Supporting Information

One-pot facile and mild construction of densely functionalized pyrimidines in water via consecutive C-C and C-N bonds formation

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Materials and methods

2.1 Experimental

All reagents such as SLS, 4-hydroxy coumarin, aldehydes etc. were analytical grade. ^{1}H and ^{13}C NMR spectra were recorded on BRUKER AVANCE II 500 NMR spectrometer using CDCl3 and DMSO-d_6 as solvent. Purity of the compound was checked by TLC. Melting points were determined in open capillary and are uncorrected.

One-pot three-component reaction

Typical procedure. A three neck round-bottomed flask was charged with aldehydes (2 mmol), 4-hydroxy coumarin (2 mmol), and urea/thiourea (2 mmol) in water (10 mL). Catalyst sodium lauryl sulphate (10 mol%) was charged in the reaction mixture. Reaction was conducted at RT for a desired period of time. Monitored the reaction mass by TLC analysis and confirmed by spectroscopic analysis.

Characterization Data

4-Pheny-3,4-dihydro-1*H*-chromeno[4,3-*d*]pyrimidine-2,5-dione **(4a)**

Off white powder, mp 160-162 ^{o}C; ^{1}H NMR (500 MHz, DMSO d_6): δ_H 6.36 (s, 1H, -CH), 7.09-7.39 (m, 9H, Ar-H), 7.60 (s, 1H, NH), 7.90 (s, 1H, NH); ^{13}C NMR (125 MHz, DMSO d_6): 36 (C-1), 103 (C-2), 115 (C-13), 116 (C-17), 121 (C-14), 122 (C-15), 124 (C-16), 125 (C-6 and 10), 126 (C-8), 126 (C-7), 128 (C-9), 131 (C-5), 140 (C-12), 152 (C-3), 164 (C-4), 165 (C-11); ESI-MS: m/z Calculated for $C_{17}H_{12}N_2O_3$ 292.29 Found $[M]^+$ 292.3; C, H and N analyses Calculated for C 69.86, H 4.14, N 9.58, Found C 70.02, H 4.18, N 9.69.

4-(2-Hydroxyhenyl)-3,4-dihydro-1*H*-chromeno[4,3-*d*]pyrimidine-2,5-dione **(4b)**

Off white powder, mp 240-242 ^{o}C; ^{1}H NMR (500 MHz, DMSO d_6): δ_H 6.25 (s, 1H, -CH), 6.49-6.56 (m, 2H, Ar-H), 6.79 (d, 2H, J = 8.0 Hz, Ar-H), 6.98 (t, 1H, J = 7.5 Hz, Ar-H), 7.28-7.34 (m, 2H, Ar-H), 7.56 (t, 1H, J = 7.0 Hz, Ar-H), 7.67 (1, 1H, -NH), 7.88 (s, 1H, -NH), 9.66 (s, 1H, OH); ^{13}C NMR (125 MHz, DMSO d_6): 35 (C-1), 104 (C-2), 111 (C-13), 112 (C-17), 113 (C-14), 115 (C-15), 117 (C-16), 117 (C-7), 123 (C-8), 129 (C-9), 131 (C-10), 141 (C-5), 152 (C-6), 154 (C-12), 157 (C-3), 164 (C-4), 165 (C-11); ESI-MS: m/z Calculated for $C_{17}H_{12}N_2O_4$ 308.29 Found $[M]^+$ 309; C, H and N analyses Calculated for C 66.23, H 3.92, N 9.09, Found C 66.32, H 3.99, N 9.15.

4-(4-Chlorophenyl)-3,4-dihydro-1*H*-chromeno[4,3-*d*]pyrimidine-2,5-dione **(4c)**

Off white powder, mp 195-197 ^{o}C; ^{1}H NMR (500 MHz, DMSO d_6): δ_H 6.28 (s, 1H, CH), 7.13 (d, 2H, J = 8.5 Hz, Ar-H), 7.54-7.34 (m, 6H, Ar-H), 7.56 (s, 1H, NH), 7.87 (s, 1H, -NH); ^{13}C NMR (125 MHz, DMSO d_6): 35 (C-1), 104 (C-2), 116 (C-13), 118 (C-17), 123 (C-14), 128 (C-15), 128 (C-16), 129 (C-7), 130 (C-9), 131 (C-10), 132 (C-5), 137 (C-8), 139 (C-12), 152 (C-3),

164 (C-4), 165 (C-11); ESI-MS: m/z Calculated for $C_{17}H_{11}ClN_2O_3$ 326.73 Found $[M]^+$ 326.7; C, H and N analyses Calculated for C 62.49, H 3.39, N 8.57, Found C 62.32, H 3.49, N 8.65.

4-(4-Dimethylamino phenyl)-3,4-dihydro-1*H*-chromeno[4,3-*d*]pyrimidine-2,5-dione **(4d)**

Off white powder, mp 235-237 ^oC; ^1H NMR (500 MHz, DMSO d_6): δ_H 3.11 (s, 6H, $N(CH_3)_2$), 6.27 (s, 1H, -CH), 7.21-7.28 (m, 8H, Ar-H), 7.51 (s 1H, -NH), 7.79 (s, 1H, -NH); ^{13}C NMR (125 MHz, DMSO d_6): 35 (C-1), 45 ($N(CH_3)_2$), 103 (C-2), 111 (C-13), 115 (C-17), 119 (C-14), 122 (C-15 and 16), 124 (C-8 and 5), 128 (C-7 and 9), 131 (C-6 and 10), 131 (C-12), 152 (C-3), 164 (C-4), 167 (C-11); ESI-MS: m/z Calculated for $C_{19}H_{17}N_3O_3$ 335.36 Found $[M]^+$ 336; C, H and N analyses Calculated for C 68.05, H 5.11, N 12.53, Found C 68.12, H 5.22, N 12.61.

4-(3-Nitrophenyl)-3,4-dihydro-1*H*-chromeno[4,3-*d*]pyrimidine-2,5-dione **(4e)**

Off white powder, mp 172-174 ^oC; ^1H NMR (500 MHz, DMSO d_6): δ_H 6.37 (s, 1H,-CH), 7.27-7.33 (m, 4H, Ar-H), 7.38 (d, 2H, J = 8.5 Hz, Ar-H), 7.56 (t, 2H, J = 8.0 Hz, Ar-H), 7.84 (s, 1H, -NH), 8.09 (s, 1H, -NH); ^{13}C NMR (125 MHz, DMSO d_6): 36 (C-1), 103 (C-2), 115 (C-13), 118 (C-17), 123 (C-14), 123 (C-15), 124 (C-16), 124 (C-5), 128 (C-6), 130 (C-10), 131 (C-7 and 9), 145 (C-8), 150 (C-12), 152 (C-3), 164 (C-4), 166 (C-11); ESI-MS: m/z Calculated for $C_{17}H_{11}N_3O_5$ 337.29 Found $[M]^+$ 337.3; C, H and N analyses Calculated for C 60.54, H 3.29, N 12.46, Found C 60.70, H 3.41, N 12.29.

4-(4-Hydroxy-3-methoxyphenyl)-3,4-dihydro-1*H*-chromeno[4,3-*d*]pyrimidine-2,5-dione **(4f)**

Off white powder, mp 208-210 ^oC; ^1H NMR (500 MHz, DMSO d_6): δ_H 3.72 (s, 3H, OCH_3), 6.39 (s, 1H, -CH), 7.16-7.39 (m, 7H, Ar-H), 7.60 (s, 1H, -NH), 7.93 (s, 1H, -NH), 10.20 (br, 1H, OH); ^{13}C NMR (125 MHz, DMSO d_6): 35 (C-1), 56 (OCH_3), 104 (C-2), 116 (C-13), 117 (C-17), 123

(C-14), 123 (C-15), 124 (C-16), 125 (C-8), 126 (C-9), 128 (C-7), 129 (C-10), 130 (C-6), 132 (C-5), 139 (C-12), 152 (C-3), 164 (C-4), 166 (C-11); ESI-MS: m/z Calculated for $C_{18}H_{14}N_2O_5$ 338.31 Found $[M]^+$ 338.3; C, H and N analyses Calculated for C 63.90, H 4.17, N 8.28, Found C 63.76, H 4.31, N 8.11.

4-Phenyl-2-thioxo-3,4-dihydro-1*H*-chromeno[4,3-*d*]pyrimidin-5-one **(4h)**

Off white powder, mp 185-187 ^oC; ^1H NMR (500 MHz, DMSO d_6): δ_H 6.34 (s, 1H, -CH), 7.24-7.39 (m, 9H, Ar-H), 7.82 (s, 1H, -NH), 8.09 (s, 1H, -NH); ^{13}C NMR (125 MHz, DMSO d_6): 36 (C-1), 103 (C-2), 115 (C-13), 119 (C-17), 123 (C-14), 123 (C-15), 124 (C-16), 127 (C-5), 131 (C-6 and 10), 132 (C-7 and 9), 145 (C-8), 150 (C-12), 152 (C-3), 164 (C-4), 166 (C-11); ESI-MS: m/z Calculated for $C_{17}H_{12}N_2O_2S$ 308.35 Found $[M]^+$ 308.3; C, H and N analyses Calculated for C 66.22, H 3.92, N 9.08, Found C 66.46, H 4.01, N 9.18.

4-(2-Hydroxyphenyl)-2-thioxo-3,4-dihydro-1*H*-chromeno[4,3-*d*]pyrimidin-5-one **(4i)**

Off white powder, mp 170-172 ^oC; ^1H NMR (500 MHz, DMSO d_6): δ_H 5.38 (s, 1H, -CH), 7.05-7.69 (m, 8H, Ar-H), 8.02 (s, 1H, -NH), 8.15 (s, 1H, -NH), 11.74 (s, 1H, OH); ^{13}C NMR (125 MHz, DMSO d_6): 35 (C-1), 102 (C-2), 109 (C-13), 110 (C-17), 111 (C-14), 113 (C-15), 115 (C-16), 115 (C-5), 121 (C-6), 127 (C-10), 129 (C-7), 139 (C-9), 150 (C-8), 152 (C-12), 155 (C-3), 162 (C-4), 163 (C-11); ESI-MS: m/z Calculated for $C_{17}H_{12}N_2O_3S$ 324.35 Found $[M]^+$ 324.4; C, H and N analyses Calculated for C 62.95, H 3.73, N 8.64, Found C 62.88, H 3.81, N 8.72.

4-(4-Chlorophenyl)-2-thioxo-3,4-dihydro-1*H*-chromeno[4,3-*d*]pyrimidin-5-one **(4j)**

Off white powder, mp 187-189 ^oC; ^1H NMR (500 MHz, DMSO d_6): δ_H 6.29 (s, 1H, -CH), 7.14 (d, 1H, J = 7.5 Hz, Ar-H), 7.24-7.35 (m, 5H, Ar-H), 7.55-7.59 (m, 2H, Ar-H), 7.88 (s, 1H, -NH), 7.93 (s, 1H, -NH); ^{13}C NMR (125 MHz, DMSO d_6): 35 (C-1), 104 (C-2), 116 (C-13), 117 (C-

17), 123 (C-14), 128 (C-15), 129 (C-16), 130 (C-5), 131 (C-6 and 10), 132 (C-7 and 9), 137 (C-8), 138 (C-12), 152 (C-3), 164 (C-4), 166 (C-11); ESI-MS: m/z Calculated for $C_{17}H_{11}ClN_2O_2S$ 342.80 Found $[M]^+$ 343; C, H and N analyses Calculated for C 59.56, H 3.23, N 8.17, Found C 60.78, H 3.31, N 8.22.

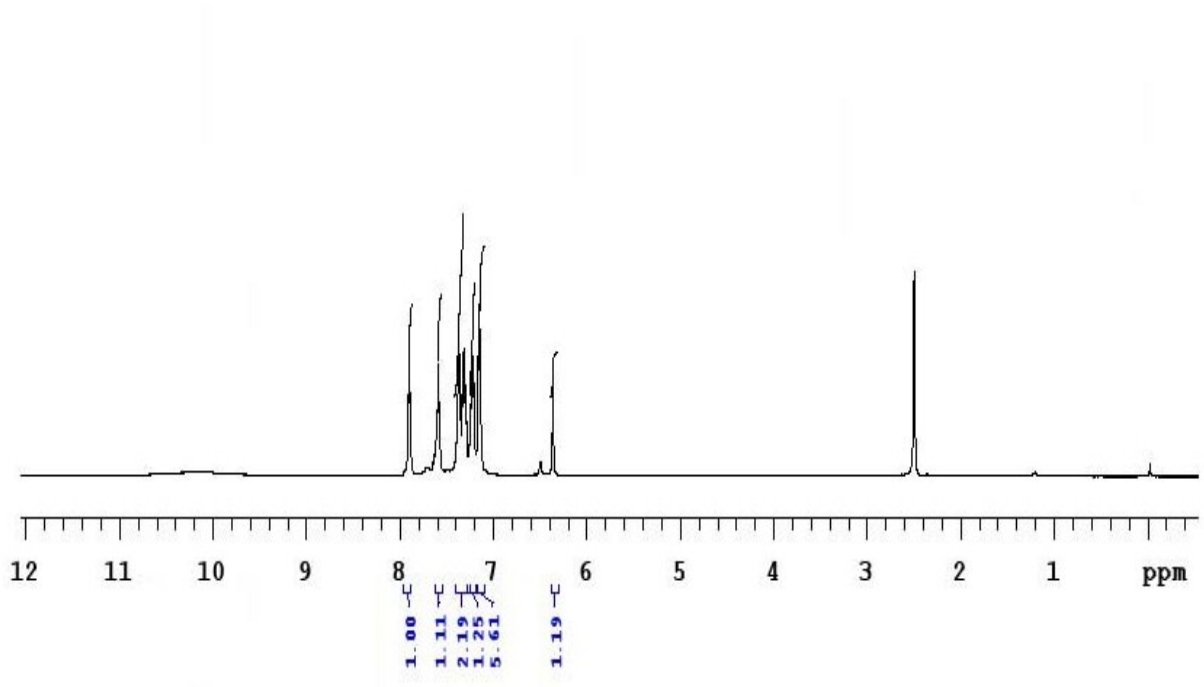
4-(4-Dimethyaminophenyl)-2-thioxo-3,4-dihydro-1*H*-chromeno[4,3-*d*]pyrimidin-5-one **(4k)**

Off white powder, mp 238-240 ^oC; ^1H NMR (500 MHz, DMSO d_6): δ_H 3.11 (s, 6H, $N(CH_3)_2$), 6.26 (s, 1H, -CH), 7.17-7.28 (m, 4H, Ar-H), 7.49-7.56 (m, 4H, Ar-H), 7.69 (s, 1H, NH), 7.80 (s, 1H, NH); ^{13}C NMR (125 MHz, DMSO d_6): 36 (C-1), 45 ($N(CH_3)_2$), 103 (C-2), 111 (C-13), 115 (C-17), 119 (C-14), 123 (C-15), 123 (C-16), 124 (C-7 and 9), 124 (C-6 and 10), 128 (C-5 and 8), 131 (C-12), 153 (C-3), 164 (C-4), 167 (C-11); ESI-MS: m/z Calculated for $C_{19}H_{17}N_3O_2S$ 351.42 Found $[M]^+$ 351.2; C, H and N analyses Calculated for C 64.94, H 4.88, N 11.96, Found C 64.78, H 4.01, N 12.10.

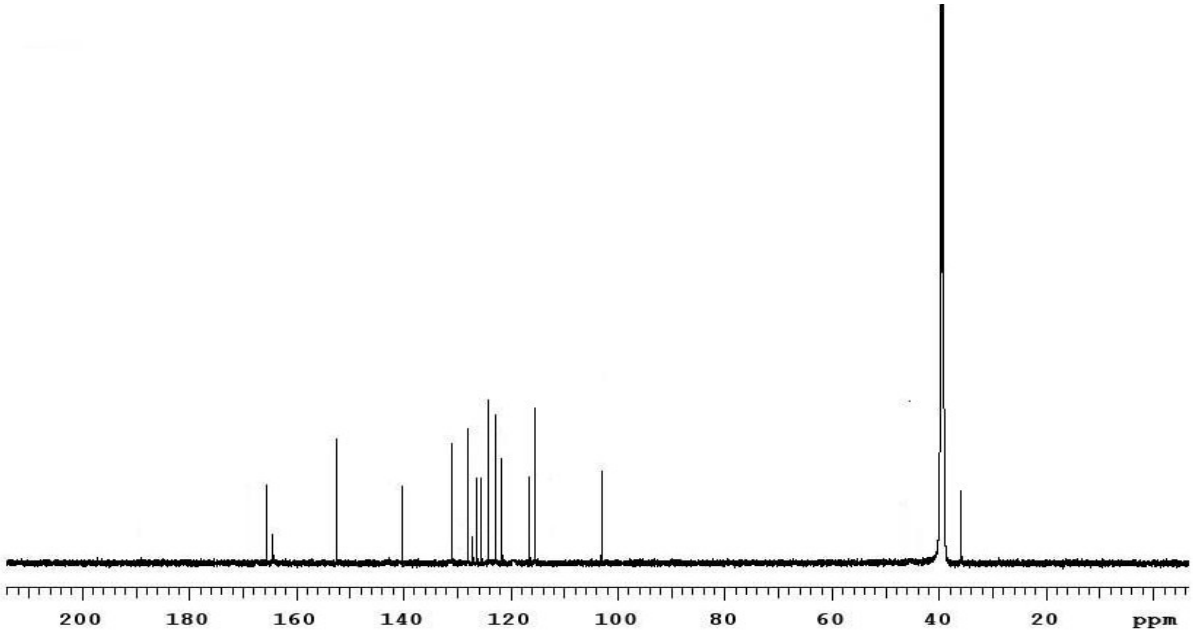
Scanned NMR Spectra

Compound 4a

H NMR



^{13}C NMR



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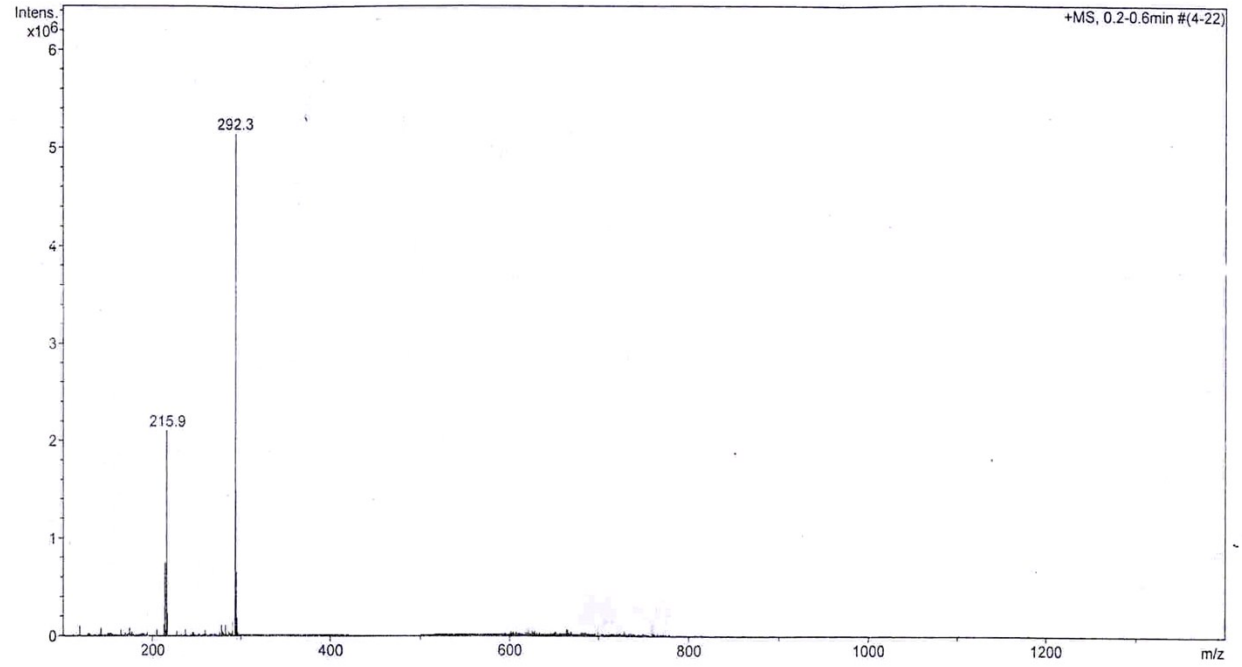

Compound 4b

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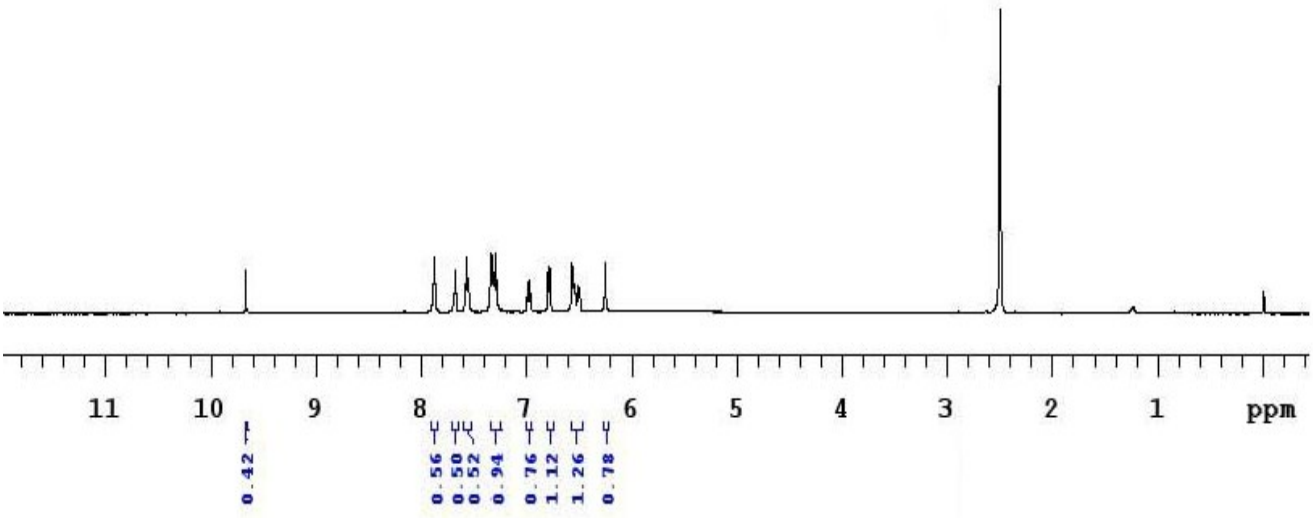

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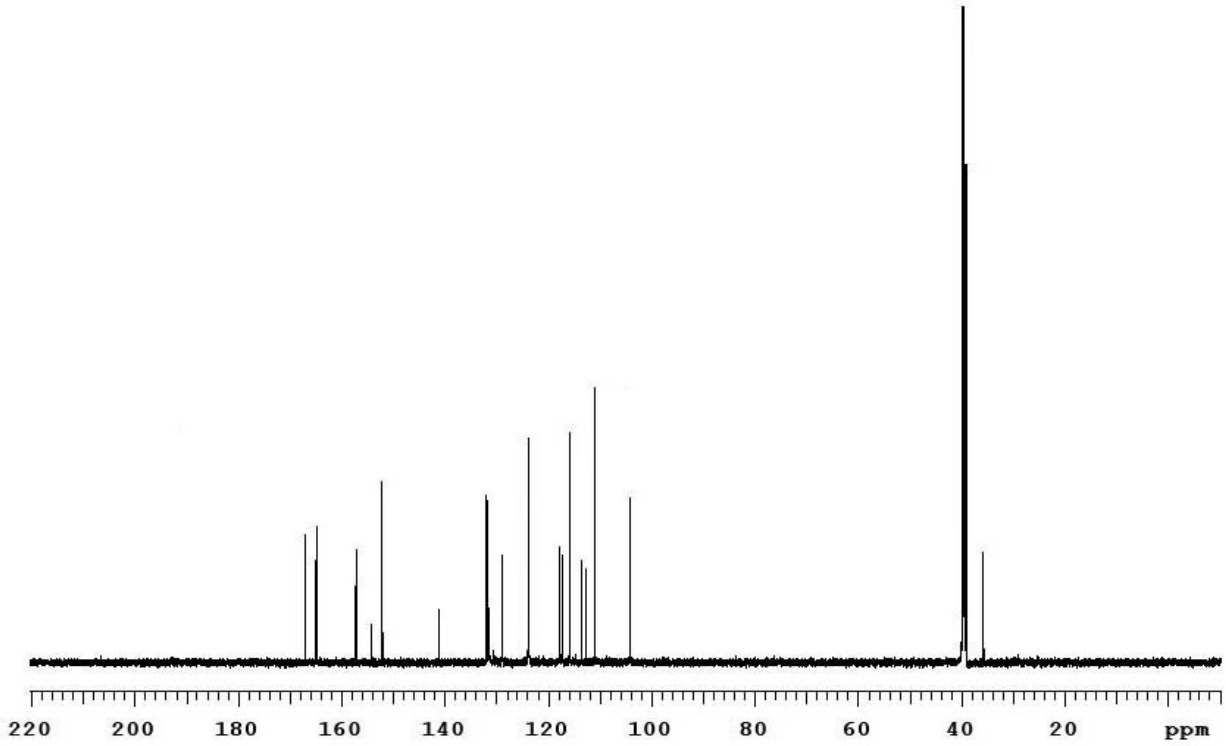
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60
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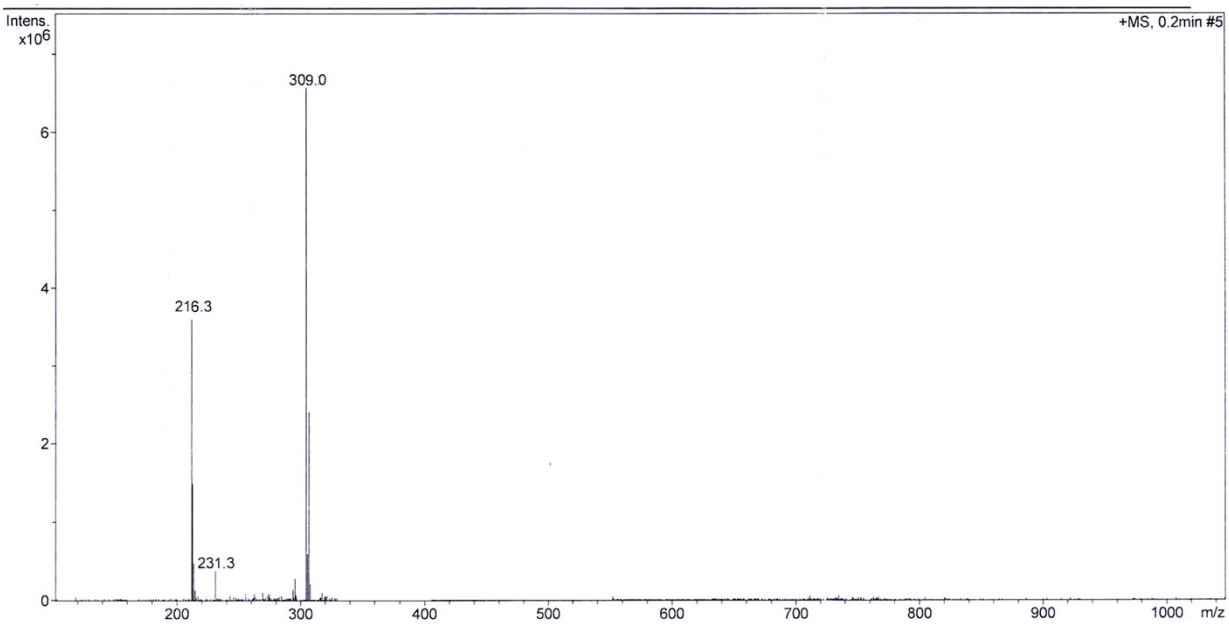
20
ppm

Mass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800
900
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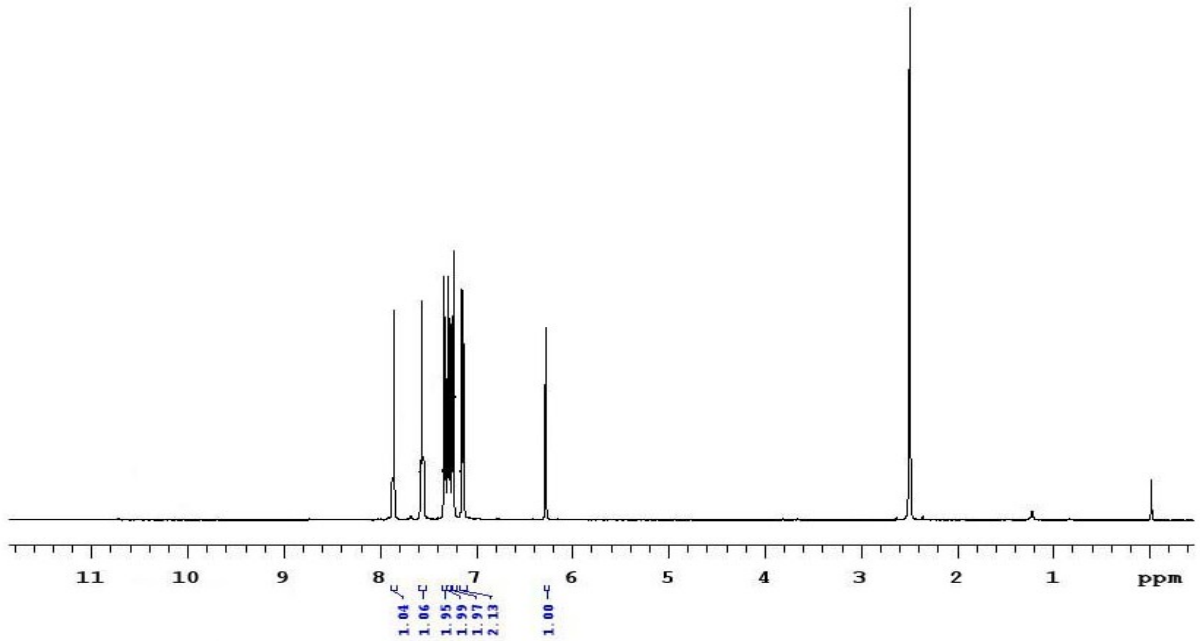
m/z

Compound 4c

H NMR



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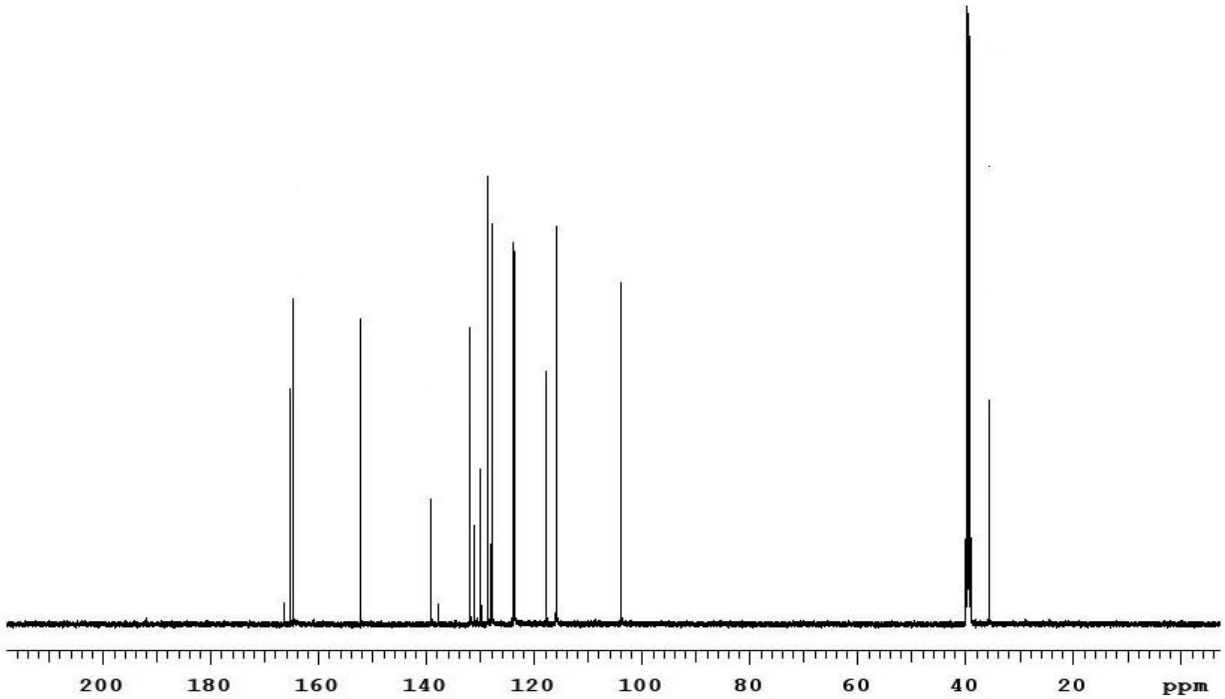

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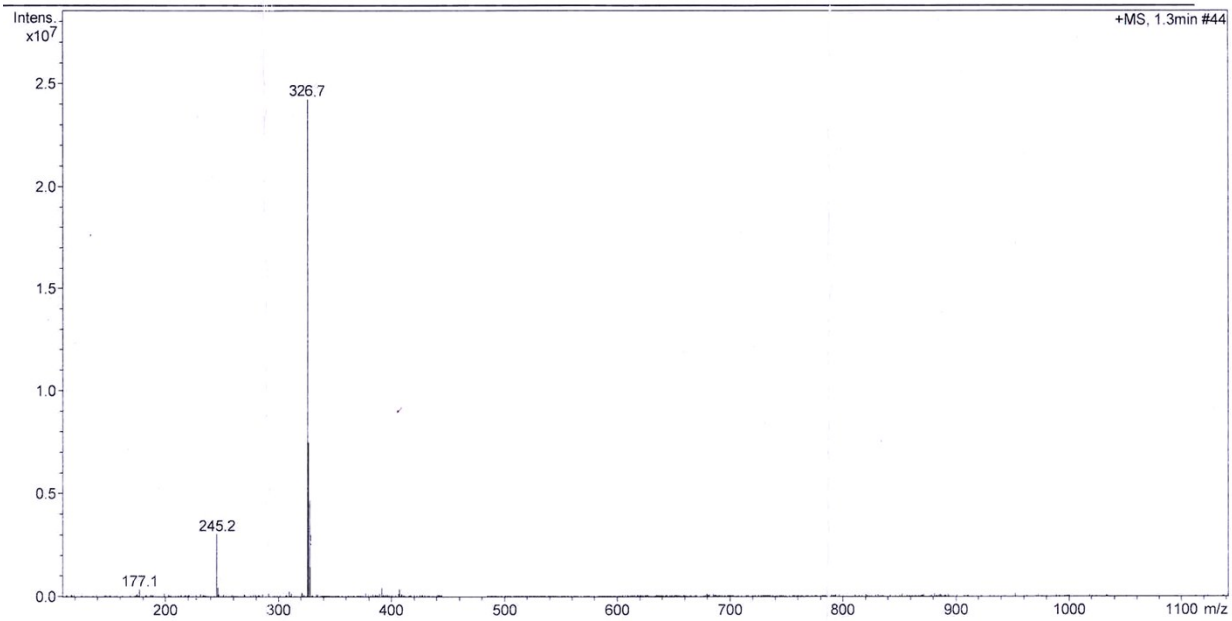
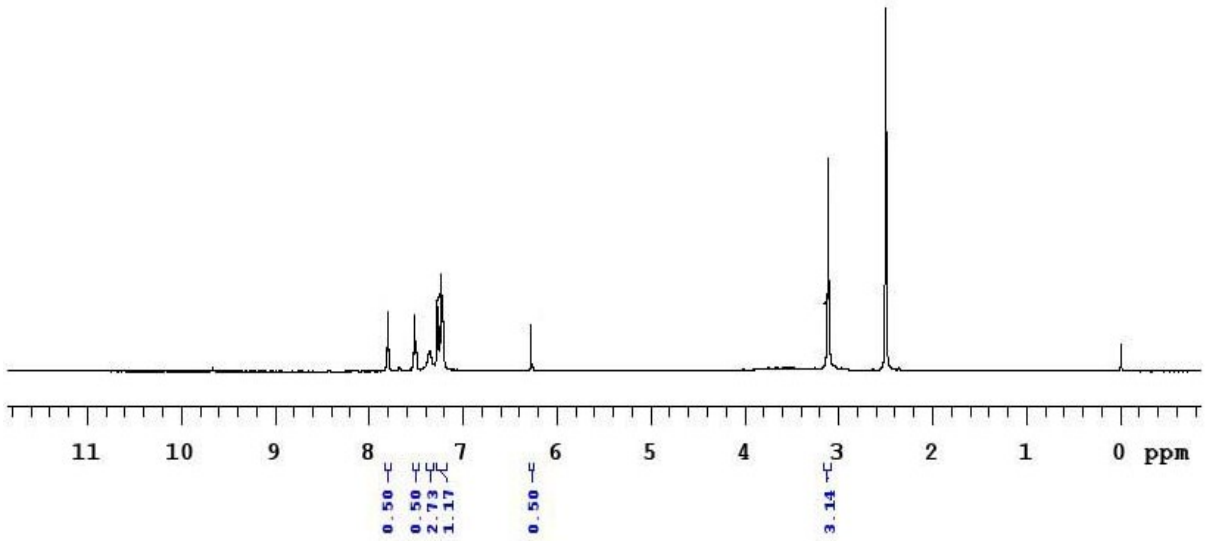


Compound 4d

H NMR



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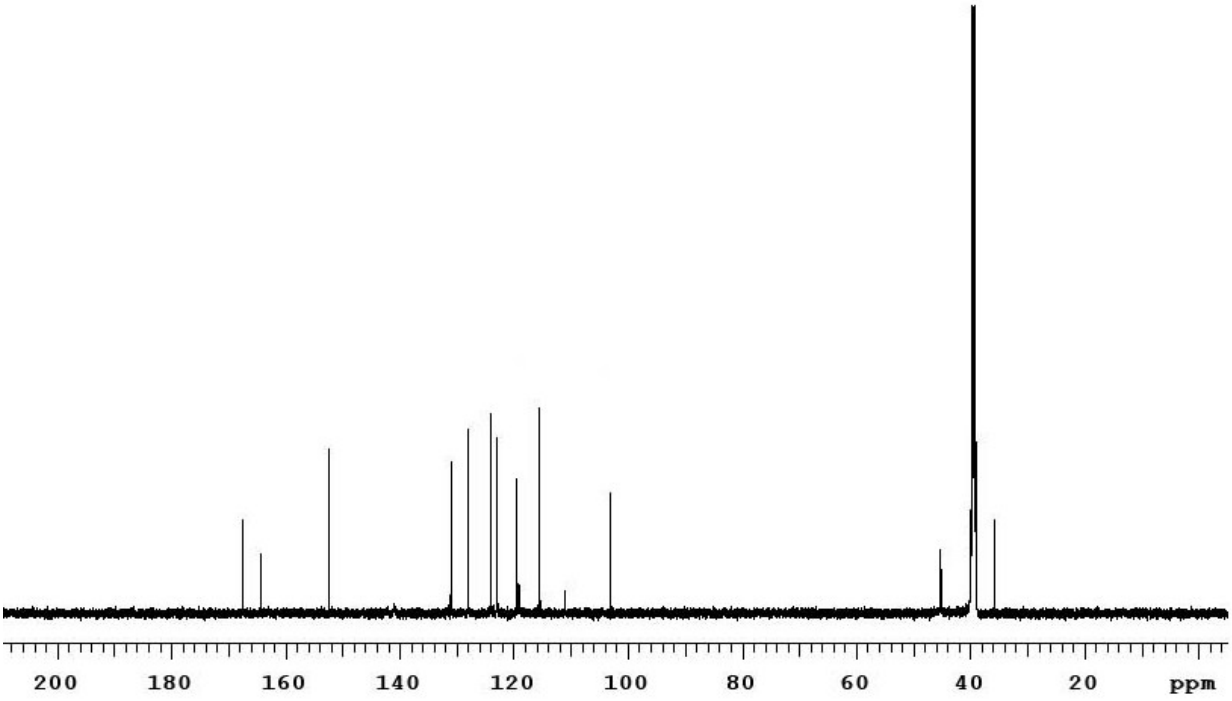
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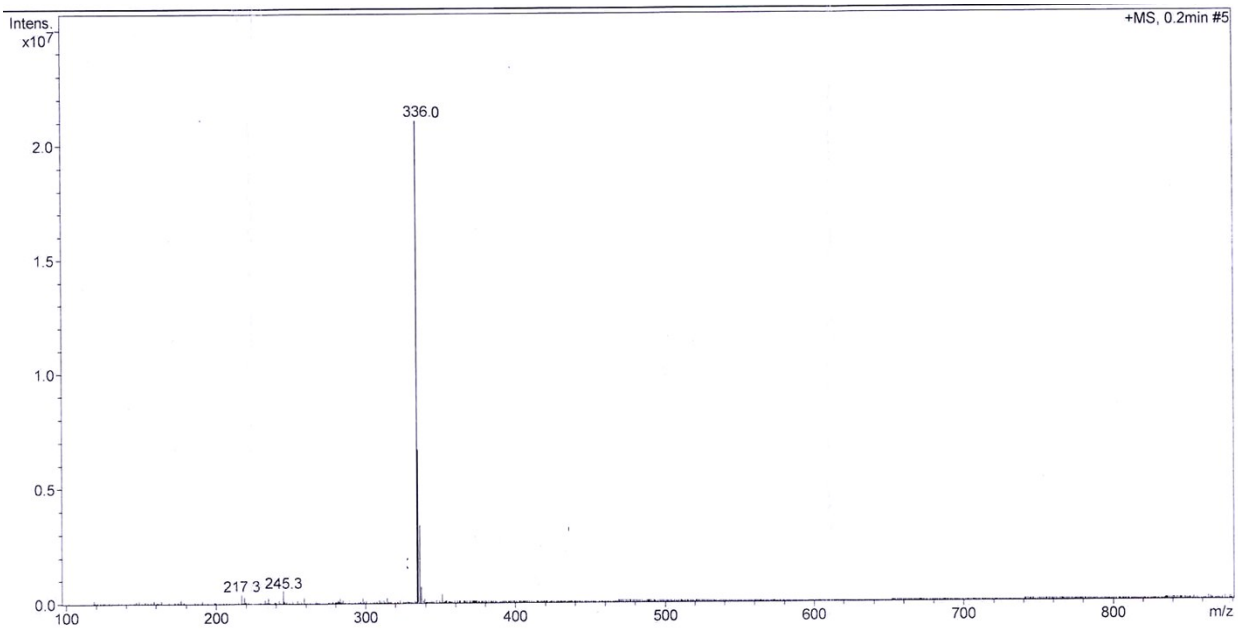
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400
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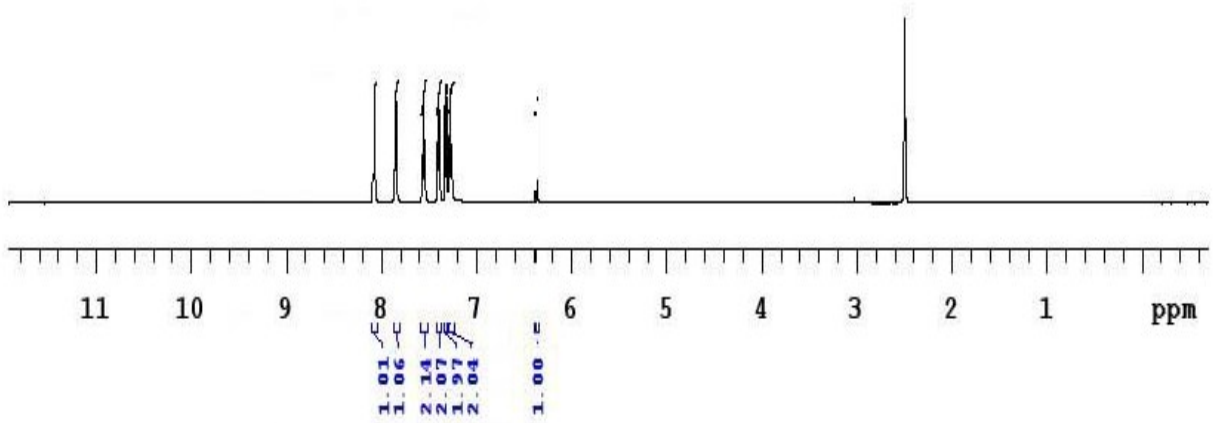
600
700
800
m/z

Compound 4e

H NMR



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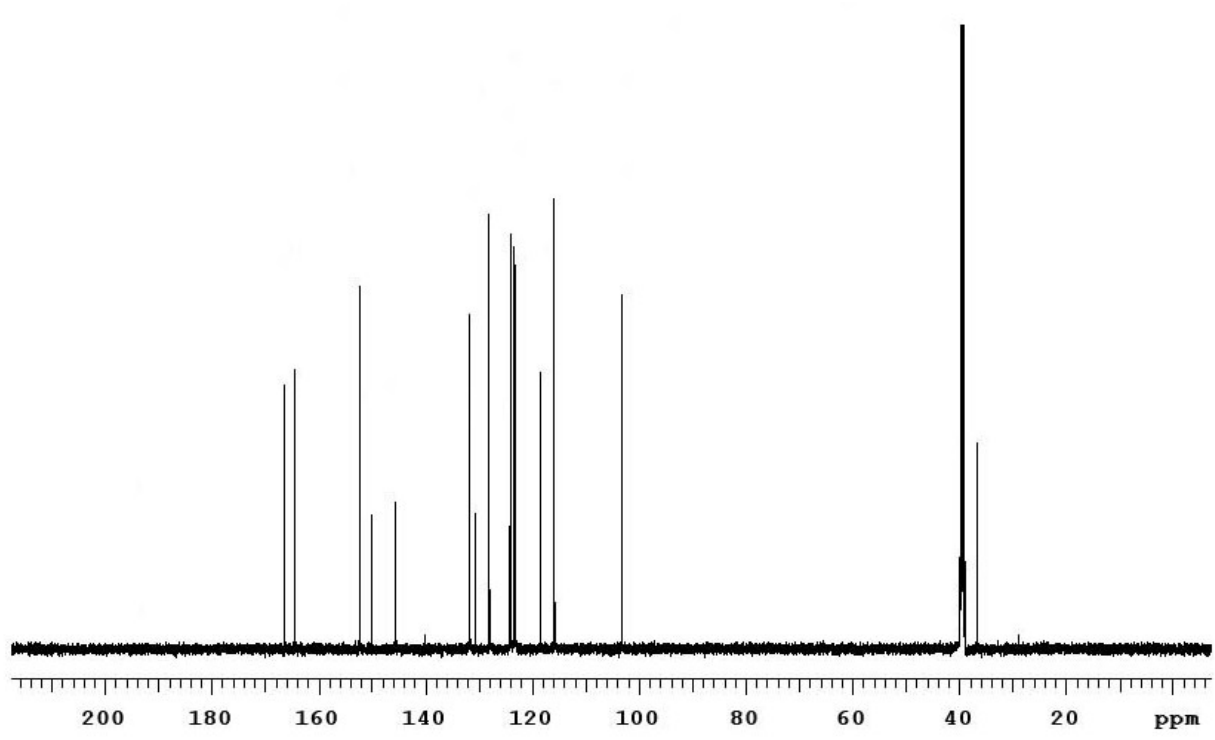

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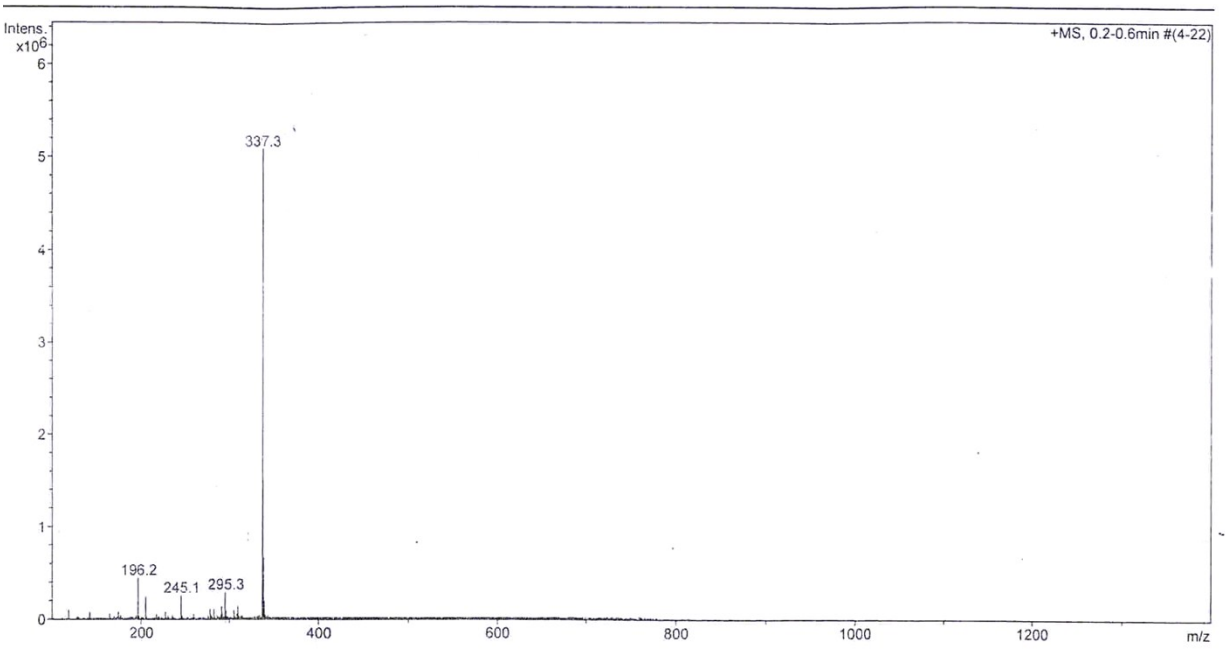
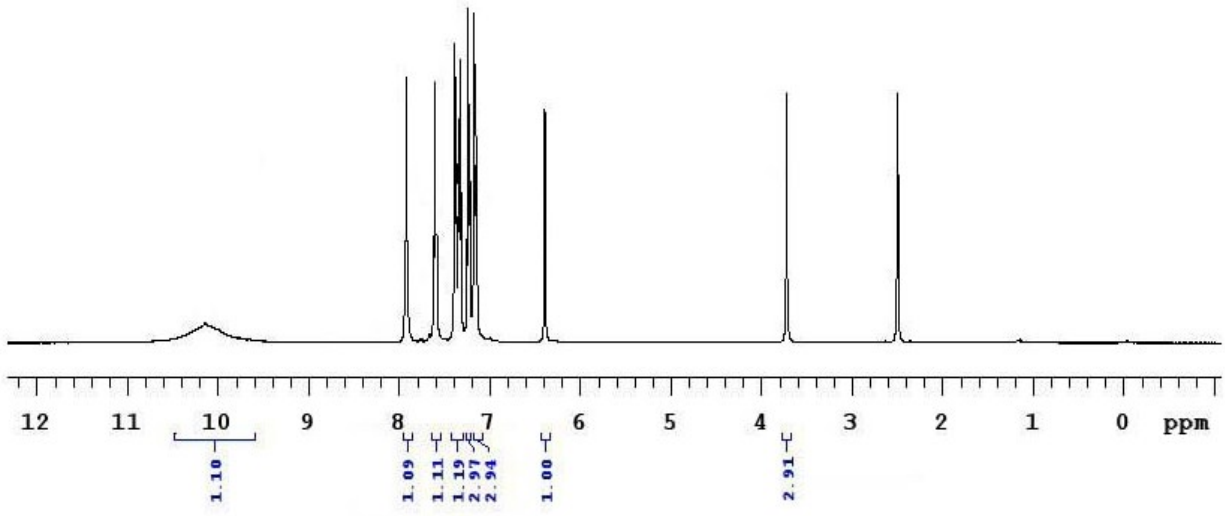


Compound 4f

H NMR



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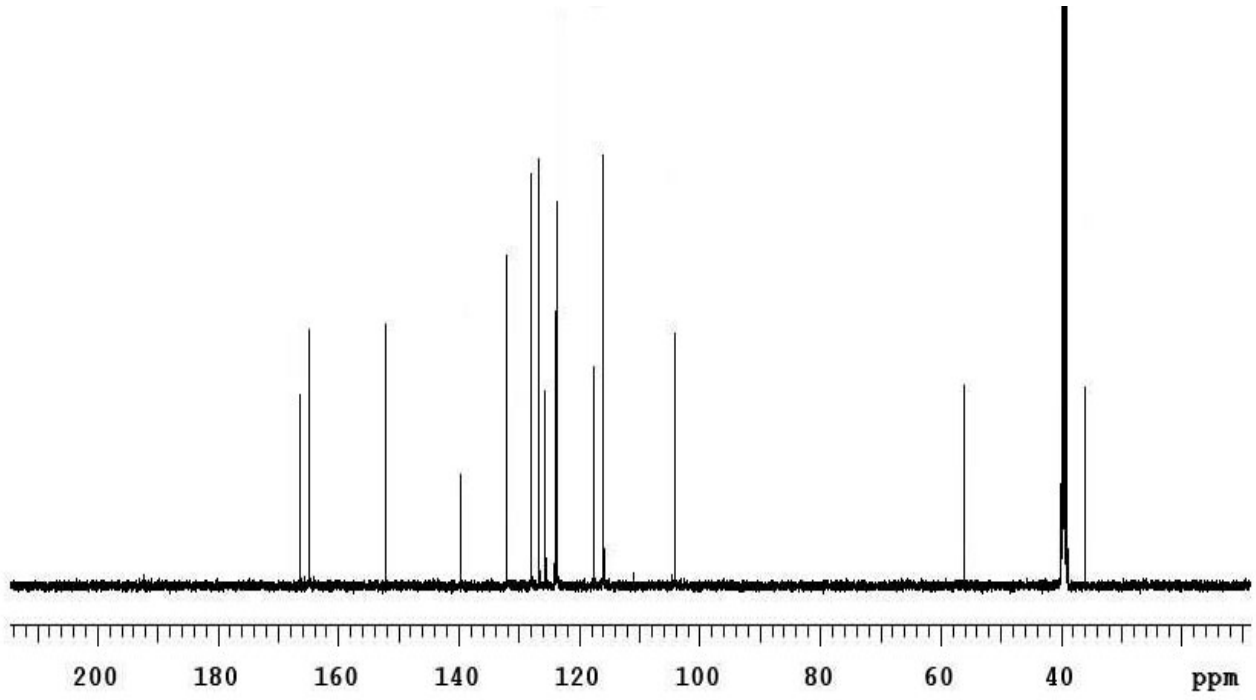
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80
60
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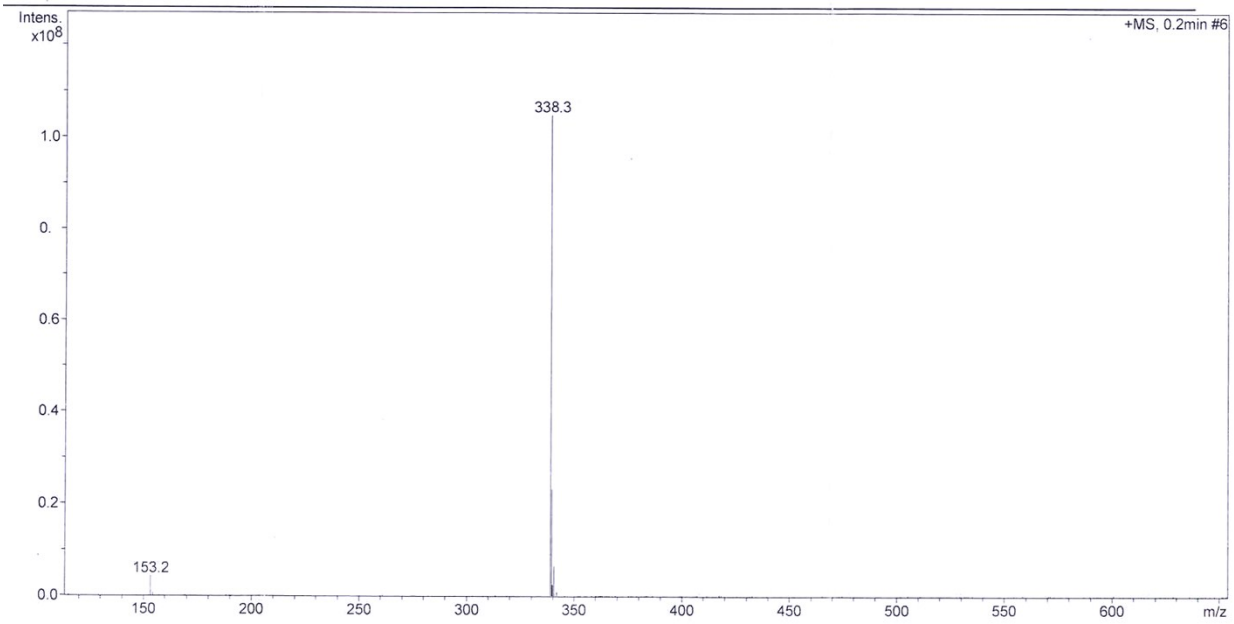
Mass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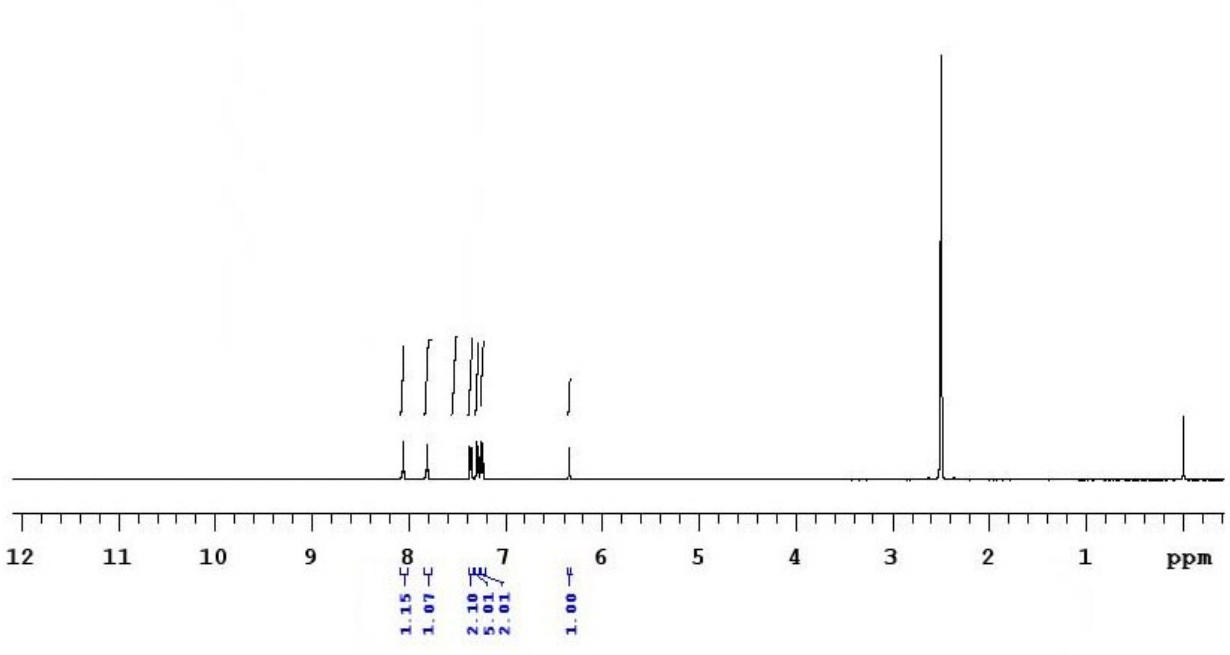
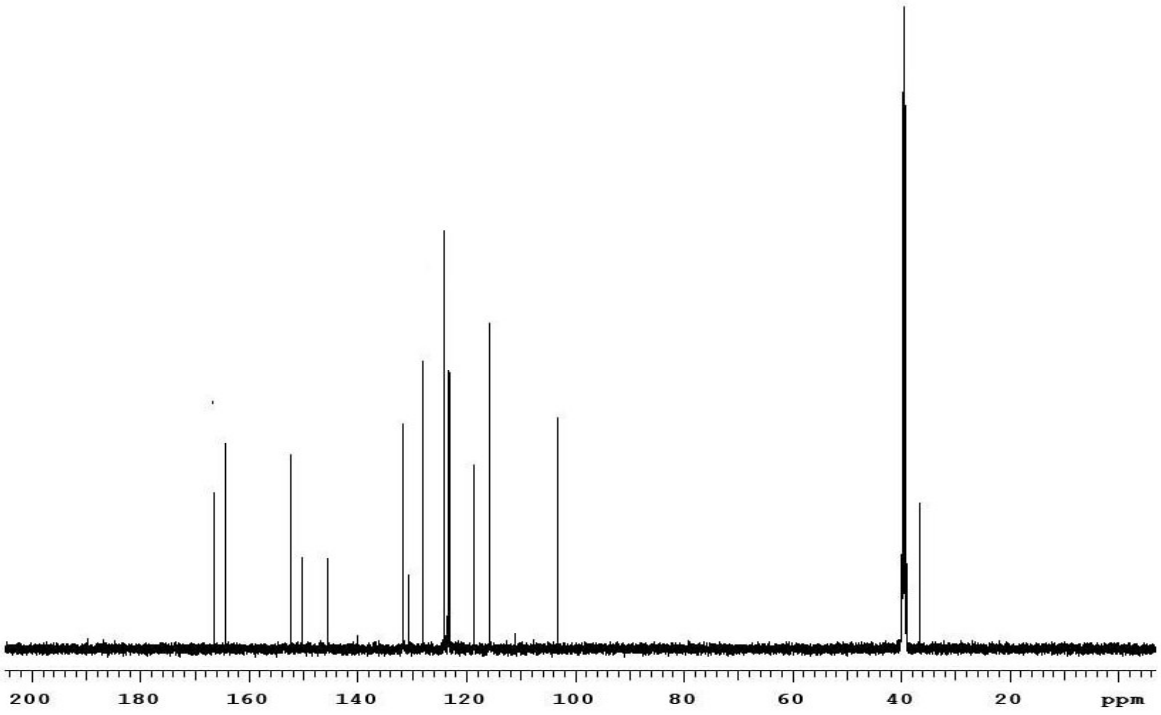
300
350
400
450
500
550
600
m/z

Compound 4h

H NMR



^{13}C NMR



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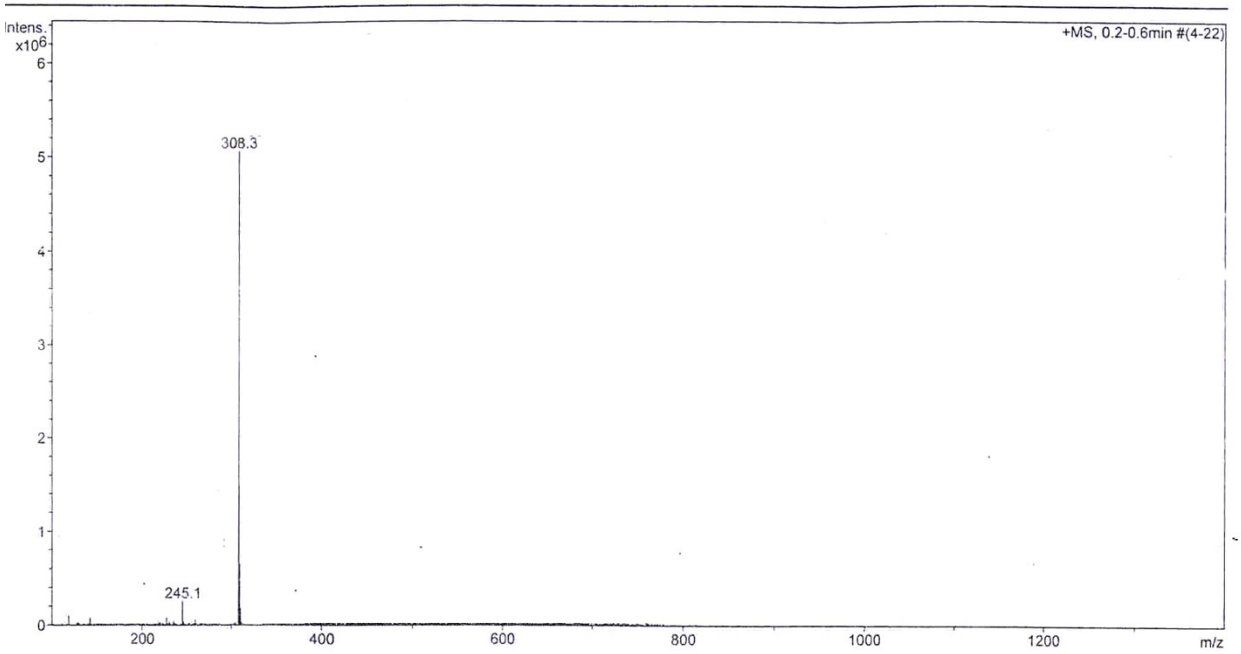
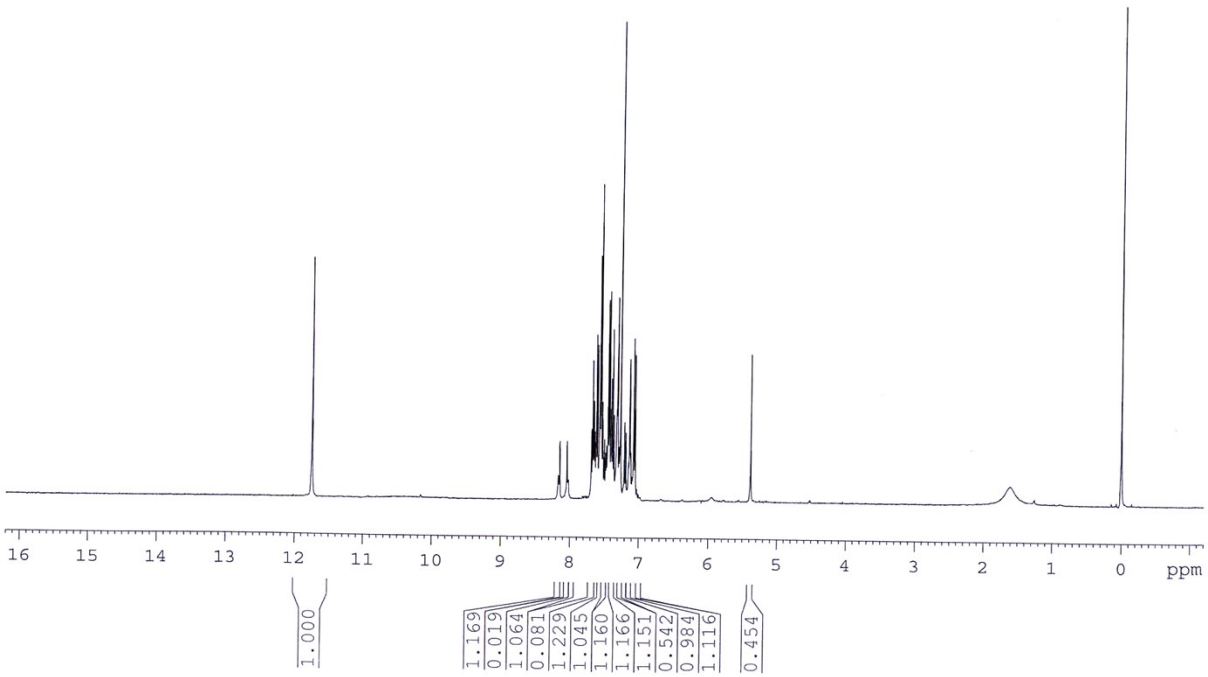


Compound 4i

H NMR



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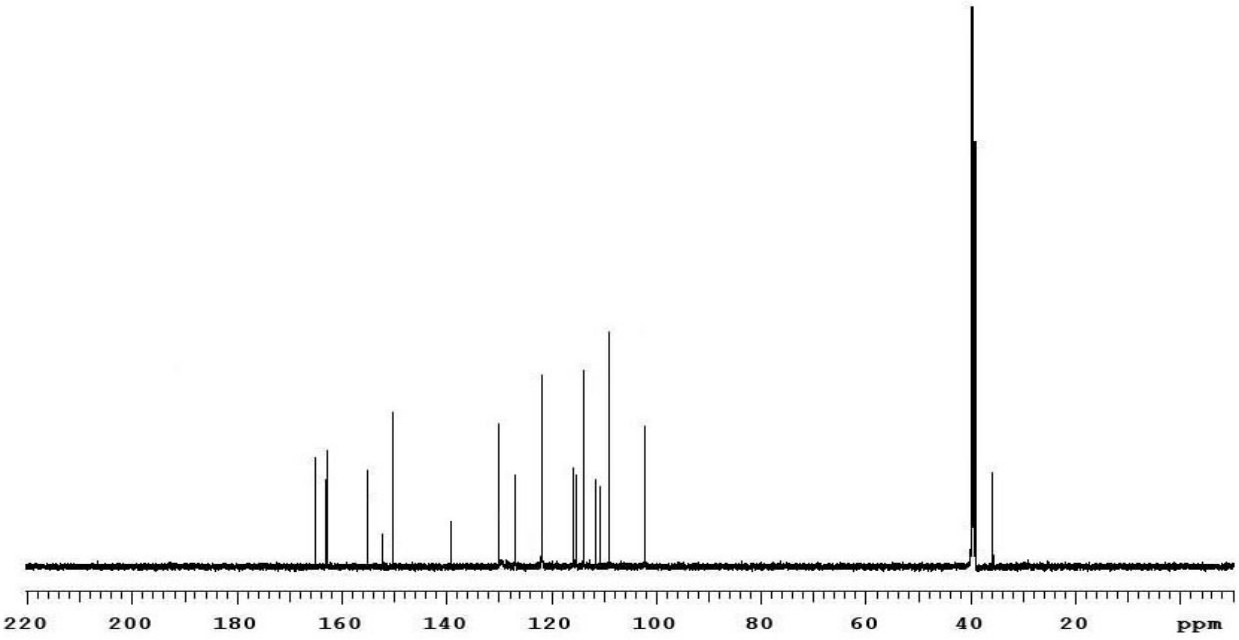
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40
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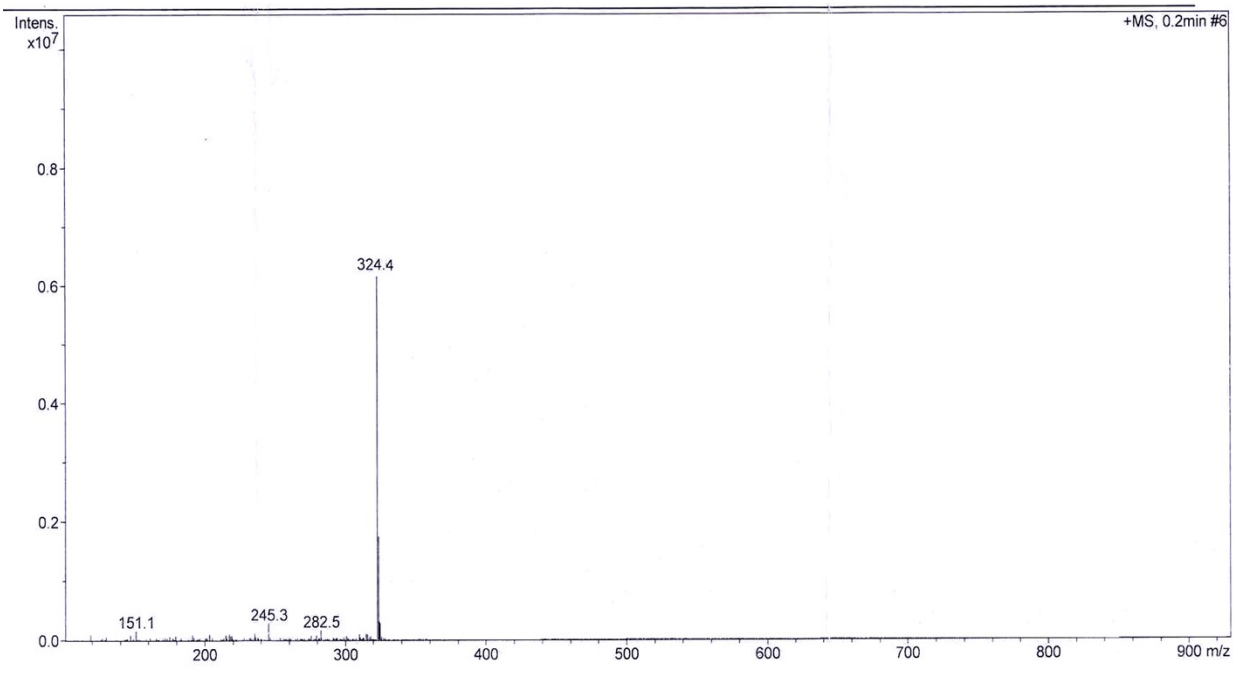
ppm

Mass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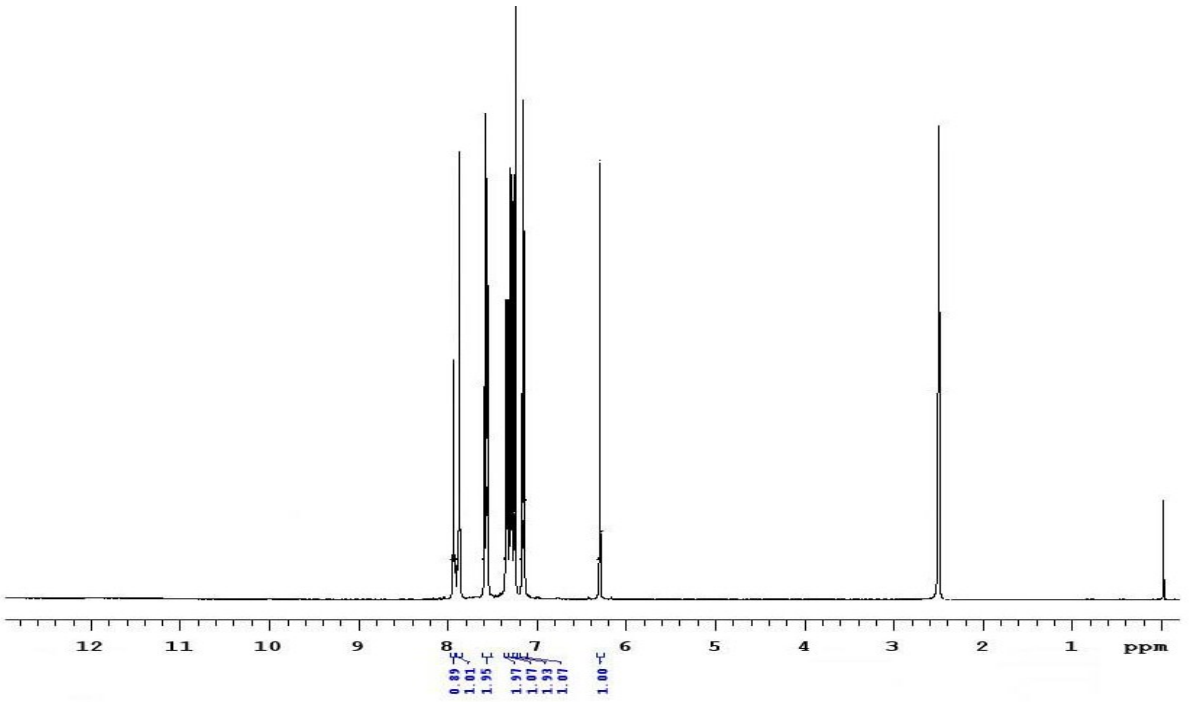
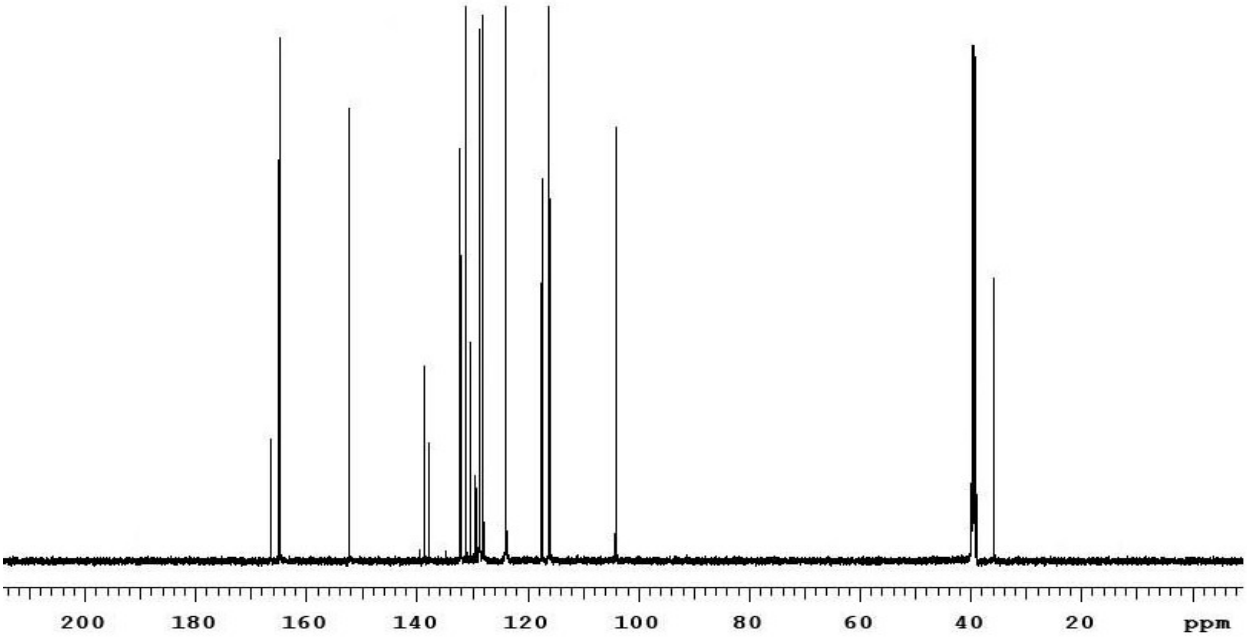
200
300
400
500
600
700
800
900 m/z

Compound 4j

H NMR



^{13}C NMR



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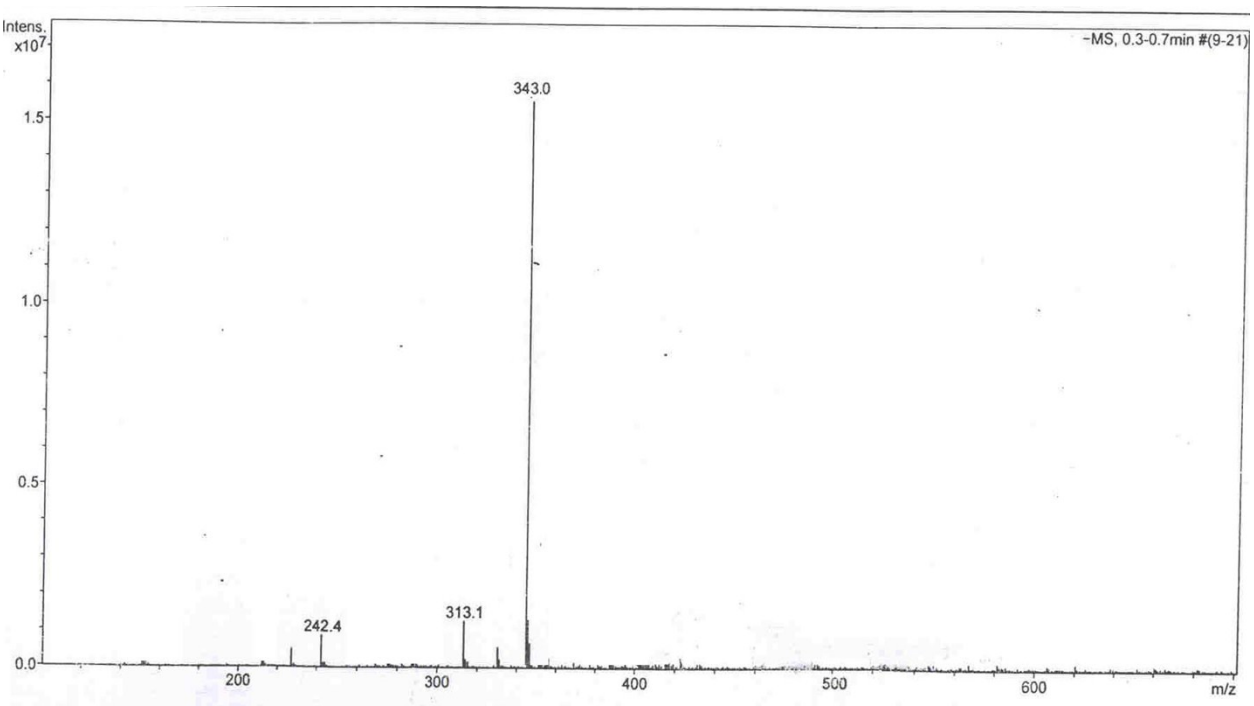
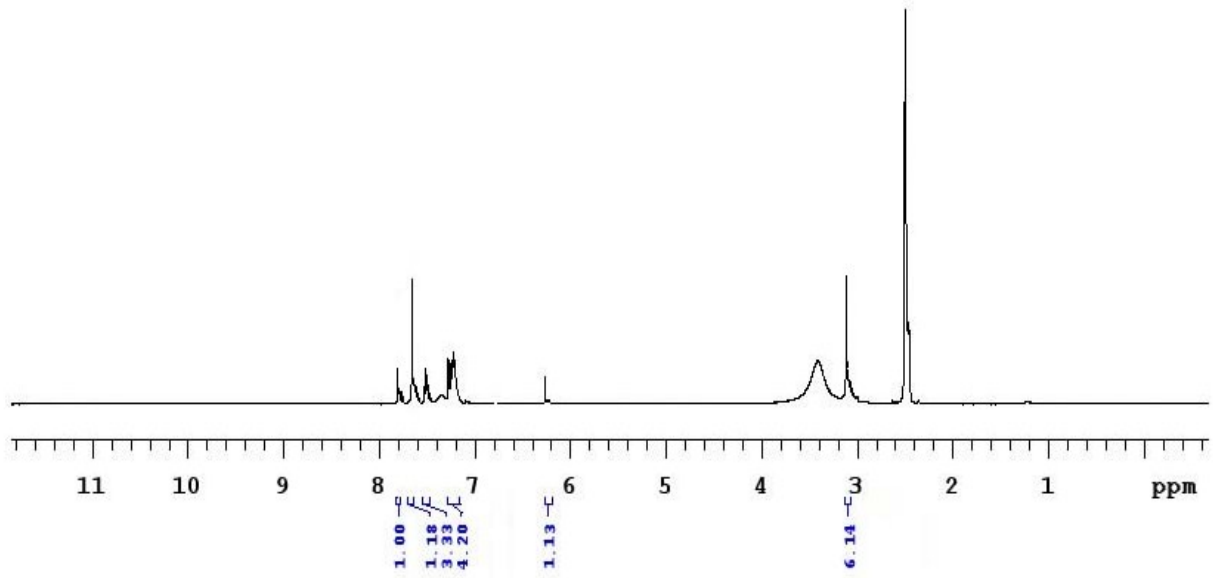
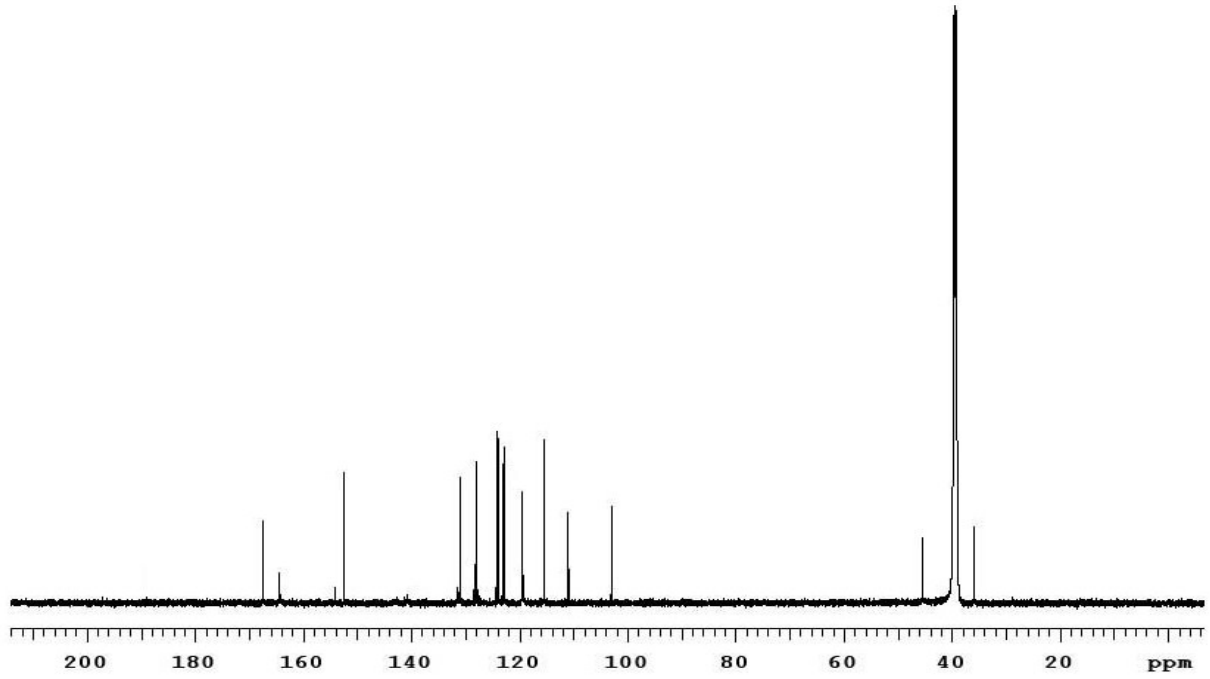


Compound 4k

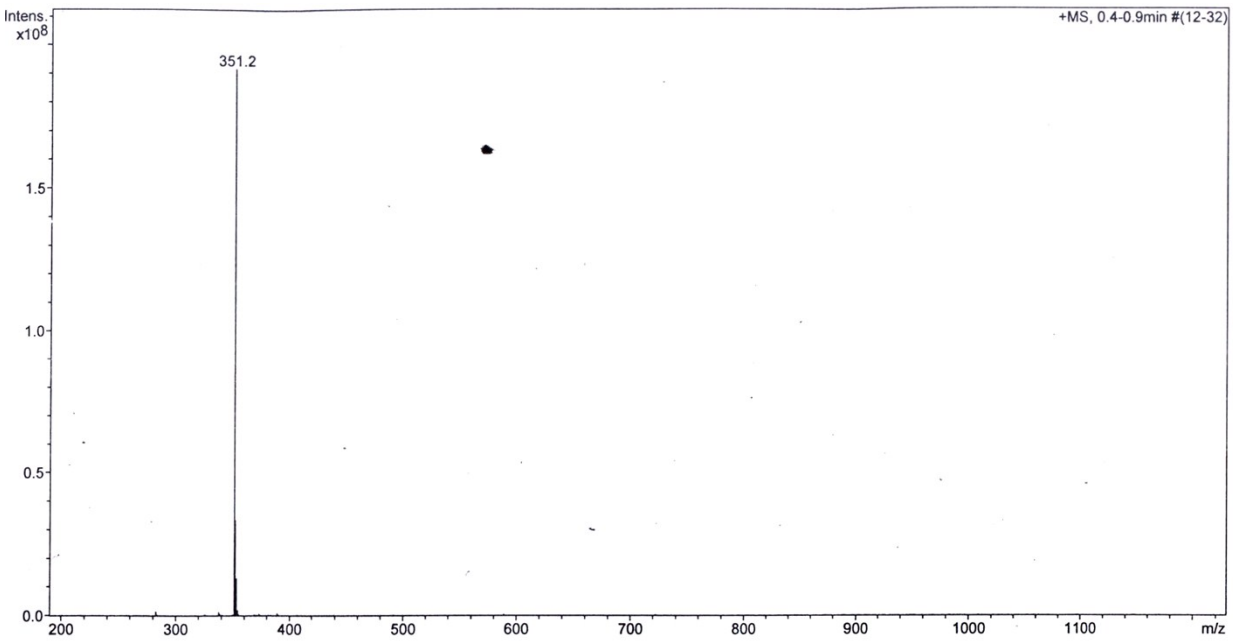
H NMR



^{13}C NMR


200
180
160
140
120
100
80
60
40
20
ppm

Mass


Intens.
x10^8
+MS, 0.4-0.9min #(12-32)
351.2
1.5
1.0
0.5
0.0
200
300
400
500
600
700
800
900
1000
1100
m/z