Supplementary Information

Ambient Arylmagnesiation of Alkynes Catalysed by Ligandless Nickel(II)

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All preparations and manipulations were performed using standard Schlenk techniques under a nitrogen atmosphere. NMR spectra were measured at 25 °C using a Bruker ACF 500 MHz NMR spectrometer. Elemental analyses were performed on the vario MICRO Elementar system. GC-MS analyses were recorded on Agilent 6890N/5973N system.

Materials: All commercial chemicals were obtained from Sigma-Aldrich or Alfa Aesar unless stated otherwise. Solvents were dried by standard procedures. Phenylmagnesium bromide solution 1.0 M in THF and 4-fluorophenylmagnesium bromide solution 1.0 M in THF were purchased from Aldrich. Other Grignard reagents, 4-Methoxyphenylmagnesium bromide solution, *o*-Tolylmagnesium bromide solution and *m*-Tolylmagnesium bromide solution were prepared from the corresponding halides and magnesium turnings in anhydrous THF and titrated before use.

(I). General method for the Preparation of Aryl(alkyl)acetylenes or Aryl(Aryl)acetylenes[1]

To a solution of the iodoarene (5 mmol) and 1-alkyne (6 mmol) in Et_3N (30 mL) was added $PdCl_2(PPh_3)_2$ (70 mmg). The mixture was then stirred for 5 min, and CuI (15 mg) was added. The resulting mixture was heated under a nitrogen atmosphere at 60 °C for 24-36h. The reaction mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel to the corresponding alkynes.

(II). General method for the Arylmagnesiation of Alkynes

After standard cycles of evacuation and back-fill with pure N_2, $NiCl_2 \cdot 6H_2O$ (0.005 mmol) as catalyst was introduced into a 25-mL Schlenk tube equipped with a magnetic stir bar. To the catalyst were added alkyne (0.5 mmol), toluene (2 mL) and then aryl Grignard solution 1.0 M in THF (0.6 mL). The resulting mixture was stirred at r.t. for 1h. The reaction was quenched with water. The organic phase was extracted with ethyl acetate (3 x 10 mL) and dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography on silica gel to the corresponding product.

(III) Characterization Data

Triphenylethylene (**3aa**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.28 (m, 8H), 7.23–7.22 (m, 2H), 7.17–7.12 (m, 3H), 7.06–7.04 (m, 2H), 6.99 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.4, 142.6, 140.3, 137.4, 130.4, 129.5, 128.6, 128.2, 128.1, 127.9, 127.6, 127.5, 127.4, 126.7. Anal. Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found C, 93.43; H, 6.26.

(*E*)-1-(1,2-diphenylvinyl)-4-fluorobenzene (**3ab**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.27 (m, 5H), 7.20–7.10 (m, 5H), 7.04–6.98 (m, 4H), 6.90 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4 (d, J = 244.6 Hz), 141.6, 140.2, 139.6 (d, J = 3.1 Hz), 137.2, 130.3, 129.5, 129.2 (d, J = 7.9 Hz), 128.7, 128.0, 127.5, 126.8, 115.0 (d, J = 21.3 Hz). Anal. Calcd. for $C_{20}H_{15}F$: C, 87.56; H, 5.51. Found C, 87.35; H, 5.66.

(*E*)-1-(1,2-diphenylvinyl)-4-methoxybenzene (**3ac**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.23 (m, 7H), 7.16–7.10 (m, 3H), 7.04–7.03 (m, 2H), 6.92 (s, 1H), 6.88 (d, *J* = 9 Hz , 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 142.1, 140.5, 137.6, 136.0, 130.4, 129.4, 128.7, 128.6, 127.9, 127.3, 126.5, 126.4, 113.6, 55.3. Anal. Calcd. for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found C, 88.11; H, 6.25.

(*E*)-1-(1,2-diphenylvinyl)-3-methylbenzene (**3ad**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.32 (m, 3H), 7.22–7.19 (m, 3H), 7.16–7.10 (m, 6H), 7.03–7.02 (m, 2H), 6.96 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.4, 142.7, 140.4, 137.7, 137.4, 130.4, 129.5, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.3, 126.6, 124.8, 21.5. Anal. Calcd. for $C_{21}H_{18}$: C, 93.29; H, 6.71. Found C, 93.77; H, 6.40.

(*E*)-1-(1,2-diphenylvinyl)-2-methylbenzene (**3ae**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.26 (m, 1H), 7.21–7.11 (m, 13H), 6.61 (s, 1H), 2.11 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 142.9, 140.2, 137.4, 136.2, 130.4, 130.2, 130.1, 129.9, 129.4, 128.2, 128.0, 127.4, 127.1, 126.7, 125.6, 20.5. Anal. Calcd. for $C_{21}H_{18}$: C, 93.29; H, 6.71. Found C, 93.30; H, 6.71.

(*Z*)-1-methyl-4-(2-phenyl-2-*p*-tolylvinyl)benzene (**3ba**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.25 (m, 5H), 7.15–7.09 (m, 4H), 7.96–7.91 (m, 5H), 2.39 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 141.7, 137.5, 136.9, 136.4, 134.7, 130.2, 129.4, 129.3, 128.7, 128.1,127.9, 127.5, 127.2, 21.3, 21.2. Anal. Calcd. for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found C, 96.65; H, 7.25.

(*E*)-1-(1,2-di*p*-tolylvinyl)-4-fluorobenzene (**3bb**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.27 (m, 2H), 7.16–7.14 (m, 2H), 7.09–7.08 (m, 2H), 7.00–6.93 (m, 6H), 6.84 (s, 1H), 2.39 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3 (d, *J* = 245.4 Hz), 140.6, 139.9 (d, *J* = 3.1 Hz), 137.3, 137.1, 136.5, 134.5, 130.1, 129.4 (d, *J* = 5 Hz), 129.1 (d, *J* = 7.9 Hz), 128.7, 127.7, 114.9 (d, *J* = 21.3 Hz). Anal. Calcd. for $C_{22}H_{19}F$: C, 87.38; H, 6.33. Found C, 87.71; H, 6.07.

(*E*)-1-(1,2-di*p*-tolylvinyl)-4-methoxybenzene (**3bc**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26–7.22 (m, 2H), 7.15–7.09 (m, 4H), 6.96-6.92 (m, 4H), 6.85–6.83 (m, 3H), 3.82 (s, 3H), 2.39 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 141.2, 137.7, 136.9, 136.5, 136.1, 134.9, 130.2, 129.3, 128.7, 128.6, 126.3, 113.5, 55.3, 21.3, 21.1. Anal. Calcd. for $C_{23}H_{22}O$: C, 87.86; H, 7.05. Found C, 87.66; H, 7.09.

(*Z*)-1-methyl-3-(1-phenyl-2-*m*-tolylvinyl)benzene (**3ca**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.30 (m, 5H), 7.26–7.24 (m, 1H), 7.17–7.16 (m, 1H), 7.06–7.02 (m, 3H), 7.96–7.95 (m, 2H), 6.91 (s, 1H), 6.84–6.83 (m, 1H), 2.33 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 142.5, 140.4, 138.2, 137.33, 137.29, 130.7, 130.5, 128.4, 128.13, 128.07, 128.0, 127.7, 127.53, 127.47, 127.4, 127.3, 126.4, 21.4, 21.3. Anal. Calcd. for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found C, 92.96; H, 7.06.

1,1,2-tri*m*-tolylethene (**3cd**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25–7.20 (m, 3H), 7.17–7.11 (m, 3H), 7.06–7.01 (m, 3H), 6.96–6.93 (m, 2H), 6.90 (s, 1H), 6.83–6.82 (m, 1H), 2.36 (s, 3H), 2.33 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 142.6, 140.4, 138.1, 137.7, 137.35, 137.29, 130.7, 130.5, 128.4, 128.1, 128.02, 128.00, 127.7, 127.40, 127.35, 126.4, 124.8, 21.5, 21.4, 21.3. Anal. Calcd. for $C_{23}H_{22}$: C, 92.57; H, 7.43. Found C, 92.71; H, 6.96.

(*Z*)-1-(2-phenyl-2-*p*-fluorophenylvinyl)-4-fluorobenzene (**3da**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.31 (m, 5H), 7.19–7.16 (m, 2H), 7.06–7.00 (m, 4H), 6.94 (s, 1H), 6.88–6.84 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2 (d, *J* = 245.4 Hz), 161.5 (d, *J* = 245.9 Hz), 143.1, 141.4, 136.0 (d, *J* = 3.5 Hz), 133.3 (d, *J* = 3.4 Hz), 132.1 (d, *J* = 7.9 Hz), 131.1 (d, *J* = 7.8 Hz), 128.3, 127.7, 127.5, 127.3, 115.7 (d, *J* = 21.3 Hz), 115.0 (d, *J* = 21.4 Hz). Anal. Calcd. for $C_{20}H_{14}F_2$: C, 82.17; H, 4.83. Found C, 82.31; H, 4.89.

(*Z*)-1-methoxy-2-(2-phenyl-2-*o*-methoxyphenylvinyl)benzene (**3ea**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.34 (m, 2H), 7.31–7.23 (m, 5H), 7.10–7.06 (m,2H), 6.90–6.87 (m, 2H), 6.83–6.77 (m, 2H), 6.60–6.57 (m, 1H), 3.82 (s, 3H), 3.55 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6, 157.5, 143.0, 138.8, 131.8, 129.6, 129.2, 128.7, 128.0, 127.9, 126.9, 126.7, 123.9, 120.8, 119.8, 111.5, 110.2, 55.51, 55.46. Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found C, 83.68; H, 6.78.

(*Z*)-1-butyl-4-(2-phenyl-2-*p*-butylphenylvinyl)benzene (**3fa**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.27 (m, 5H), 7.16–7.11 (m, 4H), 6.94–6.93 (m, 4H), 6.91 (s, 1H), 2.65 (t, *J* = 7.5, 2H), 2.53 (t, *J* = 7.5, 2H), 1.68-1.62 (m, 2H), 1.58-1.51 (m, 2H), 1.42-1.37 (m, 2H), 1.35-1.31 (m, 2H), 0.97 (t, *J* = 7.5 ,3H), 0.91 (t, *J* = 7.5, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 142.0, 141.7, 141.5, 137.7, 134.9, 130.1, 129.4, 129.3, 128.7, 128.1, 128.0, 127.9, 127.5, 127.2, 35.4, 35.3, 22.4, 14.0,13.9. Anal. Calcd. for $C_{28}H_{32}$: C, 91.25; H, 8.75. Found C, 91.46; H, 8.58.

(*E*)-1,2-diphenylhex-1-ene (**3ga**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.46 (m, 2H), 7.38-7.24 (m, 8H), 6.69 (s, 1H), 2.71 (t, *J* = 7.5 Hz, 2H), 1.45-1.39 (m, 2H), 1.36-1.29 (m, 2H), 0.85 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, CDCl3) δ 143.4, 143.2, 138.4, 128.8, 128.3, 128.2, 128.1, 127.1, 126.6, 126.5, 30.9, 30.0, 22.8, 13.9; Anal. Calcd. for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found C, 91.29; H, 8.19.

(*E*)-2-(4-fluorophenyl)-1-phenyl-1-hexene (**3gb**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.35 (m, 4H), 7.32-7.30 (m, 2H), 7.27-7.24 (m, 1H), 7.07-7.03 (m, 2H), 6.64 (s, 1H), 2.67 (t, *J* = 7.5 Hz, 2H), 1.41-1.29 (m, 4H), 0.85 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ δ 162.1 (d, *J* = 244.4 Hz), 142.3, 139.1 (d, *J* = 3 Hz), 138.1, 129.0, 128.7, 128.2, 128.15, 128.1 (d, *J* = 3.1 Hz), 127.9, 126.6, 115.1(d, *J* = 21.1 Hz), 30.8, 30.0, 22.7,13.9. Anal. Calcd. for $C_{18}H_{19}F$: C, 85.00; H, 7.53. Found C, 84.68; H, 7.63.

(*E*)-2-(4-methoxyphenyl)-1-phenyl-1-hexene (**3gc**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.38-7.35 (m, 2H), 7.31 (d, *J* = 7.0 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.65 (s, 1H), 3.84 (s, 3H), 2.68 (t, *J* = 7.5 Hz, 2H), 2.39 (s, 3H), 1.44-1.39 (m, 2H), 1.36-1.29 (m, 2H), 0.86 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 142.7, 138.5, 135.5, 128.7, 128.2, 127.6, 126.8, 126.3, 113.7, 55.3, 31.0, 29.9, 22.8, 13.9. Anal. Calcd. for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found C, 85.77; H, 7.94.

(*E*)-2-(2-methylphenyl)-1-phenyl-1-hexene (**3gd**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.35 (m, 4H), 7.29-7.20 (m, 5H), 6.36 (s, 1H), 2.60 (t, *J* = 7.5 Hz, 2H), 2.38 (s, 3H), 1.44-1.35 (m, 2H), 1.33-1.27 (m, 2H), 0.85 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, CDCl3) δ 144.1, 143.9, 138.0, 135.2, 130.1, 129.1, 128.7, 128.6, 128.2, 126.6, 126.4, 125.3, 32.4, 30.3, 22.9, 19.9, 13.9. Anal. Calcd. for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found C, 91.24; H, 8.48.

(*E*)-2-(3-methylphenyl)-1-phenyl-1-hexene (**3ge**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.31 (m, 4H), 7.27-7.23 (m, 5H), 6.67 (s, 1H), 2.69 (t, *J* = 7.5 Hz, 2H), 2.39 (s, 3H), 1.43-1.29 (m, 4H), 0.85 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 143.2, 138.4, 137.8, 131.5, 128.8, 128.8, 128.0, 127.9, 127.4, 126.4, 123.7, 30.9, 30.0, 22.8, 21.6, 13.6. Anal. Calcd. for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found C, 91.38; H, 8.44.

(*E*)-1-methyl-2-(2-phenylhex-1-enyl)benzene (**3ha**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.25–7.19 (m, 4H), 6.67 (s, 1H), 2.56 (t, *J* = 7.5 Hz, 2H), 2.29 (s, 3H), 1.34-1.29 (m, 2H), 1.25-1.20 (m, 2H), 0.78 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.9, 142.8, 137.7, 136.7, 129.7, 128.8, 128.3, 127.3, 127.0, 126.8, 126.7, 125.4, 30.7, 29.7, 22.6, 20.1, 13.8. Anal. Calcd. for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found C, 91.35; H, 8.46.

(*E*)-1-(2-phenylhex-1-enyl)naphthalene (**3ia**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04-8.02 (m, 1H), 7.89-7.87 (m, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.59-7.57 (m, 2H), 7.51-7.42 (m, 6H), 7.35-7.32 (m, 1H), 7.10 (s, 1H), 2.57 (t, 2H, *J* = 7.5 Hz), 1.36-1.30 (m, 2H), 1.21-1.15 (m, 2H), 0.72 (t, *J* = 7.5 Hz, 3H); 13C NMR (125 MHz, $CDCl_3$) δ ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 142.6, 135.8, 133.5, 128.7, 128.4, 128.3, 127.22, 127.17, 126.7, 126.1, 126.0, 125.8, 125.33, 125.25, 30.8, 30.2, 22.6, 13.7. Anal. Calcd. for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found C, 92.39; H, 7.30.

(*E*)-1-methoxy-4-(2-phenylhex-1-enyl)benzene (**3ja**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.29-7.26 (m, 3H), 6.92 (d, *J* = 9.0 Hz, 2H), 6.64 (s, 1H), 3.84 (s, 3H), 2.71 (t, *J* =8.0 Hz, 2H), 2.29 (s, 3H), 1.46-140 (m, 2H), 1.38-1.31 (m, 2H), 0.87 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.2, 143.4, 142.0, 131.0, 129.9, 128.3, 127.6, 126.9, 126.5, 113.7, 55.3, 30.9, 30.0, 22.8, 13.9. Anal. Calcd. for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found C, 85.68; H, 8.12.

(*E*)-1,2-bis(4-fluorophenyl)hex-1-ene (**3ka**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.39 (m, 2H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.07-7.03 (m, 4H), 6.58 (s, 1H), 2.63 (t, *J* = 7.5 Hz, 2H), 1.53-1.26 (m, 4H), 0.84 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2 (d, *J* = 244.1 Hz), 161.5 (d, *J* = 244.8 Hz), 142.4, 139.0, 134.2 130.3 (d, *J* = 8 Hz), 128.1 (d, *J* = 7.9 Hz), 126.9, 115.1 (d, *J* = 21.0 Hz), 30.8, 30.0, 22.7, 13.8. Anal. Calcd. for $C_{18}H_{18}F_2$: C, 79.39; H, 6.66. Found C, 79.10; H, 6.26.

(*E*)-1-methyl-3-(2-phenylhex-1-enyl)benzene (**3la**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.0 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.31–7.28 (m, 2H), 7.16–7.15 (m, 2H), 7.09 (d, *J* = 7.0 Hz, 1H), 6.69 (s, 1H), 2.73 (t, *J* = 7.5 Hz, 2H), 2.39 (s, 3H), 1.47-1.41 (m, 2H), 1.39-1.31 (m, 2H), 0.88 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.25, 143.20, 138.3, 137.7, 129.6, 128.3, 128.14, 128.09, 127.2, 127.0, 126.6, 125.7, 30.9, 30.0, 22.7, 21.5, 13.9. Anal. Calcd. for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found C, 91.46; H, 8.53.

(*E*)-1-phenyl-4-(2-phenylhex-1-enyl)benzene (**3ma**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67-7.64 (m, 4H), 7.52-7.31 (m, 10H), 6.75 (s, 1H), 2.80 (t, *J* = 8.0 Hz, 2H), 1.52-1.46 (m, 2H), 1.43-1.36 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 143.2, 140.8, 139.2, 137.4, 129.2, 128.8, 128.3, 127.6, 127.2, 127.1, 127.0, 126.9, 126.6, 31.0, 30.1, 22.8, 13.9. Anal. Calcd. for $C_{24}H_{24}$: C, 92.26; H, 7.74. Found C, 92.42; H, 7.41.

(*E*)-5-chloro-1,2-diphenylpent-1-ene (**3na**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 4H), 7.34–7.26 (m, 4H), 6.77 (s, 1H), 3.49 (t, *J* = 6.5 Hz, 2H), 2.89 (t, *J* = 7.5 Hz, 2H), 1.93-1.87 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.4, 141.4, 137.9, 129.3, 128.7, 128.5, 128.3, 127.4, 126.8, 126.6, 44.8, 31.6, 27.7. Anal. Calcd. for $C_{17}H_{17}Cl$: C, 79.52; H, 6.67. Found C,79.40; H, 6.51.

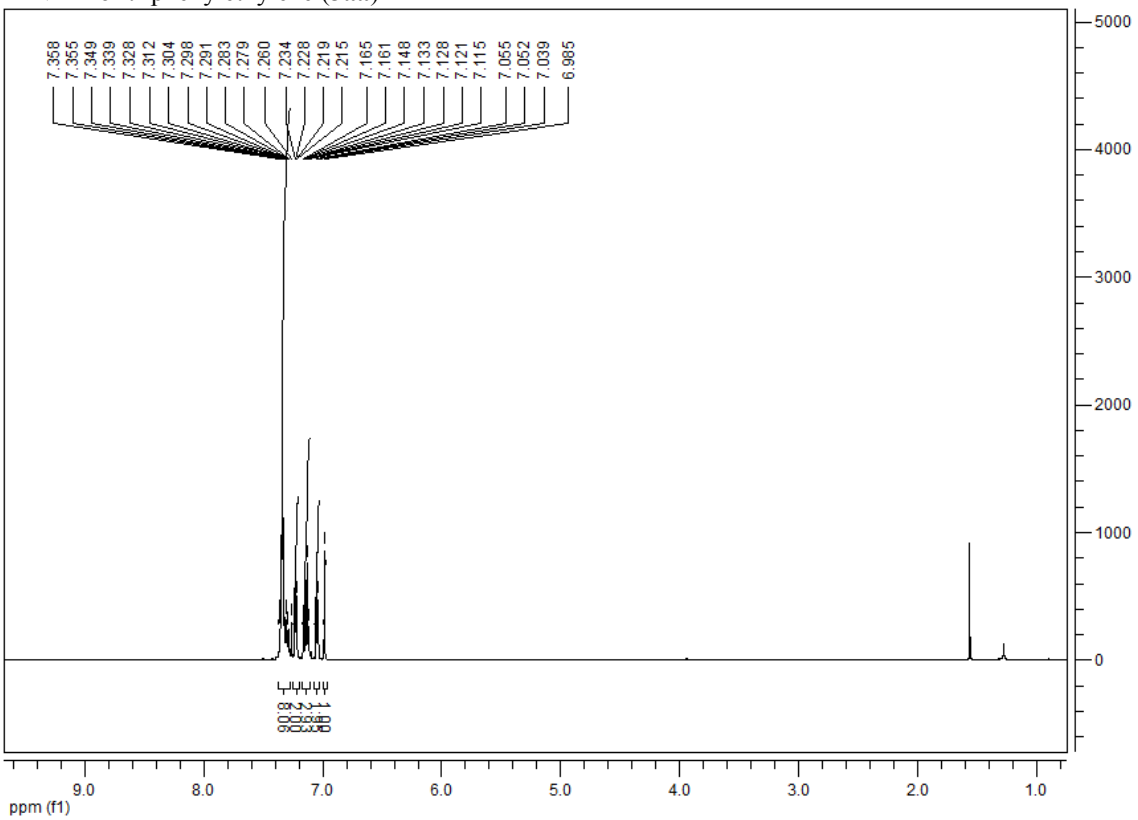
2-Deuterio-1,1,2-triphenylethene (**3aa-*d***): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.29 (m, 8H), 7.23–7.21 (m, 2H), 7.16–7.11 (m, 3H), 7.05–7.04 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.4, 142.5, 140.3, 137.3, 130.4, 129.5, 128.6, 128.2, 127.9, 127.6, 127.5, 127.4, 126.7. Anal. Calcd. for $C_{20}H_{15}D$: C, 93.34; H, 6.66. Found C, 93.51; H, 6.62.

1-Iodo-1,2,2-triphenylethene (**4aab**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.39 (m, 2H), 7.36–7.29 (m, 5H), 7.16 (t, *J* = 7.5 Hz, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.05–7.03 (m, 3H), 6.96–6.94 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.4, 147.2, 144.5, 140.3, 130.2, 130.1, 129.2, 128.3, 127.9, 127.7, 127.6, 127.5, 126.8. 101.3. Anal. Calcd. for $C_{20}H_{15}I$: C, 62.84; H, 3.96. Found C, 62.72; H, 4.42.

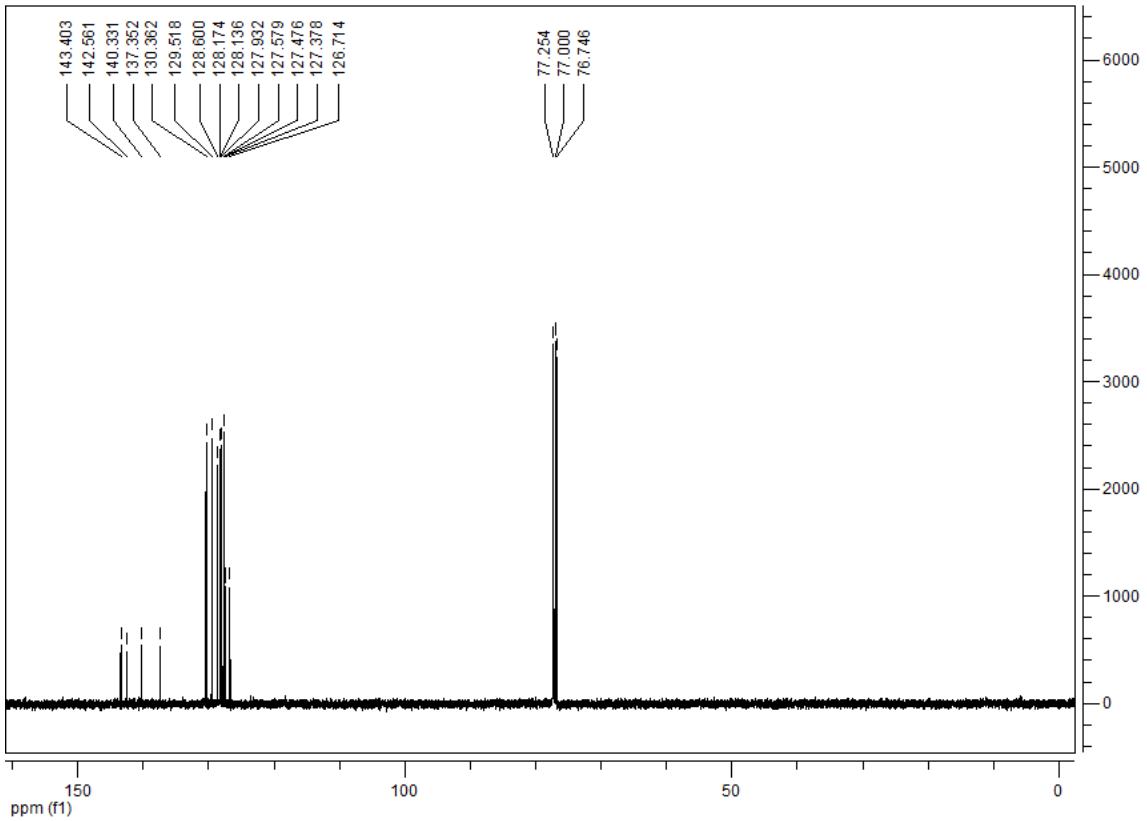
1,2,3,3-Tetraphenylprop-2-en-1-ol (**4aac**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49–7.48 (m, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.35–7.29 (m, 5H), 7.28–7.23 (m, 1H), 7.09–6.97 (m, 8H), 6.87–6.85 (m, 2H), 5.99 (d, *J* = 4.0 Hz, 1H), 2.99 (d, *J* = 6.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 142.6, 142.0, 141.9, 140.9, 137.3,131.2, 130.2, 129.6, 128.5, 128.0, 127.5, 127.4, 127.2, 126.9, 126.8, 126.3, 125.8. 73.6. Anal. Calcd. for $C_{27}H_{22}O$: C, 89.47; H, 6.12. Found C, 89.58; H,6.20.

.

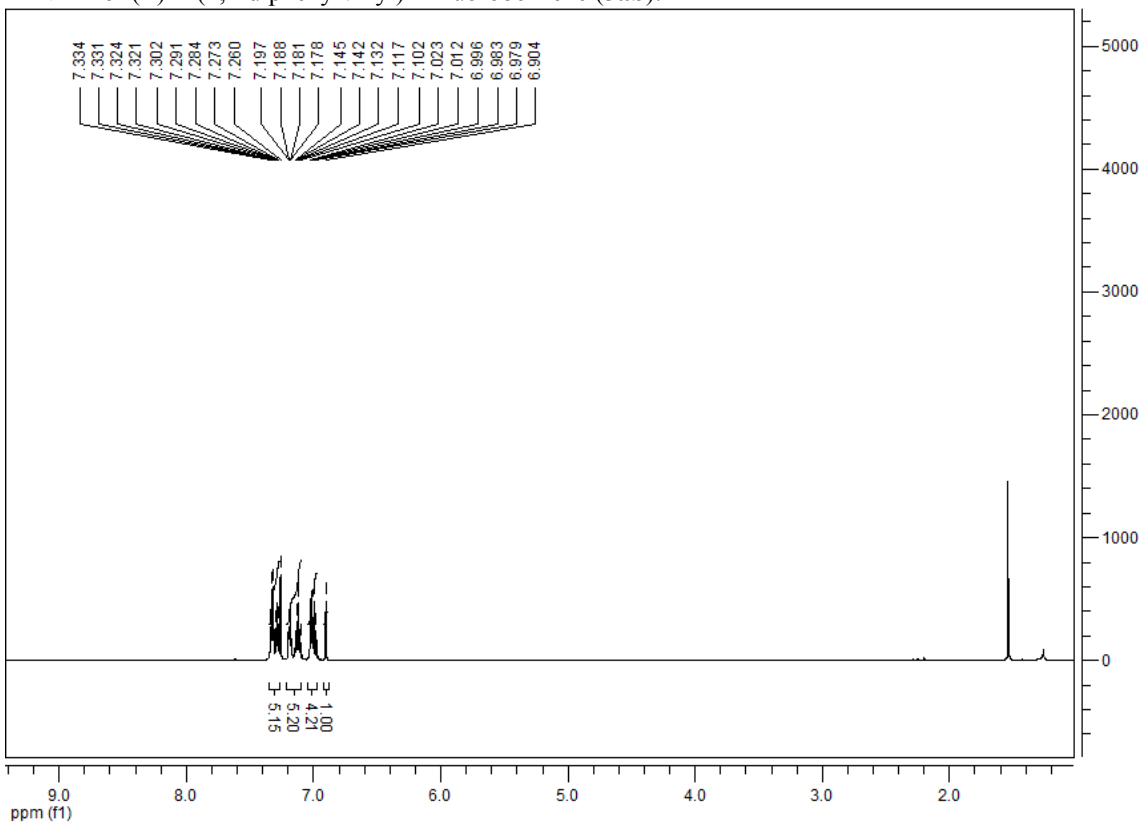
^{1}H NMR of triphenylethylene (**3aa**)



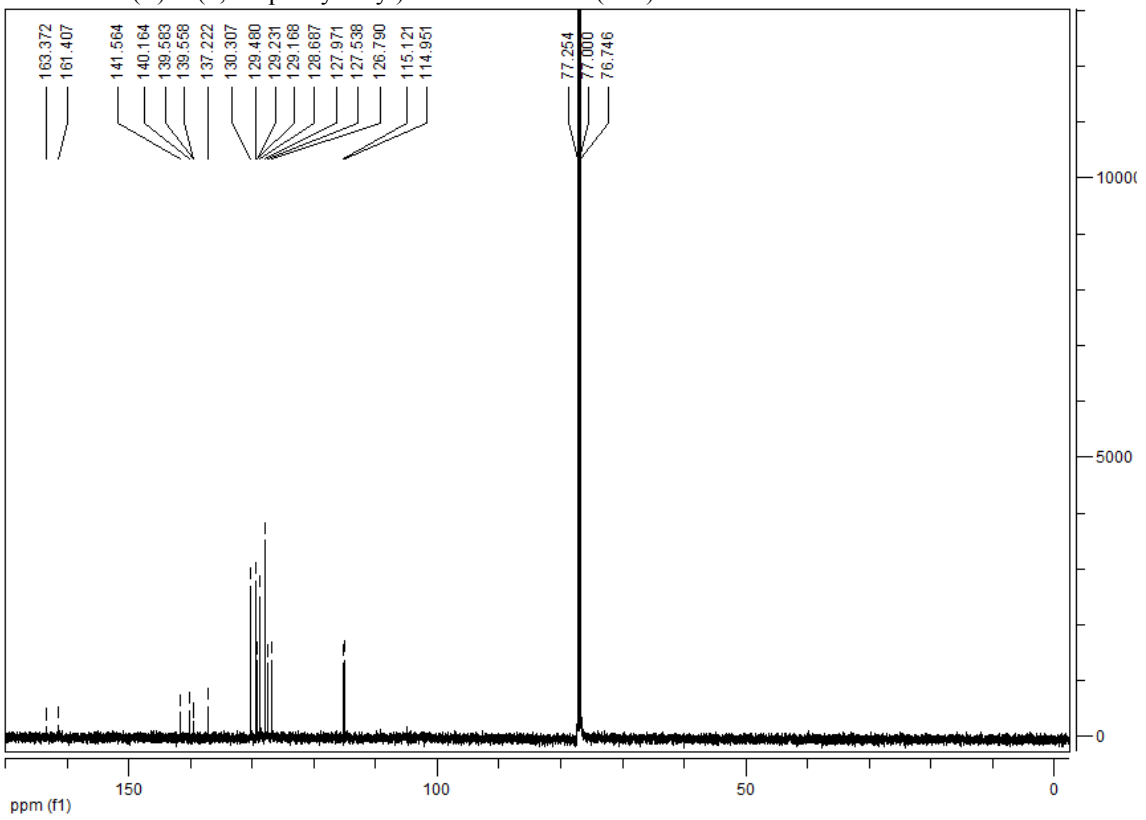
^{13}C NMR of triphenylethylene (**3aa**)



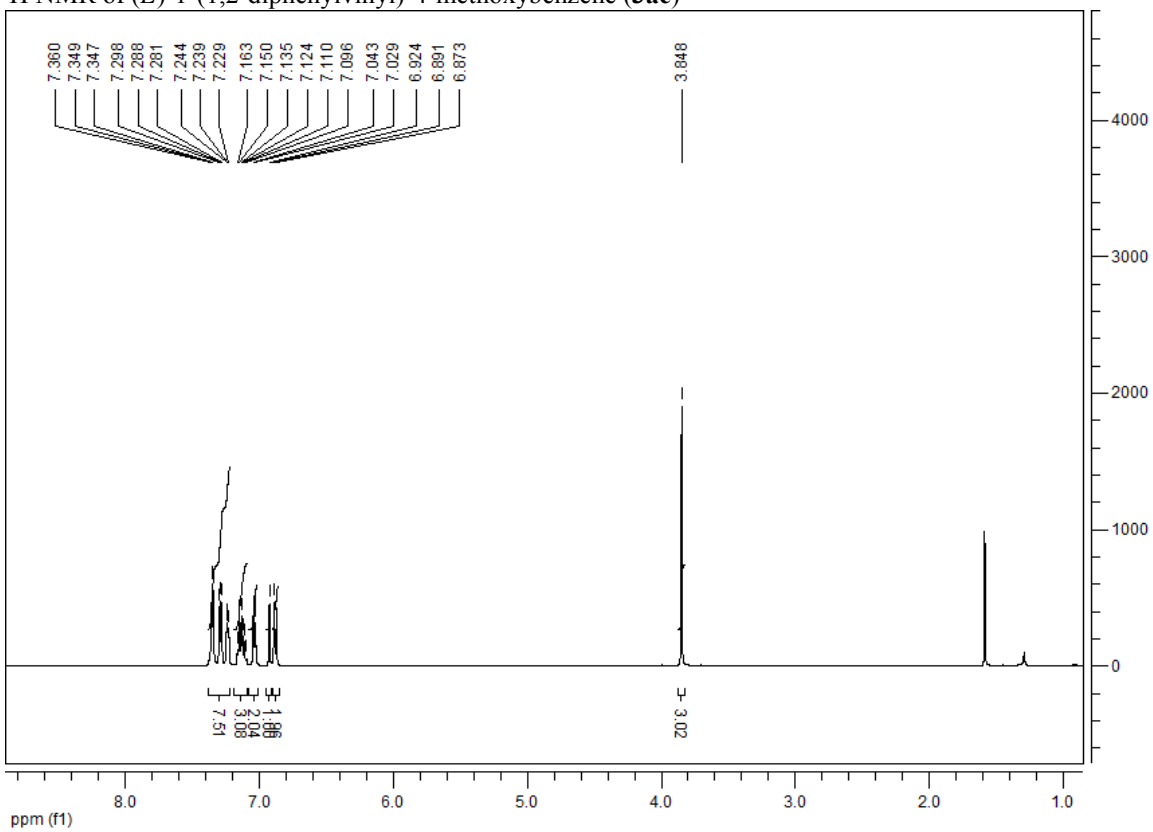
^{1}H NMR of (*E*)-1-(1,2-diphenylvinyl)-4-fluorobenzene (**3ab**):



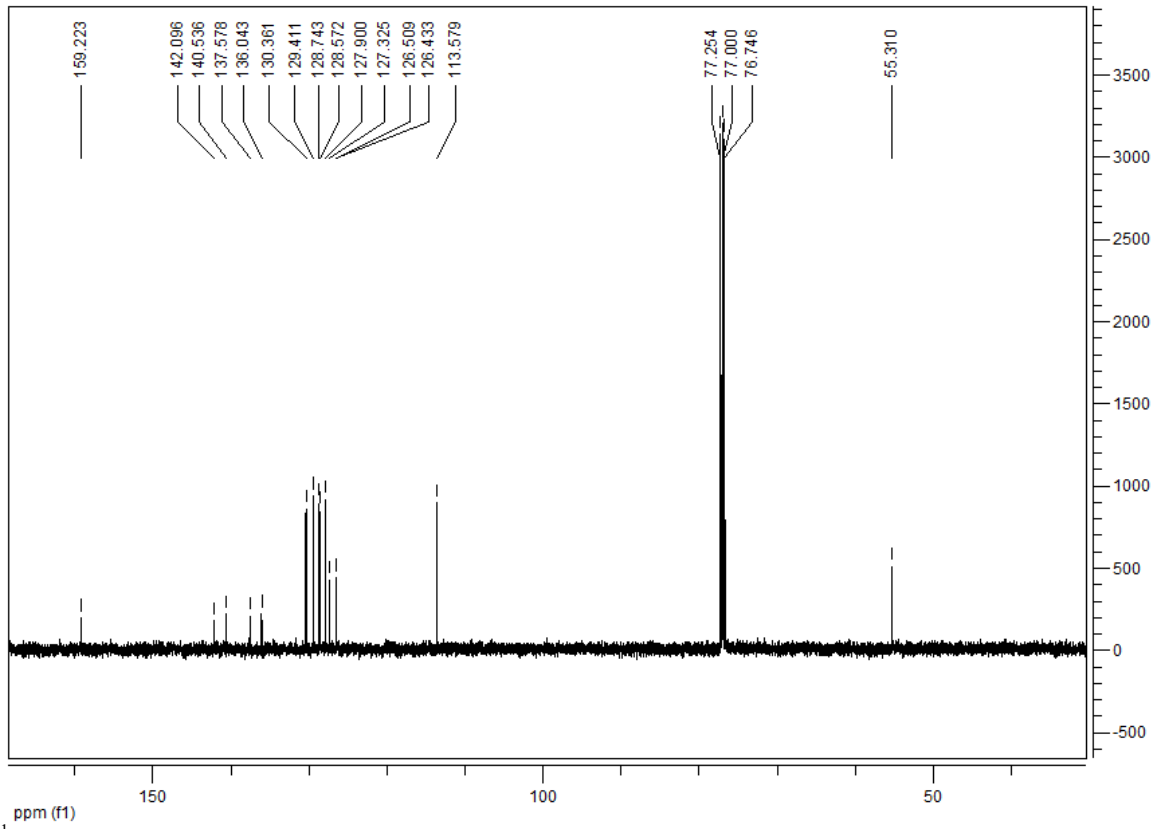
^{13}C NMR of (*E*)-1-(1,2-diphenylvinyl)-4-fluorobenzene (**3ab**):



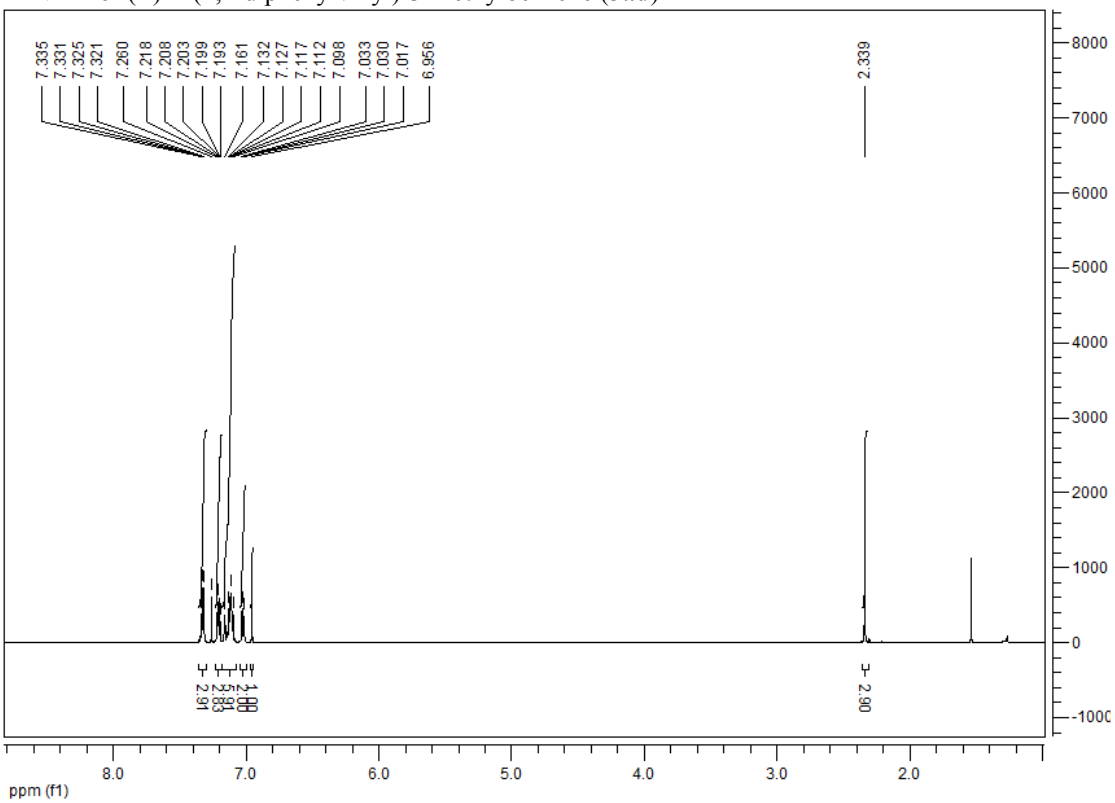
^{1}H NMR of (*E*)-1-(1,2-diphenylvinyl)-4-methoxybenzene (**3ac**)



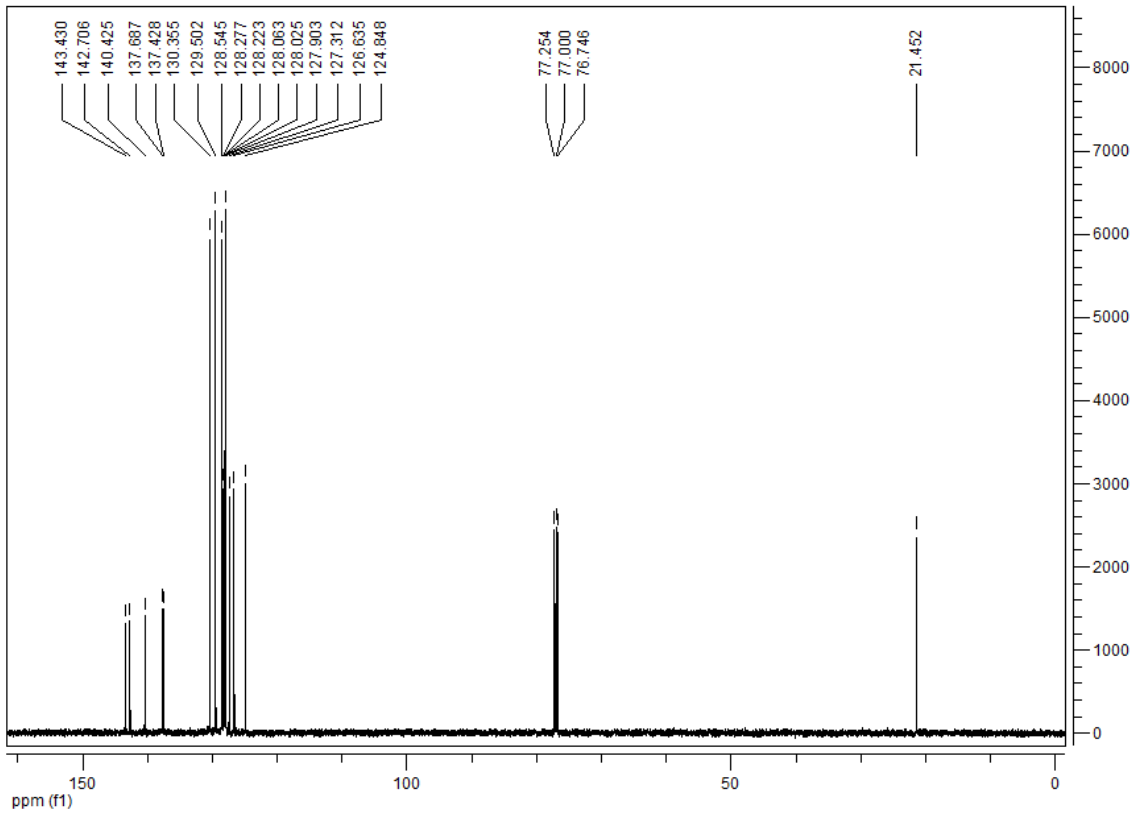
^{13}C NMR of (*E*)-1-(1,2-diphenylvinyl)-4-methoxybenzene (**3ac**)



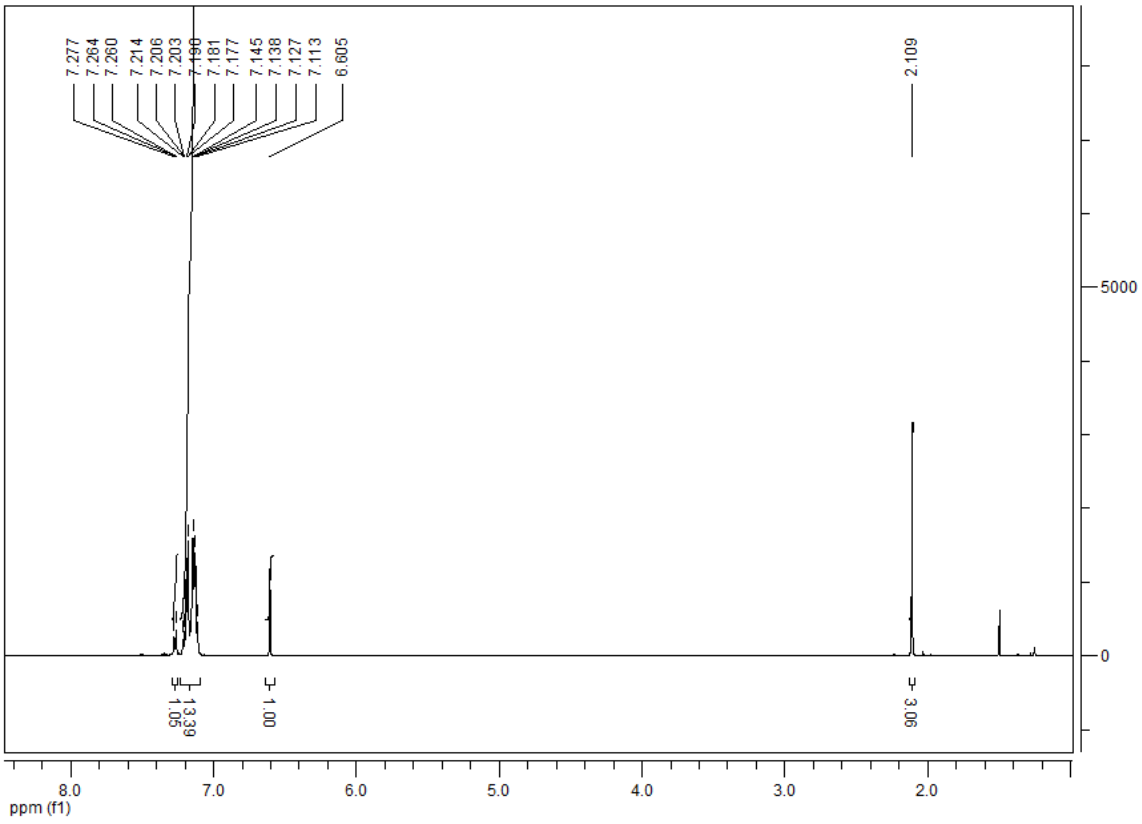
^{1}H NMR of (*E*)-1-(1,2-diphenylvinyl)-3-methylbenzene (**3ad**)



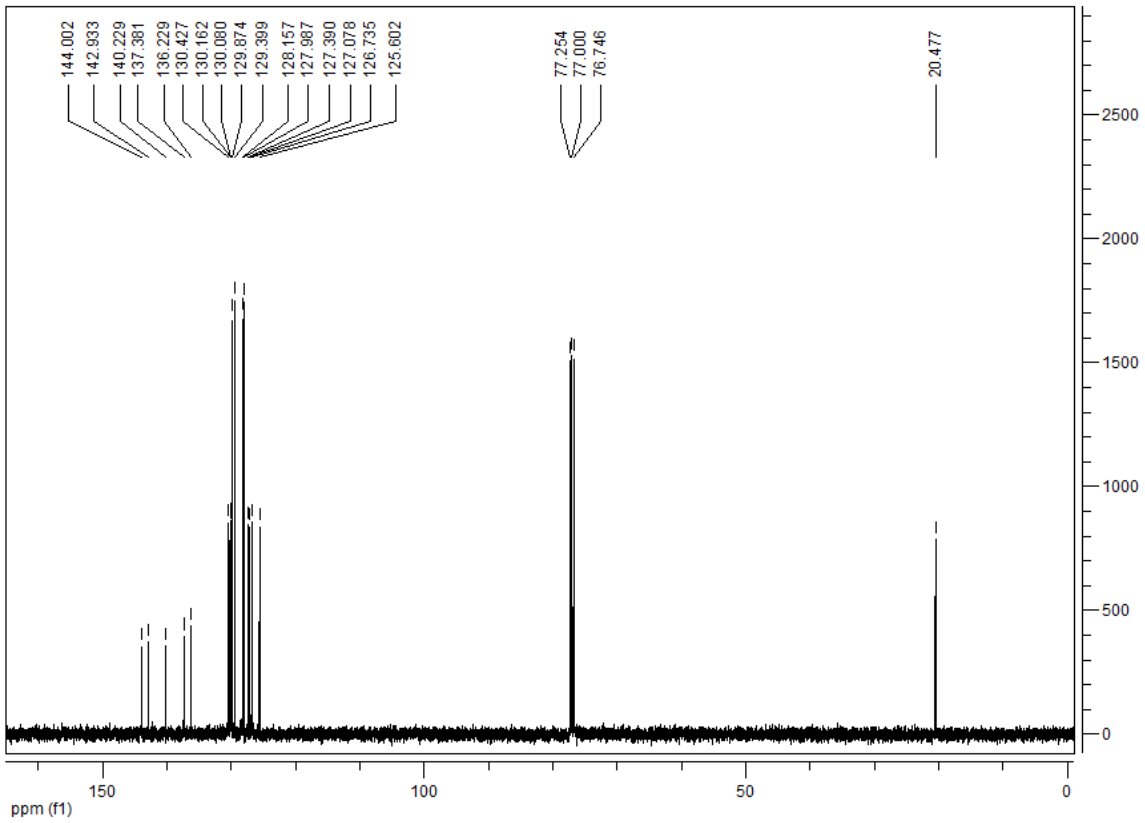
^{13}C NMR of (*E*)-1-(1,2-diphenylvinyl)-3-methylbenzene (**3ad**)



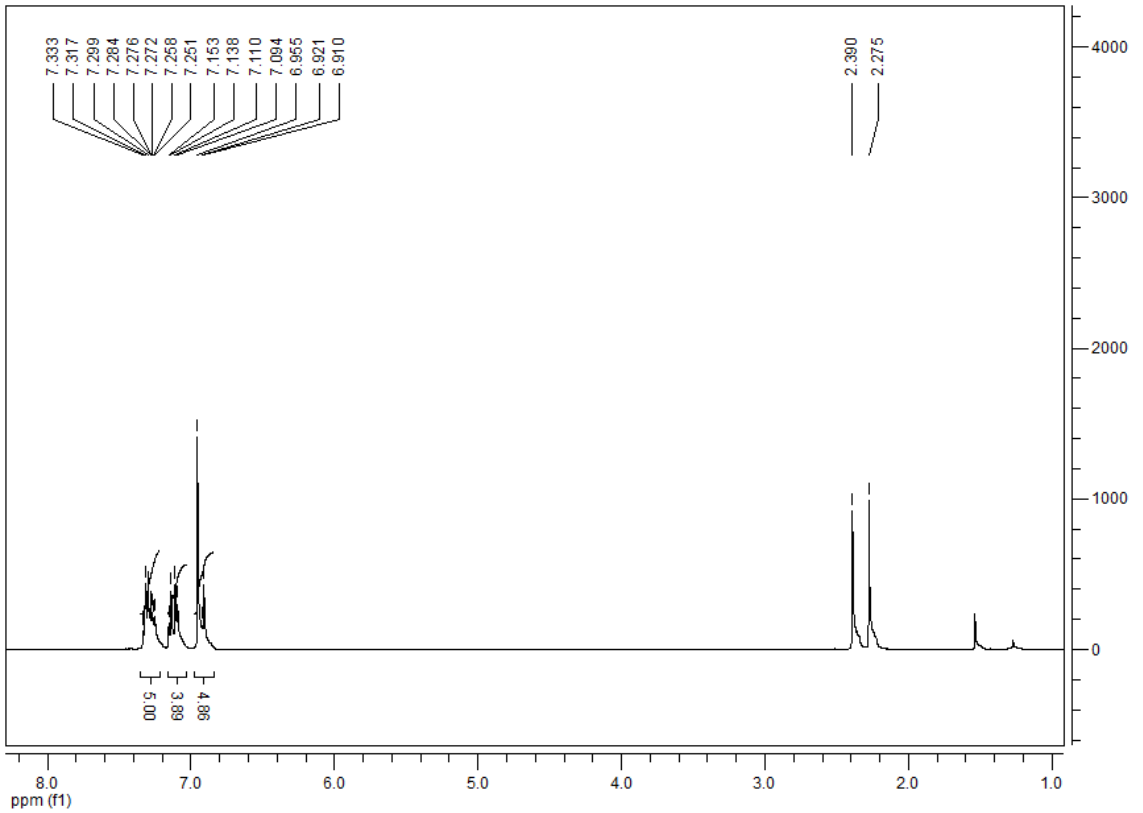
^{1}H NMR of (*E*)-1-(1,2-diphenylvinyl)-2-methylbenzene (**3ae**)



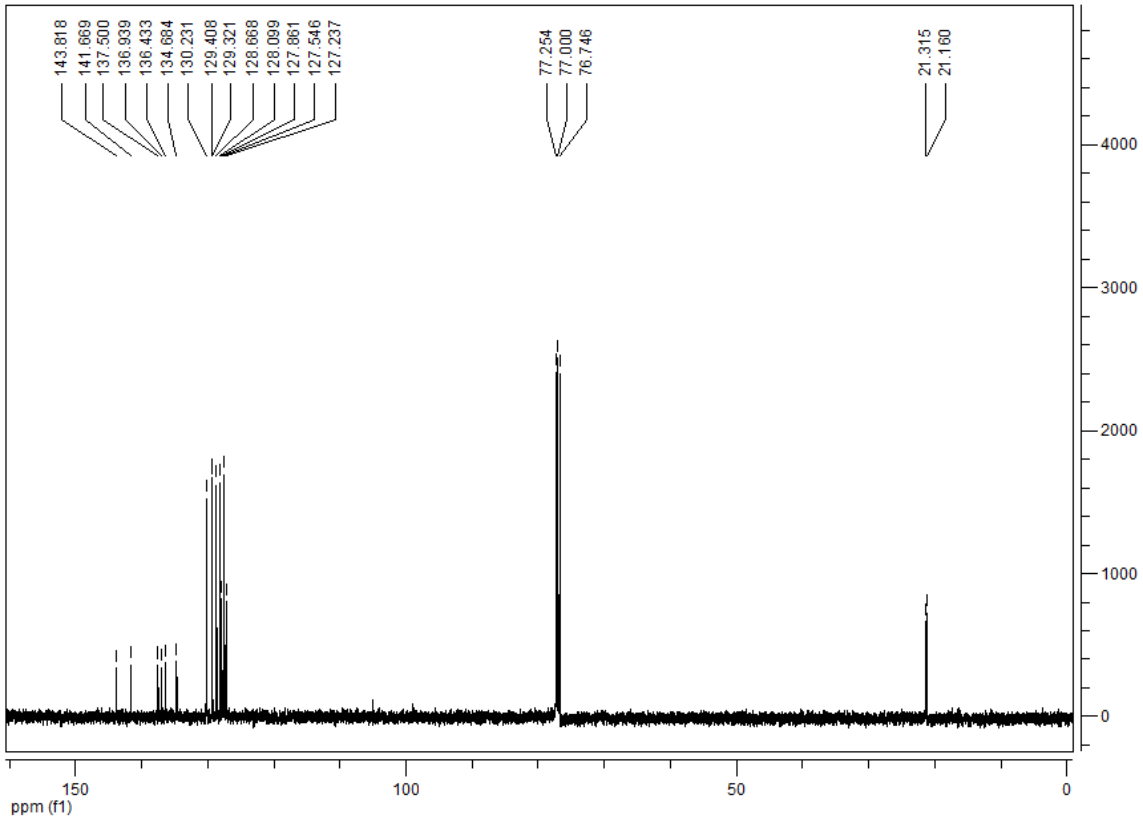
^{13}C NMR of (*E*)-1-(1,2-diphenylvinyl)-2-methylbenzene (**3ae**)



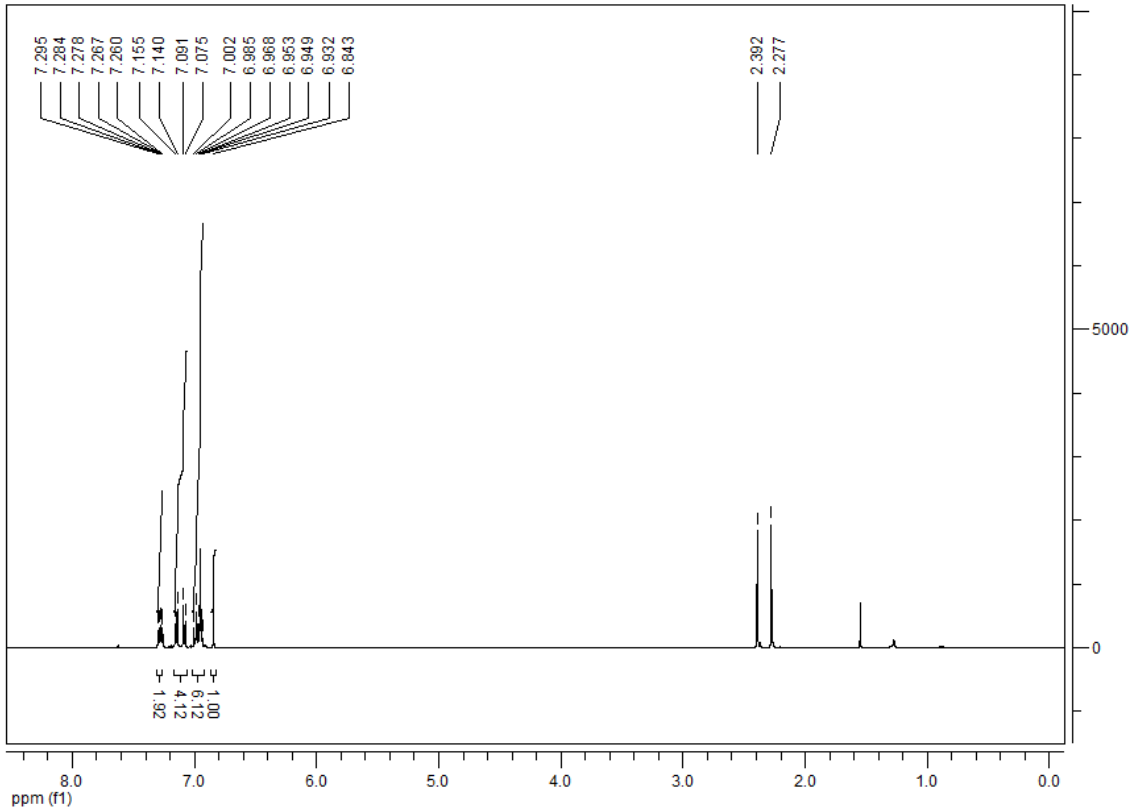
^{1}H NMR of (*Z*)-1-methyl-4-(2-phenyl-2-*p*-tolylvinyl)benzene (**3ba**)



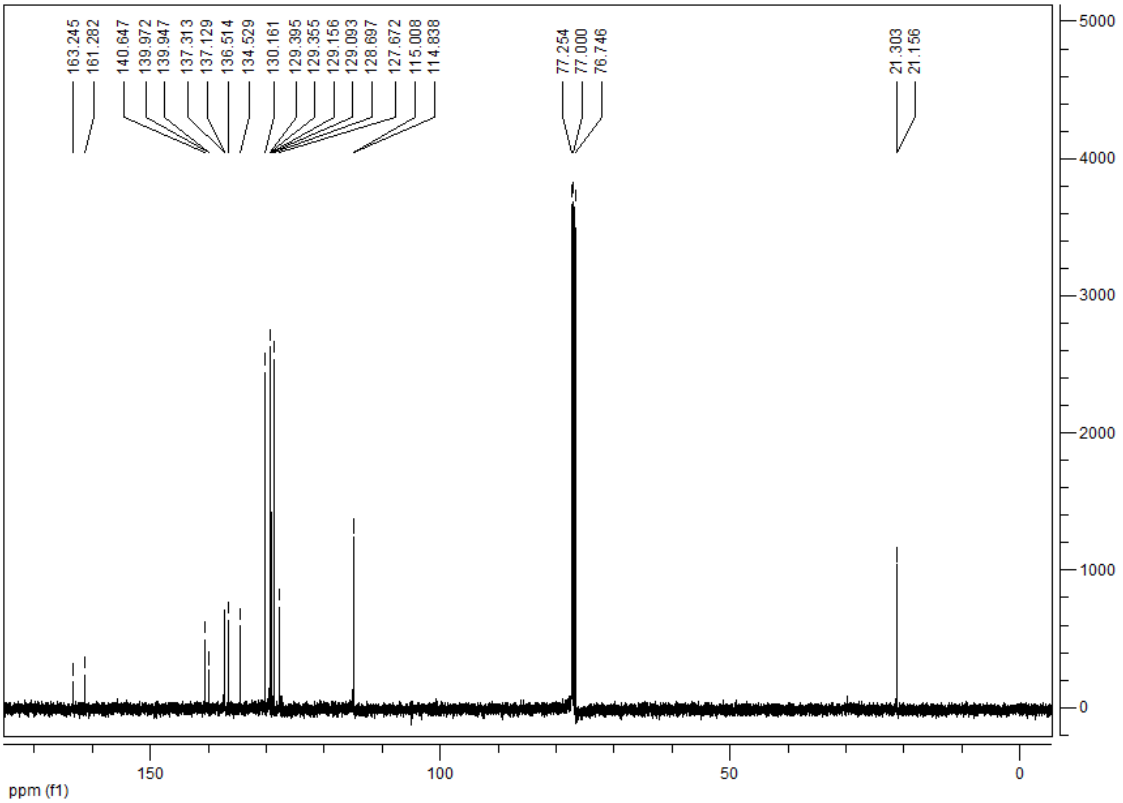
^{13}C NMR of (*Z*)-1-methyl-4-(2-phenyl-2-p-tolylvinyl)benzene (**3ba**)



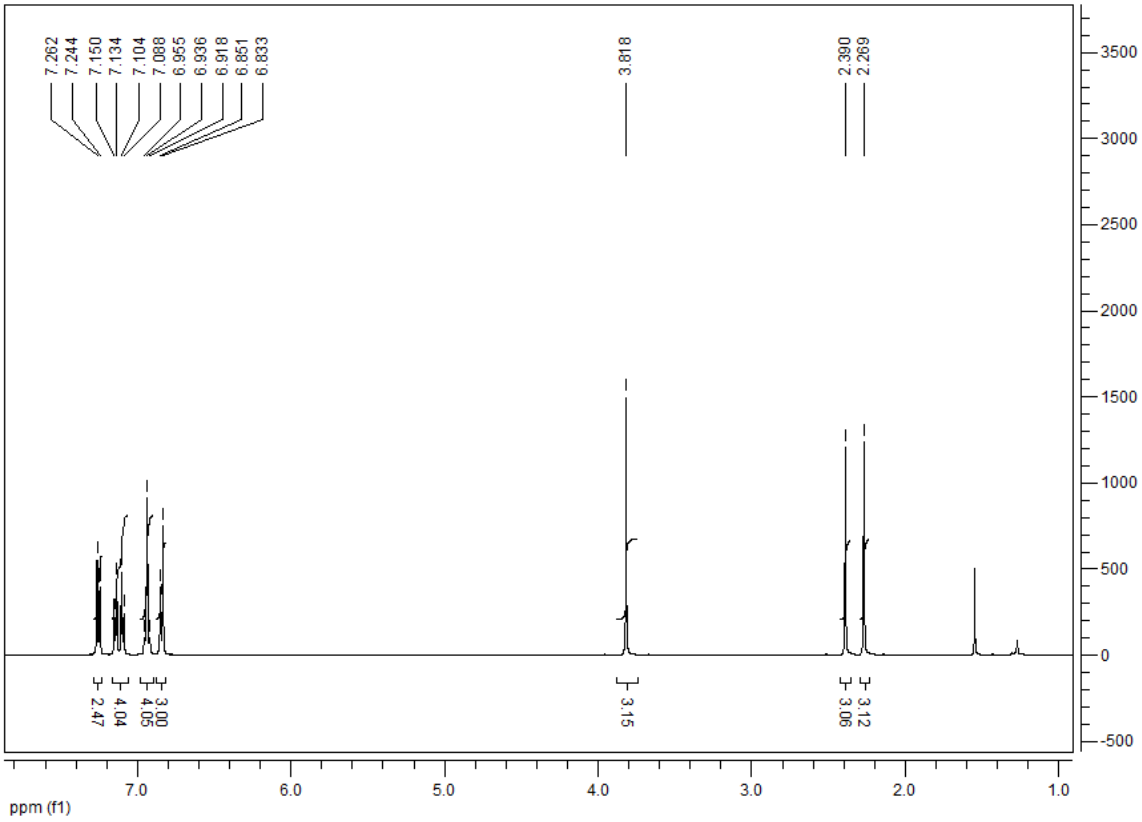
^{1}H NMR of (*E*)-1-(1, 2-di*p*-tolylvinyl)-4-fluorobenzene (**3bb**)



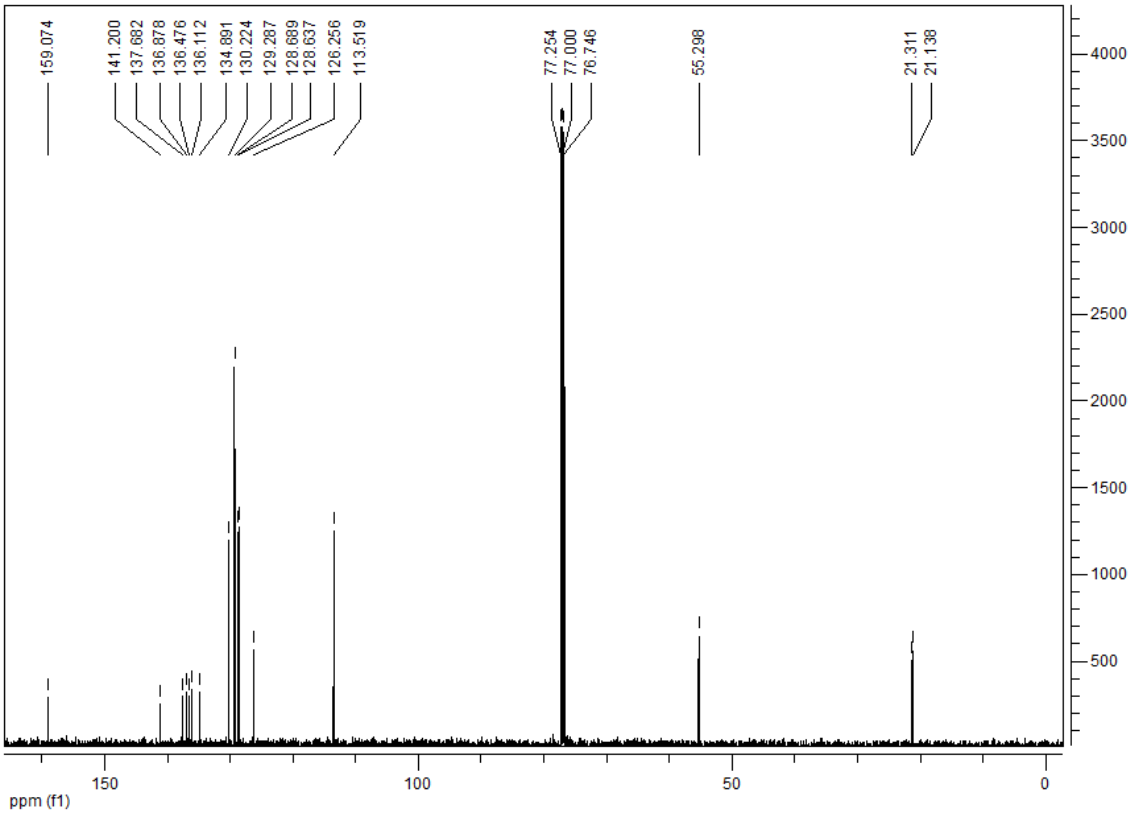
^{13}C NMR of (*E*)-1-(1, 2-di*p*-tolylvinyl)-4-fluorobenzene (**3bb**):



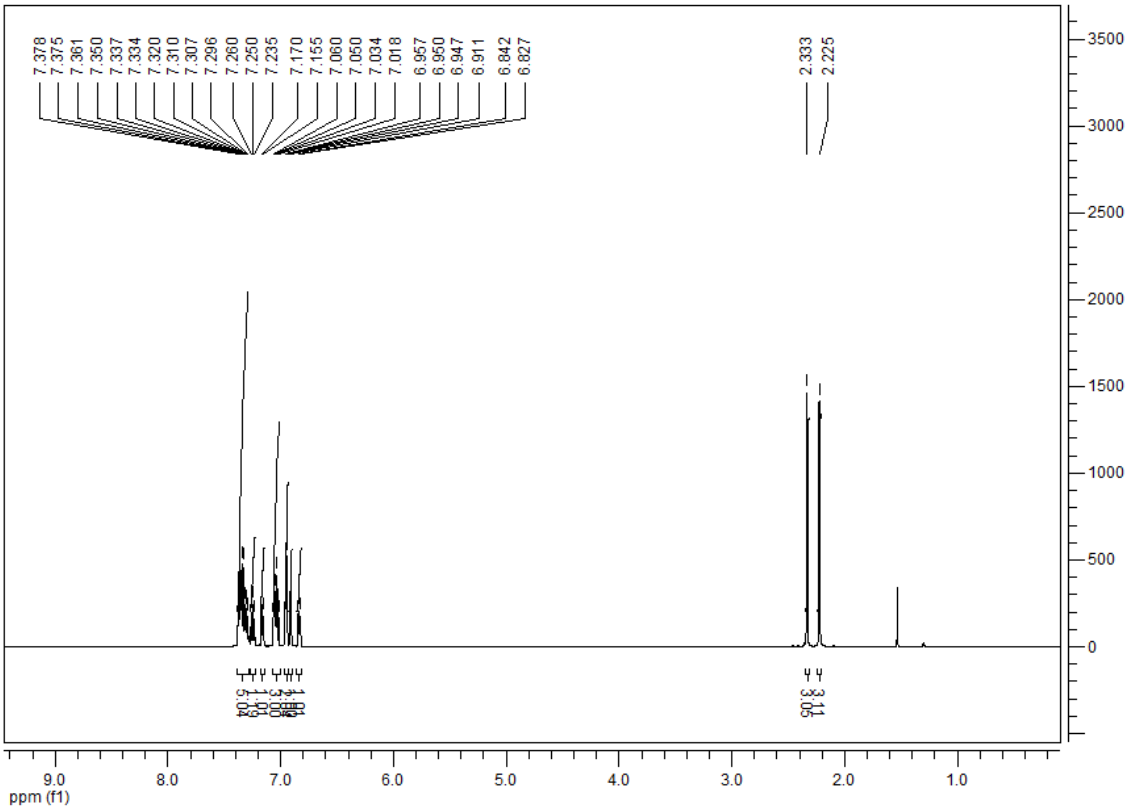
^{1}H NMR of (*E*)-1-(1,2-di*p*-tolylvinyl)-4-methoxybenzene (**3bc**):



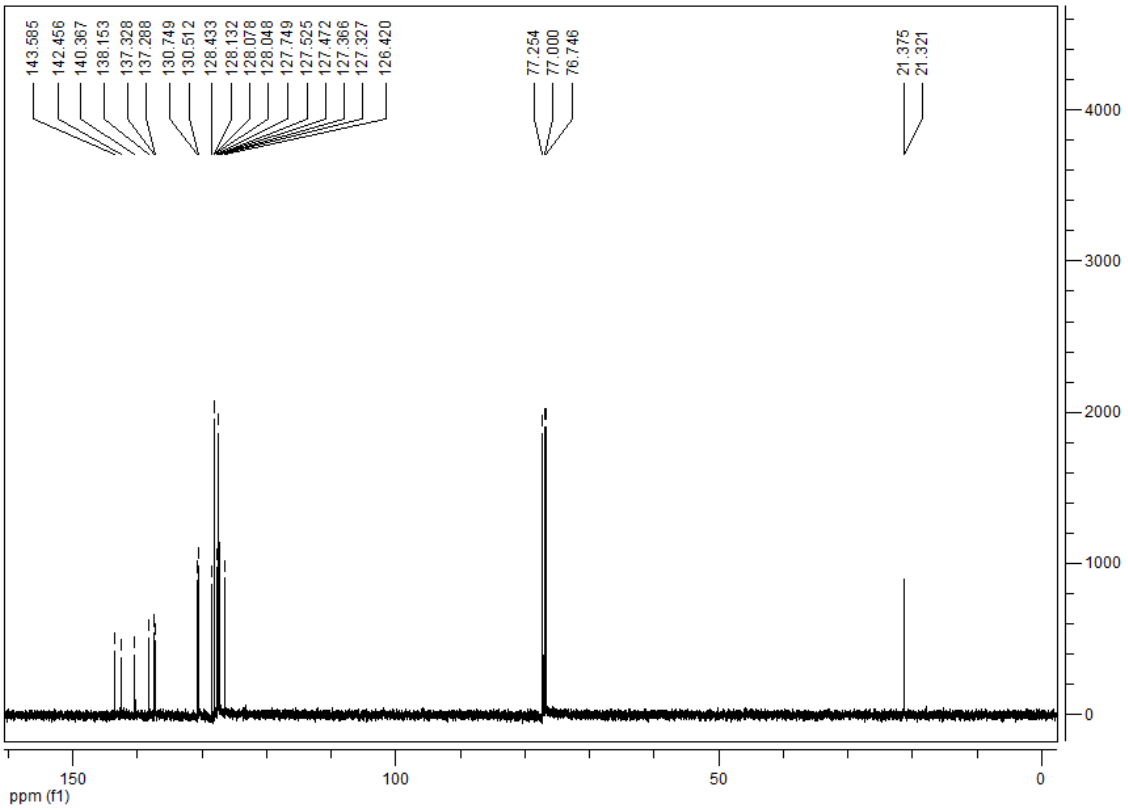
^{13}C NMR of (*E*)-1-(1,2-di*p*-tolylvinyl)-4-methoxybenzene (**3bc**):



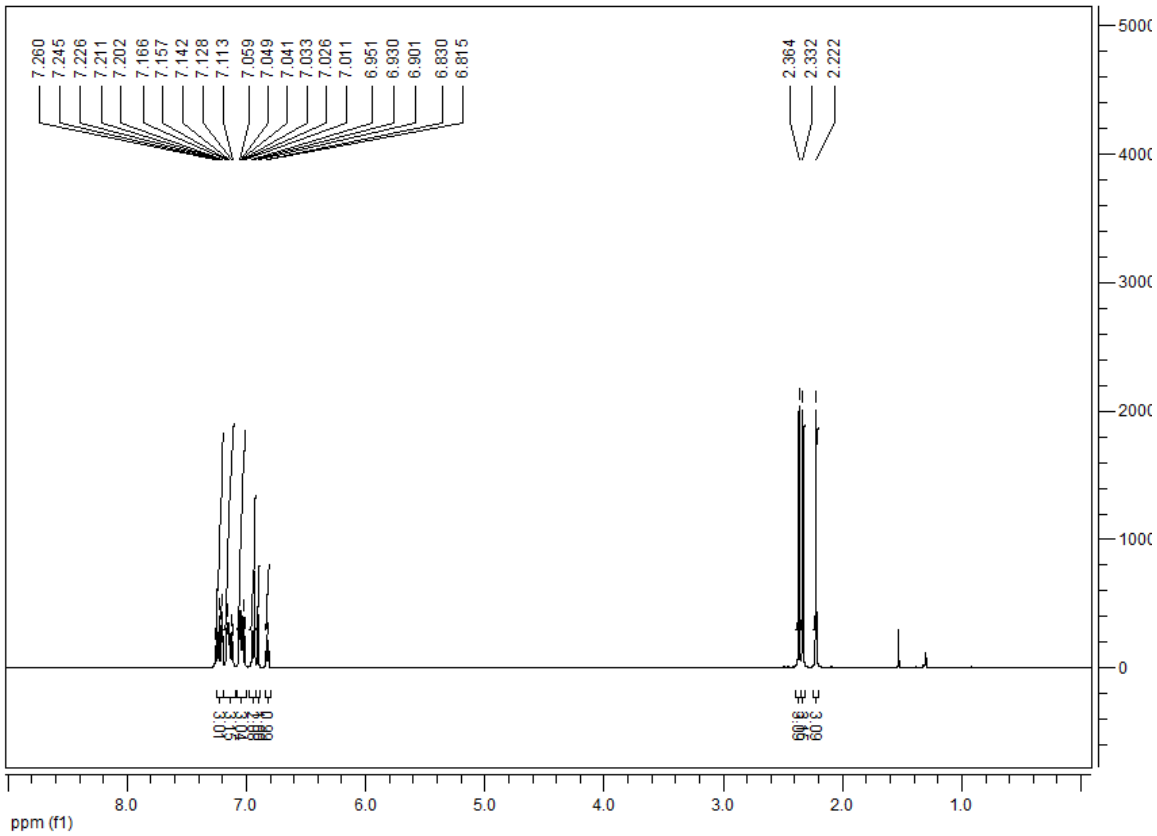
^{1}H NMR of (*Z*)-1-methyl-3-(1-phenyl-2-*m*-tolylvinyl)benzene (**3ca**):



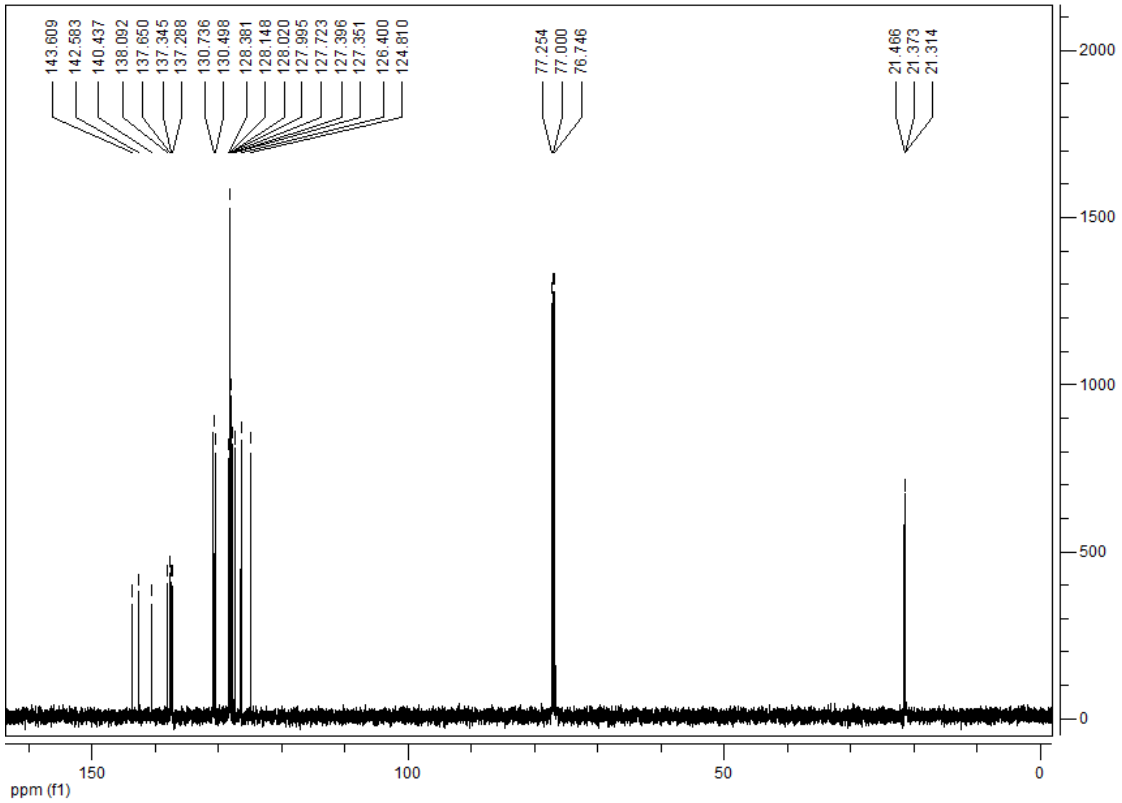
^{13}C NMR of (*Z*)-1-methyl-3-(1-phenyl-2-*m*-tolylvinyl)benzene (**3ca**):



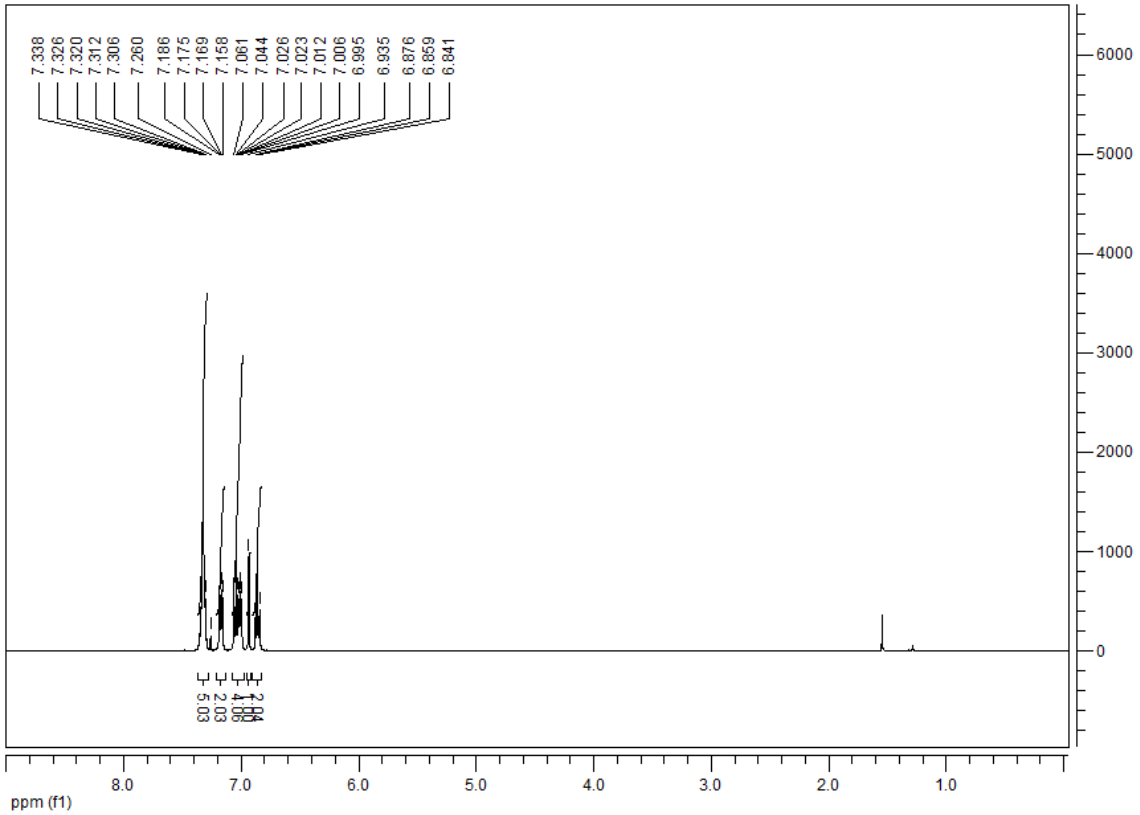
^{1}H NMR of 1,1,2-tri*m*-tolylethene (**3cd**)



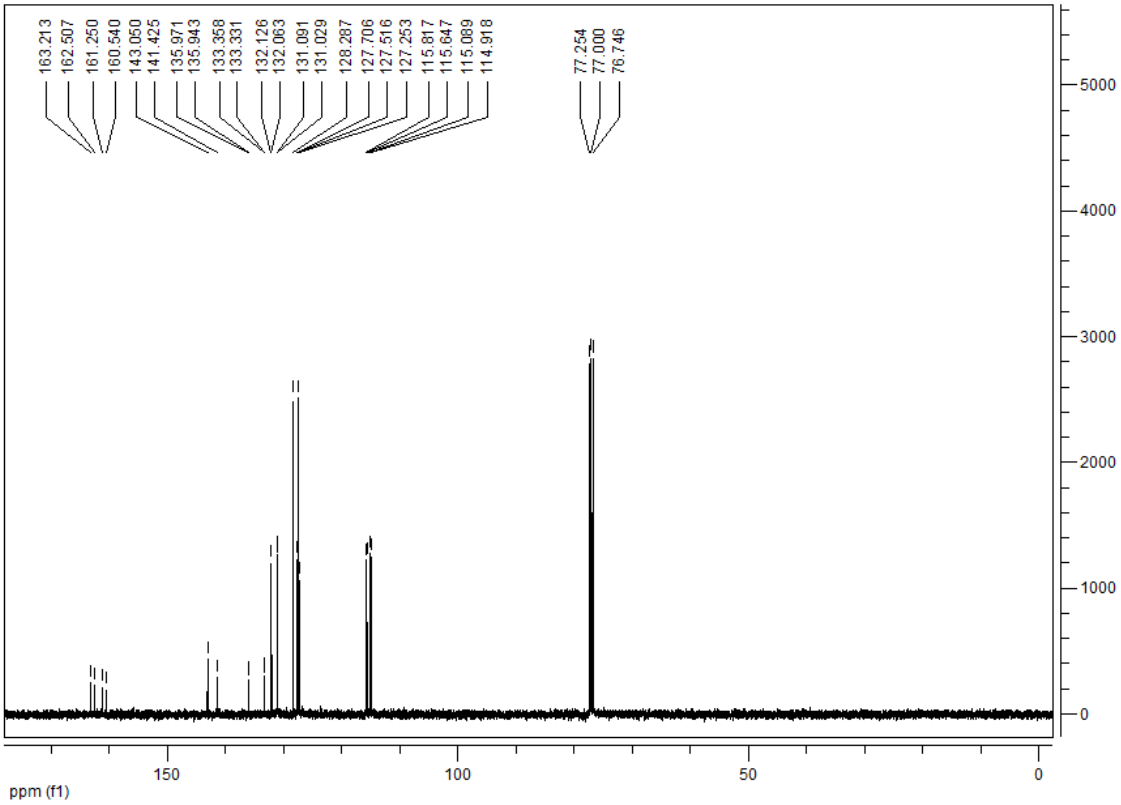
^{13}C NMR of 1,1,2-tri*m*-tolylethene (**3cd**)



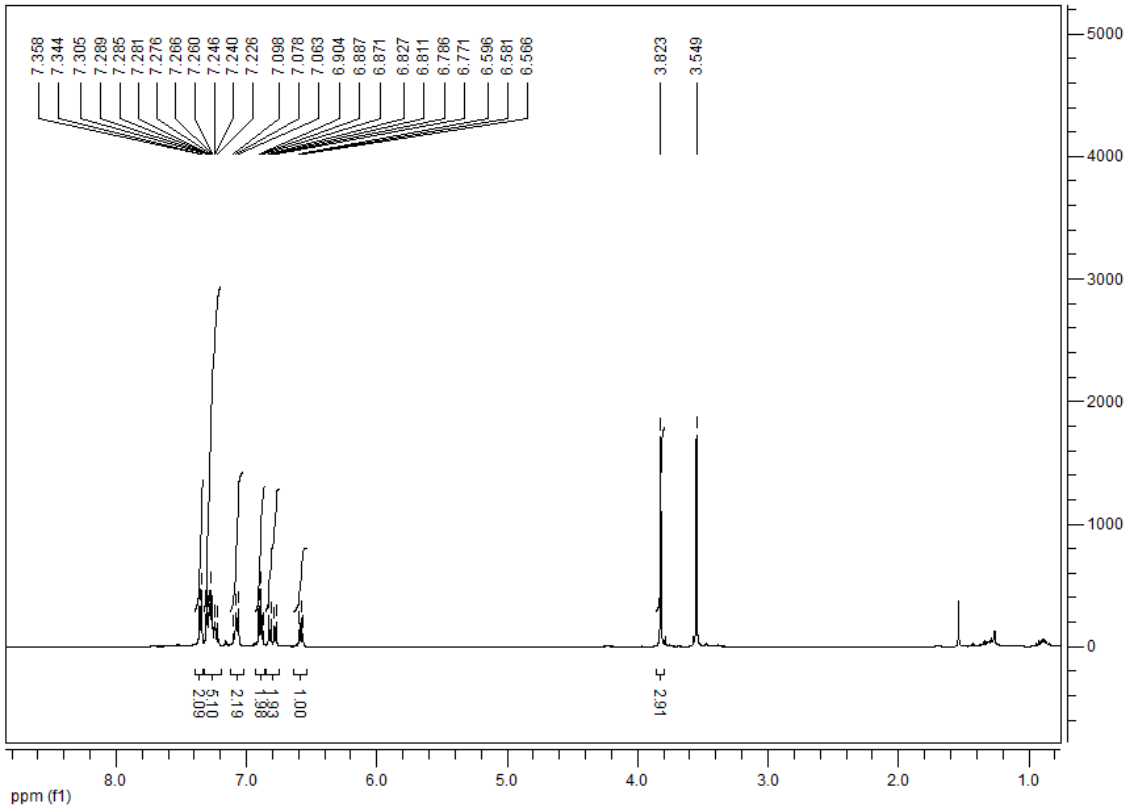
^{1}H NMR of (*Z*)-1-(2-phenyl-2-*p*-fluorophenylvinyl)-4-fluorobenzene (**3da**):



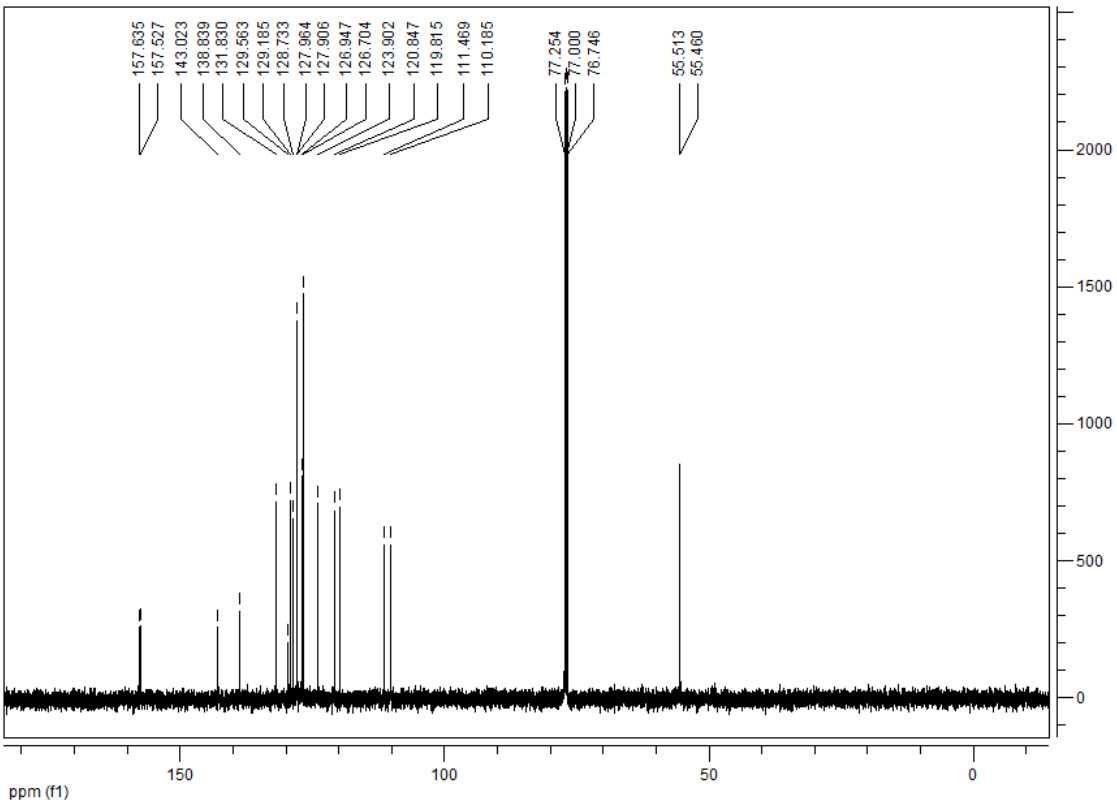
^{13}C NMR of (*Z*)-1-(2-phenyl-2-*p*-fluorophenylvinyl)-4-fluorobenzene (**3da**):



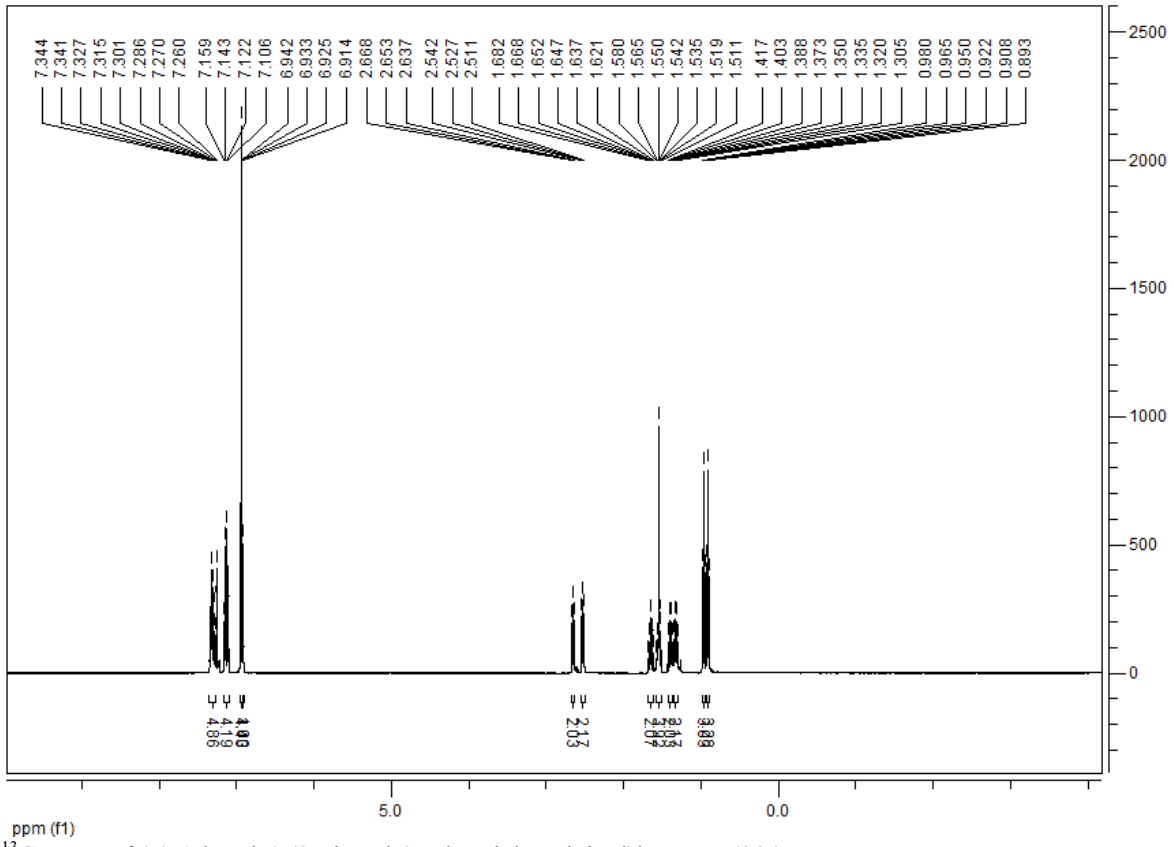
^{1}H NMR of (*Z*)-1-methoxy-2-(2-phenyl-2-*o*-methoxyphenylvinyl)benzene (**3ea**)



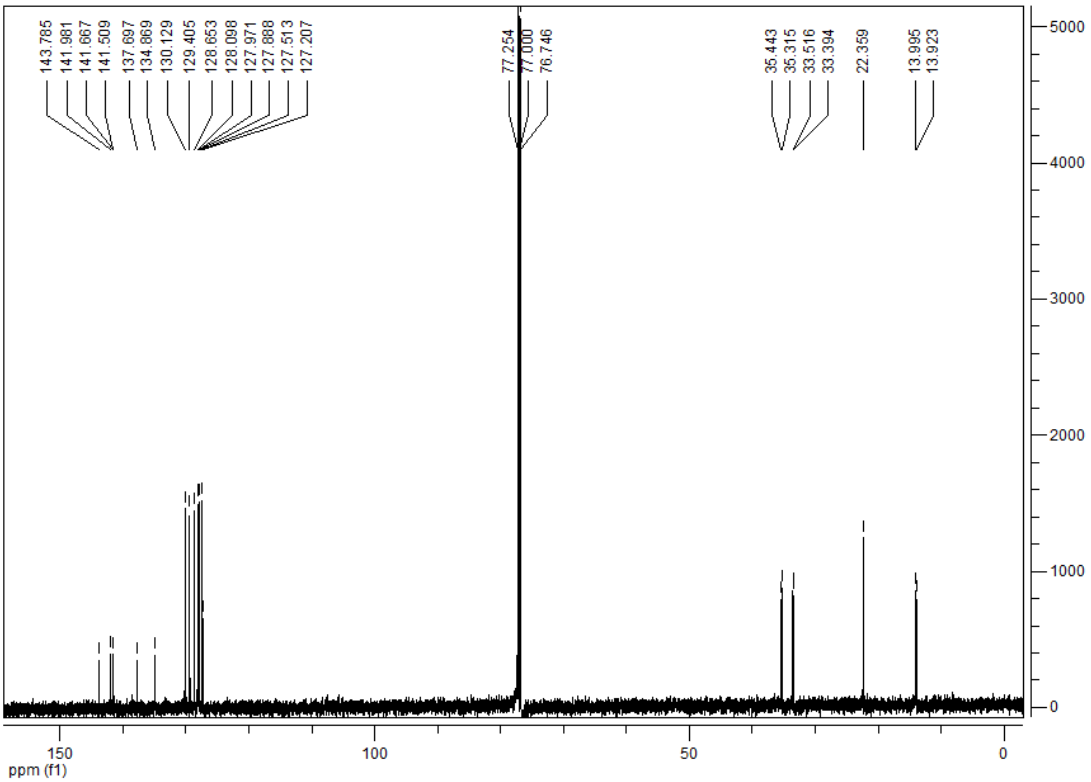
^{13}C NMR of (*Z*)-1-methoxy-2-(2-phenyl-2-*o*-methoxyphenylvinyl)benzene (**3ea**)



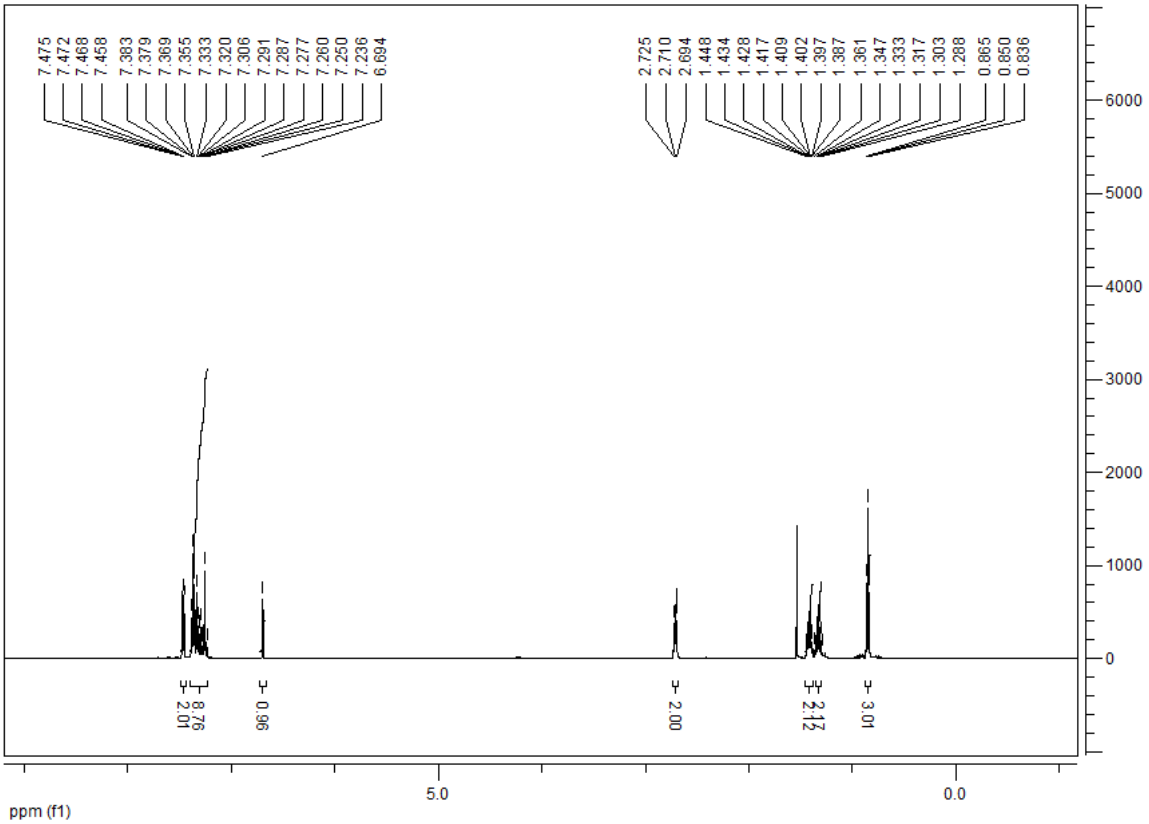
^{1}H NMR of (*Z*)-1-butyl-4-(2-phenyl-2-*p*-butylphenylvinyl)benzene (**3fa**):



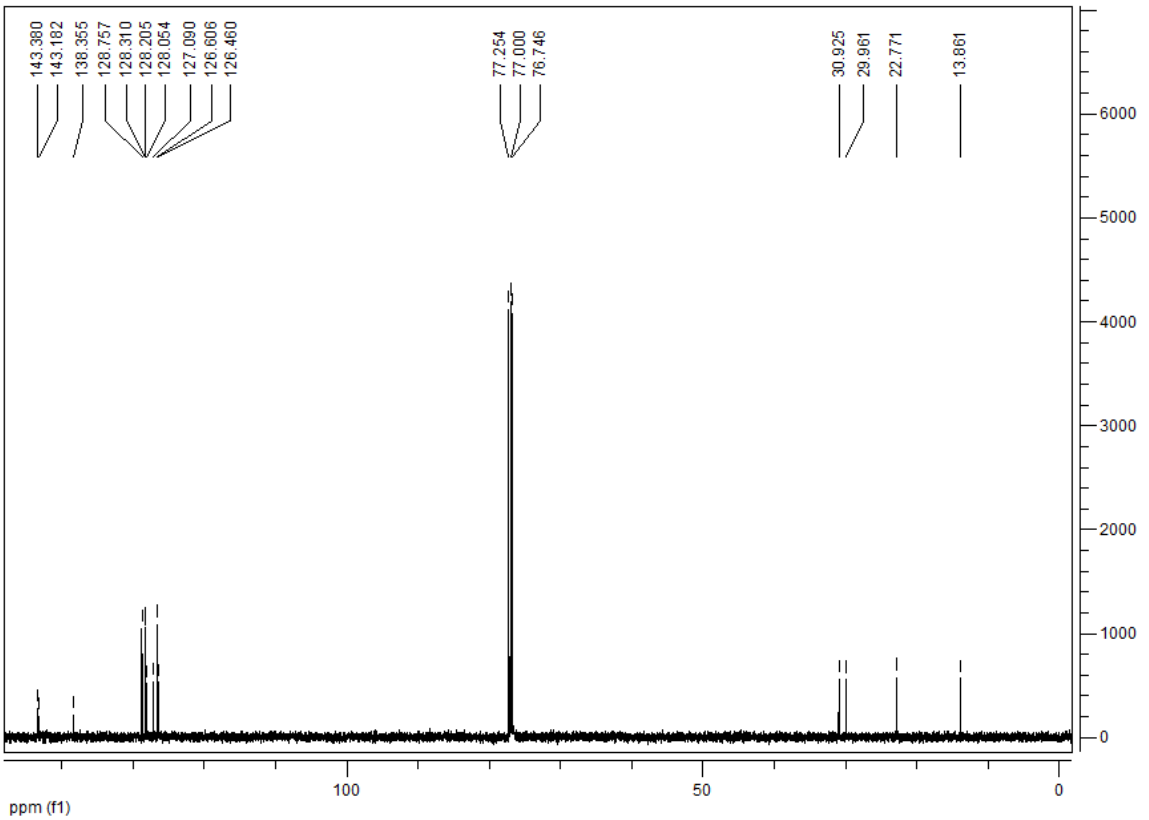
^{13}C NMR of (*Z*)-1-butyl-4-(2-phenyl-2-*p*-butylphenylvinyl)benzene (**3fa**):



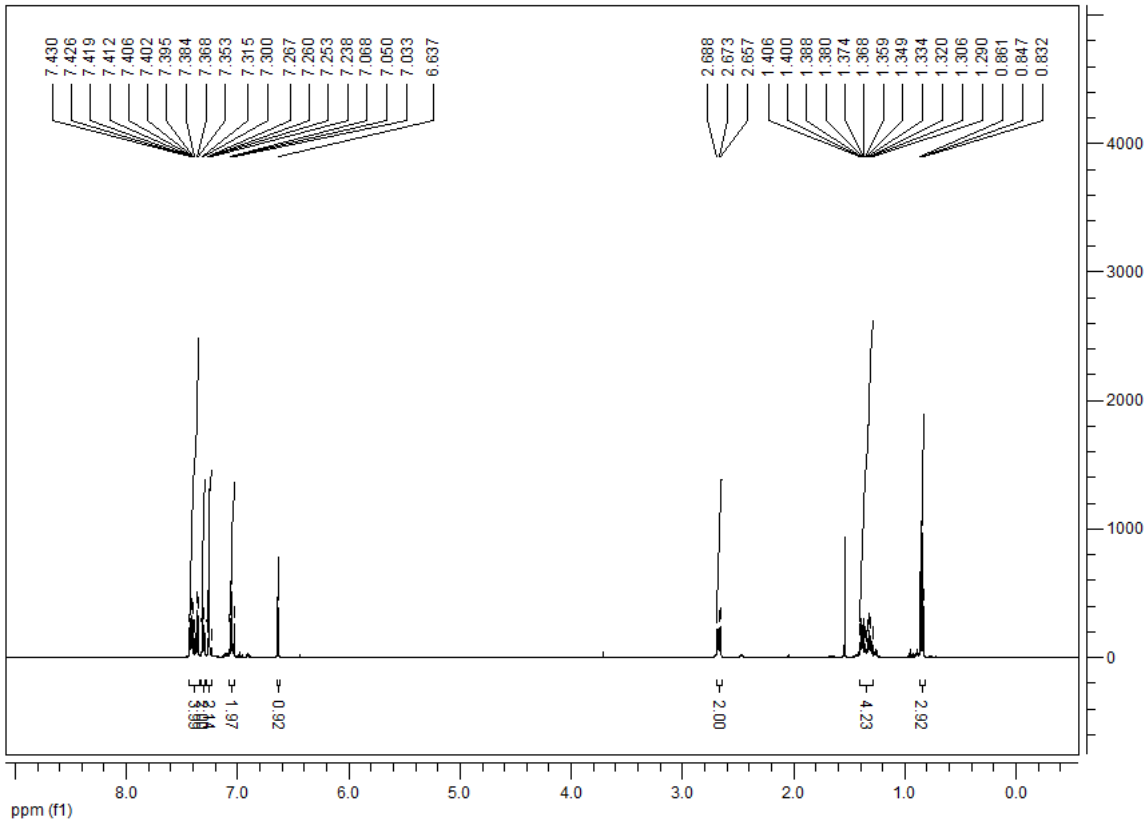
^{1}H NMR of (*E*)-1,2-diphenylhex-1-ene (**3ga**)



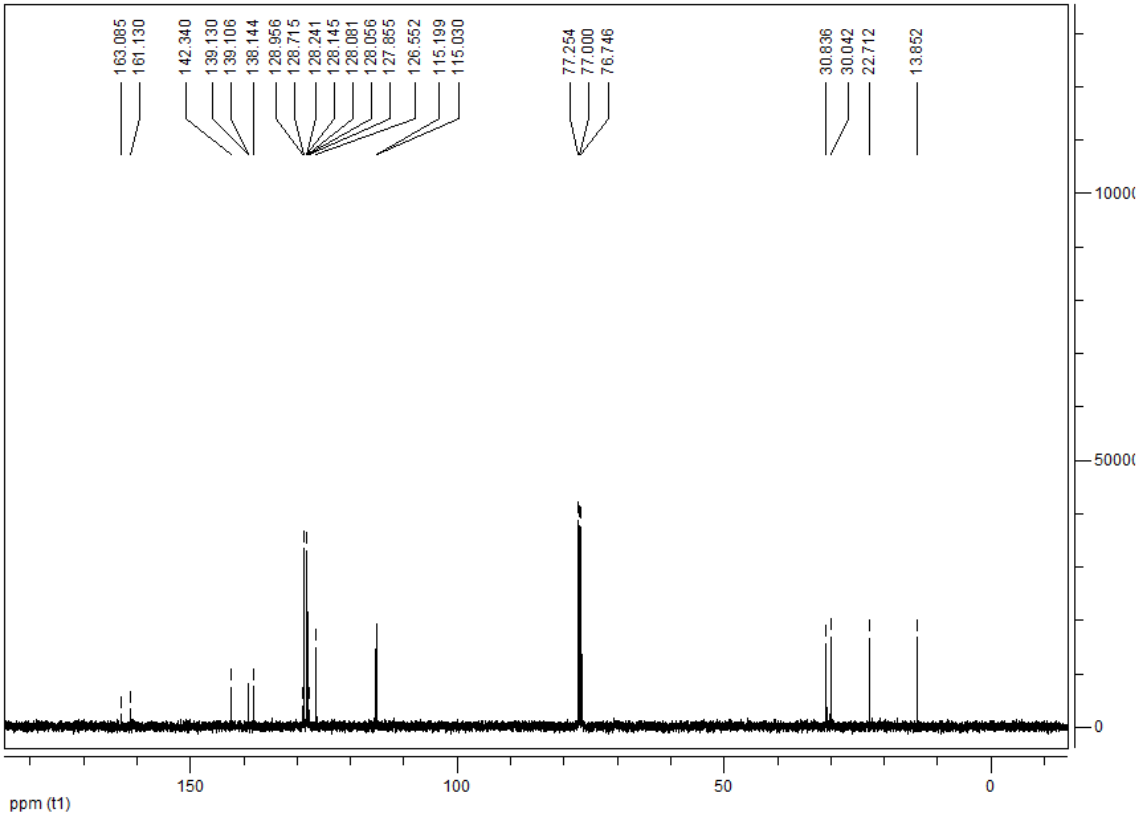
^{13}C NMR of (*E*)-1,2-diphenylhex-1-ene (**3ga**)



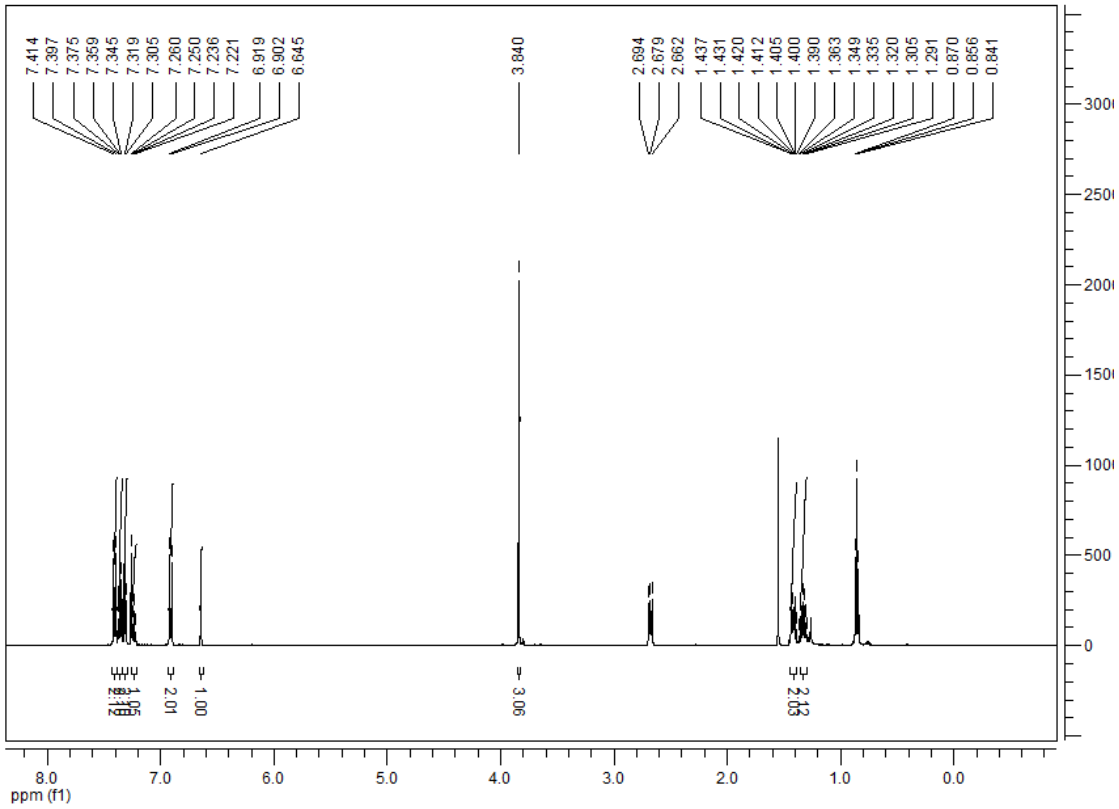
^{1}H NMR of (*E*)-2-(4-fluorophenyl)-1-phenyl-1-hexene (**3gb**):



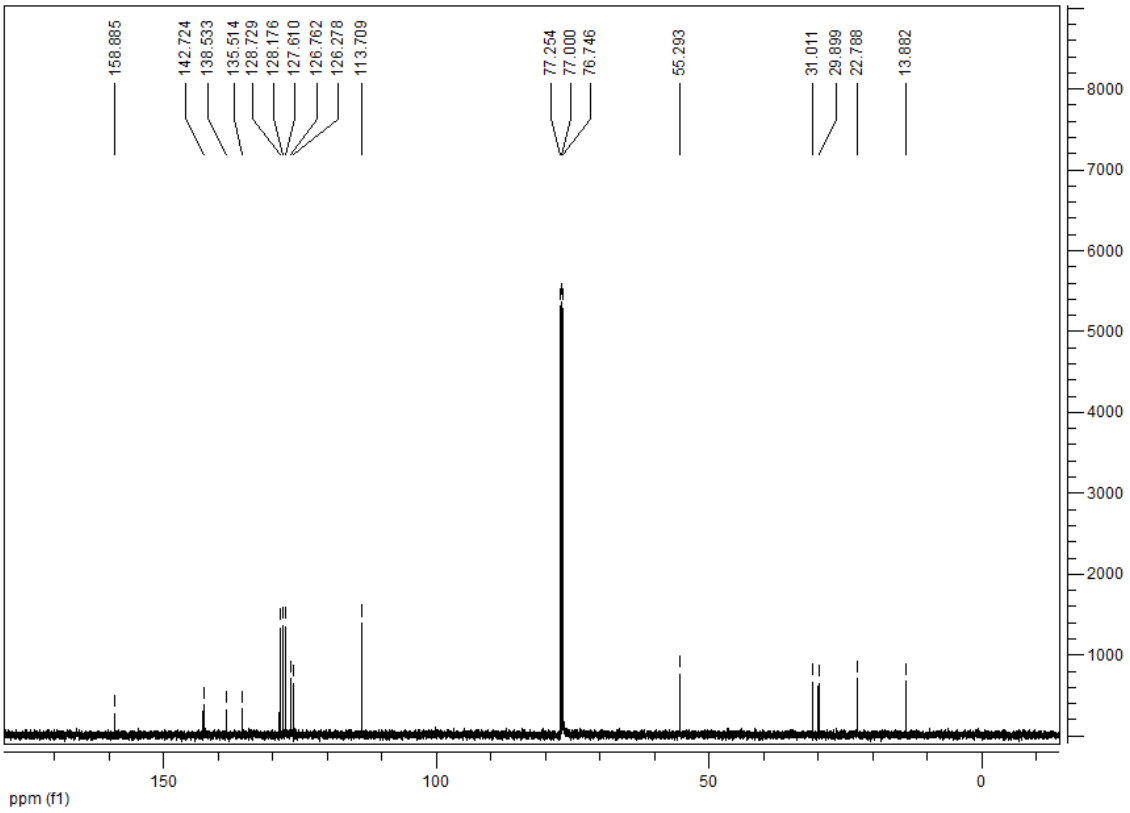
^{13}C NMR of (*E*)-2-(4-fluorophenyl)-1-phenyl-1-hexene (**3gb**):



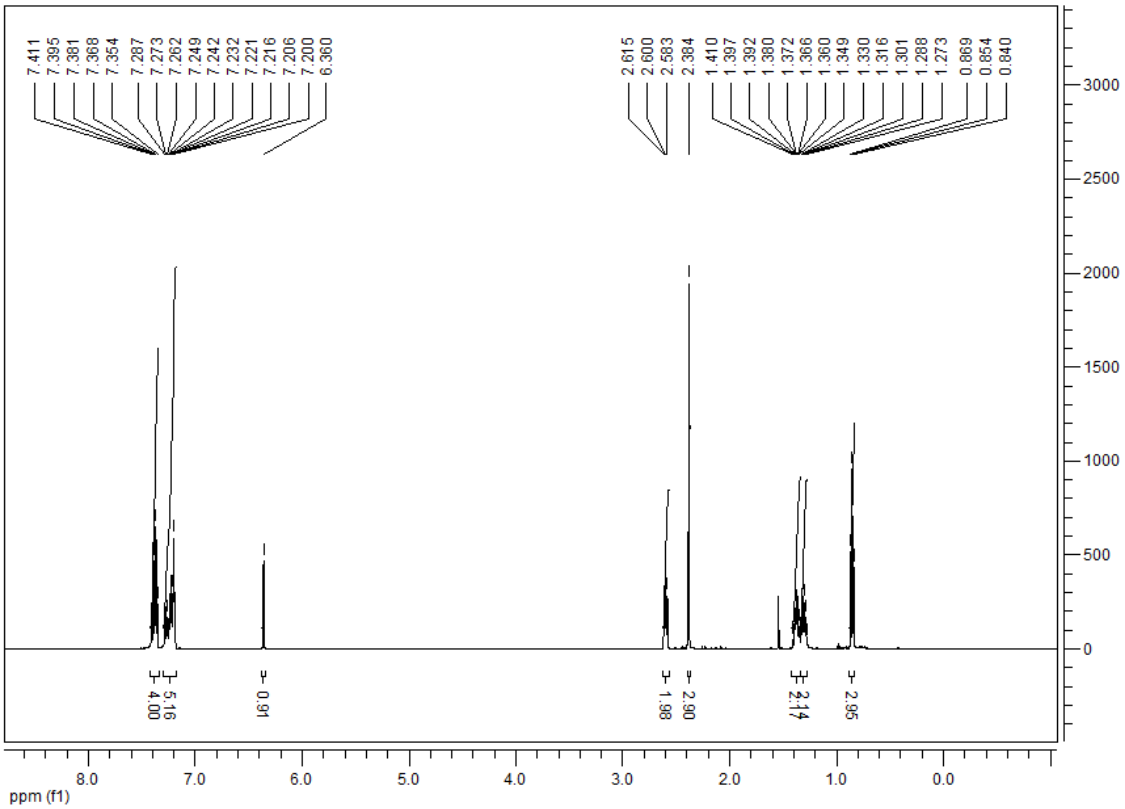
^{1}H NMR of (*E*)-2-(4-methoxyphenyl)-1-phenyl-1-hexene (**3gc**):



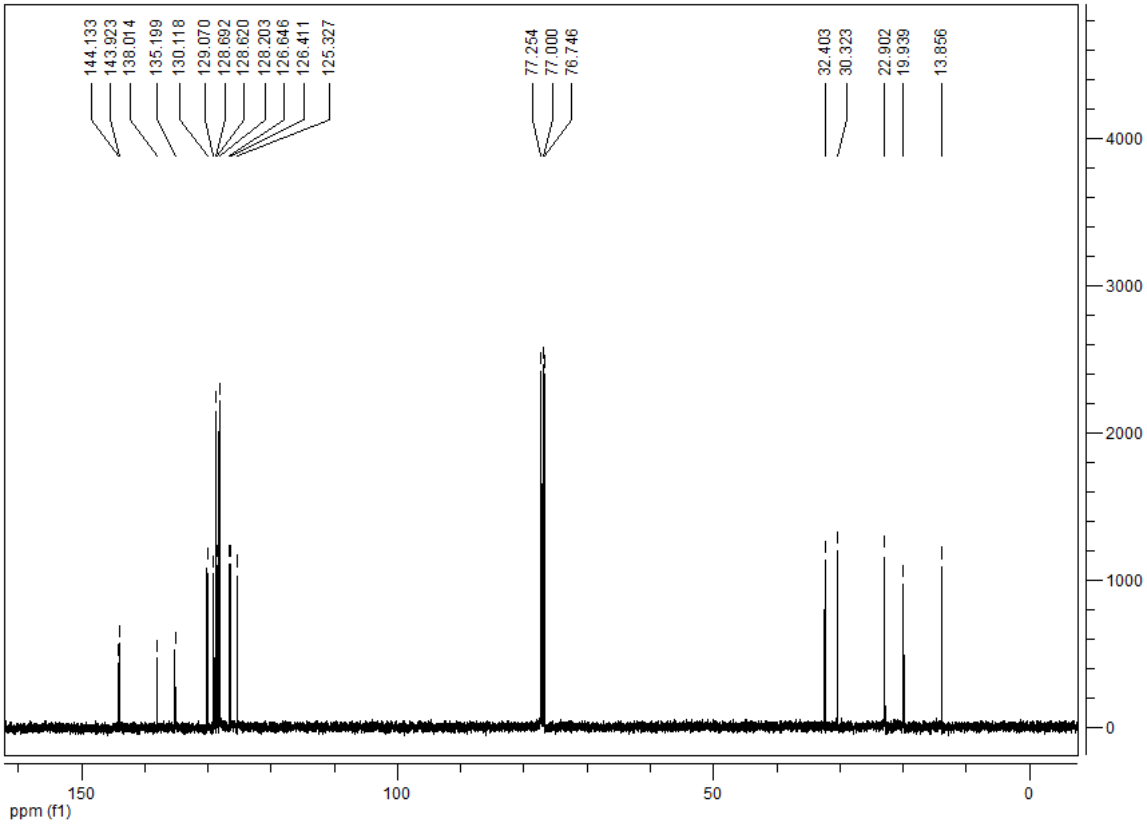
^{13}C NMR of (*E*)-2-(4-methoxyphenyl)-1-phenyl-1-hexene (**3gc**):



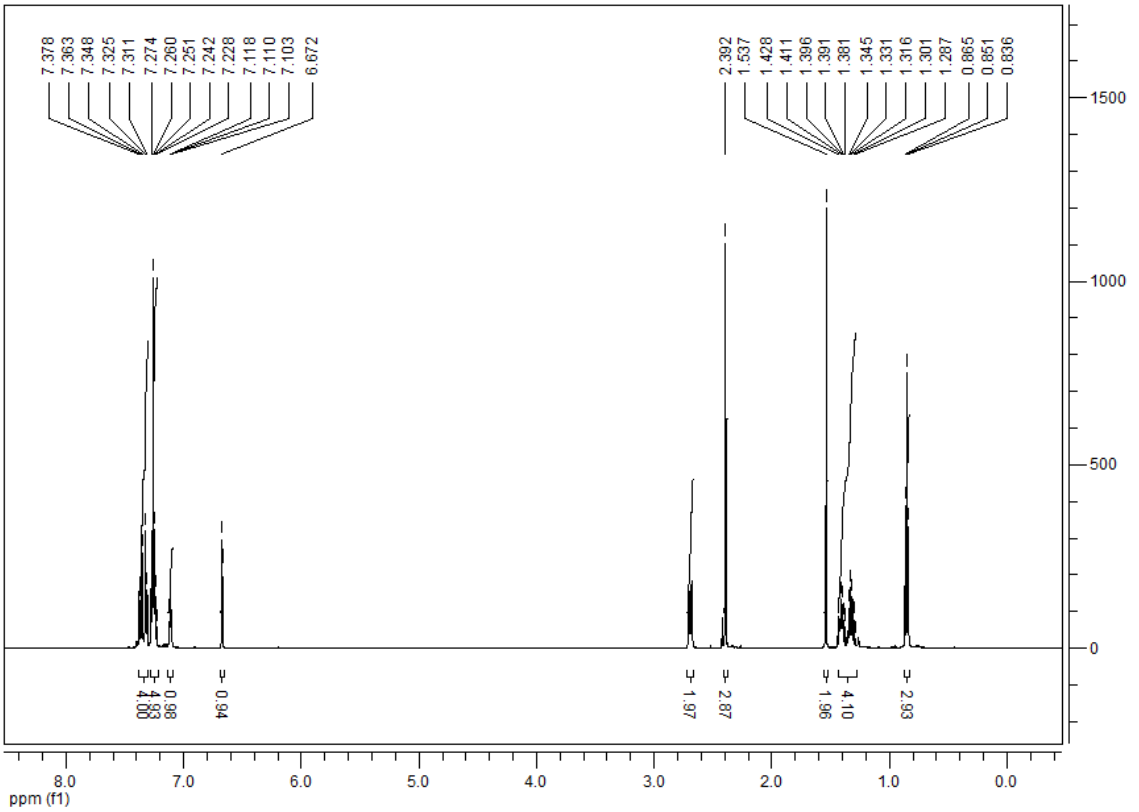
^{1}H NMR of (*E*)-2-(2-methylphenyl)-1-phenyl-1-hexene (**3gd**):



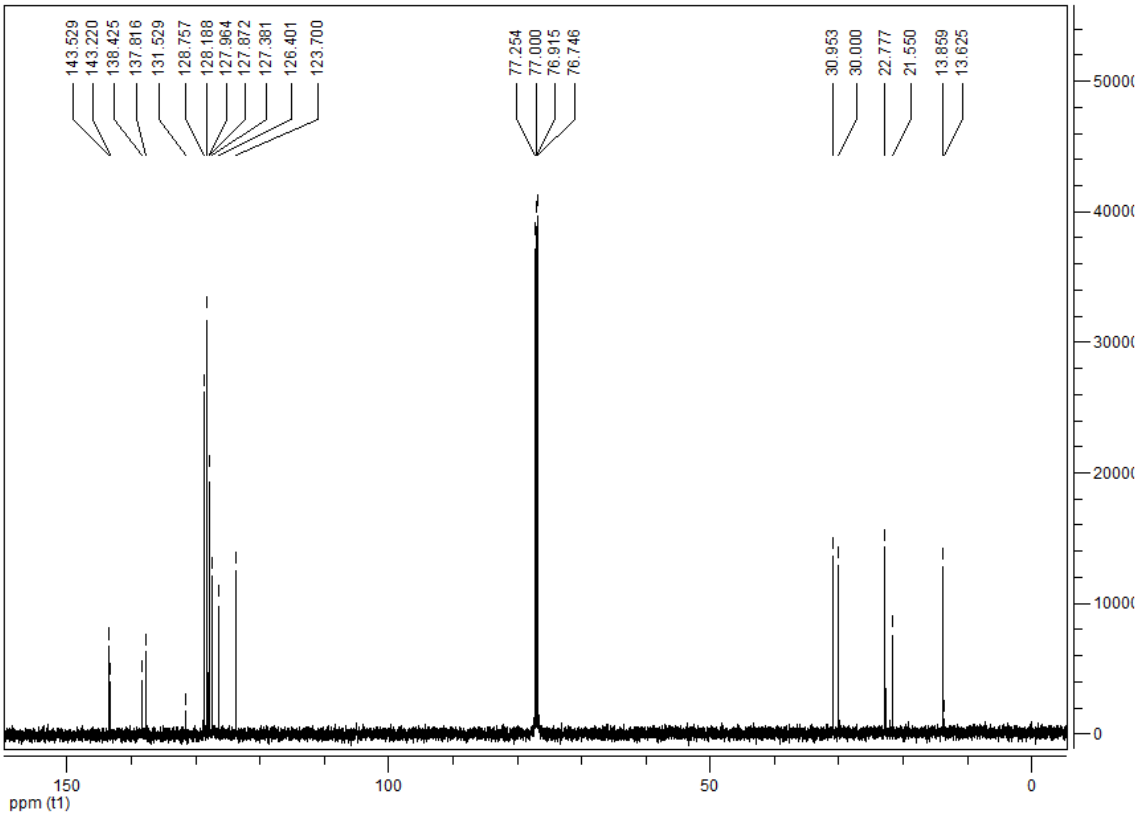
^{13}C NMR of (*E*)-2-(2-methylphenyl)-1-phenyl-1-hexene (**3gd**):



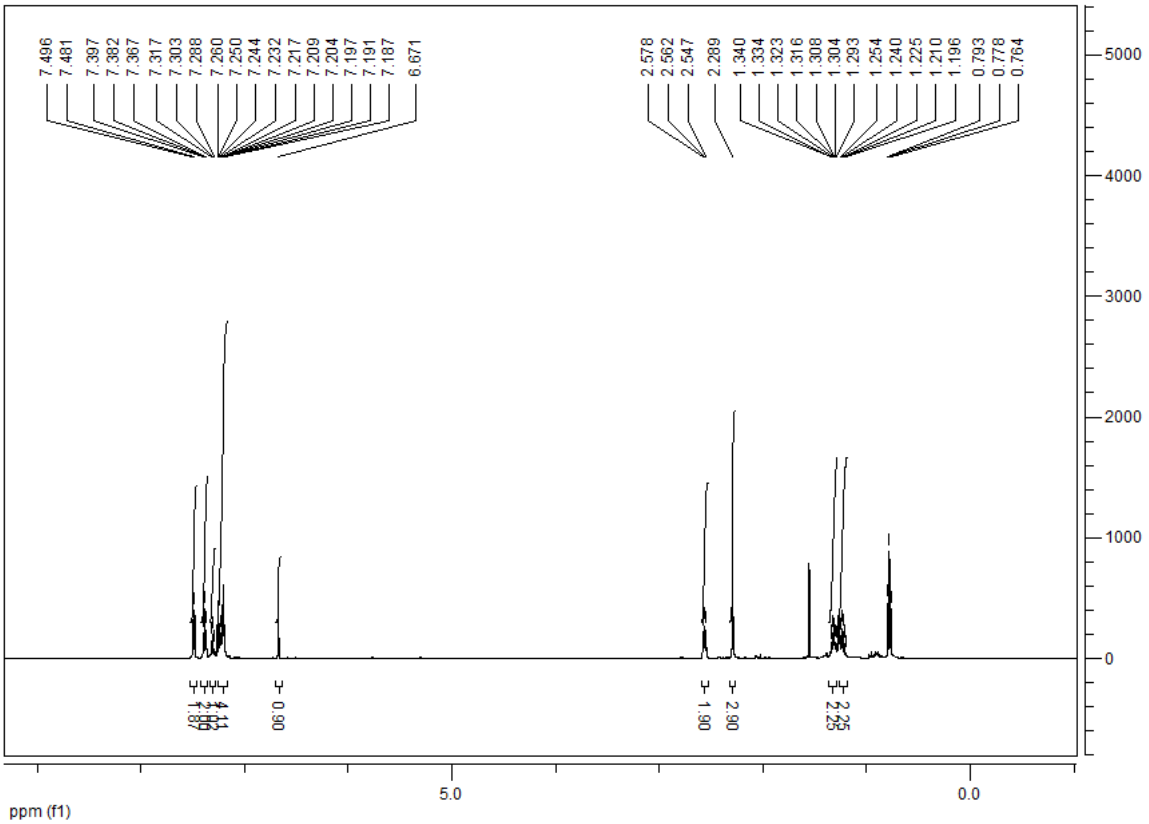
^{13}C NMR of (*E*)-2-(3-methylphenyl)-1-phenyl-1-hexene (**3ge**):



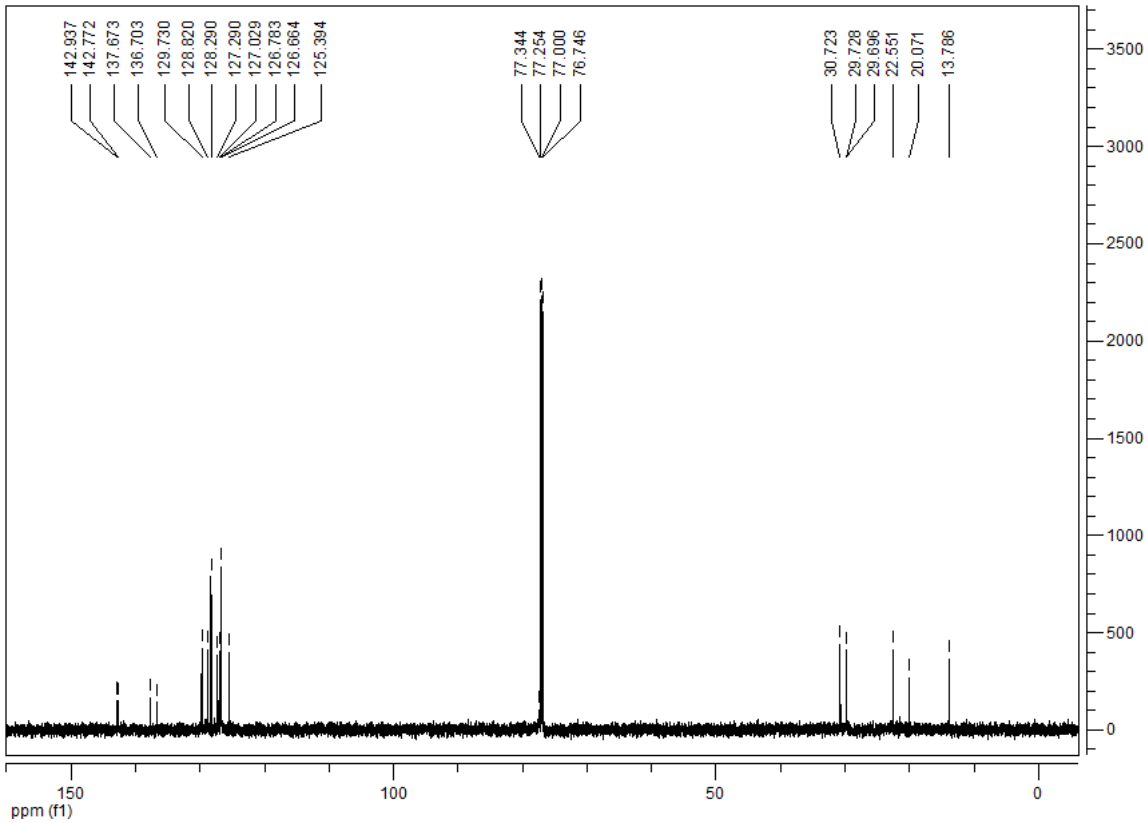
^{13}C NMR of (*E*)-2-(3-methylphenyl)-1-phenyl-1-hexene (**3ge**):



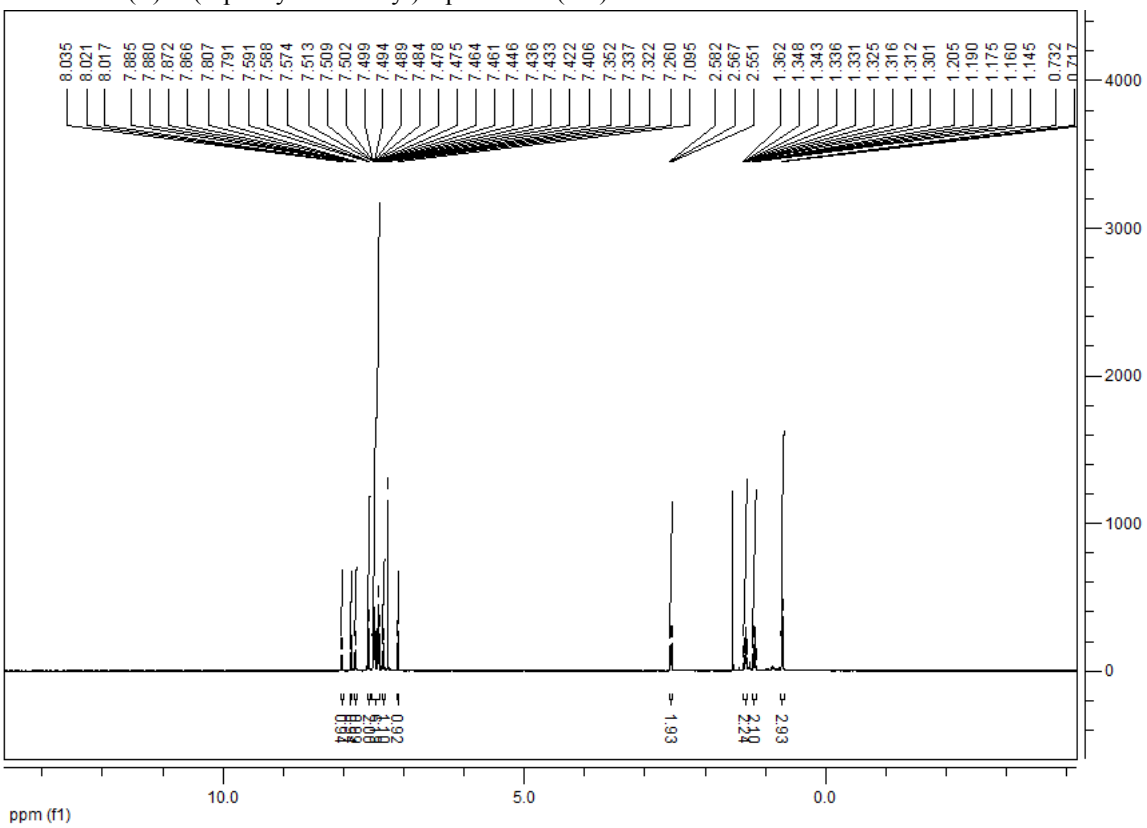
^{1}H NMR of (E)-1-methyl-2-(2-phenylhex-1-enyl)benzene (**3ha**):



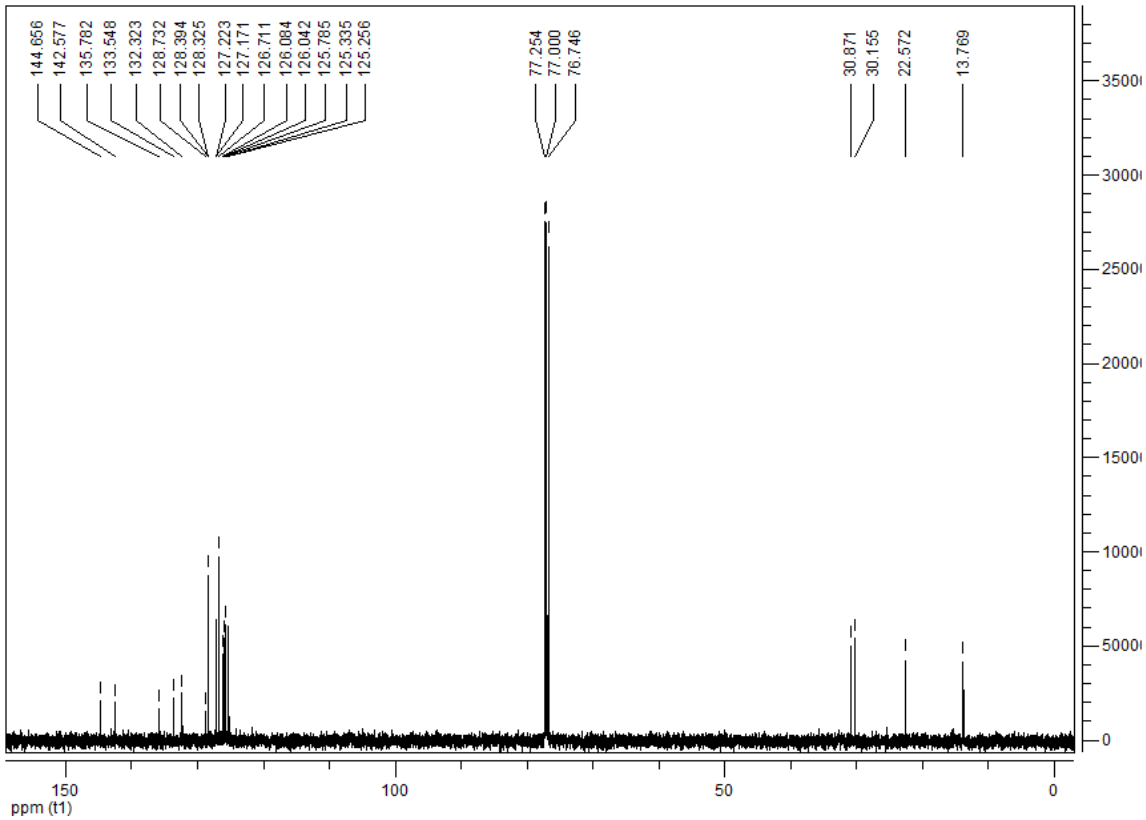
^{13}C NMR of (E)-1-methyl-2-(2-phenylhex-1-enyl)benzene (**3ha**):



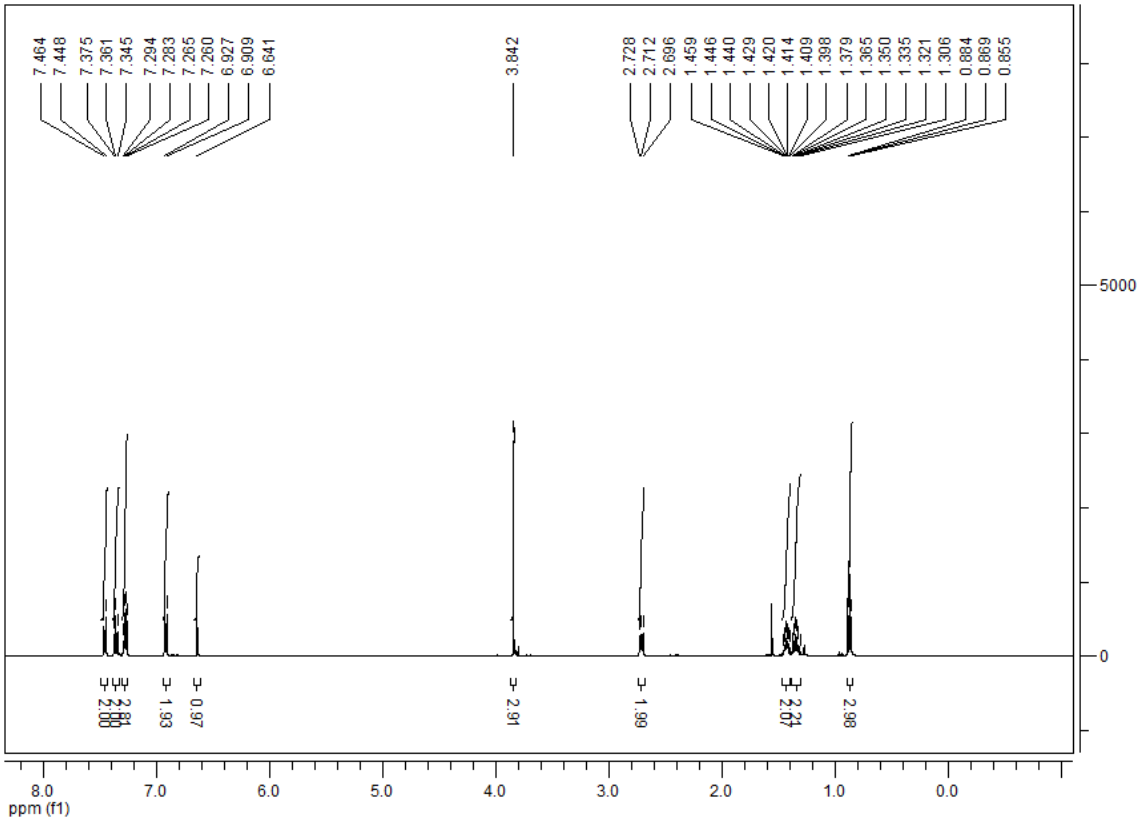
^{1}H NMR of (*E*)-1-(2-phenylhex-1-enyl)naphthalene (**3ia**):



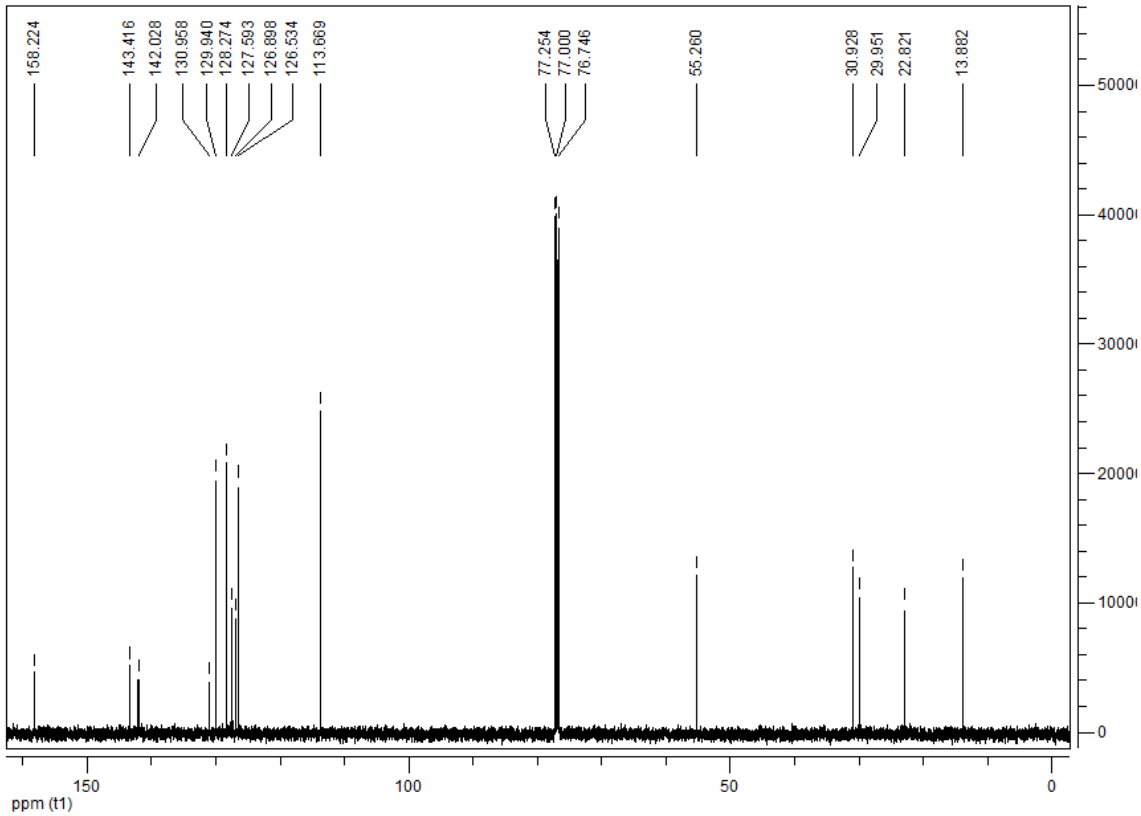
^{13}C NMR of (*E*)-1-(2-phenylhex-1-enyl)naphthalene (**3ia**):



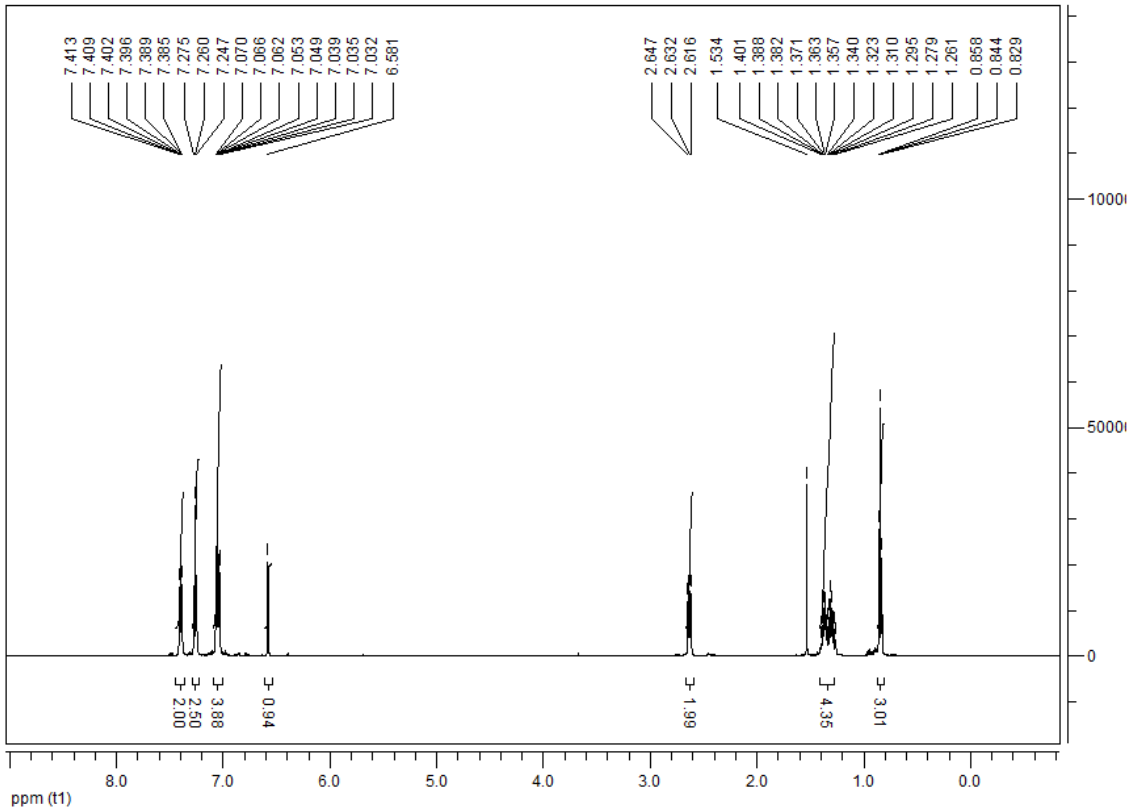
^{1}H NMR of (*E*)-1-methoxy-4-(2-phenylhex-1-enyl)benzene (**3ja**):



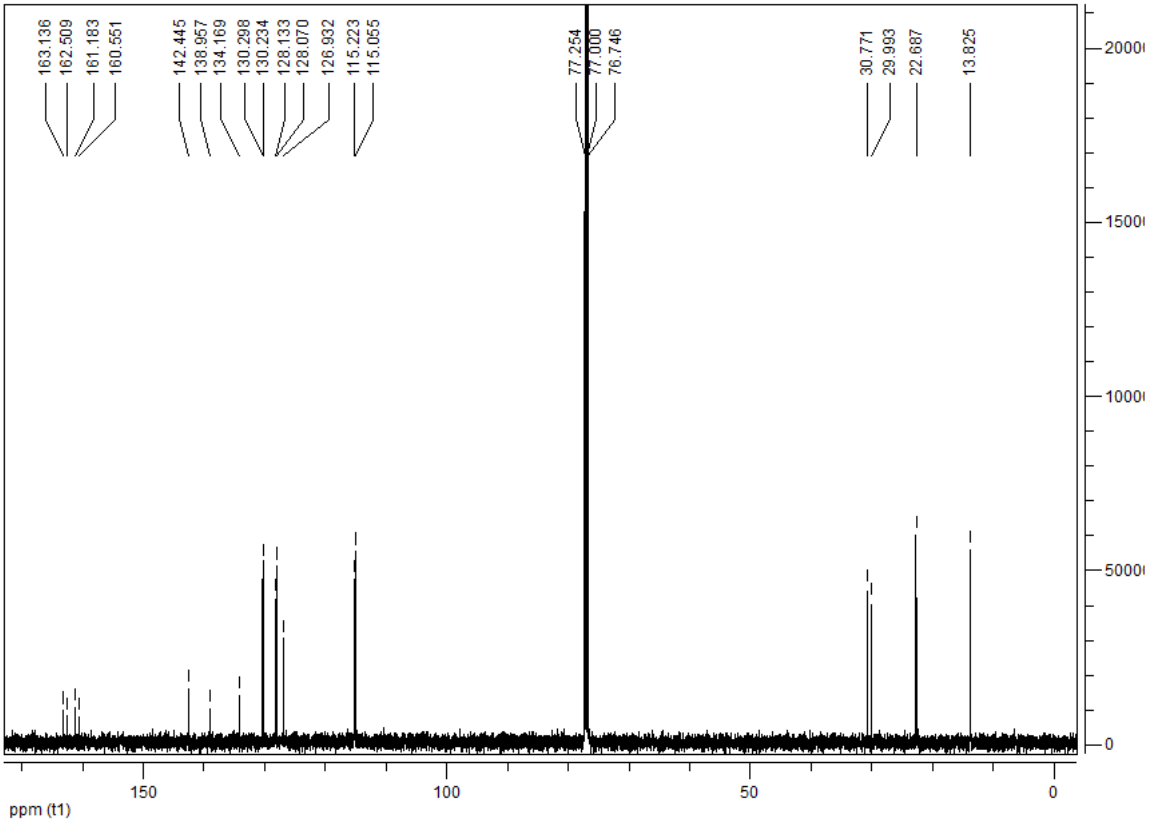
^{13}C NMR of (*E*)-1-methoxy-4-(2-phenylhex-1-enyl)benzene (**3ja**):



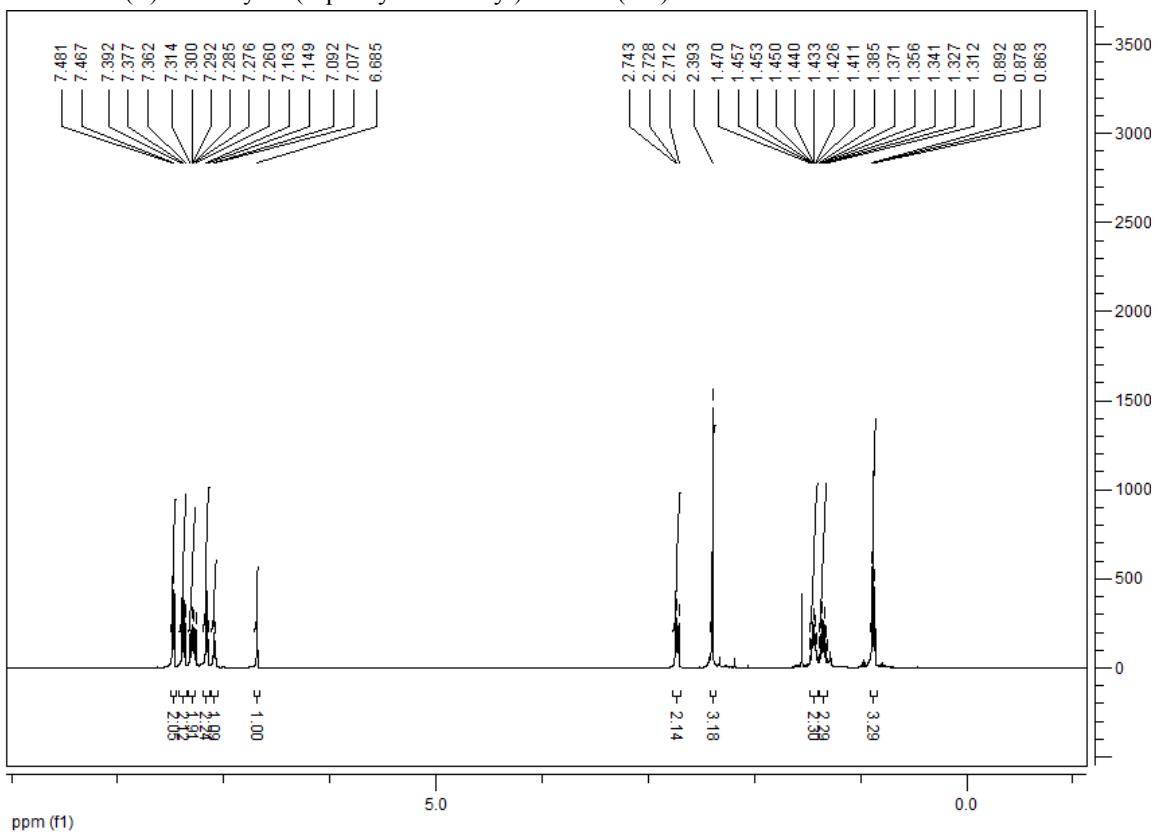
^{1}H NMR of (*E*)-1,2-bis(4-fluorophenyl)hex-1-ene (**3ka**):



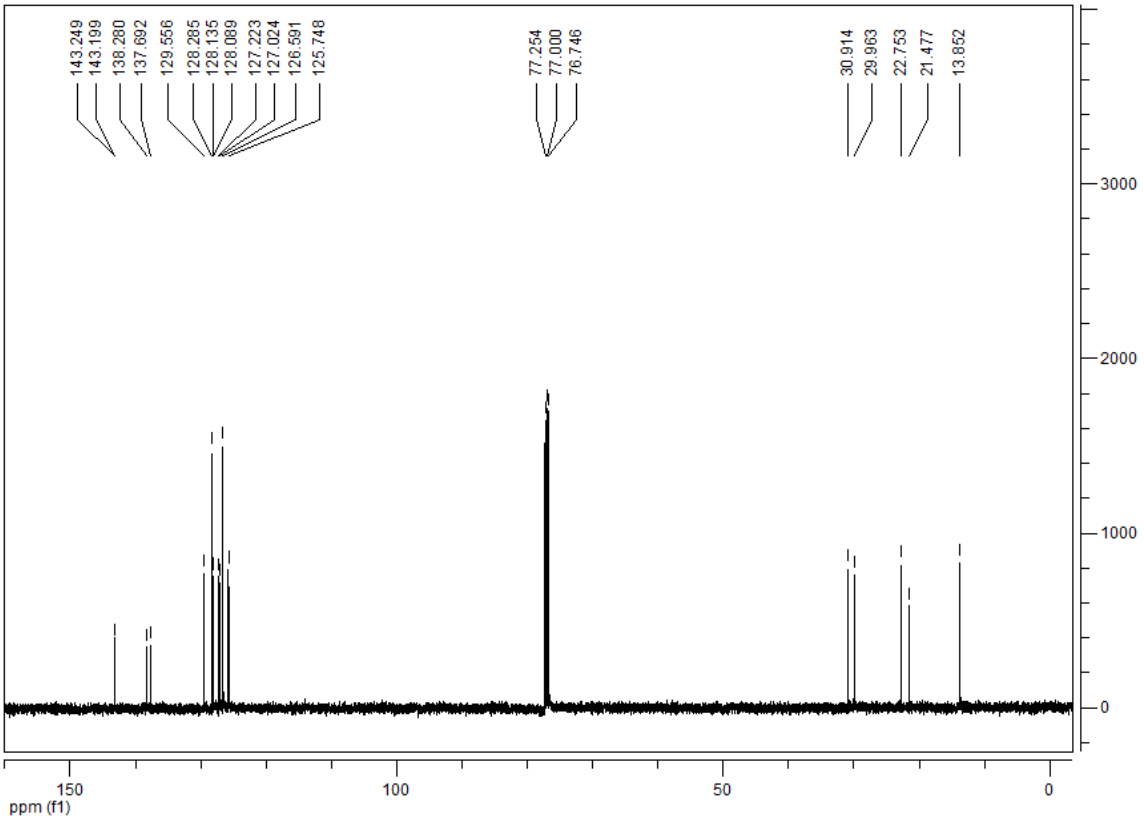
^{13}C NMR of (*E*)-1,2-bis(4-fluorophenyl)hex-1-ene (**3ka**):



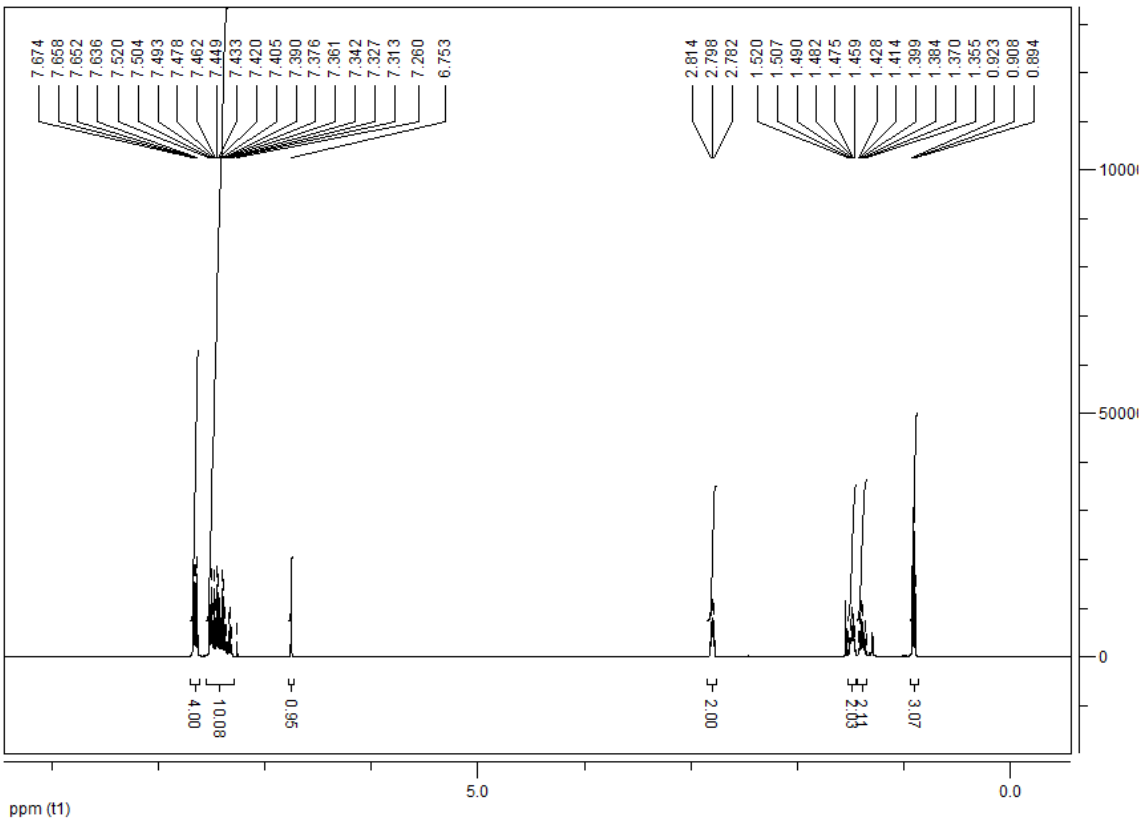
^{1}H NMR of (*E*)-1-methyl-3-(2-phenylhex-1-enyl)benzene (**3la**):



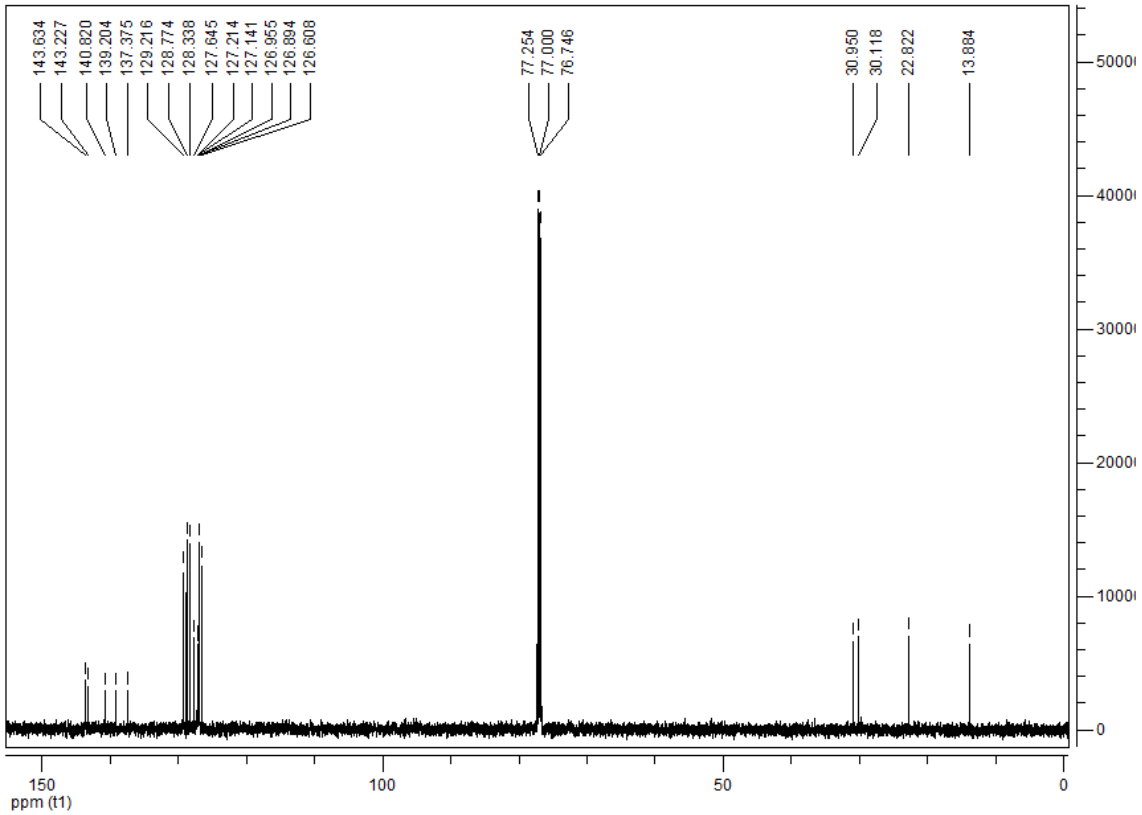
^{13}C NMR of (*E*)-1-methyl-3-(2-phenylhex-1-enyl)benzene (**3la**):



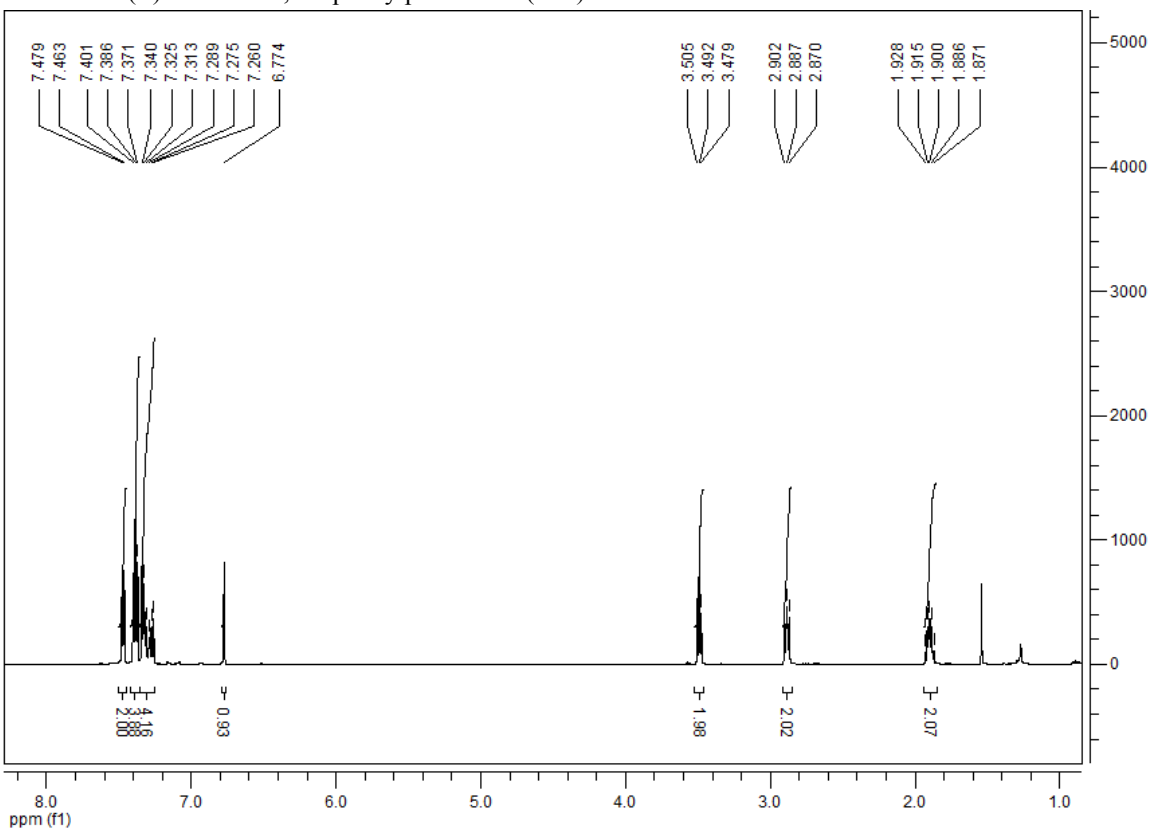
^{1}H NMR of (*E*)-1-phenyl-4-(2-phenylhex-1-enyl)benzene **(3ma)**:



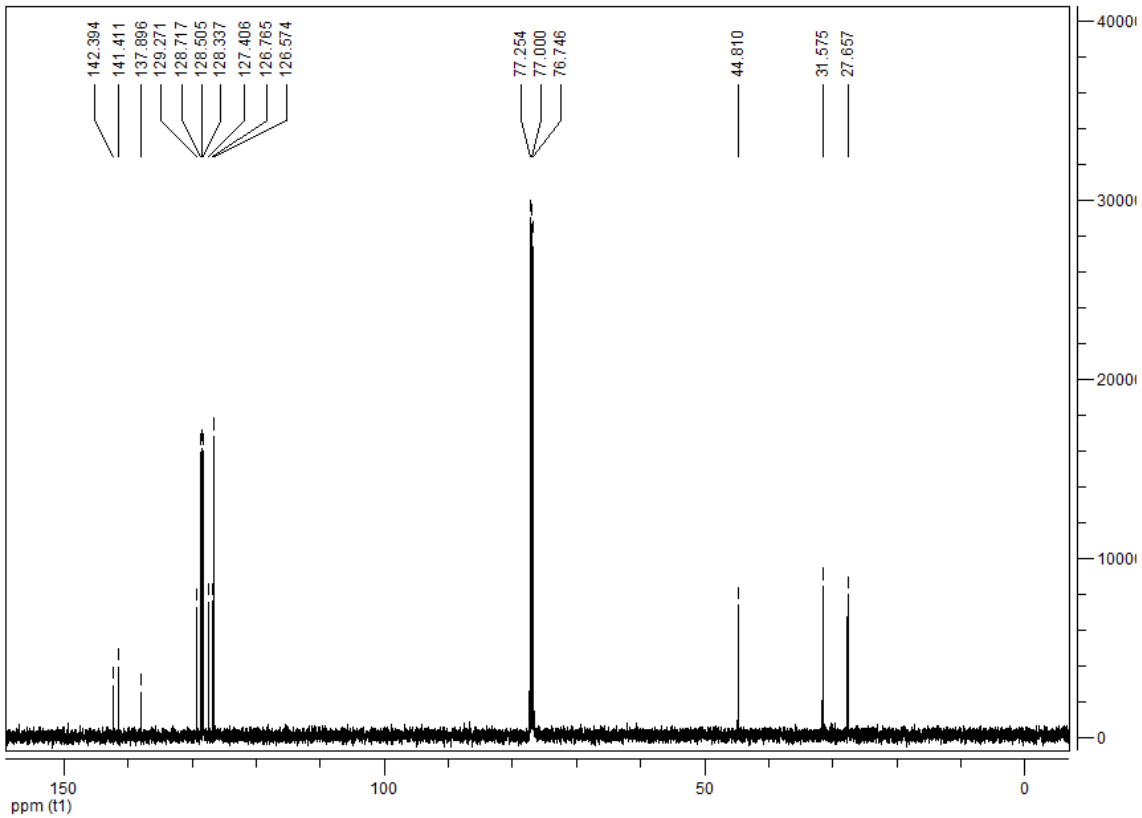
^{13}C NMR of (*E*)-1-phenyl-4-(2-phenylhex-1-enyl)benzene **(3ma)**:



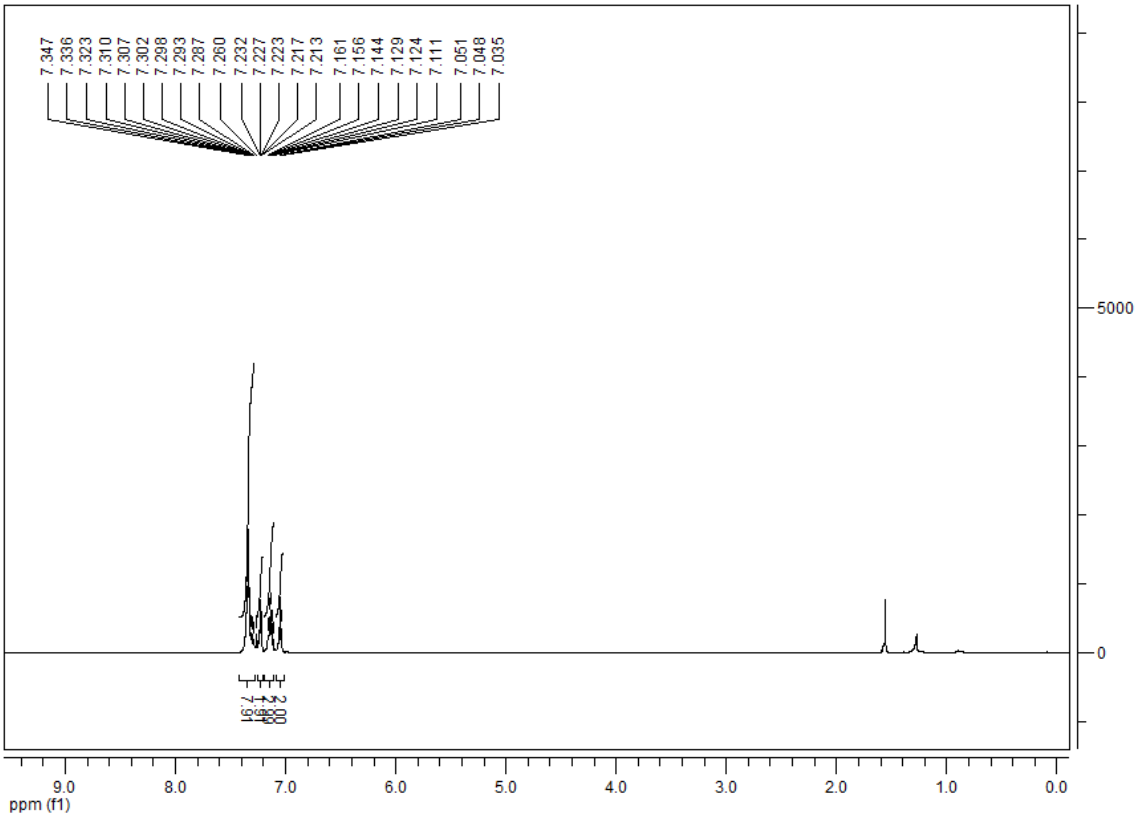
^{1}H NMR of (*E*)-5-chloro-1,2-diphenylpent-1-ene (**3na**):



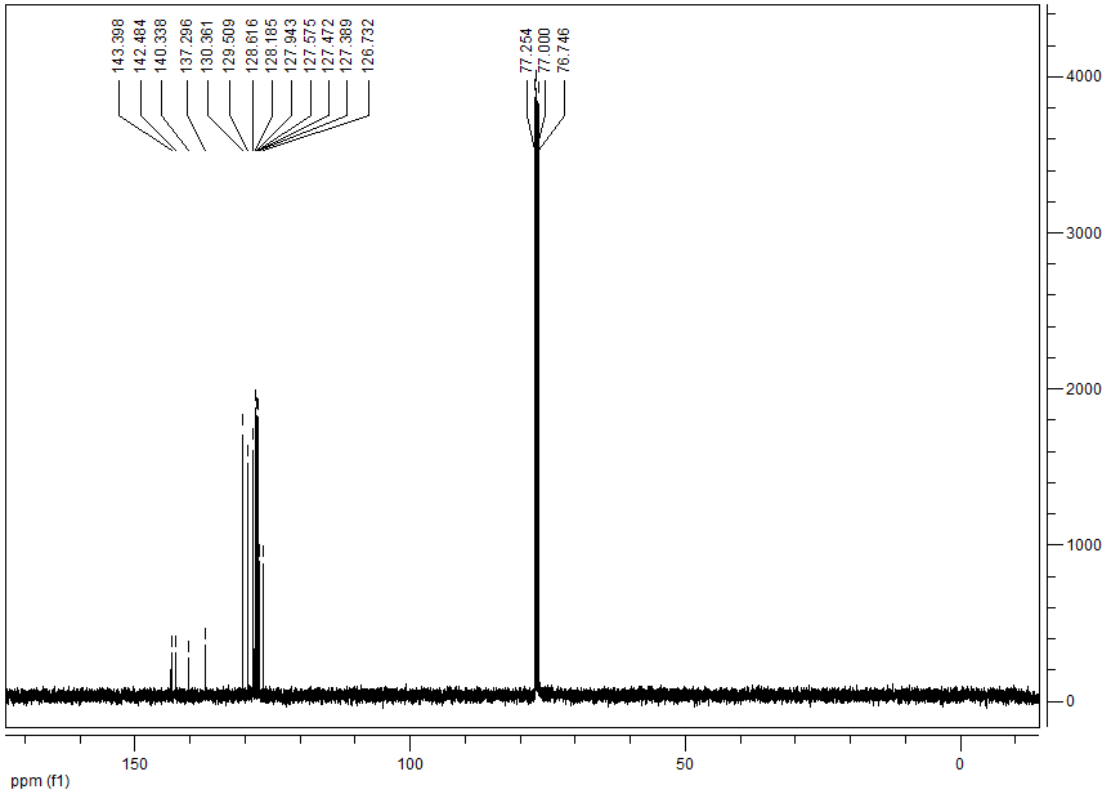
^{13}C NMR of (*E*)-5-chloro-1,2-diphenylpent-1-ene (**3na**):



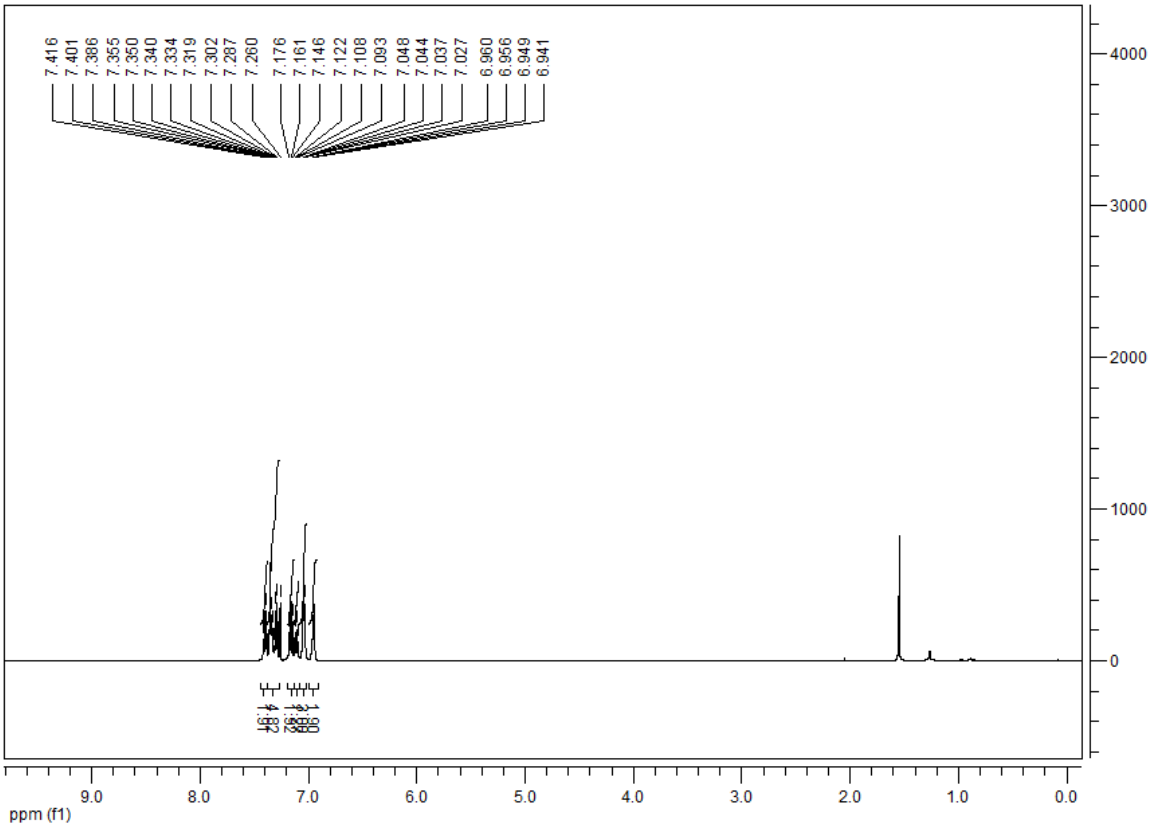
^{1}H NMR of 2-Deuterio-1,1,2-triphenylethene (**3aa-*d***):



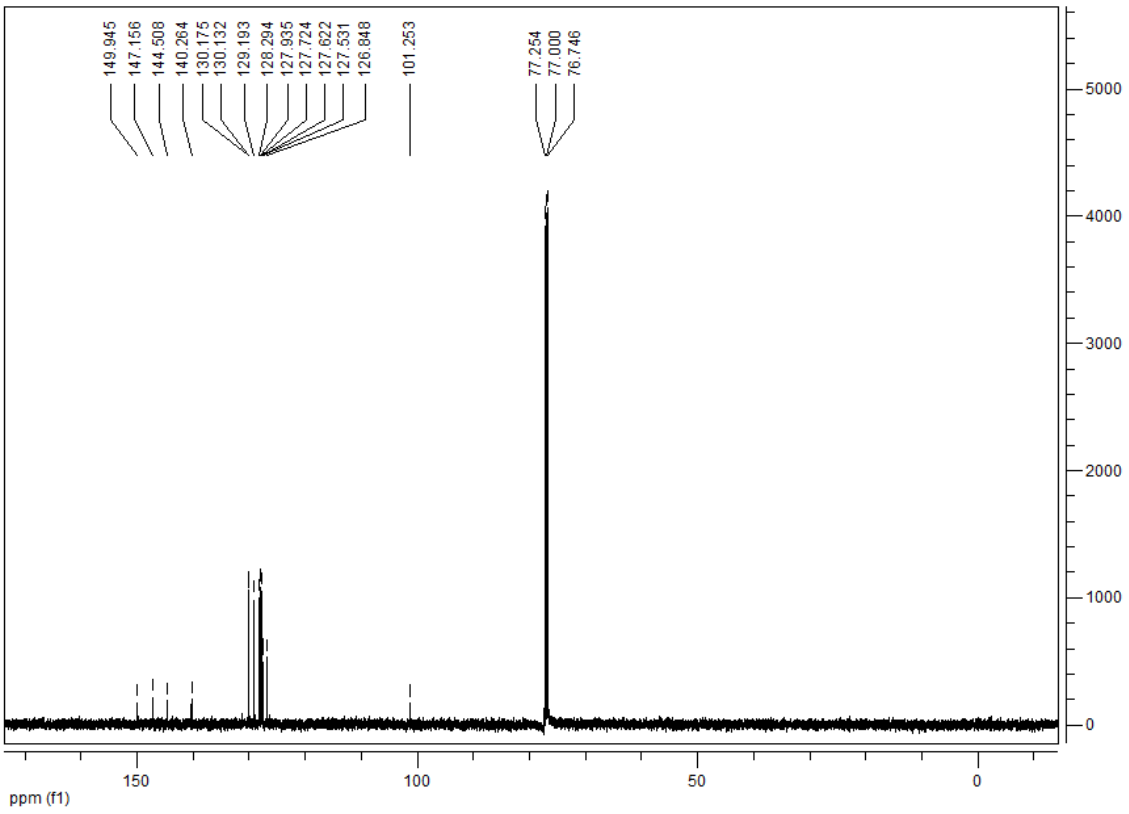
^{13}C NMR of 2-Deuterio-1,1,2-triphenylethene (**3aa-*d***):



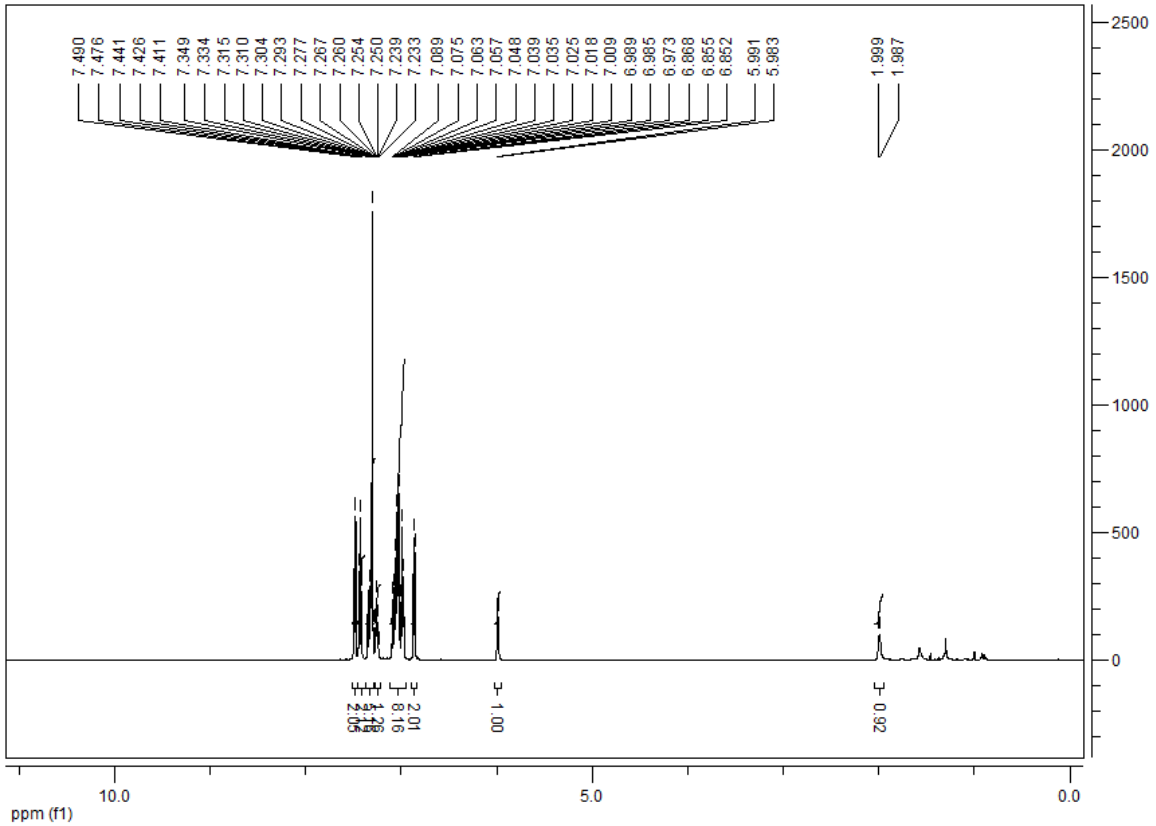
^{1}H NMR of 1-iodo-1,2,2-triphenylethene (**4aab**)



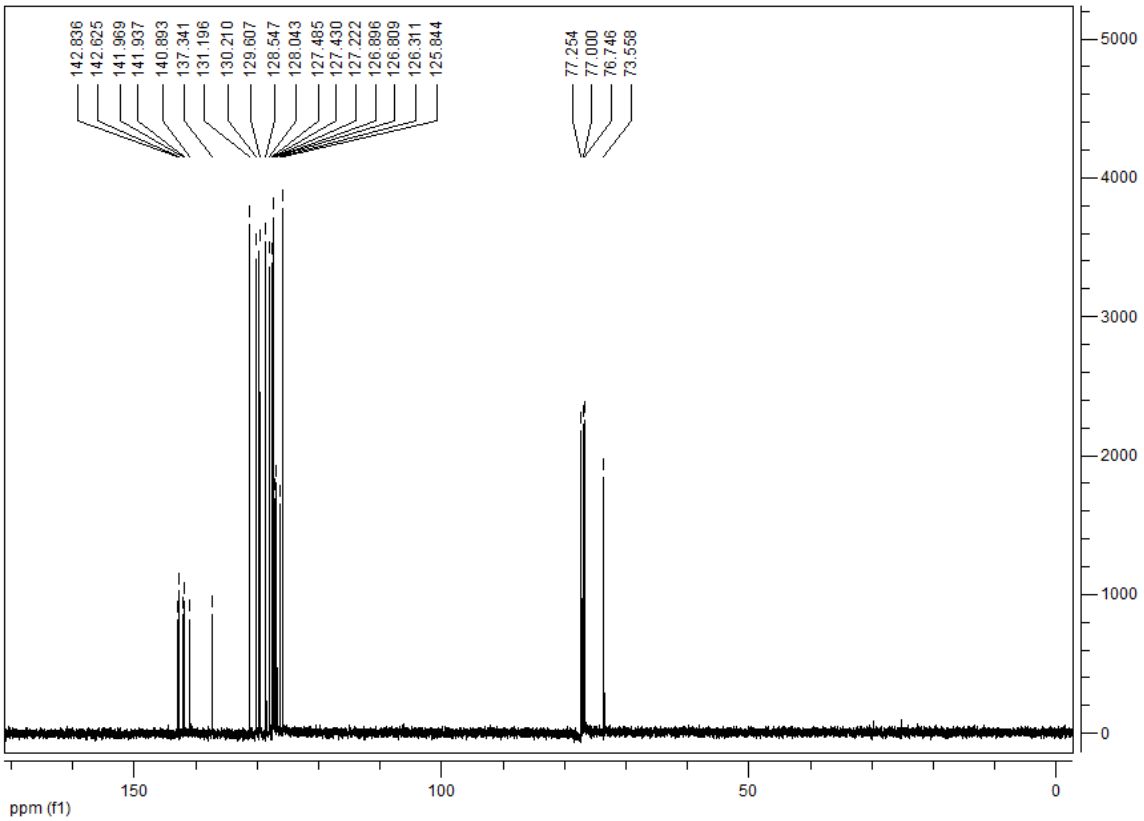
^{13}C NMR of 1-iodo-1,2,2-triphenylethene (**4aab**):



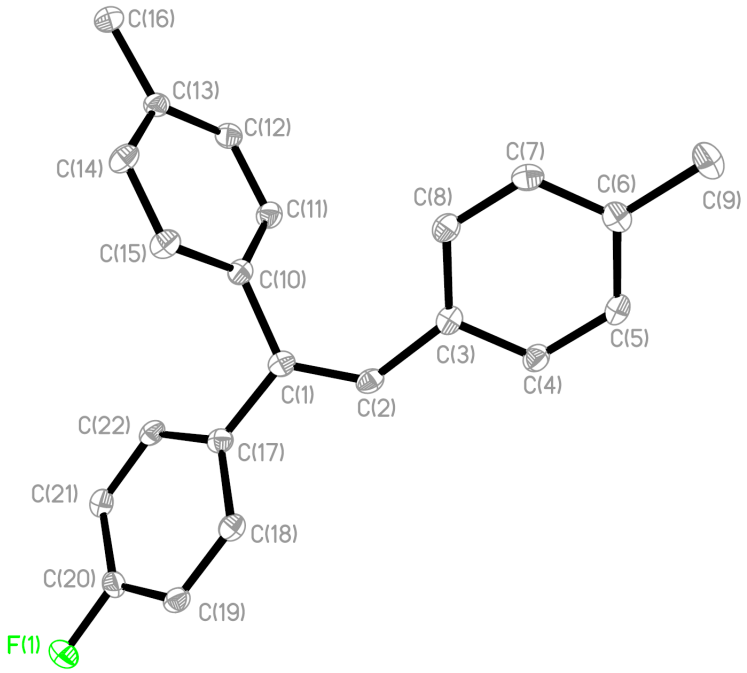
^{1}H NMR of 1,2,3,3-tetraphenylprop-2-en-1-ol (**4aac**):



^{13}C NMR of 1,2,3,3-tetraphenylprop-2-en-1-ol (**4aac**):



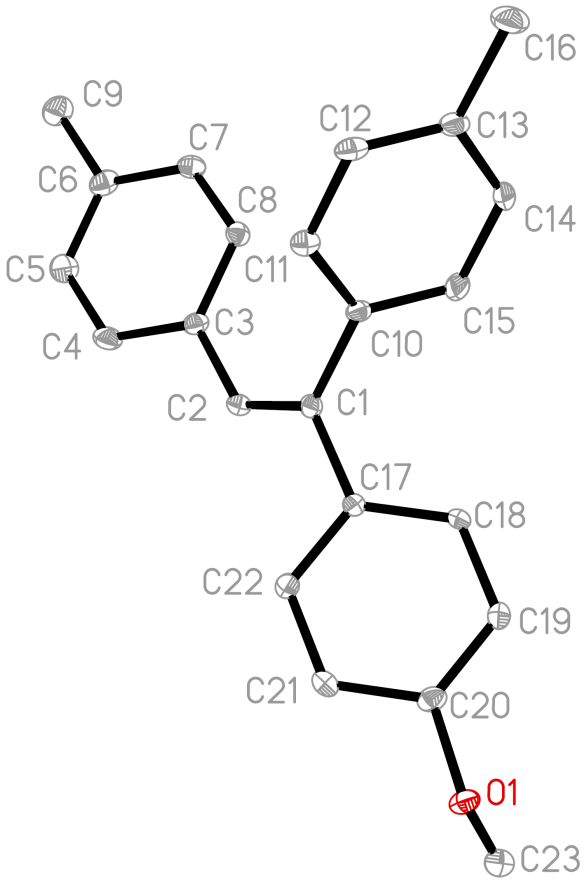
Crystal data and structure refinement for compound **3bb**



Identification code	**3bb**	
Empirical formula	C22 H19 F	
Formula weight	302.37	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.3013(8) Å	α= 78.2820(10)°.
	b = 10.3979(9) Å	β= 89.092(2)°.
	c = 17.3590(15) Å	γ = 88.732(2)°.
Volume	1643.4(2) $Å^3$	
Z	4	
Density (calculated)	1.222 Mg/m^3	
Absorption coefficient	0.077 mm^{-1}	
F(000)	640	
Crystal size	0.56 x 0.26 x 0.22 mm^3	
Theta range for data collection	2.00 to 27.50°.	
Index ranges	-12<=h<=12, -13<=k<=13, -22<=l<=22	

Reflections collected	22006
Independent reflections	7544 [R(int) = 0.0317]
Completeness to theta = 27.50°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9833 and 0.9581
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7544 / 0 / 419
Goodness-of-fit on F^2	1.085
Final R indices [I>2sigma(I)]	R1 = 0.0520, wR2 = 0.1389
R indices (all data)	R1 = 0.0674, wR2 = 0.1465
Largest diff. peak and hole	0.402 and -0.230 e.Å^{-3}

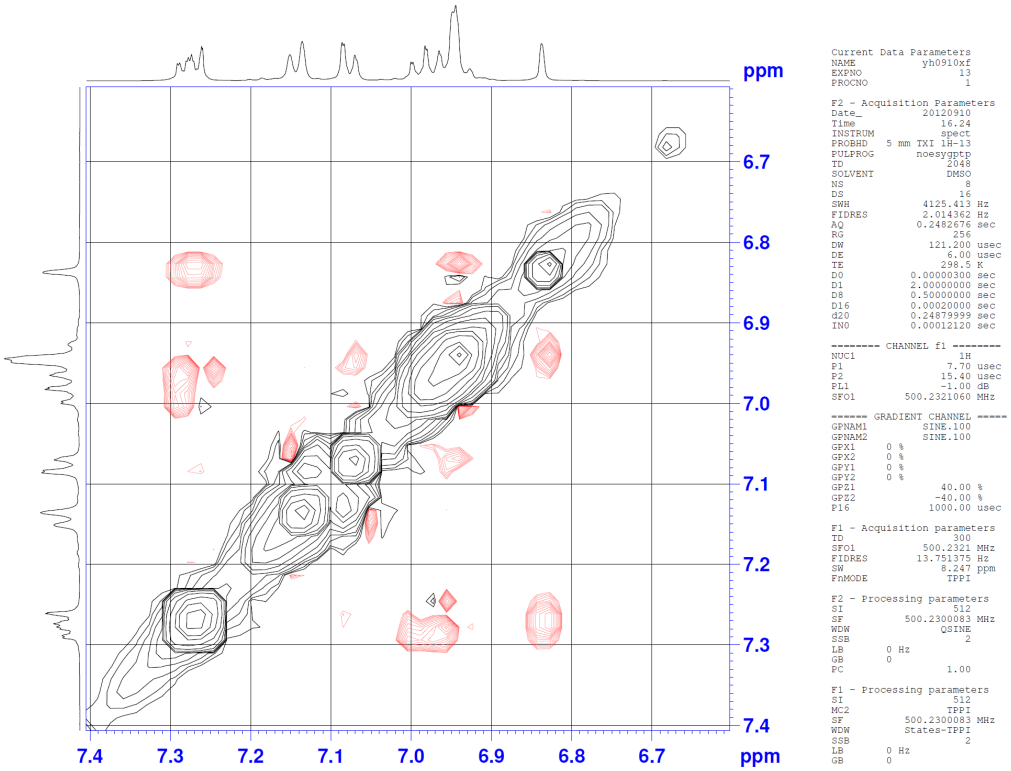
Crystal data and structure refinement for compound **3bc**



Identification code	**3bc**	
Empirical formula	C23 H22 O	
Formula weight	314.41	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 5.985(2) Å	α= 80.467(8)°.
	b = 9.373(4) Å	β= 88.504(8)°.
	c = 16.021(6) Å	γ = 77.301(8)°.
Volume	864.7(6) $Å^3$	
Z	2	
Density (calculated)	1.208 Mg/m^3	
Absorption coefficient	0.072 mm^{-1}	
F(000)	336	
Crystal size	0.34 x 0.24 x 0.12 mm^3	
Theta range for data collection	1.29 to 27.50°.	
Index ranges	-7<=h<=7, -12<=k<=12, -20<=l<=20	
Reflections collected	11285	
Independent reflections	3958 [R(int) = 0.0430]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6559	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3958 / 16 / 258	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0722, wR2 = 0.1757	
R indices (all data)	R1 = 0.0917, wR2 = 0.1933	
Largest diff. peak and hole	0.461 and -0.386 $e.Å^{-3}$	

Diffraction measurements were conducted at 100(2)–223(2) K on a Bruker AXS APEX CCD diffractometer by using Mo-Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarization effects with the SMART suite of programs and for absorption effects with SADABS.[2] Structure solutions and refinements were performed by using the programs SHELXS-97[3a] and SHELXL-97[3b]. CCDC No.: 949500 (**3bc**) and 949501(**3bb**)

NOESY of **3bb**

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Current Data Parameters
NAME                  yh0910xf
EXPNO                       13
PROCNO                       1

F2 - Acquisition Parameters
Date_               20120910
Time                   16.24
INSTRUM                spect
PROBHD   5 mm TXI 1H-13
PULPROG             noesygptp
TD                      2048
SOLVENT                 DMSO
NS                         8
DS                        16
SWH                 4125.413 Hz
FIDRES                2.014362 Hz
AQ                    0.2482676 sec
RG                        256
DW                    121.200 usec
DE                      6.00 usec
TE                    298.5 K
D0                    0.00000300 sec
D1                    2.00000000 sec
D8                    0.50000000 sec
D16                   0.00020000 sec
d20                   0.24879999 sec
IN0                   0.00012120 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                      7.70 usec
P2                     15.40 usec
PL1                    -1.00 dB
SFO1                500.2321060 MHz

====== GRADIENT CHANNEL =====
GPNAM1               SINE.100
GPNAM2               SINE.100
GPX1          0 %
GPX2          0 %
GPY1          0 %
GPY2          0 %
GPZ1                   40.00 %
GPZ2                  -40.00 %
P16                 1000.00 usec

F1 - Acquisition parameters
TD                        300
SFO1                500.2321 MHz
FIDRES             13.751375 Hz
SW                     8.247 ppm
FnMODE                  TPPI

F2 - Processing parameters
SI                        512
SF                  500.2300083 MHz
WDW                     QSINE
SSB                        2
LB            0 Hz
GB            0
PC                     1.00

F1 - Processing parameters
SI                        512
MC2                     TPPI
SF                  500.2300083 MHz
WDW               States-TPPI
SSB                        2
LB            0 Hz
GB            0
```

References

[1] Roesch, K. R., Larock, R. C.; *J. Org. Chem.* **2000**, *66*, 412-420.

[2] SADABS: Area-Detection Absorption Correction: Bruker AXS Inc., Madison, WI, 1995.

[3] (a) G. M. Sheldrick, SHELXS-97 Program for crystal structure solution, University of Göttingen, Göttingen, Germany, 1997; (b) G. M. Sheldrick, SHELXL-97 Program for crystal structure refinement, University of Göttingen, Göttingen, Germany, 1997.