

Supporting Information

PEG 400-Catalyzed C3 & O-Alkylation Reactions of 4-Hydroxycoumarin-A Study

Madhuri Pulagam¹, Hari Babu Bollikolla^{1,2,*}

¹Head, Department of Chemistry, Acharya Nagarjuna University, N Nagar-522 510, Andhra Pradesh, India

²Department of Chemistry, Andhra Kesari University-523001, Ongole, Andhra Pradesh, India

Characterization data for the synthesized compounds:

4-Hydroxy-3-(1-phenylethyl)-2H-chromen-2-one (3a):¹⁸⁻¹⁹ White amorphous solid. mp: 204-205 °C. R_f (*n*-Hexane: EtOAc, 1:1) = 0.4; IR (neat): ν = 3427 (s), 1672 (vs), 1626 (vs), 1393 (s), 1214 (s), 753 (s) cm^{-1} ; ¹H NMR (400 MHz, CDCl_3): δ = 1.73 (d, J = 7.3 Hz, 3H, CH_3CH), 4.66 (q, J = 7.3 Hz, 1H, CH_3CH), 7.14 (m, 1H), 7.25 (m, 2H), 7.29 (dd, J = 8.2 Hz, 1.0 Hz, 1H), 7.35 (ddd, J = 8.0 Hz, 7.3 Hz, 1.0 Hz, 1H), 7.41 (m, 2H), 7.60 (ddd, J = 8.2 Hz, 7.3 Hz, 1.6 Hz, 1H), 8.00 (dd, 8.0 Hz, 1.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl_3): δ = 17.2, 35.1, 111.1 (C-3), 117.1, 117.2, 123.8, 124.5, 126.7, 128.2, 128.8, 132.5, 144.9, 153.6, 160.0, 162.1; GC (HP 5-60/3-12-260/10): t_R = 25.72 min; MS (EI) m/z (%) = 266 (100) [M^+], 251 (67), 237 (4), 223 (33), 207 (10), 188 (7), 175 (51), 161 (6), 145 (20), 121 (35), 105 (39), 92 (10), 77 (11) [C_6H_5^+].

4-Hydroxy-3-(1-(4-methoxyphenyl)ethyl)-2H-chromen-2-one (3b):¹⁸⁻¹⁹ White solid; mp: 169-171 °C. IR (KBr): 3398, 2968, 1672, 1626, 1511, 1246 cm^{-1} . ¹H NMR (400 MHz, CDCl_3): δ 7.69 (d, J = 8.0 Hz, 1H), 7.52–7.48 (m, 1H), 7.40 (d, J = 8.4 Hz, 2H), 7.30–7.21 (m, 2H), 7.40 (d, J = 8.4 Hz, 2H), 6.47 (br s, 1H), 4.66 (q, J = 7.6 Hz, 1H), 3.81 (s, 3H), 1.64 (d, J = 7.6 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl_3): δ 163.5, 159.8, 159.0, 152.4, 133.0, 131.7, 128.4, 123.8, 122.8, 116.3, 116.1, 114.9, 110.0, 55.3, 33.7, 16.7 ppm. MS (ESI): m/z 295 ([$\text{M}-1$]). Anal. Calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_4$: C, 72.96; H, 5.44. Found: C, 72.95; H, 5.41.

3-(1(4-Bromophenyl)ethyl)-4-hydroxy-2H-chromen-2-one (3c):¹⁸⁻¹⁹ White amorphous solid. IR (neat): ν = 3436 (br), 1716, 1660, 1605, 1203, 754 cm^{-1} . ¹H NMR (400 MHz, CDCl_3): δ = 7.77–7.70 (m, 1 H), 7.63–7.53 (m, 3H), 7.44–7.26 (m, 4H), 6.00 (s, 1H), 4.72 (q, J = 7.3 Hz, 1H), 1.71 (d, J = 7.3 Hz, 3H). ¹³C NMR (100 MHz, CDCl_3): δ = 163.3, 159.6, 152.6, 140.7, 132.7, 132.1, 129.1, 124.0, 122.8, 116.5, 115.9, 109.7, 34.1, 16.6. MS (EI): m/z (%) = 344.0 (100) [M^+], 345.0 (22) [M^+], 346.0 (97) [M^+], 347.0 (18) [M^+]. Anal. Calcd. for $\text{C}_{17}\text{H}_{13}\text{BrO}_3$: C, 59.15; H, 3.80. Found: C, 58.91; H, 3.90.

4-Hydroxy-3-(1,2,3,4-tetrahydronaphthalen-1-yl)-2H-chromen-2-one (Coumatetralyl, B, 3d):¹⁸⁻¹⁹ White solid; mp: 188-190 °C; R_f (30% EtOAc/hexanes) 0.3; IR (neat): ν_{max} 3271, 2941, 1671, 1625, 1391, 1211, 1143, 745 cm^{-1} ; ¹H NMR (300 MHz, CDCl_3): δ 7.63 (dd, J = 1.4, 8.0 Hz, 1H), 7.49 (td, J =

1.4, 8.0 Hz, 1H), 7.35-7.12 (m, 6H), 5.73 (s, 1H), 4.59 (t, $J=6.6$ Hz, 1H), 2.93 (t, $J=5.8$ Hz, 2H), 2.33-2.14 (m, 1H), 2.03-1.79 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 163.8, 160.1, 152.7, 138.3, 134.8, 132.0, 130.8, 129.8, 128.1, 127.6, 124.0, 123.1, 116.5, 116.3, 109.6, 36.6, 30.0, 29.5, 21.9.

(E)-3-(1,3-Diphenylallyl)-4-hydroxy-2H-chromen-2-one (3e):¹⁸⁻¹⁹ White solid; mp: 155-157 °C. IR (KBr): 3327, 1671, 1624, 1610, 1494, 1392, 1201, 754 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.81 (dd, $J=6.8, 8.0$ Hz, 1H), 7.54-7.50 (m, 1H), 7.42-7.24 (m, 13H), 6.79 (dd, $J=6.0, 16.0$ Hz, 1H), 6.52 (d, $J=16.0$ Hz, 1H), 5.47 (d, $J=6.0$ Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 163.2, 160.9, 152.6, 139.6, 136.1, 133.8, 132.1, 129.2, 128.6, 128.1, 128.0, 127.6, 126.5, 124.0, 123.1, 116.5, 115.8, 106.4, 43.9 ppm. MS (ESI): m/z 353 ($[\text{M}-1]^-$).

3-((E)-3-(4-Chlorophenyl)-1-phenylallyl)-4-hydroxy-2H-chromen-2-one (3f):¹⁸⁻¹⁹ Pale yellow solid, mp: 168-171°C. IR (KBr): ν 3327, 1674, 1626, 1611, 1494, 1393, 1200, 756 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 7.81-7.72 (m, 2H), 7.57-7.28 (m, 11H), 6.78-6.68 (m, 1H), 6.48 (d, $J=16.4$ Hz, 1H), 5.46 (d, $J=6$ Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 162.9, 160.9, 152.5, 140.1, 136.2, 133.7, 132.2, 1130.0, 128.7, 128.2, 127.9, 127.6, 126.6, 124.1, 123.2, 116.5, 115.8, 106.5, 44.0 ppm. MS (ESI): m/z (rel. abund.%) 389 (M^+ , 100), 391 (M^+ , 30) ($[\text{M}+1]^+$).

3-Benzhydryl-4-hydroxy-2H-chromen-2-one (3g):¹⁸⁻¹⁹ White solid; mp: 180-181 °C. IR (KBr): 3293, 1671, 1624, 1608, 1567, 1494, 1450, 1388, 1211, 1085, 896, 756, 715 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.74 (dd, $J=6.8, 8.0$ Hz, 1H), 7.55-7.50 (m, 1H), 7.39-7.23 (m, 12H), 6.37 (br s, 1H), 5.98 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 163.2, 160.1, 152.3, 139.9, 132.1, 129.4, 128.7, 127.7, 123.9, 123.1, 116.4, 115.9, 107.7, 47.2 ppm. MS (ESI): m/z 327 ($[\text{M}-1]^-$).

4-Hydroxy-3-(1-(p-tolyl)ethyl)-2H-chromen-2-one (5a):⁴³ ^1H NMR (CDCl_3 , 400 MHz): δ 7.70-7.68 (m, 1H), 7.52-7.47 (m, 1H), 7.38 (d, $J=8$ Hz, 2H), 7.30-7.27 (m, 1H), 7.24-7.20 (m, 3H), 6.45 (s, 1H), 4.72-4.66 (m, 1H), 2.35 (s, 3H), 1.65 (d, $J=7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 163.7, 159.9, 152.6, 138.5, 137.7, 131.8, 130.5, 127.3, 123.9, 123.0, 116.4, 116.3, 110.2, 34.3, 21.1, 16.7.

3-(1-(4-Chlorophenyl)ethyl)-4-hydroxy-2H-chromen-2-one (5b):⁴³ ^1H NMR (CDCl_3 , 400 MHz): δ 7.72-7.70 (m, 1H), 7.55-7.50 (m, 1H), 7.42-7.35 (m, 4H), 7.31-7.27 (m, 1H), 7.25-7.23 (m, 1H), 6.36 (s, 1H), 4.71-4.66 (m, 1H), 1.66 (d, $J=7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 163.5, 159.9, 152.6, 140.4, 133.7, 132.2, 129.7, 128.8, 124.1, 123.0, 116.6, 116.0, 109.8, 34.0, 16.7.

4-(1-Phenylethoxy)-2H-chromen-2-one (7a).¹⁸ Off white solid; mp: 214-218 °C. IR (KBr): ν 1669, 1621, 1492, 1401, 1218, 1168, 741 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 7.64 (d, $J=12.4$ Hz, 1H), 7.64-7.43 (m, 5H), 7.64-7.42 (m, 2H), 7.23 (dd, $J=10.8$ Hz, 1H), 5.99 (s, 1H), 4.74 (q, $J=9.6$ Hz, 1H), 1.68 (d, $J=9.6$ Hz, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 163.8, 160.0, 152.6, 141.8,

132.1, 129.8, 127.7, 127.5, 123.9, 123.0, 116.3, 116.2, 110.3, 34.8, 16.8 ppm. MS (ESI): m/z (rel. abund.%) 267.3 ($[M+1]^+$, 100).

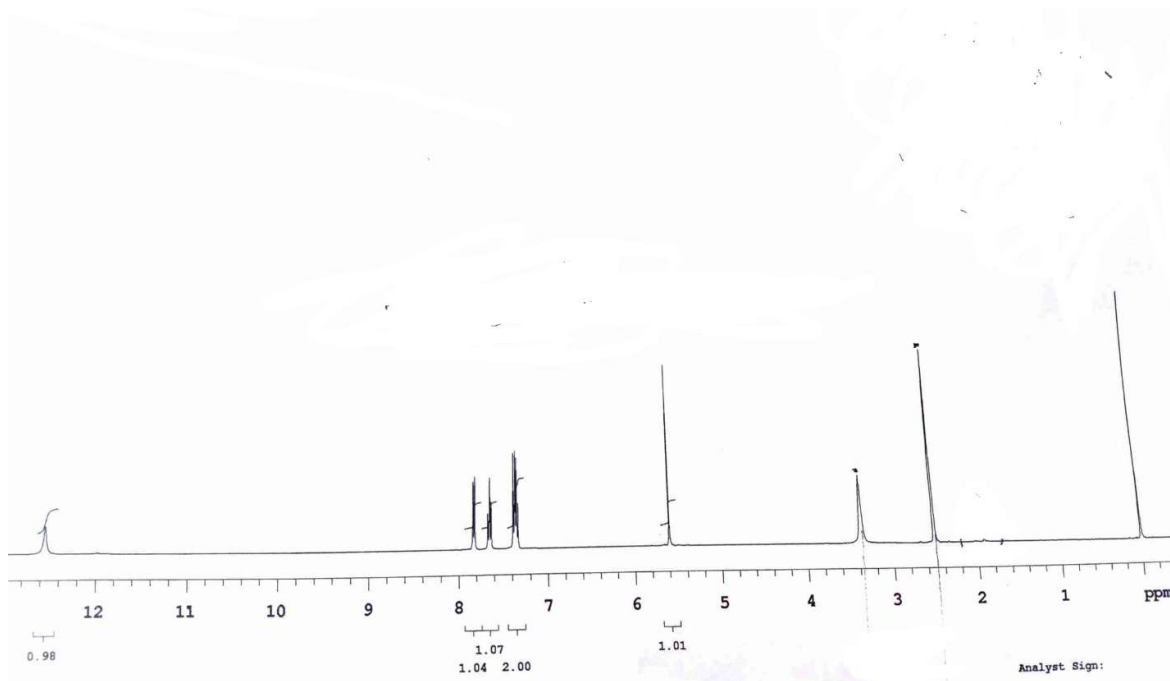
4-(1-(4-Methoxyphenyl)ethoxy)-2H-chromen-2-one (7b):¹⁸ Off white solid. mp: 180-184 °C. IR (KBr): 1673, 1628, 1514, 1249 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 7.70 (dd, $J = 8.8$ Hz, 1H), 7.48-7.52 (m, 2H), 7.41 (d, $J = 11.2$ Hz, 1H), 7.26-7.22 (m, 2H), 6.99 (d, $J = 4$ Hz, 2H), 6.04 (s, 1H), 4.65 (q, $J = 10$ Hz, 1H), 3.79 (s, 3H), 1.60 (d, $J = 9.6$ Hz, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 163.6, 159.8, 159.1, 152.3, 133.1, 131.7, 128.5, 123.8, 122.6, 116.2, 116.1, 114.9, 110.0, 55.3, 33.6, 16.8 ppm. MS (ESI): m/z (rel. abund.%) 297.2 ($[M+1]^+$, 100).

4-((E)-1,3-Diphenylallyloxy)-2H-chromen-2-one (7c):¹⁸ Pale yellow solid, mp: 132-136 °C. IR (KBr): ν 1678, 1626, 1613, 1501, 1394, 1203, 757 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 7.78 (d, $J = 7.2$ Hz, 1H), 7.55 (t, $J = 8$ Hz, 1H), 7.24-7.64 (m, 12H), 6.94 (br, s 1H), 6.67 (dd, $J = 6.4, 9.6$ Hz, 1H), 6.52 (d, $J = 16.4$ Hz, 1H), 5.47 (d, $J = 5.6$ Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 163.3, 161.5, 152.4, 139.7, 136.3, 133.9, 132.4, 129.2, 128.7, 128.2, 128.7, 127.7, 126.4, 124.4, 123.1, 116.5, 115.7, 106.4, 43.5 ppm. MS (ESI): m/z (rel. abund.%) 355.0 ($[M+1]^+$, 100).

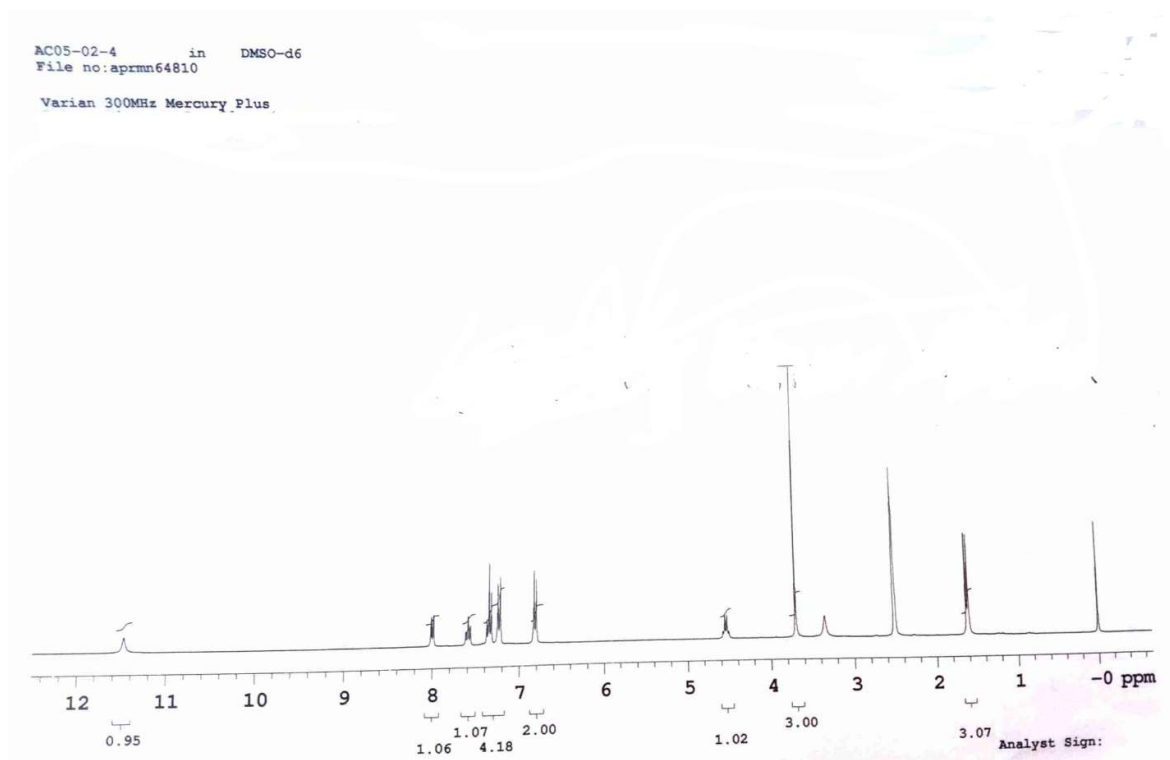
4-((E)-3-(4-Chlorophenyl)-1-phenylallyloxy)-2H-chromen-2-one (7d):¹⁸ Pale yellow solid, mp: 154-156 °C. IR (KBr): 1676, 1629, 1616, 1502, 1398, 1210, 758 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 7.75 (dd, $J = 8, 14.8$ Hz, 1H), 7.41-7.14 (m, 12H), 6.78-6.67 (m, 1H), 6.48 (d, $J = 16.4$ Hz, 1H), 6.41-6.35 (m, 1H), 5.44 (dd, $J = 5.9$ Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 163.4, 161.1, 152.8, 139.7, 136.2, 133.7, 132.4, 129.6, 128.4, 128.1, 128.0, 127.8, 126.5, 124.1, 123.3, 116.7, 115.6, 106.5, 43.9 ppm. MS (ESI): m/z (rel. abund.%) 387 (M⁺, 100), 389 (M⁺, 30) ($[M-1]^-$).

4-(1,2,3,4-Tetrahydronaphthalen-4-yloxy)-2H-chromen-2-one (7e):¹⁸ Off white solid, mp: 178-180 °C. IR (KBr): 2938, 1674, 1628, 1389, 1214, 1148, 751 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 7.65 (dd, $J = 12.8$ Hz, 1H), 7.52 (t, 1H), 7.34-7.21 (m, 6H), 5.78 (s, 1H), 4.60 (t, $J = 10$ Hz, 1H), 2.93 (t, $J = 8.8$ Hz, 2H), 2.25-2.20 (m, 1H), 1.94-1.80 (m, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 164.0, 160.3, 152.6, 138.1, 134.7, 132.0, 130.7, 129.4, 128.3, 127.8, 124.1, 123.3, 116.4, 116.1, 109.4, 36.5, 30.3, 29.8, 22.1 ppm. MS (ESI): m/z (rel. abund.%) 293 ($[M+1]^+$, 100).

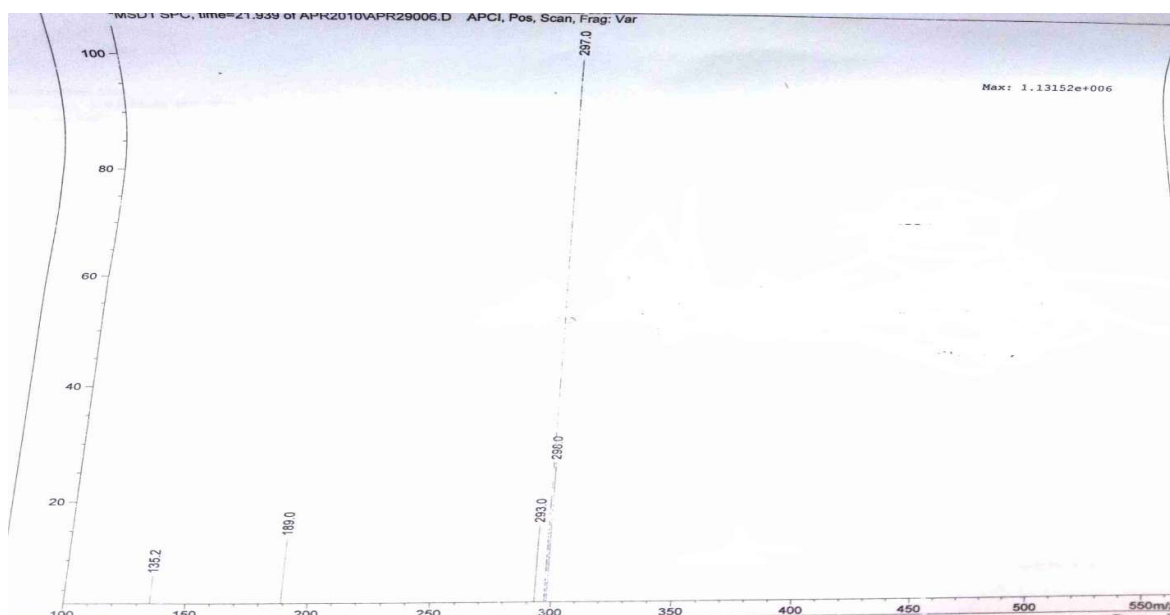
3,4-Dihydro-2,2-dimethylpyrano [3,2-c]chromen-5(2H)-one (8):¹⁸ Semi solid. IR (KBr): 1721, 1636, 1614, 1497, 1451, 1383, 1276, 1203, 1171, 1118, 1016, 764, 698 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 8.18 (dd, $J = 10$ Hz, 1H), 7.61-7.57 (m, 1H), 7.39-7.30 (m, 2H), 2.66 (t, $J = 6.8$ Hz, 2H), 1.87 (t, $J = 6.4$ Hz, 2H) 1.47 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 162.03, 60.1, 150.3, 128.4, 125.5, 121.6, 117.4, 100, 78.2, 35.5, 27.7, 15.8 ppm. MS (ESI): m/z (rel. abund.%) 231.3 ($[M+1]^+$, 100).



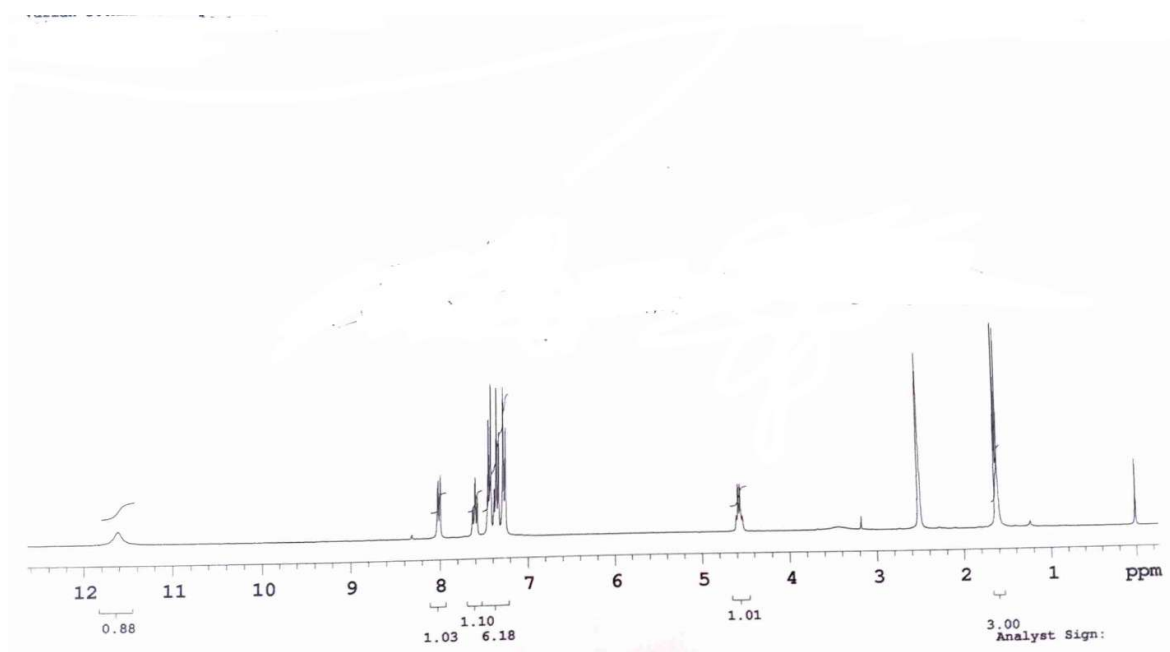
^1H NMR spectrum of **compound 1**



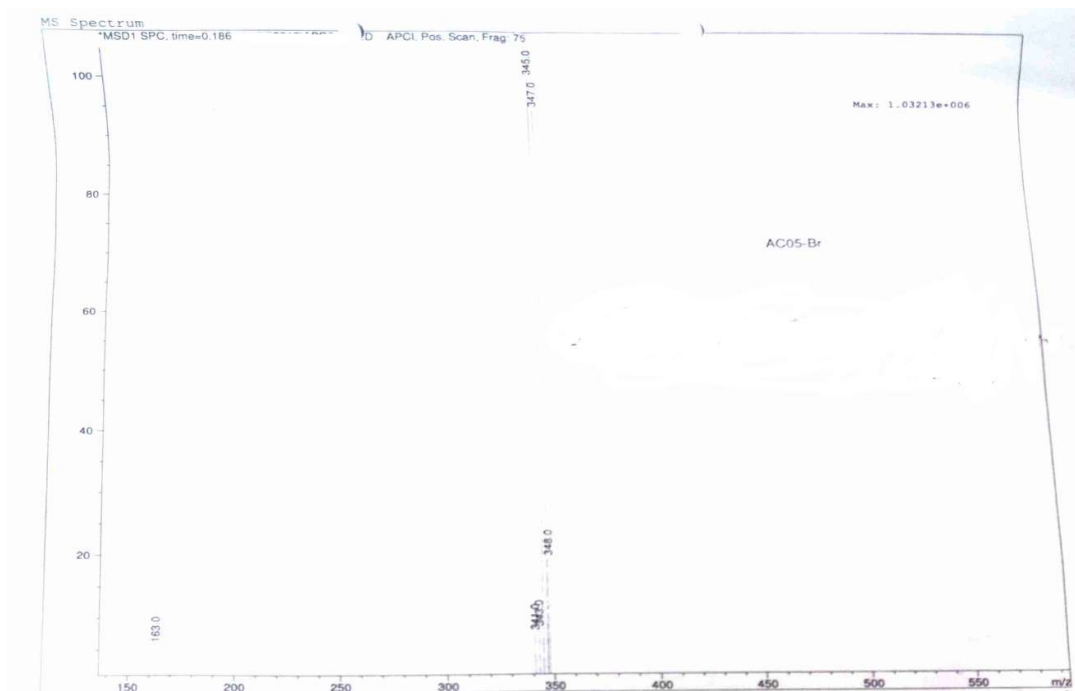
^1H NMR spectrum of **compound 3b**



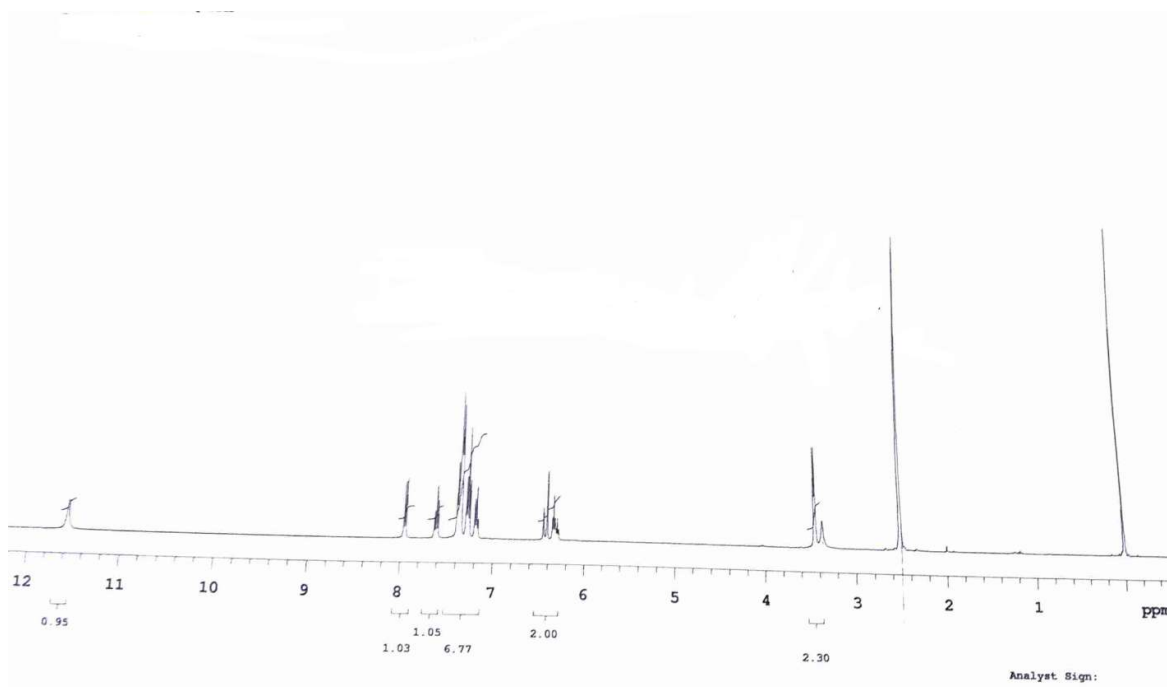
Mass spectrum of compound 3b



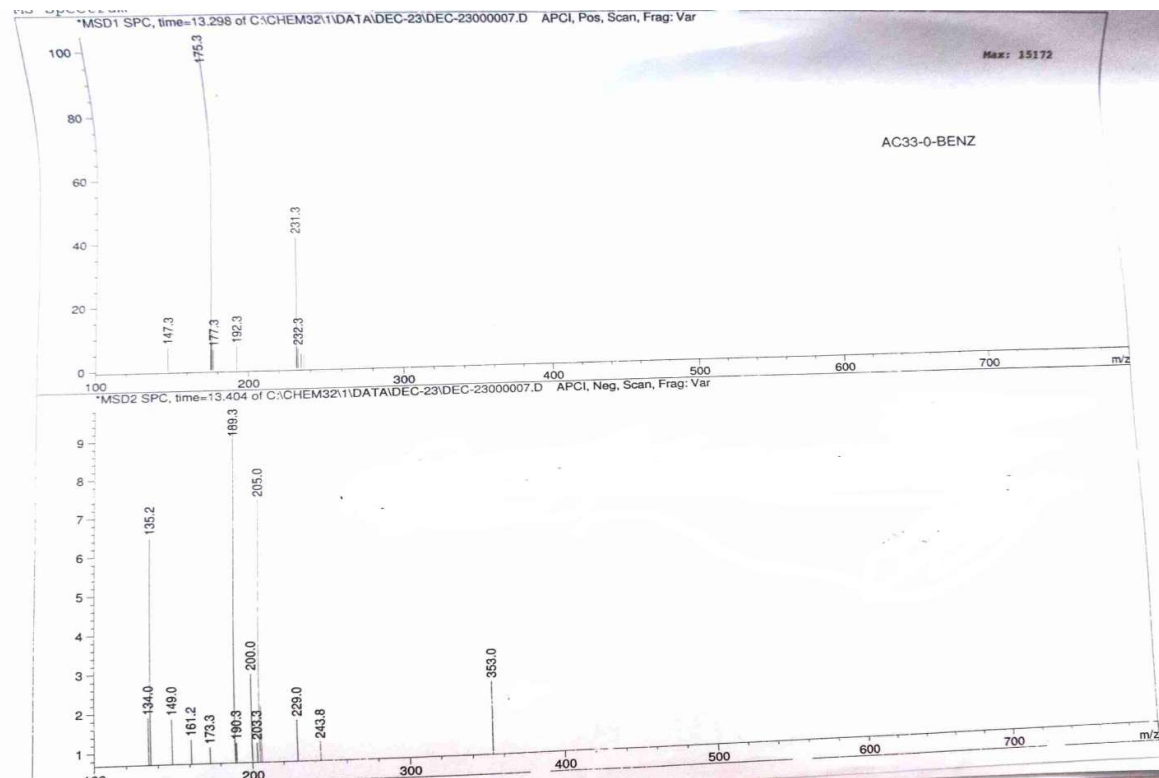
¹H NMR spectrum of compound 3c



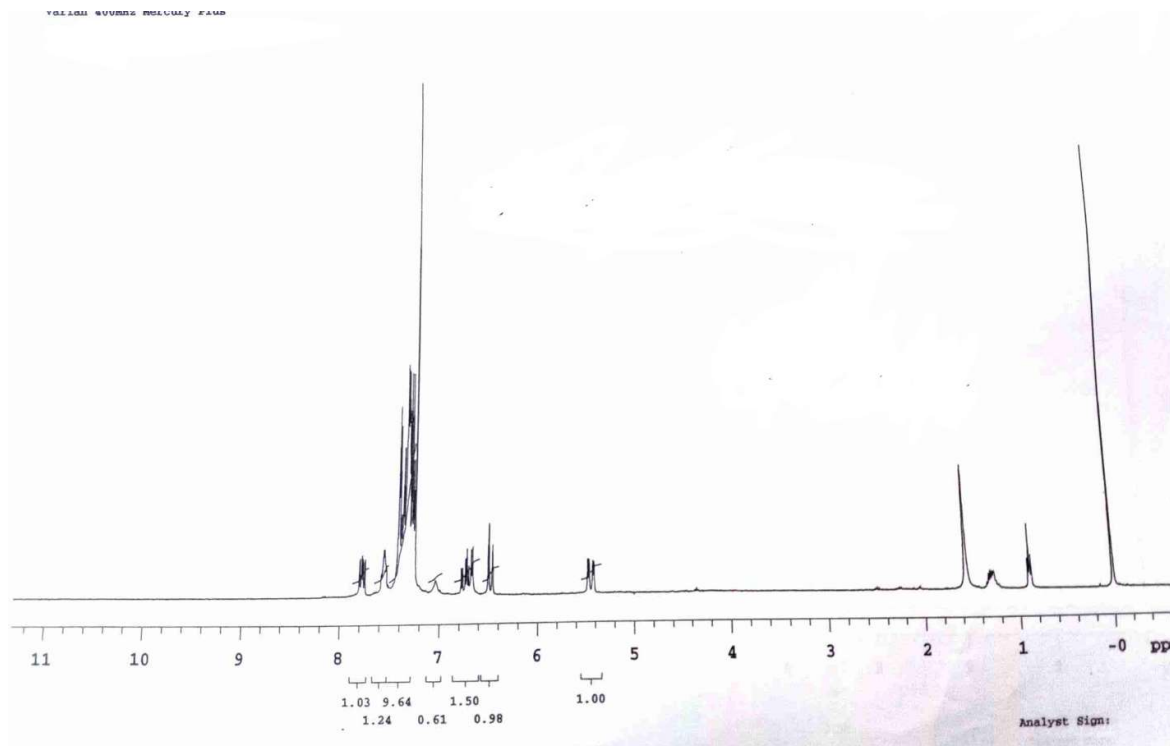
Mass spectrum of compound 3c



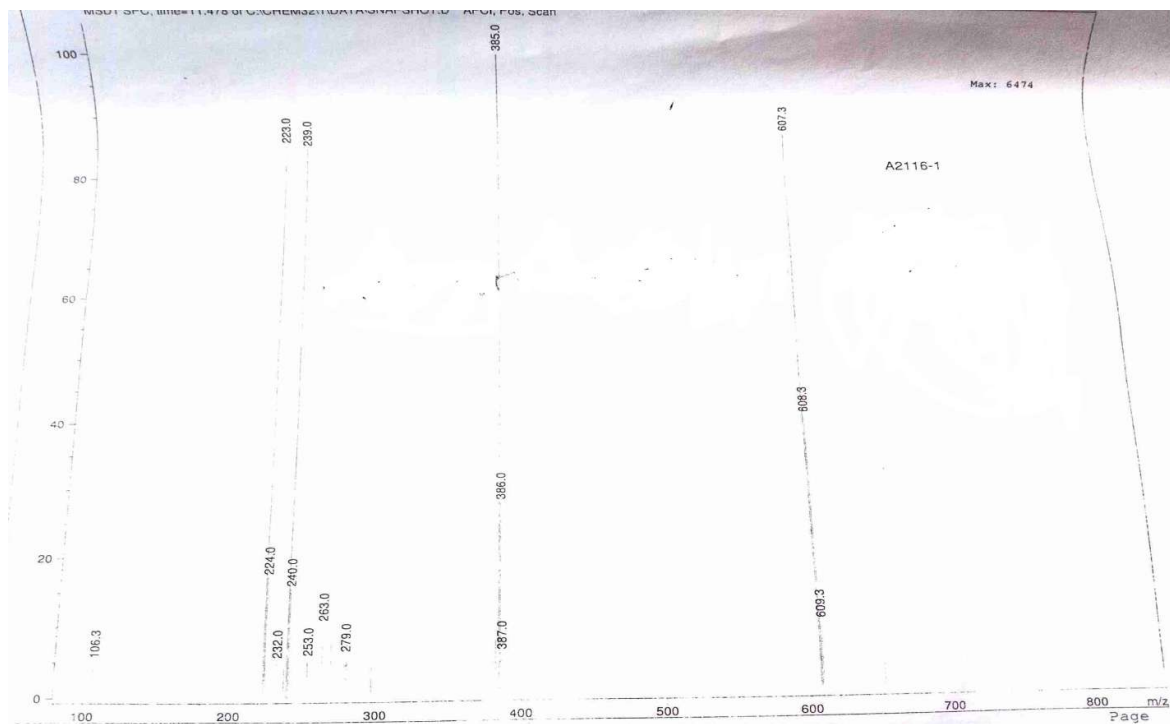
^1H NMR spectrum of compound 3c



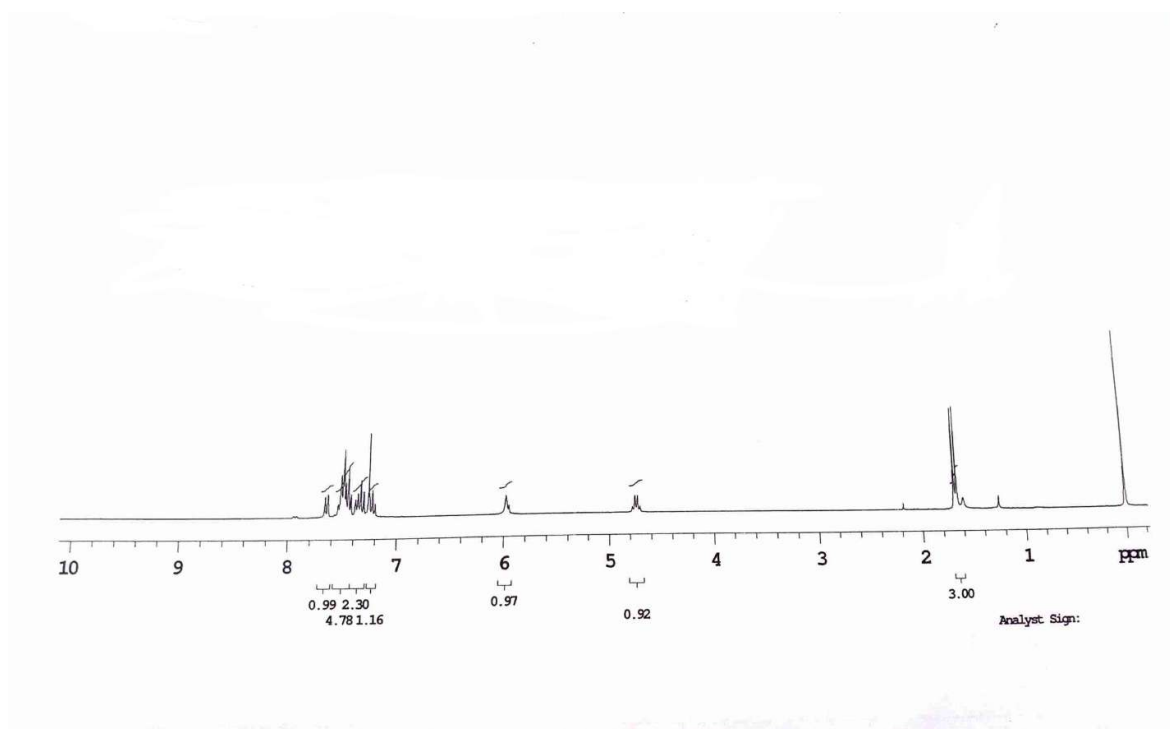
Mass spectrum of compound 3e



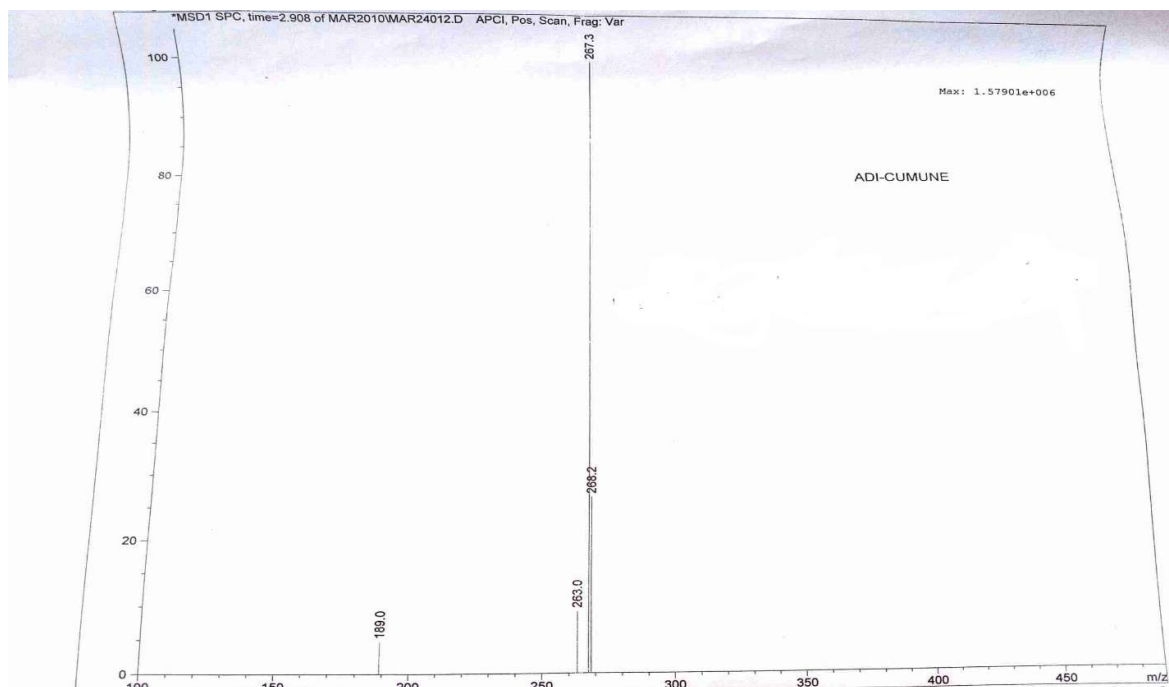
¹H NMR spectrum of compound 3f



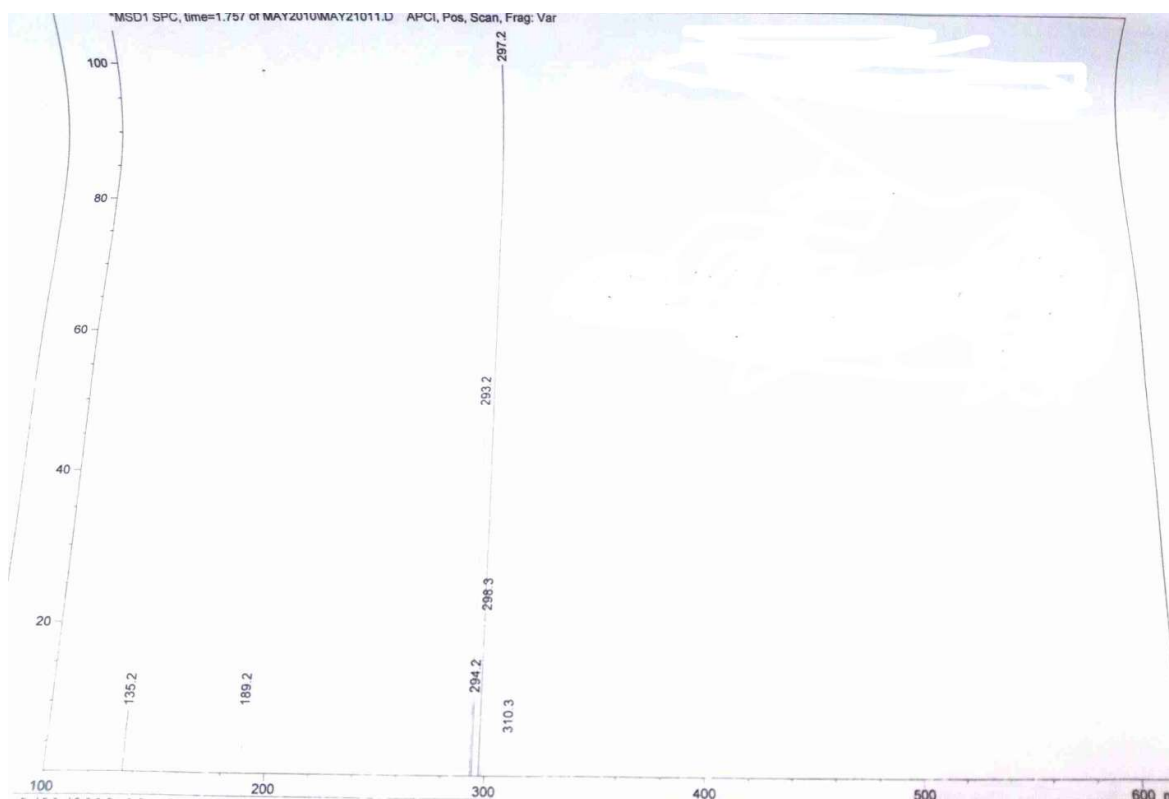
Mass spectrum of compound 3g



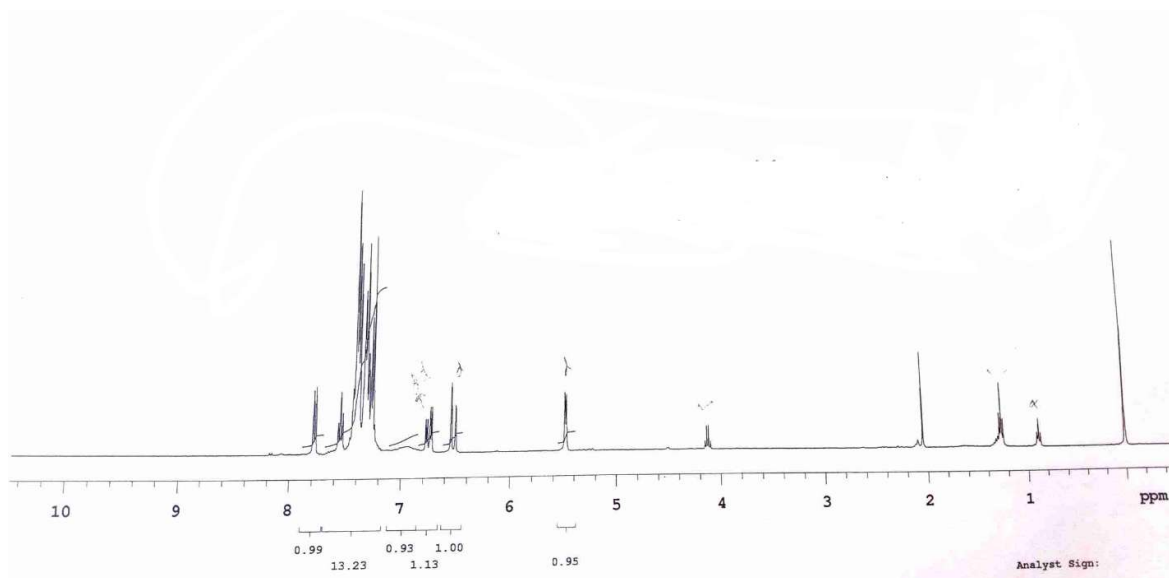
^1H NMR spectrum of compound 7a



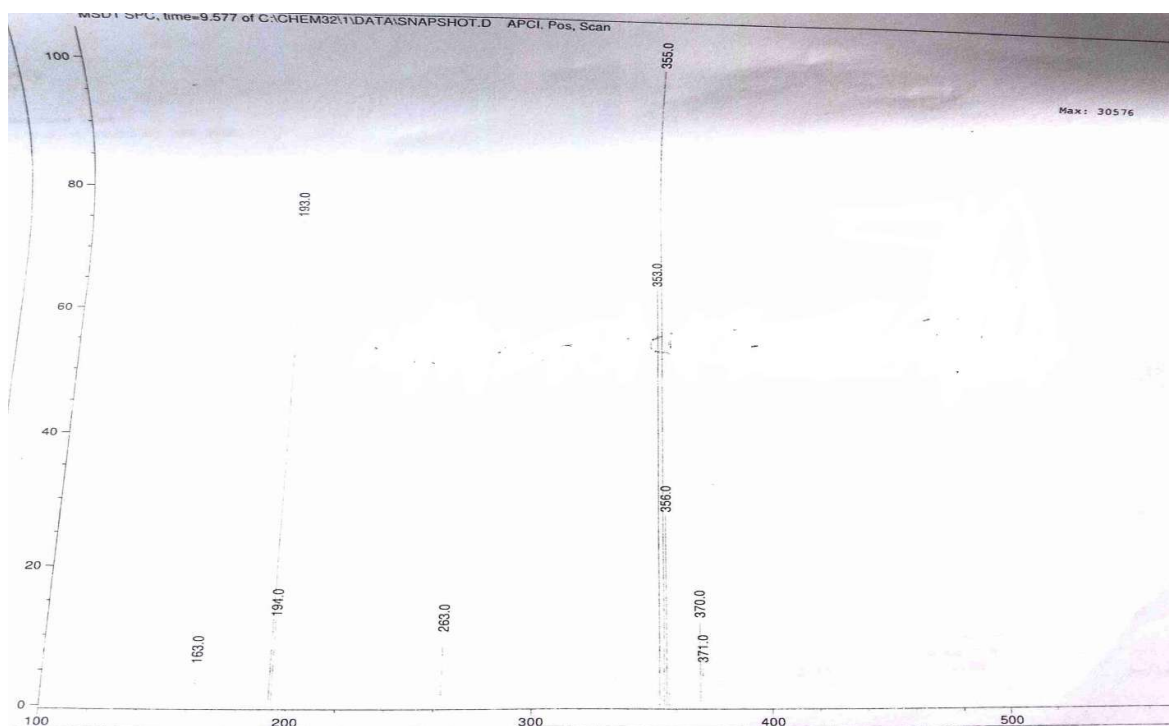
Mass spectrum of **compound 7a**



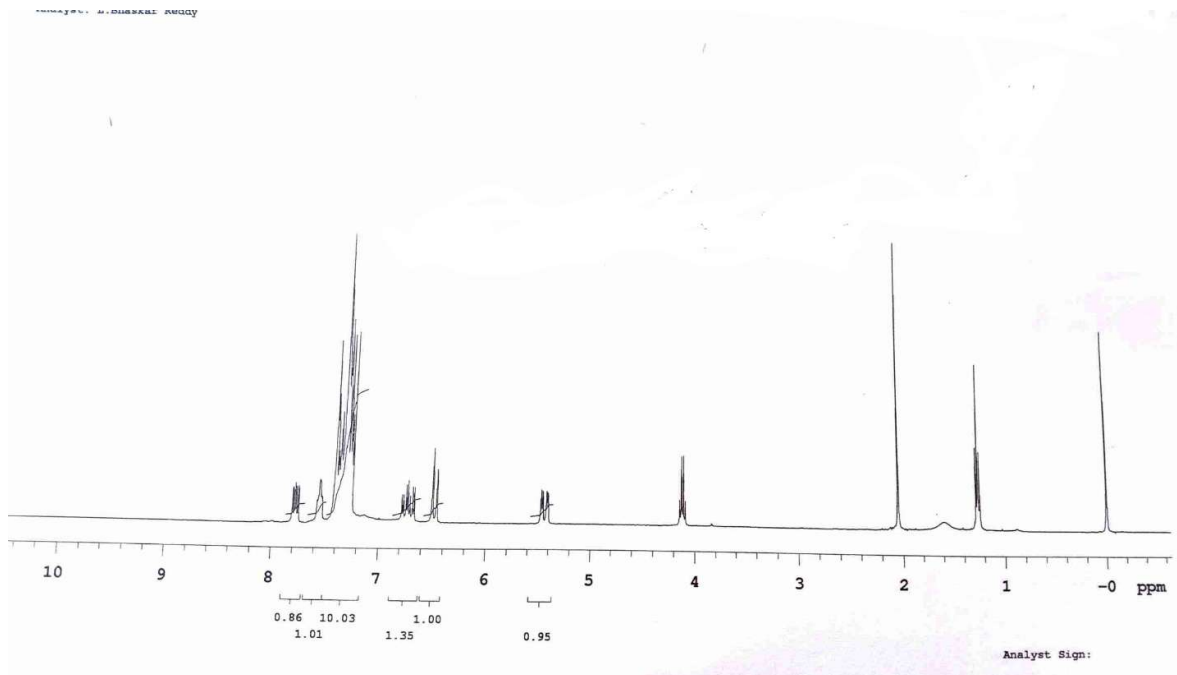
Mass spectrum of **compound 7b**



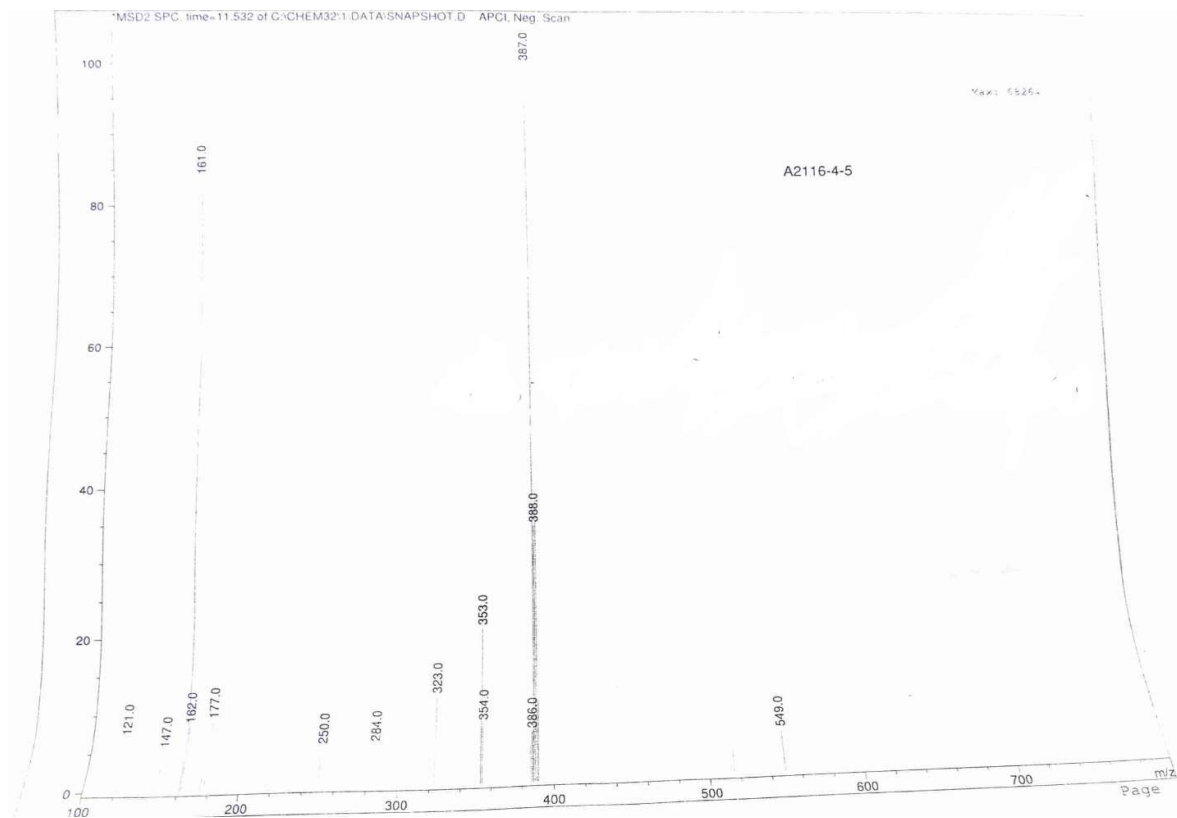
¹H NMR spectrum of **compound 7c**



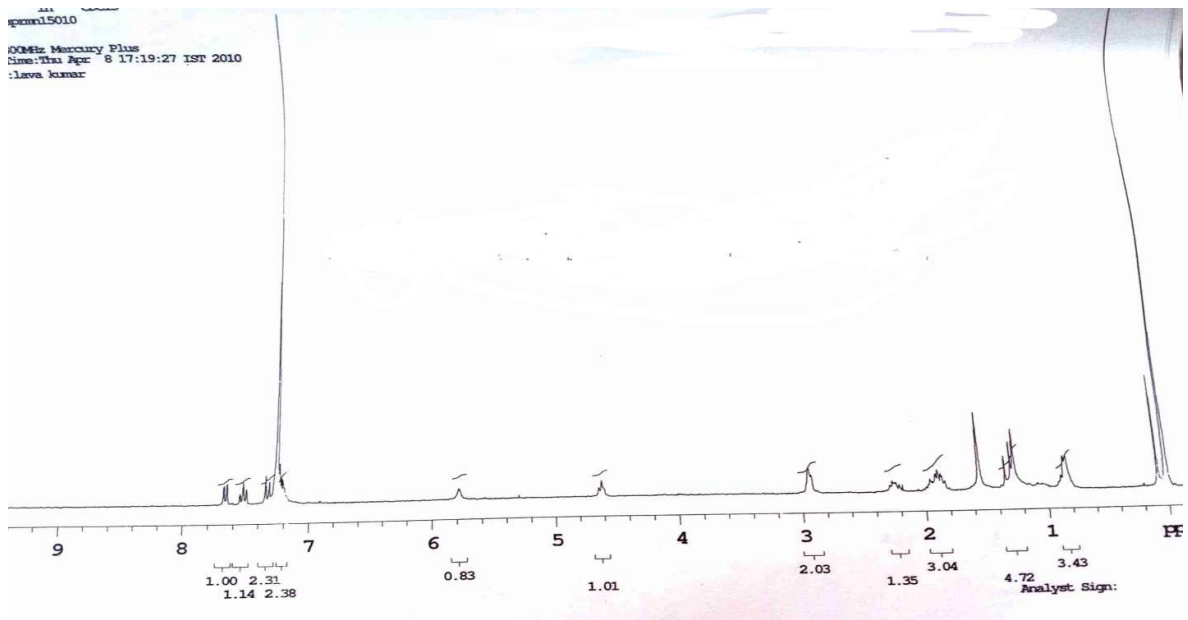
Mass spectrum of **compound 7c**



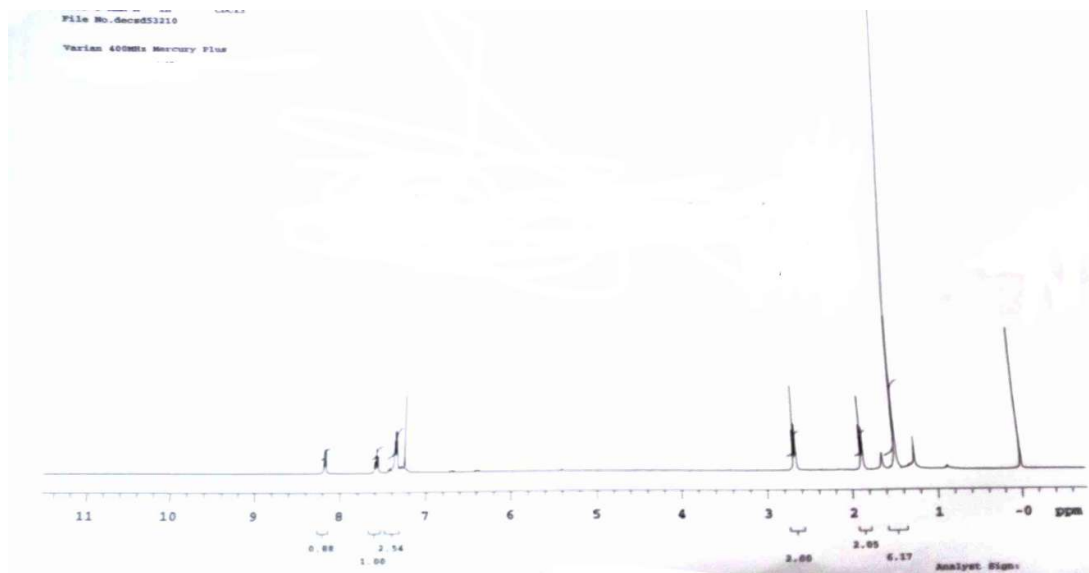
¹H NMR spectrum of compound 7d



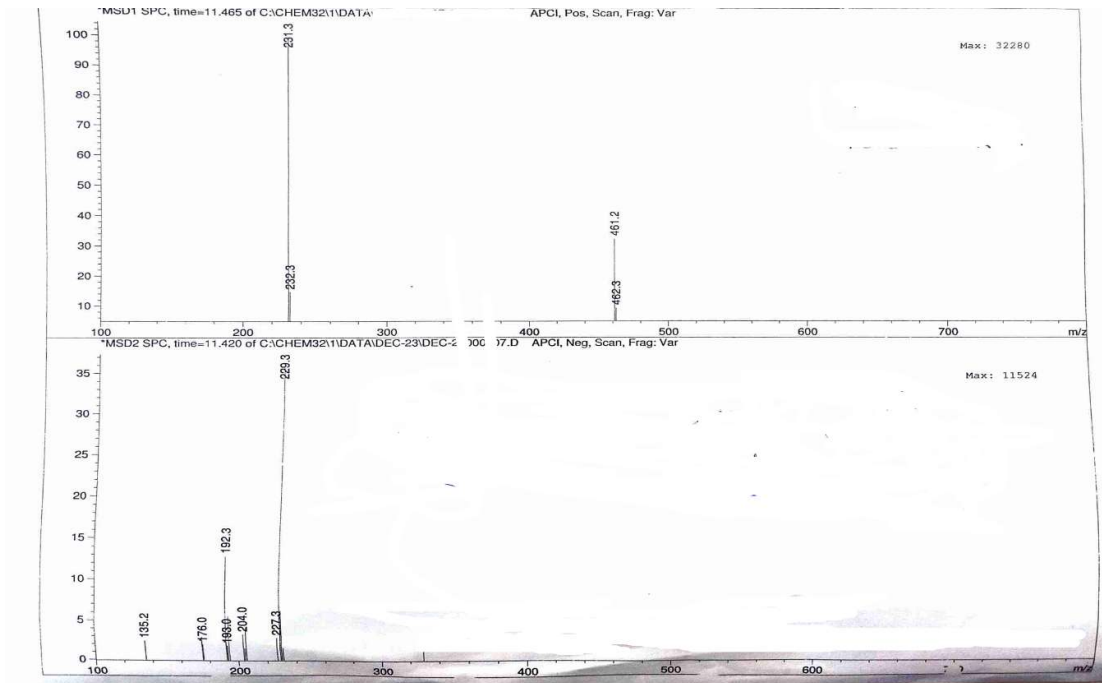
Mass spectrum of compound 7d



¹H NMR spectrum of compound 7e



¹H NMR spectrum of compound 8



Mass spectrum of compound 8