SUPPORTING INFORMATION

Iron (III)-based ionic liquid-catalyzed regioselective benzylation of arenes and heteroarenes

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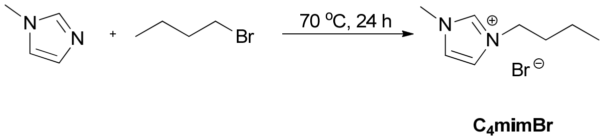
General experimental methods: All reactions were carried out without any special precautions against air.All reagents were obtained commercially without further purification. Toluene and diethyl ether were freshly distilled over sodium under nitrogen. Dichloromethane was distilled from calcium hydride. ^{1}H NMR spectra was recorded at Bruck 300 and 400 or Varian Mercury-Plus 400 spectrometer in $CDCl_3$ or D_2O and TMS (0 ppm) was used as internal reference, ^{13}C NMR was recorded at 75 MHz or 100.6 MHz in $CDCl_3$ or D_2O and $CDCl_3$ (77.0 ppm) was used as internal reference. ESI-MS were recorded on a Thermo Finnigan LCQ Advantage spectrometer in ESI mode with a spray voltage of 4.8 kV. GC-MS were recorded on a Thermo Finnigan Polaris Q GC/MS. Infrared (IR) spectra were recorded on a Bruker Tensor27 FT-IR spectrophotometer with KBr pellets. Raman spectroscopy were recorded on a Bruker RFS100/S Raman spectrometer. The products were analyzed on a gas chromatograph (Shimadzu 2014 chromatographer) equipped with a RTX-5 capillary column (30 m × 0.25 mm) using a flame ionization detector (FID). UV-Vis spectra were measured in acetonitrile (800-200 nm) on a Shimadzu UV-2450 spectrophotometer. Density values (*d*) were obtained by measuring the weight of the sample in a 1 cm^3 pycnometer held under 20 °C. ICP was measured on a ICP-9000 (N+M) Inductively coupled plasma emission spectrometer. The thermal stability of the iron-containing ionic liquids and their decomposition behaviour were measured on a PTC-10A TG-DTA analyzer (Japan, Rigaku). The samples (about 4.0-6.0 mg) were scanned from room temperature to 800 °C under air flow with a heating rate of 10 °C/min. Values for the onset degradation temperature (T_d) and peak temperature (T_p) were determined from the derivative TGA curves.

(1) Synthetic procedure of various ionic liquids:

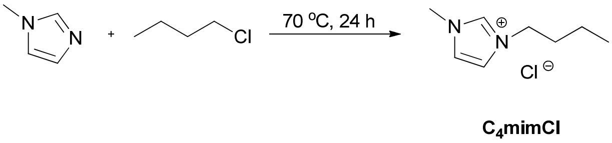
Procedure for the synthesis of 1-n-butyl-3-methylimidazolium bromide (C_4mimBr):



Scheme S1. Synthesis of C_4mimBr.

C_4mimBr was synthesized according to the reported literatures.[1] In a 100 ml round-bottom flask, 1-methylimidazole (8.21 g, 0.1 mol) was mixed with n-butyl bromide (16.44 g, 0.12 mol) and allowed to reflux for 24 h at 70 °C. The excess n-butyl bromide was distilled off under reduced pressure and the residue was finally extracted thoroughly 2-3 times (50 mL each) with diethyl ether to remove the traces of unreacted starting materials. A white solid of 1-n-butyl-3-methylimidazolium bromide was obtained in 87% yield.

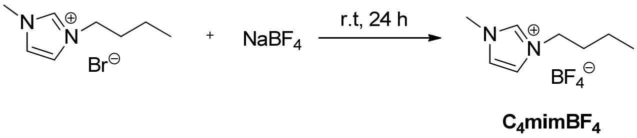
Procedure for the synthesis of C_4mimCl:



Scheme S2. Synthesis of C_4mimCl.

C_4mimCl was synthesized using the same method for the synthesis of C_4mimBr. C_4mimCl was obtained with a 72% yield.

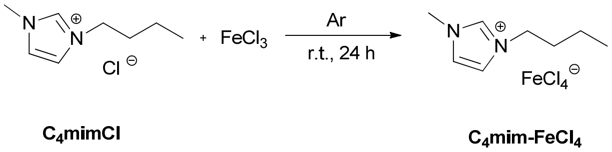
Procedure for the synthesis of C_4mimBF_4:



Scheme S3. Synthesis of C_4mimBF_4.

To a solution of C_4mimBr (2.1912 g, 10 mmol) in acetone (10 mL) at room temperature was added sodium tetrafluoroborate (1.0979 g, 10 mmol). Afer 24 h stirring, the reaction mixture was filtered and the volatiles were removed under reduced pressure. Drying in vacuo for 10 h afforded 1-butyl-3-methylimidazolium tetrafluoroborate as a light yellow liquid.

Procedure for the synthesis of $C_4mim\text{-}FeCl_4$[2]



Scheme S4. Synthesis of $C_4mim\text{-}FeCl_4$.

Synthesis of iron-containing ionic liquid with a molar ratio of 1:1 for the starting materials: Butylmethylimidazolium chloride (1.75 g, 10 mmol) and anhydrous $FeCl_3$ (1.62 g, 10 mmol) were mixed in a round bottom flask and stirred under argon atmosphere. Almost immediately an endothermic reaction took place and provided $C_4mim\text{-}FeCl_4$ as a dark brown oil. The mixture was dried for 2 days at 80 °C under vacuum for the benzylation reaction.

For the synthesis of iron containing ionic liquid with other molar ratio of the starting materials, the procedure was identical with that above. And following this method, two kinds of iron containing ionic liquids with the molar ration of the starting materials 1:1.2 and 1:2.0 could be synthesized easily.

These iron-containing IL were characterized via Raman spectroscopy and proved to be identical with authentic material reported in literature.[3]

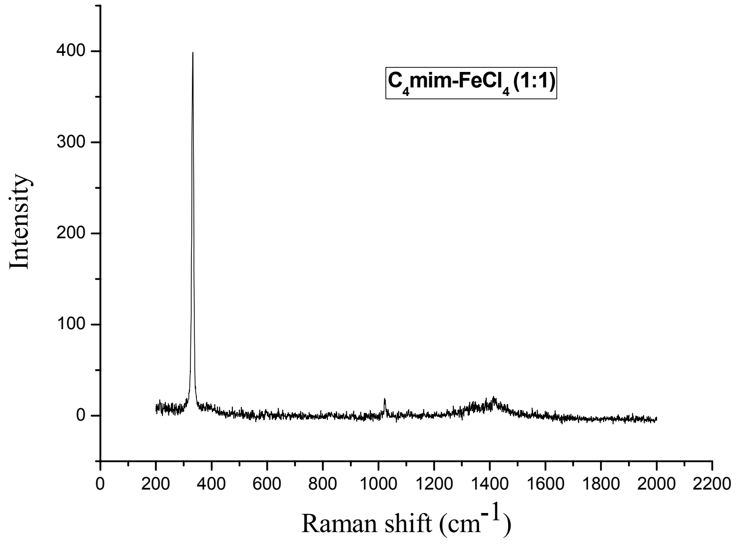


Figure S1. Raman-spectra of C_4mim-$FeCl_4$ (1:1).

The peak at 333 cm^{-1} is due to $FeCl_4^-$, indicating that the anion of this iron-containing IL is $FeCl_4^-$.

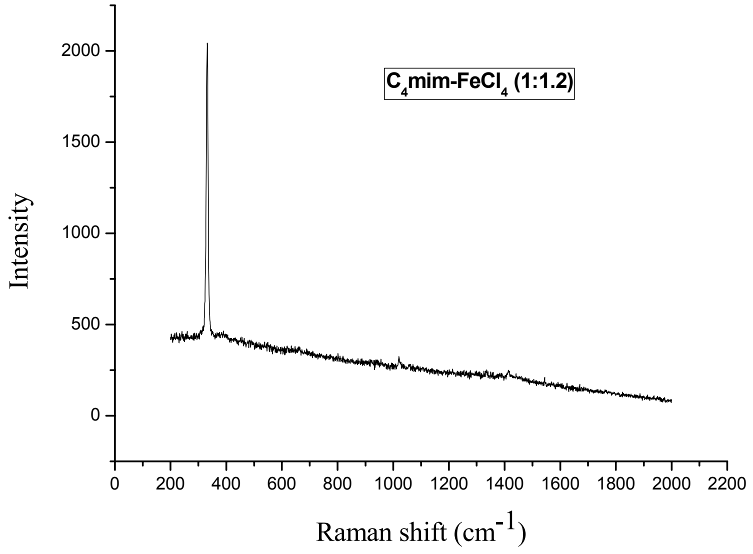


Figure S2. Raman-spectra of C$_4$mim-FeCl$_4$ (1:1.2).

The peak at 333 cm^{-1} is due to FeCl$_4^-$, indicating that the anion of this iron-containing IL is FeCl$_4^-$.

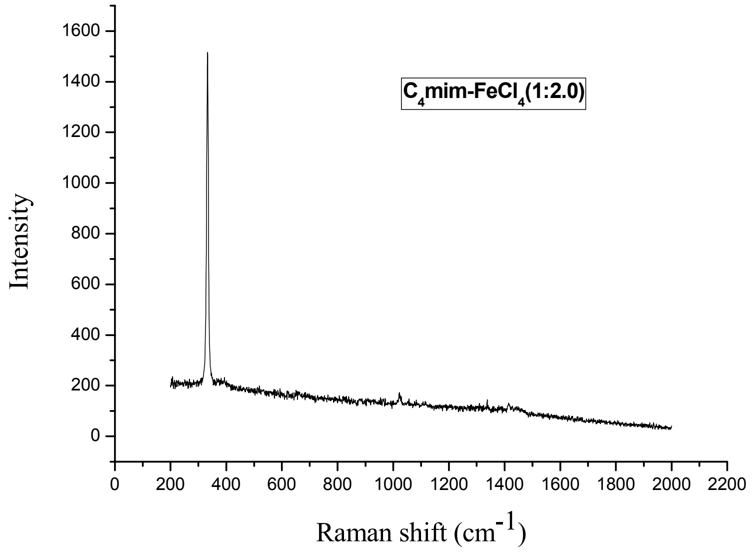
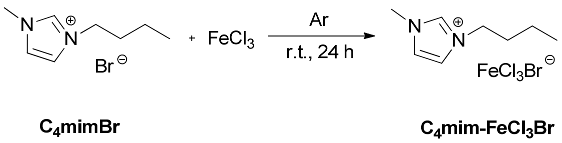


Figure S3. Raman-spectra of C$_4$mim-FeCl$_4$ (1:2.0).

The peak at 333 cm^{-1} is due to FeCl$_4^-$, indicating that the anion of this iron-containing IL is FeCl$_4^-$.

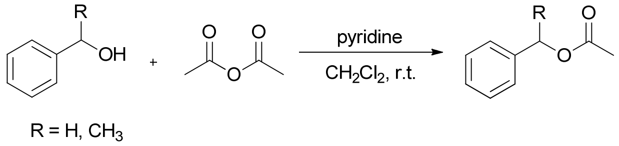
Procedure for the synthesis of C$_4$mim-FeCl$_3$Br (1:1)



Scheme S5. Synthesis of C_4mim-$FeCl_3Br$.

C_4mim-$FeCl_3Br$ (1:1) was synthesized from C_4mimBr and anhydrous $FeCl_3$ using the same method for the synthesis of C_4mim-$FeCl_4$ (1:1).

(2) Synthetic procedure for the synthesis of benzylic acetates from benzylic alcohols[4]:



Scheme S6. Synthesis of benzylic acetates from benzylic alcohols.

Into a round-bottom flask equipped with a magnetic stirbar was added the corresponding alcohol (10-50 mmol, 1.0 equiv.) and dichloromethane (50-100 mL, ~ 0.5 M). The reaction mixture was cooled to 0 °C in an ice bath and treated with pyridine (13-65 mmol, 1.3 equiv.) and then acetic anhydride (13-65 mmol, 1.3 equiv.) was added drop-wise over 10 minutes. The resulting solution was warmed to room temperature and stirred for 16 h overnight. The reaction mixture was concentrated under reduced pressure and the crude residue poured into a 250 mL separatory funnel containing 1 M aqueous HCl (125 mL) and extracted with diethyl ether (3 × 75 mL). The combined organic layers were washed with brine (75 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified by column chromatography through silica gel to afford the desired product.

(3) General procedure for the benzylation of arenes and heteroarenes:

Benzylation of *o*-xylene: In a 25 mL Schlenk tube with a magnetic stirbar, 1-phenylethyl acetate (1 mmol, 0.1642 g) and catalyst (10 mmol%, 0.1 mmol) were added. And then *o*-xylene (1 mL, 8.4 mmol) was added. After stirring for 12 h at 80 ^{o}C aliquots were taken from the reaction mixture and subjected to GC analysis for determination of yield and conversion. For isolation of the products, after the reaction, the crude was extracted with toluene, and the organic phase was dried over $MgSO_4$ and the solvents were distilled off. The product was purified by silica gel column chromatography (200-300 mesh, petroleum ether or hexane as the eluant).

Recycling of the catalyst C_4mim-$FeCl_4$: After complete reaction there are two phases including the upper *o*-xylene layer which containing the product and the nether layer which containing the iron-containing ionic liquid. The upper *o*-xylene layer containing the product was first decanted and the remaining product was extracted by washing the residue for six times with 4 mL of toluene each. After that the residue was kept under vacuum for 1 h to remove the toluene. Then fresh *o*-xylene and 1-phenylethyl acetate were added to the remaining C_4mim-$FeCl_4$ layer for the next run of the reaction. The iron content of the fresh and the recovered catalyst determined by ICP method was found to be 15.05%, 14.92%, respectively.

(4) Characterization of various ionic liquids:

1-n-butyl-3-methylimidazolium bromide (C_4mimBr):

^{1}H NMR(300 MHz, D_2O): $\delta = 0.82$(t, $^3J_{HH} = 7.4$ Hz, 3H, H); 1.23(m, 2H, H); 1.75(m, 2H, H); 3.79(s, 3H, H); 4.10(t, $^3J_{HH} = 7.2$ Hz, 2H, H); 7.33(s, 1H, H); 7.38(s, 1H, H); 8.61(s, 1H, H); ^{13}C NMR(100.6 MHz, D_2O): $\delta = 12.64$; 18.74; 31.25; 35.67; 49.27; 122.20; 123.45; 135.82; ESI-MS (4.8 kV): *m/z* (%) =139.0 (100) $[M\text{-}Br]^+$, 78.9 (100) $[M\text{-}C_8H_{15}N_2]^-$.

1-n-butyl-3-methylimidazolium chloride (C_4mimCl):

^{1}H NMR(400MHz, $CDCl_3$): $\delta = 0.93$(t, $^3J_{HH} = 7.6$ Hz, 3H, CH_3); 1.30-1.40(m, 2H, CH_2); 1.83-1.90(m, 2H, CH_2); 4.09(s, 3H, CH_3); 4.30(t, $^3J_{HH} = 7.4$ Hz, 3H, NCH_3); 7.37(s, 1H, CH); 7.50(s, 1H, CH); 10.73(s, 1H, CH); ^{13}C NMR(100.6 MHz, $CDCl_3$): $\delta = 13.36$; 19.40; 32.09; 36.51; 49.76; 121.64; 123.29; 138.24; ESI-MS (4.8 kV): *m/z* (%) =139.0 (100) $[M\text{-}Cl]^+$.

1-butyl-3-methylimidazolium tetrafluoroborate (C_4mimBF_4):

^{1}H NMR(400 MHz, D_2O): $\delta = 0.84$(t, $^3J_{HH} = 7.4$ Hz, 3H, CH_3); 1.19-1.28(m, 2H, CH_2); 1.73-1.80(m, 2H, CH_2); 3.81(s, 3H, CH_3); 4.11(t, $^3J_{HH} = 7.2$ Hz, 3H, NCH_3); 7.34(s, 1H, CH); 7.39(s, 1H, CH); 8.61(s, 1H, CH). ^{13}C NMR(100.6 MHz, D_2O): $\delta = 12.56$; 18.69; 31.21; 35.54; 49.22; 122.15; 123.41; 135.79; ESI-MS (4.8 kV): *m/z* (%) =139.0 (100) $[M\text{-}BF_4]^+$, 87.0 (100), $[M\text{-}C_8H_{15}N_2]^-$.

C_4mim-$FeCl_4$ (1:1): IR (KBr) 3149, 3116, 2960, 2933, 1641, 1567, 1164 cm^{-1}. ESI-MS (4.8 kV): *m/z* (%) = 139.25 (100) $[M\text{-}FeCl_4]^+$, 197.97 (100) $[M\text{-}C_8H_{15}N_2]^-$. UV-vis (acetonitrile) λ_{max} (ε): 359 (7.7×10^3), 307 (1.1×10^3), 268 (7.3×10^3), 262 (6.7×10^3), 213 (8.9×10^4) nm. *d*, 1.40

g cm^{-3}; T_d, 294 °C; T_p, 402 °C.

C_4mim-$FeCl_4$ (1:1.2): IR (KBr) 3160, 3117, 2964, 2939, 1641, 1569, 1166 cm^{-1}. ESI-MS (4.8 kV): *m/z* (%) = 139.25 (100) [M-$FeCl_4$]$^+$, 197.96 (100) [M-$C_8H_{15}N_2$]$^-$. UV-vis (acetonitrile) λ_{max} (ε): 358 (7.9×10^3), 307 (1.2×10^4), 241 (1.4×10^4), 213 (2.4×10^4) nm. *d*, 1.39 g cm^{-3}; T_d, 287 °C; T_p, 412 °C.

C_4mim-$FeCl_4$ (1:2.0): IR (KBr) 3164, 3119, 3002, 2966, 2941, 1641, 1570, 1168 cm^{-1}. ESI-MS (4.8 kV): *m/z* (%) = 139.25 (100) [M-$FeCl_4$]$^+$, 197.96 (100) [M-$C_8H_{15}N_2$]$^-$. UV-vis (acetonitrile) λ_{max} (ε): 357 (5.9×10^3), 309 (8.1×10^3), 238 (9.8×10^3), 212 (2.1×10^4) nm. *d*, 1.48 g cm^{-3}; T_d, 270 °C; T_p, 400 °C.

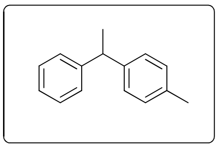
C_4mim-$FeCl_3Br$ (1:1): IR (KBr) 3149, 3116, 2960, 2933, 1641, 1567, 1164 cm^{-1}. ESI-MS (4.8 kV): *m/z* (%) = 139.0 (100) [M-$FeCl_3Br$]$^+$, 241.7 (100) [M-$C_8H_{15}N_2$]$^-$. UV-vis (acetonitrile) λ_{max} (ε): 358 (4.9×10^3), 309 (7.1×10^3), 239 (7.4×10^3), 213 (2.8×10^4) nm. *d*, 1.51 g cm^{-3}; T_d, 295 °C; T_p, 397 °C.

(5) Characterization of the benzylated reagents:

1-phenylethyl acetate: colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.54 (d, $^3J_{HH}$= 6.6 Hz, 3H, $CHCH_3$); 2.08 (s, 3H, $COCH_3$); 5.89 (q, $^3J_{HH}$= 13.2 Hz, 1H, CH); 7.29-7.32 (m, 5H, CH aromat); ^{13}H NMR(75 MHz, $CDCl_3$): δ = 21.31; 22.16; 72.28; 126.07; 127.83; 128.47; 141.69; 170.26; ESI-MS calcd for $C_{10}H_{12}O_2$ 164.20, found 350.4 (2M+Na)$^+$.

Benzyl acetate: colorless oil. ^{1}H NMR(400 MHz, $CDCl_3$): δ = 2.11 (s, 3H, $COCH_3$); 5.11 (s, 3H, CH_3); 7.33-7.37 (m, 5H, CH aromat); ^{13}C NMR(100.6 MHz, $CDCl_3$): δ = 20.99; 66.29; 128.23; 128.54; 135.90; 170.87; ESI-MS calcd for $C_9H_{12}O_2$ 150.17, found 149.0 (M-1)$^-$.

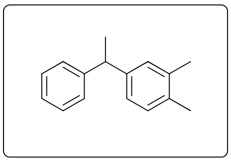
(6) Characterization of the benzylated products:



1-methyl-4-(1-phenylethyl)benzene

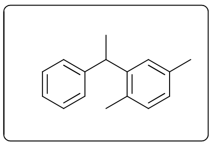
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.61 (d, $^3J_{HH}$= 6.8 Hz, 3H, $CHCH_3$); 2.29 (s, 3H, $ArCH_3$); 4.10 (q, $^3J_{HH}$ = 14.4 Hz, 1H, CH); 7.07-7.24 (m, 9H, CH aromat); ^{13}C NMR(100.6 MHz, $CDCl_3$): δ = 20.95; 21.90; 44.34; 125.91; 127.46; 127.54; 128.31; 129.02; 135.45; 143.39;

146.58; EI-MS: m/z (%): 196.07 (33) [M^+]; 181.22 (100) [$C_{14}H_{13}^+$].



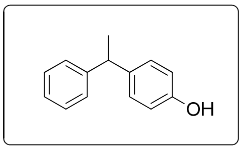
1,2-dimethyl-4-(1-phenylethyl)benzene

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.61 (d, $^3J_{HH}$= 7.2 Hz, 3H, $CHCH_3$); 2.21 (s, 6H, $2ArCH_3$); 4.08 (q, $^3J_{HH}$ = 14.4 Hz, 1H, CH); 6.94-7.29 (m, 8H, CH aromat); ^{13}C NMR(100.6 MHz, $CDCl_3$): δ =19.27; 19.83; 21.93; 44.35; 124.84; 125.85; 127.51; 128.28; 128.95; 129.58; 134.10; 136.35; 143.85; 146.63; EI-MS: m/z (%): 210.08 (44) [M^+]; 195.17 (100) [$C_{15}H_{15}^+$].



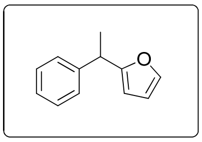
1,4-dimethyl-2-(1-phenylethyl)benzene

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.59 (d, $^3J_{HH}$= 7.2 Hz, 3H, $CHCH_3$); 2.17 (s, 3H, CH_3); 2.30 (s, 3H, CH_3); 4.27 (q, $^3J_{HH}$ = 14.2 Hz, 1H, CH); 6.91-7.24 (m, 8H, CH aromat); ^{13}C NMR(100.6 MHz, $CDCl_3$): δ = 19.26; 21.23; 22.06; 40.88; 125.72; 126.70; 127.42; 127.64; 128.25; 130.26; 132.89; 135.27; 143.67; 146.30; EI-MS: m/z (%): 210.06 (48) [M^+]; 195.20 (100) [$C_{15}H_{15}^+$].



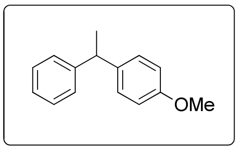
4-(1-phenylethyl)phenol

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.60 (d, $^3J_{HH}$= 7.2 Hz, 3H, $CHCH_3$); 4.09 (q, $^3J_{HH}$= 14.6 Hz, 1H, CH); 6.74 (d, $^3J_{HH}$= 8.4 Hz, 2H); 7.08 (d, $^3J_{HH}$= 8.4 Hz, 2H); 7.151-7.292 (m, 5H, aromat); ^{13}C NMR(100.6 MHz, $CDCl_3$): δ = 22.03; 43.91; 115.11; 115.25; 120.79; 125.93; 127.51; 128.32; 128.71; 129.65; 138.74; 146.70; 153.64; ESI-MS: calcd for $C_{14}H_{14}O$ 198.26, found 197.2 $(M\text{-}H)^-$. EI-MS: m/z (%): 198.12 (35) [M^+]; 183.18 (100) [$C_{13}H_{11}O^+$].



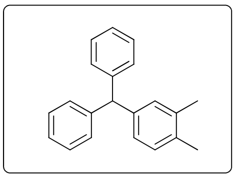
2-(1-phenylethyl)furan

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.61(d, $^3J_{HH}$= 7.2 Hz, 3H, $CHCH_3$); 4.13 (q, $^3J_{HH}$= 14.4 Hz, 1H, CH); 6.06 (d, $^3J_{HH}$= 3.2 Hz, 1H, CH); 6.30 (t, $^3J_{HH}$= 2.4 Hz, 1H, CH); 7.21-7.33 (m, 6H); ^{13}C NMR(100.6 MHz, $CDCl_3$): δ = 20.48; 39.20; 104.88; 109.90; 126.48; 127.27; 128.45; 141.29; 144.12; 158.93; EI-MS: m/z (%): 172.05 (43) [M^+]; 157.18 (100) [$C_{11}H_9O^+$].



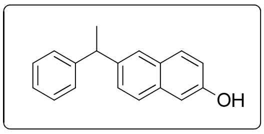
1-methoxy-4-(1-phenylethyl)benzene

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.62 (d, $^3J_{HH}$= 7.2 Hz, 3H, $CHCH_3$); 3.78 (s, 3H, CH_3); 4.10 (q, $^3J_{HH}$= 14.4 Hz, 1H, CH); 6.82-6.84 (m, 2H, CH aromat); 7.13-7.30 (m, 7H, CH aromat); ^{13}C NMR(100.6 MHz, $CDCl_3$): δ = 22.03; 43.89; 55.20; 113.68; 125.90; 127.50; 128.31; 128.48; 138.52; 146.74; 157.78; EI-MS: m/z (%): 212.12 (36) [M^+]; 197.20 (100) [$C_{14}H_{13}O^+$].



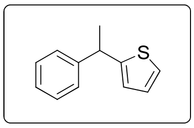
((3,4-dimethylphenyl)methylene)dibenzene

^{1}H NMR (400 MHz, $CDCl_3$): δ= 2.11 (d, $^3J_{HH}$= 13.2 Hz, 6H, $2ArCH_3$); 5.39 (s, 1H, CH); 6.74 (d, $^3J_{HH}$= 7.6 Hz, 1H, ArH); 6.82 (s, 1H, ArH); 6.94(d, $^3J_{HH}$= 7.6 Hz, 1H, ArH); 7.03 (d, $^3J_{HH}$= 7.2 Hz, 4H, ArH); 7.07-7.11 (m, 2H, ArH); 7.17 (t, $^3J_{HH}$= 7.4 Hz, 4H, ArH); ^{13}C NMR(100.6 MHz, $CDCl_3$): δ= 19.31; 19.82; 56.48; 126.13; 126.78; 128.21; 129.39; 129.52; 130.71; 134.43; 136.36; 141.32; 144.17; EI-MS: m/z (%): 272.11 (55) [M^+]; 257.19 (100) [$C_{20}H_{17}^+$].

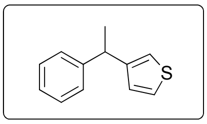


6-(1-phenylethyl)naphthalen-2-ol

^{1}H NMR (400 MHz, $CDCl_3$): δ= 1.77 (d, $^3J_{HH}$= 7.6 Hz, $CHCH_3$); 4.823 (s, 1H, OH); 5.16 (q, $^3J_{HH}$= 14.4 Hz, 1H, CH); 6.99 (d, $^3J_{HH}$= 8.8 Hz, 1H, ArH); 7.24 (d, $^3J_{HH}$= 4.8 Hz, 1H, ArH); 7.31-7.39 (m, 5H, ArH); 7.46 (t, $^3J_{HH}$= 7.6 Hz, 1H, ArH); 7.66 (d, $^3J_{HH}$= 8.8 Hz, 1H, ArH); 7.79 (d, $^3J_{HH}$= 8.4 Hz, 1H, ArH); 8.04 (d, $^3J_{HH}$= 8.8 Hz, 1H, ArH); ^{13}C NMR(100.6 MHz, $CDCl_3$): δ= 17.05; 34.81; 119.38; 122.57; 123.09; 123.77; 126.58; 126.80; 127.14; 128.70; 128.85; 129.06; 129.66; 132.83; 143.59; 151.52; ESI-MS: calcd for $C_{18}H_{16}O$ 248.32, found 247.2 $(M-H)^-$, 494.6 (2M), 495.8 $(2M-H)^-$.



2-(1-phenylethyl)thiophene



3-(1-phenylethyl)thiophene

These two isomers cannot be isolated by silica gel column chromatography. And the NMR date following are characterized to the mixture of the two isomers.

^{1}H NMR (400 MHz, $CDCl_3$): δ= 1.70 (d, $^{3}J_{HH}$= 7.2 Hz, $CHCH_3$); 4.34 (q, $^{3}J_{HH}$= 14.4 Hz, 1H, CH); 6.79 (d, $^{3}J_{HH}$= 3.6 Hz, 1H, ArH); 6.91 (q, $^{3}J_{HH}$= 6.4 Hz, 1H, ArH); 7.13 (d, $^{3}J_{HH}$= 4.4 Hz, 1H, ArH); 7.18-7.31 (m, 5H, ArH); ^{13}C NMR(100.6 MHz, $CDCl_3$): δ = 23.32 (22.22); 40.71 (40.76); 119.82; 123.46; 123.57; 125.33; 126.15; 126.49; 127.24; 127.83 (127.40); 128.46 (128.40); 146.03; 150.69; EI-MS: m/z (%): 188.08 (49) [M^+]; 173.20 (100) [$C_{11}H_9S^+$].

(7) References

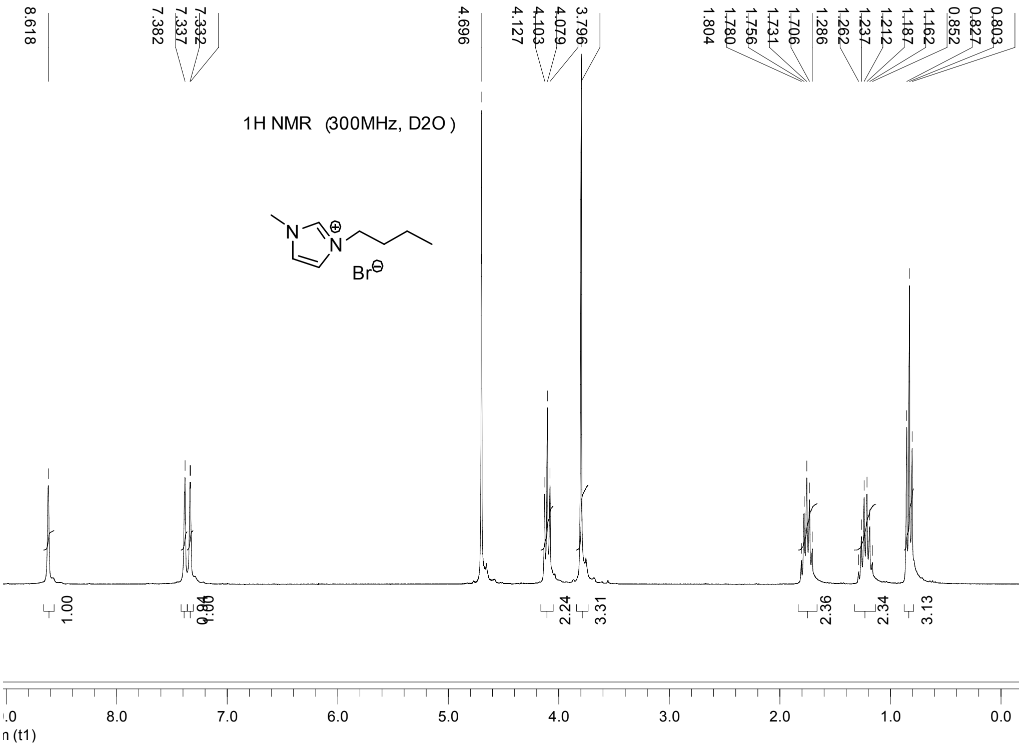
1 N. Jain, A. Kumar, S. M. S. Chauhan, Tetrahedron Lett., 2005, **46**, 2599-2602.

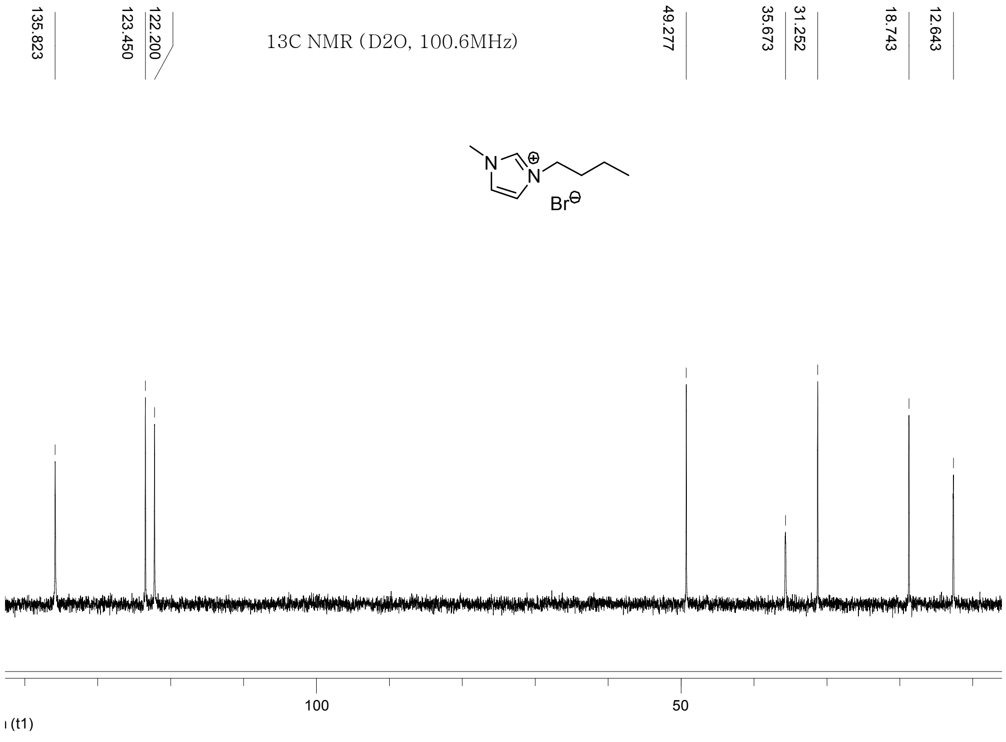
2 K. Bica, P. Gaertner, *Org. Lett.*, 2006, **8**, 733-735.

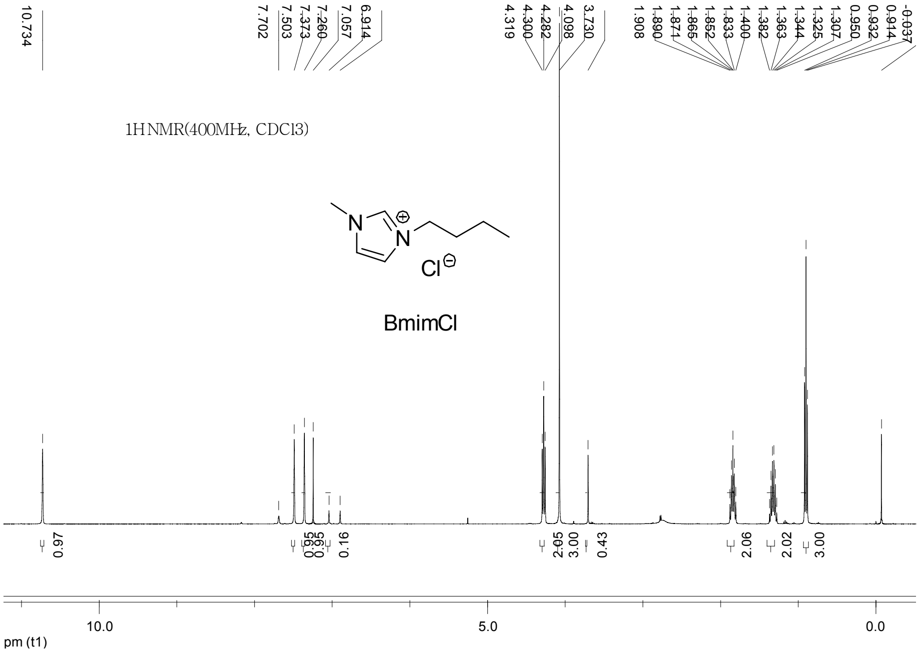
3 (a) S. Hayashi, H. Hamaguchi, *Chem. Lett.* 2004, **33**, 1590-1591. (b) M. S. Sitze, E. R. Schreiter, E. V. Patterson, R. G. Freeman, *Inorg. Chem.*, 2001**, 40**, 2298-2304.

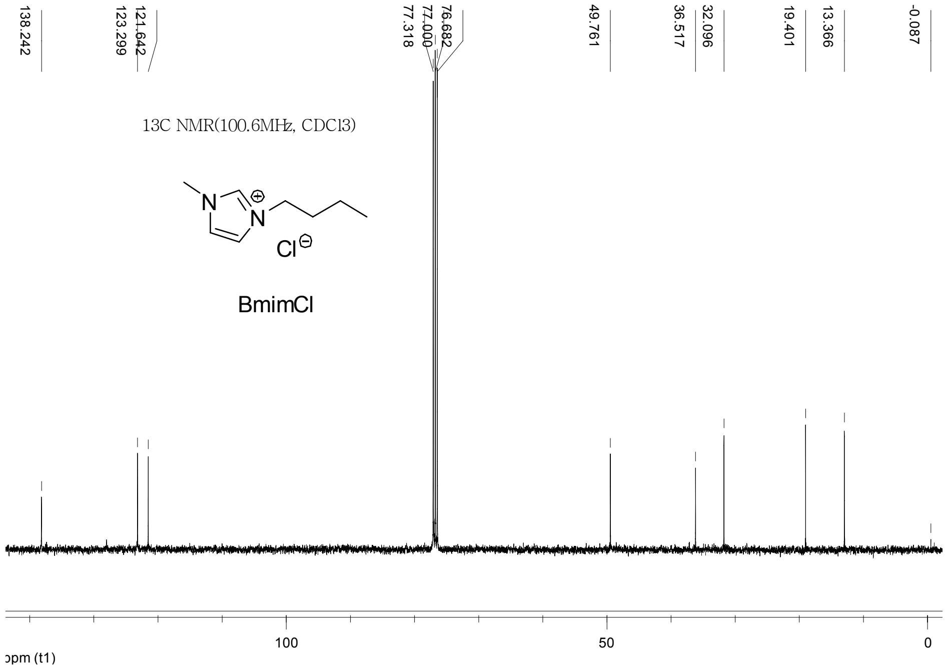
4 D. A. Powell, G. Pelletier, *Tetrahedron Lett.*, 2008, **49**, 2495-2498.

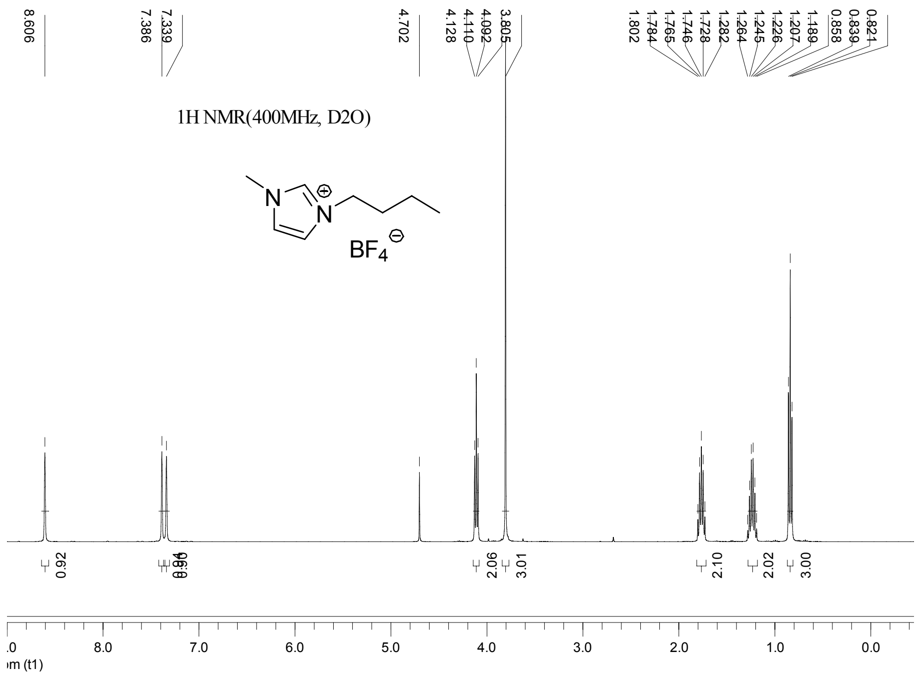
(8) The ^{1}H NMR and ^{13}C NMR charts of various ionic liquids

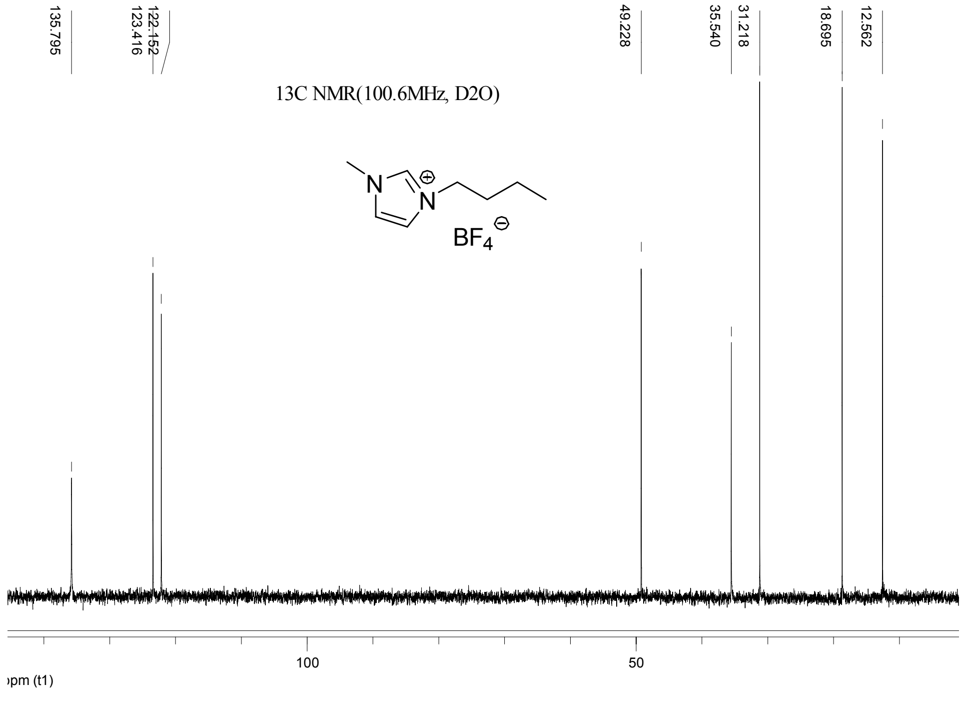




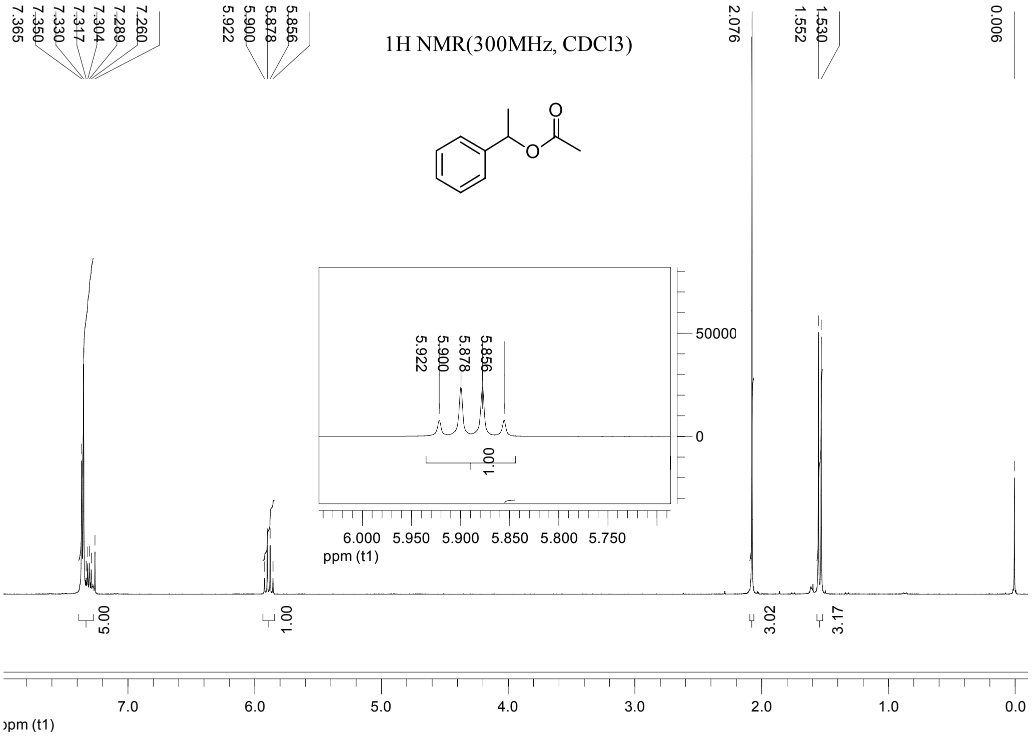

10.734
7.702
7.503
7.373
7.260
7.057
6.914
4.319
4.300
4.282
4.098
3.730
1.908
1.890
1.871
1.865
1.852
1.833
1.400
1.382
1.363
1.344
1.325
1.307
0.950
0.932
0.914
-0.037
1HNMR(400MHz, CDCl3)
N
N
⊕
Cl⊖
BmimCl
0.67
0.95
0.95
0.16
2.05
3.00
0.43
2.06
2.02
3.00
10.0
5.0
0.0
ppm (t1)

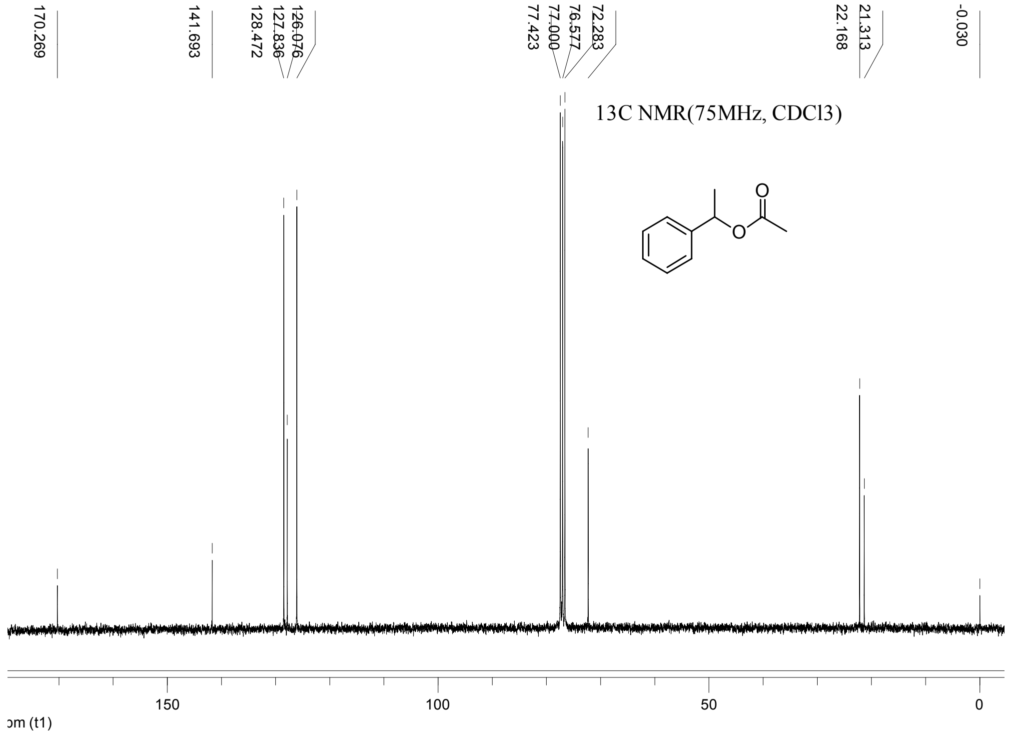

138.242
123.299
121.642
77.318
77.000
76.682
49.761
36.517
32.096
19.401
13.366
-0.087
13C NMR(100.6MHz, CDCl3)
N
N
⊕
Cl⊖
BmimCl
100
50
0
ppm (t1)

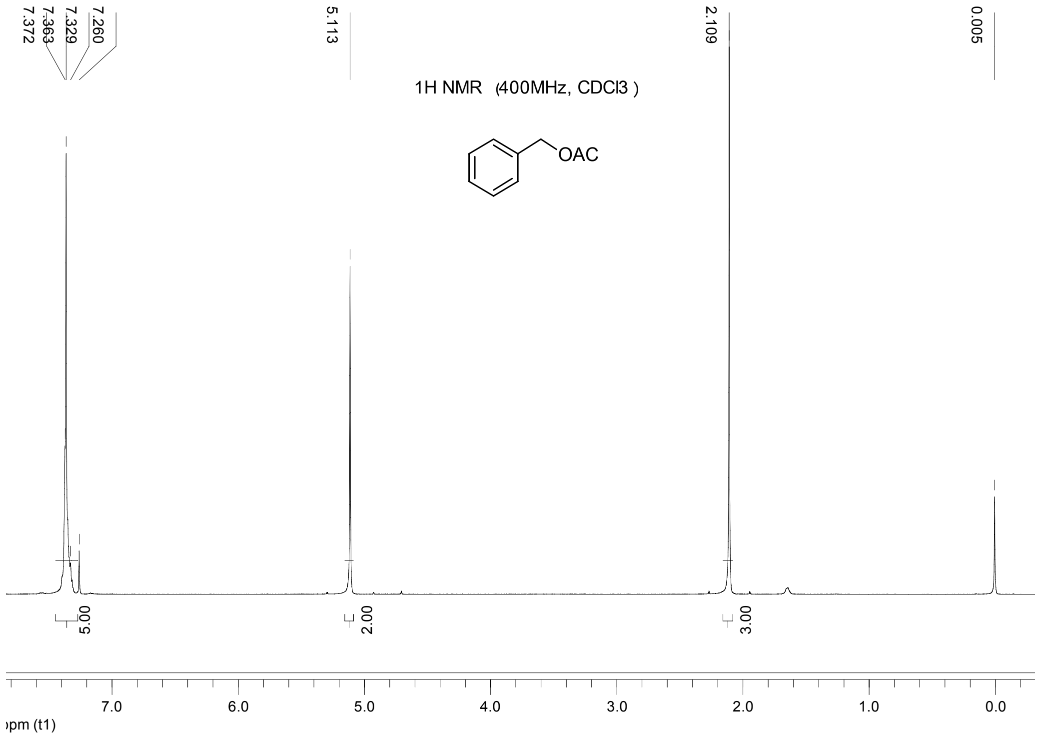

8.606
7.386
7.339
4.702
4.128
4.110
4.092
3.805
1.802
1.784
1.765
1.746
1.728
1.282
1.264
1.245
1.226
1.207
1.189
0.858
0.839
0.821
1H NMR(400MHz, D2O)
N
N
BF4
0.92
2.06
3.01
2.10
2.02
3.00
.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ım (t1)

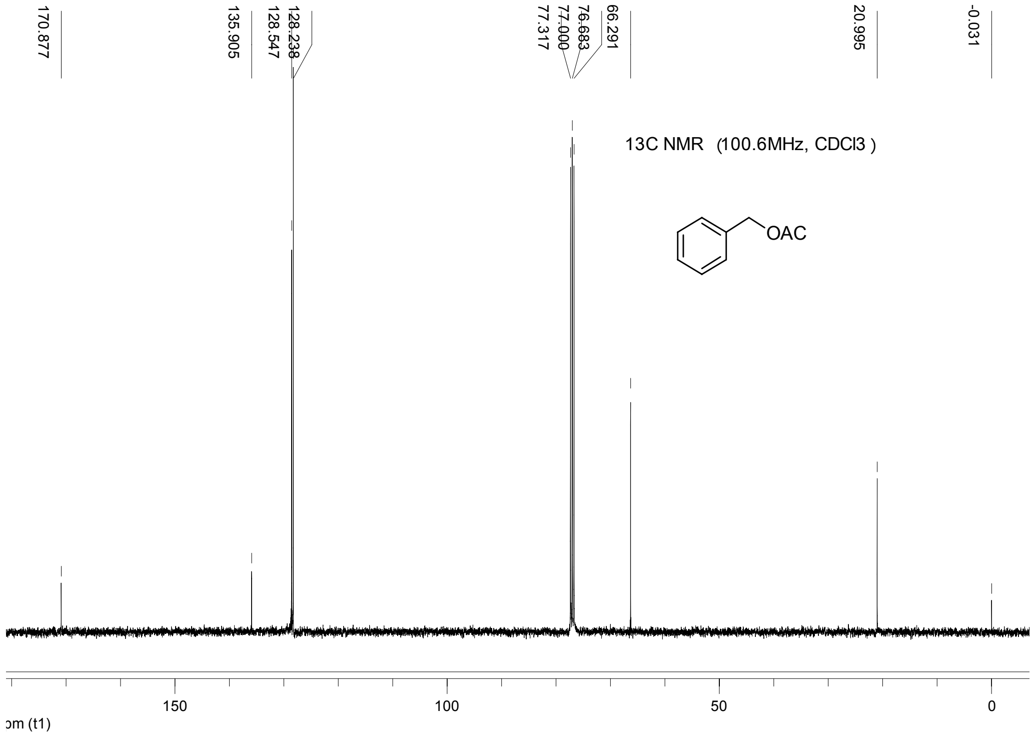

135.795
123.416
122.152
49.228
35.540
31.218
18.695
12.562
13C NMR(100.6MHz, D2O)
N
N
BF4
100
50
ɔpm (t1)

(9) The ^{1}H and ^{13}C NMR Charts of the benzylated reagents:

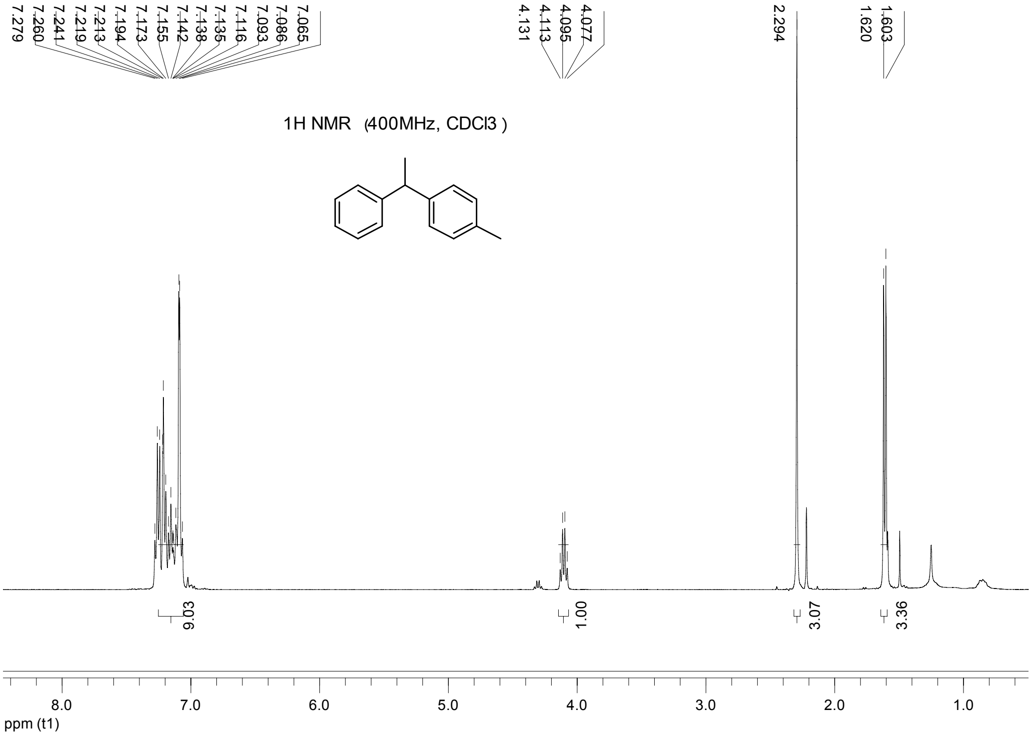


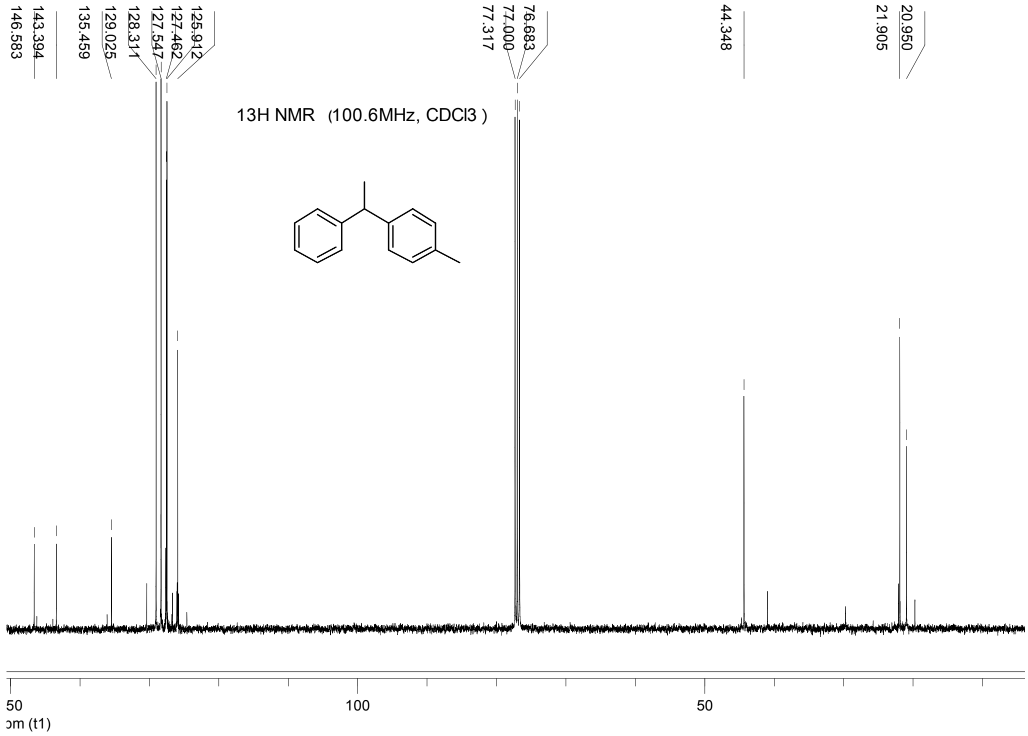


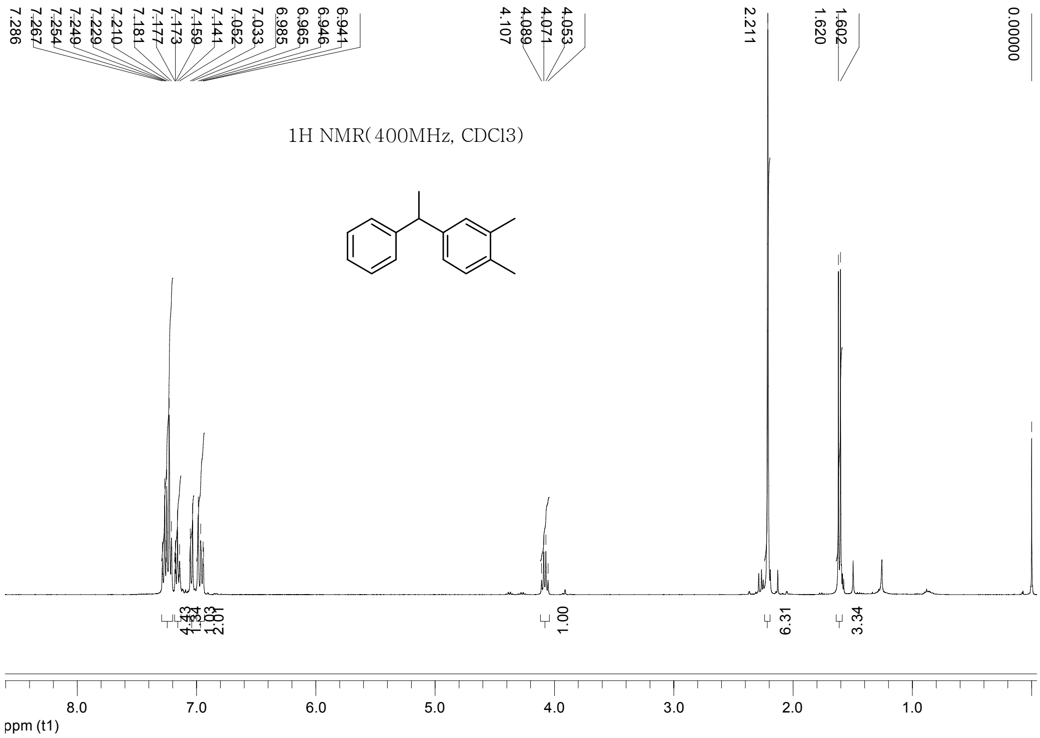

7.372
7.363
7.329
7.260
5.113
2.109
0.005
1H NMR (400MHz, CDCl3)
OAC
5.00
2.00
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

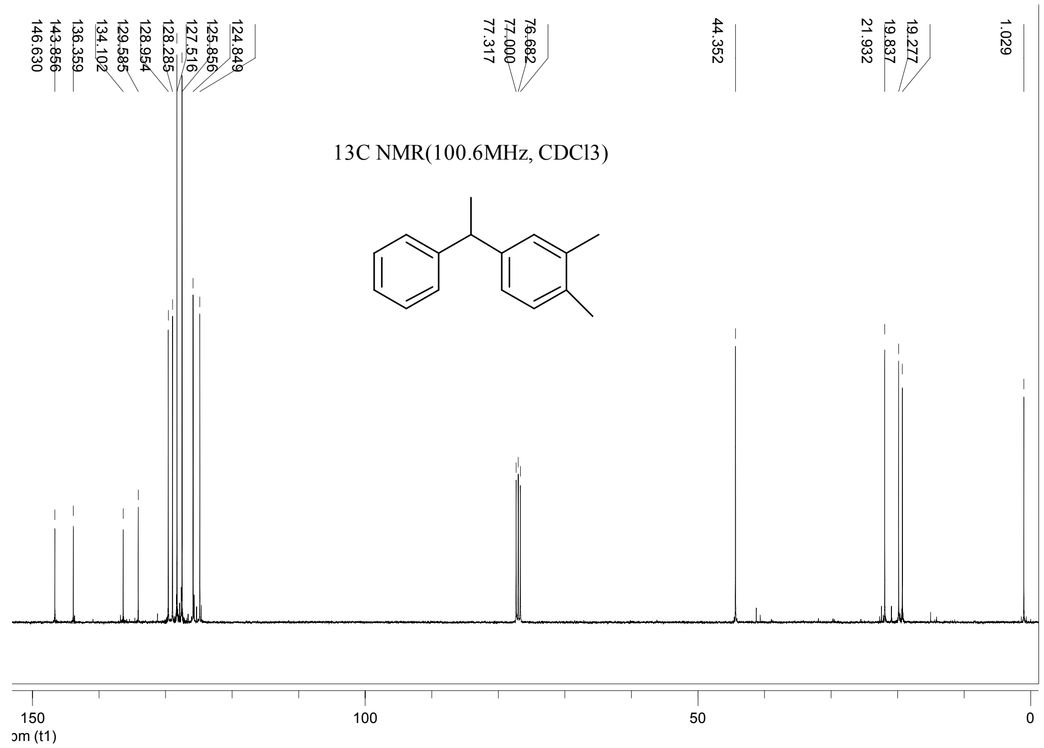

170.877
135.905
128.547
128.238
77.317
77.000
76.683
66.291
20.995
-0.031
13C NMR (100.6MHz, CDCl3)
OAC
150
100
50
0
pm (t1)

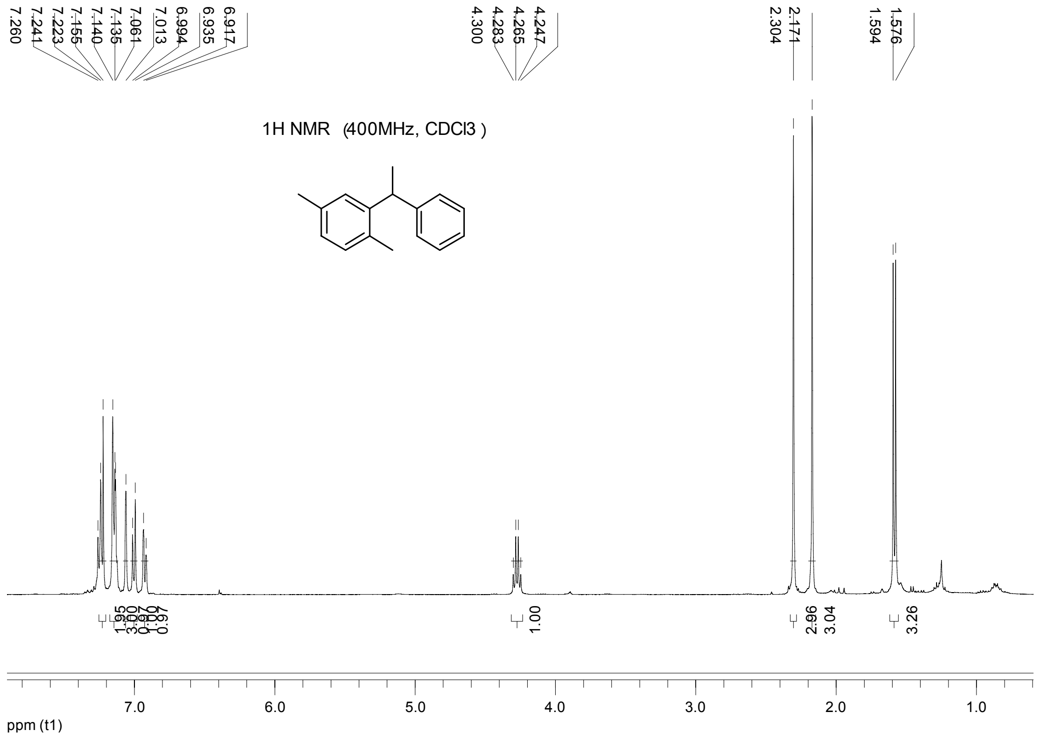
(10) The ^{1}H and ^{13}C NMR Charts of the benzylated products

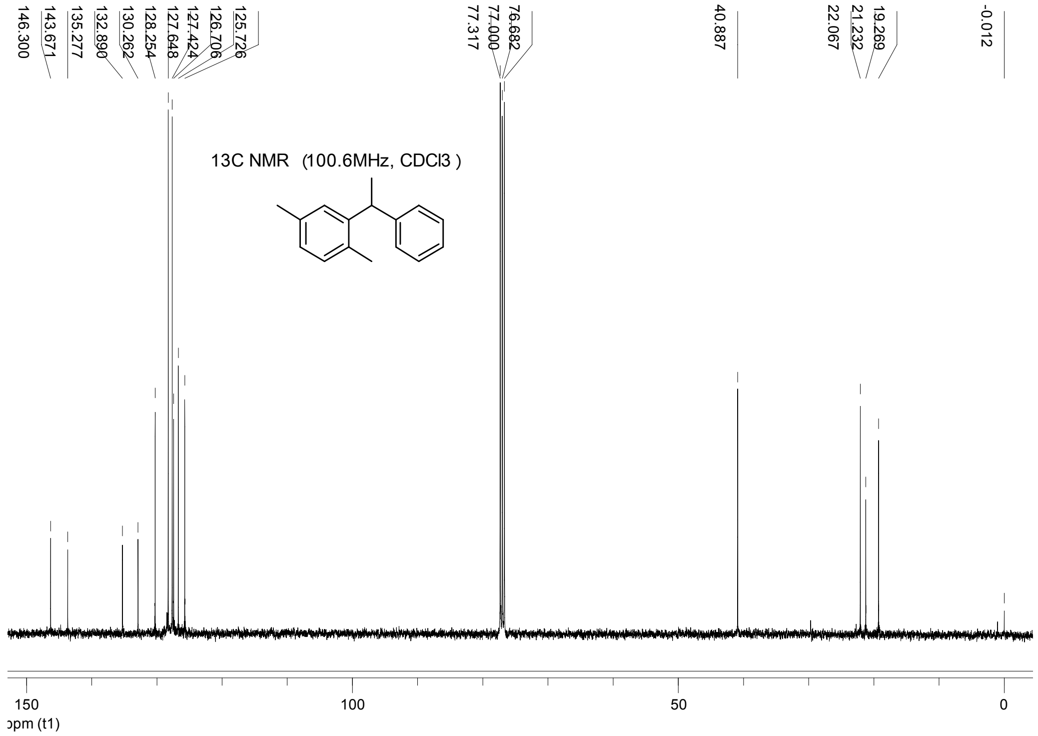


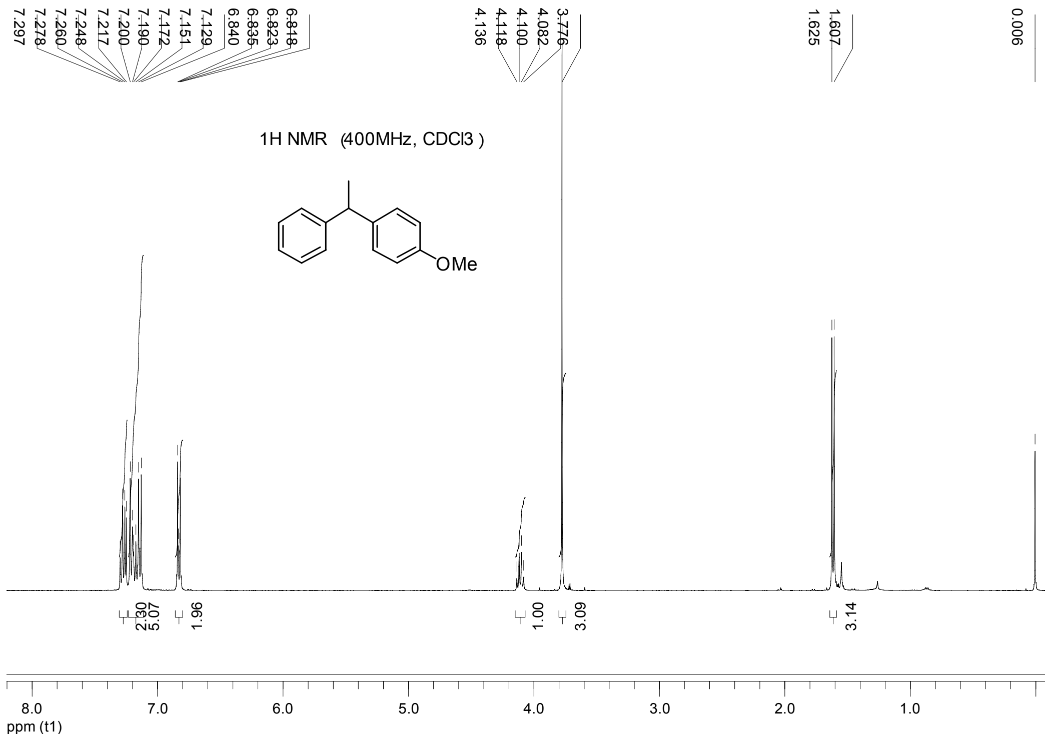


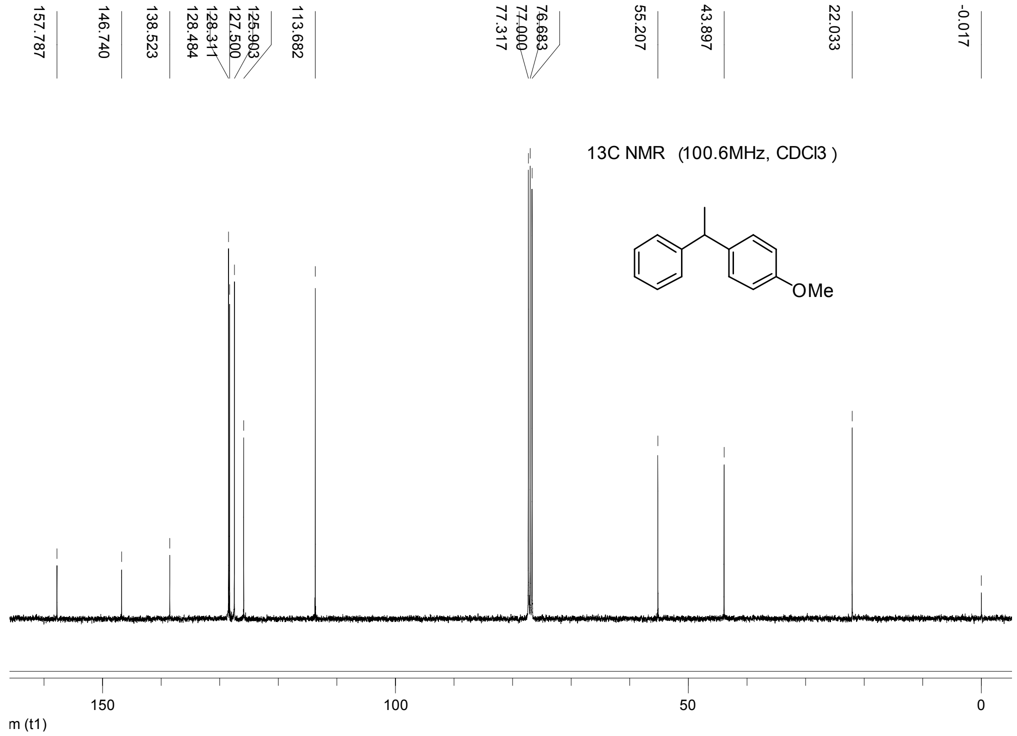

7.286
7.267
7.254
7.249
7.229
7.210
7.181
7.177
7.173
7.159
7.141
7.052
7.033
6.985
6.965
6.946
6.941
4.107
4.089
4.071
4.053
2.211
1.620
1.602
0.00000
1H NMR(400MHz, CDCl3)
4.43
1.34
1.03
2.01
1.00
6.31
3.34
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

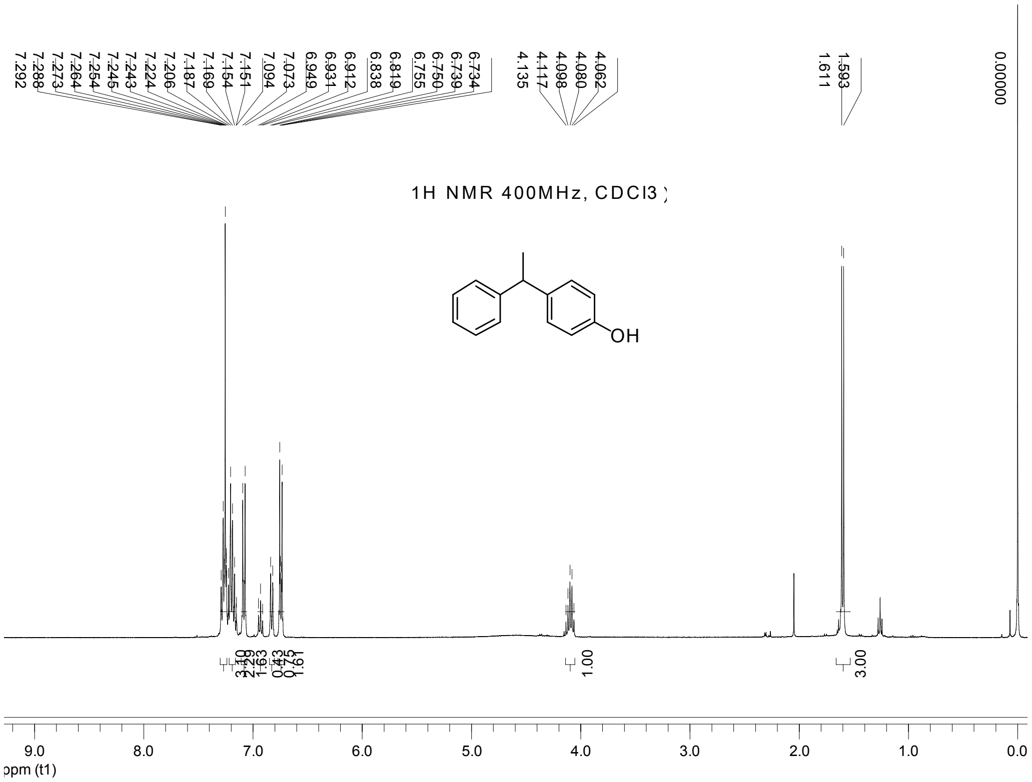

146.630
143.856
136.359
134.102
129.585
128.954
128.285
127.516
125.856
124.849
77.317
77.000
76.682
44.352
21.932
19.837
19.277
1.029
13C NMR(100.6MHz, CDCl3)
150
100
50
0
m (t1)

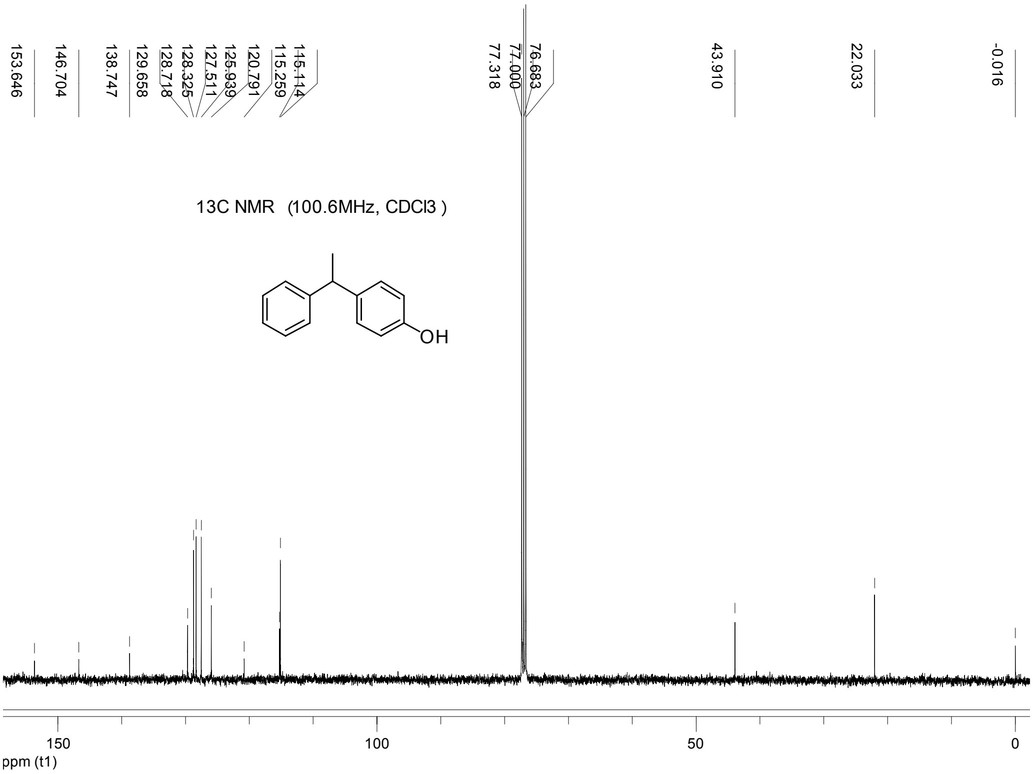

7.260
7.241
7.223
7.155
7.140
7.135
7.061
7.013
6.994
6.935
6.917
4.300
4.283
4.265
4.247
2.304
2.171
1.594
1.576
1H NMR (400MHz, CDCl3)
1.95
3.00
0.97
1.01
0.97
1.00
2.96
3.04
3.26
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

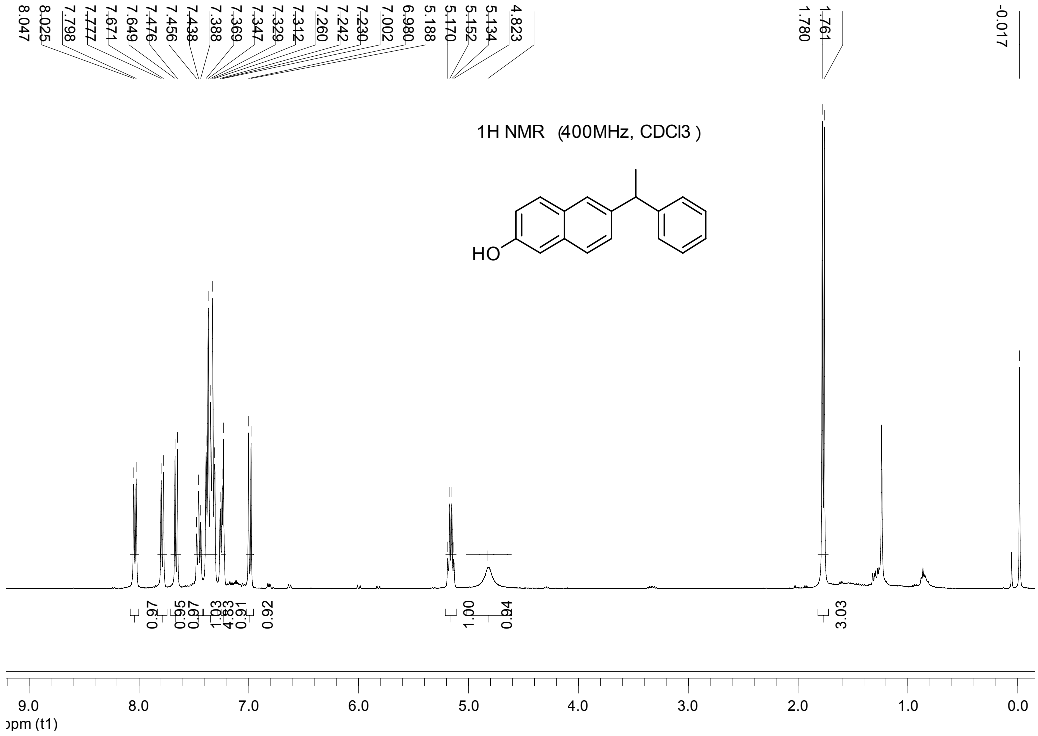

146.300
143.671
135.277
132.890
130.262
128.254
127.648
127.424
126.706
125.726
77.317
77.000
76.682
40.887
22.067
21.232
19.269
-0.012
13C NMR (100.6MHz, CDCl3)
150
100
50
0
ppm (t1)

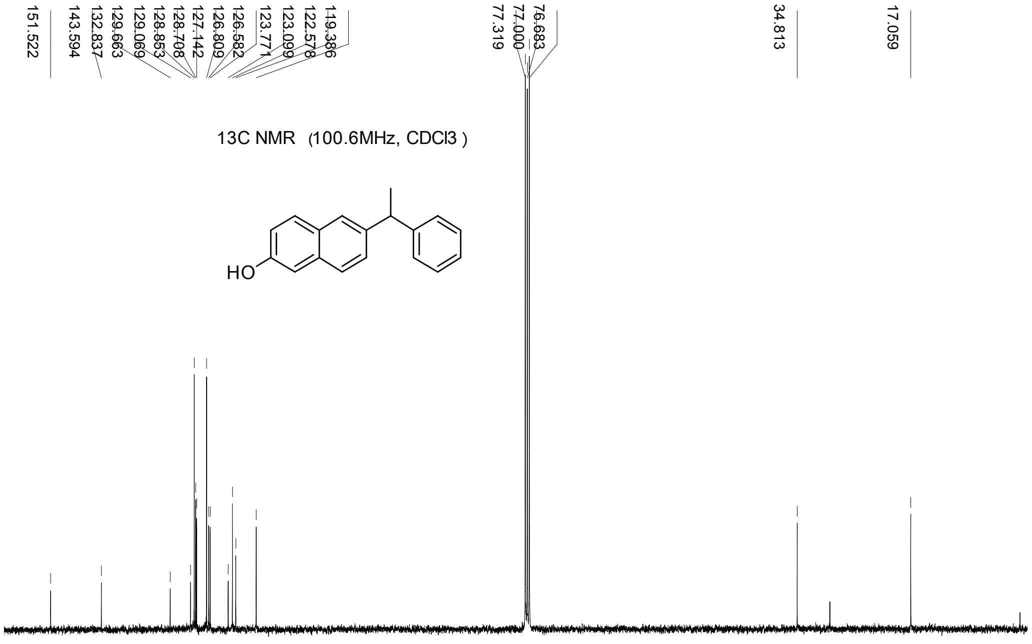

7.297
7.278
7.260
7.248
7.217
7.200
7.190
7.172
7.151
7.129
6.840
6.835
6.823
6.818
4.136
4.118
4.100
4.082
3.776
1.625
1.607
0.006
1H NMR (400MHz, CDCl3)
OMe
2.30
5.07
1.96
1.00
3.09
3.14
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

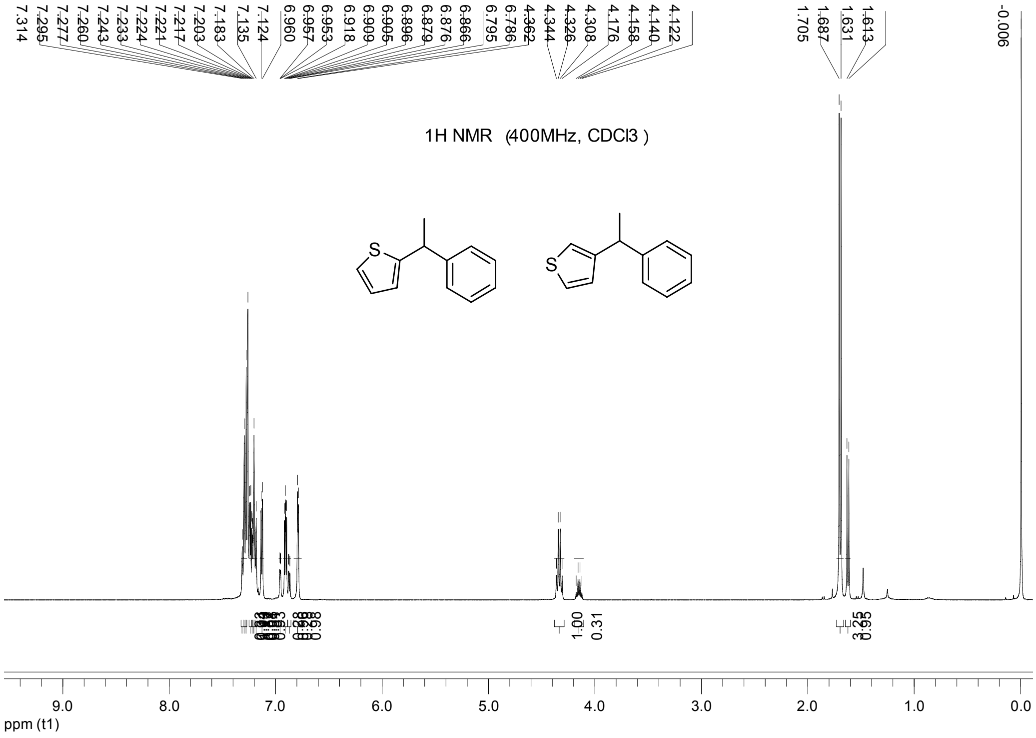

157.787
146.740
138.523
128.484
128.311
127.500
125.903
113.682
77.317
77.000
76.683
55.207
43.897
22.033
-0.017
13C NMR (100.6MHz, CDCl3)
OMe
150
100
50
0
m (t1)

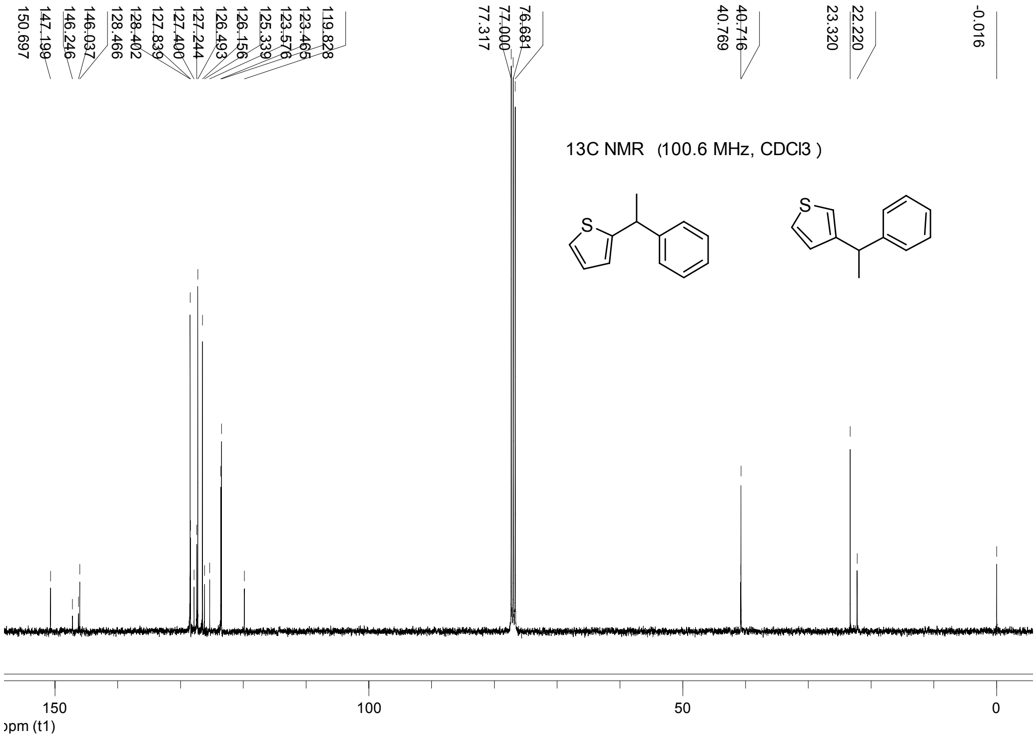

7.292
7.288
7.273
7.264
7.254
7.245
7.243
7.224
7.206
7.187
7.169
7.154
7.151
7.094
7.073
6.949
6.931
6.912
6.838
6.819
6.755
6.750
6.739
6.734
4.135
4.117
4.098
4.080
4.062
1.611
1.593
0.00000
1H NMR 400MHz, CDCl3)
OH
3.10
2.29
1.63
0.43
0.75
1.61
1.00
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

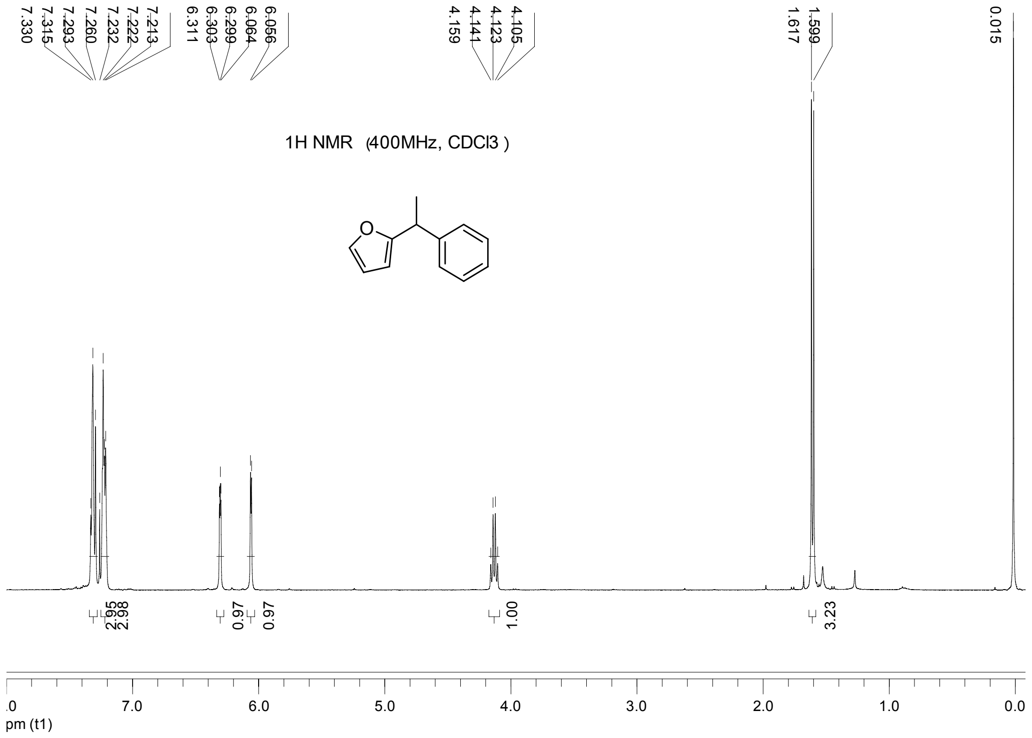

153.646
146.704
138.747
129.658
128.718
128.325
127.511
125.939
120.791
115.259
115.114
77.318
77.000
76.683
43.910
22.033
-0.016
13C NMR (100.6MHz, CDCl3)
OH
150
100
50
0
ppm (t1)

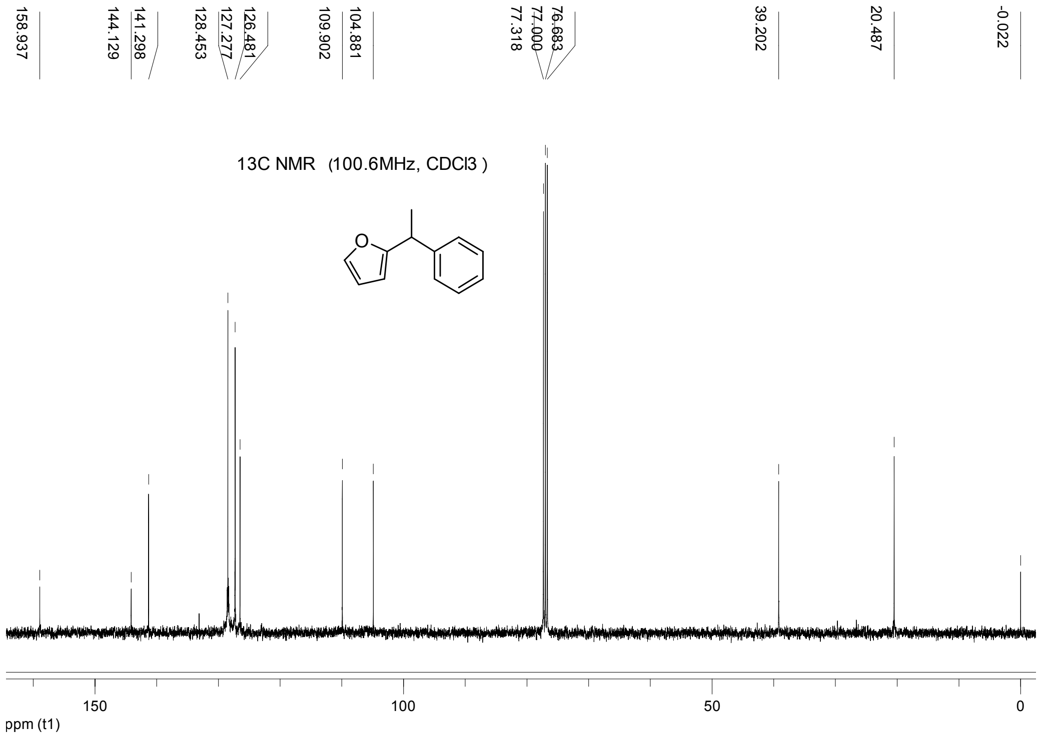

8.047
8.025
7.798
7.777
7.671
7.649
7.476
7.456
7.438
7.388
7.369
7.347
7.329
7.312
7.260
7.242
7.230
7.002
6.980
5.188
5.170
5.152
5.134
4.823
1.761
1.780
-0.017
1H NMR (400MHz, CDCl3)
HO
0.97
0.95
0.97
1.03
4.83
0.91
0.92
1.00
0.94
3.03
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

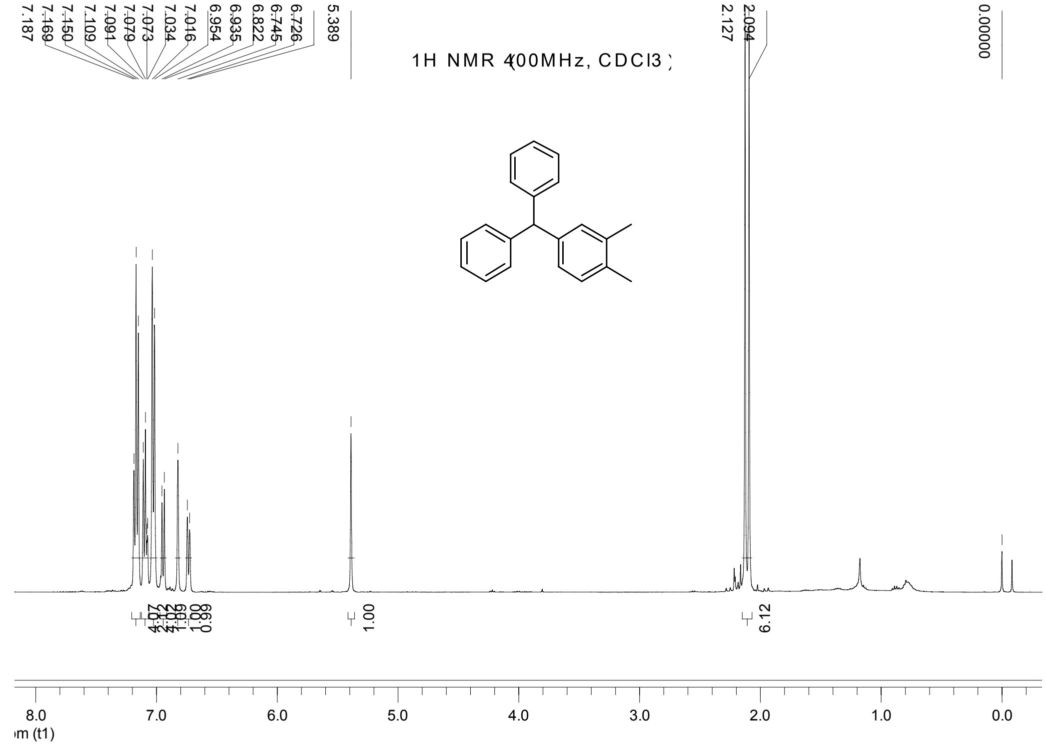

151.522
143.594
132.837
129.663
129.069
128.853
128.708
127.142
126.809
126.582
123.771
123.099
122.578
119.386
77.319
77.000
76.683
34.813
17.059
13C NMR (100.6MHz, CDCl3)
HO
150
100
50
0
ppm (t1)

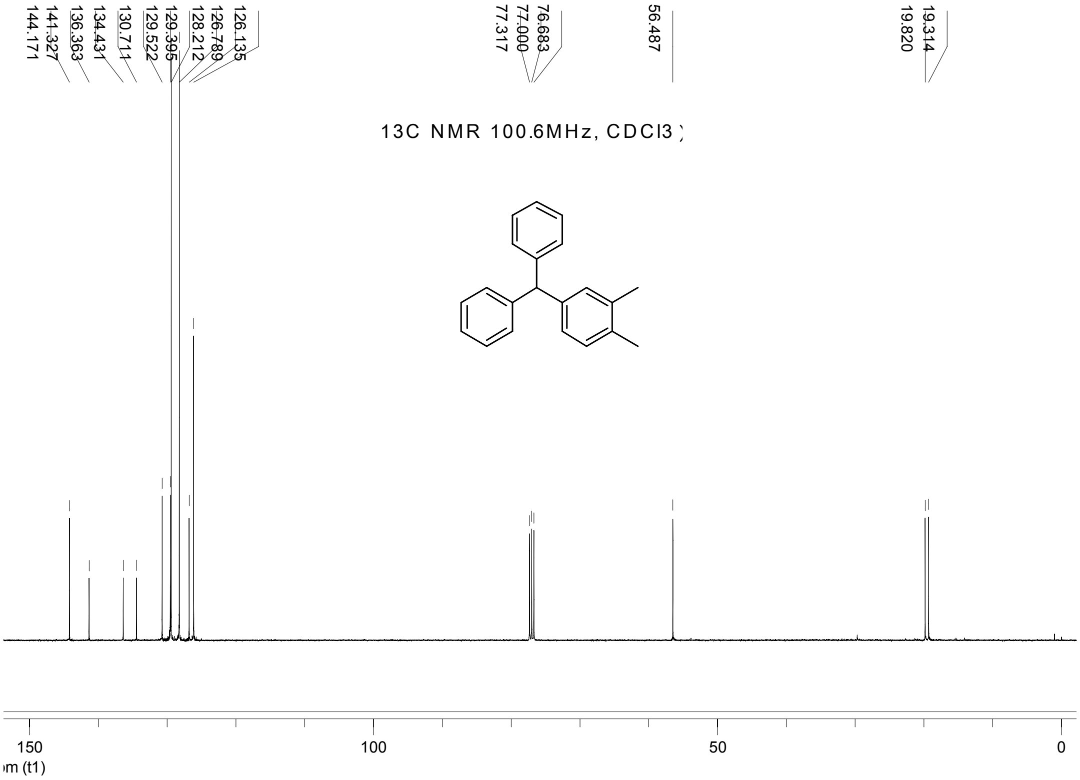

7.314
7.295
7.277
7.260
7.243
7.233
7.224
7.221
7.217
7.203
7.183
7.135
7.124
6.960
6.957
6.953
6.918
6.909
6.905
6.896
6.879
6.876
6.866
6.795
6.786
4.362
4.344
4.326
4.308
4.176
4.158
4.140
4.122
1.705
1.687
1.631
1.613
-0.006
1H NMR (400MHz, CDCl3)
S
S
1.00
0.31
3.25
0.95
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


150.697
147.199
146.246
146.037
128.466
128.402
127.839
127.400
127.244
126.493
126.156
125.339
123.576
123.465
119.828
77.317
77.000
76.681
40.716
40.769
23.320
22.220
-0.016
13C NMR (100.6 MHz, CDCl3)
S
S
150
100
50
0
ppm (t1)

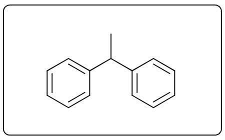

7.330
7.315
7.293
7.260
7.232
7.222
7.213
6.311
6.303
6.299
6.064
6.056
4.159
4.141
4.123
4.105
1.617
1.599
0.015
1H NMR (400MHz, CDCl3)
O
2.95
2.98
0.97
0.97
1.00
3.23
.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
pm (t1)


158.937
144.129
141.298
128.453
127.277
126.481
109.902
104.881
77.318
77.000
76.683
39.202
20.487
-0.022
13C NMR (100.6MHz, CDCl3)
O
150
100
50
0
ppm (t1)


7.187
7.169
7.150
7.109
7.091
7.079
7.073
7.034
7.016
6.954
6.935
6.822
6.745
6.726
5.389
2.127
2.094
0.00000
1H NMR (400MHz, CDCl3)
4.07
1.00
0.99
1.00
6.12
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


144.171
141.327
136.363
134.431
130.711
129.522
129.395
128.212
126.789
126.135
77.317
77.000
76.683
56.487
19.820
19.314
13C NMR 100.6MHz, CDCl3)
150
100
50
0
ppm (t1)

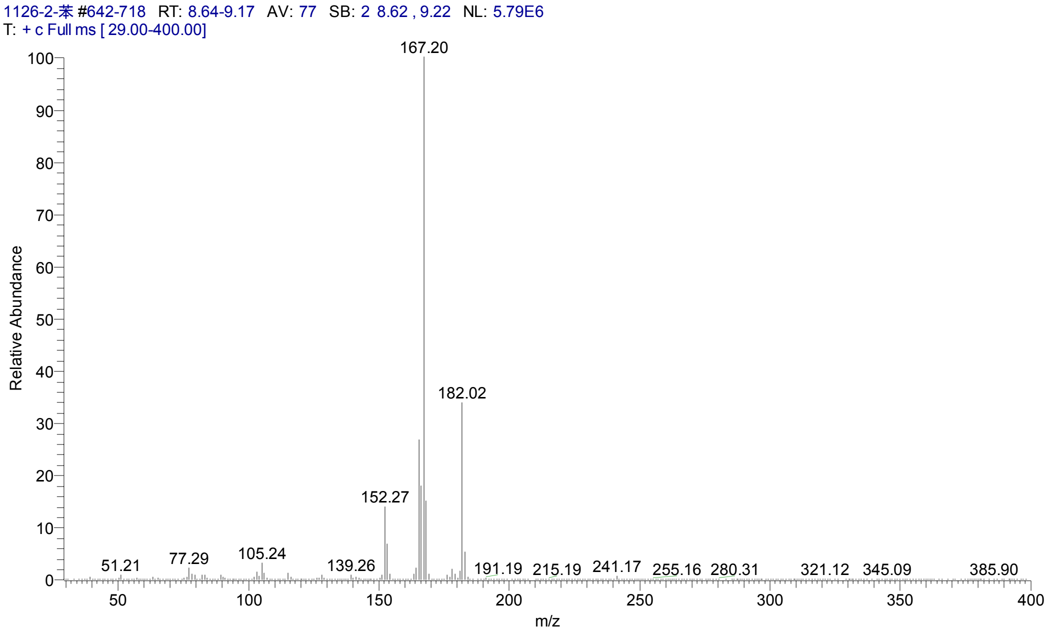
(11) The GC-MS charts of ethane-1,1-diyldibenzene and 4-benzyl-1,2-dimethylbenzene

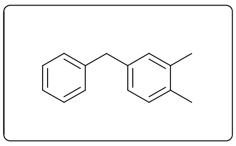


GS-MS chart of ethane-1,1-diyldibenzene:

EI-MS: m/z (%): 182.02 (34) [M^+]; 167.20 (100) [$C_{13}H_{11}^+$].

It is difficult to isolate the benzylated product of benzene, the following is the GC-MS chart of the product.

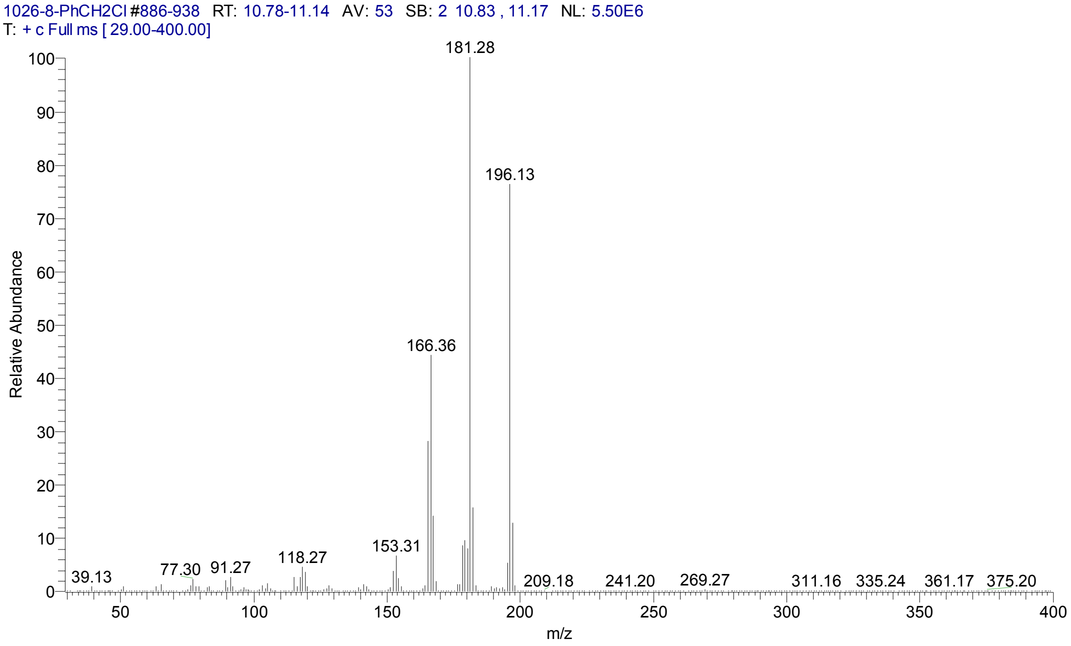




GS-MS chart of 4-benzyl-1,2-dimethylbenzene:

It is difficult to isolate the benzylated product of benzyl chloride and benzyl alcohol, the following is the GC-MS chart of the product.

EI-MS: m/z (%): 196.13 (76) [M^+]; 181.28 (100) [$C_{14}H_{13}^+$].



(12) Thermal gravimetric analysis of the iron-containing ionic liquids

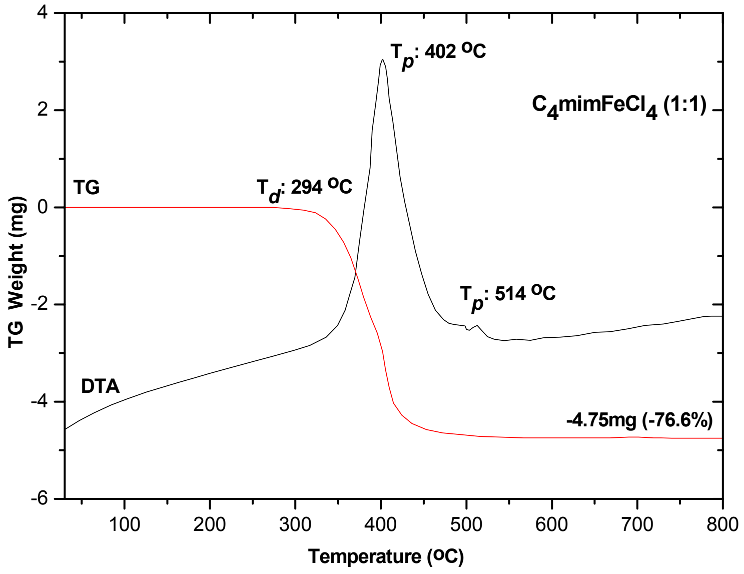


Figure S4. Thermal gravimetric analysis scan of $C_4mimFeCl_4$ (1:1).

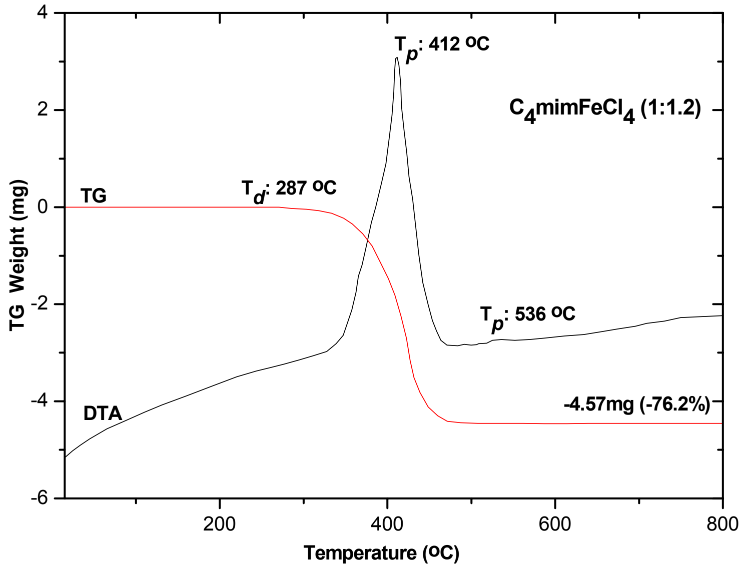


Figure S5. Thermal gravimetric analysis scan of $C_4mimFeCl_4$ (1:1.2).

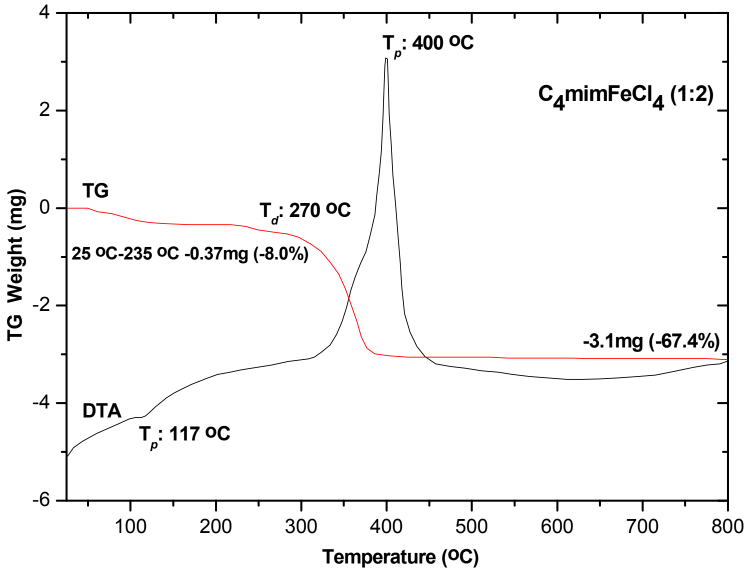


Figure S6. Thermal gravimetric analysis scan of $C_4mimFeCl_4$ (1:2.0).

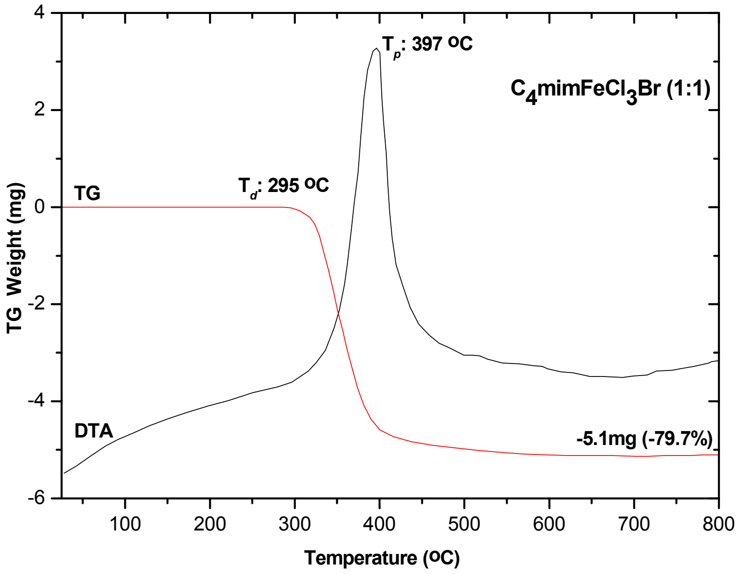


Figure S7. Thermal gravimetric analysis scan of $C_4mimFeCl_3Br$ (1:1).