Electronic Supplementary Information for RSC Advances

Alginic acid: a highly efficient renewable and heterogeneous bio-polymeric catalyst for one-pot synthesis of the Hantzsch 1,4-dihydropyridines

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1. Experimental section

1.1. Materials and methods

Melting points were determined using an Electrothermal apparatus. The FTIR spectra of alginate and its derivatives were performed with a Bruker-Equinox 55 IR spectrometer (Ettlingen, Germany) which was equipped by H.ATR accessories with a ZnSe crystal. Moreover, FTIR spectra of 1,4-dihydropyridines were recorded as KBr pellets on a Shimadzu FT IR-8400S spectrometer. The ^{1}H NMR and ^{13}C NMR spectra of 1,4-dihydropyridines and sodium alginate were recorded in deuterated chloroform ($CDCl_3$) and D_2O using spectrometers of Bruker Avance (250 MHz and 400 MHz), respectively. Analytical TLC was carried out using Merck 0.2 mm silica gel 60 F-254 Al-plates. Thermal stability of the sodium alginate and alginic acid were evaluated by the TGA technique on a Polymer Lab TGA-1500 instrument (London) under a N_2 atmosphere from room temperature to 600 °C with a heating rate of 10 °C/min.

1.2. General procedure for the fractionation of sodium alginate to its components

Sodium alginate was partially hydrolyzed according to the controlled gellification method. 1.0 gram of polysaccharide was dissolved in 100 mL of deionized water at 50 °C and heated under reflux conditions with 3 mL of HCl (3 M) for 20 min. After cooling to room temperature, the suspension was centrifuged (3000×g, 20 min) and the insoluble fraction from the centrifugation was refluxed in 100 mL of HCl (0.3 M) for 2 h. After centrifugation (8500×g, 20 min), the insoluble material was neutralized with NaOH (1 M) and the pH was adjusted to 2.85 with HCl (1 M). The soluble fraction was neutralized and added to 100 mL of EtOH. The precipitate was collected by centrifugation (8500×g, 20 min) and dried at 50 °C invacuo for 12 h (block M). The fractions obtained in the first hydrolysis step with HCl (0.3 M) and the soluble fraction at second step at pH 2.85 were rich of heteropolymeric MG and polymannuronic acid residues, respectively. Finally, the insoluble fraction at pH 2.85 was attributed to the polyguluronic acid residues.

1.3. General procedure for preparation of alginic acid (1) from sodium alginate

Alginic acid was synthesized through a procedure described by Babak et al., with some modifications. Sodium alginate (4.0 g) was added to a mixture of HCl (0.6 N, 50 mL) and EtOH (40 mL) and stirred overnight at 4 °C. The solid fracture, alginic acid, was separated by filtration under vacuum using a coarse filter paper. Then, the alginic acid was purified by washing with EtOH and acetone and dried in the oven at 60 °C.

References: (a) F. Llanes, F. Sauriol, F. G. Morin, A. S. Perlin, *Can. J. Chem*. **1997**, *75*, 585–590; (b) T. M. Aida, T. Yamagata, M. Watanabe, R. L. Smith Jr, *Carbohydr. Polym*. **2010**, *80*, 296–302; (c) T. A. Fenoradosoa, G. Ali, C. Delattre, C. Laroche, E. Petit, A. Wadouachi, P. Michaud, *J. Appl. Phycol*. **2010**, *22*, 131–137; (d) S. Holtan, Q. Zhang, W. I. Strand, G. Skjåk-Bræk, *Biomacromolecules*, **2006**, *7*, 2108-2121, (e) H. Daemi, M. Barikani, *Sci. Iran*. **2012**, *19*, 2023–2028; (f) V. G. Babak, E. A. Skotnikova, I. G. Lukina, S. Pelletier, P. Hubert, E. J. Dellacherie, *J. Colloid. Interface Sci*. **2000**, *225*, 505–510; (g) H. Daemi, M. Barikani, M. Barmar, *Int. J. Biol. Macromol*. **2014**, *66*, 212–220.

1.4. Chemical characterization of sodium alginate

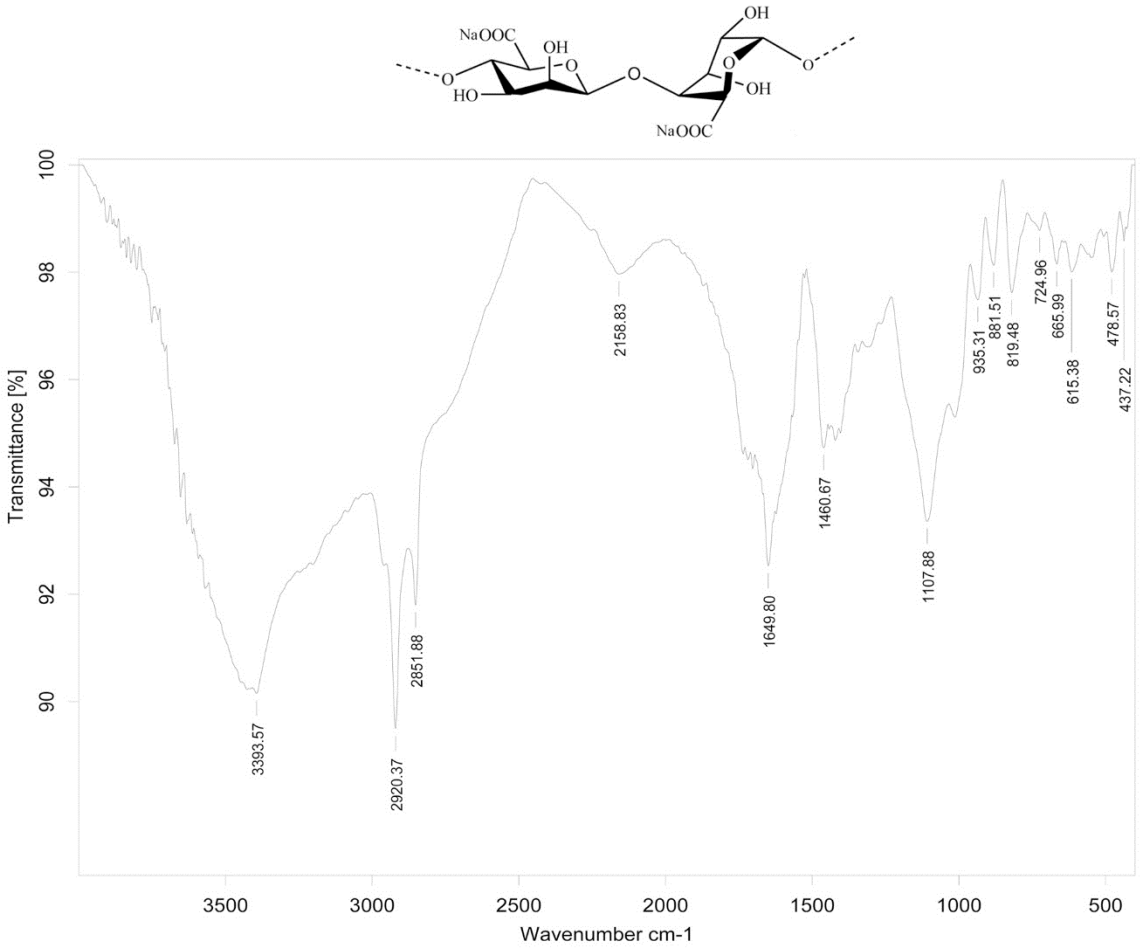


Fig. 1. FT-IR spectrum of the commercial sodium alginate.

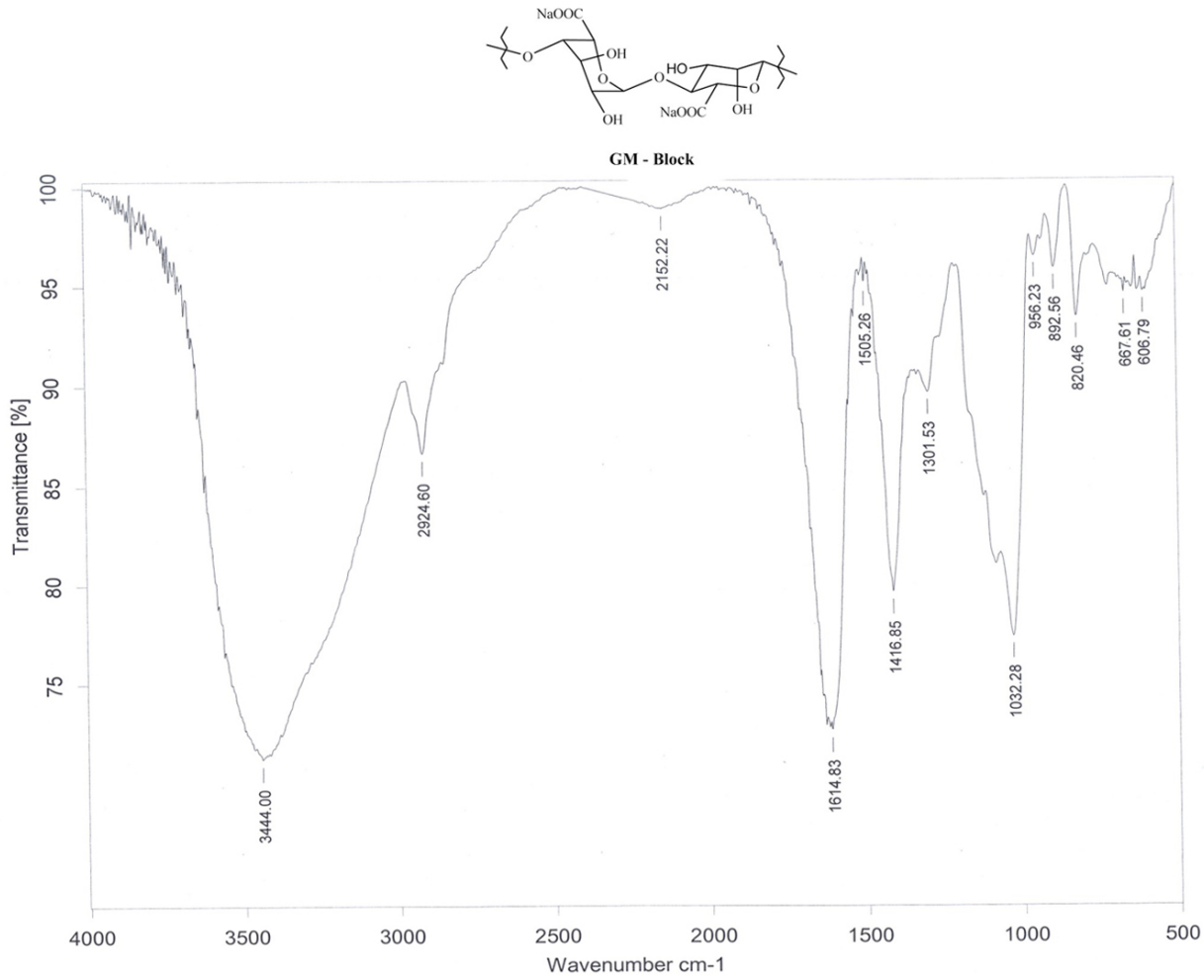


Fig. 2. FT-IR spectrum of the heterogenous copolymer containing random M and G blocks.

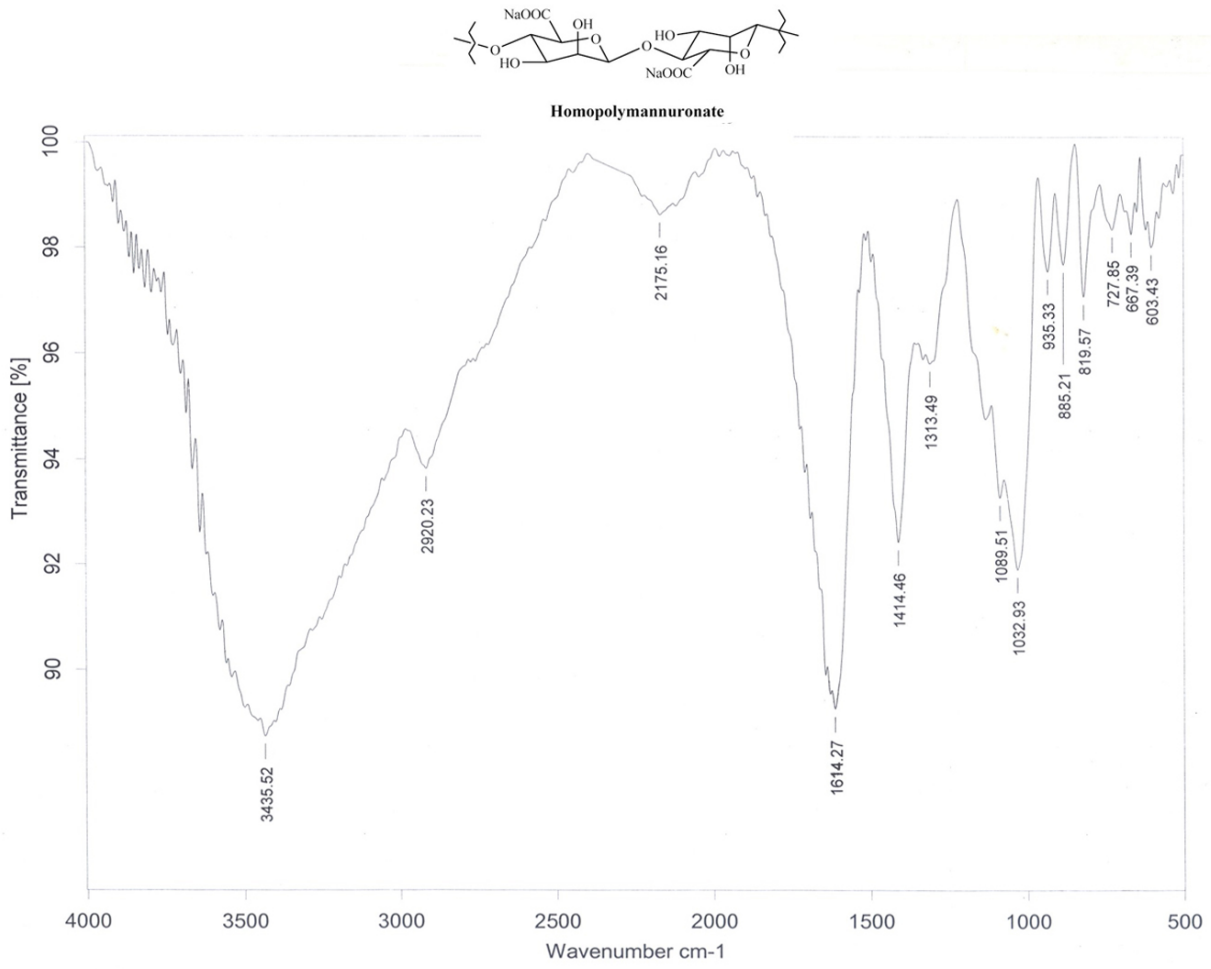


Fig. 3. FT-IR spectrum of the sodium homopolymannuronate.

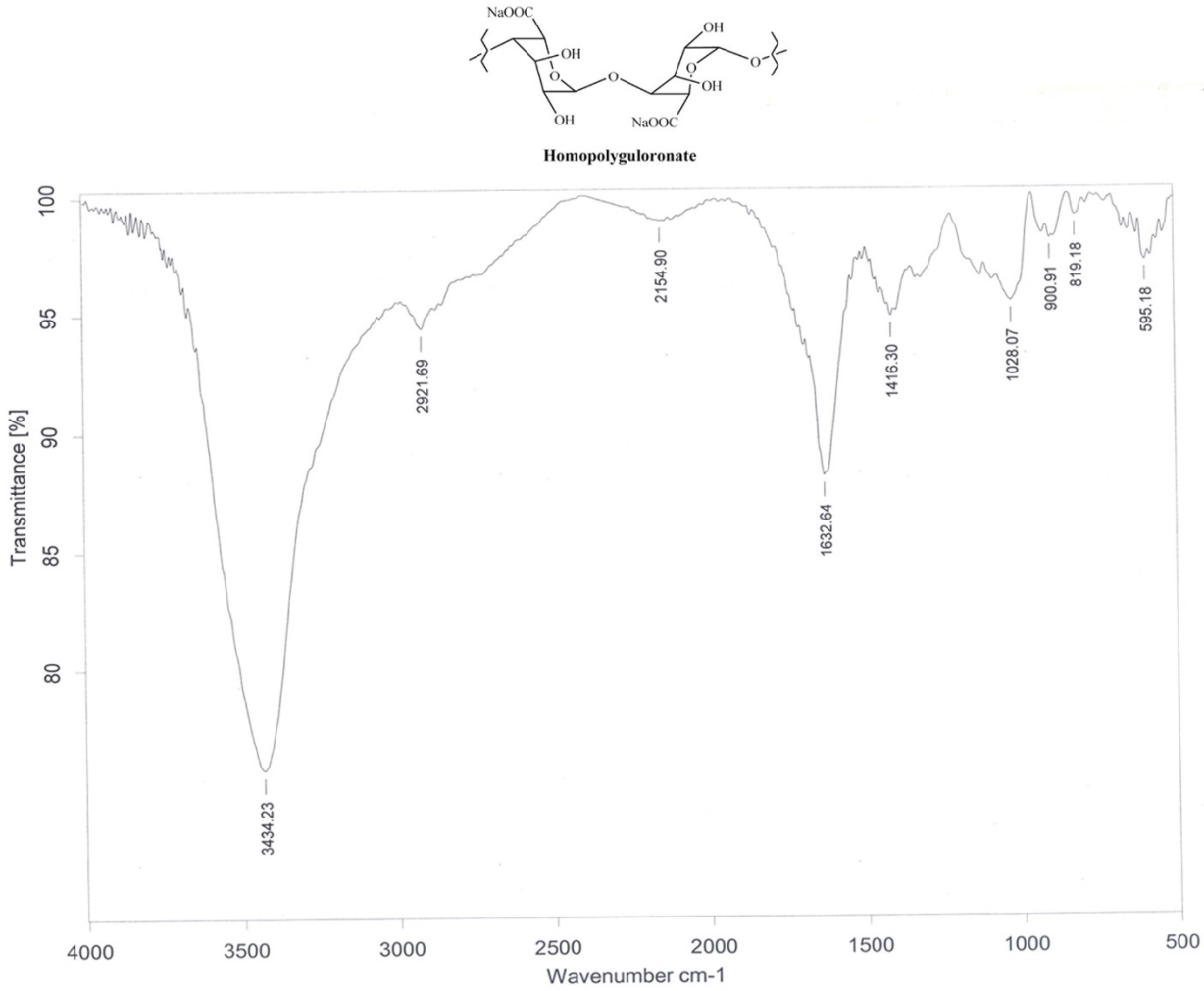


Fig. 4. FT-IR spectrum of the sodium homopolyguluronate.

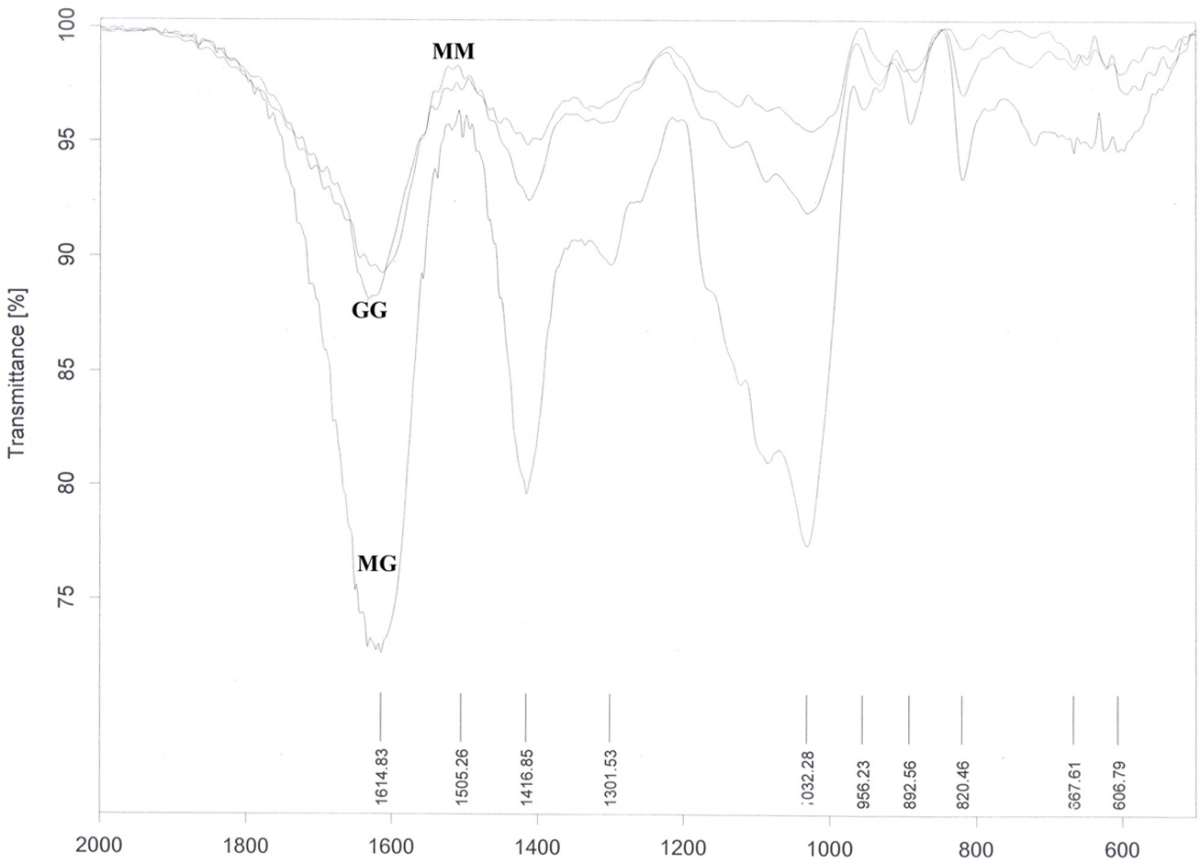


Fig. 5. A comparison between the FT-IR spectra of different constituents of the sodium alginate.

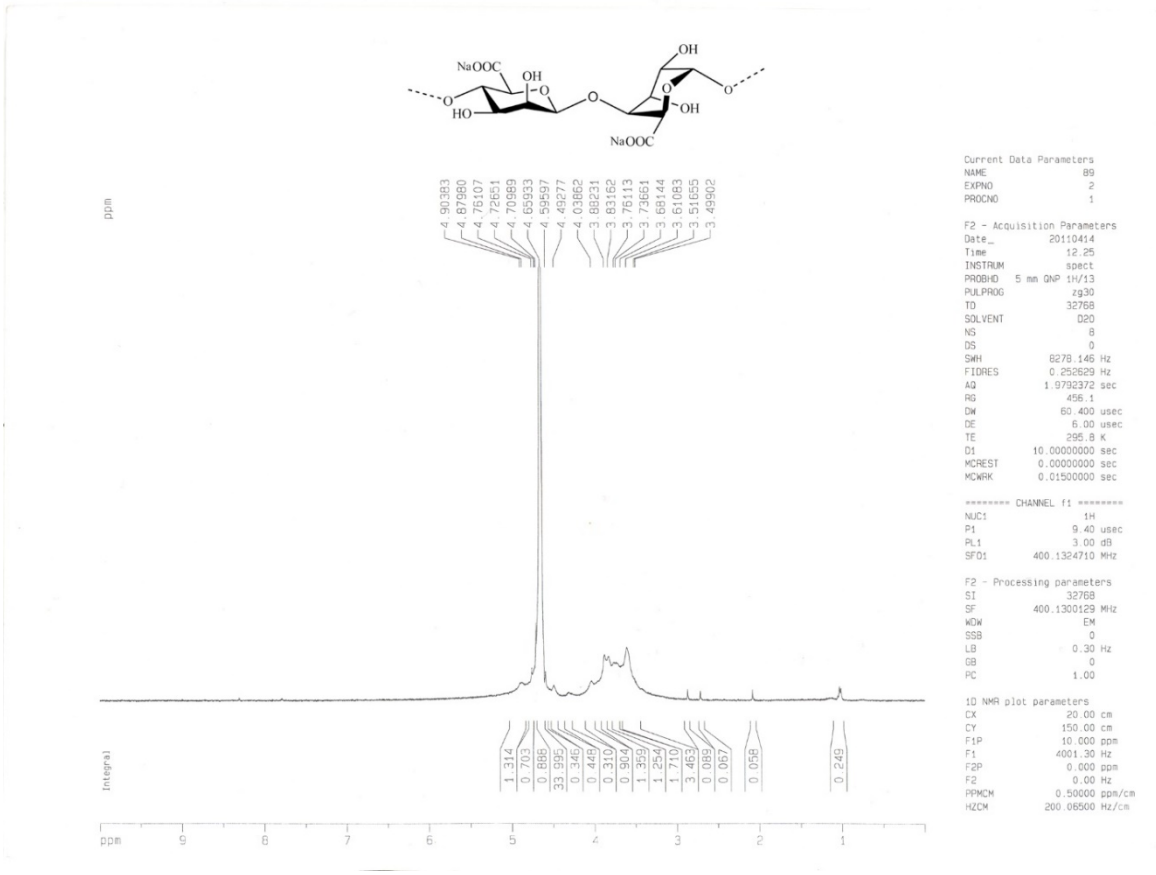


Fig. 6. ^{1}H NMR spectrum of sodium alginate.

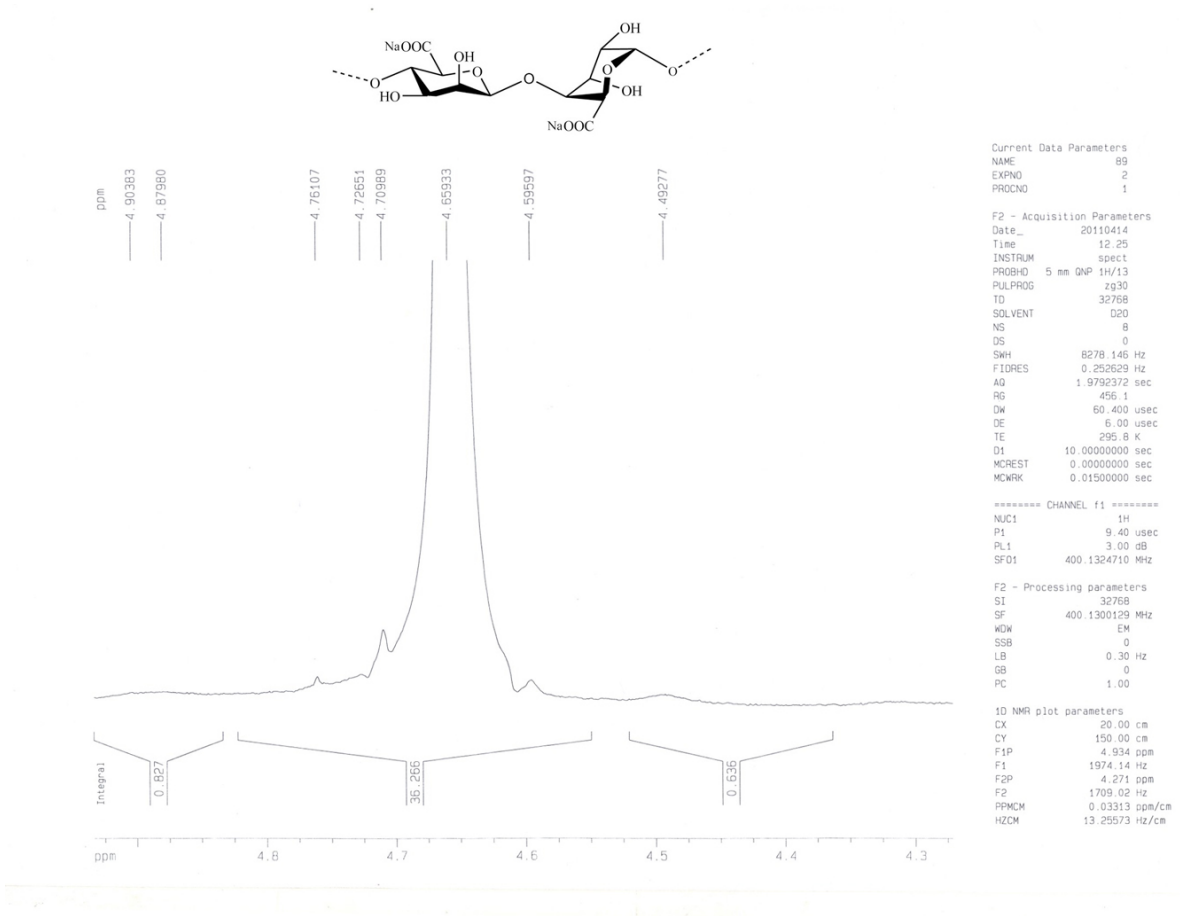


Fig. 7. ^{1}H NMR spectrum of sodium alginate (Expanded aliphatic region).

1.5. Thermo Gravimetric analysis of sodium alginate and alginic acid (1)

As seen in thermograms of sodium alginate and alginic acid, the hydrophilicity of sodium alginate is significantly more than that insoluble form, i.e. alginic acid. Therefore, the insoluble form of alginate is a more appropriate candidate as a bifunctional heterogeneous catalyst compared to its soluble form.

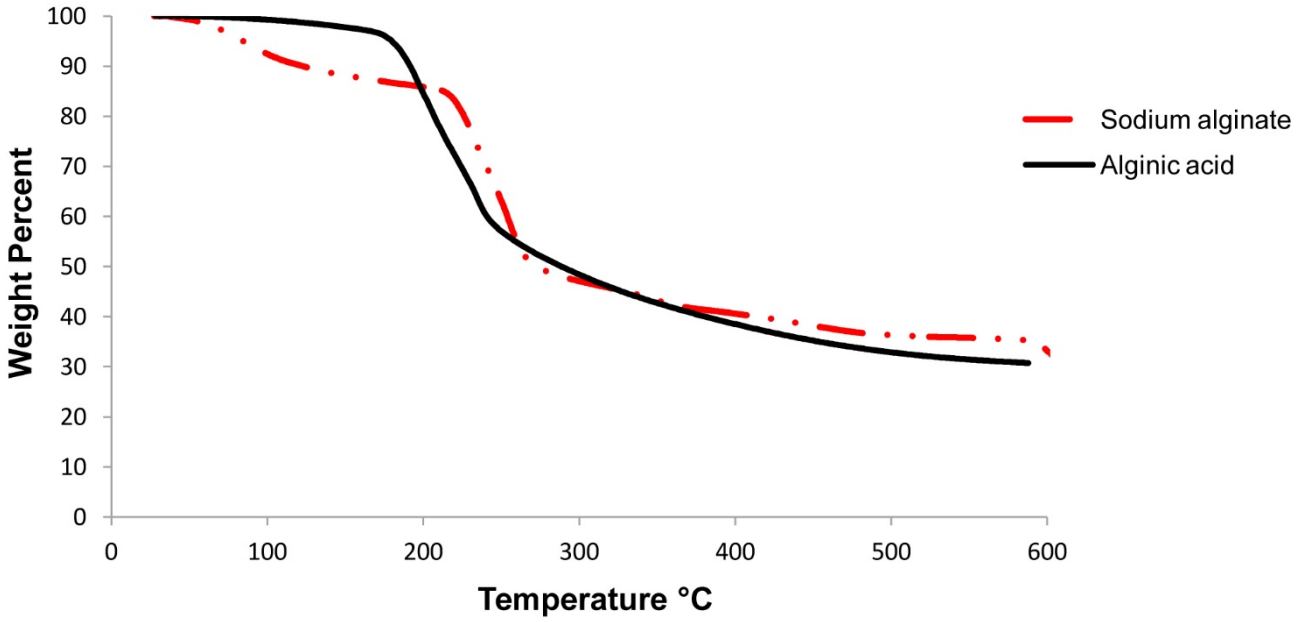


Fig. 8. TGA thermograms of sodium alginate and alginic acid (**1**).

1.6. Chemical characterization of alginic acid (1)

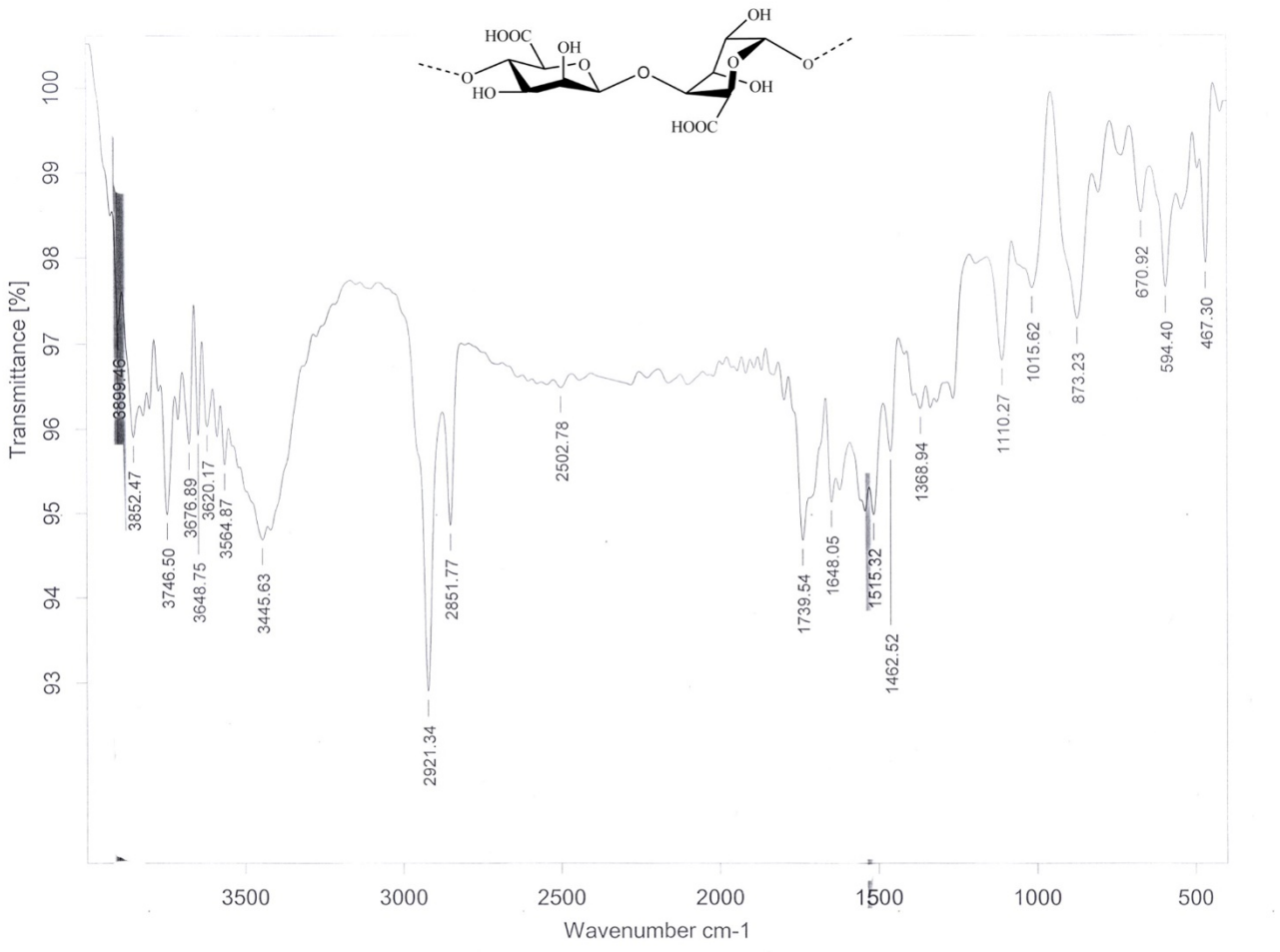


Fig. 9. FT-IR spectrum of prepared alginic acid (**1**).

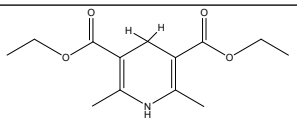
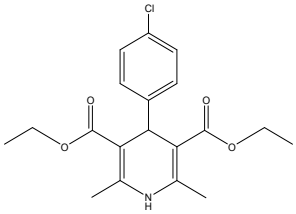
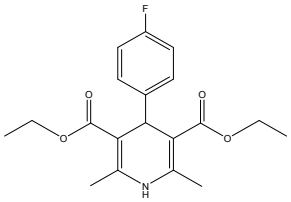
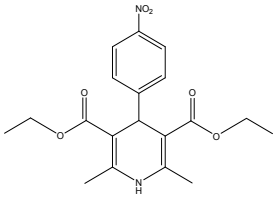
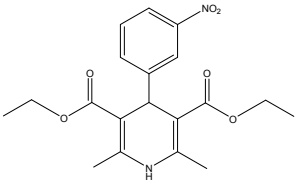
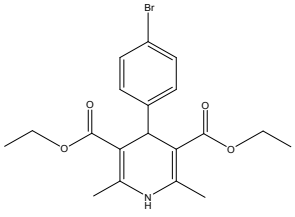
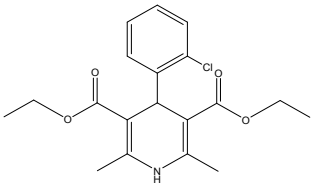
1.7. General procedure for the synthesis of 1,4-dihydropyridines (5-6) catalyzed by alginic acid (1)

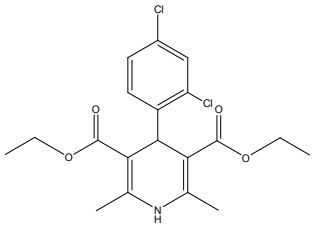
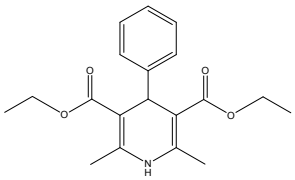
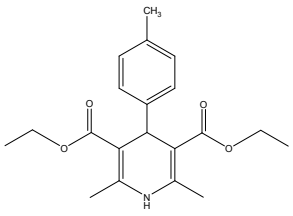
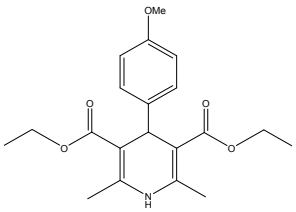
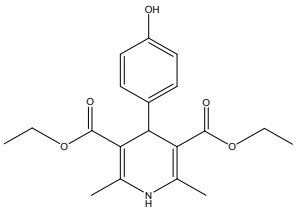
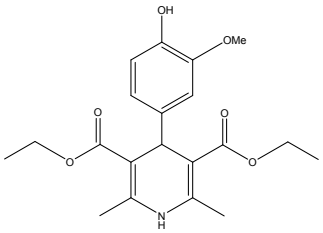
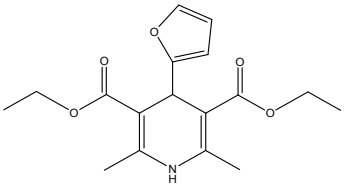
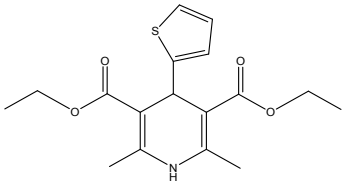
In a 5 mL round bottom flask equipped with a magnetic bar and condenser, a mixture of aldehyde (**2**, 1 mmol), β-ketoester (**3**, 2 mmol), ammonium acetate (**4a**, 1.2 mmol) and alginic acid (**1**, 17.6 mg, 10 mol% relative to the aldehyde) was added to 1 mL of 96% EtOH. The resulting mixture was stirred at reflux conditions for appropriate time indicated in Tables 1 or 2. After completion of the reaction (monitored by TLC), it was diluted with 2 mL of 96% EtOH and filtered. Then, distilled water was added dropwise with continuous stirring to the filtrate to provide crystals of 1,4-DHP **5** or **6**. The separated crystals were filtered off, washed with cold aqueous EtOH (50% v/v, 2 mL) and dried at 60 ^{o}C in an air oven for 1 h.

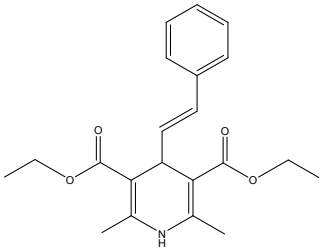
1.8. Reusability of alginic acid catalyst (1) for the Hantzsch MCR

The reusability of the catalyst **1** was investigated in the consecutive Hantzsch reaction of 4-chlorobenzaldehyde (**2a**, 1 mmol), ethyl acetoacetate (**3a**, 2 mmol) and ammonium acetate **4a** (1.2 mmol). The reactions were carried out according to the above general procedure for synthesis of 1,4-DHPs **5**. After the first run, which afforded the diethyl 4-(4-chlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**5a**) in 96% isolated yield (100% conversion), the separated catalyst was washed with fresh aliquot of EtOAc (3 x 1 mL), dried in an air oven at 60 °C, and then was subjected to a second Hantzsch reaction from which it also gave the Hantzsch reaction products in 100% conversion (95% isolated yield); the average chemical yield for six repeated runs was 94%.

Table 1. Pseudo-four-component synthesis of different diethyl 1,4-DHP-3,5-dicarboxylate (**5a-p**) catalysed by alginic acid (**1**) in EtOH under reflux conditions[a]

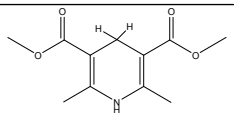
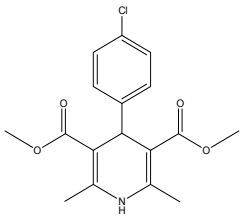
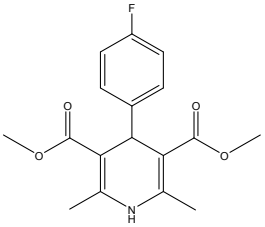
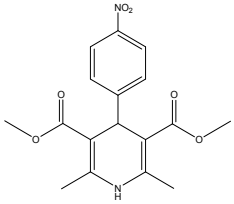
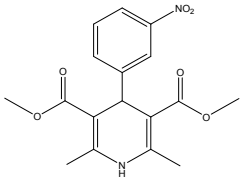
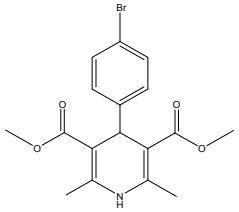
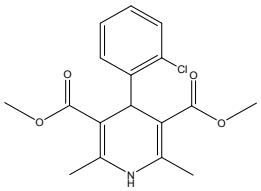
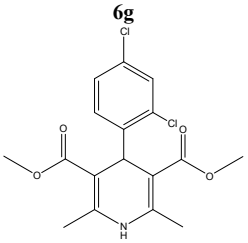
Entry	Aldehyde **2**	Product **5**[b]	Time (min)	Yield (%)[c]	M.P (Obsd) (°C)	M.P (Ref) (°C)
1	Formaldehyde **2a**	 **5a** (Diludine)	25	97	177-180	183
2	4-Chlorobenzaldehyde **2b**	 **5b**	50	96	144-145	145-146
3	4-Fluorobenzaldehyde **2c**	 **5c**	45	97	152-153	151-155
4	4-Nitrobenzaldehyde **2d**	 **5d**	50	83	125-127	136
5	3-Nitrobenzaldehyde **2e**	 **4e**	60	77	166-168	163
6	4-Bromobenzaldehyde **2f**	 **5f**	35	93	162-164	162-164
7	2-Chlorobenzaldehyde **2g**	 **5g**	60	86	131-133	129-130

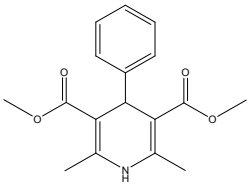
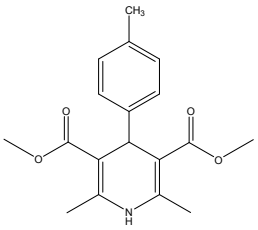
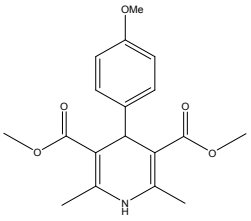
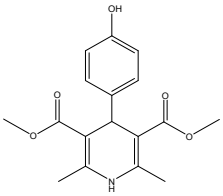
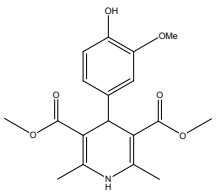
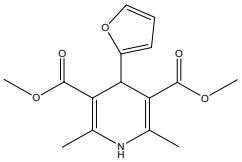
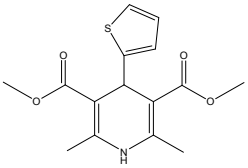
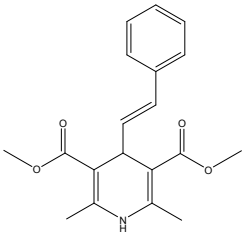
8	2,4-Dichlorobenzaldehyde **2h**	 **5h**	65	87	146-148	148-149
9	Benzaldehyde **2i**	 **5i**	45	96	156-158	157-159
10	4-Methylbenzaldehyde **2j**	 **5j**	60	92	135-137	135-138
11	4-Methoxybenzaldehyde **2k**	 **5k**	70	91	160-161	158-160
12	4-Hydroxybenzaldehyde **2l**	 **5l**	90	92	228-231	229-231
13	4-Hydroxy-3-methoxybenzaldehyde (Vanilin) **2m**	 **5m**	80	90	160-162	160-164
14	Furfural **2n**	 **5n**	55	93	160-161	160-161
15	Thiophen-2-carbaldehyde **2o**	 **5o**	70	98	169-171	172-174

16	Cinnamaldehyde **2p**	 **5p**	60	94	145-147	147

[a] Reaction conditions: Aldehyde (**2a,** 1 mmol), ethyl acetoacetate (**3a**, 2 mmol), ammonium acetate (**4a**, 1.2 mmol). [b] All the products are known compounds and were identified by comparison of their TLC, physical and spectral (IR, ^{1}H NMR) data with those of authentic samples. [c] Isolated yields.

Table 2. Pseudo-four-component synthesis of different dimethyl 1,4-DHP-3,5-dicarboxylate (**6a-p**) catalysed by alginic acid (**1**) in EtOH under reflux conditions[a]

Entry	Aldehyde **2**	Product **6**[b]	Time (min)	Yield (%)[c]	M.P (Obsd) (°C)	M.P (ref) (°C)
1	Formaldehyde **2a**	 **6a**	20	96	220-222	222-224
2	4-Chlorobenzaldehyde **2b**	 **6b**	50	94	196-198	196-198
3	4-Fluorobenzaldehyde **2c**	 **6c**	40	97	171-172	176-179
4	4-Nitrobenzaldehyde **2d**	 **6d**	60	85	196-198	196-198
5	3-Nitrobenzaldehyde **2e**	 **6e**	50	79	210-211	210-212
6	4-Bromobenzaldehyde **2f**	 **6f**	30	94	201-202	200-202
7	2-Chlorobenzaldehyde **2g**	 **6g**	60	88	184-185	185-186
8	2,4-Dichlorobenzaldehyde **2h**	 **6h**	70	93	188-190	190-192

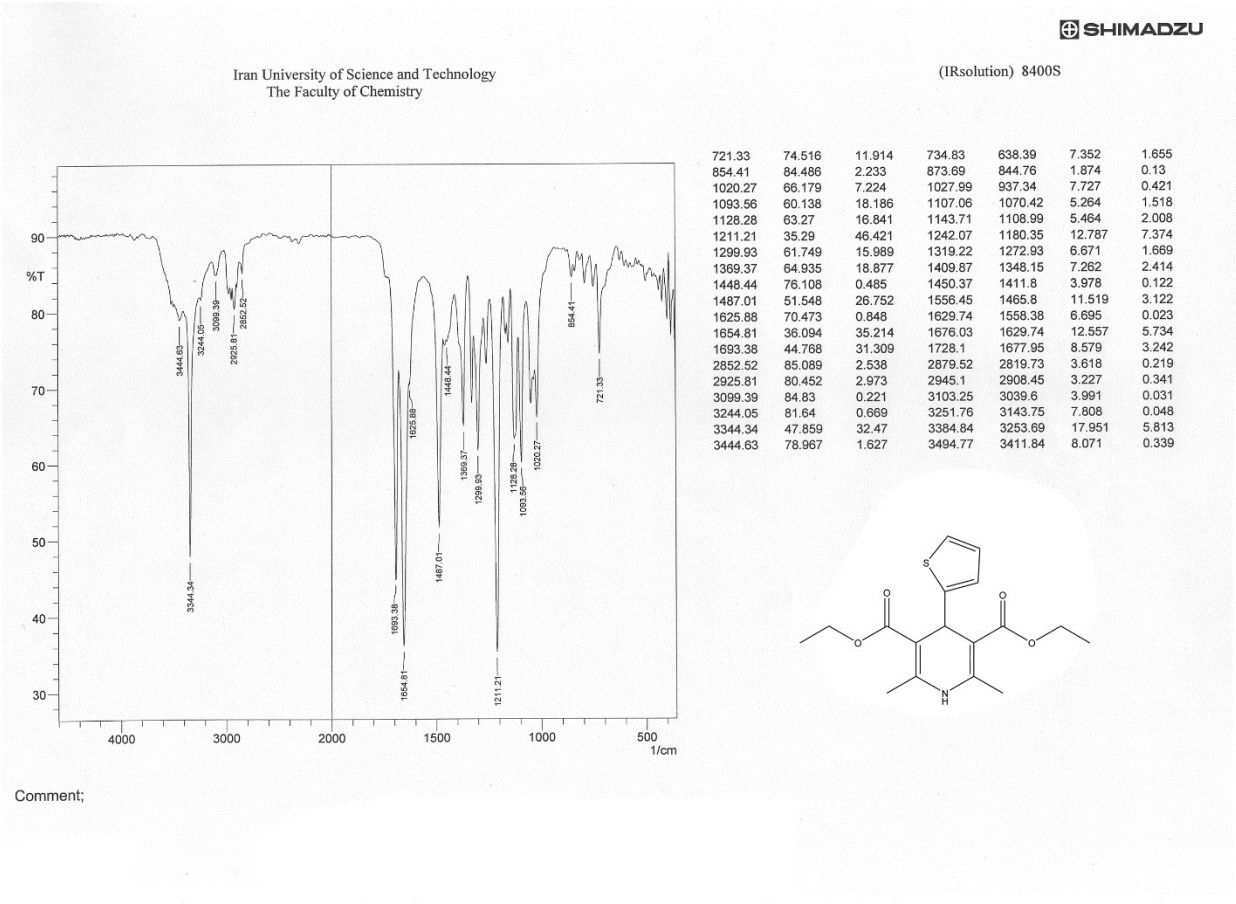
9	Benzaldehyde **2i**	 **6i**	40	95	193-194	197-198
10	4-Methylbenzaldehyde **2j**	 **6j**	55	93	175-177	173-175
11	4-Methoxybenzaldehyde **2k**	 **6k**	70	92	188-191	186-188
12	4-Hydroxybenzaldehyde **2l**	 **6l**	80	90	230-232	230-232
13	4-Hydroxy-3-methoxybenzaldehyde (Vanilin) **2m**	 **6m**	80	91	210-213	213
14	Furfural **2n**	 **6n**	50	92	191-193	192-194
15	Thiophen-2-carbaldehyde **2o**	 **6o**	60	97	200-201	201-203
16	Cinnamaldehyde **2p**	 **6p**	50	93	174-175	176-178

[a] Reaction conditions: Aldehyde (**2a,** 1 mmol), methyl acetoacetate (**3b**, 2 mmol), ammonium acetate (**4a**, 1.2 mmol). [b] All the products are known compounds and were identified by comparison of their TLC, physical and spectral (IR, ^{1}H NMR) data with those of authentic samples. [c] Isolated yields.

References: (a) S. Ghosh, F. Saikh, J. Das, A. K. Pramanik, *Tetrahedron Lett*. **2013**, *54*, 58–62; (b) B. S. Furniss, A. J. Hannaford, P. W. G. Smith, Text book of Practical Organic Chemistry, 5th ed.; Singapore: Longman Singapore, 1994. p. 1168; (c) J. Jacques, V. Eynde, F. Delfaese, A. Mayence, Y. V. Haverbeke, *Tetrahedron* **1995**, *51*, 651l–6516; (d) B. Leov, K. M. Snader, *J. Org. Chem*. **1965**, *30*, 1914–1916; (e) B. Leov, K. M. S. Lakshmi, *Bioorg. Med. Chem. Lett*. **2012**, *22*, 6016–6023; (f) P. P. Ghosh, P. Mukherjee, A. R. Das, *RSC Adv*. **2013**, *3*, 8220–8226; (g) M. Nasr-Esfahani, S. J. Hoseini, M. Montazerozohori, R. Mehrabi, H. Nasrabadi, *J. Mol. Catal. A: Chem*. **2014**, *382*, 99–105; (h) A. Debache, W. Ghalem, R. Boulcina, A. Belfaitah, S. Rhouatiand, B. Carboni, *Tetrahedron Lett*. **2009**, *50*, 5248–5250; (i) S. Patil, P. B. Pawar, S. D. Jadhav, M. B. Deshmukh, *Asian J. Chem*. **2013**, *25*, 9442–9446; (j) A. Shaabani, A. H. Rezayanand, A. Rahmati, M. Sharifi, *Monatsh. Chem*. **2006**, *137*, 77–81; (k) P. Kaur, H. Sharma, R. Rana, D.N. Prasad, R. K. Singh, *Asian J. Chem*. **2012**, *24*, 5649–5651; (l) R. H. Boecker, F. P. Guengerich. *J. Med. Chem*. **1986**, *29*, 1596–1603; (m) J. L. Wang, B. K. Liu, C. Yin, Q. Wu, X. F. Lin, *Tetrahedron* **2011**, *67*, 2689–2692; (n) B. M. Khadilkar, V. G Gaikar, A. A. Chitnavis, *Tetrahedron Lett*. **1995**, *36*, 8083–8086; (o) K. Rajesh, B. P. Reddy, V. Vijayakumar, *Can. J. Chem*. **2011**, *89*, 1236-1244; (p) H. Salehi, Q. X. Guo, *Synthetic Commun*. **2004**, *34*, 4349–4357.

Chemical characterization of diethyl 1,4-dihydro-2,6-dimethyl-4-(thiophen-2-yl)pyridine-3,5-dicarboxylate (5o)

Yellowish white crystals, mp 167–169 °C, yield: 98%, IR (KBr) cm^{-1}: 3344, 3099, 2925, 2853, 1693, 1655, 1487, 1369, 1300, 1211, 1128, 1093, 854, 721, ^1H NMR (250 MHz, $CDCl_3$): δ (ppm): 1.29 (t, *J* =7.1 Hz, 6H), 2.36 (s, 6H), 4.20 (m, 4H), 5.36 (s, 1H, C–$H_{benzylic}$), 5.77 (brs, 1H, N–H), 6.81–6.82 (d, *J* =3.5 Hz, 1H), 6.85–6.88 (t, *J* =5.0 Hz, 1H), 7.06–7.08 (dd, *J* =5.0 Hz, *J* =1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 15.9, 20.4, 32.8, 61.2, 101.3, 105.1, 111.6, 141.0, 145.9, 159.4, 166.6.



721.33	74.516	11.914	734.83	638.39	7.352	1.655
854.41	84.486	2.233	873.69	844.76	1.874	0.13
1020.27	66.179	7.224	1027.99	937.34	7.727	0.421
1093.56	60.138	18.186	1107.06	1070.42	5.264	1.518
1128.28	63.27	16.841	1143.71	1108.99	5.464	2.008
1211.21	35.29	46.421	1242.07	1180.35	12.787	7.374
1299.93	61.749	15.989	1319.22	1272.93	6.671	1.669
1369.37	64.935	18.877	1409.87	1348.15	7.262	2.414
1448.44	76.108	0.485	1450.37	1411.8	3.978	0.122
1487.01	51.548	26.752	1556.45	1465.8	11.519	3.122
1625.88	70.473	0.848	1629.74	1558.38	6.695	0.023
1654.81	36.094	35.214	1676.03	1629.74	12.557	5.734
1693.38	44.768	31.309	1728.1	1677.95	8.579	3.242
2852.52	85.089	2.538	2879.52	2819.73	3.618	0.219
2925.81	80.452	2.973	2945.1	2908.45	3.227	0.341
3099.39	84.83	0.221	3103.25	3039.6	3.991	0.031
3244.05	81.64	0.669	3251.76	3143.75	7.808	0.048
3344.34	47.859	32.47	3384.84	3253.69	17.951	5.813
3444.63	78.967	1.627	3494.77	3411.84	8.071	0.339

Fig. 10. FTIR spectrum of diethyl 1,4-dihydro-2,6-dimethyl-4-(thiophen-2-yl)pyridine-3,5-dicarboxylate (**5o**).

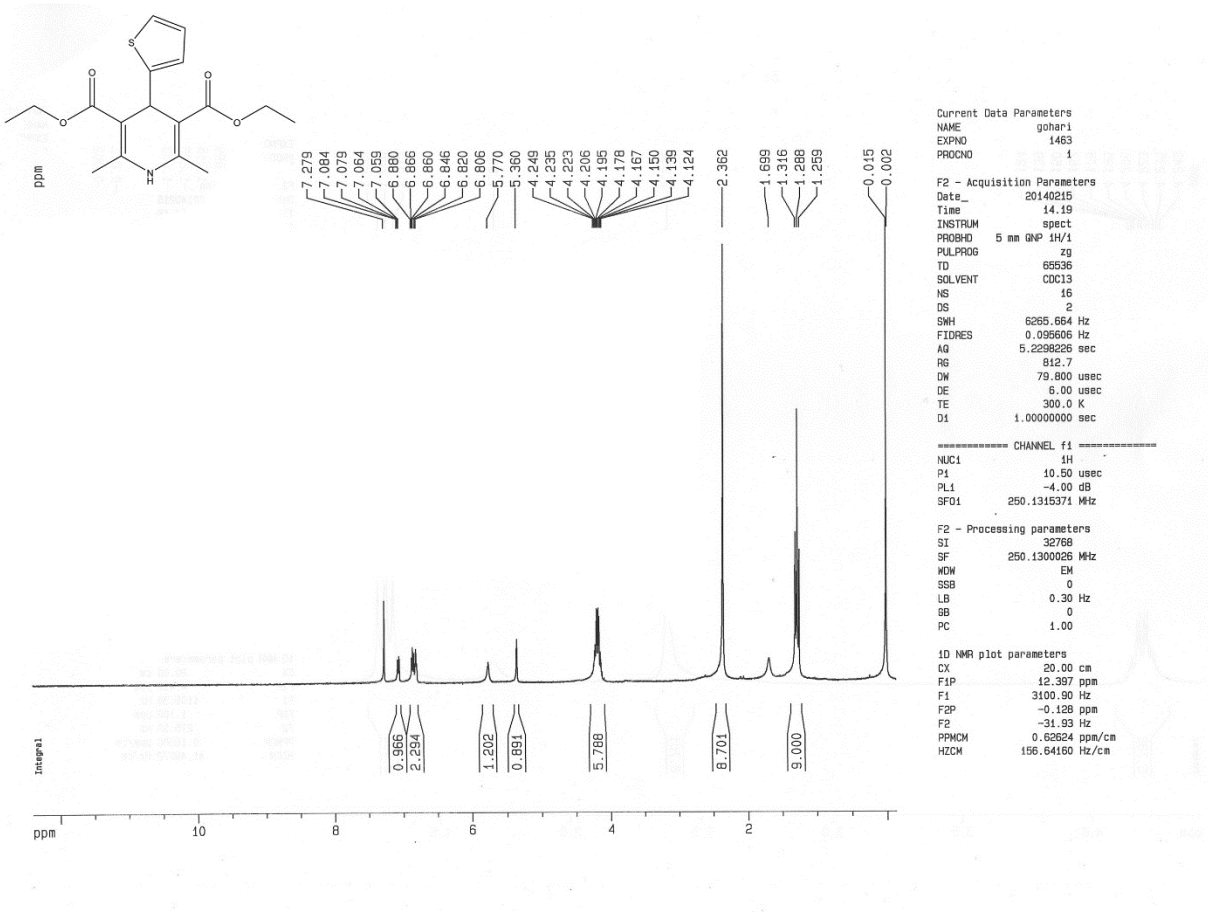


Fig. 11. ^{1}H NMR spectrum of diethyl 1,4-dihydro-2,6-dimethyl-4-(thiophen-2-yl)pyridine-3,5-dicarboxylate (**5o**) in $CDCl_3$.

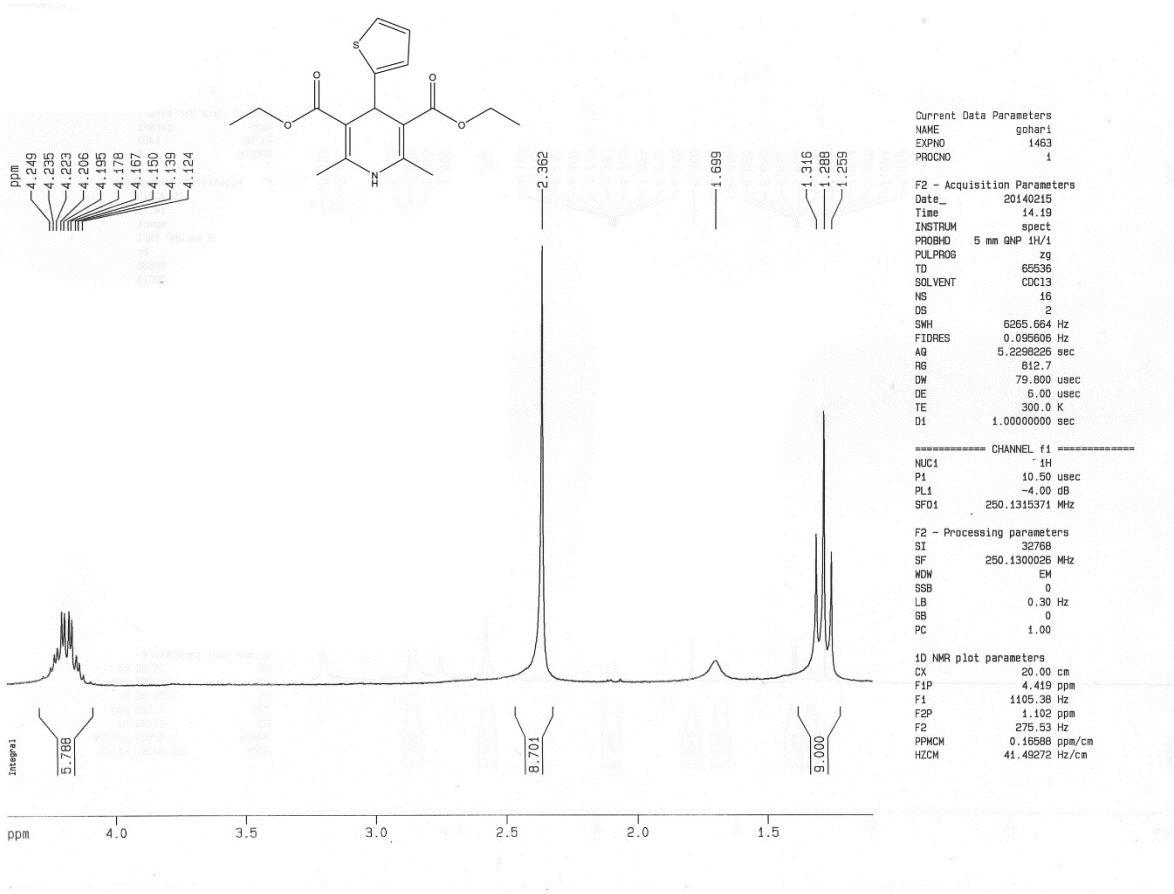


Fig. 12. ^{1}H NMR spectrum of diethyl 1,4-dihydro-2,6-dimethyl-4-(thiophen-2-yl)pyridine-3,5-dicarboxylate (**5o**) in $CDCl_3$ (Expanded aliphatic region).

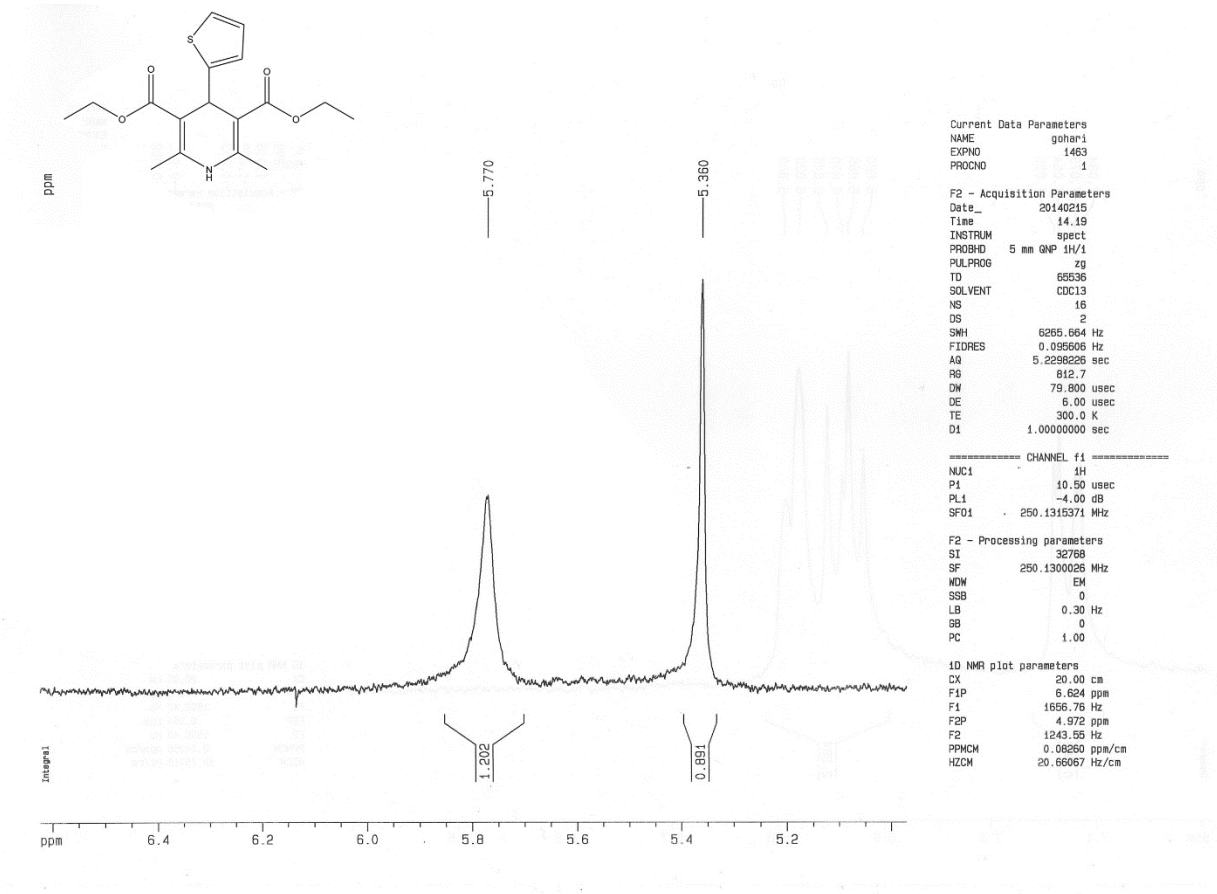


Fig. 13. ^{1}H NMR spectrum of diethyl 1,4-dihydro-2,6-dimethyl-4-(thiophen-2-yl)pyridine-3,5-dicarboxylate (**5o**) in $CDCl_3$ (Expanded aliphatic region).

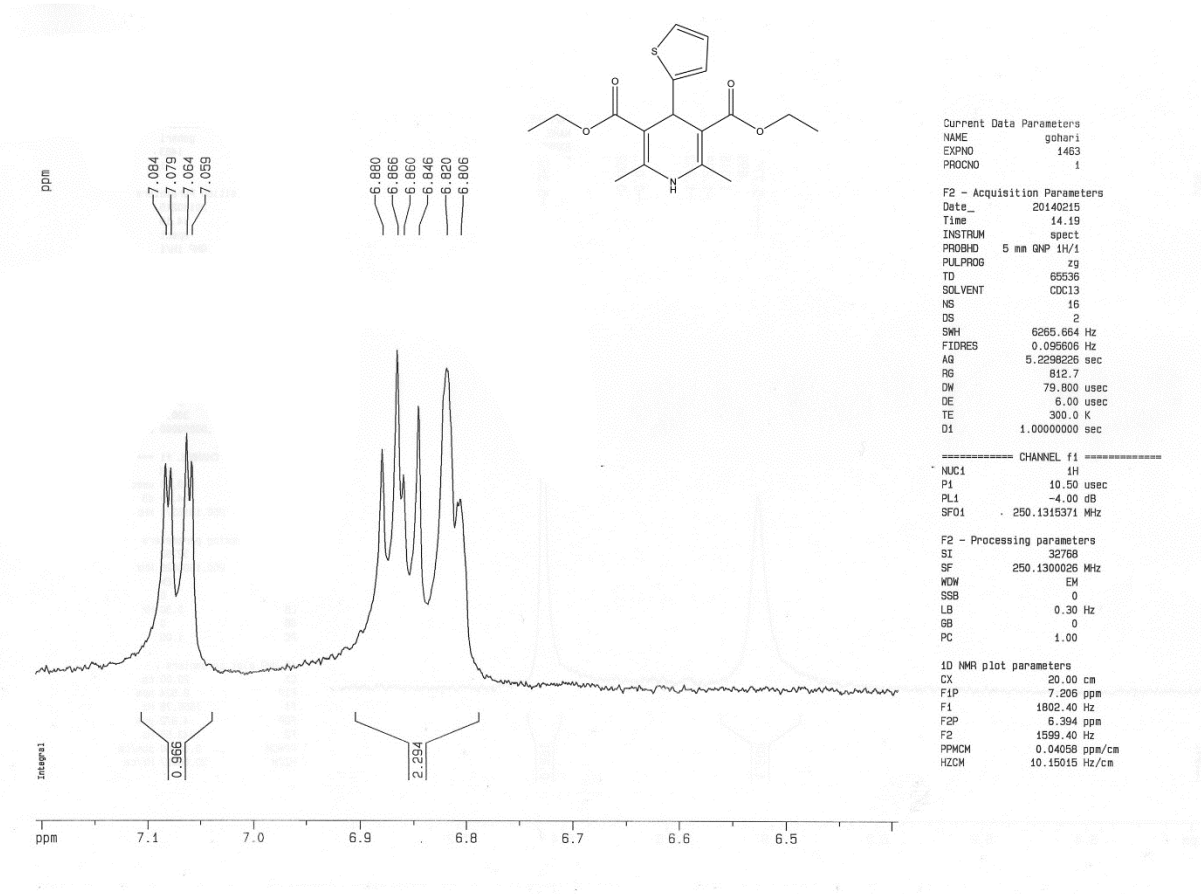
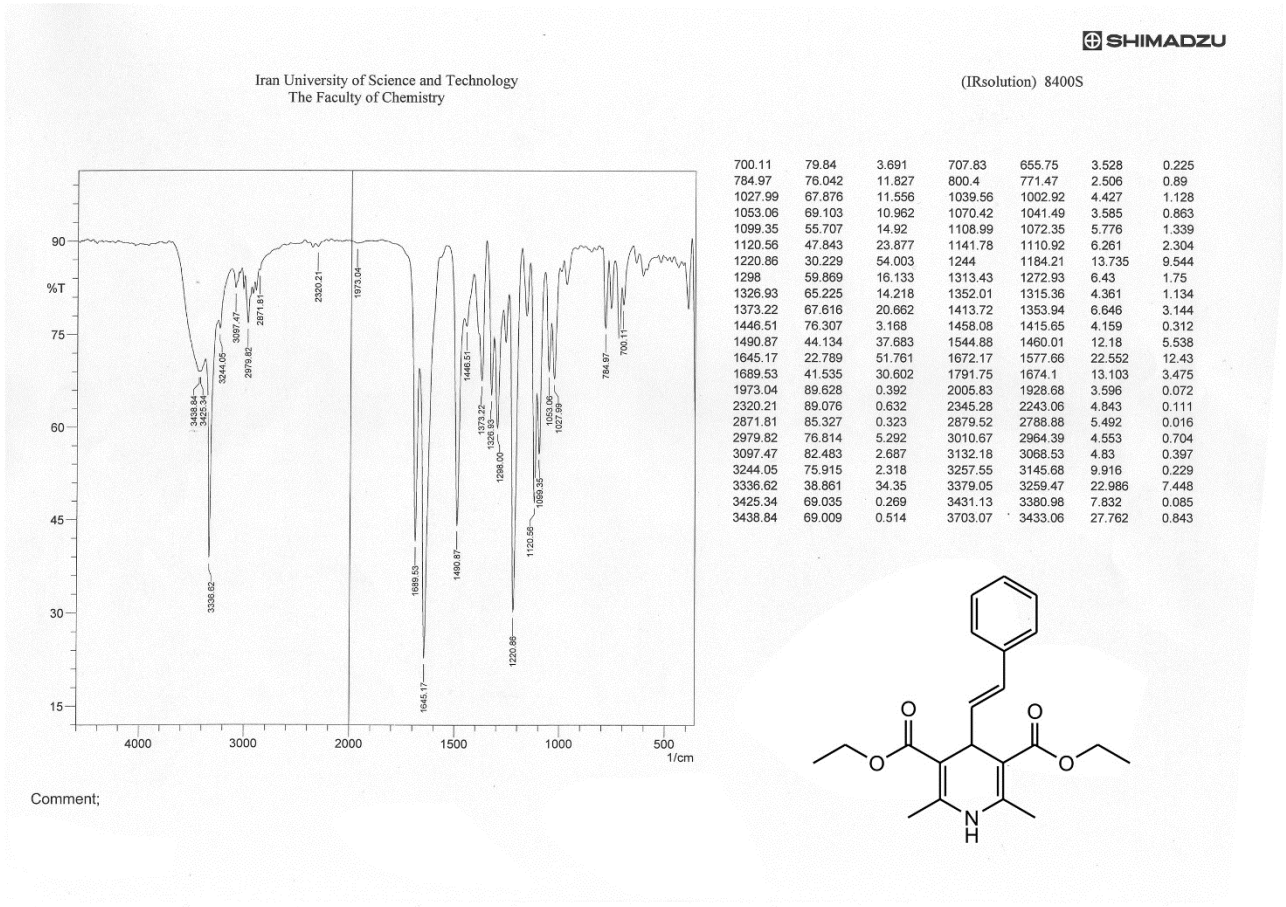


Fig. 14. ^{1}H NMR spectrum of diethyl 1,4-dihydro-2,6-dimethyl-4-(thiophen-2-yl)pyridine-3,5-dicarboxylate (**5o**) in $CDCl_3$ (Expanded aromatic region).

Chemical characterization of diethyl 2,6-dimethyl-4-styrylpyridine-1,4-dihydro-3,5-dicarboxylate (5p)

Yellow crystals, mp 145−147 °C, yield: 94%, IR (KBr) cm^{-1}: 3432, 3336, 3244, 3097, 2980, 2320, 1690, 1645, 1491, 1446, 1373, 1327, 1298, 1220, 1120, 749, ^1H NMR (250 MHz, $CDCl_3$) δ (ppm): 1.31 (t, J =7.0 Hz, 6H), 2.35 (s, 6H), 4.20 (m, 4H), 4.64 (d, J =6.0 Hz, 1H, C–$H_{benzylic}$), 5.62 (brs, 1H, N–H), 6.16- 6.29 (m, 2H), 7.14–7.36 (m, 5H), ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 14.5, 19.2, 37.1, 58.1, 102.6, 119.3, 120.2, 127.5, 128.8, 130.9, 133.0, 136.4, 147.7, 169.2.



700.11	79.84	3.691	707.83	655.75	3.528	0.225
784.97	76.042	11.827	800.4	771.47	2.506	0.89
1027.99	67.876	11.556	1039.56	1002.92	4.427	1.128
1053.06	69.103	10.962	1070.42	1041.49	3.585	0.863
1099.35	55.707	14.92	1108.99	1072.35	5.776	1.339
1120.56	47.843	23.877	1141.78	1110.92	6.261	2.304
1220.86	30.229	54.003	1244	1184.21	13.735	9.544
1298	59.869	16.133	1313.43	1272.93	6.43	1.75
1326.93	65.225	14.218	1352.01	1315.36	4.361	1.134
1373.22	67.616	20.662	1413.72	1353.94	6.646	3.144
1446.51	76.307	3.168	1458.08	1415.65	4.159	0.312
1490.87	44.134	37.683	1544.88	1460.01	12.18	5.538
1645.17	22.789	51.761	1672.17	1577.66	22.552	12.43
1689.53	41.535	30.602	1791.75	1674.1	13.103	3.475
1973.04	89.628	0.392	2005.83	1928.68	3.596	0.072
2320.21	89.076	0.632	2345.28	2243.06	4.843	0.111
2871.81	85.327	0.323	2879.52	2788.88	5.492	0.016
2979.82	76.814	5.292	3010.67	2964.39	4.553	0.704
3097.47	82.483	2.687	3132.18	3068.53	4.83	0.397
3244.05	75.915	2.318	3257.55	3145.68	9.916	0.229
3336.62	38.861	34.35	3379.05	3259.47	22.986	7.448
3425.34	69.035	0.269	3431.13	3380.98	7.832	0.085
3438.84	69.009	0.514	3703.07	3433.06	27.762	0.843

Fig. 15. FT-IR spectrum of diethyl 2,6-dimethyl-4-styrylpyridine-1,4-dihydro-3,5-dicarboxylate (**5p**).

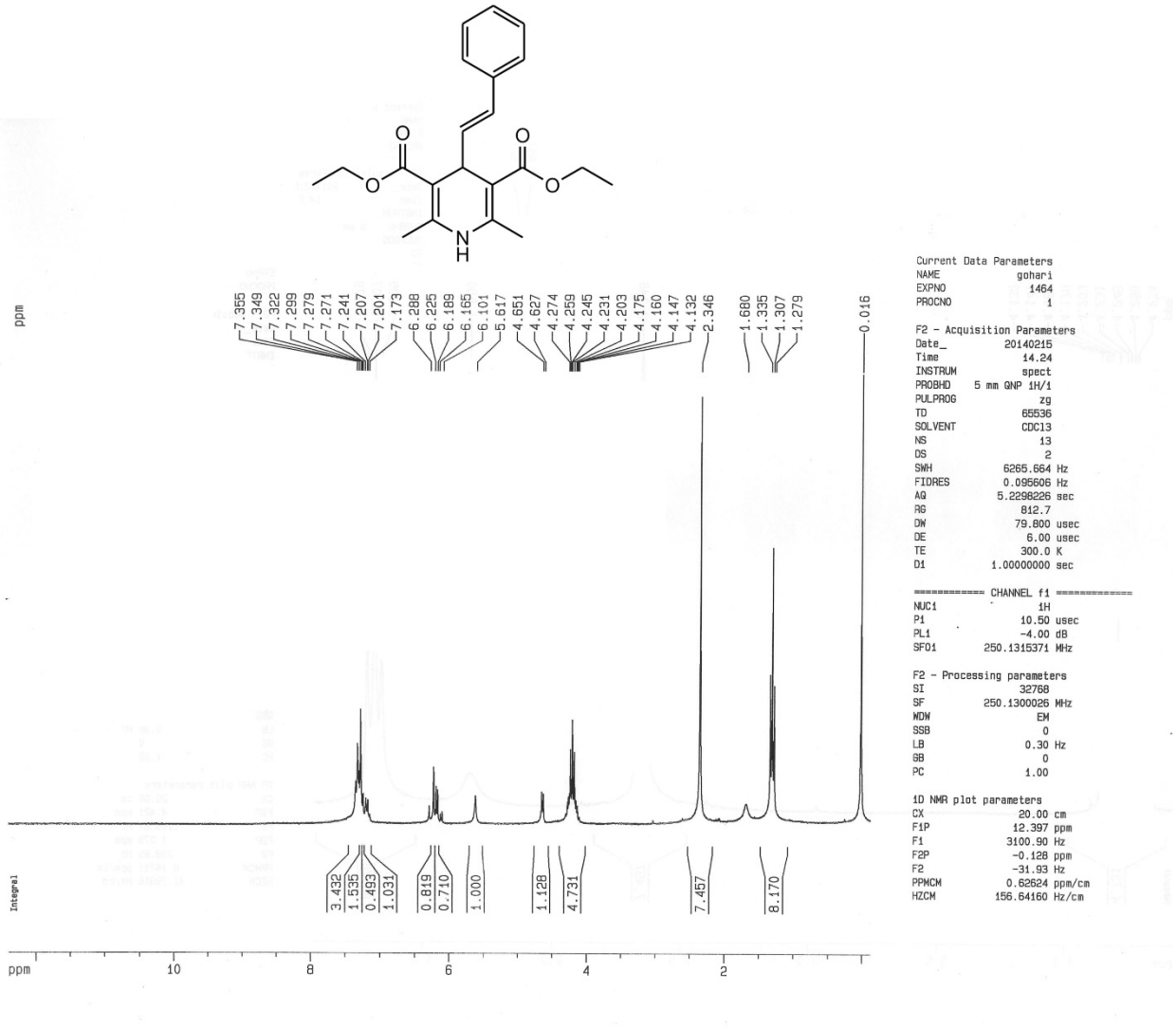


Fig. 16. ^{1}H NMR spectrum of diethyl 2,6-dimethyl-4-styrylpyridine-1,4-dihydro-3,5-dicarboxylate (**5p**) in $CDCl_3$.

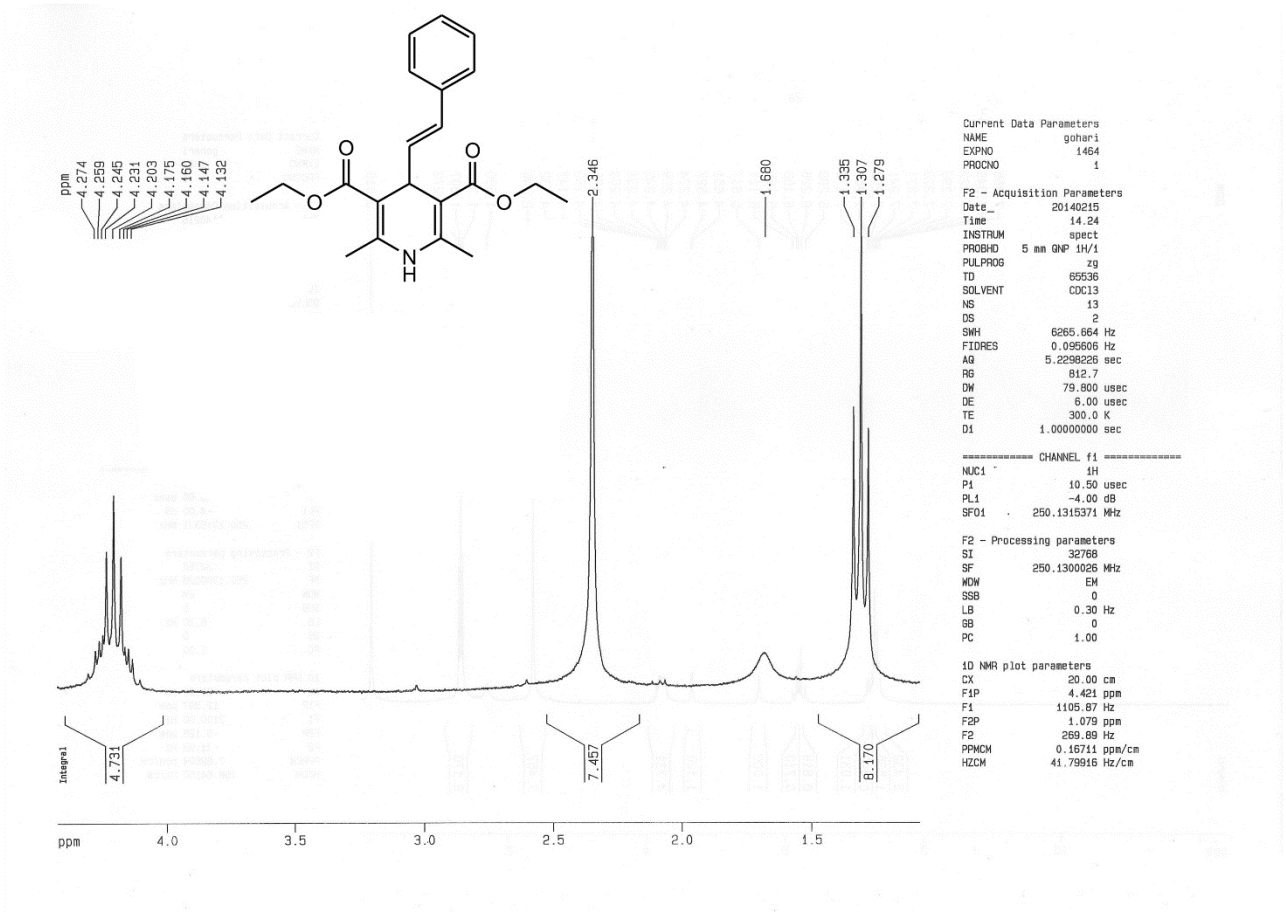


Fig. 17. ^{1}H NMR spectrum of diethyl 2,6-dimethyl-4-styrylpyridine-1,4-dihydro-3,5-dicarboxylate (**5p**) in $CDCl_3$ (Expanded aliphatic region).

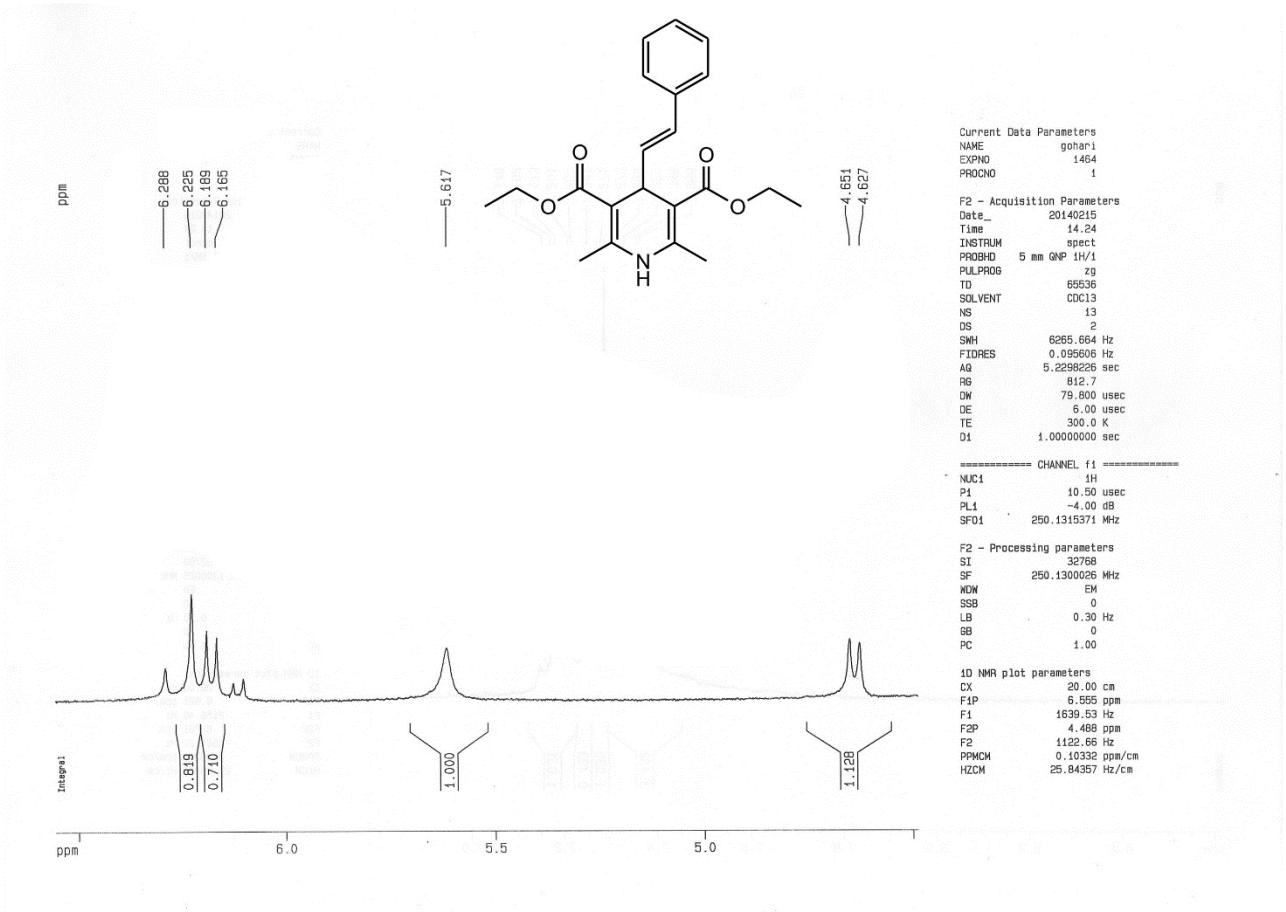


Fig. 18. ^{1}H NMR spectrum of diethyl 2,6-dimethyl-4-styrylpyridine-1,4-dihydro-3,5-dicarboxylate (**5p**) in $CDCl_3$ (Expanded aliphatic region).

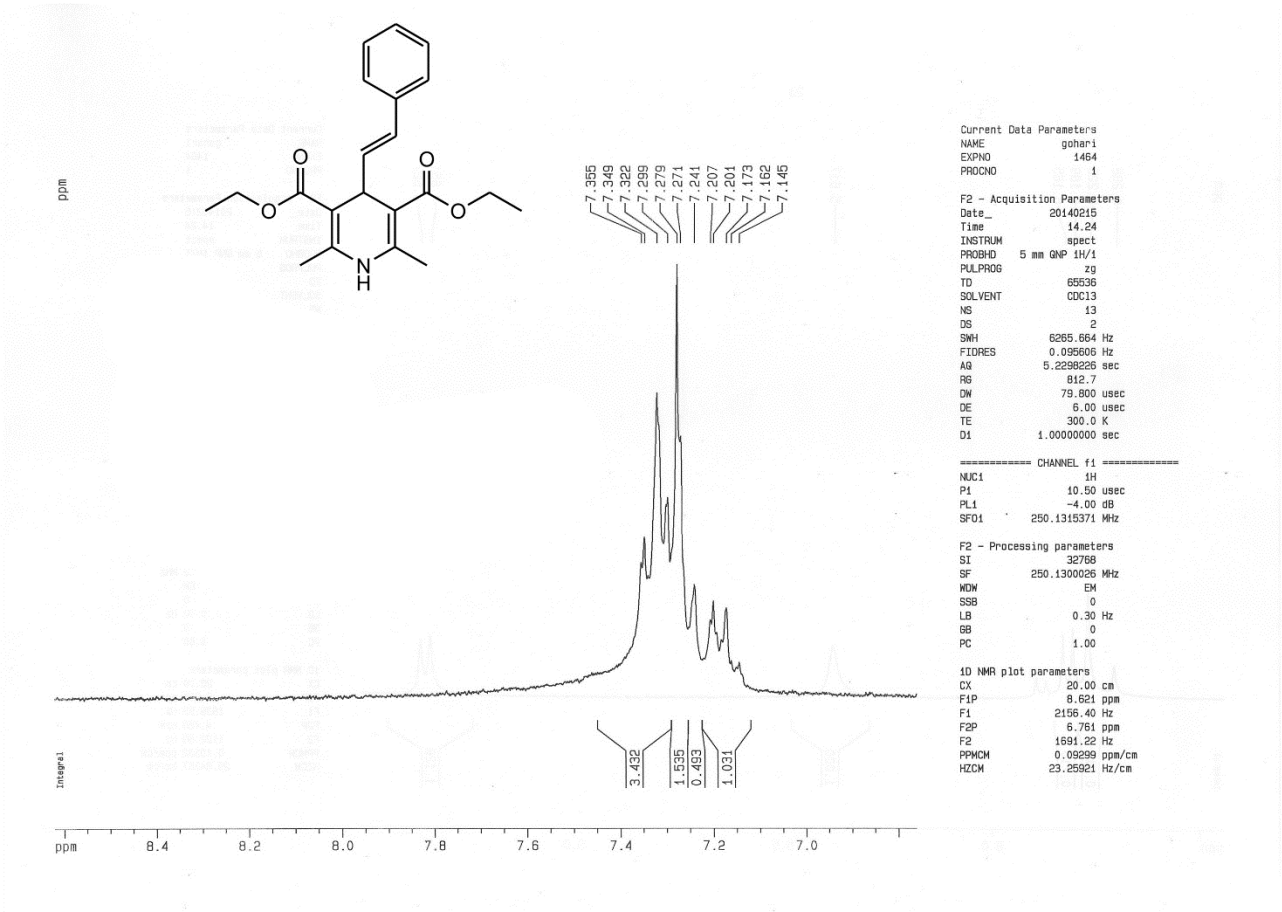
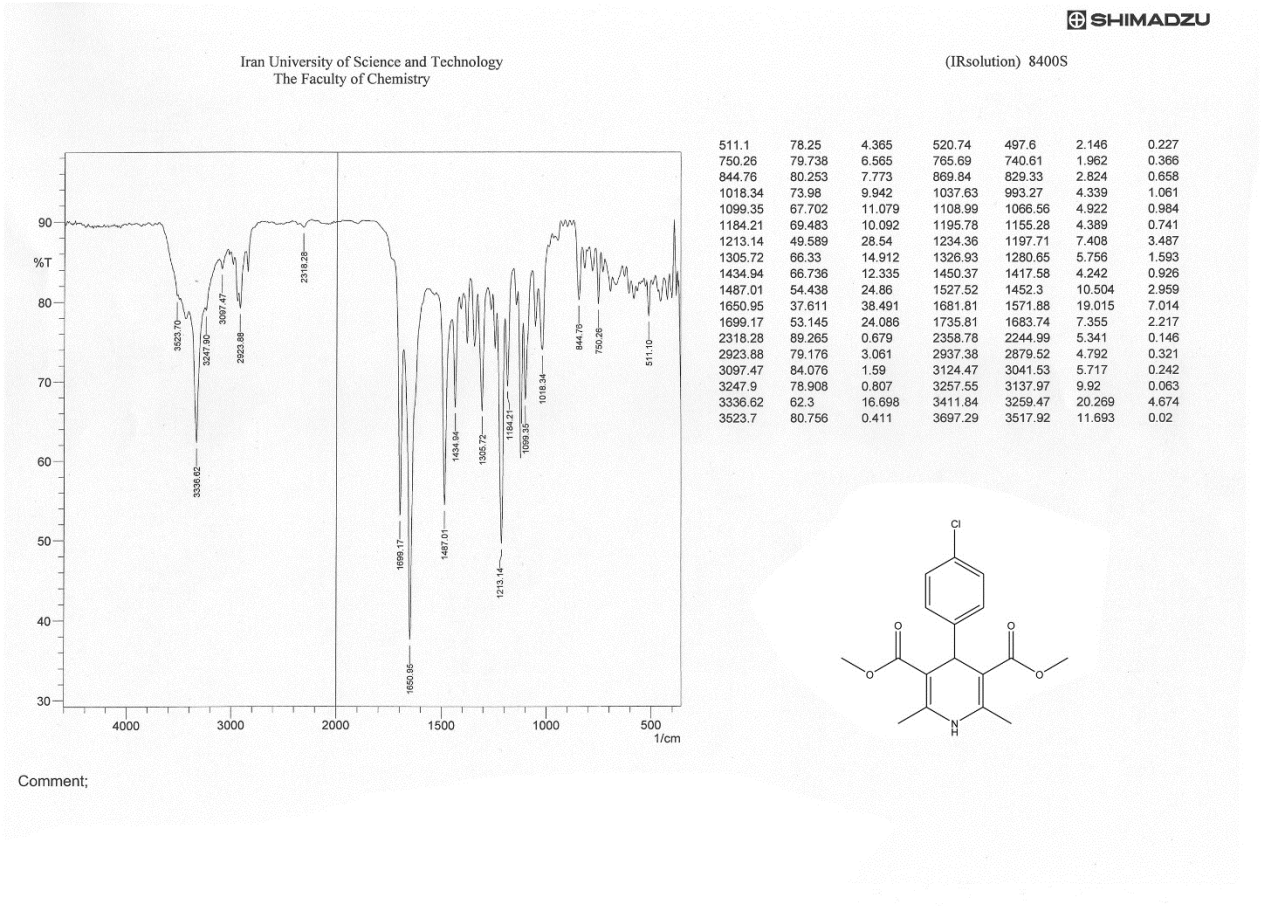


Fig. 19. ^{1}H NMR spectrum of diethyl 2,6-dimethyl-4-styrylpyridine-1,4-dihydro-3,5-dicarboxylate **(5p)** in $CDCl_3$ (Expanded aromatic region)

Chemical characterization of dimethyl 4-(4-chlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (6b)

Yellowish white crystals, mp 160−162 °C, yield: 90%, IR (KBr) cm^{-1}: 3336, 3097, 2923, 1699, 1651, 1487, 1434, 1305, 1213, 1184, 1099, 1018, 845, 750, ^1H NMR (250 MHz, $CDCl_3$): δ (ppm): 2.36 (s, 6H), 3.66 (s, 6H), 4.98 (s, 1H, C–$H_{benzylic}$), 5.63 (brs, 1H, N–H), 7.20–7.24 (d, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 20.1, 31.4, 39.9, 114.5, 127.7, 129.2, 131.1, 144.9, 195.1.



511.1	78.25	4.365	520.74	497.6	2.146	0.227
750.26	79.738	6.565	765.69	740.61	1.962	0.366
844.76	80.253	7.773	869.84	829.33	2.824	0.658
1018.34	73.98	9.942	1037.63	993.27	4.339	1.061
1099.35	67.702	11.079	1108.99	1066.56	4.922	0.984
1184.21	69.483	10.092	1195.78	1155.28	4.389	0.741
1213.14	49.589	28.54	1234.36	1197.71	7.408	3.487
1305.72	66.33	14.912	1326.93	1280.65	5.756	1.593
1434.94	66.736	12.335	1450.37	1417.58	4.242	0.926
1487.01	54.438	24.86	1527.52	1452.3	10.504	2.959
1650.95	37.611	38.491	1681.81	1571.88	19.015	7.014
1699.17	53.145	24.086	1735.81	1683.74	7.355	2.217
2318.28	89.265	0.679	2358.78	2244.99	5.341	0.146
2923.88	79.176	3.061	2937.38	2879.52	4.792	0.321
3097.47	84.076	1.59	3124.47	3041.53	5.717	0.242
3247.9	78.908	0.807	3257.55	3137.97	9.92	0.063
3336.62	62.3	16.698	3411.84	3259.47	20.269	4.674
3523.7	80.756	0.411	3697.29	3517.92	11.693	0.02

Fig. 20. FTIR spectrum of dimethyl 4-(4-chlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**6b**).

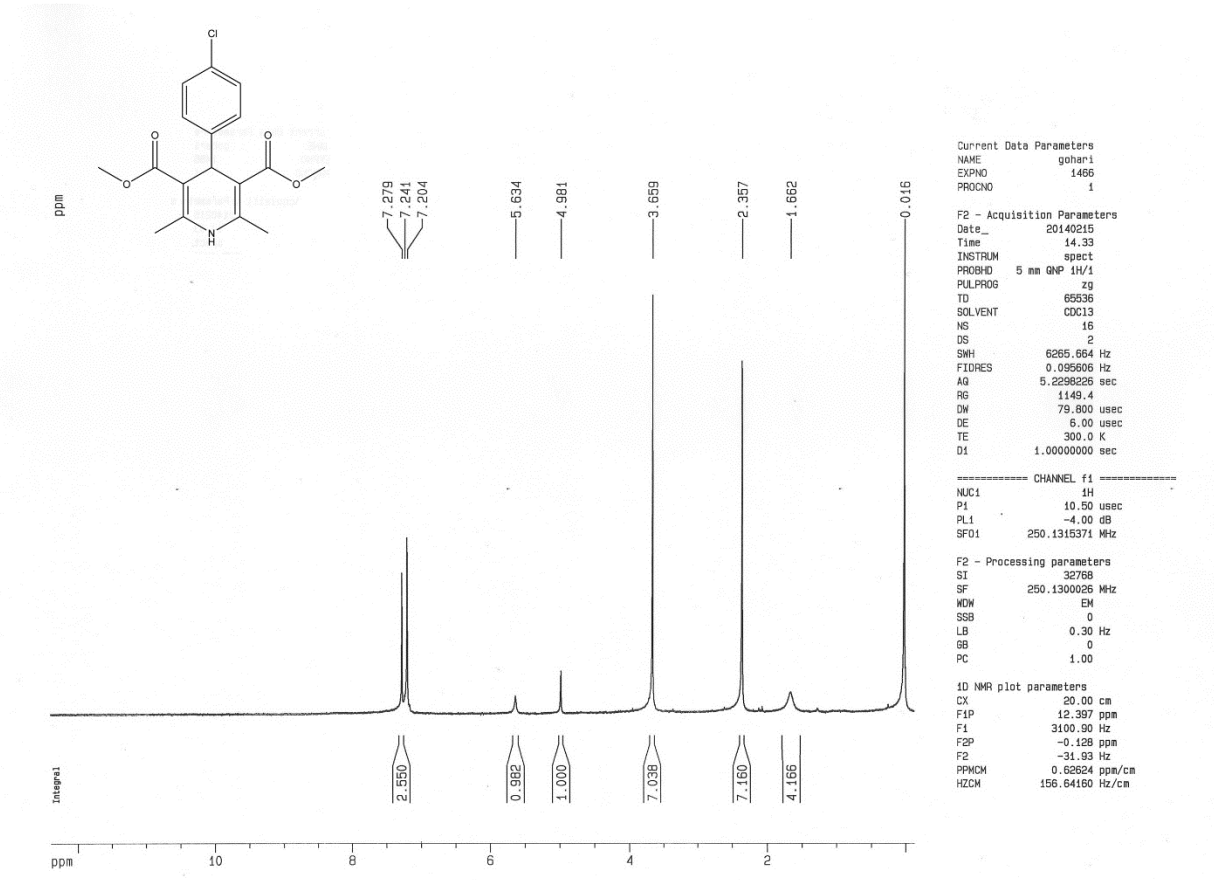


Fig. 21. ^{1}H NMR spectrum of dimethyl 4-(4-chlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**6b**) in $CDCl_3$.

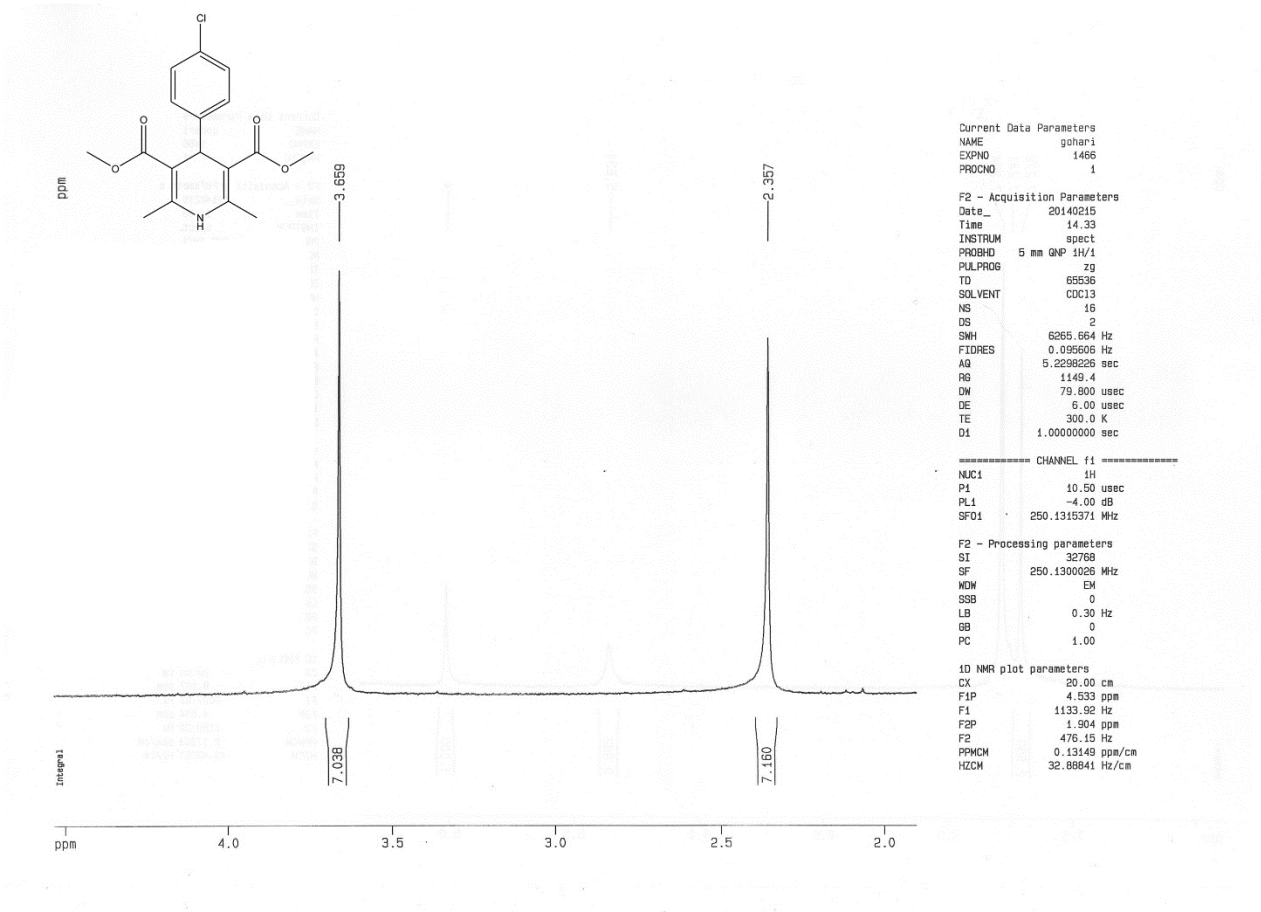


Fig. 22. ^{1}H NMR spectrum of dimethyl 4-(4-chlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**6b**) in $CDCl_3$ (Expanded aliphatic region).

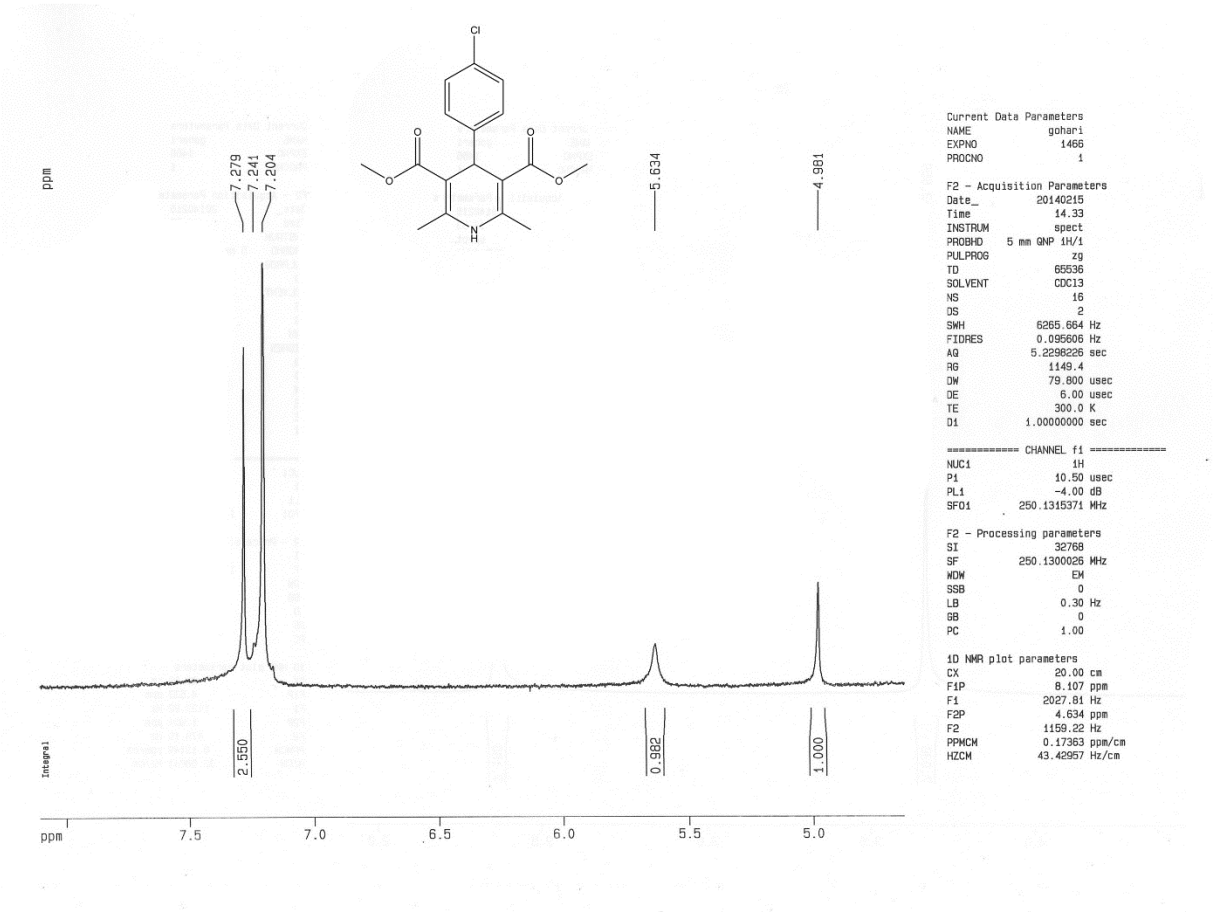


Fig. 23. ^{1}H NMR spectrum of dimethyl 4-(4-chlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**6b**) in $CDCl_3$ (Expanded aromatic region).