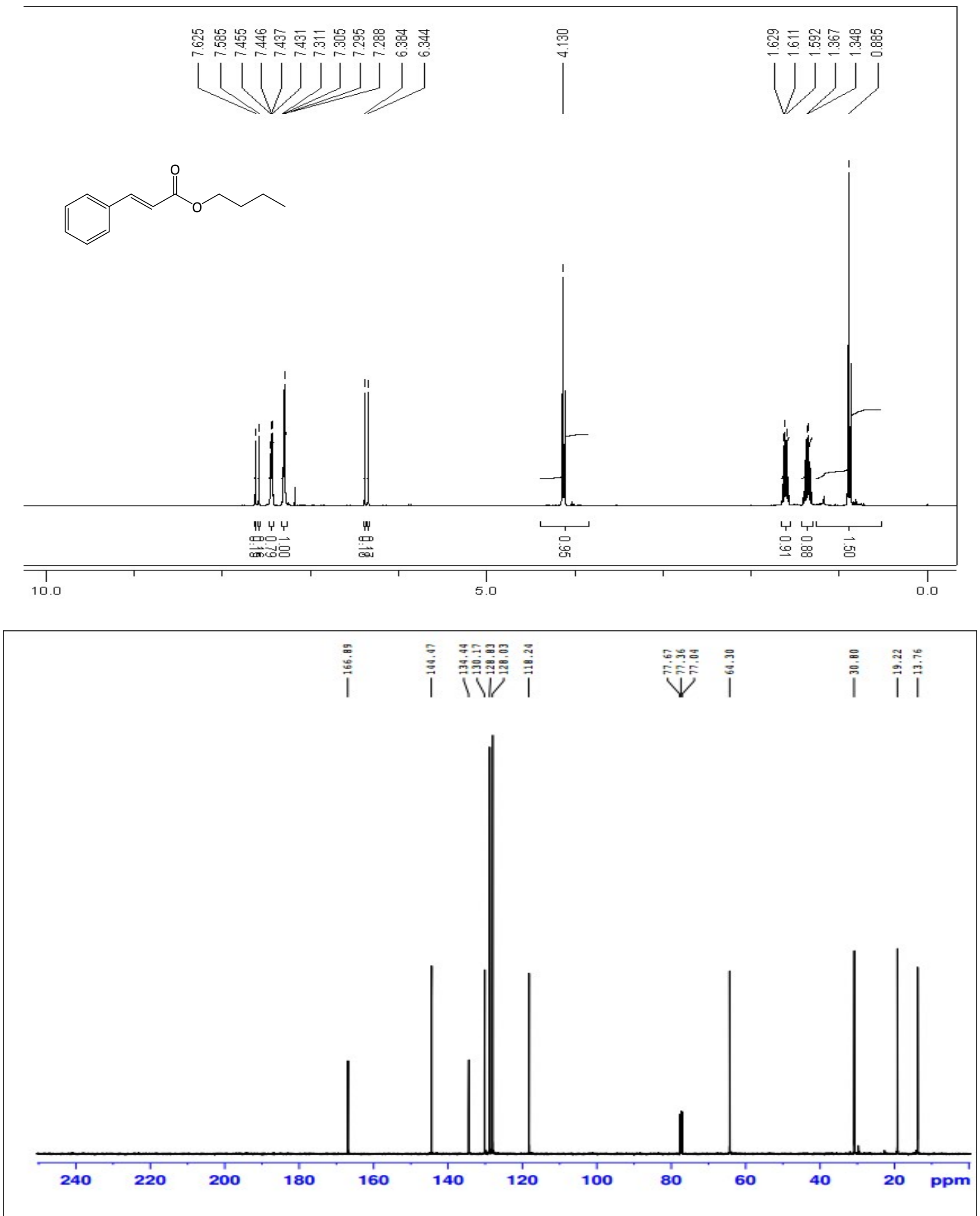
A hydrophilic heterogeneous cobalt catalyst for fluoride-free Hiyama, Suzuki, Heck and Hirao cross-coupling reactions in water

Sara Sobhani,*[a] Hadis Hosseini Moghadam,[a] Jørgen Skibsted[b] and José Miguel Sansano[c]

General information

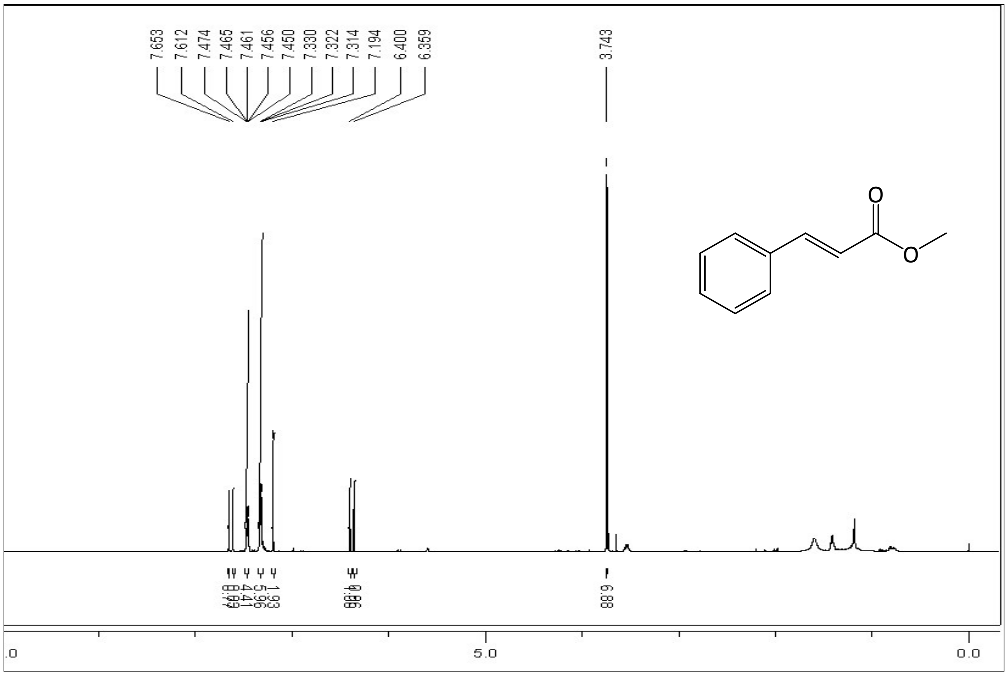
Chemicals were purchased from Merck Chemical Company. NMR spectra were recorded on a Bruker Avance DPX-400 and 300 using deutrated $CDCl_3$ and DMSO-d_6 as solvent and TMS as internal standard. The purity of the products and the progress of the reactions were accomplished by TLC on silica-gel polygram SILG/UV254 plates. TEM analysis was performed using TEM microscope (Philips EM 208S). FT-IR spectra were recorded on a Shimadzu Fourier Transform Infrared Spectrophotometer (FT-IR-8300). Thermo gravimetric analysis (TGA) was performed using a Shimadzu thermo gravimetric analyzer (TG-50). Field emission scanning electron microscopy (FE-SEM) was performed in model Mira 3-XMU. Power X-ray diffraction (XRD) was performed on a Bruker D8-advance X-ray diffractometer with Cu K_{α} (λ = 0.154 nm) radiation. XPS analyses were performed using a VG-Microtech Multilab 3000 spectrometer, equipped with an Al anode. The deconvolution of spectra was carried out by using Gaussian–Lorentzian curves. The solid-state $^{13}C\{1H\}$ CP/MAS NMR spectra was obtained on a Bruker Avance II 400 MHz (9.4 T) spectrometer using a 4 mm CP/MAS NMR probe and a spinning speed of nR = 10.0 kHz. The Co content on the catalyst was detemined by OPTIMA 7300DV ICP analyzer.

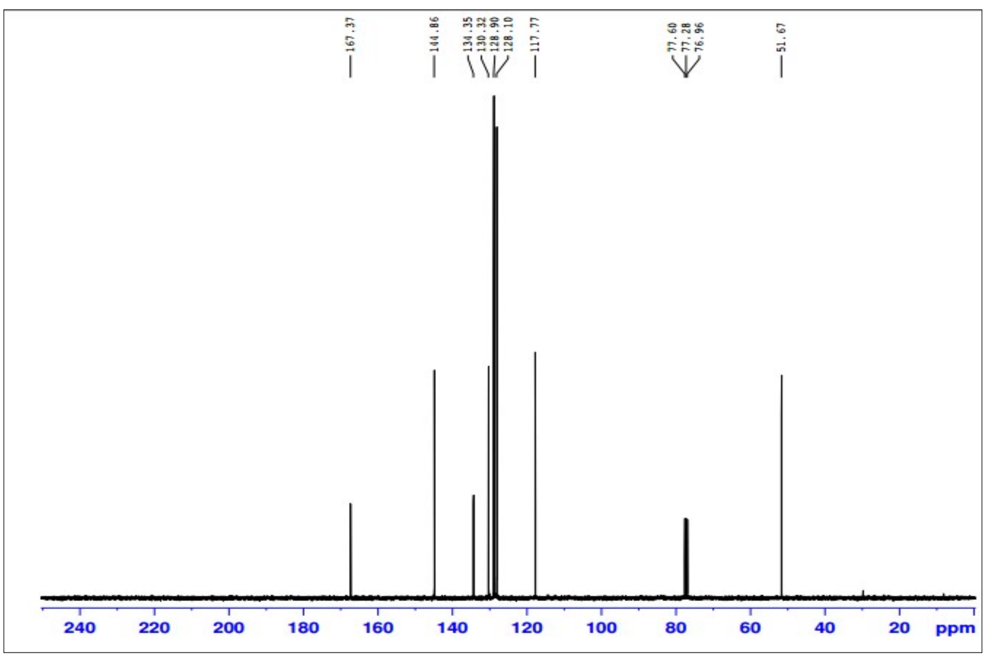
[a] *Address: Department of Chemistry, College of Sciences, University of Birjand, Birjand, Iran, email: ssobhani@birjand.ac.ir, sobhanisara@yahoo.com.*
[b] *Department of Chemistry and Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark.*
[c] *Departamento de Qu´ımica Org´anica, Facultad de Ciencias, Centro de Innovaci´on en Qu´ımica Avanzada (ORFEO-CINQA) and Instituto de S´ıntesis Org´anica (ISO), Universidad de Alicante, Apdo. 99, 03080-Alicante, Spain.*



^{1}H NMR and ^{13}C NMR spectra of (E)-*n*-butyl cinnamate

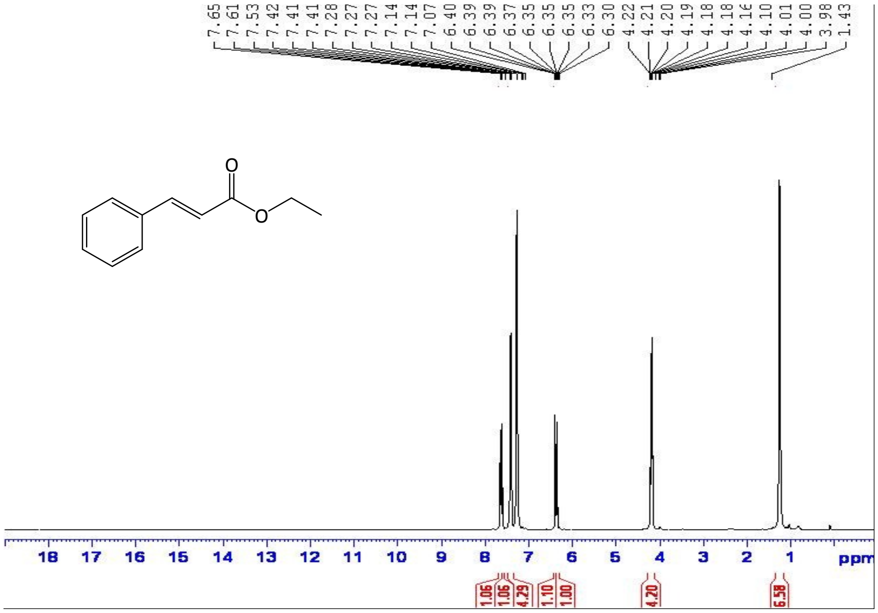
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, 1H, ^{3}J = 16.4 Hz), 7.43-7.45 (m, 2H), 7.29-7.30 (m, 3H), 6.36 (d, 1H, ^{3}J = 16.0 Hz), 4.13 (t, 2H, ^{3}J = 6.8 Hz), 1.59-1.62 (m, 2H), 1.34-1.36 (m, 2H), δ 0.88 (t, 3H, ^{3}J = 7.6 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), δ 166.8, 144.4, 134.4, 130.1, 128.8, 128.0, 118.2, 64.3, 30.8, 19.2, 13.7 ppm.

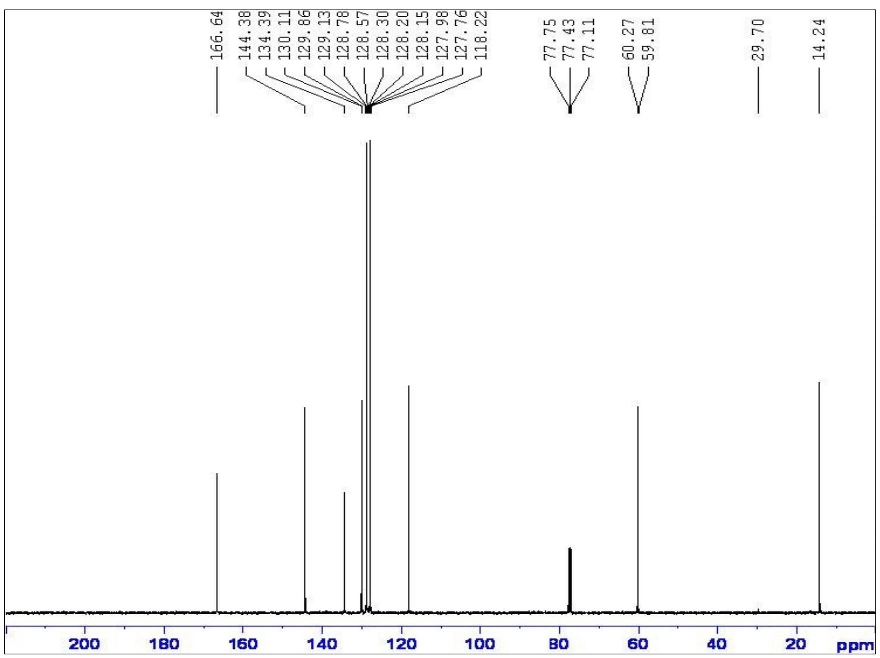




^{1}H NMR and ^{13}C NMR spectra of (E)-methyl cinnamate

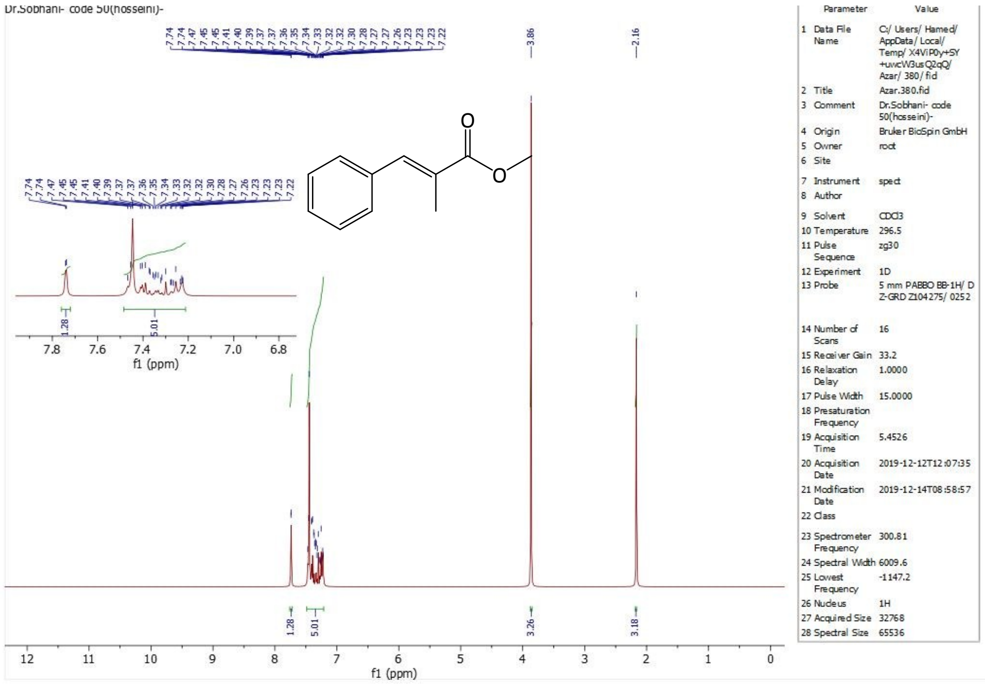
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, 1H, ^3J = 16.4 Hz), 7.45-7.47 (m, 2H), 7.31-7.33 (m, 3H), 6.38 (d, 1H, ^3J = 16.4 Hz), 3.74 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), δ 167.3, 144.8, 134.3, 130.3, 128.9, 128.1, 117.7, 51.6 ppm.

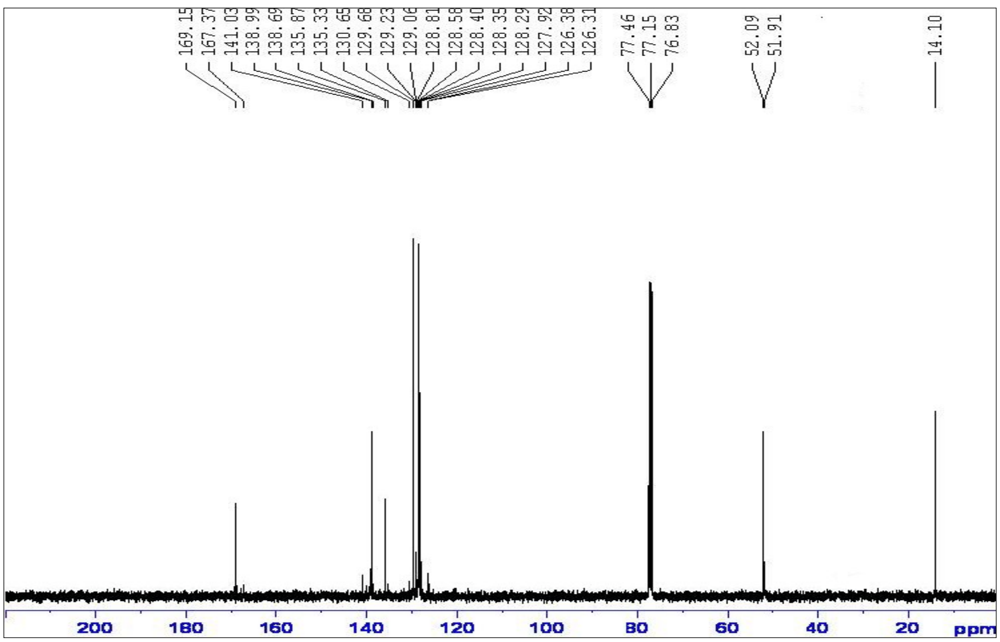




^{1}H NMR and ^{13}C NMR spectra of (E)-ethyl cinnamate

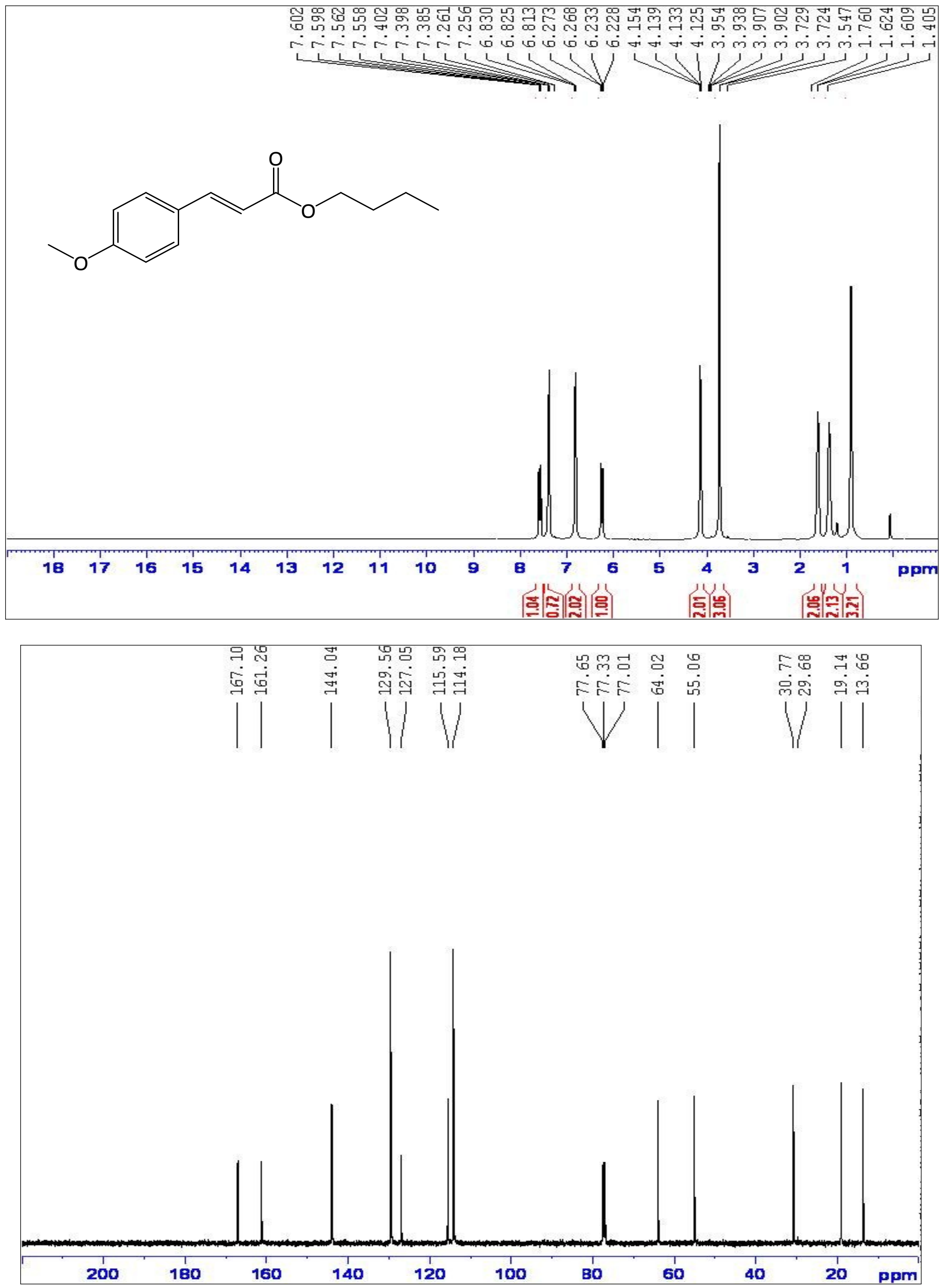
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, 1H, ^3J = 16.0 Hz), 7.41-7.42 (m, 2H), 7.27-7.28 (m, 3H), 6.35 (d, 1H, ^3J = 16.0 Hz), 4.19 (q, 2H, ^3J = 8.0 Hz), 1.43 (t, 3H, ^3J = 8.0 Hz) ppm.^{13}C NMR (100 MHz, $CDCl_3$), δ 166.6, 144.3, 134.3, 130.1, 128.7, 127.9, 118.2, 60.0, 14.2 ppm.





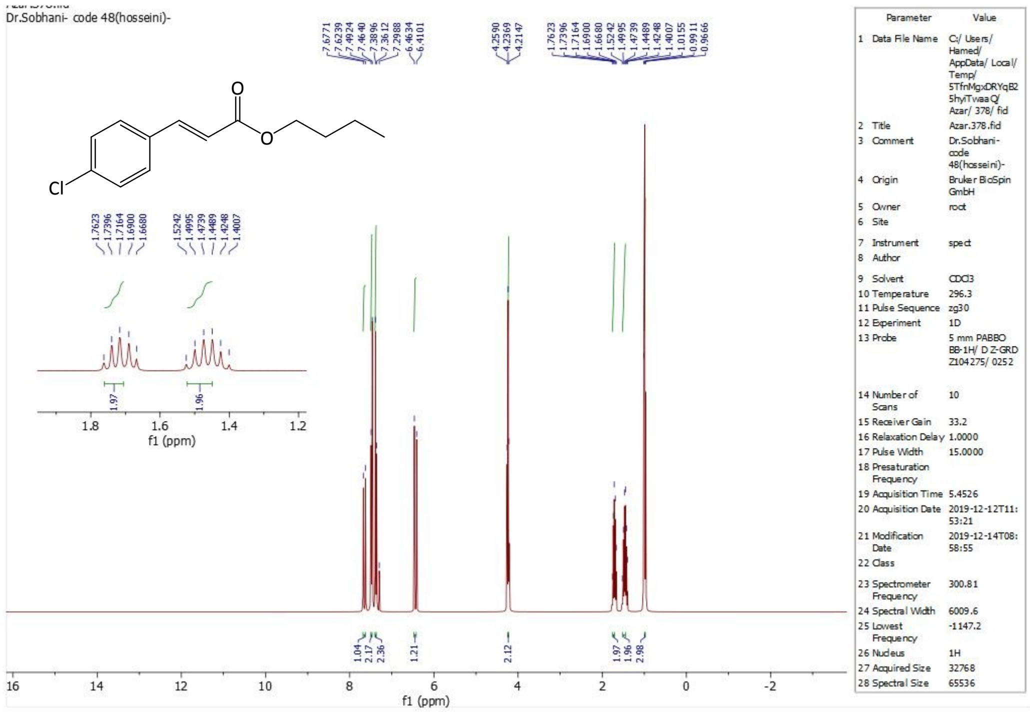
[1]H NMR and [13]C NMR spectra of (E)-methyl 2-methyl-3-phenylacrylate

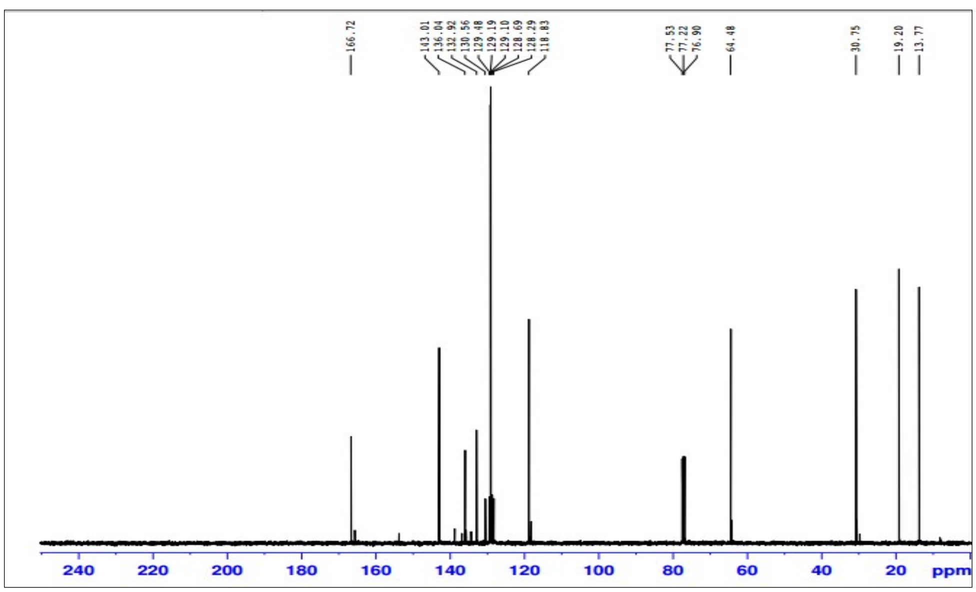
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 (s, 1H), 7.22-7.47 (m, 5H), 3.86 (s, 3H), 2.16 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), δ 169.1, 138.9, 135.8, 129.6, 127.9, 52.0, 14.1 ppm.



^{1}H NMR and ^{13}C NMR spectra of (E)-*n*-butyl 3-(4-methoxyphenyl) acrylate

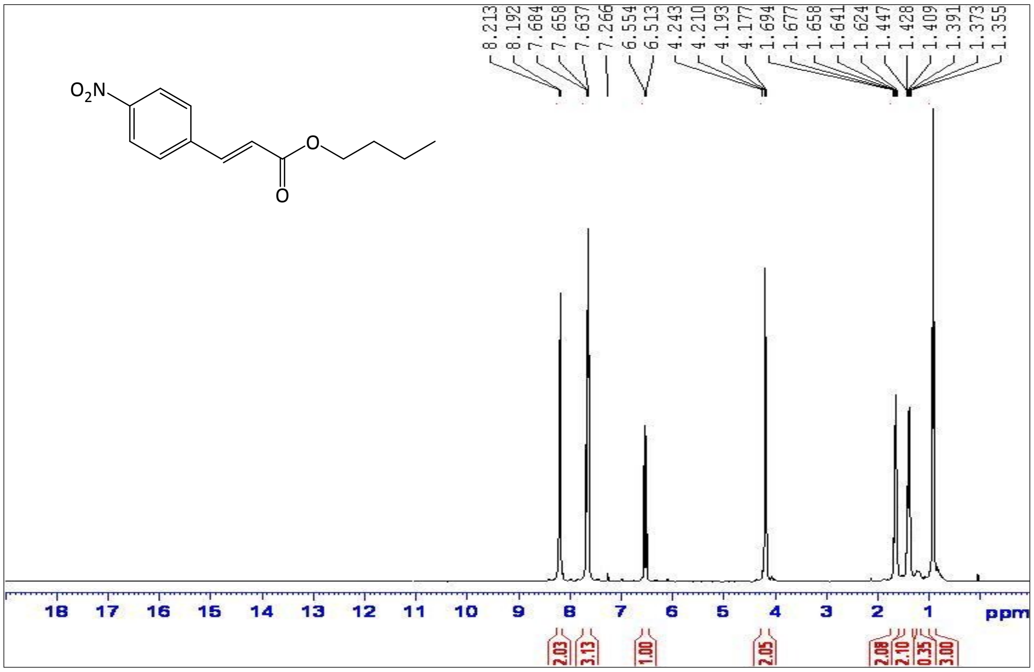
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, 1H, ^{3}J = 16.0 Hz), 7.39 (d, 3H, ^{3}J =4.2 Hz), 6.24 (d, 1H, ^{3}J = 16.0 Hz), 4.13 (m, 2H, ^{3}J =7.0 Hz), 3.72 (s, 3H), 1.60-1.62 (m, 2H), 1.35-1.40 (m, 2H), 0.91 (t, 3H, ^{3}J =7.0 Hz) ppm.^{13}C NMR (100 MHz, $CDCl_3$), δ 167.1, 161.2, 144.0, 129.5, 127.0, 115.5, 114.1, 64.0, 55.0, 30.7, 19.1, 13.6 ppm.

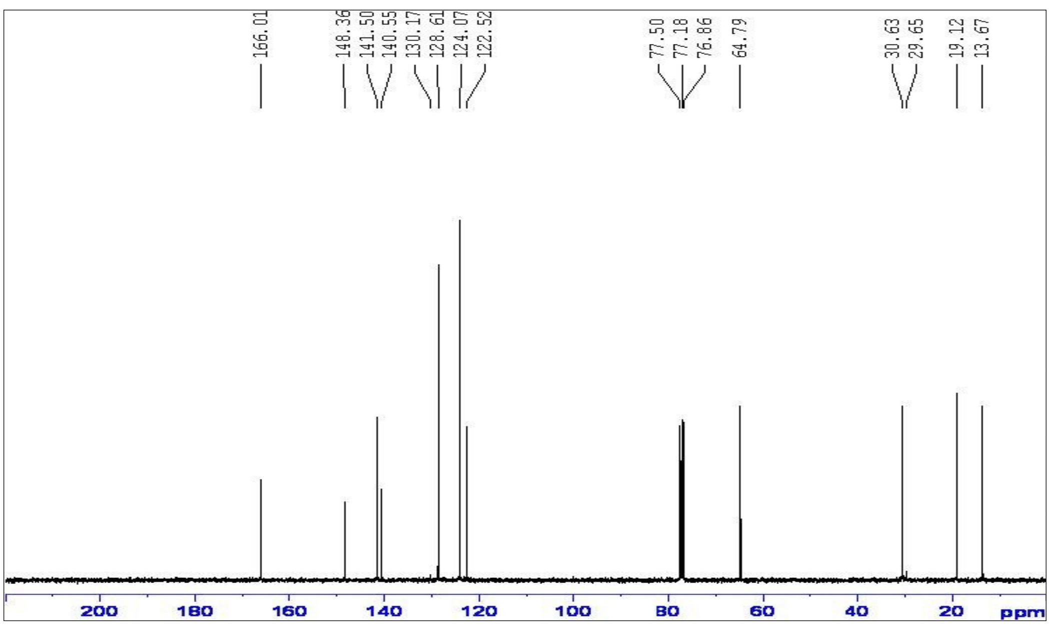




^{1}H NMR and ^{13}C NMR spectra of (E)-*n*-butyl 3-(4-chlorophenyl) acrylate

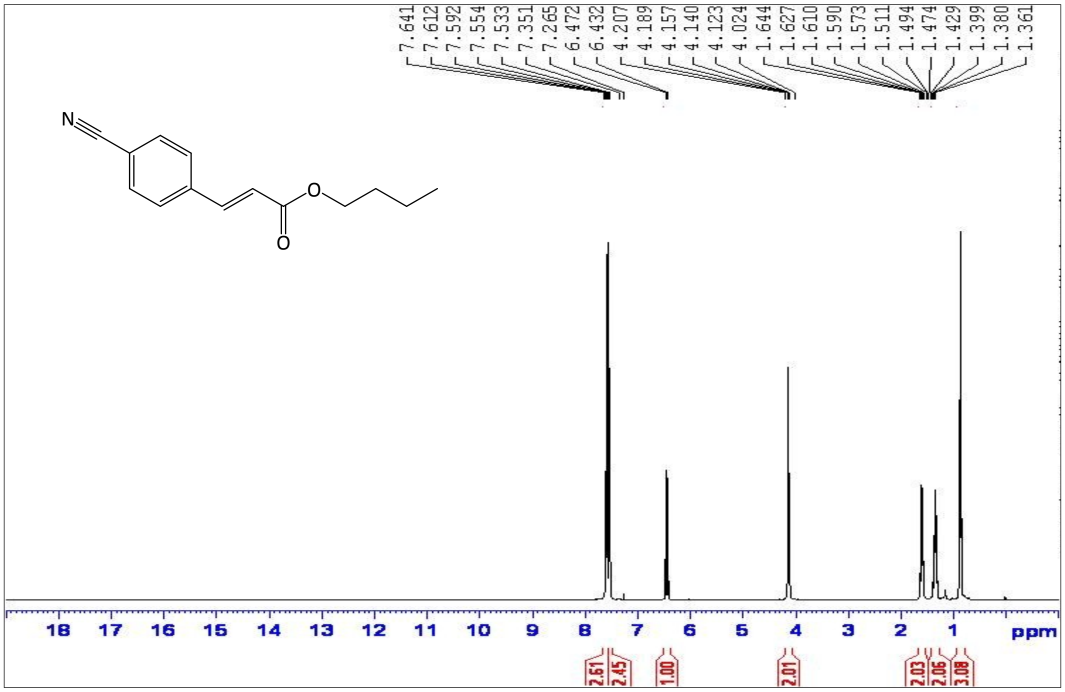
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (d, 1H, ^{3}J = 16.0 Hz), 7.47 (d, 2H, ^{3}J = 8.5 Hz), 7.37 (d, 2H, ^{3}J = 8.5 Hz), 6.43 (d, 1H, ^{3}J = 16.0 Hz), 4.24 (t, 2H, ^{3}J = 6.6 Hz), 1.40-1.52 (m, 2H), 1.67-1.76 (m, 2H), 0.99 (t, 3H, ^{3}J = 7.3 Hz) ppm.^{13}C NMR (100 MHz, $CDCl_3$), δ 166.7, 143.0, 136.0, 132.9, 129.4, 129.1, 118.8, 64.4, 30.7, 19.2, 13.7 ppm.

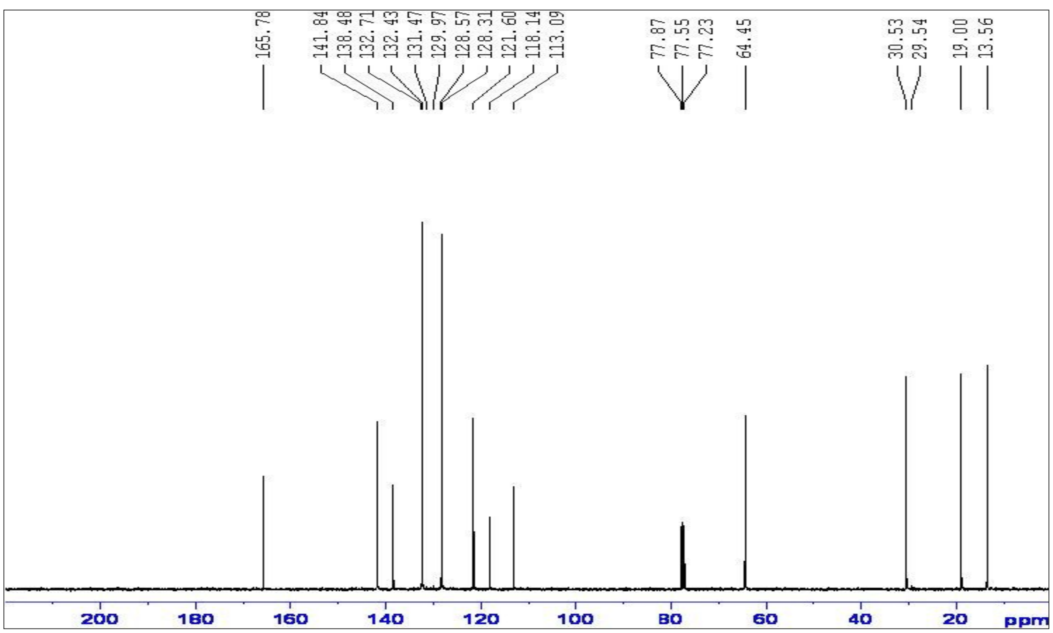




^{1}H NMR and ^{13}C NMR spectra of (E)-*n*-butyl 3-(4-nitrophenyl) acrylate

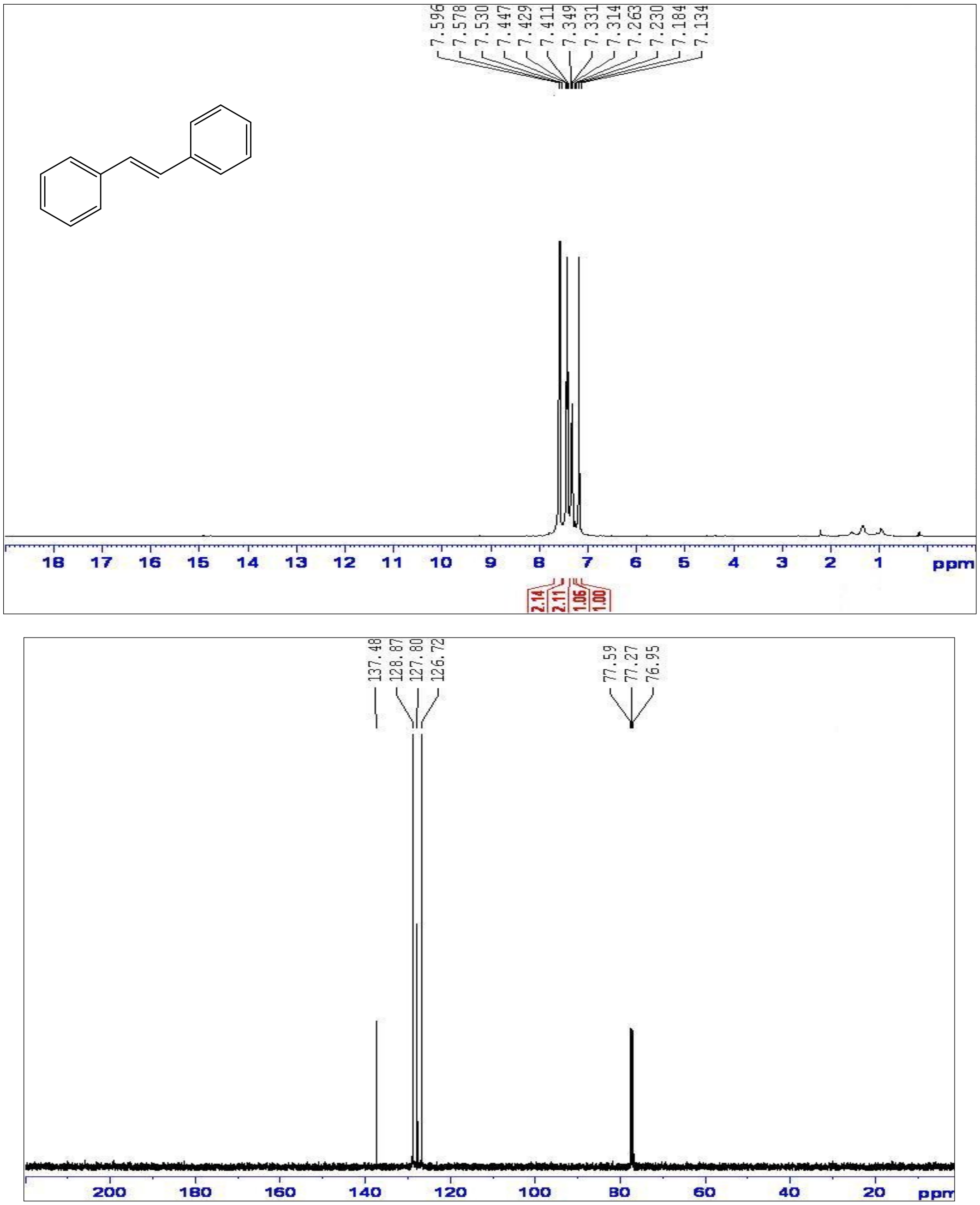
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, 2H, ^{3}J = 8.0 Hz), 7.63-7.68 (m, 3H), 6.53 (d, 1H, ^{3}J = 16.0 Hz), 4.17-4.24 (m, 2H), 1.62-1.69 (m, 2H), 1.35-1.44 (m, 2H), 0.92 (t, 3H, ^{3}J = 7.2 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), δ 166.0, 148.3, 141.5, 140.5, 128.6, 124.0, 122.5, 64.7, 30.6, 19.1, 13.6 ppm.





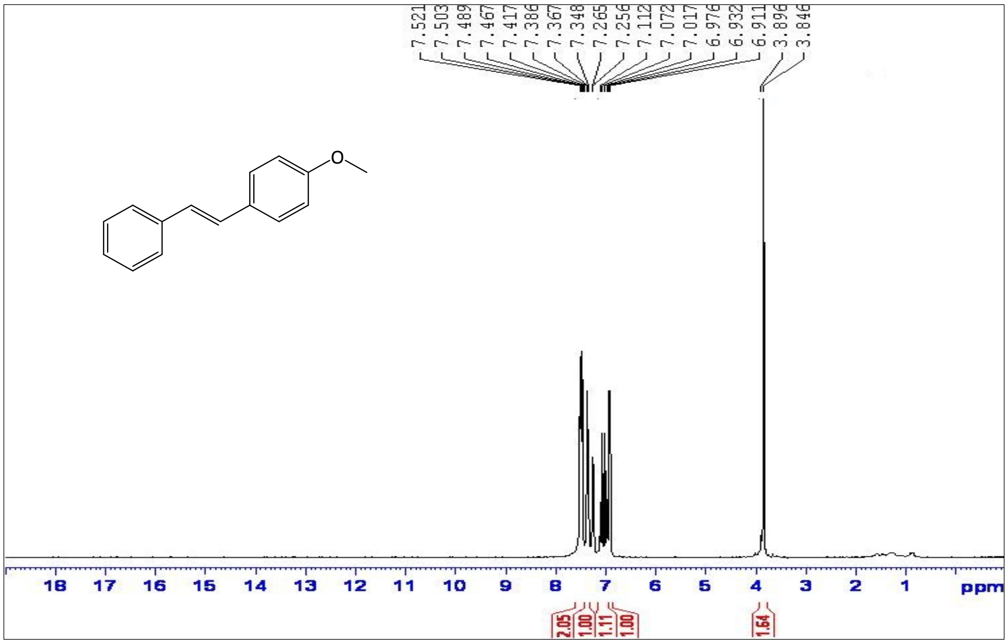
^{1}H NMR and ^{13}C NMR spectra of (E)-*n*-butyl 3-(4-cyanophenyl) acrylate

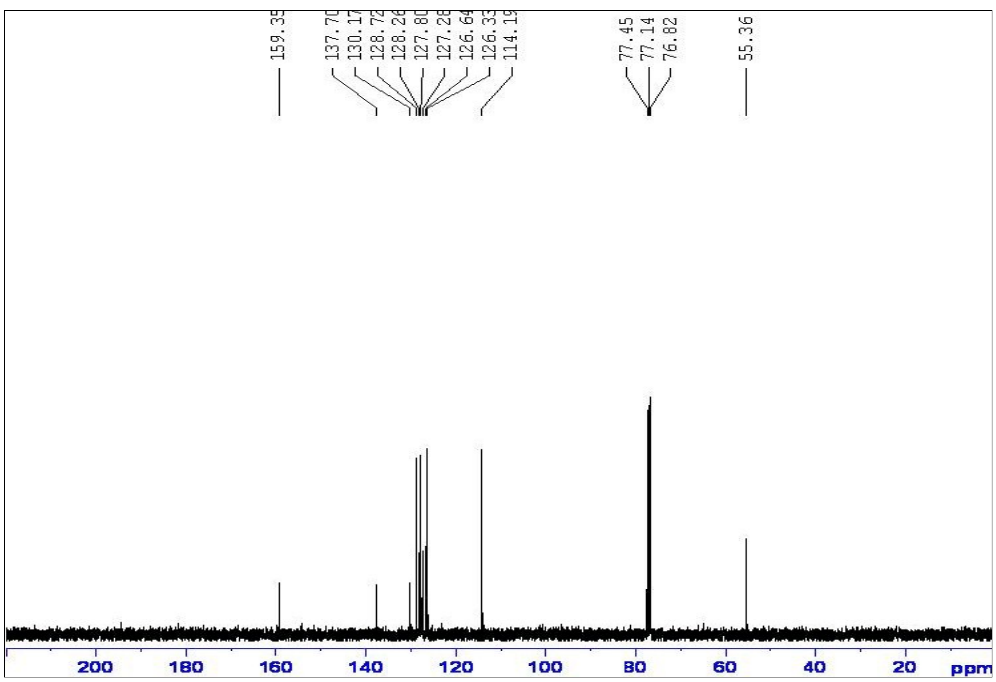
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, 2H, ^3J = 8.0 Hz), 7.57 (d, 1H, ^3J = 15.2 Hz), 7.54 (d, 2H, ^3J = 8.4 Hz), 6.45 (d, 1H, ^3J = 16.0 Hz), 4.14 (t, 2H, ^3J = 6.8 Hz), 1.57-1.64 (m, 2H), 1.30-1.38 (m, 2H), 0.77 (t, 3H, ^3J = 7.0 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), δ 165.7, 141.8, 138.4, 132.4, 128.3, 121.6, 118.1, 113.0, 64.4, 30.5, 19.0, 13.5 ppm.



^{1}H NMR and ^{13}C NMR spectra of (E)-1, 2-diphenylethene

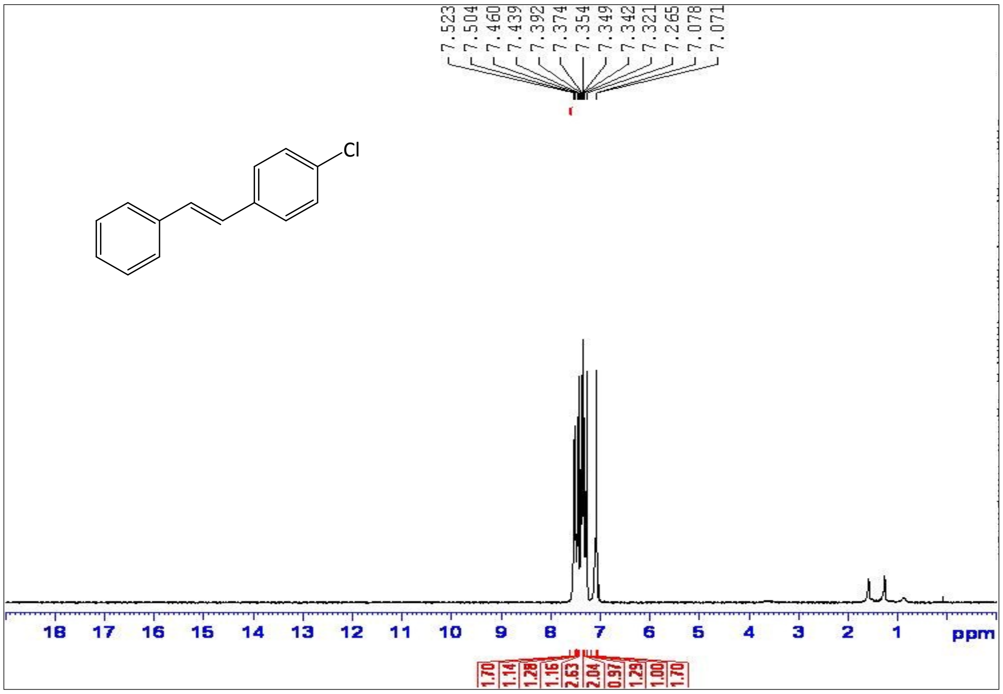
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, 4H, ^{3}J = 7.2 Hz), 7.42 (t, 4H, ^{3}J = 7.0 Hz), 7.33 (t, 2H, ^{3}J = 6.8 Hz), 7.18 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), δ 137.4, 128.8, 127.8, 126.7 ppm.

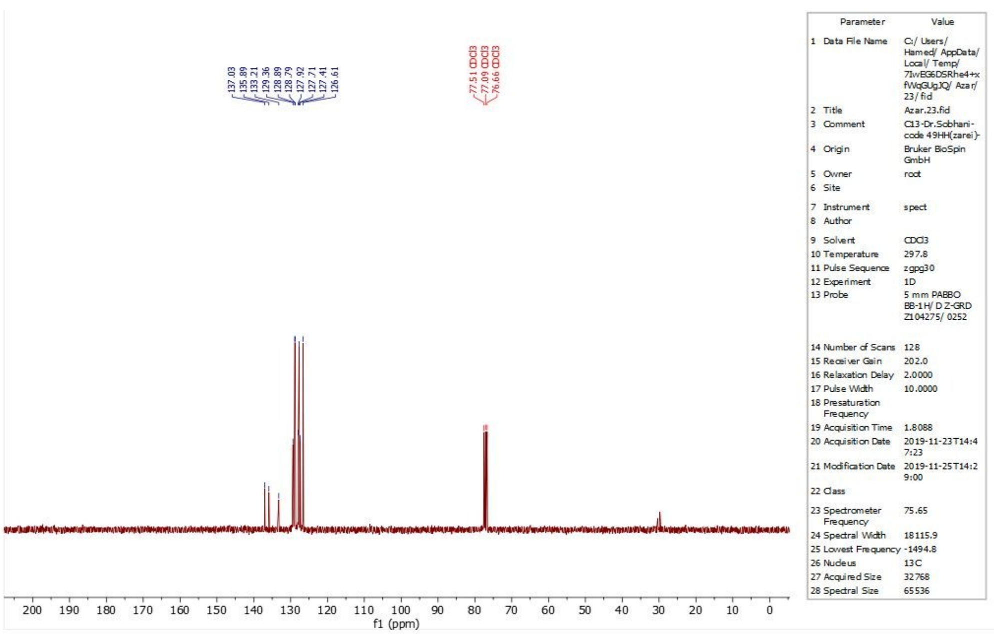




^{1}H NMR and ^{13}C NMR spectra of (E)-1-methoxy-4-styrylbenzene

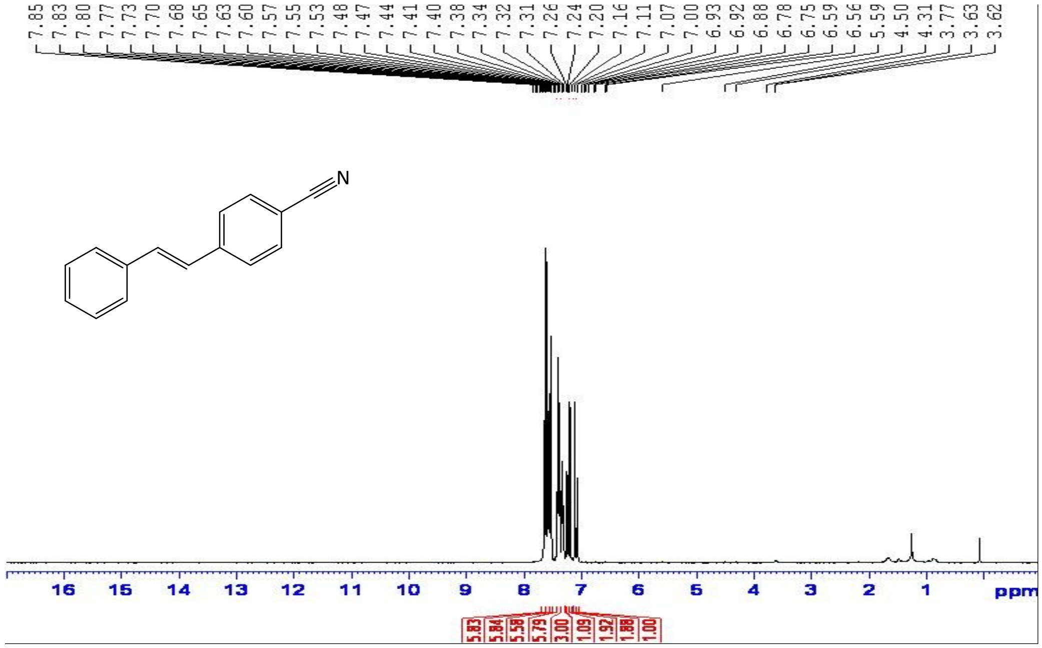
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.52 (m, 3H), 7.36 (t, 2H, ^{3}J = 7.6 Hz), 7.09 (d, 2H, ^{3}J = 16.0 Hz), 6.99 (d, 2H, ^{3}J = 16.4 Hz), 6.92 (d, 2H, ^{3}J = 8.4 Hz), 3.89 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), δ 159.3, 137.7, 130.1, 128.7, 128.2, 127.8, 127.2, 126.6, 126.3, 114.1, 55.3 ppm.

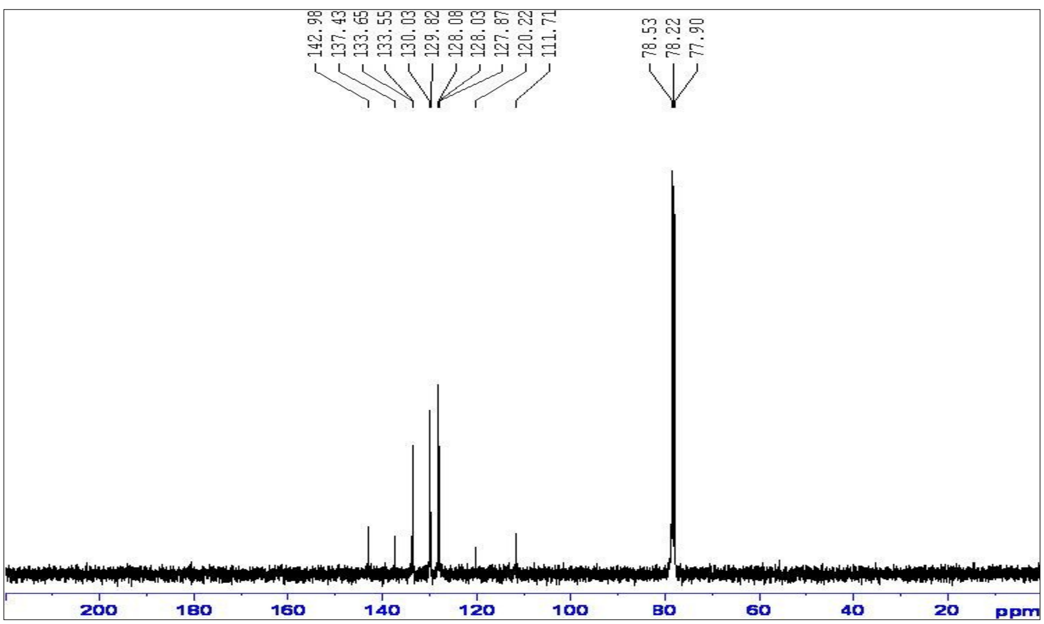




^{1}H NMR and ^{13}C NMR spectra of (E)-1-chloro-4-styrylbenzene

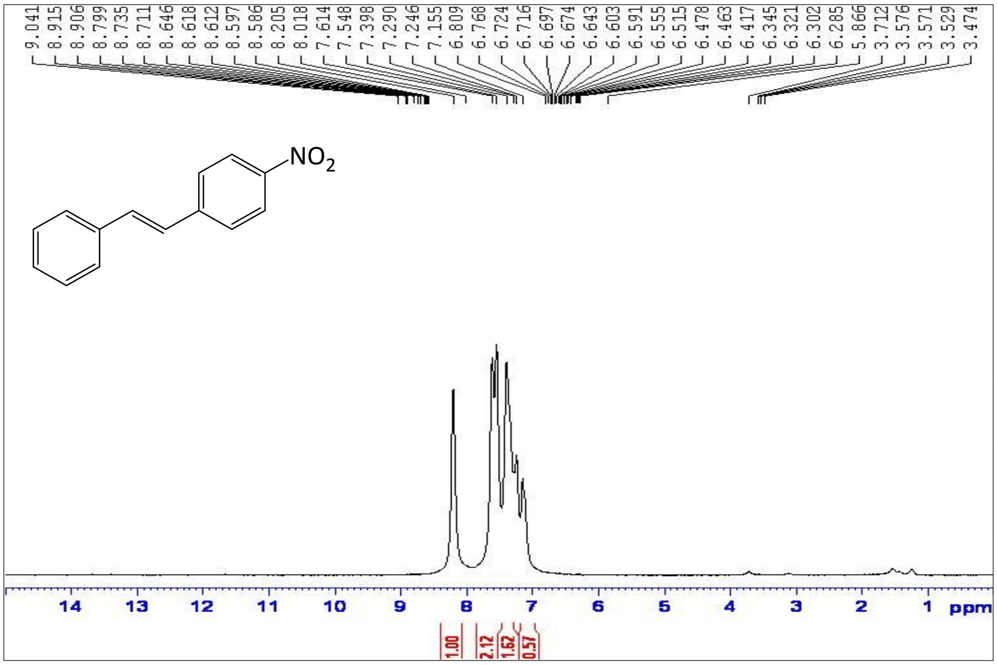
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.52 (m, 2H), 7.43-7.46 (m, 2H), 7.28-7.39 (m, 5H), 7.07 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$), δ 137.0, 135.8, 133.2, 129.3, 128.8, 128.7, 127.9, 127.7, 127.4, 126.6 ppm.

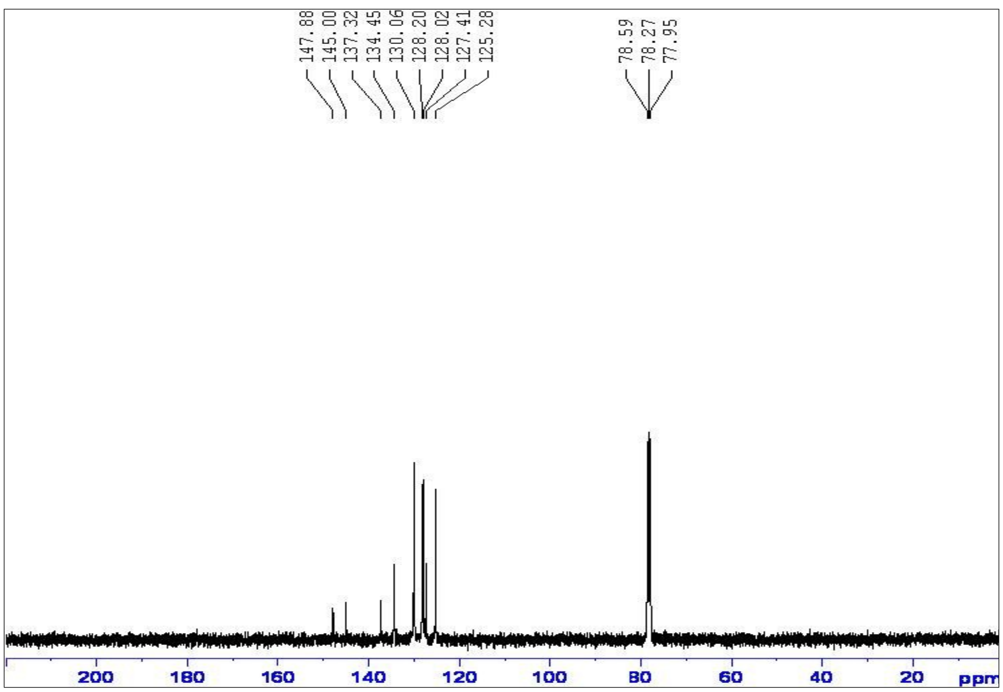




^{1}H NMR and ^{13}C NMR spectra of (E)-4-styrylbenzonitrile

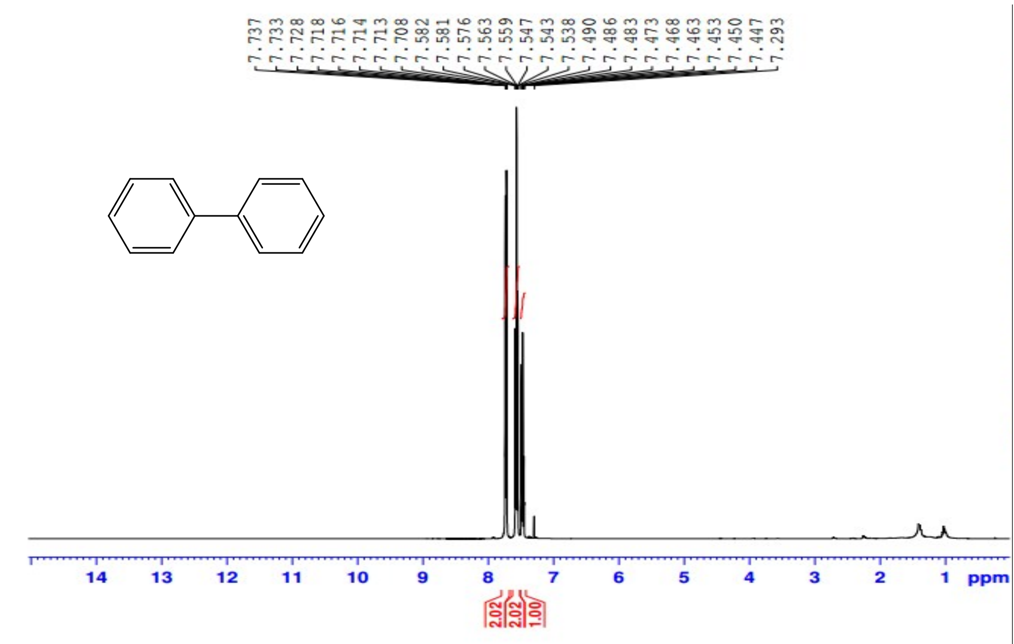
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, 2H, ^{3}J = 8.4 Hz), 7.58 (d, 2H, ^{3}J = 8.4 Hz), 7.54 (d, 2H, ^{3}J = 7.2 Hz), 7.38-7.41 (t, 2H, ^{3}J = 4.0 Hz), 7.31-7.34 (t, 1H, ^{3}J = 4.0 Hz), 7.22 (d, 1H, ^{3}J = 16.0 Hz), 7.09 (d, 1H, ^{3}J = 16.0 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), δ 142.9, 137.4, 133.6, 133.5, 130.0, 129.8, 128.1, 128.0, 127.8, 120.2, 111.7 ppm.

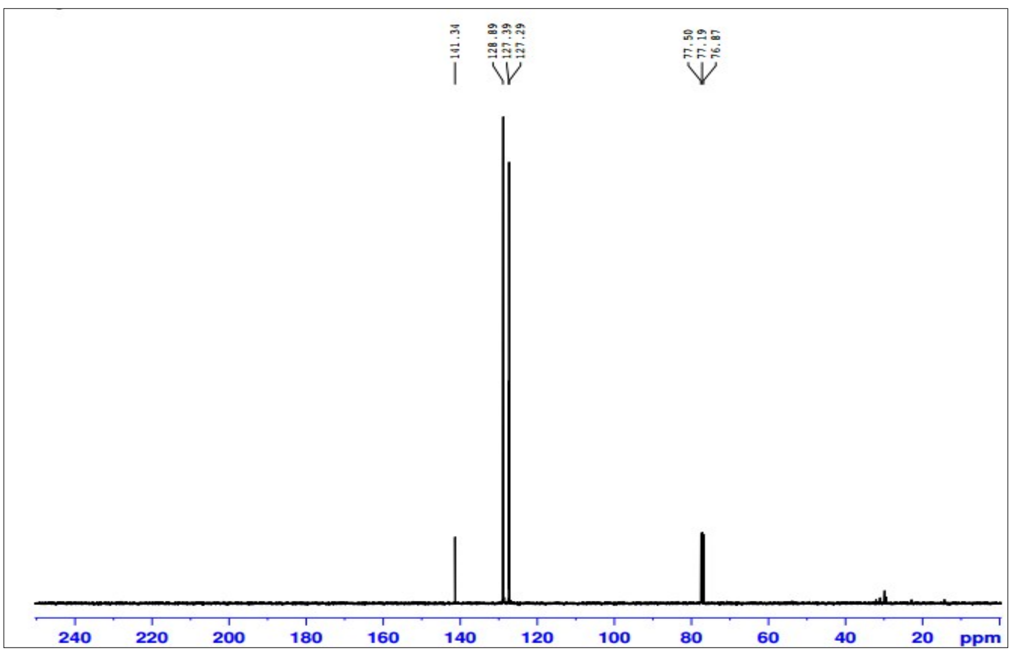




^1H NMR and ^{13}C NMR spectra of (E)-1-nitro-4-styrylbenzene

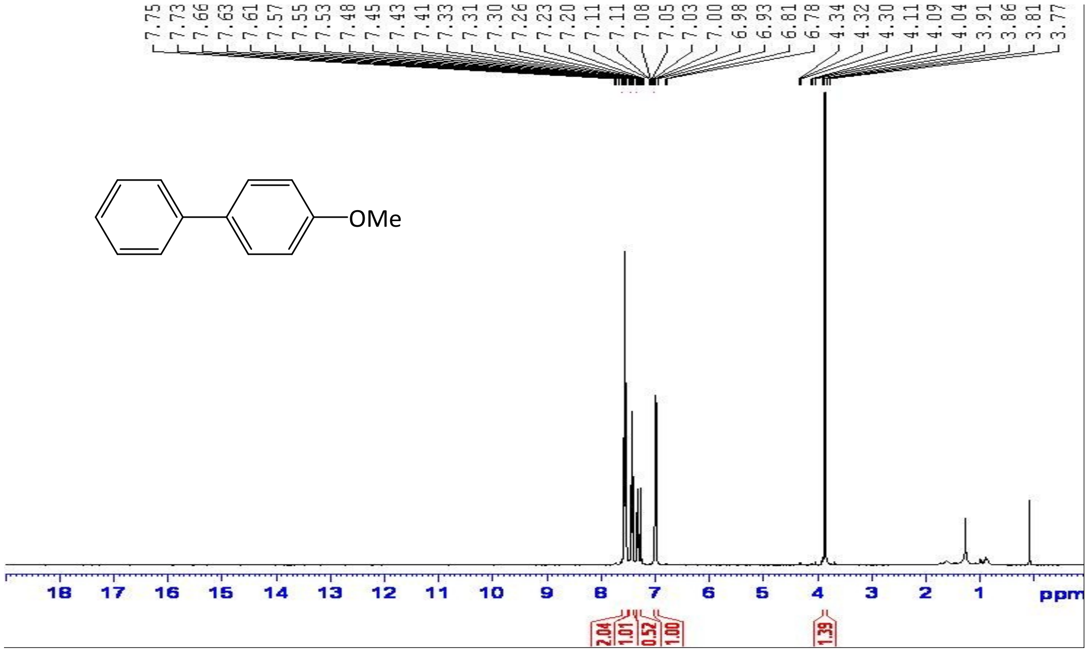
^1H NMR (400 MHz, $CDCl_3$): δ 8.15-8.26 (m, 2H), 7.49-766 (m, 4H), 7.40-7.45 (m, 4H), 7.06-7.18 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), δ 147.8, 145.0, 137.3, 134.4, 130.0, 128.2, 128.0, 127.4, 125.2 ppm.

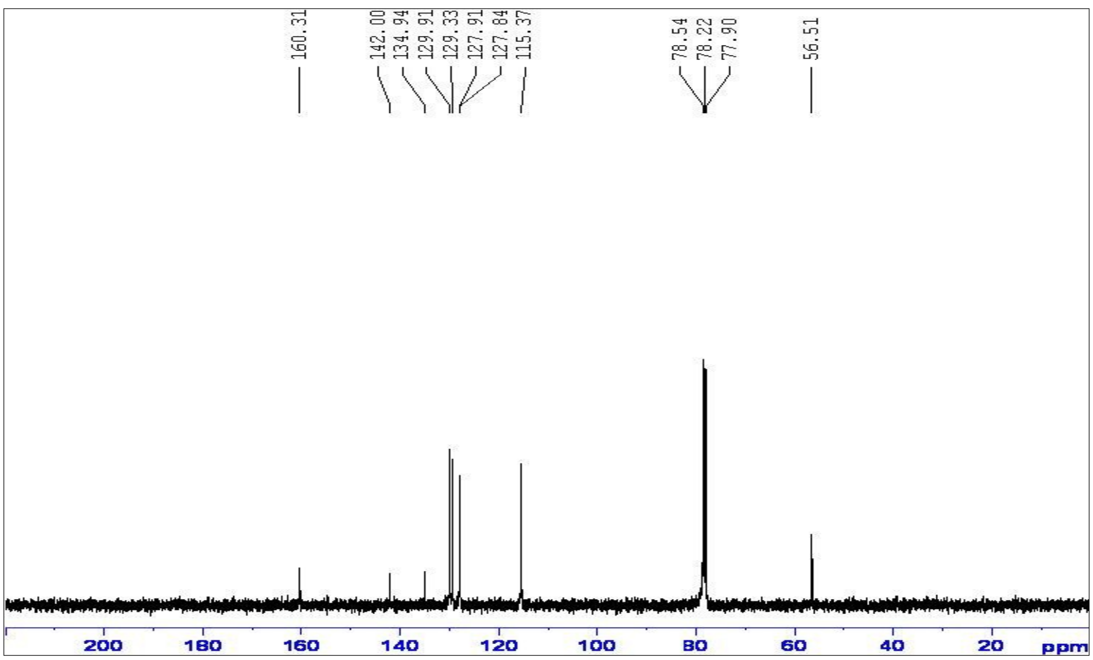




^{1}H NMR and ^{13}C NMR spectra of biphenyl

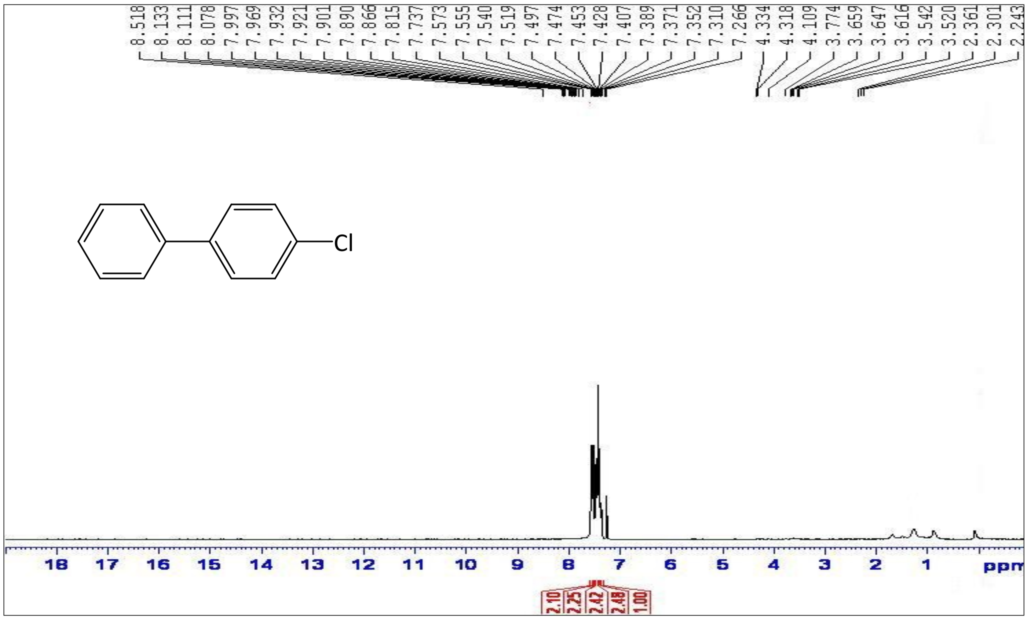
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, 4H, ^3J = 6.8 Hz), 7.56 (t, 4H, ^3J = 8.0 Hz), 7.46 (t, 2H, ^3J = 7.2 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), δ 141.3, 128.8, 127.3, 127.2 ppm (Table 2, entries 1, 5, 11).

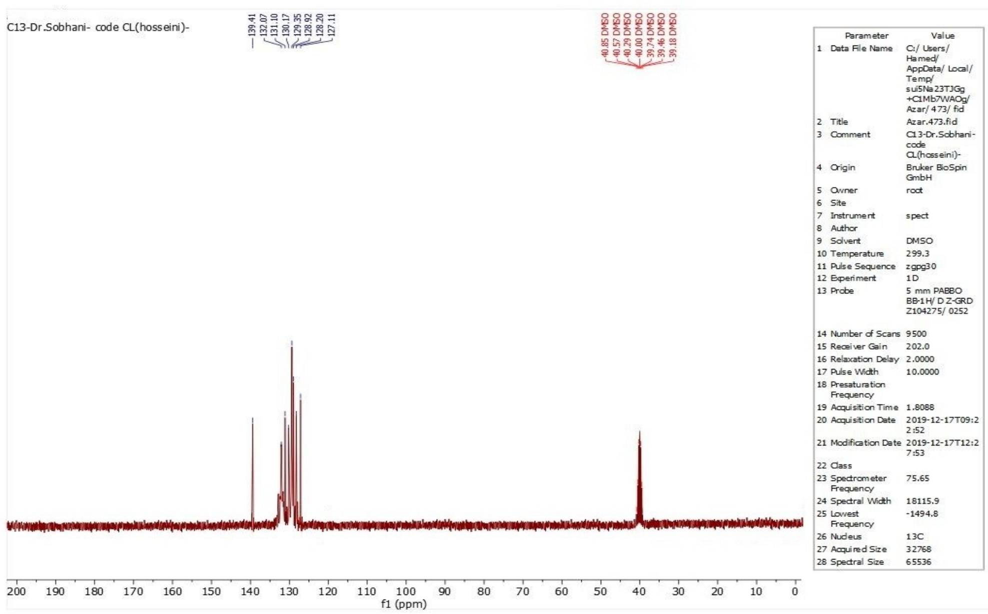




^{1}H NMR and ^{13}C NMR spectra of 4-methoxybiphenyl

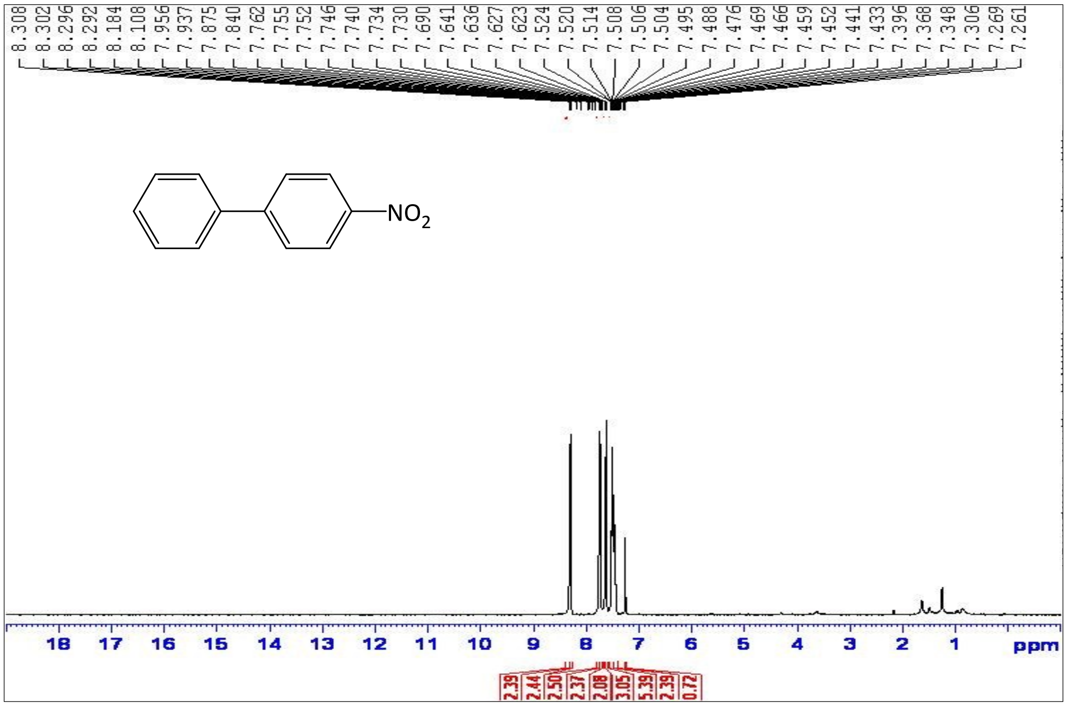
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (t, 4H, ^{3}J = 8.8 Hz), 7.43 (t, 2H, ^{3}J = 8.0 Hz), 7.31 (t, 1H, ^{3}J = 7.2 Hz), 6.99 (d, 2H, ^{3}J = 8.8 Hz), 3.83 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), δ 160.3, 142.0, 134.9, 129.9, 129.3, 127.9, 127.8, 115.3, 56.5 ppm (Table 2, entries 2, 7).

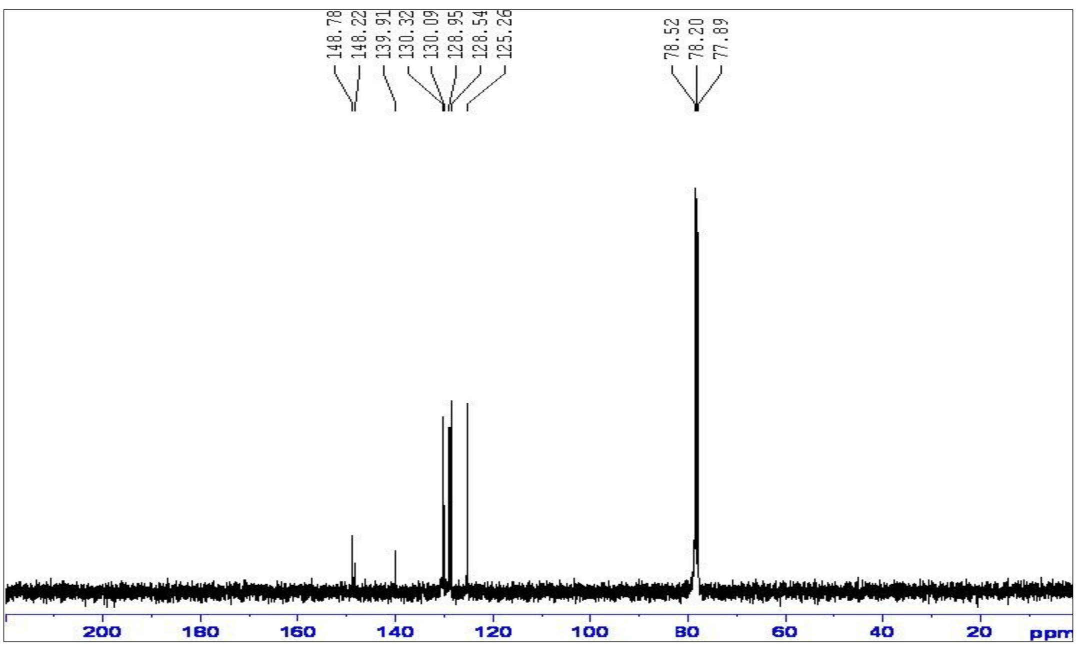




^{1}H NMR and ^{13}C NMR spectra of 4-chlorobiphenyl

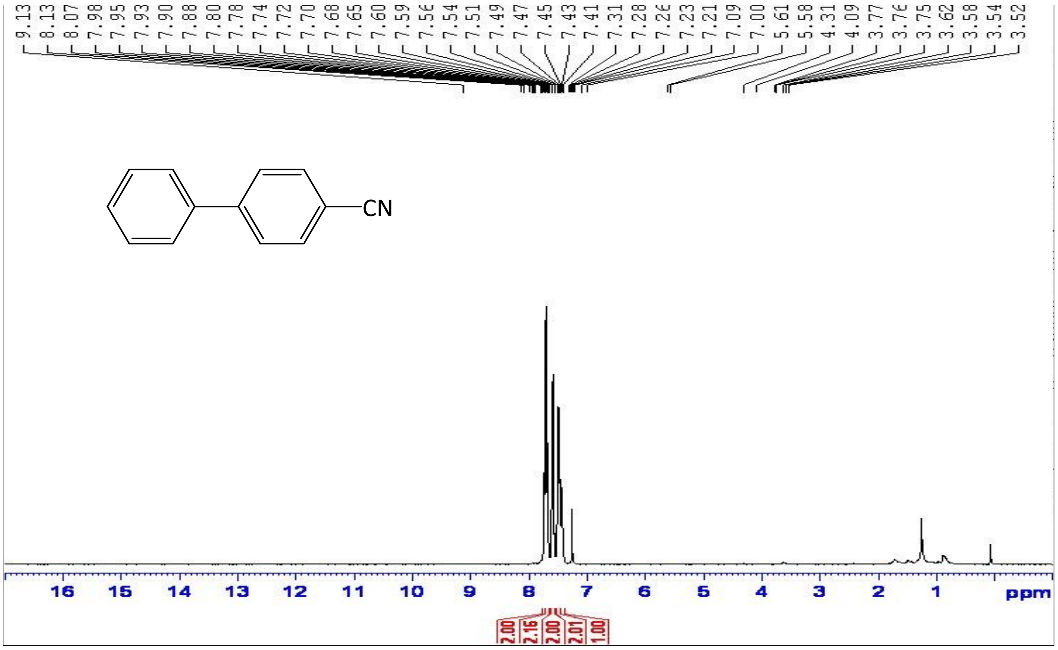
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.57 (m, 4H), 7.31-7.49 (m, 5H), ppm. ^{13}C NMR (75 MHz,DMSO-d_6), δ 139.4, 132.0, 131.1, 130.1, 129.3, 128.9, 128.2, 127.1 ppm (Table 2, entries 3, 10).

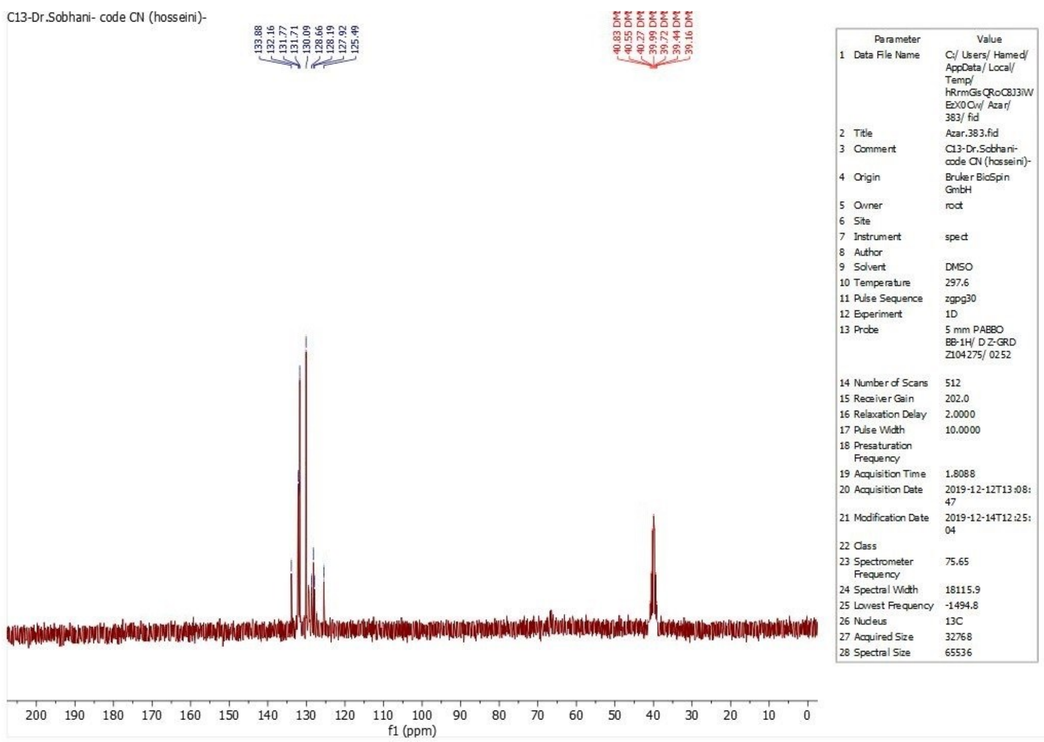




^{1}H NMR and ^{13}C NMR spectra of 4-nitrobiphenyl

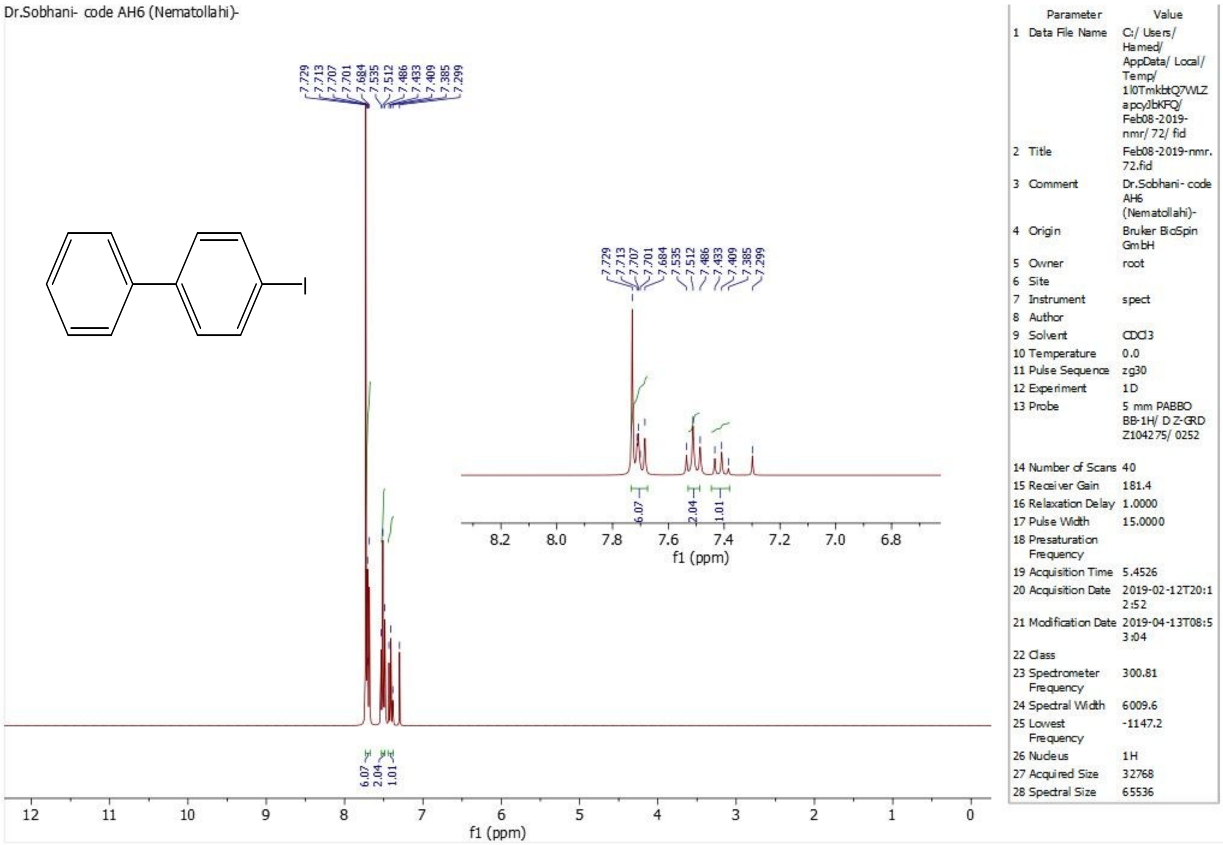
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29-8.30 (m, 2H), 7.73-7.76 (m, 2H), 7.62-7.64 (m, 2H), 7.43-7.52 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), δ 148.7, 148.2, 139.9, 130.3, 130.0, 128.9, 128.5, 125.2 ppm (Table 2, entries 8, 13).





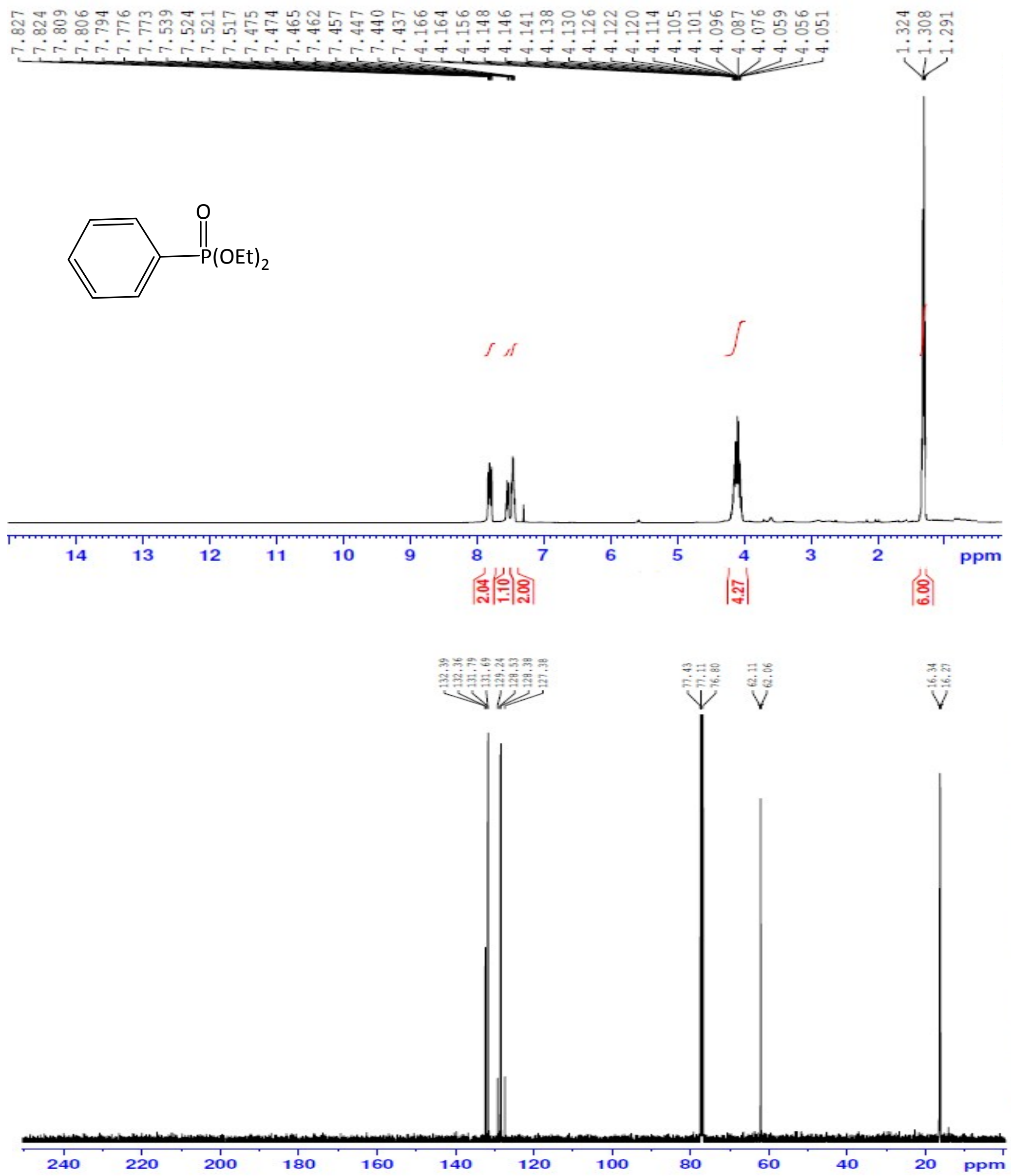
^{1}H NMR and ^{13}C NMR spectra of 4-cyanobiphenyl

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68-7.74 (m, 4H), 7.56-7.60 (m, 2H), 7.41-7.51 (m, 3H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6), δ 133.8, 132.1, 131.7, 131.7, 130.0, 128.6, 128.1, 127.9, 125.4 ppm (Table 2, entries 9, 14).



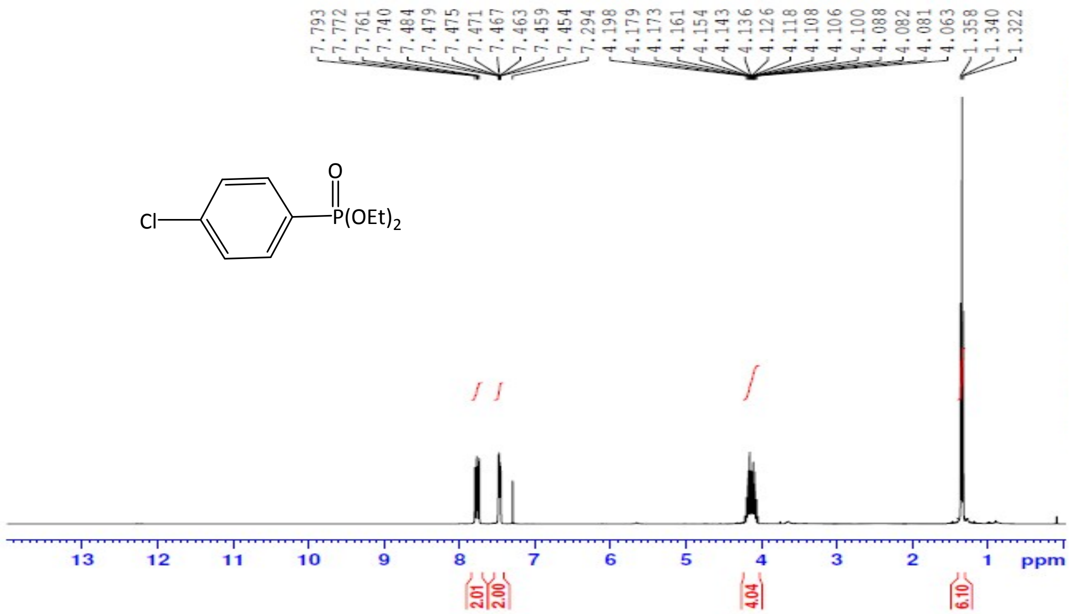
^{1}HNMR spectrum of 4-iodo-1,1'-biphenyl

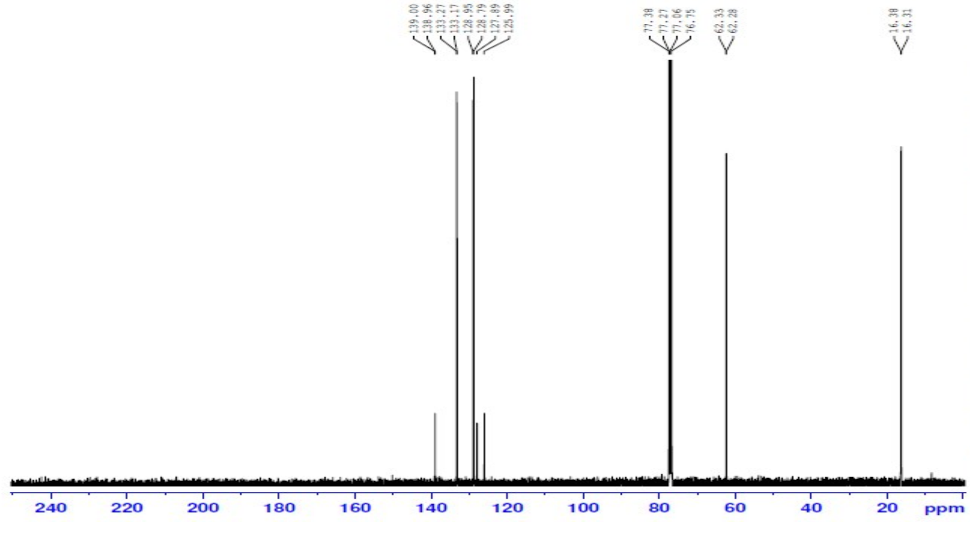
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67-7.73 (m, 6H), 7.51 (t, 2H, ^3J = 7.8 Hz), 7.40 (t, 1H, ^3J = 7.2 Hz) ppm (Table 2 entry 4).



^{1}H NMR and ^{13}C NMR spectra of diethylphenylphosphonate

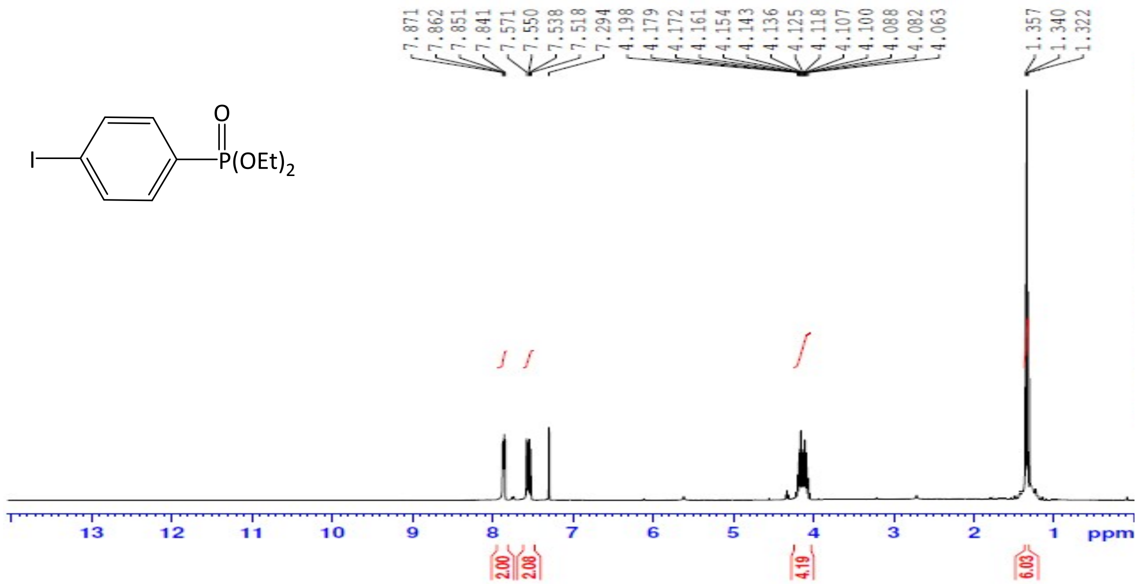
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (dd, 2H, J = 13.2, $J_{H,H}$ = 8.4), 7.53-7.51 (m, 1H), 7.47-7.42 (m, 2H), 4.16-4.05 (m, 4H), 1.30 (t, 6H, $J_{H,H}$ = 6.8 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.3 (d, J_{CP} = 3.0 Hz), 131.7 (d, J_{CP} = 10.0 Hz), 128.4 (d, J_{CP} = 15.0 Hz), 128.3 (d, J_{CP} = 186.0 Hz), 62.0 (d, J_{CP} = 5.0 Hz), 16.3 (d, J_{CP} = 7.0 Hz) ppm (Table 8, entries 1, 4, 10).

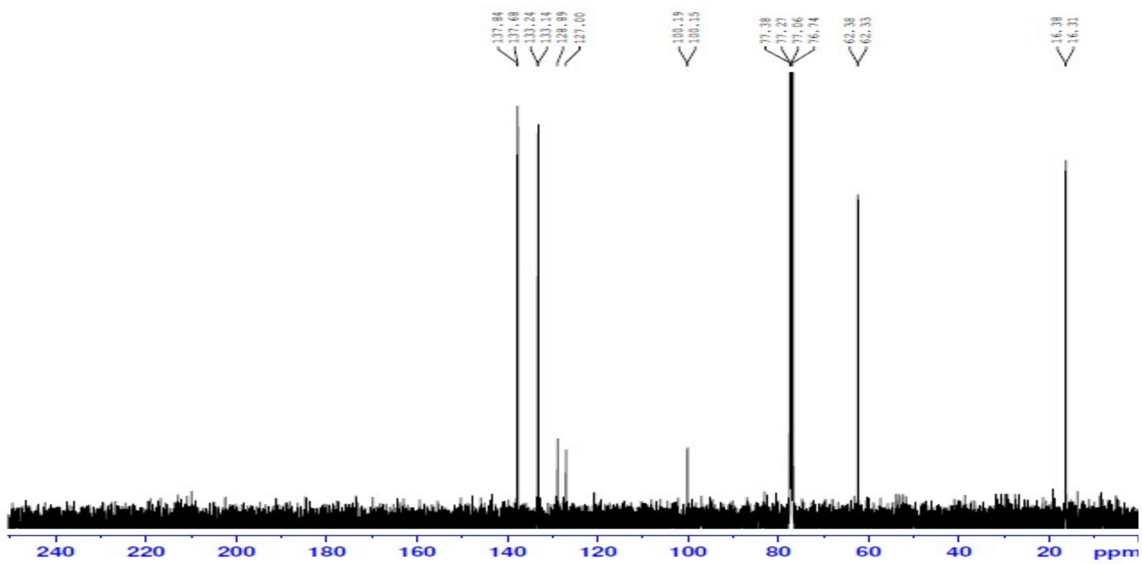




^{1}H NMR and ^{13}C NMR spectra of diethyl 4-chlorophenylphosphonate

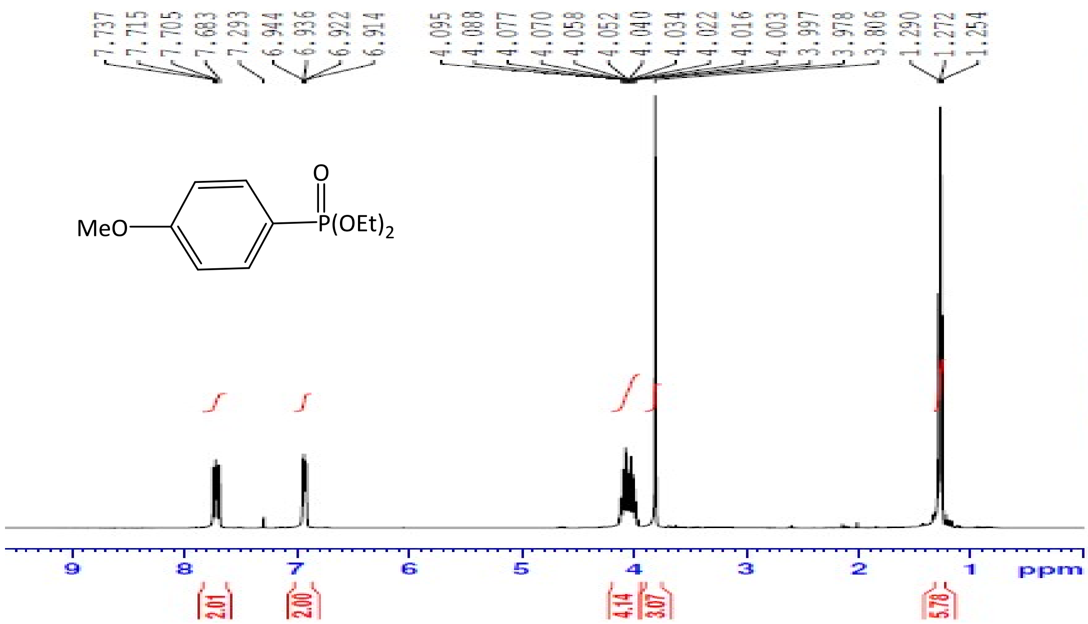
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (dd, 2H, J_{HH} = 12.8 Hz, J_{HH} = 8.4 Hz), 7.46 (dd, 2H, J_{HH} = 8.2 Hz, J_{HH} = 3.6 Hz), 4.19-4.06 (m, 4H), 1.34 (t, 6H, J_{HH} = 7.2 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9 (d, J_{CP} = 4.0 Hz), 133.2 (d, J_{CP} = 10.0 Hz), 128.8 (d, J_{CP} = 16.0 Hz), 126.9 (d, J_{CP} = 190.0 Hz), 62.2 (d, J_{CP} = 5.0 Hz), 16.3 (d, J_{CP} = 7.0 Hz) ppm (Table 8, entry 2).

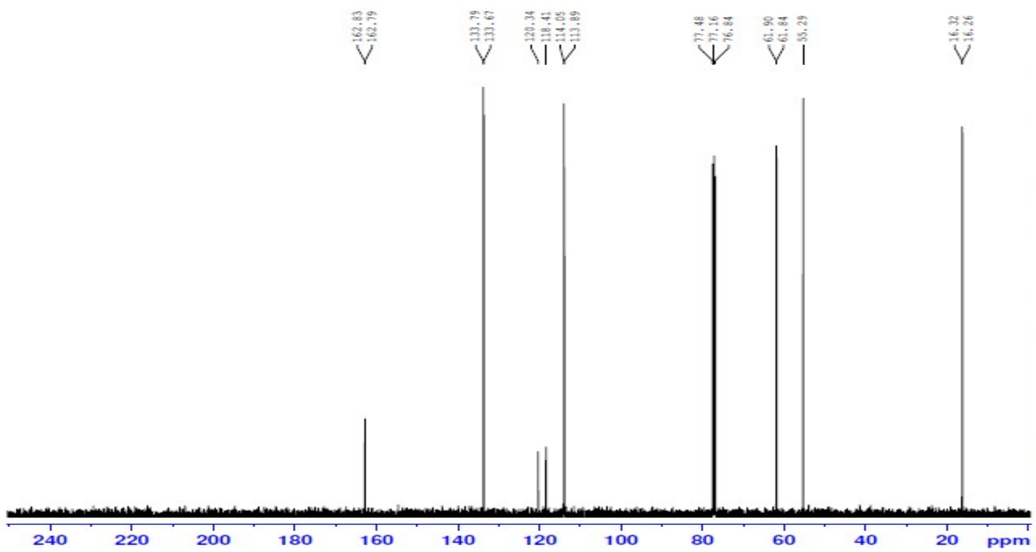




^{1}H NMR and ^{13}C NMR spectra of diethyl 4-iodophenylphosphonate

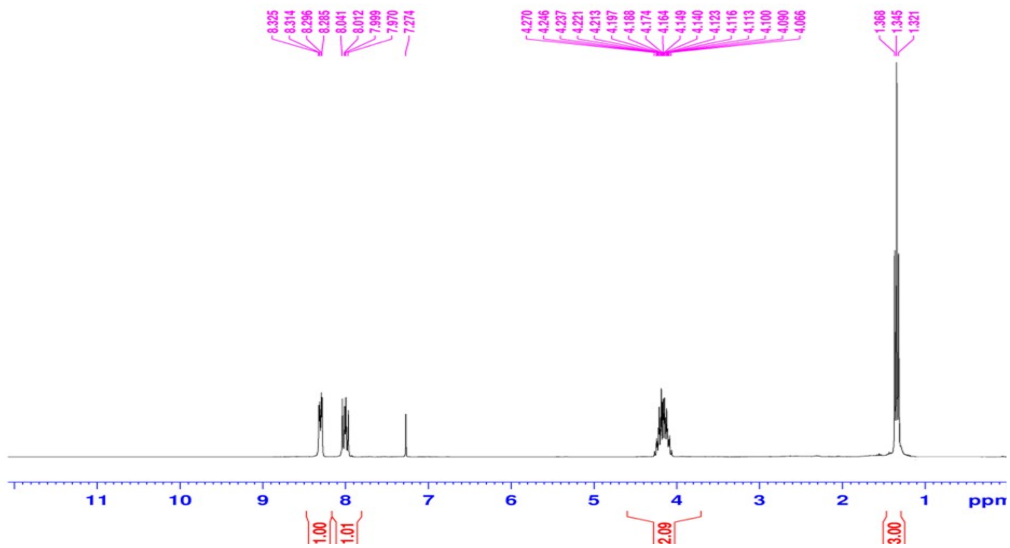
^{1}HNMR (400 MHz, $CDCl_3$): δ 7.85 (dd, 2H, J_{HH} = 8.2 Hz, J_{HH} = 3.6 Hz), 7.54 (dd, 2H, J_{HH} = 13 Hz, J_{HH} = 8.0 Hz), 4.19-4.06 (m, 4H), 1.34 (t, 6H, J_{HH} = 6.8 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7 (d, J_{CP} = 16.0 Hz), 133.1 (d, J_{CP} = 10.0 Hz), 127.4 (d, J_{CP} = 189.0 Hz), 100.1 (d, J_{CP} = 4.0 Hz), 62.3 (d, J_{CP} = 5.0 Hz), 16.3 (d, J_{CP} = 7.0 Hz) ppm (Table 8 entry 3).

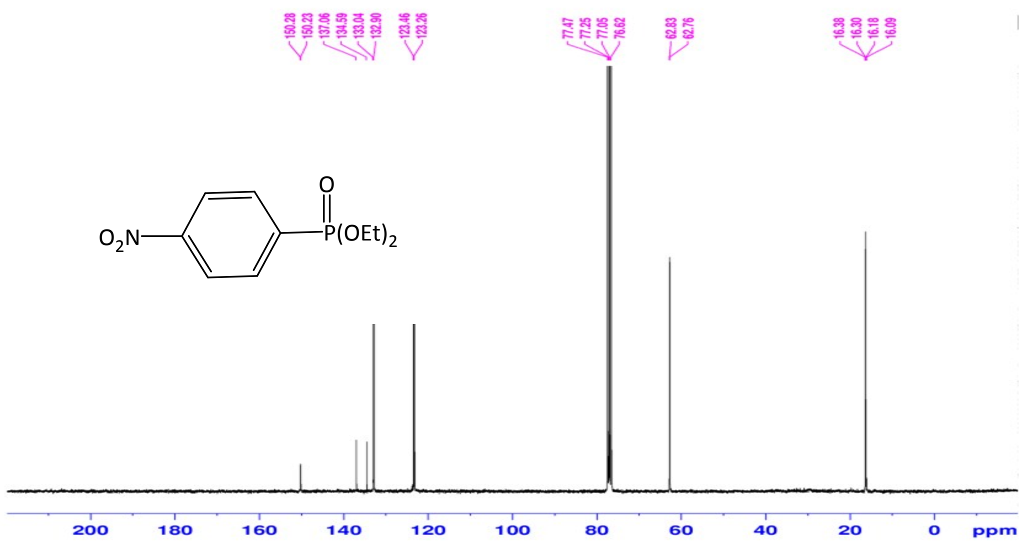




^{1}H NMR and ^{13}C NMR spectra of diethyl 4-methoxyphenylphosphonate

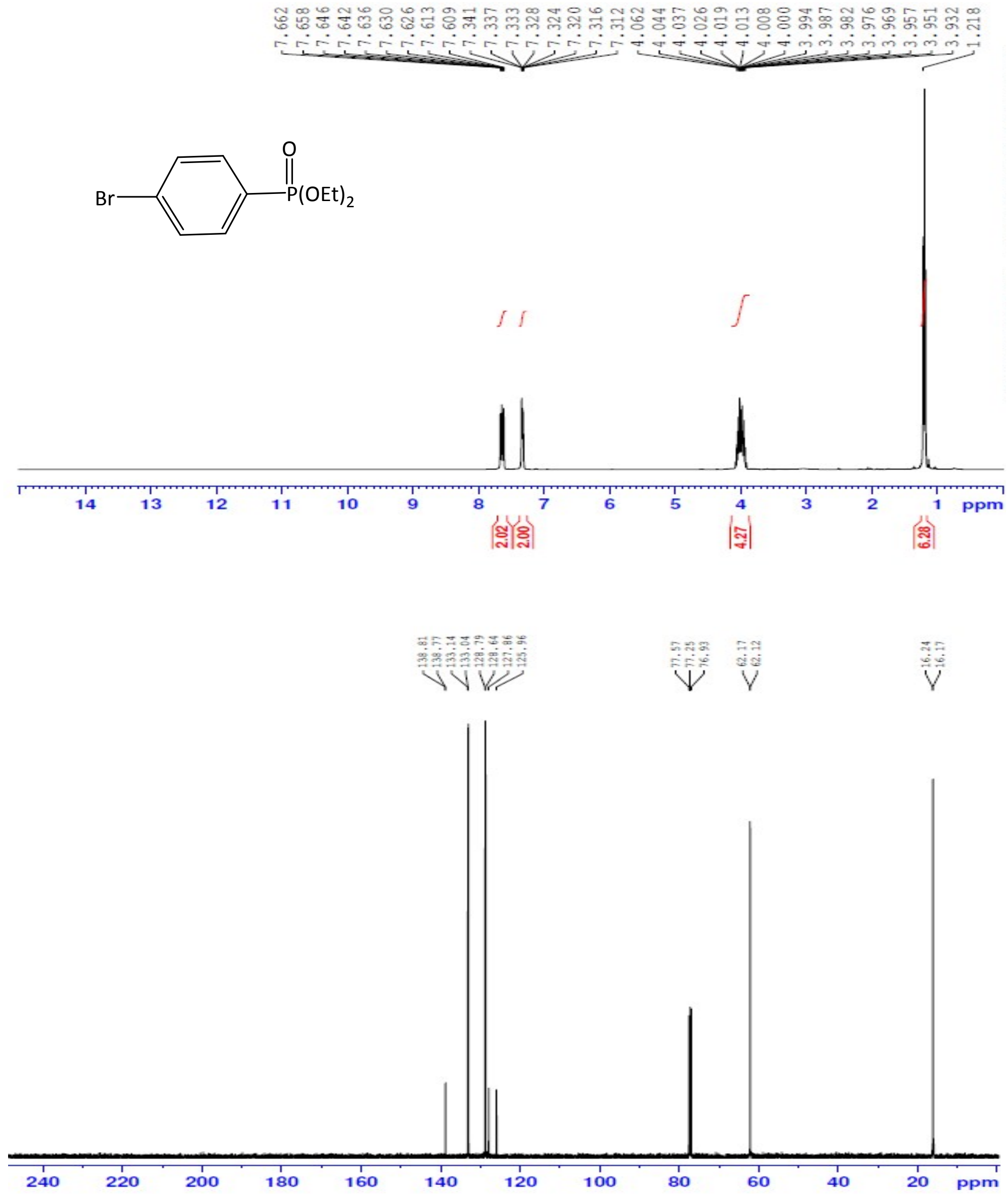
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.30 (dd, 1H, J_{HH} = 8.7 Hz, J_{HH} = 3.3 Hz), 8.00 (dd, 1H, J_{HH} = 12.7 Hz, J_{HH} = 8.7 Hz), 4.27-4.06 (m, 4H), 1.34 (t, 6H, J_{HH} = 6.9 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.2 (d, J_{CP} = 3.7 Hz), 135.8 (d, J_{CP} =185.2 Hz), 133.0 (d, J_{CP} = 10.5 Hz), 123.3 (d, J_{CP} = 15.0 Hz), 62.7 (d, J_{CP} = 5.2 Hz), 16.3 (d, J_{CP} = 6.0 Hz), 16.1 (d, J_{CP} = 6.7 Hz) ppm (Table 8, entry 5).





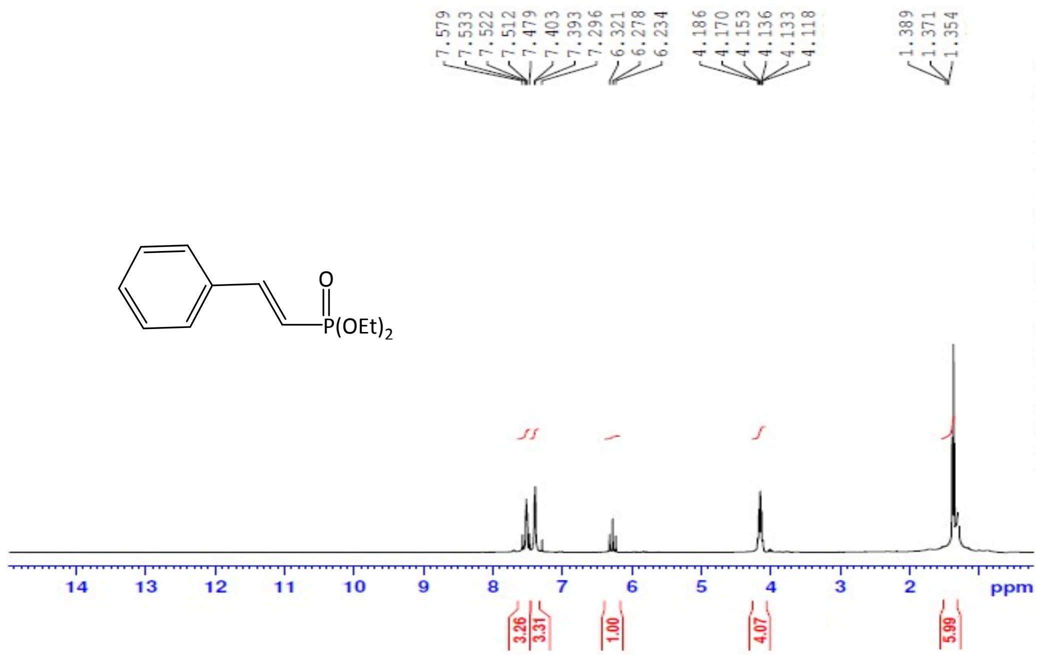
^{1}H NMR and ^{13}C NMR spectra of diethyl (4-nitrophenyl)phosphonate

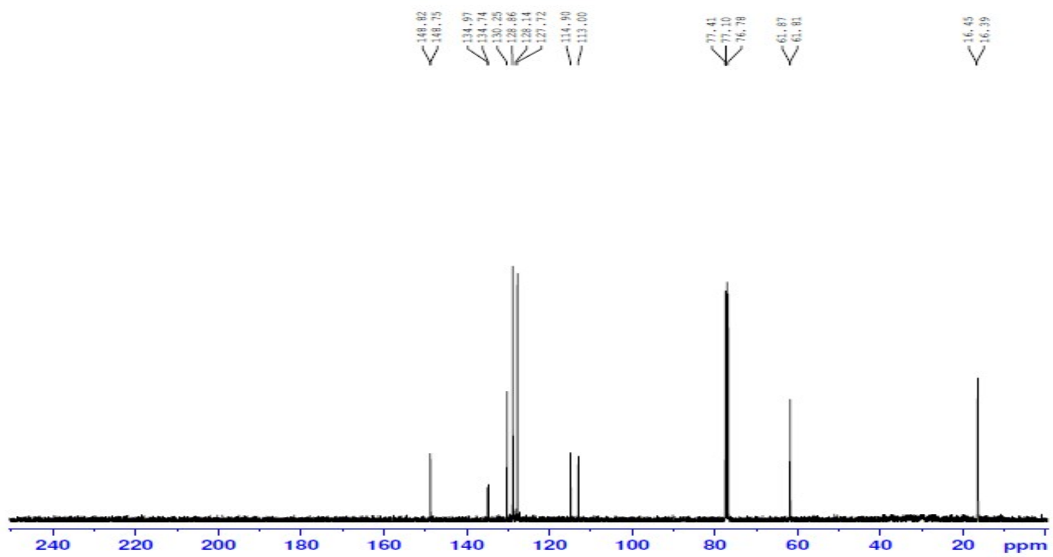
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.30 (dd, 1H, J_{HH} = 8.7 Hz, J_{HH} = 3.3 Hz), 8.00 (dd, 1H, J_{HH} = 12.7 Hz, J_{HH} = 8.7 Hz), 4.27-4.06 (m, 4H), 1.34 (t, 6H, J_{HH} = 6.9 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.2 (d, J_{CP} = 3.7 Hz), 135.8 (d, J_{CP} =185.2 Hz), 133.0 (d, J_{CP} = 10.5 Hz), 123.3 (d, J_{CP} = 15.0 Hz), 62.7 (d, J_{CP} = 5.2 Hz), 16.3 (d, J_{CP} = 6.0 Hz), 16.1 (d, J_{CP} = 6.7 Hz) ppm (Table 8, entries 6, 11).



^{1}H NMR and ^{13}C NMR spectra of diethyl 4-bromophenylphosphonate

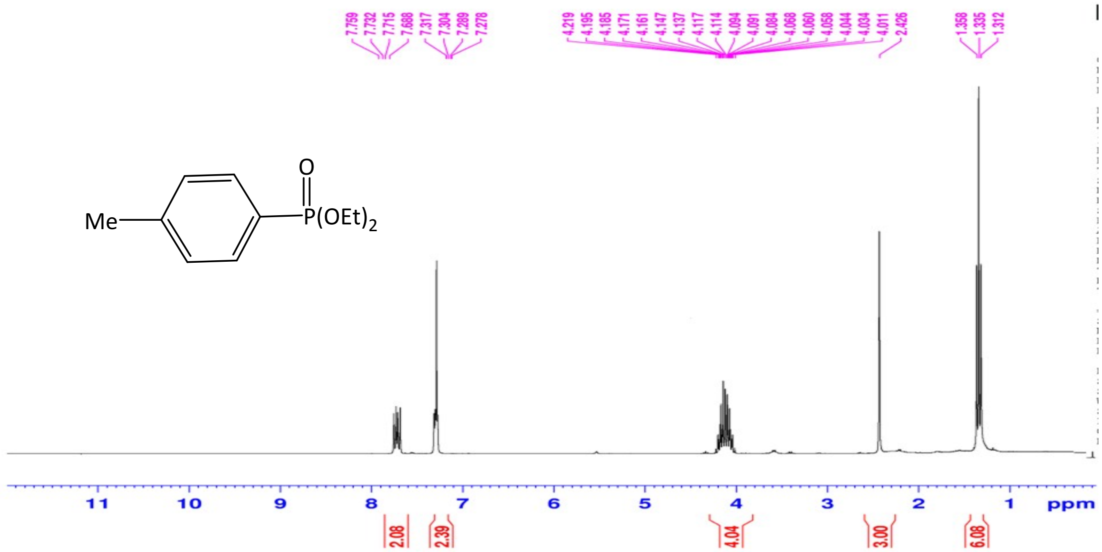
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (dd, 2H, J_{HH} = 13.2 Hz, J_{HH} = 8.4 Hz), 7.32 (dd, 2H, J_{HH} = 8.4 Hz, J_{HH} = 3.2 Hz), 4.06-3.93 (m, 4H), 1.20 (t, 6H, J_{HH} = 7.2 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7 (d, J_{CP} = 4.0 Hz), 133.0 (d, J_{CP} = 10.0 Hz), 128.7 (d, J_{CP} = 15.0 Hz), 126.9 (d, J_{CP} = 190.0 Hz), 62.1 (d, J_{CP} = 5.0 Hz), 16.2 (d, J_{CP} = 7.0 Hz) ppm (Table 8, entry 8).

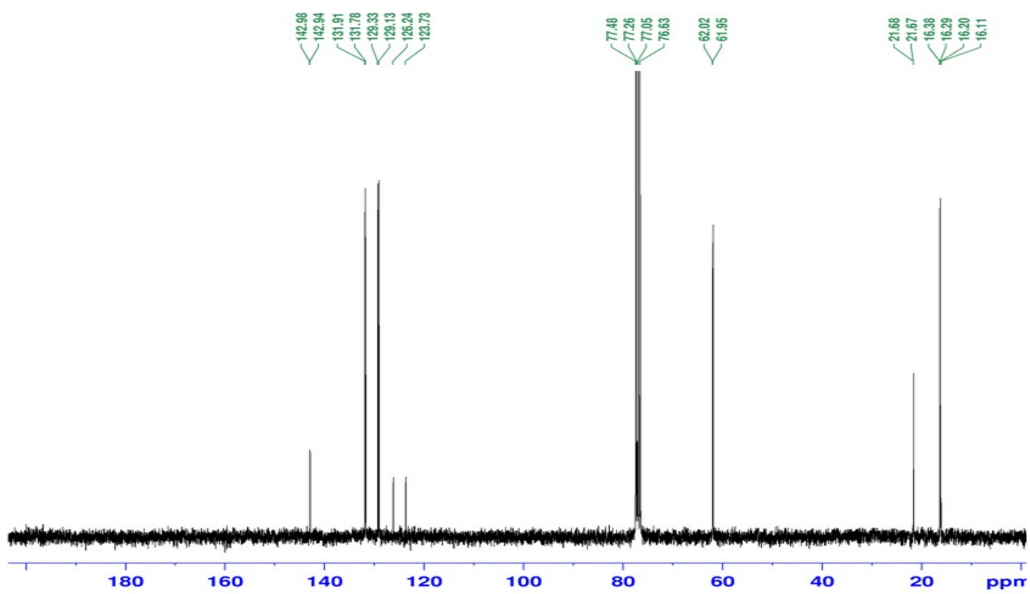




^{1}H NMR and ^{13}C NMR spectra of diethyl 2-phenylvinylphosphonate

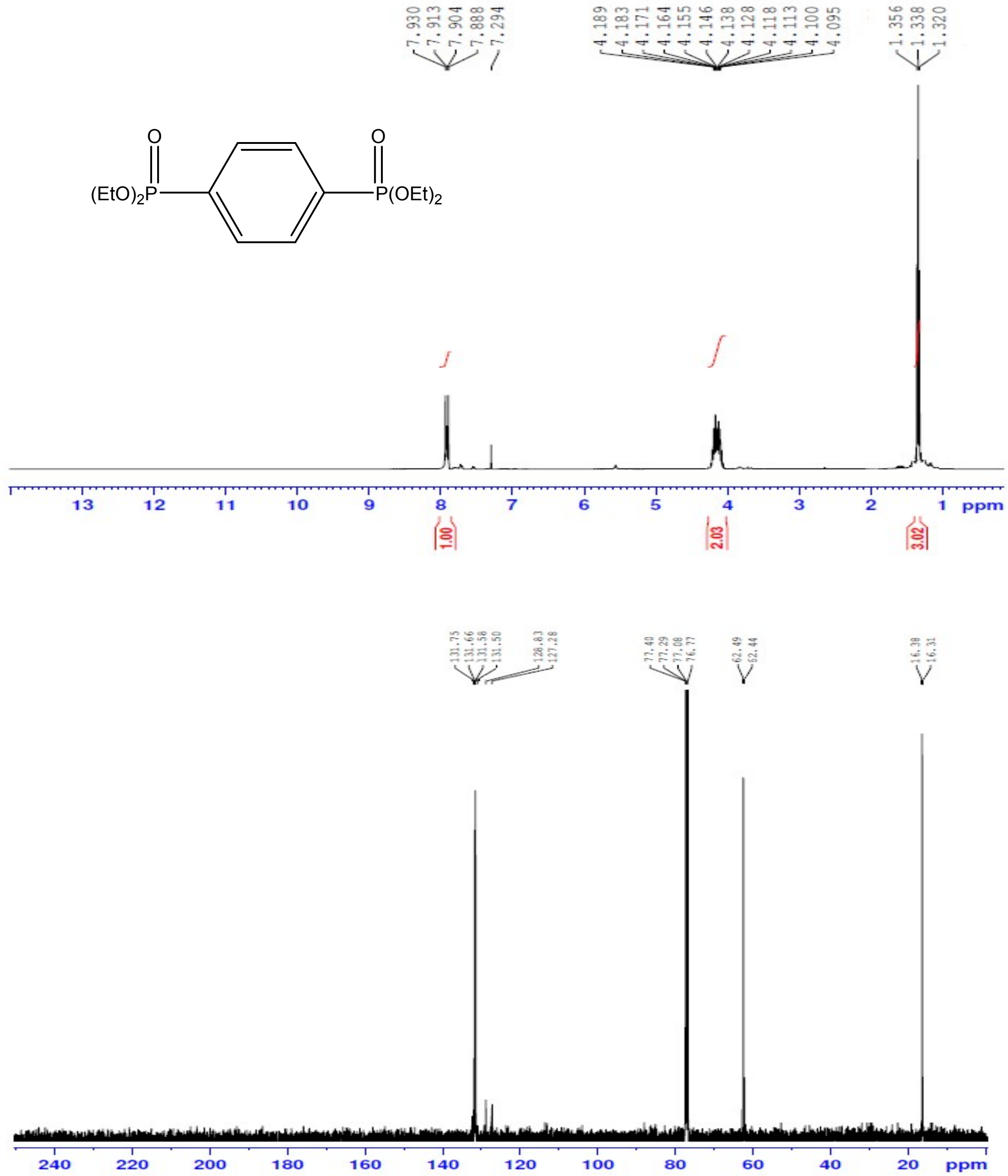
^{1}HNMR (400 MHz, $CDCl_3$): δ 7.57-7.39 (m, 6H), 6.3 (t, 1H, J_{HH} = J_{HP} = 17.6), 4.18-4.11 (m, 4H), 1.37 (t, 6H, J_{HH}= 6.8 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7 (d, J_{CP} = 7.0 Hz), 134.9, 134.7, 130.2, 128.8, 128.1, 127.7, 113.8 (d, J_{CP} = 190.0 Hz), 61.8 (d, J_{CP} = 6.0 Hz), 16.4 (d, J_{CP} = 6.0 Hz) ppm (Table 8, entry 9).





[1]H NMR and [13]C NMR spectra of diethyl 4-tolylphosphonate

[1]H NMR (300 MHz, $CDCl_3$): δ 7.72 (dd, 2H, J_{HH} = 13.2 Hz, J_{HH} = 8.1 Hz), 7.29 (dd, 2H, J_{HH} = 8.1 Hz, J_{HH} = 3.3 Hz), 4.21-4.01 (m, 4H), 2.42 (s, 3H), 1.33 (t, , 6H, J_{HH} = 6.9 Hz) ppm.[13]C NMR (75 MHz, $CDCl_3$): δ 142.9 (d, J_{CP} = 3.0 Hz), 131.8 (d, J_{CP} = 9.7 Hz), 129.2 (d, J_{CP} = 15.0 Hz), 124.9 (d, J_{CP} = 188.2 Hz), 61.9 (d, J_{CP} = 5.2 Hz), 21.6, 16.3 (d, J_{CP} = 6.7 Hz), 16.1 (d, J_{CP} = 6.7 Hz) ppm (Table 8, entry 7).



^{1}H NMR and ^{13}C NMR spectra of tetraethylphenylbis(phosphonate)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (dd, 4H, J_{HH} = 10.2 Hz, J_{HH} = 6.8 Hz), 4.18 - 4.09 (m, 8H), 1.33 (t, 12H, J_{HH} = 7.2 Hz), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.6 (dd, J_{CP} = 16.5 Hz, J_{CP} = 8.0 Hz), 128.0 (d, J_{CP} = 155.0 Hz), 62.4 (d, J_{CP} = 5.0 Hz), 16.3 (d, J_{CP} = 7.0 Hz) ppm (Table 8, entries 13, 14).