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Supporting Information

Pd-Catalysed Synthesis of Oxomalonamides Through Adjacent Triple Carbonylation of Tertiary Amines

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1. Experimental section

General

Unless otherwise noted, the chemicals and solvents were purchased from commercial supplier and used without further purification. All the reactions were performed in a 100 mL stainless steel reactor. The progress of the reaction was monitored on GC-MS, GC and thin layer chromatography using Merck silica gel 60 F254 plates. The obtained products are purified by column chromatography on silica gel (100-200 mesh). The ^{1}H NMR spectra of isolated products were recorded in $CDCl_3$ recorded on Agilent 400 and 500 MHz and ^{13}C NMR spectra 101 and 126 MHz. The chemical shifts are reported in ppm (δ) relative to the internal standard tetramethylsilane (TMS). The coupling constant J values are described in Hz. Splitting patterns of proton are depicted as s (singlet), d (doublet), t (triplet), and m (multiplet). The products are characterised by GC-MS, ^{1}H and ^{13}C NMR spectra and HRMS was recorded on Micromass ESI TOF (time of flight) mass spectrometer.

(Note: Because of the high toxicity of carbon monoxide, all the reactions should be performed in an autoclave. The laboratory should be well-equipped with a CO detector and alarm system.)

2. General experimental procedure for oxidative triple carbonylation of tertiary amines:

To a 100 mL stainless steel reactor, tertiary amine (1 mmol), additive (0.6 mmol), base (1 mmol), and catalyst (3 mol%) in 10 mL solvent were added and the reactor was closed tightly. At room temperature, the autoclave was pressurised with oxygen (1 atm) and carbon monoxide (7 atm) (8 atm, CO/O_2) without flushing. (Note: The autoclave was pressurised with oxygen followed by carbon monoxide. The CO/O_2 may form an explosive mixture under certain conditions.). Then, the reaction mixture was heated to 100 ℃ and stirred with a mechanical stirrer for 16 h. Afterward, the reactor was cooled to room temperature and pressure was released carefully. After the reaction, the reaction mixture was diluted with ethyl acetate and solvent content was evaporated under a rotary evaporator. The crude product was purified by column chromatography using EtOAc/petroleum ether as eluent. All the purified compounds were confirmed by ^{1}H, ^{13}C NMR spectroscopy, and HRMS analysis.

3. General experimental procedure for cross-experiment between two tertiary amines

In a 100 mL stainless reactor, triethyl amine (1 mmol), tripropyl/triamyl amine (1 mmol), KI (1.2 equiv.), Na_2CO_3 (2 equiv.) and catalyst (6 mol %) in 10 mL acetonitrile solvent were added. Then the reactor was closed tightly and pressurised with 14 atm of CO/O_2 (7:1) at room temperature. The reaction mixture was stirred with a mechanical stirrer and heated to 100 ℃ for 24 h. Then the autoclave was cooled to room temperature and pressure was released carefully. The reactor vessel was washed with ethyl acetate to remove the traces of product and catalyst if present. Afterwards, the solvent was evaporated by a rotary evaporator and residue was purified by column chromatography using EtOAc/petroleum ether as eluent. Obtained products was analysed with GCMS, ^{1}H and ^{13}C NMR and HRMS analysis.

4. General procedure for hydrogenation of N^1,N^1,N^3,N^3-tetraethyl-2-oxomalonamide (3a) (i and ii)

i. The target product was synthesised according to the literature report: N^1,N^1,N^3,N^3-tetraethyl-2-oxomalonamide (0.2 mmol) was dissolved in methanol (3 mL), then kept the flask into ice bath. Then, an excess amount of sodium borohydride $NaBH_4$ (6 equiv, excess) was added to the solvent at 0 ℃. The reaction mixture stirred for 2.5 h at room temperature. The 1 M HCl was added to quench the reaction. The solvent was evaporated under reduced pressure and residue was purified by column chromatography.

ii. In a 100 mL stainless reactor, N^1,N^1,N^3,N^3-tetraethyl-2-oxomalonamide (3a) (0.5 mmol), Ru-MACHO (0.01 mmol) catalyst, KO^tBu (0.05 mmol) base and 10 mL toluene solvent were added. Then autoclave was closed tightly and flushed three times with nitrogen atmosphere. At room temperature, the autoclave was flushed twice with H_2 atm. and pressurised H_2 to 50 atmosphere. Then the reaction was carried out at 160 ℃ for 24 h. The 98% conversion of N^1,N^1,N^3,N^3-tetraethyl-2-oxomalonamide (3a) was detected by GC, GCMS analysis. The residue was further purified by column chromatography.

5. General procedure for oxamide synthesis

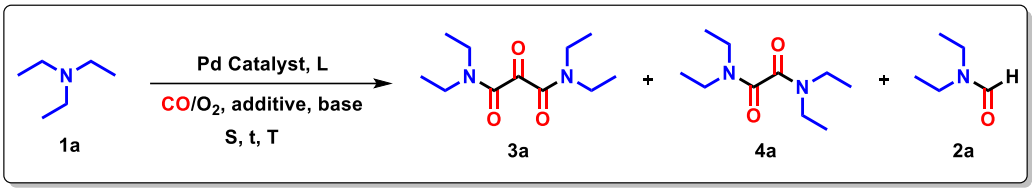
Diethyl amine (1 mmol), KI (0.6 mmol), K_2CO_3 (1 equiv.), catalyst (2.5 mol%) in 10 mL acetonitrile solvent was charged to a 100 mL stainless steel reactor. The reactor was closed tightly and was pressurised with oxygen (1 atm), and carbon monoxide (4 atm) at room

temperature. The reaction mixture was stirred with mechanical stirrer at 100 °C for 16 h. The reactor was cooled to room temperature and the pressure was vented carefully. The reactor vessel washed with ethyl acetate and solvent was evaporated using a rotary evaporator. The residue was purified by column chromatography and product was characterised with GCMS, ^{1}H and ^{13}C NMR spectroscopy.

6. General procedure for oxamate synthesis

To a 100 mL stainless steel reactor, triethyl amine (1 mmol), ethyl alcohol (1 mL), KI (0.6 mmol), K_2CO_3 (1 equiv.), catalyst (2.5 mol%) and 9 mL acetonitrile solvent was added. The reactor was closed tightly and pressurised with oxygen (1 atm) and carbon monoxide (4 atm) at room temperature. Then the reaction mixture was stirred with a mechanical stirrer at 100 °C for 24 h. Afterward, the remaining pressure was released carefully at room temperature. The reactor vessel was washed with ethyl acetate and solvent was evaporated using a rotary evaporator. The residue was purified by column chromatography. The obtained product was analysed with GC-MS, ^{1}H and ^{13}C NMR spectroscopy.

7. Detailed optimization of reaction parameters for triple carbonylation (Table. T1)



Sr. No.	Catalyst	Ligand (L)	Solvent	Additive	Conv. (%)	Selectivity (%)			
						2a	3a	4a	5a (Unknown)
1	$Pd(PPh_3)_4$	-	ACN	KI	100	5	36	20	39
2	$PdCl_2$	Johnphos	ACN	KI	100	2	38	4	56
3	$PdCl_2$	Sphos	ACN	KI	100	3	42	3	52
4	$PdCl_2$	Di(1-adamantyl)-n-butylphosphine	ACN	KI	98	5	44	7	44
5	$PdCl_2$	Pcy_3	ACN	KI	100	7	40	6	47
6	$PdCl_2$	PPh_3	ACN	KI	100	5	45	7	43
7	$PdCl_2$	dppf	ACN	KI	98	7	22	6	65

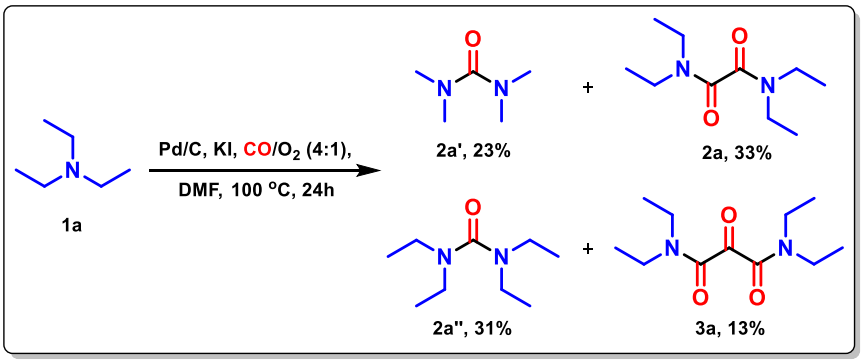
8	$PdCl_2$	dppe	ACN	KI	99	5	23	10	62
9	$PdCl_2$	DPEphos	ACN	KI	100	2	27	4	67
10	$PdCl_2$	Xantphos	ACN	KI	100	5	14	8	73
11	$PdCl_2$	dppb	ACN	KI	100	8	26	9	57
12	$PdCl_2$	PPh_3	THF	KI	trace	-	-	-	-
13	$PdCl_2$	PPh_3	1,4-dioxane	KI	40	16	trace	trace	84
14	$PdCl_2$	PPh_3	Toluene	KI	ND	-	-	-	-
15	$PdCl_2$	PPh_3	PEG-400	KI	ND	-	-	-	-
16	$Pd(OAc)_2$	PPh_3	ACN	KI	100	3	54	6	37
17	$Pd(OTf)_2$	PPh_3	ACN	KI	100	4	46	8	42
18	$Pd(acac)_2$	PPh_3	ACN	KI	100	5	52	6	37
19	$Pd(PPh_3)_2Cl_2$	PPh_3	ACN	KI	100	11	38	18	33
20	Pd/C	PPh_3	ACN	KI	100	6	27	38	29
21	$Pd(OAc)_2$	PPh_3	ACN	NaI	100	15	25	4	56
22	$Pd(OAc)_2$	PPh_3	ACN	TBAI	100	5	38	5	52
23	$Pd(OAc)_2$	PPh_3	ACN	CuI	100	2	20	6	72
24	$Pd(OAc)_2$	PPh_3	DMF	KI	100	-	12	22	66
25	$Pd(OAc)_2$	PPh_3, K_2CO_3	ACN	KI	100	2	53	10	35
26	$Pd(OAc)_2$	K_2CO_3	ACN	KI	100	6	51	6	37
27[c]	$Pd(OAc)_2$	K_2CO_3	ACN	KI	100	6	58	8	28
28[c]	$PdBr_2$	K_2CO_3	ACN	KI	98	5	22	6	67
29[c]	PdI_2	K_2CO_3	ACN	KI	100	4	34	22	40
30[c]	$Pd(OAc)_2$	Cs_2CO_3	ACN	KI	100	2	10	3	85
31[c]	$Pd(OAc)_2$	Na_2CO_3	ACN	KI	100	2	64	6	28
32[c]	$Pd(OAc)_2$	KO^tBu	ACN	KI	100	6	25	4	65
33[c]	$Pd(OAc)_2$	NaOAc	ACN	KI	100	5	59	8	28
34[c]	$Pd(OAc)_2$	Na_2CO_3, PPh_3	ACN	KI	100	5	56	9	30
35[c,d]	$Pd(OAc)_2$	Na_2CO_3	ACN	KI	100	6	46	5	43

36[c], N_2	$Pd(OAc)_2$	Na_2CO_3	ACN	KI	trace	-	-	-	-
37[c]	$Pd(OAc)_2$	-	ACN	KI	100	6	54	10	30
38[c],[e]	$Pd(OAc)_2$	Na_2CO_3	ACN	-	35	1	2	4	93
39[f]	$Pd(OAc)_2$	Na_2CO_3	ACN	KI	82	4	66	10	20

[a]**Reaction conditions:** tertiary amine 1a (1 mmol), catalyst (3 mol%), base (1 mmol), additive (0.6 mmol), solvent (10 mL), 5 atm CO/O_2 (4:1), [b]conversion and selectivity determined by GC, GC-MS, [c]8 atm of CO/O_2 (7:1) pressure, [d]air as an oxidant, [e]without additive, [f]13 atm of CO/O_2 (12:1) pressure, 100 °C for 16-24 h, (5a-undefined products).

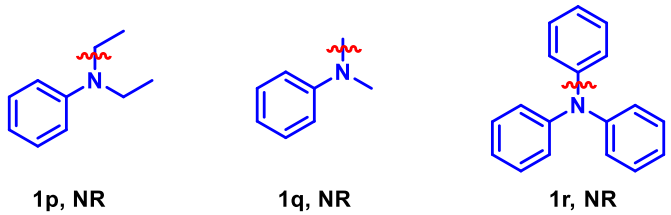
8. Reaction of tertiary amine in Pd/C, DMF solvent

The reaction of triethyl amine (tertiary amine) is carried out using Pd/C as catalyst, KI as an additive in DMF solvent under the 5 atm pressure of CO/O_2 (4:1). The mixture of carbonylated products formation was observed such as 1,1,3,3-tetramethylurea (from DMF), 1,1,3,3-tetraethylurea, oxamide and oxomalonamide and were detected by GC-MS.



Scheme S1. Reaction of tertiary amine using Pd/C catalyst, KI additive, 5 atm. pressure of CO/O_2 (4:1) in DMF solvent for 24 h.

Unsuccessful tertiary amines substrates in oxidative triple carbonylation transformation

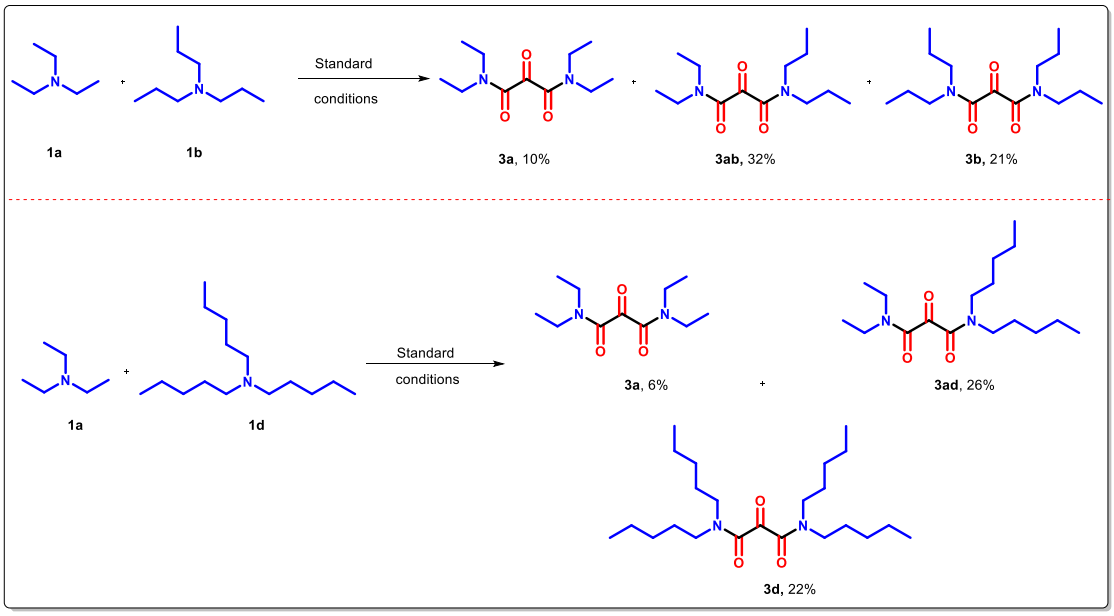


Scheme S2. Unsuccessful tertiary amine in this transformation

The oxidative triple carbonylation transformation using aromatic tertiary amines like *N*,*N*-diethyl aniline (**1p**), *N*,*N*-dimethyl aniline (**1q**) and also with triphenylamine (**1r**) were

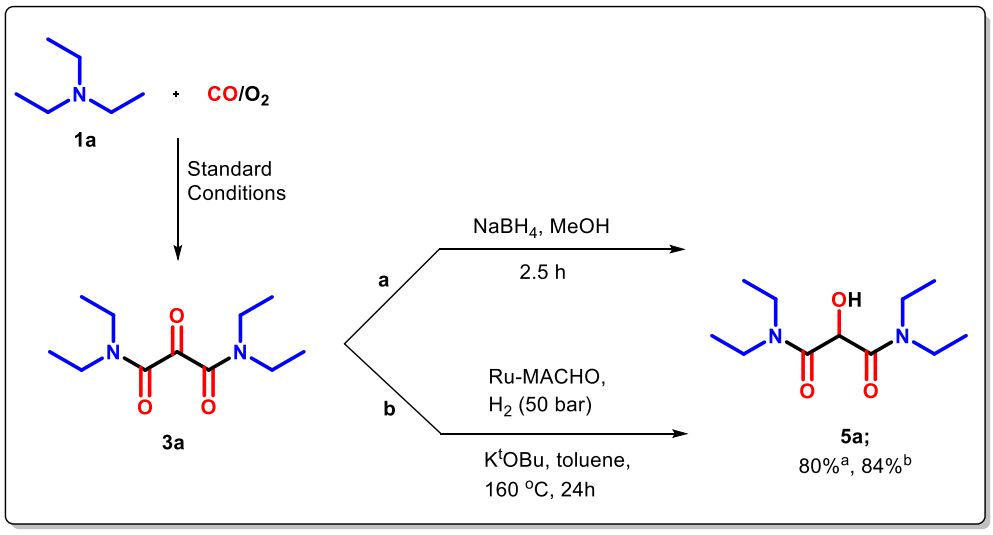
performed under standard conditions. Unfortunately, the reaction did not produce the respective oxomalonamide products, this could be because of lack of α hydrogen atom to the nitrogen and lone pair of nitrogen are conjugated to the phenyl ring, which indicates that the sp^2 C-N bond does not cleave under these standard reaction conditions.

9. Cross-coupling between two different tertiary amines



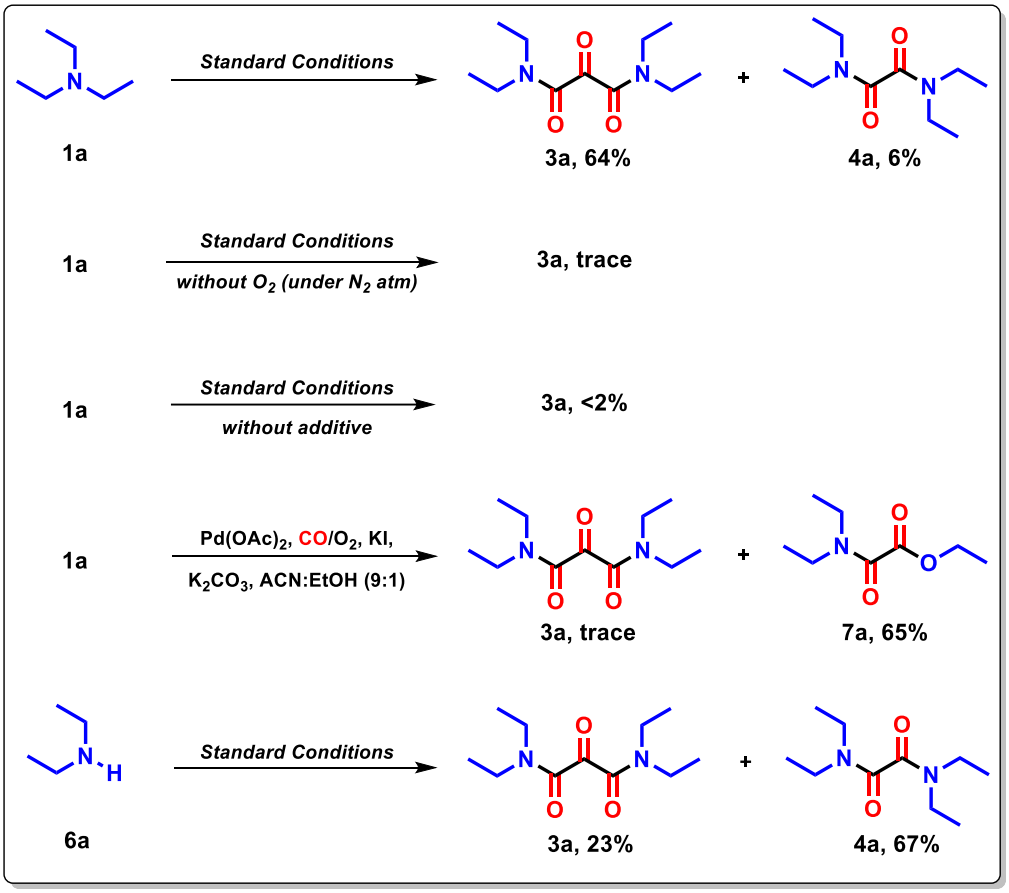
Scheme S3. Cross-coupling between two different tertiary amines

10. Hydrogenation reaction of 3a



Scheme S4. Hydrogenation reaction of 3a

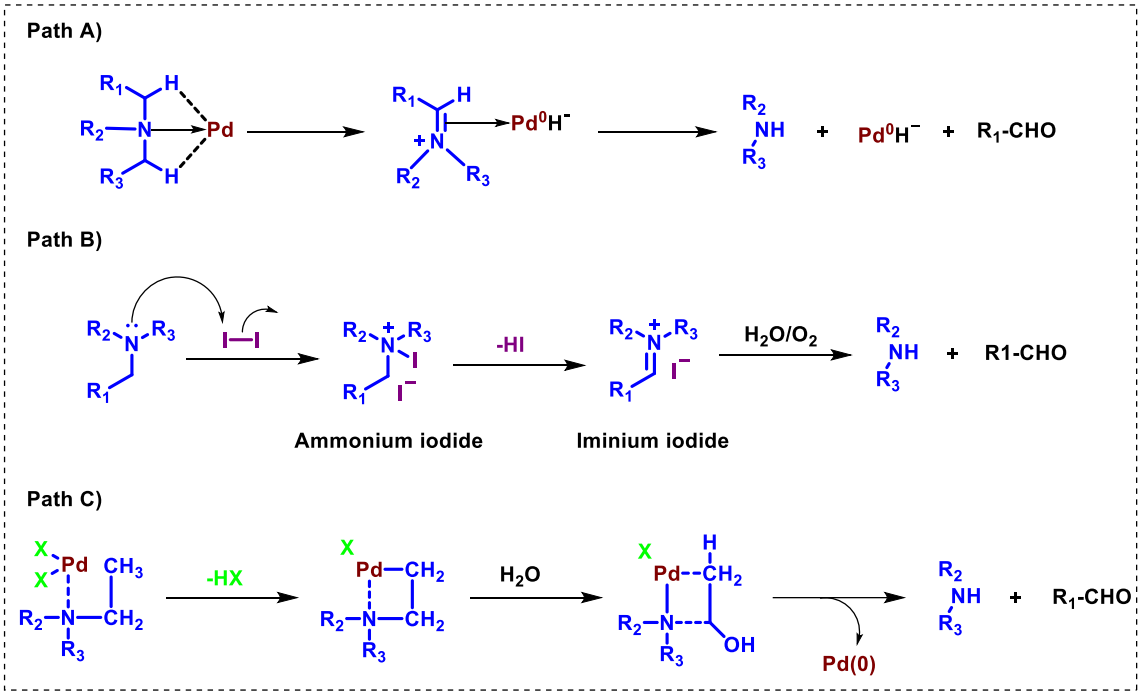
11. Control Experiments



Scheme S5. Some control experiments

12. Reaction pathways for the cleavage of tertiary amine to secondary amine

We propose pathways to yield secondary amine from the *N*-dealkylation of tertiary amine. In path A, the nitrogen of tertiary amines coordinates with Pd(0) to form a Pd-iminium type intermediate. Further, the hydrolyses of iminium intermediate affords aldehyde and secondary amine. In path B, the reaction between tertiary amine and iodine forms ammonium iodide intermediate. Then iminium iodide could be formed from ammonium iodide with the elimination of HI. Then the iminium iodide was hydrolysed to give secondary amine and aldehyde. In path C, Pd(II) might be the active species to accelerate the C-N bond cleavage, in which amine coordinates with Pd and forms the Pd-C bond[1]. Then the nucleophilic attack of OH^- followed by rearrangement to secondary amine and aldehyde.



Scheme S6. Pathways for cleavage of tertiary amine to secondary amine

13. Spectroscopic data of products

N^1,N^1,N^3,N^3-tetraethyl-2-oxomalonamide (3a), 56%, 16 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.43 (q, *J* = 7.2 Hz, 8H), 1.21 (dt, *J* = 27.9, 7.2 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 183.31, 165.58, 42.33, 39.46, 14.25, 12.49. **HRMS** (ESI) *m/z* calcd for $C_{11}H_{20}N_2O_3$ $[M + H]^+$, 229.1552, found 229.1548. **GC-MS** (EI, 70 eV) *m/z* (%) 228 (10, M^+), 200 (3), 171 (2), 100 (100), 72 (98), 44 (39). **IR** (cm^{-1}) 2978, 2938, 2879, 1714, 1632,1461.

2-oxo-N^1,N^1,N^3,N^3-tetrapropylmalonamide (3b), 55%, 16 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.36 – 3.17 (m, 8H), 1.69 – 1.50 (m, 8H), 0.84 (q, *J* = 7.5 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 183.10, 166.01, 49.36, 46.49, 22.02, 20.39, 11.12, 10.88. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{28}N_2O_3$ $[M + H]^+$, 285.2178, found 285.2175. **GC-MS** (EI, 70 eV) *m/z* (%) 284 (22, M^+), 256 (5), 128 (100), 100 (51), 86 (94), 43 (100). **IR** (cm^{-1}) 2966, 2936, 2877, 1715, 1634, 1456.

N^1,N^1,N^3,N^3-tetrabutyl-2-oxomalonamide (3c), 48%, 16 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.45 – 3.18 (m, 8H), 1.57 (ddt, *J* = 27.2, 15.3, 7.6 Hz, 8H), 1.28 (tt, *J* = 18.2, 7.5 Hz, 8H), 0.88 (td, *J* = 7.3, 3.5 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 183.19, 165.89, 47.59, 44.73, 30.89, 29.23, 20.04, 19.81, 13.64 (d, *J* = 8.9 Hz). **HRMS** (ESI) *m/z* calcd for $C_{19}H_{36}N_2O_3$ $[M + H]^+$, 341.2804, found 341.2782. **GC-MS** (EI, 70 eV) *m/z* (%) 340 (44, M^+), 255 (10), 156 (100), 128 (96), 100 (100), 57 (98). **IR** (cm^{-1}) 2959, 2933, 2874, 1715, 1636, 1460.

2-oxo-N^1,N^1,N^3,N^3-tetrapentylmalonamide (3d), 43% 16 h.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.37 (ddd, *J* = 15.7, 11.4, 4.4 Hz, 8H), 1.73 – 1.58 (m, 8H), 1.38 – 1.25 (m, 16H), 0.97 – 0.84 (m, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 183.22, 165.82, 47.83, 44.98, 28.93, 28.70, 28.52, 26.81, 22.27 (d, *J* = 11.3 Hz), 13.87 (t, *J* = 1.9 Hz). **HRMS** (ESI) *m/z* calcd for $C_{23}H_{44}N_2O_3$ $[M + H]^+$, 397.3430, found 397.3381. **GC-MS** (EI, 70 eV) *m/z* (%) 396 (82, M^+), 368 (8), 297 (22), 185 (100), 156 (98). **IR** (cm^{-1}) 2930, 2957, 2861, 1715, 1638, 1462.

N^1,N^1,N^3,N^3-tetrahexyl-2-oxomalonamide (3e), 40%, 24 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.31 (dd, *J* = 15.8, 8.6 Hz, 8H), 1.57 (dd, *J* = 24.3, 10.8 Hz, 8H), 1.25 (s, 24H), 0.83 (t, *J* = 6.3 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 183.30, 165.86, 47.88, 45.03, 31.34 (d, *J* = 10.4 Hz), 28.82, 27.10, 26.46, 26.26, 22.44, 13.86 (d, *J* = 2.2 Hz). **HRMS** (ESI) *m/z* calcd for $C_{27}H_{52}N_2O_3$ $[M + H]^+$, 453.4056, found 453.4009. **GC-MS** (EI, 70 eV) *m/z* (%) 452 (8, M^+), 212 (85), 184 (45), 128 (14), 85 (92), 43 (100). **IR** (cm^{-1}) 2956, 2928, 2858, 1715, 1638, 1464.

N^1,N^1,N^3,N^3-tetraoctyl-2-oxomalonamide (3f), 26%, 24 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21 – 5.09 (m, 2H), 3.35 – 3.21 (m, 4H), 3.20 – 3.05 (m, 4H), 1.28 (dd, *J* = 23.1, 8.5 Hz, 48H), 0.85 (t, *J* = 6.4 Hz, 10H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.96, 162.02, 69.86, 48.02, 44.44, 31.69 (d, *J* = 4.9 Hz), 29.15 (dd, *J* = 9.5, 3.9 Hz), 28.68, 27.13, 26.75 (d, *J* = 17.8 Hz), 22.55 (d, *J* = 2.8 Hz), 21.53, 13.99 (d, *J* = 2.4 Hz). **HRMS** (ESI) *m/z* calcd for $C_{35}H_{68}N_2O_3$ $[M + H]^+$, 565.5308, found 565.5252. **IR** (cm^{-1}) 2953, 2925, 2856, 1735, 1657, 1464.

N^1,N^1,N^3,N^3-tetraisobutyl-2-oxomalonamide (3g), 41%, 16 h.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.26 (dd, *J* = 15.8, 7.7 Hz, 8H), 2.10 – 1.99 (m, 4H), 0.93 (dd, *J* = 6.7, 3.3 Hz, 24H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 181.77, 165.70, 53.56, 50.48, 26.03, 25.10, 18.90 (d, *J* = 19.0 Hz). **HRMS** (ESI) *m/z* calcd for $C_{19}H_{36}N_2O_3$ $[M + H]^+$, 341.2804, found 341.2769. **GC-MS** (EI, 70 eV) *m/z* (%) 340 (44, M^+), 355 (10), 156 (100), 128 (96), 100 (100), 57 (98). **IR** (cm^{-1}) 2962, 2931, 2873, 1717, 1636, 1467.

N^1,N^1,N^3,N^3-tetraisopropyl-2-oxomalonamide (3h), 25%, 16 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.09 (dq, *J* = 13.3, 6.7 Hz, 2H), 3.52 (dp, *J* = 13.6, 6.9 Hz, 2H), 1.44 (d, *J* = 6.9 Hz, 12H), 1.25 (d, *J* = 6.6 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.65, 166.23, 50.38, 46.03, 20.63, 20.07. **HRMS** (ESI) *m/z* calcd for $C_{15}H_{28}N_2O_3$ $[M + H]^+$, 285.2178, found 285.2143. **GC-MS** (EI, 70 eV) *m/z* (%) 284 (3, M^+), 213 (22), 128 (48), 86 (100), 43 (63). **IR** (cm^{-1}) 2976, 2929, 2857, 1707, 1638, 1450.

N^1-ethyl-N^1,N^3,N^3-triisopropyl-2-oxomalonamide (3i), 14%, 16 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.42 – 4.04 (m, 2H), 3.55 – 3.30 (m, 3H), 1.43 (d, *J* = 6.8 Hz, 5H), 1.31 – 1.10 (m, 16H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 182.42, 166.10 (d, *J* = 17.2 Hz), 50.45 (d, *J* = 5.0 Hz), 49.67, 46.88, 46.04, 39.07, 35.32, 29.63, 21.19, 20.54 (d, *J* = 1.9 Hz), 20.07 (d, *J* = 5.4 Hz), 16.64, 14.28. **HRMS** (ESI) *m/z* calcd for $C_{14}H_{26}N_2O_3$ $[M + H]^+$, 271.2021, found 271.2004. **GC-MS** (EI, 70 eV) *m/z* (%) 270 (2, M^+), 199 (10), 125 (39), 86 (89), 43 (100). **IR** (cm^{-1}) 2976, 2936, 2856, 1710, 1635, 1450.

N^1,N^3-diethyl-N^1,N^3-dimethyl-2-oxomalonamide (3j), 17%, 24 h.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.47 (dqd, *J* = 14.2, 7.2, 1.6 Hz, 4H), 3.12 – 2.88 (m, 6H), 1.28 (t, *J* = 7.1 Hz, 4H), 1.20 (td, *J* = 7.2, 1.1 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 183.20, 165.70, 165.25, 44.85 (d, *J* = 5.5 Hz), 41.96 (d, *J* = 5.7 Hz), 34.43 (d, *J* = 5.6 Hz), 31.63 (d, *J* = 5.3 Hz), 13.60, 11.73. **HRMS** (ESI) *m/z* calcd for $C_9H_{16}N_2O_3$ $[M + H]^+$, 201.1239, found 201.1216. **GC-MS** (EI, 70 eV) *m/z* (%) 200 (22, M^+), 172 (3), 144 (10), 86 (80), 59 (100). **IR** (cm^{-1}) 2975, 2938, 2858, 1717, 1634, 1449.

N^1,N^1,N^3-triethyl-N^3-methyl-2-oxomalonamide (3k), 11%, 24 h.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.47 (dtt, *J* = 9.2, 7.0, 4.6 Hz, 6H), 3.05 (d, *J* = 53.5 Hz, 3H), 1.29 – 1.27 (m, 6H), 1.22 – 1.20 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 183.29, 165.83, 165.53, 44.78, 42.35 (d, *J* = 6.6 Hz), 41.90, 39.50 (d, *J* = 5.3 Hz), 34.35, 31.87, 31.53, 14.26, 13.52, 12.48, 11.66. **HRMS** (ESI) *m/z* calcd for $C_{10}H_{18}N_2O_3$ $[M + H]^+$, 215.1395, found 215.1373. **GC-MS** (EI, 70 eV) *m/z* (%) 214 (16, M^+), 186 (4), 158 (4), 100 (100), 72 (95). **IR** (cm^{-1}) 2973, 2927, 2855, 1716, 1639, 1461.

N^1,N^1-diethyl-2-oxo-N^3,N^3-dipropylmalonamide (3ab), 32%, 24 h.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.49 – 3.42 (m, 4H), 3.39 – 3.31 (m, 4H), 1.68 (ddq, *J* = 33.4, 14.9, 7.5 Hz, 4H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 0.92 (dt, *J* = 9.5, 7.4 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 183.17, 165.99, 165.59, 49.44, 46.54, 42.34, 39.49, 22.09, 20.46, 14.30, 12.52, 11.23, 10.98. **HRMS** (ESI) *m/z* calcd for $C_{13}H_{24}N_2O_3$ $[M + H]^+$, 257.1865, found 257.1849. **GC-MS** (EI, 70 eV) *m/z* (%) 256 (94, M^+), 228 (35), 199 (24), 129 (100), 101 (100). **IR** (cm^{-1}) 2969, 2936, 2877, 1715, 1634, 1460.

N^1,N^1-diethyl-2-oxo-N^3,N^3-dipentylmalonamide (3ad), 26%, 24 h.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.53 – 3.25 (m, 8H), 1.71 – 1.59 (m, 4H), 1.34 – 1.21 (m, 14H), 0.90 (td, *J* = 6.8, 3.2 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 183.32, 165.76 (d, *J* = 23.9 Hz), 47.91, 45.06, 42.31, 39.44, 28.98, 28.74, 28.55, 26.84, 22.27 (d, *J* = 9.7 Hz), 14.26, 13.87 (d, *J* = 2.5 Hz), 12.50. **HRMS** (ESI) *m/z* calcd for $C_{17}H_{32}N_2O_3$ $[M + H]^+$, 313.2491, found 313.2474. **GC-MS** (EI, 70 eV) *m/z* (%) 312 (80, M^+), 284 (18), 255 (15), 185 (100), 156 (98). **IR** (cm^{-1}) 2957, 2928, 2858, 1716, 1638, 1462.

N^1,N^1,N^3,N^3-tetraethyl-2-hydroxymalonamide (4a), 84%, 24 h.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.87 (d, *J* = 4.7 Hz, 1H), 4.77 (d, *J* = 5.6 Hz, 1H), 3.49 – 3.26 (m, 8H), 1.23 – 1.14 (m, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.80, 69.65, 41.31, 40.58, 13.85, 12.50. **HRMS** (ESI) *m/z* calcd for $C_{11}H_{22}N_2O_3$ $[M + H]^+$, 231.1708, found 231.1691. **GC-MS** (EI, 70 eV) *m/z* (%) 230 (70, M^+), 201 (16), 173 (22), 157 (68), 131 (100), 101 (100). **IR** (cm^{-1}) 3363, 2974, 2936, 2876, 1634.

N^1,N^1,N^2,N^2-tetraethyloxalamide (5a)[2]**,** 67%, 16 h.

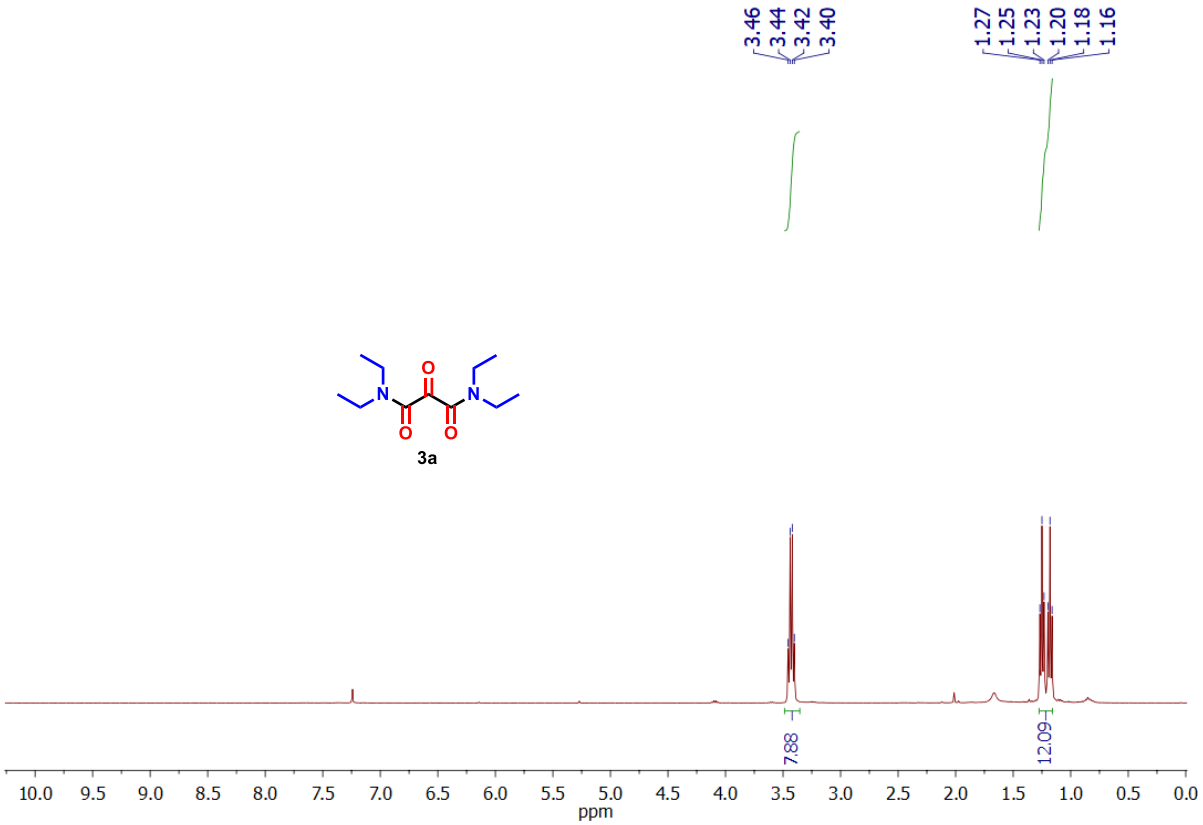
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.45 (q, *J* = 7.2 Hz, 4H), 3.29 (q, *J* = 7.1 Hz, 4H), 1.25 – 1.16 (m, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.64, 42.23, 38.22, 13.89, 12.48. **GC-MS** (EI, 70 eV) *m/z* (%) 200 (64, M^+), 171 (12), 101 (100), 72 (100).

ethyl 2-(diethylamino)-2-oxoacetate (6a)[3]**,** 65%, 24 h.

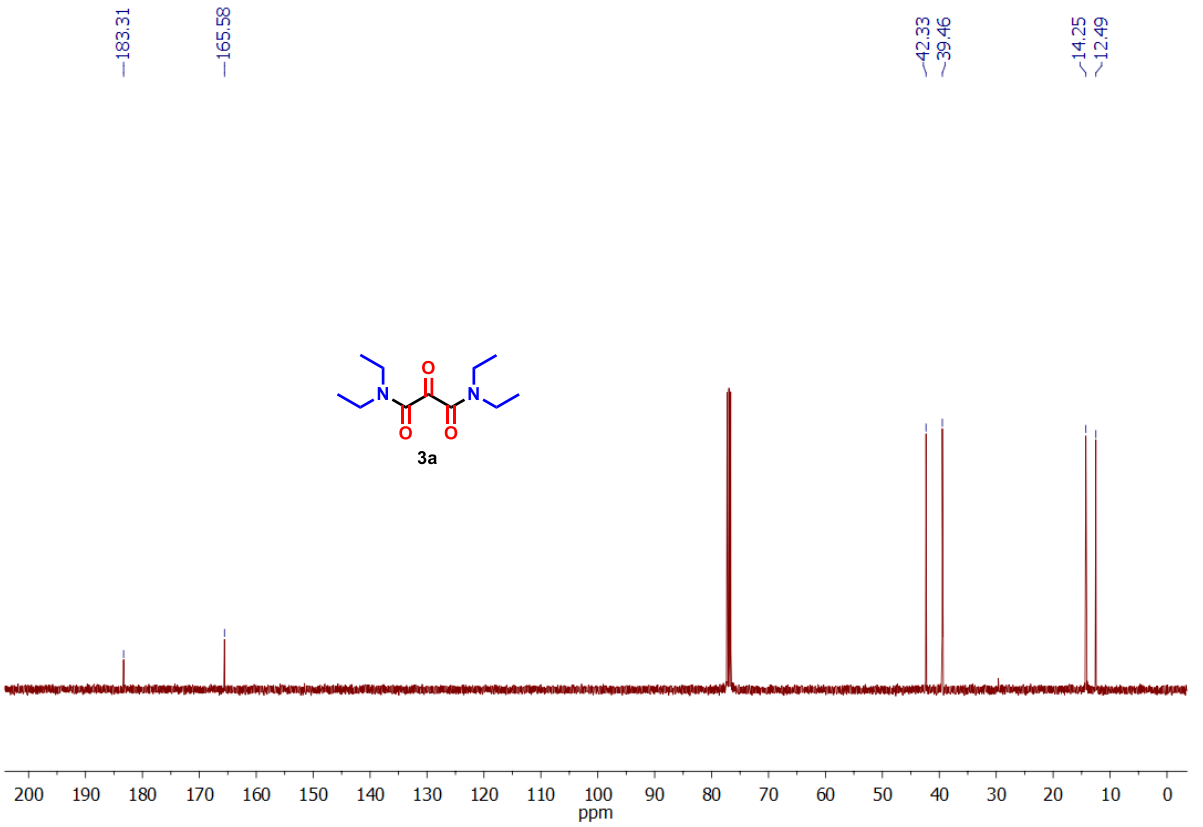
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.34 (q, *J* = 7.1 Hz, 2H), 3.47 – 3.41 (m, 2H), 3.29 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.23 – 1.17 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.23, 161.46, 61.89, 42.47, 39.03, 14.16, 13.98, 12.51. **GC-MS** (EI, 70 eV) *m/z* (%) 173 (10, M^+), 144 (12), 100 (100), 72 (98).

14. ^{1}H and ^{13}C NMR spectra of products

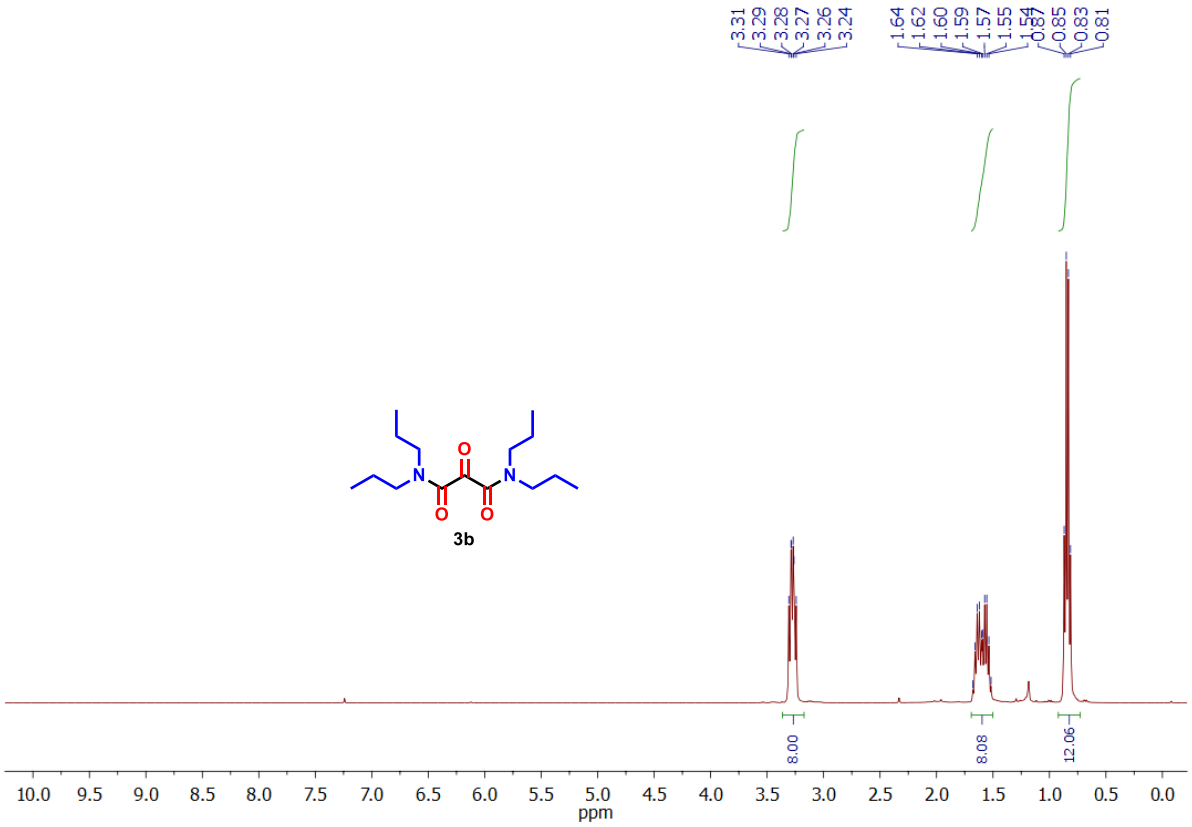
^{1}H NMR of N^1,N^1,N^3,N^3-tetraethyl-2-oxomalonamide (3a)



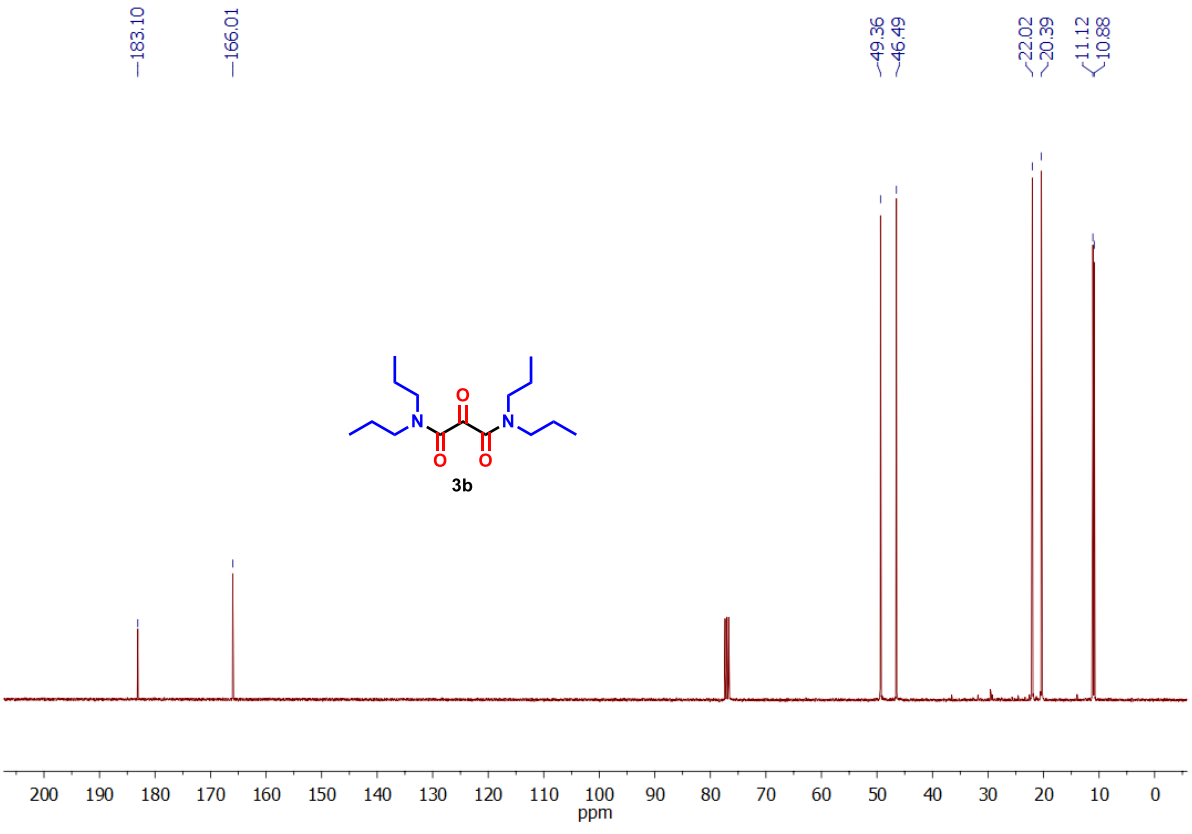
^{13}C NMR of N^1,N^1,N^3,N^3-tetraethyl-2-oxomalonamide (3a)



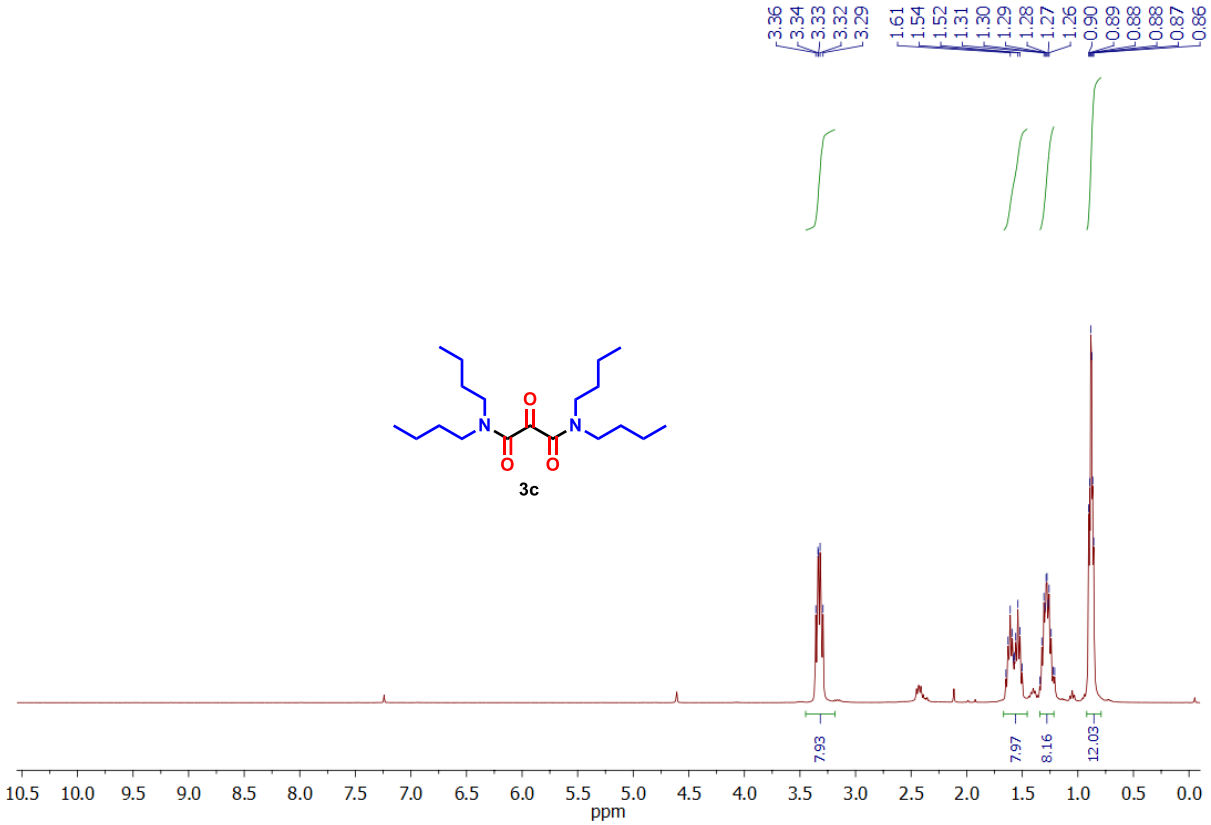
^{1}H NMR of 2-oxo-N^{1},N^{1},N^{3},N^{3}-tetrapropylmalonamide (3b)



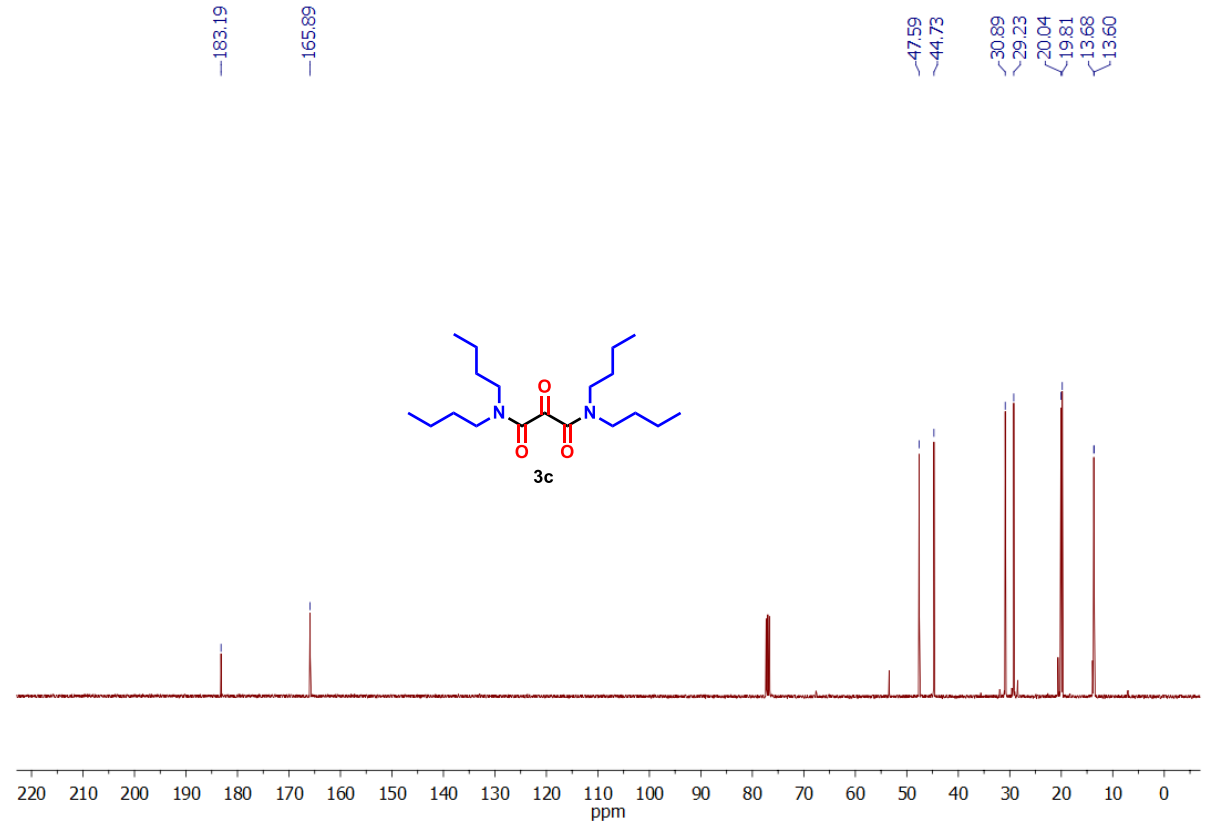
^{13}C NMR of 2-oxo-N^{1},N^{1},N^{3},N^{3}-tetrapropylmalonamide (3b)



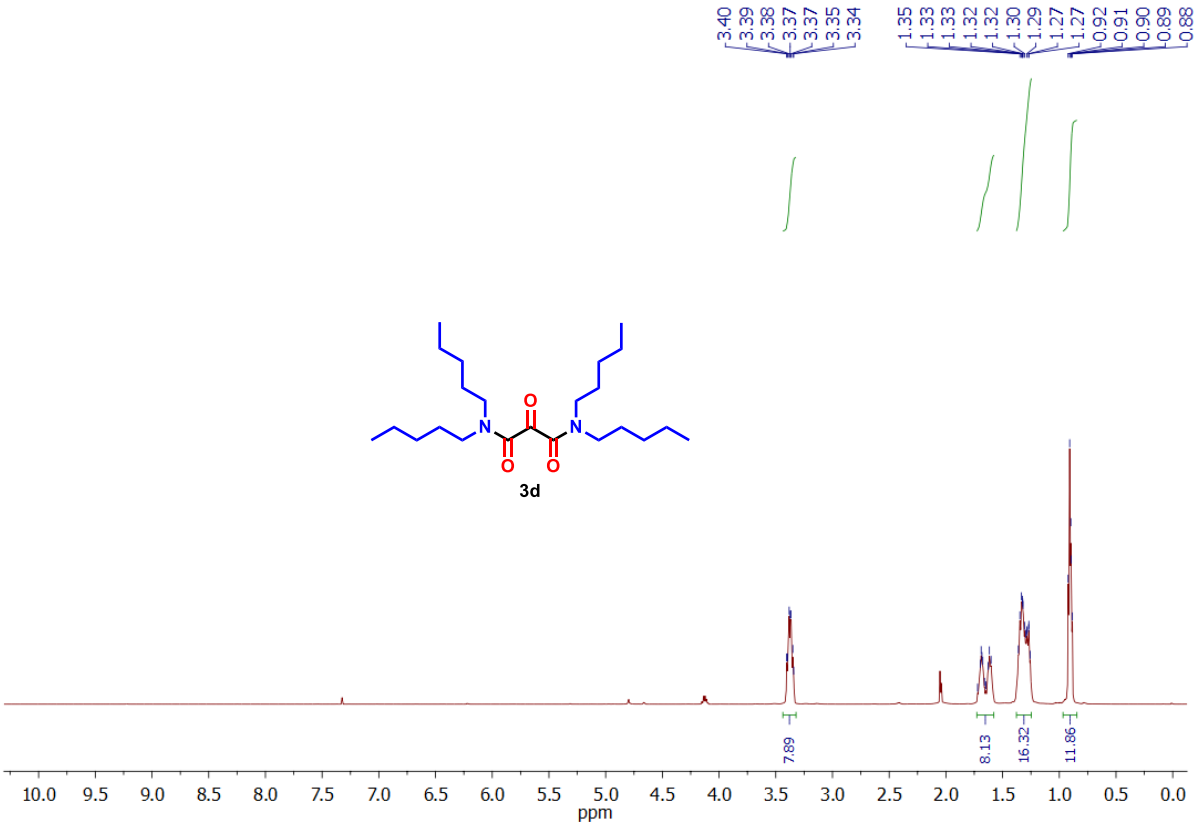
^{1}H NMR of N^1,N^1,N^3,N^3-tetrabutyl-2-oxomalonamide (3c)



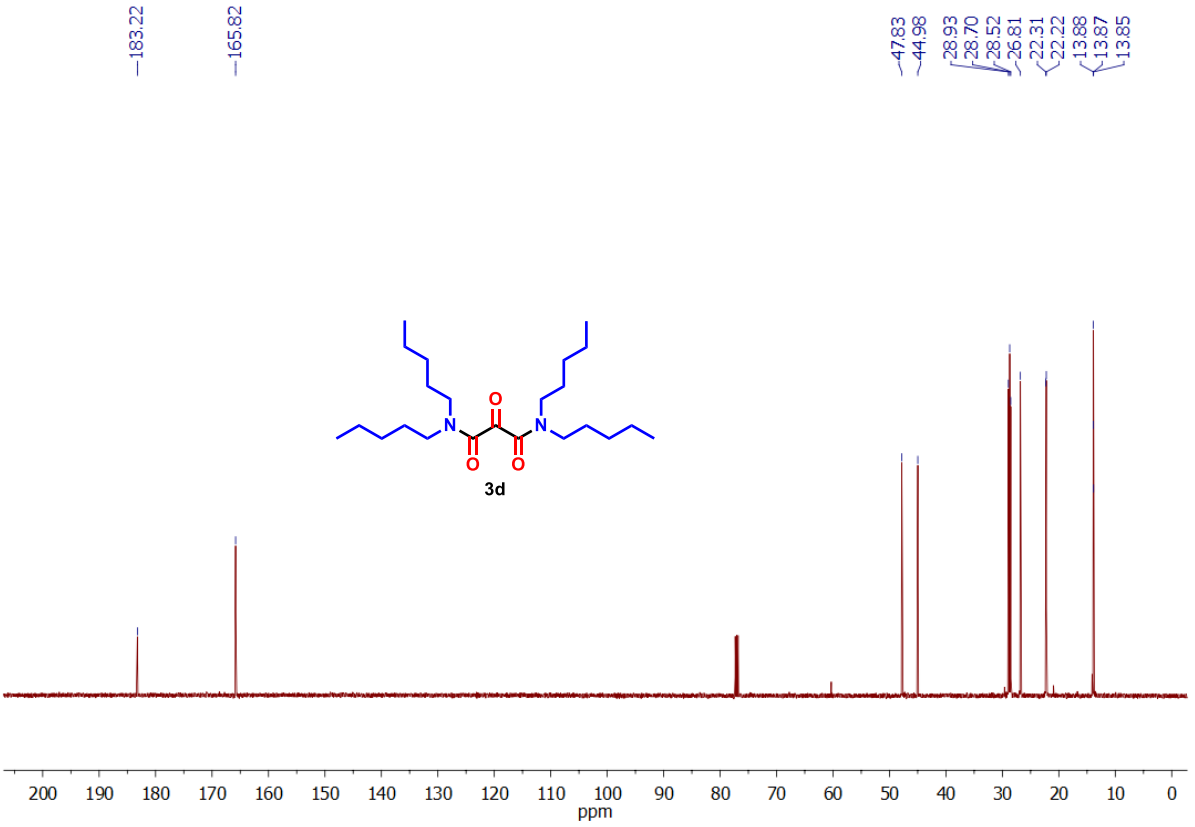
^{13}C NMR of N^1,N^1,N^3,N^3-tetrabutyl-2-oxomalonamide (3c)



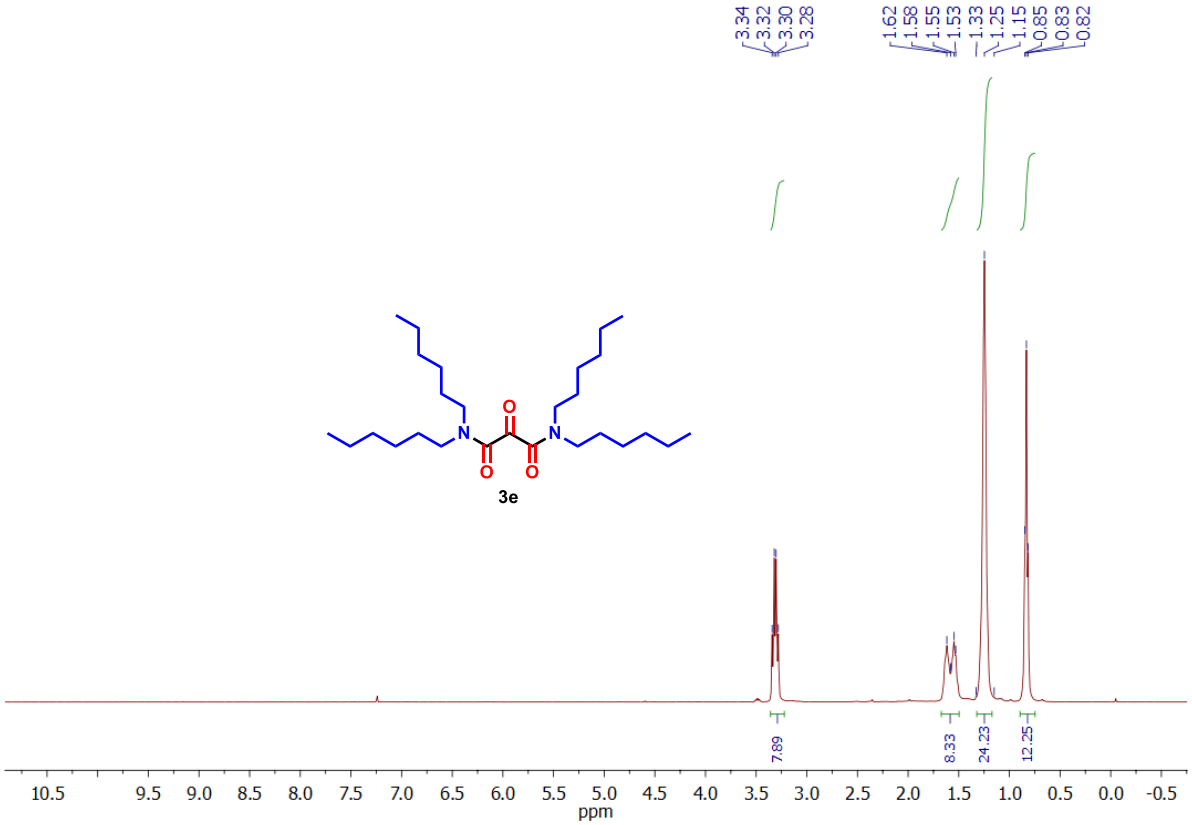
^{1}H NMR of 2-oxo-N^{1},N^{1},N^{3},N^{3}-tetrapentylmalonamide (3d)



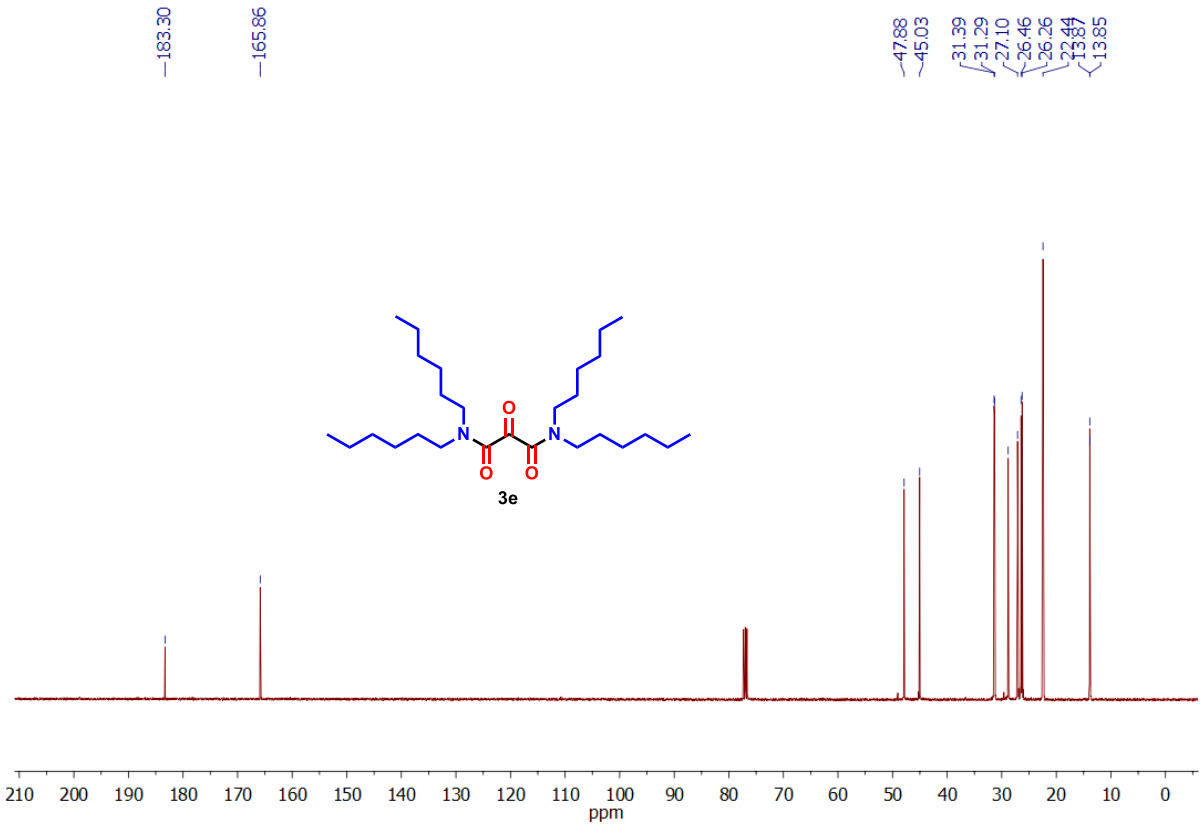
^{13}C NMR of 2-oxo-N^{1},N^{1},N^{3},N^{3}-tetrapentylmalonamide (3d)



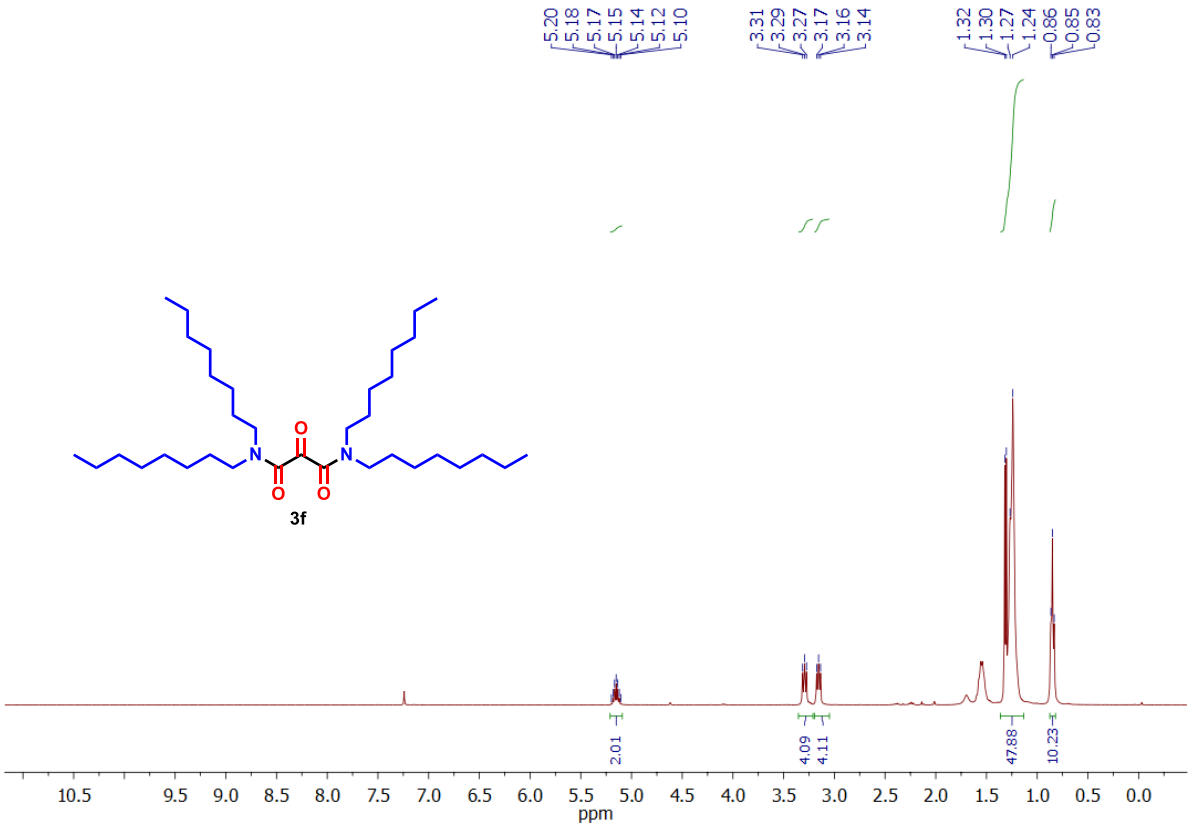
^{1}H NMR of N^1,N^1,N^3,N^3-tetrahexyl-2-oxomalonamide (3e)



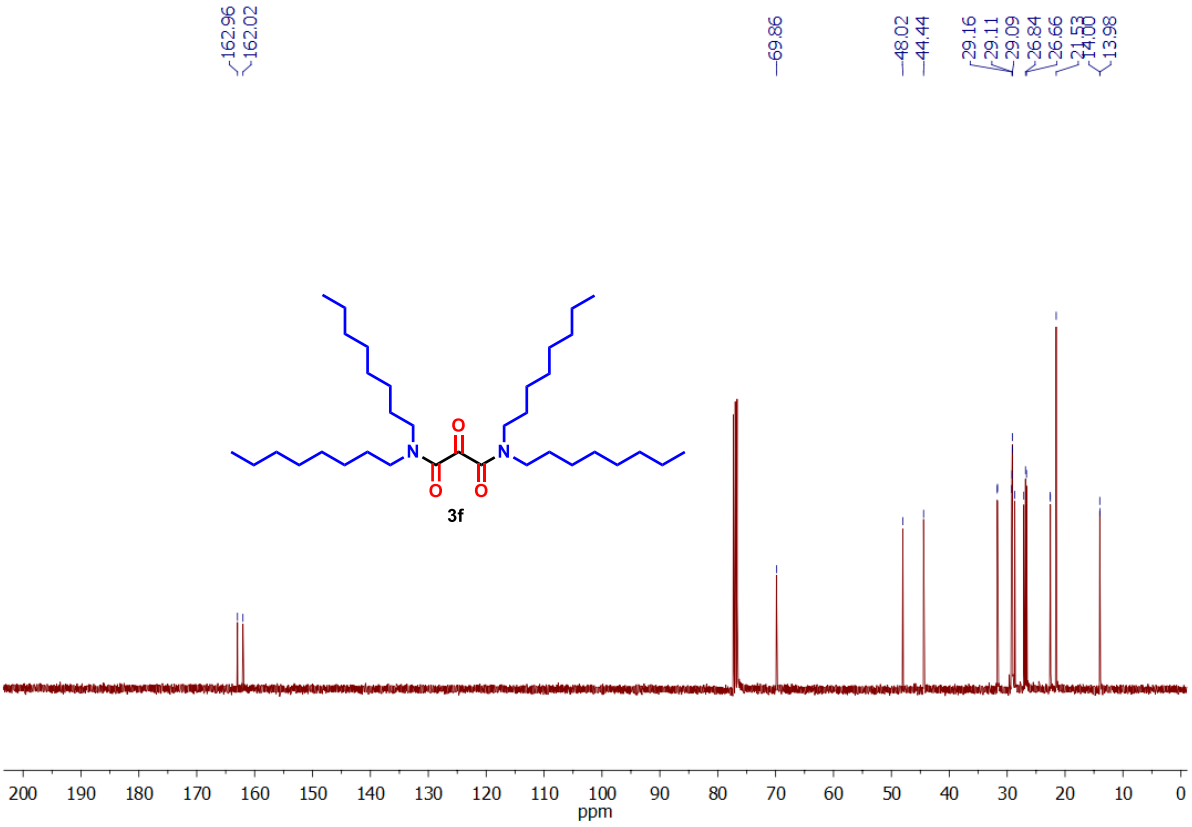
^{13}C NMR of N^1,N^1,N^3,N^3-tetrahexyl-2-oxomalonamide (3e)



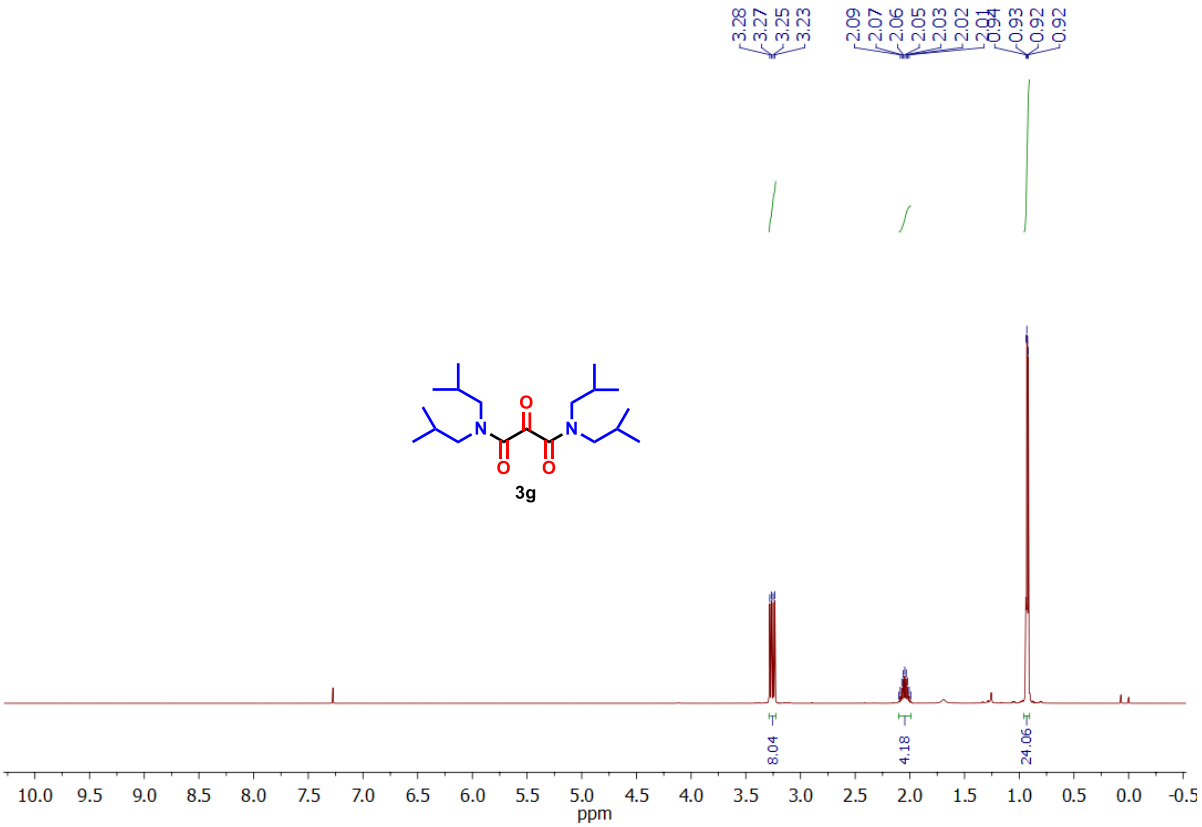
^{1}H NMR of N^{1},N^{1},N^{3},N^{3}-tetraoctyl-2-oxomalonamide (3f)



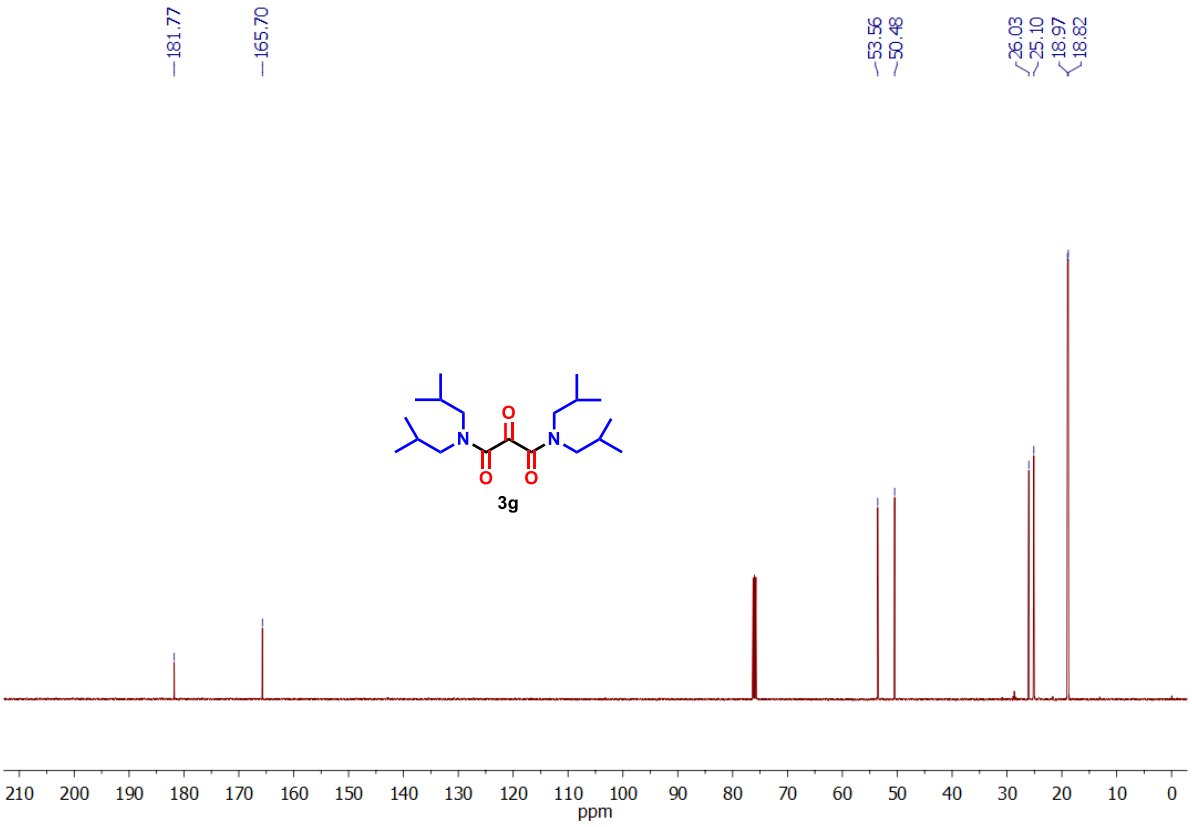
^{13}C NMR of N^{1},N^{1},N^{3},N^{3}-tetraoctyl-2-oxomalonamide (3f)



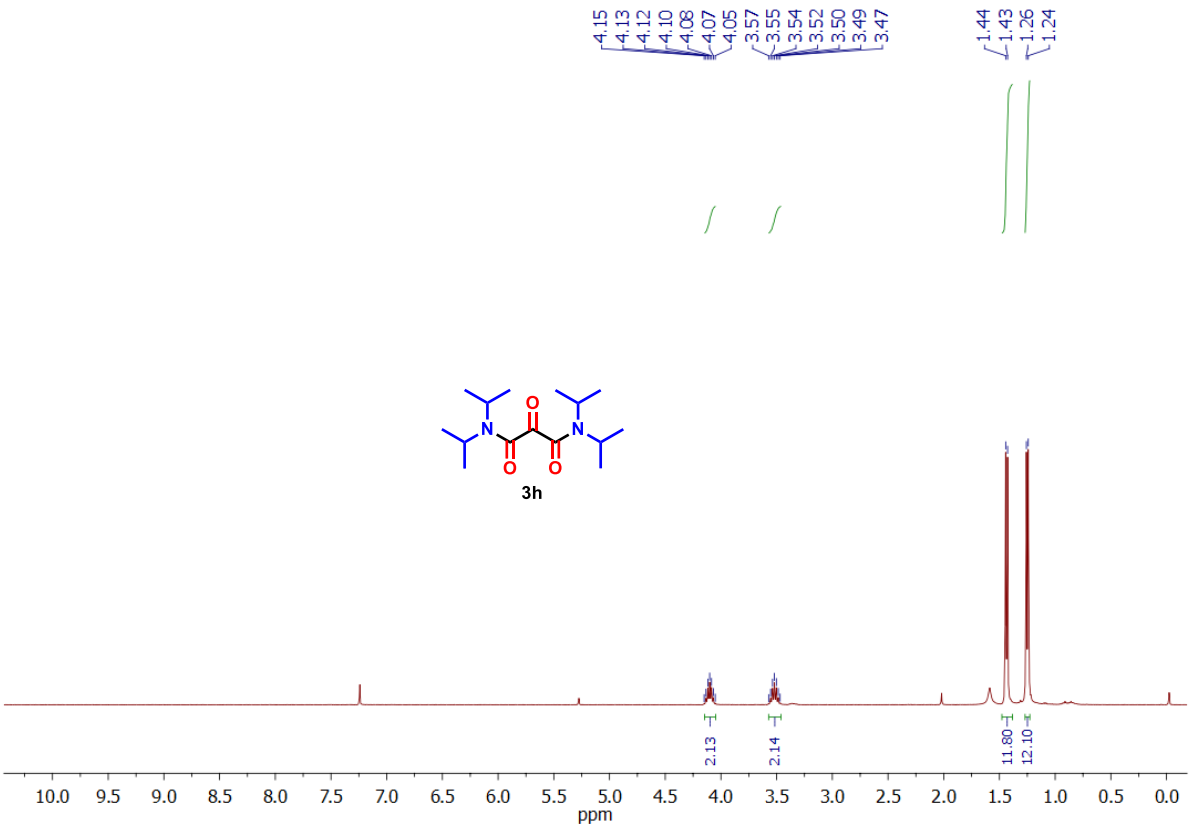
^{1}H NMR of N^1,N^1,N^3,N^3-tetraisobutyl-2-oxomalonamide (3g)



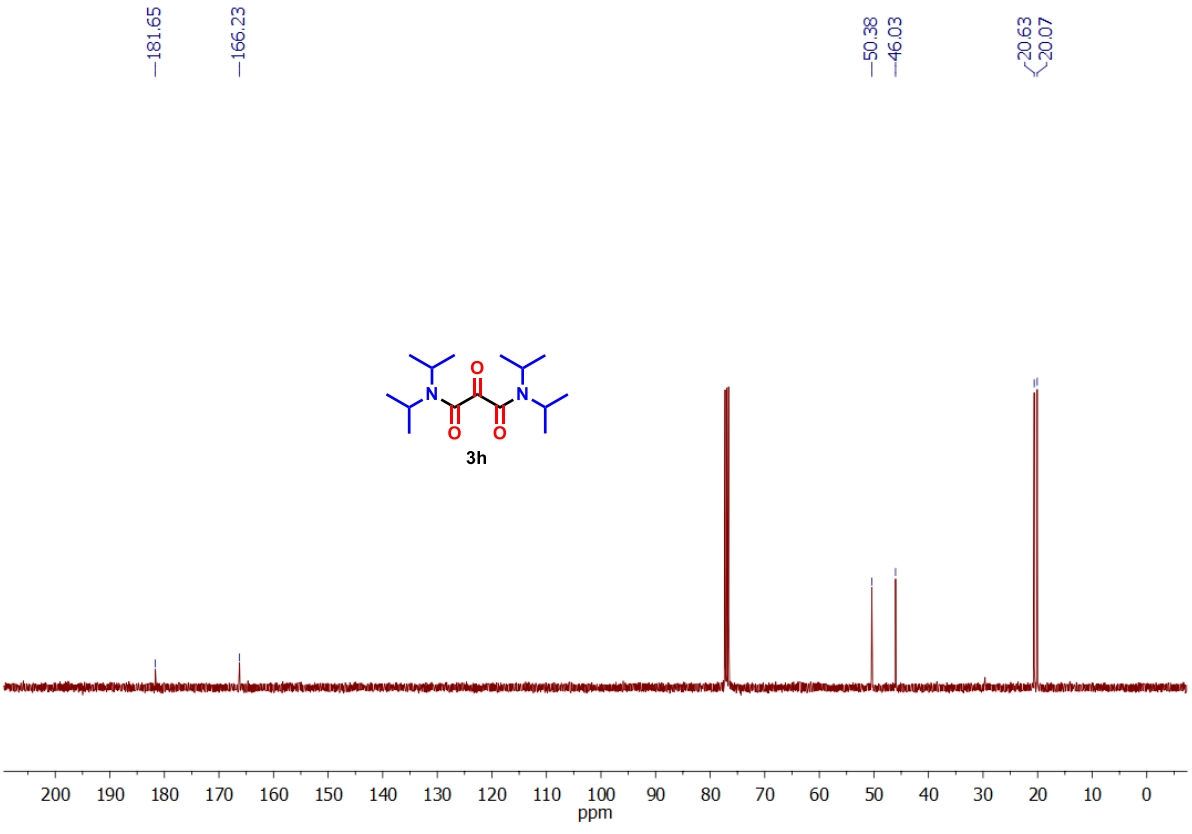
^{13}C NMR of N^1,N^1,N^3,N^3-tetraisobutyl-2-oxomalonamide (3g)



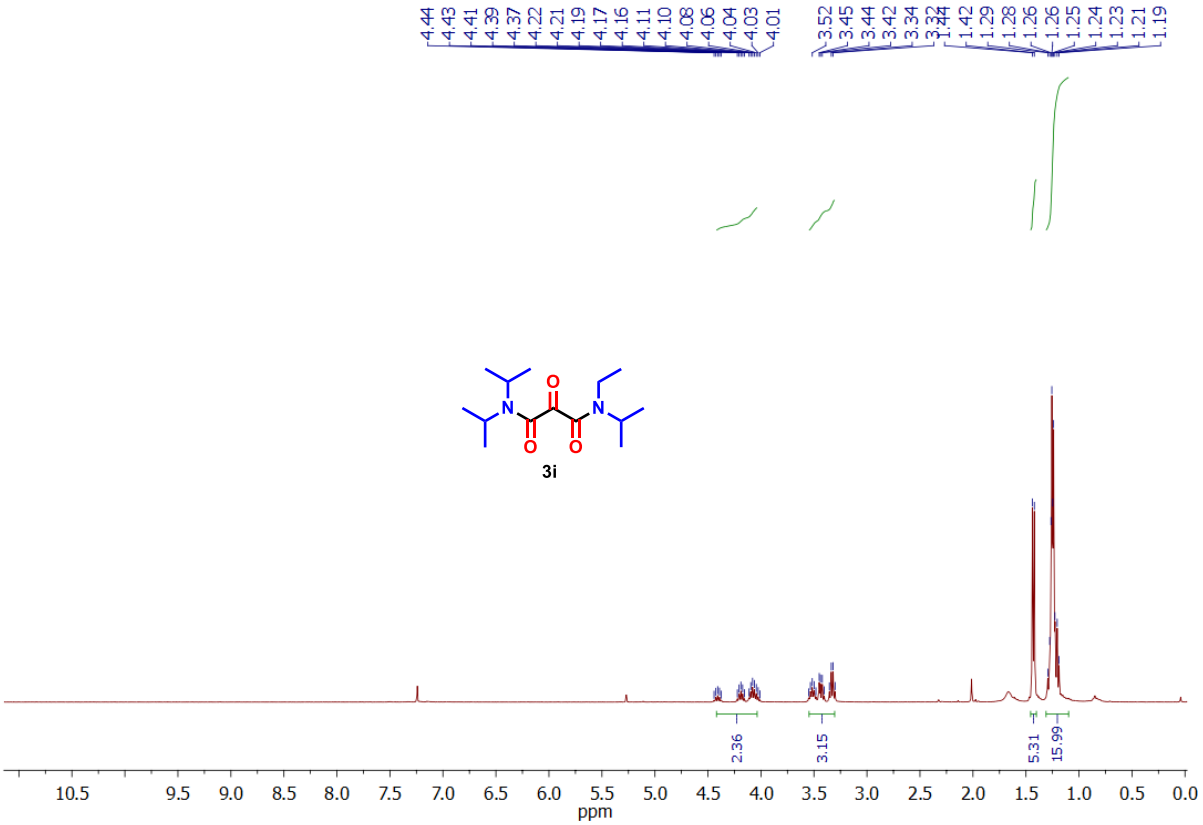
^{1}H NMR of N^1,N^1,N^3,N^3-tetraisopropyl-2-oxomalonamide (3h)



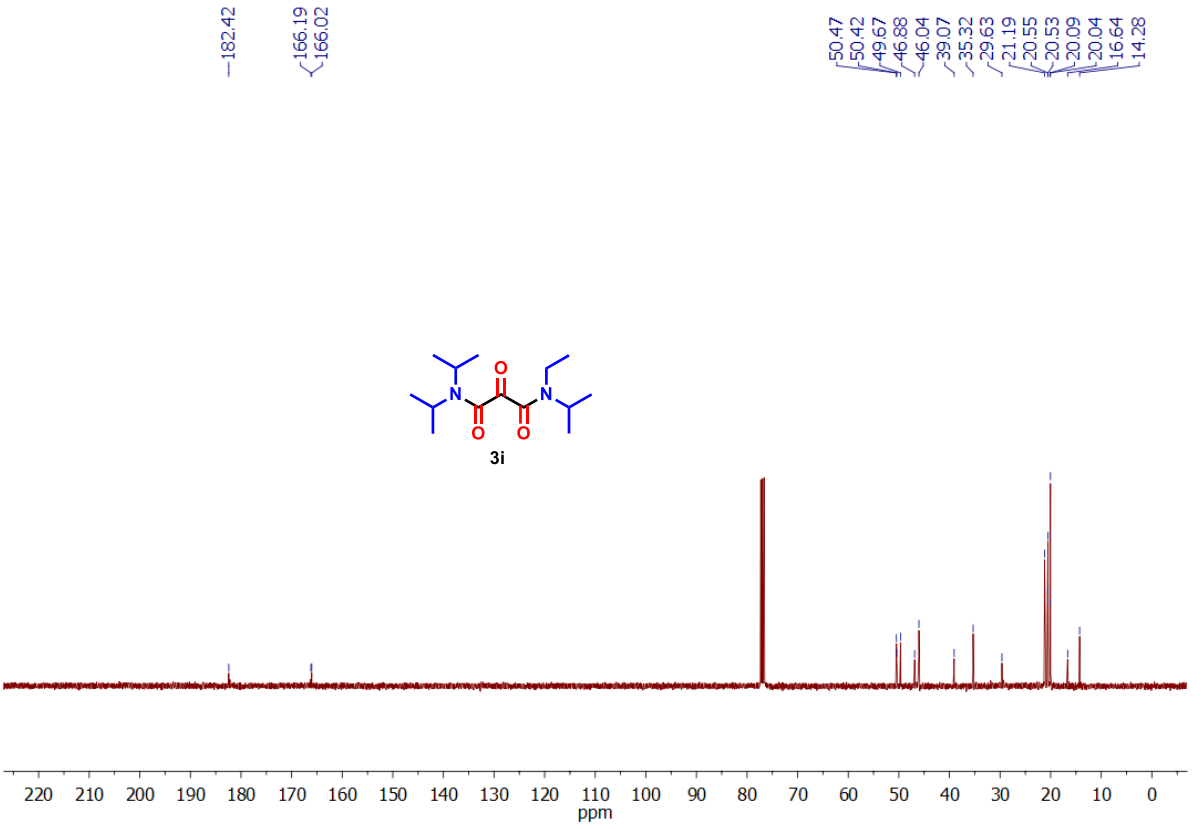
^{13}C NMR of N^1,N^1,N^3,N^3-tetraisopropyl-2-oxomalonamide (3h)



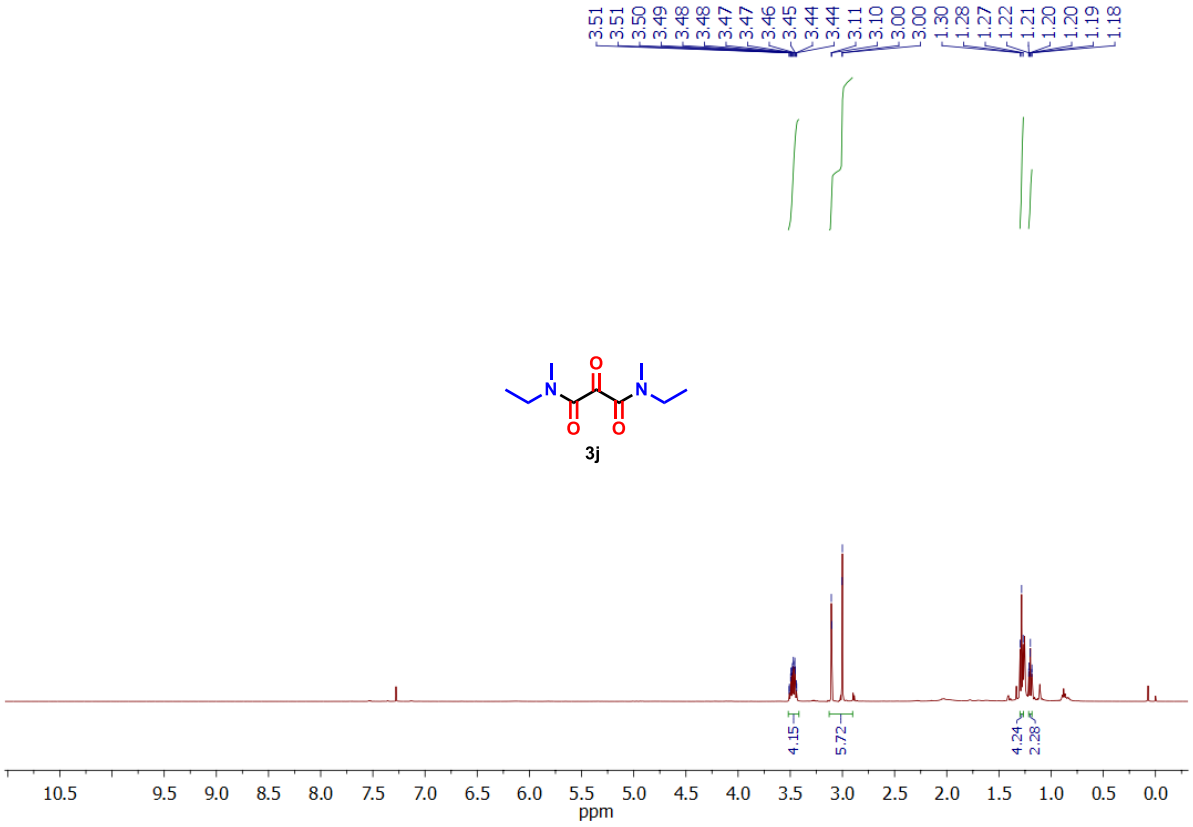
^{1}H NMR of N^{1}-ethyl-N^{1},N^{3},N^{3}-triisopropyl-2-oxomalonamide (3i)



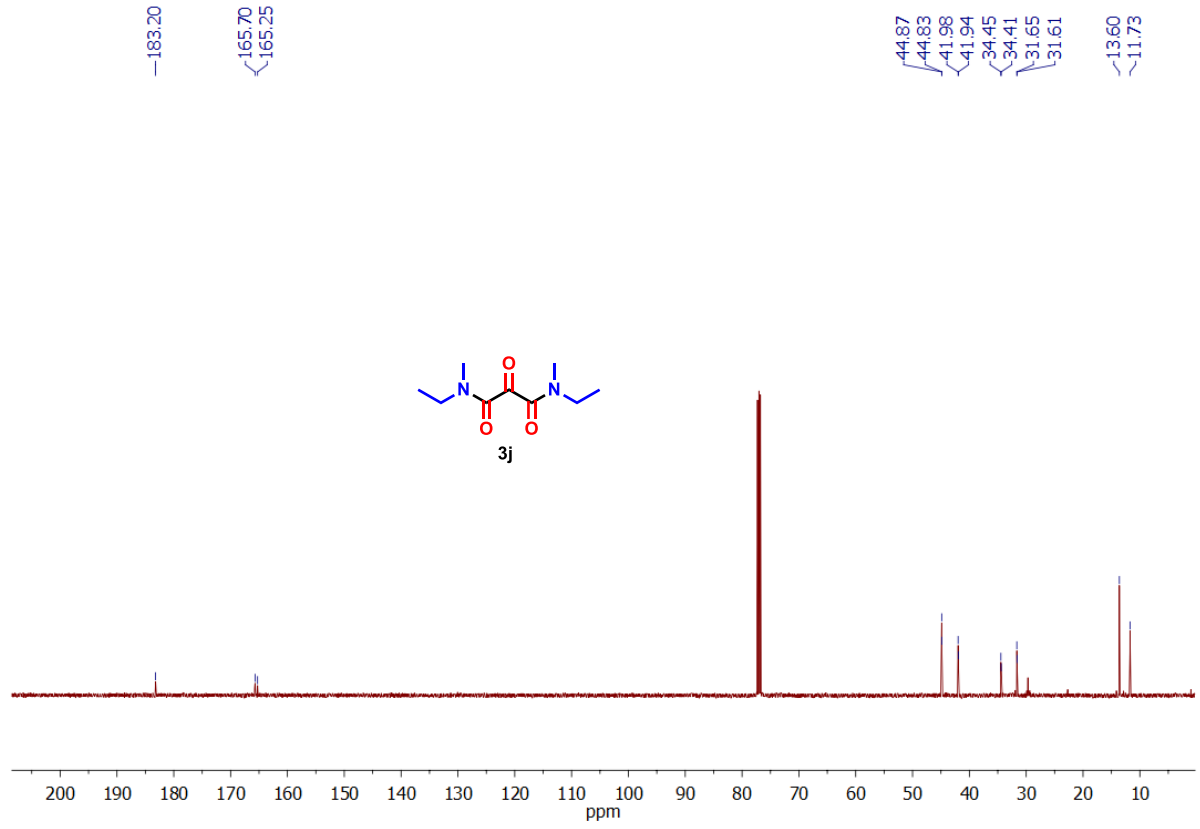
^{13}C NMR of N^{1}-ethyl-N^{1},N^{3},N^{3}-triisopropyl-2-oxomalonamide (3i)



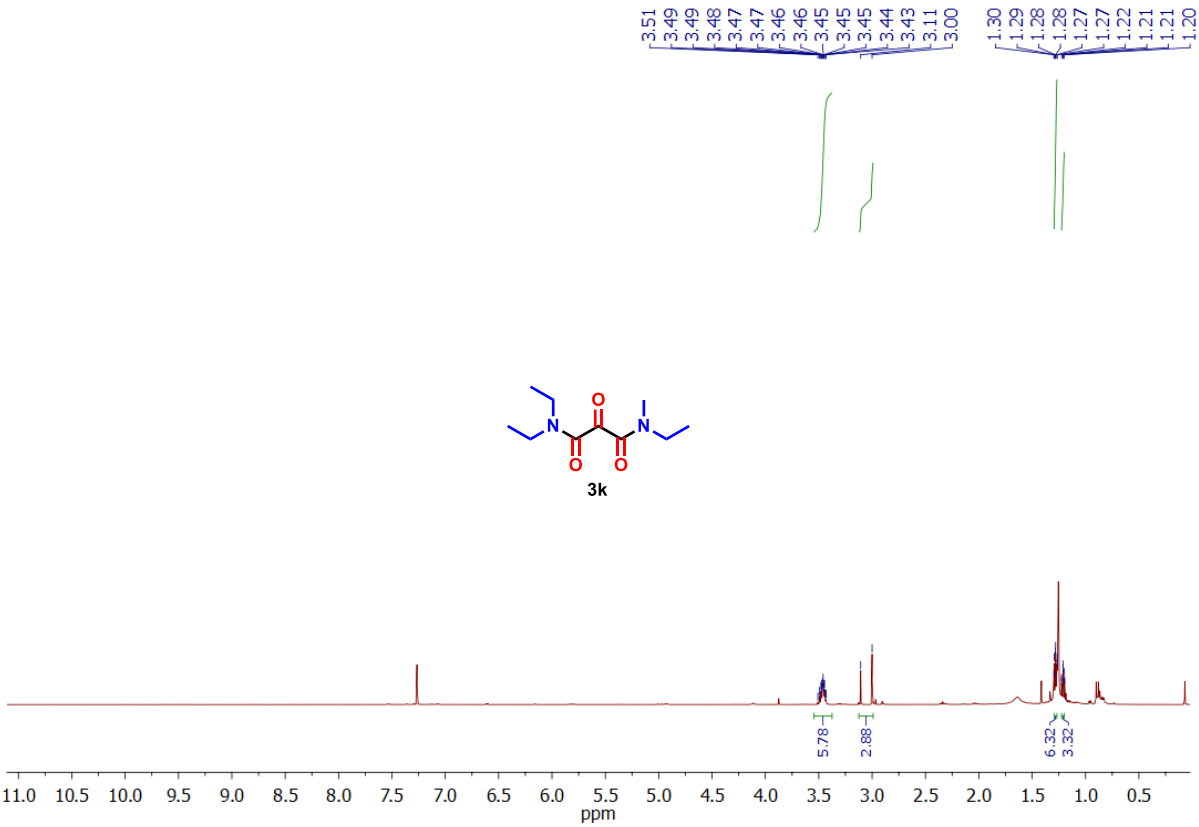
^{1}H NMR of N^{1},N^{3}-diethyl-N^{1},N^{3}-dimethyl-2-oxomalonamide (3j)



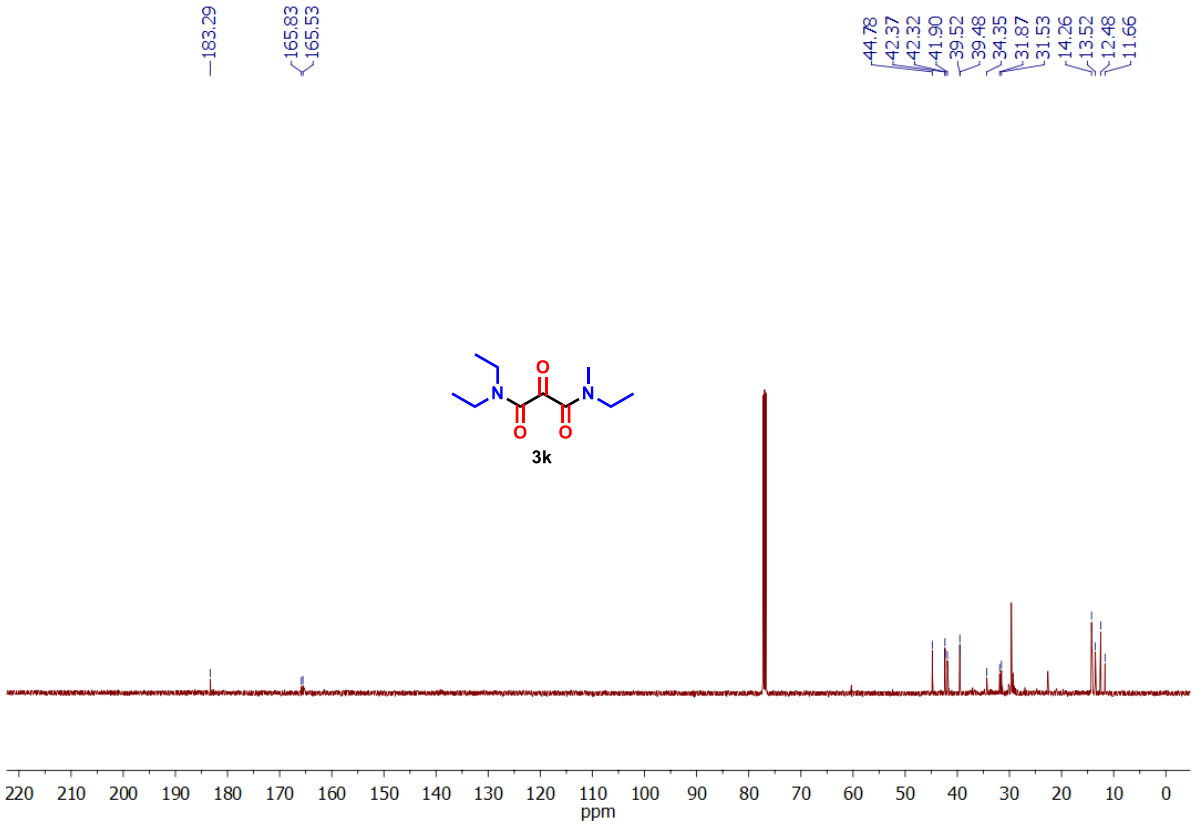
^{13}C NMR of N^{1},N^{3}-diethyl-N^{1},N^{3}-dimethyl-2-oxomalonamide (3j)



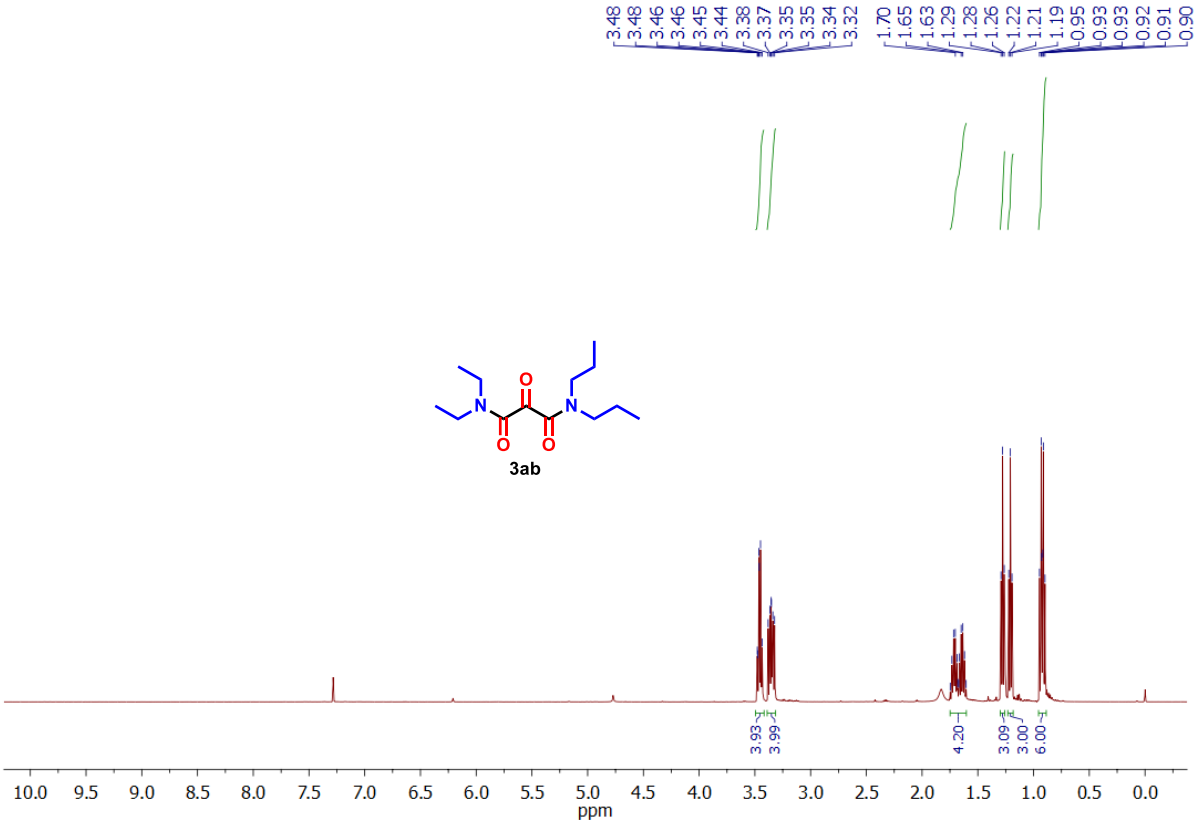
^{1}H NMR of N^{1},N^{1},N^{3}-triethyl-N^{3}-methyl-2-oxomalonamide (3k)



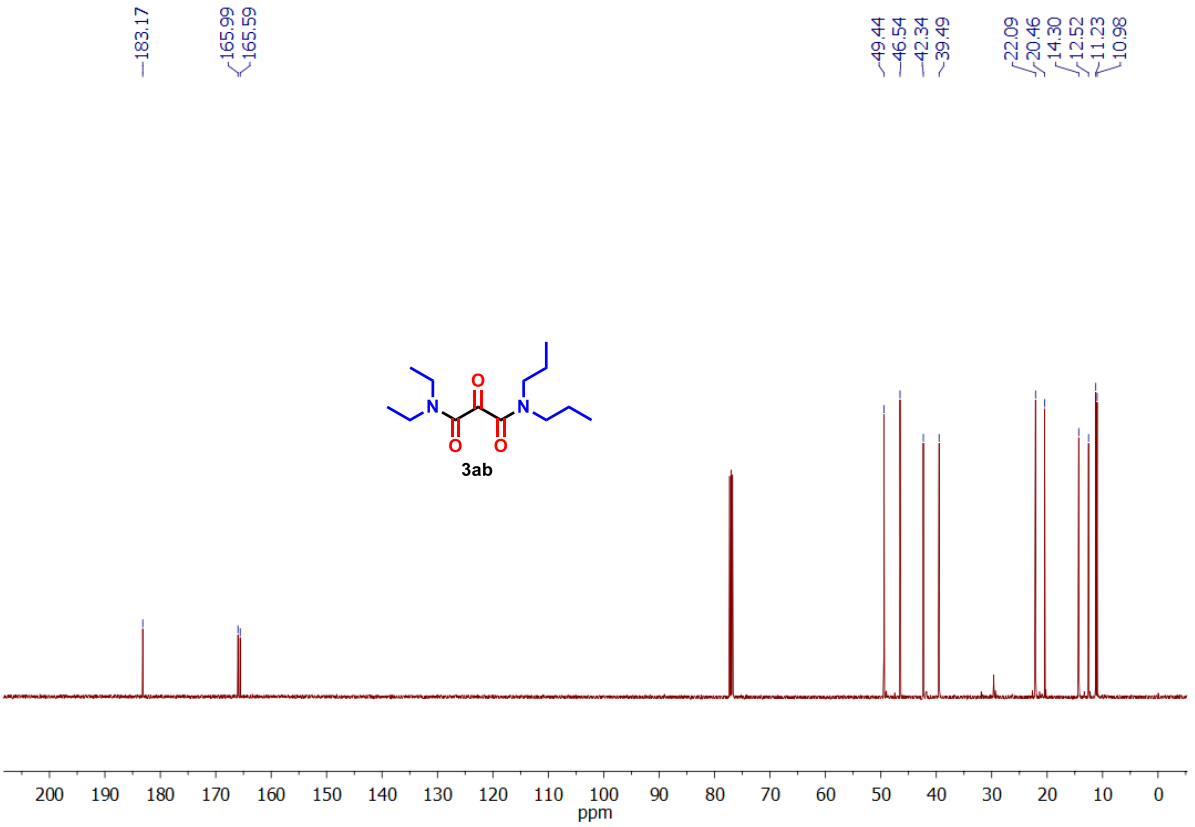
^{13}C NMR of N^{1},N^{1},N^{3}-triethyl-N^{3}-methyl-2-oxomalonamide (3k)



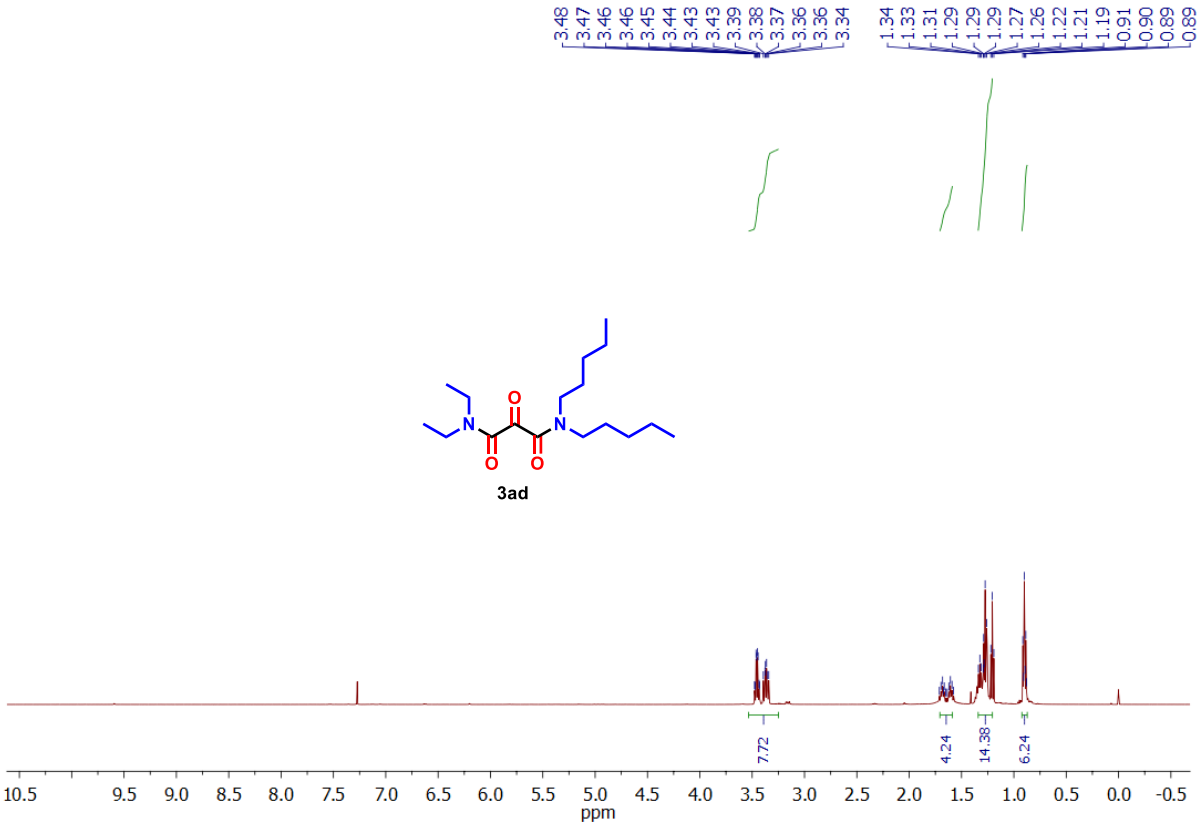
^{1}H NMR of N^{1},N^{1}-diethyl-2-oxo-N^{3},N^{3}-dipropylmalonamide (3ab)



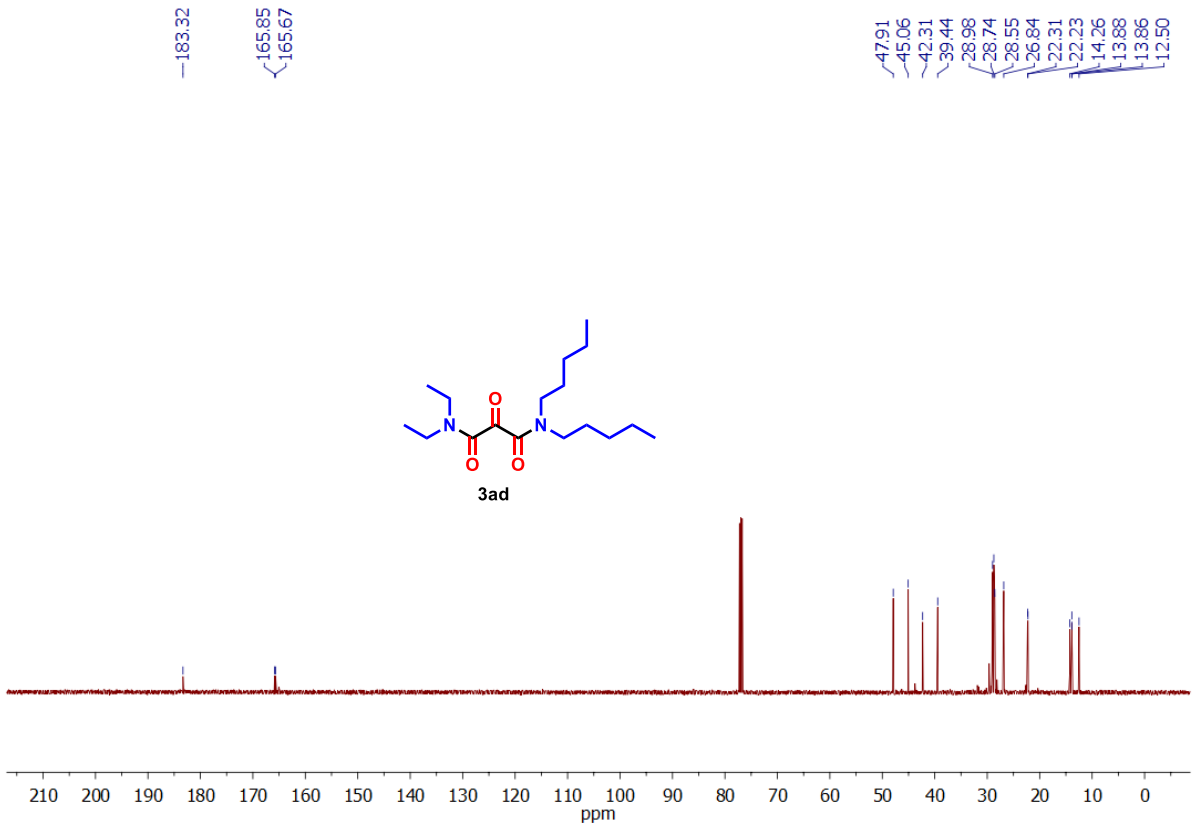
^{13}C NMR of N^{1},N^{1}-diethyl-2-oxo-N^{3},N^{3}-dipropylmalonamide (3ab)



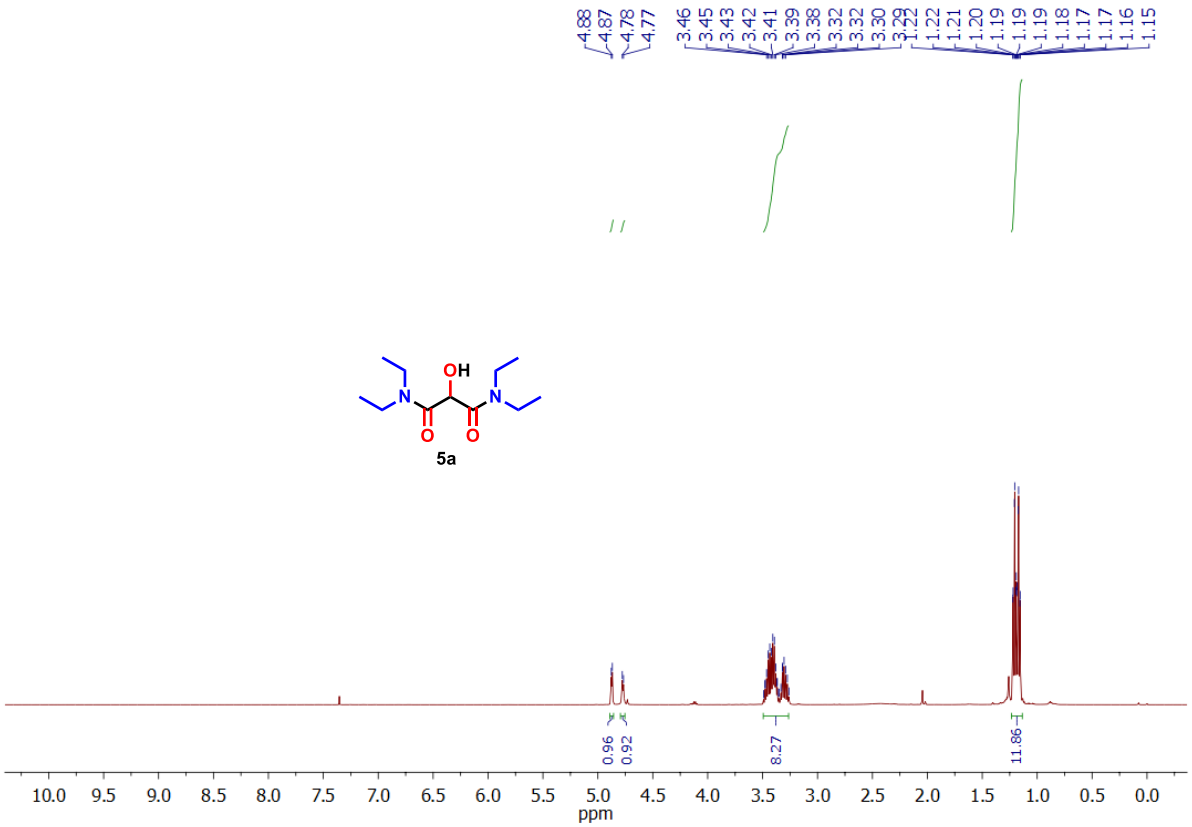
^{1}H NMR of N^{1},N^{1}-diethyl-2-oxo-N^{3},N^{3}-dipentylmalonamide (3ad)



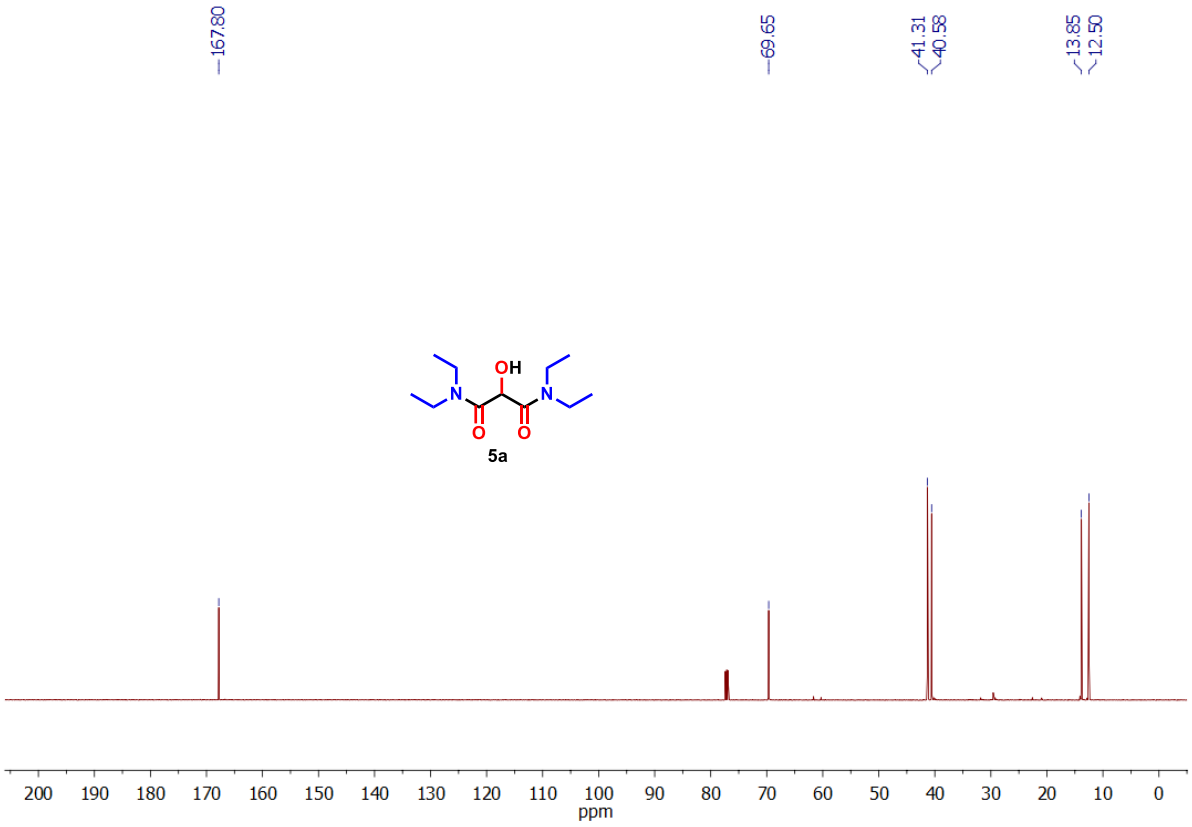
^{13}C NMR of N^{1},N^{1}-diethyl-2-oxo-N^{3},N^{3}-dipentylmalonamide (3ad)



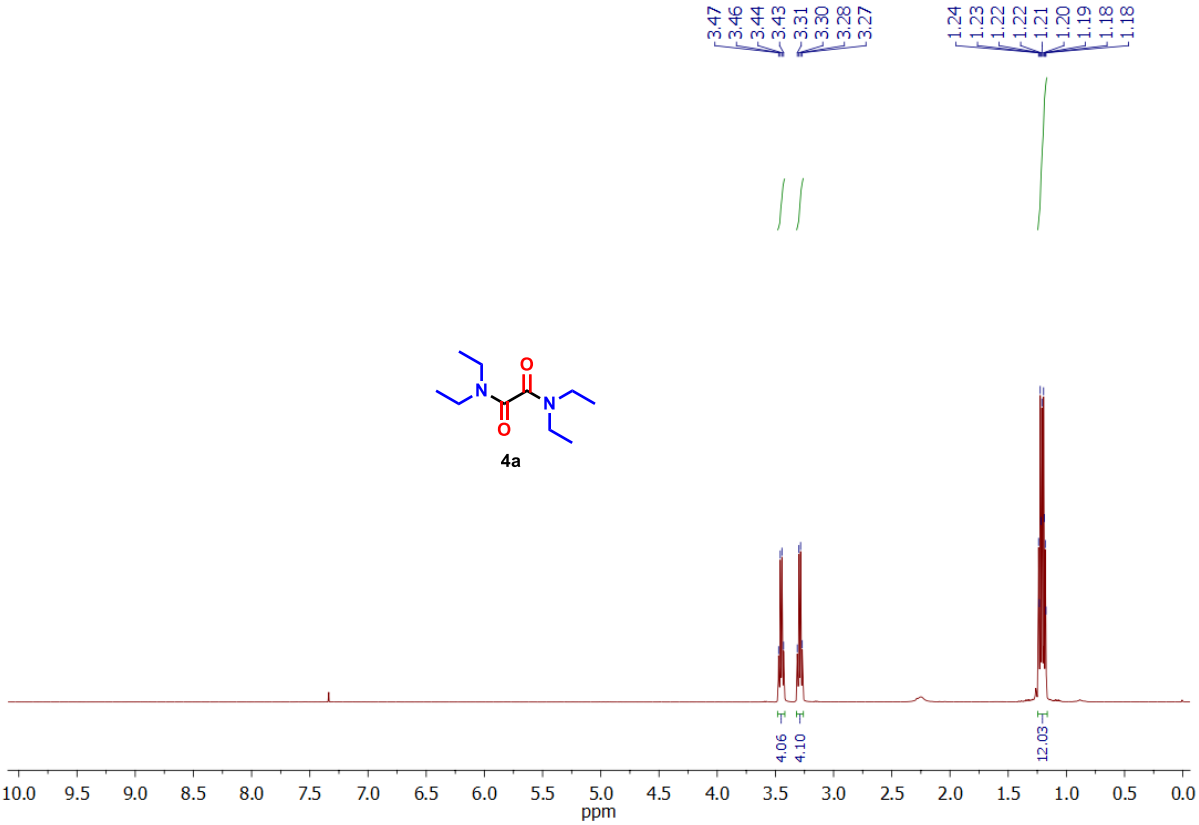
^{1}H NMR of N^{1},N^{1},N^{3},N^{3}-tetraethyl-2-hydroxymalonamide (5a)



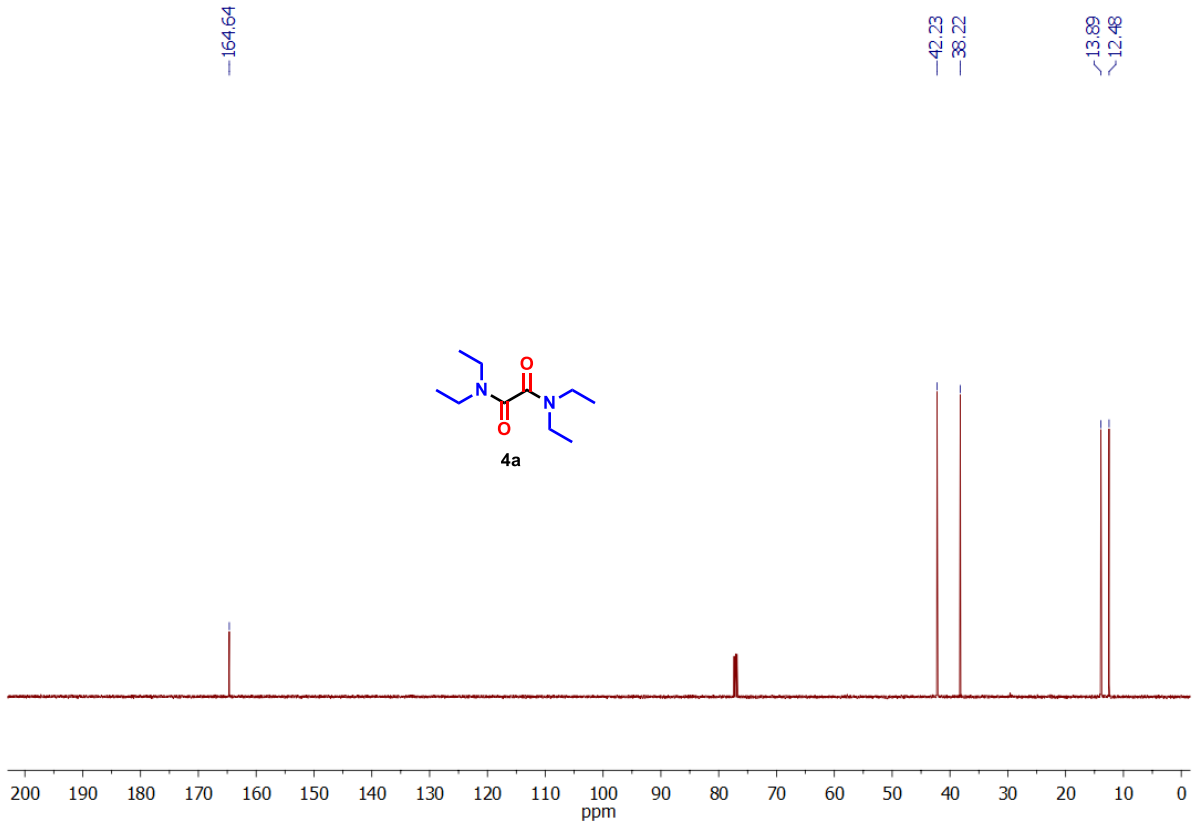
^{13}C NMR of N^{1},N^{1},N^{3},N^{3}-tetraethyl-2-hydroxymalonamide (5a)



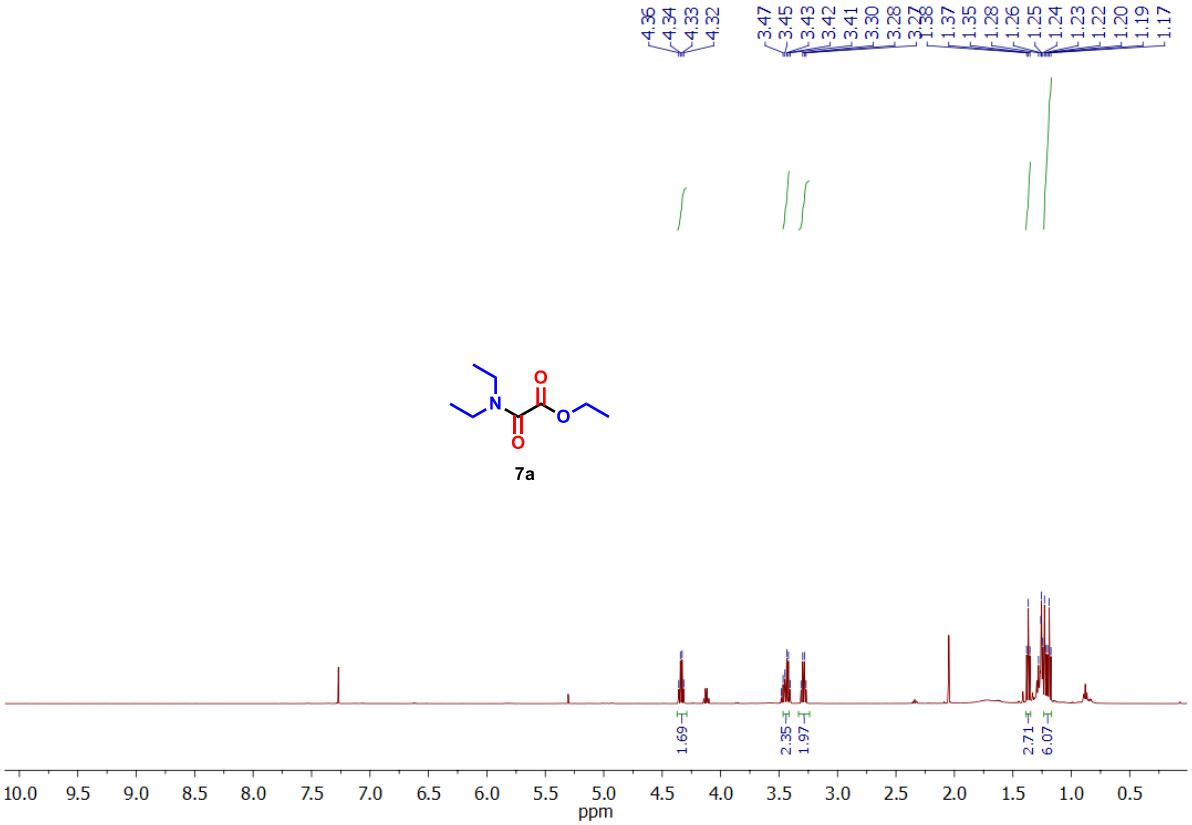
^{1}H NMR of N^{1},N^{1},N^{2},N^{2}-tetraethyloxalamide (4a)



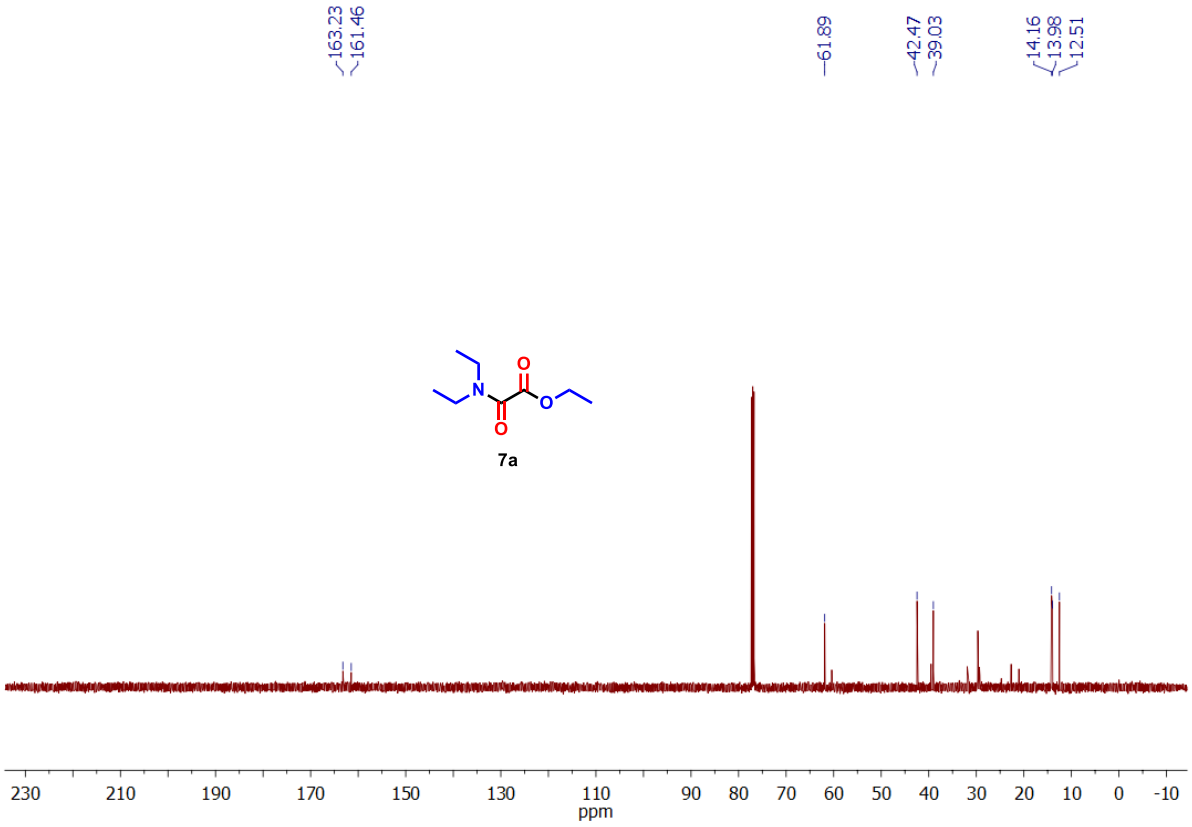
^{13}C NMR of N^{1},N^{1},N^{2},N^{2}-tetraethyloxalamide (4a)



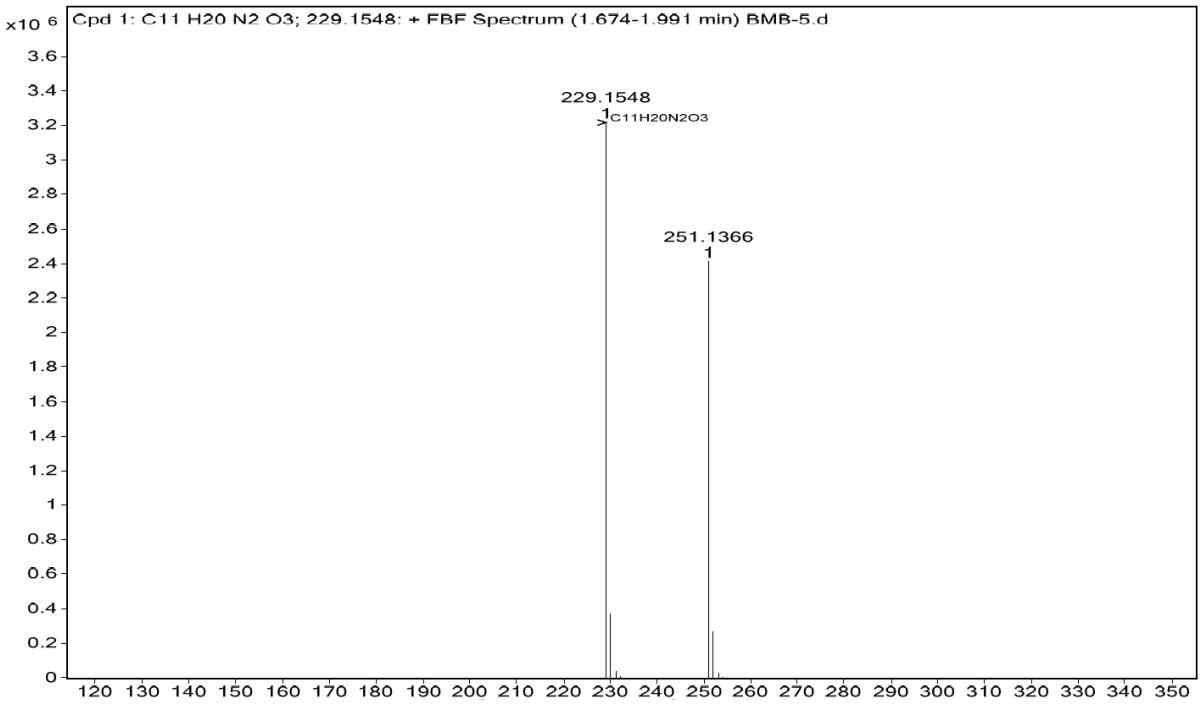
^{1}H NMR of ethyl 2-(diethylamino)-2-oxoacetate (7a)



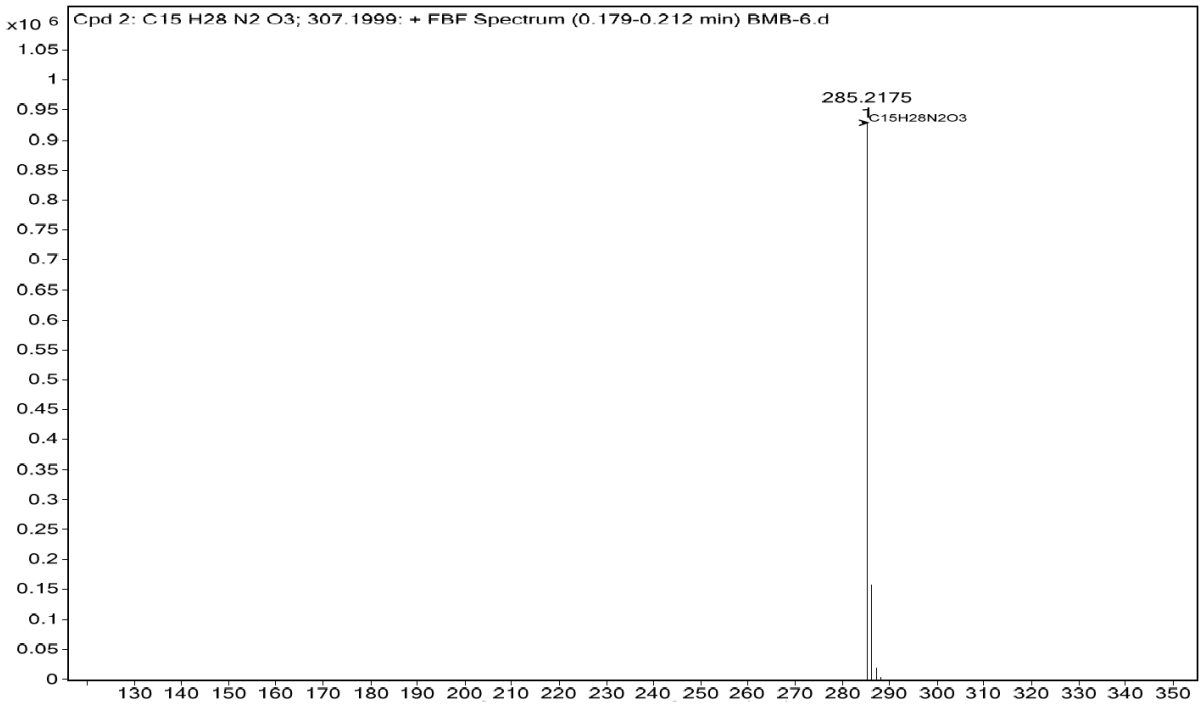
^{13}C NMR of ethyl 2-(diethylamino)-2-oxoacetate (7a)



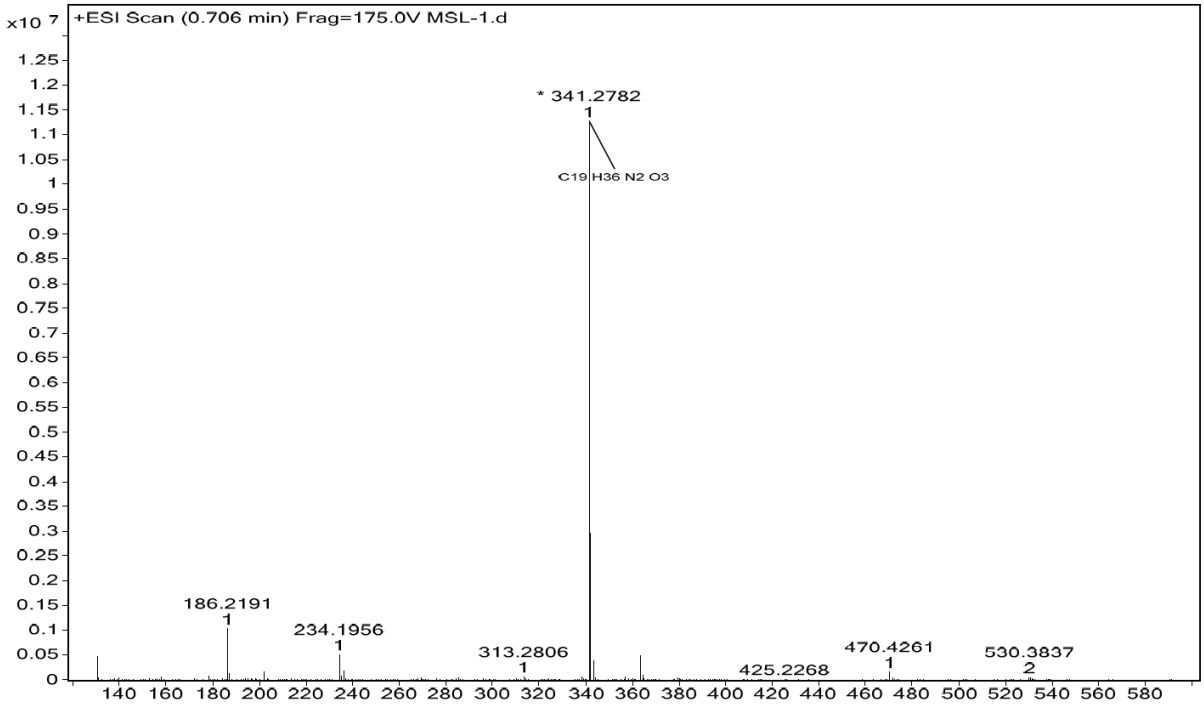
15. HRMS images of the products



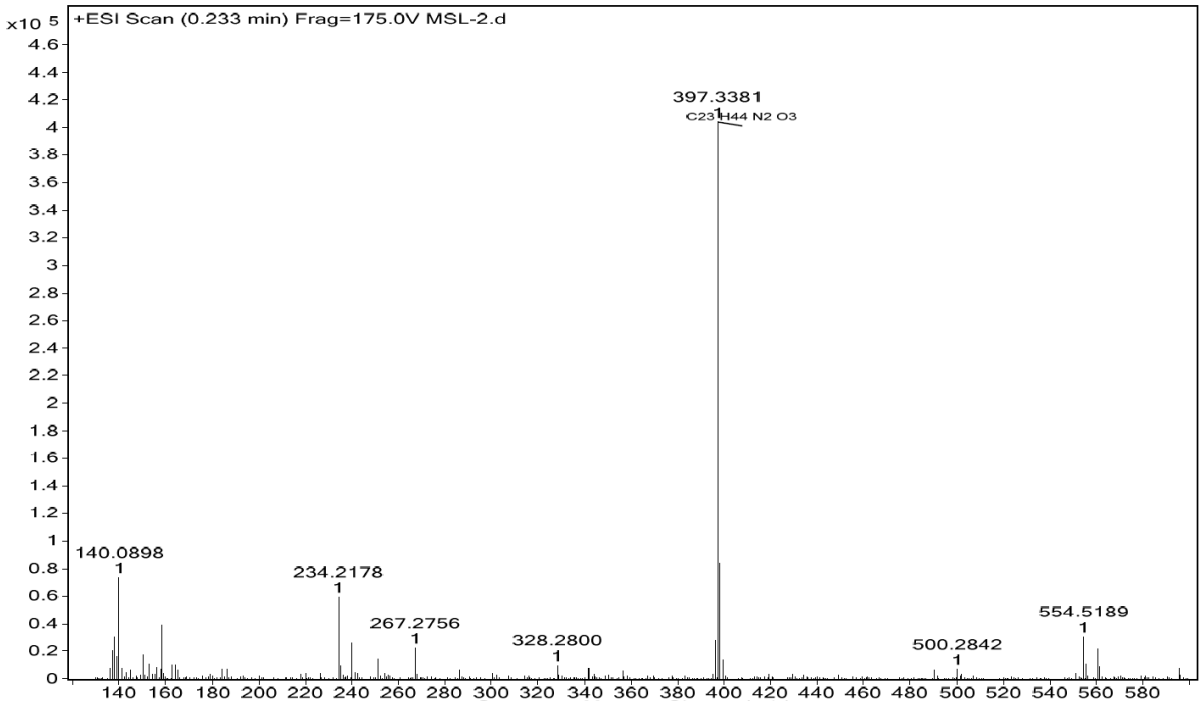
HRMS (ESI) m/z calcd for $C_{11}H_{20}N_2O_3$ $[M+H]^+$, 229.1552, found 229.1548 **HRMS of 3a**



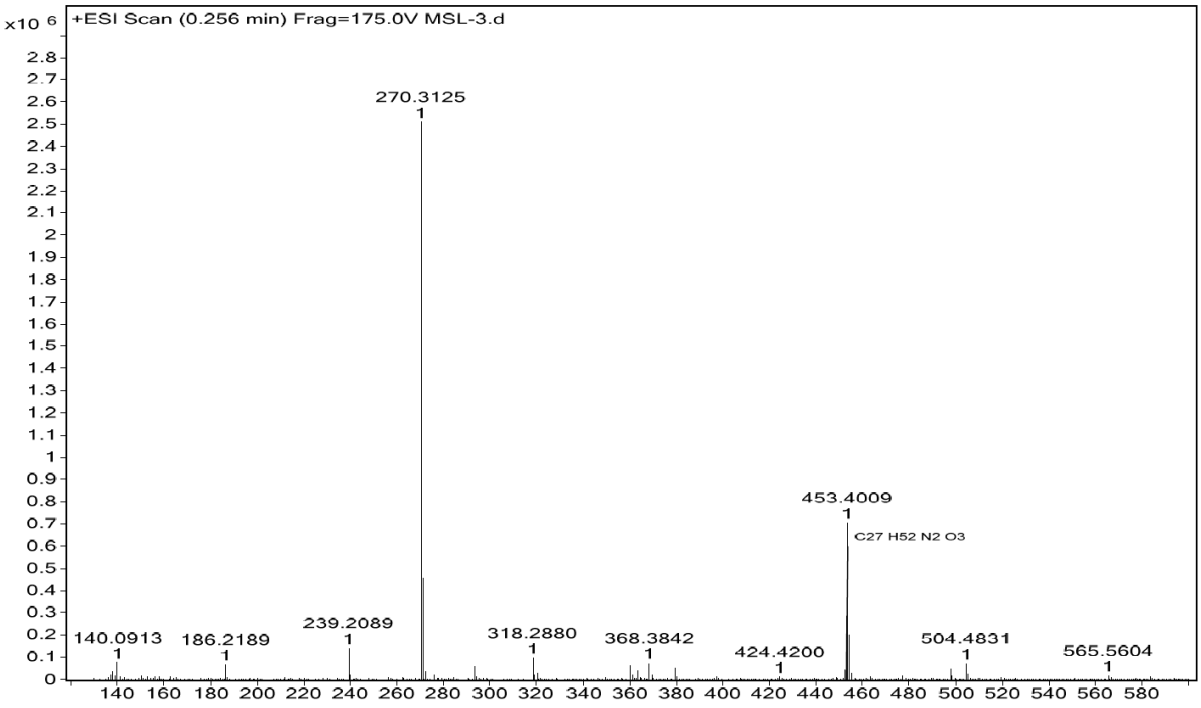
HRMS (ESI) m/z calcd for $C_{15}H_{28}N_2O_3$ $[M + H]^+$, 285.2178, found 285.2175 **HRMS of 3b**



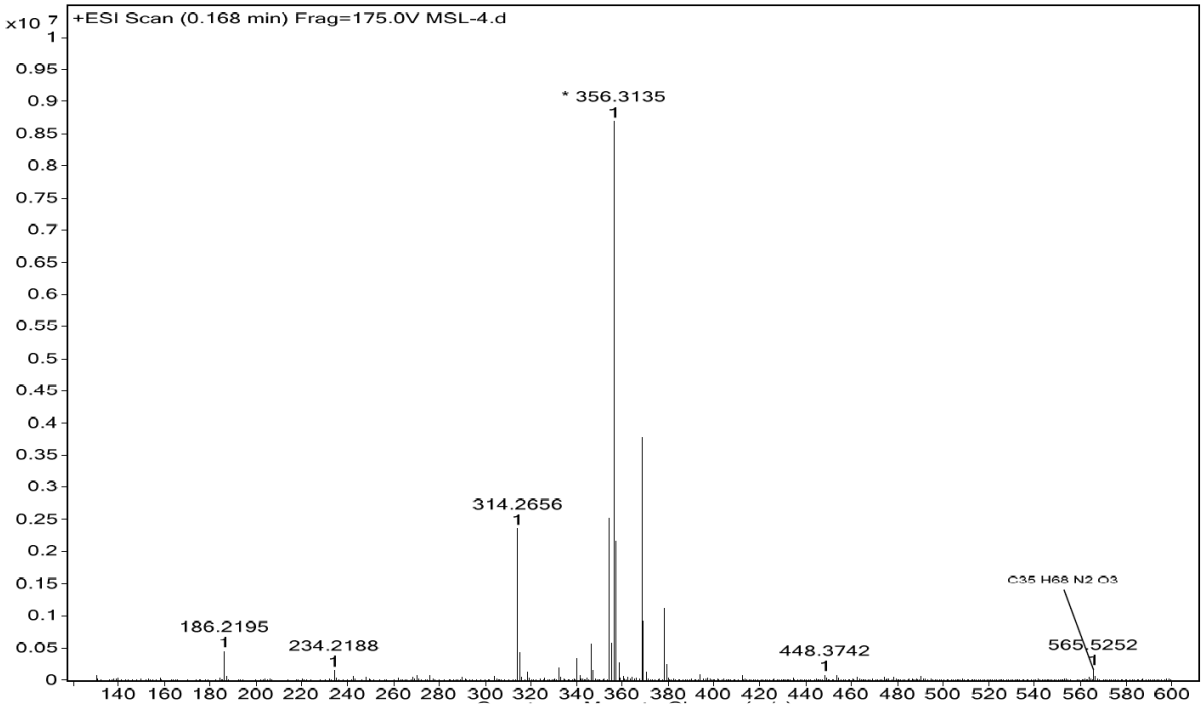
HRMS (ESI) m/z calcd for $C_{19}H_{36}N_2O_3$ $[M + H]^+$, 341.2804, found 341.2782 **HRMS of 3c**



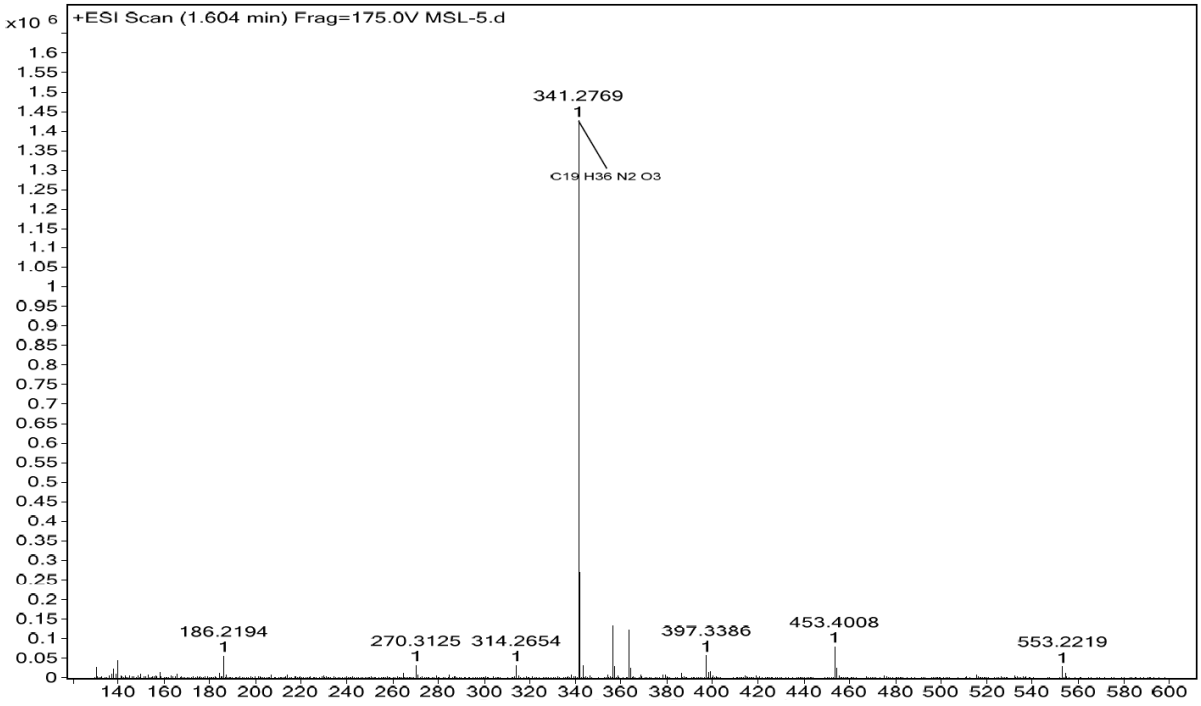
HRMS (ESI) m/z calcd for $C_{23}H_{44}N_2O_3$ $[M + H]^+$, 397.3430, found 397.3381 **HRMS of 3d**



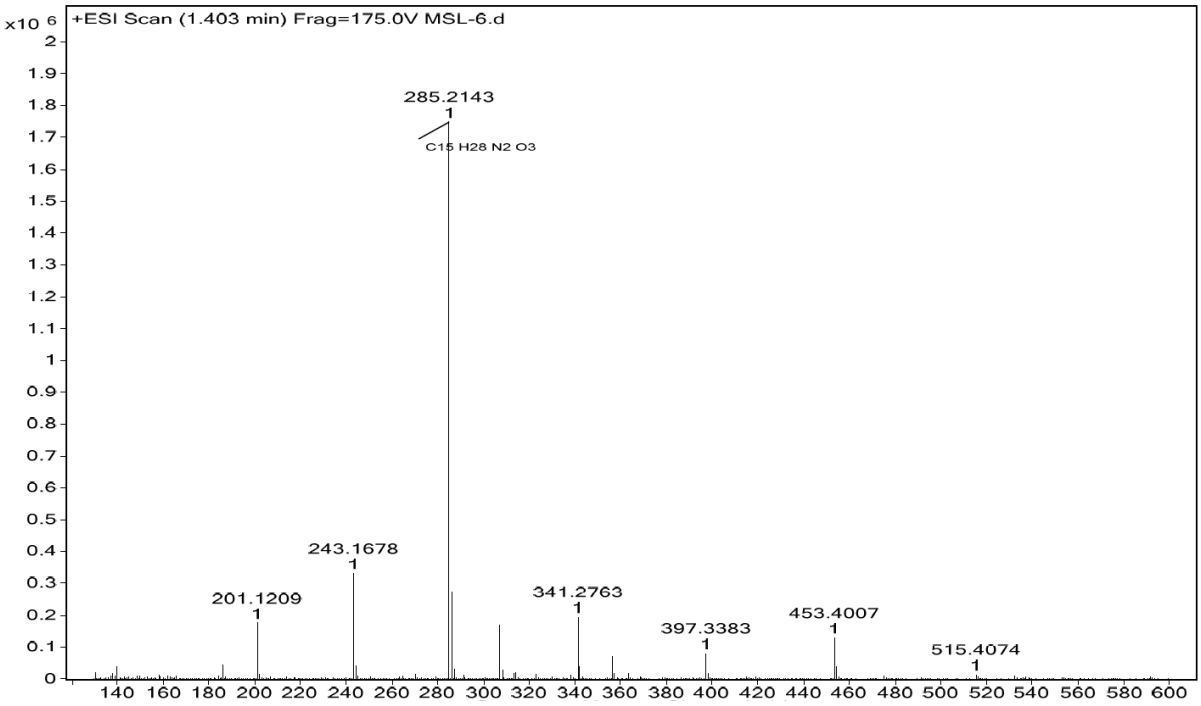
HRMS (ESI) m/z calcd for $C_{27}H_{52}N_2O_3$ $[M + H]^+$, 453.4056, found 453.4009 **HRMS of 3e**



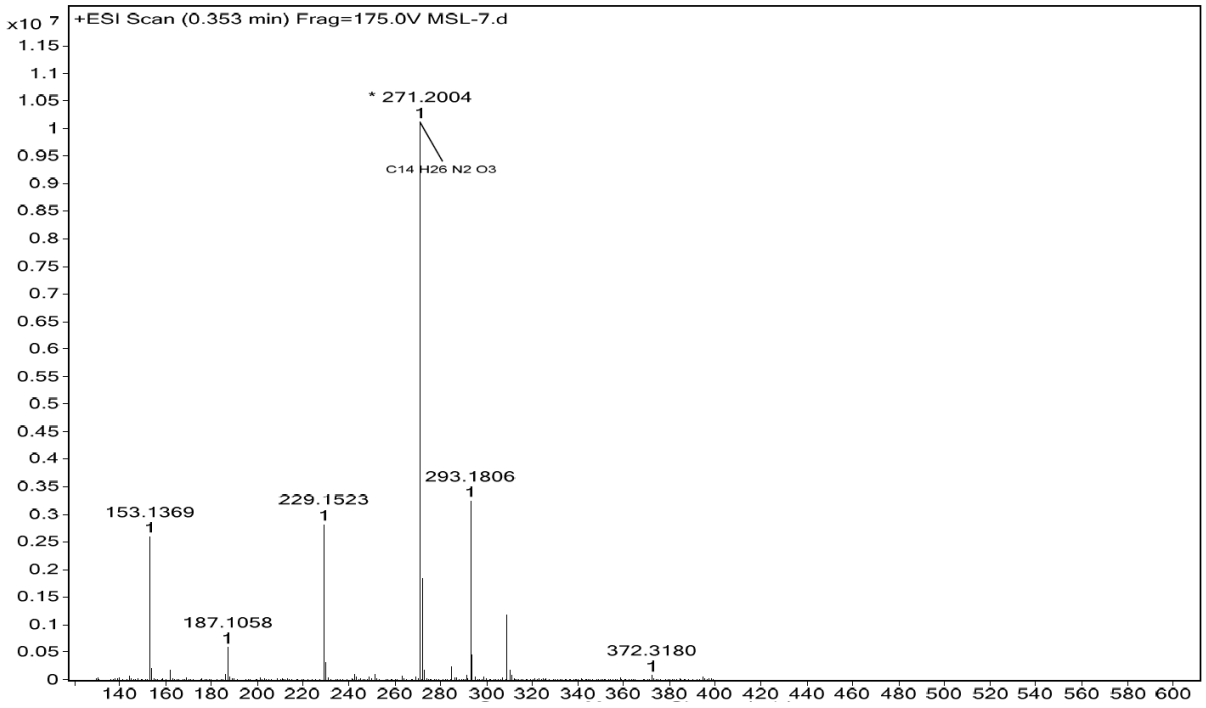
HRMS (ESI) m/z calcd for $C_{35}H_{68}N_2O_3$ $[M + H]^+$, 565.5308, found 565.5252 **HRMS of 3f**



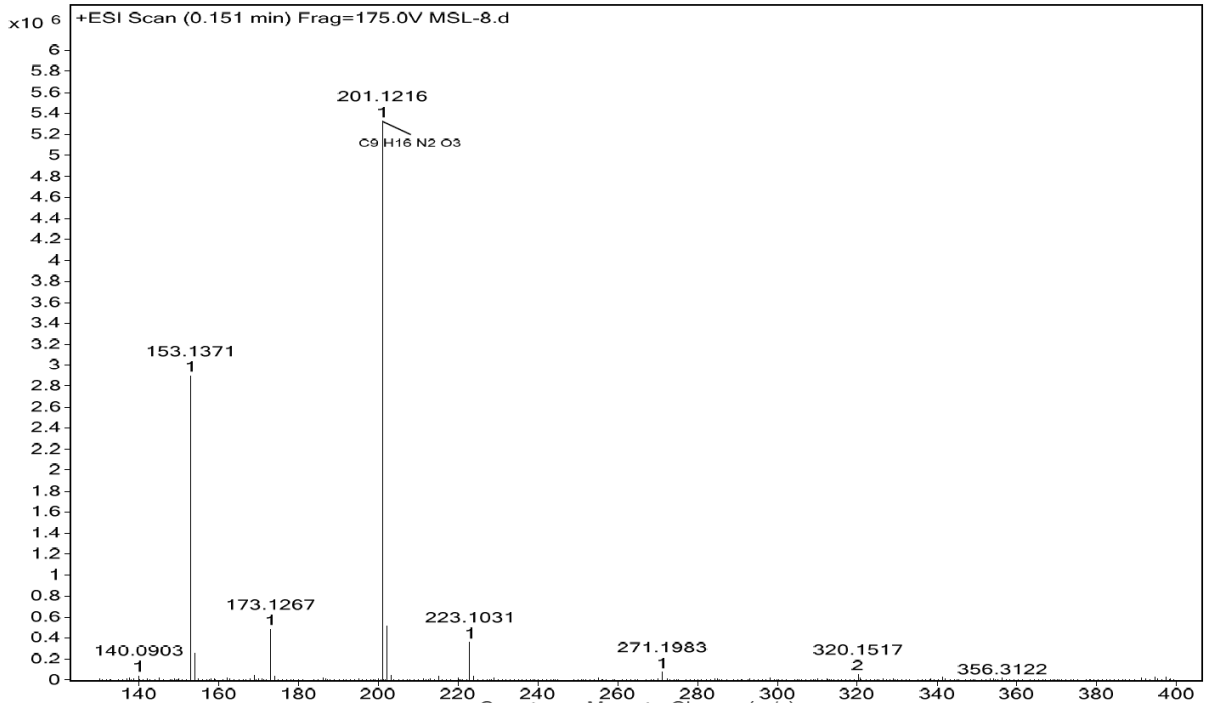
HRMS (ESI) m/z calcd for $C_{19}H_{36}N_2O_3$ $[M + H]^+$, 341.2804, found 341.2769 **HRMS of 3g**



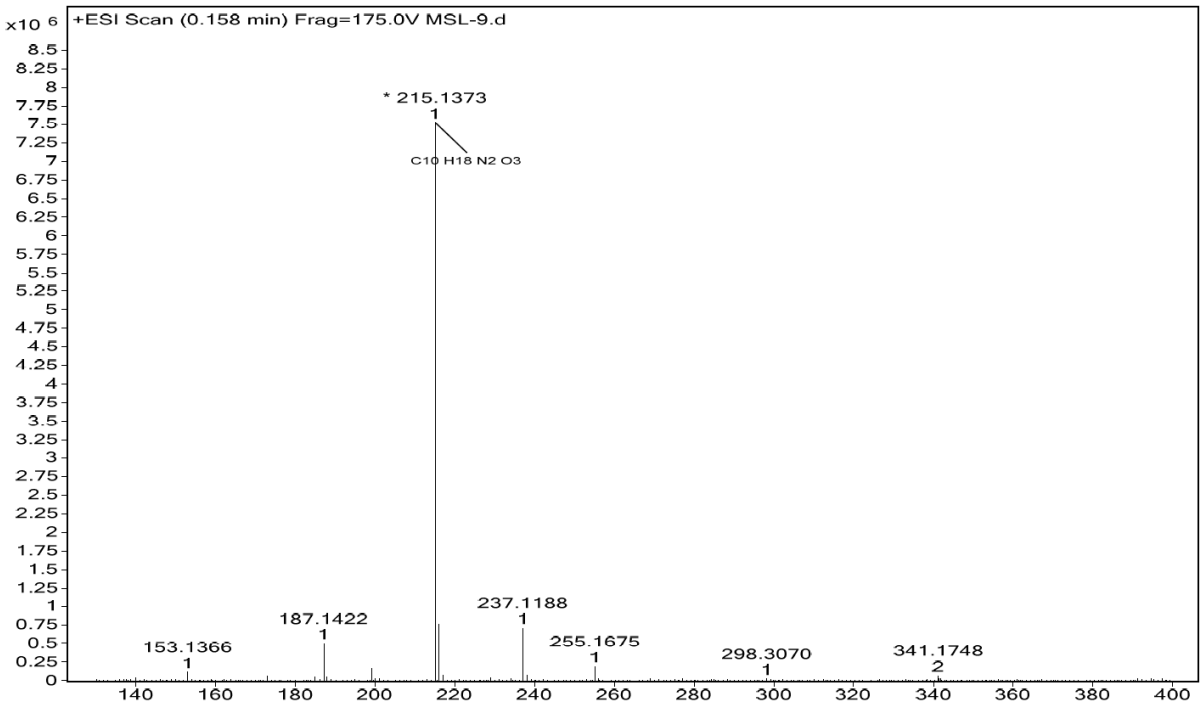
HRMS (ESI) m/z calcd for $C_{15}H_{28}N_2O_3$ $[M + H]^+$, 285.2178, found 285.2143 **HRMS of 3h**



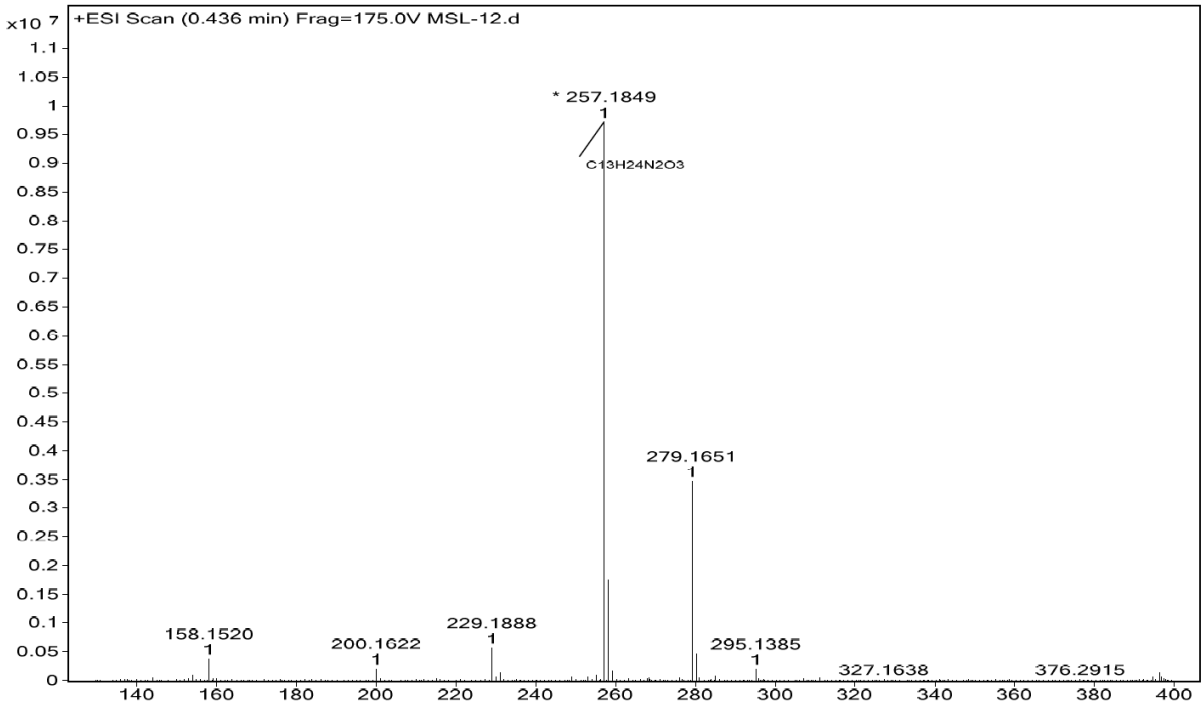
HRMS (ESI) m/z calcd for $C_{14}H_{26}N_2O_3$ $[M + H]^+$, 271.2021, found 271.2004 **HRMS of 3i**



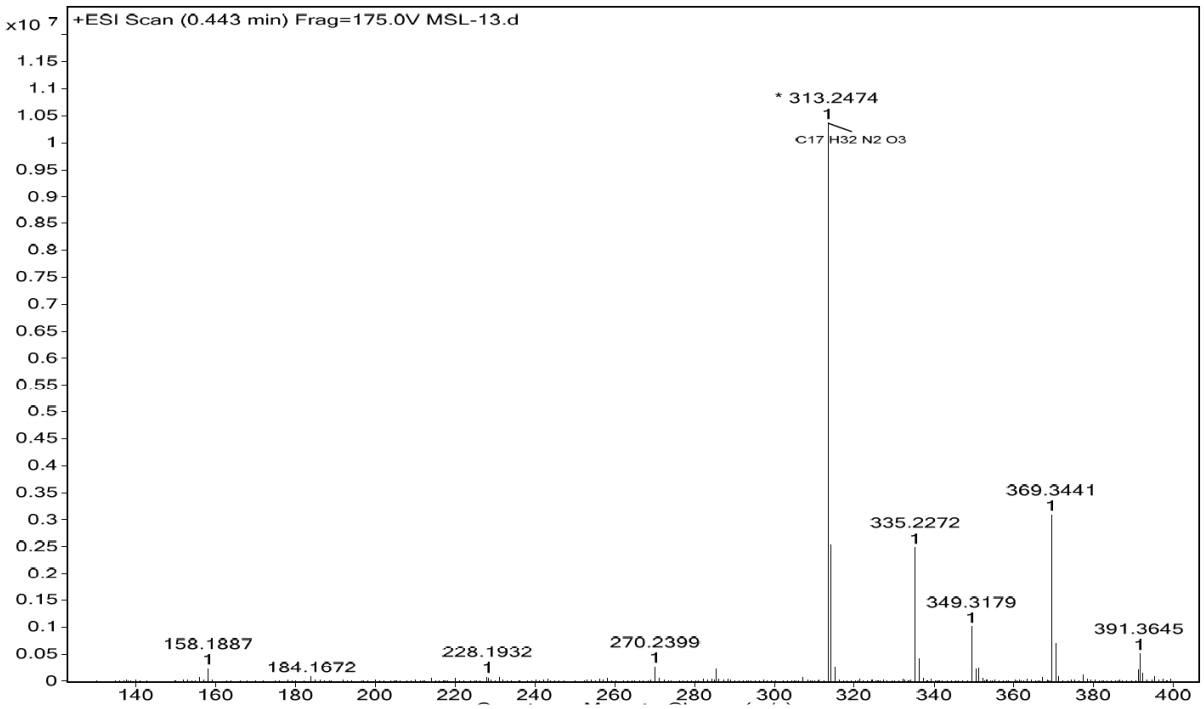
HRMS (ESI) m/z calcd for $C_9H_{16}N_2O_3$ $[M + H]^+$, 201.1239, found 201.1216 **HRMS of 3j**



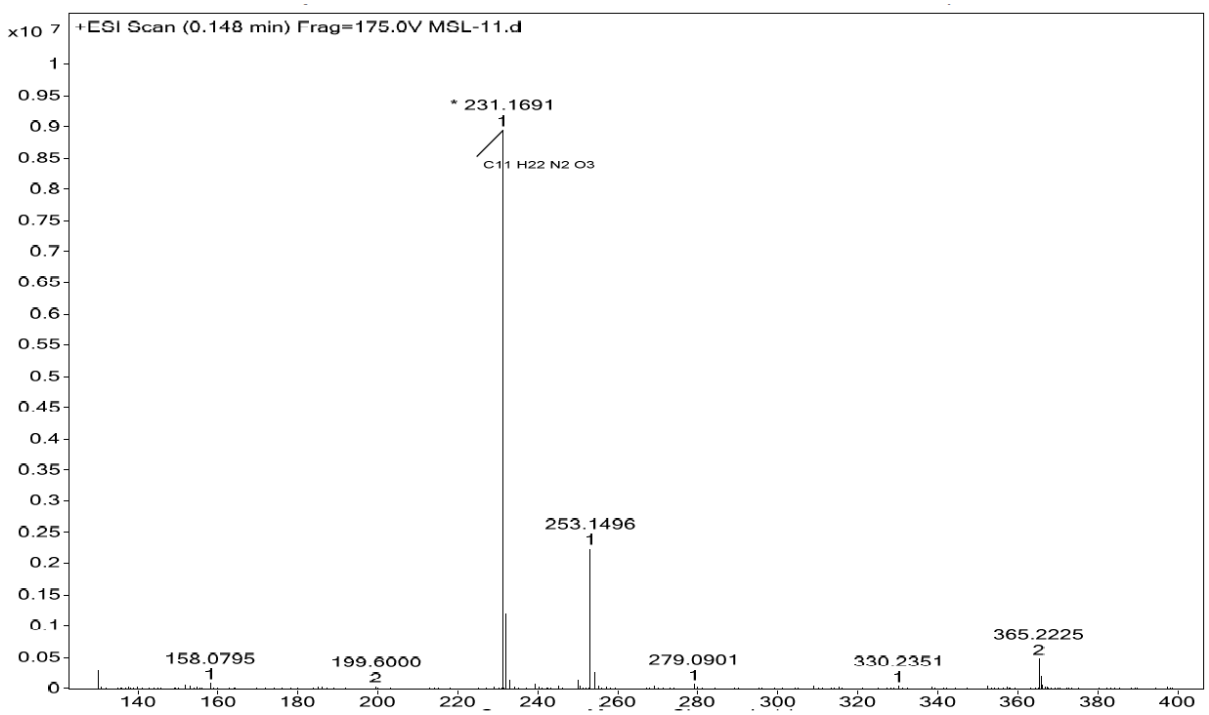
HRMS (ESI) m/z calcd for $C_{10}H_{18}N_2O_3$ $[M + H]^+$, 215.1395, found 215.1373 **HRMS of 3k**



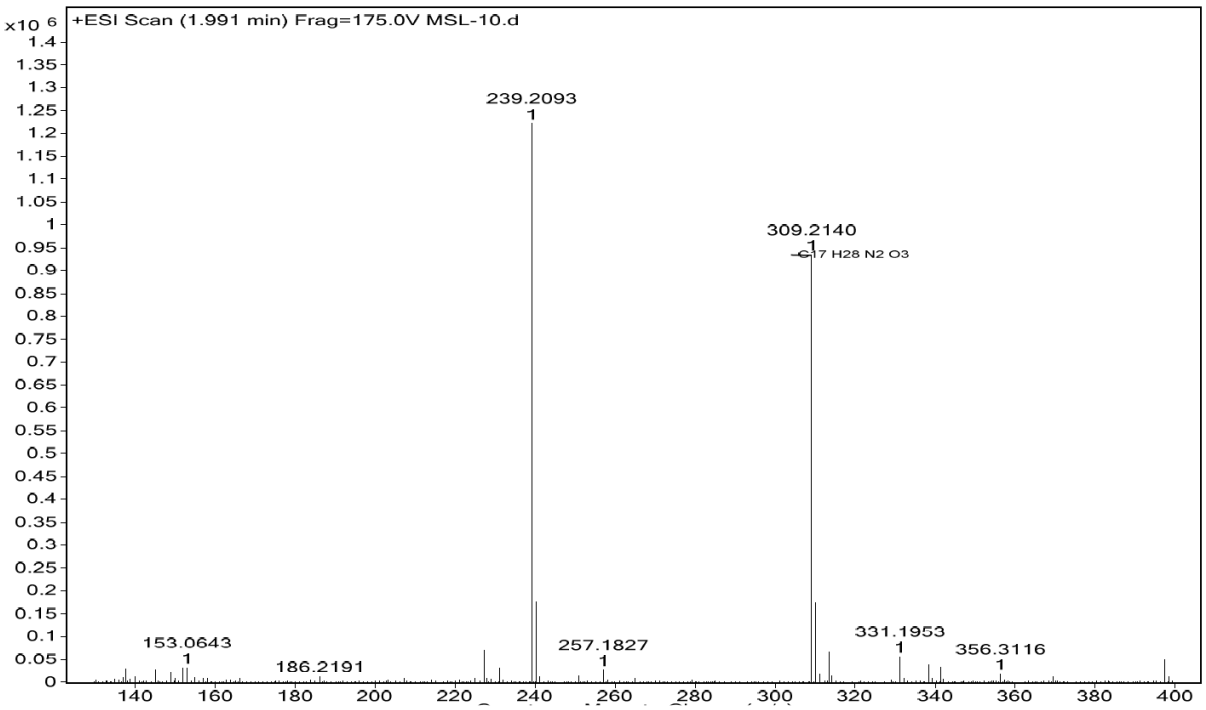
HRMS (ESI) m/z calcd for $C_{13}H_{24}N_2O_3$ $[M + H]^+$, 257.1865, found 257.1849 **HRMS of 3ab**



HRMS (ESI) m/z calcd for $C_{17}H_{32}N_2O_3$ $[M + H]^+$, 313.2491, found 313.2474 **HRMS of 3ad**

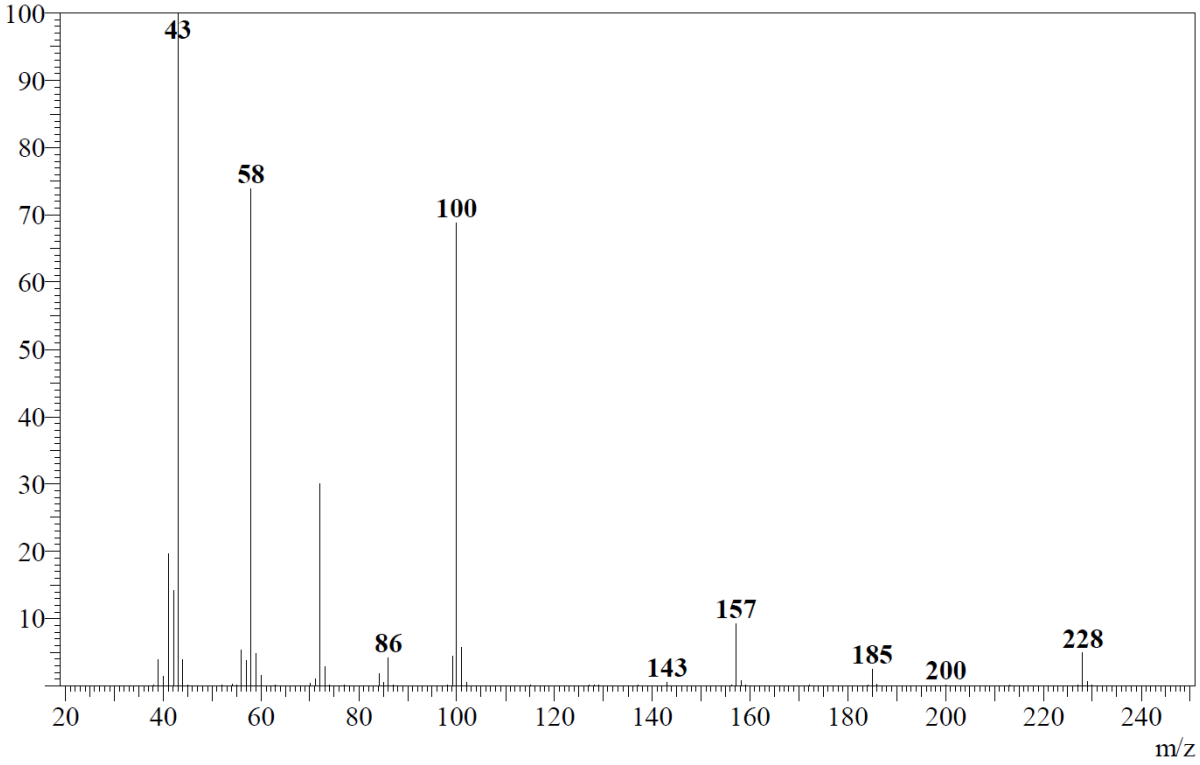


HRMS (ESI) m/z calcd for $C_{11}H_{22}N_2O_3$ $[M + H]^+$, 231.1708, found 231.1691 **HRMS of 5a**

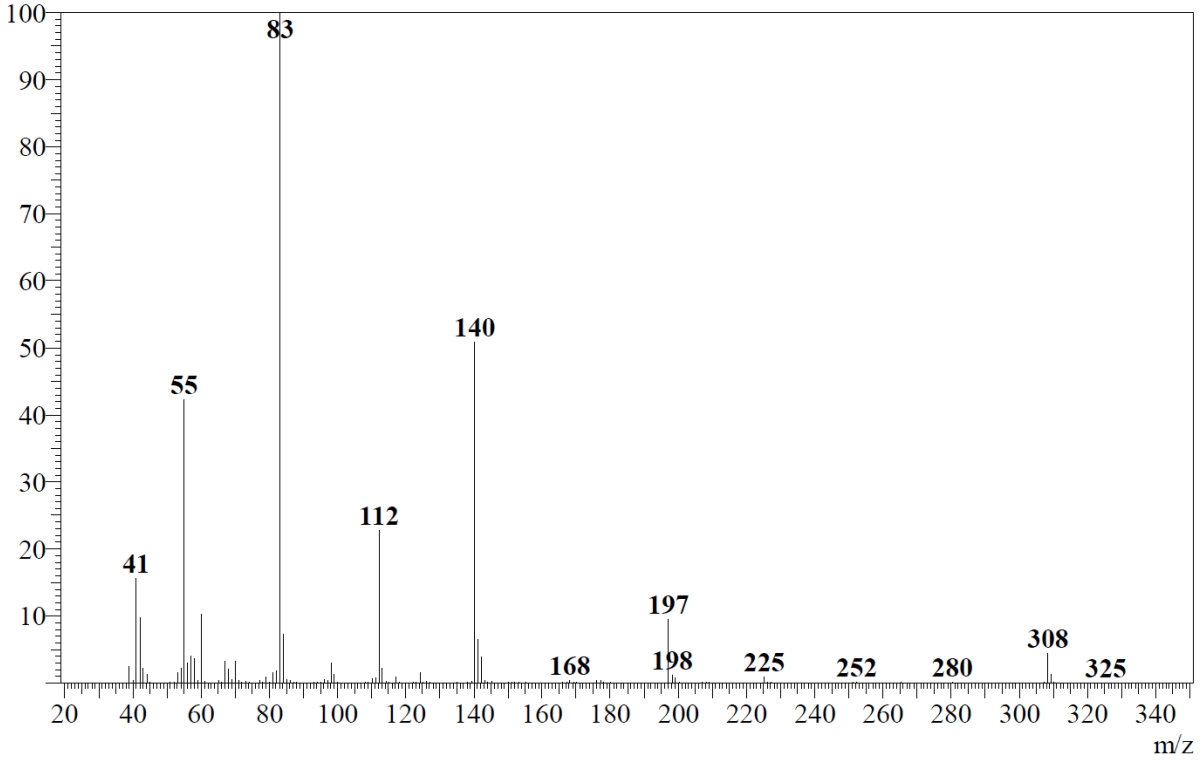


HRMS (ESI) m/z calcd for $C_{17}H_{28}N_2O_3$ $[M+H]^+$, 309.2178, found 309.2140 **HRMS of 3m**

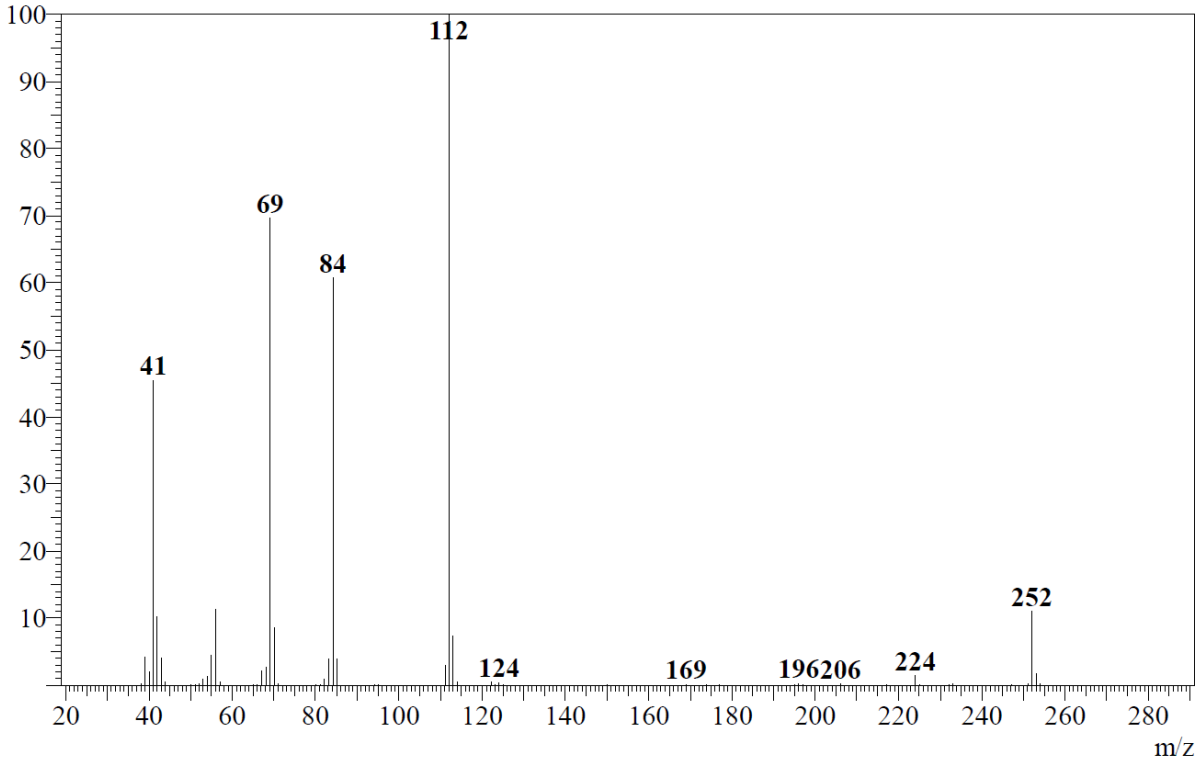
16.GCMS images of 3l, 3m, 3n and 3o compounds



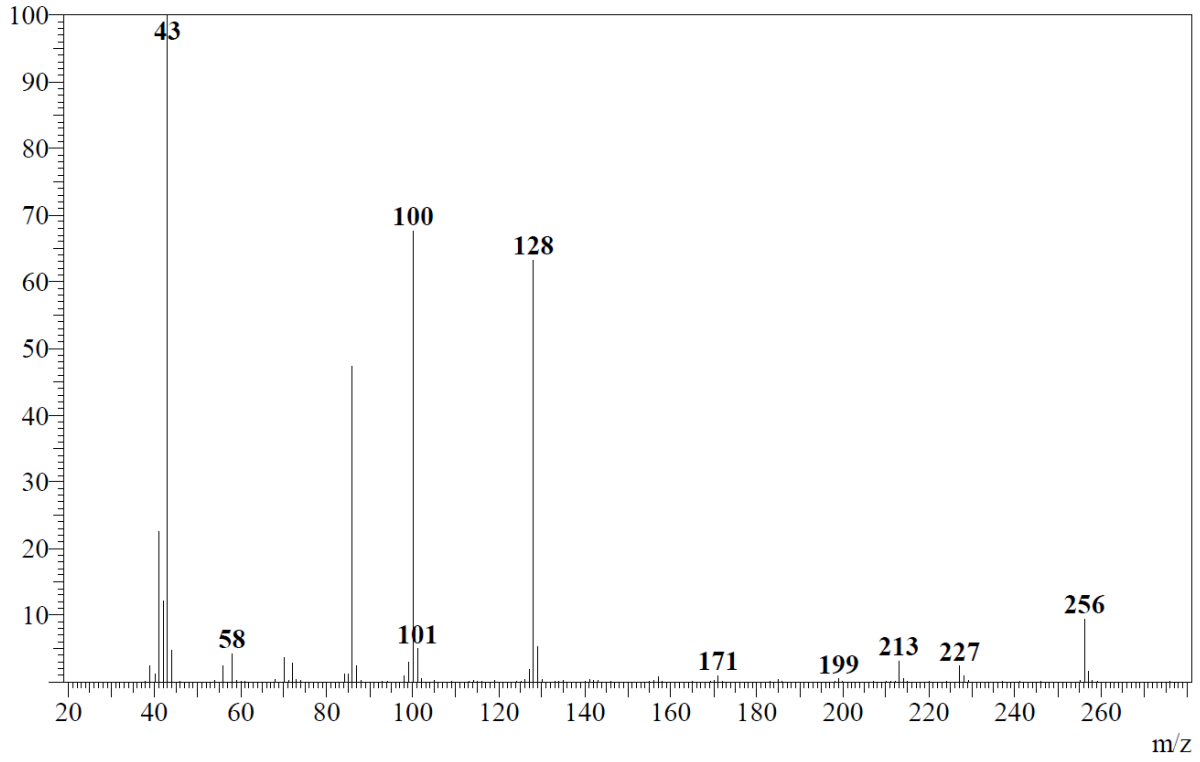
GCMS of spectra of N^1,N^3-diisopropyl-N^1,N^3-dimethyl-2-oxomalonamide (3l)



GCMS spectra of N^1,N^3-dicyclohexyl-N^1,N^3-dimethyl-2-oxomalonamide (3m)



GCMS spectra of 1,3-di(piperidin-1-yl)propane-1,2,3-trione (3n)



GCMS spectra of 1,3-dimorpholinopropane-1,2,3-trione (3o)

17. References

1 (a) R. S. Mane and B. M. Bhanage, J. Org. Chem., 2016, 81, 4974–4980; (b) R. S. Mane and B. M. Bhanage, Adv. Synth. Catal., 2017, 359, 2621–2629; (c) M. A. Idris and S. Lee, *Org. Chem. Front.*, 2020, **7**, 2737–2743.

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3 Y. A. Kolekar and B. M. Bhanage, New J. Chem., 2019, 43, 18072–18078.