Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information:

Regioselective Heck Reaction catalyzed by Pd nanoparticles immobilized on DNA-modified MWCNTs

Abdol R. Hajipour[a,b]*, Zahra Khorsandi[a] , Hossein Farrokhpour*c

[a]*Pharmaceutical Research Laboratory, Department of Chemistry ,Isfahan University of Technology, Isfahan 84156, Iran*

[b]*Department of Neuroscience, University of Wisconsin, Medical School, Madison, WI53706-1532, USA*

1. Experimental details

1.1. General

All the reagents and solvents were purchased from Merck chemical company. Salmon testes DNA (stDNA) was purchased from Sigma-Aldrich Chem Co.(USA). The state of palladium was determined by X-ray diffractometer (XRD, Xpert MPD), X-ray diffractometer using CuKα radiation. The size and morphology of catalyst were observed using transmission electron microscopy (TEM) EM208S micro-scope with an accelerating voltage of 100 KV. The palladium quantity on the carriers was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Varian vista-mpx). Reaction yields were analyzed by gas chromatography (GC, Agilent Technologies). The selectivity was also investigated using GC. The FT-IR spectra were recorded on a Jasco-680 (Japan) spectrophotometer in KBr pellets and reported in cm^{-1}. UV−vis spectroscopy was carried out with a JASCO V-550 UV/vis spectrometer. Scanning electron micrographs of the support and catalyst were taken on a SEM EM 3200 instrument. the ^{1}H NMR of the products was recorded on a 500 MHz Bruker-avance in $CDCl_3$.

1.2. General procedure for the preparation of Pd on DNA-functionalized MWCNTs (Pd/DNA@MWCNTs)

Multi walled carbon nanotubes oxide was synthesized using solution of H_2SO_4 and H_2O_2. The DNA-functionalized MWCNTs have been prepared using Qu's strategy follows the steps described in Scheme 1.[1] The stDNA was heated at 95 °C for 1−2 h to obtain single-stranded DNA. The CO_2H-MWCNTs dispersion was mixed with single-stranded DNA (10 mL, 2 mg mL^{-1}), and $NaBH_4$ was added (8 μL, 75 wt %; $NaBH_4$/ MWCNTs-O); the mixture refluxed at 100 °C for 1 h. Then, the solution was centrifuged and washed several times with double-distilled water and dried in vacuum overnight at 60 ºC. The aqueous solution (0.5 M) of palladium(II) acetate and HCl was prepared and added to aqueous solution of the

DNA@MWCNTs and then 20 μL of freshly prepared $NaBH_4$ solution (5 mg/200 μL H_2O) was added and stirred for only 1 min at room temperature. Then, the solution was centrifuged and the solid was washed several times with double-distilled water and ethanol to remove the unreacted palladium diacetate and dried in the vacuum overnight at 60 ºC to afford the desired catalyst.

1.3. General procedure for the Heck reaction of aryl halides with olefins

Aryl halide (1 mmol) was added to a stirred mixture of KOH (3 mmol), olefin (1.5 mmol) and DMF:H_2O (1:2, 3 mL), followed by adding 5 mg of catalyst. The mixture was then stirred at 50 °C in an oil bath, and the extent of the reaction was monitored by TLC (thin-layer chromatography, n-hexane / ethyl acetate, 5:1) and gas chromatography (GC). After completion of the reaction, the mixture was diluted with dichloromethane and water. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. Finally, the product was isolated by chromatography on a column of silica gel (n-hexane / ethyl acetate, 5:1) to obtain the corresponding products. The products were characterized by comparing their physical properties m.p., IR, ^1H, ^{13}C NMR spectra with those found in the literatures.[2,3]

2.4. General procedure for the Heck reaction of aryl iodide with 2,3-dihydrofuran

The Pd/DNA@MWCNTs (10 mg) was dispersed in THF (2 mL) by sonication and then aryl iodide (1 mmol), 2,3-dihydrofuran (1.5 mmol) and Li_2CO_3 (1.5 mmol) was added and stirred at 50 ºC for 48 h. After completion, the reaction mixture was diluted with hexane (5 mL) and the catalyst was separated by centrifuging. The isomeric ratio of the product was determined by GC before purification. In final, the residue was purified by column chromatography (n-hexane / ethyl acetate, 6:1) to afford the products. All the products are known and their structures were secured on the basis of their analytical and/or spectral data, compared with literature data.[4,5]

2. Characterization of catalyst

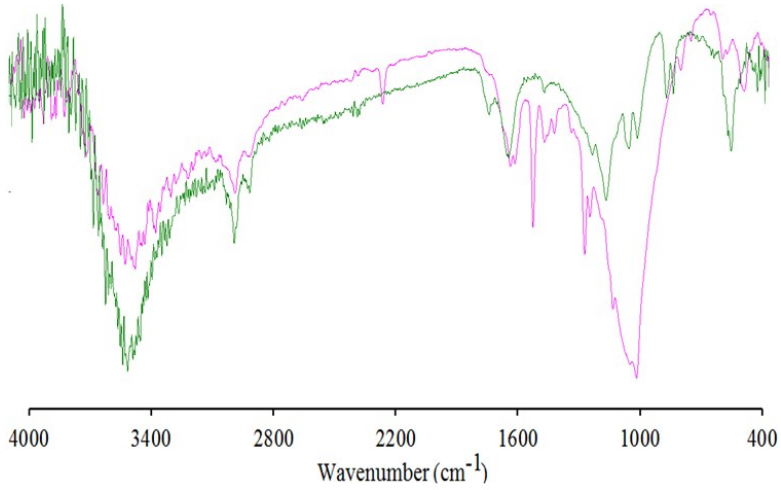


Figure S1. The FT-IR spectra of MWCNT-COOH (green) and Pd/DNA@MWCNTs (pink)

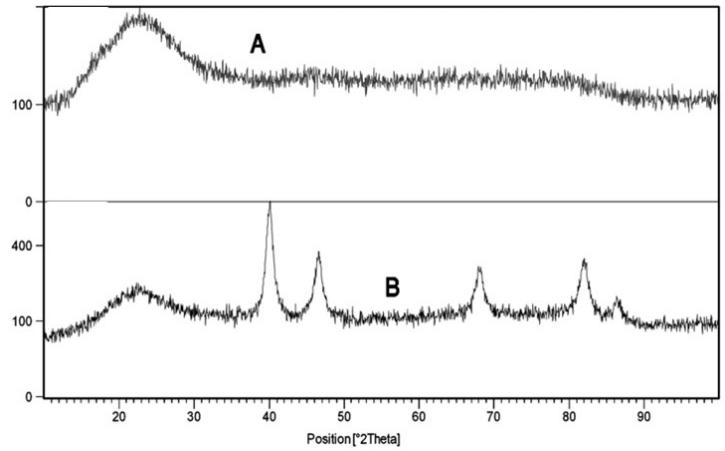


Figure S2. XRD pattern of the MWCNTs up (A) and Pd/DNA@MWCNTs down (blue)

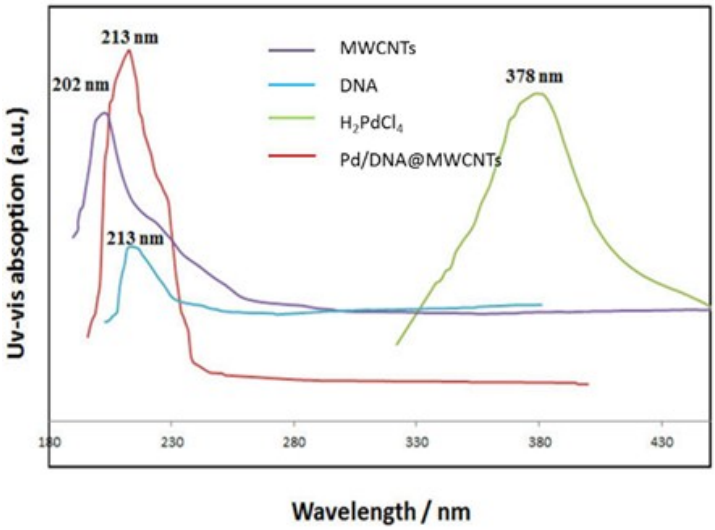


Figure S3. UV−vis absorption of MWCNT-COOH (violet), DNA (blue), H_2PdCl_4 (green), Pd/DNA@MWCNTs (red).

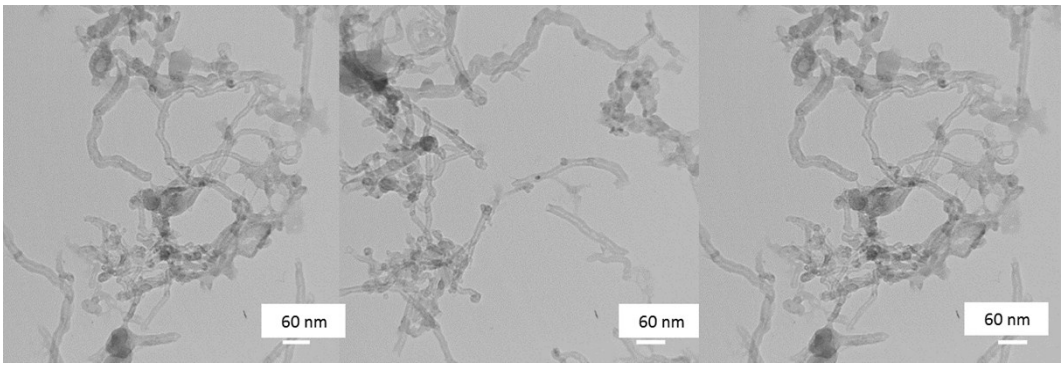
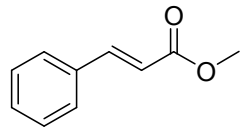
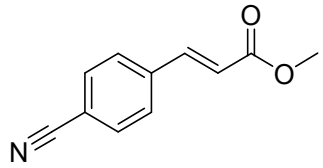


Fig. S4. TEM image of Pd/DNA@MWCNTs recovered after nine run

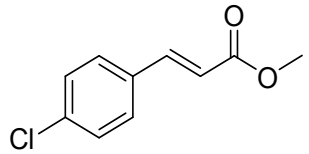
3. Characterization of products



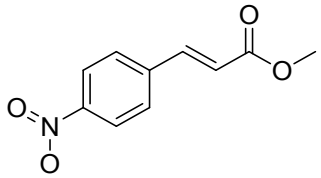
Methyl cinnamate, Yellow solid; m.p. 34 ºC; ^{1}H NMR (500 MHz, ppm, $CDCl_3$, TMS) δ = 7.69 (d, J=0.16 Hz, 1H), 7.55 -7.35 (m, 5H), 6.43 (d, J= 0.16 Hz, 1H), 3.79 (s, 3H). IR (KBr, cm^{-1}): ν =685 ,770 ,1167 ,1205 ,1458 ,1641 ,1718 ,2841 ,2944 ,3069.



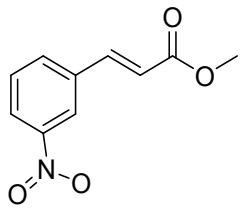
Methyl 3-(4-cyanophenyl)acrylate, White solid; mp 111-114 ºC; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.57-7.70 (m, 5H), 6.62 (d, J= 16. 1Hz, 1H), 6.48 (d, J= 16.1 Hz, 1H), 3.81 (s, 3H). IR (KBr, cm^{-1}): ν = 3011, 2961, 2869, 1723, 1641, 1322, 832, 549.



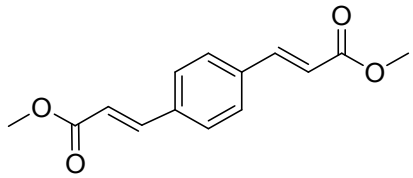
Methyl 3-(4-chlorophenyl)acrylate, Yellow solid, mp 73-75 ºC; ^{1}H NMR (500 MHz, $CDCl_3$, ppm, TMS): δ = 7.59 (d, J= 16.0 Hz, 1H), 7.40 (d, J= 8.4 Hz, 2H), 7.30 (d, J= 8.4 Hz, 2H), 6.34 (d, J= 16.0 Hz, 1H), 3.79 (s, 3H). IR (KBr, cm^{-1}): ν = 3031, 3005, 2948, 1769, 1635, 1491, 1315, 1201, 1002, 829, 305.



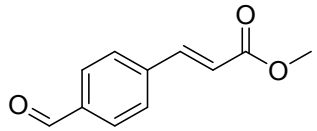
Methyl 3-(4-nitrophenyl)acrylate, Yellow solid, mp 159-160 ºC; ^{1}H NMR (500 MHz, $CDCl_3$, ppm, TMS): δ = 8.54 (m, 2H), 7.64 (m, 3H), 6.58 (d, J= 16 Hz, 1H), 3.86 (s, 3H). IR (KBr, cm^{-1}): ν = 2956, 1718, 1640, 1512, 1343, 841.



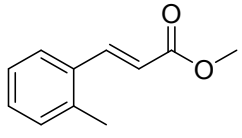
Methyl 3-(3-nitrophenyl)acrylate, Yellow solid, mp 158-159 ºC; ^{1}H NMR (500 MHz, $CDCl_3$, ppm, TMS): δ = 8.36 (s, 1H), 8.19 (d, J= 8 Hz, 1H), 7.79 (d, J= 8 Hz, 1H), 7.68 (d, J= 16 Hz, 1H), 7.58 (m, 1H), 6.52 (d, J= 16 Hz, 1H), 3.82 (s, 3H). IR (KBr, cm^{-1}): 3089, 2961, 1709, 1641, 1526, 1357, 1211, 992, 814, 747.



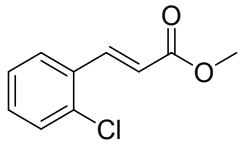
Methyl 3-(4- methyl acrylate)acrylate, White solid; ^{1}H NMR (500 MHz, $CDCl_3$, ppm, TMS): δ = 8.14 = (d, J= 16 Hz, 2H), 7.21 (s, 4H), 6.87 (d, J= 16 Hz, 2H), 3.89 (s, 6H). IR (KBr, cm^{-1}): ν = 3001, 2945, 1709, 1630, 1326, 1206, 1181, 1002, 832.



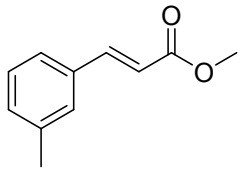
Methyl 3-(4-formylphenyl)acrylate, White solid; mp 82-84 ºC, ^{1}H NMR (500 MHz, $CDCl_3$, ppm, TMS): δ = 10.02 (s, 1H), 8.01 (d, J= 8.0 Hz, 2H), 7.69 (d, J= 15.9 Hz, 1H),7.69 (d, J= 8.0 Hz, 2H), 6.61 (d, J= 15.9 Hz, 1H), 3.85 (s, 3H).



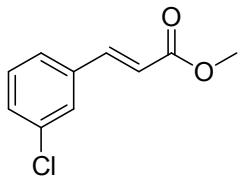
Methyl 3-o-tolylacrylate, yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$, ppm, TMS): δ = 7.96 (d, J= 15.0 Hz, 1H), 7.53 (d, J= 6.0 Hz, 1H), 7.23 (m, 3H), 6.34 (d, J= 15.0 Hz, 1H), 3.81 (s, 3H), 2.46 (s, 3H).



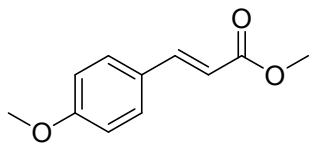
Methyl 3-(2-chlorophenyl)acrylate, yellow liquid, ^{1}H NMR (500 MHz, $CDCl_3$, ppm, TMS): δ = 8.04 (d, *J*= 16 Hz, 1H), 7.61 (d, *J*= 7.3 Hz, 1 H), 7.38 (d, *J*= 7.3 Hz, 1H), 7.29 (m, 2H), 6.41 (d, *J*= 16Hz, 1H), 3.89 (s, 3H).



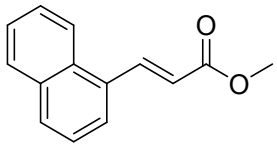
Methyl 3-m-tolylacrylate, yellow liquid, ^{1}H NMR (500 MHz, $CDCl_3$, ppm, TMS): δ = 7.65 (d, J= 16 Hz, 1H), 7.32 (m, 2H), 7.25 (m, 1H), 7.19 (m, 1H), 6.39 (d, J= 16 Hz, 1H), 3.84 (s, 3H), 2.34 (s, 3H).



3-(3-Chloro -phenyl)-acrylic acid methyl ester, yellow liquid, ^{1}H NMR (500 MHz, $CDCl_3$, ppm, TMS): δ = 7.67 (d, J= 16 Hz, 1H), 7.48 (s, 1H), 7.38 (m, 2H), 6.48 (d, J= 16 Hz, 1H), 3.84 (s, 3H).

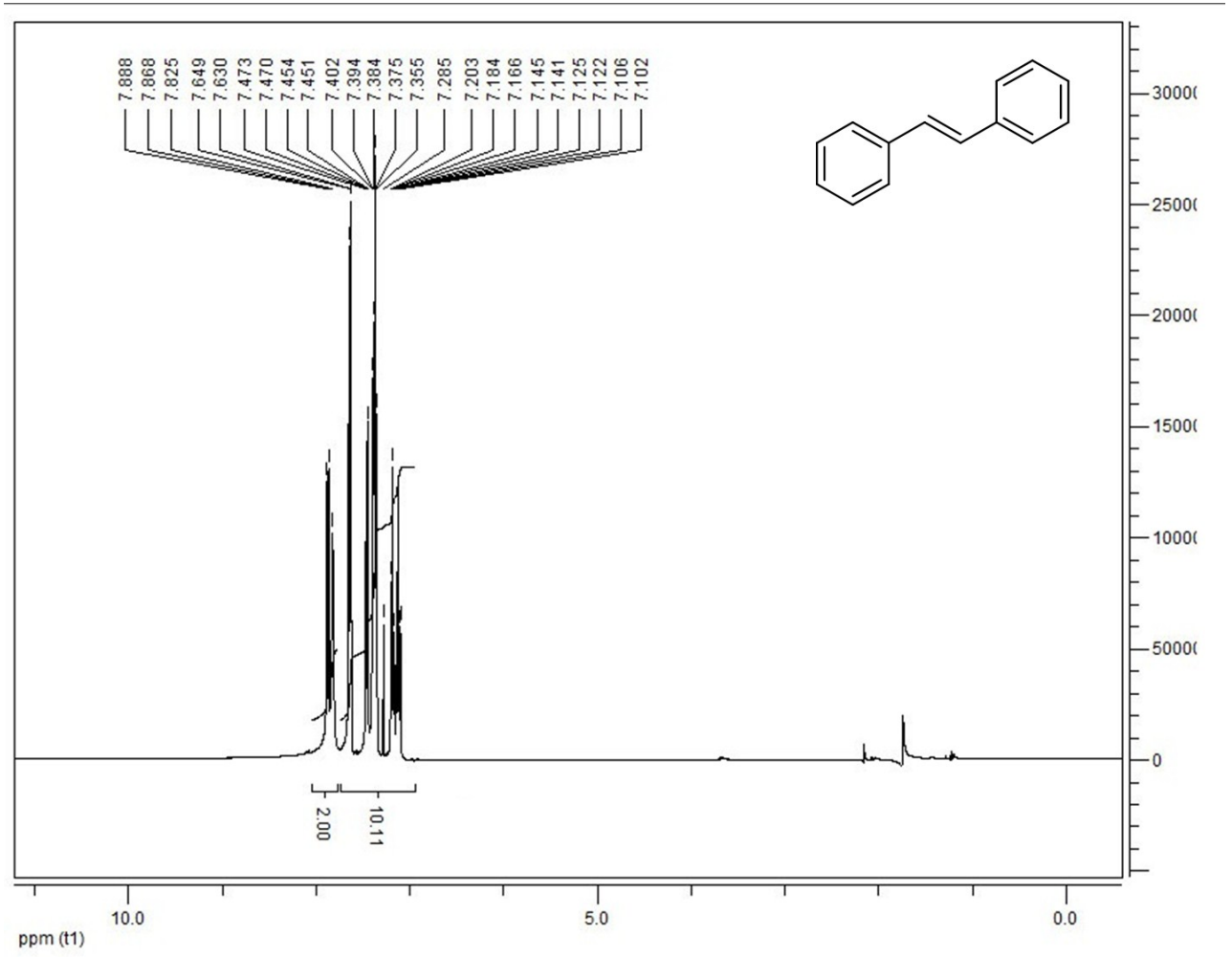


Methyl 3-(4-methoxyphenyl)acrylate, Yellow solid, mp 88 ºC, ^{1}H NMR (500 MHz, $CDCl_3$, ppm, TMS): δ = 7.62 (d, J= 16 Hz, 1H), 7.43 (d, J= 7 Hz, 2H), 6.87 (d, J= 7 Hz, 2H), 6.29 (d, J= 16 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H). IR (KBr, cm^{-1}), 3031, 1987, 2958, 2934, 1708, 1638, 1601, 1290, 1202, 1031, 983.

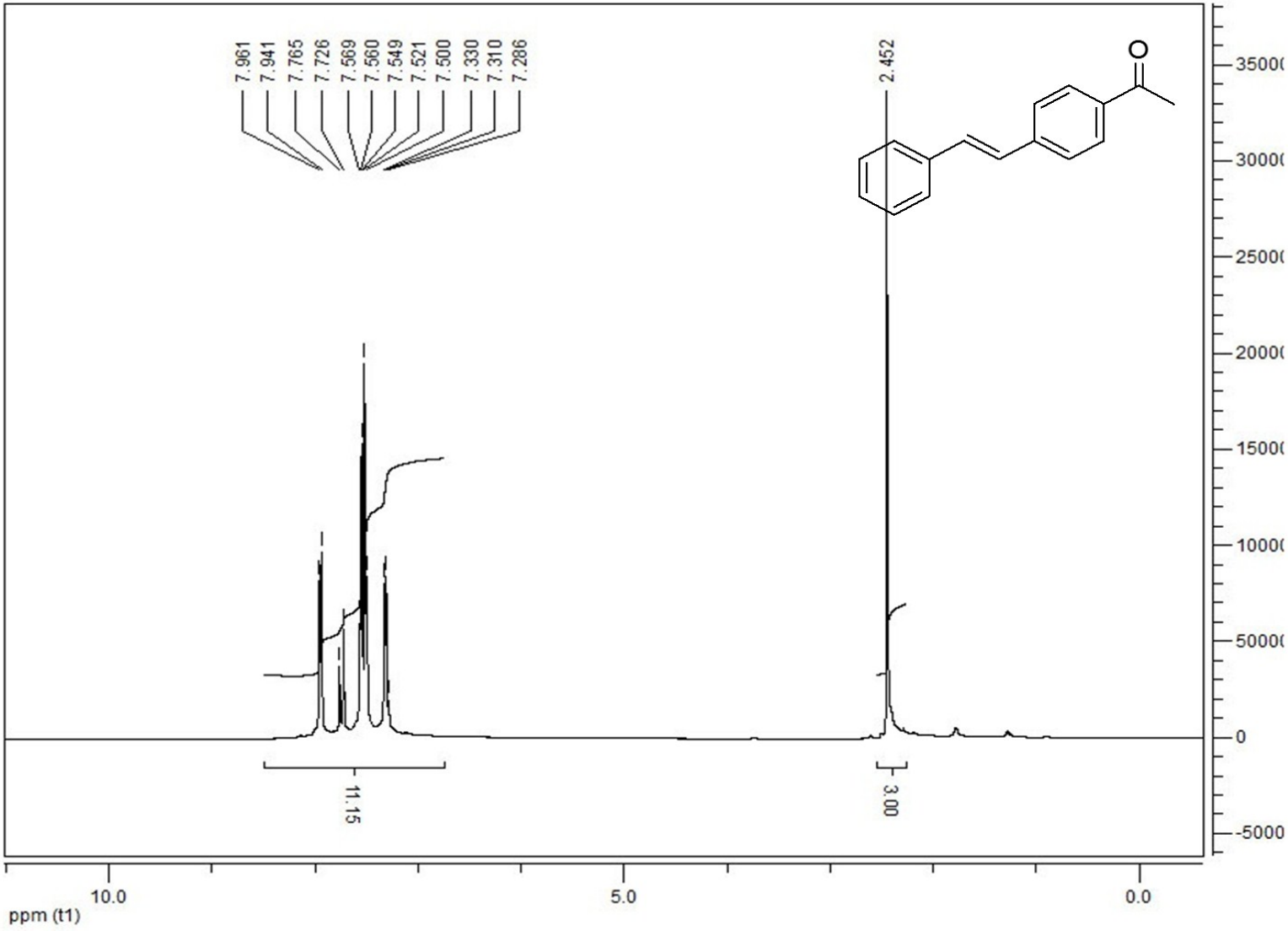


Methyl 3-(naphthalen-4-yl)acrylate, yellow liquid, ^{1}H NMR (500 MHz, $CDCl_3$, ppm, TMS): δ = 8.51 (d, J= 16 Hz, 1H), 8.17 (m, 1H), 7.85 (m, 2H), 7.68 (d, J= 7 Hz, 1 H), 7.62 (m, 3H), 6.53 (d, J= 16 Hz, 1H), 3.82 (s, 3H).

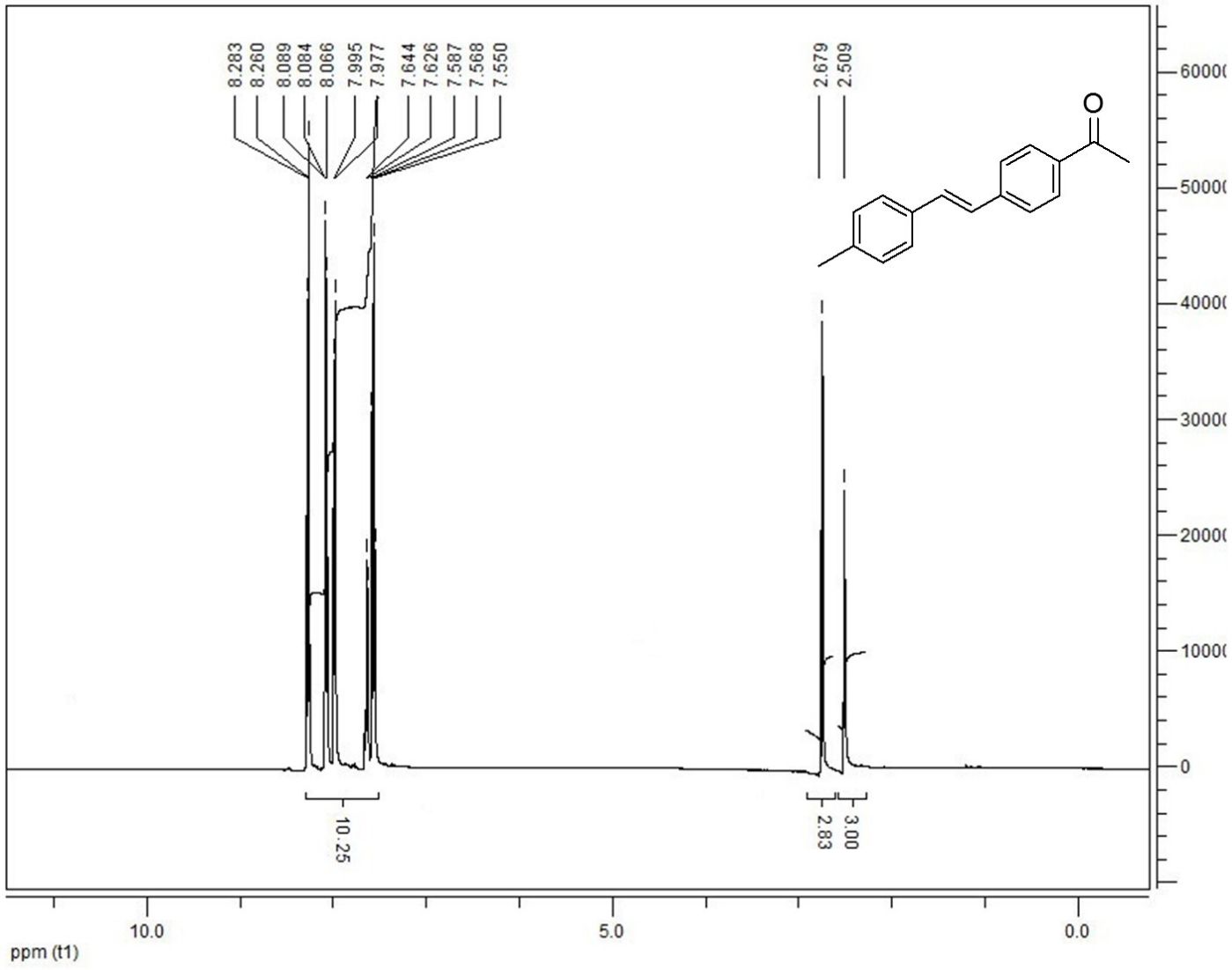
Selected spectra



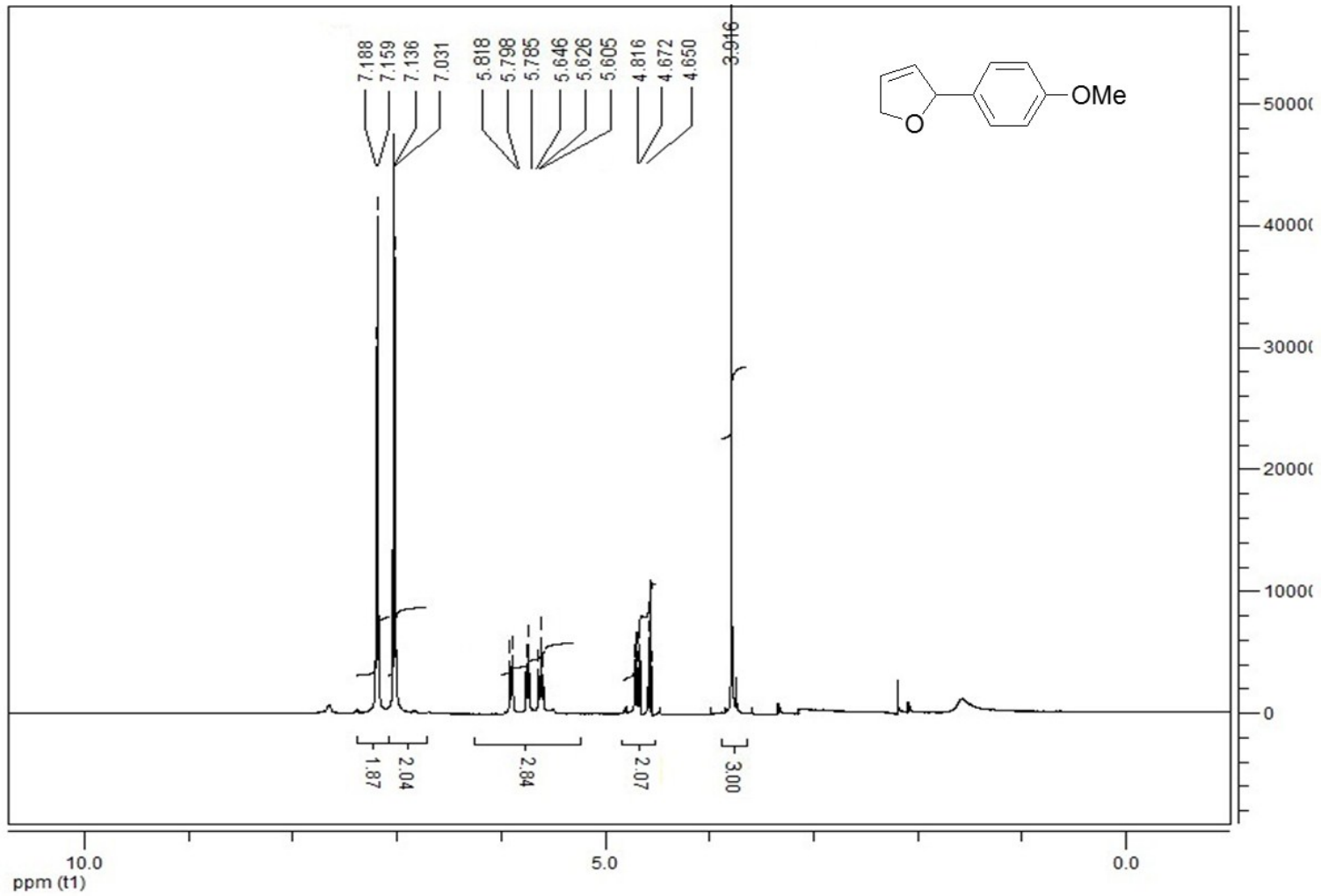
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of (E)-stilbene



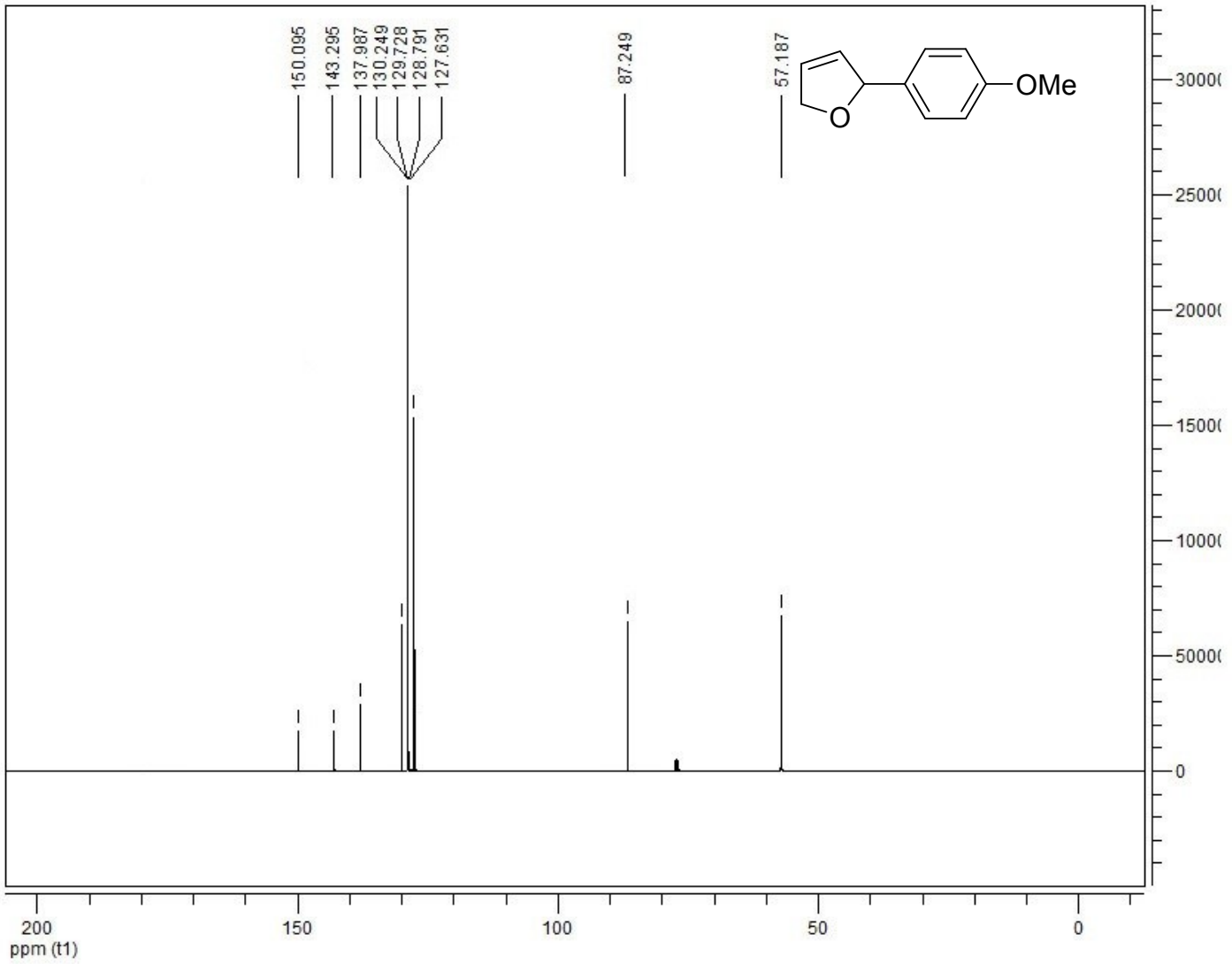
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of 1-(4-styryl phenyl)ethanone



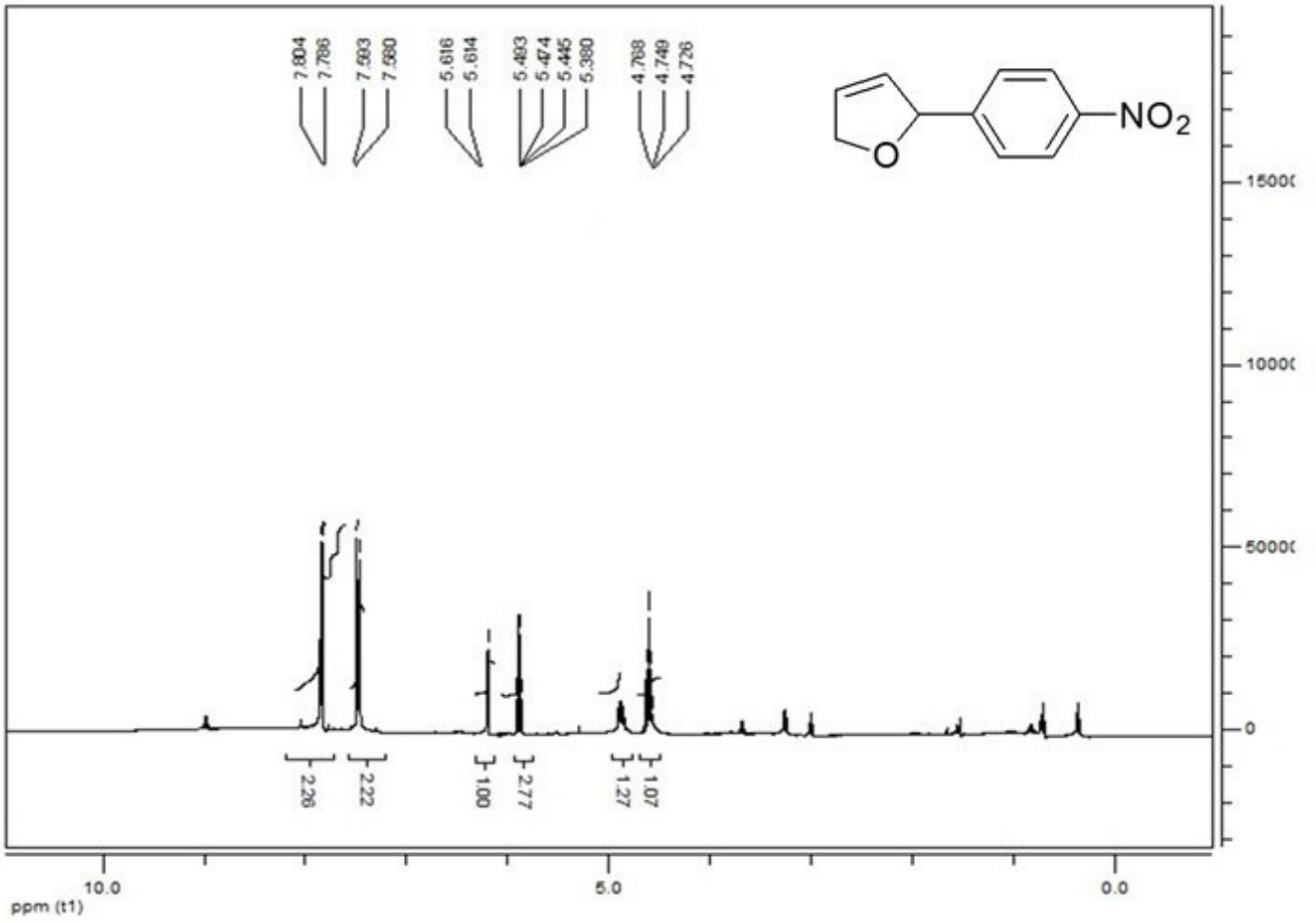
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of 4-(4-methylstyrene)acetophenone



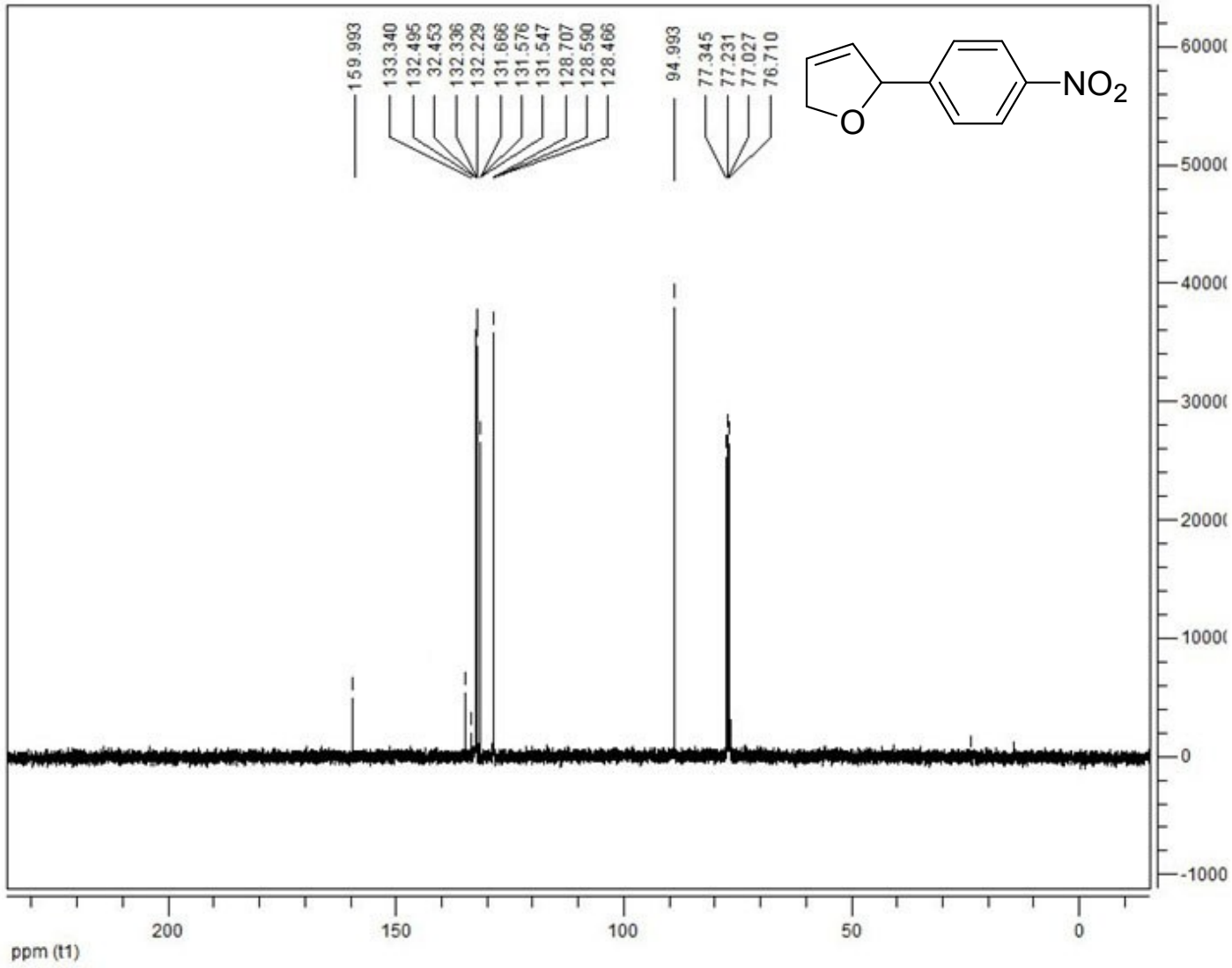
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of 2-(p-anisyl)-2,5-dihydrofuran



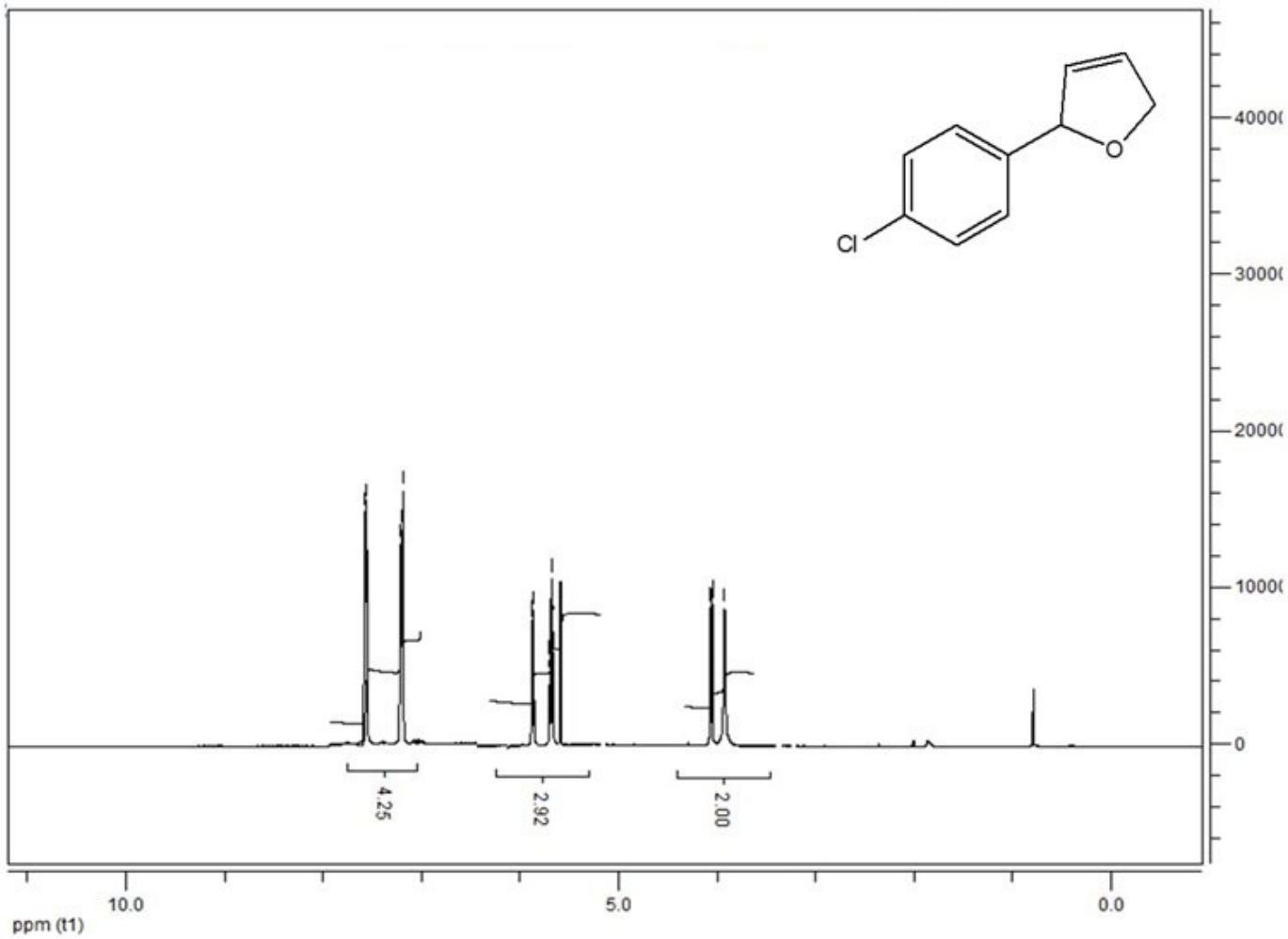
^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of 2-(p-anisyl)-2,5-dihydrofuran



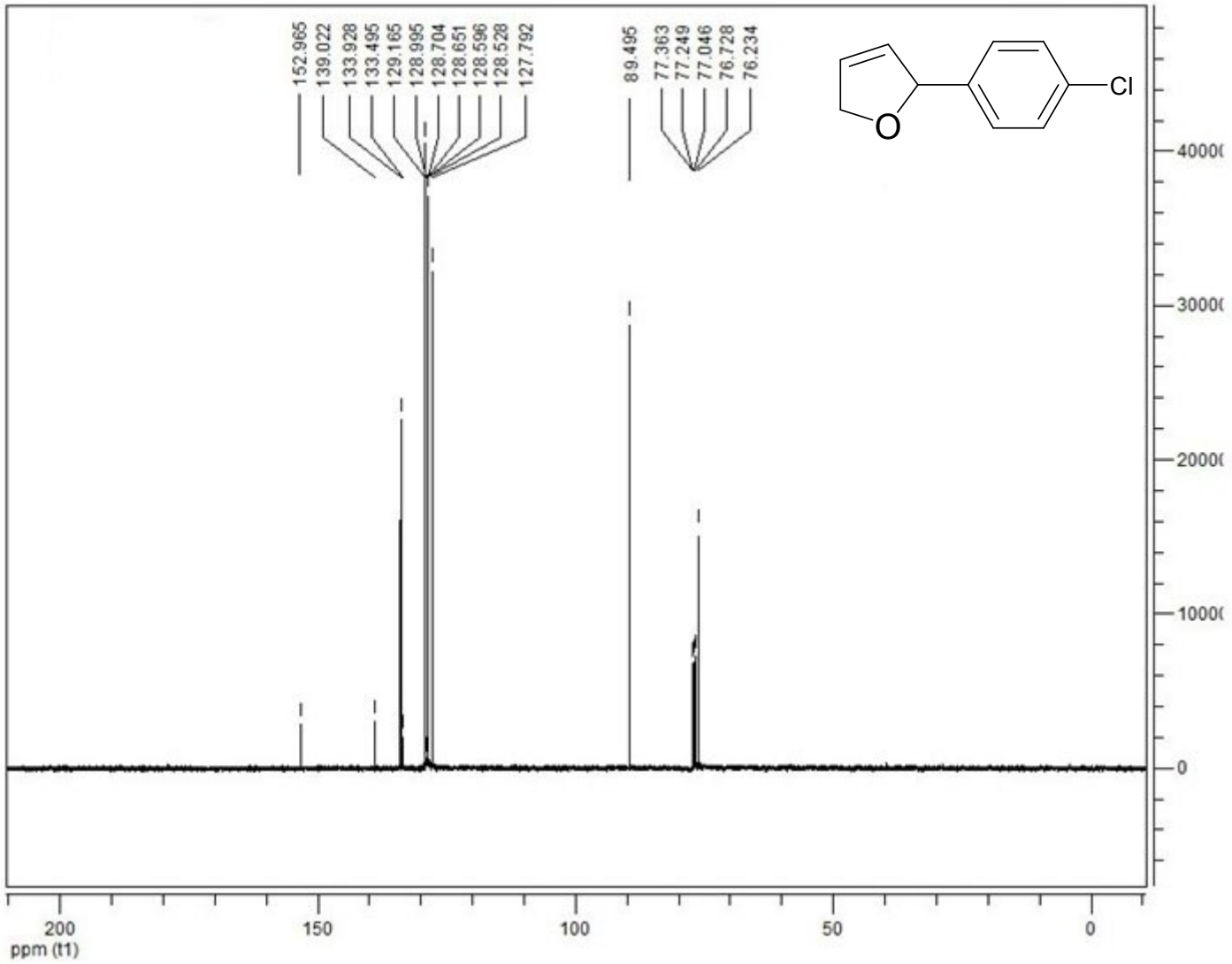
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of 2-(4-nitro-phenyl)-2,5-dihydro-furan (3c).



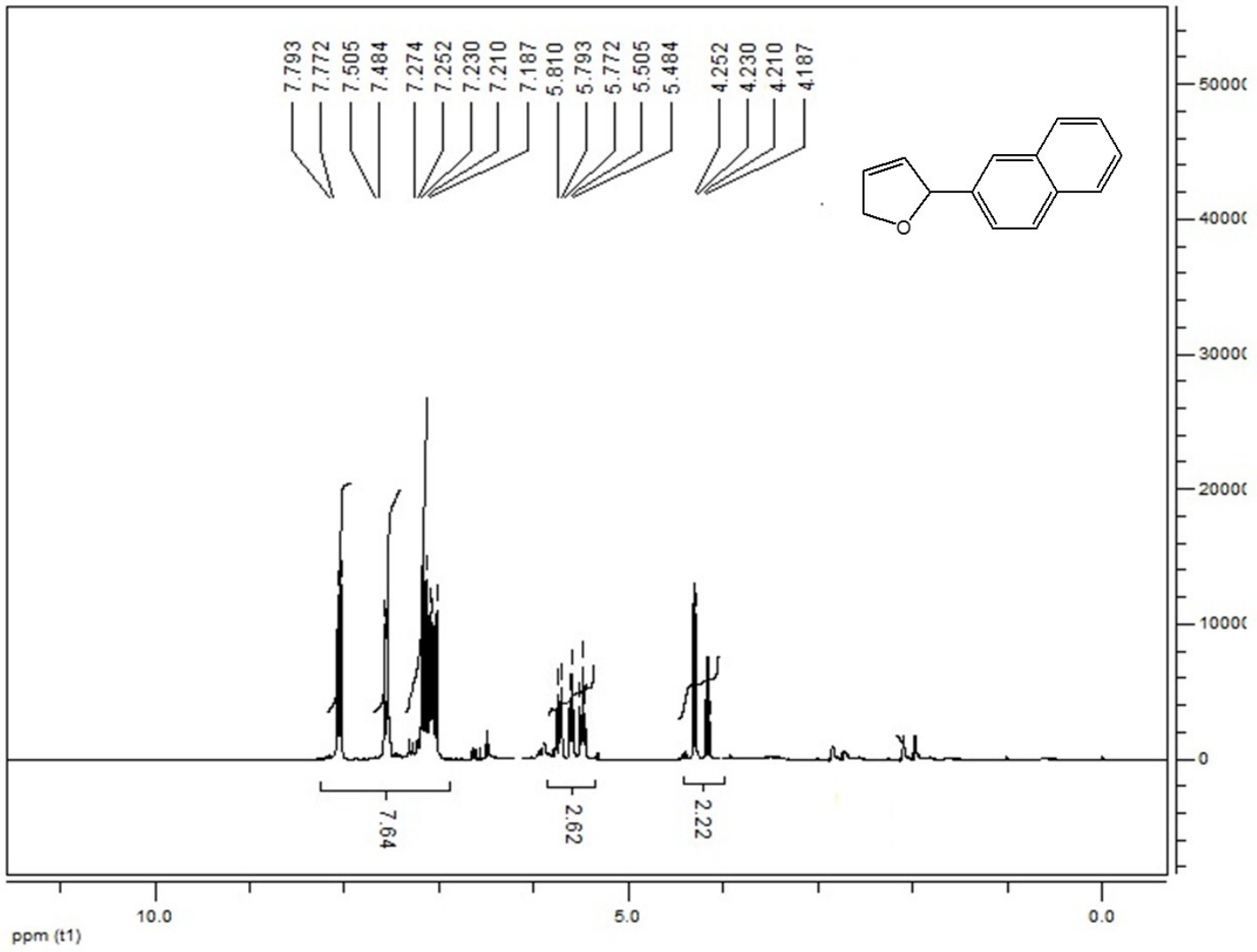
^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of 2-(4-nitro-phenyl)-2,5-dihydro-furan (3c).



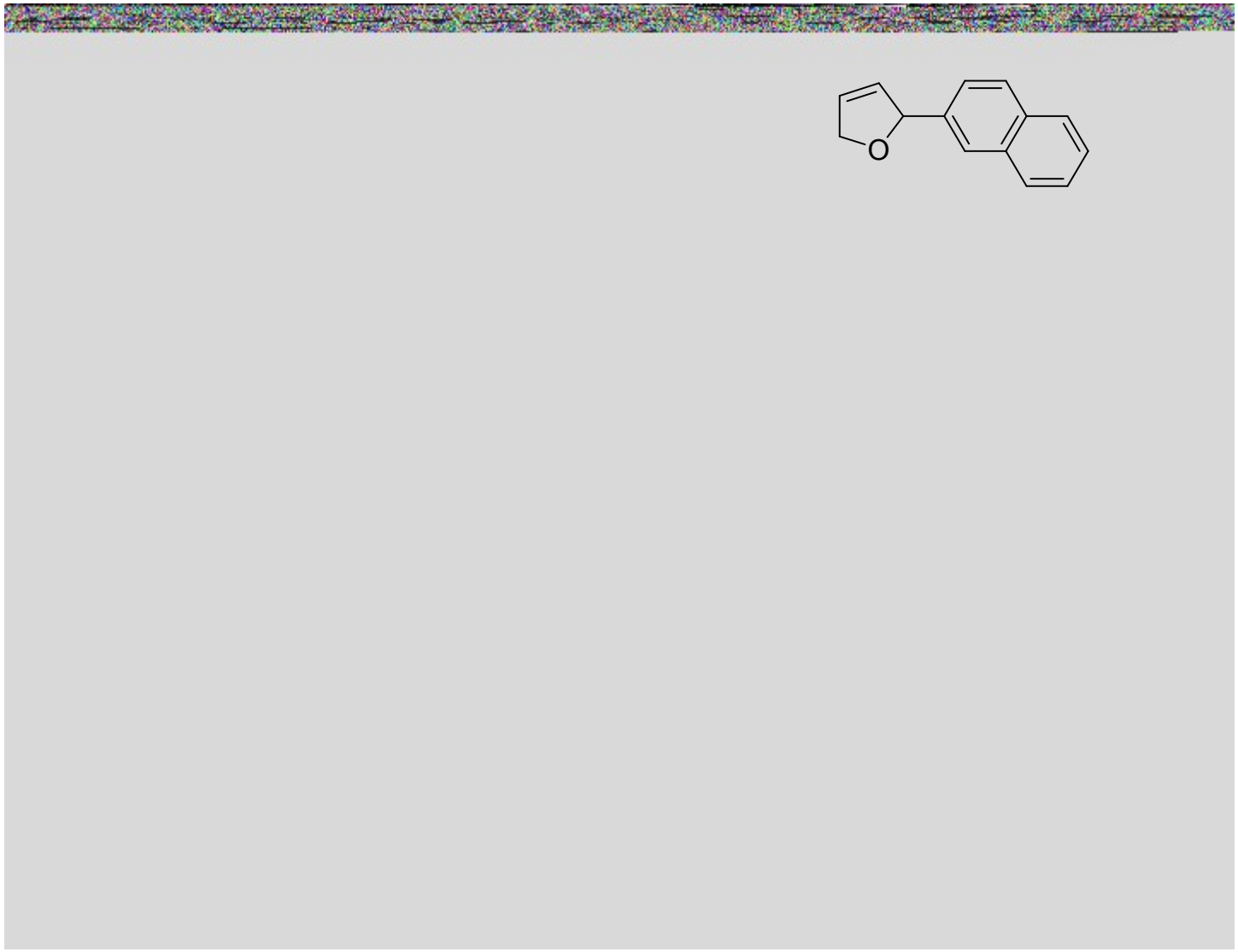
1H NMR Spectrum (500 MHz, CDCl3) of 4-(4-methylstyrene)acetophenone



^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of 4-(4-methylstyrene)acetophenone



^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of 2-(1-naphthyl)-2,5-dihydrofuran



^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of 2-(1-naphthyl)-2,5-dihydrofuran

Reference

1. Qu, K.; Wu. L.; Ren. J.; Qu, X. *ACS Appl Mater Inter*, **2012**, *4*, 5001−5009.
2. Hajipour, A. R.; Azizi, G.; *Green Chem*., **2013**, *15*, 1030–1034.
3. Isfahani, A. L.; Baltork, I. M.; Mirkhani, V.; Khosropour A. R.; Moghadam, M.; Tangestaninejad, S.; Kia, R. *Adv. Synth. Catal*. **2013**, *355*, 957–972.
4. Lauer, M. G.; Thompson, M. K.; Shaughnessy, K. H. *J. Org. Chem.* **2014**, *79*, 10837–10848.
5. Wu, C.; Zhou, J. *J. Am. Chem. Soc*. **2014**, *136*, 650−652.
6. Tu, T.; Deng, W. P.; Hou, X. L.; Dai, L. X.; Dong, X. C. *Chem. Eur. J*. **2003**, *9*, 3073-3081.