Electronic Supplementary Information (ESI) for

Catalyst-free domino reaction in water/ethanol: An efficient, regio- and chemoselective one-pot multi-component synthesis of pyranopyrazole derivatives

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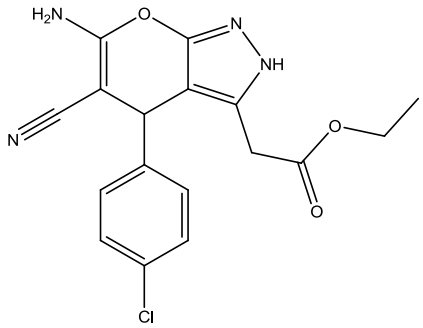
General Information

All starting materials were obtained from Merck or Fluka, and were used without further purification. Melting points were determined on an Electrothermal 9100 apparatus and were not corrected. IR spectra were obtained as potassium bromide pellets with a BOMEM-MB-series FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker-DRX-300-Avance spectrometer at and 300 and 75 MHz, respectively, in DMSO and in the presence of TMS as internal standard. HR-ESIMS spectra were acquired on a Bruker MicroTOF ESI-MS system. Elemental analyses were performed using a Heraeus CHN-O Rapid analyzer.

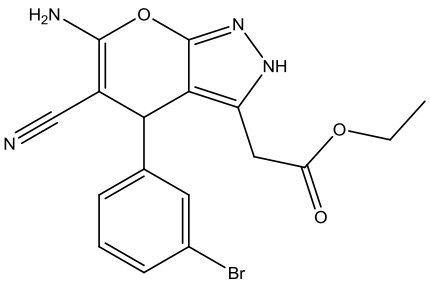
General procedure for the synthesis of 5: A mixture of the hydrazine hydrate (**2**, 1 mmol, 0.05 mL) and dialkyl-3-oxopentanedioate (**1**, 1 mmol) in water/ethanol (10 mL/ 8:2) was magnetically stirred for 30 min at 60 ^{o}C followed by the addition of aldehyde (**3**, 1 mmol) and malononitril (**4**, 1 mmol). The reaction mixture was stirred for 12 h at 60 ^{o}C. Then, the mixture was cooled to r.t. and 10 ml of water was added and the resulting mixture was stirred for 30 min. The precipitated product was filtered, washed with water. The products were further purified by recrystallization in ethanol.

Typical procedure for the synthesis of ethyl 2-(6-amino-4-(4-chlorophenyl)-5-cyano-2,4-dihydropyrano[2,3-c]pyrazol-3-yl)acetate (5a): A mixture of the hydrazine hydrate (1 mmol, 0.05 mL) and diethyl-3-oxopentanedioate (1 mmol , 0.18 mL) in water/ethanol (10 mL/ 8:2) was magnetically stirred for 30 min at 60 ^{o}C followed by the addition of 4-chlorobenzaldehyde (1 mmol, 0.14 g) and malononitril (1 mmol, 0.07 g). The reaction mixture was stirred for 12 h at 60 ^{o}C. Then, the mixture was cooled to room temperature and 10 ml of water was added and the

resulting mixture was stirred for 30 min. The precipitated product was filtered, washed with water. The products were further purified by recrystallization in ethanol.

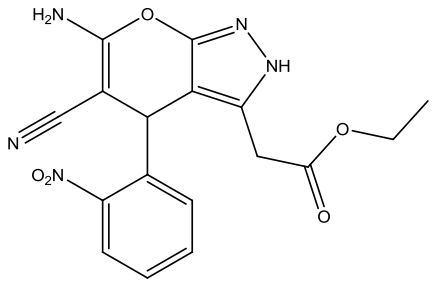


Ethyl 2-(6-amino-4-(4-chlorophenyl)-5-cyano-2,4-dihydropyrano[2,3-c]pyrazol-3-yl)acetate (5a). Yield: 75%, mp 197-199 °C; IR (KBr): 3270, 3114, 3098, 2183, 1729, 1620; ^{1}H NMR (300 MHz, DMSO-d_6) δ_H 1.08 (*t*, *J* = 7.0 Hz, 3H), 3.18 (*d*, *J* = 17.1 Hz, 2H), 3.41 (*d*, *J* = 17.1 Hz, 2H), 3.87-3.90 (*m*, 2H), 4.65 (*s*, 1H), 6.99 (*s*, 2H), 7.15 (*d*, *J* = 8.0 Hz, 2H), 7.34 (*d*, *J* = 8.0 Hz, 2H), 12.40 (*s*, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C 13.8, 30.1, 35.5, 56.7, 60.6, 98.4, 120.5, 128.4, 129.4, 131.3, 132.6, 143.1, 160.8, 168.0. HR-MS (ESI) Calcd for $C_{17}H_{15}ClN_4O_3$ [M+1] 259.0911 found 259.0912. Anal. Calcd. for $C_{17}H_{15}ClN_4O_3$: C, 56.91; H, 4.21; N, 15.62%. found: C, 56.89; H, 4.20; N, 15.61%.

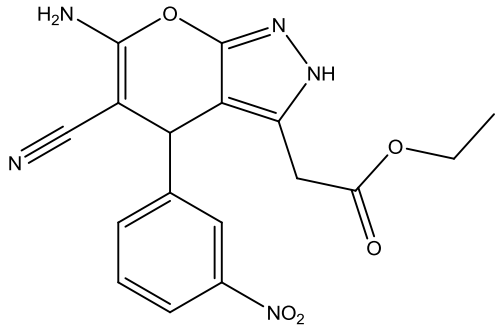


Ethyl 2-(6-amino-4-(3-bromophenyl)-5-cyano-2,4-dihydropyrano[2,3-c]pyrazol-3-yl)acetate (5b). Yield: 78%, mp 194-196 °C; IR (KBr): 3477, 3273, 3100, 2182, 1729, 1642, 1594. ^{1}H NMR (300 MHz, DMSO-d_6) δ_H 1.09 (*t*, *J* = 5.0 Hz, 3H), 3.20 (*d*, *J* = 20.0 Hz, 2H), 3.48 (*d*, *J* = 20.0 Hz, 2H), 3.85-3.91 (*m*, 2H), 4.66 (*s*, 1H), 7.02 (*s*, 2H), 7.14-7.16 (*m*, 1H), 7.26-7.30 (*m*, 2H), 7.42-7.44 (*m*, 1H), 12.44 (*s*, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C 13.8, 30.1, 35.7, 56.4, 60.7, 98.2, 120.5, 121.7, 126.7, 129.7, 130.1, 130.7, 132.5, 146.8, 154.5, 160.9, 168.0. HR-MS (ESI)

Calcd for $C_{17}H_{15}BrN_4O_3$ [M+Na] 425.0225 found 425.0230. Anal. Calcd. for $C_{17}H_{15}BrN_4O_3$: C, 50.64; H, 3.75; N, 13.89%. found: C, 50.66; H, 3.78; N, 13.92%.

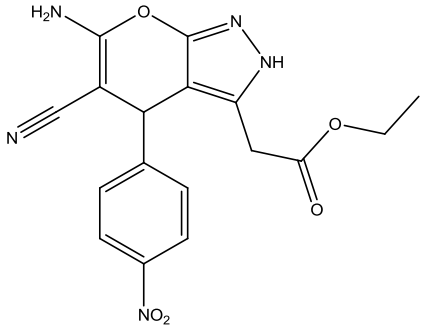


Ethyl 2-(6-amino-5-cyano-4-(2-nitrophenyl)-2,4-dihydropyrano[2,3-c]pyrazol-3-yl)acetate (5c). Yield: 60%, mp 192-194 °C; IR (KBr): 3418, 3332, 3201, 2190, 1742, 1639, 1593. ^{1}H NMR (300 MHz, DMSO-d_6) δ_H 1.03 (*t*, *J* = 6.9 Hz, 3H), 3.09 (*d*, *J* = 17.4 Hz, 2H), 3.41 (*d*, *J* = 17.7 Hz, 2H), 3.80-3.83 (*m*, 2H), 5.13 (*s*, 1H), 7.07 (*s*, 1H), 7.25-7.27 (*m*, 1H), 7.47 (*m*, 1H), 7.61-7.63 (*m*, 1H), 7.84-787 (*m*, 1H), 12.45 (*s*, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C 14.26, 30.63, 31.67, 56.56, 61.16, 98.20, 120.50, 124.1, 128.8, 131.9, 134.0, 138.0, 149.2, 161.5, 168.3. HR-MS (ESI) Calcd for $C_{17}H_{15}N_5O_5$ [M+1] 370.1151 found 370.1159. Anal. Calcd. for $C_{17}H_{15}N_5O_5$: C, 55.28; H, 4.09; N, 18.96%. found: C, 55.30; H, 4.07; N, 18.98%.

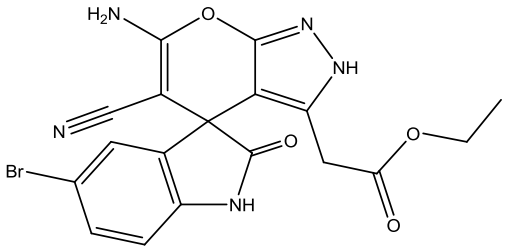


Ethyl 2-(6-amino-5-cyano-4-(3-nitrophenyl)-2,4-dihydropyrano[2,3-c]pyrazol-3-yl)acetate (5d). Yield: 68%, mp 187-189 °C. IR (KBr): 3474, 3230, 2189, 1730, 1638, 1598. ^{1}H NMR (300 MHz, DMSO-d_6) δ_H 1.01 (*t*, *J* = 7.1 Hz, 3H), 3.23 (*d*, *J* = 17.1 Hz, 2H), 3.48 (*d*, *J* = 17.1 Hz, 2H), 3.72-3.83 (*m*, 2H), 4.87 (*s*, 1H), 7.10 (*s*, 1H), 7.61-7.66 (*m*, 2H), 7.99 (*s*, 1H), 8.09-8.10 (*m*, 1H), 7.84-787 (*m*, 1H), 12.44 (*s*, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C 13.7, 30.6, 35.4, 56.7, 61.0, 97.2, 120.1, 122.4, 129.2, 132.2, 135.1, 138.3, 139.2, 140.6, 148.0, 161.2, 167.8. HR-MS (ESI) Calcd for $C_{17}H_{15}N_5O_5$ [M+1] 370.1151 found 370.1158.

Anal. Calcd. for $C_{17}H_{15}N_5O_5$: C, 55.28; H, 4.09; N, 18.96%. found: C, 55.31; H, 4.06; N, 18.98%.

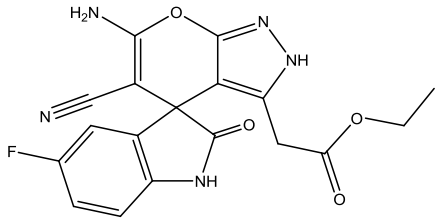


Ethyl 2-(6-amino-5-cyano-4-(4-nitrophenyl)-2,4-dihydropyrano[2,3-c]pyrazol-3-yl)acetate (5e). Yield: 65%, mp 185-188 °C; IR (KBr): 3429, 3336, 3234, 2189, 1733, 1621, 1508. ^{1}H NMR (300 MHz, DMSO-d_6) δ_H 1.04 (*t*, *J* = 7.0 Hz, 3H), 3.24 (*d*, *J* = 17.2 Hz, 2H), 3.47 (*d*, *J* = 17.2 Hz, 2H), 3.80-3.84 (*m*, 2H), 4.85 (*s*, 1H), 7.09 (*s*, 2H), 7.45 (*d*, *J* = 8.6 Hz, 2H), 8.21 (*d*, *J* = 8.6 Hz, 1H), 12.42 (*s*, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C 13.7, 30.2, 35.9, 55.9, 60.6, 97.7, 123.8, 128.9, 132.6, 146.4, 151.8, 161.0, 162.0, 168.0. HR-MS (ESI) Calcd for $C_{17}H_{15}N_5O_5$ [M+1] 370.1151 found 370.1148. Anal. Calcd. for $C_{17}H_{15}N_5O_5$: C, 55.28; H, 4.09; N, 18.96%. found: C, 55.32; H, 4.12; N, 18.92%.

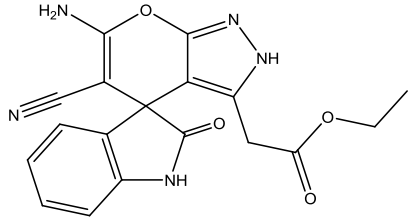


Ethyl 2-(6'-amino-5-bromo-5'-cyano-2-oxo-2'*H*-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-yl)acetate (5f). Yield: 85%, mp 234-236 °C; IR (KBr): 3310, 3174, 2194, 1730, 1629, 1596. ^{1}H NMR (300 MHz, DMSO-d_6) δ_H 1.07 (*t*, *J* = 7.5 Hz, 3H), 3.06 (*d*, *J* = 17.5 Hz, 2H), 3.85 (*d*, *J* = 17.5 Hz, 2H), 6.05-7.50 (*m*, 3H, 2H), 10.73 (*s*, 1H), 12.61 (*s*, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C 13.8, 29.8, 47.4, 54.6, 60.8, 95.6, 111.8, 114.1, 118.5, 127.6, 131.6, 131.9, 134.3, 140.8, 155.2, 162.5, 167.4, 177.3. HR-MS (ESI) Calcd for $C_{18}H_{14}BrN_5O_4$ [M+1] 444.0302 found 444.0309.

Anal. Calcd. for $C_{18}H_{14}BrN_5O_4$: C, 48.67; H, 3.18; N, 15.76%. found: C, 48.69; H, 3.22; N, 15.73%.

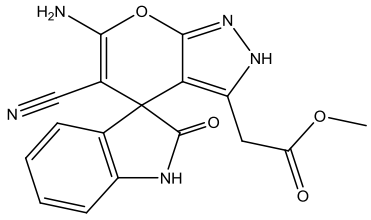


Ethyl 2-(6'-amino-5'-cyano-5-fluoro-2-oxo-2'*H*-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-yl)acetate (5g). Yield: 82%, mp 254-256 °C; IR (KBr): 3433, 3320, 2190, 1719, 1641, 1582. ^{1}H NMR (300 MHz, DMSO-d_6) δ_H 1.06 (*t*, *J* = 7.5 Hz, 3H), 2.87-3.15 (*m*, 2H), 3.80-3.88 (*m*, 2H), 6.89-6.94 (*m*, 1H), 7.33 (*s*, 1H), 10.60 (*s*, 1H), 12.58 (*s*, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C 13.7, 29.8, 47.6, 54.8, 60.7, 95.8, 110.7 (*d*, $^3J_{C\text{-}F}$ = 31.0 Hz), 112.5 (*d*, $^2J_{C\text{-}F}$ = 100.0 Hz), 115.4 (*d*, $^2J_{C\text{-}F}$ = 100.0 Hz), 115.6, 118.5, 131.6, 131.6, 133.6 (*d*, $^3J_{C\text{-}F}$ = 15.5 Hz), 137.7 (*d*, $^4J_{C\text{-}F}$ = 5.0 Hz), 155.2, 157.5, 159.4, 162.5, 167.4, 177.7. HR-MS (ESI) Calcd for $C_{18}H_{14}FN_5O_4$ [M+H] 384.1158 found 384.1153. Anal. Calcd. for $C_{18}H_{14}FN_5O_4$: C, 56.40; H, 3.68; F, 4.96; N, 18.27%. found: C, 56.39; H, 3.69; N, 18.26%.

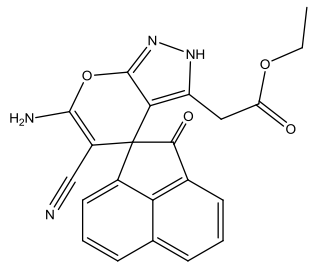


Ethyl 2-(6'-amino-5'-cyano-2-oxo-2'*H*-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-yl)acetate (5h). Yield: 85%, mp 233-235 °C; IR (KBr): 3549, 3164, 2191, 1723, 1612, 1486. ^{1}H NMR (300 MHz, DMSO-d_6) δ_H 1.05 (*t*, *J* = 7.5 Hz, 3H), 2.96 (AB*q*, *J* = 17.5 Hz, 2H), 3.85-3.85 (*m*, 2H), 6.88-6.90 (*m*, 1H), 6.99 (*s*, 1H), 7.23-7.27 (*m*, 3H), 10.54 (*s*, 1H), 12.53 (*s*, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C 13.8, 29.7, 47.1, 55.3, 60.7, 96.3, 109.7, 118.6, 122.3, 124.7, 129.0, 131.6, 131.8, 141.6, 155.2, 162.4, 167.4, 177.7. HR-MS (ESI) Calcd for

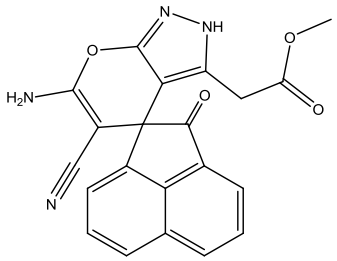
$C_{18}H_{15}N_5O_4$ [M+Na] 388.1022 found 388.1031. Anal. Calcd. for $C_{18}H_{15}N_5O_4$: C, 59.18; H, 4.14; N, 19.17%. found: C, 59.17; H, 4.15; N, 19.17%.



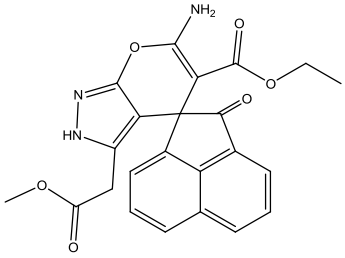
Methyl 2-(6'-amino-5'-cyano-2-oxo-2'*H*-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-yl)acetate (5i). Yield: 75%, mp 268-270 °C; IR (KBr): 3549, 3164, 2191, 1723, 1612, 1486. ^{1}H NMR (300 MHz, DMSO-d_6) δ_H 2.41 (*d, J* = 17.5 Hz, 2H), 2.67 (*d, J* = 17.1 Hz, 2H), 3.04 (*s*, 3H), 7.36-7.43 (*m*, 1H), 7.72-8.07 (*m*, 4H), 8.36-8.40 (*m*, 1H), 12.53 (*s*, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C 30.0, 47.6, 52.3, 55.8, 96.8, 110.3, 119.0, 122.8, 125.2, 129.5, 132.0, 132.2, 142.0, 155.7, 162.9, 168.3, 178.1. HR-MS (ESI) Calcd for $C_{17}H_{13}N_5O_4$ [M+1] 352.1042 found 352.1046. Anal. Calcd. for $C_{17}H_{13}N_5O_4$: C, 58.12; H, 3.73; N, 19.93;%. found: C, 58.10; H, 3.71; N, 19.90%.



Ethyl 2-(6'-amino-5'-cyano-2-oxo-2*H*,2'*H*-spiro[acenaphthylene-1,4'-pyrano[2,3-c]pyrazole]-3'-yl)acetate (5j). Yield: 87%, mp 219-221 °C; IR (KBr): 3408, 3130, 2189, 1728, 1644, 1593. ^{1}H NMR (300 MHz, DMSO-d_6) δ_H 0.84 (*t, J* = 7.5 Hz, 3H), 2.43 (*d, J* = 17.5 Hz, 2H), 2.68 (*d, J* = 17.5 Hz, 2H), 3.41-3.49 (*m*, 2H), 7.38 (*s*, 1H), 7.43-7.45 (*m*, 1H), 7.77-7.81 (*m*, 1H), 7.89-7.92 (*m*, 1H), 8.02-8.07 (*m*, 2H), 8.39-8.40 (*m*, 1H), 12.53 (*s*, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C 13.5, 29.7, 51.7, 56.1, 60.4, 97.3, 118.7, 121.6, 122.6, 125.1, 129.0, 129.31, 130.5, 131.7, 132.4, 140.1, 155.3, 162.5, 167.1, 203.2. HR-MS (ESI) Calcd for $C_{22}H_{16}N_4O_4$ [M+Na] 423.1069 found 423.1066. Anal. Calcd. for $C_{22}H_{16}N_4O_4$: C, 66.00; H, 4.03; N, 13.99%. found: C, 65.99; H, 4.02; N, 13.98%.



Methyl 2-(6'-amino-5'-cyano-2-oxo-2*H*,2'*H*-spiro[acenaphthylene-1,4'-pyrano[2,3-c]pyrazole]-3'-yl)acetate (5k). Yield: 76%, mp 239-241 °C; IR (KBr): 3388, 3148, 2188, 1730, 1642, 1591. ^{1}H NMR (300 MHz, DMSO-d_6) δ_H 2.93 (*d*, *J* = 17.5 Hz, 2H), 3.05 (*d*, *J* = 17.1 Hz, 2H), 6.86-6.89 (*m*, 1H), 6.98 (*s*, 1H), 7.23-7.27 (*m*, 3H), 10.55 (*s*, 1H), 12.53 (*s*, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C 30.0, 52.0, 56.5, 61.2, 97.8, 119.2, 122.0, 123.0, 125.6, 129.4, 129.8, 130.5, 131.0, 132.1, 140.5, 141.3, 155.8, 163.0, 168.0, 203.7. HR-MS (ESI) Calcd for $C_{21}H_{14}N_4O_4$ [M+1] 387.1088 found 387.1076. Anal. Calcd. for $C_{21}H_{14}N_4O_4$: C, 65.28; H, 3.65; N, 14.50%. found: C, 65.26; H, 3.67; N, 14.46%.



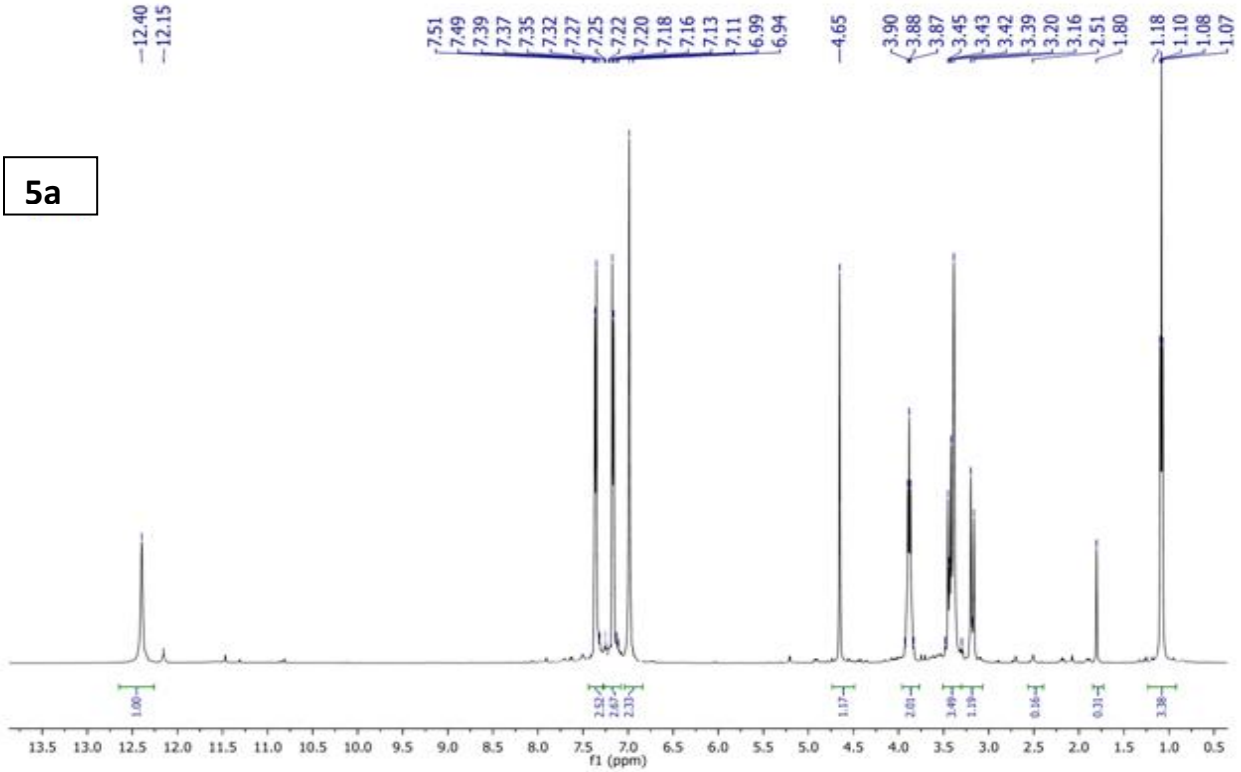
Eethyl 6'-amino-3'-(2-methoxy-2-oxoethyl)-2-oxo-2*H*,2'*H*-spiro[acenaphthylene-1,4'-pyrano[2,3-c]pyrazole]-5'-carboxylate (5l). Yield: 68%, mp 147-150 °C; IR (KBr): 3549, 3164, 2191, 1723, 1612, 1486. ^{1}H NMR (300 MHz, DMSO-d_6) δ_H -0.14 (*t*, *J* = 7.1 Hz, 3H), 2.32 (*d*, *J* = 17.4 Hz, 2H), 3.09 (*s*, 3H), 3.29-3.30 (*m*, 2H), 7.19-7.22 (*m*, 1H), 7.57-7.62 (*m*, 1H), 7.83-7.95 (*m*, 3H), 8.10 (br*s*, 2H), 8.27-8.29 (*m*, 1H), 12.35 (*s*, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C 12.5, 29.9, 51.9, 58.8, 75.4, 99.9, 119.8, 121.8, 124.1, 128.8, 129.4, 130.2, 131.9, 132.7, 140.7, 145.4, 163.3, 167.8, 168.5, 204.7. HR-MS (ESI) Calcd for $C_{23}H_{19}N_3O_6$ [M+Na] 456.1166 found 456.1172. Anal. Calcd. for $C_{23}H_{19}N_3O_6$: C, 63.74; H, 4.42; N, 9.70%. found: C, 63.77; H, 4.41; N, 9.73%.

X-ray crystal structure analysis of 5f

Crystal	5f
Empirical formula	C18 H14 Br1 N5 O4
Color, habit	Colorless , Block
Crystal dimensions (mm)	0.42 x 0.40 x 0.17
Crystal system	Triclinic
Space group	P-1
Z	2
a (Å)	8.4317(8)
b(Å)	12.8686(11)
c(Å)	13.2953(14)
β (°)	81.684(8)
Temperature (K)	120
Volume ($Å^3$)	1257.4(2)
D_{calcd} ($Mg\ m^{-3}$)	1.173
Radiation (Å)	Mo Kα 0.71073
Absorption coeff. (μ) (mm^{-1})	1.661
Absorption correction	Numerical
F (000)	448
θ range for data collection (°)	2.45 to 27.00
Goodness-of-fit on F^2	0.865
Final *R* indices (I>2σ(I))	R1 = 0.0814, wR2 = 0.1825
Largest diff. peak and hole (e $Å^{-3}$)	0.654 and -0.830

Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC: 823135 (5n). Copy of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge DB2 1EZ,UK (fax:+ 44 (1223) 336033; e-mail: deposit@ccdc.cam.ac.uk).

5a


12.40
12.15
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7.25
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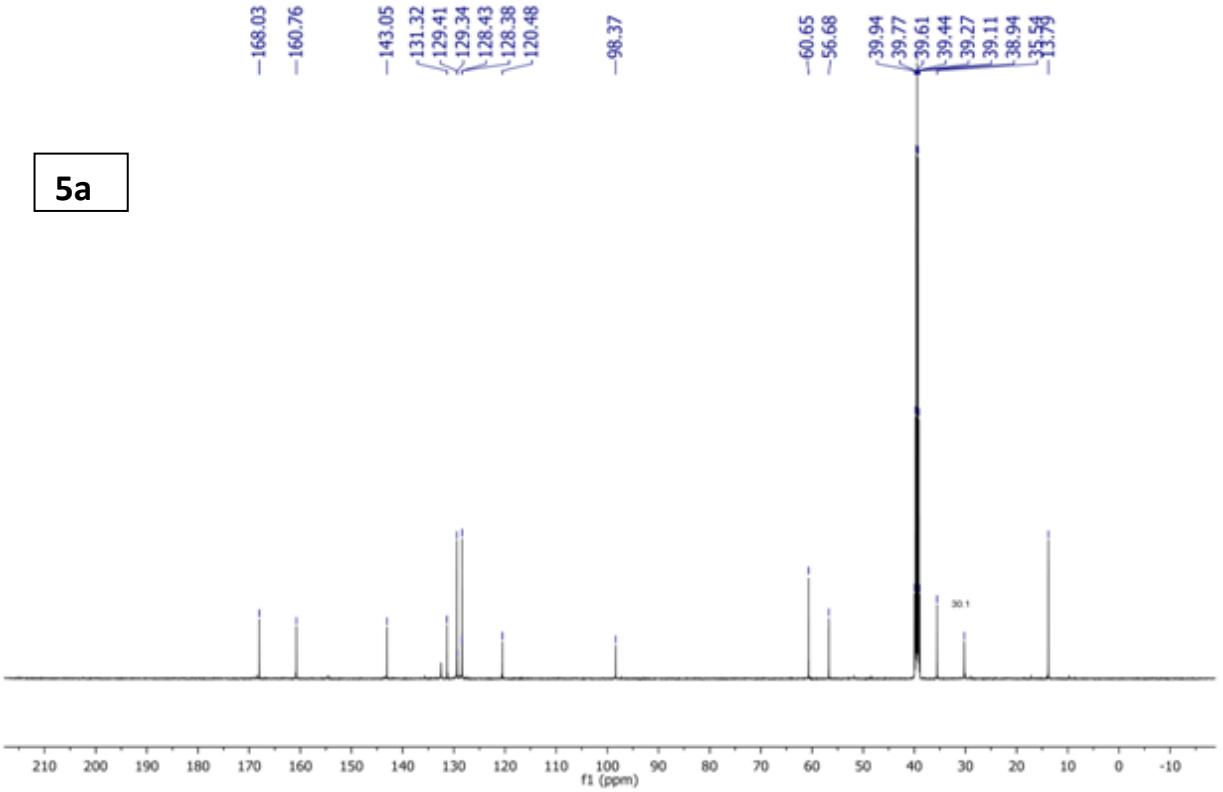
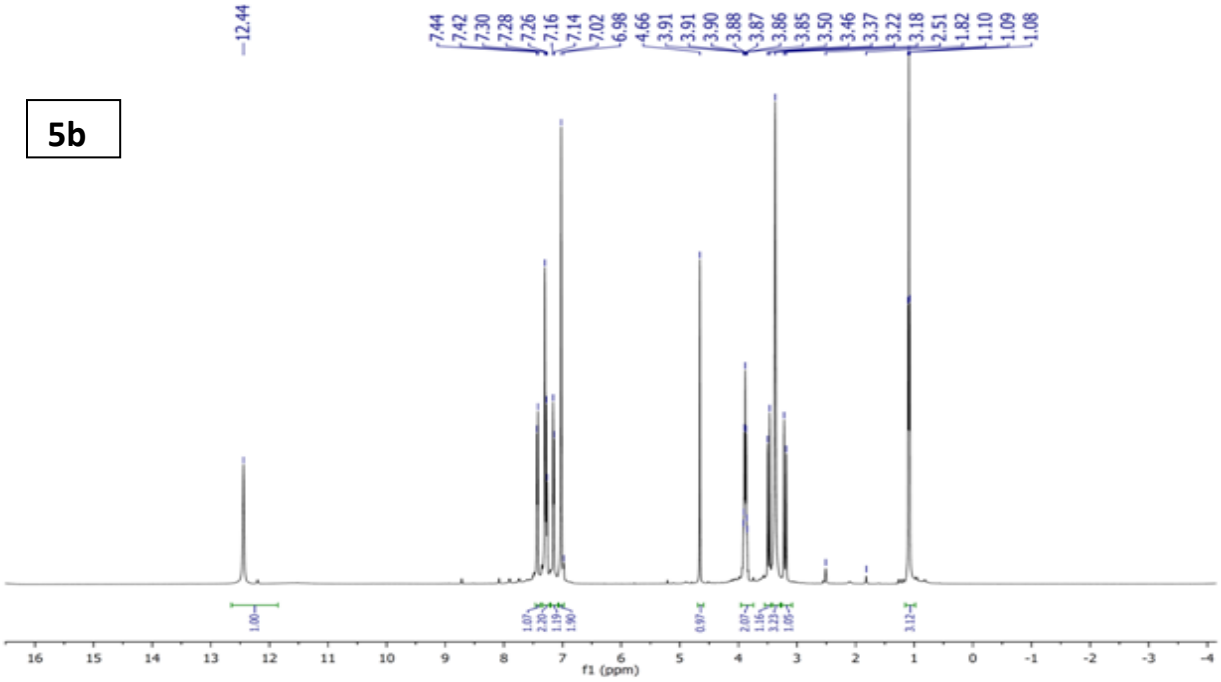
3.42
3.39
3.20
3.16
2.51
1.80
1.18
1.10
1.08
1.07
f1 (ppm)

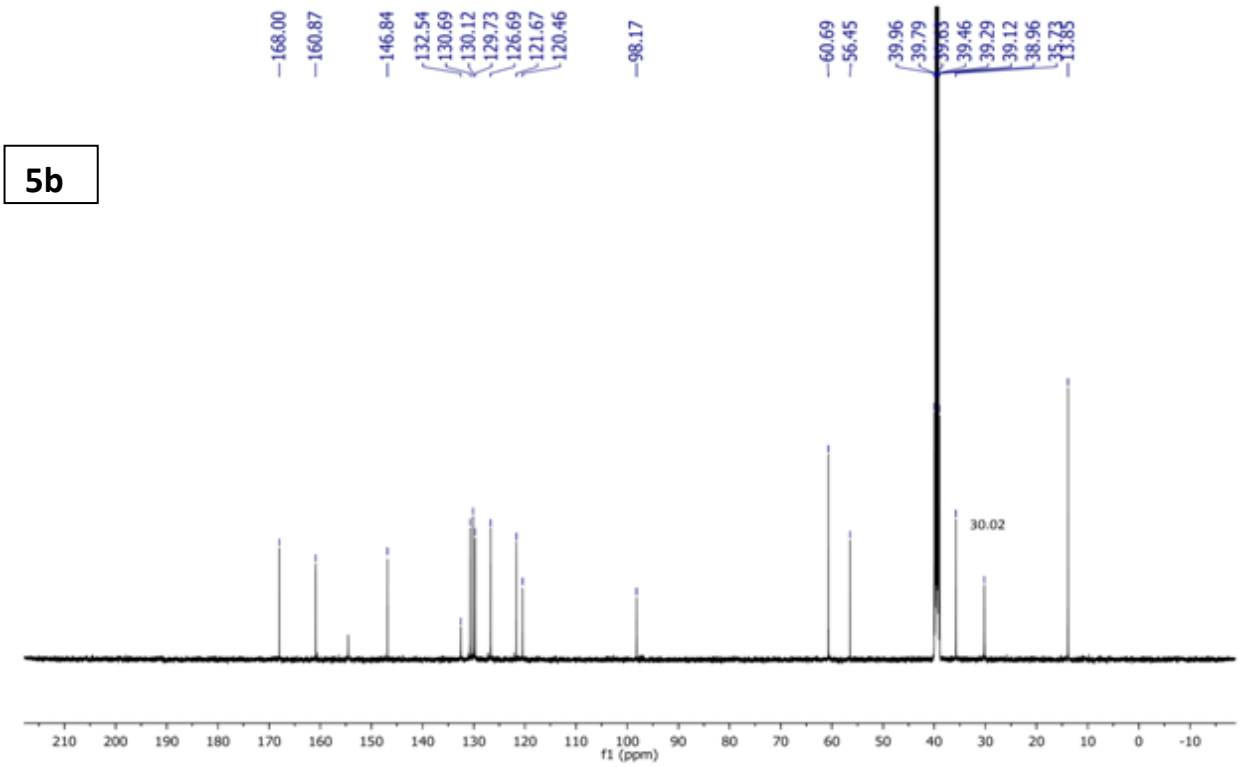
5a

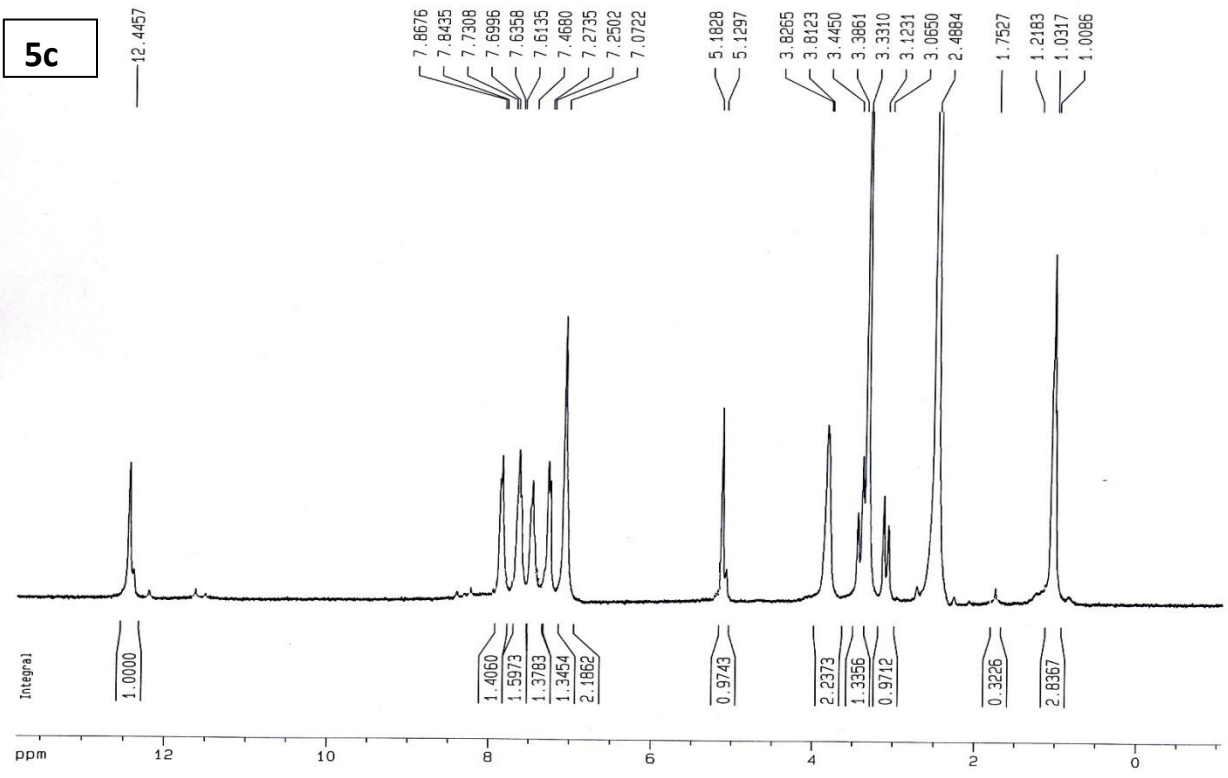

168.03
160.76
143.05
131.32
129.41
129.34
128.43
128.38
120.48
98.37
60.65
56.68
39.94
39.77
39.61
39.44
39.27
39.11
38.94
30.1
13.79
f1 (ppm)

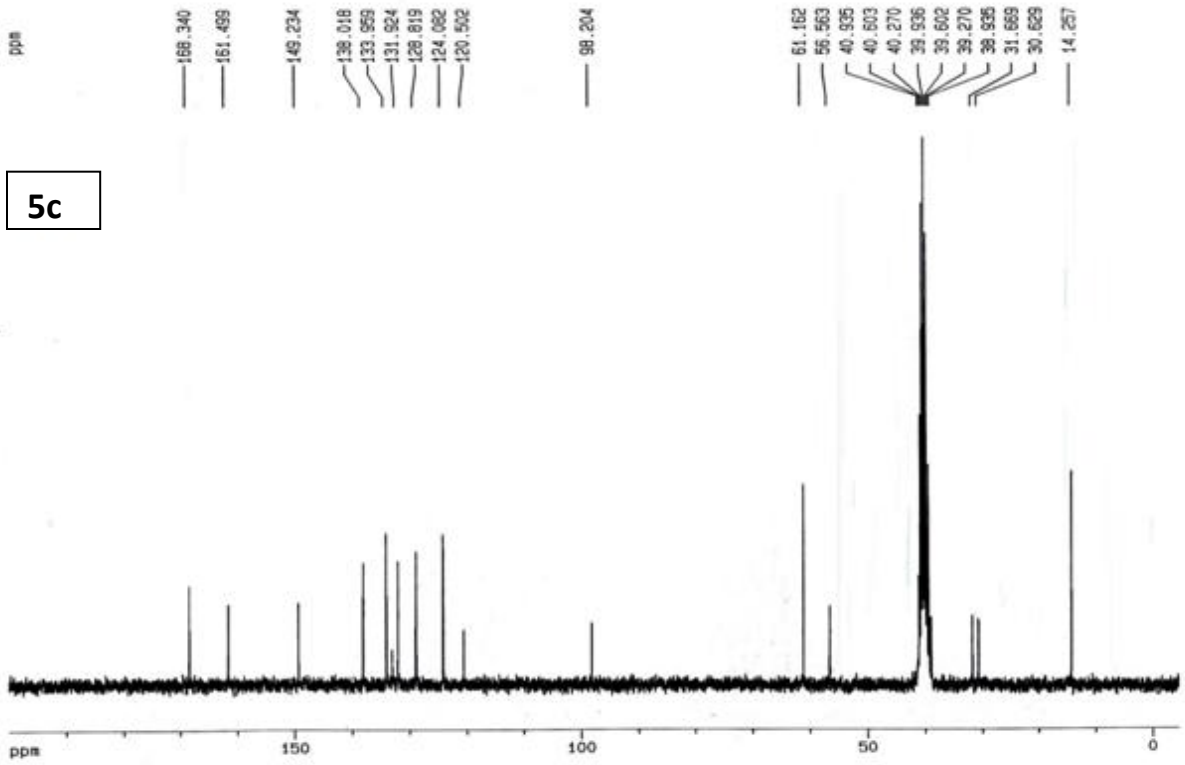
5b

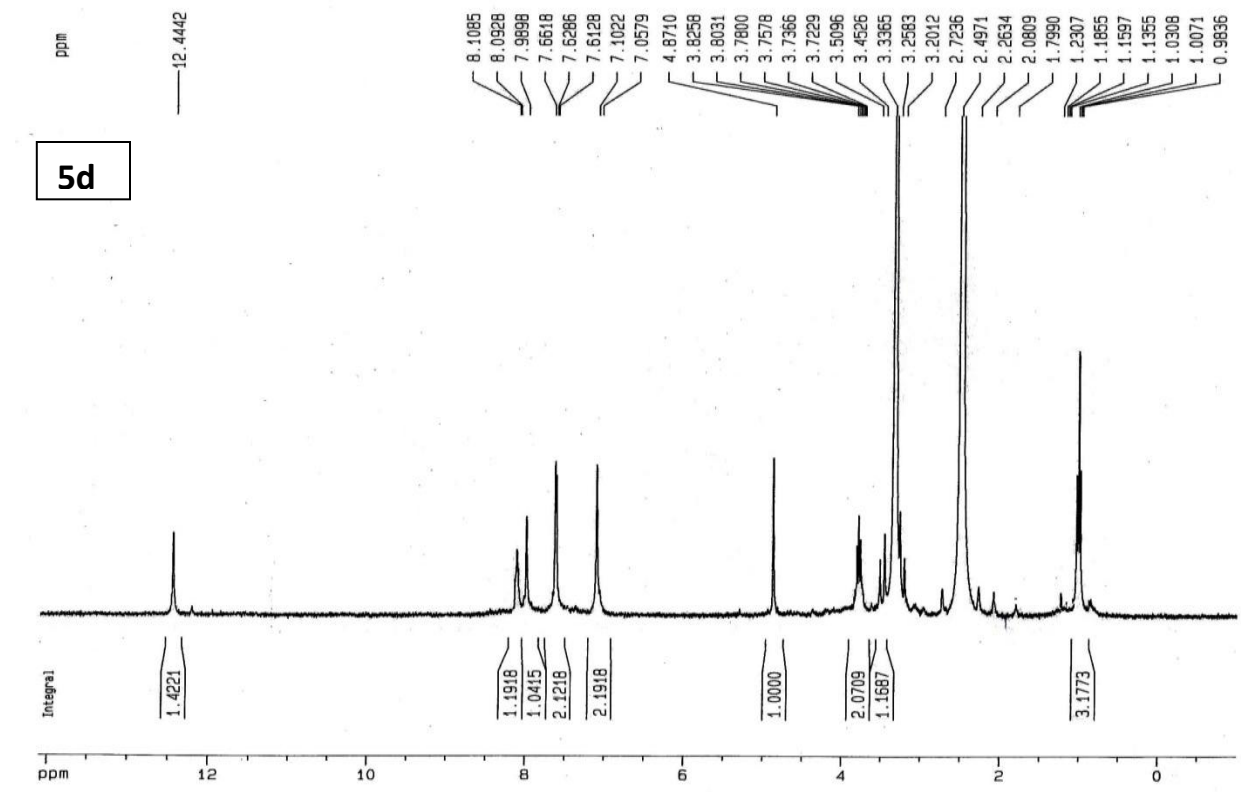

12.44
7.44
7.42
7.30
7.28
7.26
7.16
7.14
7.02
6.98
4.66
3.91
3.91
3.90
3.88
3.87
3.86
3.85
3.50
3.46
3.37
3.22
3.18
2.51
1.82
1.10
1.09
1.08
f1 (ppm)

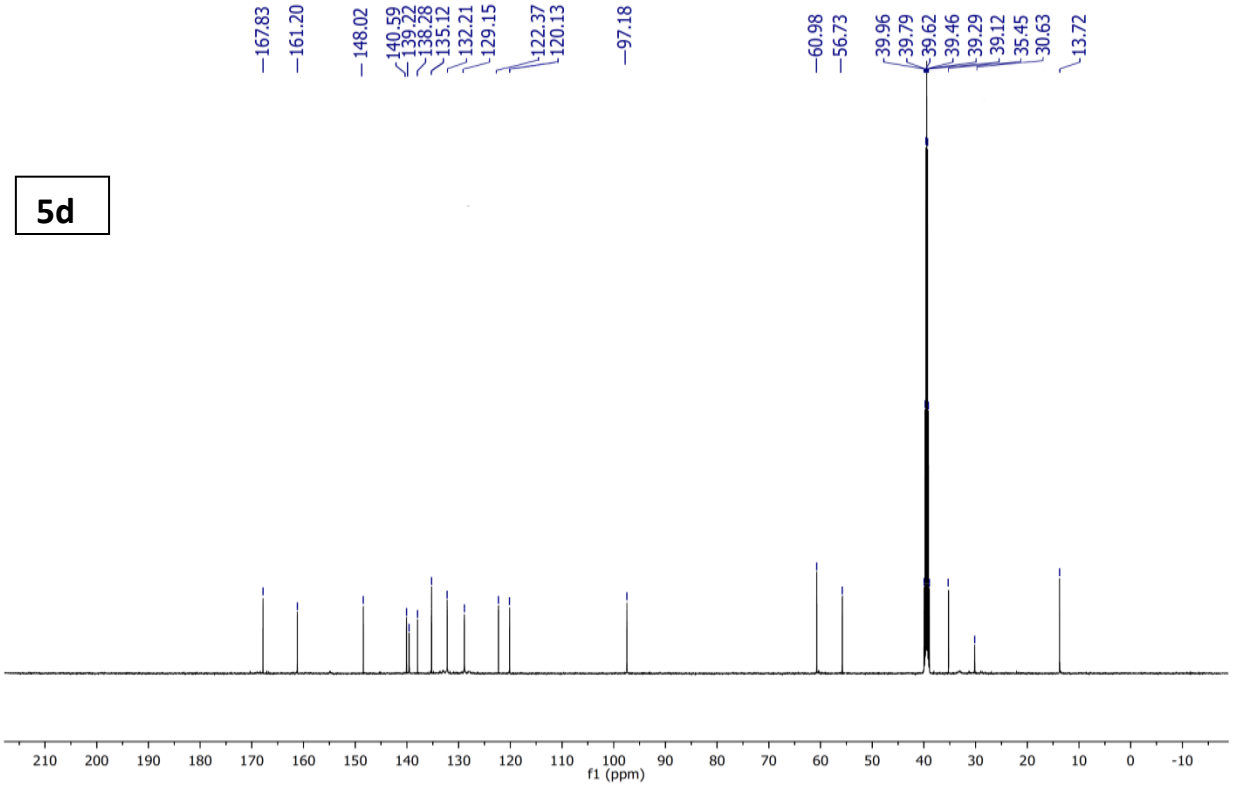
5b


168.00
160.87
146.84
132.54
130.69
130.12
129.73
126.69
121.67
120.46
98.17
60.69
56.45
39.96
39.79
39.63
39.46
39.29
39.12
38.96
35.73
13.85
30.02
f1 (ppm)

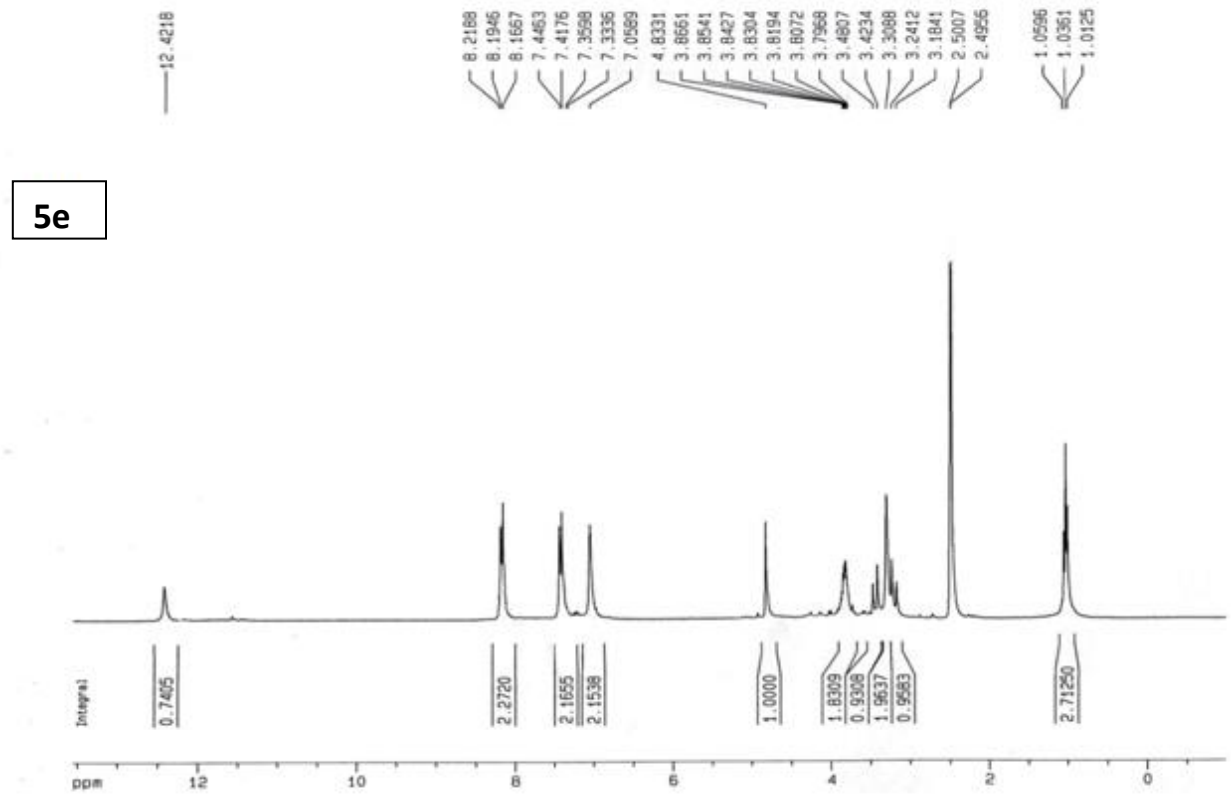

5c
12.4457
7.8676
7.8435
7.7308
7.6996
7.6358
7.6135
7.4680
7.2735
7.2502
7.0722
5.1828
5.1297
3.8265
3.8123
3.4450
3.3861
3.3310
3.1231
3.0650
2.4884
1.7527
1.2183
1.0317
1.0086
Integral
1.0000
1.4060
1.5973
1.3783
1.3454
2.1862
0.9743
2.2373
1.3356
0.9712
0.3226
2.8367
ppm
12
10
8
6
4
2
0


ppm
168.340
161.499
149.234
138.018
133.959
131.924
128.819
124.082
120.502
98.204
61.162
56.563
40.935
40.603
40.270
39.936
39.602
39.270
38.935
31.669
30.629
14.257
5c
ppm
150
100
50
0

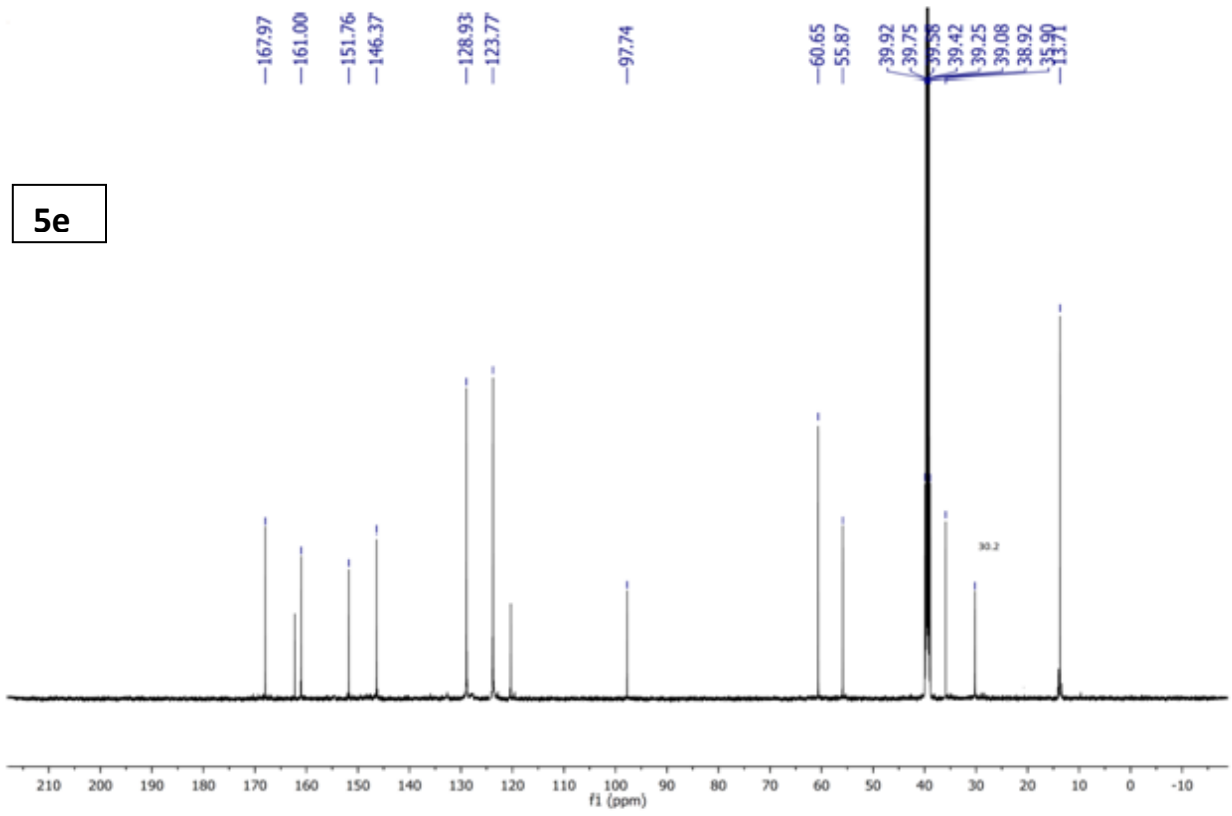

5d
ppm
12.4442
8.1085
8.0928
7.9898
7.6618
7.6286
7.6128
7.1022
7.0579
4.8710
3.8258
3.8031
3.7800
3.7578
3.7366
3.7229
3.5096
3.4526
3.3365
3.2583
3.2012
2.7236
2.4971
2.2634
2.0809
1.7990
1.2307
1.1855
1.1597
1.1355
1.0308
1.0071
0.9836
Integral
1.4221
1.1918
1.0415
2.1218
2.1918
1.0000
2.0709
1.1687
3.1773
ppm
12
10
8
6
4
2
0

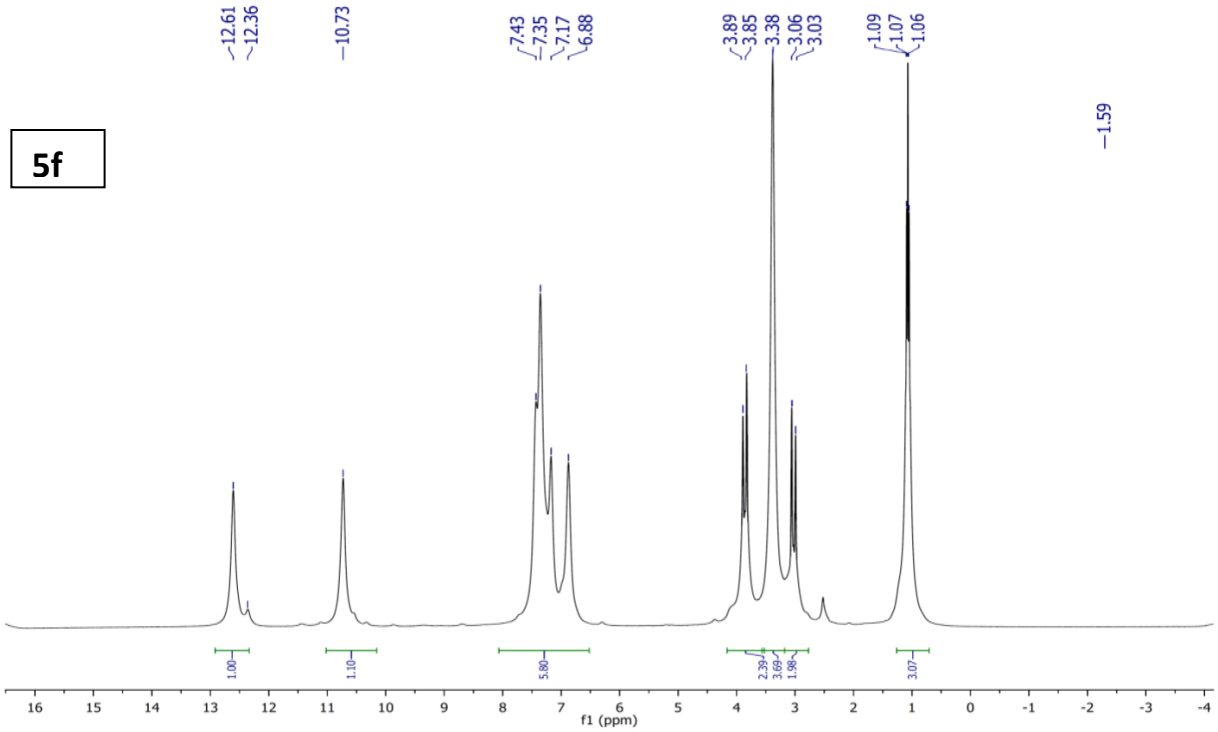

5d
167.83
161.20
148.02
140.59
139.22
138.28
135.12
132.21
129.15
122.37
120.13
97.18
60.98
56.73
39.96
39.79
39.62
39.46
39.29
39.12
35.45
30.63
13.72
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

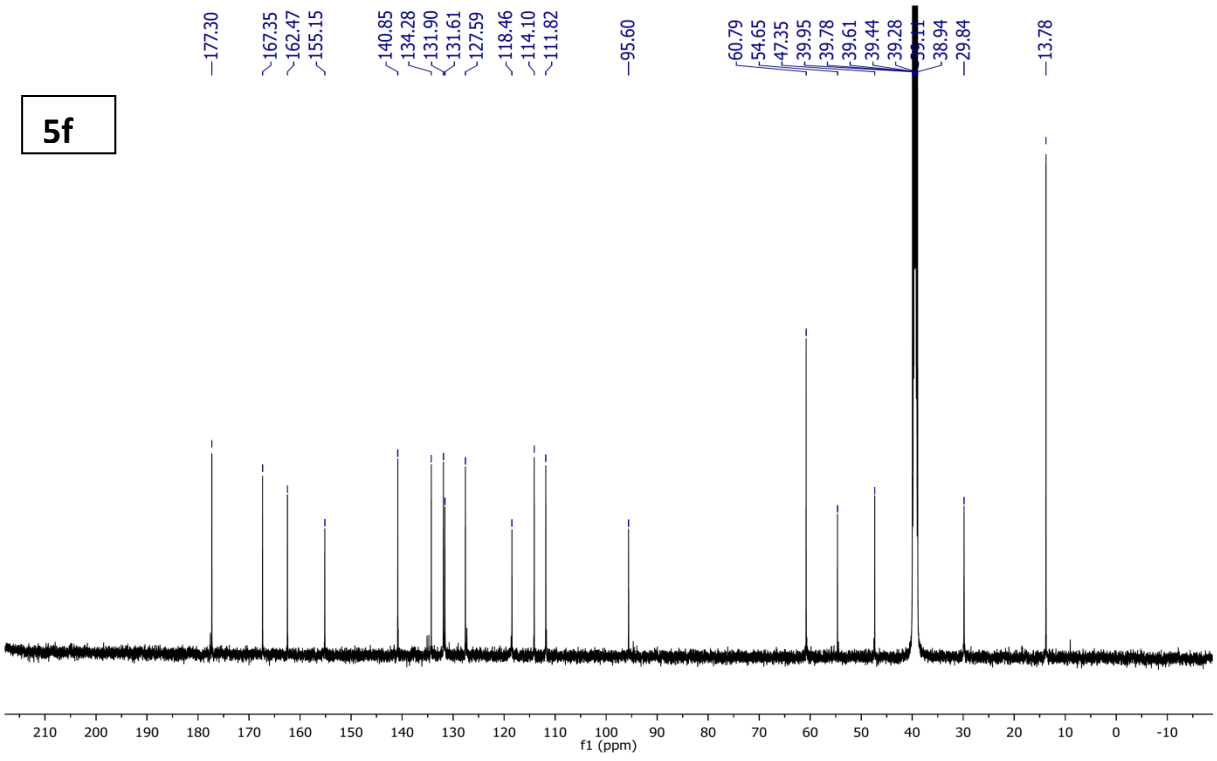
5e

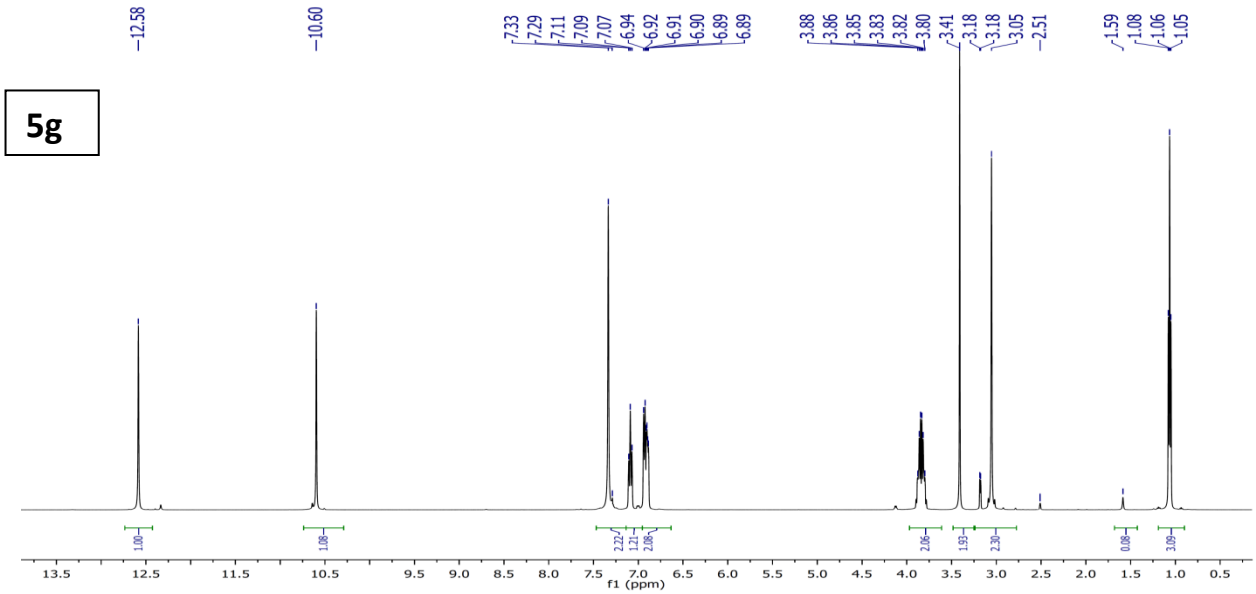

12.4218
8.2188
8.1945
8.1667
7.4463
7.4176
7.3598
7.3336
7.0589
4.8331
3.8661
3.8541
3.8427
3.8304
3.8194
3.8072
3.7968
3.4807
3.4234
3.3088
3.2412
3.1841
2.5007
2.4956
1.0596
1.0361
1.0125
Integral
0.7405
2.2720
2.1655
2.1538
1.0000
1.8309
0.9308
1.9637
0.9583
2.71250
ppm
12
10
8
6
4
2
0

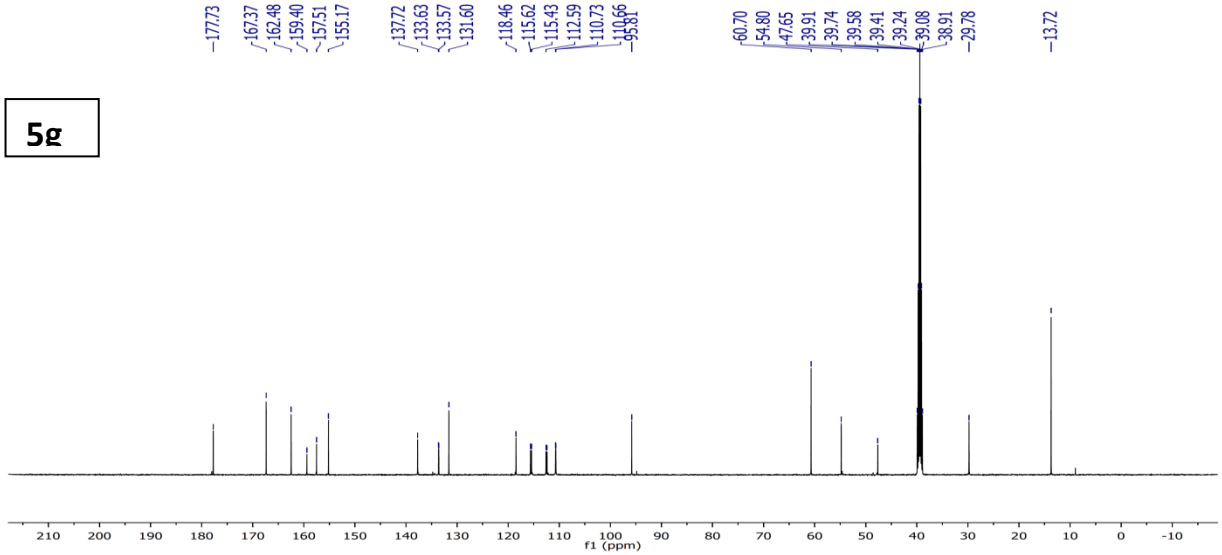
5e

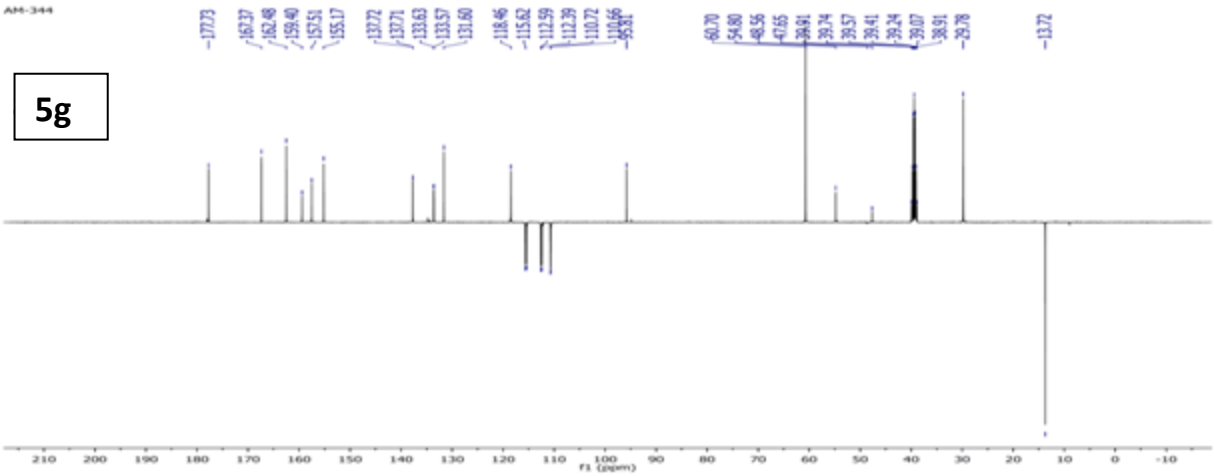

167.97
161.00
151.76
146.37
128.93
123.77
97.74
60.65
55.87
39.92
39.75
39.42
39.25
39.08
38.92
35.90
13.71
30.2
f1 (ppm)

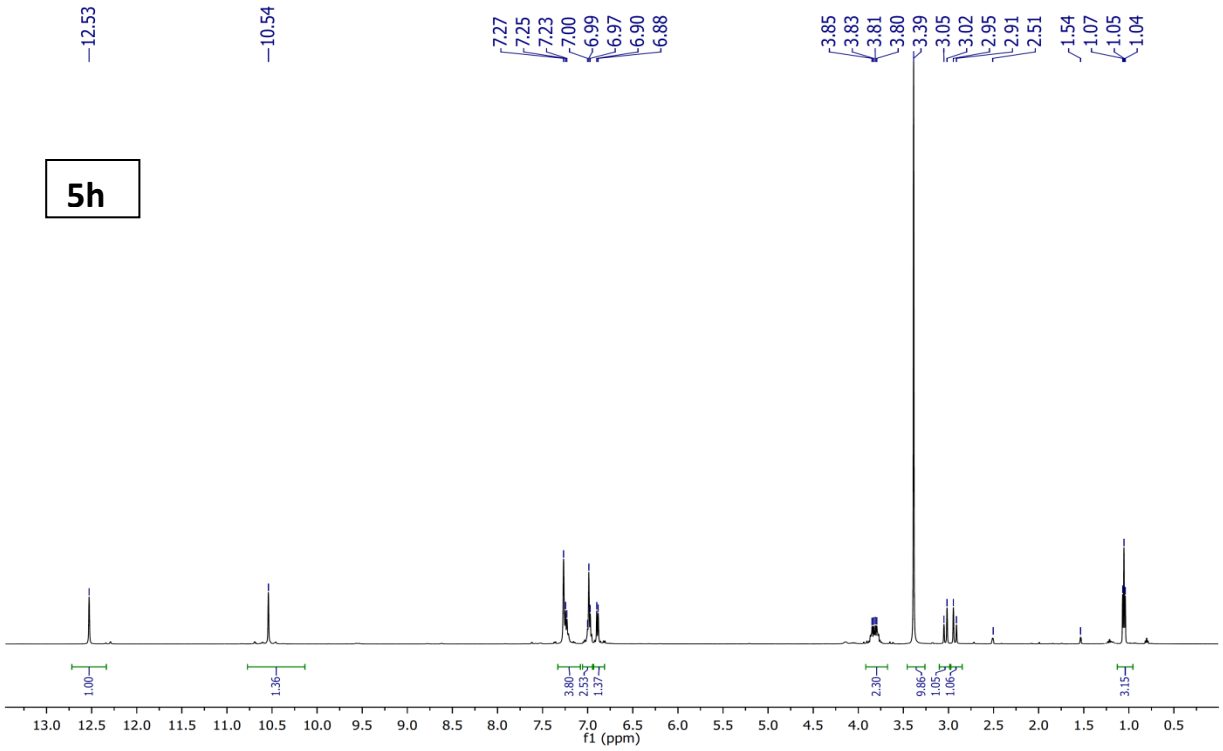

5f
12.61
12.36
10.73
7.43
7.35
7.17
6.88
3.89
3.85
3.38
3.06
3.03
1.09
1.07
1.06
1.59
1.00
1.10
5.80
2.39
3.69
1.98
3.07
f1 (ppm)

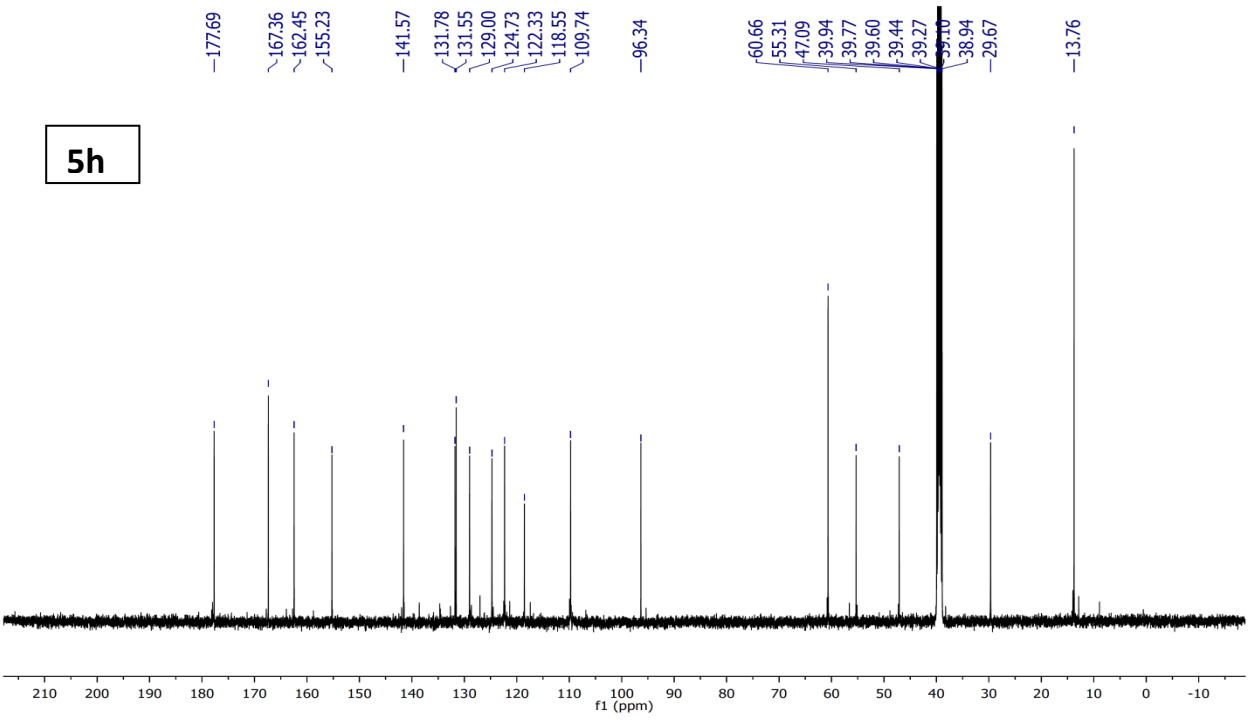

5f
177.30
167.35
162.47
155.15
140.85
134.28
131.90
131.61
127.59
118.46
114.10
111.82
95.60
60.79
54.65
47.35
39.95
39.78
39.61
39.44
39.28
39.11
38.94
29.84
13.78
f1 (ppm)

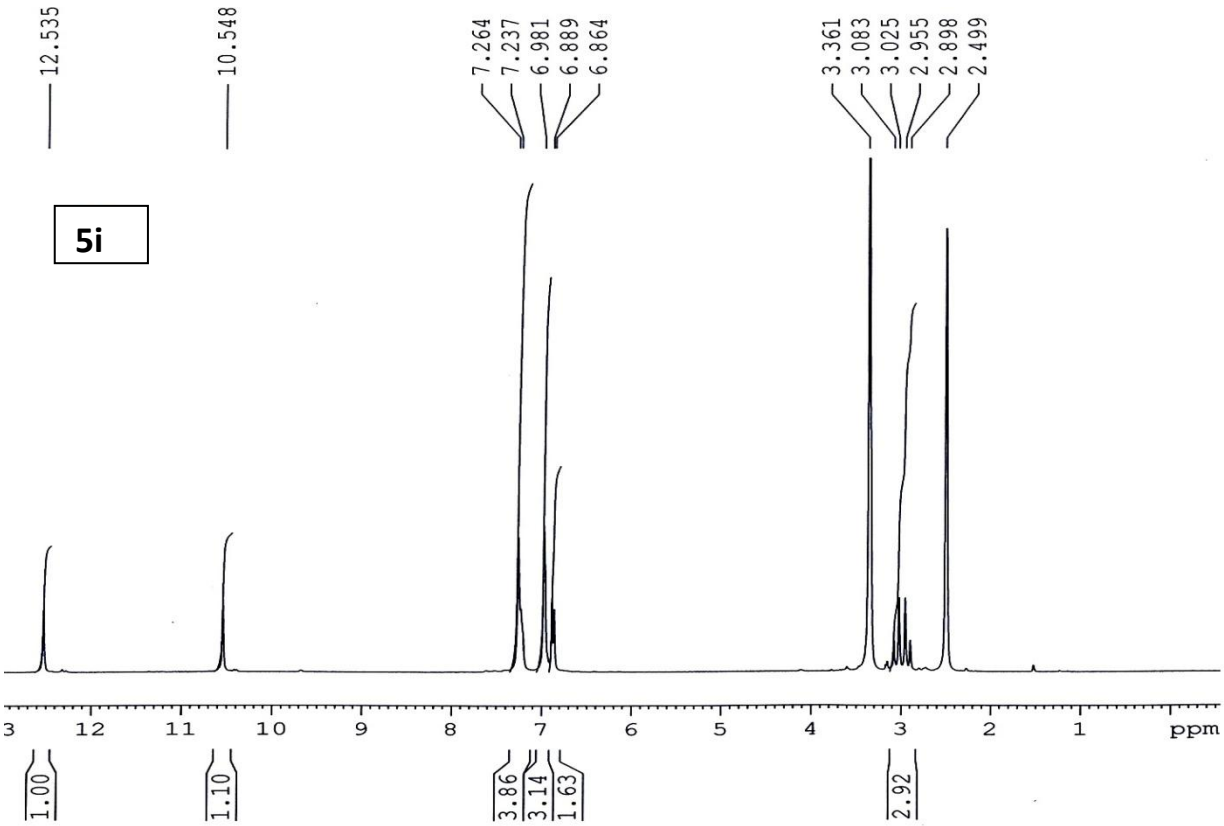

5g
12.58
10.60
7.33
7.29
7.11
7.09
7.07
6.94
6.92
6.91
6.90
6.89
6.89
3.88
3.86
3.85
3.83
3.82
3.80
3.41
3.18
3.18
3.05
2.51
1.59
1.08
1.06
1.05
1.00
1.08
2.22
1.21
2.06
2.06
1.93
2.30
0.98
3.09
f1 (ppm)

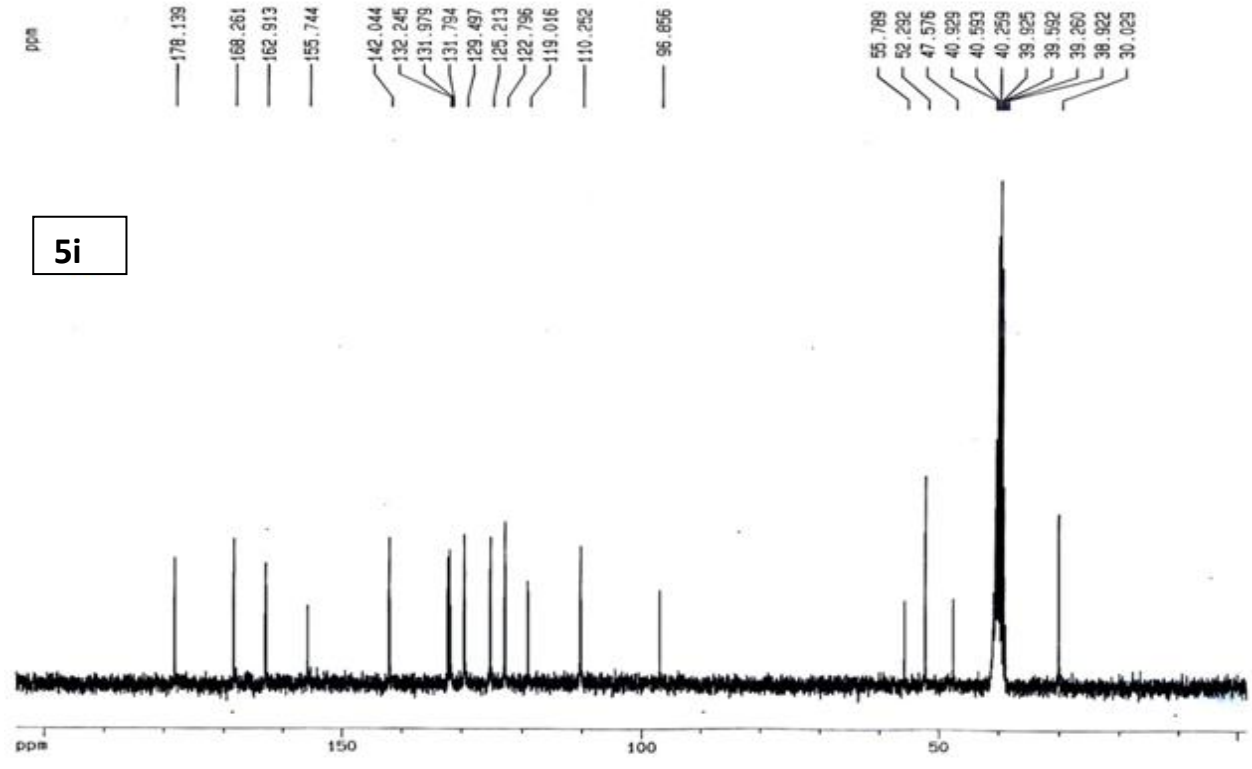

5g
177.73
167.37
162.48
159.40
157.51
155.17
137.72
133.63
133.57
131.60
118.46
115.62
115.43
112.59
110.73
110.66
95.81
60.70
54.80
47.65
39.91
39.74
39.58
39.41
39.24
39.08
38.91
29.78
13.72
f1 (ppm)

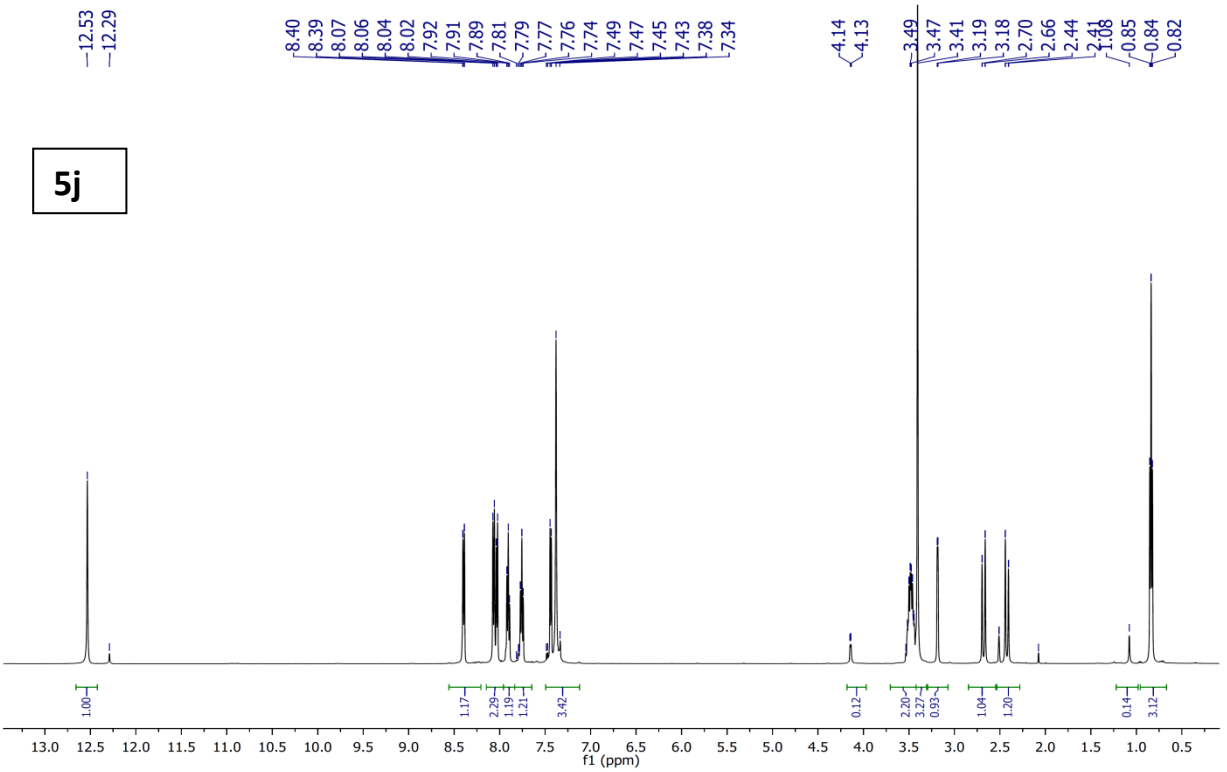

AM-344
5g
177.73
167.37
162.48
159.40
157.51
155.17
137.72
137.71
133.63
133.57
131.60
118.46
115.62
112.59
112.39
110.72
110.66
95.81
60.70
54.80
48.56
47.65
39.91
39.74
39.57
39.41
39.24
39.07
38.91
29.78
13.72
f1 (ppm)

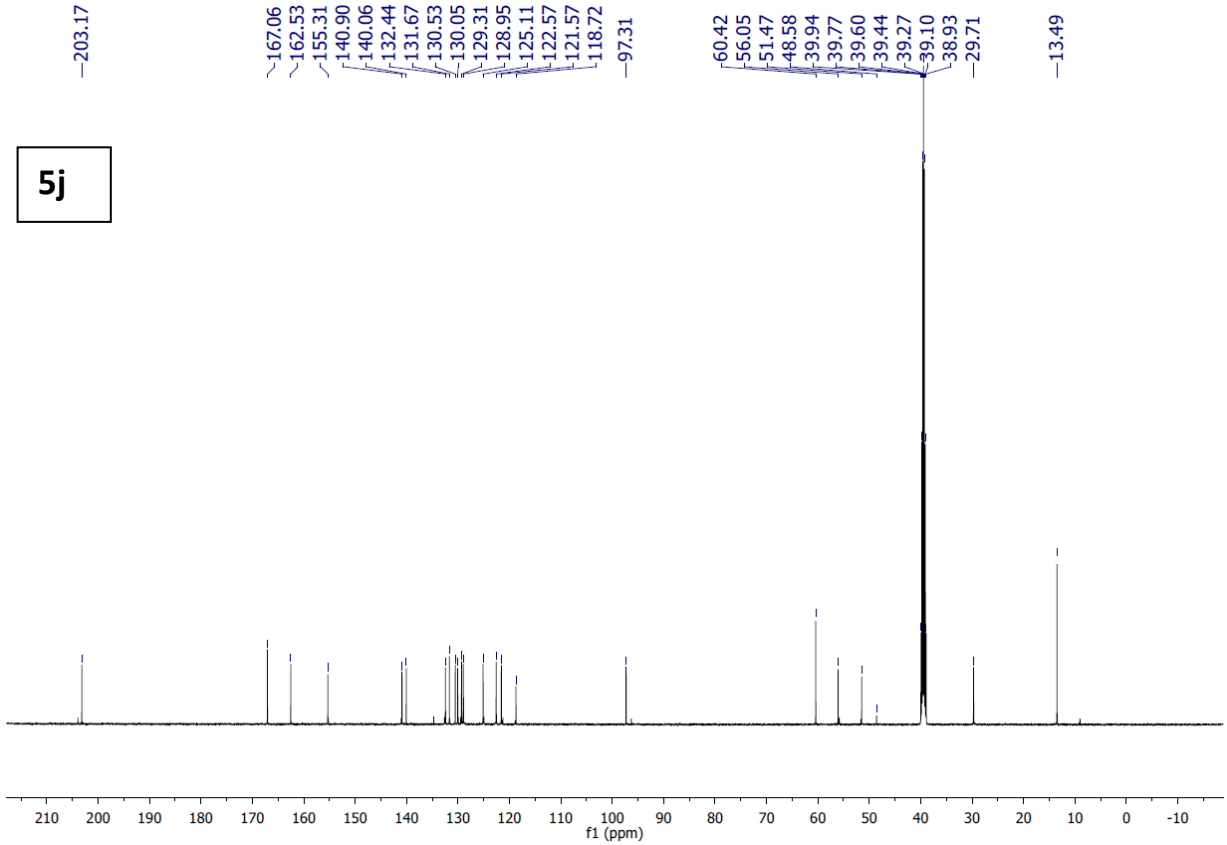

12.53
10.54
7.27
7.25
7.23
7.00
6.99
6.97
6.90
6.88
3.85
3.83
3.81
3.80
3.39
3.05
3.02
2.95
2.91
2.51
1.54
1.07
1.05
1.04
5h
1.00
1.36
3.80
2.53
1.37
2.30
9.86
1.05
1.06
3.15
f1 (ppm)

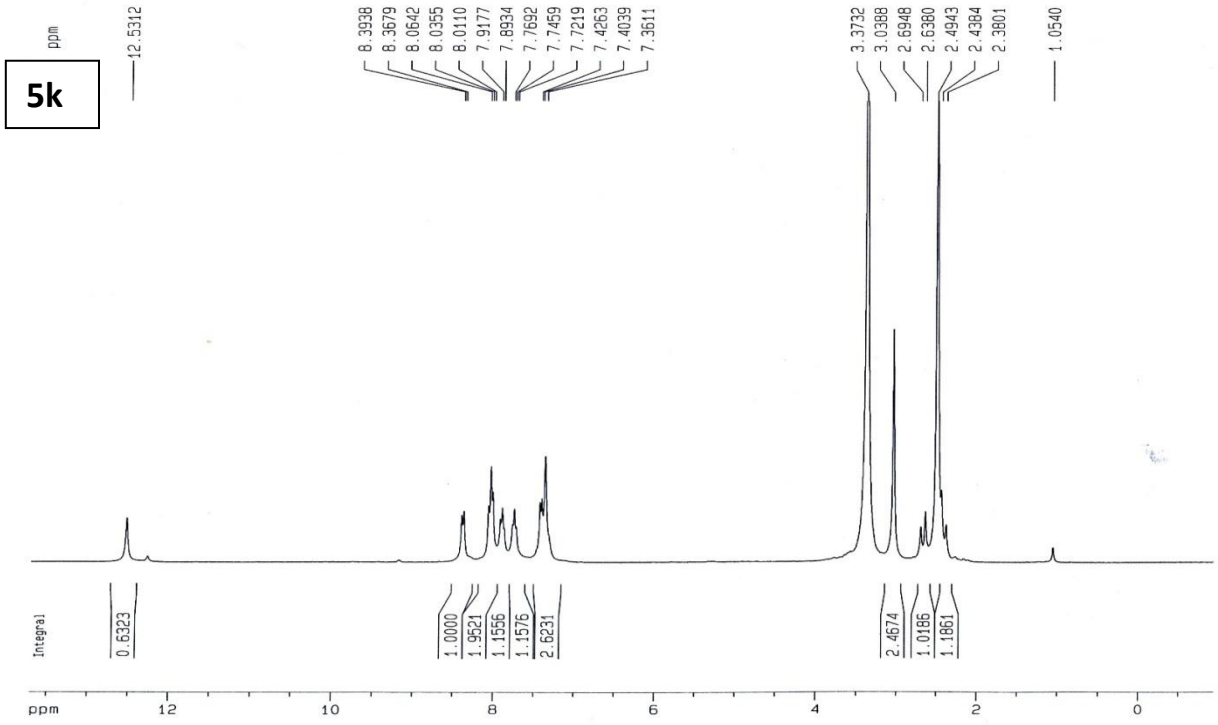

177.69
167.36
162.45
155.23
141.57
131.78
131.55
129.00
124.73
122.33
118.55
109.74
96.34
60.66
55.31
47.09
39.94
39.77
39.60
39.44
39.27
39.10
38.94
29.67
13.76
5h
f1 (ppm)

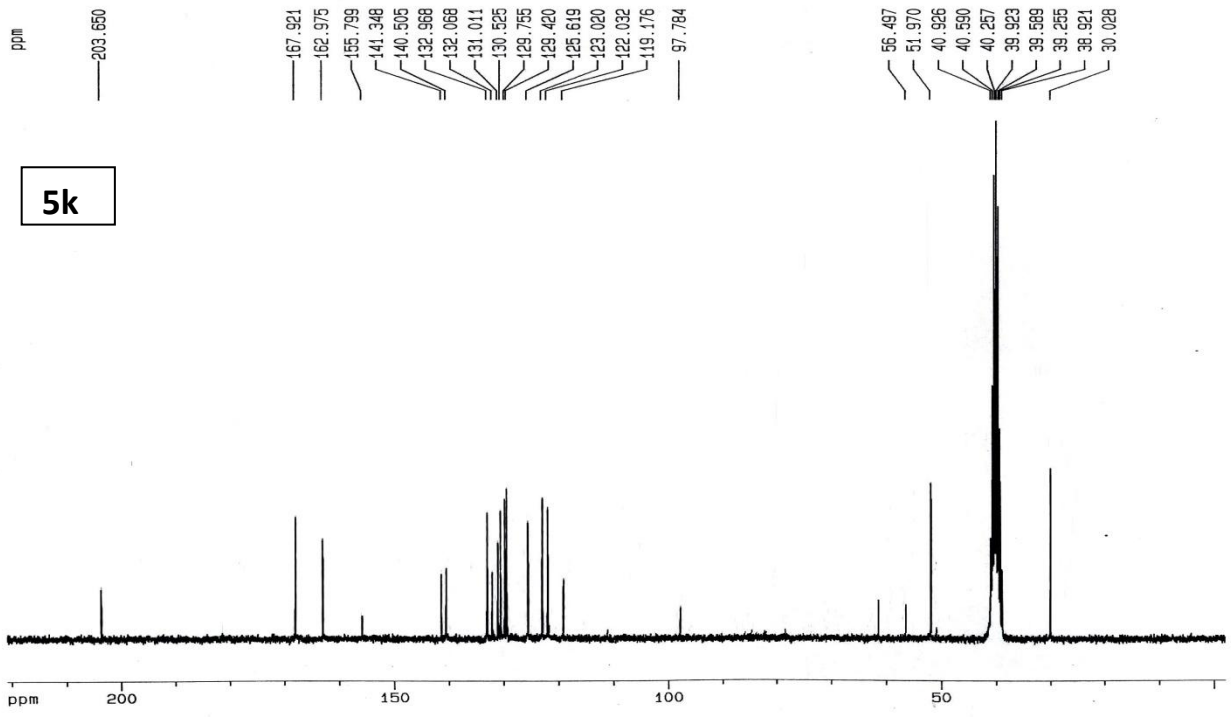

12.535
10.548
7.264
7.237
6.981
6.889
6.864
3.361
3.083
3.025
2.955
2.898
2.499
5i
ppm
1.00
1.10
3.86
3.14
1.63
2.92


ppm
178.139
168.261
162.913
155.744
142.044
132.245
131.979
131.794
129.497
125.213
122.796
119.016
110.262
96.856
55.789
52.292
47.576
40.929
40.593
40.259
39.925
39.592
39.260
38.922
30.029
5i
ppm
150
100
50

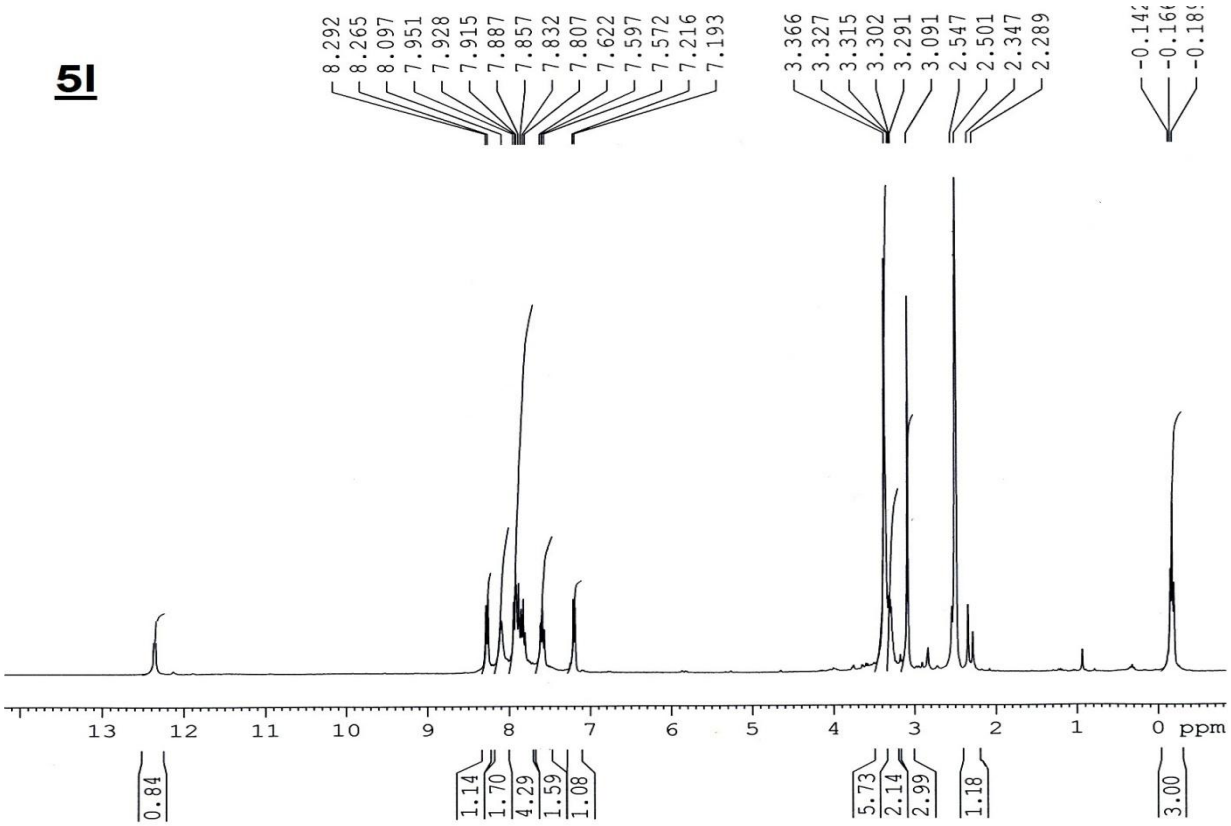

5j
12.53
12.29
8.40
8.39
8.07
8.06
8.04
8.02
7.92
7.91
7.89
7.81
7.79
7.77
7.76
7.74
7.49
7.47
7.45
7.43
7.38
7.34
4.14
4.13
3.49
3.47
3.41
3.19
3.18
2.70
2.66
2.44
2.41
1.08
0.85
0.84
0.82
1.00
1.17
2.29
1.19
1.21
3.42
0.12
2.20
3.27
0.93
1.04
1.20
0.14
3.12
f1 (ppm)

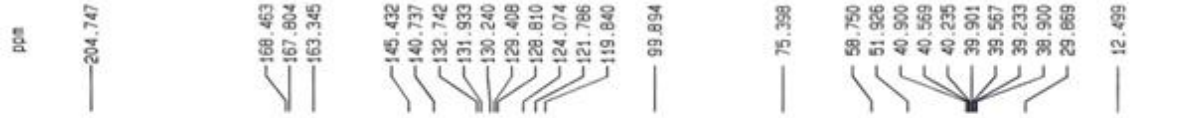

5j
203.17
167.06
162.53
155.31
140.90
140.06
132.44
131.67
130.53
130.05
129.31
128.95
125.11
122.57
121.57
118.72
97.31
60.42
56.05
51.47
48.58
39.94
39.77
39.60
39.44
39.27
39.10
38.93
29.71
13.49
f1 (ppm)


5k
ppm
12.5312
8.3938
8.3679
8.0642
8.0355
8.0110
7.9177
7.8934
7.7692
7.7459
7.7219
7.4263
7.4039
7.3611
3.3732
3.0388
2.6948
2.6380
2.4943
2.4384
2.3801
1.0540
Integral
0.6323
1.0000
1.9521
1.1556
1.1576
2.6231
2.4674
1.0186
1.1861
ppm
12
10
8
6
4
2
0

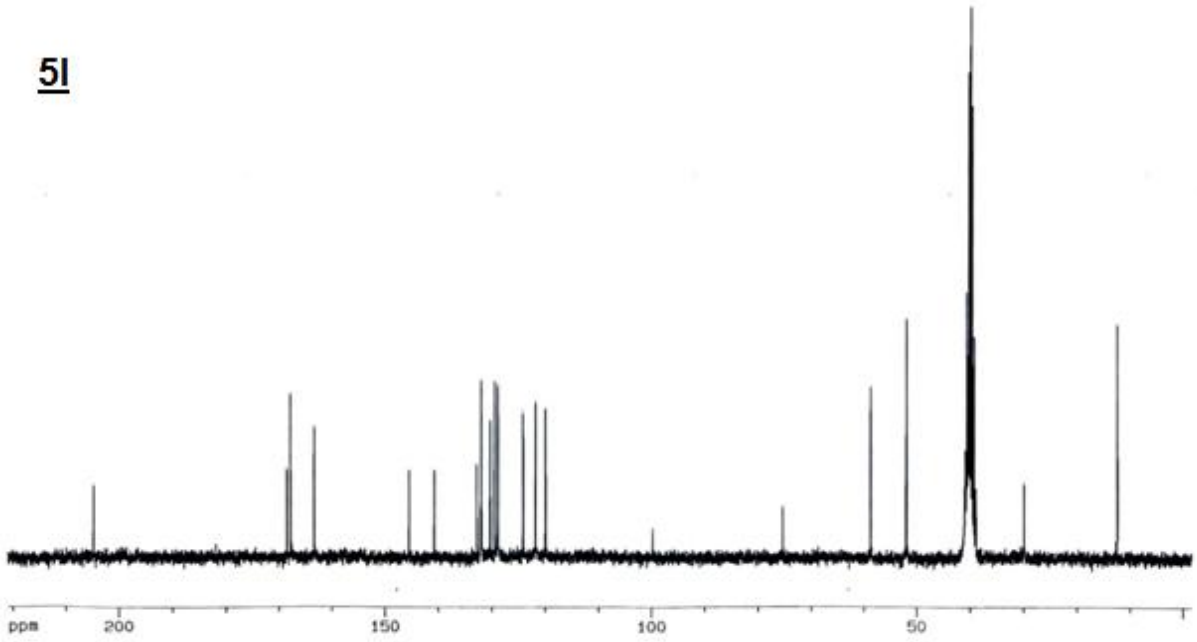

5k
ppm
203.650
167.921
162.975
155.799
141.348
140.505
132.968
132.068
131.011
130.525
129.755
128.420
125.619
123.020
122.032
119.176
97.784
56.497
51.970
40.926
40.590
40.257
39.923
39.589
39.255
38.921
30.028
ppm
200
150
100
50

5l


8.292
8.265
8.097
7.951
7.928
7.915
7.887
7.857
7.832
7.807
7.622
7.597
7.572
7.216
7.193
3.366
3.327
3.315
3.302
3.291
3.091
2.547
2.501
2.347
2.289
-0.142
-0.166
-0.185
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.84
1.14
1.70
4.29
1.59
1.08
5.73
2.14
2.99
1.18
3.00


ppm
204.747
168.463
167.804
163.345
145.432
140.737
132.742
131.933
130.240
129.408
128.810
124.074
121.786
119.840
99.894
75.398
58.750
51.926
40.900
40.569
40.235
39.901
39.567
39.233
38.900
29.869
12.499

5l


ppm
200
150
100
50