Supporting Information

Nature Inspired Singlet Oxygen Generation to Access the *α*-Amino Carbonyl Compounds via 1,2-Acyl Migration

Waldemar Schilling[b], Yu Zhang[a,b], Prakash Kumar Sahoo[a], Samir Kumar Sarkar[b], Gandhi Sivaraman[c], and Shoubhik Das*[a]

[a] Y. Zhang, P. Sahoo, and Prof. S. Das

Department of Chemistry

University of Antwerpen

Groenenborgerlaan 171, 2020 Antwerpen, Belgium

Email: shoubhik.das@uantwerpen.be

[b] W. Schilling, Y. Zhang, and Dr. S. Sarkar.

Institute for Biomolecular and Organic Chemistry

Georg-August-Universität Göttingen

Tammanstraße 2, 37077 Göttingen, Germany

[c] Dr. G. Sivaraman

Department of Chemistry

Gandhigram Rural Institute

Gandhigram, 624032, Tamilnadu, India.

Corresponding Author

*E-mail: shoubhik.das@uantwerpen.be

Contents:

1. Materials, methods

Commercial reagents were used without the purification and reactions were run under ambient atmosphere with the exclusion of moisture from the reagents using standard techniques for the air-sensitive compounds. ^{1}H NMR spectra (300, 400 and 500 MHz) and ^{13}C NMR spectra (75.58, 100.62 and 125.71 MHz) were recorded using Bruker spectrometers AVANCE III 300, AVANCE III HD 400, AVANCE III 400, AVANCE III HD 500 and Varian spectrometers Mercury VX 300, VNMRS 300 and Inova 500 with $CDCl_3$ and DMSO-d_6 as solvent. NMR spectra were calibrated using the solvent residual signals ($CDCl_3$: δ ^{1}H = 7.26, δ ^{13}C = 77.16). ESI mass spectra were recorded on Bruker Daltonic spectrometers maXis (ESI-QTOF-MS) and micrOTOF (ESI-TOF-MS). GC-MS mass spectra were recorded on Thermo Finnigan spectrometers TRACE (Varian GC Capillary Column; wcot fused silica coated CP-SIL 8CB for amines; 30 m x 0.25 mm x 0.25 µm) and DSQ (Varian FactorFour Capillary Column; VF-5ms 30 m x 0.25 mm x 0.25 µm). Gas chromatography was performed on an Agilent Technologies chromatograph 7890A GC System (Supelcowax 10 Fused Silica Capillary Column; 30 m x 0.32 mm x 0.25 µm). GC calibrations were carried out with authentic samples and *n*-dodecane as an internal standard. Absorption-emission spectra were recorded on a Jasco FP-8500 Spectrofluorometer and UV/Vis spectra were recorded on a Jasco V-770 Spectrophotometer. Reference for reported products is given after the name of the product.

2. Setup for photocatalytic reactions

The reaction setup is depicted in **Figure S1**. The reaction setup consists of a self-constructed light source configuration, made up of a crystallizing dish with a diameter of 140 mm. Inside of the crystallizing dish, commercially available 5 m LED-Strip is glued with separable LED elements. In total, 3 m LED strip is used in a crystallizing dish, with a total power of 24 W. Light intensity of the light source can be adjusted by a self-constructed dimmer. Construction of the reaction setup and the dimmer was performed by the electronic services of the faculty for chemistry of the Georg-August-Universität Göttingen. Cooling of the setup is performed by a commercially available 120 mm fan. To ensure the constant room temperature, the dimmer setting was used at 80% (19.2 W). During the first experiment, the temperature was monitored inside the crystallizing dish and did not exceed room temperature (25–32 °C). Magnetic stirring was performed at 250 rpm. The wavelength of the blue LED setup is ranging from 404 nm to 553 nm with a maximum at 456 nm.

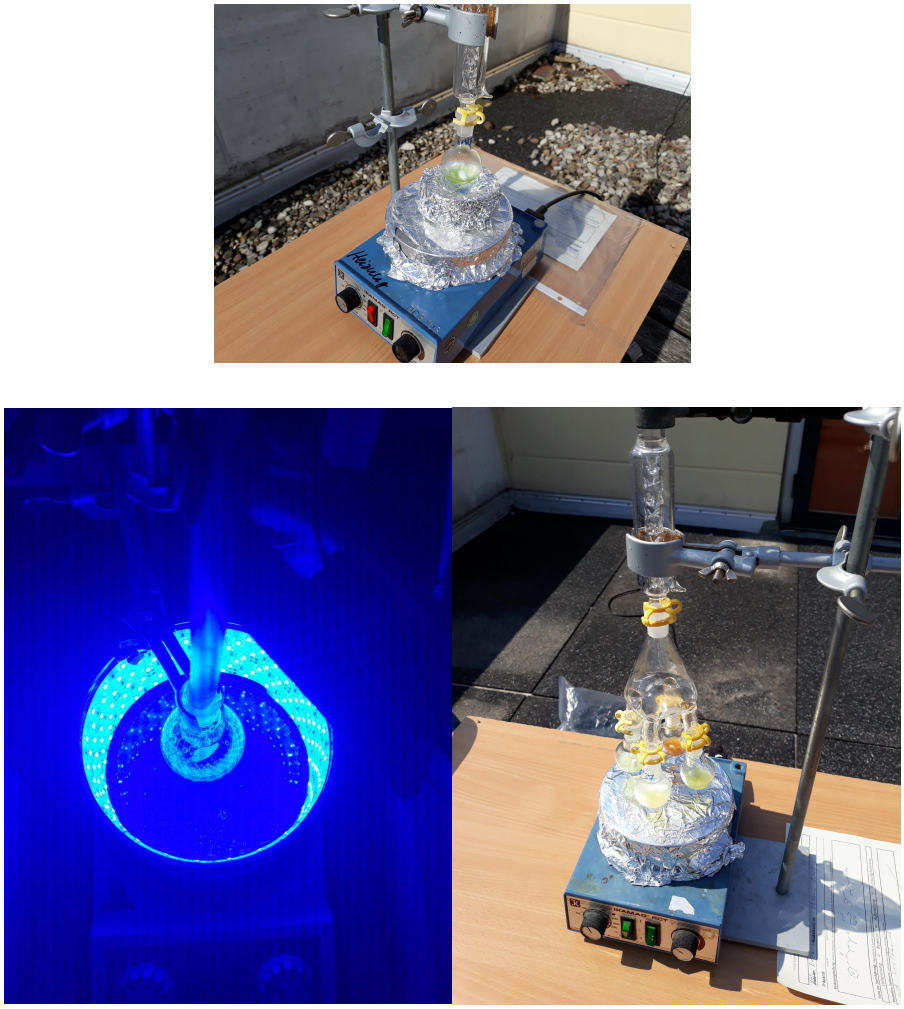
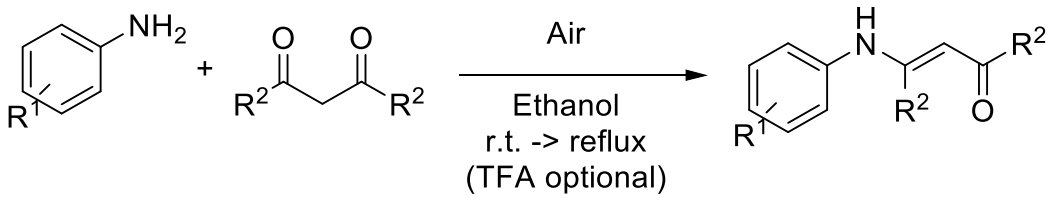


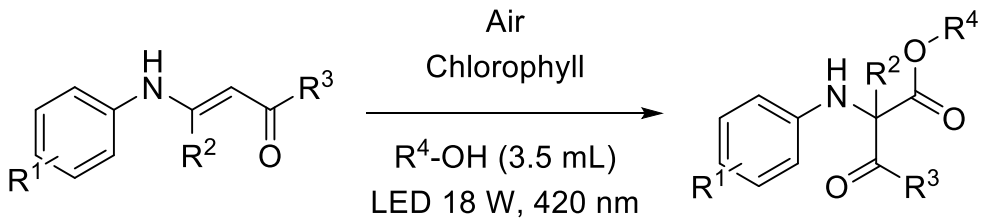
Figure S1: Led and Sunlight reaction setup.

3.1 General procedure for the synthesis of secondary enaminones



A 25 mL flask containing a stirring bar was charged with aryl amines (5 mmol) and the corresponding diketone substrate (7.5 mmol) in ethanol (20 ml). Resulting mixture was stirred for 24–72 h. In case of unsatisfying yields, the reaction was heated to reflux condition and stirred for further 24–72 h. Addition of trifluoro acetic acid increased the reaction speed and yield of the reaction.[1]

3.2 General procedure for the photocatalytic reaction of secondary enaminones



10 mL two-neck flask containing a stirring bar was charged with the substrate (0.25 mmol), chlorophyll (6%-mass content) and alcohol (3.5 mL). The resulting mixture was stirred for 4–24 h under the irradiation of blue LED (the progress was monitored *via* TLC, or GC-MS). A Vigreux column was attached to minimize the evaporation of the solvent. Then, the resulting mixture underwent an aqueous workup (using distilled water) and was extracted three times with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Products were purified using silica gel chromatography with ethyl acetate and *n*-pentane as solvents (typically ranging from 5:95 to 20:80 ethyl acetate:*n*-pentane).

In case of sunlight experiments, the LED setup was removed and replaced by a cork ring wrapped in aluminum foil.

Additional information: In one case of a new batch of chlorophyll, the catalyst showed a lower reactivity. However, after removing the top layer of the bottle, the reactivity was restored. In some cases, a base contamination was present, in those cases, lower reactivity was observed. Further repetition of the experiments (without base contamination) always showed normal activity.

Chlorophyll information: Supplier: TCI, Product Number: C0780, this product is a natural pigment from a plant-derived chlorophyll. The natural pigment consists of chlorophyll contained substances (extracted from a plant), Gum Arabic and Lactose.

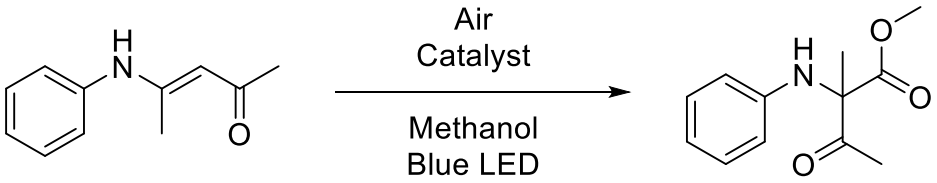
Handling of the catalyst was performed without any additional requirement. Filtration of the catalyst before the reaction resulted in minor reduction in the yield, but afforded a clear solution.

3.3 General procedure for the singlet oxygen mediated organic transformation of various substrates.

A 10 mL two-neck flask equipped with a stirring bar was charged with chlorophyll (6%-mass content) and substrates (0.25 mmol). The flask was evacuated and refilled with O_2(x 3times). The respective solvents (1 mL) were added and the mixture was stirred for24 h under the irradiation of blue LED (the progress was monitored *via* TLC, or GC-MS).Then, the resulting mixture underwent an aqueous workup (using distilled water) and was extracted three times with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Products were purified using silica gel chromatography with ethyl acetate and *n*-heptane as solvents (typically ranging from 5:95 to 30:80 ethylacetate:*n*-heptane).

4. Optimization table

Table S1: Optimization table for the 1,2-Acyl migration reaction of secondary enaminones utilizing chlorophyll [a]



Entry	Catalyst	Cat. Load. / mol%	V solv. / mL	Yield / %
1	Chlorophyll TCI 6%	0.12	2.0	42
2	Chlorophyll TCI 6%	0.24	2.0	52
3	Chlorophyll TCI 6%	0.30	2.0	54
4	Chlorophyll TCI 6%	0.30	1.5	59
5	Chlorophyll TCI 6%	0.30	2.5	56
6	Chlorophyll TCI 6%	0.30	3.0	68
7	Chlorophyll TCI 6%	0.30	3.5	92
8	Acriflavine	5.0	2.0	<2
9	Methylene blue	0.30	3.5	0
10	Eosin Y	5.0	2.0	<2
11	Rose bengal	0.30	3.5	55
12[b]	Chlorophyll TCI 6%	0.30	3.5	0
13[c]	Chlorophyll TCI 6%	0.30	3.5	0
14[d]	Chlorophyll TCI 6%	0.30	3.5	31

[a] Reaction conditions: Substrate (0.25 mmol), catalyst, MeOH, excitation with LED stipes adjusted to 19.2 W output, 6 h. All the yields were determined by GC-FID using *n*-dodecane as an internal standard. [b] catalyst loading was 5 mol%. [c] Solvent was changed to DMSO. [d] Solvent was changed to DMF. [e] Solvent was DMSO with 10 Vol% MeOH.

5. Mechanistic experiments

Stern-Volmer quenching experiments

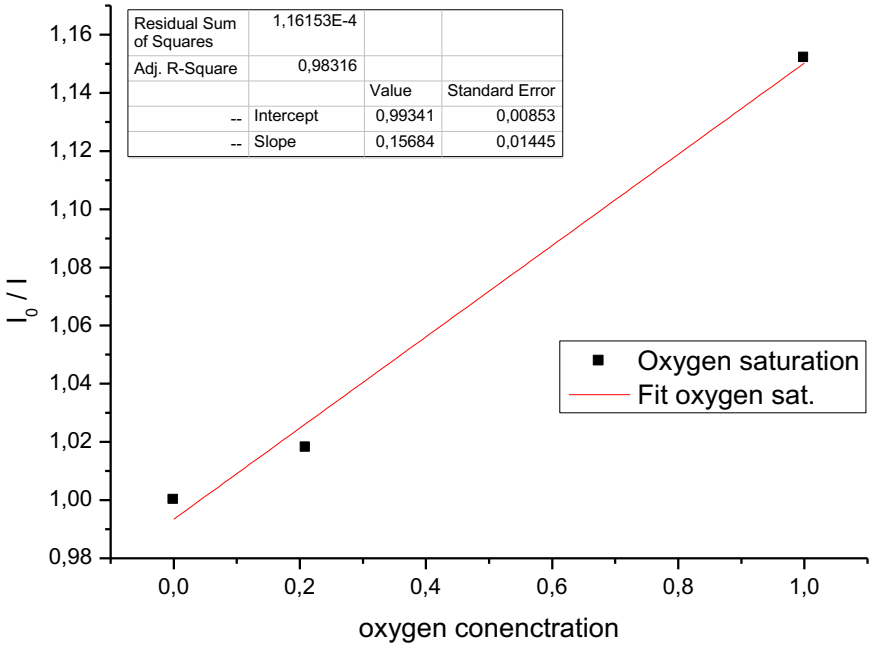


Figure S2: Stern-Volmer plot of chlorophyll in methanol depending on oxygen saturation.

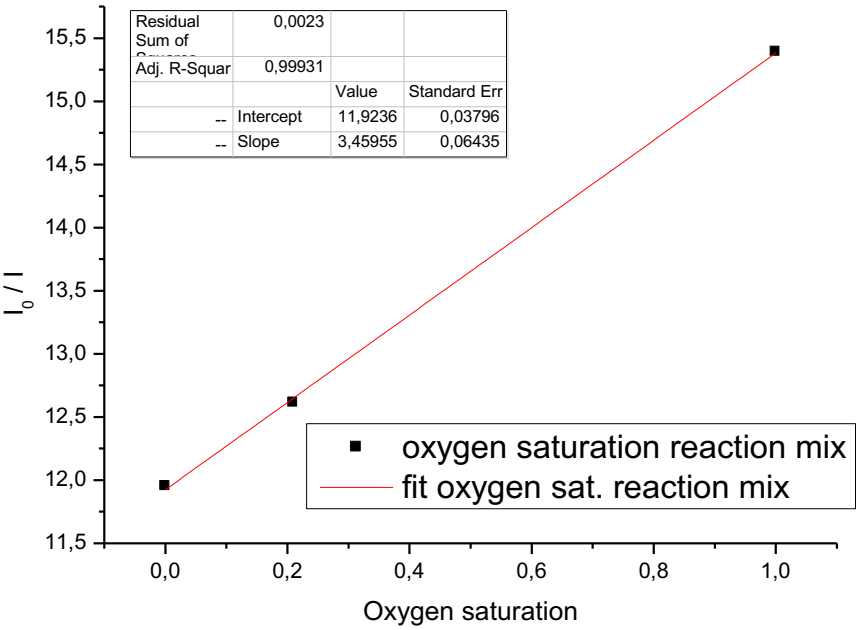


Figure S3: Stern-Volmer plot of reaction mixture depending on oxygen saturation.

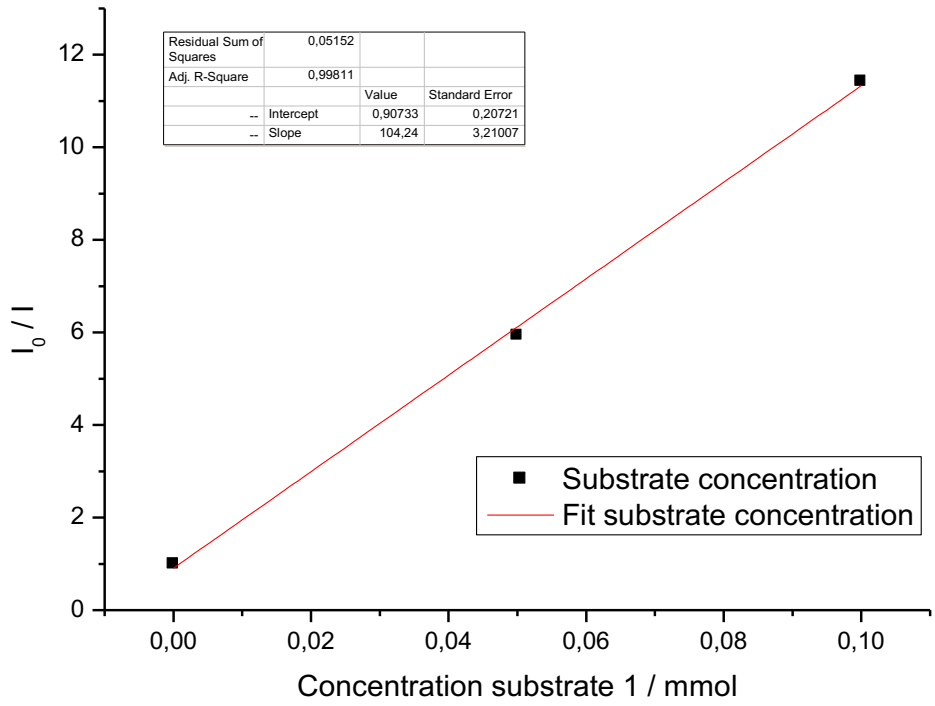


Figure S4: Stern-Volmer plot of reaction mixture depending on concentration of substrate under air conditions.

Time- and light-dependent kinetics

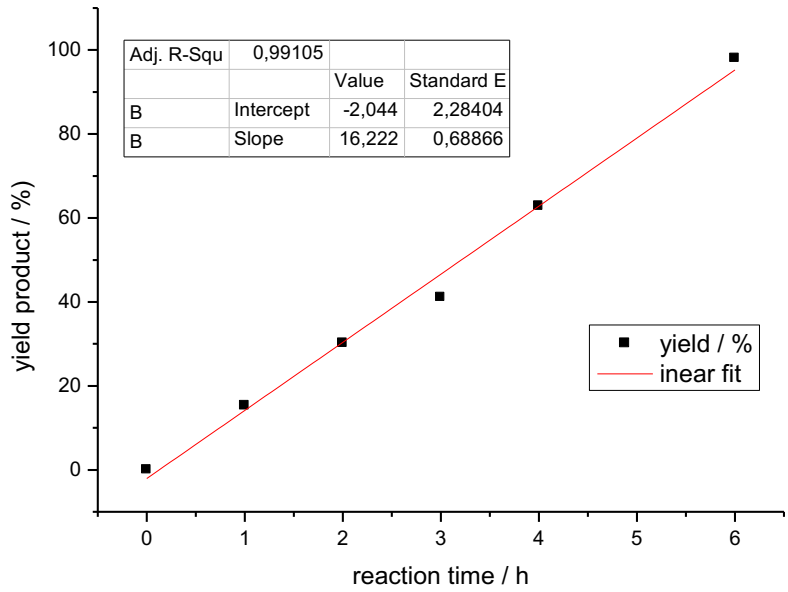


Figure S5: Time-dependent yield of the reaction. Each entry is a separate reaction with yield determined by GC-FID using *n*-dodecane as internal standard.

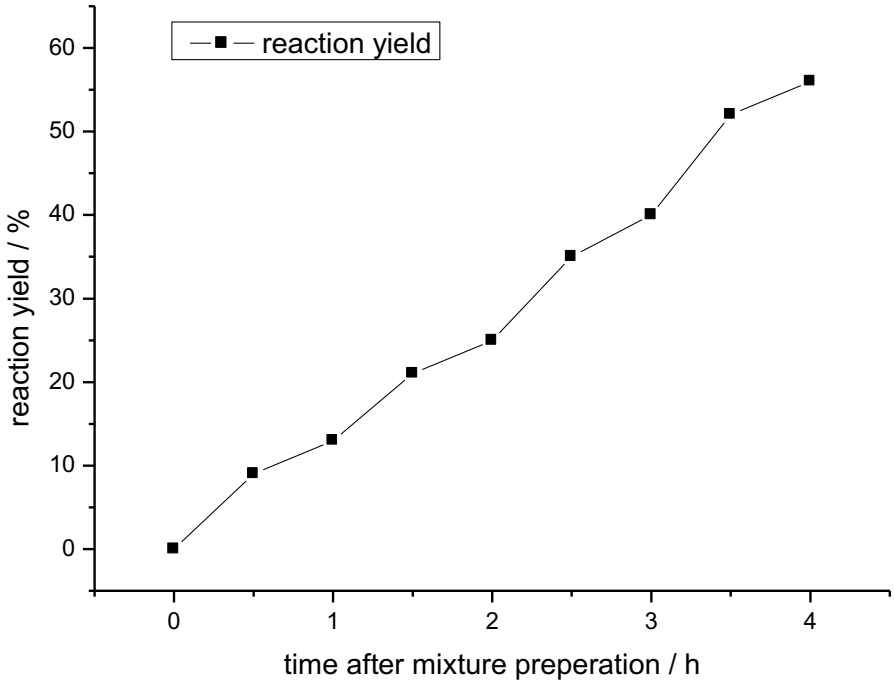


Figure S6: Time-dependent yield of the reaction with alternating 30 minutes of irradiation and 30 minutes of darkness periods. Reaction at 1 mmol scale, Chlorophyll (0.3 mol%), 14 mL MeOH. Sample size 0.1 mL reaction mixture, yield was determined by GC-FID using *n*-dodecane as internal standard.

Calculation of TON and TOF values

Calculation of the product-based TON and TOF values was performed

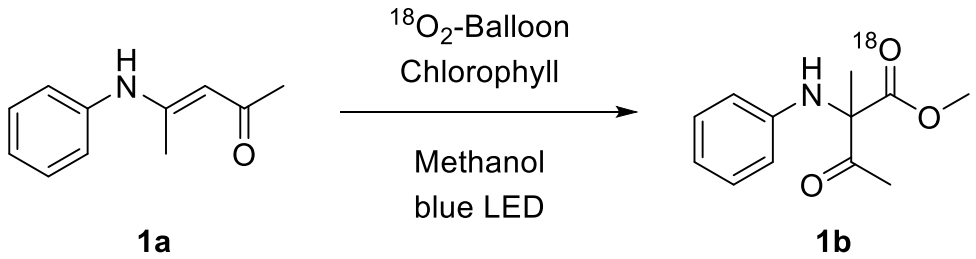
1.1 $$\frac{m_P \cdot M_P}{n_{catalyst}} = \mathrm{TON}$$

Alternatively: $$\frac{\mathrm{yield}_{GC}}{n_{catalyst}} = \mathrm{TON}$$

1.2 $$\frac{\mathrm{TON}}{t} = \mathrm{TOF}$$

m_p: weight of the product after isolation in g
M_p: molar mass of the product in g * mol^{-1}
$n_{catalyst}$: effective amount of catalyst in mol
TON: Turn over number
$yield_{GC}$: Yield of the reaction determined by GC-FID calibration, *n*-dodecane as internal standard. In mol
t: reaction time in h
TOF: turn over frequency in h^{-1}

Labeling experiment under $^{18}O_2$-Atmosphere



Secondary enaminone **1a** was transformed by following the procedure described in section **3.1.** under $^{18}O_2$ atmosphere. After 6 h, the resulting products were characterized by GC-MS, HRMS and ESI. Yield was 86 % for the labelled product.

MS (ESI): calcd. for $C_{12}H_{15}N^{16}O_2{}^{18}O$ [M+H$^+$]: 224.1165, found: 244.1167.

MS (ESI): calcd. for $C_{12}H_{15}N^{16}O_2{}^{18}O$ [M+Na$^+$]: 246.0990, found: 246.0987.

Associated information of DFT calculations

The hybrid UB3LYP[1] functional has been used in all calculations as incorporated in *Gaussian 09* package[2], mixing the exact Hartree-Fock-type exchange with Becke's exchange functional[3] and that proposed by Lee-Yang-Parr for the correlation contribution.[4] The 6-311++g(d,p) basis set was used for all the atoms which provides reasonably high quality results in moderate timescales. All ground state geometry optimizations were followed by subsequent frequency test to ascertain stationary points.

For **A**

Zero-point correction= 0.217279 (Hartree/Particle)
Thermal correction to Energy= 0.229954
Thermal correction to Enthalpy= 0.230898
Thermal correction to Gibbs Free Energy= 0.176987
Sum of electronic and zero-point Energies= -556.742850
Sum of electronic and thermal Energies= -556.730176
Sum of electronic and thermal Enthalpies= -556.729231
Sum of electronic and thermal Free Energies= -556.783142

C	-1.98077	0.57226	-1.46055
C	-0.98768	1.26957	-2.16159
C	-0.82824	2.64797	-1.9654
C	-1.6619	3.32908	-1.06816
C	-2.65499	2.63178	-0.36712
C	-2.81443	1.25337	-0.56331
H	-2.10251	-0.48018	-1.61035
H	-0.35117	0.74953	-2.84666
H	-0.07	3.18038	-2.50066
H	-3.2915	3.15182	0.31795
H	-3.57267	0.72096	-0.02805
N	-1.49466	4.77496	-0.86236
H	-0.5365	5.02329	-1.00473
C	-1.89275	5.12399	0.50899
C	-1.30586	6.17027	1.13941
H	-1.65875	7.15592	0.91841
C	0.07279	6.02469	1.81004
O	0.15199	5.84412	3.0529
C	1.35451	6.10008	0.95969
H	2.11668	5.49847	1.40922
H	1.15008	5.73859	-0.02643
H	1.68733	7.11555	0.90544
C	-2.97673	4.30069	1.22925
H	-3.50109	4.92788	1.9196
H	-3.66478	3.90951	0.50921
H	-2.51746	3.49265	1.75939

For **B**

Zero-point correction= 0.224857 (Hartree/Particle)
Thermal correction to Energy= 0.239236
Thermal correction to Enthalpy= 0.240180
Thermal correction to Gibbs Free Energy= 0.182573

Sum of electronic and zero-point Energies= -707.066345
Sum of electronic and thermal Energies= -707.051966
Sum of electronic and thermal Enthalpies= -707.051022
Sum of electronic and thermal Free Energies= -707.108629

C	-0.97795	-1.25805	0.75447
C	0.23014	-0.7735	0.24599
C	0.40866	0.60046	0.04418
C	-0.63222	1.49227	0.33333
C	-1.8431	1.00645	0.84259
C	-2.01334	-0.3677	1.0568
H	-1.10947	-2.30888	0.91327
H	1.02118	-1.45275	0.01121
H	-0.50331	2.54086	0.16728
H	-2.63913	1.68404	1.07008
H	-2.93361	-0.7358	1.45135
N	1.69705	1.08745	-0.46797
H	2.11144	0.38045	-1.04133
C	2.58501	1.38244	0.66866
C	2.31154	2.51507	1.47761
H	1.5871	2.42687	2.26183
C	2.65646	0.07296	1.47841
H	1.67064	-0.19913	1.79635
H	3.06188	-0.70704	0.86633
H	3.28485	0.21519	2.33674
O	3.88396	1.92692	0.46277
O	3.71042	2.53532	1.76649
C	1.8981	3.75667	0.66362
C	2.97306	4.57344	-0.07518
H	2.54233	5.02912	-0.94327
H	3.35488	5.33306	0.57533
H	3.77067	3.92368	-0.37371
O	0.68728	4.10225	0.60115

For **C**
Zero-point correction= 0.222947 (Hartree/Particle)
Thermal correction to Energy= 0.238509
Thermal correction to Enthalpy= 0.239453
Thermal correction to Gibbs Free Energy= 0.178293
Sum of electronic and zero-point Energies= -707.073147
Sum of electronic and thermal Energies= -707.057585
Sum of electronic and thermal Enthalpies= -707.056641
Sum of electronic and thermal Free Energies= -707.117802

C	-2.27555	0.58264	-1.76506
C	-1.3239	1.30906	-2.49348
C	-0.95671	2.59617	-2.07824
C	-1.54116	3.15687	-0.93458
C	-2.49281	2.43045	-0.20616
C	-2.86001	1.14333	-0.6214
H	-2.55592	-0.40011	-2.0821
H	-0.87766	0.88095	-3.36669
H	-0.2301	3.15081	-2.63441
H	-2.93906	2.85855	0.66705

H	-3.58662	0.58869	-0.06524
N	-1.15599	4.50699	-0.49902
C	-1.6955	5.02456	0.55666
C	-1.29199	6.43897	1.01296
C	-0.09962	6.34478	1.98301
O	-0.30213	6.23189	3.21987
C	1.34058	6.38874	1.43942
H	1.9814	5.82054	2.08082
H	1.36266	5.97274	0.45384
H	1.67834	7.40348	1.4059
C	-2.74126	4.22629	1.35713
H	-3.42917	4.90301	1.81945
H	-3.27277	3.57285	0.69727
H	-2.24846	3.64838	2.11083
H	-2.11893	6.90342	1.5083
O	-0.91934	7.21911	-0.12607
O	0.10081	6.64615	-0.73714
H	0.84411	6.58743	-0.13244

For **D**

Zero-point correction= 0.196407 (Hartree/Particle)
Thermal correction to Energy= 0.210218
Thermal correction to Enthalpy= 0.211162
Thermal correction to Gibbs Free Energy= 0.153292
Sum of electronic and zero-point Energies= -630.764034
Sum of electronic and thermal Energies= -630.750223
Sum of electronic and thermal Enthalpies= -630.749278
Sum of electronic and thermal Free Energies= -630.807148

C	-3.26223	0.60257	-1.80557
C	-2.55545	1.22542	-2.84308
C	-1.77512	2.35878	-2.57756
C	-1.70157	2.86929	-1.27452
C	-2.40835	2.24643	-0.23701
C	-3.18868	1.11307	-0.50253
H	-3.85803	-0.26278	-2.0083
H	-2.61161	0.83564	-3.83798
H	-1.23548	2.83435	-3.36972
H	-2.35219	2.63621	0.75788
H	-3.72832	0.6375	0.28963
N	-0.88304	4.05813	-0.99601
C	-0.81516	4.52936	0.20679
C	0.04234	5.77482	0.49857
C	0.12316	6.33582	1.93048
O	-0.5115	5.77652	2.86212
C	0.98066	7.58127	2.22226
H	1.34911	7.53353	3.22569
H	1.80495	7.6144	1.54083
H	0.38371	8.46123	2.10299
C	-1.59183	3.8449	1.34692
H	-1.86216	4.57381	2.08212
H	-2.47682	3.39046	0.95299
H	-0.97617	3.09487	1.79781
O	0.677	6.33412	-0.43307

For **E**

Zero-point correction= 0.252734 (Hartree/Particle)
Thermal correction to Energy= 0.269208
Thermal correction to Enthalpy= 0.270152
Thermal correction to Gibbs Free Energy= 0.207444
Sum of electronic and zero-point Energies= -746.450429
Sum of electronic and thermal Energies= -746.433956
Sum of electronic and thermal Enthalpies= -746.433012
Sum of electronic and thermal Free Energies= -746.495720

C	-2.29845	0.70765	-1.93927
C	-1.26919	1.42373	-2.56519
C	-0.86893	2.66594	-2.05467
C	-1.49792	3.19207	-0.91824
C	-2.52718	2.47598	-0.29232
C	-2.92744	1.23377	-0.80284
H	-2.60406	-0.24081	-2.32906
H	-0.78894	1.02203	-3.43289
H	-0.08307	3.21269	-2.53258
H	-3.00743	2.87769	0.57537
H	-3.7133	0.68702	-0.32494
N	-1.07806	4.49508	-0.38273
C	-1.65867	4.98074	0.66628
C	-1.21882	6.3458	1.22729
C	-0.09638	6.13838	2.26108
O	-0.38231	5.96835	3.47471
C	1.37597	6.13905	1.80965
H	1.94717	5.50486	2.45497
H	1.44111	5.77704	0.80485
H	1.76262	7.13569	1.85546
C	-2.78973	4.19383	1.3541
H	-3.47301	4.87819	1.81201
H	-3.30836	3.60524	0.62644
H	-2.37368	3.55132	2.10175
O	-0.73807	7.16725	0.16006
O	-2.3334	6.98451	1.85552
C	-1.92496	8.25206	2.37646
H	-1.56524	8.86672	1.5779
H	-2.75895	8.72998	2.84654
H	-1.14509	8.10795	3.09474
H	0.01018	6.73847	-0.26169

For **F**

Zero-point correction= 0.254362 (Hartree/Particle)
Thermal correction to Energy= 0.270800
Thermal correction to Enthalpy= 0.271744
Thermal correction to Gibbs Free Energy= 0.209869
Sum of electronic and zero-point Energies= -746.480894
Sum of electronic and thermal Energies= -746.464456
Sum of electronic and thermal Enthalpies= -746.463512
Sum of electronic and thermal Free Energies= -746.525387

C	-2.46076	0.46647	-1.89045
C	-2.15603	1.35397	-2.93131
C	-1.80553	2.67959	-2.64181

C	-1.75976	3.1177	-1.31144
C	-2.06449	2.2302	-0.27057
C	-2.41499	0.90458	-0.56008
H	-2.72837	-0.54567	-2.11149
H	-2.19098	1.01946	-3.94708
H	-1.57287	3.35722	-3.43653
H	-2.02954	2.56471	0.7452
H	-2.64765	0.22695	0.23465
N	-1.39211	4.50821	-1.00776
C	-0.73074	4.56491	0.30384
C	-0.34558	6.02164	0.62197
C	0.68058	7.50271	2.10739
H	0.71553	7.83722	3.12315
H	1.63973	7.1225	1.82389
H	0.41937	8.32213	1.47082
C	-1.69189	4.03992	1.38651
H	-2.57348	4.64601	1.4051
H	-1.9595	3.02778	1.16547
H	-1.21049	4.08119	2.34121
O	-0.07195	6.81858	-0.31268
O	-0.29887	6.46869	1.97949
H	-0.76799	4.84912	-1.7108
C	0.53809	3.69259	0.27708
O	1.52366	3.99321	0.99947
C	0.6008	2.45239	-0.63372
H	1.61293	2.28333	-0.9369
H	0.24138	1.59835	-0.09861
H	-0.00834	2.61377	-1.49848

DFT calculations for the photocatalytic behavior of chlorophyll and Intrinsic Reaction Coordinate (IRC) calculations

DFT calculations were carried out with the Gaussian09 program package. Ground state geometry optimization and frequency calculations were performed at the gradient-corrected DFT level using B3LYP correlation functional sets and LANL2DZ sub sets. The excited state geometries were optimized using Time dependent –DFT (TDDFT) using aforementioned functional basis sets. Intrinsic reaction coordinate (IRC) calculations were carried out to confirm that the transition state structures connect the reactants and the respective products.

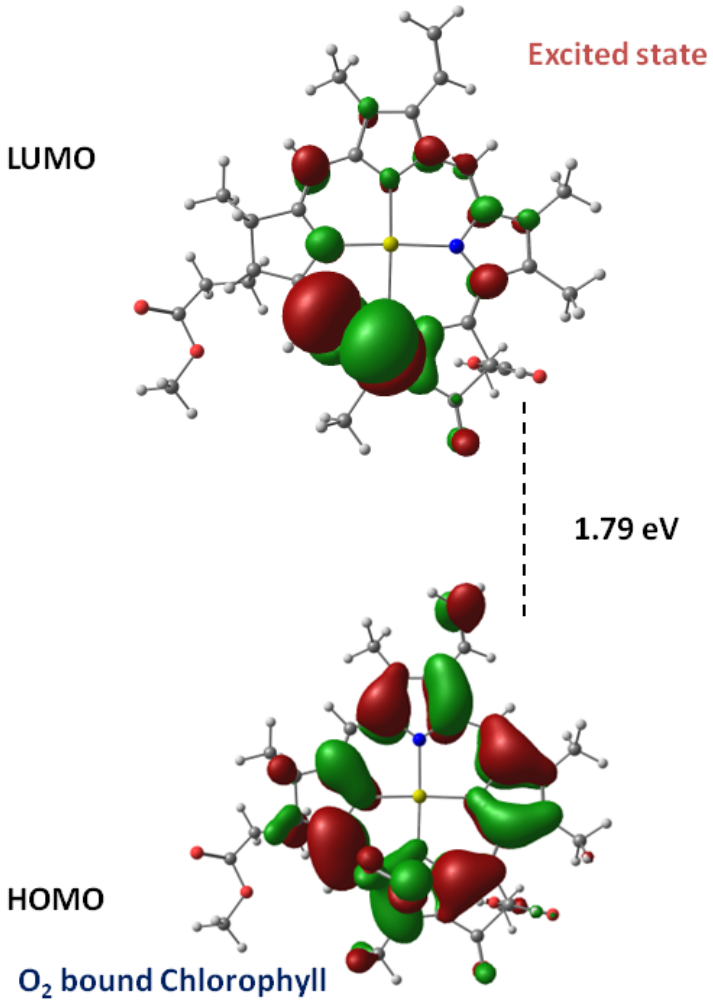


Fig S7: Frontier molecular orbitals of O_2 bound chlorophyll-A in Excited state.

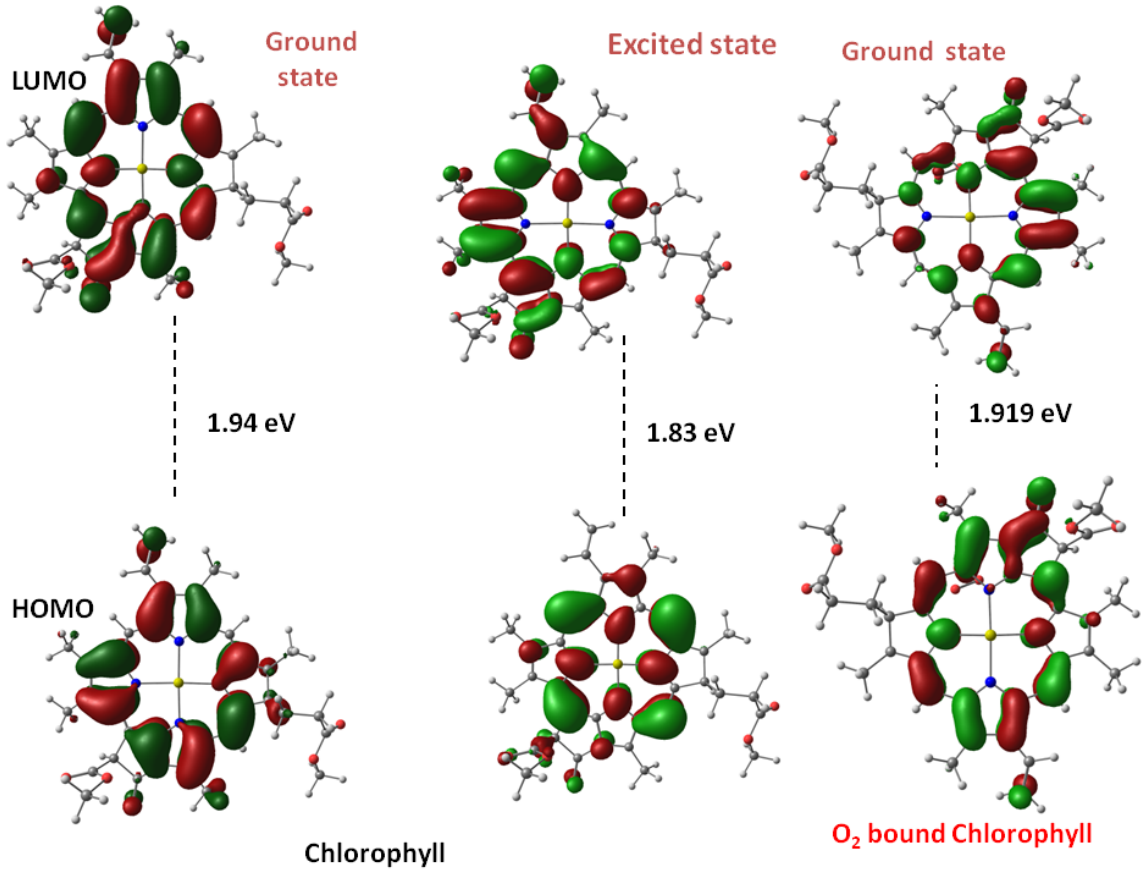


Fig S8: Frontier molecular orbitals of chlorophyll and O_2 bound chlorophyll in ground state and Excited state.

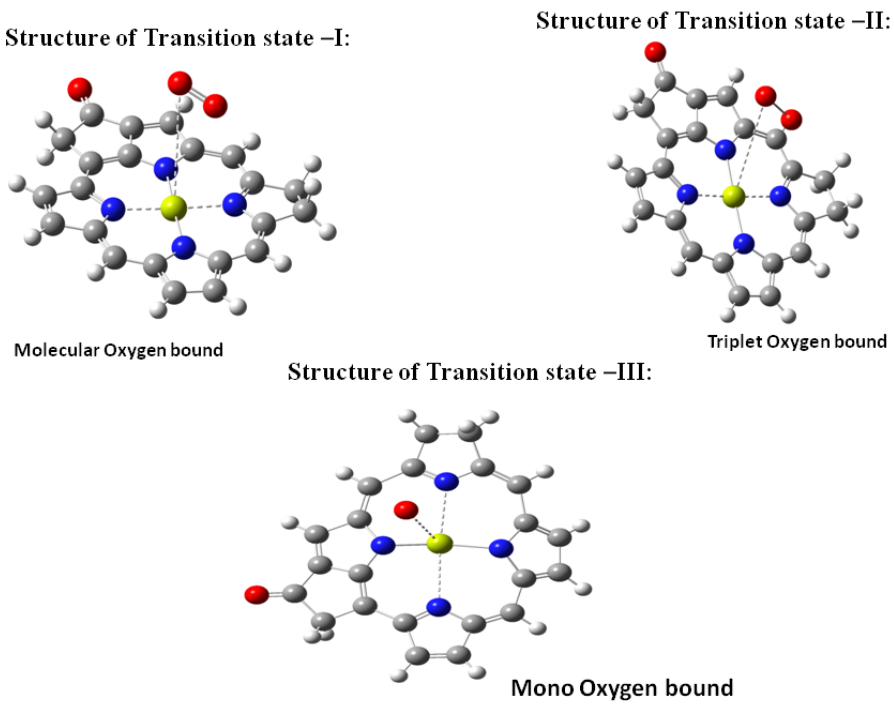


Fig S9: Structure of the transition states for the conversion of O_2 into singlet oxygen.

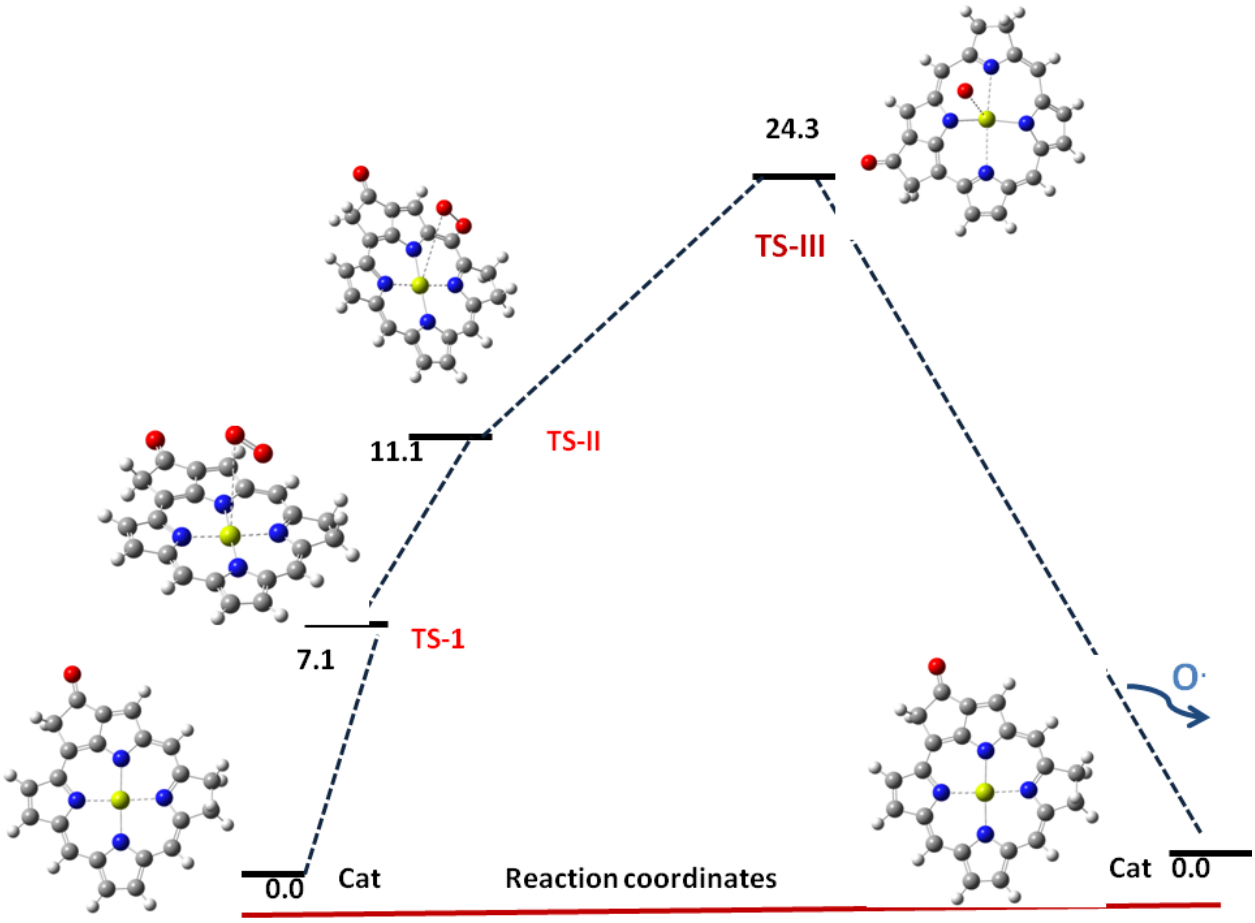
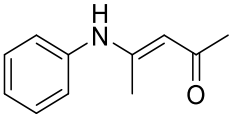
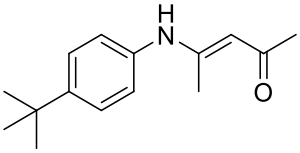


Fig S10: Molecular oxygen conversion into singlet oxygen mechanism by chlorophyll calculated using B3LYP level. Relative free energies are given in kcal/mol.

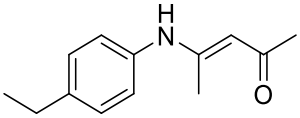
6. Characterizations of the starting materials and the products



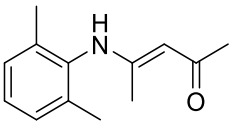
(E)-4-(phenylamino)pent-3-en-2-one[5] (1a): **^{1}H NMR** (300 MHz, $CDCl_3$) δ 12.47 (s, 1H), 7.32 (dd, *J* = 8.5, 7.1 Hz, 2H), 7.21 – 7.14 (m, 1H), 7.09 (dd, *J* = 7.3, 1.5 Hz, 2H), 5.18 (s, 1H), 2.09 (s, 3H), 1.98 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 196.2, 160.3, 138.8, 129.2, 125.6, 124.8, 97.7, 29.2, 19.9; **MS (GC-MS)**: *m/z* 175 (M^+); **reaction time:** 6 h; 99% yield.



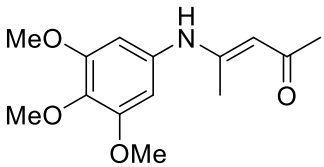
(E)-4-((4-(tert-butyl)phenyl)amino)pent-3-en-2-one [5] (7a): **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 12.43 (s, 1H), 7.34 (d, *J* = 8.6 Hz, 2H), 7.03 (d, *J* = 8.6 Hz, 2H), 5.16 (s, 1H), 2.09 (s, 3H), 1.98 (s, 3H), 1.31 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): *δ* 195.9, 160.9, 148.8, 136.1, 126.0, 124.5, 97.4, 34.6, 31.4, 29.2, 20.0; **MS (GC-MS)**: *m/z* 231 (M^+); 96% yield.



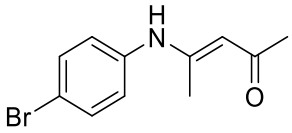
(E)-4-((4-ethylphenyl)amino)pent-3-en-2-one[5] (8a): **^{1}H NMR** (400 MHz, $CDCl_3$): δ 12.43 (s, 1H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 5.18 (s, 1H), 2.65 (d, *J* = 7.6 Hz, 2H), 2.10 (s, 3H), 1.98 (s, 3H), 1.24 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): *δ* 195.8, 160.9, 141.9, 136.2, 128.5, 124.9, 97.2, 29.0, 28.3, 19.8, 15.5; **MS (GC-MS)**: *m/z* 203 (M^+); 87% yield.



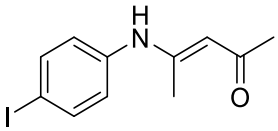
(E)-4-((2,6-dimethylphenyl)amino)pent-3-en-2-one (9a)[6]: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 11.96 (s, 1H), 7.11 (q, *J* = 5.4 Hz, 3H), 5.23 (s, 1H), 2.22 (s, 6H), 2.13 (s, 3H), 1.64 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): *δ* 196.1, 162.9, 136.6, 136.2, 128.3, 127.5, 95.9, 29.1, 18.9, 18.3; **MS (GC-MS)**: *m/z* 203 (M^+); 78% yield.



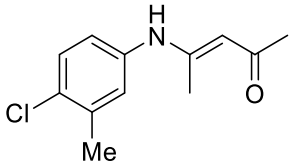
(E)-4-((3,4,5-trimethoxyphenyl)amino)pent-3-en-2-one[5] (10a): **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 12.38 (s, 1H), 6.33 (s, 2H), 5.18 (s, 1H), 3.83 (s, 6H), 3.80 (s, 3H), 2.10 (s, 3H), 1.99 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 196.3, 160.8, 153.5, 136.3, 134.6, 103.0, 97.5, 92.8, 61.1, 56.3, 29.3, 20.0; **MS (GC-MS)**: *m/z* 265 (M^+); 90 % yield.



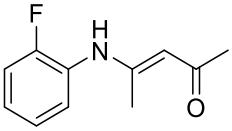
(E)-4-((4-(tert-bromo)phenyl)amino)pent-3-en-2-one [7] (11a): **^{1}H NMR** (400 MHz, $CDCl_3$): δ 12.39 (s, 1H), 7.41 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 5.17 (s, 1H), 2.06 (s, 3H), 1.95 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.6, 159.8, 137.9, 132.2, 126.1, 118.8, 98.3, 29.2, 19.8; **MS (GC-MS)**: *m/z* 253 (M^+); 91 % yield.



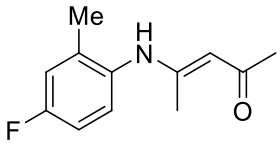
(E)-4-((4-(tert-iodo)phenyl)amino)pent-3-en-2-one[5] (12a): **^{1}H NMR** (400 MHz, $CDCl_3$): δ 12.57 – 12.23 (bs, 1H), 7.65 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.22 (s, 1H), 2.11 (s, 3H), 2.01 (s, 3H).; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.7, 159.5, 138.3, 126.4, 117.4, 98.5, 89.5, 29.4, 20; **MS (GC-MS)**: *m/z* 301 (M^+); 92% yield.



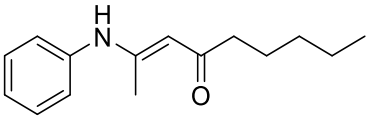
(E)-4-((4-chloro-3-methylphenyl)amino)pent-3-en-2-one (13a): **^{1}H NMR** (400 MHz, $CDCl_3$): δ 12.19 (s, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.75 (d, *J* = 2.6 Hz, 1H), 6.65 (dd, *J* = 8.5, 2.6 Hz, 1H), 4.98 (s, 1H), 2.13 (s, 3H), 1.89 (s, 3H), 1.76 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.3, 160.1, 137.2, 137.0, 131.3, 129.5, 127.0, 123.3, 97.9, 29.5, 20.1, 19.8; **MS (GC-MS)**: *m/z* 223 (M^+); 54% yield.



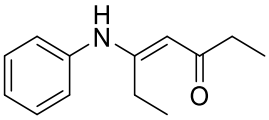
(E)-4-((2-fluorophenyl)amino)pent-3-en-2-one[8] (14a): **^{1}H NMR** ((300 MHz, $CDCl_3$) δ 12.25 (s, 1H), 7.32 – 6.94 (m, 4H), 5.27 (s, 1H), 2.12 (s, 3H), 1.95 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 196.8, 160.6, 156.8 (d, *J* = 248.0 Hz), 127.3 (d, *J* = 11.0 Hz), 124.4 (d, *J* = 4.0 Hz), 116.4 (d, *J* = 20.2 Hz), 98.3, 29.3, 19.6; **MS (GC-MS)**: *m/z* 193 (M^+); 92% yield.



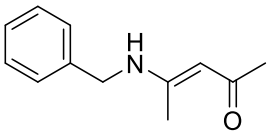
(E)-4-((4-fluoro-2-methylphenyl)amino)pent-3-en-2-one (15a): **^{1}H NMR** (400 MHz, $CDCl_3$): δ 12.12 (s, 1H), 7.00 (dd, *J* = 8.7, 5.4 Hz, 1H), 6.93 – 6.88 (m, 1H), 6.87 – 6.79 (m, 1H), 5.17 (s, 1H), 2.21 (s, 3H), 2.06 (s, 3H), 1.77 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.2, 161.7, 161.0 (d, *J* = 245.6 Hz), 135.1 (d, *J* = 325.9 Hz), 128.2, 117.3 (d, *J* = 22.2 Hz), 113.2 (d, *J* = 22.5 Hz), 97.0, 29.0, 19.5, 18.2; **MS (GC-MS)**: *m/z* 207 (M^+); **ESI-HRMS:** *m/z* calcd. For $C_{12}H_{14}FNO[M+H]^+$: 208.1132, found: 208.1132; 90 % yield.



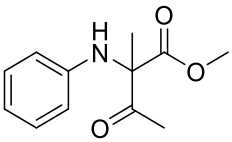
(E)-2-(phenylamino)non-2-en-4-one (16a): **^{1}H NMR** (300 MHz, $CDCl_3$) δ 12.56 (s, 1H), 7.33 (dd, *J* = 8.3, 7.2 Hz, 2H), 7.24 – 7.15 (m, 1H), 7.15 – 7.06 (m, 2H), 5.19 (s, 1H), 2.41 – 2.28 (m, 2H), 2.01 (s, 3H), 1.76 – 1.57 (m, 2H), 1.44 – 1.28 (m, 4H), 1.02 – 0.85 (m, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 199.4, 160.1, 138.9, 129.1, 125.4, 124.5, 97.3, 42.3, 31.8, 25.7, 22.6, 20.0, 14.0; **MS (GC-MS)**: *m/z* 231 (M^+); **ESI-HRMS:** *m/z* calcd. For $C_{15}H_{21}NO[M+H]^+$: 232.1696, found: 232.1700; 87% yield.



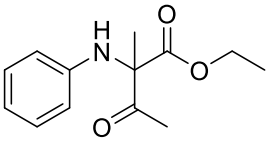
(E)-5-(phenylamino)hept-4-en-3-one (17a)[9]: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 12.52 (s, 1H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.25 – 7.18 (m, 1H), 7.17 – 7.09 (m, 2H), 5.24 (s, 1H), 2.48 – 2.25 (m, 4H), 1.13 (m, 6H)**^{13}C NMR** (100 MHz, $CDCl_3$): *δ* 200.2, 165.9, 138.7, 129.1, 125.7, 125.2, 94.4, 35.3, 25.2, 12.5, 9.9; **MS (GC-MS)**: *m/z* 203 (M^+); 91% yield.



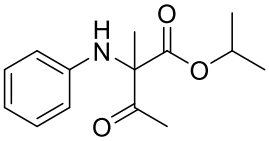
(E)-4-(benzylamino)pent-3-en-2-one (18a): **^{1}H NMR** (400 MHz, $CDCl_3$): δ 11.15 (s, 1H), 7.41 – 7.14 (m, 5H), 5.05 (s, 1H), 4.45 (d, *J* = 6.3 Hz, 2H), 2.02 (s, 3H), 1.92 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): *δ* 195.3, 163.4, 138.0, 128.8, 127.4, 126.7, 95.9, 46.7, 28.8, 18.9; **MS (GC-MS)**: *m/z* 169 (M^+); **ESI-HRMS:** *m/z* calcd. For $C_{12}H_{15}NO[M+H]^+$: 190.1226, found: 190.1228; 61% yield.



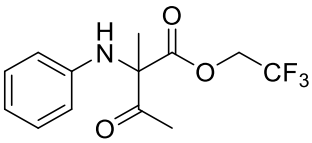
3-Oxo-*N*-phenyl-isovaline methyl ester[10] (1b): **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.17 (dd, *J* = 8.6, 7.3 Hz, 2H), 6.78 – 6.73 (m, 1H), 6.55 (dt, *J* = 7.7, 1.0 Hz, 2H), 5.17 (bs, 1H) 3.81 (s, 3H), 2.22 (s, 3H), 1.71 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): *δ* 203.5, 171.7, 143.9, 129.4, 118.4, 114.1, 69.6, 53.6, 24.7, 18.4; **MS (GC-MS)**: *m/z* 221 (M^+); **reaction time:** 8 h; 92% yield, **TON**: 307.



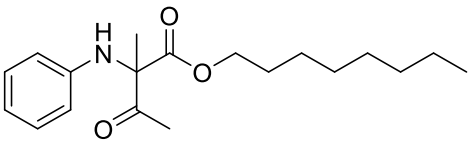
Ethyl 3-oxo-2-(phenylamino)butanoate[11] (2b): **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.14 (dd, *J* = 8.6, 7.3 Hz, 2H), 6.73 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.57 – 6.47 (m, 2H), 5.28 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.20 (s, 3H), 1.68 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): *δ* 203.9, 171.3, 144.1, 129.5, 118.5, 114.3, 69.8, 62. 9, 24.8, 18.7, 14.1 ; **MS (GC-MS)**: *m/z* 235 (M^+); **reaction time:** 8 h; 72% yield, **TON:** 240.



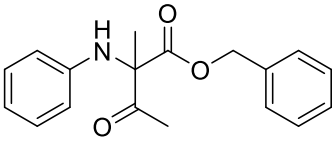
Isopropyl 3-oxo-2-(phenylamino)butanoate[10] (3b): **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.16 (dd, J = 8.6, 7.3 Hz, 2H), 6.75 (tt, J = 7.4, 1.0 Hz, 1H), 6.63 – 6.49 (m, 2H), 5.28 (bs, 1H), 5.12 (p, J = 6.2 Hz, 1H), 2.20 (s, 3H), 1.68 (s, 3H), 1.27 (d, J = 6.2 Hz, 3H), 1.19 (d, J = 6.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 203.8, 170.6, 144.2, 129.4, 118.3, 114.2, 70.6, 24.6, 21.4, 21.3, 18.5; **MS (GC-MS)**: *m/z* 249 (M^+); **ESI-HRMS:** *m/z* calcd. For $C_{14}H_{19}NO_3[M+H]^+$: 250.1438, found: 250.1441; **reaction time:** 8h; 51% yield, **TON:** 170.



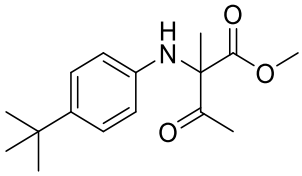
2,2,2-Trifluoroethyl 3-oxo-2-(phenylamino)butanoate (4b): **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.19 – 7.13 (m, 2H), 6.80 – 6.74 (m, 1H), 6.58 – 6.51 (m, 2H), 5.24 (s, 1H), 4.65 (dq, J = 12.6, 8.2 Hz, 1H), 4.47 (dq, J = 12.6, 8.2 Hz, 1H), 2.24 (s, 3H) 1.75 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.85, 170.17, 143.68, 129.55, 122.50 (d, J = 277.7 Hz), 118.94, 114.48, 69.86, 61.43 (q, J = 37.1 Hz), 24.50, 19.07; **MS (GC-MS)**: *m/z* 289 (M^+); **ESI-HRMS:** *m/z* calcd. For $C_{13}H_{14}F_3NO_3[M+H]^+$: 312.0816, found: 312.0820; **reaction time:** 6 h; 68% yield, **TON:** 227.



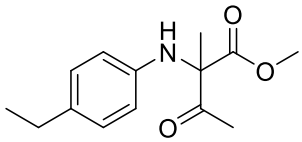
Octyl 3-oxo-2-(phenylamino)butanoate (5b): **^{1}H NMR** (400 MHz, $CDCl_3$): δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.11 (m, 2H), 6.75 (tt, J = 7.3, 1.1 Hz, 1H), 6.59 – 6.51 (m, 2H), 5.33 (s, 1H), 4.20 (td, J = 6.6, 1.7 Hz, 2H), 2.22 (s, 3H), 1.71 (s, 3H), 1.61 (hept, J = 6.7, 6.0 Hz, 2H), 1.38 – 1.22 (m, 10H), 0.90 (t, J = 6.9 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 203.6, 171.2, 144.0, 129.4, 118.3, 114.1, 69.7, 66.9, 31.7, 29.1, 28.4, 25.6, 24.7, 22.6, 18.6, 14.1; **MS (GC-MS)**: *m/z* 319 (M^+); **ESI-HRMS:** *m/z* calcd. For $C_{19}H_{29}NO_3[M+H]^+$: 320.1326, found: 320.1332; **reaction time:** 8 h; 89% yield, **TON:** 297; **5b-s: 5 mmol scale, sunlight**, 5h, 82 %, **TON:** 273.



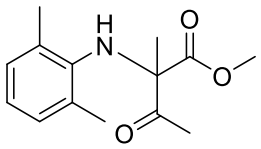
Benzyl 3-oxo-2-(phenylamino)butanoate[12] (6b): **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41 – 7.31 (m, 3H), 7.31 – 7.24 (m, 2H), 7.16 (dd, J = 8.6, 7.3 Hz, 2H), 6.76 (tt, J = 7.3, 1.1 Hz, 1H), 6.54 (dt, J = 7.7, 1.1 Hz, 2H), 5.33 (s, 1H), 5.23 (s, 2H), 2.11 (s, 3H), 1.72 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 203.2, 171.0, 143.9, 134.7, 129.4, 128.7, 128.4, 118.4, 114.2, 69.8, 68.2, 24.6, 18.7; **MS (GC-MS)**: *m/z* 297 (M^+); **reaction time:** 10 h; 68% yield, **TON:** 227.



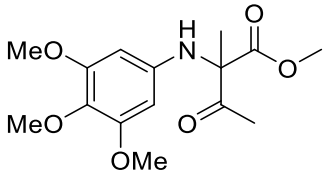
Methyl 2-((4-(tert-butyl)phenyl)amino)-3-oxobutanoate[10] (7b): **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.19 (d, *J* = 8.7 Hz, 2H), 6.49 (d, *J* = 8.8 Hz, 2H), 5.19 (d, *J* = 2.8 Hz, 1H), 3.81 (s, 3H), 2.22 (s, 3H), 1.69 (s, 3H), 1.28 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): *δ* 203.2, 203.9, 171.9, 141.2, 126.1, 114.0, 69.7, 53.5, 31.5, 24.8, 18.7; **MS (GC-MS)**: *m/z* 277 (M^+); **reaction time:** 8 h; 62% yield, **TON:** 207. (An impurity of around 6 % is present, the yield is corrected by this value, **MS (GC-MS)**: *m/z* 277 (M^+) with no other mass present; signals at **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.36, 7.34, 7.05, 7.03, 6.57, 6.55, 3.73, results indicate that the *m-tert*-butyl-isomer product is present, the origin of the isomer is unknown)



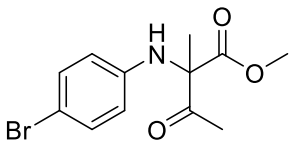
Methyl 2-((4-ethylphenyl)amino)-2-methyl-3-oxobutanoate[10] (8b): **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.07 – 6.97 (m, 2H), 6.53 – 6.45 (m, 2H), 5.17 (s, 1H), 3.81 (s, 3H), 2.55 (q, *J* = 7.6 Hz, 2H), 2.22 (s, 3H), 1.69 (s, 3H), 1.20 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): *δ* 204.0, 172.0, 141.8, 134.4, 128.8, 114.5, 69.8, 53.6, 28.0, 24.9, 18.8, 15.9; **MS (GC-MS)**: *m/z* 249 (M^+); **reaction time:** 8 h; 69% yield, **TON:** 230. (An impurity of around 3 % present, the yield is corrected by this value, signals at **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.00, 6.45, 6.47, **MS (GC-MS)**: *m/z* 249 (M^+) with no other mass present, results indicate that an unknown isomer product is present, the origin of the isomer is unknown)



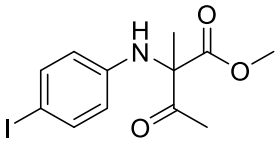
Methyl 2-((2,6-dimethylphenyl)amino)-2-methyl-3-oxobutanoate[10] (9b): **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.97 (d, *J* = 7.4 Hz, 2H), 6.89 (dd, *J* = 8.2, 6.6 Hz, 1H), 4.93 (s, 1H), 3.83 (s, 3H), 2.30 (d, *J* = 1.2 Hz, 3H), 2.17 (s, 6H), 1.17 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): *δ* 203.6, 171.9, 154.1, 140.6, 91.9, 61.2, 56.1, 53.7, 34.3, 24.9, 22.5, 18.9, 14.2; **MS (GC-MS)**: *m/z* 249 (M^+); **ESI-HRMS:** *m/z* calcd. For $C_{14}H_{19}NO_3[M+H]^+$: 250.1438, found: 250.1441; **reaction time:** 6 h; 65% yield, **TON:** 217; **9b-s:** 5h 82 %; **TON-s:** 273.



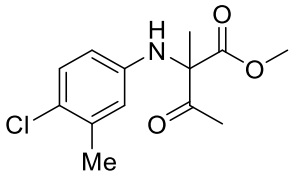
Methyl 2-methyl-3-oxo-2-((3,4,5-trimethoxyphenyl)amino)butanoate (10b): **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 5.76 (s, 2H) 3.80-3.75 (m, 12H), 2.20 (s, 3H) 0.88 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): *δ* 203.6, 171.9, 154.1, 140.6, 91.9, 61.2, 56.1, 53.7, 34.3, 24.9, 22.5, 18.9, 14.2; **MS (GC-MS)**: *m/z* 311 (M^+); **ESI-HRMS:** *m/z* calcd. For $C_{15}H_{21}NO_6[M+H]^+$: 312.1442, found: 312.1431; **reaction time:** 12 h; 82% yield, **TON:** 273.



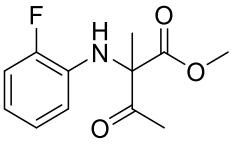
Methyl 2-((4-iodophenyl)amino)-3-oxobutanoate[11] (11b): **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.29 – 7.22 (m, 2H), 6.61 – 6.32 (m, 2H), 3.80 (s, 3H), 2.21 (s, 3H), 1.68 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.8, 171.4, 142.9, 132.1, 115.6, 110.2, 69.5, 53.6, 30.9, 24.6, 18.5 ; **MS (GC-MS)**: *m/z* 299 (M^+); **reaction time:** 12 h, 48% yield, **TON:** 160.



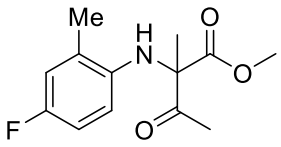
Methyl 2-((4-iodophenyl)amino)-3-oxobutanoate (12b)[13]: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51 – 7.32 (m, 2H), 6.42 – 6.21 (m, 2H), 5.36 (s, 1H), 3.78 (d, *J* = 1.4 Hz, 3H), 2.18 (d, *J* = 1.3 Hz, 3H), 1.66 (d, *J* = 1.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.8, 171.5, 143.6, 138.1, 116.3, 79.4, 69.5, 53.8, 24.7, 18.6; **MS (GC-MS)**: *m/z* 347 (M^+); **ESI-HRMS:** *m/z* calcd. For $C_{12}H_{14}INO_3[M+H]^+$: 348.0091, found: 348.0093; **reaction** time: 6h, 64% yield, **TON:** 213. (An impurity of around 4 % present, the yield is corrected by this value, signals at **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43, 6.40, 6.37, 3.73; **MS (GC-MS)**: *m/z* 347 (M^+) with no other mass present, results indicate that an unknown isomer product is present, the origin of the isomer is unknown)



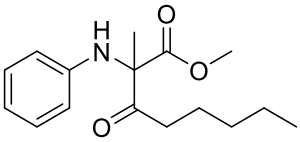
Methyl 2-((4-chloro-3-methylphenyl)amino)-2-methyl-3-oxobutanoate[13] (13b): **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.08 (d, *J* = 8.6 Hz, 1H), 6.48 – 6.39 (m, 1H), 6.27 (dd, *J* = 8.6, 2.9 Hz, 1H), 3.78 (s, 3H), 2.26 (s, 3H), 2.19 (s, 3H), 1.66 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 203.1, 171.5, 142.5, 136.9, 129.6, 123.6, 116.7, 112.6, 69.5, 53.6, 24.6, 20.3, 18.6; **MS (GC-MS)**: *m/z* 269 (M^+); **ESI-HRMS:** *m/z* calcd. For $C_{13}H_{16}ClNO_3[M+H]^+$: 270.0891, found: 270.0894; **reaction time:** 7 h; 41% yield, **TON:** 137.



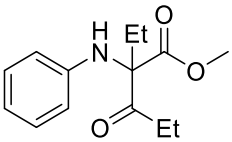
Methyl 2-((2-fluorophenyl)amino)-2-methyl-3-oxobutanoate[11] (14b): **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.03-6.99 (m, 1H), 6.92.6.87 (m, 1H), 6.70-6.62 (m, 1H), 6.48 – 6.35 (m, 1H), 3.80 (s, 3H), 2.21 (s, 3H), 1.68 (s, 3H).; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.93, 171.34, 152.06 (d, *J* = 239.8 Hz), 132.40, 124.43, 118.06 (d, *J* = 6.9 Hz), 115.06 (d, *J* = 18.9 Hz), 113.35, 69.29, 53.61, 24.61, 18.66; **MS (GC-MS)**: *m/z* 239 (M^+); **reaction time:** 8 h; 78% yield, **TON:** 260.



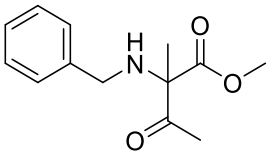
Methyl 2-((4-fluoro-2-methylphenyl)amino)-3-oxobutanoate (15b): **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 6.83 (dd, *J* = 9.2, 3.1 Hz, 1H), 6.71 (td, *J* = 8.5, 3.1 Hz, 1H), 6.22 (dd, *J* = 8.8, 4.7 Hz, 1H), 5.15 (s, 1H), 3.78 (d, *J* = 0.9 Hz, 3H), 2.24 (s, 3H), 2.19 (s, 3H), 1.66 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): *δ* 203.38, 171.92, 155.71 (d, *J* = 236.1 Hz), 138.16, 125.44 (d, *J* = 7.1 Hz), 117.51 (d, *J* = 22.4 Hz), 112.74 (d, *J* = 21.7 Hz), 111.98 (d, *J* = 7.8 Hz), 69.78, 53.54, 24.54, 18.74, 17.78; **MS (GC-MS)**: *m/z* 253 (M^+); **ESI-HRMS:** *m/z* calcd. For $C_{13}H_{16}FNO_3[M+H]^+$: 254.1187, found: 254.1188; **reaction time:** 6 h 62% yield; **TON:** 207; **15b-s: sunlight**; **reaction time:** 5 h, 72 % yield, **TON:** 240.



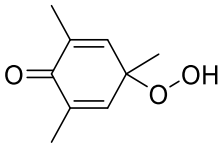
Methyl 2-methyl-3-oxo-2-(phenylamino)octanoate (16b): **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.20 – 7.07 (m, 2H), 6.81 – 6.66 (m, 1H), 6.54 – 6.46 (m, 2H), 5.33 (s, 1H), 3.76 (s, 3H), 2.55 – 2.41 (m, 2H), 1.68 (s, 3H), 1.57 (h, *J* = 7.0 Hz, 2H), 1.27 – 1.18 (m, 4H), 0.85 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): *δ* 205.77, 171.88, 143.93, 129.35, 118.24, 114.10, 69.45, 53.38, 36.85, 31.09, 23.52, 22.35, 18.66, 13.86; **MS (GC-MS)**: *m/z* 277 (M^+); **ESI-HRMS:** *m/z* calcd. For $C_{16}H_{23}NO_3[M+H]^+$: 278.1751, found: 278.1748; **reaction time:** 8h; 71% yield, **TON:** 237.



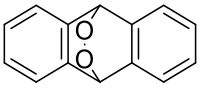
Methyl 2-ethyl-3-oxo-2-(phenylamino)pentanoate[11] (17b): ^{1}H NMR (400 MHz, CDCl3) *δ* 7.20 – 7.08 (m, 2H), 6.79 – 6.65 (m, 1H), 6.54 – 6.46 (m, 2H), 3.77 (s, 3H), 2.58 – 2.43 (m, 2H), 2.36 – 2.29 (m, 2H), 1.04 (t, *J* = 7.3 Hz,3H), 0.66 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.74, 171.13, 143.94, 129.41, 125.12, 118.20, 114.13, 94.41, 53.34, 30.25, 22.64, 8.26, 7.13. **MS (GC-MS)**: *m/z* 249 (M^+); **reaction time:** 6h; 81% yield, **TON:** 270. (An impurity of around 6 % present, the yield is corrected by this value, signals at **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 5.32, 5.22, 1.17, 1.15, **MS (GC-MS)**: *m/z* 249 (M^+) with no other mass present, results indicate substance is present, the origin of the impurity could degradation of the product to a cleavage product)



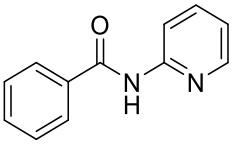
Methyl 2-(benzylamino)-2-methyl-3-oxobutanoate (18b): **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38 – 7.30 (m, 5H), 3.76 (s, 3H), 3.64 (s, 2H), 2.24 (s, 3H), 1.57 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): *δ* 204.9, 172.4, 139.8, 128.6, 128.4, 127.4, 72.1, 52.9, 47.9, 25.2, 19.0; **MS (GC-MS)**: *m/z* 235 (M^+); **ESI-HRMS:** *m/z* calcd. For $C_{13}H_{17}NO_3[M+H]^+$: 236.1281, found: 236.1280; **reaction time:** 7h; 71% yield, **TON:** 237.



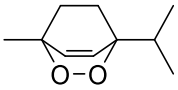
4-Hydroperoxy-2,4,6-trimethyl-2,5-cyclohexadien-1-one (19b) [14]: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81 (s, 1H), 6.62 (s, 2H), 1.92 (s, 6H); 1.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 186.7, 144.1, 137.0, 78.8, 23.2, 16.1; **MS (GC-MS)**: *m/z* 168 (M^+); **reaction time:** 24h; 81% yield.



Anthracene-9,10-endoperoxide (20b) [15]: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43-7.41 (m, 4H), 7.30-7.28 (m, 4H), 6.02 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 138.2, 128.1, 123.7, 79.5; **MS (GC-MS)**: *m/z* 210 (M^+); **reaction time:** 24h; 78% yield.



N-(pyridin-2-yl)benzamide (21b) [16]: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.70 (br, 1H), 8.40 (d, J = 8.4 Hz, 1H), 8.31 (d, J = 4.8 Hz, 1H), 7.95-7.93 (m, 2H), 7.79 – 7.75 (m, 1H). 7.60 – 7.56 (m, 1H), 7.53 – 7.47 (m, 2H), 7.10 – 7.07 (m,1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.7, 151.6, 147.8, 138.6, 134.3, 132.3, 128.8, 127.2, 119.9, 114.2; **MS (GC-MS)**: *m/z* 198 (M^+); **reaction time:** 24h; 62% yield.



Ascaridole (22b) [17]: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.49 (d, J = 8.4 Hz, 1H), 6.41 (d, J = 8.4 Hz, 1H), 2.10 – 1.98 (m, 2H), 1.94 – 1.89 (m, 1H), 1.56 – 1.46 (m, 2H), 1.37 (s, 3H), 1.0 (d, J = 8.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): *δ* 136.5, 133.2, 79.9, 74.5, 32.3, 29.7, 25.7, 21.5, 17.4, 17.3; **MS (GC-MS)**: *m/z* 235 (M^+); **MS (GC-MS)**: *m/z* 168 (M^+); **reaction time:** 24h; 83% yield.

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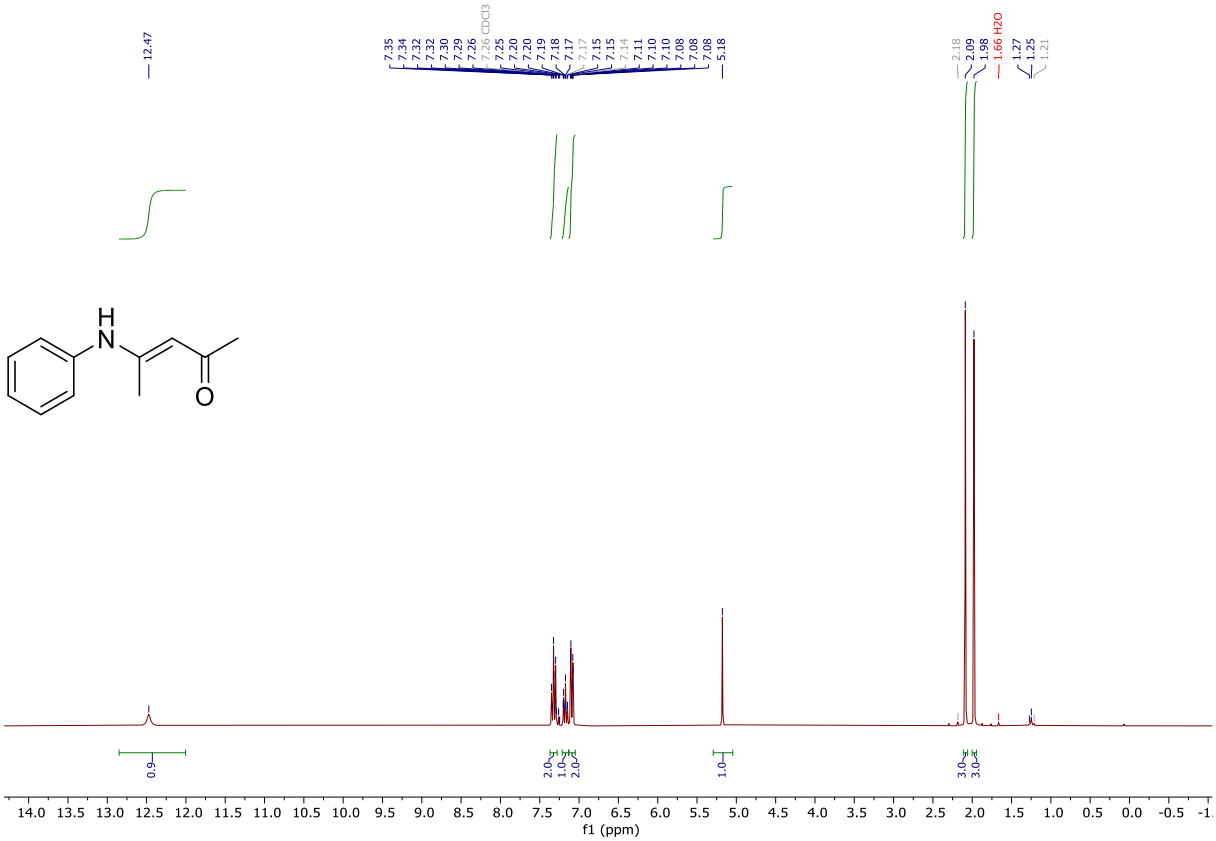
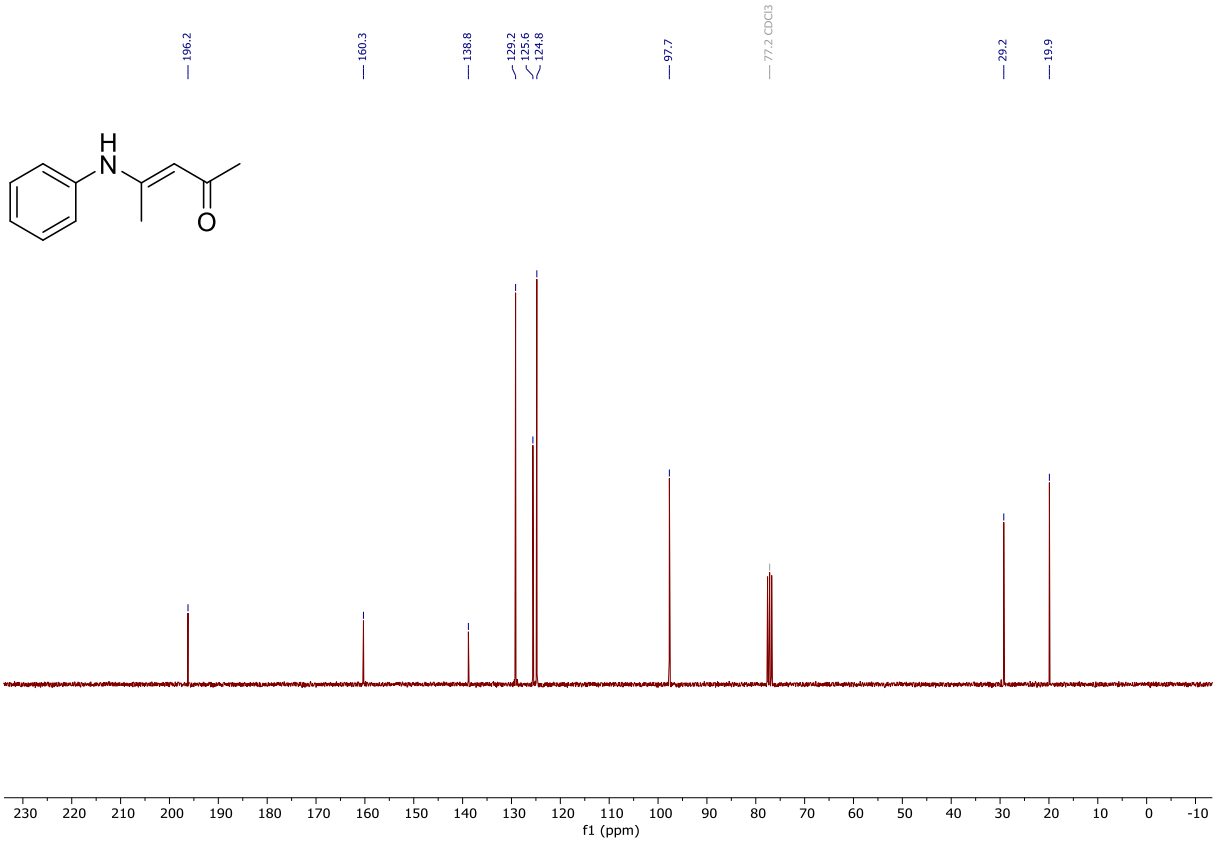
1a

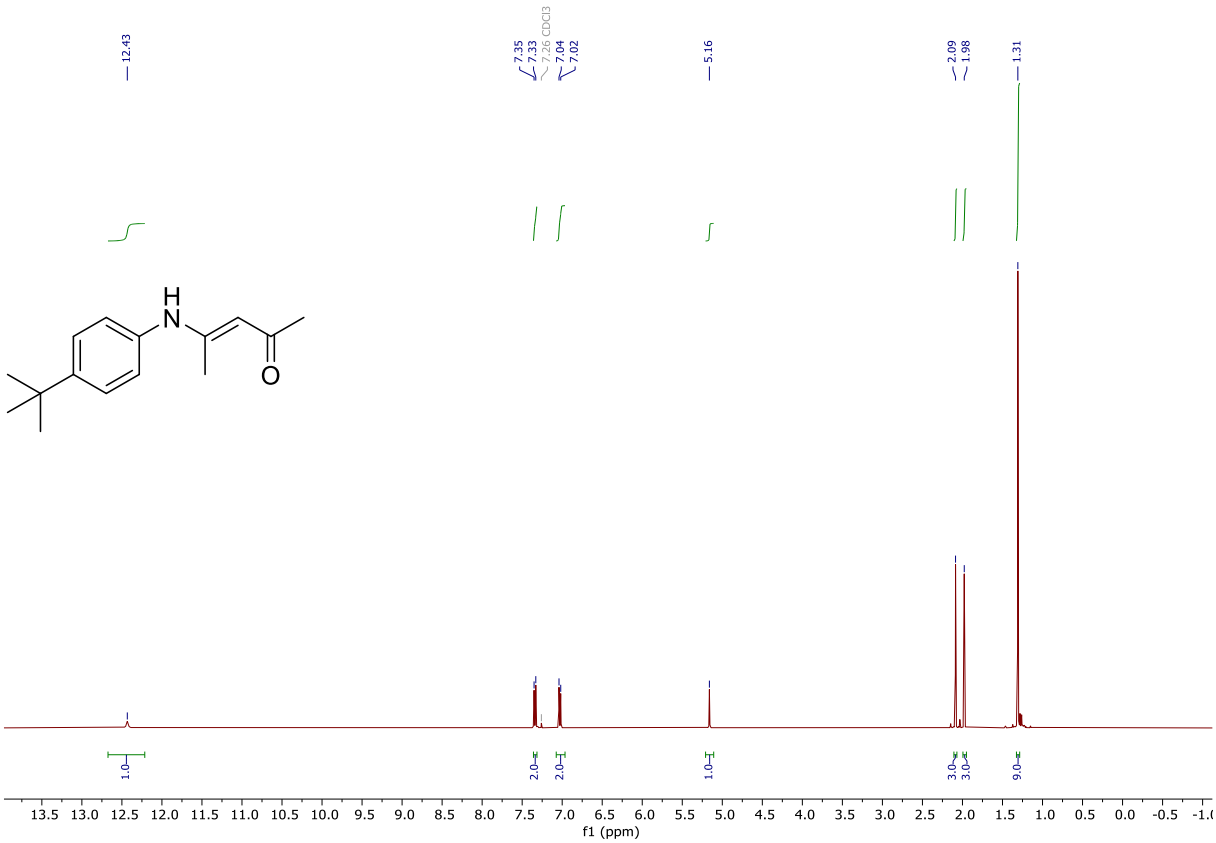


^{1}H-NMR in $CDCl_3$.



^{13}C-NMR in $CDCl_3$.

7a



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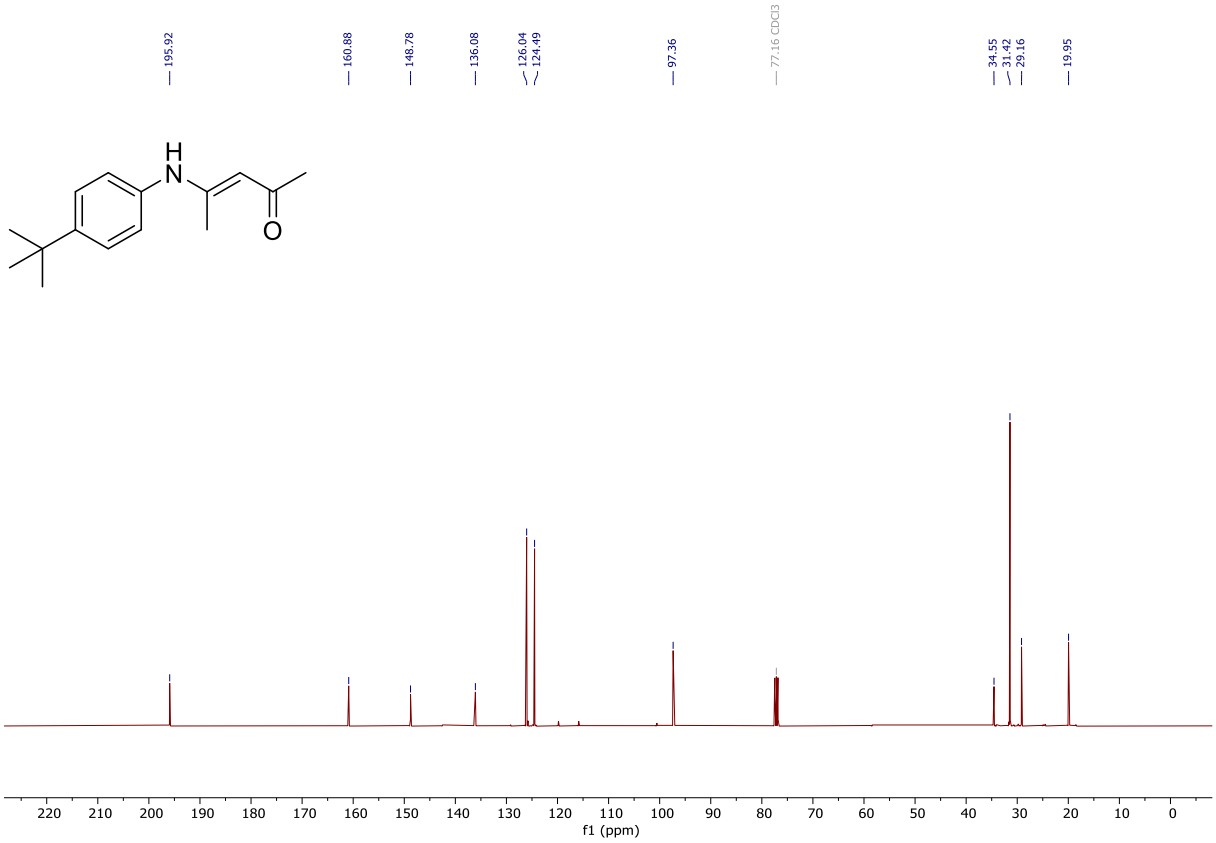

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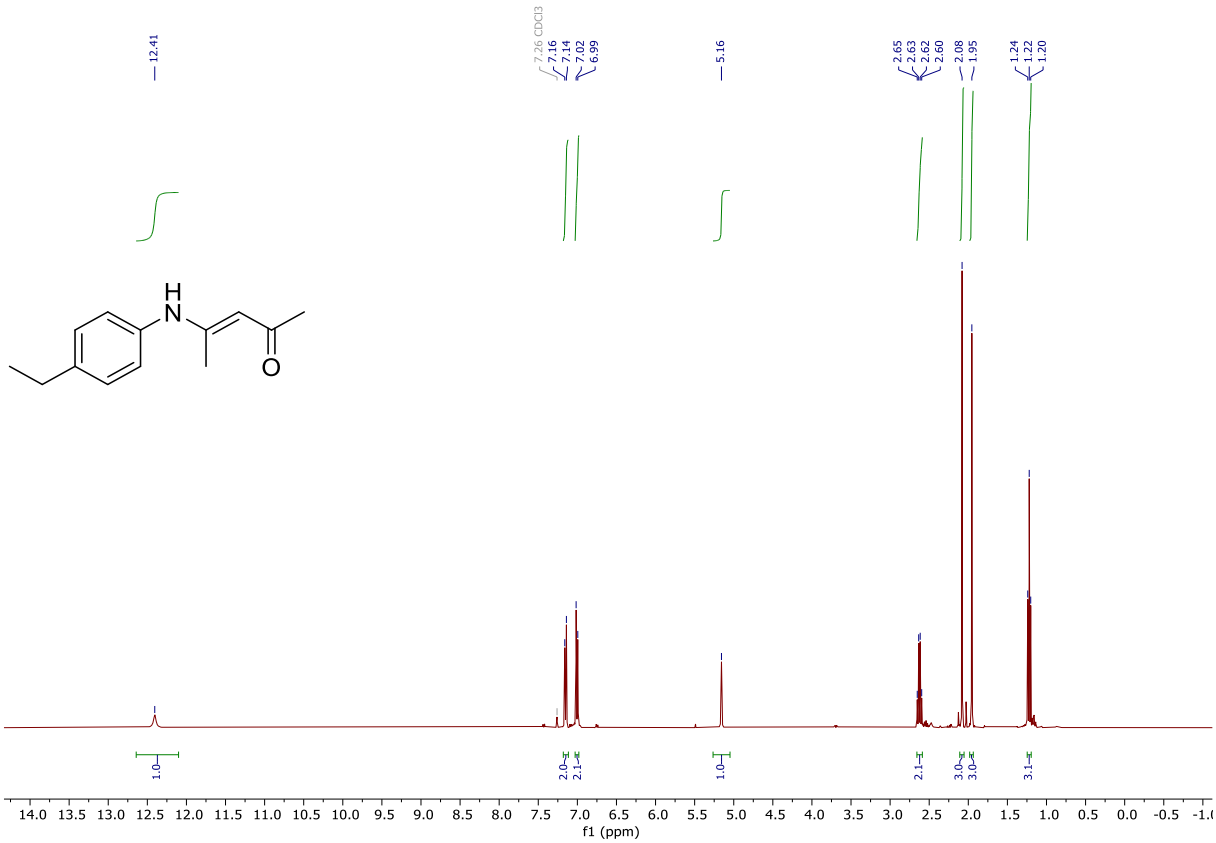
8a



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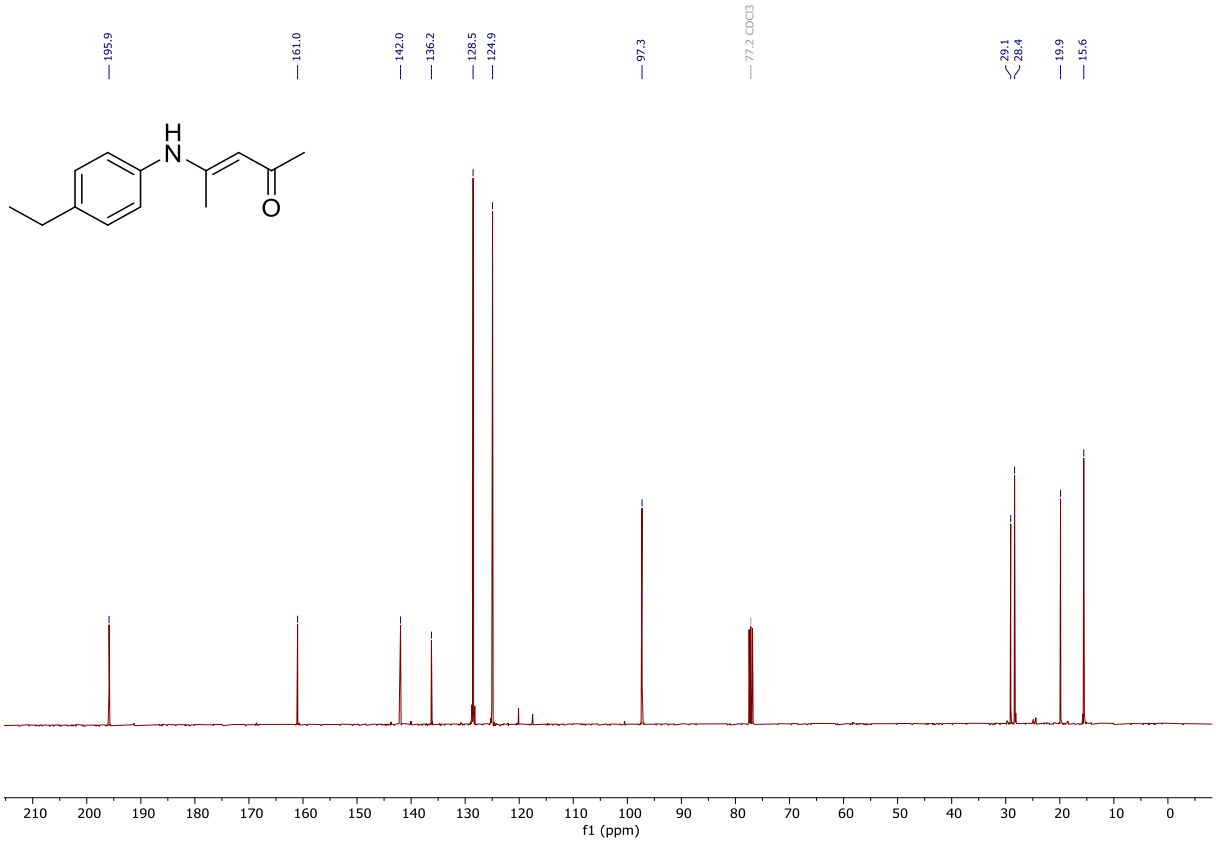

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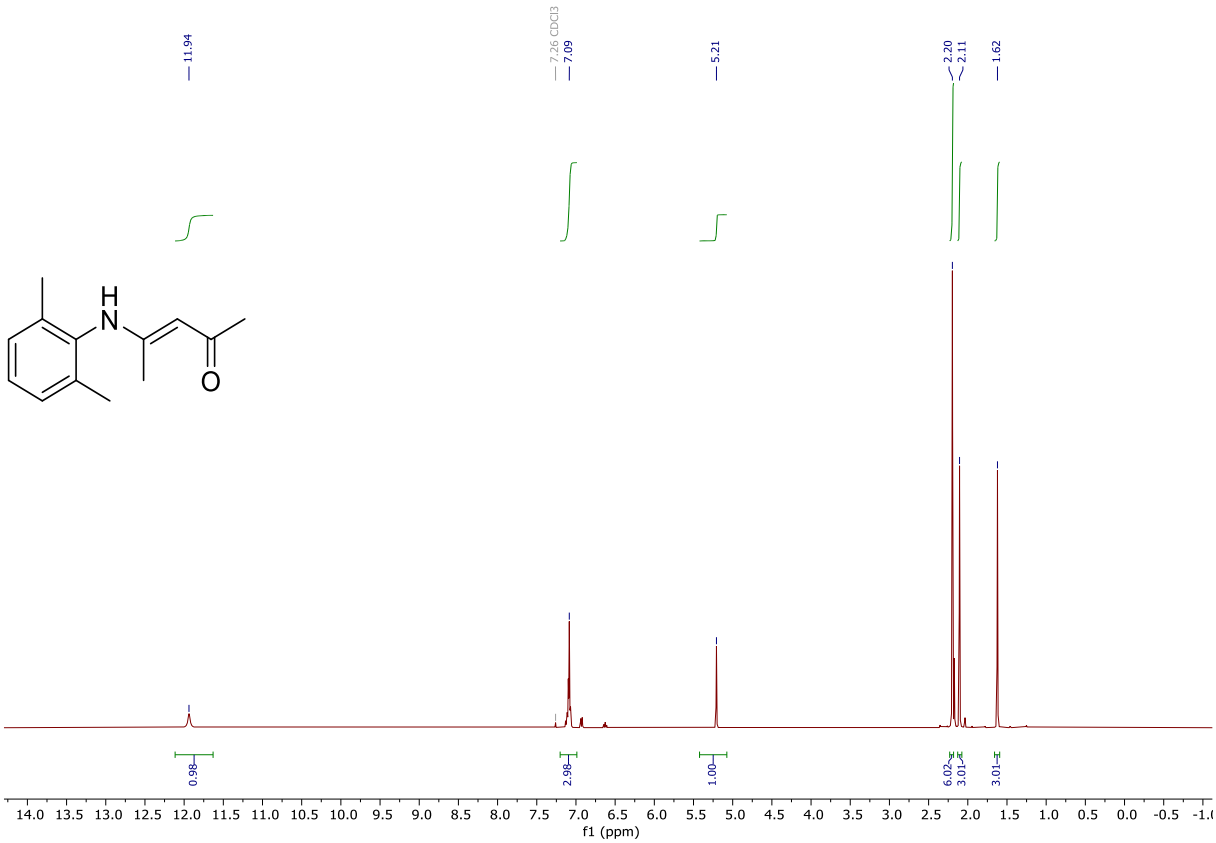
9a



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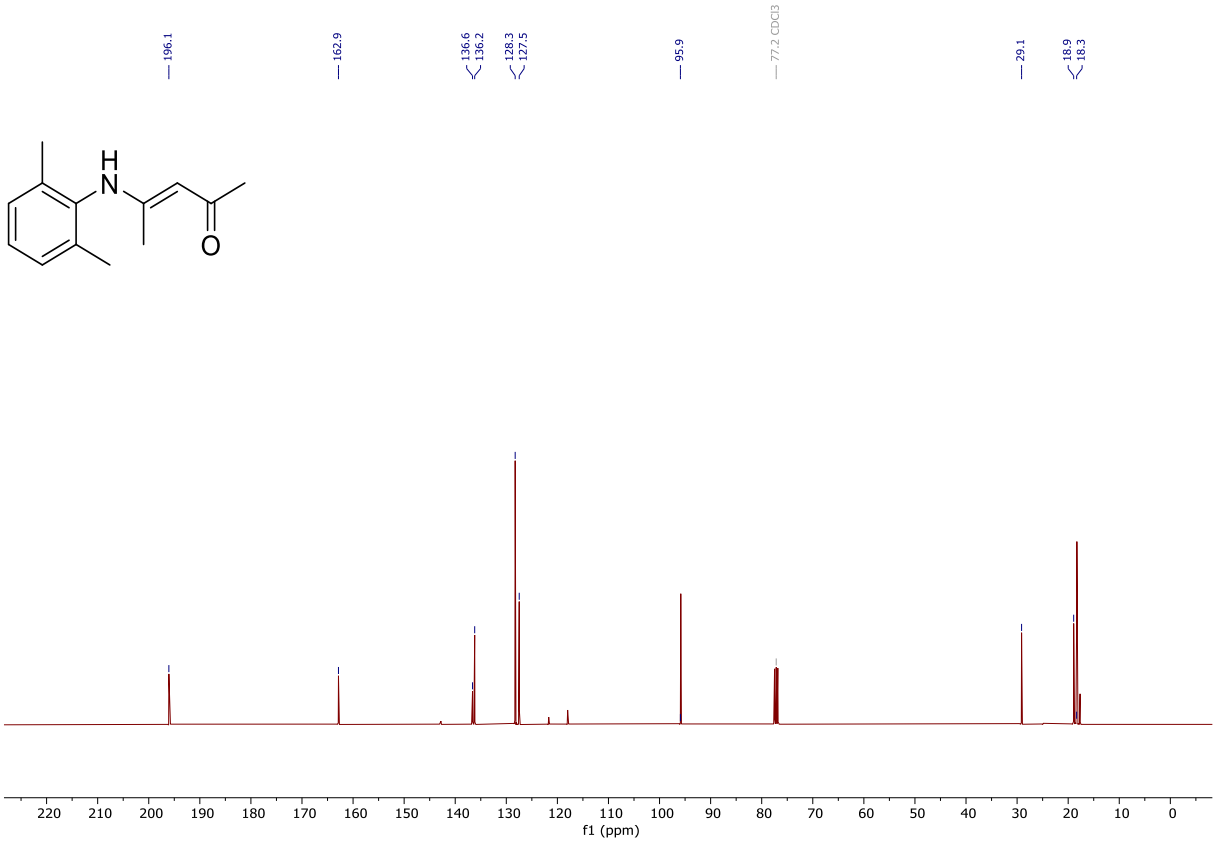

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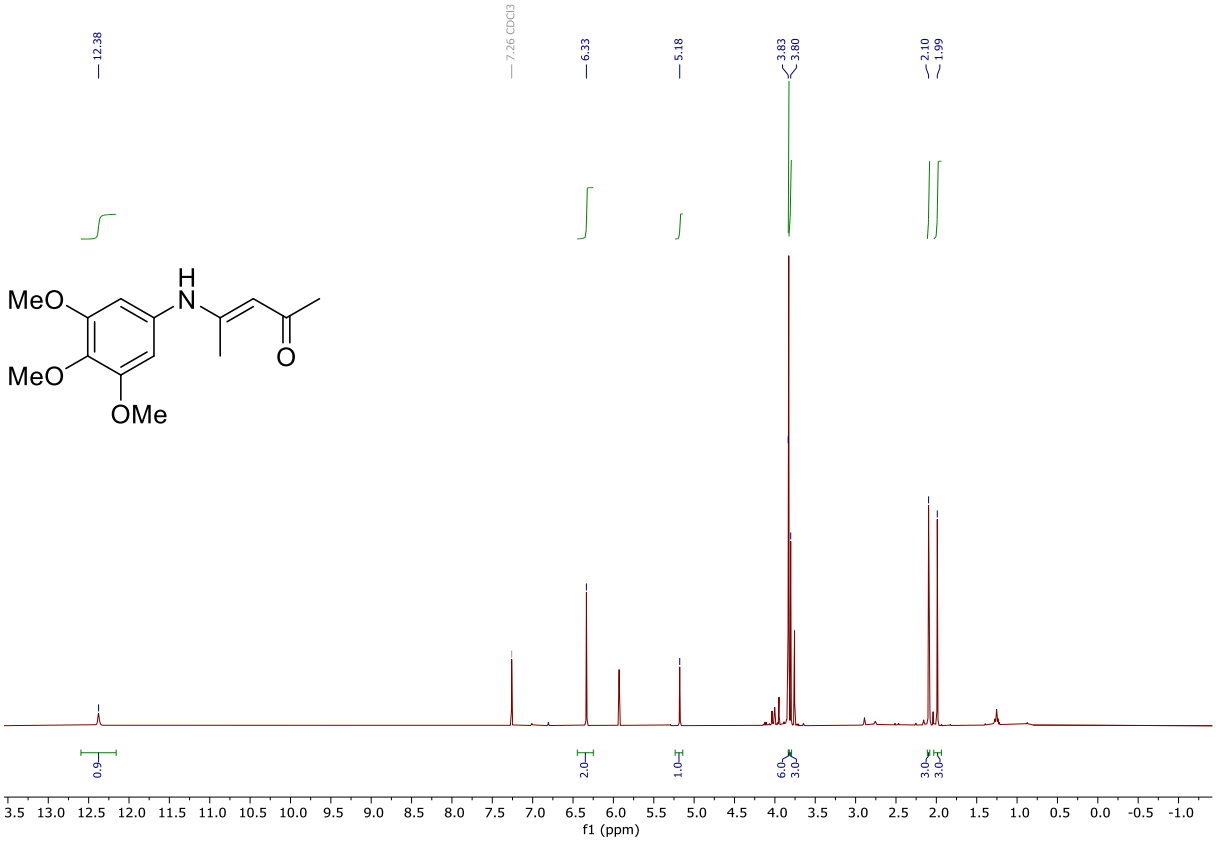
10a



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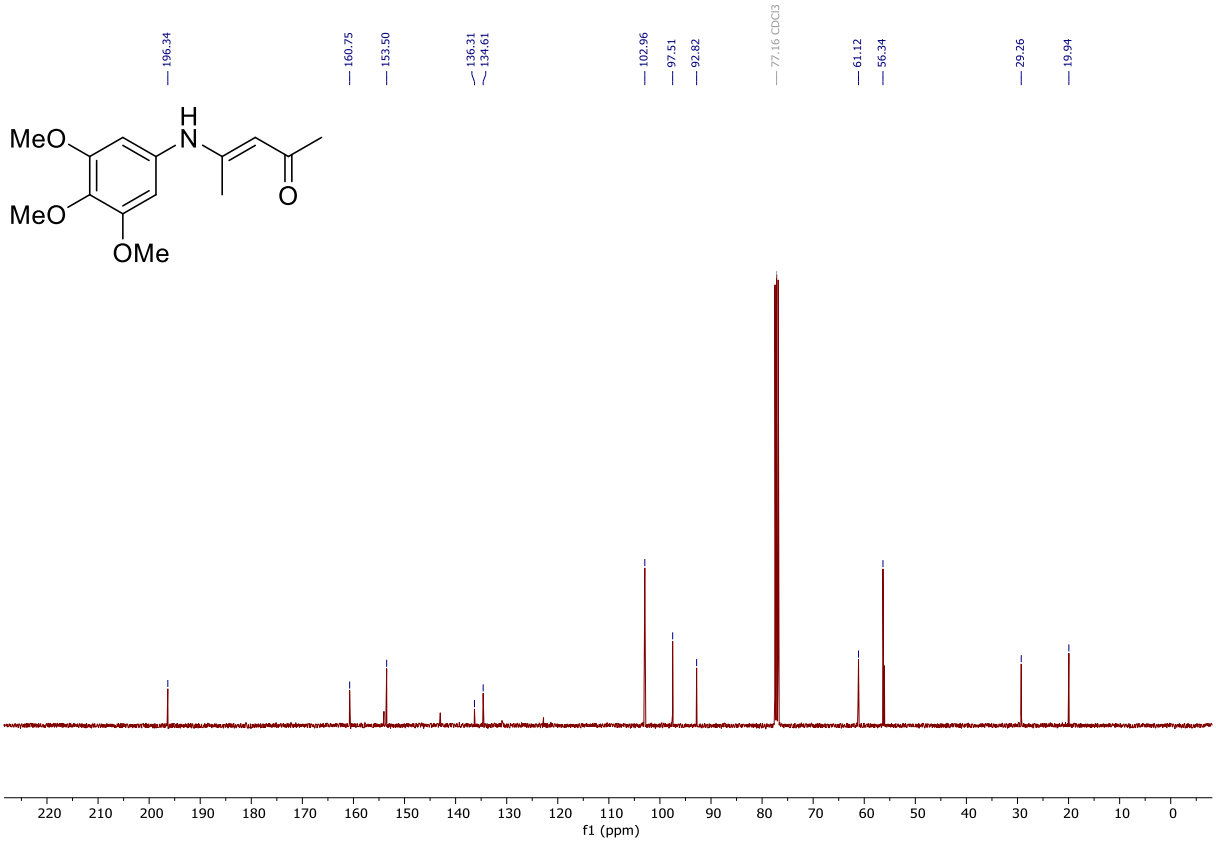

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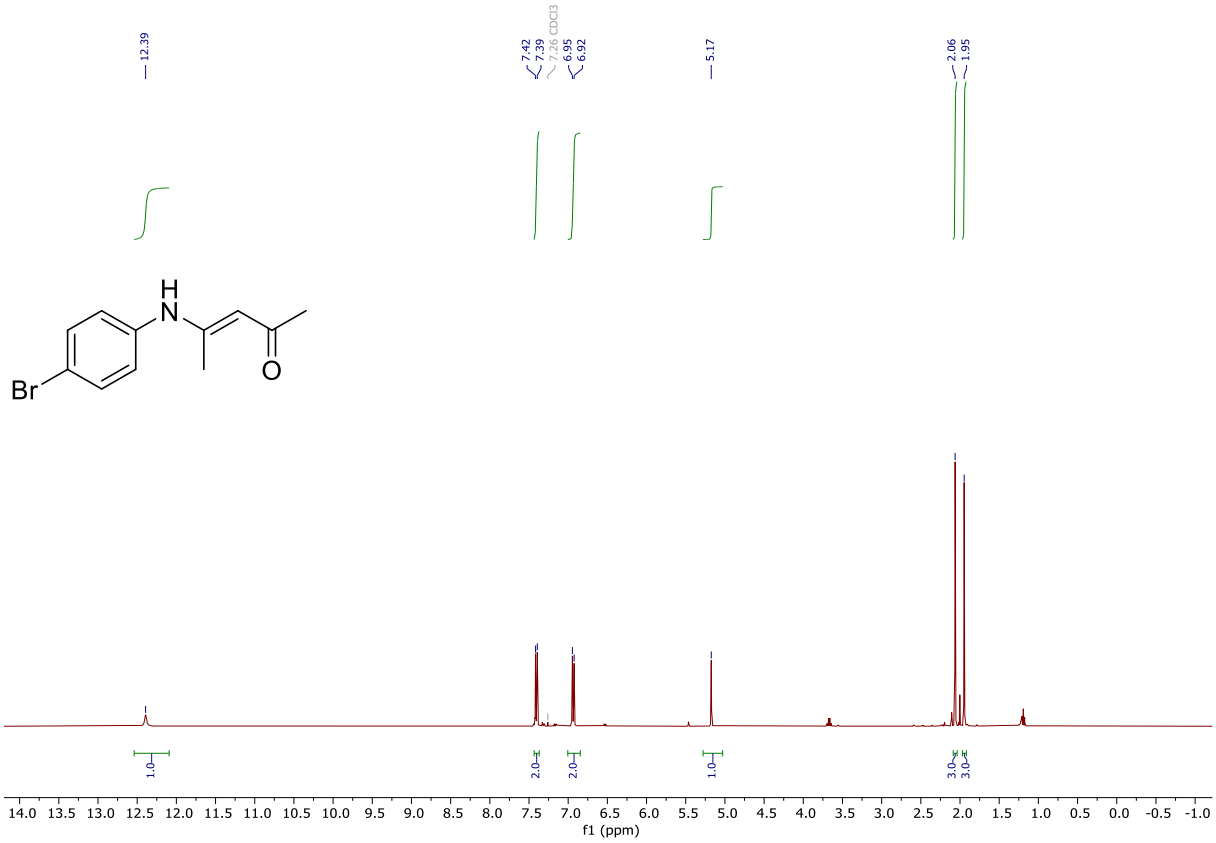
11a



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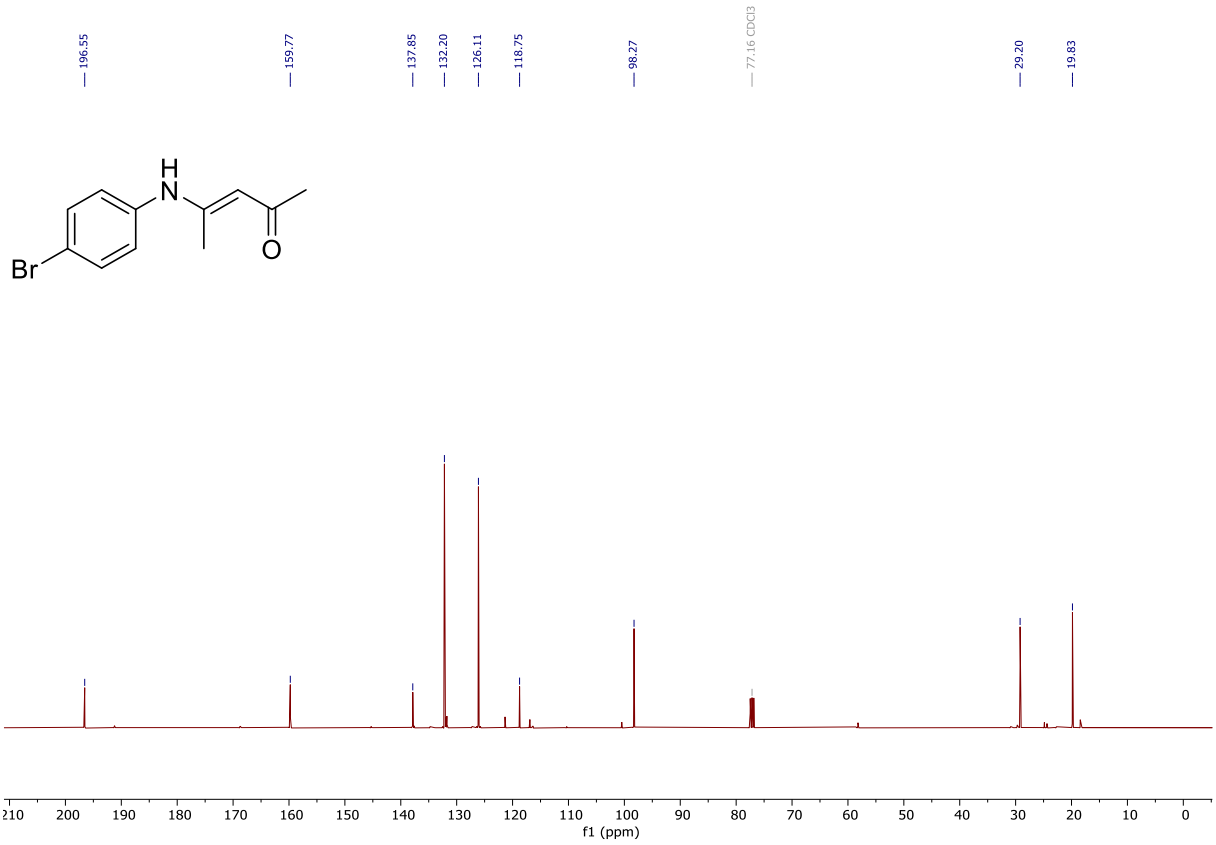

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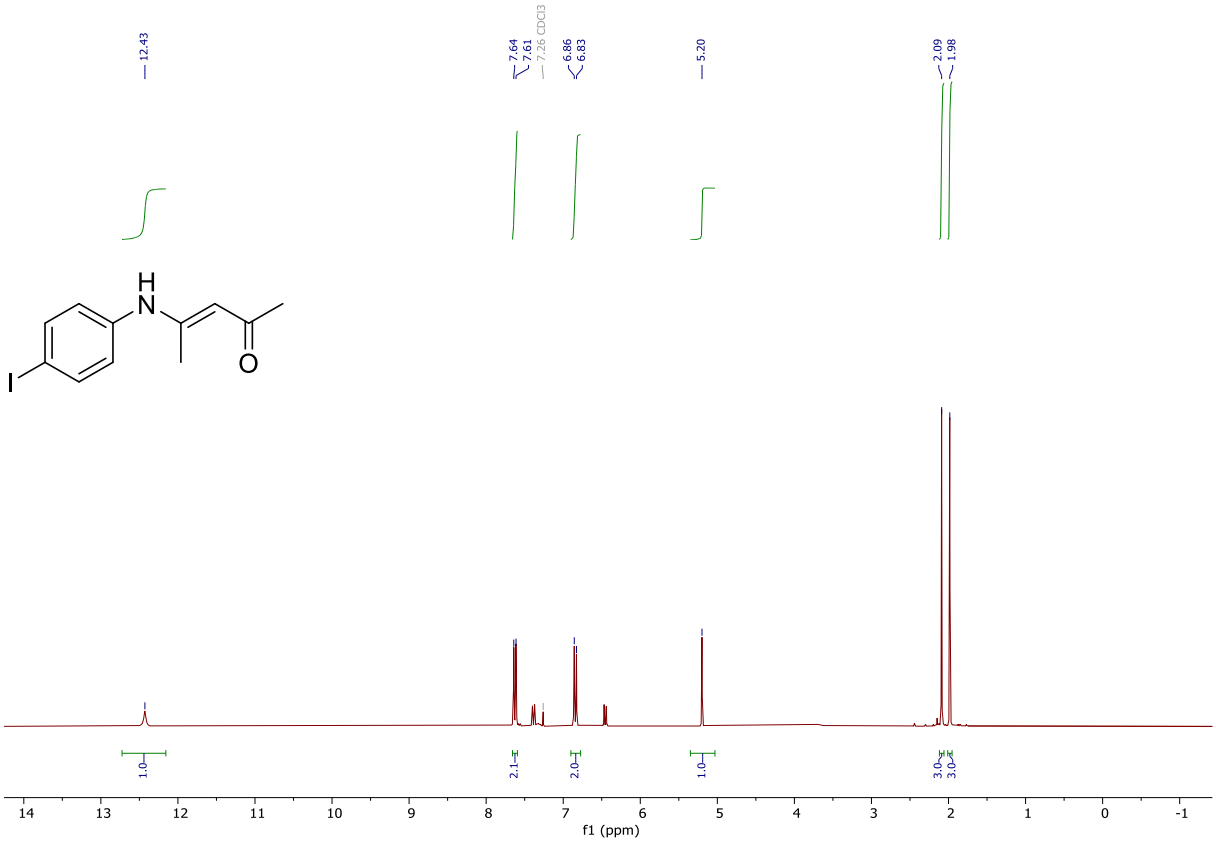
12a



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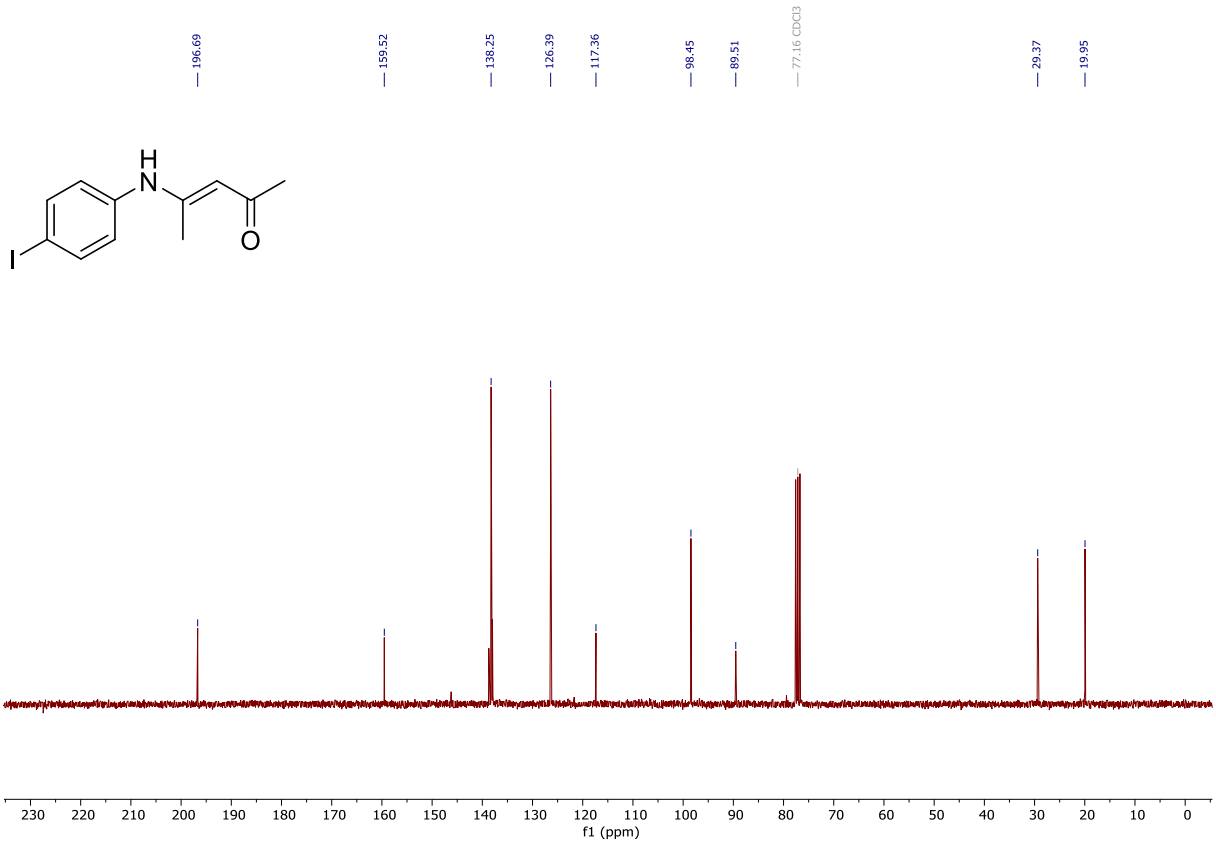

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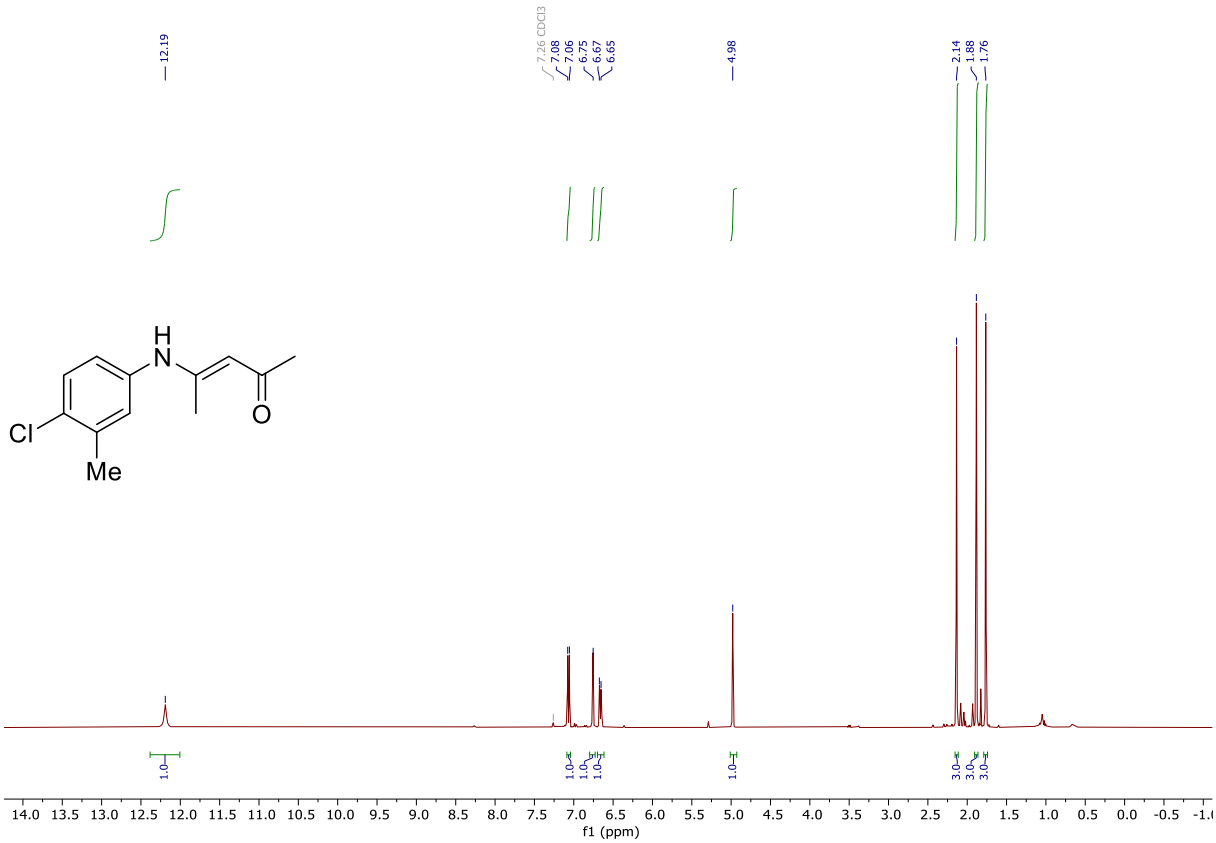
13a



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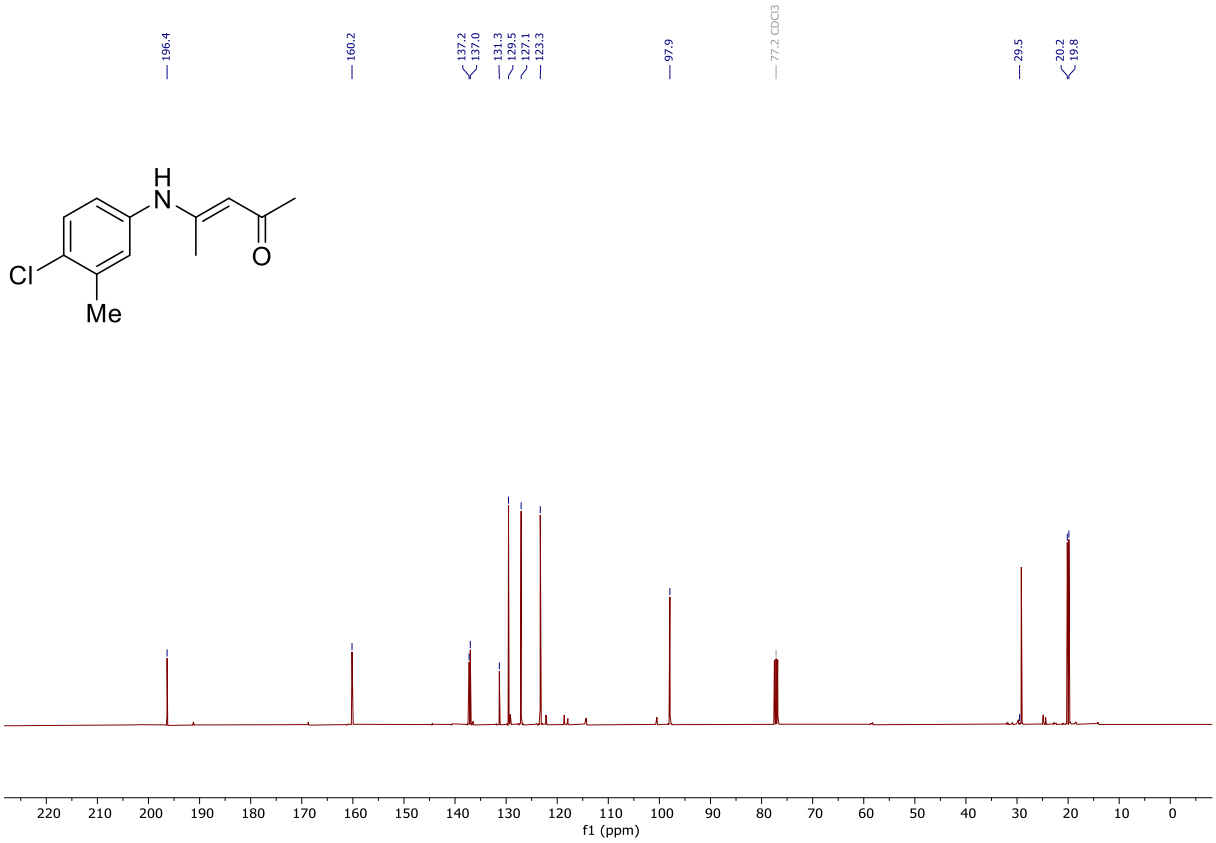

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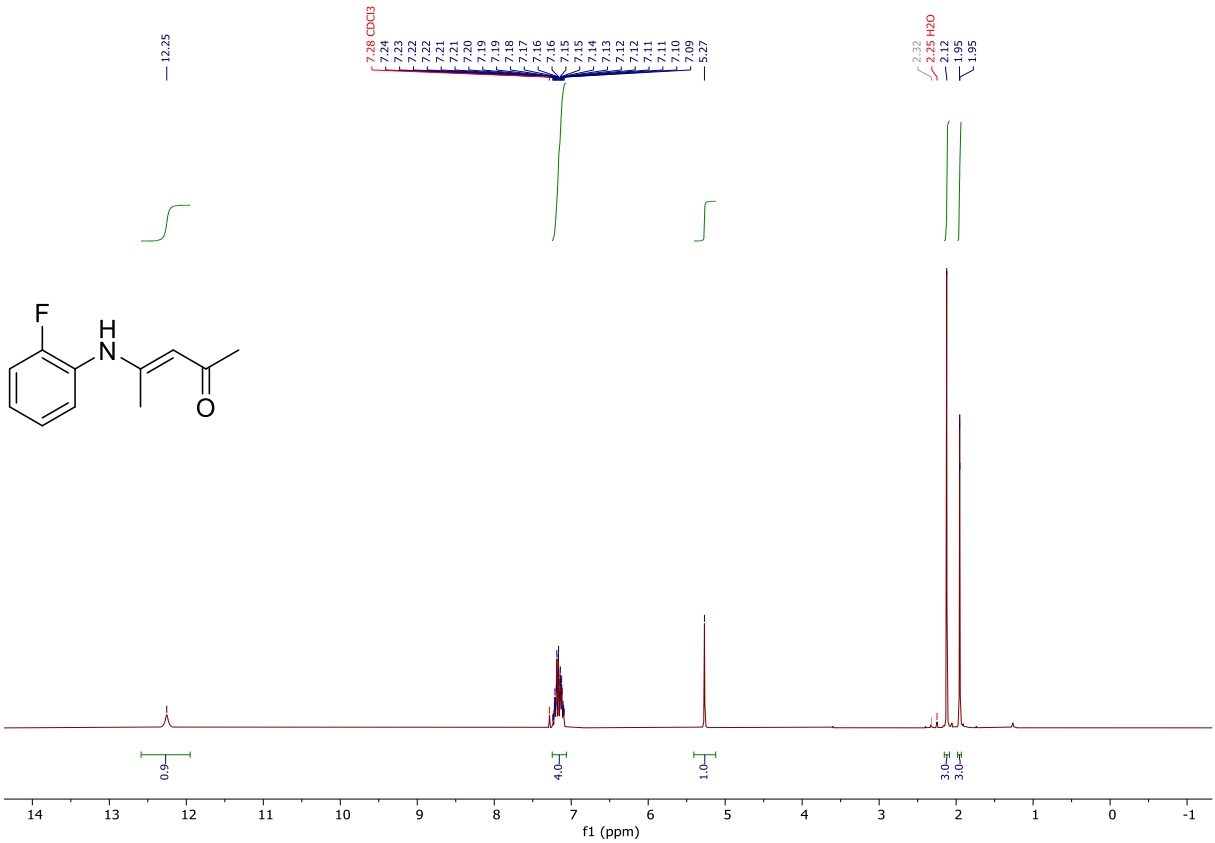
14a



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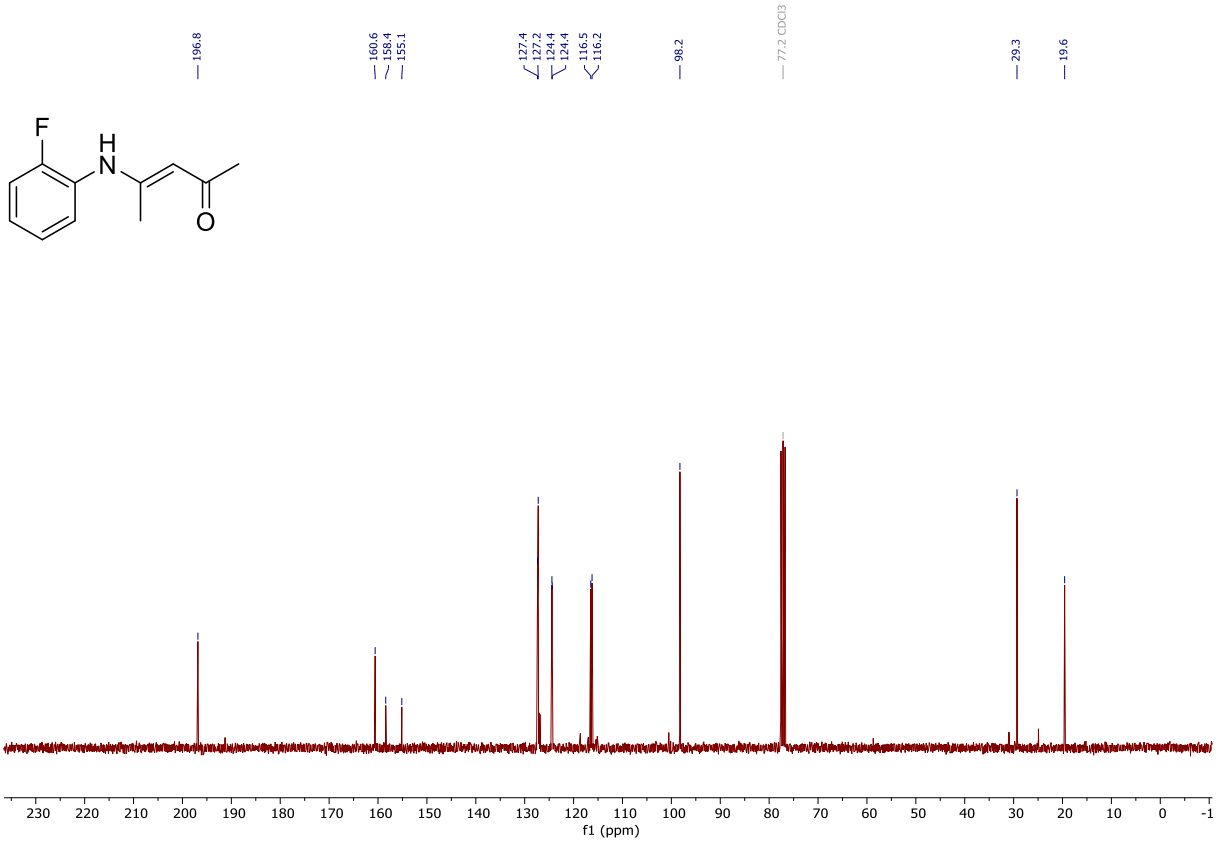

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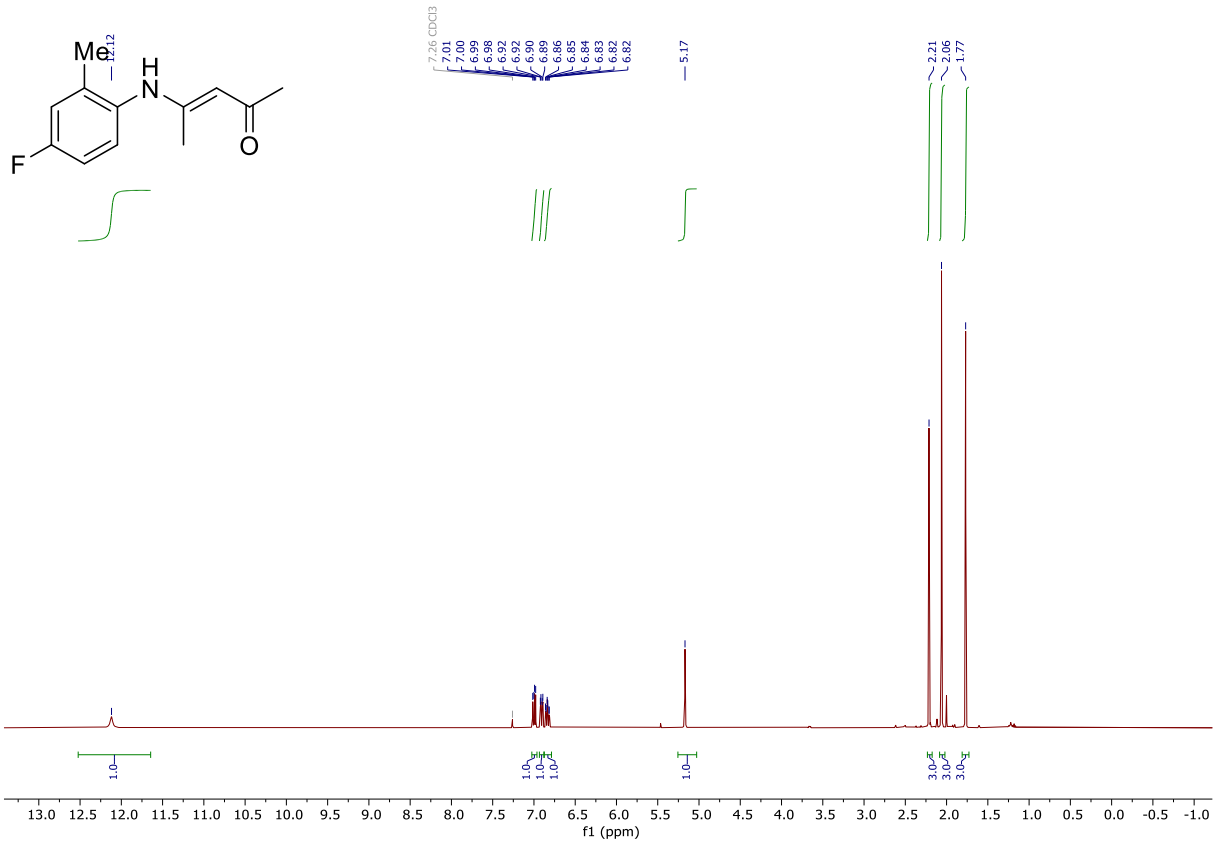
15a



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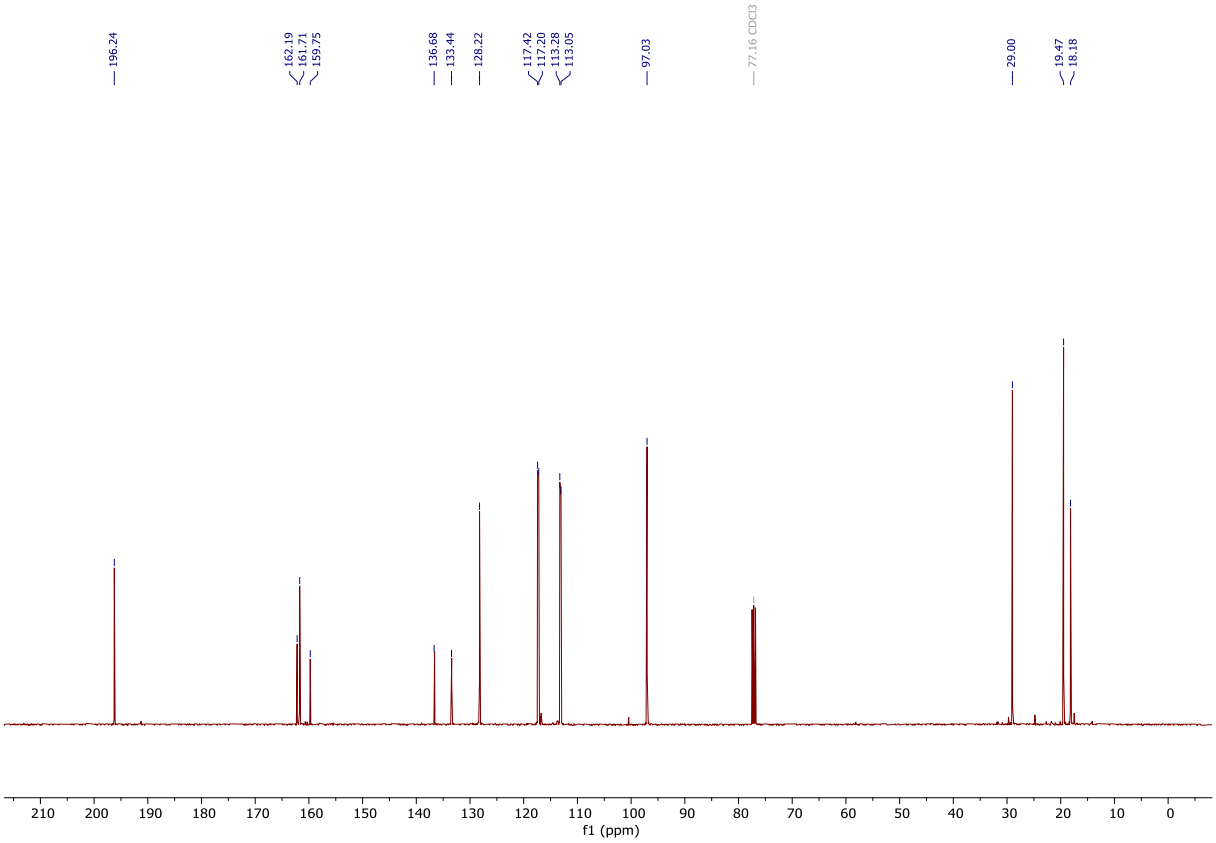

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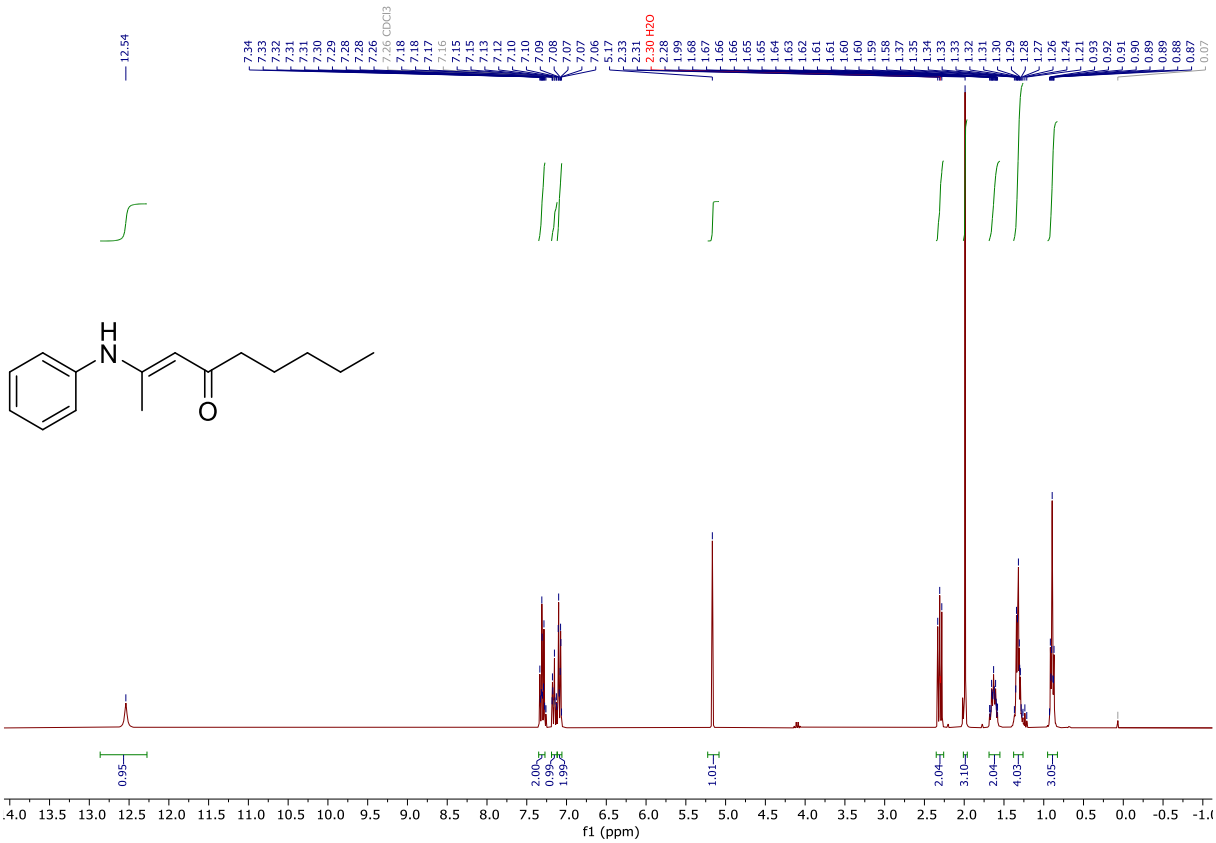
16a



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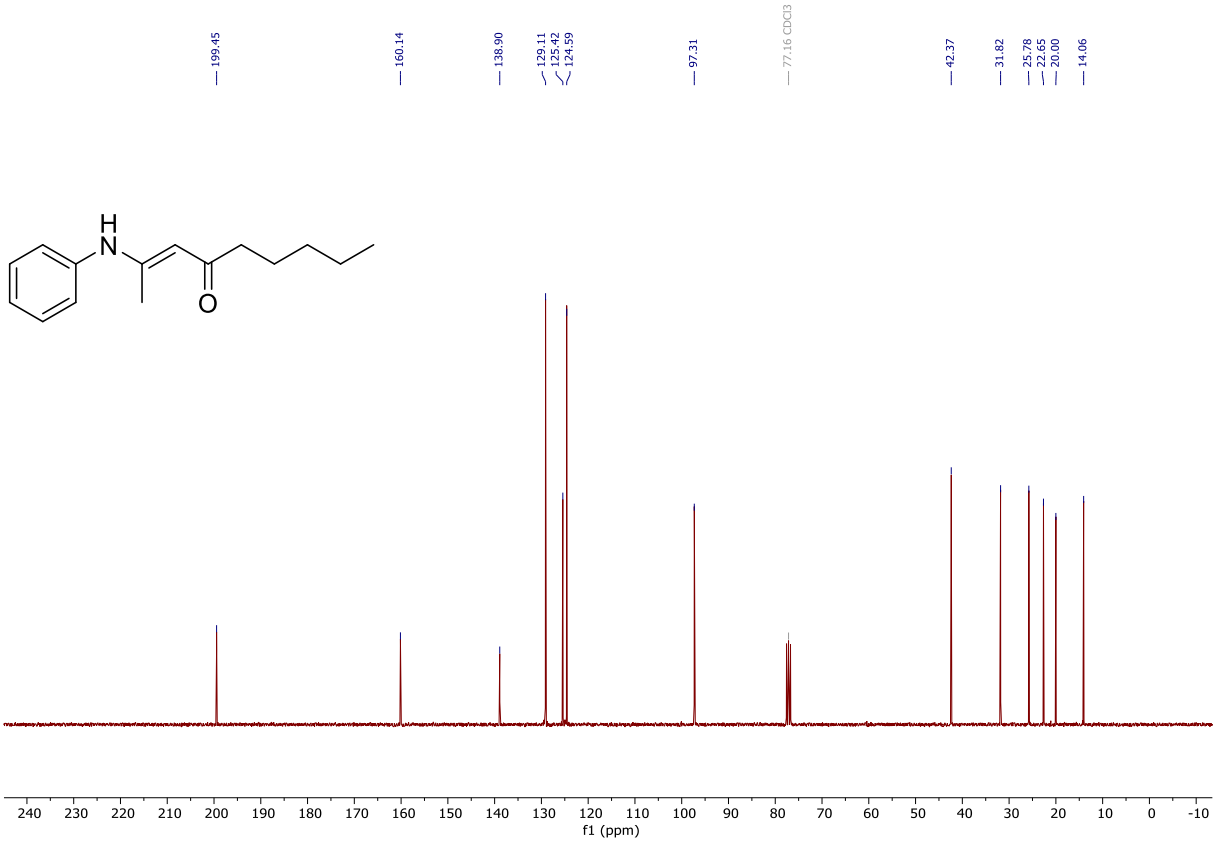

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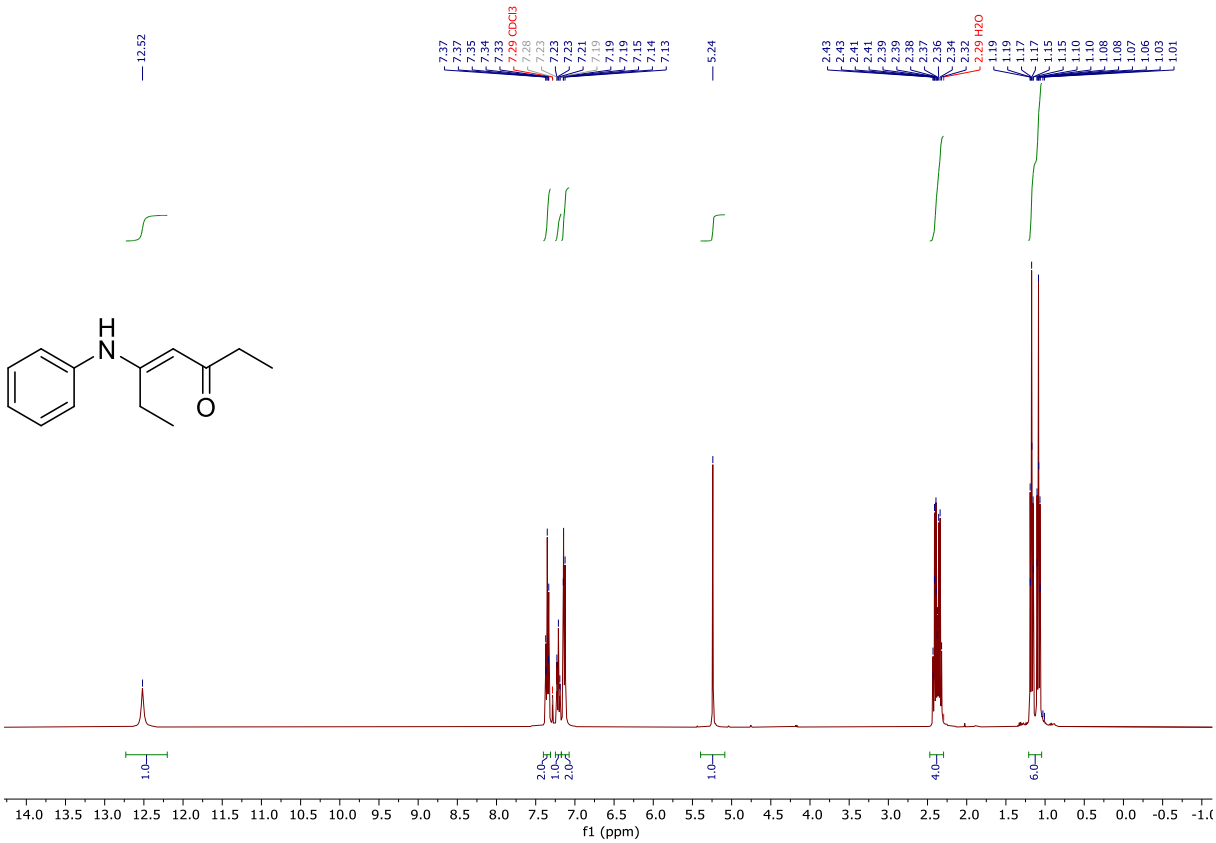
17a



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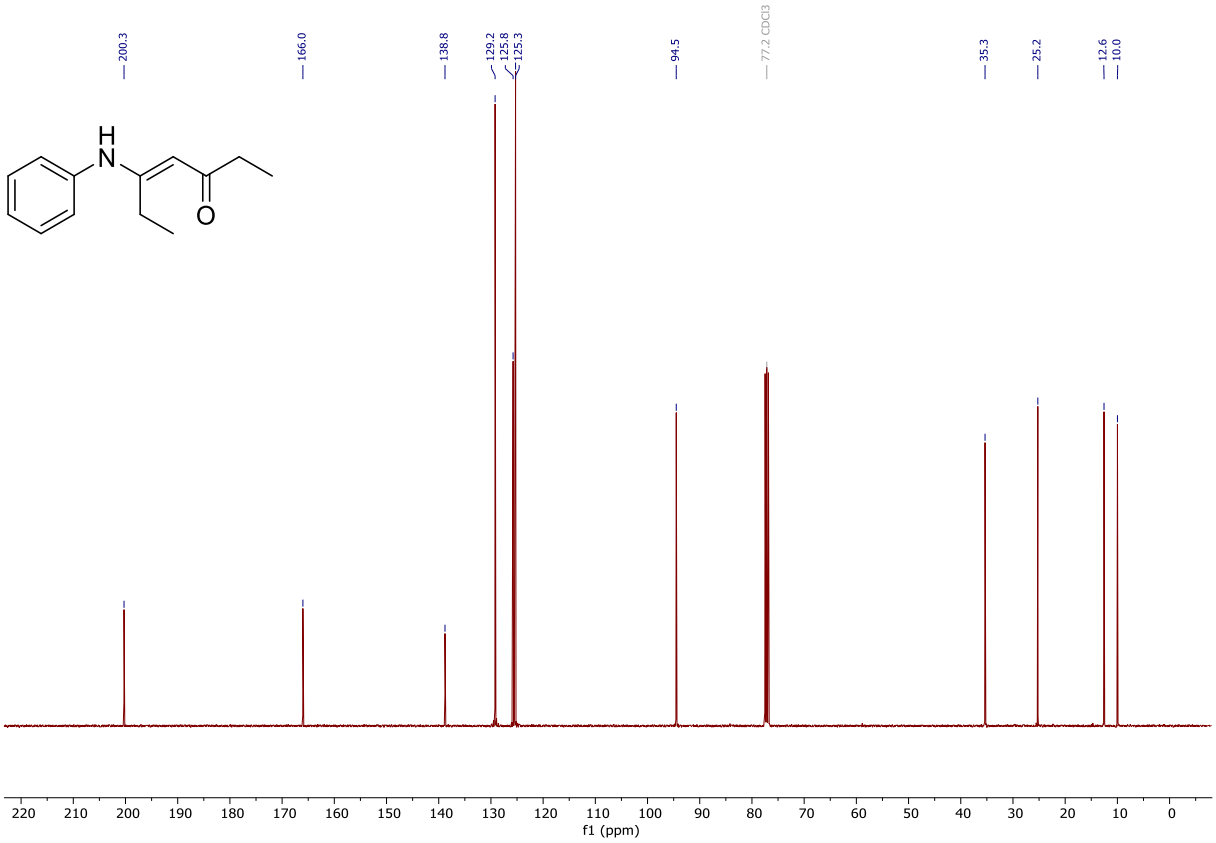

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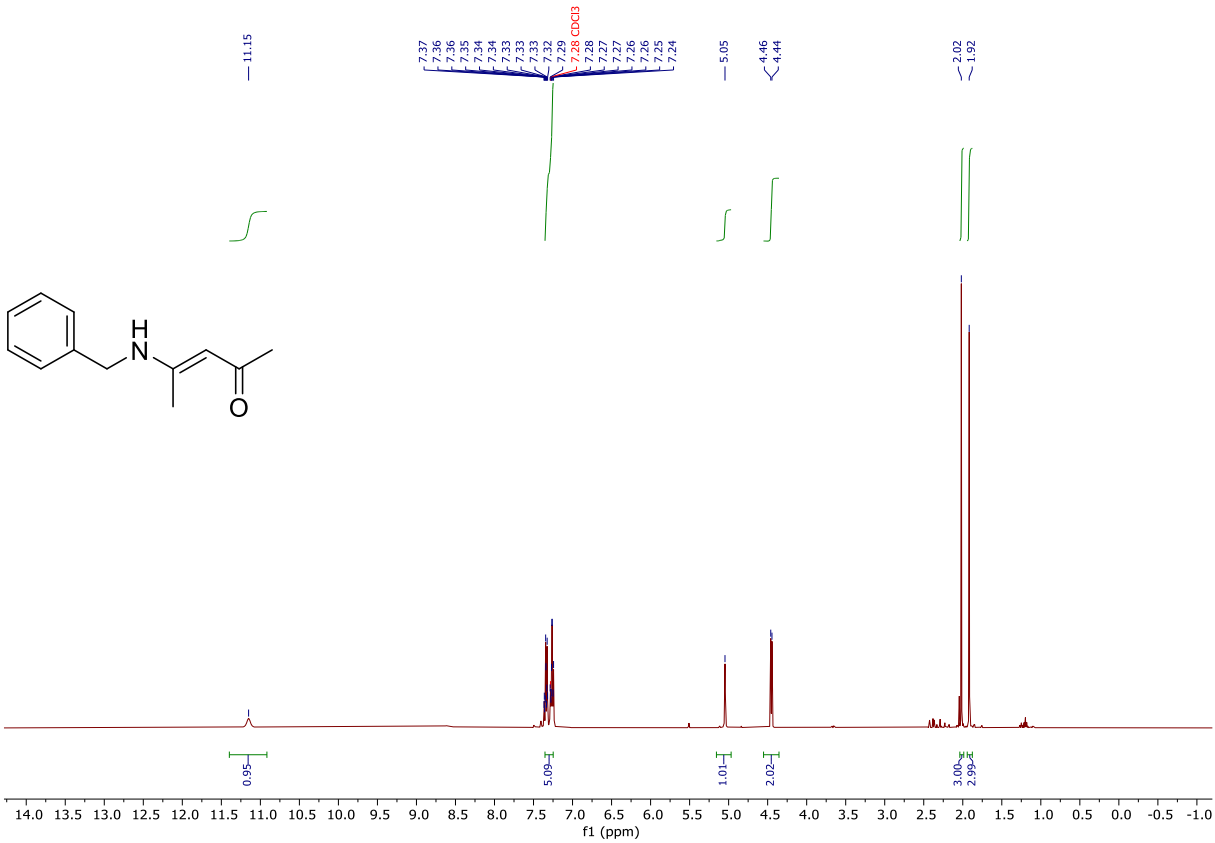
18a



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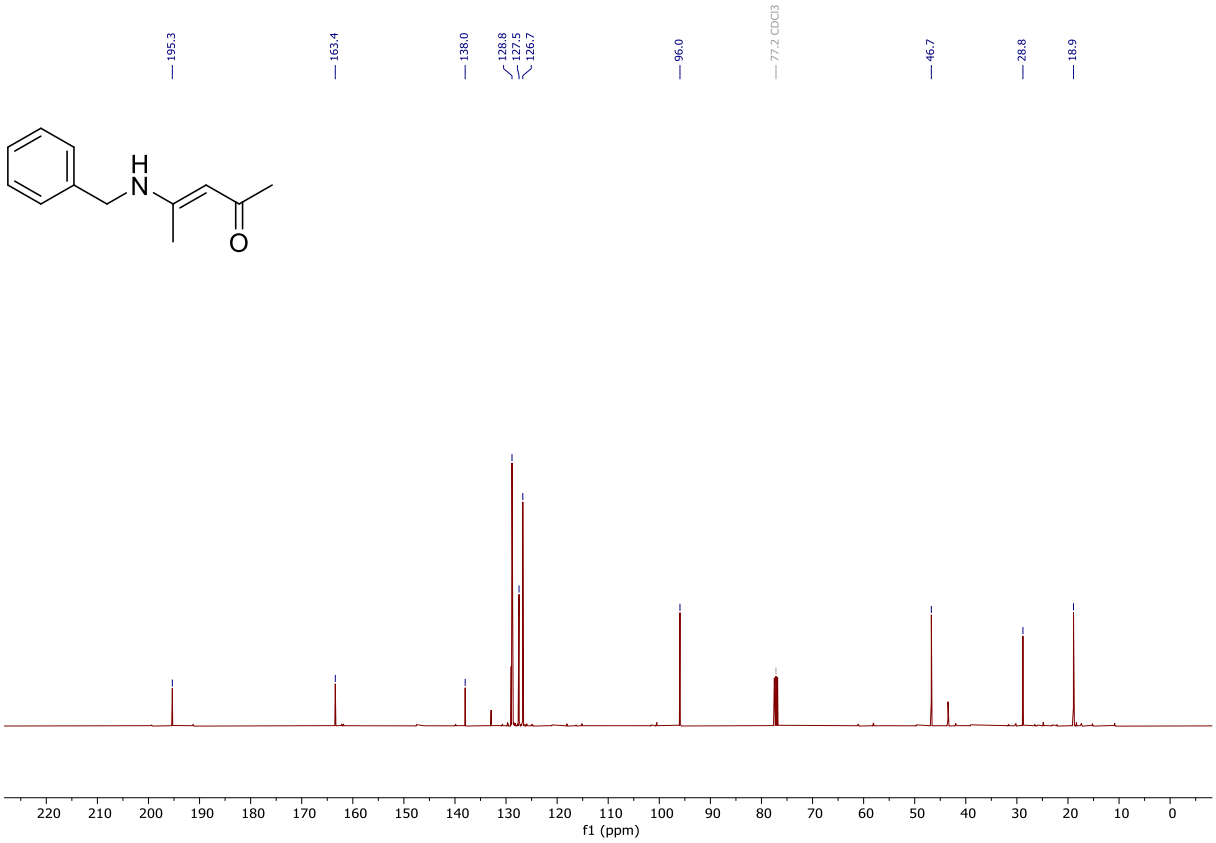

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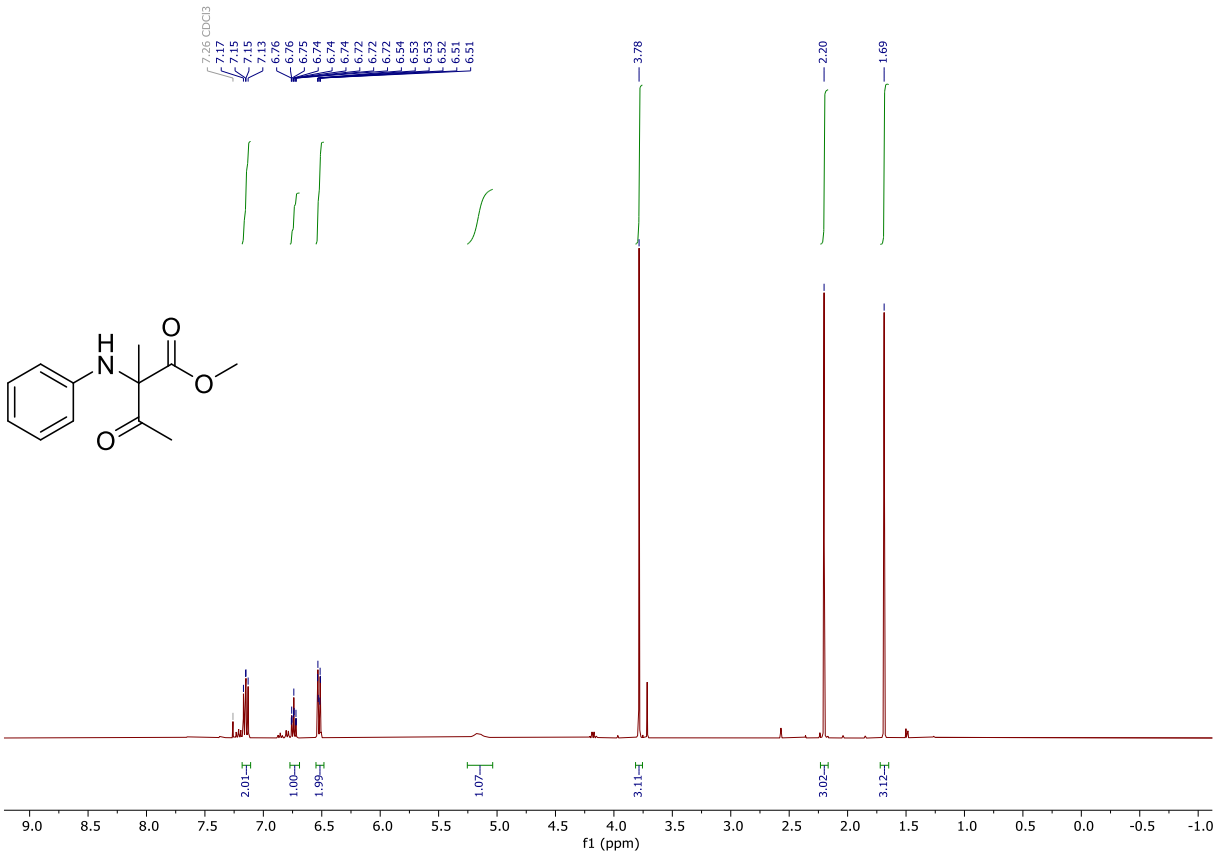
1b



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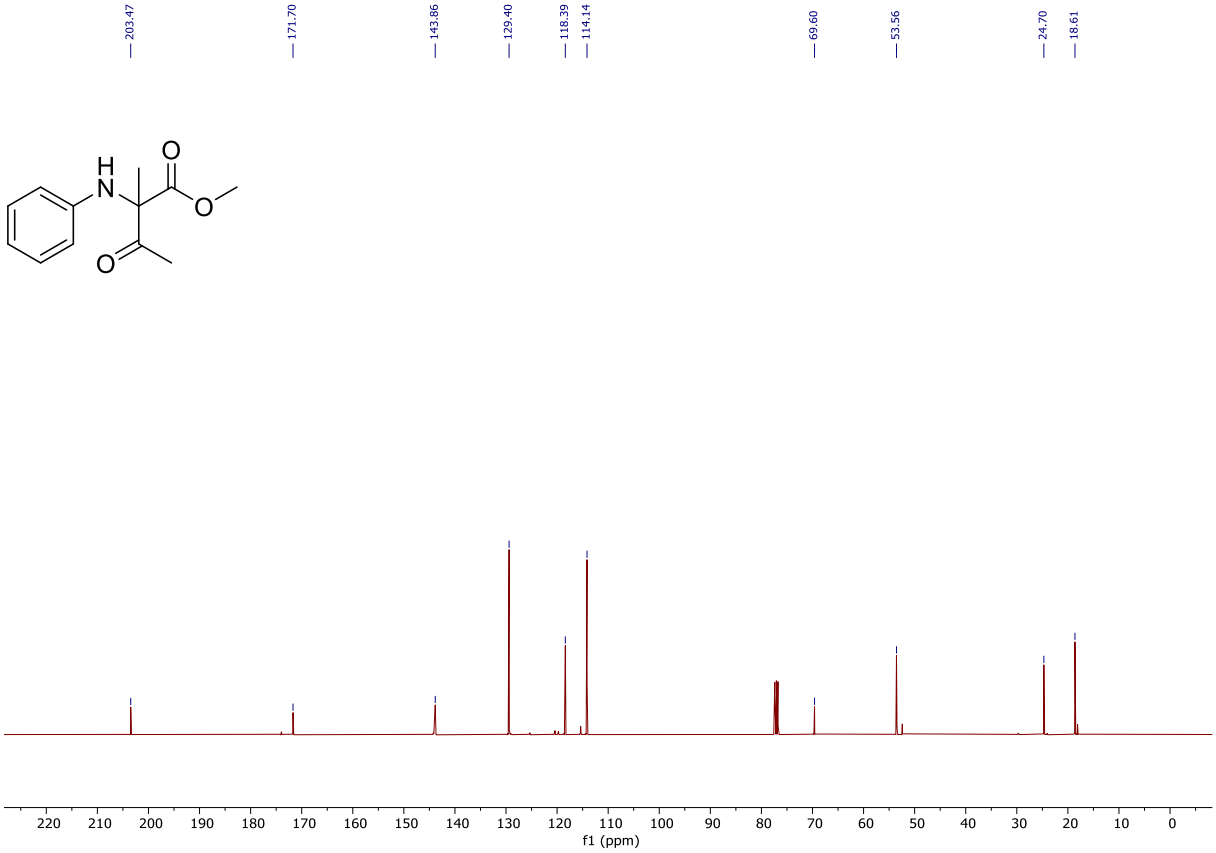

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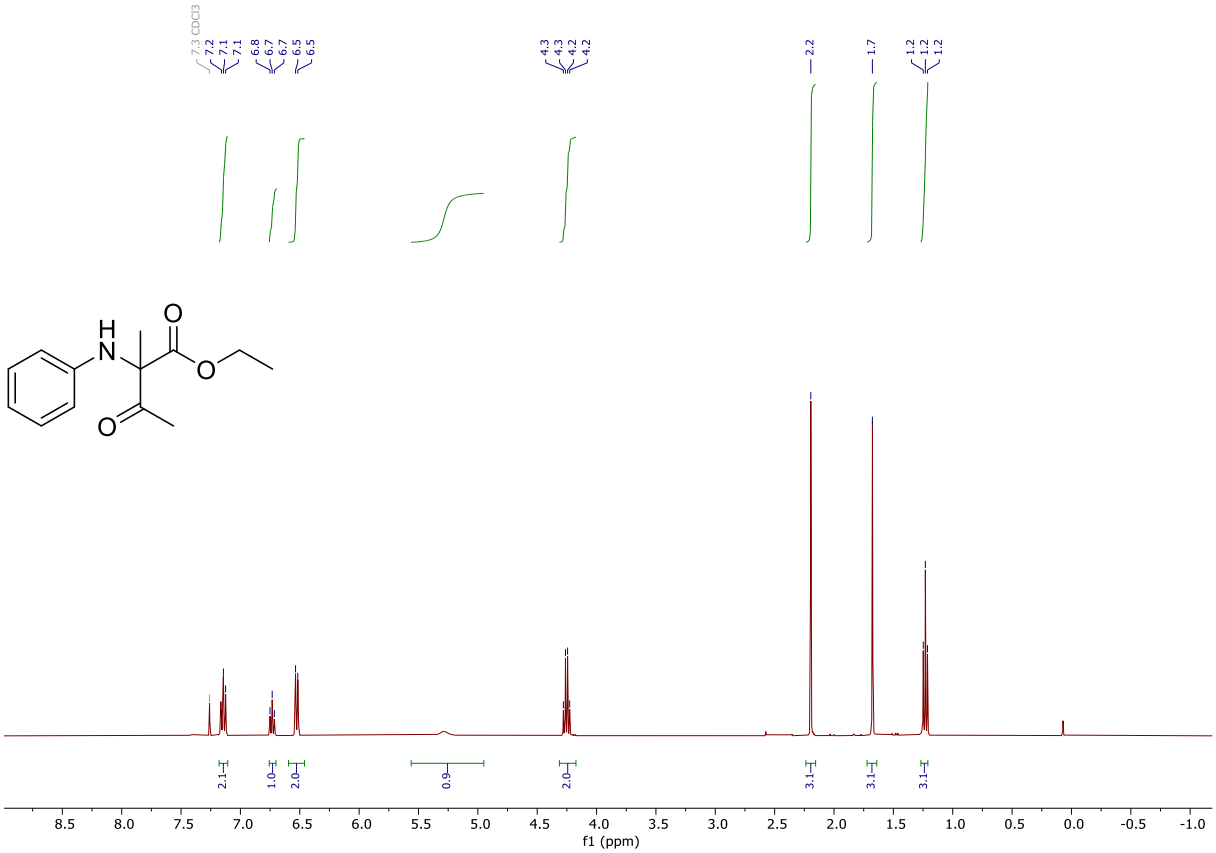
2b



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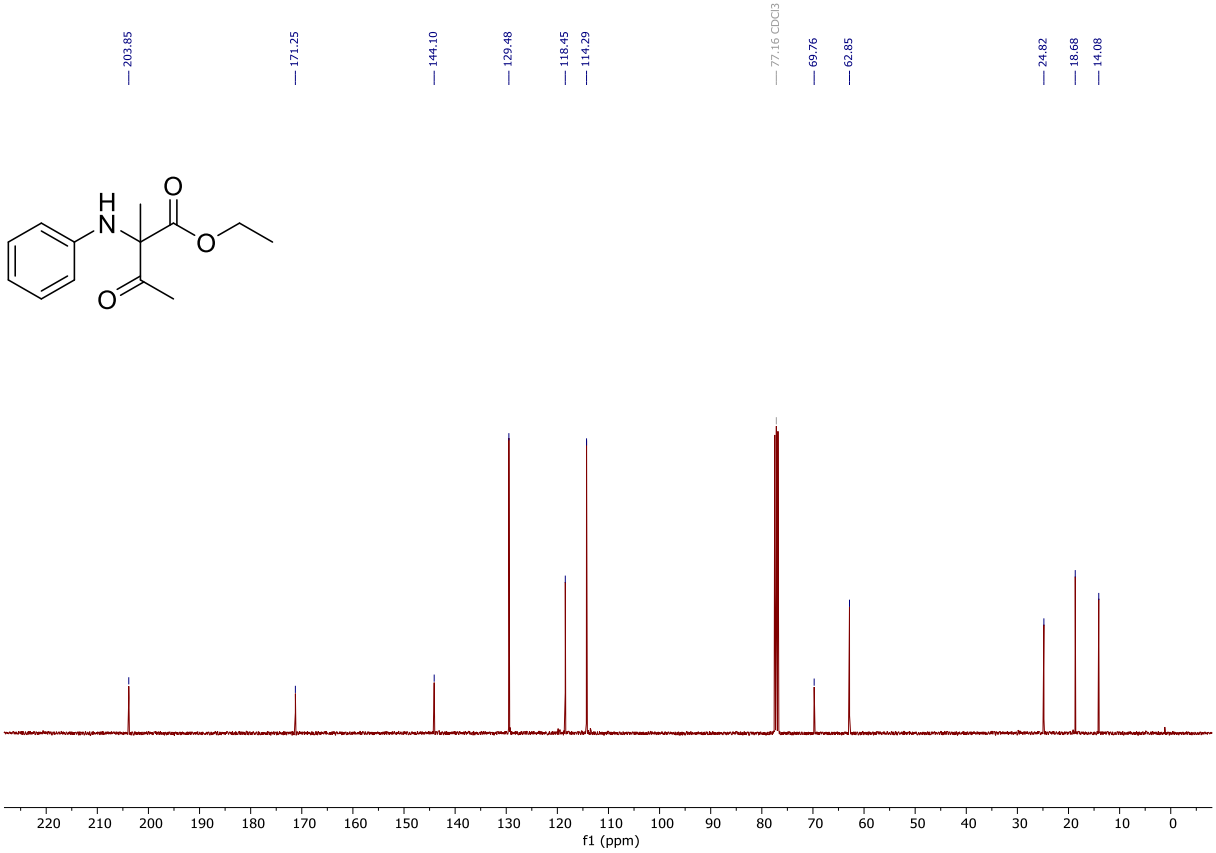
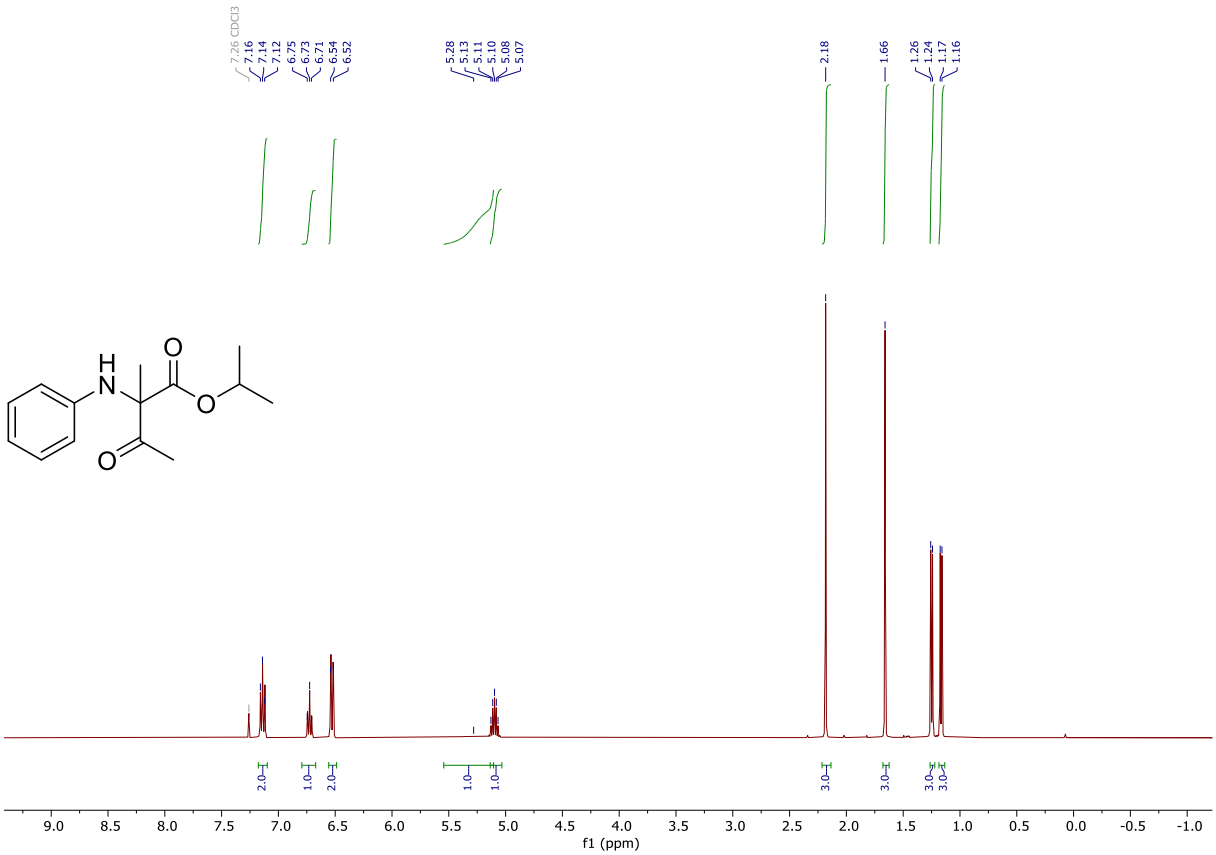
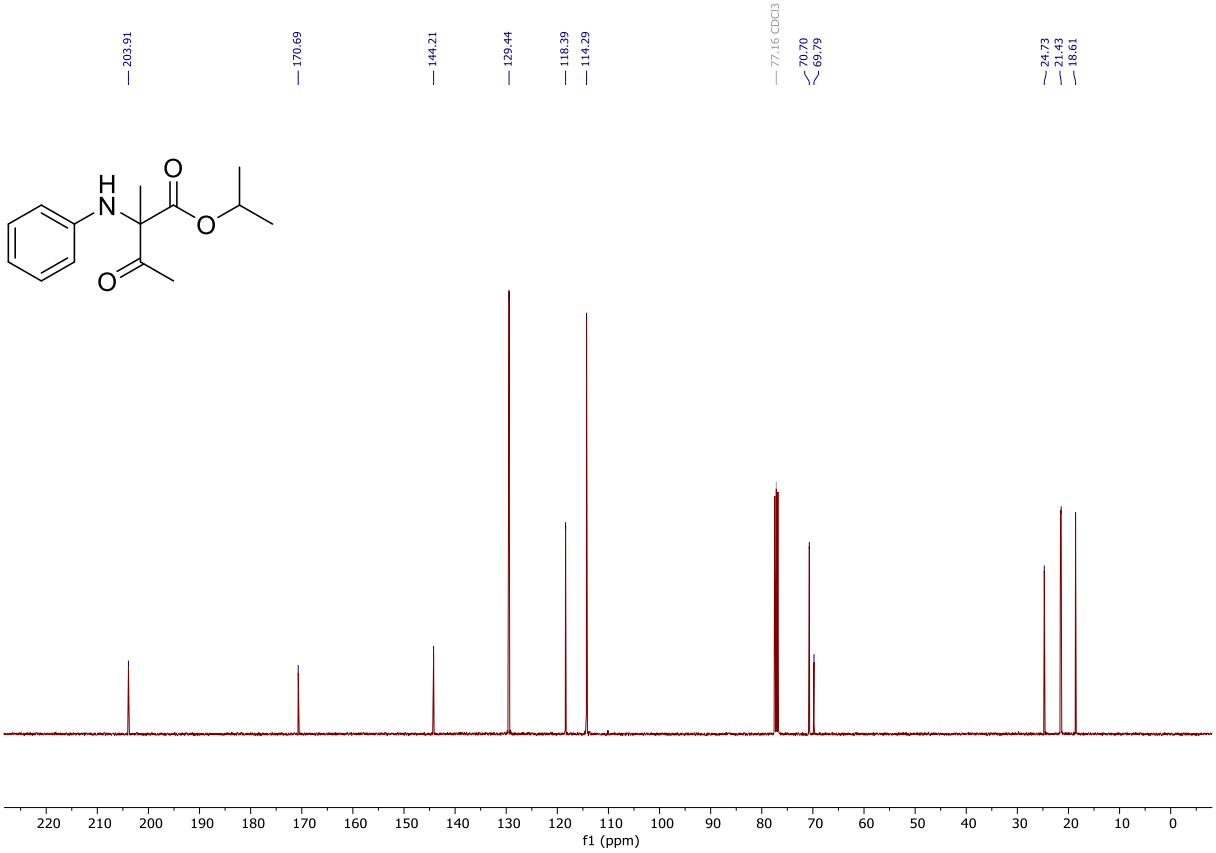


^{13}C-NMR in $CDCl_3$.

3b

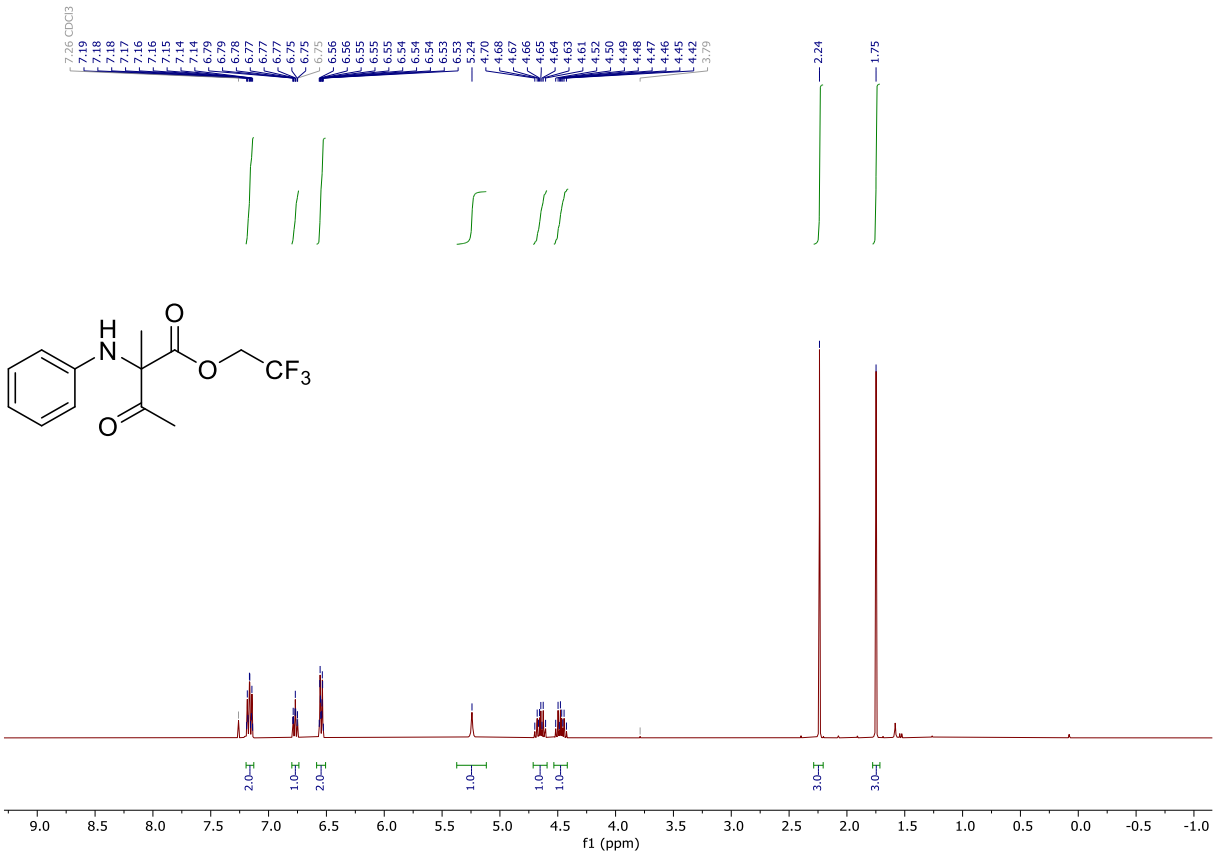


^{1}H-NMR in $CDCl_3$.

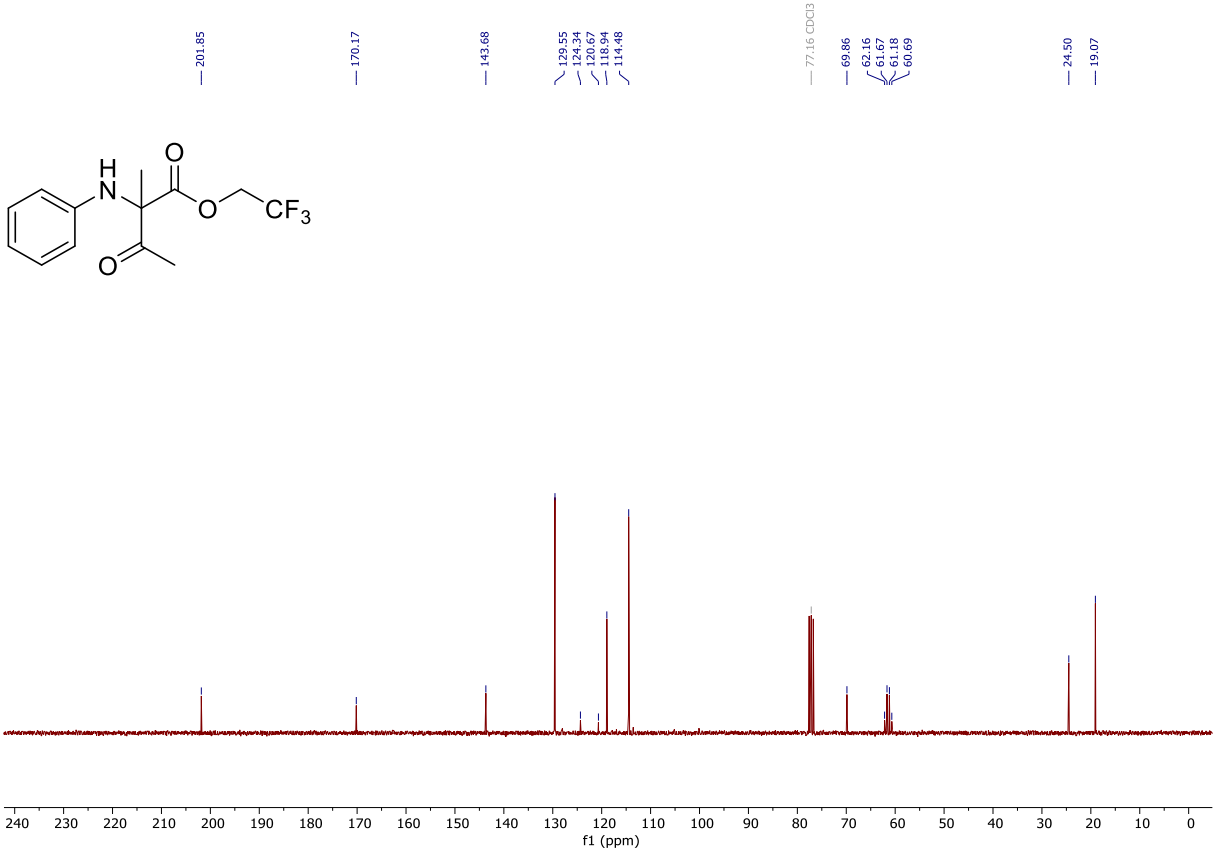


^{13}C-NMR in $CDCl_3$.

4b



^{1}H-NMR in $CDCl_3$.



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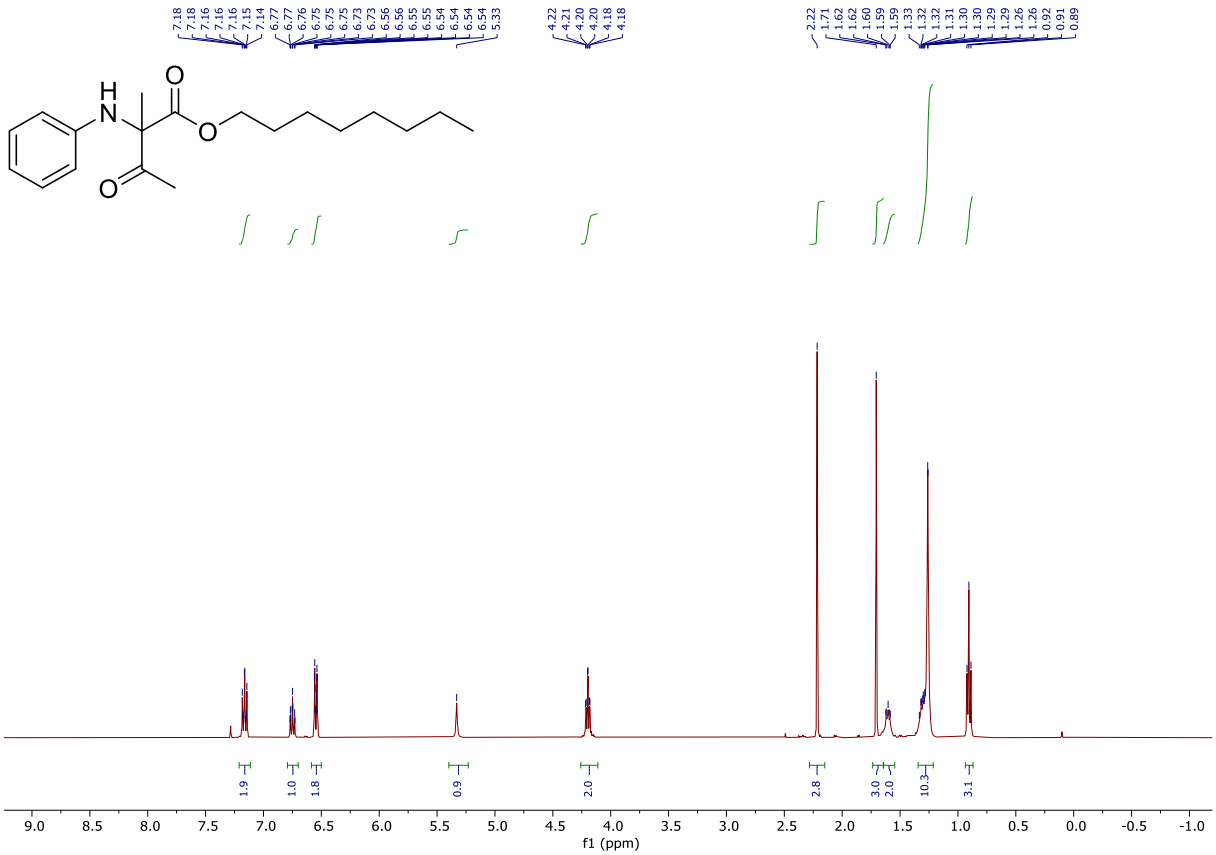
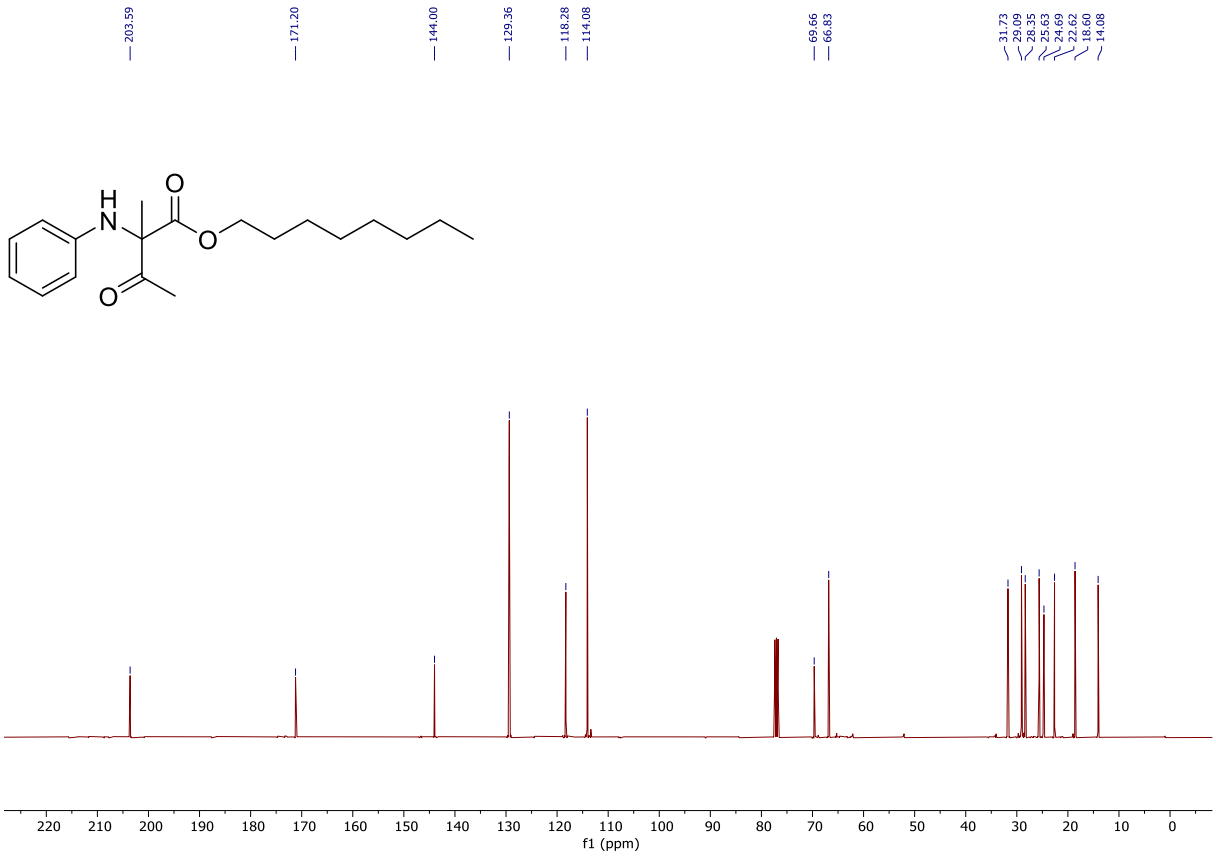
5b



^{1}H-NMR in $CDCl_3$.



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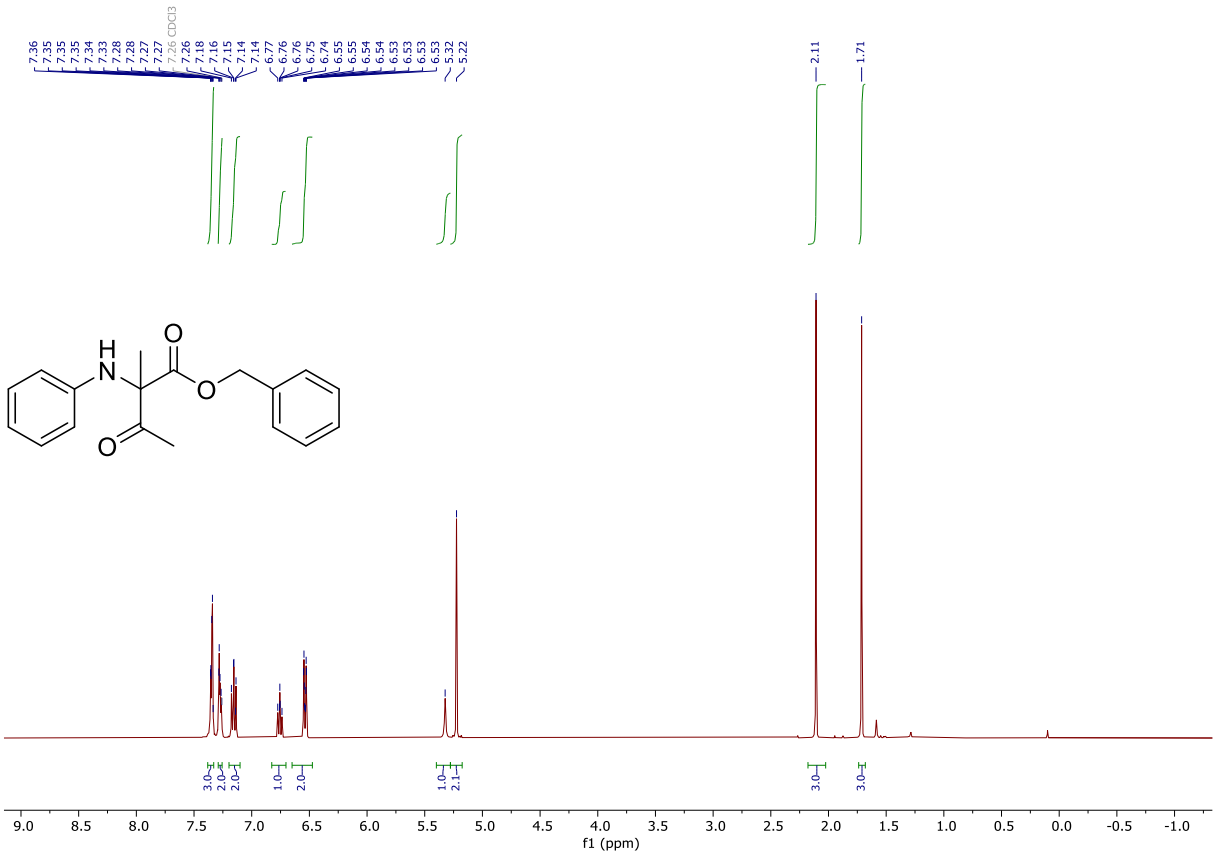
6b



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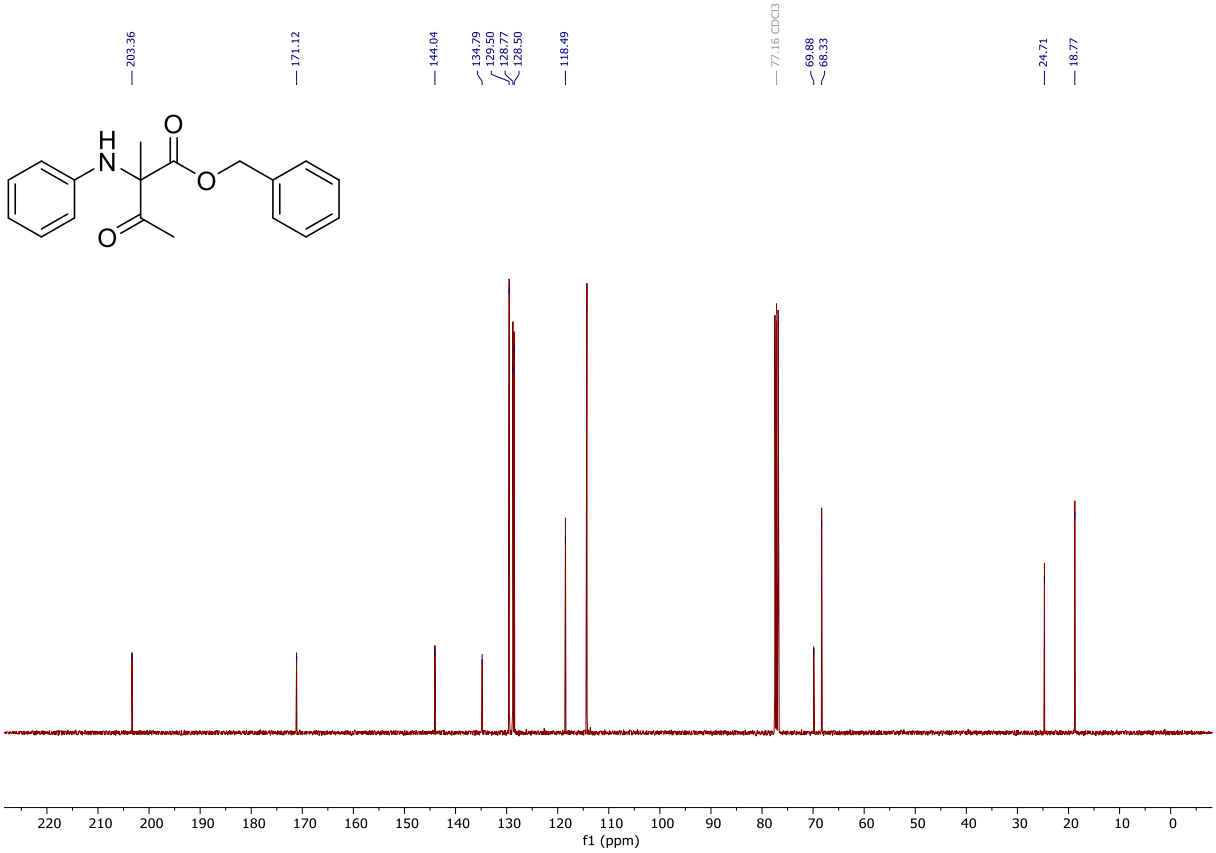
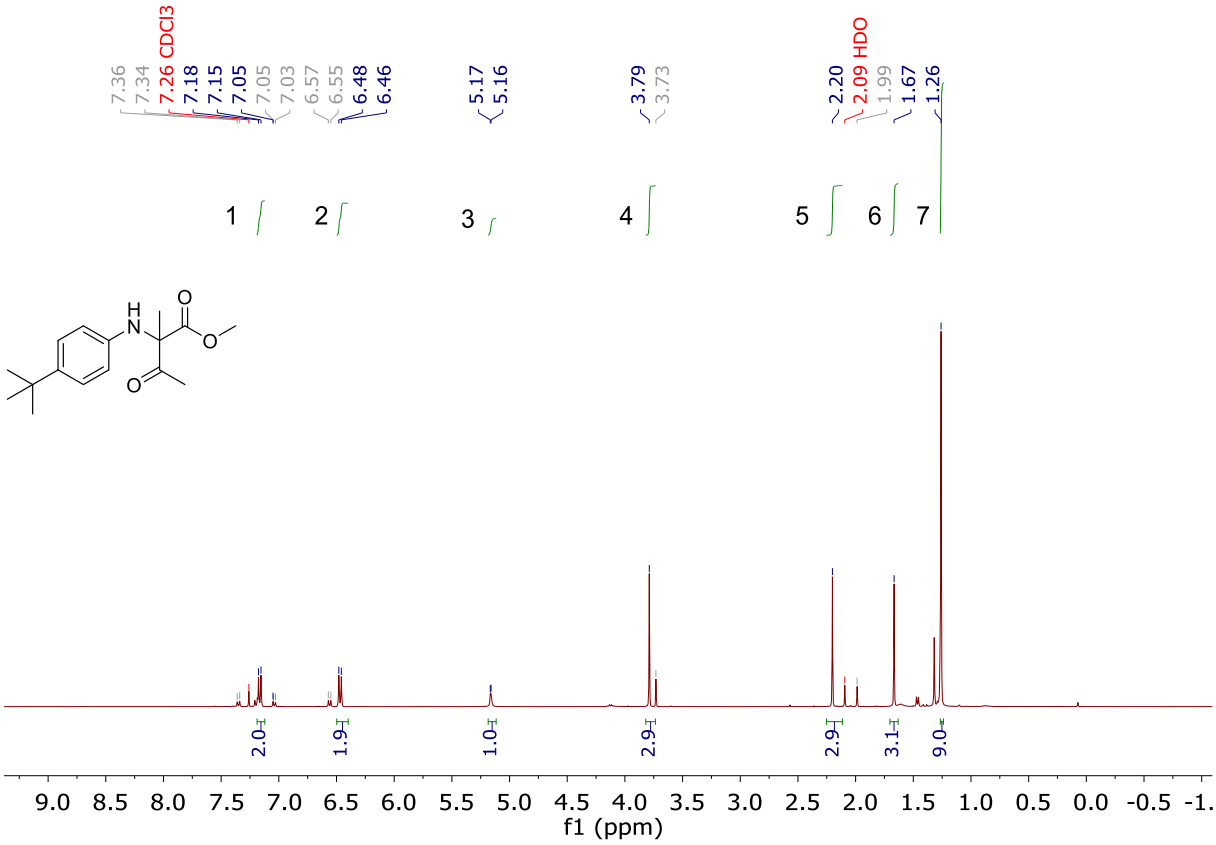


^{13}C-NMR in $CDCl_3$.

7b



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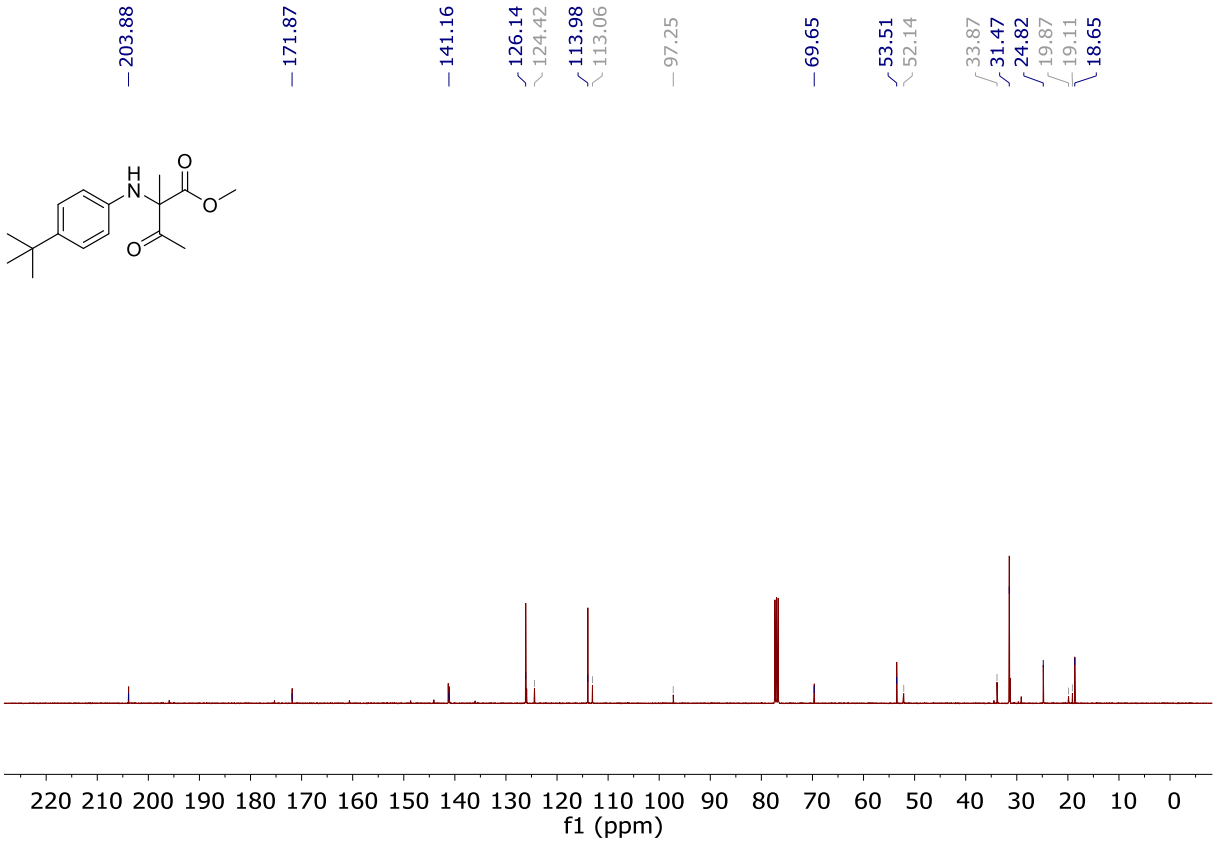

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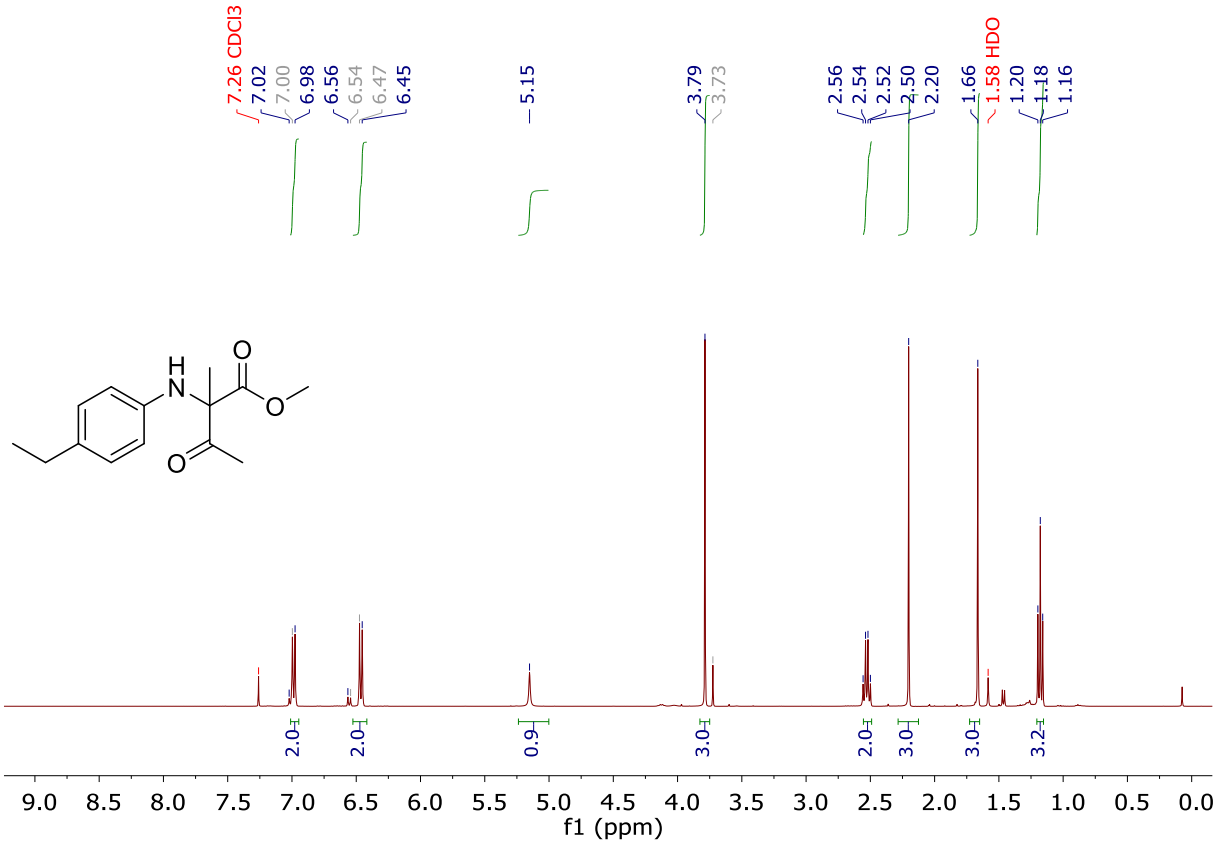
8b



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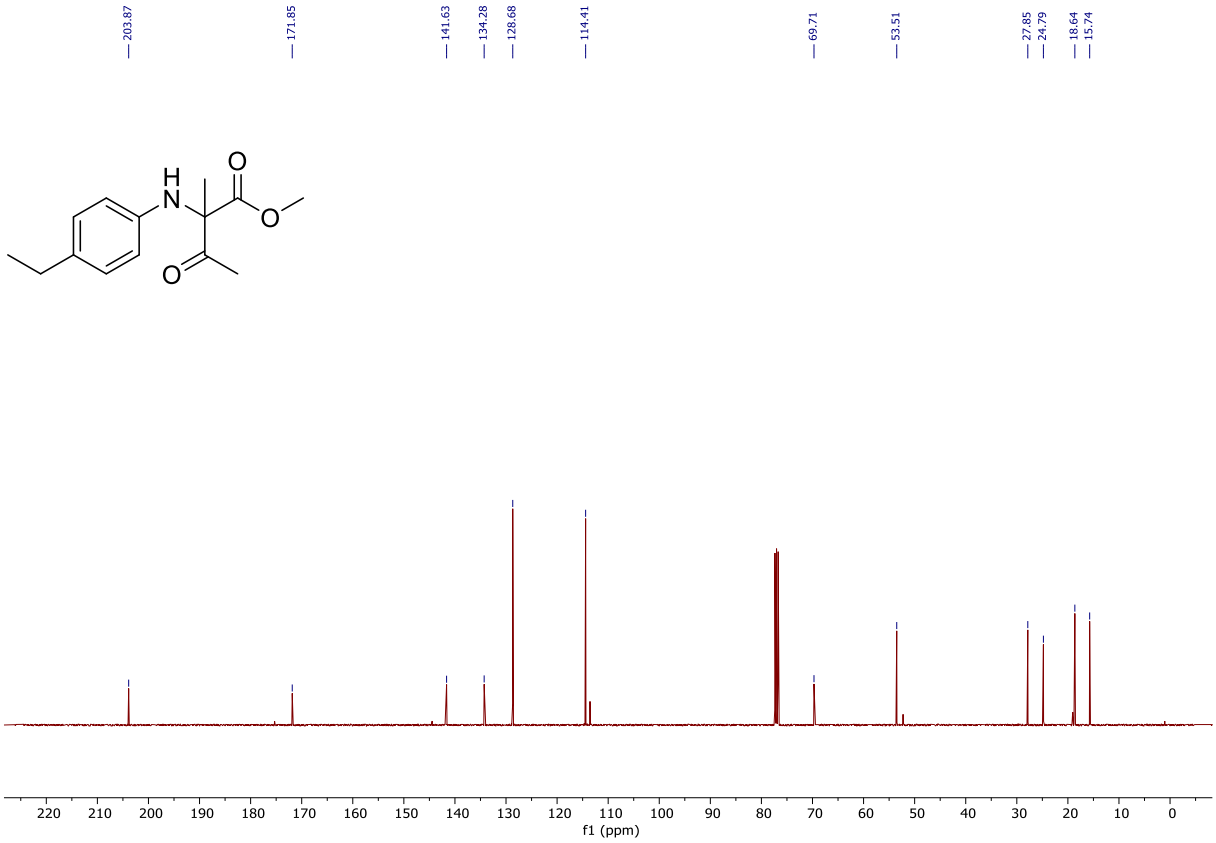
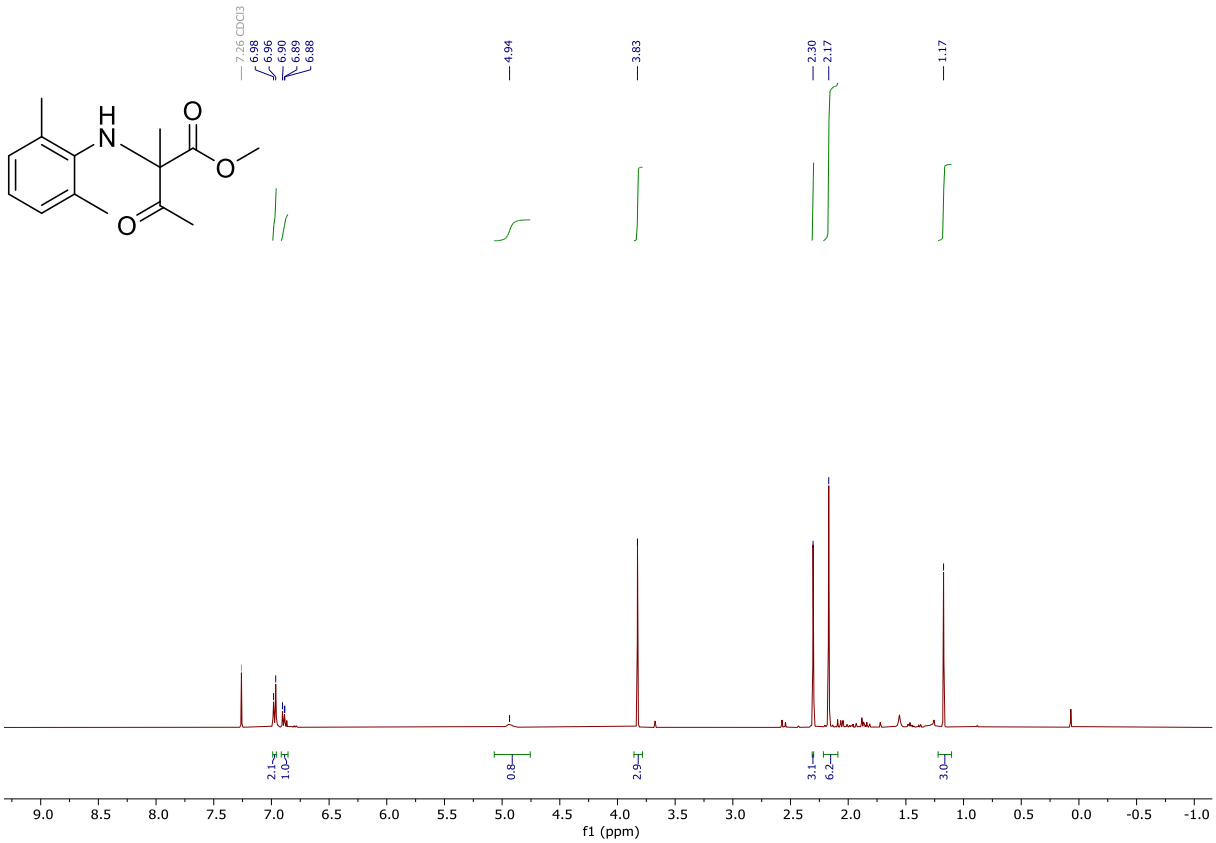


^{13}C-NMR in $CDCl_3$.

9b



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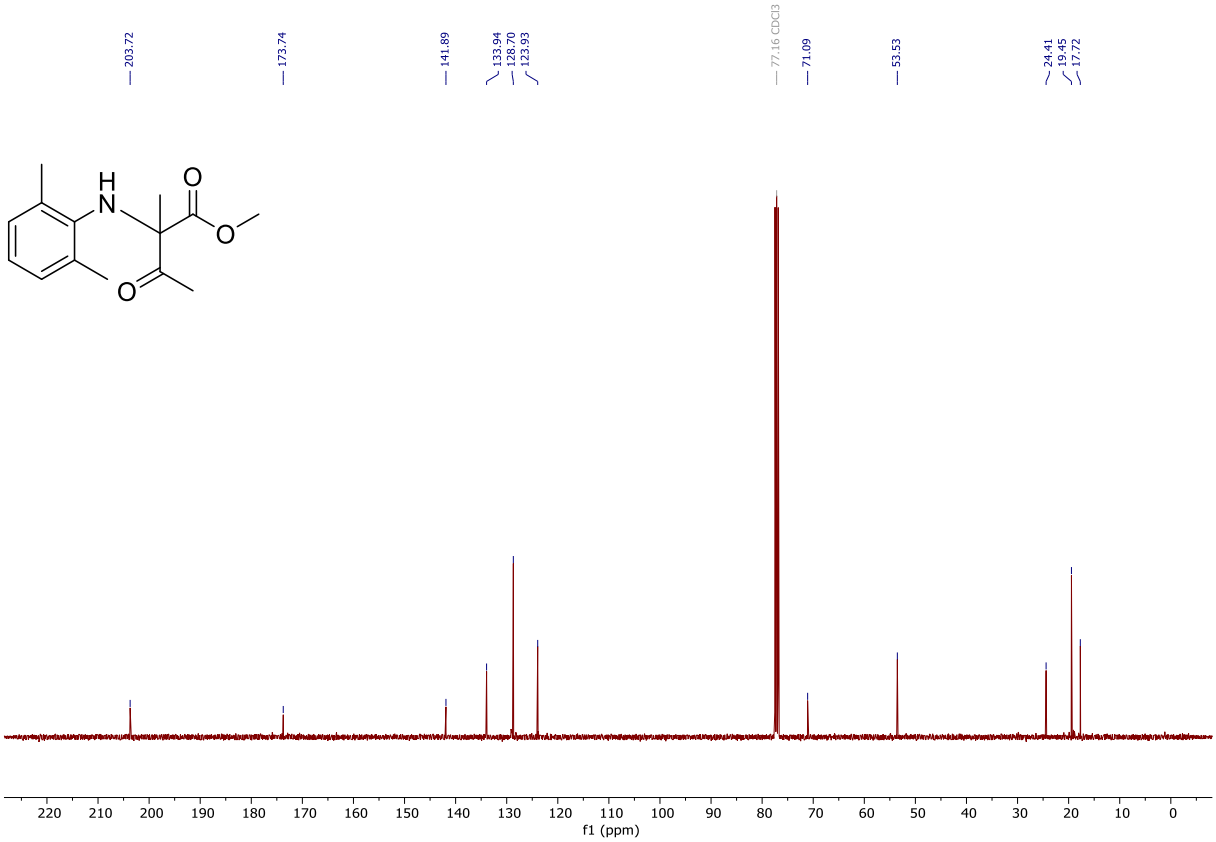

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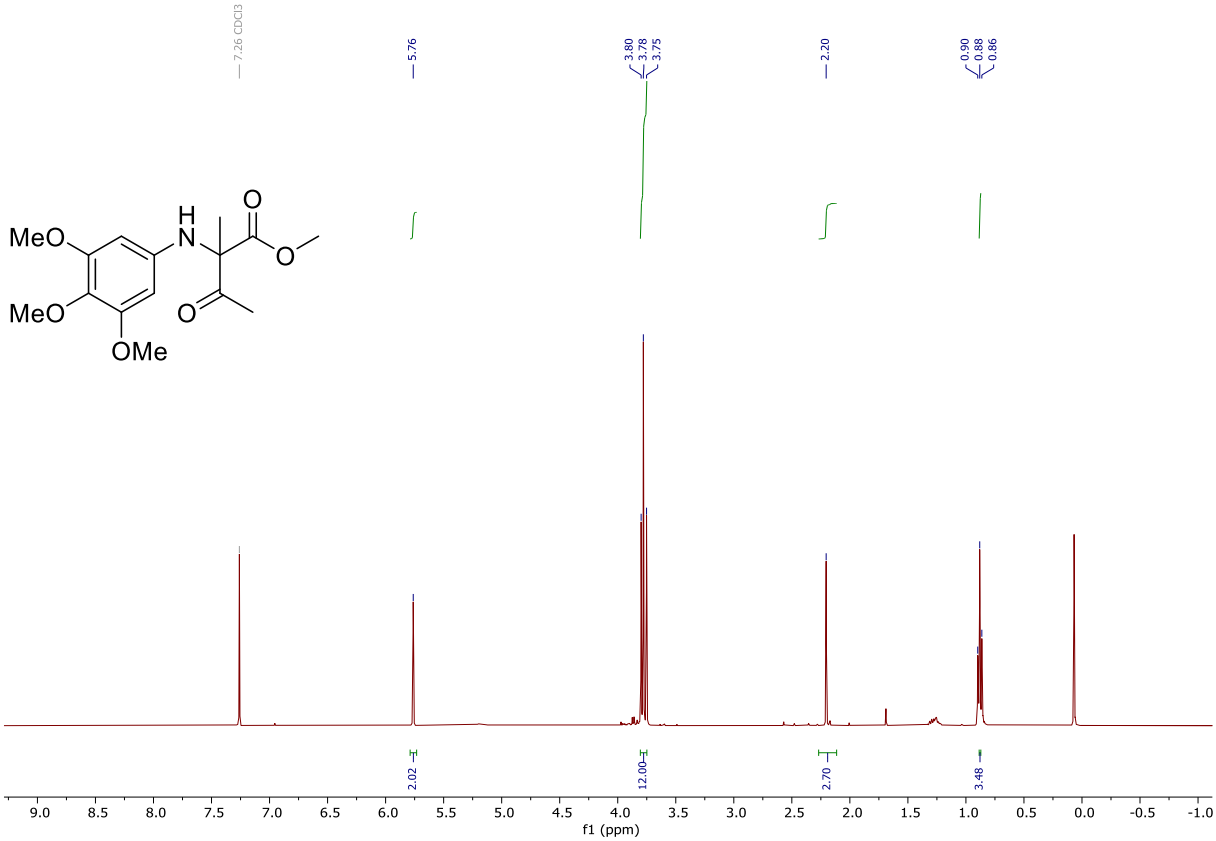
10b



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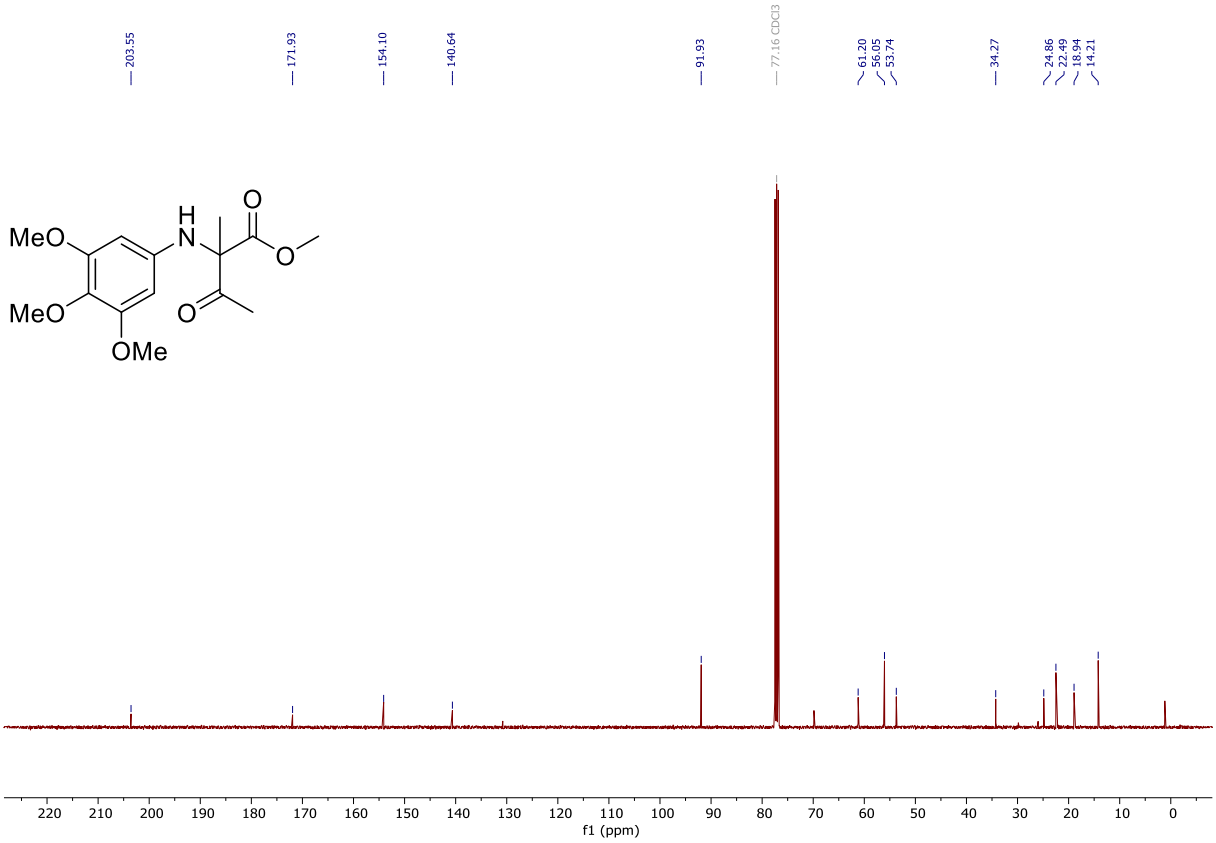

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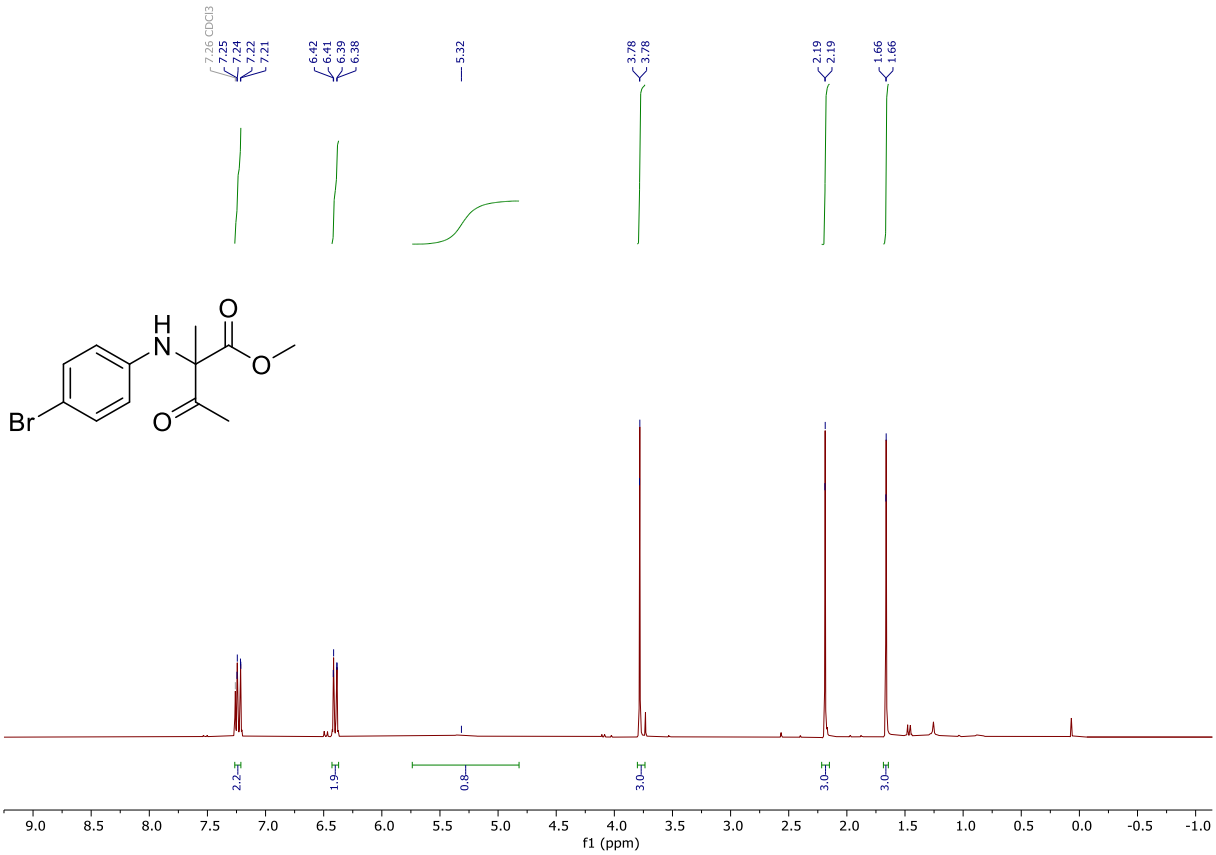
11b



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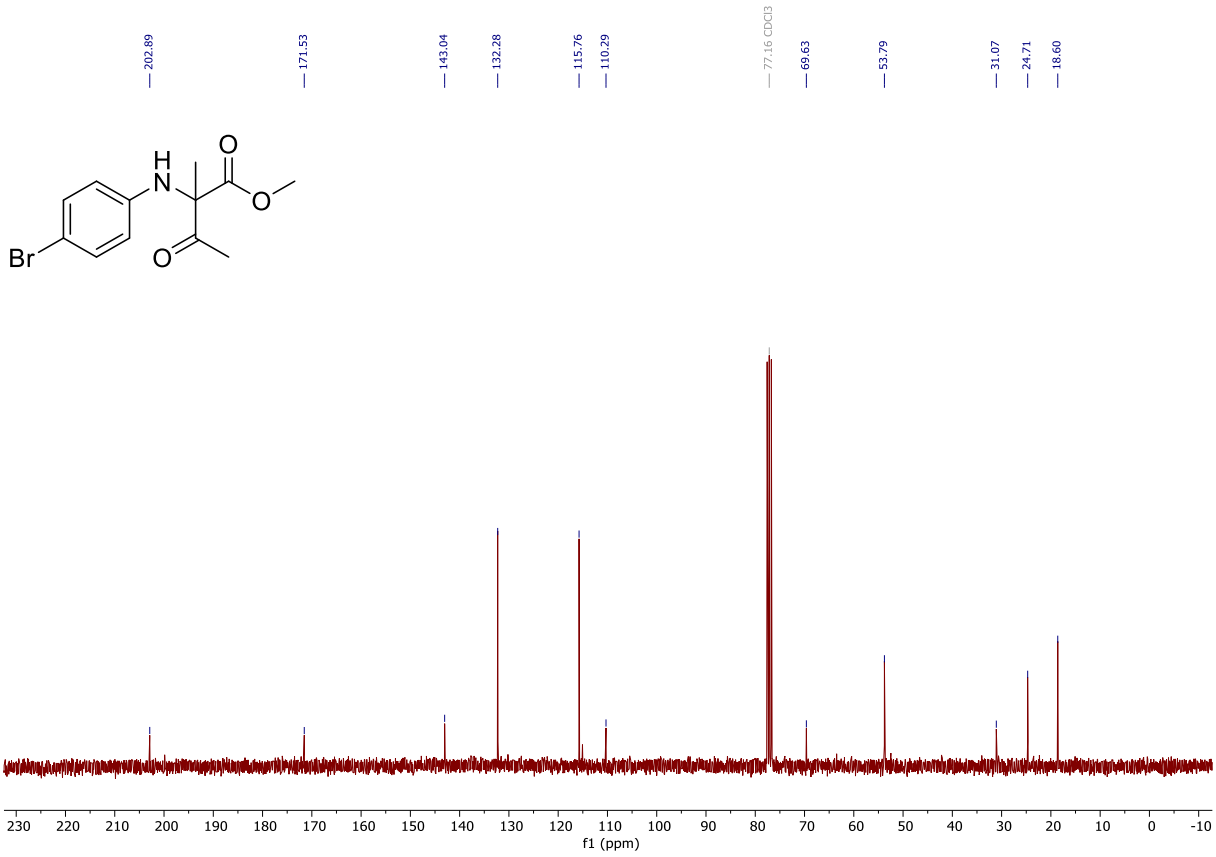

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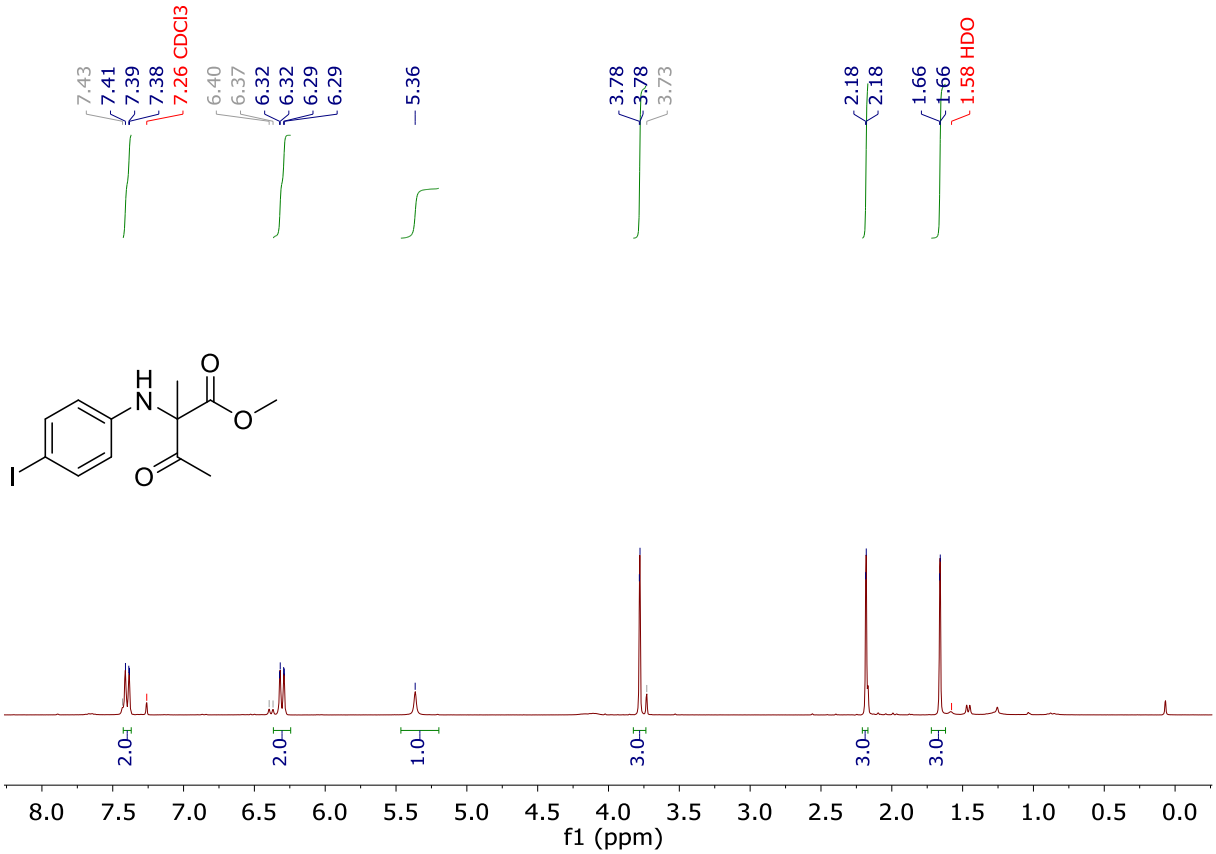
12b



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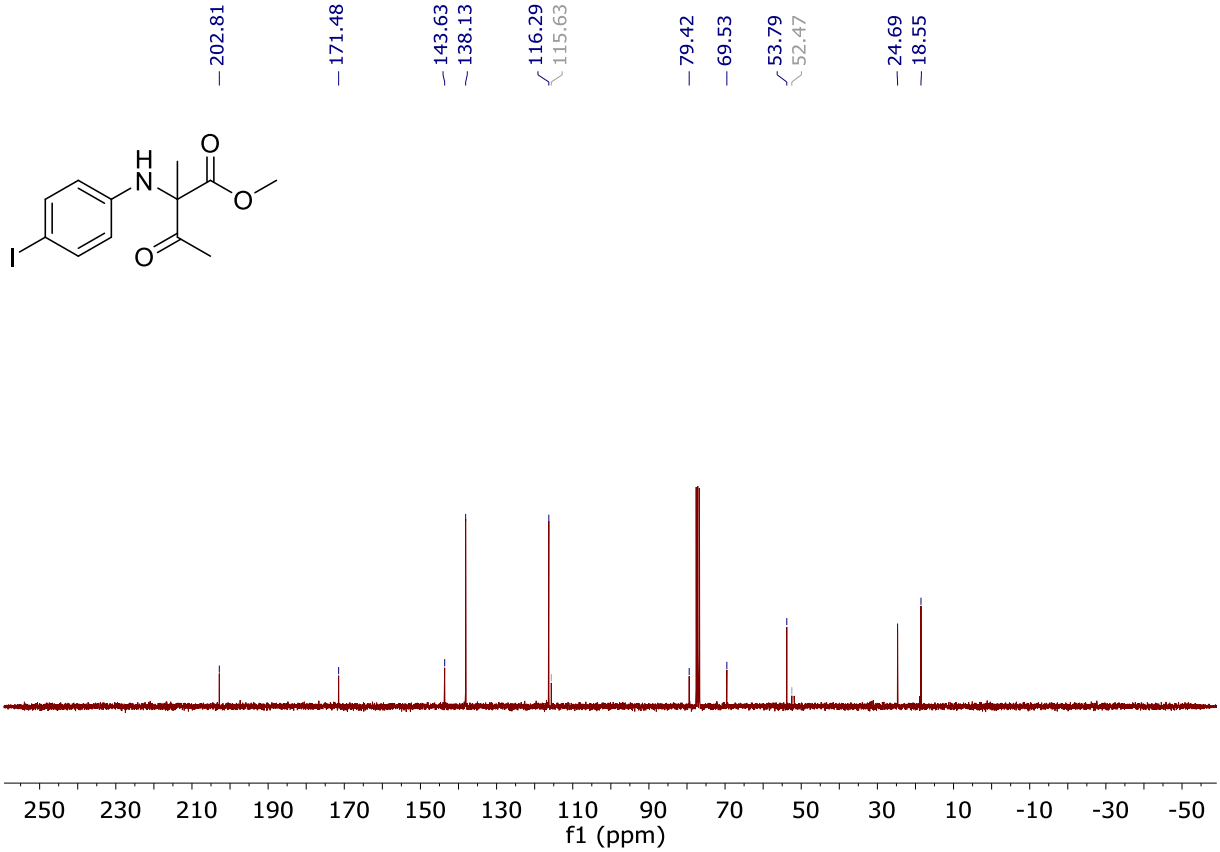

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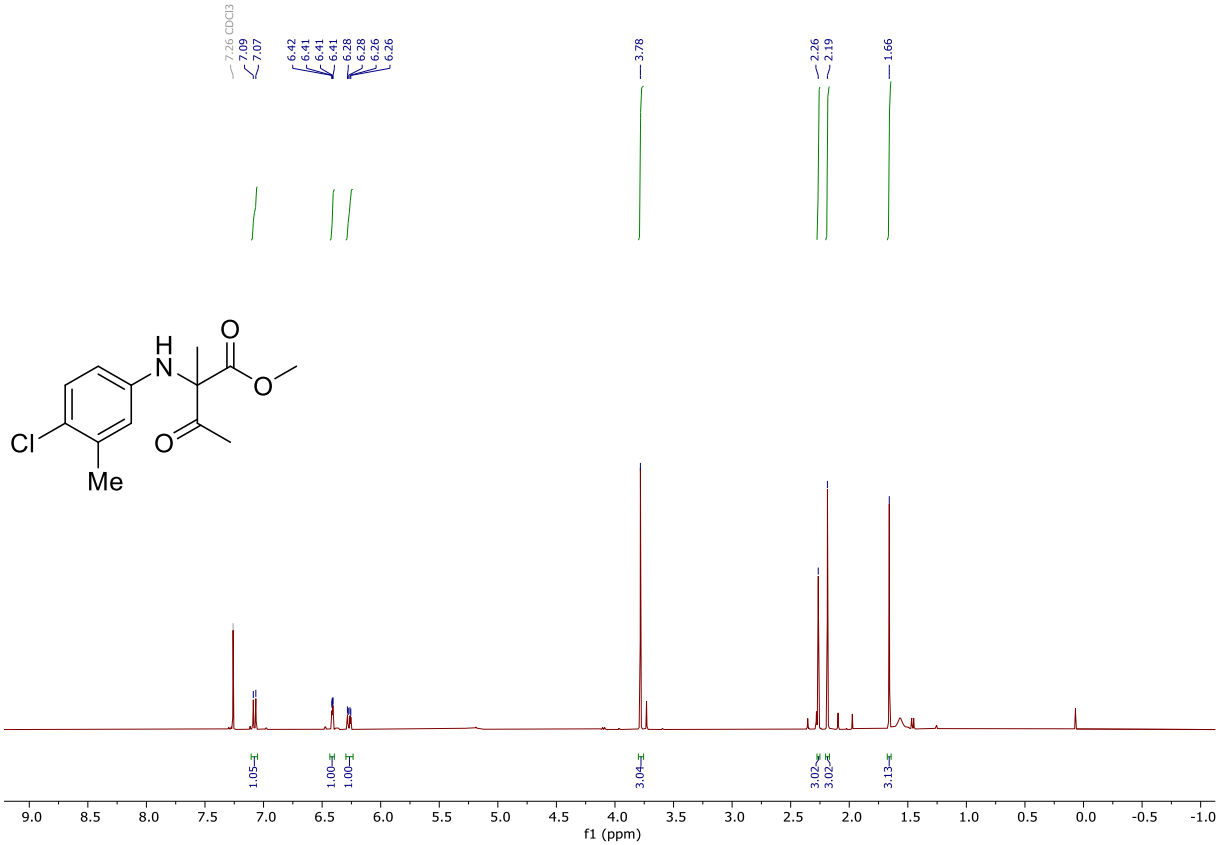
13b



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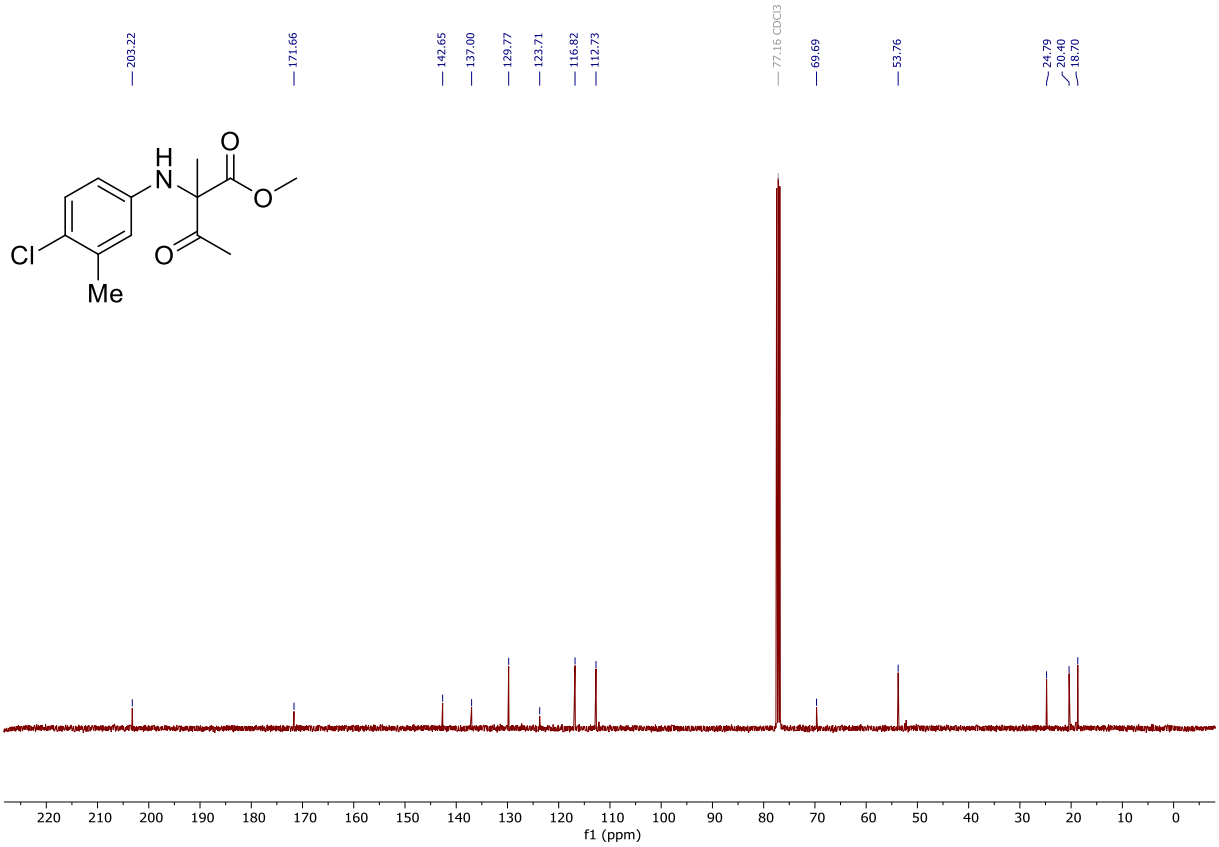

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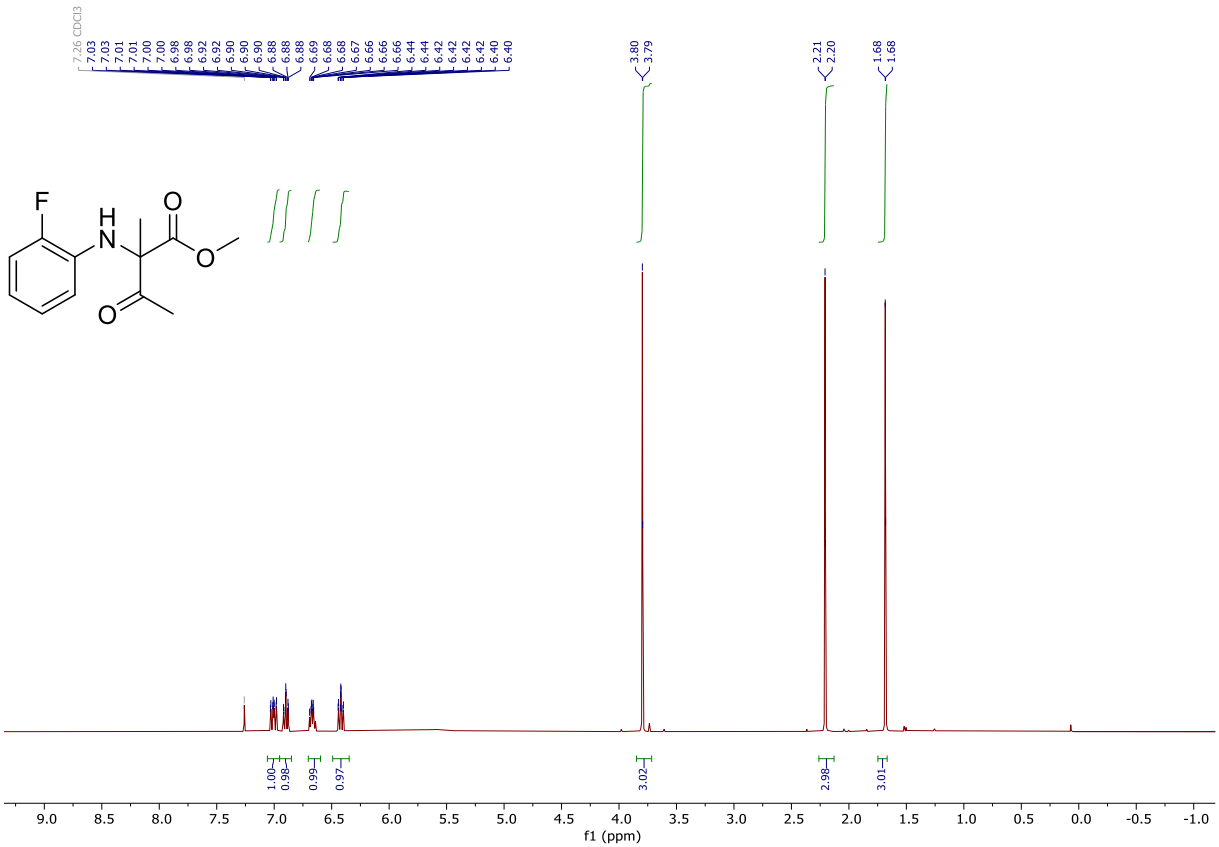
14b



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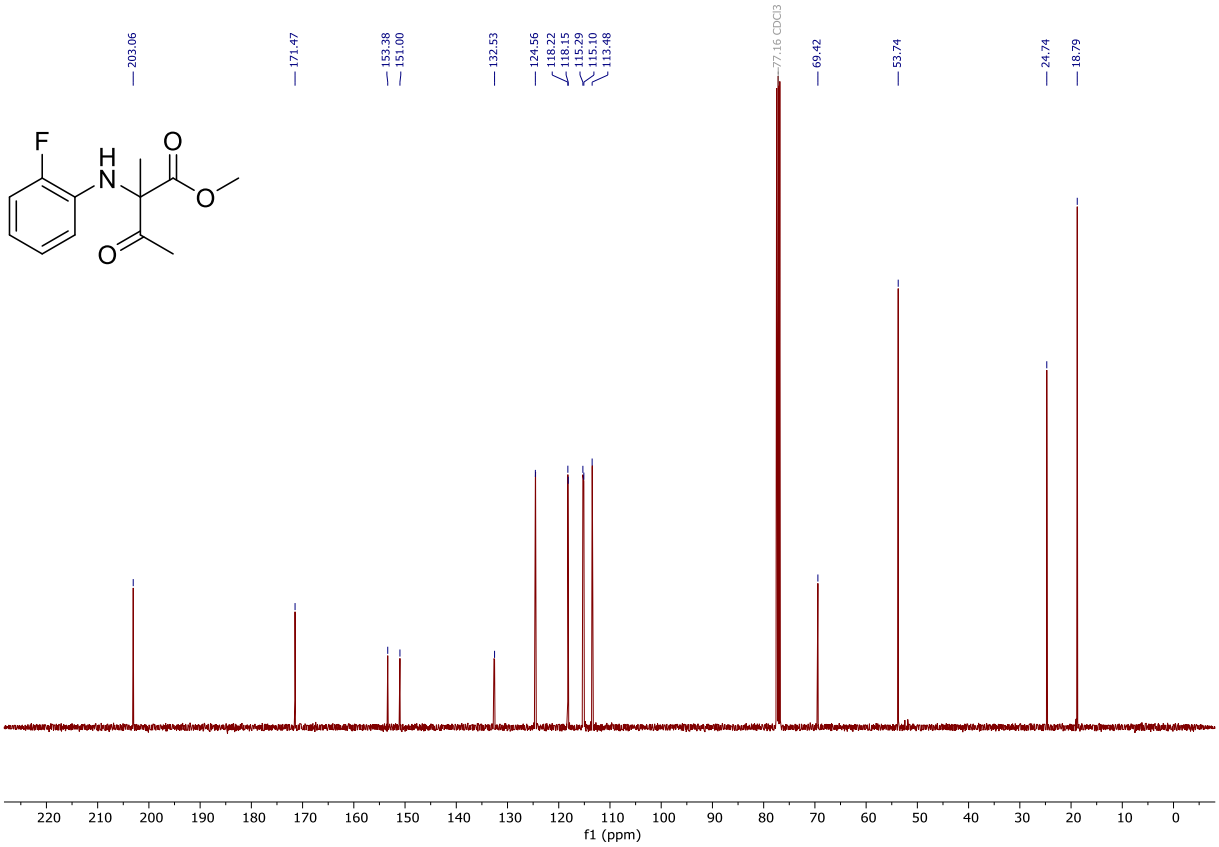

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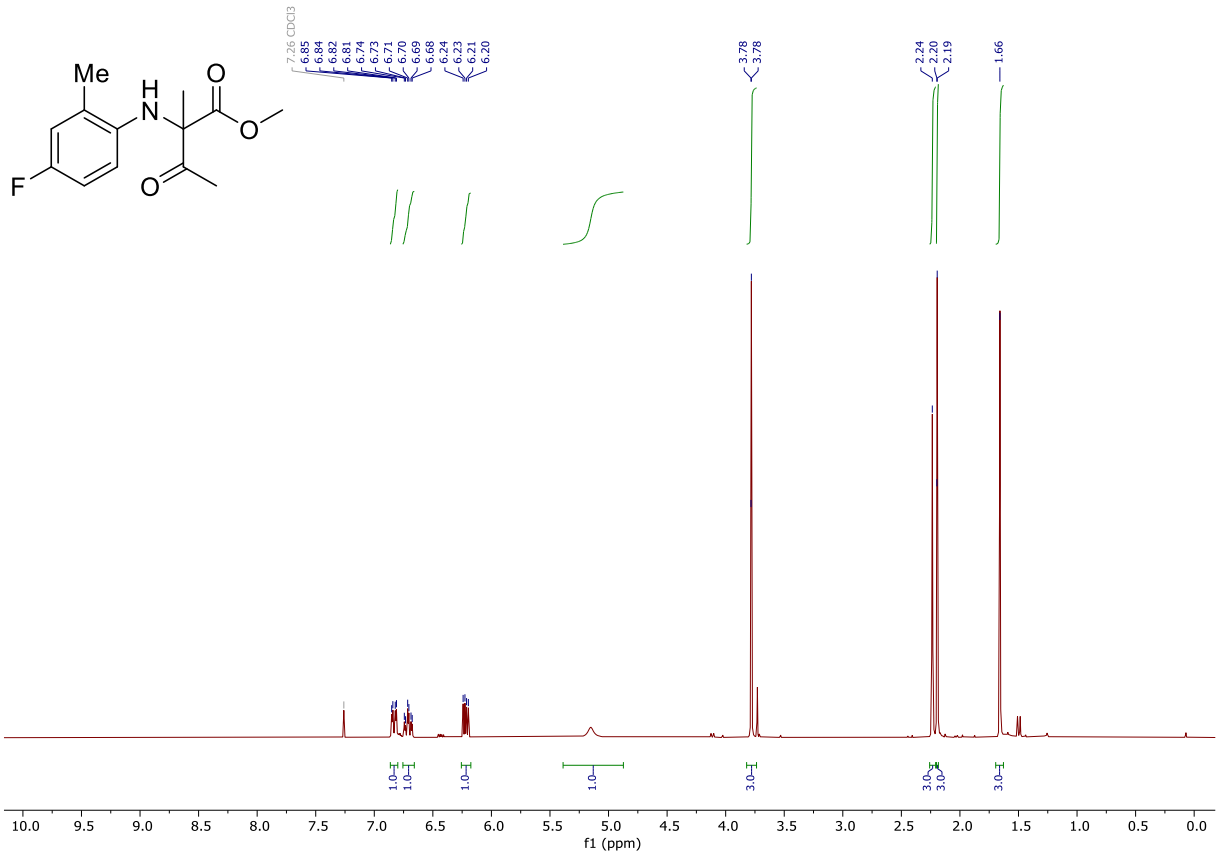
15b



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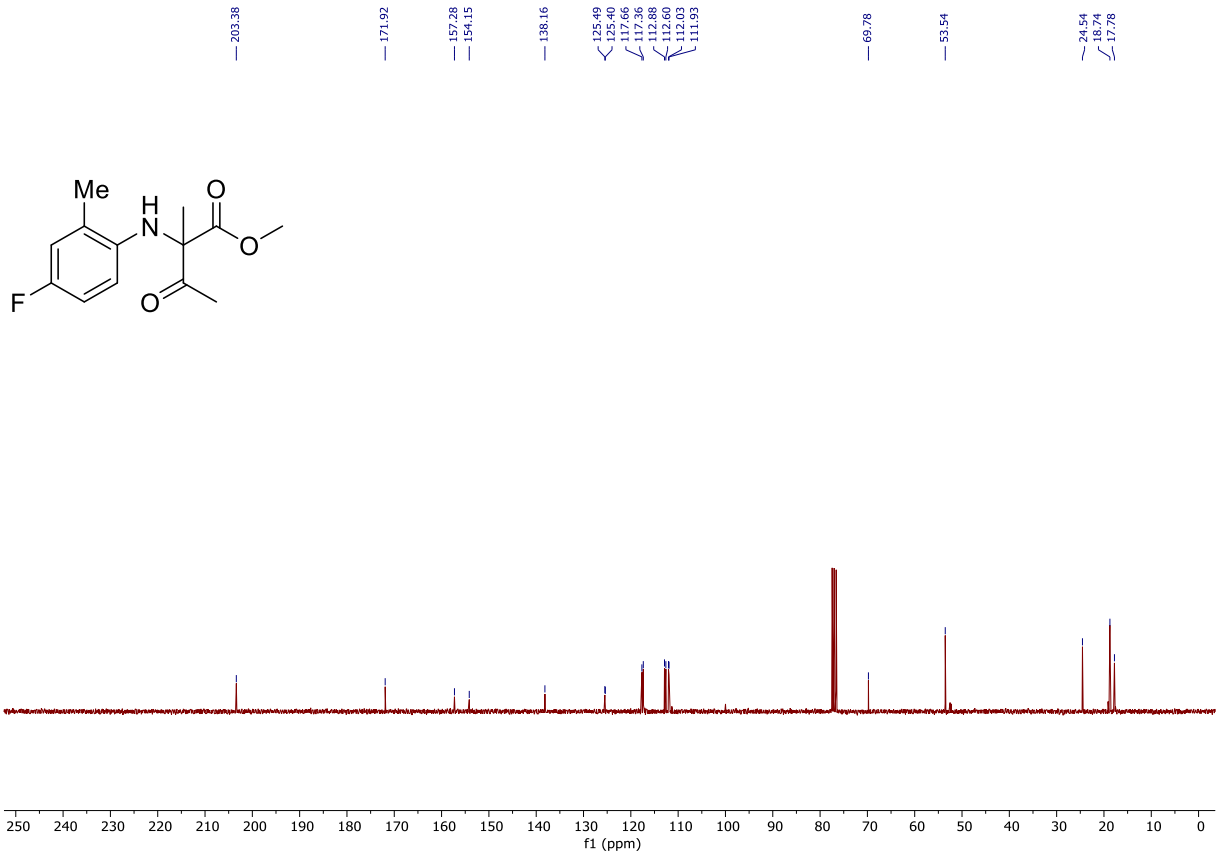
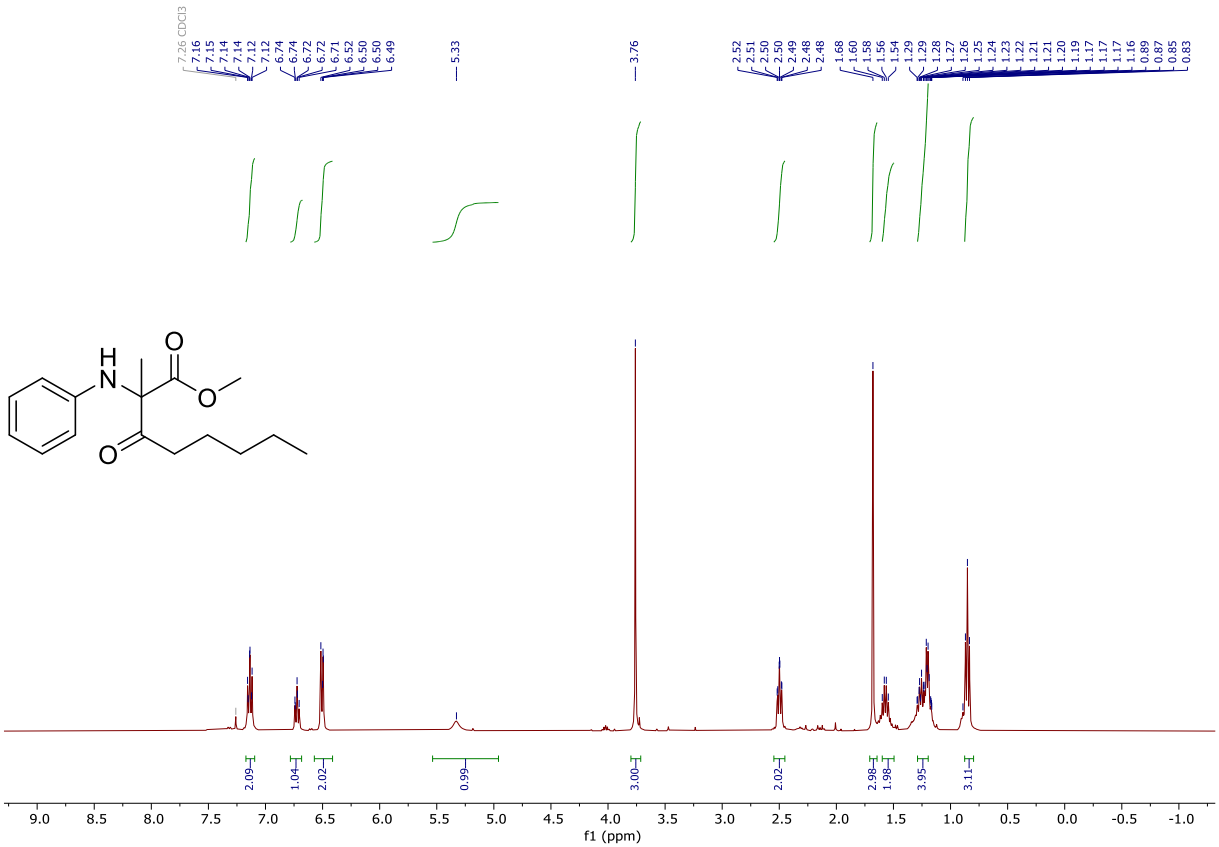
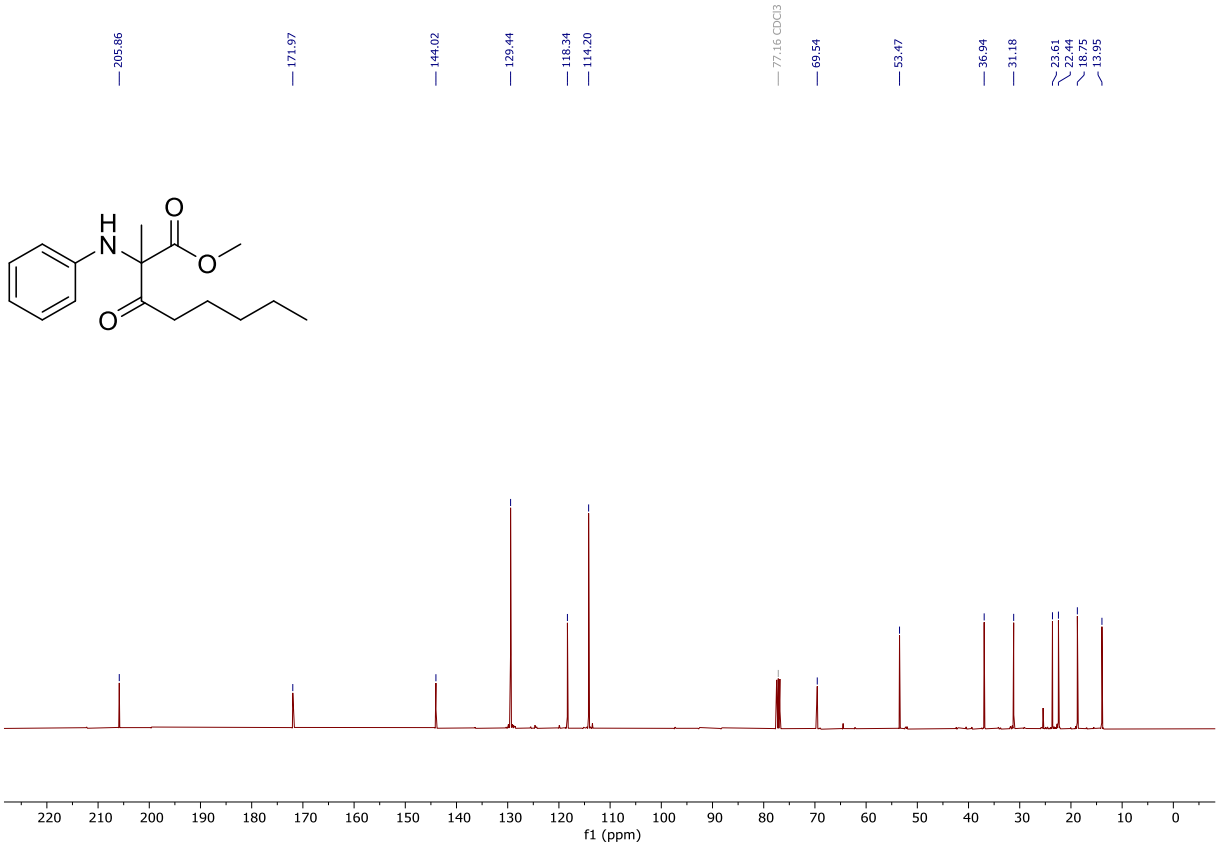


^{13}C-NMR in $CDCl_3$.

16b

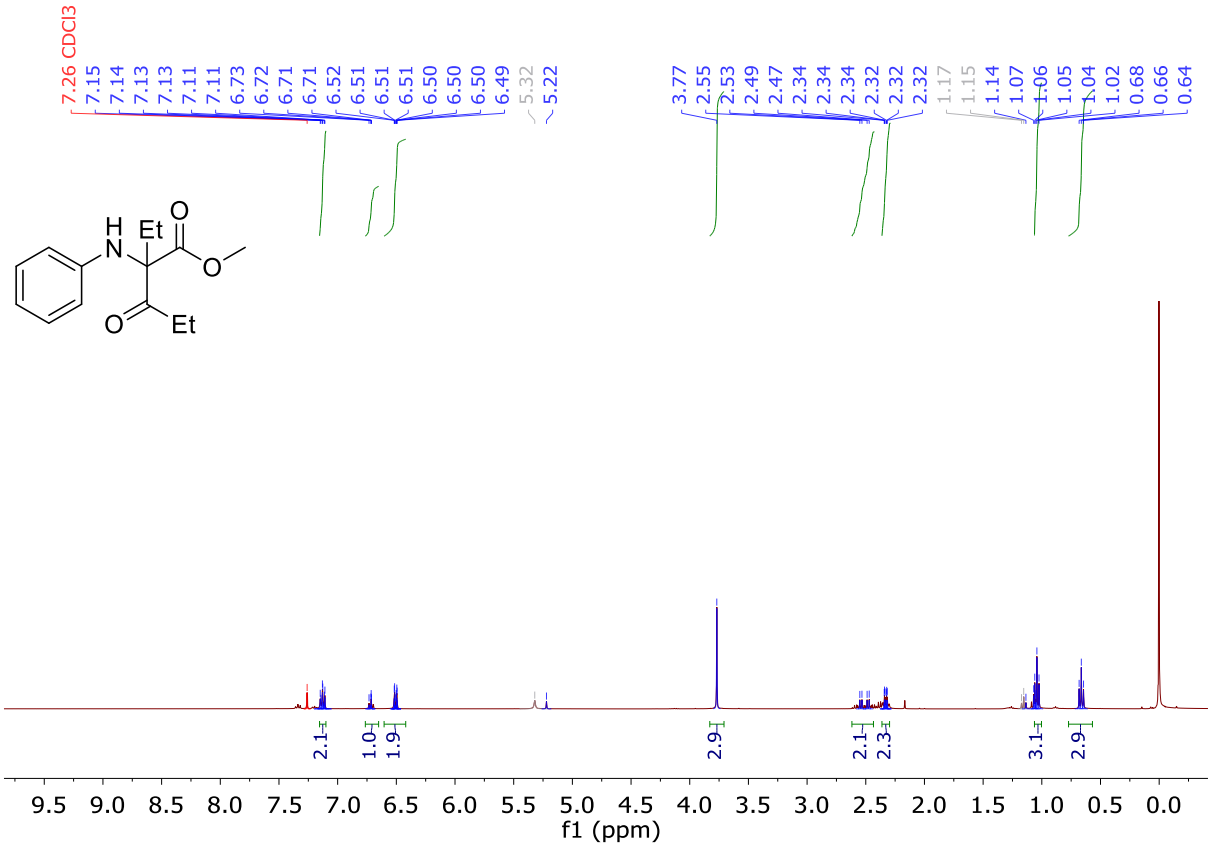


^{1}H-NMR in $CDCl_3$.

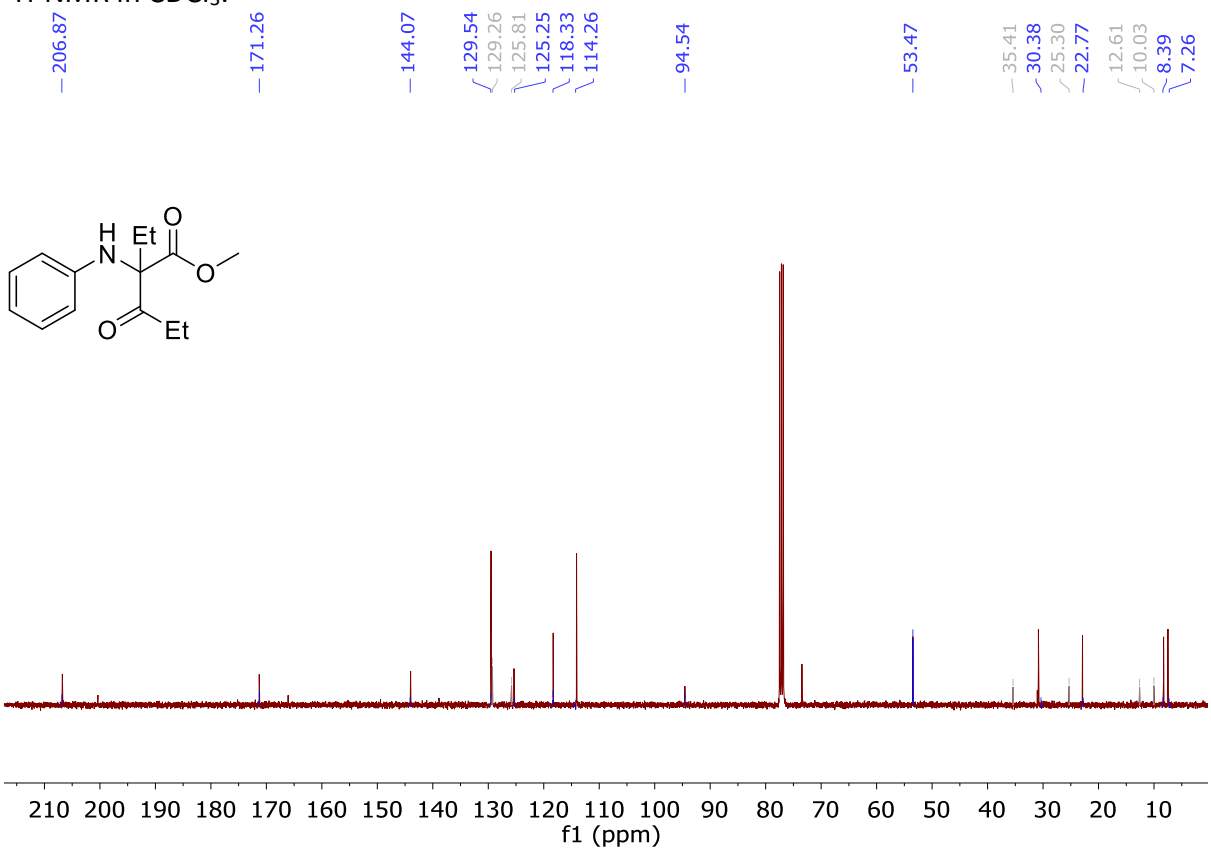


^{13}C-NMR in $CDCl_3$.

17b

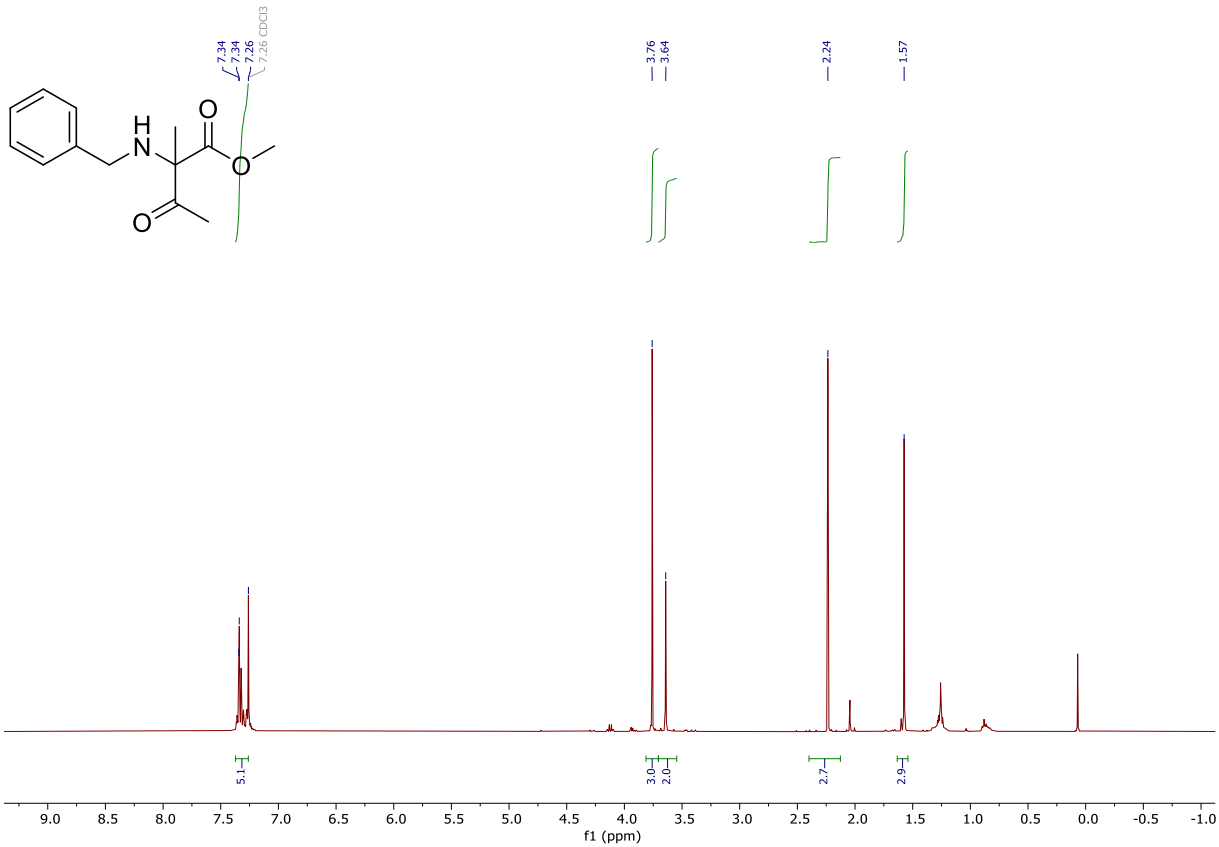


^{1}H-NMR in $CDCl_3$.

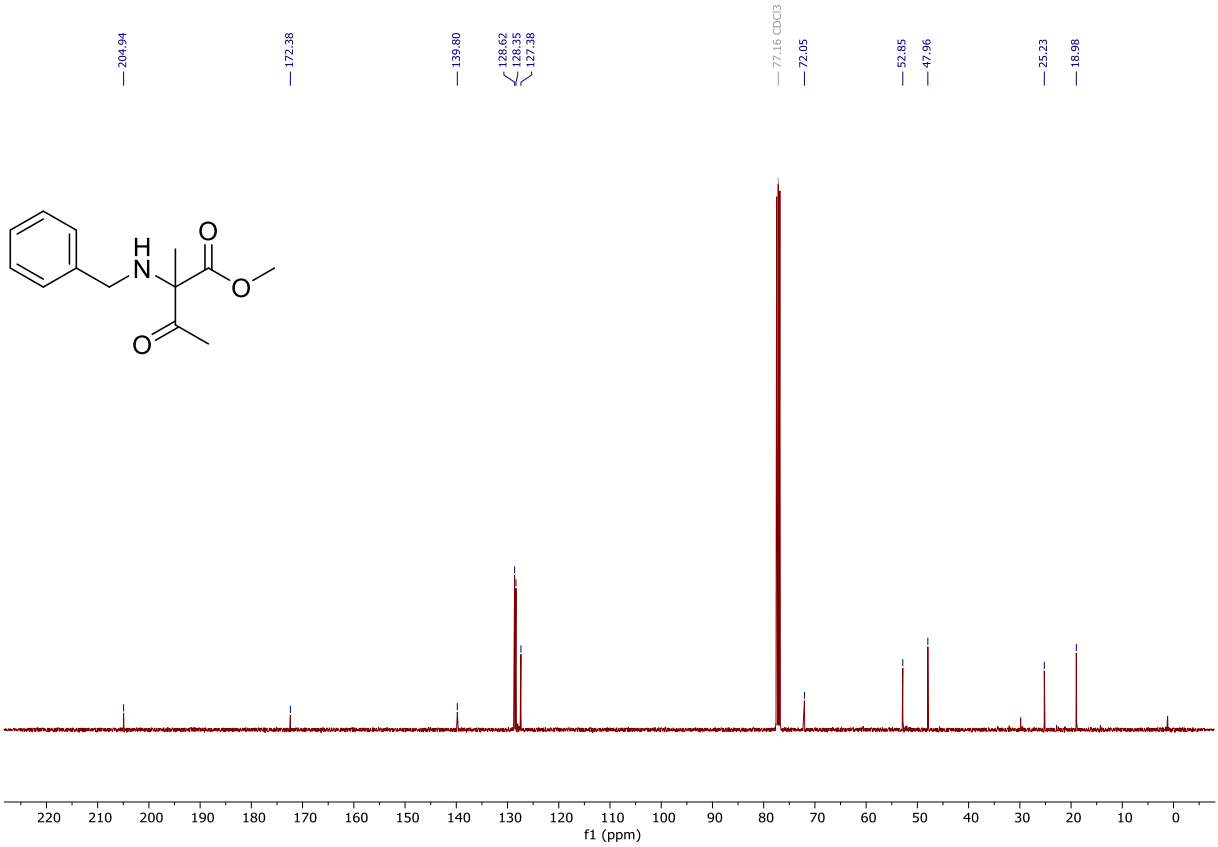


^{13}C-NMR in $CDCl_3$.

18b

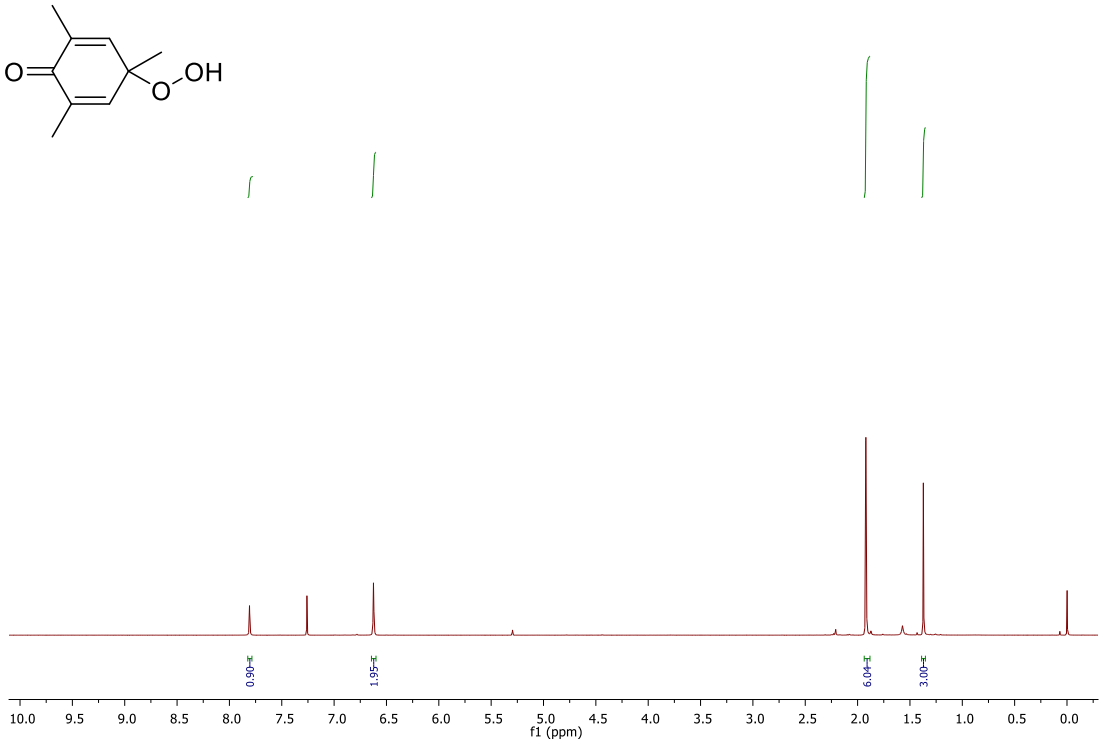


^{1}H-NMR in $CDCl_3$.

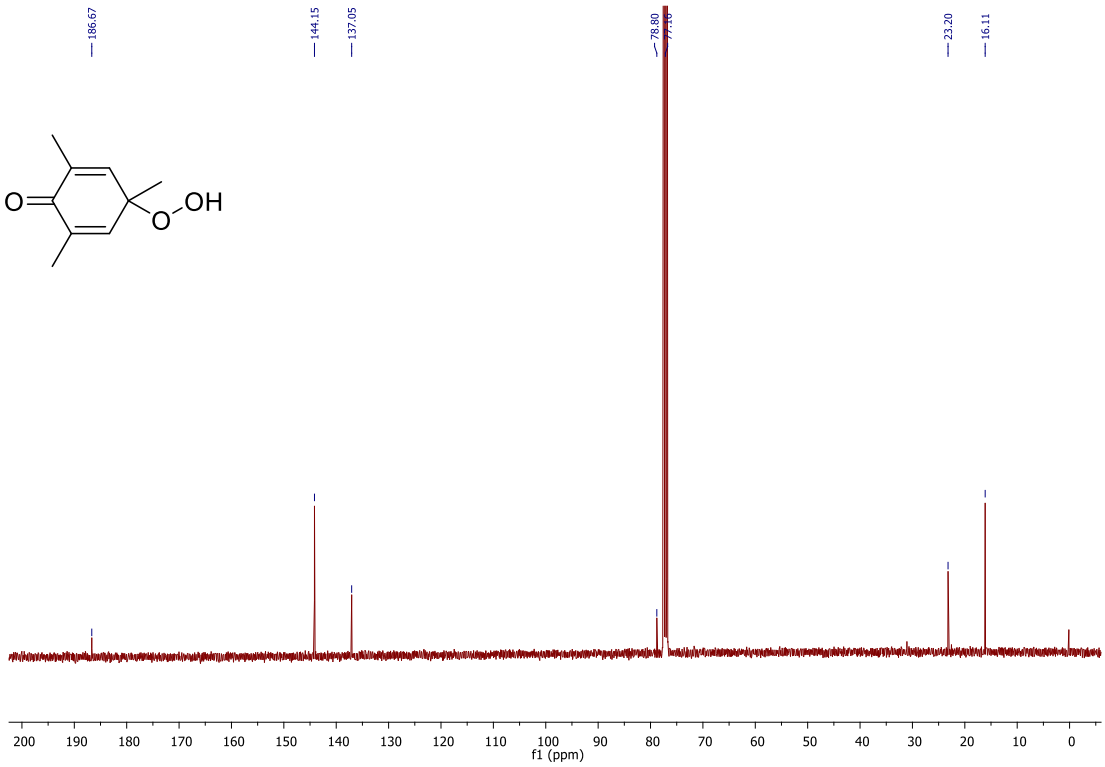


^{13}C-NMR in $CDCl_3$.

19b

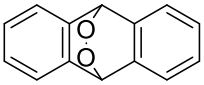


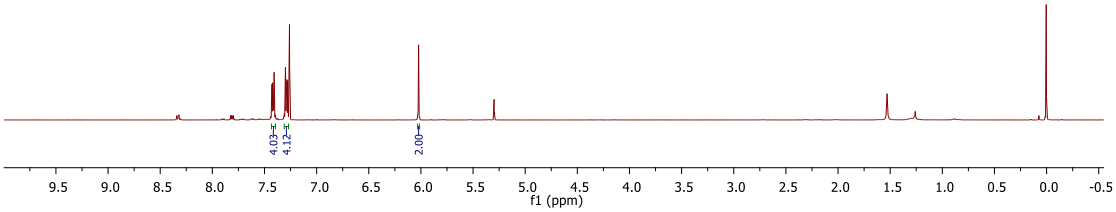
^{1}H-NMR in $CDCl_3$.



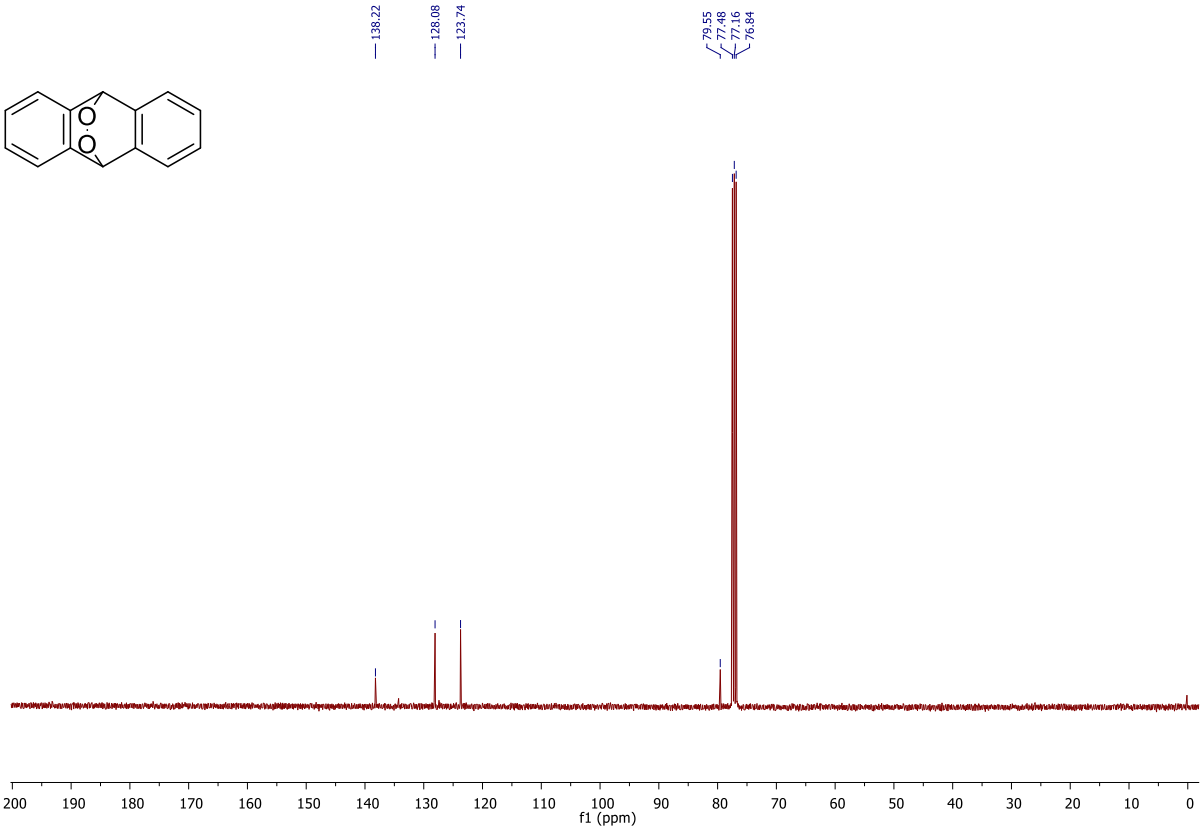
^{13}C-NMR in $CDCl_3$.

20b



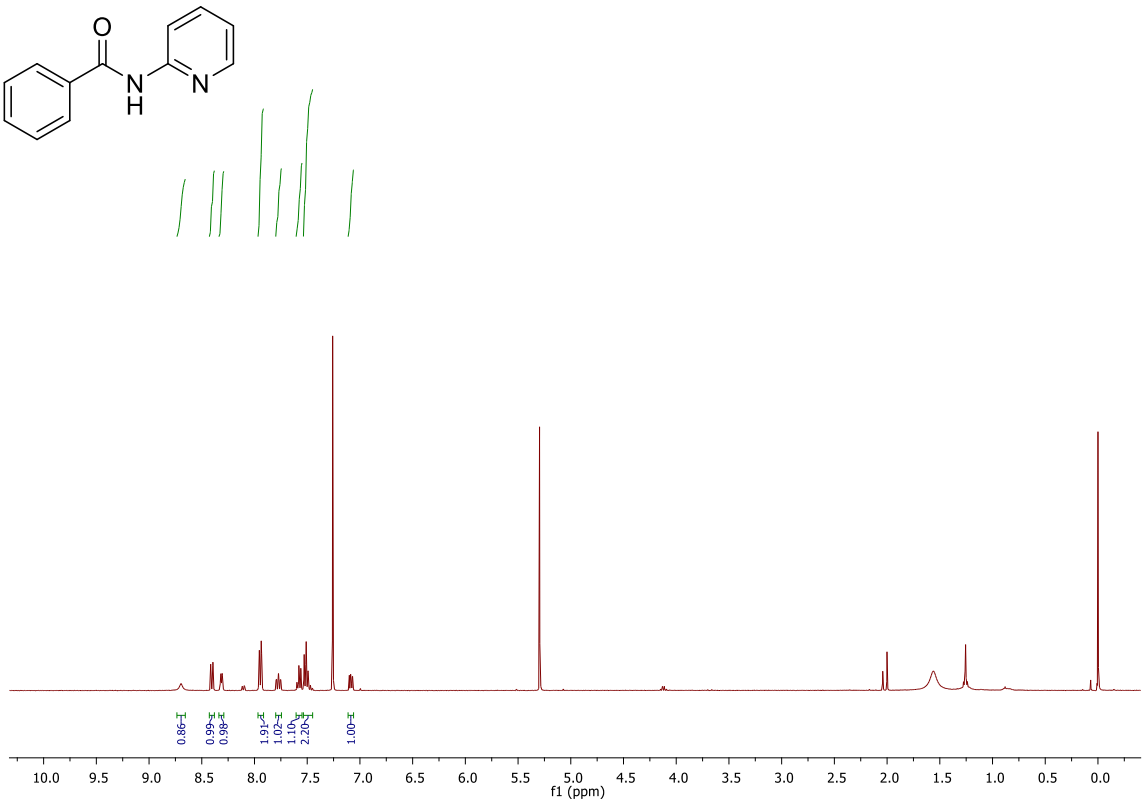


^{1}H-NMR in $CDCl_3$.

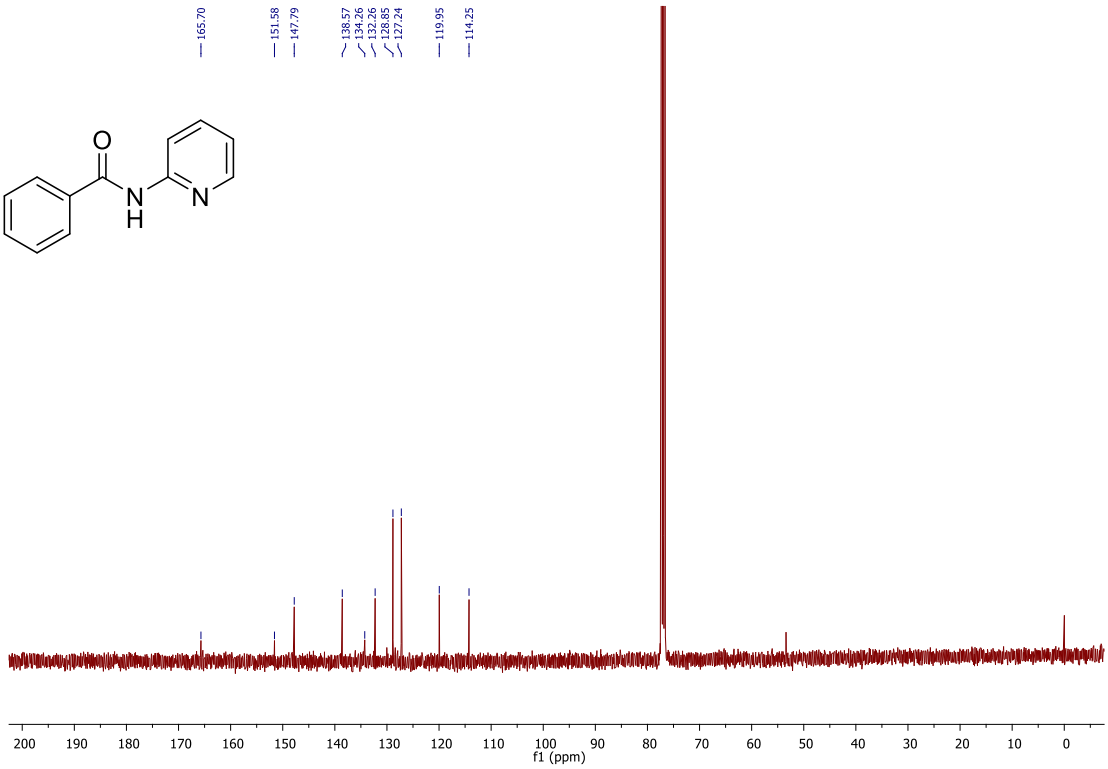


^{13}C-NMR in $CDCl_3$.

21b

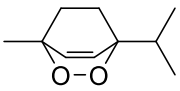


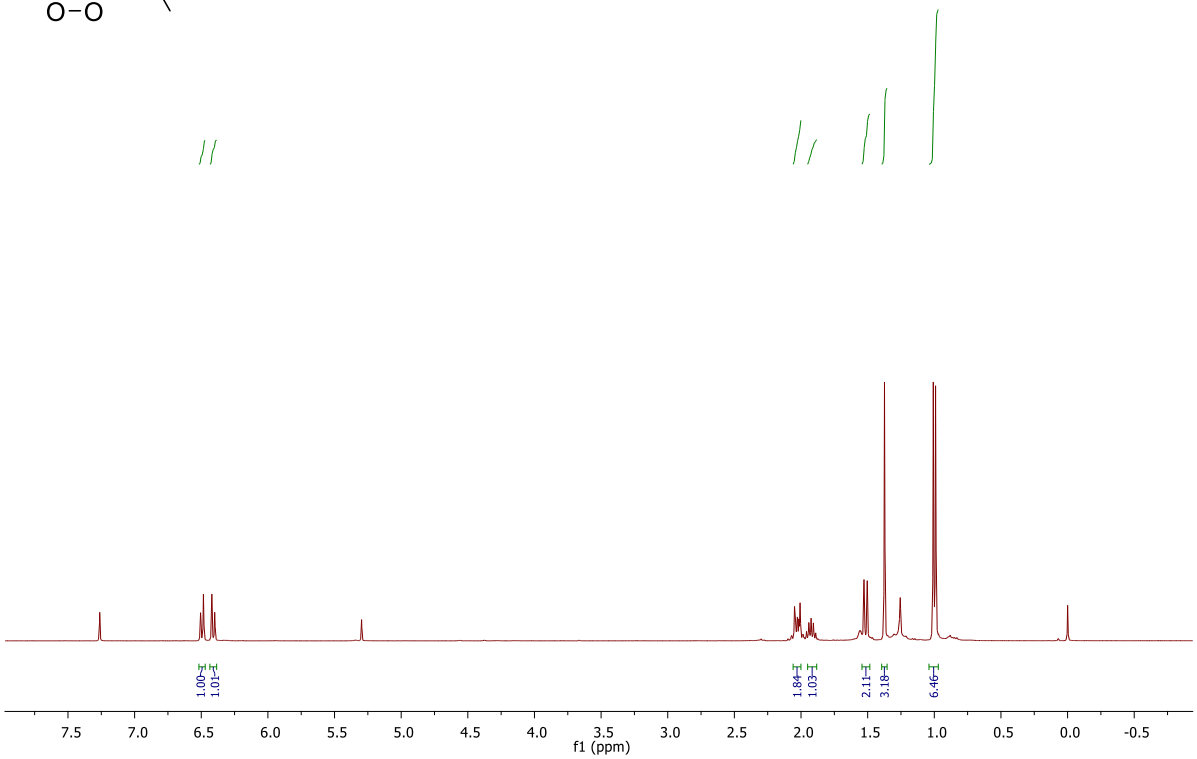
^{1}H-NMR in $CDCl_3$.



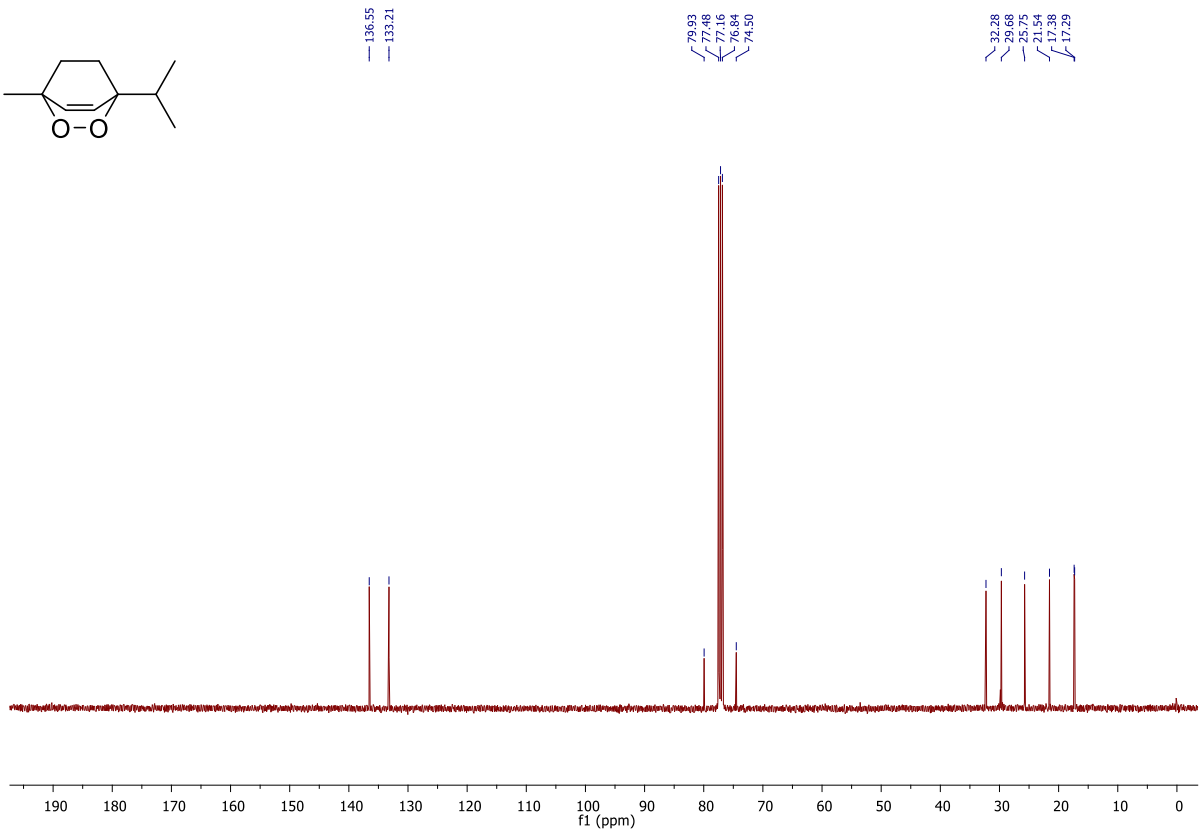
^{13}C-NMR in $CDCl_3$.

22b





^{1}H-NMR in $CDCl_3$.



^{13}C-NMR in $CDCl_3$.