Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Cu/Al(O)OH-Catalyzed Formation of β-Enamino Ketones / Esters Under Solvent, Ligand and Base Free Conditions – Experimental and Computational Studies

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Supporting Infomations

Catalyst Characterization:

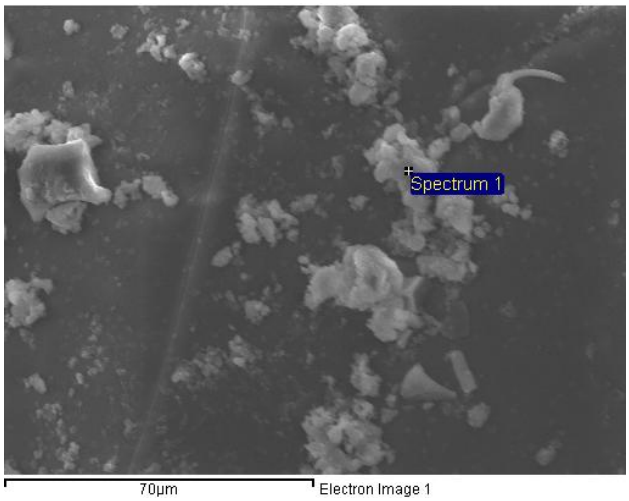

Fig. S1 SEM image of Cu/AlO(OH).

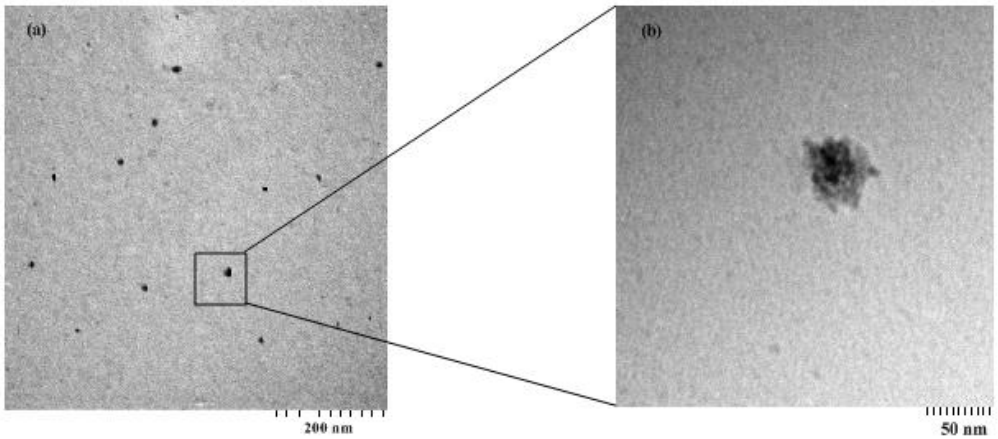

Fig. S2 HR-TEM Image: (a) low resolution (20 nm bar scale), (b) high resolution (5 nm bar scale).

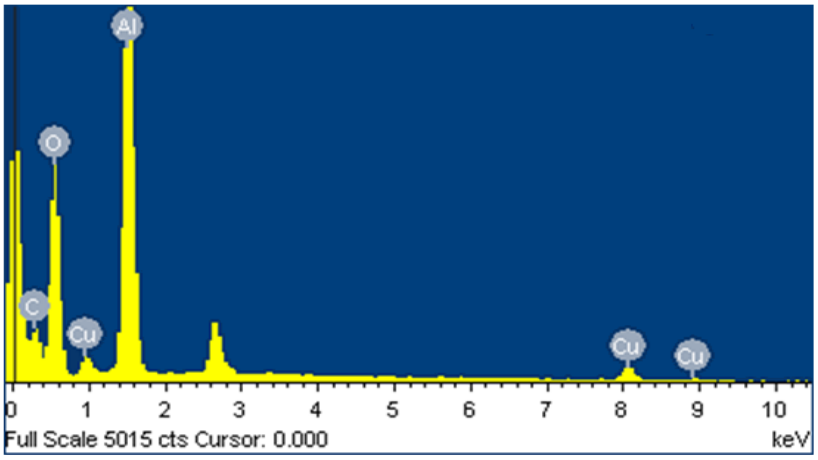

Fig. S3 SEM-EDX result of Cu/AlO(OH).

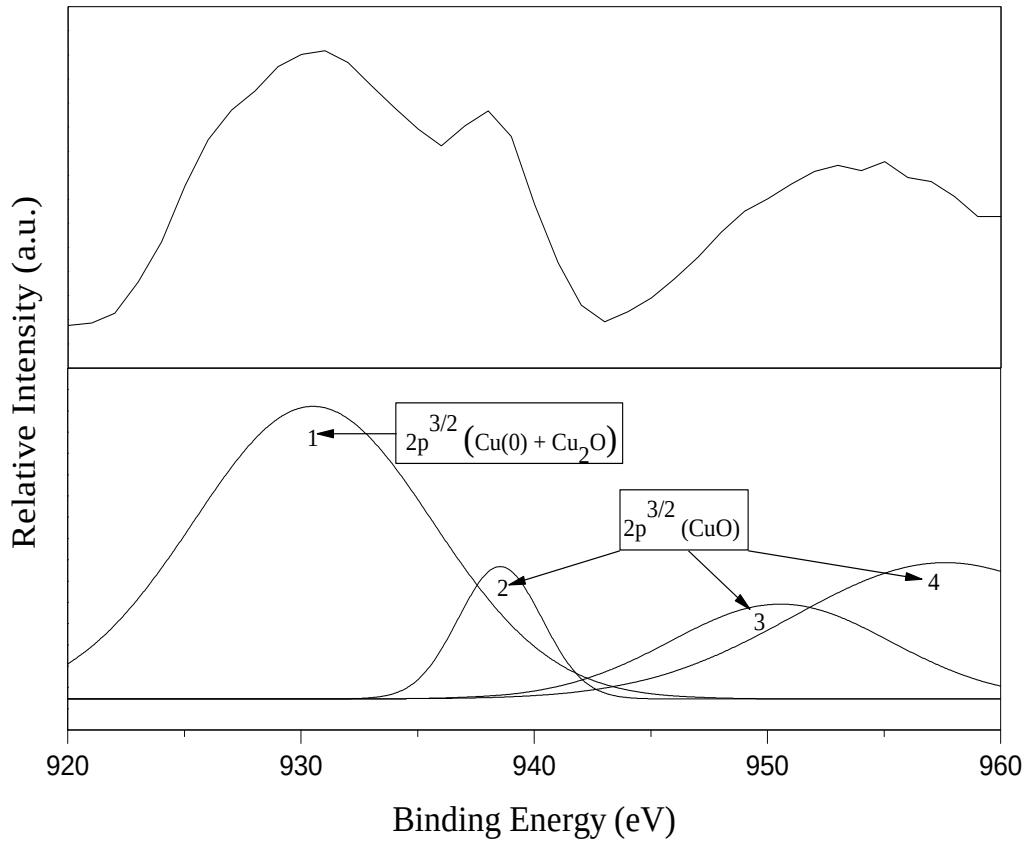

Fig. S4 XPS spectrum of Cu/AlO(OH).

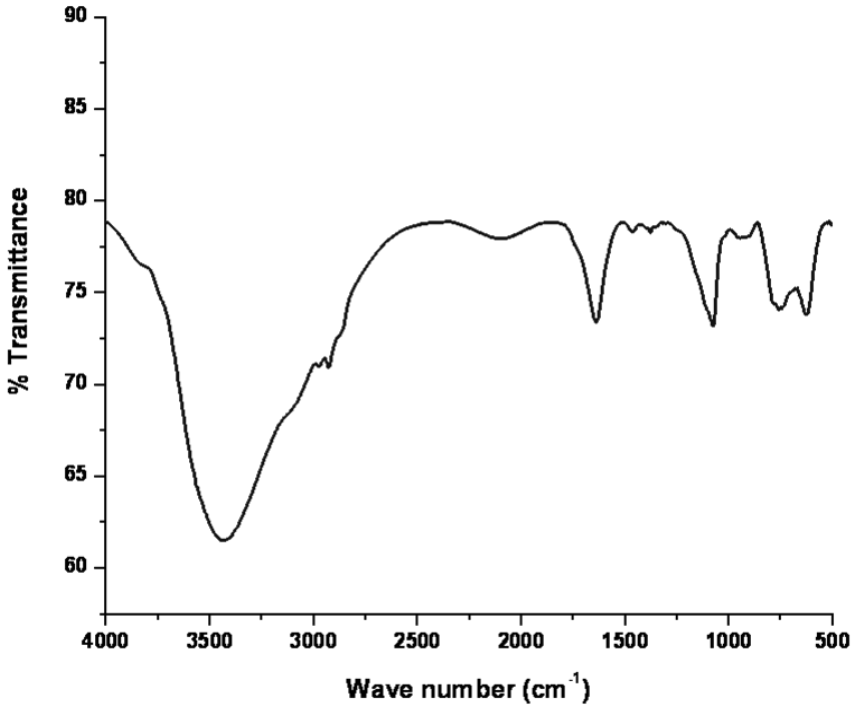

Fig. S5 FT-IR Spectrum of Cu/AlO(OH).

Peak at 3400 cm^{-1} corresponds to OH stretching frequency. The peak at 1075 cm^{-1} has been assigned as due to Al=O stretching frequency. The other peaks at 1644 cm^{-1}, 1111 cm^{-1}, 624 cm^{-1} and 516 cm^{-1} correspond to Al-O stretching and bending frequencies.

GC Conditions:

GC (Shimadzu-2010) is equipped with 5% diphenyl and 95% dimethyl siloxane, Restek capillary column (60 m length, 0.32 mm dia) and a flame ionization detector (FID). The column temperature was 220°C. The temperatures of the injection port and FID were kept constant at 250°C and 280°C, respectively during product analysis.

GC DATA

1. Condensation of acetyl acetone and aniline (Table 2, entry 1)

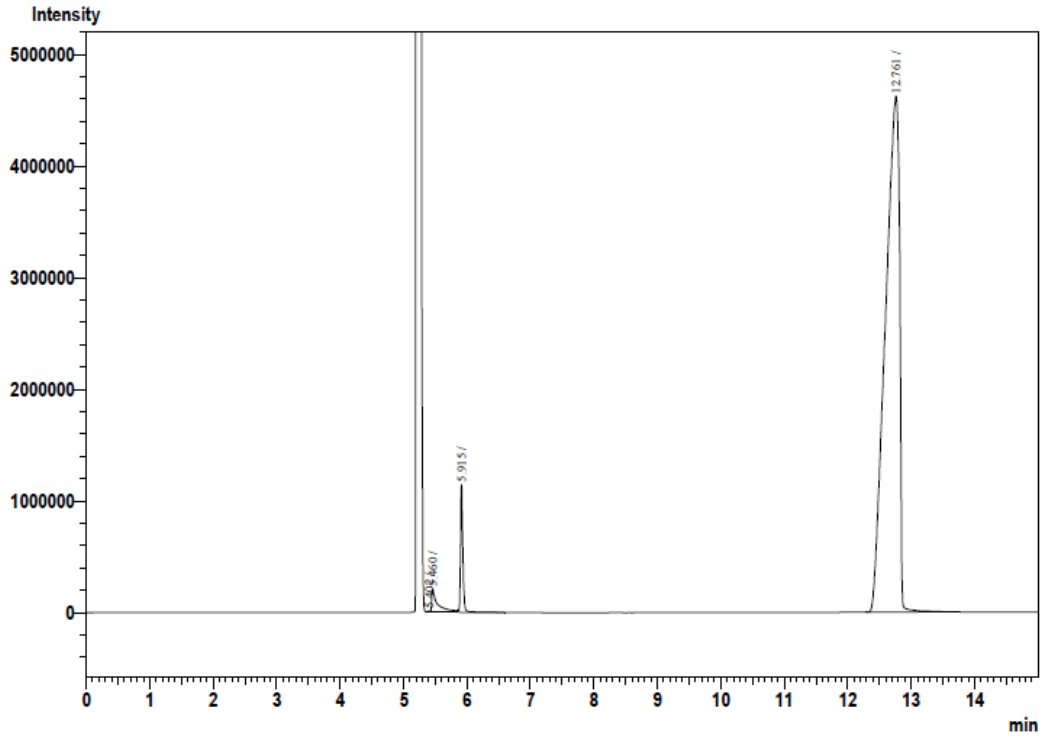

Fig. S6 GC data for condensation of acetyl acetone and aniline

GC data for condensation of acetyl acetone and aniline

Peak#	Ret.Time	Area	Height	Area%
1	5.402	21255	11289	0.0279
2	5.460	1404185	204179	1.8457
3	5.915	2936351	1138087	3.8597
4	12.761	71716132	4622075	94.2667
Total		76077923	5975630	100.0000

2. Condensation of ethyl acetoacetate and aniline (Table 2, entry 2)

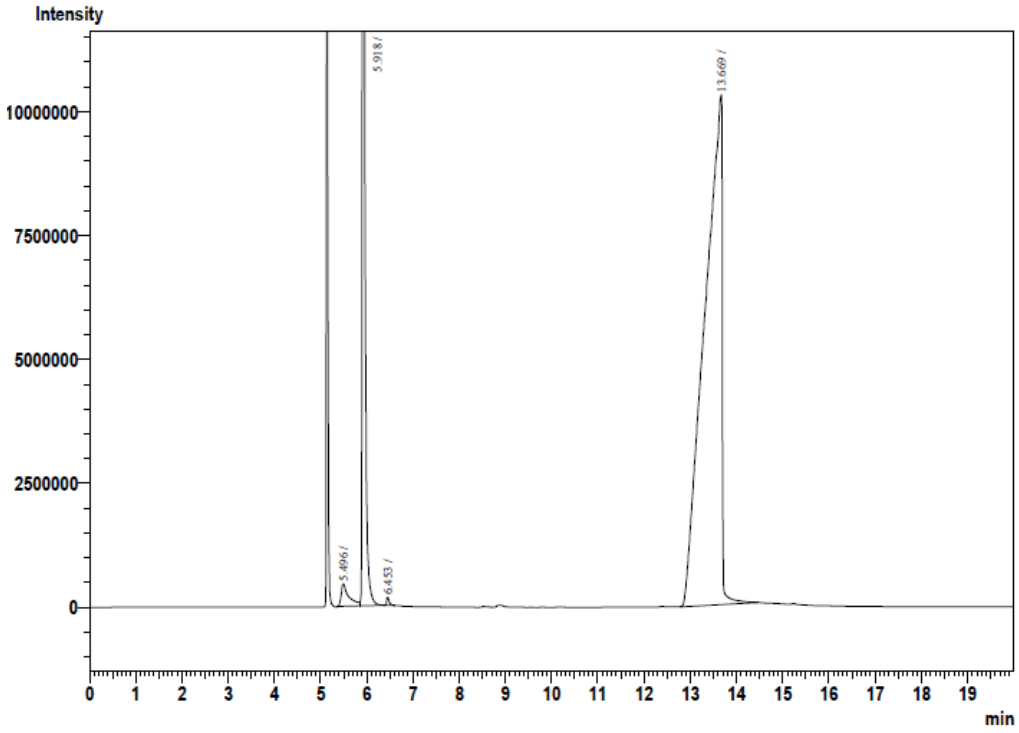

Fig. S7 GC DATA for Condensation of ethylacetoacetate and aniline

GC data for Condensation of ethylacetoacetate and aniline

Peak#	Ret.Time	Area	Height	Area%
1	5.496	5126790	449602	1.3939
2	5.918	92142417	25779115	25.0515
3	6.453	616068	160379	0.1675
4	13.669	269926771	10282438	73.3871
Total		367812046	36671534	100.0000

3. Condensation of trifluoroacetylacetate and aniline (Table 2, entry 3)

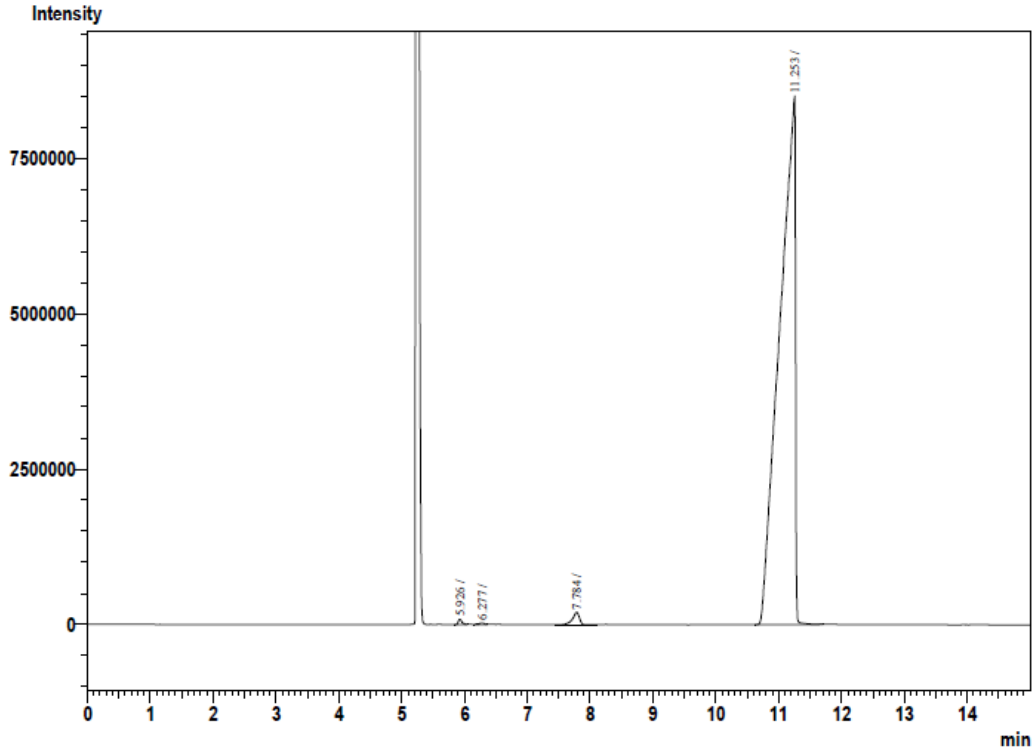

Fig. S8 GC DATA for Condensation of trifluoroacetylacetate and aniline

GC data for Condensation of trifluoroacetylacetate and aniline

Peak#	Ret.Time	Area	Height	Area%
1	5.926	334221	82503	0.2248
2	6.277	141336	25258	0.0951
3	7.784	1530359	200271	1.0293
4	11.253	146680722	8495269	98.6509
Total		148686638	8803301	100.0000

4. Condensation of methyl acetoacetate and aniline (Table 2, entry 4)

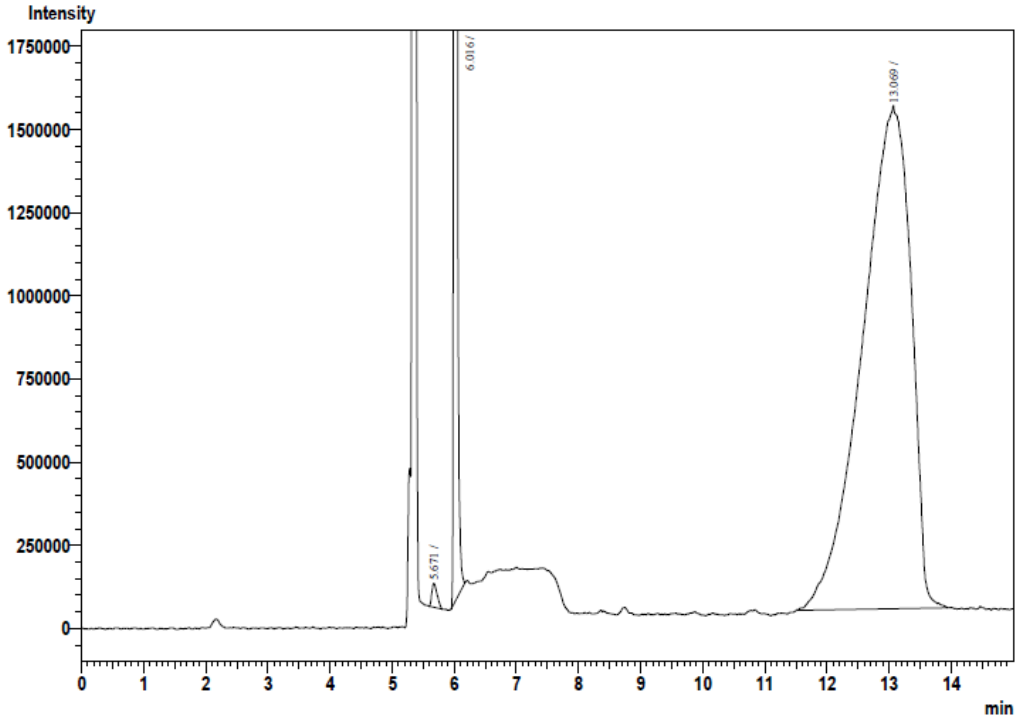

Fig. S9 GC DATA for Condensation of methyl acetoacetate and aniline

GC data for Condensation of methyl acetoacetate and aniline

Peak#	Ret.Time	Area	Height	Area%
1	5.671	422854	71712	0.3982
2	6.016	23708957	7761063	22.3247
3	13.069	82068723	1512746	77.2771
Total		106200534	9345521	100.0000

5. Condensation of acetylacetone and cyclohexylamine (Table 2, entry 5)

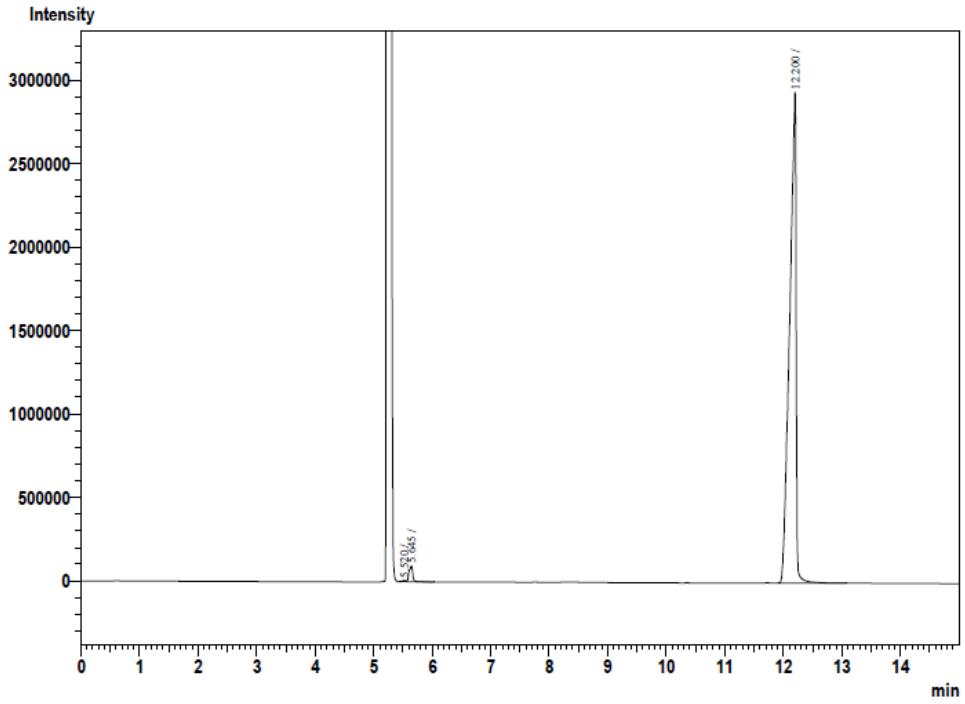

Fig. S10 GC DATA for Condensation of acetylacetone and cyclohexylamine

GC data for Condensation of acetylacetone and cyclohexylamine

Peak#	Ret.Time	Area	Height	Area%
1	5.520	33750	7930	0.1472
2	5.645	417821	95935	1.8219
3	12.200	22481168	2931881	98.0309
Total		22932739	3035746	100.0000

6. Condensation of ethylacetoacetate and cyclohexylamine (Table 2, entry 6)

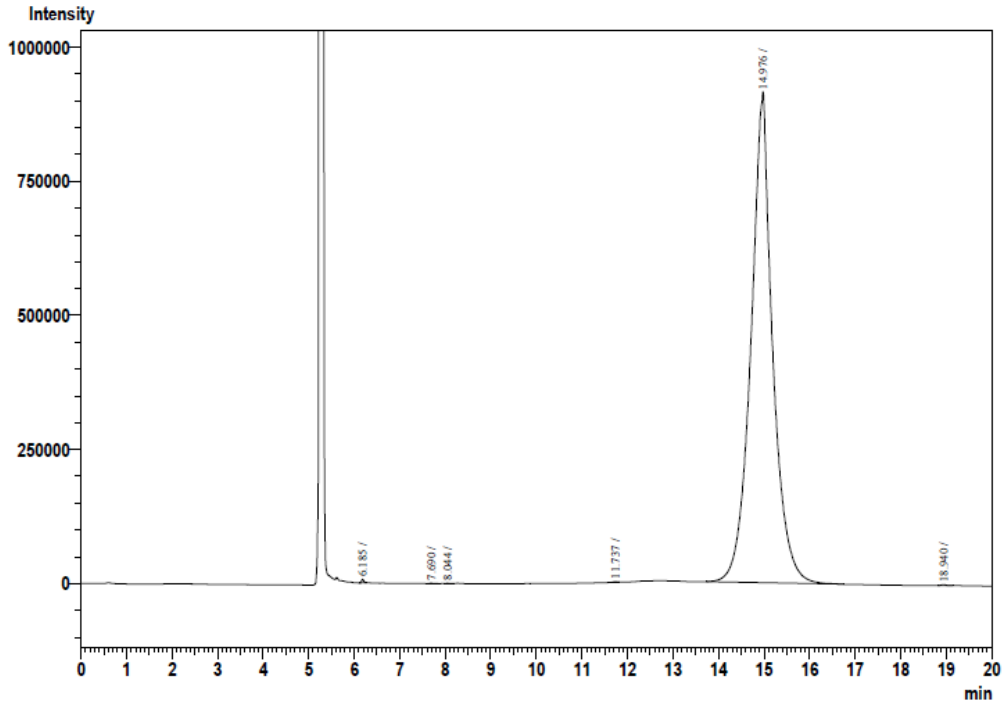

Fig. S11 GC DATA for Condensation of ethylacetoacetate and cyclohexylamine

GC data for Condensation of ethylacetoacetate and cyclohexylamine

Peak#	Ret.Time	Area	Height	Area%
1	6.185	22594	6551	0.0749
2	7.690	7613	1353	0.0252
3	8.044	4828	1045	0.0160
4	11.737	6637	1365	0.0220
5	14.976	30119213	914567	99.8249
6	18.940	11163	1382	0.0370
Total		30172048	926263	100.0000

7. Condensation of trifluroacetylacetate and cyclohexylamine (Table 2, entry 7)

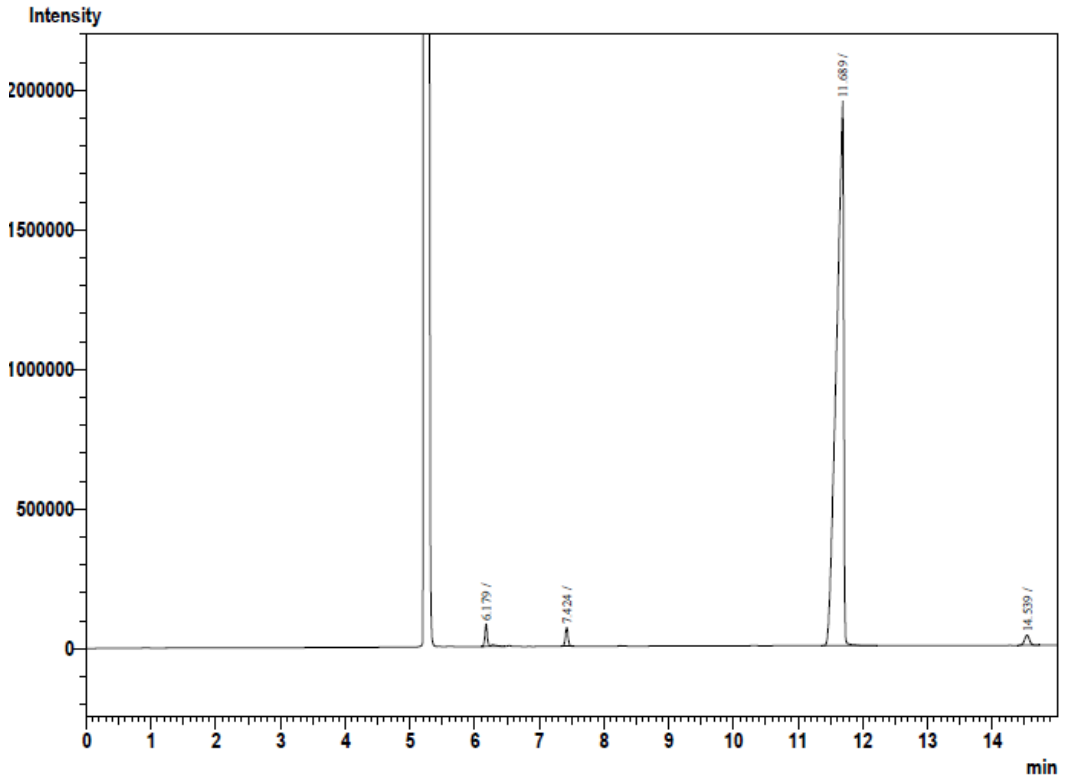

Fig. S12 GC DATA for Condensation of trifluroacetylacetate and cyclohexylamine

GC data for Condensation of trifluroacetylacetate and cyclohexylamine

Peak#	Ret.Time	Area	Height	Area%
1	6.179	232050	79332	1.4921
2	7.424	193411	66905	1.2436
3	11.689	14939433	1943871	96.0586
4	14.539	187518	35793	1.2057
Total		15552412	2125901	100.0000

8. Condensation of methyl acetoacetate and cyclohexylamine (Table 2, entry 8)

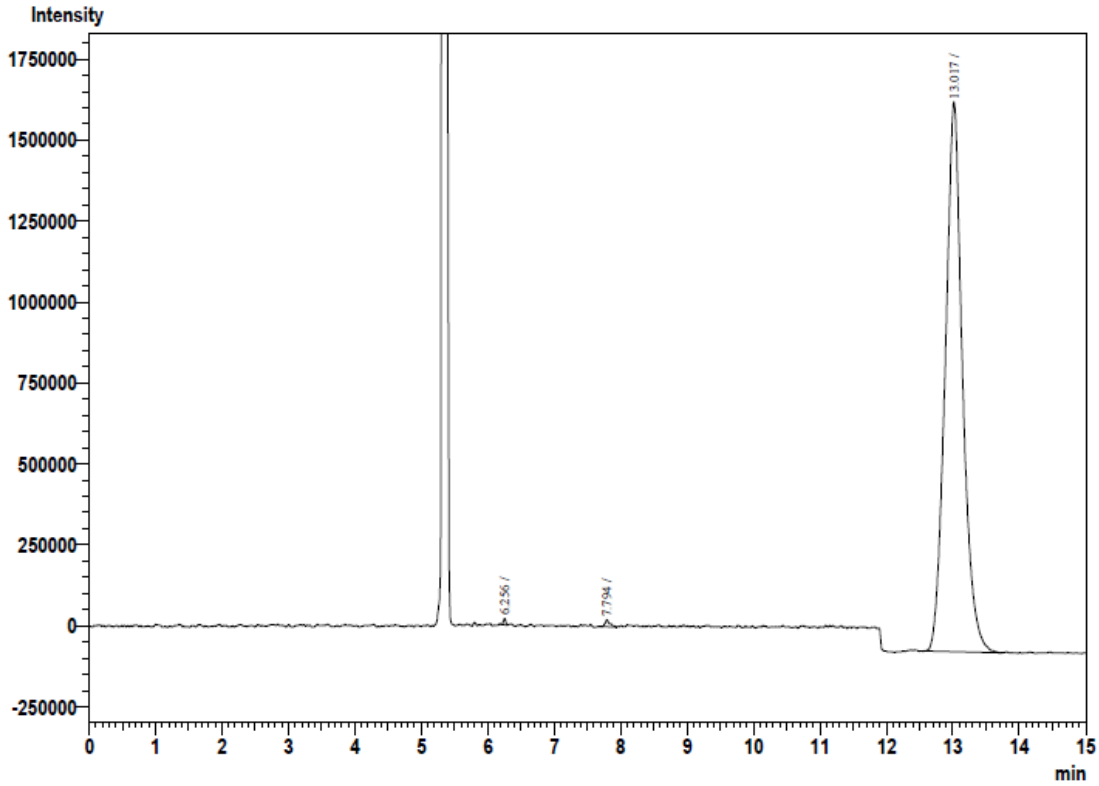

Fig. S13 GC DATA for Condensation of methyl acetoacetate and cyclohexylamine

GC data for Condensation of methyl acetoacetate and cyclohexylamine

Peak#	Ret.Time	Area	Height	Area%
1	6.256	47913	20190	0.1555
2	7.794	107977	21762	0.3504
3	13.017	30660148	1696333	99.4941
Total		30816038	1738285	100.0000

9. Condensation of acetylacetone and n-butylamine (Table 2, entry 7)

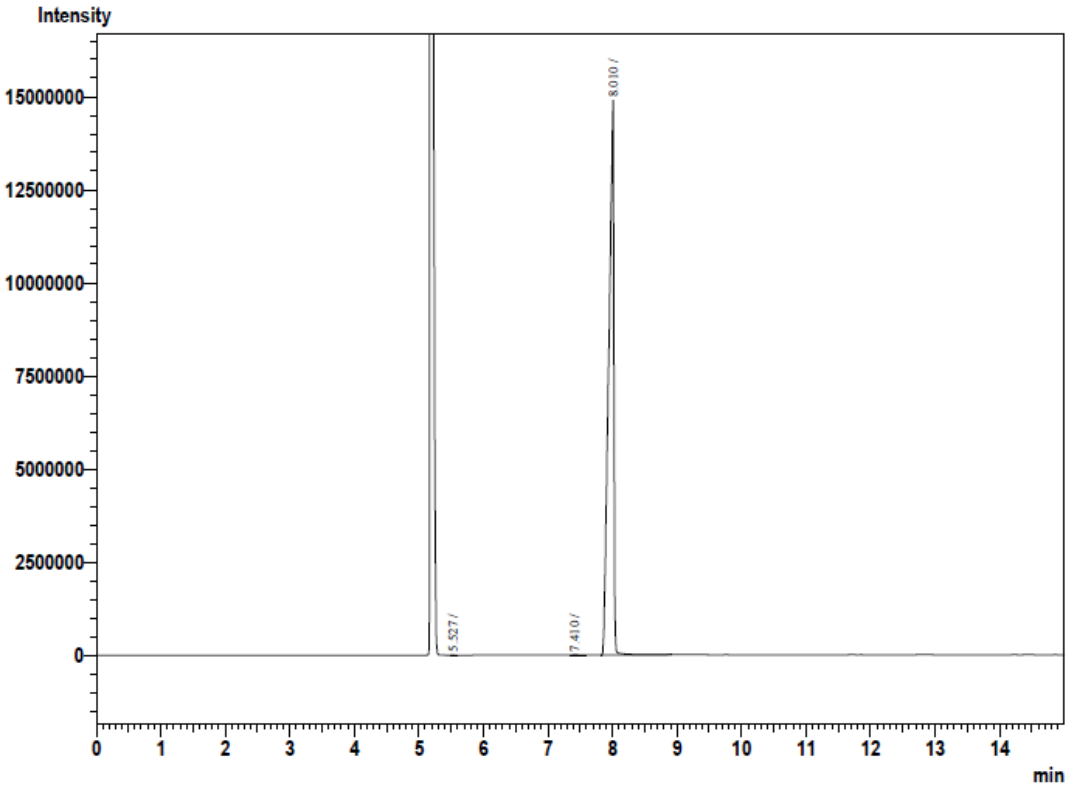

Fig. S14 GC DATA for Condensation of acetylacetone and n-butylamine

GC data for Condensation of acetylacetone and n-butylamine

Peak#	Ret.Time	Area	Height	Area%
1	5.527	9509	3545	0.0117
2	7.410	62658	17115	0.0769
3	8.010	81417106	14851755	99.9114
Total		81489273	14872415	100.0000

10. Condensation of ethylacetoacetate and n-butylamine (Table 2, entry 8)

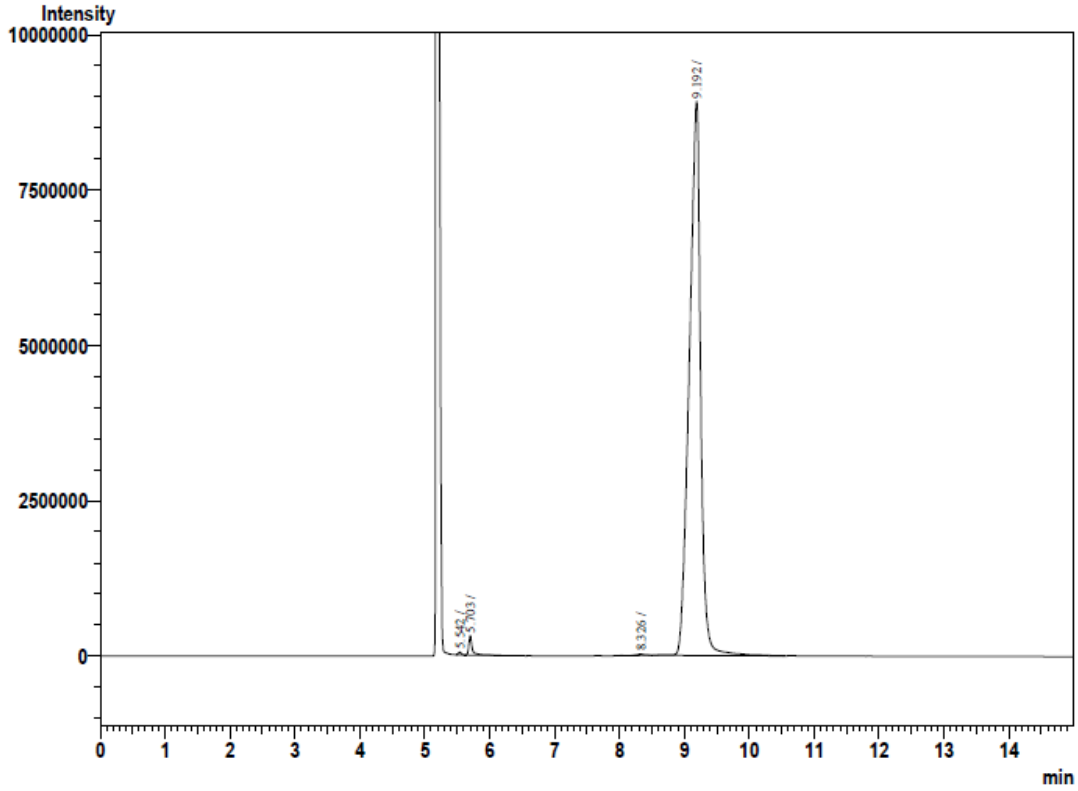

Fig. S15 GC DATA for Condensation of ethylacetoacetate and n-butylamine

GC data for Condensation of acetylacetone and n-butylamine

Peak#	Ret.Time	Area	Height	Area%
1	5.542	128780	43313	0.1174
2	5.703	1199472	309589	1.0937
3	8.326	165681	20131	0.1511
4	9.192	108176508	8915059	98.6378
Total		109670441	9288092	100.0000

11. Condensation of trifluoroacetoacetate and n-butylamine (Table 2, entry 9)

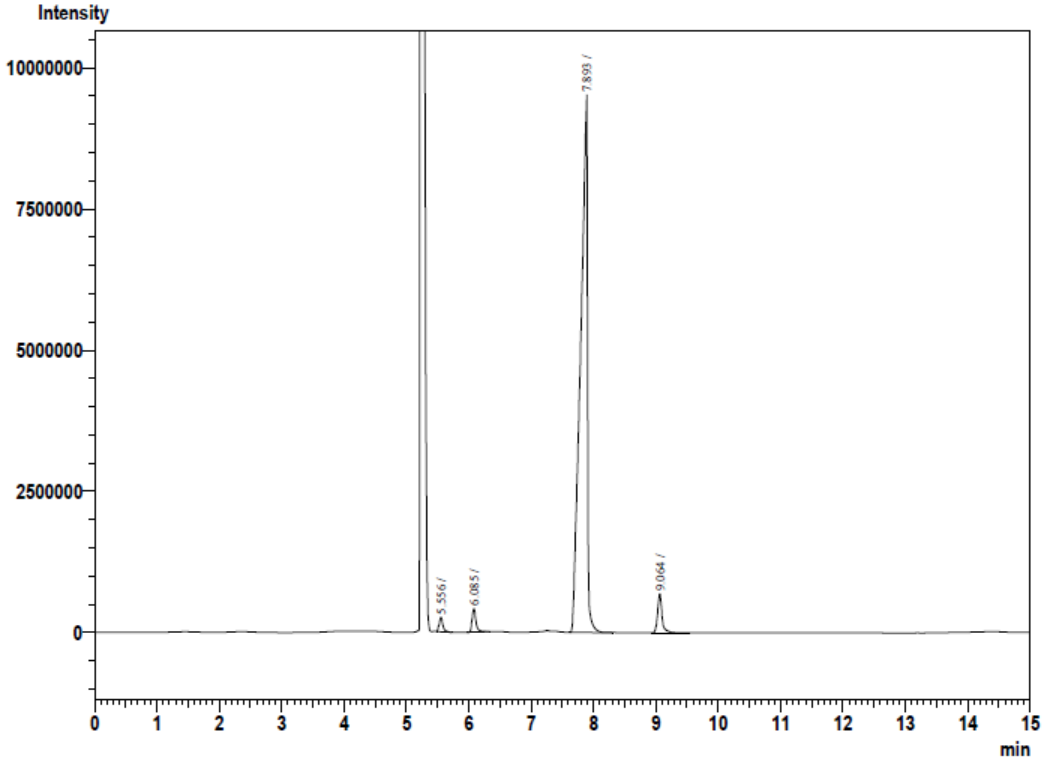

Fig. S16 GC DATA for Condensation of trifluoroacetoacetate and n-butylamine

GC data for Condensation of trifluoroacetoacetate and n-butylamine

Peak#	Ret.Time	Area	Height	Area%
1	5.556	1037038	258144	1.3141
2	6.085	1785654	414085	2.2628
3	7.893	72669650	9400022	92.0868
4	9.064	3421961	689381	4.3363
Total		78914303	10761632	100.0000

12. Condensation of methyl acetoacetate and n-butylamine (Table 2, entry 12)

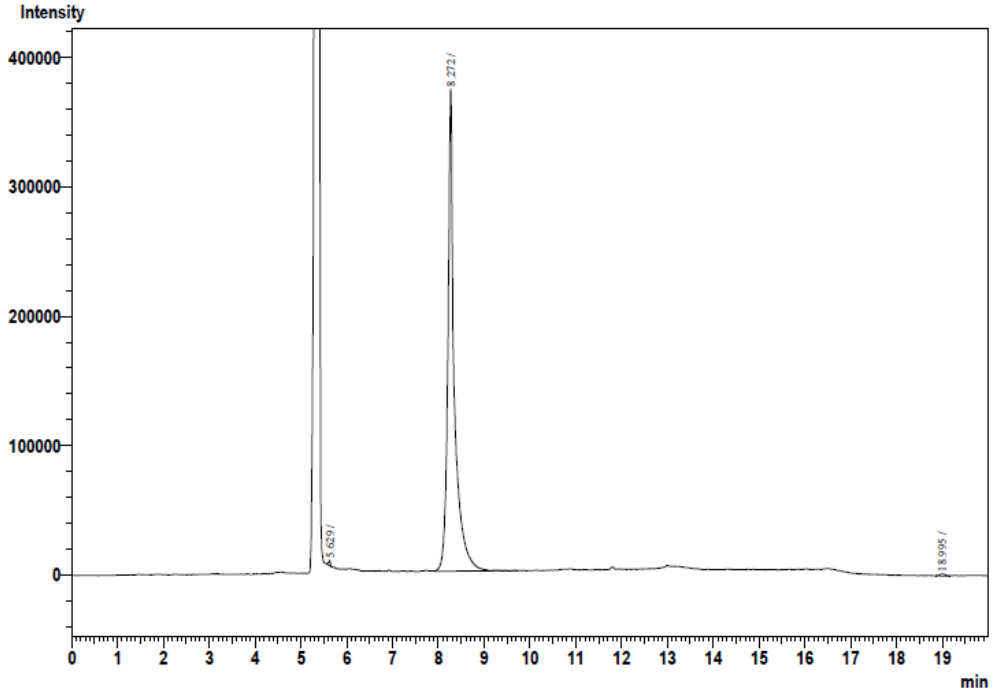

Fig. S17 GC DATA for Condensation of methyl acetoacetate and n-butylamine

GC data for Condensation of methyl acetoacetate and n-butylamine

Peak#	Ret.Time	Area	Height	Area%
1	5.629	10818	3979	0.2912
2	8.272	3690704	372385	99.3442
3	18.995	13547	1568	0.3646
Total		3715069	377932	100.0000

13. Condensation of methyl benzoyl acetate and n-butylamine (Table 2, entry 13)

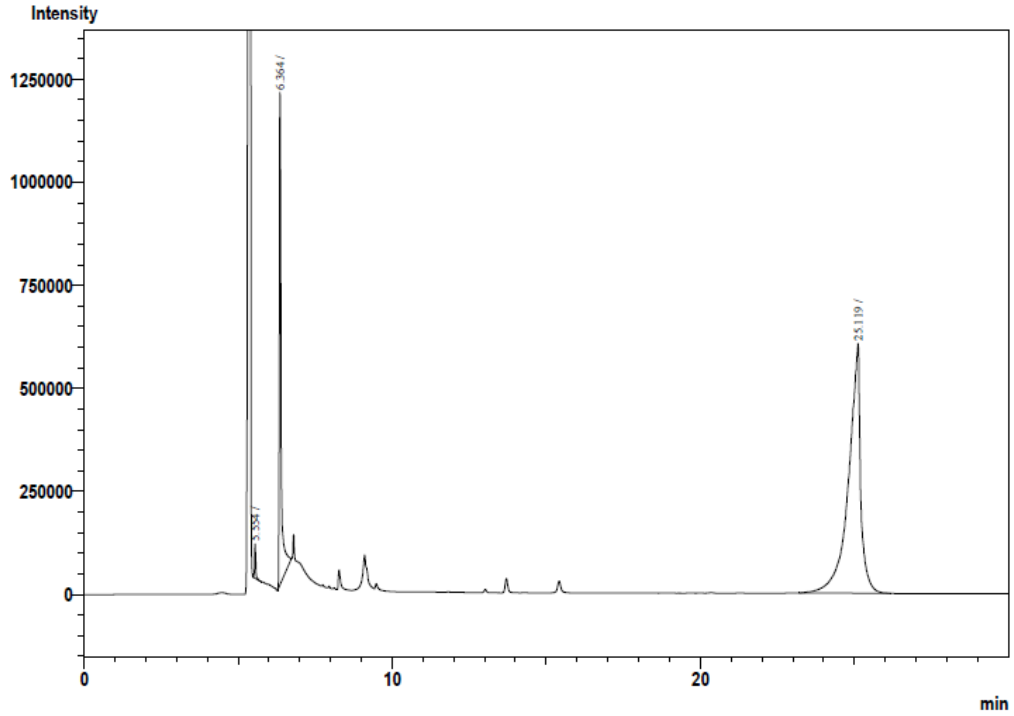

Fig. S18 GC DATA for Condensation of methyl benzoyl acetate and n-butylamine

GC data for Condensation of methyl benzoyl acetate and n-butylamine

Peak#	Ret.Time	Area	Height	Area%
1	5.554	215541	82353	0.9972
2	6.364	4738113	1191921	21.9215
3	25.119	16660302	606024	77.0812
Total		21613956	1880298	100.0000

14. Condensation of acetyl acetone and 2-chloroaniline (Table 2, entry 14)

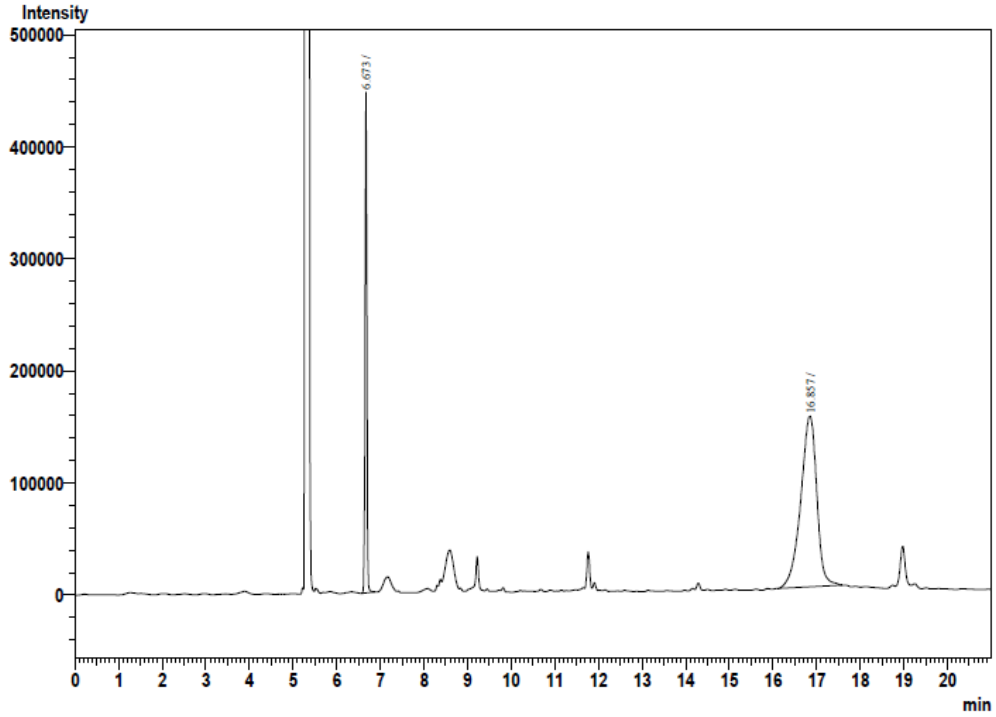

Fig. S19 GC DATA for Condensation of acetyl acetone and 2-chloroaniline

GC data for Condensation of acetyl acetone and 2-chloroaniline

Peak#	Ret.Time	Area	Height	Area%
1	6.673	1269026	445327	24.5330
2	16.857	3903708	152227	75.4670
Total		5172734	597554	100.0000

15. Condensation of trifluoro acetyl acetone and 2-chloroaniline (Table 2, entry 15)

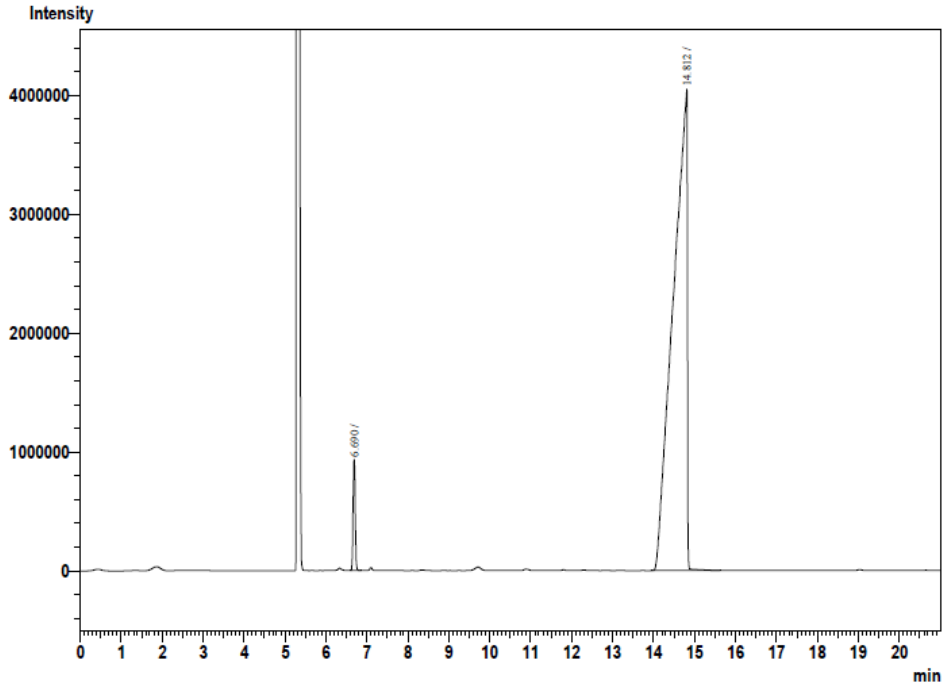

Fig. S20 GC DATA for Condensation of trifluoro acetyl acetone and 2-chloroaniline

GC data for Condensation of trifluoro acetyl acetone and 2-chloroaniline

Peak#	Ret.Time	Area	Height	Area%
1	6.690	3405186	933074	3.4126
2	14.812	96377961	4044235	96.5874
Total		99783147	4977309	100.0000

16. Condensation of acetyl acetone and m-toludine (Table 2, entry 16)

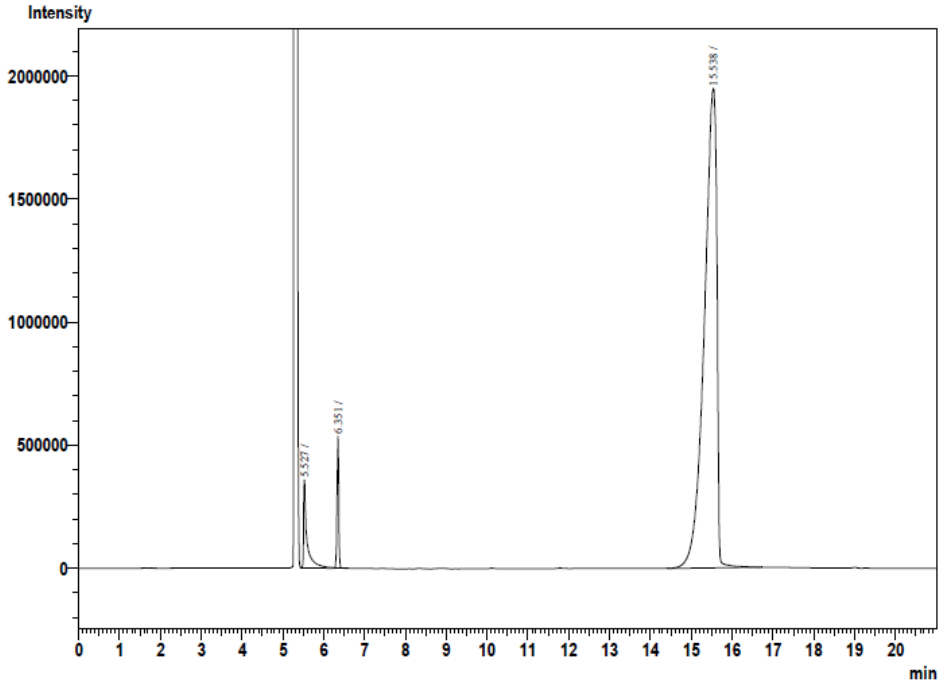

Fig. S21 GC DATA for Condensation of acetyl acetone and m-toludine

GC data for Condensation of acetyl acetone and m-toludine

Peak#	Ret.Time	Area	Height	Area%
1	5.527	2062374	356347	4.5742
2	6.351	1583090	534112	3.5112
3	15.538	41441512	1947276	91.9146
Total		45086976	2837735	100.0000

17. Condensation of trifluoro acetyl acetone and m-toludine (Table 2, entry 17)

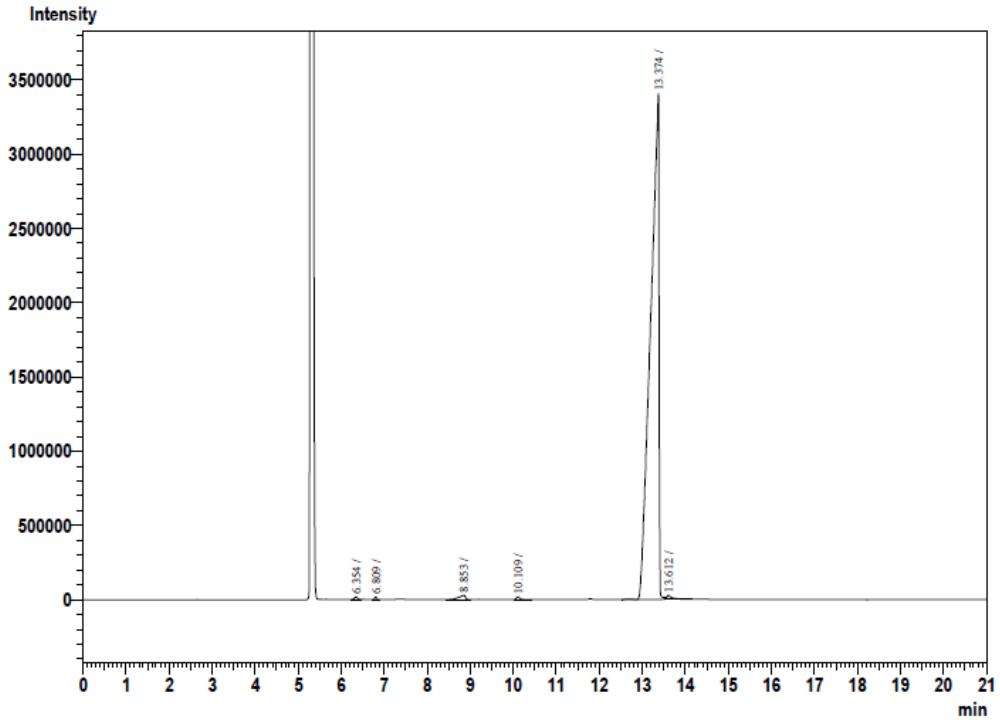

Fig. S22 GC DATA for Condensation of trifluoro acetyl acetone and m-toludine

GC data for Condensation of trifluoro acetyl acetone and m-toludine

Peak#	Ret.Time	Area	Height	Area%
1	6.354	89647	17830	0.1918
2	6.809	55007	17978	0.1177
3	8.853	309734	29223	0.6625
4	10.109	105187	19430	0.2250
5	13.374	45930946	3399990	98.2477
6	13.612	259629	27468	0.5554
Total		46750150	3511919	100.0000

18. Condensation of acetyl acetone and o-anisidine (Table 2, entry 17)

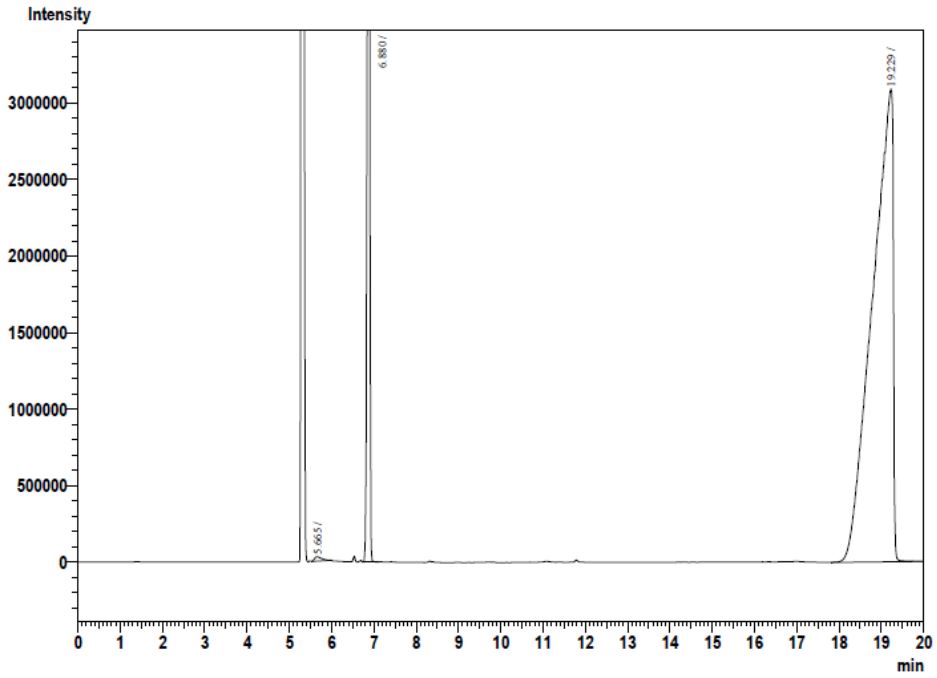

Fig. S23 GC DATA for Condensation of acetyl acetone and o-anisidine

GC data for Condensation of acetyl acetone and o-anisidine

Peak#	Ret.Time	Area	Height	Area%
1	5.665	327595	27747	0.2338
2	6.880	34672372	10138115	24.7459
3	19.229	105113382	3088428	75.0202
Total		140113349	13254290	100.0000

NMR spectra of representative products

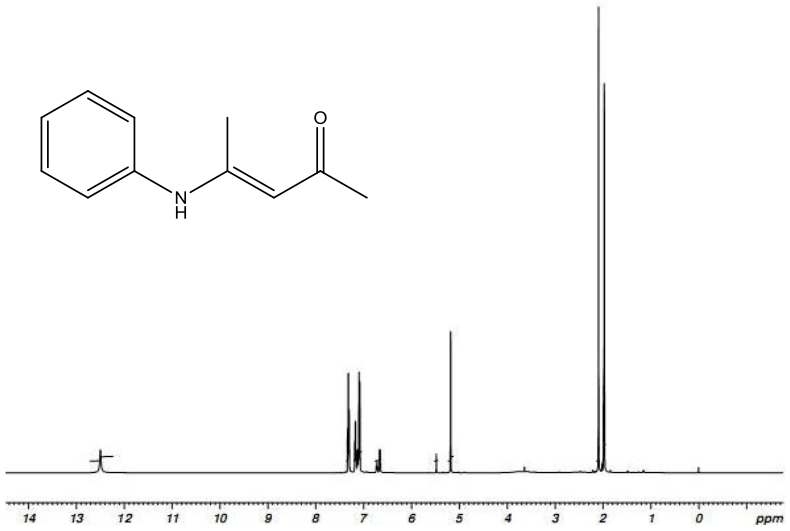

Fig. S24 ^{1}H-NMR spectrum of 4-(phenylamino)pent-3-en-2-one

^{1}H NMR (400 MHz, $CDCl_3$): 1.990 (s, 3H), 2.095 (s, 3H), 5.185 (s, 1H), 5.483(s, 2H), 6.722 (m, 1H), 7.320 (t, 2H), 12.493 (s, 1H).

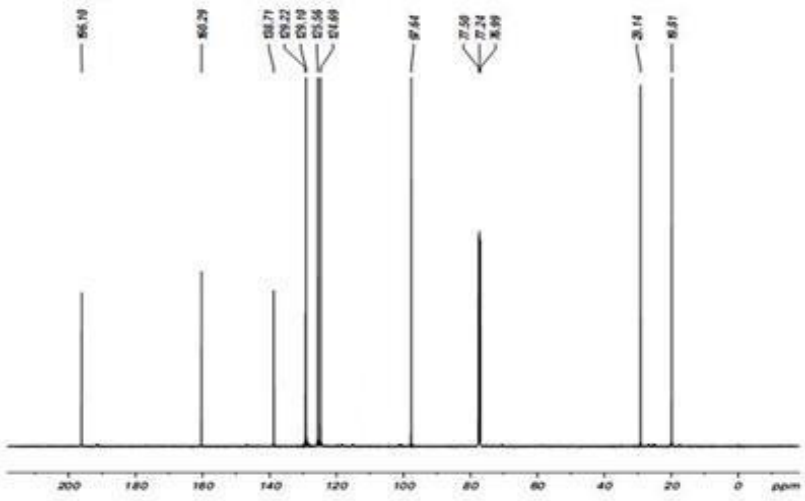

Fig. S25 ^{13}C-NMR spectrum of 4-(phenylamino)pent-3-en-2-one

^{13}C NMR (100 MHz, $CDCl_3$): 19.51 (-CH_3), 20.14 (-CH_3), 97.64 (-CH), 125.56 (-CH), 129.22 (-CH), 138.71 (-CH), 160.29 (-CH), 186.10 (-C=O).

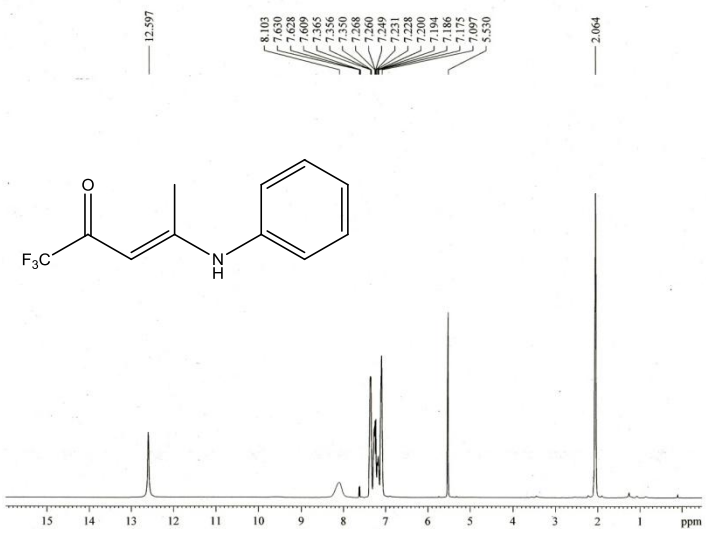

Fig. S26 ^{1}H-NMR spectrum of 1,1,1-trifluoro-4-(phenylamino)pent-3-en-2-one

^{1}H NMR (400 MHz, $CDCl_3$): 2.063 (s, 3H), 5.530 (s, 1H), 7.097-78.103(m, 5H), 12.597 (s, 1H).

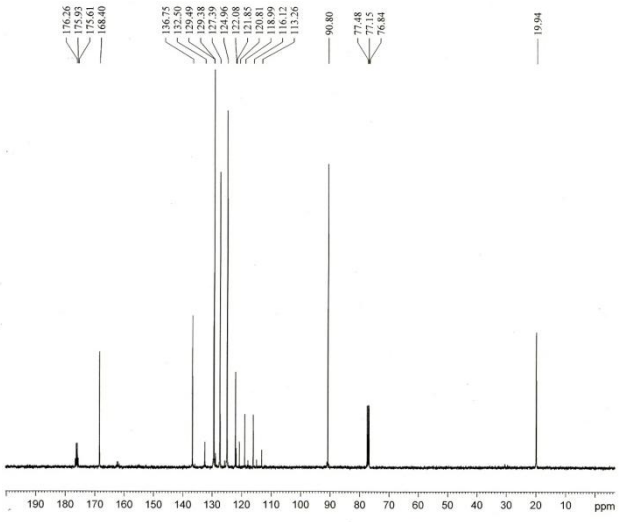

Fig. S27 ^{13}C-NMR spectrum of 1,1,1-trifluoro-4-(phenylamino)pent-3-en-2-one

^{13}C NMR (100 MHz, $CDCl_3$): 19.94 (-CH_3), 90.80 (-CH), 124.96 (-CH), 127.39 (-CH), 129.49 (-C), 136.75 (-C), 168.40 (-C=O), 175.93 (-CF_3).

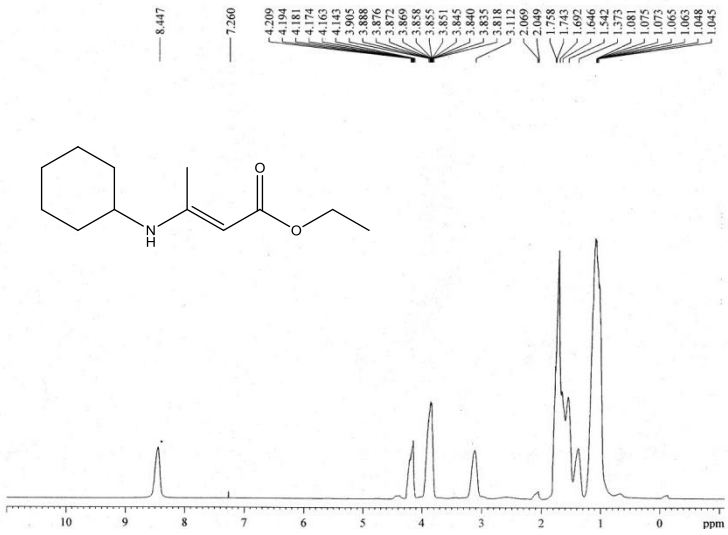

Fig. S28 ^{1}H-NMR spectrum of ethyl-3-(cyclohexylamino)-but-2-enoate

^{1}H NMR (400 MHz, $CDCl_3$): 1.045-1.081(m, 4H), 1.373 (m, 3H), 1.542-1.649 (m, 4H), 1.743-1.758 (m, 2H), 2.069 (s, 3H), 3.112 (m, 1H), 3.855 (s, 1H) 4.143-4.209 (m, 2H), 8.447 (s, 1H).

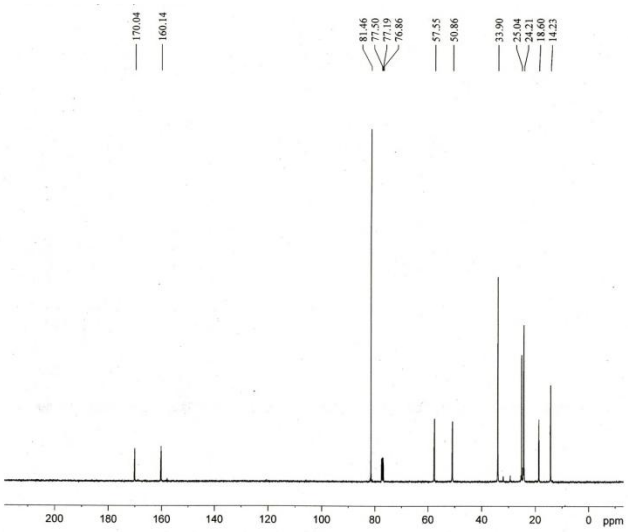

Fig. S29 ^{13}C-NMR spectrum of ethyl-3-(cyclohexylamino)-but-2-enoate

^{13}C NMR (100 MHz, $CDCl_3$): 14.23 (-CH_3), 18.60 (-CH_3), 24.21-25.04 (-CH_2), 33.90 (-CH_2), 50.86(-CH), 57.55 (-CH_2), 81.46 (-CH), 160.14 (-C), 170.04 (-C=O).

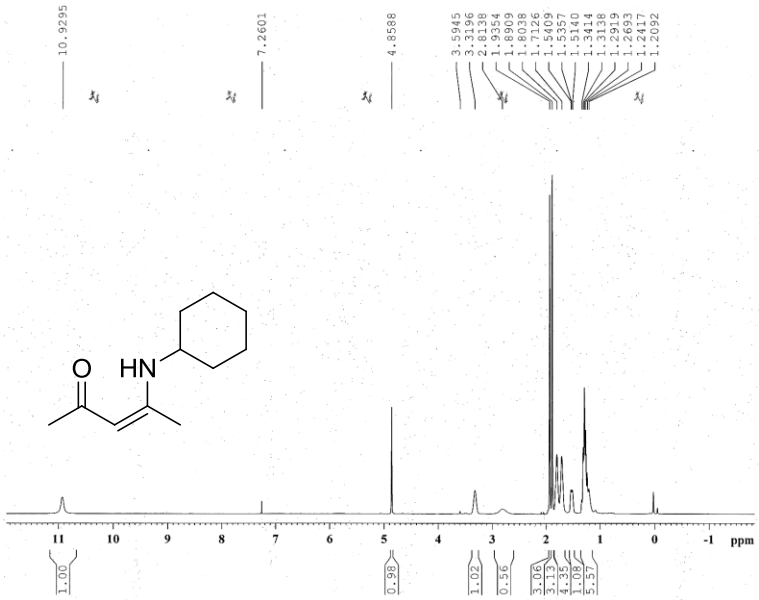

Fig. S30 ^{1}H-NMR spectrum of 4-(cyclohexylamino)pent-3-en-2-one

^{1}H NMR (400 MHz, $CDCl_3$): 1.269 (m, 4H), 1.341 (m, 2H), 1.54-1.803 (m, 4H), 1.890 (s, 3H), 1.935 (s, 3H), 3.594 (s, 1H), 4.858 (s, 1H), 10.929 (s, 1H).

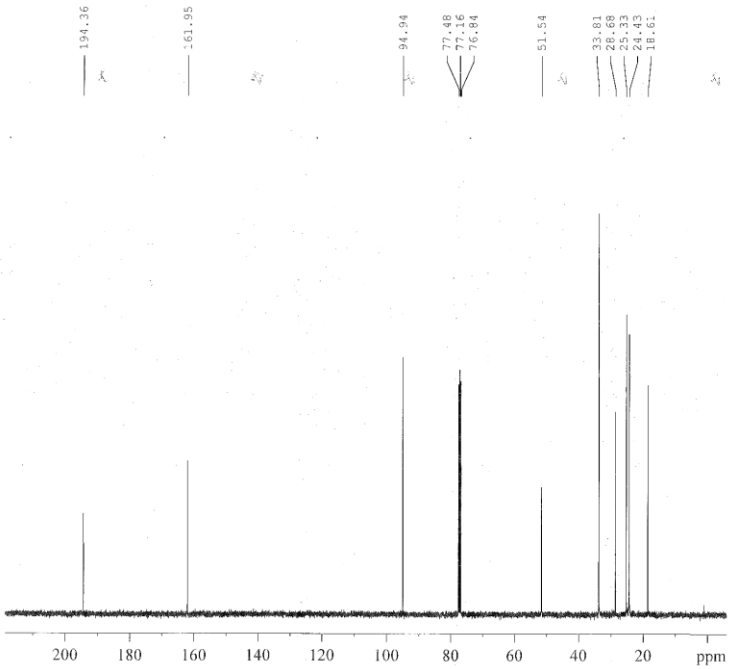

Fig. S31 ^{13}C-NMR spectrum of 4-(cyclohexylamino)pent-3-en-2-one

^{13}C NMR (100 MHz, $CDCl_3$): 18.61 ($-CH_3$), 24.43 ($-CH_2$), 25.33 ($-CH_2$), 28.68 ($-CH_3$), 33.81 ($-CH_2$), 51.54 (-CH), 94.94 (-CH), 161.95 (-C), 194.36 (-C=O).

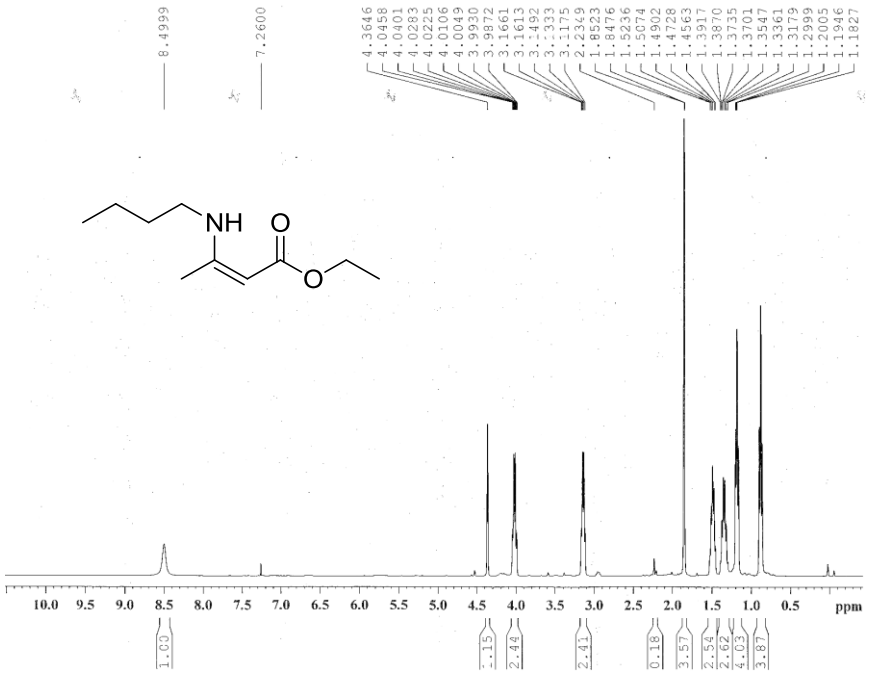

Fig. S32 ^{1}H-NMR spectrum of Ethyl 3-(butylamino)but-2-enoate

^{1}H NMR (400 MHz, $CDCl_3$): 1.194 (t, 3H), 1.317 (t, 3H), 1.373 (q, 2H), 1.490 (q, 2H), 1.852 (d, 3H), 3.149 (q, 2H), 4.010 (m, 2H), 4.364 (s, 1H), 8.499 (s, 1H).

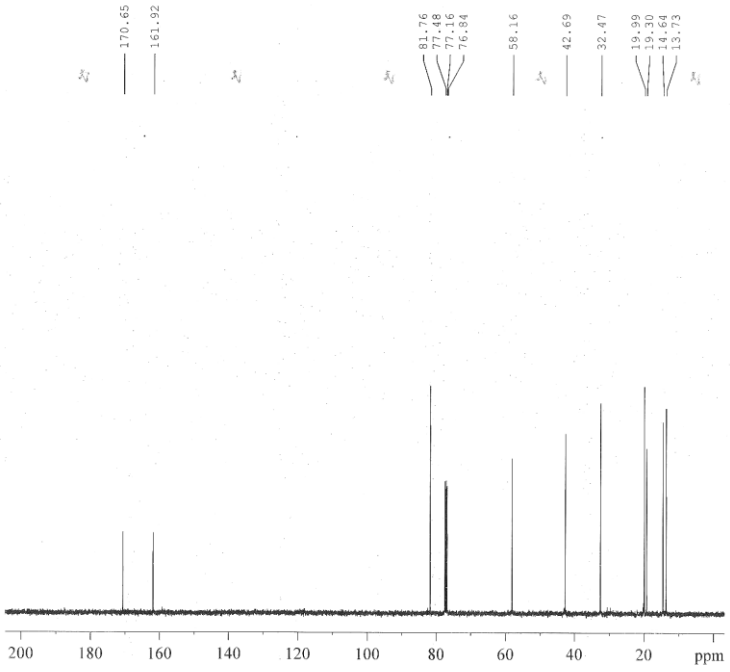

Fig. S33 ^{13}C-NMR spectrum of Ethyl 3-(butylamino)but-2-enoate

^{13}C NMR (100 MHz, $CDCl_3$): 13.73 (-CH_3), 14.64 (-CH_3), 19.30 (-CH_2), 19.99 (-CH_3), 32.47 (-CH), 42.69 (-CH_2), 58.16 (-CH_2), 81.76 (-CH), 161.92 (-C), 170.65 (-C=O).