Controlled synthesis of uniform palladium nanoparticles on novel micro-porous carbon as a recyclable heterogeneous catalyst for Heck reaction

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† Electronic Supplementary Information (ESI) available: Experimental details of the synthesis of C-(KTB-Pd), C-(KB-Pd), C-(CPR-Pd). XPS characterises, Pore size distribution and 1H NMR data. See DOI: 10.1039/b000000x

Experiment section

Materials: Benzene, $FeCl_3$ (anhydrous), methanol and 1,2-dichloroethane (DCE) were obtained from National Medicines Corporation Ltd of China, all of which were of analytical grade and were used as received. Chloromethyl Polystyrene Resin (CPR, Aladdin, 100-200 mesh), Formaldehydedimethyl acetal (FDA, Alfa Aesar, 98%) and 1,3,5-triphenylbenzene (AlfaAesar,98%) were also used as received.

Synthesis of KB: $FeCl_3$（anhydrous 9.75g, 0.06mol） was added to a solution of benzene (1.56g, 0.02mol) and FDA (4.56g, 0.06mol) in 20 mL DCE. The resulting mixture were stirred at room temperature for good mix, and then were stirred at 45°Cfor 5h to form original network, and then heated at 80°C for 19 h to react completely. The resulting precipitate was washed three times with methanol, then washed with methanol in a Soxhlet for 24 h, and finally dried under reduced pressure at 60°C for 24 h.

Synthesis of KTB: $FeCl_3$（anhydrous 4.87 g, 0.03mol） was added to a solution of 1,3,5-Triphenylbenzene (1.53g, 0.005mol) and FDA (2.28g, 0.03mol) in 10mL DCE. The resulting mixture were stirred at room temperature for good mix, and then were stirred at 45 °C for 5h to form original network, and then heated at 80°Cfor 19h to react completely. The resulting precipitate was washed three times with methanol, then was washed with methanol in a Soxhlet for 24h, and finally dried under reduced pressure at 60°C for 24h.

Prepared C-(KTB-Pd) catalyst: The C-(KTB-Pd) catalyst was prepared using an impregnation method. In a typical synthesis, 10 mg $PdCl_2$ was dissolved in 2 ml acetonitrile at a flask, after the solution changed to bright yellow, 80 mg of KTB was dispersed in it and mixing for 12h, the suspension was centrifugal separation and washed by acetone for three times. The slurry was dried in an oven at 60°C for 6h, than the resulting powder was heated in a tube furnace at 500°C under flowing N_2 for 4 h, the heating rate is 2^{o}C/min and then reduction at 400°C under an H_2 atmosphere for 2h. At last the sample was cooled to room temperature at a N_2 atmosphere.

Prepared C-(KB-Pd) catalyst: The C-(KB-Pd) catalyst was prepared using an impregnation method. In a typical synthesis, 10 mg $PdCl_2$ was dissolved in 2 ml acetonitrile at a flask, after the solution changed to bright yellow, 80 mg of KB was dispersed in it and mixing for 12h, the suspension was centrifugal separation and washed by acetone for three times. The slurry was dried in an oven at 60°C for 6h, than the resulting powder was heated in a tube furnace at 500°C under flowing N_2 for 4 h, the heating rate is 2^{o}C/min and then reduction at 400°C under an H_2 atmosphere for 2h. At last the sample was cooled to room temperature at a N_2 atmosphere.

Prepared C-(CPR-Pd) catalyst: The C-(CPR-Pd) catalyst was prepared using an impregnation method. In a typical synthesis, 10 mg $PdCl_2$ was dissolved in 2 ml acetonitrile at a flask, after the solution changed to bright yellow, 80 mg of CPR was dispersed in it and mixing for 12h, the suspension was centrifugal separation and washed by acetone for three times. The slurry was dried in an oven at 60°C for 6h, than the resulting powder was heated in a tube furnace at 500°C under flowing N_2 for 4 h, the heating rate is 2^oC/min and then reduction at 400°C under an H_2 atmosphere for 2h. At last the sample was cooled to room temperature at a N_2 atmosphere.

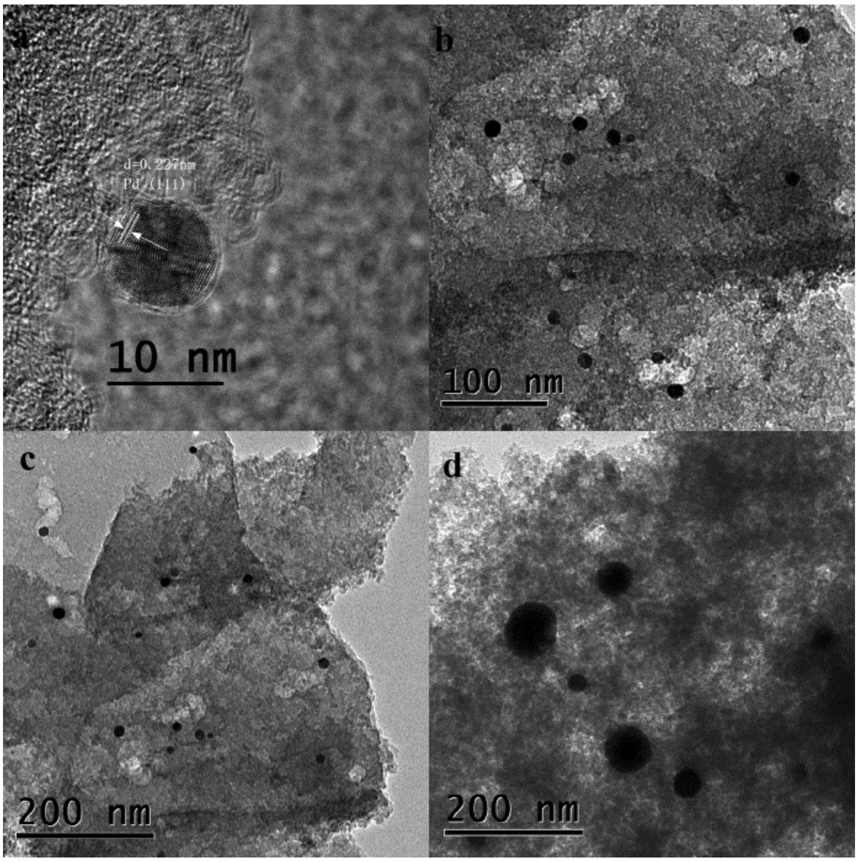


Figure S1.The carbonization of C-(KTB-Pd) at different temperature. a) 500 °C, b) 600 °C, c) 700 °C, and d) 800 °C.

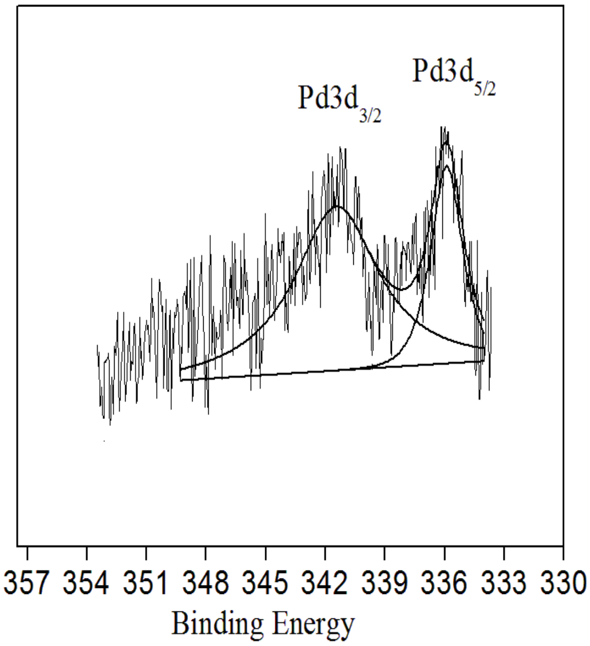


Figure S2. XPS experiments of C-(KTB-Pd)

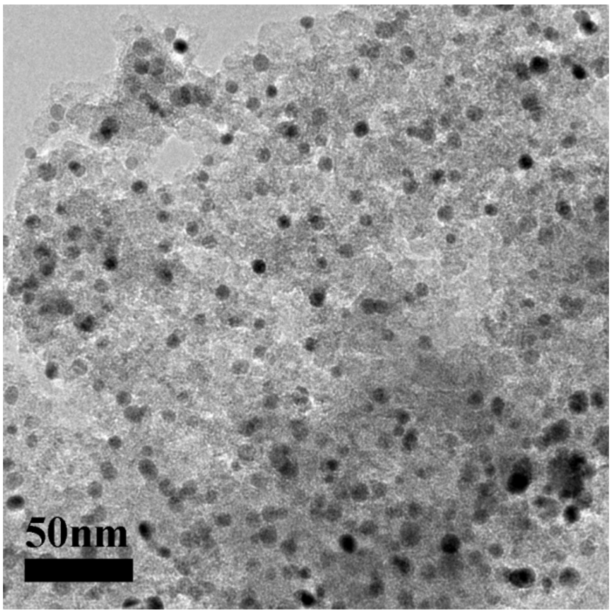


Figure S3 TEM images of C-(KTB-Pd) after recycling for 10 times

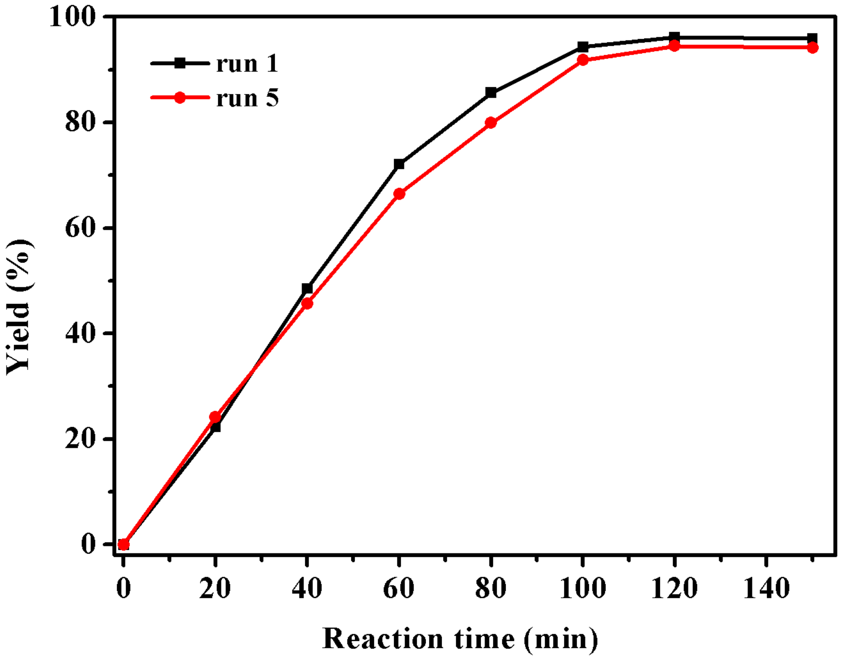
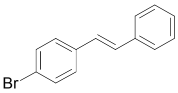


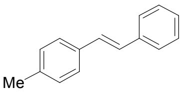
Figure S4 Kinetic studies of catalyst C-(KTB-Pd) in Heck reaction.

Due to Pd catalyst is very activity for Heck reaction. We did kinetic study to research the recycle performance of catalyst C-(KTB-Pd). We select fresh and fifth catalyst make seven groups of parallel test, and stop the reaction at 20, 40, 60 , 80, 100, 120 and 150 minutes. The reaction condition was the same to the manuscript except for reaction time.

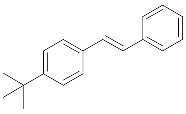
^{1}H NMR



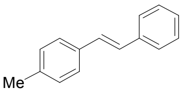
^{1}H NMR ($CDCl_3$, 400 MHz), 7.51-7.46 (m, 4H), 7.38-7.35 (m, 4H), 7.28 (d, 1H), 7.11-7.01 (m, 2H).



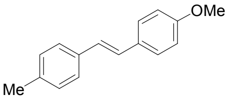
^{1}H NMR ($CDCl_3$, 400 MHz), 7.5 (d, J = 4 Hz, 2H), 7.44 (d, J = 4 Hz, 2H), 7.40 (t, J = 4 Hz, 2H), 7.31-7.28 (t, 3H), 7.22 (d, J = 8 Hz, 2H), 7.16-7.10 (m, 2H), 2.41 (s, 3H).



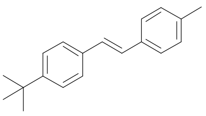
^{1}H NMR ($CDCl_3$, 400 MHz), 7.55-7.49 (m, 4H), 7.43-7.37 (m, 4H), 7.29-7.28 (m, 1H), 7.15-7.09 (m, 2H), 1.37 (s, 9H).



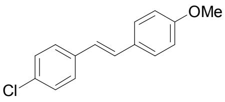
^{1}H NMR ($CDCl_3$, 400 MHz), 7.59 (d, J = 8 Hz, 2H), 7.51 (d, J = 4 Hz, 2H), 7.37 (t, J = 4 Hz, 2H), 7.26 (t, J = 4Hz, 1H), 7.24-7.18 (m, 4H), 2,31 (s, 3H)



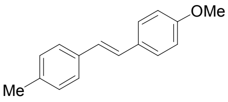
^{1}H NMR ($CDCl_3$, 400 MHz), 7.52 (d, J = 8 Hz, 2H), 7.45 (d, J = 8 Hz, 2H), 7.14-7.04 (m, 4H), 6.94 (d, J = 4 Hz, 2H), 3.77 (s, 3H), 2.30 (s, 3H).



^{1}H NMR ($CDCl_3$, 400 MHz), 7.51-7.49 (dd, J = 4 Hz, 4 Hz, 3H), 7.39 (d, J = 4 Hz, 2H), 7.22-7.16 (m, 5H), 2.31 (s, 3H), 1.29 (s, 9H).



^{1}H NMR ($CDCl_3$, 400 MHz), 7.60-7.54 (m, 4H), 7.41 (d, J = 4 Hz, 2H), 7.23 (d, J = 12 Hz, 1H), 7.10 (d, J = 12 Hz, 1H), 6.96 (d, J = 4 Hz, 1H), 3.77 (s, 3H).



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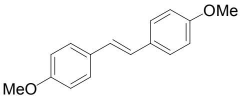
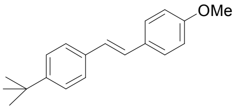
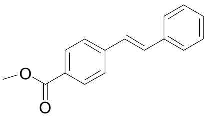


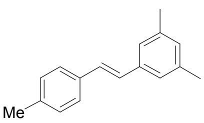
^{1}H NMR ($CDCl_3$, 400 MHz), 7.22 (d, J = 4 Hz, 4H), 6.93 (t, J = 4 Hz, 6H), 3.77 (s, 6H).



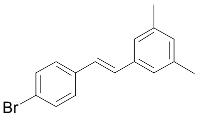
^{1}H NMR ($CDCl_3$, 400 MHz), 7.60-6.80 (m, 10H), 3.75 (d, 3H), 1.28 (s, 9H).



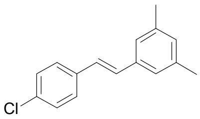
^{1}H NMR (d6-DMSO, 400 MHz), 7.97 (d, J = 4 Hz, 2H), 7.76 (d, J = 4 Hz, 2H), 7.66 (d, J = 4 Hz, 2H), 7.46-7.32 (m, 5H), 3.86 (s, 3H).



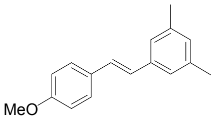
^{1}H NMR ($CDCl_3$, 400 MHz), 7.51 (d, J = 8 Hz, 2H), 7.27-7.24 (m, 4H), 7.20-7.10 (dd, J = 12 Hz, 2H), 7.00 (s, 1H), 2.33 (s,1H), 2.31 (s, 1H).



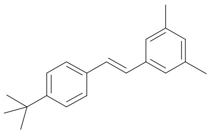
^{1}H NMR ($CDCl_3$, 400 MHz), 7.51-7.48 (m, 1H), 7.44 (d, J = 4 Hz, 1H), 7.36-7.33 (, 2H), 7.26-7.23 (m, 1H), 7.22-7.11 (m, 2H), 7.00 (d, J = 4 Hz, 1H), 6.91 (s, 1H), 2.32 (s, 6H).



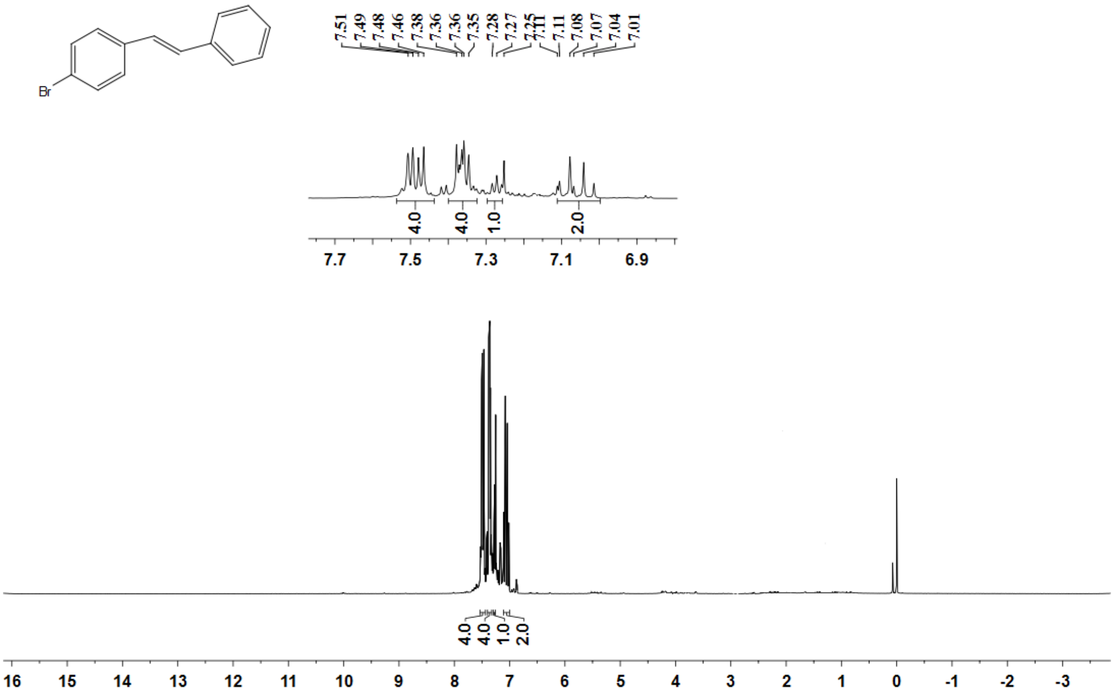
^{1}H NMR ($CDCl_3$, 400 MHz), 7.36 (d, J = 4 Hz, 2H), 7.27 (d, J = 4 Hz, 2H), 7.09 (s, 2H), 6.97 (s, 2H), 6.88 (s, 1H), 2.30 o(s, 6H).



^{1}H NMR ($CDCl_3$, 400 MHz), 7.46 (d, J = 8 Hz, 2H), 7.14 (s, 2H), 7.07 (d, J = 12 Hz, 1H), 6.95-6.91 (m, 4H), 3.84 (s, 3H), 2.35 (s, 6H).



^{1}H NMR ($CDCl_3$, 400 MHz), 7.48 (d, J = 8 Hz, 2H), 7.42 (d, J = 4 Hz, 2H), 7.17 (s, 2H), 7.13-7.04 (dd, 2H), 6.93 (s, 1H), 2.33 (s, 6H), 1.33 (s, 9H).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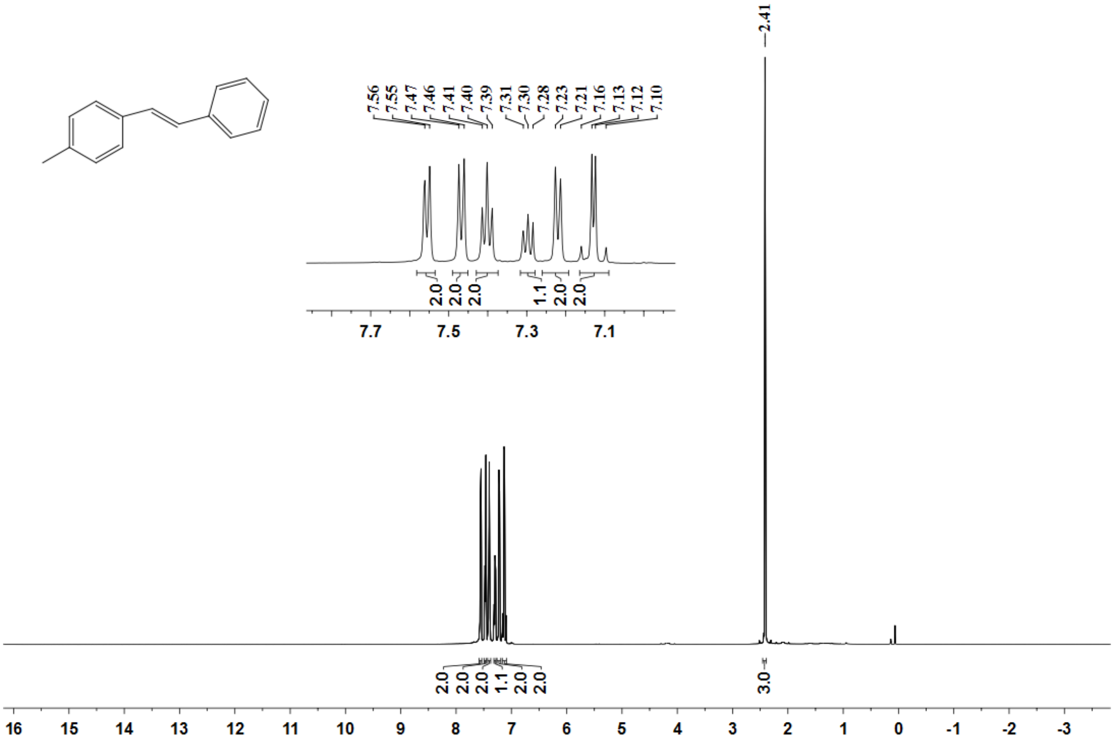
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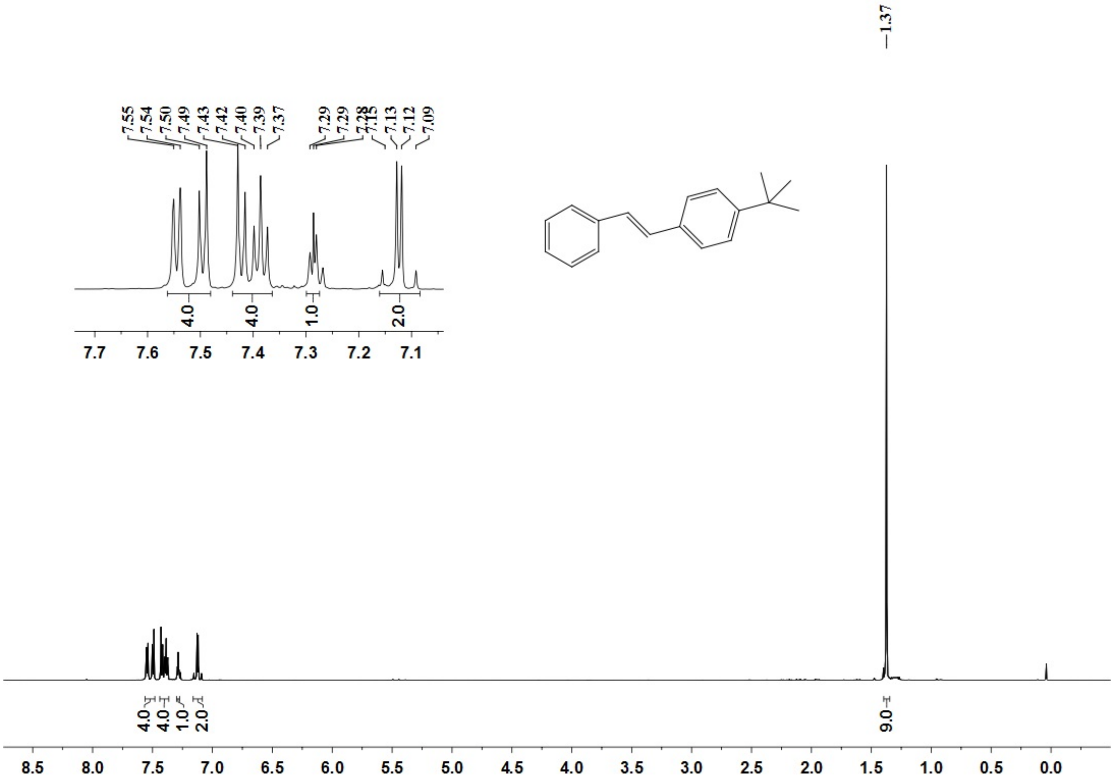

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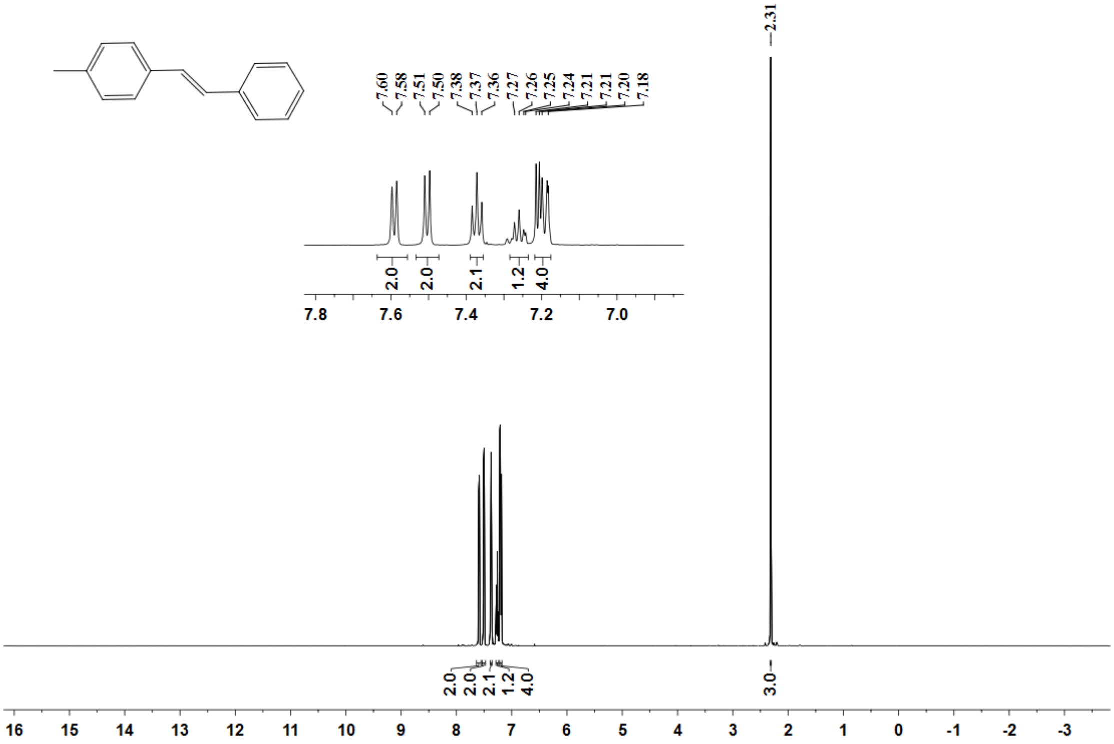

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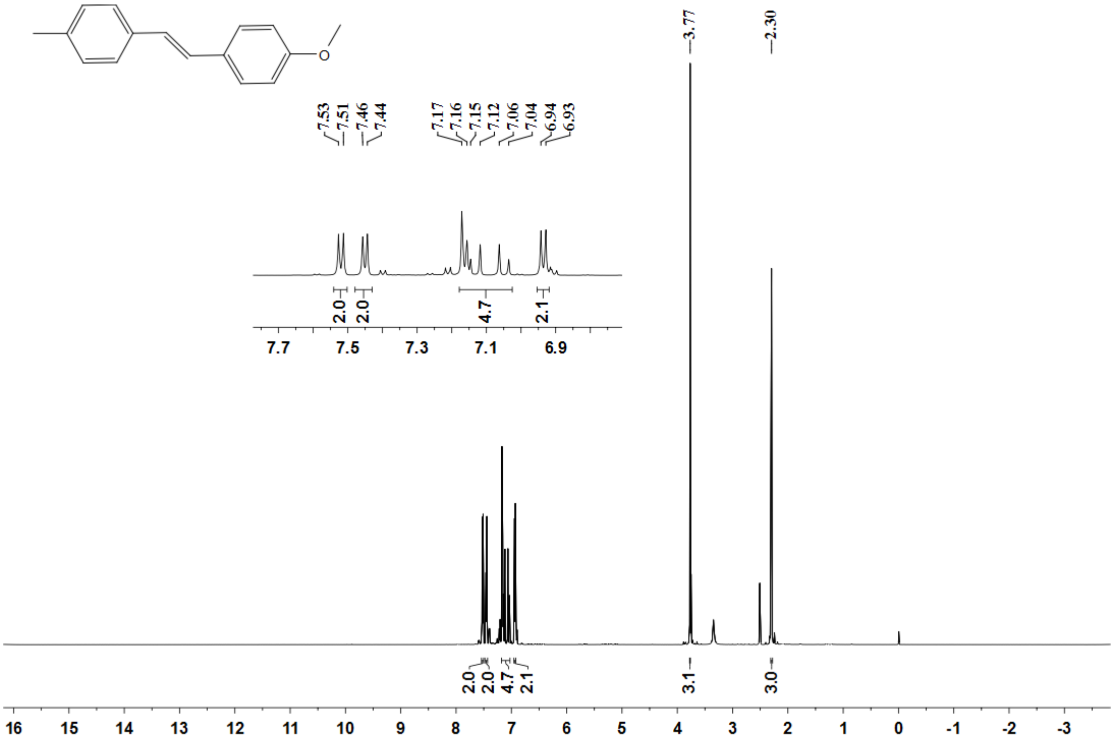
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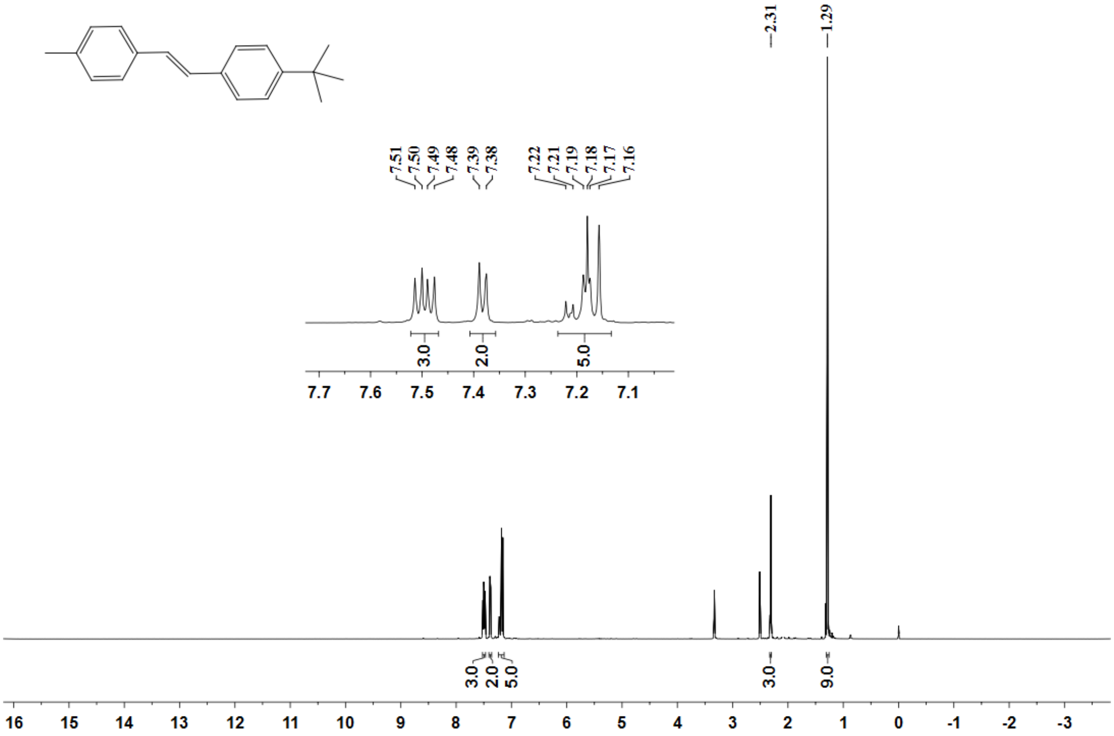
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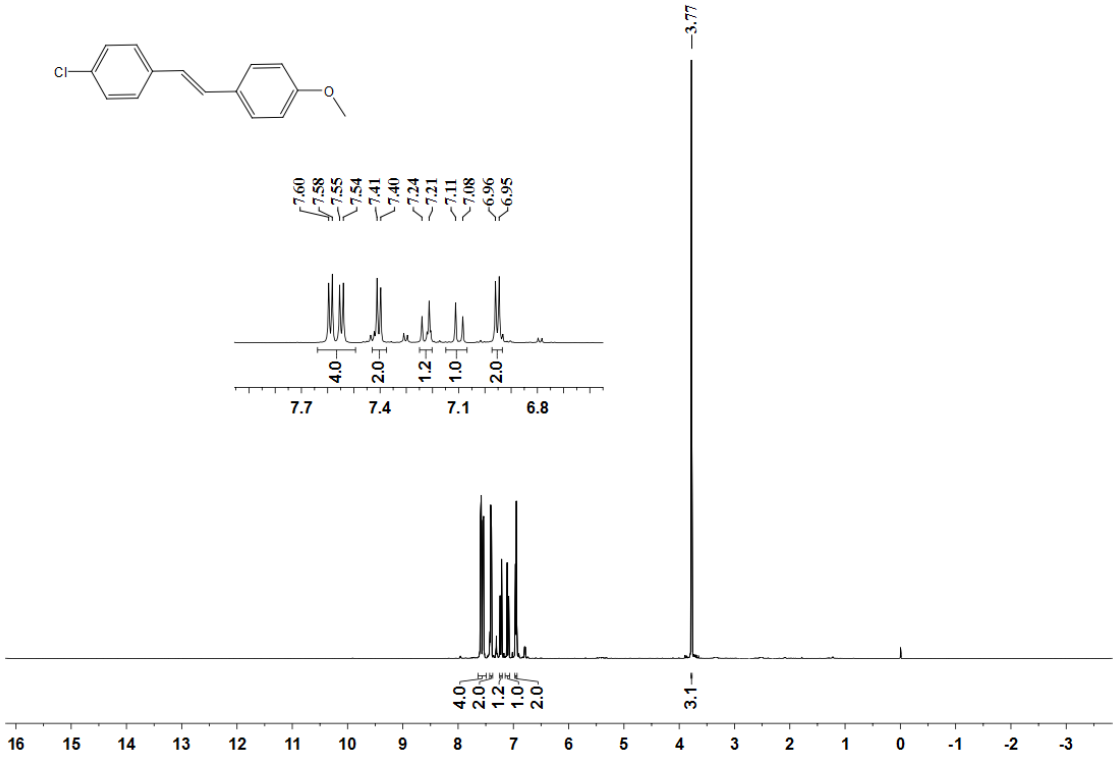
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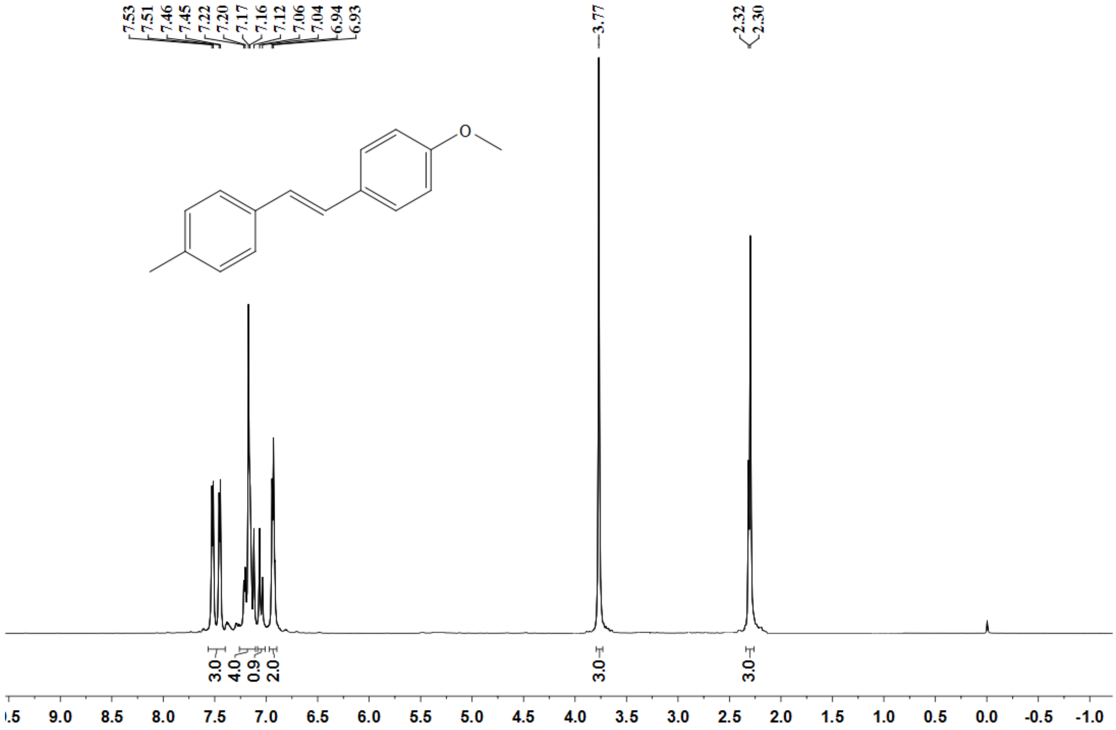
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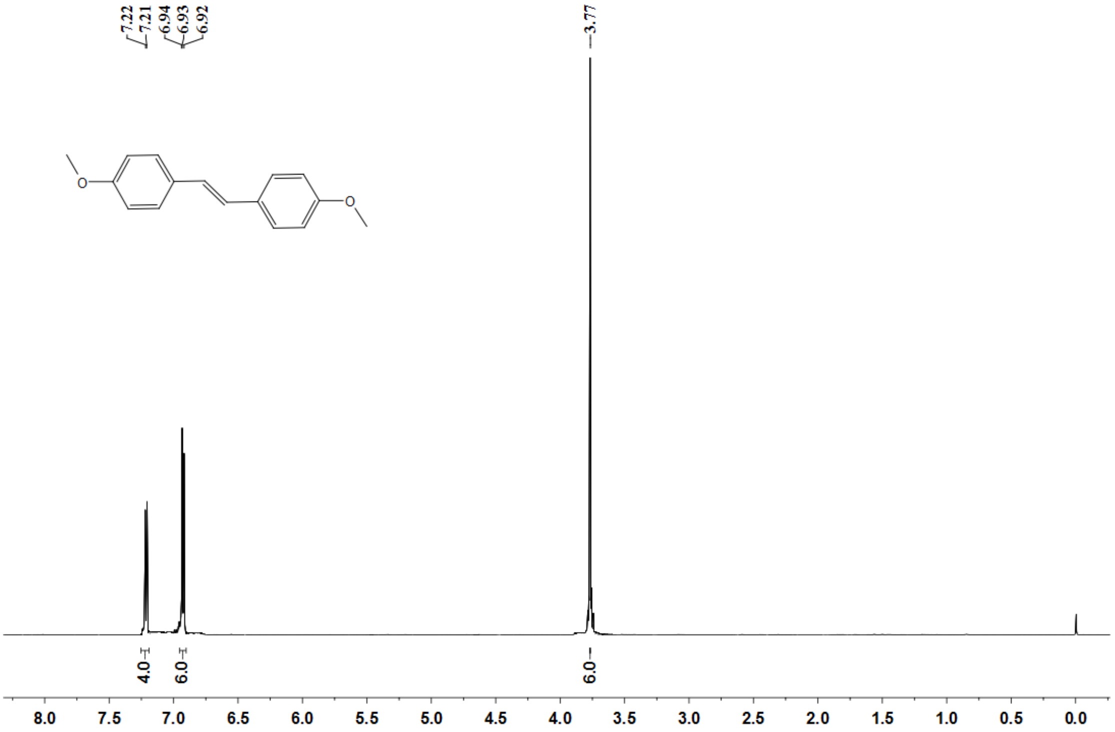
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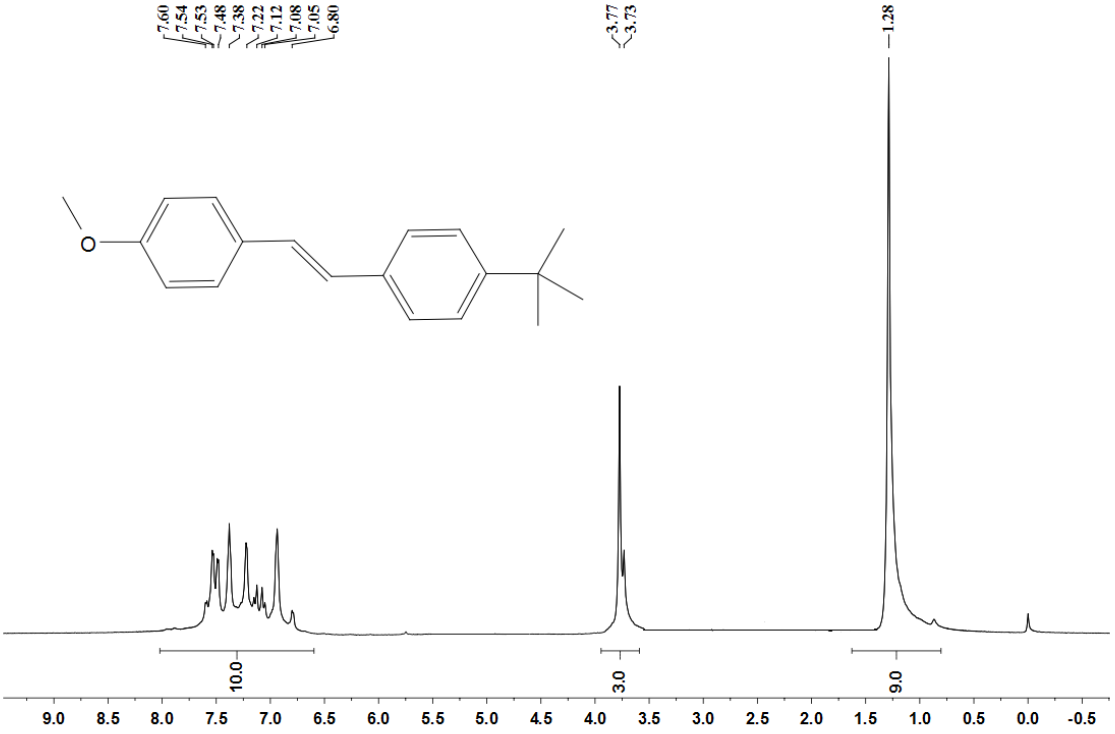
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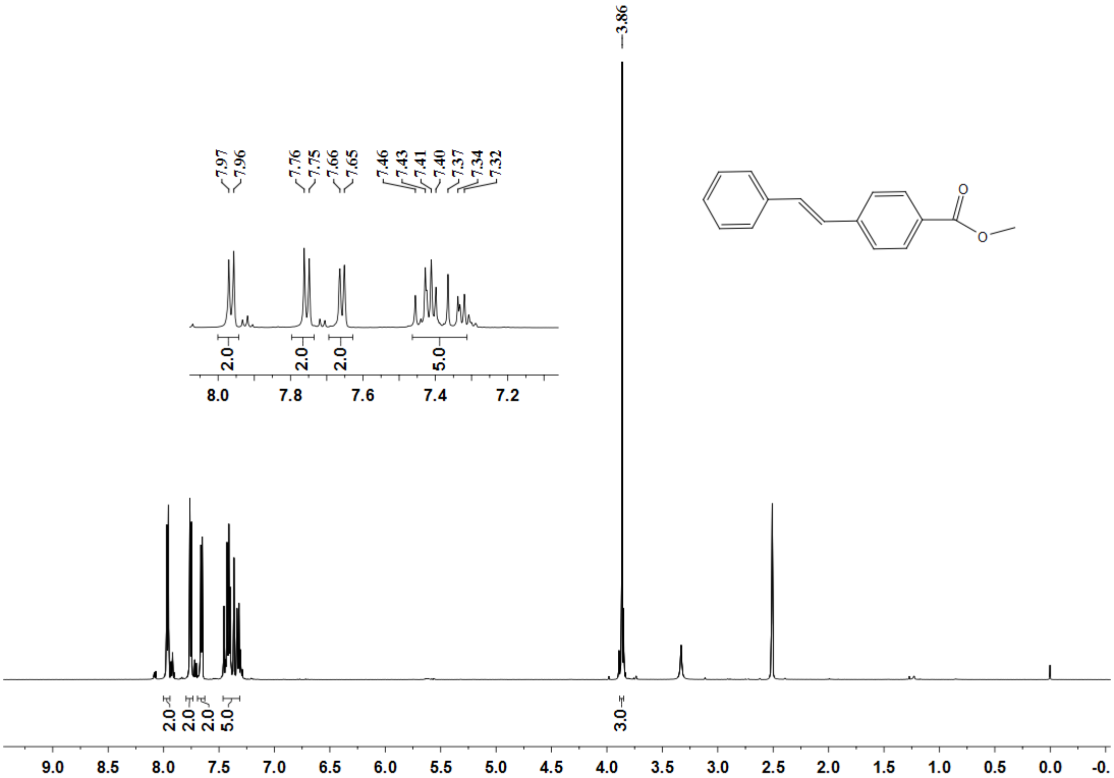
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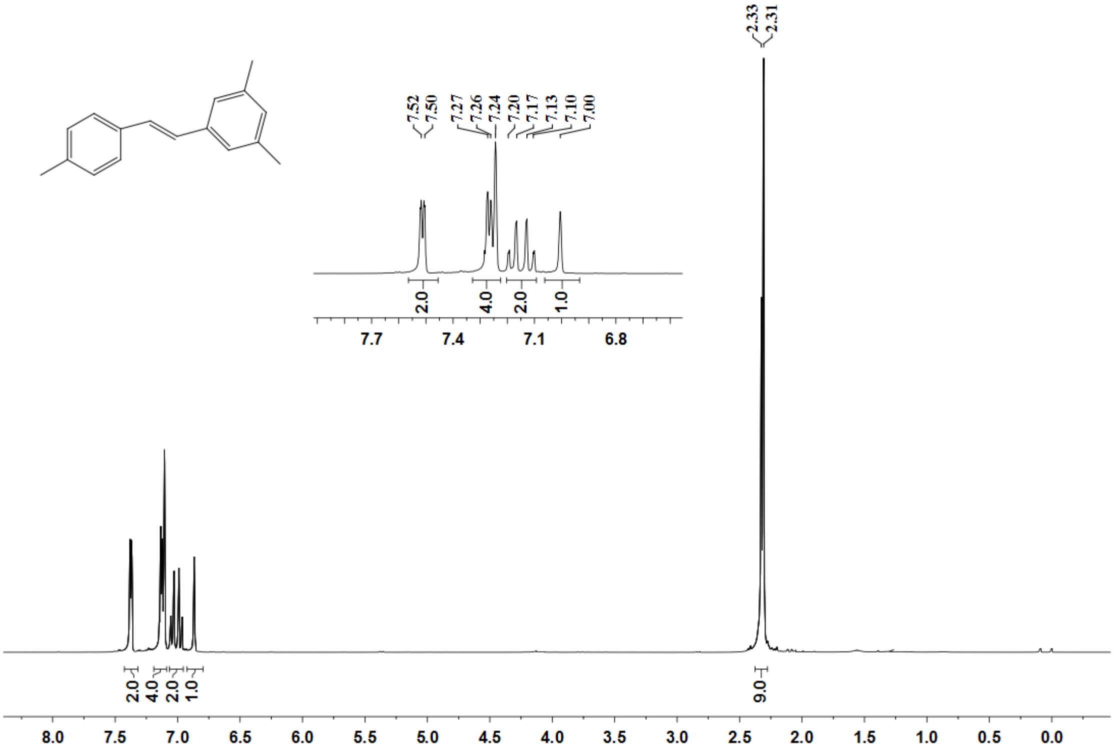
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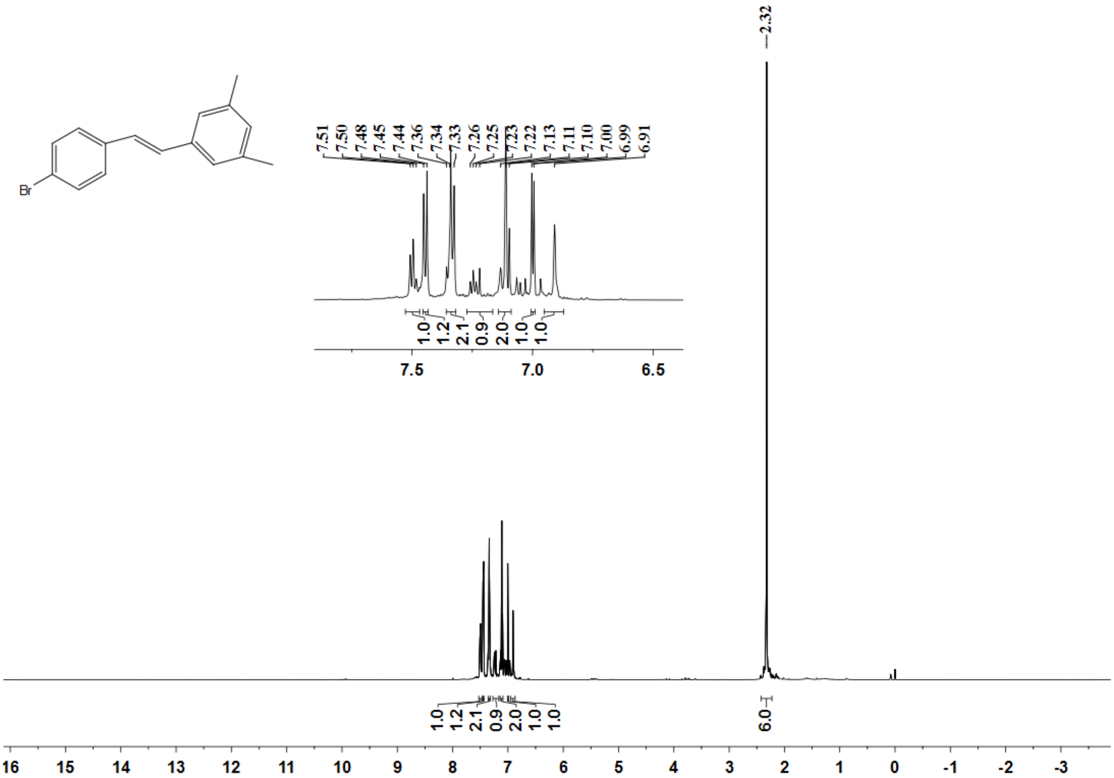
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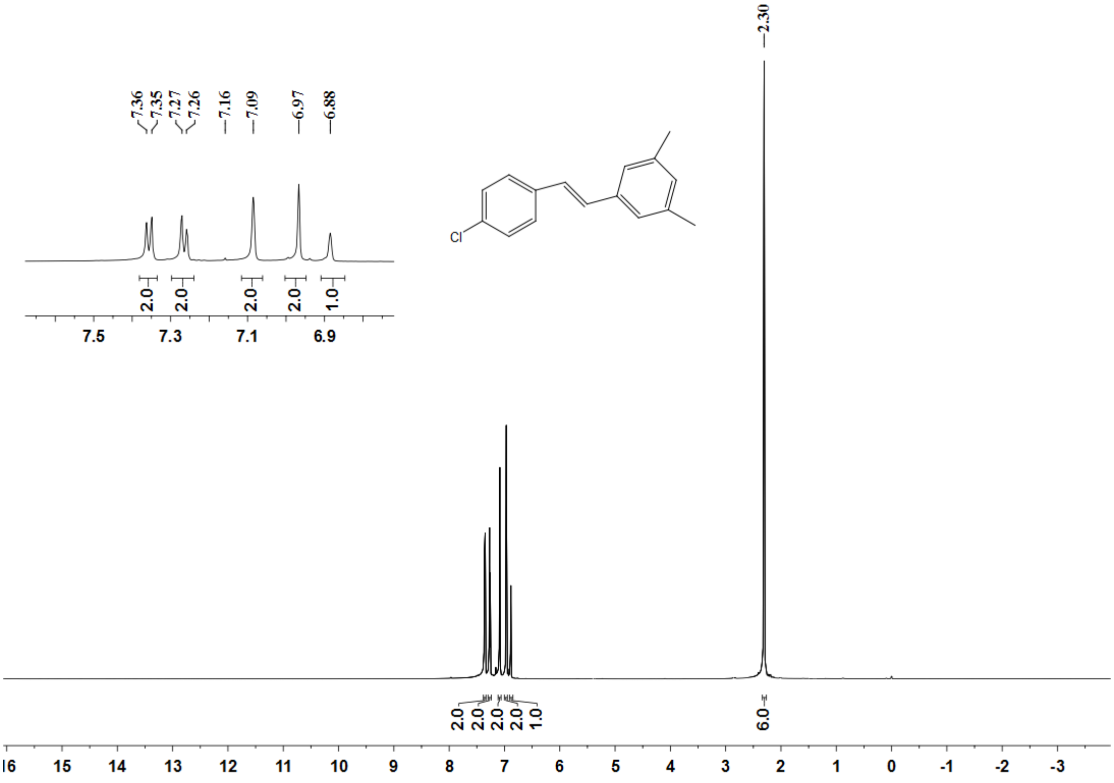
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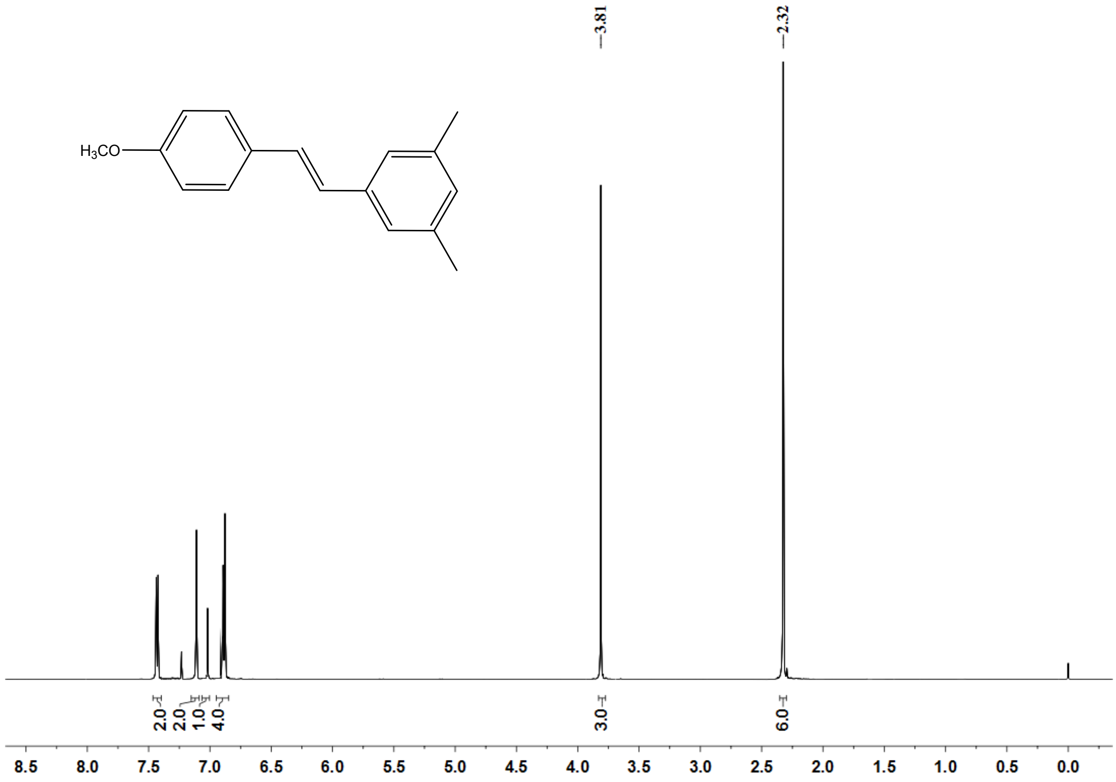

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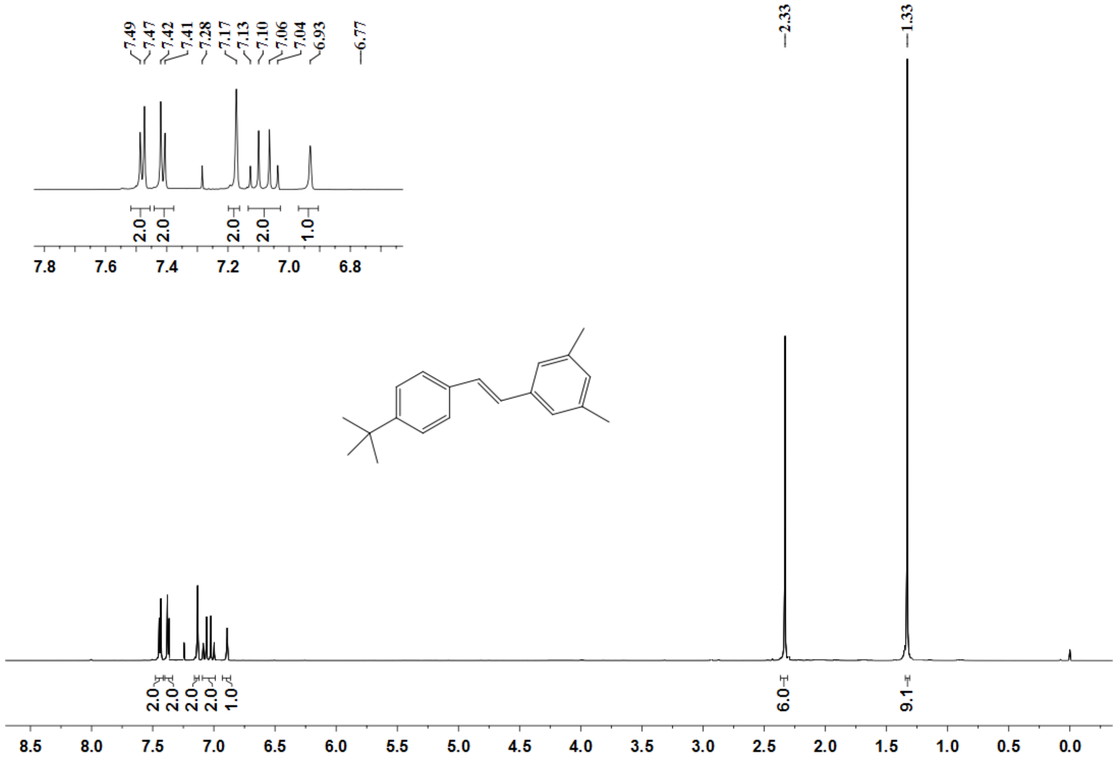

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