Benzoylation for recovery of structure directing agent (Di-n-propylamine) from process effluent of aluminophosphate synthesis

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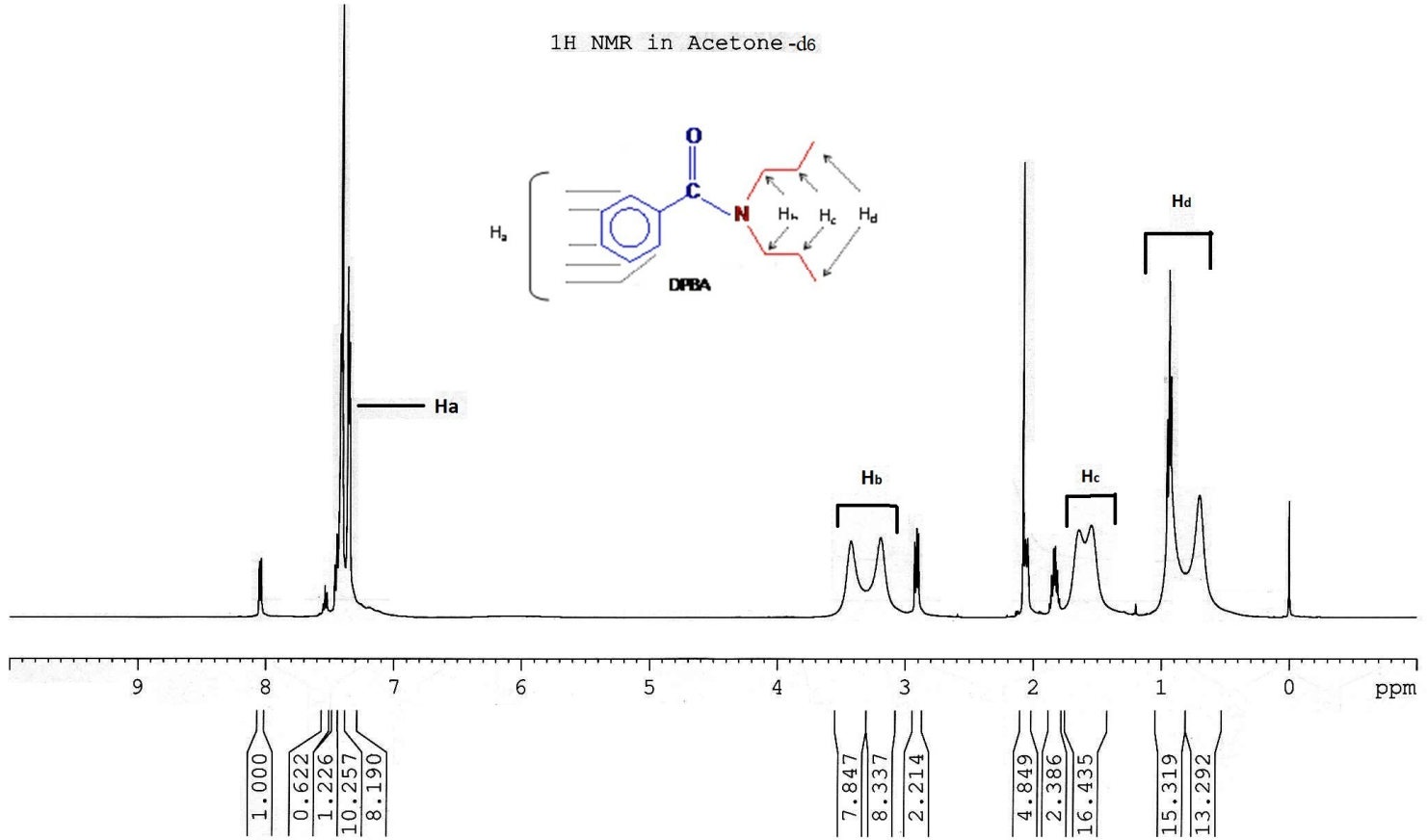
Supplementary Information Page- S1

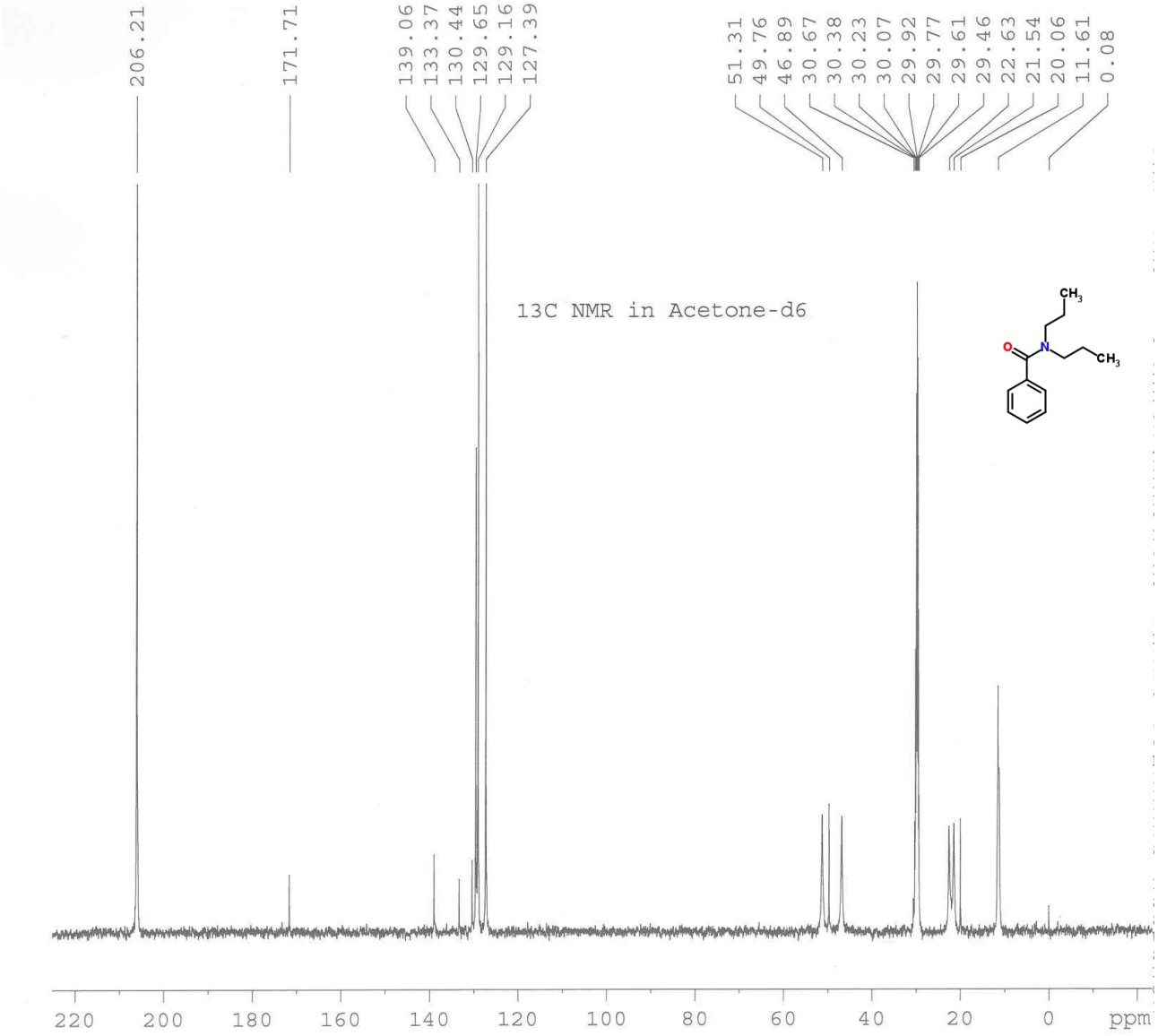
(Assignment of ^{1}H-NMR spectrum to the product, DPBA**)**



The ^{1}H NMR spectrum displayed resonances attributable to DPBA [δ (ppm, aromatic, 5H), 7.40-7.42, 7.34-7.36; δ(-N-CH_2, 4H), 3.42 & 3.19; δ(-CH_2-, 4H), 1.64 & 1.54; δ(-CH_3, 6H), 0.92-0.95 & 0.7-0.81. It appears that both the propyl groups experience 'dissimilar environment', probably arising from 'allylic strain' and rotation about amide bond. In addition, impurities are also identifiable; benzoyl chloride (δ 8.03-8.5, 7.52-7.55 ppm); dipropylamine (δ 2.92-2.89, 2.04, 1.76-1.87, 1.20 ppm) and solvent peak at δ 2.08 ppm.

Supplementary Information Page- S2

(Assignment of ^{13}C-NMR spectrum of product, DPBA)



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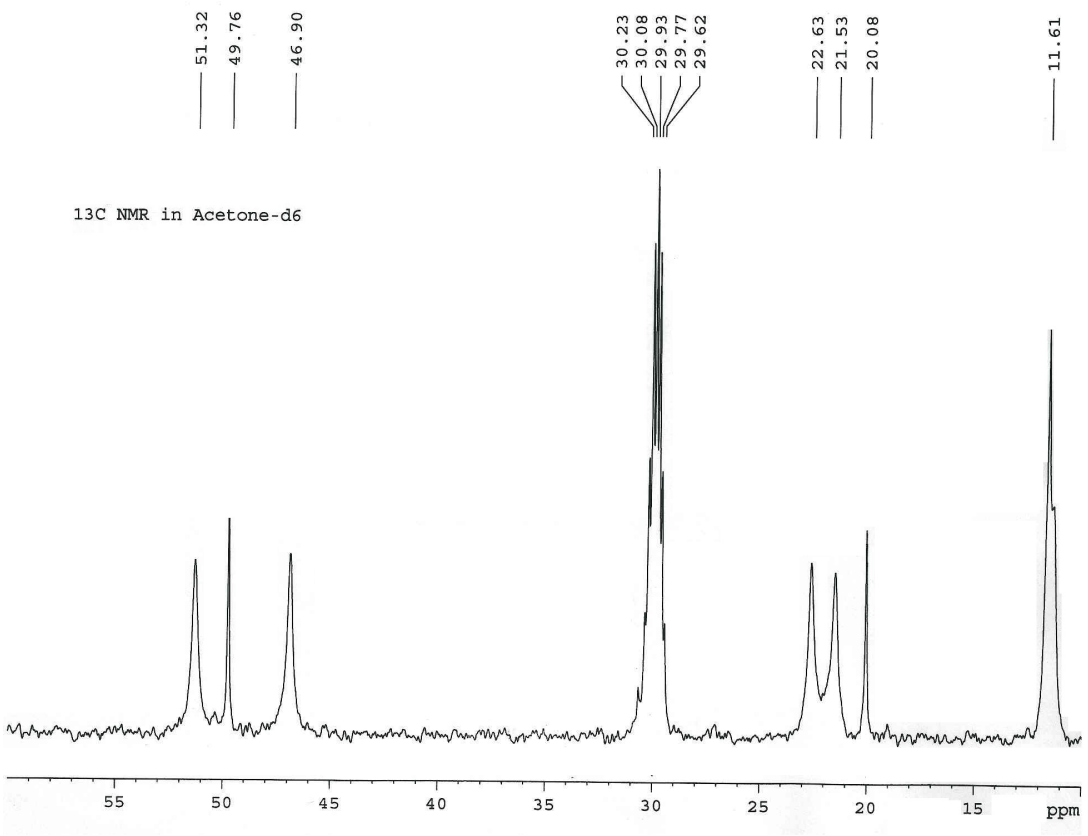
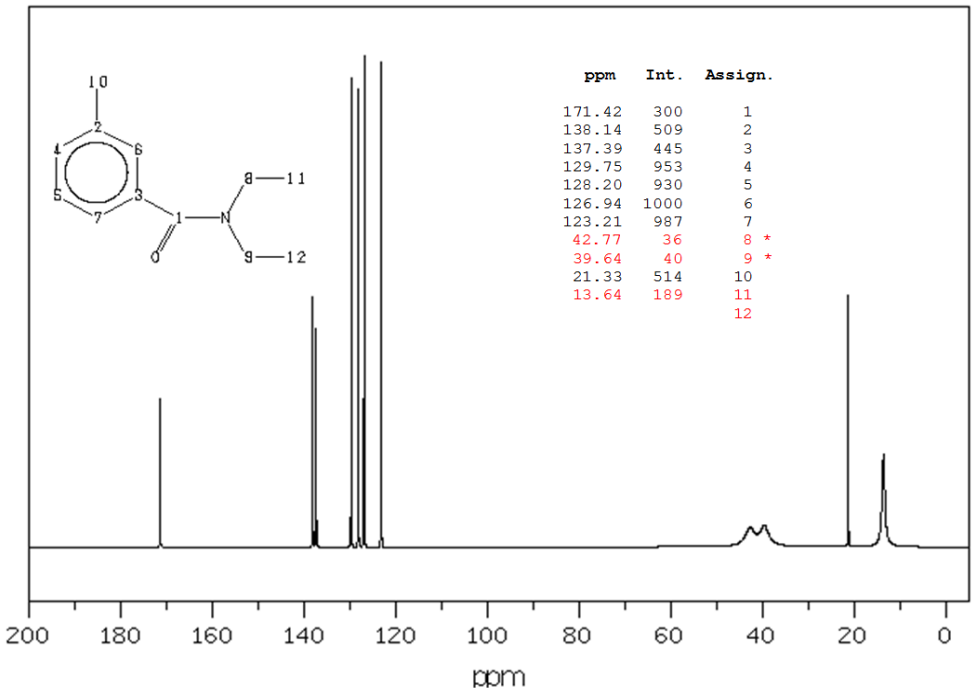
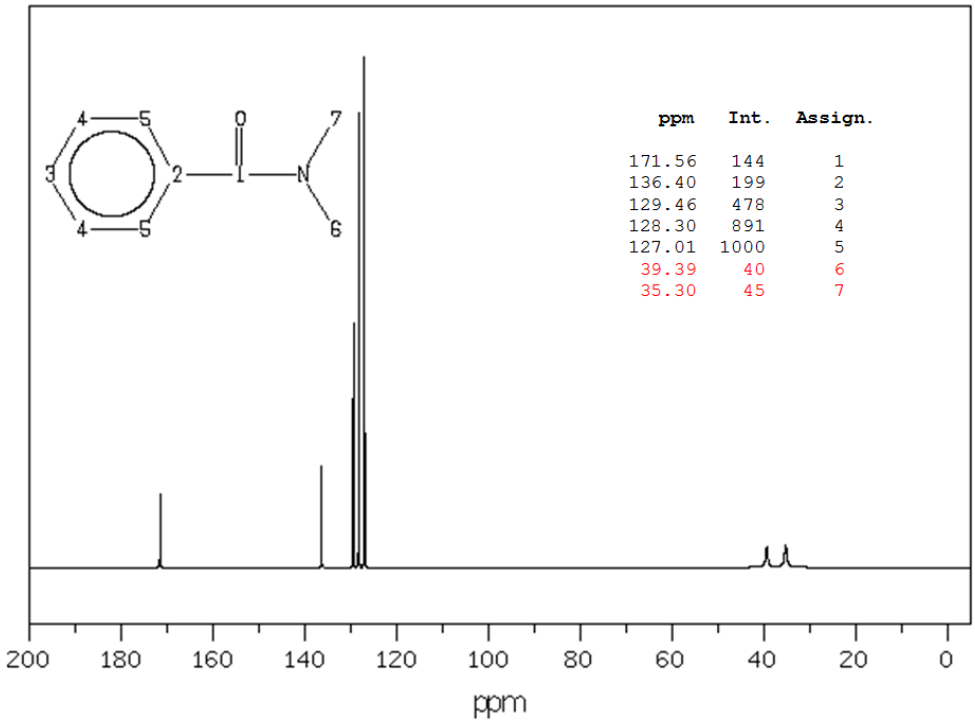


Explanation for ^{13}C-NMR

Generally, 8 different carbons are predicted represented by eight different peaks in the ^{13}C-NMR spectrum of DPBA. The dipropyl groups should have given rise to 3 different peaks; however, surprisingly we observed 6 different peaks indicating that these groups experience **'dissimilar environment'**. The methylene carbons immediately next to N-atom appeared at 50.36 & 47.58, and the ones next to this carbon showed up at 22.14 & 20.73 ppm. The end methyl groups appear to be nearly in the same 'environment' and show up at 12.28 & 11.86(shoulder). In the published literature also similar observations were reported (http://sdbs.riodb.aist.go.jp/sdbs/cgi-bin/cre_index.cgi, see spectra for diethylbenzamide and dimethylbenzamide (next page); www.rsc.org/suppdata/cc/c1/c1cc11635e/c1cc11635e.pdf, Electronic Supplementary Material (ESI) for Chemical Communications, the Royal Society of Chemistry 2011). It is also reported in the case of diethylbenzamide that this could be due to strong steric squeezing of the ethyl groups (allylic strain) leading to the amide group turn and attenuated π-electronic coupling between of aromatic group and amide moieties [P. Majewskaa, J. Paja¸ka, M. Rospenka and A. Filarowski, J. Phys. Org. Chem. 2009, 22 130–137. (www.interscience.wiley.com) DOI 10.1002/poc. 1437; P. Kawski, A. Kochel, M. G. Perevozkina, A. Filarowski, J. Mol. Struct. 2006, 790, 65]. In view of this, we are convinced that our assignment of ^{13}C-NMR is correct.

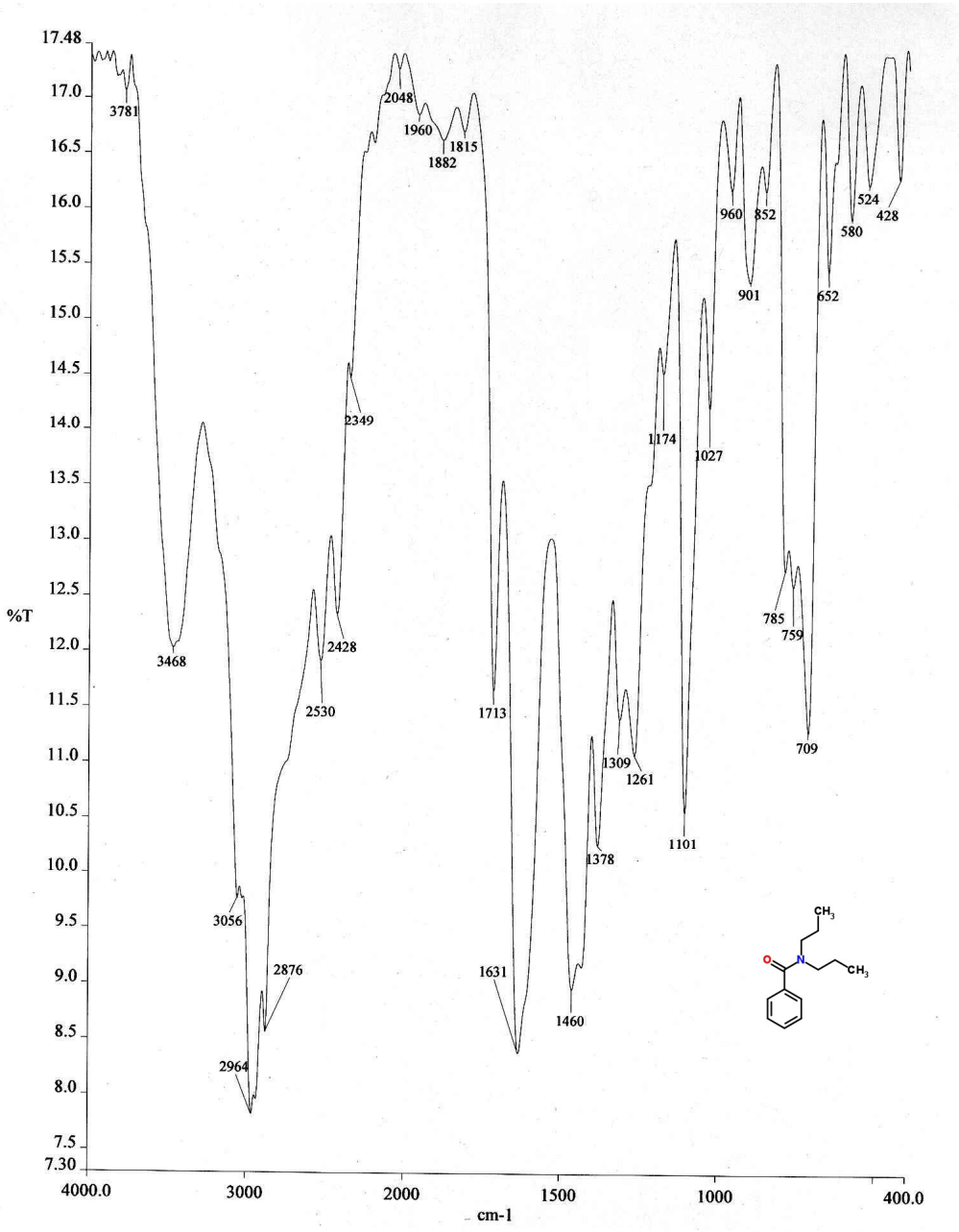
http://sdbs.riodb.aist.go.jp/sdbs/cgi-bin/cre_index.cgi





Supplementary Information Page- S3

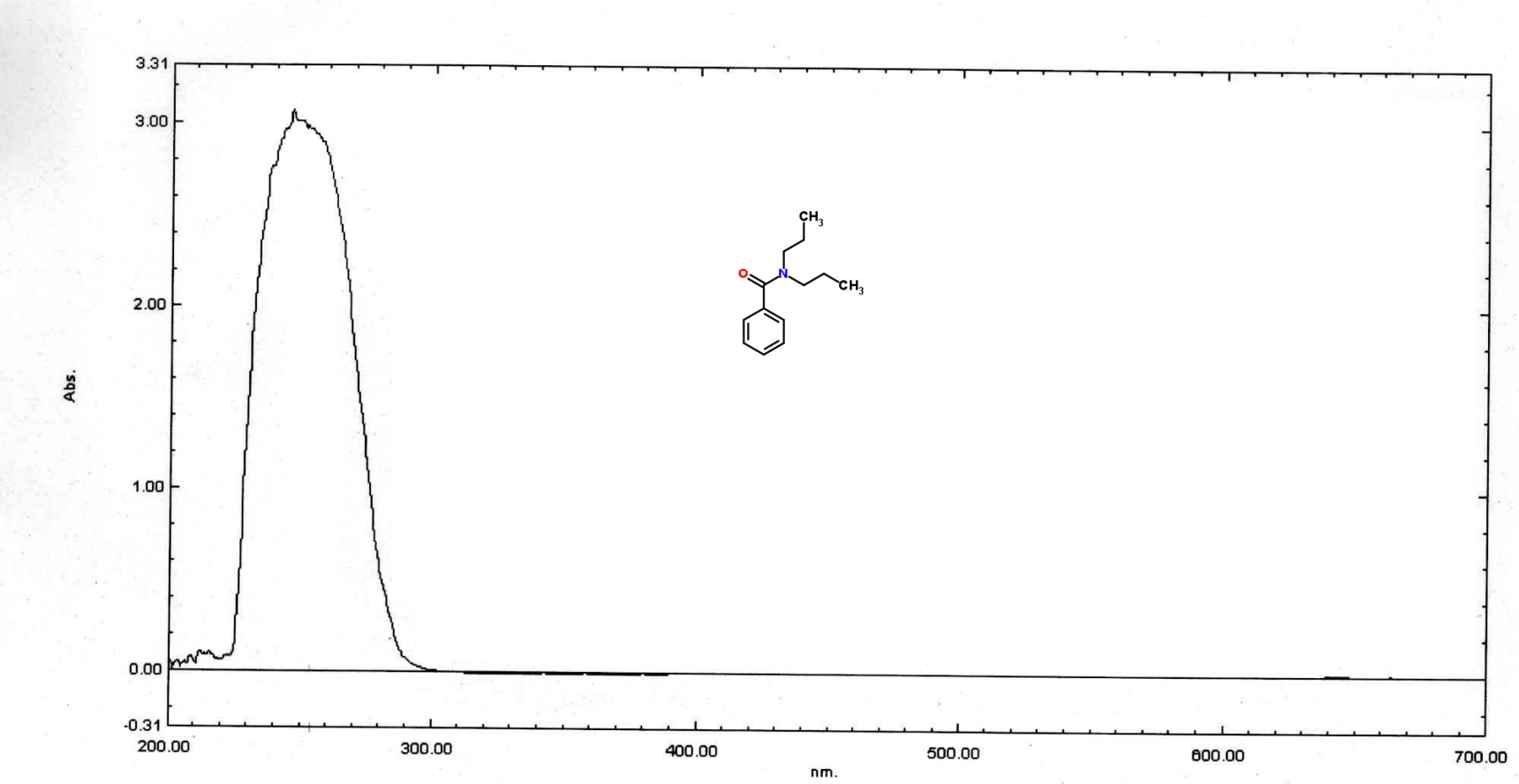
(FT-IR spectrum of the product DPBA, KBr disc)



Major IR absorption peaks observed at 3056-2876, 1631-1460, 1378-1300, 1101, 785, 759 & 709 cm^{-1} may be attributed to ν_{CH} (sp^2 & sp^3), $\nu_{C=O}$, $\nu_{C=C}$ (aromatic), ν_{CH_3}, $_{CH_2}$ (bend), ν_{C-C} (stretch) of the compound, DPBA. The ν_{CH} (bends) were observed at 785-709 cm^{-1}. The absorption at 1713 and 652 cm^{-1} may be due to $\nu_{C=O}$ and ν_{C-Cl} of benzoyl chloride impurities.

Supplementary Information Page- S4

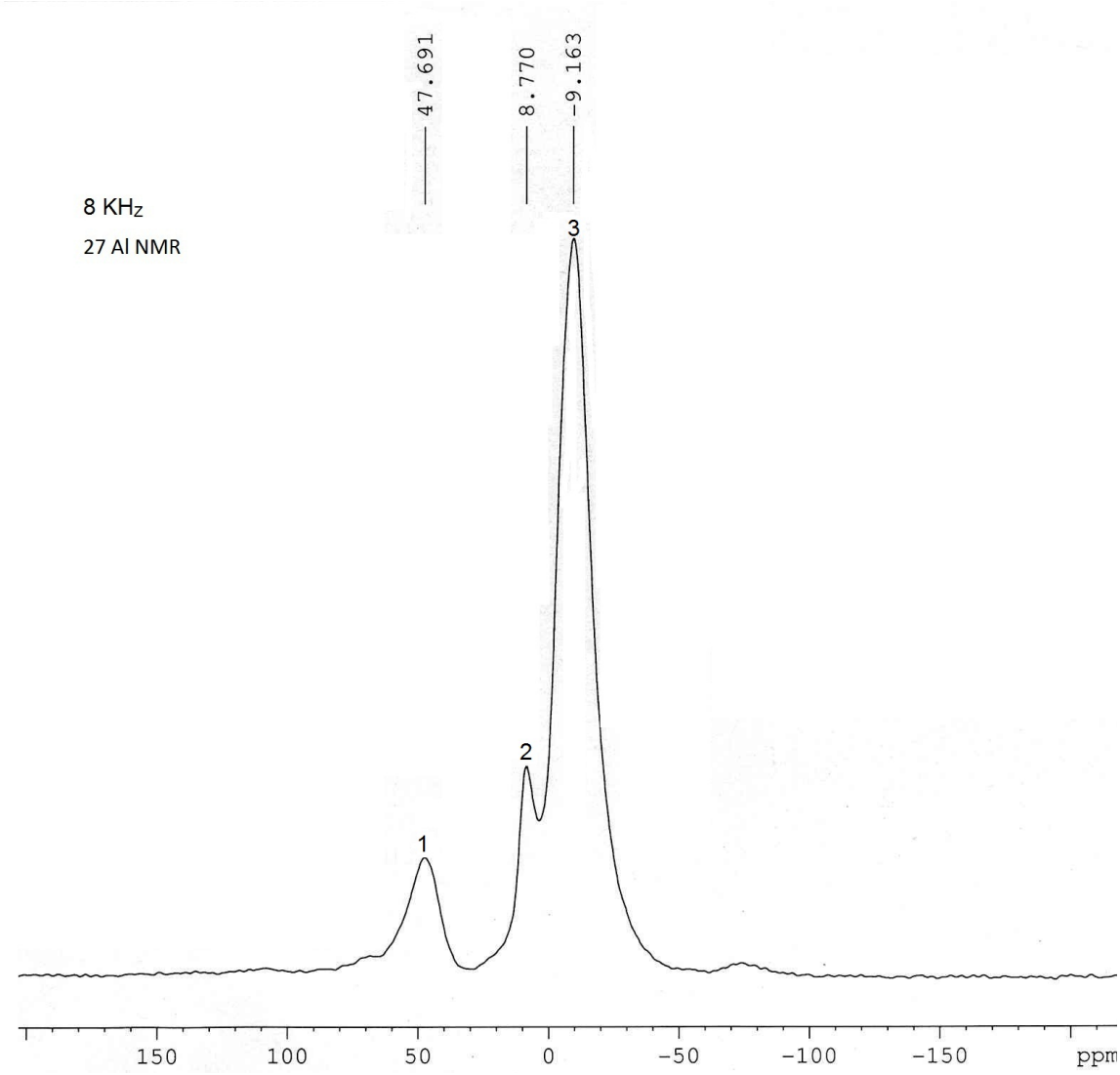
(Electronic spectrum of DPBA in acetone)



The broad absorption band in the range 230-290 nm may be attributed to π-π* transition due to aromatic and –C=O groups in the compound.

Supplementary Information Page- S5

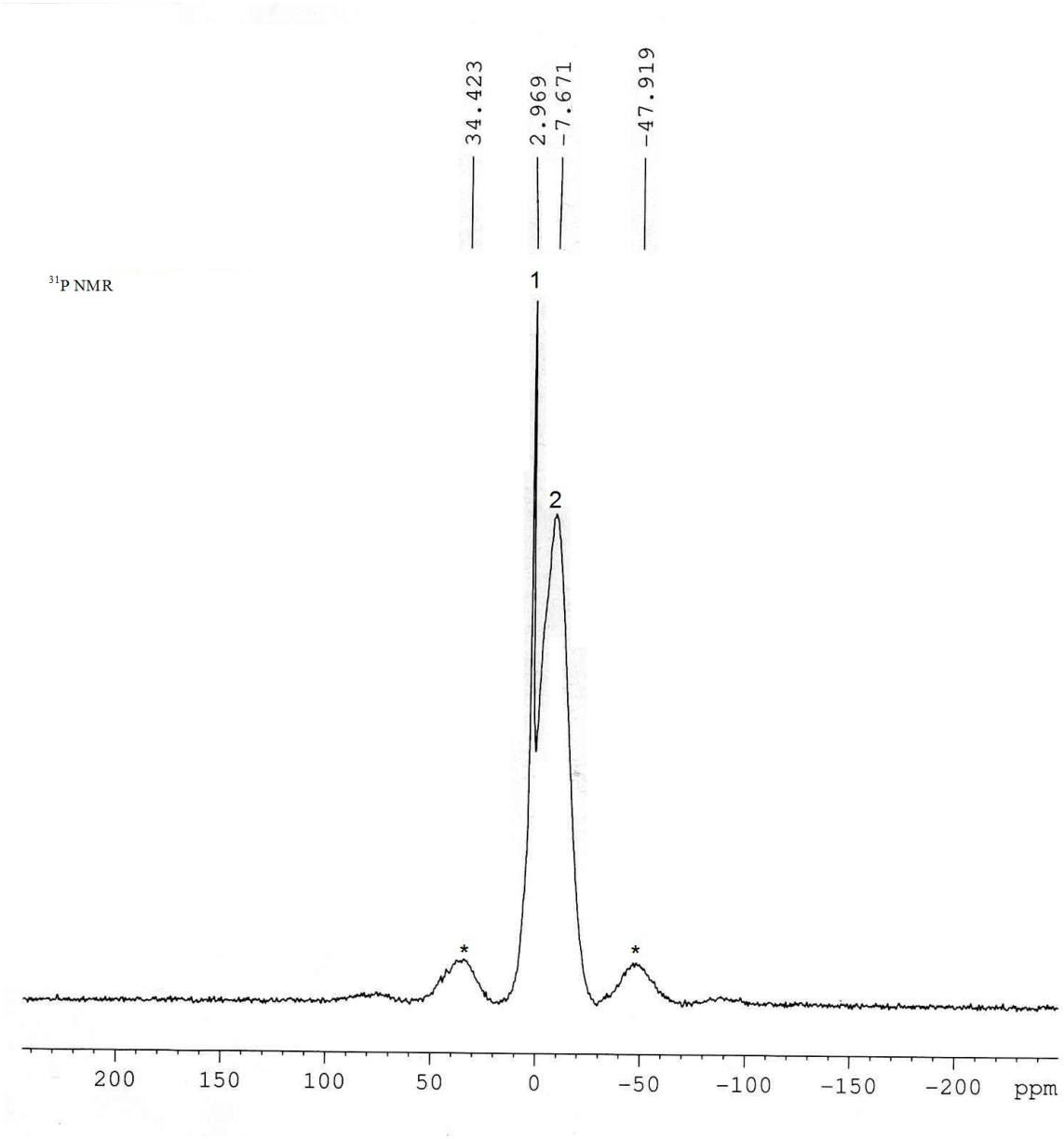
(^{27}Al-NMR Spectrum for the recoverd $AlPO_4$, 8 kHz)



The MAS ^{27}Al NMR spectrum displayed three resonance signals at δ 47.69, 8.77 and -9.16 ppm. They can be attributed Al in tetrahedral, pentagonal and octagonal geometries made up of AlO_X polyheydra. The most intense peak -9.16 ppm is characteristic of hydrated $AlPO_4$ [J. Mol. Str. 470 (1-2), 1998, 221-228; Bleam et al., Phy. Chem. Minerals (1989), 16: 809-816].

Supplementary Information Page- S6

(^{31}P SS-NMR MAS = 8K) spectrum for the recovered $AlPO_4$)

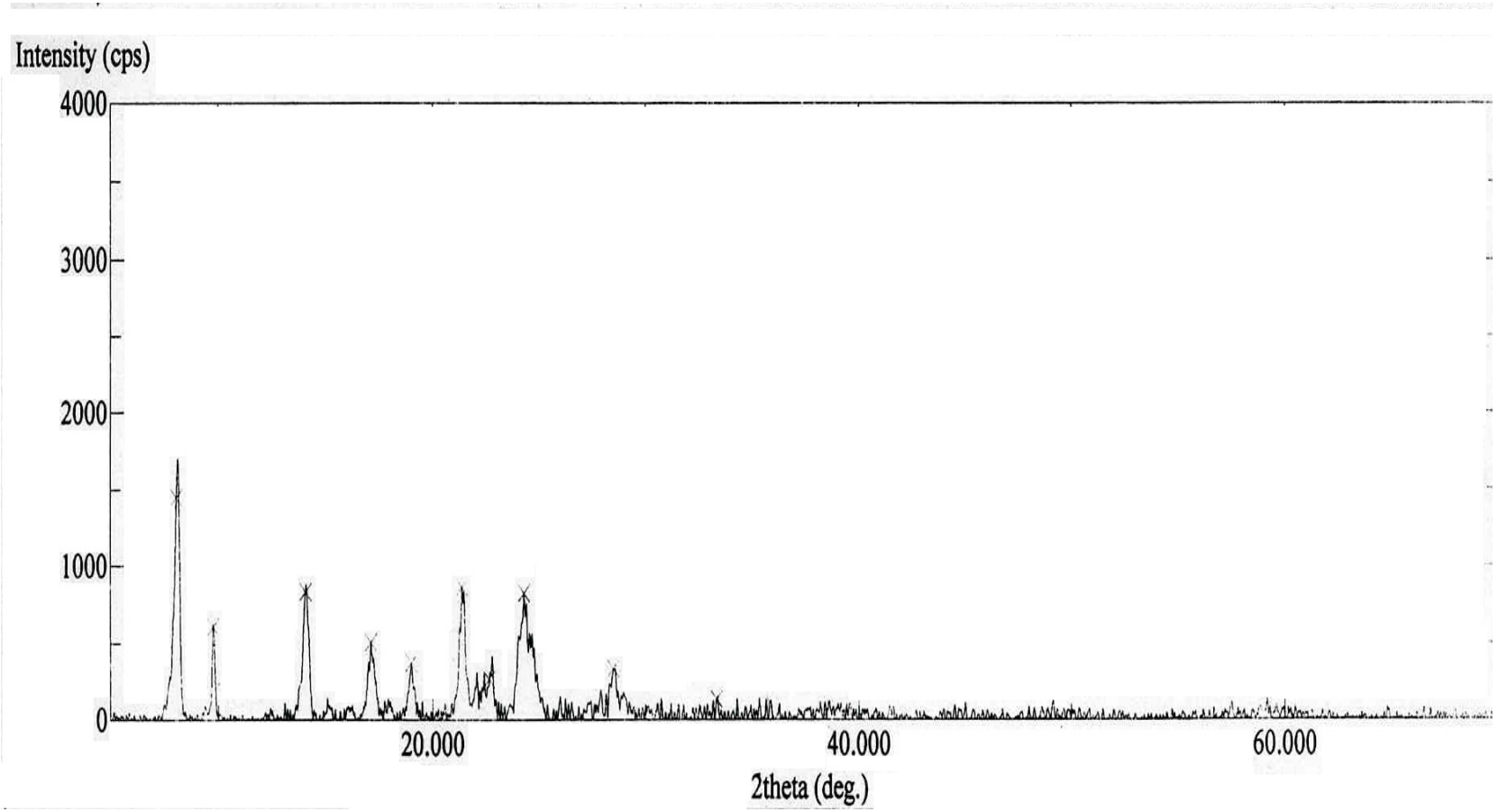


* Spinning side bands

The ^{31}P MAS NMR spectra showed two resonance at δ 2.97 and -7.67 ppm, apart from spinning side bands on either side. These signals can be attributed to PO_4^{3-} polyhedra; the former appears to be due to protonated PO_4^{3-} [Bleam et al., Phy. Chem. Minerals (1989), 16: 809-816].

Supplementary Information Page- S7

(Powder XRD of the product $AlPO_4$, X-ray:Cu Kα, 30 kV/15 mA, Kb filter, scan speed, 5.0 deg/min)



The powder XRD indicated crystalline powder which displayed diffractions at 2θ = 8.06, 9.76, 14.04, 17.08, 18.98, 21.38, 22.66, 24.3, 28.48 and 33.32 deg. Several of these diffractions match with reported XRD of $AlPO_4$ [Li and Davis, J. Chem. Soc. Faraday Trans. 1933, 89, pp. 957-964].

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