Electronic Supplementary Information (ESI)

Title: Nanostructured Molybdenum Oxides and their Catalytic Performance in Alkylation of Arenes

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Content

All chemicals were purchased from Wako Pure Chemical Industries, Ltd. These chemicals were used as purchase without further purification unless indicated. All reagents were A.R. grade. Distilled water was prepared by using Yamato Autostill WG25 (Tokyo, Japan).

Preparation of MP

Add 3.5 gram of $(NH_4)_6Mo_7O_{24}.4H_2O$ (AHM) into 500 mL water in a 2 liter beaker. Stir for 4.5 min at RT to realize dissolution of the salt. Add 1.0 liter acetone under stirring. Stir for 7 min and filter out the catalyst, wash in the sequence of acetone 100 mL × 2 times, pentane 20 mL × 2 times, dry in a 60 ^oC–oven for 14 h and then calcine at 350 ^oC for 2 h in a 10 ^oC/min ramping rate in a 50 mL/min flow speed of air.

Preparation of MH

The preparation of MH was modified from literature.[1] Commercial MoO_3 and 30% aqueous hydrogen peroxide were used as precursors. In a typical procedure, MoO_3 powder (2.88 g, 20 mmol) reacted with 30% aqueous H_2O_2 (24.0 mL) and dissolved completely after stirring for 24 h at 30 ^oC of water bath (It is strongly suggested that at least 8 h is needed for completely decomposing remained H_2O_2, otherwise it will decompose in the following hydrothermal treatment and generate high pressure inside autoclave), forming a transparent orange-green solution. The above acid solution was diluted with equal volume of water. The 30 mL of resultant precursor solution was transferred into a 300 mL Teflon-lined stainless steel autoclave. The autoclave was then sealed and maintained at 175 ^oC for 48 h. After cooling naturally to room temperature in ambient surroundings, the precipitate was collected after centrifuging, washed with deionized water, and dried at 40 ^oC.

Preparation of MM

2 gram of $(NH_4)_6Mo_7O_{24}.4H_2O$ (AHM) was caclined in a crucible in a static air at 500 ^oC for 12 h.

Preparation of β-MoO_3

The preparation of β-MoO_3 was modified from literature.[2] The precursory solution of molybdic acid was prepared from a 1 mol/L solution of $Na_2MoO_4{\cdot}2H_2O$. 1 L of the solution was passed through a column packed with 500 mL of cation-exchange (CE) resin (Amberlite IR120B H) to exchange Na^+ ions. The resin was regenerated with 1 mol/L HCl solution (1 L) and washed with distilled water until the pH was 7. These operations were repeated for 10 times. 30 mL of the obtained precursory solution was then transferred into a 300–mL vessel and evaporated to dryness at 60 ^oC and 1500–2000 Pa after addition of 1% HNO_3 solution. The drying was done within 2 h. Molybdenum oxide was produced by heating 0.5 gram of the dried powder at 300 ^oC

for 1 h in an oxygen stream (50 mL/min).

Catalyst characterization

Powder XRD patterns were recorded on a diffractometer (Rigaku, RINT Ultima+) with CuKα radiation (Kα 1.54056 Å). Scanning electron microscopy (SEM) was performed on a JSM–7400F (JEOL). ^{1}H NMR sprectra were recorded using JEOL ECX–600 or JEOL ECX–400 at CRIS center of Hokkaido University. Reactant and product concentratons were measued by gas chromatography using flame ionization detection (Shimazu Classic–5000, 60m TC WAX column). The detector voltage is 1.5 kV.

Catalytic test

A 50 mL round-bottom three-neck flask equipped with a reflux condenser was used as a stirred bed reactor to test the catalytic activities of the material. Add 0.3 gram catalyst and Teflon coated magnetic stir bar into the reactor. Seal and purge the reactor with N_2 gas (10 mL/min) under desired temperature for 5 min. Remove oil bath and let the reactor cool down to room temperature. Add a mixture of benzyl alcohol (0.24 mL), arene (15 mL) and internal standard hexadecane (0.1 mL) into the reactor. Purge N_2 gas (10 mL/min) through liquid phase for 3 min. Reduce the N_2 flow rate to 5 mL/min. Put the reactor in pre-heated oil bath. The resulting mixture was heated with stirring until the reaction had reached completion, as judged by TLC and GC/MS. Aliquots (0.1 mL) were collected at interval. The crude mixture was concentrated *in vacuo* to yield the crude product. Purification of product was carried out on silica gel using pure hexane to remove remaining solvent followed by washing with effluent of hexane/ethyl acetate (2.5:1) to give the desired diphenylmethanes compound. The ^{1}H NMR and ^{13}C NMR were conducted in $CDCl_3$ at ambient condition with TMS standard (1% wt in $CDCl_3$) or with $CHCl_3$ as reference (δ=7.26) or TMS. The spectra of known compounds (**Table 2**, and **Table 3**) were identical to the reported literatures, and unavailable spectra and the spectra of new compounds (**Table 4, entries 2-7**) were appended in the following.

Catalyst recycling and reuse

Reaction mixture was filtered out using 0.2 μm membrane filter (Toyo Roshi Kaisha Ltd., Japan). The solid catalyst was then rinsed with toluene (5×3 mL). Suspend the collected catalyst in fresh benzyl alcohol (0.24 mL) and toluene (15 mL) and conduct reaction. The 3rd, 4th, 5th, 6th and 7th recycling tests were carried out in the same procedure as the 2nd reaction. In all reuse tests, the sampling time was 20 min for convenience.

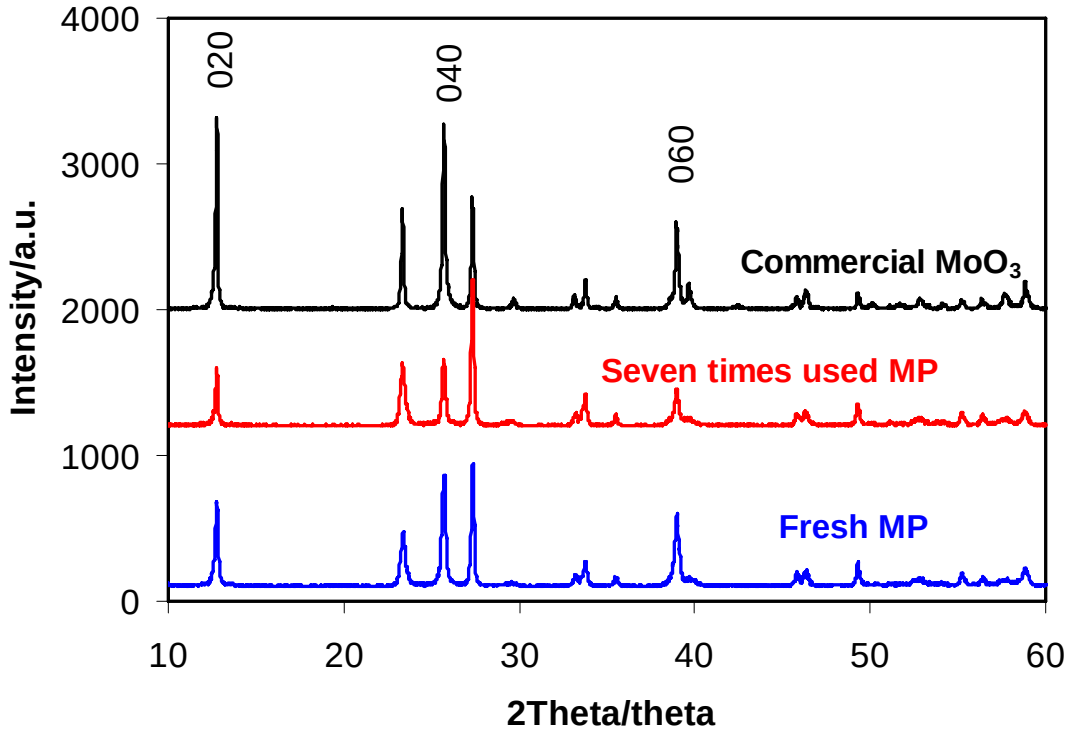


Fig S1. XRD patterns of MP, seven times used MP and commercial MoO_3 (MC–MoO_3)

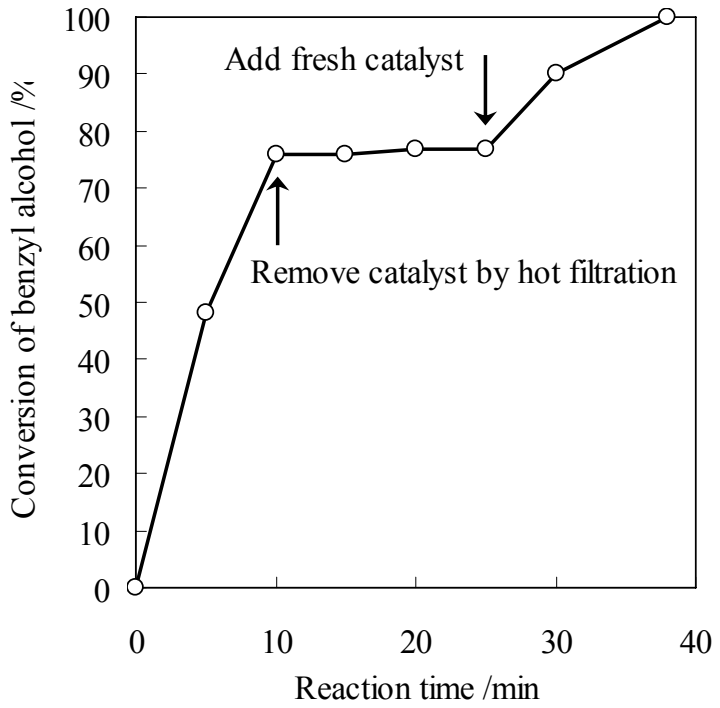


Fig. S2 Catalyst separation at 10 min and catalyst triggering at 25 min.

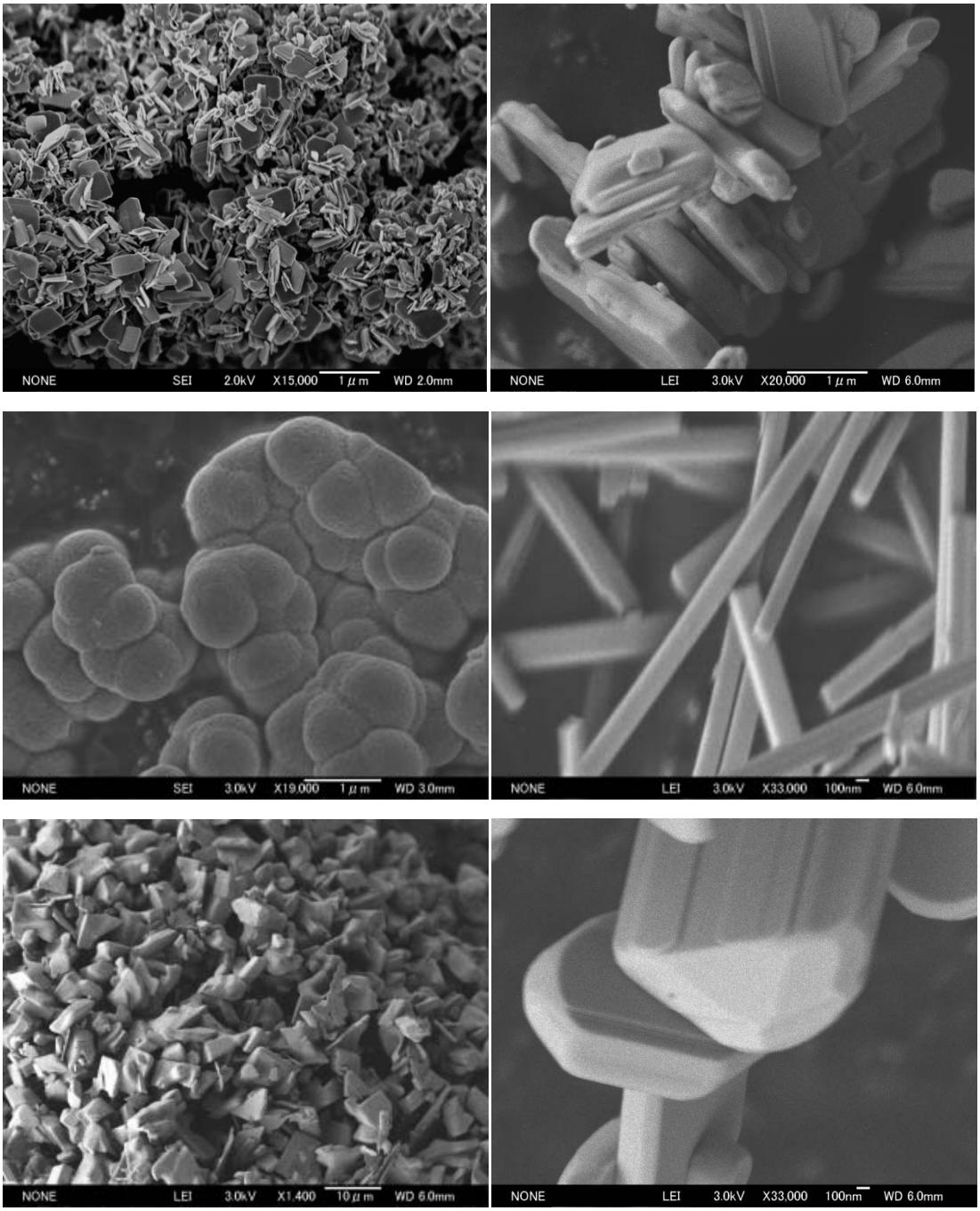


Fig. S3 Representative SEM images of MP (upper left), CM-MoO_3 (upper right), β-MoO_3 (middle left), MH (middle right), MC-MoO_2 (lower left) and MM (lower right).

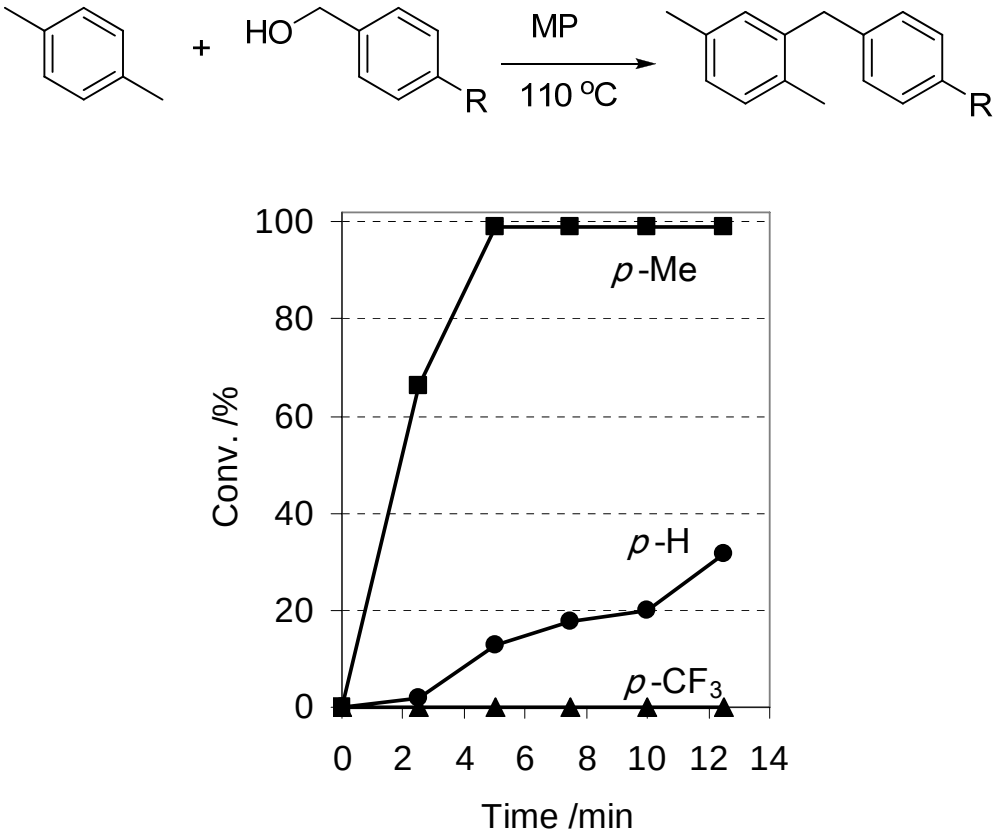
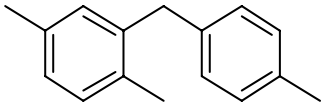
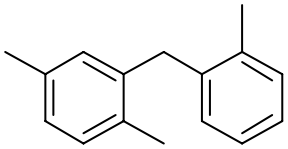


Fig. S4 The competitive activities of para-substituted benzyl alcohol as the alkylating agent.

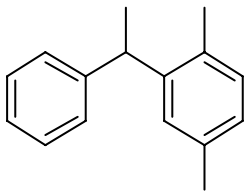
Characterization details on some compounds



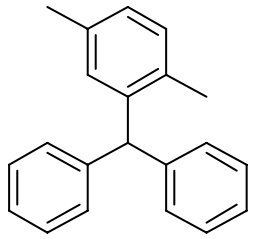
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.8-7.1 (m, 7 H), 3.9 (s, 2H), 2.3 (s, 3H), 2.3 (s, 3H), 2.2 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 138.91, 137.42, 135.31, 135.27, 133.38, 130.66, 130.12, 129.02, 128.55, 126.96; For ^{1}H NMR and ^{13}C NMR spectra see the appendix.
MS m/z (%): calculated for $C_{16}H_{18}$: 210.14, found: 210.20 (71.70) [M^+], 195.15 (100) [M^+-CH_3], 180.15 (30.8), 165.15 (23.54), 118.15 (91.39).



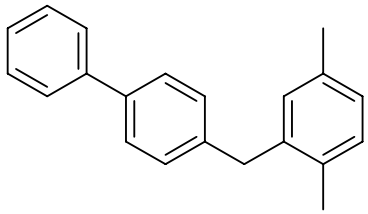
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.8-7.1 (m, 7 H), 3.8 (s, 2H), 2.2 (s, 3H), 2.1 (s, 3H), 2.1 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 138.52, 138.11, 136.50, 135.40, 133.42, 130.00, 129.96, 128.96, 128.88, 126.86, 126.09, 125.97, 36.59, 20.99, 19.60, 19.07; For ^{1}H NMR and ^{13}C NMR spectra see the appendix.
MS m/z (%): calculated for $C_{16}H_{18}$: 210.14, found: 210.20 (45.55) [M^+], 195.25 (37.61) [M^+-CH_3], 118.15 (53.45), 117.15 (20.54), 105.15 (23.48), 104.10 (100.00), 77.10 (21.10)



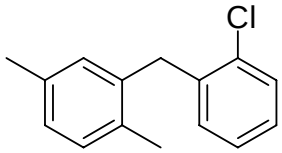
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.9-7.3 (m, 8 H), 4.3 (q, H), 2.2 (s, 3H), 2.1 (s, 3H), 2.1 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 138.52, 138.11, 136.50, 135.40, 133.42, 130.00, 129.96, 128.96, 128.88, 126.86, 126.09, 125.97, 36.59, 20.99, 19.60, 19.07; For ^{1}H NMR and ^{13}C NMR spectra see the appendix.
MS m/z (%): calculated for $C_{16}H_{18}$: 210.14, found: 210.20 (43.36) [M^+], 195.15 (100) [M^+-CH_3], 180.15 (30.84), 165.15 (25.30), 89.10 (25.62)



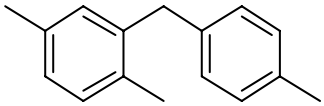
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.9-7.3 (m, 13H), 5.6 (s, 1H), 2.2 (s, 3H), 2.2 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.50, 142.06, 135.05, 133.48, 130.28, 130.12, 129.63, 128.91, 128.25, 127.04, 126.17, 53.48, 21.22, 19.49; For ^{1}H NMR and ^{13}C NMR spectra see the appendix.
MS m/z (%): calculated for $C_{21}H_{20}$: 272.16, found: 272.15 (76.1) [M^+], 257.2 (100) [M^+-CH_3], 195.11 (19.11), 179.2 (51.24), 165.05 (63.54), 106.15 (20.53), 77.1 (18.12).

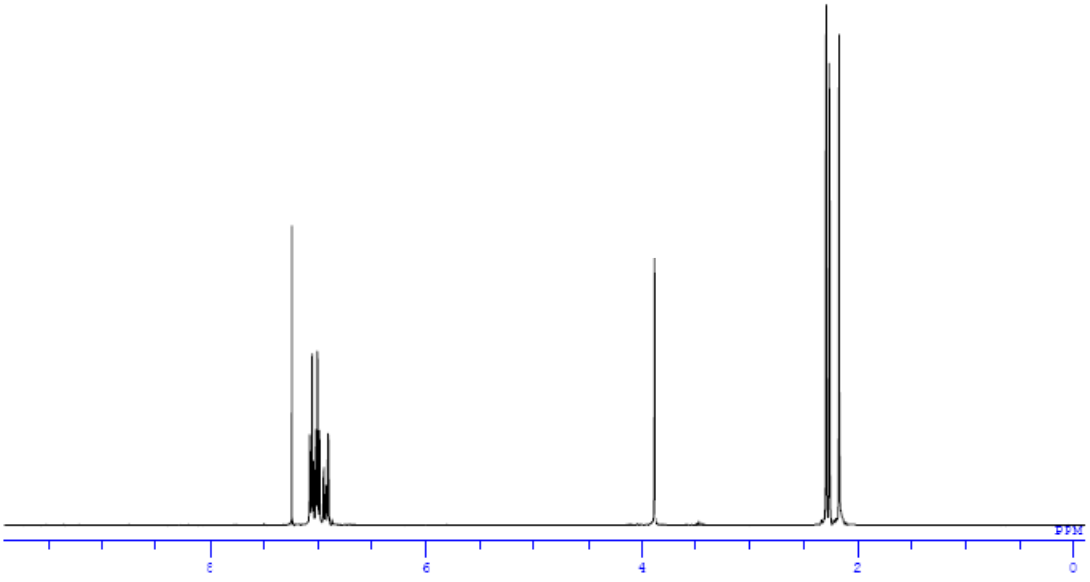


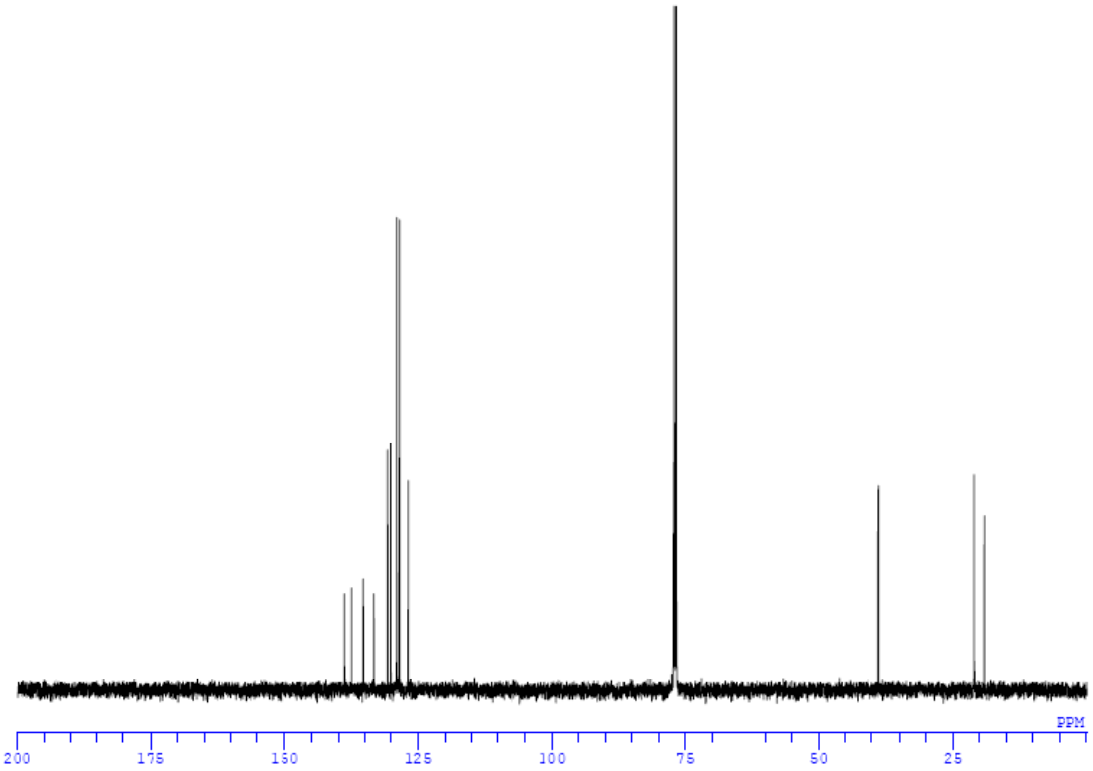
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.9-7.6 (m, 12H), 4.0 (s, 2H), 2.3 (s, 3H), 2.3 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.03, 139.69, 138.80, 138.57, 135.46, 134.68, 133.46, 130.78, 130.24, 129.08, 128.91, 128.71, 127.17, 127.10, 127.03, 126.99; For ^{1}H NMR and ^{13}C NMR spectra see the appendix.
MS m/z (%): calculated for $C_{21}H_{20}$: 272.16, found: 272.10 (23.84) [M^+], 257.15 (30.24) [M^+-CH_3], 105.15 (37.16), 91.05 (100).

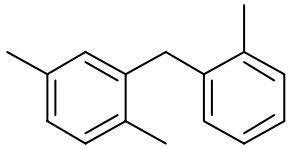


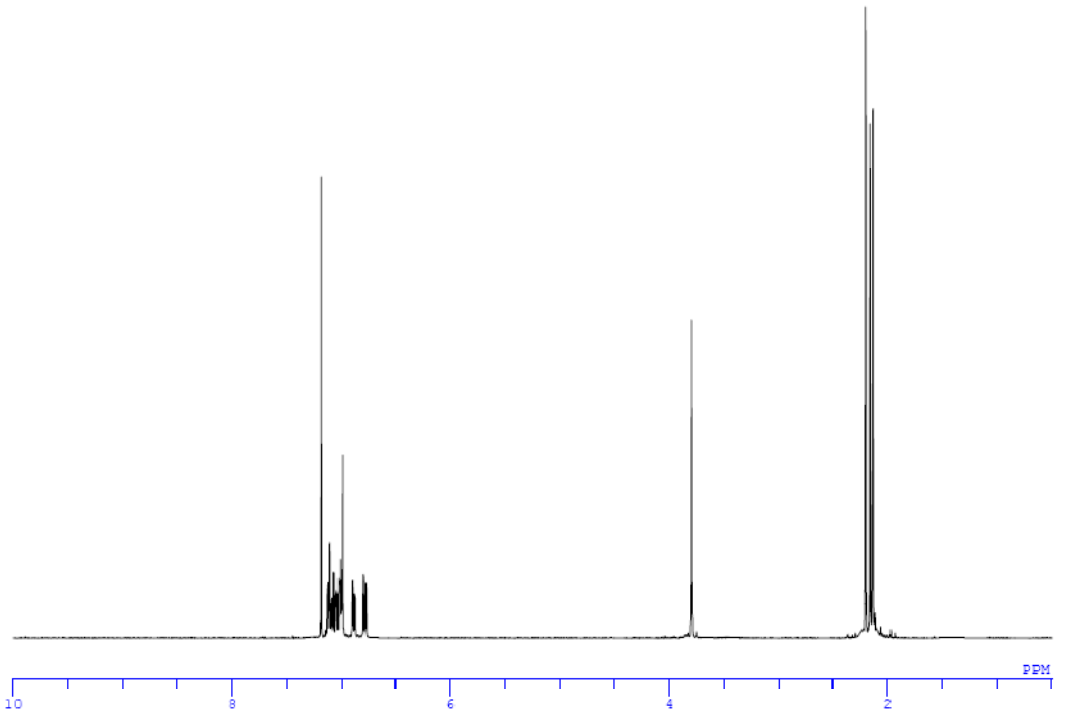
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.8-7.4 (m, 7H), 4.0 (s, 2H), 2.3 (s, 3H), 2.2 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 138.15, 137.20, 135.50, 134.25, 133.62, 130.55, 130.17, 129.27, 128.91, 127.37, 127.29, 126.75; For ^{1}H NMR and ^{13}C NMR spectra see the appendix.
MS m/z (%): calculated for $C_{15}H_{15}Cl$: 230.09, found: 230.15 (85.78) [M^+], 215.10 (52.42) [M^+-CH_3], 195.20 (100) [M^+-Cl], 180.15 (69.49), 118.1 (51.01), 117.05 (12.35), 82.25 (41.02).

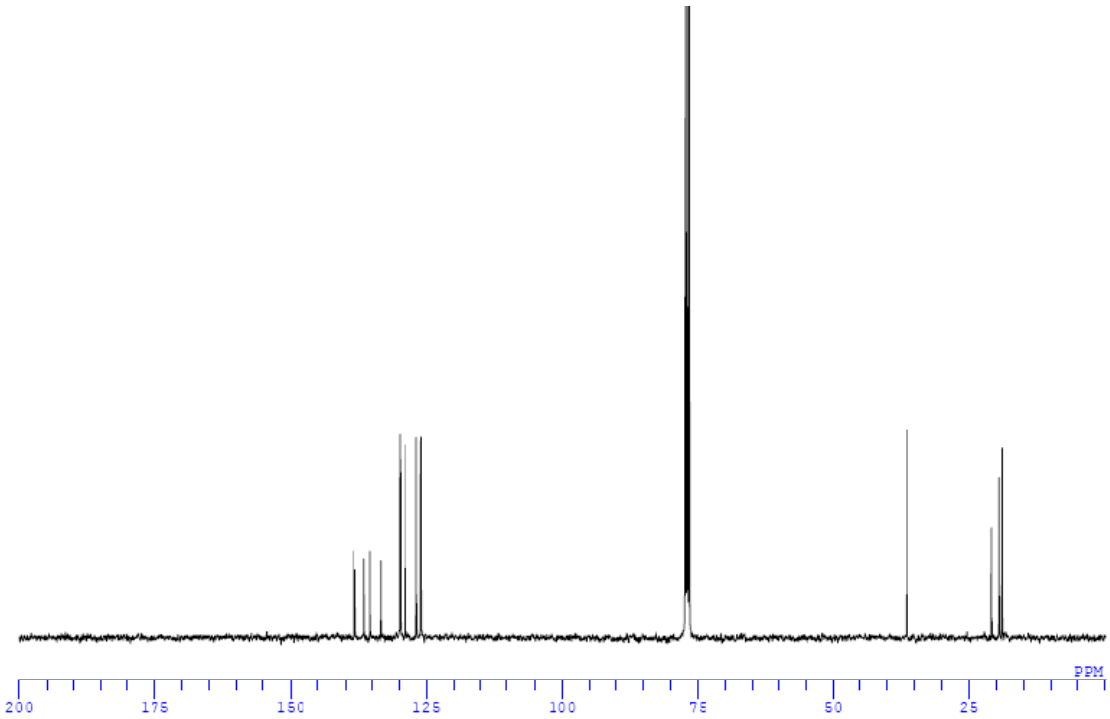


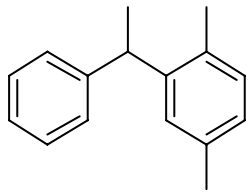


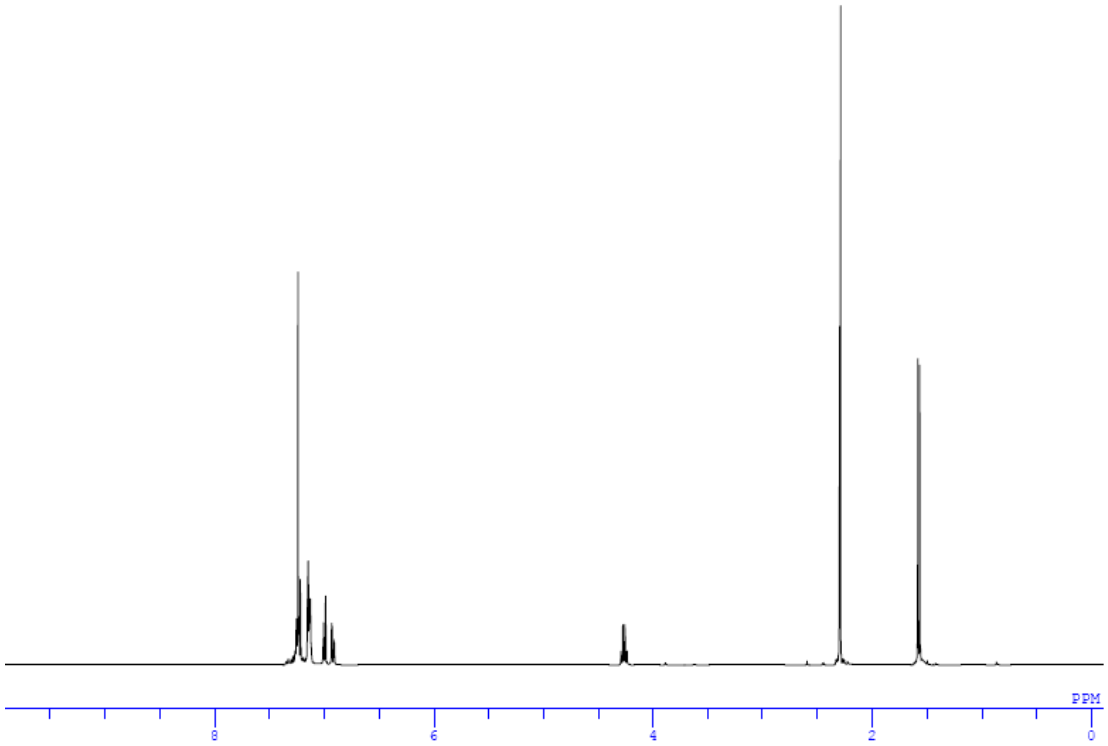


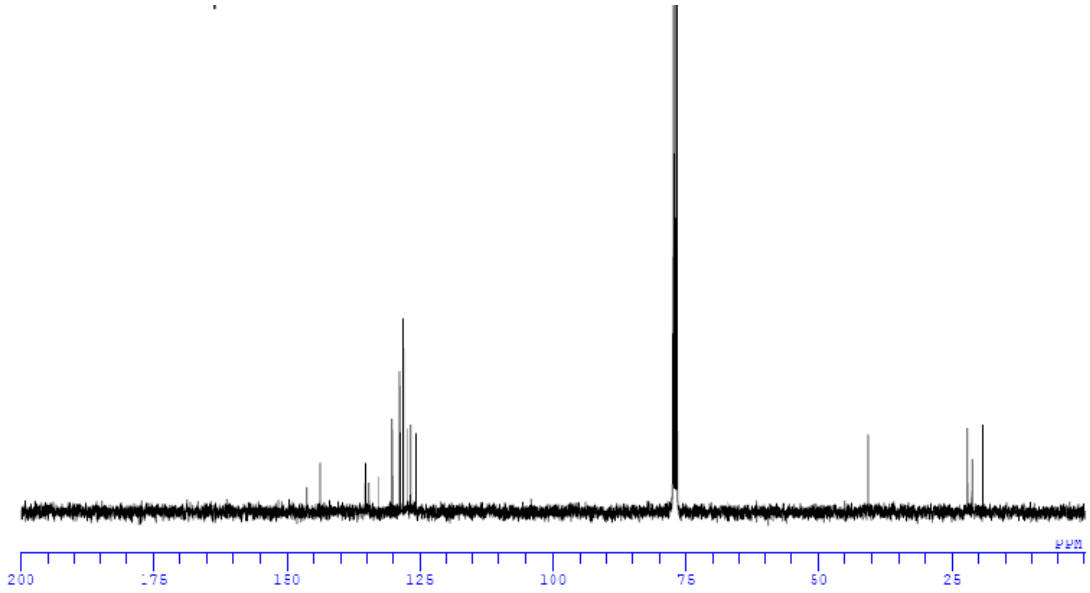


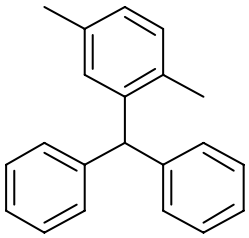


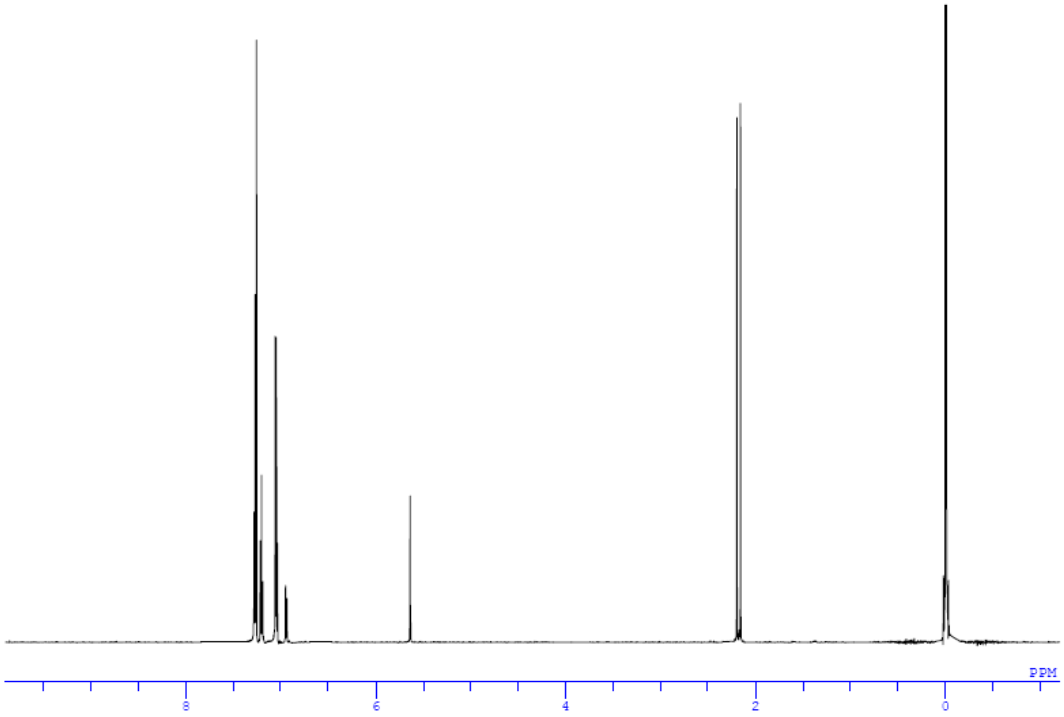








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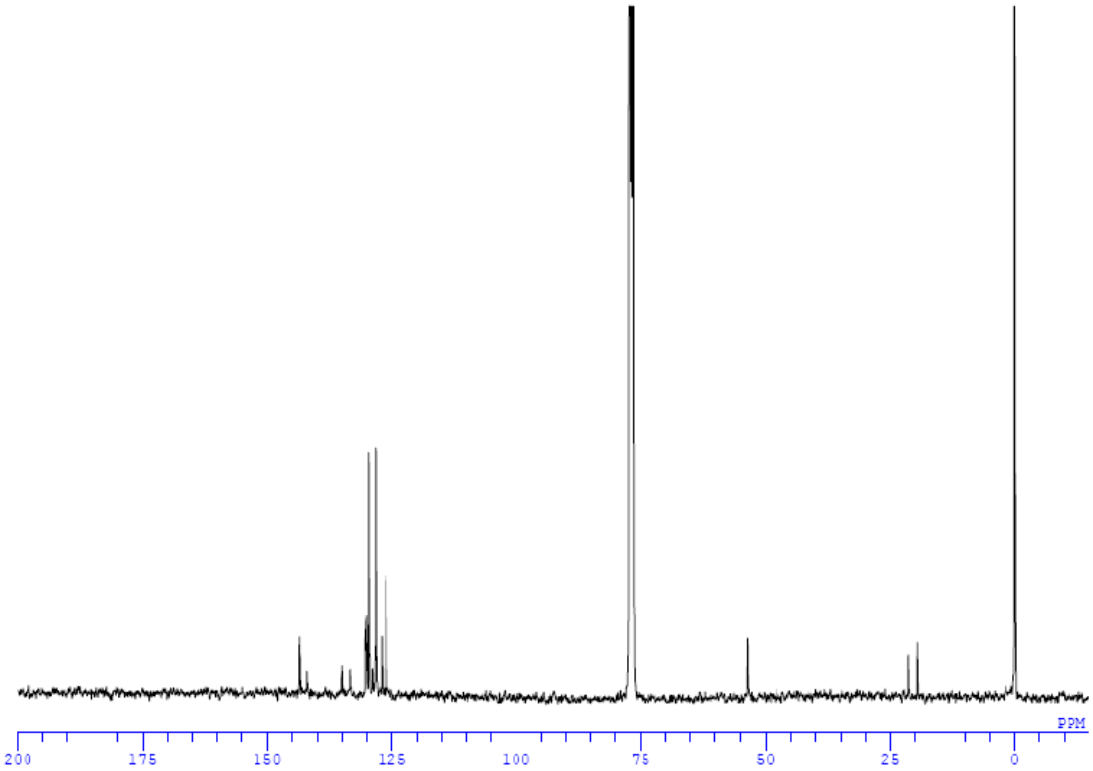
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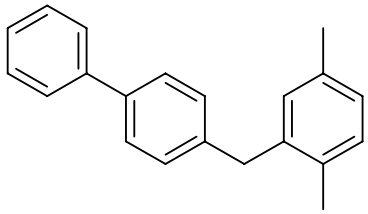

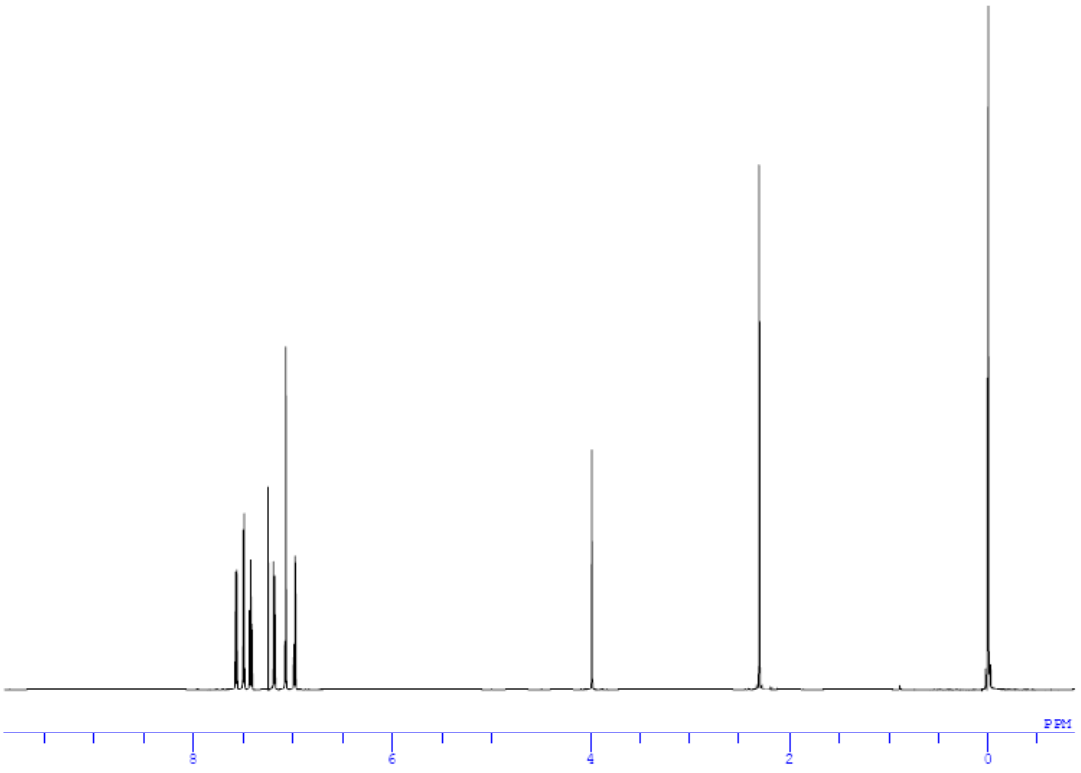
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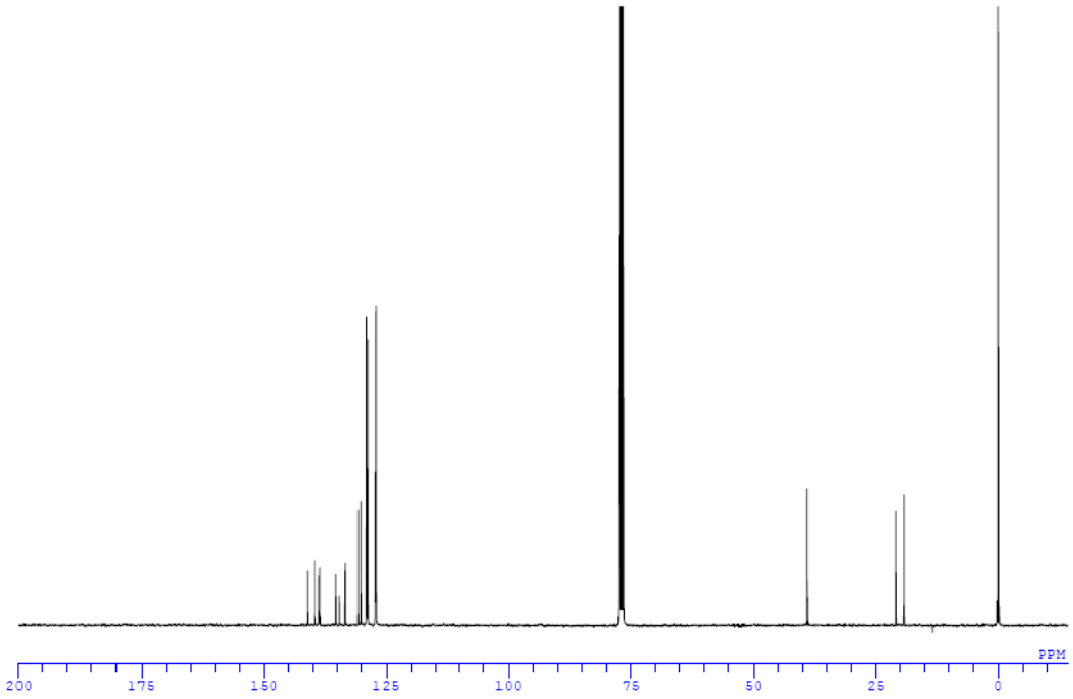
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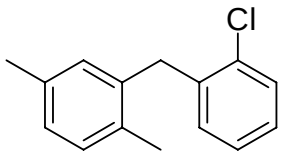
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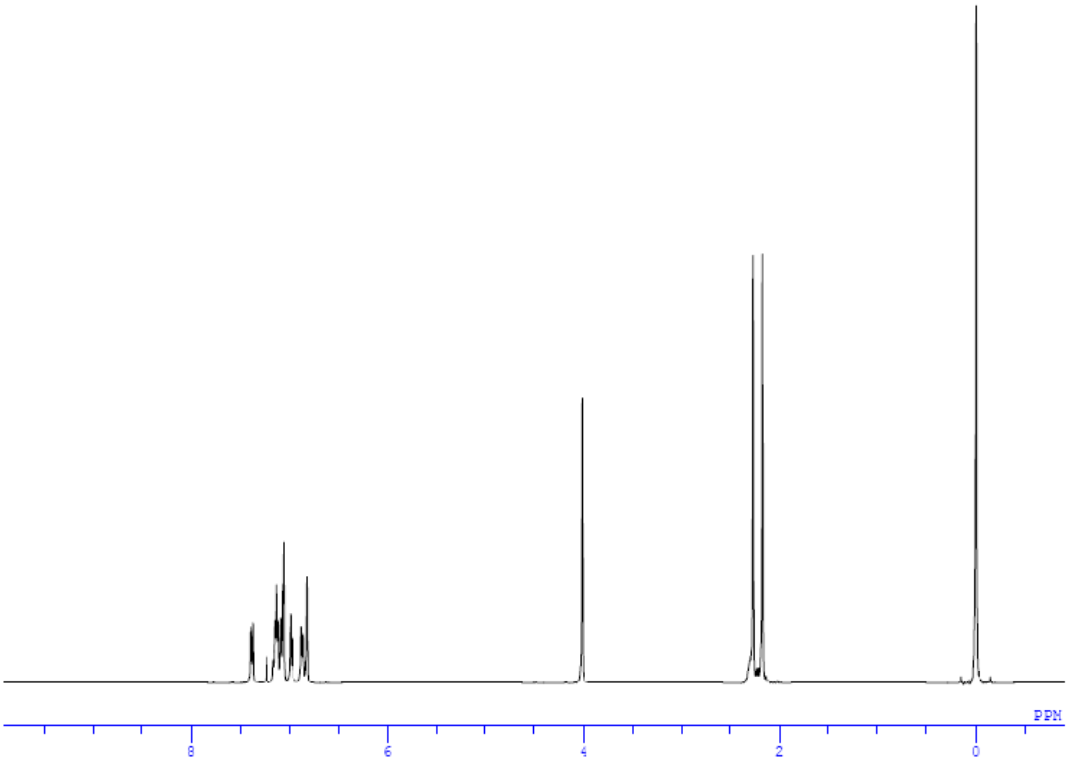
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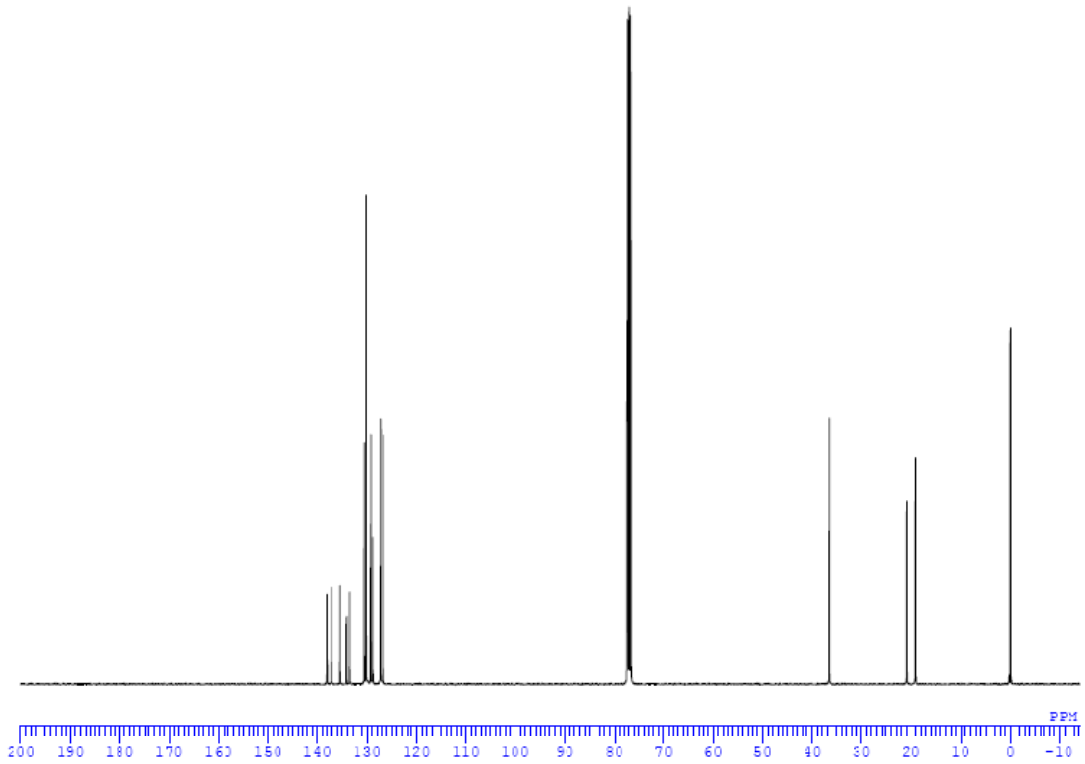
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Reference

1 L. Fang, Y. Y. Shu, A. Q. Wang and T. Zhang, *J. Phys. Chem. C*, 2007, **111**, 2401-2408.

2 T. Mizushima, K. Fukushima, H. Ohkita and N. Kakuta, *Appl. Catal. A*, 2007, **326**, 106-112.