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Electronic Supplementary Information

N-doped Porous Carbon Nanotubes: Synthesis and Their Application in Catalysis

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1. General experimental methods

Materials

All reagents and solvents were purchased from commercial sources and were used without further purification, unless indicated otherwise. 2,6-di(9H-carbazol-9-yl)pyridine (**CarPy**) and **CarPy-CMP** were prepared following procedures reported in the literature as shown below.

Instrumentation

Liquid ^{1}H NMR spectra was recorded in $CDCl_3$ using the residual $CHCl_3$ as internal reference (7.26 ppm) on Bruck 400 spectrometer. Liquid ^{13}C NMR was recorded at 100.6 MHz in $CDCl_3$ using the residual $CHCl_3$ as internal reference (77.0 ppm). Solid-state NMR experiments were performed on a Bruker WB Avance II 400 MHz spectrometer. The ^{13}C CP/MAS NMR spectra were recorded with a 4-mm double-resonance MAS probe and with a sample spinning rate of 10.0 kHz; a contact time of 2 ms (ramp 100) and pulse delay of 3 s were applied. FTIR spectra of the samples were collected on a TENSOR 27 FTIR at a resolution of 2 cm^{-1}. Gas sorption isotherms were obtained with Micromeritics TriStar II 3020 and Micromeritics ASAP 2020 M+C accelerated surface area and porosimetry analyzers at certain temperature. The samples were outgassed at 120 ^{o}C for 8 h before the measurements. Surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) methods. The pore-size-distribution curves were obtained from the adsorption branches using non-local density functional theory (NLDFT) method. Field emission scanning electron microscopy (SEM) observations were performed on a Hitachi S-4800 microscope operated at an accelerating voltage of 15.0 kV. (HR) Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-1011 and JEM-2011F instrument operated at 200 kV. The thermal properties of the materials were evaluated using a thermogravimetric analysis (TGA) instrument (STA PT1600 Linseis) over the temperature range of 25 to 800 °C under air and N_2 atmosphere with a heating rate of 10 °C/min. X-ray photoelectron spectroscopy (XPS) was performed on an ESCAL Lab 220i-XL spectrometer at a pressure of ~3×10^{-9} mbar (1 mbar = 100 Pa) using Al Ka as the excitation source (1486.6 eV) and operated at 15 kV and 20 mA. The binding energies were referenced to the C_{1s} line at 284.8 eV from adventitious carbon. The XRD analysis was performed on a D/MAX-RC diffractometer operating at 30 kV and 100 mA with $Cu_{K\alpha}$ radiation. Raman spectra were recorded on a Renishaw system 1000 Raman spectrometer with a laser wavelength of 514 nm. The reaction mixture was analyzed by means of GC (Agilent 4890D) with a FID detector and a nonpolar capillary column (DB-5) (30 m × 0.25 mm × 0.25 μm). The column oven was temperature-programmed with a 2 min initial hold at 323 K, followed by the temperature increase to 538K at a rate of 20 K/min and kept at 538 K for 10 min. High purity nitrogen was used as a carrier gas.

2. Synthetic procedures

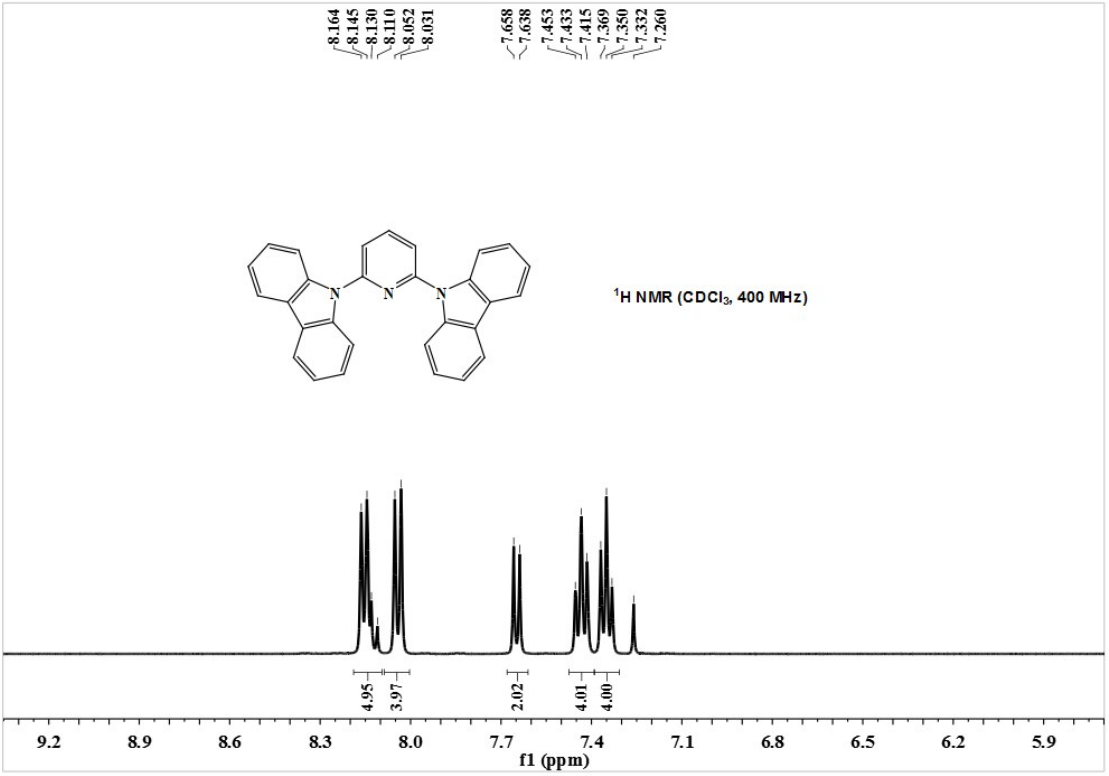
(1) Synthesis of 2,6-di(9H-carbazol-9-yl)pyridine (CarPy)

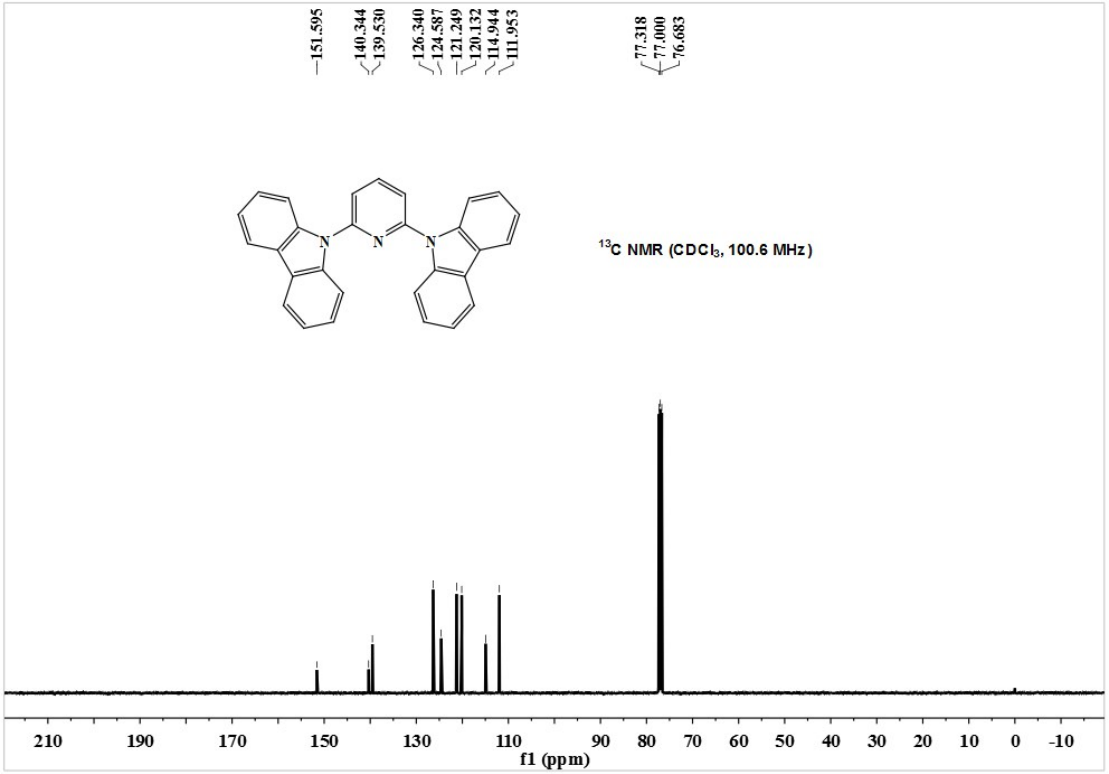
Ref.: *Chem. Mater.*, 2013, **25**, 3414-3426.

Carbazole (6.69 g, 40 mmol, 2 equiv.), 2,6-dibromo-pyridine (4.74 g, 20 mmol, 1 equiv.), potassium phosphate (12.7 g, 60 mmol, 3 equiv.), copper iodide (762 mg, 4 mmol, 20 mol%) and trans-1,2-diaminocyclohexane (DACH, 0.960 mL, 8 mmol, 40 mol%) were refluxed in 100 mL dioxane under nitrogen for 72 h. The reaction mixture was diluted with ethyl acetate and filtrated over silica. Removal of the solvent under reduced pressure

gave a crude product, which was washed with boiling methanol (3 x 100 mL) and recrystallized from ethyl acetate. The product was obtained as white solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35 (t, ^{3}J = 7.6 Hz, 4H), 7.43 (t, ^{3}J = 8 Hz, 4H), 7.65 (d, ^{3}J = 8 Hz, 2H), 8.04 (d, ^{3}J = 8.4 Hz, 4H), 8.11-8.16 (m, 5H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 111.95, 114.94, 120.13, 121.25, 124.59, 126.34, 139.53, 140.34, 151.95.





(2) Synthesis of CarPy-CMP

Ref.: *J. Am. Chem. Soc.*, 2012, **134**, 6084-6087.

CarPy (200 mg) was dissolved in 90 mL of anhydrous chloroform and then transferred dropwise to a suspension of ferric chloride (954 mg,) in 60 mL of anhydrous chloroform. The solution mixture was stirred under refluxing condition (oil bath: 80 ^{o}C) for 24 h under nitrogen protection, and then 100 mL of methanol was added to the above reaction mixture after cooling down to room temperature. The resulting mixture was kept stirring for 1 h and the precipitate was collected by filtration. After washed with methanol, the obtained solid was stirred vigorously in hydrochloric acid solution (10 wt%) for 2 h and then $NH_3 \cdot H_2O$ (10 wt%) for 2 h. The suspension was then filtered and washed with water and methanol. After extracted in a Soxhlet extractor with methanol, H_2O and THF for 48 h, the desired polymer was collected and dried in vacuum oven at 140 °C for 24 h with 90% yield.

(3) Synthesis of N-CNTs-t

The sample **CarPy-CMP** (0.3 g) was transferred into a ceramic boat and placed in a temperature-programmed furnace under an nitrogen flow. The sample was heated slowly from room temperature to 400/600/800 ^{o}C with a ramping rate of 3 ^{o}C and then kept at the designed temperature for 2 h under flowing nitrogen gas. The furnace was allowed to cool to room temperature naturally in a nitrogen atmosphere. The resultant black carbon material (carbon nanotubes) was collected directly from the ceramic boat and used without further purification.

(4) Typical procedures for C-H arylation of benzene catalyzed by N-CNTs-800

For a typical procedure (entry 2, Table 1), **N-CNTs-800** (0.0100 g), *t*-BuOK (0.1347 g, 1.2 mmol), iodobenzene (0.0816 g, 0.4 mmol) and benzene (4 mL) were put into a 15 mL thick-wall glass tube with a cap successively, which was sealed tightly and then heated to 120 ^{o}C. After reacting for 24 h, the reaction mixture was cooling to room temperature, and then dodecane (internal standard) (0.05 g) and CH_2Cl_2 (8 mL) was added, stirred vigorously and centrifuged. The upper liquid was analyzed by GC and the details were shown below. For catalyst recycling, the catalyst was recycled by filtration, washed with CH_2Cl_2, H_2O and EtOH, and then dried under vacuum at 100 ^{o}C for 24 h, followed by being reused for the next run.

(5) Typical procedure for benzyl alcohol amination with aniline

In a glovebox, aniline (1 mmol), benzyl alcohol (2 mmol), **N-CNTs-800** (10.0 mg), KOH (0.5 mmol) and toluene (2 mL) were put into a 15 mL thick-wall glass tube with a cap successively, which was sealed tightly and then heated to 130 ^{o}C. After reacting for 24 h, the reaction mixture was cooling to room temperature, and then dodecane (internal standard) (0.05 g) and CH_2Cl_2 (8 mL) was added, stirred vigorously and centrifuged. The upper liquid was analyzed by GC and the details were shown below.

(6) Typical procedure for nitrobenzene reduction

The reaction was conducted with similar procedures for benzyl alcohol amination with aniline. The quantity of the reactants was nitrobenzene (1 mmol), **N-CNTs-800** (10.0 mg), KOH (3 mmol) and isopropanol (2 mL).

(7) Typical procedure for oxidation of ethylbenzene

Ethylbenzene (0.5 mmol), **N-CNTs-800** (5.0 mg), TBHP (*tert*-butyl hydroperoxide, 500 uL, 70 wt% in water), and water (1 mL) were introduced into a 15 mL thick-wall glass tube with a cap successively, which was sealed tightly and then heated to 80 ^{o}C. After reacting for 12 h, the reaction mixture was cooling to room temperature, and then dodecane (internal standard) (0.05 g) and CH_2Cl_2 (8 mL) was added, stirred vigorously and centrifuged. The upper liquid was analyzed by GC and the details were shown below.

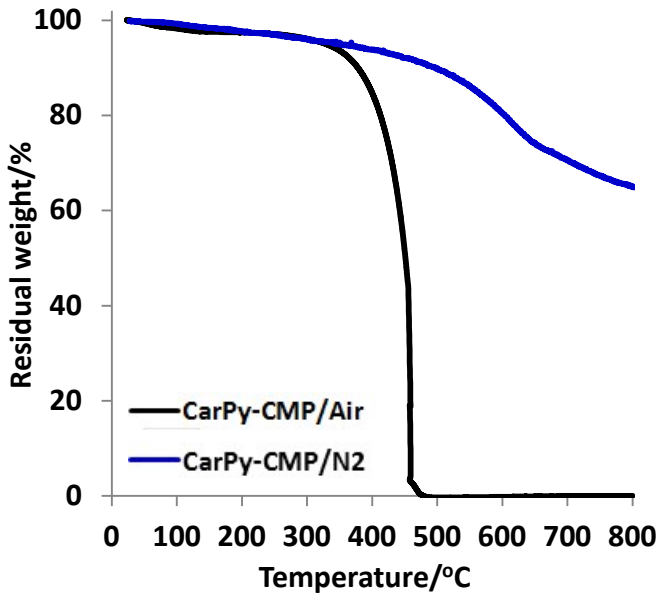


Figure S1. Thermogravimetric analysis (TGA) of **CarPy-CMP** under air and N_2 up to 800 °C at a ramping rate of 10 °C min^{-1}.

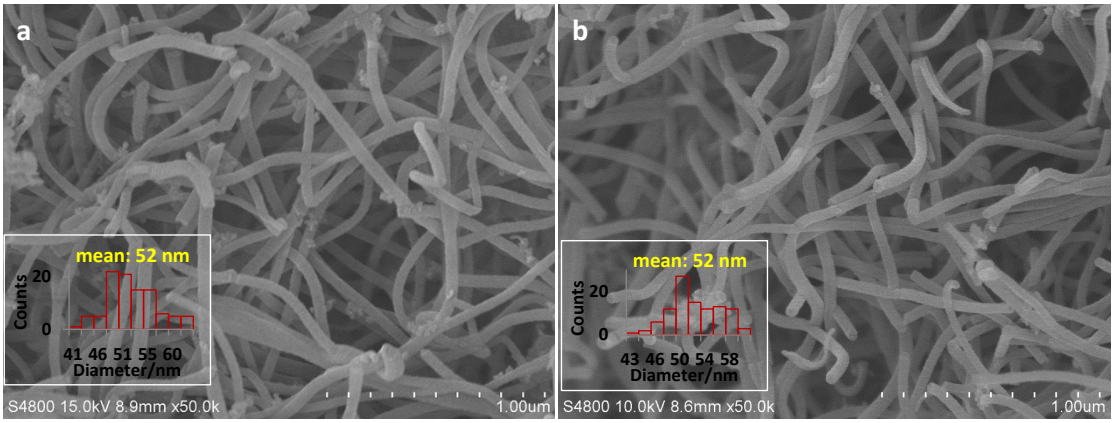


Figure S2. SEM images of a) **N-CNTs-400** and b) **N-CNTs-600**.

Table S1. Summary of elemental (CHN) analysis of **CarPy-CMP** and **N-CNTs-t**

Sample	Element		
	C/%	H/%	N/%
CarPy-CMP	83.19	4.03	9.14
N-CNTs-400	84.18	2.73	8.91
N-CNTs-600	86.24	2.24	5.85
N-CNTs-800	89.61	2.14	4.40

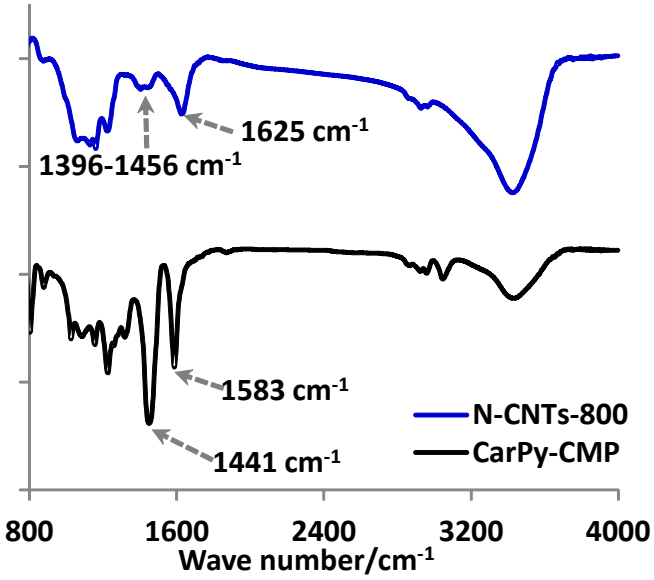


Figure S3. FTIR spectra of **CarPy-CMP** and **N-CNTs-800**. The spectra were recorded as KBr pellets. The existence of pyridine rings was confirmed by the appearance of two strong absorption bands at 1583 and 1441 cm^{-1}.

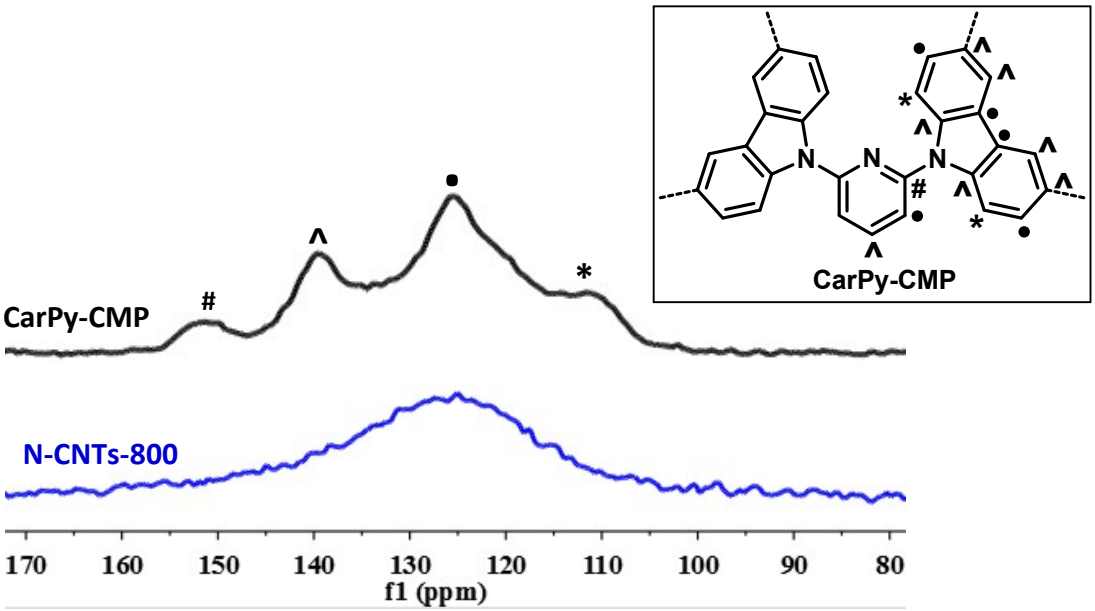


Figure S4. CP/MAS ^{13}C NMR spectra for **CarPy-CMP** (111.0, 125.6, 139.7, 151.7) and **N-CNTs-800** (125.0).

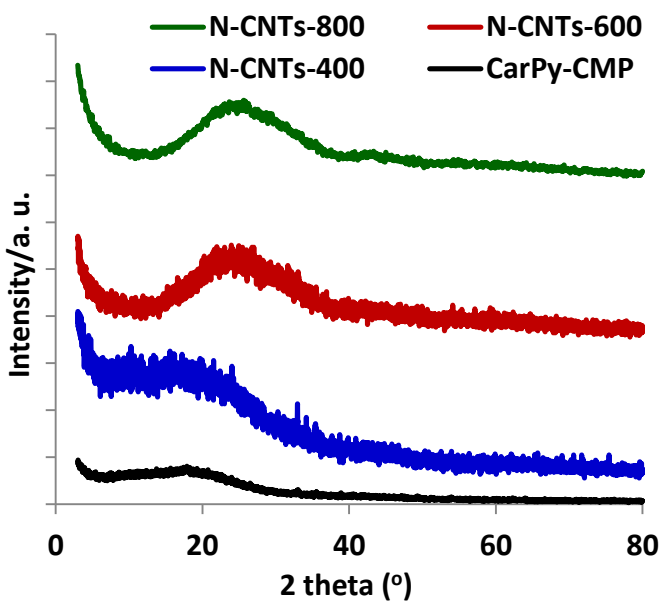


Figure S5. PXRD-pattern of **CarPy-CMP** and **N-CNTs-400/600/800**.

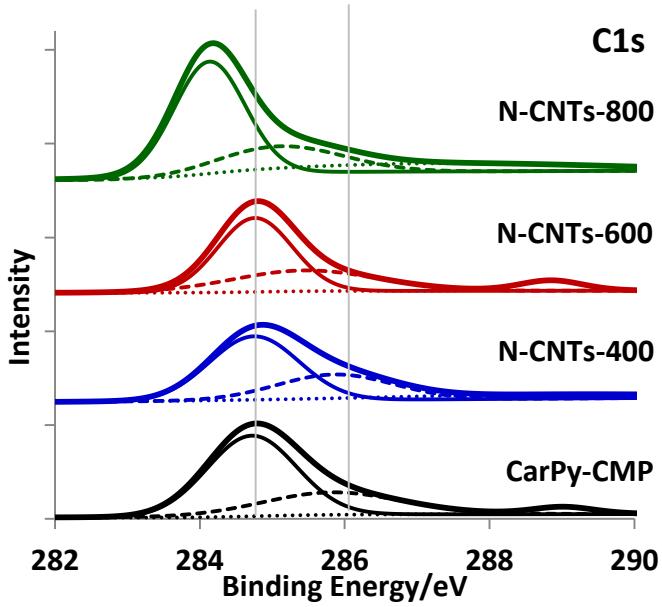


Figure S6. XPS spectra of C1s for **CarPy-CMP** and **N-CNTs-t**.

Table S2. Porosity parameters of **CarPy-CMP** and **N-CNTs-800**.

Material	SABET [m^2 g^{-1}][a]	V_{total}(V_{micro}) [cm^3 g^{-1}][b]	V_{meso}/V_{total} [%][b]
CarPy-CMP	993	1.08(0.25)	77
N-CNTs-800	1176	1.13(0.28)	75

[a] For BET plots, see Figure S7 as shown below. [b] V_{total}: total pore volume, calculated at P/P_0 = 0.99; V_{micro}: micropore volume, calculated over the relative pressure range P/P_0 = 0.2~0.4; V_{meso}: mesopore volume (=V_{total}-V_{micro}); V_{meso}/V_{total}: mesopore volume proportion.

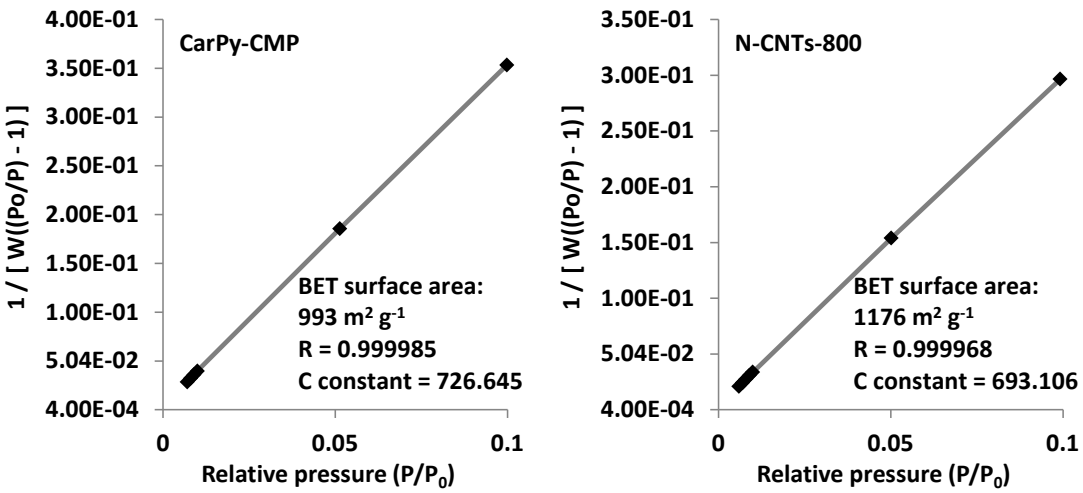
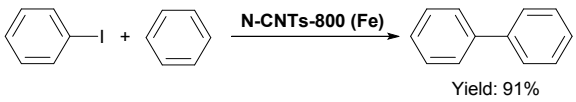


Figure S7. BET plot (P/P_0 = 0.006-0.1) of **CarPy-CMP** and **N-CNTs-800**.



Scheme S1. Influence of Fe impurities in **N-CNTs-800** on the arylation reaction of benzene. Reaction conditions: PhI 0.4 mmol, benzene 4 mL, *t*-BuOK 1.2 mmol, **N-CNTs-800 (Fe)** 10 mg, 120 °C, 24 h. **N-CNTs-800 (Fe)** was prepared by impregnation method, adding $FeCl_3$ (1.0 wt%) to **CarPy-CMP** before carbonization (800 °C) in a nitrogen flow. However, no obvious effect on catalytic activity was observed, indicating the residual Fe has no impact on the catalyst performance of **N-CNTs-800**. In fact, the residual Fe content in **N-CNTs-800** was lower than 0.001 wt% as determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis.

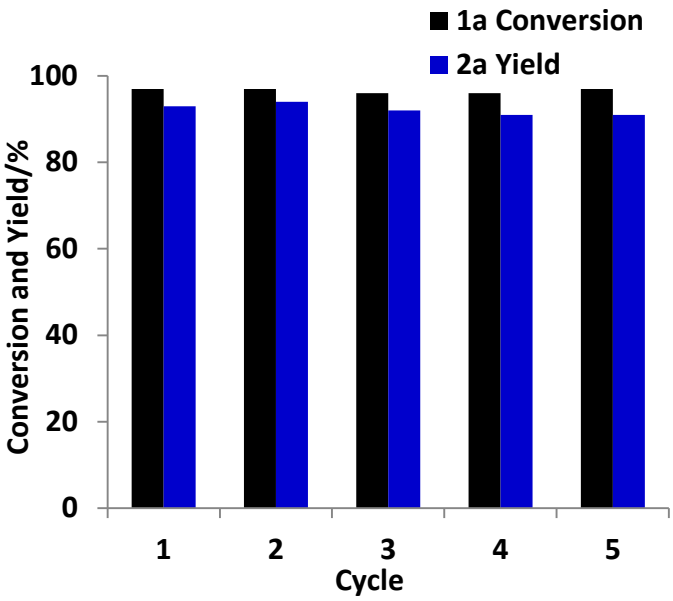


Figure S8. Recyclability test of **N-CNTs-800**. Reaction conditions: Iodobenzene 0.4 mmol, benzene 4 mL, *t*-BuOK 1.2 mmol, **N-CNTs-800** 0.01 g, 120 °C, 24 h. Conversions and Yields were determined by GC using dodecane as an internal standard.

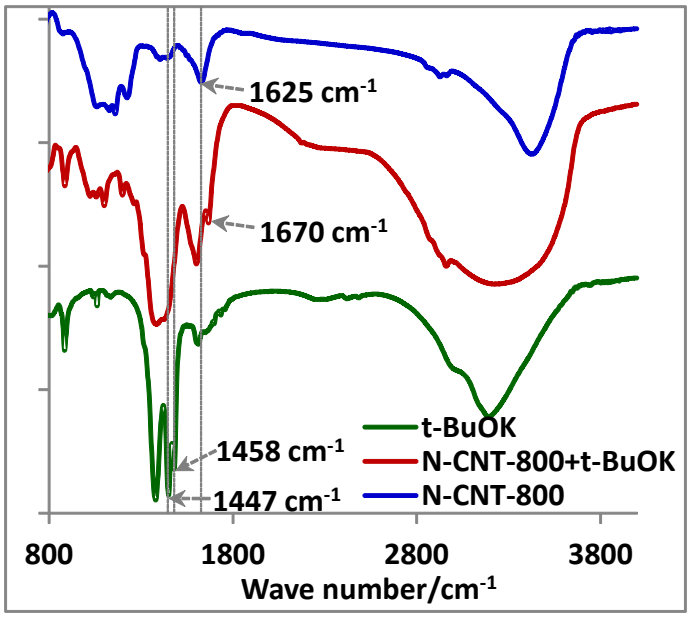


Figure S9. FTIR spectra of **N-CNTs-800**, *t*-BuOK and their mixture. The spectra were recorded as KBr pellets. The mixture was prepared by adding **N-CNTs-800** (0.01 g) to 10 mL tetrahydrofuran solution of *t*-BuOK (1.2 mmol) and stirring for 5 h at room temperature. Then the solvent was evaporated and the mixture was dried under vacuum at 60 °C for 12 h.

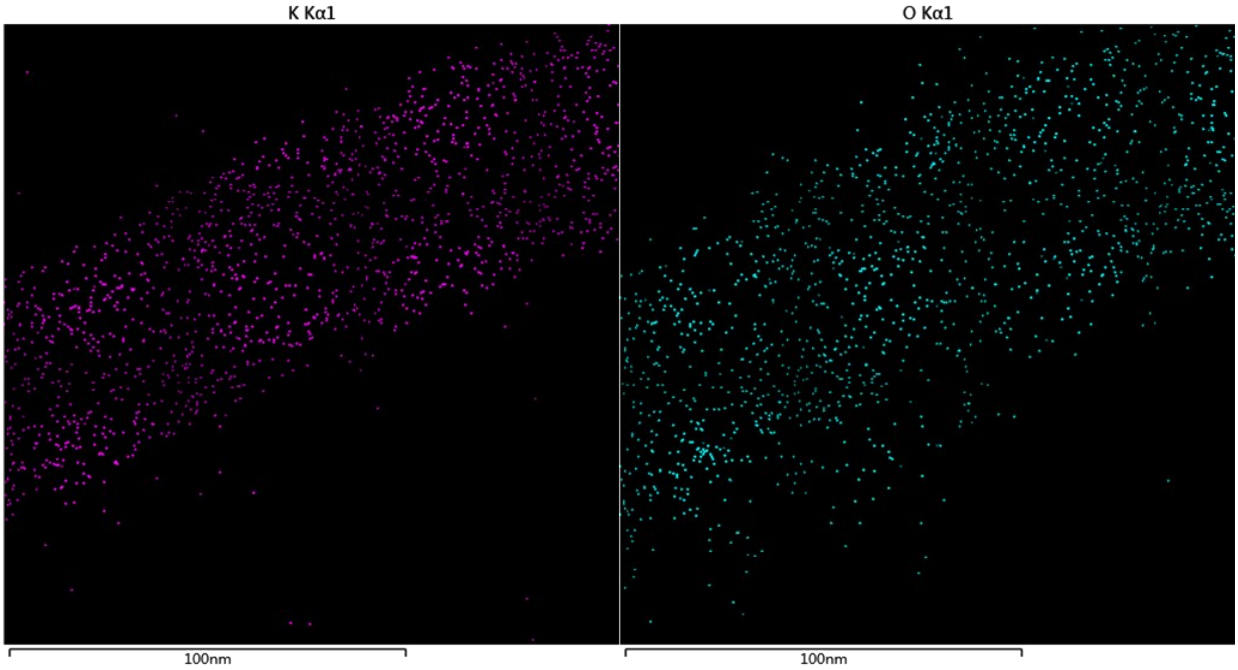
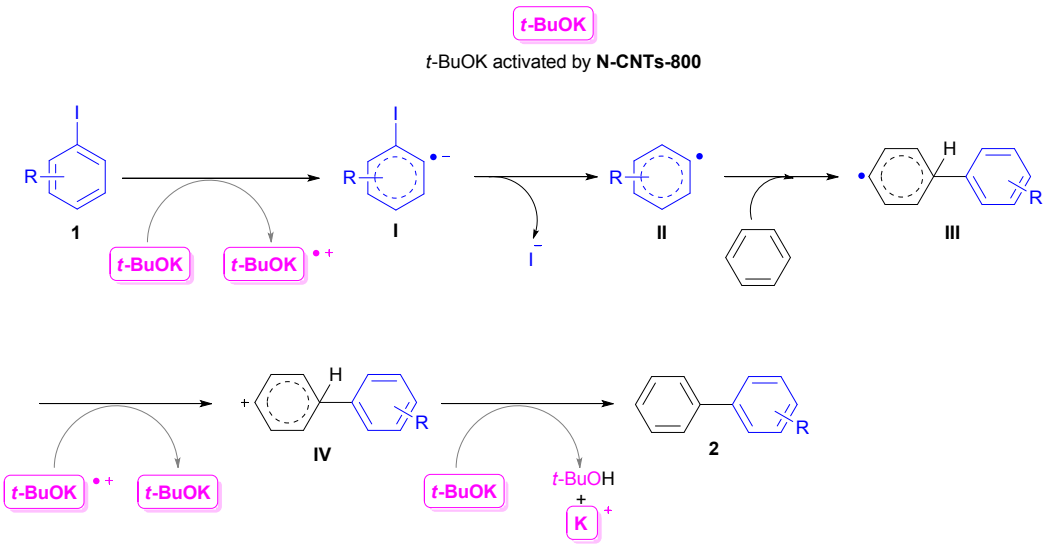
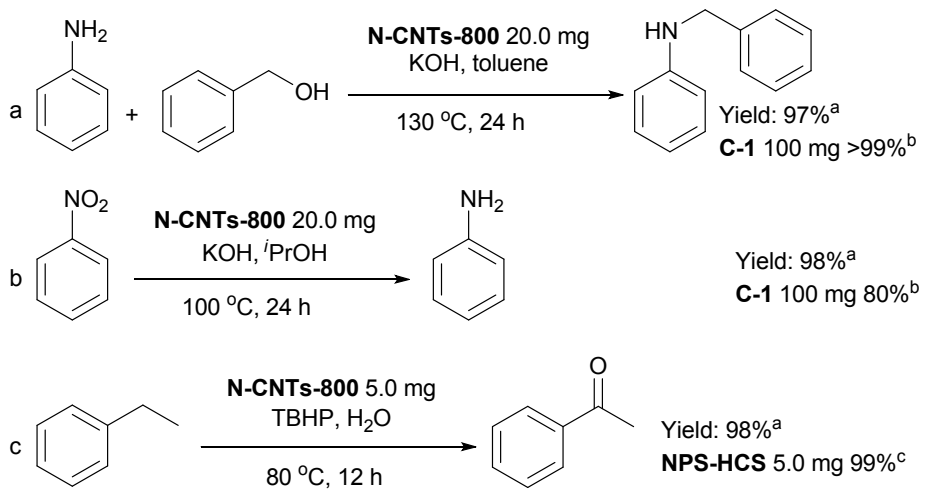


Figure S10. EDS mapping of K (purple) and O (blue) for the *t*-BuOK coordinated N-CNTs-800. The sample was prepared by adding **N-CNTs-800** (0.01 g) to 10 mL tetrahydrofuran solution of *t*-BuOK (1.2 mmol) and stirring for 5 h at room temperature. Then the mixture was filtered and washed with water and tetrahydrofuran. After being extracted in a Soxhlet extractor with tetrahydrofuran for 48 h, the sample was collected and dried in vacuum oven at 80 °C for 24 h.



Scheme S2. Proposed mechanism for the **N-CNTs-800**/*t*-BuOK catalyzed C-H arylation. Firstly, *t*-BuOK was activated by the the skeleton of **N-CNTs-800**, which subsequently transferred a single electron to aryl iodide **1**, affording the intermediate aryl radical anion **I**. And then, aryl radical **II** was formed by departure of iodide anion, and then reacted with benzene to generate a biary radical **III**. Oxidation of **III** by the previously formed radical cation of *t*-BuOK produced the biaryl cation **IV**. Finally, deprotonation of **IV** by a *tert*-butoxide anion furnished the biary product **2**. (Ref. *Chem. Commun.*, 2015, **51**, 545-548; *J. Am. Chem. Soc.*, 2016, **138**, 7402-7410; *Angew. Chem. Int. Ed.*, 2016, **55**, 4492-4496; *Angew. Chem. Int. Ed.*, 2016, **55**, 3124-3128.)



Scheme S3. Utilization of N-CNTs-800 as the catalyst in the reductive hydrogen atom transfer reaction and oxidation reaction. [a] Yields were determined by GC using dodecane as an internal standard. [b] Data from Ref. (Nat. Commun., 2015, 6, 6478). [c] Data from Ref. (Angew. Chem. Int. Ed., 2016, 55, 4016-4020).

3. Determination of the product yields

The structures of the products for C-H arylation, reductive hydrogen atom transfer reaction and oxidation reaction were characterized by GC-MS and comparing the retention time with the authentic compound. The

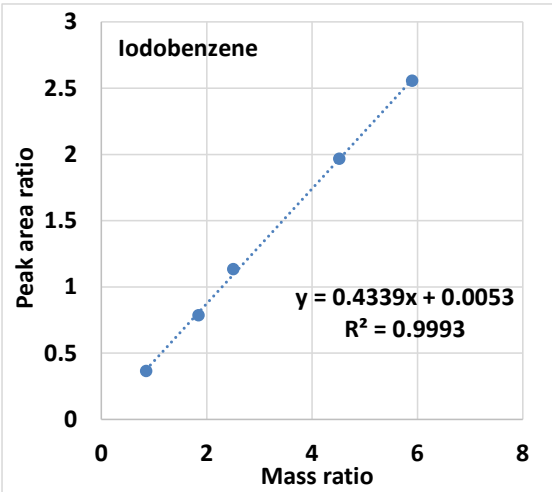
yields of the products for each reaction were determined by GC using dodecane as the internal standard and calculated through the calibartion curves as shown below.

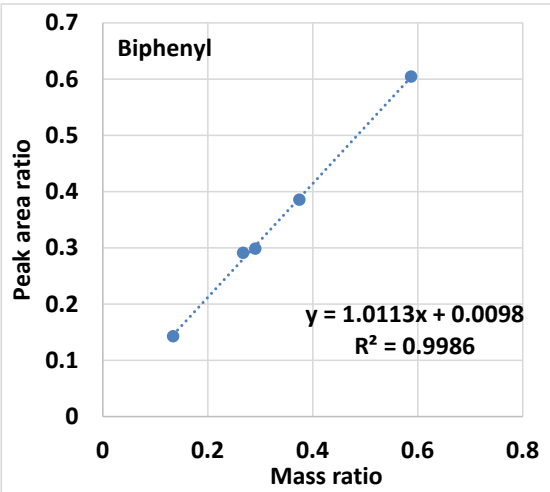
3.1 Reaction of iodobenzene with benzene to produce biphenyl

Calibration Curve

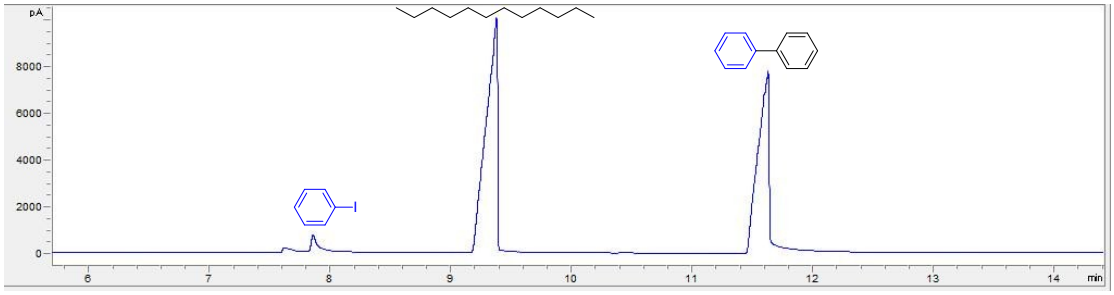
Standard Solution	iodobenzene/g	dodecane/g
1	0.0624	0.0488
2	0.1289	0.0502
3	0.2231	0.0491
4	0.3471	0.0509
5	0.4696	0.0502

Standard Solution	biphenyl/g	dodecane/g
1	0.01	0.0745
2	0.0213	0.0796
3	0.0266	0.071
4	0.0313	0.1077
5	0.0466	0.0793

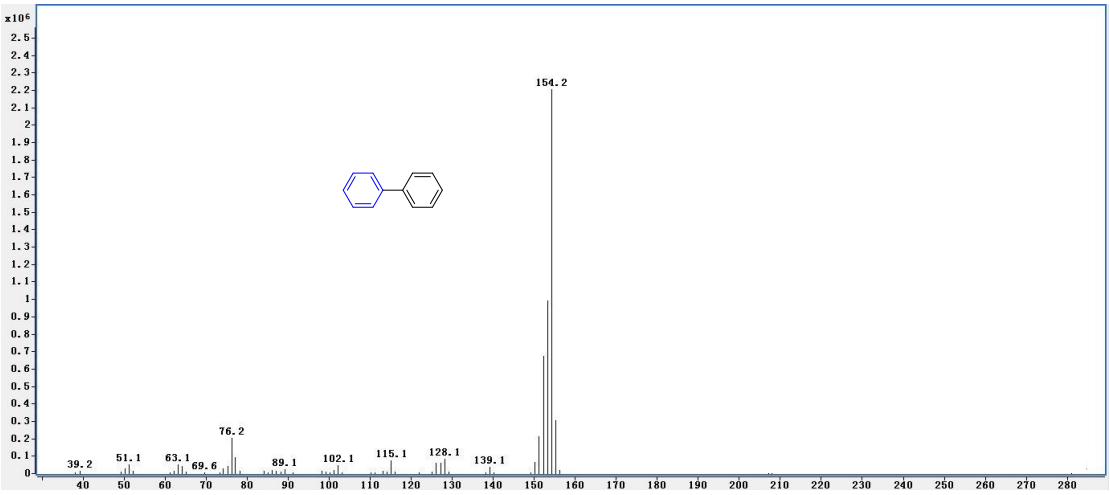




GC spectra



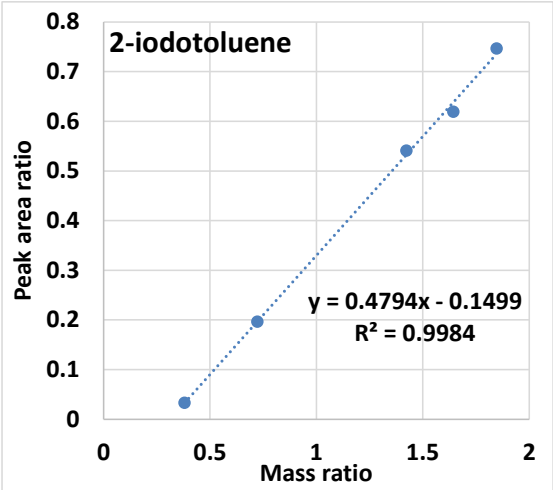
MS spectra

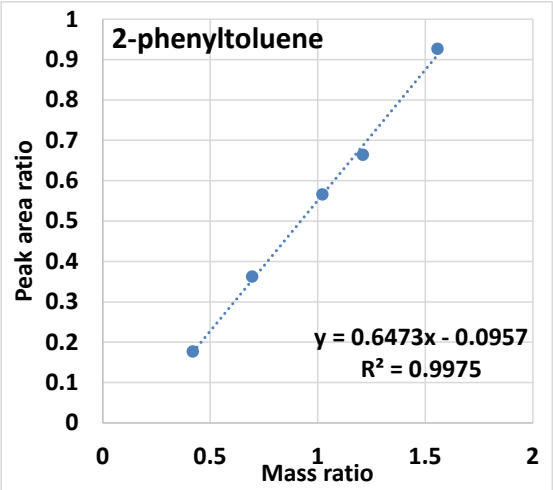


3.2 Reaction of 2-iodotoluene with benzene to produce 2-phenyltoluene

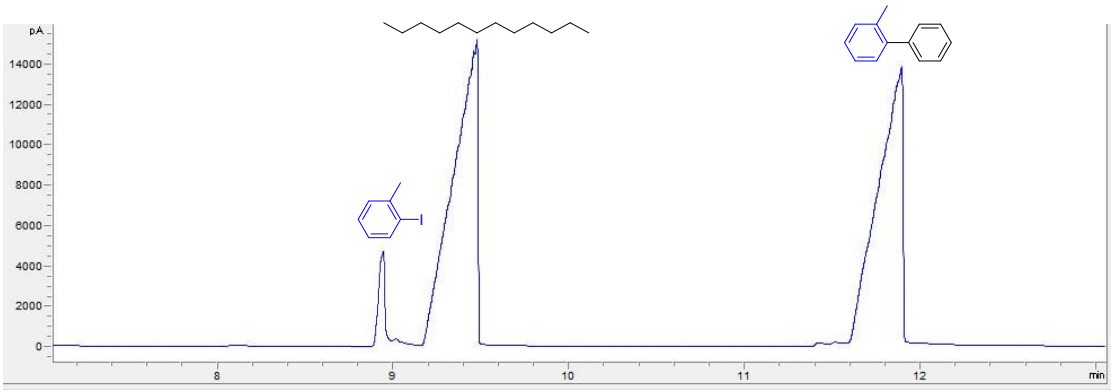
Calibration Curve

Standard Solution	2-iodotoluene/g	2-phenyltoluene/g	dodecane/g
1	0.0187	0.0206	0.0491
2	0.0349	0.0336	0.0483
3	0.0753	0.0468	0.0458
4	0.0582	0.0637	0.0409
5	0.0905	0.0593	0.049

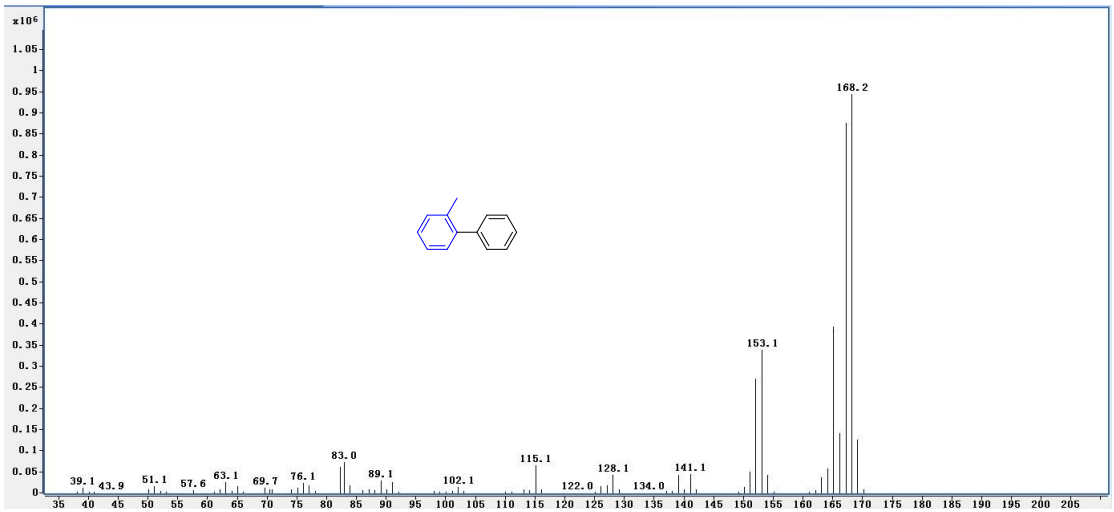




GC Spectra



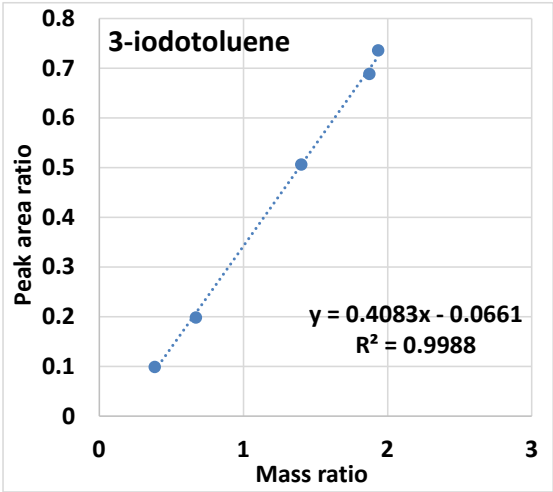
MS spectra

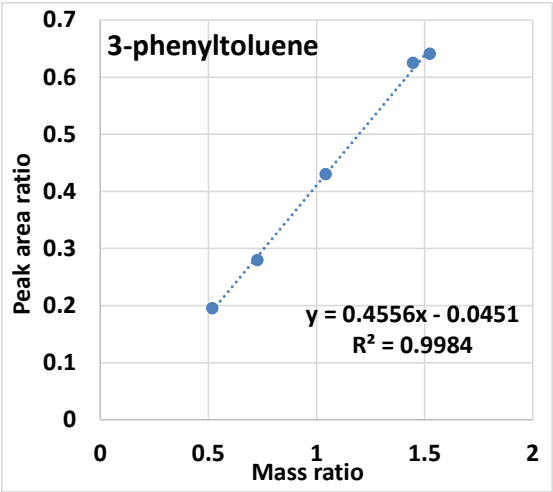


3.3 Reaction of 3-iodotoluene with benzene to produce 3-phenyltoluene

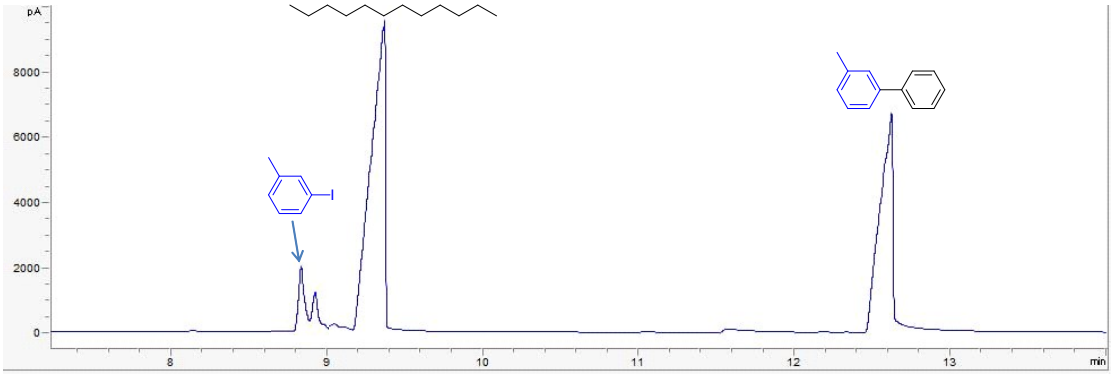
Calibration Curve

Standard Solution	3-iodotoluene/g	3-phenyltoluene/g	dodecane/g
1	0.0179	0.0241	0.0465
2	0.0327	0.0355	0.0488
3	0.0681	0.0507	0.0486
4	0.0776	0.0631	0.0414
5	0.0944	0.0706	0.0488

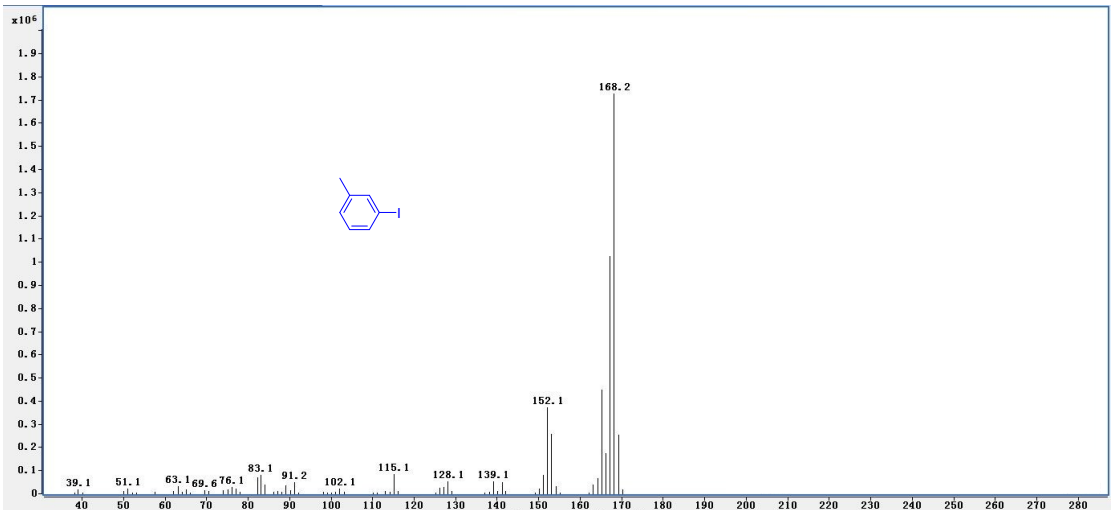




GC Spectra



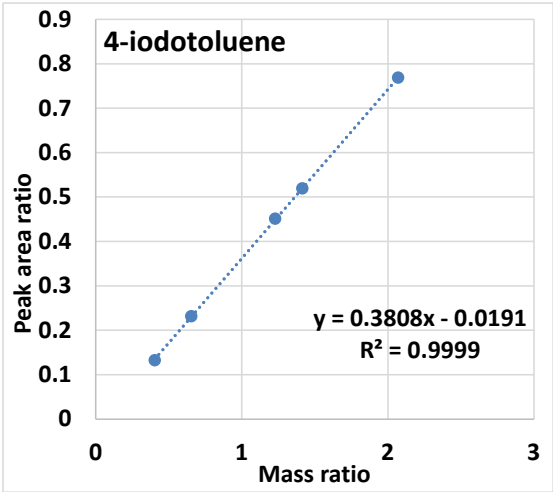
MS spectra

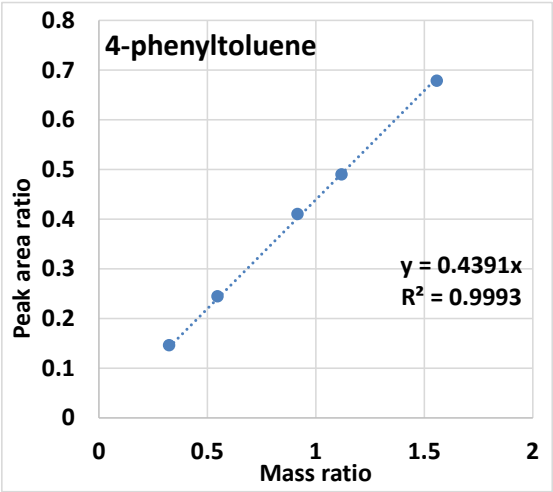


3.4 Reaction of 4-iodotoluene with benzene to produce 4-phenyltoluene

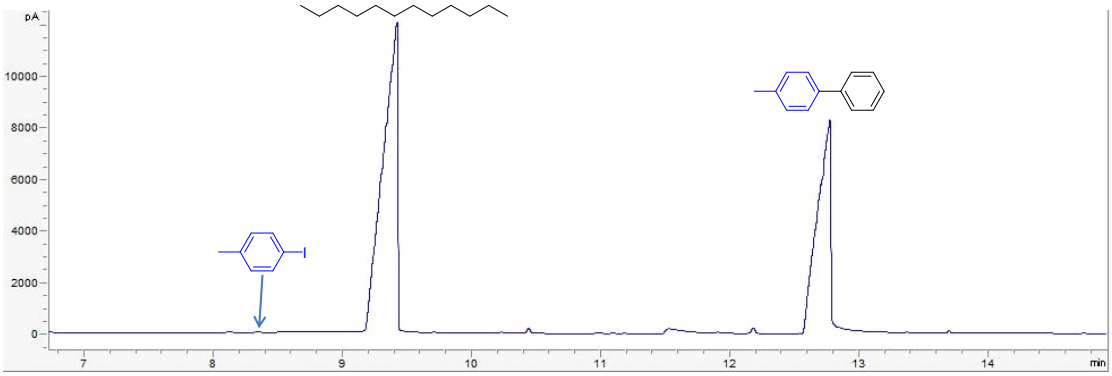
Calibration Curve

Standard Solution	4-iodotoluene/g	4-phenyltoluene/g	dodecane/g
1	0.0177	0.0142	0.0438
2	0.0322	0.0269	0.0492
3	0.0617	0.046	0.0502
4	0.07	0.0554	0.0495
5	0.0984	0.074	0.0475

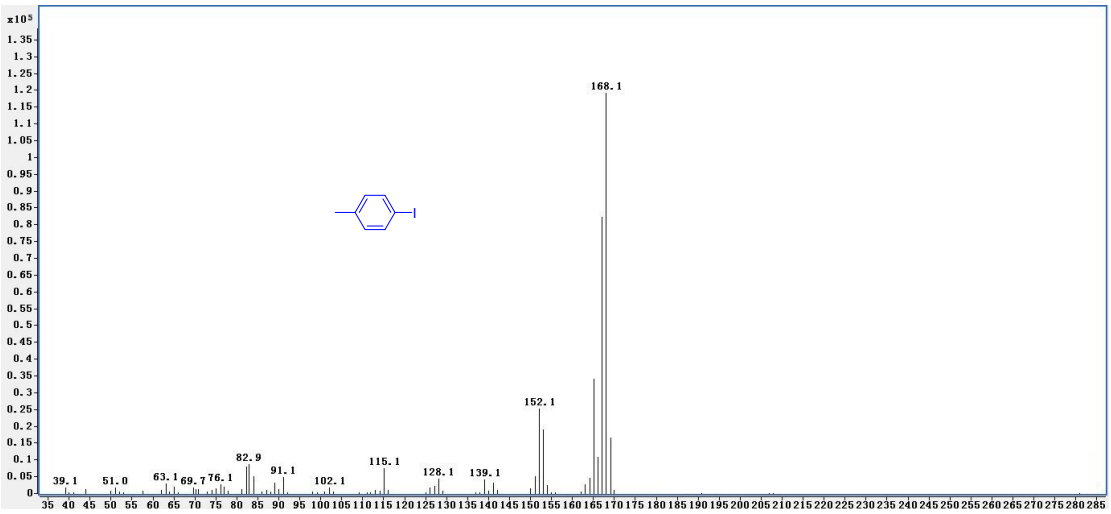




GC Spectra



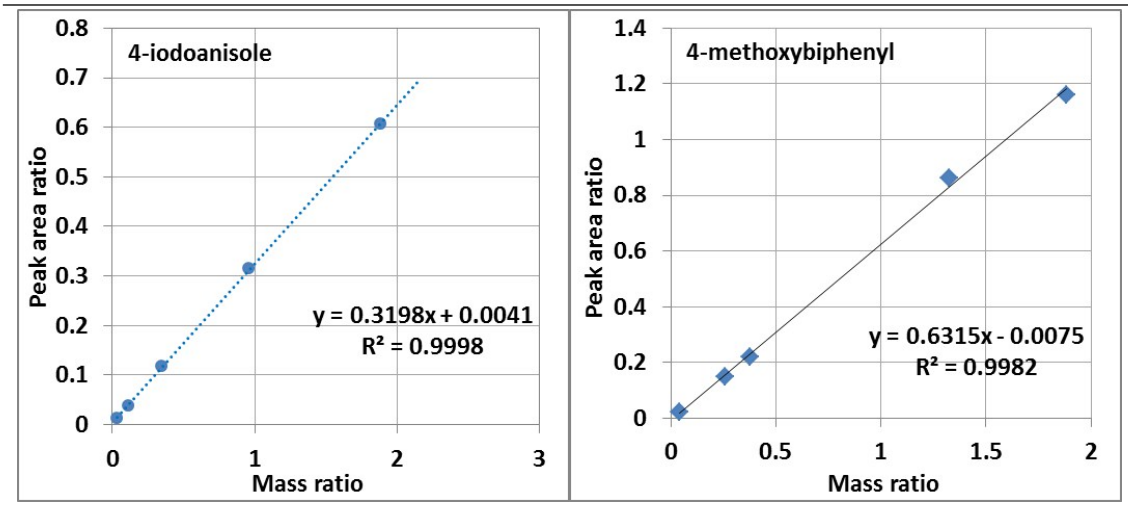
MS spectra



3.5 Reaction of 4-iodoanisole with benzene to produce 4-methoxybiphenyl

Calibration Curve

Standard Solution	4-iodoanisole/g	4-methoxybiphenyl/g	dodecane/g
1	0.0017	0.002	0.0498
2	0.0058	0.0129	0.0499
3	0.017	0.0186	0.0491
4	0.0478	0.066	0.0498
5	0.1071	0.0933	0.0495



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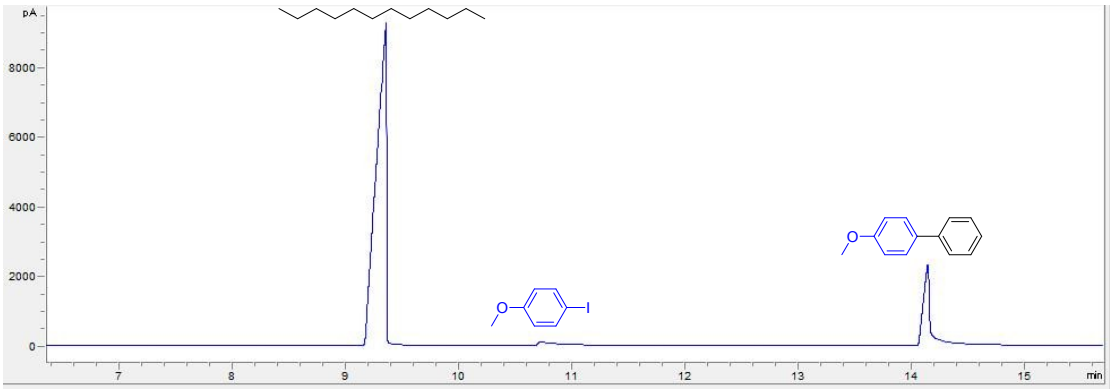
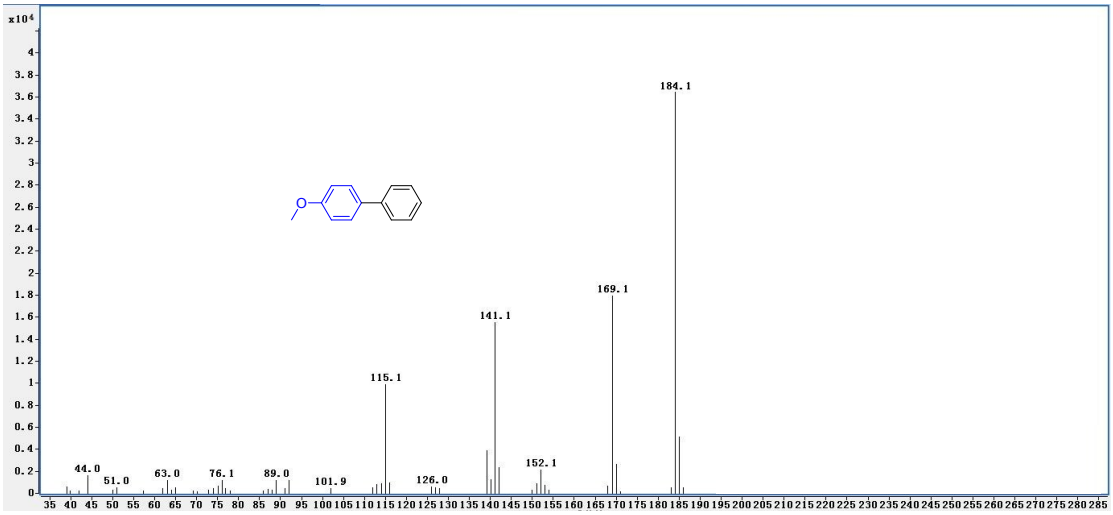


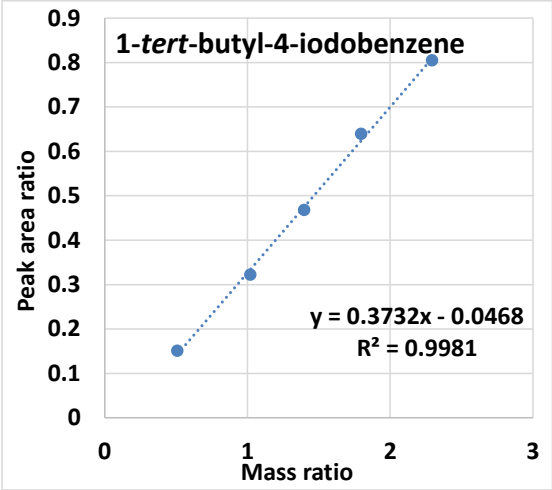
MS spectra

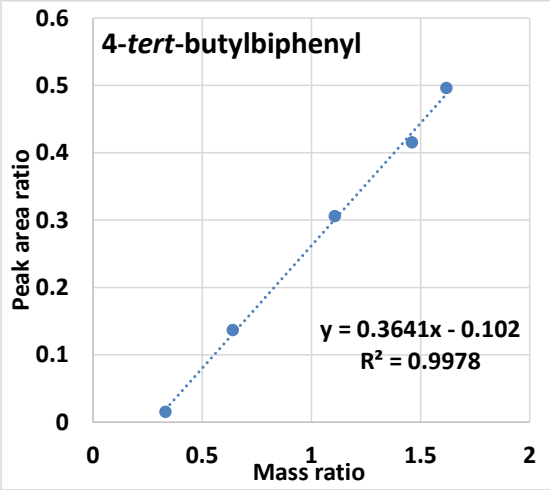


3.6 Reaction of 1-*tert*-butyl-4-iodobenzene with benzene to produce 4-*tert*-butylbiphenyl

Calibration Curve

Standard Solution	1-*tert*-butyl-4-iodobenzene/g	4-*tert*-butylbiphenyl/g	dodecane/g
1	0.0248	0.0162	0.0487
2	0.0522	0.0328	0.0512
3	0.0689	0.0546	0.0493
4	0.09	0.0732	0.0501
5	0.1149	0.0811	0.0501





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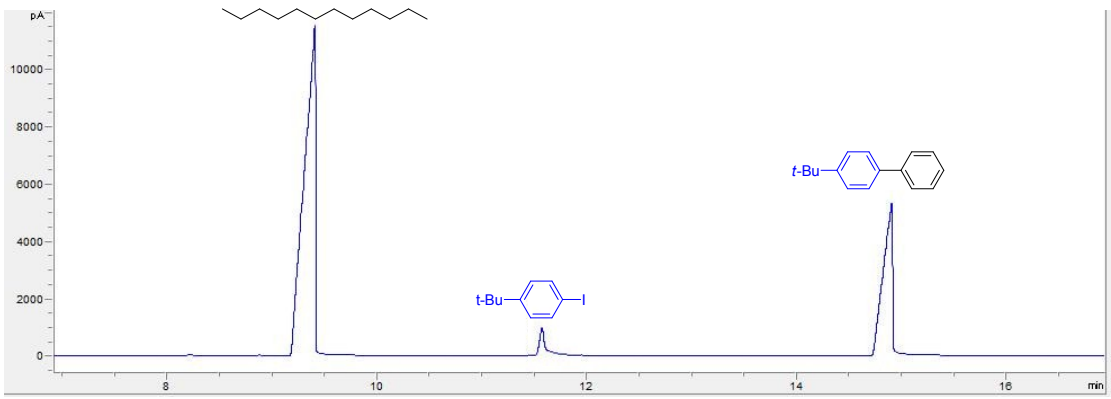
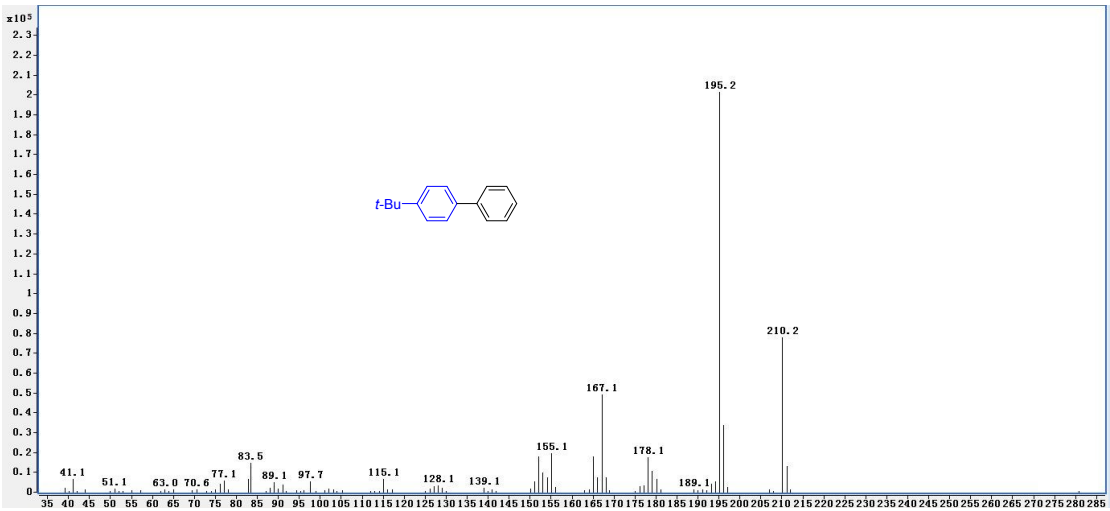


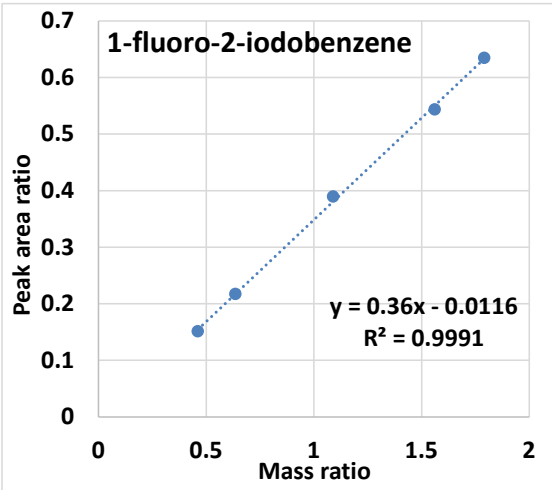
MS spectra

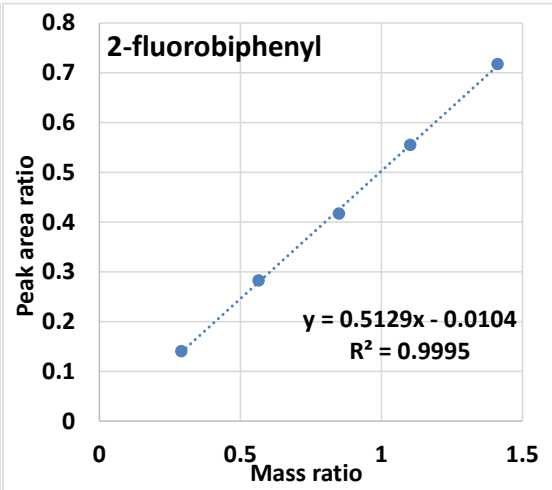


3.7 Reaction of 1-fluoro-2-iodobenzene with benzene to produce 2-fluorobiphenyl

Calibration Curve

Standard Solution	1-fluoro-2-iodobenzene/g	2-fluorobiphenyl/g	dodecane/g
1	0.0525	0.014	0.0482
2	0.0322	0.0286	0.0506
3	0.0228	0.042	0.0494
4	0.0773	0.0546	0.0495
5	0.0899	0.0709	0.0502





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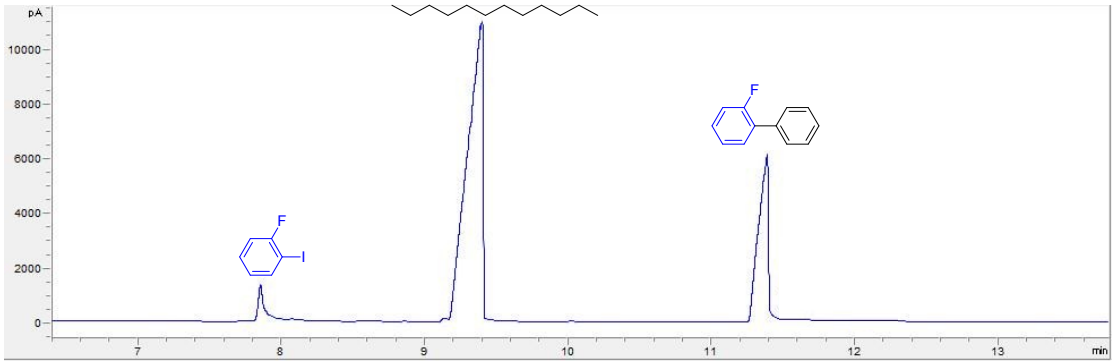

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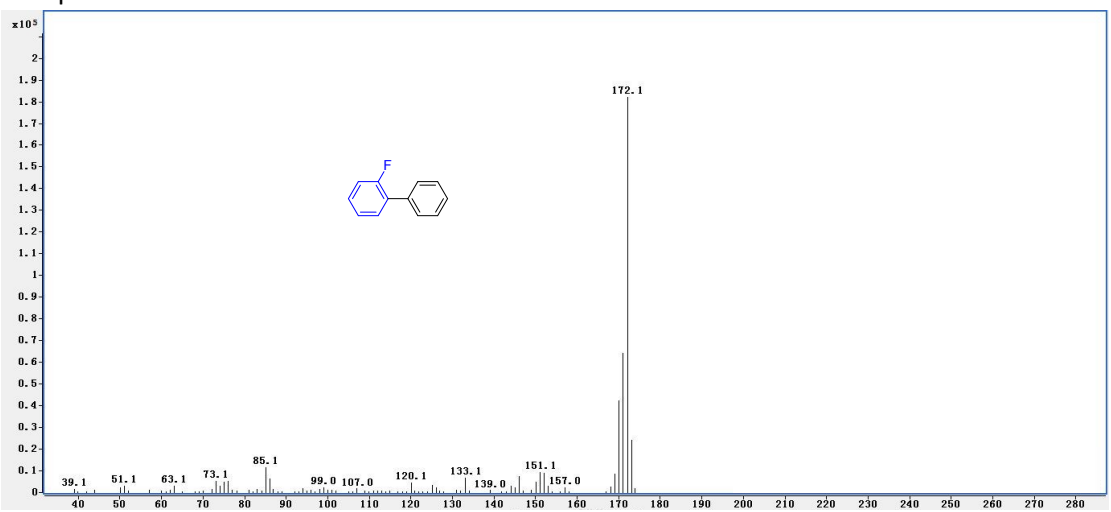
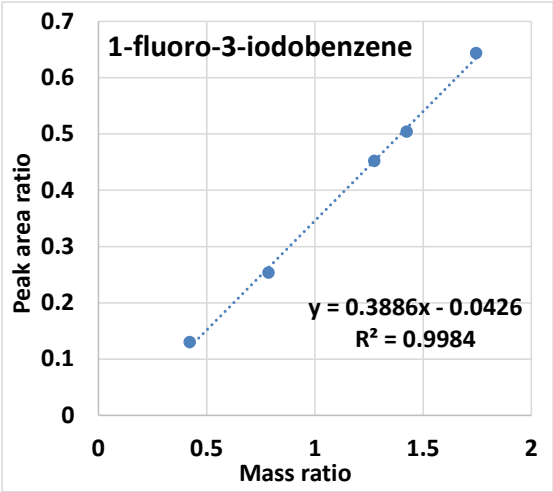
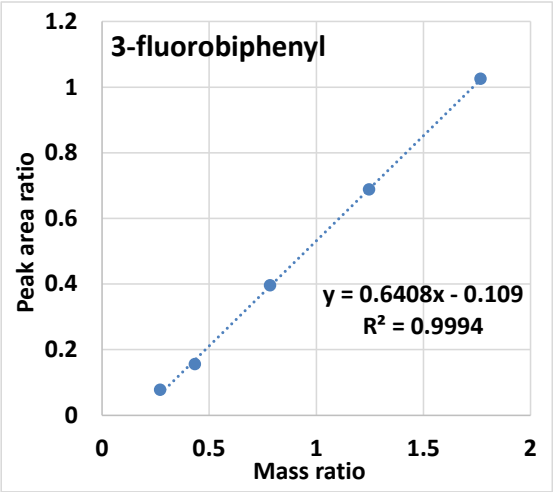


3.8 Reaction of 1-fluoro-3-iodobenzene with benzene to produce 3-fluorobiphenyl

Calibration Curve

Standard Solution	1-fluoro-3-iodobenzene/g	3-fluorobiphenyl/g	dodecane/g
1	0.0203	0.0131	0.0481
2	0.0383	0.0382	0.0487
3	0.0622	0.0212	0.0488
4	0.085	0.0607	0.0487
5	0.0698	0.0866	0.049





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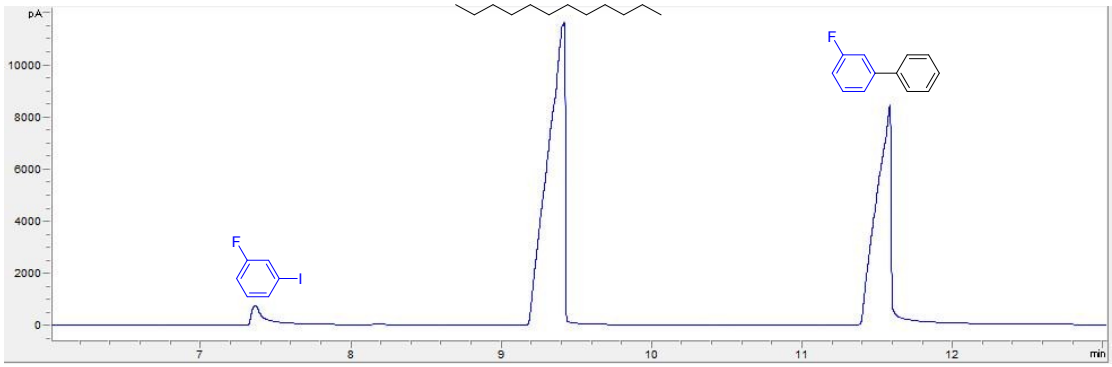
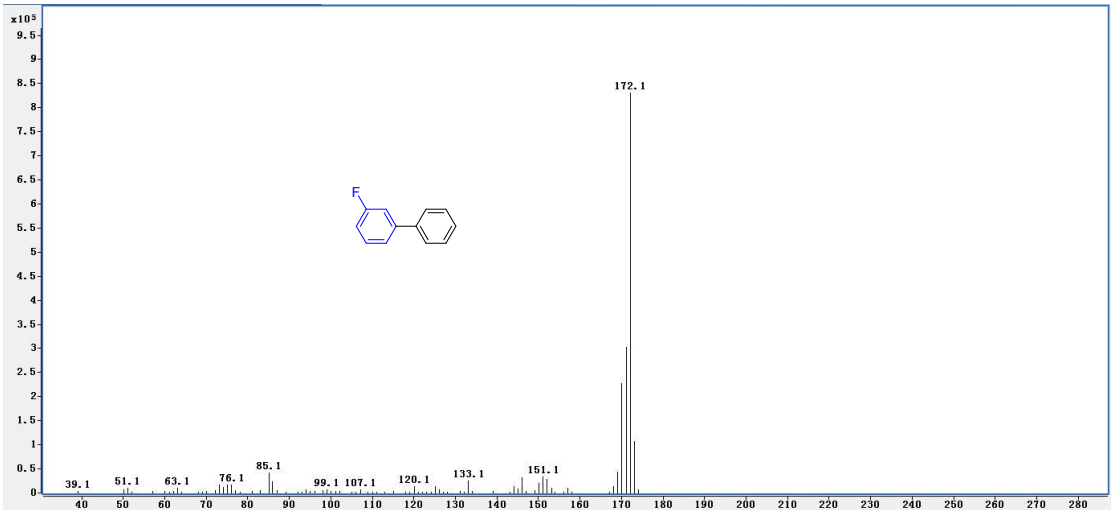


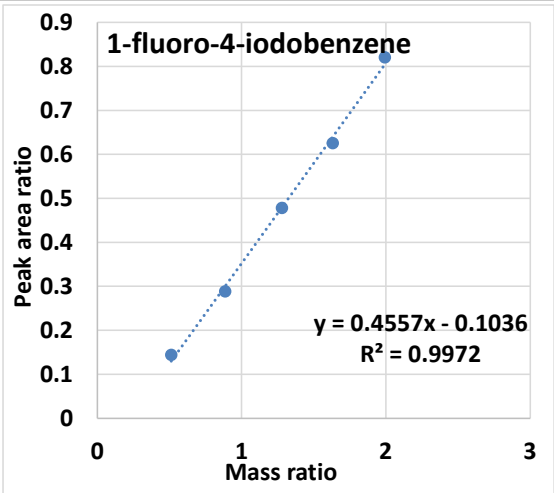
MS spectra

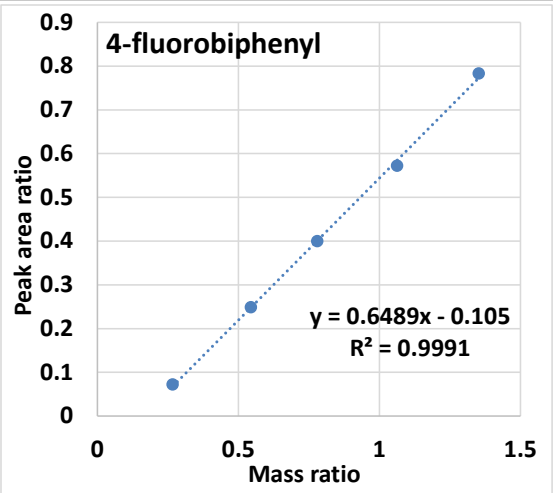


3.9 Reaction of 1-fluoro-4-iodobenzene with benzene to produce 4-fluorobiphenyl

Calibration Curve

Standard Solution	1-fluoro-4-iodobenzene/g	4-fluorobiphenyl/g	dodecane/g
1	0.0263	0.0137	0.0513
2	0.044	0.027	0.0496
3	0.064	0.039	0.0500
4	0.0824	0.0537	0.0505
5	0.0995	0.0675	0.0499





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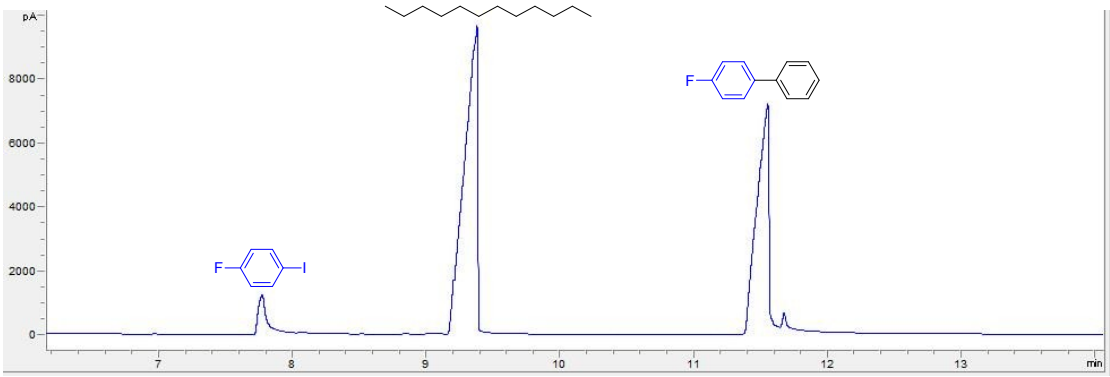

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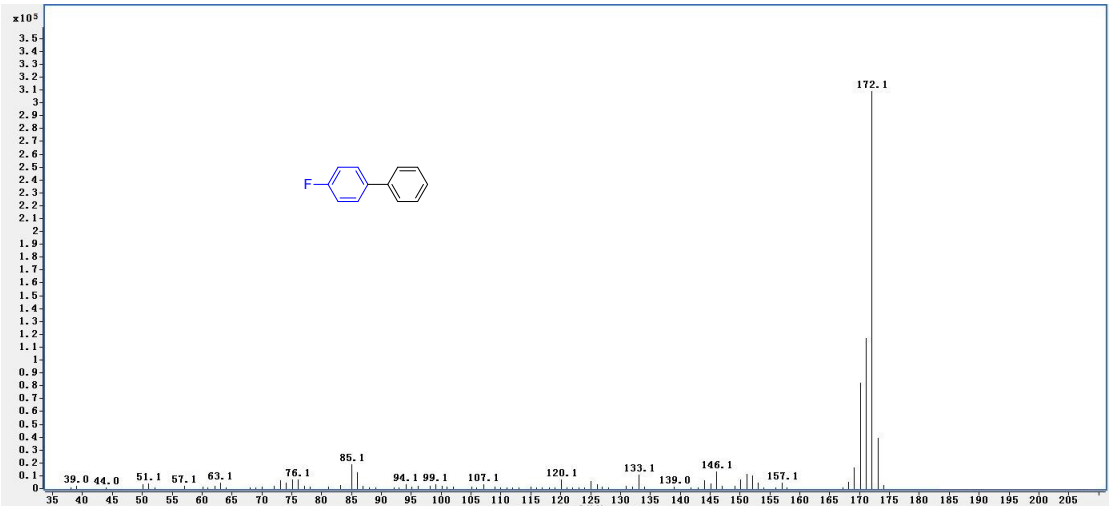
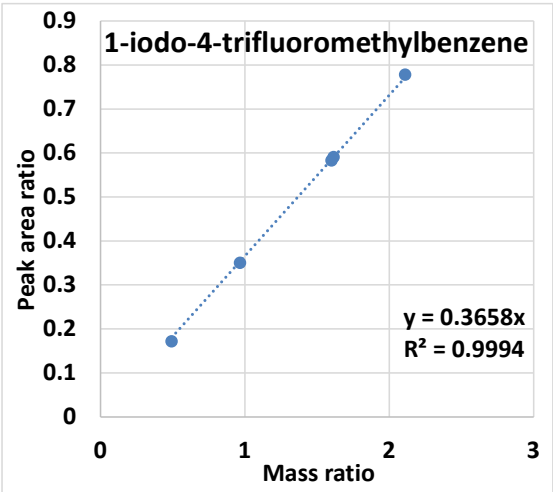
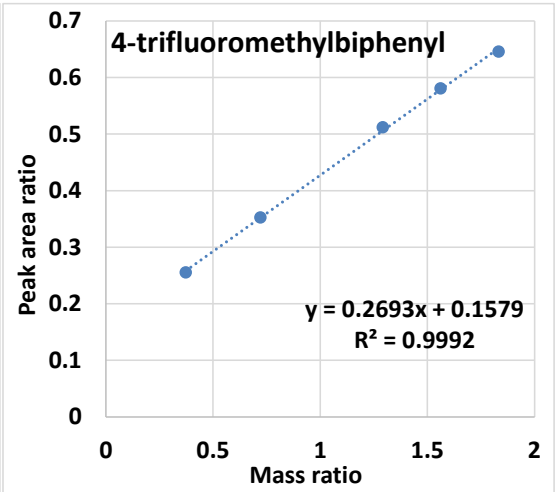


3.10 Reaction of 1-iodo-4-trifluoromethylbenzene with benzene to produce 4-trifluoromethylbiphenyl

Calibration Curve

Standard Solution	1-iodo-4-trifluoromethylbenzene/g	4-trifluoromethylbiphenyl/g	dodecane/g
1	0.0801	0.0185	0.0496
2	0.0251	0.0368	0.051
3	0.068	0.0549	0.0425
4	0.0463	0.0748	0.0479
5	0.1072	0.0931	0.0508





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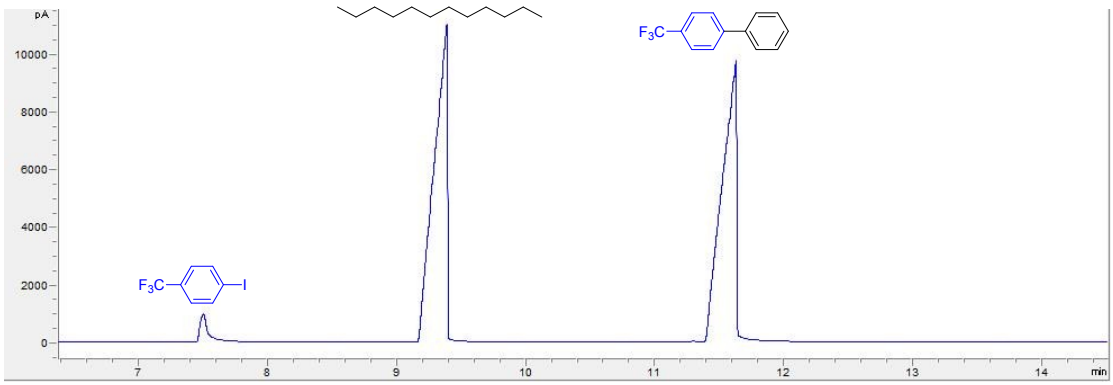
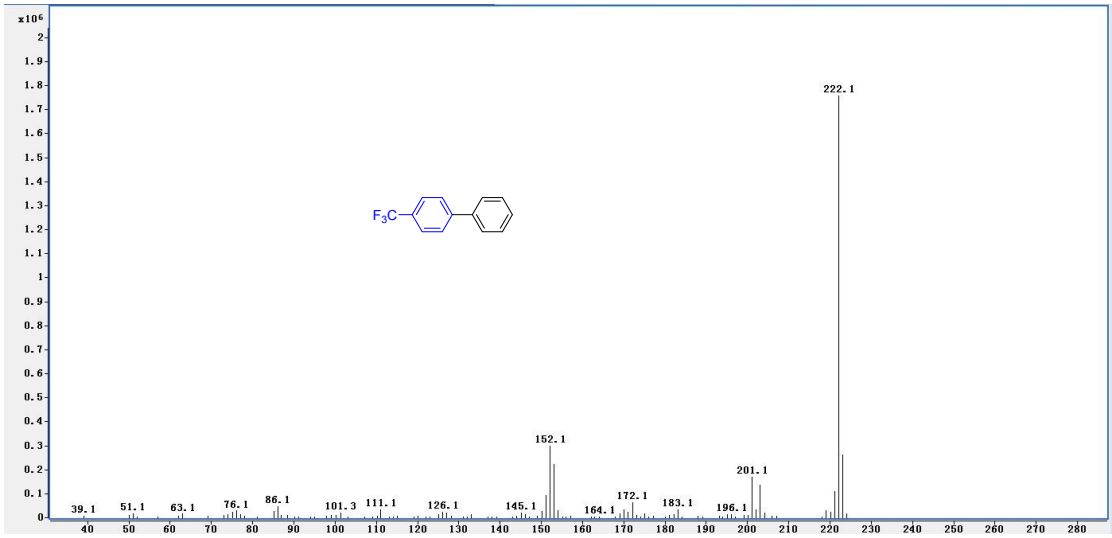


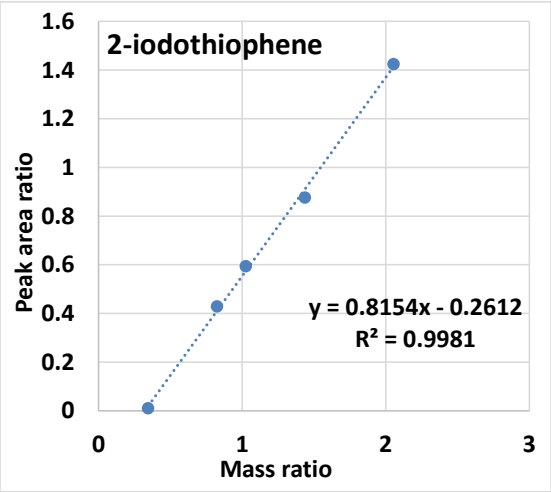
MS spectra

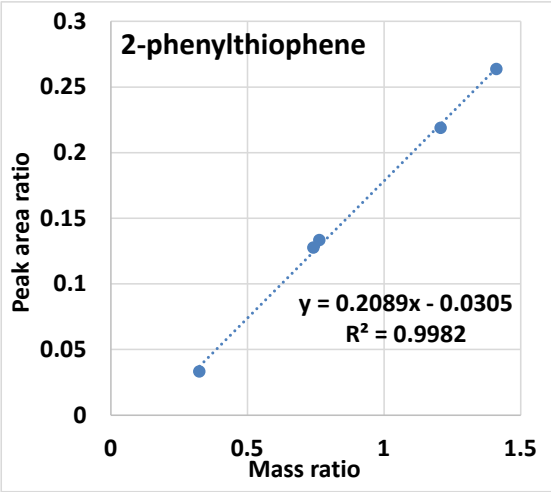


3.11 Reaction of 2-iodothiophene with benzene to produce 2-phenylthiophene

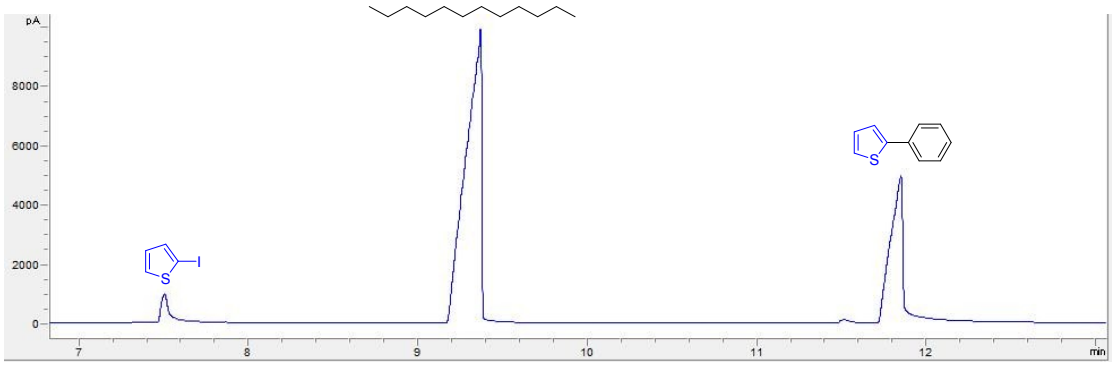
Calibration Curve

Standard Solution	2-iodothiophene/g	2-phenylthiophene/g	dodecane/g
1	0.0166	0.0156	0.0481
2	0.0335	0.0301	0.0406
3	0.0713	0.0599	0.0496
4	0.0507	0.0377	0.0494
5	0.0949	0.0652	0.0462

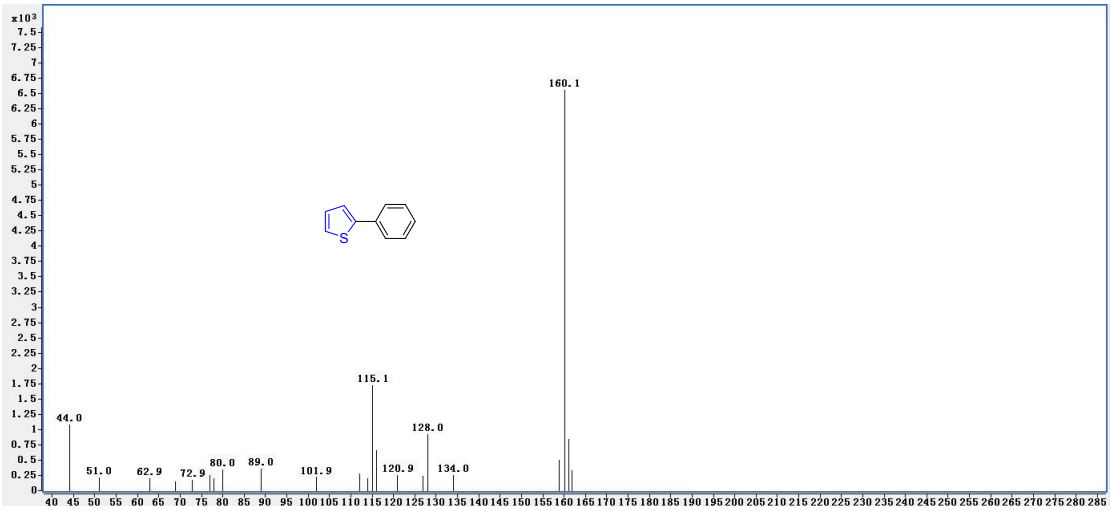




GC Spectra

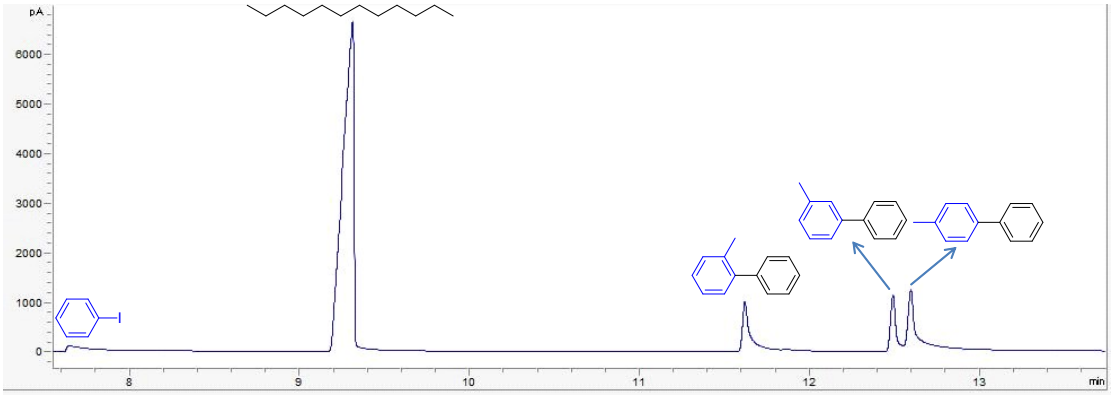


MS spectra



3.12 Reaction of iodobenzene with toluene to produce 2/3/4-methylbiphenyl

GC Spectra

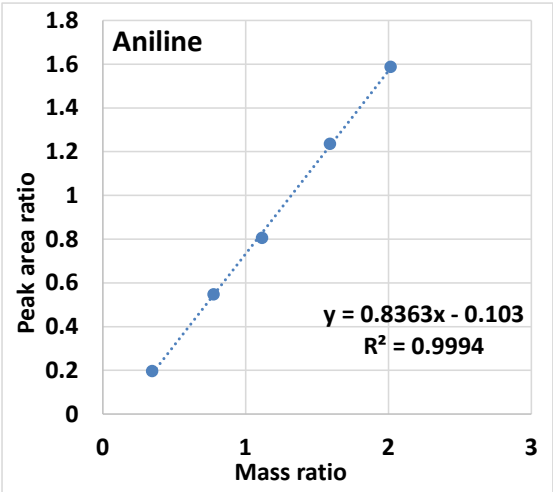


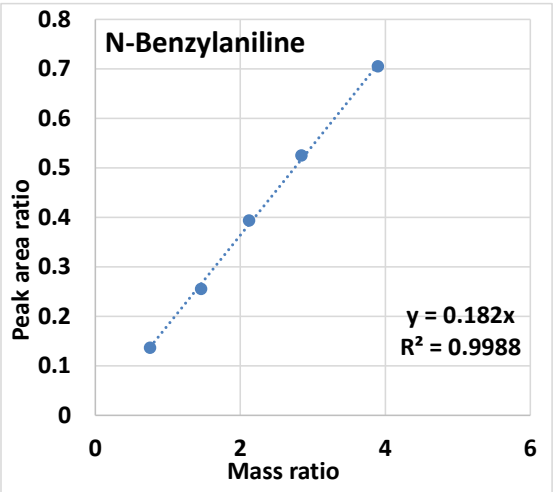
3.13 Reaction of aniline with benzyl alcohol to produce N-benzylaniline

Calibration Curve

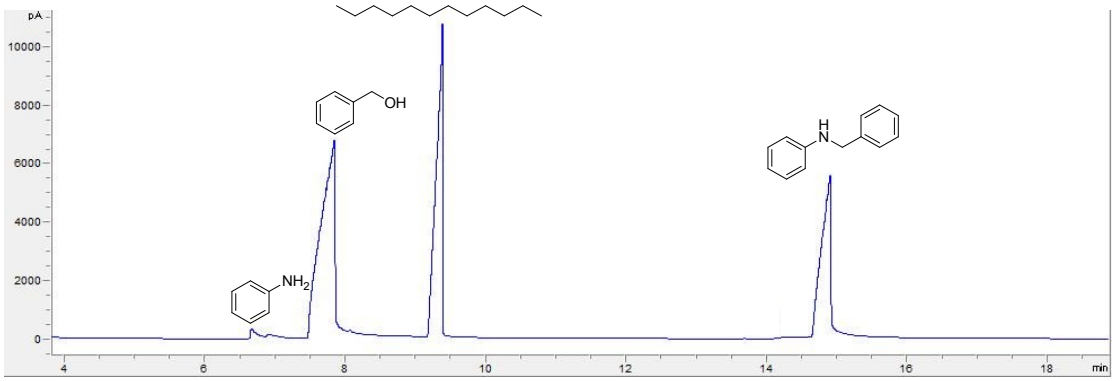
Standard Solution	Aniline/g	dodecane/g
1	0.017	0.0491
2	0.038	0.049
3	0.0554	0.0497
4	0.0789	0.0496
5	0.1002	0.0497

Standard Solution	N-Benzylaniline/g	dodecane/g
1	0.0382	0.0504
2	0.0735	0.0503
3	0.1045	0.0492
4	0.1433	0.0504
5	0.193	0.0495

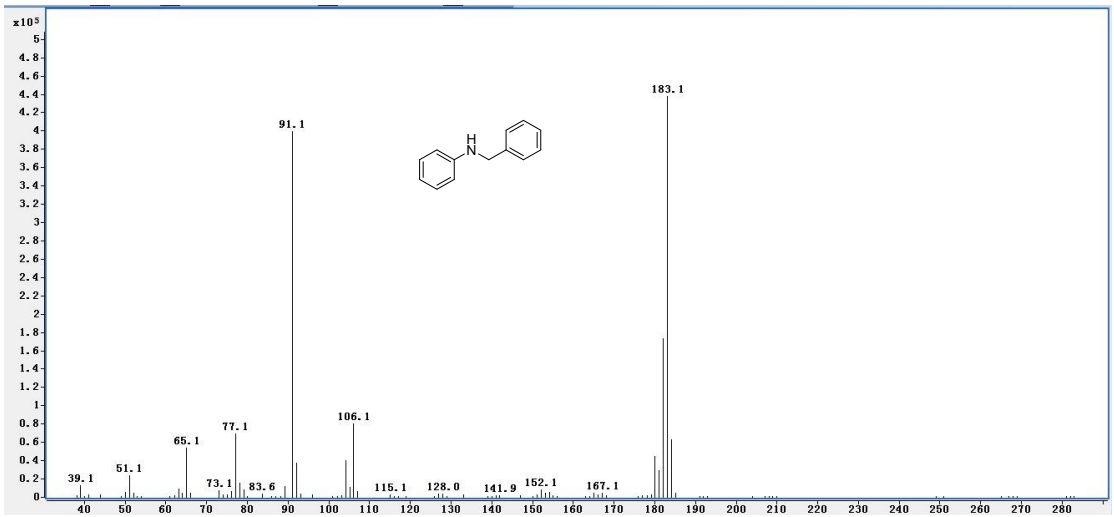




GC Spectra



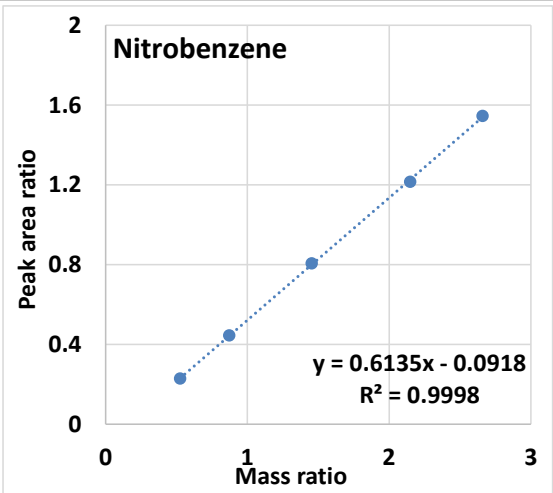
MS spectra



3.14 Reduction of nitrobenzene to produce aniline

Calibration Curve

Standard Solution	nitrobenzene/g	dodecane/g
1	0.0241	0.0459
2	0.0438	0.0502
3	0.0699	0.0481
4	0.1051	0.0489
5	0.1311	0.0493



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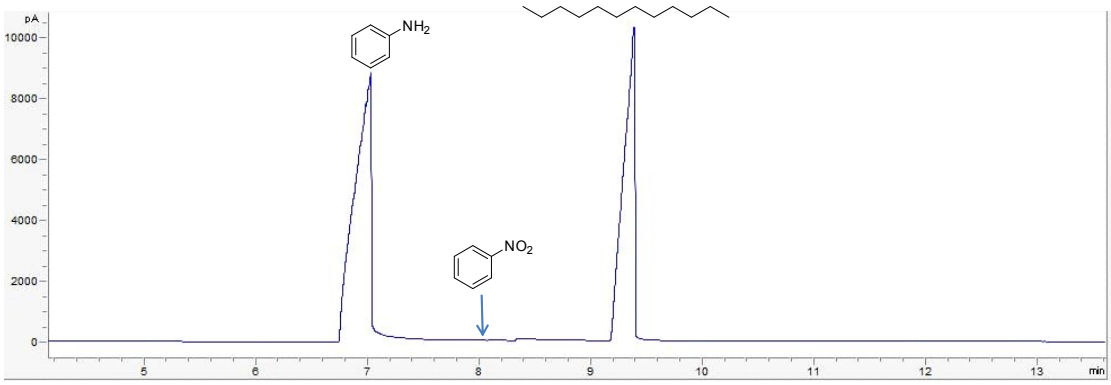

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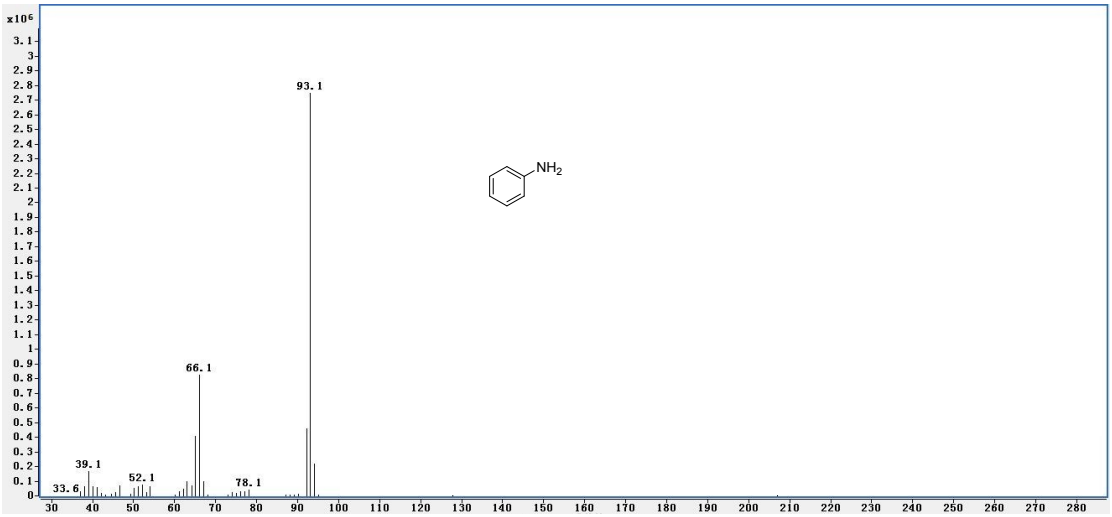
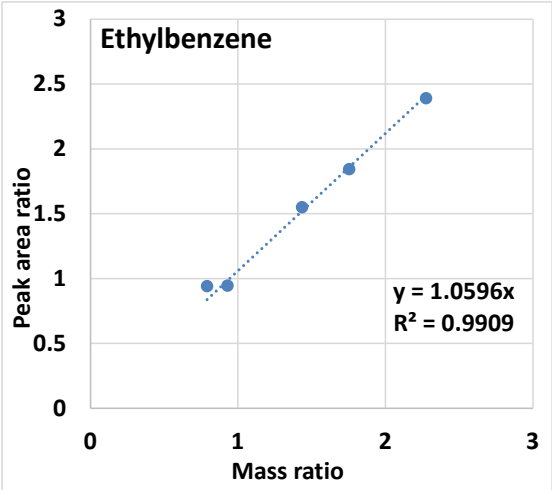
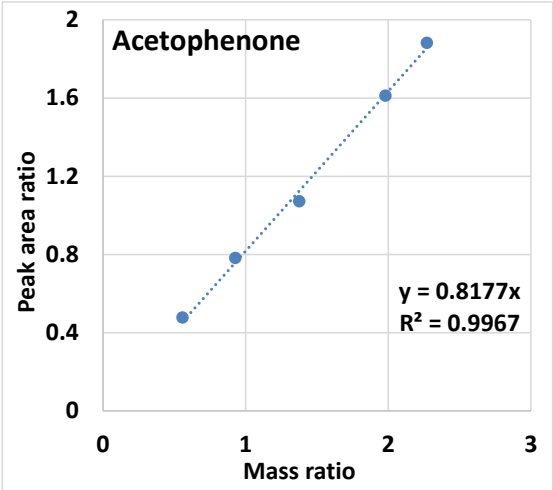


3.15 Oxidation of ethylbenzene to produce acetophenone

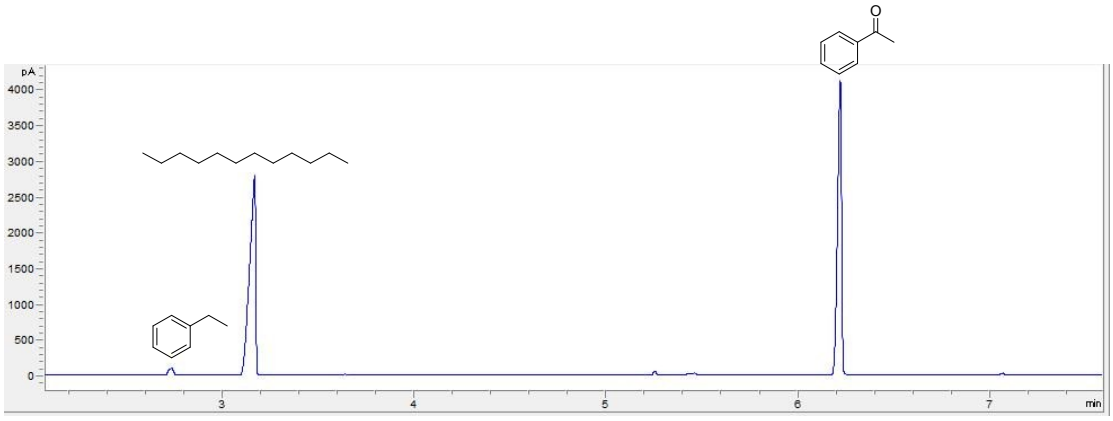
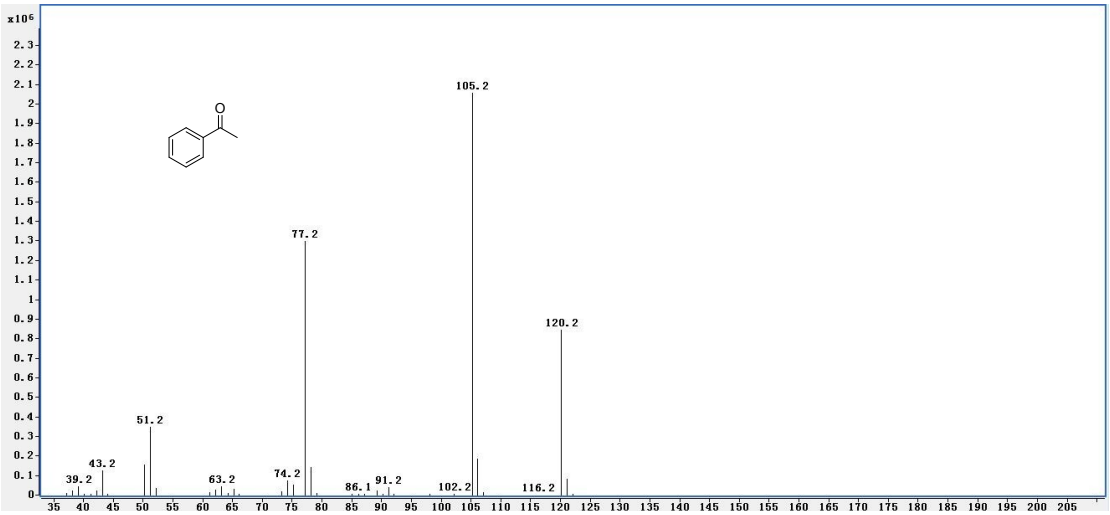
Calibration Curve

Standard Solution	ethylbenzene/g	acetophenone/g	dodecane/g
1	0.0402	0.0699	0.0508
2	0.0457	0.0274	0.0491
3	0.0683	0.1081	0.0476
4	0.0834	0.0441	0.0475
5	0.1102	0.0959	0.0484





GC Spectra



MS spectra