

Supporting information

On catalysis by ionic liquids

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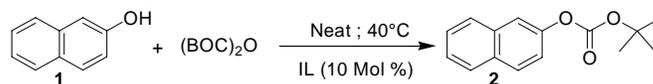
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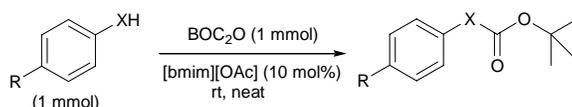
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Table 1: Screening of Ionic Liquids (ILs) for *O-t*-Boc Formation.^a

| entry | ionic liquid (IL) | δ of C ₂ -H in (ppm) ^c | time (h) | yield (%) ^b |
|-------|---------------------------|---|----------|------------------------|
| 1 | Nil | ----- | 2 | Nil ^d |
| 2 | [bmim][BF ₄] | 9.385 | 2 | 10 ^d |
| 3 | [bmim][OAc] | 10.205 | 2 | 97 |
| 4 | [bmim][HSO ₄] | 10.271 | 2 | 20 ^d |
| 5 | NaCl | ----- | 2 | Nil ^d |
| 6 | NH ₄ Cl | ----- | 2 | Nil ^d |
| 7 | [bdmim][OAc] | ----- | 2 | 30 ^d |
| 8 | NH ₄ OAc | ----- | 2 | 40 ^d |

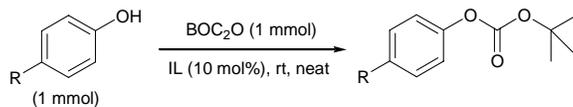
^a 2-Naphthol **1** (0.144 g, 1 mmol) was treated with Boc₂O (0.218 g, 1 mmol, 1equiv) in presence of the IL (0.1 mmol, 10 mol %). ^b Yield of *tert*-butyl-naphthalen-2-yl carbonate **2** (characterized by IR, ¹H NMR). ^c NMR was taken in CDCl₃. ^d The unreacted starting material was recovered.

Table A. The [bmim][OAc] Catalysed *O/S-tert*-butoxycarbonylation of a Few Representative Phenols/Thiols having Varying pK_a Values.^a

| entry | substrate | pK _a ^b | time (h) | yield (%) ^c |
|-------|-----------------------------|------------------------------|----------|------------------------|
| 1 | R = H; X = O | 10.02 ^d | 2 | 91 |
| 2 | R = H; X = S | 6.61 ^e | 3 | 90 |
| 3 | R = Me; X = O | 10.19 ^f | 1.25 | 90 |
| 4 | R = Me; X = S | 6.82 ^e | 2.5 | 92 |
| 5 | R = NO ₂ ; X = O | 7.15 ^d | 4 | 94 ^{g,h,i} |
| 6 | R = NO ₂ ; X = S | 4.71 ^e | 5 | 89 |

^aThe phenol/thiol (1 mmol) was treated with Boc₂O (1 mmol) at rt under neat condition in the presence of [bmim][OAc] (10 mol%). ^bThe pK_a values of the corresponding phenol/thiol as reported in the literature. ^cThe yield of the isolated pure (IR, NMR and MS) product. ^dModern Physical Organic Chemistry by E. V. Anslyn and D. A. Dougherty **2006**, Univ. Sci. Books, CA, 279. ^e*J. Org. Chem.* **1982**, *47*, 3224. ^fCompiled by R. Williams. ^gThe *O-t*-Boc formation did not take place in carrying out the reaction in the absence of any IL and the starting 4-nitrophenol remained unchanged. ^hThe *O-t*-Boc was formed in 40% yield in carrying out the reaction in the presence of [bmim]Cl (10 mol%) instead of [bmim][OAc] and the starting 4-nitrophenol was recovered (55%) unchanged. ⁱNo *O-t*-Boc was formed in carrying out the reaction separately in the presence of NaCl (10 mol%) and NH₄Cl (10 mol%) instead of [bmim][OAc] and the starting 4-nitrophenol was recovered unchanged.

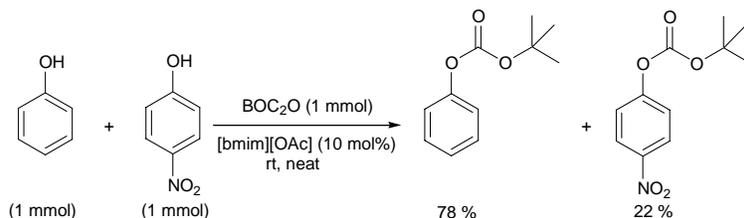
Table B. The Comparison of the Catalytic Efficiency of [bmim][OAc] and [bdmim][OAc] during *O*-*tert*-Butoxycarbonylation of a Few Representative Phenols.^a



| entry | substrate | IL | time (h) | yield (%) ^b |
|-------|-------------------------|--------------|----------|------------------------|
| 1 | R = Me | [bmim][OAc] | 1.25 | 90 |
| 2 | R = Me | [bdmim][OAc] | 1.25 | 15 ^c |
| 3 | R = OMe | [bmim][OAc] | 1 | 89 |
| 4 | R = OMe | [bdmim][OAc] | 1 | 10 ^c |
| 5 | R = OCH ₂ Ph | [bmim][OAc] | 2 | 89 |
| 6 | R = OCH ₂ Ph | [bdmim][OAc] | 2 | 40 ^c |
| 7 | R = NO ₂ | [bmim][OAc] | 4 | 94 |
| 8 | R = NO ₂ | [bdmim][OAc] | 4 | 45 ^c |

^a The phenol (1 mmol) was treated with Boc₂O (1 mmol) at rt under neat condition in the presence of the IL (10 mol%). ^b The yield of the isolated pure (IR, NMR and MS) product. ^c The unreacted starting material was recovered.

Scheme A. Inter-molecular Competition for [bmim][OAc] Catalysed *O*-*t*-Boc Formation at a Phenolic OH with Better Hydrogen Bond Donor Ability but having Higher *pK_a*.



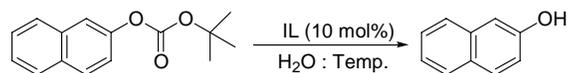
The mixture of phenol (94 mg, 1 mmol) and 4-nitrophenol (139 mg, 1 mmol) was treated with Boc₂O (218 mg, 1 mmol) under neat condition at 40 °C for 2 h in the presence of [bmim][OAc] (20 mg, 10 mol%). The ¹H NMR of an aliquot sample of the reaction mixture revealed it to be a 78:22 mixture of the *O*-*t*-Boc of the phenol and 4-nitrophenol, respectively, based on the integral values of the protons *ortho* to the NO₂ group in 4-nitrophenol and its *O*-*t*-Boc derivative [the protons *ortho* to the NO₂ group in 4-nitrophenol appear as doublet at δ 8.17 but the corresponding protons in the *O*-*t*-Boc derivative of 4-nitrophenol appear as doublet at δ 8.27]. This reflects selective *O*-*t*-Boc formation of the phenol OH group that has higher *pK_a* (10.02) value compared to that of 4-nitrophenol (7.15).

Reusability of [bmim][OAc] for *O*-*t*-Boc Formation.

The [bmim][OAc] (0.05 g, 0.25 mmol, 10 mol %) was added to a magnetically stirred mixture of 2-naphthol (0.360 g, 2.5 mmol) and Boc₂O (0.54 g, 1 equiv, 2.5 mmol) at 40 °C. After completion of the reaction, the reaction mixture was diluted with EtOAc (5 mL) followed by addition of a 1 mL of water (to dissolved the catalyst). The EtOAc layer was separated and the ionic liquid was recovered by concentrating the aqueous layer/portion under vacuum at 80° C for 40 min. The recovered [bmim][OAc]

was found to be identical (spectral data) with an authentic sample (unused ionic liquid). The recovered [bmim][OAc] was reused for three consecutive fresh batches of reactions of 2-naphthol (0.360 g, 2.5 mmol) and Boc₂O (0.54 g, 1equiv, 2.5 mmol) at 40 °C to afford *tert*-butyl naphthalen-2-yl carbonate in 93, 90 and 88% yields, respectively.

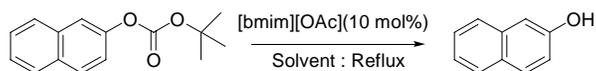
Table 2: Screening of Ionic Liquids (ILs) for *O*-*t*-Boc Deprotection.



| entry | ionic liquid (IL) | temp | time (h) | yield (%) ^b |
|-------|---------------------------|---------------|----------|------------------------|
| 1 | NIL | 40 °C | 3 | Trace ^c |
| 2 | NIL | 60 °C | 3 | Trace ^c |
| 3 | NIL | Reflux | 3 | 10 ^c |
| 4 | [bmim][BF ₄] | Reflux | 3 | 89 |
| 5 | [bmim][OAc] | Reflux | 3 | 98 |
| 6 | [bmim][OAc] | 60 °C | 3 | 20 ^c |
| 7 | [bmim][OAc] | 40 °C | 3 | Trace ^c |
| 8 | [bdmim][OAc] | Reflux | 3 | 30 ^c |
| 9 | AcOH | Reflux | 3 | 50 ^c |
| 10 | NH ₄ OAc | Reflux | 3 | 40 ^c |
| 11 | [bmim][HSO ₄] | Reflux | 3 | 60 ^c |

^a *tert*-Butyl naphthalen-2-yl carbonate (0.243 g, 1 mmol) was refluxed with water (2 mL) in presence of IL (0.02 g, 0.1 mmol, 10 mol %). ^b Isolated yield of the parent phenol (2-naphthol: characterized by spectral data). ^c The unreacted starting material was recovered.

Table 3: Effect of Solvents on *O*-*t*-Boc Deprotection.



| entry | solvent | time (h) | yield (%) ^b |
|-------|-----------------------|----------|------------------------|
| 1 | H₂O | 3 | 98 |
| 2 | MeOH | 3 | 15 ^c |
| 3. | EtOH | 3 | 25 ^c |
| 4. | ^t BuOH | 3 | 10 ^c |
| 5. | MeCN | 3 | 20 ^c |
| 6. | PhMe | 3 | 5 ^c |

^a Boc protected 2-naphthol (0.243 g, 1 mmol) was heated under reflux in the respective solvent (2 mL) in the presence of IL (0.02 g, 0.1 mmol, 10 mol %). ^b Isolated yield of the parent phenol (2-naphthol: characterized by spectral data). ^c The unreacted starting material was recovered.

Reusability of the [bmim][OAc] for *O*-*t*-Boc deprotection.

To a magnetically stirred mixture of *tert*-butyl naphthalen-2-yl carbonate (0.244 g, 1 mmol) and water (2 mL), [bmim][OAc] (0.02 g, 0.1 mmol, 10 mol%) was added at reflux condition. After completion of the reaction, the reaction mixture was diluted with EtOAc (5 mL). The ionic liquid was recovered by

concentrating the aqueous layer/portion under vacuum at 80° C for 40 min. The recovered [bmim][OAc] was found to be identical (spectral data) with an authentic sample (unused ionic liquid). The recovered [bmim][OAc] was reused thrice for fresh batches of reactions of *tert*-butyl naphthalen-2-yl carbonate (0.244 g, 1 mmol) and water (2 mL) at reflux condition to afford 2-naphthol in 92, 90 and 80% yields, respectively.

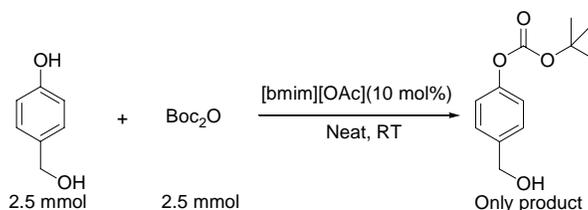
Typical Experimental Procedures:

Typical procedure for *O*-*t*-BOC formation:

The [bmim][OAc] (0.05 g, 0.25 mmol, 10 mol %) was added to a magnetically stirred mixture of 2-naphthol (0.360 g, 2.5 mmol) and Boc₂O (0.54 g, 1equiv, 2.5 mmol) at 40 °C. After completion of the reaction (2 h, monitored by TLC), the reaction mixture was diluted with EtOAc (5 mL) followed by addition of a few drops of water (to dissolved the catalyst). The supernatant EtOAc solution was decanted off. The aqueous layer/portion was extracted with EtOAc (2×5 mL). The combined EtOAc extracts were dried (Na₂SO₄) and concentrated under vacuum to afford the *tert*-butyl naphthalen-2-yl carbonate (0.590 g, 97 %), off white solid, Mp: 68 °C. IR (KBr) ν : 3401, 1756, 1277, 1258, 1239, 1146 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 27°C, TMS) δ : 1.59 (s, 9 H; O-Boc), 7.29-7.33 (m, 1 H, ArCH), 7.46-7.50 (m, 2 H, ArCH), 7.69 (d, ³*J*(H,H)=2.1 Hz, 1 H, ArCH) 7.79-7.86 (m, 3 H, ArCH); ¹³C NMR (CDCl₃, 100 MHz) δ : 27.75, 83.62, 118.16, 120.90, 125.69, 126.55, 127.70, 129.39, 131.40, 133.74, 148.73, 152.01; Mass (EI) *m/z*: 244 [M⁺].

The ionic liquid was recovered by concentrating the aqueous layer/portion under vacuum at 80° C for 40 min and reused for the fresh batches of reaction, three times without any significant loss of catalytic activity.

Selective *O*-*t*-Boc formation with phenolic OH in the presence of alcoholic OH:



The [bmim][OAc] (0.05 g, 0.25 mmol, 10 mol %) was added to a magnetically stirred mixture of 4-hydroxybenzyl alcohol (0.310 g, 2.5 mmol) and Boc₂O (0.54 g, 1equiv, 2.5 mmol) at 40 °C. After completion of the reaction (4 h, monitored by TLC), the reaction mixture was diluted with EtOAc (5 mL) followed by addition of a few drops of water (to dissolved the catalyst). The supernatant EtOAc solution was decanted off. The aqueous layer/portion was extracted with EtOAc (2×5 mL). The combined EtOAc extracts were dried (Na₂SO₄) and concentrated under vacuum to afford the carbonic acid *tert*-butyl ester 4-hydroxymethyl-phenyl ester carbonate (0.392 g, 70 %), Yellow liquid, yield 70 %. IR (KBr) ν : 3472, 2983, 1753, 1743, 1512, 1453, 1395, 1368, 1276, 1255, 1224, 1149 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 27°C, TMS) δ : 1.56 (s, 9 H; O-Boc), 4.62 (s, 2 H, CH₂), 7.13-7.15 (m, 2 H, ArCH), 7.32-7.35 (m, 2 H, ArCH); Mass (EI) *m/z*: 224 [M⁺]

Recovery of starting material (Table 1 entry7):

The [bdmim][OAc] (0.05 g, 0.25 mmol, 10 mol %) was added to a magnetically stirred mixture of 2-naphthol (0.360 g, 2.5 mmol) and Boc₂O (0.54 g, 1 equiv, 2.5 mmol) at 40 °C. After 2 h, the reaction mixture was diluted with EtOAc (5 mL) followed by addition of a few drops of water (to dissolved the catalyst). The supernatant EtOAc solution was decanted off. The aqueous layer/portion was extracted with EtOAc (2×5 mL). The combined EtOAc extracts were dried (Na₂SO₄) and concentrated under vacuum. The crude product was subjected to column chromatography on silica gel (60-120 mesh, 10 g). Elution with hexane (200 mL) eliminated any unreacted Boc₂O. Further elution with eluted 9:1 hexane: EtOAc (250 mL) afforded the *O-t*-Boc product (70 mg, 30%). The unreacted 2-naphthol (0.094 g, 65%) was eluted next with EtOAc (150 mL) and was found to be identical (spectral) with an authentic sample.

Typical procedure for *O-t*-Boc deprotection:

To a magnetically stirred mixture of *tert*-butyl naphthalen-2-yl carbonate (0.244 g, 1 mmol) and water (2 mL), [bmim][OAc] (0.02 g, 0.1 mmol, 10 mol%) was added at reflux condition. After completion of the reaction (3 h, monitored by TLC), the reaction mixture was diluted with EtOAc (5 mL). The supernatant EtOAc solution was decanted off. The aqueous layer/portion was extracted with EtOAc (2×5 mL). The combined EtOAc extracts were dried (Na₂SO₄) and concentrated under vacuum to afford 2-Naphthol (0.138 g, 98%). Off white solid, Mp: 121 °C. IR (KBr) ν : 3402, 1275, 1260, 1238, 1145 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 27°C, TMS) δ : 4.99 (s, 1 H; OH), 7.08-7.14 (m, 2 H, ArCH), 7.30-7.34 (m, 1 H, ArCH), 7.40-7.44 (m, 1 H, ArCH), 7.66-7.68 (m, 2 H, ArCH), 7.73-7.77 (m, 1 H, ArCH); Mass (EI) m/z : 114 [M⁺].

The ionic liquid was recovered by concentrating the aqueous layer/portion under vacuum at 80° C for 40 min and reused for the fresh batches of reaction, three times without any significant loss of catalytic activity.

Synthesis of Ionic Liquid; 1-Butyl-2,3-dimethylimidazolium acetate [bdmim][OAc]:

A mixture of 1,2-dimethyl imidazole (5 mmol) and n-butyl bromide (5 mmol, 1 equiv) was dissolved in PhCH₃ and heated at 80 °C to afford 3-butyl-1,2-dimethyl imidazolium bromide [bdmim][Br]. A mixture of [bdmim][Br] (2.5 mmol, 1 equiv) and NaOAc (2.5 mmol, 1.5 equiv) was dissolved in distilled water (5 mL) and stirred at rt for 72 hrs. The aqueous mixture was subjected to rotary evaporation at 80 °C under reduced pressure for 1 hr. Then MeCN was added, the organic layer was filtered and concentrated under reduced pressure to afford the pure [bdmim][OAc]. Clear viscous liquid, 0.96 (t, ³*J*(H,H)=7.5 Hz, 3 H, CH₃), 1.38 (q, 2 H, CH₂), 1.81 (q, 2 H, CH₂), 2.82 (s, 3H, CH₃), 4.03 (s, 3 H, N-CH₃), 4.24 (t, ³*J*(H,H)=7.5 Hz, 2 H, CH₂), 7.57 (d, ³*J*(H,H)=1.8 Hz, 1 H, CH), 7.76 (d, ³*J*(H,H)=1.8 Hz, 1 H, CH).

Experimental Procedure for Ion-fishing using MALDI-TOF MS (+ve mode):

A mixture of 4-benzyloxyphenol (0.200 g, 1 mmol) and Boc₂O (0.22 g, 1equiv, 1 mmol) was stirred magnetically at 40 °C in the presence of [bmim][OAc] (0.05 g, 0.1 mmol, 10 mol %). After 45 min, an aliquot portion of the reaction mixture was taken out by capillary and dissolved in DCM. A stock solution (1 μ L) of the matrix [prepared from 2,5-dihydroxybenzoic acid (10 mg), TFA (600 μ L of 0.1%

aq. soln) and MeCN (300 μ L)] was added to the solution (1 μ L) of the reaction mixture in DCM and the resultant solution (1 μ L) was added on the MALDI plate. The solvent was evaporated on air drying (10 min) and the spectra were recorded in advance Bruker Daltonics® MALDI-TOF-TOF mass spectrometer.

Experimental Procedure for NMR study:

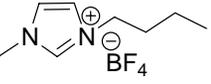
A mixture of 4-methylphenol (0.134 g, 1 mmol) and Boc_2O (0.22 g, 1 equiv, 1 mmol) was stirred magnetically at 40 °C in the presence of [bmim][OAc] (0.198 g, 1 equiv, 1 mmol). An aliquots of the reaction mixture (40 μ L) was taken out immediately after the addition of the phenol to the mixture of Boc_2O and the IL (0 min), followed by withdrawal of samples after 15, 30, and 45 min intervals and subjected to record of ^1H NMR (400 MHz) in CDCl_3 as solvent.

Experimental Procedure for IR study:

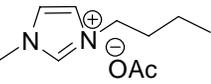
A mixture of 4-methylphenol (0.134 g, 1 mmol) and Boc_2O (0.22 g, 1 equiv, 1 mmol) was stirred magnetically at 40 °C in the presence of [bmim][OAc] (0.198 g, 1 equiv, 1 mmol). Aliquots of the reaction mixture (10 μ L) was taken out immediately after the addition of the phenol to the mixture of Boc_2O and the IL (0 min), followed by withdrawal of samples after 15, 30, and 45 min intervals and subjected to record IR.

Characterization of the compounds:

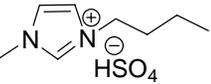
1-Butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]):

 Clear liquid, ^1H NMR (300 MHz, CDCl_3 , 27°C, TMS) δ : 0.95 (t, $^3J(\text{H,H})=9$ Hz, 3 H, CH_3), 1.35 (q, 2 H, CH_2), 1.87 (q, 2 H, CH_2), 4.01(s, 3 H, N- CH_3), 4.24 (t, $^3J(\text{H,H})=6$ Hz, 2 H, CH_2), 7.41(s, 1 H, CH), 7.47(s, 1 H, CH), 9.38 (s, 1 H, $\text{C}_2\text{-H}$).

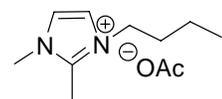
1-Butyl-3-methylimidazolium acetate ([bmim][OAc]):

 Clear liquid, 0.96 (t, $^3J(\text{H,H})=6$ Hz, 3 H, CH_3), 1.40 (q, 2 H, CH_2), 1.91 (q, 2 H, CH_2), 2.61 (s, 3H, OAc), 4.13 (s, 3 H, N- CH_3), 4.35 (t, $^3J(\text{H,H})=9$ Hz, 2 H, CH_2), 7.54(s, 1 H, CH), 7.66(s, 1 H, CH), 10.20 (s, 1 H, $\text{C}_2\text{-H}$); IR (KBr) v: 3403, 2969, 1643, 1017; Mass (EI) m/z : 139 [bmim]⁺

1-Butyl-3-methylimidazolium hydrogensulphate ([bmim][HSO₄]):

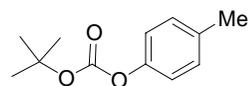
 Clear viscous liquid, 0.98 (bs, 3 H, CH_3), 1.41 (bs, 2 H, CH_2), 1.94 (bs, 2 H, CH_2), 4.14 (s, 3 H, N- CH_3), 4.35 (bs, 2 H, CH_2), 7.46 (s, 1 H, CH), 7.54 (s, 1 H, CH), 10.27 (s, 1 H, $\text{C}_2\text{-H}$).

1-Butyl-2,3-dimethylimidazolium acetate ([bdmim][OAc]):



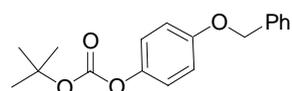
Clear viscous liquid, 0.96 (t, $^3J(H,H)=7.5$ Hz, 3 H, CH₃), 1.38 (q, 2 H, CH₂), 1.81 (q, 2 H, CH₂), 2.82 (s, 3H, CH₃), 4.03 (s, 3 H, N-CH₃), 4.24 (t, $^3J(H,H)=7.5$ Hz, 2 H, CH₂), 7.57 (d, $^3J(H,H)=1.8$ Hz, 1 H, CH), 7.76 (d, $^3J(H,H)=1.8$ Hz, 1 H, CH).

tert-Butyl *p*-tolyl carbonate²:



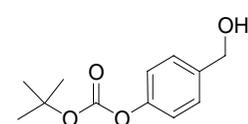
White solid, yield 90 %. Mp: 41°C. IR (KBr) v: 3493, 2982, 2933, 1758, 1247, 1150 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 27°C, TMS) δ: 1.55 (s, 9 H; O-Boc), 2.33 (s, 3 H, CH₃), 7.04 (d, $^3J(H,H)=8.3$ Hz, 2 H, ArCH), 7.16 (d, $^3J(H,H)=7.97$ Hz, 2 H, ArCH); Mass (EI) *m/z*: 208 [M⁺]

4-(Benzyloxy)phenyl *tert*-butyl carbonate²:



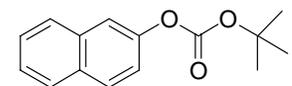
White solid, yield 85 %. Mp: 89°C. IR (KBr) v: 3469, 2982, 1752, 1506, 1242, 1105, 1014 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 27°C, TMS) δ: 1.55 (s, 9 H; O-Boc), 5.04 (s, 2 H, CH₂), 6.94 (d, $^3J(H,H)=8$ Hz, 2 H, ArCH), 7.07 (d, $^3J(H,H)=8$ Hz, 2 H, ArCH), 7.37-7.40 (m, 5H, ArCH); Mass (EI) *m/z*: 300 [M⁺]

tert-Butyl 4-(hydroxymethyl)phenyl carbonate²:



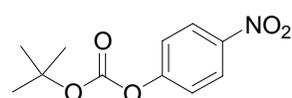
Yellow liquid, yield 70 %. IR (KBr) v: 3472, 2983, 1753, 1743, 1512, 1453, 1395, 1368, 1276, 1255, 1224, 1149 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 27°C, TMS) δ: 1.56 (s, 9 H; O-Boc), 4.62 (s, 2 H, CH₂), 7.13-7.15 (m, 2 H, ArCH), 7.32-7.35 (m, 2 H, ArCH); Mass (EI) *m/z*: 224 [M⁺]

tert-Butyl naphthalen-2-yl carbonate¹:



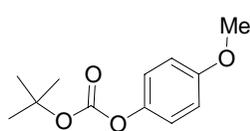
Off white solid, yield 97 %. Mp: 68 °C. IR (KBr) v: 3401, 1756, 1277, 1258, 1239, 1146 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 27°C, TMS) δ: 1.59 (s, 9 H; O-Boc), 7.29-7.33 (m, 1 H, ArCH), 7.46-7.50 (m, 2 H, ArCH), 7.69 (d, $^3J(H,H)=2.1$ Hz, 1 H, ArCH) 7.79-7.86 (m, 3 H, ArCH); ¹³C NMR (CDCl₃, 100 MHz) δ: 27.75, 83.62, 118.16, 120.90, 125.69, 126.55, 127.70, 129.39, 131.40, 133.74, 148.73, 152.01; Mass (EI) *m/z*: 244 [M⁺]

tert-Butyl 4-nitrophenyl carbonate²:



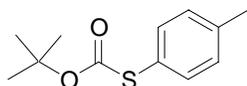
Off white solid, yield 85 %. Mp: 72°C. IR (KBr) v: 3436, 2983, 1756, 1525, 1220, 1143 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 27°C, TMS) δ: 1.58 (s, 9 H; O-Boc), 7.36 (d, $^3J(H,H)=7.2$ Hz, 2 H, ArCH), 8.26 (d, $^3J(H,H)=7.2$ Hz, 2 H, ArCH); Mass (EI) *m/z*: 239 [M⁺]

tert-Butyl 4-methoxyphenyl carbonate¹:



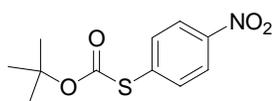
Off white solid, yield 85 %. Mp: 61 °C. IR (KBr) v: 3400, 1751, 1509, 1286, 1249, 1210, 1161 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 27°C, TMS) δ: 1.55 (s, 9 H; O-Boc), 3.79 (s, 3 H, OCH₃), 6.87 (d, ³J(H,H)=9 Hz, 2 H, ArCH), 7.07 (d, ³J(H,H)=9 Hz, 2 H, ArCH); Mass (EI) m/z: 224 [M⁺]

O-tert-Butyl S-p-tolyl carbonothioate²:



Yellow liquid, yield 90 %, IR (KBr) v: 3448, 2980, 1725, 1698, 1121, 1092 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 27°C, TMS) δ: 1.49 (s, 9 H; O-Boc), 2.36 (s, 3 H, CH₃), 7.19 (d, ³J(H,H)=7.8 Hz, 2 H, ArCH), 7.40 (d, ³J(H,H)=8.1 Hz, 2 H, ArCH) ; Mass (EI) m/z: 224 [M⁺]

O-tert-Butyl S-4-nitrophenyl carbonothioate²:

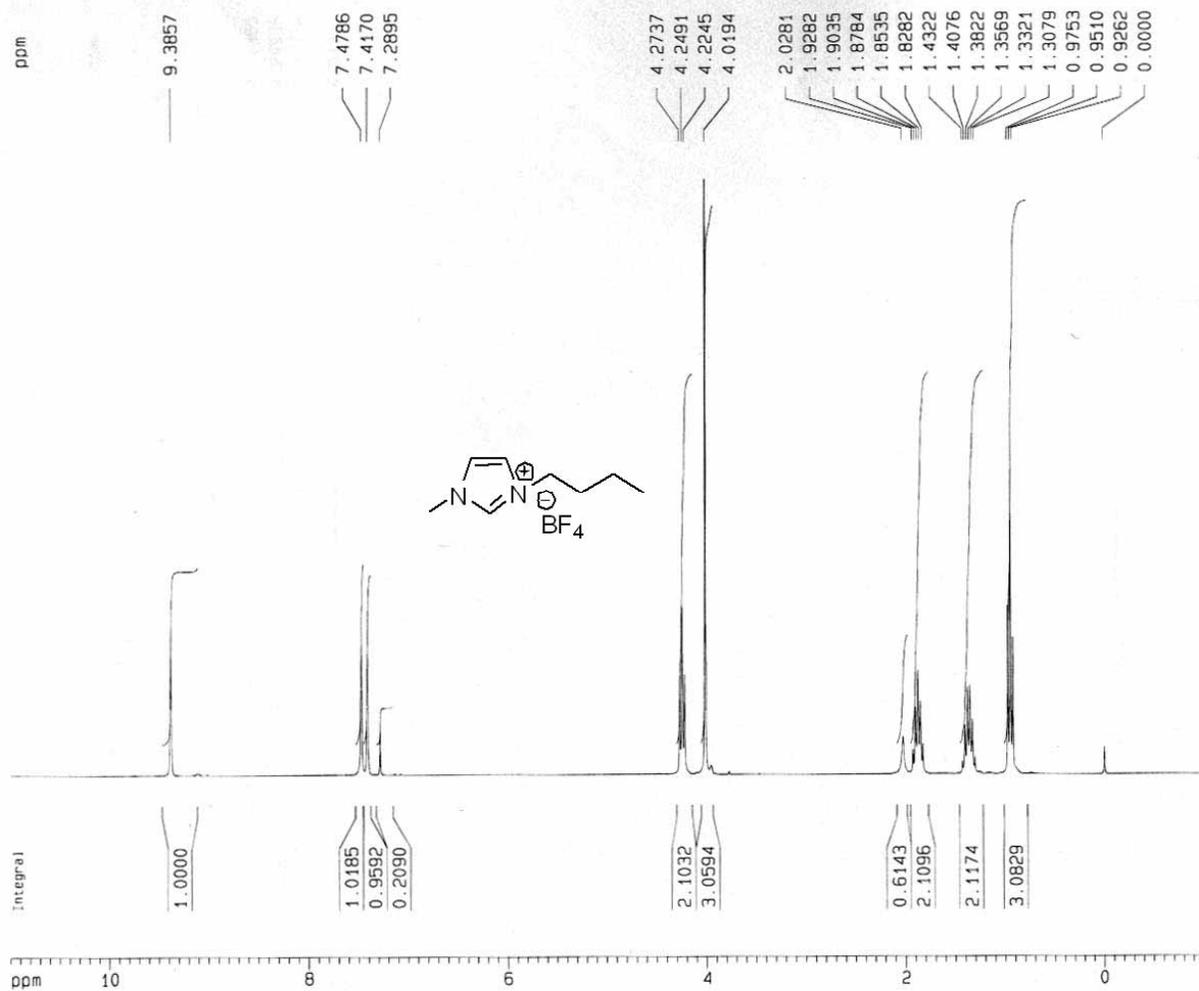


Yellow solid, yield 89 %. Mp: 62°C. IR (KBr) v: 3842, 3444, 2982, 2934, 1724, 1588, 1518, 1345, 1200, 1124 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 27°C, TMS) δ: 1.53 (s, 9 H; O-Boc), 7.71 (d, ³J(H,H)=8.7 Hz, 2 H, ArCH), 8.22 (d, ³J(H,H)=8.7 Hz, 2 H, ArCH) ; Mass (EI) m/z: 255 [M⁺]

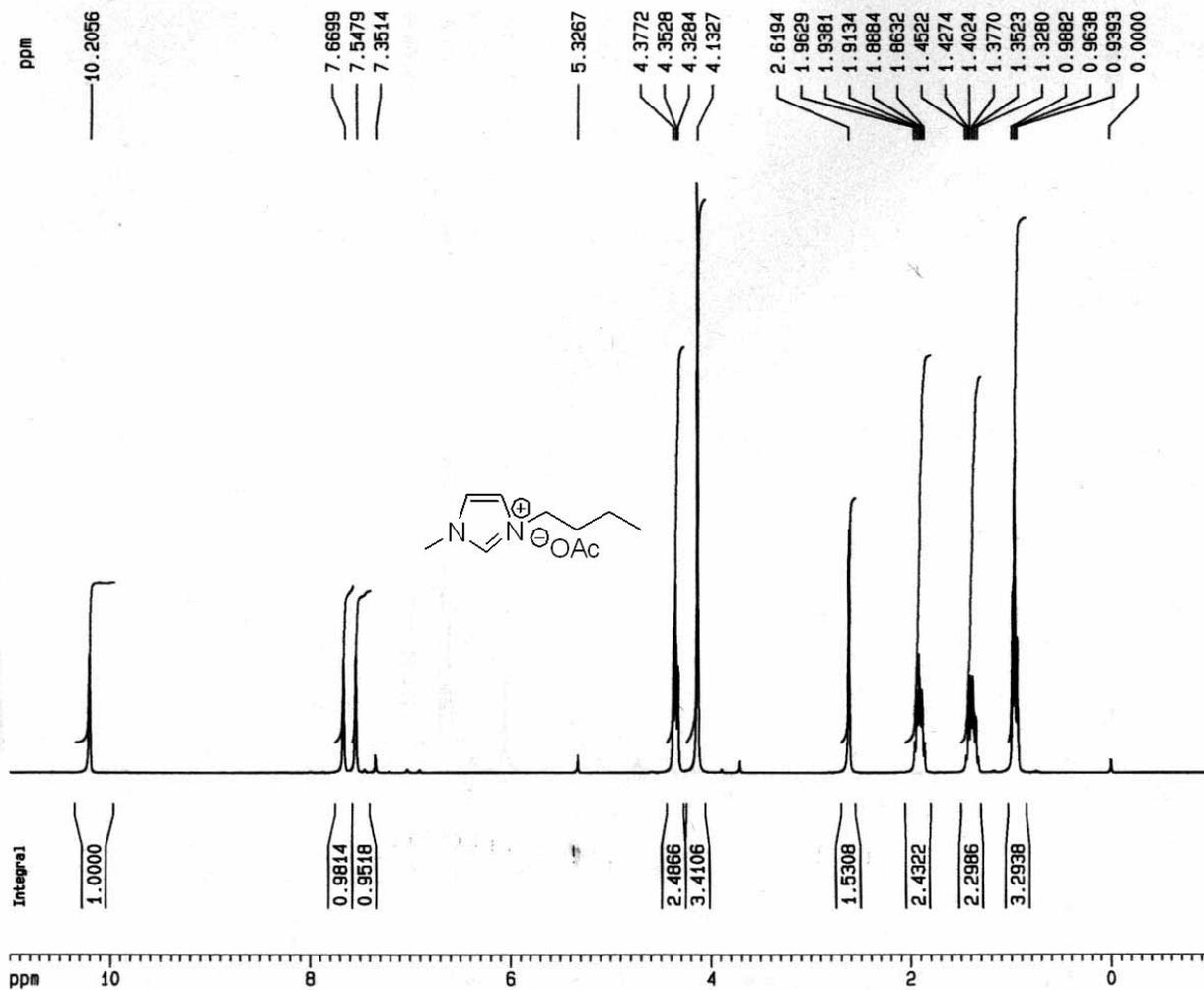
References:

- [1] Bartoli, G.; Bosco, M.; Carlone, A.; Dalpozzo, R.; Locatelli, M.; Melchiorre, P.; Palazzi, P.; Sambri, L.; *Synlett*. **2006**, 2104.
[2] Chebolu, R.; Chankeshwara, S. V.; Chakraborti, A. K.; *Synthesis*, **2008**, 1448.

[bmim][BF₄]: ¹H NMR (300 MHz, CDCl₃, 27 °C, TMS)



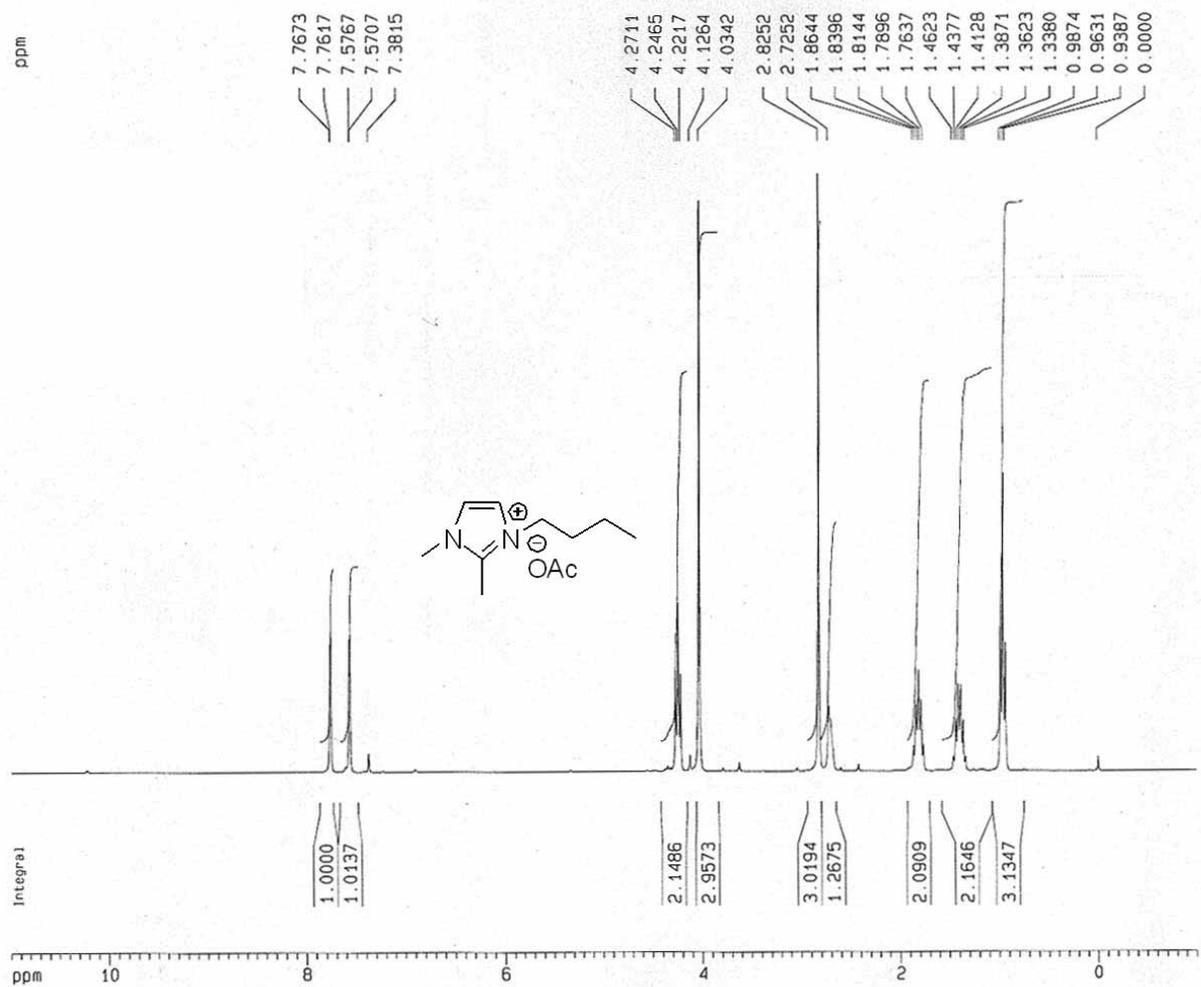
[bmim][OAc]: ¹H NMR (300 MHz, CDCl₃, 27°C, TMS)



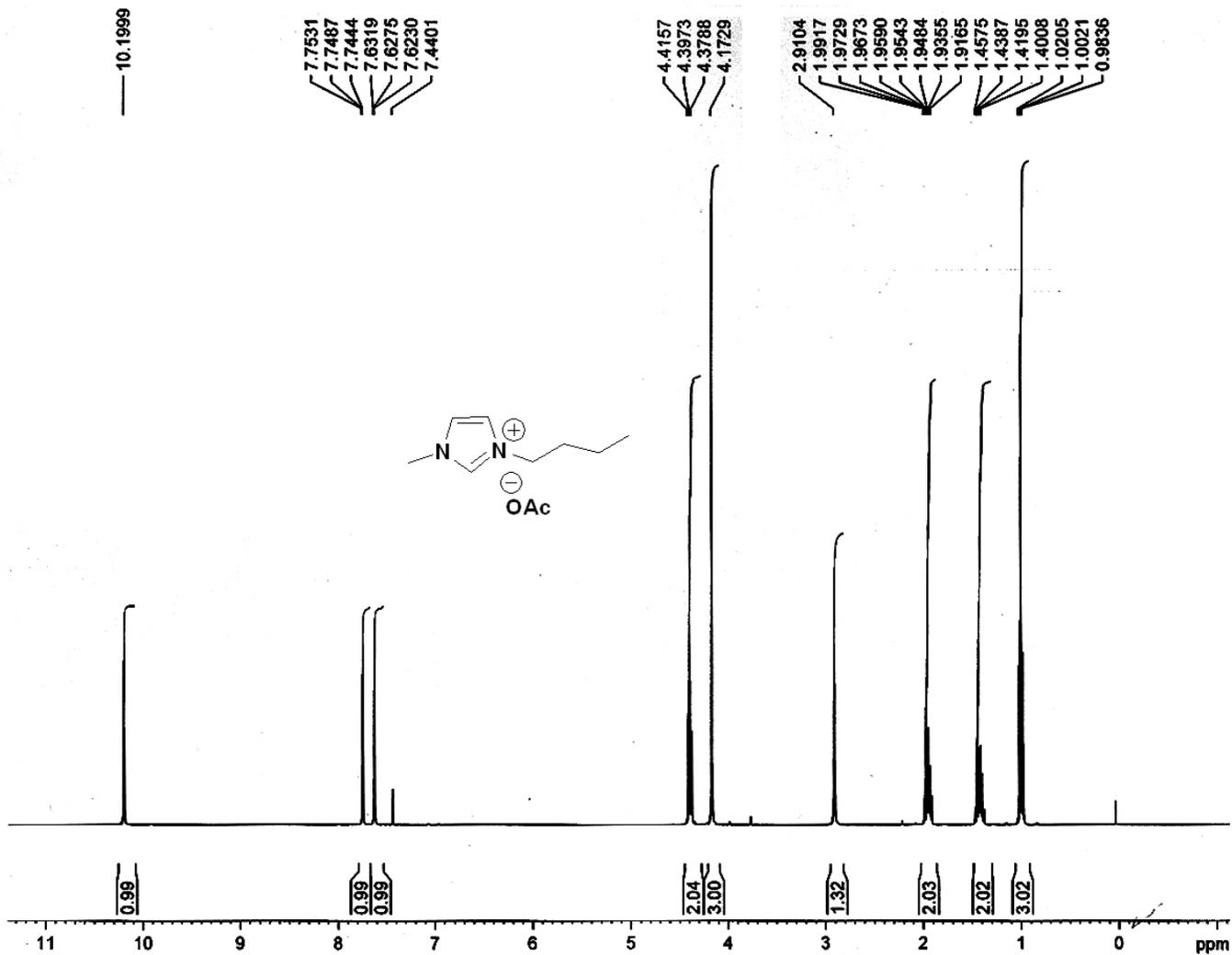
[bmim][HSO₄]: ¹H NMR (300 MHz, CDCl₃, 27°C, TMS)



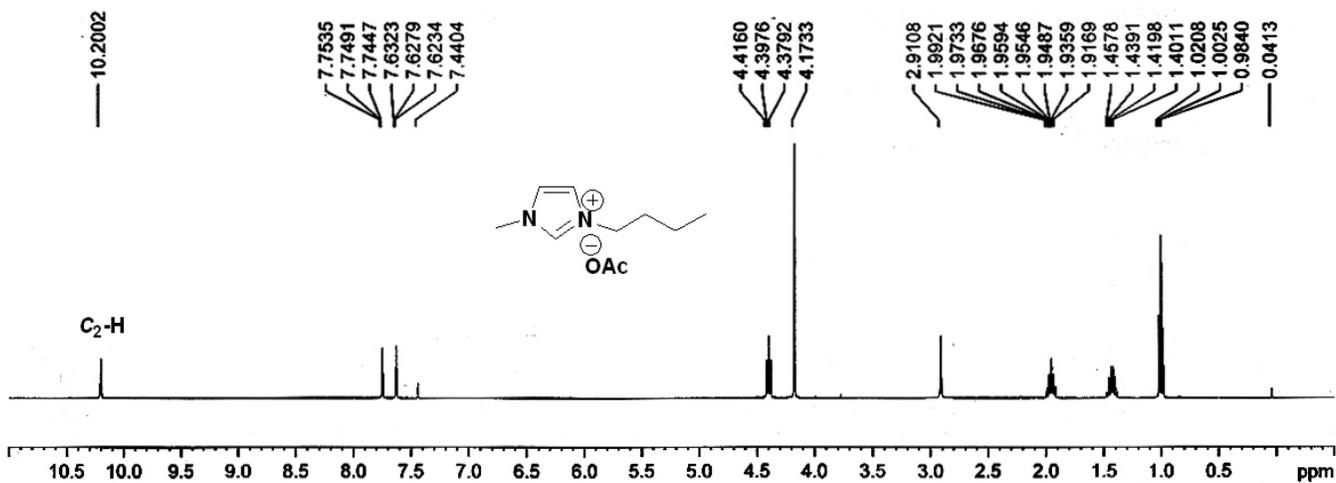
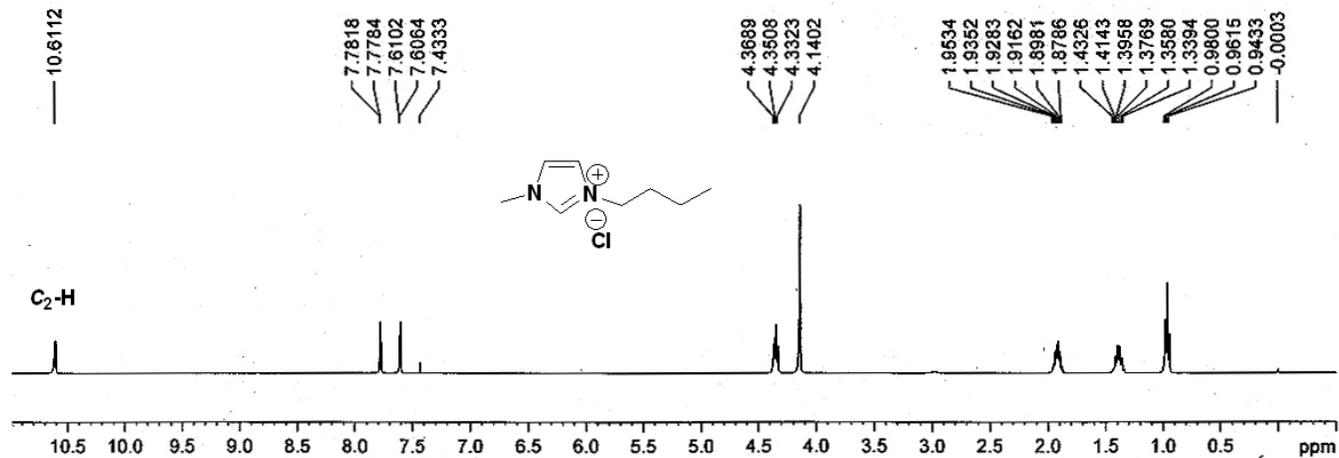
[bdmim][OAc]: ^1H NMR (300 MHz, CDCl_3 , 27°C , TMS)



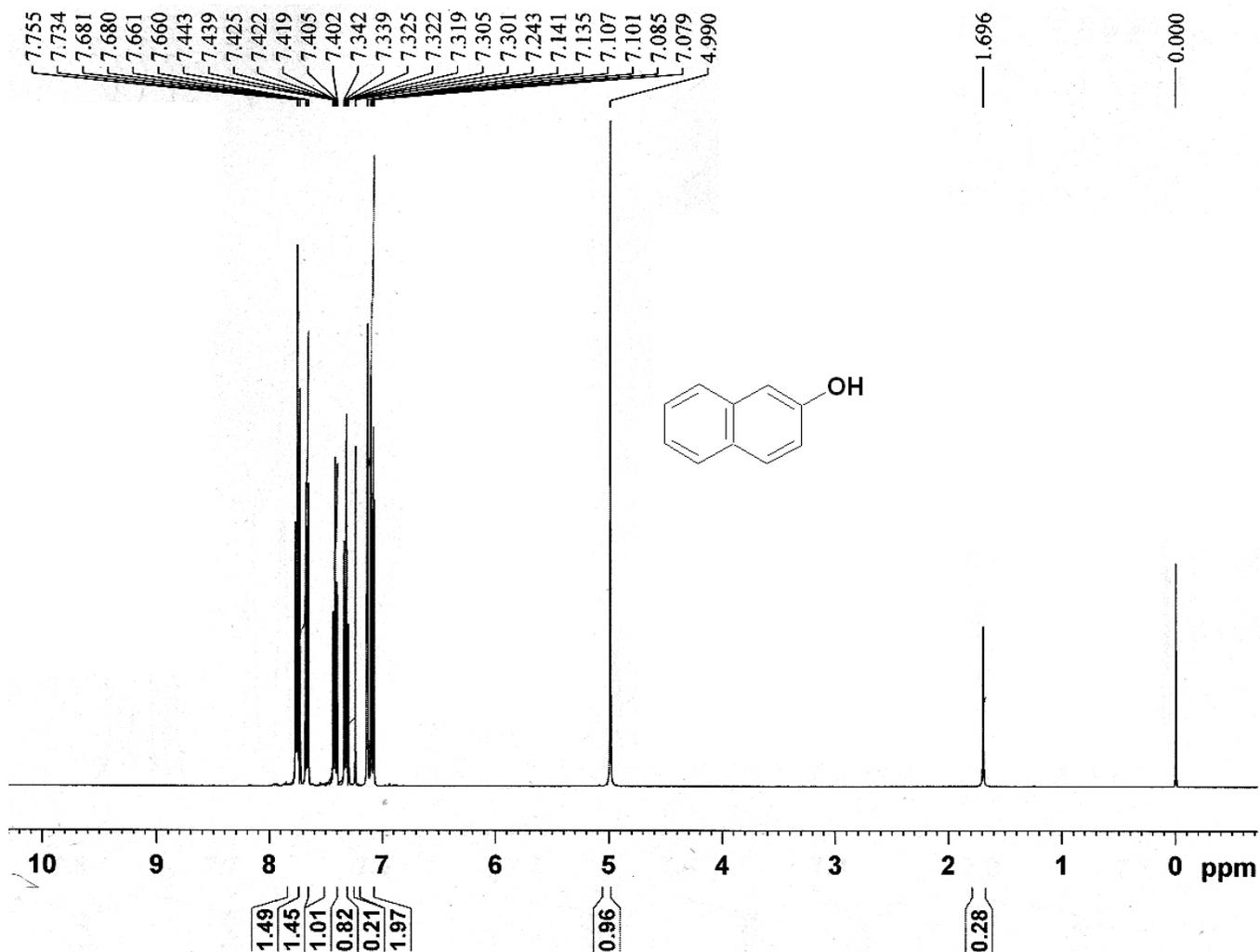
Recovered [bmim][OAc]: ^1H NMR (400 MHz, CDCl_3 , 27°C , TMS)



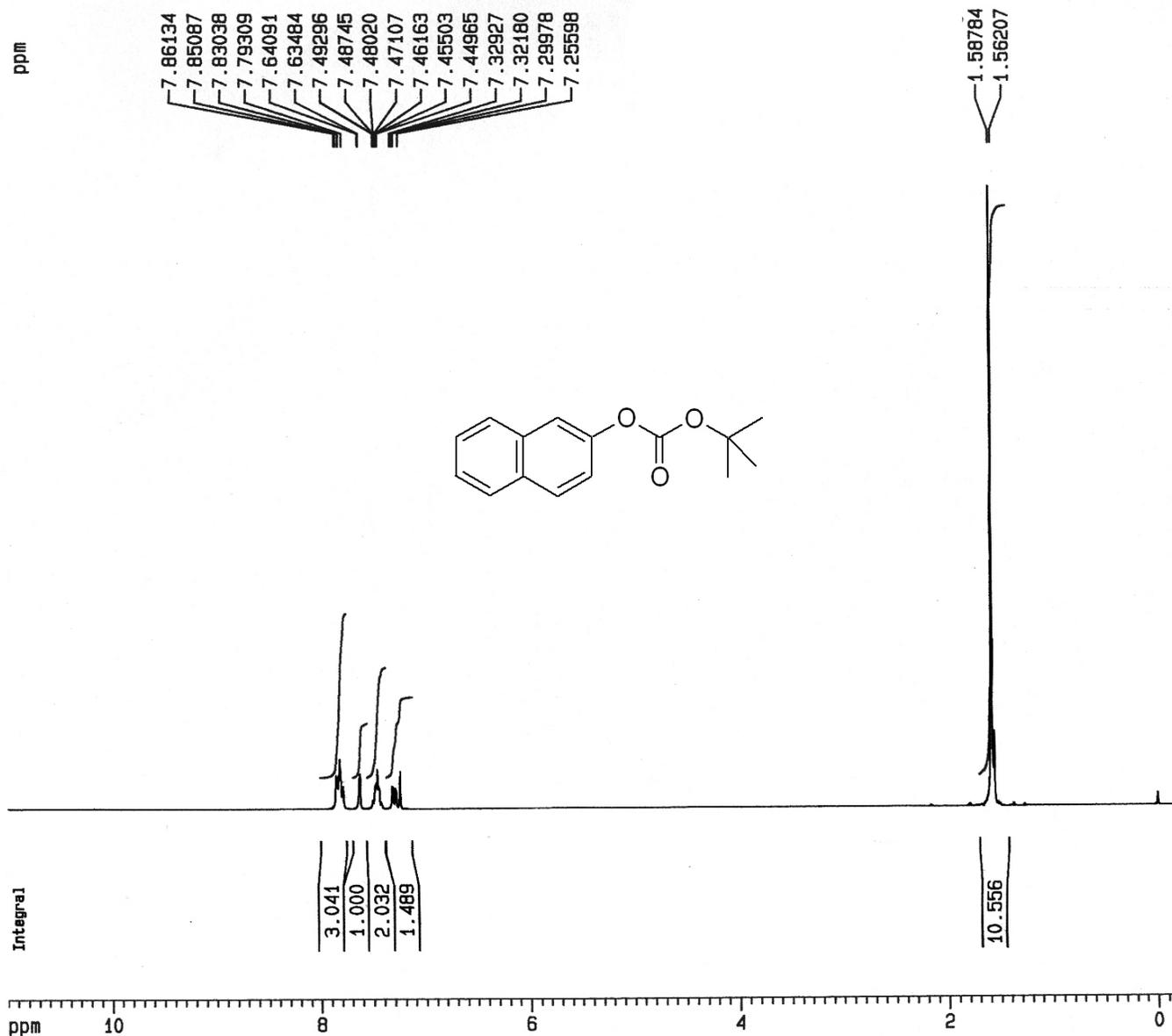
Spectral Comparison of Authentic Samples of [bmim][Cl] & [bmim][OAc]: ¹H NMR
(400 MHz, CDCl₃, 27°C, TMS)



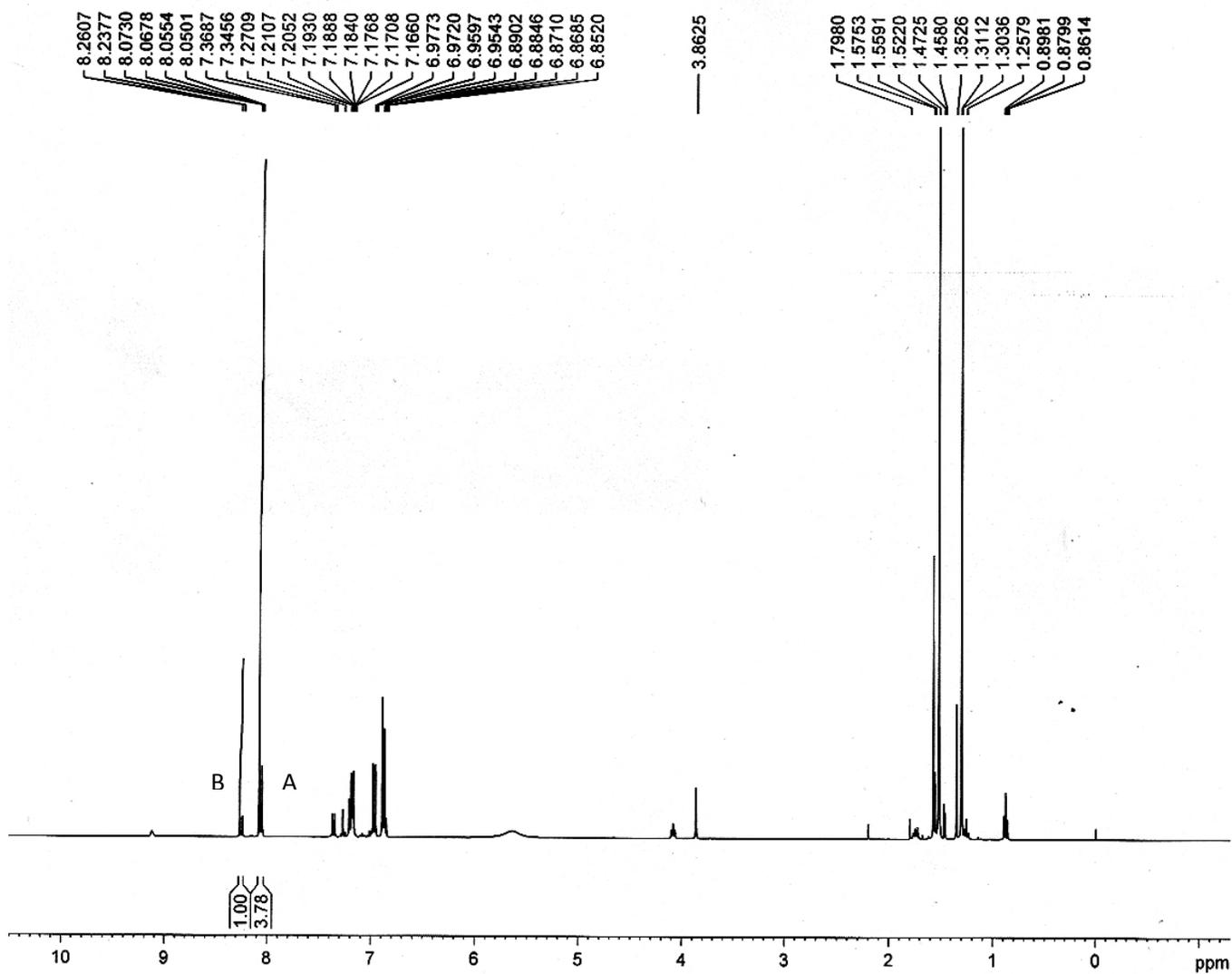
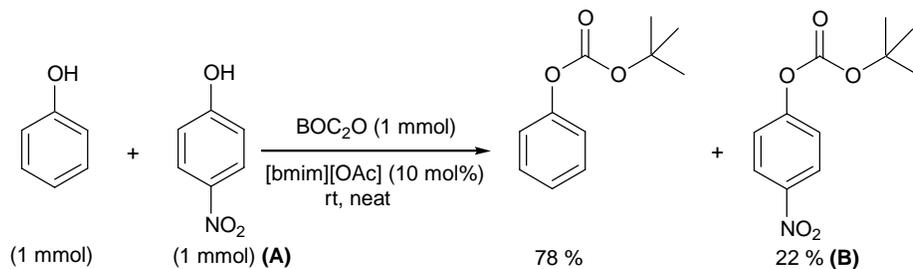
Characterisation of the Recovered Starting Material (Table 1, entry 7): ^1H NMR
(400 MHz, CDCl_3 , 27°C , TMS)



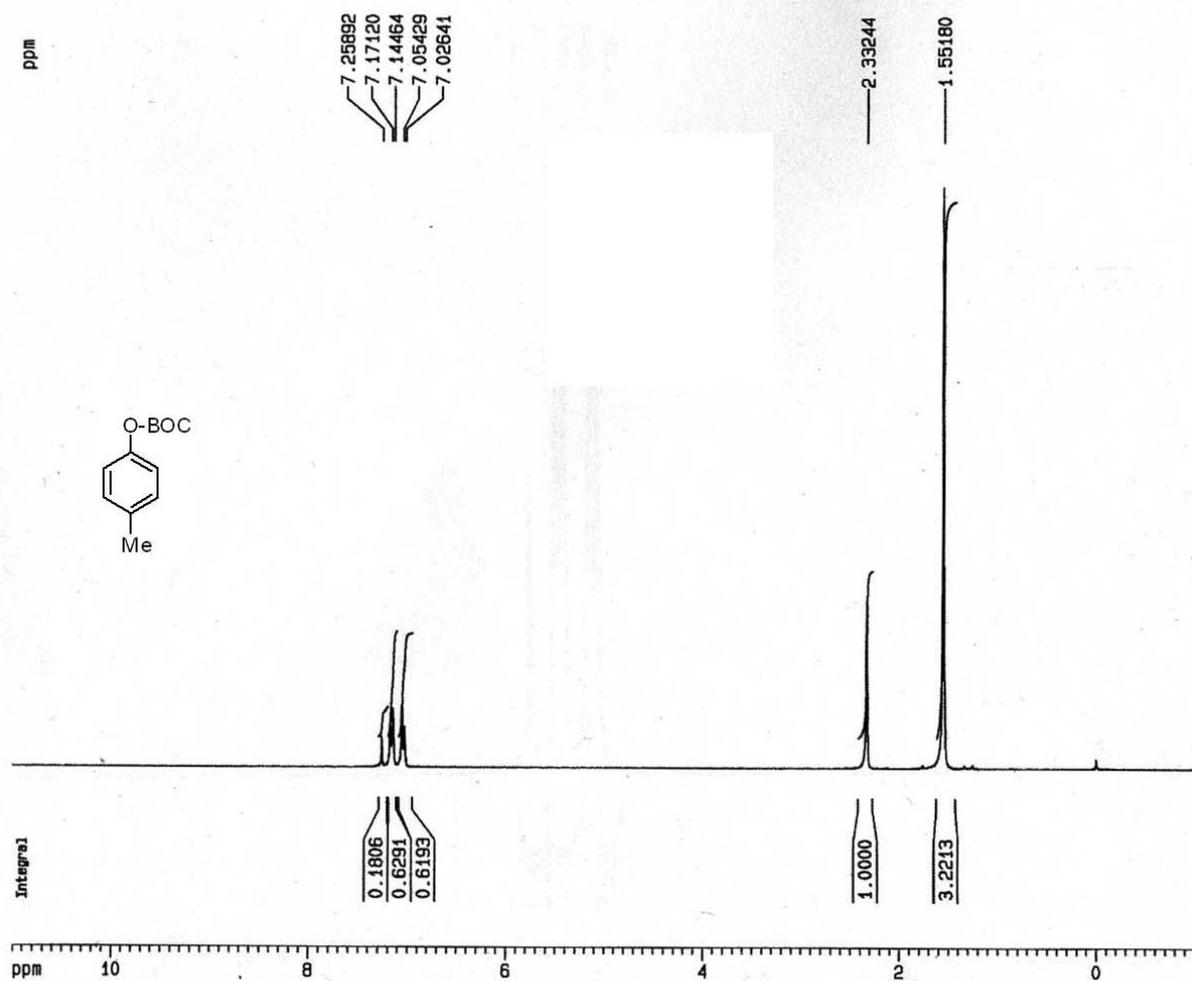
Characterisation of the Recovered Starting Material (Table 2, entry 3): ^1H NMR
(300 MHz, CDCl_3 , 27°C , TMS)



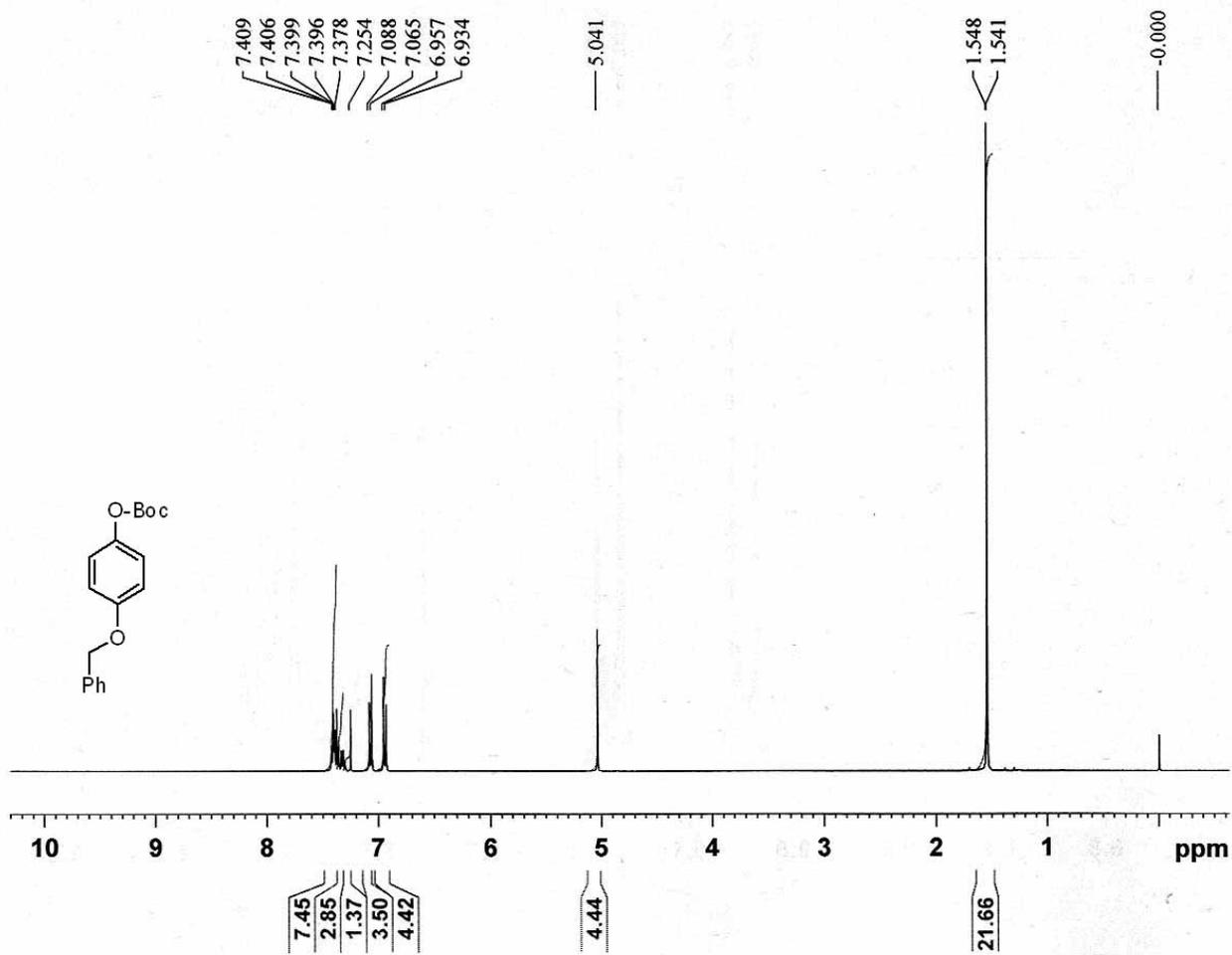
Inter-molecular competition for [bmim][OAc] catalysis (Scheme A): ^1H NMR (400 MHz, CDCl_3 , 27°C , TMS)



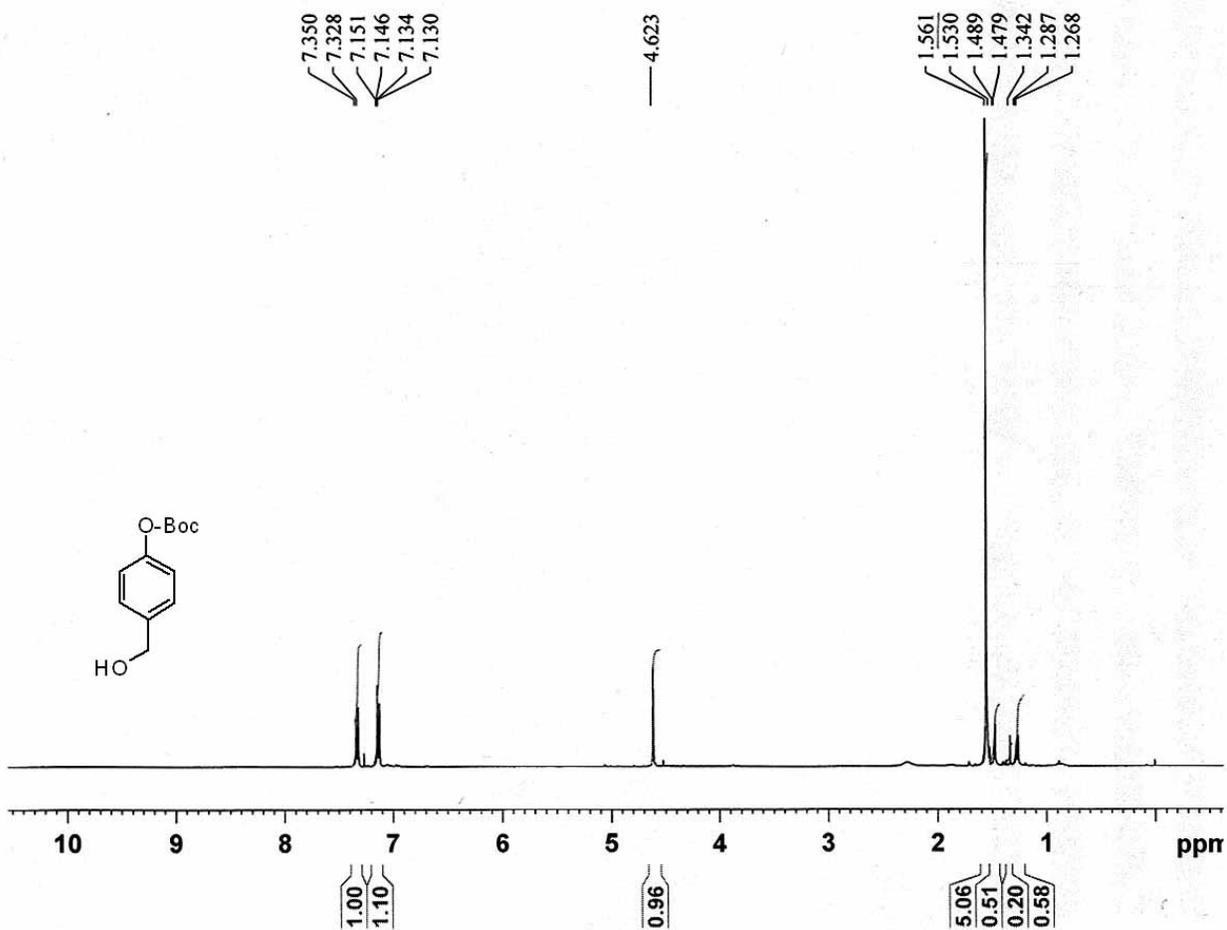
tert-Butyl 4-methylphenyl carbonate: ^1H NMR (300 MHz, CDCl_3 , 27°C , TMS)



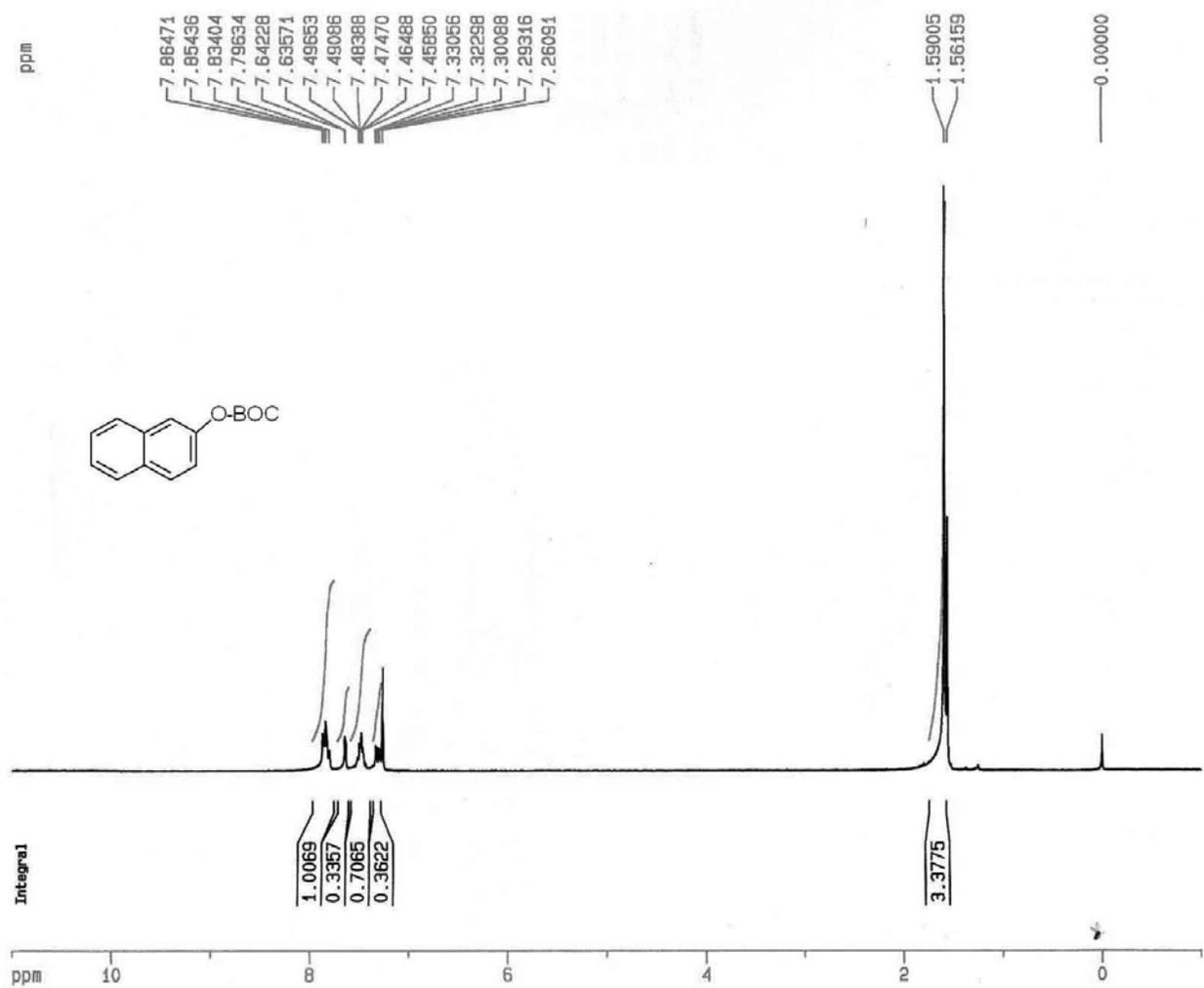
4-(Benzyloxy)phenyl *tert*-butyl carbonate: ^1H NMR (400 MHz, CDCl_3 , 27°C , TMS)



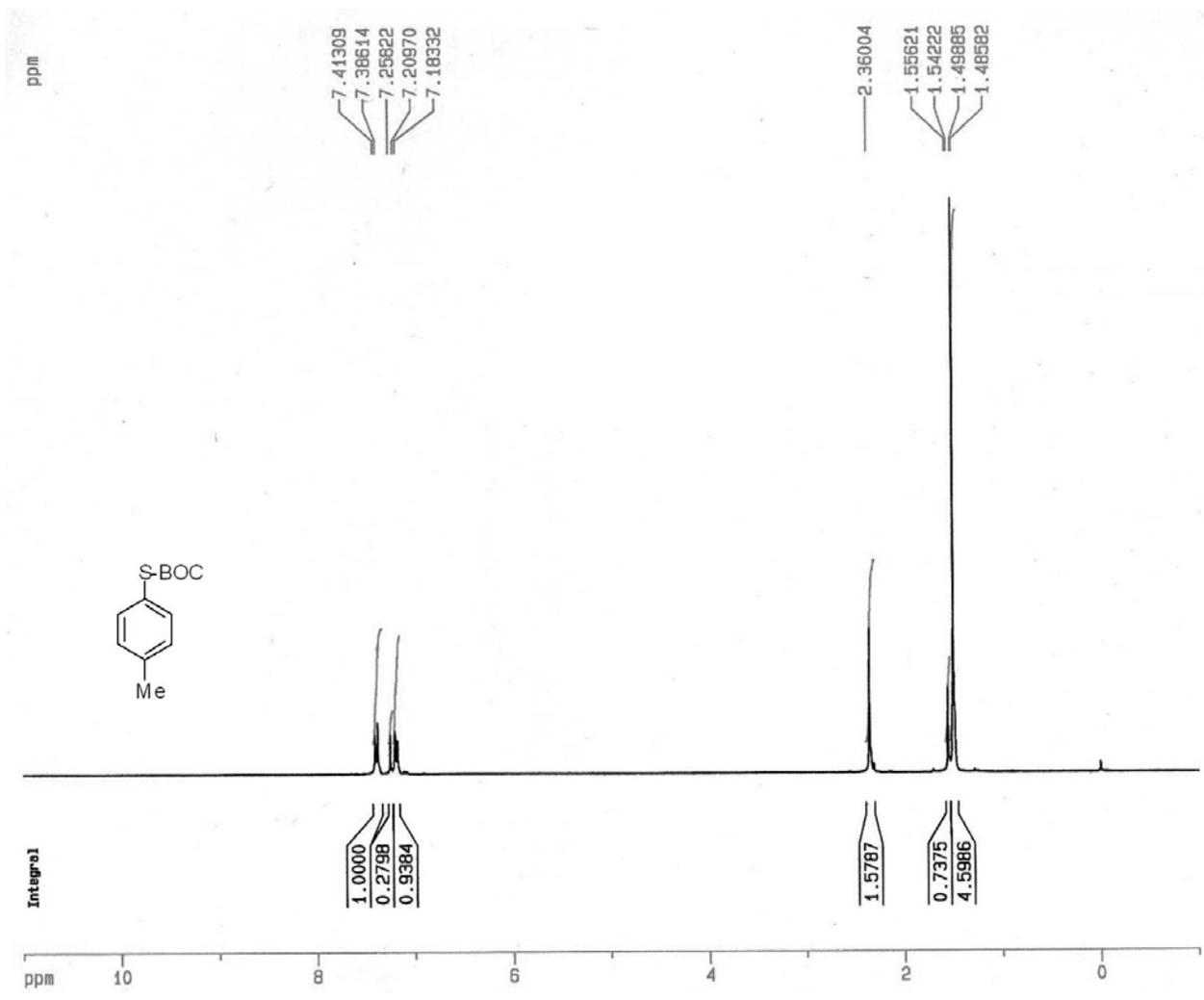
***tert*-Butyl 4-(hydroxymethyl)phenyl carbonate: ¹H NMR (400 MHz, CDCl₃, 27°C, TMS)**



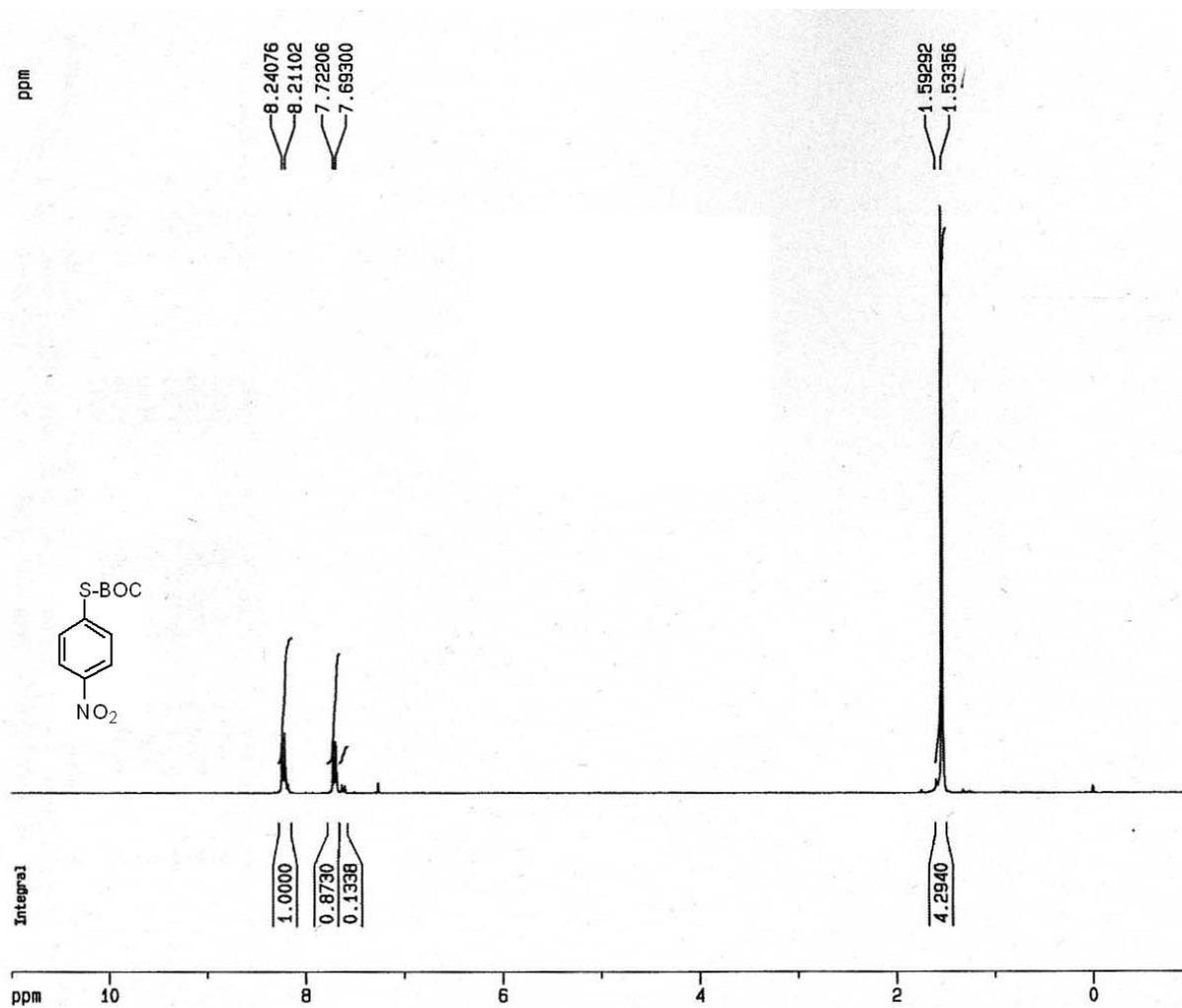
***tert*-Butyl naphthalen-2-yl carbonate: ^1H NMR (300 MHz, CDCl_3 , 27°C, TMS)**



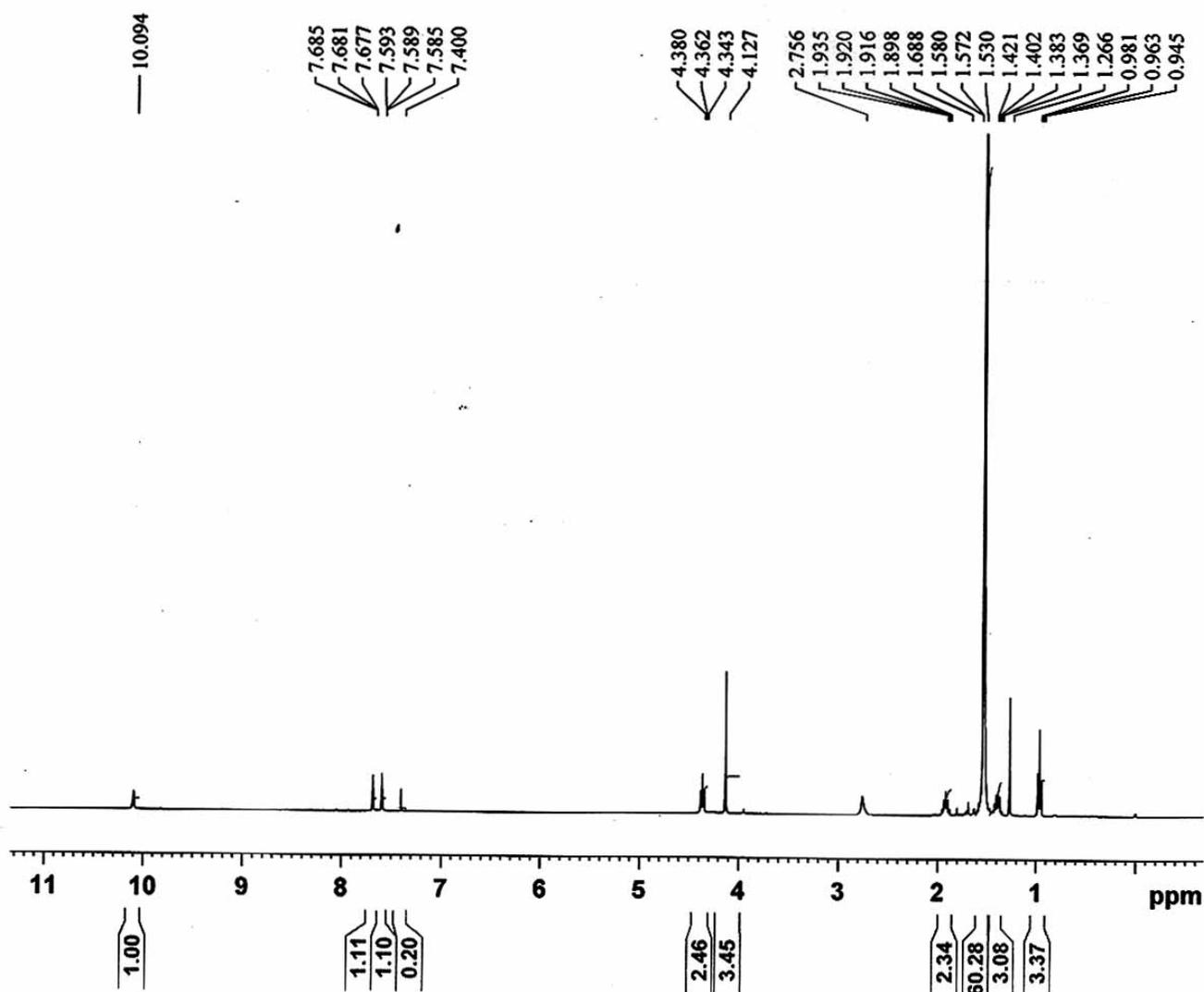
***O*-tert-Butyl *S*-4-methylphenyl carbonothioate: ¹H NMR (300 MHz, CDCl₃, 27°C, TMS)**



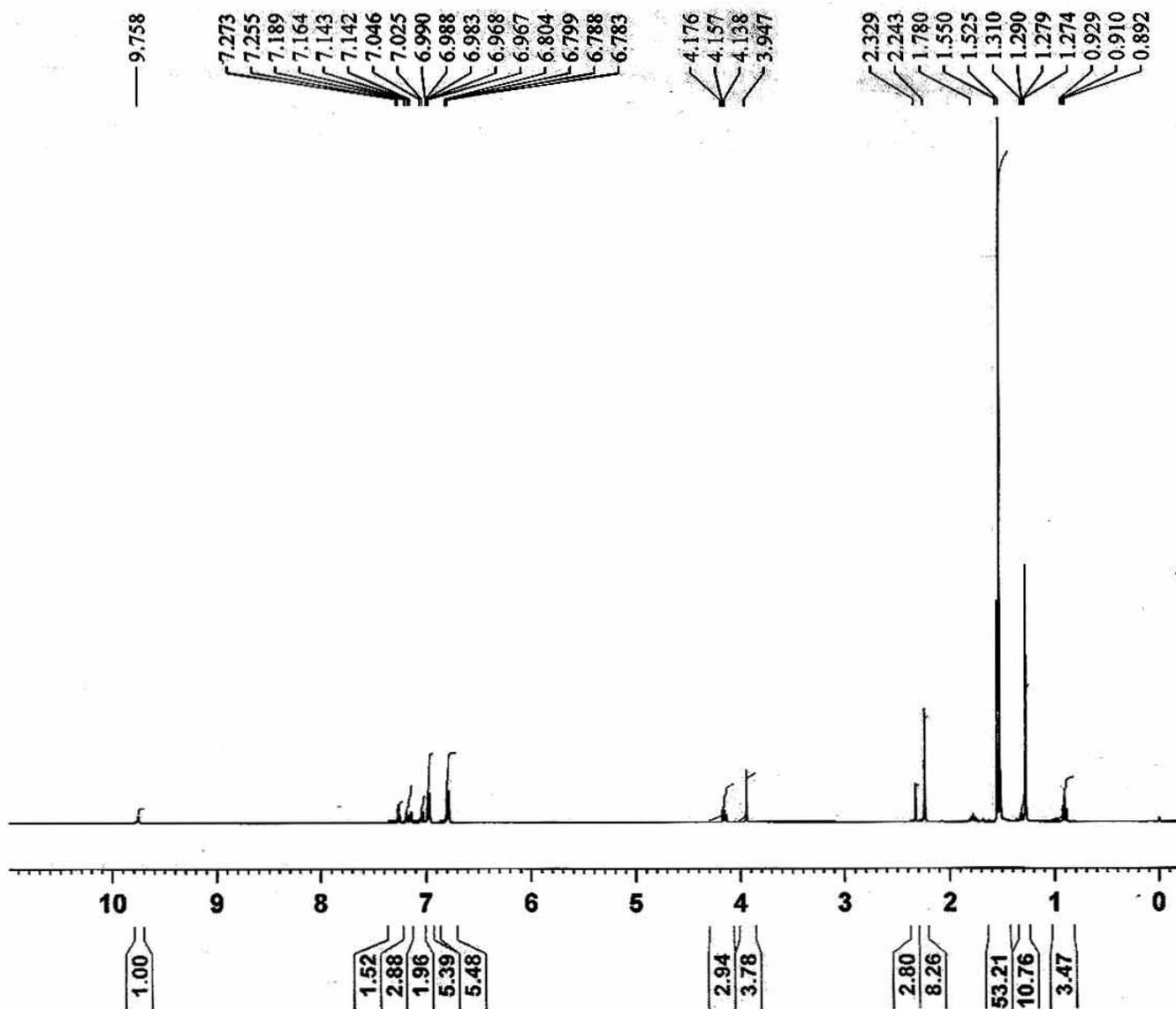
***O*-tert-Butyl *S*-4-nitrophenyl carbonothioate: ¹H NMR (300 MHz, CDCl₃, 27°C, TMS)**



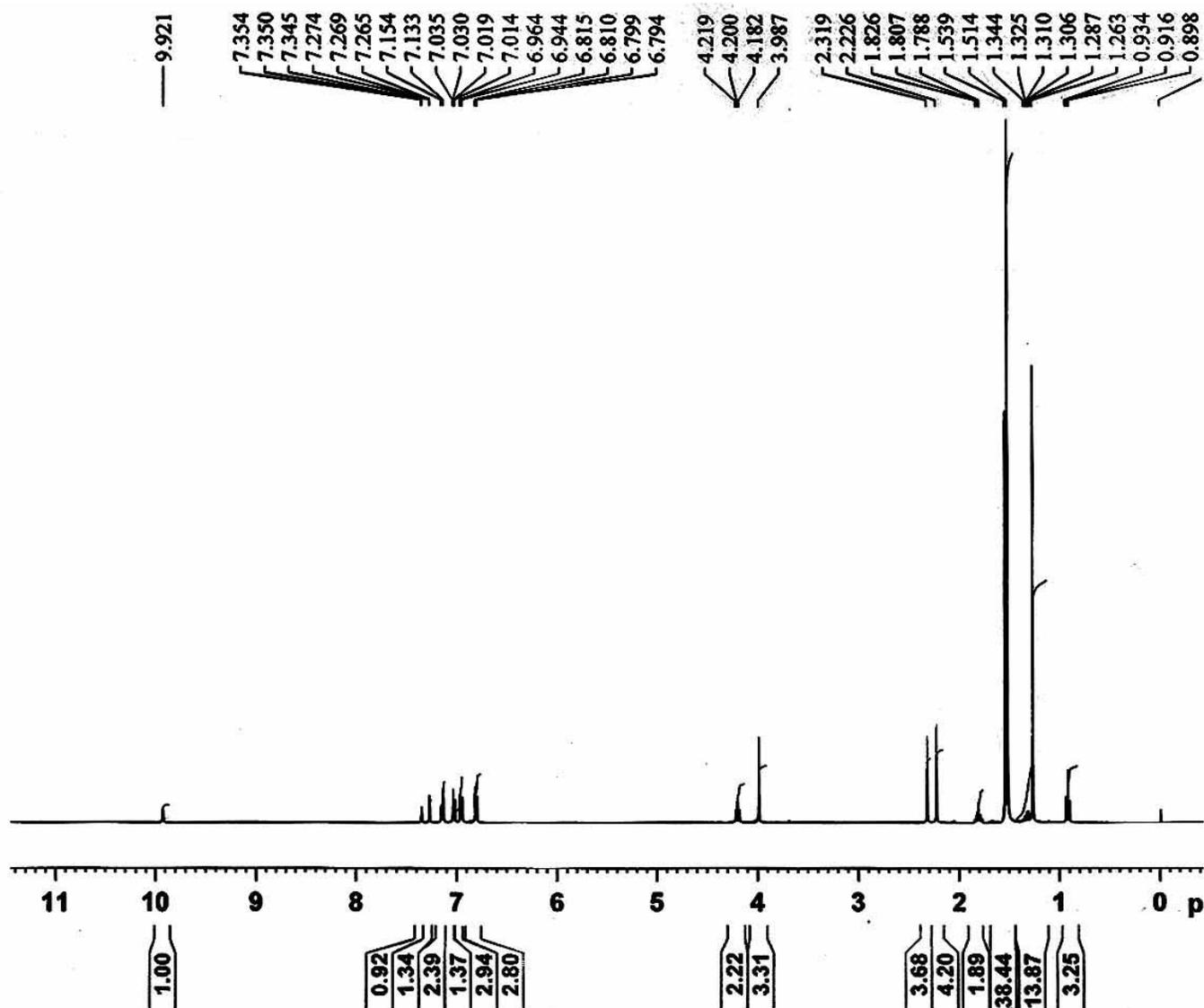
¹H NMR of aliquot mixture of Boc₂O and IL (400 MHz, CDCl₃, 27°C, TMS)



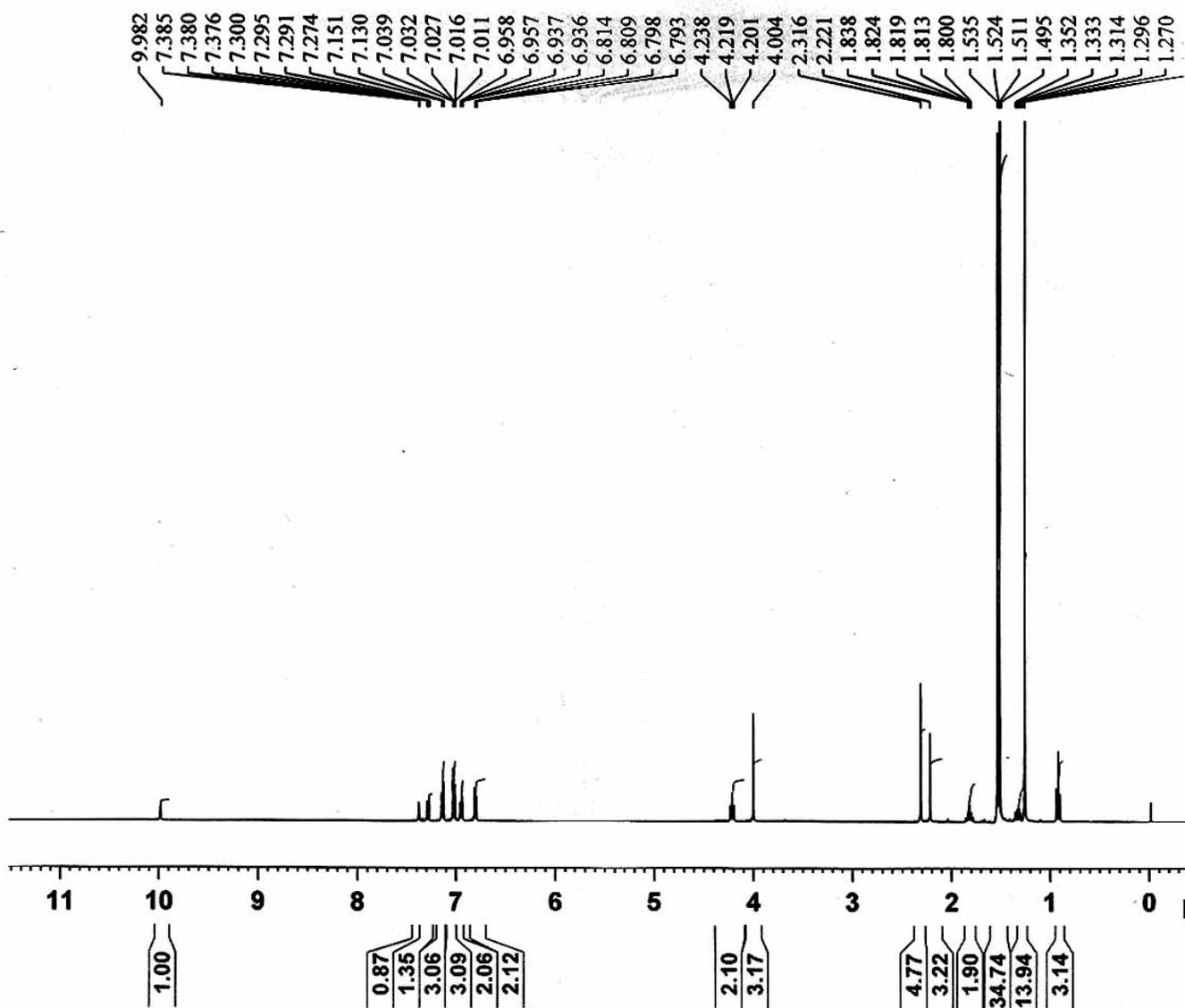
¹H NMR of aliquot of sample withdrawn at 0 min (400 MHz, CDCl₃, 27°C, TMS)



¹H NMR of aliquot of sample withdrawn at 15 min (400 MHz, CDCl₃, 27°C, TMS)



¹H NMR of aliquot of sample withdrawn at 30 min (400 MHz, CDCl₃, 27°C, TMS)



^1H NMR of aliquot of sample withdrawn at 45 min (400 MHz, CDCl_3 , 27°C, TMS)

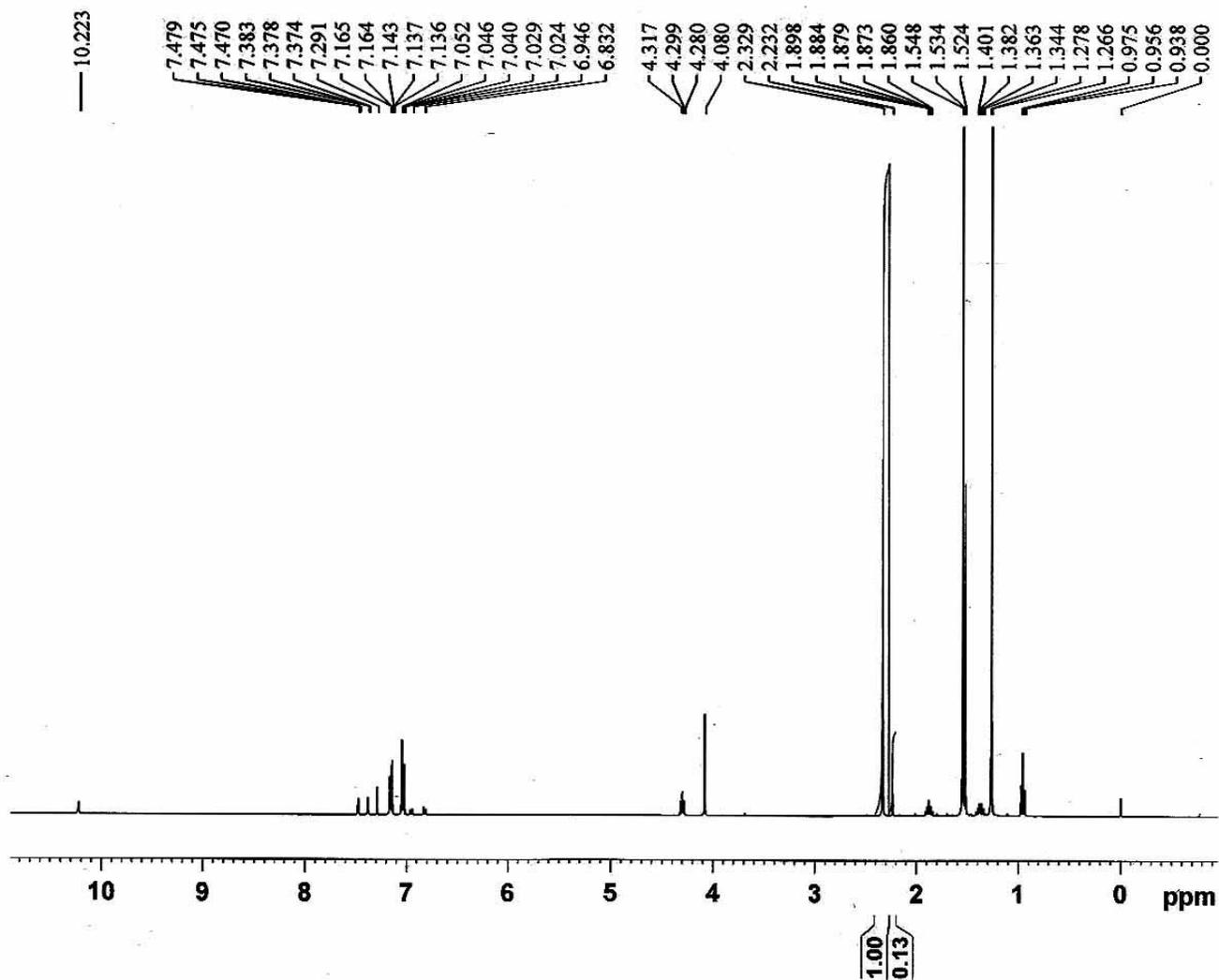


Figure A: IR of aliquots of sample withdrawn after various time intervals during the reaction of 4-methylphenol with Boc₂O in the presence of [bmim][OAc]

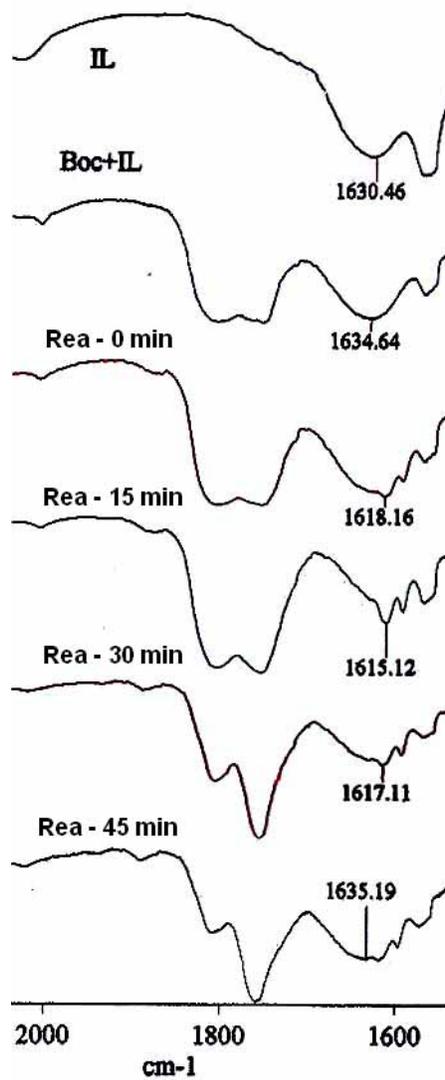


Figure 2: MALDI-TOF-TOF MS of aliquot sample after 45 min of reaction of 4-benzyloxyphenol with Boc₂O in the presence of [bmim][OAc].

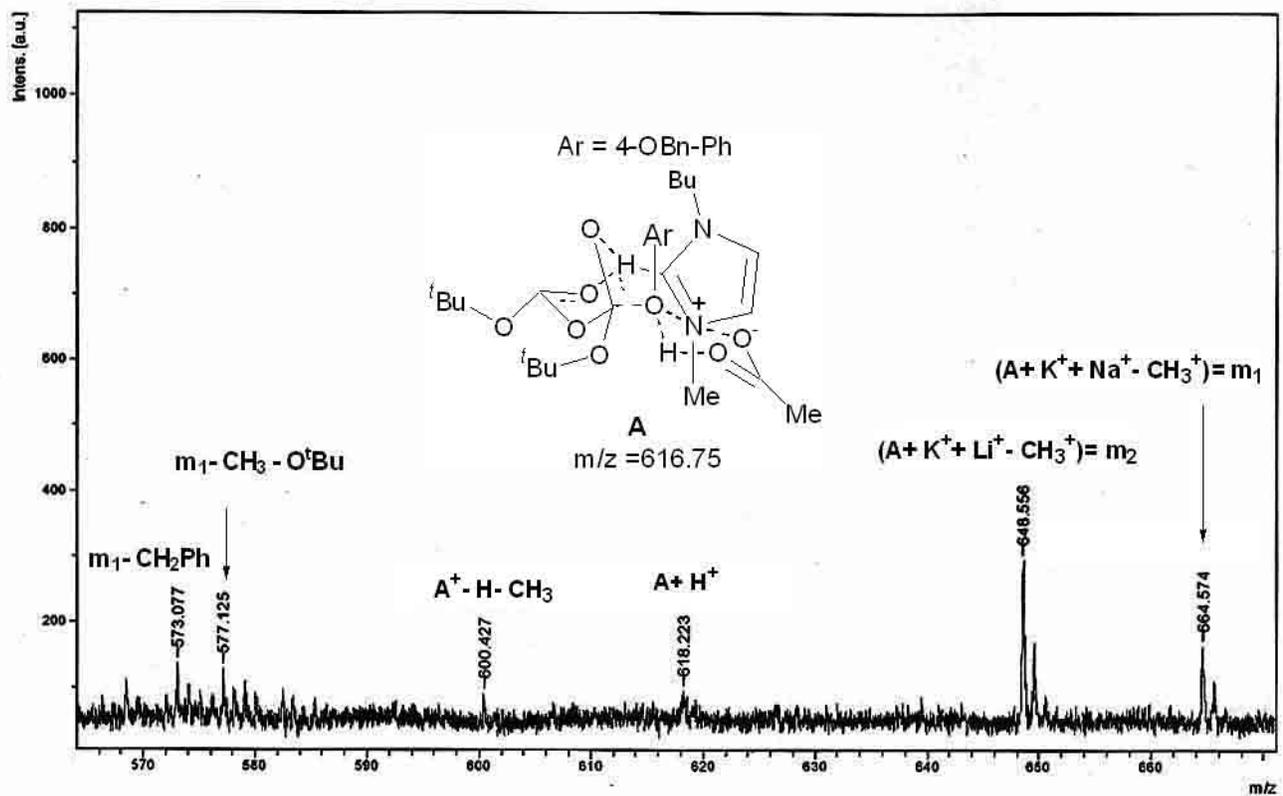


Figure B: MALDI-TOF-TOF MS MS OF m_1 of Figure 2 of Manuscript Text:

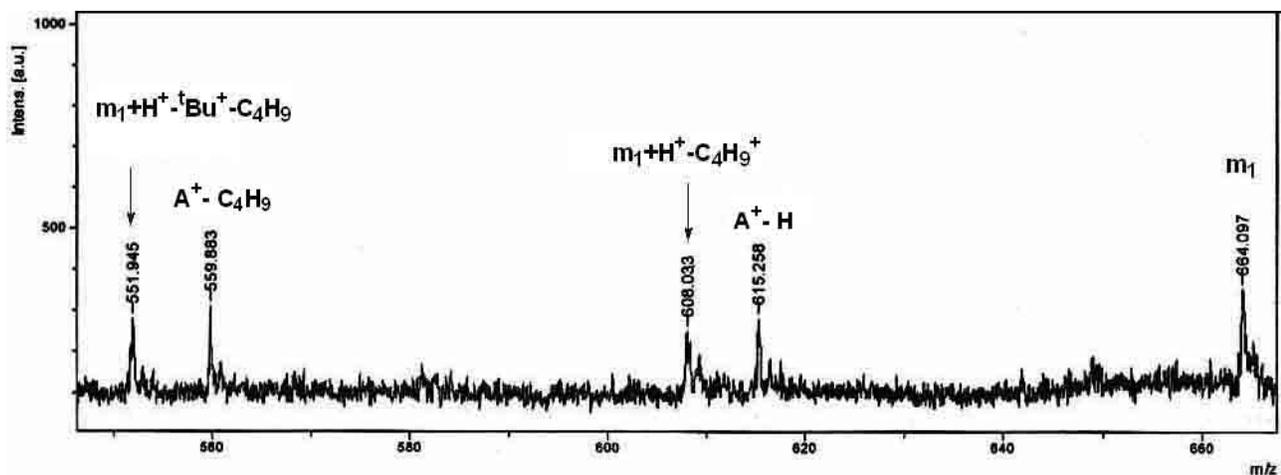


Figure C: MALDI-TOF-TOF MS² OF m_2 of Figure 2 of Manuscript Text:

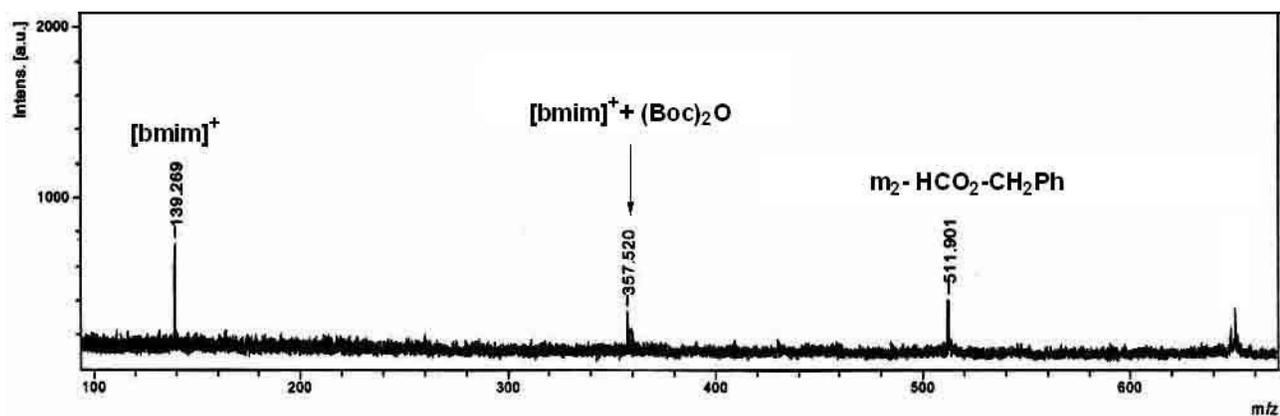


Figure 3. MALDI-TOF-TOF MS of aliquot sample after 90 min for the reaction of 2 in water in the presence of [bmim][OAc]:

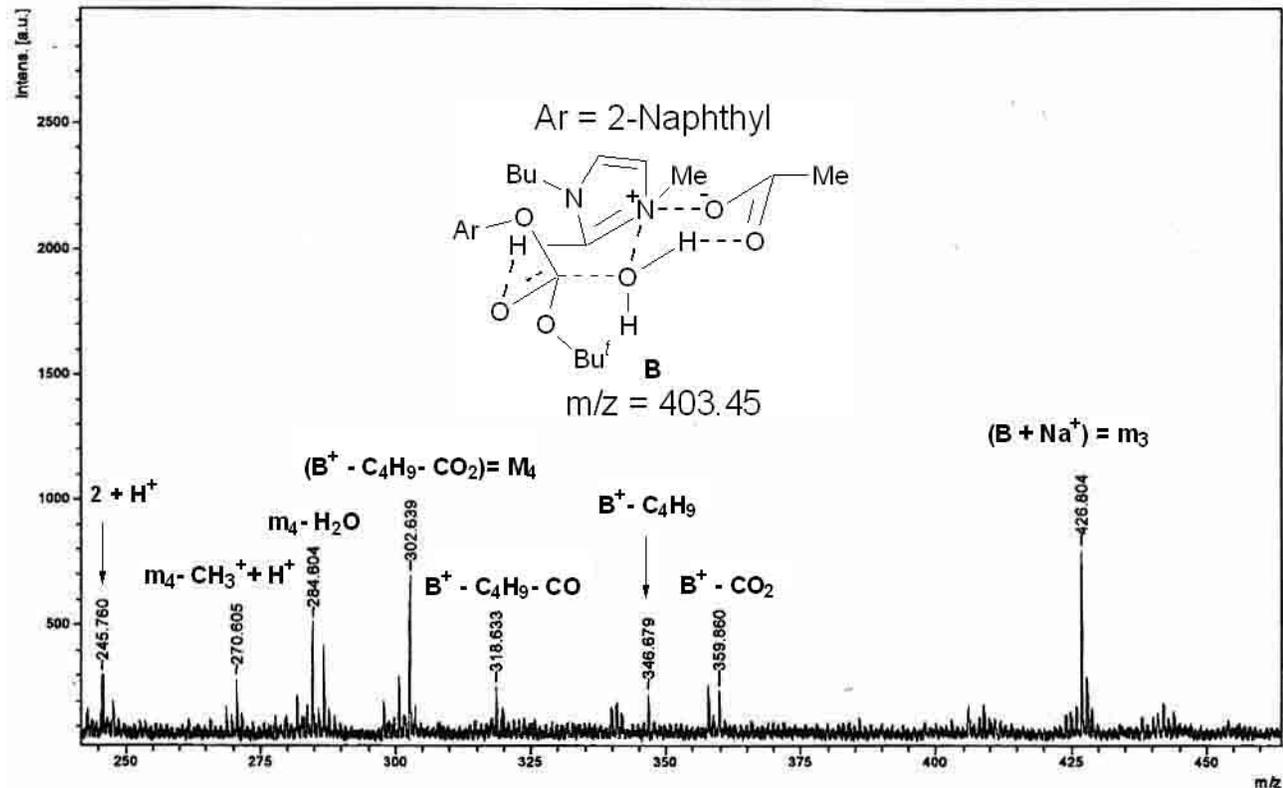


Figure C: MALDI-TOF-TOF MS² OF m_3 of Figure 3 of Manuscript Text:

