_2+H]^+$: 373.0675, found: 373.0673; IR (KBr) cm^{-1}: 1202.3, 1318.6, 1388.1, 1606.0, 1633.8, 1706.1, 2947.7.

(*Z*)-ethyl 2-((*Z*)-3-(9-ethyl-9*H*-carbazol-3-yl)-4-oxo-2-(phenylimino)thiazolidin-5-ylidene)acetate (4e)

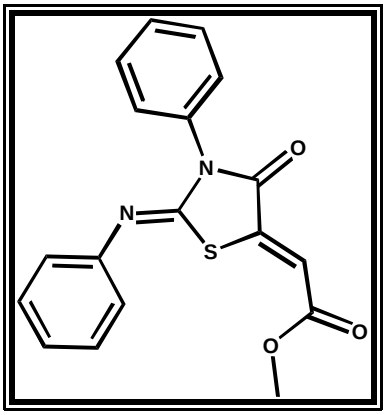


Yield: 91%, (0.427 g); M.p. 102 ^{0}C; Characteristics: Yellow crystalline solid;

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06-8.01 (m, 2H), 7.98-6.87 (m, 11H), 4.31-4.16 (m, 4H), 1.35 (t, 3H, *J*=

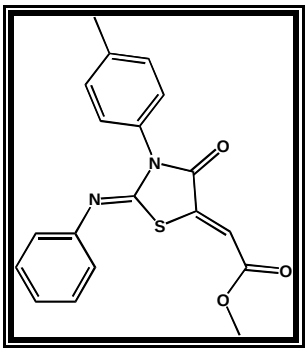
7.2 Hz), 1.24(t, 3H, *J*=6.9Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.3, 152.6, 147.7, 141.5, 140.5, 139.8, 129.2, 126.3, 125.1, 125.0, 123.5, 121.1, 121.0, 120.9, 120.2, 119.4, 118.8, 116.8, 112.6, 109.1, 108.7, 61.7, 37.7, 14.2, 13.8; HRMS (ESI-TOF) m/z Calculated for $[C_{27}H_{23}N_3O_3S+H]^+$: 470.1533, found: 470.1536; IR (KBr) cm^{-1}: 1193.7, 1314.7, 1484.1, 1647.0, 1693.6, 1720.4, 2974.5, 3429.2.

(*Z*)-methyl 2-((*Z*)-4-oxo-3-phenyl-2-(phenylimino)thiazolidin-5-ylidene)acetate (4f)



Yield: 95%, (0.321 g); M.p. 116 ^{0}C; Characteristics: Yellow crystalline solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44-7.13 (m, 7H), 7.09-7.00 (m, 1H), 6.89-6.82 (m, 3H), 3.71 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.3, 164.6, 151.6, 147.4, 141.4, 137.5, 134.1, 129.6, 129.3, 129.0, 127.9, 125.3, 120.9, 116.5, 52.6 ; HRMS (ESI-TOF) m/z Calculated for $[C_{18}H_{14}N_2O_3S+H]^+$: 339.0798, found: 339.0795; IR (KBr) cm^{-1}: 1267.1, 1371.3, 1614.7, 1645.0, 1727.4, 2953.8, 3032.3

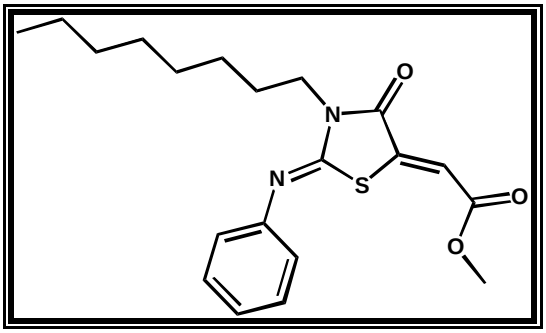
(*Z*)-methyl 2-((*Z*)-4-oxo-2-(phenylimino)-3-(p-tolyl)thiazolidin-5-ylidene)acetate (4g)



Yield: 93%, (0.327 g); M.p. 88 ^{0}C; Characteristics: Yellow crystalline solid;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (d, 1H, *J*=7.2 Hz), 7.42-7.32 (m, 2H), 7.06-6.96 (m, 4H), 6.87-6.82 (m, 2H), 6.74 (d, 1H, *J*= 8.1 Hz), 3.71(s, 3H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.1, 152.0, 147.3, 144.7, 141.4, 139.1, 137.4, 131.2, 130.1, 129.9, 129.4, 129.2, 127.7, 127.3, 125.0, 120.8, 116.2, 53.3, 21.1; HRMS (ESI-TOF) m/z Calculated for $[C_{19}H_{16}N_2O_3S +H]^+$: 353.0954, found: 353.0955; IR (KBr) cm^{-1}: 1265.3, 1366.2, 1602.9, 1652.5, 1730.6, 2960.0, 3033.4.

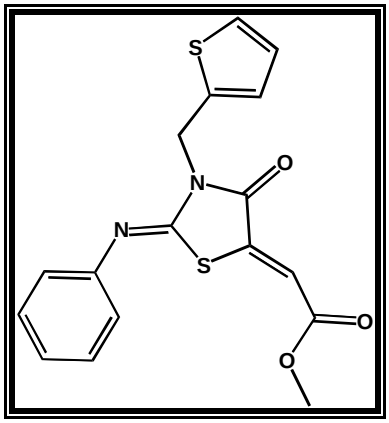
(*Z*)-methyl 2-((*Z*)-3-octyl-4-oxo-2-(phenylimino)thiazolidin-5-ylidene)acetate (4h)



Yield: 97%, (0.363 g); Characteristics: Yellow liquid;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27-7.17 (m, 2H), 7.08-6.86 (m, 3H), 6.79 (s, 1H), 3.86 (t, 2H, *J*=7.4Hz), 3.66 (s, 3H), 1.66-1.64 (m, 2H), 1.24-1.17 (m, 10H), 0.78-0.76 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.3, 164.8, 150.9, 147.4, 141.8, 137.4, 130.3, 129.4, 127.4, 125.1, 121.1, 115.7, 52.4, 43.2, 31.8, 29.1, 27.4, 26.8, 22.6, 14.1; HRMS (ESI-TOF) m/z Calculated for $[C_{20}H_{26}N_2O_3S +H]^+$: 375.1737, found: 375.1735; IR (KBr) cm^{-1}: 1202.9, 1289.2, 1322.3, 1594.2, 1637.3, 1718.2, 2855.8, 2927.2.

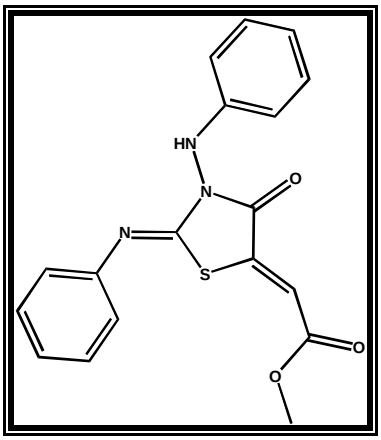
(*Z*)-methyl 2-((*Z*)-4-oxo-2-(phenylimino)-3-(thiophen-2-ylmethyl)thiazolidin-5-ylidene)acetate (4i)



Yield: 96%, (0.344g); M.p. 80 ^{0}C; Characteristics: Yellow amorphous solid;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (d, 1H, *J*=7.2 Hz), 7.53-7.03 (m, 5H), 6.96-6.80 (m, 2H), 6.78 (s, 1H), 5.15 (s, 2H), 3.62 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.2, 164.2, 150.2, 147.1, 141.6, 137.6, 136.7, 130.4, 129.5, 128.9, 127.5, 126.6, 125.5, 121.3, 116.3, 52.5, 40.5 ; HRMS (ESI-TOF) m/z Calculated for $[C_{17}H_{14}N_2O_3S_2+H]^+$: 359.0519, found: 359.0518; IR (KBr) cm^{-1}: 1202.2, 1319.0, 1389.1, 1633.8, 1706.2, 2948.1.

(*Z*)-methyl 2-((*Z*)-4-oxo-3-(phenylamino)-2-(phenylimino)thiazolidin-5-ylidene)acetate (4j)

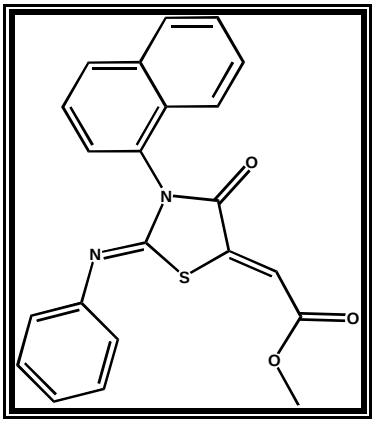


Yield: 94%, (0.332 g); M.p. 98 ^{0}C; Characteristics: Yellow crystalline solid;

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.51 (s, 1H), 7.89 (m, 2H), 7.67-7.60 (m, 2H), 7.54-7.42 (m, 2H), 7.34-

7.29 (m, 2H), 7.14-7.09 (m, 3H), 3.71 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.1, 152.1, 150.9, 137.4, 136.7, 133.9, 130.2, 129.5, 129.3, 129.2, 129.1, 128.9, 127.2, 125.6, 125.1, 124.1, 119.6, 53.4 ; HRMS (ESI-TOF) m/z Calculated for $[C_{18}H_{15}N_3O_3S+H]^+$: 354.0907, found: 354.0905; IR (KBr) cm^{-1}: 1251.3, 1444.0, 1499.4, 1550.4, 1598.9, 1698.4, 3245.7.

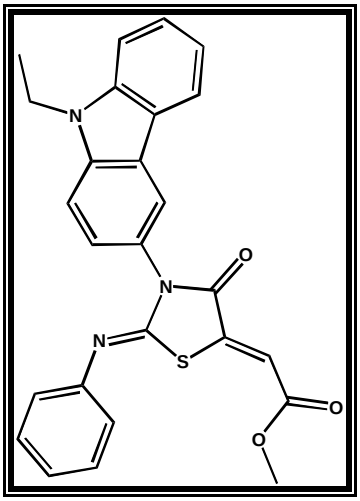
(*Z*)-methyl 2-((*Z*)-3-(naphthalen-1-yl)-4-oxo-2-(phenylimino)thiazolidin-5-ylidene)acetate (4k)



Yield: 92%, (0.357 g); M.p. 102 ^{0}C; Characteristics: Yellow crystalline solid;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73-7.37 (m, 11H), 7.08-6.99 (m, 2H), 3.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.7, 143.7, 141.4, 134.3, 129.5, 129.3, 128.0, 128.9, 127.4, 126.5, 125.9, 125.6, 125.5, 123.2, 116.7, 115.4, 52.5 ; HRMS (ESI-TOF) m/z Calculated for $[C_{22}H_{16}N_2O_3S+H]^+$: 389.0954, found: 389.0953; IR (KBr) cm^{-1}: 1262.3, 1344.6, 1605.7, 1656.5, 1705.8, 2956.8, 3029.2.

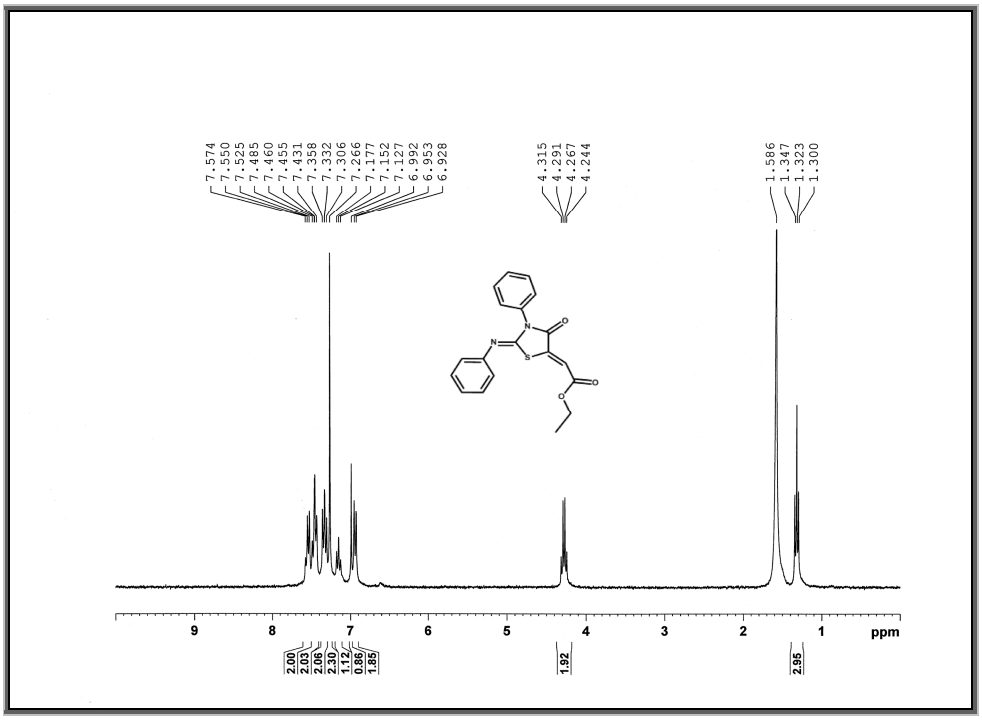
(*Z*)-methyl 2-((*Z*)-3-(9-ethyl-9*H*-carbazol-3-yl)-4-oxo-2-(phenylimino)thiazolidin-5-ylidene)acetate (4l)



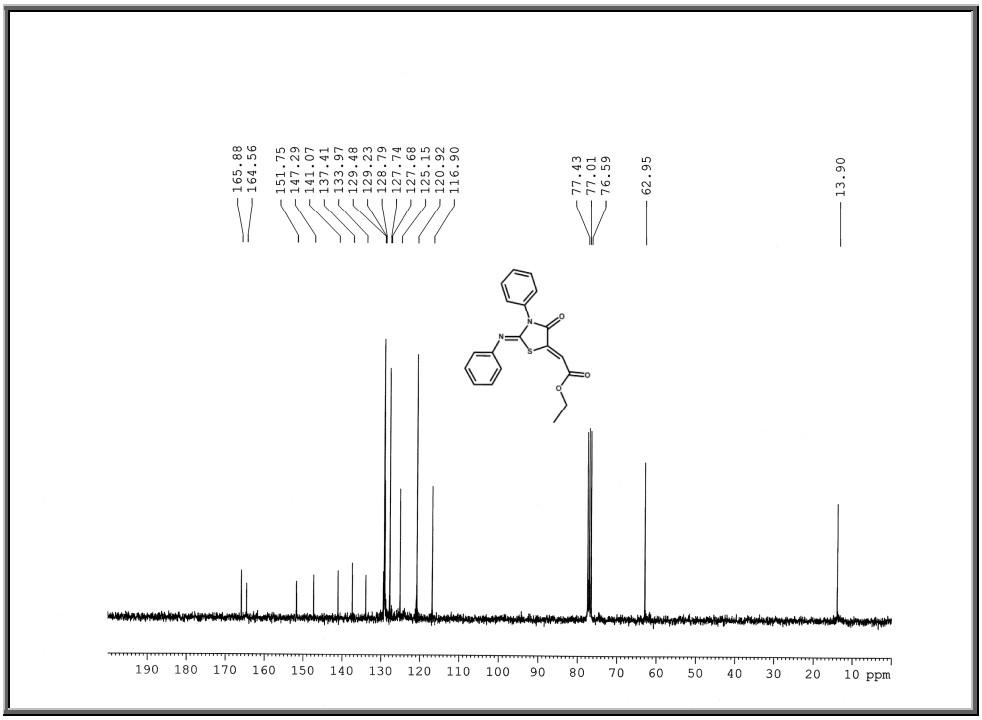
Yield: 95%, (0.432 g); M.p. 120 ^{0}C; Characteristics: Yellow crystalline solid;

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11-8.04 (m, 2H), 7.59-6.93 (m, 11H), 4.37 (q, 2H, *J*=7.1 Hz), 3.82(s, 3H), 1.43 (t, 3H, *J*=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 147.6, 141.7, 140.5, 129.2, 126.3, 125.1, 124.9, 122.7, 121.0, 120.8, 120.2, 119.3, 116.3, 109.1, 108.7, 52.5, 37.8, 13.9 ; HRMS (ESI-TOF) m/z Calculated for $[C_{26}H_{21}N_3O_3S+H]^+$: 456.1376, found: 456.1377; IR (KBr) cm^{-1}: 1196.3, 1310.6, 1616.0, 1642.4, 1722.0, 2970.1, 3421.1.

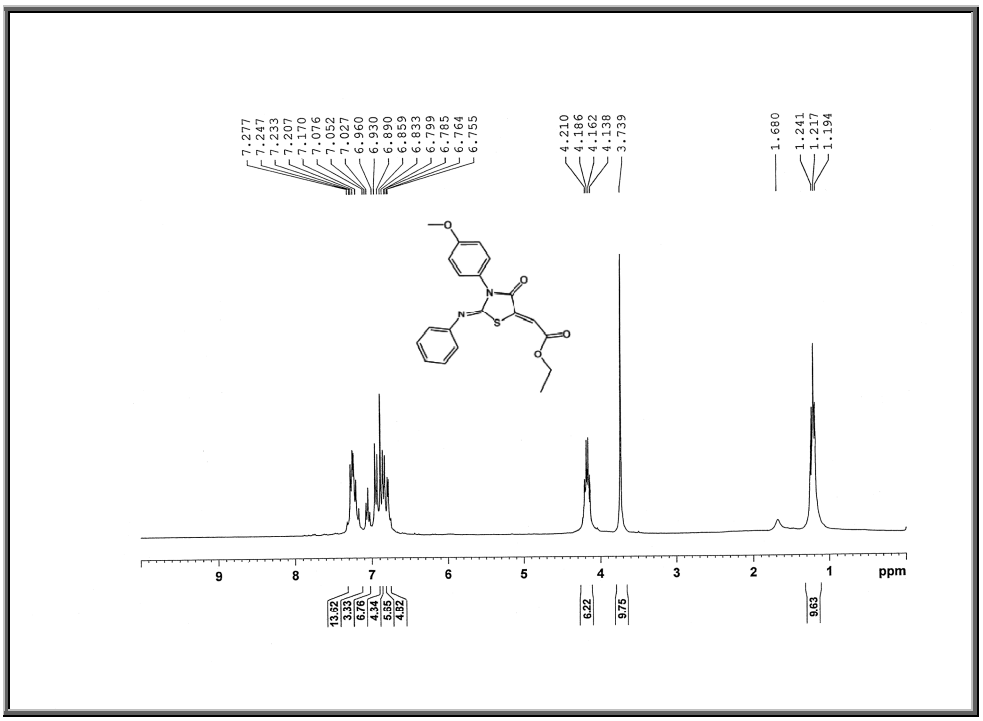
[1]HNMR, [13]CNMR Spectra of the Compounds (4a-4l):



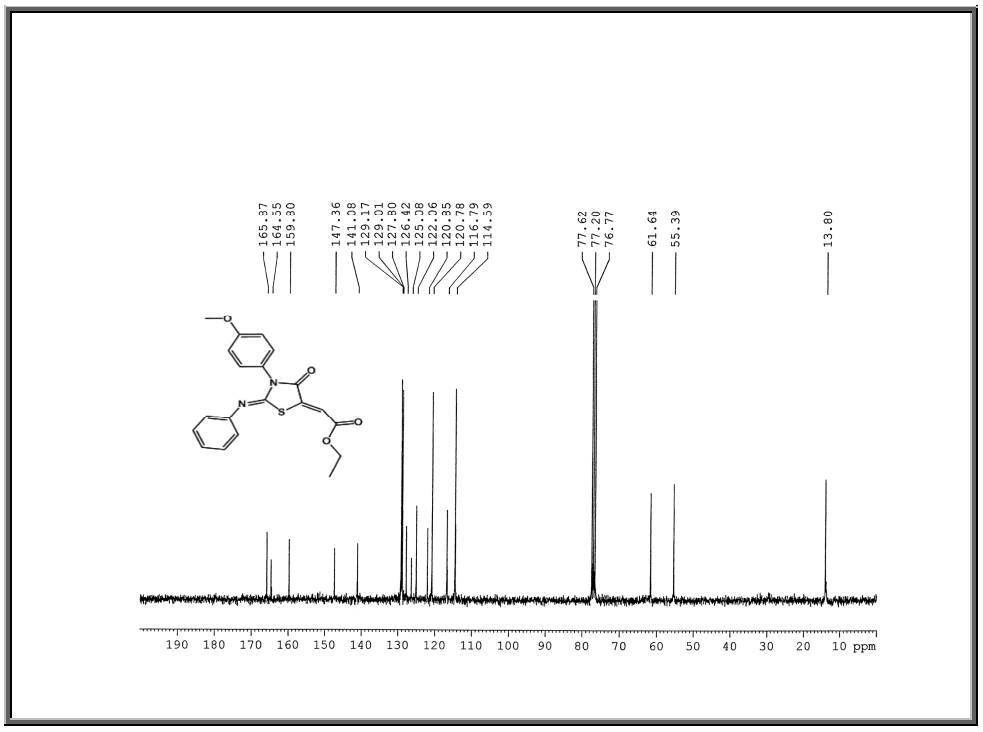
[1]H NMR of Compound 4a



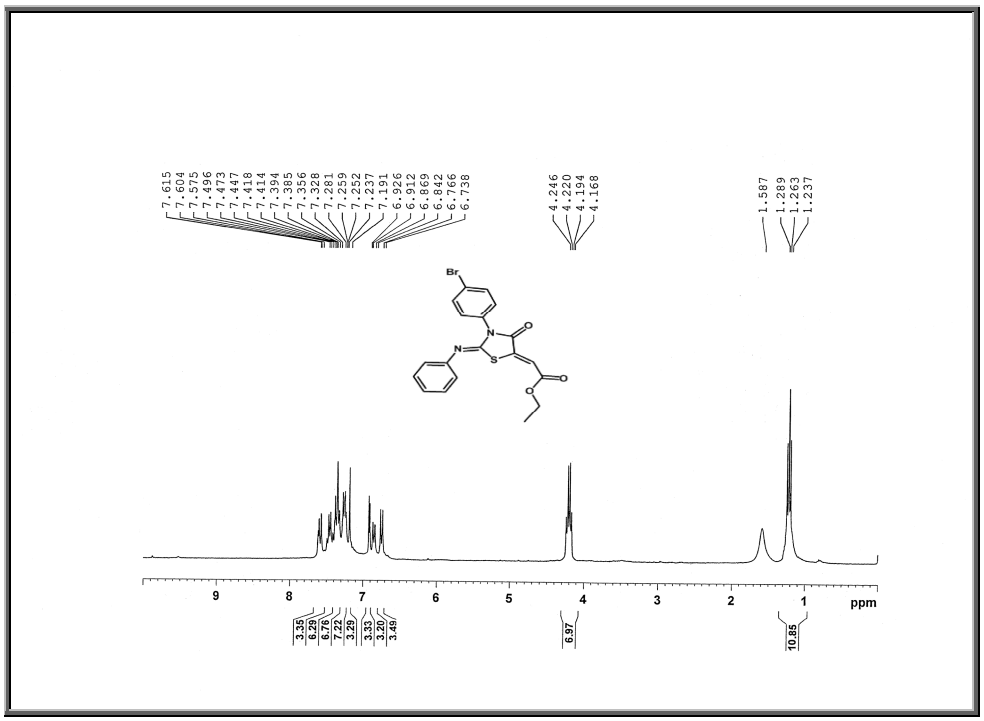
[13]C NMR of Compound 4a



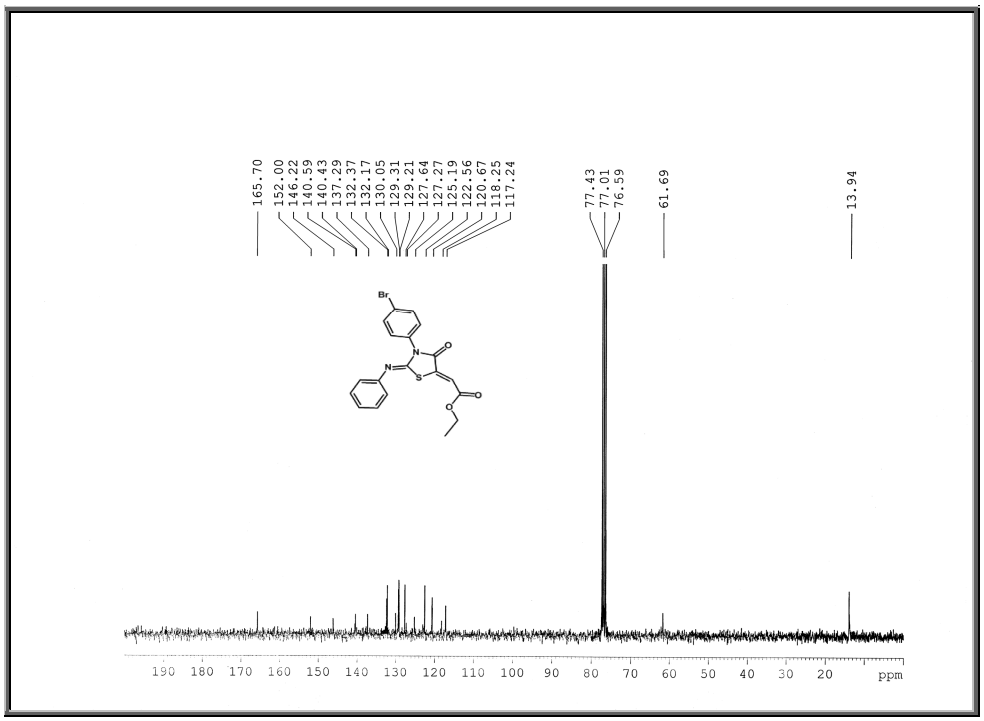
[1] H NMR of Compound 4b



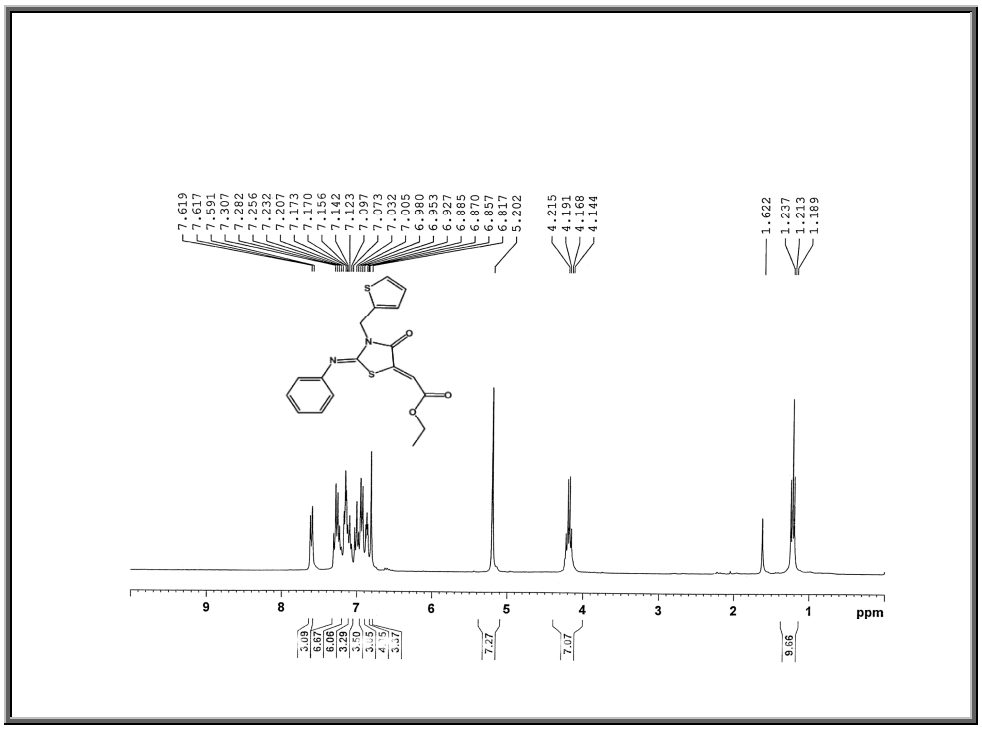
[13]C NMR of Compound 4b



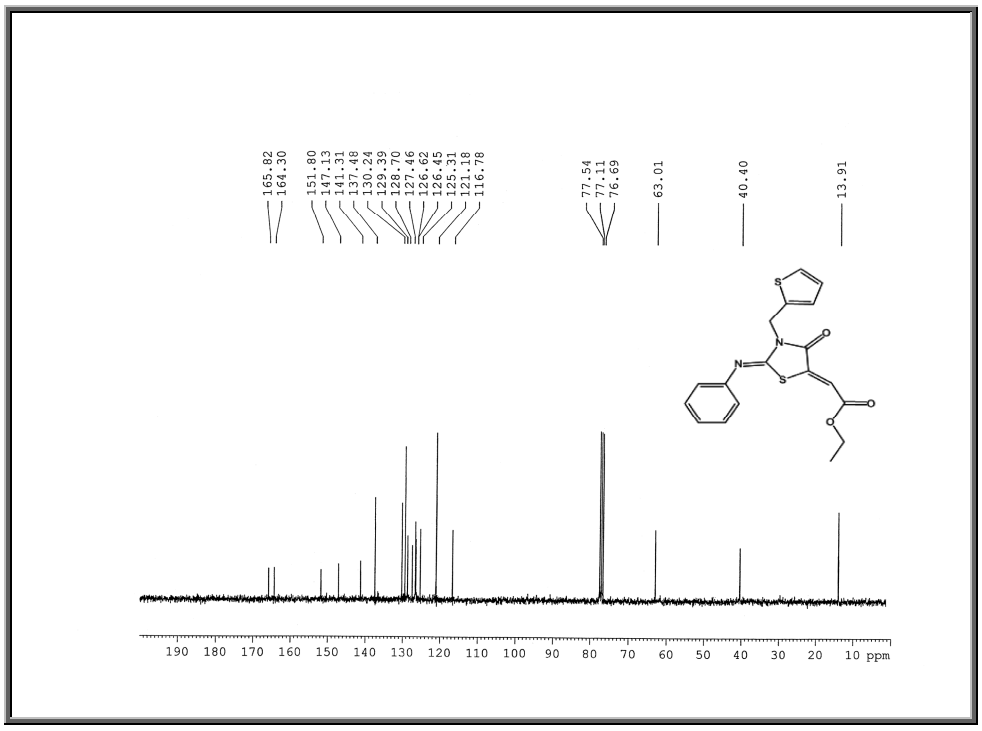
^{1}H NMR of Compound 4c



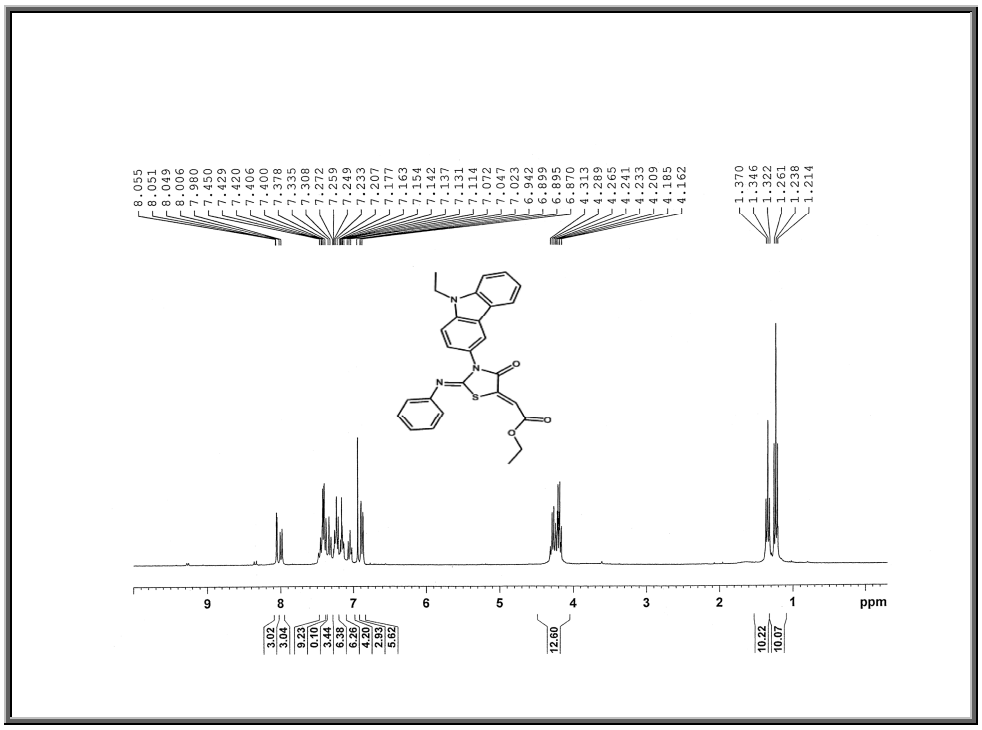
^{13}C NMR of Compound 4c



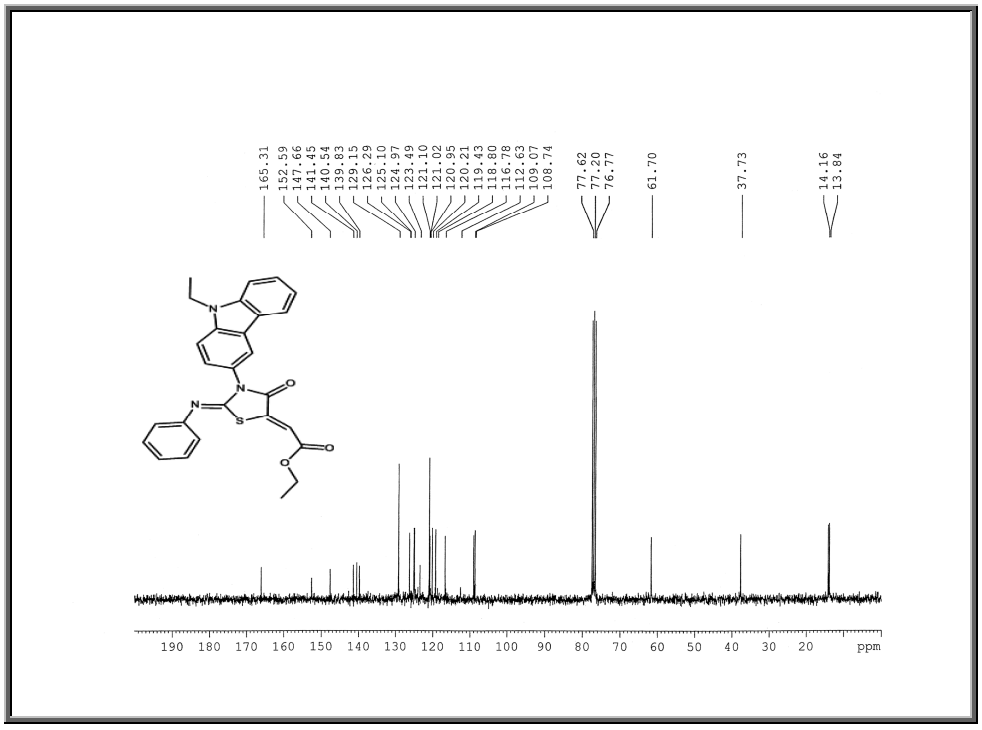
^{1}H NMR of Compound 4d



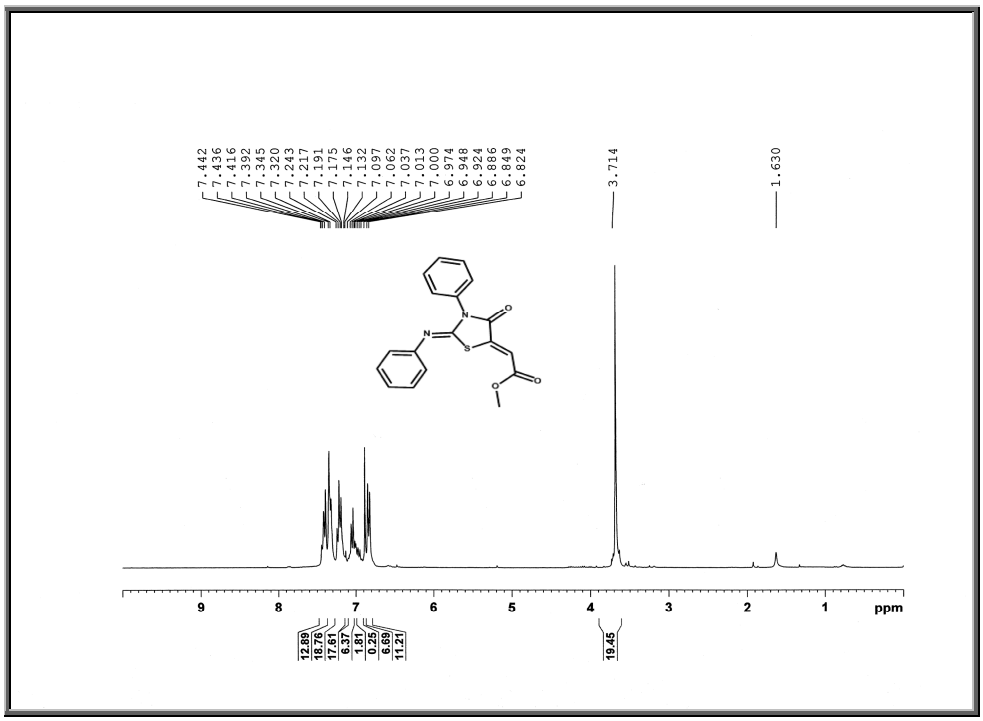
^{13}C NMR of Compound 4d



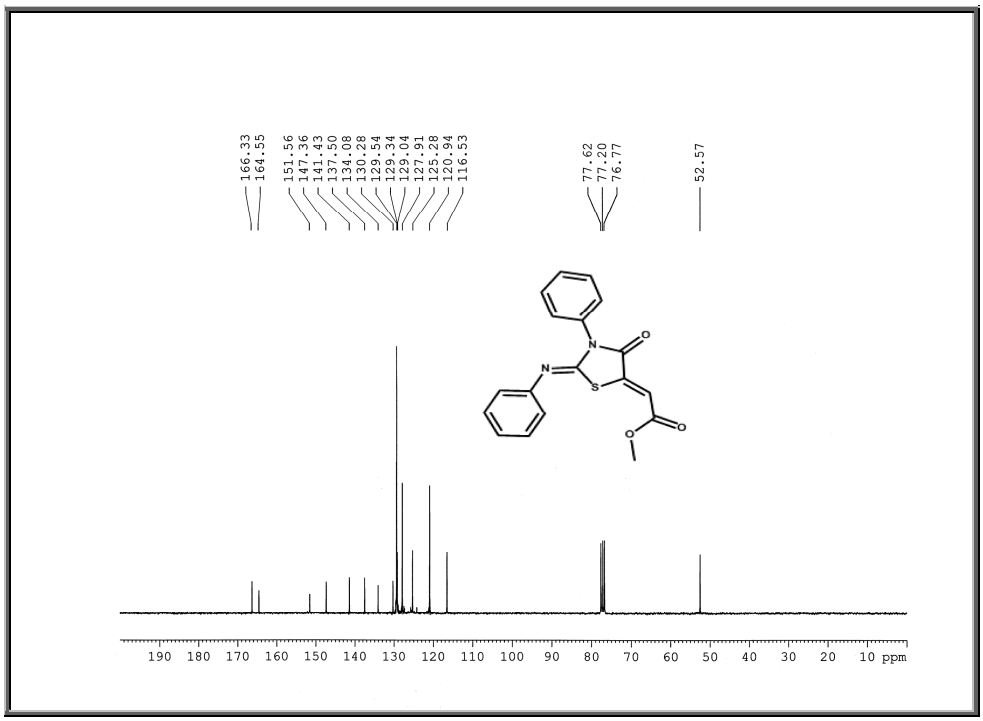
^{1}H NMR of Compound 4e



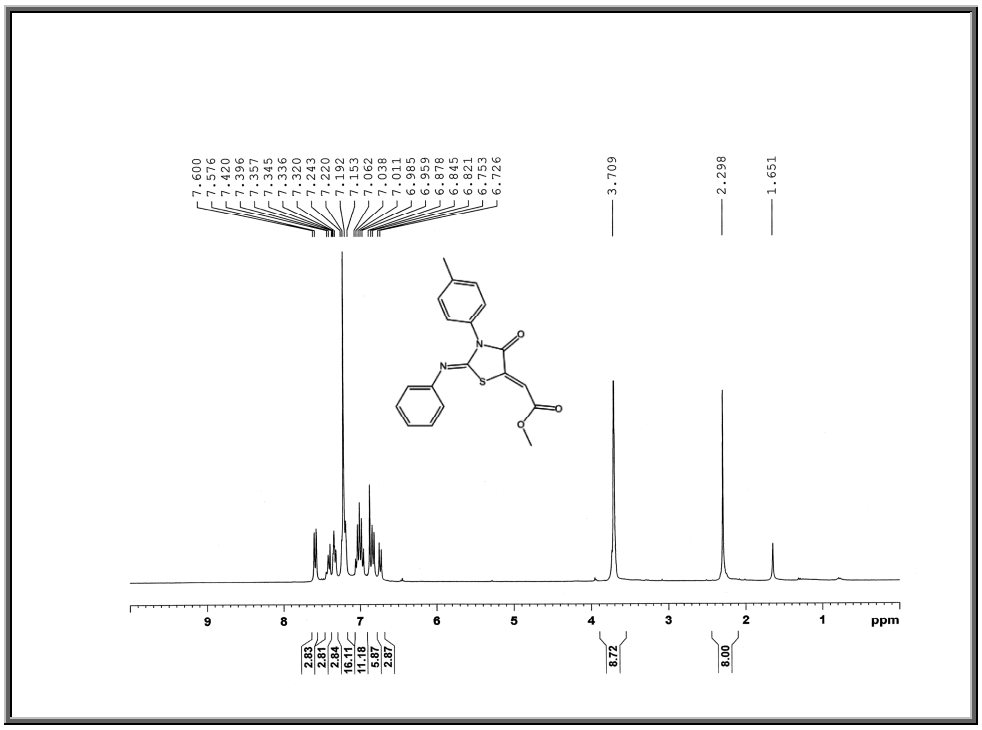
^{13}C NMR of Compound 4e



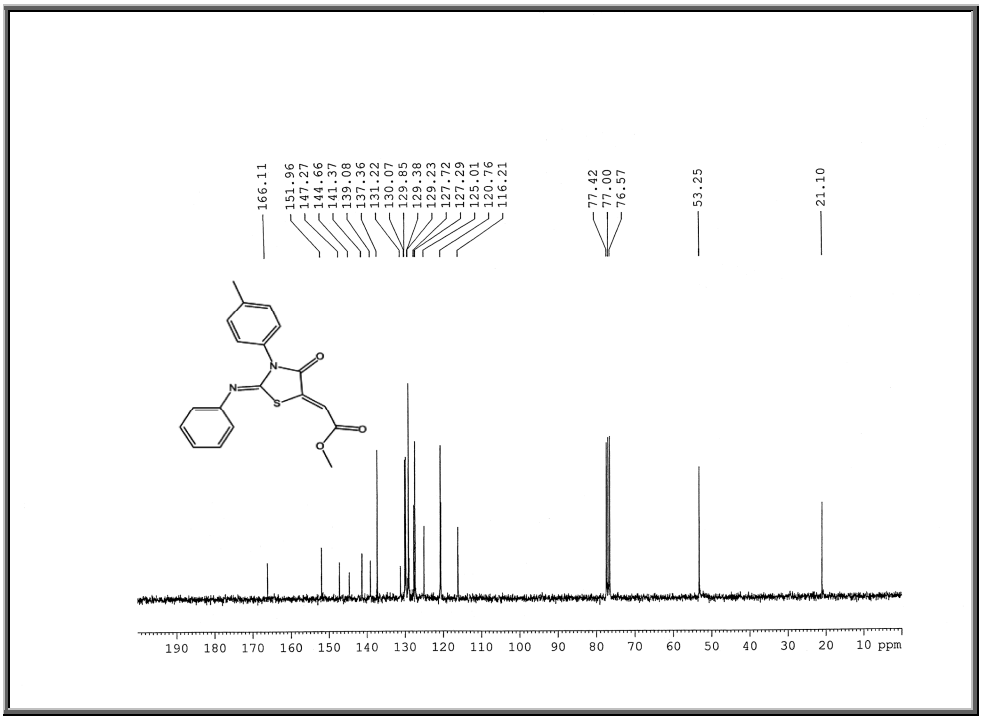
^{1}H NMR of Compound 4f



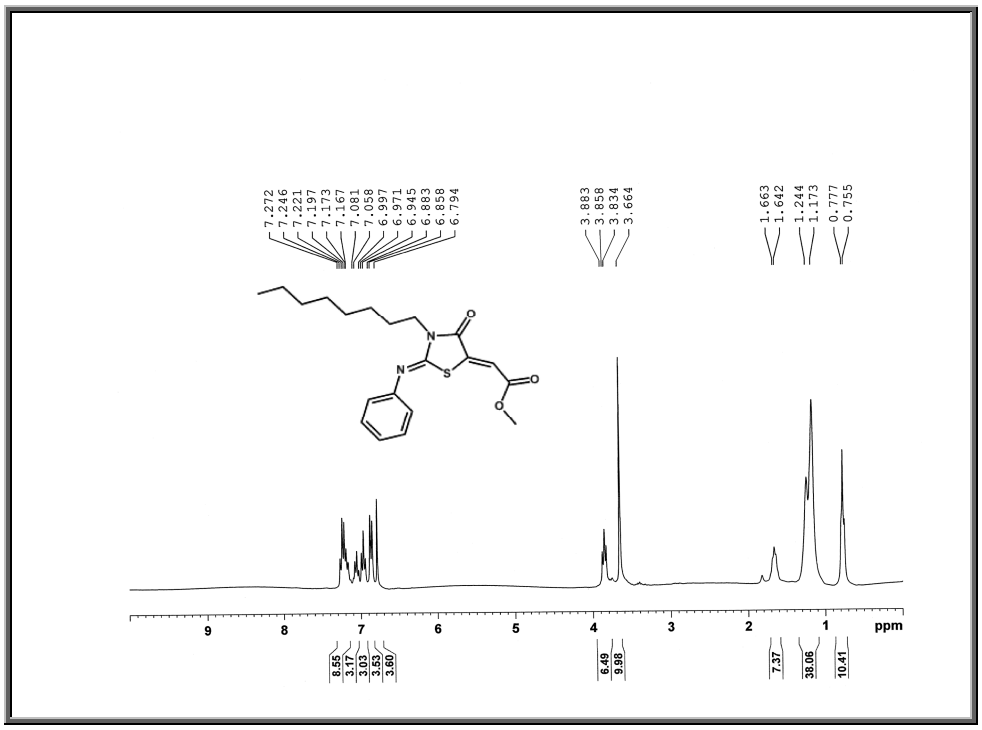
^{13}C NMR of Compound 4f



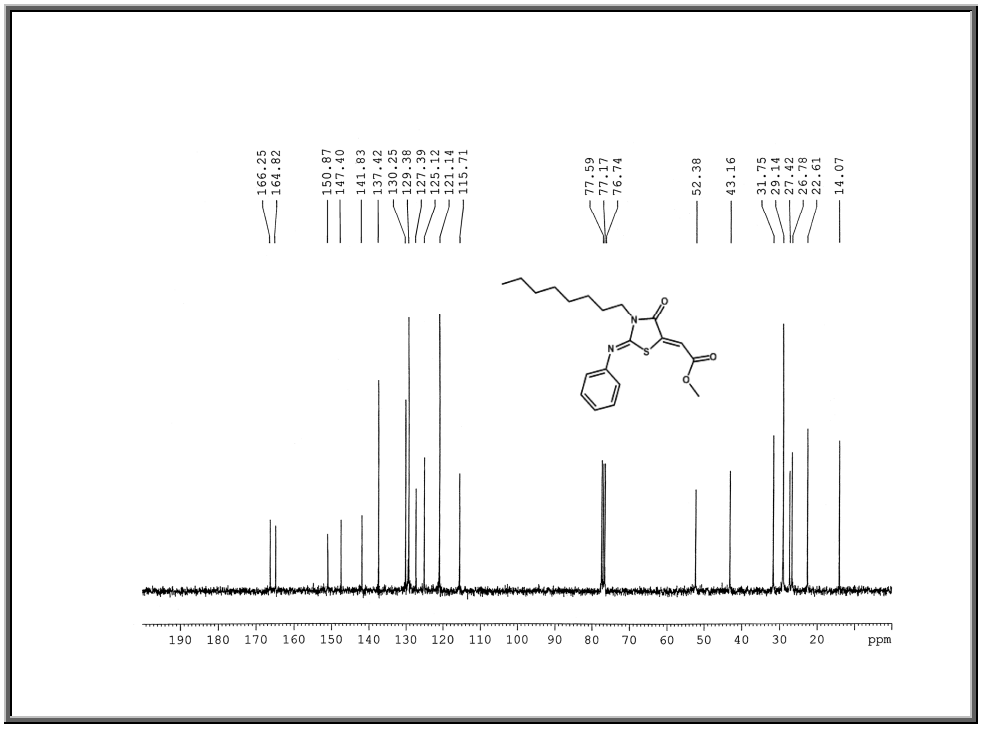
^{1}H NMR of Compound 4g



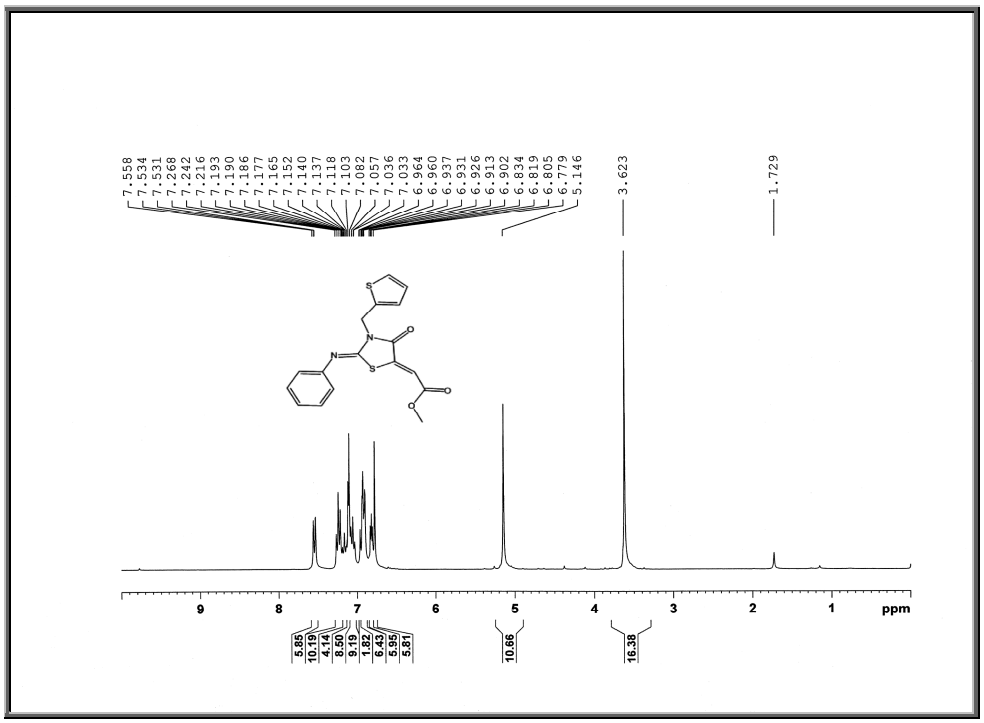
^{13}C NMR of Compound 4g



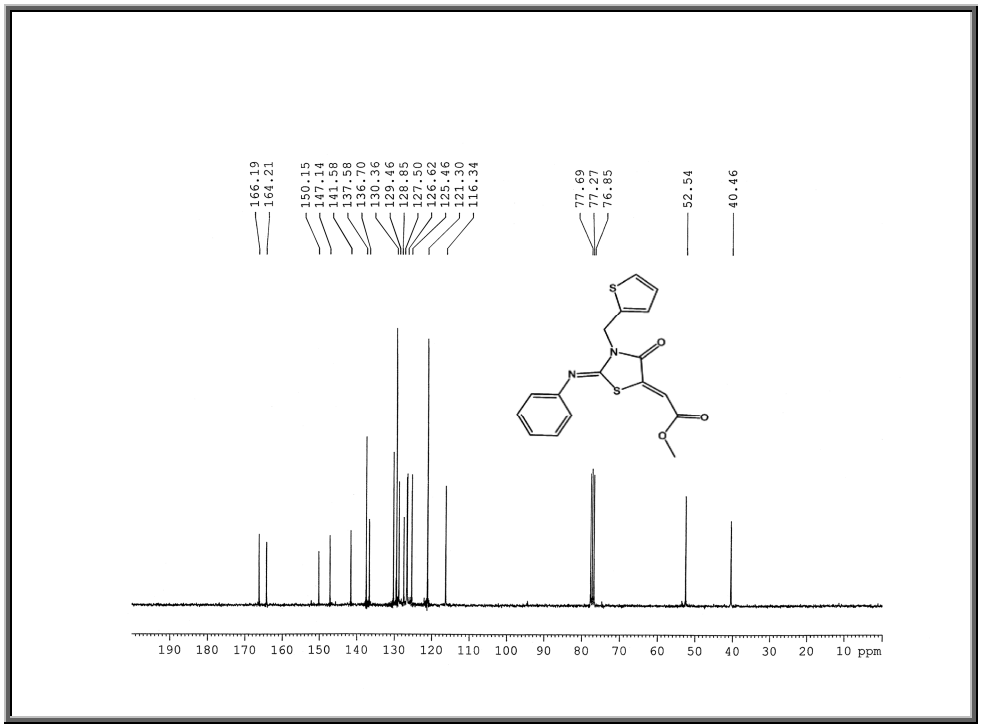
^{1}H NMR of Compound 4h



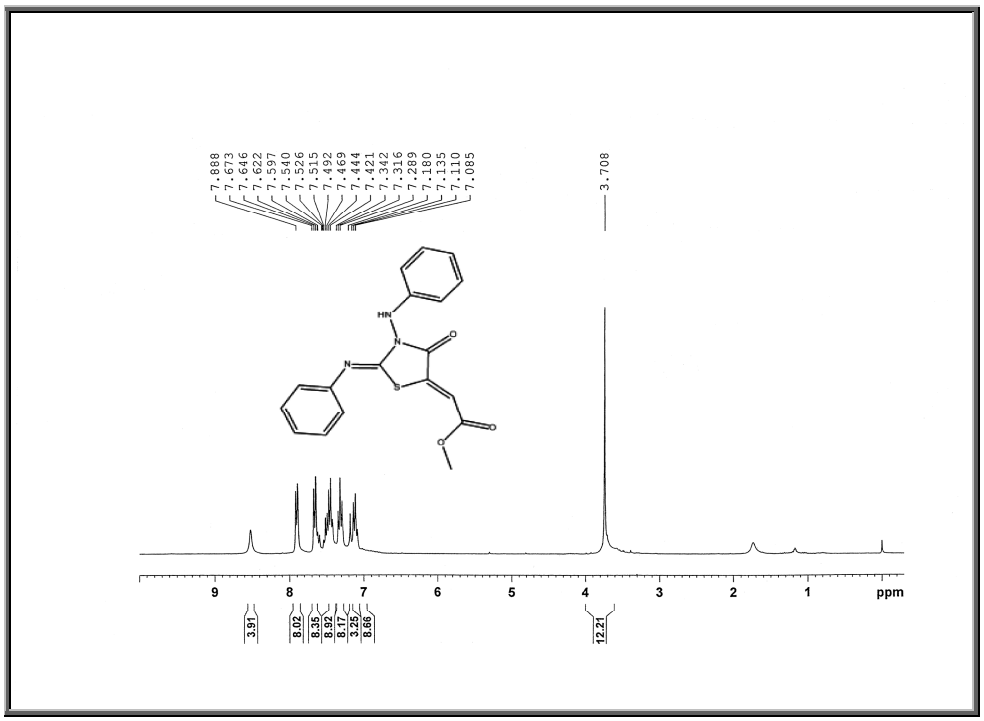
^{13}C NMR of Compound 4h



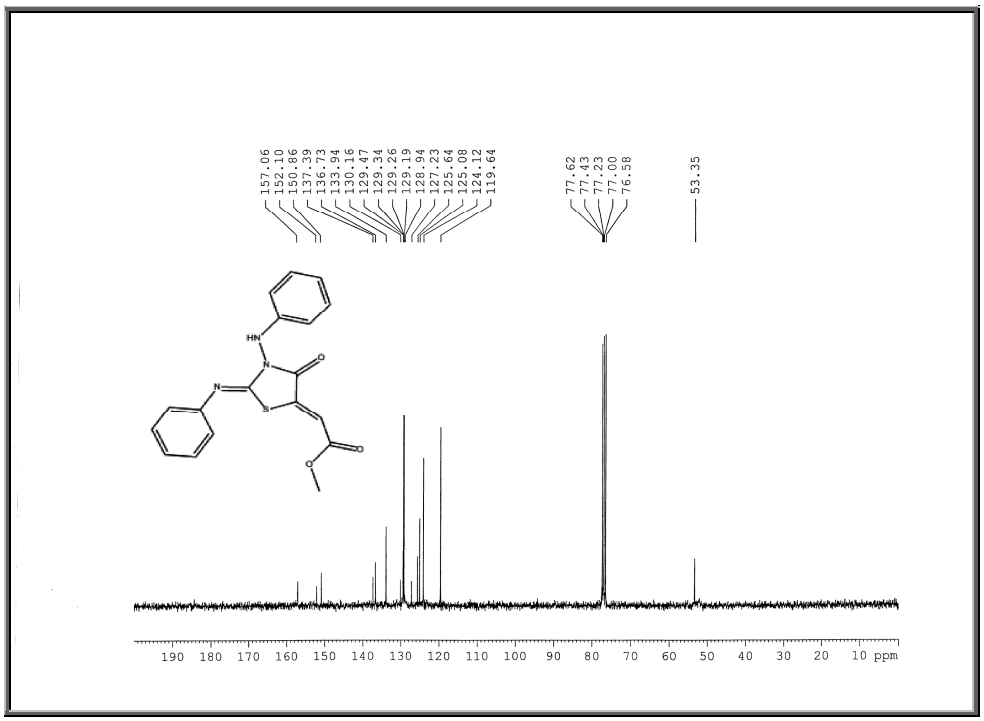
^{1}H NMR of Compound 4i



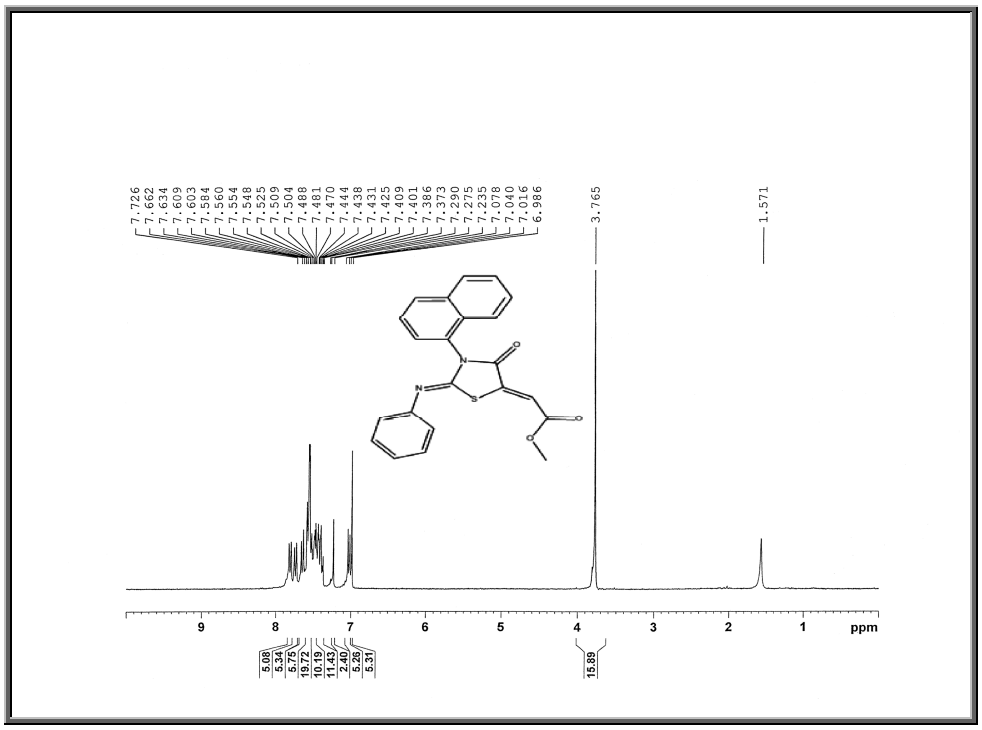
^{13}C NMR of Compound 4i



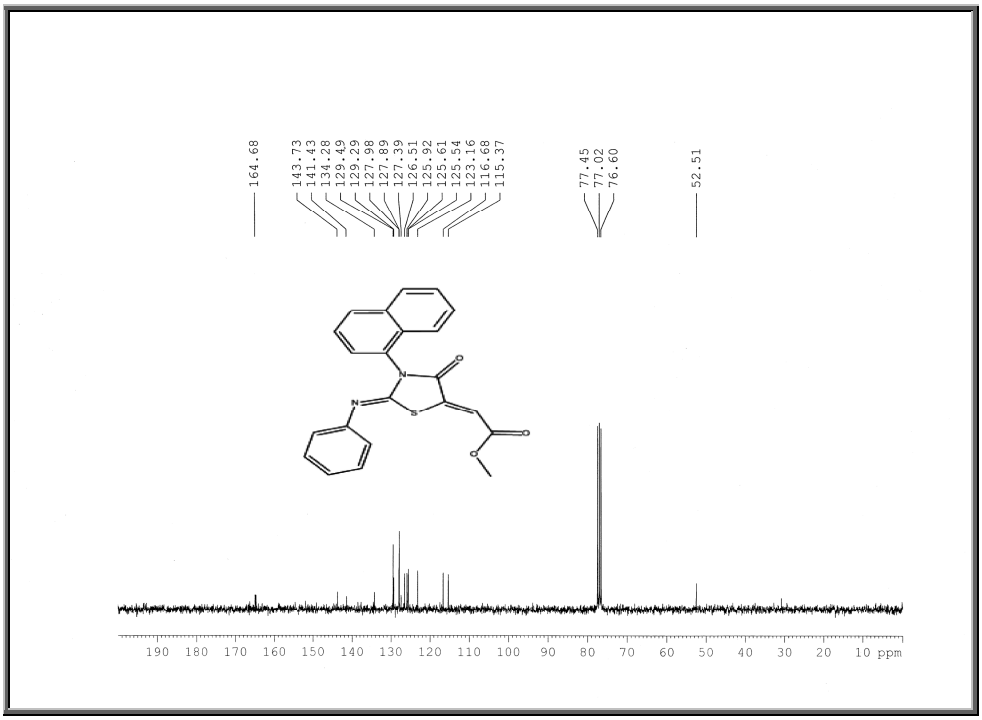
^{1}H NMR of Compound 4j



^{13}C NMR of Compound 4j



^{1}H NMR of Compound 4k



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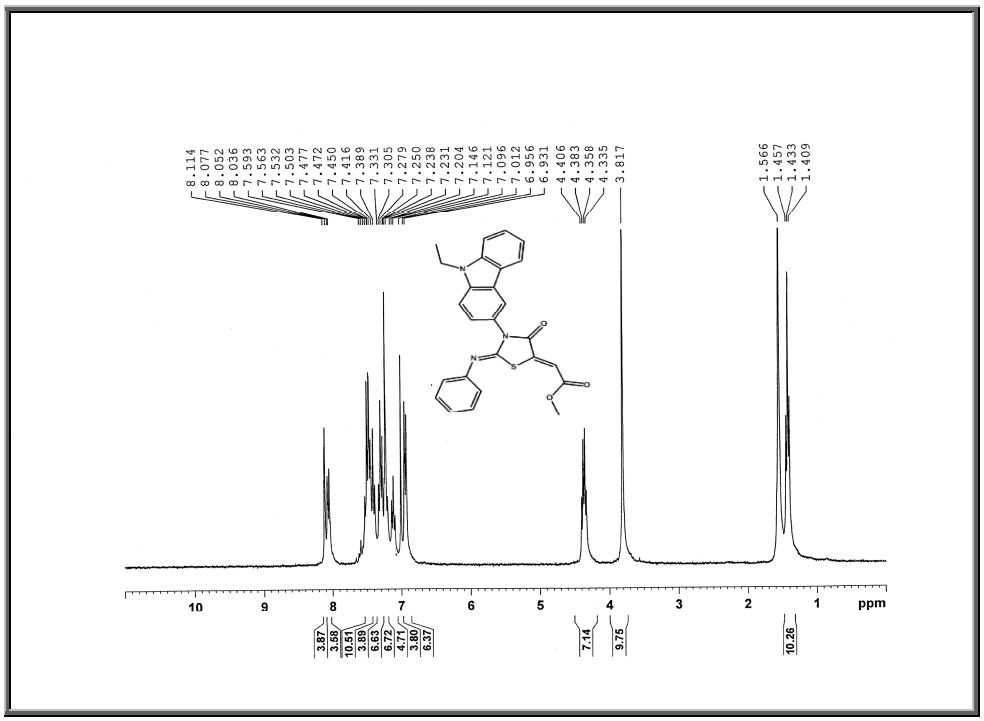
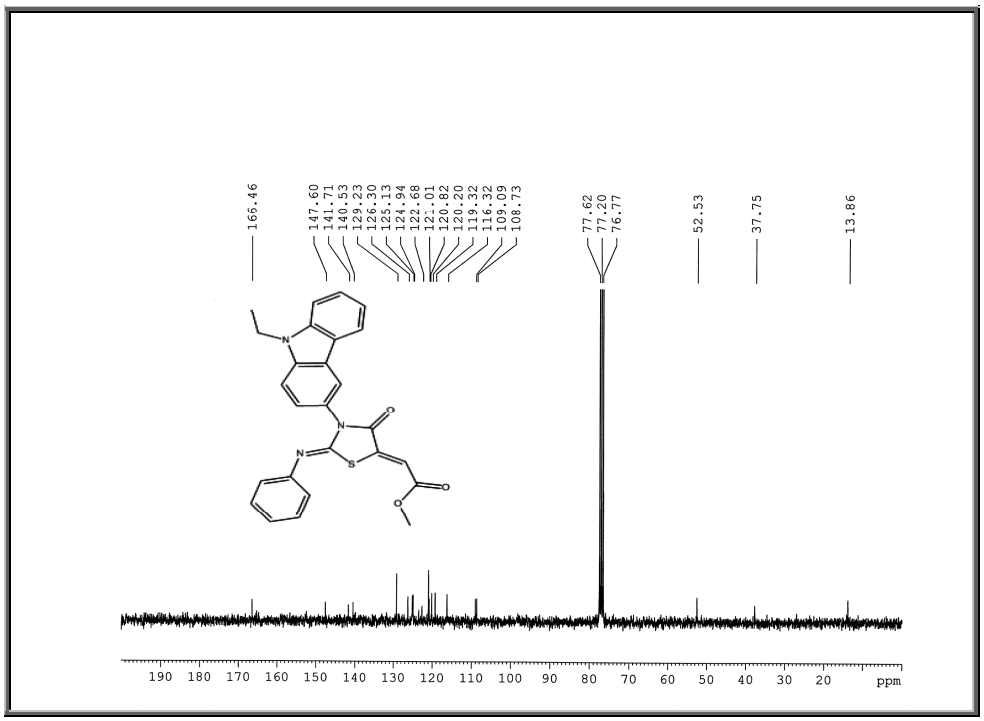


^{1}H NMR of Compound 4l



^{13}C NMR of Compound 4l