Supporting Information

Water Mediated Heck and Ullmann Couplings by Supported Palladium Nanoparticles: Importance of Surface Polarity of the Carbon Spheres

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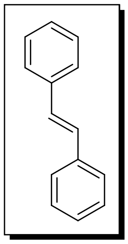
Characterization:

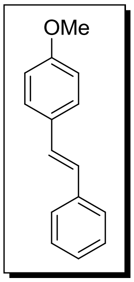
Transmission electron microscope (TEM) (Philips Tecnai G2 FEI F12, operating at 80–100 kV) was used to investigate morphology and size of the nanoparticles. The samples for TEM were prepared by dispersing the material in water and drop-drying onto a Formvar resin coated copper grid. XPS spectra were recorded on a KRATOS AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg Kα anode. For elemental analysis, a Perkin Elmer Analyst 300 atomic absorption spectrometer was used. Thermo gravimetric analysis was carried out with Mettler Toledo star TG analyzer under an N_2 atmosphere, with a heating rate of 10 ^{o}C min^{-1} from 25–1000 ^{o}C. Temperature programmed desorption of ammonia (TPD) was carried out on an Autochem 2910 instrument (Micromeritics, USA). ^{1}H NMR spectra were recorded on a Varian Gemini 200 MHz and Avance 300 MHz spectrometers. Chemical shifts (*δ*) are reported in parts per million (ppm) using TMS as an internal standard.

Spectral Data



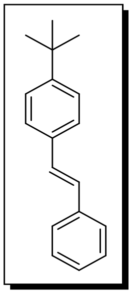
(*E*)-1,2-Diphenylethene.[1]

White crystalline solid, mp 122–124 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.04 (s, 2H), 7.16–7.21 (m, 2H), 7.29 (t, *J* = 7.55, 7.17 Hz, 4H), 7.46 (d, *J* = 7.17 Hz, 4H) ppm; ^{13}C NMR (50 MHz, CDCl$_3$): δ 126.4, 127.5, 128.5, 128.6, 137.2 ppm.



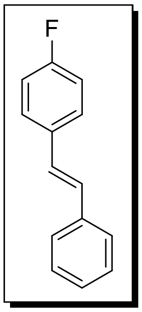
(*E*)-1-Methoxy-4-styrylbenzene.[1]

White crystalline solid, mp 131–134 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.81(s, 3H), 6.82 (d, *J* = 9.06 Hz, 2H), 6.88–7.04 (dd, *J* = 15.86, 16.61 Hz, 2H), 7.18 (t, *J* = 7.55, 6.79 Hz, 1H), 7.29 (t, *J* = 8.30, 6.79 Hz, 2H), 7.38–7.45 (m, 4H) ppm; ^{13}C NMR (50 MHz, CDCl$_3$): δ 55.2, 114.0, 126.2, 126.5, 127.1, 127.6, 128.1, 128.5, 130.0, 137.6, 159.2 ppm.



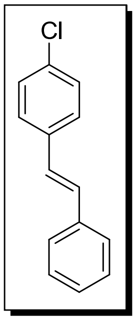
(*E*)-1-*tert*-Butyl-4-styrylbenzene.[2]

White crystalline solid, mp 94–96 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.33 (s, 9H), 7.02 (s, 2H), 7.16–7.23 (m, 1H), 7.27–7.33 (m, 4H), 7.39 (d, *J* = 8.30 Hz, 2H), 7.46 (d, *J* = 7.55 Hz, 2H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): δ 31.3, 34.5, 125.5, 126.1, 126.3, 127.3, 127.8, 128.4, 128.5, 134.5, 137.4, 150.7 ppm.



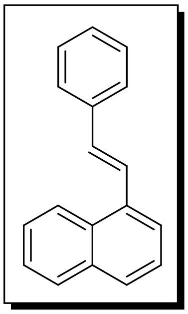
(*E*)-1-Fluoro-4-styrylbenzene.[3]

White crystalline solid, mp 120–121 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.92–7.0 (m, 4H), 7.19–7.23 (m, 1H), 7.30 (t, *J* = 7.80, 6.83 Hz, 2H), 7.42–7.44 (m, 4H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): δ 115.4, 115.7, 126.3, 127.4, 127.5, 127.8, 127.9, 128.4, 128.6, 133.4, 137.1, 160.6, 163.9 ppm.



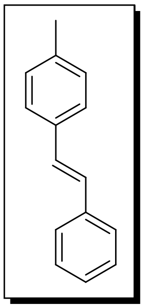
(*E*)-1-Chloro-4-styrylbenzene.[1]

White crystalline solid, mp 120–121 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.01 (s, 2H), 7.19–7.39 (m, 5H), 7.39–7.46 (m, 4H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 126.5, 127.3, 127.6, 127.8, 128.6, 128.9, 129.2, 133.1, 135.8, 136.9 ppm.



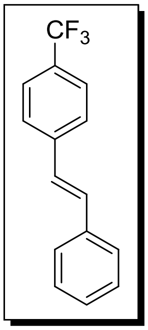
(*E*)-2-Styrylnaphthalene.[4]

White crystalline solid, mp 70–71 ^{o}C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.19–7.24 (m, 3H), 7.32 (t, *J* = 7.80, 7.80 Hz, 2H), 7.37–7.43 (m, 2H), 7.50 (d, *J* = 7.80 Hz, 2H), 7.68 (d, *J* = 8.78 Hz, 1H), 7.74–7.77 (m, 3H), 7.80 (s, 1H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): δ 123.4, 125.8, 126.2, 126.4, 126.5, 127.6, 127.9, 128.3, 128.6, 128.9, 132.9, 133.6, 134.7, 137.2 ppm.



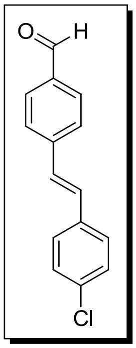
(*E*)-1-Methyl-4-styrylbenzene.[2]

White crystalline solid, mp 119–122 ^{o}C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.36 (s, 3H), 7.02 (s, 2H), 7.11 (d, *J* = 7.93 Hz, 2H), 7.16–7.24 (m, 1H), 7.29 (t, *J* = 7.74, 7.11 Hz, 2H), 7.34 (d, *J* = 8.12 Hz, 2H), 7.45 (d, *J* = 7.74 Hz, 2H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): δ 21.2, 126.3, 127.3, 127.6, 128.6, 129.3, 134.5, 137.4 ppm.



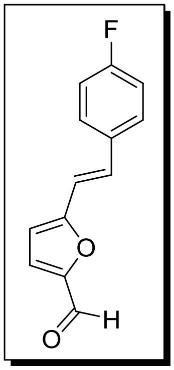
(*E*)-1-Styryl-4-(trifluoromethyl)benzene.[2]

White crystalline solid, mp 62–63 ^{o}C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.98 (d, *J* = 15.86 Hz, 1H) , 7.08 (d, *J* = 16.61 Hz, 1H), 7.17–7.21 (m, 1H), 7.22–7.27 (m, 2H), 7.30–7.35 (m, 3H), 7.47 (t, *J* = 7.55, 9.06 Hz, 3H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): δ 126.5, 127.3, 127.6, 127.8, 128.6, 128.7, 129.2, 133.1, 135.8, 136.9 ppm.



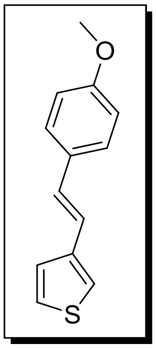
(*E*)-4-(4-Chlorostyryl)benzaldehyde.[5]

White crystalline solid, mp 129–131 ^{o}C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.07 (d, *J* = 16.2 Hz, 1H), 7.17 (d, *J* = 16.43 Hz, 1H), 7.31 (d, *J* = 8.49 Hz, 2H), 7.43 (d, *J* = 8.49 Hz, 2H), 7.63 (d, *J* = 8.12 Hz, 2H), 7.86 (d, *J* = 8.12 Hz, 2H), 9.97 (s, 1H) ppm, ^{13}C NMR (75 MHz, CDCl$_3$): δ 126.8, 127.8, 127.9, 128.9, 130.2, 130.7, 134.0, 134.9, 135.4, 142.9, 191.5 ppm.



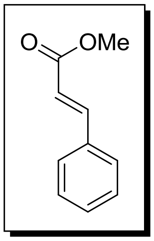
(*E*)-2-(4-Fluorostyryl)furan.

Pale red colour solid, mp 120–121 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.49 (d, *J* = 3.77 Hz, 1H), 6.81 (d, *J* = 16.24 Hz, 1H), 7.04 (t, *J* = 8.49, Hz, 2H), 7.20 (d, *J* = 3.58 Hz, 1H), 7.28 (d, *J* = 16.24 Hz, 1H), 7.46 (dd, *J* = 5.47, 8.49 Hz, 2H), 9.59 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 110.5, 114.7, 115.8, 116.1, 128.5, 128.6, 132.0, 158.3, 161.3, 164.6, 176.7 ppm; HRMS (ESI): m/z: calcd. for $C_{13}H_{10}O_2F$ 217.0664; found: 217.0674 $[M]^{+\cdot}$.



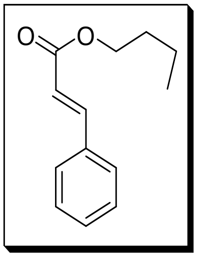
(*E*)-3-(4-Methoxystyryl)thiophene.[6]

Pale yellow solid, mp147–149 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.80 (s, 3H), 6.83 (dd, J = 14.16, 8.49 Hz, 4H), 7.14 (s, 1H), 7.24–7.28 (m, 2H), 7.33 (d, *J* = 8.68 Hz, 2H,) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.2, 114.06, 120.8, 121.4, 124.8, 125.9, 127.3, 128.2, 130.0, 140.3, 159.1 ppm.



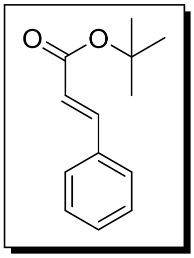
(*E*)-Methyl cinnamate.[7]

White liquid, ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.79 (s, 3H), 6.38 (d, *J* = 15.53 Hz, 1H), 7.34–7.37 (m, 3H), 7.49–7.50 (M, 2H), 7.65 (d, *J* = 16.45 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 51.5, 117.6, 127.9, 128.7, 130.1, 134.1, 144.6, 167.2 ppm.



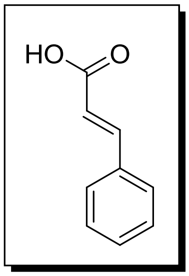
(*E*)-n-Butyl cinnamate.[7]

Yellow liquid, ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.98 (t, *J* = 7.36 Hz, 3H), 1.38–1.93 (m, 2H), 1.63–1.73 (m, 2H), 4.18 (t, *J* = 6.61 Hz, 2H), 6.39 (d, *J* = 15.86 Hz, 1H), 7.32–7.38 (m, *J* = 3H), 7.49 (dd, *J* = 4.15, 2.07, Hz, 2H), 7.60 (d, *J* = 16.05 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.5, 18.9, 30.5, 64.1, 118.0, 127.8, 128.6, 129.9, 134.2, 144.3, 166.8 ppm.



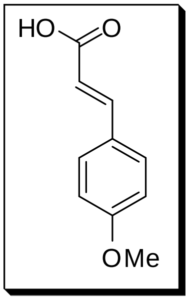
***tert*-Butyl cinnamate.[7]**

Yellow liquid, ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.52 (s, 9H), 6.32 (d, *J* = 15.86 Hz, 1H), 7.32–7.37 (m, 3H), 7.46–7.56 (m, 3H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): δ 28.1, 80.4, 120.1, 127.8, 128.7, 129.8, 134.5, 143.4, 166.2 ppm.



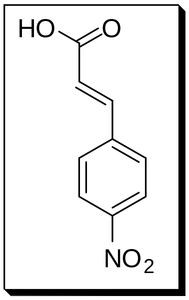
***trans*-Cinnamic acid.**[8]

White crystalline solid, mp118–120 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.43 (d, *J* = 15.86 Hz, 1H), 7.34–7.41 (m, 3H), 7.52–7.55 (m, 2H), 7.79 (d, *J* = 15.86 Hz, 1H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): δ 117.3, 128.3, 128.8, 130.6, 133.9, 147.0, 172.7 ppm.



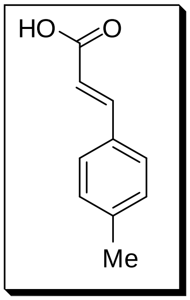
***(E)*-3-(4-methoxyphenyl)acrylic acid.**[8]

Pale brown crystalline solid, mp171–173 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.85 (s, 3H), 6.42 (d, *J* = 15.86 Hz, 1H), 6.99 (d, *J*= 7.62 Hz, 2H), 7.58 (d, *J*= 7.62 Hz, 2H), 7.82 (d, *J* = 15.86 Hz, 1H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): δ 55.2, 114.0, 117.2, 128.4, 130.2, 134.2, 147.0, 172.3 ppm.



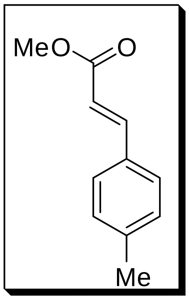
***(E)*-3-(4-nitrophenyl)acrylic acid.**[8]

Pale yellow solid, mp 202–204 °C; ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 6.48 (d, *J* = 15.86 Hz, 1H), 7.62 (d, *J*= 9.06 Hz, 2H), 7.79 (d, *J* = 15.86 Hz, 1H), 8.20 (d, *J*= 9.06 Hz, 2H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): δ 120.2, 128.6, 130.4, 143.0, 148.2, 160.0, 172.3 ppm.



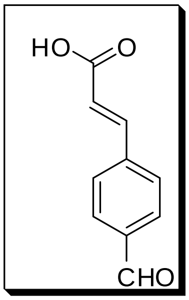
***(E)*-3-*p*-tolylacrylic acid.**[8]

White solid, mp 197–199 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.31 (s, 3H), 6.45 (d, *J* = 15.86 Hz, 1H), 7.04 (d, *J*= 8.3 Hz, 2H), 7.62 (d, *J*= 8.3 Hz, 2H), 7.80 (d, *J* = 15.86 Hz, 1H), ppm; ^{13}C NMR (75 MHz, CDCl$_3$): δ 21.8, 118.8, 128.9, 130.2, 132.1, 139.9, 144.6, 168.7 ppm.



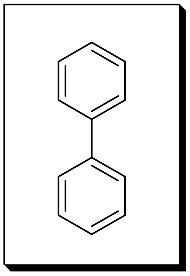
***(E)*-methyl 3-*p*-tolylacrylate.**[7]

White liquid; ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.30 (s, 3H), 3.79 (s, 3H), 6.44 (d, *J* = 15.84 Hz, 1H), 7.03 (d, *J*= 7.8 Hz, 2H), 7.60 (d, *J*= 8.3 Hz, 2H), 7.76 (d, *J* = 15.84 Hz, 1H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): δ 21.8, 51.5, 118.7, 128.8, 130.1, 131.9, 139.7, 144.5, 168.5 ppm.



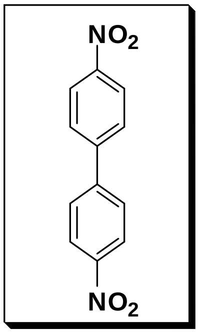
***(E)*-3-(4-formylphenyl)acrylic acid.**[8]

White solid, mp 200–202 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.42 (d, *J* = 15.86 Hz, 1H), 7.72 (d, *J*= 15.86 Hz, 1H), 7.80–7.85 (m, 4H), 9.97 (s, 1H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): δ 116.9, 129.6, 130.1, 136.2, 141.2, 144.5, 171.5, 191.5 ppm.



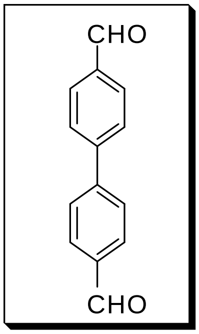
Biphenyl.[9]

White solid, mp118–120 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.29 (t, *J*=6.78 Hz, 2H), 7.39 (t, *J*=7.63 Hz, 4H), 7.53 (d, *J*=7.63 Hz, 4H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ=127.10, 127.18, 128.67, 141.15 ppm.



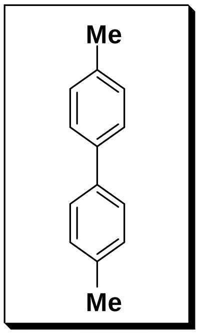
4,4'-dinitrobiphenyl.[10]

Yellow color solid; ^{1}H NMR (CDCl$_3$, 300 MHz): δ=7.14 (d, *J*=9.06 Hz, 4H), 8.30 (d, *J*=9.06 Hz, 4H); ^{13}C NMR (DMSO, 75 MHz): δ=119, 126.4, 143, 160 ppm.



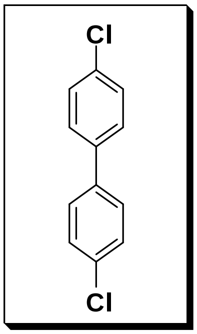
Biphenyl-4,4'-dicarbaldehyde.[11]

White solid, mp118–120 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.80 (d, *J* = 8.3 Hz, 4H), 7.99 (d, *J* = 8.3 Hz, 4H), 10.00 (s, 2H) ppm; ^{13}C NMR (75 MHz, CDCl$_3$): δ 128.1, 130.4, 136.2, 145.7, 192.0 ppm.



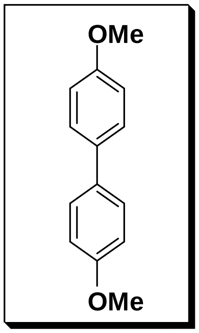
4,4'-dimethylbiphenyl.[12]

White solid, mp118–120 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 6H), 7.23 (d, *J* = 7.7 Hz, 4H), 7.46(d, *J* = 7.7 Hz, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.1, 126.8, 129.6, 136.7, 138.4 ppm.



4,4'-dichlorobiphenyl.[13]

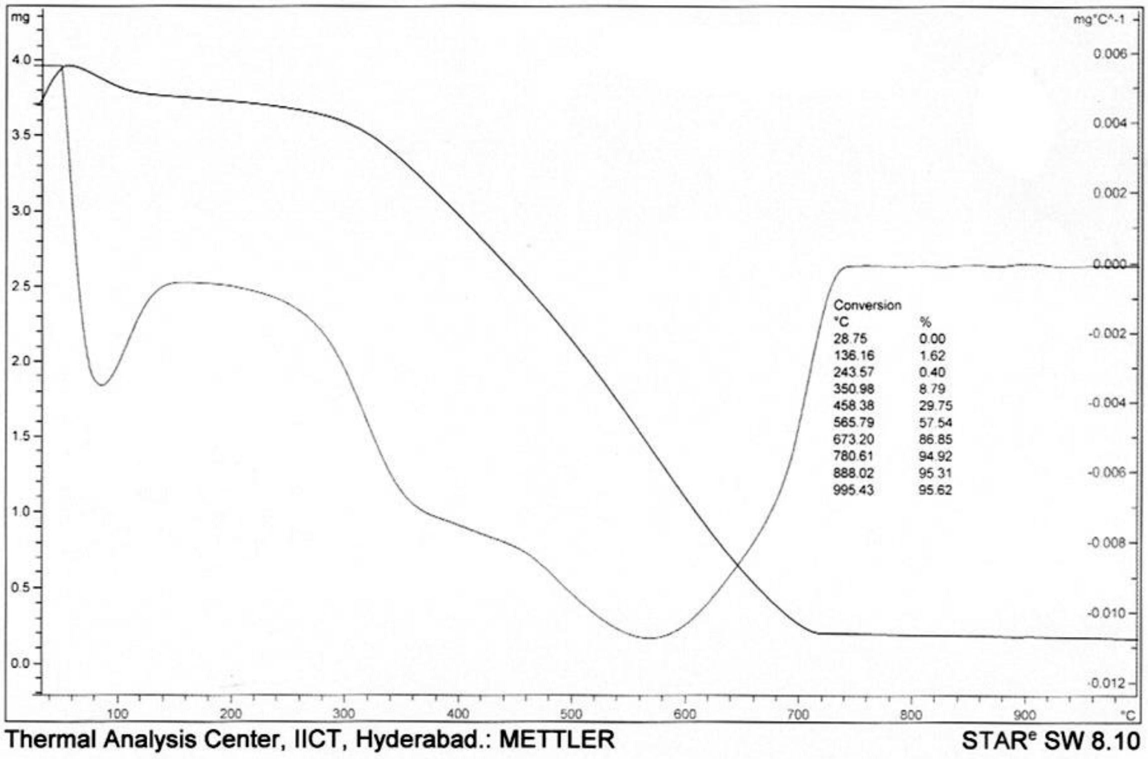
White solid, mp147–149 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.5 Hz, 4H), 7.48 (d, *J* = 8.5 Hz, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 128.2, 129.0, 133.7, 138.4 ppm.



4,4'-dimethoxybiphenyl.[14]

White solid, mp168–170 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ 3.82 (s, 6H), 6.95 (d, *J* = 8.8 Hz, 4H), 7.48(d, *J* = 8.8 Hz, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.3, 114.1, 127.6, 133.5, 158.7 ppm.

TGA analysis of Pd/CSP:



Conversion

°C	%
28.75	0.00
136.16	1.62
243.57	0.40
350.98	8.79
458.38	29.75
565.79	57.54
673.20	86.85
780.61	94.92
888.02	95.31
995.43	95.62

Kinetic analysis data for the “homeopathic catalysis” (0.05 mol% of Pd@CSP) in water:

Time (h)	Conversion (%)
4	25
8	36
12	50
16	59
20	67
24	70

E-factor calculations:

The E factor represents the actual amount of waste produced in the process, defined as everything but the desired product. Put quite simply, it is the total mass of raw materials minus the total mass of product, all divided by the total mass of product.[14, 15]

Table 1 Heck reaction of iodo benzene with styrene under different reaction conditions: Searching for relatively green conditions.[a]

Entry	Iodo benzene (mmol)	Styrene (mmol)	TEA (mmol)	TBAB (mmol)	Isolated yield (%)[b]	Time (h)	E factor (kg waste/kg product)[c]
1	0.32	0.416	0.64	0.64	95	6.5	5.88
2	0.32	0.32	0.64	0.64	86	6.5	6.38
3	0.32	0.416	0.48	0.64	93	7.0	5.71
4	0.32	0.416	0.48	0.48	90	6.5	5.00
5	0.32	0.32	0.48	0.48	80	6.5	5.43
6	0.32	0.416	0.48	0.32	90	7.0	4.05

[a]All reactions are performed with 0.5 mol% *vs.* iodobenzene of Pd@CSP in 4 mL of water. [b]Isolated yields. [c]Exclusion of ethanol used for work up procedure, exclusion of the amount of the Pd@CSP used, and exclusion of ingredients used for flash chromatography.

Note (Regarding Table 1 and 2, SI): When the Authors have not reported the amount of solvent used in the work-up procedure, we have not accounted for the meaningful comparisons with literature review and considered that solvent can be recovered. By considering these heterogeneous Pd catalysts are recyclable and hence, waste is essentially eliminated.

For Entry 6, Table1 (SI)

E = [0.065 g (iodobenzene) + 0.043 g (styrene) + 0.048 g (TEA) + 0.102 g (TBAB) – 0.051g (product × yield)] / 0.051 g

= 4.05.

E = [0.065 g (iodobenzene) + 0.043 g (styrene) + 0.048 g (TEA) + 0.102 g (TBAB) + 2.34 g (ethanol) – 0.051g (product × yield)] / 0.051 g

= 49.94 (inclusion of amount of ethanol used for work up procedure).

E = [0.065 g (iodobenzene) + 0.043 g (styrene) + 0.048 g (TEA) + 0.102 g (TBAB) + 0.005 g (Pd) – 0.051g (product × yield)] / 0.051 g

= 4.15 (weight of Pd@CSP is considered. Due to the solubilization of CSP over extended recycling and leaching of Pd species in to the solution, it is considered as the waste).

For Entry 1 Table 2 (manuscript)

E= [0.065 g (iodobenzene) + 0.043 g (styrene) + 0.064 g (TEA) + 3.77 g (DMF) – 0.056g (product × yield)] / 0.056 g

= 68.32 (inclusion of DMF).

For Entry 1 Table 4 (manuscript)

E= [0.065 g (iodobenzene) + 0.088 g (K_2CO_3) + 0.205 g (TBAB) – 0.025g (product × yield)] / 0.025 g

= 13.32.

Table 2 Comparison of E-factor for the Heck coupling reaction over different supported palladium catalysts.

Entry	Catalyst	E factor (kg waste/kg product	Reference
1	Pd/C	5.50[c]	*Adv. Synth. Catal.*, 2002, **344**, 344–348.
2	*In situ* Pd nanoparticles	6.92[a]	*J. Org. Chem.*, 2006, **71**, 4339–4342.
3	Pd/activated carbon	13.25[b]	*Chem. Eur. J.*, 2002, **8**, 622–631.
4	Pd/ pH-responsive colloid	3.81[d], 3.67[d, e]	*Journal of Catalysis*, 2007, **250**, 324–330.
5	Pd@SPB	7.28[a]	*Adv. Synth. Catal.*, 2008, **350**, 493 – 500.
6	Pd@CSP	4.05[a]	*present protocol*
7	Pd/MPTAT	29.67[f]	*Green Chem.*, 2011, **13**, 1317–1331.
8	Pd-PHEMA/CMK	5.26[a]	*Appl. Catal. A: Gen.*, 2012, **423-424,** 78-90.

[a]Reaction between iodo benzene and styrene in water. [b]Reaction between bromo benzene and styrene in DMAc. [c]Reaction between chloro benzene and styrene in water. [d]Reaction between iodo benzene and methyl acrylate in water. [e]Rection between iodo benzene and methy acrylate with Pd@CSP in water. [f]Reaction between iodo benzene and styrene in water and ethanol (inclusion of ethanol and exclusion of water).

- *Adv. Synth. Catal.*, 2002, **344**, 344–348.

E = 4.95 g (chloro benzene) + 4.60 g (styrene) + 4.76 g (HCOONa) + 6.62 g (Na_2CO_3) + 1.5 g (PEG) – 3.45 g (product × yield)/3.45 g

= 5.50.

- *J. Org. Chem.*, 2006, **71**, 4339–4342.

E = [0.20 g (iodobenzene) + 0.20 g (styrene) + 0.317 g (Na_2CO_3) + 0.321 g (TBAB) – 0.135 g (product × yield)]/0.135 g

= 6.92.

- *Chem. Eur. J.*, 2002, **8**, 622–631.

E = [1.55 g (bromo benzene) + 1.562 g (styrene) + 0.984 g (NaOAc) + 9.3 g (DMAc) – 0.94 g (product × yield)]/0.94 g

= 13.25.

- *Journal of Catalysis*, 2007, **250**, 324–330.

E = [0.407 g (iodobenzene) + 0.258 g (methyl acrylate) + 0.828 g (K_2CO_3) – 0.420 g (product × yield)] / 0.420 g

= 3.81.

Present protocol

E = [0.065 g (iodobenzene) + 0.035 g (methyl acrylate) + 0.048 g (TEA) + 0.10 g (TBAB) – 0.053 g (product × yield)] / 0.053 g

= 3.67.

- *Adv. Synth. Catal.*, 2008, **350**, 493 – 500.

E = [0.204 g (iodobenzene) + 0.104 g (styrene) + 0.829 g (TEA) + 0.322 g (TBAB) – 0.176 g (product × yield)] / 0.176 g
= 7.28.

- *Green Chem.*, 2011, **13**, 1317–1331.

E = [0.204g (iodobenzene) + 0.104 g (styrene) + 0.829 g (K_2CO_3) + 0.322 g (TBAB) + 3.94 g (ethanol) – 0.176 g (product × yield)] / 0.176 g

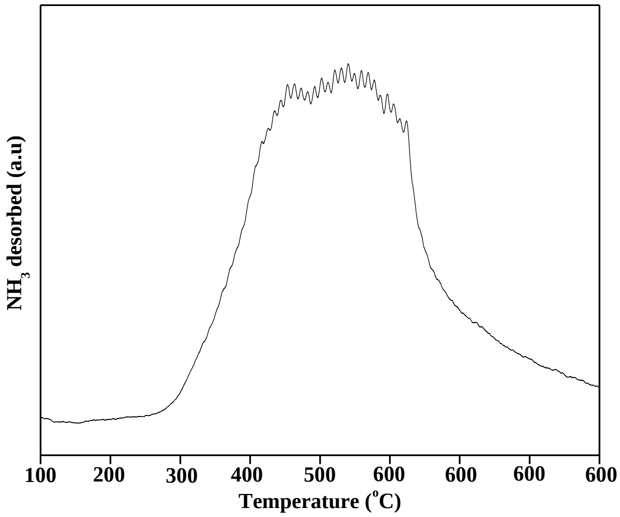
= 29.67.

- *Appl. Catal. A: Gen.*, 2012, **423-424,** 78-90.

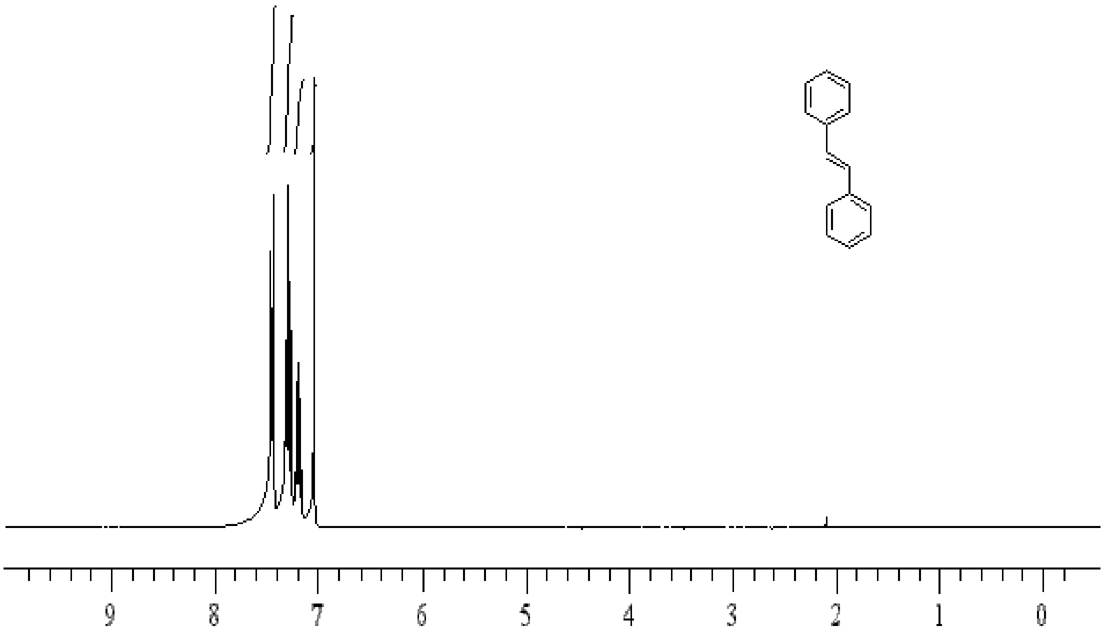
E = [0.204g (iodobenzene) + 0.208 g (styrene) + 0.690 g (K_2CO_3) – 0.176 g (product × yield)] / 0.176 g

= 5.26.

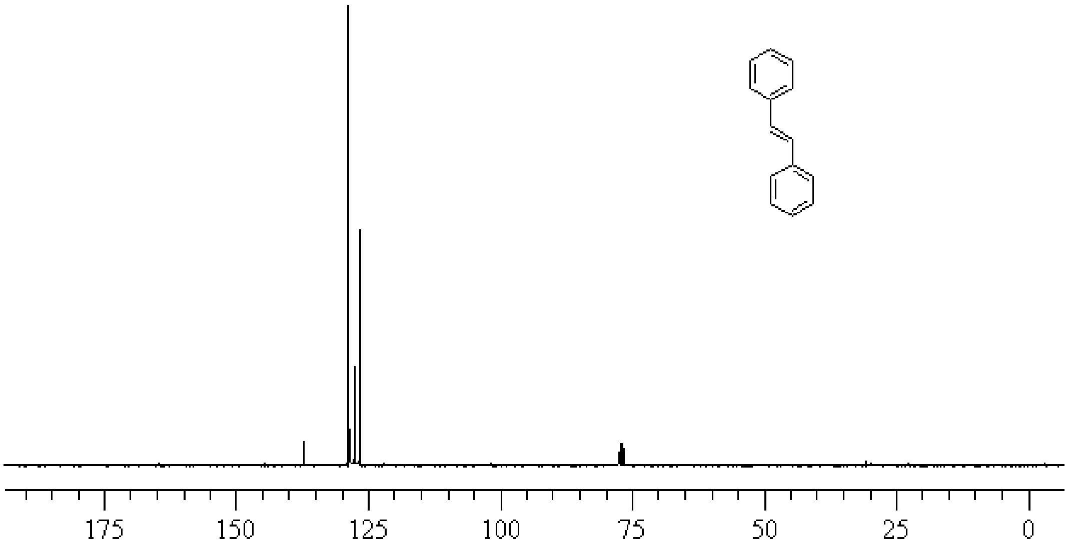
A Graph of ammonia TPD of CSP:



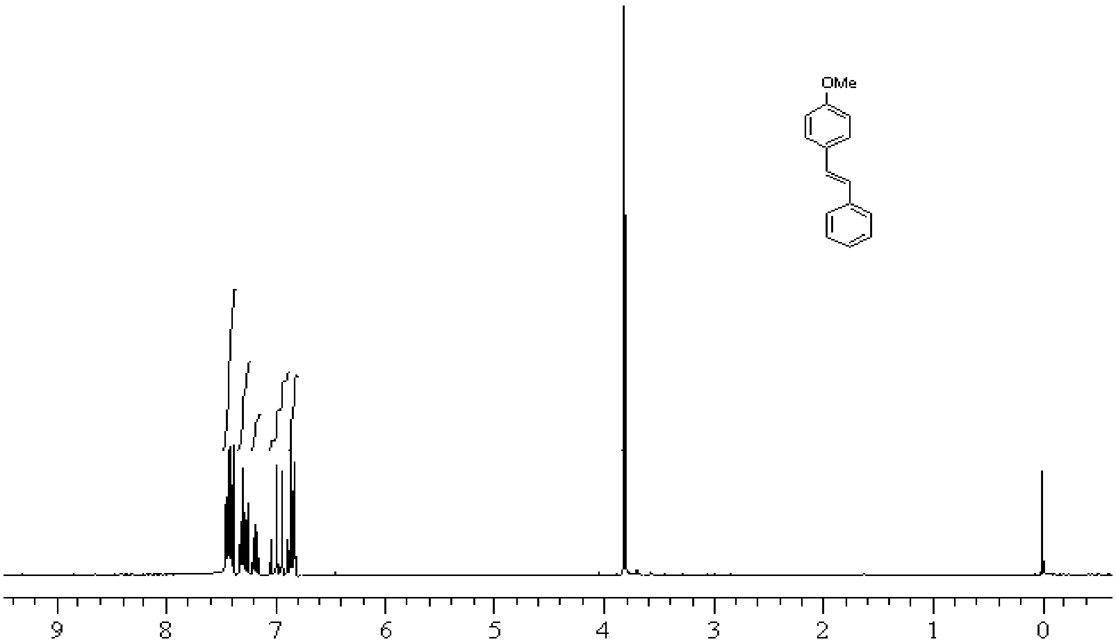
The structural characterizations of support (CSPs) are well established.[16] Ammonia TPD analysis has been carried out in order to prove the presence of -COOH functionalities on the support. In a typical experiment, temperature programmed desorption of ammonia (NH_3-TPD) was performed in a laboratory built equipment containing programmable temperature controller and GC with TCD. The sample was pretreated at 200 °C for 1 h in He flow (60 ml/min). After pretreatment, the sample was saturated with anhydrous ammonia (10% NH_3 balance He) at 100°C for 1 h and subsequently flushed with He for 50 min at the same temperature to remove physisorbed ammonia. Then, the temperature of the sample was raised up to 600 °C at a heating rate 10 ^{o}C/min. The desorbed NH$_3$ gas was monitored with gas chromatography by using thermal conductivity detector. A broad ammonia desorption profile in the range of 280–600^{o} C is observed (SI). This broad peak is an indication for the presence of - COOH functional groups.[17]



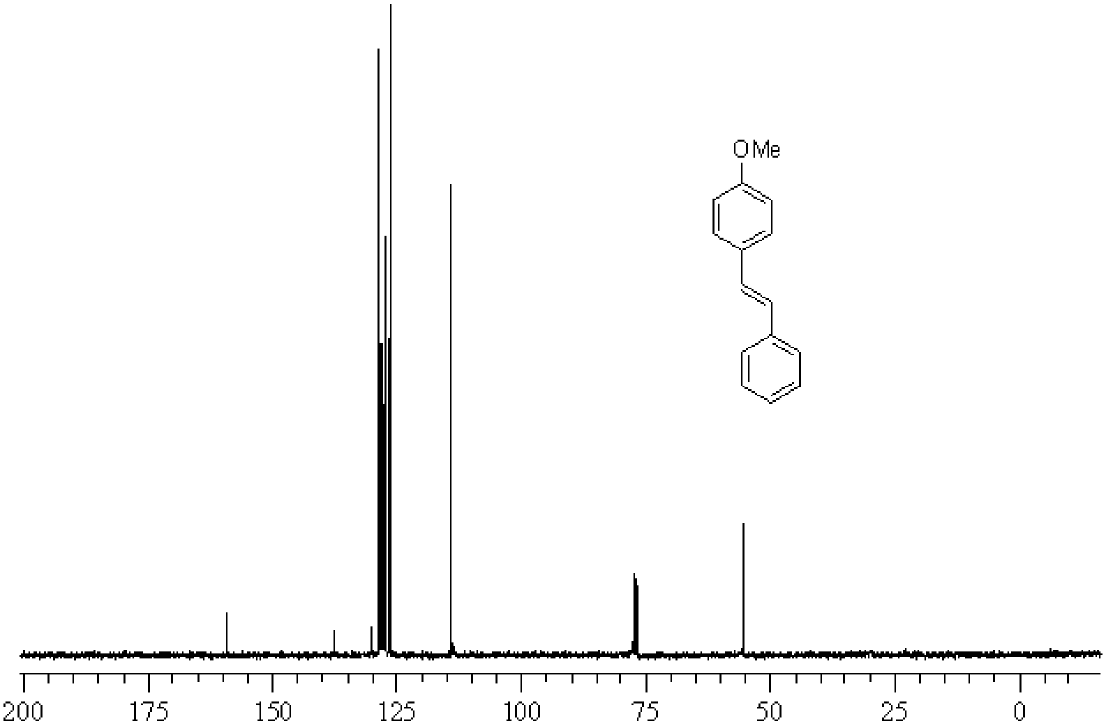
^{1}H NMR (300 MHz, CDCl$_3$) spectra of (*E*)-1,2-diphenylethene (**1**)



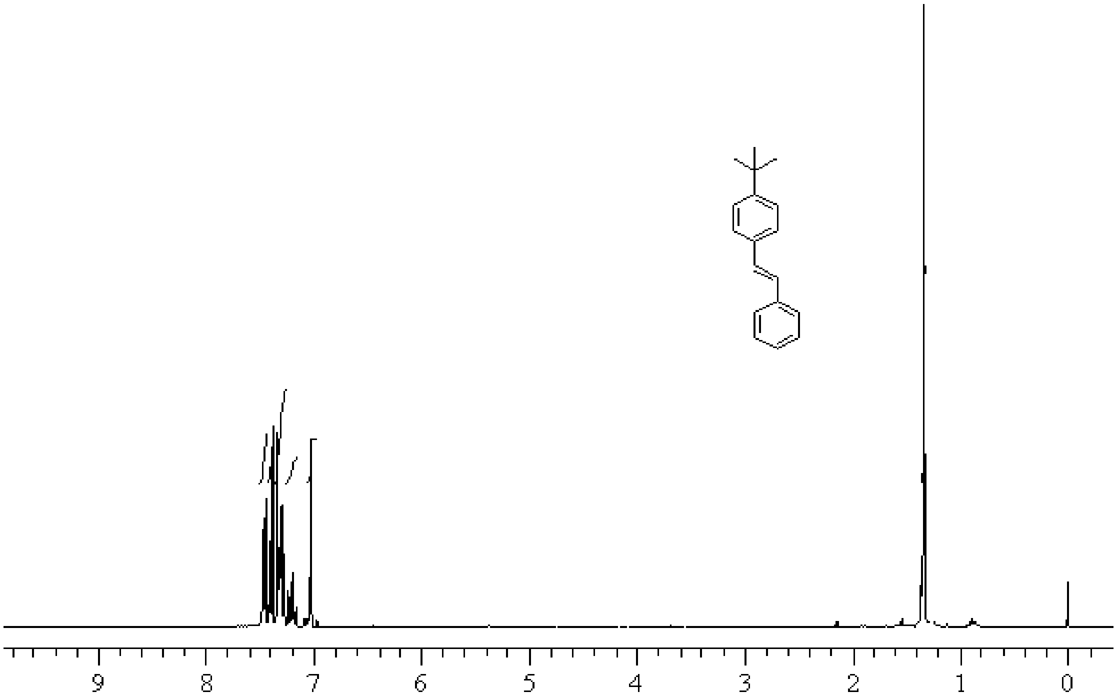
^{13}C NMR (50 MHz, CDCl$_3$) spectra of (*E*)-1,2-diphenylethene (**1**)



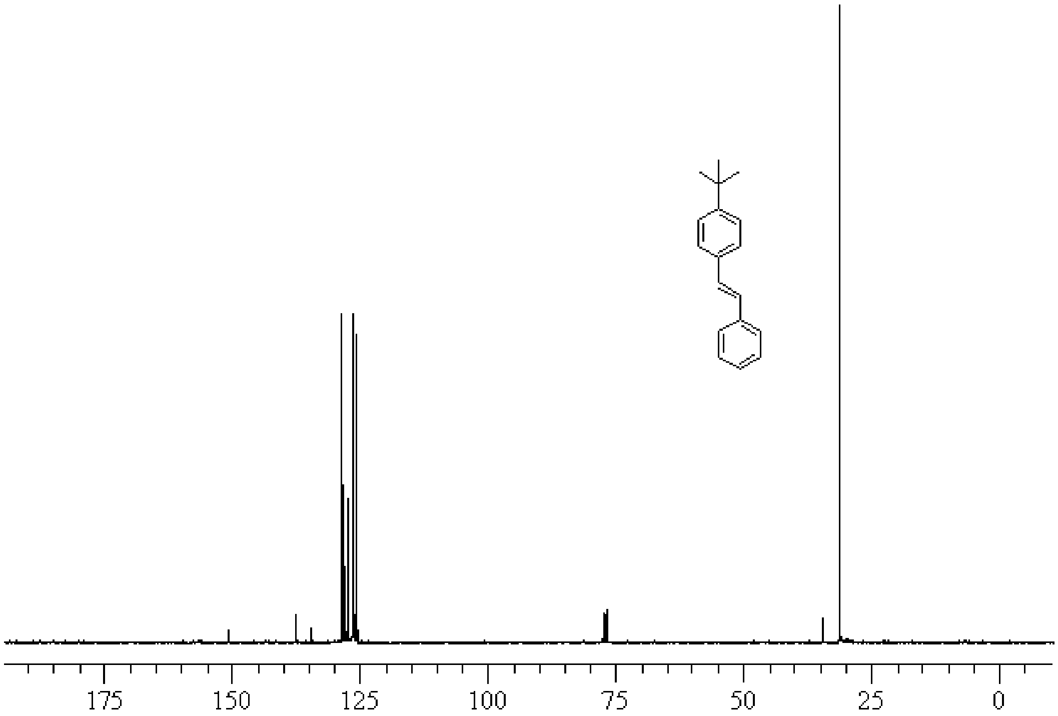
^{1}H NMR (300 MHz, $CDCl_3$) spectra of (*E*)-1-methoxy-4-styrylbenzene (**2**)



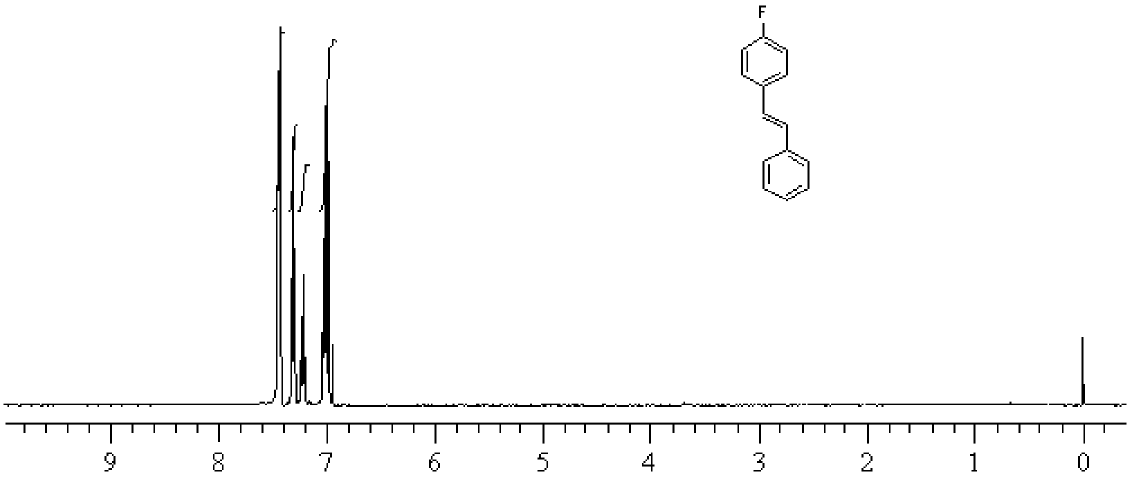
^{13}C NMR (50 MHz, $CDCl_3$) spectra of (*E*)-1-methoxy-4-styrylbenzene (**2**)



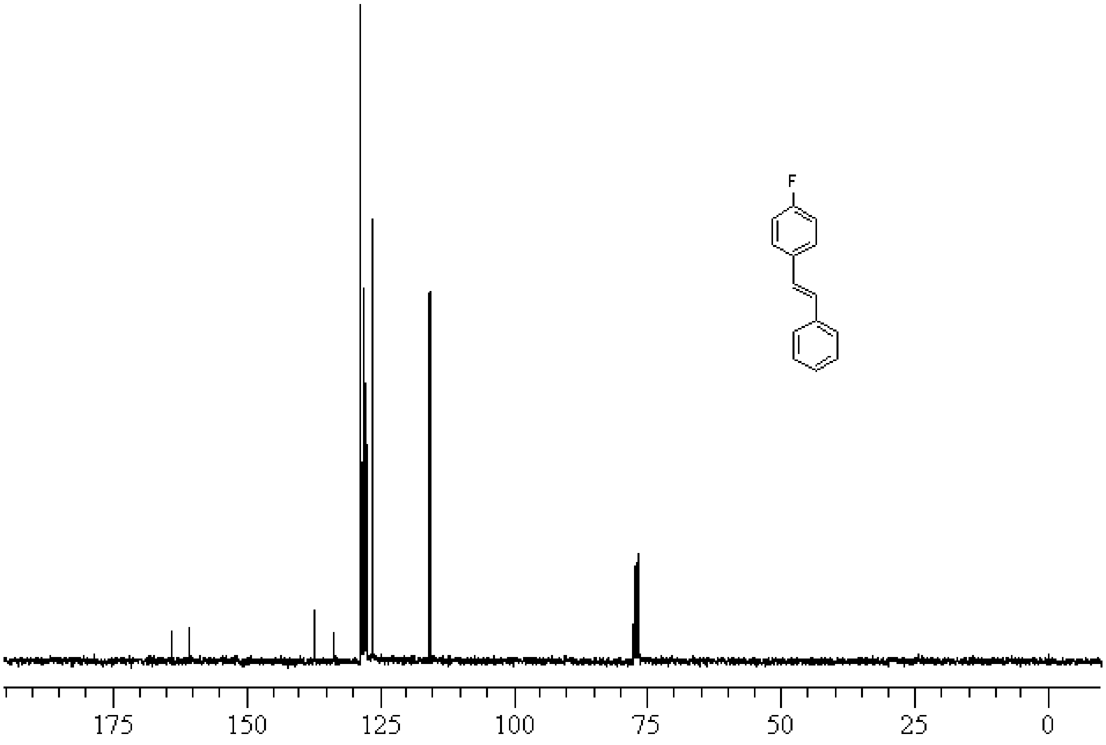
^{1}H NMR (300 MHz, $CDCl_3$) spectra of (*E*)-1-*tert*-butyl-4-styrylbenzene (**3**)



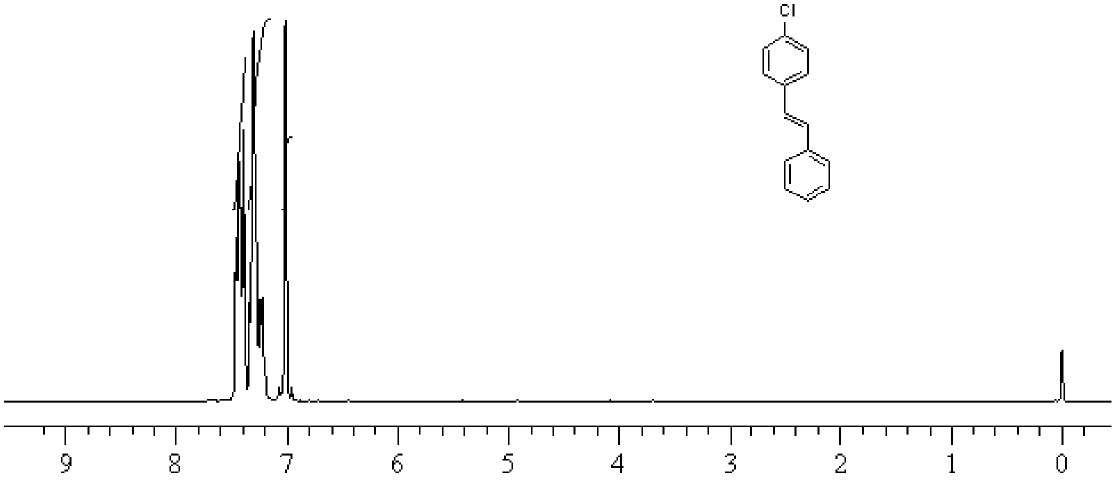
^{13}C NMR (75 MHz, $CDCl_3$) spectra of (*E*)-1-tert-butyl-4-styrylbenzene (**3**)



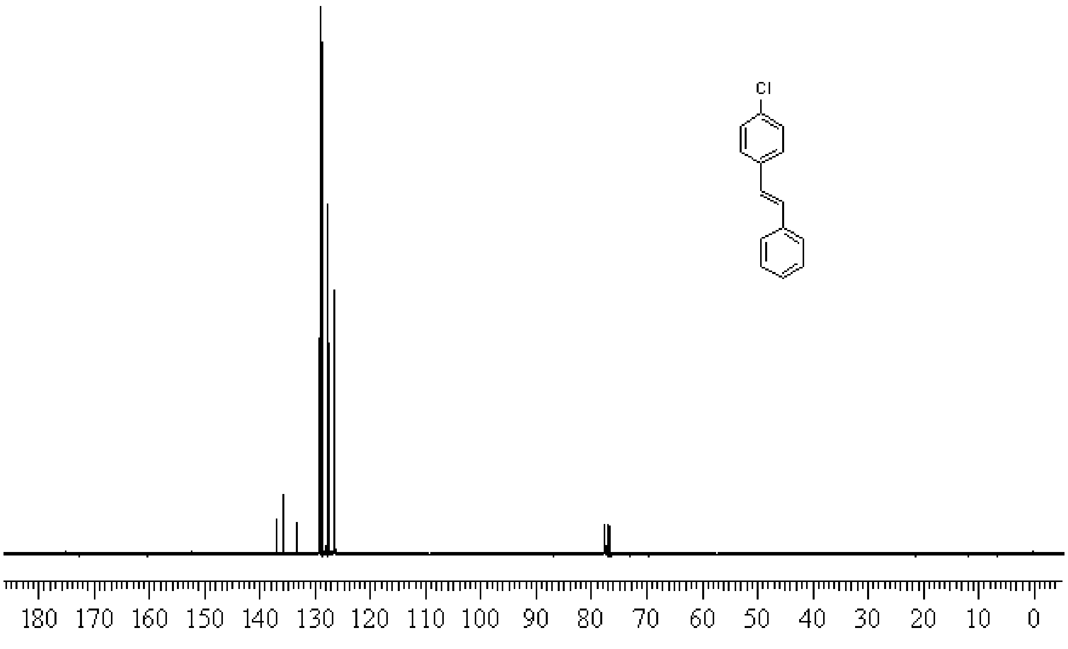
^{1}H NMR (300 MHz, CDCl$_3$) spectra of (*E*)-1-fluoro-4-styrylbenzene (**4**)



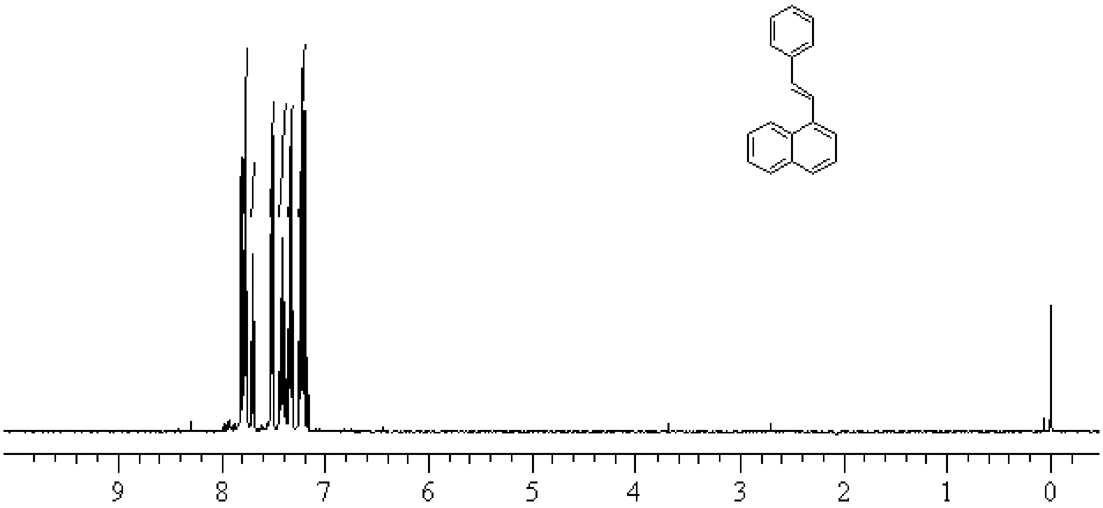
^{13}C NMR (75 MHz, CDCl$_3$) spectra of (*E*)-1-fluoro-4-styrylbenzene (**4**)



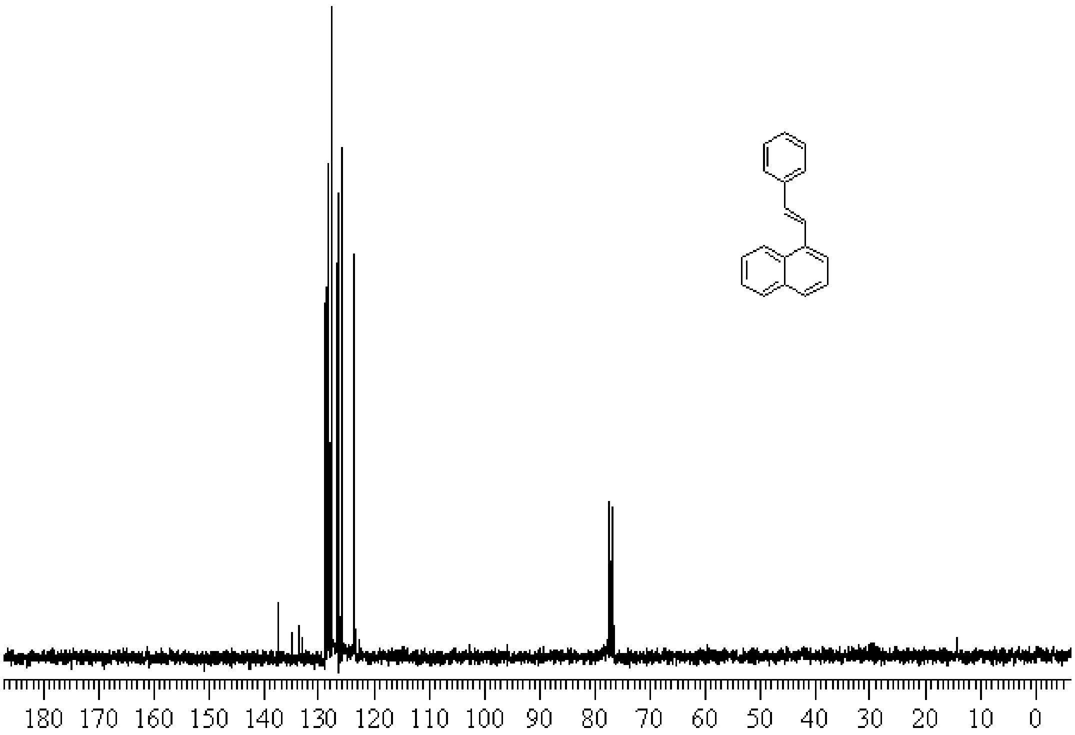
^{1}H NMR (300 MHz, $CDCl_3$) spectra of (*E*)-1-chloro-4-styrylbenzene (**5**)



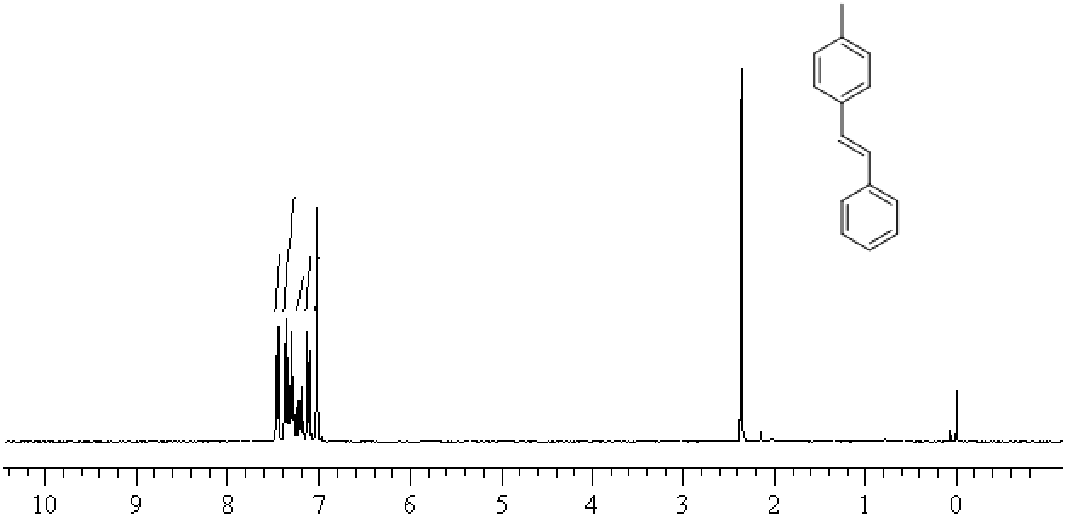
^{13}C NMR (75 MHz, $CDCl_3$) spectra of (*E*)-1-chloro-4-styrylbenzene (**5**)



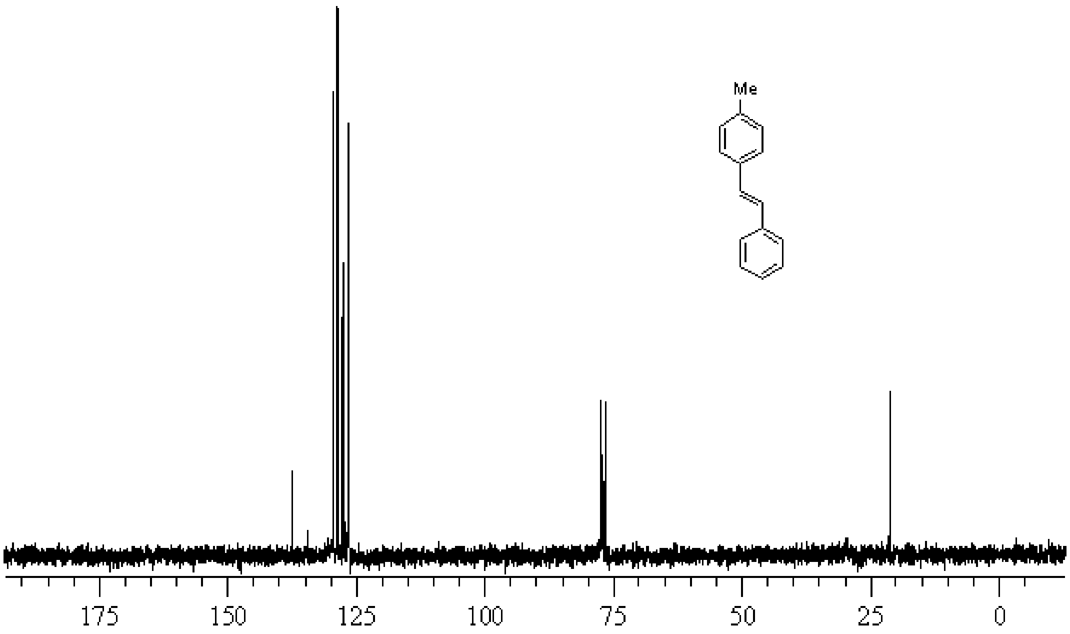
^{1}H NMR (300 MHz, $CDCl_3$) spectra of (*E*)-2-styrylnaphthalene (**6**)



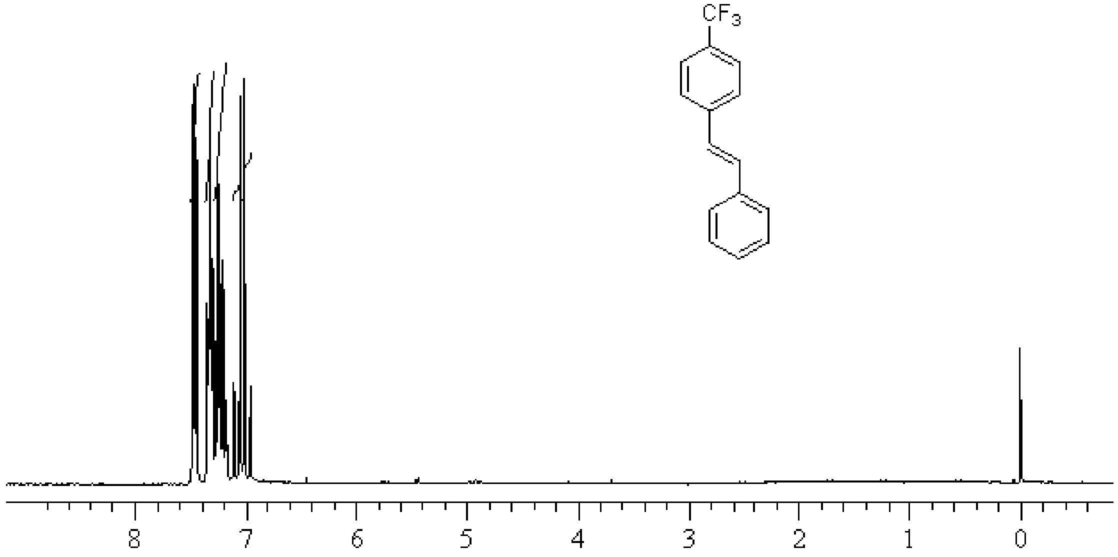
^{13}C NMR (75 MHz, $CDCl_3$) spectra of (*E*)-2-styrylnaphthalene (**6**)



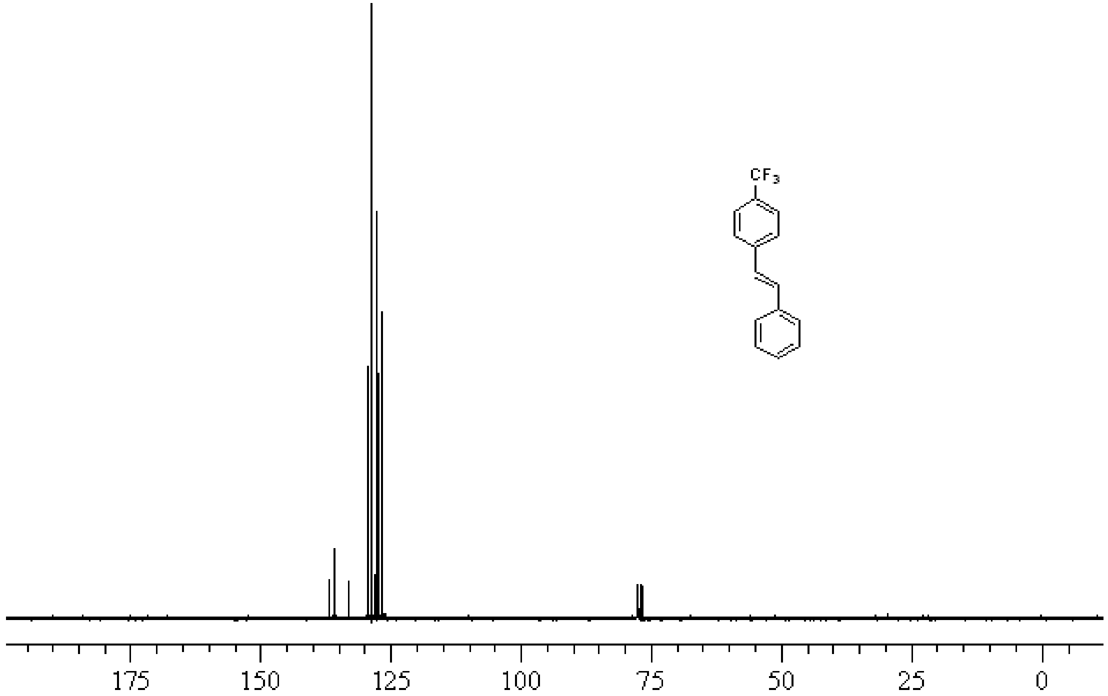
^{1}H NMR (300 MHz, CDCl$_3$) spectra of (*E*)-1-methyl-4-styrylbenzene (**7**)



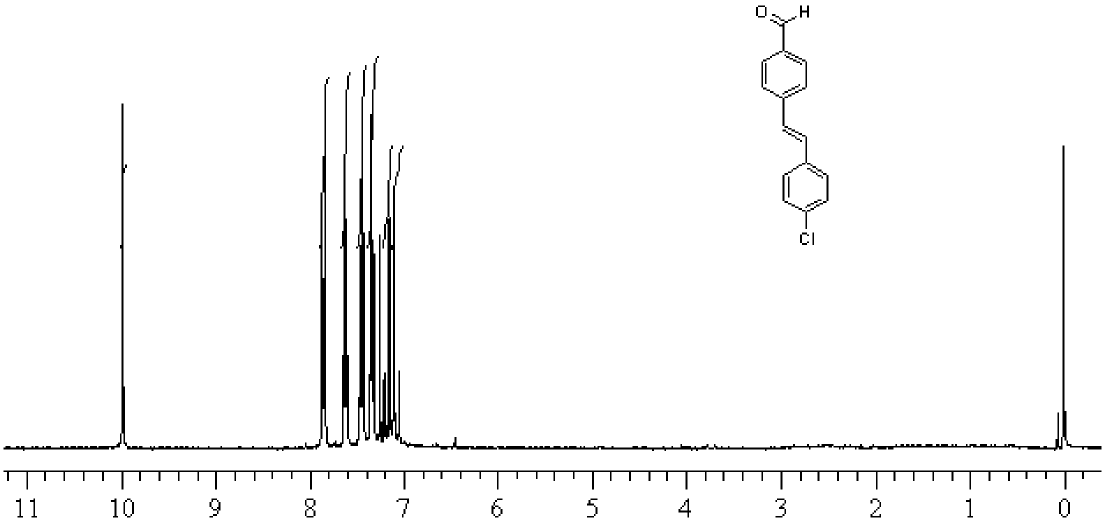
^{13}C NMR (75 MHz, CDCl$_3$) spectra of (*E*)-1-methyl-4-styrylbenzene (**7**)



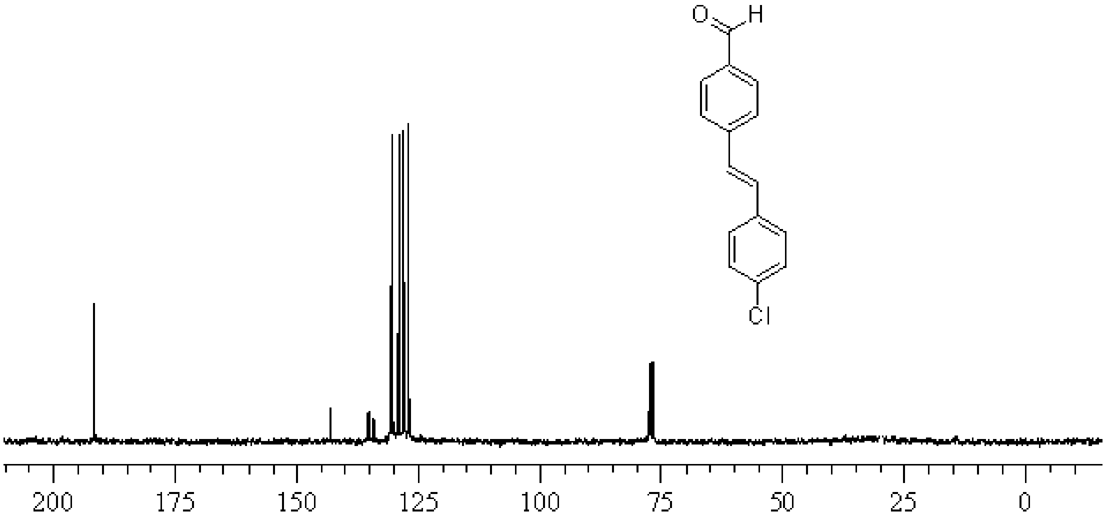
^{1}H NMR (300 MHz, $CDCl_3$) spectra of (*E*)-1-styryl-4-(trifluoromethyl)benzene (**8**)



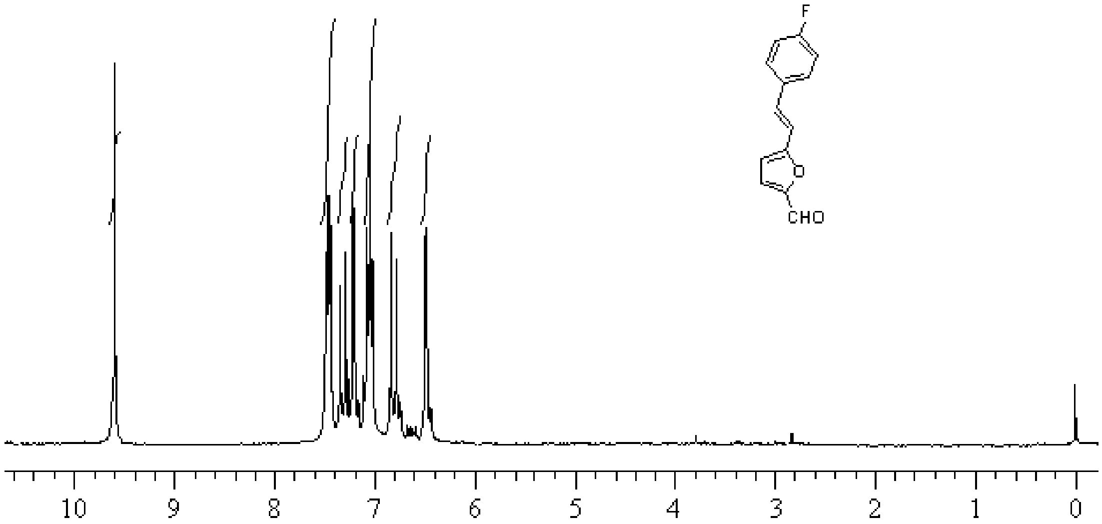
^{13}C NMR (75 MHz, $CDCl_3$) spectra of (*E*)-1-styryl-4-(trifluoromethyl)benzene (**8**)



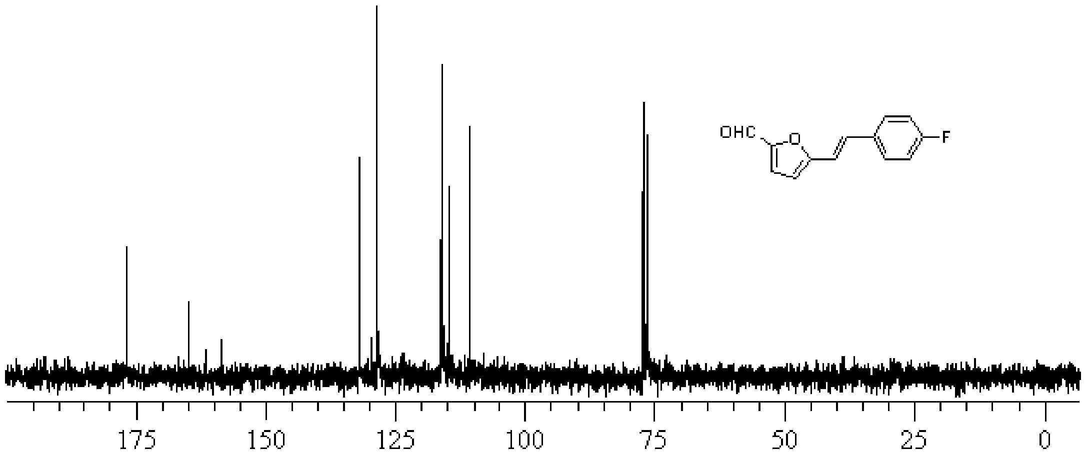
^{1}H NMR (300 MHz, CDCl$_3$) spectra of (*E*)-1-methyl-4-styrylbenzene (**9**)



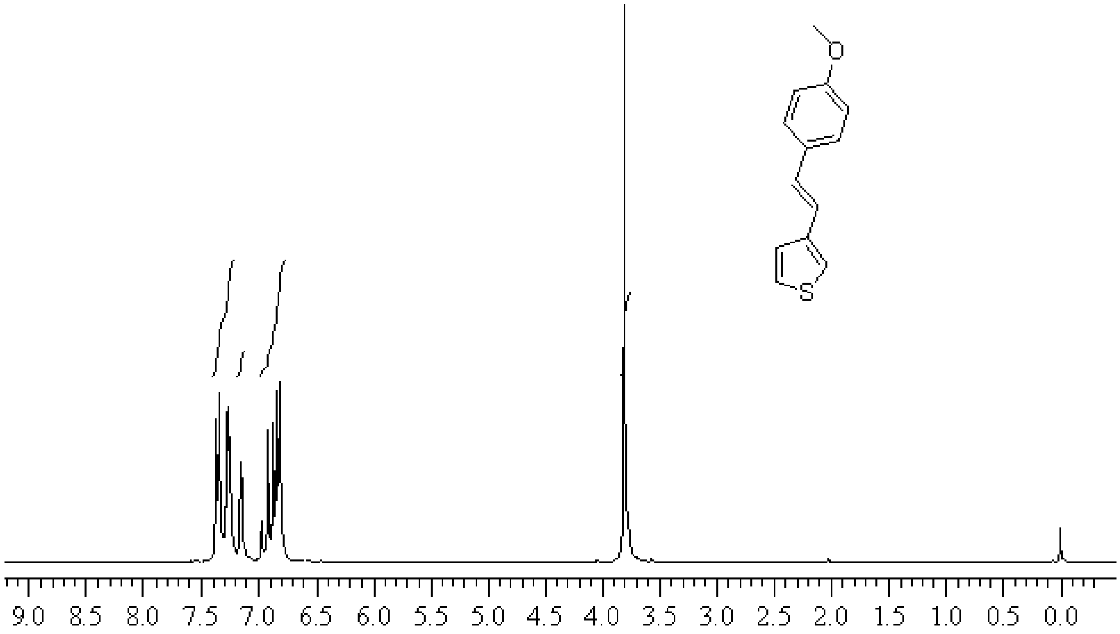
^{13}C NMR (75 MHz, CDCl$_3$) spectra of (*E*)-1-methyl-4-styrylbenzene (**9**)



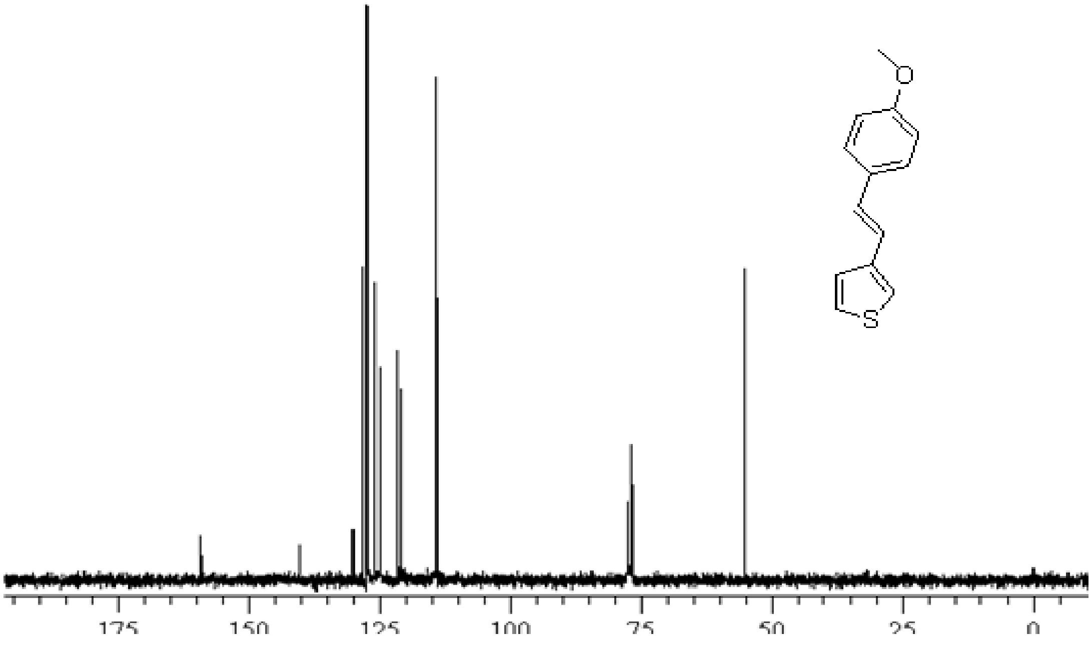
^{1}H NMR (300 MHz, $CDCl_3$) spectra of (*E*)-2-(4-fluorostyryl)furan (**10**)



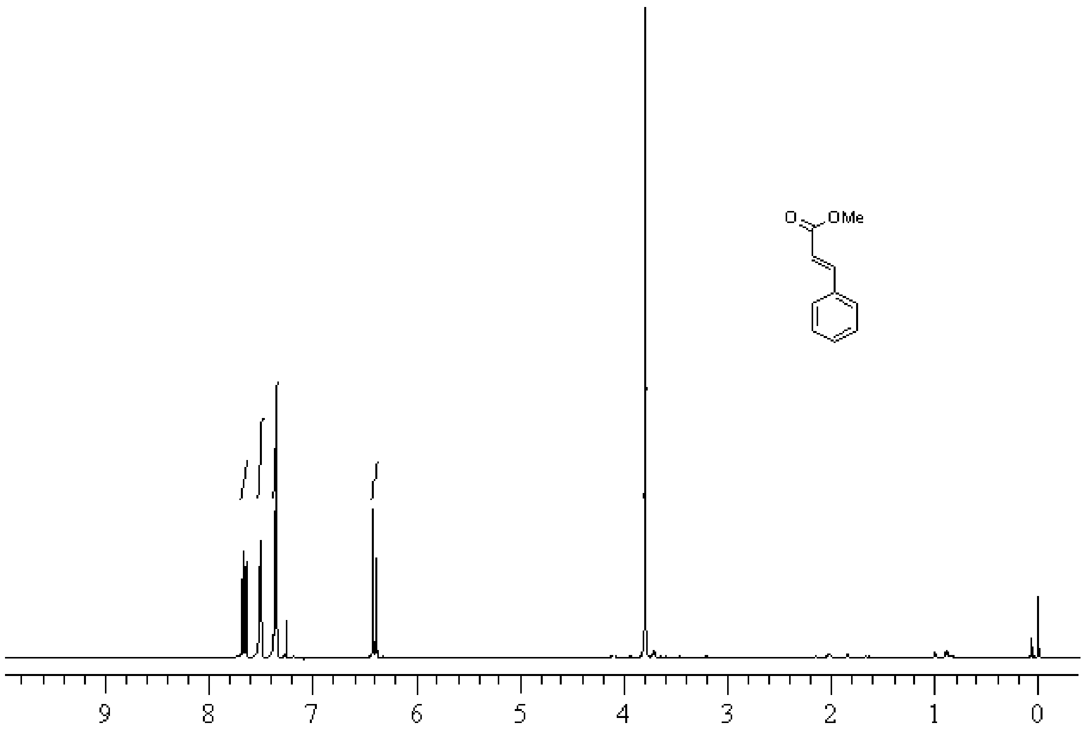
^{13}C NMR (75 MHz, $CDCl_3$) spectra of (*E*)-2-(4-fluorostyryl)furan (**10**)



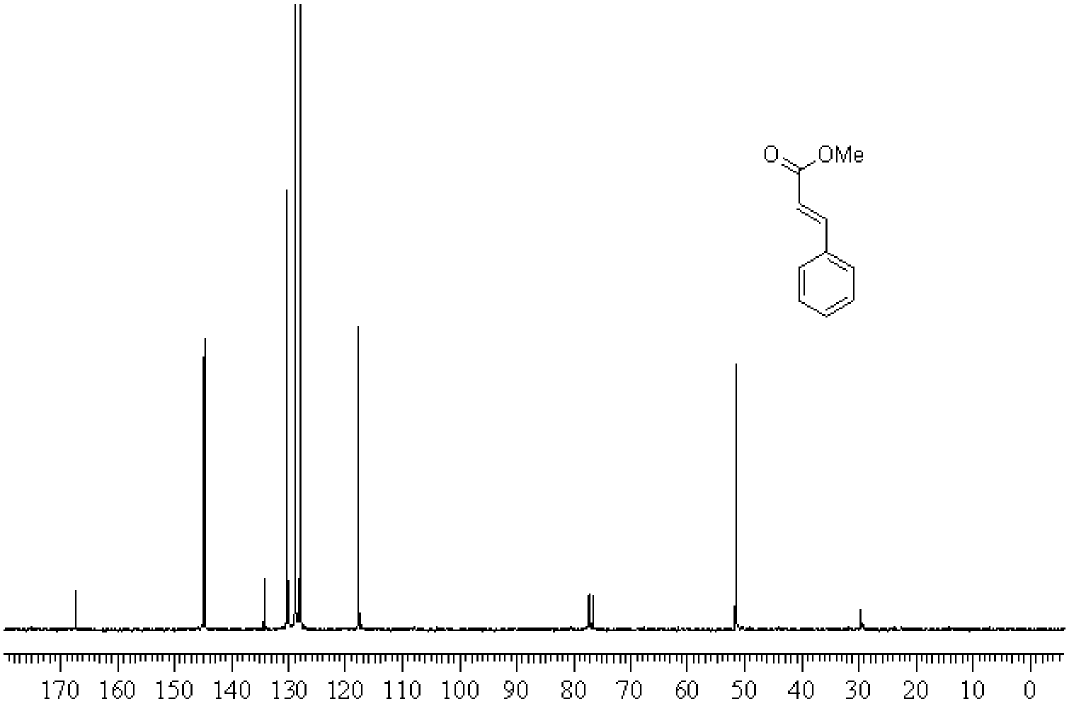
^{1}H NMR (300 MHz, $CDCl_3$) spectra of (*E*)-3-(4-methoxystyryl)thiophene (**11**)



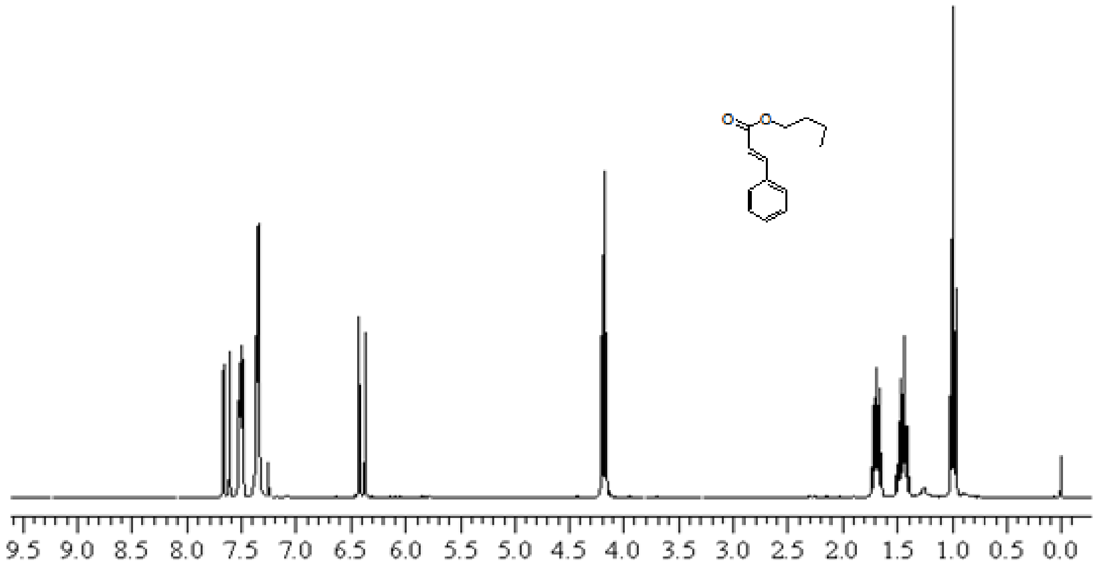
^{13}C NMR (75 MHz, $CDCl_3$) spectra of (*E*)-3-(4-methoxystyryl)thiophene (**11**)



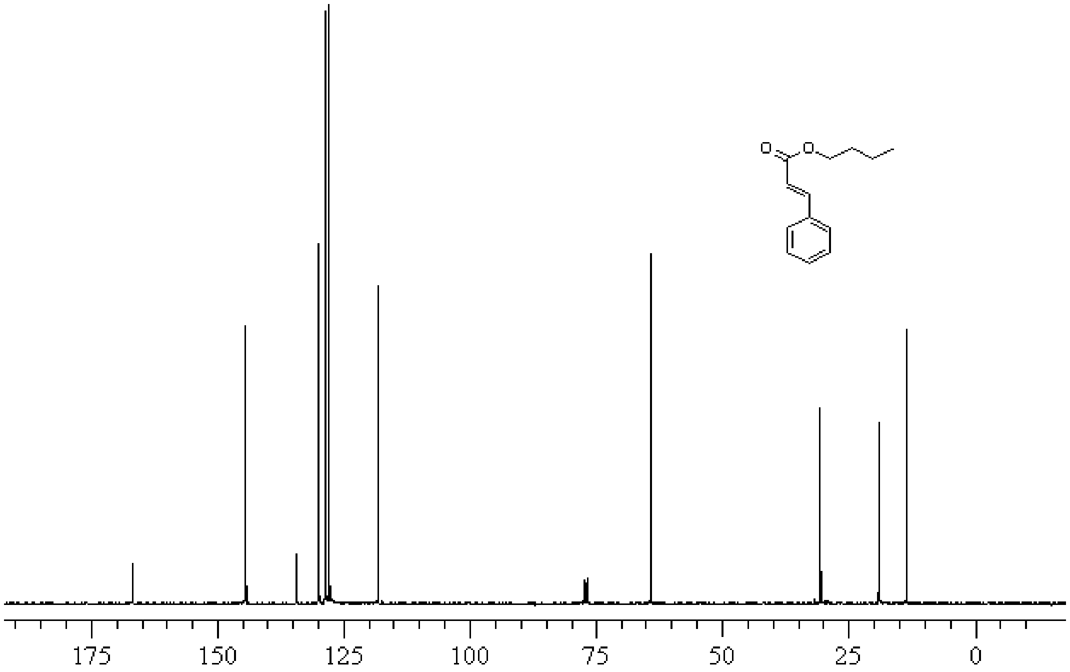
^{1}H NMR (300 MHz, CDCl$_3$) spectra of (*E*)-methyl cinnamate (**12**)



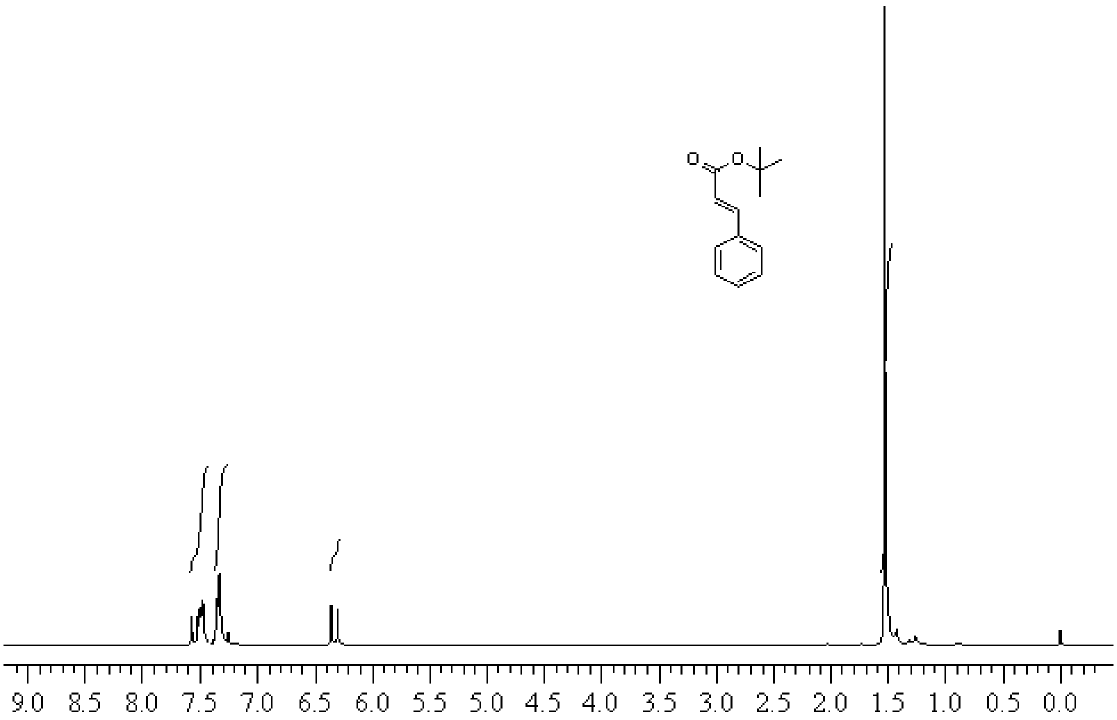
^{13}C NMR (75 MHz, CDCl$_3$) spectra of (*E*)-methyl cinnamate (**12**)



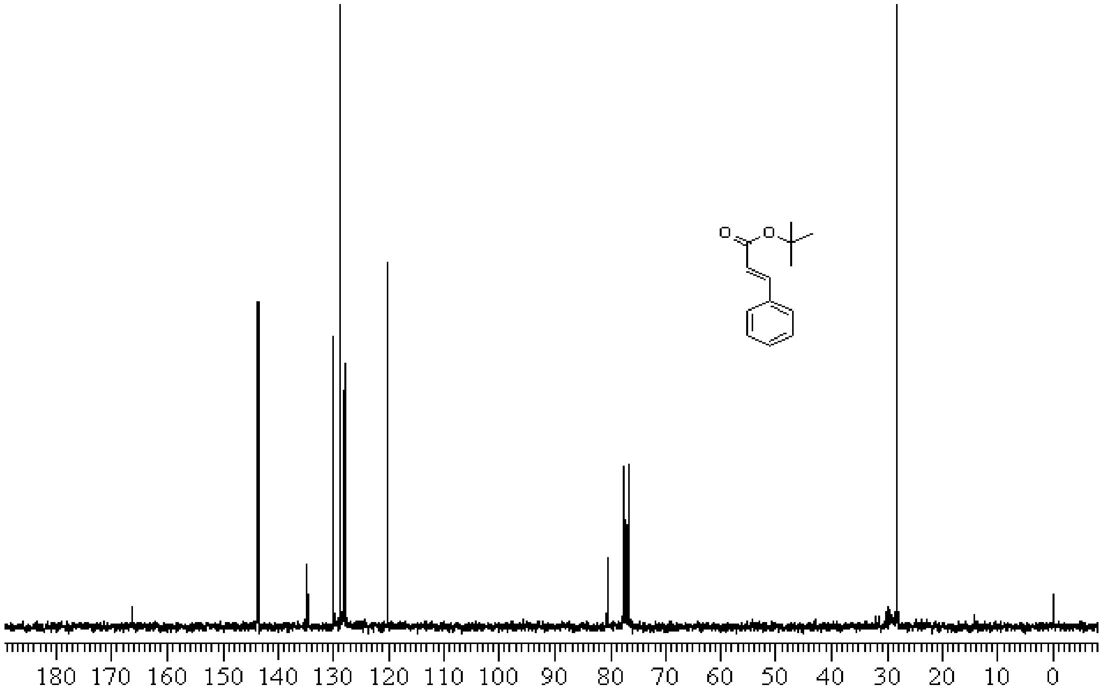
^{1}H NMR (300 MHz, $CDCl_3$) spectra of (*E*)-n-butyl cinnamate (**13**)



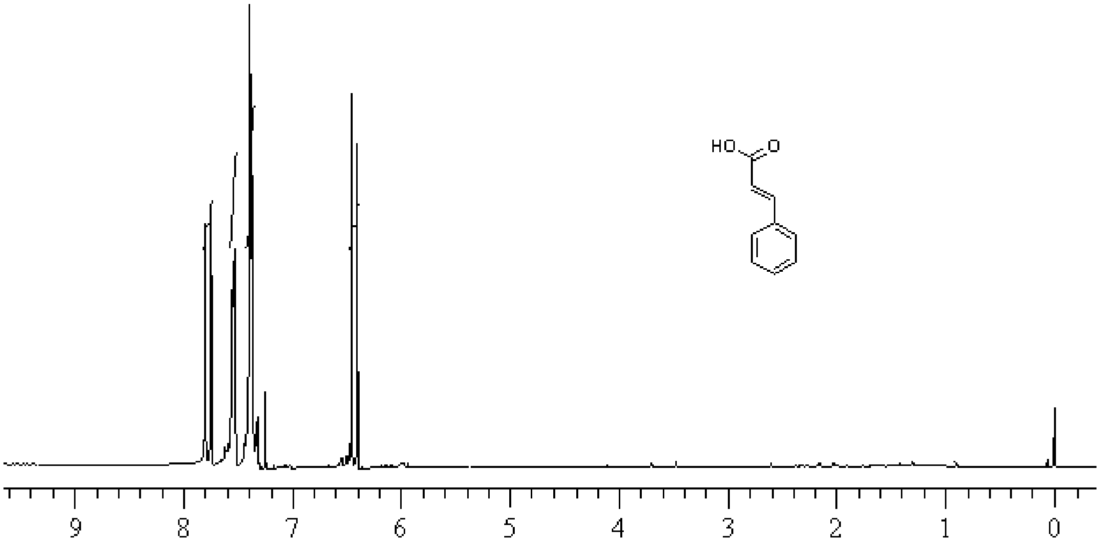
^{13}C NMR (75 MHz, $CDCl_3$) spectra of (*E*)-n-butyl cinnamate (**13**)



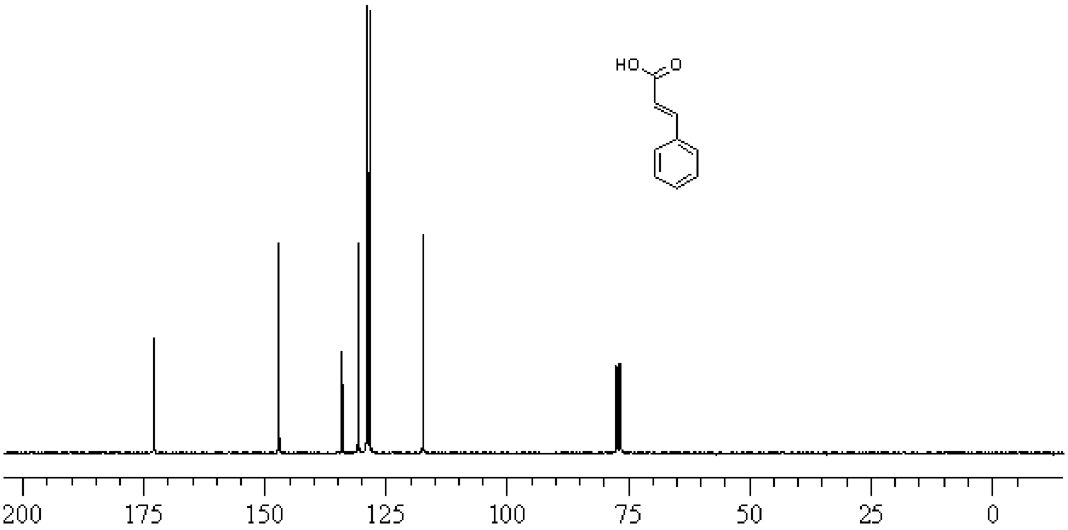
^{1}H NMR (300 MHz, CDCl$_3$) spectra of *tert*-butyl cinnamate (**14**)



^{13}C NMR (75 MHz, CDCl$_3$) spectra of *tert*-butyl cinnamate (**14**)



^{1}H NMR (300 MHz, $CDCl_3$) spectra of *trans* cinnamic acid (**15**)



^{13}C NMR (75 MHz, $CDCl_3$) spectra of *trans* cinnamic acid (**15**)

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