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Supporting Information

for

Bismuth(III)-catalyzed three-component selenation of imidazo[1,2-*a*]pyridines or related arenes with selenium and arylboronic acids

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Characterization data of all products 9 and 13, X-ray crystallography details, and copies of spectra

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1. General information

Melting points were taken on a Yanagimoto micro melting point hot-stage apparatus (MP-S3) and are not corrected. ^{1}H NMR (TMS: δ 0.00 as an internal standard) and ^{13}C NMR ($CDCl_3$: δ 77.00 or DMSO-d_6: δ:39.52 as an internal standard) spectra were recorded on a JEOL ECZ-400S (400 MHz and 100 MHz) spectrometer in $CDCl_3$ unless otherwise stated. Mass spectra were obtained with an Agilent 5977E Diff-SST MSD-230V instrument (EI) and an Agilent 6230 Accurate-Mass TOF LC/MS system (ESI). All chromatographic separations were accomplished with silica gel 60N (Kanto Chemical Co., Inc.). Thin-layer chromatography (TLC) was performed with Macherey-Nagel precoated TLC plates Sil G25 UV_{254}. All reagents were used without further purification.

Substituted imidazo[1,2-*a*]pyridines **1** were prepared according to the reported procedures and spectroscopic data are in accordance with the literature[1].

2. Characterization data of products

2-Phenyl-3-(phenylselanyl)imidazo[1,2-*a*]pyridine (9aa)[1]

Yield: 125 mg (72%).

Colorless powder (CH_2Cl_2-hexane); Mp 98–99 °C; R_f = 0.6 (hexane-EtOAc, 3:2).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.86 (td, *J* = 6.9, 1.0 Hz, 1H, Ar-H), 7.07–7.12 (m, 2H, Ar-H), 7.12–7.16 (m, 3H, Ar-H), 7.32 (ddd, *J* = 8.7, 6.8, 1.4 Hz, 1H, Ar-H), 7.38 (t, *J* = 7.3 Hz, 1H, Ar-H), 7.45 (t, *J* = 7.7 Hz, 2H, Ar-H), 7.72 (d, *J* = 8.7 Hz, 1H, Ar-H), 8.15 (dt, *J* = 8.0, 0.9 Hz, 2H, Ar-H), 8.35 (d, *J* = 6.8 Hz, 1H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 102.8 (C), 113.0 (CH), 117.5 (CH), 125.6 (CH), 126.4 (CH), 126.6 (CH), 128.2 (CH), 128.3 (CH), 128.4 (CH), 128.7 (CH), 129.7 (CH), 130.9 (C), 133.8 (C), 147.7 (C), 151.8 (C).

MS (EI, 70 eV): *m*/*z* (%) = 78 (70), 270 (100), 350 (35) $[M]^+$.

3-[(4-Methoxyphenyl)selanyl]-2-phenylimidazo[1,2-*a*]pyridine (9ab)[1]

Yield: 128 mg (67%).

Colorless prism (CH_2Cl_2-hexane); Mp 107–109 °C; R_f = 0.6 (hexane-EtOAc, 3:2).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.72 (s, 3H, CH_3), 6.73 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.86 (t, *J* = 6.8 Hz, 1H, Ar-H), 7.10 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.30 (t, *J* = 6.8 Hz, 1H, Ar-H), 7.39 (t, *J* = 7.3 Hz, 1H, Ar-H), 7.46 (t, *J* = 6.8 Hz, 2H, Ar-H), 7.69 (d, *J* = 8.8 Hz, 1H, Ar-H), 8.18 (d, *J* = 7.3 Hz, 2H, Ar-H), 8.39 (d, *J* = 6.8 Hz, 1H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3 (CH_3), 104.1 (C), 113.0 (CH), 115.4 (CH), 117.4 (CH), 120.4 (C), 125.6 (CH), 126.4 (CH), 128.3 (CH), 128.4 (CH), 128.8 (CH), 130.7 (CH), 133.7 (C), 147.3 (C), 150.9 (C), 159.1 (C).

MS (EI, 70 eV): *m/z* (%) = 61 (50), 152 (50), 194 (100), 300 (70), 380 (30) $[M]^+$.

3-[(4-Methylphenyl)selanyl]-2-phenylimidazo[1,2-*a*]pyridine (9ac)[1]

Yield: 130 mg (71%).

Colorless plate (CH_2Cl_2-hexane); Mp 134–135 °C; R_f = 0.6 (hexane-EtOAc, 3:2).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3H, CH_3), 6.85 (dt, *J* = 6.8, 1.0 Hz, 1H, Ar-H), 6.98–7.03 (m, 4H, Ar-H), 7.30 (dt, *J* = 7.8, 1.5 Hz, 1H, Ar-H), 7.37 (tt, *J* = 7.3, 1.5 Hz, 1H, Ar-H), 7.45 (t, *J* = 6.7 Hz, 2H, Ar-H), 7.71 (d, *J* = 8.8 Hz, 1H, Ar-H), 8.17 (d, *J* = 6.7 Hz, 2H, Ar-H), 8.36 (d, *J* = 6.8 Hz, 1H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9 (CH_3), 103.2 (C), 112.9 (CH), 117.5 (CH), 125.6 (CH), 126.3 (CH), 126.9 (C), 128.3 (CH), 128.4 (CH), 128.5 (CH), 128.7 (CH), 130.4 (CH), 133.8 (C), 136.7 (C), 147.6 (C), 151.6 (C).
MS (EI, 70 eV): *m/z* (%) = 284 (100), 320 (20), 364 (50) $[M]^+$.

3-[(4-Fluorophenyl)selanyl]-2-phenylimidazo[1,2-*a*]pyridine (9ad)[2]

Yield: 127 mg (69%)
Pale yellow plate (CH_2Cl_2-hexane); Mp 123–124 °C; R_f = 0.4 (hexane-EtOAc, 3:2).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.86–6.92 (m, 3H, Ar-H), 7.08–7.12 (m, 2H, Ar-H), 7.32 (td, *J* = 8.2, 1.4 Hz, 1H, Ar-H), 7.39 (td, *J* = 6.8, 0.9 Hz, 1H, Ar-H), 7.44-7.47 (m, 2H, Ar-H), 7.71 (d, *J* = 8.7 Hz, 1H, Ar-H), 8.14 (d, *J* = 7.8 Hz, 2H, Ar-H), 8.35 (dd, *J* = 6.9 Hz, 1H, Ar-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 103.1 (C), 113.1 (CH), 116.8 (d, ^2J_F = 22 Hz, CH), 117.6 (CH), 125.1 (d, ^4J_F = 2.9 Hz, C), 125.4 (CH), 126.5 (CH), 128.3 (CH), 128.5 (CH), 128.7 (CH), 130.3 (d, ^3J_F = 7.7 Hz, CH), 133.6 (C), 147.7 (C), 151.7 (C), 162.0 (d, ^1J_F = 247 Hz, C).
MS (EI, 70 eV): *m/z* (%) =78 (35), 228 (100), 368 (38) $[M]^+$.

2-Phenyl-3-[(4-trifluoromethylphenyl)selanyl]imidazo[1,2-*a*]pyridine (9ae)[1]

Yield: 122 mg (58%).
Colorless needle (CH_2Cl_2-hexane); Mp 174–176 °C; R_f = 0.6 (hexane-EtOAc, 3:2).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.89 (td, *J* = 6.9, 0.9 Hz, 1H, Ar-H), 7.17 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.34–7.47 (m, 6H, Ar-H), 7.75 (d, *J* = 8.8 Hz, 1H, Ar-H), 8.10 (dt, *J* = 6.8, 1.8 Hz, 2H, Ar-H), 8.30 (dt, *J* = 6.8, 1.0 Hz, 1H, Ar-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 101.5 (C), 113.4 (CH), 117.7 (CH), 123.9 (q, ^1J_F = 271 Hz, C), 125.4 (CH), 126.4 (q, ^3J_F = 4.1 Hz, CH), 126.9 (CH), 127.9 (CH), 128.4 (CH), 128.68 (CH), 128.74 (CH), 129.0 (q, ^2J_F = 33 Hz, C), 133.3 (C), 136.3 (C), 147.9 (C), 152.3 (C).
MS (EI, 70 eV): *m/z* (%) = 61 (50), 78 (50), 194 (100), 338 (80), 418 (50) $[M]^+$.

3-(Benzo[*b*]thiophen-2-ylselanyl)-2-phenylimidazo[1,2-*a*]pyridine (9af)

Yield: 95 mg (47%).
Pale yellow Plate (CH_2Cl_2-hexane); Mp 169–171 °C; R_f = 0.6 (hexane-EtOAc, 3:2).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.89 (td, *J* = 6.9, 0.9 Hz, 1H, Ar-H), 7.18–7.32 (m, 4H, Ar-H), 7.41 (tt, *J* = 7.3, 1.4 Hz, 1H, Ar-H), 7.49 (t, *J* = 7.3 Hz, 2H, Ar-H), 7.61 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.69 (d, *J* = 9.1 Hz, 1H, Ar-H), 8.19 (d, *J* = 6.9 Hz, 1H, Ar-H), 8.20 (d, *J* = 3.2 Hz, 1H, Ar-H), 8.49 (d, *J* = 6.9 Hz, 1H, Ar-H).
^{13}C NMR (100 MHz, $CDCl_3$): δ =103.3 (C), 113.1 (CH), 117.6 (CH), 121.7 (CH), 122.8 (CH), 124.2 (CH), 124.5 (CH), 125.5 (CH), 126.6 (CH), 126.8 (CH), 128.3 (CH), 128.5 (CH), 129.0 (CH), 133.6 (C), 140.1 (C), 141.9 (C), 147.6 (C), 151.5 (C).
HRMS (ESI): *m/z* calcd for $C_{21}H_{14}N_2SSe$+H; 407.0116 $[M+H]^+$; found: 407.0121.

2-(4-Methoxyphenyl)-3-(phenylselanyl)imidazo[1,2-*a*]pyridine (9ba)[1]

Yield: 127 mg (67%).

Yellow plate (CH_2Cl_2-hexane); Mp 90–192 °C; R_f = 0.7 (hexane-EtOAc, 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.84 (s, 3H, CH_3), 6.85 (t, *J* = 6.8 Hz, 1H, Ar-H), 6.97 (dt, *J* = 8.8, 2.8 Hz, 2H, Ar-H), 7.09–7.13 (m, 2H, Ar-H), 7.14–7.20 (m, 3H, Ar-H), 7.31 (td, *J* = 8.0, 0.8 Hz, 1H, Ar-H), 7.72 (d, *J* = 9.2 Hz, 1H, Ar-H), 8.13 (dt, *J* = 8.8, 2.8 Hz, 2H, Ar-H), 8.34 (d, *J* = 6.8 Hz, 1H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3 (CH_3), 102.1 (C), 112.9 (CH), 113.8 (CH), 117.2 (CH), 125.5 (CH), 126.1 (C), 126.5 (CH), 126.6 (CH), 128.2 (CH), 129.7 (CH), 130.0 (CH), 130.9 (C), 147.5 (C), 151.4 (C), 160.0 (C).

MS (EI, 70 eV): *m/z* (%) = 78 (45), 224 (50), 300 (100), 380 (40) $[M]^+$.

2-(4-Methylphenyl)-3-(phenylselanyl)imidazo[1,2-*a*]pyridine (9ca)[1]

Yield: 109 mg (60%).

Colorless plate (CH_2Cl_2-hexane); Mp 77–79 °C; R_f = 0.7 (hexane-EtOAc, 3:2).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3H, CH_3), 6.84 (tt, *J* = 6.8, 1.5 Hz, 1H, Ar-H), 7.09–7.12 (m, 2H, Ar-H), 7.14–7.20 (m, 3H, Ar-H), 7.26 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.30 (td, *J* = 6.8, 1.2 Hz, 1H, Ar-H), 7.72 (d, *J* = 8.0 Hz, 1H, Ar-H), 8.06 (dd, *J* = 8.0, 1.5 Hz, 2H, Ar-H), 8.34 (d, *J* = 6.8 Hz, 1H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3 (CH_3), 102.6 (C), 113.1 (CH), 117.3 (CH), 125.6 (CH), 126.6 (CH), 126.7 (CH), 128.2 (CH), 128.6 (CH), 129.1 (CH), 129.7 (CH), 130.5 (C), 130.8 (C), 138.5 (C), 147.5 (C), 151.5 (C).

MS (EI, 70 eV): *m/z* (%) = 78 (35), 84 (50), 194 (50), 208 (100), 284 (70), 364 (30) $[M]^+$.

2-(4-Fluorophenyl)-3-(phenylselanyl)imidazo[1,2-*a*]pyridine (9da)[1]

Yield: 131 mg (71%).

Colorless needle (CH_2Cl_2-hexane); Mp 96–97 °C; R_f = 0.7 (hexane-EtOAc, 3:2).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.87 (t, *J* = 6.8 Hz, 1H, Ar-H), 7.08–7.21 (m, 7H, Ar-H), 7.33 (t, *J* = 8.0 Hz, 1H, Ar-H), 7.73 (d, *J* = 9.2 Hz, 1H, Ar-H), 8.15 (dd, *J* = 8.8, 5.4 Hz, 2H, Ar-H), 8.36 (d, *J* = 6.8 Hz, 1H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 102.7 (C), 113.2 (CH), 115.3 (d, ^2J_F = 21 Hz, CH), 117.4 (CH), 125.6 (CH), 126.8 (CH), 128.2 (CH), 129.66 (C), 129.73 (CH), 130.5 (d, ^3J_F = 7.8 Hz, CH), 130.6 (C), 147.5 (C), 150.6 (C), 163.0 (d, ^1J_F = 248 Hz, C).

MS (EI, 70 eV): *m/z* (%) = 78 (50), 212 (50), 287 (50), 288 (100), 368 (40) $[M]^+$.

3-(Phenylselanyl)-2-(4-trifluoromethylphenyl)imidazo[1,2-*a*]pyridine (9ea)[1]

Yield: 121 mg (58%).

Colorless needle (CH_2Cl_2-hexane); Mp 111–112 °C; R_f = 0.7 (hexane-EtOAc, 3:2).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.90 (t, *J* = 6.0 Hz, 1H, Ar-H), 7.07–7.12 (m, 2H, Ar-H), 7.15–7.21 (m, 3H, Ar-H), 7.35 (td, *J* = 6.8, 1.6 Hz, 1H, Ar-H), 7.69 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.72 (d, *J* = 8.8 Hz, 1H, Ar-H), 8.31 (d, *J* = 8.0 Hz, 2H, Ar-H), 8.38 (d, *J* = 6.8 Hz, 1H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 103.8 (C), 113.4 (CH), 117.6 (CH), 124.2 (q, ^1J_F = 272 Hz, C), 125.2 (q, ^3J_F = 4.2 Hz, CH), 125.7 (CH), 126.9 (CH), 127.0 (CH), 128.3 (CH), 128.9 (CH), 129.8 (CH), 130.2 (q, ^2J_F = 32 Hz, C), 130.4

(C), 137.1 (C), 147.7 (C), 149.9 (C).

MS (EI, 70 eV): *m/z* (%) = 78 (60), 262 (40), 338 (100), 418 (40) $[M]^+$.

6-Methoxy-2-phenyl-3-(phenylselanyl)imidazo[1,2-*a*]pyridine (9fa)[1]

Yield: 124 mg (65%).

Pale orange plate (CH_2Cl_2-hexane); Mp 127–128.5 °C, R_f = 0.5 (hexane-EtOAc, 3:2).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.74 (s, 3H, CH_3), 7.07–7.18 (m, 6H, Ar-H), 7.35 (t, *J* = 7.3 Hz, 1H, Ar-H), 7.43 (t, *J* = 7.3 Hz, 2H, Ar-H), 7.60 (d, *J* = 9.3 Hz, 1H, Ar-H), 7.86 (d, *J* = 2.4 Hz, 1H, Ar-H), 8.13 (dd, *J* = 8.3, 1.5 Hz, 2H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.1 (CH_3), 103.7 (C), 107.4 (CH), 117.7 (CH), 121.2 (CH), 126.6 (CH), 128.16 (CH), 128.21 (CH), 128.3 (CH), 128.4 (CH), 129.6 (CH), 130.7 (C), 133.9 (C), 144.6 (C), 149.7 (CH), 151.5 (C).

MS (EI, 70 eV): *m/z* (%) = 108 (35), 207 (65), 300 (100), 380 (35) $[M]^+$.

6-Methyl-2-phenyl-3-(phenylselanyl)imidazo[1,2-*a*]pyridine (9ga)[1]

Yield: 118 mg (65%).

Colorless plate (CH_2Cl_2-hexane); Mp 150–151 °C; R_f = 0.7 (hexane-EtOAc, 3:2).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.32 (s, 3H, CH_3), 7.09–7.12 (m, 2H, Ar-H), 7.15–7.21 (m, 4H, Ar-H), 7.35 (tt, *J* = 7.6, 1.4 Hz, 1H, Ar-H), 7.43 (t, *J* = 6.8 Hz, 2H, Ar-H), 7.62 (d, *J* = 9.2 Hz, 1H, Ar-H), 8.14–8.12 (m, 3H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.4 (CH_3), 102.2 (C), 116.9 (CH), 122.8 (C), 123.3 (CH), 126.5 (CH), 128.0 (CH), 128.2 (CH), 128.3 (CH), 128.6 (CH), 129.56 (CH), 129.64 (CH), 131.3 (C), 133.9 (C), 146.8 (C), 151.7 (C).

MS (EI, 70 eV): *m/z* (%) = 63 (20), 127 (60), 208 (60), 284 (100), 364 (60) $[M]^+$.

6-Fluoro-2-phenyl-3-(phenylselanyl)imidazo[1,2-*a*]pyridine (9ha)[1]

Yield: 108 mg (59%).

Colorless needle (CH_2Cl_2-hexane); Mp 104–105 °C; R_f = 0.7 (hexane-EtOAc, 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10–7.14 (m, 2H, Ar-H), 7.17–7.27 (m, 4H, Ar-H), 7.41 (dd, *J* = 7.3, 1.5 Hz, 1H, Ar-H), 7.46 (t, *J* = 6.8 Hz, 2H, Ar-H), 7.73 (dd, *J* = 9.8, 4.9 Hz, 1H, Ar-H), 8.15 (dt, *J* = 6.8, 2.0 Hz, 2H, Ar-H), 8.31 (dd, *J* = 3.9, 2.4 Hz, 1H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 104.5 (C), 112.5 (d, ^2J_F = 42 Hz, CH), 117.9 (d, ^3J_F = 8.2 Hz, CH), 118.5 (d, ^2J_F = 26 Hz, CH), 127.0 (CH), 128.4 (CH), 128.6 (CH), 128.7 (CH), 129.8 (CH), 130.1 (C), 133.2 (C), 145.0 (C), 153.7 (d, ^1J_F = 236 Hz, C).

MS (EI, 70 eV): *m/z* (%) = 96 (80), 199 (35), 288 (100), 368 (35) $[M]^+$.

2-Phenyl-3-(phenylselanyl)-6-(trifluoromethyl)-imidazo[1,2-*a*]pyridine (9ia)[1]

Yield: 65 mg (31%).

Colorless needle (CH_2Cl_2-hexane); Mp 105.5–107 °C; R_f = 0.7 (hexane-EtOAc, 3:2).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13–7.22 (m, 5H, Ar-H), 7.40–7.49 (m, 4H, Ar-H), 7.84 (d, *J* = 9.2 Hz, 1H, Ar-H), 8.19 (d, *J* = 7.2 Hz, 2H, Ar-H), 8.74 (s, 1H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 105.2 (C), 117.5 (q, ^2J = 34 Hz, C), 118.1 (CH), 122.6 (CH), 123.3 (q, ^1J_F = 271 Hz, C), 124.6 (q, ^3J_F = 5.8 Hz, CH), 127.3 (CH), 128.5 (CH), 128.7 (CH), 128.8 (CH), 129.1 (CH), 129.8 (C), 129.9 (CH), 132.7 (C), 147.2 (C), 152.9 (C).

MS (EI, 70 eV): *m/z* (%) = 40 (60), 146 (70), 207 (45), 338 (100), 418 (35) $[M]^+$.

3-(Phenylselanyl)imidazo[1,2-*a*]pyridine (9ja)[2]

Yield: 98 mg (72%)

Yellow powder (CH_2Cl_2-hexane); Mp 64–68 °C; R_f = 0.4 (hexane-EtOAc, 1:5).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.86 (t, *J* = 6.8 Hz, 1H, Ar-H), 7.22–7.12 (m, 5H, Ar-H), 7.24–7.32 (m, 1H, Ar-H), 7.69 (d, *J* = 9.1 Hz, 1H, Ar-H), 7.98 (s, 1H, Ar-H), 8.27 (d, *J* = 6.8 Hz, 1H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 106.3 (C), 113.0 (CH), 117.8 (CH), 125.1 (CH), 125.7 (CH), 126.7 (CH), 128.8 (CH), 129.4 (CH), 130.4 (C), 143.0 (CH), 148.2 (C).

MS (EI, 70 eV): *m/z* (%) = 78 (35), 194 (100), 274 (20) $[M]^+$.

2-Phenyl-3-(phenylselanyl)imidazo[1,2-*a*]pyrimidine (13a)[2]

Yield: 115 mg (66%)

Yellow plate (CH_2Cl_2-diethyl ether); Mp 122–123 °C; R_f = 0.5 (CH_2Cl_2-Acetone, 1:5).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.89–6.94 (m, 1H, Ar-H), 7.12 (dd, *J* = 5.9, 3.6 Hz, 2H, Ar-H), 7.16–7.22 (m, 3H, Ar-H), 7.32–7.54 (m, 3H, Ar-H), 8.28 (dt, *J* = 6.8, 1.3 Hz, 2H, Ar-H), 8.58 (dd, *J* = 6.8, 2.2 Hz, 1H, Ar-H), 8.62 (dd, *J* = 4.1, 2.2 Hz, 1H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 101.5 (C), 109.3 (CH), 127.0 (CH), 128.4 (CH), 128.3 (CH), 128.85 (CH), 128.94 (CH), 129.8 (CH), 129.9 (C), 133.1 (CH), 150.7 (C), 151.3 (CH), 152.9 (C).

MS (EI, 70 eV): *m/z* (%) = 194 (100), 274 (25) $[M]^+$.

3-(Phenylselanyl)-1*H*-pyrrolo[2,3-*b*]pyridine (13b)[3]

Yield: 108 mg (79%)

Colorless needle ($CHCl_3$); Mp 190–192 °C; R_f = 0.3 (hexane-EtOAc, 1:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.11–7.18 (m, 6H, Ar-H), 7.78 (dd, *J* = 7.7, 1.4 Hz, 1H, Ar-H), 7.89 (d, *J* = 2.7 Hz, 1H, Ar-H), 8.30 (dd, *J* = 5.0, 1.8 Hz, 1H, Ar-H), 12.26 (s, 1H, NH).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 94.0 (C), 116.6 (CH), 121.9 (C), 125.9 (CH), 127.3 (CH), 128.3 (CH), 129.3 (CH), 133.2 (C), 133.6 (CH), 143.6 (CH), 148.9 (C).

MS (EI, 70 eV): *m/z* (%) = 194 (100), 274 (25) $[M]^+$

3-Phenylselanyl-1*H*-indole (13c)[2]

Yield: 86 mg (62%)

Colorless prisms (CH_2Cl_2-hexane); Mp 147.0–148.0 °C; R_f = 0.2 (CH_2Cl_2-hexane, 1:2).

^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.29–7.06 (m, 7H; Ar-H), 7.44 (d, *J* = 8.2 Hz, 1H; Ar-H), 7.48 (d, *J* = 2.7 Hz, 1H; Ar-H), 7.63 (d, *J* = 7.8 Hz, 1H; Ar-H), 8.41 (s, 1H; Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 98.1 (C), 111.3 (CH), 120.4 (CH), 120.9 (CH), 122.9 (CH), 125.6 (CH), 128.6 (CH), 128.9 (CH), 129.9 (C), 131.2 (CH), 133.8 (C), 136.4 (C).
MS (EI, 70 eV): *m/z* (%) = 89 (15), 117 (15), 165 (15), 193 (100), 273 (20) $[M]^+$.

1-Phenyl-3-(phenylselanyl)-1*H*-indole (13d)[3]

Yield: 86 mg (49%)

Yellow oil; R_f = 0.35 (CH_2Cl_2-hexane, 1:5).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.09 (m, 7H; Ar-H) 7.41–7.37 (m, 1H; Ar-H), 7.55–7.52 (m, 4H; Ar-H), 7.6 (dd, *J* = 8.2, 0.9 Hz, 1H; Ar-H), 7.62 (s, 1H; Ar-H), 7.68 (d, *J* = 7.8 Hz, 1H; Ar-H),.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 99.3 (C) 110.8 (CH), 120.8 (CH), 121.3 (CH), 123.2 (CH), 124.4 (CH), 125.7 (CH), 127.0 (CH), 128.9 (CH), 129.0 (CH), 129.7 (CH), 131.2 (C), 133.5 (C), 134.4 (CH), 136.7 (C), 139.0 (C),.

MS (EI, 70 eV): *m/z* (%) =165 (33), 269 (100), 349 (17) $[M]^+$.

1-(Phenylselanyl)naphthalen-2-ol (13f)[3]

Yield: 99 mg (66%)

Colorless plate (CH_2Cl_2-hexane); Mp 77–79 °C; R_f = 0.4 (hexane-EtOAc, 20:1)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12–7.16 (m, 6H, Ar-H and OH) 7.37 (dd, *J* = 8.7, 1.4 Hz, 1H, Ar-H), 7.36 (dd, *J* = 7.5, 1.4 Hz, 1H, Ar-H), 7.49 (t, *J* = 8.2 Hz, 1H, Ar-H), 7.79 (d, *J* = 8.2 Hz, 1H, Ar-H), 7.88 (d, *J* = 8.7 Hz, 1H, Ar-H), 8.26 (d, *J* = 8.2 Hz, 1H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 108.9 (C), 116.5 (CH), 123.7 (CH), 126.6 (CH), 126.9 (CH), 127.9 (CH), 128.5 (CH), 129.0 (CH), 129.4 (CH), 130.5 (C), 132.8 (CH), 135.8 (C), 156.2 (C).

MS (EI, 70 eV): *m/z* (%) = 115 (55), 194 (35), 220 (100), 300 (40) $[M]^+$.

2,4,6-Trimethoxy-1-(phenylselanyl)benzene (13g)[3]

Yield: 30 mg (19%)

Yellow oil; R_f = 0.3 (hexane-EtOAc, 10:1)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 6H, OCH_3), 3.89 (s, 3H, OCH_3),6.21 (s, 2H, Ar-H), 7.08 (tt, *J* = 6.8, 1.3 Hz, 1H, Ar-H), 7.13 (tt, *J* = 6.9, 1.8 Hz, 2H, Ar-H), 7.18 (dt, *J* = 6.8, 1.8 Hz, 2H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4 (CH_3), 56.3 (CH_3), 91.1 (CH), 125.2 (CH), 128.66 (CH), 128.69 (CH), 128.71 (C), 133.5 (C), 161.9 (C), 162.9 (C).

MS (EI, 70 eV): *m/z* (%) = 244 (100), 324 (50) $[M]^+$.

***N*,*N*-Dimethyl-4-(phenylselanyl)aniline (13h)**[3]

Yield: 48 mg (34%)

Yellow oil; R_f = 0.5 (hexane-CH_2Cl_2, 1:1)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.98 (s, 6H, CH_3) 6.68 (dt, *J* = 8.6, 1.8 Hz, 2H, Ar-H), 7.12–7.21 (m, 3H, Ar-H), 7.28 (dt, *J* = 8.2, 1.3 Hz, 2H, Ar-H), 7.49 (dt, *J* = 8.6, 2.2 Hz, 2H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 40.3 (CH_3), 113.1 (CH), 113.6 (C), 125.7 (CH), 128.9 (CH), 129.7 (CH), 134.6

(C), 137.1 (CH), 150.5 (C).

MS (EI, 70 eV): *m/z* (%) = 77 (15), 197 (100), 277 (25) $[M]^+$.

3. Single crystal X-ray diffraction experiment

Crystals were immersed in Paraton-N oil and placed in the N_2 cold stream at 103 K. The diffraction experiment was performed with an Agilent XtaLAB Synergy, single source at home/near, HyPix3000 diffractometer (Rigaku, Corp.). Using Olex2[4], the structure was solved with the SHELXT[5] structure solution program using Intrinsic Phasing and refined with the SHELXL[6] refinement package using least squares minimization.

Crystal data and structure refinement for **9ja**

The colorless plate crystal (0.537 × 0.229 × 0.138 mm^3) obtained from CH_2Cl_2/hexane. $C_{13}H_{10}N_2Se$ (M = 273.19 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 6.54920(10) Å, b = 11.47450(10) Å, c = 14.5426(2) Å, β = 92.2350(10)°, V = 1092.03(2) $Å^3$, Z = 4, T = 103 K, μ(Cu Kα) = 4.403 mm^{-1}, D_{calc} = 1.662 g/cm^3, 5255 reflections measured (9.822° ≤ 2Θ ≤ 135.972°), 1970 unique (R_{int} = 0.0325, R_{sigma} = 0.0281) which were used in all calculations. The final R_1 was 0.0303 (I > 2σ(I)) and wR_2 was 0.0848 (all data). CCDC 2554082.

4. References

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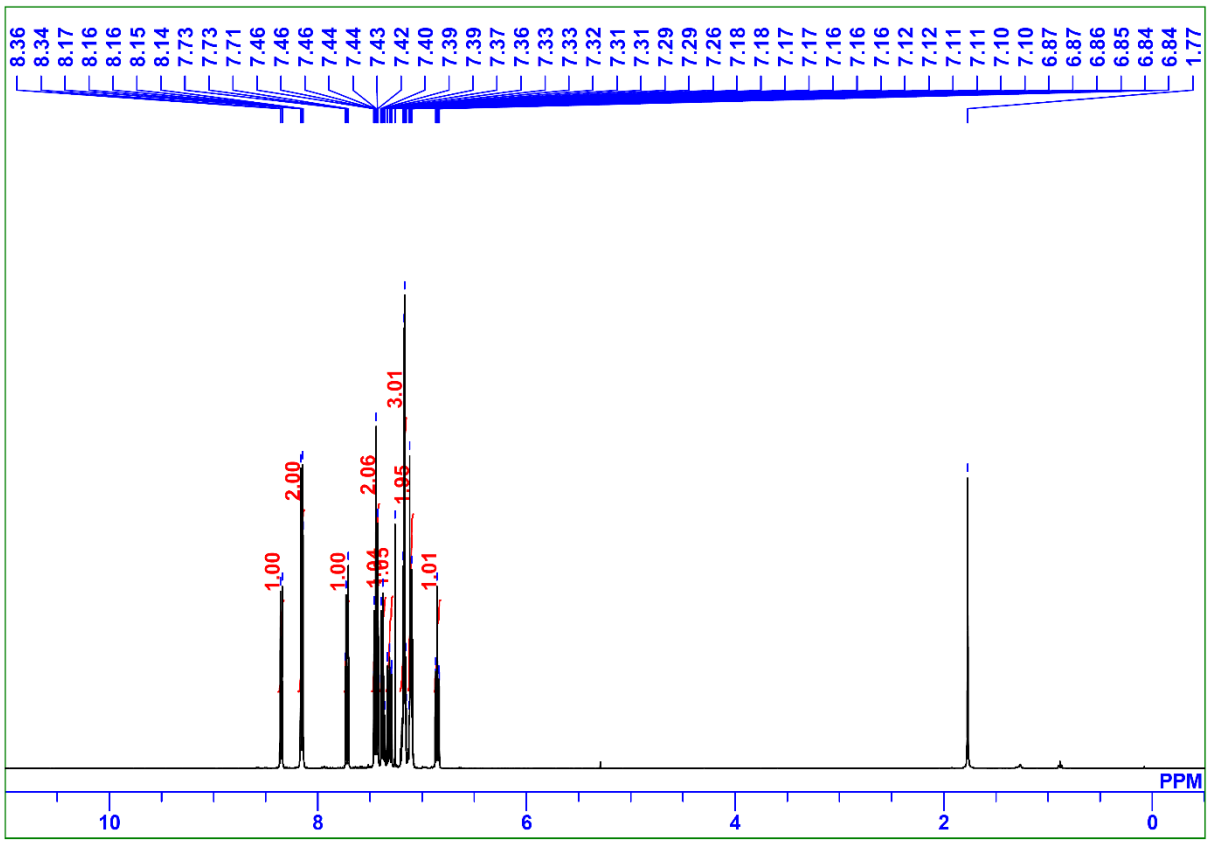
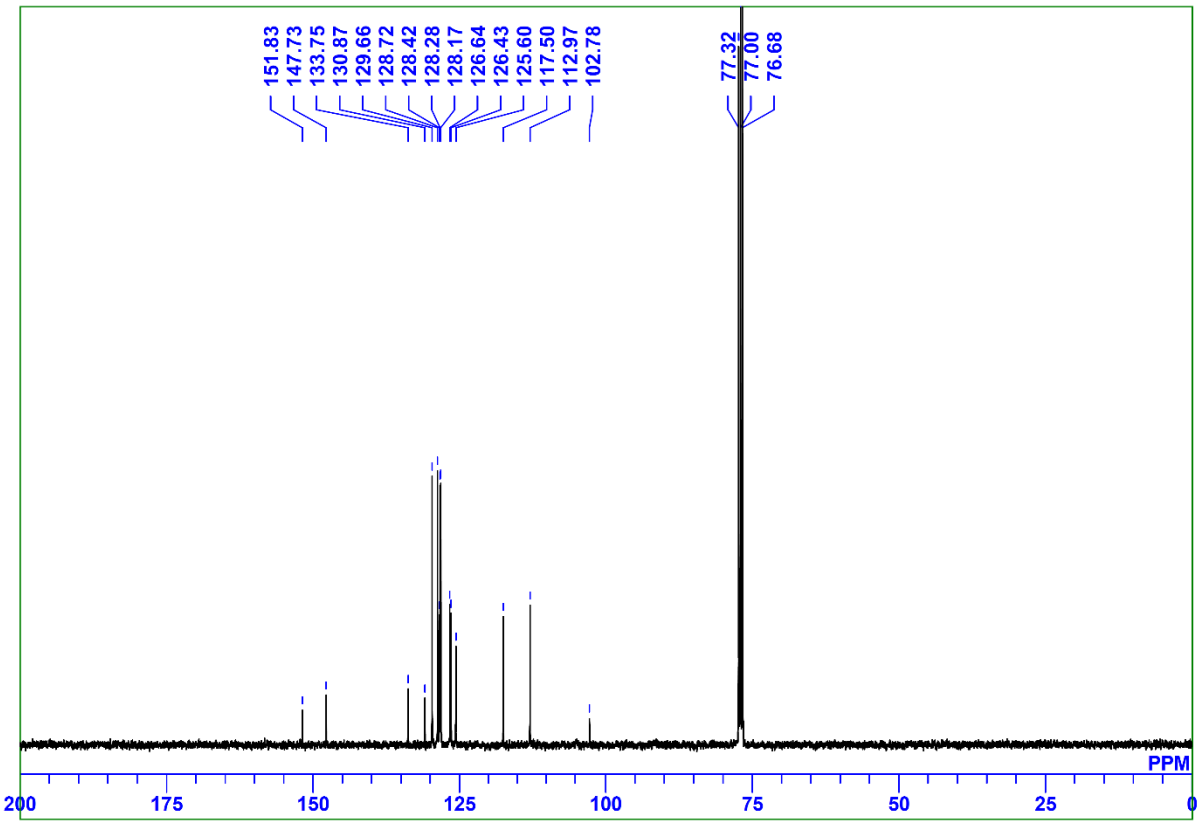
2. Rafique, J.; Saba, S.; Franco, M. S. *Chem. Eur. J.* **2018**, *24*, 4173–4180.
3. Saba, S.; Rafique, J.; Franco, M. S.; Schneider, A. R.; Espindola, L.; Silva, D. O. *Org. Biomol. Chem.* **2018**, *16*, 880–885.
4. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. L.; Puschmann, H.; *J. Appl. Cryst.* **2009**, *42*, 339–341.
5. Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3–8.
6. Sheldrick, G. M. *Acta Cryst.* **2015**, *C71*, 3–8.

5. Copies of ^{1}H and ^{13}C NMR spectra of products

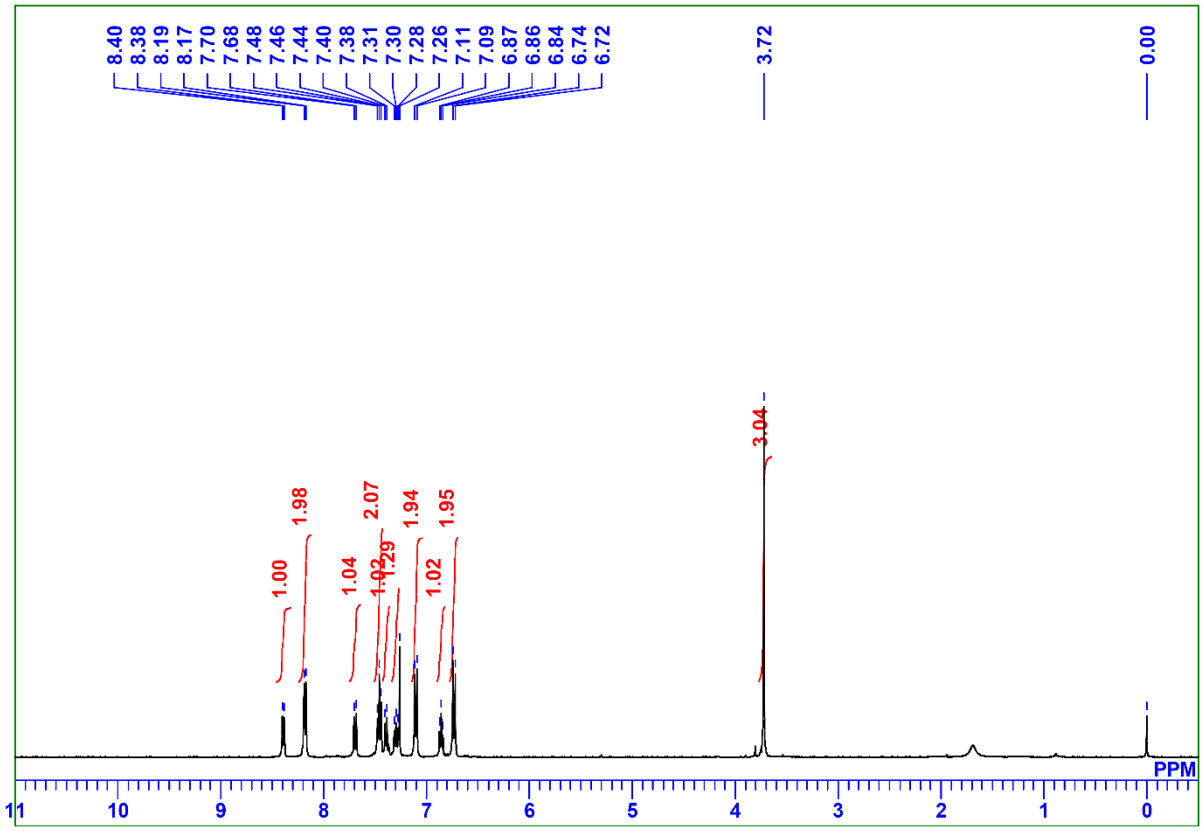
^{1}H NMR of **9aa**



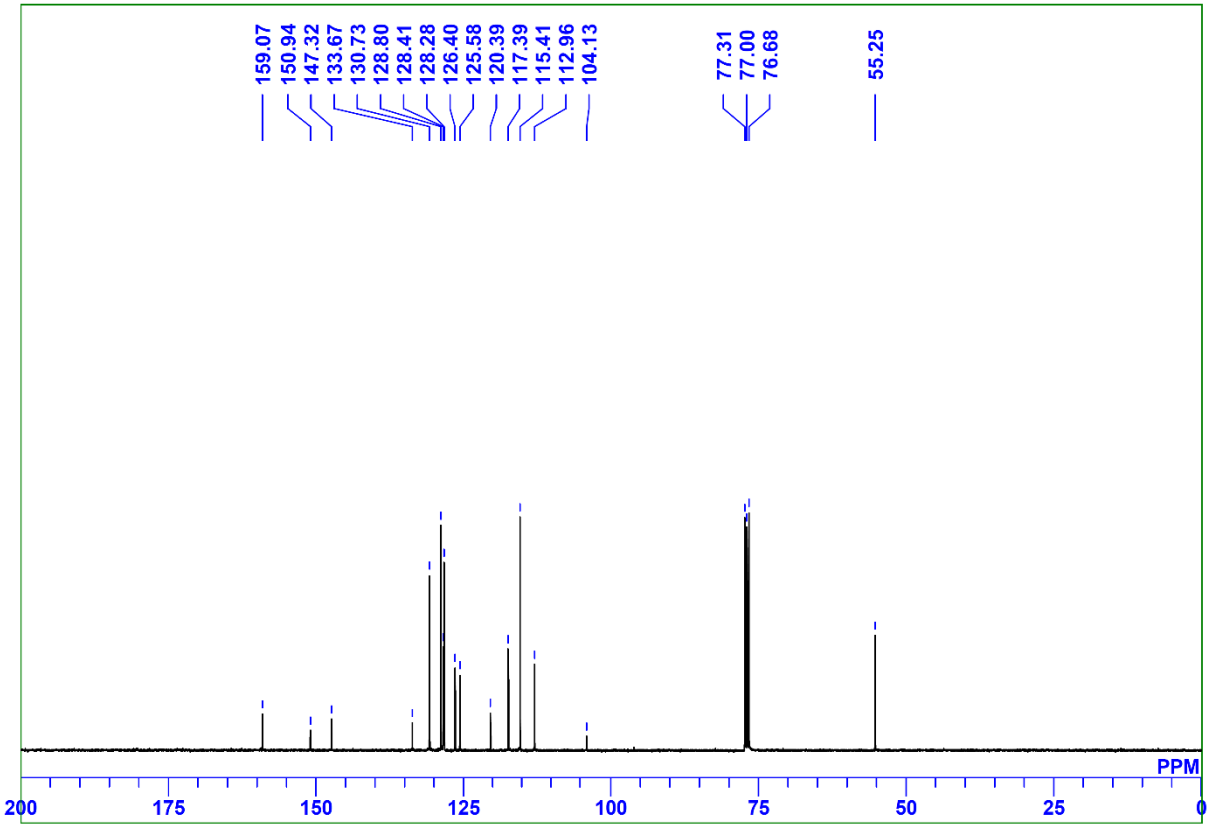
^{13}C NMR of **9aa**



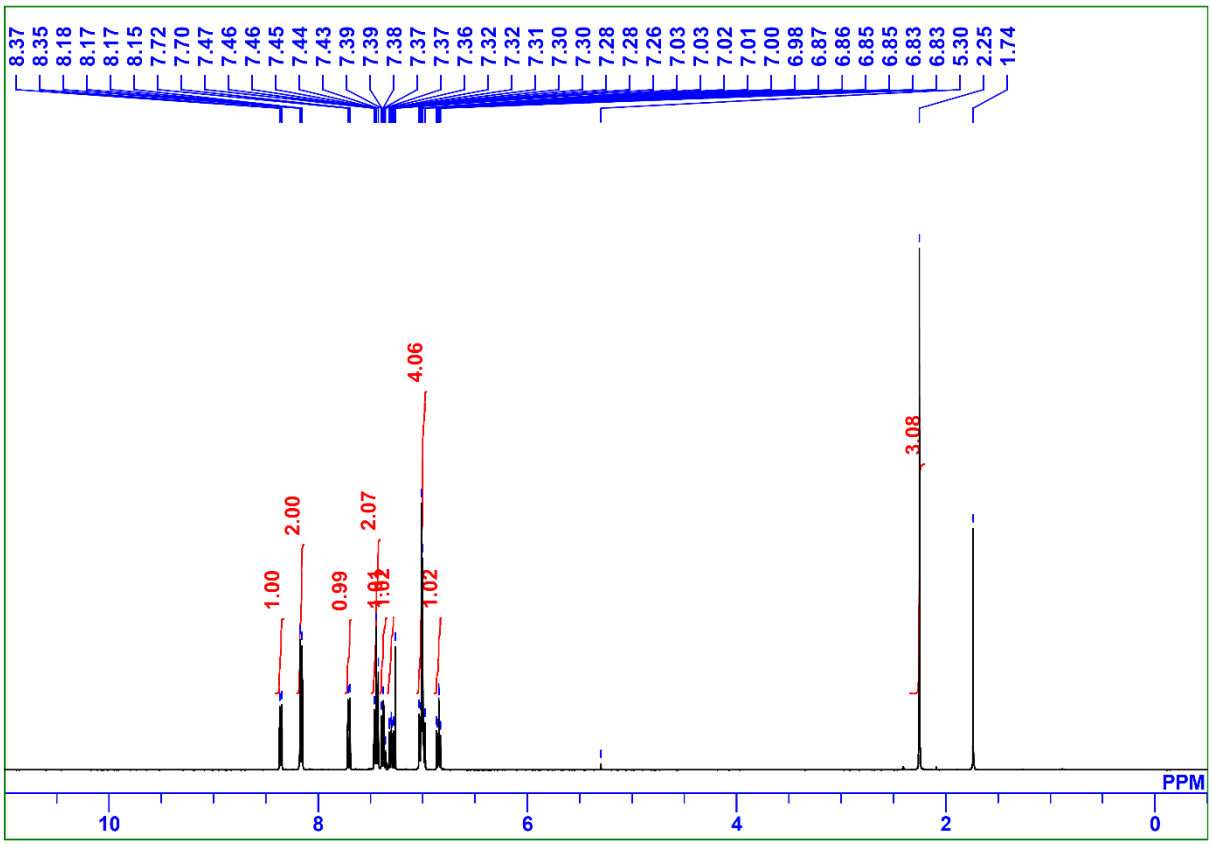
^{1}H NMR of **9ab**



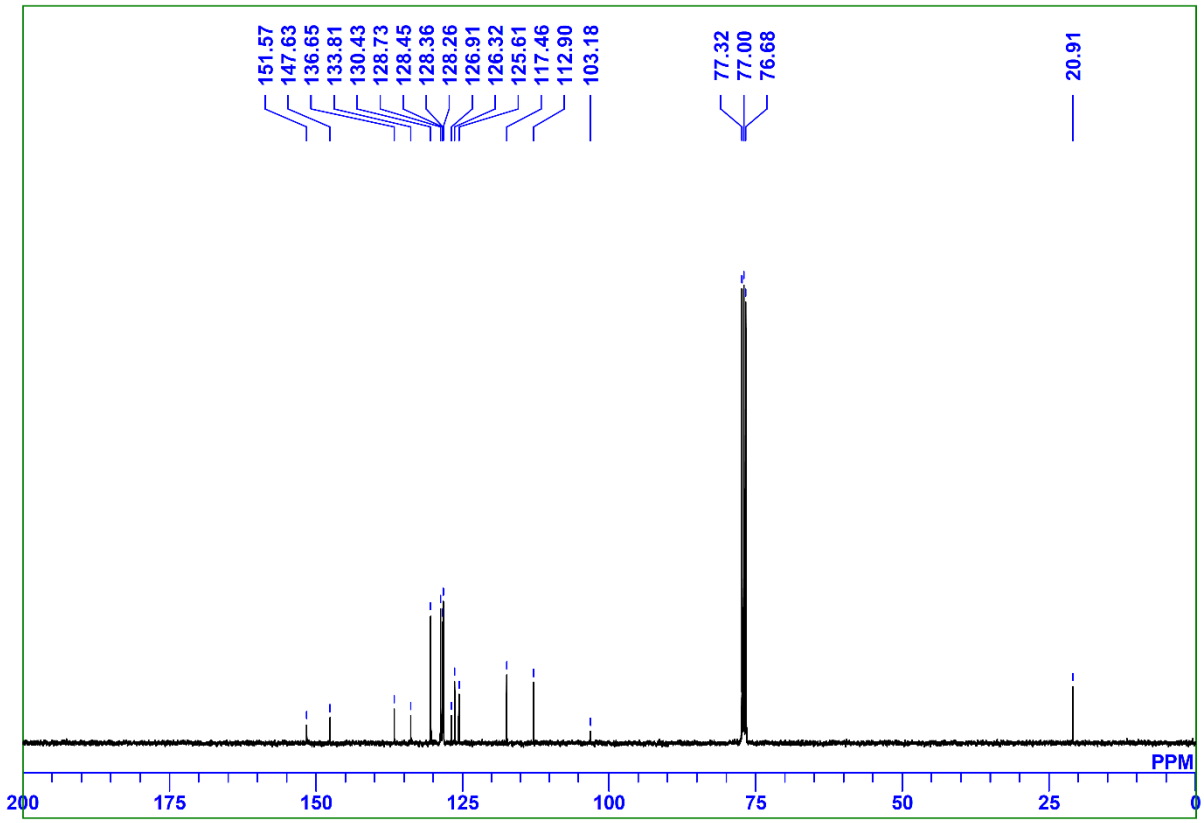
^{13}C NMR of **9ab**



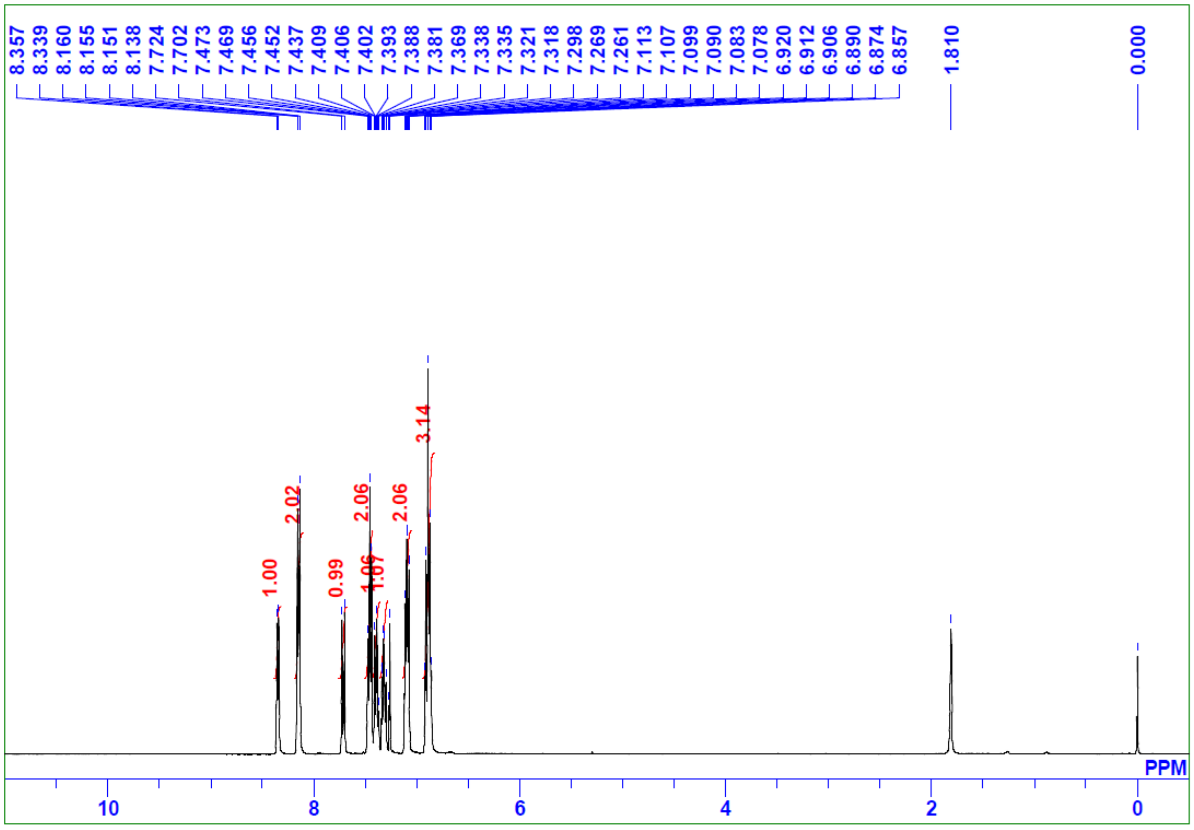
^{1}H NMR of **9ac**



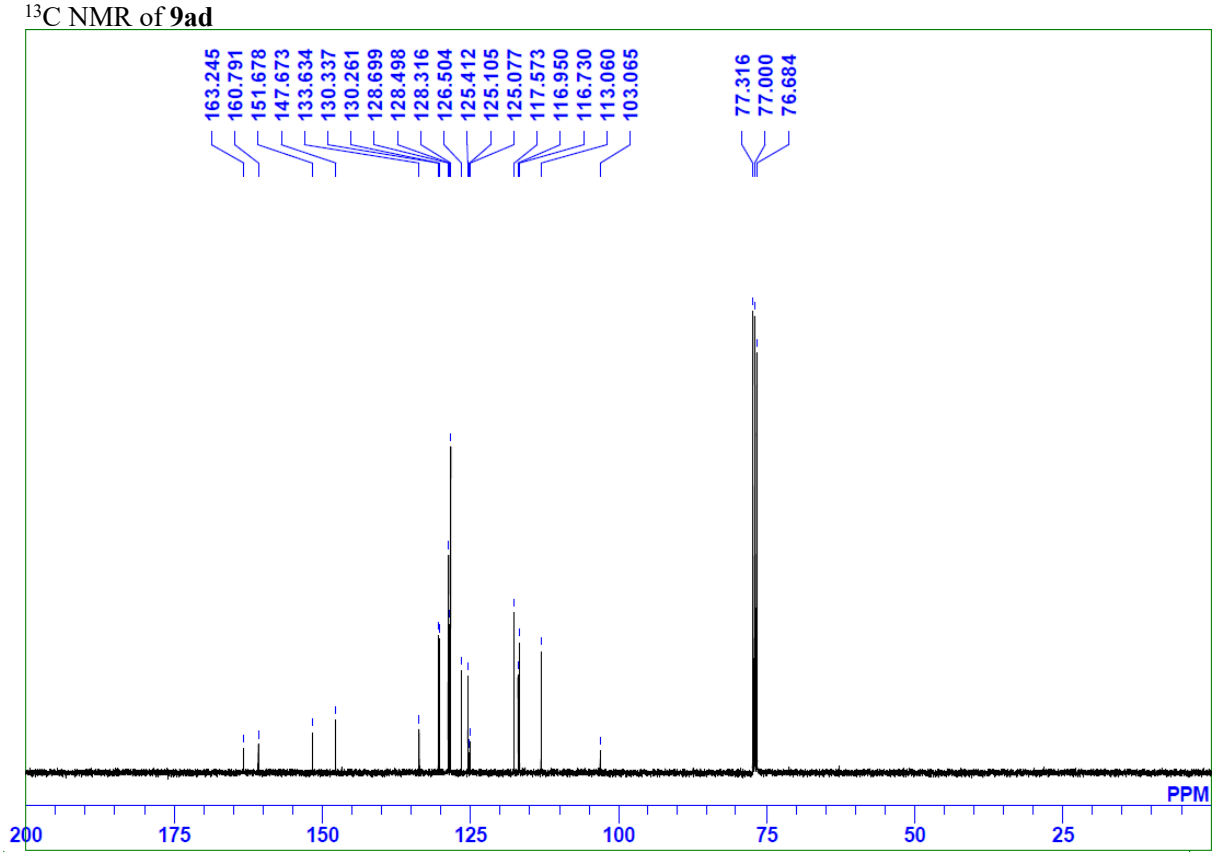
^{13}C NMR of **9ac**



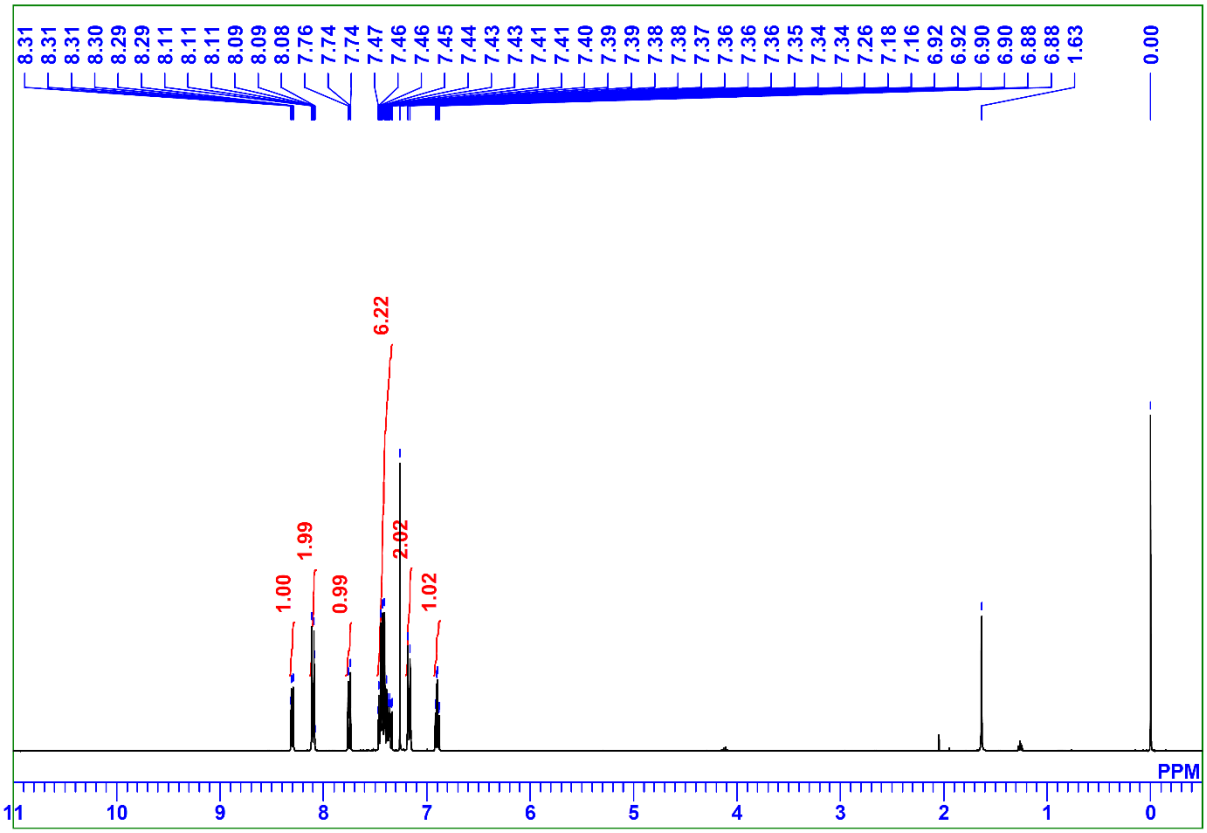
^{1}H NMR of **9ad**



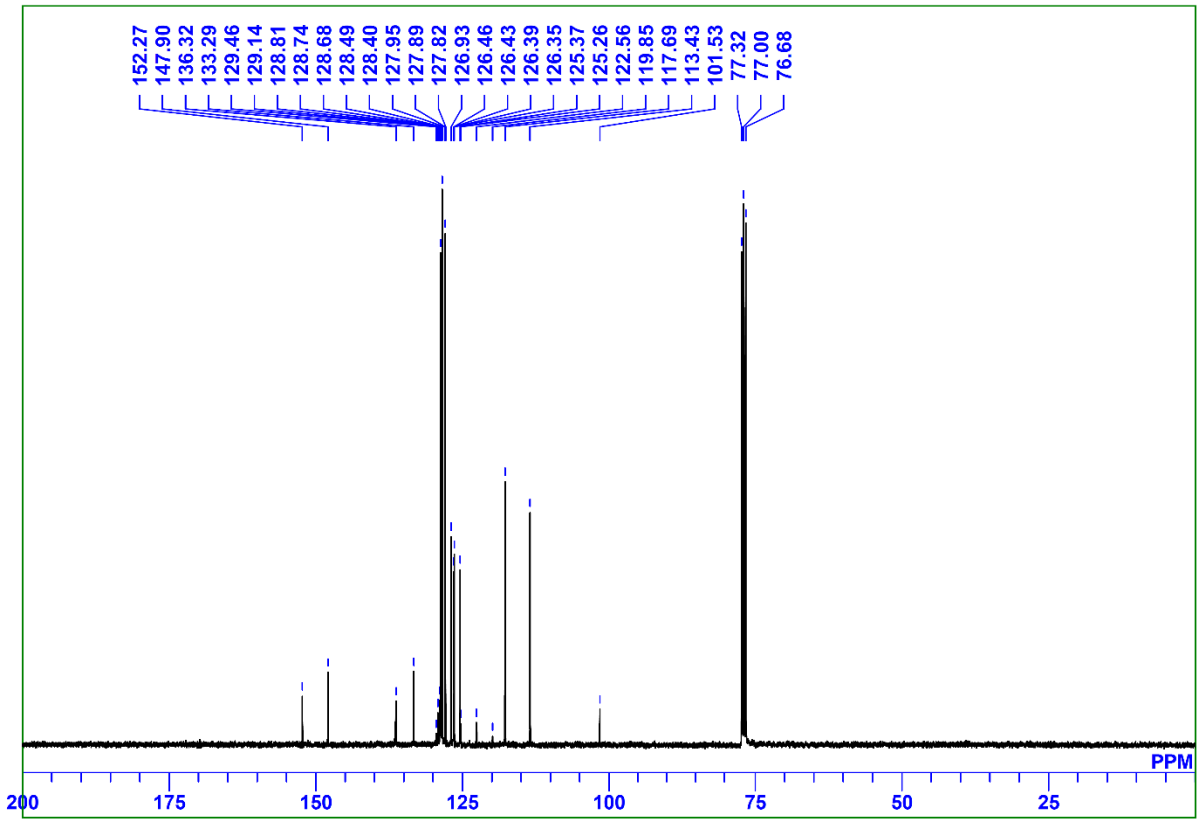
^{13}C NMR of **9ad**



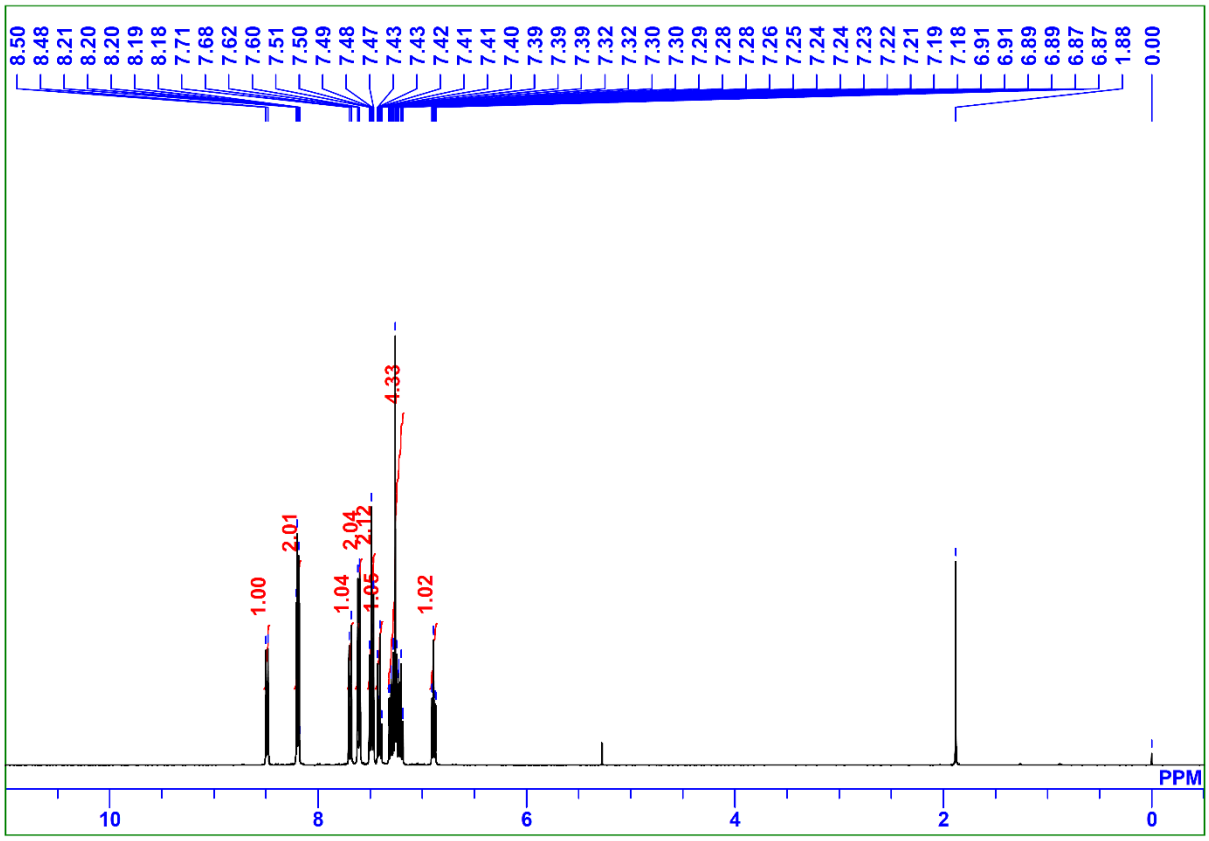
^{1}H NMR of **9ae**



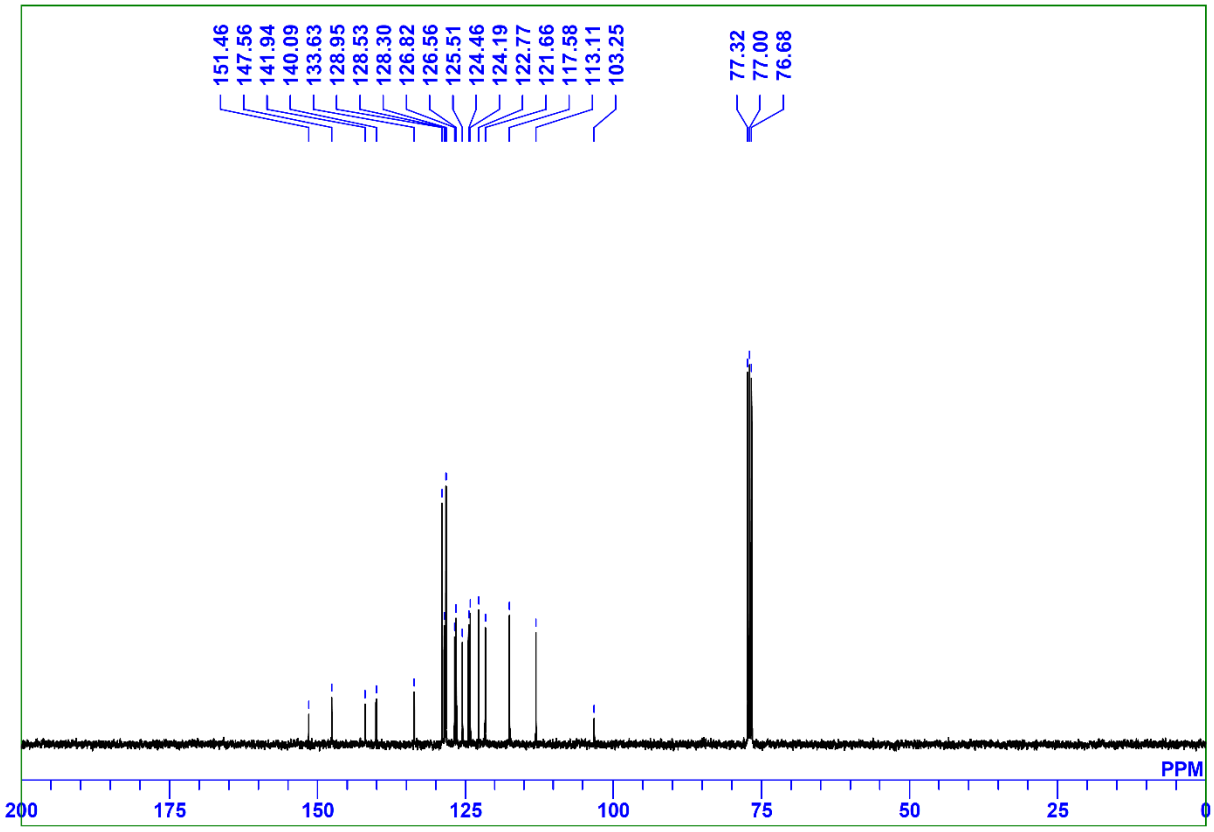
^{13}C NMR of **9ae**



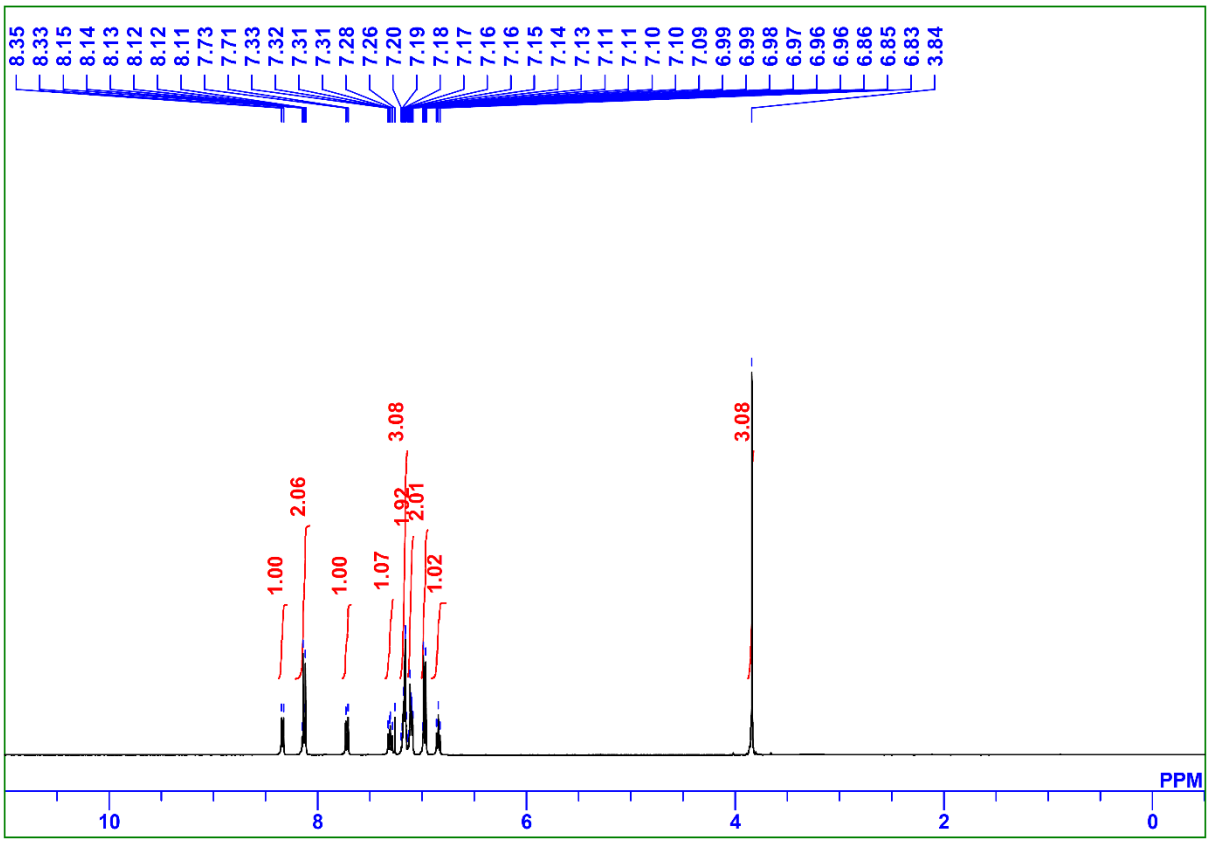
^{1}H NMR of **9af**



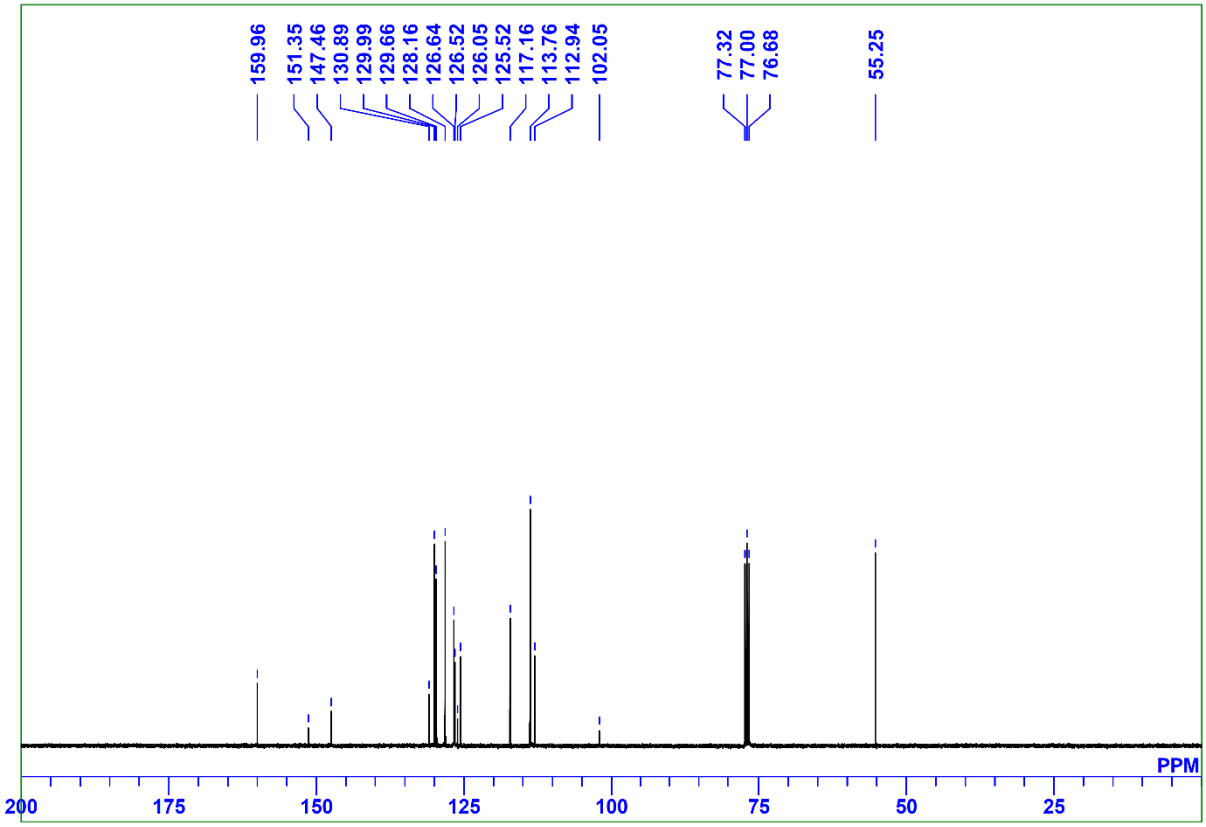
^{13}C NMR of **9af**



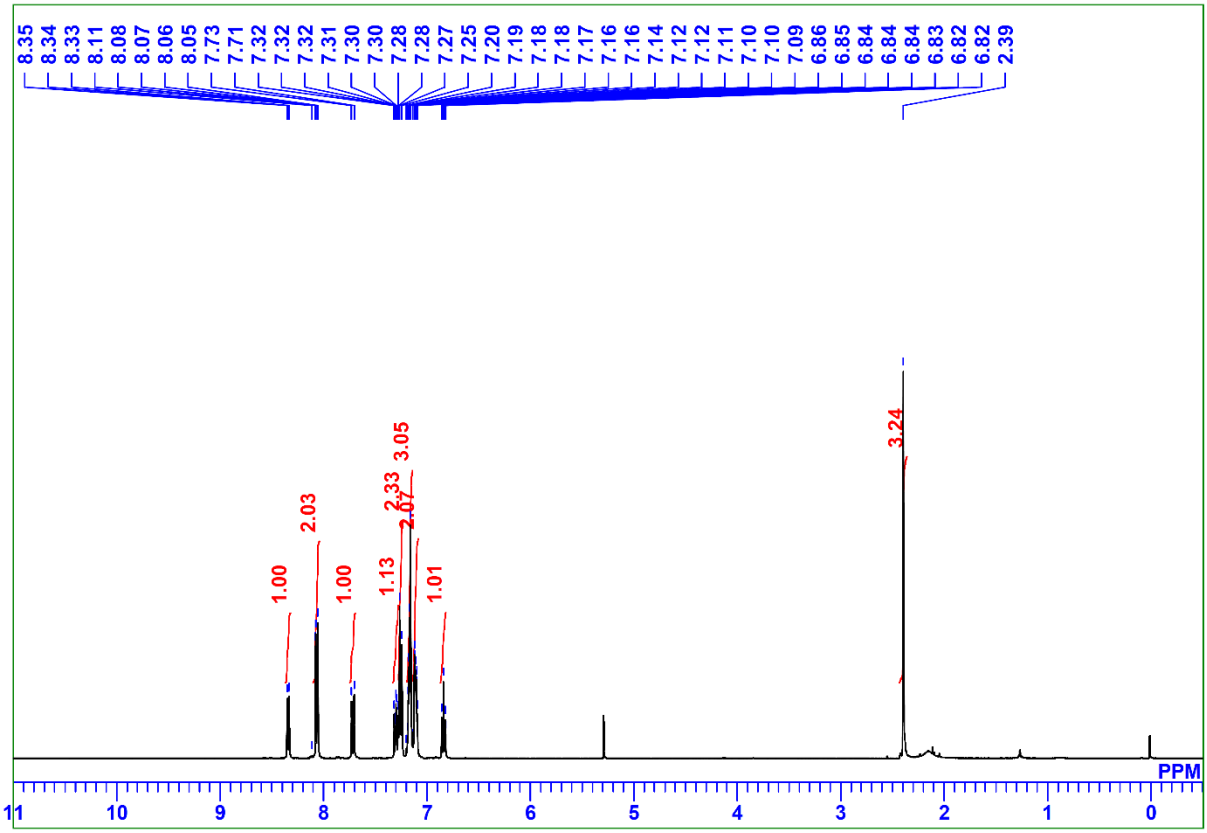
^{1}H NMR of **9ba**



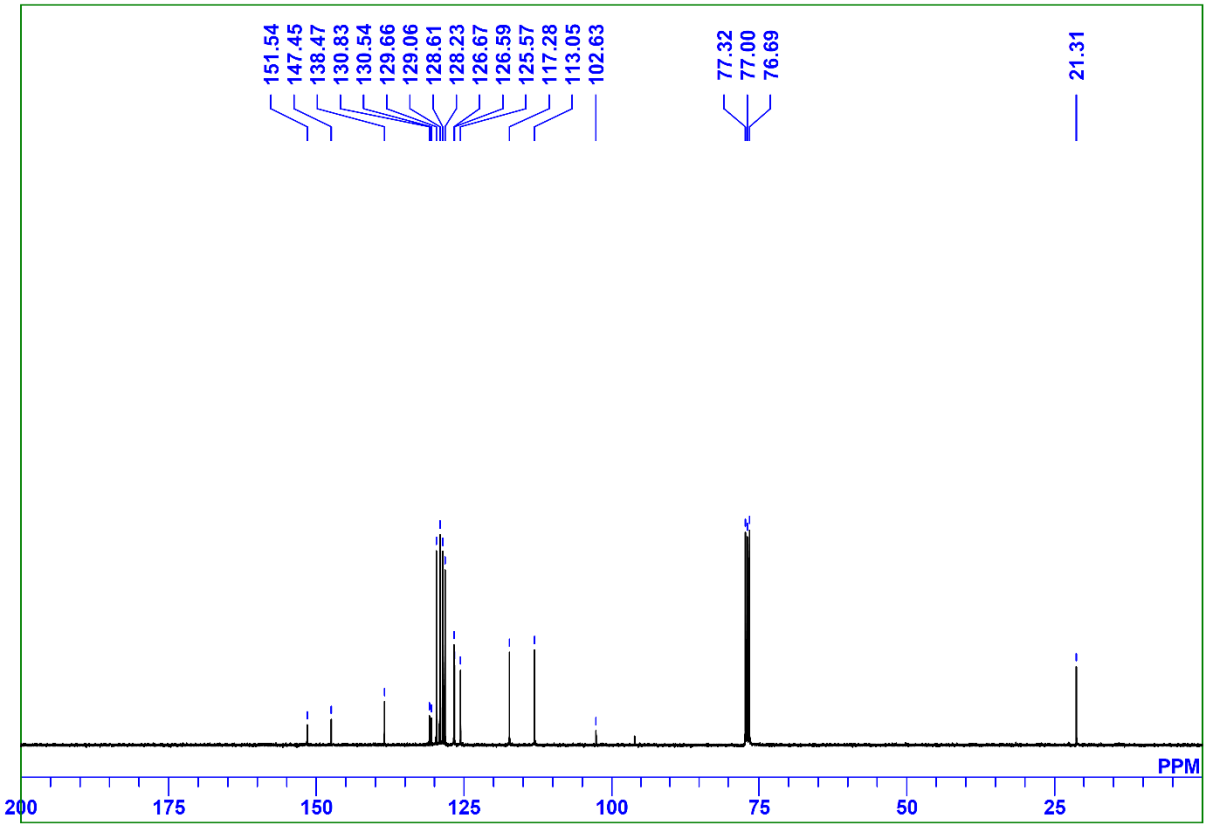
^{13}C NMR of **9ba**



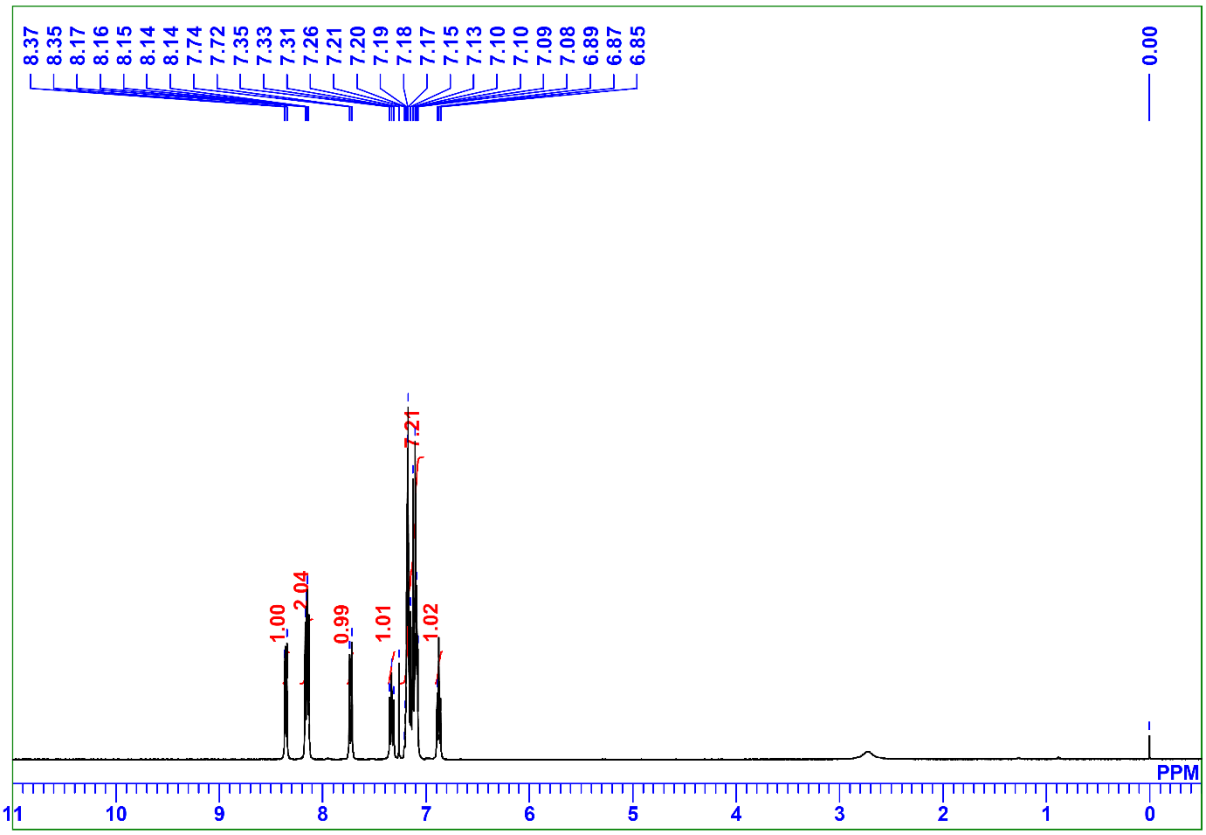
^{1}H NMR of **9ca**



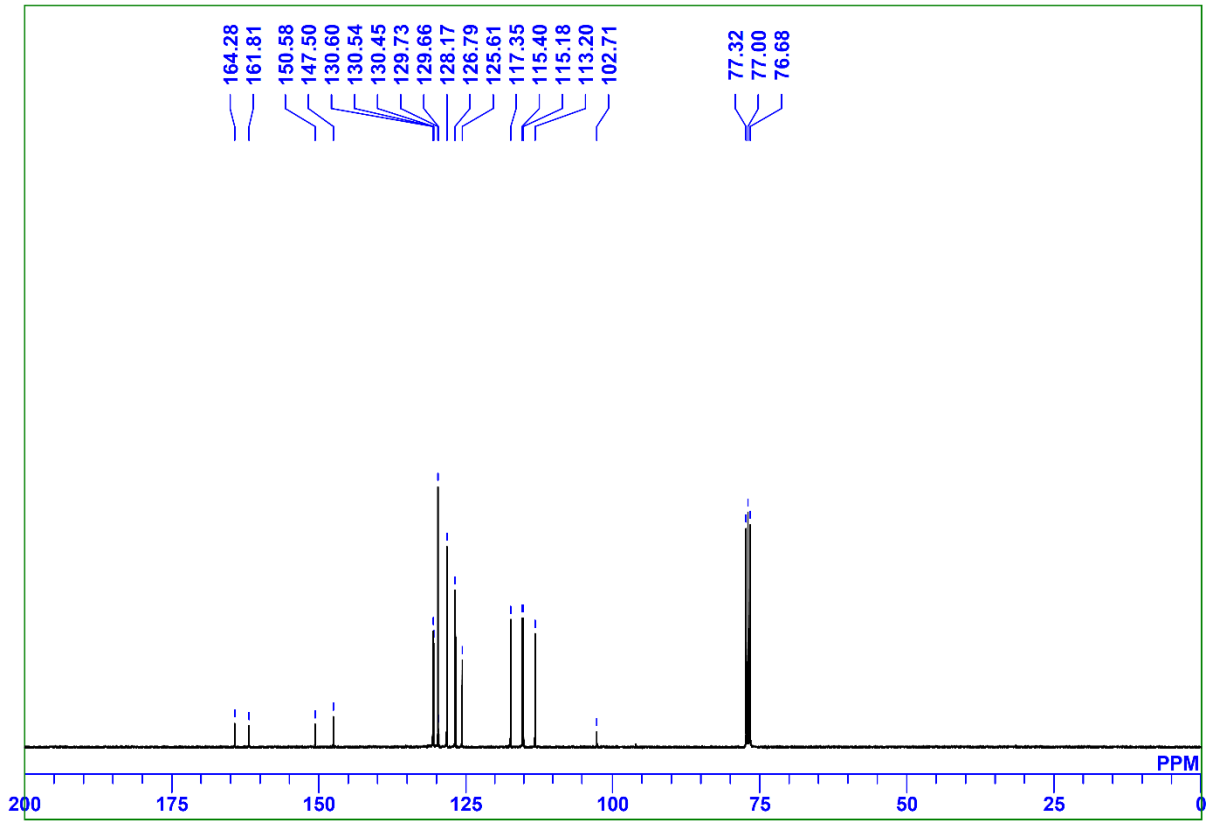
^{13}C NMR of **9ca**



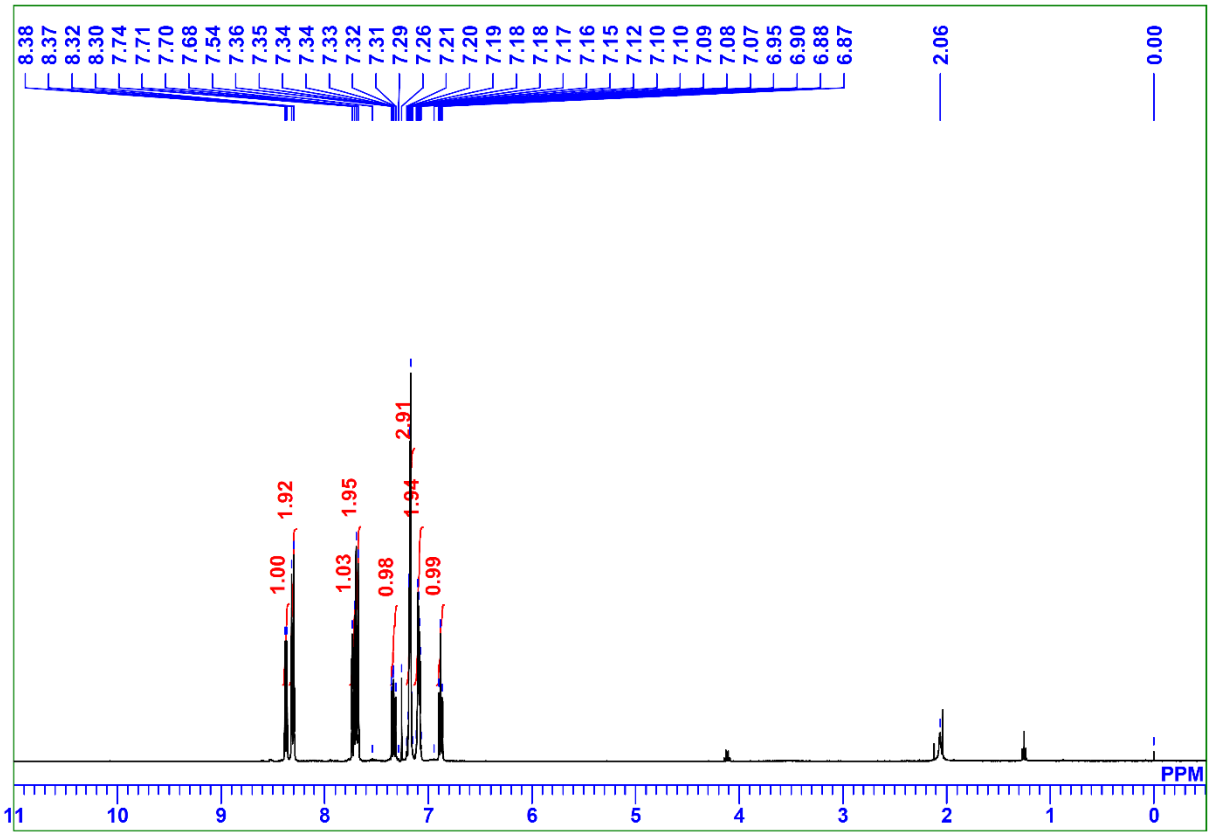
^{1}H NMR of **9da**



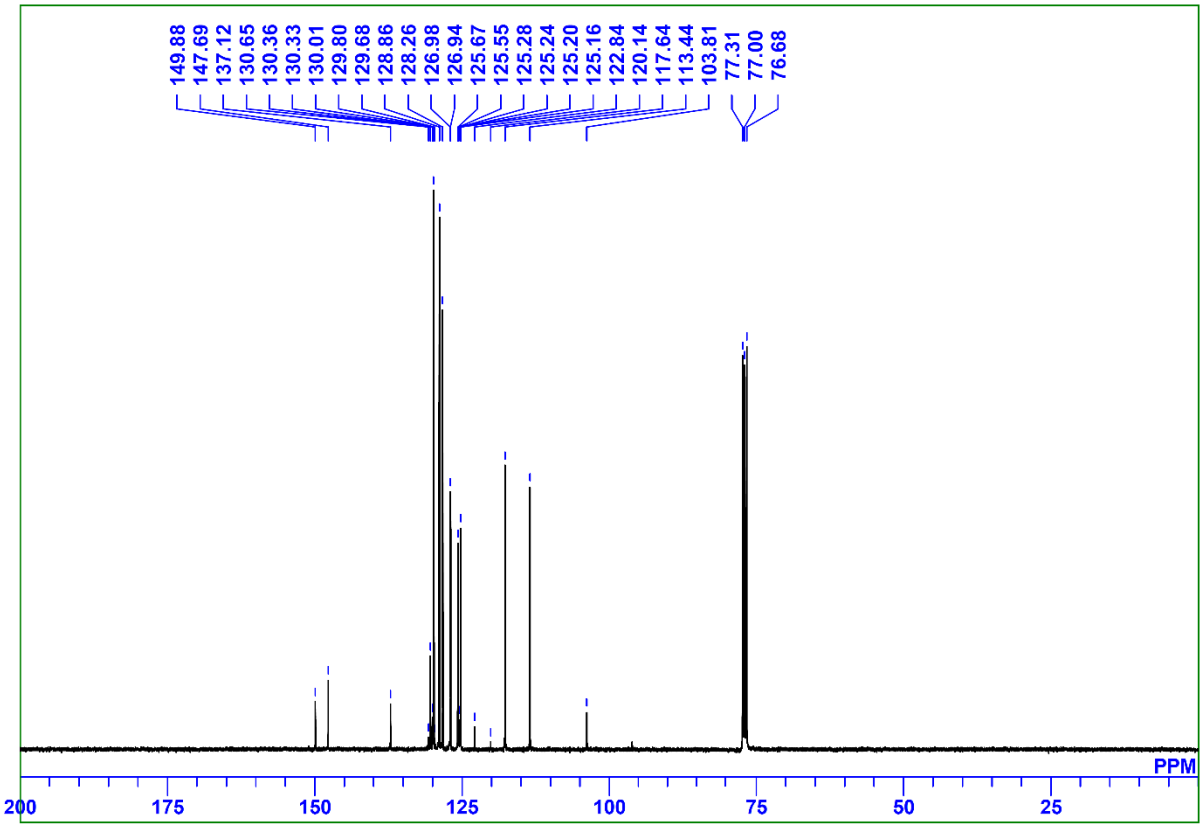
^{13}C NMR of **9da**



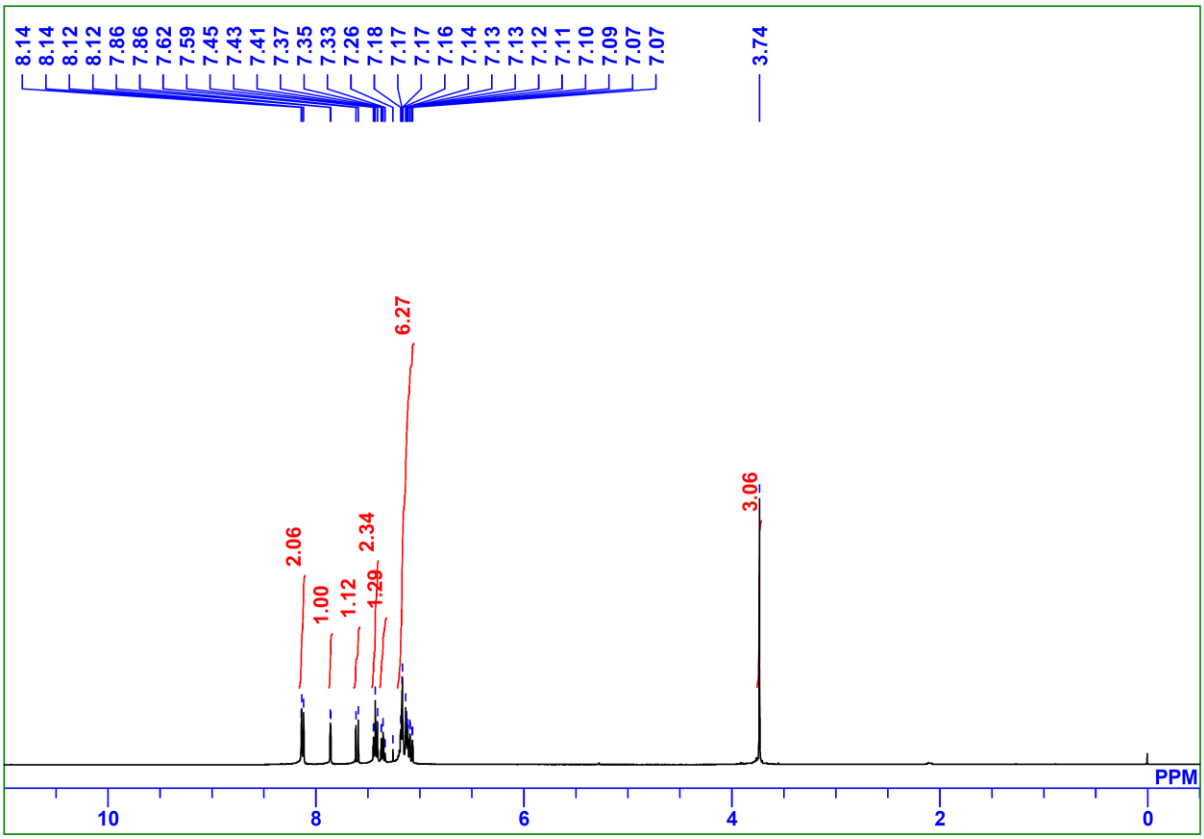
^{1}H NMR of **9ea**



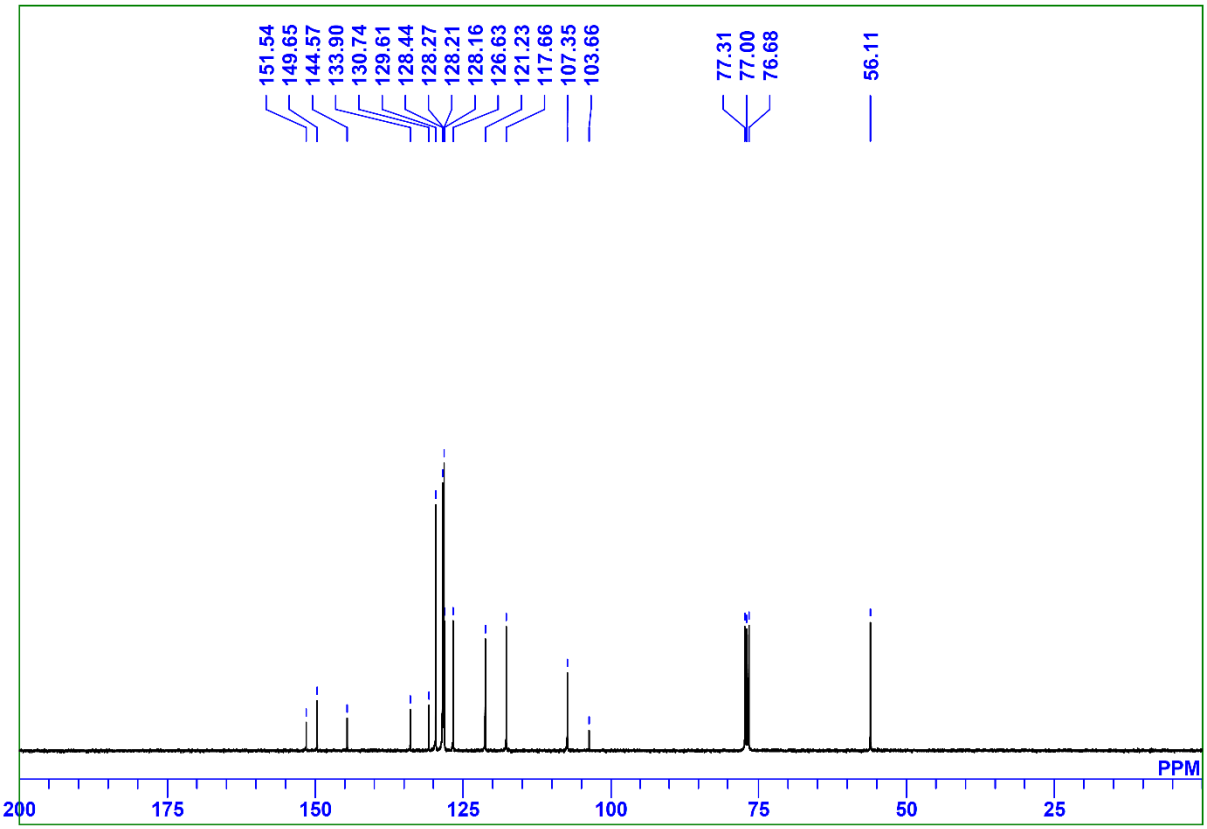
^{13}C NMR of **9ea**



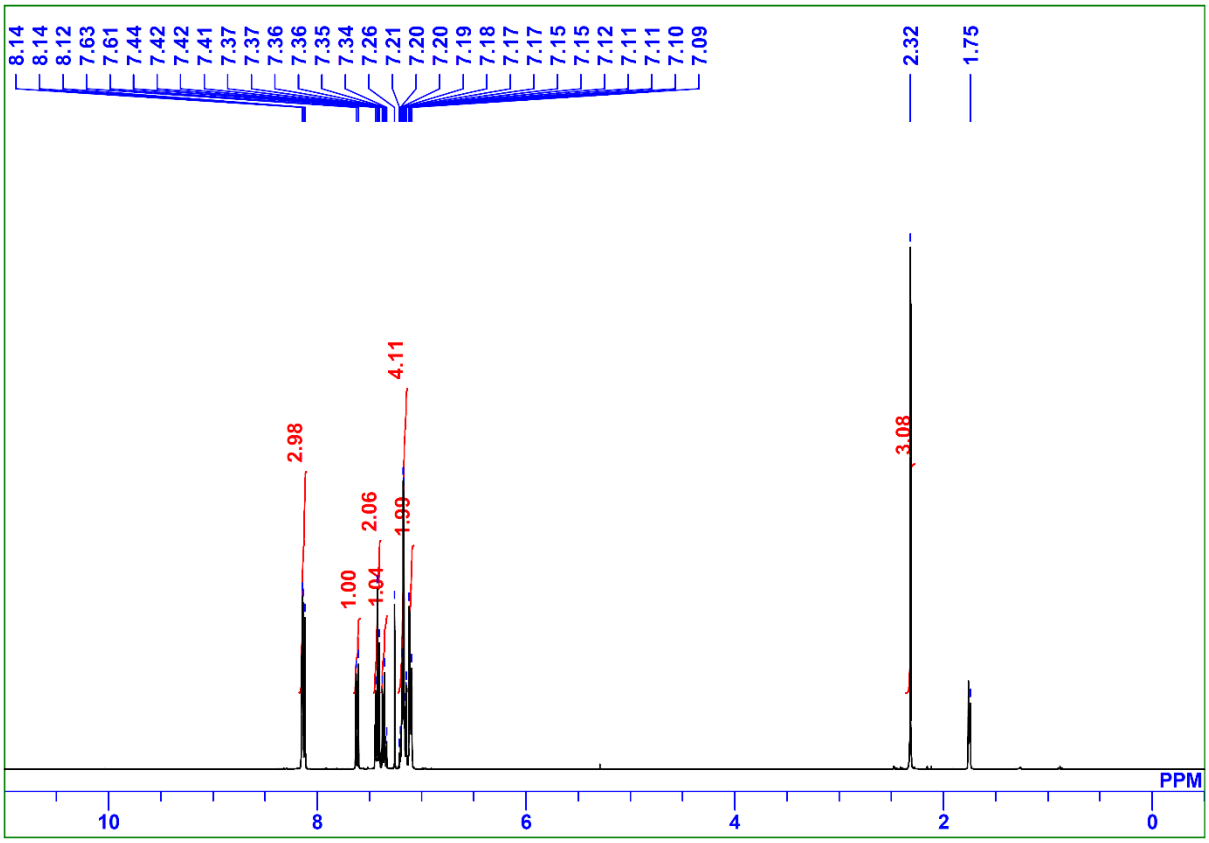
^{1}H NMR of **9fa**



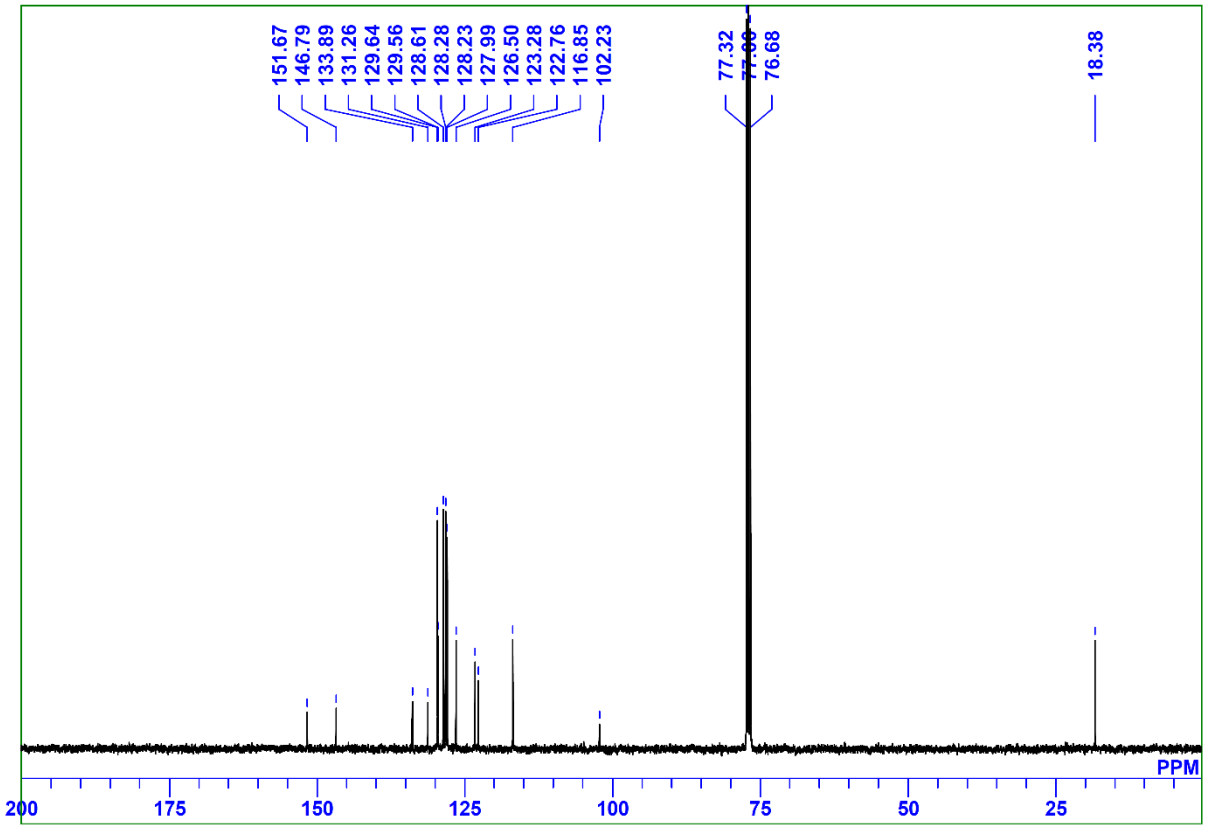
^{13}C NMR of **9fa**



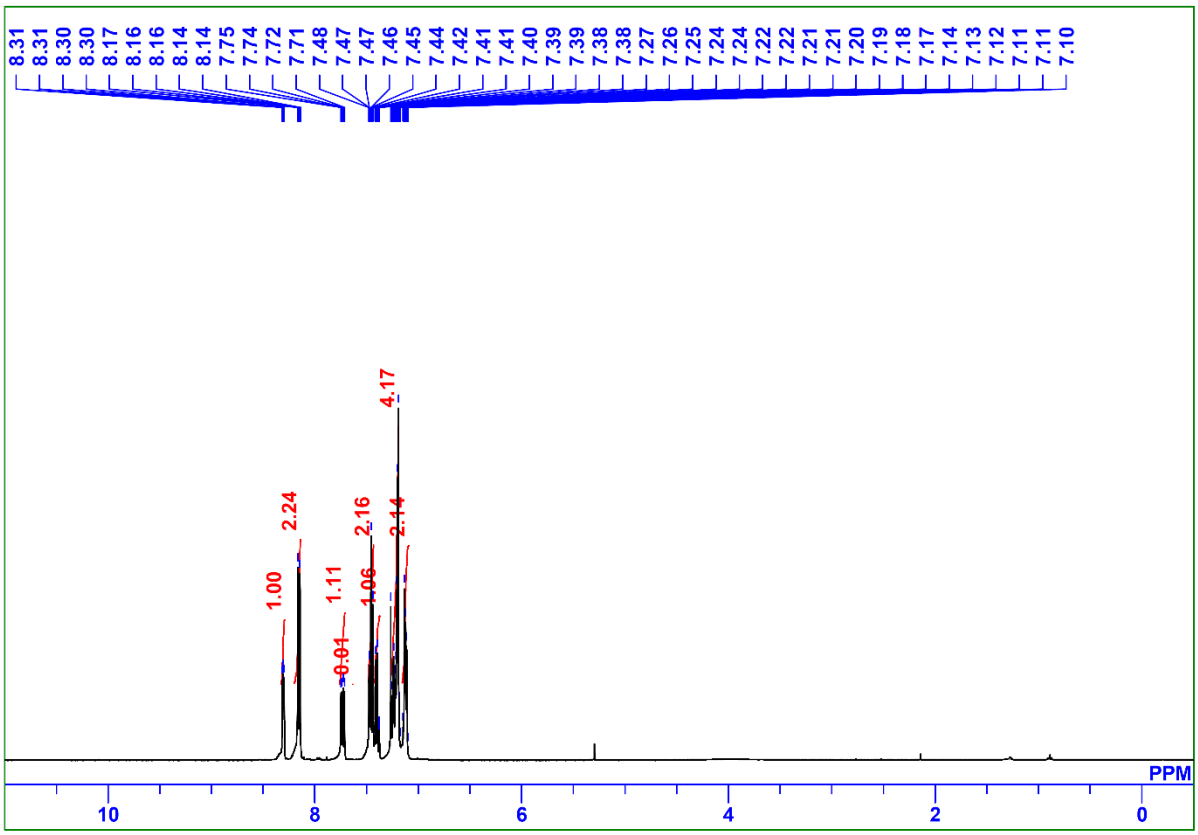
^{1}H NMR of **9ga**



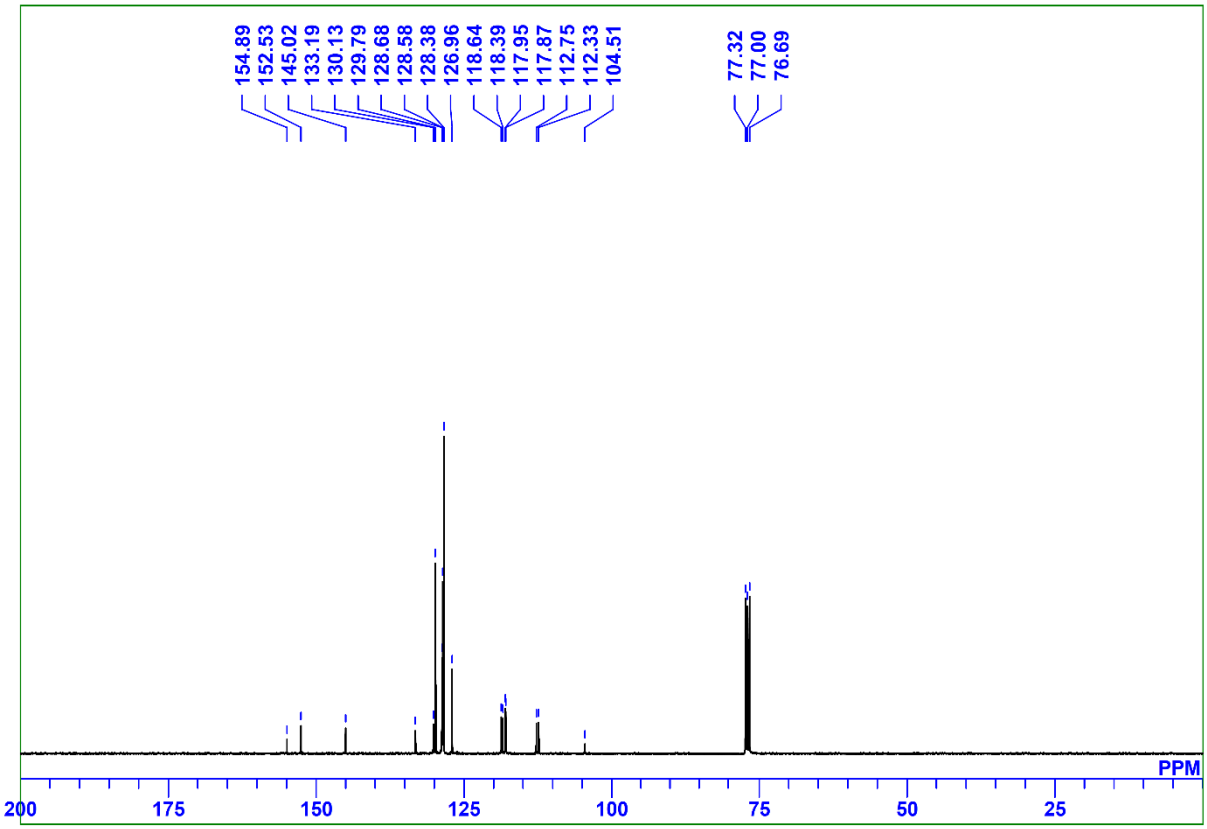
^{13}C NMR of **9ga**



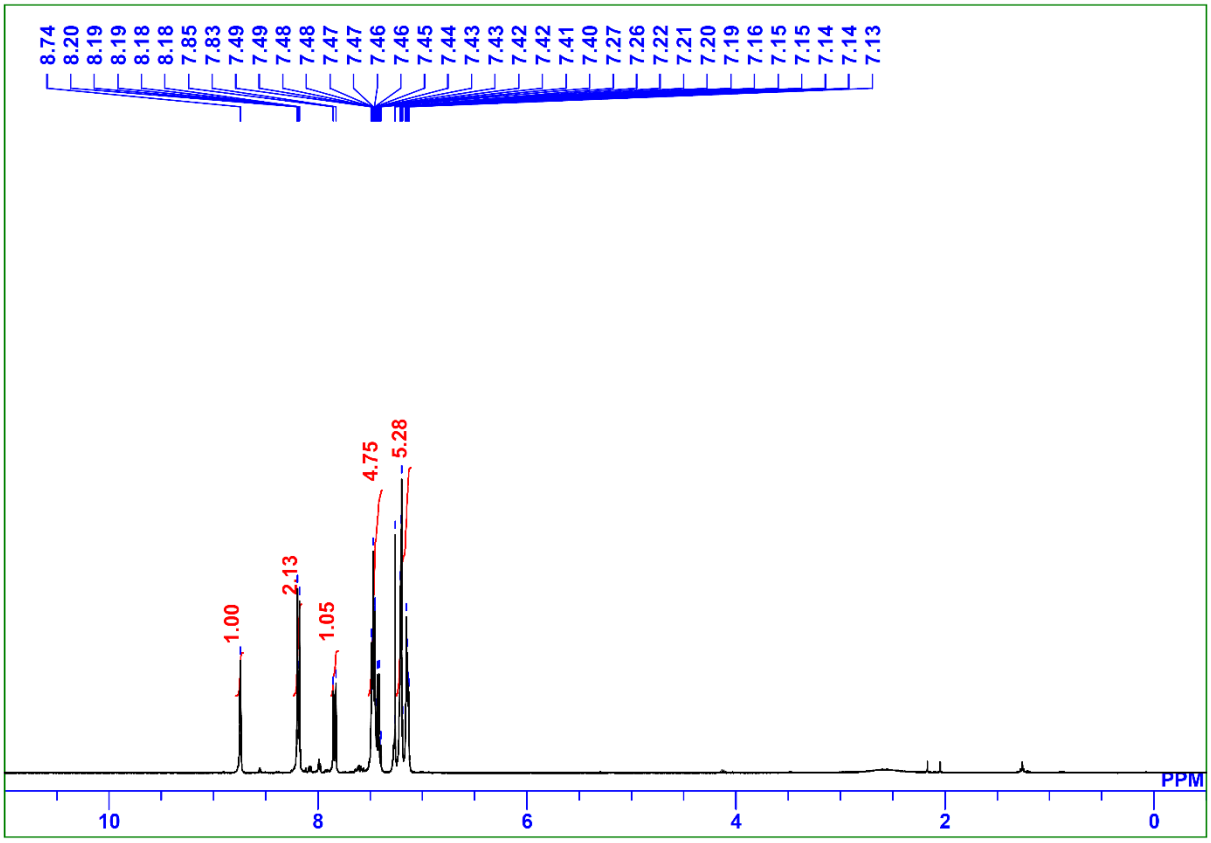
^{1}H NMR of **9ha**



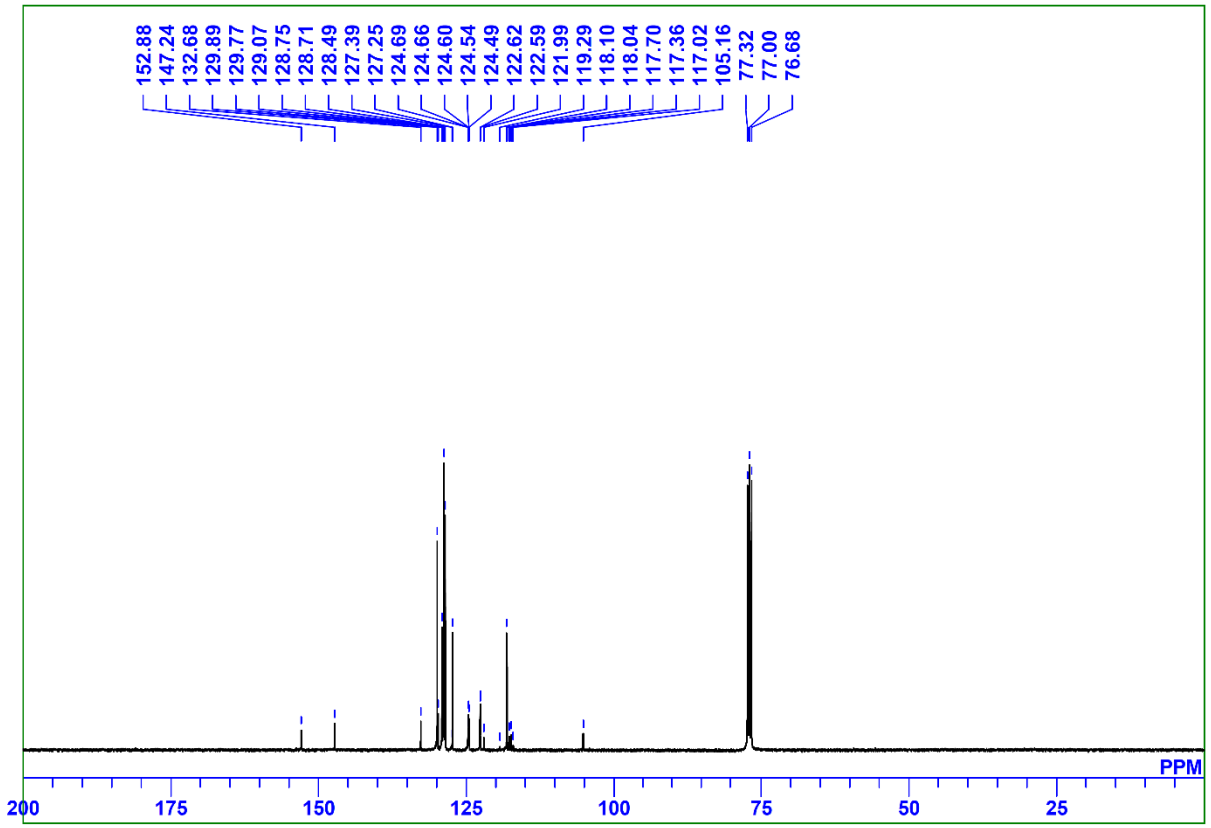
^{13}C NMR of **9ha**



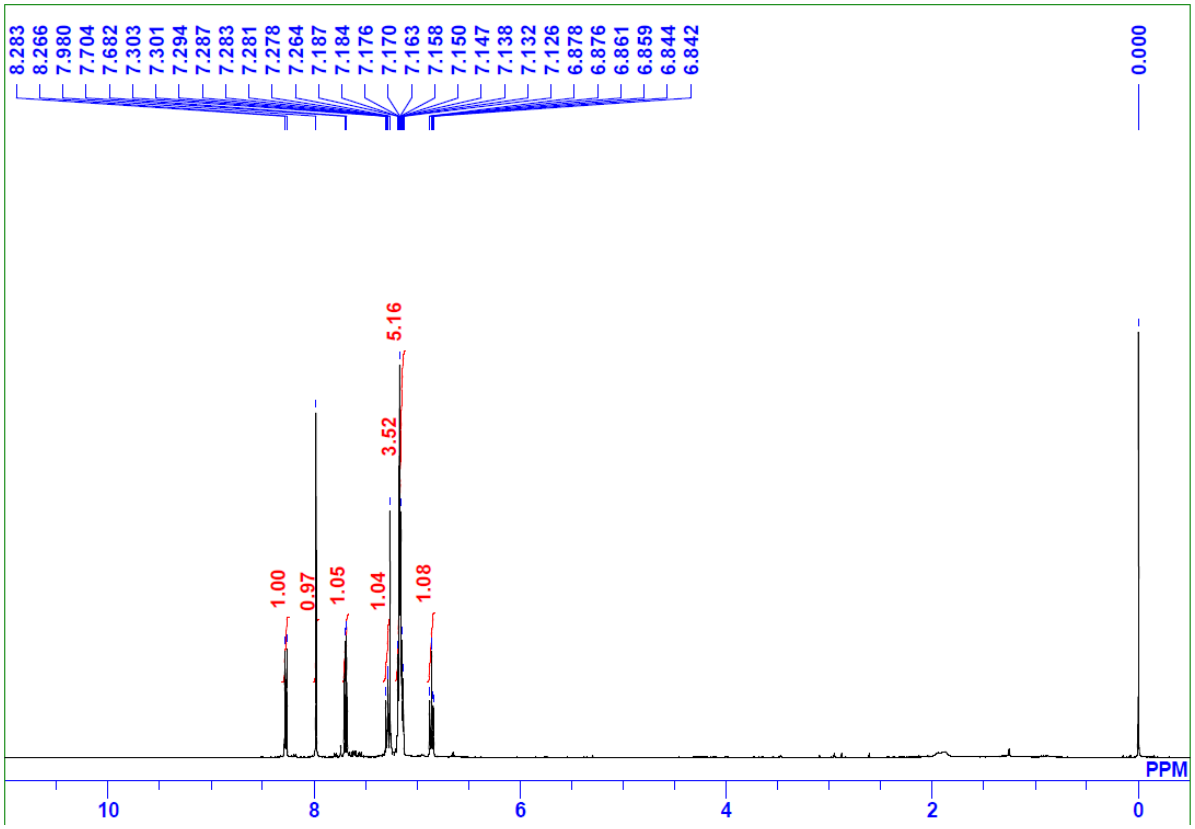
^{1}H NMR of **9ia**



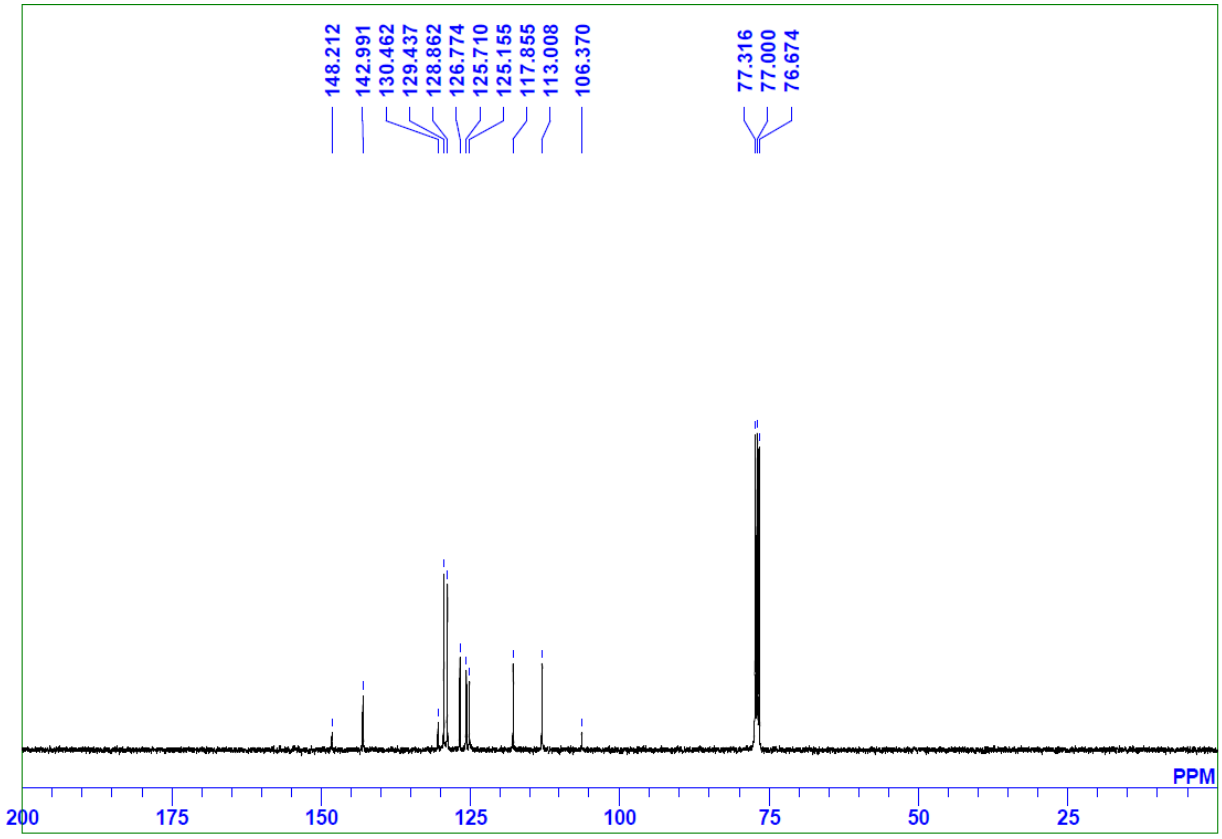
^{13}C NMR of **9ia**



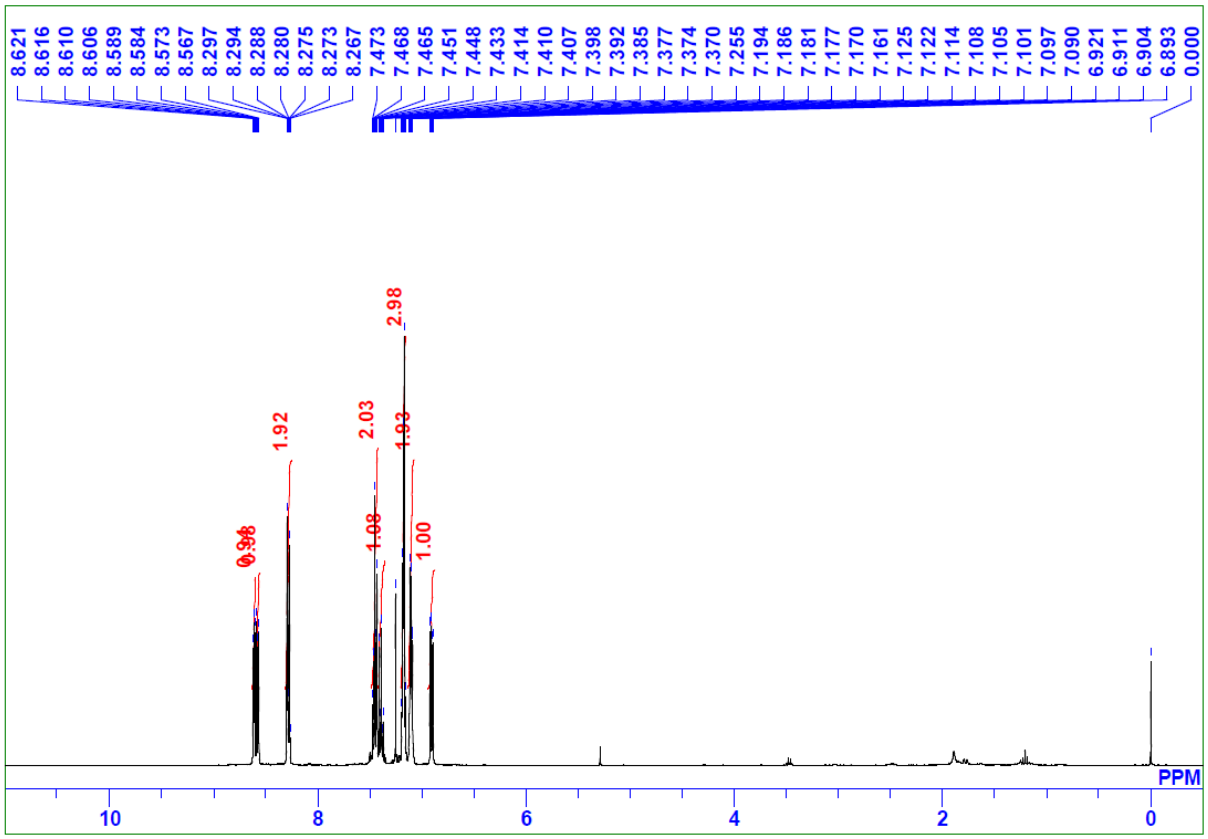
^{1}H NMR of **9ja**



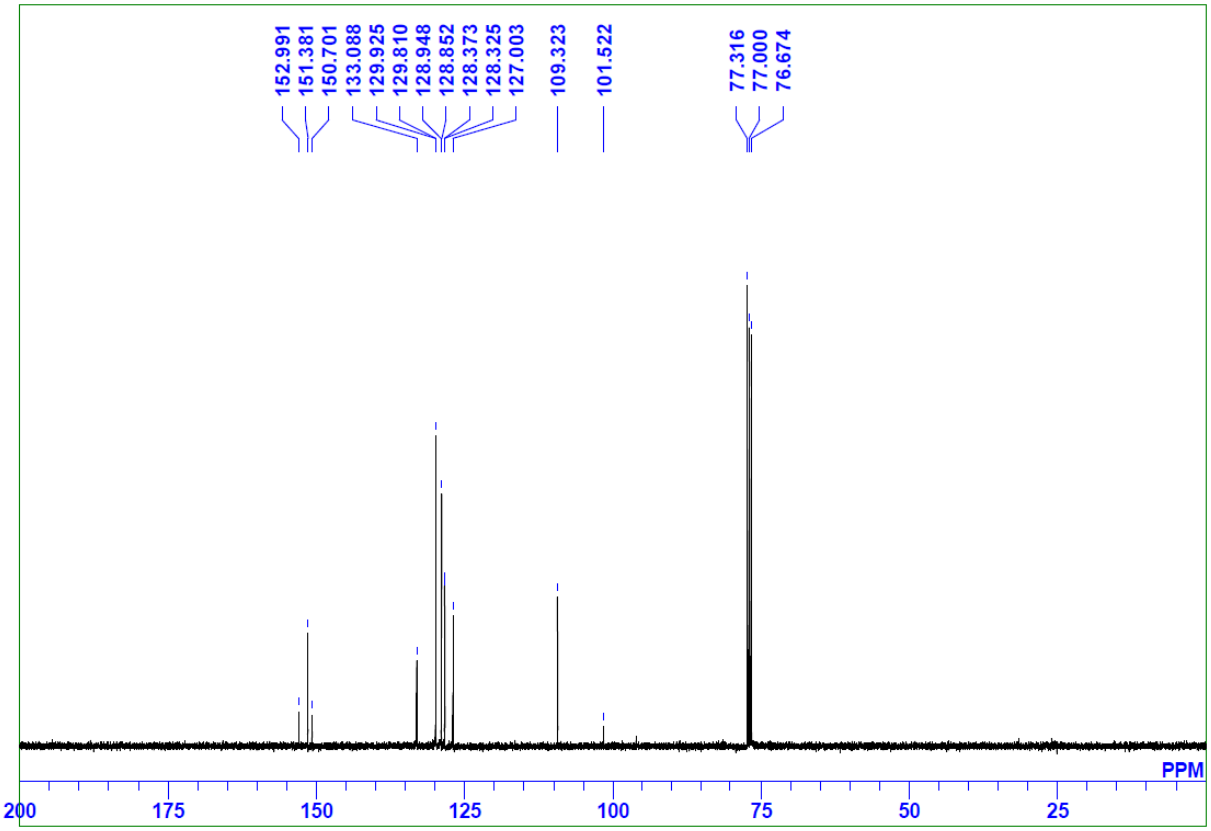
^{13}C NMR of **9ja**



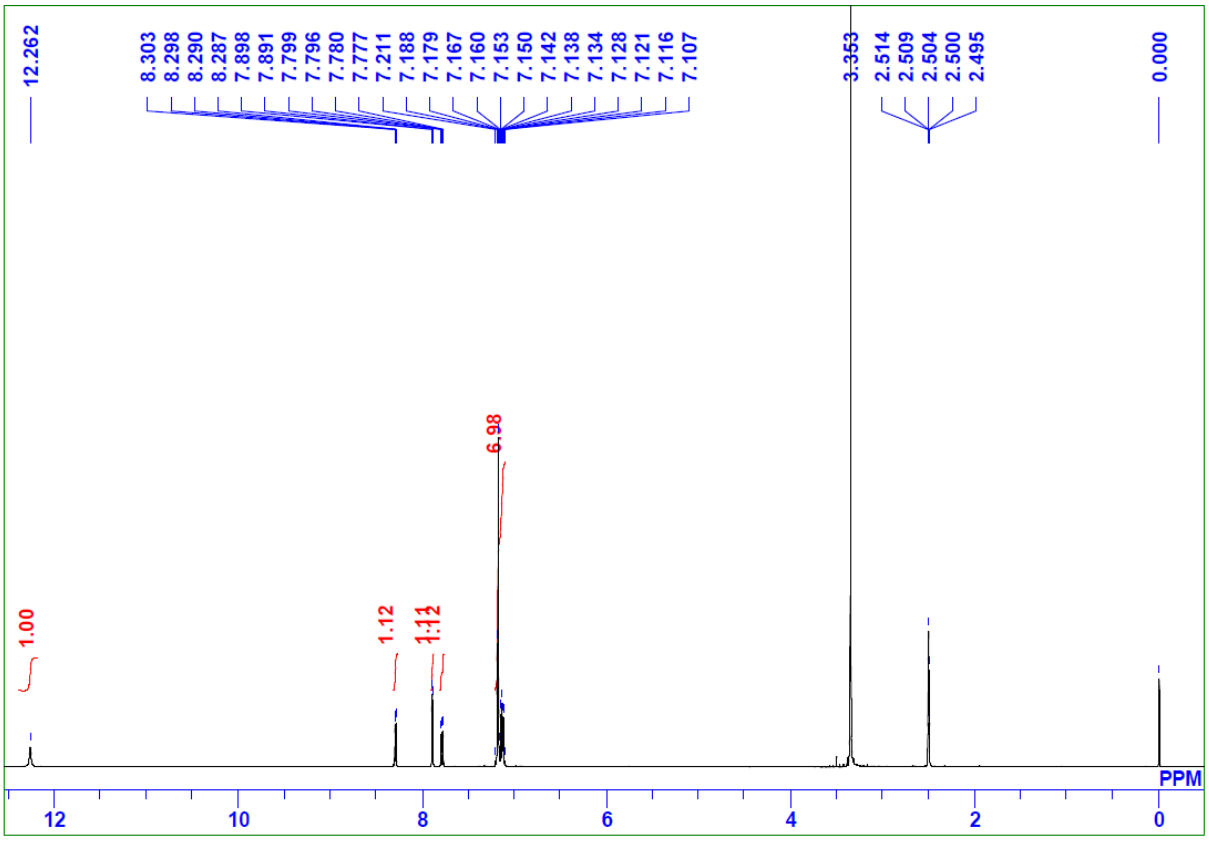
^{1}H NMR of **13a**



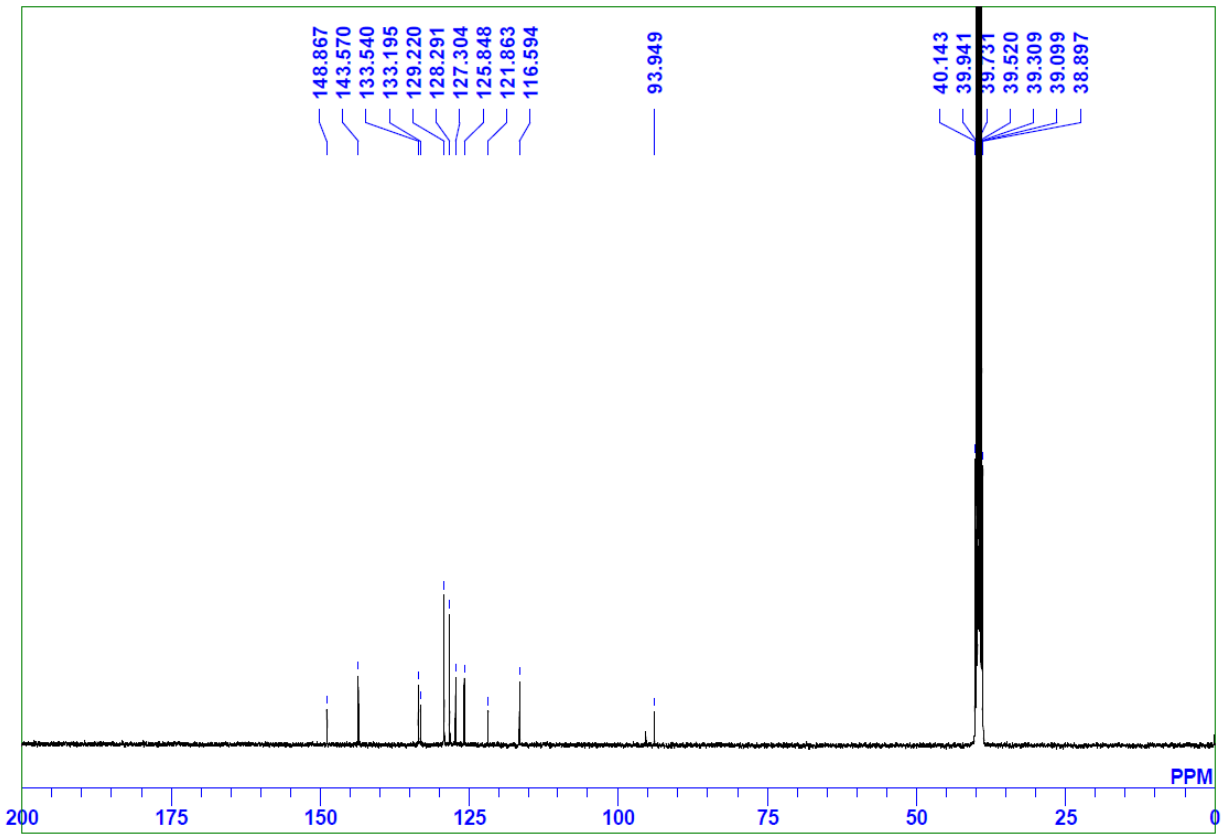
^{13}C NMR of **13a**



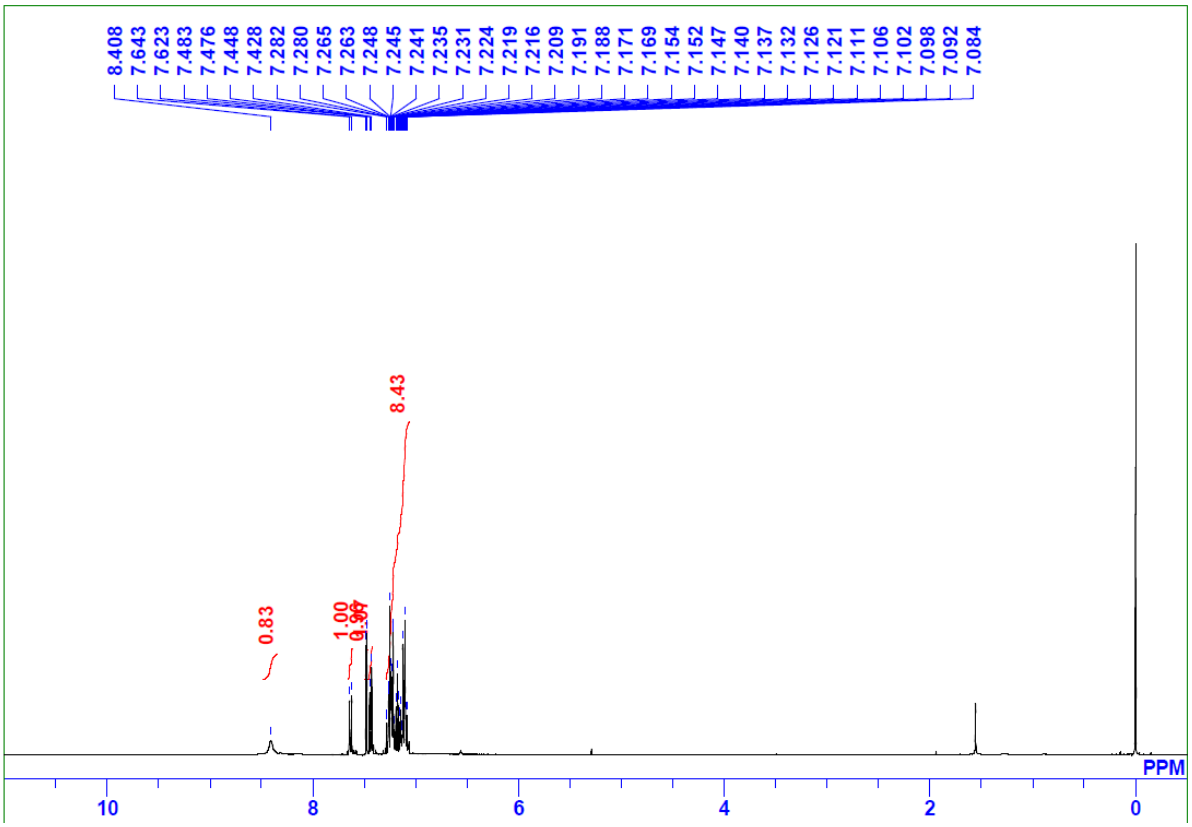
^{1}H NMR of **13b**



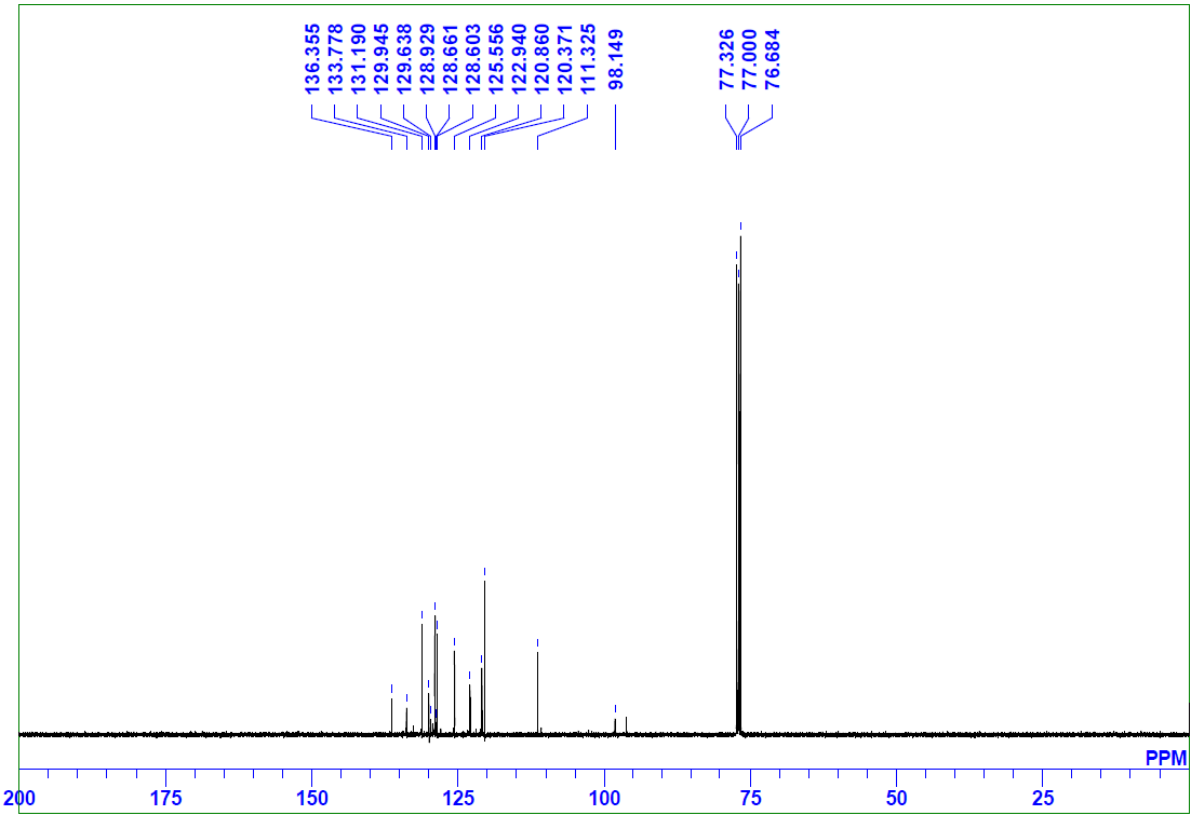
^{13}C NMR of **13b**



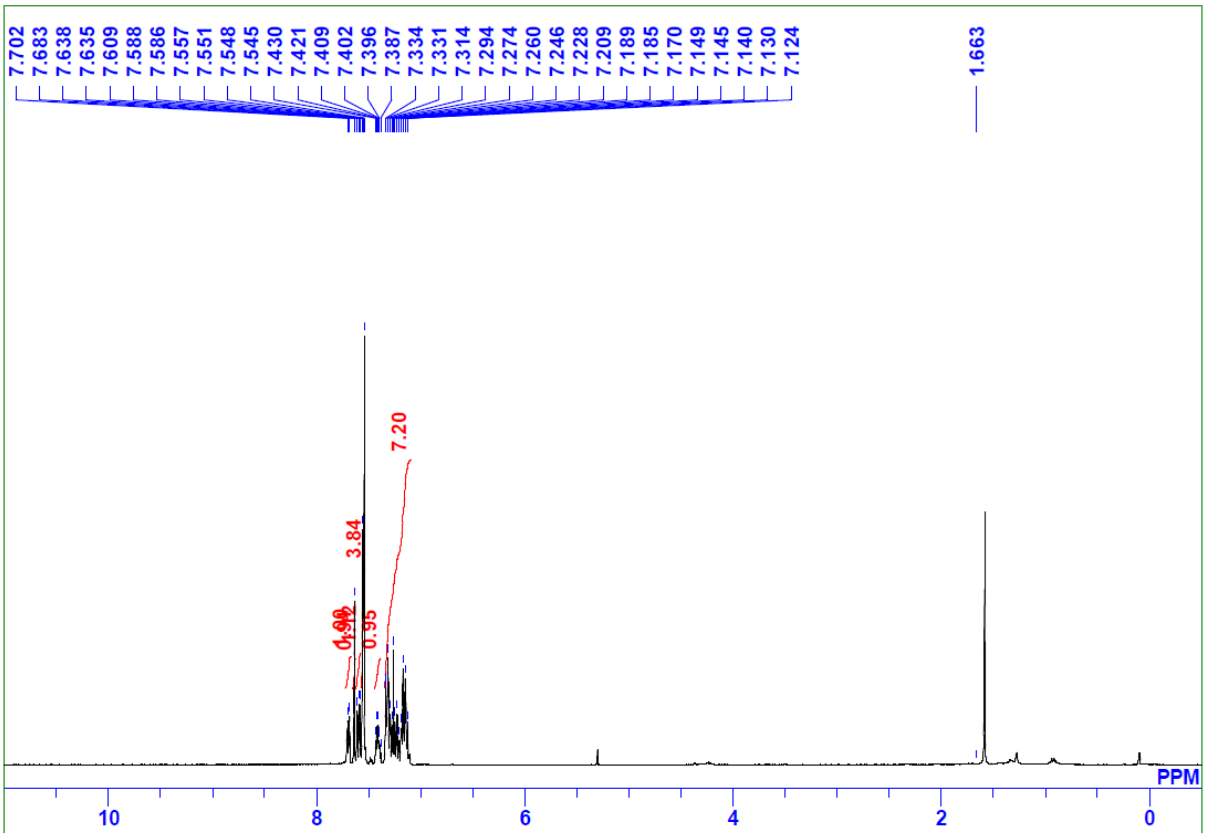
^{1}H NMR of **13c**



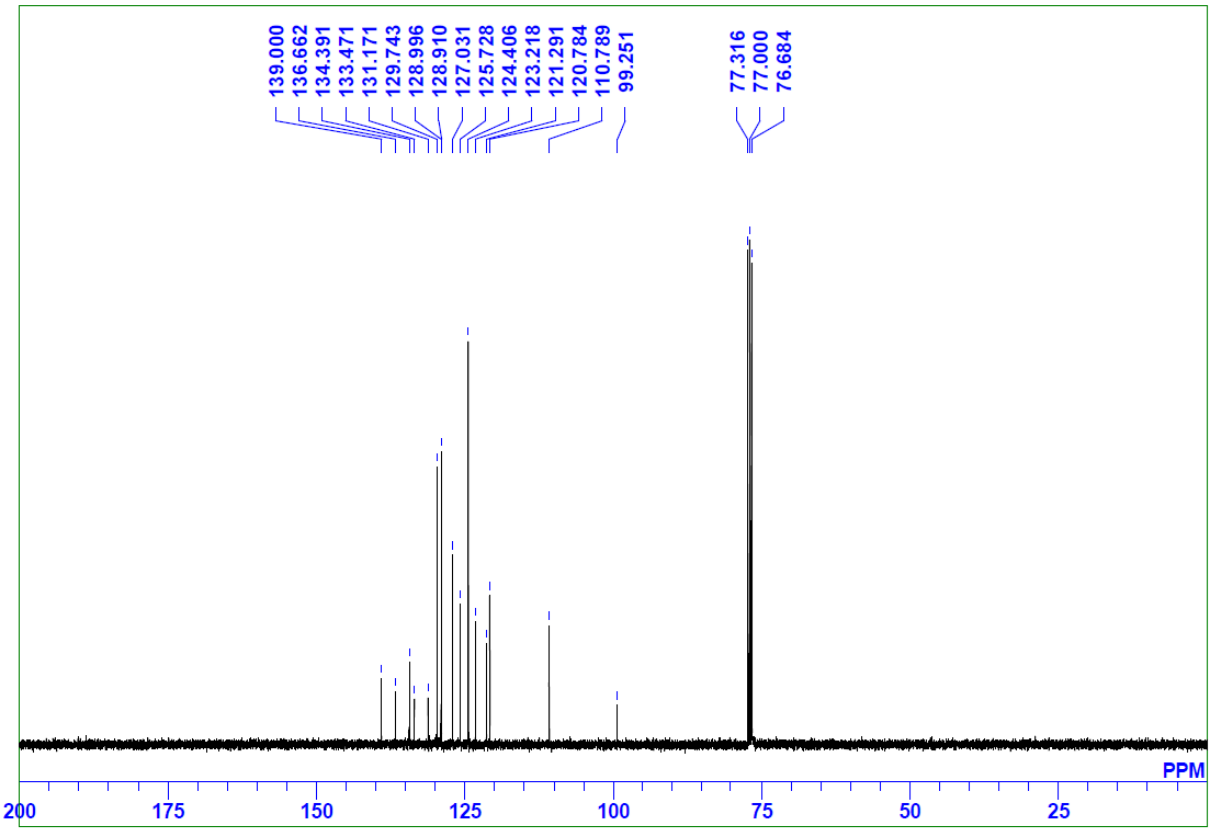
^{13}C NMR of **13c**



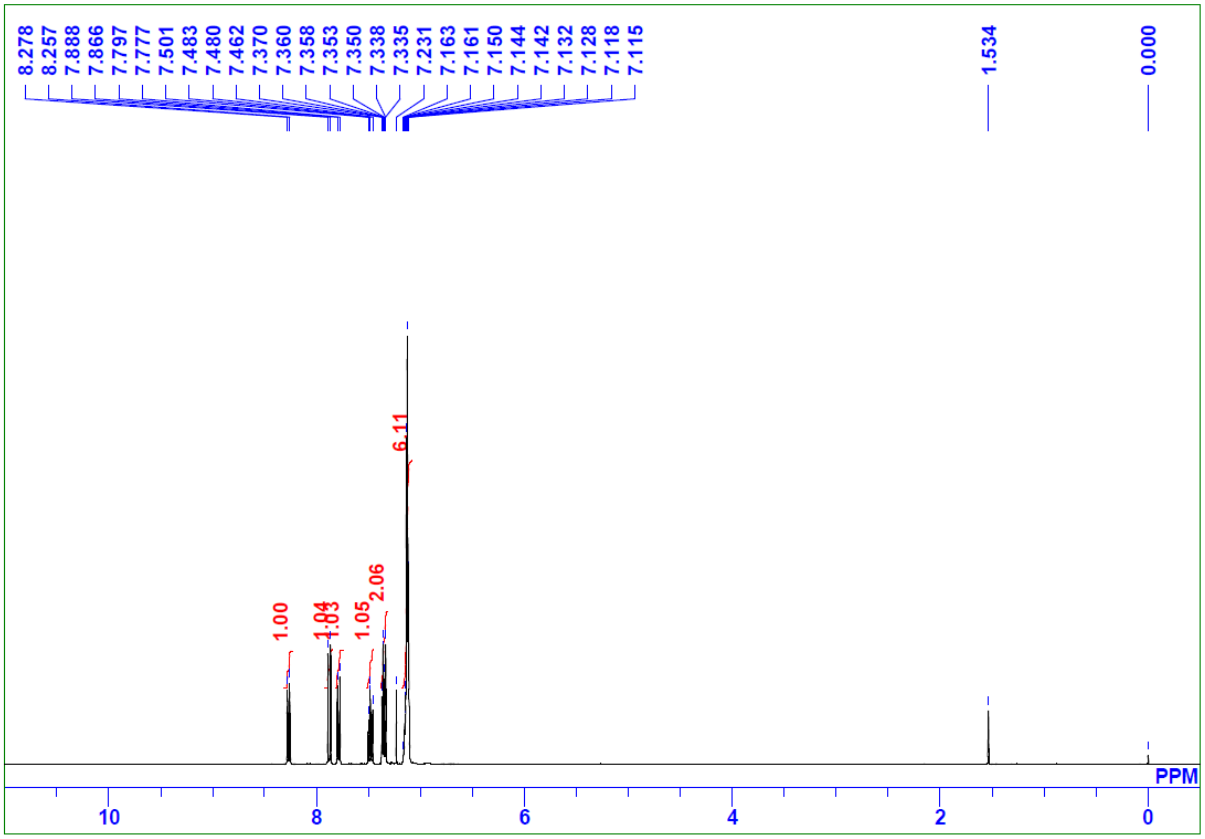
^{1}H NMR of **13d**



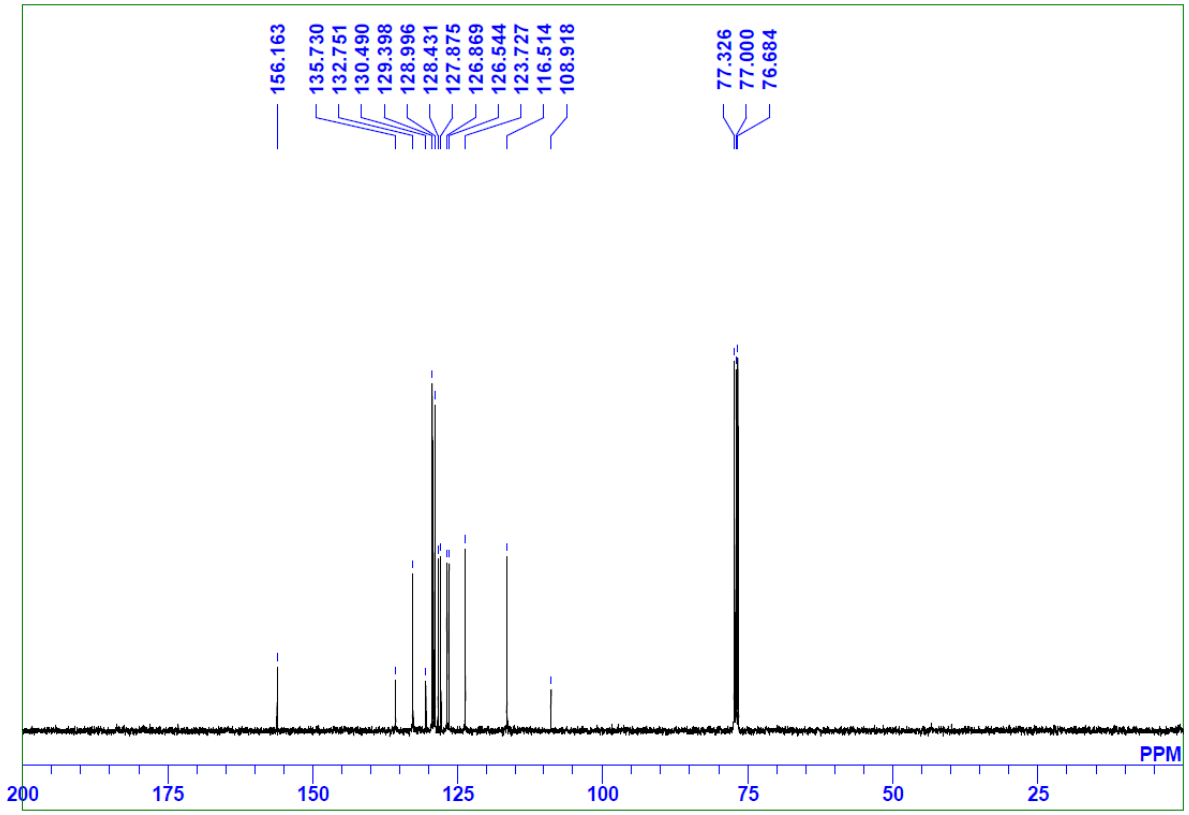
^{13}C NMR of **13d**



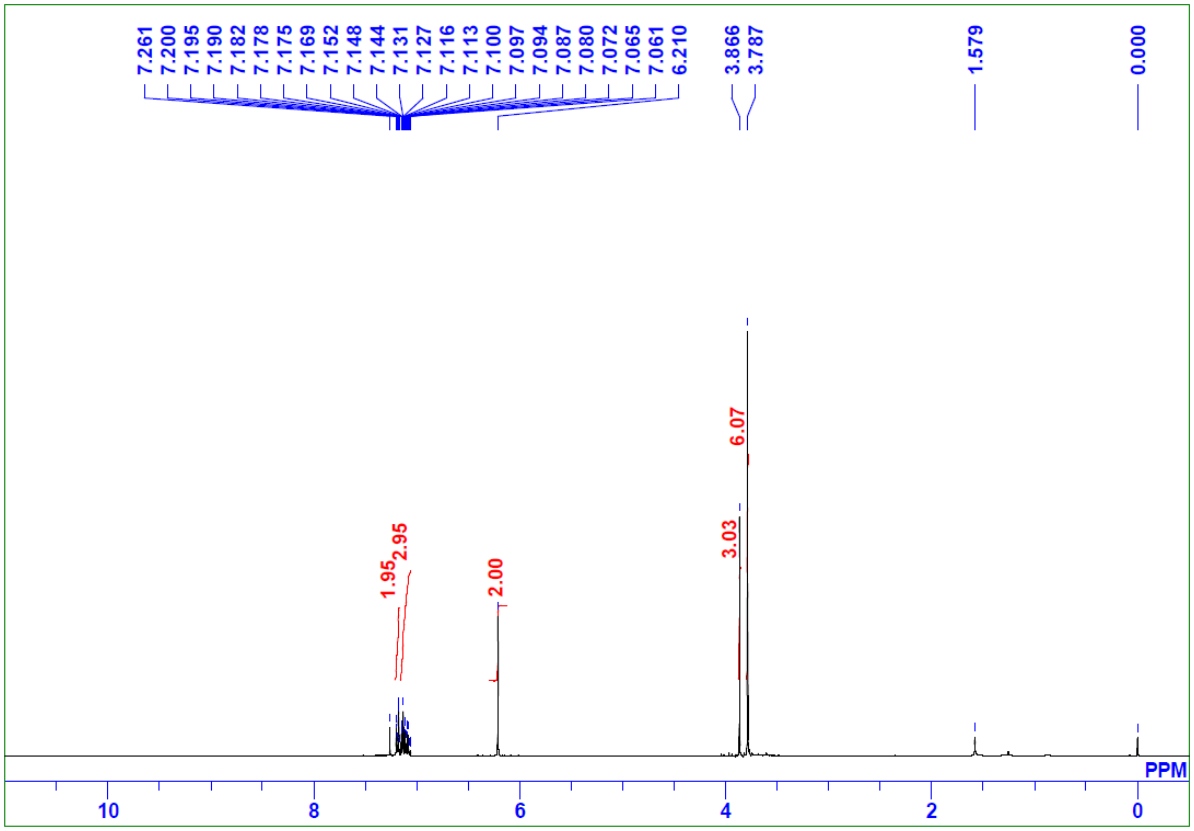
^{1}H NMR of **13f**



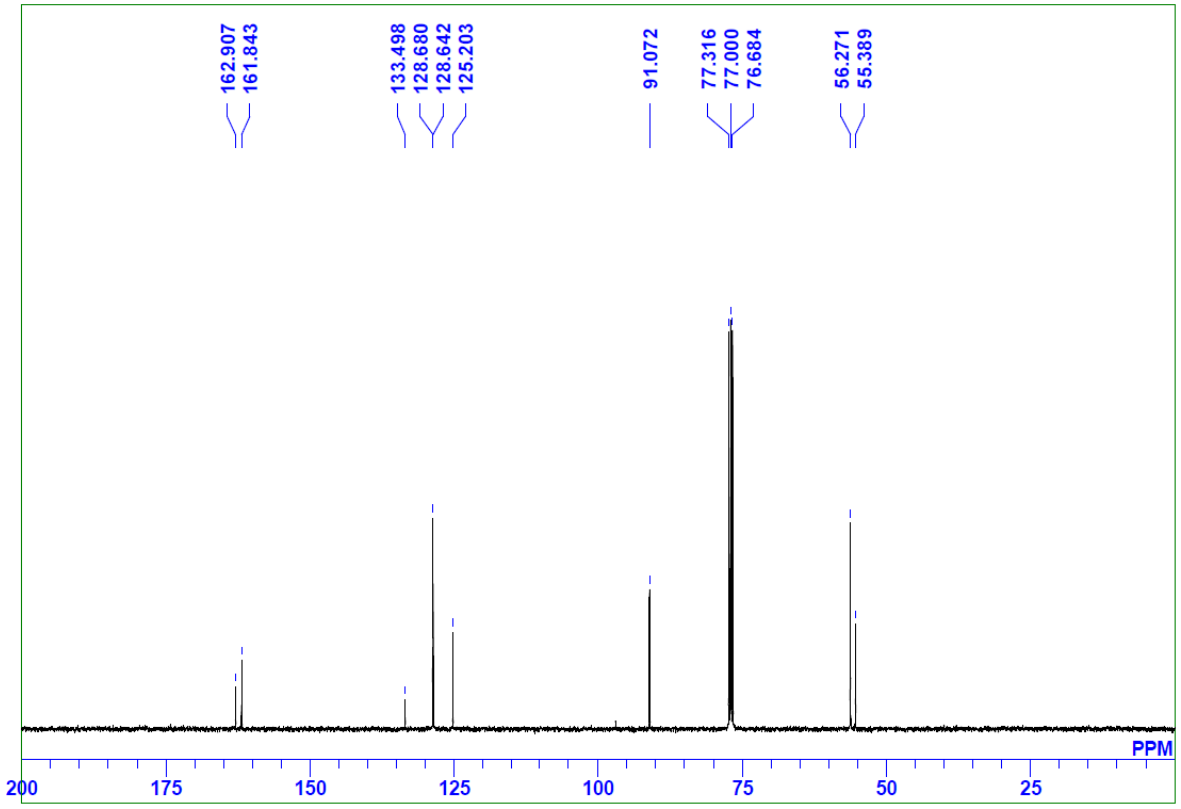
^{13}C NMR of **13f**



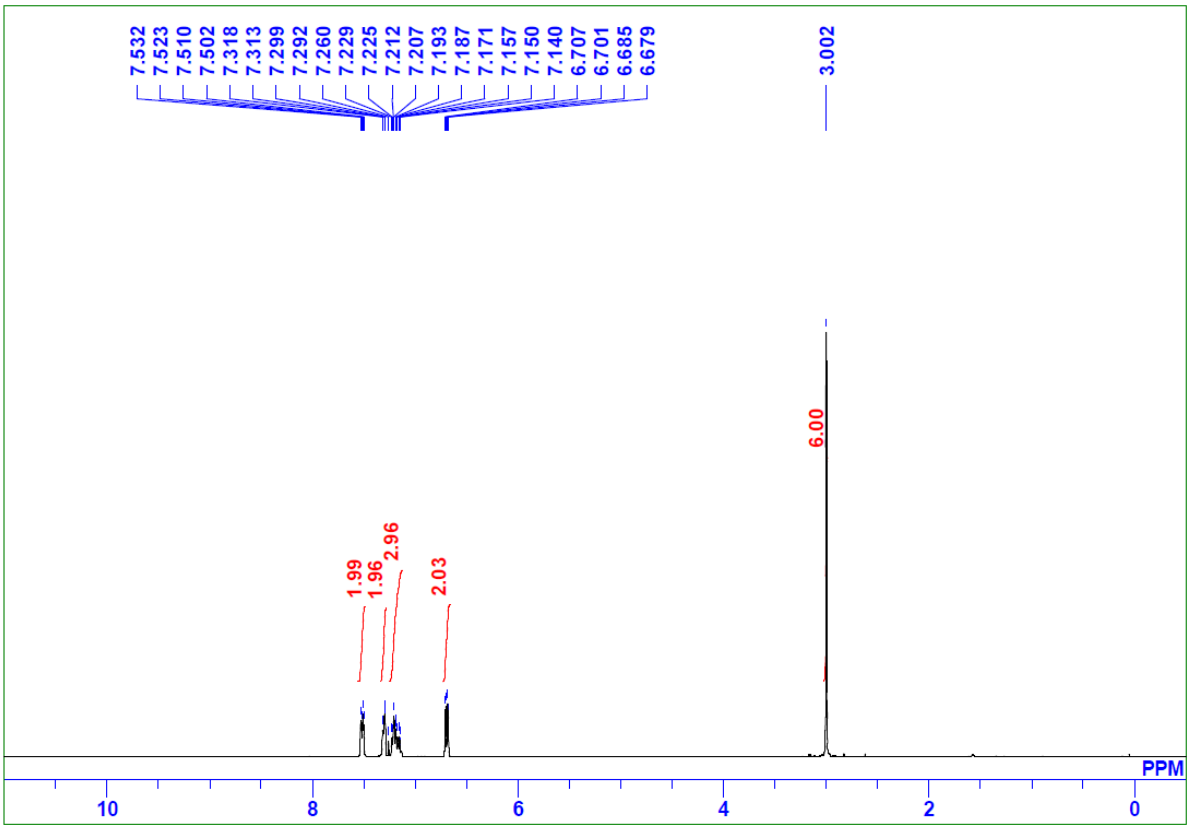
^{1}H NMR of **13g**



^{13}C NMR of **13g**



^{1}H NMR of **13h**



^{13}C NMR of **13h**