Supplementary Information for:

Gelatin as a Bioorganic Reductant, Ligand and Support for Palladium Nanoparticles. Application as a Catalyst for Ligand- and Amine-Free Sonogashira-Hagihara Reaction

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Instrumentation, Analysis and Starting Materials:

Experimental:

General: All chemicals were purchased from Merck, Fluka or acros companies and used without any further purification. NMR spectra were recorded with a Bruker Avance DPX- 250 spectrometer (^{1}H NMR 250 MHz and ^{13}C NMR 62.9 MHz) in pure deuteriated chloroform with tetramethylsilane (TMS) as the internal standard. UV spectra (PerkinElmer, Lambda 25, UV/Vis spectrometer) were used to ensure the complete conversion of Pd(II) to Pd(0). Scanning electron micrographs were obtained by SEM (SEM, XL-30 FEG SEM, Philips, at 20 KV). Transmission electron microscope, TEM (Philips CM10) was also used to obtain TEM images. X-ray diffraction (XRD, D8, Advance, Bruker, axs) spectra were used to characterize the heterogeneous catalyst. Atomic force microscope, AFM (DME, Dual Scope^{TM} DS 95-200-E) was also used to obtain AFM images. Palladium content was measured by ICP analyzer (Varian, Vista-pro) and atomic absorption analysis.

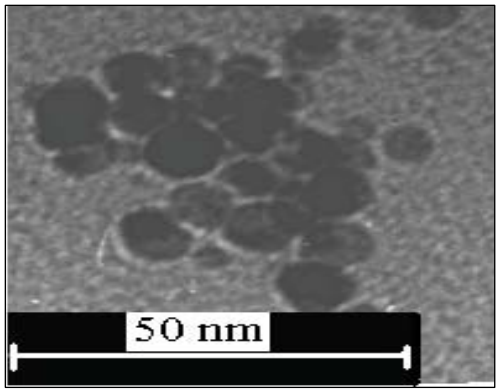
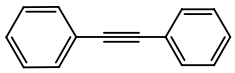


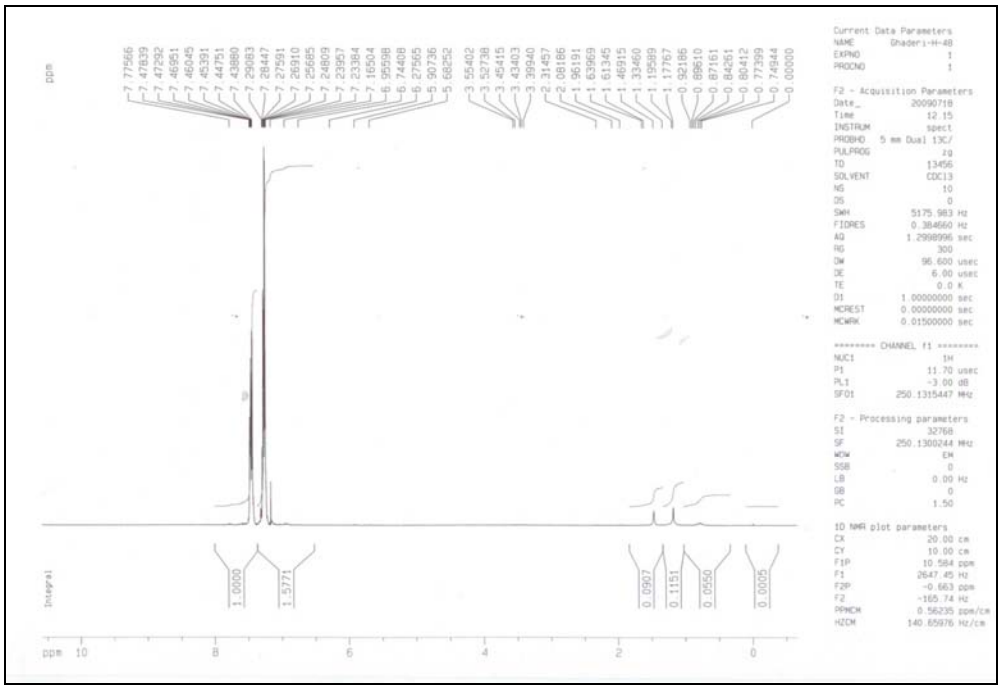
Figure S1. Close view of the TEM picture of the freshly prepared palladium nanoparticles supported on gelatin

Spectral data:

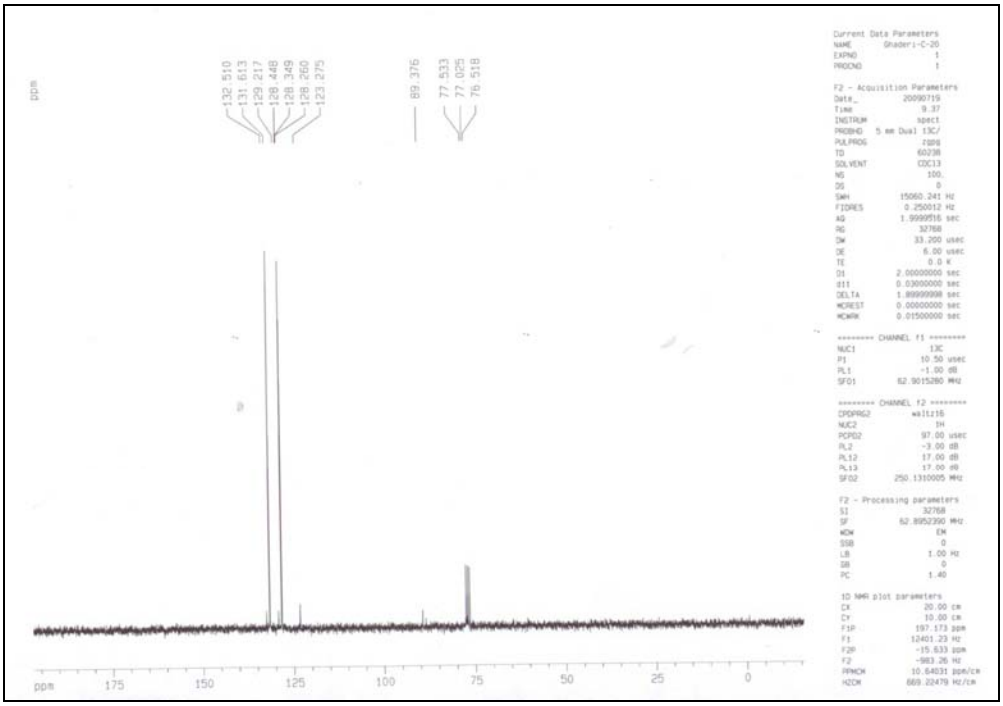
(3a)[1]



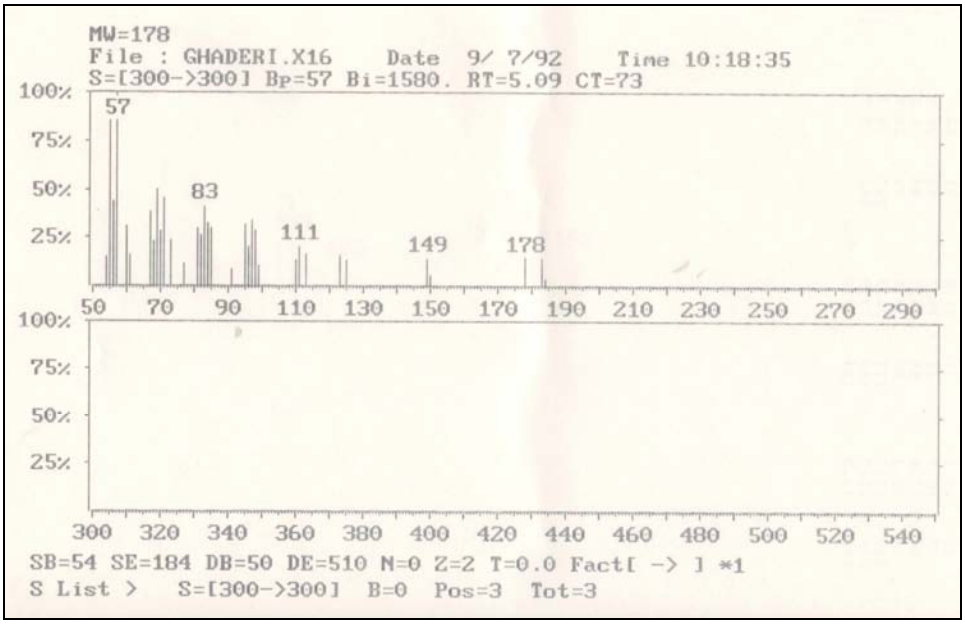
White solid (mp: 58-59 ºC); ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 7.35 (m, 6 H), 7.54 (m, 4 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm): 89.38, 123.27, 128.35, 129.21, 131.61; MS (m/e)= 178 [M^+]; Elemental Analysis: Calcd. C: 94.33, H: 5.67, Found. C: 94.01, H: 5.66.



^{1}H NMR of 3a

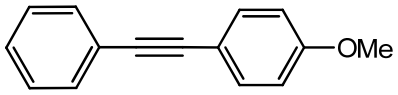


^{13}C NMR of 3a

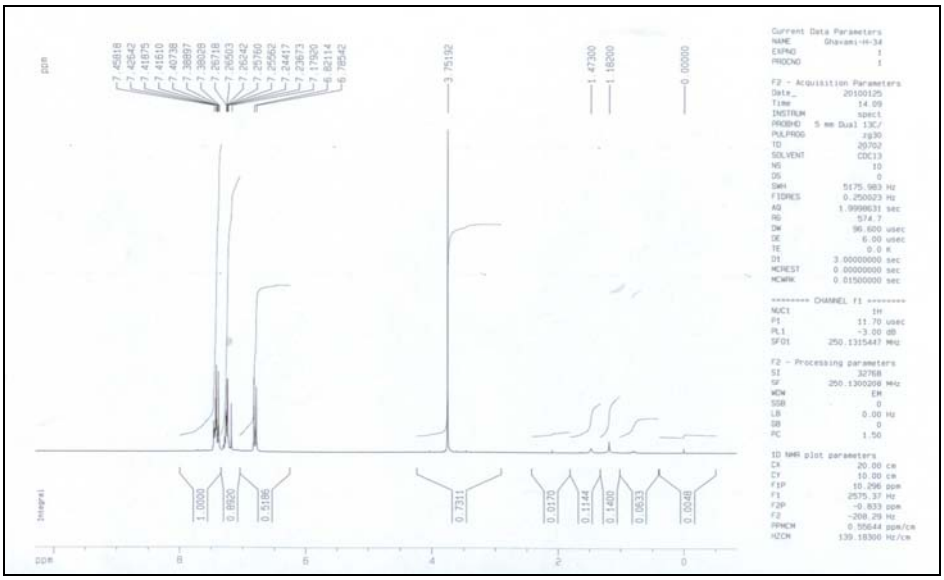


Mass spectrum of 3a

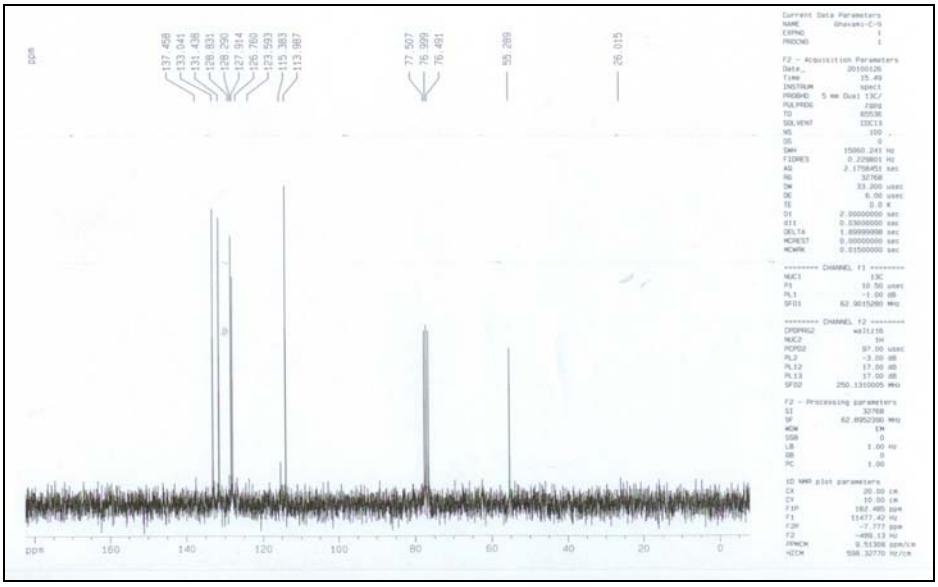
(**3b**)[1]



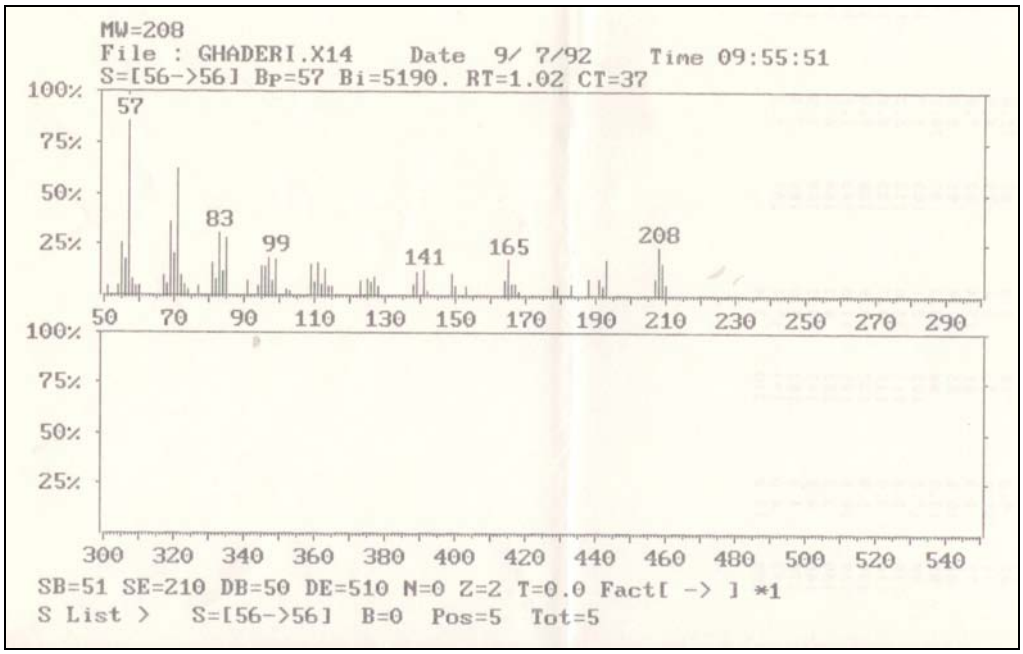
Yellow solid (mp: 55-56 ºC); ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 3.75 (s, 3 H), 6.80 (d, 2 H, J= 10 Hz), 7.18-7.46 (m, 7 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm): 55.29, 89.22, 98.31, 113.99, 115.38, 123.59, 126.76, 127.91, 128.29, 128.83, 131.44, 133.04, 137.46; MS (m/e)= 208 [M^+]; Elemental Analysis: Calcd. C: 86.50, H: 5.82, Found. C: 86.31, H: 5.80.



^{1}H NMR of 3b

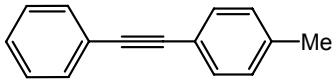


^{13}C NMR of 3b

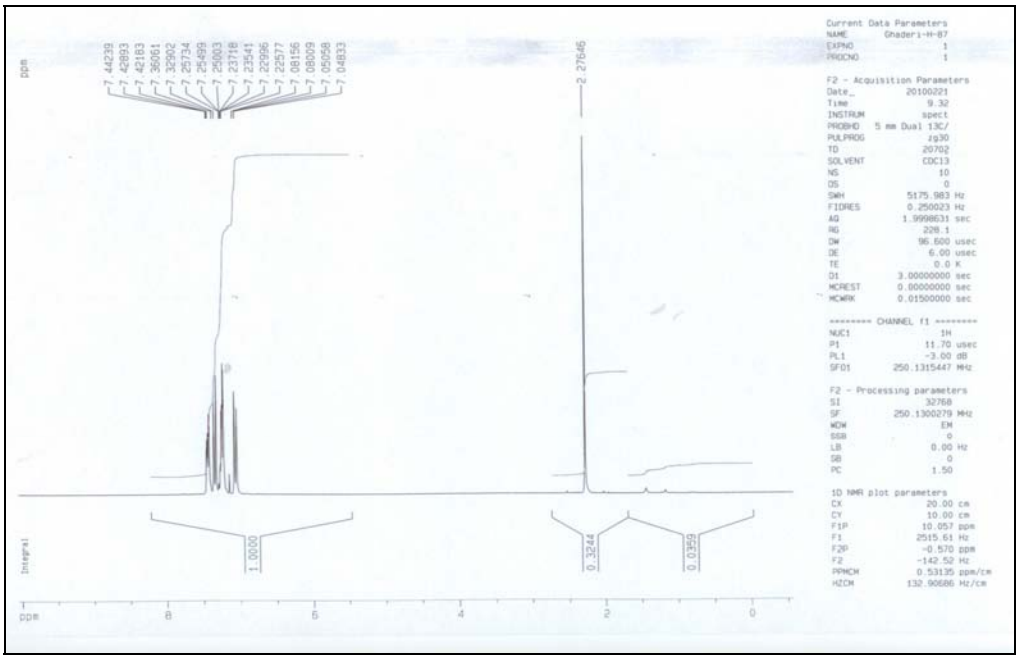


Mass spectrum of 3b

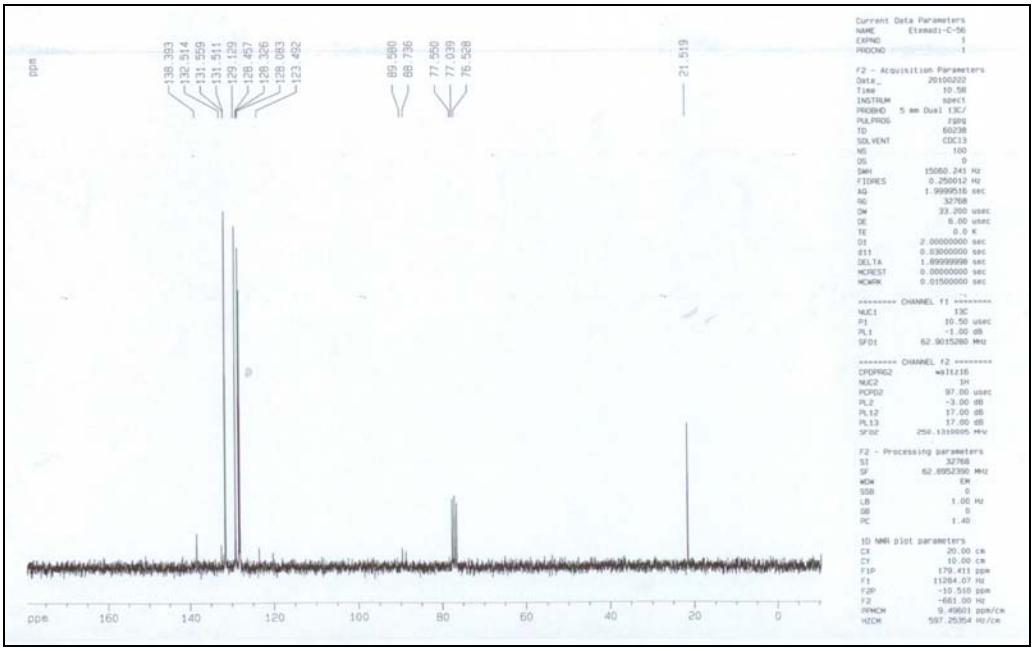
(**3c**)[1]



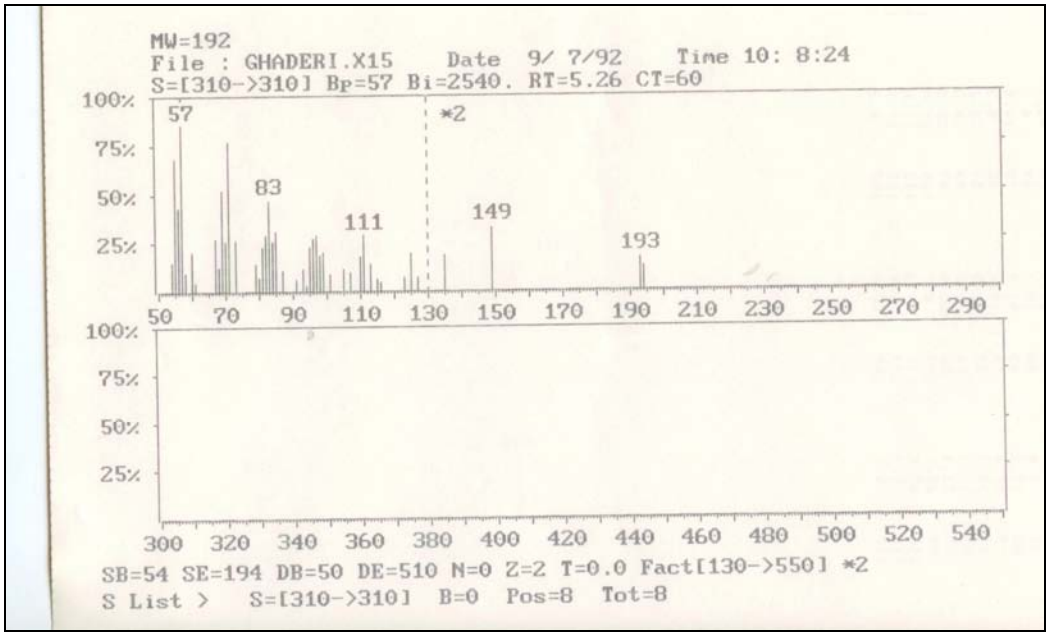
Yellow solid (mp: 49-50 ºC); ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 2.28 (s, 3 H), 7.07 (dd, 2 H, J= 7.84 Hz, J´= 0.56 Hz), 7.22-7.44 (m, 7 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm): 21.52, 88.74, 89.58, 123.49, 128.08, 128.33, 128.46, 129.13, 131.51, 131.56, 132.51, 138.39; MS (m/e)= 192 [M^+]; Elemental Analysis: Calcd. C: 93.70, H: 6.30, Found. C: 93.43, H: 6.28.



^{1}H NMR of 3c

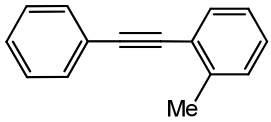


^{13}C NMR of 3c

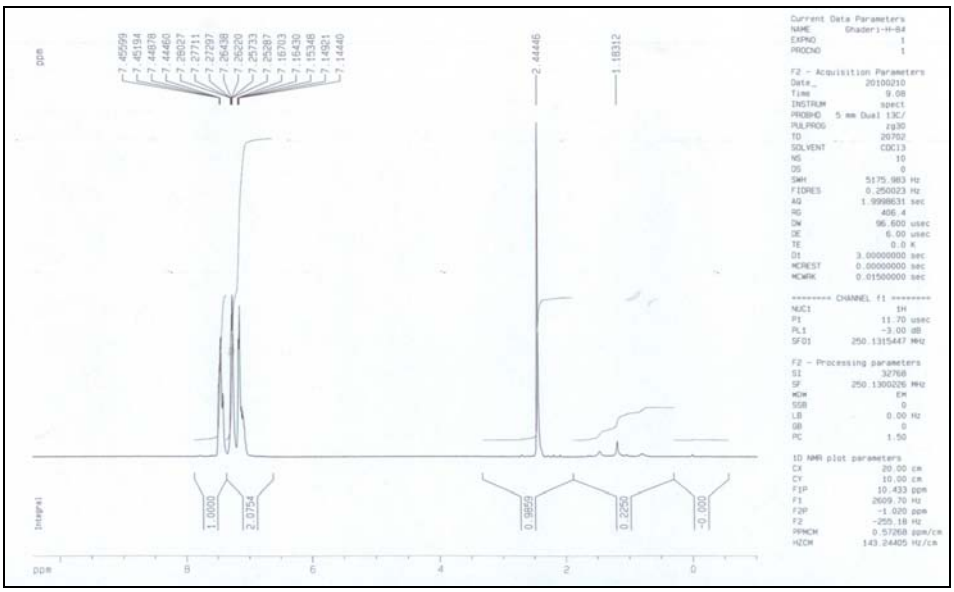


Mass spectrum of 3c

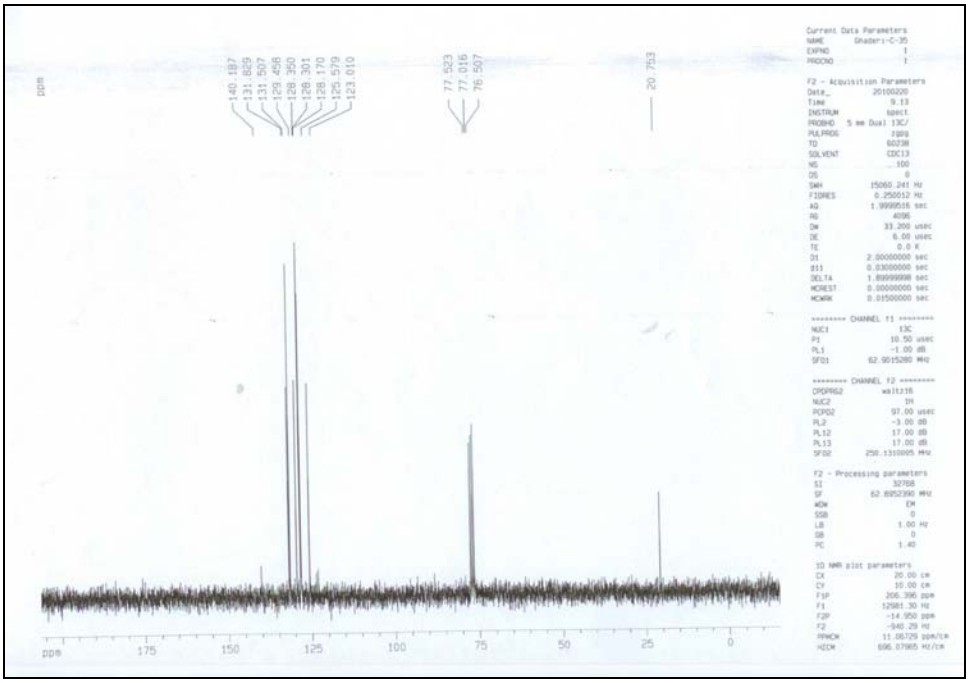
(**3d**)[1]



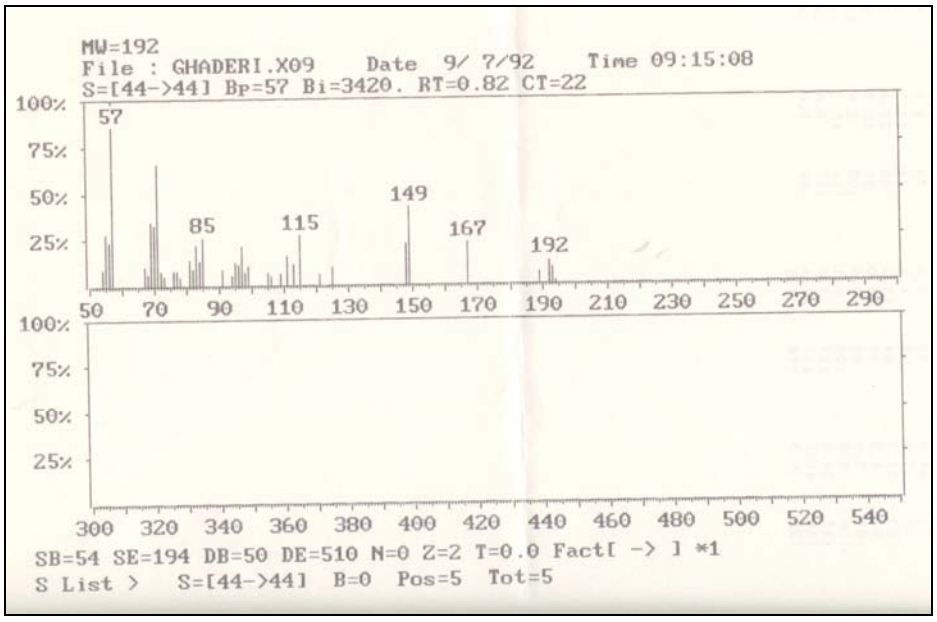
Viscose pale yellow oil; ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 2.44 (s, 3 H), 7.14-7.46 (m, 9 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm): 20.75, 86.01, 94.25, 123.01, 125.58, 128.17, 128.30, 128.35, 129.46, 131.51, 131.83, 140.19; MS (m/e)= 192 [M^+]; Elemental Analysis: Calcd. C: 93.70, H: 6.30, Found. C: 94.03, H: 6.15.



^{1}H NMR of 3d

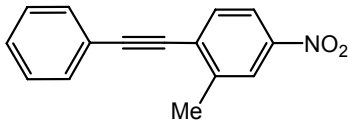


^{13}C NMR of 3d

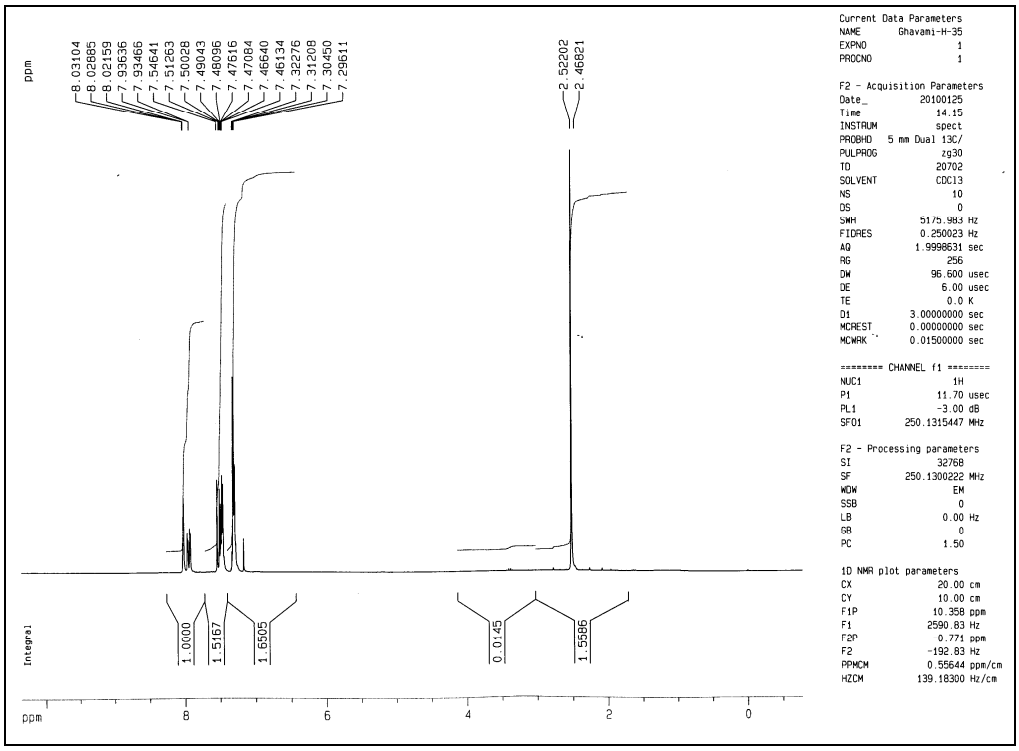


Mass spectrum of 3d

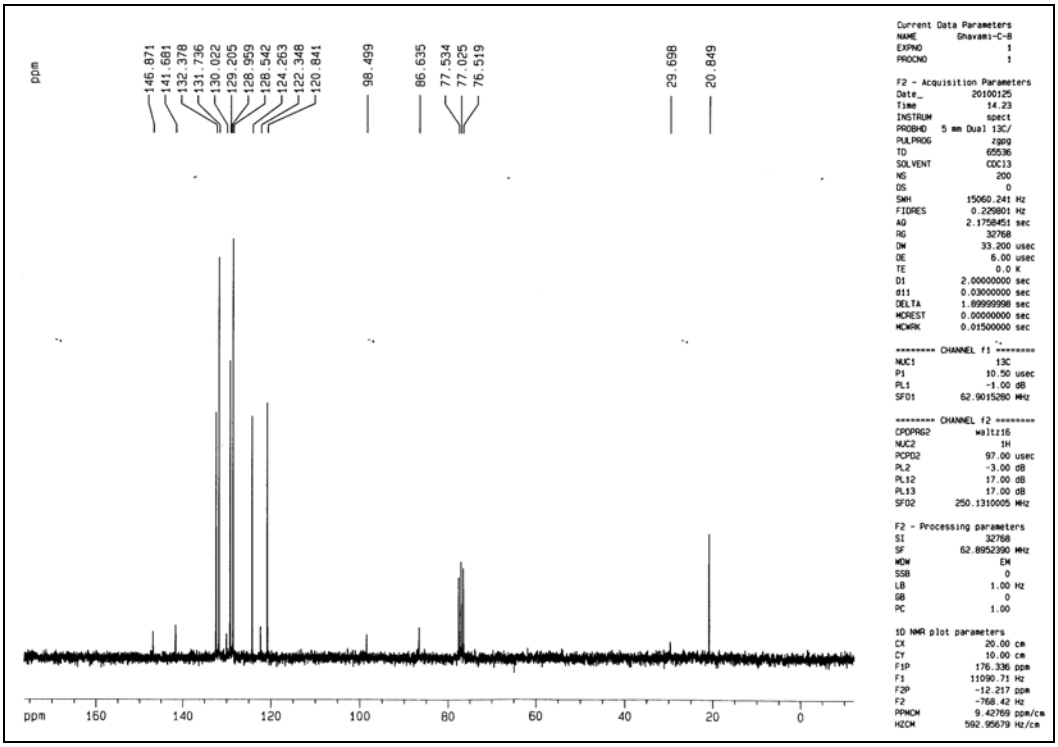
(**3e**)



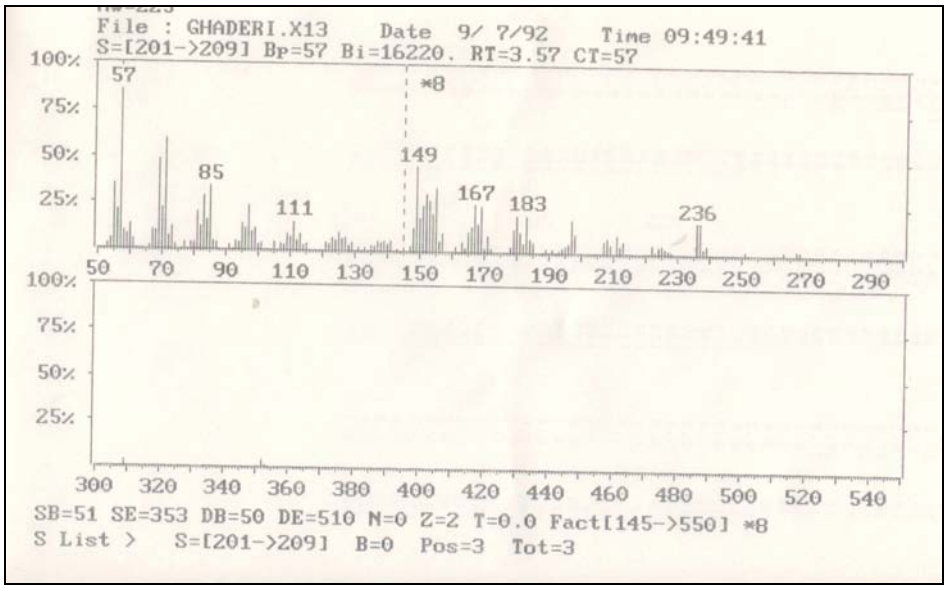
Yellow solid (mp: 101-102 ºC); ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 2.52 (s, 3 H), 7.30-7.32 (m, 3 H), 7.46-7.55 (m, 3 H), 7.93-8.03 (m, 2 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm): 20.85, 86.64, 98.50, 120.84, 122.35, 124.26, 128.54, 128.95, 130.02, 131.74, 132.38, 141.68, 146.87; MS (m/e)= 237 [M^+]; Elemental Analysis: Calcd. C: 75.93, H: 4.68, N: 5.90, Found. C: 75.95, H: 4.71, N: 5.89.



^{1}H NMR of 3e

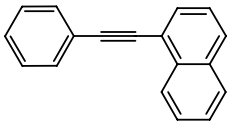


^{13}C NMR of 3e

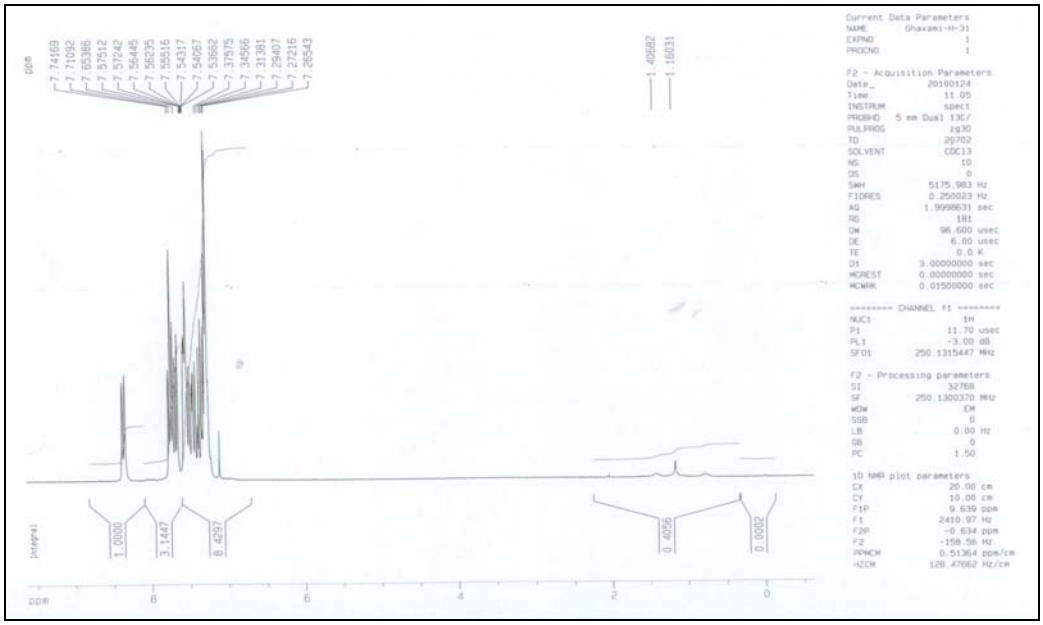


Mass spectrum of 3e

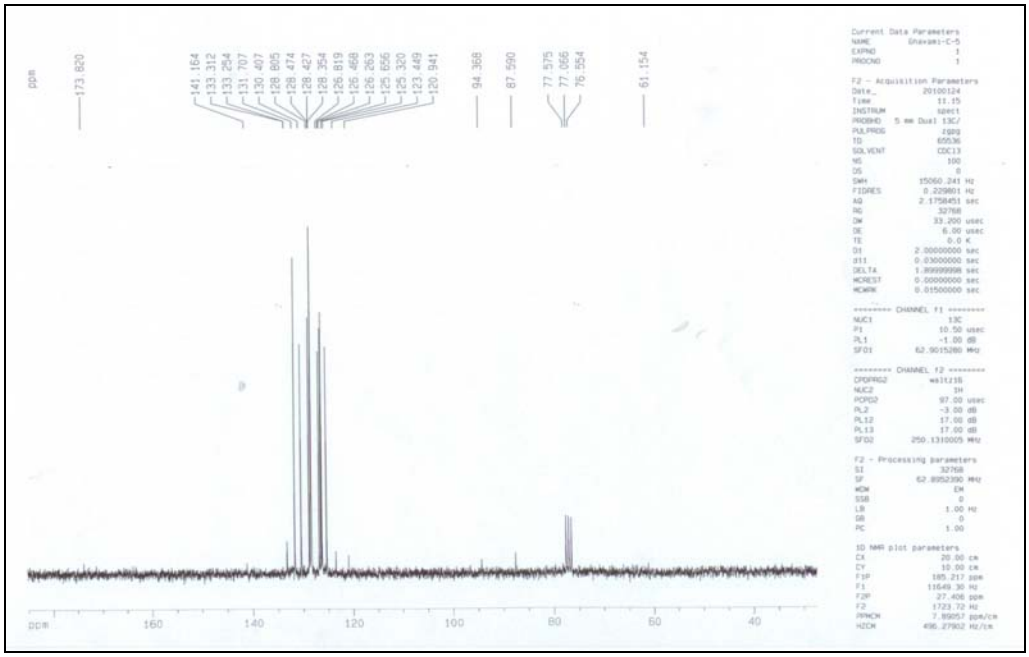
(3g)[1]



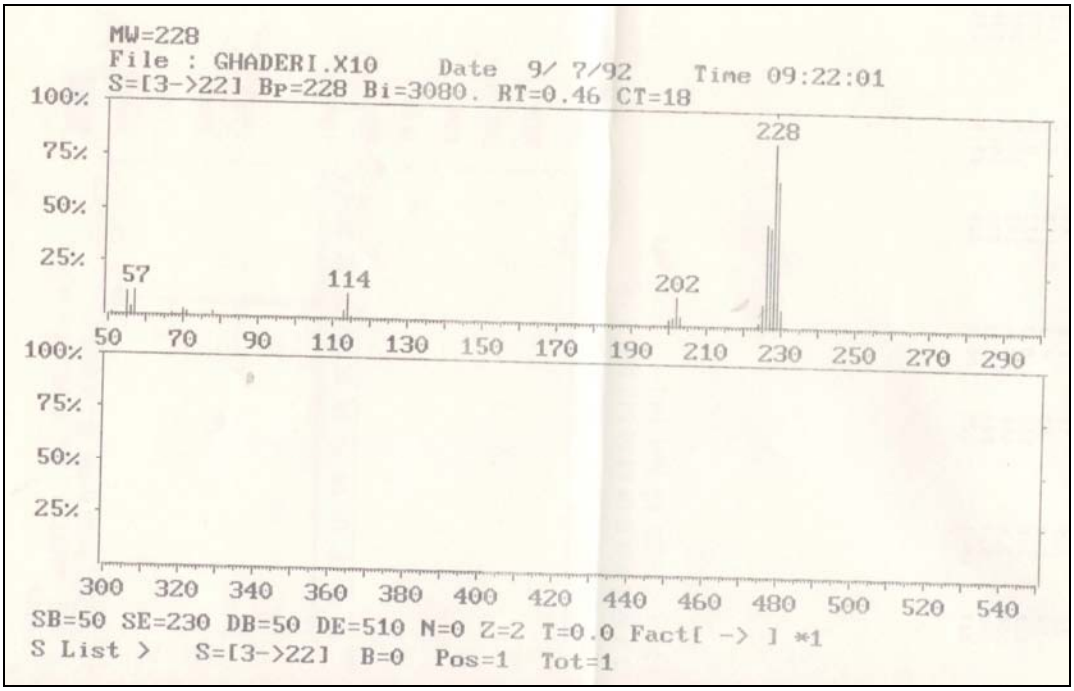
Viscose yellow oil; ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm):7.26-7.74 (m, 11 H), 8.36 (d, 1 H, J= 8.2 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm): 87.59, 94.37, 120.94, 123.45, 125.32, 125.66, 126.26, 126.47, 126.82, 128.35, 128.43, 128.47, 128.81, 130.41, 131.71, 133.25, 133.31, 141.16; MS (m/e)= 228 [M^+]; Elemental Analysis: Calcd. C: 94.69, H: 5.31, Found. C: 94.83, H: 5.61.



^{1}H NMR of 3g

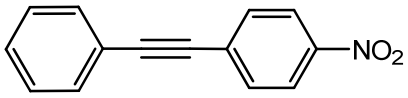


^{13}C NMR of 3g

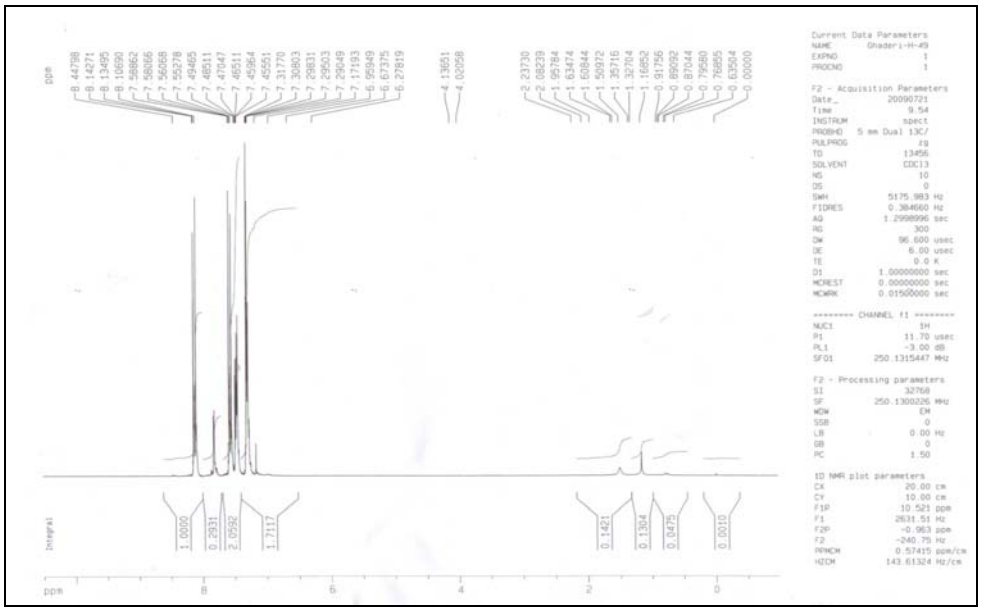


Mass spectrum of 3g

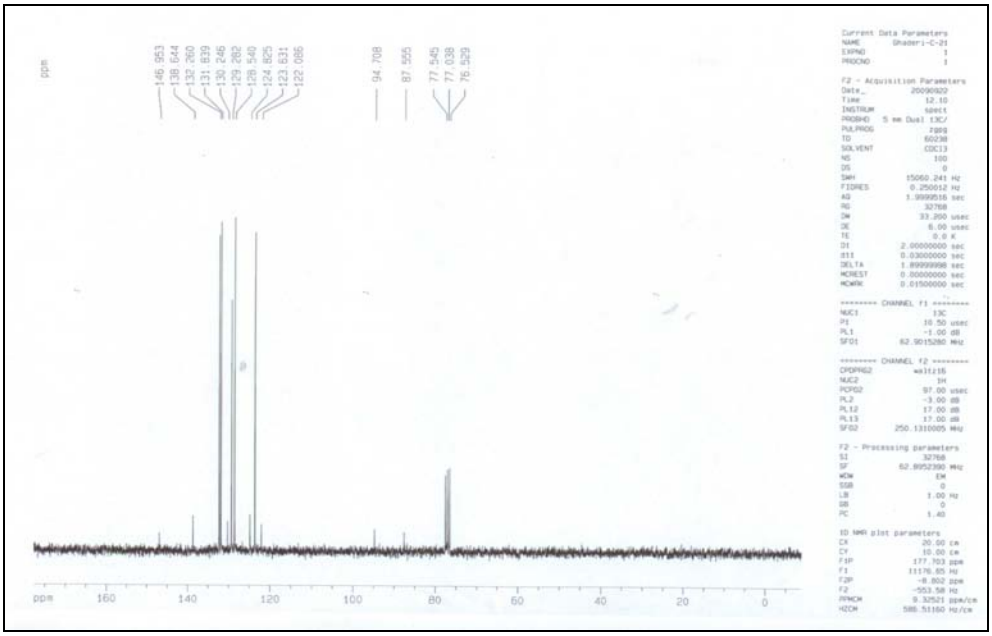
(**3h**)[1]



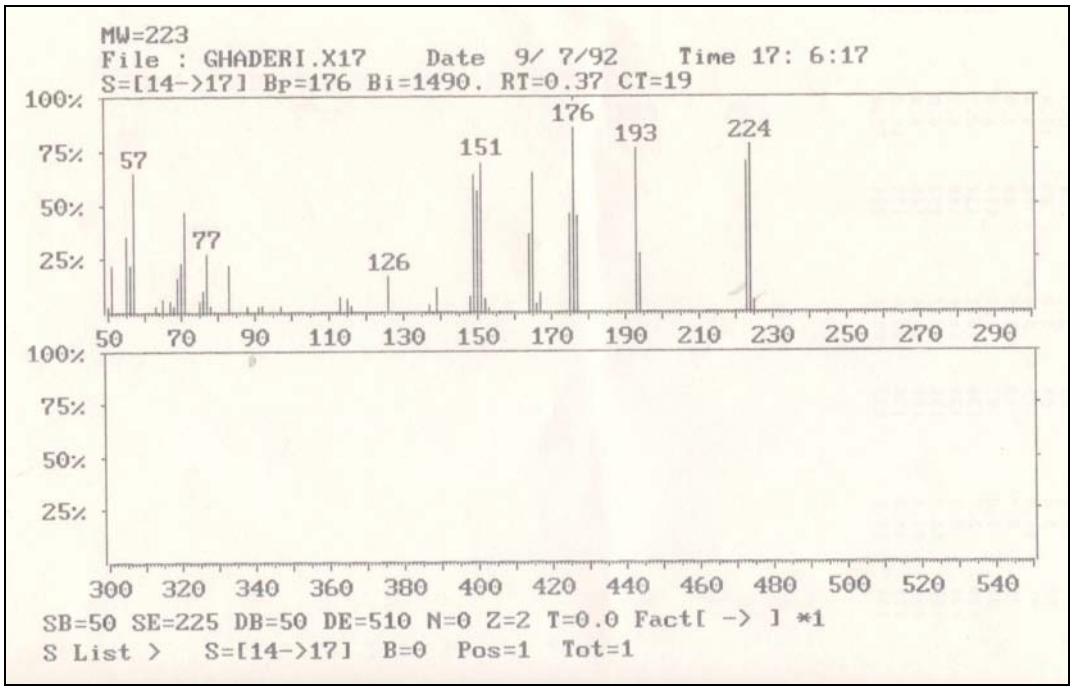
Yellow solid (mp: 121-122 ºC); ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 7.31-7.59 (m, 7 H), 8.12 (d, 2 H, J= 7.5 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm): 87.55, 94.71, 122.09, 123.63, 124.83, 128.54, 129.28, 130.25, 131.84, 132.26, 138.64, 146.95; MS (m/e)= 224 [M^+]; Elemental Analysis: Calcd. C: 75.32, H: 4.07, N: 6.27, Found. C: 75.52, H: 4.02, N: 6.03.



^{1}H NMR of 3h

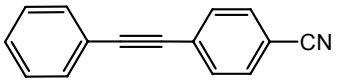


^{13}C NMR of 3h

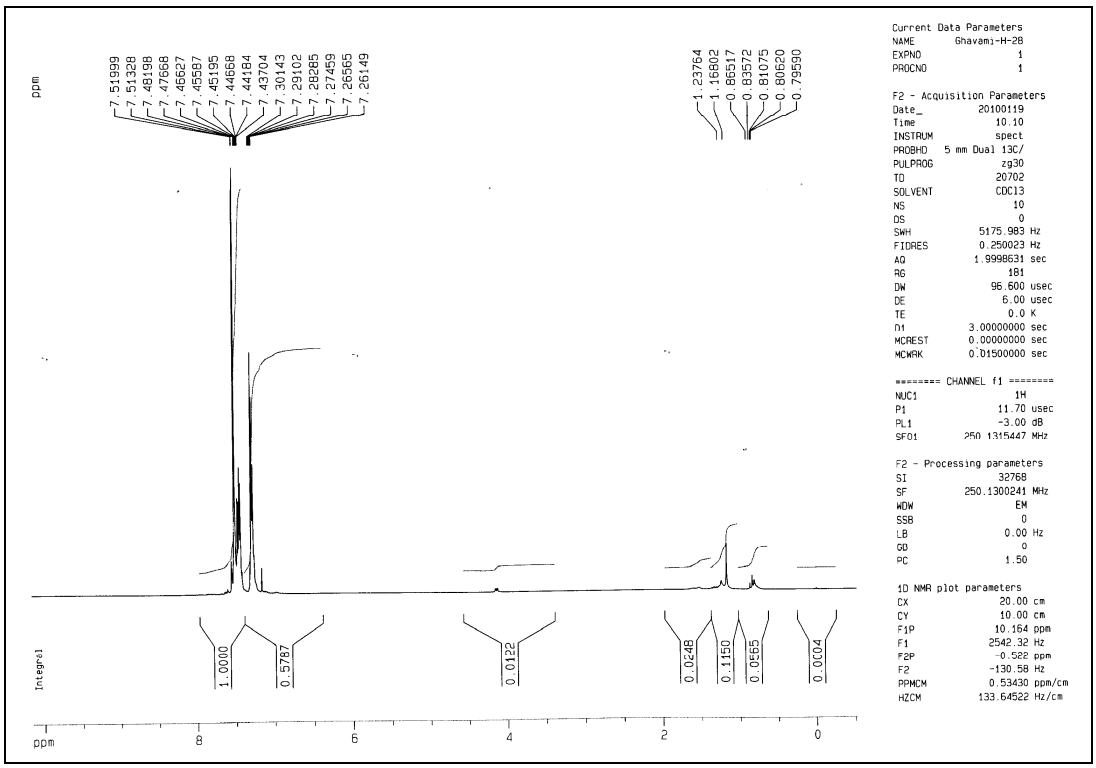


Mass spectrum of 3h

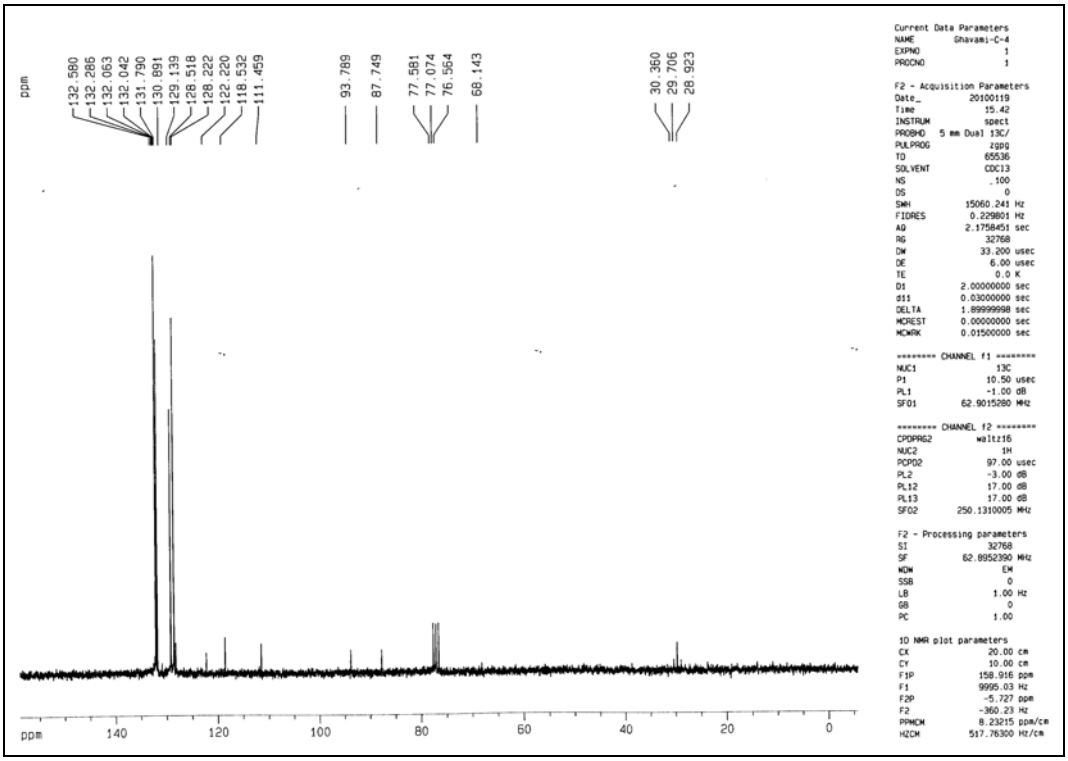
(3i)[1]



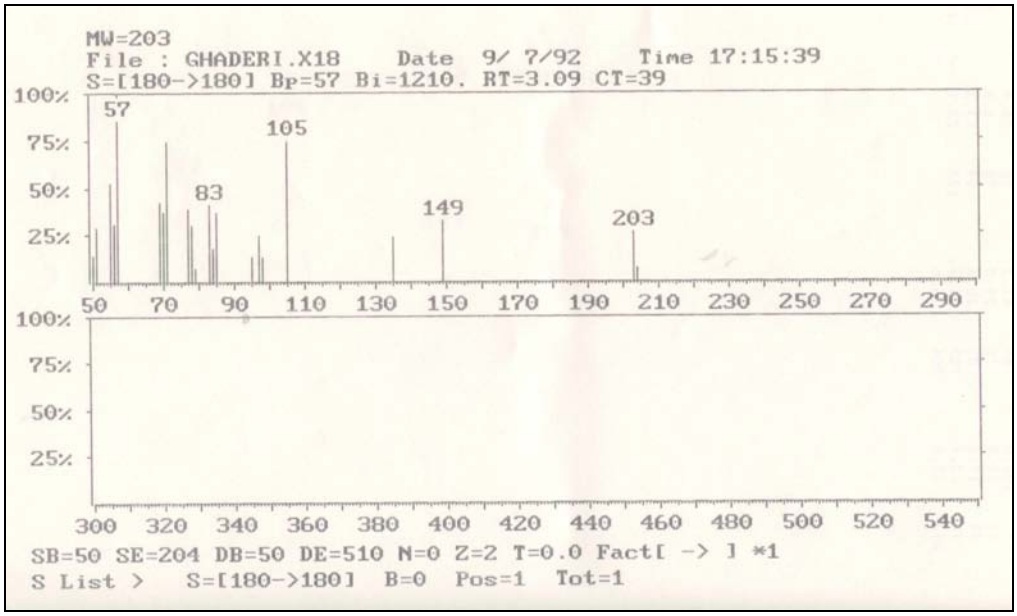
^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 7.26-7.52 (m, 9 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm):87.75, 93.79, 111.46, 118.53, 122.22, 128.52, 130.89, 131.79, 132.04, 132.29, 132.58; MS (m/e)= 203 [M^+]; Elemental Analysis: Calcd. C: 88.64, H: 4.47, N: 6.89, Found. C: 88.50, H: 4.18, N: 6.53.



^{1}H NMR of 3i

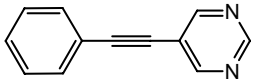


^{13}C NMR of 3i

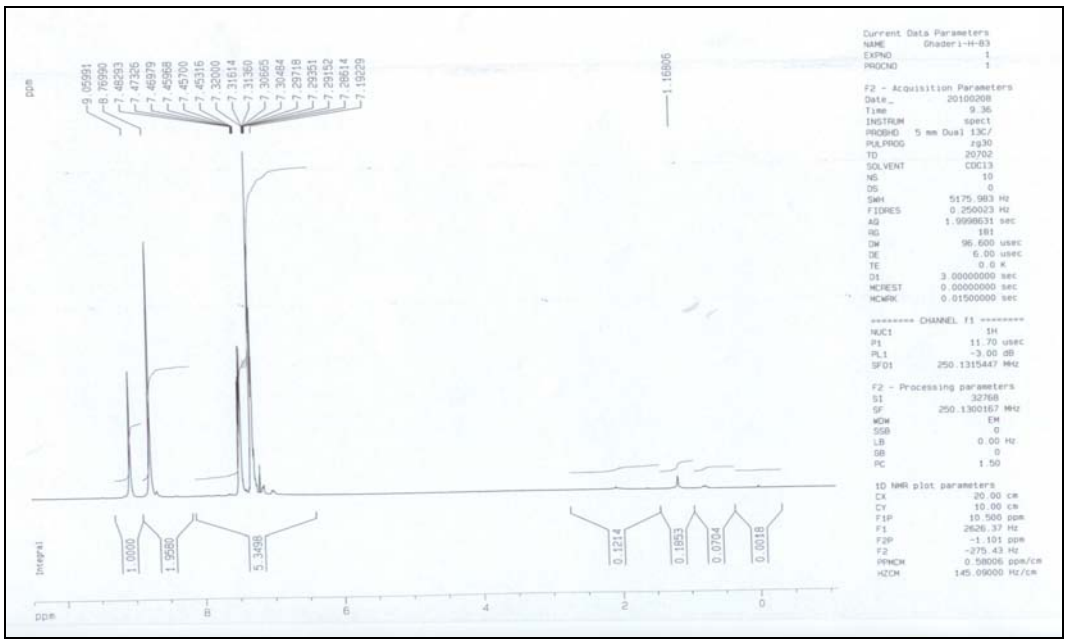


Mass spectrum of 3i

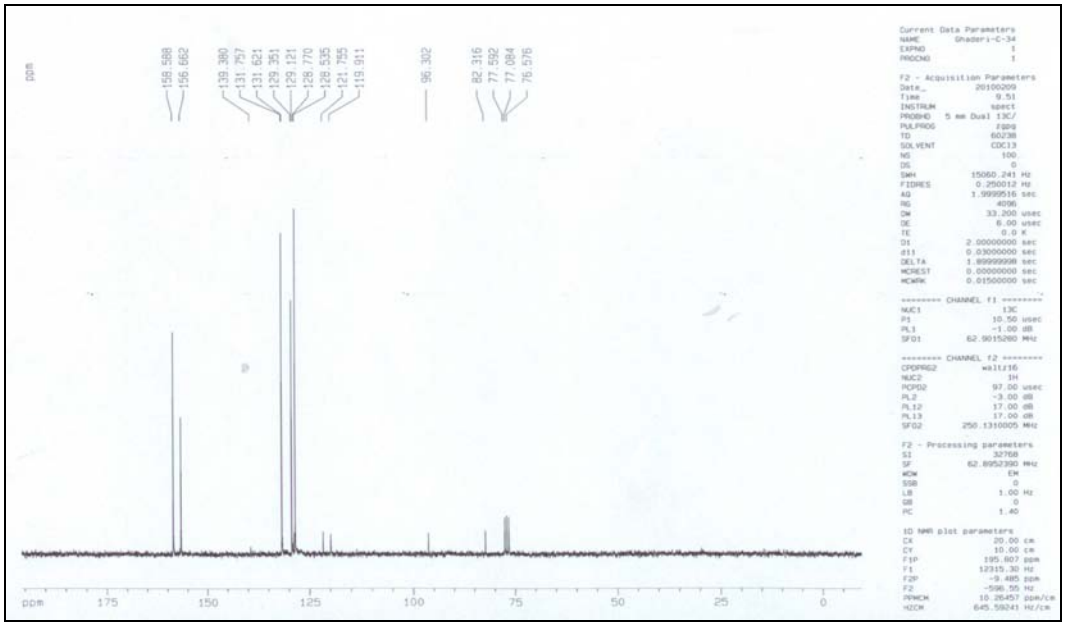
(**3j**)[2]



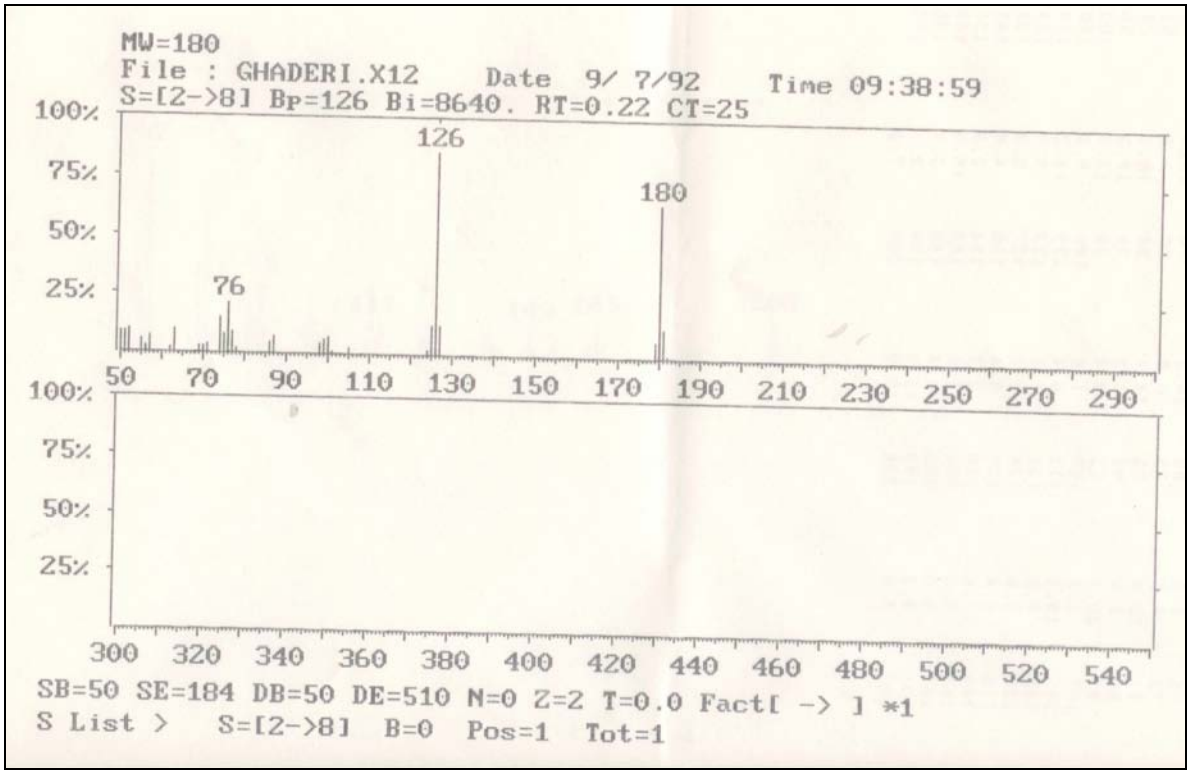
Dark yellow oil; ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 7.29-7.32 (m, 3 H), 7.45-7.48 (m, 2 H), 8.77 (s, 2 H), 9.06 (s, 1 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm): 82.32, 96.30, 119.91, 121.75, 129.12, 131.76, 139.38, 156.66, 158.59; MS (m/e)= 180 [M^+]; Elemental Analysis: Calcd. C: 79.98, H: 4.48, N: 15.54, Found. C: 79.99, H: 4.77, N: 15.54.



^{1}H NMR of 3j

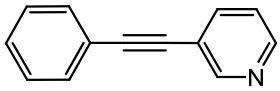


^{13}C NMR of 3j

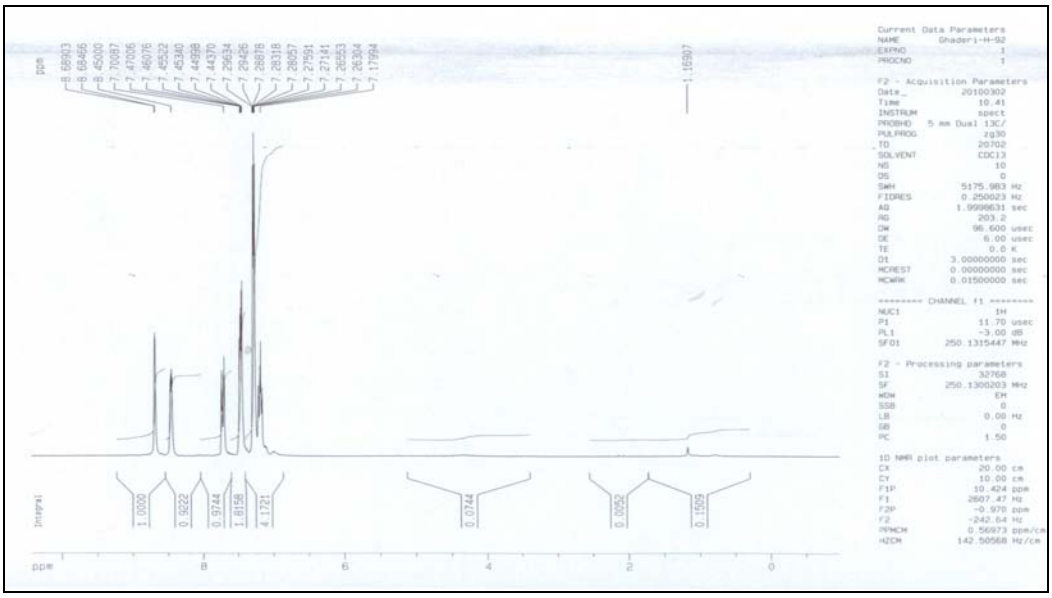


Mass spectrum of 3j

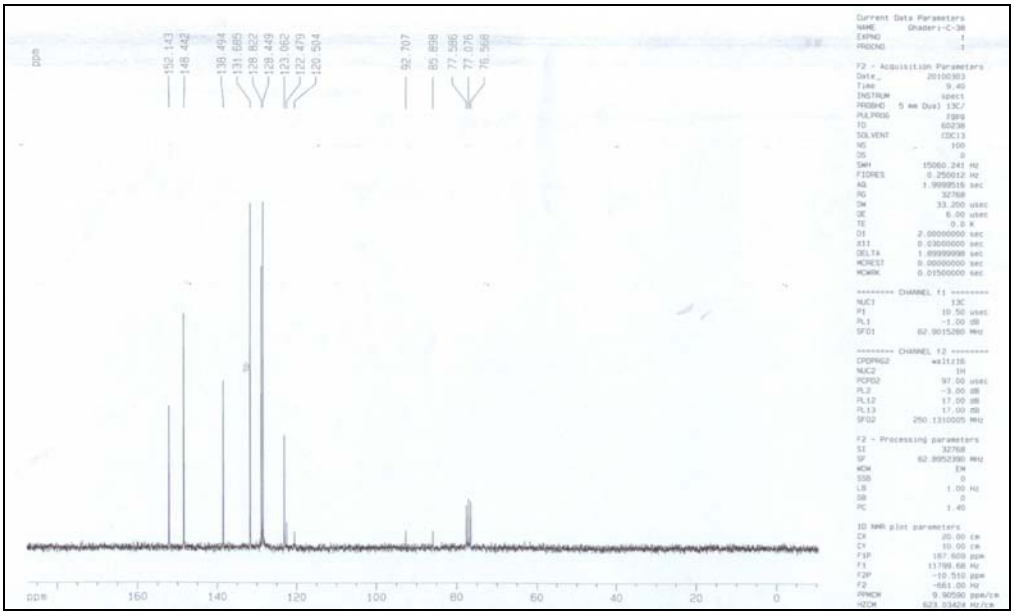
(3k)[3]



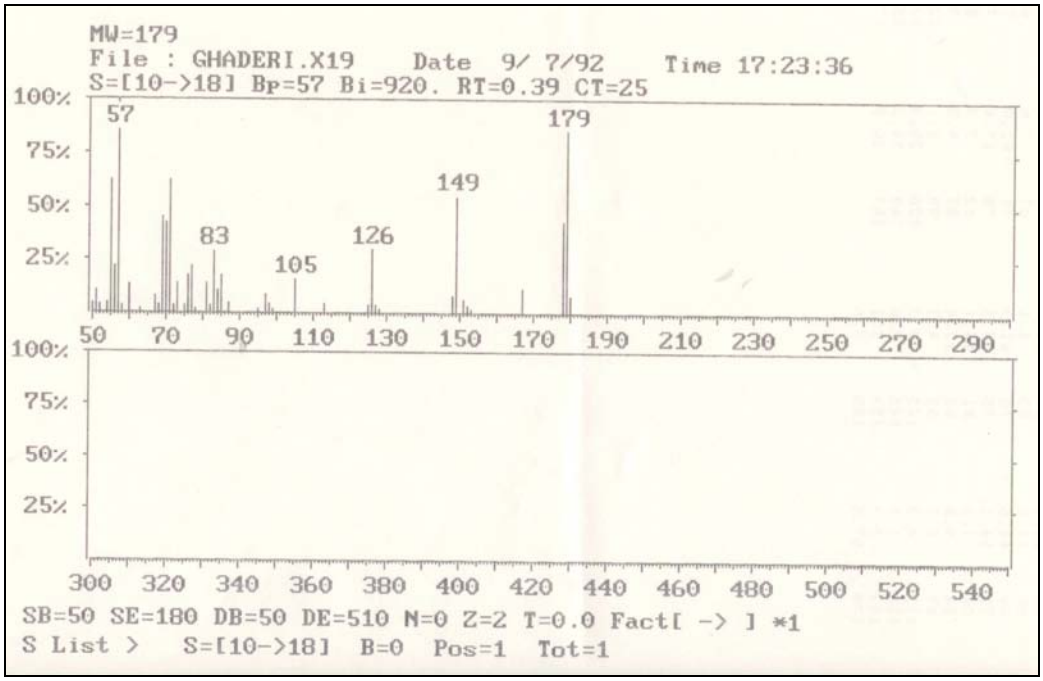
^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 7.29 (m, 4 H), 7.45 (m, 2 H), 7.70 (m, 2H), 8.45 (m, 2 H), 8.68 (s, 1 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm): 85.90, 92.71, 120.50, 122.48, 123.06, 128.45, 128.82, 131.68, 138.49, 148.44, 152.14; MS (m/e)= 179 [M^+]; Elemental Analysis: Calcd. C: 87.12, H: 5.07, N: 7.81, Found. C: 87.47, H: 4.89, N: 7.73.



^{1}H NMR of 3k

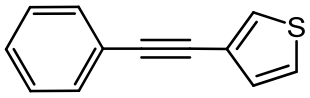


^{13}C NMR of 3k

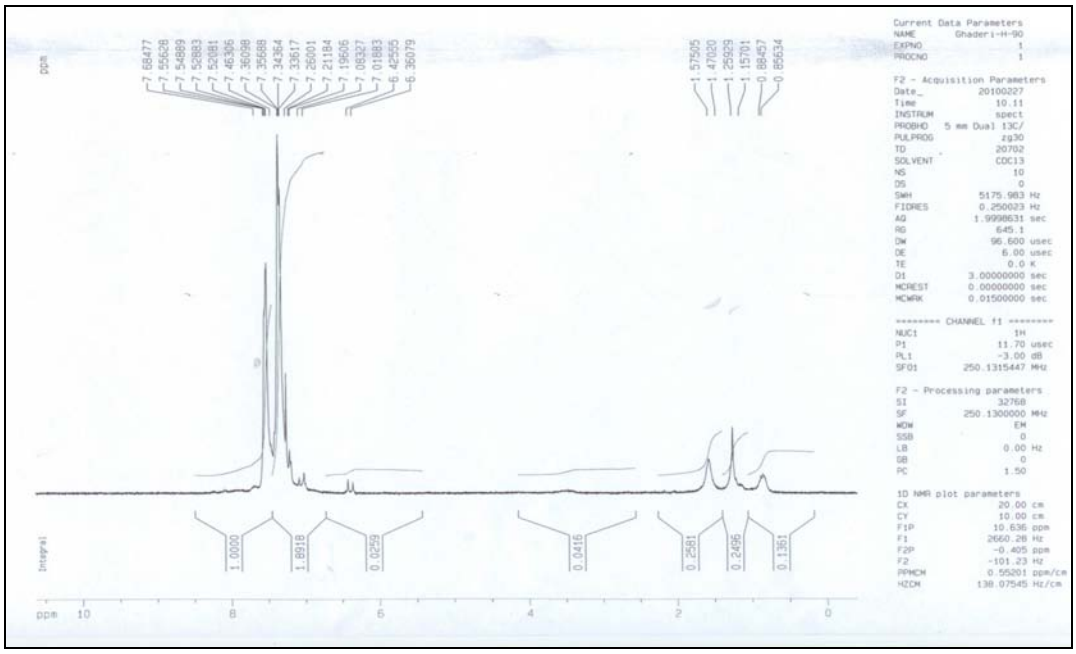


Mass spectrum of 3k

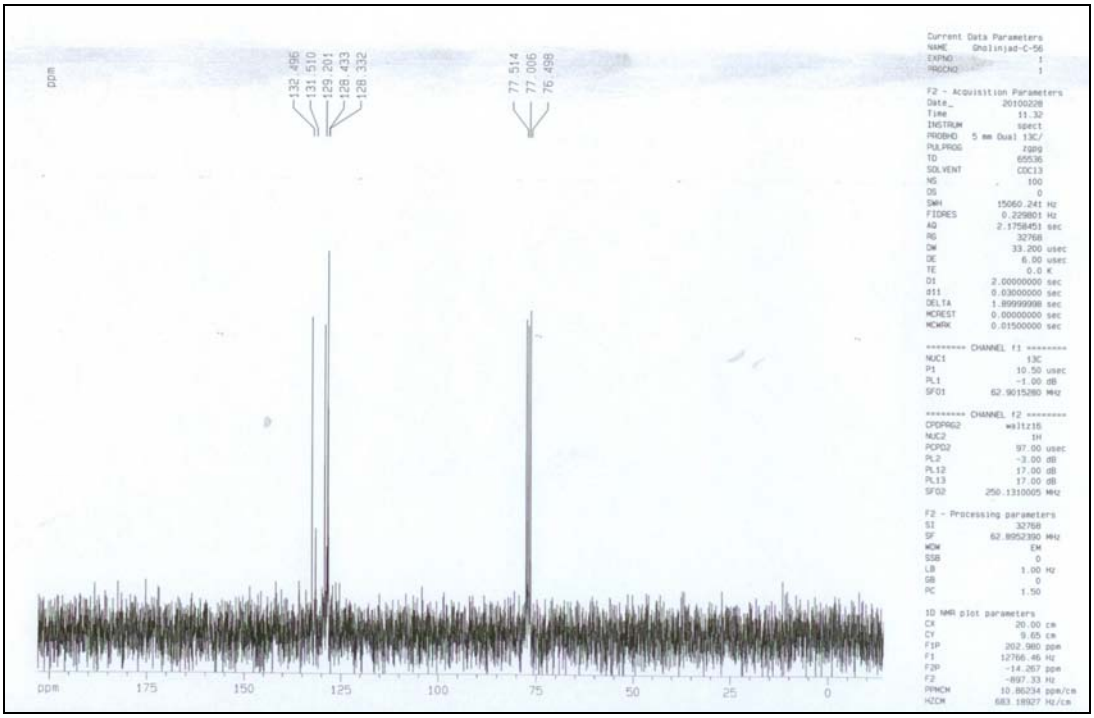
(3l)[3]



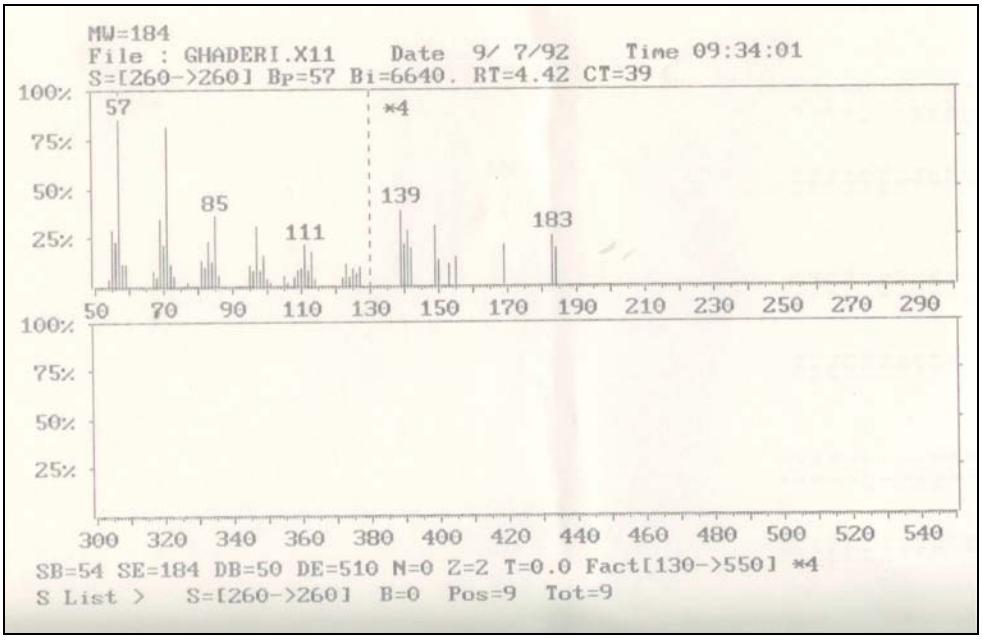
Viscose yellow oil; ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 7.01-7.68 (m, 8 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm): 87.30, 94.51, 128.33, 128.43, 129.20, 131.51, 132.50; MS (m/e)= 184 [M^+]; Elemental Analysis: Calcd. C: 78.22, H: 4.39, Found. C: 78.43, H: 4.08.



^{1}H NMR of 3l

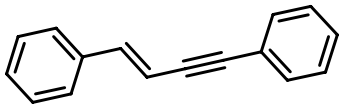


^{13}C NMR of 3l

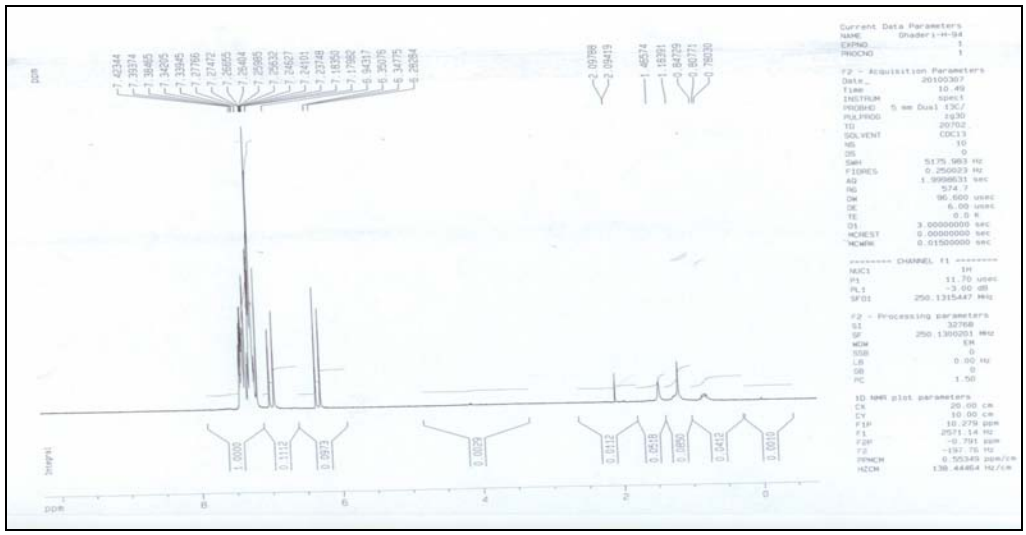


Mass spectrum of 3l

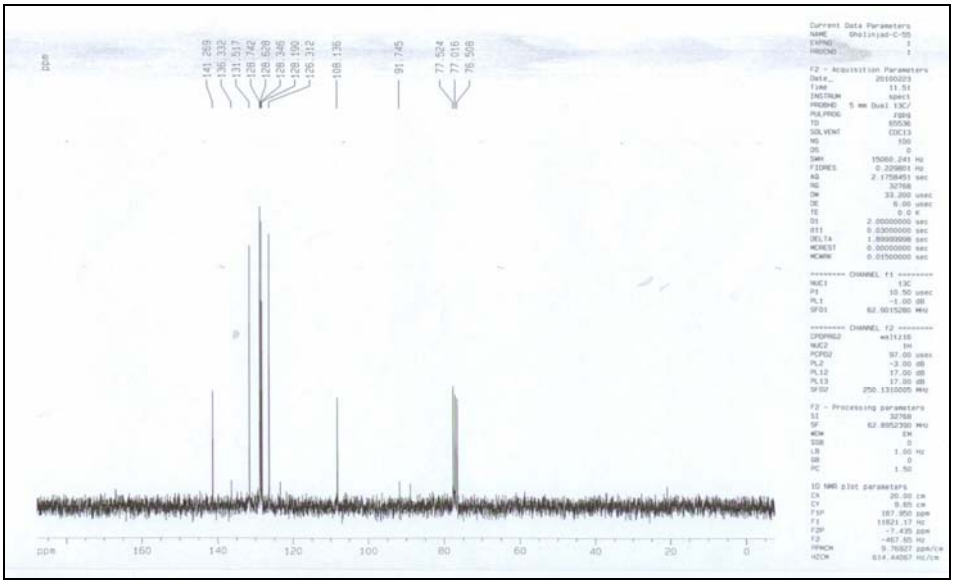
(3m)[4]



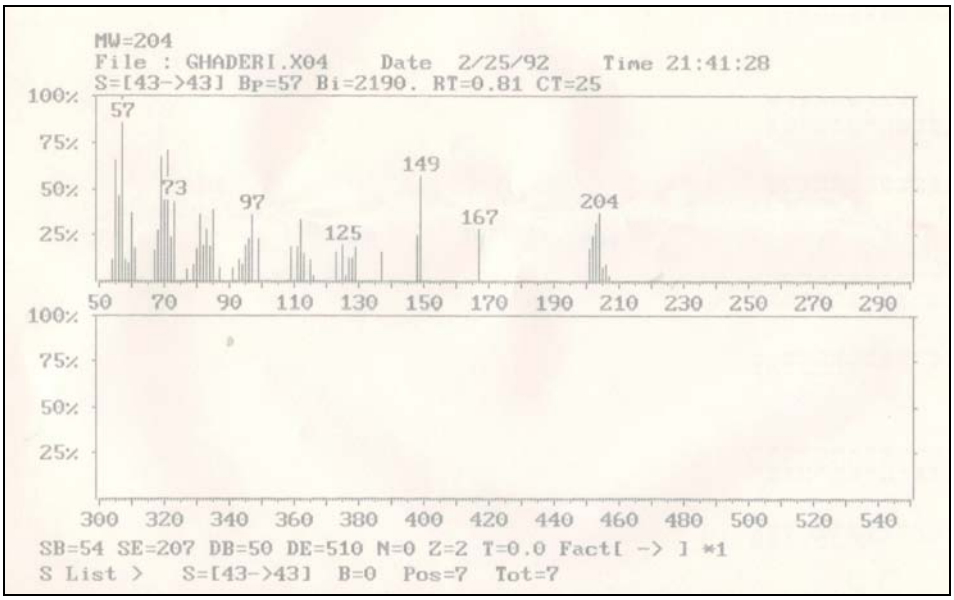
^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 6.31 (d, 1 H, J= 16.25 Hz), 6.97 (d, 1 H, J= 16.25 Hz), 7.18-7.61 (m, 10 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm): 85.00, 97.12, 108.17, 126.30, 128.18, 128.33, 128.62, 128.73, 131.50, 141.25; MS (m/e)= 204 [M^+]; Elemental Analysis: Calcd. C: 94.07, H: 5.93, Found. C: 93.85, H: 6.06.



^{1}H NMR of 3m



^{13}C NMR of 3m



Mass spectrum of 3m

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