Electronic Supplementary Information

Facile Separation Catalyst System: Direct Diastereoselective Synthesis of (*E*)-*α,β*-Unsaturated Ketones Catalyzed by an Air-Stable Lewis Acidic/Basic Bifunctional Organobismuth Complex in Ionic Liquids

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1. General

The chemicals were purchased from Aldrich. Co., Ltd. and used as received unless otherwise indicated. $[S(CH_2C_6H_4)_2BiCl]$ (**2**), the precursor of $[S(CH_2C_6H_4)_2Bi(OH_2)]^+[BF_4]^-$ (**1**), was prepared according to the procedure described elsewhere.[1] The catalytic reactions were carried out in ambient environment. The NMR spectra were recorded at 25 ^oC over an INOVA-400M (Varian) instrument calibrated using tetramethylsilane (Me_4Si) as internal standard. Elemental analysis was performed over VARIO EL III (Elementar). Single-crystal X-ray diffraction analysis of **1** was performed over a SMART 1000 instrument stationed in the Hong Kong Baptist University. TG-DSC analysis was performed on a NETZSCH-STA-449C equipment (Operation condition: N_2, 5 ˚C/min heating rate). Melting points were determined over a XT-4 micro melting point apparatus (Beijing Tech Instrument Co., Ltd.). The acidity was measured by the Hammett indicator method.[2] The employed indicators included crystal violet (pK_a = 0.8), dimethyl yellow (pK_a = 3.3), methyl red (pK_a = 4.8), neutral red (pK_a = 6.8), bromothymol blue (pK_a = 7.2), and thymol blue (pK_a = 8.9). Acid/base strength was expressed by Hammett acidity function (H_0) and Hammett basicity function (H_-), respectively scaled by pK_a value of the indicators.

2. TG-DSC analysis of organobismuth complex 1

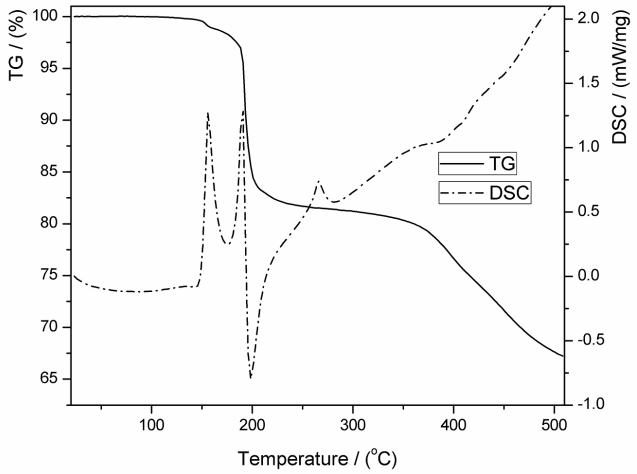


Fig. S1 TG-DSC curves of complex **1**.

The thermal behavior of complex **1** was investigated by TG-DSC in a N_2 atmosphere (Fig. S1). The TG-DSC curves show three stages of weight loss. The endothermic step below 150 ˚C can be assigned to the removal of H_2O molecules. The material is stable up to about 200 ˚C. The weight loss of exothermic nature at 200 ˚C is plausibly due to the oxidation of organic entities. Based on the TG results, the empirical formula of the complex is estimated to be $[S(CH_2C_6H_4)_2Bi(OH_2)]^+[BF_4]^-$ (**1**).

3. Crystal data refinements

Refinement of F^2 against all reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors (gt), *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on all data should be even larger. Hydrogen site location: inferred from neighbouring sites, H atoms treated by a mixture of independent and constrained refinement. Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) adopted to solve structure: SHELXS97 (Sheldrick, 1990); program(s) adopted to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: Bruker *SHELXTL*; software used to prepare material for publication: Bruker *SHELXTL*.

4. Typical procedure for synthesis of *(E)-α,β*-unsaturated ketones in various solvents catalyzed by catalyst 1

To a 50 mL round bottomed flask were added catalyst **1** (0.0526 mg, 0.1 mmol), PhCHO (**4a**, 1.060 g, 10.0 mmol), *n*-$PrNH_2$ (0.590 g, 10.0 mmol), cyclohexanone (**5a**, 2.940 g, 30.0 mmol) and solvent (1.0 mL). Then the mixture was stirred for 6 h under TLC analysis until PhCHO as well as the intermediate imine obtained from PhCHO and *n*-$PrNH_2$ were almost consumed completely. The mixture was subject to column chromatography on silica gel (200–300 meshes) (petroleum ether/ethyl acetate = 5/1, v/v).

5. Typical procedure for synthesis of *(E)-α,β*-unsaturated ketones in ionic liquids catalyzed by catalyst 1

To a 50 mL round bottomed flask were added catalyst **1** (0.0526 mg, 0.1 mmol), PhCHO (**4a**, 1.060 g, 10.0 mmol), *n*-$PrNH_2$ (0.590 g, 10.0 mmol), cyclohexanone (**5a**, 2.940 g, 30.0 mmol) and [Bmim]BF_4 (1.0 mL). Then the mixture was stirred for 6 h under TLC analysis until PhCHO as well as the intermediate imine obtained from PhCHO and *n*$PrNH_2$ were consumed completely. Then the mixture was allowed to settle for 5 min, and the resulting mixture was found self-separated into two phases. The upper layer comprises reactants and products, and the lower layer ionic liquids, catalyst, and water (generated

during reaction). After simple separation by decantation, the upper phase was subject to column chromatography on silica gel (200-300 meshes) (petroleum ether/ethyl acetate = 5/1, v/v). The yield of **6a** was 1.825 g (98% based on PhCHO). All the products were characterized by comparison of ^{1}H and ^{13}C NMR spectral data.[3]

6. Characterization data of *(E)-α,β*-unsaturated ketones

6.1 (*E*)-2-Benzylidenecyclohexanone (6a)

δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.77–1.78 (2H, m, CH_2), 1.92–1.94 (2H, m, CH_2), 2.54 (2H, t, J = 6.8 Hz, CH_2), 2.84–2.85 (2H, m, CH_2), 7.32–7.35 (1H, m, ArH), 7.36–7.40 (4H, m, ArH), 7.50 (1 H, t, J = 2.4 Hz, ArCH). δ_C (100 MHz, $CDCl_3$; Me_4Si) 23.40, 23.87, 28.92, 40.33, 128.31, 128.50, 130.27, 135.56, 136.66, 201.78.

6.2 (*E*)-2-(4-Methylbenzylidene)cyclohexanone (6b)

δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.75–1.78 (2H, m, CH_2), 1.91–1.94 (2H, m, CH_2), 2.37 (3H, s, CH_3), 2.51–2.55 (2H, t, J= 6.8 Hz, CH_2), 2.82–2.86 (2H, m, CH_2), 7.18–7.20 (2H, d, J = 8.0 Hz, ArH), 7.30–7.33 (2H, d, J = 8.4 Hz, ArH), 7.49 ppm (1 H, s, ArCH). δ_C (100 MHz, $CDCl_3$; Me_4Si) 21.38, 23.36, 23.89, 29.00, 40.28, 129.11, 130.45, 132.82, 135.83, 138.81, 159.98, 202.11.

6.3 (*E*)-2-(4-Chlorobenzylidene)cyclohexanone (6c)

δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.61–1.69 (2H, m, CH_2), 1.77–1.85 (2H, m, CH_2), 2.42 (2H, t, J = 6.8 Hz, CH_2), 2.68 (2H, m, CH_2), 7.19–7.25 (4H, m, ArH), 7.32 (1H, t, J = 2.2 Hz, Ar-CH=C). δ_C (100 MHz, $CDCl_3$; Me_4Si) 23.23, 23.74, 28.85, 40.20, 128.53, 131.47, 134.02, 134.34, 137.07, 201.08.

6.4 (*E*)-2-(4-(Trifluoromethyl)benzylidene)cyclohexanone (6d)

δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.80 (2H, t, J = 6.8 Hz, CH_2), 1.96 (2H, t, J = 9.6 Hz, CH_2), 2.56 (2H, t, J = 6.8Hz, CH_2), 2.82 (2H, t, J = 6.4 Hz, CH_2), 7.52 (2H, d, J = 8.0 Hz, ArH), 7.64 (2H, d, J = 8.0 Hz, ArH), 7.88 (1H, s, ArCH=). δ_C (100 MHz, $CDCl_3$; Me_4Si) 23.30, 23.87, 28.93, 40.32, 124.09, 129.11, 130.45, 132.92, 135.73, 138.82, 161.13, 200.98.

6.5 (*E*)-2-(Furan-2-ylmethylene)cyclohexanone (6e)

δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.84 (2H, d, J = 5.6 Hz, CH_2); 1.91 (2H, d, J = 5.2 Hz, CH_2), 2.51 (2H, t, J = 6.8 Hz, CH_2), 2.92 (2H, s, CH_2), 6.51 (1H, d, J = 1.6 Hz, FuranH), 6.63 (1H, s, FuranH), 7.39 (1H, s, FuranH), 7.55 (1H, s, CH=C). δ_C (100 MHz, $CDCl_3$; Me_4Si) 22.94, 28.39, 30.90, 39.90, 109.77, 112.24, 122.99, 132.52, 144.53, 152.40, 200.46.

6.6 (*E*)-2-(3-Phenylpropylidene)cyclohexanone (6f)

δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.68–1.62 (2H, m, CH_2), 1.84–1.77 (2H, m, CH_2), 2.44–2.36 (6H, m, -CH_2-CH_2Ph, CH_2), 2.75 (2H, t, J = 8.0 Hz, CH_2), 6.65 (1H, t, J = 2.8 Hz, CH=C), 7.21–7.16 (3H, m, ArH), 7.28 (2H, t, J = 7.2 Hz, ArH). δ_C (100 MHz, $CDCl_3$; Me_4Si) 23.51, 23.64, 26.82, 29.90, 34.83, 40.29, 126.26, 128.61, 137.04, 138.13, 138.06, 141.47, 201.42.

6.7 (*E*)-2-Octylidenecyclohexanone (6g)

δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.88 (3H, t, J = 6.0 Hz, CH_3), 1.25–1.38 (12H, m), 1.76–1.83 (2H, m, CH_2), 2.36–2.42 (4H, m, C=CH-CH_2, CH_2), 2.76 (2H, t, J = 8.4 Hz, CH_2), 6.55 (1H, t, J = 2.8 Hz, CH=C). δ_C (100 MHz, $CDCl_3$; Me_4Si) 14.02, 22.68, 23.33, 23.64, 25.17, 26.68, 27.82, 28.5, 29.14, 31.81, 40.02, 135.93, 139.67, 200.79.

6.8 (*E*)-2-Benzylidenecyclopentanone (6h)

δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.06 (2H, t, J = 7.6 Hz, CH_2), 2.44 (2H, t, J = 8.0 Hz, CH_2), 3.00 (2H, t, J = 7.2 Hz, CH_2), 7.30-7.48 (4H, m, ArCH and ArCH=C), 7.56–7.59 (2H, m, ArH). δ_C (100 MHz, $CDCl_3$; Me_4Si) 20.20, 29.36, 37.79, 128.73, 128.36, 130.55, 132.42, 135.57, 136.12, 208.24.

6.9 Diethyl 2-benzylidenemalonate (6i)

δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.27–1.35 (6H, m, 2CH_3), 4.30 (4H, m, 2CH_2), 7.37–7.40 (3H, m, ArH), 7.44–7.47 (2H, t, J = 4.8 Hz, ArH), 7.74 ppm (1H, s, CH). δ_C (100 MHz, $CDCl_3$; Me_4Si) 13.86, 14.12, 61.62, 61.67, 126.30, 128.75, 129.42, 130.49, 132.88, 142.11, 164.11, 166.66.

6.10 Dimethyl 2-benzylidenemalonate (6j)

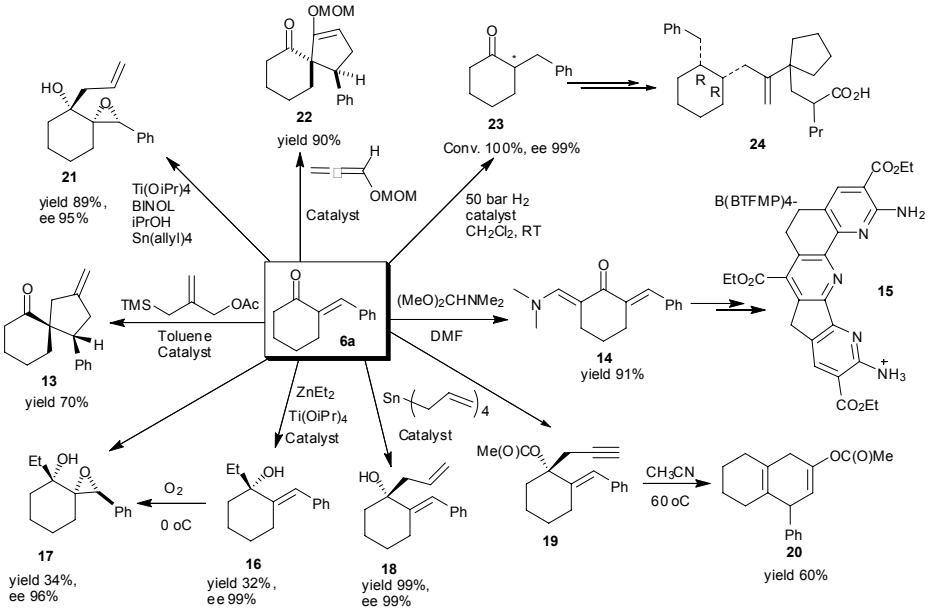
δ_H (400 MHz; $CDCl_3$; Me_4Si) 3.84 (3 H, s, CH_3), 3.87 (3H, s, CH_3), 7.38-7.40 (3H, m, ArH), 7.45 (2H, t, J = 5.0 Hz, ArH), 7.77 (1H, s, ArCH=C). δ_C (100 MHz, $CDCl_3$; Me_4Si) 60.92, 60.97, 126.32, 128.77, 129.41, 130.47, 132.89, 142.12, 164.12, 166.69.

6.11 3-Benzylidenepentane-2,4-dione (6k)

δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.24 (3H, s, CH_3), 2.38 (3H, s, CH_3), 7.36 (5H, m, ArH), 7.44 (1H, s, ArCH=C). δ_C (100 MHz, $CDCl_3$; Me_4Si) 26.22, 31.33, 128.71, 129.39, 130.41, 132.68, 139.62, 142.51, 196.47, 205.31.

7. Meaningful transformations of product

To demonstrate the value of high-stereoselective (*E*)-*α,β*-unsaturated ketones, several meaningful transformations of product **6a** have been developed (Scheme 2). For example, 1,2- addition of (*E*)-2-benzylidene-cyclohexanone (**6a**) with 2-((trimethylsilyl)methyl)allyl acetate produces compound **13** (a synthetically useful spirobicyclic material, the corresponding 1,2-addition adducts) in moderate yield (70%).[4] Polyaza-receptors such as **15** were used to determine the optimum cavity size for complexing phosphoric acid diesters which is synthesized from cyclic *α,β*-unsaturated ketones **6a** (developed by Anslyn *et al*.[5]). Asymmetric addition of alkylzinc reagents to cyclic *α,β*-unsaturated ketones was also reported before.[6] The resulting tertiary allylic alcohols **16** are valuable intermediates that can be further converted through directed epoxidation reactions to **17** with excellent diastereoselectivities (Jeon and Walsh).[6a] Catalytic asymmetric allylation of cyclic *α,β*-unsaturated ketones utilizing titanium tetraisopropoxide, BINOL, 2-propanol additive, and tetraallylstannane as allylating agent produced tertiary homoallylic alcohol **18** in excellent yield (99%) and with high levels of enantioselectivity (ee 99%).[7] When 1 equiv of *tert*-butyl hydroperoxide is added, the directed epoxidation of the allylic double bond ensures the formation of epoxy alcohol **19** with high diastereoselectivity.[7a] Compound **20** can be ramified from **6a**, and cycloisomerized to cyclohexadienyl carbonate **21** in a fair yield.[8] Another synthetically useful spirobicyclic compound (**22**) can be readily prepared in high yield (90%) from allenyl MOM ((methoxyl)methyl) ether and a cyclic *α,β*-unsaturated ketones through a two-step formal [3+2] cycloaddition, a highly diastereoselective process developed by Zhang *et al*.[9] Hou *et al.* developed a method for the installation of chiral centers at the α-position of ketones **23** by Ir-catalyzed asymmetric hydrogenation of *α,β*-unsaturated ketones **6a**;[10] high enantioselectivity (ee 99%) was achieved even under an atmospheric pressure of hydrogen. These ketones with a chiral carbon centers are important compounds in drug synthesis such as the synthesis of **24**.[11]



Scheme 2 Utilization of (*E*)-*α,β*-unsaturated ketone **6a** in the highly-enantioselective synthesis of spirobicyclic compounds, allylic alcohols, epoxy alcohols, chiral ketones, polyaza-receptors, and other building blocks of chemical synthesis.

8. Large scale synthesis using the self-separation catalyst system

Due to the high demand, it is desirable to prepare *α,β*-unsaturated ketones in large scale. The method described by us for the cross-condensation reaction is energy efficient and atom economic, and only H_2O is generated as a side-product. Using the self-separation catalytic system, it is possible to directly produce and isolate *α,β*-unsaturated ketones at room

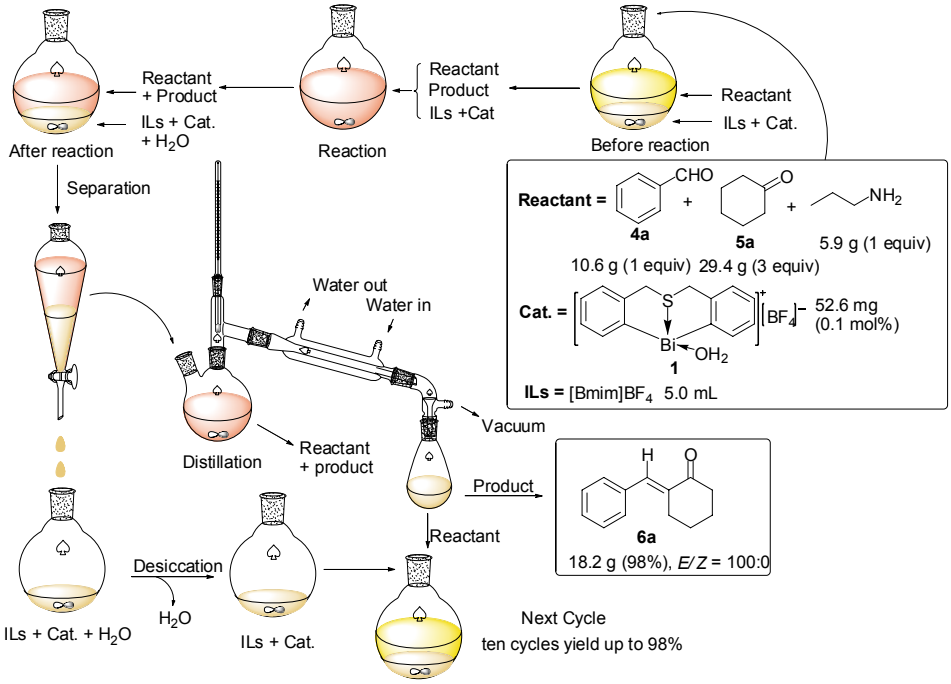


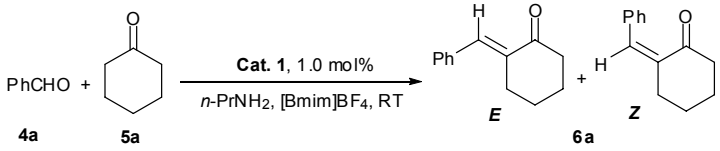
Fig. 2 Scaled-up cross-condensation reaction of benzaldehyde and cyclohexanone catalyzed by 0.1 mol% of **1** in the presence of *n*-$PrNH_2$.

temperature. The products can be collected by direct distillation, and the tedious procedures described in our previous study (catalyzed by $[S(CH_2C_6H_4)_2Bi(OH_2)]^+[OSO_2C_8F_{17}]^-$) such as extraction using an organic solvent, drying of the organic phase with a dehydrating reagent, filtration and evaporation of the organic solvent can be avoided. As shown in Fig. 2, at large scale (by 5 times), the catalyst loading can be lowered to 0.1 mol% with the self-separation of catalytic system unaffected. The desirable *(E)-α,β*-unsaturated ketones (**6a**, 18.2 g, yield 98%, *E/Z* = 100:0) can be collected by means of distillation under vacuum, and the unconsumed reactants used directly in the next cycle.

9. The large scale preparation of *(E)-α,β*-unsaturated ketones (6a) and catalyst system recycle

To a 100 mL round bottomed flask were added catalyst **1** (0.0526 g, 0.1 mmol), PhCHO (**4a**, 10.6 g, 100.0 mmol), *n*-$PrNH_2$ (5.9 g, 100.0 mmol), cyclohexanone (**5a**, 29.4 g, 100.0 mmol) and $[Bmim]BF_4$ (5.0 mL). Then the mixture was stirred for 12 h under TLC analysis until PhCHO as well as the intermediate (*E*)-*N*-benzylidenepropan-1-amine obtained from PhCHO and *n*-$PrNH_2$ were completely consumed. The mixture was allowed to settle for 5 min for self-separation into two phases. After simple separation, the lower layer was subject to evaporation under vacuum at room temperature for water removal and then the catalyst and ionic liquid was ready for the next reaction cycle. The upper layer was distilled under vacuum for the collection of (*E*)-2-benzylidenecyclohexanone (**6a**, 18.2 g, yield 98%).

Table S1 Recycling of catalyst **1** in a large-scale synthesis of *α,β*-unsaturated ketones.[a]



Cycle[b]	Yield (%)[c]	*E*/*Z*[d]	Cycle[e]	Yield (%)[c]	*E*/*Z*[d]
1	98	100/0	1	98	100/0
2	99	100/0	2	99	100/0
3	98	100/0	3	99	100/0
4	97	100/0	4	98	100/0
5	98	100/0	5	97	100/0
6	97	100/0	6	97	100/0
7	98	100/0			
8	99	100/0			
9	97	100/0			
10	96	100/0			

[a] **4a**, 100 mmol; *n*-$PrNH_2$, 100 mmol (for the first cycle only, for the next cycle 10 mmol of *n*-$PrNH_2$ was added because the recovered *n*-$PrNH_2$ was also added into the reaction system); **5a**, 300 mmol (for the first cycle only, for the next cycle 100 mmol of **5a** was added because the recovered **5a** was also added into the reaction system); **1**, 0.1 mmol; [Bmim]BF_4, 5.0 mL; RT. [b] The recovered catalyst was treated with desiccation. [c] Isolated yield. [d]Determined by ^{1}H NMR. [e]The recovered catalyst was used directly for the next cycle without any treatment.

10. ^{1}H NMR study of the interaction of catalyst and ionic liquids

a) To a NMR tube was added catalyst **1** (0.05 mmol, 26.3 mg) in acetone-d_6 (0.5 mL) (Me_4Si as an internal standard), then the solution was analyzed at 25°C over an INOVA-400M (Varian) instrument calibrated using Me_4Si. δ_H (400 MHz; acetone-d_6; Me_4Si) 3.64 (2H, s, H_2O), 4.82 (2H, d, J = 16.0 Hz, $ArCH_2$), 5.15 (2H, d, J = 16.0 Hz, $ArCH_2$), 7.45 (2H, t, J = 7.2, 7.6 Hz, ArH), 7.56 (2H, d, J = 6.8 Hz, ArH), 7.88 (2H, d, J = 7.8 Hz, ArH), 8.23 (2H, d, J = 6.8 Hz, ArH).

b) To another tube was added [Bmim]BF_4 (0.05 mmol, 11.3 mg) in acetone-d_6 (0.5 mL) (Me_4Si as an internal standard), then the solution was analyzed at 25°C over an INOVA-400M (Varian) instrument calibrated using Me_4Si. δ_H (400 MHz; acetone-d_6; Me_4Si) 0.94 (3H, t, J = 7.2, 7.6 Hz, CH_3), 1.39 (2H, m, CH_2), 1.92 (2H, t, J = 7.2, 7.6 Hz, CH_2), 4.05 (3H, s, CH_3), 4.36 (2H, t, J = 7.2 Hz, CH_2), 7.72 (1H, s, Imidazolyl H), 7.78 (1H, s, Imidazolyl H), 9.04 (1H, s, Imidazolyl H).

c) To a catalyst **1** (0.05 mmol, 26.3 mg) in acetone-d_6 (0.5 mL) (Me_4Si as an internal standard) solution was added [Bmim]BF_4 (0.05 mmol, 11.3 mg), then the solution was analyzed at 25°C over an INOVA-400M (Varian) instrument calibrated using Me_4Si. δ_H (400 MHz; acetone-d_6; Me_4Si) 0.94 (3H, t, J = 7.6, 7.2 Hz, CH_3), 1.34–1. 40 (2H, m, CH_2), 1.89–1.92 (2H, m, CH_2), 3.60 (2H, s, H_2O), 4.02 (3H, s, CH_3), 4.33 (2H, t, J = 7.2, 7.6 Hz, CH_2), 4.81 (2H, d, J = 15.6 Hz, $ArCH_2$), 5.14 (2H, d, J = 16.0 Hz, $ArCH_2$), 7.45 (2H, t, J = 7.6, 7.2 Hz, ArH), 7.56 (2H, d, J = 6.8 Hz, ArH), 7.69 (1H, t, J = 1.6 Hz, Imidazolyl H), 7.74 (1H, t, J = 1.6 Hz, Imidazolyl H), 7.88 (2H, d, J = 7.6 Hz, ArH), 8.23 (2H, d, J = 7.2 Hz, ArH), 8.98 (1H, s, Imidazolyl H).

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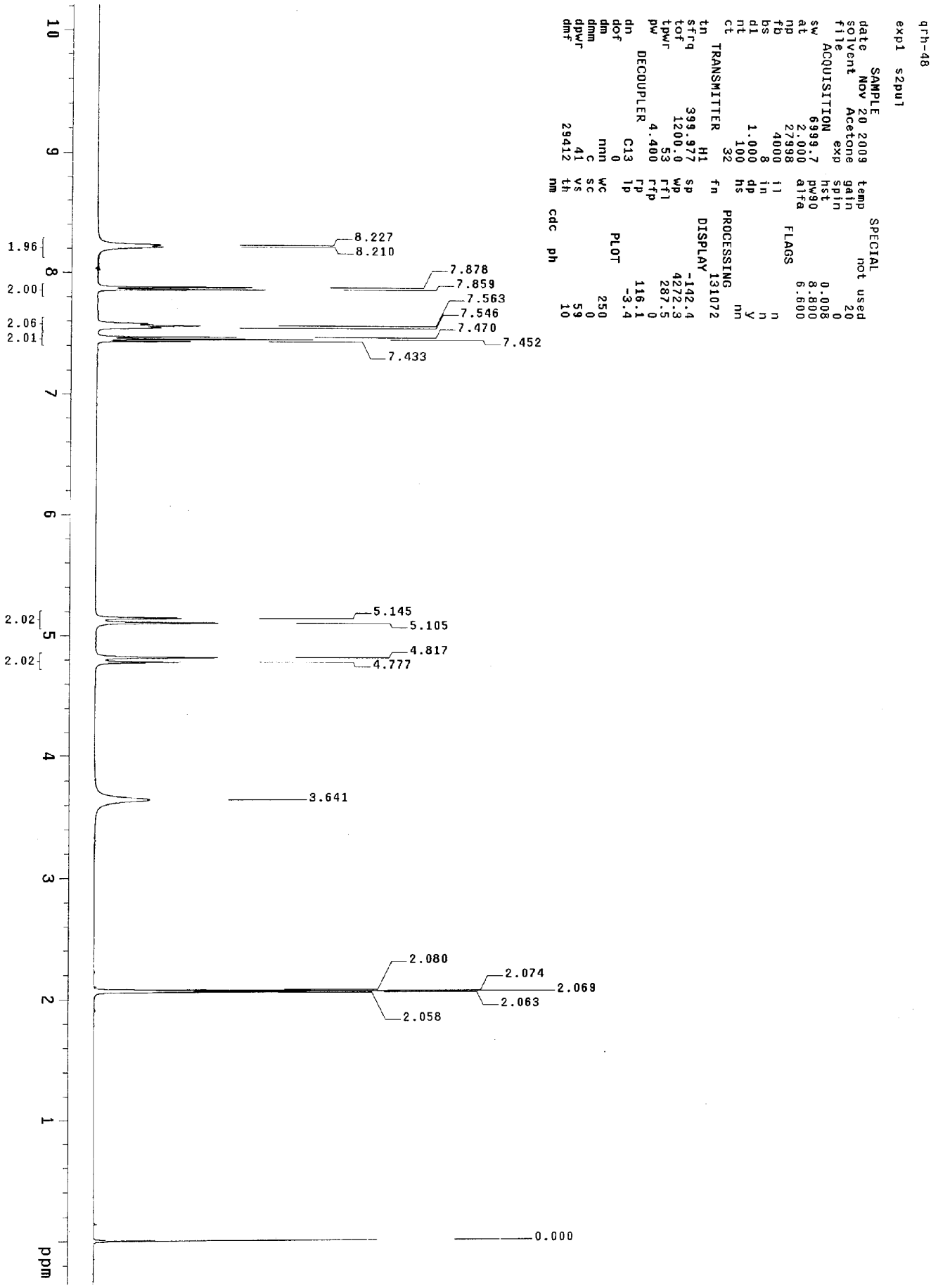
Appendix ^{1}H NMR analysis

1. Chart 1 (^{1}H NMR of Complex **1**)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date Nov 20 2009
solvent Acetone
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at 2.000
np 27998
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d1 1.000
nt 100
ct 32
TRANSMITTER
tn H1
sfrq 399.977
tof 1200.0
tpwr 53
pw 4.400
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 41
dmf 29412
nm cdc
SPECIAL
temp not used
gain 20
spin 0
hst 0.008
pw90 8.800
alfa 6.600
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in n
dp y
hs nn
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th 10
ph
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2.00
2.06
2.01
2.02
2.02
8.227
8.210
7.878
7.859
7.563
7.546
7.470
7.452
7.433
5.145
5.105
4.817
4.777
3.641
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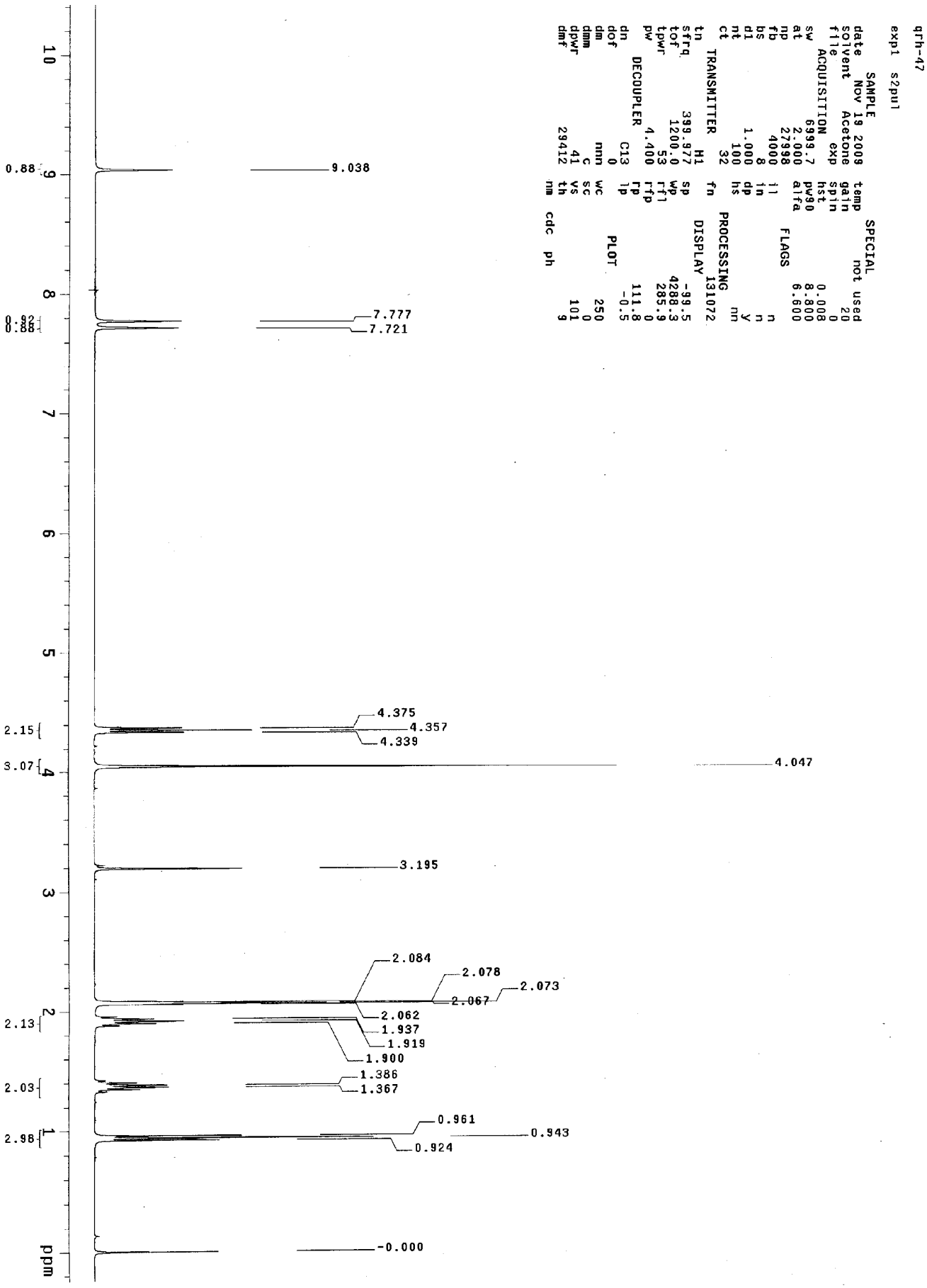
2.069
2.063
2.058
0.000
ppm

2. Chart 2 (^{1}H NMR of [Bmim]BF_4)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nt 100
ct 32
TRANSMITTER
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sfrq 399.977
tof 1200.0
tpwr 53
pw 4.400
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 41
dmf 29412
SPECIAL
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hst 0.008
pw90 8.800
alfa 6.600
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in n
dp y
hs nn
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rfl 285.9
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vs 101
th 9
nm cdc ph
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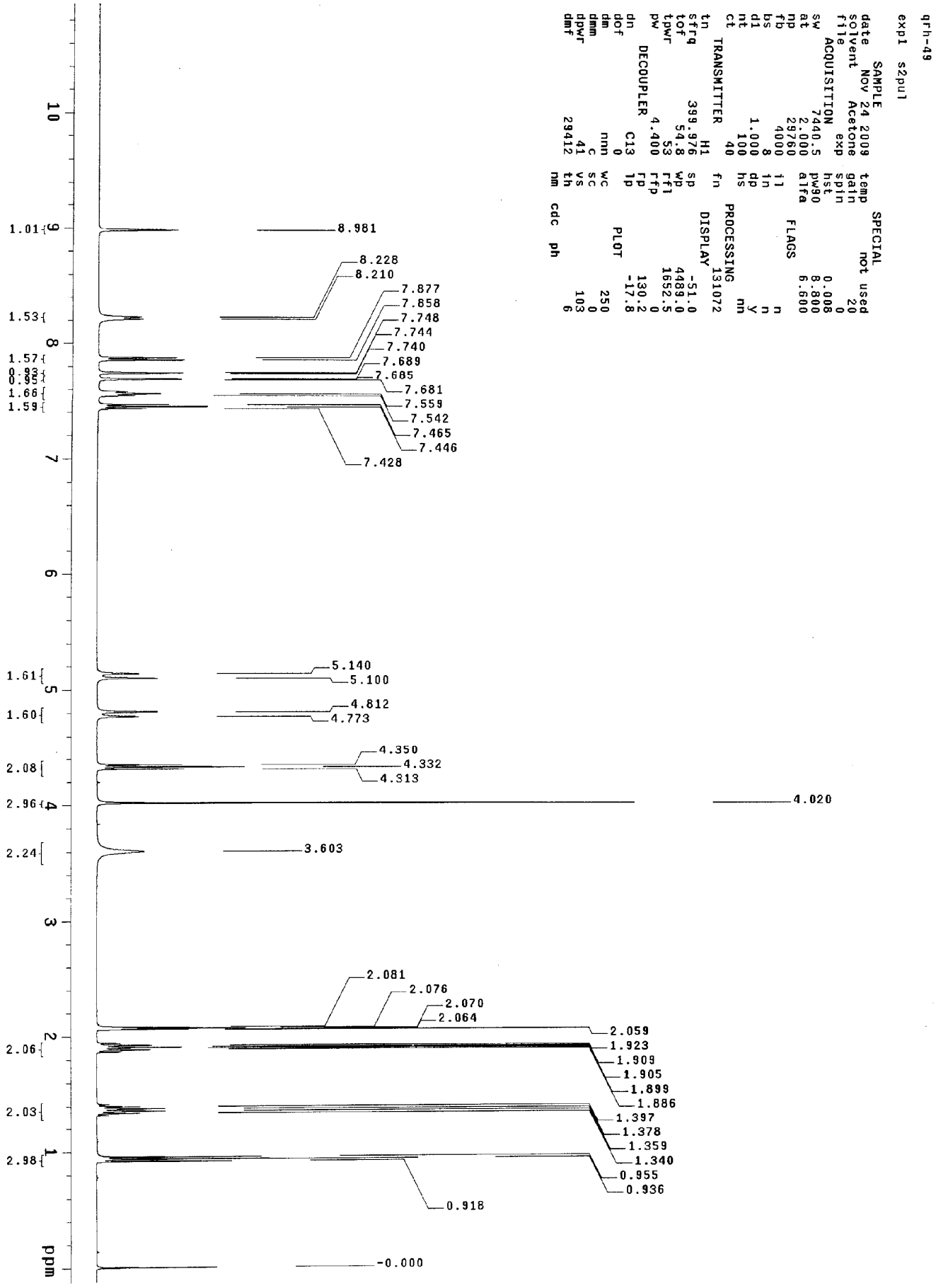
7.777
7.721
4.375
4.357
4.339
4.047
3.195
2.084
2.078
2.073
2.067
2.062
1.937
1.919
1.900
1.386
1.367
0.961
0.943
0.924
-0.000
0.88
0.92
0.88
2.15
3.07
2.13
2.03
2.98
ppm

.3. Chart 3 (^{1}H NMR of Complex **1** and [Bmim]BF_4)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solvent Acetone
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d1 1.000
nt 100
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TRANSMITTER
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sfrq 399.976
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tpwr 53
pw 4.400
DECOUPLER
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dmm c
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PLOT
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SPECIAL
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gain 20
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pw90 8.800
alfa 6.600
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dp y
hs nn
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1652.5
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vs
th
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8.210
7.877
7.858
7.748
7.744
7.740
7.689
7.685
7.681
7.559
7.542
7.465
7.446
7.428
5.140
5.100
4.812
4.773
4.350
4.332
4.313
4.020
3.603
2.081
2.076
2.070
2.064
2.059
1.923
1.909
1.905
1.899
1.886
1.397
1.378
1.359
1.340
0.955
0.936
0.918
-0.000
1.01
1.53
1.57
0.93
0.95
1.66
1.59
1.61
1.60
2.08
2.96
2.24
2.06
2.03
2.98
ppm