Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Base free synthesis of iron oxide supported on boron nitride for the construction of highly functionalized pyrans and spirooxindoles

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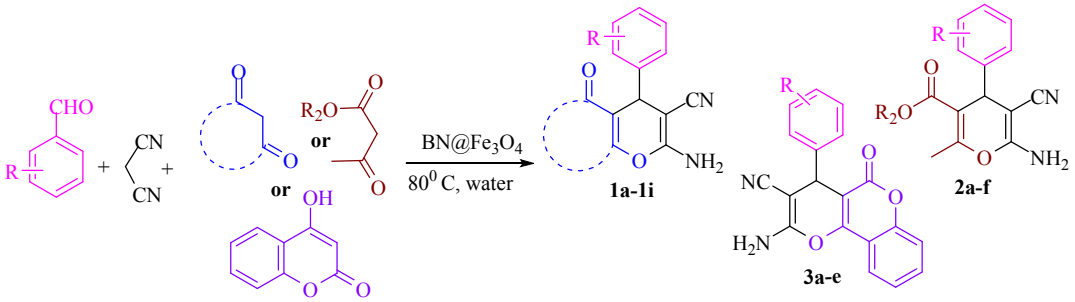
General

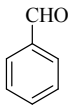
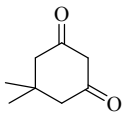
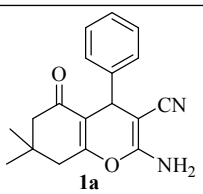
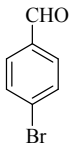
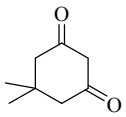
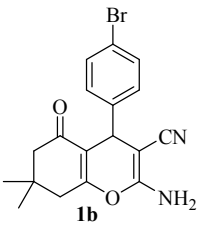
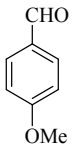
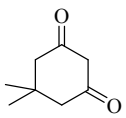
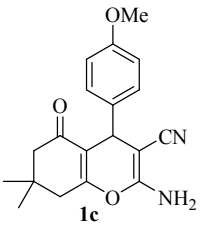
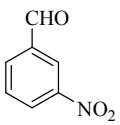
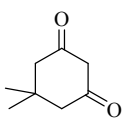
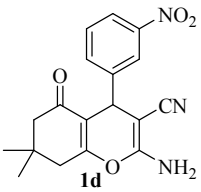
All reagents were purchased either from Sigma or Alfa Aesar. IR spectra were recorded in KBr on a Shimadzu IR Afinity I or in UATR mode on a Perkin Elmer, Spectrum-400. SEM images were obtained from a Hitachi S-4800 microscope at an operating voltage of 15Kv. The sample was coated with platinum for effectual imaging before being charged. X-ray powder diffraction study was carried out on a Rigaku X-Ray diffractometer at a voltage of 35 Kv using Cu Kα radiations (λ=0.15418 nm) at scanning rate of 1.00°/minute in the 2θ range 10-80°. BET measurement was performed using Smart Instruments; model no- Smart Sorb 92/93. Melting points were recorded on a SRS-EZ-Melt melting point apparatus and are uncorrected. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker 400 MHz and 500 MHz spectrometer in $CDCl_3$ or DMSO-d^6 using TMS as an internal reference and chemicals shifts are reported in parts per million (ppm). ^{1}H NMR Spectra are reported in the order: multiplicity as s (singlet), d (doublet), t (triplet), m (multiplet), brs (broad singlet), coupling constant (*J* value) in hertz (Hz) and no of protons. Elemental analyses were carried out in a Perkin Elmer 2400 automatic CHN analyzer or Elementer Vario EL III.

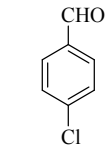
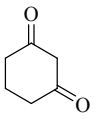
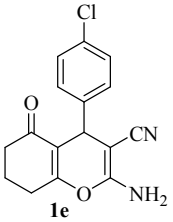
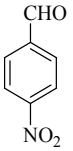
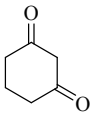
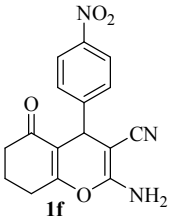
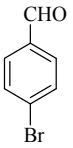
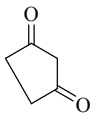
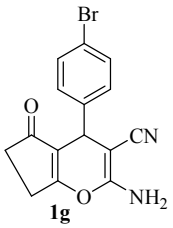
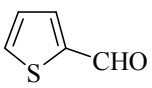
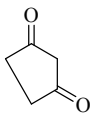
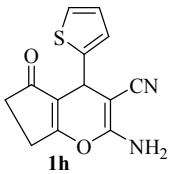
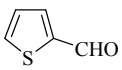
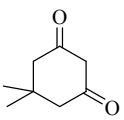
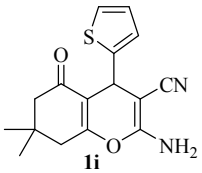
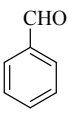
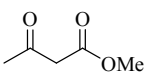
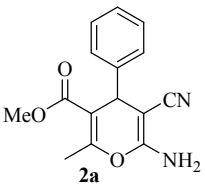
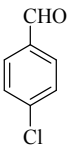
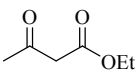
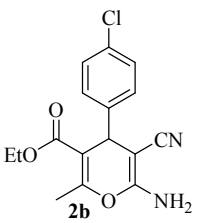
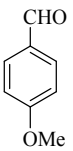
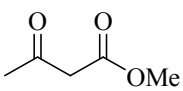
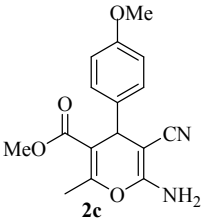
General Procedure for Multicomponent reaction using BN@Fe_3O_4

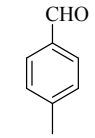
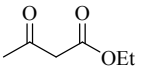
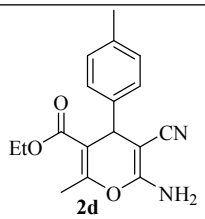
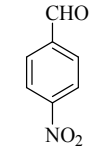
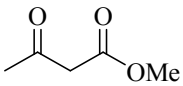
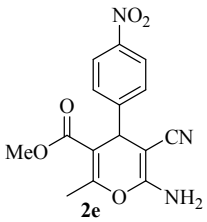
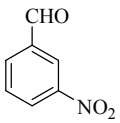
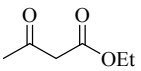
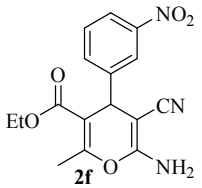
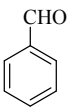
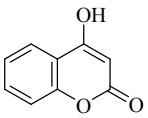
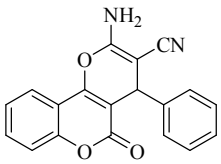
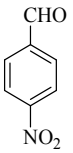
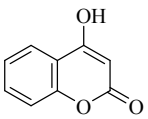
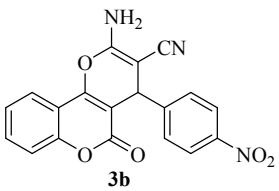
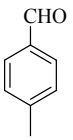
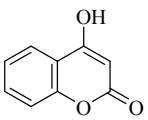
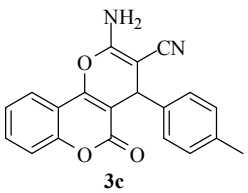
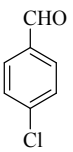
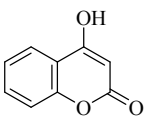
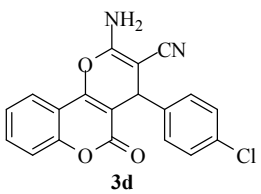
Experimental procedure for the synthesis of highly functionalised pyran andsSpirooxindole derivatives: To malononitrile (1.1 mmol) dissolved in water (3 mL) was added an aldehyde/isatin (1.0 mmol) followed by BN@Fe_3O_4 (15mg) and active methylenic diketo compound (1.0mmol) (dimidone or 4-hydroxy coumarin or cycloalkan-1,3-dione or ethyl acetoacetate/methyl acetoacetate). The reaction mixture was stirred at 80° C. The progress of the reaction was monitored by TLC and after completion of the reaction the solid precipitate was filtered off and dissolved in ethyl acetate and was filtered again to separate the catalyst. Product was collected under reduce pressure using ethyl acetate or CH_2Cl_2. All the products were characterised using NMR, IR and melting point analysis.

Table S1. BN@Fe_3O_4 catalyzed synthesis of pyran derivatives with aldehydes, malononitrile and cycloalkane-1,3-dione (**1a-i**)[a] or 1,3-diketoesters (**2a-f**)[a] or 4-hydroxycoumarine (**3a-e**)[a]



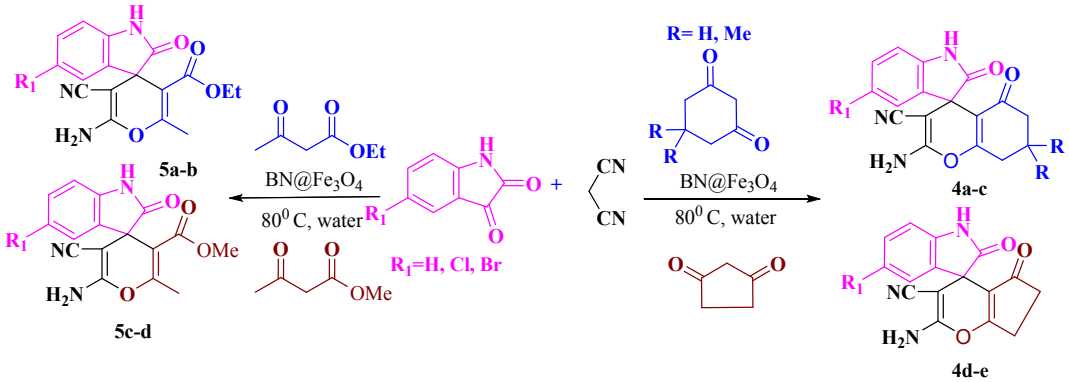
Run	Aldehyde	Diketones/ 4-hydroxy coumarine	Product	Time (min)	Yield[b] (%)	CAS No
01			 **1a**	10	97 92[c]	915297-78-8
02			 **1b**	10	95	107753-01-5
03			 **1c**	10	93	129354-36-5
04			 **1d**	15	91	144036-36-2

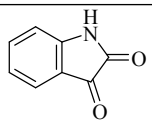
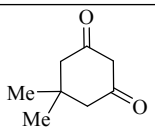
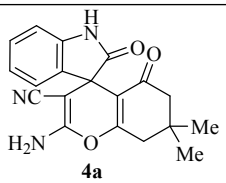
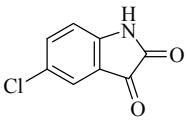
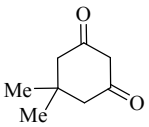
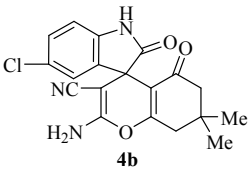
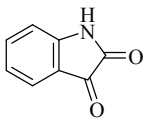
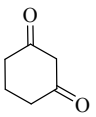
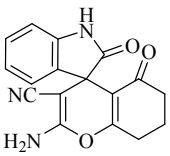
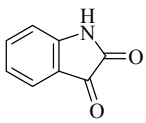
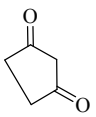
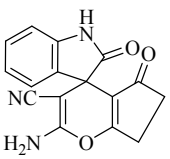
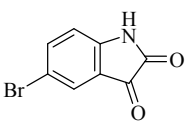
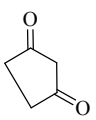
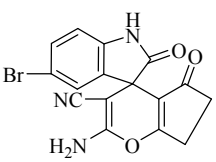
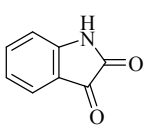
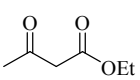
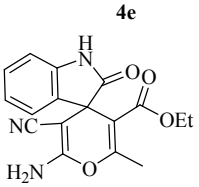
05			 **1e**	10	92	107752-92-1
06			 **1f**	15	90	156176-90-8
07			 **1g**	15	89	1099640-03-5
08			 **1h**	20	86	1266549-91-0
09			 **1i**	15	88	153790-54-6
10			 **2a**	15	95 91[c]	176106-06-2
11			 **2b**	15	94	89809-77-8
12			 **2c**	15	93	176106-12-0

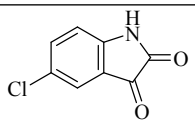
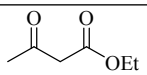
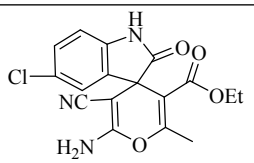
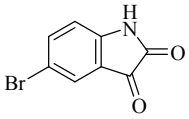
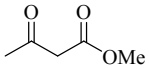
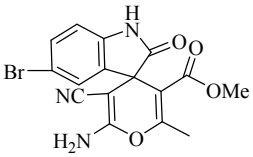
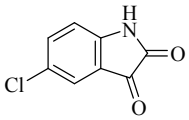
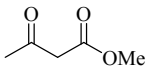
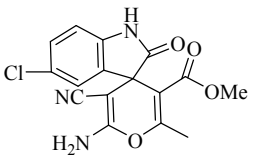
13			 **2d**	15	94	89809-75-6
14			 **2e**	20	92	300587-72-8
15			 **2f**	20	90	72568-54-8
16			 **3a**	20	95 90[c]	96767-93-0
17			 **3b**	25	90	177028-91-0
18			 **3c**	20	92	177028-90-9
19			 **3d**	10	94	177028-89-6

[a] [a]Reaction conditions: Aldehyde (1.0 mmol), malononitrile (1.1mmol) and cyclic diketones/ 1,3-diketoesters (1.0 mmol) or 4-hydroxycoumarine in 3 ml water at 80° C, [b]Isolated yield, [c]Yield after 5[th] cycle.

Table S2. $BN@Fe_3O_4$ catalyzed synthesis of highly functionalized spirooxindole with isatin, malononitrile and cycloalkane-1,3-dione (**4a-e**)[a] or 1,3-diketoesters (**5a-d**)[a]

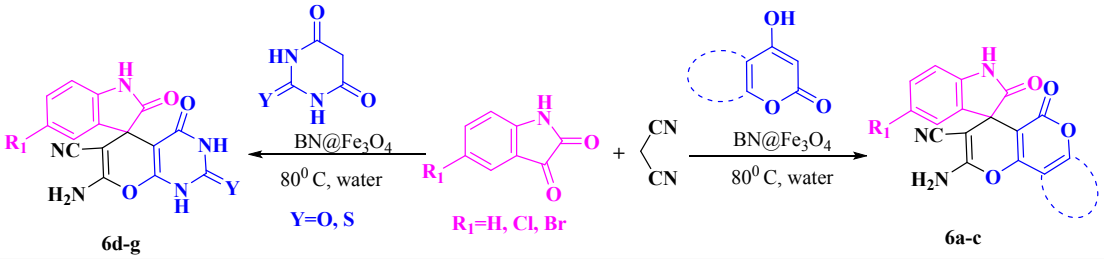


Run	Isatin	Active Methylene	Diketones	Product	Time (min)	Yield[b] (%)	CAS No
01				 **4a**	30	92 88[c]	119771-51-6
02				 **4b**	30	91	303039-26-1
03				 **4c**	30	90	74647-54-4
04				 **4d**	45	88	1206598-84-6
05				 **4e**	45	87	1217902-67-4
06				 **5a**	60	93 89[c]	74647-49-7

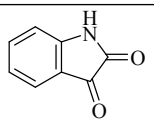
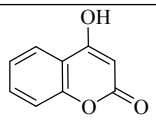
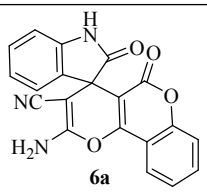
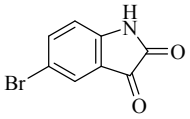
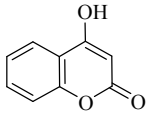
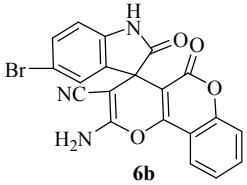
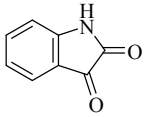
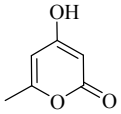
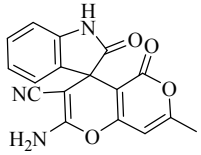
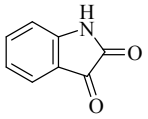
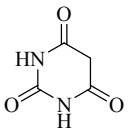
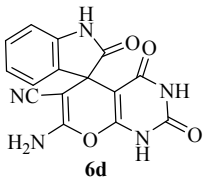
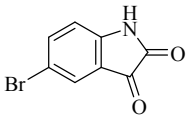
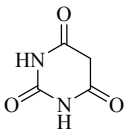
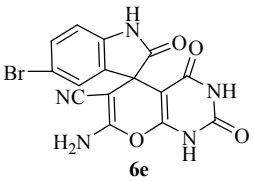
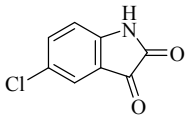
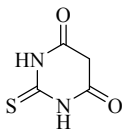
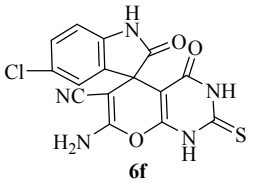
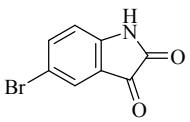
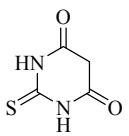
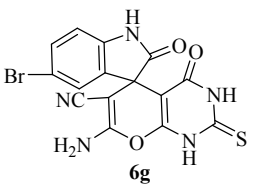
07				 **5b**	60	88	313382-04-6
08				 **5c**	60	90	329716-42-9
09				 **5d**	60	89	313382-08-0

[a]Reaction conditions: Isatin derivatives (1.0 mmol), malononitrile (1.1 mmol) and cyclic-1,3-diketone or 1,3-diketoesters (1.0 mmol) in 3 ml water under 80° C, [b]Isolated yield, [c]Yield after 5th cycle

Table S3. $BN@Fe_3O_4$ catalyzed synthesis of highly functionalized spirooxindole with isatin, malononitrile and 4-hydroxy-derivatives or barbituric acid or 2-thiobarbituric (**6a-g**)[a]

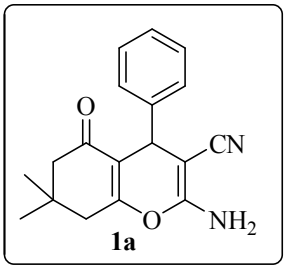


6d-g **6a-c**

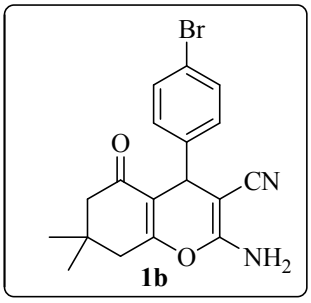
Run	Isatin	4-hydroxy Derivatives or barbituric/ thiobarbituric acid	Product	Time (min)	Yield[b] (%)	CAS No
01			 **6a**	45	88 84[c]	126115-65-9
02			 **6b**	45	86	313381-87-2
03			 **6c**	60	85	331950-46-0
04			 **6d**	45	88	74647-56-6
05			 **6e**	45	86	413575-36-7
06			 **6f**	60	90	1796569-42-0
07			 **6g**	60	90	1226674-87-8

[a]Reaction conditions: Isatin derivatives (1.0 mmol), malononitrile (1.1 mmol) and 4-hydroxy derivatives or barbituric acid/ thiobarbituric acid (1.0 mmol) in 3 ml water under 80 °C, [b]Isolated yield, [c]Yield after 5[th] cycle.

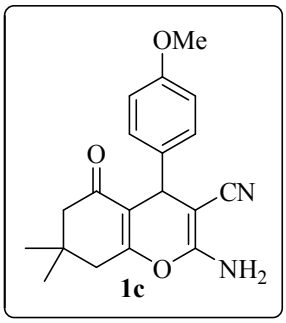
Spectral data of all compounds

1. 

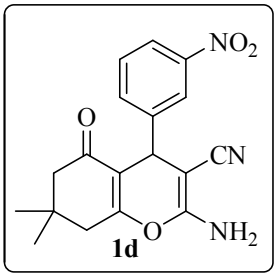
1a ***2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (1a)*****:** Yield 97%. m.p. 232-234°C. IR ν_{max} (KBr): 3398, 3324, 3210, 2963, 2199, 1679, 1662, 1602, 1467, 1370, 1034 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.04 (s, 3H), 1.11 (s, 3H), 2.21-2.23 (m, 2H), 2.45 (brs, 2H), 4.40 (s, 1H), 4.57 (brs, 2H), 7.17-7.31 (m, 5H) ppm.

2. 

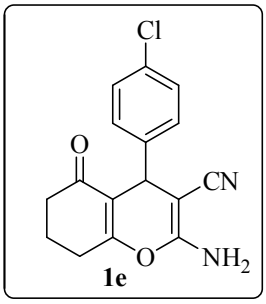
1b ***2-amino-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile(1b):*** Yield 95%. Solid, m.p. 204-206°C. IR ν_{max} (KBr): 3395, 3321, 3210, 2965, 2193, 1684, 1662, 1608, 1408, 1369, 1040 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.03 (s, 3H), 1.11 (s, 3H), 2.21-2.23 (m, 2H), 2.45 (brs, 2H), 4.37 (s, 1H), 4.54 (brs, 2H), 7.12 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H) ppm.

3. 

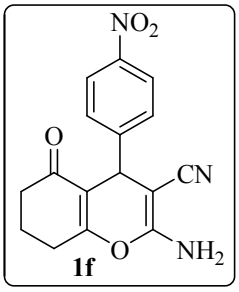
1c ***2-amino-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (1c):*** Yield 93%. Solid, m.p. 199°C. IR ν_{max} (KBr): 3379, 3307, 3185, 2965, 2188, 1690, 1646, 1607, 1464, 1365, 1034 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.03 (s, 3H), 1.11 (s, 3H), 2.21-2.23 (m, 2H), 2.44 (s, 2H), 3.76 (s. 3H), 4.36 (s, 1H), 6.82 (d, J = 8.8 Hz, 2H), 6.87 (brs, 2H), 7.15 (d, J = 8.8 Hz, 2H) ppm.

4. 

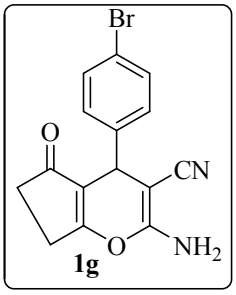
1d ***2-amino-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (1d):*** Yield 91%. Solid, m.p. 215°C. IR ν_{max} (KBr): 3472, 3334, 3185, 2961, 2194, 1690, 1664, 1596, 1469, 1373, 1042 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.98 (s, 3H), 1.08 (s, 3H), 2.08-2.22 (m, 2H), 2.44-2.45 (m, 2H), 4.71 (brs, 2H), 5.18 (s, 1H), 7.30-7.36 (m, 2H), 7.48-7.54 (m, 1H), 7.79 (d, *J* = 8.4 Hz, 1H) ppm.

5. 

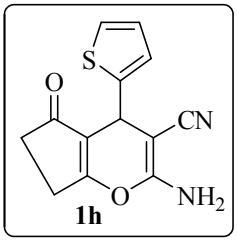
1e ***2-amino-4-(4-chlorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (1e):*** Yield 92%. Solid, m.p. 240° C. IR ν_{max} (KBr): 3415, 3334, 3215, 2196, 1685, 1650, 1601, 1247, 1003 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 1.90-2.05 (m, 2H), 2.25-2.31 (m, 2H), 2.59-2.65 (m, 2H), 4.24 (s, 1H), 6.84 (brs, 2H), 7.17-7.20 (m, 2H), 7.25-7.29 (m, 2H) ppm.

6. 

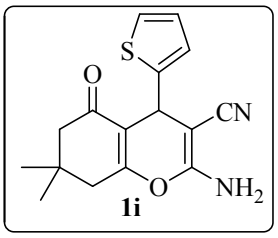
1f ***2-amino-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (1f):*** Yield 90%. Solid, m.p. 235°C. IR ν_{max} (KBr): 3417, 3336, 3217, 2196, 1682, 1651, 1601, 1362, 1006 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 1.97-2.09 (m, 2H), 2.31-2.35 (m, 2H), 2.62-2.69 (m, 2H), 4.42 (s, 1H), 6.79 (brs, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 8.13 (d, *J* = 6.8 Hz, 2H) ppm.

7. 

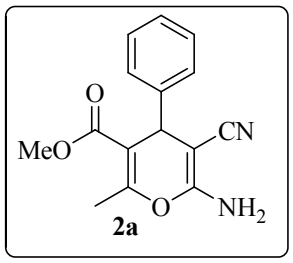
1g ***2-amino-4-(4-bromophenyl)-5-oxo-4,5,6,7-tetrahydrocyclopenta[b]pyran-3-carbonitrile (1g):*** Yield 89%. Solid, m.p. 218°C. IR ν_{max} (KBr): 3409, 3325, 3210, 2195, 1673, 1639, 1599, 1369, 1011 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 2.43-2.45 (m, 2H), 2.72-2.80 (m, 2H), 4.24 (s, 1H), 6.86 (brs, 2H), 7.15-7.18 (m, 2H), 7.40-7.44 (m, 2H) ppm.

8. 

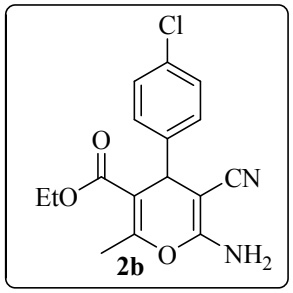
1h ***2-amino-5-oxo-4-(thiophen-2-yl)-4,5,6,7-tetrahydrocyclopenta[b]pyran-3-carbonitrile (1h):*** Yield 86%. Solid, m.p. 218°C. IR ν_{max} (KBr): 3383, 3316, 3202, 2192, 1665, 1647, 1592, 1376, 1094 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 2.41-2.46 (m, 2H), 2.67-2.77 (m, 2H), 4.57 (s, 1H), 6.85 (brs, 2H), 6.89-6.92 (m, 1H), 6.96 (d, *J* = 2.8 Hz, 1H), 7.20 (d, *J* = 2.8 Hz, 1H) ppm.

9. 

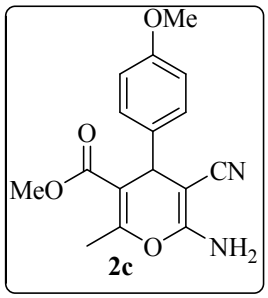
1i ***2-amino-7,7-dimethyl-5-oxo-4-(thiophen-2-yl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (1i):*** Yield 88%. Solid, m.p. 210°C. IR ν_{max} (KBr): 3382, 3248, 2959, 2199, 1680, 1660, 1603, 1375, 1213, 1036 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 1.03 (s, 3H), 1.10 (s, 3H), 2.12-2.29 (m, 2H), 2.40-2.55 (m, 2H), 4.60 (s, 1H), 6.69 (brs, 2H), 6.86-6.88 (m, 2H), 7.16 (d, *J* = 3.6 Hz, 1H) ppm.

10. 

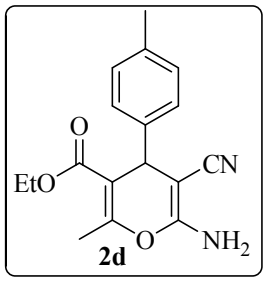
2a ***methyl 6-amino-5-cyano-2-methyl-4-phenyl-4H-pyran-3-carboxylate (2a):*** Yield 95%. Solid, m.p. 175°C. IR ν_{max} (KBr): 3416, 3331, 3202, 2952, 2199, 1711, 1672, 1607, 1408, 1334, 1266, 1179, 1062 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$: δ = 2.46 (s, 3H), 3.63 (s, 3H), 4.53-4.59 (brs, 3H), 7.28-7.31 (m, 2H), 7.36-7.39 (m, 3H) ppm.

11. 

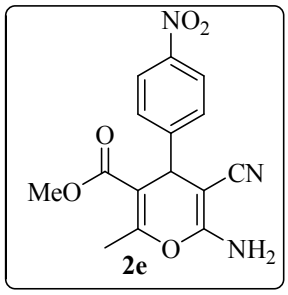
2b ***ethyl 6-amino-4-(4-chlorophenyl)-5-cyano-2-methyl-4H-pyran-3-carboxylate (2b):*** Yield 94%. Solid, m.p. 170°C. IR ν_{max} (KBr): 3422, 3319, 3206, 2981, 2197, 1717, 1646, 1608, 1489, 1338, 1273, 1177, 1121 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.12 (t, *J* = 7.2 Hz, 3H), 2.38 (s, 3H), 4.00-4.07 (m, 2H), 4.43 (s, 1H), 4.50 (s, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.27-7.29 (m, 2H) ppm.

12. 

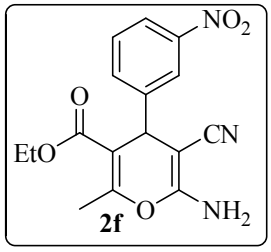
2c ***methyl 6-amino-5-cyano-4-(4-methoxyphenyl)-2-methyl-4H-pyran-3-carboxylate (2c):*** Yield 93%. Solid, m.p. 152° C. IR ν_{max} (KBr): 3425, 3336, 3207, 2951, 2196, 1725, 1676, 1607, 1409, 1342, 1262, 1177, 1059 cm-1. 1H NMR (400 MHz, CDCl3): δ= 2.35 (s, 3H), 3.59 (s, 3H), 3.78 (s, 3H), 4.39 (s, 1H), 4.48 (s, 2H), 6.82 (d, *J* = 9.2 Hz, 2H), 7.11 (d, *J* = 9.2 Hz, 2H) ppm.

13. 

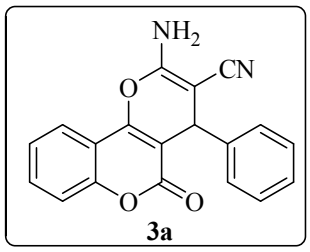
2d ***ethyl 6-amino-5-cyano-2-methyl-4-p-tolyl-4H-pyran-3-carboxylate (2d):*** Yield 94%. Solid, m.p. 180°C. IR ν_{max} (KBr): 3412, 3331, 3227, 2981, 2198, 1707, 1689, 1610, 1331, 1262, 1179, 1062 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.12 (t, *J* = 7.2 Hz, 3H), 2.31 (s, 3H), 2.36 (s, 3H), 4.00-4.07 (m, 2H), 4.41 (s, 1H), 4.43 (s, 2H), 7.06-7.09 (m, 4H) ppm.

14. 

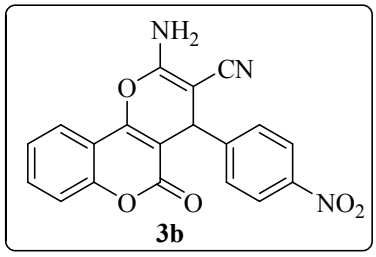
2e ***methyl 6-amino-5-cyano-2-methyl-4-(4-nitrophenyl)-4H-pyran-3-carboxylate (2e):*** Yield 92%. Solid, m.p. 165–167°C. IR ν_{max} (KBr): 3399, 3328, 3202, 2956, 2204, 1707, 1672, 1644, 1521, 1340, 1274, 1178, 1057 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 2.34 (s, 3H), 3.57 (s, 3H), 4.32 (s, 1H), 6.57 (s, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H) ppm.

15. 

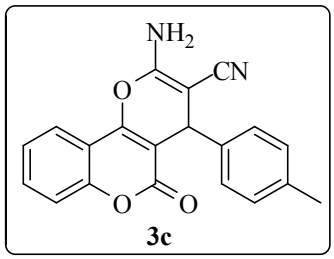
2f ***ethyl 6-amino-5-cyano-2-methyl-4-(3-nitrophenyl)-4H-pyran-3-carboxylate (2f):*** Yield 90%. Solid, m.p. 170°C. IR ν_{max} (KBr): 3404, 3328, 3221, 2989, 2194, 1702, 1645, 1603, 1440, 1347, 1270, 1179, 1061 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.12 (t, *J* = 6.8 Hz, 3H), 2.42 (s, 3H), 4.04-4.08 (m, 2H), 4.58 (s, 1H), 4.62 (s, 2H), 7.49-7.58 (m, 2H), 8.05-8.08 (m, 2H) ppm.

16. 

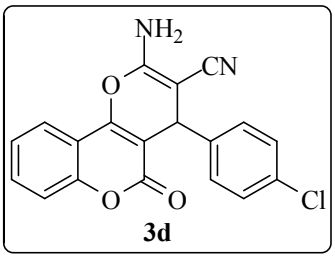
3a ***2-amino-5-oxo-4-phenyl-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (3a):*** Yield 95%. Solid, m.p. 270°C. IR ν_{max} (KBr): 3377, 3286, 3179, 2198, 1708, 1676, 1605, 1381, 1211, 1058 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 4.49 (s, 1H), 7.09 (s, 2H), 7.27-7.31 (m, 4H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.95-7.96 (m, 2H) ppm.

17. 

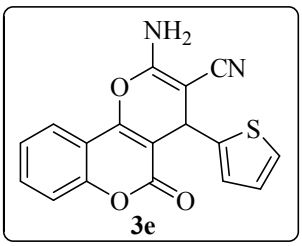
3b ***2-amino-4-(4-nitrophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (3b):*** Yield 90%. Solid, m.p. 260°C. IR ν_{max} (KBr): 3482, 3429, 3370, 3334, 2195, 1718, 1670, 1607, 1377, 1055 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): *δ* = 4.69 (s, 1H), 7.47-7.53 (m, 2H), 7.55 (s, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.72-7.76 (m, 1H), 7.91-7.93 (m, 1H), 8.19 (d, *J* = 9.0 Hz, 2H) ppm.

18. 

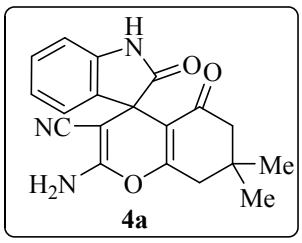
3c ***2-amino-5-oxo-4-p-tolyl-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (3c):*** Yield 92%. Solid, m.p. 256°C. IR ν_{max} (KBr): 3387, 3294, 3192, 3036, 2225, 1715, 1672, 1588, 1352, 1095 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 2.45 (s, 3H), 4.45 (s, 1H), 7.09 (s, 2H), 7.34-7.38 (m, 4H), 7.59-7.64 (m, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.97-8.00 (m, 1H) ppm.

19. 

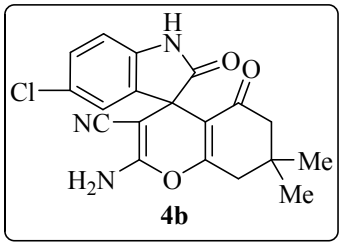
3d ***2-amino-4-(4-chlorophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (3d):*** Yield 94%. Solid, m.p. 260°C. IR ν_{max} (KBr): 3382, 3311, 3259, 3189, 2193, 1715, 1676, 1611, 1377, 1961 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 4.51 (s, 1H), 7.12 (s, 2H), 7.29 (brs, 4H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 1H) ppm.

20. 

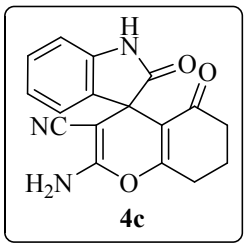
3e ***2-amino-5-oxo-4-(thiophen-2-yl)-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (3e):*** Yield 89%. Solid, m.p. 220°C. IR ν_{max} (KBr): 3367, 3280, 3174, 2200, 1710, 1669, 1636, 1601, 1383, 1360, 1171, 1056 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 4.83 (s, 1H), 6.93-6.95 (m, 1H), 7.04 (d, *J* = 3.2, 1H), 7.32 (d, *J* = 4.0 Hz, 1H), 7.39-7.45 (m, 4H), 7.65-7.69 (m, 1H), 7.89-7.91 (m, 1H) ppm.

21. 

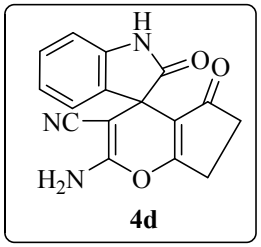
4a ***2-amino-7,7-dimethyl-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carbonitrile (4a):*** Yield 92%. Solid, m.p. 304-306°C (305-307°C). IR ν_{max} (Neat): 3376, 3313, 3139, 2959, 2191, 1719, 1682, 1654, 1622, 1604, 1471, 1391, 1348, 1326, 1298, 1222, 1165, 1054 cm^{-1}. ^1H NMR (400 MHz, DMSO-d^6): *δ* =1.02 (s, 3H), 1.05 (s, 3H), 2.06-2.18 (m, 2H), 2.48-2.58 (m, 2H), 6.79 (d, *J* = 7.6, 1H), 6.88 (t, *J* = 7.2, 1H), 6.95 (d, *J* = 7.2, 1H), 7.11 (s, 2H), 7.12-7.14 (m, 1H), 10.37 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d^6+$CDCl_3$) : 27.1, 27.7, 31.8, 46.8, 50.1, 57.5, 78.9, 109.2, 110.8, 117.2, 121.5, 122.8, 127.9, 134.3, 141.9, 158.7, 163.9, 178.0, 194.5 ppm.

22. 

4b ***2-amino-5'-chloro-7,7-dimethyl-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carbonitrile (4b):*** Yield 91%. Solid, m.p. 293-295°C (294-296°C). IR ν_{max} (Neat): 3282, 3150, 2957, 2192, 1723, 1679, 1652, 1602, 1477, 1349, 1328, 1224, 1166, 1057 cm^{-1}. ^1H NMR (400 MHz, DMSO-d^6): δ = 1.04 (s, 3H), 1.09 (s, 3H), 2.48-2.60 (m, 2H), 3.53 (s, 2H), 6.80 (d, *J* = 7.2, 1H), 7.05 (d, *J* = 6.8, 1H), 7.13-7.16 (m, 1H), 7.23 (s, 2H),10.52 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d^6+$CDCl_3$) : 27.3, 27.5, 31.9, 47.1, 49.9, 56.7, 78.5, 110.3, 110.5, 117.1, 123.1, 125.7, 127.9, 136.2, 140.9, 158.8, 164.3, 177.7, 194.8 ppm.

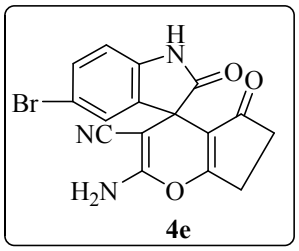
23. 

4c ***2-amino-2',5-dioxo-5,6,7,8-tetrahydrospiro[chromene-4,3'-indoline]-3-carbonitrile (4c):*** Yield 90%. Solid, m.p. 310-312°C (312-313°C). IR ν_{max} (Neat): 3367, 3156, 2954, 2196, 2008, 1711, 1682, 1656, 1607, 1479, 1465, 1352, 1334, 1313, 1256, 1218, 1196, 1078 cm^{-1}. ^1H NMR (400 MHz, DMSO-d^6): δ = 1.91-1.97 (m, 2H), 2.18-2.26 (m, 2H), 2.63-2.67 (m, 2H), 6.78 (d, *J* = 7.2, 1H), 6.88 (t, *J* = 7.2, 1H), 6.98 (d, *J* = 7.2, 1H), 7.10-7.12 (m, 1H), 7.13 (s, 2H), 10.38 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d^6+$CDCl_3$) : 19.7, 26.8, 36.4, 46.9, 57.5, 109.1, 111.9, 117.3, 121.5, 123.0, 127.9, 134.4, 141.9, 158.6, 165.8, 178.1, 194.7 ppm.

24. 

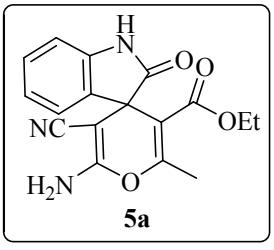
4d ***2-amino-2',5-dioxo-6,7-dihydro-5H-spiro[cyclopenta[b]pyran-4,3'-indoline]-3-carbonitrile (4d):*** Yield 88%. Solid, m.p. >300°C (>300°C). IR ν_{max} (Neat): 3346, 3229, 3140, 2192, 1716, 1660, 1596, 1470, 1344, 1232, 1218, 1015 cm^{-1}. ^1H NMR (400 MHz, DMSO-d^6): δ = 2.27-2.31 (m, 2H), 2.73-2.75 (m, 2H), 6.77 (d,

J = 7.2, 1H), 6.85-6.89 (m, 1H), 6.97 (d, *J* = 6.8, 1H), 7.10-7.14 (m, 1H), 7.37 (s, 2H), 10.49 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d^6+$CDCl_3$) : 24.9, 33.1, 46.6, 56.5, 109.5, 114.9, 117.4, 121.9, 124.1, 128.7, 131.9, 141.9, 160.5, 176.9, 177.3, 199.5 ppm.



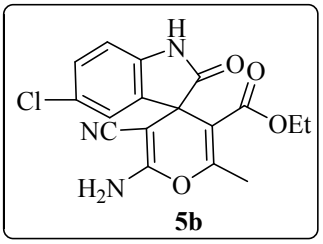
4e

25. ***2-amino-5'-bromo-2',5-dioxo-6,7-dihydro-5H-spiro[cyclopenta[b]pyran-4,3'-indoline]-3-carbonitrile (4e):*** Yield 87%. Solid, m.p. 299-301°C. IR ν_{max} (Neat): 3288, 3360, 3193, 2922, 2191, 1879, 1704, 1674, 1635, 1589, 1477, 1339, 1234, 1033 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d^6): δ = 2.39-2.51 (m, 2H), 2.80-2.81 (m, 2H), 6.81 (d, *J* = 8.0, 1H), 7.33-7.40 (m, 2H), 7.59 (brs, 2H), 10.73 (s, 1H)ppm. ^{13}C NMR (100 MHz, DMSO-d^6) : 24.9, 33.2, 46.7, 55.8, 111.4, 113.7, 114.2, 117.4, 127.1, 131.6, 134.4, 141.3, 160.7, 176.4, 177.9, 199.9 ppm. Elemental Analysis for $C_{16}H_{10}BrN_3O_3$ calculated C, 51.63; H, 2.71; N, 11.29; obtained C, 51.59; H, 2.72; N, 11.32.

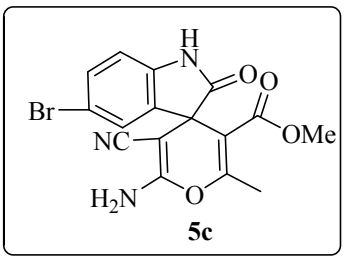


5a

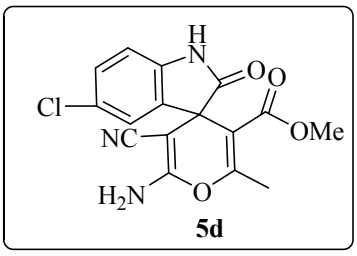
26. ***ethyl 2'-amino-3'-cyano-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (5a):*** Yield 93%. Solid, m.p. 260-262°C (258-260°C). IR ν_{max} (Neat): 3481**,** 3277, 3156, 2981, 2844, 2191, 1720, 1698, 1674, 1618, 1595, 1470, 1381, 1287, 1211, 1069, 1033 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d^6): δ = 0.78 (t, *J*= 7.0, 3H), 2.31 (s, 3H), 3.72-3.81 (m, 2H), 6.79 (d, *J*= 7.5, 1H), 6.91-6.94 (m, 1H), 7.04-7.05 (m, 1H), 7.12 (brs, 2H), 7.16-7.17 (m, 1H), 10.38 (s, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d^6) : 14.6, 19.8, 49.7, 56.3, 64.3, 105.7, 114.5, 118.2, 123.2, 130.6, 134.7, 138.8, 147.2, 157.9, 159.1, 163.7, 180.3 ppm.

27. 

5b ***ethyl 2'-amino-5-chloro-3'-cyano-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (5b):*** Yield 88%. Solid, m.p. 301-303°C (>260°C). IR ν_{max} (Neat): 3374, 3147, 2945, 2188, 1721, 1670, 1602, 1478, 1420, 1374, 1287, 1173, 1071 cm^{-1}. ^1H NMR (400 MHz, DMSO-d^6): δ = 0.71-0.84 (m, 3H), 2.31 (s, 3H), 3.79-3.83 (m, 2H), 6.81-6.82 (m, 1H), 7.17-7.24 (m, 4H), 10.54 (s, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d^6) : 13.1, 18.8, 49.4, 56.0, 60.4, 101.6, 103.8, 117.4, 130.6, 136.8, 141.0, 147.2, 158.9, 159.5, 163.7, 164.4, 178.4 ppm.

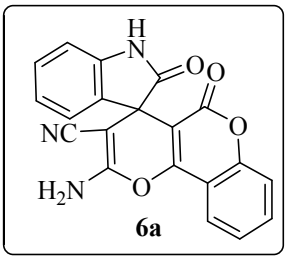
28. 

5c ***methyl 2'-amino-5-bromo-3'-cyano-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (5c):*** Yield 90%. Solid, m.p. 240-242°C. IR ν_{max} (Neat): 3356, 3235, 3180, 2192, 1976, 1702, 1645, 1592, 1478, 1422, 1379, 1298, 1215, 1175, 1053 cm^{-1}. ^1H NMR (400 MHz, DMSO-d^6): δ = 2.20 (s, 3H), 2.36 (s, 3H), 6.74-6.76 (m, 1H), 7.11-7.22 (m, 3H), 7.31-7.33 (m, 1H), 10.51 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d^6) : 19.8, 31.5, 49.6, 56.2, 107.4, 111.2, 113.3, 117.3, 125.9, 130.9, 137.1, 141.3, 158.1, 159.0, 160.4, 178.2 ppm. Elemental Analysis for $C_{16}H_{12}BrN_3O_4$ calculated C, 49.25; H, 3.10; N, 10.77; obtained C, 49.24; H, 3.11; N, 10.79.

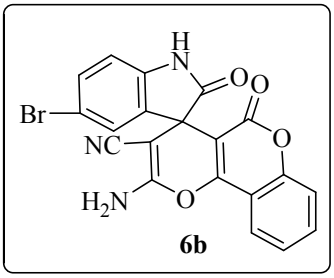
29. 

5d ***methyl 2'-amino-5-chloro-3'-cyano-6'-methyl-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (5d):*** Yield 89%. Solid, m.p. 301-303°C (>260°C). IR ν_{max} (Neat): 3374, 3147, 2945, 2188, 1721, 1670, 1602, 1478, 1420, 1374, 1287, 1173, 1071 cm^{-1}. ^1H NMR (400 MHz, DMSO-d^6): δ = 2.34 (s, 3H),

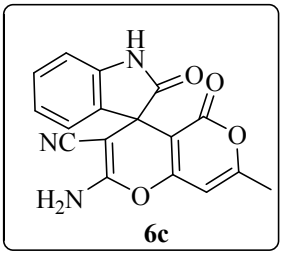
3.37 (s, 3H), 6.82 (d, *J*=8.4, 1H), 7.18-7.25 (m, 4H), 10.56 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d^6) : 19.0, 49.4, 51.5, 55.9, 103.9, 110.7, 117.3, 123.5, 125.7, 128.4, 136.7, 140.8, 158.9, 159.5, 164.9, 178.3 ppm.

30. 

6a ***2'-amino-2,5'-dioxo-5'H-spiro[indoline-3,4'-pyrano[3,2-c]chromene]-3'-carbonitrile (6a):*** Yield 88%. Solid, m.p. 291-293°C (290-291°C). IR ν_{max} (Neat): 3356, 3292, 3195, 2206, 1729, 1708, 1670, 1602, 1471, 1357, 1217, 1168, 1104, 1081 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d^6): δ = 6.82 (d, *J* = 8.0, 1H), 6.90 (t, *J* = 8.5, 1H), 7.16-7.19 (m, 2H), 7.44-7.52 (m, 2H), 7.63 (brs, 2H), 7.73 (t, *J* = 8.5, 1H), 7.91 (t, *J* = 7.5, 1H), 10.65 (s, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d^6) :48.1, 57.5, 101.9, 110.1, 112.9, 117.2, 117.5, 122.6, 123.2, 124.6, 125.5, 129.4, 133.5, 134.2, 142.7, 152.5, 155.6, 158.8, 158.9, 177.7 ppm.

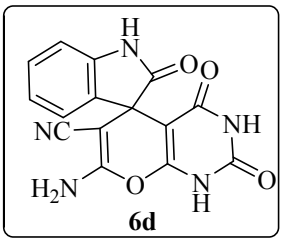
31. 

6b ***2'-amino-5-bromo-2,5'-dioxo-5'H-spiro[indoline-3,4'-pyrano[3,2-c]chromene]-3'-carbonitrile (6b):*** Yield 86%. Solid, m.p. 330-332°C (>300°C). IR ν_{max} (Neat): 3708, 3681, 3317, 3245, 3187, 2923, 2844, 2826, 2199, 1709, 1668, 1604, 1471, 1357, 1219, 1166, 1085, 1055, 1033 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d^6): δ = 6.42-6.44 (m, 2H), 6.58-6.60 (m, 1H), 7.04-7.20 (m, 4H), 7.71 (brs, 2H), 10.94 (s, 1H) ppm.^{13}C NMR (125 MHz, DMSO-d^6) : 48.3, 56.9, 101.3, 111.9, 113.1, 114.3, 117.2, 117.4, 123.3, 125.5, 127.8, 132.2, 134.2, 135.9, 142.0, 152.6, 155.9, 159.0, 159.1, 177.4 ppm.

32. 

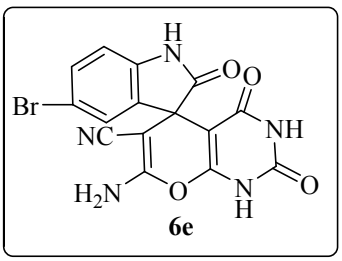
6c

2'-amino-7'-methyl-2,5'-dioxo-5'H-spiro[indoline-3,4'-pyrano[4,3-b]pyran]-3'-carbonitrile (6c): Yield 85%. Solid, m.p. 277-279°C (278-280°C). IR ν_{max} (Neat): 3288, 3133, 2192, 2000, 1728, 1703, 1674, 1609, 1471, 1362, 1348, 1214, 1167, 1046 cm^{-1}. ^1H NMR (500 MHz, DMSO-d^6): δ = 2.20 (s, 3H), 6.32 (s, 1H), 6.78 (d, *J* = 7.5, 1H), 6.89 (t, *J* = 7.5, 1H), 7.06 (d, *J* = 8.0, 1H), 7.15 (t, *J* = 7.5, 1H), 7.41 (brs, 2H), 10.55 (s, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d^6) :19.8, 47.5, 57.4, 98.4, 98.9, 109.9, 117.7, 122.5, 124.4, 129.3, 133.6, 142.7, 159.1, 160.1, 160.5, 164.3, 177.8 ppm.

33. 

6d

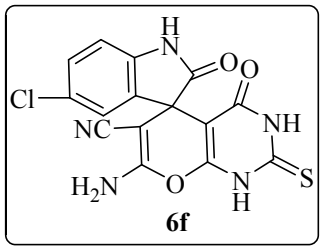
7'-amino-2,2',4'-trioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-d]pyrimidine]-6'-carbonitrile (6d): Yield 88%. Solid, m.p. 270-272°C (275-276°C). IR ν_{max} (Neat): 3353, 3306, 3142, 2829, 2204, 1717, 1694, 1672, 1616, 1536, 1466, 1393, 1338, 1113 cm^{-1}. ^1H NMR (500 MHz, DMSO-d^6): δ = 6.70-6.88 (m, 3H), 7.07-7.13 (m, 2H), 7.30 (brs, 2H), 10.43 (s, 1H), 11.02 (s, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d^6) : 47.2, 58.2, 87.2, 109.8, 117.6, 122.3, 124.3, 128.9, 134.1, 142.6, 150.2, 154.3, 158.9, 162.1, 178.3 ppm.

34. 

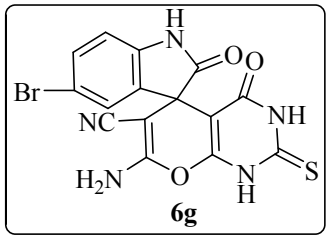
6e

7'-amino-5-bromo-2,2',4'-trioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-d]pyrimidine]-6'-carbonitrile (6e): Yield 86%. Solid, m.p. 222-224°C (220-222°C). IR ν_{max} (Neat): 3708, 3681, 3351, 2973, 2922, 2865, 2844, 2202, 1730, 1689, 1648, 1617, 1540, 1474, 1403, 1340, 1297, 1249, 1215, 1164, 1125, 1054 cm^{-1}. ^1H NMR (500 MHz, DMSO-d^6): δ = 6.74-6.75

(m, 1H), 7.31-7.37 (m, 5H), 10.59 (s, 1H), 10.87 (s, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d^6) : 47.5, 60.3, 86.5, 111.7, 114.1, 117.5, 127.3, 131.6, 136.6, 141.9, 150.2, 154.6, 159.1, 162.2, 178.0 ppm.

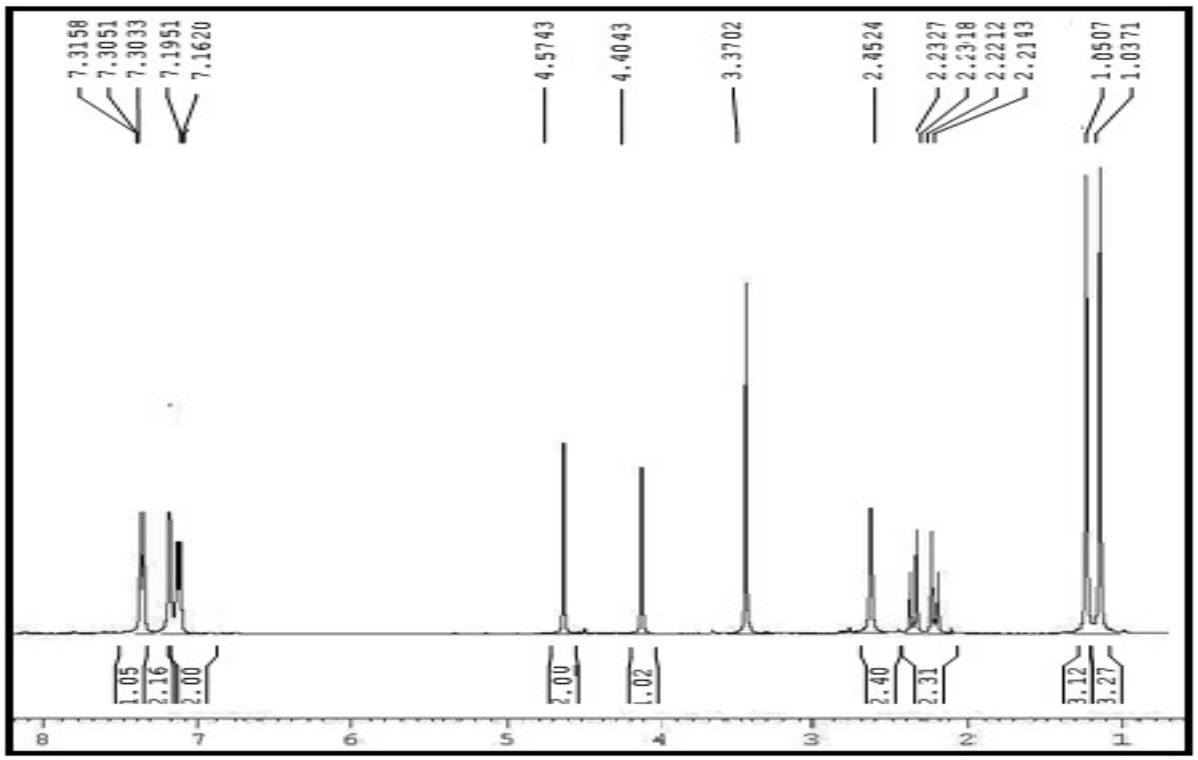
35. 

6f ***7'-amino-5-chloro-2,4'-dioxo-2'-thioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-d]pyrimidine]-6'-carbonitrile (6f):*** Yield 90%. Solid, m.p. 260-262°C. IR ν_{max} (Neat): 3437, 3357, 3267, 3147, 2196, 1673, 1620, 1569, 1497, 1477, 1396, 1339, 1273, 1223, 1175, 1129, 1111, 1068, 1051cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d^6): δ = 6.76 (d, *J*= 7.5, 1H), 7.15-7.21 (m, 3H), 7.31 (brs, 2H), 10.55 (s, 1H), 11.88 (s, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d^6) : 47.7, 56.9, 90.9, 111.2, 117.6, 124.6, 126.3, 128.7, 136.1, 141.6, 155.5, 159.4, 160.5, 175.7, 178.1 ppm. Elemental Analysis for $C_{15}H_8ClN_5O_3S$ calculated C, 48.20; H, 2.16; N, 18.74; obtained C, 48.18; H, 2.13; N, 18.75.

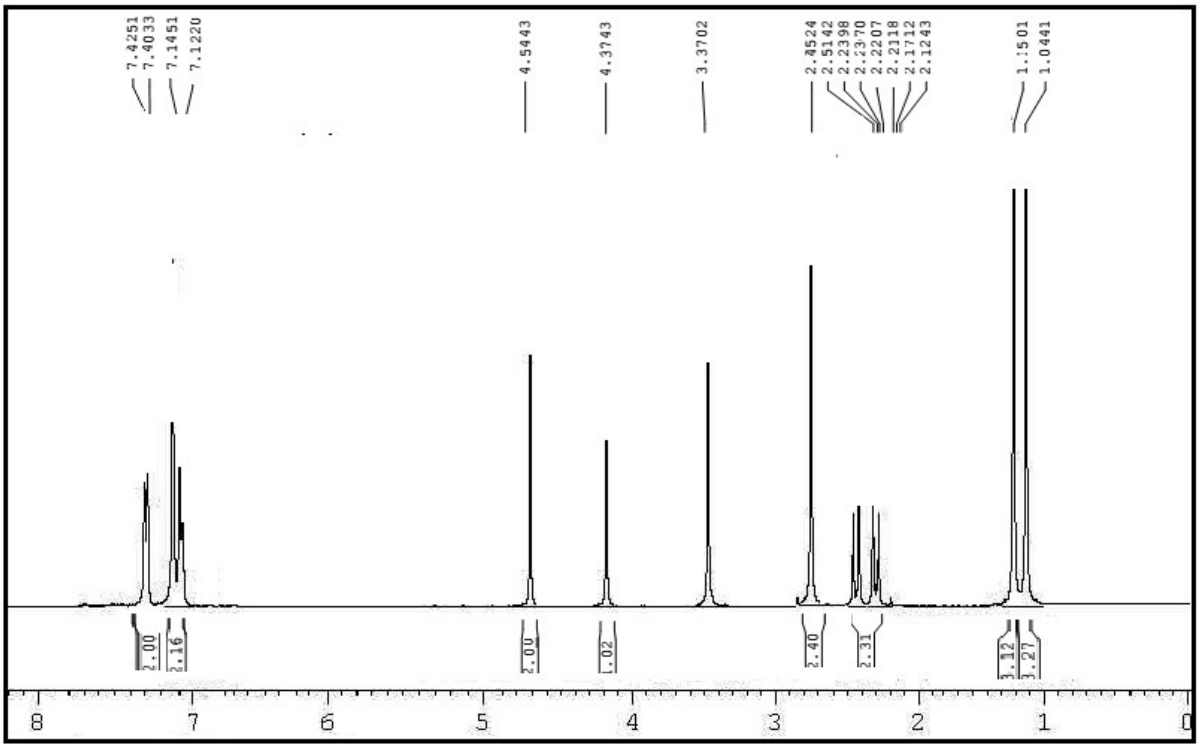
36. 

6g ***7'-amino-5-bromo-2,4'-dioxo-2'-thioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-d]pyrimidine]-6'-carbonitrile (6g):*** Yield 90%. Solid, m.p. 245-247°C (246-248°C). IR ν_{max} (Neat): 3333, 3163, 2842, 2200, 1683, 1661, 1616, 1575, 1497, 1474, 1396, 1339, 1274, 1212, 1168, 1131, 1110, 1052 cm^{-1}. δ = 6.72-6.73 (m, 1H), 7.29-7.36 (m, 5H), 10.58 (s, 1H), 12.05 (s, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d^6) : 47.6, 57.1, 91.2, 111.7, 114.1, 117.5, 127.4, 131.7, 136.3, 141.9, 154.8, 159.2, 160.3, 175.3, 177.7 ppm.

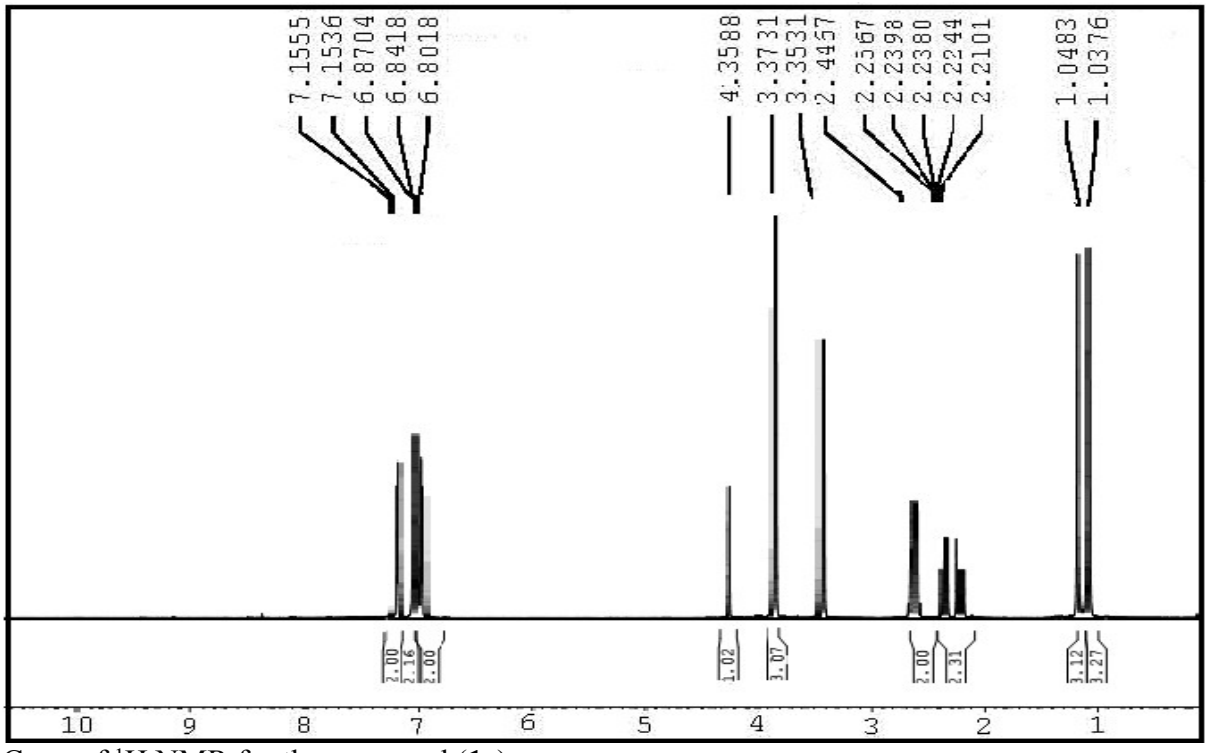
Copies of ^{1}H and ^{13}C NMR spectra of Selected Compounds



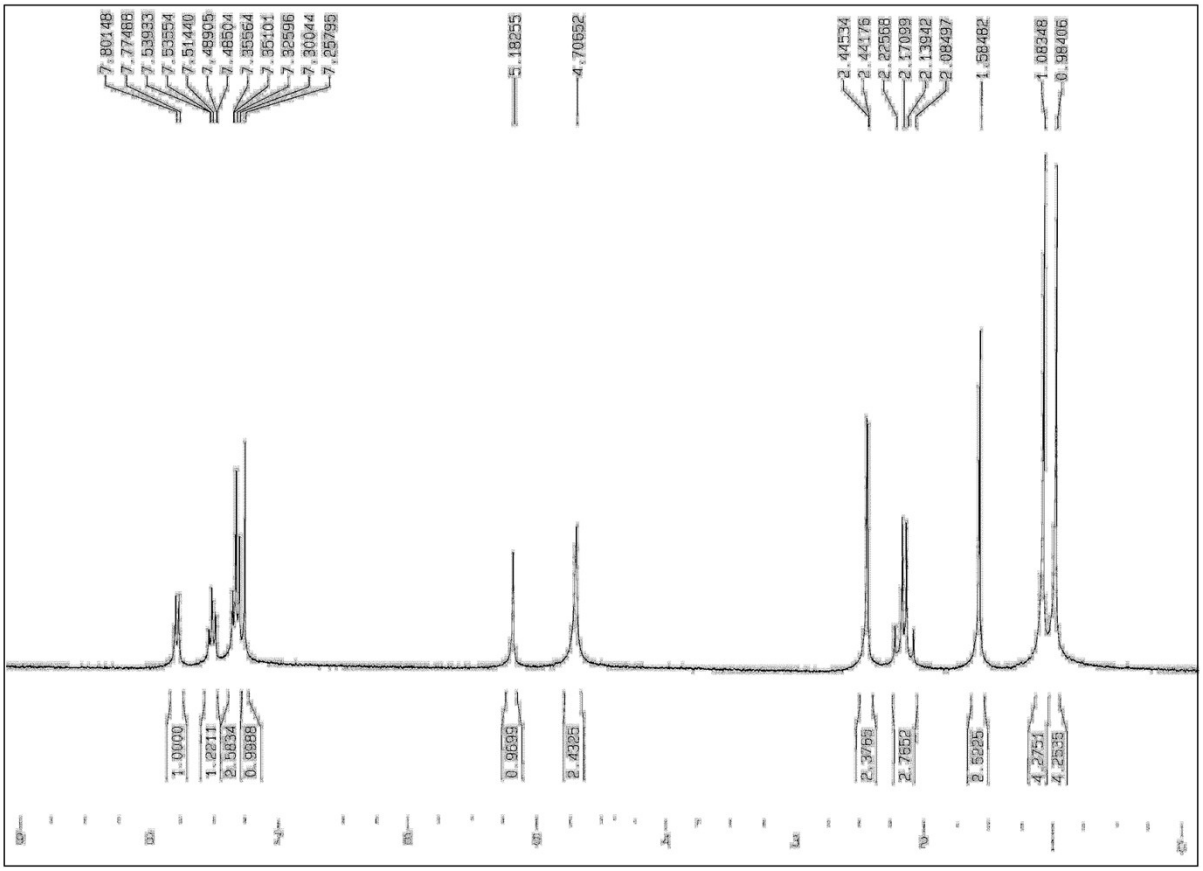
Copy of ^{1}H NMR for the compund (**1a)**



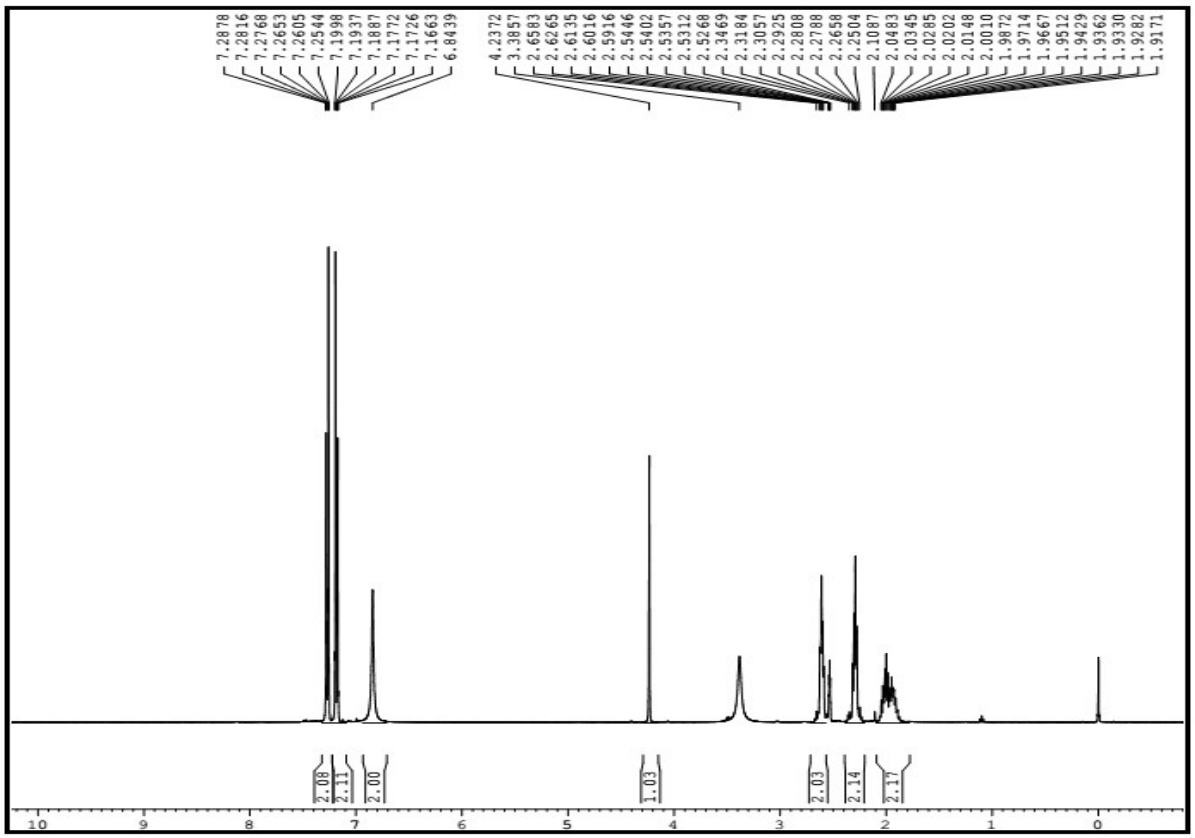
Copy of ^{1}H NMR for the compund (**1b**).



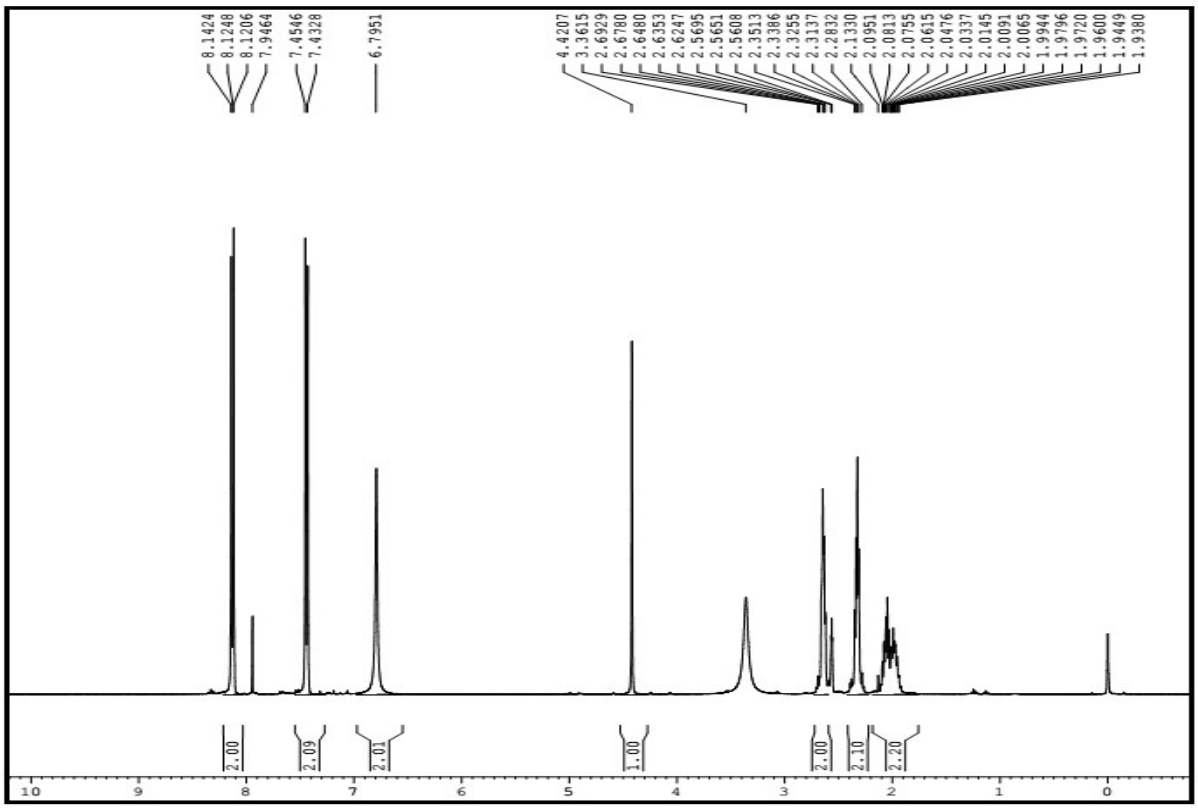
Copy of ^{1}H NMR for the compund (**1c**).



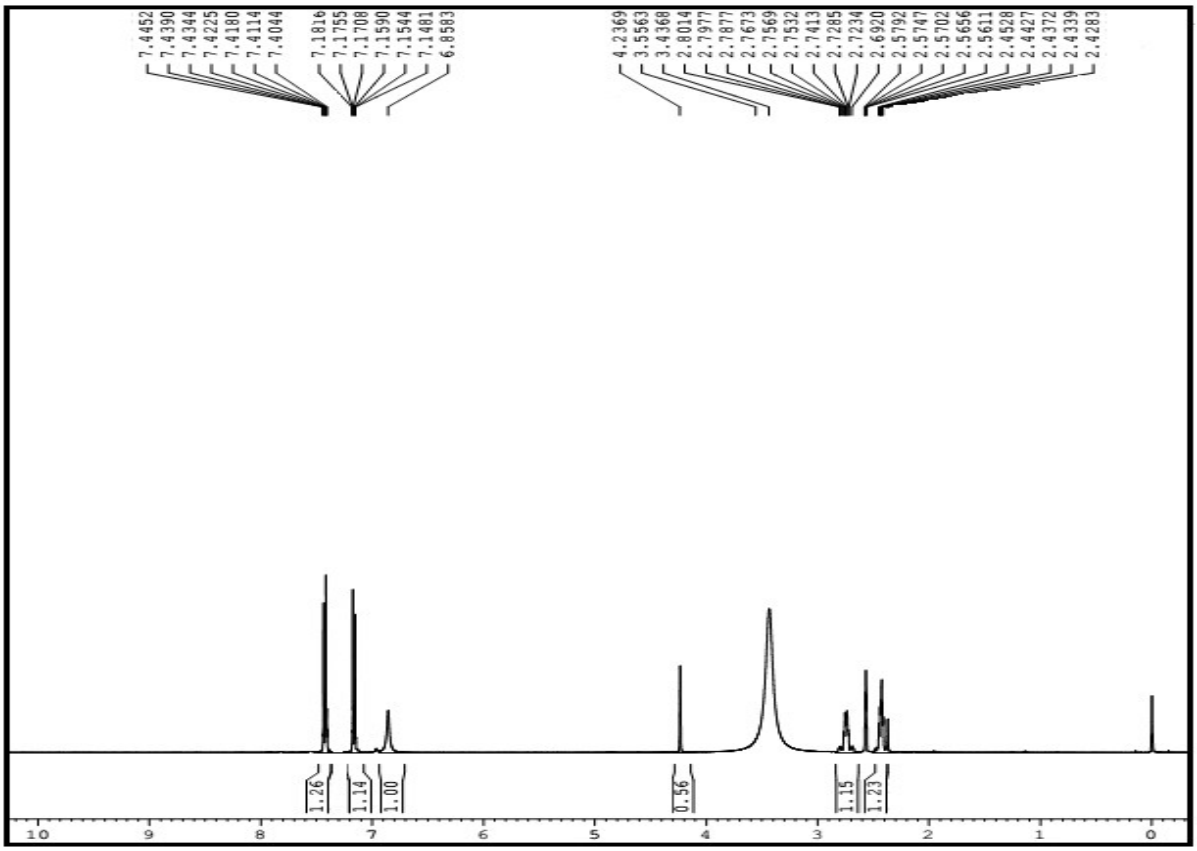
Copy of ^{1}H NMR for the compund (**1d**).



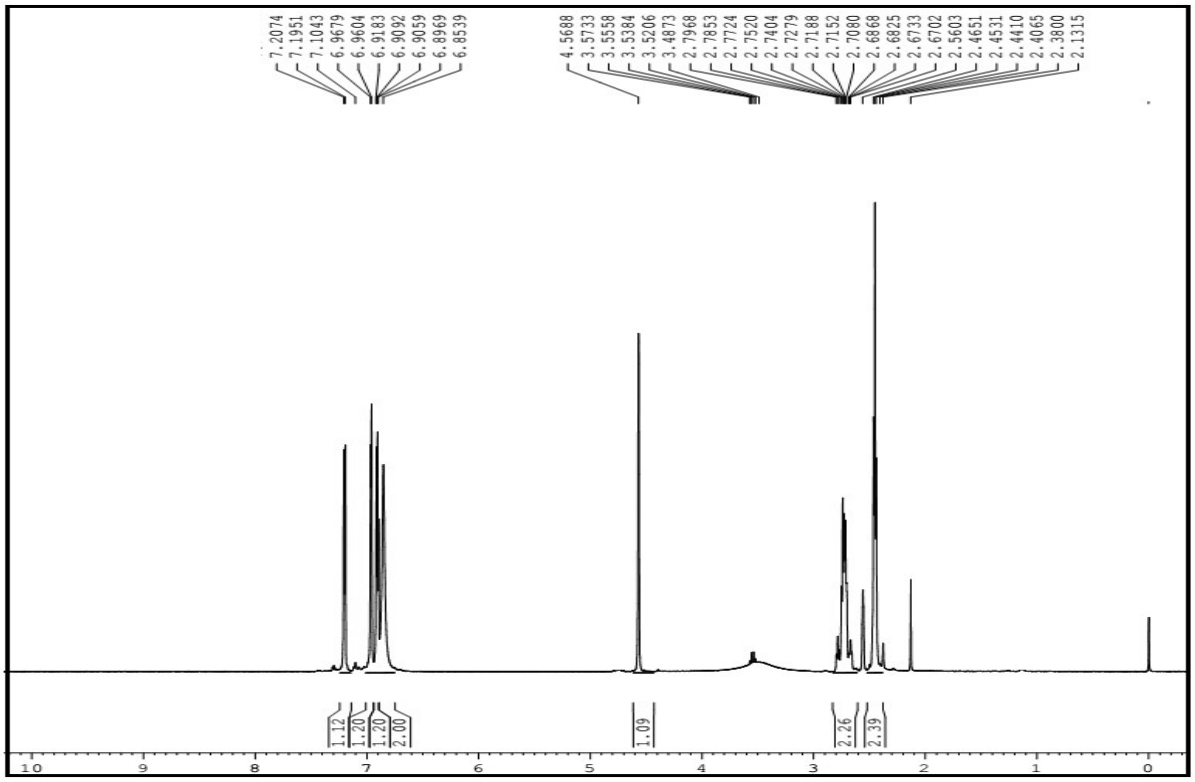
Copy of ^{1}H NMR for the compund (**1e**).



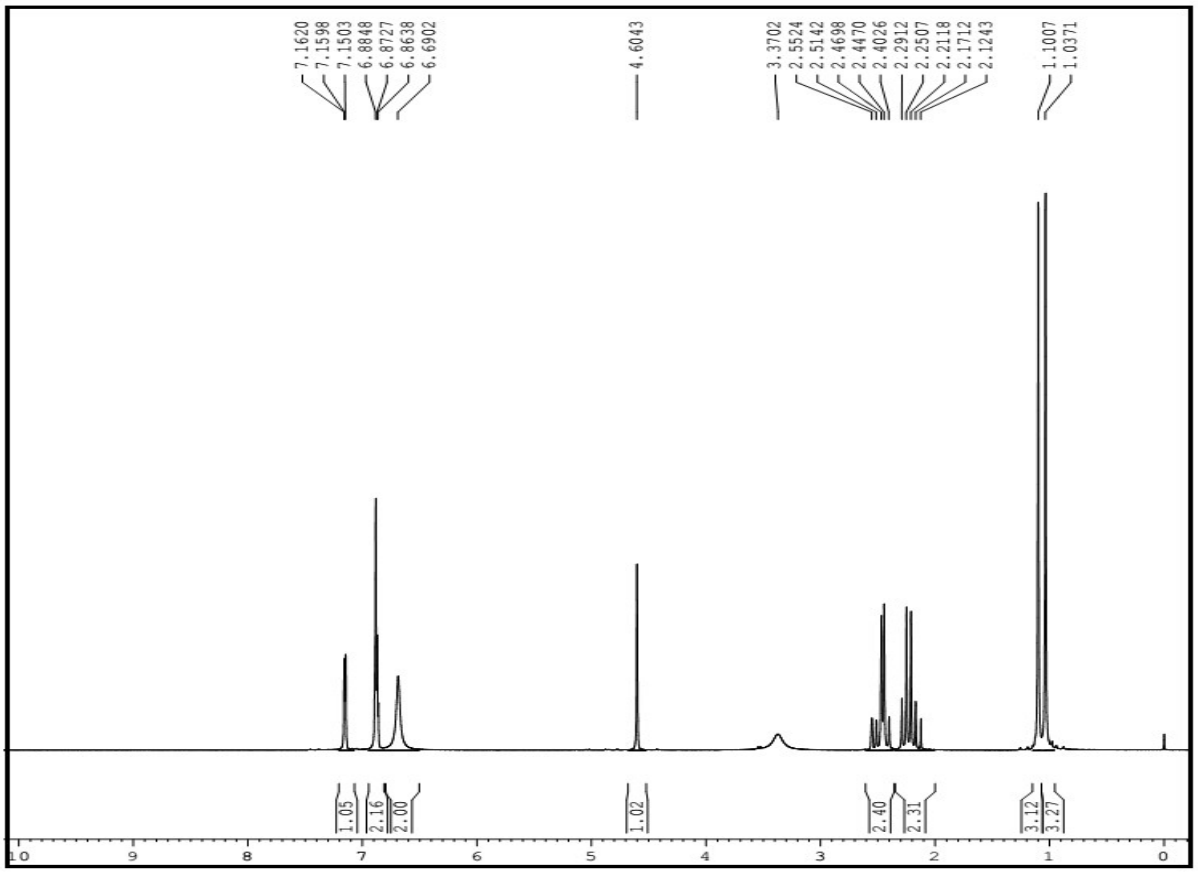
Copy of ^{1}H NMR for the compund (**1f**).



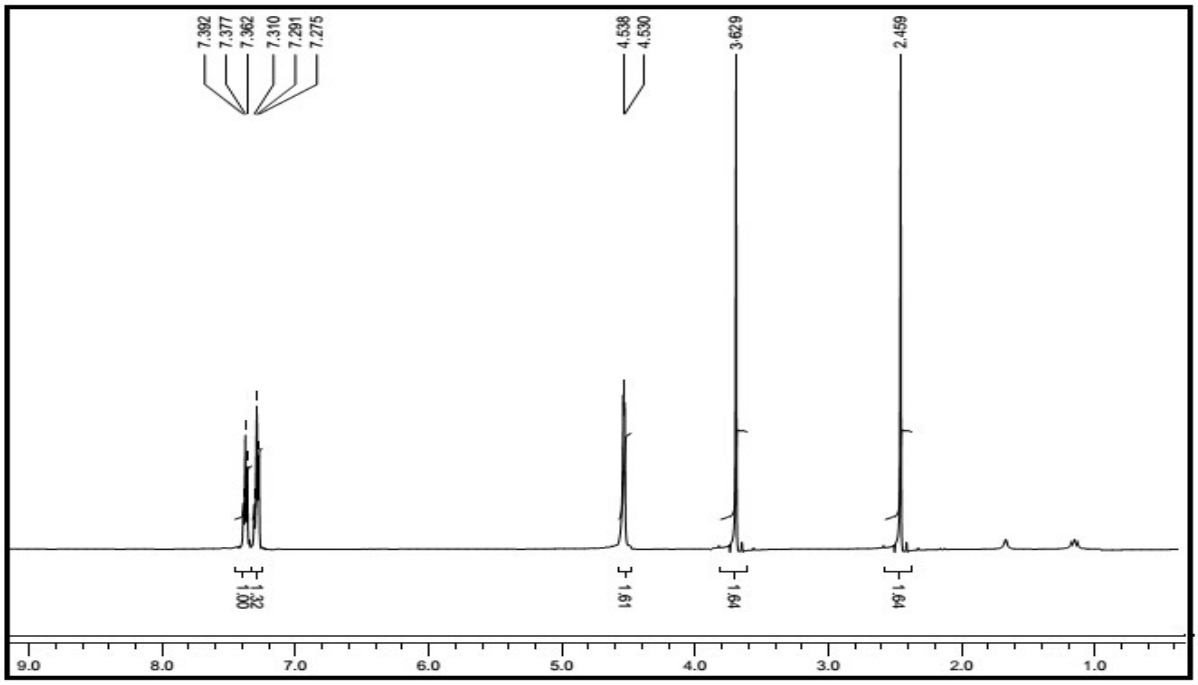
Copy of ^{1}H NMR for the compund (**1g**).



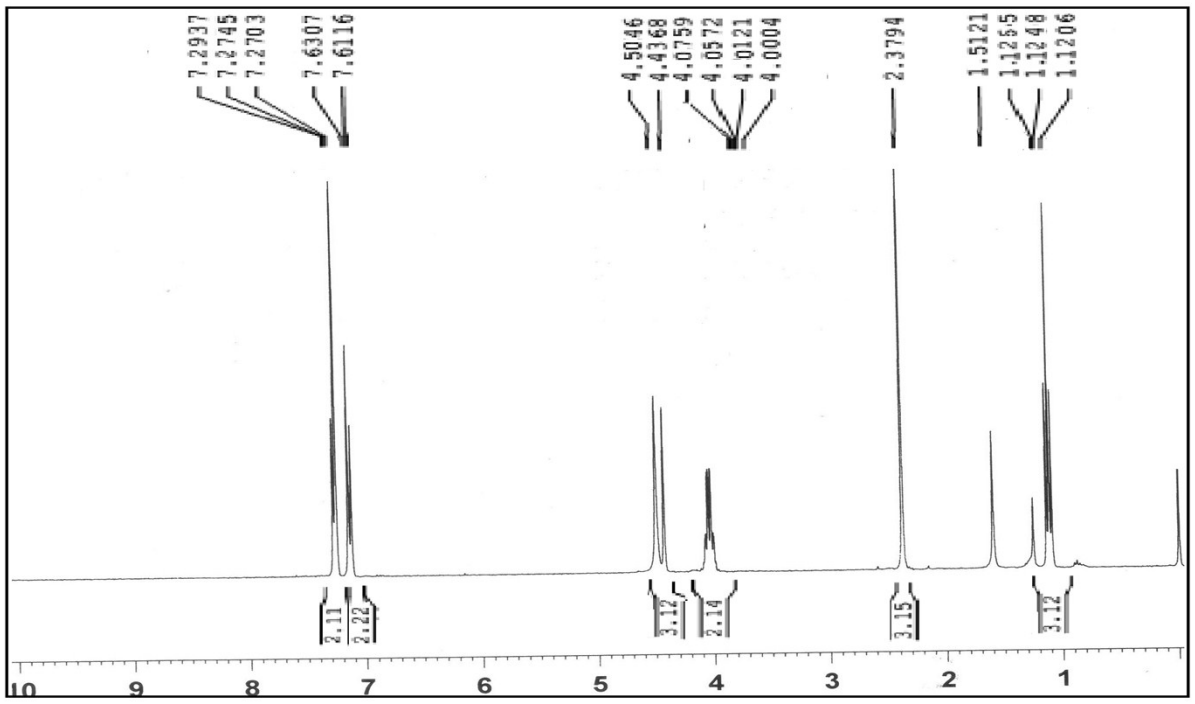
Copy of ^{1}H NMR for the compund (**1h**).



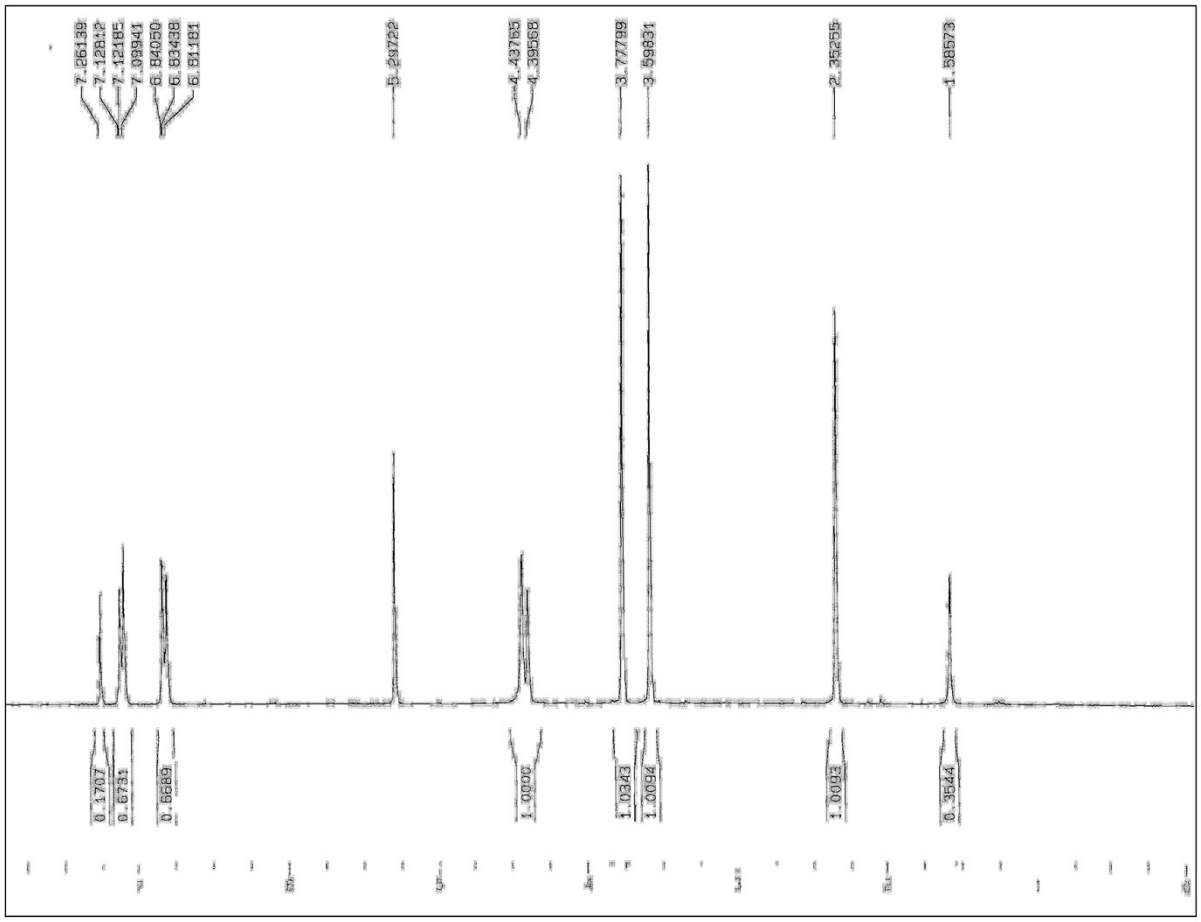
Copy of ^{1}H NMR for the compund (**1i**).



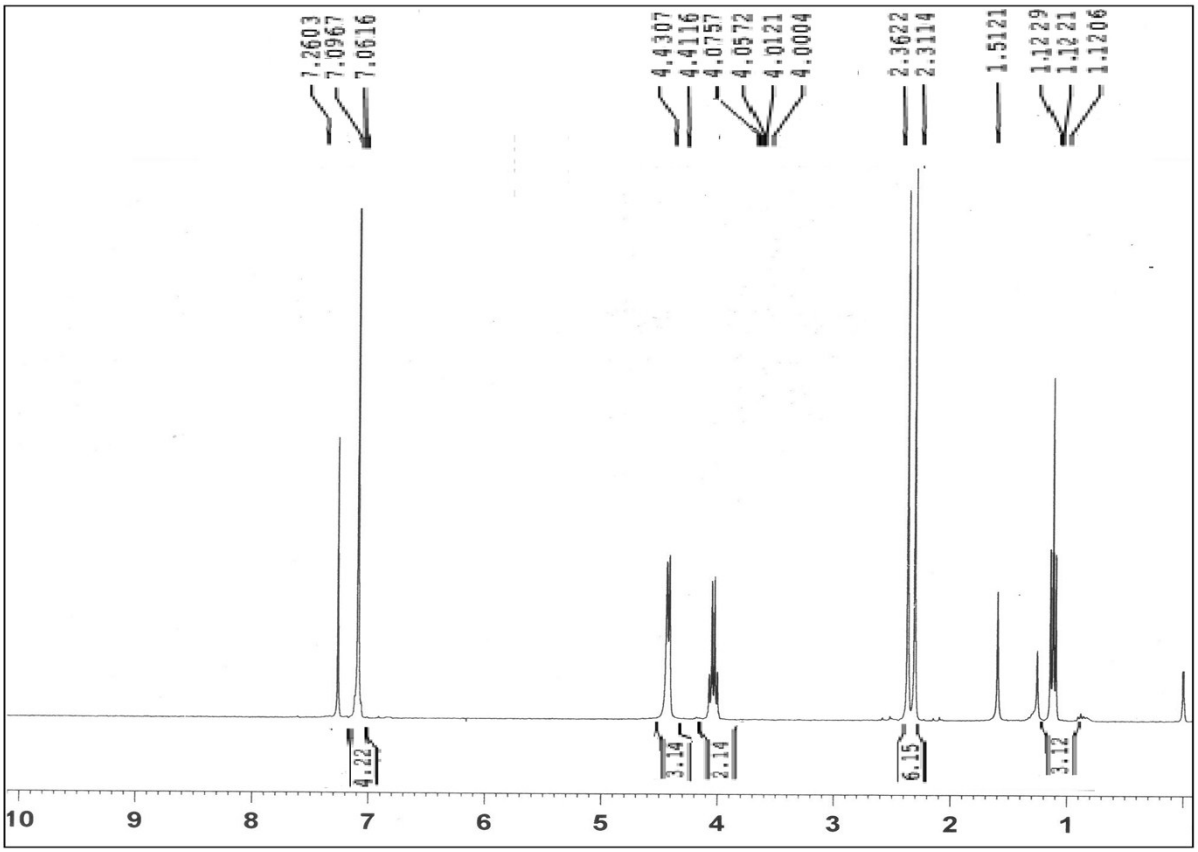
Copy of ^{1}H NMR for the compund (**2a**).



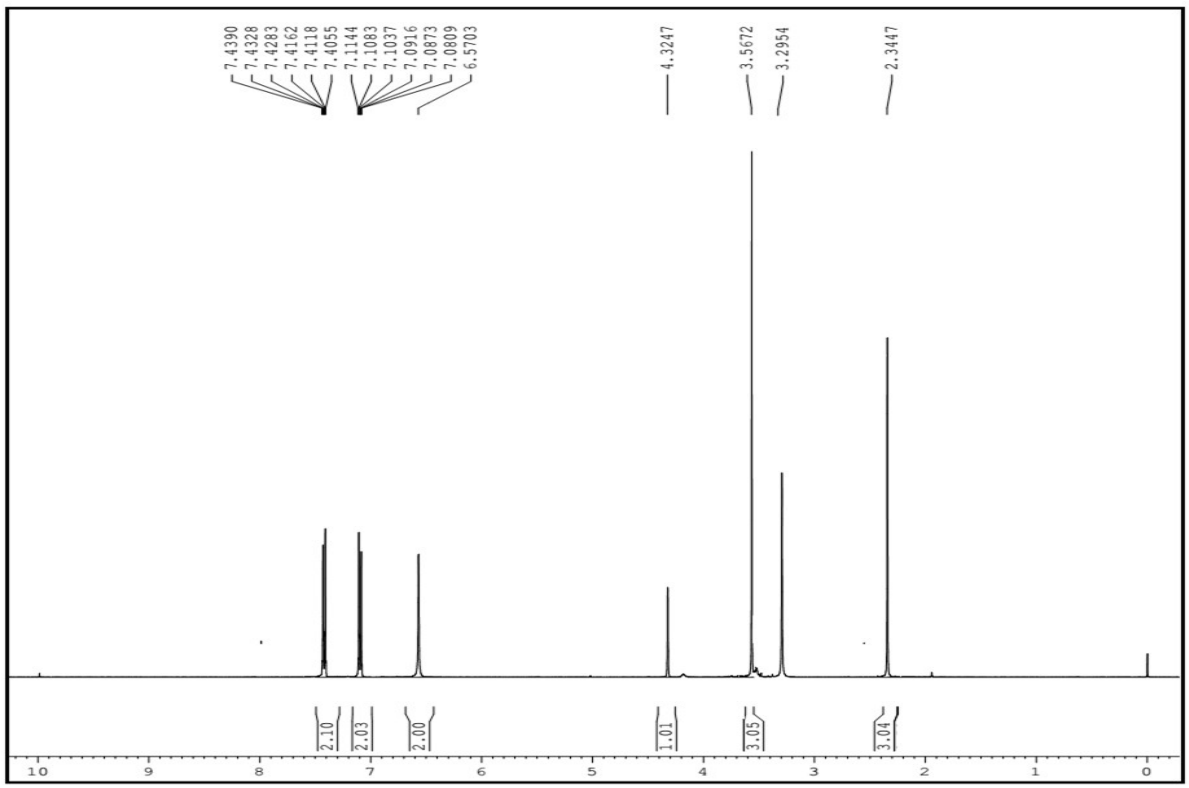
Copy of ^{1}H NMR for the compund (**2b**).



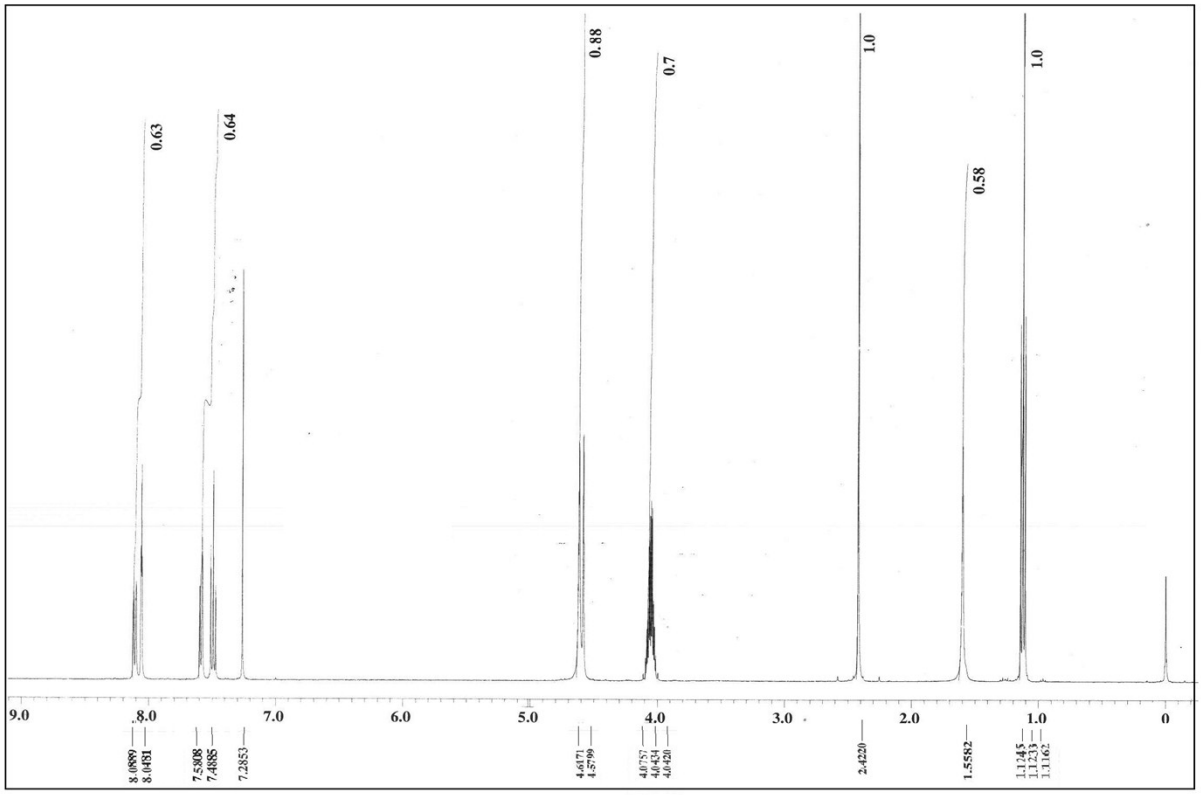
Copy of ^{1}H NMR for the compund (**2c**).



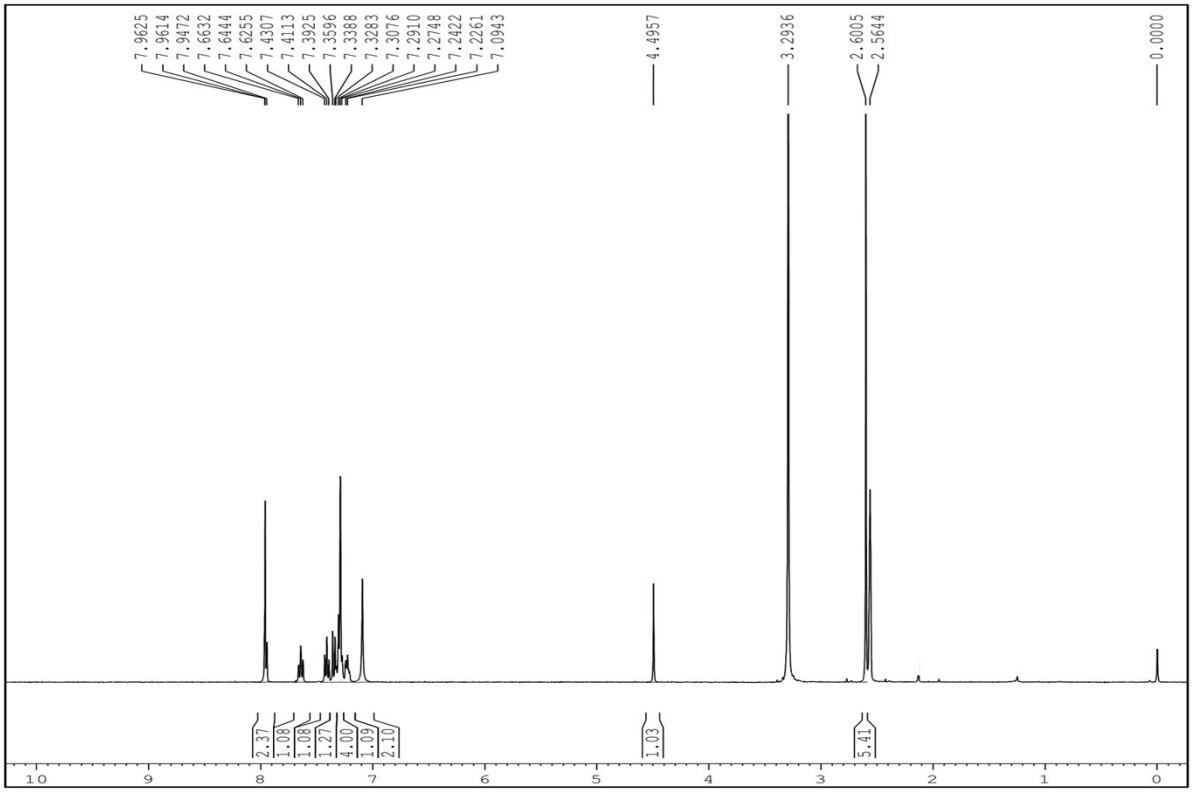
Copy of ^{1}H NMR for the compund (**2d**).



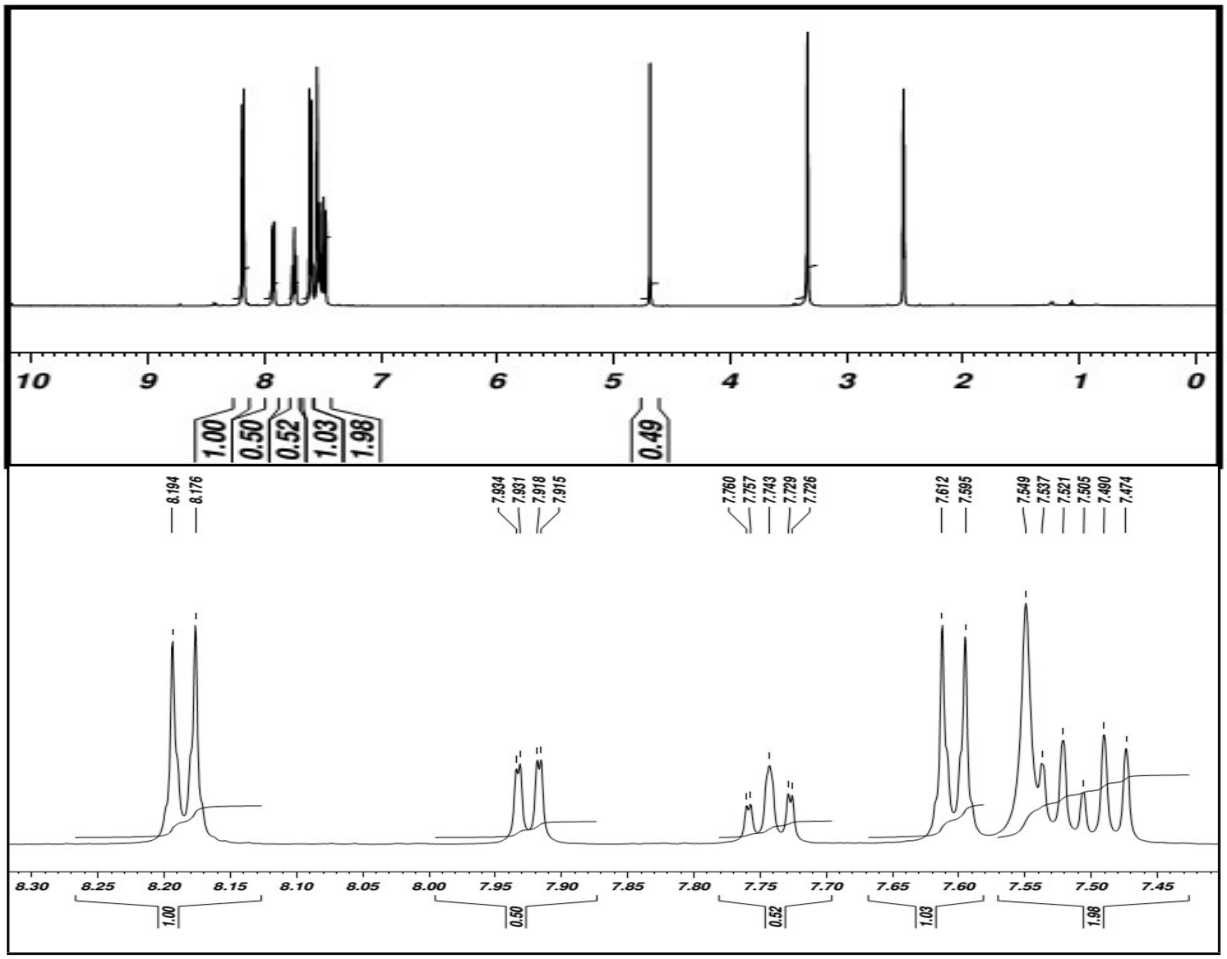
Copy of ^{1}H NMR for the compund (**2e**).



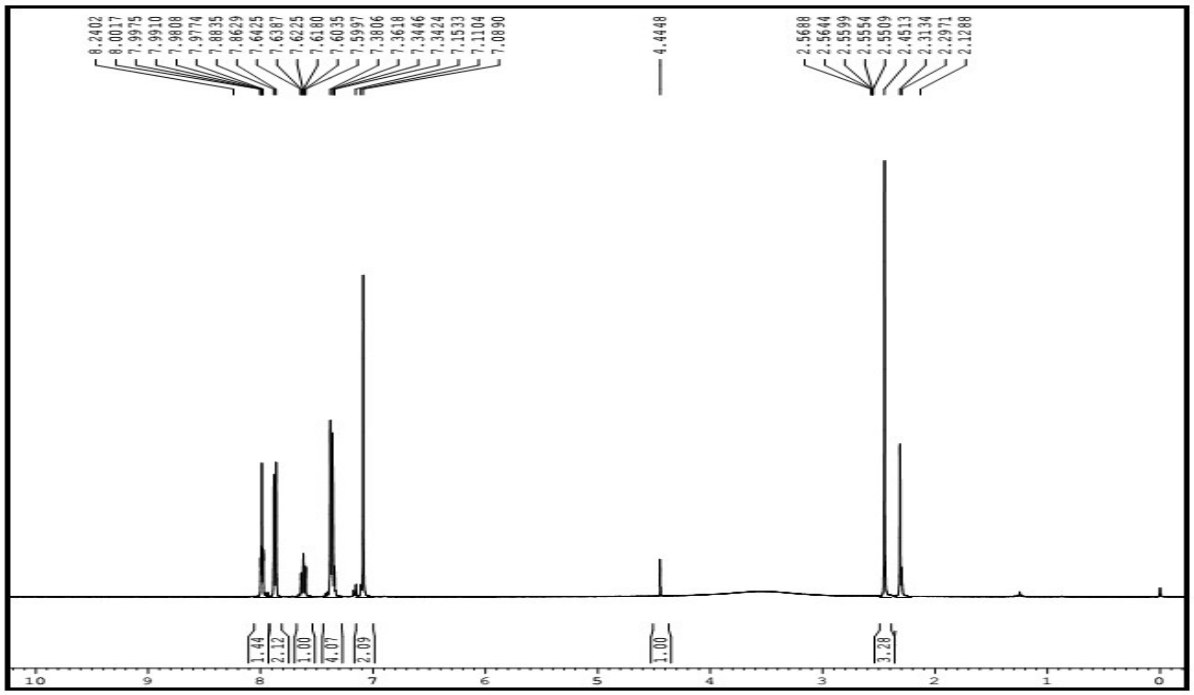
Copy of ^{1}H NMR for the compund (**2f**).



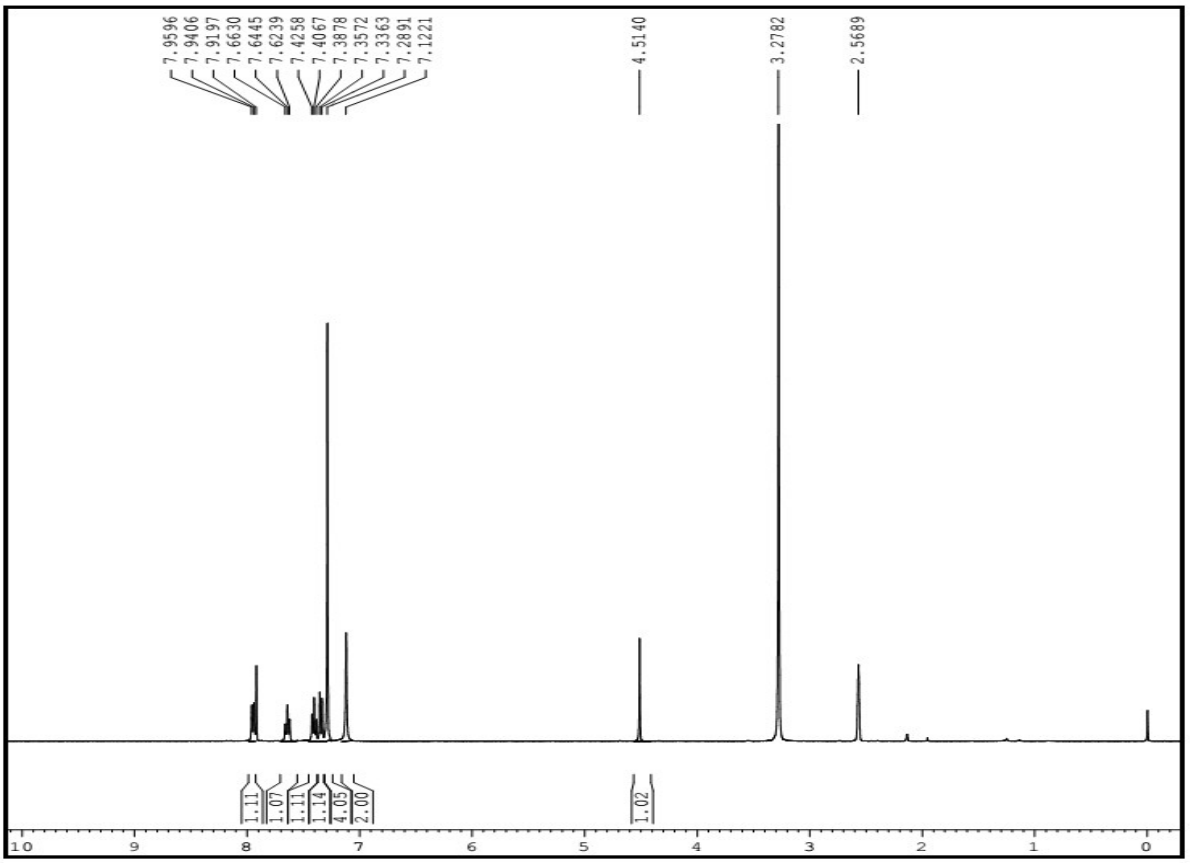
Copy of ^{1}H NMR for the compund (**3a**).



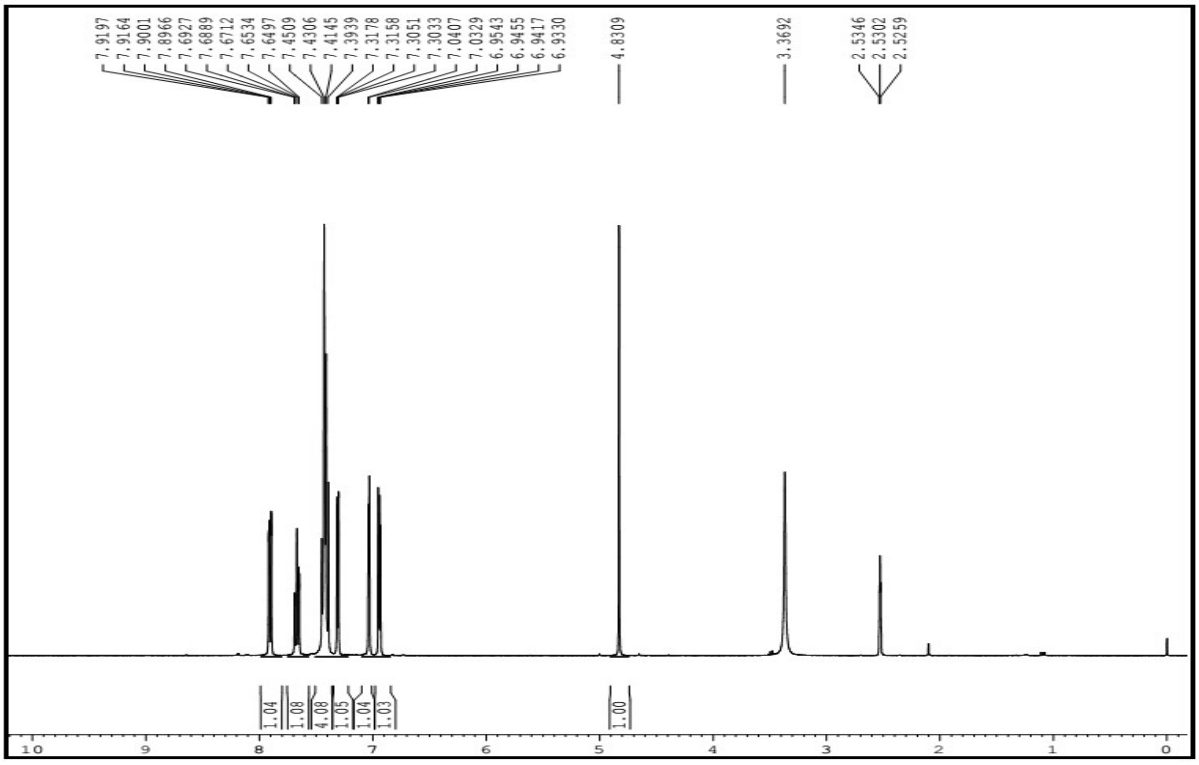
Copy of ^{1}H NMR for the compund (**3b**).



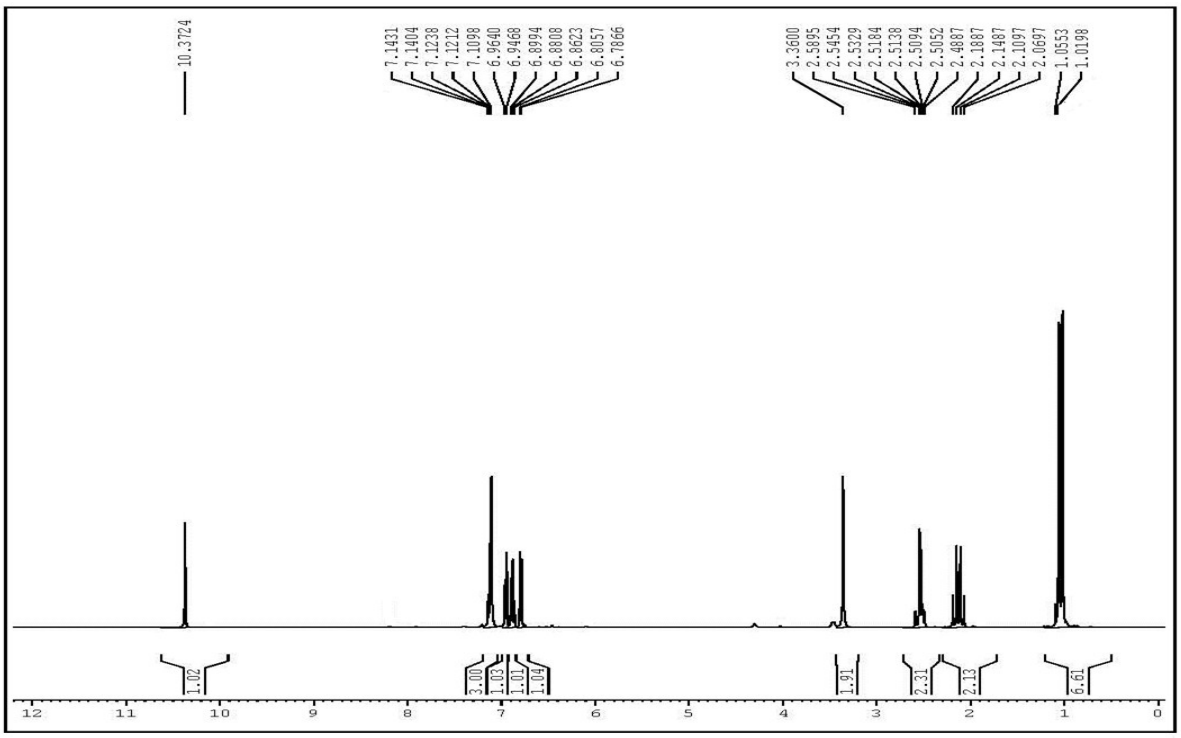
Copy of ^{1}H NMR for the compund (**3c**).



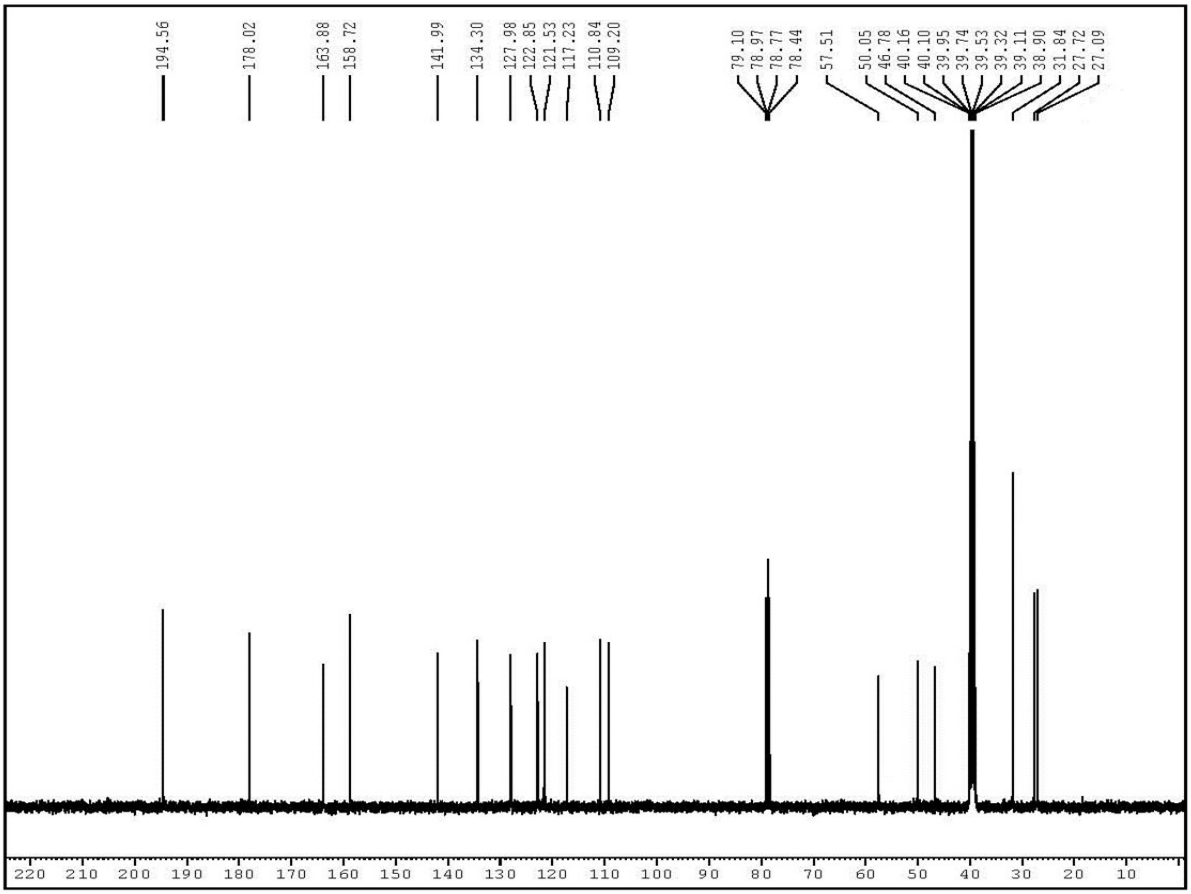
Copy of ^{1}H NMR for the compund (**3d**).



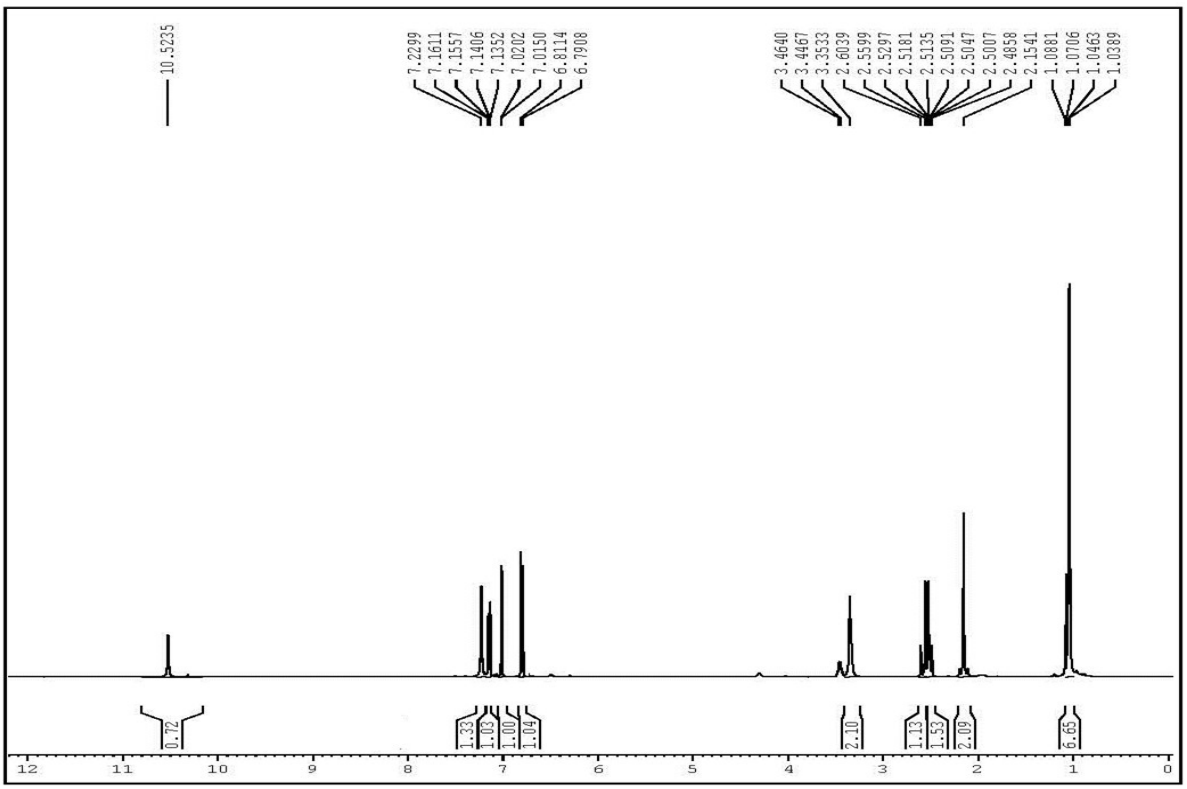
Copy of ^{1}H NMR for the compund (**3e**).



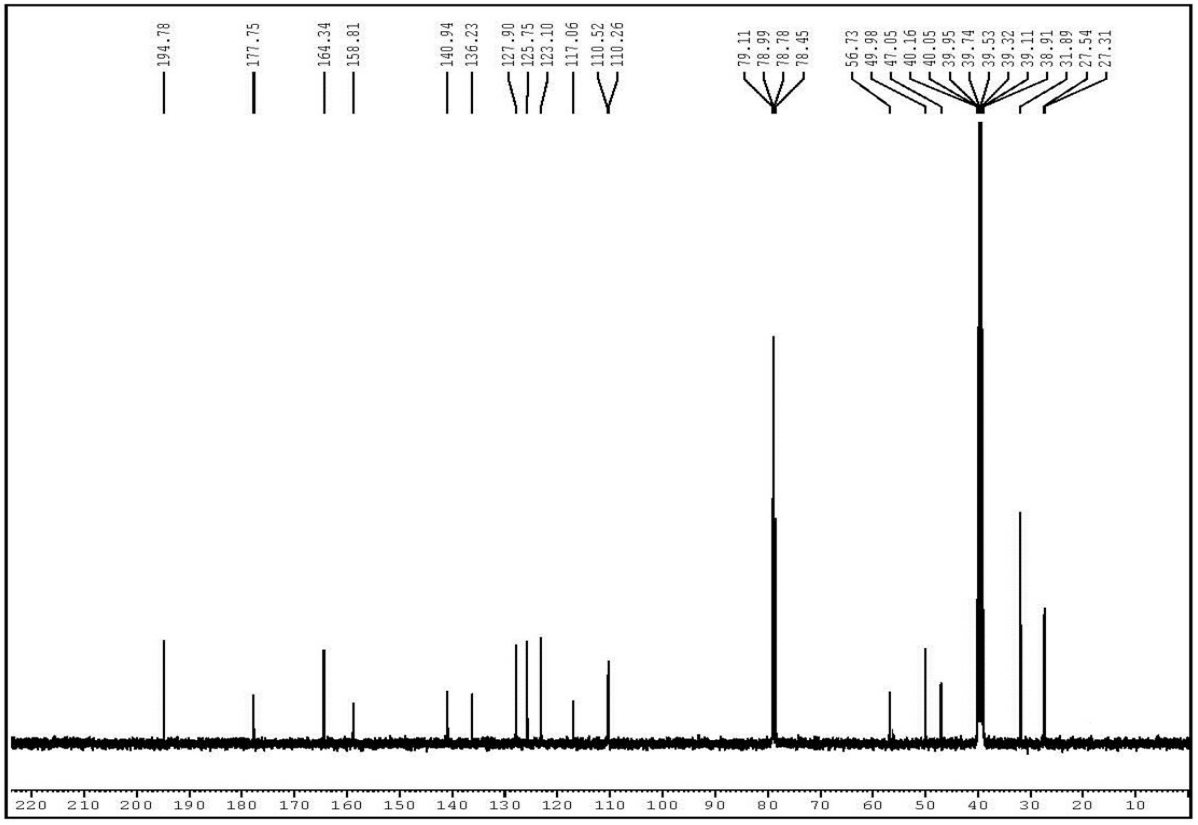
Copy of ^{1}H NMR for the compund (**4a**).



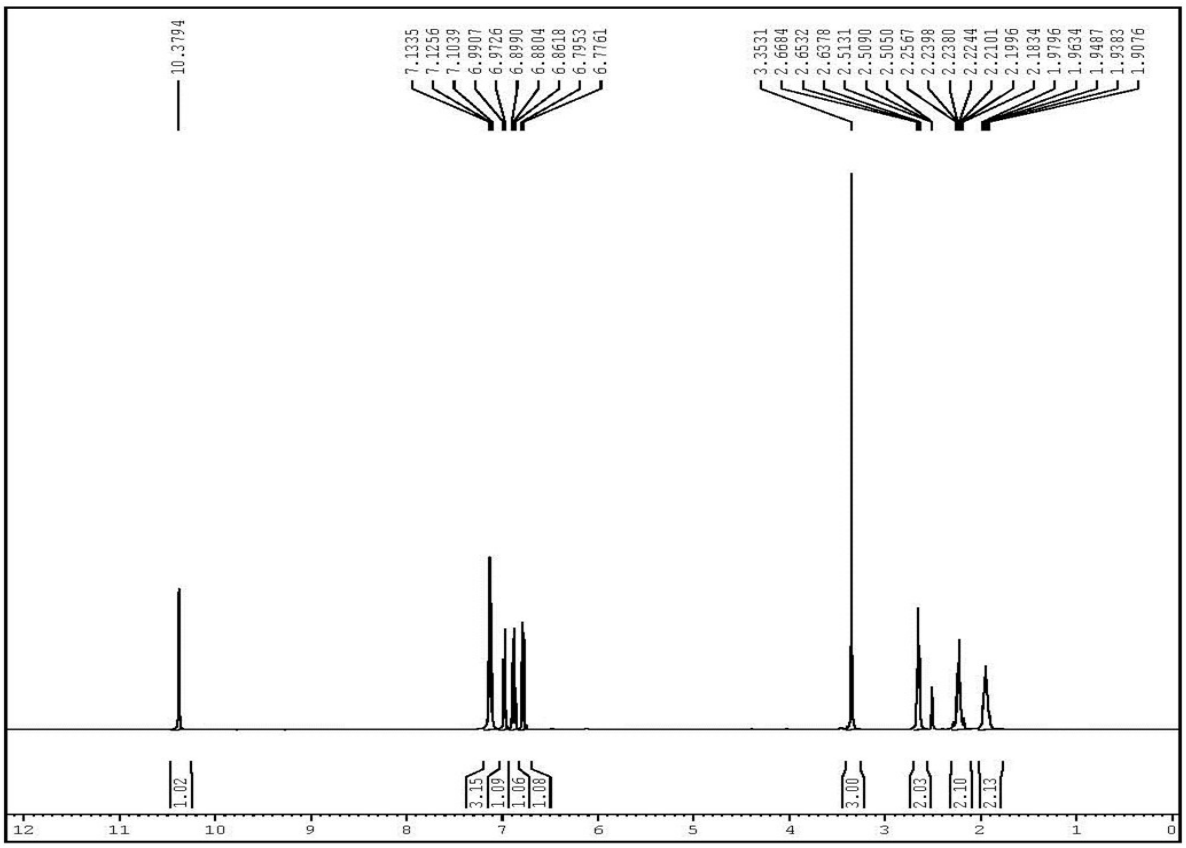
Copy of ^{13}C NMR for the compund (**4a**).



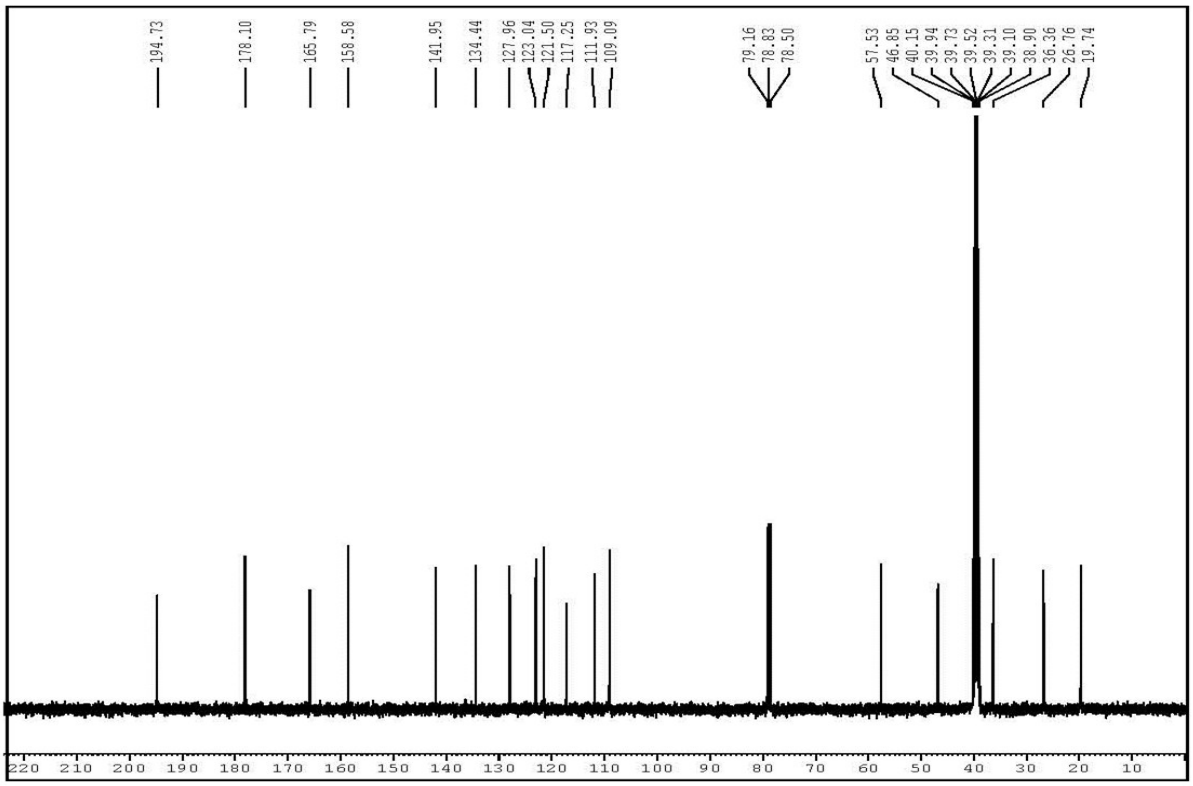
Copy of ^{1}H NMR for the compund (**4b**).



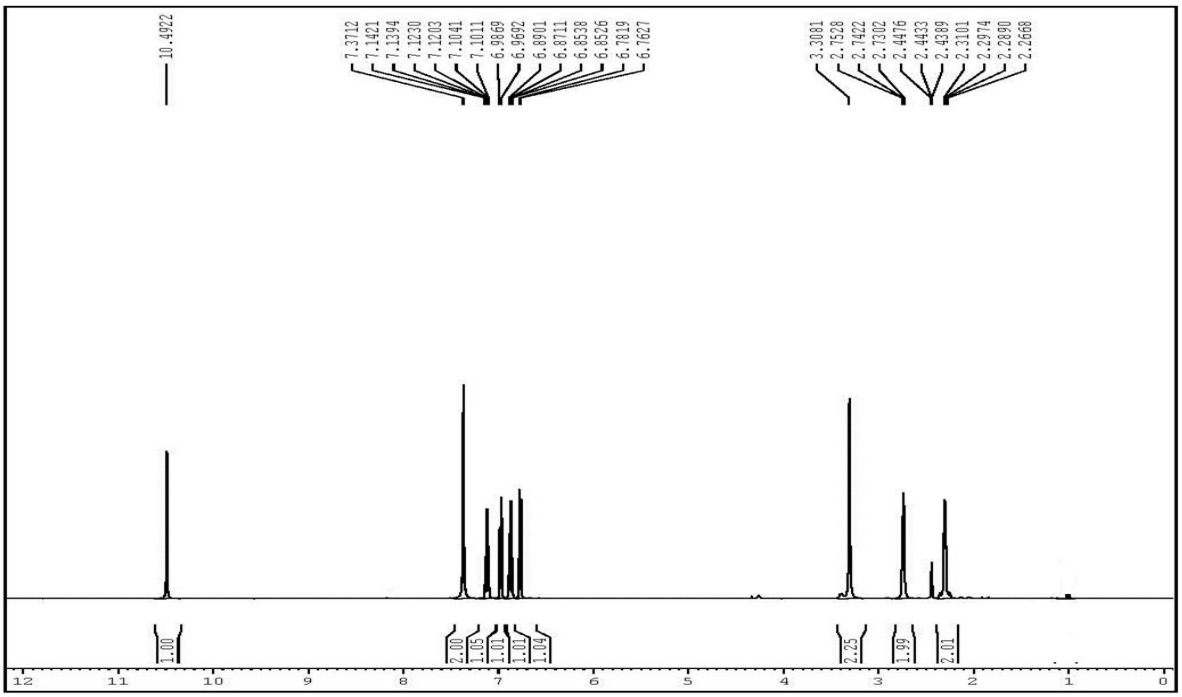
Copy of ^{13}C NMR for the compund (**4b**).



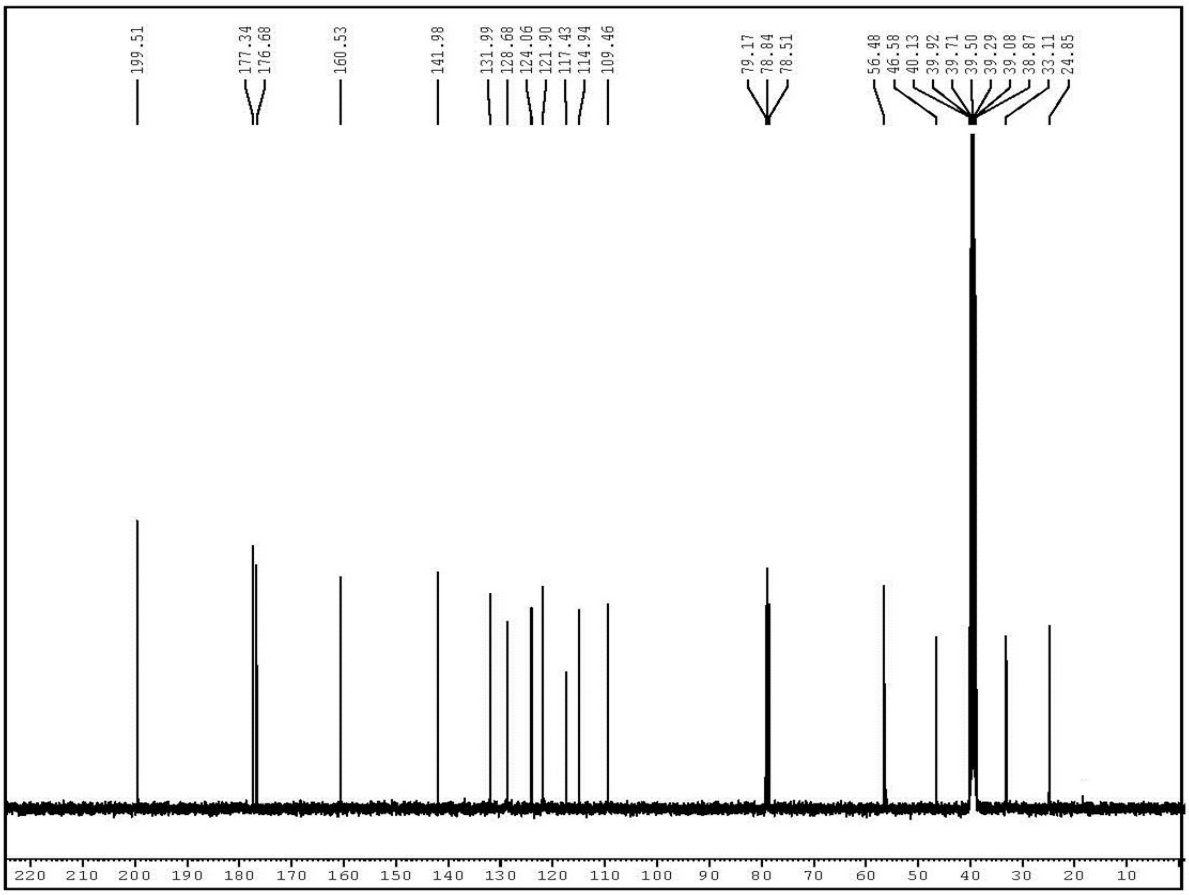
Copy of ^{1}H NMR for the compund (**4c**).



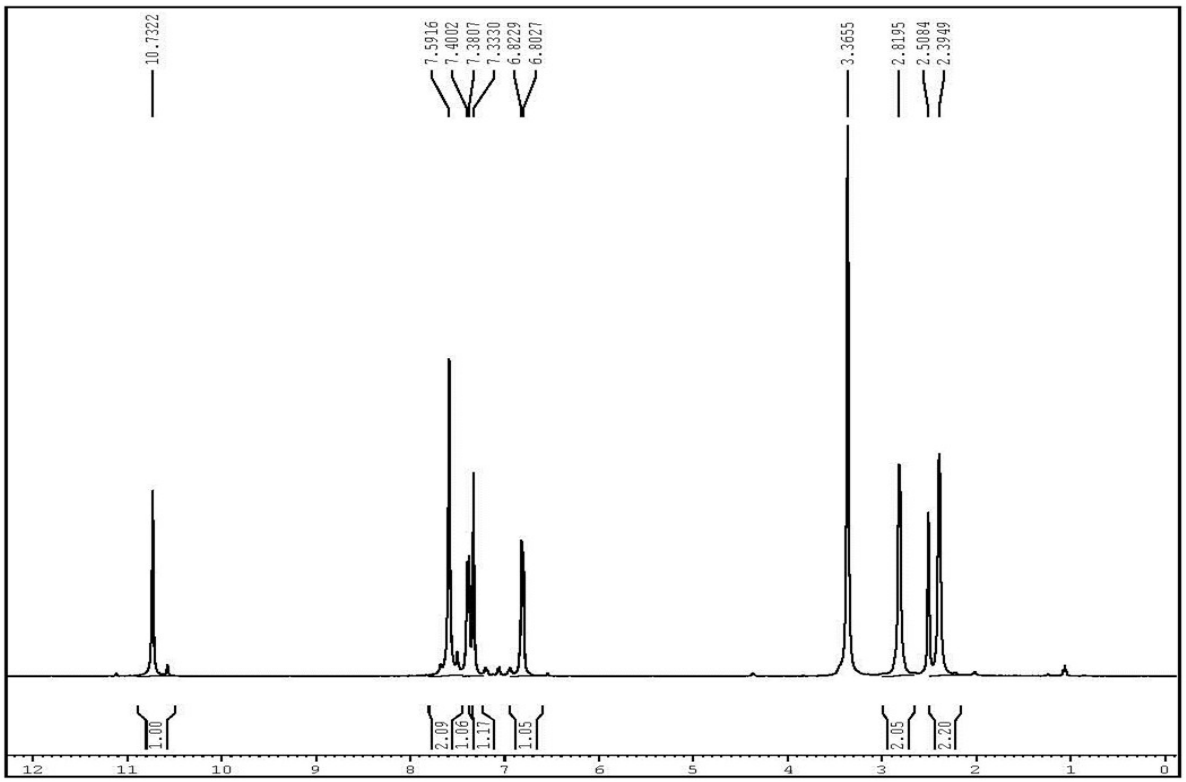
Copy of ^{13}C NMR for the compund (**4c**).



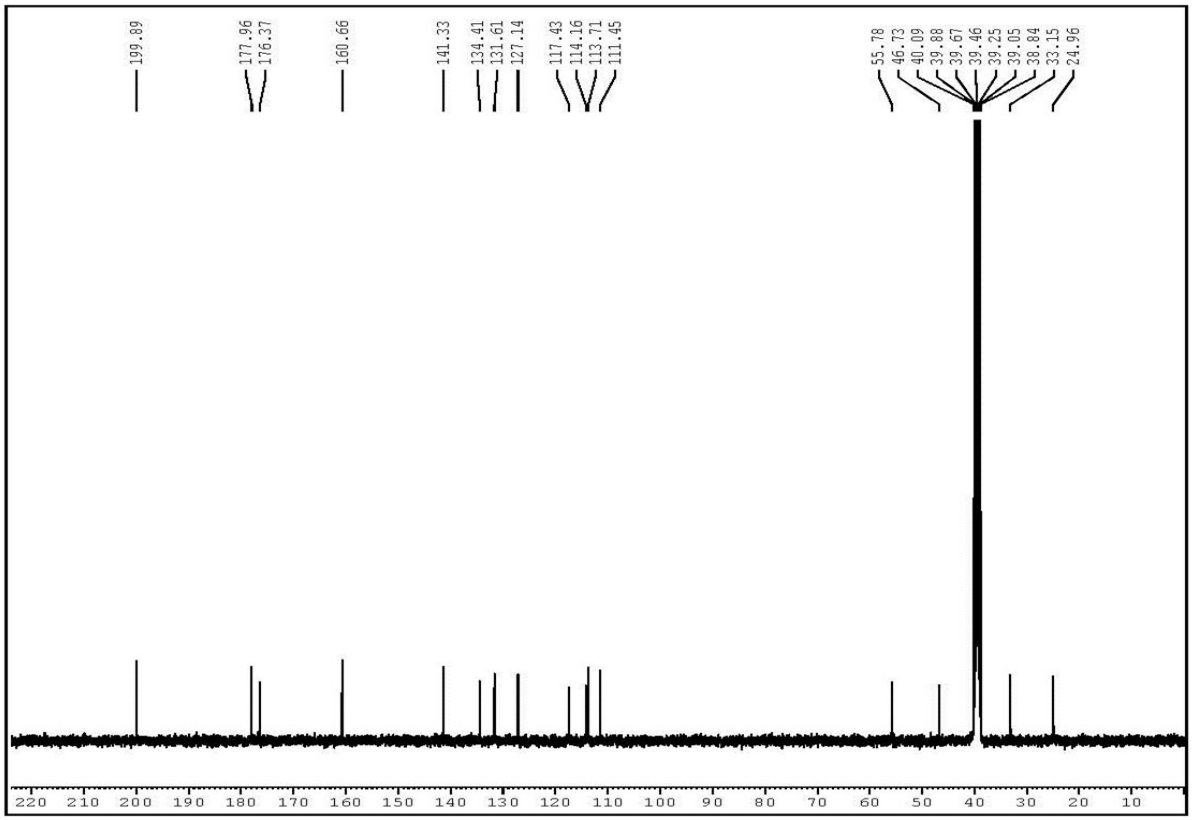
Copy of ^{1}H NMR for the compund (**4d**).



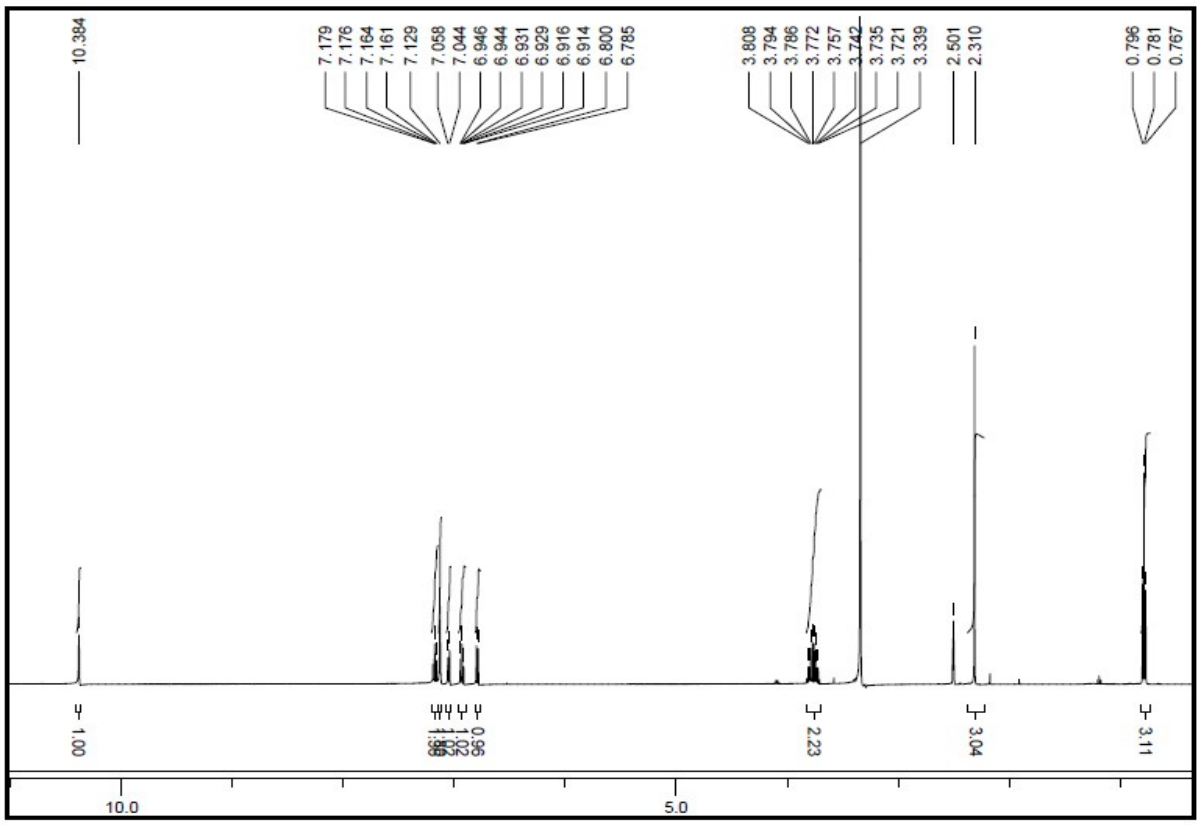
Copy of ^{13}C NMR for the compund (**4d**).



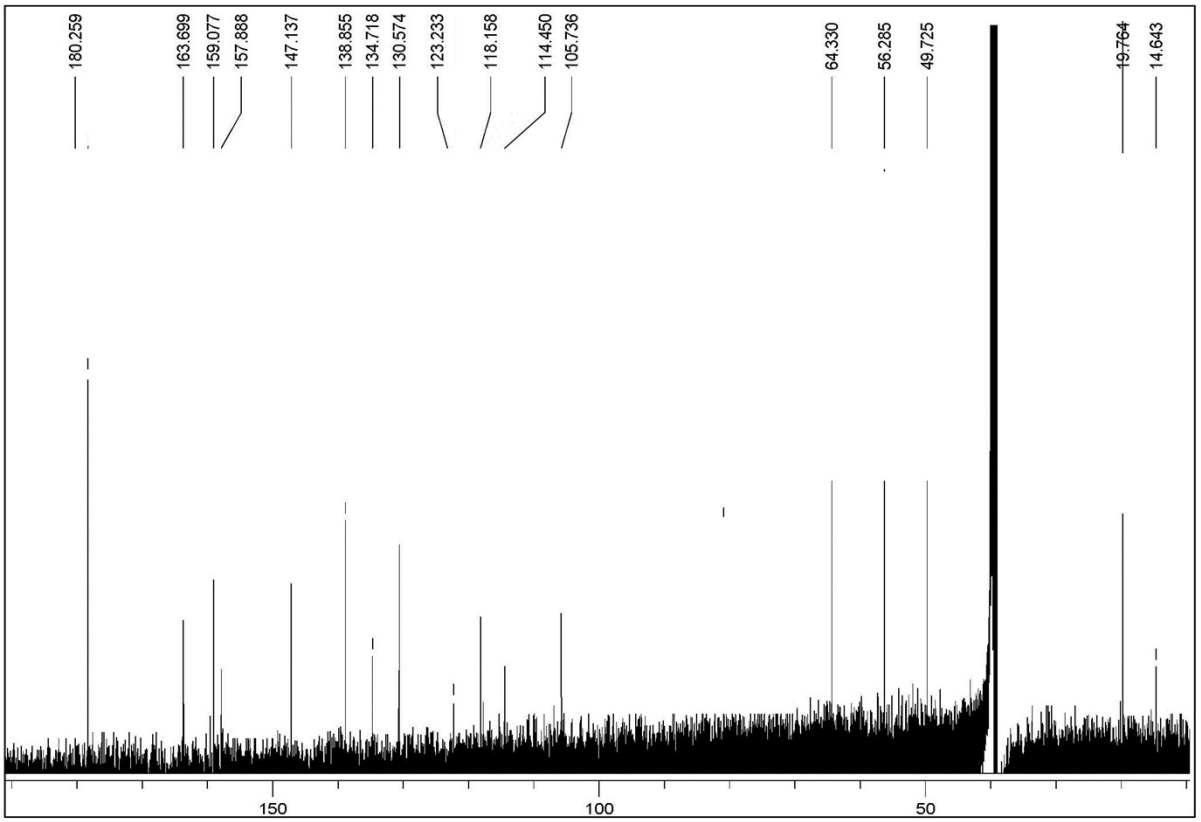
Copy of ^{1}H NMR for the compund (**4e**).



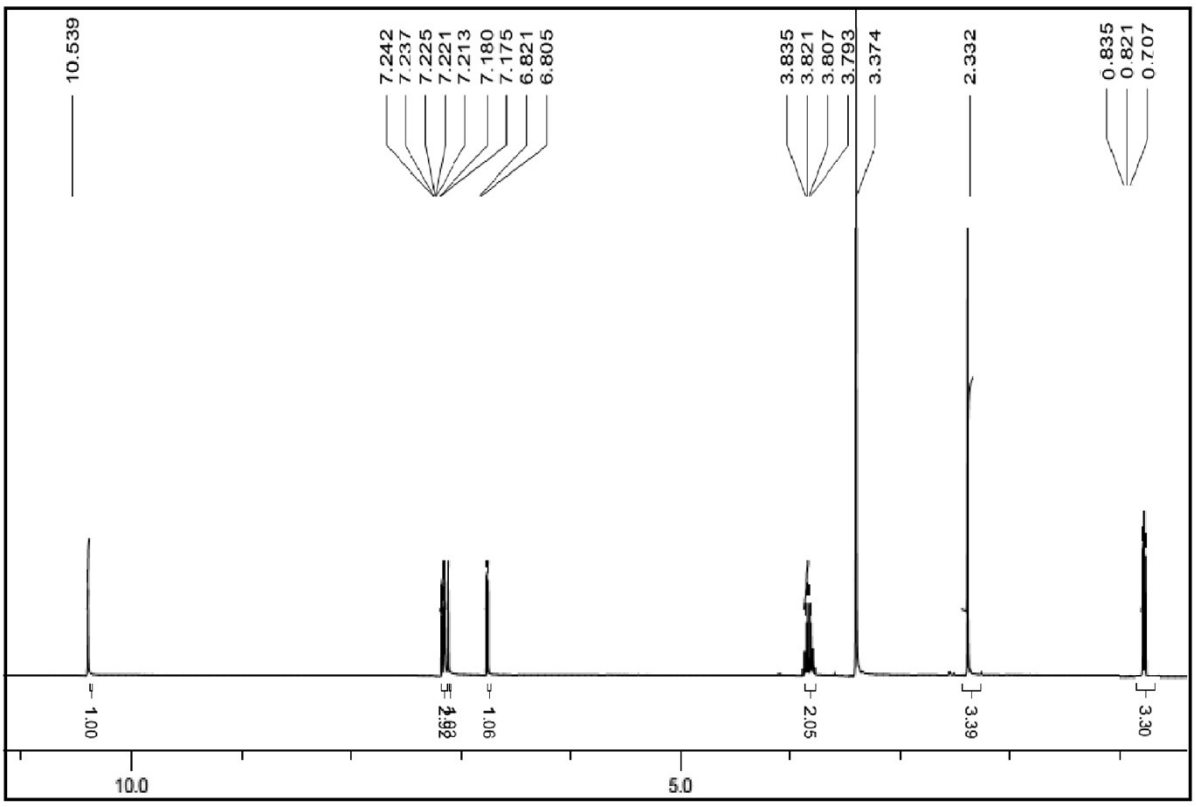
Copy of ^{13}C NMR for the compund (**4e**).



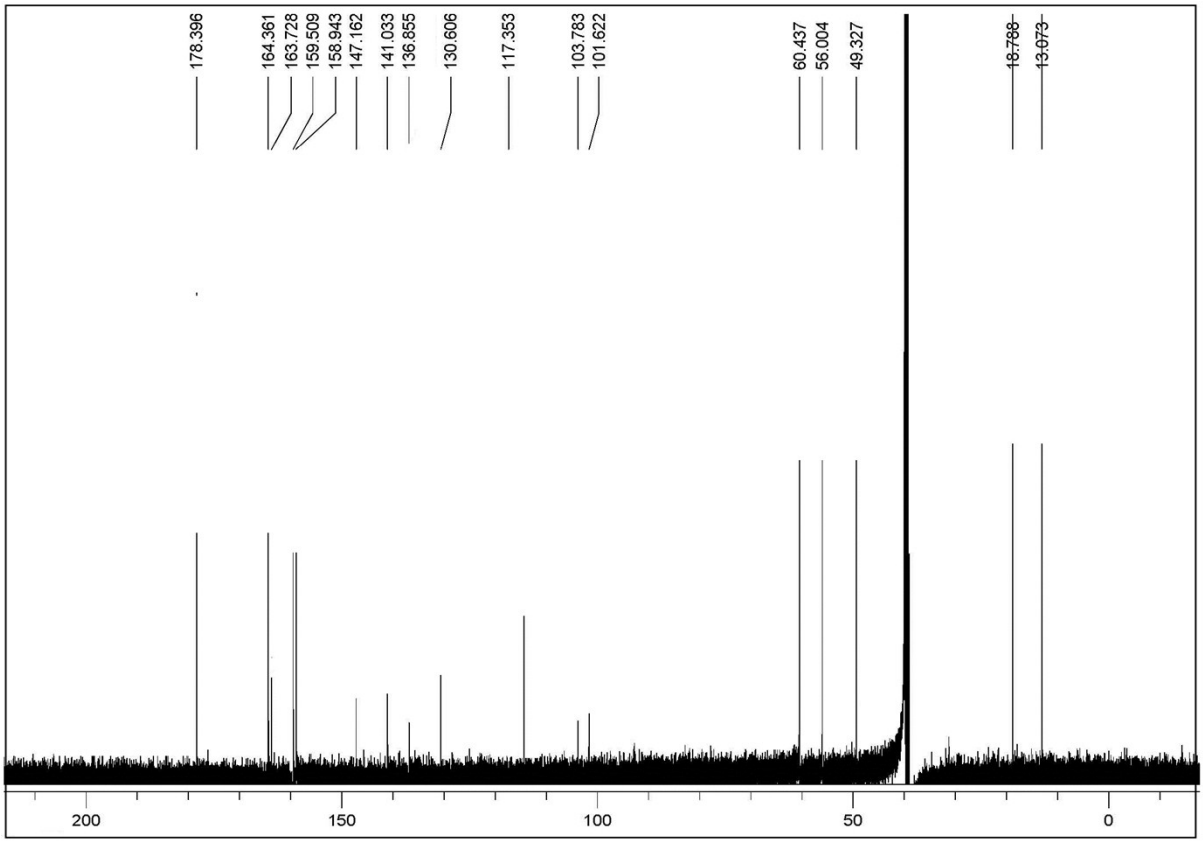
Copy of ^{1}H NMR for the compund (**5a**).



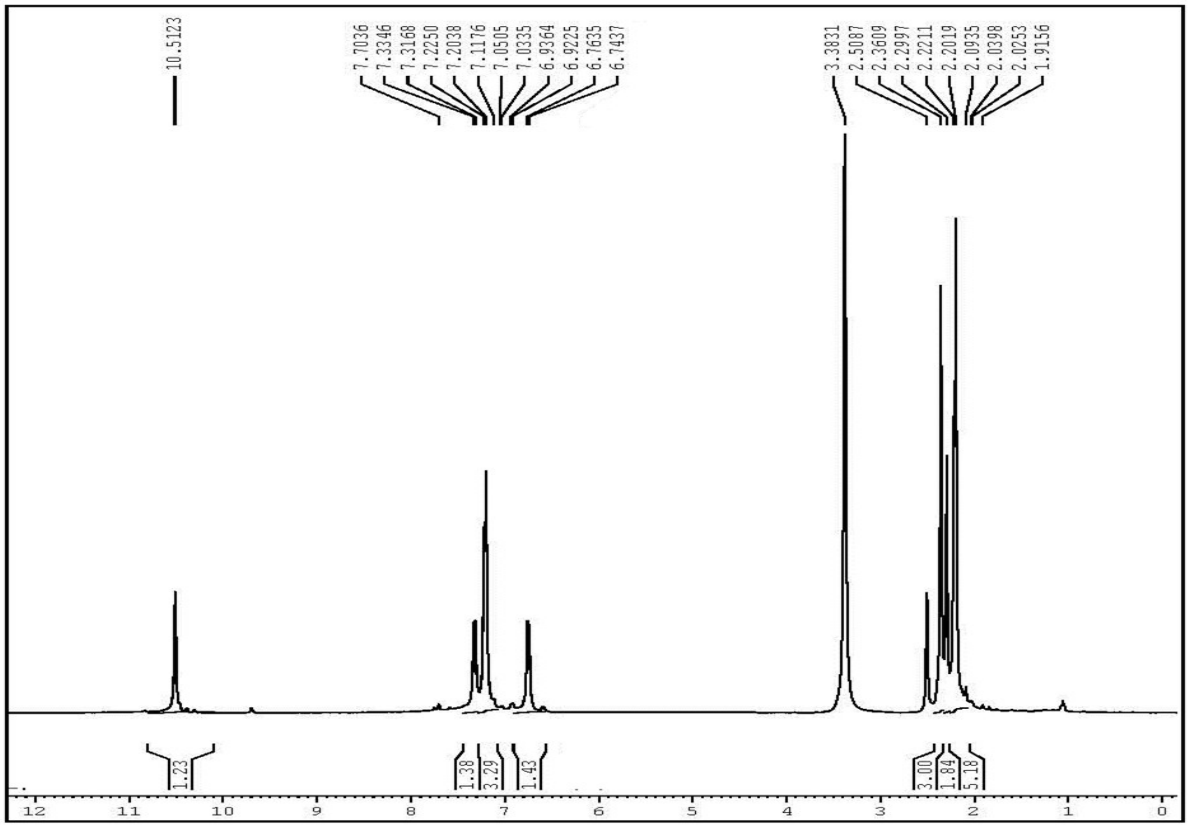
Copy of ^{13}C NMR for the compund (**5a**).



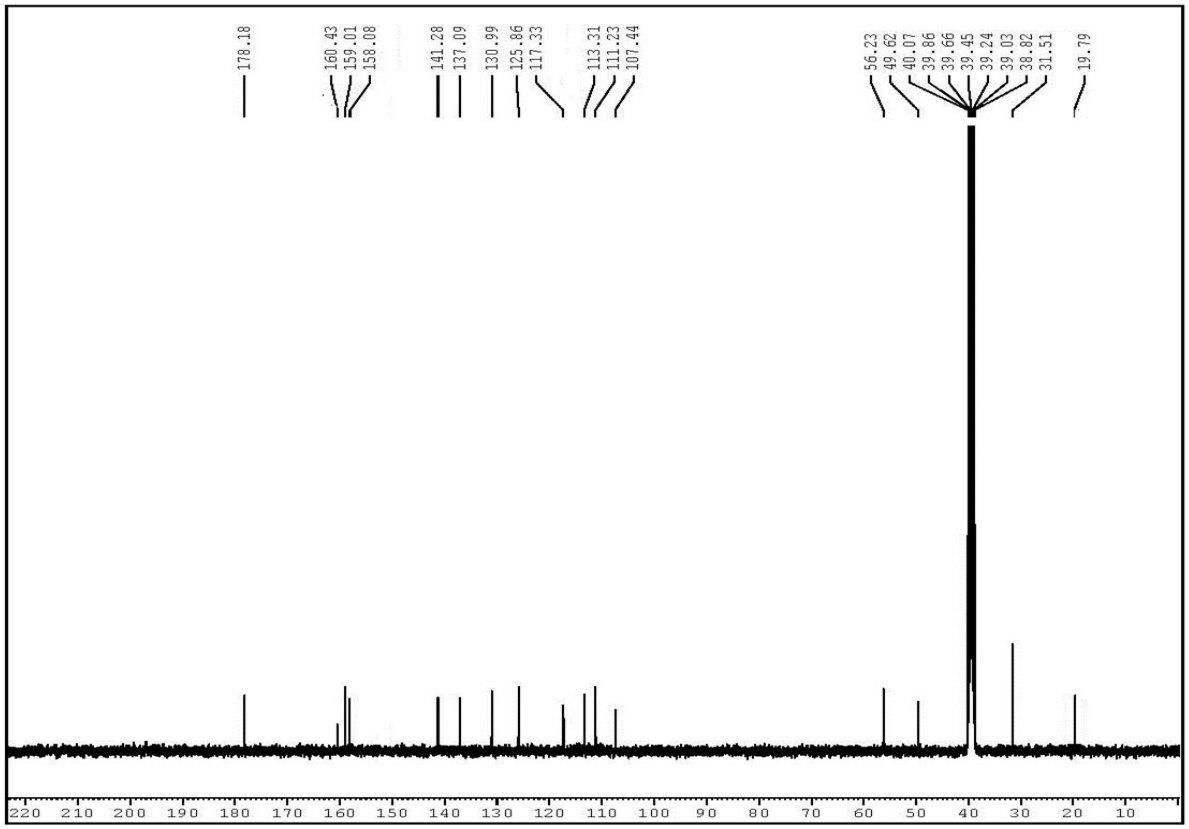
Copy of ^{1}H NMR for the compund (**5b**).



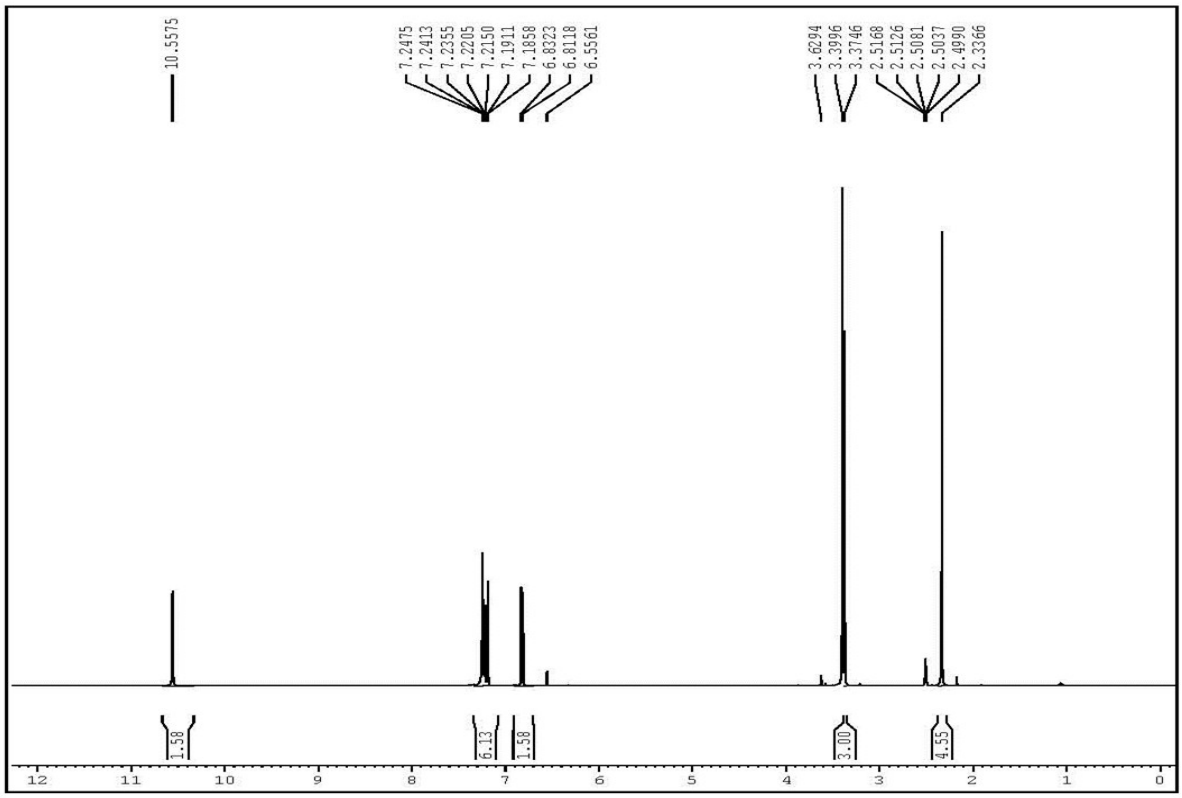
Copy of ^{13}C NMR for the compund (**5b**).



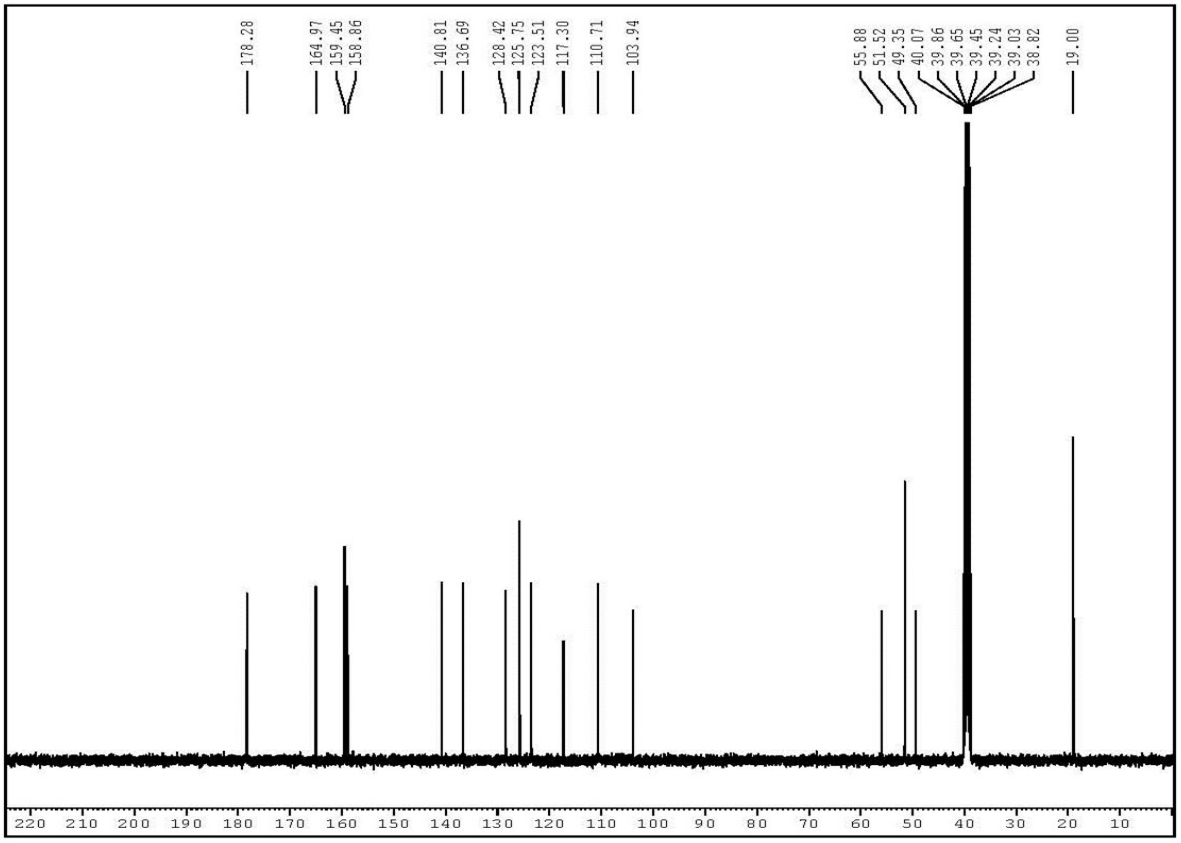
Copy of ^{1}H NMR for the compund (**5c**).



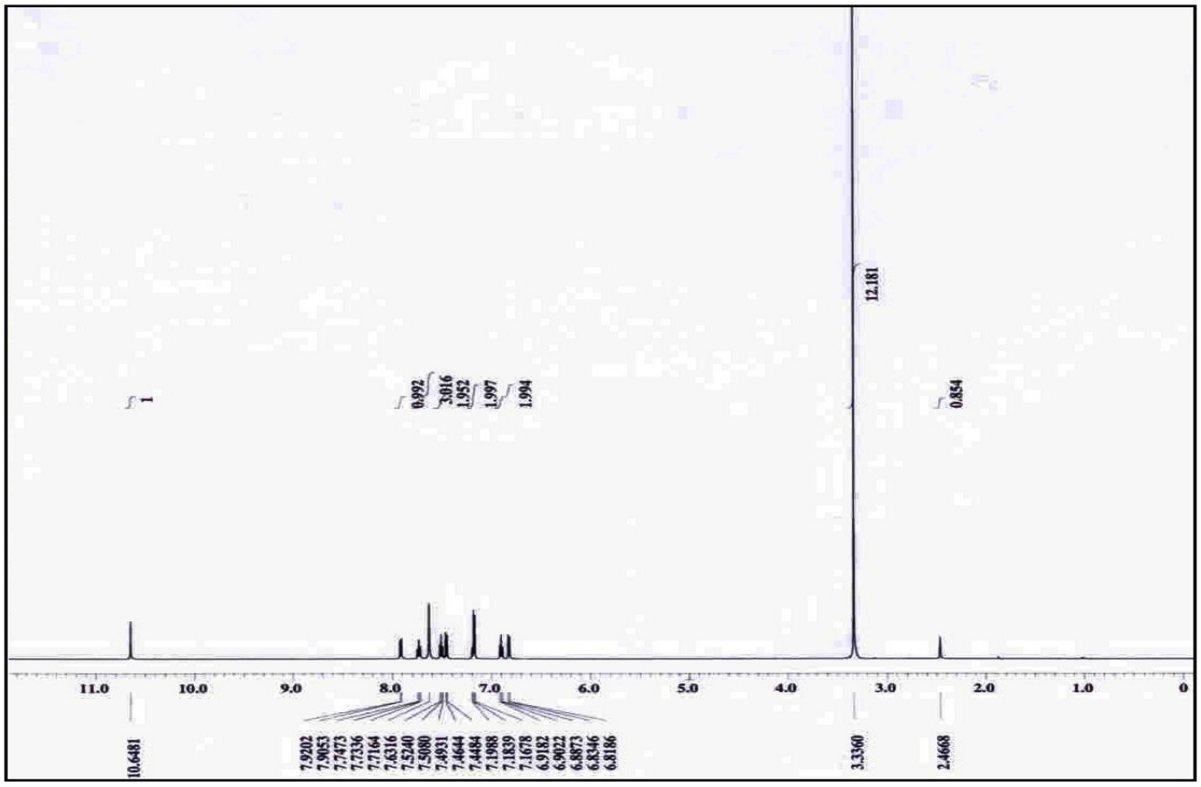
Copy of ^{13}C NMR for the compund (**5c**).



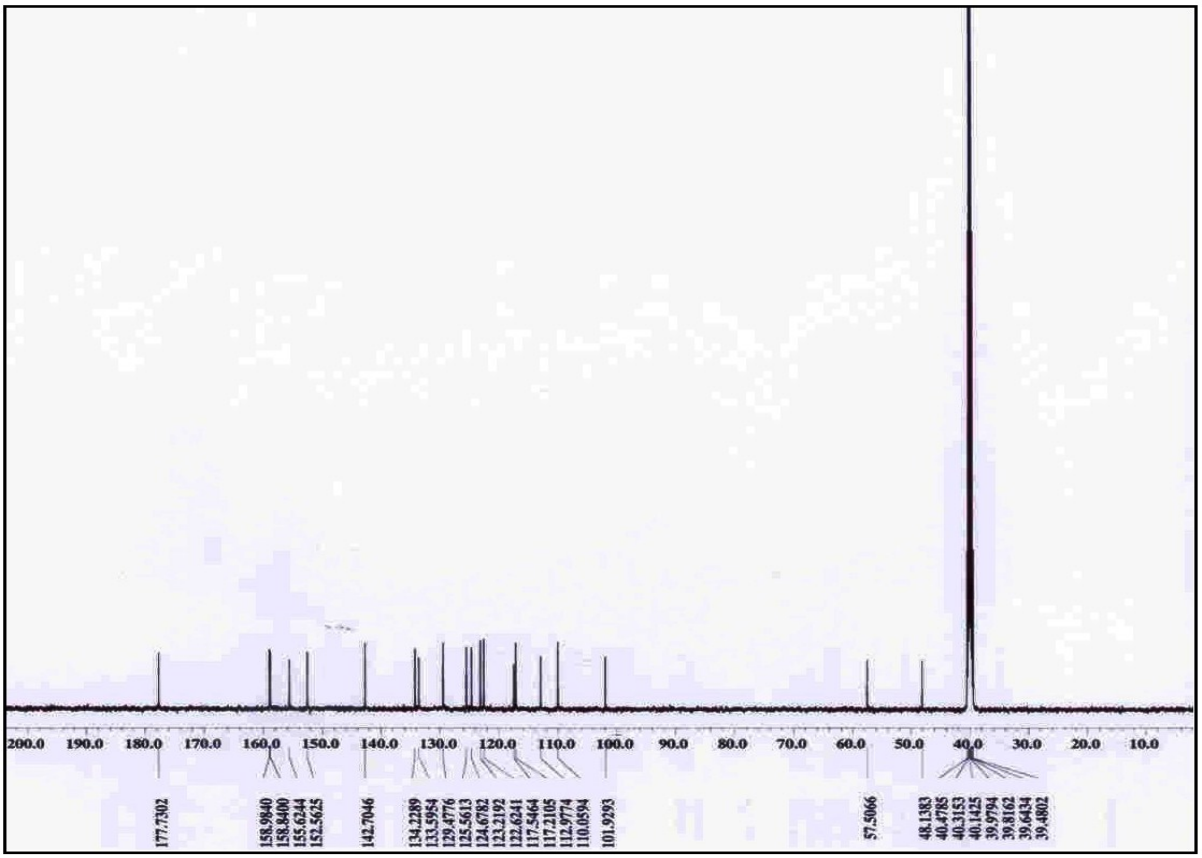
Copy of ^{1}H NMR for the compund (**5d**).



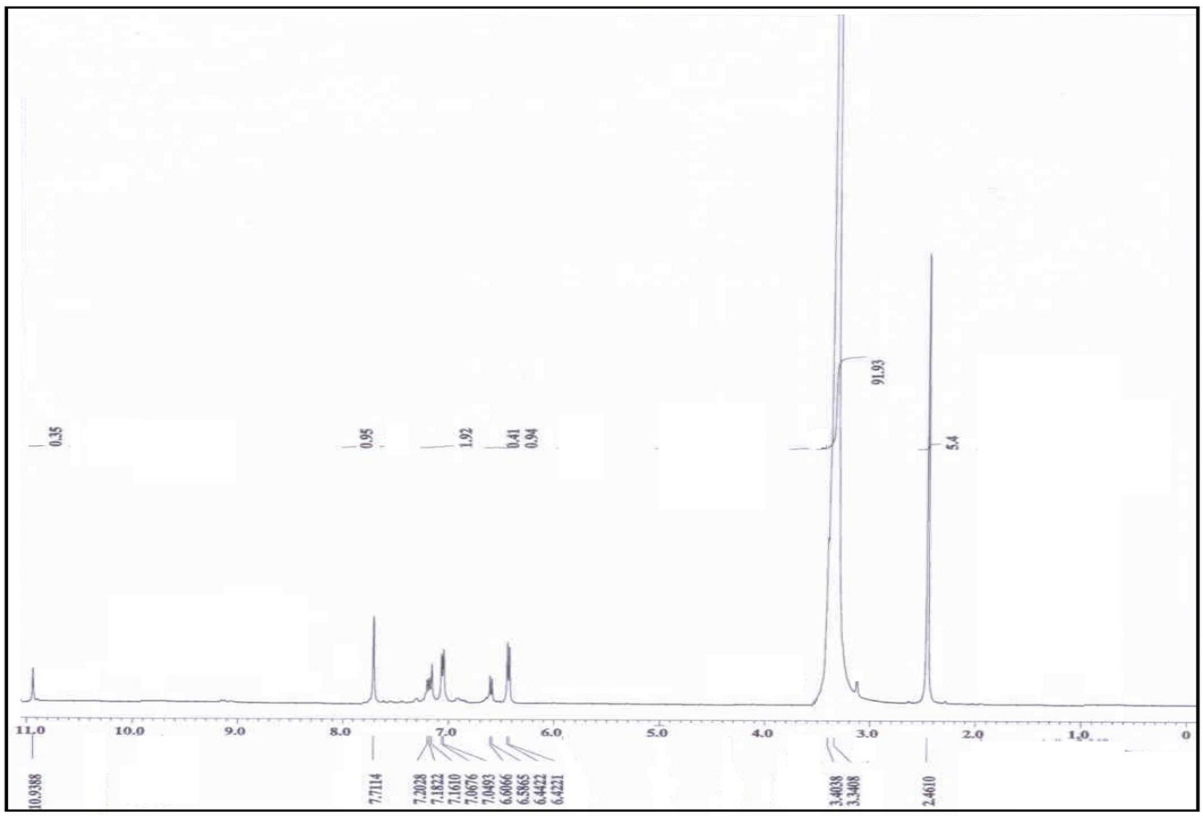
Copy of ^{13}C NMR for the compund (**5d**).



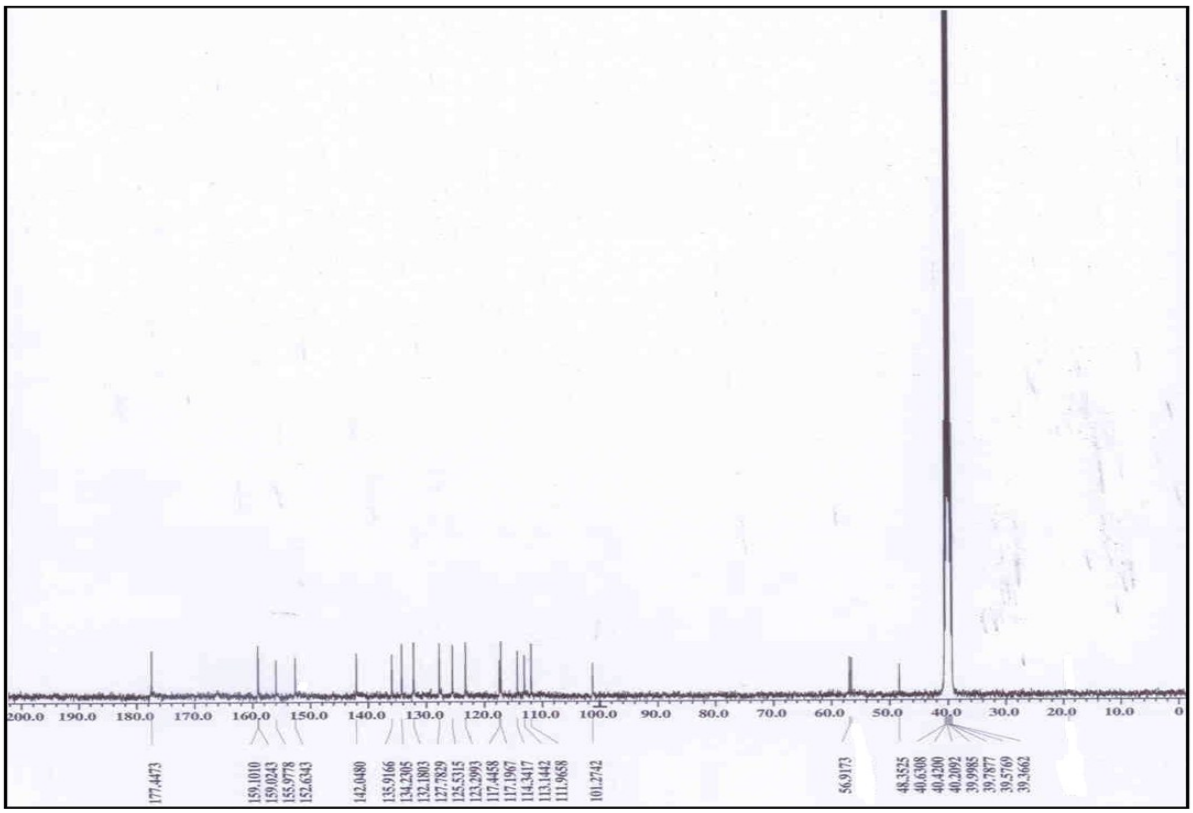
Copy of ^{1}H NMR for the compund (**6a**).



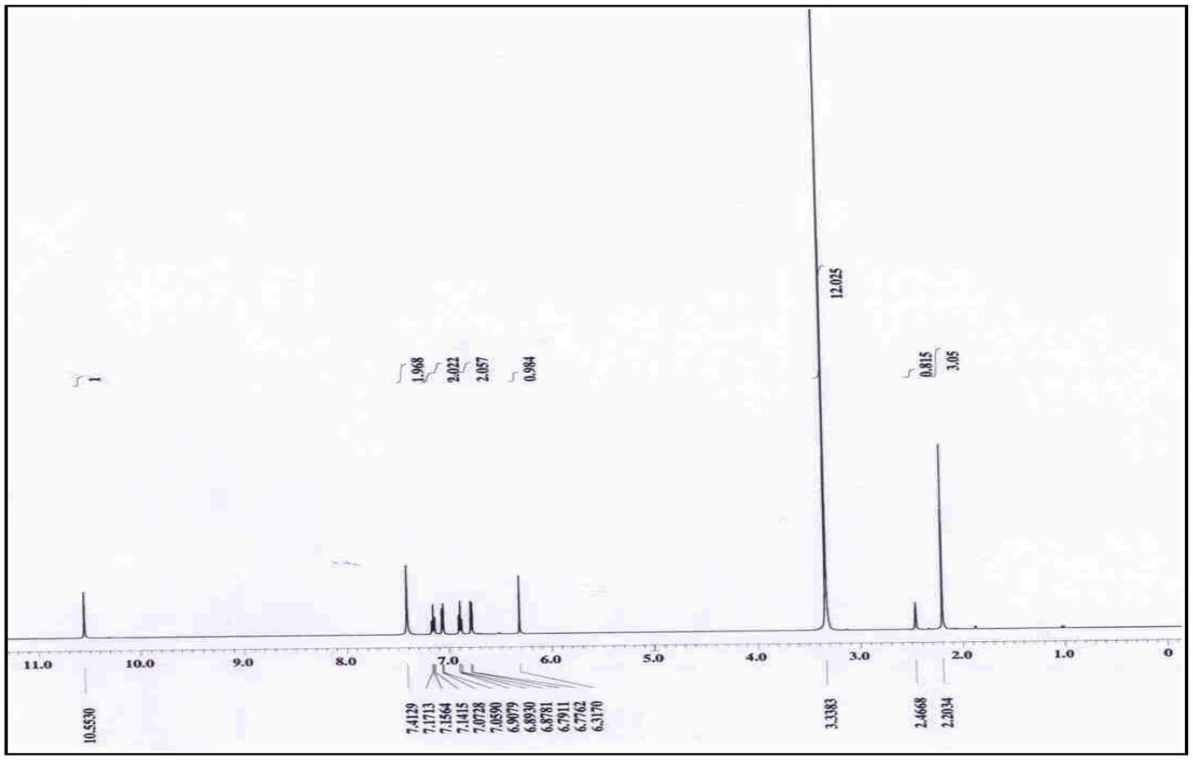
Copy of ^{13}C NMR for the compund (**6a**).



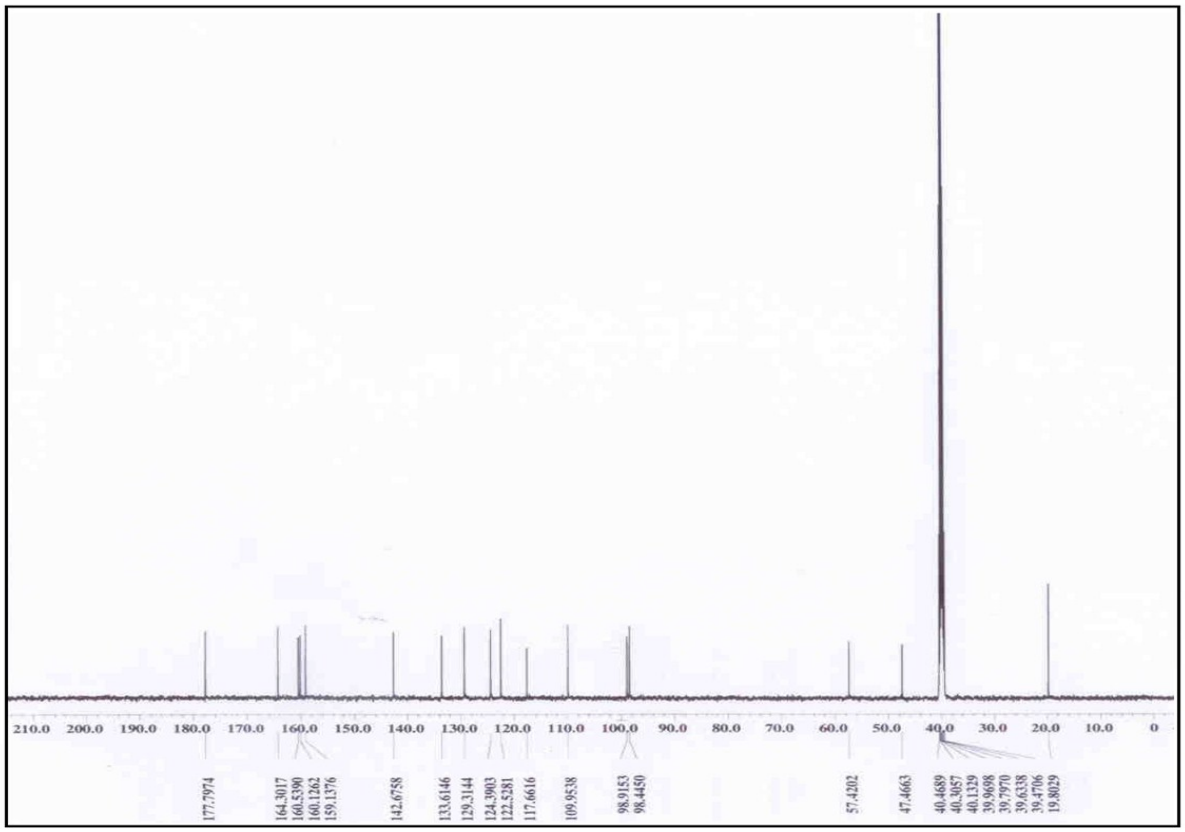
Copy of ^{1}H NMR for the compund (**6b**).



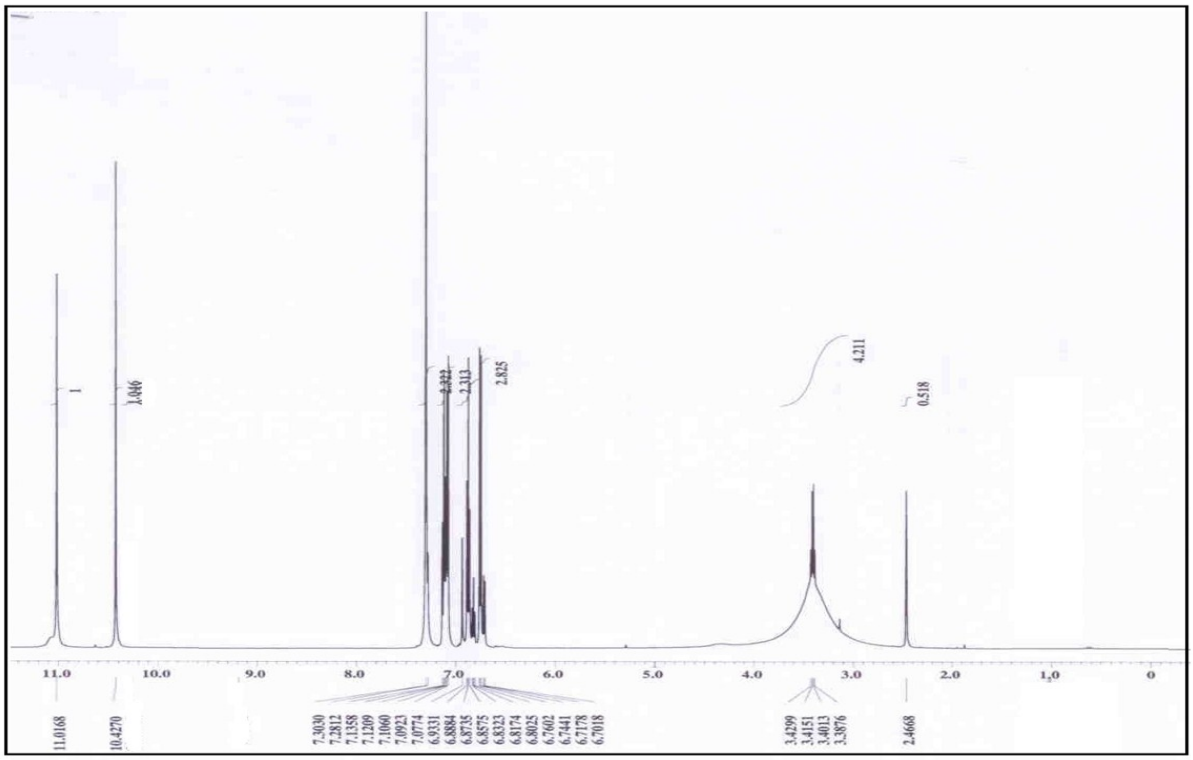
Copy of ^{13}C NMR for the compund (**6b**).



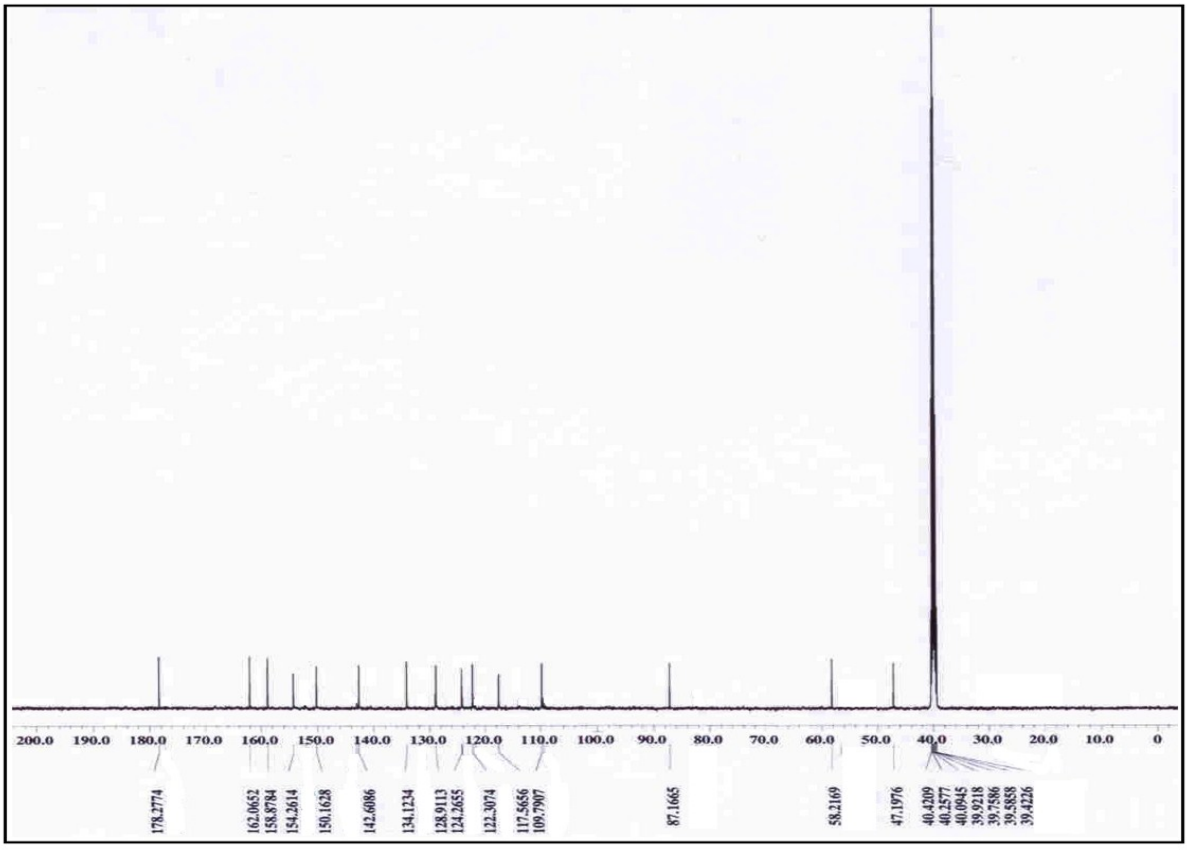
Copy of ^{1}H NMR for the compund (**6c**).



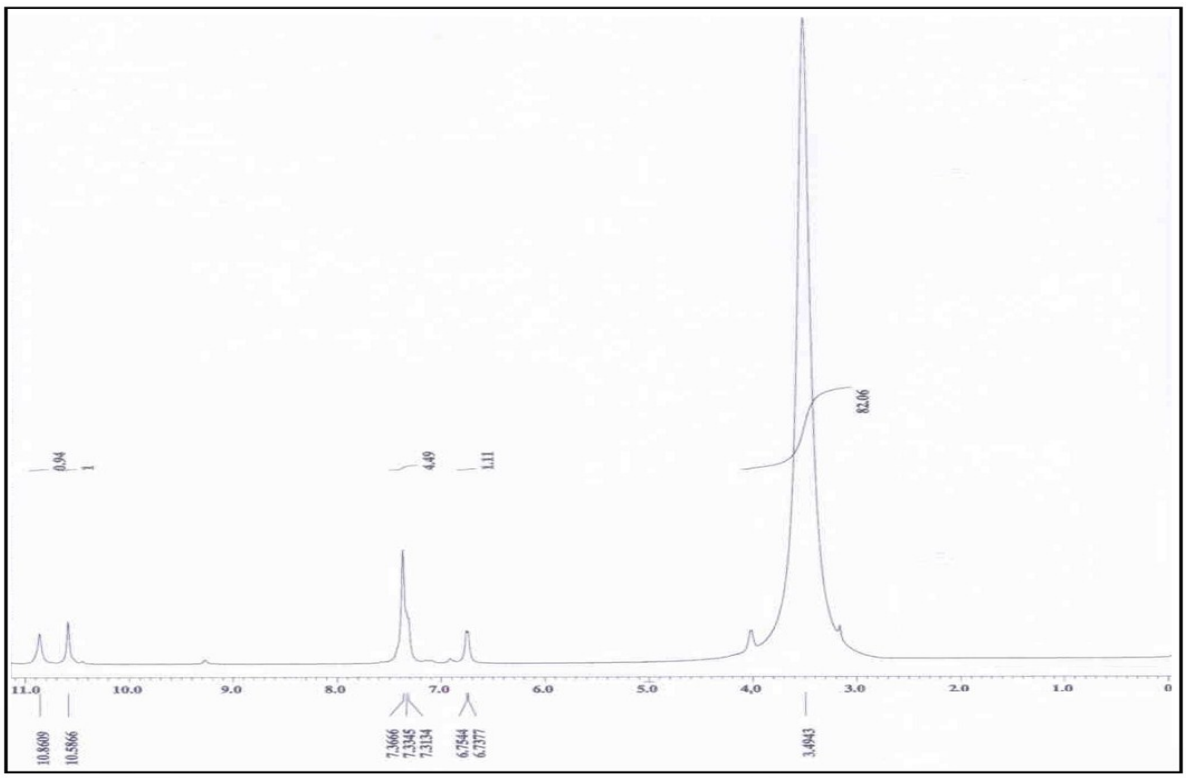
Copy of ^{13}C NMR for the compund (**6c**).



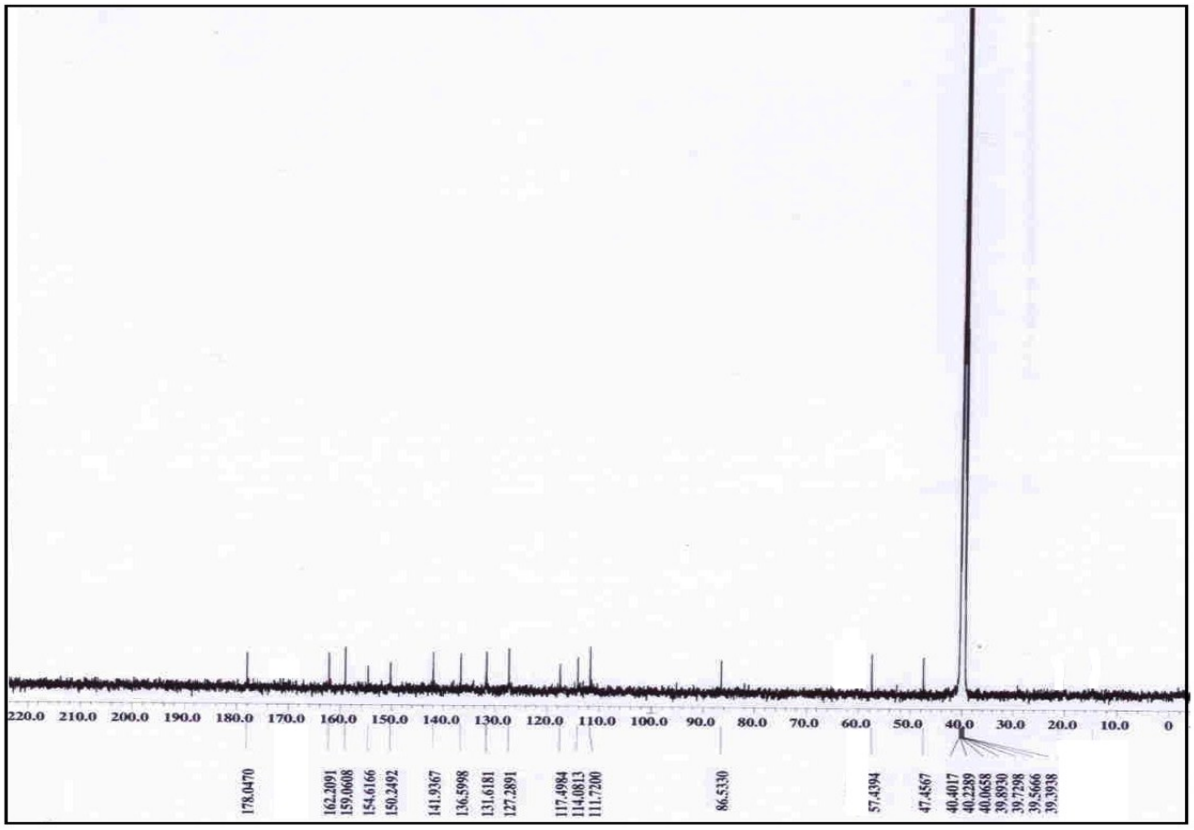
Copy of ^{1}H NMR for the compund (**6d**).



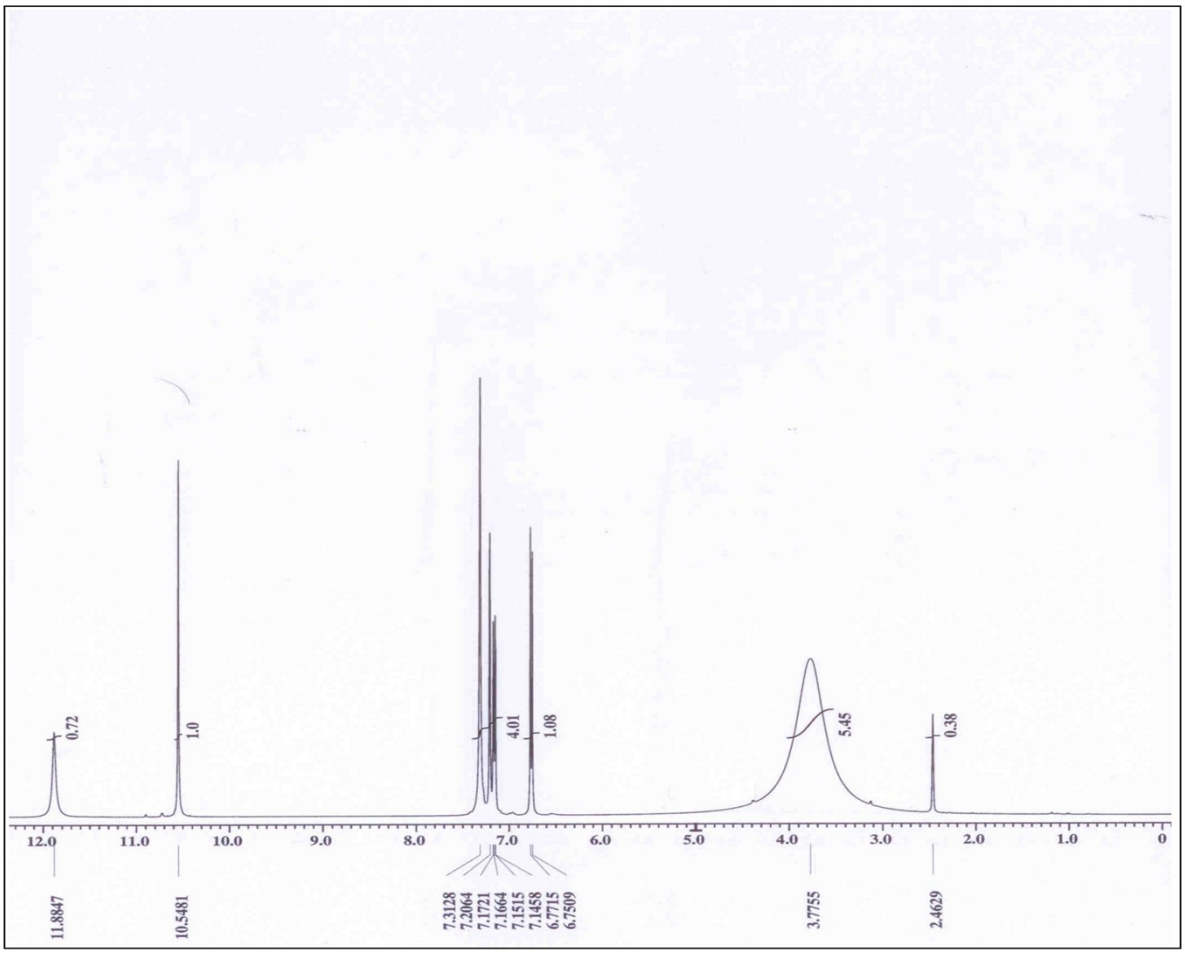
Copy of ^{13}C NMR for the compund (**6d**).



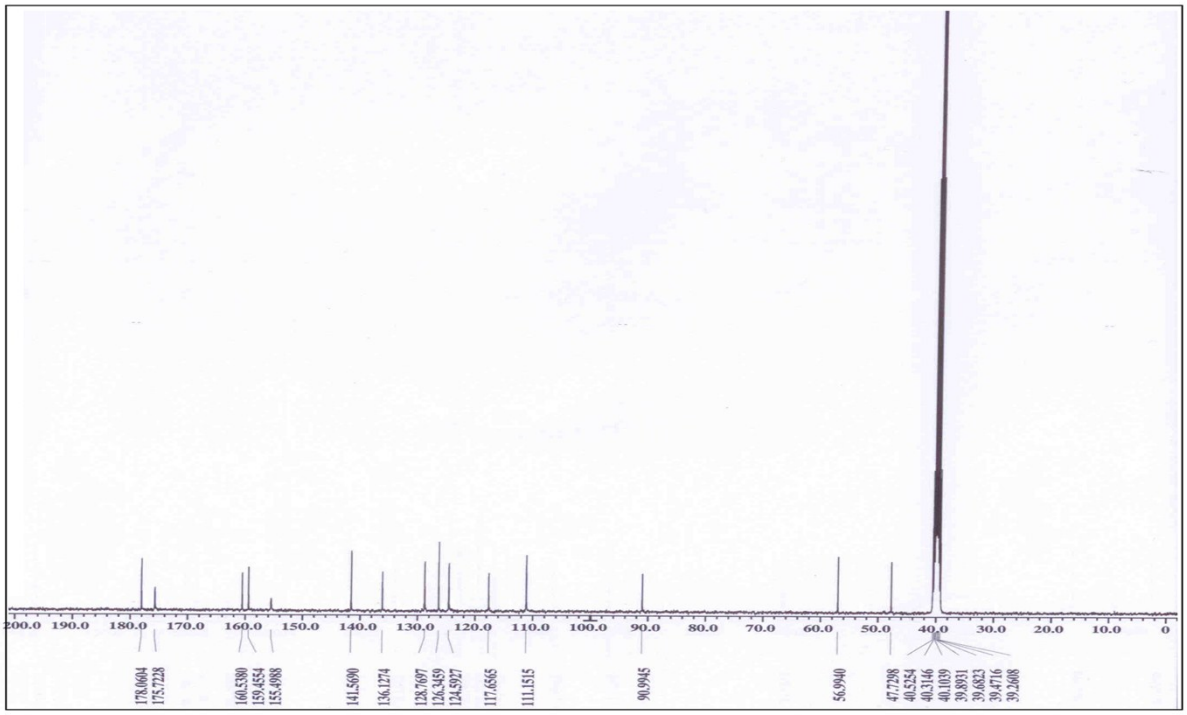
Copy of ^{1}H NMR for the compund (**6e**).



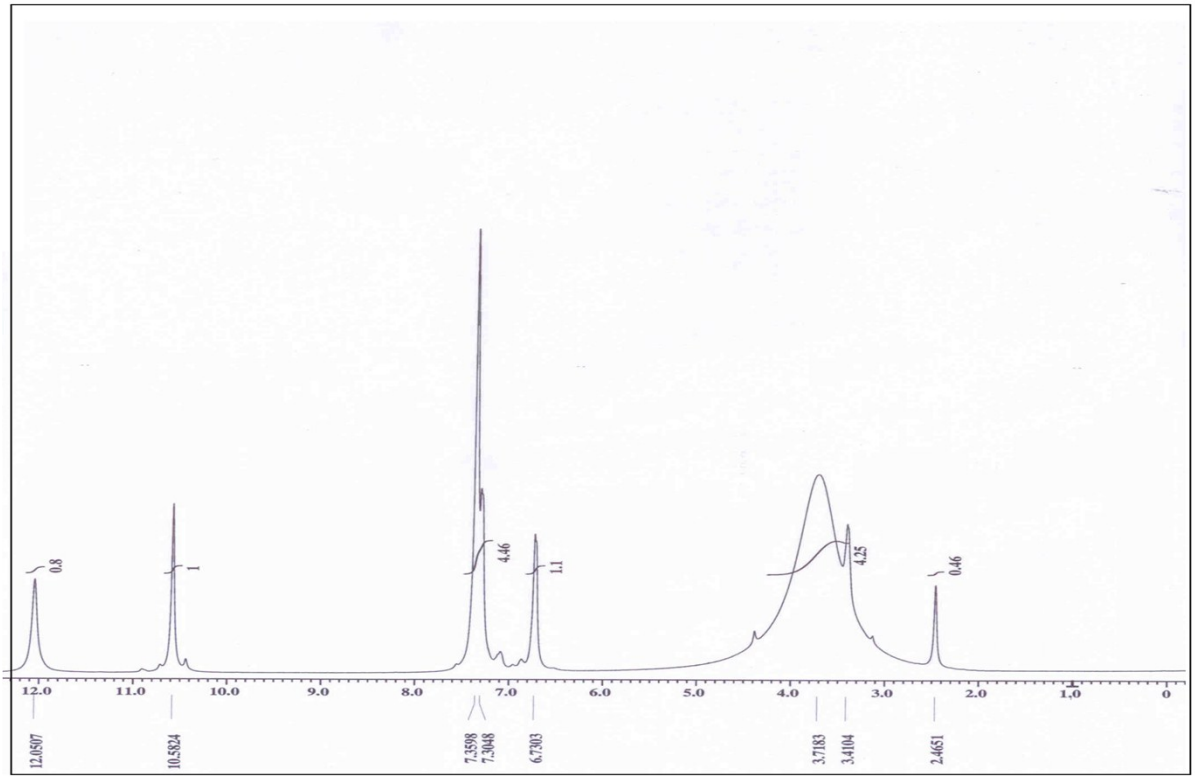
Copy of ^{13}C NMR for the compund (**6e**).



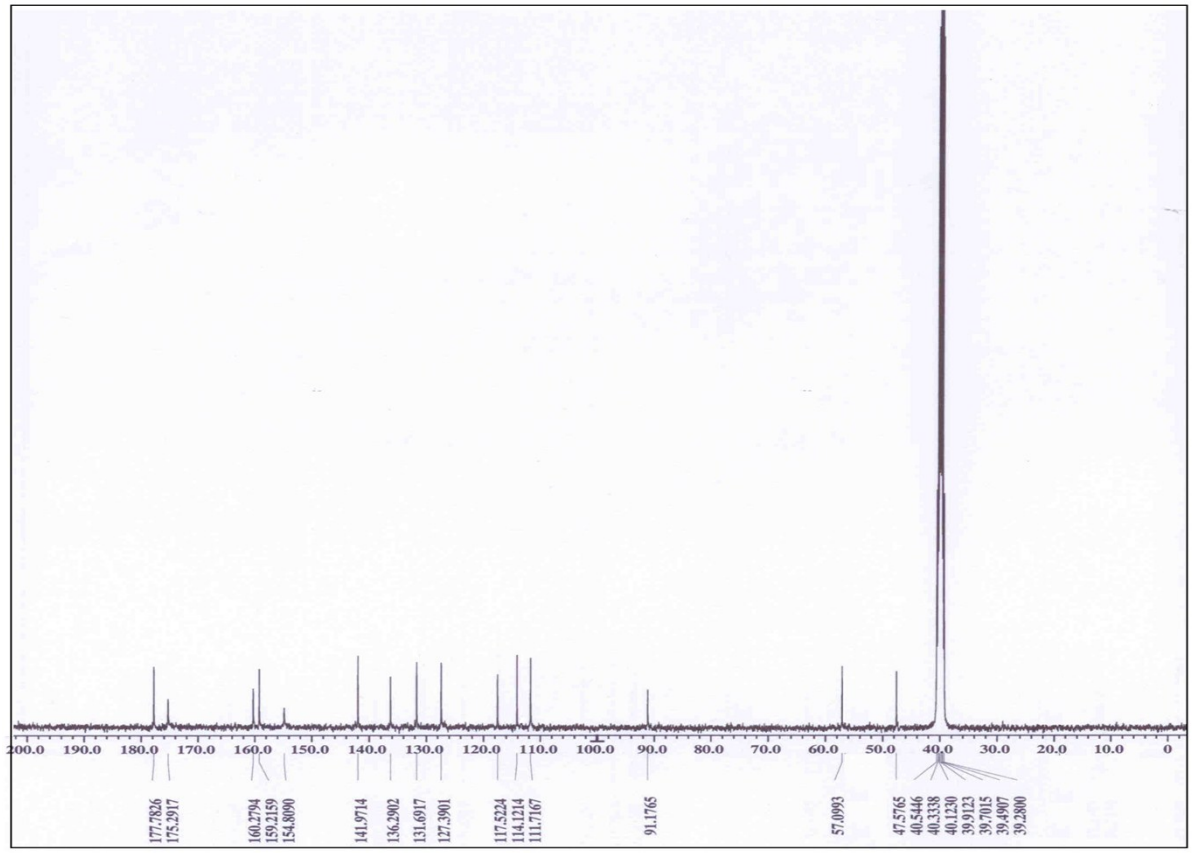
Copy of ^{1}H NMR for the compund (**6f**).



Copy of ^{13}C NMR for the compund (**6f**).



Copy of ^{1}H NMR for the compund (**6g**).



Copy of ^{13}C NMR for the compund (**6g**).