Supplementary Information

Iron/Iron Oxide Nanoparticles: A Versatile Support for Catalytic Metals and Their Application in Suzuki-Miyaura Cross-Coupling Reactions

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1. Reagents and Materials

Iron (III) chloride ($FeCl_3$, 97%), Palladium (II) nitrate hydrate ($Pd(NO_3)_2{\cdot}xH_2O$), sodium borohydride ($NaBH_4$, 99%) and all aryl halides, aryl boronic acids were purchased from Sigma-Aldrich. K_2CO_3 was purchased from Mallinckrodt. KOH and Na_2SO_4 were obtained from Caledon. All reagents were used without further purification. Typically, in-house distilled water was employed for all syntheses and reactions, whereas 18.2 $M\Omega{\cdot}cm^{-1}$ deionized water was used for ICP-MS studies.

2. Preparation of $Fe@Fe_xO_y$ nanoparticles

$Fe@Fe_xO_y$ were prepared using a modified literature procedure. Briefly, $FeCl_3$ (21 mmol) was dissolved in 400 mL of deionized water. A solution of $NaBH_4$ (2.24 g, 59 mmol) in 30 mL of water was added dropwise while the iron (III) chloride solution was stirred vigorously. The orange solution became dark, and a black precipitate formed. The precipitate was vacuum-filtered and washed with 500 mL of deionized water followed by 50 mL of 95% ethanol. The resulting black paste was transferred to a round-bottom flask and dried *in vacuo* for 2 days to yield a black powder. The $Fe@Fe_xO_y$ powder was ground using a mortar and pestle to break up large aggregates in an argon-filled glovebox (0.6 ppm H_2O, 0.6 ppm O_2). Yield: 0.98 g.

3. Preparation of $Fe@Fe_xO_y$ supported Pd catalyst ($Fe@Fe_xO_y/Pd$)

0.01 mmol of $Pd(NO_3)_2$, 2 mg of $Fe@Fe_xO_y$, and 5 mL of aqueous KOH solution (pH 10.5) were mixed under argon and sonicated for 20 minutes. The reaction mixture was subsequently centrifuged, and the black precipitate was washed with distilled water once and directly used in the Suzuki-Miyaura coupling reactions under investigation. The Pd loading amount was determined by inductively coupled plasma mass spectrometry (ICP-MS). After filtering the reaction mixture (Whatman No. 2 filter papers), the colorless filtrate was acidified with concentrated nitric acid and analyzed by ICP-MS to determine the amount of unreacted Pd (0.05 % compared to initial amount). In conclusion, $Pd(NO_3)_2$ is almost completely deposited on $Fe@Fe_xO_y$ and the catalyst Pd content corresponds to the initial amount of $Pd(NO_3)_2$ (0.01 mmol on 2 mg $Fe@Fe_xO_y$).

4. General procedure for Suzuki-Miyaura coupling reactions

Aryl halide (2.0 mmol) and aryl boronic acid (2.4 mmol) were dissolved in 5 ml ethanol. K_2CO_3 (5 mmol) in 2 mL distilled water was added to the solution. $Fe@Fe_xO_y/Pd$ (0.5 mol%) were sonicated in 3 mL distilled water and also added. The reaction mixture was stirred at room temperature in air for the indicated time. After reaction, the mixture was diluted with H_2O (20 mL) and diethyl ether (20 mL). The catalyst was separated by gravity filtration (Whatman No. 2 filter papers) or centrifugation (when catalyst was reused), and the mixture was extracted with diethyl ether (4 × 25 mL). The organic layers were combined, dried with anhydrous Na_2SO_4 and the solvent was removed on a rotary evaporator to yield the crude product. If necessary, the crude product was purified by column chromatography on silica gel to give the desired products. Products were identified by GC-MS and ^1H and ^{13}C NMR.

While these reactions were performed in air, the catalyst may undergo slow oxidation in solution upon prolonged (i.e., >>48 hours) exposure to air, and should not be exposed to air when dry.

5. Assay of residual Pd in the crude product

The reaction procedures are the same as above, except that membrane filters (Millipore, 0.45 μm) were used to filter off the catalyst rather than Whatman No. 2 filter papers. The crude product was heated to 625□ for several hours to remove organic components. The residues were dissolved in concentrated nitric acid and analyzed by ICP-MS.

6. Characterization

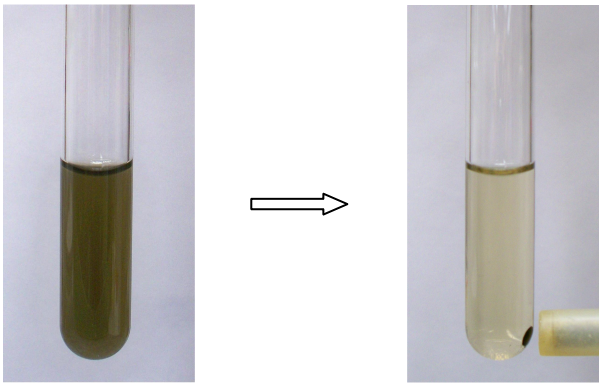
^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Inova 400 spectrometer at 400 MHz and 100 MHz, respectively. Spectra were referenced to $CHCl_3$ (7.26 ppm) and $CDCl_3$ (77.06 ppm), respectively. Chemical shifts are recorded in parts per million (ppm, δ).

Gas chromatography-mass spectrometry (GC-MS) was performed on a HP 5890 with a 5970 MSD using electron ionization. 1 μL of an acetone solution of the product was injected into a DB-5MS column with a 0.25 μm film. The carrier gas was helium at 1 mL/min. The injection port was at 280□ and a linear temperature profile (50□ - 280□ at 10□/minute) was employed.

Transmission electron microscopy (TEM) was performed using a JEOL 2010 Transmission Electron Microscope with an accelerating voltage of 200 keV and a LaB_6 thermionic emission filament. The instrument was fitted with an Energy Dispersive X-Ray (EDX) detector for elemental analysis. TEM samples were prepared by suspending particles in distilled water by sonication and dropcoating the solution onto carbon-coated, 200-mesh Cu grids (SPI Supplies).

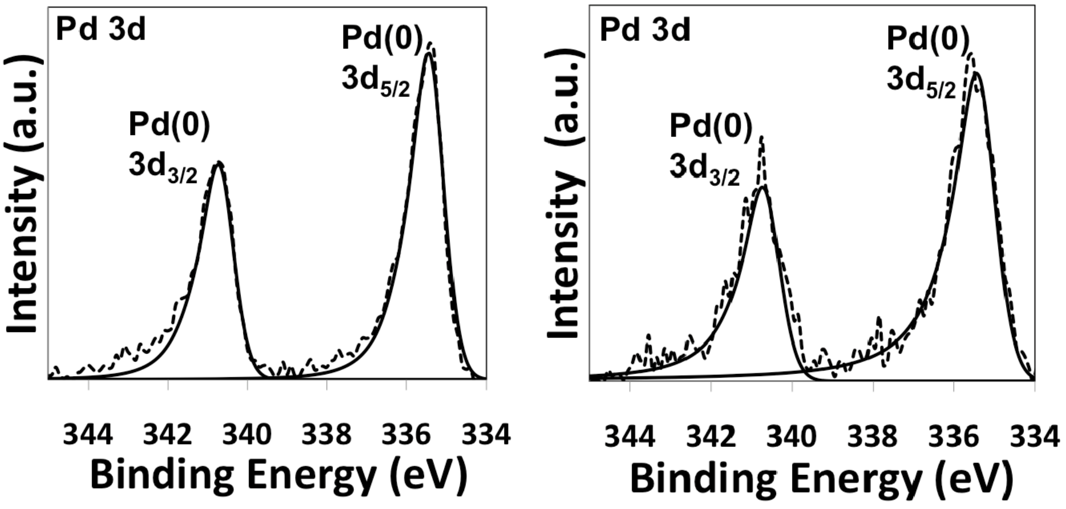
X-ray photoelectron spectroscopy (XPS) was performed on an AXIS-165 XPS spectrometer from Kratos Analytical. The base pressure and operating pressure in the chamber were maintained at $\leq 10^{-7}$ Pa. A monochromatic Al Kα X-ray ($\lambda = 8.34$Å) was used to irradiate the samples, and the spectra were obtained with an electron takeoff angle of 90°. Samples were pressed into carbon tape. To control sample charging, the charge neutralizer filament was used during the experiment. The pass energy for the survey and the high-resolution spectra were 160 and 20 eV, respectively. Spectra were calibrated to the C 1s emission at 284.8 eV using CasaXPS (VAMAS) software. Following calibration, the background of each spectrum was subtracted using a Shirley-type background to remove most of the extrinsic loss structure. Fitting was carried out using 70% Lorentzian/30% Gaussian line shapes for metal zero-oxidation states, and Gaussian line shapes for higher oxidation states. Binding Energy values and orbital splitting were consistent with literature values obtained from the NIST database (http://srdata.nist.gov/xps/).

Inductively coupled plasma mass spectrometry (ICP-MS) was performed on a Perkin Elmer Elan 6000 ICP-MS. Sample solvents were evaporated and the organic components were removed by heating at 625℃ for several hours. The residues were dissolved in concentrated nitric acid and analyzed by ICP-MS. The flow rate on the instrument was 1 mL/min and dual detector mode was employed. A blank was subtracted after internal standard correction and the values reported are an average of three readings (35 sweeps per reading).



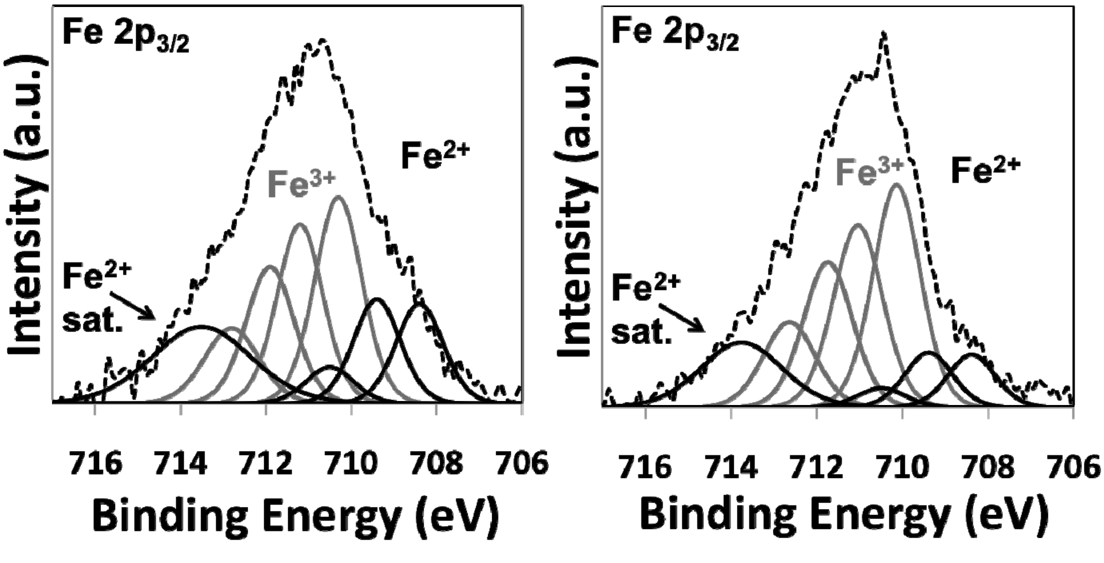
Before After

Figure S1. Magnetic separation of the catalyst from the reaction mixture.



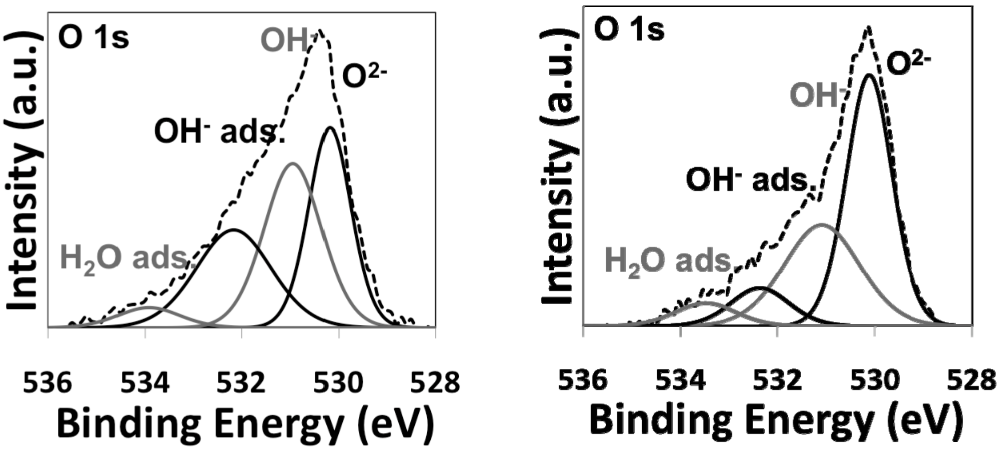
(a) (b)

Figure S2. Background-subtracted high-resolution Pd 3d region of the XP spectra of Fe@Fe$_x$O$_y$/Pd (a) before reaction (b) after reaction. Experimental (dotted line) and fit (solid line) data indicate metallic Pd(0). FWHM range from 0.85 to 1.05. Note that reduced sample size after reaction leads to reduced signal-to-noise ratio.



(a) (b)

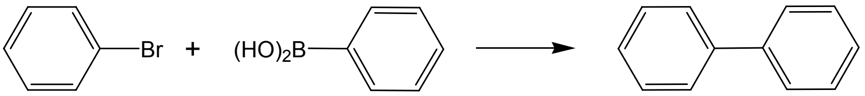
Figure S3. Shirley background-subtracted high-resolution Fe 2p$_{3/2}$ region of the XP spectra (dotted line) of Fe@Fe$_x$O$_y$/Pd (a) before reaction and (b) after reaction. The fitting (solid lines) indicates the presence of mixed oxides Fe$_3$O$_4$ and FeOOH. A slight decrease in Fe(II) is observed after reaction.



(a) **(b)**

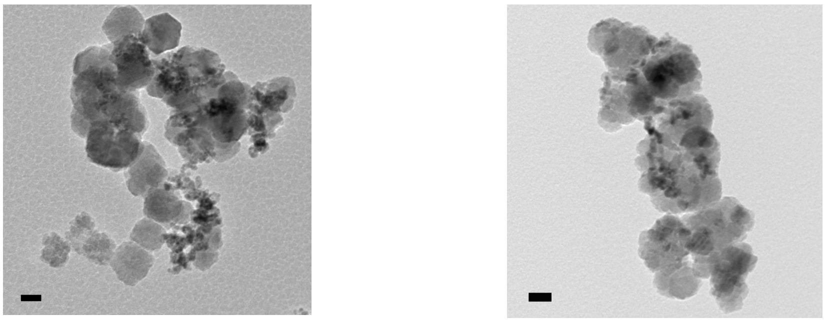
Figure S4. Shirley background-subtracted high-resolution O 1s region of the XP spectra of Fe@Fe_xO_y/Pd (dotted line) (a) before reaction and (b) after reaction. Solid lines show fits. The peak fit to crystalline OH^- confirms the presence of FeOOH alongside Fe_3O_4.

Table S1. Suzuki-Miyaura coupling reactions catalyzed by Pd/C and Fe@Fe_xO_y/Pd.[a]



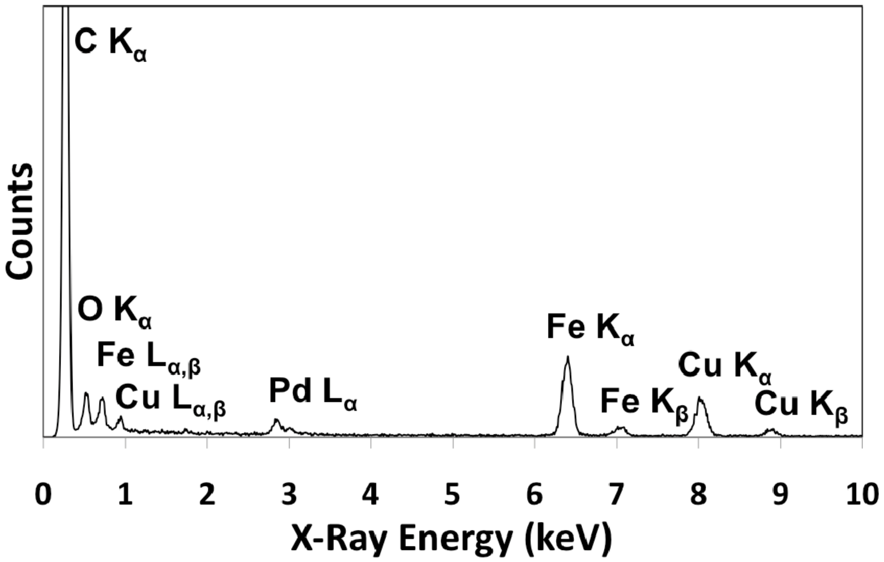
Catalyst	Time (h)	Yield (%)[b]
Pd/C	4	90
Fe@Fe_xO_y/Pd	4	95

[a] Reaction conditions: 2.0 mmol bromobenzene, 2.4 mmol phenylboronic acid, 5.0 mmol K_2CO_3, 0.5 mol % catalyst, H_2O/EtOH (1:1), room temperature. [b] Isolated yield.

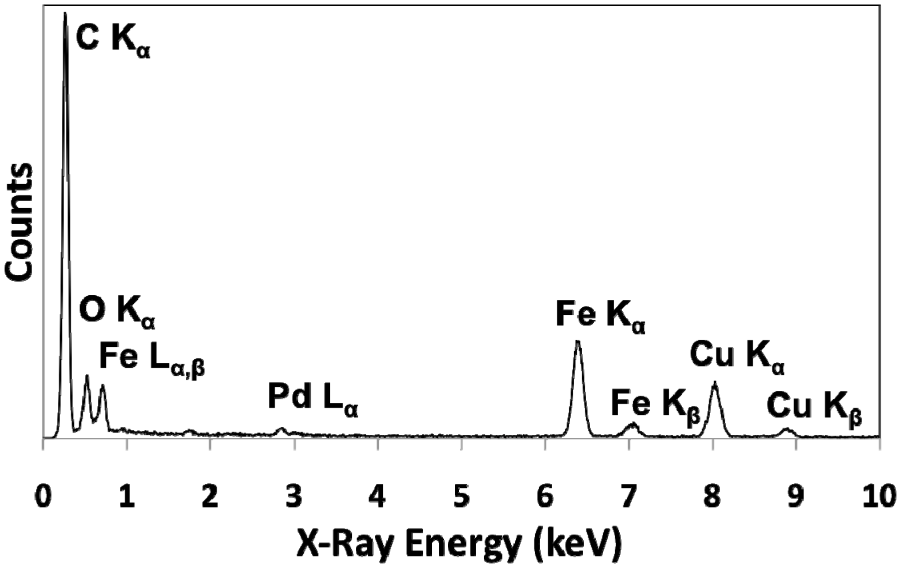


(a) **(b)**

Figure S5. TEM images of Fe@Fe_xO_y/Pd (a) before reaction and (b) after 5 reactions, showing no significant change in catalyst morphology. Scale bar: 20 nm.



(a)



(b)

Figure S6. EDX spectra of Fe@Fe_xO_y/Pd (a) before reaction and (b) after 5 reactions, showing no significant change in catalyst composition.

Biphenyl. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.4 Hz, 4H), 7.49 (t, *J* = 7.5 Hz, 4H), 7.39 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 128.8, 127.3, 127.2.

2-Methylbiphenyl. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.46 (m, 2H), 7.41 (t, *J* = 7.6 Hz, 3H), 7.35-7.30 (m, 4H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0, 141.9, 135.4, 130.4, 129.8, 129.2, 128.1, 127.3, 126.8, 125.8, 20.5.

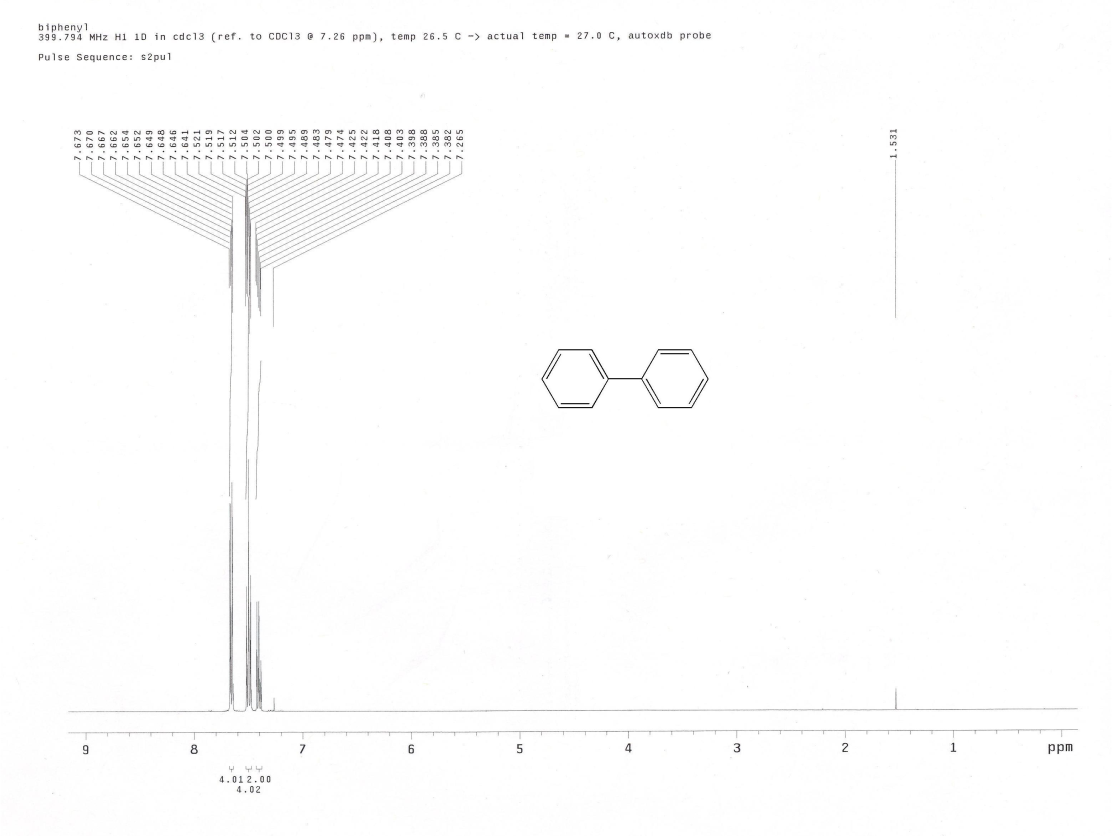
2-Methoxybiphenyl. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.0 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.38-7.34 (m, 3H), 7.09-7.01 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.5, 138.6, 130.9, 130.8, 129.6, 128.6, 128.0, 126.9, 120.9, 111.3, 55.6.

3-Methoxybiphenyl. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.41 (m, 2H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.20 (s, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 142.8, 141.2, 129.8, 128.8, 127.5, 127.2, 119.7, 113.0, 112.7, 55.3.

4-Methoxybiphenyl. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.55 (m, 4H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 140.8, 133.8, 128.7, 128.2, 126.7, 126.6, 114.2, 55.4.

4-Acetylbiphenyl. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.1 Hz, 1H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 145.8, 139.9, 135.9, 129.0, 128.9, 128.2, 127.3, 127.2, 26.7.

4-Nitrobiphenyl. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 6.9 Hz, 2H), 7.53-7.44 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 147.1, 138.8, 129.1, 128.9, 127.8, 127.4, 124.1.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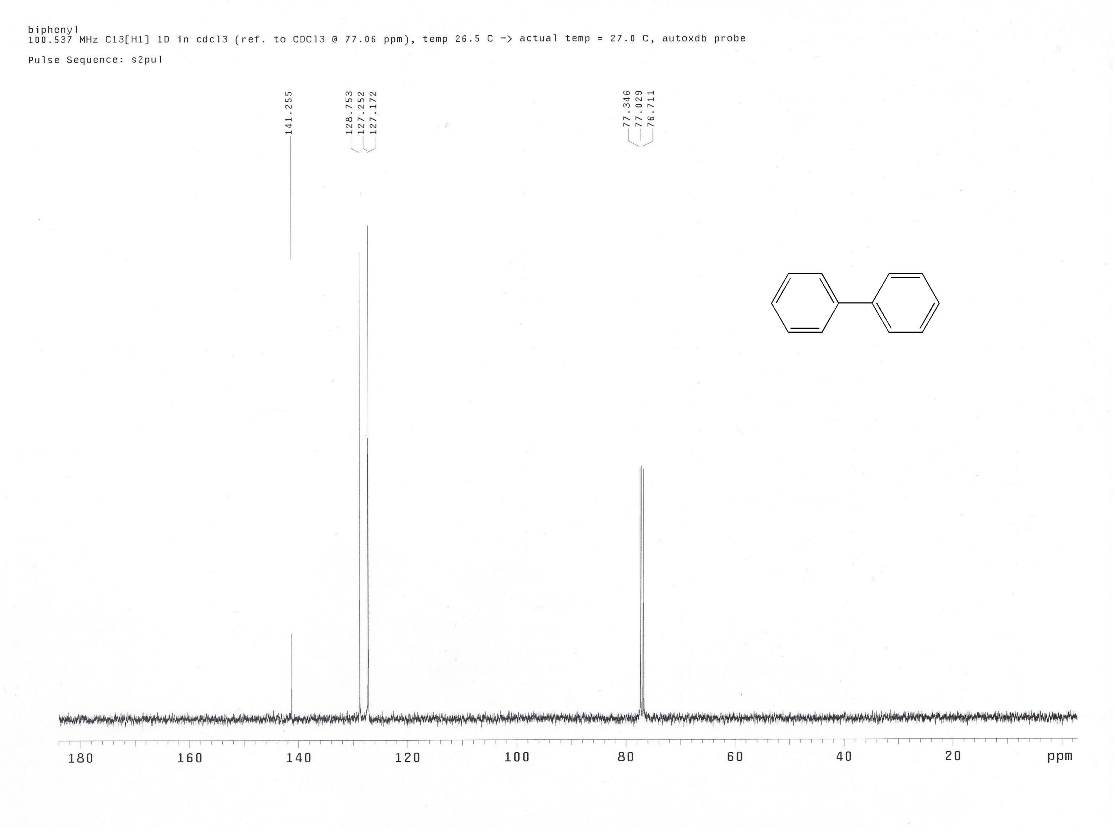
biphenyl
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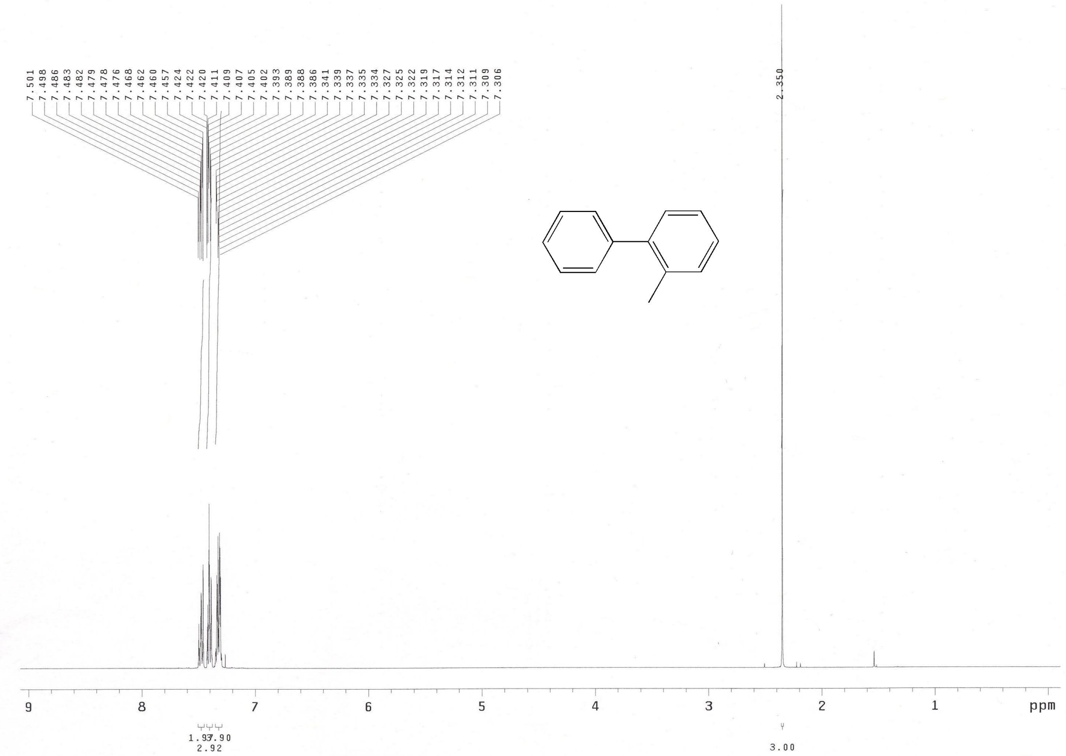

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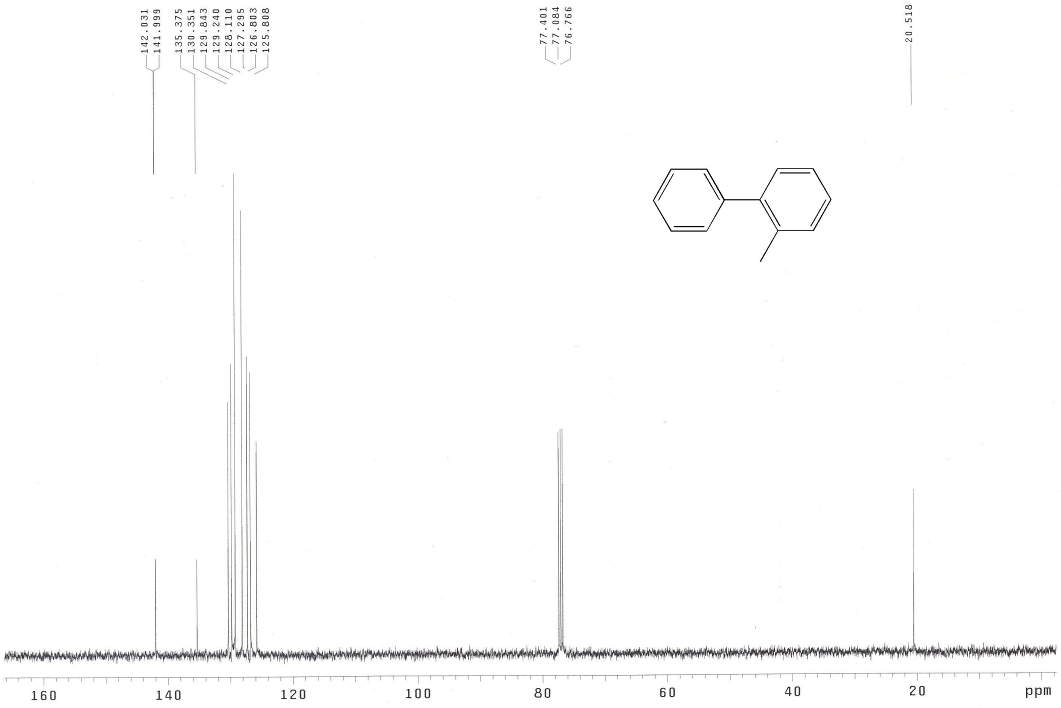

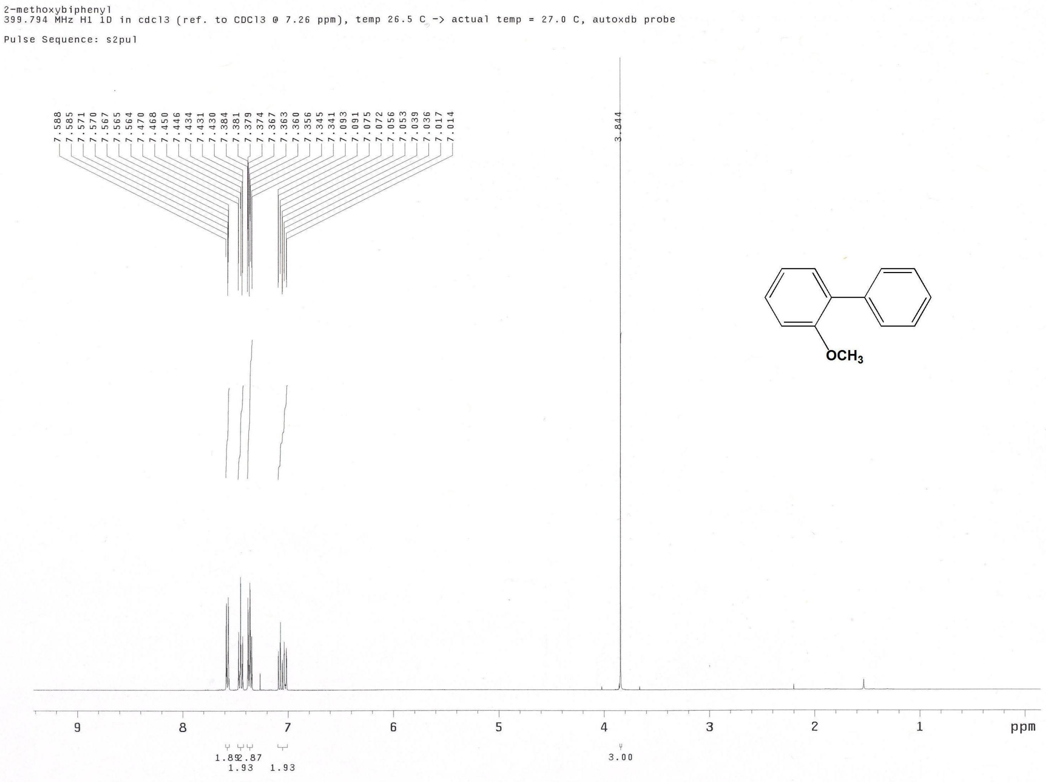

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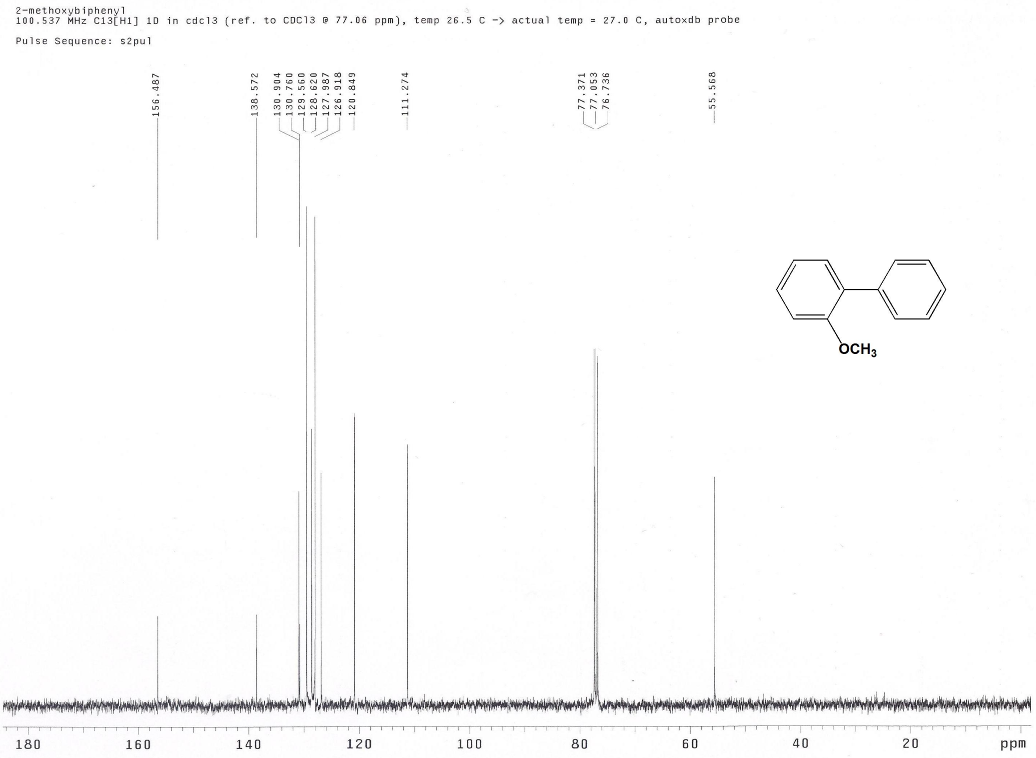

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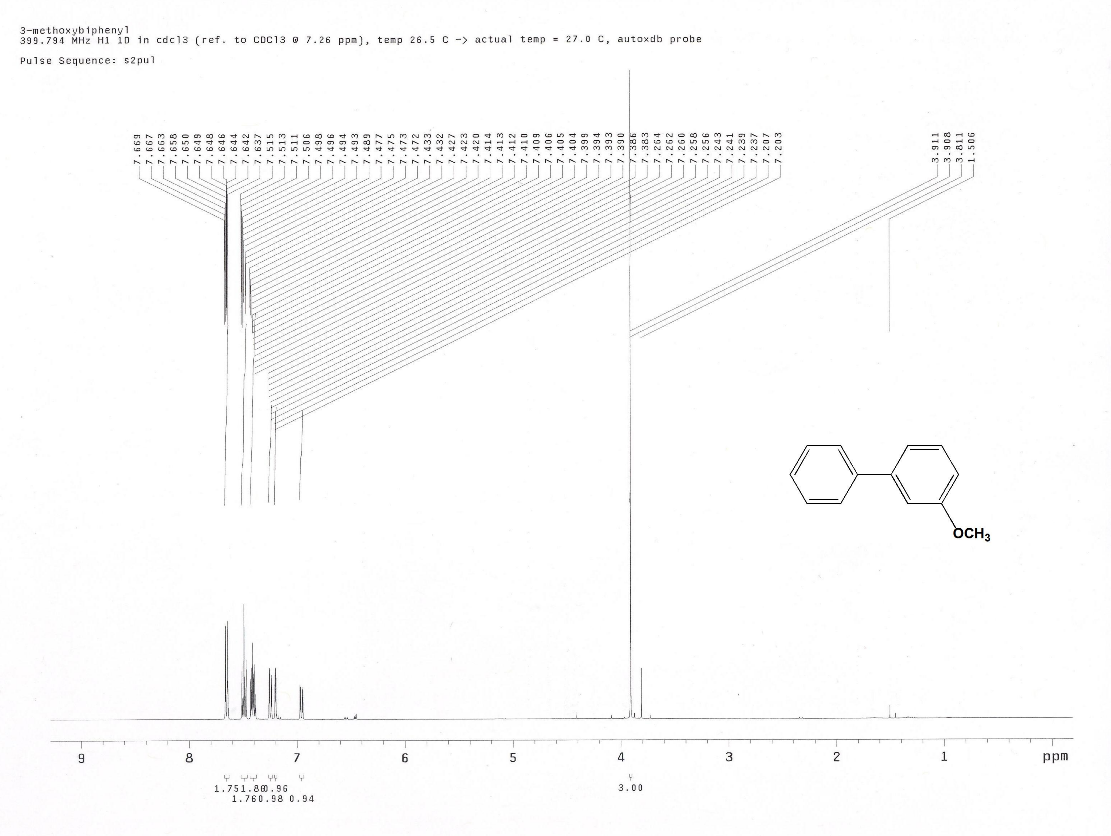
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7.648
7.646
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7.637
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7.513
7.511
7.506
7.498
7.496
7.494
7.493
7.489
7.477
7.475
7.473
7.472
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7.432
7.427
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7.390
7.386
7.383
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7.262
7.260
7.258
7.256
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7.237
7.207
7.203
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3.908
3.811
1.506
OCH3
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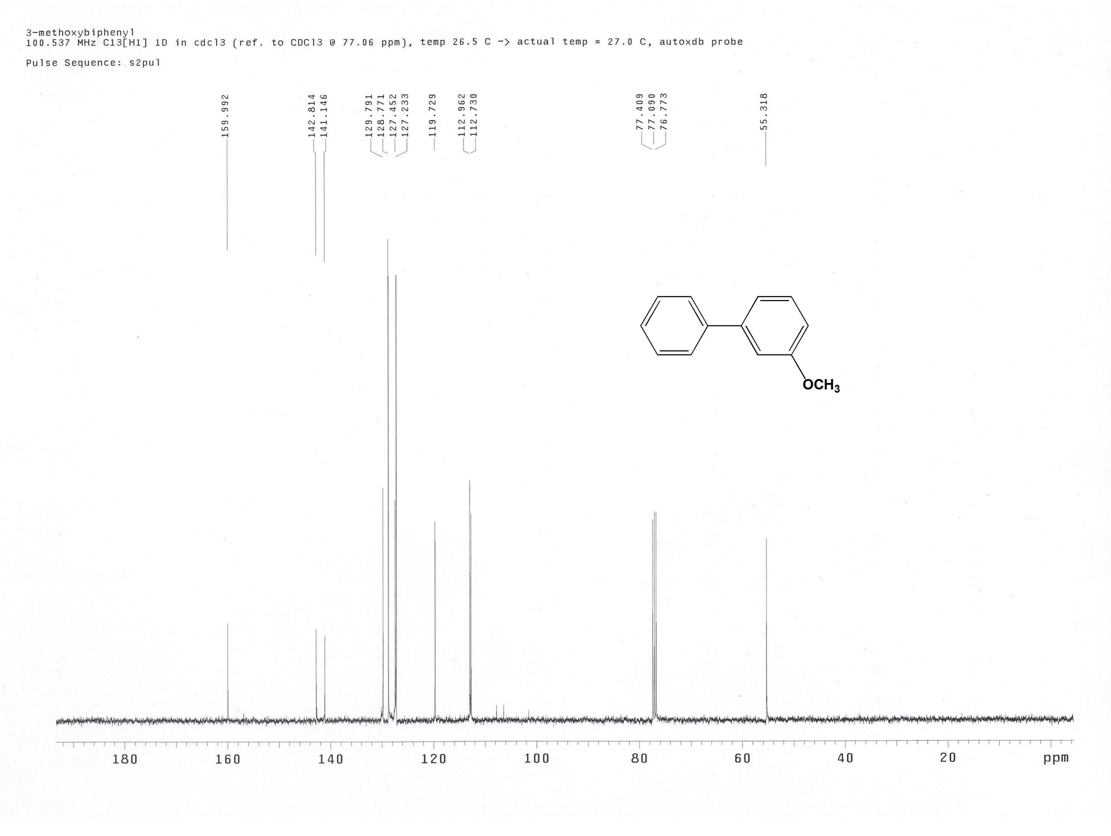
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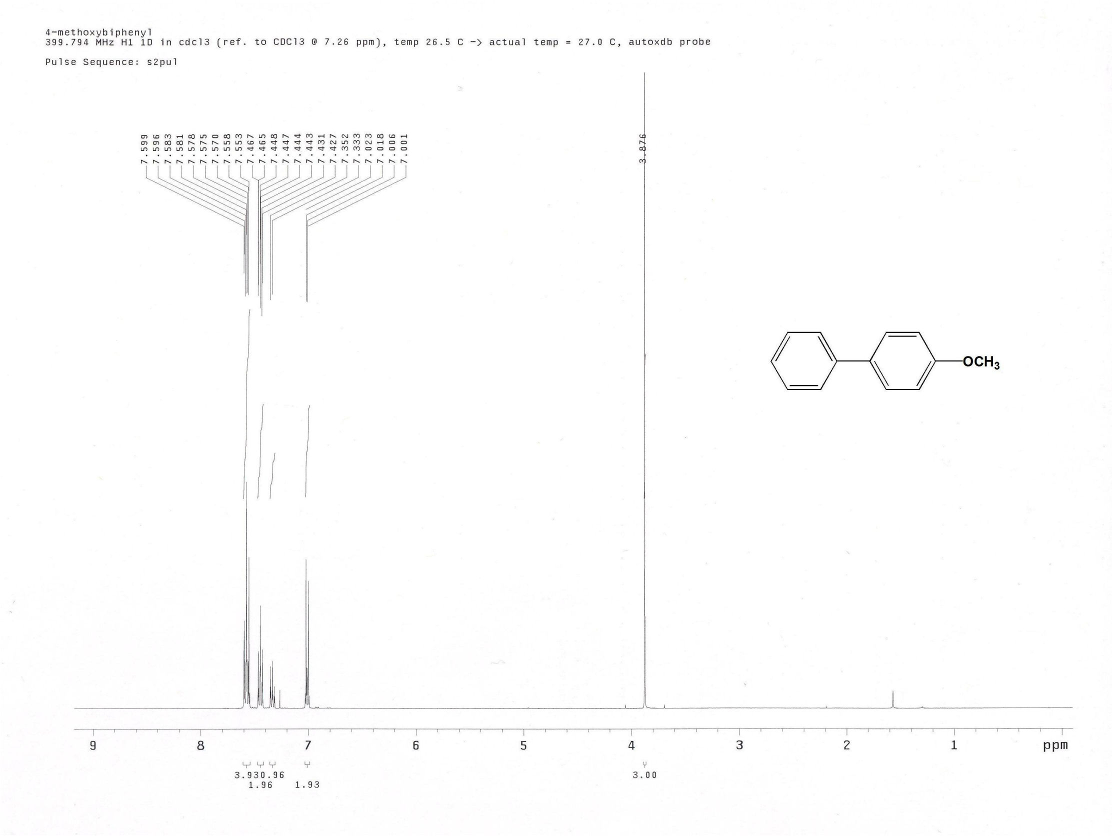
ppm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7.443
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7.006
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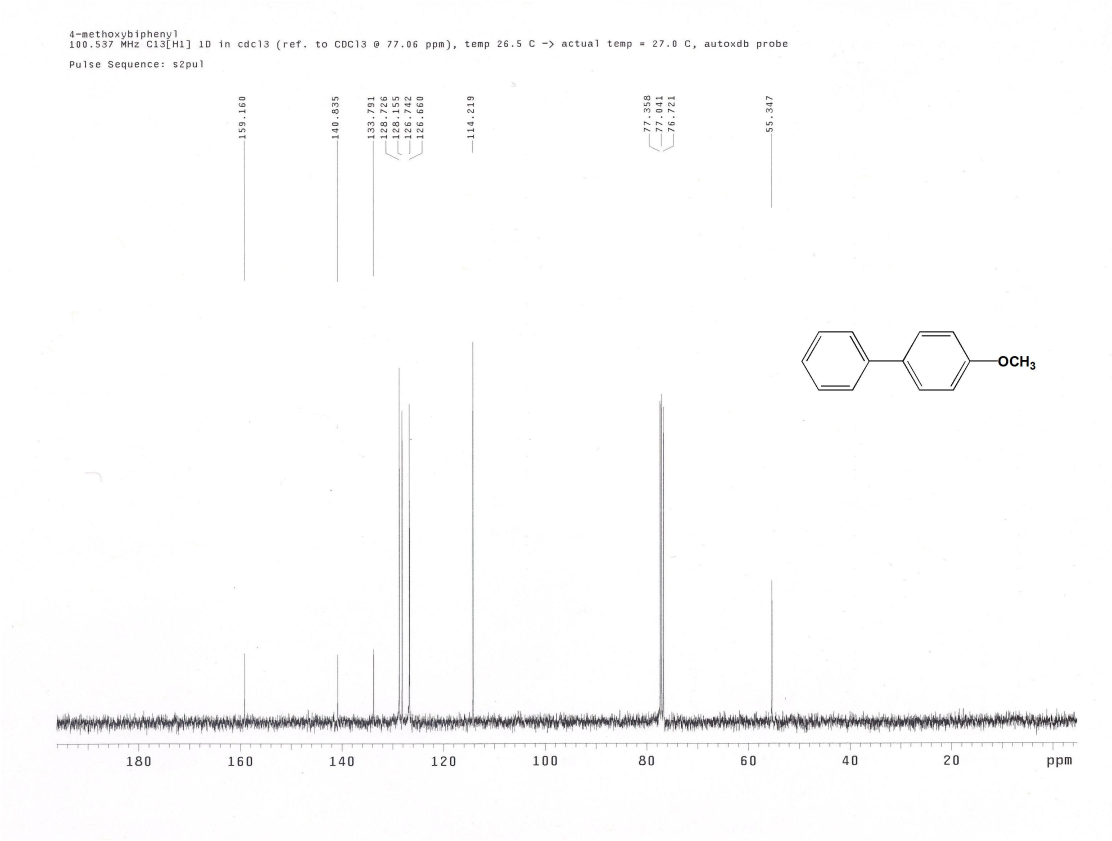
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77.358
77.041
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55.347
OCH3
180
160
140
120
100
80
60
40
20
ppm

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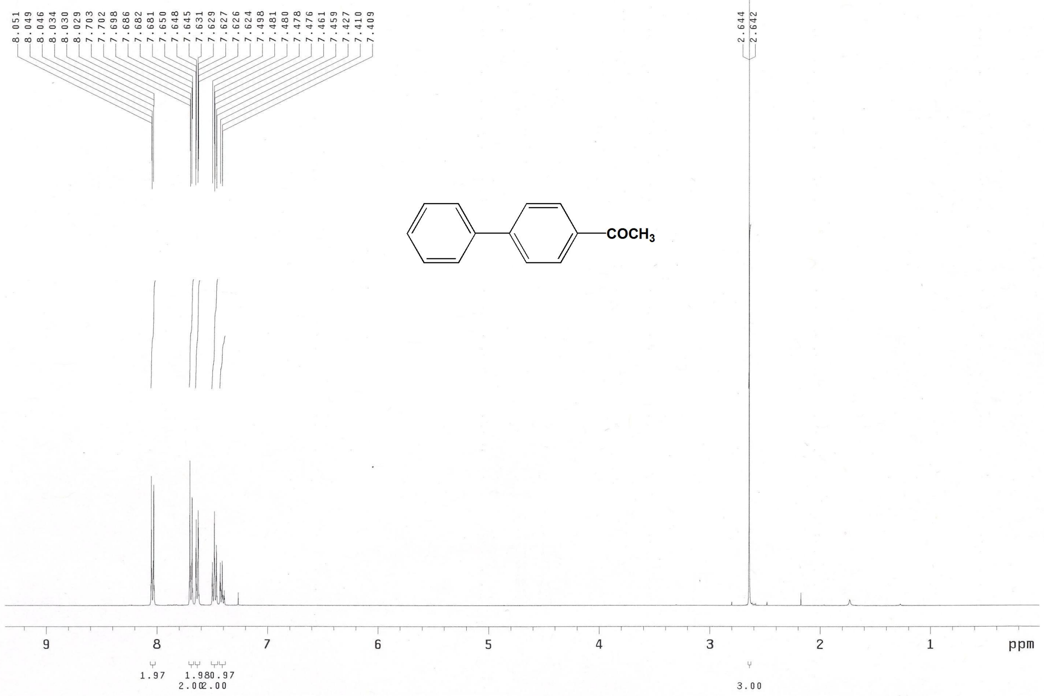

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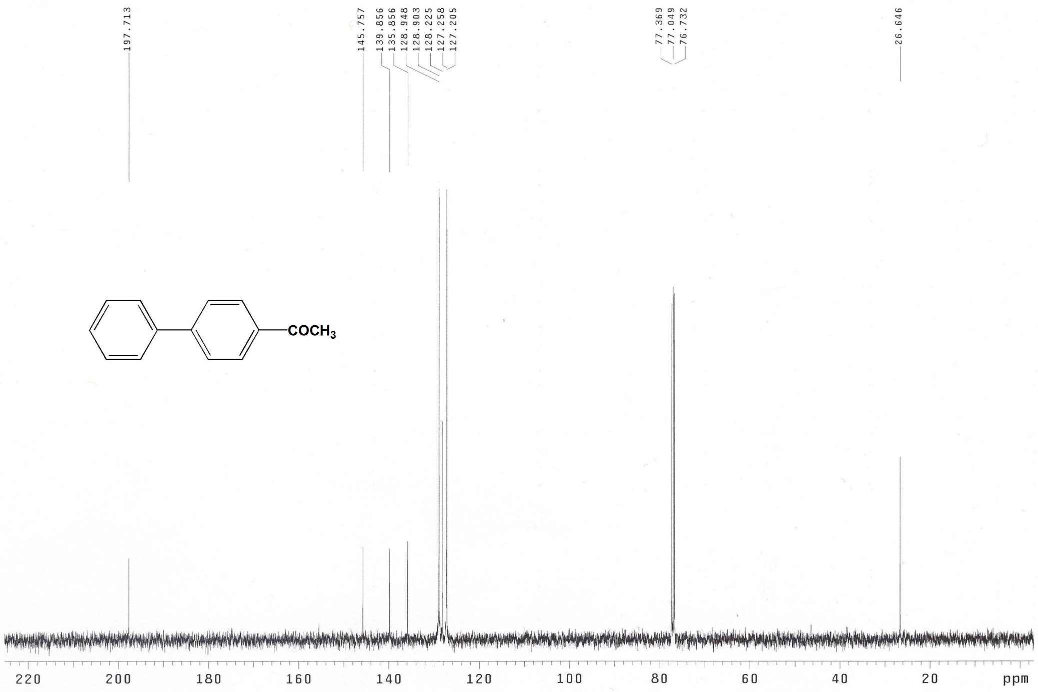

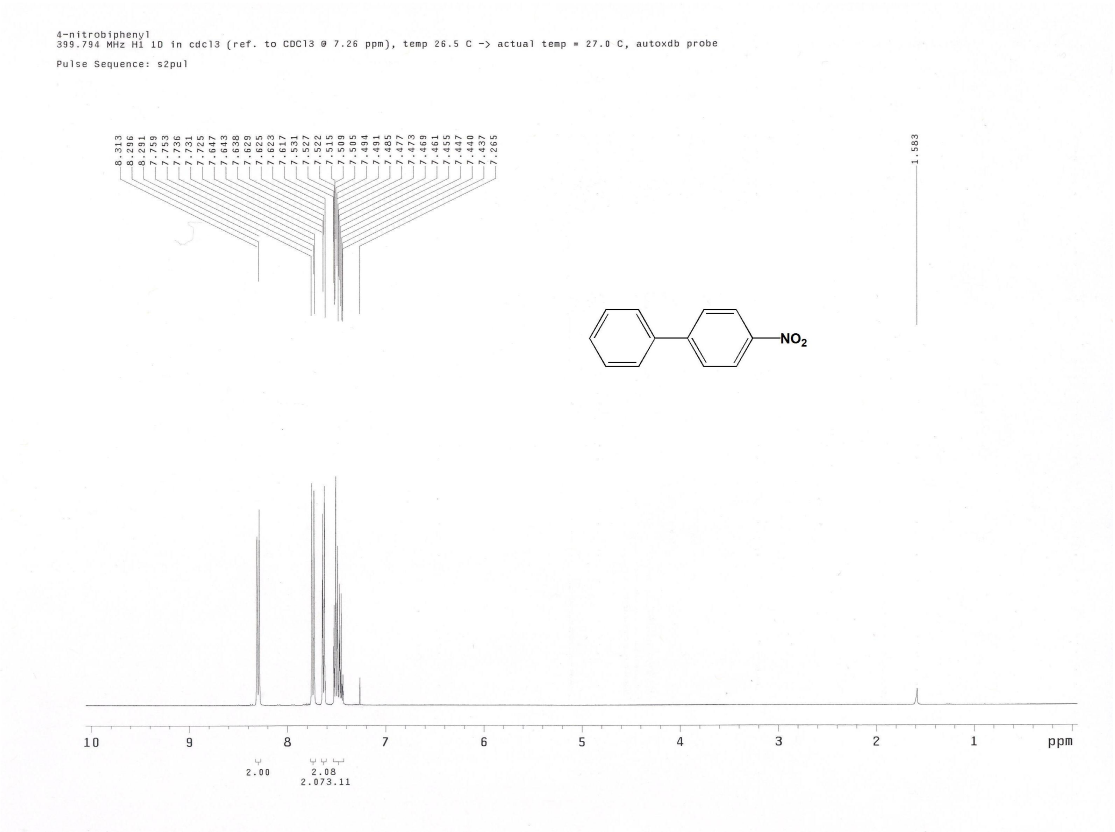
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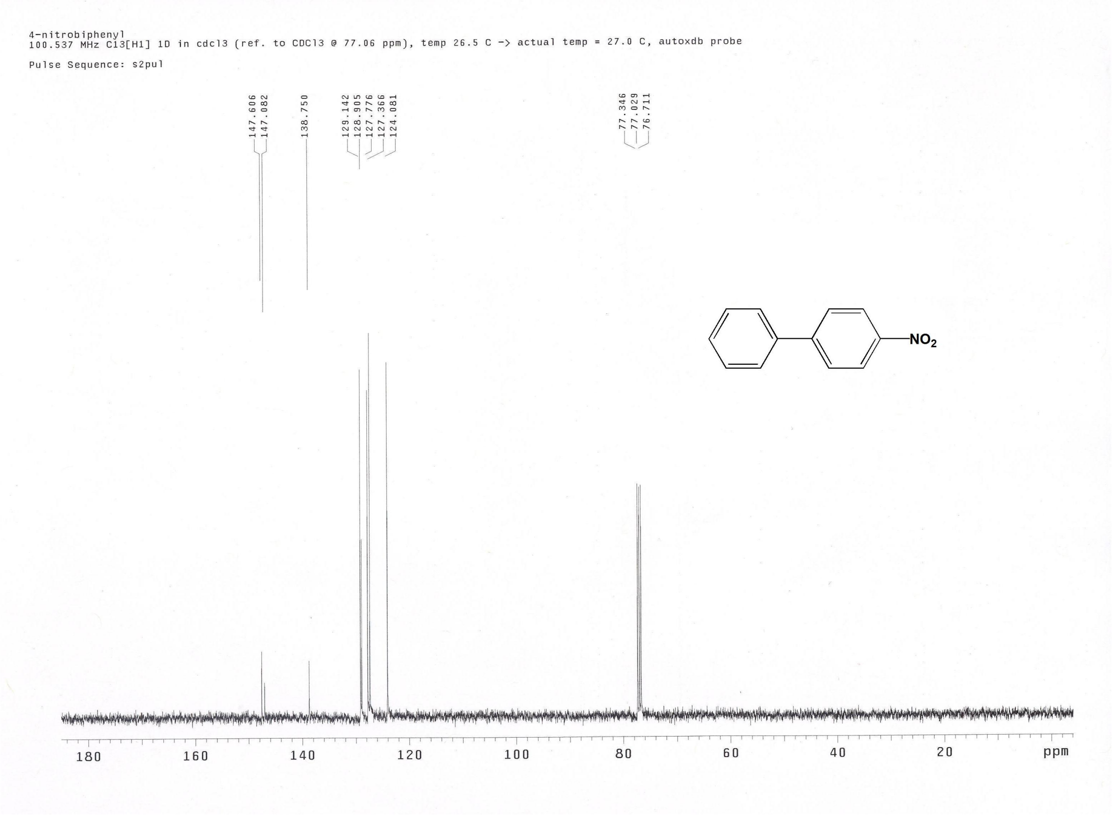
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129.142
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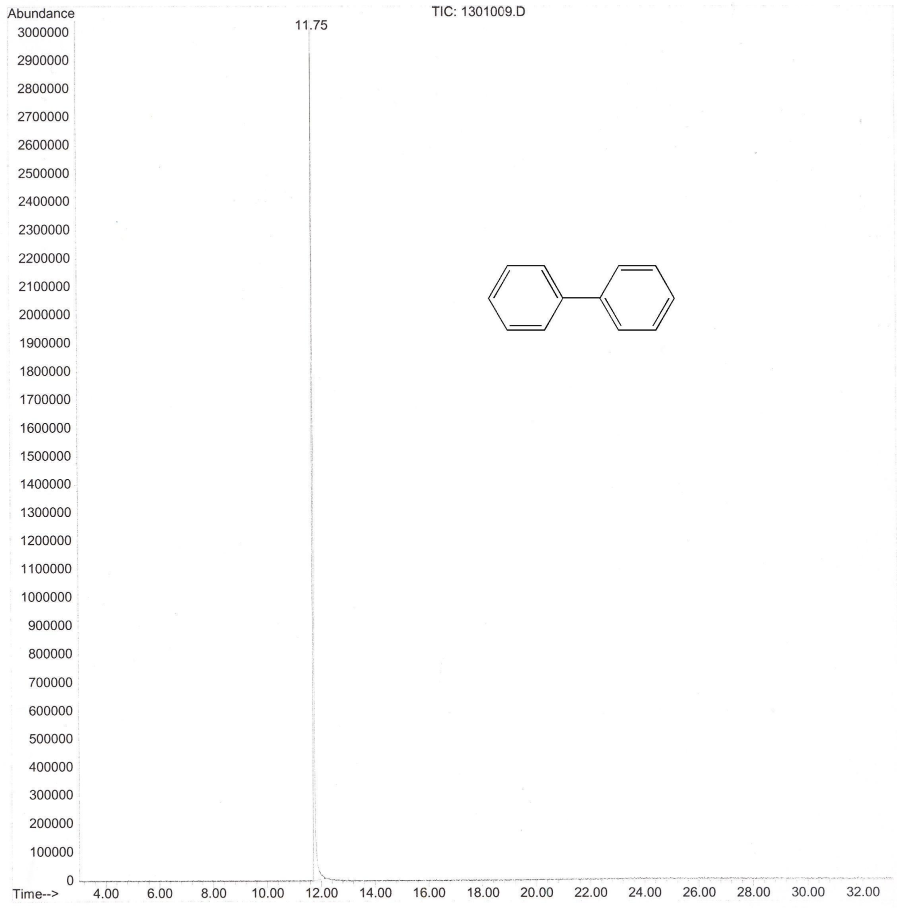

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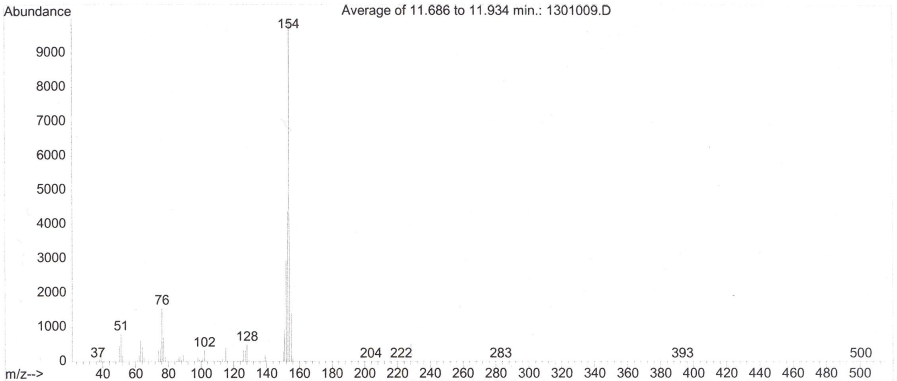

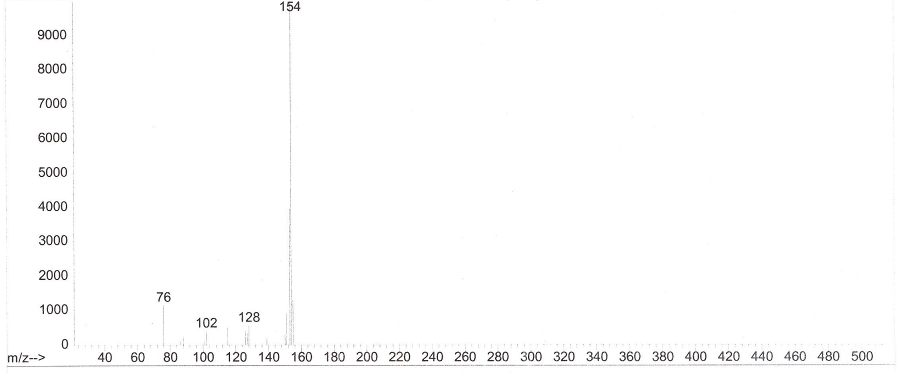

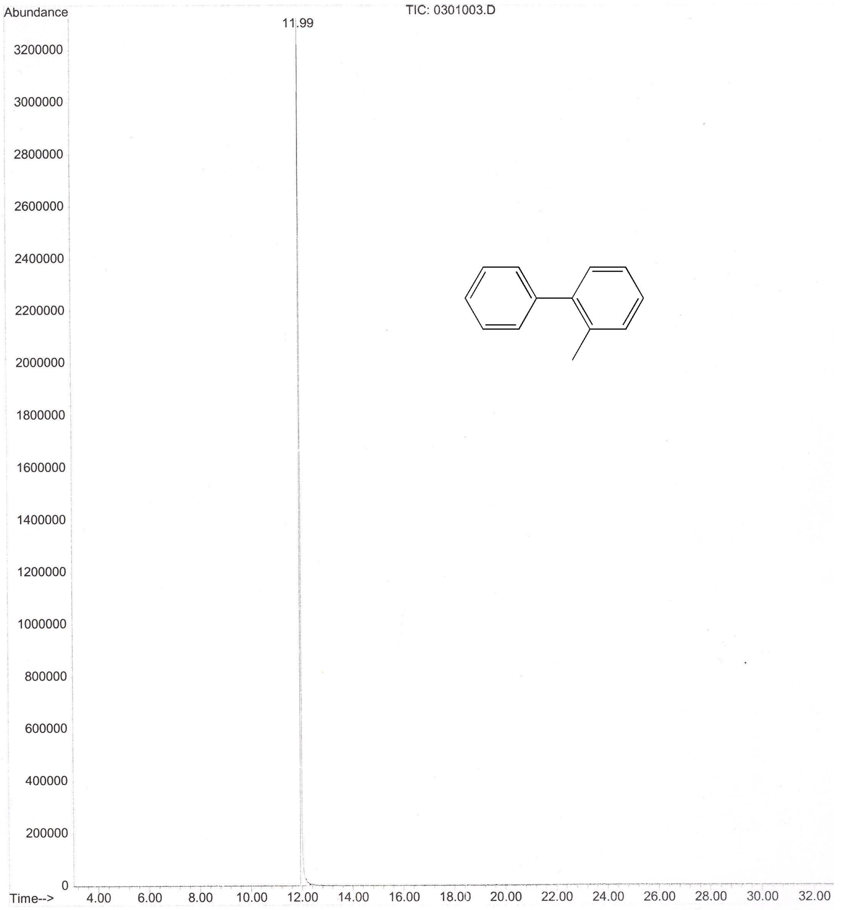

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Quality          : 92
ID               : 1,1'-Biphenyl, 2-methyl-
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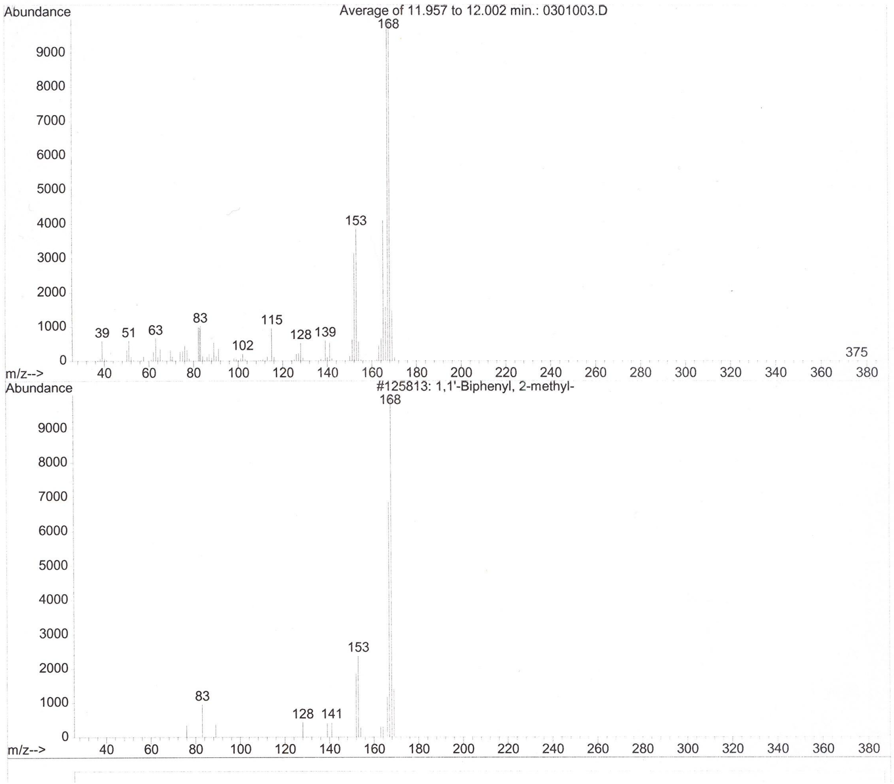

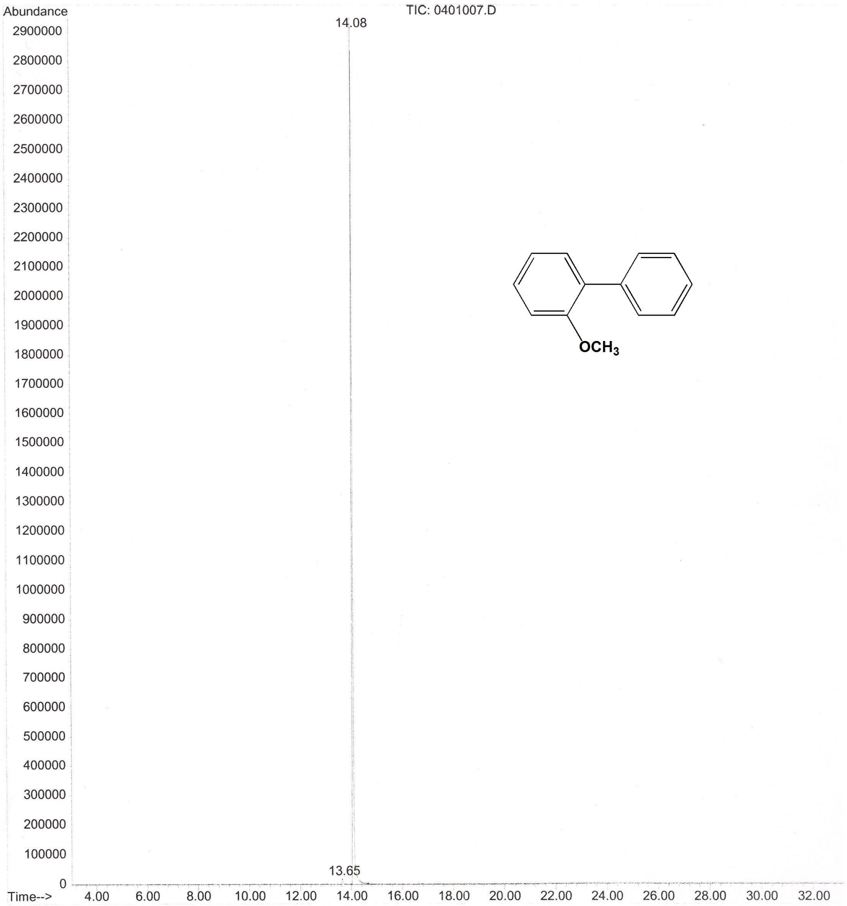

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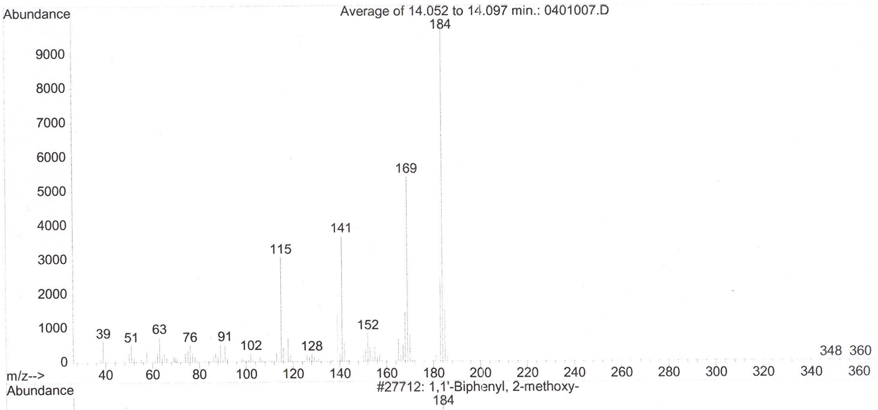

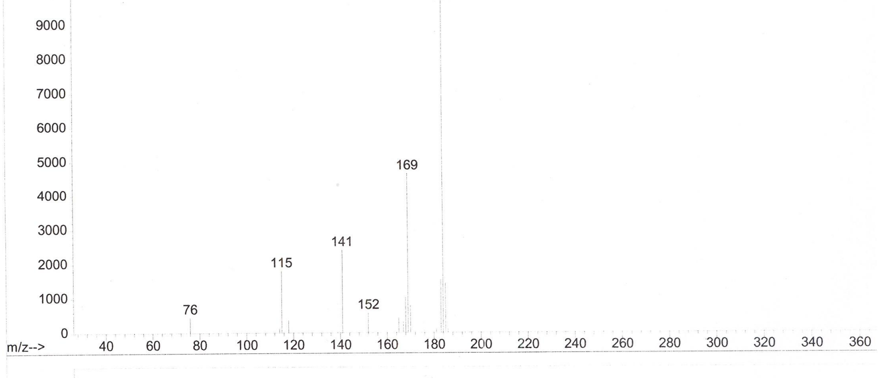

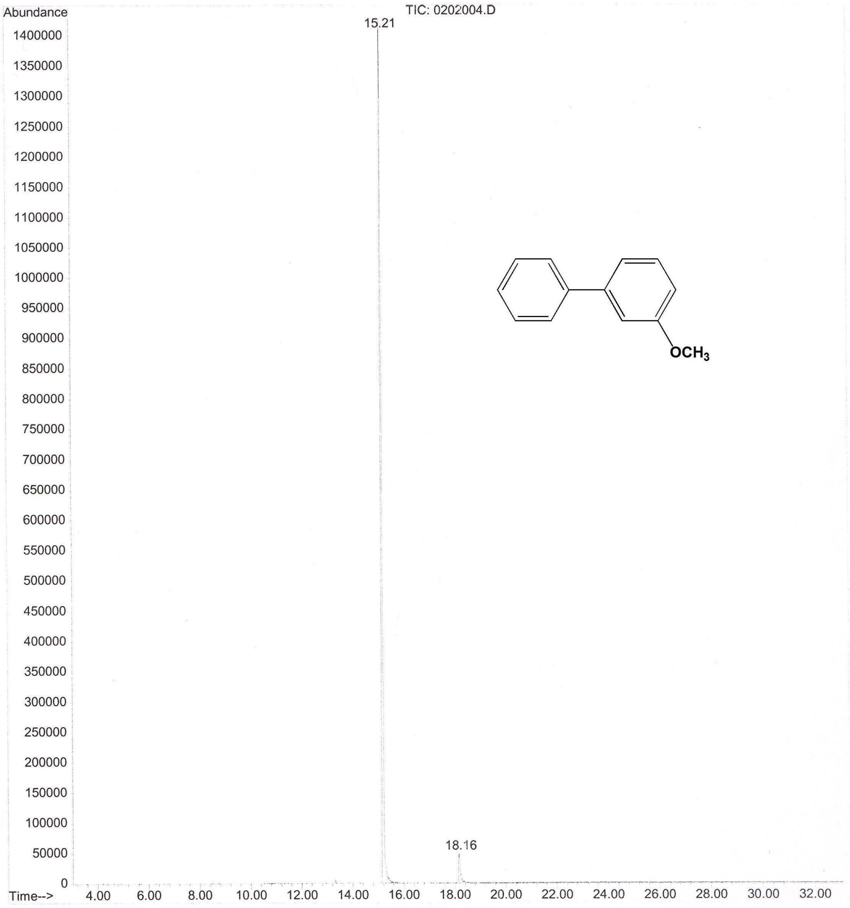

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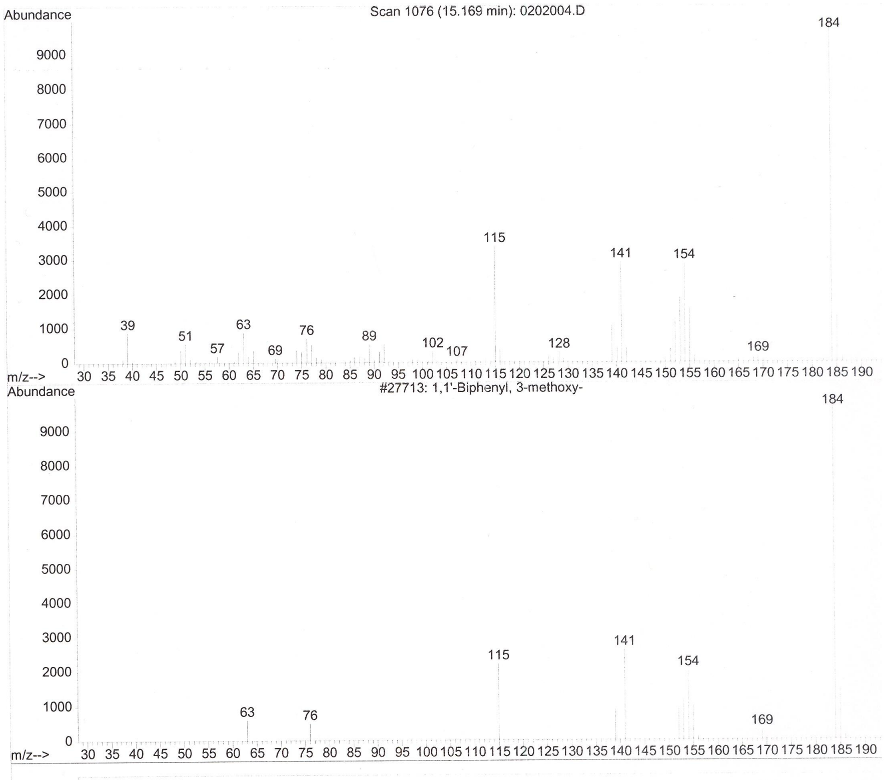

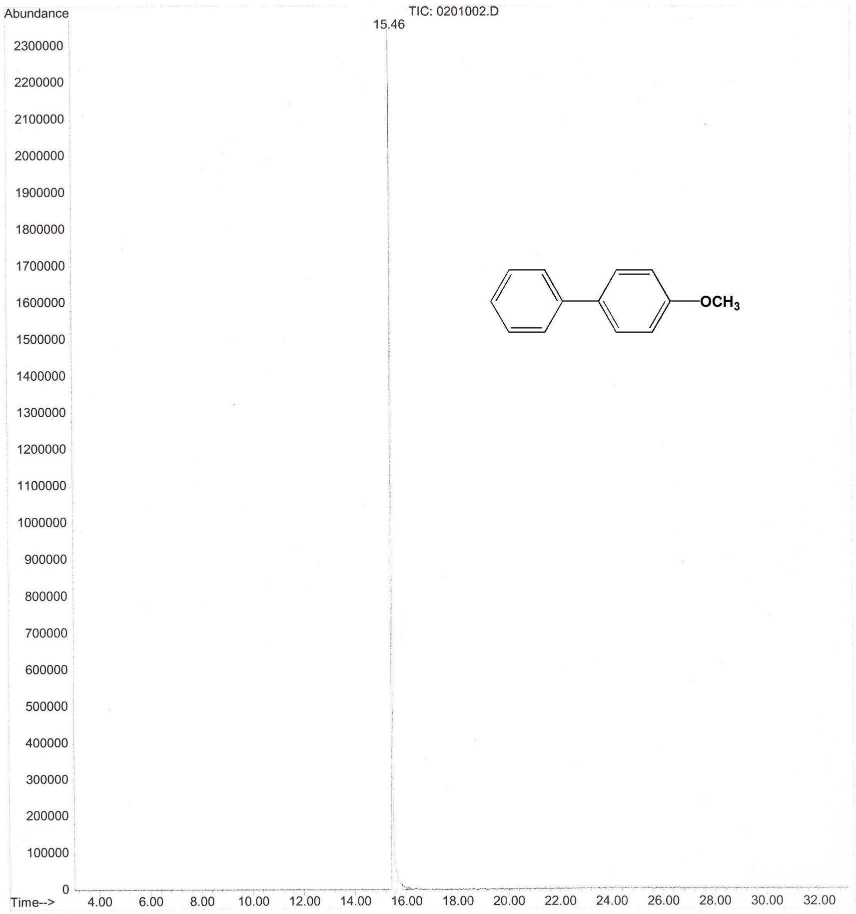

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ID               : 1,1'-Biphenyl, 4-methoxy-
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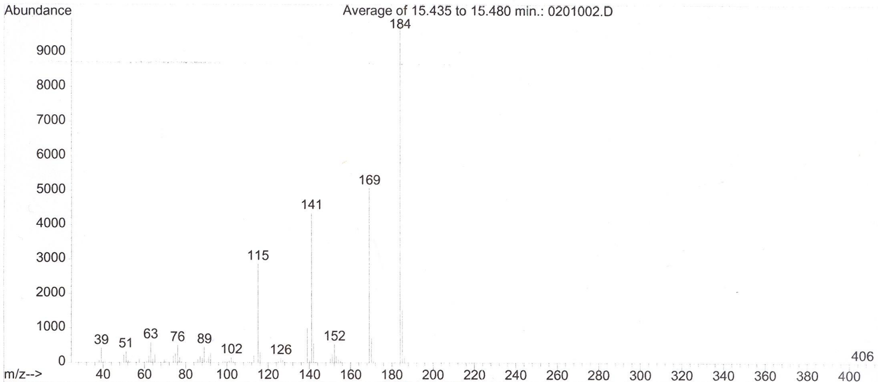

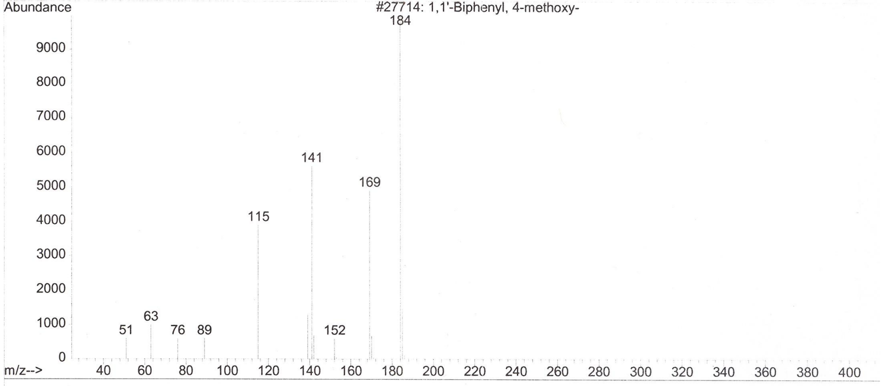

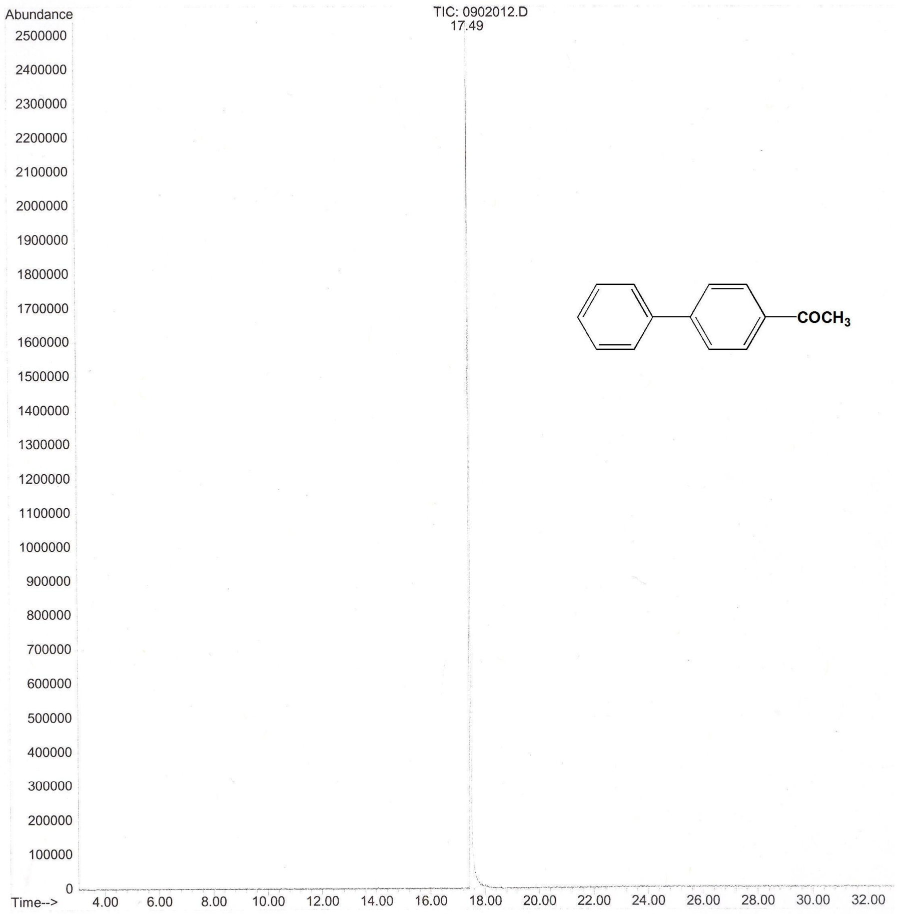

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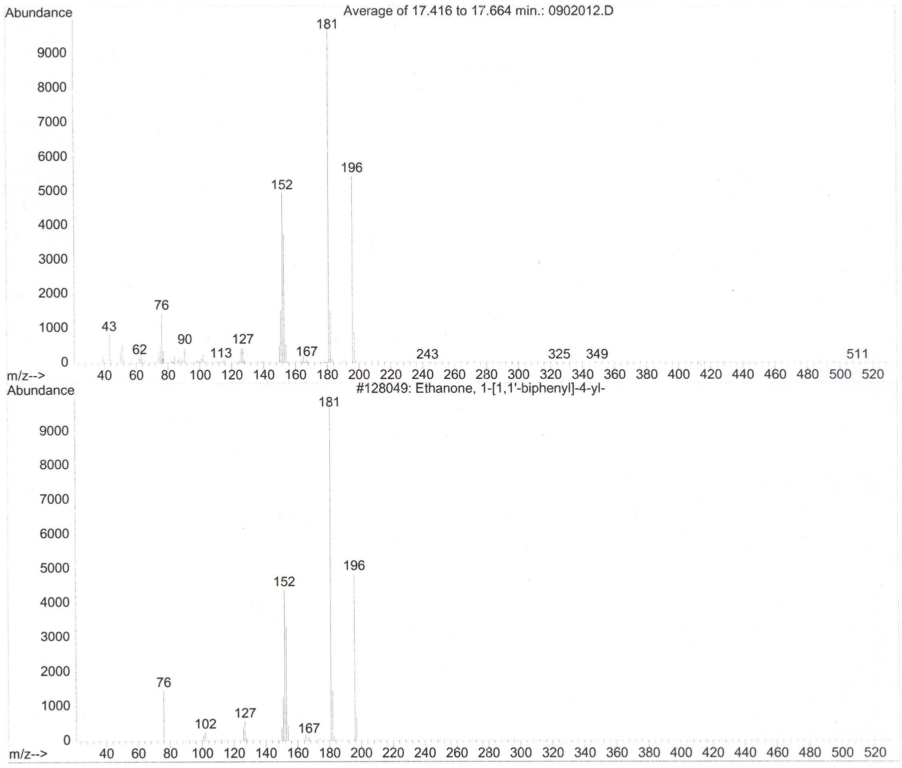

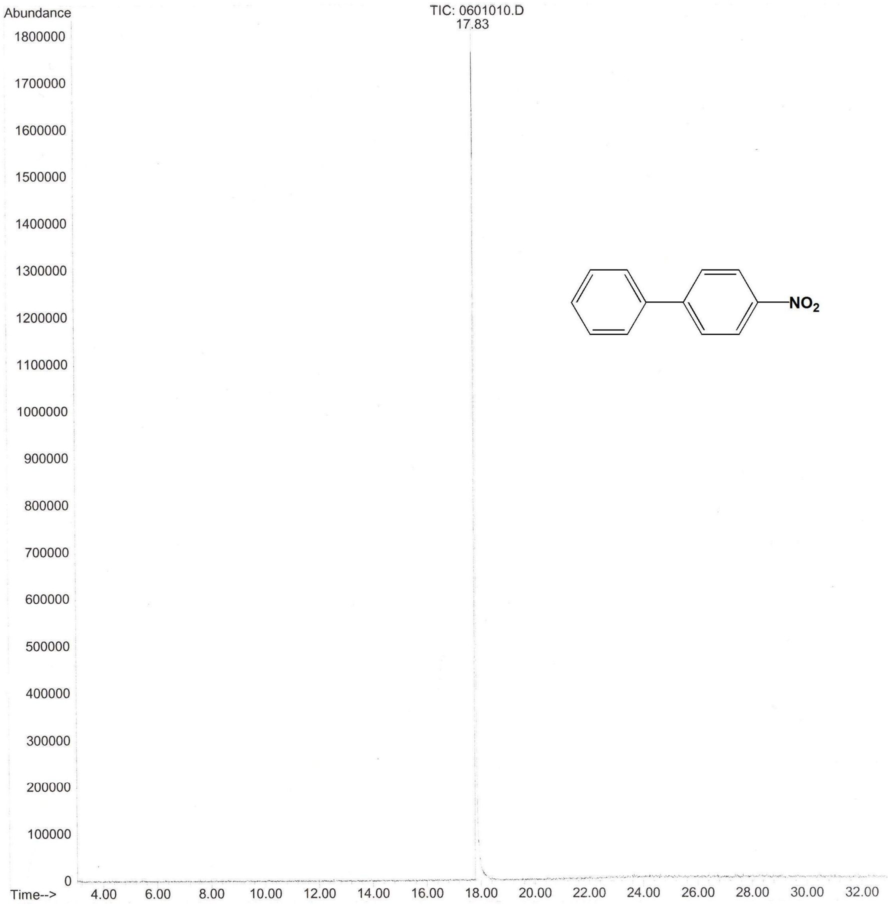

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Library Searched : C:\DATABASE\WILEY138.L
Quality          : 98
ID               : 1,1'-Biphenyl, 4-nitro-
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