Regioselective nitration of aromatic substrates in zeolite cages

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Abstract. Phenol is nitrated regioselectively by fuming nitric acid inside the cages of faujasite zeolites (dependent on the loading level) and a remarkable ortho-selectivity is observed in solid state nitration. Toluene and chlorobenzene also containing ortho-/para-orienting substituents, undergo faster nitration, though the regioselectivity is less significant in zeolite media. The results are explained on the basis of diffusion and binding of phenol inside zeolite, which facilitate regioselectivity (and which is absent in toluene and chlorobenzene). Other advantages of employing zeolites as media for mild and selective nitration are also highlighted.

Keywords. Phenol, toluene, chlorobenzene, regioselective nitration, zeolites.

1. Introduction

Among all electrophilic substitutions, nitration of aromatic substrates is a widely studied reaction of great industrial significance as many nitroaromatics are extensively utilized as chemical feedstock for a wide range of useful materials such as dyes, pharmaceuticals etc. However, earlier technologies[1] involve the use of corrosive liquid phase nitric acid–sulphuric acid mixture, responsible for the generation of large amounts of wastes, which are expensive to treat. Other associated problems are overnitration, oxidation of byproducts and poor selectivity. This necessitates the need for new, novel and simpler methods for nitration which can overcome the problems. Use of nitrogen dioxide and benzene in gas phase over solid catalysts such as SiO_2–Al_2O_3, supported sulphates, supported benzenesulphonic and ZSM-5 zeolite[2] has led to nitrobenzene and the yields are generally moderate.

Liquid-phase applications involve *in situ* generated acyl nitrates and their bulkiness is believed to lead to improved selectivity. Environmentally friendly heterogeneous catalysts based on aluminosilicates are other attractive alternates in liquid phase. Claycop (copper(II) nitrate supported on K10-montmorillonite) has been used[3] in the nitration of toluene with high para-selectivity in the presence of acetic anhydride in carbon tetrachloride. Choudary *et al* have effectively used Fe^{3+}-exchanged montmorillonite catalyst for the selective nitration of chlorobenzene (up to 92% para-selectivity) and reported an isolated yield of 90% in the presence of a mixture of fuming nitric acid–acetic anhydride as nitrating agent.[4] Lanthanide(III) triflate which operates by generating triflic acid is also employed[5] but chlorinated solvents are required and the selectivity is poor. In this context, zeolites containing cages and channels find extensive applications[6–8]

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in organic reactions, either as active participants or as inert supports. Zeolite-based solid acids are potentially attractive due to the easy removability of substrate/product, catalyst recycling and possible regioselectivity due to their constraining environment. For example, in nitration of toluene using benzoyl nitrate in carbon tetrachloride, large pore mordenites[9] gives 60% selectivity. Smith *et al* have used zeolite H-***b*** and acetyl nitrate to yield highly regioselective para-nitration of toluene.[10,11] Other advantages of using zeolites include quantitative yield of mononitration under mild conditions, very good selectivity, recovery and reuse of the catalysts. For the nitration of deactivated aromatic compounds also, novel nitration systems composing of nitric acid, trifluroacetic anhydride and H-***b*** are reported.[12] With emphasis on achieving higher para-selectivity to meet market demand, Choudary *et al* have achieved a zeolite-based methodology for the nitration of aromatic compounds.[13] They have carried out nitration of toluene with various zeolite catalysts and zeolite beta of different Si/Al ratios. Zeolite beta has proved to be the best catalyst among the zeolites used in terms of space-time yield and para-selectivity. Increased Brönsted acidity that reduces the available space is attributed to the improved para-selectivity. Same catalyst is found to nitrate aromatic substrates efficiently containing electron-withdrawing substituents as well. Halogenobenzenes undergo para-selective nitration with a nitrogen dioxide-oxygen-zeolite H-***b***/HY as a solid inorganic catalyst.[14] Recently zeolite-assisted nitration of neat toluene and chlorobenzene with a nitrogen dioxide/molecular oxygen system is reported[15] and a remarkable enhancement of para-selectivity is observed. In the double Kyodai nitration of the same substrates over zeolites, high preference for the 2,4-dinitro isomer is observed at the second nitration stage.[16]

It is significant to note that many of the earlier studies employ polar solvents such as acetonitrile, which tend to retain the substrate in the solvent phase rather than in the interior of the zeolite cages. Also nitration of arenes with strongly activating groups (wherein polynitration is a serious handicap to selective nitration) in zeolite environment is not explored. With these goals in mind, we have reported[17] recently regioselective nitration of phenol inside the cages/channels of zeolite media using fuming nitric acid. In our attempts to delineate the mechanism in detail and also to generalize the applicability of this procedure to other aromatic compounds, we have chosen two more substrates, namely toluene and chlorobenzene, which are also ortho-/para-orienting but with reduced activation of the aryl ring and the salient features of this study are presented below.

2. Results and discussion

2.1 *Nitration of phenol*

In the present study, unlike earlier studies of zeolite-induced nitration of deactivated/ weakly activated aromatic substrates, HPLC grade hexane (nonpolar) is chosen as the solvent of choice, which ensures the presence of phenol predominantly inside the more polar cages/channels of zeolite (scheme 1). To demonstrate this unequivocally, nitration is carried out at two different loading levels. At a lower loading level (which corresponds to 3·6 molecules per supercage) in NaY, picric acid (**1d**) is the major product followed by the *p*-nitrophenol (**1c**). With NaX zeolites, the selectivity is less pronounced compared to solution reaction and the amount of the *o*-isomer (**1a**) increases at the expense of (**1c**) and (**1d**). However, when the reaction carried out inside the narrow channels of molecular sieves 5 A and also in CsY (with much larger cations which reduce the cage size and are

X = OH, CH$_3$, Cl

1   2   3   **(a)**   **(b)**   **(c)**   **(d)**

Scheme 1.
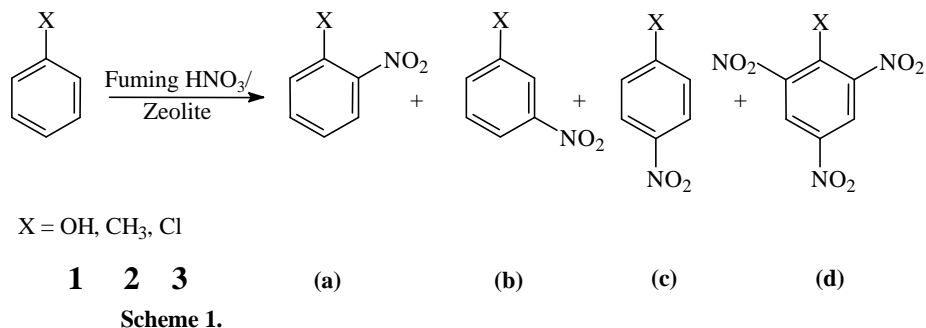
expected to exert steric hindrance to nitration), the formation of the *p*-isomer (**1c**) is more pronounced. With more acidic CaY zeolites, conversion is low (isolated yield is only 50%) indicating stronger binding of the reaction mixture with the zeolite, thus limiting their utility in the present study. There is no reaction when 1 : 1 dil. HNO$_3$ is added, as the cages are blocked by water molecules.

At a higher loading level of phenol (corresponding to 39 molecules per supercage), the influence of the zeolite environment is insignificant. As the results in table 1 indicate, in both the faujasite zeolites (NaY and NaX), an identical products distribution, (in which *o*-nitrophenol (**1a**) is the major product followed by significant amount of picric acid), is obtained. Thus with excess amount of phenol, most of them are forced to stay outside the zeolite cage and nitration occurs, predominantly in the solution phase. This assumption is supported by the observation of a similar product distribution in the absence of zeolites under identical conditions. When a narrow channel molecular sieve (inner diameter of ~ 5 A) is used, the amount of *p*-nitrophenol (**1c**) has increased. It is relevant to note here that zeolite-mediated *p*-selectivity within narrow pore zeolites such as ZSM-5 is well known.[15]

A remarkable regioselectivity in nitration is observed, when phenol is treated with fuming nitric acid in the presence of NaY zeolite in solid state. With a loading level corresponding to 8 molecules per supercage, the *o*-isomer (**1a**) is the exclusive product. The significantly higher loading level coupled with the constrained environment of zeolite in solid state forbids free mobility of phenol inside the supercage and this results in exclusive formation of *o*-nitrophenol. An increase in the amount of nitric acid, while increasing the percentage conversion, decreases the regioselectivity. The amount of *o*-isomer decreases, with a concomitant increase in the amount of picric acid, regioselectivity in the solid state is also observed in the X-type faujasites too. For example, solid state nitration of phenol in NaX zeolite yields only *o*-nitro phenol, (with a slight decreased percentage conversion, 19% compared to 23% in NaY zeolite). The result is also independent on the amount of zeolite. For example, doubling the amount of zeolite and the reagents, has also resulted in the same *o*-nitro phenol (20% conversion), without sacrificing the selectivity.

2.2 *Nitration of toluene and chlorobenzene*

Successful regioselective nitration of phenol has prompted us to extend the nitration studies to toluene (weakly activating and *o*-/*p*-orienting). In an earlier work, Laszlo has

Table 1. Percentage conversion and products distribution in nitration of phenol (**1**) by fuming nitric acid [a].

Zeolite	Amount of		Conversion (%)	Product proportions of [b]			
	HNO_3 (ml)	Zeolite (mg)		**1a**	**1c**	**1d**	X^c
At lower loading level of PhOH[d]							
Nil	0·6	500	100	50	19	10	21
NaY	0·6	500	100	17	37	41	5
NaX	0·6	500	44	43	21	36	–
CaY[e]	0·6	500	57	8	2	–	90
CsY	0·6	500	76	16	76	8	–
Mol. Sieve 5 A	0·6	500	100	11	72	16	1
1 : 1 dil. HNO_3	0·6	500	nil	–	–	–	–
At higher loading level of PhOH[f]							
Nil	0·06	500	100	59	23	9	9
NaY	0·06	500	100	52	32	16	–
NaX	0·06	500	79	57	33	4	6
CaY	0·06	500	100	56	33	10	–
CsY	0·06	500	100	58	32	8	2
Mol. Sieve 5 A	0·06	500	100	48	43	8	1
Solid state nitration of PhOH[g]							
NaY	0·03	500	23	100	–	–	–
NaY	0·03	750	19	100	–	–	–
NaY	0·03	1000	12	100	–	–	–
NaY	0·03	500	13	100	–	–	–
NaY	0·06	500	40	69	17	11	3
NaY	0·09	500	59	52	16	27	5
NaY	0·12	500	58	25	9	54	12

[a] As hexane slurry, at 0–5°C for 30 min: analysed by GC; error limit ± 2%
[b] Percentage conversions are normalised to 100; for structures of **1a–1d** refer scheme 1
[c] Unidentified products
[d] With 70 mg of **1** (corresponds to a loading level of 3·6 molecules per supercage)
[e] Isolated yield is ~ 50%
[f] With 800 mg of **1** (corresponds to a loading level of 39 molecules per supercage)
[g] 0·15 ml (1·75 mmol) of **1** in 500 mg of NaY zeolite (corresponds to a loading level of 7·5 molecules per supercage). After the addition of HNO_3 at 0–5°C for a period of 5 min, the solid sample was kept at room temperature for 30 min

developed Claycop ($Cu(NO_3)_2$/montmorillonite-K10) that selectively nitrates toluene in acetic anhydride/CCl_4 with an isomer distribution of ortho 23, meta 1 and para 76%.[18] Smith has shown that mordenite and zeolite *b* can play an important role in the selective mononitration of toluene, where the *p* selectivity of 67% by using benzoyl nitrate[9] and the *o/p* isomer ratio of 0·23 by using acetyl nitrate[10,11] have been achieved. Toluene has also been nitrated with isopropyl nitrate in the presence of HZSM-5, producing predominantly the *p*-isomer (95%).[20] In the presence of molecular oxygen and HZSM-5, neat toluene has reacted with liquid nitrogen dioxide in a regioselective manner at room temperature to yield mononitrotoluenes as main products, where the *p*-isomer predominates up to 90%.[16]

With an objective of finding replacement of liquid sulphuric acid in the nitration of toluene and nitrotoluenes, Vassena *et al*[20] have used solid acids such as silica-impregnated sulphuric acid, H-beta, mordenite, ZSM-5 and ZSM-12 under vapour phase conditions. Zeolite-beta has provided a higher 4-nitrotoluene to 2-nitrotoluene ratio than ZSM-5, ZSM-12 and mordenite, but becomes deactivated after 5-10 h on-stream.

In the present study, solution nitration of toluene produces *o*- and *p*-nitrotoluenes in a 56 : 39 ratio (table 2) as in previous studies of nitration. Nitration in various cation-exchanged zeolites in hexane slurry causes a marginal improvement in the yield of the *p*-isomer (**2c**) and this is more significant in solid state nitration. Neither cation-size nor the pore dimensions of zeolite seems to influence further the selectivity of the reaction. Similarly variation in loading level of the substrate also has no effect. Though the selectivity is not as dramatic as in the case of phenol nitration, the present method of nitration of toluene has other advantages. The reaction is faster compared to solution nitration (due to the confinement of reagent and substrate inside the cage) and polynitration is totally suppressed. The poorer selectivity may be attributed to the weakly polar nature of the alkyl group, which destabilizes any interaction with the polar zeolite environment and this may have forced bulk of the substrate into the solution phase.

Nitration is also extended to a deactivated, *o-/p*-orienting substrate namely chlorobenzene (table 3). Though the selectivity is not as significant as expected, the conversion is faster and quantitative. However in the solid state the yield of *o*-isomer increases considerably compared to solution nitration. Increased deactivation of the aryl ring (compared to phenol and toluene), has resulted in a marked improvement in the selectivity in solution phase nitration and an *o-/p*-ratio of 27/71 (0·38) is observed, in

Table 2. Percentage conversion and products distribution in nitration of toluene (**2**) by fuming nitric acid [a,b].

| Zeolite | Conversion (%) | Product proportions of [c] | | | | ortho/para ratio |
		2a	**2b**	**2c**	X[d]	
Solution	57	56	5	39	–	1·44
NaY	100	48	5	44	3	1·09
NaX	100	53	3	44	–	1·20
Mol. Sieve 5 A	100	56	4	40	–	1·40
RbY	100	57	4	39	–	1·46
CsY	99	55	4	40	1	1.38
NaY[e]	100	54	4	42	–	1·29
NaY[f]	100	52	4	44	4	1·18
NaY[g]	70	49	1	50	–	0·98

[a] As a hexane slurry, at room temperature for 30 min, with 500 mg of zeolite and 0·6 ml of fuming nitric acid, with 800 mg of **2** (corresponds to a loading level of 32 molecules per supercage)
[b] Analysed by GC; Error limit ± 2%
[c] Percentage conversion are normalized to 100; for structures of **2a–2c** refer scheme 1
[d] Unidentified products
[e] With 80 mg of **2** (corresponds to a loading level of 3·6 molecules per supercage)
[f] Solid state nitration of **2** (0·18 ml), with 0·12 ml of fuming nitric acid
[g] Solid state nitration of **2** (0·18 ml), with 0·03 ml of fuming nitric acid

Table 3. Percentage conversion and products distribution in nitration of chlorobenzene (**3**) by fuming nitric acid [a,b].

| Zeolite | Conversion (%) | Product proportions of [c] | | | ortho/para ratio |
		3a	**3c**	X[d]	
Solution	2	27	71	2	0·38
NaY	100	22	78	–	0·28
NaX	100	23	77	–	0·29
RbY	100	25	75	–	0·33
CsY	100	28	72	–	0·39
NaY[e]	100	25	75	–	0·33
NaY[f]	100	33	67	–	0·49
NaY[g]	67	39	61	–	0·64

[a] As a hexane slurry, at room temperature for 30 min, with 500 mg of zeolite and 0·6 ml of fuming nitric acid, with 800 mg of **3** (corresponds to a loading level of 35 molecules per supercage)
[b] Analysed by GC; error limit ± 2%
[c] Percentage conversion are normalized to 100; for structures of **3a–3c** refer scheme 1
[d] Unidentified products
[e] With 80 mg of **3** (corresponds to a loading level of 3·3 molecules per supercage)
[f] Solid state nitration of **3** (0·14 ml), with 0·12 ml of fuming nitric acid
[g] Solid state nitration of **3** (0·14 ml), with 0·03 ml of fuming nitric acid

accordance with the greater thermodynamic stability of the *p*-isomer. Here also, as in toluene nitration, variation in cation size as well as loading level has not resulted in any significant variation in reaction selectivity.

Of the three substrates, phenol is the most reactive. However, it is striking to note that it is also the more selective, contrary to expectations based on reactivity-selectivity principle. This is more remarkable in solid phase nitration at a lower loading level and the other two substrates, namely toluene and chlorobenzene are insensitive to loading level variations. To account for this behaviour, we propose that phenol being more polar, enters more readily into the zeolite cages (compared to the other two substrates) and binds to the basic sites. Subsequent interaction with the active nitrating species (scheme 2) has resulted in *o*-nitration and this is more favoured in the solid state. The weakly polar nature of toluene and chlorobenzene leads to poor binding and has resulted in free mobility in and out of the cage. Consequently, loading level has no effect on nitration of these two substrates as nitration now takes place predominantly in solution phase.

Thus the observed results clearly indicate regioselective nitration of phenol and faster reactivity in toluene and nitrobenzene, in different zeolite environment. While solid state nitration ensures exclusive *ortho*-nitrophenol formation in NaY, the same reaction in slurry in the presence of molecular sieve (5 A) and also with CsY (with bulkier cations) leads to predominant formation of *p*-nitrophenol. The yield of the various products also depends on the loading level of the substrate inside the supercage. By using chemical evidences, the results also demonstrate for the first time that diffusion into the cage followed by binding (more significant in lower loading level) can lead to remarkable regioselectivity in nitration. It is relevant to note here that in previous studies on nitration of phenol, *p*-substitution is achieved regioselectively and in contrast to them, the present
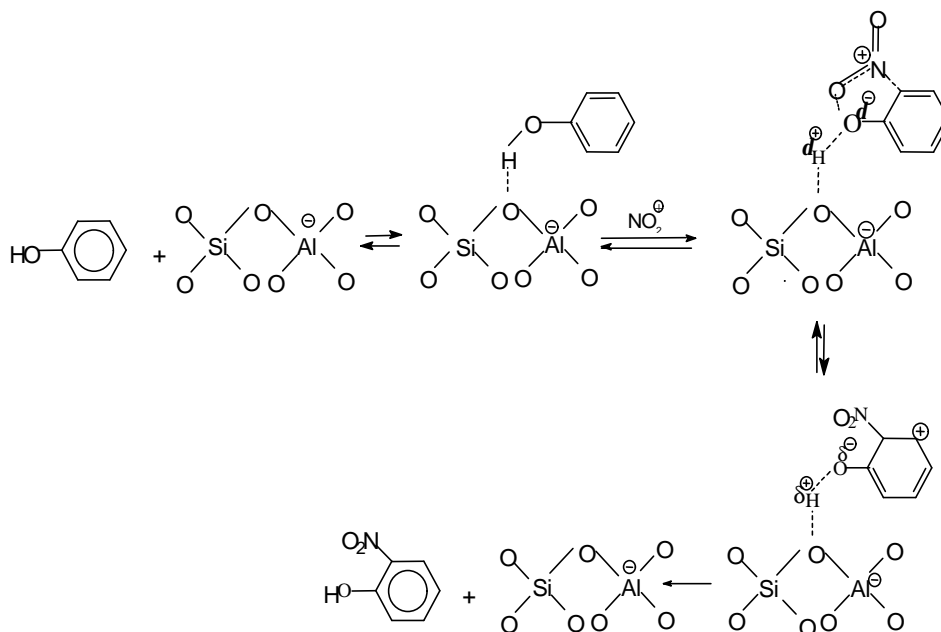
Scheme 2. Mechanism of nitration of phenol in solid phase.

study enables exclusive formation of *o*-isomer. Other advantages include significant reduction in polynitration, absence of mixed nitrating agents (no need for *in situ* generation of active nitrating species) and demonstration of the reaction inside the supercage (as evident from the absence of any significant variation in product distribution at a higher loading level, in which case the reaction is predominantly outside the cage). Thus zeolites provide an ideal platform for mild, safer and regioselective nitration of an electron-rich substrate too, as in the case of phenol. They are also reusable (through a thermal treatment) and are environmentally benign. Another interesting factor which differentiates zeolites from other constrained media is that as molecular sieves, they help in retaining the byproduct water in their cages.

3. Experimental

3.1 *General*

Toluene, phenol and chlorobenzene (E-merck) were employed after distillation. NaY zeolite was obtained from Aldrich; Molecular sieve 5 A was obtained from E Merck. The cations of interest were exchanged into the NaY powder by stirring with the corresponding nitrate (10%) solution at 70°C for about 12 h. The exchange was repeated at least four times. Each time after exchange, the zeolite powder was washed repeatedly with distilled water and then dried. All the zeolites were preheated at 500°C, in muffle furnace for 6 h, before use.

3.2   *Nitration procedure*

3.2a   *Nitration of phenol in solution:*   In a typical experiment, to a solution of a phenol in 5 ml of hexane kept at 0–5°C, 500 mg of activated zeolite (preheated to 450°C in a muffle furnace) was added and kept stirring as a hexane slurry. Known amount of fuming nitric acid was added and the solution was magnetically stirred for 30 min while maintaining the temperature at 0–5°C. After bringing the reaction mixture to room temperature, the hexane portion was removed. Overnight extraction of the zeolite using dichloromethane was carried out. The combined hexane and dichloromethane portions, after removal of the solvent, was analysed by GC.

3.2b   *Solid state nitration of phenol:*   To a solution of phenol in 5 ml hexane, activate zeolite was added and stirred for 6 h. Then the solvent was removed by rotary evaporation. To this solid sample (kept at 0–5°C), nitric acid was added for a period of 5 min, with continuous shaking. The reaction mixture was kept aside for 30 min at room temperature and then subjected to overnight extraction with dichloromethane. Products were identified by their retention times and also by coinjection with authentic samples. In all the zeolites, except CaY, recovered mass balance was about 90%.

3.2c   *Nitration of toluene and chlorobenzene in solution:* Aromatic substrates (17·5 mmol) and preheated zeolite (500 mg) were mixed in 5 ml hexane (HPLC grade) and stirred together for 5 min. After that known volume of fuming nitric acid was added drop wise for 15 min at room temperature. After the addition was over the mixture was stirred for 30 min. Overnight extraction of the zeolite using dichloromethane was carried out.

3.2d   *Solid state nitration of toluene and chlorobenzene:*   The substrates and preheated zeolite were stirred with 5 ml hexane for 1 h at room temperature and allowed to settle for 1 h. The hexane portion was removed. The solid portion was washed with 2 ml of hexane and removed again the hexane portion. The mixture was dried in air for 2–3 min and then nitrogen gas was passed through it for 5 min. Known amount of fuming nitric acid was added to it, the solid sample was kept at room temperature for 30 min. Overnight extraction of the zeolite using dichloromethane was carried out.

3.3   *Analysis of the reaction mixture*

All GC analyses were carried out on a Shimadzu 17 A model gas chromatograph unit (SE-30 10% capillary column, FID detector) and high purity nitrogen as the carrier gas. Retention times of phenol, toluene and chlorobenzene were taken as the internal reference. Products were identified by their retention times and also by coinjection with authentic samples.

3.4   *Spectral data of products*

In many cases products were isolated from the reaction mixture carried out in bulk. They were identified by their ^{1}H-NMR spectra and also by their GC-retention times.

(**1a**) 90 MHz CDCl$_3$ 7·8 ***d*** (*d*, 1H), 7·4 ***d*** (*t*, 1H), 6·9 ***d*** (*t*, 1H), 6·7 ***d*** (*d*, 1H), 6·6 ***d*** (*s*, 1H).

(**1c**) 90 MHz Acetone d_6 7·4 **d** (*d*, 2H), 6.4 **d** (*s*, 1H), 6.2 **d** (*d*, 2H).
(**1d**) 90 MHz DMSO d_6 8·2 **d** (*s*, 1H), 7·4 **d** (*s*, 2H).
(**2a**) 90 MHz CDCl$_3$ 7·7 **d** (*d*, 1H), 7·6 **d** (*d*, 1H), 7·3 **d** (*t*, 1H), 7·1 **d** (*t*, 1H), 2·4 **d** (*s*, 3H).
(**2b**) 90 MHz CDCl$_3$ 7·8 **d** (*s*, 1H), 7·3 **d** (*t*, 1H), 7·2 **d** (*d*, 1H), 7·1 **d** (*d*, 1H), 2·3 **d** (*s*, 3H).
(**2c**) 90 MHz CDCl$_3$ 7·8 **d** (*d*, 2H), 7·1 **d** (*d*, 2H), 2·3 **d** (*s*, 3H).
(**3a**) 90 MHz CDCl$_3$ 7·8 **d** (*d*, 1H), 7·7 **d** (*d*, 1H), 7·5 **d** (*t*, 1H), 7·3 **d** (*t*, 1H).
(**3c**) 90 MHz CDCl$_3$ 7·9 **d** (*d*, 2H), 7·4 **d** (*d*, 2H).

Acknowledgements

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