Synthesis and Structure Characterization of L-Prolinol Derived Chiral Eutectic Mixtures as Sustainable Solvents in Asymmetric Organocatalysis

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Supplementary Information

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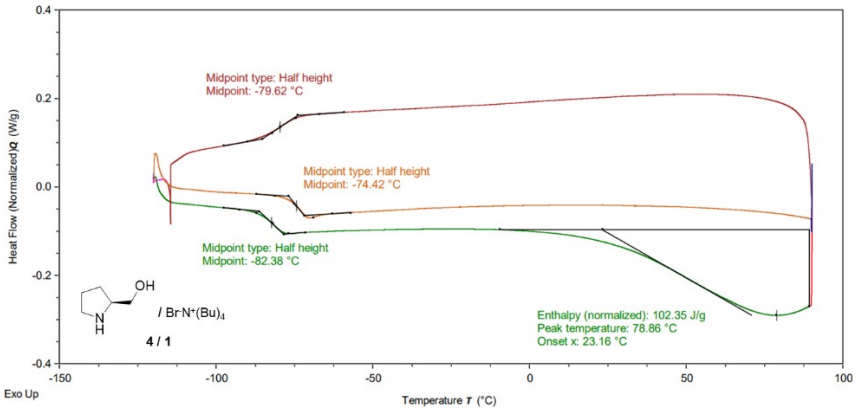
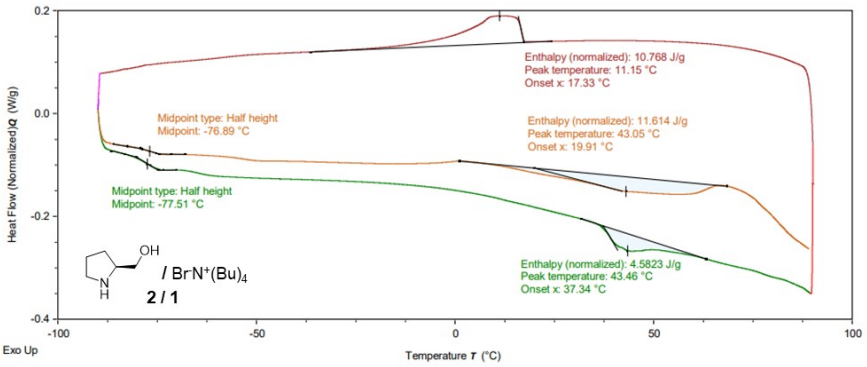
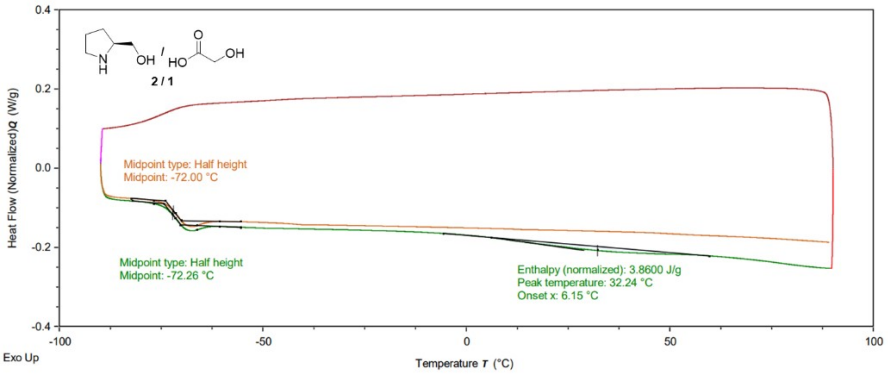
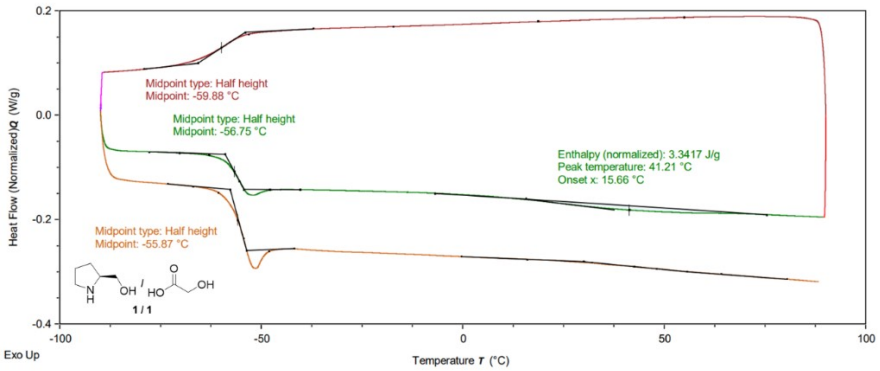




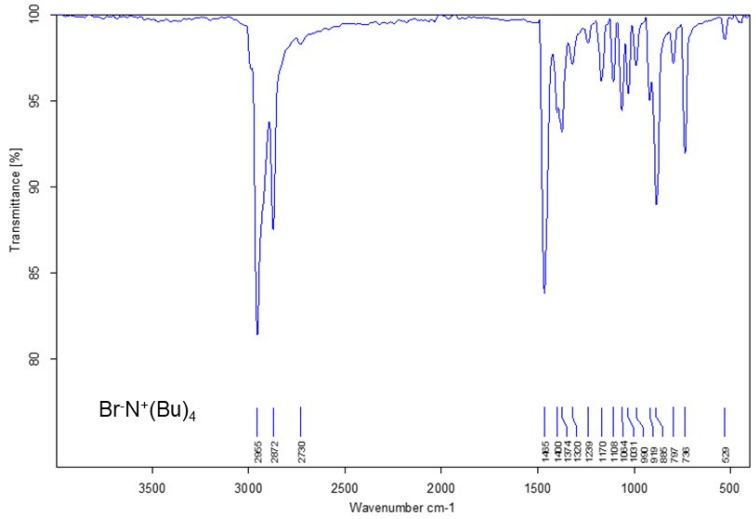
1.2. L-Prolinol/GA mixtures

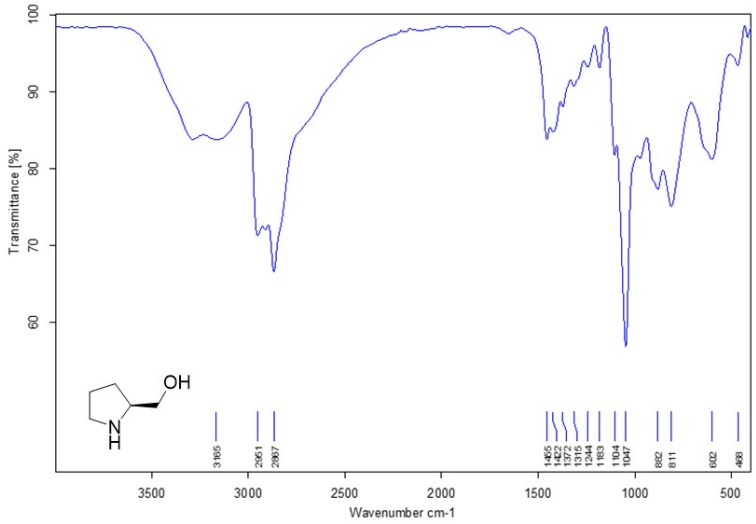


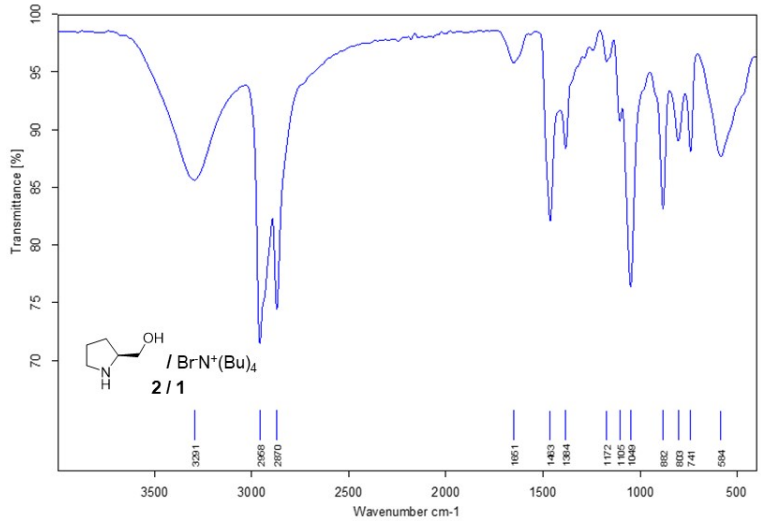


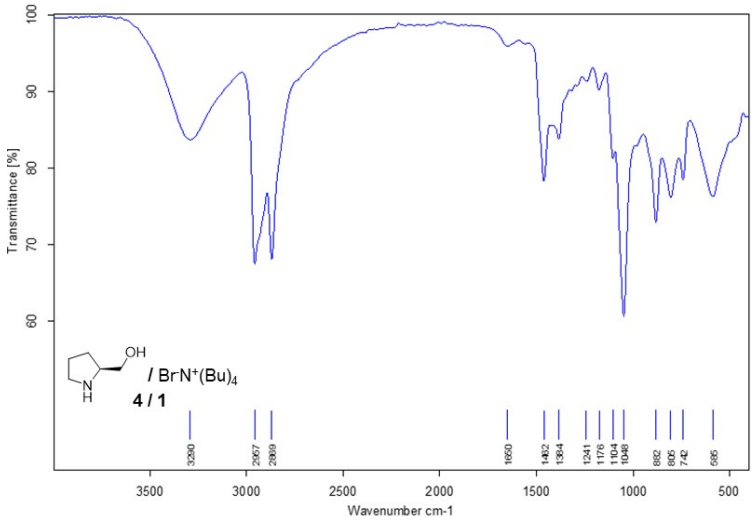
2. IR spectra

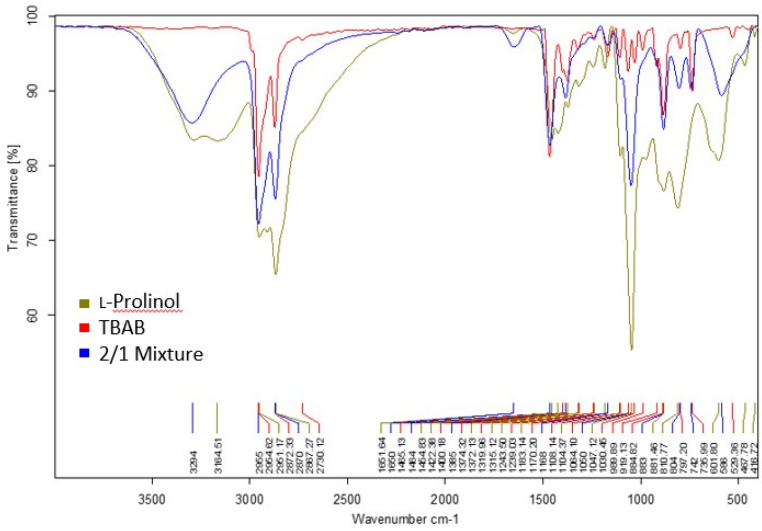
2.1. L-Prolinol/TBAB mixtures

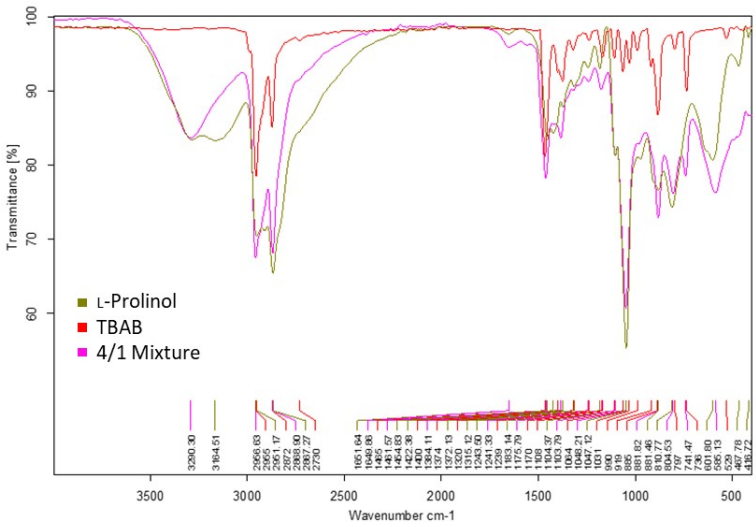


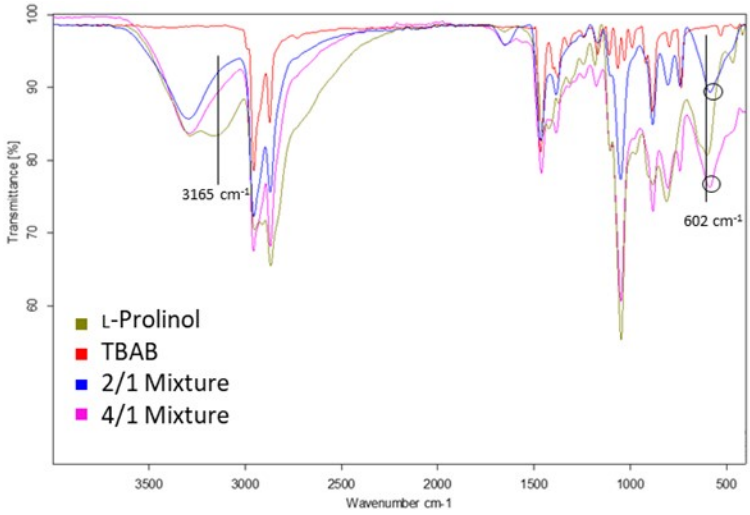





Transmittance [%]
Wavenumber cm-1
/ Br⁻N⁺(Bu)4
4 / 1

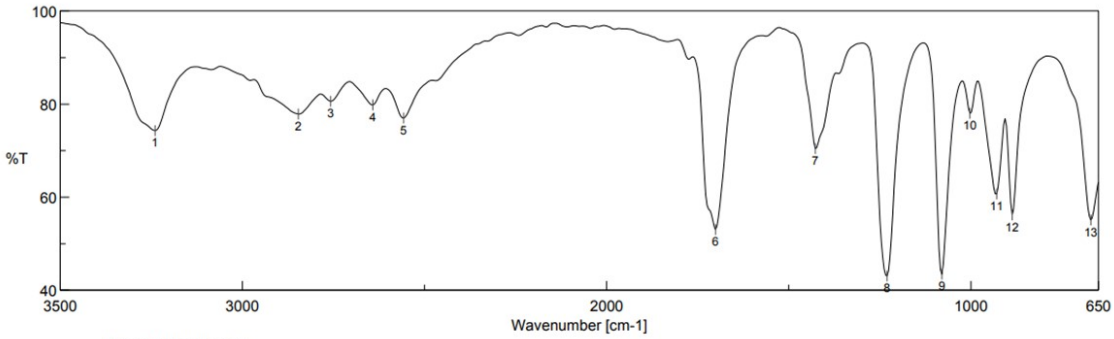

Transmittance [%]
Wavenumber cm-1
L-Prolinol
TBAB
2/1 Mixture


Transmittance [%]
Wavenumber cm-1
L-Prolinol
TBAB
4/1 Mixture



2.2. L-Prolinol/GA mixtures

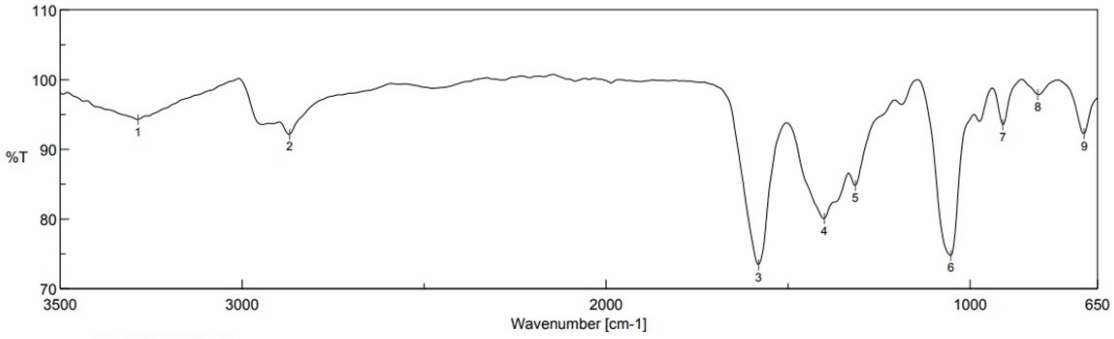
Glycolic Acid



[Result of Peak Picking]

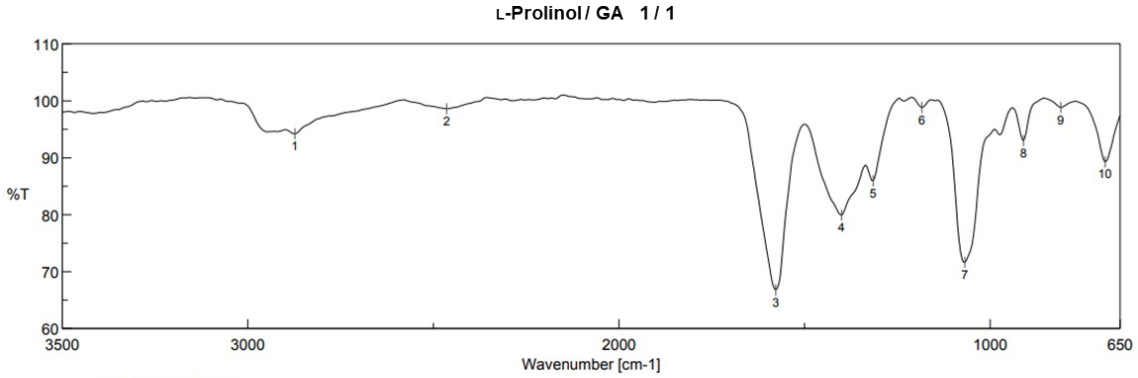
No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3239.82	74.29	2	2846.42	77.85	3	2757.71	80.59	4	2642	79.79	5	2557.15	76.96
6	1700.91	53.01	7	1427.07	70.40	8	1230.36	43.07	9	1079.94	43.44	10	1002.8	78.00
11	929.521	60.66	12	887.095	56.17	13	671.106	55.09						

L-Prolinol-GA 2:1



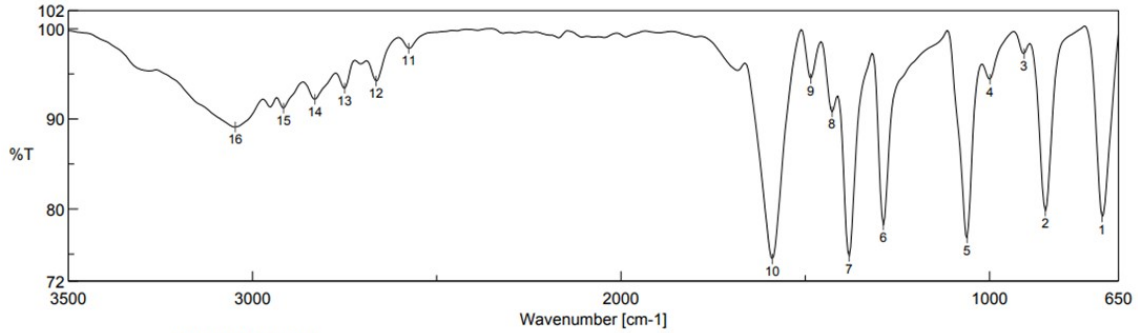
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3286.11	94.26	2	2869.56	92.13	3	1581.34	73.42	4	1400.07	80.05	5	1315.21	84.77
6	1052.94	74.75	7	910.236	93.50	8	813.813	97.83	9	686.534	92.23			



[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2873.42	94.19	2	2464.58	98.60	3	1577.49	66.78	4	1400.07	79.91	5	1315.21	85.94
6	1184.08	98.82	7	1068.37	71.60	8	910.236	93.01	9	809.956	98.83	10	690.391	89.26



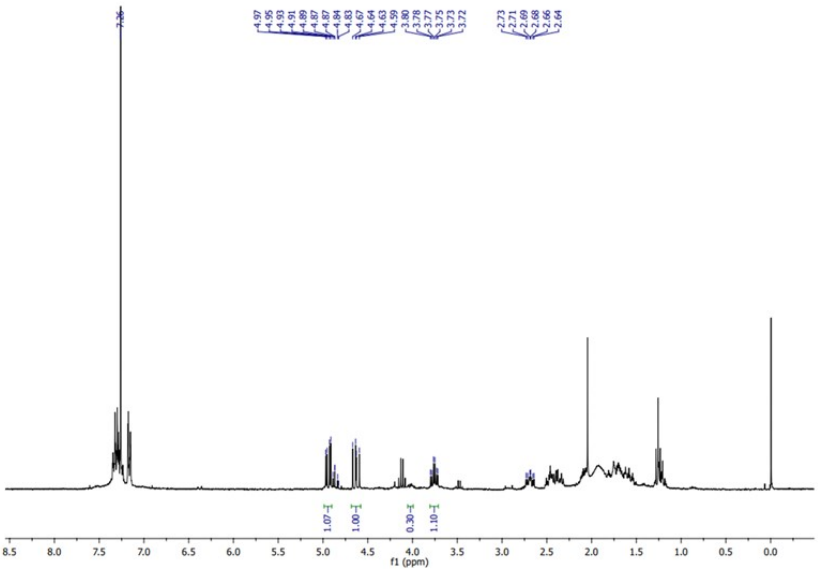
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	694.248	79.11	2	848.525	79.77	3	906.379	97.23	4	998.946	94.39
5	1060.66	76.79	6	1288.22	78.21	7	1380.78	74.73	8	1427.07	90.77
9	1484.92	94.46	10	1589.06	74.44	11	2576.43	97.82	12	2665.14	94.18
13	2749.99	93.37	14	2830.99	92.15	15	2915.84	91.18	16	3046.98	89.08

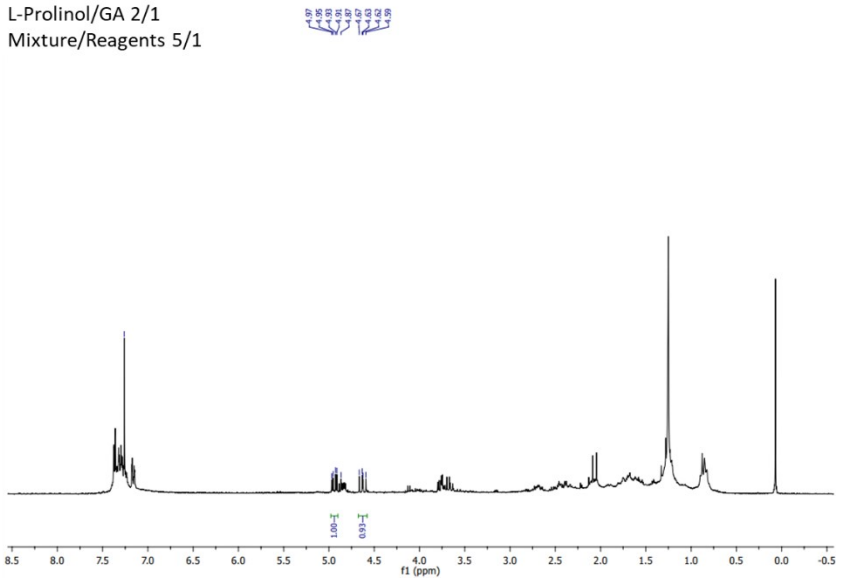
3. Selected ^{1}H-NMR spectra of crude reactions

3.1. L-Prolinol/GA 1/1

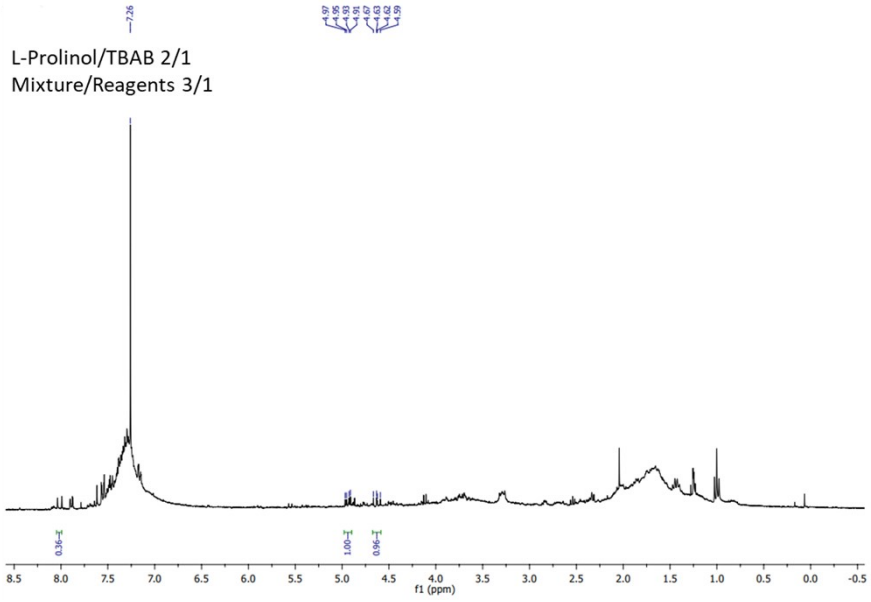
L-Prolinol/GA 1/1
Mixture/Reagents 5/1



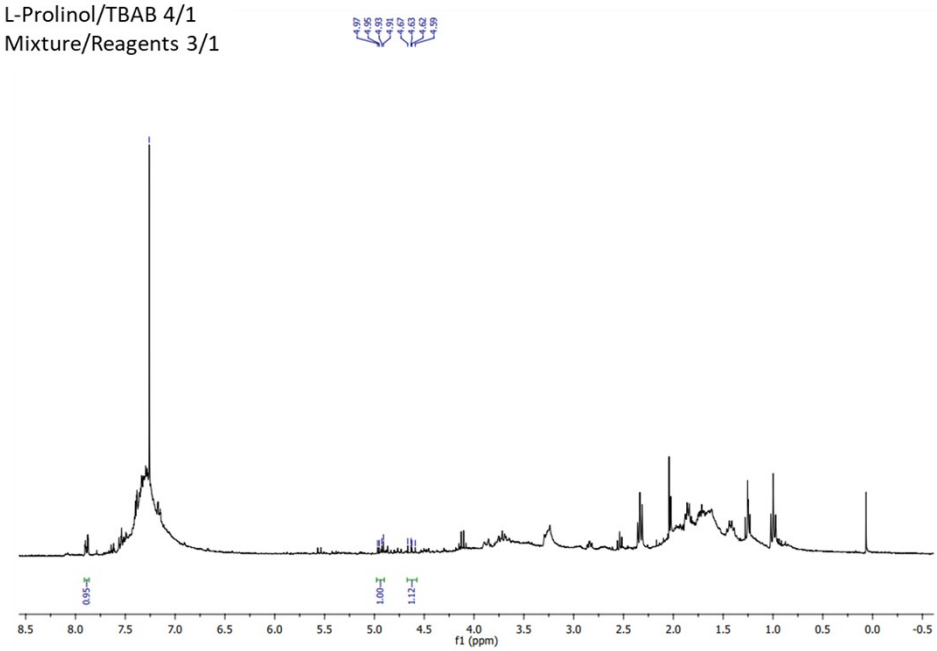
3.2. L-Prolinol/GA 2/1



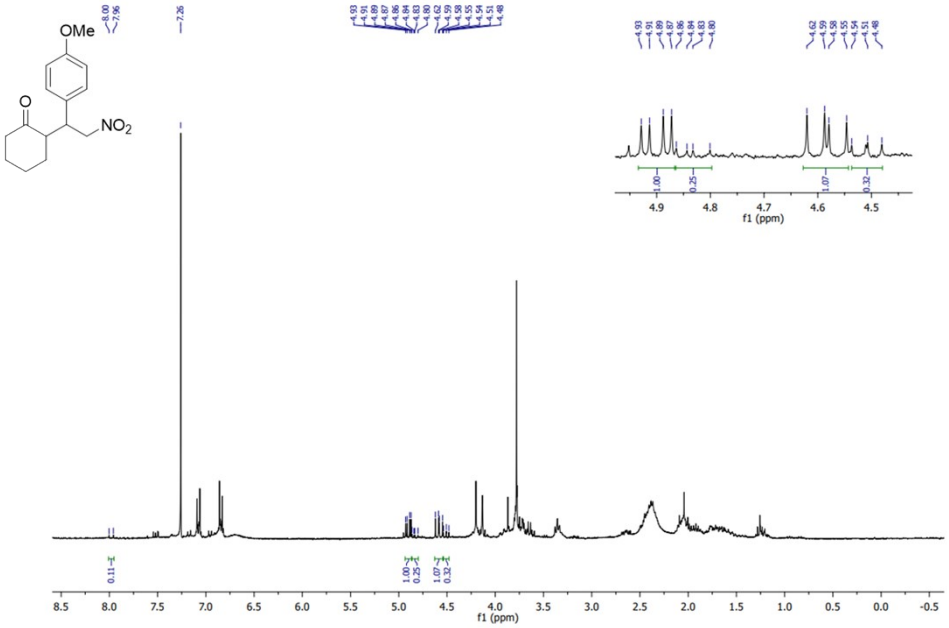
3.3. L-Prolinol/TBAB 2/1

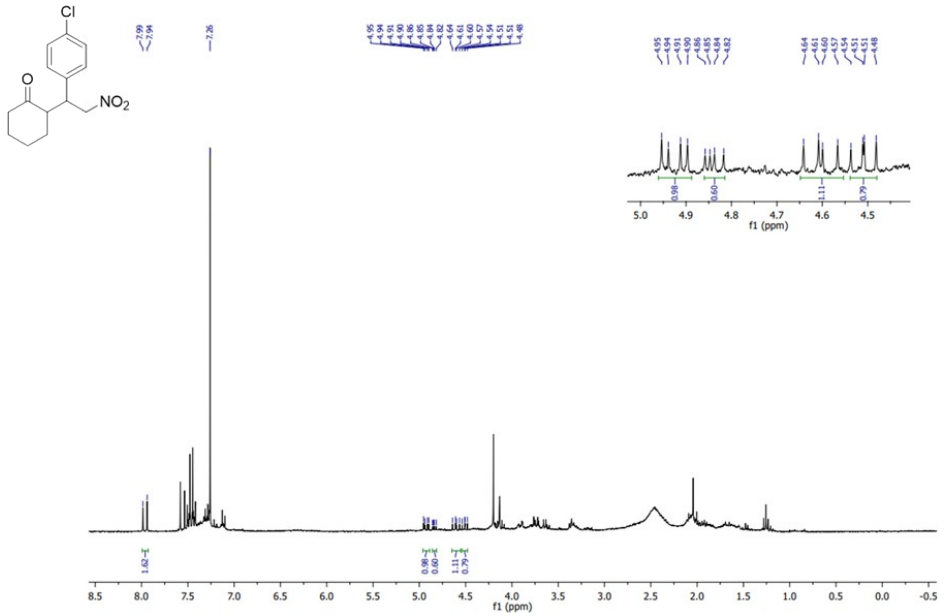


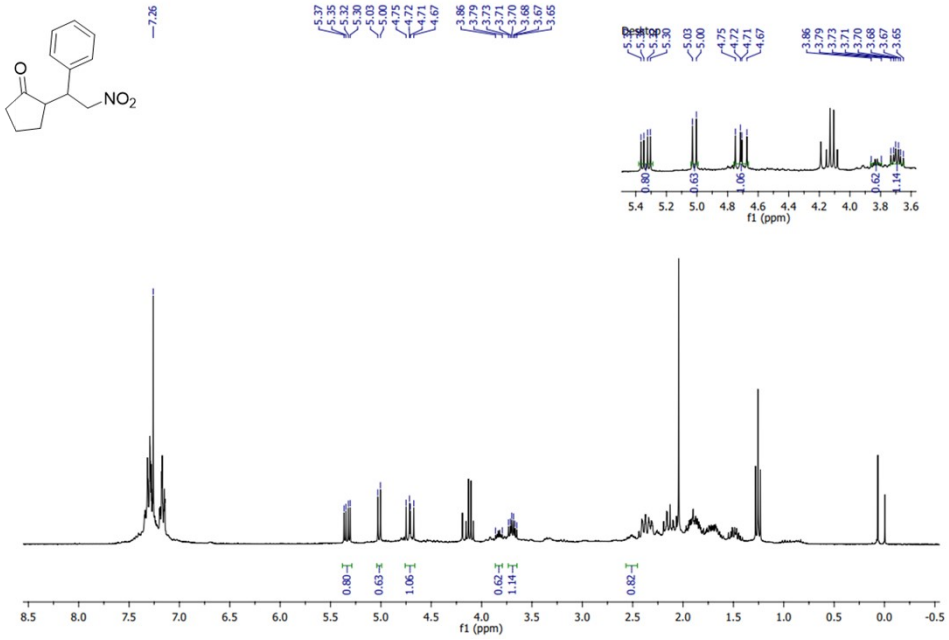
3.4. L-Prolinol/TBAB 4/1



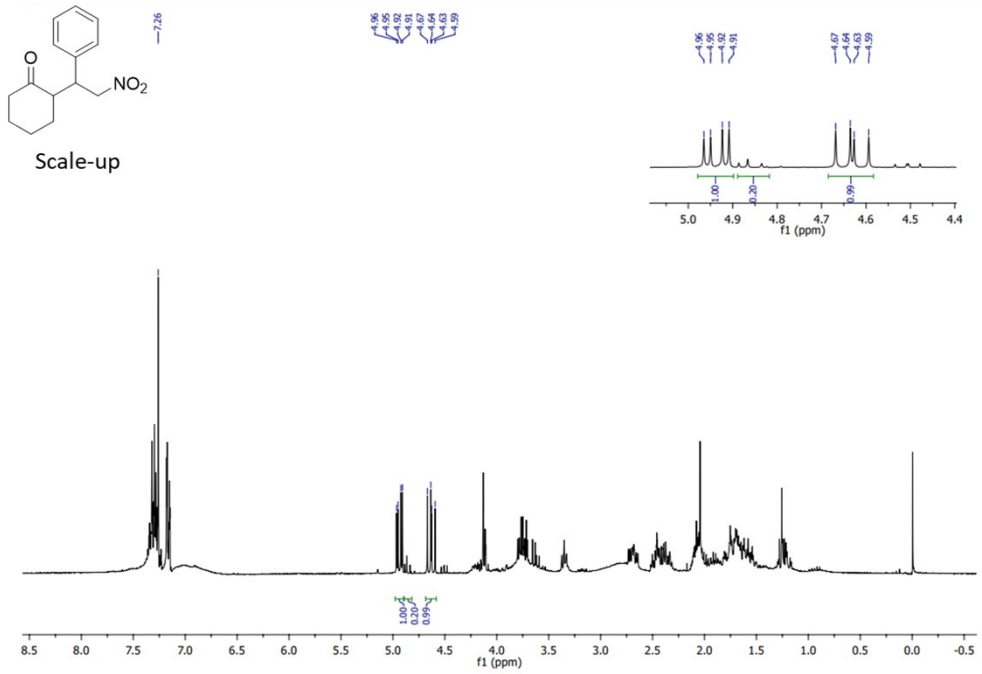
3.5. Michael addition of ketones to b-nitrostyrenes employing L-Prolinol/GA 1/1 mixture in a 5/1 mass ratio of chiral mixture to reagents



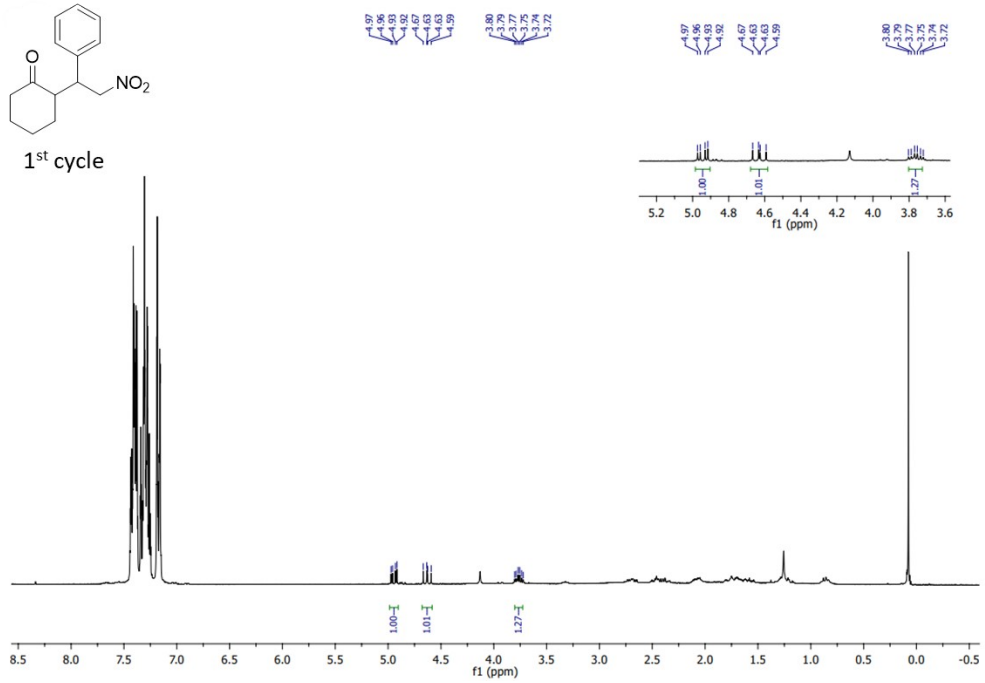

Cl
O
NO2
f1 (ppm)

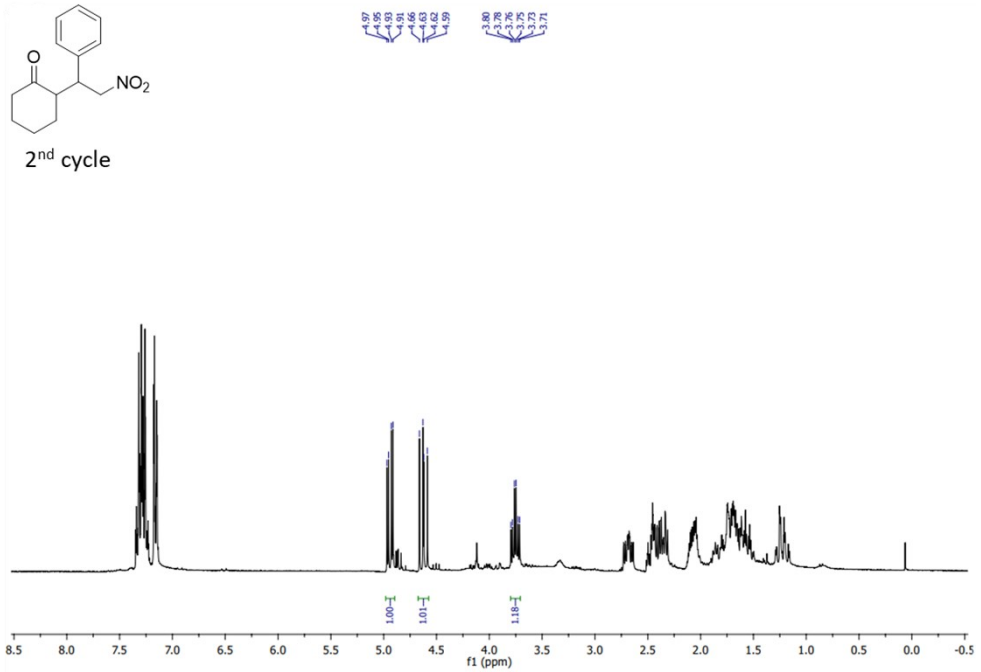

O
NO2
Desktop
f1 (ppm)

3.6. Scale-up of cyclohexanone to β-nitrostyrene Michael addition employing L-Prolinol/GA 1/1 mixture in a 5/1 mass ratio of chiral mixture to reagents.

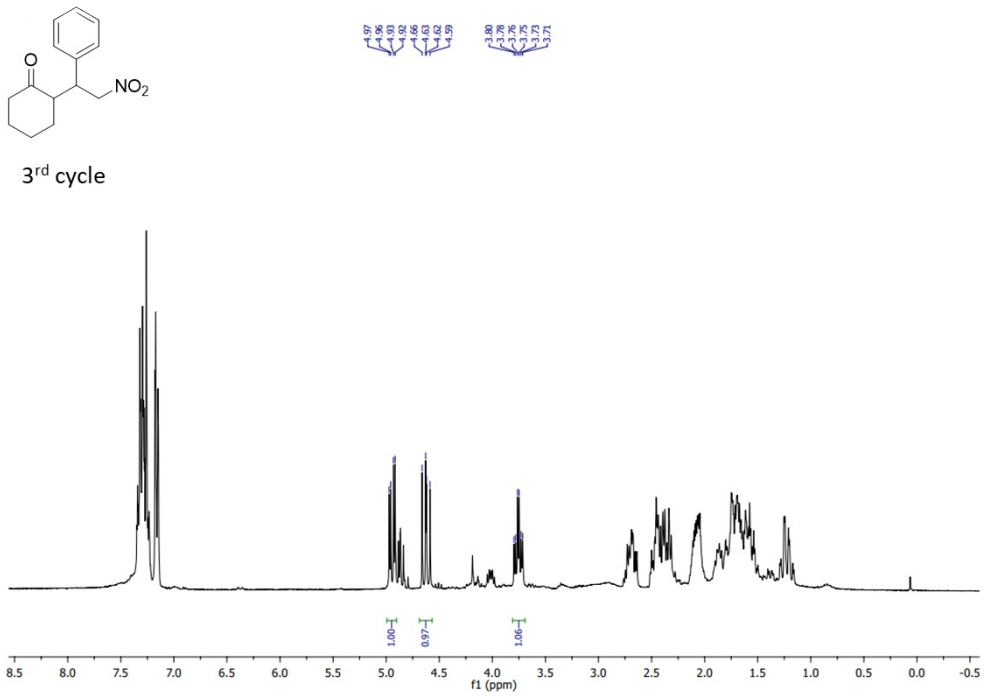


3.7. Recycling studies of cyclohexanone to β-nitrostyrene Michael addition employing L-Prolinol/GA 1/1 mixture in a 5/1 mass ratio of chiral mixture to reagents.

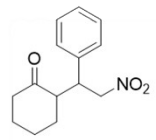




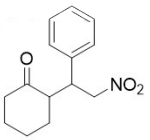
2nd cycle



3rd cycle



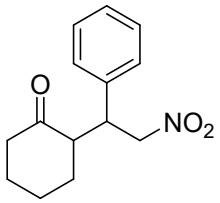
4th cycle

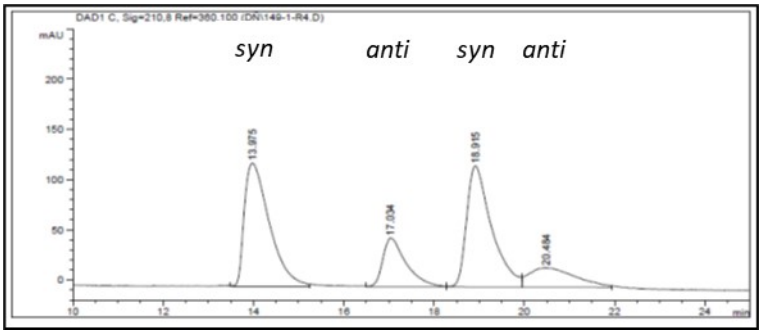


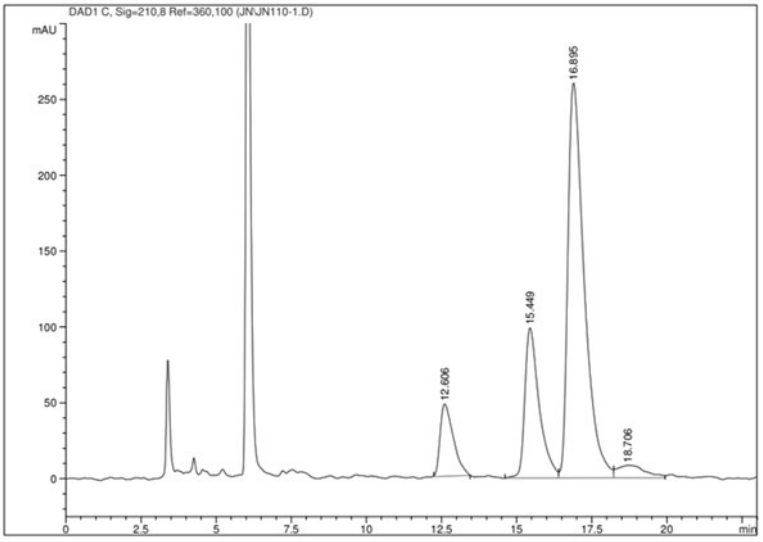
5th cycle

4. Chiral HPLC spectra of crude reaction mixtures.

4.1. (*S*)-2-((*R*)-2-nitro-1-phenylethyl)cyclohexanone (major product).[1]

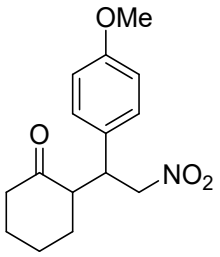


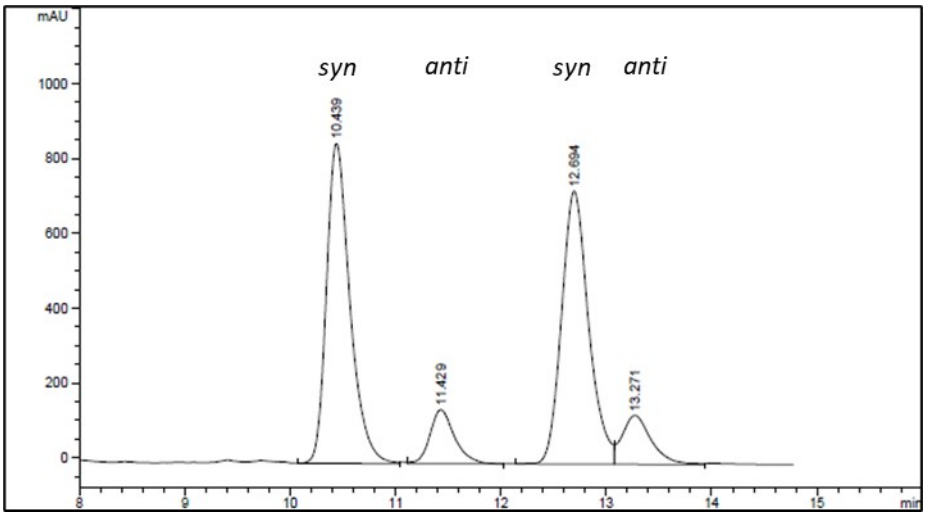


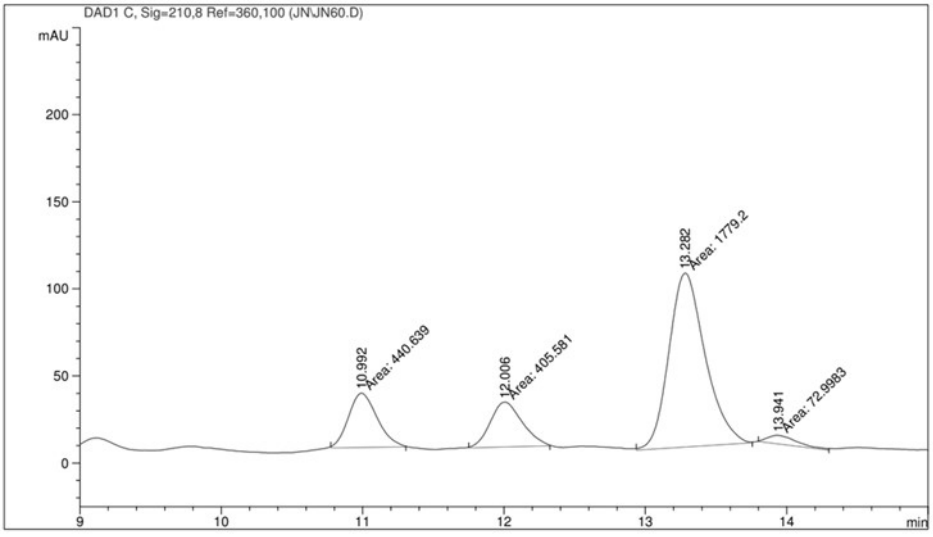


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.606	MM	0.5073	1451.62292	47.69149	9.6052
2	15.449	PV	0.4922	3277.74731	99.00982	21.6884
3	16.895	VB	0.5611	9846.47070	260.43976	65.1527
4	18.706	BV	0.7689	537.07117	8.29995	3.5537
Totals :				1.51129e4	415.44101	

4.2. (*S*)-2-((*R*)-1-(4-methoxyphenyl)-2-nitroethyl)cyclohexanone (major product).[1]

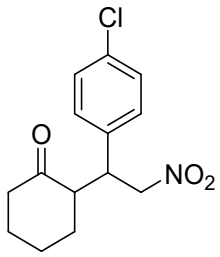


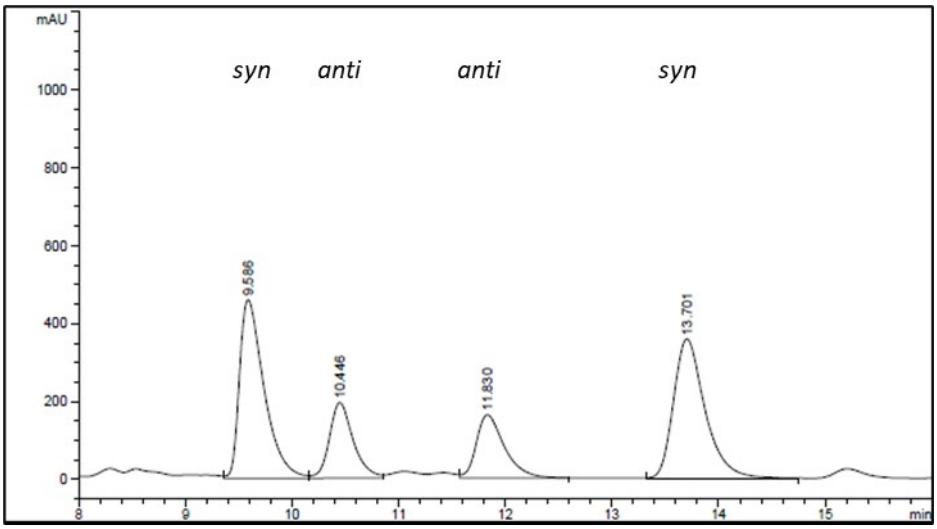


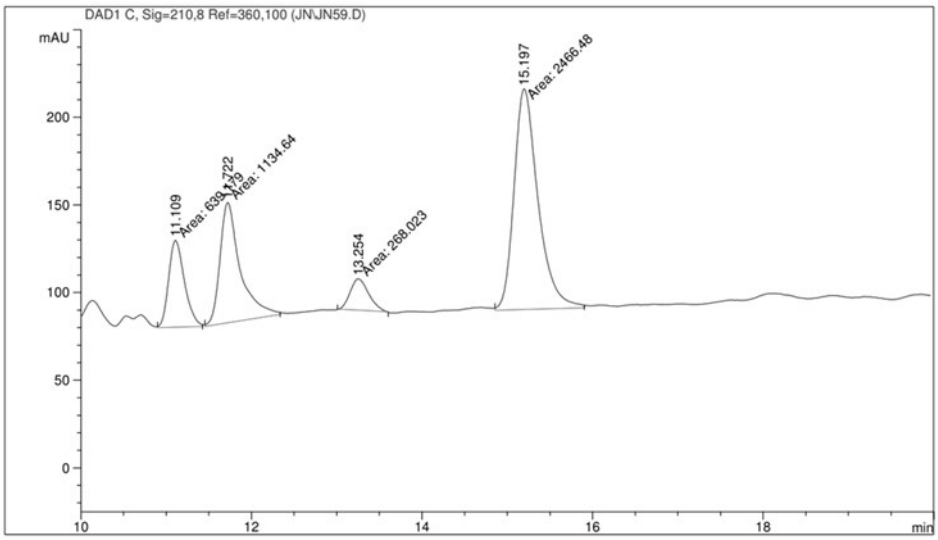


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.992	MM	0.2350	440.63882	31.25068	16.3295
2	12.006	MM	0.2621	405.58099	25.79507	15.0303
3	13.282	MM	0.2971	1779.20483	99.82589	65.9350
4	13.941	MM	0.2450	72.99831	4.96668	2.7052
Totals :				2698.42297	161.83832	

4.3. (*S*)-2-((*R*)-1-(4-chlorophenyl)-2-nitroethyl)cyclohexanone (major product).[1]

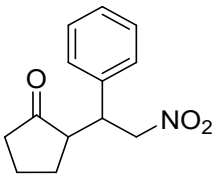


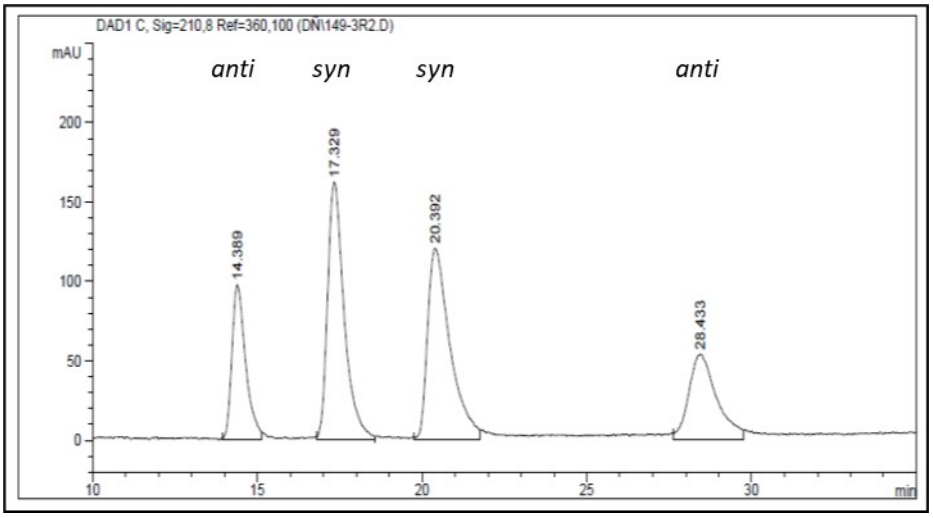


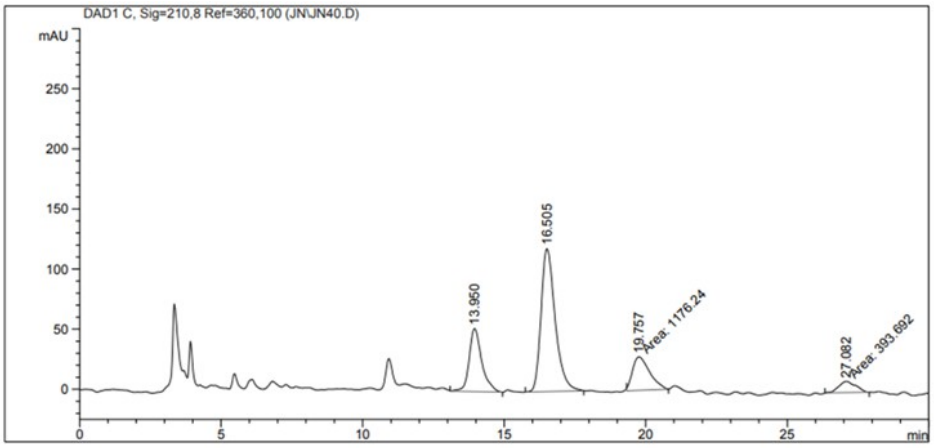


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.109	MM	0.2153	639.17908	49.47757	14.1778
2	11.722	MM	0.2756	1134.64038	68.60476	25.1677
3	13.254	MM	0.2497	268.02289	17.88955	5.9451
4	15.197	MM	0.3266	2466.47949	125.88364	54.7095
Totals :				4508.32184	261.85551	

4.4. (*S*)-2-((*R*)-2-Nitro-1-phenylethyl)cyclohexanone (major product).[1]

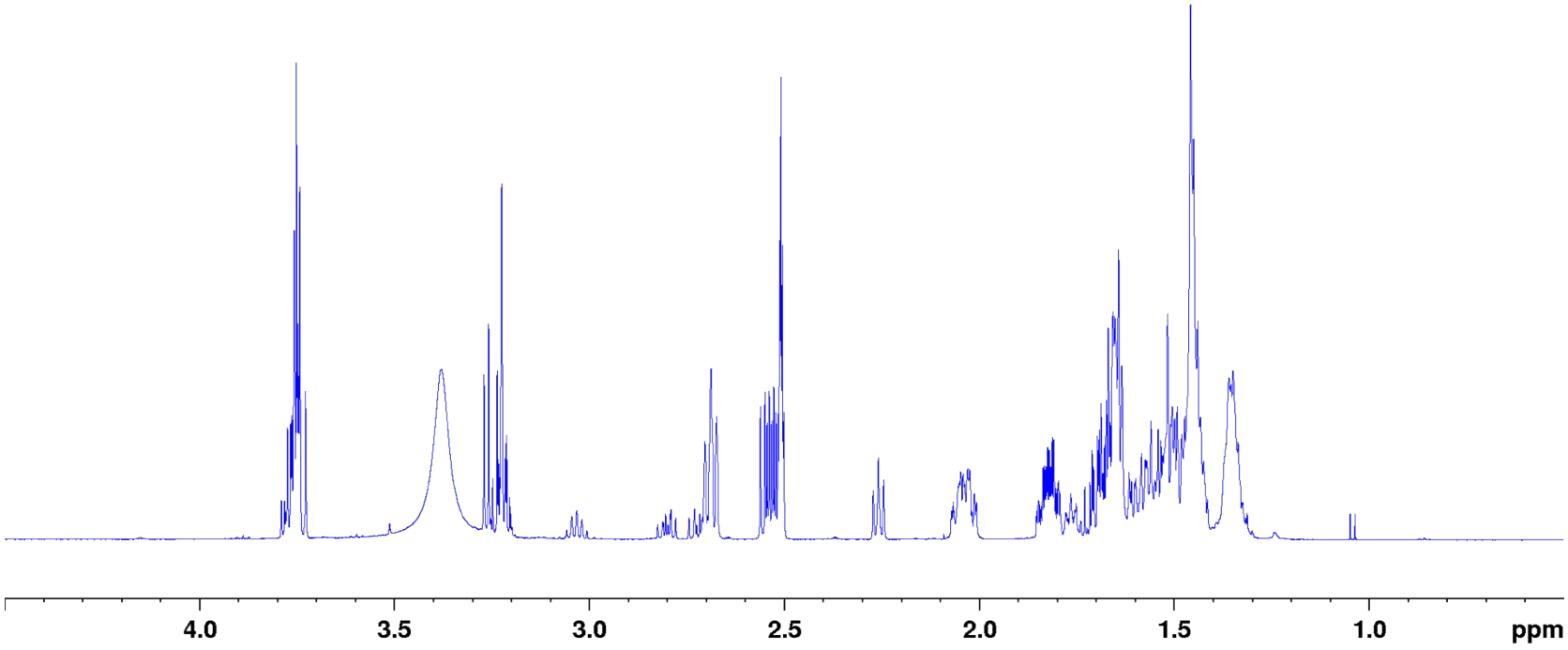




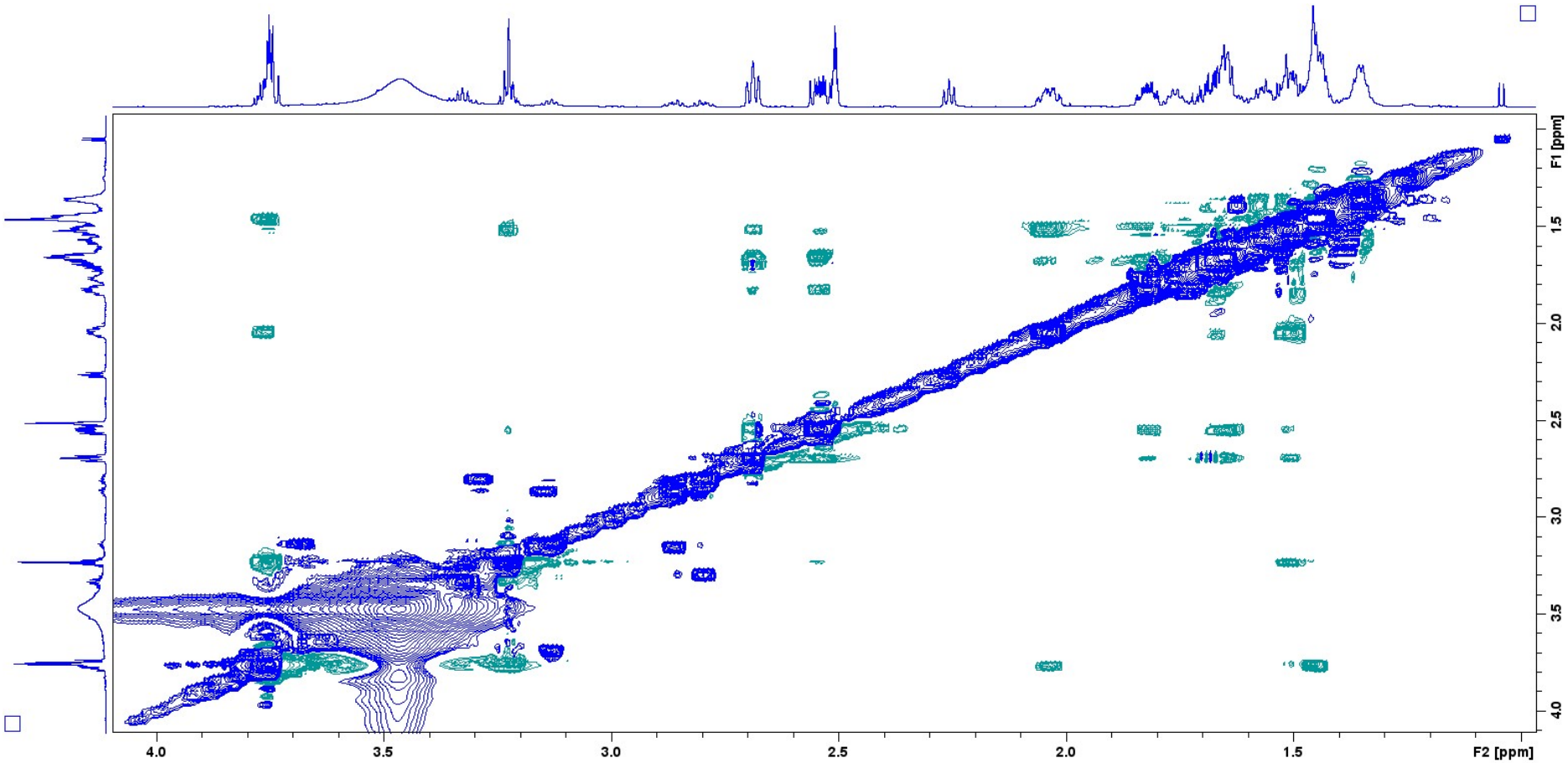


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.950	VP	0.4729	1635.98901	52.59710	22.2802
2	16.505	BB	0.5260	4136.86768	118.88335	56.3392
3	19.757	MM	0.7021	1176.23901	27.92154	16.0190
4	27.082	PP	0.7013	393.69220	9.35669	5.3616
Totals :				7342.78790	208.75868	

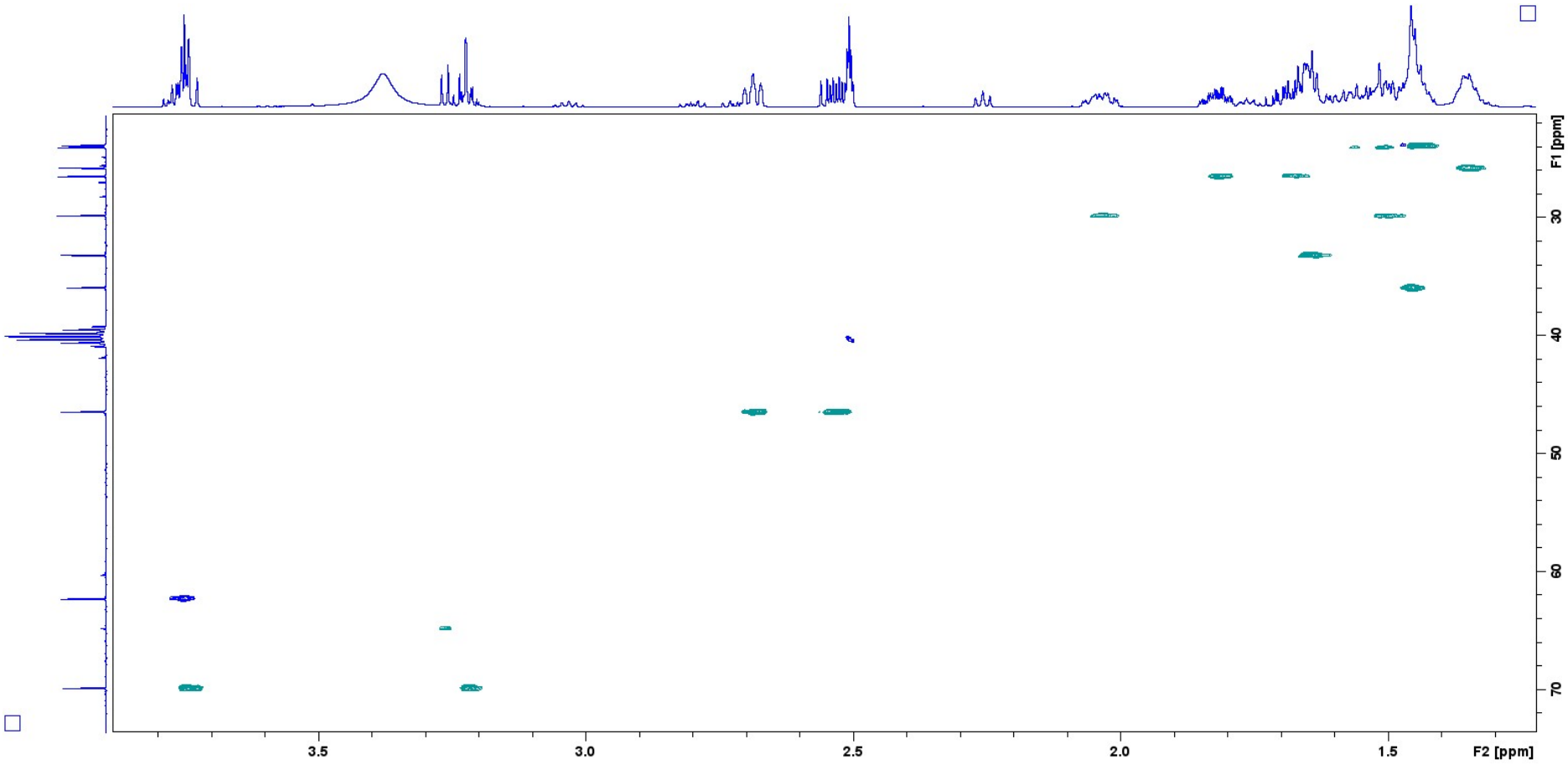
5. In situ NMR mechanistic studies: Oxazolidine intermediate formation.



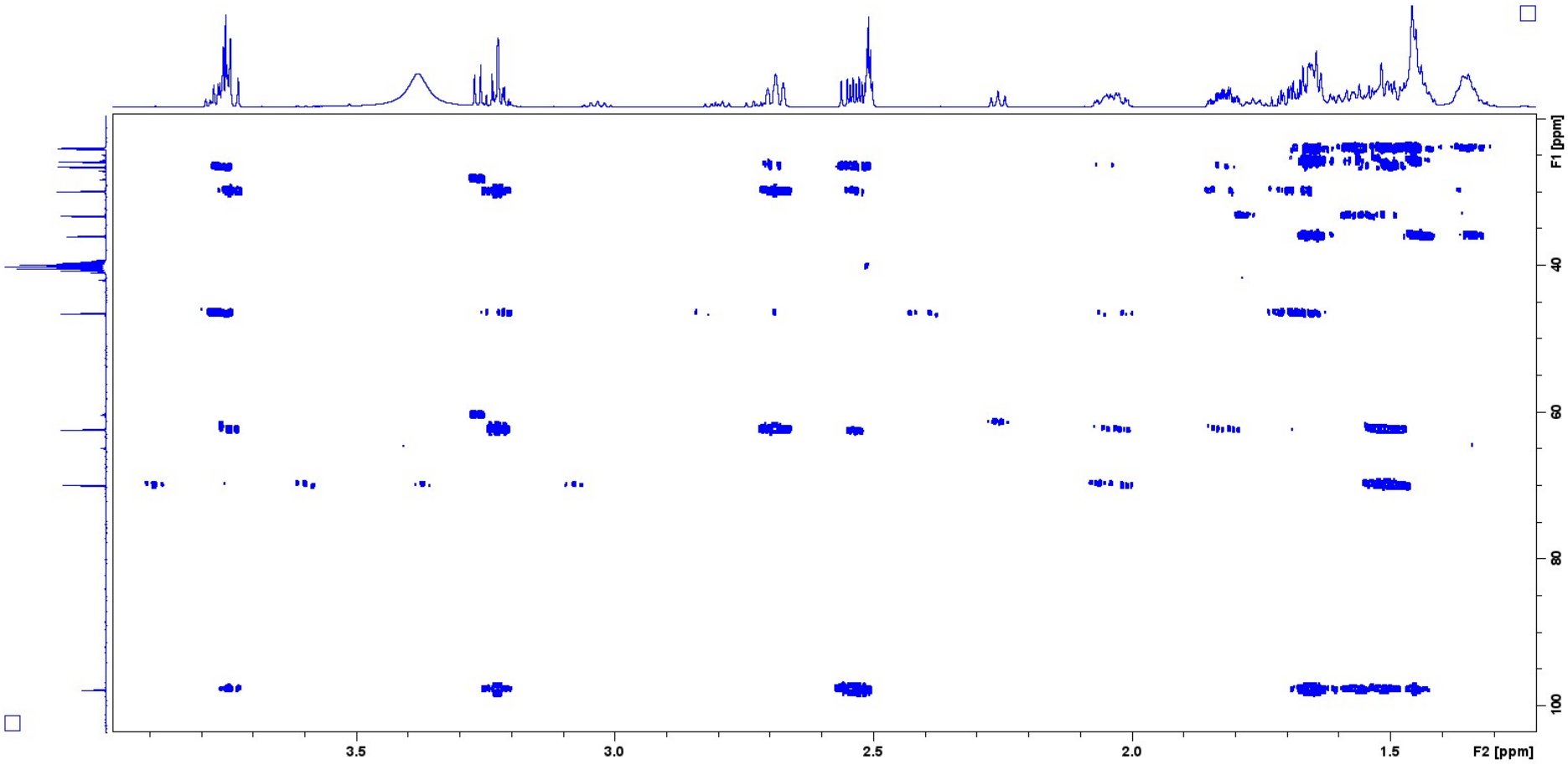
^{1}H NMR of the reaction between L-Prolinol and cyclohexanone obtained after 20 h.



2D ^{1}H,^{1}H gNOESY spectrum of the reaction between L-Prolinol and cyclohexanone obtained after 20 h.



2D Edited $^{1}H,^{13}C$ gHSQC of the reaction between L-Prolinol and cyclohexanone obtained after 20 h.



2D $^{1}H,^{13}C$ gHMBC of the reaction between L-Prolinol and cyclohexanone obtained after 20 h.

6. References.

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