Electronic Supporting Information

for

Mechanochemical reactions studied by *in situ* Raman spectroscopy: base catalysis in liquid-assisted grinding

by

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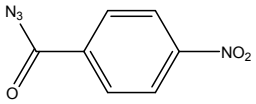
EXPERIMENTAL

General comments. The infrared (IR) spectra were recorded using PerkinElmer Spectrum RX I Fourier-transform (FT) IR System spectrometer (KBr pellets technique) and using PerkinElmer System2000 FT-IR spectrometer (as suspensions in Nujol applied on NaCl windows). The ^{1}H and ^{13}C spectra (in DMSO-d_6 at RT) were measured on Bruker Avance (300 or 600 MHz) spectrometers with tetramethylsilane as an internal standard.

Synthesis of 4-nitrobenzoyl azide 1

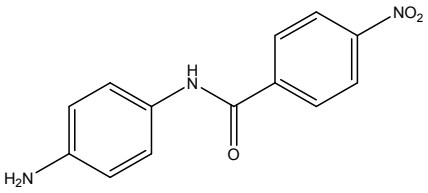


A solution of 4-nitrobenzoyl chloride (8.0 g, 43.1 mmol in 15 mL) was gradually added to an aqueous solution of sodium azide (4.2 g, 64.6 mmol in 20 mL). The resulting reaction mixture was stirred at room temperature for 40 minutes. The precipitate was collected by filtration and dissolved in dichloromethane. This solution was extracted with $NaHCO_3$ (3x20 mL). Collected organic layers were dried over Na_2SO_4 and solvent evaporated to dryness. Product **1** was obtained as light yellow crude in 90% yield (7.461 g).

NMR data: δ_H(300 MHz; d_6-DMSO; Me_4Si) 8.18 (m, 2H, Arom), 8.36 (m, 2H, Arom). δ_C(75 MHz; d_6-DMSO; Me_4Si) 124.06, 130.43, 135.25, 150.86, 170.69.

IR data: ν_{max}/cm^{-1} : 3367(vw), 3108(vw), 2348(w), 2180(w), 2137(m), 1703(m), 1605(w), 1536(m), 1247(m), 1235(m), 1178(m), 1105(w), 996(m), 870(w), 845(m), 719(w), 709(m).

Synthesis of *N*-(4-aminophenyl)-4-nitrobenzamide in solution



1,4-Diaminobenzene (0.050 g, 0.925 mmol) and 4-nitrobenzoyl azide (0.08885 g, 0.9249 mmol) were dissolved in ethanol (3 mL). The resulting solution was stirred at room

temperature for 2 h. The precipitate formed was collected by filtration and washed with cold ethanol to yield 0.140 g (59 %) of an orange product.

NMR data: δ_H(300 MHz; d_6-DMSO; Me_4Si) 4.97(s, 2H, NH_2), 6.55 (d, 2H, *J* 8.59, Ar), 7.39 (d, 2H, *J* 8.52, Ar), 8.15 (d, 2H, *J* 8.62, Ar), 8.34 (d, 2H, *J* 8.95, Ar), 10.16 (s, 1H, NH-CO). δ_C(150 MHz; d_6-DMSO; Me_4Si) 113,66, 122.16, 123.40, 127.62, 128.85, 129.12, 140.99, 145.44, 147.82, 162.81.

IR data: ν_{max}/cm^{-1} 3422(vw, broad), 3334(w, broad), 3190(vw, broad) , 1643(m), 1598(w), 1541(m), 1516(m), 1350(w), 1329(w), 1316(vw),1300(vw), 1285(w), 1266(w), 1108(w), 1014(vw), 900(vw), 865(w), 856(w), 822(w).

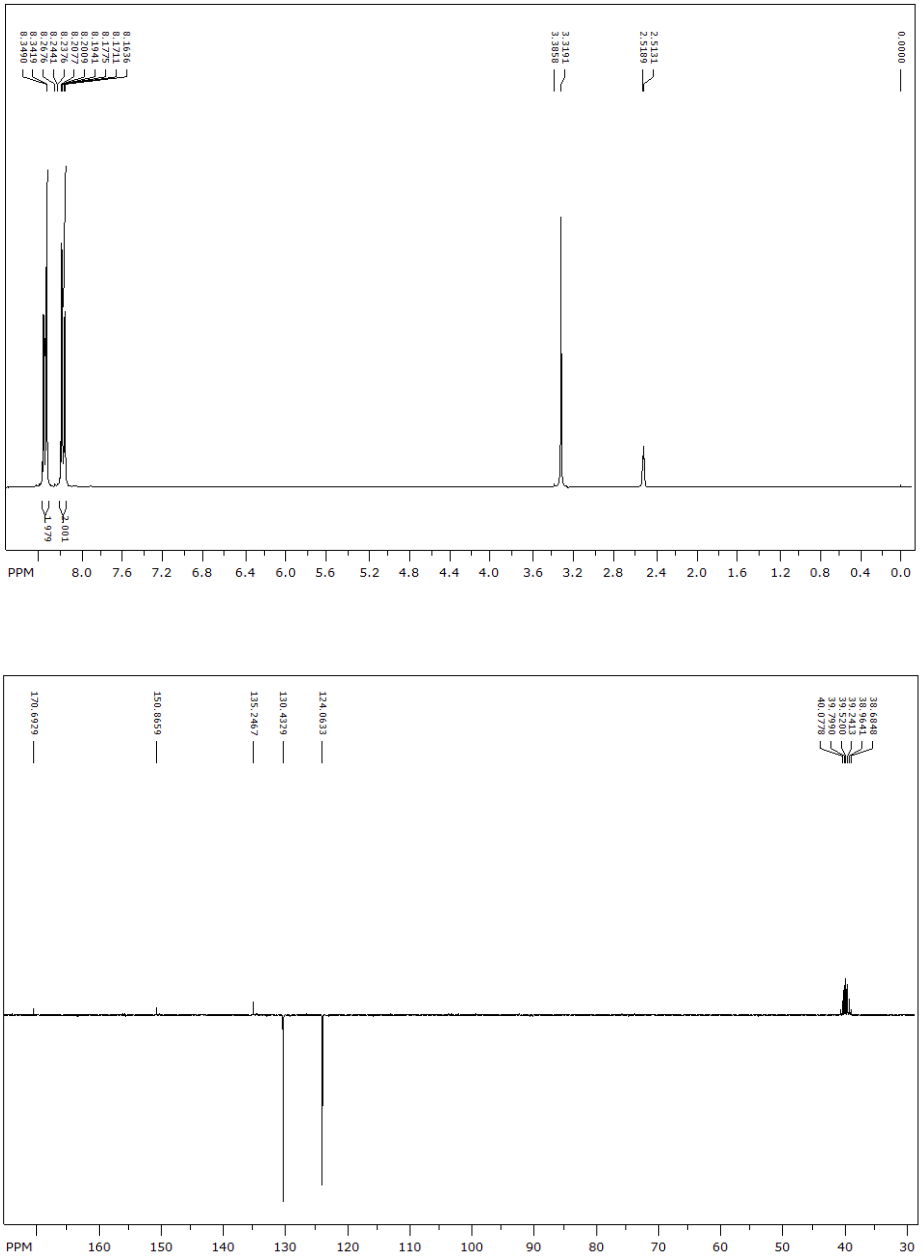
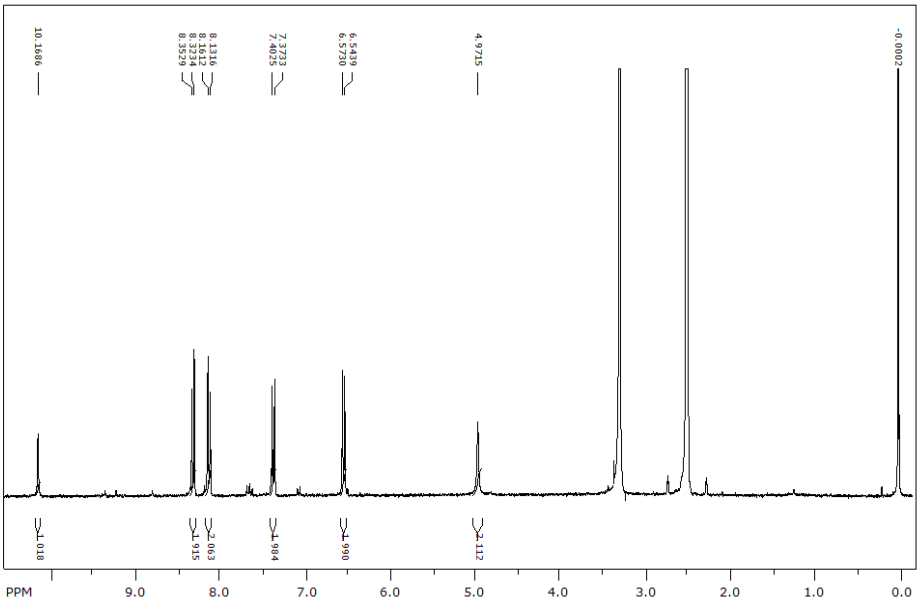
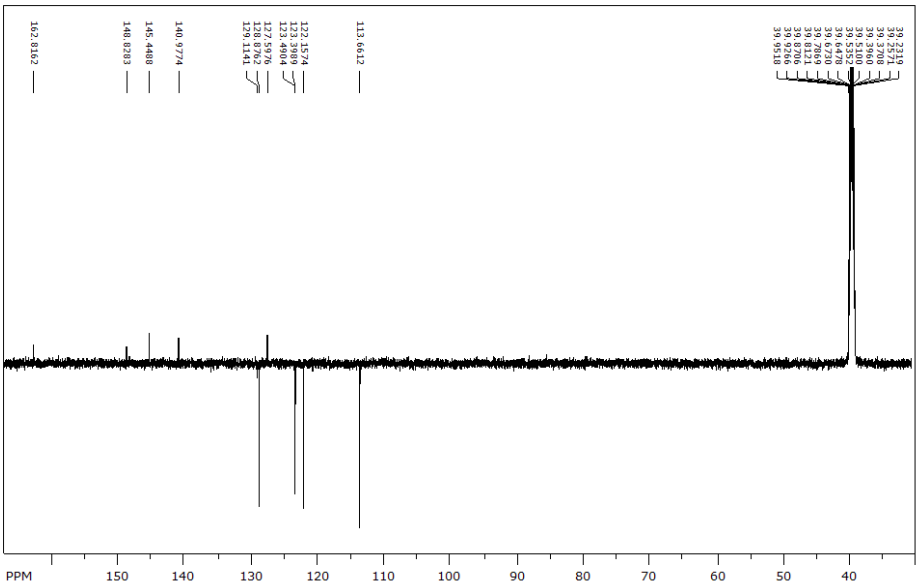


Figure 1. ^{1}H and ^{13}C NMR spectra of 4-nitrobenzoyl azide.


10.1686
8.3529
8.3334
8.1316
8.1122
7.4029
7.3733
6.5730
6.5439
4.9715
-0.0002
1.018
1.915
2.063
1.984
1.990
5.112
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

a)


162.8162
148.8283
145.4488
140.9774
129.1141
128.9742
127.5976
123.4904
123.3989
122.1574
113.6612
39.9518
39.9926
39.8706
39.8121
39.6730
39.6478
39.5359
39.5101
39.2960
39.3708
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PPM
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140
130
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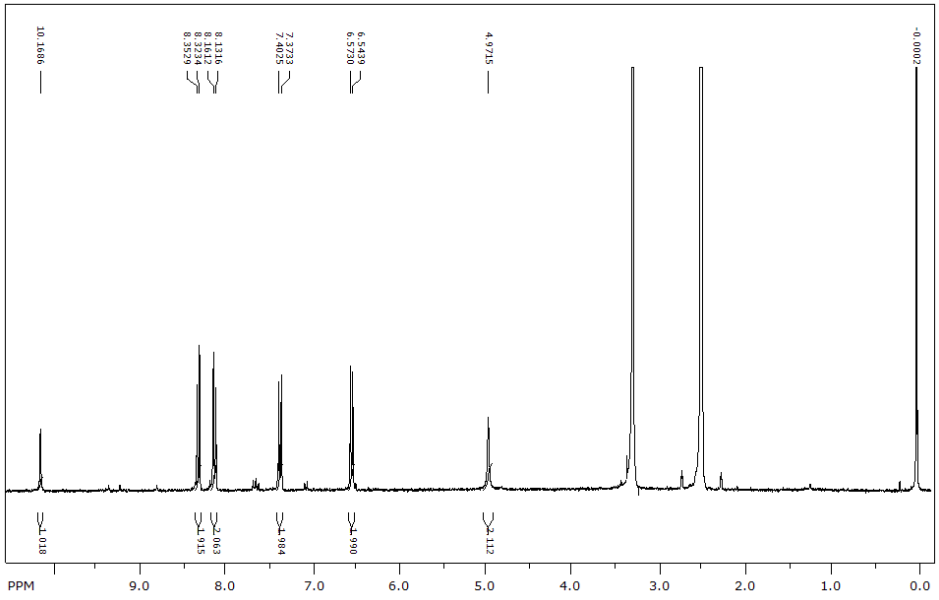
110
100
90
80
70
60
50
40

b)



c)

Figure 2. ^{1}H and ^{13}C NMR spectra of *N*-(4-aminophenyl)-4-nitrobenzamide: a) and b) the product obtained by milling; c) product obtained from solution.

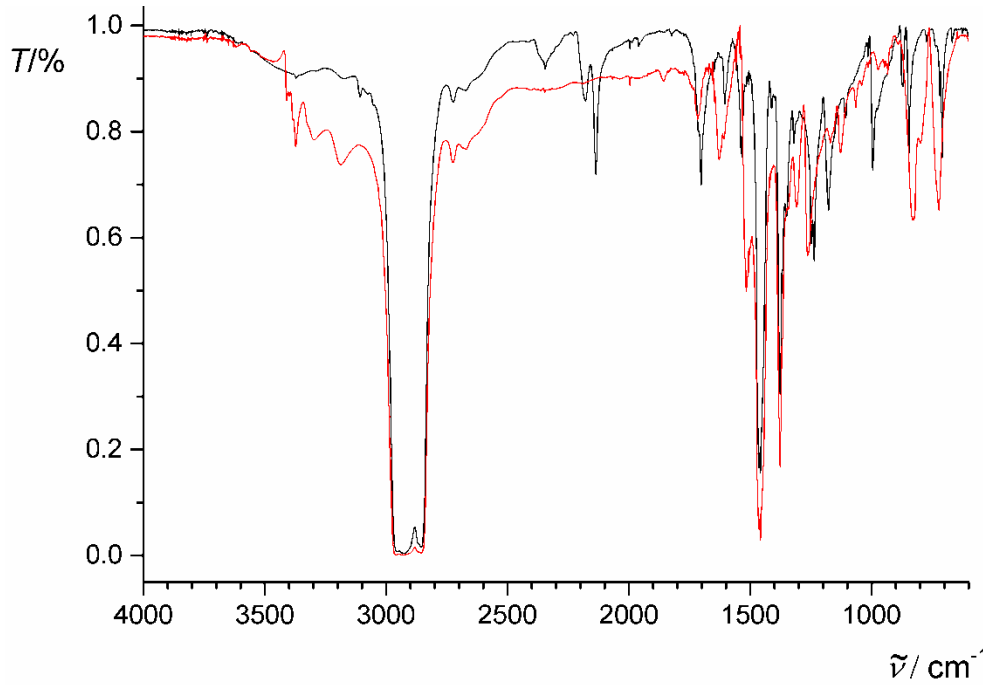


Figure 3. IR spectra for azide (black) and amide (red) collected in Nujol using a FT-IR spectrometer.

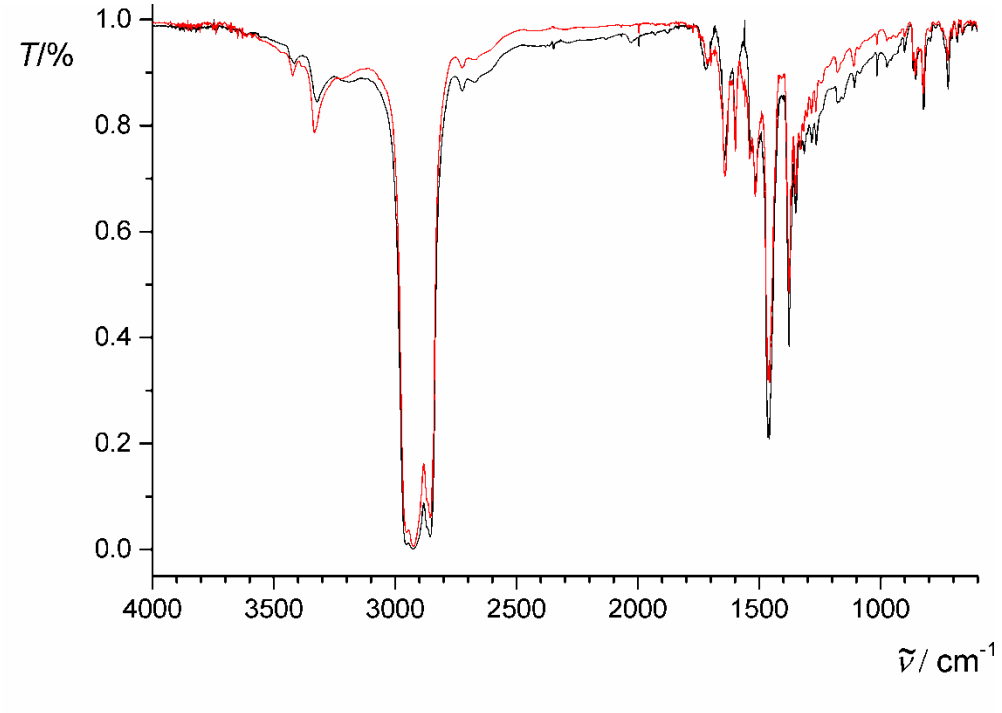


Figure 4. IR spectra of amide products obtained from mechanochemical synthesis (black) and from solution (red) collected in Nujol using a FT-IR spektrometer.

COMPUTATIONAL DETAILS

Optimized geometries

Amine – C_{2h} symmetry

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	1	0.303641	3.254193	0.829290
2	1	0.303641	3.254193	-0.829290
3	1	-0.303641	-3.254193	0.829290
4	7	0.084483	-2.826019	0.000000
5	6	0.004337	-0.695175	1.197699
6	1	0.014621	-1.226398	2.144664
7	6	0.006412	-1.420072	0.000000
8	7	-0.084483	2.826019	0.000000
9	6	-0.006412	1.420072	0.000000
10	6	-0.004337	0.695175	1.197699
11	1	-0.014621	1.226398	2.144664
12	6	0.004337	-0.695175	-1.197699
13	1	0.014621	-1.226398	-2.144664
14	6	-0.004337	0.695175	-1.197699
15	1	-0.014621	1.226398	-2.144664
16	1	-0.303641	-3.254193	-0.829290

HF=-343.050306

ZeroPoint=0.1329956

Thermal=0.1404432

Azide

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.962131	1.478419	0.015992
2	6	-0.575683	1.591624	0.007920
3	6	-0.015143	2.860467	0.000728
4	6	-0.836550	3.994370	0.001638
5	6	-2.228949	3.853283	0.009831
6	6	-2.800346	2.586977	0.017089
7	1	0.032109	0.697974	0.007411
8	1	1.058856	2.993999	-0.005659
9	1	-2.857730	4.733365	0.010501
10	1	-3.871685	2.445018	0.023516
11	6	-0.167913	5.326971	-0.006334
12	8	1.029493	5.484798	-0.013316
13	7	-1.104870	6.403847	-0.004815
14	7	-0.595822	7.538911	-0.011148
15	7	-0.233170	8.602436	-0.016500
16	7	-2.568978	0.123497	0.023727
17	8	-3.789232	0.052946	0.030829
18	8	-1.808701	-0.833455	0.022489

HF=-713.8637391

ZeroPoint=0.1157373

Thermal=0.1271137

Amide

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.075467	1.623353	0.034427
2	6	-0.703475	1.504978	0.231891
3	6	0.082217	2.645193	0.144866
4	6	-0.495810	3.892785	-0.117085
5	6	-1.877655	3.977209	-0.330216
6	6	-2.676194	2.842319	-0.254943
7	1	-0.278142	0.534165	0.444182
8	1	1.155716	2.591999	0.271097
9	1	-2.341350	4.920568	-0.594510
10	1	-3.742876	2.883110	-0.424397
11	6	0.440198	5.073962	-0.208246
12	8	1.616567	4.914772	-0.493694
13	7	-0.134993	6.286128	0.064386
14	7	-2.922724	0.412225	0.122391
15	8	-4.124533	0.548518	-0.062537
16	8	-2.368484	-0.647820	0.376300
17	1	-1.082370	6.263857	0.408053
18	6	0.460132	7.571120	0.055662
19	6	-0.324825	8.651800	0.474221
20	6	1.775092	7.816649	-0.357243
21	6	0.179855	9.943176	0.484455
22	1	-1.347867	8.482548	0.797938
23	6	2.275062	9.112590	-0.345082
24	1	2.395381	6.993187	-0.674875
25	6	1.496465	10.200250	0.074332
26	1	-0.453583	10.762311	0.808572
27	1	3.295807	9.283246	-0.672109
28	7	1.991473	11.503903	0.023561
29	1	1.544610	12.160002	0.647030
30	1	2.997375	11.582555	0.052962

HF=-892.0903426

ZeroPoint=0.2268527

Thermal=0.2429433

Urea

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.958973	5.253092	0.005402
2	8	2.151004	5.239609	0.243461
3	7	0.200773	6.392430	-0.139867
4	1	-0.782501	6.282371	-0.332432
5	6	0.624202	7.742829	-0.045070
6	6	-0.351705	8.734459	-0.192795
7	6	1.947569	8.135172	0.183092
8	6	-0.025358	10.080916	-0.117963
9	1	-1.386246	8.452821	-0.369010
10	6	2.267729	9.485428	0.258574
11	1	2.713706	7.385510	0.302576
12	6	1.296987	10.485104	0.112092
13	1	-0.803503	10.826532	-0.243753
14	1	3.301201	9.768169	0.431952
15	1	-0.789986	4.204371	-0.350993
16	7	0.192620	4.090655	-0.154910
17	6	0.613800	2.761478	-0.079368
18	6	-0.364994	1.768292	-0.276914
19	6	1.940650	2.374302	0.178715
20	6	-0.038549	0.426039	-0.220534
21	1	-1.391865	2.057964	-0.476615
22	6	2.264274	1.026881	0.234565
23	1	2.694486	3.129435	0.330804
24	6	1.280744	0.063259	0.036226
25	1	-0.782931	-0.343071	-0.370871
26	1	3.279219	0.710769	0.431748
27	7	1.635299	-1.360132	0.097933
28	8	0.739789	-2.178709	-0.082308
29	8	2.804419	-1.648282	0.325806
30	7	1.644933	11.838488	0.126535
31	1	0.899346	12.469300	0.382355
32	1	2.498915	12.052769	0.620628

HF=-947.4715436

ZeroPoint=0.2433013

Thermal=0.2609688

Isocyanate

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.968144	-0.033164	0.000074
2	6	1.303794	1.187132	0.000111
3	6	-0.086666	1.201935	0.000035
4	6	-0.759632	-0.012671	-0.000077
5	6	-0.101279	-1.236715	-0.000114
6	6	1.285758	-1.246261	-0.000037
7	1	1.874345	2.105074	0.000198
8	1	-0.632027	2.137523	0.000061
9	1	-0.675080	-2.154074	-0.000202
10	1	1.844332	-2.171440	-0.000062
11	7	3.447327	-0.044074	0.000157
12	8	4.001869	-1.133898	0.000125
13	8	4.018825	1.036677	0.000245
14	8	-2.163880	-0.095726	-0.000160
15	6	-2.859800	0.992980	-0.000133
16	7	-3.522056	1.940389	-0.000108

HF=-604.3374888

ZeroPoint=0.1052637

Thermal=0.1149033

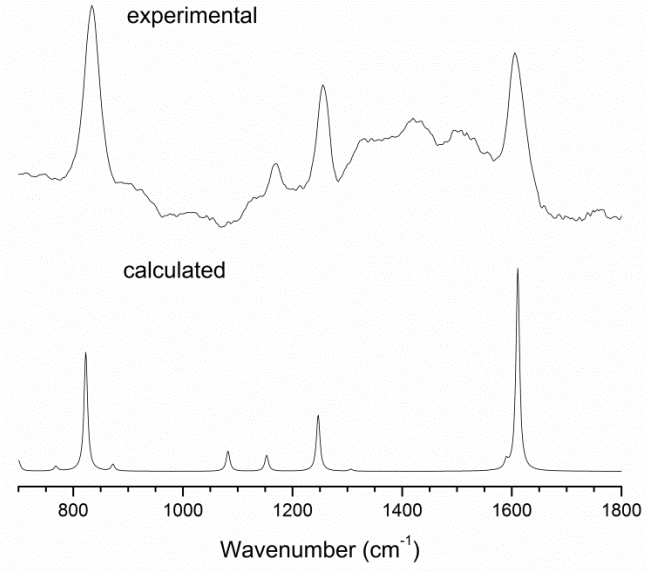


Figure 5. Experimental and calculated Raman spectrum of 1,4-diaminobenzene. Raman bands of amine have low intensities and are thus barely observed in the reaction mixture with azide.

RAMAN SPECTROSCOPY

Table 1. Assignment of Raman bands in range 2500-1000 cm^{-1}.

1		**2**		**Product**	**3**	**Isocyanate**	**Urea**	**Assignment**
Obs.	Calc.[a]	Obs.	Calc.[b]	Obs.	Calc.[c]	Calc.[d]	Calc.[d]	
–	–	–	–	–	–	2323	–	isocyanate group: ν_{as}(NCO)
2135	2232	–	–	–	–	–	–	azide group: ν_{as}(NNN)
1695	1718	–	–	–	1708	–	1743	amide I: ν(C=O)
–	–	1607	1611	1643	1643	–	1640 1624	$\nu(C=C)_{PhNH2}$ + $\delta(NH_2)$
–	–	–	–	1620	1625	–	1617	$\nu_{as}(NO_2)$ + $\nu(C=C)_{PhNO2}$ + $\nu(C=C)_{PhNH2}$ + $\delta(NH_2)$
1599	1600	–	–	1600	1611	1602	1611	„ring mode“: $\nu(C=C)_{PhNO2}$
–	–	–	–	1527	1534	–	1532	amide II: $\nu(C_{CO}–N)_{PhNH2}$ + δ(NH)
–	–	–	–	–	–	–	1513	amide II: $\nu(C_{CO}–N)_{PhNO2}$ + δ(NH)
–	–	–	–	1435	1436	–	–	ν(C=N) + δ(NH) + $\nu(C=C)_{PhNH2}$ + $\delta(CH)_{PhNH2}$
1353	1347	–	–	1354	1355	1352	1347	$\nu_s(NO_2)$
–	–	–	–	–	–	–	1333	$\nu_s(NO_2)$ + ν(C=C)
–	–	–	–	1328	1321	–	1315	$\nu(C=C)_{PhNH2}$ + $\delta(CH)_{PhNH2}$
1265	1260	1256	1247	1266	1288	–	1282	$\nu(C–N_{NH2})$
1239	1216	–	–	–	–	–	–	azide group: ν_s(NNN) + ν(CC)
–	–	–	–	1239	1240	–	1263	amide III: $\nu(C_{Ph}–N)$+ δ(NH) + $\nu(CC_{Ph})$
–	–	–	–	–	–	–	1226	ν(C–N)
–	–	–	–	–	–	1207	–	ν(C–O)
1174	1163	1170	1153	1175	1184	1131	1181	ρ(CCH)
1111	1088	–	–	1110	1098	1099	1103	$\nu(C–N_{NO2})$

[a] Scaled by 0.975; [b] scaled by 0.960; [c] scaled by 0.983; [d] scaled by 0.980.

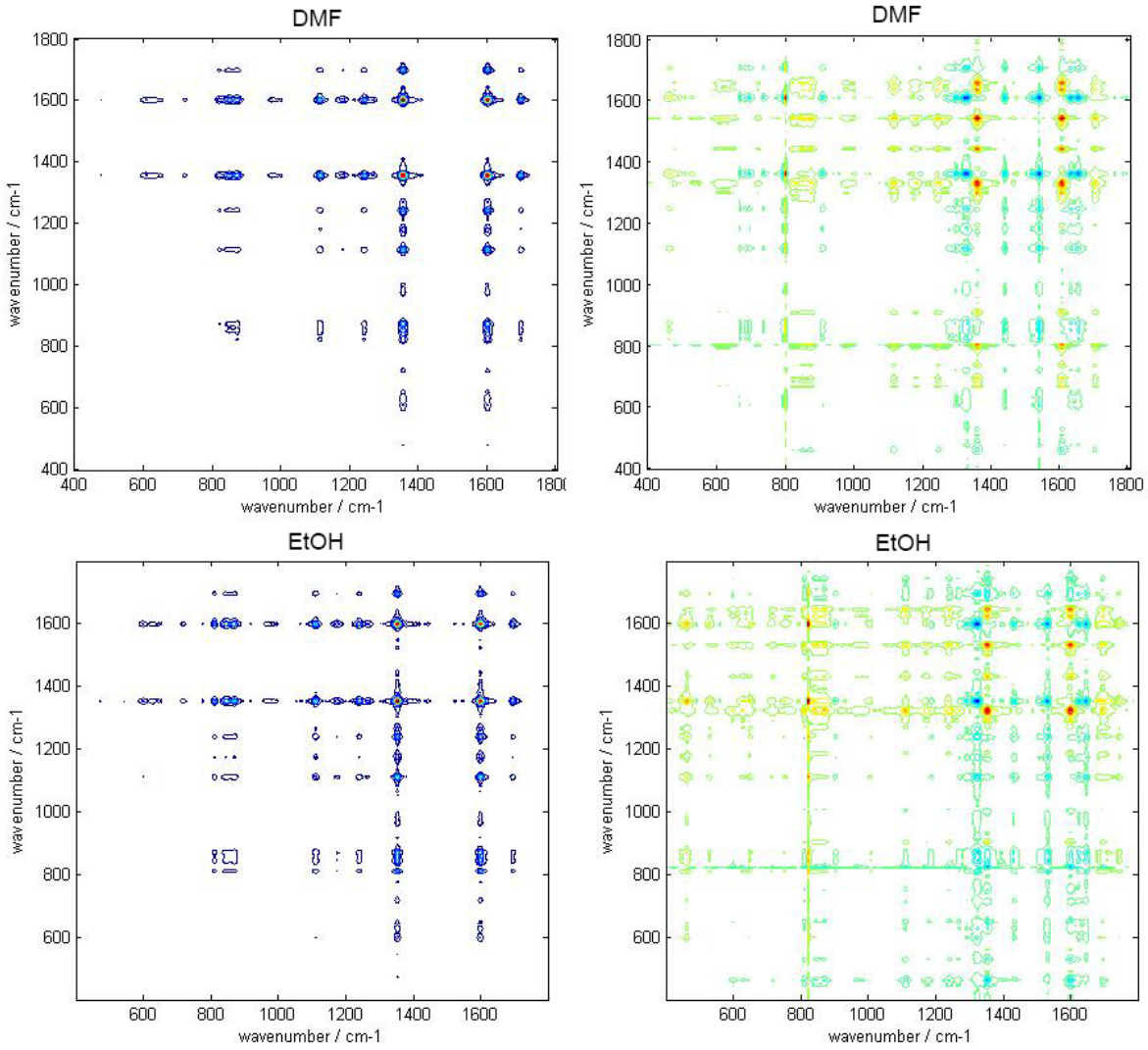


Figure 6. Synchronous (left) and asynchronous (right) spectra for LAG milling reactions using DMF and ethanol as liquid additives.

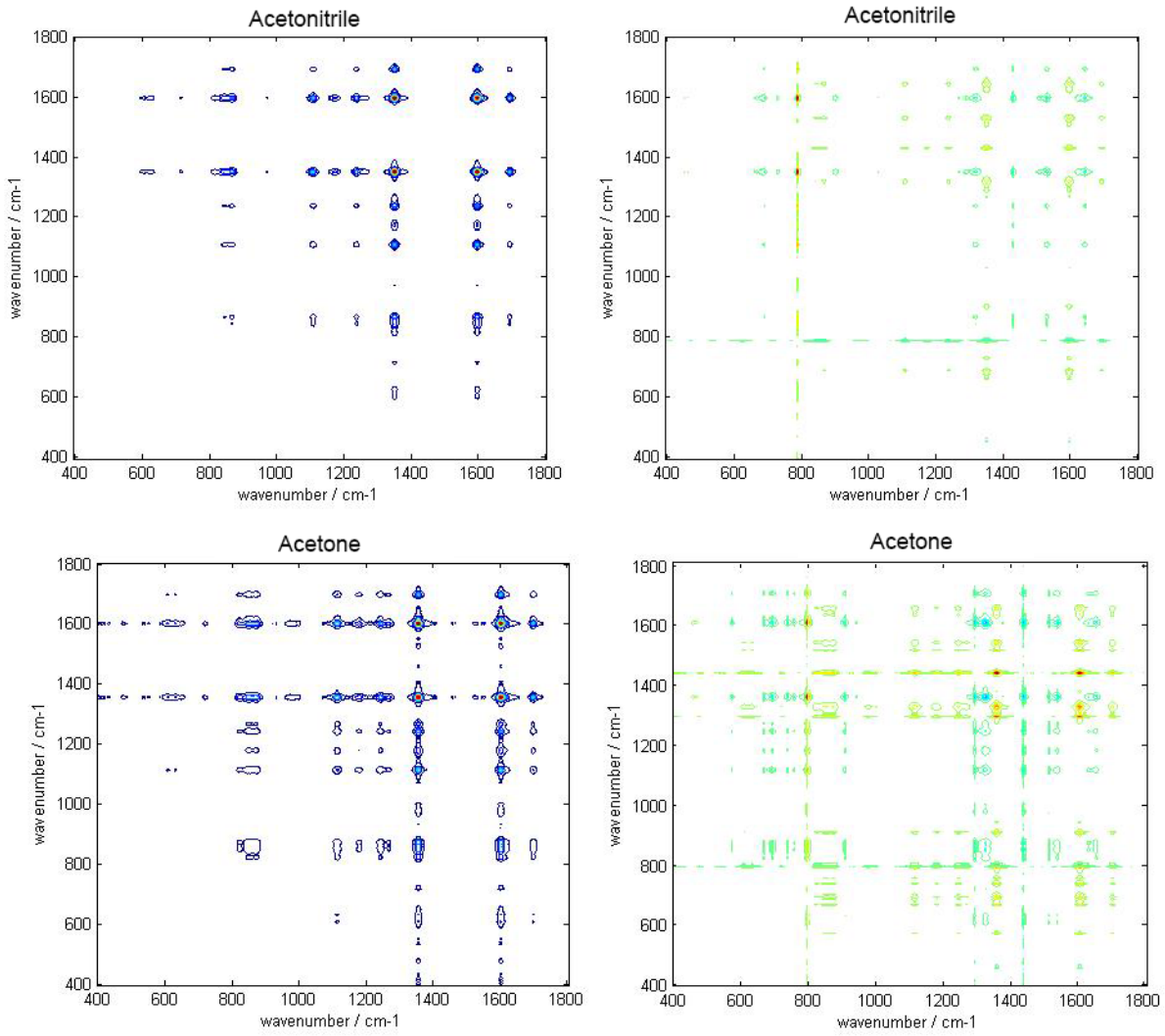


Figure 7. Synchronous (left) and asynchronous (right) spectra for LAG milling reactions using acetonitrile and acetone as liquid additives.

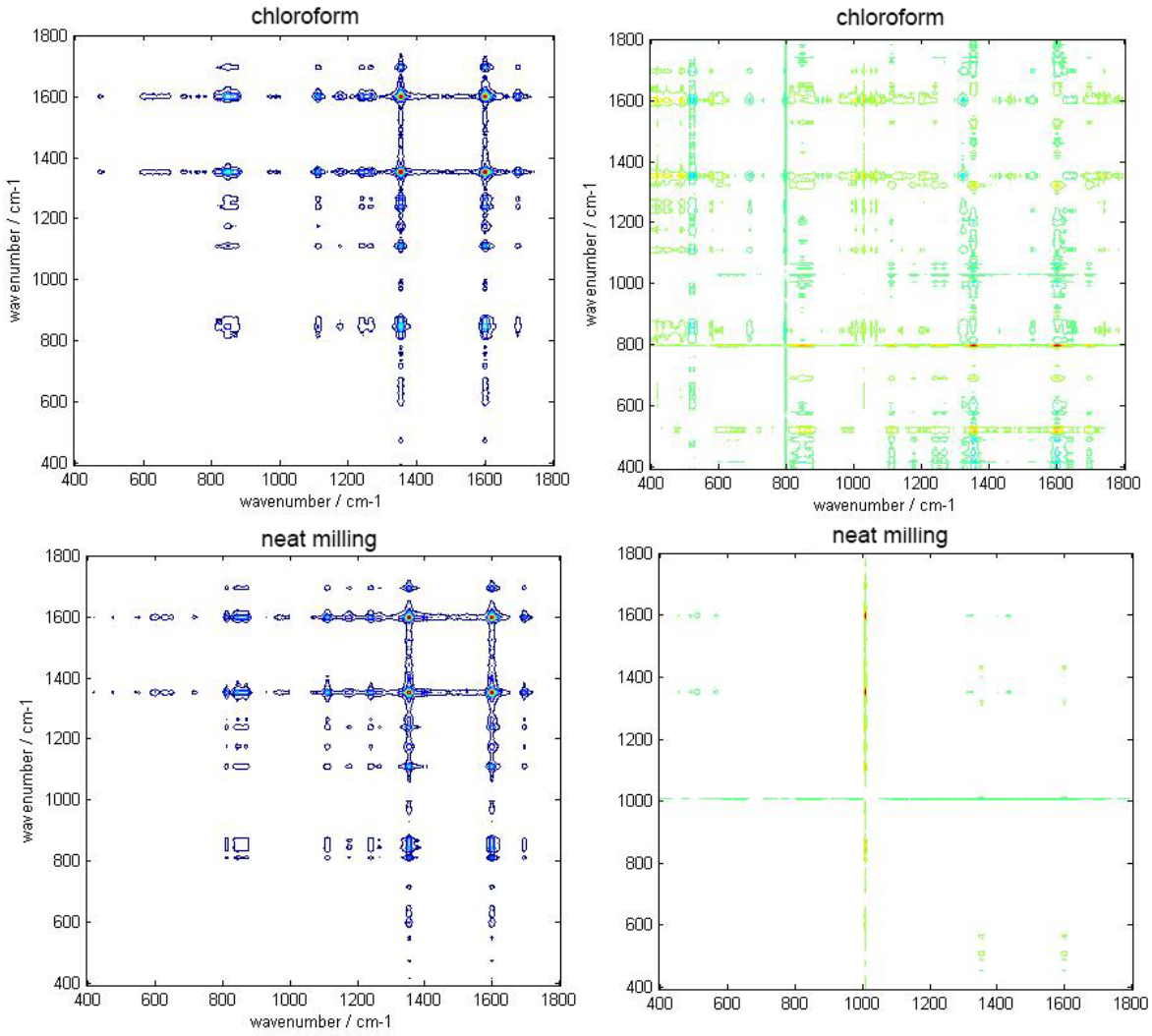


Figure 8. Synchronous (left) and asynchronous (right) spectra for LAG milling reaction using chloroform as the liquid additive and neat milling reaction.

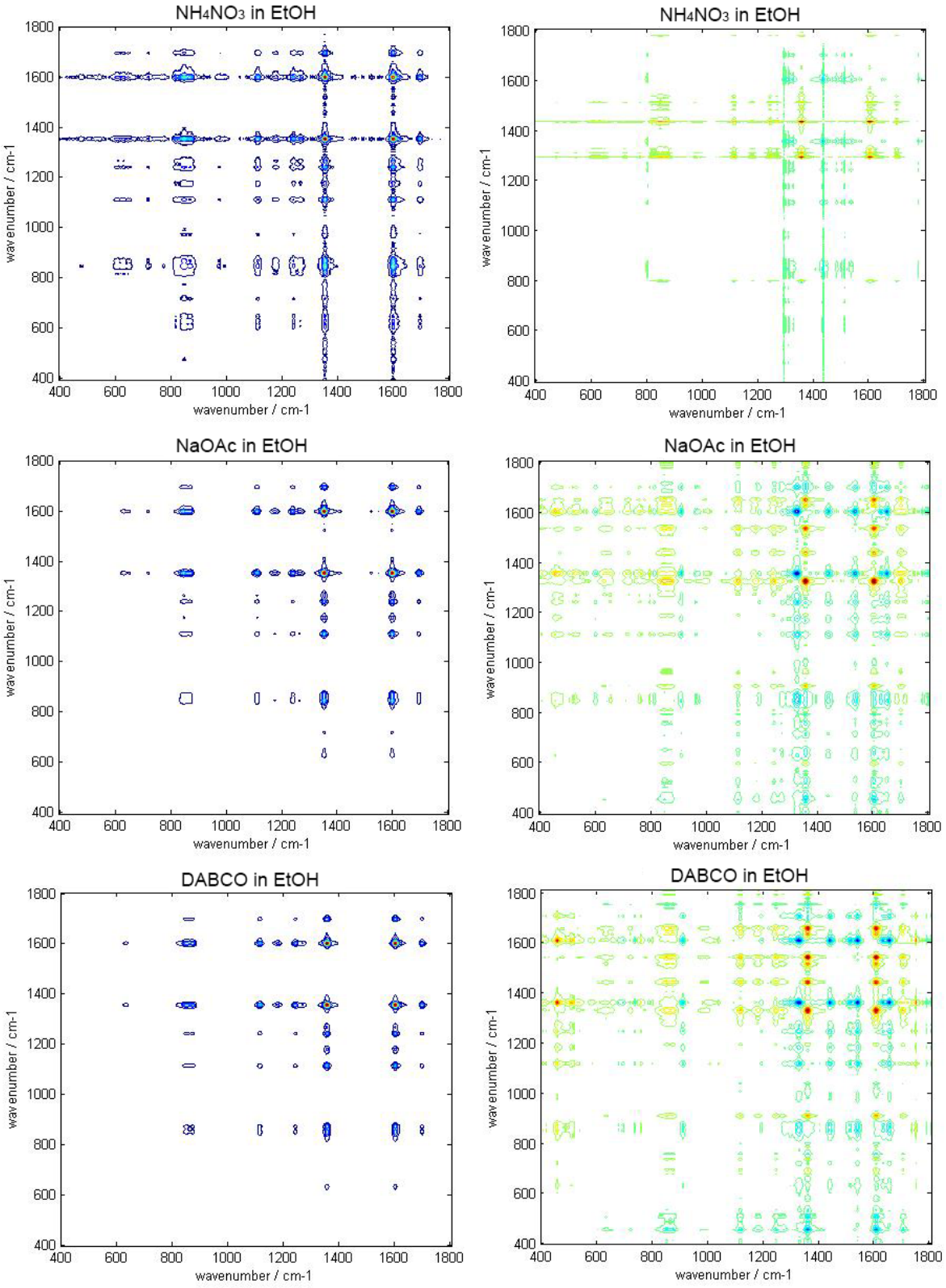


Figure 9. Synchronous (left) and asynchronous (right) spectra for ILAG milling reactions ethanol as liquid additives and (from top) ammonium nitrate, sodium acetate and dabco as additives.

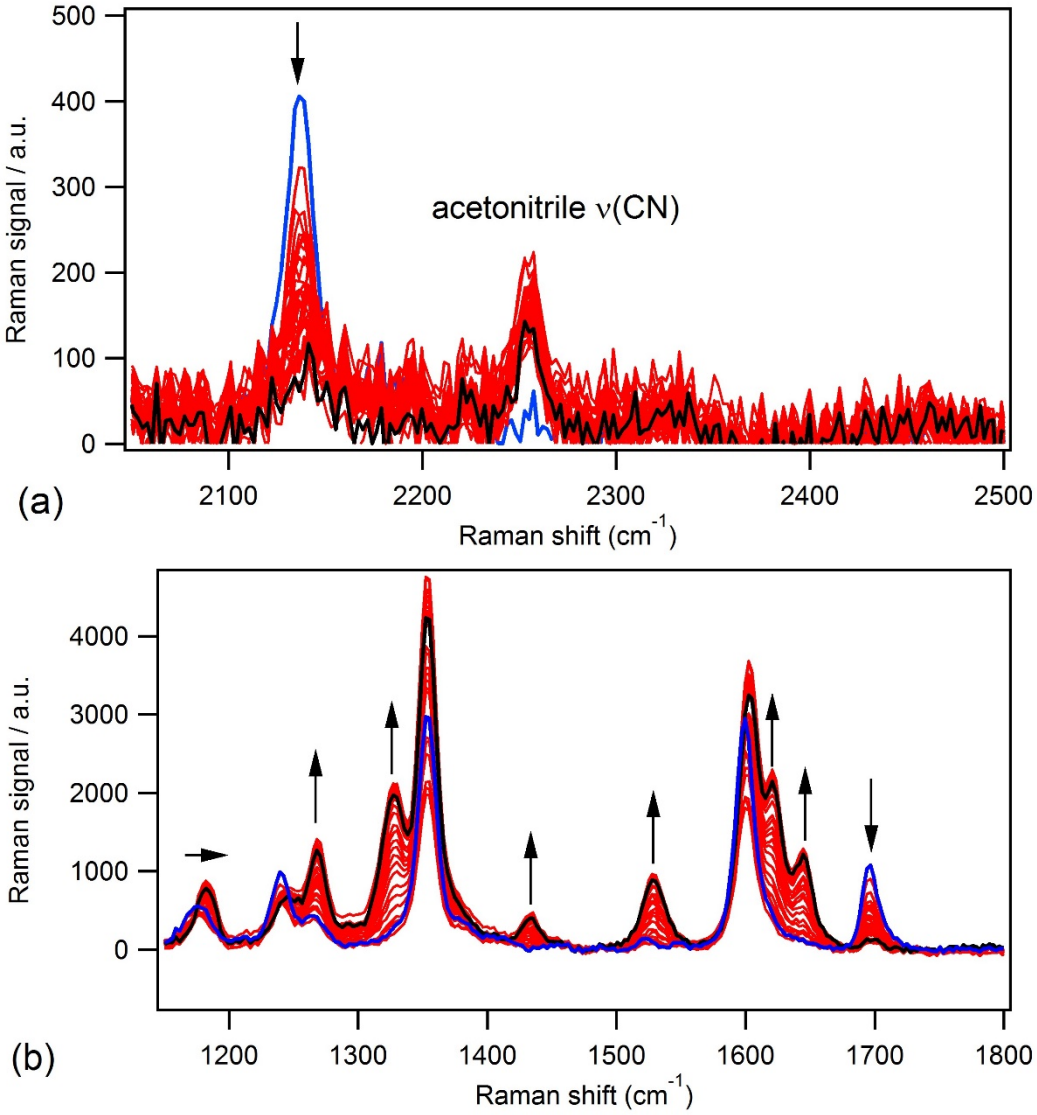


Figure 10. Time-resolved Raman spectra in the LAG reaction using acetonitrile. (a) Region with most significant changes and (b) region with azide group vibration. Spectrum taken at t = 0 s is represented by the blue line, while the final spectrum with the black line. Direction of the change of the band's intensity with time is indicated by arrows. Possible band at ca. 2320 cm^{-1} which would belong to isocyanate stretching of the possible isocyanate intermediate, does not appear. The band at 2255 cm^{-1} belongs to acetonitrile and does not change in shape and intensity (except changes which can be attributed to changing amount of the sample irradiated) during milling. Acetonitrile band is not visible in the first (blue) spectrum due to reaction mixture not being homogenous yet.

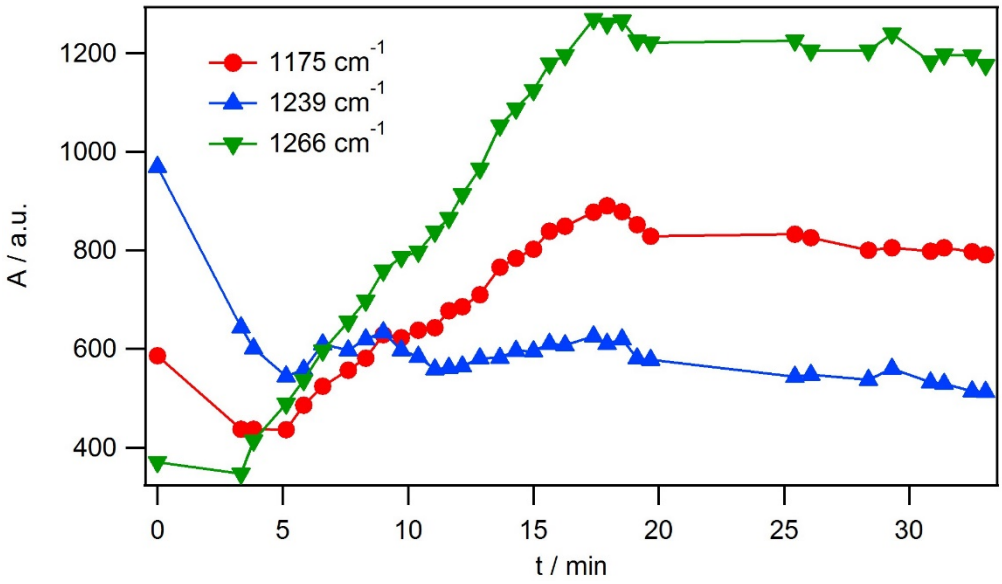


Figure 11. Intensity change of selected bands during LAG reaction using acetonitrile.

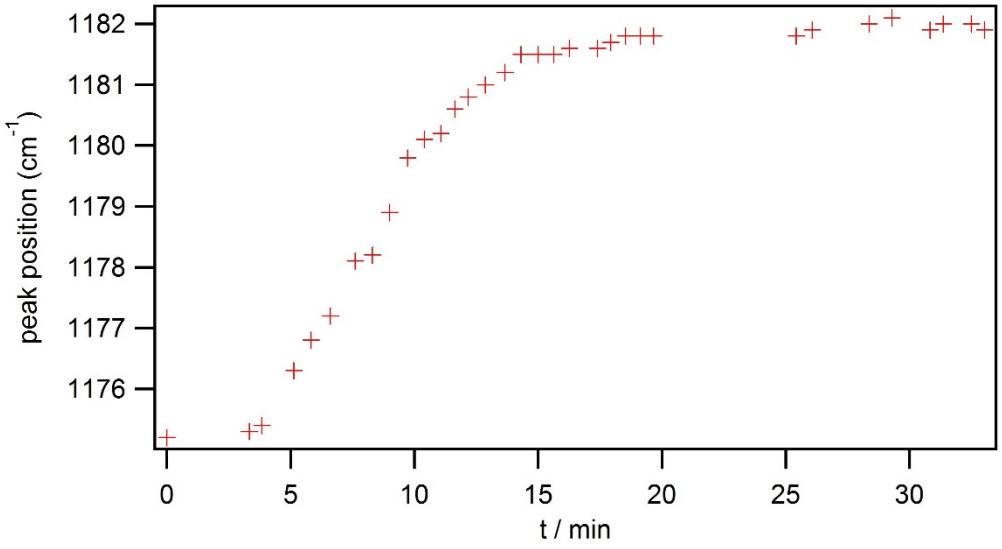


Figure 12. Change of the band position belonging to aromatic ring rocking vibration during LAG reaction with acetonitrile.

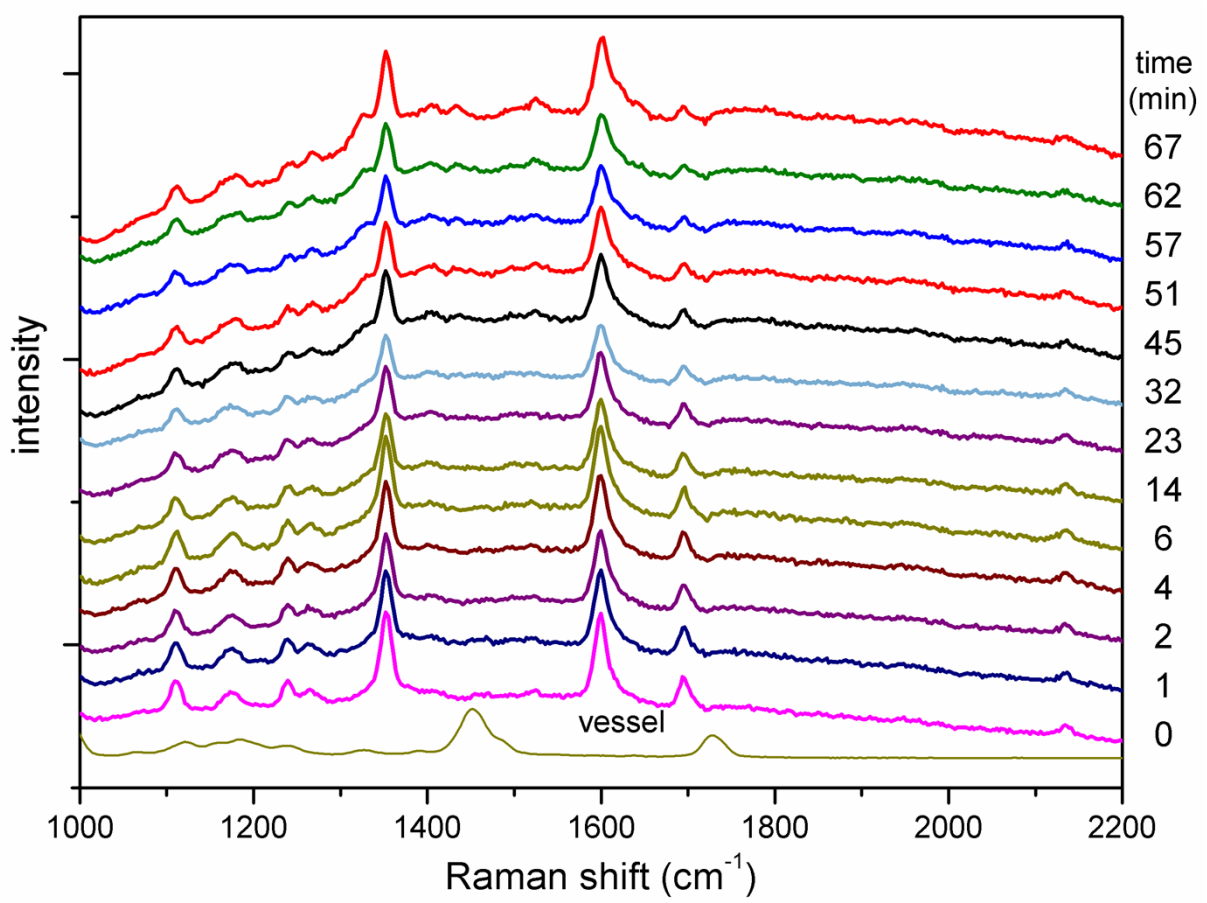


Figure 13. Neat grinding reaction of **1** and **2** yielding minor amounts of **3** after milling for an hour.

SOLUBILITIES

Table 2. Solubilities[a)] of **1**, **2** and **3** expressed as mass of compound soluble in given liquid's volume (mg/ml).

	1	**2**	**3**
Ethanol	30	8	22
DMF	400	120	36
Acetone	880	340	120
Acetonitrile	65	18	7
Chloroform	90	4	4

[a] Solubilities were determined by preparing saturated solutions of each compound in specific solvent and determining the solution composition. For this, clear saturated solution was put in a separate test tube, solution weighed, the solvent evaporated, and the remaining precipitate weighed.

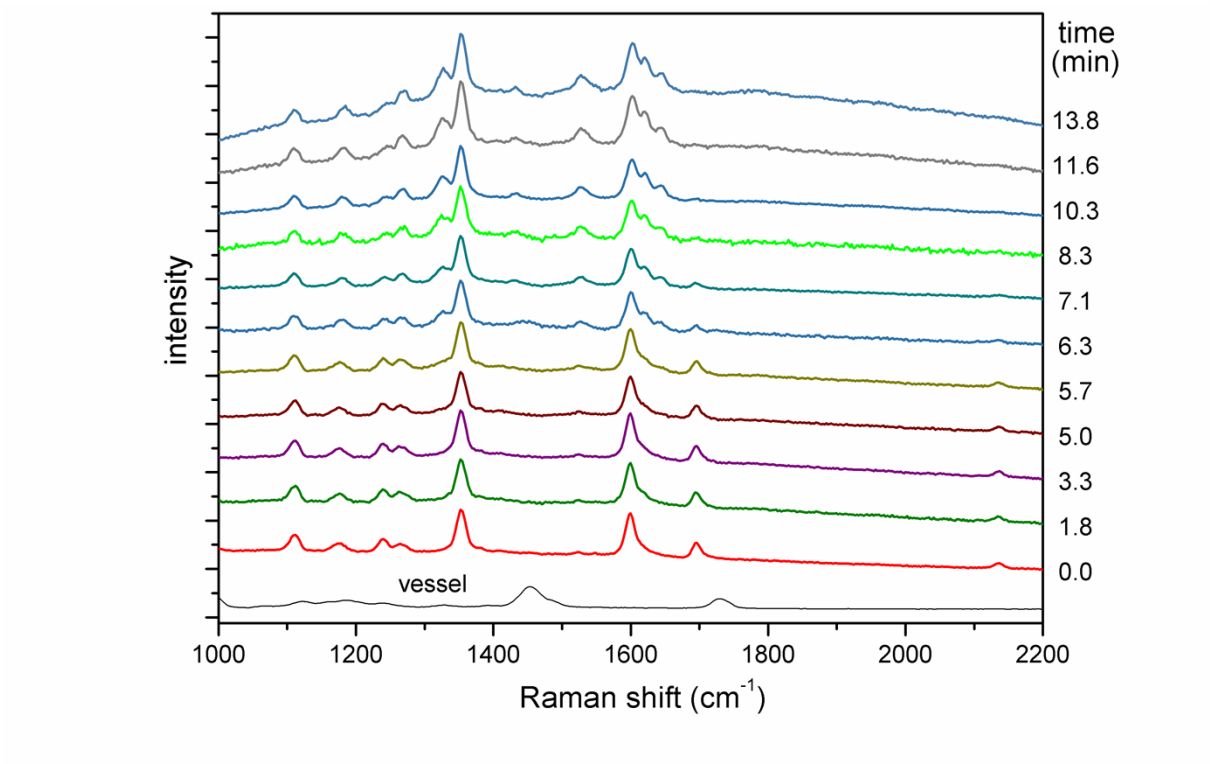


Figure 14. Time resolved Raman spectra during milling reaction of **1** and **2** yielding **3** under ILAG reaction conditions using ethanol and 10 mol% sodium acetate with respect to reactants.

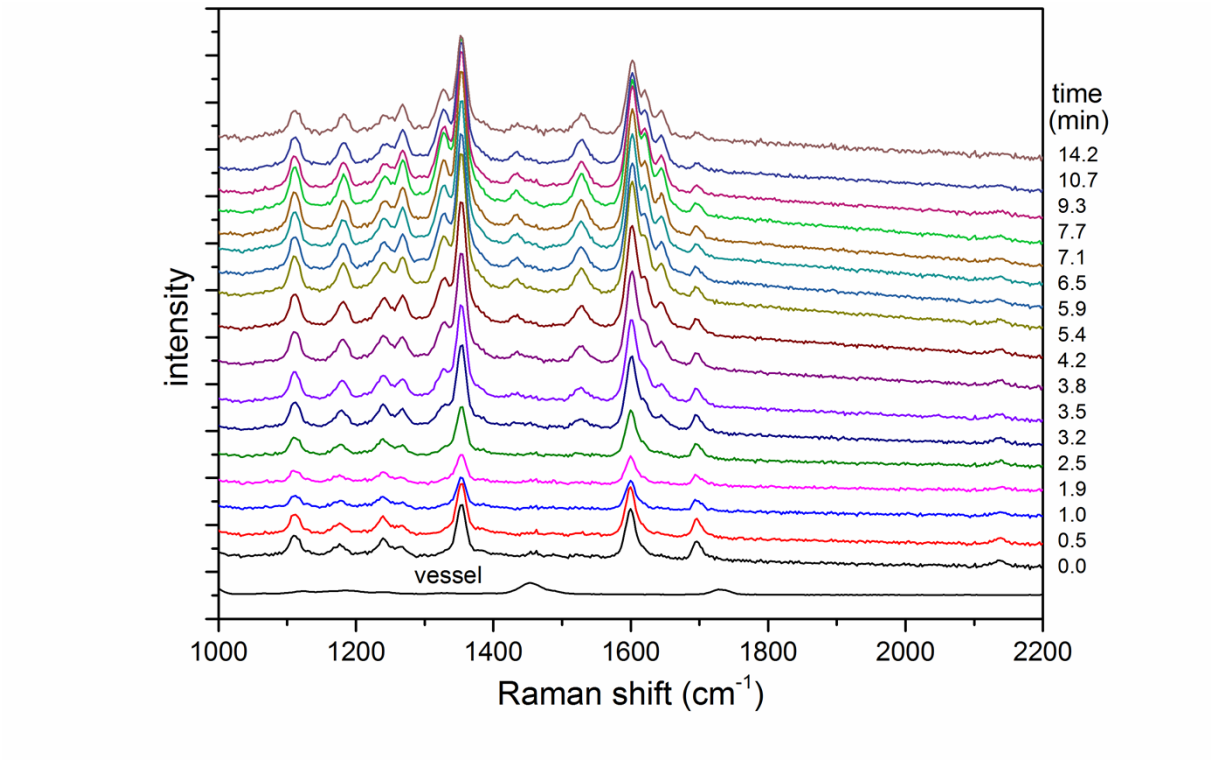


Figure 15. Time resolved Raman spectra during milling reaction of **1** and **2** yielding **3** under ILAG reaction conditions using ethanol and 10 mol% dabco with respect to reactants.

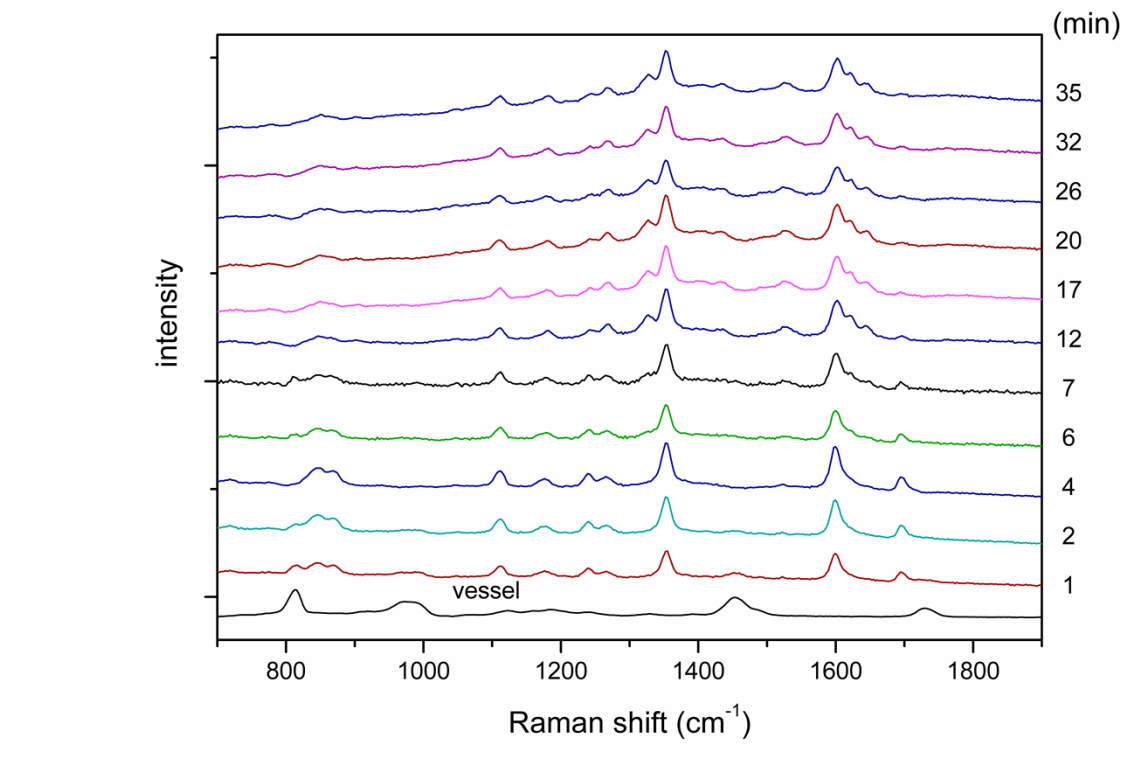


Figure 16. Time resolved Raman spectra during milling reaction of **1** and **2** yielding **3** under ILAG reaction conditions using ethanol and 10 mol% ammonium nitrate with respect to reactants.

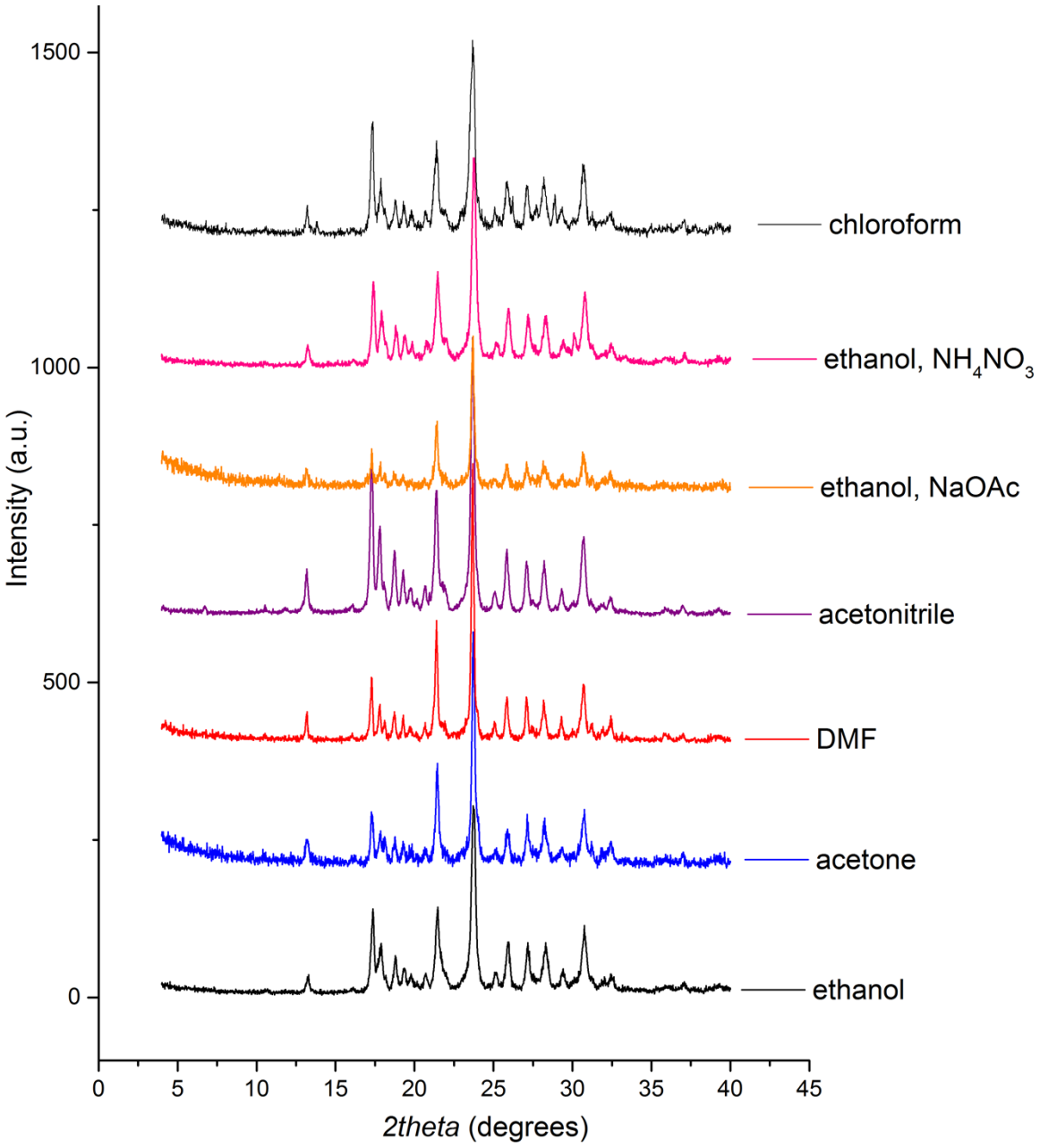


Figure 17. Characterisation of solid products of milling reactions by powder X-ray diffraction showing that the same solid phase is obtained in all milling reactions. Patterns were collected *ex situ* within few days after preparation. Formation of the product in the experiment with chloroform is attributed to aging reaction.