Supplementary Material (ESI) for Chemical Communications

Biphasic hydroformylation in ionic liquids: Interaction between phosphane ligands and imidazolium triflate, toward an asymmetric process

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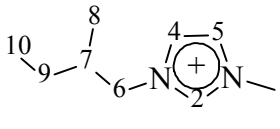
General methods.

All reactions were carried in oven-dried glassware under nitrogen, using standard Schlenk and vacuum line techniques. The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded using an Advance 300 Brucker, at 300.13, 75.49 and 121.49 MHz respectively. Chemical shifts are given in ppm (δ) and measured relative to residual solvent, for ^{1}H and ^{13}C, and to external reference (H_3PO_4 in D_2O) for $^{31}P\{^{1}H\}$ NMR. The 2D T-ROESY experiments were run using the software supplied by Brucker. Mixing times for T-ROESY experiments were set at 300 ms. The data matrix for the T-ROESY was made of 512 free induction decays, 1 K points each, resulting from the co-addition of 64 scans. The real resolution was 1.5-6.0 Hz/point in F2 and F1 dimension, respectively. They are transformed in the non-phase – sensitive mode after QSINE window processing. Elemental analysis were performed by "Service Central d'Analyse du CNRS". Optical rotations were performed with a Perkin Elmer 343 (589 nm) polarimeter. IR analysis were performed with a Nicolet 510 FTIR.

Materials.

D_2O (99.95 % isotopic purity), $CDCl_3$, [D_8] THF were obtained from Euriso-top. The sodium salt of the *meta*-substituted trisulfonated triphenylphosphine (TPPTS) was synthesized as reported by Gärtner et al.[1] The sodium salt of the *meta*-substituted monosulfonated triphenylphosphine (TPPMS) was prepared by a literature method.[2] The purity of the sulfonated ligands were carefully controlled. In particular, ^{31}P solution NMR indicated that the product was a mixture of phosphine (ca. 98%) and its oxide (ca. 2%). Trifluoromethanesulfonic anhydride was freshly prepared prior to use by distillation of a 1:1 w/w mixture of trifluoromethanesulfonic acid and phosphorus pentoxide.[3] The 1-methylimidazole was freshly distilled under KOH. All other chemicals were purchased from Acros, Aldrich, Fluka, Solvionic or Strem and used without further purification. Solvents were distilled under positive pressure of dry nitrogen before use and dried by standard methods : dichloromethane from CaH_2, toluene from Na/Hg amalgam.

Synthesis of 1-[(*S*)-2-methylbutyl]-3-methylimidazolium triflate [MBMIM][TfO].



TfO^-

A dry flask (1L), equipped with a magnetic stir bar and a septum-inlet for nitrogen, was charged with a solution of (*S*)-2-methylbutanol (6.28 g, 71.2 mmol) in dichloromethane (300 mL), poly(vinylpyridine) (18.0 g, 63.8 mmol) was added. At 0°C, we added the trifluoromethanesulfonic anhydride (8.6 g, 30.6 mmol) in a dropwise fashion. The reaction mixture was stirred for 5 minutes to 0°C then at room temperature, then filtered under gravity. The poly(vinylpyridinium triflate) precipitate was washed with 5 mL of dichloromethane. The organic layer was washed with a saturated $NaHCO_3$ solution and when the organic layer became transparency, we dried ($MgSO_4$) and concentrated under vacuum to give the (*S*)-2-methylbutyltriflate (yellowish oil). The methylene group adjacent to the triflate group give a characteristic dd at 4.38 ppm (2H) in the ^1H NMR spectrum, but this compound was not very stable. This oil was dissolved in anhydrous toluene under a nitrogen atmosphere and the solution was cooled to 0 °C. The 1-methylimidazole (6.18 g, 75.2 mmol) was added and the resulting solution was stirred an hour. The ionic liquid layer appeared beneath the toluene. After extraction, the ionic liquid was washed with toluene to remove unreacted 1-methylimidazole. The pale-yellow ionic liquid was dried overnight at 120°C in vacuum. The product was stored under dry nitrogen (21.28 g, 99%).

$[\alpha]_D^{20}$ = + 1,4 (*c* 1.01 CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$, 20°C, TMS): δ 0.6-0.8 (m, 6H; 8, 10), 0.9 (qd, ^3J(H,H)=7.3 Hz, ^3J(H,H)=9.1 Hz, 1H; 9), 1.2 (qd, ^3J(H,H)=7.3 Hz, ^3J(H,H)=9.1 Hz, 1H; 9), 1.7 (m, 1H; 7), 3.8 (s, 3H; N-CH_3), 3.9-4.1 (m, 2H; 6), 7.2 (s, 1H; 4/5), 7.3 (s, 1H; 4/5), 8.8 (s, 1H; 2); ^{13}C NMR (75 MHz, $CDCl_3$, 20°C): δ 10.6 (10), 15.9 (8), 26.0 (9), 35.3 (N-CH_3), 36.0 (7), 55.2 (6), 122.7 (4/5), 123.6 ppm (4/5), 136.4 (2); IR: $\tilde{\nu}$= 3115 and 3155 cm^{-1} (C-H···F); Anal. Calc. for $C_{10}H_{17}F_3N_2O_3S$: C, 39.73%; H, 5.67%. Found: C, 39,83%; H, 5.70%.

General hydroformylation experiments.

All catalytic reactions were performed under nitrogen using standard Schlenk techniques. All solvents and liquid reagents were degassed by bubbling nitrogen for 15 min before each use

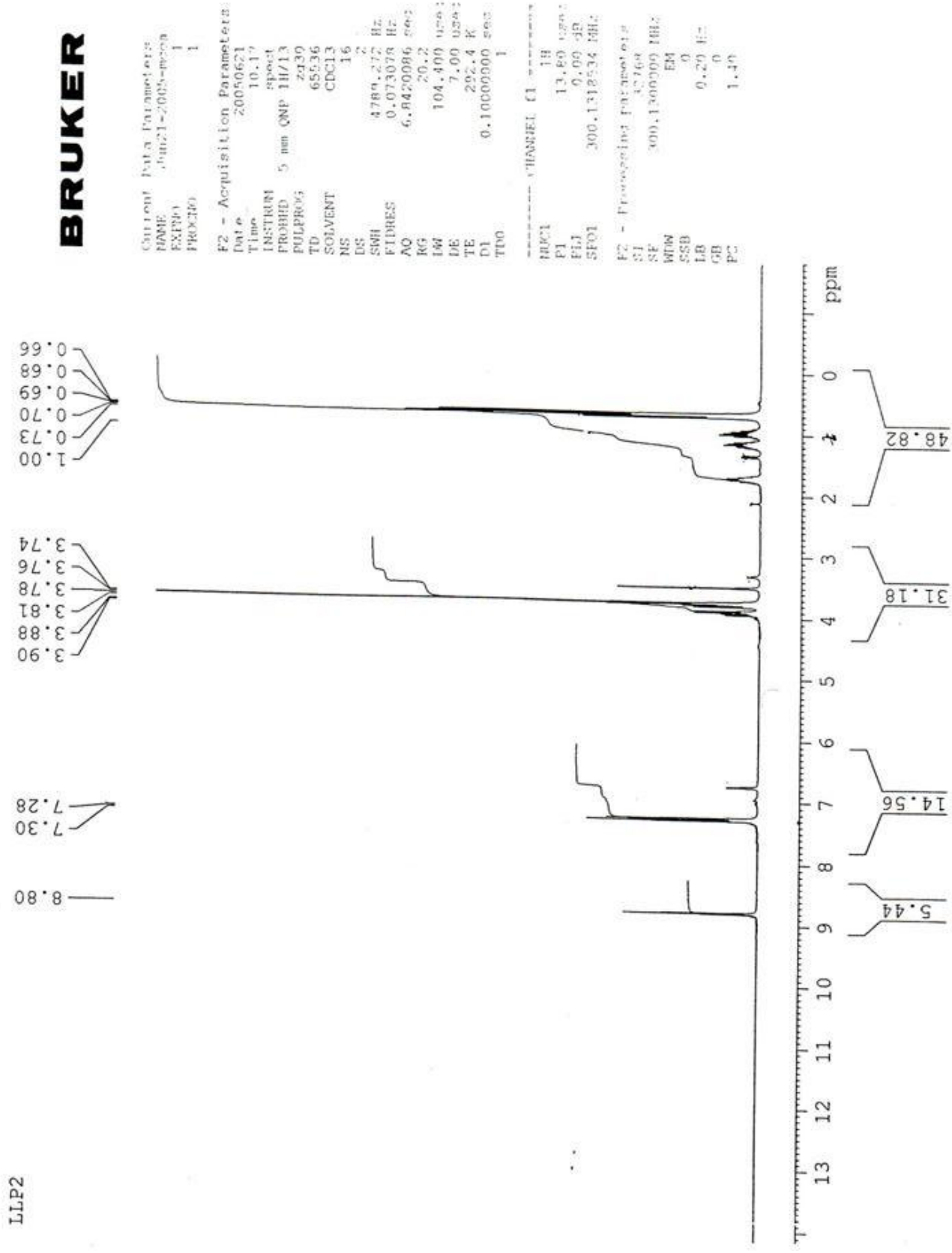
or by two freeze-pump-thaw cycles before use. $Rh(acac)(CO)_2$ (2.0×10^{-2} mmol) and phosphane ligand (0.105 mmol) were dissolved in 4.0 mL of ionic liquid. The resulting ionic phase and an organic phase composed of olefin (20.60 mmol) and undecane (2.03 mmol - GC internal standard) were charged under an atmosphere of nitrogen into the 25 mL reactor which was heated at 80°C. Mechanical stirring equipped with a multipaddle unit was then started (1500 rpm) and the autoclave was pressurized with 50 atm of CO/H_2 (1/1) from a gas reservoir connected to the reactor through a high pressure regulator valve allowing to keep constant the pressure in the reactor throughout the whole reaction. The reaction medium was sampled during the reaction for GC analyses of the organic phase after decantation. For styrene hydroformylation, the aldehydes are reduced in alcohol using aluminium lithium hydride in THF. The enantiomeric excess is obtained by GC analyses on Chrompack CP-9300® (Chirasil-Dex (25 m × 0.32 mm)).

References.

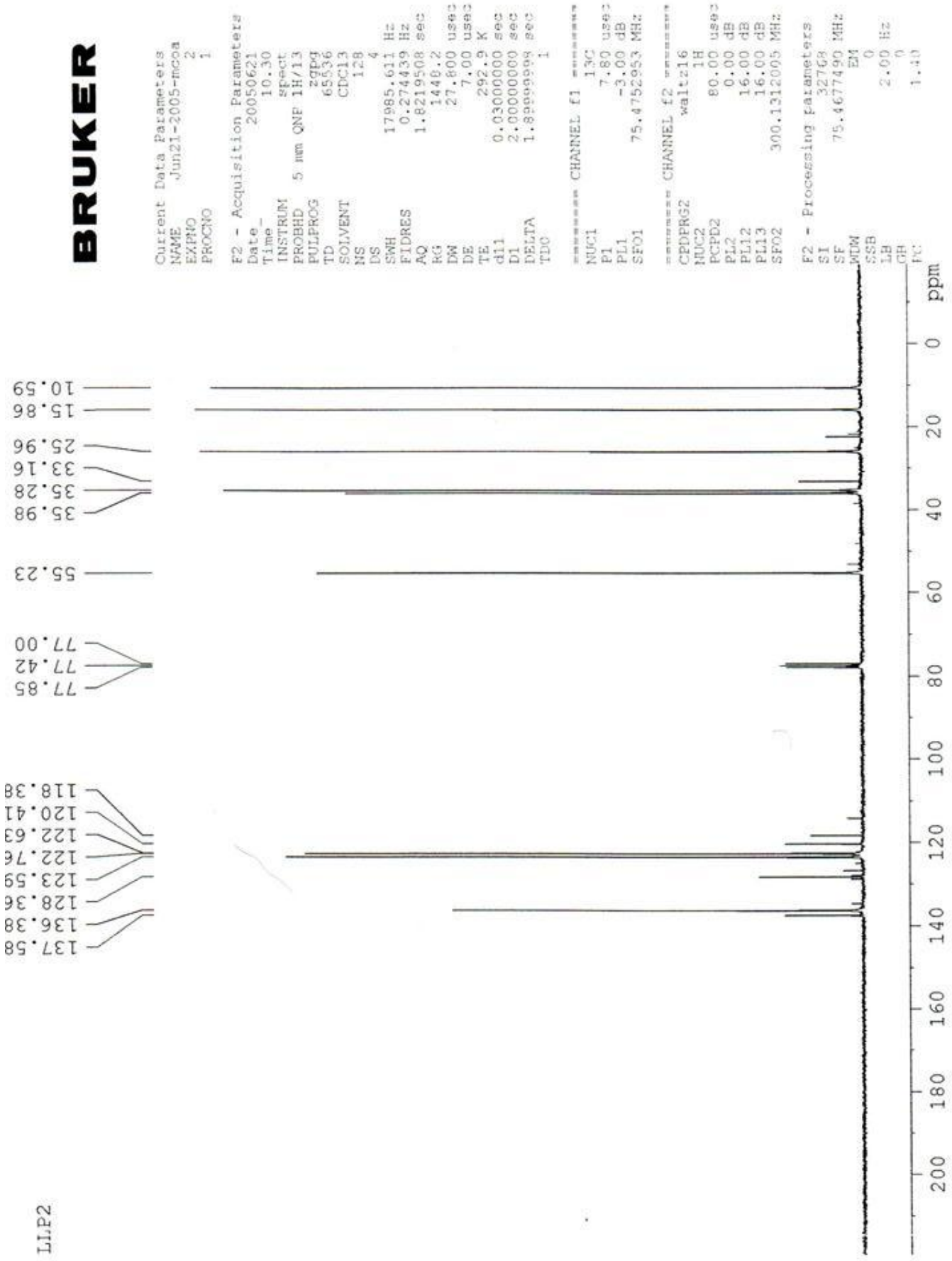
[1] R. Gärtner, B. Cornils, H. Springer, P. Lappe, DE pat 3235030, **1982**.

[2] F. Ahrland, J. Chatt, N.R. Davies, A.A. Williams, *J. Chem. Soc.* **1958**, 276.

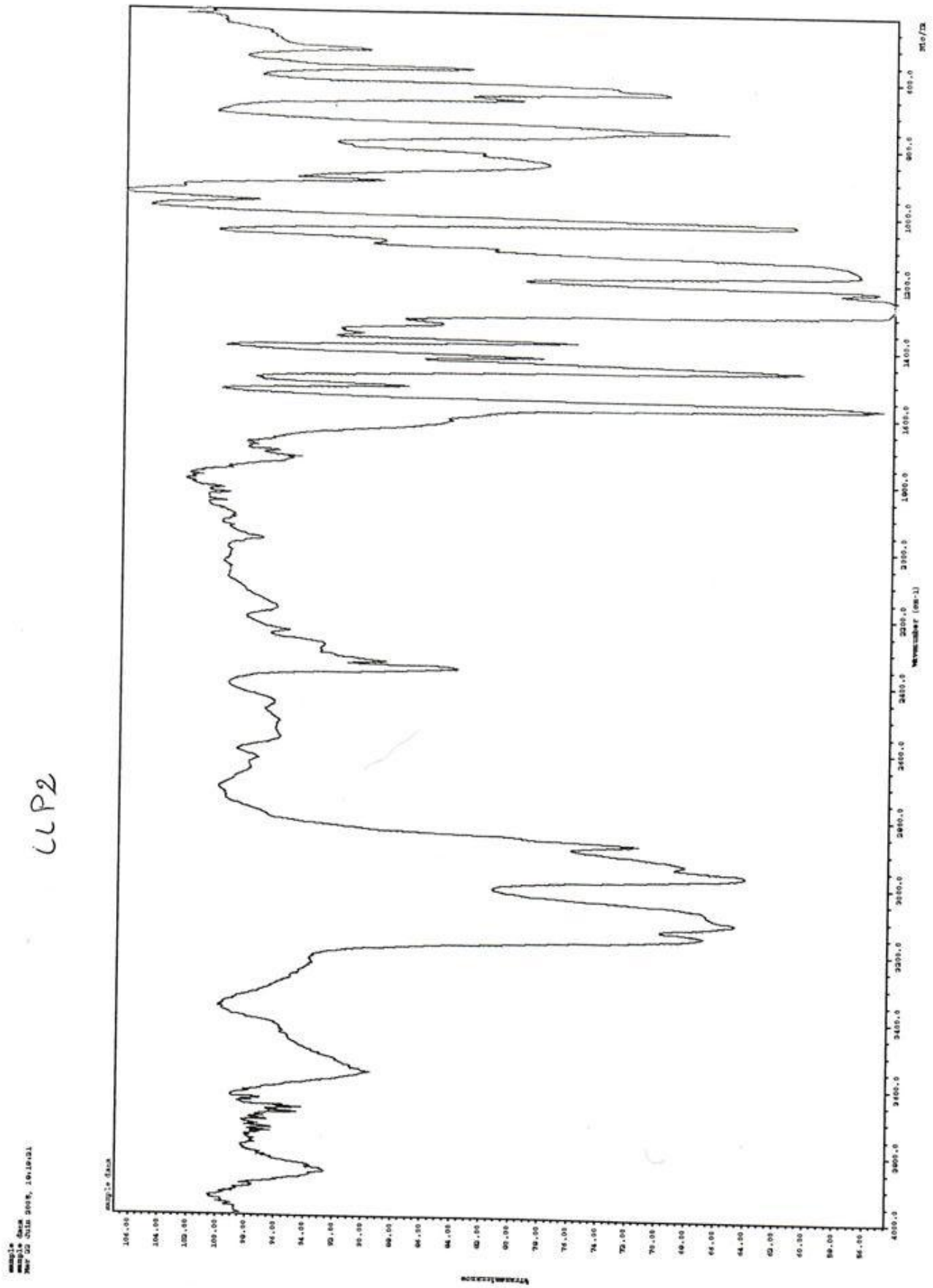
[3] P.J. Stang, T.E. Dueber, *Org. Synth.* **1987**, Coll. Vol. VI, 757.



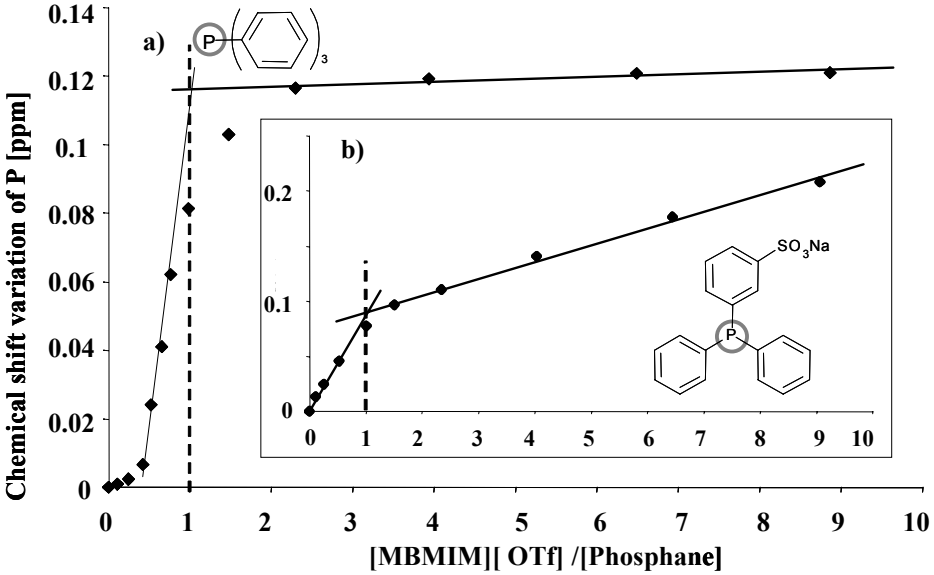
^{1}H NMR ($CDCl_3$) of 1-[(*S*)-2-methylbutyl]-3-methylimidazolium triflate (MBMIM).



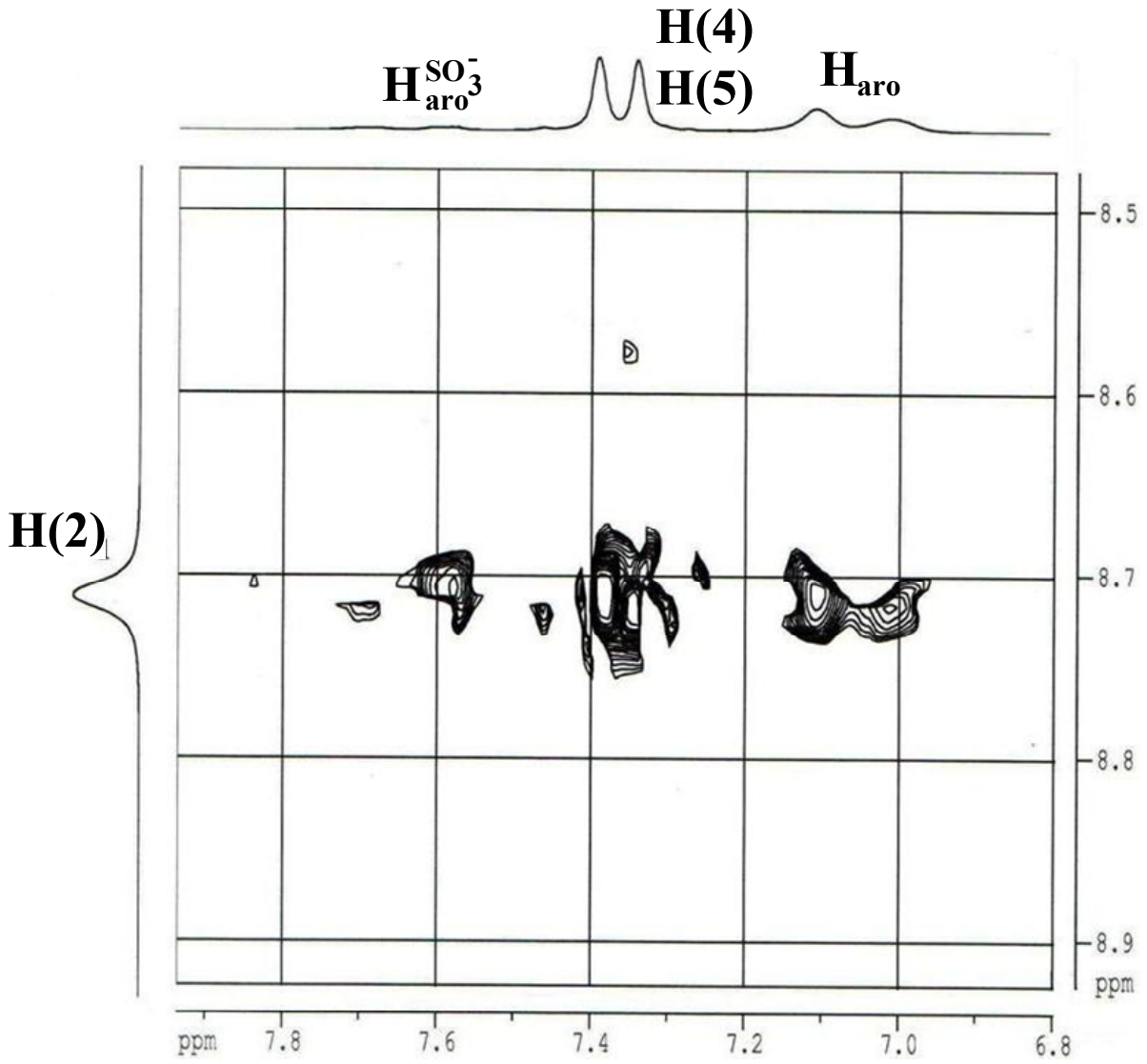
^{13}C NMR ($CDCl_3$) of 1-[(*S*)-2-methylbutyl]-3-methylimidazolium triflate (MBMIM).



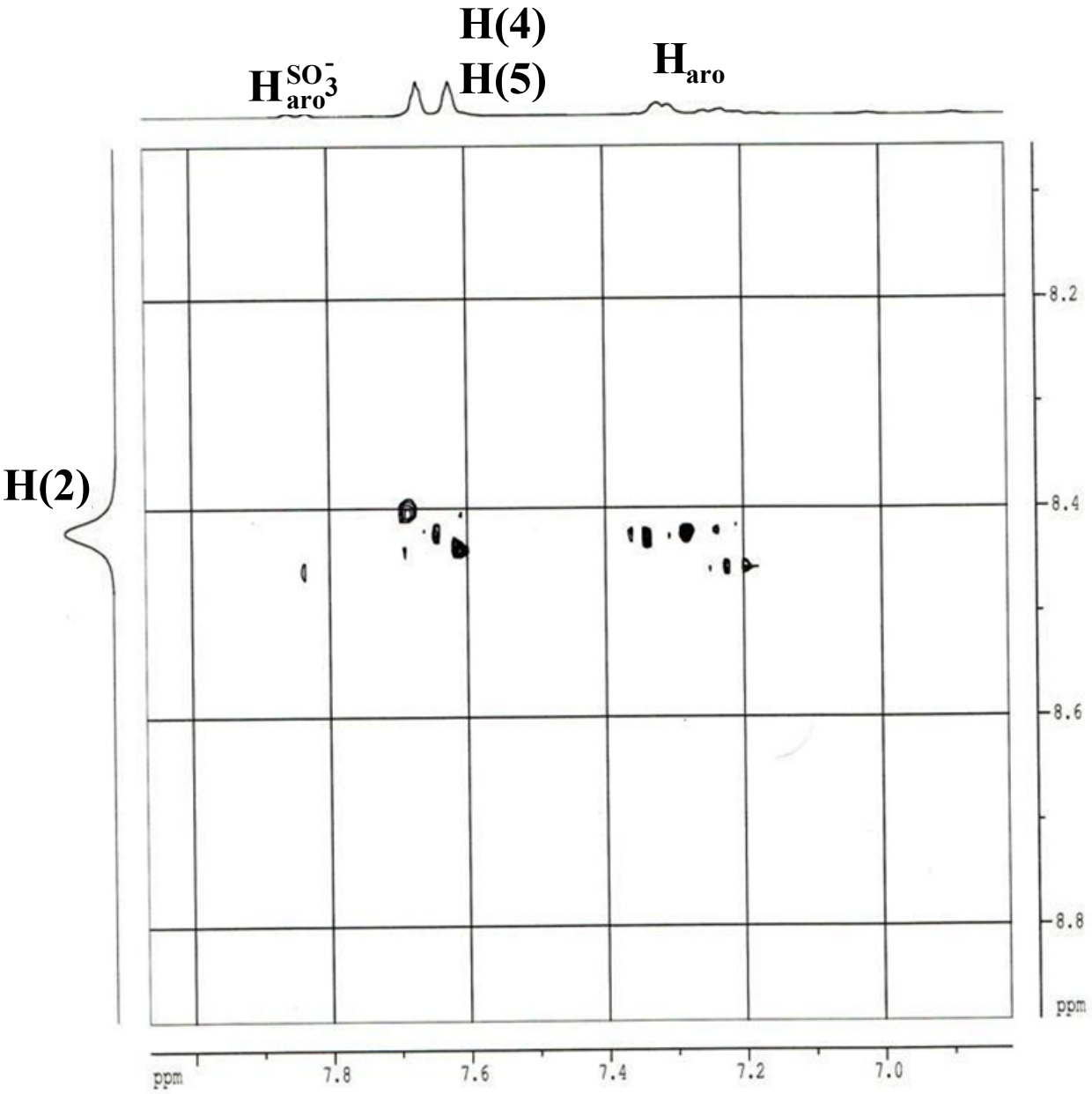
IR of 1-[(*S*)-2-methylbutyl]-3-methylimidazolium triflate (MBMIM).



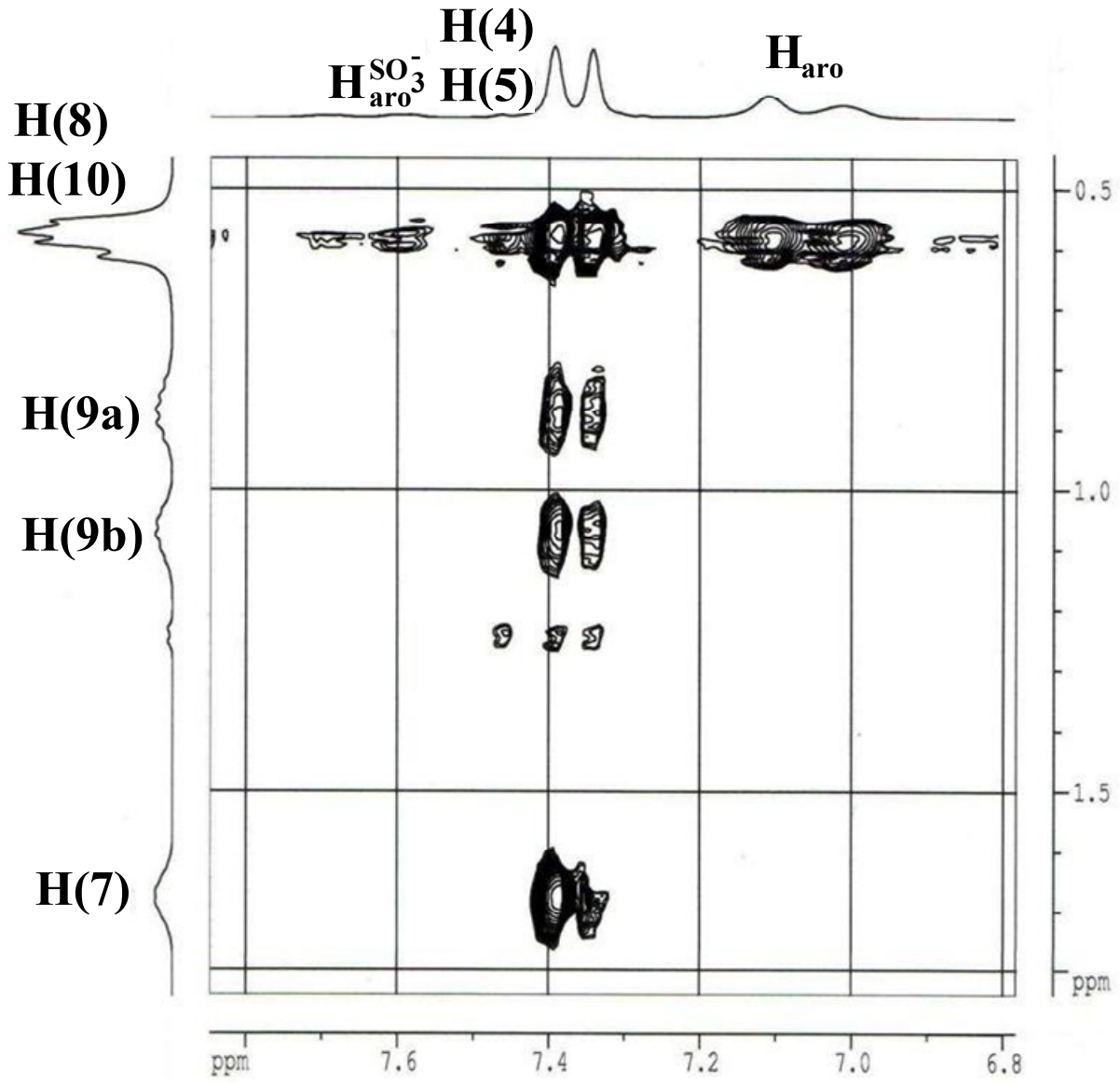
^{31}P NMR titration profile for addition of [MBMIM][TfO] to phosphane in [D_8]THF at 300K.



Partial contour plot of T-ROESY spectrum of mixture containing TPPMS and MBMIM 16% (m/m) at 300K with a 300 ms mixing time (external lock: D_2O).



Partial contour plot of T-ROESY spectrum of mixture containing TPPMS and MBMIM 16% (m/m) at 300K with a 300 ms mixing time in 50% [D8]THF (V/V).



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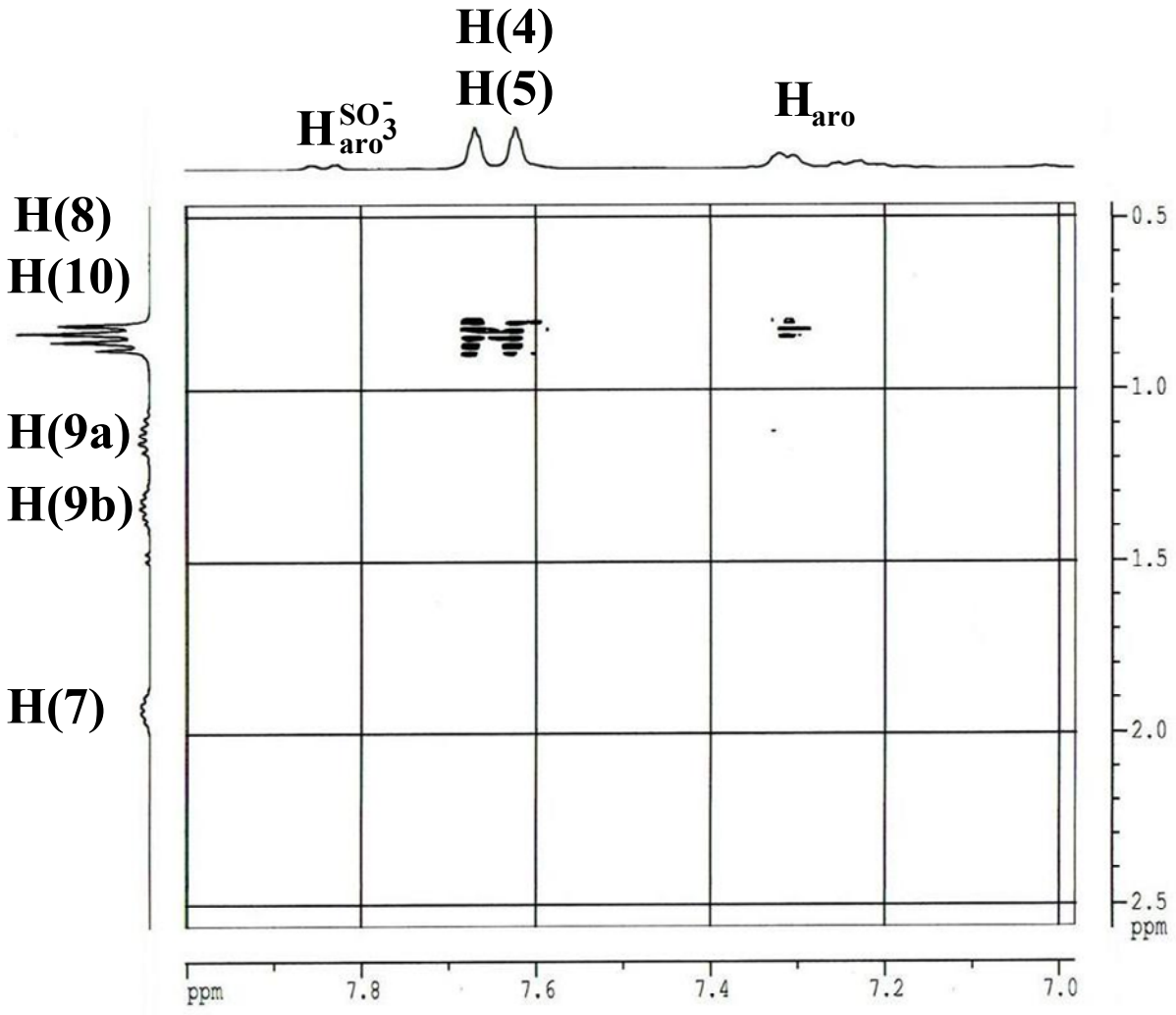
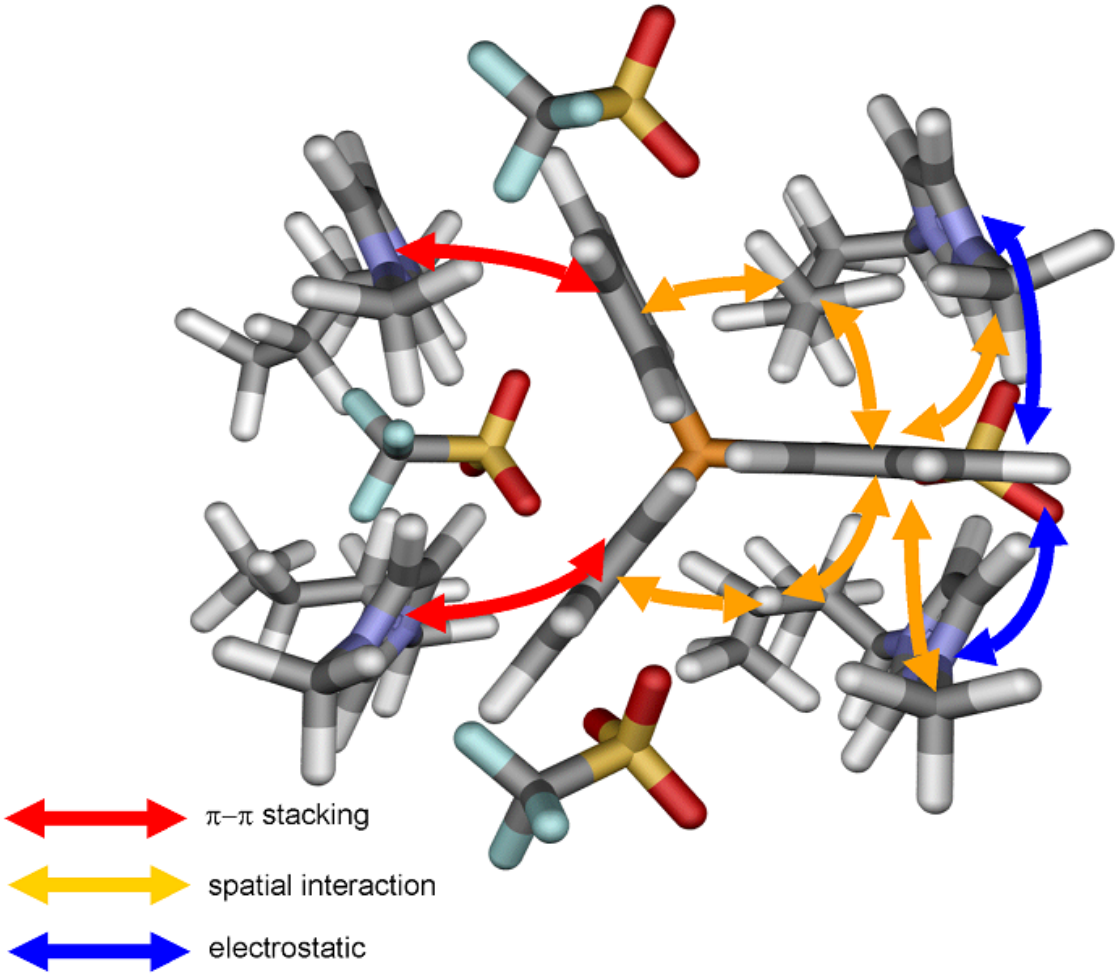


Partial contour plot of T-ROESY spectrum of mixture containing TPPMS and MBMIM 16% (m/m) at 300K with a 300 ms mixing time in 50% [D8]THF (V/V).



(*S*)-MBMIM/TPPMS complex structure and principal interactions deduced from the T-ROESY spectra of a mixture containing TPPMS and (*S*)-MBMIM (hydrogen bonds are not seen in this figure).