

Supplementary Materials

Pd–Co Nanoparticles Supported on Calcined Mg–Fe Hydrotalcites for the Suzuki–Miyaura Reaction in Water with High Turnover Numbers

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1 General information

All reagents were of analytical grade and purchased from Aladdin Industrial Inc. The chemicals were used without further purification. NMR spectra were recorded at room temperature in CDCl₃ on 400 MHz spectrometers. TEM images were recorded on a JEOL 2100F instrument operating at 120 kV. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was tested on an IRIS Intrepid II XSP instrument (Thermo Electron Corp.).

2 Experimental Section

2.1 Catalyst preparation

Synthesis of Pd–Co–CHT

Pd–Co–HT with a ratio of Mg/Fe = 3 was prepared by a conventional co-precipitation method. The two solutions, A and B, were synchronously added dropwise into 100 mL of deionized water with vigorous stirring. Solution A (200 mL) contained MgCl₂·6H₂O (1.2 mol/L), FeCl₃·6H₂O (0.4 mol/L), PdCl₂ (7.5×10⁻³ mol/L) and CoCl₂ (1.4×10⁻² mol/L) added into the solution A. Solution B (200 mL) contained enough NaOH and Na₂CO₃ to precipitate the solution A completely. The co-precipitation temperature was carried out at 40 °C, while the pH was kept constant in 10–11 by adding NaOH. Then the resulting slurry was aged at 65 °C for 18 h to obtain the final precipitate, which was centrifuged several times with deionized water, till

the specific conductance of the supernate were below 300 $\mu\text{s}/\text{cm}$. Finally, the solid was dried at 105 °C for 8 h in air and product was denoted as Pd-Co-HT. Then the Pd-Co-HT powder was calcined in a muffle furnace at 500 °C for 5 h and then reduced at 200 °C for 2 h under flowing H_2 and N_2 (flow rate: 50/150 mL/min). The final product was noted as Pd/Co-CHT.

The X-ray diffraction analysis (XRD) was collected on a D8 Advance using a Cu $K\alpha$ radiation from 5 ° to 80 ° (2θ). The surface area, average pore volume, and pore diameter were measured via the Brunner-Emmett-Teller (BET) method with TriStar Π 3020 (Micromeritics, USA). The High Resolution Transmission electron microscope (HR-TEM) were detected by (JEOL 2100F).

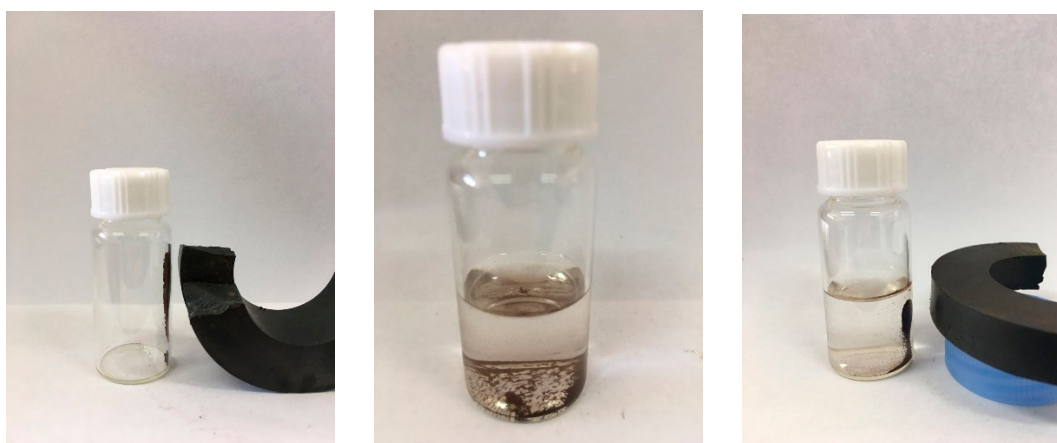


Figure S1. Magnetic separation of catalyst

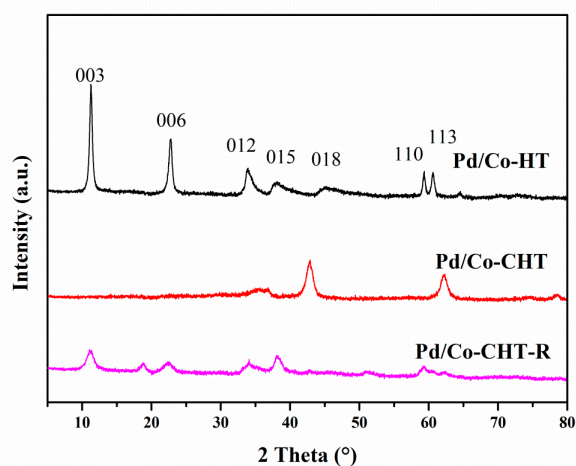


Figure S2. Typical XRD patterns of Pd-Co-HT, Pd-Co-CHT.

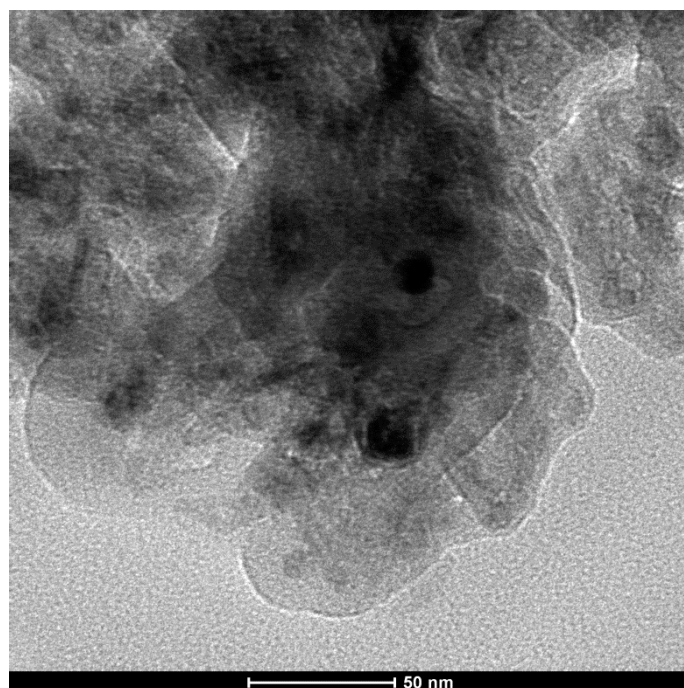
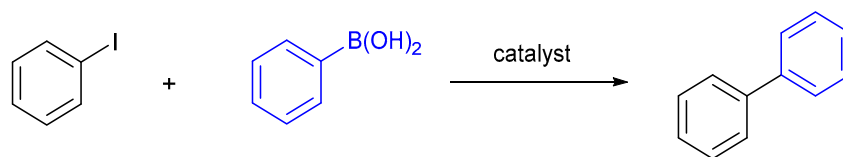


Figure S3. HRTEM image of the Pd–Co–CHT powder.

2.2 General experimental procedure for Suzuki cross coupling reactions catalyzed by Pd–Co–CHT

Aryl halide (5.0 mmol), boronic acids (7.5 mmol), 10 mmol K_2CO_3 and 10 mg of nano Pd–Co–CHT catalyst were added in 5 mL water and the reaction was carried at 80 °C for 6h. The progress of the reaction was monitored by TLC. Upon completion of the reaction, the catalyst was separated and the filtrate was extracted with diethyl ether. The catalyst was easily recovered by simple filtration or by magnetic separation, washed by water and diethyl ether, and dried for next runs. The products were isolated by column chromatography using pure petroleum ether as the eluent. The recyclability study was ran subsequently by reused catalyst. The products were characterized by 1H NMR and MS.

Table S1. Comparison between previous reported works and the present work for Suzuki coupling reaction of aryl halide with phenyl boronic acid.

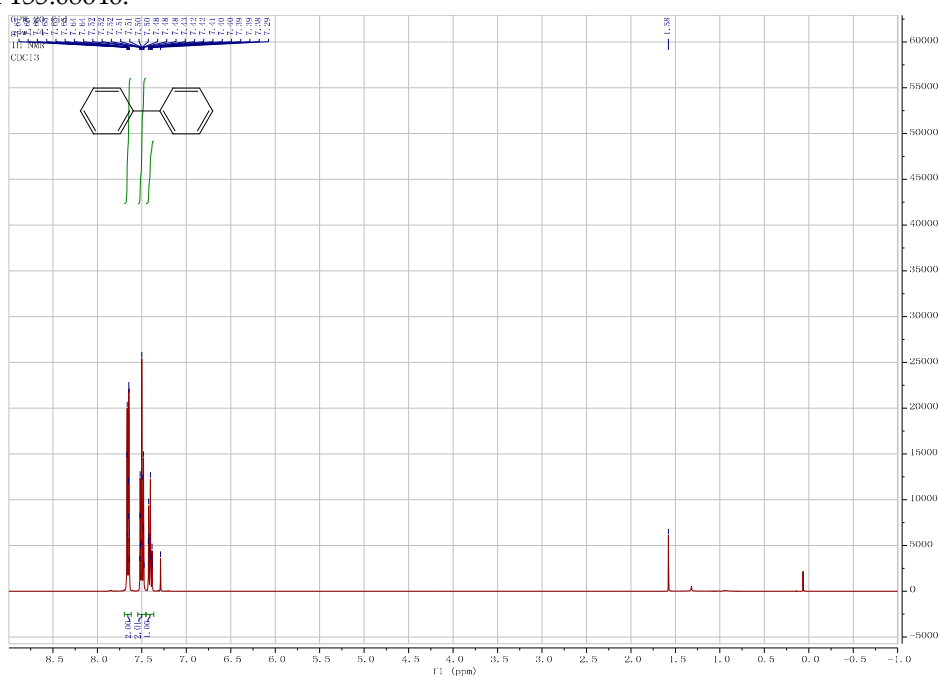


entry	catalyst	Pd Loding	yield	Reference
1	Pd/COF-LZU1	0.5mol%	97%	1
2	$Fe_3O_4@SiO_2@mSiO_2$ -Pd	0.075mol%	98%	2
3	$Pd^{II}/UOF-1$	0.5mol%	97%	3
4	Nano Pd– $Fe_3O_4@Alg$ beads	0.05mol%	97%	4
5	Pd@PNP	0.2mol%	96%	5
6	nano tetraimine Pd(0)	0.2mol%	95%	6

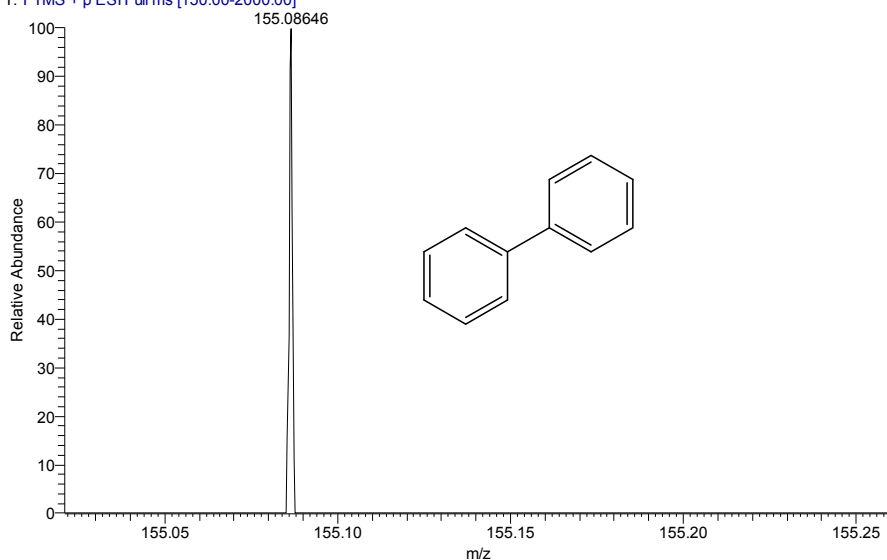
7	Fe ₃ O ₄ @SiO ₂ -Pd	0.03mol%	96%	7
8	PdNPs@COF	0.1mol%	99%	8
9	Pd-Mg-Al-HT	3 atom%	99%	9
10	(Pd ^{II} -NHCs) _n @nSiO ₂	0.27mol%	97%	10
11	Pd@UPOP-1	1 mol%	99%	11
12	Pd@PANI	0.021mol%	96%	12
13	Pd/CNP	0.5mol%	87%	13
14	Pd-Co-CHT	0.009mol%	99%	This work

3 Characterization of products by mass spectra and ¹H NMR

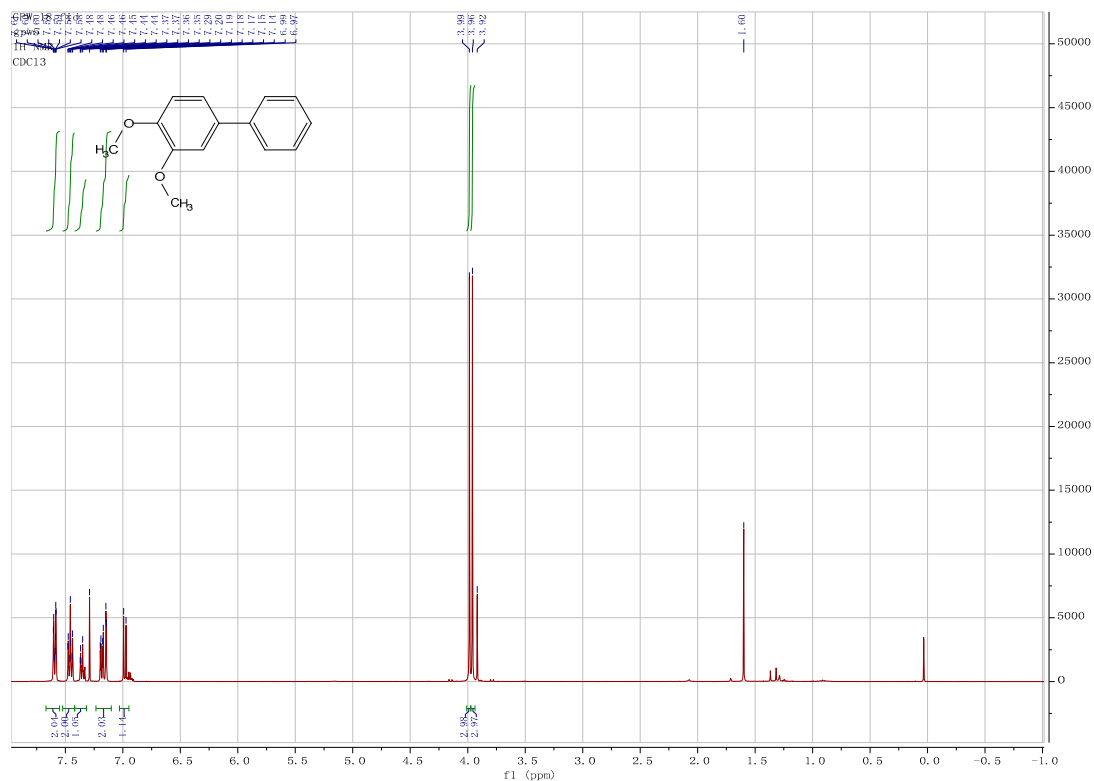
Compound **3a** was prepared according to the general procedure and purified by column chromatography to give a white solid. ¹H NMR (400 MHz, Chloroform-d) δ 7.70 – 7.62 (m, 2H), 7.55 – 7.45 (m, 2H), 7.45 – 7.37 (m, 1H). HRMS (ESI) m/z calcd for C₁₂H₁₁⁺ (M+H)⁺ 155.08553, found 155.08646.



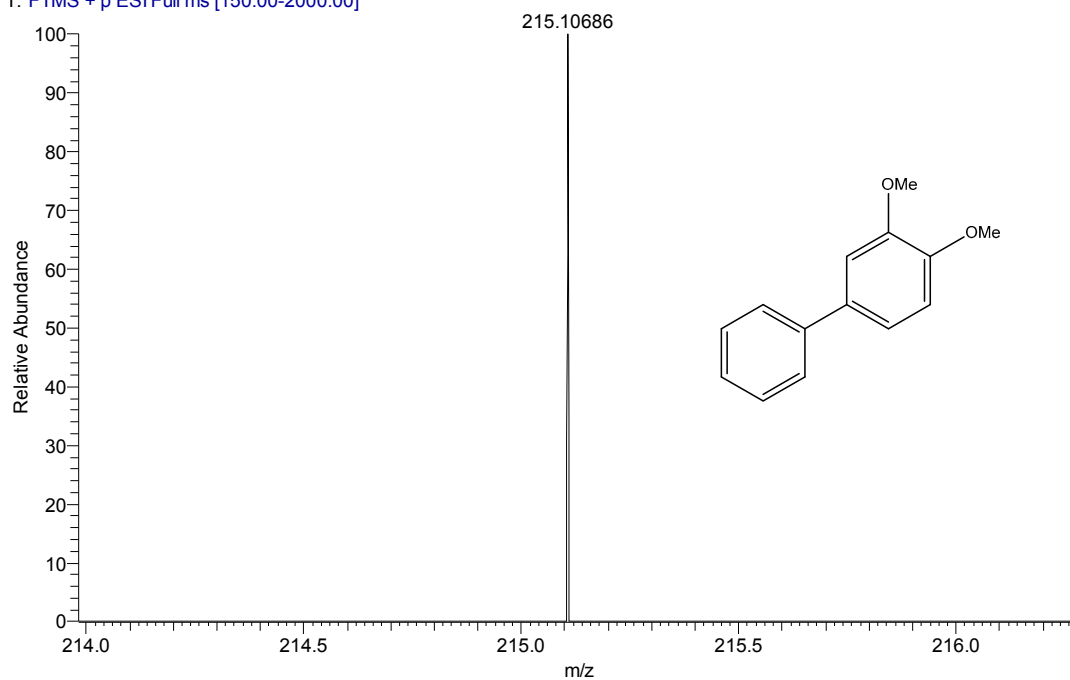
385 #10 RT: 0.17 AV: 1 NL: 3.44E3
T: FTMS + p ESI Full ms [150.00-2000.00]



3b ^1H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.55 (m, 2H), 7.52 – 7.42 (m, 2H), 7.42 – 7.32 (m, 1H), 7.23 – 7.10 (m, 2H), 6.98 (d, $J = 8.3$ Hz, 1H), 3.99 (s, 3H), 3.96 (s, 3H). HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{15}\text{O}_2^+$ ($\text{M}+\text{H}$) $^+$ 215.10666, found 215.10686.

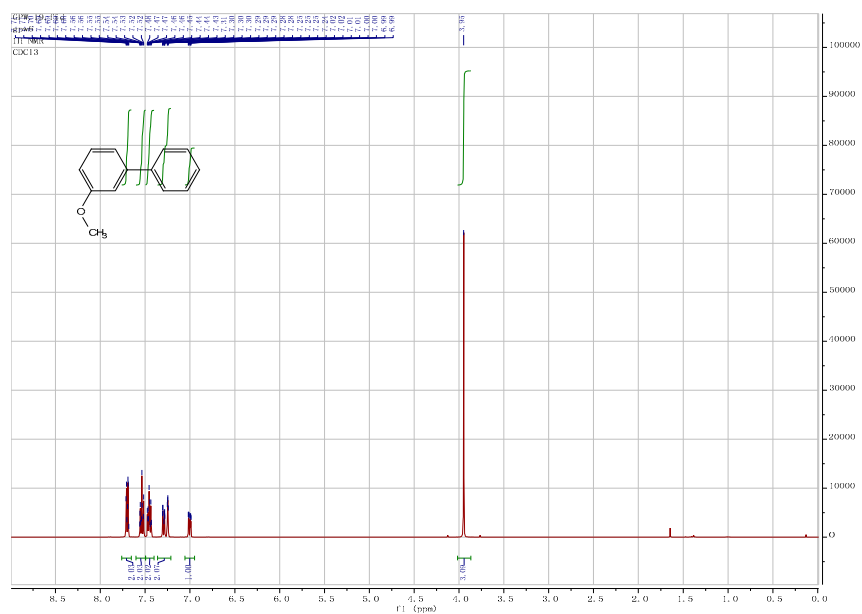
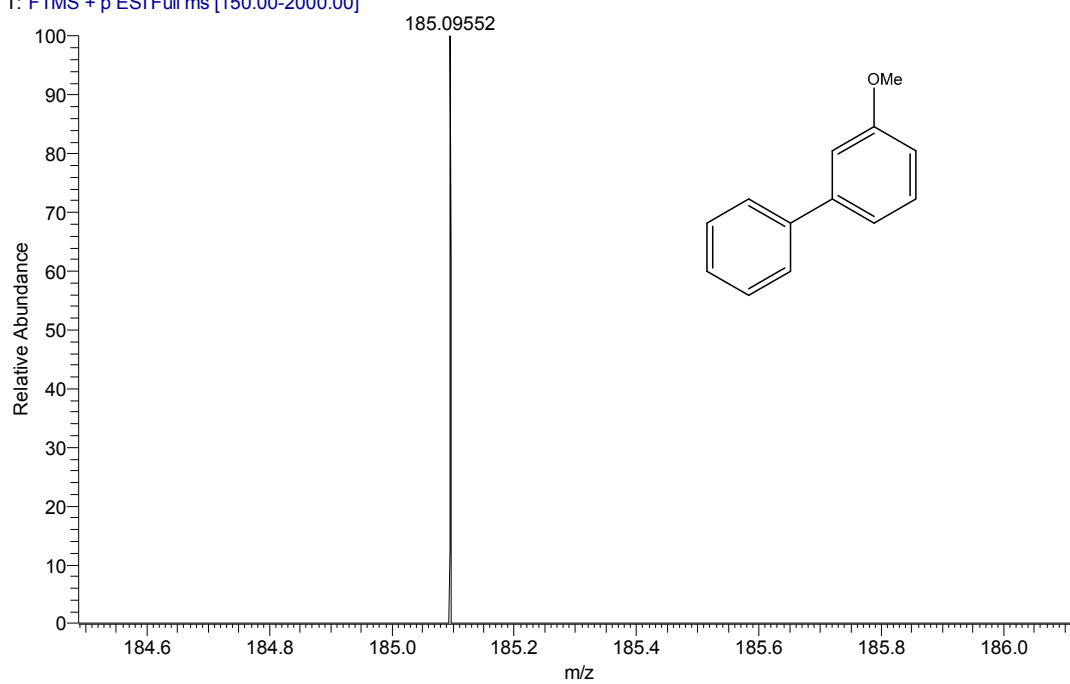


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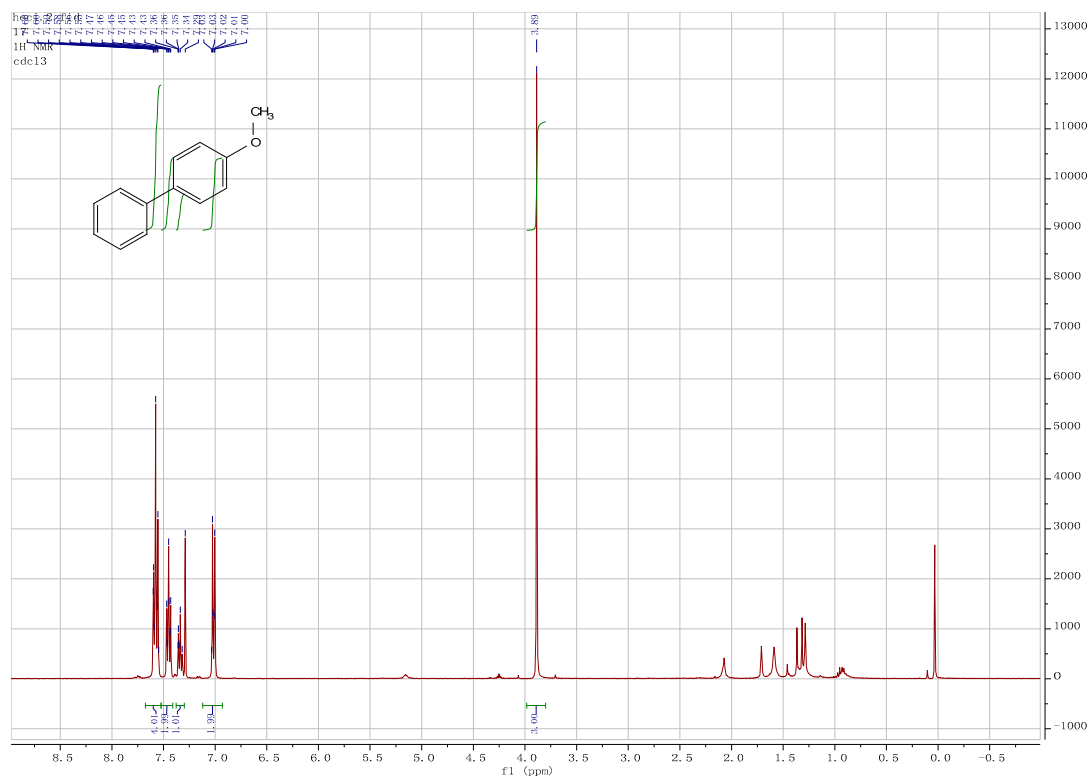
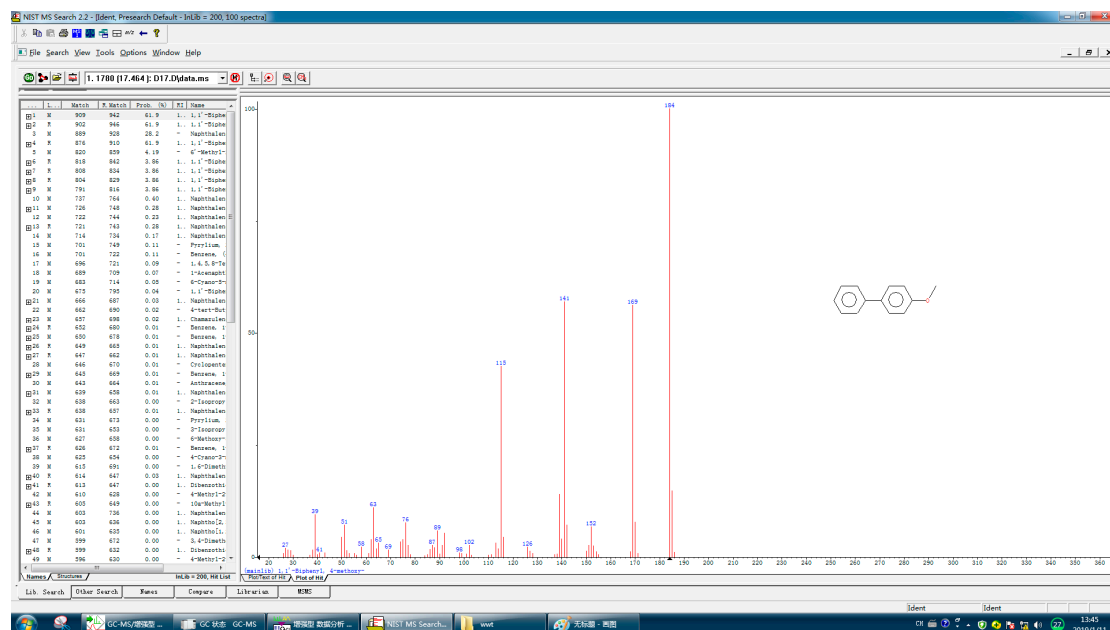


3c ^1H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.65 (m, 2H), 7.60 – 7.50 (m, 2H), 7.45 (tt, $J = 7.4$, 2.4 Hz, 2H), 7.36 – 7.21 (m, 2H), 7.00 (ddd, $J = 8.2$, 2.6, 0.9 Hz, 1H), 3.95 (s, 3H). HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{13}\text{O}^+$ ($\text{M}+\text{H}$) $^+$ 185.09609, found 185.09552.

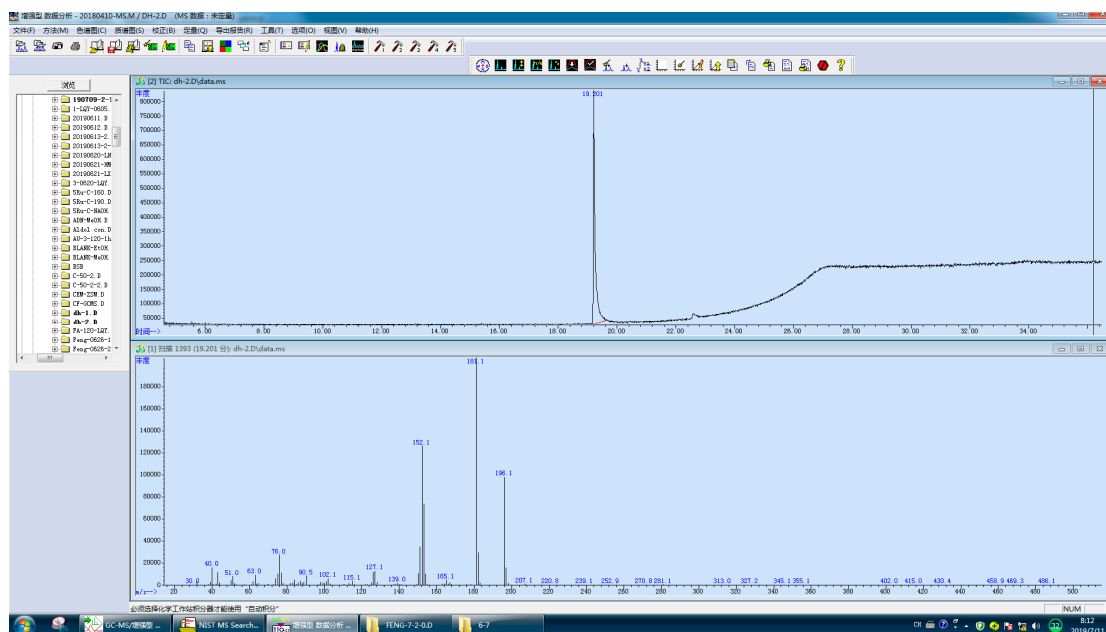
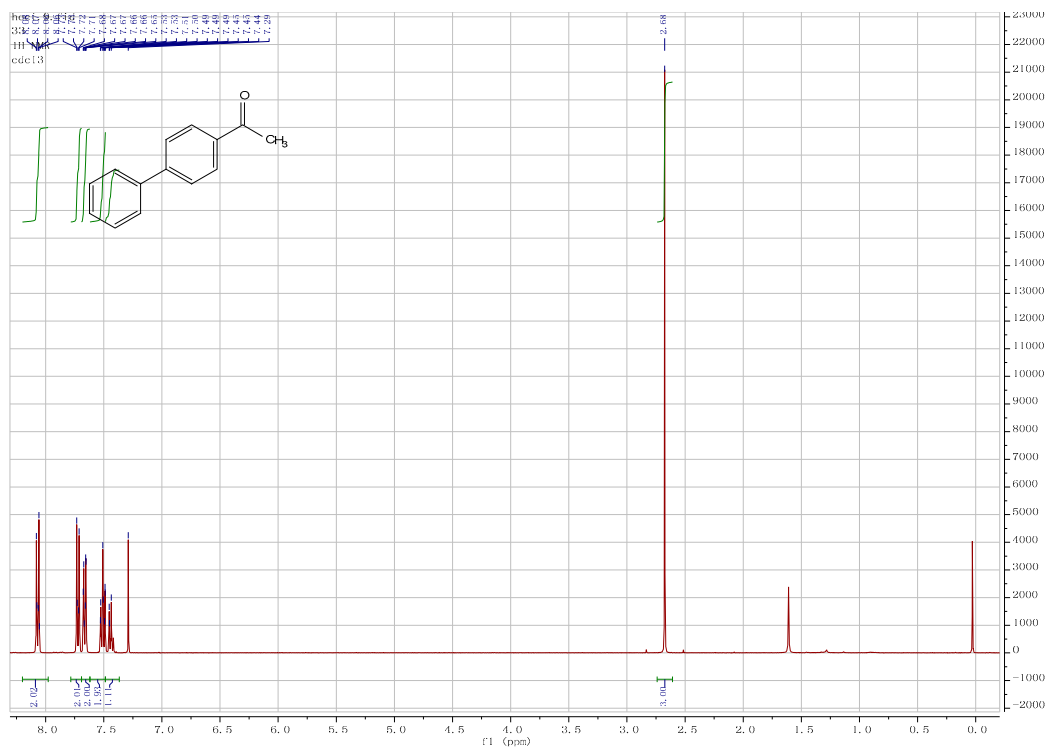
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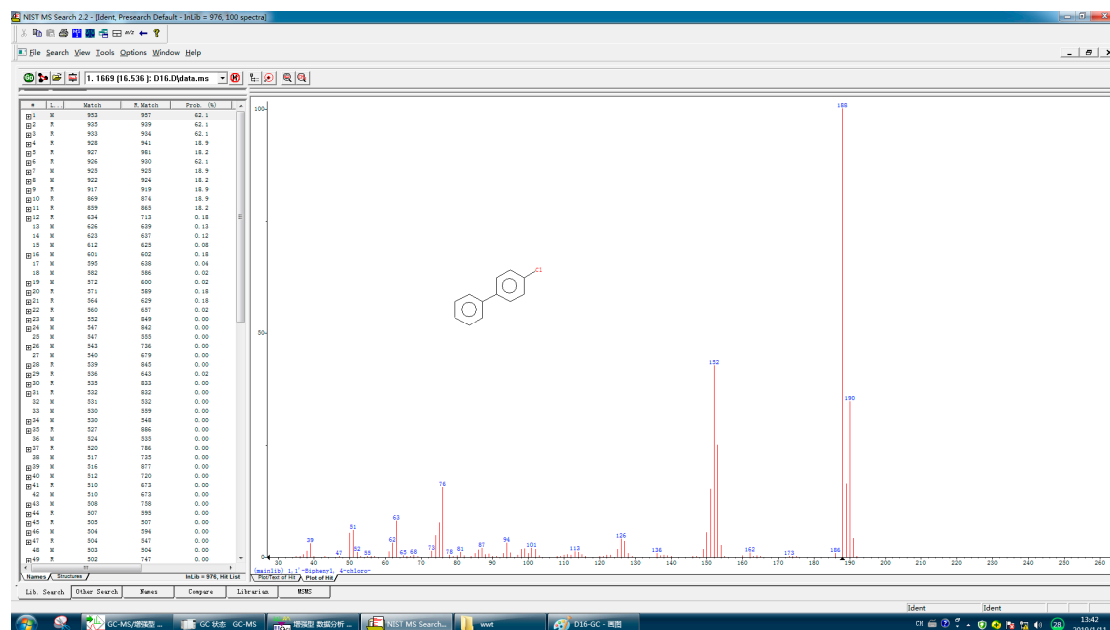
3d ^1H NMR (400 MHz, CDCl_3) δ 7.68 – 7.52 (m, 4H), 7.45 (dd, $J = 8.5, 6.9$ Hz, 2H), 7.38 – 7.30 (m, 1H), 7.12 – 6.93 (m, 2H), 3.89 (s, 3H). calcd for $\text{C}_{13}\text{H}_{12}\text{O}$ 184, found 184.



3f ¹H NMR (400 MHz, Chloroform-d) δ 8.20 – 7.98 (m, 2H), 7.78 – 7.69 (m, 2H), 7.69 – 7.62 (m, 2H), 7.62 – 7.49 (m, 2H), 7.49 – 7.37 (m, 1H), 2.68 (s, 3H). calcd for C₁₄H₁₂O 196.09, found 196.1.

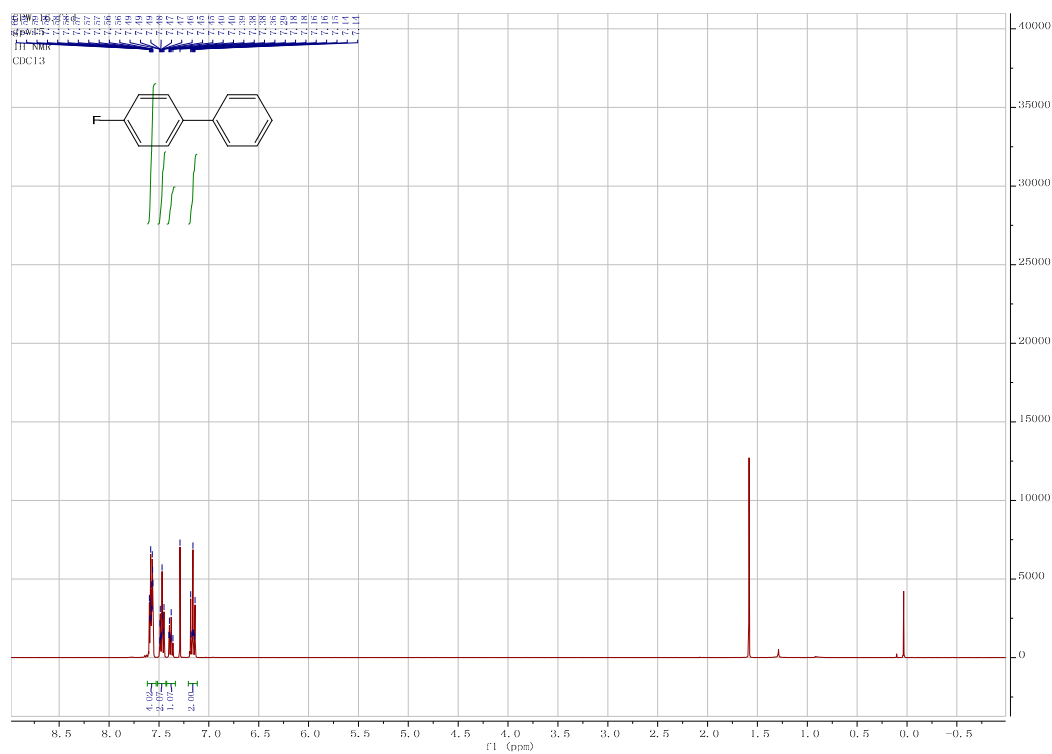
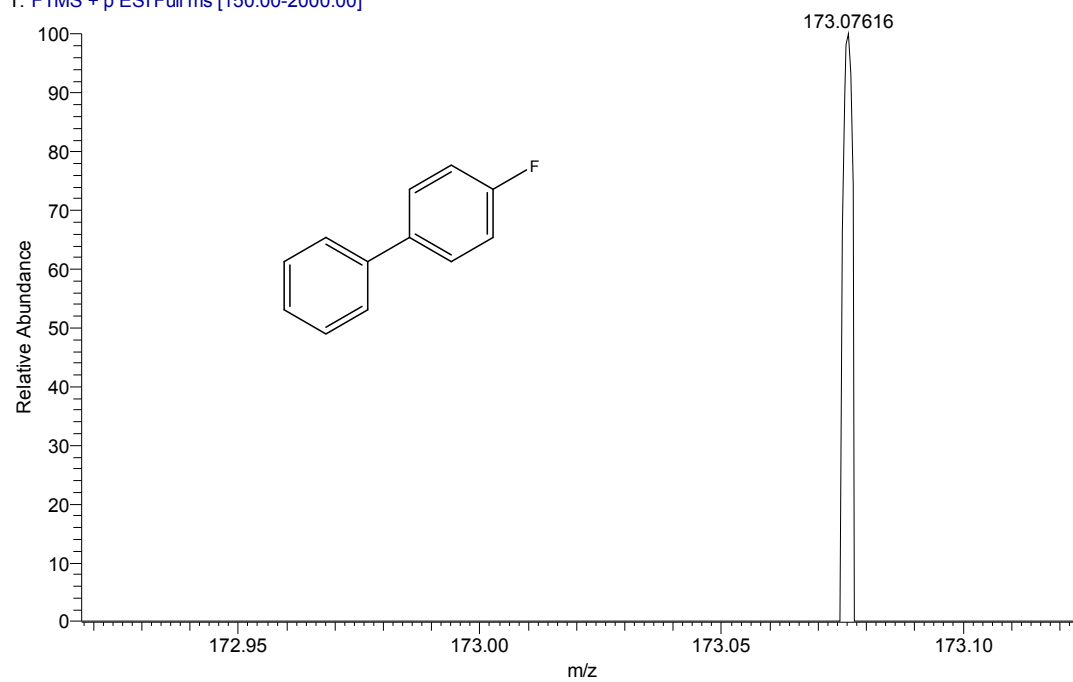


3g calcd for $\text{C}_{12}\text{H}_9\text{Cl}$ 188, found 188. $^1\text{H NMR}$ (400 MHz, $\text{Chloroform-}d$) δ 7.64 – 7.55 (m, 4H), 7.54 – 7.40 (m, 6H).

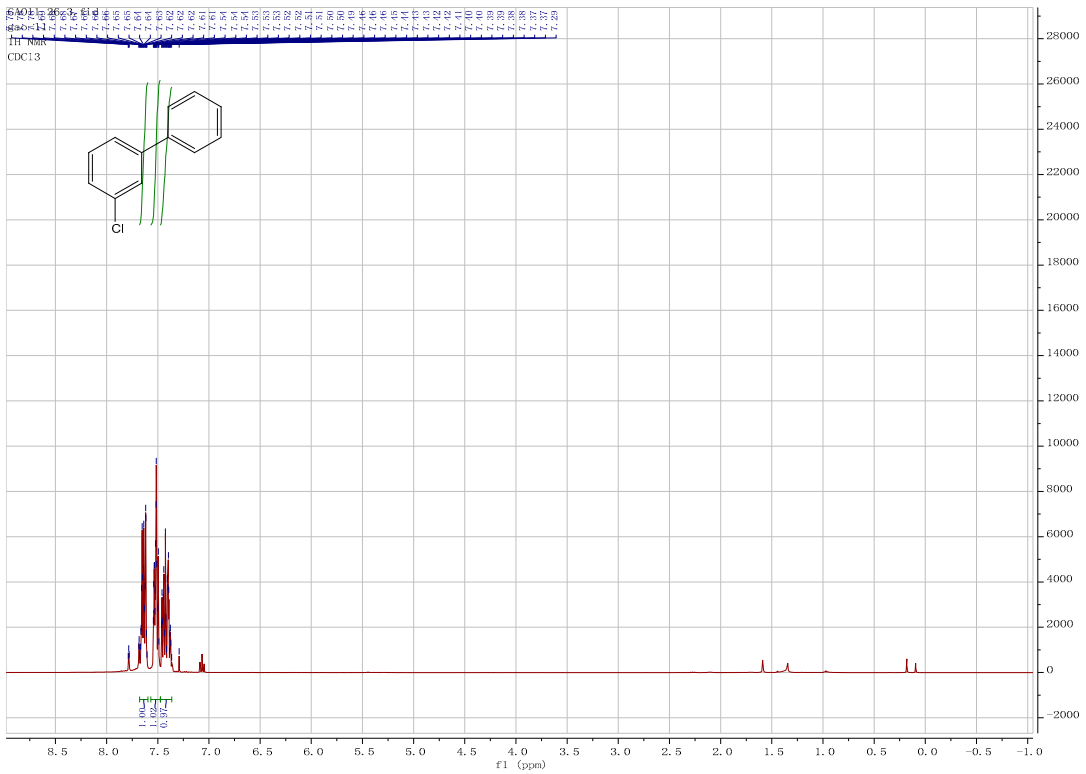
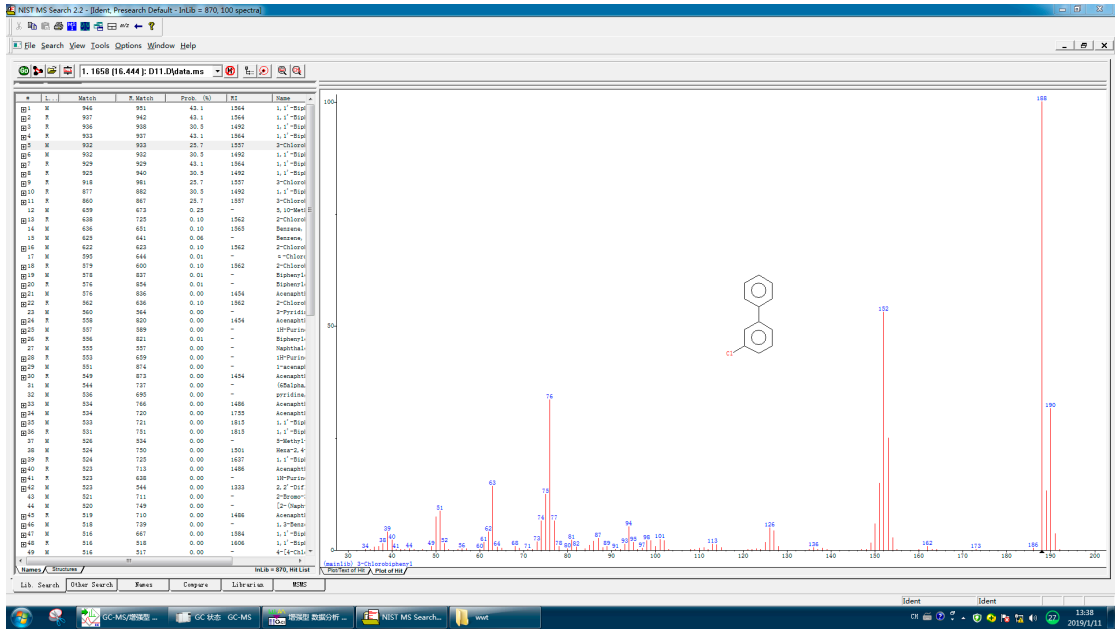


3h HRMS (ESI) m/z calcd for $C_{12}H_{10}F^+$ ($M+H$)⁺ 173.07610, found 173.07616. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.53 (m, 4H), 7.51 – 7.43 (m, 2H), 7.42 – 7.34 (m, 1H), 7.21 – 7.12 (m, 2H).

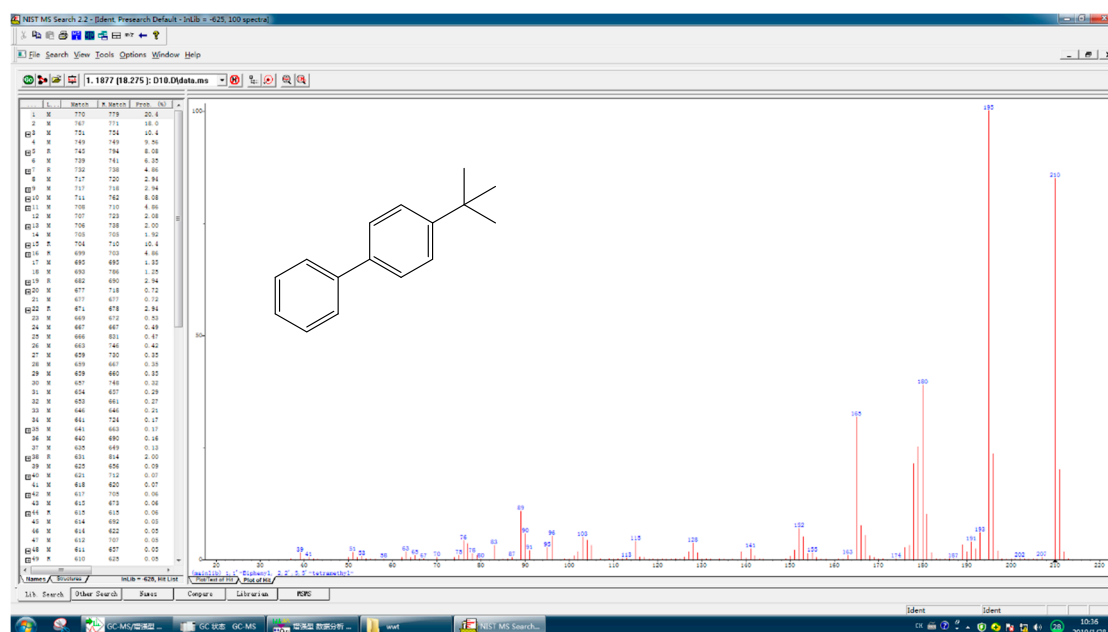
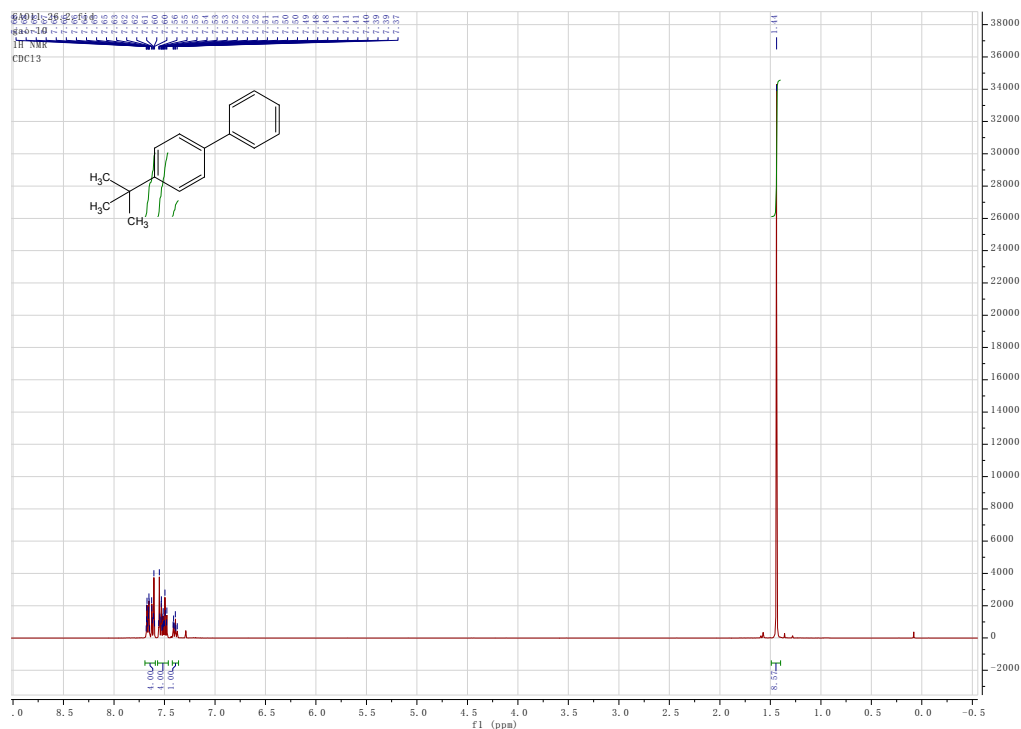
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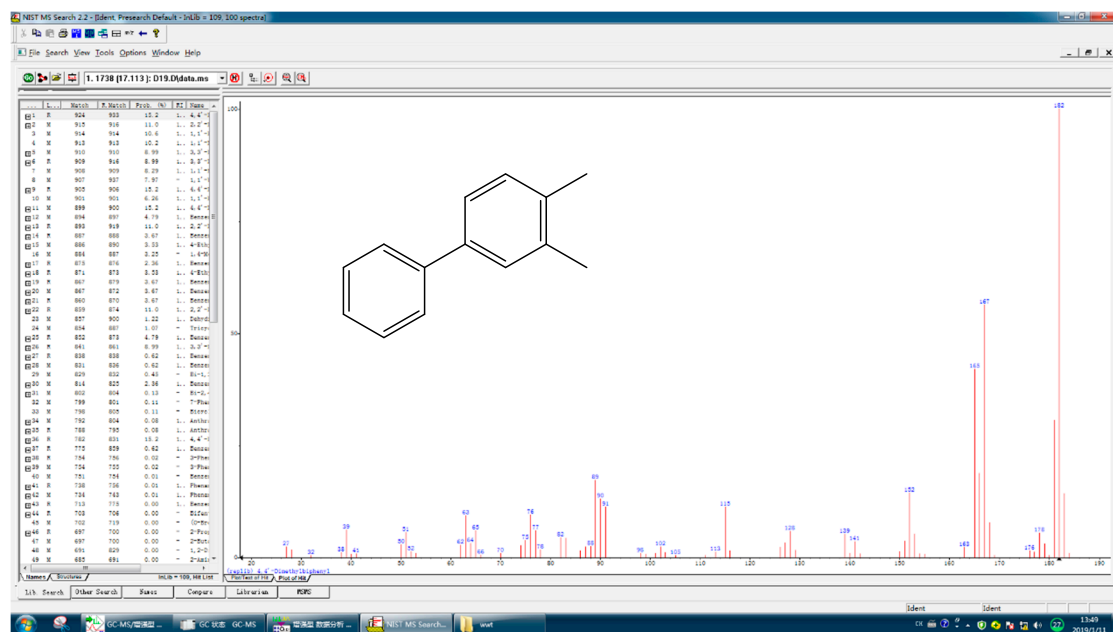
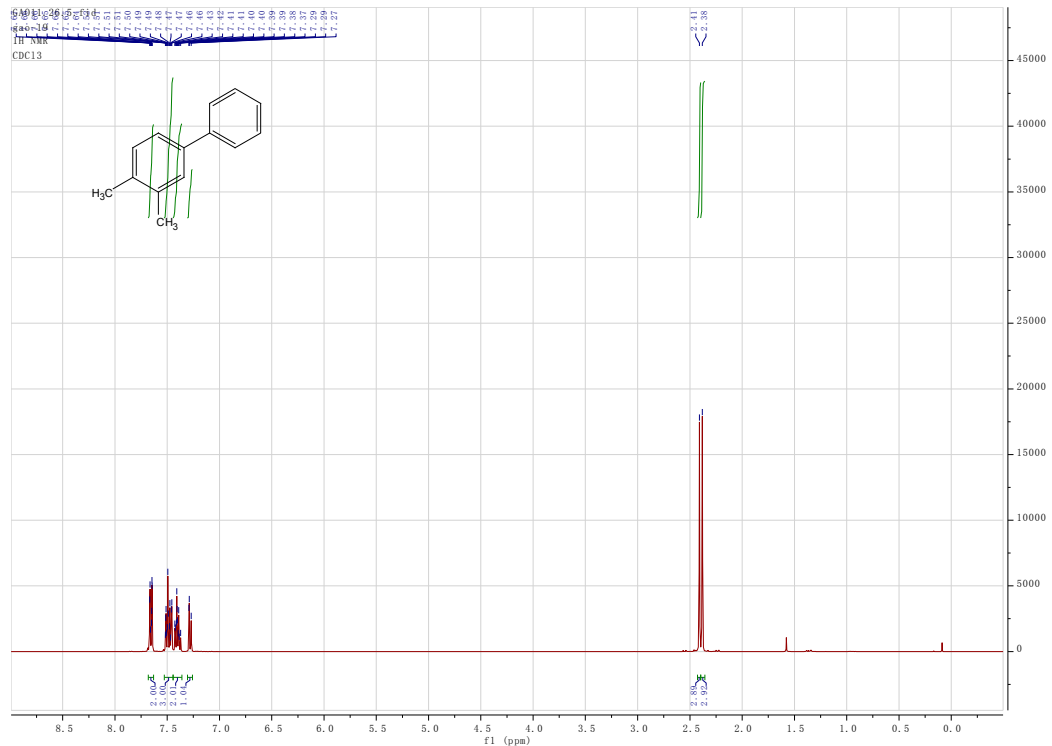
3i calcd for C₁₂H₉Cl 188, found 188. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.60 (m, 1H), 7.57 – 7.47 (m, 1H), 7.47 – 7.36 (m, 1H).



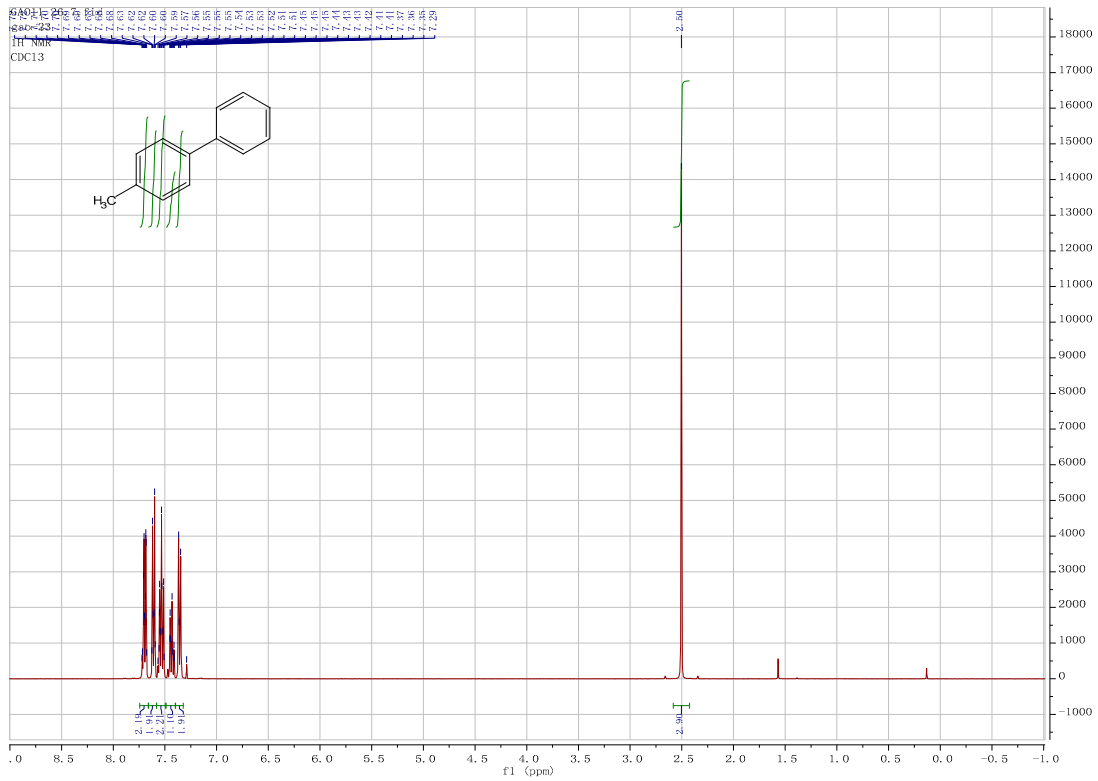
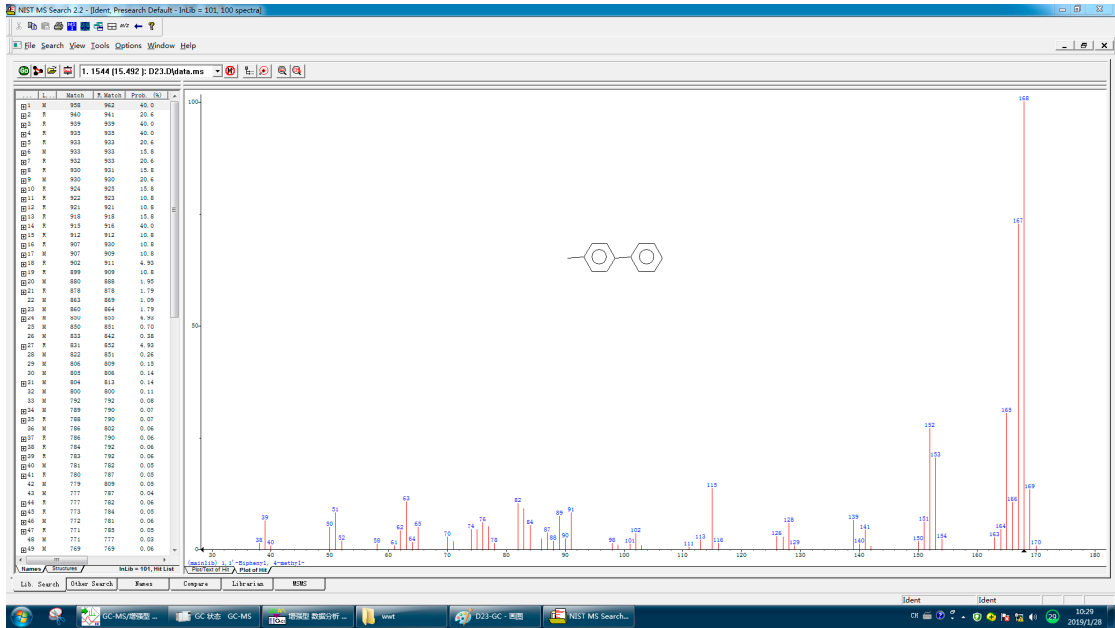
3j calcd for C₁₆H₁₈ 210, found 210. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.59 (m, 4H), 7.57 – 7.46 (m, 4H), 7.42 – 7.36 (m, 1H), 1.44 (s, 9H).



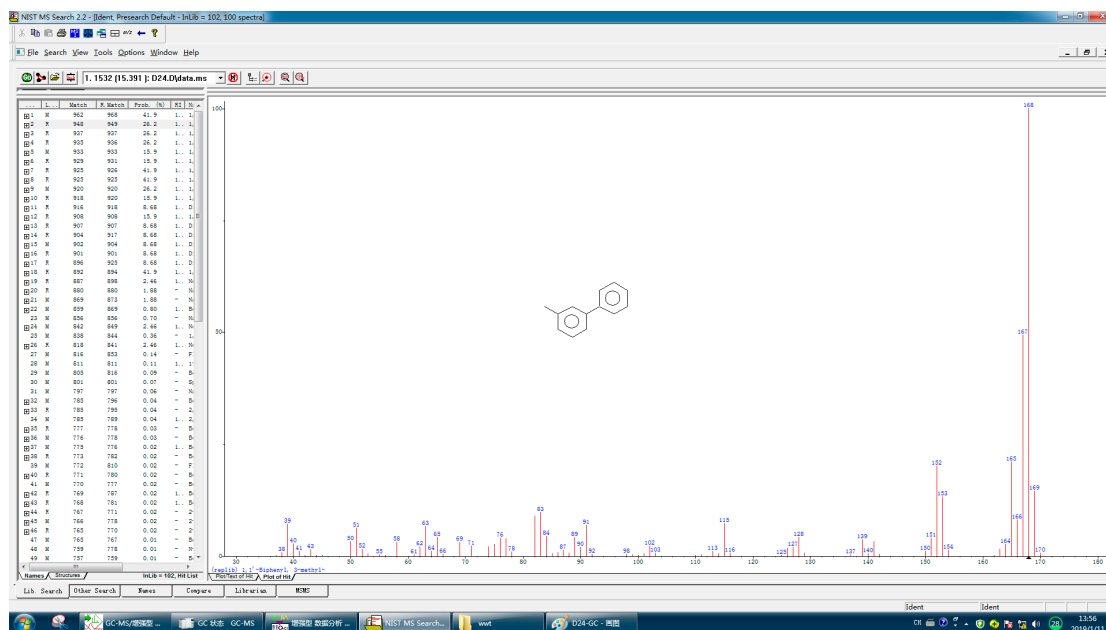
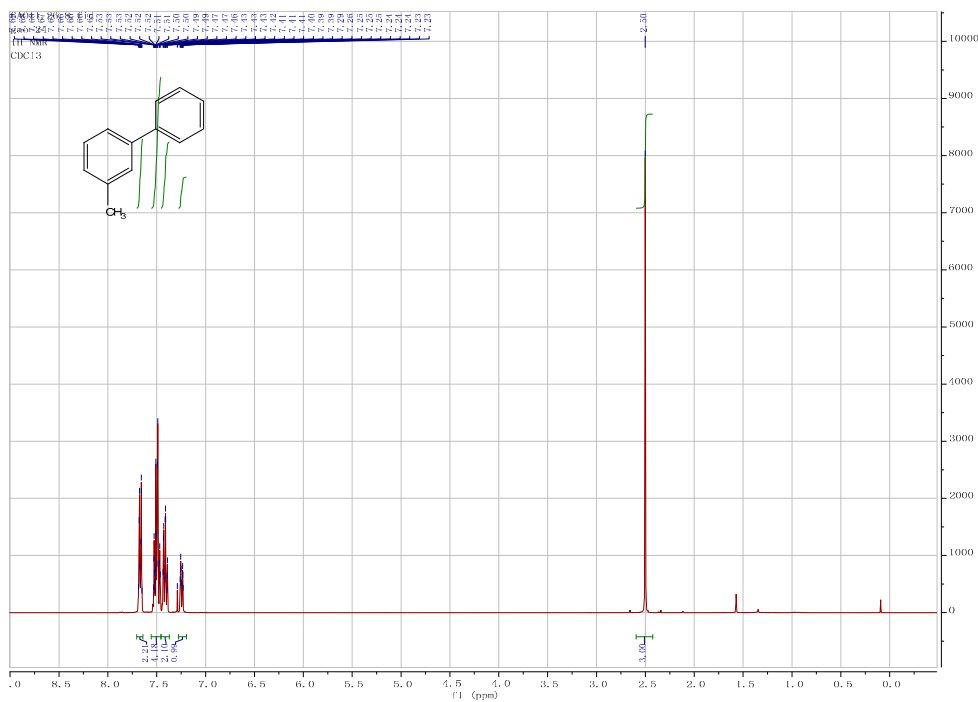
3k calcd for C₁₄H₁₄ 182, found 182. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.63 (m, 2H), 7.53 – 7.44 (m, 3H), 7.44 – 7.36 (m, 2H), 7.31 – 7.26 (m, 1H), 2.41 (s, 3H), 2.38 (s, 3H).



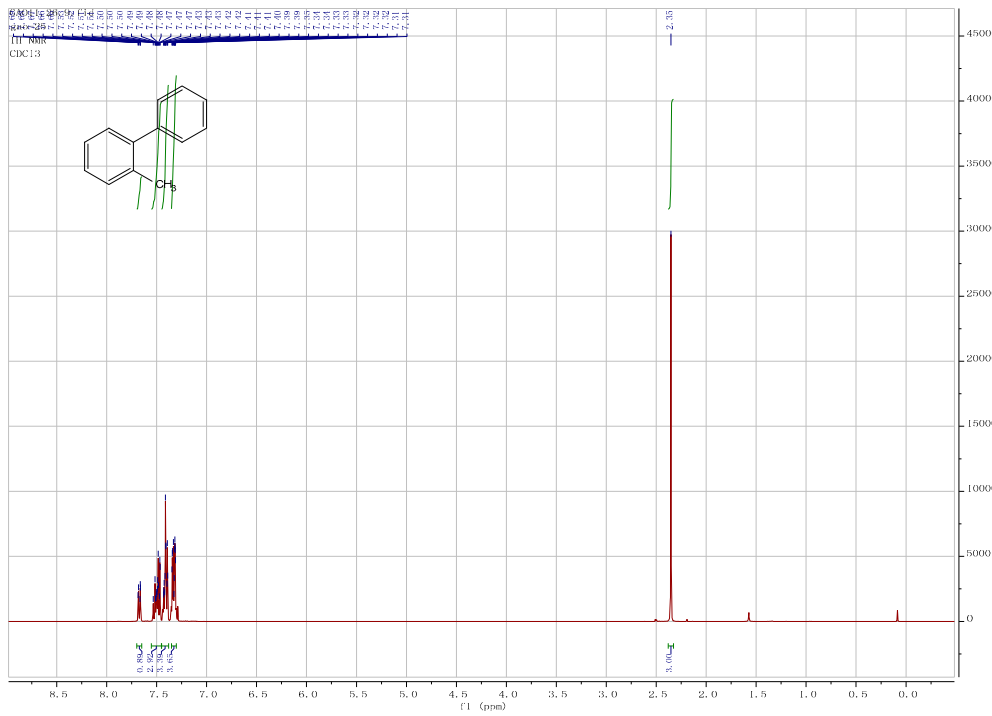
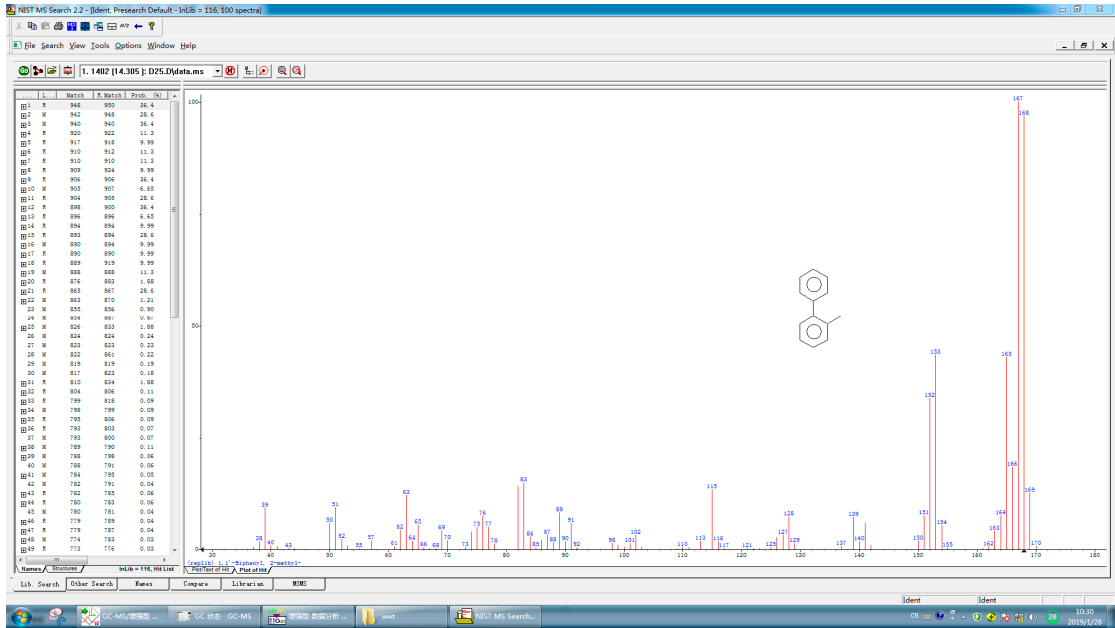
31 calcd for $\text{C}_{13}\text{H}_{12}$ 168, found 168. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.66 (m, 2H), 7.66 – 7.58 (m, 2H), 7.58 – 7.50 (m, 2H), 7.49 – 7.40 (m, 1H), 7.36 (d, J = 8.0 Hz, 2H), 2.50 (s, 3H).



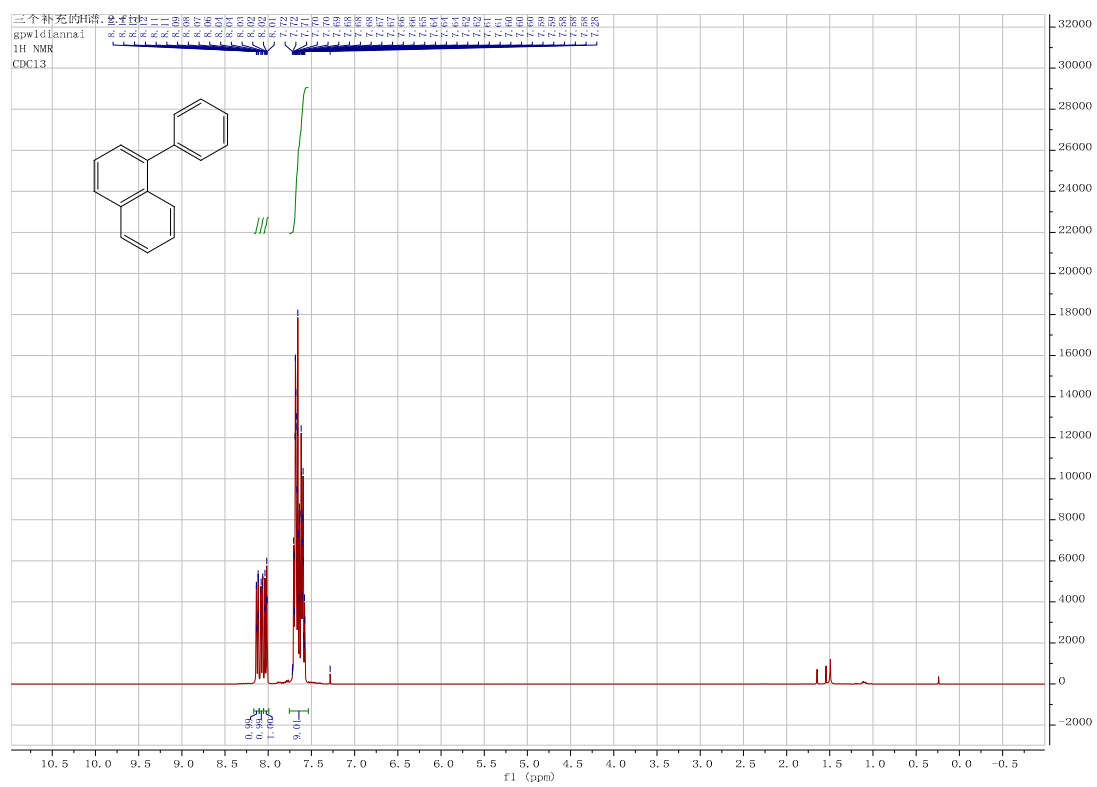
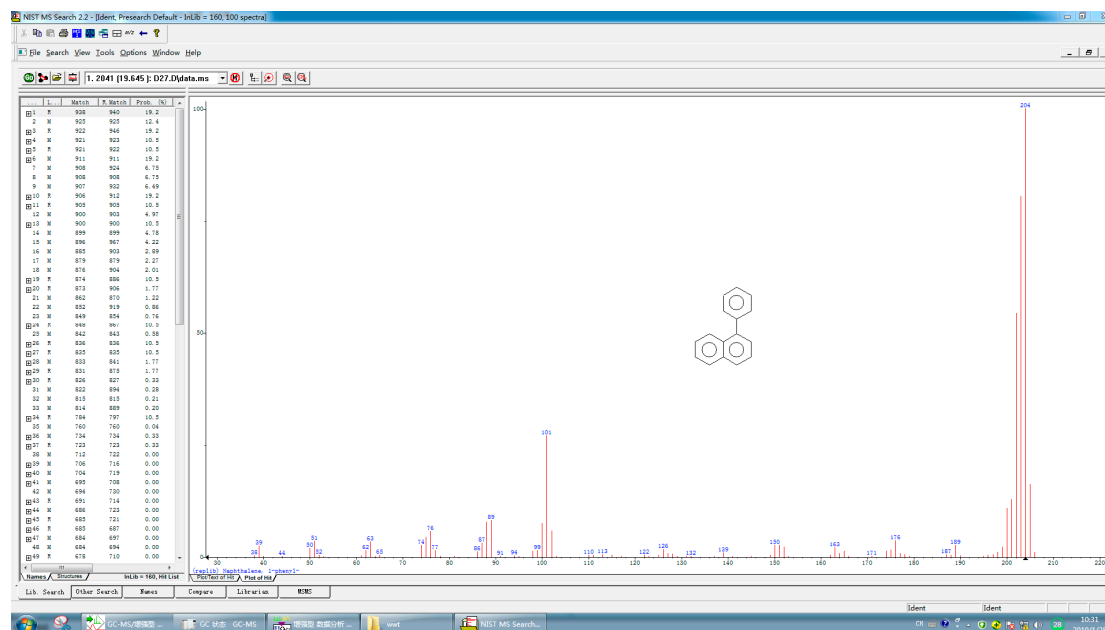
3m calcd for $C_{13}H_{12}$ 168, found 168. 1H NMR (400 MHz, Chloroform-d) δ 7.71 – 7.64 (m, 2H), 7.56 – 7.46 (m, 4H), 7.41 (ddt, J = 7.8, 6.9, 1.4 Hz, 2H), 7.28 – 7.20 (m, 1H), 2.50 (s, 3H).



3n calcd for $C_{13}H_{12}$ 168, found 168. 1H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.65 (m, 1H), 7.55 – 7.45 (m, 3H), 7.45 – 7.38 (m, 3H), 7.35 – 7.30 (m, 4H), 2.35 (s, 3H).



3o calcd for C₁₆H₁₂ 204, found 204. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.17 – 8.10 (m, 1H), 8.07 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.03 (dt, *J* = 8.2, 1.2 Hz, 1H), 7.76 – 7.54 (m, 9H).



References

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