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Electronic Supplementary Information

Polyurea derived from CO_2 and diamines: highly efficient catalysts for C-H arylation of benzene

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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. Tetra-*n*-butylammonium tungstate was synthesized based on the reported procedure (Inorg. Chem. 1985, 24, 4055).

Instrumentation

Liquid ^1H NMR and ^{13}C NMR spectra was recorded on Bruck 400 spectrometer. Solid-state NMR experiments were performed on a Bruker WB Avance III 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}. Field emission scanning electron microscopy (SEM) observations were performed on a Hitachi S-4800 microscope operated at an accelerating voltage of 15.0 kV. Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-1011 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 atmosphere with a heating rate of 10 °C/min. ESI-MS were recorded on a Thermo Finnigan LCQ Advantage spectrometer in ESI mode with a spray voltage of 4.8 kV. 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 the polyurea

Ref. *J. Colloid Interf. Sci*, 2014, **424**, 44-48

In this work, PU was synthesized via the copolymerization of CO_2 with 1,4-butanediamine, 1,4-cyclohexanediamine and *p*-xylylenediamine, respectively, catalyzed by $[n\text{-}Bu_4N]_2WO_4$ using N-methyl pyrrolidone (NMP) as solvent. In a typical procedure, 5 mmol diamine, 0.25 mmol tetra-*n*-butylammonium tungstate as catalyst, and 1 mL NMP as solvent were loaded into a Teflon-lined stainless steel reactor of 15 mL inner volume with a magnetic stirrer. After sealing the reactor, 3 MPa CO_2 was charged at room temperature. The reactor was put into an oven and heated at 160 ^oC for 12 h. After reaction, the reactor was cooled down in cold water and the gas inside was slowly vented. The solid obtained was washed with deionized water and ethanol for several times. After drying in vacuum at 100 ^{o}C for 24 h, white PU powders were finally obtained.

(2) Typical procedures for C-H arylation of benzene catalyzed by PU

For typical procedure (entry 2, Table 1), PU-Benz powders (0.0125 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 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. 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.

Table S1. Elemental analysis results of PU

PU	C	H	N	urea unit /mmol g^{-1}
PU-Benz	65.39	6.50	15.83	5.65
PU-^{c}Hex	56.97	8.79	18.28	6.53
PU-^{n}Bu	51.08	8.76	21.78	7.78

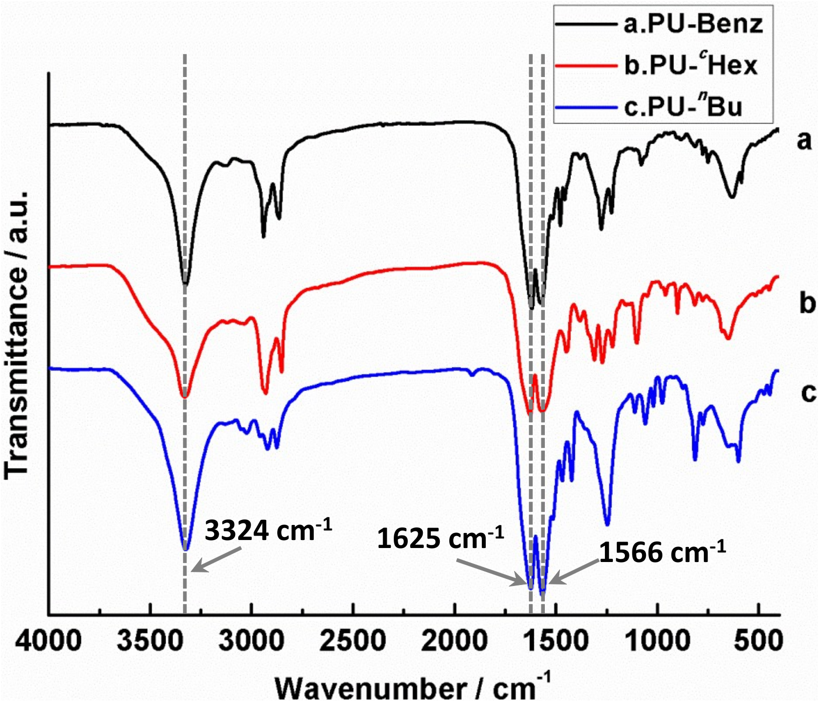


Figure S1. FTIR spectra of PU. The spectra were recorded as KBr pellets.

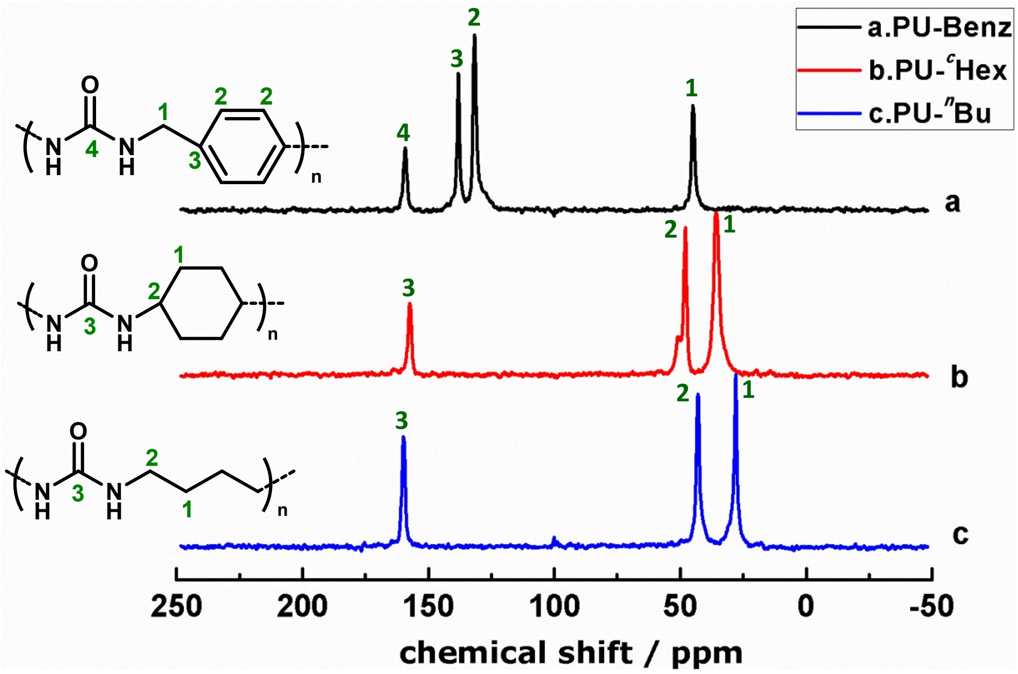


Figure S2. Solid-state ^{13}C NMR spectra for PU.

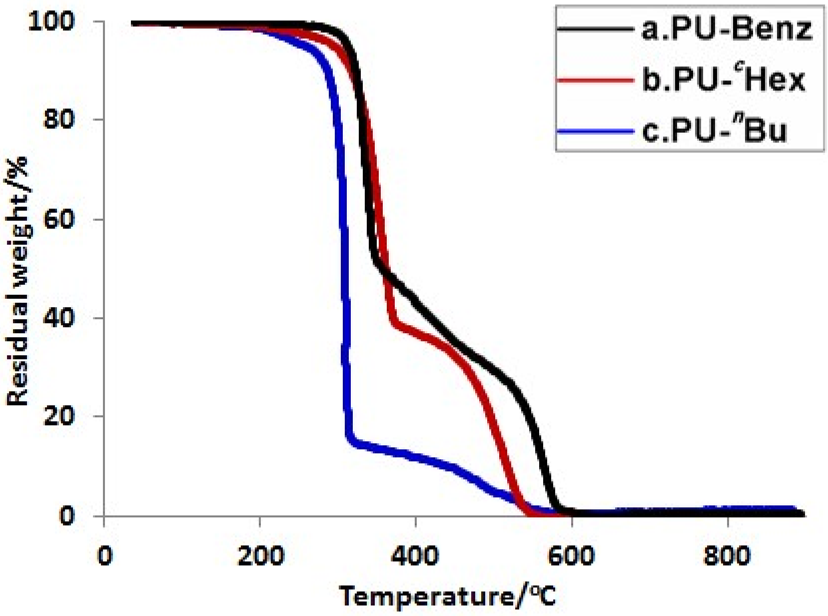


Figure S3. Thermogravimetric analysis (TGA) of PU in air up to 900 °C at a ramping rate of 10 °C min^{-1}.

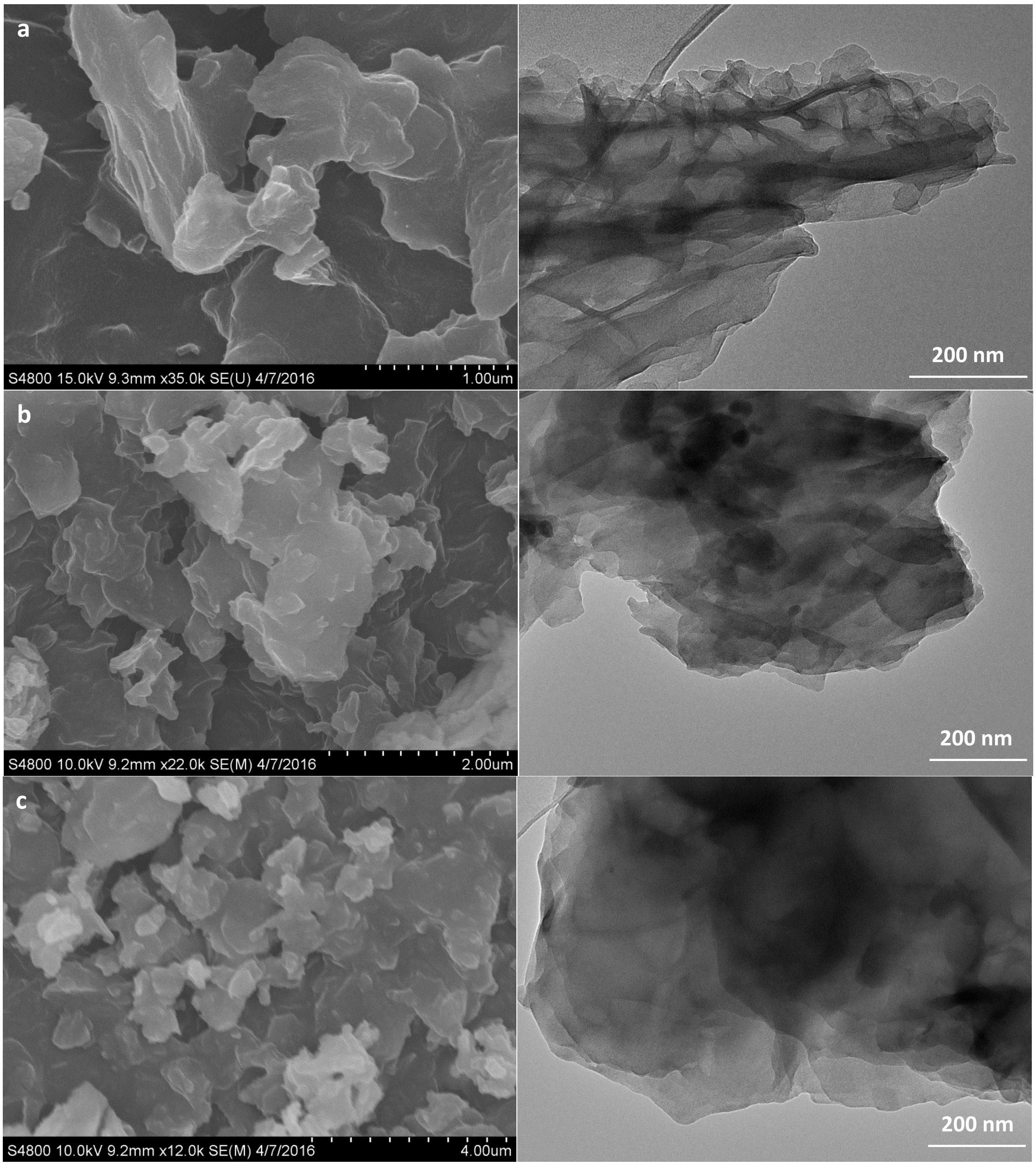
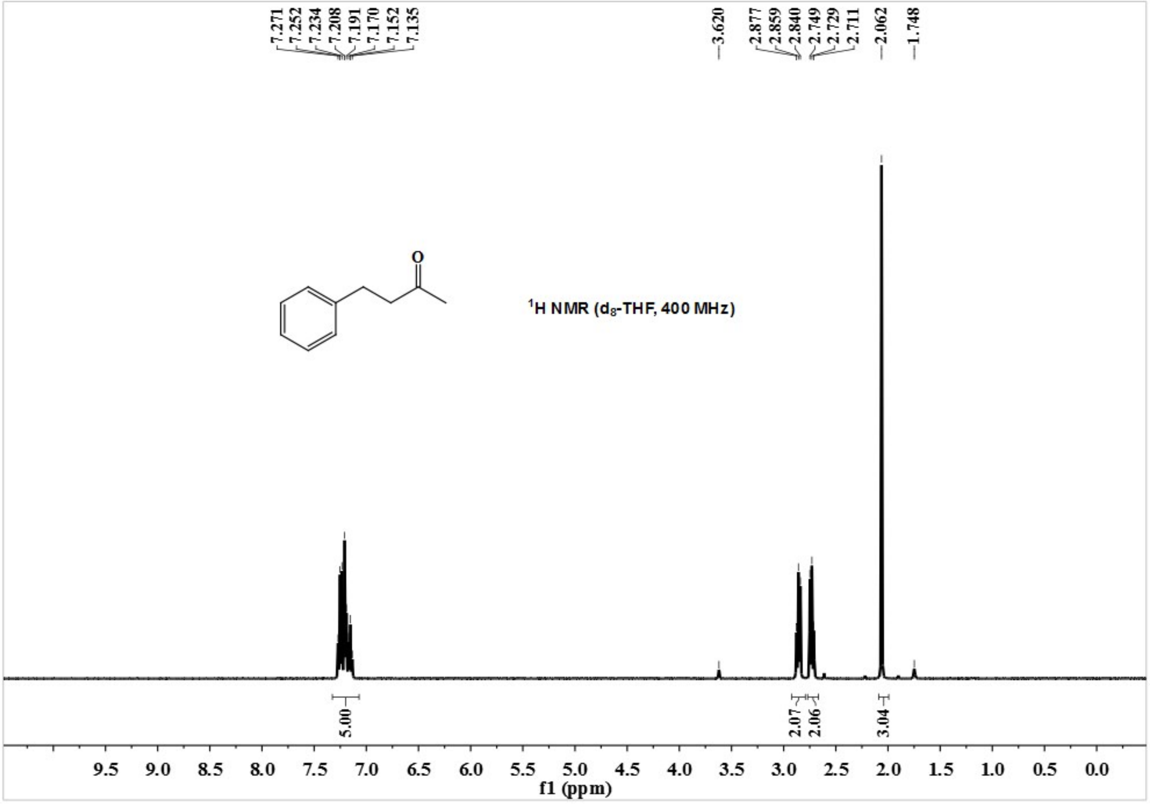
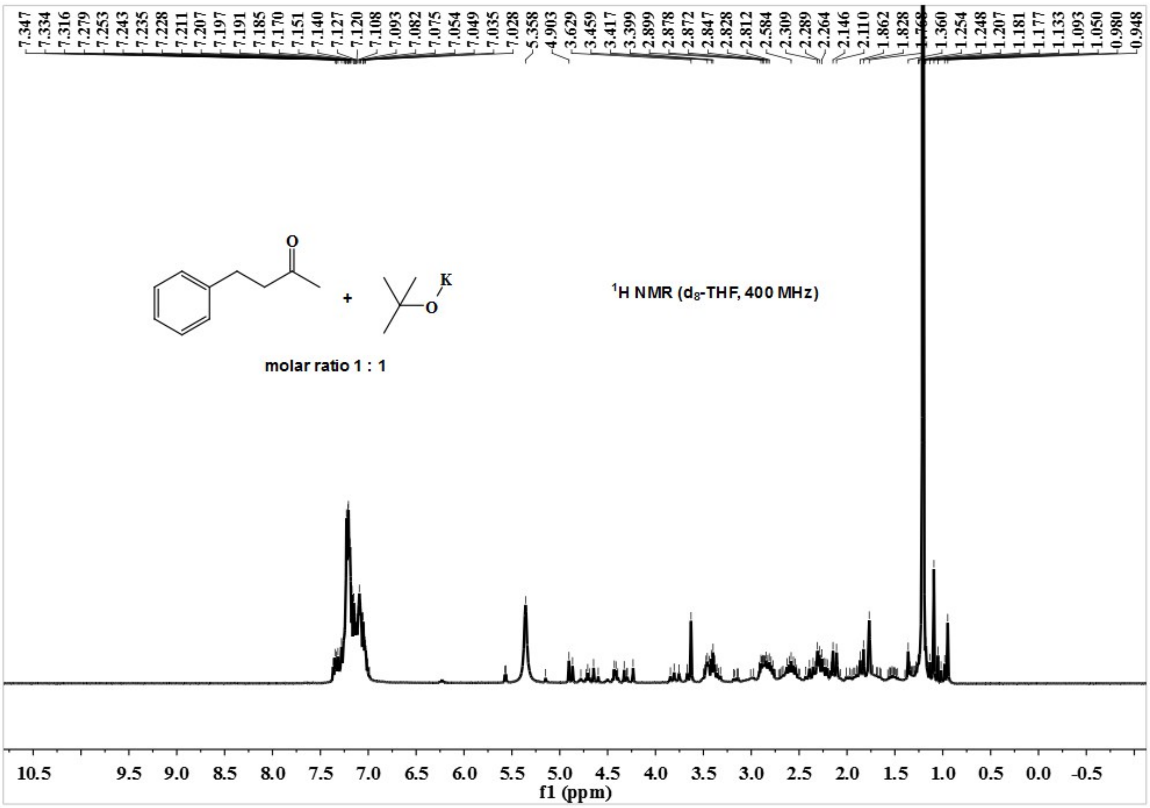


Figure S4. SEM (left) and TEM images (right) of (a) **PU-Benz**, (b) **PU-^{c}Hex** and (c) **PU-^{n}Bu**.


7.271
7.252
7.234
7.208
7.191
7.170
7.152
7.135
3.620
2.877
2.859
2.840
2.749
2.729
2.711
2.062
1.748
O
¹H NMR (d₈-THF, 400 MHz)
5.00
2.07
2.06
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


7.347
7.334
7.316
7.279
7.253
7.243
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7.228
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7.170
7.151
7.140
7.127
7.120
7.108
7.093
7.082
7.075
7.054
7.049
7.035
7.028
5.358
4.903
3.629
3.459
3.417
3.399
2.899
2.878
2.872
2.847
2.828
2.812
2.584
2.309
2.289
2.264
2.146
2.110
1.862
1.828
1.768
1.360
1.254
1.248
1.207
1.181
1.177
1.133
1.093
1.050
0.980
0.948
O
+
K
O
molar ratio 1 : 1
¹H NMR (d₈-THF, 400 MHz)
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

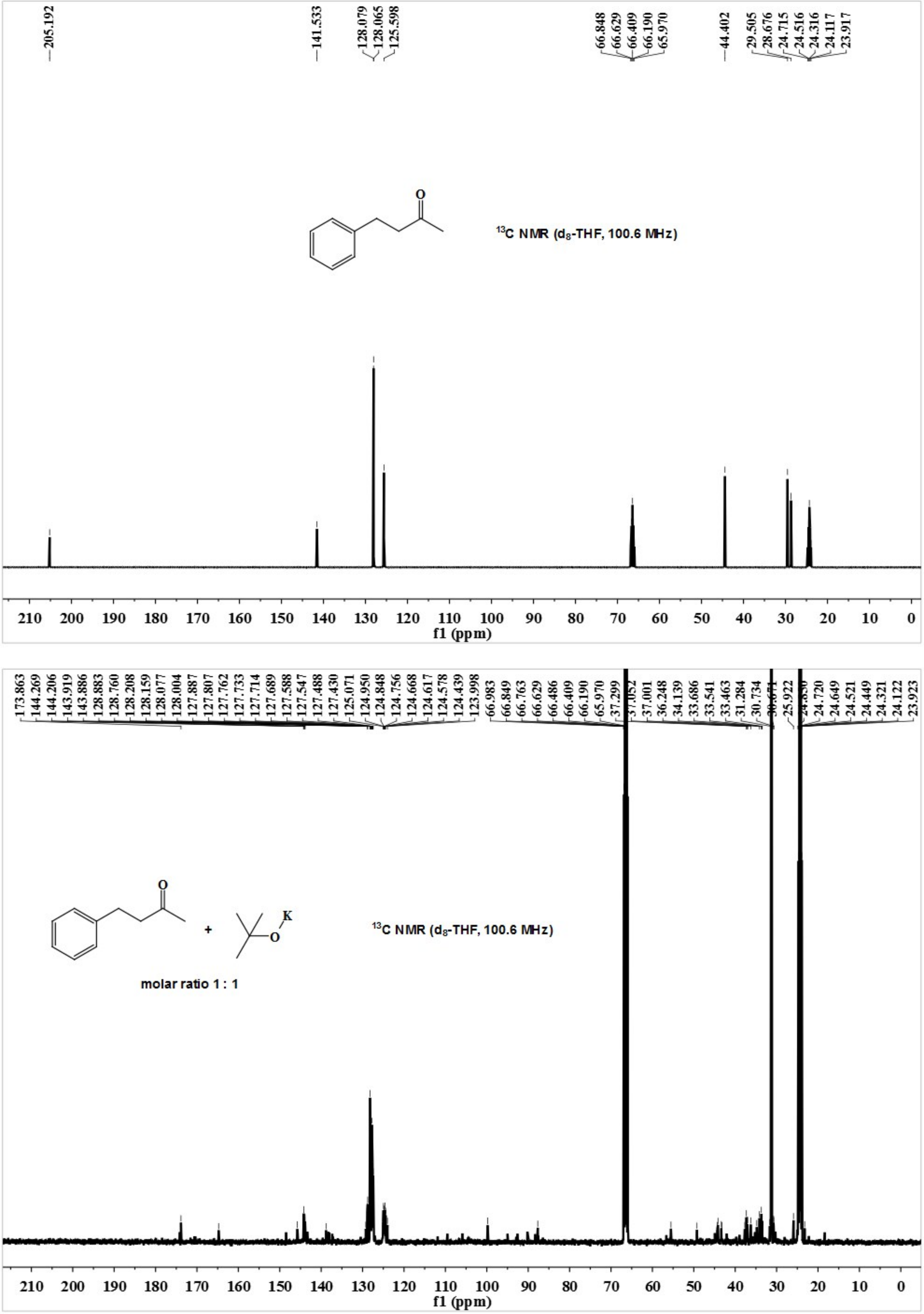


Figure S5. ^{1}H NMR (d$_8$-THF, 400 MHz) and ^{13}C NMR (d$_8$-THF, 100.6 MHz) spectra of 4-phenylbutan-2-one and its mixture with *t*-BuOK (molar ratio 1:1).

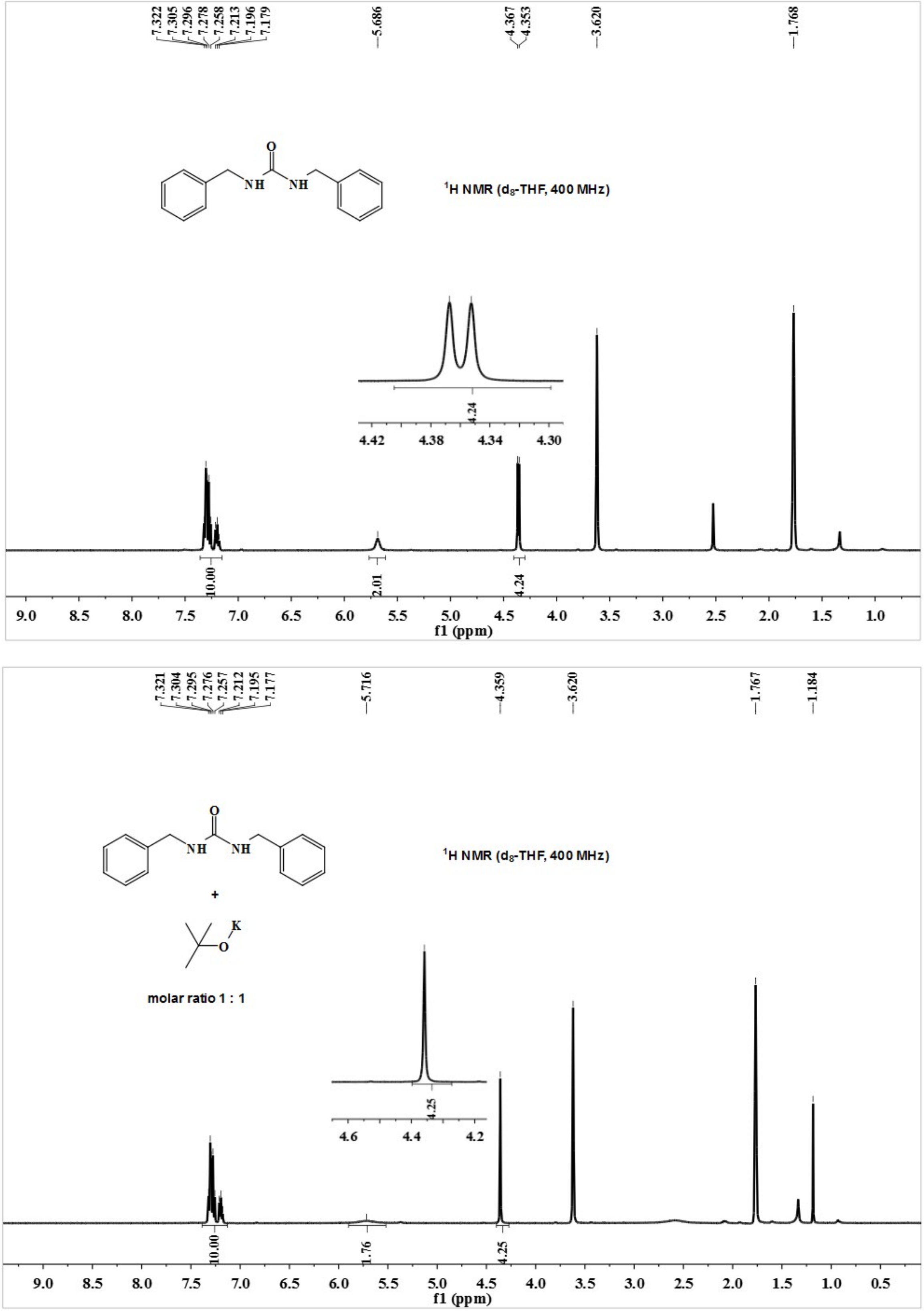


Figure S6. ^{1}H NMR (d_8-THF, 400 MHz) spectra of **U-Benz** and its mixture with *t*-BuOK (molar ratio 1:1).

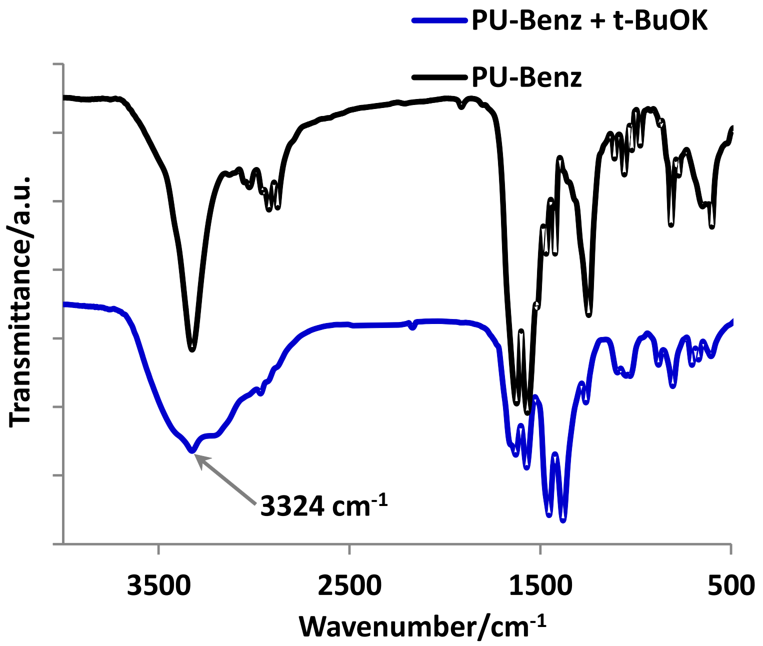


Figure S7. FTIR spectra of **PU-Benz** and its physical mixture with *t*-BuOK.

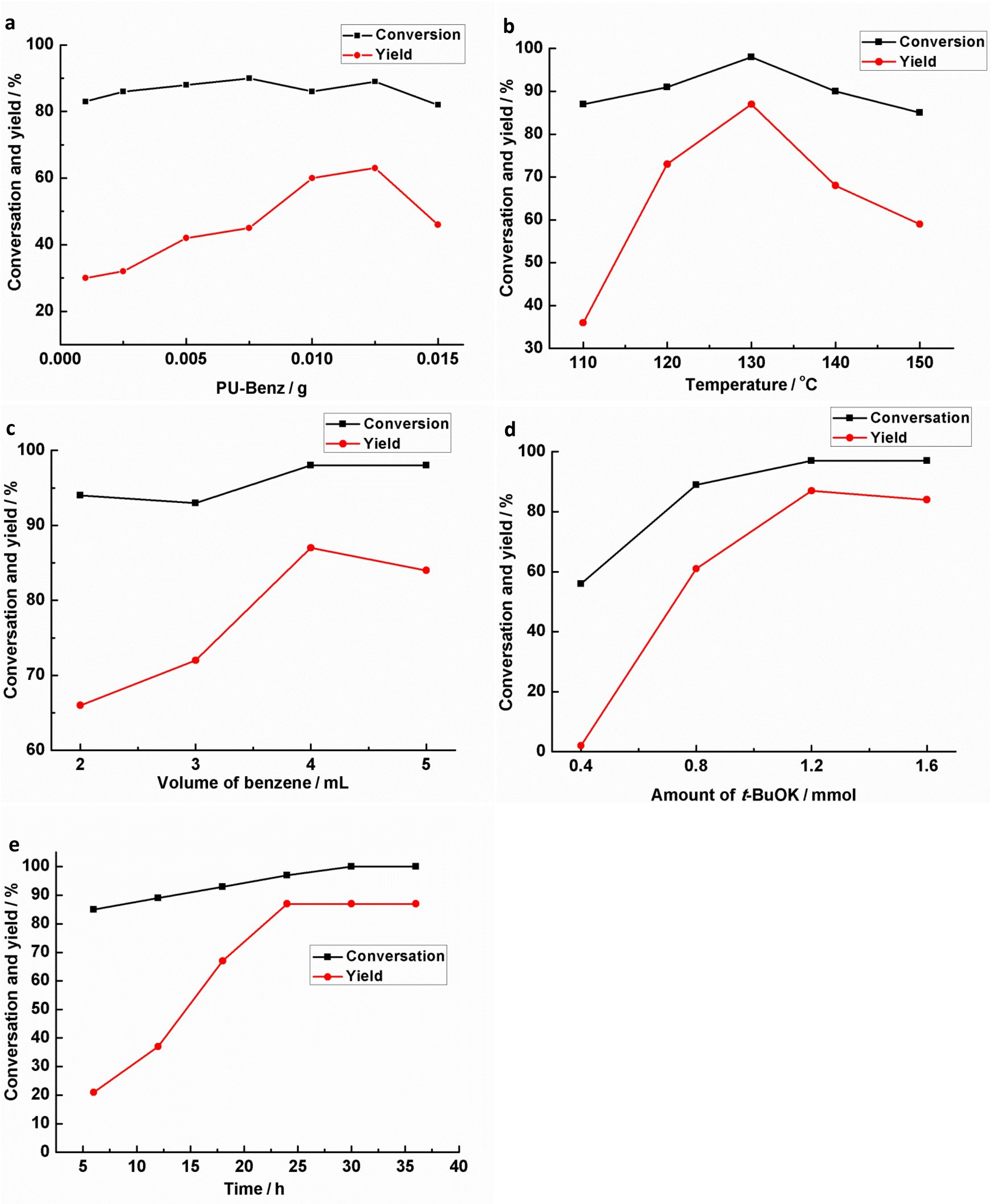


Figure S8. Influence of different reaction parameters. Reaction conditions: (a) PhI 0.4 mmol, benzene 4 mL, t-BuOK 1.2 mmol, 120 °C, 24 h; (b) PhI 0.4 mmol, benzene 4 mL, t-BuOK 1.2 mmol, **PU-Benz** 0.0125 g, 24 h; (c) PhI 0.4 mmol, *t*-BuOK 1.2 mmol, **PU-Benz** 0.0125 g, 130 °C, 24 h; (d) PhI 0.4 mmol, benzene 4 mL, **PU-Benz** 0.0125 g, 130 °C, 24 h; (e) PhI 0.4 mmol, benzene 4 mL, *t*-BuOK 1.2 mmol, **PU-Benz** 0.0125 g, 130 °C. Conversion of PhI and yield of biphenyl was determined by GC using dodecane as an internal standard.

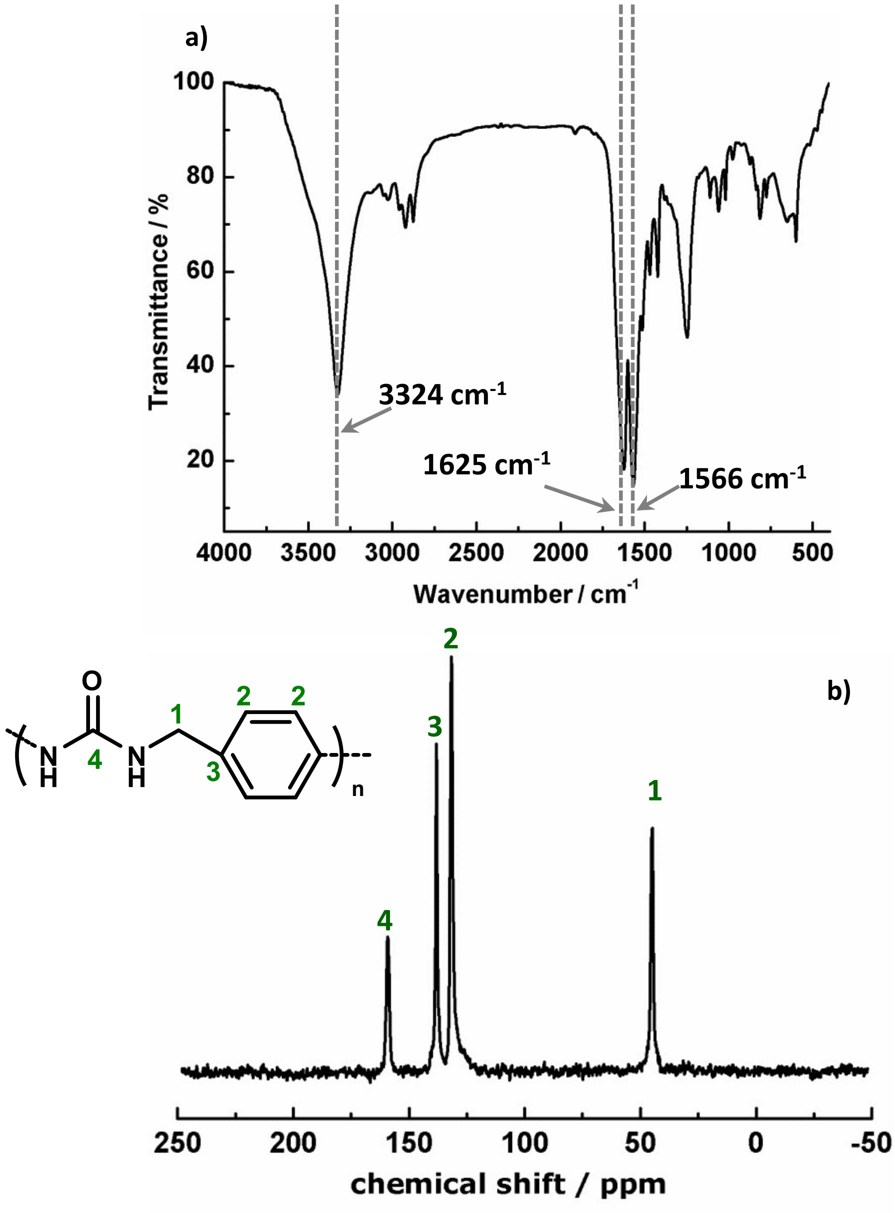
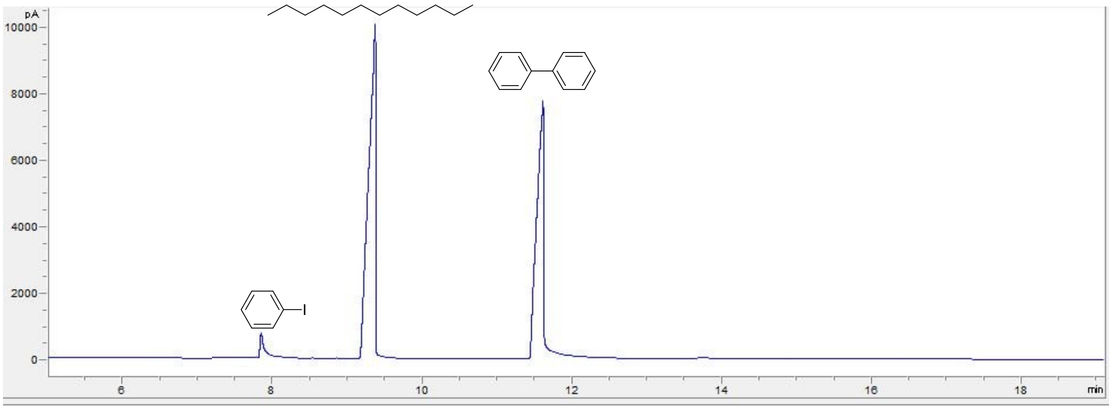


Figure S9. a) FTIR and b) solid-state ^{13}C NMR spectra of **PU-Benz** after being reused for five times.

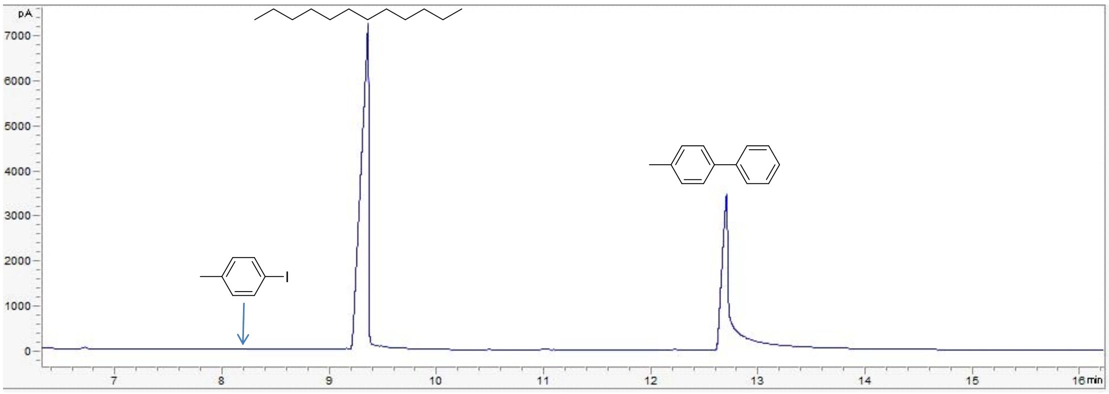
3. GC spectra of the reaction solutions for substrate scope screening

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

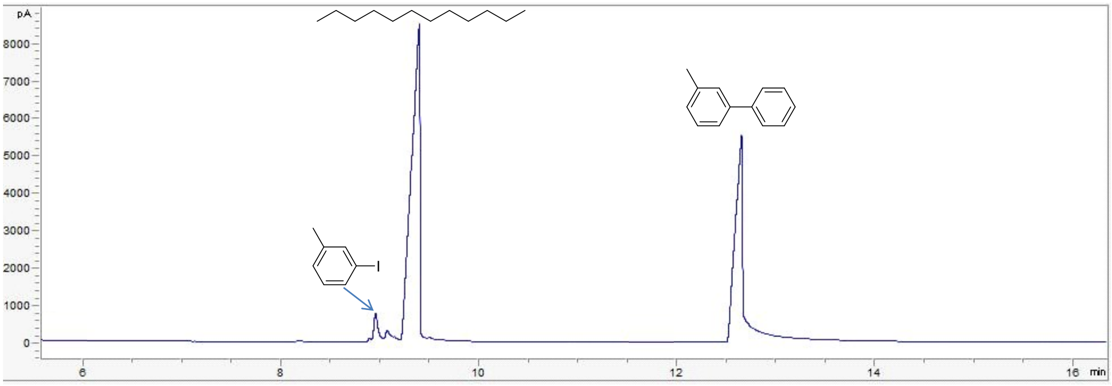
3.1 Reaction of iodobenzene with benzene to produce biphenyl



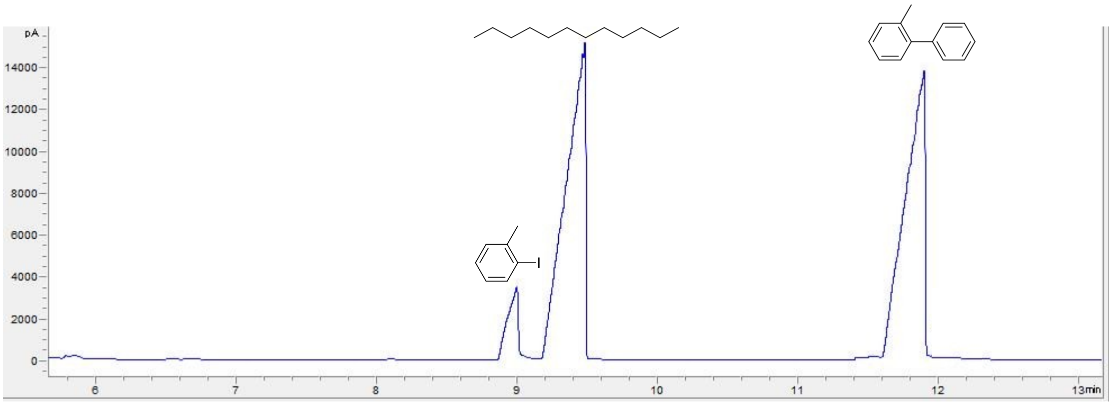
3.2 Reaction of 4-iodotoluene with benzene to produce 4-phenyltoluene



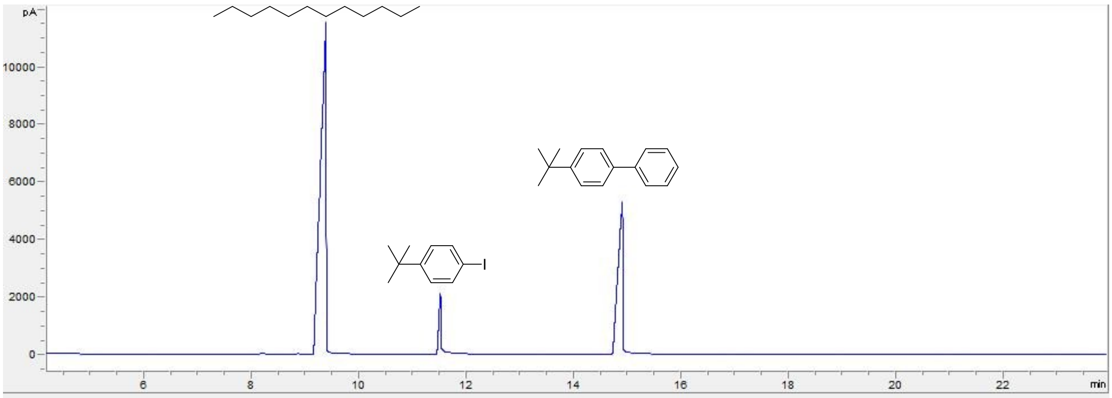
3.3 Reaction of 3-iodotoluene with benzene to produce 3-phenyltoluene



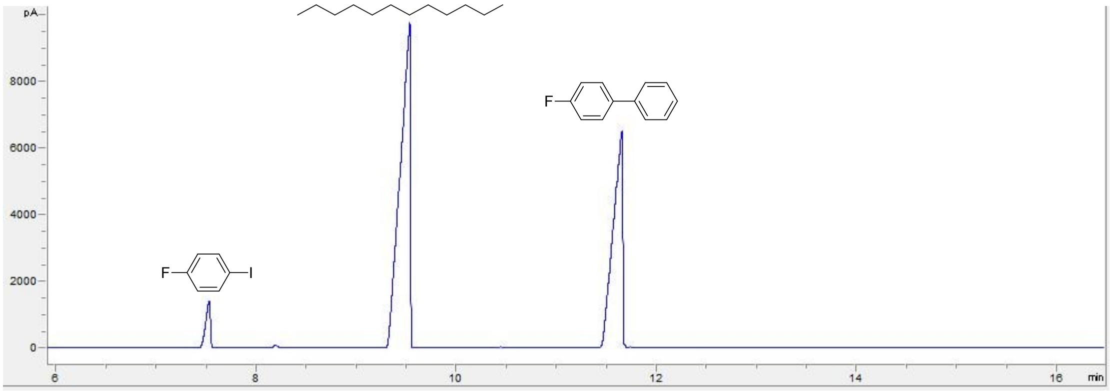
3.4 Reaction of 2-iodotoluene with benzene to produce 2-phenyltoluene



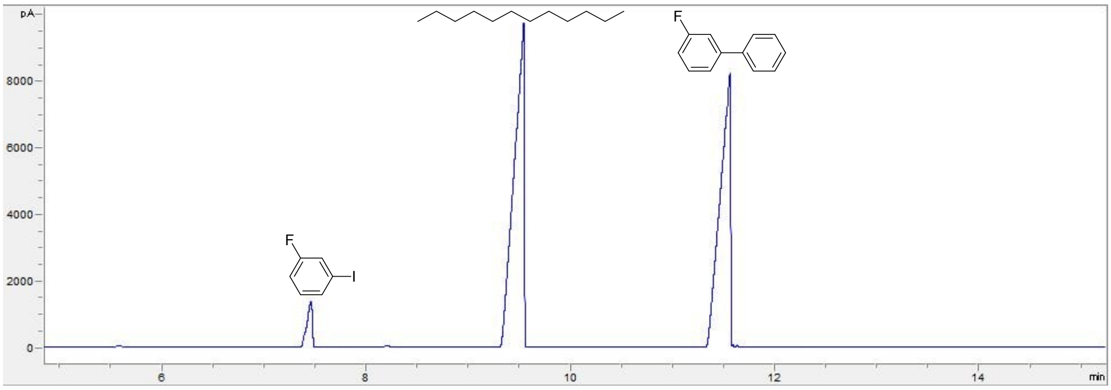
3.5 Reaction of 1-tert-butyl-4-iodobenzene with benzene to produce 4-tert-butylbiphenyl



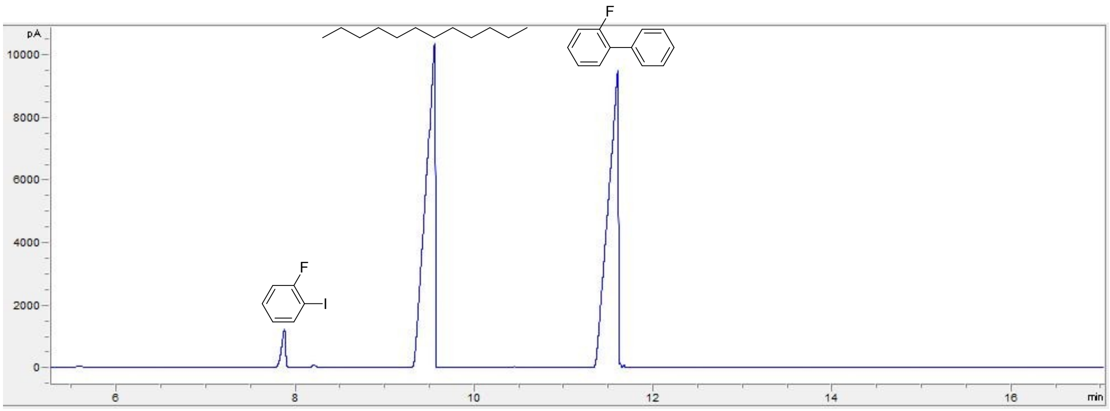
3.6 Reaction of 1-fluoro-4-iodobenzene with benzene to produce 4-fluorobiphenyl



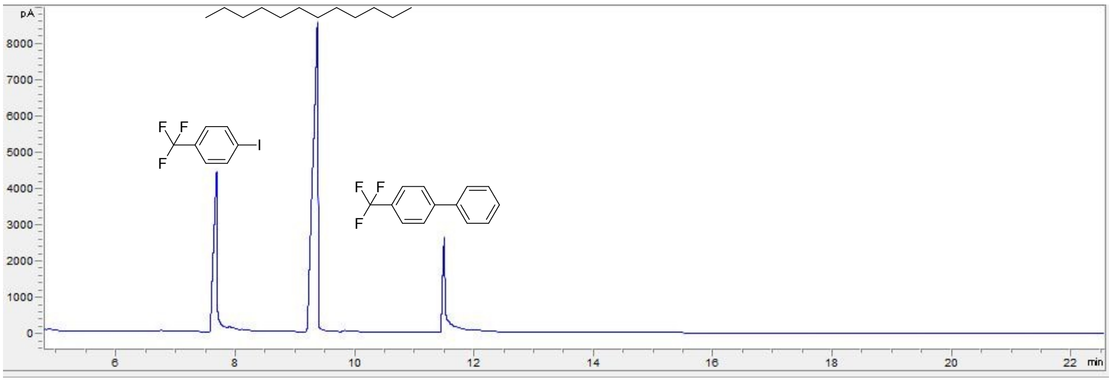
3.7 Reaction of 1-fluoro-3-iodobenzene with benzene to produce 3-fluorobiphenyl



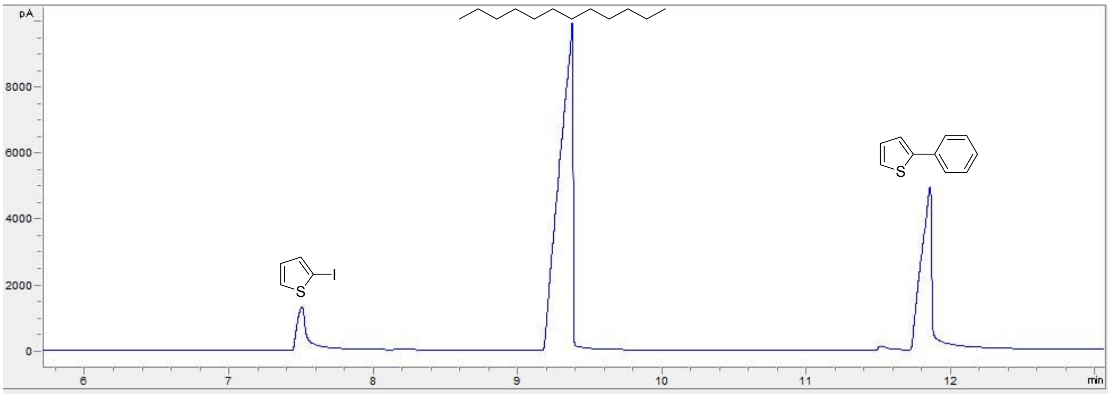
3.8 Reaction of 1-fluoro-2-iodobenzene with benzene to produce 2-fluorobiphenyl



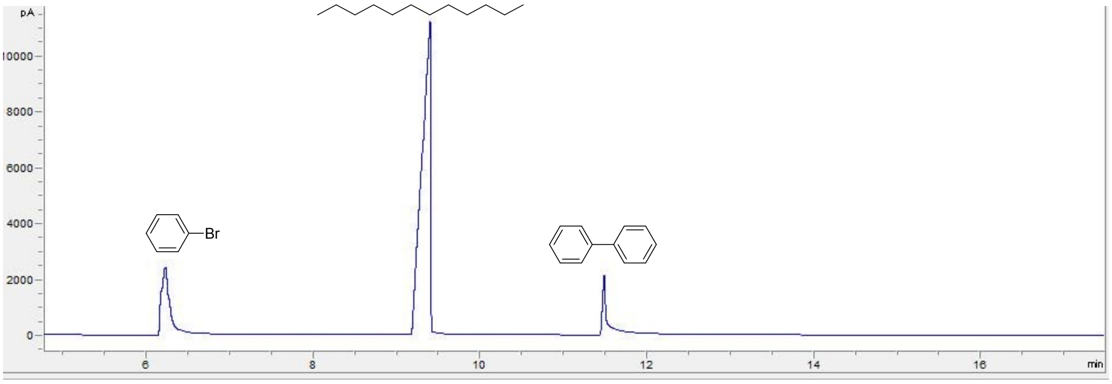
3.9 Reaction of 1-iodo-4-trifluoromethylbenzene with benzene to produce 4-trifluoromethylbiphenyl



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



3.11 Reaction of bromobenzene with benzene to produce biphenyl



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