Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Aryl alkyl carbene-Pd complex assisted C-Cl bond activation: An unprecedented cross-coupling route to *trans*-stilbenes

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1. Experimental Section

All starting materials were commercially available and were used without further purification. 1-(bromoethyl)benzene was prepared by reaction of styrene with hydrobromic acid in acetic acid. 1-(hydroxyethyl)benzene was prepared by reduction of acetophenone with sodium borohydride in methanol. 1-(iodoethyl)benzene and 1-(chloroethyl)benzene were prepared by reaction of 1-(hydroxyethyl)benzene with molecular iodine and concentrated hydrochloric acid respectively. All reactions were done under Microwave irradiation using CEM Discover system microwave at a *MW* power of 50 watts. The products were purified by column chromatography on silica gel. ^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX-300 MHz spectrometer (^{1}H 300 MHz, ^{13}C 75 MHz), using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts are given in δ relative to TMS, the coupling constants J are given in Hz**.** δ given in ppm. UV spectra was obtained in hexane on Perkin Elmer (Lamda Bio 20) spectrophotometer. The ESI -MS was performed on MICROTOF II mass instrument. LCMS was performed on Waters 2767 sample manager with waters ZQ mass detector. Molecular mass (GC-MS) of compounds were measured on Perkin Elmer Clarus 600 C. The size of nanoparticles was determined by Malvern DLS. IR spectra were recorded on Nicolet 460 (Protege) spectrophotometer in range 4000-400 cm^{-1}.

General procedure for the synthesis of *trans*–stilbenoids (3a-l)

In a typical procedure, to **1a** (1.08 mmol) procured from Alfa aeser, 30% styrene (0.46 mmol) was added at the beginning of the reaction. The contents were taken in 5 mL microwave tube containing 1.0 mL DMF. To it, aryl chloride (4.64 mmol) and then KOH (4.64 mmol) dissolved in 1mL water was added. This was followed by addition of $Pd(OAc)_2$ (0.5 mol%) to the reaction mixture. The contents were irradiated in microwave for 50 min at 140 ^{o}C where after the reaction mixture was extracted with hexane (3 x 25 mL). The combined organic layers were washed with water, dried over Na_2SO_4 and concentrated under reduced pressure. Chromatography on silica gel afforded pure product.

In an alternate procedure, product mixture of synthesized **1a** (containing 0.7 equiv. **1a** and 0.3 equiv. styrene) was taken in 1 mL DMF in a 5.0 mL microwave tube. To it, aryl chloride (3.0 equiv.) and KOH (3.0 equiv.) dissolved in 1.0 mL water were added. This was followed by addition of $Pd(OAc)_2$ (0.5 mol%) to the reaction mixture. The contents were irradiated in microwave for 50 minutes at 140 ^{o}C where after the reaction mixture was extracted with hexane (3 x 25 mL). The combined organic layers were washed with water, dried over Na_2SO_4 and concentrated under reduced pressure. Chromatography on silica gel afforded pure product.

General procedure for the synthesis of *trans*–stilbenoids (3m, 3n, 3o):

To 1-(bromoethyl)naphthalene (**1a′**) (1.49 mmol) prepared from 2-vinyl naphthalene, 30% styrene (0.64 mmol) was added at the beginning of the reaction. The contents were taken in 5 mL microwave tube containing 1 mL DMF. To it, aryl chloride (6.39 mmol) followed by KOH (6.39 mmol) dissolved in 1 mL water was added. This was followed by addition of $Pd(OAc)_2$ (0.5 mol%) to the reaction mixture. The contents were irradiated in microwave for 50 min at 140 ^{o}C where after the reaction mixture was extracted with hexane (3 x 25 mL). The combined organic layers were washed with water, dried over Na_2SO_4 and concentrated under reduced pressure. Chromatography on silica gel afforded pure product.

Experimental procedure for quenching reaction using TEMPO:

To **1a** (1.08 mmol) procured from Alfa Aeser, 30% styrene (0.46 mmol) was added. The contents were taken in 5 mL microwave tube containing 1.0 mL DMF. To it, aryl chloride (4.64 mmol), TEMPO (1.54 mmol), and KOH (4.64 mmol) dissolved in 1mL water was added. This was followed by addition of $Pd(OAc)_2$ (0.5 mol%) to the reaction mixture. The contents were irradiated in microwave for 50 min at 140 ^{o}C where after the reaction mixture was extracted with hexane (2 x 5 mL). The contents were then concentrated under reduced pressure.

General procedure for time dependent NMR studies:

To **1a** (0.36mmol) procured from Alfa Aeser, 30% styrene (0.15 mmol) was added at the beginning of the reaction. The contents were taken in 5 mL microwave tube containing 1.0 mL DMF. To it, aryl chloride (1.54 mmol) followed by KOH (1.54 mmol) dissolved in 1.0 mL water was added. $Pd(OAc)_2$ (0.5 mol%) was added to the reaction mixture. The contents were stirred well for 1-2 minutes, extracted with 5.0 mL hexane, dried over Na_2SO_4 and then concentrated under reduced pressure which resulted in loss of most of the styrene as it is highly volatile. ^{1}H NMR of this sample was taken in $CDCl_3$. This was considered to be reaction at zero minutes. The same procedure was repeated eight more times after irradiating the reaction mixture in microwave at 140 ^{o}C for different reaction times: 1, 2, 5, 10, 20, 30, 40 and 50 minutes. After each reaction, work up was done as described above and ^{1}H NMR of the sample was taken in $CDCl_3$.

Experimental procedures for the synthesis of starting materials and characterization data of *trans*–stilbenoids:

1-(Bromoethyl)benzene (1a): Styrene (43.2 mmol) was taken in 50 mL R.B. flask containing 1.0 mL acetic acid. 33% hydrobromic acid in acetic acid (43.2 mmol) was added drop-wise with continuous shaking at rt. The contents were then stirred at rt for 4 h. The progress of reaction was monitored through TLC. After completion of reaction, the reaction mixture was neutralized with aqueous sodium bicarbonate solution. Product was extracted with dichloromethane and concentrated under reduced pressure. % conversion was determined by HPLC (Fig. S4). Light brown liquid; yield = 5.56 g, 70%; ^{1}H NMR (300 MHz, $CDCl_3$)[1] δ (ppm) 7.38 (d, *J* = 7.2 Hz, 2H), 7.20-7.30 (m, 3H), 5.15 (q, *J* = 6.6 Hz, 1H), 1.97 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 143.0, 128.5, 128.2, 126.6, 49.4, 26.7. LRMS-ESI exact mass calcd. For $C_8H_{10}Na^+$ $[M+H+Na]^+$ equires *m/z* 129.0680, found *m/z* 129.0550.

2-(1-bromoethyl)naphthalene (1a′): 2-Vinylnaphthalene (3.26 mmol) was taken in 50 mL round bottom flask containing 1 mL acetic acid. 33% hydrobromoic acid in acetic acid (3.25 mmol) was added dropwise with proper shaking at room temperature. The contents were there after stirred at room temperature for 4 h. After completion of reaction, the reaction mixture was neutralized by aqueous sodium bicarbonate solution. The product was extracted with dichloromethane and concentrated under reduced pressure. Light brown liquid; yield = 748 mg, 98%; ^{1}H NMR (300MHz, $CDCl_3$)[2] δ (ppm) 7.83 (t, *J* = 6.6 Hz, 4H), 7.58-7.61 (m, 1H), 7.47-7.50 (m, 2H), 5.40 (q, *J* = 6.9 Hz, 1H), 2.14 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 140.5, 133.2, 133.1, 128.7, 128.2, 127.7, 126.5, 125.2, 125.1, 50.1, 26.8. EI-MS (*m/z*): 155.

1-(Iodoethyl)benzene (1c): 1-(hydroxyethyl)benzene (4.1 mmol) was mixed properly with a crushed mixture of triphenylphosphene (4.1 mmol) and iodine (4.1 mmol). The entire contents were taken in microwave tube and irradiated in microwave for 5 minutes. Product was extracted in hexane-water mixture and concentrated under reduced pressure. Pure **1c** was obtained and was characterized by NMR and mass. Dark yellow orange liquid; yield = 913 mg, 96%; ^{1}H NMR (300MHz, $CDCl_3$)[3] δ (ppm) 7.39-7.55 (m, 5H), 5.51 (q, *J* = 6.3 Hz, 1H), 2.31 (d, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 145.5, 128.9, 128.1, 126.8, 29.2, 26.6. EI-MS (*m/z*): 105.

1-(Chloroethyl)benzene (1d): 1-(hydroxyethyl)benzene (16.4 mmol) was shaken with 45 mL concentrated hydrochloric acid in separating funnel for 20 minutes. The aqueous layer was removed and an additional 25 mL of conc. HCl was added to the organic layer and again shaken for 20 minutes. The aqueous layer was removed and organic layer was washed four times with 25 mL water followed by a wash with 20 mL of 5% $NaHCO_3$. The organic layer was dried under reduced pressure. Pure **1d** was obtained and was characterized by NMR and mass. Light yellow liquid; yield = 2.25 g, 98%; ^{1}H NMR (300MHz, $CDCl_3$)[4] δ (ppm) 7.20-7.36 (m, 5H), 5.00 (q, J = 6.6 Hz, 1H), 1.76 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 143.0, 128.8, 128.4, 126.7, 58.9, 26.7. EI-MS (*m/z*): 105.

1-(Hydroxyethyl)benzene (1e): Acetophenone (66.67 mmol) was taken in 100 mL round bottle flask containing 40 mL methanol. $NaBH_4$ (131.58 mmol) was added in portions. Reaction mixture was stirred at room temperature for 1 h and quenched with water. The mixture was extracted with DCM, dried over $MgSO_4$, and solvent was evaporated to afford the product as colourless oil. Further purification by column chromatography on silica gel afforded pure **1e**. Colorless liquid; yield = 6.84 g, 84%; ^{1}H NMR (300MHz, $CDCl_3$)[5] δ (ppm) 7.34-7.38 (m, 4H), 7.27-7.30 (m, 1H), 4.91 (q, J = 6.3 Hz, 1H), 1.51 (d, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 146.2, 128.5, 127.3, 125.7, 70.1, 25.3. EI-MS (*m/z*): 122.

(*E*)-1,2-Diphenylethylene (3a): White crystalline solid; yield = 167 mg, 86%; ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm)[6] 7.59 (d, J = 7.5 Hz 2H), 7.43 (t, J = 7.5 Hz, 2H), 7.28-7.36 (m, 1H), 7.18 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 137.5, 128.9, 128.8, 127.8, 126.7. EI-MS (*m/z*): 179.

(*E*)-1-Chloro-4-styrylbenzene (3b): White solid; yield = 194 mg, 84%; ^{1}H NMR (300MHz, $CDCl_3$)[7] δ (ppm) 7.42 (d, J = 7.2 Hz 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.17-7.30 (m, 5H), 6.93 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, δ (ppm) 136.9, 135.8, 133.2, 129.3, 128.8, 128.7, 127.9, 127.6, 127.4, 126.5.

(*E*)-1–Nitro-4-styrylbenzene (3c): Yellowish solid; yield = 219 mg, 90%; ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm) 8.24 (d, J = 9 Hz, 2H), 7.65 (d, J = 9 Hz, 2H), 7.57 (d, J = 7.5Hz, 2H), 7.28-7.45 (m, 4H), 7.11 (d, J = 13.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, δ (ppm) 146.7, 143.8, 136.1, 133.2, 128.8, 128.8, 126.9, 126.8, 126.2, 124.09. HRMS-ESI exact mass calcd. For $C_{14}H_{11}NO_2Na^+$ $[M+Na]^+$ requires m/z 248.0682, found *m/z* 248.0685.

(*E*)-1-Cyano-4-styrylbenzene (3d): White solid; yield = 188 mg, 85%; ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm) 7.55-7.67 (m, 6H), 7.32-7.44 (m, 3H), 7.24 (d, *J* = 16.2 Hz, 1H), 7.10 (d, *J* = 16.5Hz, 1H);^{13}C NMR (75 MHz,$CDCl_3$, δ (ppm) 141.8, 136.2, 132.4, 132.3, 128.8, 128.6, 126.9, 126.8, 126.7, 118.9, 110.5, HRMS-ESI exact mass calcd. For $C_{15}H_{12}N^+$ $[M]^+$ requires *m/z* 206.0964, found *m/z* 206.0958.

(*E*)-1-Styryl-4-trifluoromethylbenzene (3e): White solid; yield = 220 mg, 82%; ^{1}H NMR (300MHz, $CDCl_3$)[8] δ (ppm) 7.51 (d, *J* = 16.8 Hz, 3H), 7.34 (t, *J* = 6.9 Hz, 3H), 7.16-7.29 (m,3H), 7.09 (d, *J* = 9.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, δ (ppm) 140.8, 136.7, 131.2, 129.5, 128.8, 128.3,127.2, 126.8, 126.6, 125.7. LRMS-ESI exact mass calcd. For $C_{15}H_{12}F_3K^+$ $[M+H+K]^+$ requires *m/z* 288.35, found *m/z* 288.25.

(*E*)-(4-Styrylphenyl)ethanone (3f): White solid; yield = 192 mg, 80%; ^{1}H NMR (300MHz, $CDCl_3$)[6] δ (ppm) 7.97 (d, *J* = 7.8 Hz, 2H) 7.54-7.62 (m, 4H), 7.40 (t, *J* = 6.9 Hz, 2H), 7.33 (d, *J* = 6.9 Hz, 1H), 7.25 (d, *J* = 16.2 Hz, 1H), 714 (d, *J* = 16.2 Hz, 1H), 2.62 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ (ppm) 197.5, 142.0, 136.7, 135.9, 131.5, 128.9, 128.8, 128.3, 127.5, 126.8, 126.5, 26.6. LRMS-ESI exact mass calcd. For $C_{16}H_{15}O^+$ $[M+H]^+$ requires *m/z* 223.11, found *m/z* 223.12.

(*E*)-1-Methyl-4-stryrylbenzene (3g): White solid; yield = 155 mg, 74%; ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm) 7.60 (d, *J* = 7.2 Hz, 2H), 7.43 – 7.53 (m, 4H), 7.32-7.37 (m, 1H), 7.26 (d, *J* = 7.5 Hz, 2H), 7.18 (s, 2H), 2.46 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ (ppm) 137.6, 137.5, 134.6, 129.5, 128.7, 127.8, 127.4, 126.5, 126.4, 21.3. EI-MS (*m/z*): 194.

(*E*)-1-Methyl-2-styrylbenzene (3h): White solid; yield = 147 mg, 70%; ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm)[9] 7.47 (d, *J* = 5.1 Hz, 2H), 7.39 (d, *J* = 5.7 Hz, 2H), 7.19-7.24 (m, 2H), 7.06-7.16 (m, 4H), 6.88 (d, *J* = 1.2 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ (ppm) 137.8, 136.5, 135.9, 130.6, 130.1, 128.8, 128.6, 128.5, 127.74, 127.71, 126.7, 126.6, 126.4, 125.5, 20.1. EI-MS (*m/z*): 194.

(*E*)-1-Methoxy-4-styrylbenzene (3i): White solid; yield = 45 mg, 20%; ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm) 7.22 – 7.55 (m, 4H), 6.93 – 7.15 (m, 7H), 3.98 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ (ppm) 159.0, 137.4, 129.8, 128.3, 127.9, 127.4, 126.9, 126.3, 125.9, 113.8, 54.9. HRMS-ESI exact mass calcd. For $C_{15}H_{15}O^+$ $[M+H]^+$ requires *m/z* 211.1115, found *m/z* 2011.1117.

(*E*)-2-Styrylpyridine (3j): White crystalline solid; yield = 145 mg, 74%; ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm) 8.54 (d, *J* = 4.5 Hz, 1H), 7.59 (t, *J* = 6.9 Hz, 1H), 7.52 (d, *J* = 9.3 Hz, 3H), 7.31 (t, *J*= 7.5 Hz, 3H),7.24 (d, *J* = 6.9 Hz, 1H), 7.13-7.19 (m, 1H), 7.08 (t, *J* = 5.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, δ (ppm) 155.6, 149.7, 136.6, 136.5, 132.7, 128.7, 128.3, 127.9, 127.1, 122.09, 122.06. HRMS-ESI exact mass calcd. For $C_{13}H_{12}N^+$ $[M]^+$ requires *m/z* 180.0964, found *m/z* 180.0973.

(*E*)-2-Styrylthiophene (3k): White crystalline solid; yield = 141 mg, 70%; ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm) 7.47 (d, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 6.6 Hz, 3H),7.07 (d, *J* = 3 Hz, 1H), 7.00 (t, *J* = 3.6 Hz, 1H), 6.93 (d, *J* = 16.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, δ (ppm) 142.9, 137.0, 128.8, 128.4, 127.6, 126.4, 126.1, 124.4, 121.8. HRMS-ESI exact mass calcd. For $C_{12}H_{10}SNa^+$ $[M+Na]^+$ requires *m/z* 209.0401, found *m/z* 209.1065.

(*E*)-1-Styrylnaphthalene (3l): White crystalline solid; yield = 274 mg, 80%; ^{1}H NMR (300MHz, $CDCl_3$)[7] δ (ppm) 8.25 (d, *J* = 7.5 Hz, 1H), 7.89-7.95 (m, 2H), 7.77-7.85 (m, 2H),7.64 (d, *J* = 7.5 Hz, 2H),7.49-7.59 (m, 3H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.18 (d, *J* = 16.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm) 137.6, 135.0, 133.7, 131.8, 131.4, 128.8, 128.6, 128.4, 128.0, 127.8, 126.7, 126.1, 125.8, 125.7, 123.8, 123.6. EI-MS (*m/z*): 230.

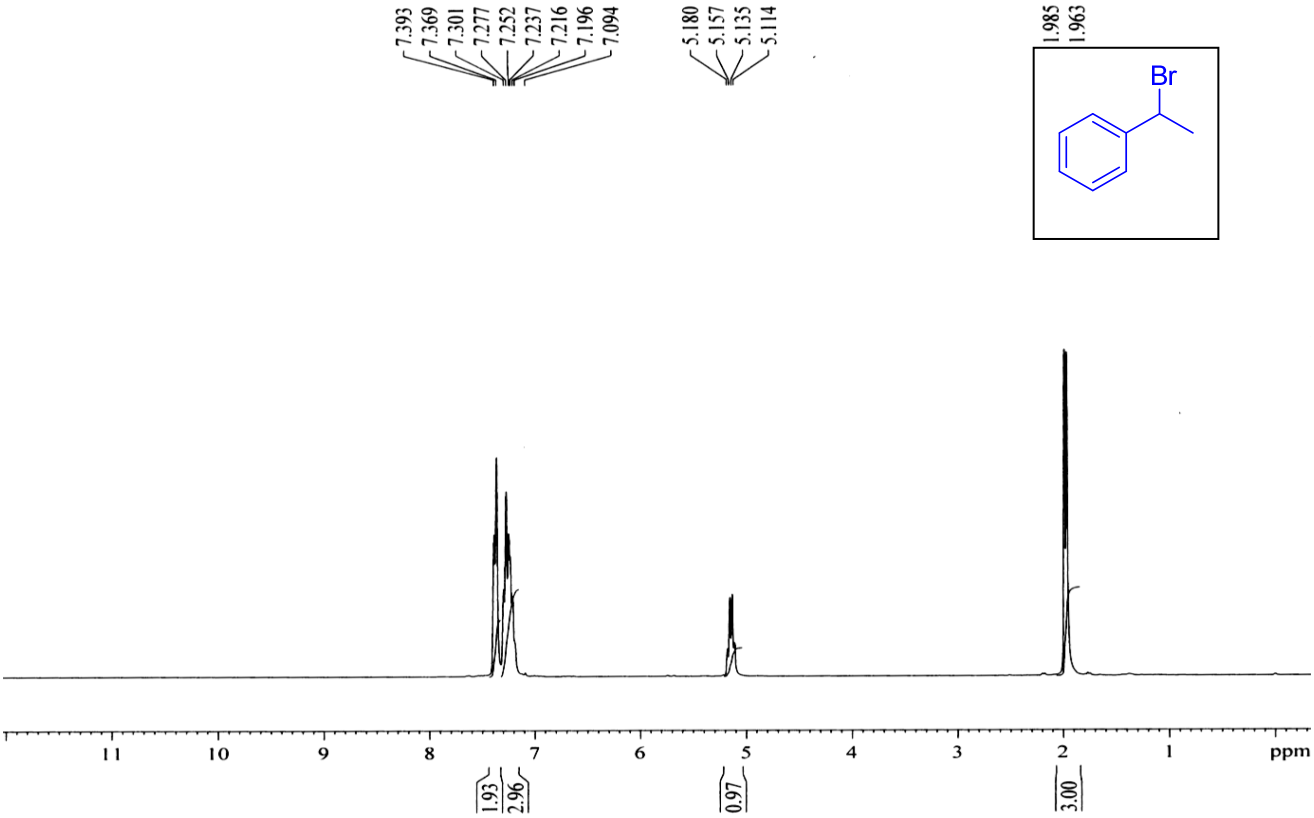
(*E*)-2-Styrylnaphthalene (3m): White crystalline solid; yield = 288 mg, 84%; ^{1}H NMR (300MHz, DMSO)[10] δ (ppm) 8.41 (d, *J* = 7.2 Hz, 1H), 8.08 (d, *J* = 16.2 Hz, 1H), 7.88-7.97 (m, 3H), 7.78 (d, *J* = 7.5 Hz, 2H),7.53-7.62 (m, 3H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.27-7.34 (m, 2H); ^{13}C NMR (75 MHz, DMSO), δ (ppm) 137.0, 134.6, 133.3, 132.6, 128.9, 128.7, 128.4, 128.2, 127.8, 127.7, 127.6, 126.5, 126.4, 126.3, 125.9, 123.6. EI-MS (*m/z*): 230.

(*E*)-1-(1-Naphthyl)-2-(2-naphthyl)ethylene (3n): White crystalline solid; yield = 260 mg, 74%; ^{1}H NMR (300MHz, DMSO) δ (ppm) 7.80-789 (m, 5H), 7.65-7.79 (m, 3H), 7.59 (d, *J* = 8.7 Hz, 1H), 7.41-7.52 (m, 4H), 7.25-7.38 (m, 2H), 7.04-7.2 (m, 1H);^{13}C NMR (75 MHz, DMSO), δ (ppm) 123.6, 123.8, 124.1, 124.8, 125.4, 125.5, 125.7, 125.9, 126.2, 127.1, 127.4, 127.5, 127.7, 127.94, 127.99, 128.4, 131.8, 132.3, 133.2, 134.6, 135.8, 142.9. EI-MS (*m/z*): 281.

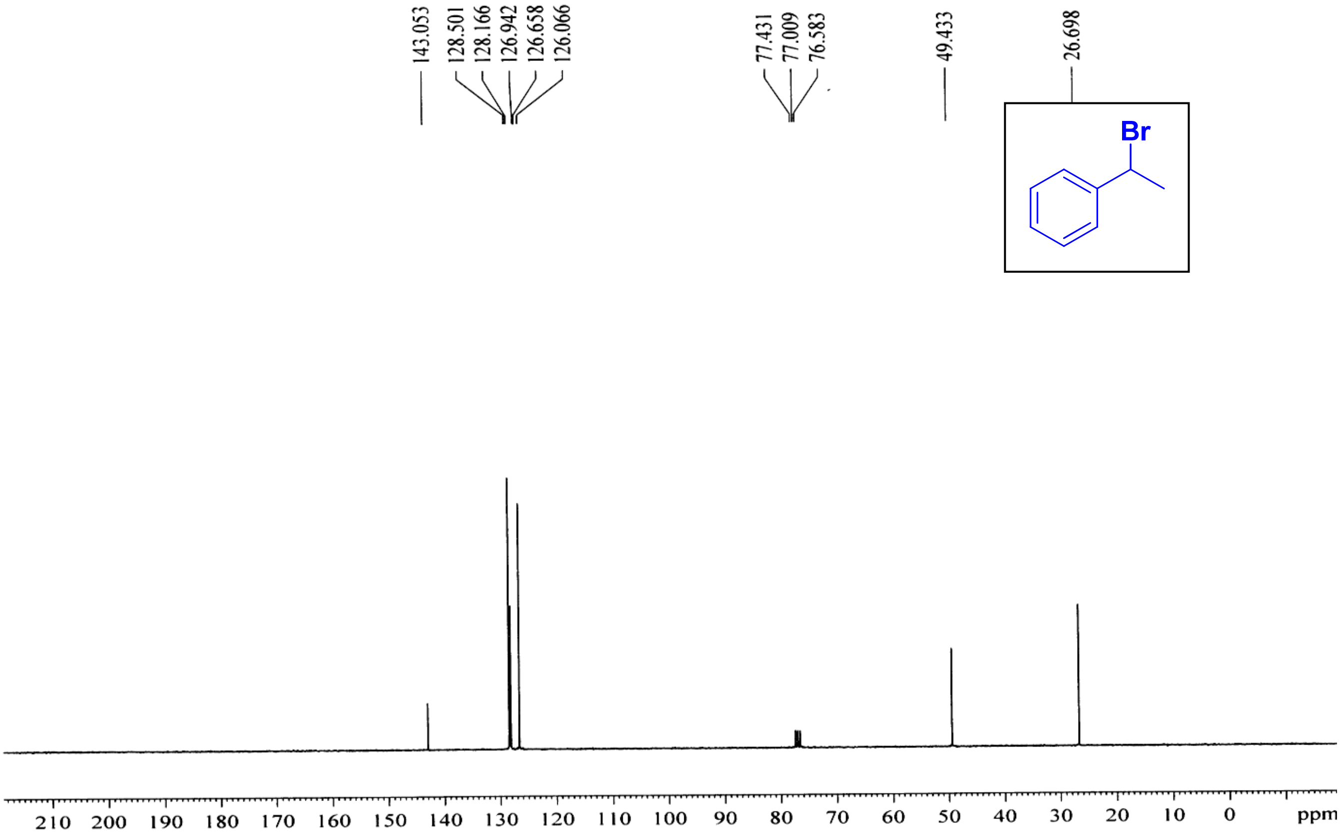
(*E*)-2-(2-Naphthalen-2-yl-vinyl)thiophene (3o): White crystalline solid; yield = 317 mg, 76%; ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm) 7.13-7.23 (m, 1H), 7.27-7.41 (m, 2H), 7.43-7.45

(m, 3H), 7.57-7.73 (m, 2H), 7.75-7.82 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, δ (ppm) 123.6, 125.3, 125.4, 125.6, 125.8, 125.9, 126.2, 126.4, 127.5, 127.6, 127.7, 127.8, 128.1, 128.9, 133.7, 135.6. EI-MS (*m/z*): 236.

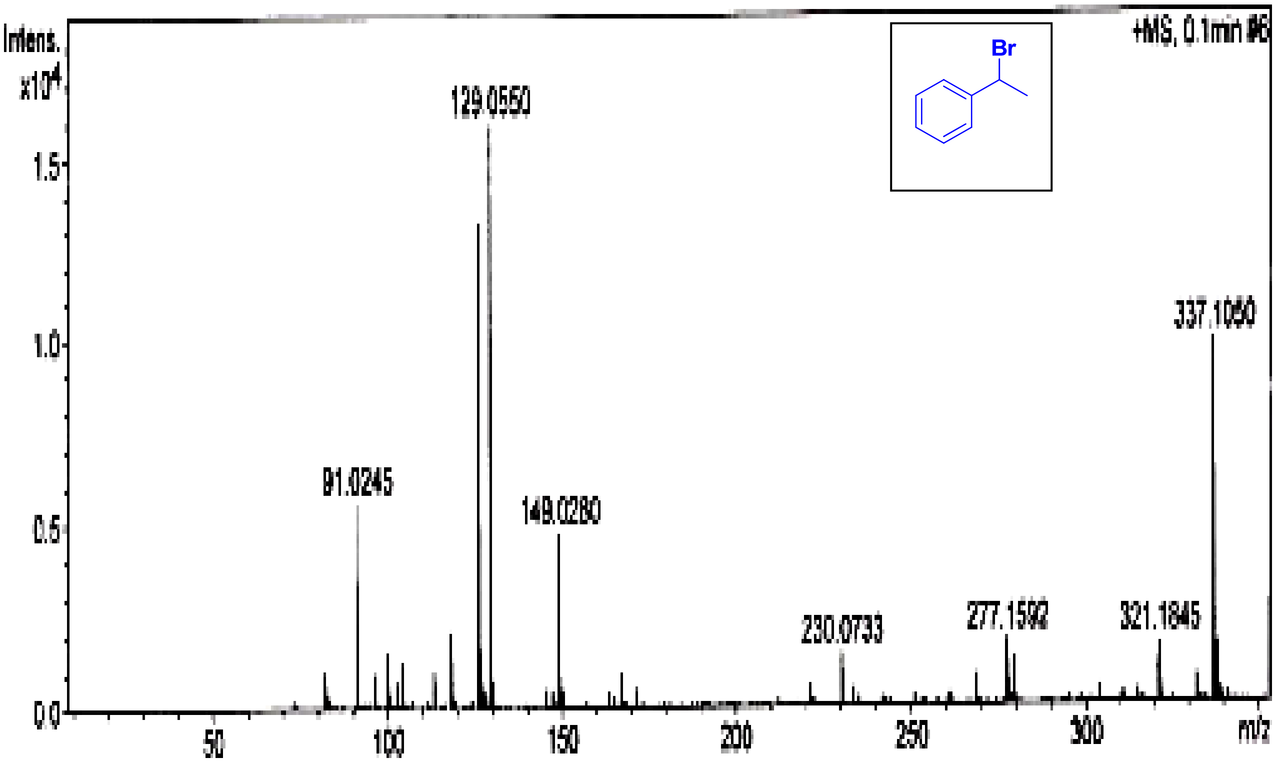
2. Copies of ^{1}H NMR, ^{13}C NMR and Mass Spectra:



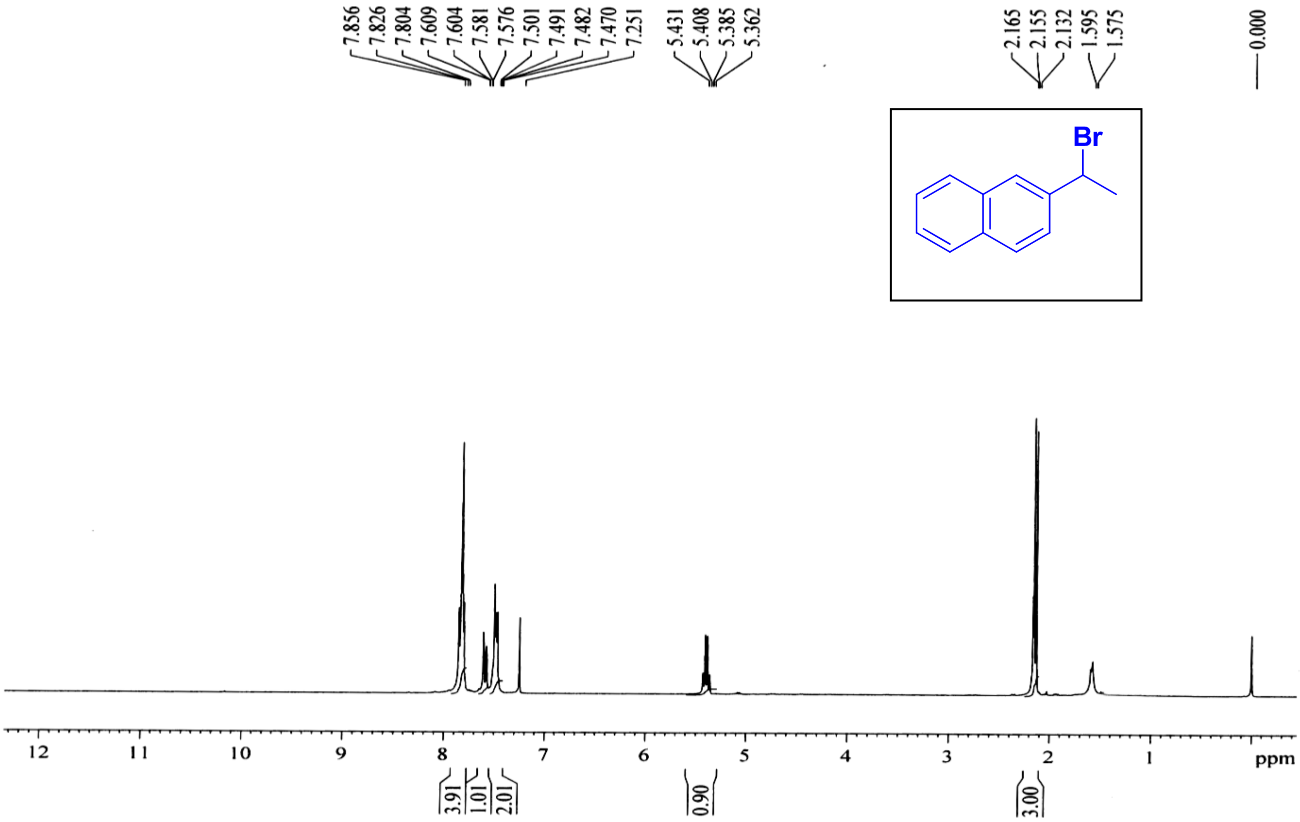
Spectrum 1. 300 MHz ^{1}H NMR of compound **1a**



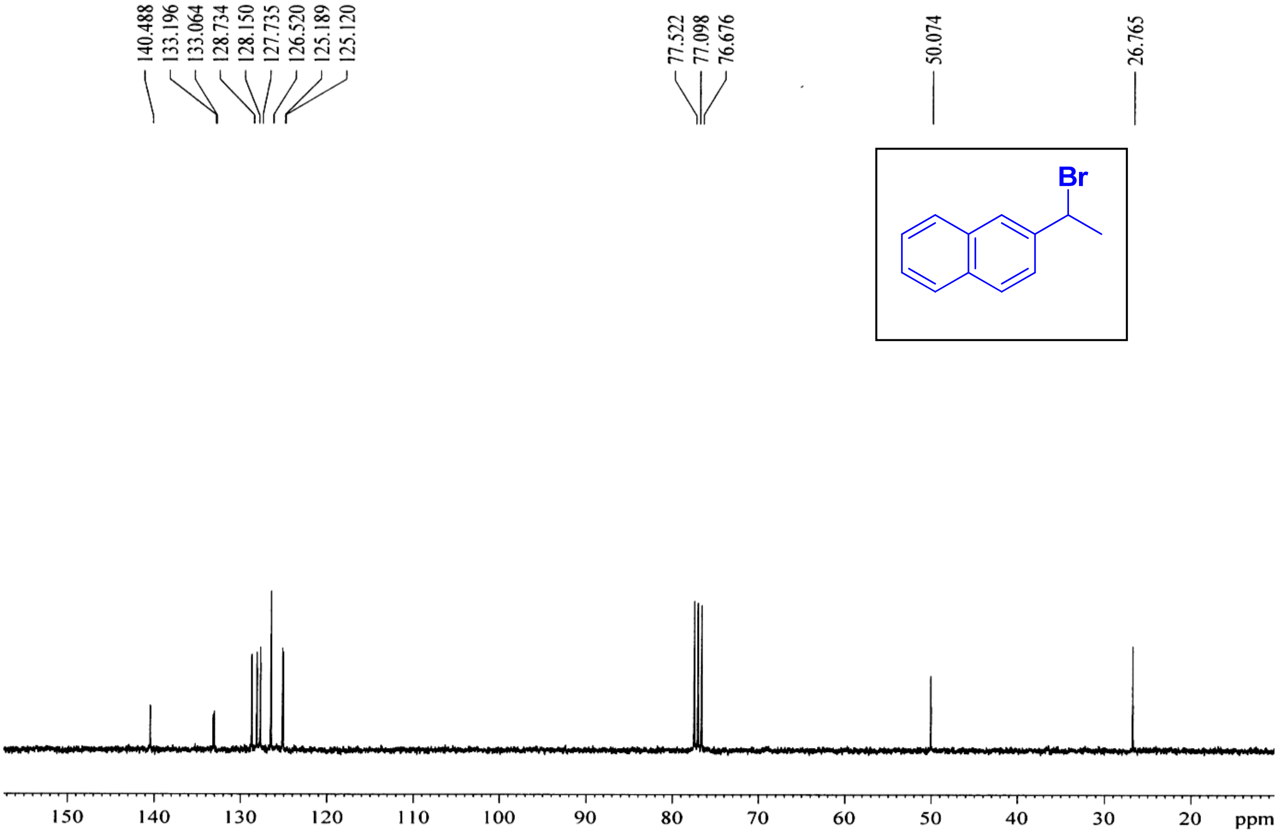
Spectrum 2. 75 MHz ^{13}C NMR of compound **1a**



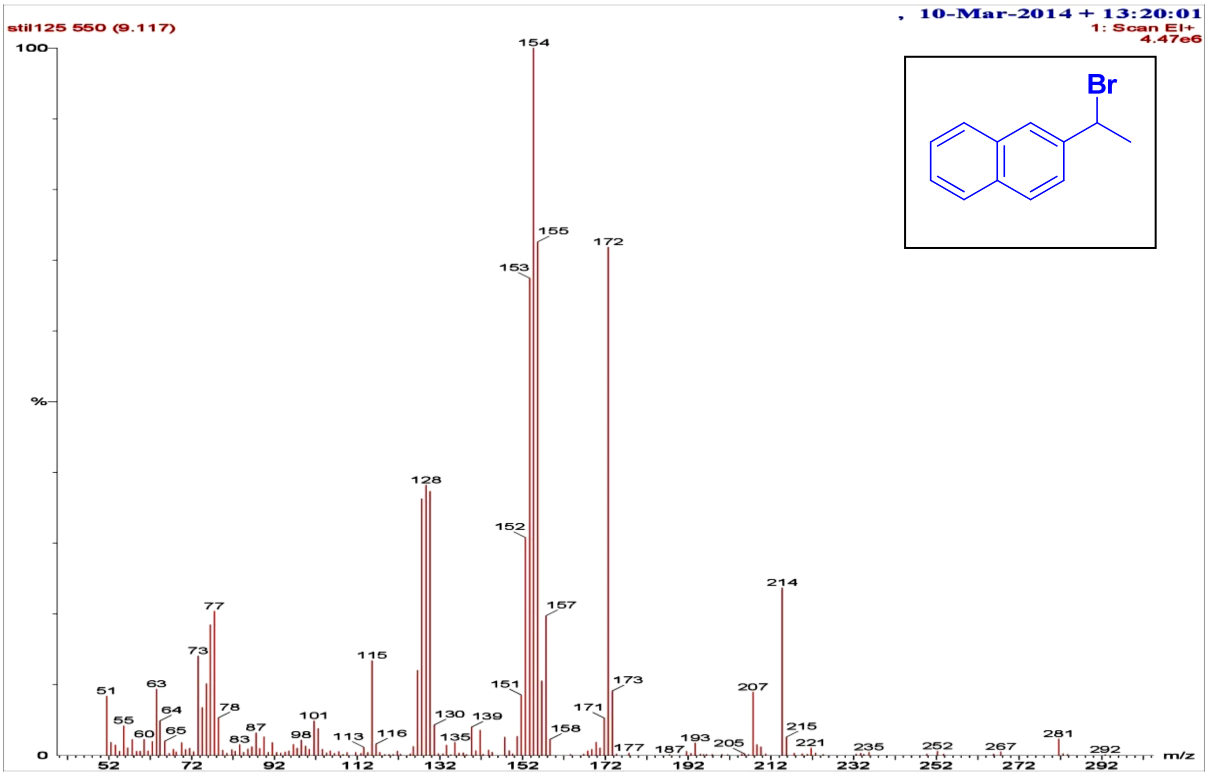
Spectrum 3. LRMS-ESI of compound **1a**



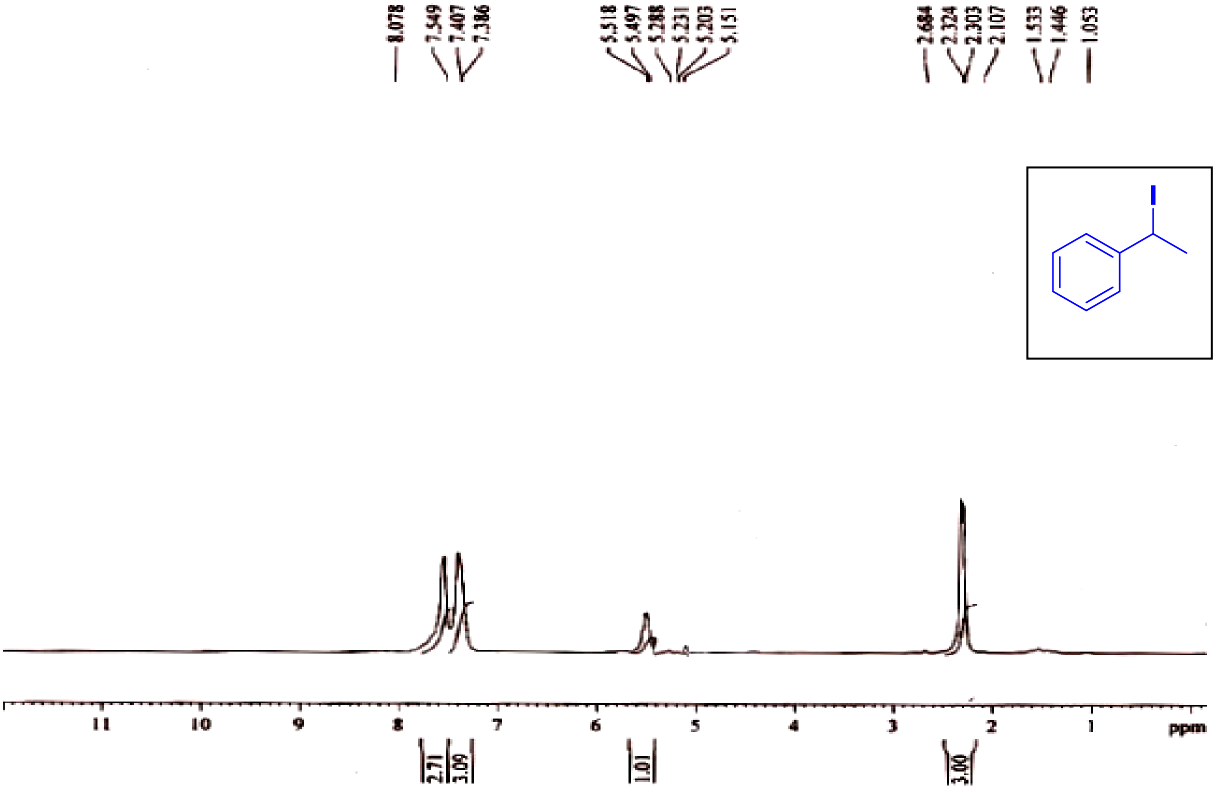
Spectrum 4. 300 MHz ^{1}H NMR of compound **1a´**



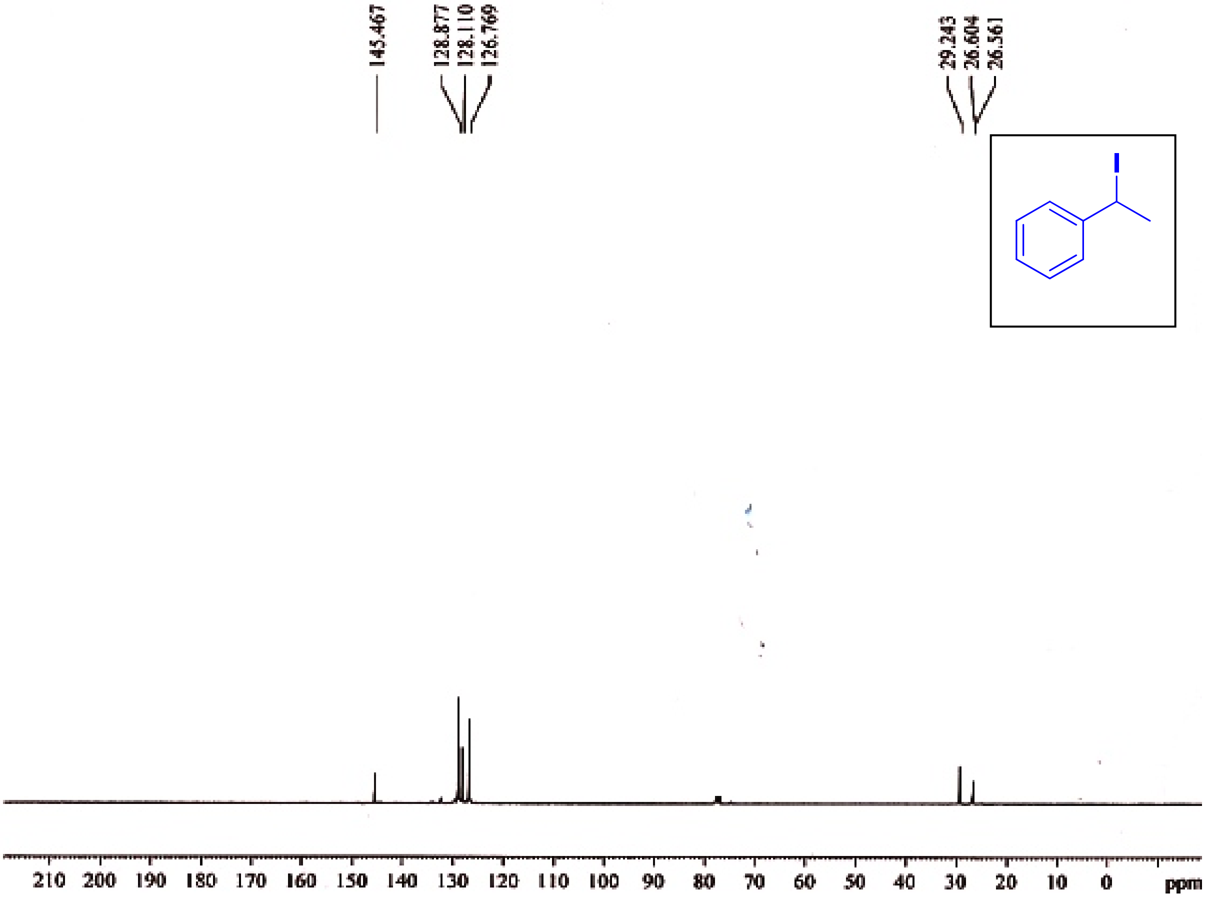
Spectrum 5. 75 MHz ^{13}C NMR of compound **1a´**



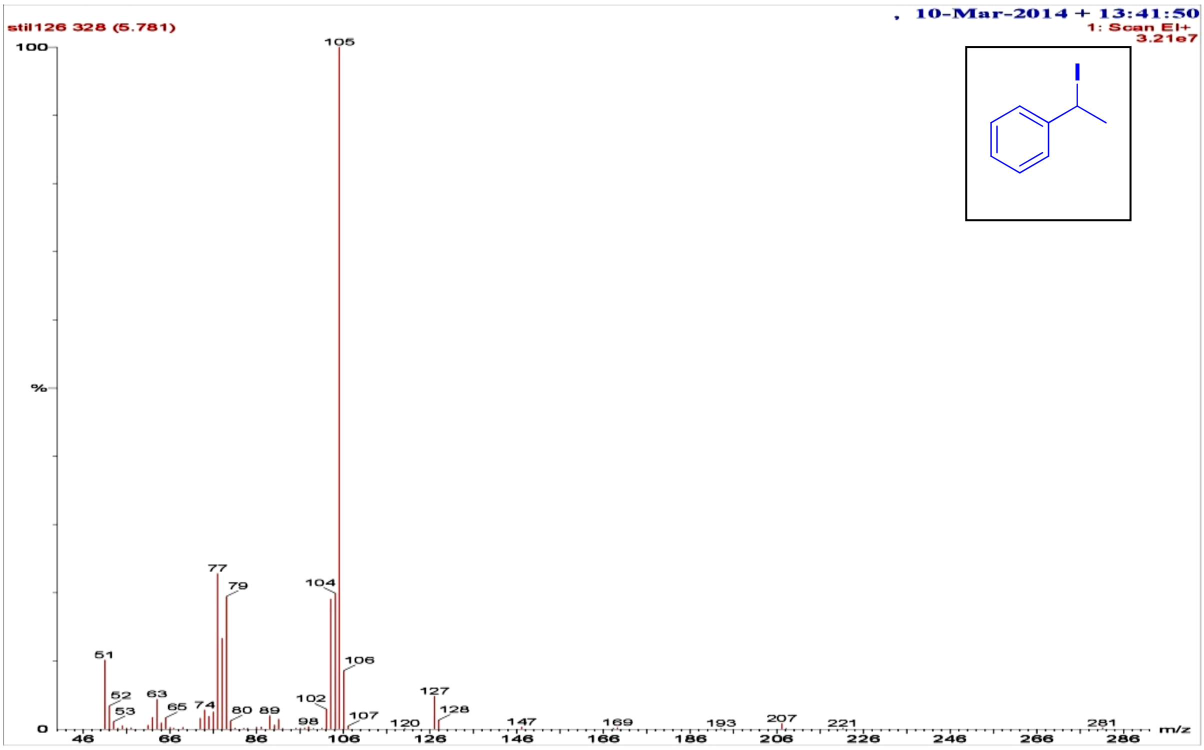
Spectrum 6. EI-MS of compound **1a´**



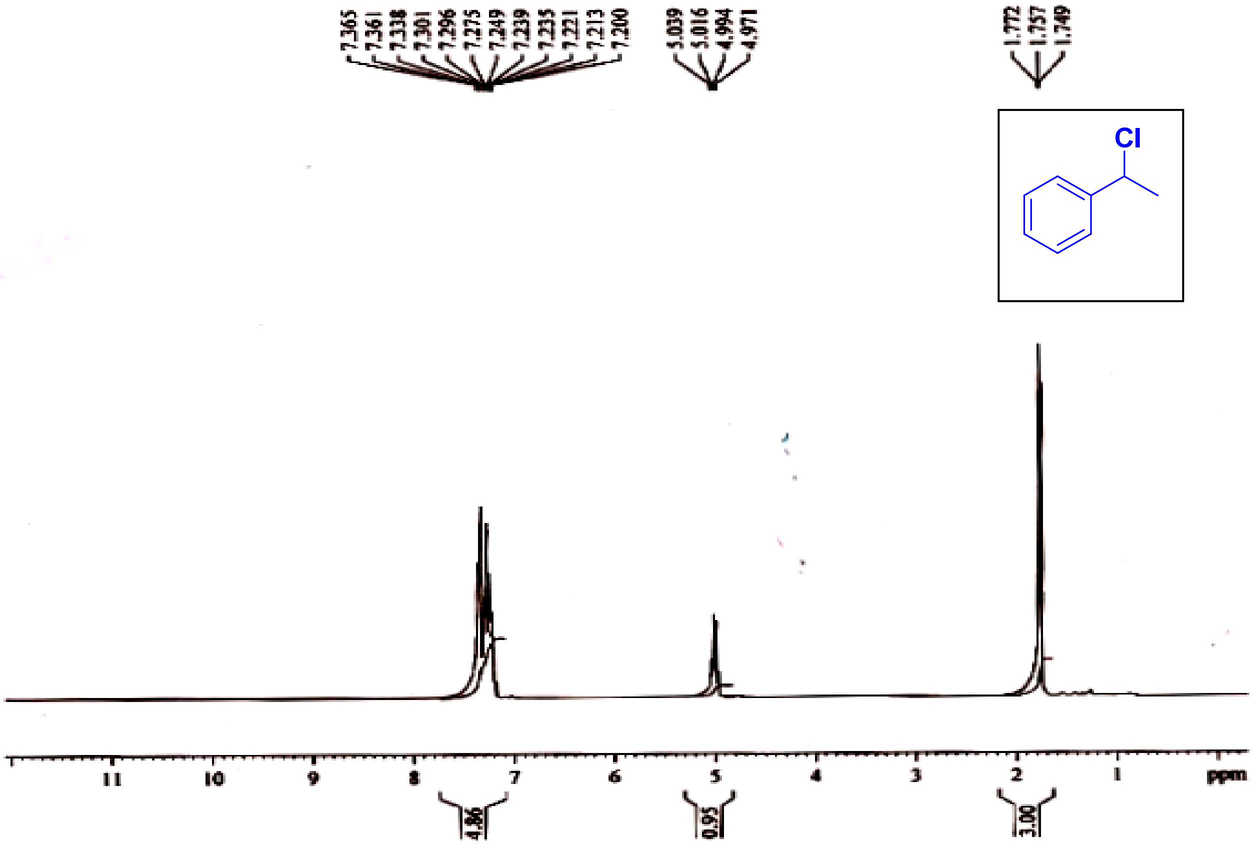
Spectrum 7. 300 MHz ^{1}H NMR of compound **1b**



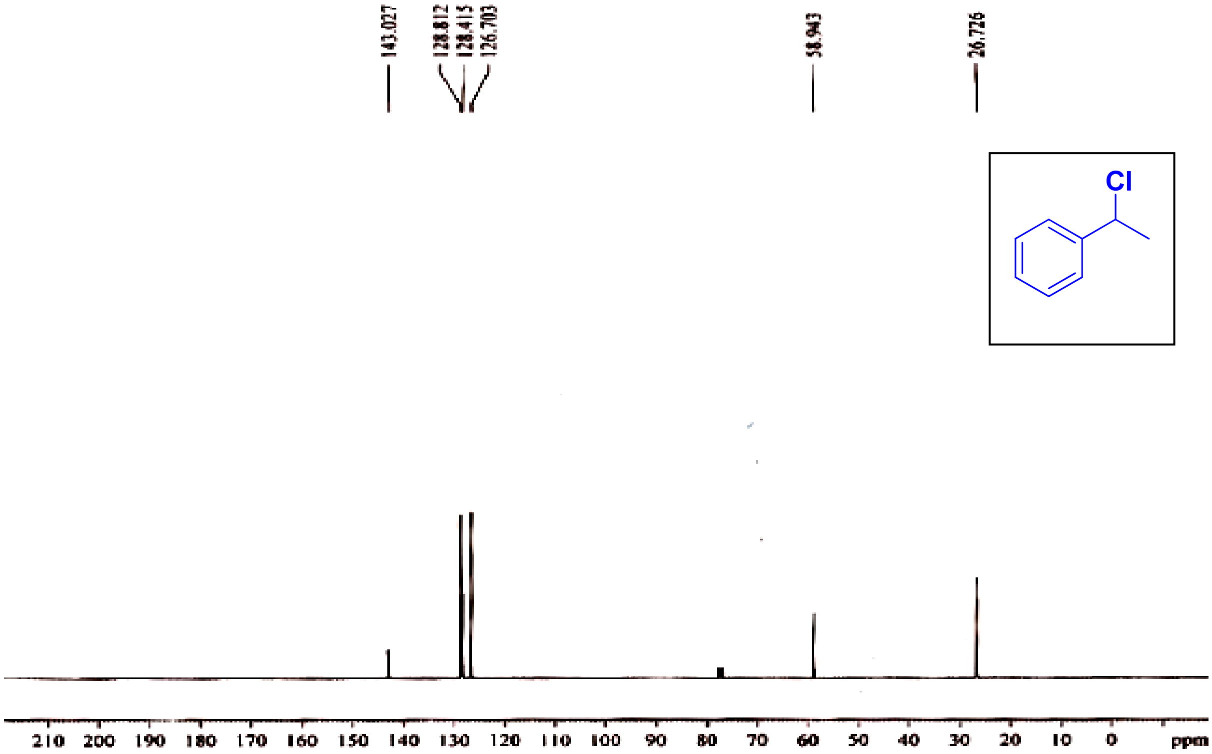
Spectrum 8. 75 MHz ^{13}C NMR of compound **1b**



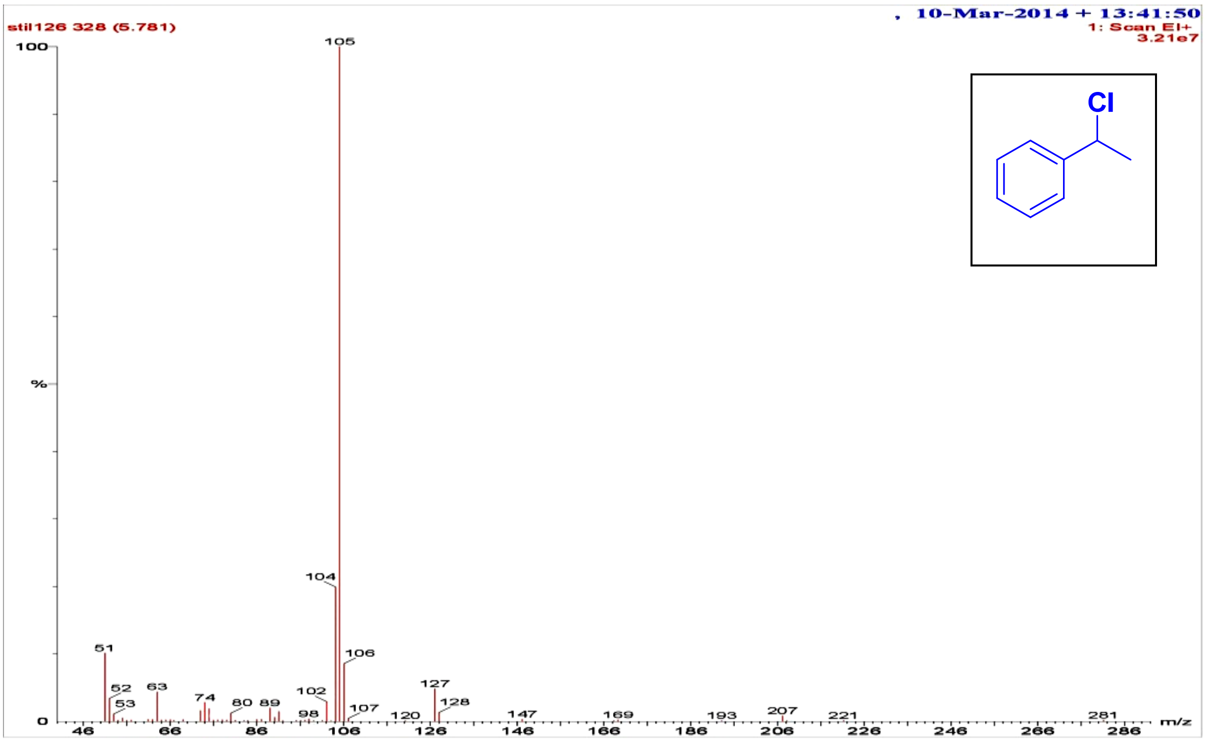
Spectrum 9. EI-MS of compound **1b**



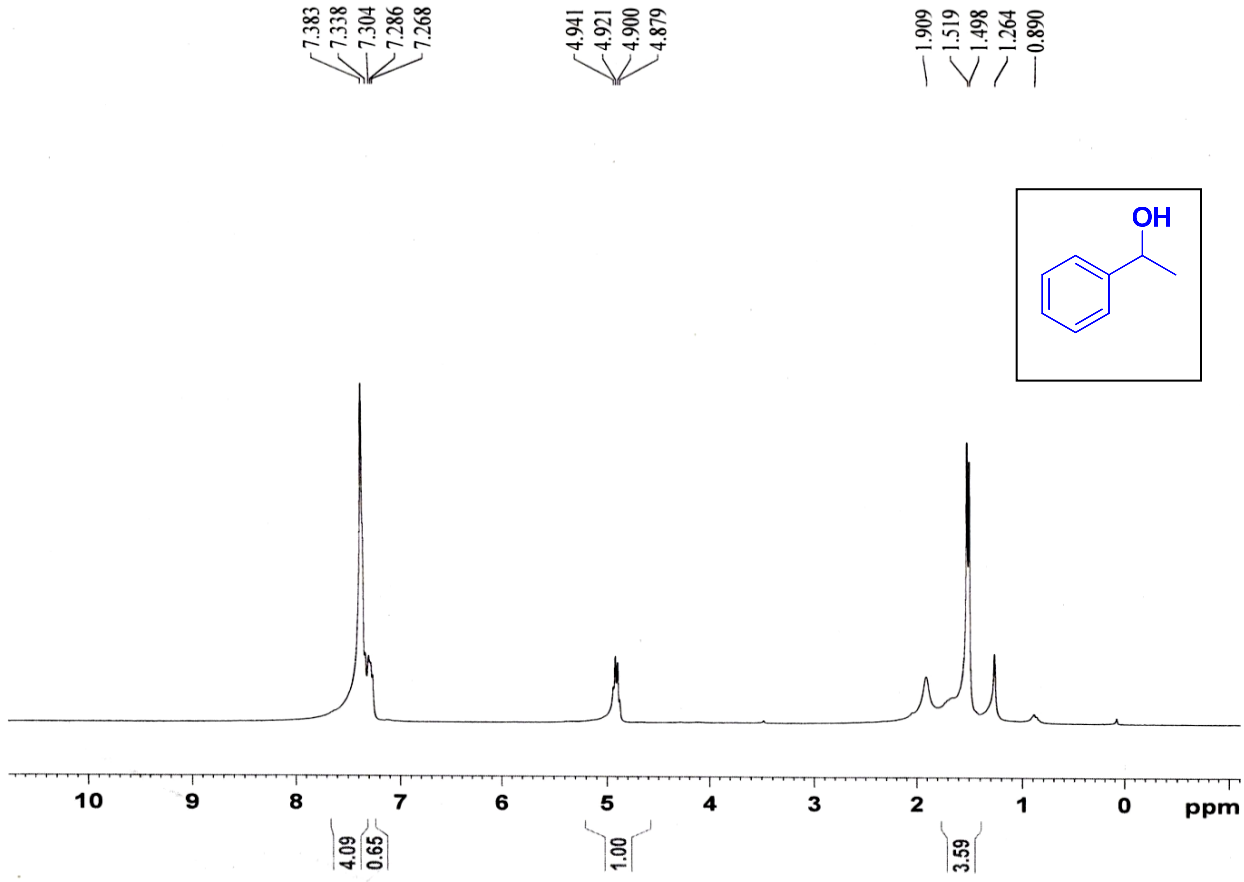
Spectrum 10. 300 MHz ^{1}H NMR of compound **1c**



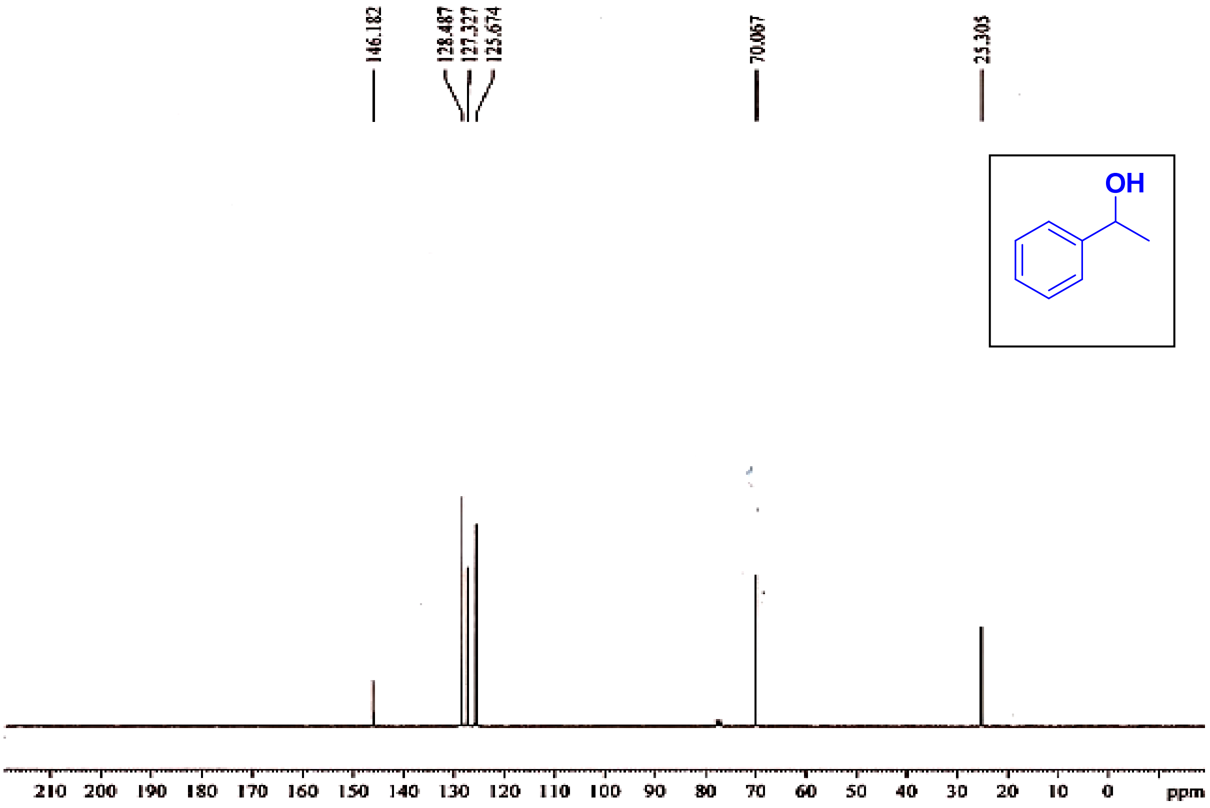
Spectrum 11. 75 MHz ^{13}C NMR of compound **1c**



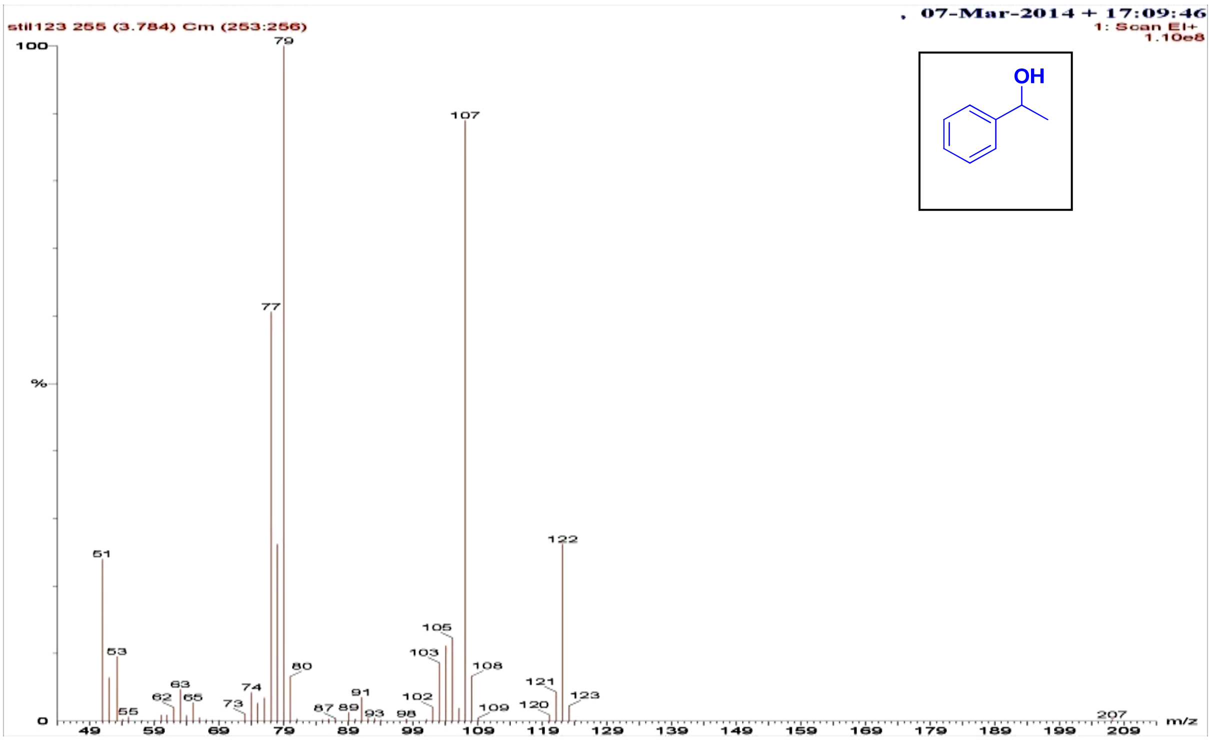
Spectrum 12. EI-MS of compound **1c**



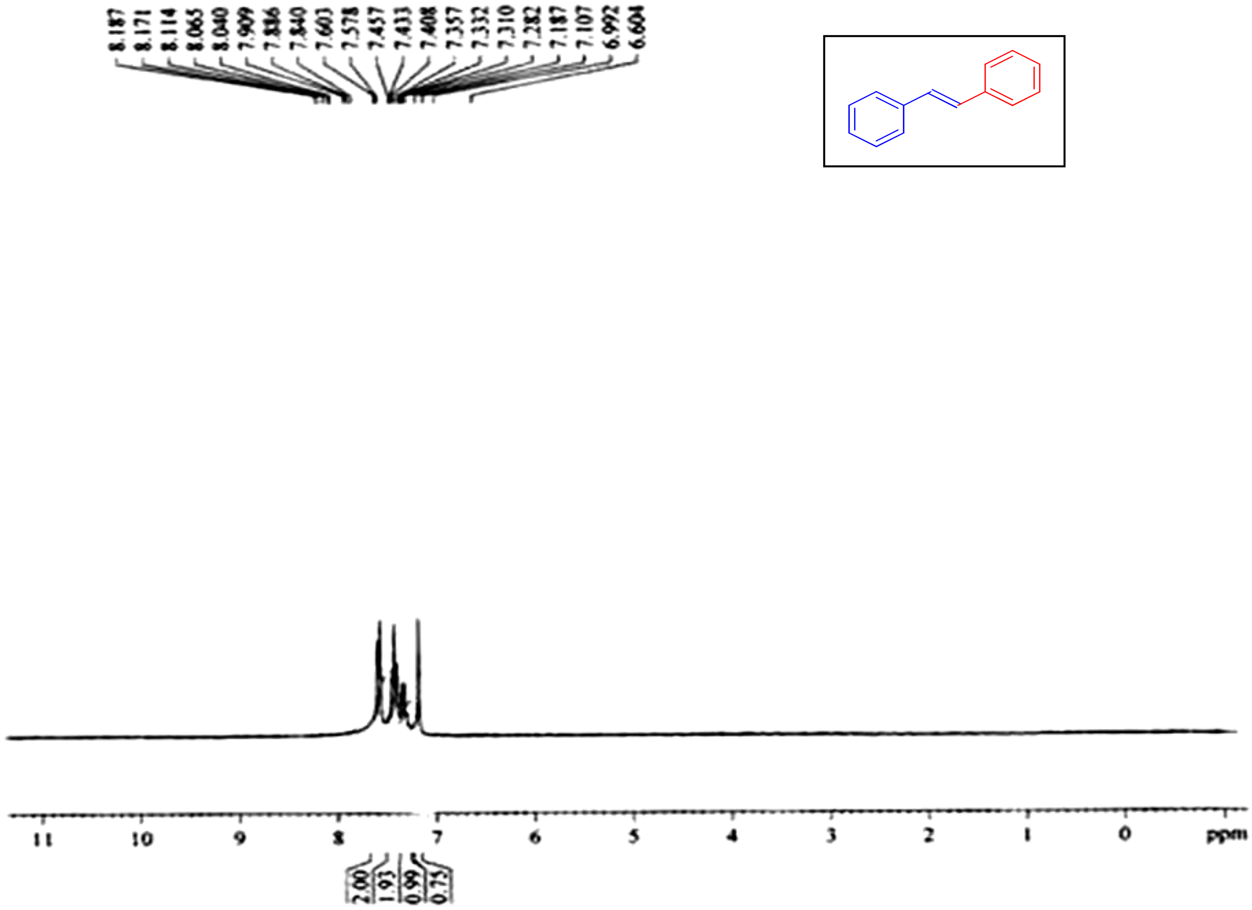
Spectrum 13. 300 MHz ^{1}H NMR of compound **1d**



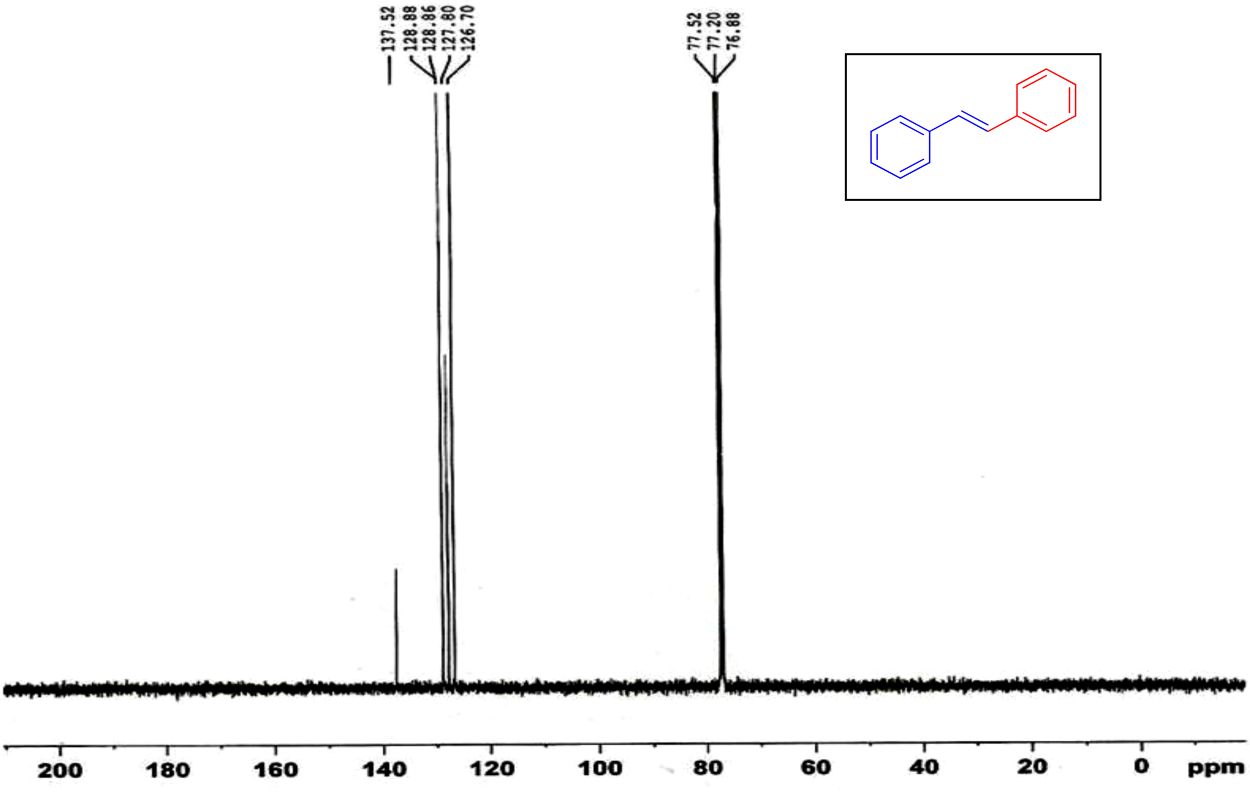
Spectrum 14. 75 MHz ^{13}C NMR of compound **1d**



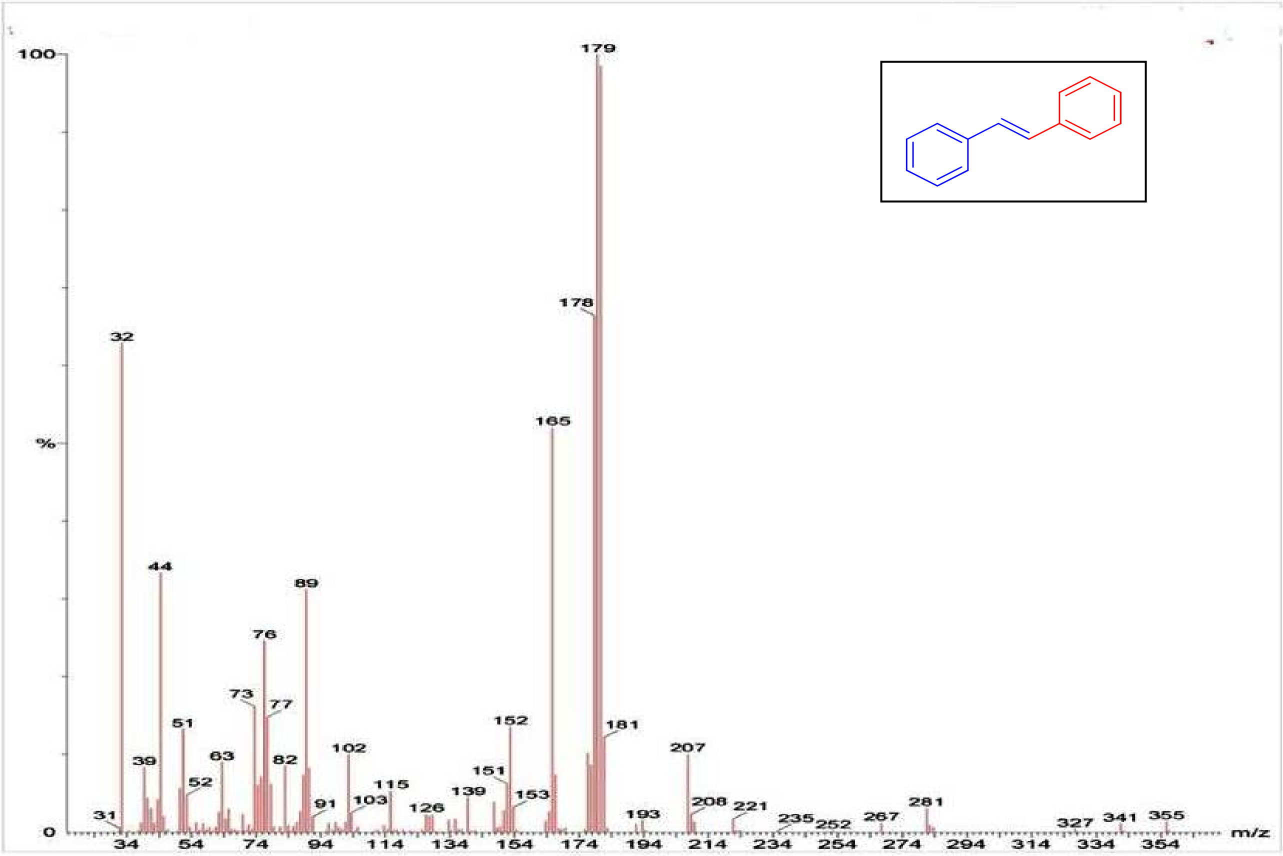
Spectrum 15. EI-MS of compound **1d**



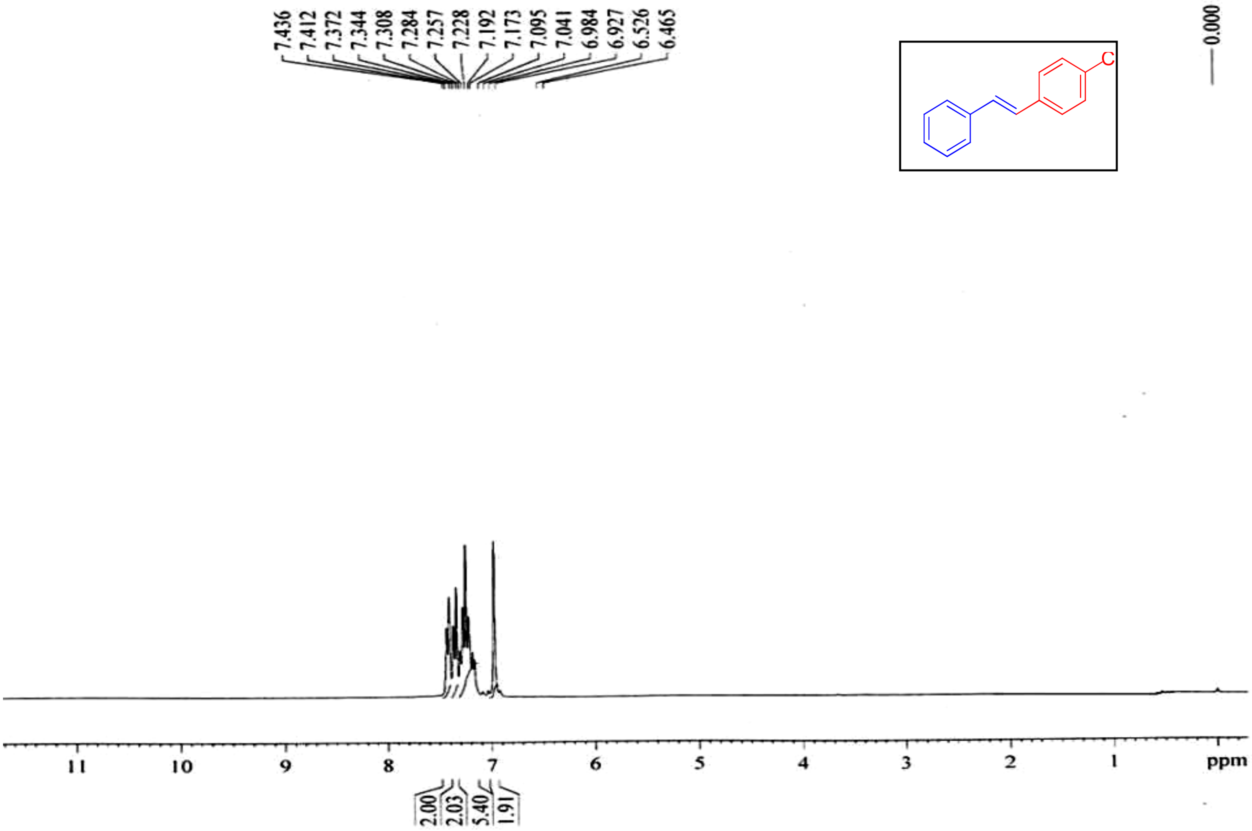
Spectrum 16. 300 MHz ^{1}H NMR of compound **3a**



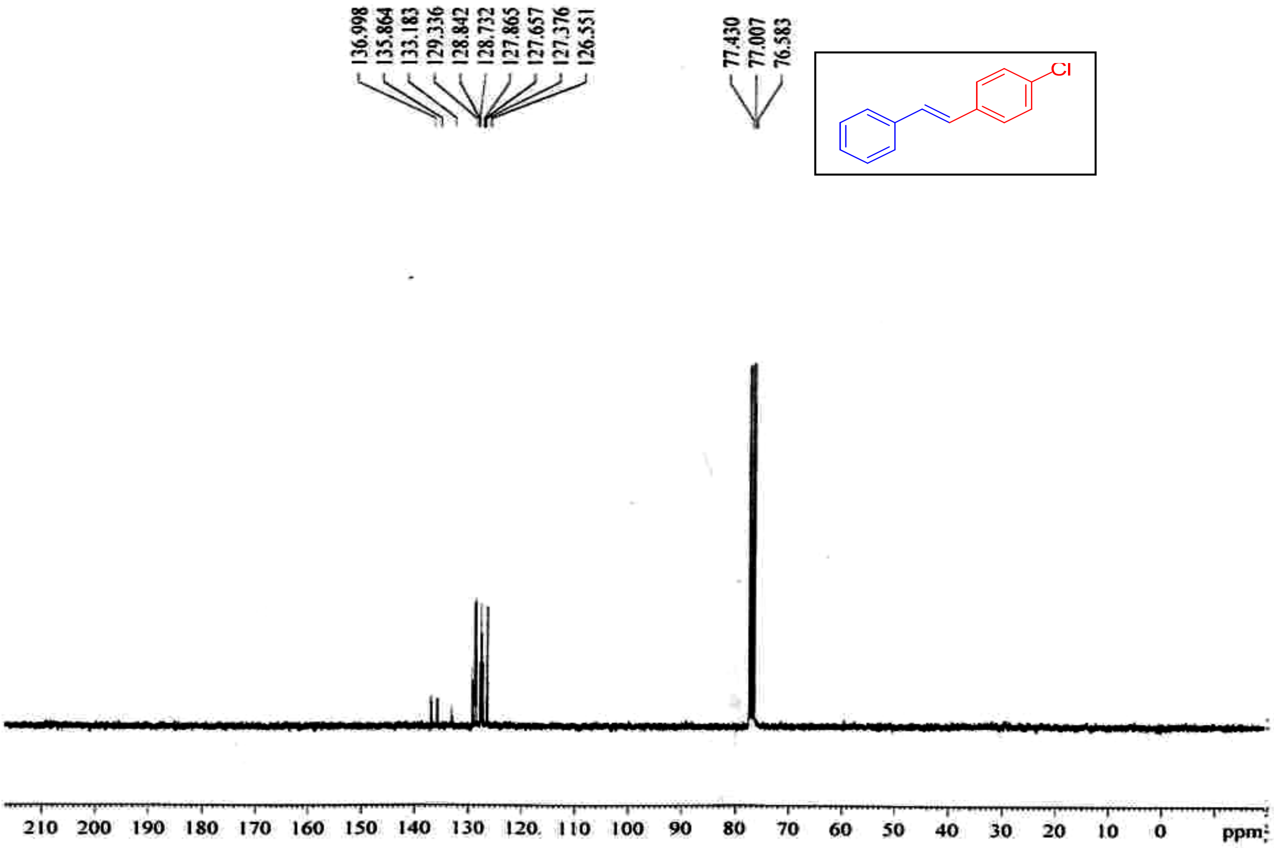
Spectrum 17. 75 MHz ^{13}C NMR of compound **3a**



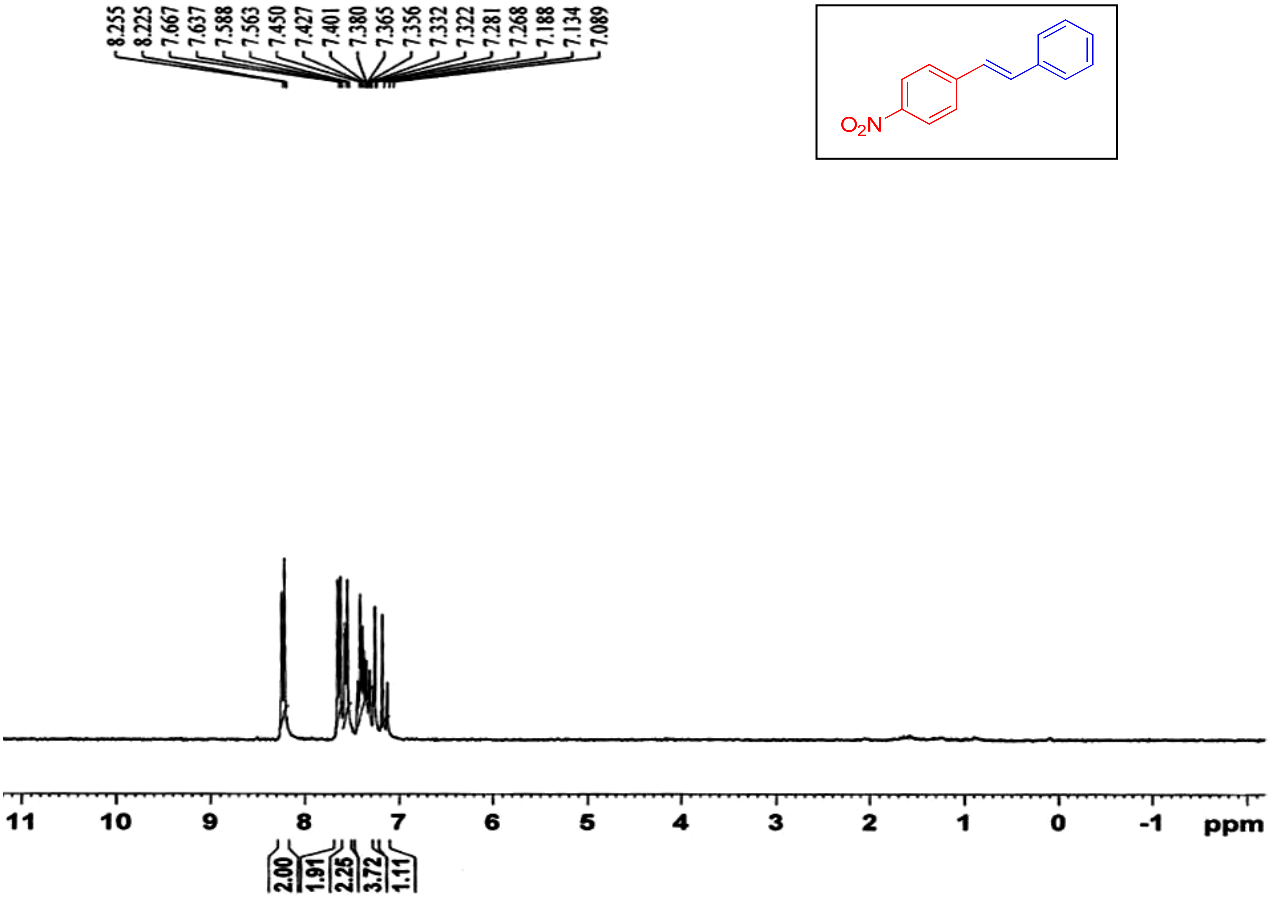
Spectrum 18. EI-MS of compound **3a**



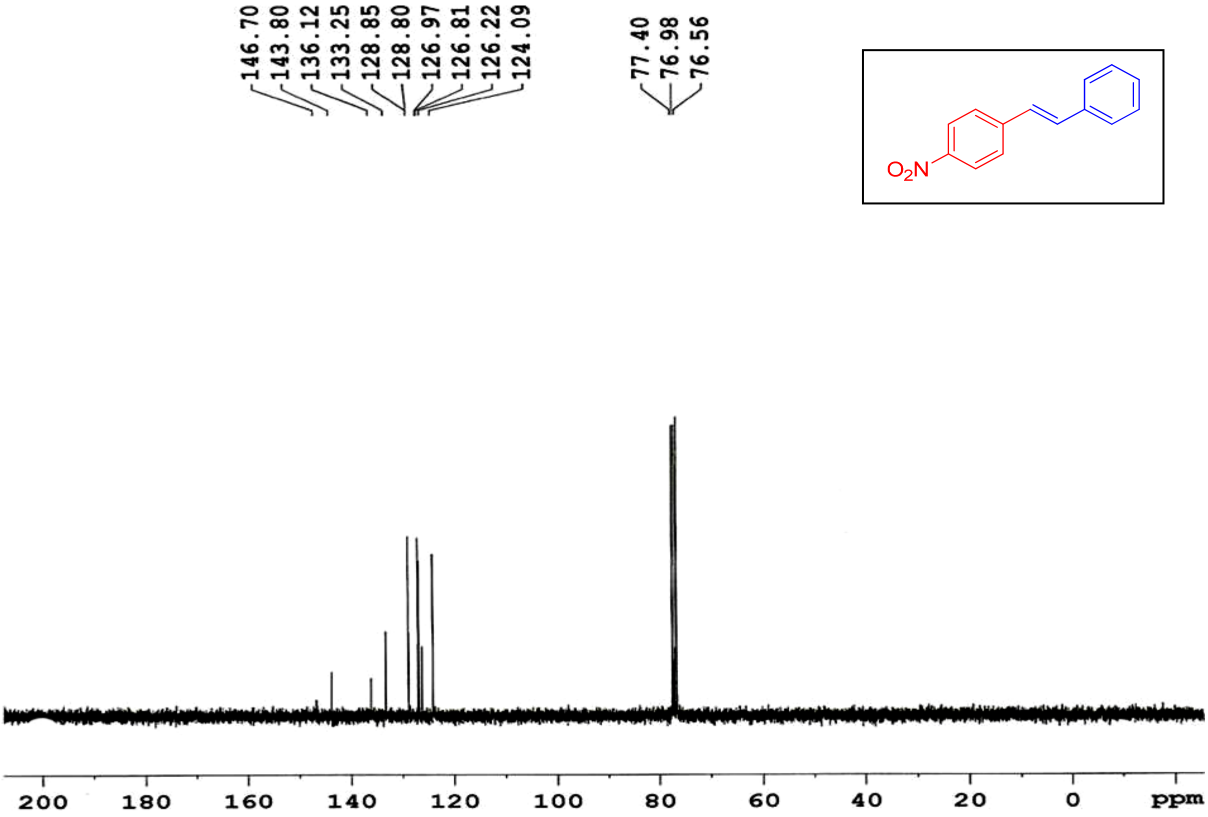
Spectrum 19. 300 MHz ^{1}H NMR of compound **3b**



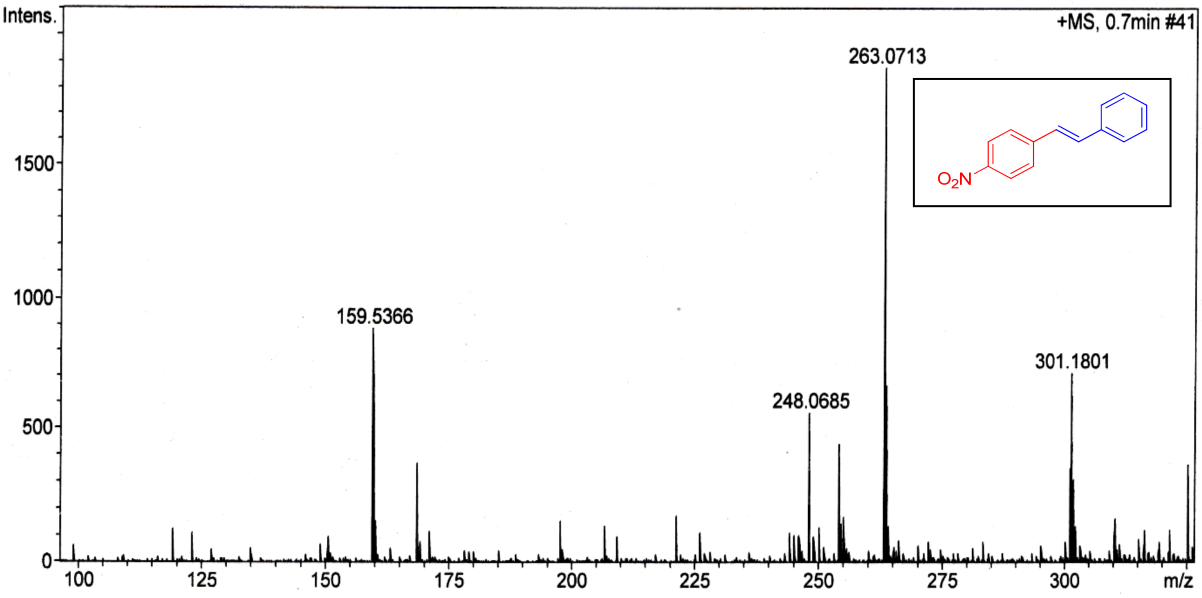
Spectrum 20. 75 MHz ^{13}C NMR of compound **3b**



Spectrum 21. 300 MHz ^{1}H NMR of compound **3c**

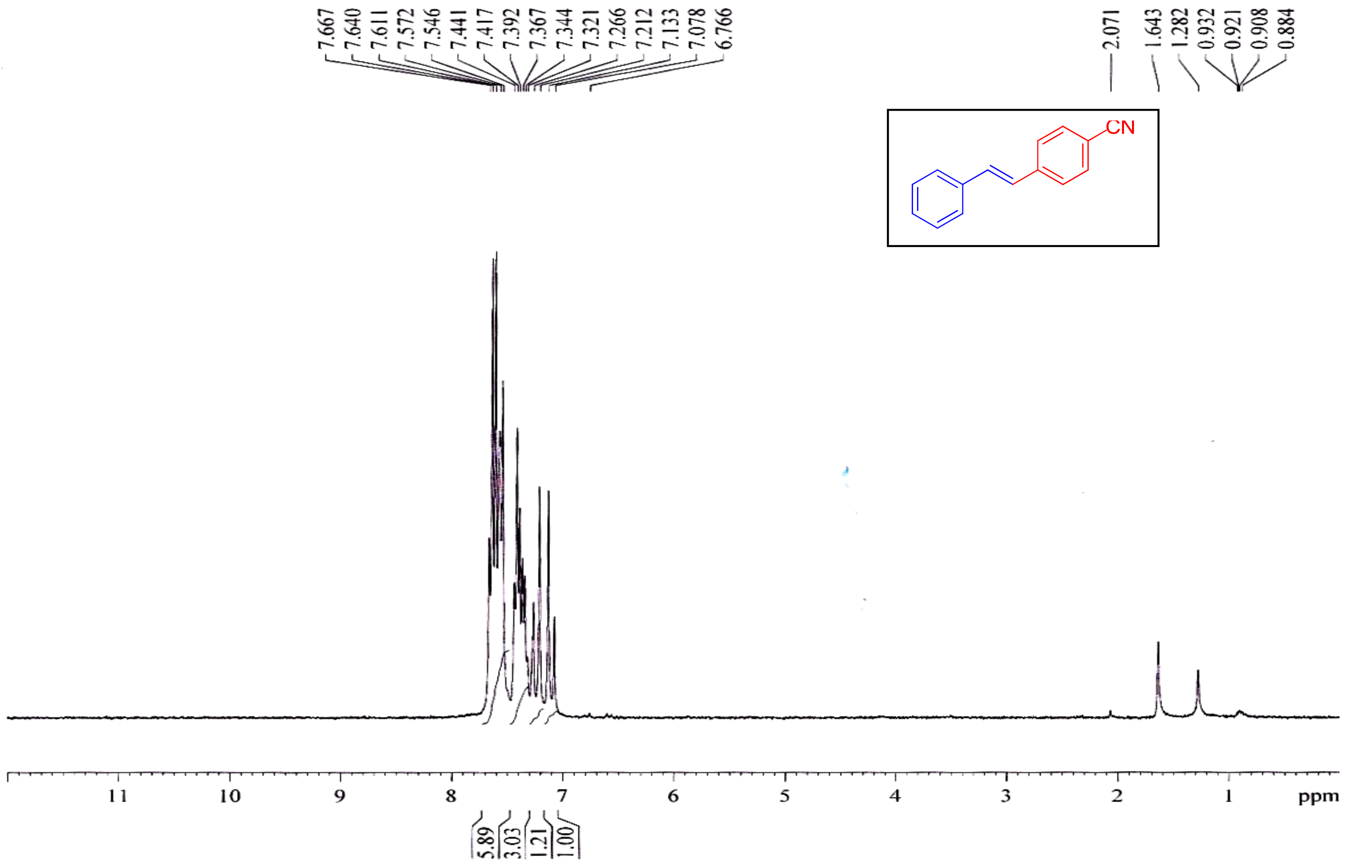


Spectrum 22. 75 MHz ^{13}C NMR of compound **3c**

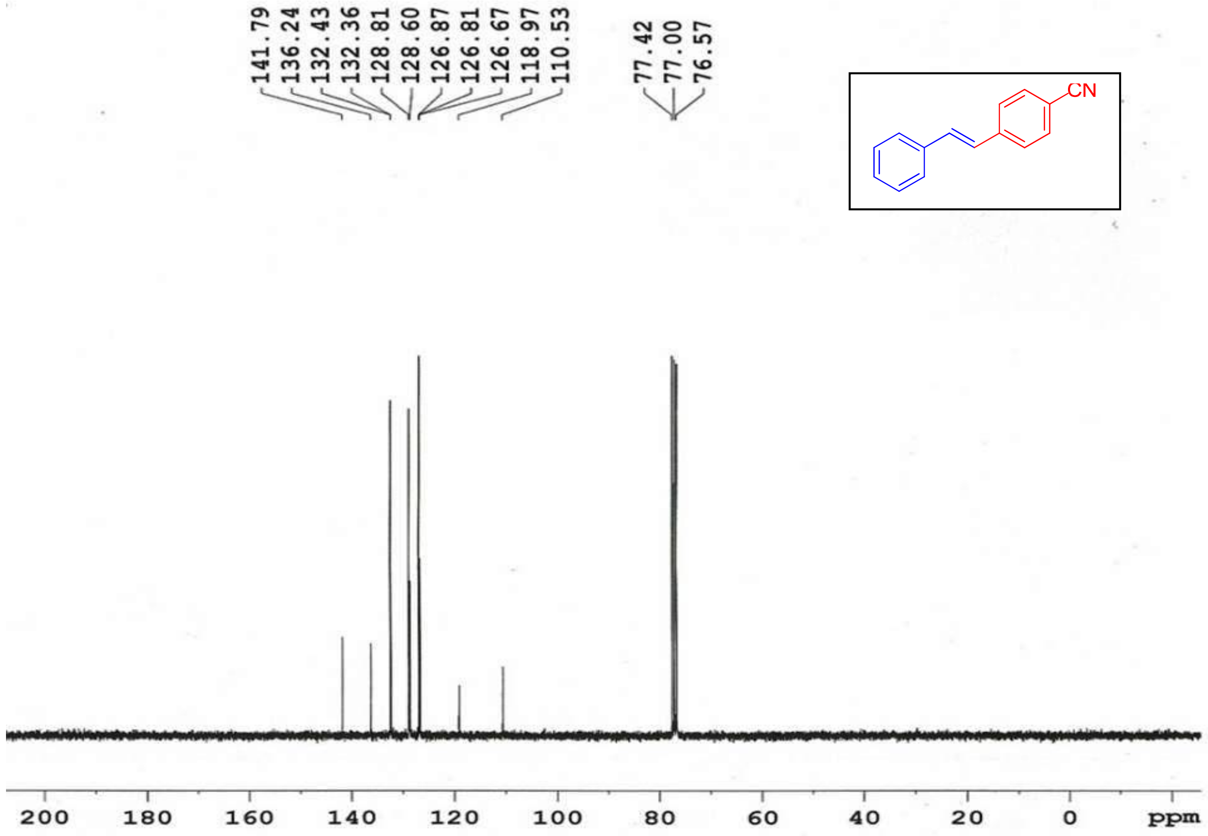


Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e$^-$ Conf	N-Rule
248.0685	1	C 14 H 11 N Na O 2	100.00	248.0682	-1.2	-1.2	90.0	9.5	even	ok

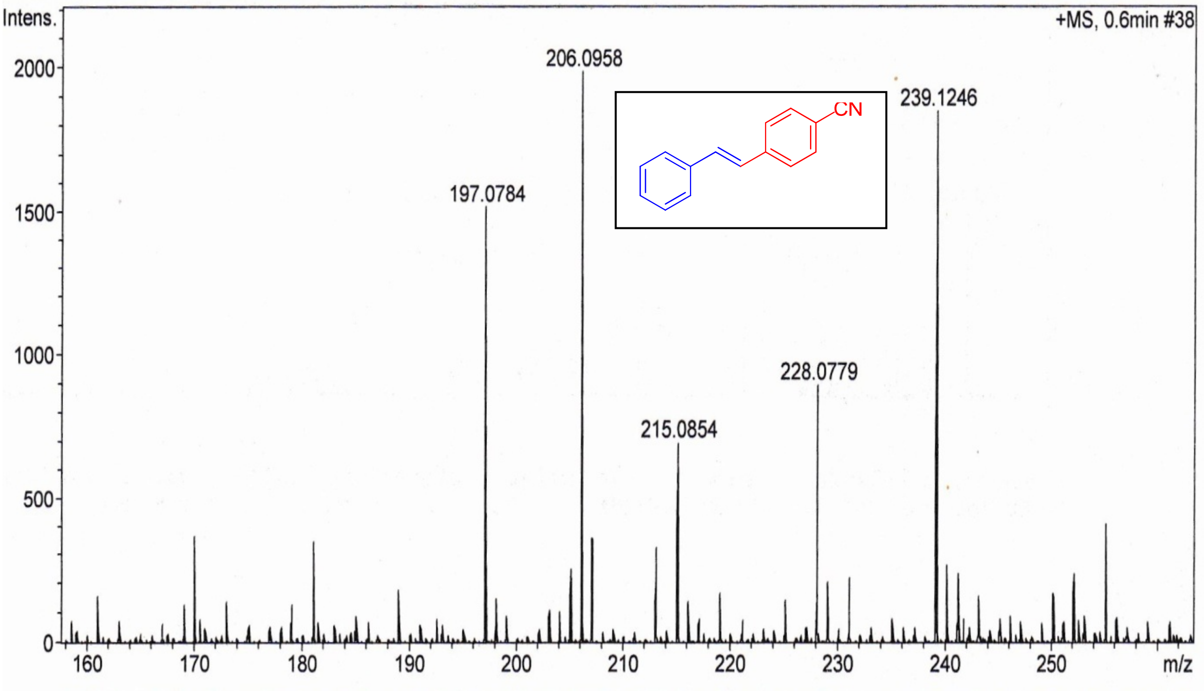
Spectrum 23. HRMS-ESI of compound **3c**



Spectrum 24. 300 MHz ^{1}H NMR of compound **3d**

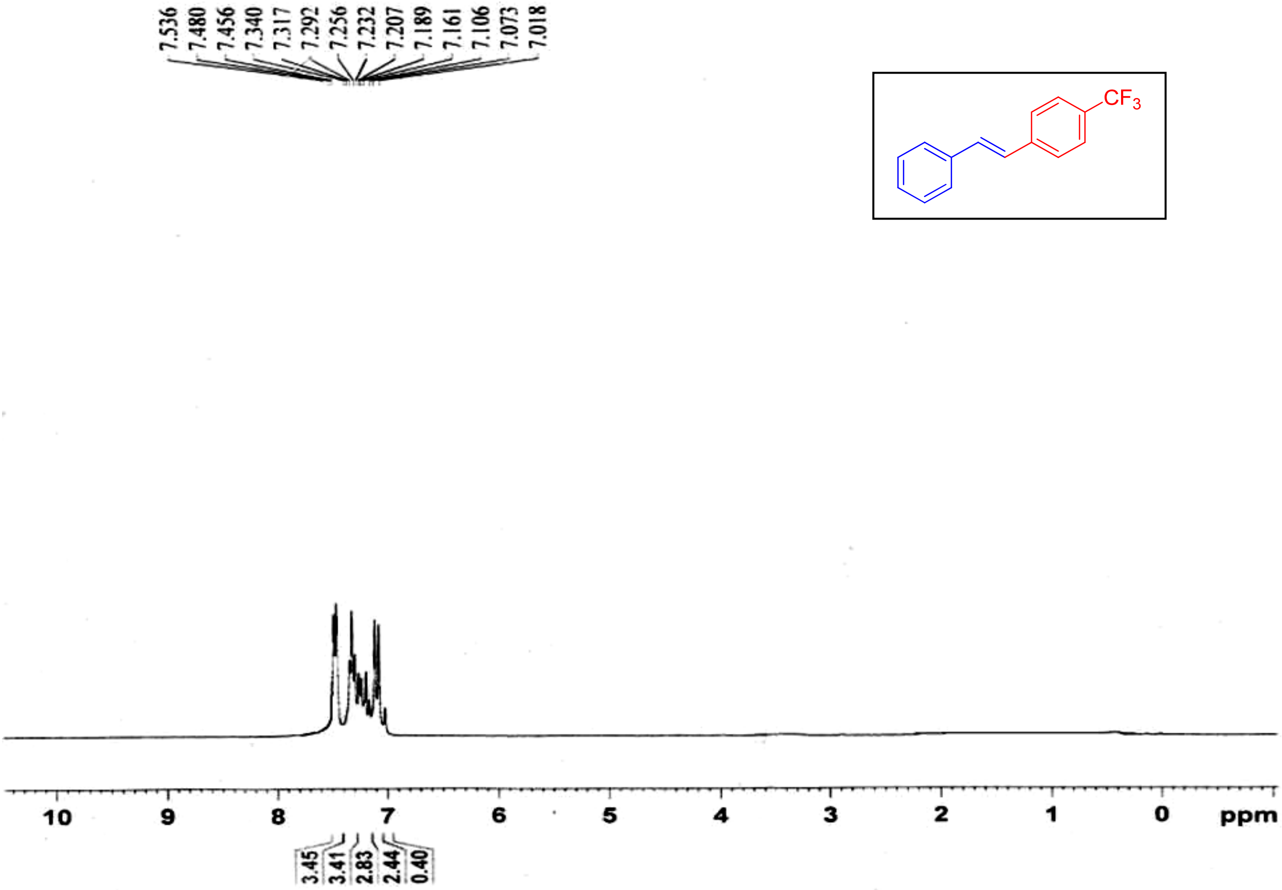


Spectrum 25. 75 MHz ^{13}C NMR of compound **3d**

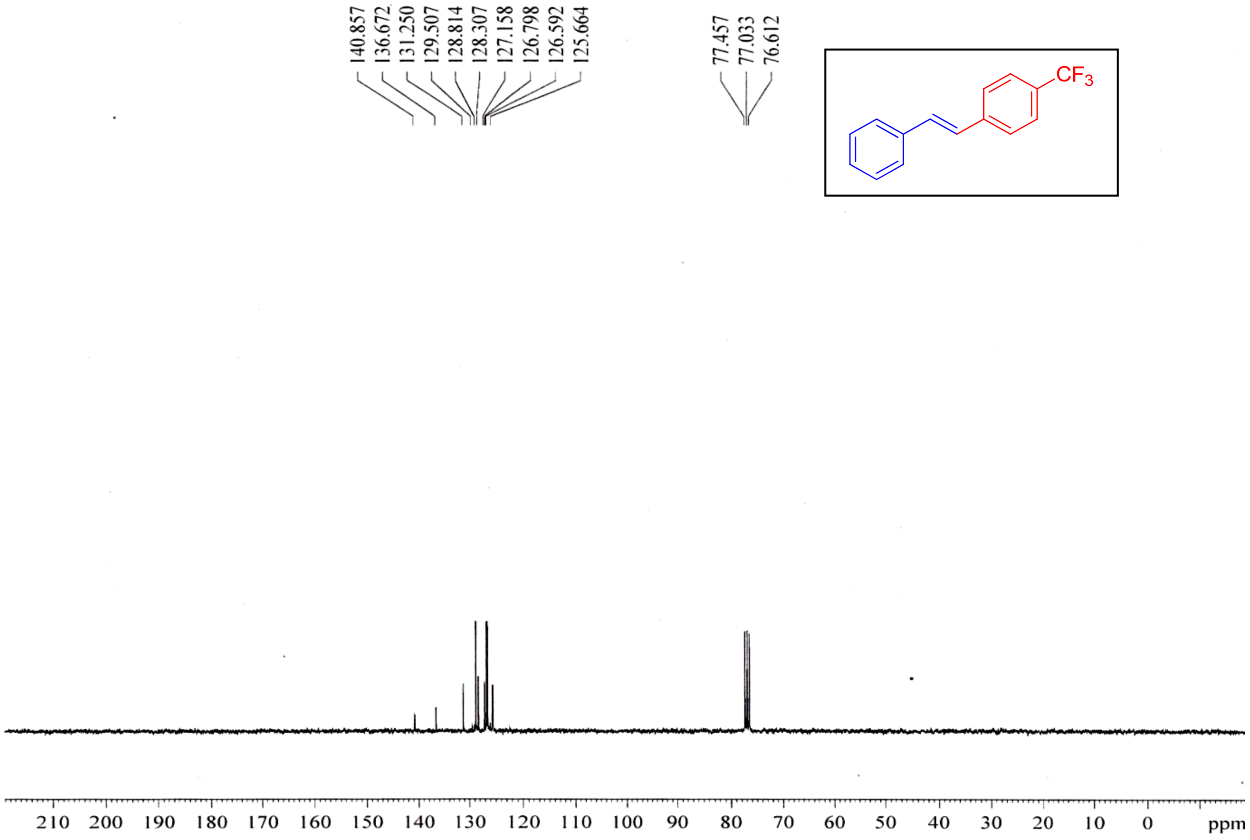


Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e^- Conf	N-Rule
206.0958	1	C 15 H 12 N	100.00	206.0964	2.9	2.9	96.1	10.5	even	ok

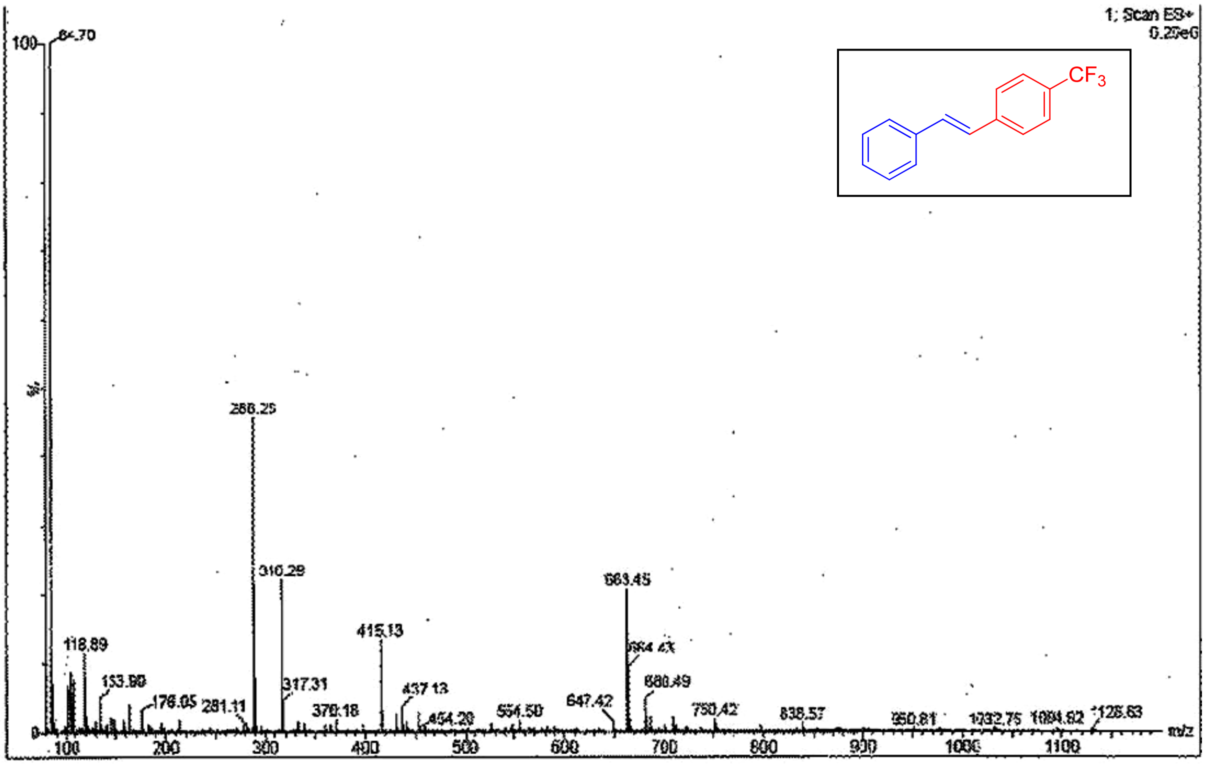
Spectrum 26. HRMS-ESI of compound **3d**



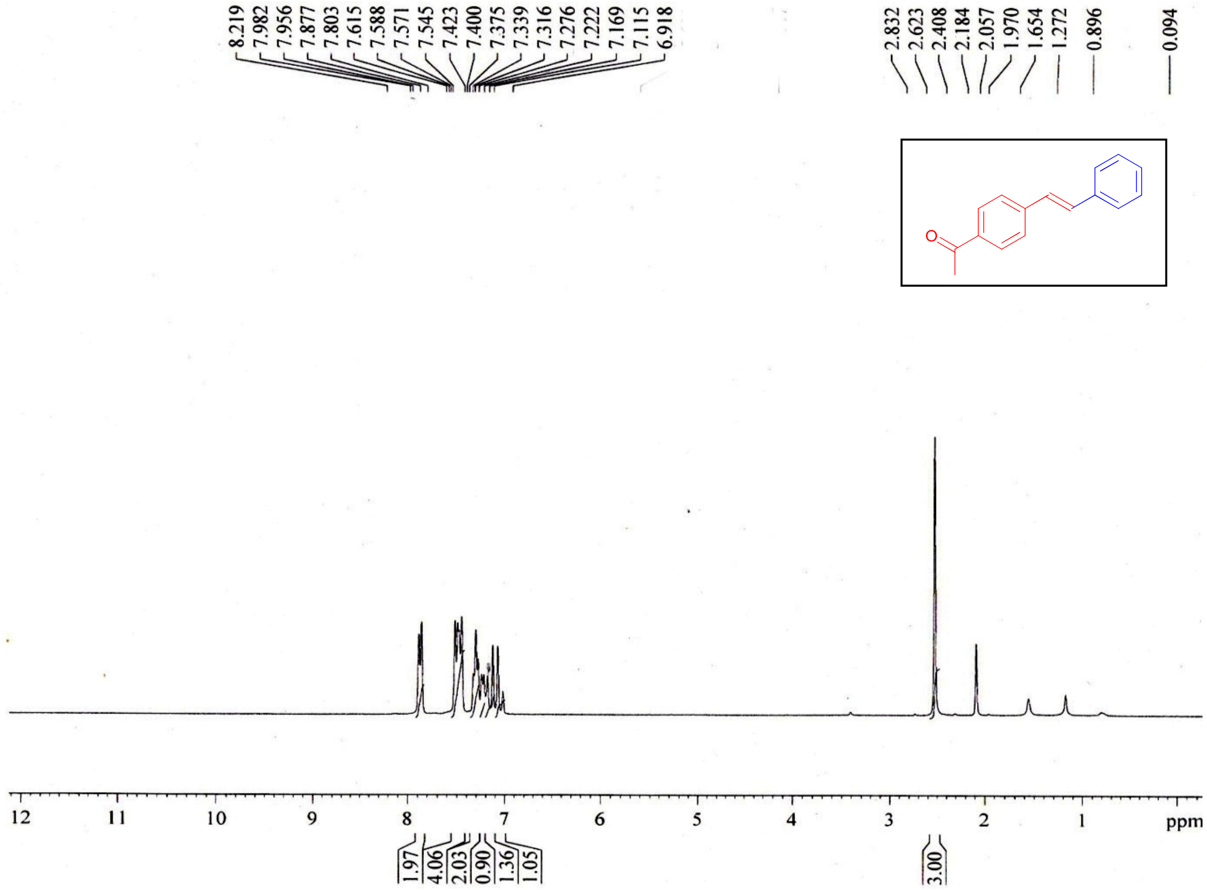
Spectrum 27. 300 MHz ^{1}H NMR of compound **3e**



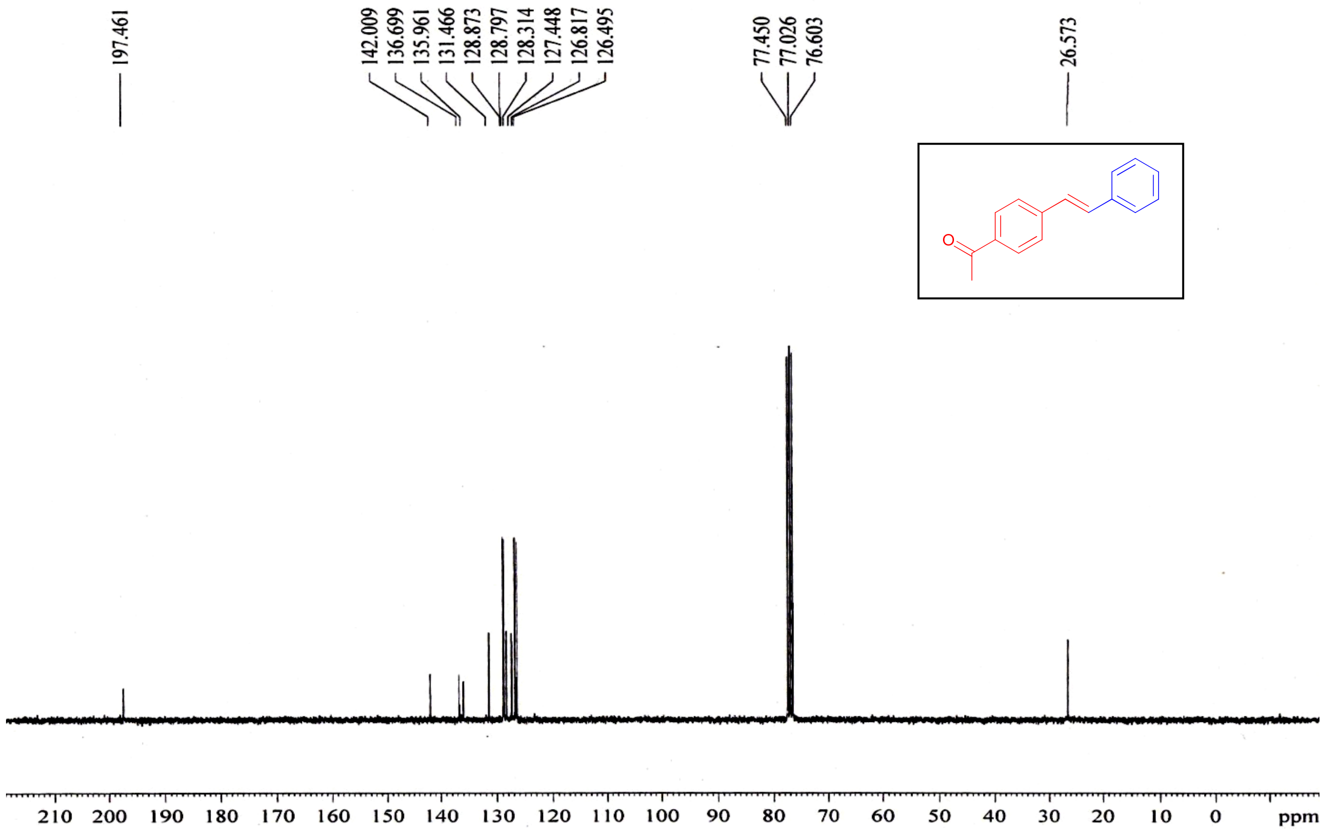
Spectrum 28. 75 MHz ^{13}C NMR of compound **3e**



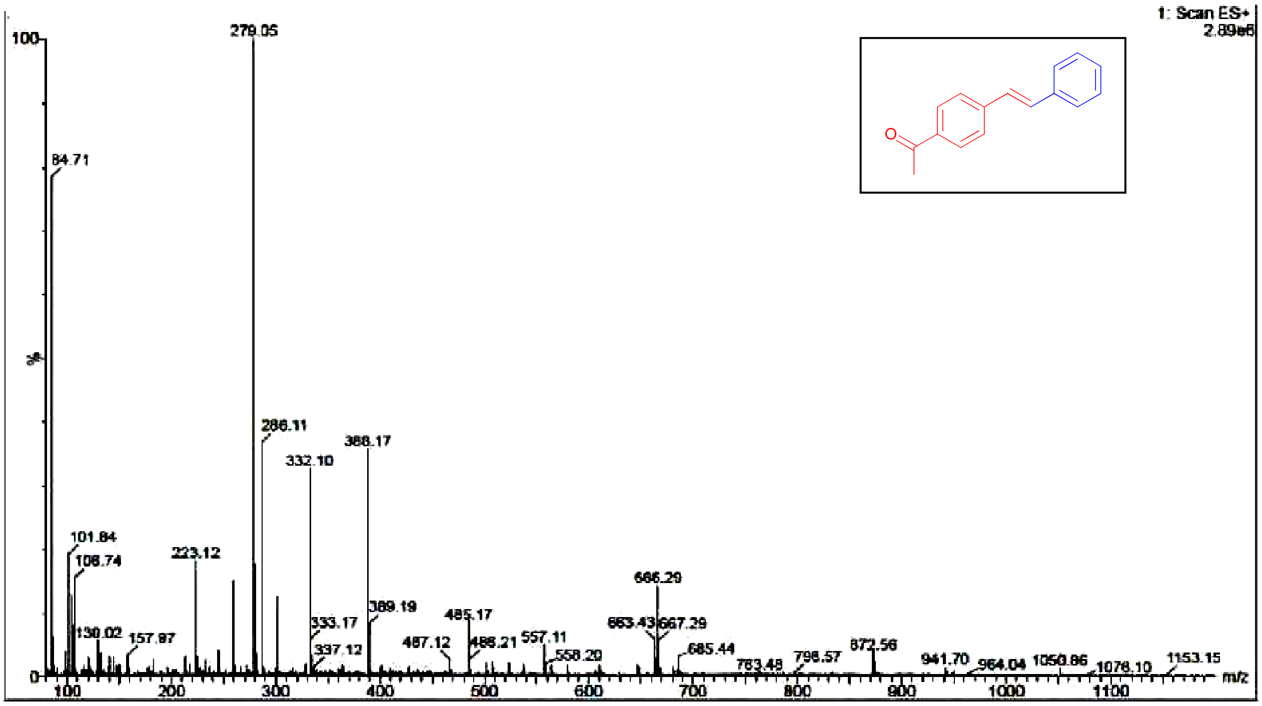
Spectrum 29. LRMS-ESI of compound **3e**



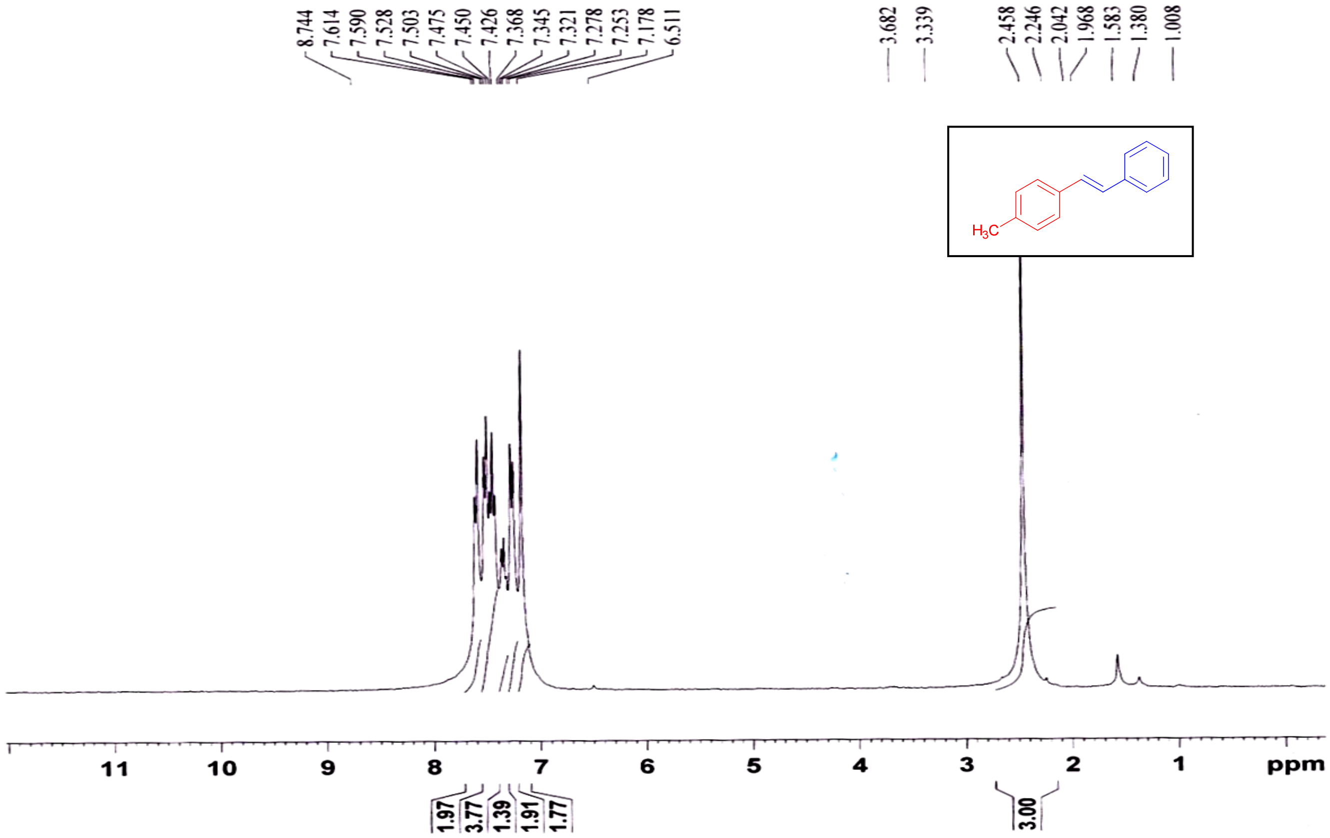
Spectrum 30. 300 MHz ^{1}H NMR of compound **3f**



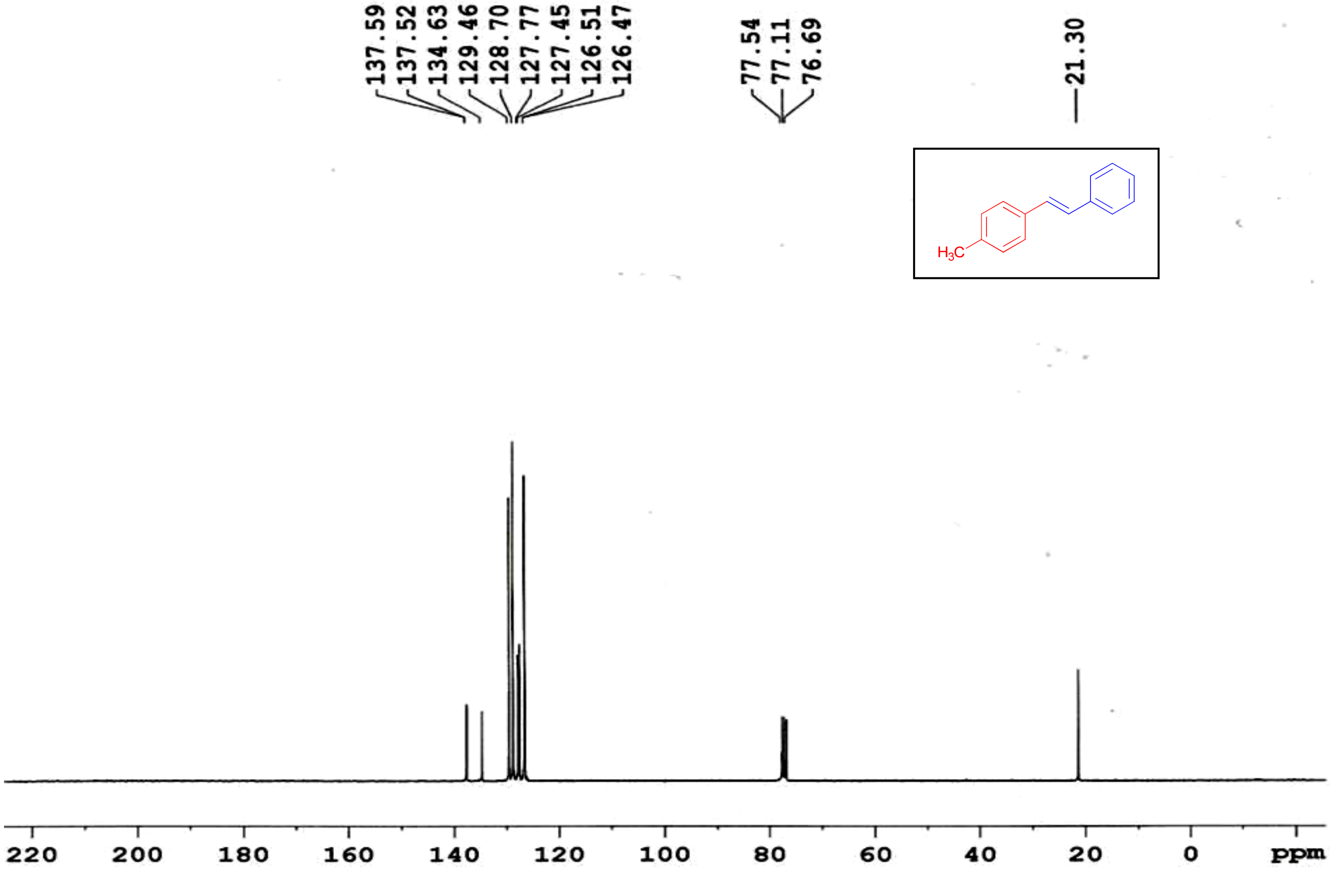
Spectrum 31. 75 MHz ^{13}C NMR of compound **3f**



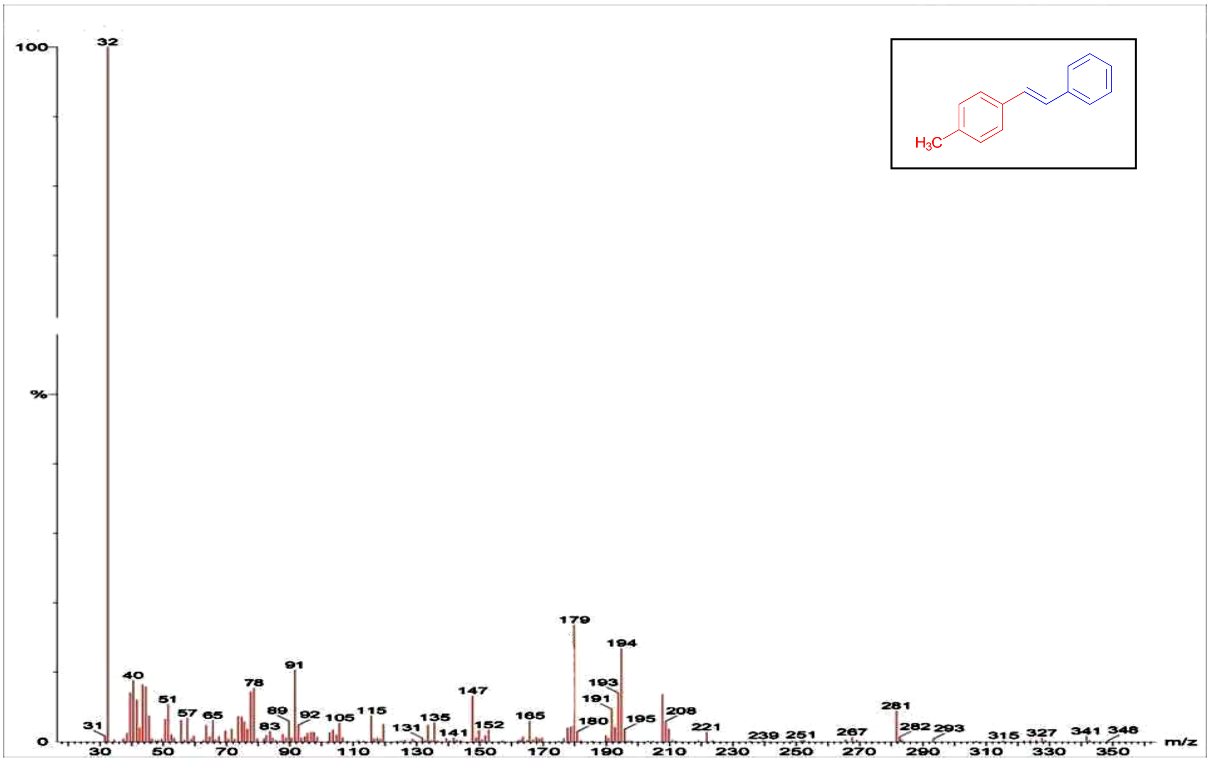
Spectrum 32. LRMS-ESI of compound **3f**



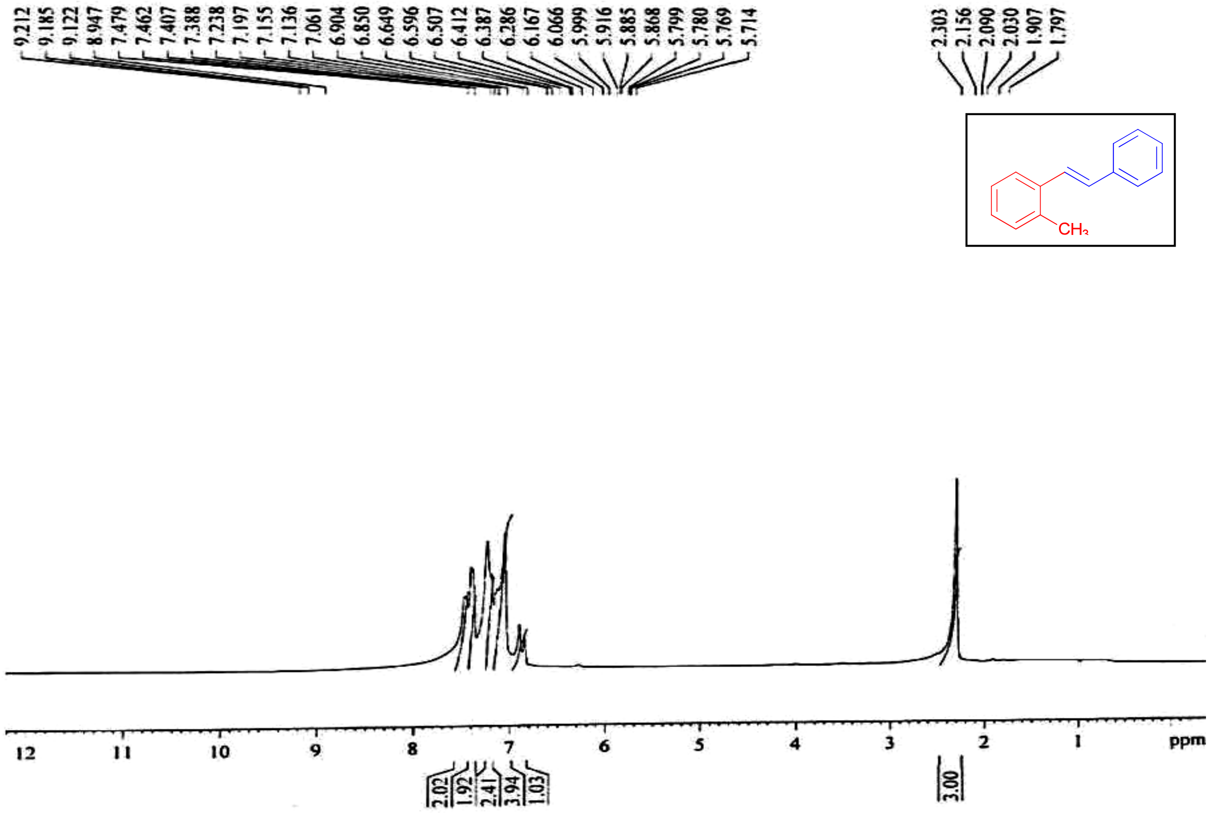
Spectrum 33. 300 MHz ^{1}H NMR of compound **3g**



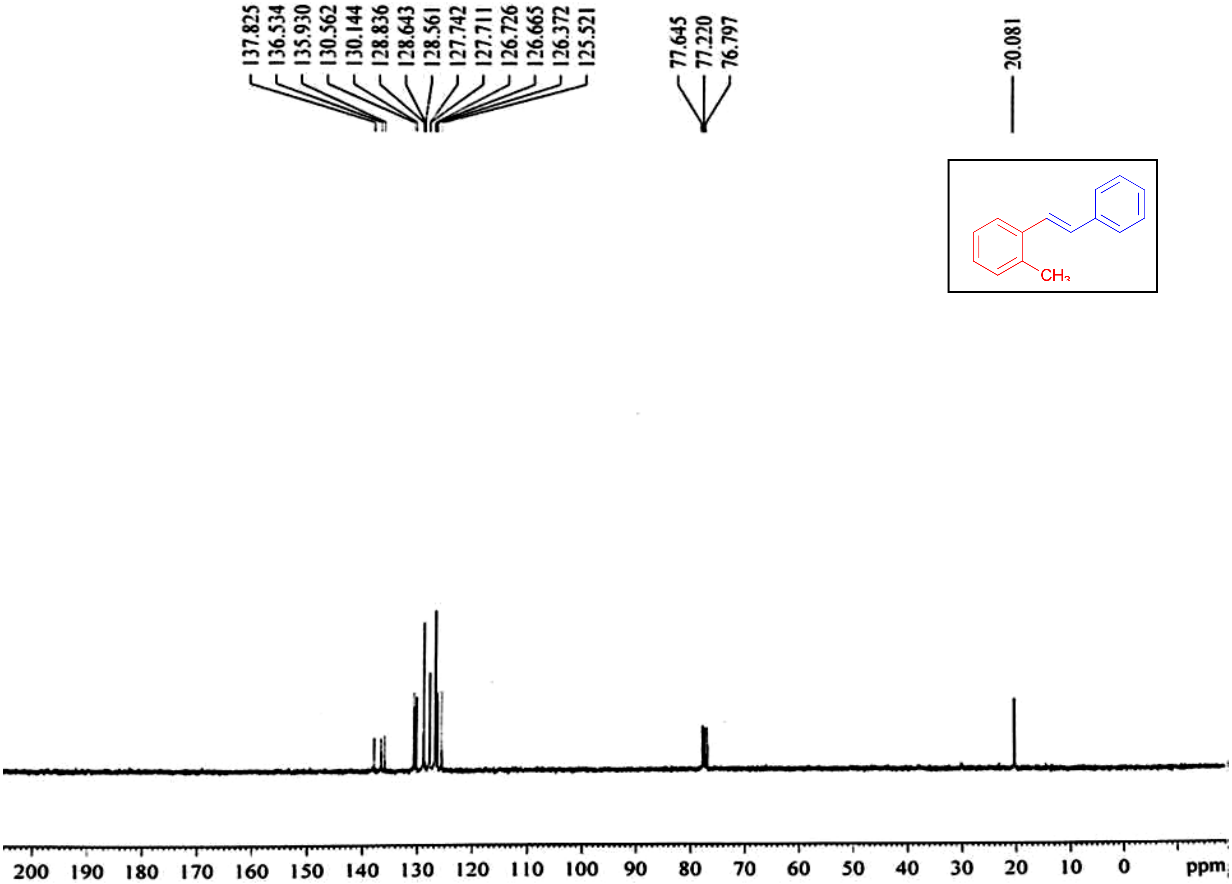
Spectrum 34. 75 MHz ^{13}C NMR of compound **3g**



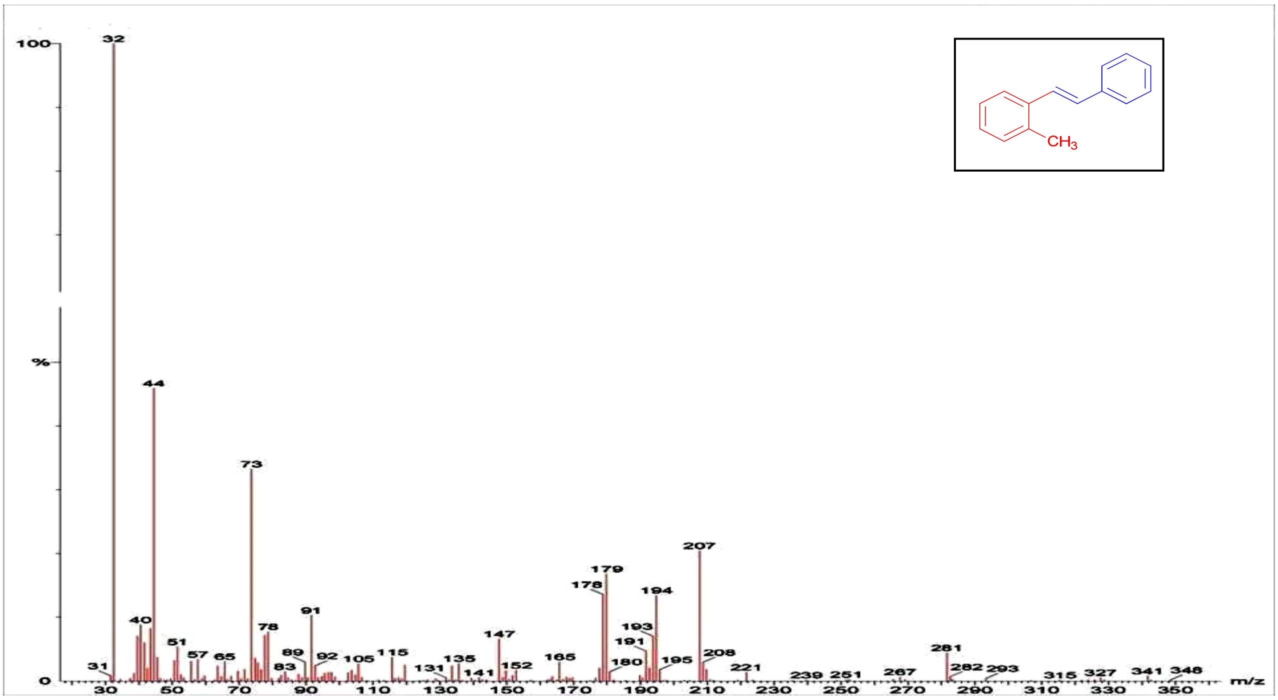
Spectrum 35. EI-MS of compound **3g**



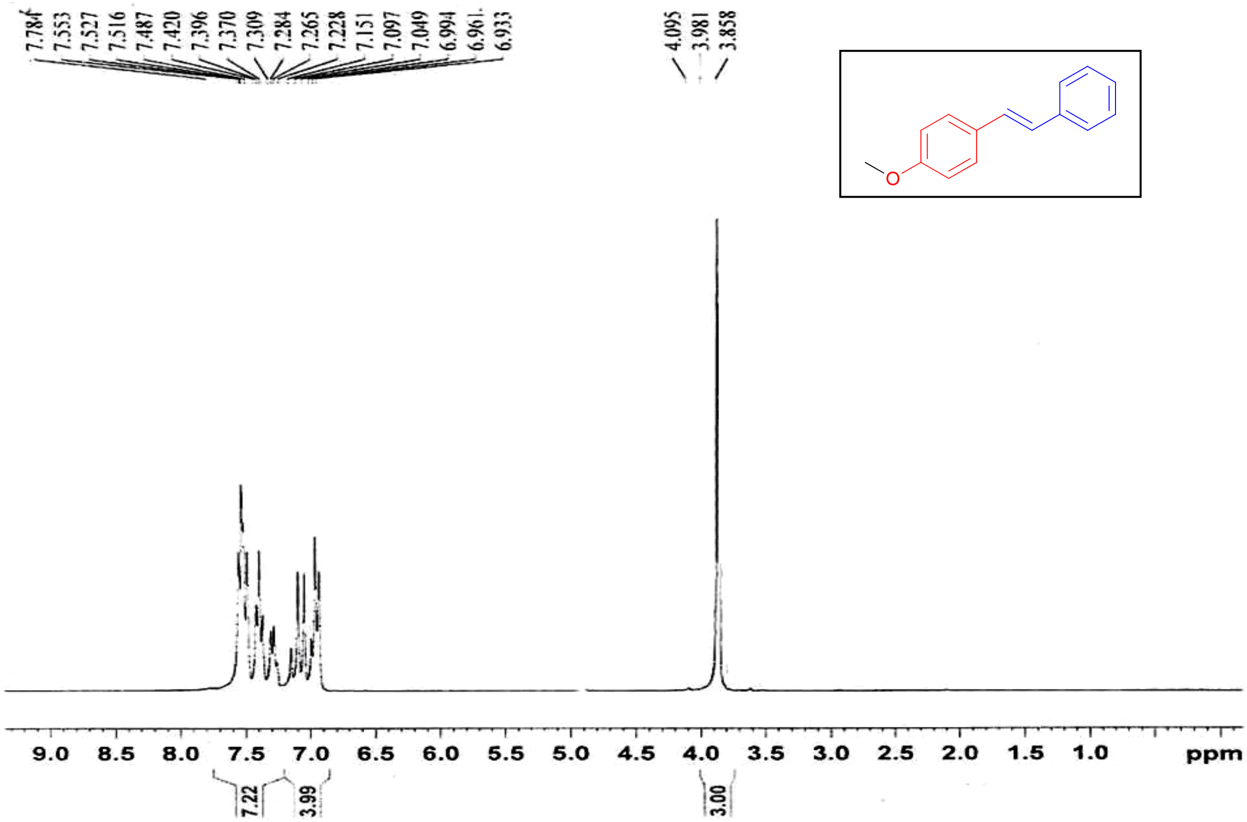
Spectrum 36. 300 MHz ^{1}H NMR of compound **3h**



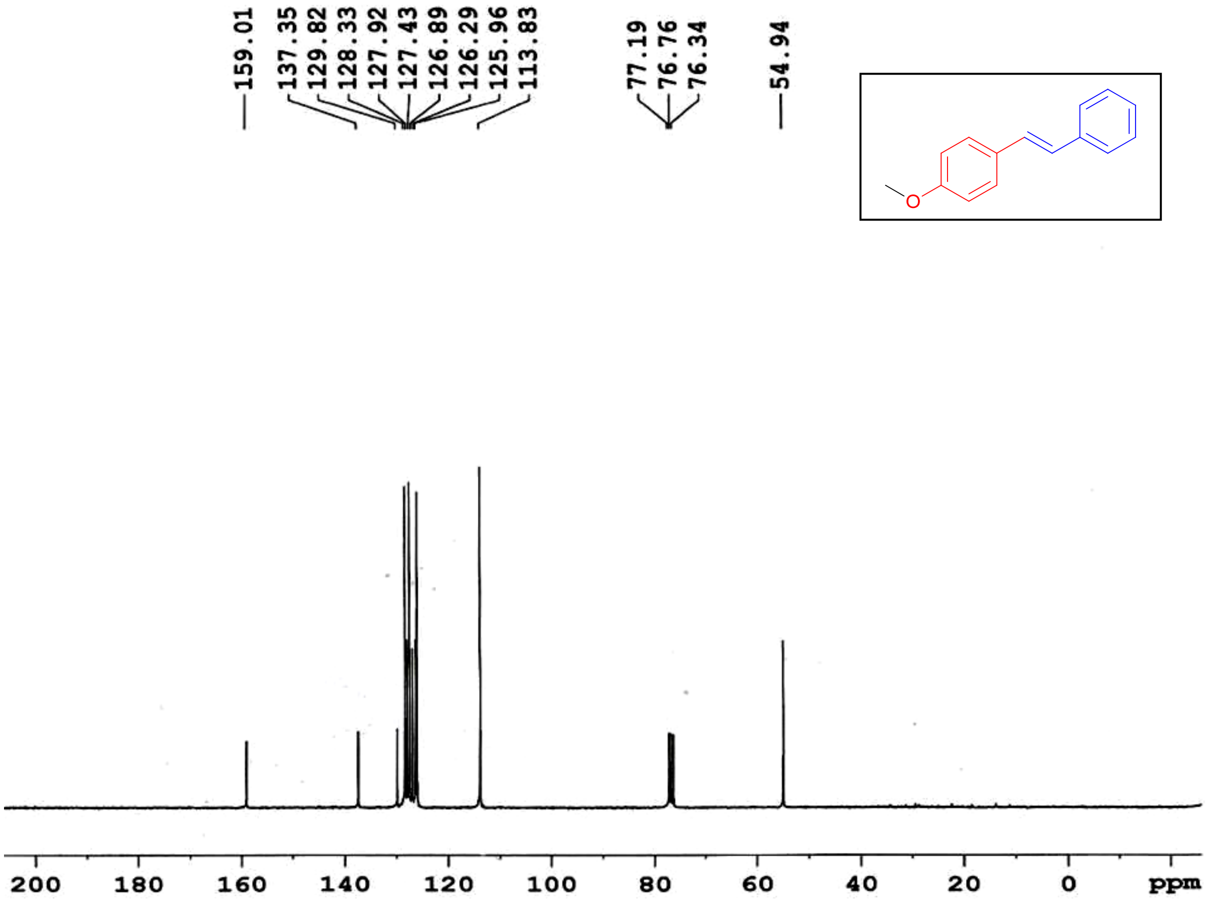
Spectrum 37. 75 MHz ^{13}C NMR of compound **3h**



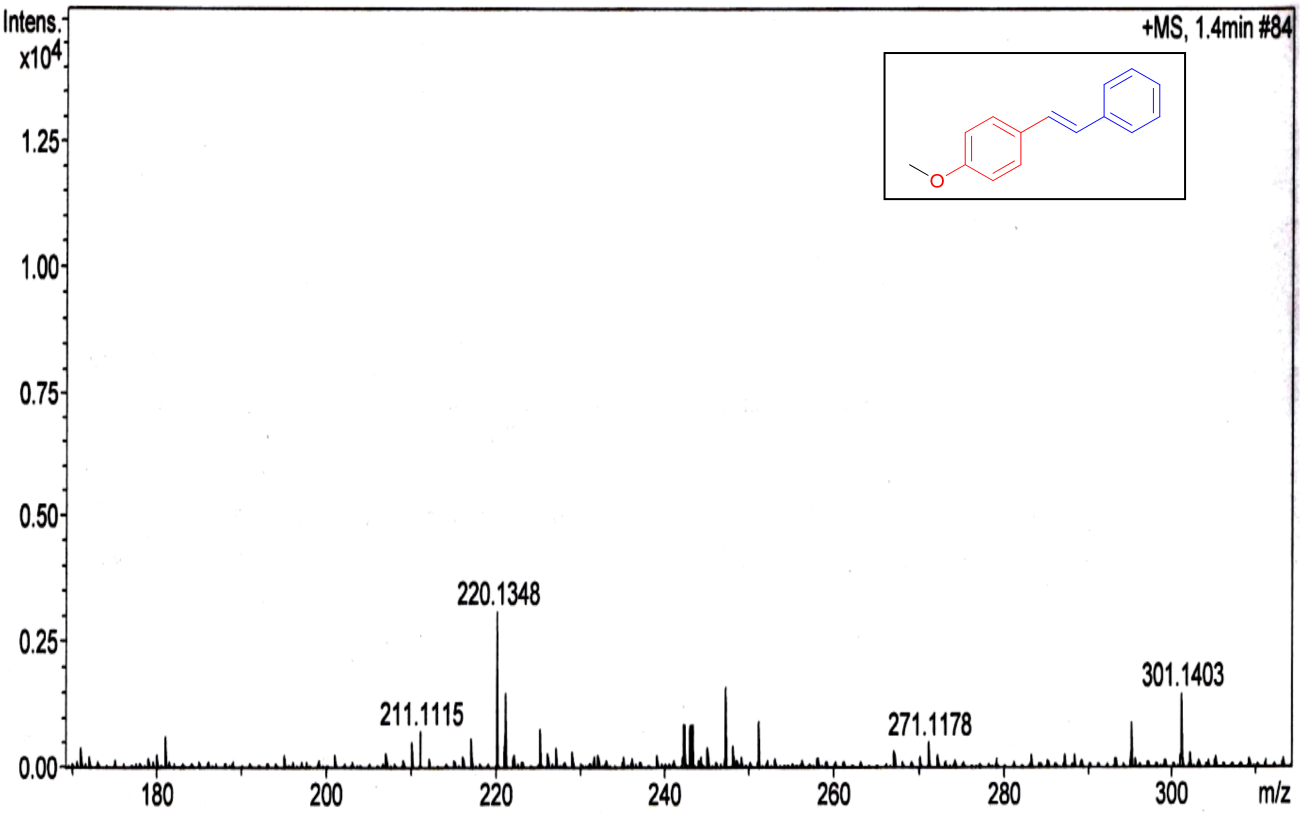
Spectrum 38. EI-MS of compound **3h**



Spectrum 39. 300 MHz ^{1}H NMR of compound **3i**

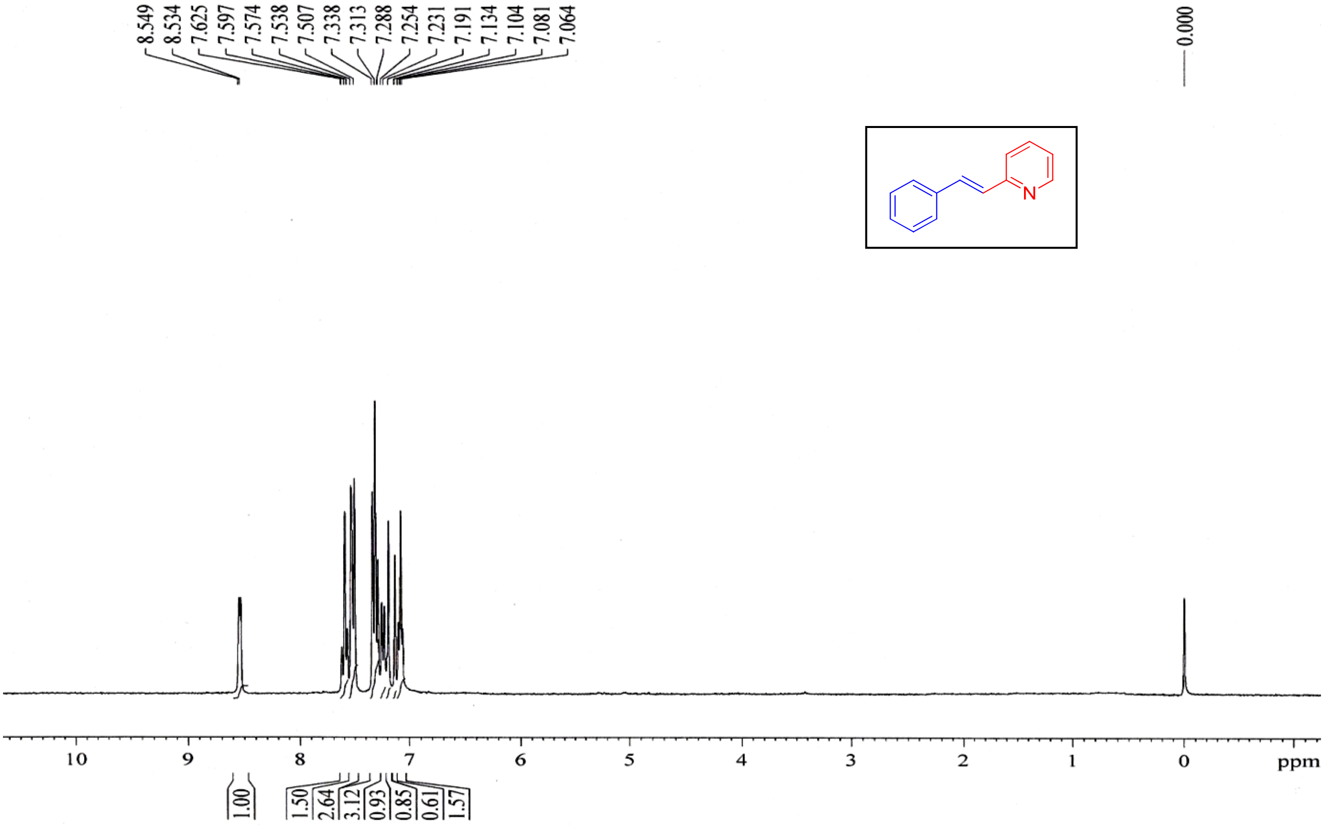


Spectrum 40. 75 MHz ^{13}C NMR of compound **3i**

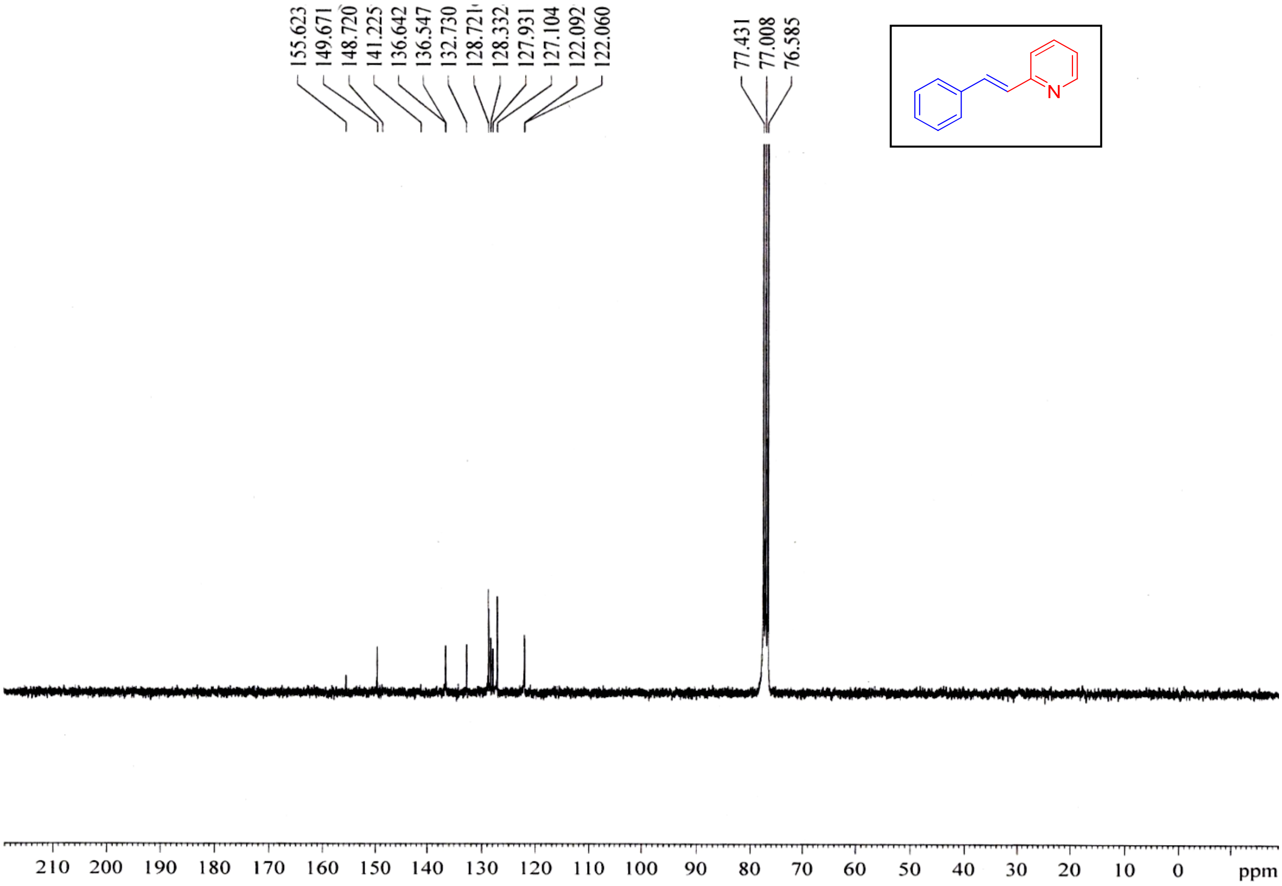


Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
211.1115	1	C 15 H 15 O	100.00	211.1117	1.1	1.1	93.9	8.5	even	ok

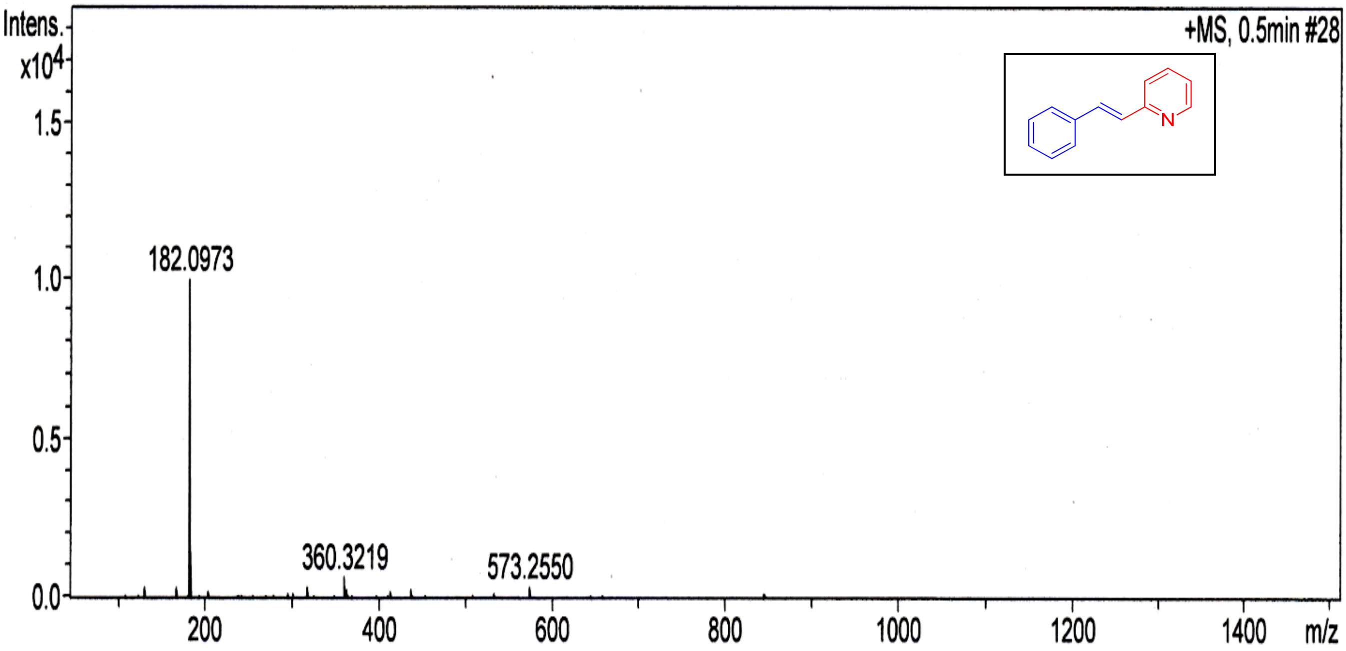
Spectrum 41. HRMS-ESI of compound **3i**



Spectrum 42. 300 MHz ^{1}H NMR of compound **3j**

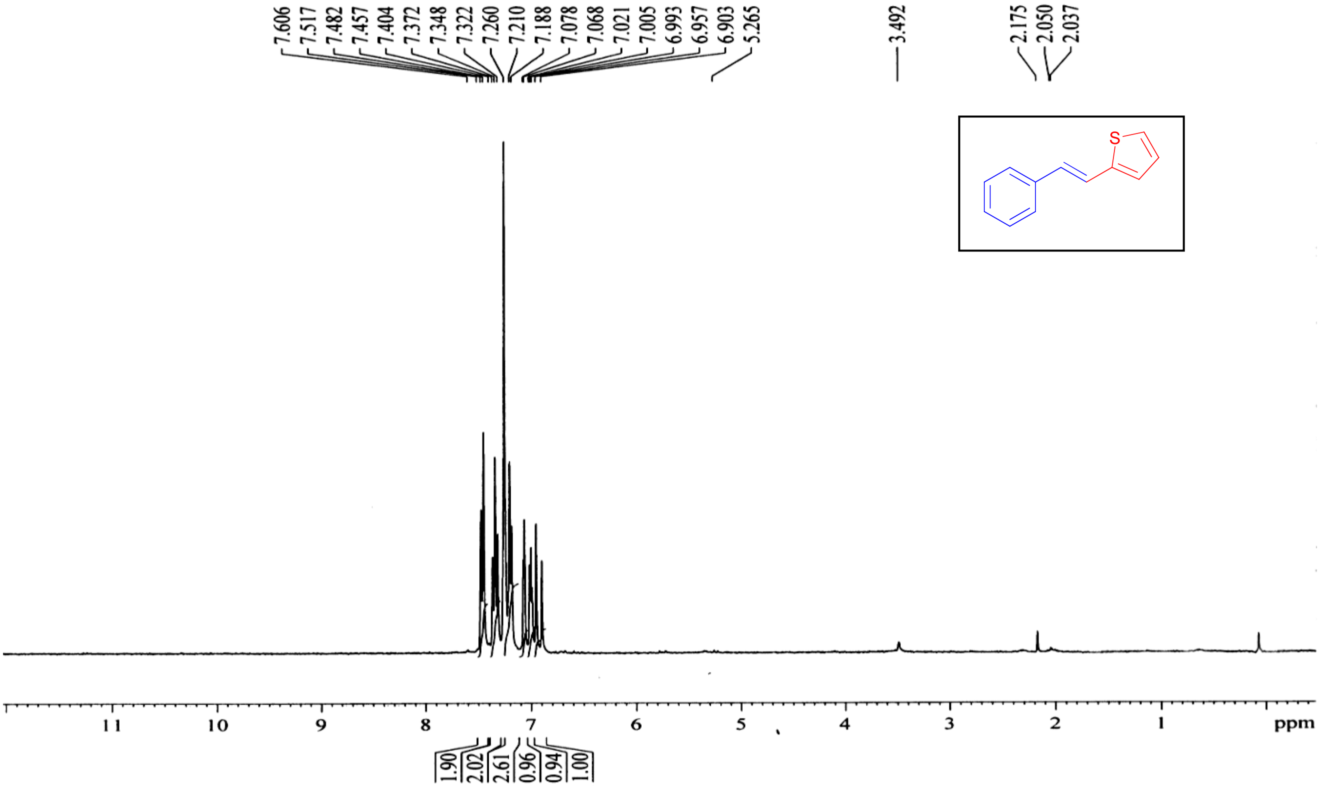


Spectrum 43. 75 MHz ^{13}C NMR of compound **3j**

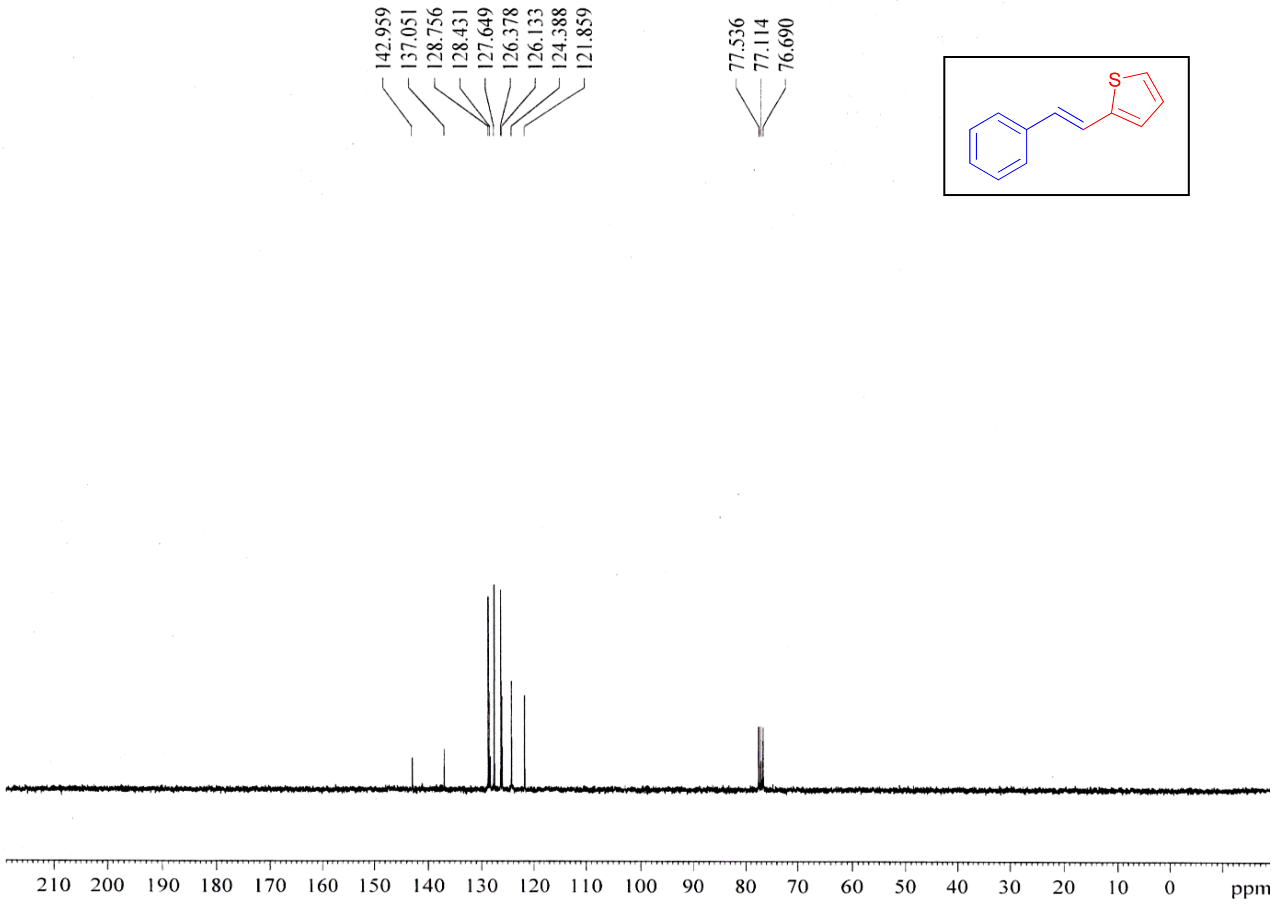


Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
182.0973	1	C 13 H 12 N	100.00	182.0964	-4.8	-4.5	12.3	8.5	even	ok

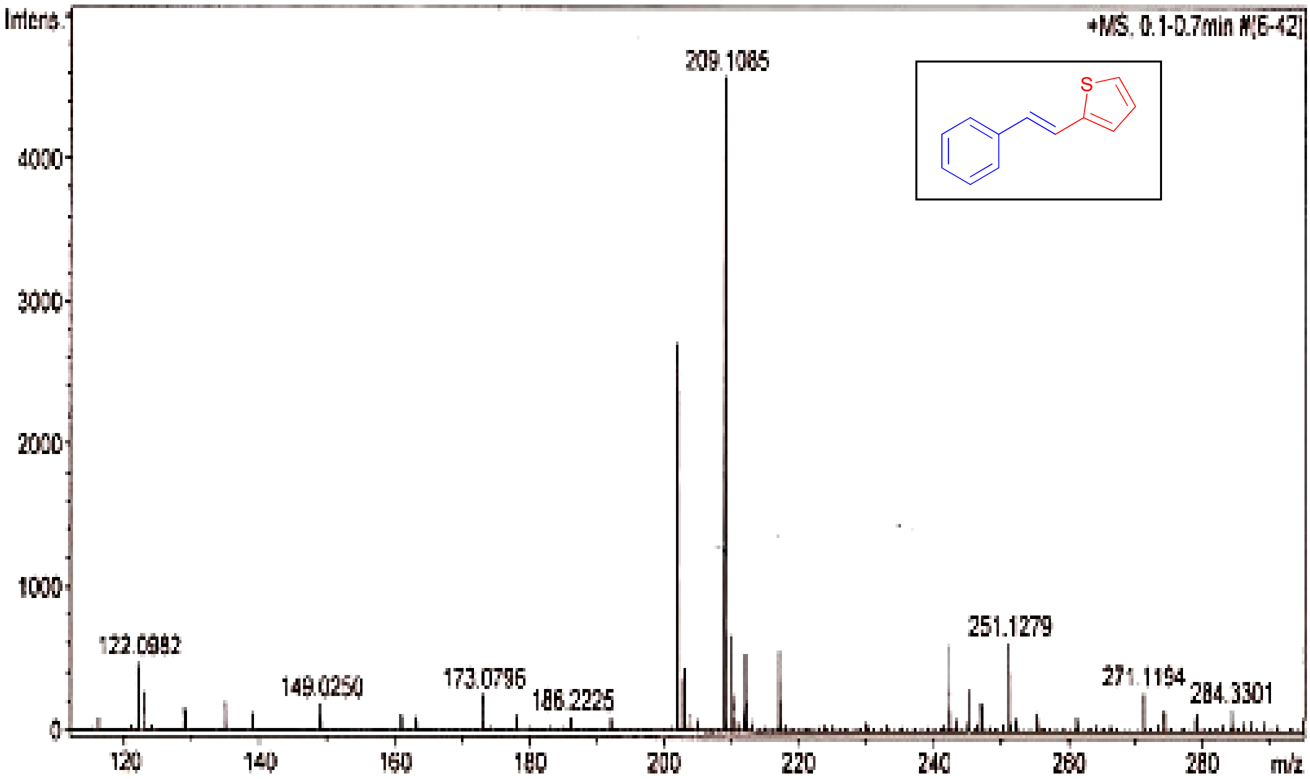
Spectrum 44. HRMS-ESI of compound **3j**



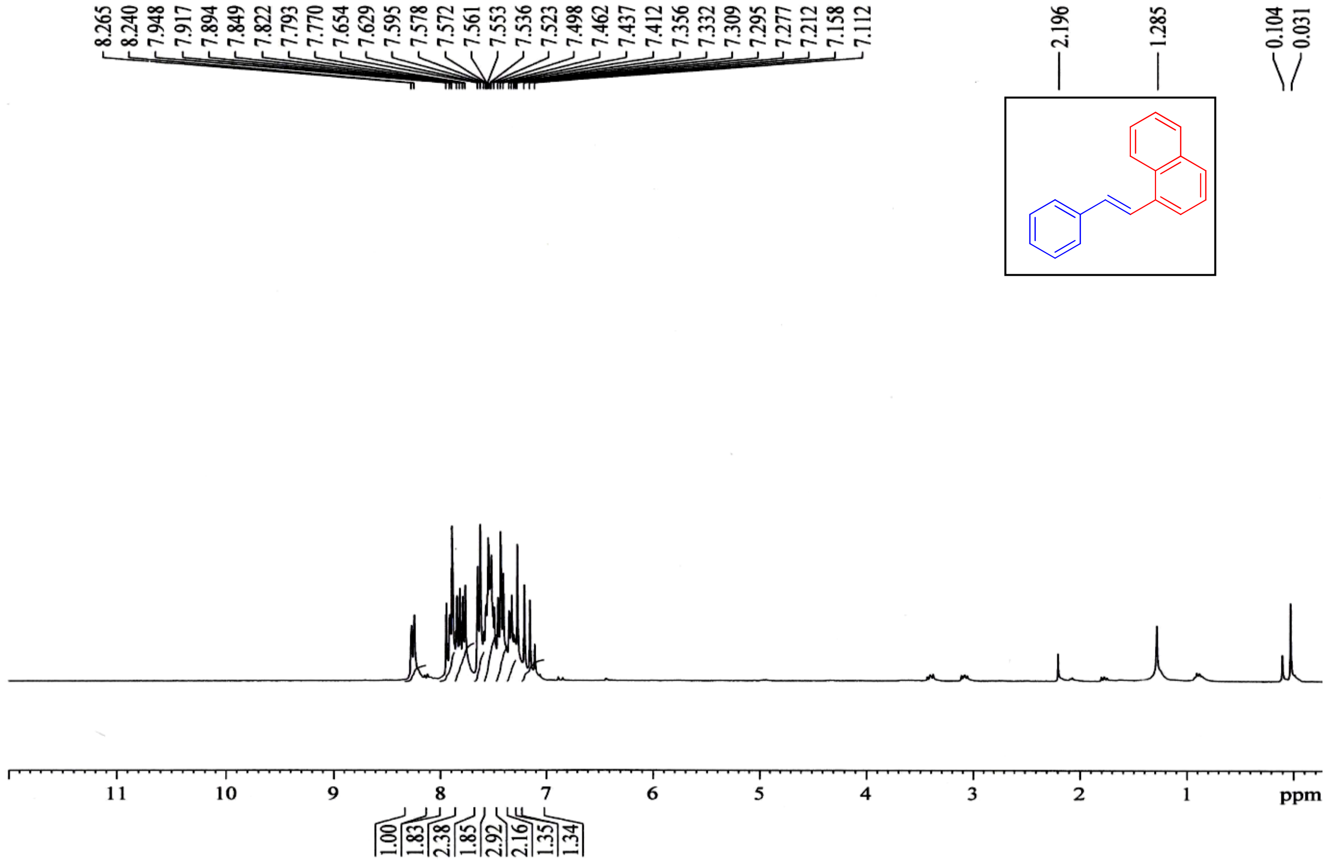
Spectrum 45. 300 MHz ^{1}H NMR of compound **3k**



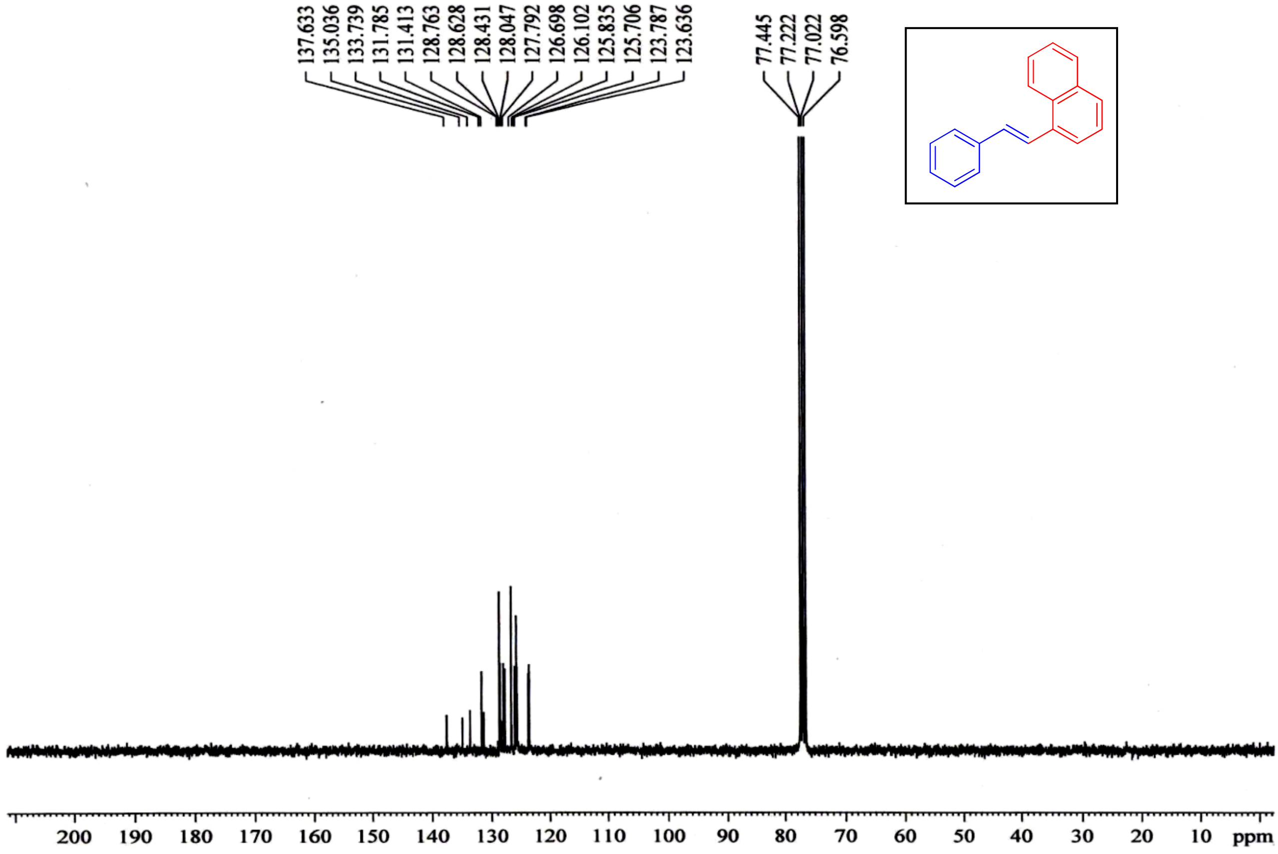
Spectrum 46. 75 MHz ^{13}C NMR of compound **3k**



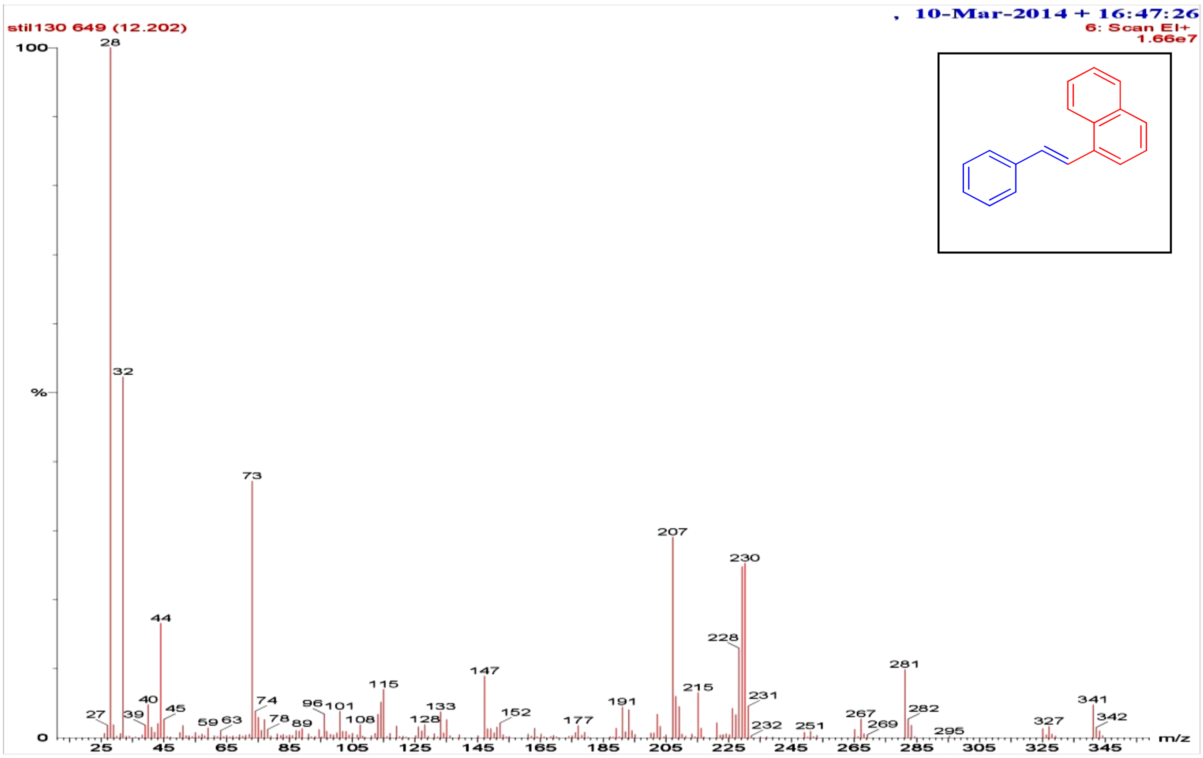
Spectrum 47. HRMS-ESI of compound **3k**



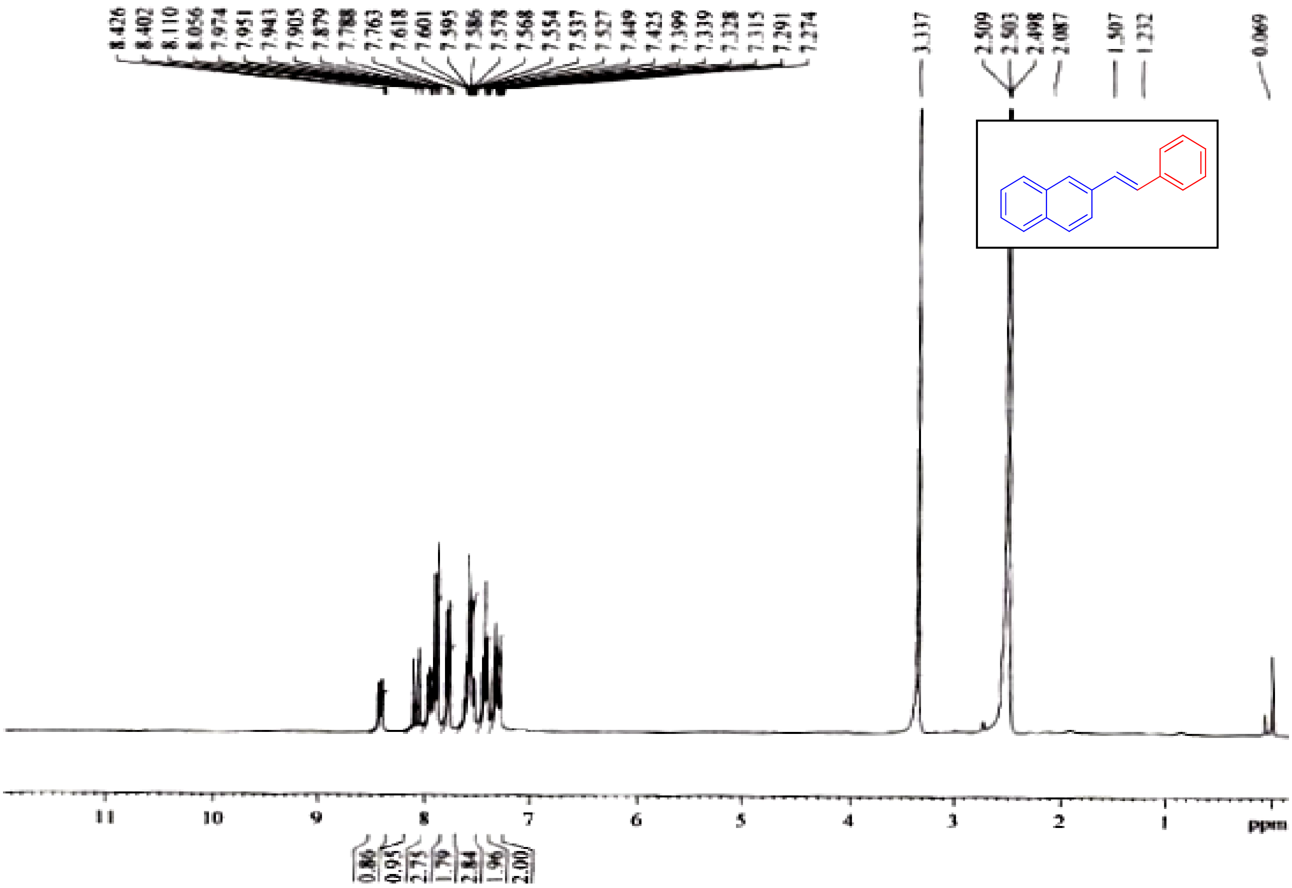
Spectrum 48. 300 MHz ^{1}H NMR of compound **3l**



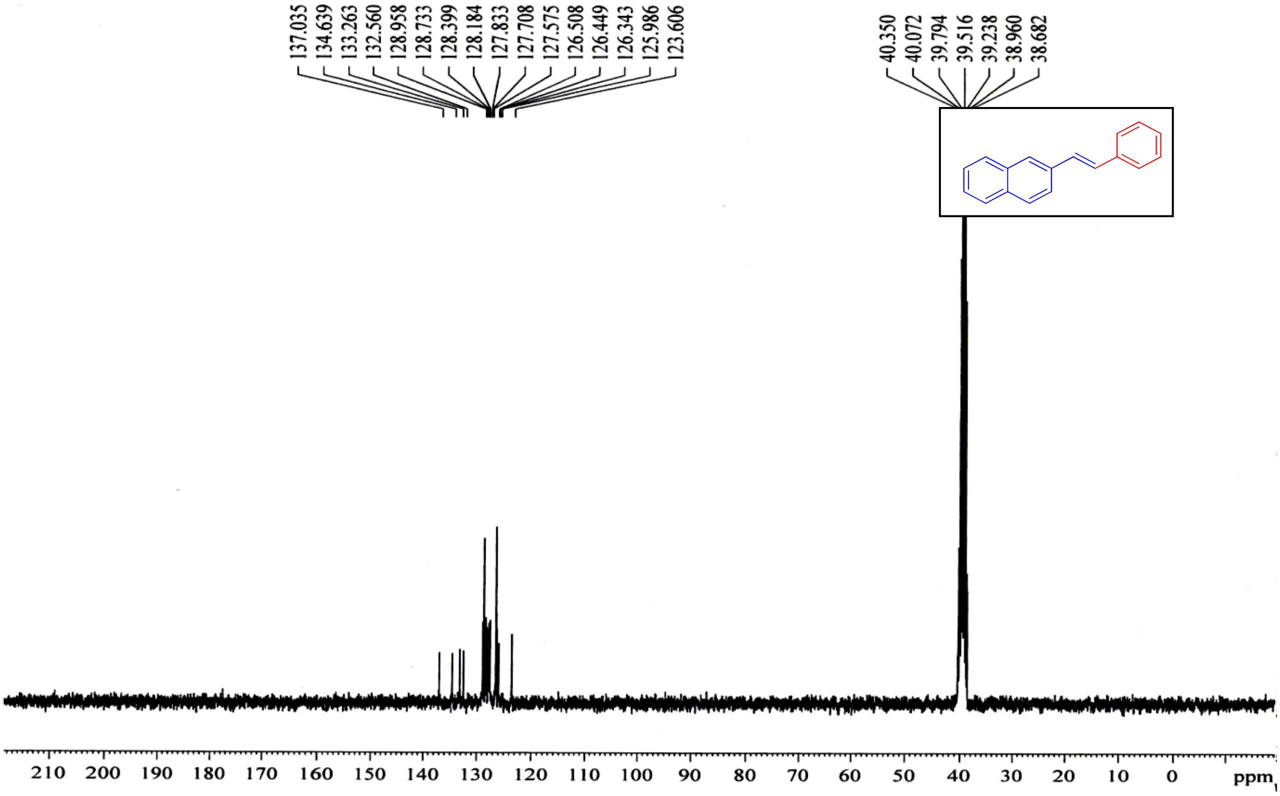
Spectrum 49. 75 MHz ^{13}C NMR of compound **3l**



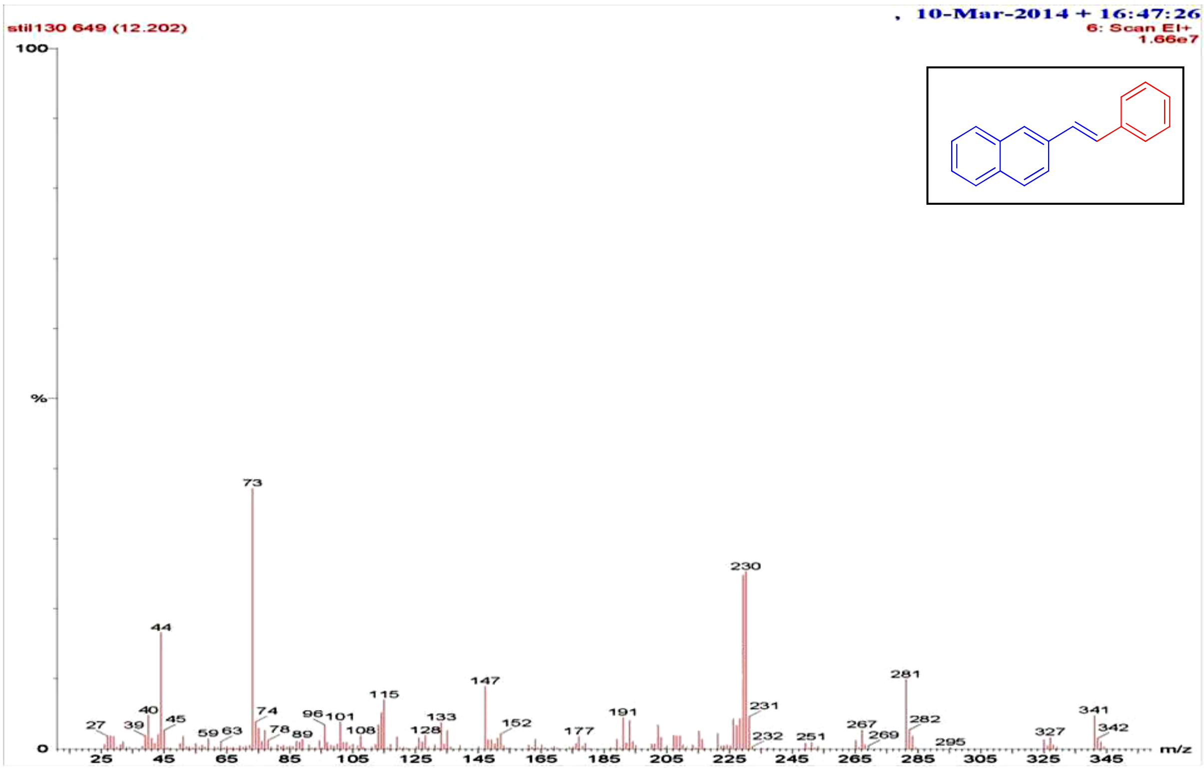
Spectrum 50. EI-MS of compound **3l**



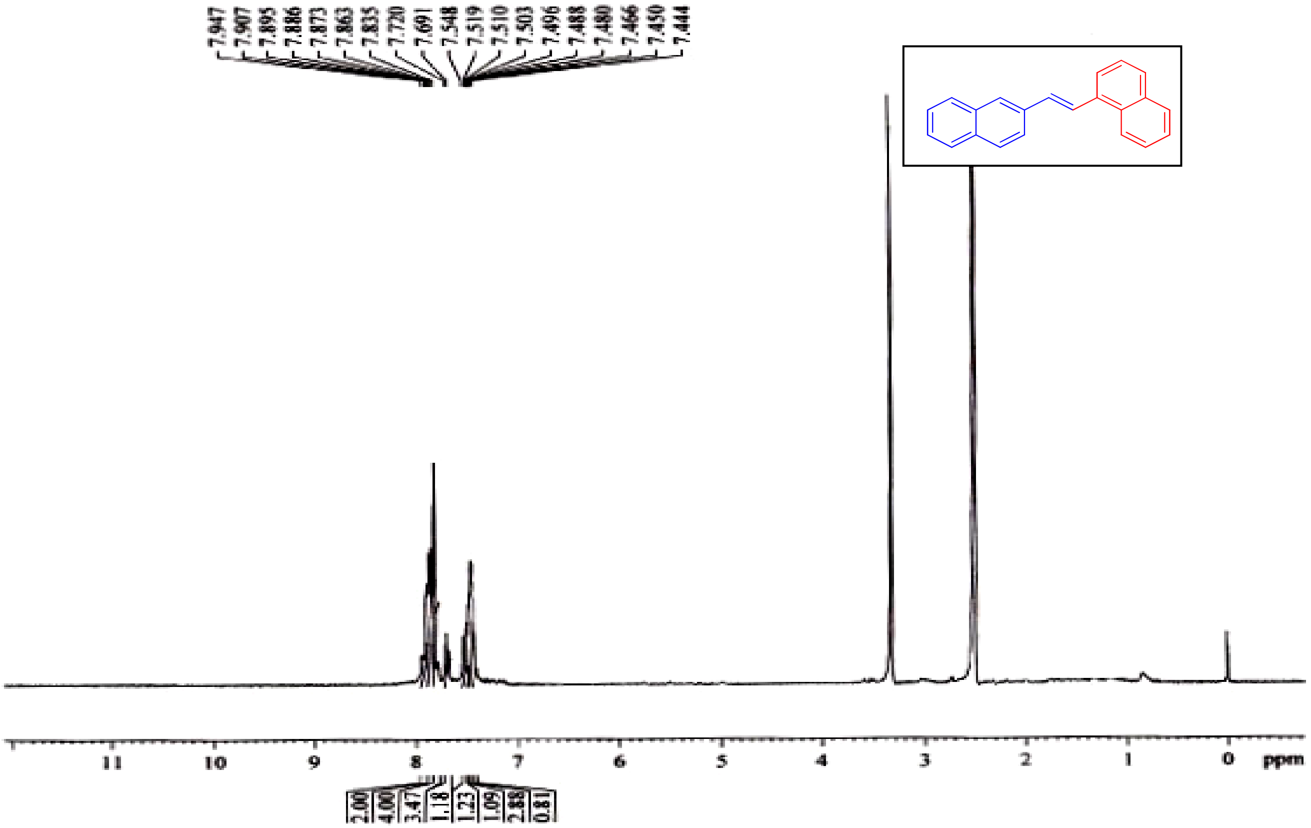
Spectrum 51. 300 MHz ^{1}H NMR of compound **3m**



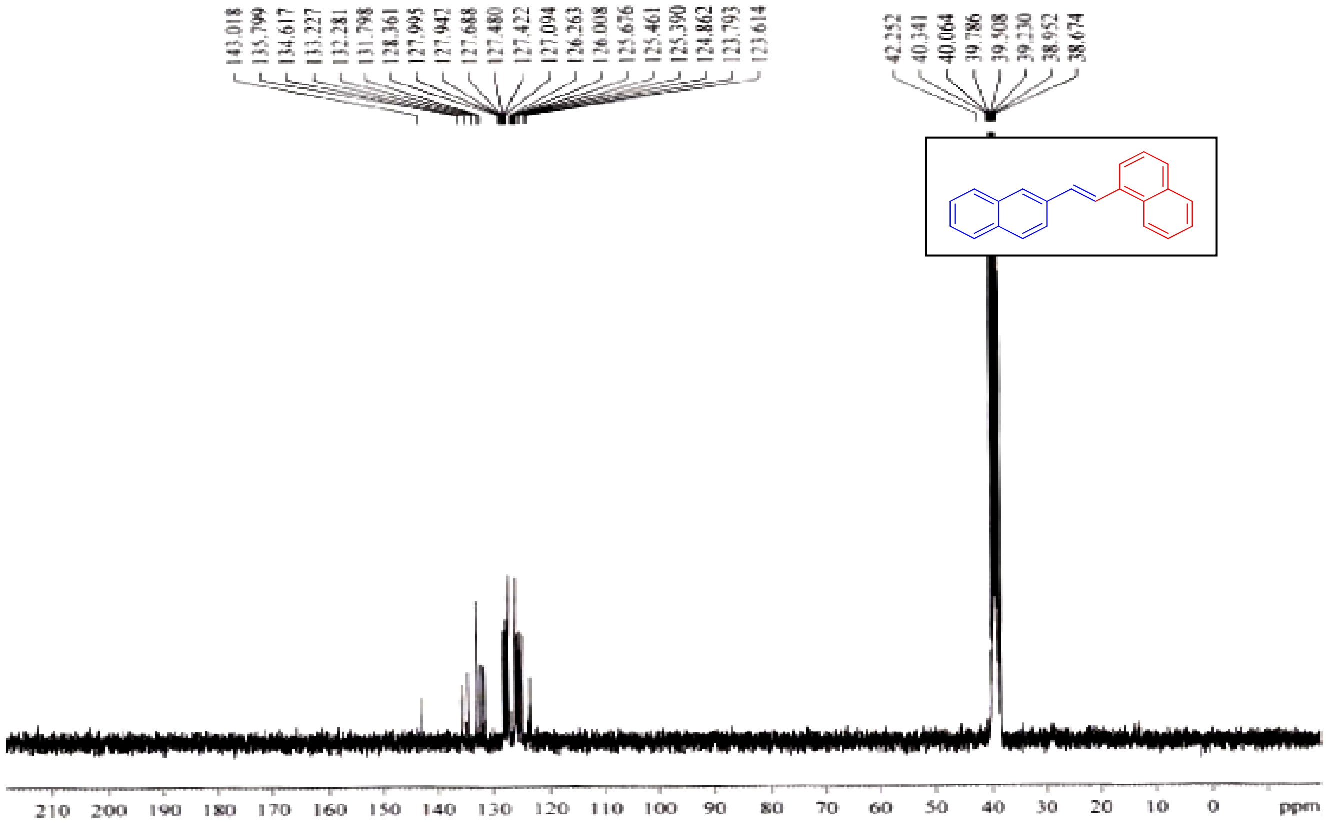
Spectrum 52. 75 MHz ^{13}C NMR of compound **3m**



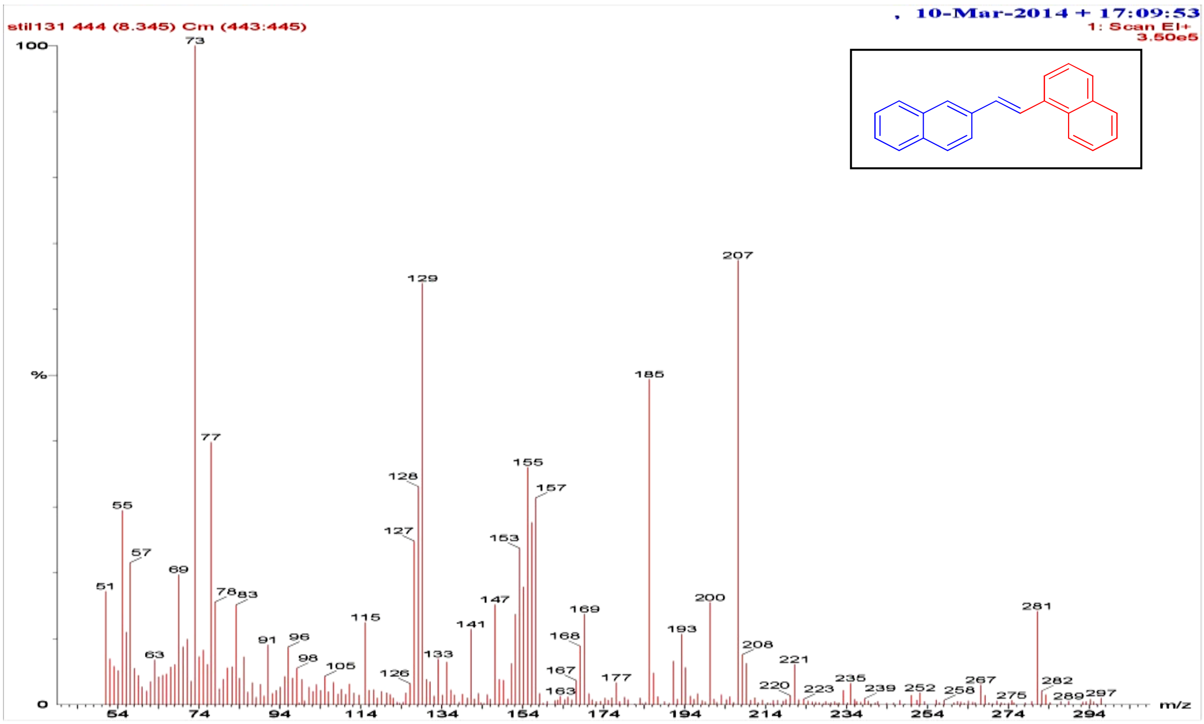
Spectrum 53. EI-MS of compound **3m**



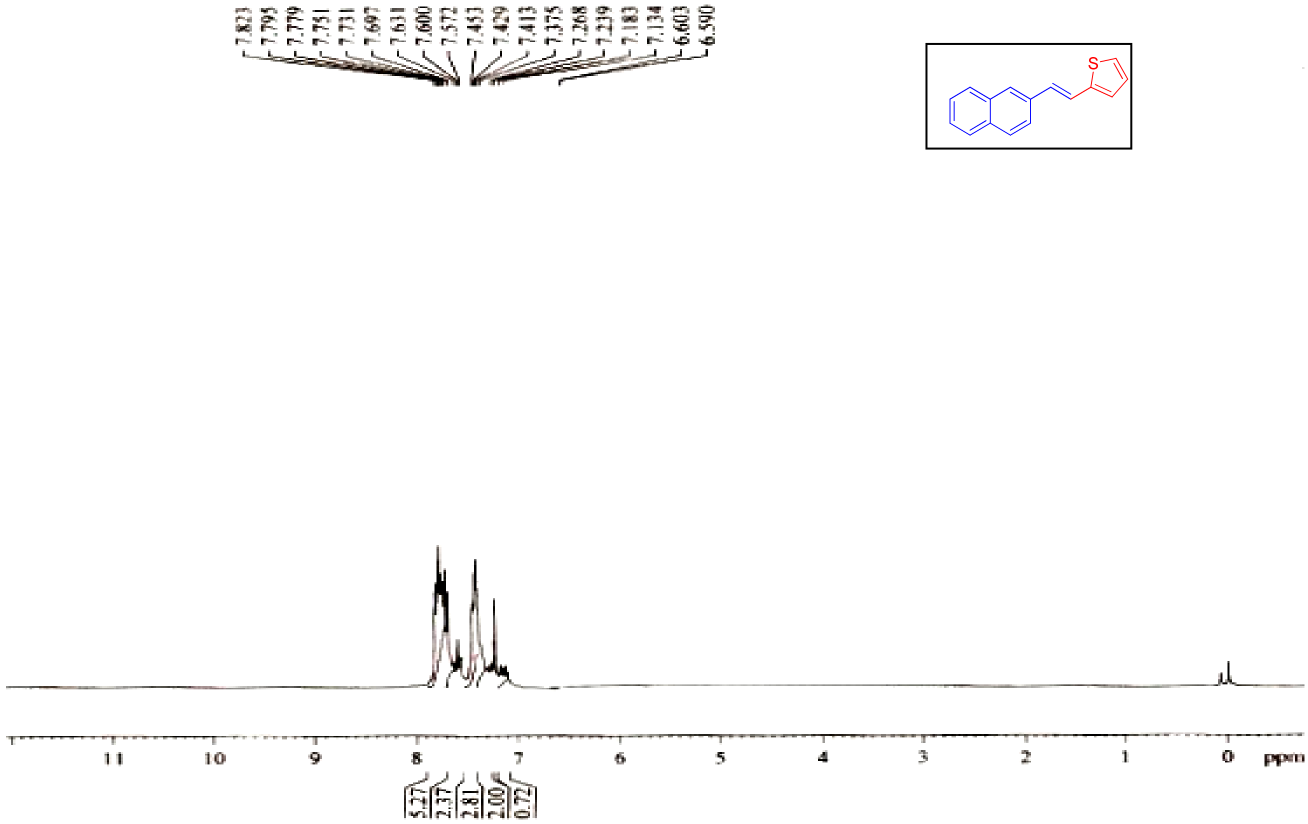
Spectrum 54. 300 MHz ^{1}H NMR of compound **3n**



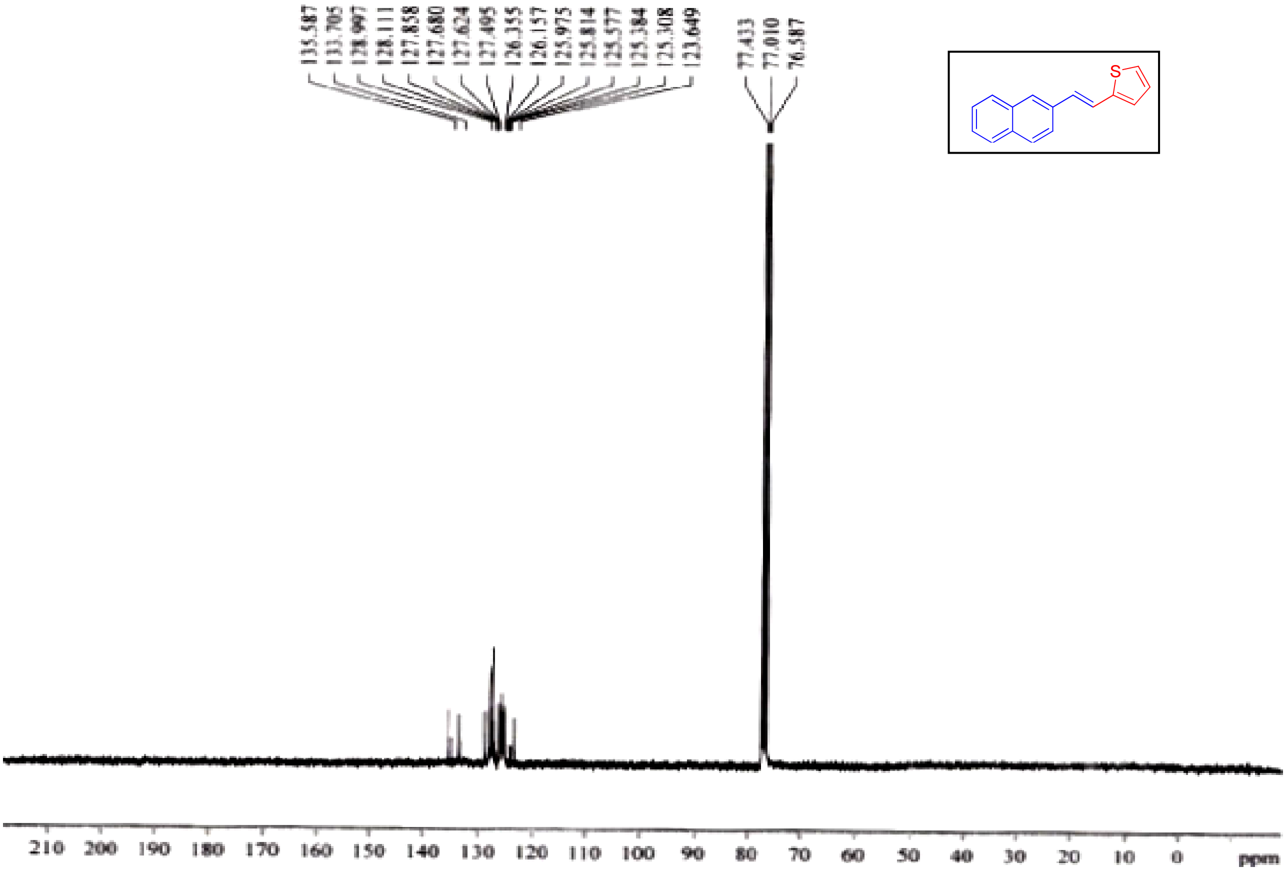
Spectrum 55. 75 MHz ^{13}C NMR of compound **3n**



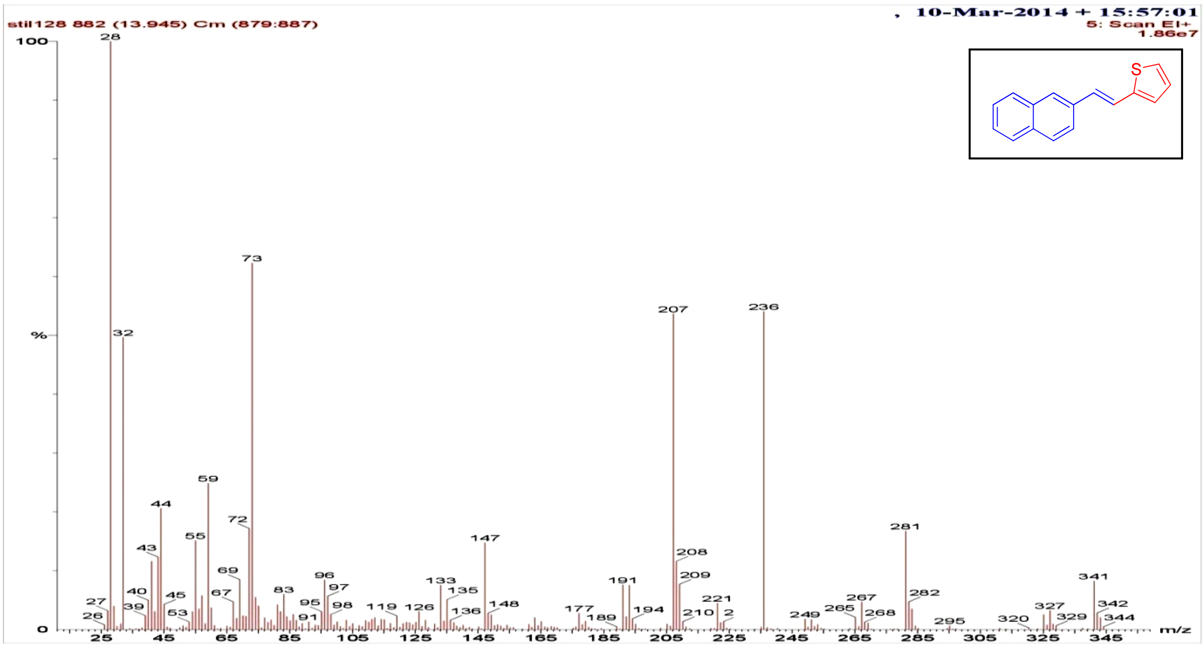
Spectrum 56. EI-MS of compound **3n**



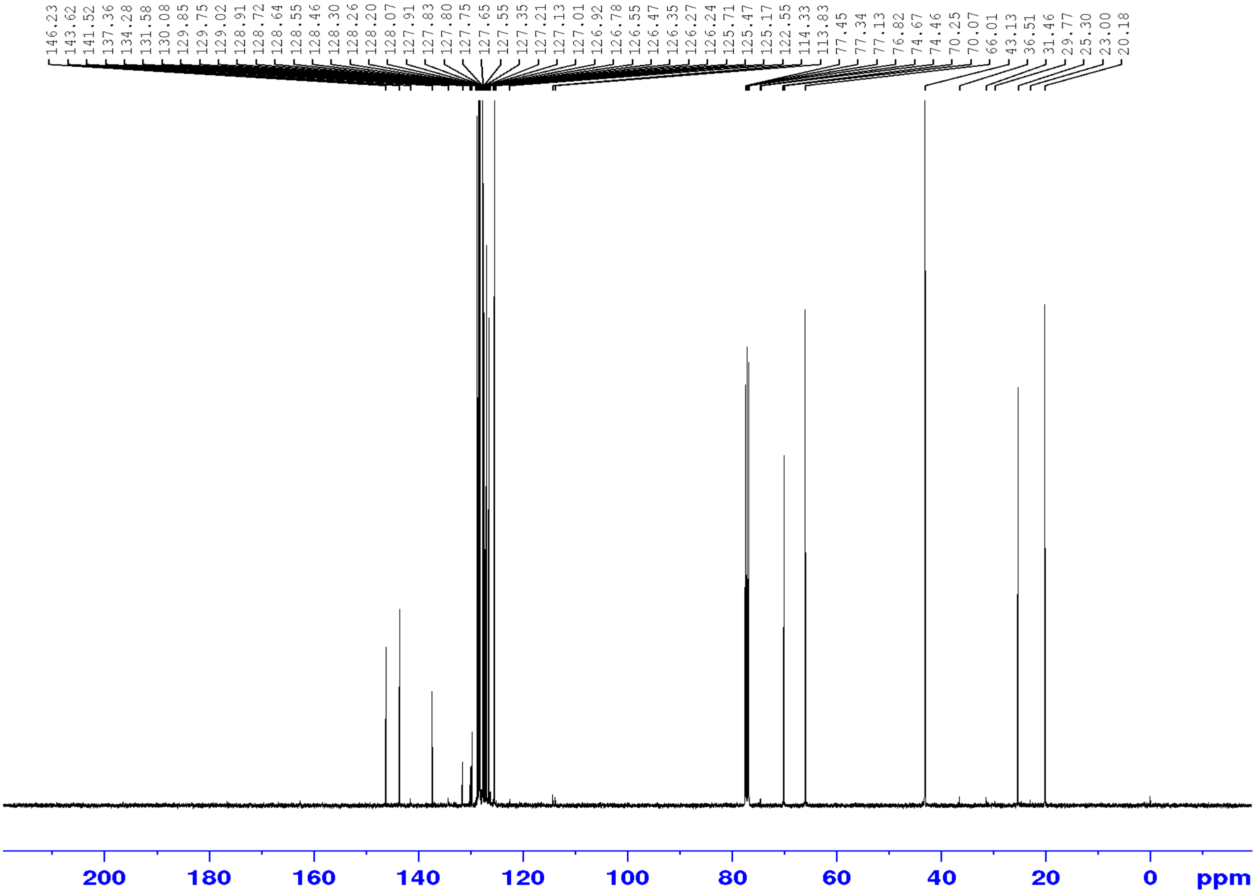
Spectrum 57. 300 MHz ^{1}H NMR of compound **3o**



Spectrum 58. 75 MHz ^{13}C NMR of compound **3o**

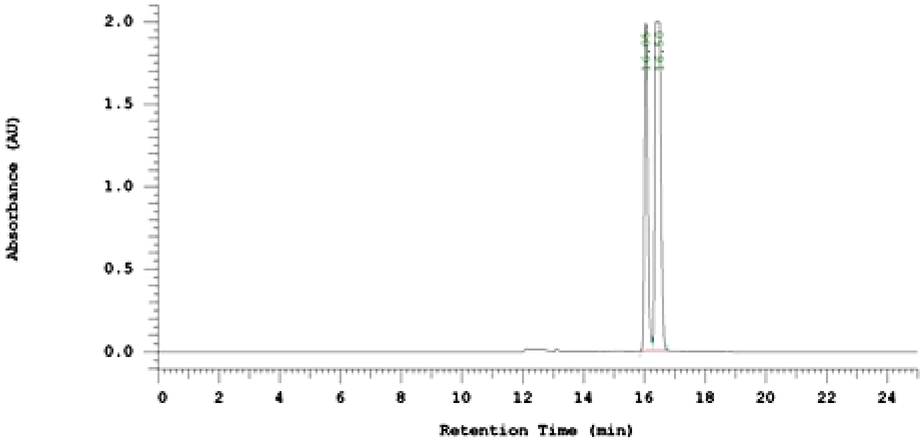


Spectrum 59. EI-MS of compound **3o**



Spectrum 60. ^{13}C NMR of reaction mixture at 10 minutes

3. HPLC data



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                 Chrom Type: Best Chromatogram
Peak Quantitation: AREA
Calculation Method: AREA%

No.                 RT                  Area                Area %
----------------------------------------------------------------------
  1                16.05               7432921              35.282
  2                16.50              13634484              64.718
----------------------------------------------------------------------
                                       21067405             100.000
----------------------------------------------------------------------
```

Figure S1: HPLC profile showing percentage conversion of styrene to 1-(bromoethyl)benzene (1a).

4. UV-visible Spectrum

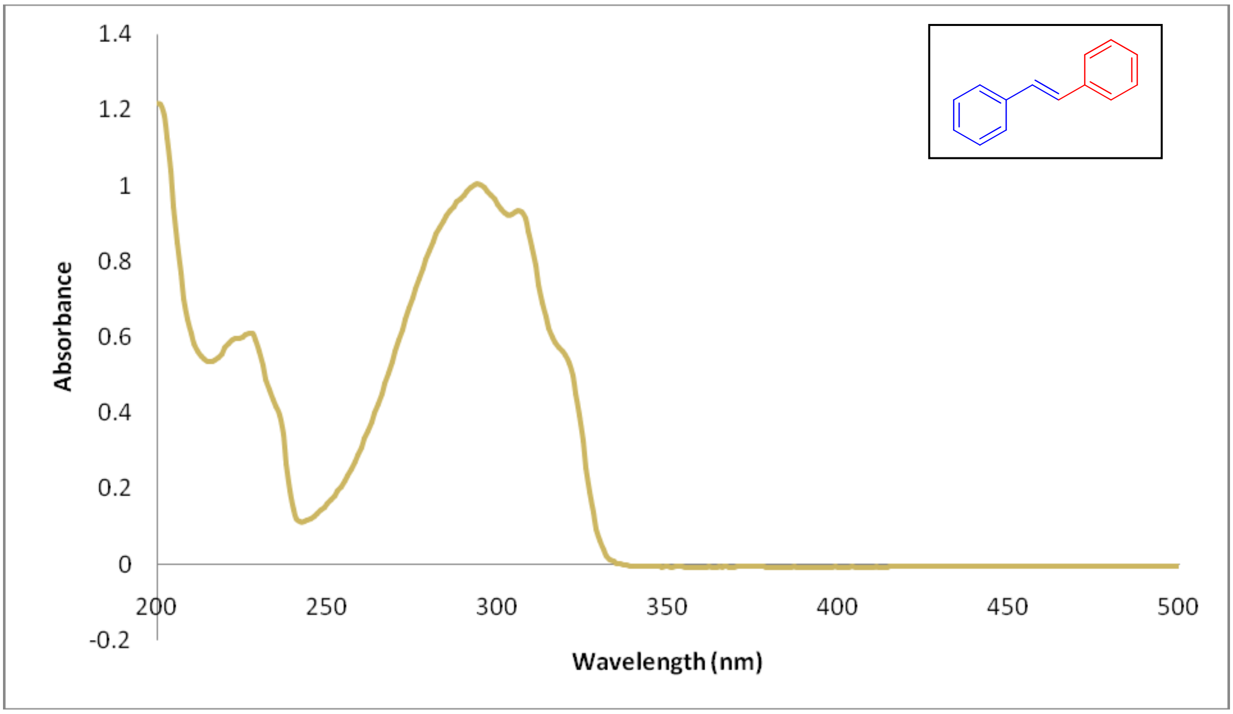


Figure S2: UV-visible spectrum of compound 3a.

5. DLS data

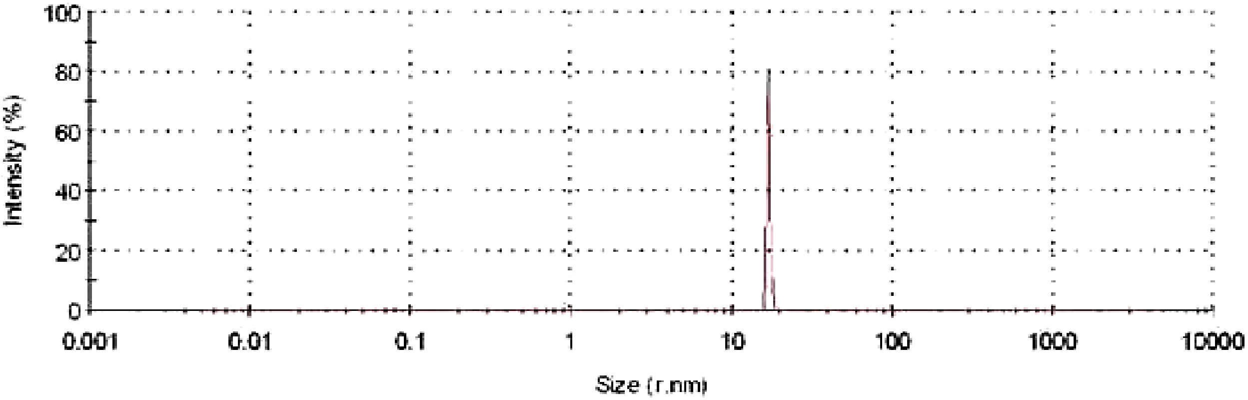
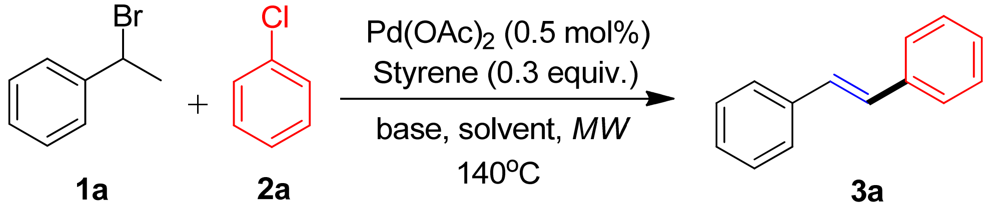


Figure S3: DLS of Pd catalyst during reaction (50 min in MW)

6. COSY45 spectrum



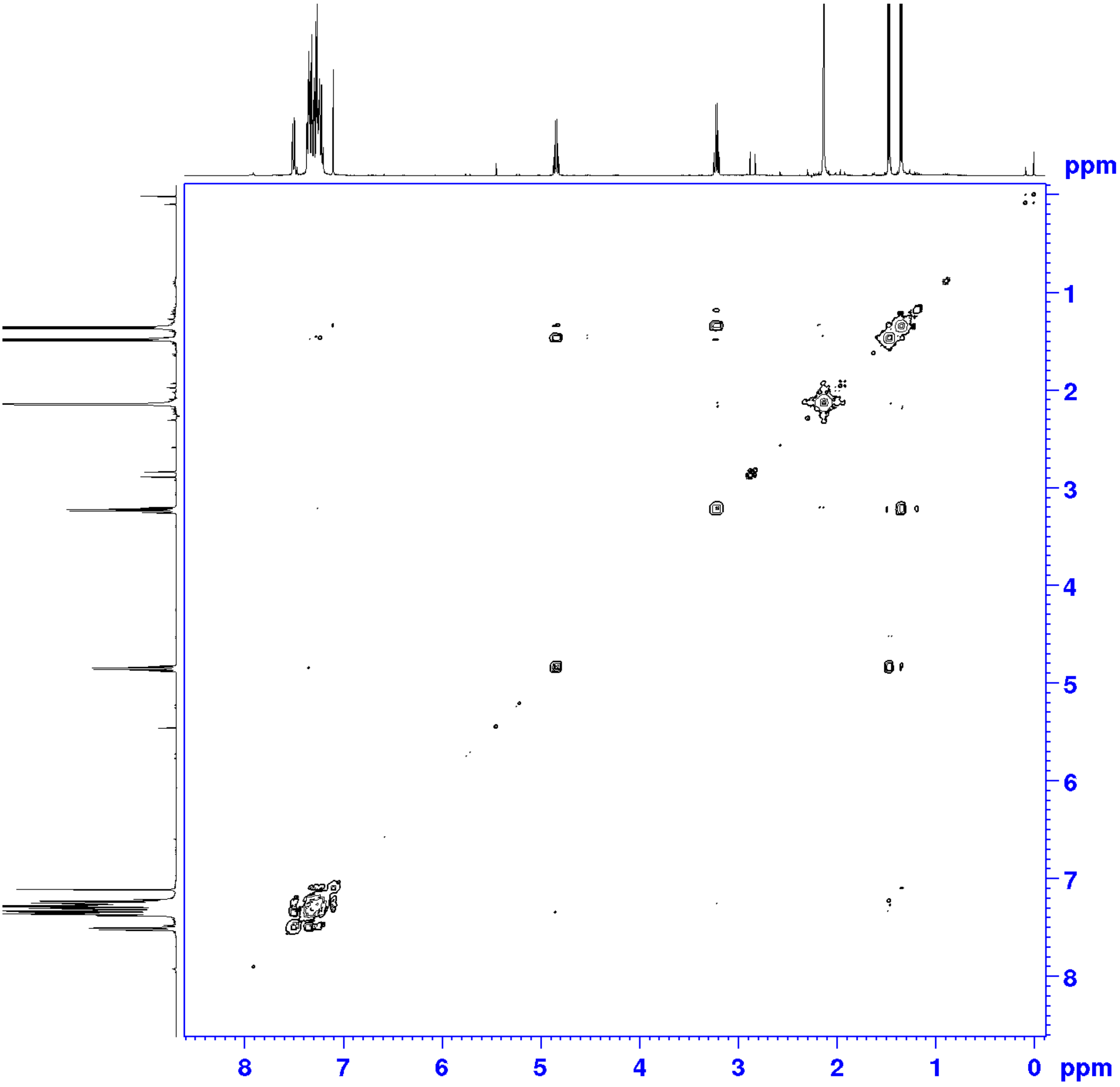


Figure S4: COSY45 of reaction mixture at 10 min

7. DEPT 90 spectra

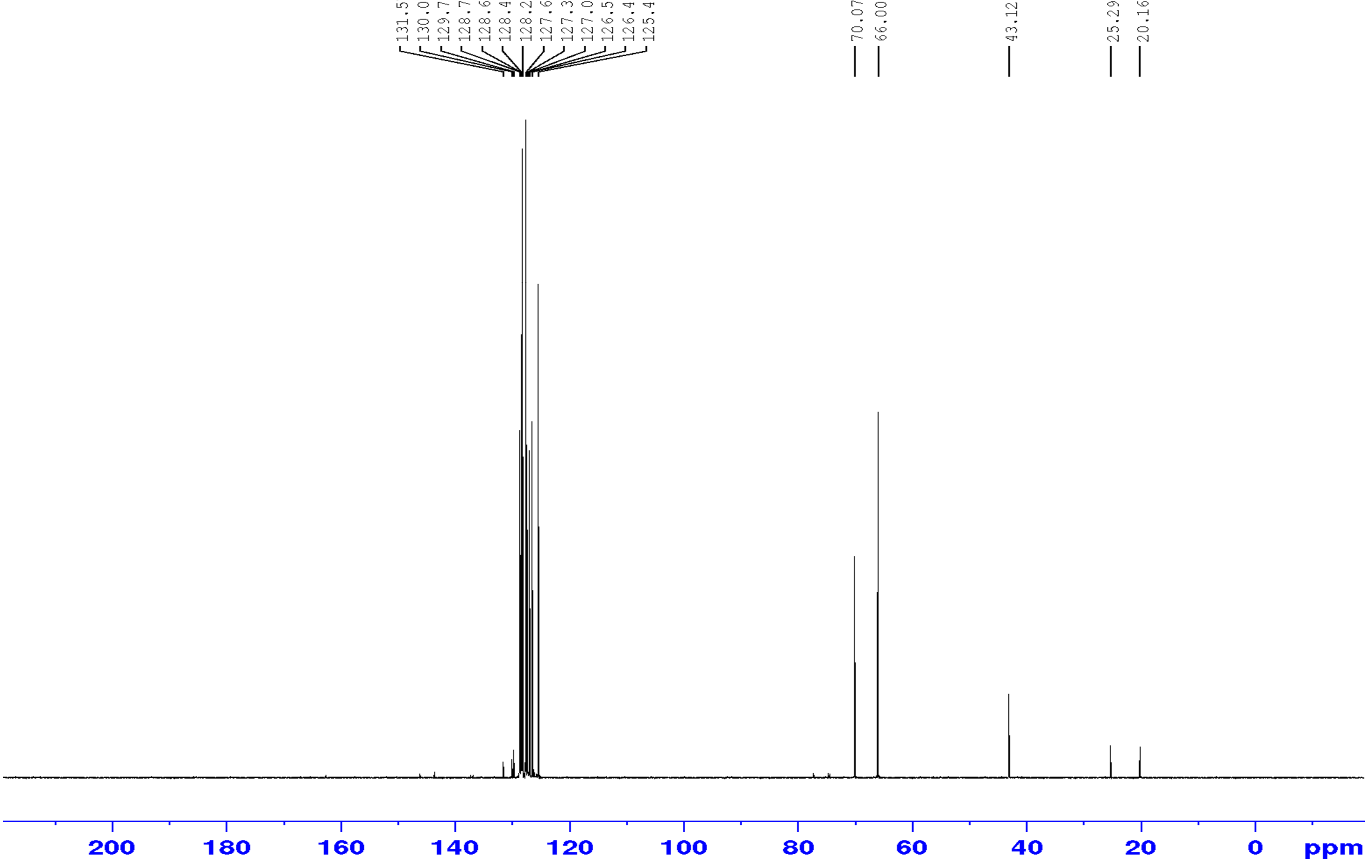


Figure S5: DEPT 90 of reaction mixture at 10 min

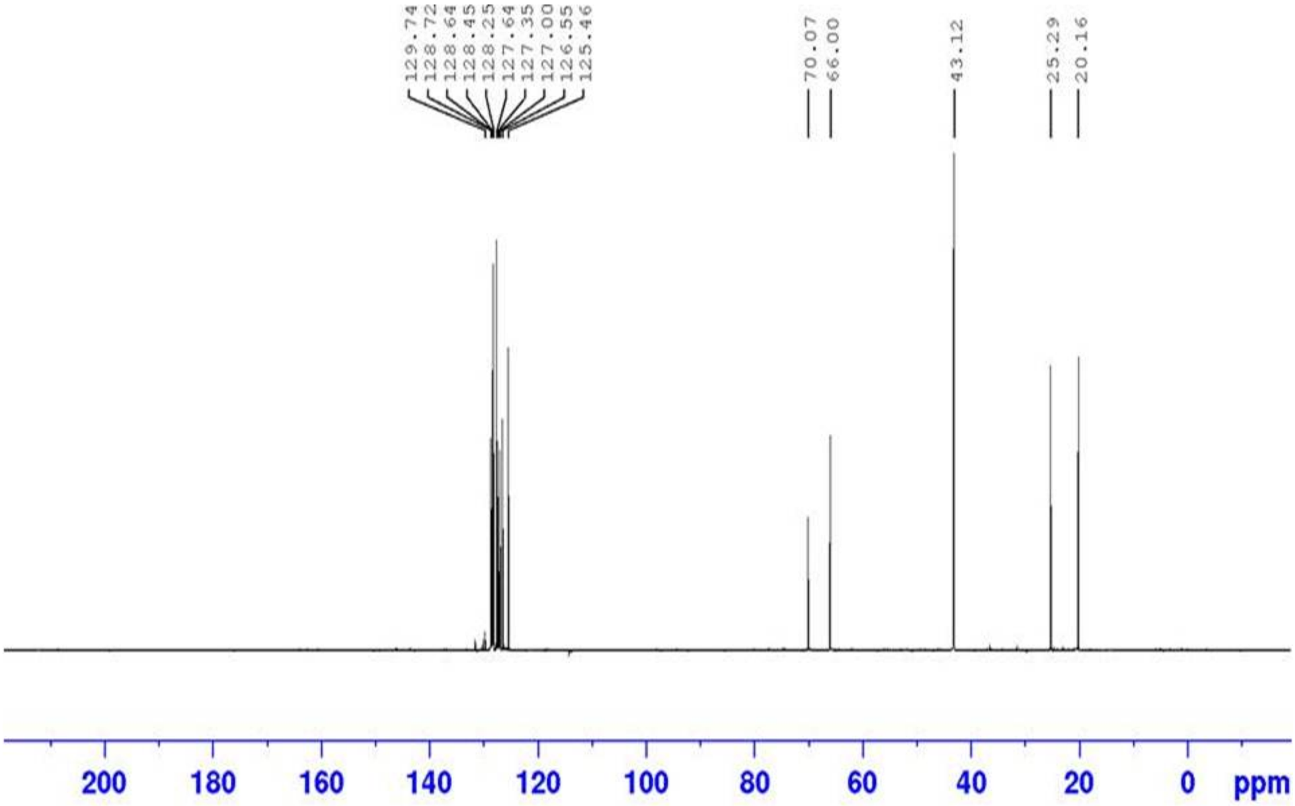
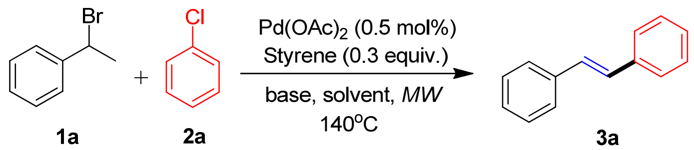
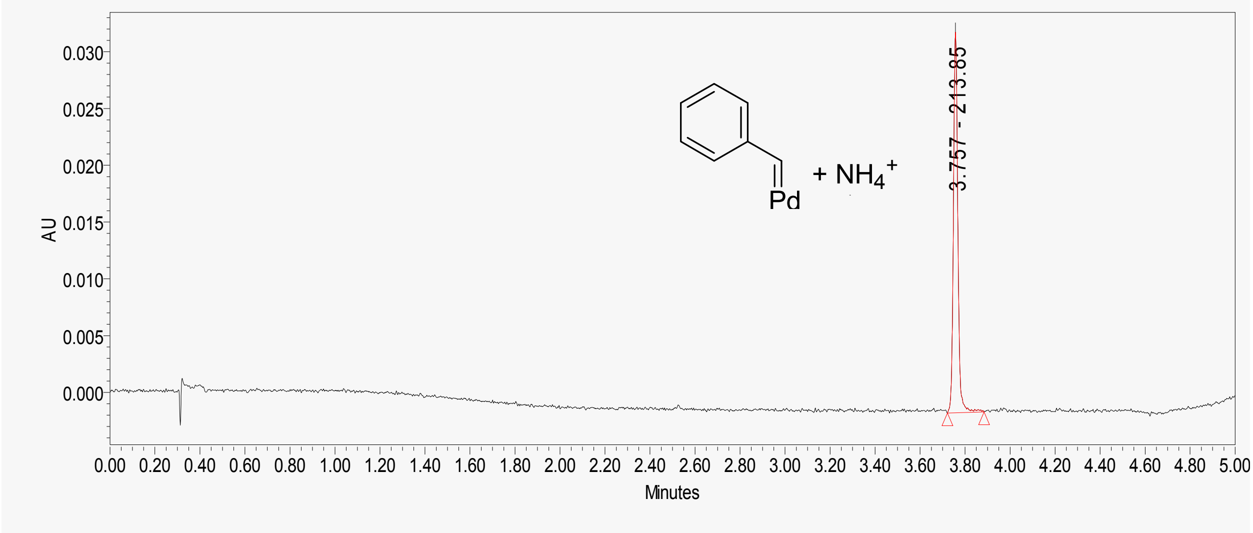


Figure S6: DEPT 135 of reaction mixture at 10 min

8. Sequential LC-MS data of the reaction mixture at 1, 5, and 10 minutes

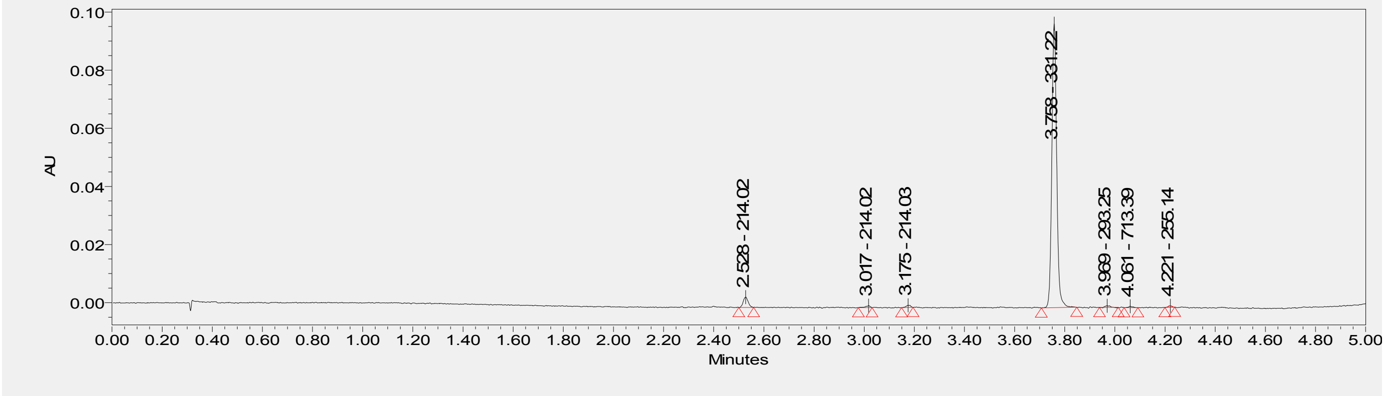


1a **2a** **3a**



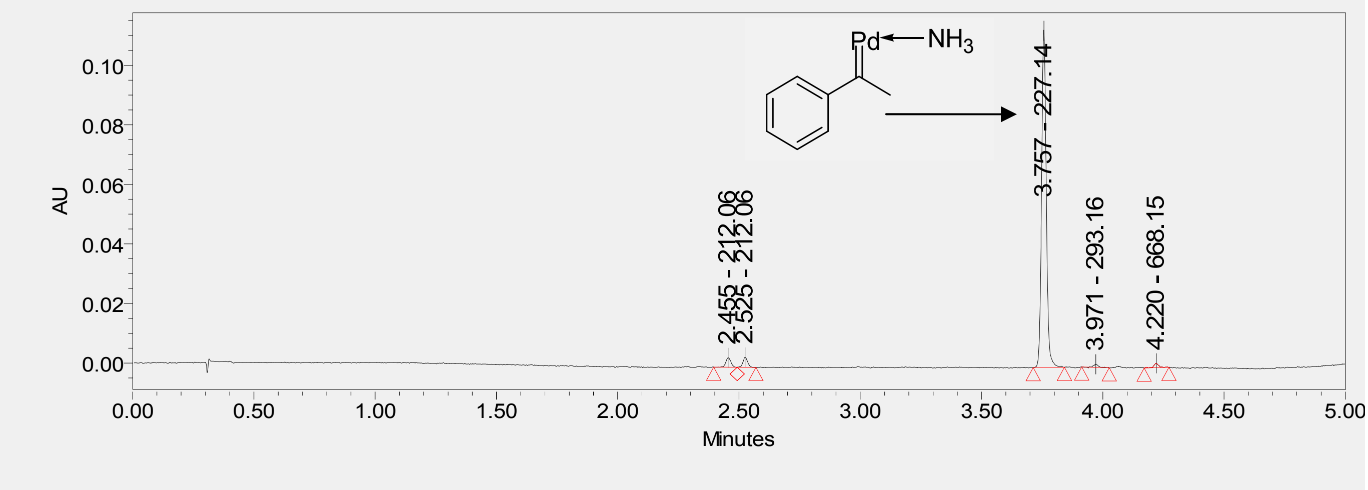
SN	Retention Time	Area	% Area	Base Peak
1	3.757	46004	100.00	213.85

Figure S7: LC-MS data of the reaction mixture at 1 minute



SN	Retention Time	Area	% Area	Base Peak
1	2.528	4875	3.47	214.02
2	3.017	968	0.69	214.02
3	3.175	916	0.65	214.03
4	3.758	131788	93.80	331.22
5	3.969	914	0.65	293.25
6	4.061	526	0.37	713.39
7	4.221	507	0.36	255.14

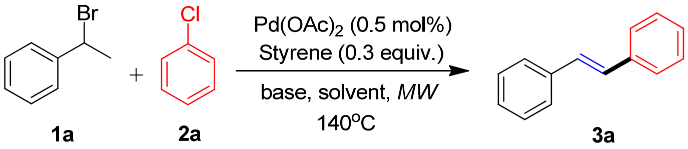
Figure S8: LC-MS data of the reaction mixture at 5 minute

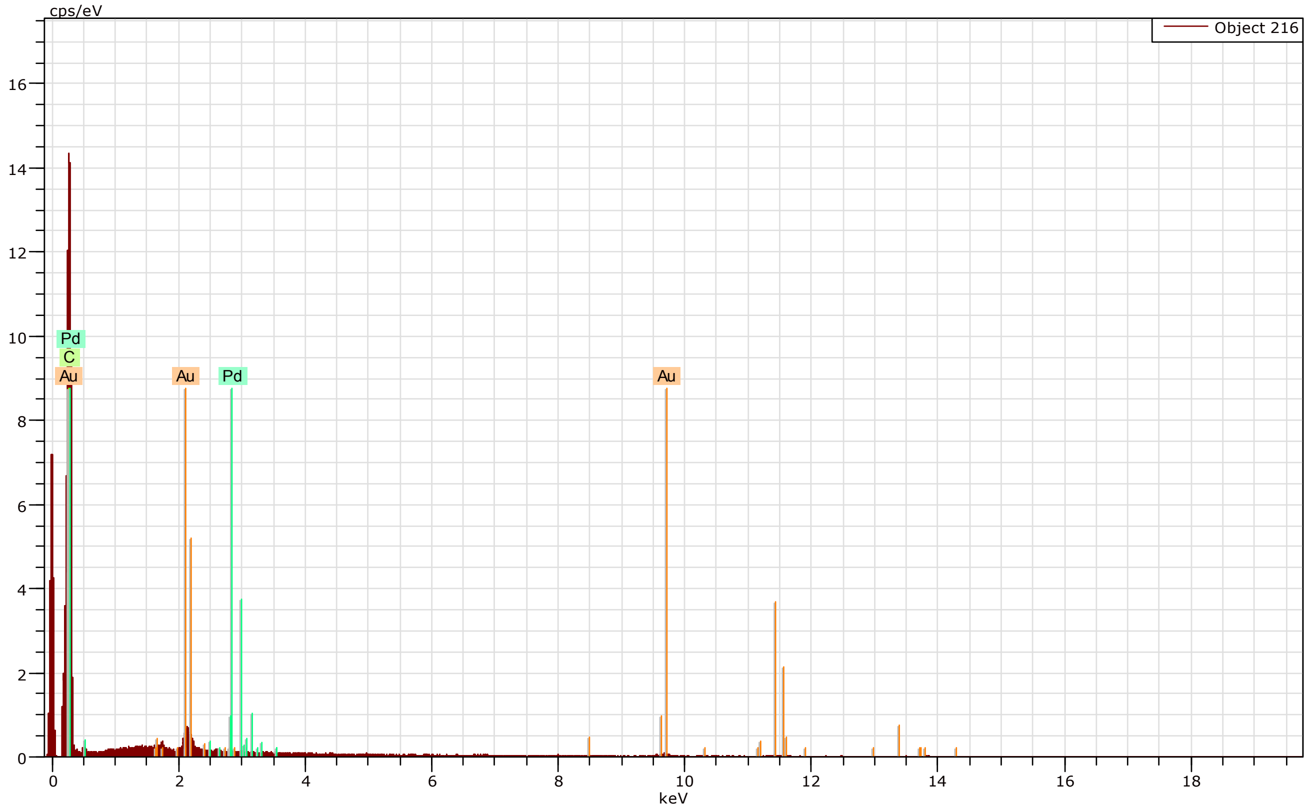


	Retention Time	Area	% Area	Base Peak
1	2.455	4633	2.80	212.06
2	2.525	4598	2.78	212.06
3	3.757	152531	92.24	227.14
4	3.971	1619	0.98	293.16
5	4.220	1973	1.19	668.15

Figure S9: LC-MS of the reaction mixture at 10 minute

9. EDAX of reaction mixture after 5 minutes





AN Series	unn. C [wt.%]	norm.C [wt.%]	Atom. C [at.%]	Error [%]
Au 79 L-series	53.83	56.30	8.24	3.9
C 6 K-series	35.90	37.55	90.10	62.2
Pd 46 L-series	5.89	6.15	1.67	0.5
Total	95.62	100.00	100.00	---

Figure S10: EDAX of reaction mixture after 5 minutes

10. Single-Crystal X-Ray experimental details:

Data Collection and Refinement

Single-crystal X-ray data of compounds were collected on Bruker SMART CCD-Diffractometer using graphite monochromated Mo*K*α radiation (λ = 0.71073 Å). The structures were solved by the direct method and then refined on F^2 by the full matrix least-squares technique with the SHELX-97 set of software[11] using the WinGX (version 1.80.05) program package.[12] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as riding atoms using SHELX default parameters. Further information on the crystal structure determination (excluding structure factors) has been given as table S1 and also deposited in the Cambridge Crystallographic Data Centre as supplementary publications no. **1028616**. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033. e-mail: deposit@ccdc.cam.ac.uk) or via internet.

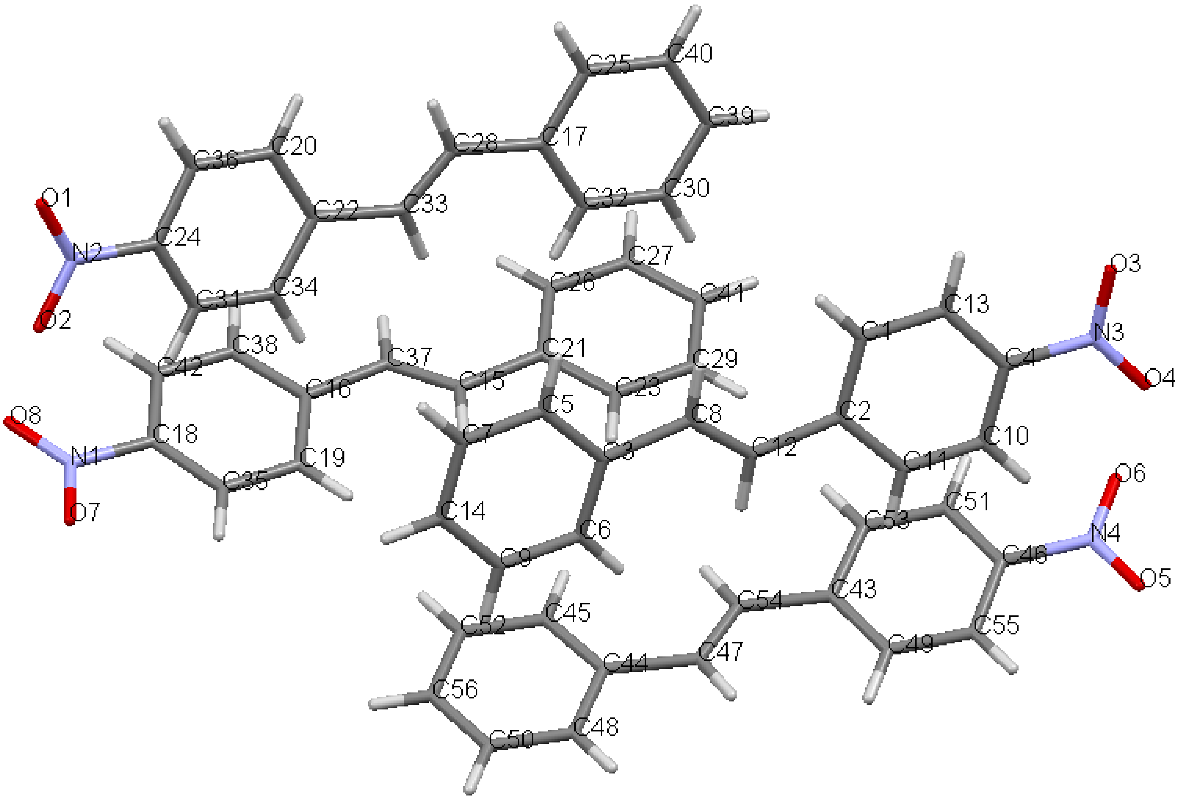


Figure S11. Single crystal X-ray structure of **c**ompound **3c** shown in capped stick model.

Table S1. Crystallographic refinement data for compound **3c**

Property	**Data 3c**
Empirical Formula	C14 H11 N O2
Formula Weight	225.24
Crystal System	Monoclinic
Space group	P -1
a (Å)	7.890(3)
b (Å)	10.185(4)
c (Å)	28.422(9)
α, β, γ (^{o})	90, 90, 90
V (Å^3)	2284.0(14)
Z	8
Density (calc)	1.310
F(000)	944.0
μ (mm^{-1})	0.088
Crystal Size [mm]	0.24 x 0.17 x 0.15
Temperature (K)	273(2)
Radiation / λ	Mo*K*\α / 0.71073
θ Min-Max [^{o}]	0.982,0.987
h, k, l	-9:9; -12:12; -33:33
Tot.,UniqData, R(int)	22049, 8046, 0.099
Obs. data [I > 2.0 σ(I)]	2999
Nref, Npar	8046, 613
R1, wR2, S	0.0952, 0.2695, 0.993
Min. - Max. resd. dens. [e/ Å^3]	-0.170, 0.368
CCDC	**1028616**

11. Computational details:

To support our mechanistic pathway shown in figure 5 (main text) the density functional theory (DFT)[13] studies with GAUSSIAN 09 program[14] have been performed. Working within the framework of first-principles DFT, the free energies were determined using the B3LYP hybrid functional. The 6-311++G (2d,p) basis set[15] was chosen to describe H, C, O, Cl, and Br atoms and the effective core potential of Hay and Wadt[16] with double-ζ valence basis set (LANL2DZ) was used for the palladium (Pd) . The structure of the molecules was optimized in *N*,*N*-dimethylformamide-water (DMF-H_2O) binary solvent *via* direct inversion in iterative subspace (DIIS), as implemented in the GAUSSIAN 09 program, until the largest component of the ionic forces attained a value 0.00045 a.u.. In order to confirm it as local minima, frequency calculations were performed at the same level of the theory. The polarisable continuum model (PCM)[17] using the integral equation formalism variant (IEFPCM) was employed to investigate the effect of the solvent. The solvent descriptors were assumed to vary linearly with the molar fraction of each component of the homogeneous mixture (binary solvent).

The free energies for the optimized structures in binary solvent are given in Table S2 of the supplementary data. Then, the relative free energies ($G°_{rel}$) were computed, based on stoichiometric considerations. The free energy of the starting material 1-(bromoethyl)benzene **1a** was arbitrarily taken as zero and the energy of other intermediate molecules and complexes in figure 5 (main text) was normalized to **1a**. The free energy of Pd-carbene complex with different ligands in figure S12 was normalized to A ($G°_A = 0.0$).

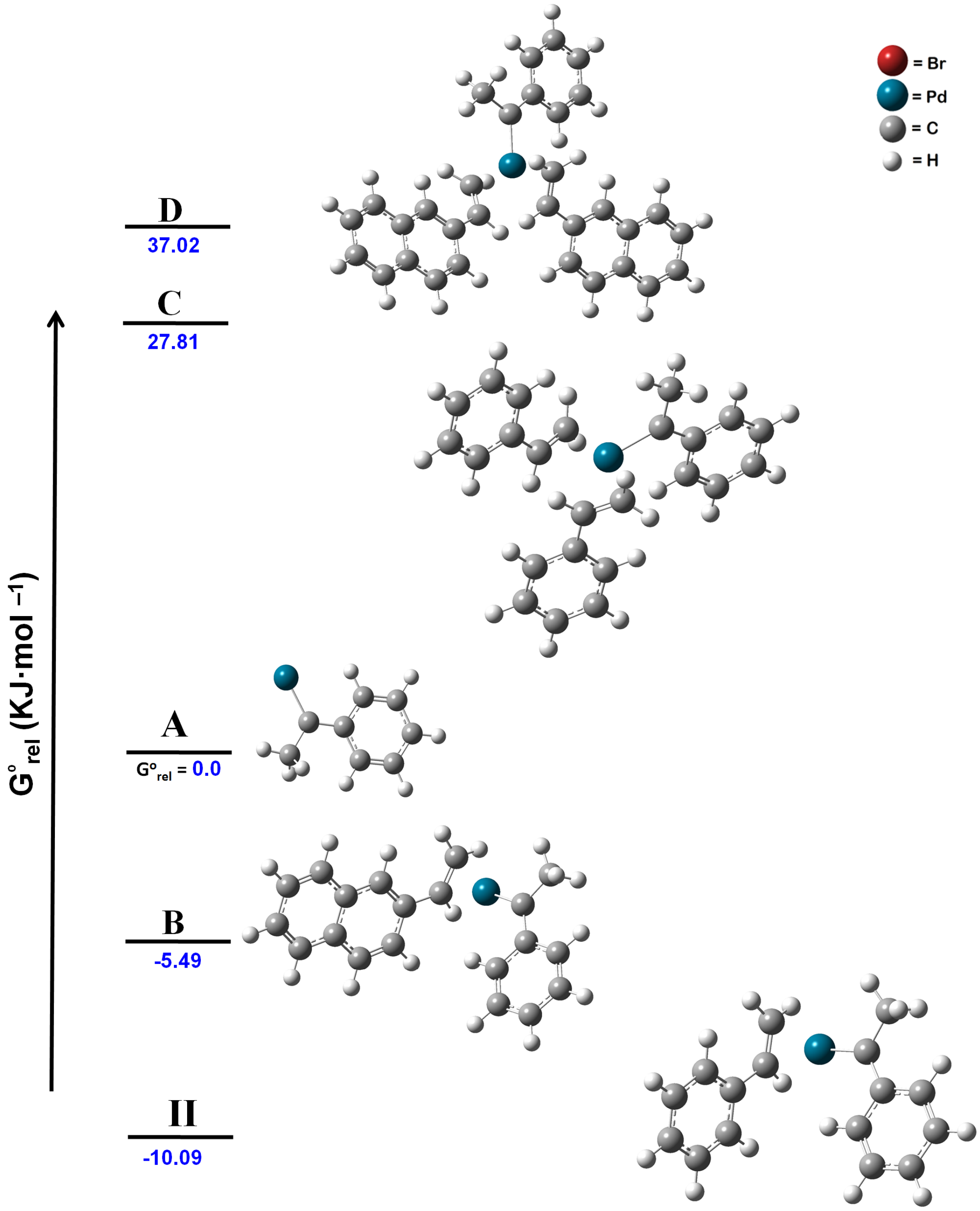
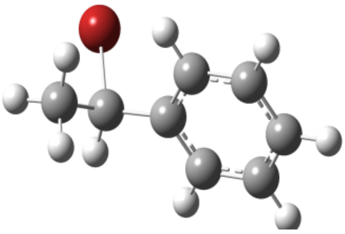
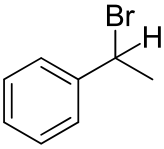
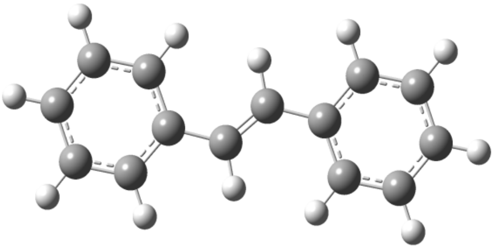
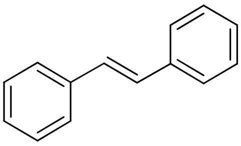
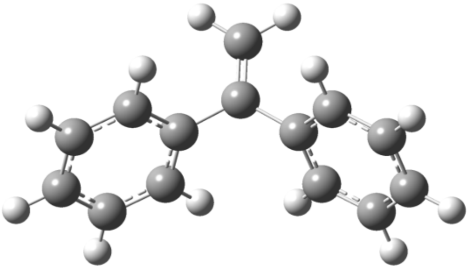
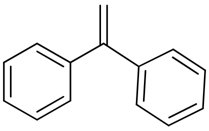
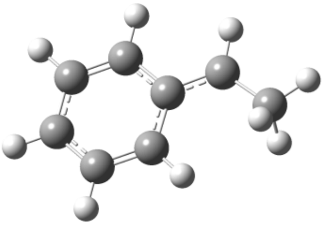
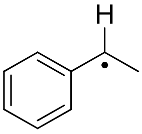
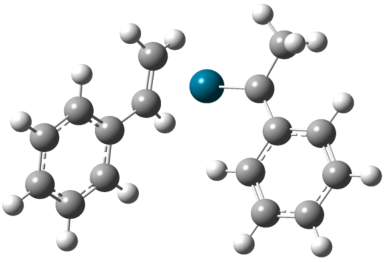
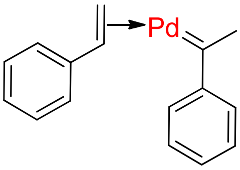
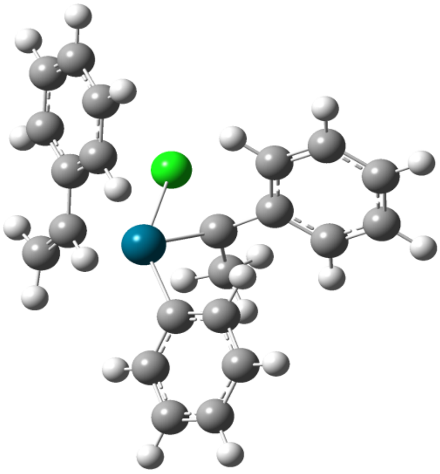
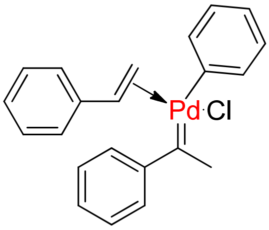
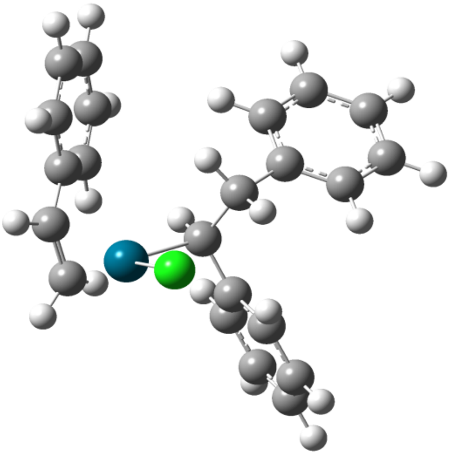
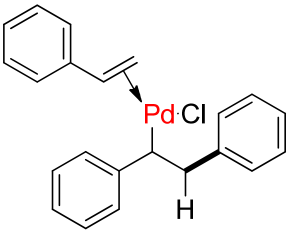
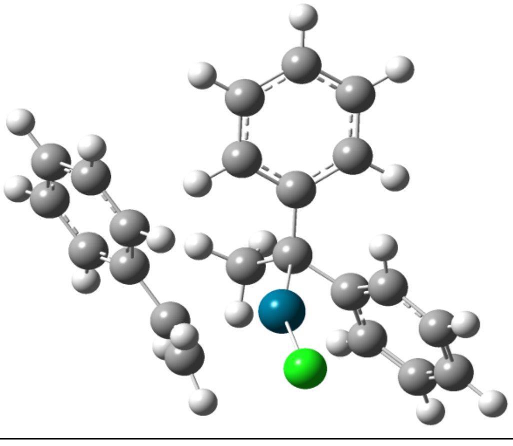
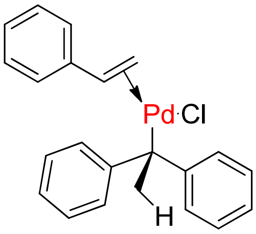
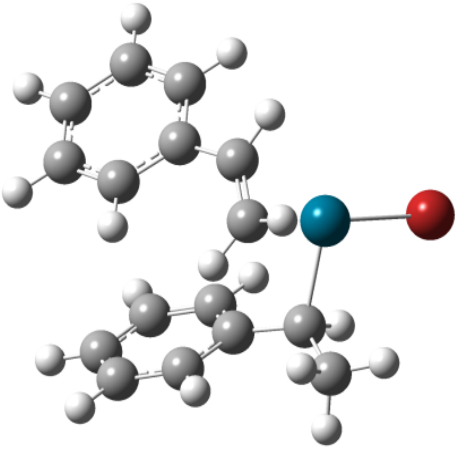
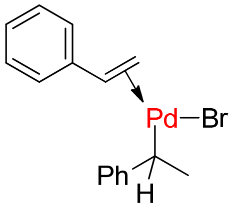
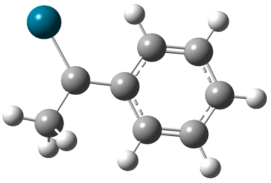
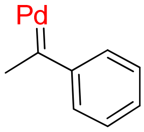
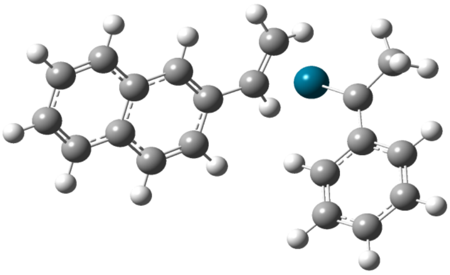
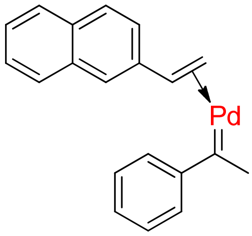
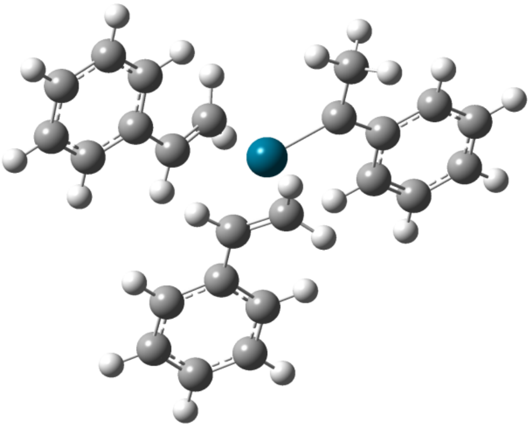
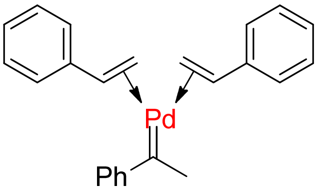


Figure S12. Optimized geometries and their Relative Gibbs Free energy ($G°_{rel}$) profile diagram of Pd-carbene complexes, showing relative stability of Pd-carbene complex with different ligands. $G°_{rel}$ calculated w.r.t. A ($G°_A = 0.0$) in binary solvent DMF-H_2O.

Table S2. Optimized molecular geometries

Sl. No.	Comp.	Optimized geometry	Structure
1	1a		
2	3a		
3	3a′		
4	I		
5	II		

6	**III**		
7	**IV**		
8	**IVa**		

9	**VI**		
10	**A**		
11	**B**		
12	**C**		

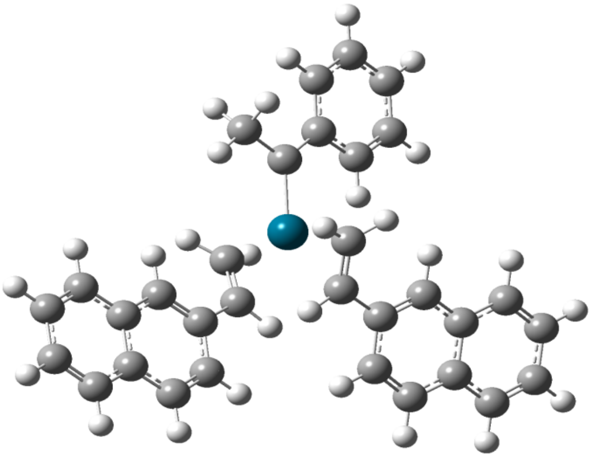
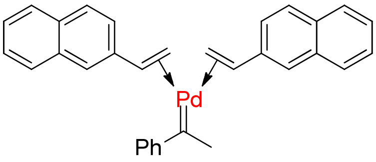
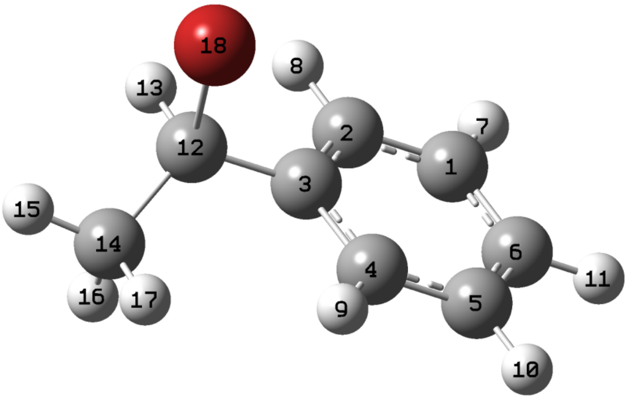
13	**D**		

Table S3. Free energies for the optimized structures in binary solvent

			Binary Solvent (DMF-H_2O)	
Sl. No.	Structure/ Compound No.	G° (a.u.)	Relative Gibbs Free Energy (a.u.)	(kJ. mol^{-1})
		Data for figure 5		
1	**1a**	-2884.406693	0.0	0.0
2	**I**	-310.217757	{G_{I} – (G_{1a} -G_{Br})} = [(-310.217757) – {(-2884.406693) – (-2574.119103)}] = 0.069833	183.35
3	**II**	-746.004891	{G_{II} – (G_{1a} -G_{HBr} + G_{pd} + $G_{styrene}$)} = [(-746.008200) – {(-2884.406693) – (-2574.764920) + (-126.724511) + (-309.641916)}] = 0.003309	8.69
4	**III**	-1437.897323	{G_{III} – (G_{1a} + G_{pd} -G_{HBr} + G_{phCl}+ $G_{styrene}$)} = [(-1437.897323) – {(-2884.406693) + (-126.724511) - (-2574.764920) + (-691.885164) + (-309.641916)}] = -0.003959	-10.39
5	**IV**	-1437.958018	{G_{IV} – (as above)} = {(-1437.958018) – (---)} = -0.064654	-169.75
6	**IVa**	-1437.952824	{G_{IVa} – (as above)} = {(-1437.952824) – (---)} = -0.05946	-156.11
7	**VI**	-3320.835476	{G_{VI} – (G_{1a} + G_{pd} + $G_{styrene}$)} = [(-3320.835476) – {(-2884.406693) + (-126.724511) + (-309.641916)}]	-163.72

			= -0.062356	
8	*Trans*-Stilbene (3a)	-540.693233	{G_{3a} – (G_{1a} + G_{phCl} - G_{HCl} -G_{HBr})} = [(-540.693233) – {(-2884.406693) + (-691.885164) - (-460.850000) - (- 2574.764920)}] = -0.016296	-42.78
9	1,1-diphenyl ethane (3a’)	-540.682965	{$G_{3a'}$ – (-as above)}= {(540.682965) – (---)}= -0.006028	-15.83
		Data for figure S12		
10	**A**	-436.359133	0.0	0.0
11	**B**	-899.645431	{G_B – (G_A + $G_{vinylnaphthalene}$)} = [(-899.645431) – {(-436.359133) + (-463.284205)}] = -0.002093	-5.49
12	**C**	-1055.632373	{G_C – (G_A + (2 x $G_{styrene}$)} = [(-1055.632373) – { (-436.359133) + 2 x (-309.641916)}] = -0.010592	27.81
13	**D**	-1362.913444	{G_D – (G_A + 2 x $G_{vinylnaphthalene}$)} = [(-1362.913444) – {(-436.359133) + 2 x (-463.284205)}] = 0.014099	37.02
14	**II**	-746.004891	{G_{II} – (G_A + $G_{styrene}$)} = [(-746.004891) – {(-436.359133) + (-309.641916)}] = -0.003842	-10.09
		Others		
15	Chlorobenzene	-691.885164		-
16	HBr	-2574.764920		-
17	HCl	-460.850000		-
18	Bromine atom	-2574.119103		-

19	Palladium atom	-126.724511		-
20	Styrene	-309.641916		-
21	2-Vinyl naphthalene	-463.284205		-



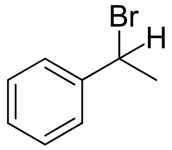


Figure S13. Optimized molecular geometry of **1a** by DFT at B3LYP

Table S4. X, Y, Z-Cordinates of optimized compound **1a** calculated by DFT at B3LYP

```
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
   1          6           0        2.802593   -0.892344    0.769104
   2          6           0        1.488852   -0.605472    1.126005
   3          6           0        0.706524    0.250853    0.346202
   4          6           0        1.267736    0.813102   -0.805117
   5          6           0        2.578394    0.524680   -1.164713
   6          6           0        3.350644   -0.328465   -0.378653
   7          1           0        3.396234   -1.554659    1.387672
   8          1           0        1.066215   -1.047512    2.021408
   9          1           0        0.679083    1.472919   -1.430399
  10          1           0        2.999359    0.966891   -2.059737
  11          1           0        4.372903   -0.550793   -0.660174
  12          6           0       -0.691495    0.559686    0.781079
  13          1           0       -0.872069    0.162443    1.774858
  14          6           0       -1.137567    2.003838    0.683914
  15          1           0       -2.158688    2.119774    1.045454
  16          1           0       -0.478791    2.611790    1.311586
  17          1           0       -1.084260    2.386544   -0.334940
  18         35           0       -2.003259   -0.586362   -0.320076
 ---------------------------------------------------------------------
```

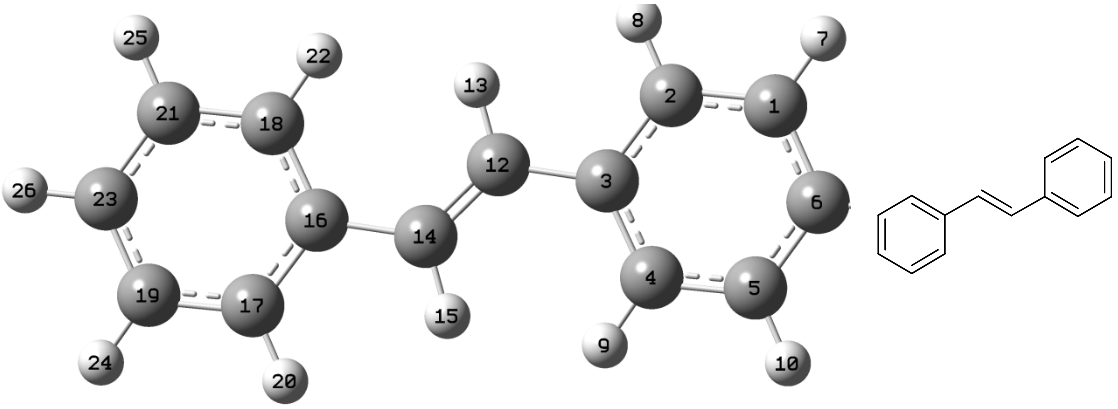


Figure S14. Optimized molecular geometry of **3a** by DFT at B3LYP

Table S5. X, Y, Z-Cordinates of optimized compound **3a** calculated by DFT at B3LYP

```
---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        4.199418   -1.085732    0.000026
      2          6           0        2.821944   -1.274759    0.000047
      3          6           0        1.935800   -0.185738    0.000023
      4          6           0        2.487441    1.107374   -0.000024
      5          6           0        3.861828    1.296189   -0.000046
      6          6           0        4.727223    0.201646   -0.000018
      7          1           0        4.859874   -1.944899    0.000046
      8          1           0        2.419608   -2.281943    0.000084
      9          1           0        1.839292    1.974960   -0.000041
     10          1           0        4.263281    2.302848   -0.000078
     11          1           0        5.799816    0.353865   -0.000032
     12          6           0        0.495582   -0.453547    0.000046
     13          1           0        0.240719   -1.509532    0.000123
     14          6           0       -0.495588    0.453563   -0.000028
     15          1           0       -0.240745    1.509551   -0.000100
     16          6           0       -1.935801    0.185733   -0.000021
     17          6           0       -2.821958    1.274763    0.000036
     18          6           0       -2.487426   -1.107366   -0.000068
     19          6           0       -4.199417    1.085731    0.000054
     20          1           0       -2.419614    2.281944    0.000065
     21          6           0       -3.861827   -1.296191   -0.000044
     22          1           0       -1.839283   -1.974959   -0.000131
     23          6           0       -4.727219   -0.201664    0.000018
     24          1           0       -4.859890    1.944884    0.000098
     25          1           0       -4.263253   -2.302861   -0.000081
     26          1           0       -5.799814   -0.353872    0.000033
---------------------------------------------------------------------
```

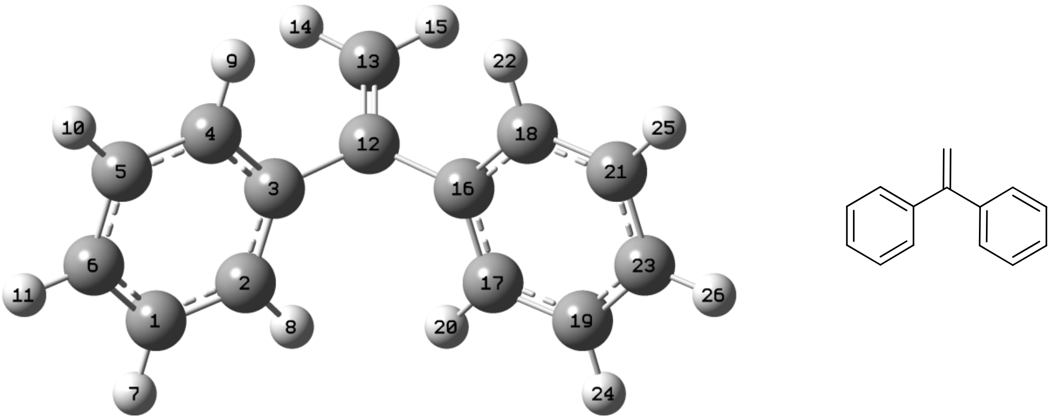


Figure S15. Optimized molecular geometry of **3a′** by DFT at B3LYP

Table S6. X, Y, Z-Cordinates of optimized compound **3a′** calculated by DFT at B3LYP

```
---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
   1          6           0        3.598324    0.120302   -0.634897
   2          6           0        2.389887    0.805176   -0.707683
   3          6           0        1.279928    0.388271    0.037961
   4          6           0        1.414920   -0.747741    0.847102
   5          6           0        2.624320   -1.429032    0.925896
   6          6           0        3.721805   -0.998034    0.184859
   7          1           0        4.441821    0.456046   -1.226666
   8          1           0        2.298924    1.663513   -1.362245
   9          1           0        0.569142   -1.092992    1.429305
  10          1           0        2.709664   -2.298238    1.567429
  11          1           0        4.662137   -1.533350    0.240321
  12          6           0       -0.000017    1.149602    0.000041
  13          6           0       -0.000059    2.489813    0.000053
  14          1           0        0.920737    3.055671    0.066311
  15          1           0       -0.920694    3.055903   -0.066102
  16          6           0       -1.279909    0.388100   -0.037875
  17          6           0       -2.390093    0.805389    0.707223
  18          6           0       -1.414690   -0.748183   -0.846610
  19          6           0       -3.598517    0.120520    0.634371
  20          1           0       -2.299387    1.664074    1.361367
  21          6           0       -2.624096   -1.429510   -0.925457
  22          1           0       -0.568820   -1.093720   -1.428505
  23          6           0       -3.721790   -0.998180   -0.184947
  24          1           0       -4.442205    0.456548    1.225711
  25          1           0       -2.709260   -2.298964   -1.566677
  26          1           0       -4.662139   -1.533455   -0.240472
 --------------------------------------------------------------------
```

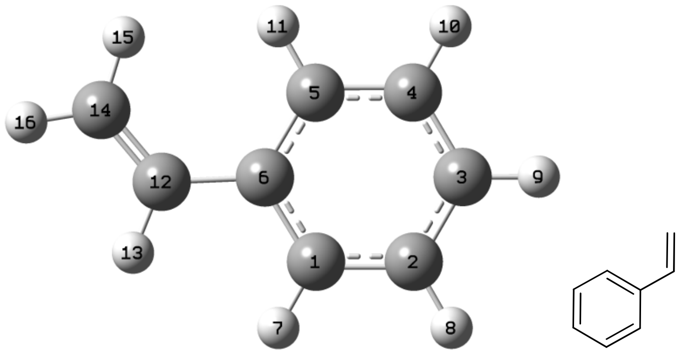


Figure S16. Optimized molecular geometry of **styrene** by DFT at B3LYP

Table S7. X, Y, Z-Cordinates for optimized geometry of **styrene** calculated by DFT at B3LYP

```
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
    1          6           0        5.503298   -0.407478    0.000141
    2          6           0        6.893467   -0.461409    0.000478
    3          6           0        7.635915    0.714930   -0.000119
    4          6           0        6.975093    1.943741   -0.001052
    5          6           0        5.588274    1.995818   -0.001383
    6          6           0        4.823846    0.818517   -0.000786
    7          1           0        4.930526   -1.328501    0.000607
    8          1           0        7.395018   -1.421985    0.001196
    9          1           0        8.718709    0.678356    0.000135
   10          1           0        7.546091    2.864859   -0.001529
   11          1           0        5.096832    2.961135   -0.002128
   12          6           0        3.352653    0.813555   -0.001086
   13          1           0        2.905766   -0.177678   -0.000751
   14          6           0        2.535923    1.869218   -0.001697
   15          1           0        2.895905    2.891578   -0.002043
   16          1           0        1.461443    1.735605   -0.001864
```

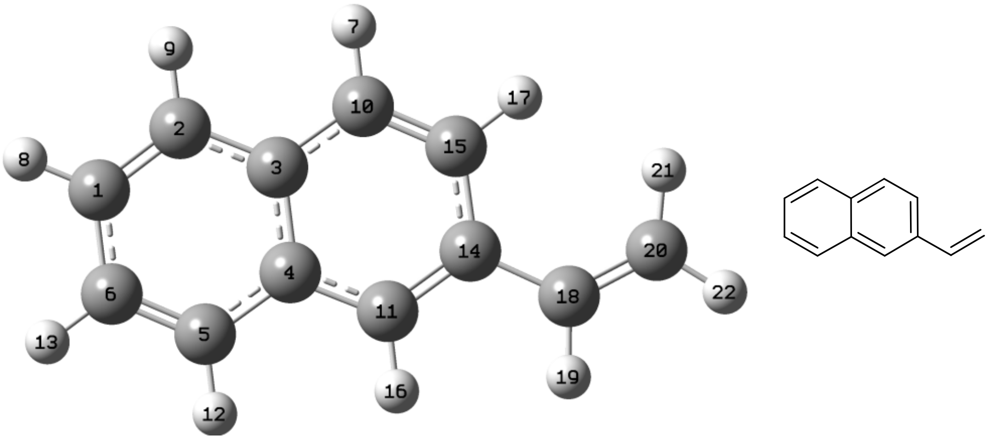


Figure S17. Optimized molecular geometry of **2-vinylnaphthalene** by DFT at B3LYP

Table S8. X, Y, Z-Cordinates of optimized 2-vinylnaphthalene molecule, calculated by DFT at B3LYP

```
---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
   1          6           0        3.236131    0.043126    0.000000
   2          1           0        3.821136    0.959359   -0.000002
   3          6           0        3.894036   -1.118271    0.000001
   4          1           0        4.976557   -1.138272    0.000000
   5          1           0        3.391795   -2.078776    0.000002
   6          6           0        1.778816    0.250231    0.000000
   7          6           0        1.289042    1.586410    0.000000
   8          6           0        0.860704   -0.783061    0.000000
   9          6           0       -0.053983    1.857140    0.000000
  10          1           0        2.002457    2.403080    0.000000
  11          6           0       -0.531395   -0.540799    0.000000
  12          1           0        1.196482   -1.813715   -0.000001
  13          6           0       -1.006070    0.807822    0.000000
  14          1           0       -0.403377    2.883618    0.000000
  15          6           0       -1.479607   -1.598753    0.000000
  16          1           0       -1.121145   -2.622165    0.000000
  17          6           0       -2.403534    1.045820    0.000000
  18          1           0       -2.759680    2.070002    0.000000
  19          6           0       -3.293027    0.000670    0.000000
  20          1           0       -4.359081    0.193988    0.000000
  21          6           0       -2.825515   -1.334779    0.000000
  22          1           0       -3.538734   -2.150443    0.000000
---------------------------------------------------------------------
```

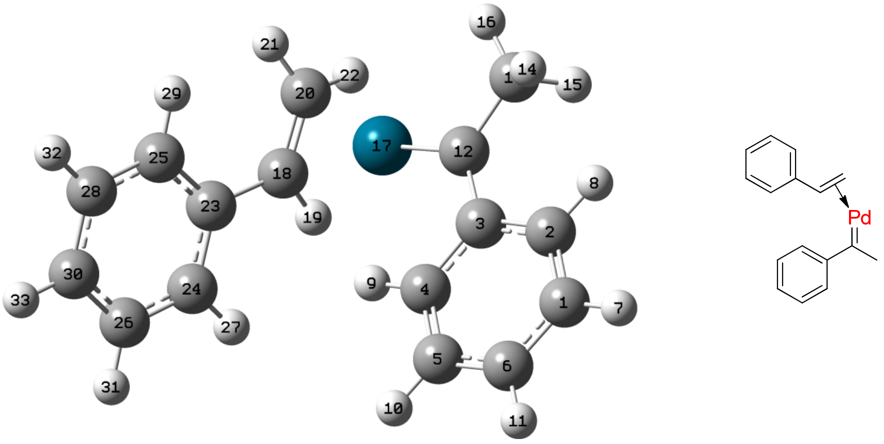


Figure S18. Optimized molecular geometry of **II** by DFT at B3LYP

Table S9. X, Y, Z-Cordinates of optimized intermediate **II,** calculated by DFT at B3LYP

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.306880	0.810092	1.205375
2	6	0	1.597646	1.568113	0.288246
3	6	0	0.385627	1.098131	-0.267188
4	6	0	-0.070924	-0.170685	0.150086
5	6	0	0.634607	-0.928729	1.070898
6	6	0	1.827136	-0.439202	1.600343
7	1	0	3.234657	1.188017	1.617573
8	1	0	1.989405	2.533643	-0.001593
9	1	0	-0.999567	-0.537256	-0.272525
10	1	0	0.261534	-1.898310	1.377126
11	1	0	2.383563	-1.028722	2.319425
12	6	0	-0.404442	1.851600	-1.232950
13	6	0	0.121335	3.208711	-1.591936
14	1	0	0.232092	3.835767	-0.697405
15	1	0	1.123650	3.129706	-2.034098
16	1	0	-0.518629	3.730409	-2.298181
17	46	0	-2.081972	1.210814	-2.098074
18	6	0	-3.927998	0.091178	-2.853185
19	1	0	-3.484160	-0.790701	-3.306002
20	6	0	-3.812950	1.282267	-3.524921
21	1	0	-4.397021	2.155118	-3.259372
22	1	0	-3.335336	1.309501	-4.496549
23	6	0	-4.796660	-0.192941	-1.694713
24	6	0	-4.875893	-1.509423	-1.219127
25	6	0	-5.570133	0.787017	-1.053371
26	6	0	-5.691141	-1.838127	-0.141486
27	1	0	-4.288935	-2.282305	-1.703142
28	6	0	-6.385649	0.459078	0.021115
29	1	0	-5.534580	1.814488	-1.393555
30	6	0	-6.450545	-0.854658	0.484777
31	1	0	-5.734469	-2.863369	0.206905
32	1	0	-6.974825	1.231848	0.500919
33	1	0	-7.087560	-1.106417	1.324108

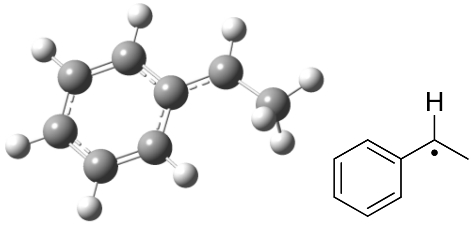


Figure S19. Optimized molecular geometry of **IVa** by DFT at B3LYP

Table S10. X, Y, Z-Cordinates of optimized intermediate **IVa,** calculated by DFT at B3LYP

```
---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
   1          6           0       -1.334968    1.362203    0.000003
   2          6           0        0.015264    1.056374    0.000022
   3          6           0        0.461274   -0.294467    0.000018
   4          6           0       -0.539399   -1.306925    0.000011
   5          6           0       -1.884083   -0.989042   -0.000007
   6          6           0       -2.296555    0.348255   -0.000020
   7          1           0       -1.648047    2.400124    0.000005
   8          1           0        0.742455    1.858792    0.000036
   9          1           0       -0.228892   -2.346126    0.000014
  10          1           0       -2.623635   -1.781583   -0.000016
  11          1           0       -3.351168    0.595077   -0.000036
  12          6           0        1.828852   -0.644481    0.000006
  13          1           0        2.069443   -1.701969    0.000002
  14          6           0        2.958547    0.331297   -0.000020
  15          1           0        2.933337    0.989558    0.877192
  16          1           0        3.919641   -0.182734   -0.000060
  17          1           0        2.933274    0.989579   -0.877215
---------------------------------------------------------------------
```

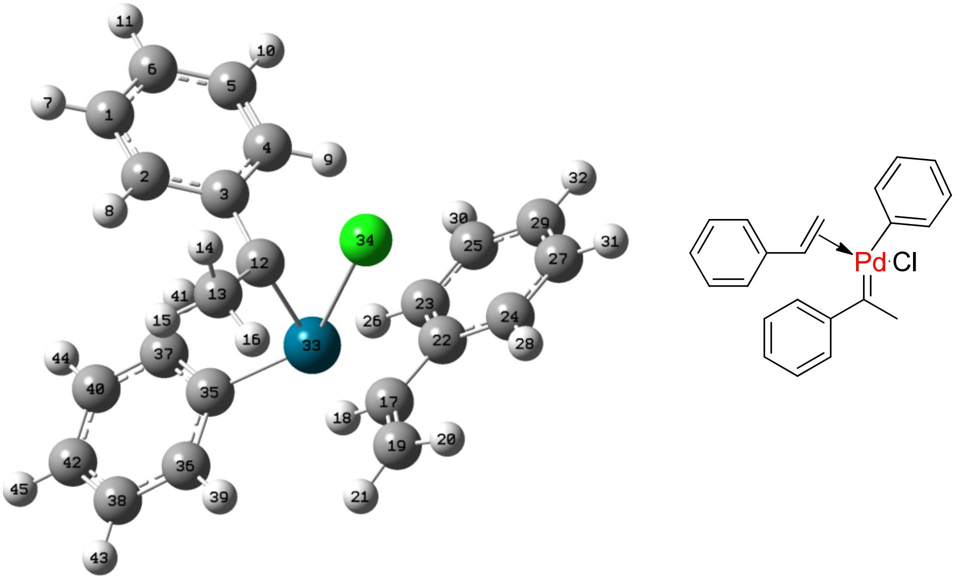


Figure S20. Optimized molecular geometry of **III** by DFT at B3LYP

Table S11. X, Y, Z-Cordinates of optimized intermediate **III,** calculated by DFT at B3LYP

```
---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
    1          6           0        3.317367    2.965500    1.005594
    2          6           0        2.902073    2.135226   -0.034572
    3          6           0        1.544704    1.855944   -0.240548
    4          6           0        0.619006    2.446989    0.635527
    5          6           0        1.030519    3.281923    1.662912
    6          6           0        2.386914    3.546190    1.857112
    7          1           0        4.375118    3.159328    1.141300
    8          1           0        3.652400    1.702579   -0.681741
    9          1           0       -0.437158    2.247952    0.503014
   10          1           0        0.291624    3.726745    2.319351
   11          1           0        2.708991    4.195336    2.662510
   12          6           0        1.108445    0.918528   -1.321741
   13          6           0        2.151788    0.530692   -2.345761
   14          1           0        2.628351    1.403770   -2.805072
   15          1           0        2.925919   -0.068390   -1.862136
   16          1           0        1.712612   -0.077313   -3.135010
   17          6           0       -1.936589   -1.813922    0.361515
   18          1           0       -1.433312   -2.119877    1.272752
   19          6           0       -1.605918   -2.455301   -0.792825
   20          1           0       -2.157092   -2.307710   -1.713740
   21          1           0       -0.903764   -3.277183   -0.776933
   22          6           0       -3.027951   -0.843924    0.559631
   23          6           0       -3.245651   -0.336487    1.847822
   24          6           0       -3.875157   -0.419541   -0.475053
   25          6           0       -4.272485    0.566678    2.097941
   26          1           0       -2.601865   -0.657377    2.659053
   27          6           0       -4.898989    0.483477   -0.225609
   28          1           0       -3.737705   -0.796202   -1.480983
   29          6           0       -5.102797    0.981040    1.061238
   30          1           0       -4.424210    0.945227    3.101658
```

31	1	0	-5.544168	0.799587	-1.036595
32	1	0	-5.904471	1.684240	1.251966
33	46	0	-0.148047	-0.611608	-0.725904
34	17	0	-0.308127	1.767865	-2.312767
35	6	0	1.355613	-1.571493	0.204050
36	6	0	2.047752	-2.602104	-0.438211
37	6	0	1.678531	-1.272826	1.529778
38	6	0	3.035361	-3.323439	0.234766
39	1	0	1.827217	-2.853899	-1.469310
40	6	0	2.662848	-1.997896	2.203574
41	1	0	1.171035	-0.468560	2.049907
42	6	0	3.345857	-3.025398	1.558753
43	1	0	3.561485	-4.119328	-0.281517
44	1	0	2.896798	-1.752465	3.234013
45	1	0	4.113057	-3.585314	2.080773

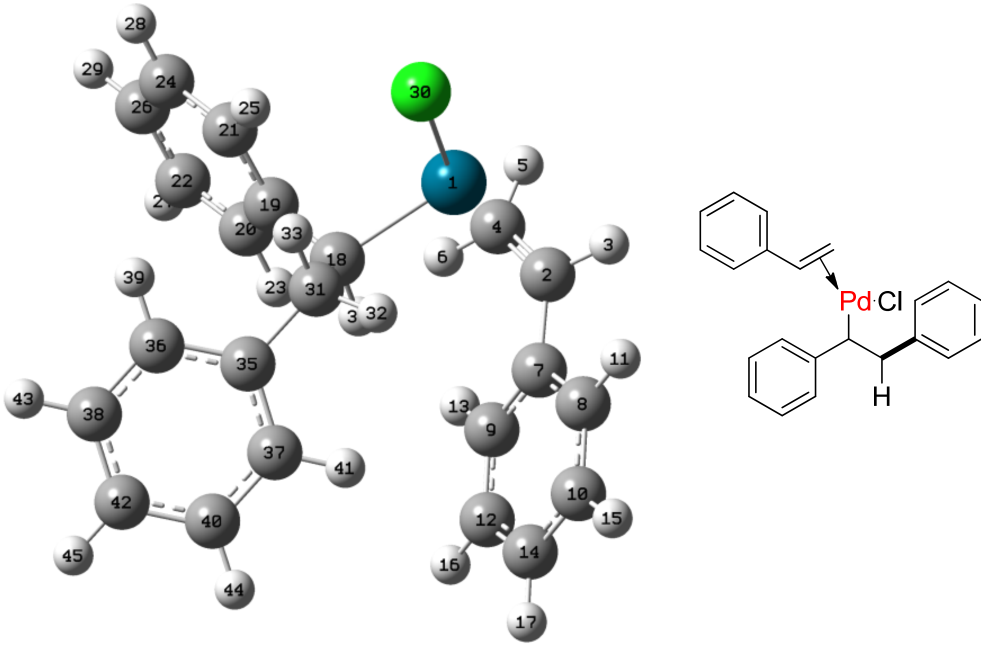


Figure S21. Optimized molecular geometry of **IV** by DFT at B3LYP

Table S12. X, Y, Z-Cordinates of optimized intermediate **IV,** calculated by DFT at B3LYP

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	0.025095	-1.990231	-0.323930
2	6	0	2.058171	-2.040129	0.694814
3	1	0	2.436316	-2.883724	0.122819
4	6	0	1.039990	-2.285998	1.599020
5	1	0	0.737909	-3.305805	1.808141
6	1	0	0.752229	-1.551576	2.339058
7	6	0	2.895788	-0.832349	0.611332
8	6	0	3.738139	-0.665741	-0.497804
9	6	0	2.929381	0.135240	1.625148
10	6	0	4.570811	0.440425	-0.601729
11	1	0	3.733288	-1.412268	-1.283919

12	6	0	3.765033	1.240853	1.521844
13	1	0	2.320837	0.015234	2.512520
14	6	0	4.585576	1.400028	0.408000
15	1	0	5.211776	0.552671	-1.467818
16	1	0	3.782865	1.975039	2.318300
17	1	0	5.238654	2.260958	0.331975
18	6	0	-0.488533	-0.019907	0.095358
19	6	0	-1.845169	-0.117695	0.682314
20	6	0	-1.996899	-0.038969	2.077161
21	6	0	-3.002315	-0.269883	-0.099715
22	6	0	-3.251476	-0.104148	2.668251
23	1	0	-1.120096	0.092803	2.700429
24	6	0	-4.255944	-0.338214	0.491337
25	1	0	-2.913750	-0.360811	-1.173775
26	6	0	-4.387205	-0.256334	1.876673
27	1	0	-3.344219	-0.032772	3.745304
28	1	0	-5.135765	-0.458352	-0.129541
29	1	0	-5.367464	-0.310288	2.334800
30	17	0	-1.196014	-2.326118	-2.441834
31	6	0	-0.283444	0.798651	-1.178884
32	1	0	0.721759	0.603082	-1.557886
33	1	0	-0.982467	0.487922	-1.952163
34	1	0	0.240159	0.268361	0.849912
35	6	0	-0.432286	2.288881	-0.913487
36	6	0	-1.607046	2.962790	-1.255093
37	6	0	0.604207	3.015833	-0.321168
38	6	0	-1.744140	4.327320	-1.013401
39	1	0	-2.420316	2.418682	-1.721516
40	6	0	0.470487	4.379203	-0.076343
41	1	0	1.527737	2.513297	-0.055701
42	6	0	-0.705986	5.040177	-0.420784
43	1	0	-2.661499	4.832982	-1.291646
44	1	0	1.287546	4.926769	0.378921
45	1	0	-0.810469	6.102242	-0.233328

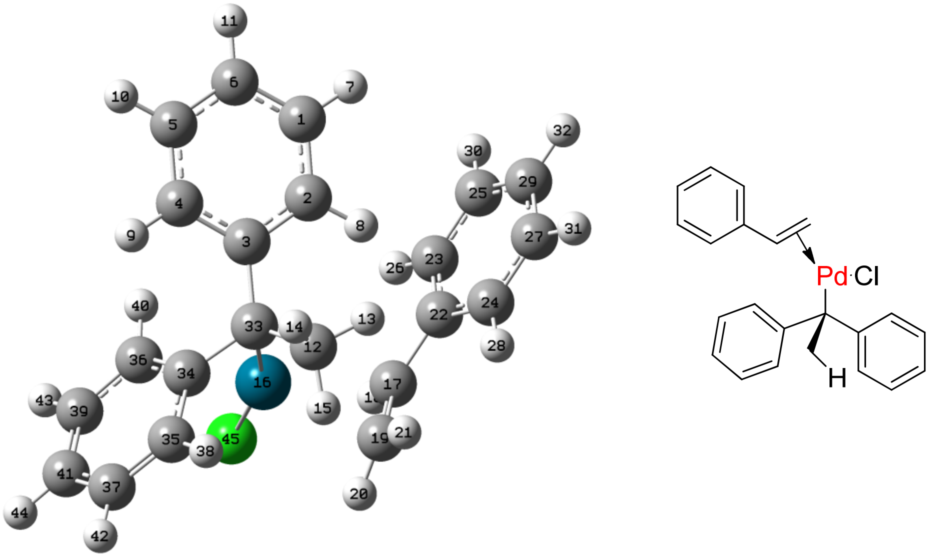
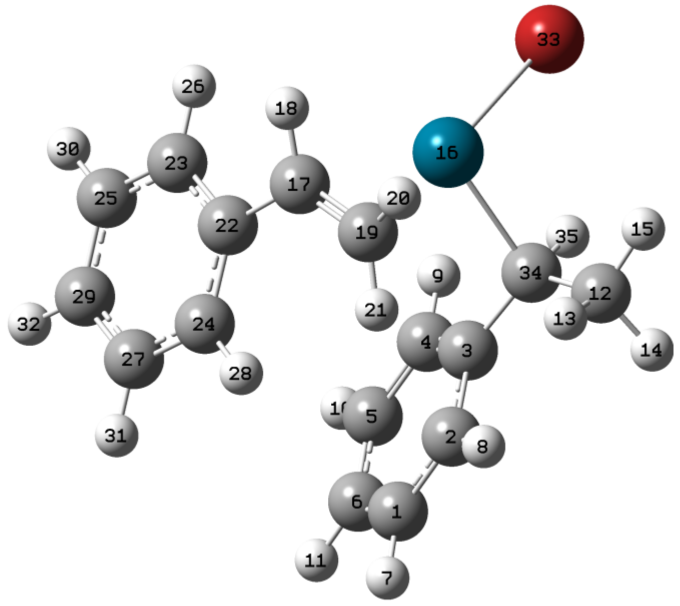


Figure S22. Optimized molecular geometry of **IVa** by DFT at B3LYP

Table S13. X, Y, Z-Cordinates of optimized intermediate **IVa,** calculated by DFT at B3LYP

```
---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
    1          6           0        2.100984    2.965340   -0.754205
    2          6           0        1.429052    1.955514   -0.075767
    3          6           0        0.050075    2.035980    0.156784
    4          6           0       -0.625833    3.182268   -0.288513
    5          6           0        0.048121    4.197310   -0.958367
    6          6           0        1.414003    4.090971   -1.200494
    7          1           0        3.165574    2.872685   -0.932015
    8          1           0        1.981255    1.090641    0.264359
    9          1           0       -1.684345    3.293110   -0.091474
   10          1           0       -0.496328    5.075867   -1.283730
   11          1           0        1.939399    4.880286   -1.724495
   12          6           0       -0.174223    0.898466    2.389467
   13          1           0        0.909769    0.787871    2.414170
   14          1           0       -0.408981    1.828293    2.920741
   15          1           0       -0.618687    0.070282    2.937887
   16         46           0       -0.728118   -0.867842   -0.146850
   17          6           0        1.310266   -2.186907    0.201595
   18          1           0        1.114741   -2.793325   -0.675799
   19          6           0        0.427709   -2.282888    1.242377
   20          1           0       -0.347714   -3.037966    1.226573
   21          1           0        0.620487   -1.810304    2.195830
   22          6           0        2.611124   -1.502786    0.205442
   23          6           0        3.283733   -1.322364   -1.011906
   24          6           0        3.236248   -1.066330    1.382824
   25          6           0        4.525263   -0.700984   -1.057070
   26          1           0        2.820320   -1.667476   -1.929165
   27          6           0        4.478368   -0.446633    1.337614
   28          1           0        2.760462   -1.227548    2.341973
   29          6           0        5.125537   -0.256420    0.118080
   30          1           0        5.025497   -0.565070   -2.008361
   31          1           0        4.948140   -0.118956    2.257216
   32          1           0        6.095168    0.225562    0.086239
   33          6           0       -0.667946    0.992026    0.961595
   34          6           0       -2.077845    0.757513    0.681091
   35          6           0       -3.042321    0.423141    1.672689
   36          6           0       -2.473341    0.668236   -0.687776
   37          6           0       -4.318655    0.062535    1.315189
   38          1           0       -2.775578    0.483820    2.718861
   39          6           0       -3.779498    0.269097   -1.027197
   40          1           0       -1.828760    1.054966   -1.466898
   41          6           0       -4.692362   -0.025789   -0.040714
   42          1           0       -5.047514   -0.159013    2.085339
   43          1           0       -4.062237    0.219505   -2.070985
   44          1           0       -5.703135   -0.314711   -0.301099
   45         17           0       -1.414402   -2.735974   -1.740380
---------------------------------------------------------------------
```



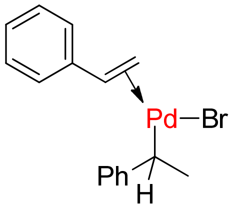


Figure S23. Optimized molecular geometry of **VI** by DFT at B3LYP

Table S14. X, Y, Z-Cordinates of optimized intermediate **VI,** calculated by DFT at B3LYP

```
---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
   1          6           0        1.916239   -0.315202    0.961483
   2          6           0        0.820134    0.528499    0.828334
   3          6           0       -0.098049    0.356494   -0.219688
   4          6           0        0.117618   -0.704187   -1.117910
   5          6           0        1.207094   -1.550927   -0.980131
   6          6           0        2.114878   -1.356747    0.059752
   7          1           0        2.620747   -0.155364    1.769049
   8          1           0        0.697361    1.343877    1.529568
   9          1           0       -0.576471   -0.848323   -1.938103
  10          1           0        1.356359   -2.357342   -1.688114
  11          1           0        2.971829   -2.011284    0.164104
  12          6           0       -1.153653    2.678925    0.137551
  13          1           0       -1.077476    2.671954    1.224556
  14          1           0       -0.274488    3.209330   -0.251388
  15          1           0       -2.032980    3.259889   -0.140265
  16         46           0       -3.076312    0.503740    0.056767
  17          6           0       -3.016572   -0.916450    1.869151
  18          1           0       -4.090439   -1.085755    1.796418
  19          6           0       -2.604526    0.340527    2.247103
  20          1           0       -3.325643    1.064757    2.606376
  21          1           0       -1.567028    0.543744    2.473138
  22          6           0       -2.213182   -2.142278    1.781505
  23          6           0       -2.751859   -3.261503    1.128235
  24          6           0       -0.957686   -2.263057    2.390816
  25          6           0       -2.047951   -4.455951    1.064497
  26          1           0       -3.729806   -3.186286    0.666264
  27          6           0       -0.256625   -3.460380    2.331853
  28          1           0       -0.535222   -1.425719    2.930164
  29          6           0       -0.795499   -4.558819    1.666478
```

30	1	0	-2.477106	-5.308580	0.552209
31	1	0	0.710401	-3.539727	2.813472
32	1	0	-0.247596	-5.492591	1.626278
33	35	0	-4.123518	1.091505	-2.211160
34	6	0	-1.204511	1.297172	-0.474770
35	1	0	-1.418626	1.344605	-1.539342

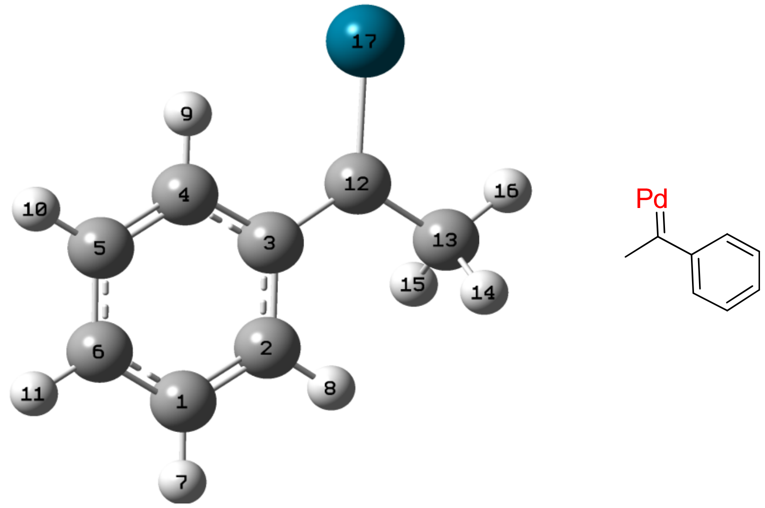


Figure S24. Optimized molecular geometry of **A** by DFT at B3LYP

Table S15. X, Y, Z-Cordinates of optimized geometry **A** calculated by DFT at B3LYP

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.552830	-1.559456	-0.105046
2	6	0	1.252851	-1.079056	-0.125932
3	6	0	0.974488	0.299766	-0.033204
4	6	0	2.073857	1.176482	0.089587
5	6	0	3.374850	0.696035	0.129046
6	6	0	3.619848	-0.672282	0.027999
7	1	0	2.738501	-2.623773	-0.185236
8	1	0	0.409856	-1.754706	-0.217496
9	1	0	1.912642	2.243175	0.166487
10	1	0	4.201828	1.387845	0.236142
11	1	0	4.637087	-1.044763	0.054529
12	6	0	-0.415953	0.765915	-0.064111
13	6	0	-0.605341	2.254265	-0.153721
14	1	0	-0.246270	2.729557	0.769723
15	1	0	-0.021227	2.689360	-0.974591
16	1	0	-1.647519	2.531111	-0.282499
17	46	0	-1.933684	-0.379300	0.040114

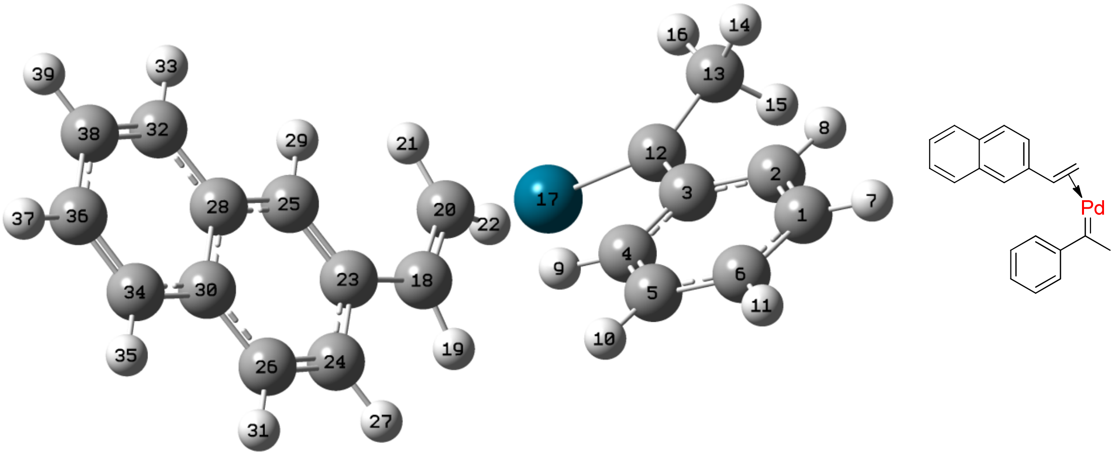


Figure S25. Optimized molecular geometry of **B** by DFT at B3LYP

Table S16. X, Y, Z-Cordinates of optimized intermediate **B,** calculated by DFT at B3LYP

```
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        1.971100    0.938637    1.570821
      2          6           0        1.481732    1.554445    0.430590
      3          6           0        0.305085    1.092447   -0.202110
      4          6           0       -0.349156   -0.017572    0.374409
      5          6           0        0.137813   -0.634257    1.515836
      6          6           0        1.301081   -0.156775    2.116665
      7          1           0        2.875161    1.307951    2.039647
      8          1           0        2.018553    2.401875    0.026402
      9          1           0       -1.252516   -0.377107   -0.105268
     10          1           0       -0.383028   -1.484286    1.939181
     11          1           0        1.686668   -0.635974    3.008820
     12          6           0       -0.257785    1.701178   -1.401027
     13          6           0        0.480092    2.889574   -1.939630
     14          1           0        0.541401    3.683070   -1.182837
     15          1           0        1.516663    2.625902   -2.188292
     16          1           0        0.012402    3.302959   -2.828929
     17         46           0       -1.867663    1.042795   -2.375684
     18          6           0       -3.667917   -0.043523   -3.266886
     19          1           0       -3.286261   -1.051196   -3.401230
     20          6           0       -3.243714    0.924037   -4.143609
     21          1           0       -3.724672    1.892376   -4.213944
     22          1           0       -2.594284    0.657209   -4.967927
     23          6           0       -4.765788    0.066781   -2.287515
     24          6           0       -5.069804   -1.073275   -1.490486
     25          6           0       -5.528495    1.207170   -2.116242
     26          6           0       -6.084195   -1.053626   -0.570930
     27          1           0       -4.479765   -1.973462   -1.621747
     28          6           0       -6.582289    1.262155   -1.175924
     29          1           0       -5.330627    2.092217   -2.709507
     30          6           0       -6.871694    0.109591   -0.381112
     31          1           0       -6.297753   -1.935049    0.023548
     32          6           0       -7.369378    2.430609   -0.994874
     33          1           0       -7.151892    3.306020   -1.596783
     34          6           0       -7.930604    0.168748    0.558559
```

35	1	0	-8.147079	-0.708078	1.158823
36	6	0	-8.672098	1.314362	0.709344
37	1	0	-9.479439	1.348699	1.431071
38	6	0	-8.387774	2.456069	-0.075890
39	1	0	-8.980385	3.354065	0.052527

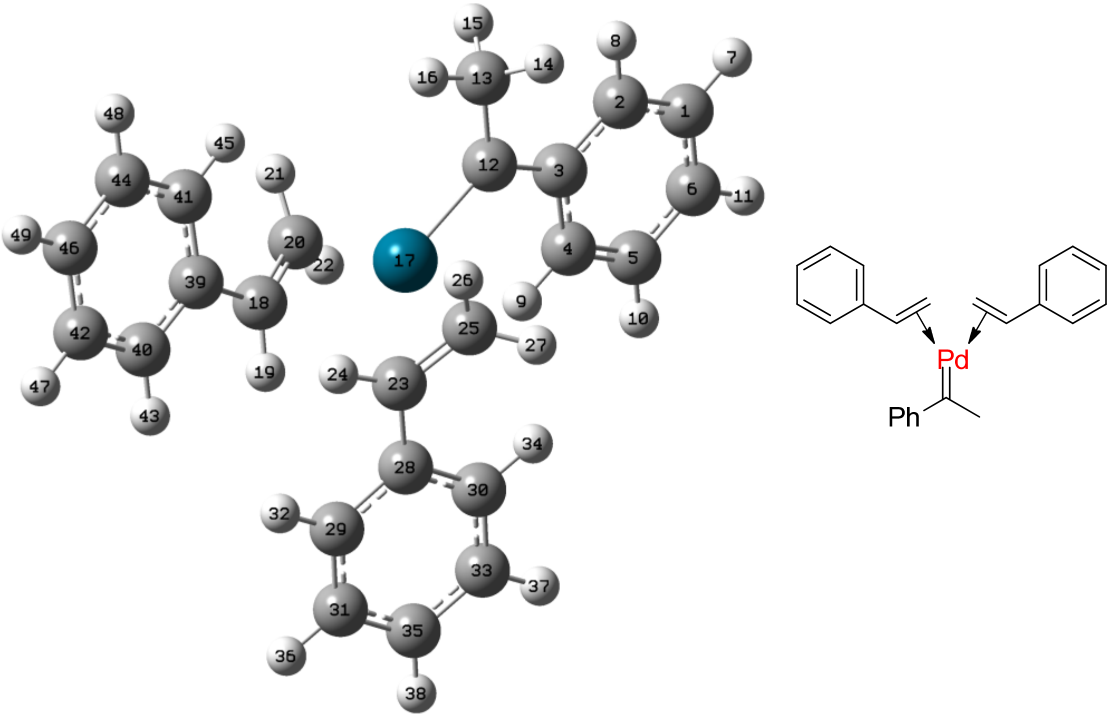


Figure S26. Optimized molecular geometry of **C** by DFT at B3LYP

Table S17. X, Y, Z-Cordinates of optimized intermediate **C,** calculated by DFT at B3LYP

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-5.712975	-1.061454	-0.120214
2	6	0	-4.493433	-1.592581	0.272183
3	6	0	-3.284104	-0.903776	0.032661
4	6	0	-3.367796	0.342660	-0.621940
5	6	0	-4.584741	0.875504	-1.015850
6	6	0	-5.762852	0.173331	-0.765308
7	1	0	-6.628137	-1.607421	0.075229
8	1	0	-4.482235	-2.551924	0.771568
9	1	0	-2.445236	0.877555	-0.813047
10	1	0	-4.620677	1.834657	-1.517989
11	1	0	-6.716765	0.586218	-1.071636
12	6	0	-1.972607	-1.417573	0.425642
13	6	0	-1.970840	-2.761291	1.092415
14	1	0	-2.584065	-2.749642	2.002935
15	1	0	-2.415308	-3.521684	0.437028
16	1	0	-0.969803	-3.088810	1.362618
17	46	0	-0.226664	-0.482979	0.180987
18	6	0	1.564525	-0.513798	-1.346420
19	1	0	1.763052	0.531980	-1.552796

20	6	0	0.415519	-1.074309	-1.881643
21	1	0	0.306741	-2.146823	-1.980904
22	1	0	-0.219357	-0.479094	-2.525725
23	6	0	1.057528	1.072211	1.399917
24	1	0	2.026528	0.596017	1.499605
25	6	0	0.004443	0.562667	2.143820
26	1	0	0.186352	-0.246595	2.839979
27	1	0	-0.887247	1.147102	2.331561
28	6	0	1.077587	2.391974	0.749123
29	6	0	2.304206	2.938514	0.339997
30	6	0	-0.080494	3.159341	0.535938
31	6	0	2.374817	4.191950	-0.258286
32	1	0	3.214548	2.373031	0.504058
33	6	0	-0.010192	4.411060	-0.061240
34	1	0	-1.046678	2.770592	0.832457
35	6	0	1.217046	4.936875	-0.464038
36	1	0	3.337239	4.588298	-0.561047
37	1	0	-0.919334	4.981011	-0.215578
38	1	0	1.268136	5.913623	-0.929945
39	6	0	2.708424	-1.271385	-0.813102
40	6	0	3.949552	-0.632023	-0.668890
41	6	0	2.630104	-2.629292	-0.459138
42	6	0	5.064129	-1.313837	-0.192193
43	1	0	4.040236	0.412381	-0.945373
44	6	0	3.742903	-3.310458	0.016022
45	1	0	1.687086	-3.154725	-0.545962
46	6	0	4.968106	-2.658522	0.154169
47	1	0	6.009988	-0.793434	-0.094472
48	1	0	3.654382	-4.357159	0.283954
49	1	0	5.833983	-3.192831	0.526317

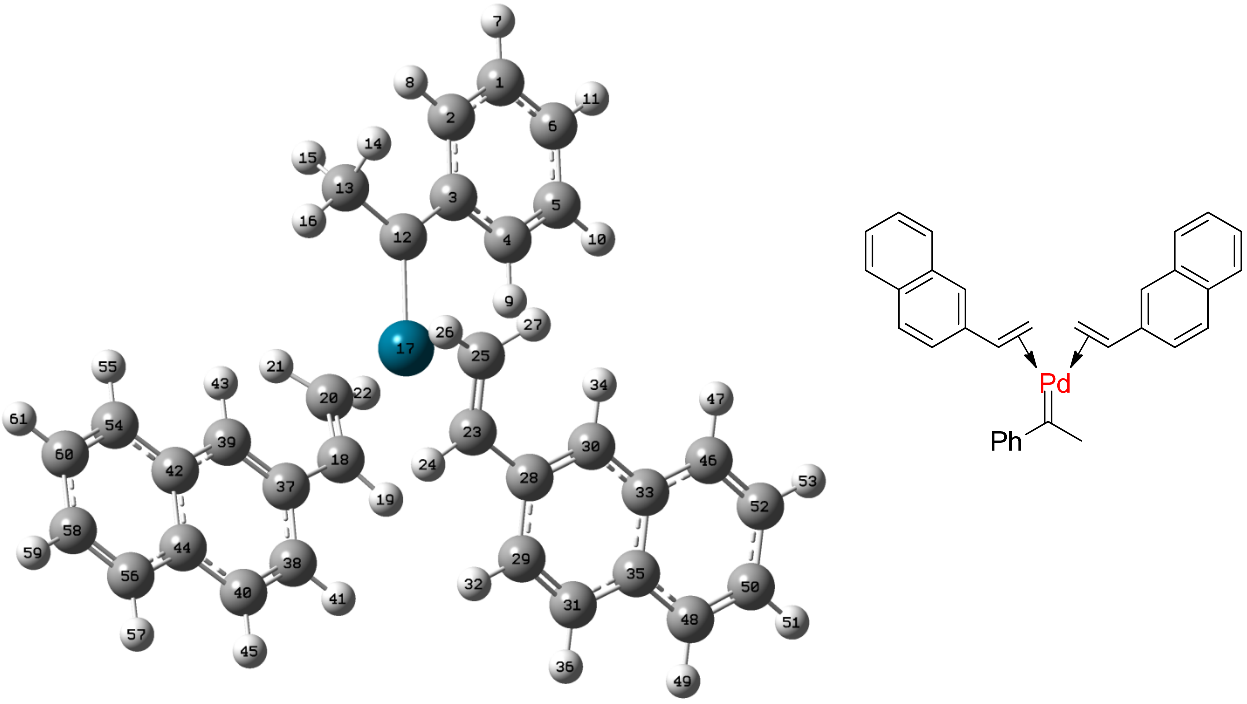


Figure S27. Optimized molecular geometry of **D** by DFT at B3LYP

Table S18. X, Y, Z-Cordinates of optimized intermediate **D,** calculated by DFT at B3LYP

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.151963	5.458690	-0.179347
2	6	0	1.920538	4.911323	0.147622
3	6	0	1.676806	3.526739	0.012753
4	6	0	2.734524	2.725928	-0.465672
5	6	0	3.966881	3.269761	-0.790267
6	6	0	4.178654	4.640421	-0.648288
7	1	0	3.316216	6.523893	-0.069462
8	1	0	1.140730	5.567458	0.509941
9	1	0	2.555696	1.662897	-0.574347
10	1	0	4.763016	2.632220	-1.155009
11	1	0	5.140179	5.070472	-0.902736
12	6	0	0.397797	2.899401	0.338834
13	6	0	-0.667975	3.815824	0.860747
14	1	0	-0.327639	4.347705	1.758557
15	1	0	-0.906257	4.591021	0.120653
16	1	0	-1.586328	3.287611	1.105042
17	46	0	-0.030679	0.959961	0.157011
18	6	0	-1.117831	-0.402830	-1.429002
19	1	0	-0.459988	-1.255281	-1.555343
20	6	0	-0.717508	0.809845	-1.968272
21	1	0	-1.428688	1.604647	-2.153813
22	1	0	0.200611	0.862060	-2.539668
23	6	0	0.192908	-0.964967	1.494528
24	1	0	-0.807228	-1.382040	1.528538
25	6	0	0.432793	0.201471	2.205736
26	1	0	-0.354848	0.622495	2.818072
27	1	0	1.438507	0.504044	2.468232
28	6	0	1.225804	-1.869576	0.967144
29	6	0	0.834413	-3.169381	0.532978
30	6	0	2.568792	-1.539977	0.891927
31	6	0	1.743935	-4.072615	0.051387
32	1	0	-0.211504	-3.446262	0.598715
33	6	0	3.534417	-2.447251	0.399146
34	1	0	2.908599	-0.561218	1.209626
35	6	0	3.120725	-3.745294	-0.034720
36	1	0	1.417214	-5.056358	-0.267839
37	6	0	-2.483224	-0.728753	-0.988367
38	6	0	-2.830420	-2.098305	-0.803782
39	6	0	-3.463750	0.223165	-0.764616
40	6	0	-4.088584	-2.476661	-0.417074
41	1	0	-2.076458	-2.855383	-0.986464
42	6	0	-4.771736	-0.131698	-0.363482
43	1	0	-3.237476	1.276346	-0.883927
44	6	0	-5.100054	-1.511542	-0.182508
45	1	0	-4.325483	-3.527248	-0.288684
46	6	0	4.912863	-2.112170	0.318945
47	1	0	5.231591	-1.128902	0.647300
48	6	0	4.091874	-4.651033	-0.528075
49	1	0	3.771375	-5.634203	-0.855318
50	6	0	5.416917	-4.295355	-0.592423
51	1	0	6.151253	-4.995997	-0.971585

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    52          6           0        5.829639   -3.012258   -0.163613
    53          1           0        6.877668   -2.741969   -0.218341
    54          6           0       -5.779406    0.842341   -0.129341
    55          1           0       -5.534820    1.890199   -0.265049
    56          6           0       -6.412011   -1.862364    0.221046
    57          1           0       -6.654682   -2.910843    0.356137
    58          6           0       -7.362964   -0.895672    0.438692
    59          1           0       -8.363237   -1.175215    0.747286
    60          6           0       -7.041352    0.470266    0.260943
    61          1           0       -7.799347    1.224832    0.435505
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