

Supporting Information

Novel chitosan-based/montmorillonite/palladium hybrid microspheres as heterogeneous catalyst for Sonogashira reactions

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1. EXPERIMENTAL DETAILS

1.1 Materials

Chitosan was supplied by Zhejiang Aoxing Biotechnology Co., Ltd., China, with a deacetylation degree of 95% and molecular weight of 1.2×10^5 . G-105 type Na-MMT was supplied by Nanocor Co., USA. PdCl_2 was supplied by Zhejiang Metallurgical Research Institute Co., Ltd., China. All the chemical reagents and solvents were in analytical grade and used without further purification.

1.2 Preparation of CS/MMT/Pd hybrid microspheres

Certain amount of CS (0.75g and 0.5g) was dissolved in 100 ml 2 wt% acetic acid solution under magnetic stirring for 2h. Then, certain amounts of MMT (0.25g and 0.5g) was added to the CS solution and stirred for another 2h. Afterwards, 1.5 ml Na_2PdCl_4 solution was carefully dropped into 30 ml CS/MMT blend solution under magnetic stirring. Na_2PdCl_4 solution was prepared as follows: 0.15 g PdCl_2 and 1g NaCl were dissolved in 50 ml deionized water. The resultant CS/MMT/Pd mixing solution was dropped into 5wt% NaOH solution bath with a needle of 0.7 mm in diameter. CS/MMT/Pd hybrid microspheres precipitated quickly in the NaOH solution. The microspheres were filtered out and then washed to pH = 7.0 with deionized water. Finally, the microspheres were dried in 60 °C oven.

1.3 Characterizations of the CS/MMT/Pd hybrid microspheres

Fourier transform infrared spectroscopy (FTIR) analysis of the microspheres was performed with a Nicolet 740 spectrometer (Nicolet Instrument, US) using KBr tablet compressing method. The X-ray diffraction (XRD) analysis of the microspheres was performed with an Empyrean X-ray Diffraction System (Panalytical Company, the Netherlands) at a scanning rate of 10 °/min in the 2θ ranged from 3 to 70 °. Thermogravimetric analysis (TGA) was performed with a TG/DTA 6300 Seiko instrument (Seiko Instruments Inc., Japan) in air atmosphere from 50 °C to 750 °C at a heat rate of 20 °C /min. Binding energy of the Pd element of CS/MMT/Pd hybrid microspheres was determined with a Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Scientific, US). The morphology of the CS/MMT/Pd hybrid microspheres was observed with a JEM-6360 (Japan) scanning electron microscope (SEM). The phase dispersion behavior of the CS/MMT/Pd hybrid microspheres was observed with a JEM-2100F (Japan) high resolution transmission electron microscope (HR-TEM). The Pd element content within CS/MMT/Pd hybrid

microspheres was determined by a Leemann ICP-AES Prodigy XP inductively coupled plasma-atomic emission spectrometer (ICP, US). During the tests, CS/MMT/Pd hybrid microspheres were firstly treated with a mixture of fuming HNO₃ and concentrated HCl (v/v: 1 ml/3 ml) to dissolve out the Pd component. Then the solution was diluted 25 times and determined with ICP. According to the ICP results, the Pd content of the fresh CS/MMT/Pd hybrid microspheres was 1.2 wt%.

1.4 Catalysis application of the CS-based/MMT/Pd hybrid microspheres

To a 20 ml round bottom flask were added 1 mmol aromatic halide, 1.2 mmol alkyne, CS/MMT/Pd (75/25/1.2) hybrid microspheres (0.026g, about 60 pieces of microspheres, containing 3 μmol Pd as determined with ICP), 3 mmol base (potassium acetate), in 3+0.2 ml (DMSO + ethylene glycol) solvent. The reactions were performed in 110 °C oil bath under magnetic stirring for 5 h. TLC and/or GC/MS analysis was used to monitor the reaction progress. The workup and product characterization were followed by the same procedures with our former work. For the recycling experiments, after each reaction run, CS/MMT/Pd hybrid microspheres were filtrated out the reaction solution and rinsed with ethanol. And then they were put into a new reaction run.

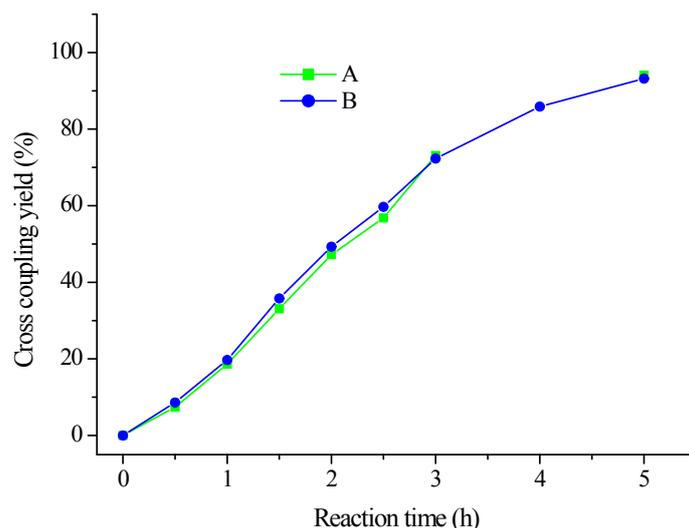
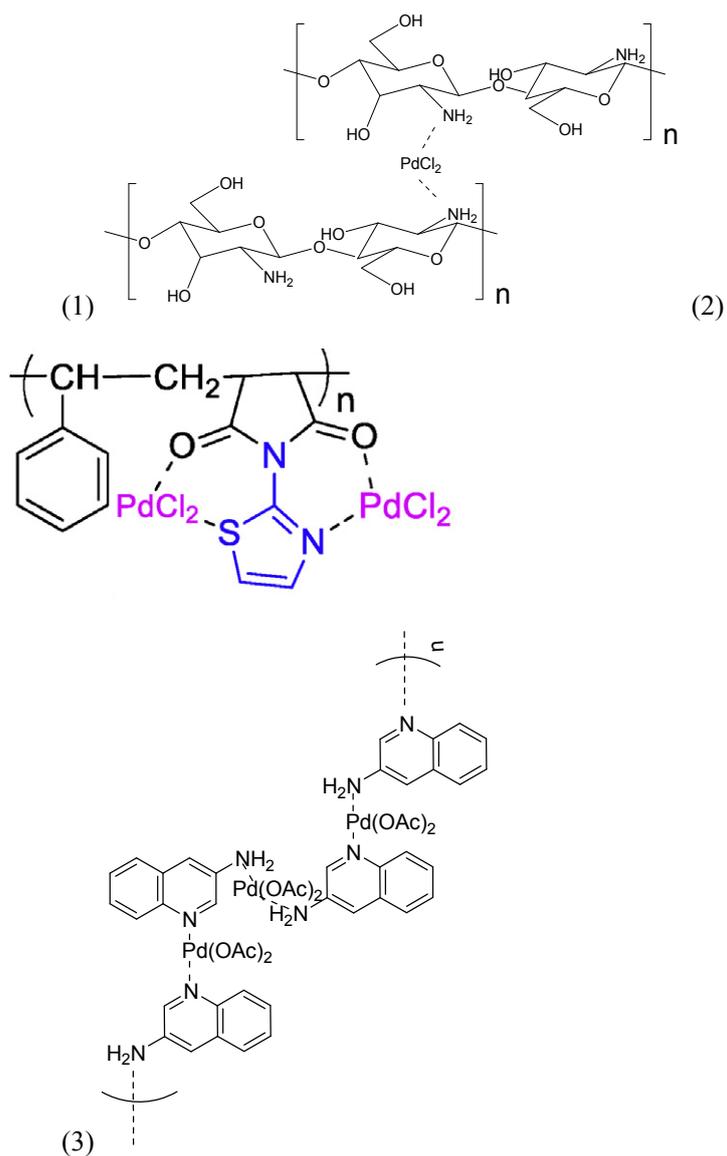


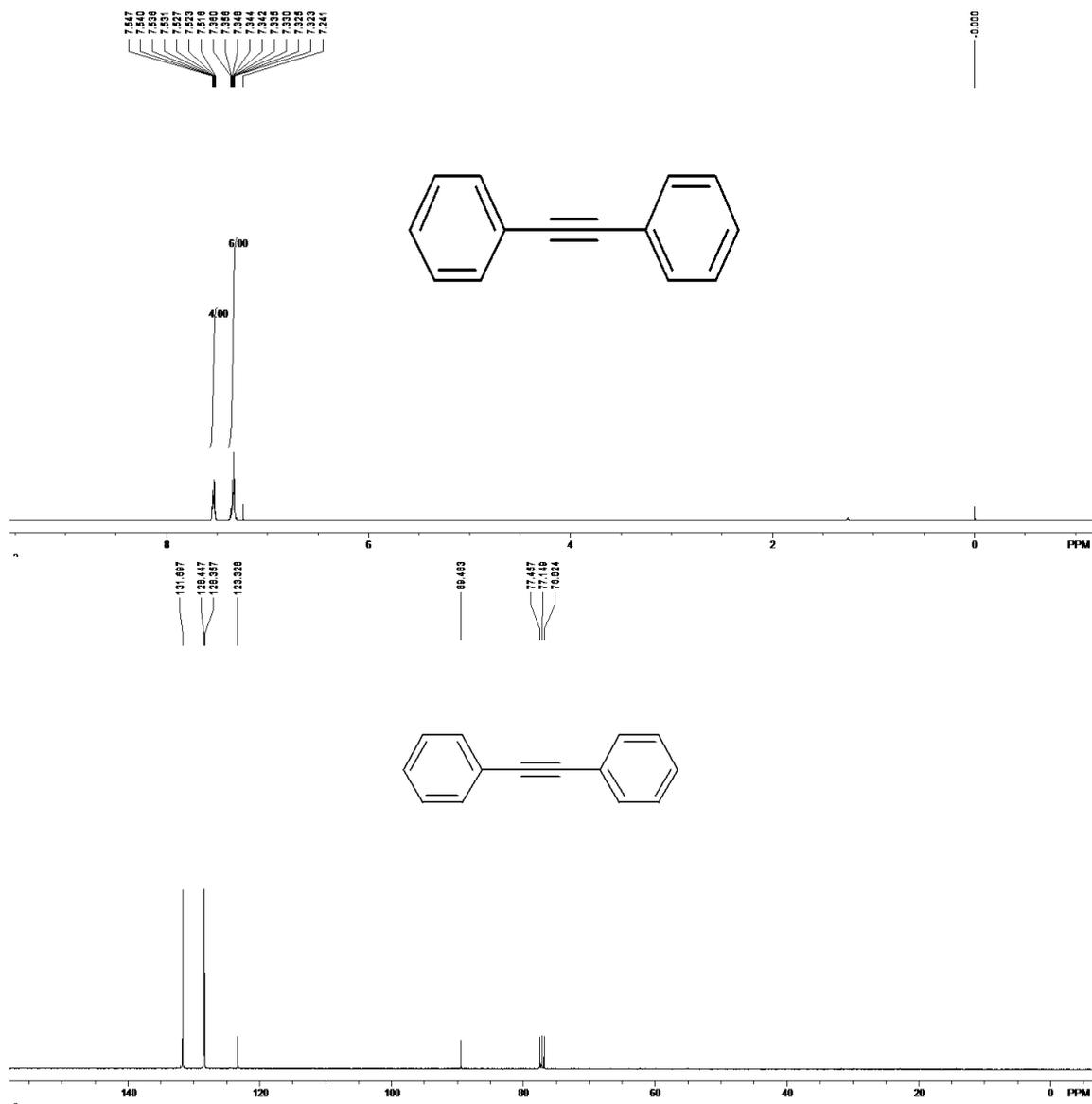
Fig. 1S Cross-coupling yields of iodobenzene with phenyl acetylene catalyzed with CS/MMT/Pd hybrid microspheres as a function with reaction time: A. CS/MMT/Pd (75/25/1.2); B. CS/MMT/Pd (50/50/1.2).



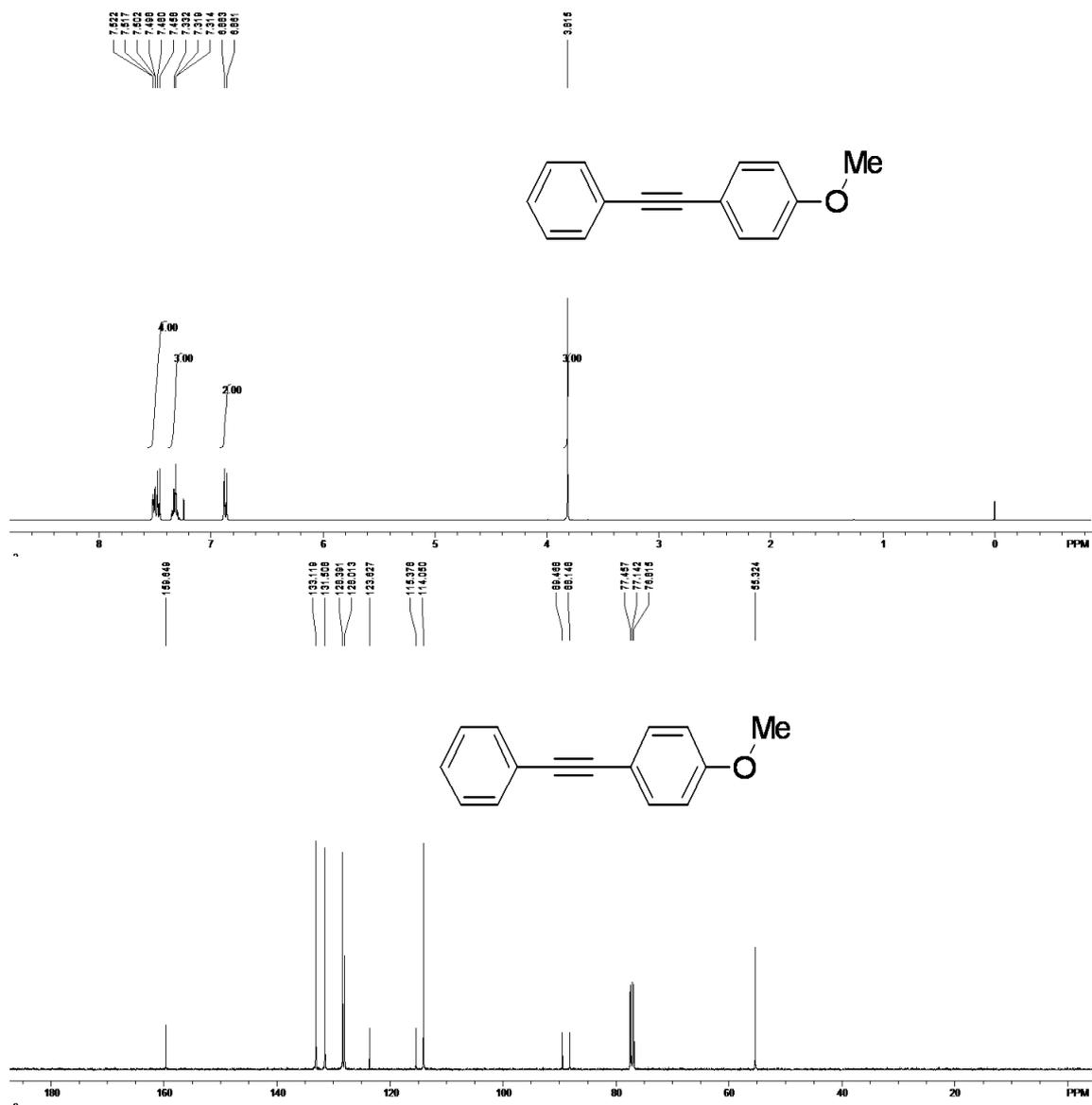
Scheme 1S The scheme of the complexation interactions between Pd species and polymer supports: (1) chitosan (**this study**); (2) poly(styrene-co-maleic anhydride) (**ref. 35**); (3) poly(3-aminoquinoline) (**ref. 34**).

2. ^1H NMR and ^{13}C NMR spectra of the coupling products

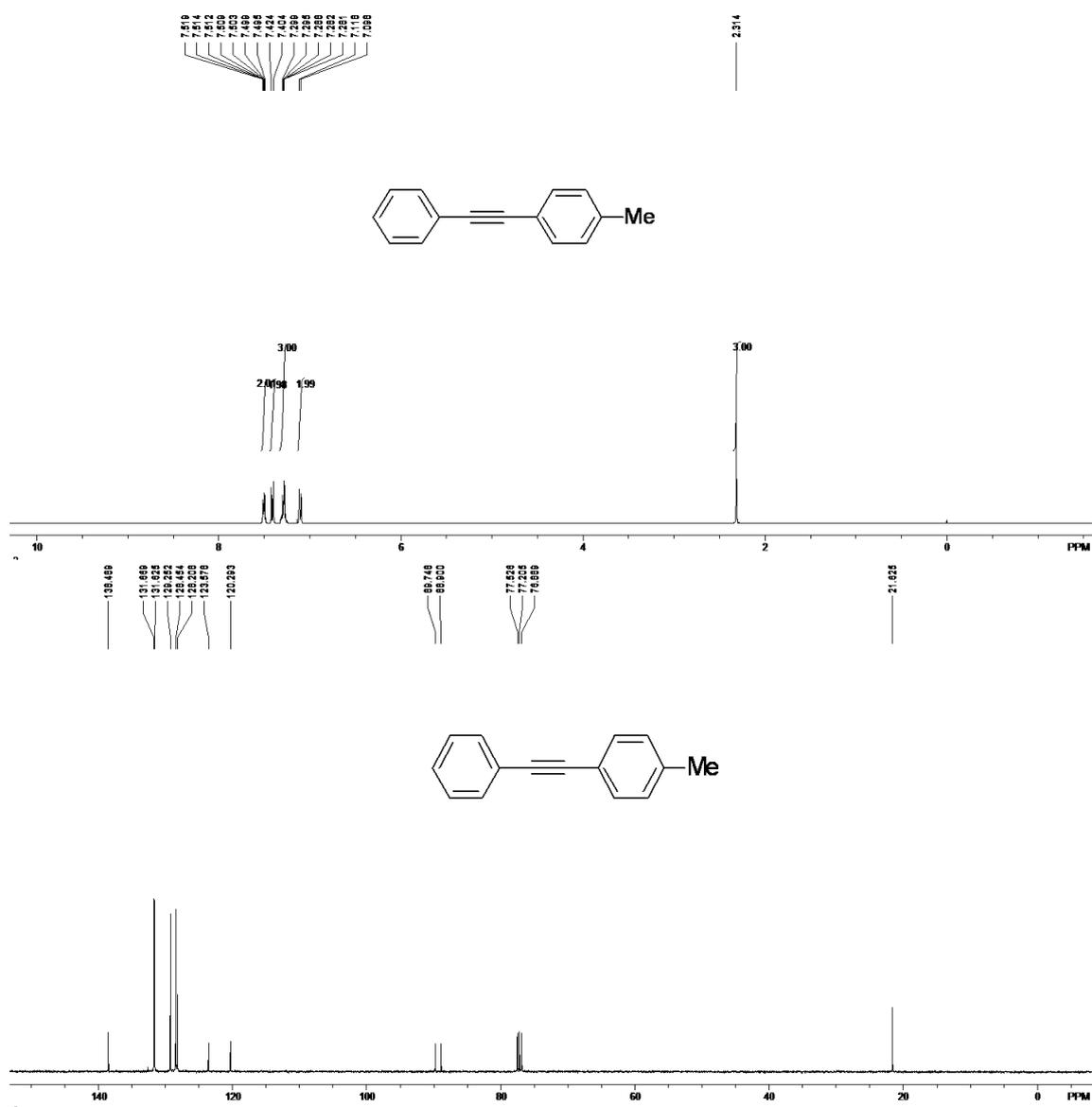
1,2-diphenylethyne white solid mp ($^{\circ}\text{C}$) 98-99; ^1H NMR (400 Hz, CDCl_3 , TMS) δ 7.32–7.38 (m, 6H), 7.52–7.55 (m, 4H); ^{13}C NMR (100 Hz, CDCl_3 , TMS) δ 89.5, 123.3, 128.4 (2C), 131.7.



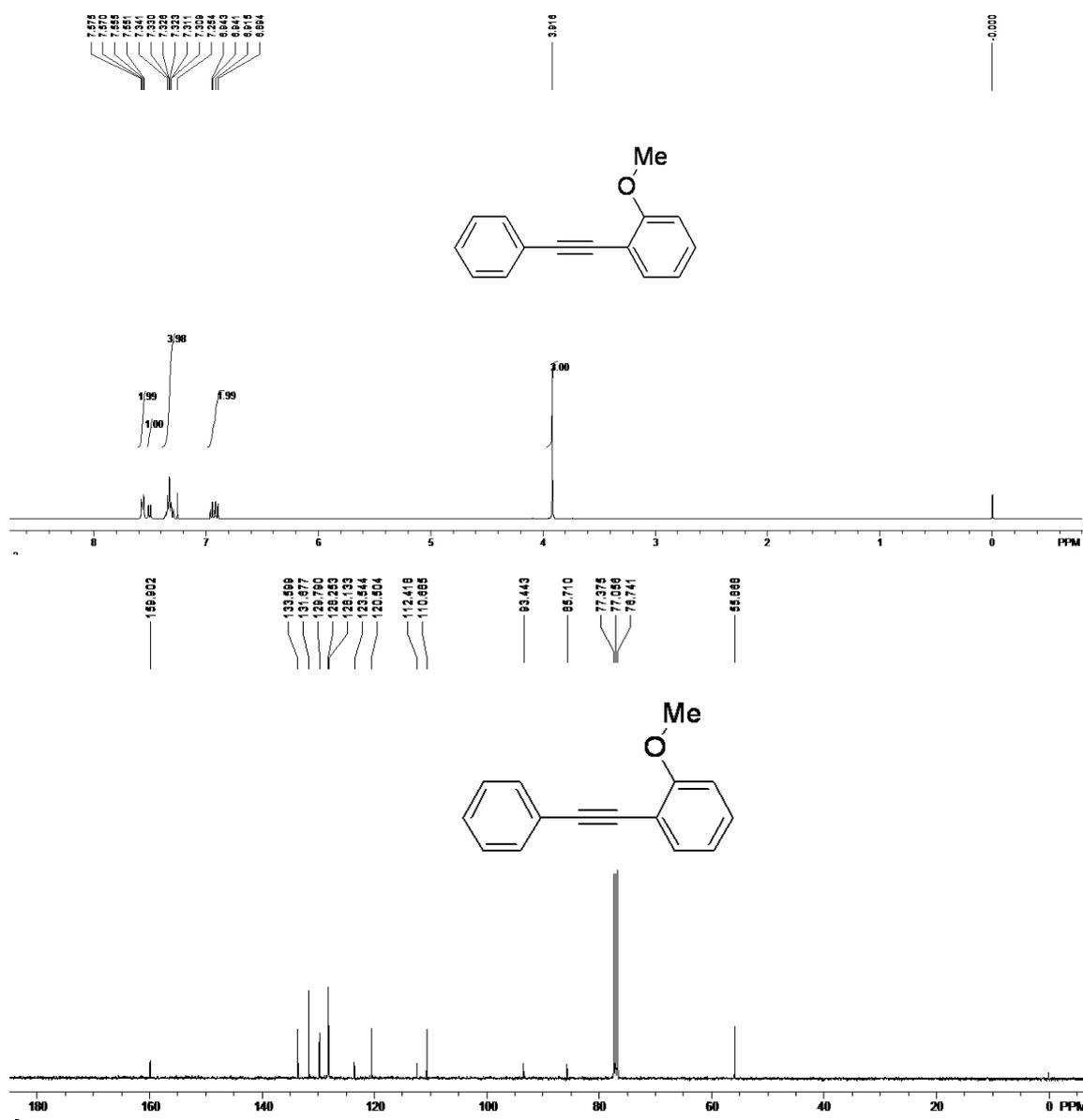
1-methoxy-4-(phenylethynyl)benzene yellow solid; mp (°C) 72-73; ^1H NMR (400 Hz, CDCl_3 , TMS) δ 3.82 (s, 3H), 6.85–6.88 (m, 2H), 7.31–7.33 (m, 3H), 7.46–7.52 (m, 4H); ^{13}C NMR (100 Hz, CDCl_3 , TMS) δ 55.3, 88.1, 89.5, 114.1, 115.4, 123.6, 128.0, 128.4, 131.5, 133.1, 159.6.



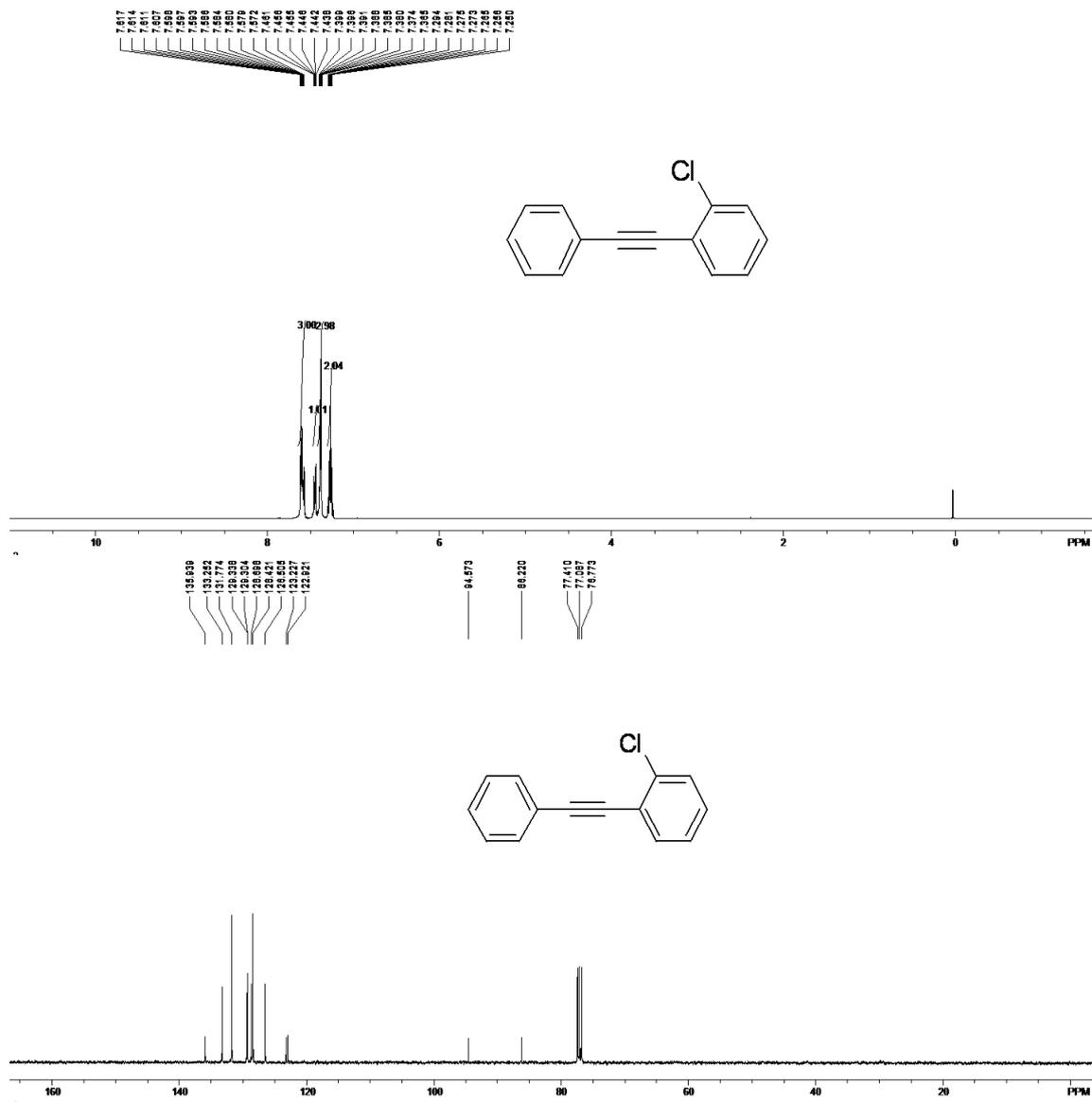
1-methyl-4-(phenylethynyl)benzene white solid; mp (°C) 85-86; ^1H NMR (400 Hz, CDCl_3 , TMS) δ 2.31 (s, 3H), 7.10–7.12 (m, 2H), 7.28–7.30 (m, 3H), 7.40–7.42 (m, 2H), 7.50–7.52 (m, 2H); ^{13}C NMR (100 Hz, CDCl_3 , TMS) δ 21.6, 88.9, 89.7, 120.3, 123.6, 128.2, 128.4, 129.2, 131.6, 131.7, 138.5.



1-methoxy-2-(phenylethynyl)benzene yellow solid; mp (°C) 78-79; ¹H NMR (400 Hz, CDCl₃, TMS) δ 3.91 (s, 3H), 6.90–6.94 (m, 2H), 7.31–7.34 (m, 4H), 7.51 (m, 1H), 7.57 (m, 2H); ¹³C NMR (100 Hz, CDCl₃, TMS) δ 55.9, 85.7, 93.4, 110.7, 112.4, 120.5, 123.5, 128.1, 128.3, 129.8, 131.7, 133.6, 159.9.



1-chloro-2-(phenylethynyl)benzene white oil; ^1H NMR (400 Hz, CDCl_3 , TMS) δ 7.25–7.29 (m, 2H), 7.37–7.40 (m, 3H), 7.44–7.46 (m, 1H), 7.57–7.62 (m, 3H); ^{13}C NMR (100 Hz, CDCl_3 , TMS) δ 86.2, 94.6, 122.9, 123.2, 126.5, 128.4, 128.7, 129.3 (2C), 131.7, 133.3, 135.9.



1-fluoro-4-(phenylethynyl)benzene yellow solid; mp (°C) 124-125; ¹H NMR (400 Hz, CDCl₃, TMS) δ 7.02–7.05 (m, 2H), 7.33–7.35 (m, 3H), 7.49–7.53 (m, 4H); ¹³C NMR (100 Hz, CDCl₃, TMS) δ 88.3, 89.0, 115.6, 115.8, 119.4, 123.1, 128.4, 131.6, 131.8, 133.5, 161.3, 163.7.

