Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Alkylation of the α-amino C−H bonds of anilines photocatalyzed by a DMEDA-Cu-Benzophenone complex: Reaction scope and mechanistic studies

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A- General information

All reagents were obtained from commercial sources and used as received, except when specified.

NMR analyses were carried out on a Bruker AvanceII-300 spectrometer (300 MHz for ^{1}H, 75 MHz for ^{13}C and 282 MHz for ^{19}F). The chemical shifts (δ) for carbon and proton resonances are given compared to the residual solvent peak and are expressed in ppm. The following abbreviations were used to explain the multiplicities : s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Mass spectra were recorded at the CESAMO (ISM, University of Bordeaux, France, http://cesamo.ism.u-bordeaux1.fr/) using electrospray ionisation (ESI) or Field Ionisation. HRMS ESI spectra were obtained on a QStar Elite mass spectrometer (Applied Biosystems) using positive polarity electrospray ionization mode. Electronic absorption spectra were recorded on a Varian Cary 5000 spectrophotometer in 1 cm pathlength quartz cells.

B- Irradiation setups

Illumination sources employed in the study :

- Luzchem® HUV LED/illuminator setup (https://www.luzchem.com); $\lambda_{max\ em}$ 365 nm; Sample situated at ca. 3 cm from the light source; Used for optimization reactions and reaction scope.

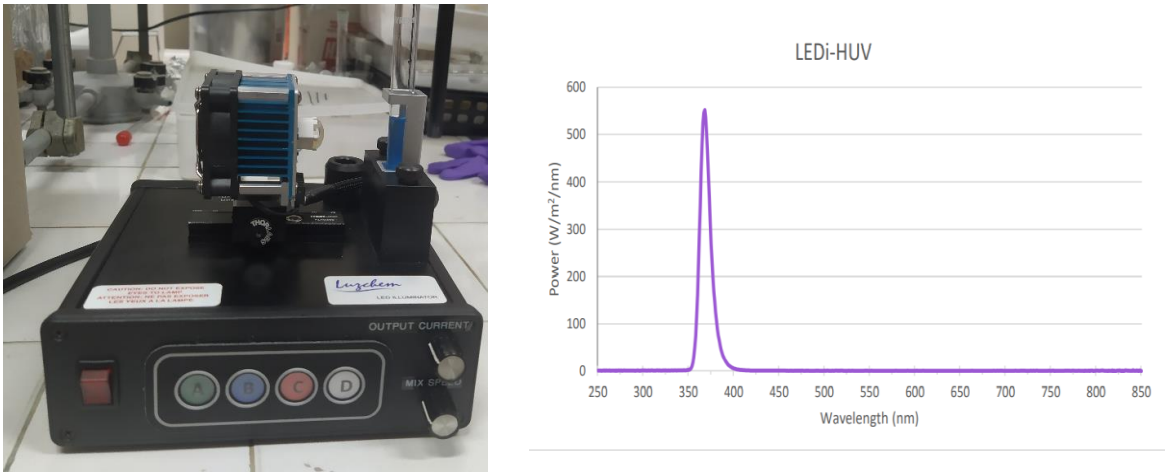


Figure S1. Photograph of the Luzchem® irradiation setup, and emission spectrum of the 365 nm LED (from https://www.luzchem.com).

- PR160L Kessil® LEDs (https://www.kessil.com); $\lambda_{max\ em}$ 370 nm (43 W) or 390 nm (52 W) (Fig. S2); Sample situated at ca. 15 cm from the light source; Used for optimization reactions.

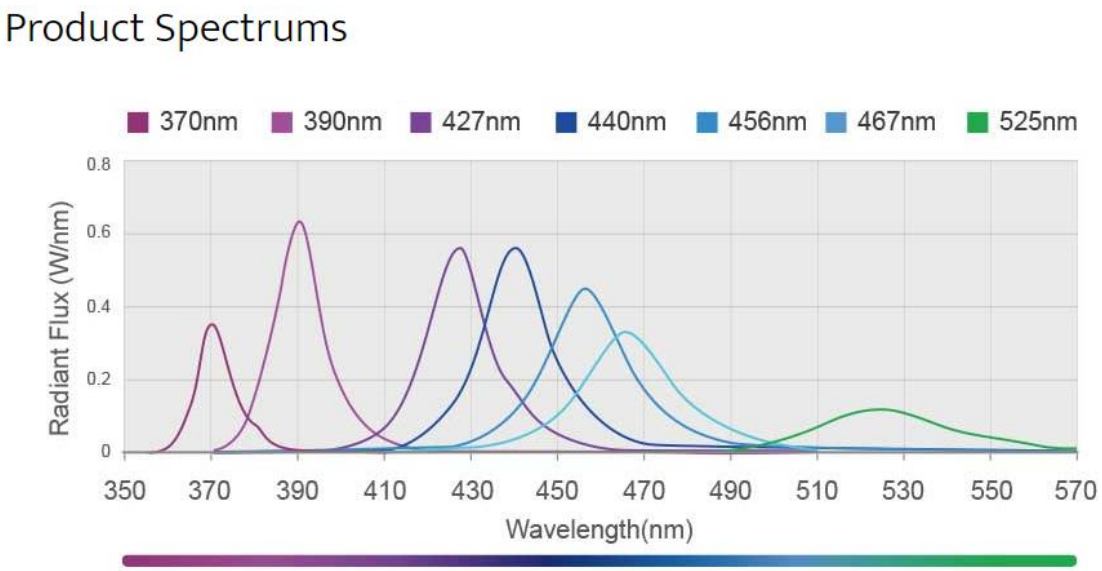
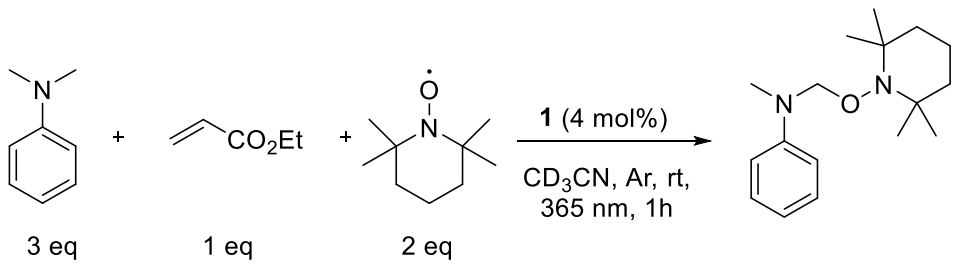


Figure S2. Emission spectra of the 370 and 390 nm LEDs used in this study (from https://www.kessil.com).

- Fisher Bioblock low pressure mercury lamp (type "TLC", Thin layer Chromatography; 6 W), $\lambda_{max\ em}$ 365 nm (emisssion spectrum 320-390 nm); Sample situated at ca. 1 cm from the lamp; Used for optimization reactions.
- Compact Fluorescent Light (CFL) bulb (24 W); Sample situated at ca. 1 cm from the lamp; Used for optimization reactions.

C- Mechanistic experiments

C-1 Radical trapping with TEMPO



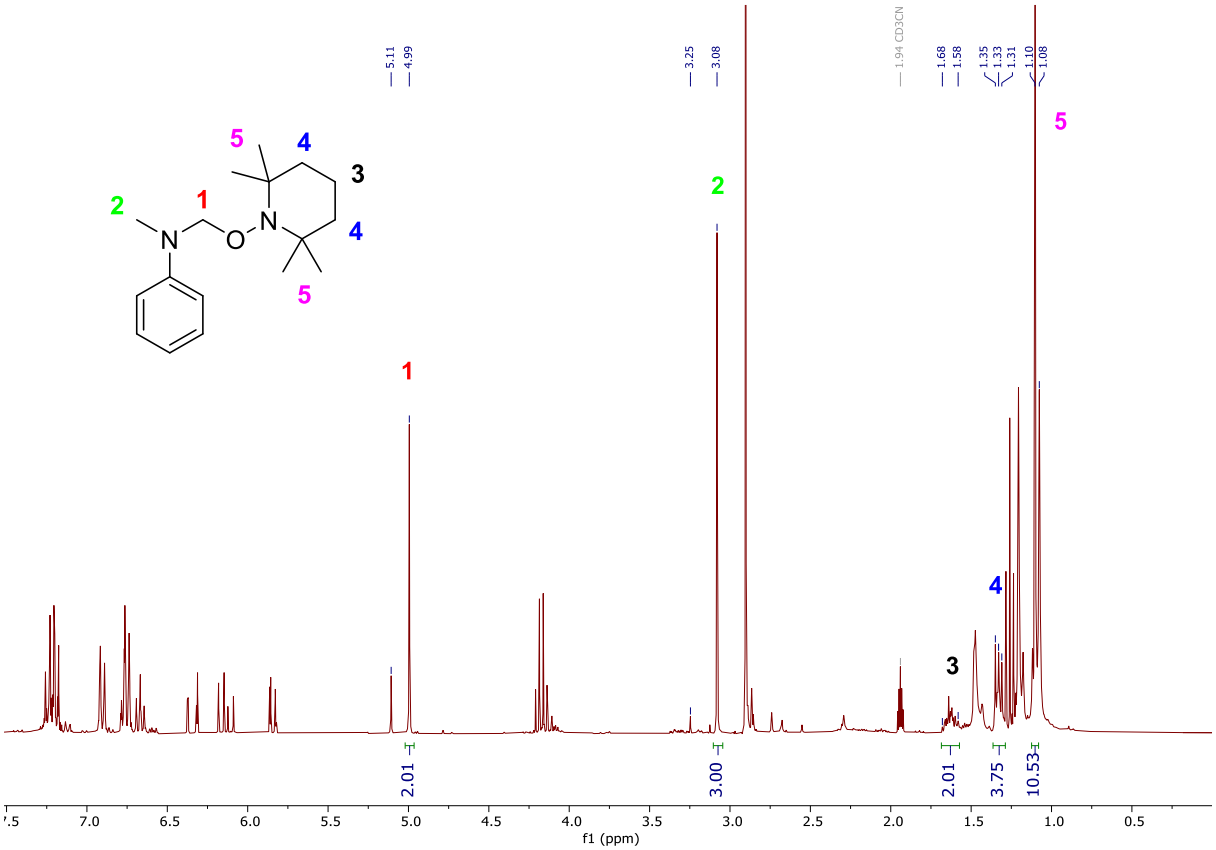


Figure S3: ^{1}H NMR of the reaction mixture after one hour of irradiation following the general procedure A conducted in the presence of two equivalents of TEMPO, along with the tentative peak assignments of the TEMPO-aniline coupling product.

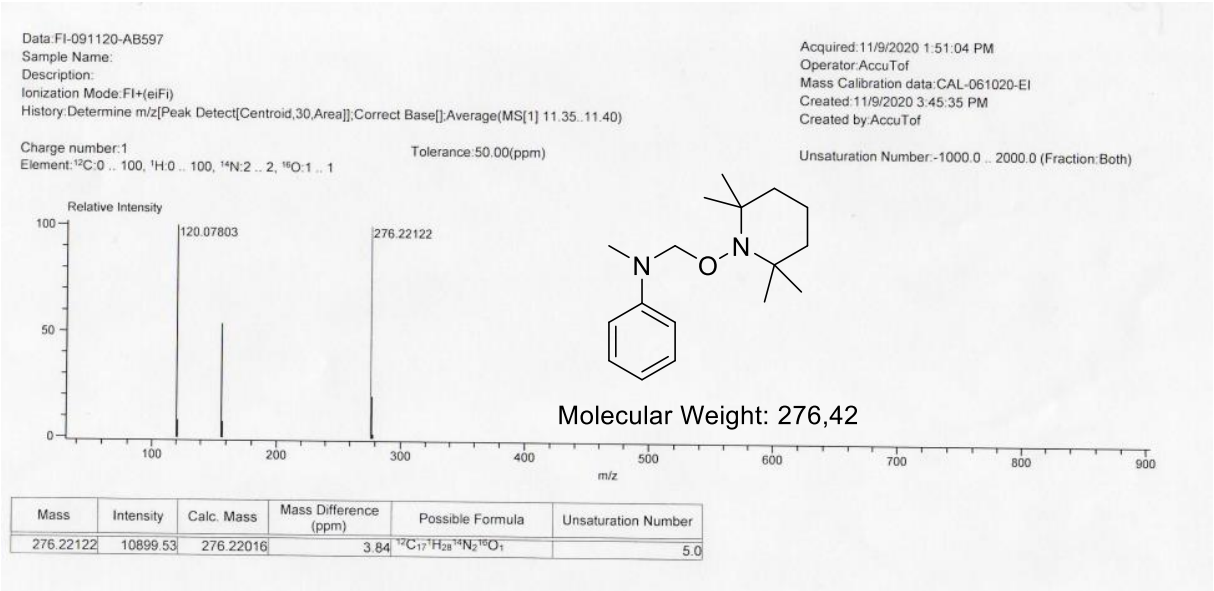
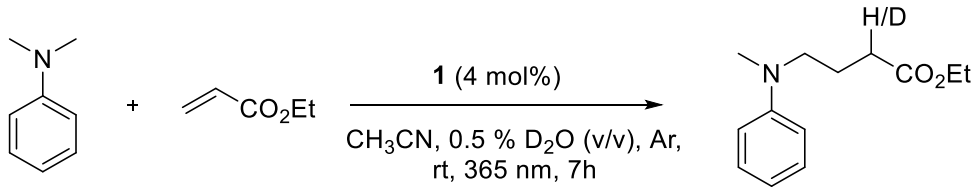


Figure S4. HRMS (Field Ionisation) of the reaction mixture showing the presence of the TEMPO-aniline coupling product.

C-2 Product deuteration with D_2O



Following general procedure B except that the reagents were dissolved in acetonitrile (1.990 mL) containing D_2O (0.01 mL). The crude was purified by silica gel column chromatography with petroleum ether/ethyl acetate (90/10, v/v) as the eluent. The incorporation of deuterium was assessed by ^{1}H, ^{13}C NMR and mass spectrometry (Fig. S13, S14).

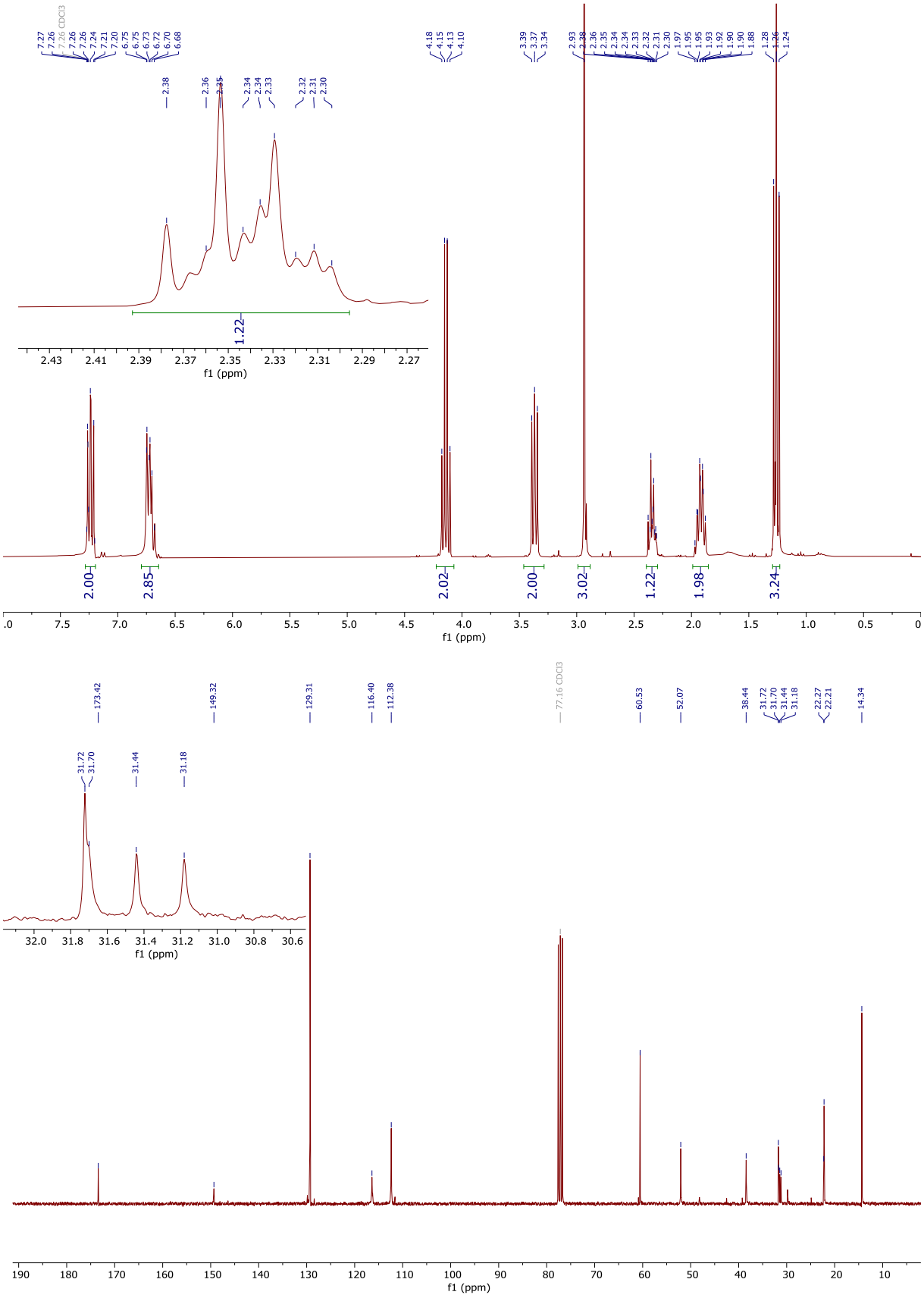
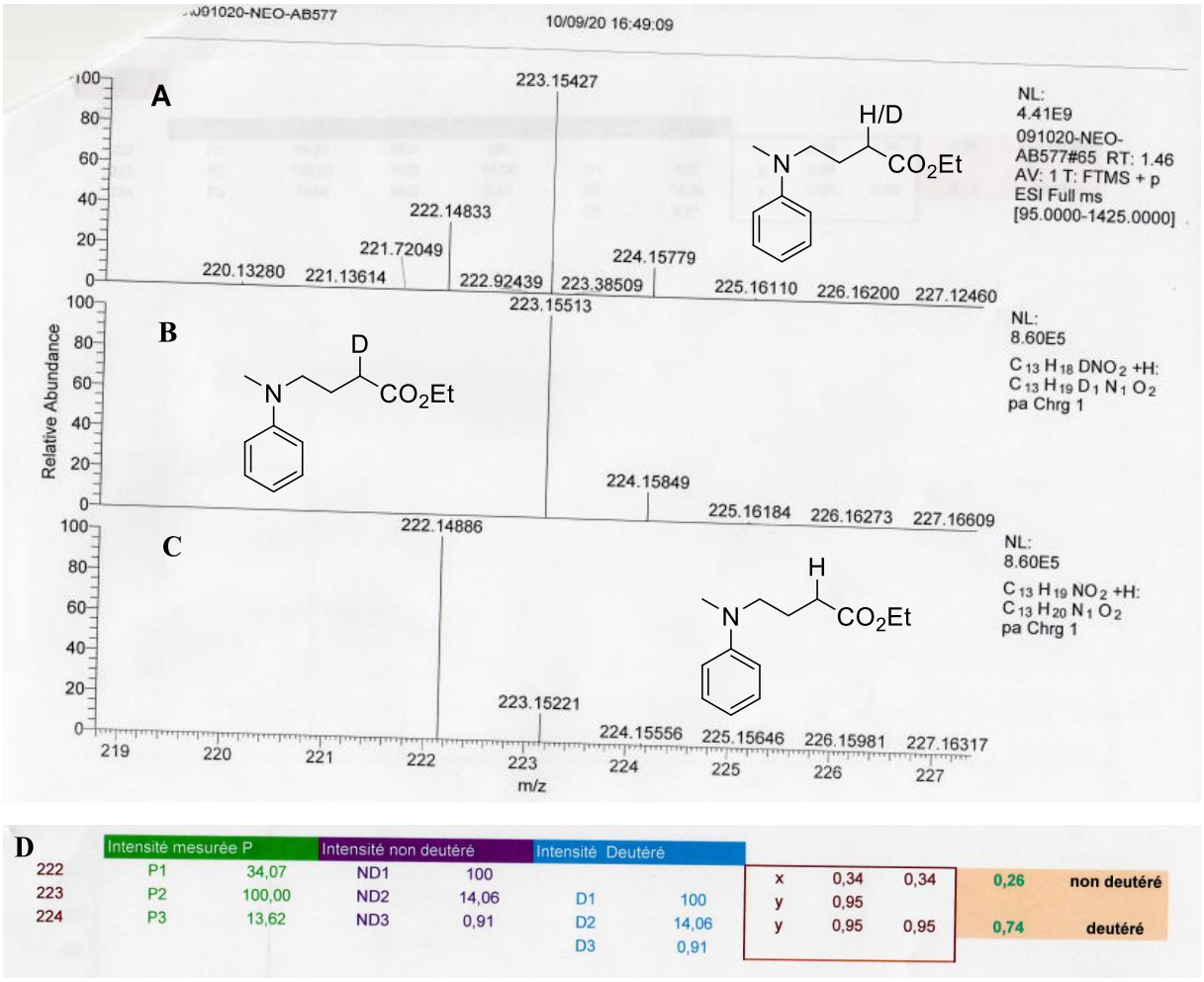


Figure S5: ^{1}H and ^{13}C NMR spectra of the isolated product revealing a ~ 75:25 ratio between the mono-deuterated product and the fully hydrogenated product. On the ^{1}H NMR spectrum the integral value of the peak at 2.35 ppm should be 2 if no deuteration had occurred.



D

	Intensité mesurée P		Intensité non deutéré		Intensité Deutéré					
222	P1	34,07	ND1	100			x	0,34	0,34	0,26 non deutéré
223	P2	100,00	ND2	14,06	D1	100	y	0,95		
224	P3	13,62	ND3	0,91	D2	14,06	y	0,95	0,95	0,74 deutéré
					D3	0,91				

Figure S6. Experimental MS spectra of the isolated aniline product (**A**), and calculated isotope patterns for the mono-deuterated (**B**) and fully hydrogenated anilines (**C**). **D**: Intensity of the various peaks that affords a 74:26 ratio between the mono-deuterated and fully hydrogenated products.

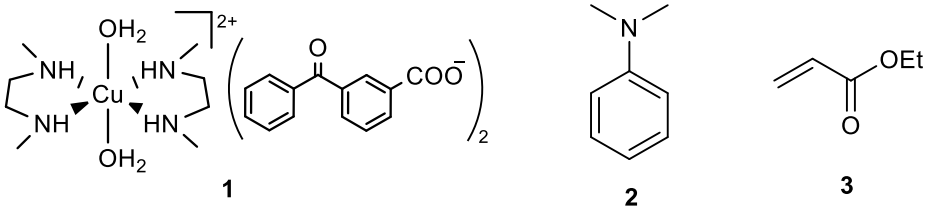
C-3 Transient absorption spectroscopy (TRABS)

The transient absorption / time-resolved luminescence set-up was built as follows : a frequency tripled Nd:YAG amplified laser system (30 ps, 30 mJ @1064 nm, 20 Hz, Ekspla model PL 2143) output was used to pump an optical parametric generator (Ekspla model PG 401) producing tunable excitation pulses in the range 410 – 2300 nm. For longer timescales, a tunable nanosecond laser (5 ns, 135 mJ @355 nm from Nd:YAG amplified laser pumping OPO, 10 Hz, Ekspla model NT342B-10-WW); produced tunable excitation pulses in the range 410-2300 nm. The residual fundamental laser radiation was focused in a high pressure Xe filled breakdown cell where a white light pulse for sample probing was produced. All light signals were analyzed by a spectrograph (Princeton Instruments Acton model SP2300) coupled with a high dynamic range streak camera (Hamamatsu C7700, 1ns-1ms). Accumulated sequences (sample emission, probe without and with excitation) of pulses were recorded and treated by HPDTA (Hamamatsu) software to produce two-dimensional maps (wavelength *vs* delay) of transient absorption intensity in the range 300 – 800 nm. Typical measurement error was better than 10^{-3} O. D. Data were analysed using home-made software developed in LabVIEW 2014 system-design platform and development environment. The trust-region dogleg algorith[i] (supported by

LabVIEW 2014) was applied to determine the set of parameters that best fit the set of input data. The trust-region dogleg algorithm was used instead of Levenberg-Marquardt algorithm, the latter being less stable in most cases during optimization process, because trust region methods are robust, and can be applied to ill-conditioned problems.

The samples were measured in acetonitrile, exciting at 355 nm:

- BP (0.01 M) – **2** (0.3 M)
- **1** (0.04 M) – **2** (0.3 M) – **3** (0.1 M)



The TRABS maps are shown below:

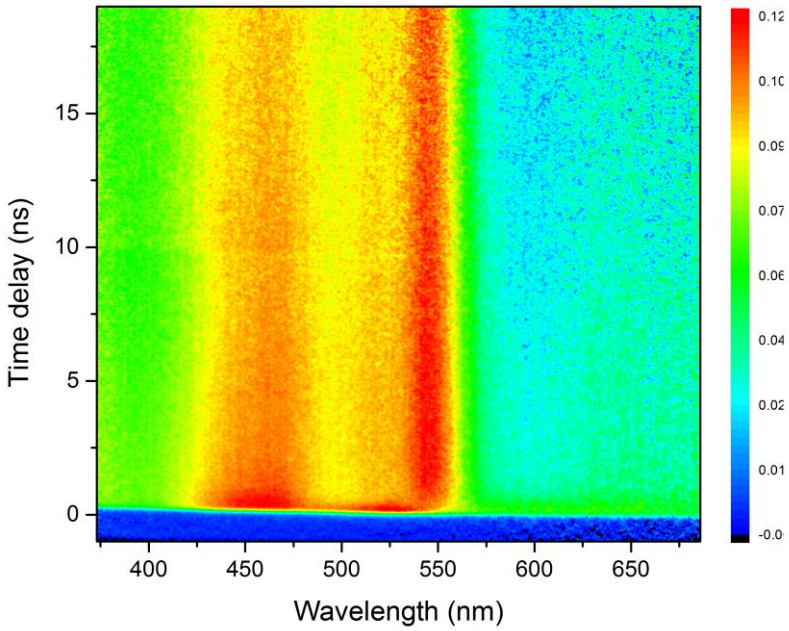


Figure S7. TRABS map of BP (0.01 M) – **2** (0.3 M) on a 20 ns timescale in acetonitrile (λ_{exc} = 355 nm).

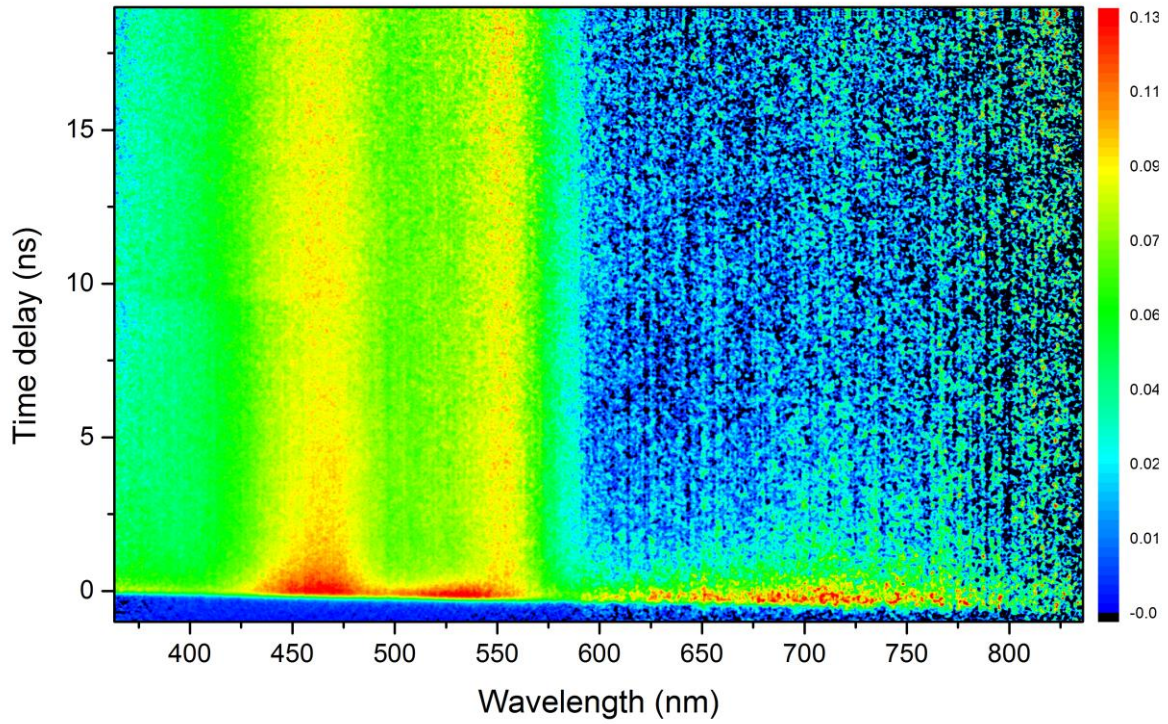


Figure S8. TRABS map of **1** (0.04 M) – **2** (0.3 M) – **3** (0.1 M) on a 20 ns timescale in acetonitrile (λ_{exc} = 355 nm). (Note: The spectrum combines two individual spectra at different wavelength ranges).

Several spectral bands are seen on the maps and the attribution of all these bands were provided previously: Miyasaka, H.; Morita, K.; Kamada, K.; Mataga, N. *Bull. Chem. Soc. Jpn*. **1990**, *63*, 3385-3397.

Central wavelength	**Attribution**
460 nm	**2** radical cation
520 - 525 nm	BP triplet
550 - 560 nm	BP ketyl radical
650 – 700 nm	BP radical anion

The temporal evolution of signals is very complicated with many overlapping signals and comprises on shorter timescales the decay of rapidly formed BP triplet signal along with the rise of BP ketyl radical, **2** radical cation and BP radical anion signals attributed to a bimolecular / dissociated donor-acceptor system. Concerning the excited BP-**2** complex (formed in the ground state), the fast decay superposed with bands at 460, 520, 550 and 700 nm. The initial decay time of BP radical anion band correlates quite well with the decay time of **2** radical cation band at the beginning of the kinetic, which is ascribed to a competitive back electron transfer process. Subsequently, the signals of the **2** radical cation and BP ketyl radical are persistent and do not appear to decay from ca. 10 ns to 200 ns. (A solvated electron signal is strongly affecting all the signals on timescales longer than 200 ns).

The principal difference seen on the TRABS maps is the difference of decay time of BP radical anion in BP – **2** (similar to the previously reported Mataga sample) compared with **1** – **2** and **1** – **2** – **3** samples. The only similarity found in the kinetics of all 3 samples for this band is a fast component (τ = 0.6 ns) probably due to relaxation of the singlet excited state of complex BP-**2**, formed in the ground state.

D- Procedures of catalytic reactions

D-1 Optimization reactions (procedure A)

In a vial (2 mL) protected from light by aluminum foil, complex **1** (0.004 mmol, 0.04 eq), *N*,*N*-dimethylaniline **2** (0.3 mmol, 38.0 µL) and ethyl acrylate **3** (0.1 mmol, 10.9 µL) were dissolved in CD_3CN (1 mL). The solution was transferred into a NMR tube, and the tube was capped with a rubber septum. The reaction medium was deaerated by gentle argon bubbling during 10 minutes. The reaction was initiated by irradiating the tube with the chosen irradiation setup. After solvent evaporation, the crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (95/5 to 90/10, v/v) as the eluent.

D-2 Scope reactions (procedure B)

In a test tube (pyrex, 1 cm diameter, 10 cm length) protected from light by aluminum foil, equipped with a magnetic stirrer, complex **1** (0.008 mmol, 5.81 mg) was dissolved in dry acetonitrile (2 mL) and sonicated for 1 minute. Then the acceptor (0.2 mmol, 1 eq) and the aniline (0.6 mmol, 3 eq) were added, and the tube was capped with a rubber septum. The reaction medium was deaerated by gentle argon bubbling during 10 minutes. The reaction was initiated by irradiating the tube at 365 nm with the Luzchem® illuminator setup. After stirring under irradiation at room temperature for 3-48 h, the solvent was removed under reduced pressure, and the crude product was purified by column chromatography over silica gel.

D-3 Synthesis of **4** on 1 mmol scale reaction

In a test tube (1.5 cm diameter, 16 cm length) protected from light by aluminum foil, equipped with a magnetic stirrer, complex **1** (0.04 mmol, 29.1 mg) was dissolved in dry acetonitrile (10 mL) and sonicated for 1 minute. Then ethyl acrylate (1 mmol, 1 eq) and *N*,*N*-dimethyl aniline (3 mmol, 3 eq) were added, and the tube was capped with a rubber septum. The reaction medium was deaerated by gentle argon bubbling during 10 minutes. The reaction was initiated by irradiating the tube at 365 nm with the Luzchem® illuminator setup (tube placed at ~ 10 cm from the LED). After stirring under irradiation at room temperature for 17 h, the solvent was removed under reduced pressure, and the crude purified by column chromatography over silica gel.

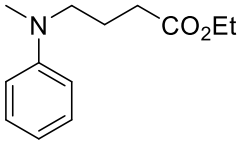
D-4 C(sp^3)−H/CuAAC reactions

In a test tube (pyrex, 1 cm diameter, 10 cm length) protected from light by aluminum foil, equipped with a magnetic stirrer, complex **1** (0.008 mmol, 5.81 mg) was dissolved in dry acetonitrile (2 mL) and sonicated for 1 minute. Then the propargyl acrylate (0.2 mmol, 1 eq), the benzyl azide (0.2 mmol, 1 eq) and the aniline (0.6 mmol, 3 eq) were added, and the tube was capped with a rubber septum. The reaction medium was deaerated by gentle argon bubbling during 10 minutes. The reaction was initiated by irradiating the tube at 365 nm with the

Luzchem® illuminator setup. After stirring under irradiation at room temperature for 3 h, the solvent was removed under pressure, and the crude product was purified by column chromatography over silica gel.

E- Characterization data of compounds 4, 6-37

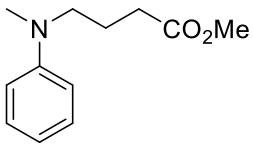
Ethyl 4-[methyl(phenyl)amino]butanoate, **4** :[1]



Synthesis was carried out according to the general procedure with N,N-dimethylaniline (0.6 mmol, 76.1 µL) and ethyl acrylate (0.2 mmol, 21.7 µL). The mixture was stirred under irradiation for 3 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (95/5 to 90/10; v/v) as the eluent to afford compound **4** as a colorless oil (40.3 mg, 91 % yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 7.26-7.21 (m, 2H), 6.75-6.68 (m, 3H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.37 (t, *J* = 7.2 Hz, 2H), 2.93 (s, 3H), 2.35 (t, *J* = 7.3 Hz, 2H), 1.97-1.87 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 173.4, 149.3, 129.3, 116.4, 112.4, 60.5, 52.1, 38.5, 31.7, 22.3, 14.3 ppm. **HRMS** (ESI): Calcd. for $C_{13}H_{20}O_2N$ $[M+H]^+$: 222.1489; Found : 222.1484.

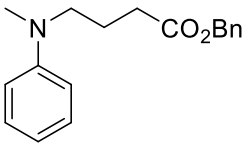
Methyl 4-[methyl(phenyl)amino]butanoate, **6** :[2]



Synthesis was carried out according to the general procedure with N,N-dimethylaniline (0.6 mmol, 76.1 µL) and methyl acrylate (0.2 mmol, 18.0 µL). The mixture was stirred under irradiation for 4 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (95/5 to 90/10, v/v) as the eluent to afford compound **6** as a colorless oil (31.5 mg, 76% yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 7.27-7.20 (m, 2H), 6.77-6.67 (m, 3H), 3.68 (s, 3H), 3.37 (t, *J* = 7.3 Hz, 2H), 2.93 (s, 3H), 2.37 (t, *J* = 7.3 Hz, 2H), 1.97-1.87 (m, 2H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 173.9, 149.3, 129.3, 116.4, 112.4, 52.1, 51.7, 38.5, 31.4, 22.3 ppm. **HRMS** (ESI): Calcd. for $C_{12}H_{18}O_2N$ $[M+H]^+$: 208.1332; Found : 208.1330.

Benzyl 4-[methyl(phenyl)amino]butanoate, **7**:

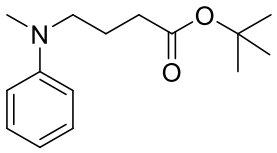


Synthesis was carried out according to the general procedure with N,N-dimethylaniline (0.6 mmol, 76.1 µL) and benzyl acrylate (0.2 mmol, 30.6 µL). The mixture was stirred under irradiation for 4 hours. The crude product was purified by column chromatography over silica

gel with petroleum ether/ethyl acetate (95/5, v/v) as the eluent to afford compound **7** as a colorless oil (41.4 mg, 73% yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 7.42-7.33 (m, 5H), 7.26-7.21 (m, 2H), 6.74-6.69 (m, 3H), 5.14 (s, 2H), 3.37 (t, *J* = 7.3 Hz, 2H), 2.92 (s, 3H), 2.43 (t, *J* = 7.3 Hz, 2H), 2.01-1.91 (m, 2H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 173.2, 149.3, 136.0, 129.3, 128.7, 128.4, 128.4, 116.4, 112.4, 66.4, 52.0, 38.4, 31.7, 22.3 ppm. **HRMS** (ESI): Calcd. for $C_{18}H_{22}O_2N$ $[M+H]^+$: 284.1645; Found : 284.1636.

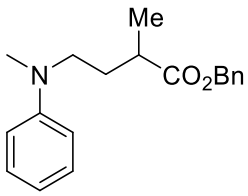
tert-Butyl 4-[methyl(phenyl)amino]butanoate, **8** :[3]



Synthesis was carried out according to the general procedure with N,N-dimethylaniline (0.6 mmol, 76.1 µL) and *tert*-butyl acrylate (0.2 mmol, 29.3 µL). The mixture was stirred under irradiation for 3 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (95/5, v/v) as the eluent to afford compound **8** as a colorless oil (36 mg, 72 % yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 7.26-7.21 (m, 2H), 6.75-6.68 (m, 3H), 3.36 (t, *J* = 7.4 Hz, 2H), 2.94 (s, 3H), 2.28 (t, *J* = 7.2 Hz, 2H), 1.93-1.83 (m, 2H), 1.46 (s, 9H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 172.8, 149.4, 129.3, 116.3, 112.3, 80.5, 52.1, 38.4, 33.0, 28.2, 22.4 ppm. **HRMS** (ESI): Calcd. for $C_{15}H_{24}O_2N$ $[M+H]^+$: 250.1802; Found : 250.1799.

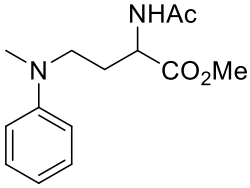
Benzyl 2-methyl-4-[methyl(phenyl)amino]butanoate, **9** :



Synthesis was carried out according to the general procedure with N,N-dimethylaniline (0.6 mmol, 76.1 µL) and benzyl methacrylate (0.2 mmol, 33.9 µL). The mixture was stirred under irradiation for 9 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (95/5, v/v) as the eluent to afford compound **9** as a colorless oil (27.1 mg, 46 % yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 7.40-7.30 (m, 5H), 7.24-7.18 (m, 2H), 6.73-6.63 (m, 3H), 5.12 (s, 2H), 3.38-3.25 (m, 2H), 2.87 (s, 3H), 2.61-2.49 (m, 1H), 2.04-1.91 (m, 1H), 1.76-1.67 (m, 1H), 1.23 (d, *J* = 6.9 Hz, 3H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 176.1, 149.2, 136.2, 129.3, 128.7, 128.4, 128.4, 116.5, 112.5, 66.4, 50.8, 38.4, 37.6, 30.6, 17.7 ppm. **HRMS** (ESI): Calcd. for $C_{19}H_{24}O_2N$ $[M+H]^+$: 298.1802; Found : 298.1798.

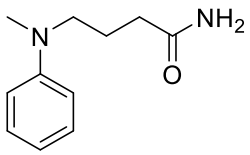
Methyl 2-acetamido-4-[methyl(phenyl)amino]butanoate, **10**:



Synthesis was carried out according to the general procedure with N,N-dimethylaniline (0.6 mmol, 76.1 µL) and methyl-2-acetamidoacrylate (0.2 mmol, 28.6 mg). The mixture was stirred under irradiation for 24 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (30/70, v/v) as the eluent to afford compound **10** as a colorless oil (33.8 mg, 64 % yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 7.26-7.22 (m, 2H), 6.77-6.71 (m, 3H), 6.28 (d, *J* = 6.6 Hz, 1H), 4.67-4.61 (m, 1H), 3.69 (s, 3H), 3.45-3.37 (m, 2H), 2.89 (s, 3H), 2.24-2.12 (m, 1H), 2.03 (s, 3H), 2.04-1.91 (m, 1H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 172.8, 170.1, 149.0, 129.4, 117.4, 113.1, 52.5, 50.9, 49.6, 39.0, 29.4, 23.3 ppm. **HRMS** (ESI): Calcd. for $C_{14}H_{21}O_3N_2$ $[M+H]^+$: 265.1547; Found : 265.1542.

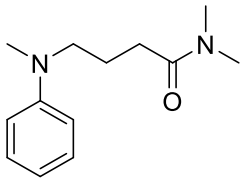
4-[Methyl(phenyl)amino]butanamide, **11**:



Synthesis was carried out according to the general procedure with N,N-dimethylaniline (0.6 mmol, 76.1 µL) and acrylamide (0.2 mmol, 14.2 mg). The mixture was stirred under irradiation for 4 hours. The crude product was purified by column chromatography over silica gel with ethyl acetate as the eluent to afford compound **11** as a colorless oil (29.9 mg, 78 % yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 7.25-7.19 (m, 2H), 6.76-6.67 (m, 3H), 5.74-5.52 (m, 2H), 3.37 (t, *J* = 7.2 Hz, 2H), 2.92 (s, 3H), 2.25 (t, *J* = 7.2 Hz, 2H), 1.97-1.87 (m, 2H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 175.1, 149.4, 129.3, 116.6, 112.5, 52.0, 38.4, 33.0, 22.8 ppm. **HRMS** (ESI): Calcd. for $C_{11}H_{17}ON_2$ $[M+H]^+$: 193.1335; Found : 193.1333.

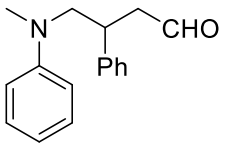
N,N-Dimethyl-4-[methyl(phenyl)amino]butanamide, **12**:



Synthesis was carried out according to the general procedure with N,N-dimethylaniline (0.6 mmol, 76.1 µL) and N,N-dimethylacrylamide (0.2 mmol, 20.6 µL). The mixture was stirred under irradiation for 4 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (30/70, v/v) as the eluent to afford compound **12** as a colorless oil (35.9 mg, 81 % yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 7.25-7.19 (m, 2H), 6.82-6.61 (m, 3H), 3.39 (t, *J* = 7.2 Hz, 2H), 2.94 (s, 3H), 2.93 (s, 6H), 2.33 (t, *J* = 7.2 Hz, 2H), 1.98-1.88 (m, 2H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 172.5, 149.5, 129.2, 116.2, 112.4, 52.1, 38.2, 37.2, 35.9, 30.3, 22.3 ppm. **HRMS** (ESI): Calcd. for $C_{13}H_{21}ON_2$ $[M+H]^+$: 221.1648 ; Found : 221.1644.

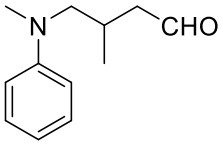
4-[Methyl(phenyl)amino]-3-phenylbutanal, **13**:



Synthesis was carried out according to the general procedure with N,N-dimethylaniline (0.6 mmol, 76.1 µL) and *trans*-cinnamaldehyde (0.2 mmol, 25.2 µL). The mixture was stirred under irradiation for 17 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (90/10, v/v) as the eluent to afford compound **13** as a colorless oil (30.1 mg, 59% yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 9.59 (t, *J* = 2.2 Hz, 1H), 7.37-7.32 (m, 2H), 7.31-7.23 (m, 5H), 6.80-6.74 (m, 3H), 3.80-3.72 (m, 1H), 3-58-3.40 (m, 2H), 2.88-2.79 (m, 2H), 2.76 (s, 3H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 200.7, 149.1, 141.7, 129.4, 129.0, 127.7, 127.3, 117.1, 112.7, 59.9, 47.6, 40.0, 39.2 ppm. **HRMS** (ESI): Calcd. for $C_{17}H_{20}ON$ $[M+H]^+$: 254.1539; Found : 254.1538.

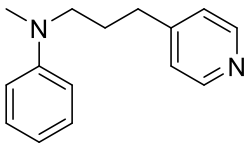
3-Methyl-4-[methyl(phenyl)amino]butanal, **14**:



Synthesis was carried out according to the general procedure with N,N-dimethylaniline (0.6 mmol, 76.1 µL) and *trans*-crotonaldehyde (0.2 mmol, 16.6 µL). The mixture was stirred under irradiation for 4 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (95/5 to 90/10, v/v) as the eluent to afford compound **14** as a colorless oil (28.2 mg, 74 % yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 9.61 (t, *J* = 2.1 Hz, 1H), 7.28-7.22 (m, 2H), 6.80-6.67 (m, 3H), 3.25-3.07 (m, 2H), 2.90 (s, 3H), 2.67-2.56 (m, 1H), 2.50-2.25 (m, 2H), 1.01 (d, *J* = 6.9 Hz, 3H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 201.7, 149.7, 129.4, 117.0, 112.7, 59.7, 49.3, 39.9, 28.3, 18.1 ppm. **HRMS** (ESI): Calcd. for $C_{12}H_{18}ON$ $[M+H]^+$: 192.1383; Found : 192.1385.

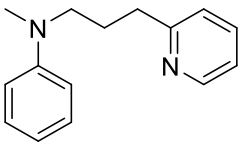
N-Methyl-N-[3-(pyridin-4-yl)propyl]aniline, **15**:



Synthesis was carried out according to the general procedure with N,N-dimethylaniline (0.6 mmol, 76.1 µL) and 4-vinylpyridine (0.2 mmol, 21.6 µL). The mixture was stirred under irradiation for 3 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (50/50 to 40/60, v/v) as the eluent to afford compound **15** as a colorless oil (29.7 mg, 66% yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 8.50 (d, *J* = 5.2 Hz, 2H), 7.26-7.19 (m, 2H), 7.13 (d, *J* = 5.5 Hz, 2H), 6.73-6.62 (m, 3H), 3.35 (t, *J* = 7.2 Hz, 2H), 2.92 (s, 3H), 2.66 (t, *J* = 7.2 Hz, 2H), 1.98-1.88 (m, 2H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 151.2, 149.6, 149.3, 129.3, 124.0, 116.6, 112.5, 52.2, 38.5, 32.8, 27.3 ppm. **HRMS** (ESI): Calcd. for $C_{15}H_{19}N_2$ $[M+H]^+$: 227.1543; Found : 227.1538.

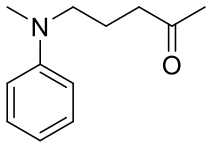
N-Methyl-N-[3-(pyridin-2-yl)propyl]aniline, **16**:



Synthesis was carried out according to the general procedure with N,N-dimethylaniline (0.6 mmol, 76.1 µL) and 2-vinylpyridine (0.2 mmol, 21.0 mg) - (purified by column chromatography with petroleum ether/ethyl acetate (80/20, v/v) as the eluent prior to use). The mixture was stirred under irradiation for 14 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (60/40 to 50/50, v/v) as the eluent to afford compound **16** as a colorless oil (29.6 mg, 65% yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 8.55-8.52 (m, 1H), 7.59 (td, *J* = 7.8 Hz, 1.8 Hz, 1H), 7.25-7.18 (m, 2H), 7.16-7.09 (m, 2H), 6.72-6.65 (m, 3H), 3.40 (t, *J* = 7.7 Hz, 2H), 2.93 (s, 3H), 2.84 (t, *J* = 7.8 Hz, 2H), 2.09-1.99 (m, 2H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 161.6, 149.3, 136.6, 129.3, 122.9, 121.3, 116.2, 116.2, 112.4, 52.4, 38.5, 35.8, 26.9 ppm. **HRMS** (ESI): Calcd. for $C_{15}H_{19}N_2$ $[M+H]^+$: 227.1543; Found : 227.1538.

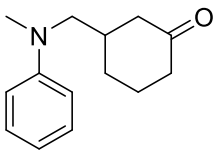
5-[Methyl(phenyl)amino]pentan-2-one, **17**:[4]



Synthesis was carried out according to the general procedure with N,N-dimethylaniline (0.6 mmol, 76.1 µL) and methyl vinyl ketone (0.2 mmol, 16.5 µL) - (methyl vinyl ketone was dried over K_2CO_3, then filtered and distilled under reduced pressure prior to use). The mixture was stirred under irradiation for 4 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (90/10, v/v) as the eluent to afford compound **17** as a colorless oil (22.2 mg, 58% yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 7.28-7.19 (m, 2H), 6.77-6.66 (m, 3H), 3.32 (t, *J* = 7.2 Hz, 2H), 2.91 (s, 3H), 2.47 (t, *J* = 7.2 Hz, 2H), 2.12 (s, 3H), 1.92-1.82 (m, 2H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 208.5, 149.4, 129.3, 116.4, 112.4, 51.9, 40.8, 38.3, 30.1, 21.1 ppm. **HRMS** (ESI): Calcd. for $C_{12}H_{18}ON$ $[M+H]^+$: 192.1383; Found : 192.1379.

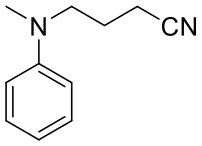
3-{[Methyl(phenyl)amino]methyl}cyclohexan-1-one, **18**:



Synthesis was carried out according to the general procedure with N,N-dimethylaniline (0.6 mmol, 76.1 µL) and cyclohexen-2-one (0.2 mmol, 19.4 µL). The mixture was stirred under irradiation for 3 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (90/10 to 85/15, v/v) as the eluent to afford compound **18** as a colorless oil (32.2 mg, 74 % yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 7.26-7.20 (m, 2H), 6.73-6.67 (m, 3H), 3.33-3.20 (m, 2H), 2.97 (s, 3H), 2.48-2.19 (m, 4H), 2.14-2.03 (m, 2H), 2.00-1.95 (m, 1H), 1.70-1.57 (m, 1H), 1.47-1.34 (m, 1H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 211.0, 149.2, 129.4, 116.5, 112.2, 58.8, 46.1, 41.6, 39.9, 38.4, 29.6, 25.3 ppm. **HRMS** (ESI): Calcd. for $C_{12}H_{19}ONNa$ $[M+Na]^+$: 240.1359 ; Found : 240.1356.

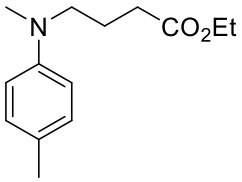
4-[Methyl(phenyl)amino]butanenitrile, **19**:[5]



Synthesis was carried out according to the general procedure with N,N-dimethylaniline (0.6 mmol, 76.1 µL) and acrylonitrile (0.2 mmol, 13.1 µL). The mixture was stirred under irradiation for 3 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (90/10 to 85/15, v/v) as the eluent to afford compound **19** as a colorless oil (33.5 mg, 96 % yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 7.29-7.24 (m, 2H), 6.78-6.74 (m, 3H), 3.47 (t, *J* = 7.0 Hz, 2H), 2.96 (s, 3H), 2.39 (t, *J* = 6.9 Hz, 2H), 2.01-1.91 (m, 2H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 149.0, 129.4, 119.5, 117.2, 112.8, 51.4, 38.9, 23.2, 14.8 ppm. **HRMS** (ESI): Calcd. for $C_{11}H_{15}N_2$ $[M+H]^+$: 175.1230 ; Found : 175.1229.

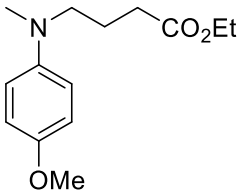
Ethyl 4-[methyl(p-tolyl)amino]butanoate, **20**:



Synthesis was carried out according to the general procedure with 4,N,N-trimethylaniline (0.6 mmol, 86.6 µL) and ethyl acrylate (0.2 mmol, 21.7 µL). The mixture was stirred under irradiation for 24 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (95/5 to 90/10, v/v) as the eluent to afford compound **20** as a colorless oil (37.7 mg, 80% yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.0 Hz, 2H), 6.65 (d, *J* = 8.0 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.32 (t, *J* = 7.4 Hz, 2H), 2.90 (s, 3H), 2.34 (t, *J* = 7.2 Hz, 2H), 2.25 (s, 3H), 1.95-1.85 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 173.4, 147.4, 129.8, 125.8, 112.9, 60.5, 52.5, 38.6, 31.8, 22.2, 20.3, 14.4 ppm. **HRMS** (ESI): Calcd. for $C_{14}H_{22}O_2N$ $[M+H]^+$: 236.1645; Found : 236.1644.

Ethyl 4-[(4-methoxyphenyl)(methyl)amino]butanoate, **21**:

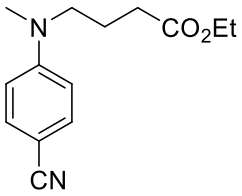


Synthesis was carried out according to the general procedure with 4-(dimethylamino)anisole (0.6 mmol, 90.3 mg) and ethyl acrylate (0.2 mmol, 21.7 µL). The mixture was stirred under irradiation for 24 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (90/10, v/v) as the eluent to afford compound **21** as a colorless oil (29.9 mg, 59% yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 6.86-6.81 (m, 2H), 6.76-6.70 (m, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.76 (s, 3H), 3.26 (t, *J* = 7.5 Hz, 2H), 2.85 (s, 3H), 2.34 (t, *J* = 7.5 Hz, 2H), 1.93-1.83 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 173.5, 152.0, 144.3, 114.9, 60.5,

55.9, 53.4, 39.2, 31.8, 22.2, 14.4 ppm. **HRMS** (ESI): Calcd. for $C_{14}H_{22}O_3N$ $[M+H]^+$: 252.1594; Found : 252.1587.

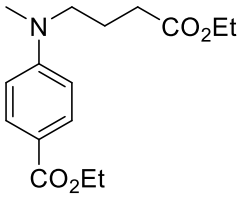
Ethyl 4-[(4-cyanophenyl)(methyl)amino]butanoate, **22**:



Synthesis was carried out according to the general procedure with 4-(dimethylamino)benzonitrile (0.6 mmol, 87.7 mg) and ethyl acrylate (0.2 mmol, 21.7 µL). The mixture was stirred under irradiation for 24 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (80/20, v/v) as the eluent to afford compound **22** as a colorless oil (45.5 mg, 92 % yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 7.47-7.42 (m, 2H), 6.69-6.64 (m, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.41 (t, *J* = 7.5 Hz, 2H), 2.99 (s, 3H), 2.33 (t, *J* = 7.3 Hz, 2H), 1.95-1.85 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 173.0, 151.5, 133.6, 120.7, 111.6, 97.7, 60.7, 51.5, 38.4, 31.3, 22.0, 14.3 ppm. **HRMS** (ESI): Calcd. for $C_{14}H_{18}O_2N_2Na$ $[M+Na]^+$: 269.1261; Found : 269.1258.

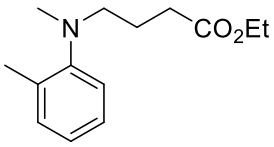
Ethyl 4-[(4-ethoxy-4-oxobutyl)(methyl)amino]benzoate, **23**:



Synthesis was carried out according to the general procedure with ethyl 4-dimethylaminobenzoate (0.6 mmol, 115.9 mg) and ethyl acrylate (0.2 mmol, 21.7 µL). The mixture was stirred under irradiation for 17 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (90/10 to 80/20, v/v) as the eluent to afford compound **23** as a colorless oil (42.8 mg, 73% yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.9 Hz, 2H), 6.65 (d, *J* = 8.9 Hz, 2H), 4.30 (q, *J* = 7.2 Hz, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.42 (t, *J* = 7.3 Hz, 2H), 2.99 (s, 3H), 2.33 (t, *J* = 7.3 Hz, 2H), 1.96-1.87 (m, 2H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 173.1, 167.0, 152.2, 131.4, 117.5, 110.7, 60.6, 60.2, 51.6, 38.5, 31.4, 22.2, 14.6, 14.3 ppm. **HRMS** (ESI): Calcd. for $C_{16}H_{24}O_4N$ $[M+H]^+$: 294.1699; Found : 294.1696.

Ethyl 4-[methyl(o-tolyl)amino]butanoate, **24**:

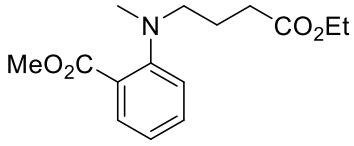


Synthesis was carried out according to the general procedure with N,N,2-trimethylaniline (0.6 mmol, 87.3 mg) and ethyl acrylate (0.2 mmol, 21.7 µL). The mixture was stirred under irradiation for 3 hours. The crude product was purified by column chromatography over silica

gel with petroleum ether/ethyl acetate (95/5, v/v) as the eluent to afford compound **24** as a colorless oil (35.3 mg, 75% yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 7.18-7.13 (m, 2H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.99-6.94 (m, 1H), 4.12 (q, *J* = 7.4 Hz, 2H), 2.92 (t, *J* = 7.4 Hz, 2H), 2.66 (s, 3H), 2.36 (t, *J* = 7.4 Hz, 2H), 2.31 (s, 3H), 1.91-1.81 (m, 2H), 1.25 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 173.8, 152.3, 133.5, 131.2, 126.5, 123.2, 120.2, 60.4, 55.3, 42.0, 31.9, 23.0, 18.3, 14.4 ppm. **HRMS** (ESI): Calcd. for $C_{14}H_{21}NO_2Na$ $[M+Na]^+$: 258.1465; Found : 258.1457.

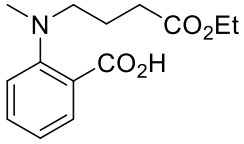
Methyl 2-[(4-ethoxy-4-oxobutyl)(methyl)amino]benzoate, **25**:



Synthesis was carried out according to the general procedure with methyl 2-(dimethylamino)benzoate (0.6 mmol, 107.5 mg) and ethyl acrylate (0.2 mmol, 21.7 µL). The mixture was stirred under irradiation for 17 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (90/10 to 80/20, v/v) as the eluent to afford compound **25** as a colorless oil (15.0 mg, 27% yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 7.5 Hz,1.7 Hz, 1H), 7.38-7.30 (m, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.88 (t, *J* = 7.6 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.88 (s, 3H), 3.14 (t, *J* = 7.4 Hz, 2H), 2.81 (s, 3H), 2.32 (t, *J* = 7.4 Hz, 2H), 1.94-1.85 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 173.6, 169.1, 151.9, 132.2, 131.4, 123.0, 119.7, 118.8, 60.5, 54.9, 52.2, 41.3, 31.6, 22.7, 14.3 ppm. **HRMS** (ESI): Calcd. for $C_{15}H_{22}O_4N$ $[M+H]^+$: 280.1543; Found : 280.1538.

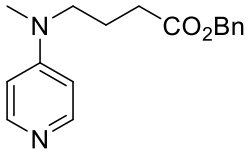
2-[(4-Ethoxy-4-oxobutyl)(methyl)amino]benzoic acid, **26**:



Synthesis was carried out according to the general procedure with 2-dimethylaminobenzoic acid (0.6 mmol, 99.1 mg) and ethyl acrylate (0.2 mmol, 21.7 µL). The mixture was stirred under irradiation for 48 hours. The crude product was purified by column chromatography over silica gel with ethyl acetate as the eluent to afford compound **26** as a yellowish oil (20.6 mg, 39% yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 7.8 Hz, 1.8 Hz, 1H), 7.64-7.59 (m, 1H), 7.44-7.39 (m, 2H), 4.10 (q, *J* = 7.3 Hz, 2H), 3.13 (t, *J* = 7.5 Hz, 2H), 2.83 (s, 3H), 2.31 (t, *J* = 7.4 Hz, 2H), 1.84-1.74 (m, 2H), 1.22 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 172.5, 167.5, 150.0, 134.2, 132.3, 128.0, 125.9, 122.2, 60.8, 57.2, 44.7, 31.5, 22.3, 14.3 ppm. **HRMS** (ESI): Calcd. for $C_{14}H_{20}NO_4$ $[M+H]^+$: 266.1387; Found : 266.1384.

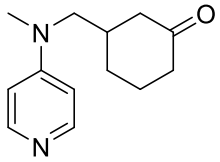
Benzyl 4-[methyl(pyridin-4-yl)amino]butanoate, **27**:



Synthesis was carried out according to the general procedure with 4-dimethylaminopyridine (0.6 mmol, 73.3 mg) and benzyl acrylate (0.2 mmol, 30.6 µL). The mixture was stirred under irradiation for 9 hours. The crude product was purified by column chromatography over silica gel with ethyl acetate/triethylamine (98/2, v/v) as the eluent to afford compound **27** as a colourless oil (31.7 mg, 56% yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 6.6 Hz, 2H), 7.40-7.30 (m, 5H), 6.47 (d, *J* = 6.6 Hz, 2H), 5.12 (s, 2H), 3.38 (t, *J* = 7.5 Hz, 2H), 2.94 (s, 3H), 2.40 (t, *J* = 7.5 Hz, 2H), 1.97-1.87 (m, 2H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 172.8, 153.6, 149.6, 135.8, 128.8, 128.5, 128.5, 106.6, 66.6, 50.6, 37.5, 31.3, 22.0 ppm. **HRMS** (ESI): Calcd. for $C_{17}H_{21}O_2N_2$ $[M+H]^+$: 285.1598; Found : 285.1590.

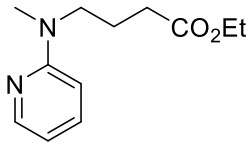
3-[(Methyl(pyridin-4-yl)amino)methyl]cyclohexan-1-one, **28**:



Synthesis was carried out according to the general procedure with 4-dimethylaminopyridine (0.6 mmol, 73.3 mg) and cyclohexen-2-one (0.2 mmol, 19.4 µL). The mixture was stirred under irradiation for 3 hours. The crude product was purified by column chromatography over silica gel with ethyl acetate/triethylamine (95/5, v/v) as the eluent to afford compound **28** as a yellowish oil (25.9 mg, 59% yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 8.19 (d, *J* = 6.5 Hz, 2H), 6.47 (d, *J* = 6.5 Hz, 2H), 3.38-3.23 (m, 2H), 3.00 (s, 3H), 2.43-2.35 (m, 2H), 2.33-2.17 (m, 2H), 2.12-2.03 (m, 2H), 1.95-1.88 (m, 1H), 1.72-1.56 (m, 1H), 1.48-1.34 (m, 1H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 220.1, 153.7, 149.3, 106.7, 57.2, 45.8, 41.4, 39.0, 38.1, 29.4, 25.1 ppm. **HRMS** (ESI): Calcd. for $C_{13}H_{19}ON_2$ $[M+H]^+$: 219.1492; Found : 219.1487.

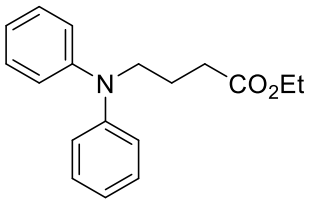
Ethyl 4-[methyl(pyridin-2-yl)amino]butanoate, **29**:



Synthesis was carried out according to the general procedure with 2-dimethylaminopyridine (0.6 mmol, 72.6 µL) and ethyl acrylate (0.2 mmol, 21.7 µL). The mixture was stirred under irradiation for 4 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (90/10 to 80/20, v/v) as the eluent to afford compound **29** as a colorless oil (33.8 mg, 76% yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 8.14-8.12 (m, 1H), 7.45-7.39 (m, 1H), 6.54-6.48 (m, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.57 (t, *J* = 7.4 Hz, 2H), 3.03 (s, 3H), 2.34 (t, *J* = 7.4 Hz, 2H), 1.97-1.88 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 173.5, 158.6, 147.9, 137.4, 111.5, 105.8, 60.9, 49.3, 36.5, 31.7, 22.7, 14.4 ppm. **HRMS** (ESI): Calcd. for $C_{12}H_{19}O_2N_2$ $[M+H]^+$: 223.1441; Found : 223.1438.

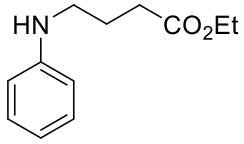
Ethyl 4-(diphenylamino)butanoate, **30**:



Synthesis was performed according to the general procedure with N-methyl-N-phenylaniline (0.6 mmol, 104.7 µL) and ethyl acrylate (0.2 mmol, 21.7 µL). The mixture was stirred under irradiation for 17 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (95/5 to 90/10, v/v) as the eluent to afford compound **30** as a colorless oil (42.1 mg, 74% yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 7.31-7.25 (m, 4H), 7.04-6.98 (m, 4H), 6.98-6.94 (m, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.80-3.74 (m, 2H), 2.39 (t, *J* = 7.5 Hz, 2H), 2.06-1.96 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 173.3, 148.0, 129.4, 121.5, 121.1, 61.0, 51.6, 31.7, 22.8, 14.4 ppm. **HRMS** (ESI): Calcd. for $C_{18}H_{22}O_2N$ $[M+H]^+$: 284.1645; Found : 284.1641.

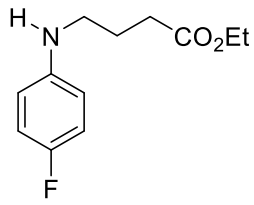
Ethyl 4-(phenylamino)butanoate, **31**:[6]



Synthesis was performed according to the general procedure with N-methylaniline (0.6 mmol, 65.0 µL) and ethyl acrylate (0.2 mmol, 21.7 µL). The mixture was stirred under irradiation for 18 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (90/10 to 80/20, v/v) as the eluent to afford compound **31** as a colorless oil (33 mg, 79% yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 7.21-7.14 (m, 2H), 6.71 (tt, *J* = 7.3 Hz, 1.1 Hz, 1H), 6.64-6.60 (m, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.19 (t, *J* = 6.8 Hz, 2H), 2.43 (t, *J* = 6.9 Hz, 2H), 2.00-1.91 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 173.5, 148.1, 129.4, 117.6, 113.0, 60.6, 43.5, 32.1, 24.8, 14.4 ppm. **HRMS** (ESI): Calcd. for $C_{12}H_{18}O_2N$ $[M+H]^+$: 208.1332; Found : 208.1332.

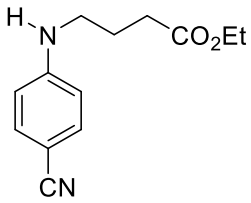
Ethyl 4-[(4-fluorophenyl)amino]butanoate, **32**:



Synthesis was performed according to the general procedure with 4-fluoro-N-methylaniline (0.6 mmol, 72.2 µL) (purified by column chromatography with petroleum ether/ethyl acetate (90/10, v/v) as the eluent prior to use) and ethyl acrylate (0.2 mmol, 21.7 µL). The mixture was stirred under irradiation for 24 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (90/10 to 85/15, v/v) as the eluent to afford compound **32** as a colorless oil (20.4 mg, 45% yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 6.92-6.84 (m, 2H), 6.58-6.51 (m, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.13 (t, *J* = 7.0 Hz, 2H), 2.42 (t, *J* = 7.0 Hz, 2H), 1.98-1.89 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H) ppm. **^{19}F NMR** : (282 MHz, $CDCl_3$) : -128.1 ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 173.6, 156.0 (d, $^{1}J_{C\text{-}F}$ = 230 Hz), 144.5, 115.8 (d, $^{2}J_{C\text{-}F}$ = 22 Hz), 113.8 (d, $^{3}J_{C\text{-}F}$ = 8 Hz), 60.7, 44.2, 32.0, 24.7, 14.4 ppm. **HRMS** (ESI): Calcd. for $C_{12}H_{17}O_2NF$ $[M+H]^+$: 226.1238; Found : 226.1230.

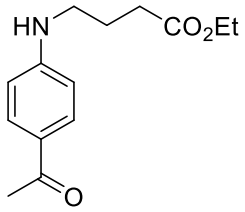
Ethyl 4-[(4-cyanophenyl)amino]butanoate, **33**:



Synthesis was performed according to the general procedure with 4-(methylamino)benzonitrile (0.6 mmol, 79.3 mg) and ethyl acrylate (0.2 mmol, 21.7 µL). The mixture was stirred under irradiation for 20 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (75/25 to 70/30) as the eluent to afford compound **33** as a white solid (33 mg, 71% yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 7.42-7.37 (m, 2H), 6.58-6.53 (m, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.21 (t, *J* = 7.1 Hz, 2H), 2.42 (t, *J* = 7.1 Hz, 2H), 1.99-1.90 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 173.4, 151.3, 133.8, 120.6, 112.6, 98.7, 60.8, 42.8, 31.8, 24.2, 14.3 ppm. **HRMS** (ESI): Calcd. for $C_{13}H_{17}O_2N_2$ $[M+H]^+$: 233.1285; Found : 233.1280.

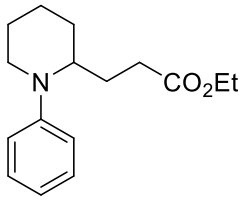
Ethyl 4-[(4-acetylphenyl)amino]butanoate, **34**:



Synthesis was performed according to the general procedure with (4-(methylamino)phenyl)ethanone (0.6 mmol, 90.0 mg) and ethyl acrylate (0.2 mmol, 21.7 µL). The mixture was stirred under irradiation for 16 hours. The crude product was purified by conducting two successive column chromatographies over silica gel with petroleum ether/ethyl acetate (70/30, v/v) as the eluent to afford compound **34** as a yellowish oil (18.2 mg, 36% yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 7.85-7.78 (m, 2H), 6.59-6.53 (m, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.25 (t, *J* = 7.2 Hz, 2H), 2.49 (s, 3H), 2.42 (t, *J* = 7.2 Hz, 2H), 2.01-1.94 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 196.5, 173.5, 152.0, 131.0, 127.0, 111.6, 60.8, 43.0, 31.9, 26.1, 24.4, 14.4 ppm. **HRMS** (ESI): Calcd. for $C_{14}H_{20}O_3N$ $[M+H]^+$: 250.1438; Found : 250.1436.

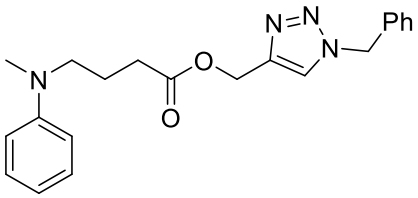
Ethyl 3-(1-phenylpiperidin-2-yl)propanoate, **35**:



Synthesis was performed according to the general procedure with N-phenylpiperidine (0.6 mmol, 96.7 mg) (purified by column chromatography with petroleum ether/ethyl acetate (95/5) as the eluent prior to use) and ethyl acrylate (0.2 mmol, 21.7 µL). The mixture was stirred under irradiation for 24 hours. The crude product was purified by conducting two successive column chromatographies over silica gel with petroleum ether/ethyl acetate (90/10, v/v) as the eluent to afford compound **35** as a colorless oil (28.1 mg, 54% yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 7.25-7.18 (m, 2H), 6.88 (d, *J* = 7.8 Hz, 2H), 6.76 (t, *J* = 7.5 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.90-3.80 (m, 1H), 3.40-3.31 (m, 1H), 3.09-2.97 (m, 1H), 2.29-2.23 (m, 2H), 2.03-1.91 (m, 1H), 1.87-1.75 (m, 2H), 1.71-1.56 (m, 5H), 1.21 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 173.7, 151.2, 129.3, 118.4, 116.6, 60.5, 55.3, 43.6, 31.8, 28.0, 25.2, 23.6, 19.6, 14.3 ppm. **HRMS** (ESI): Calcd. for $C_{16}H_{24}O_2N$ $[M+H]^+$: 262.1802; Found : 262.1799.

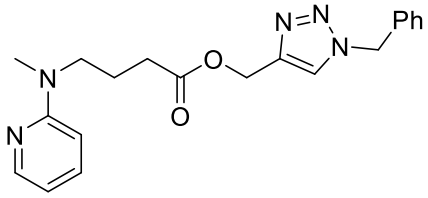
(1-Benzyl-1H-1,2,3-triazol-4-yl)methyl 4-[methyl(phenyl)amino]butanoate, **36**:



Synthesis was performed according to the general procedure with N,N-dimethylaniline (0.6 mmol, 76.1 µL), propargyl acrylate (0.2 mmol, 22.1 µL) and benzyl azide (0.2 mmol, 25.0 µL). The mixture was stirred under irradiation for 4 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (70/30 to 60/40, v/v) as the eluent to afford compound **36** as a colorless oil (53.1 mg, 73% yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.39-7.33 (m, 3H), 7.28-7.16 (m, 4H), 6.72-6.63 (m, 3H), 5.50 (s, 2H), 5.17 (s, 2H), 3.30 (t, *J* = 7.4 Hz, 2H), 2.87 (s, 3H), 2.35 (t, *J* = 7.4 Hz, 2H), 1.94-1.84 (, 2H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 173.2, 149.3, 143.3, 134.5, 129.3, 129.3, 129.0, 128.3, 123.7, 116.4, 112.4, 57.7, 54.3, 52.0, 38.5, 31.6, 22.2 ppm. **HRMS** (ESI): Calcd. for $C_{22}H_{24}O_2N_4$ $[M+H]^+$: 365.1972; Found : 365.1960.

(1-Benzyl-1H-1,2,3-triazol-4-yl)methyl 4-[methyl(pyridin-2-yl)amino]butanoate, **37**:



Synthesis was performed according to the general procedure with 2-dimethylaminopyridine (0.6 mmol, 72.6 µL), propargyl acrylate (0.2 mmol, 22.1 µL) and benzyl azide (0.2 mmol, 25.0 µL). The mixture was stirred under irradiation for 4 hours. The crude product was purified by column chromatography over silica gel with petroleum ether/ethyl acetate (50/50, v/v) as the eluent to afford compound **37** as a colorless oil (48.3 mg, 66% yield).

^{1}H NMR : (300 MHz, $CDCl_3$) δ 8.10-8.07 (m, 1H), 7.49 (s, 1H), 7.43-7.32 (m, 4H), 7.28-7.23 (m, 2H), 6.53-6.46 (m, 2H), 5.50 (s, 2H), 5.17 (s, 2H), 3.53 (t, *J* = 7.4 Hz, 2H), 2.98 (s, 3H), 2.35 (t, *J* = 7.4 Hz, 2H), 1.95-1.85 (m, 2H) ppm. **^{13}C NMR** : (75 MHz, $CDCl_3$): δ 173.3, 158.4, 147.7, 143.4, 137.5, 134.5, 129.3, 129.0, 128.3, 123.7, 111.6, 105.8, 57.7, 54.4, 49.2, 36.5, 31.5, 22.7 ppm. **HRMS** (ESI): Calcd. for $C_{20}H_{24}O_2N_5$ $[M+H]^+$: 366.1925; Found : 366.1913.

F – References

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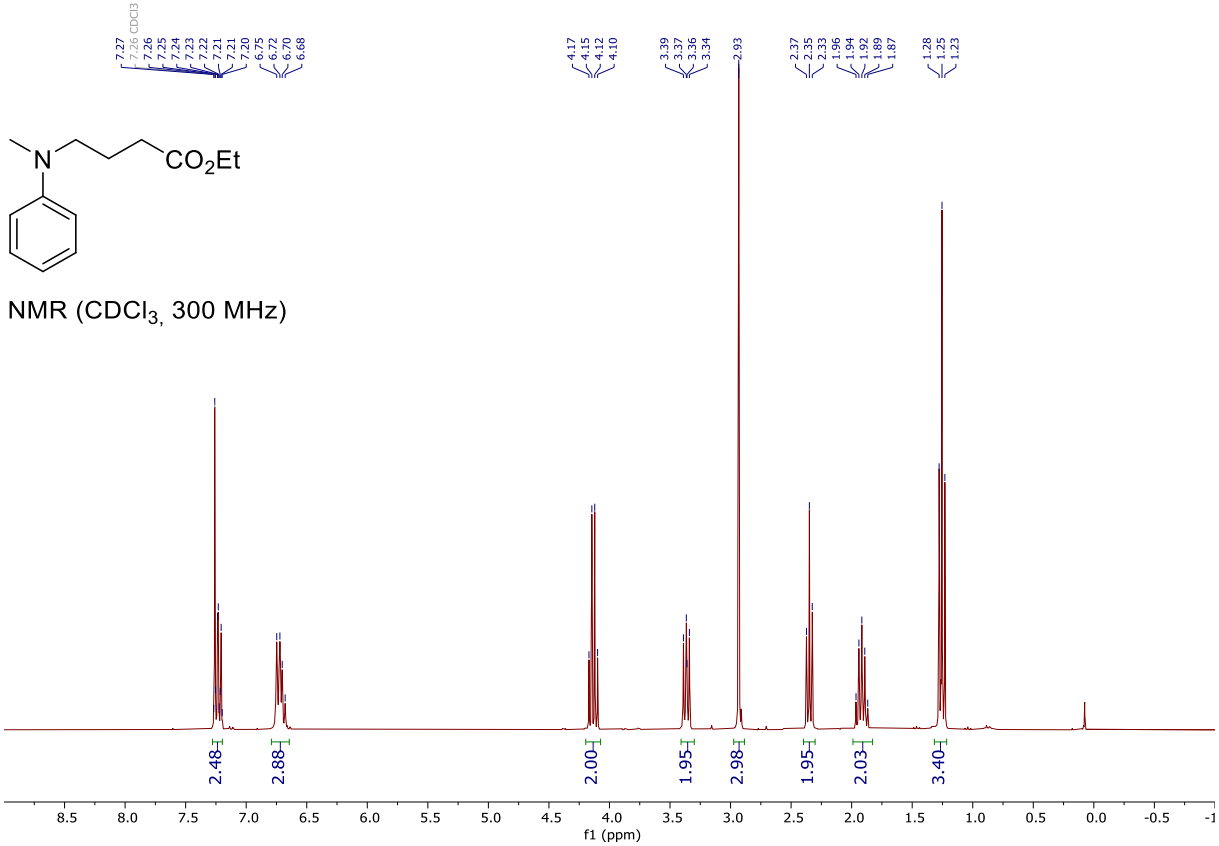
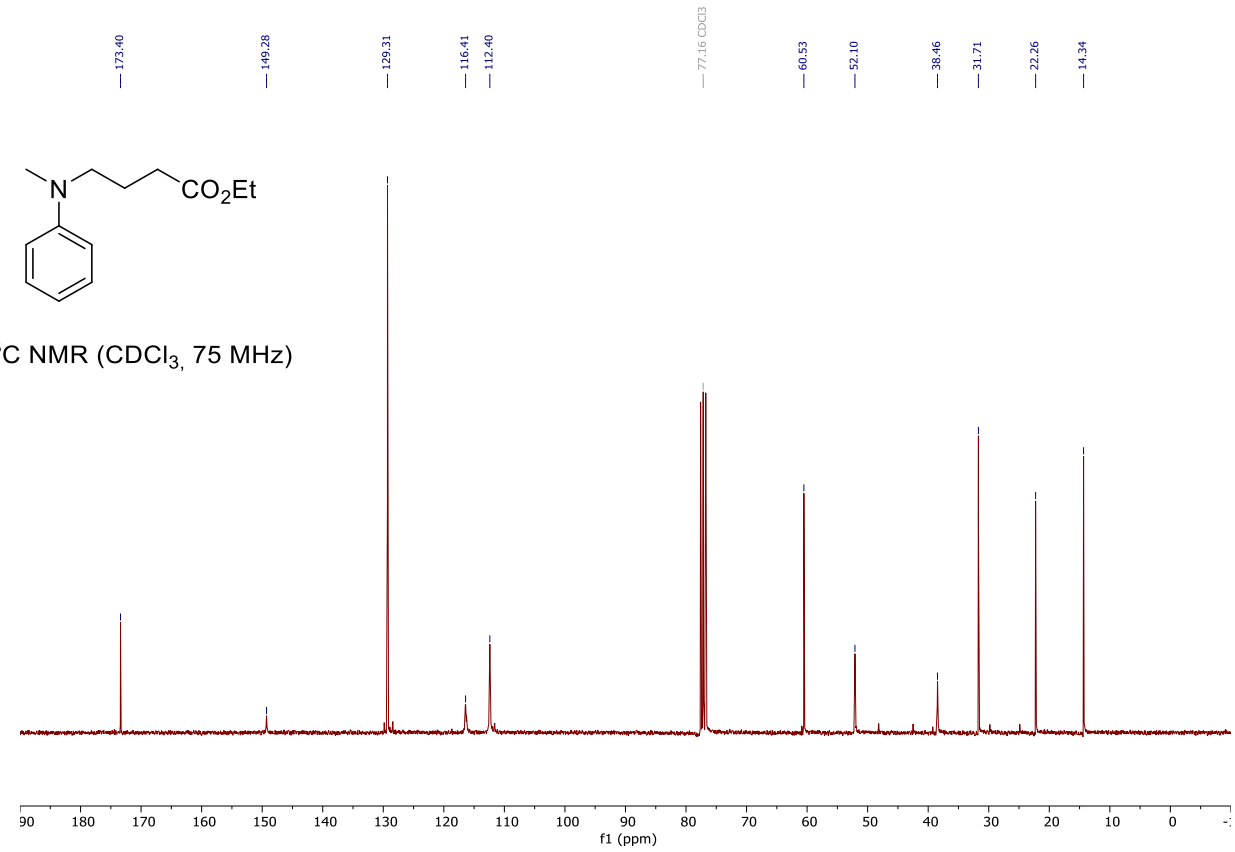
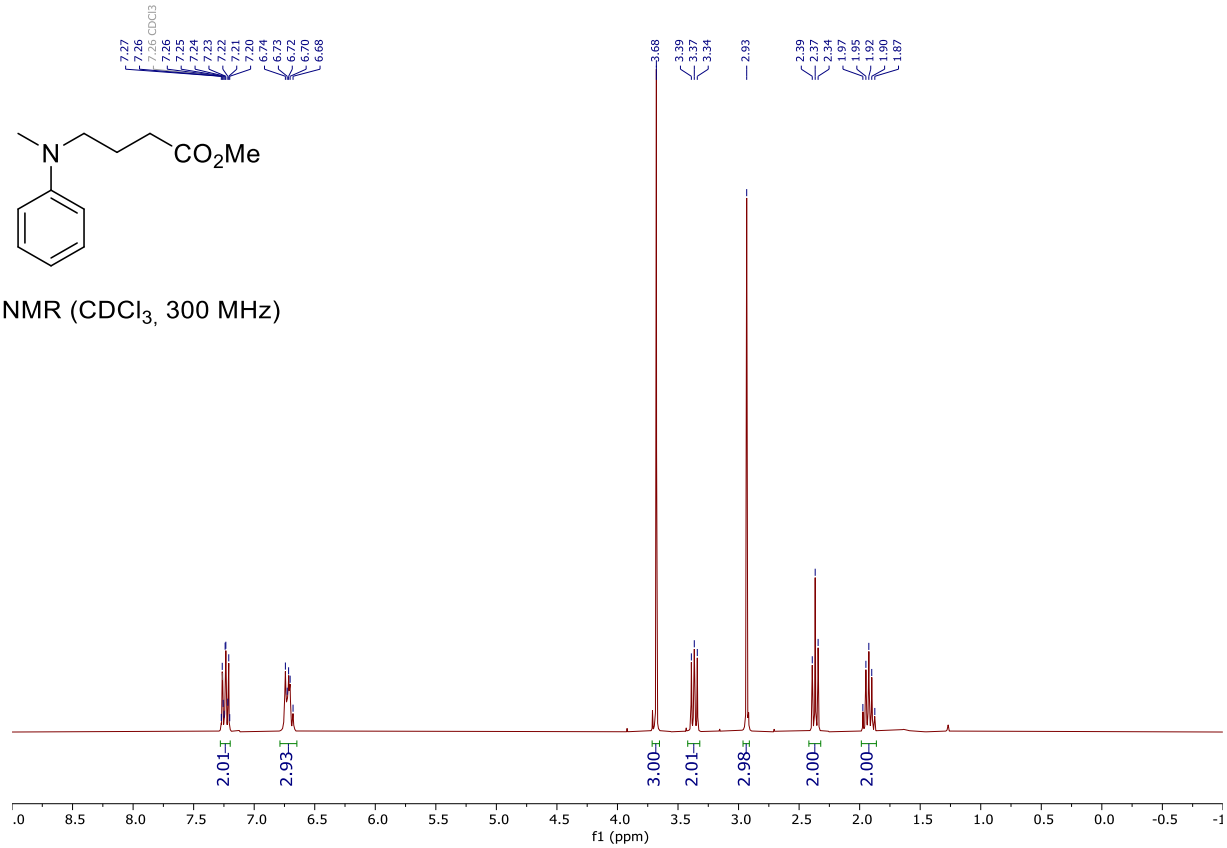
G- NMR spectra



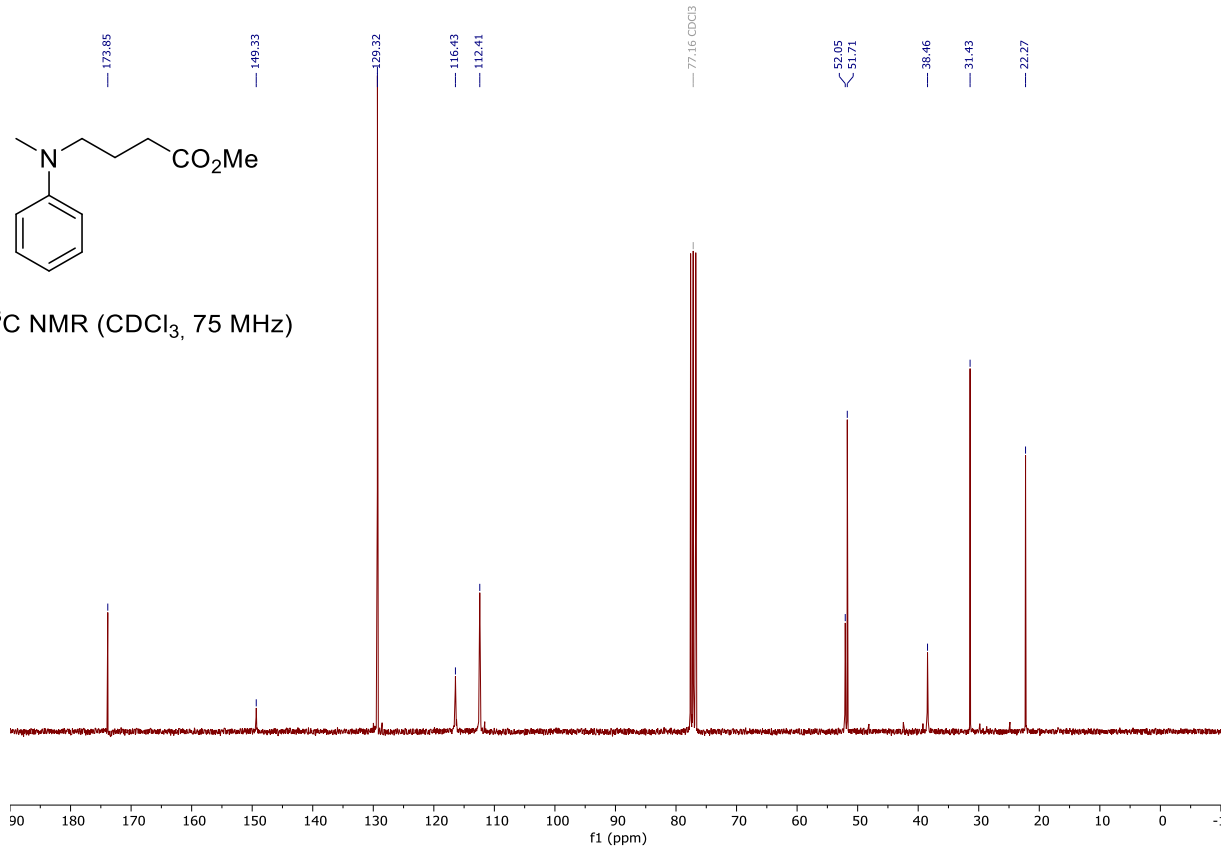
4, ^{1}H NMR ($CDCl_3$, 300 MHz)



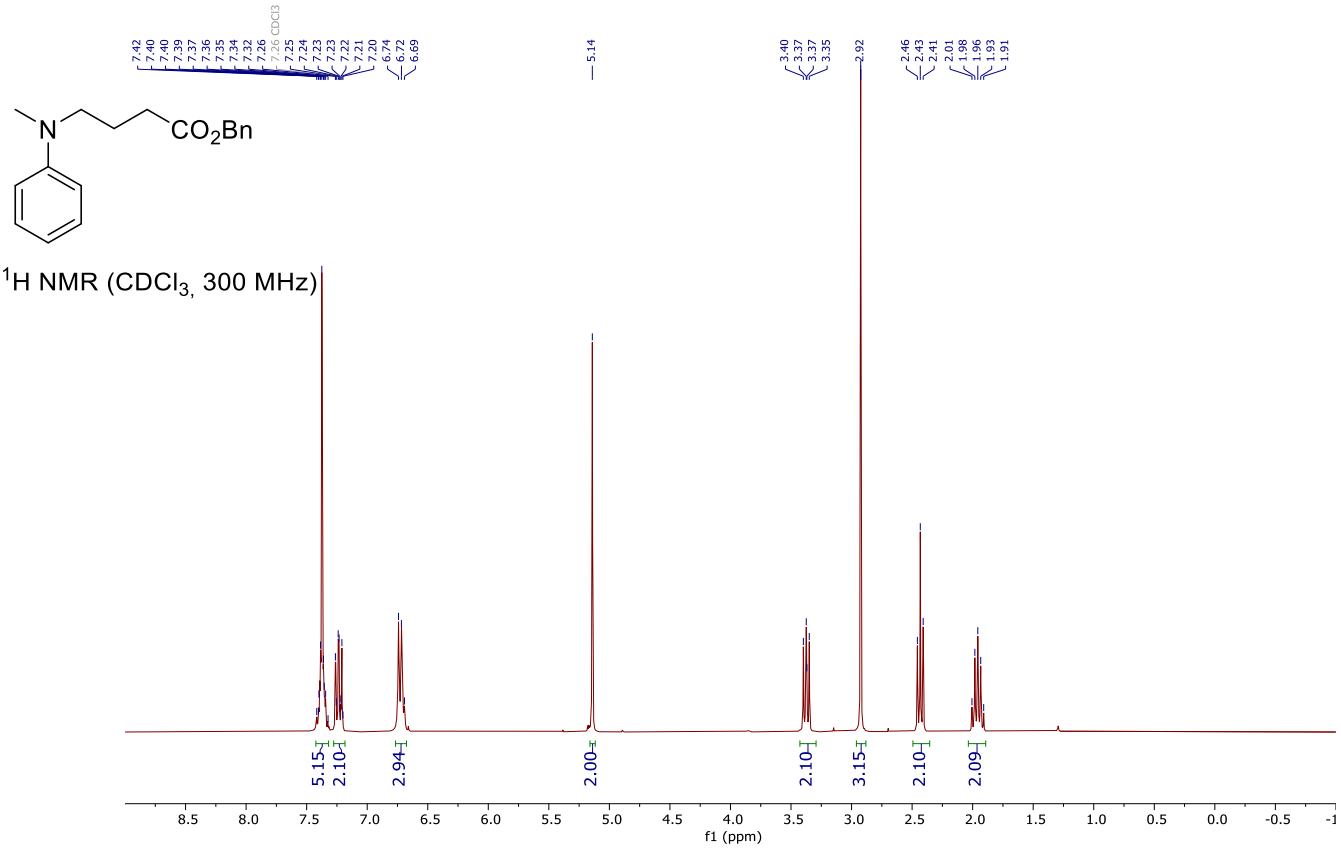
4, ^{13}C NMR ($CDCl_3$, 75 MHz)



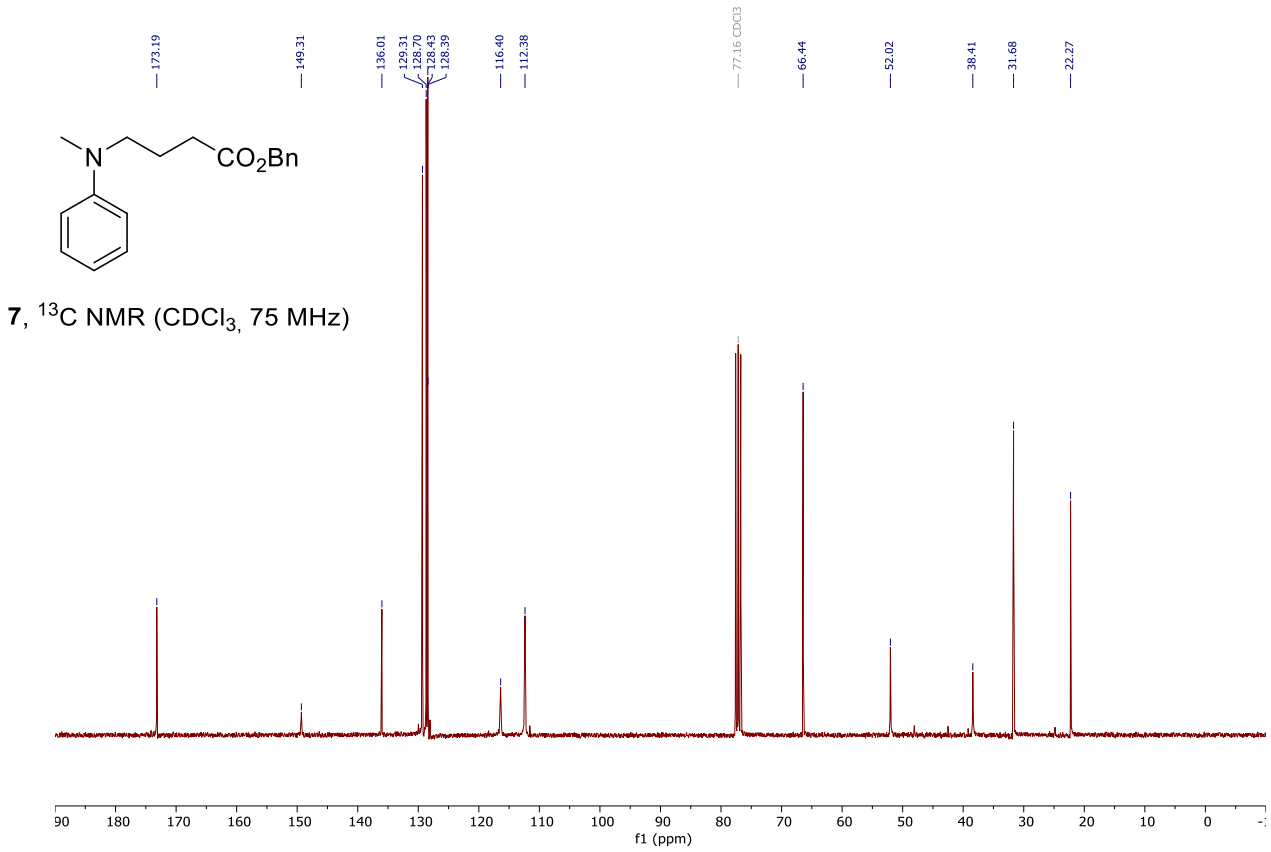
6, ^{1}H NMR ($CDCl_3$, 300 MHz)



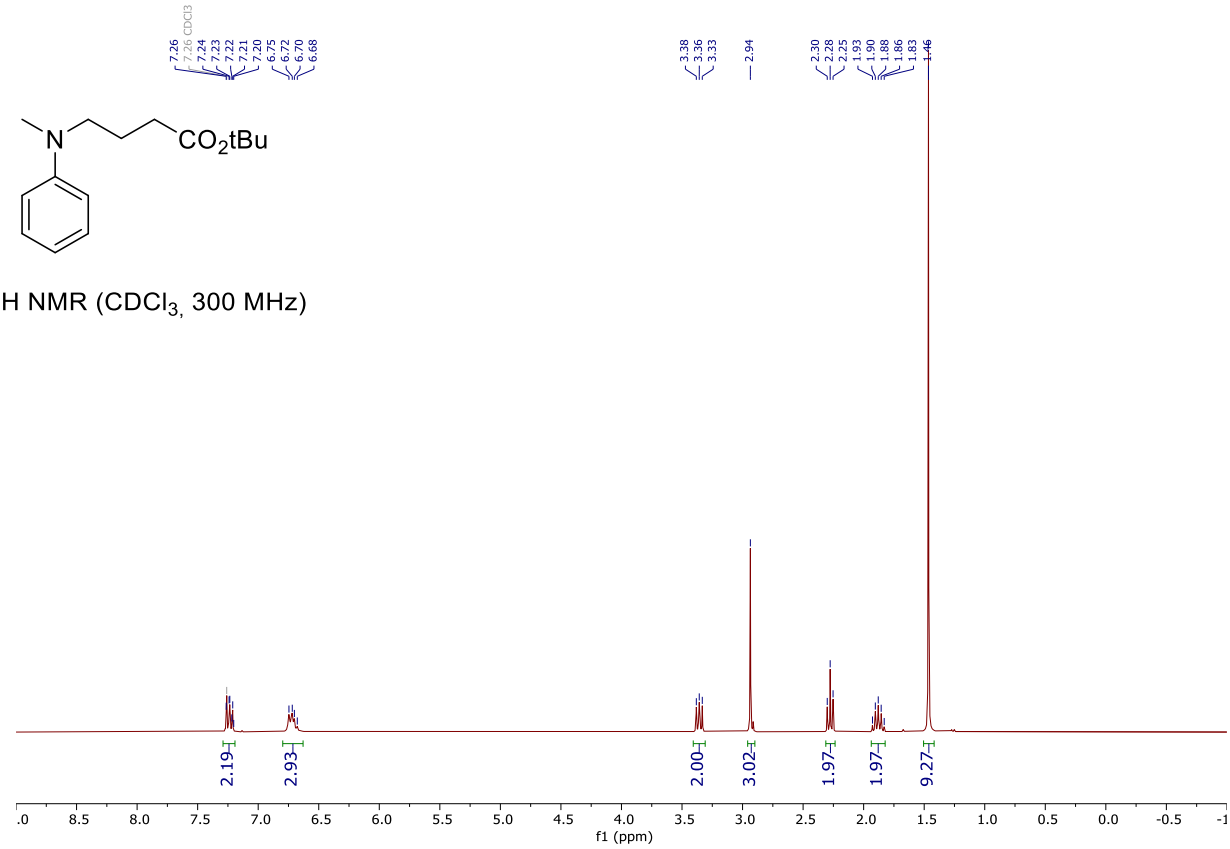
6, ^{13}C NMR ($CDCl_3$, 75 MHz)



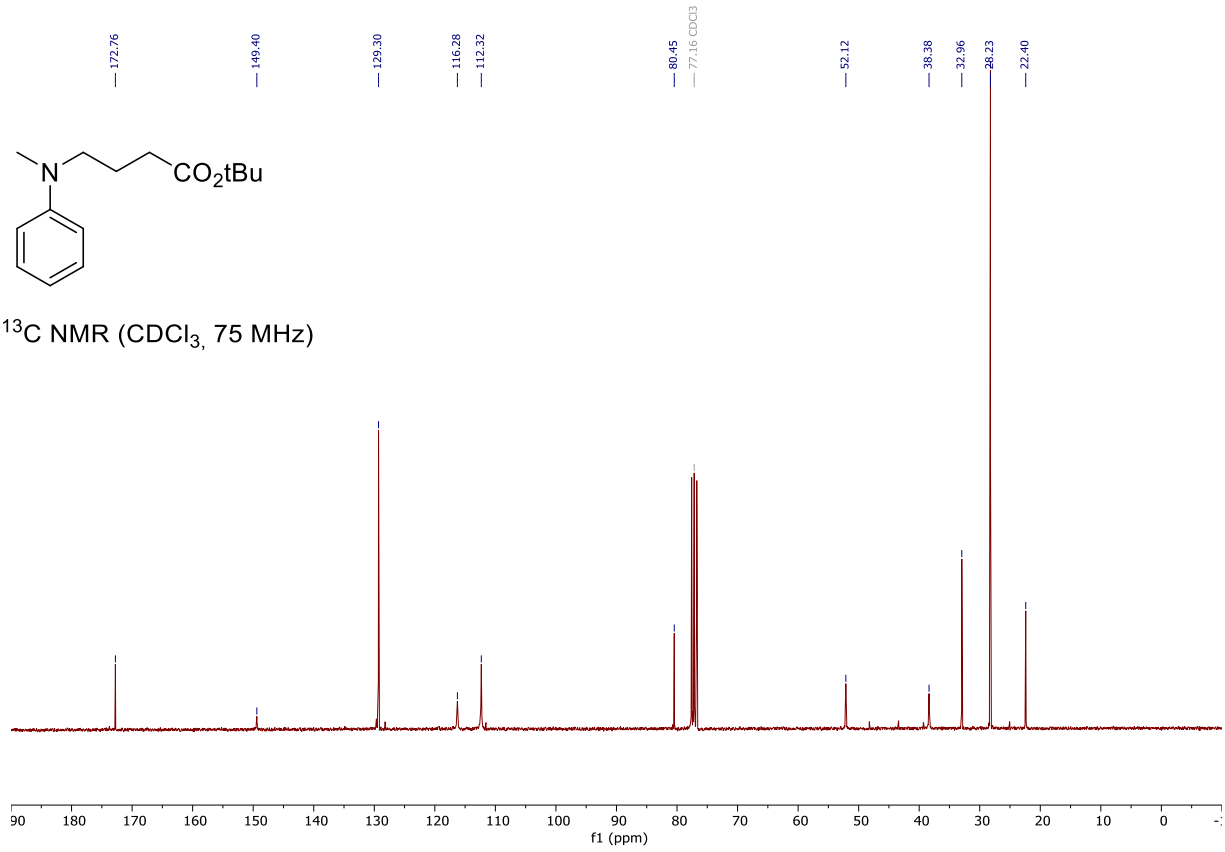
7, ^{1}H NMR ($CDCl_3$, 300 MHz)



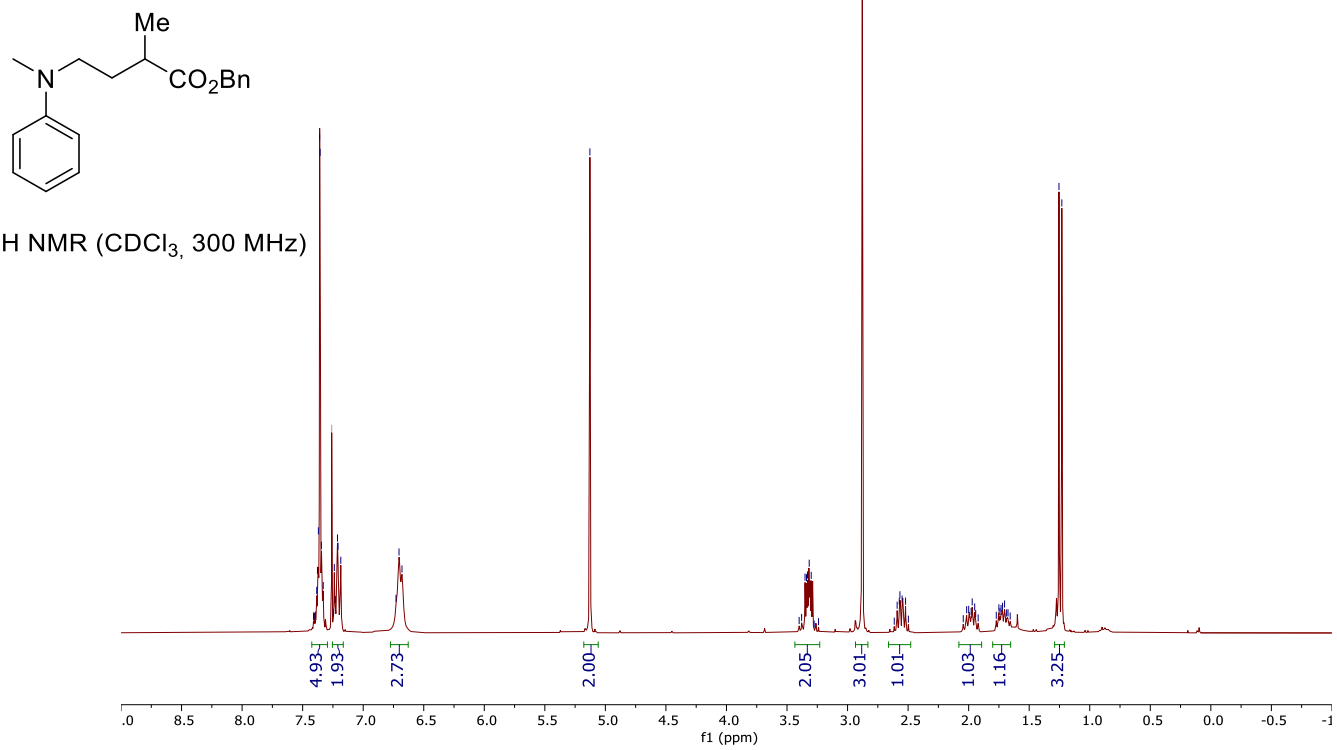
7, ^{13}C NMR ($CDCl_3$, 75 MHz)



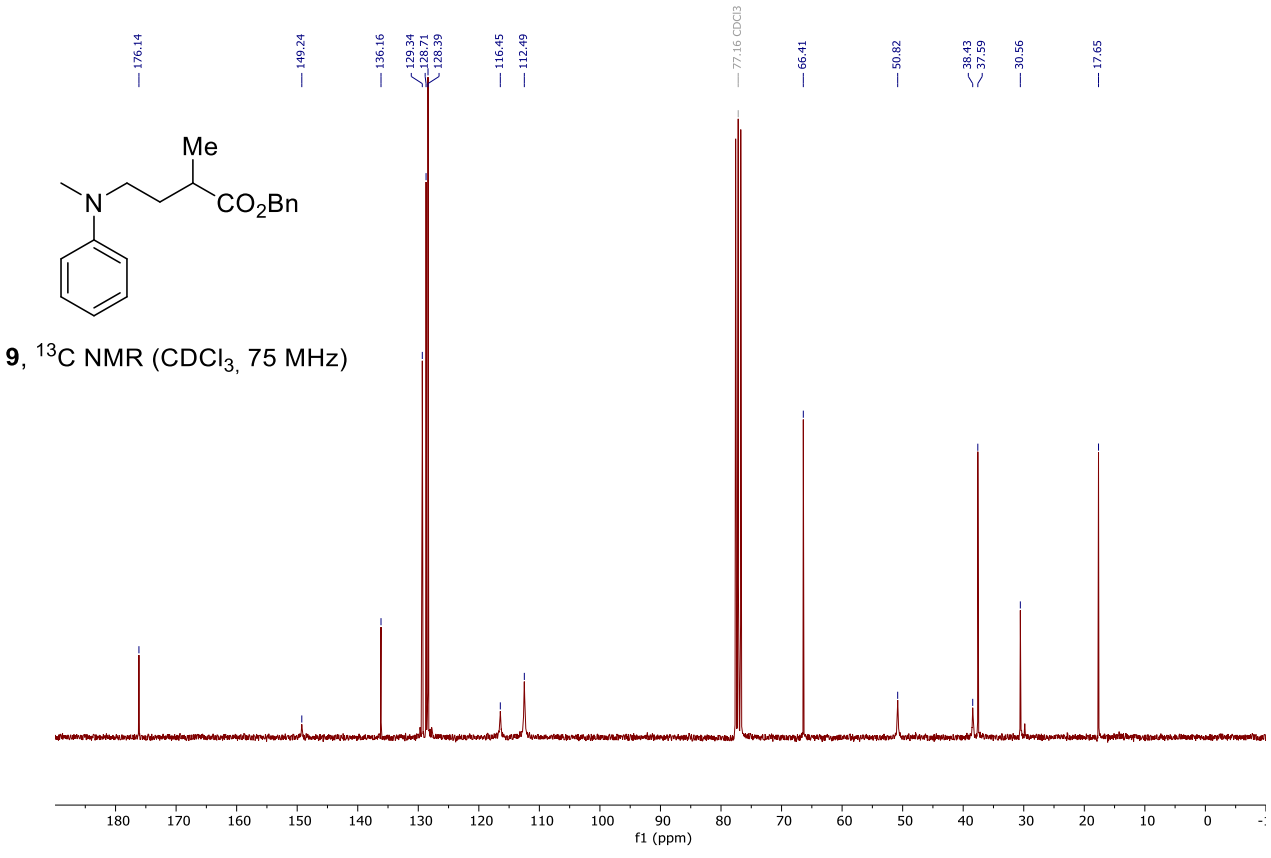
8, ^{1}H NMR ($CDCl_3$, 300 MHz)



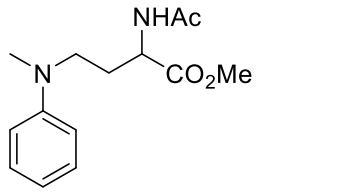
8, ^{13}C NMR ($CDCl_3$, 75 MHz)



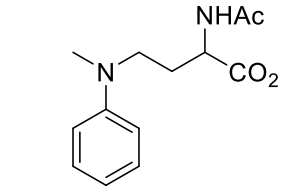
9, ^{1}H NMR ($CDCl_3$, 300 MHz)



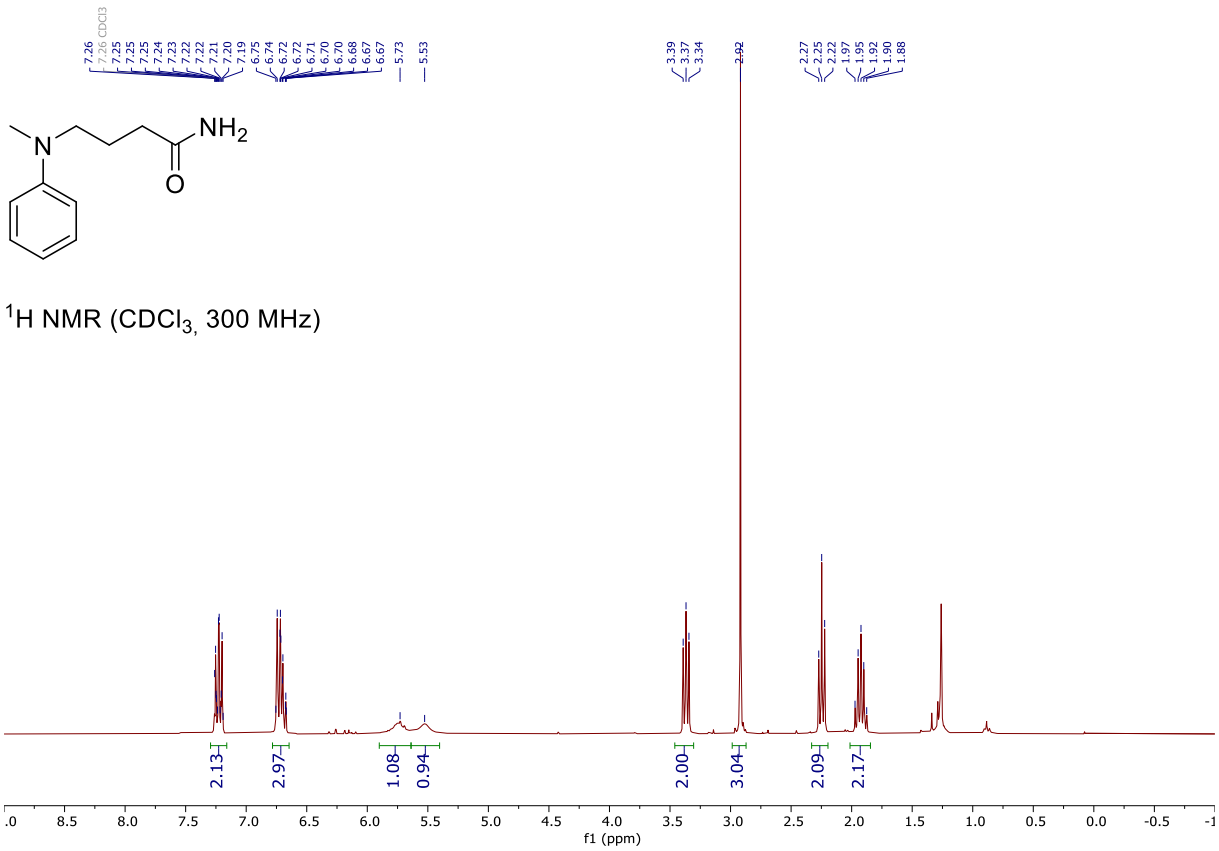
9, ^{13}C NMR ($CDCl_3$, 75 MHz)



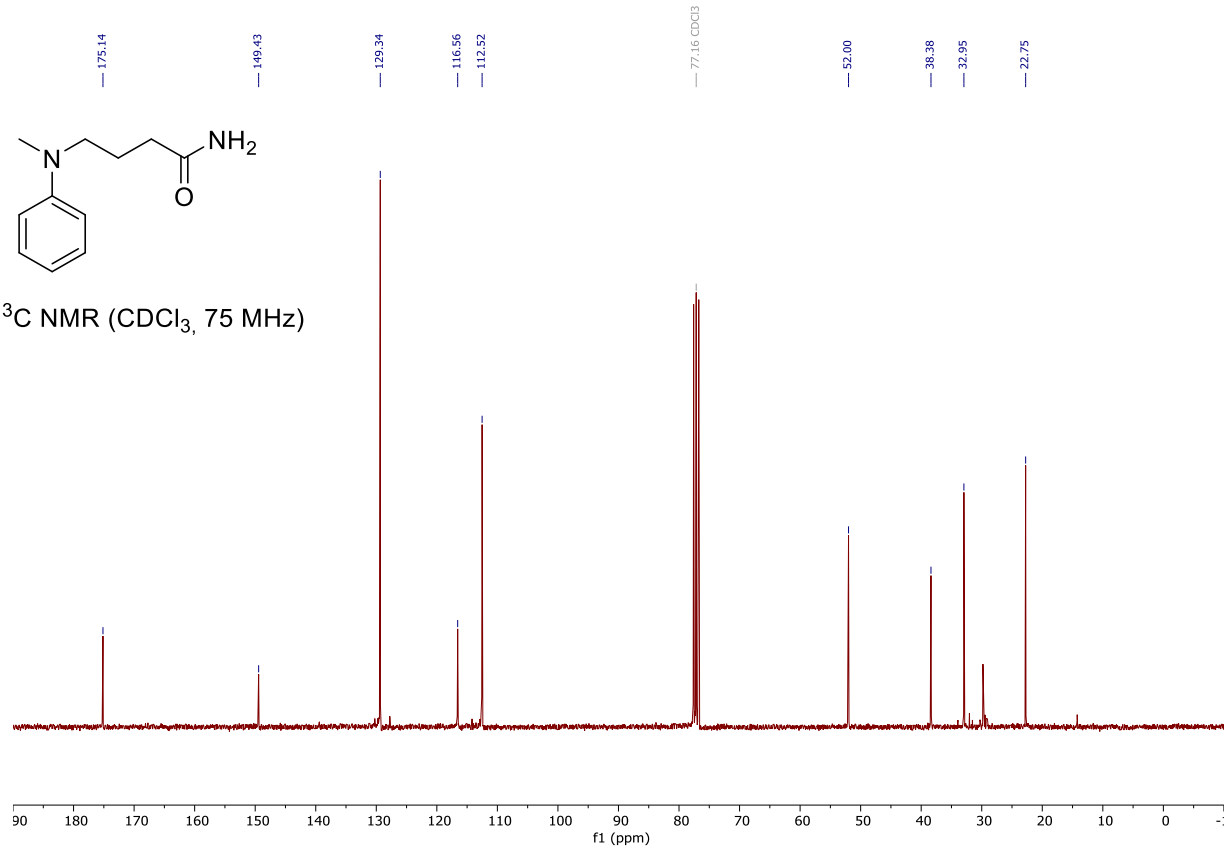
10, ^{1}H NMR ($CDCl_3$, 300 MHz)



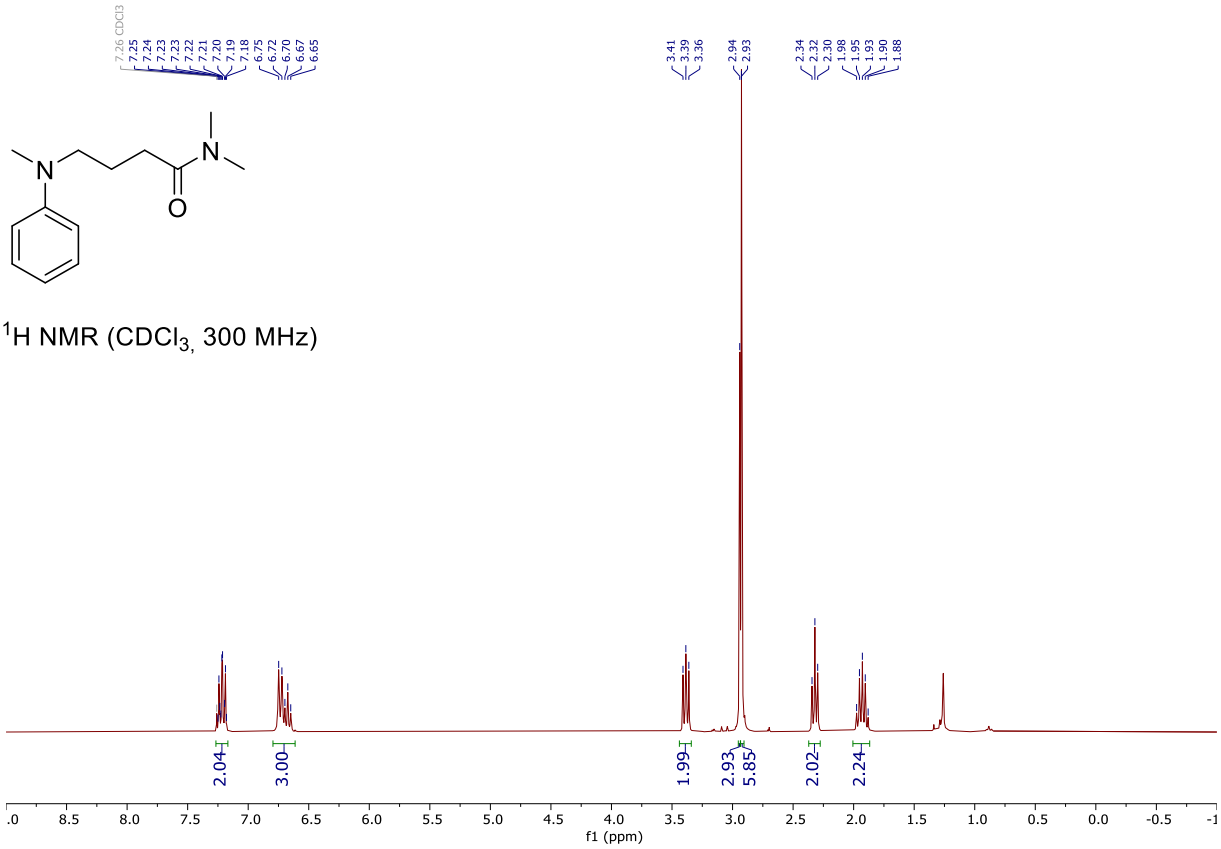
10, ^{13}C NMR ($CDCl_3$, 75 MHz)



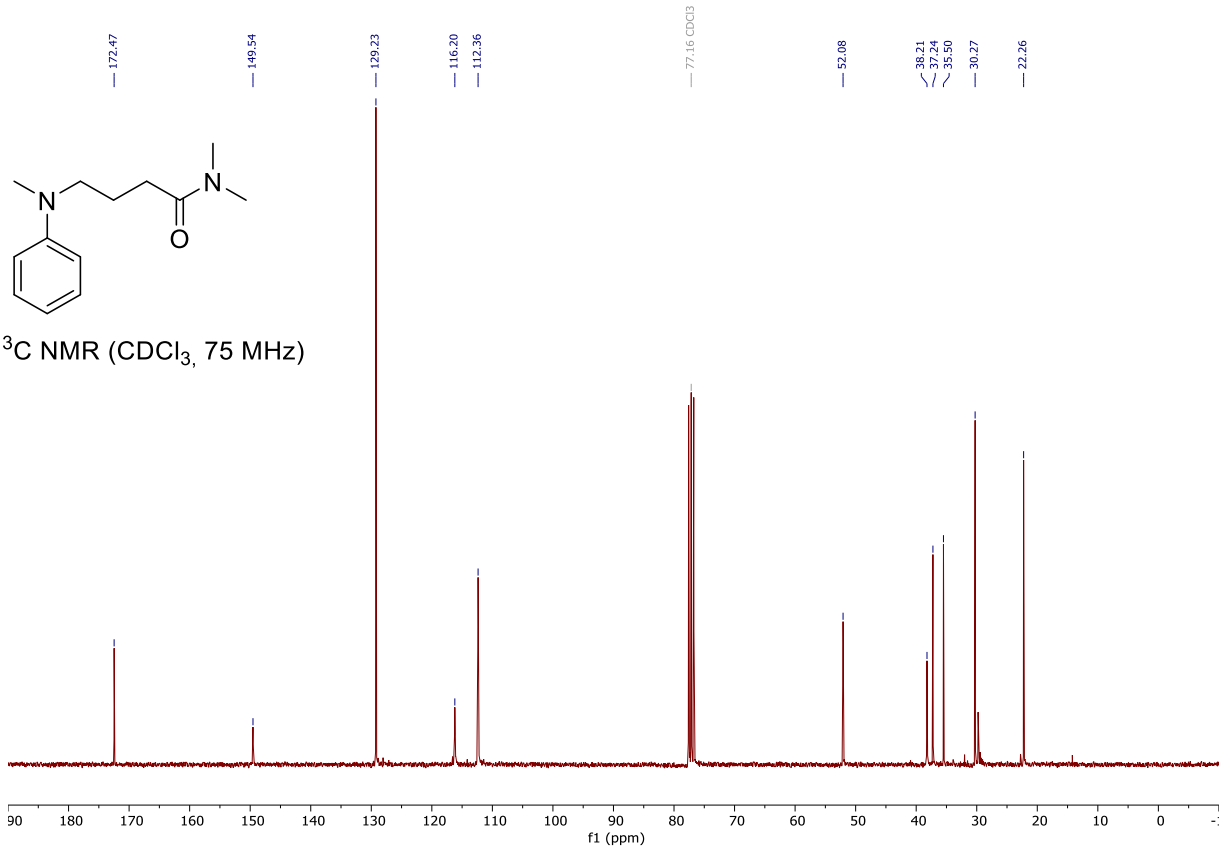
11, ^{1}H NMR ($CDCl_3$, 300 MHz)



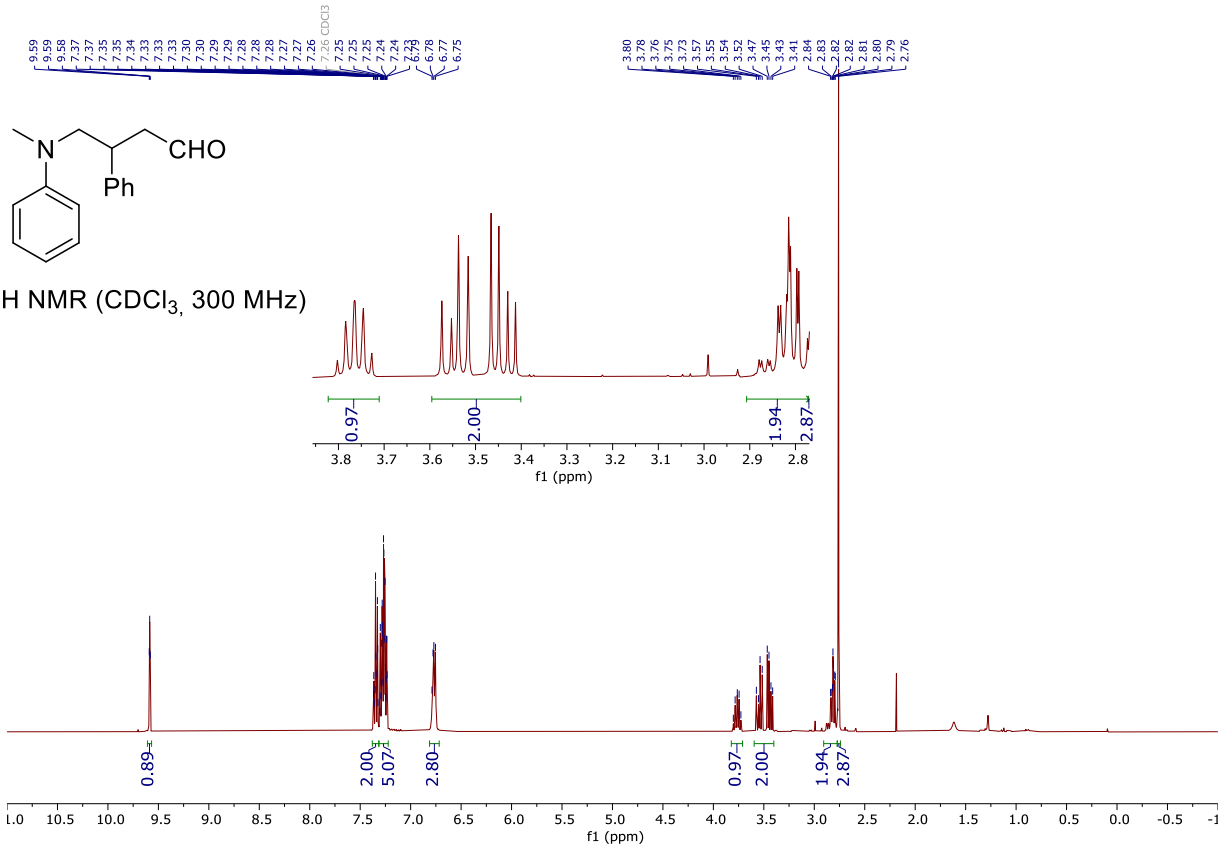
11, ^{13}C NMR ($CDCl_3$, 75 MHz)



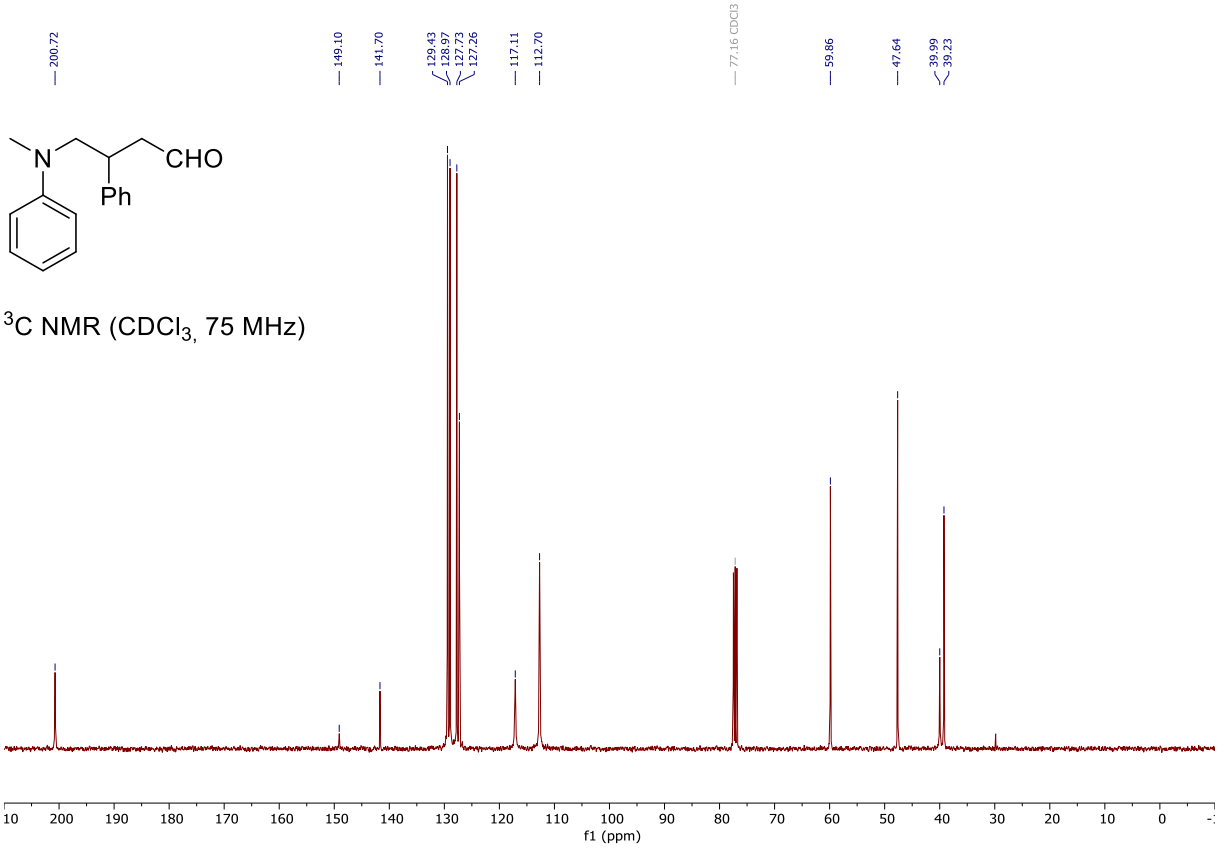
12, ^{1}H NMR ($CDCl_3$, 300 MHz)



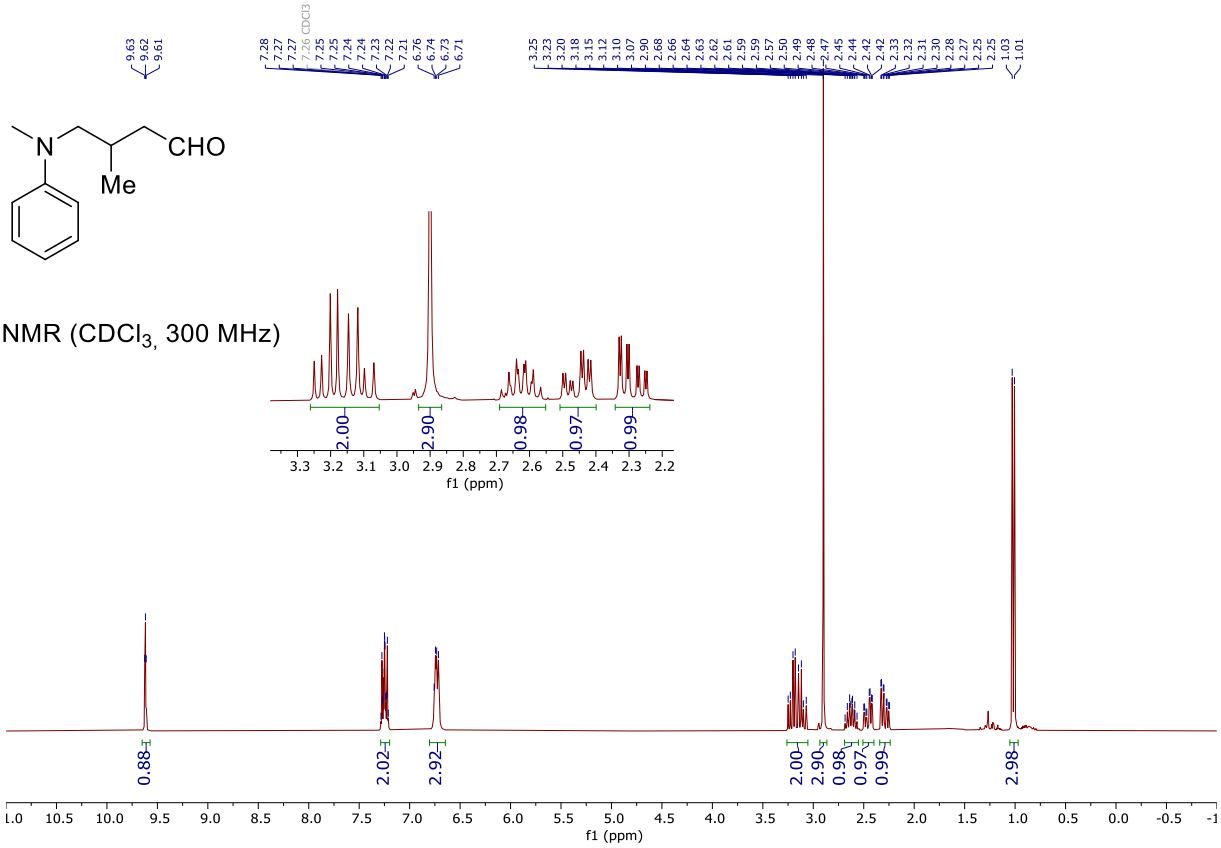
12, ^{13}C NMR ($CDCl_3$, 75 MHz)



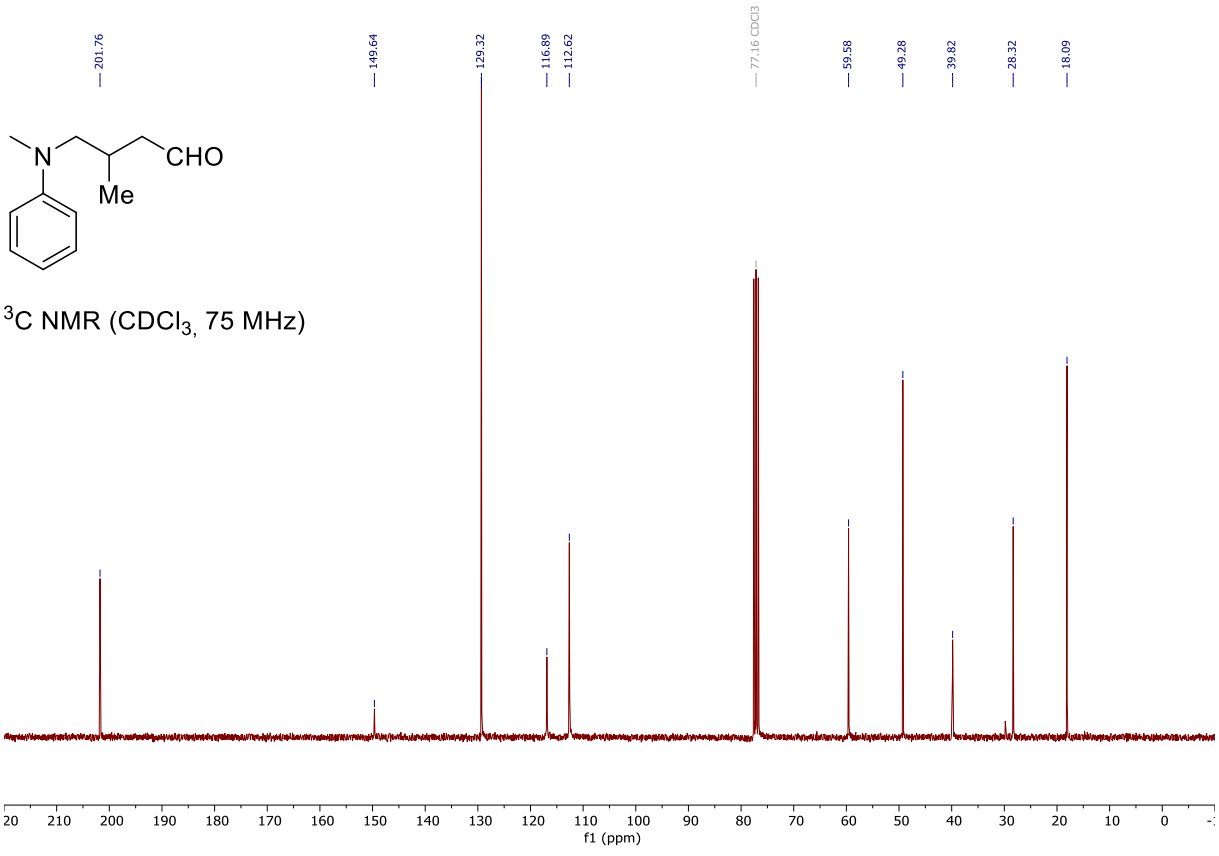
13, ^{1}H NMR ($CDCl_3$, 300 MHz)



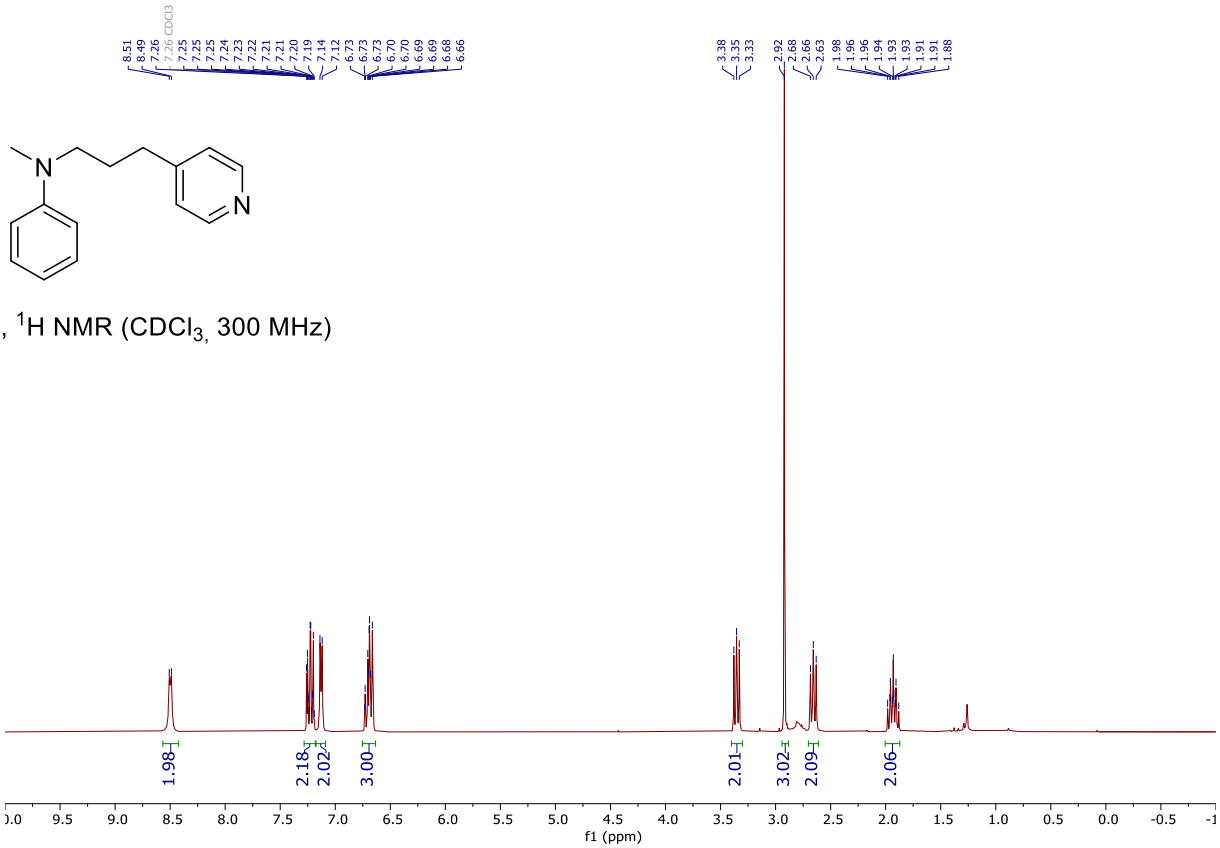
13, ^{13}C NMR ($CDCl_3$, 75 MHz)



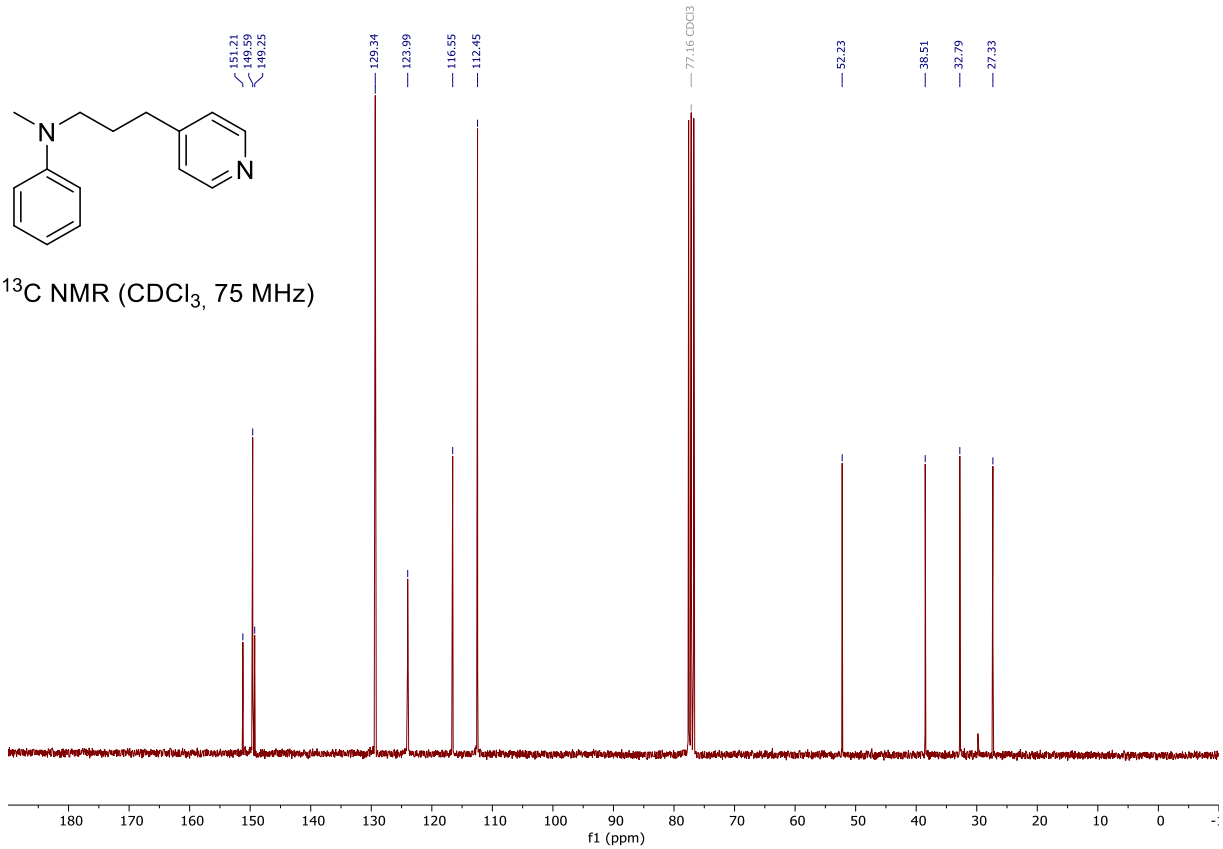
14, ^{1}H NMR ($CDCl_3$, 300 MHz)



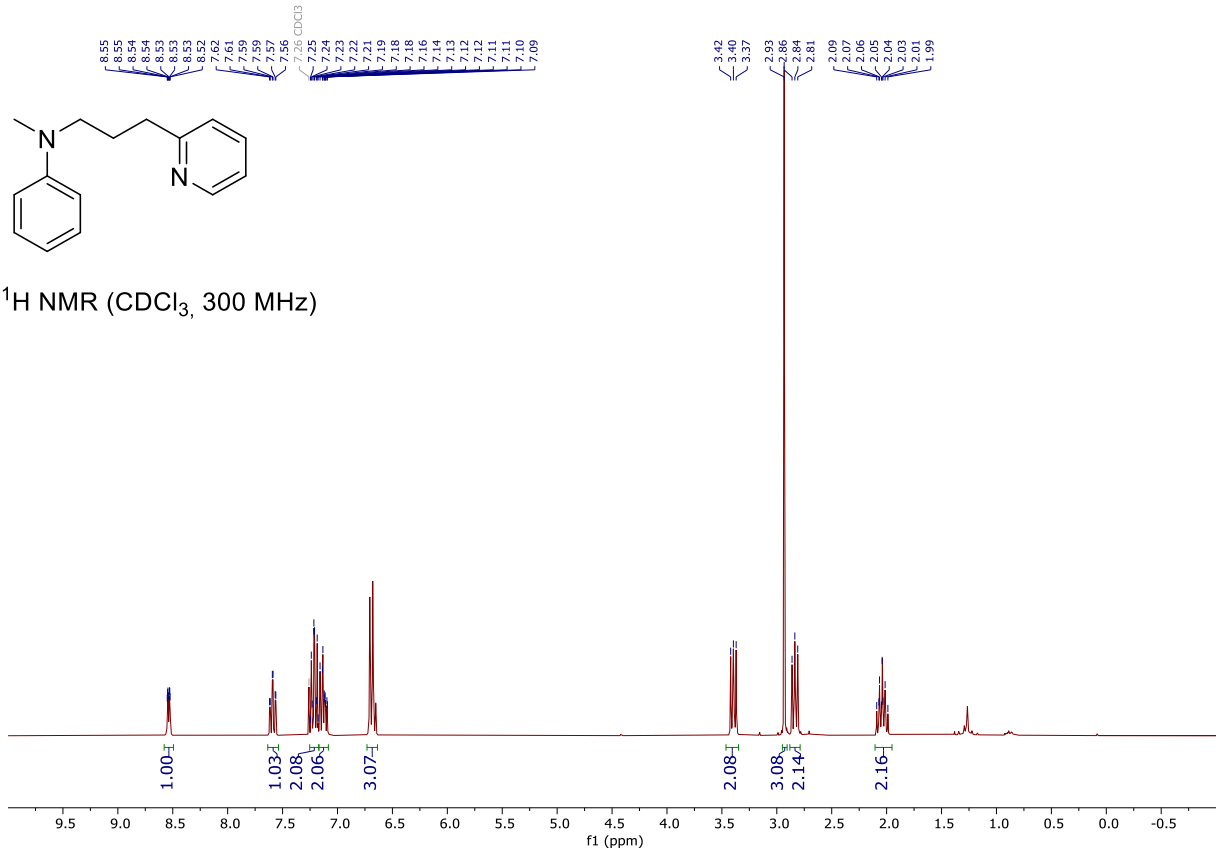
14, ^{13}C NMR ($CDCl_3$, 75 MHz)



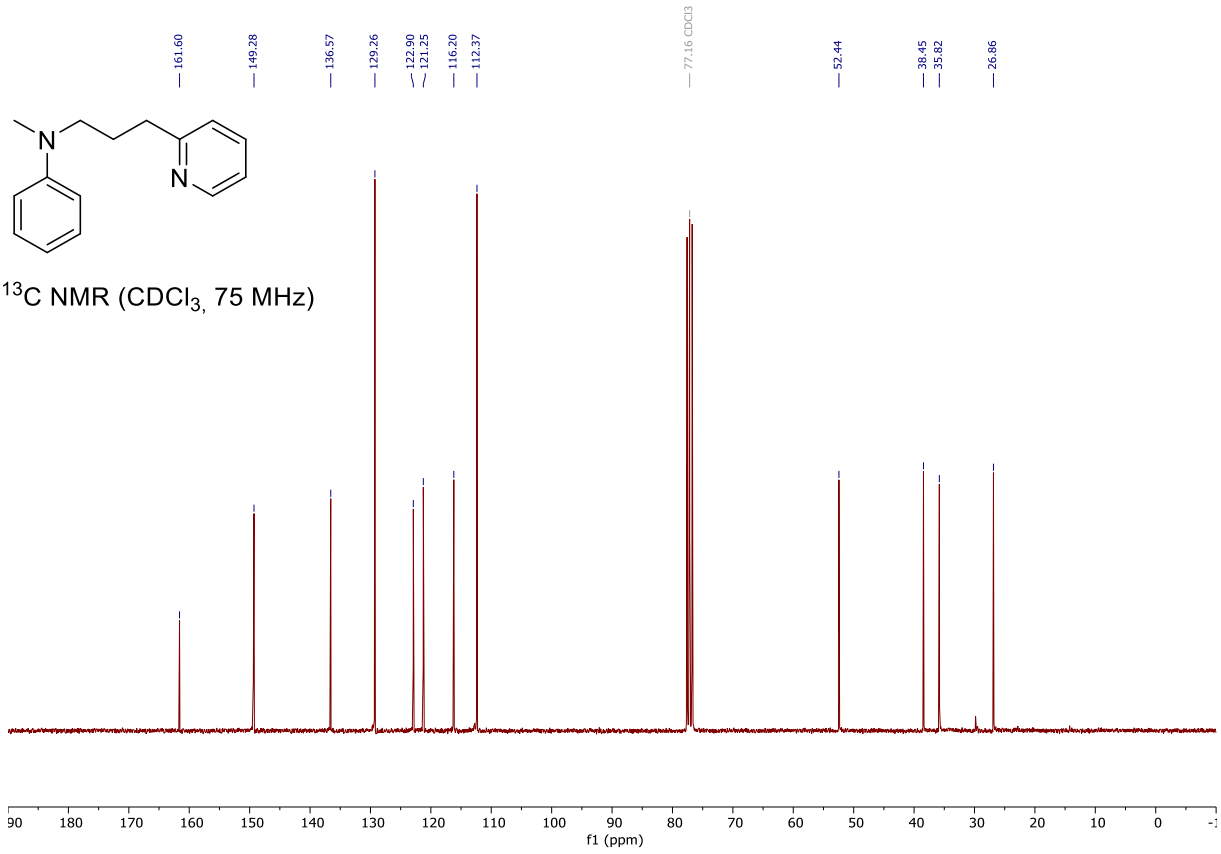
15, ^{1}H NMR ($CDCl_3$, 300 MHz)



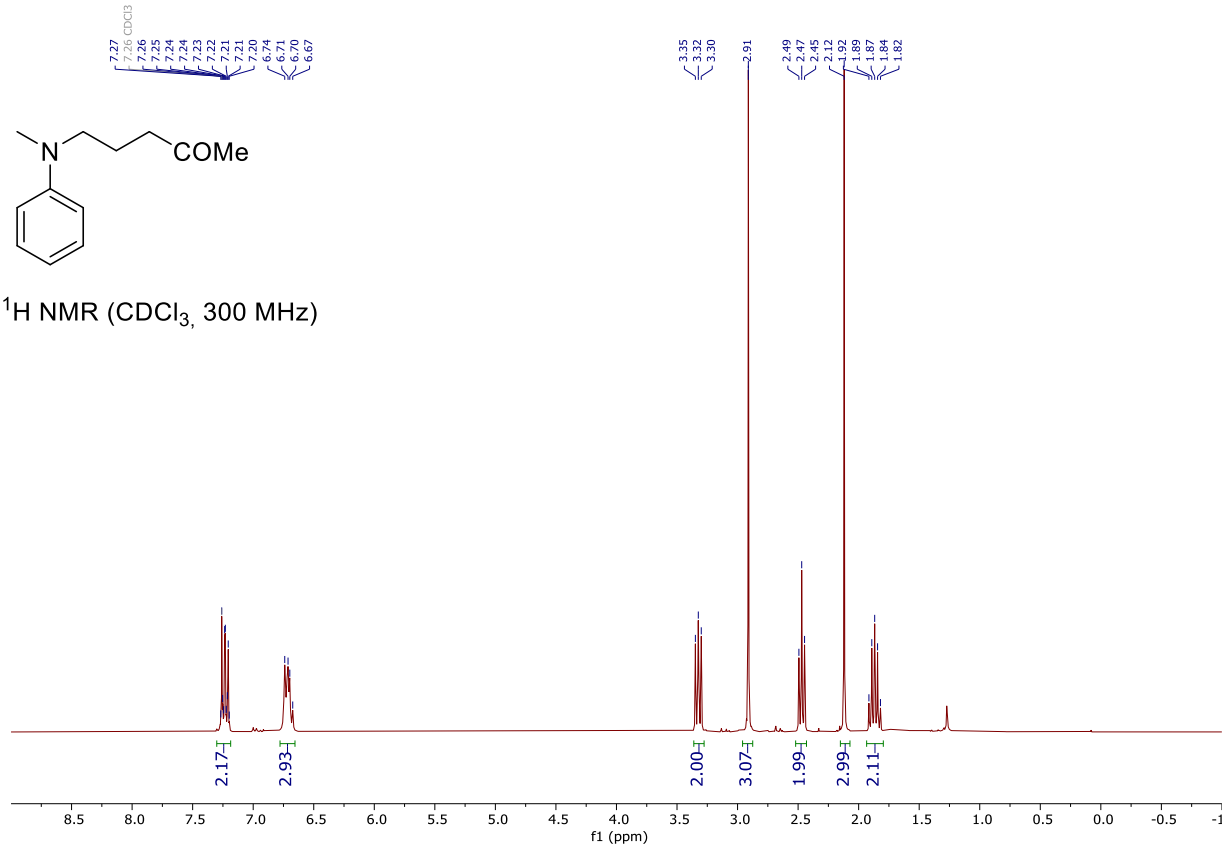
15, ^{13}C NMR ($CDCl_3$, 75 MHz)



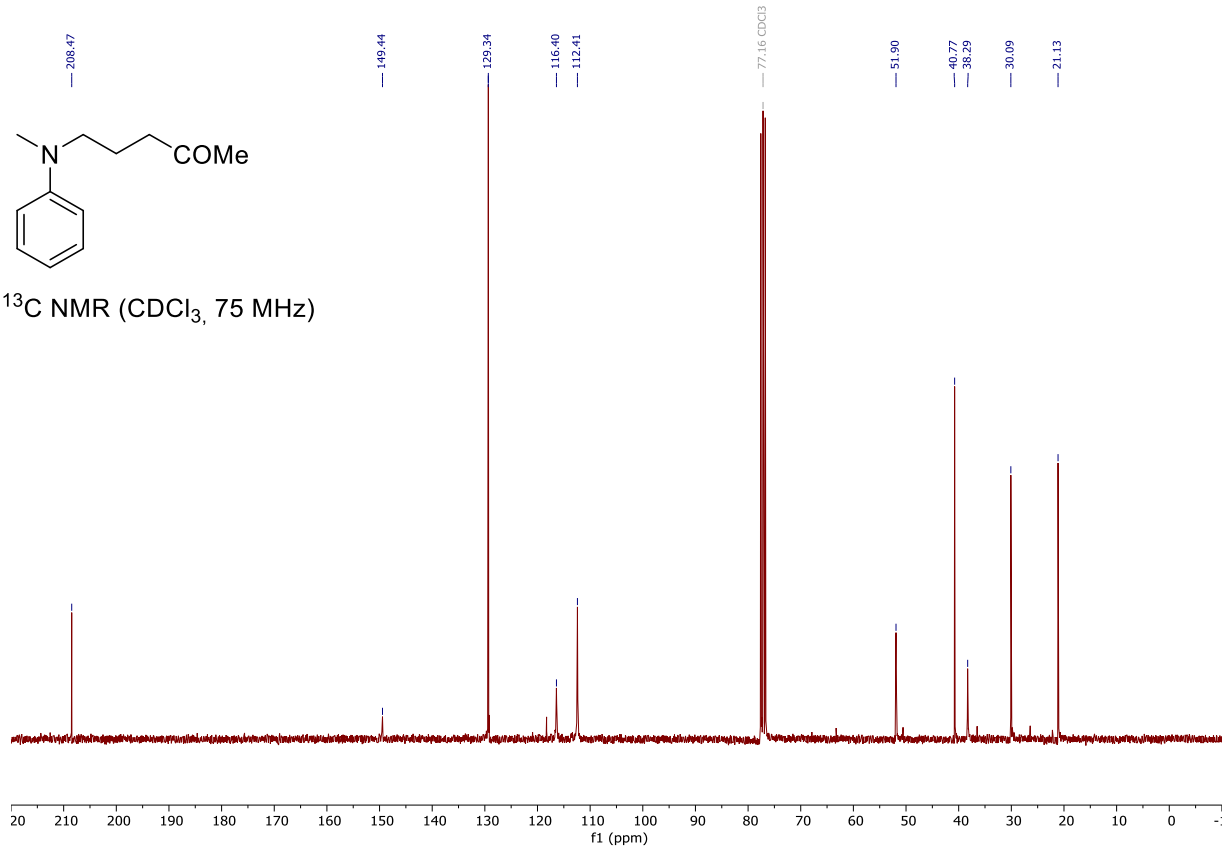
16, ^{1}H NMR ($CDCl_3$, 300 MHz)



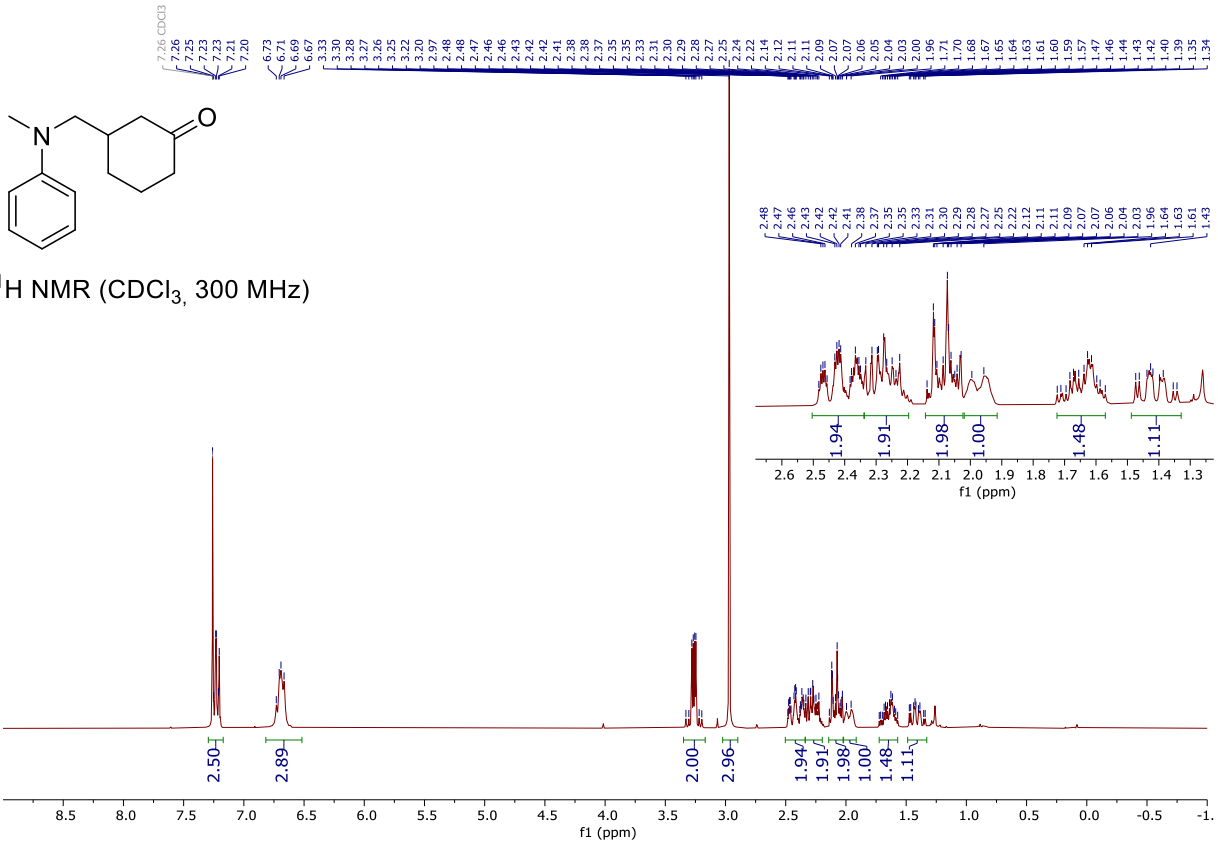
16, ^{13}C NMR ($CDCl_3$, 75 MHz)



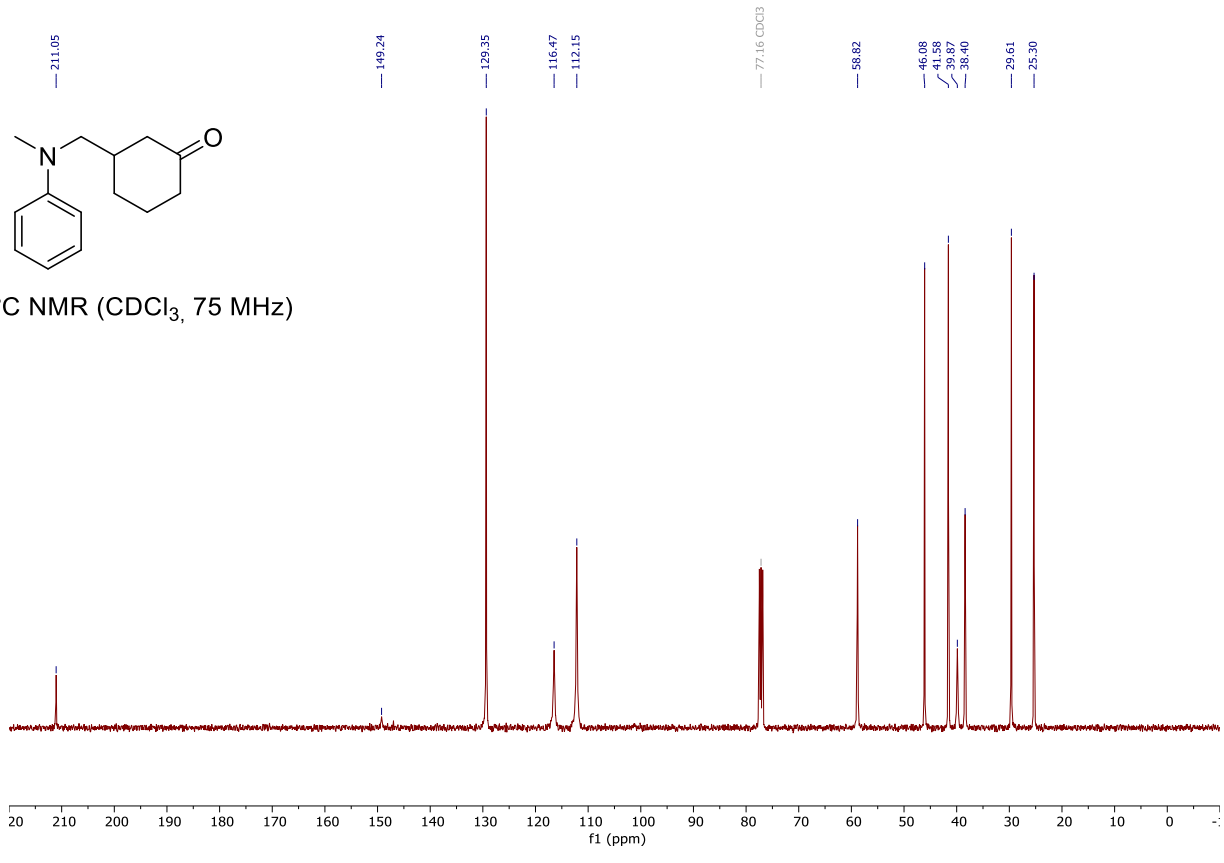
17, ^{1}H NMR ($CDCl_3$, 300 MHz)



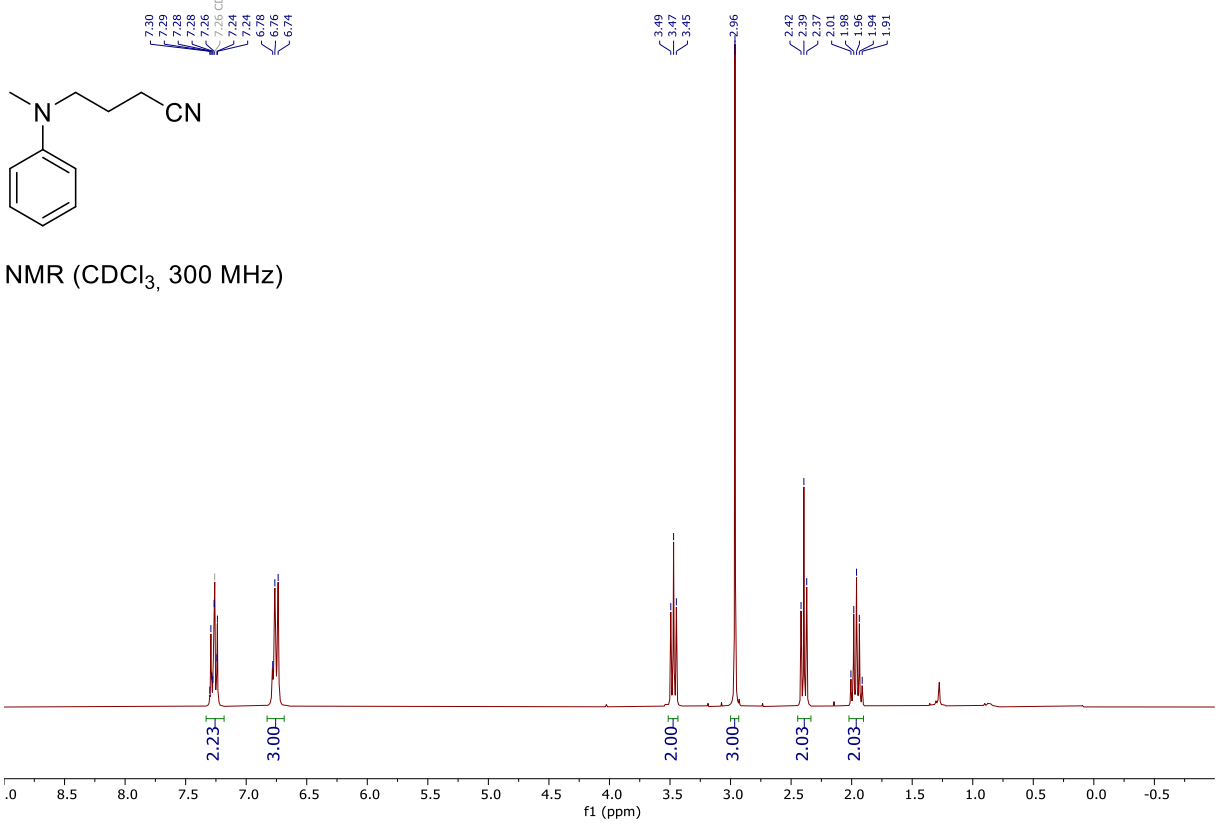
17, ^{13}C NMR ($CDCl_3$, 75 MHz)



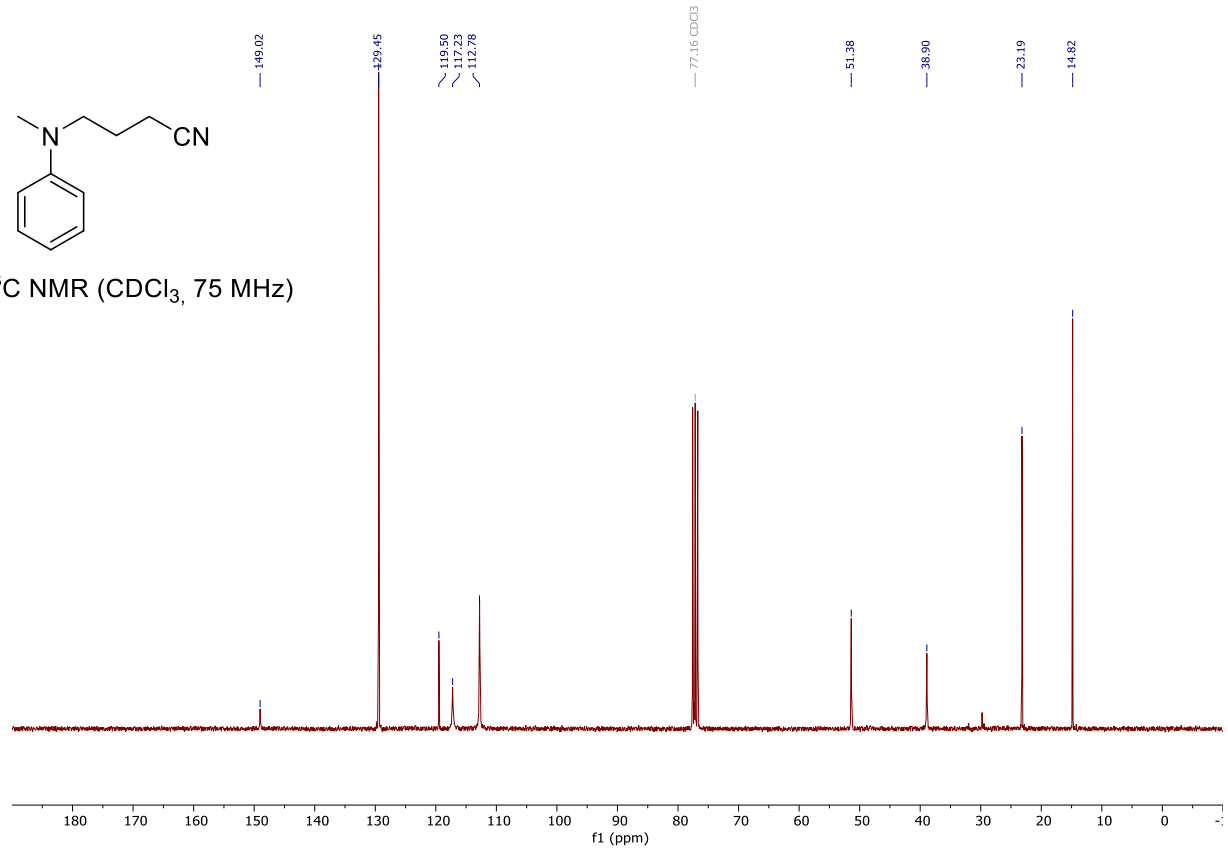
18, ^{1}H NMR ($CDCl_3$, 300 MHz)



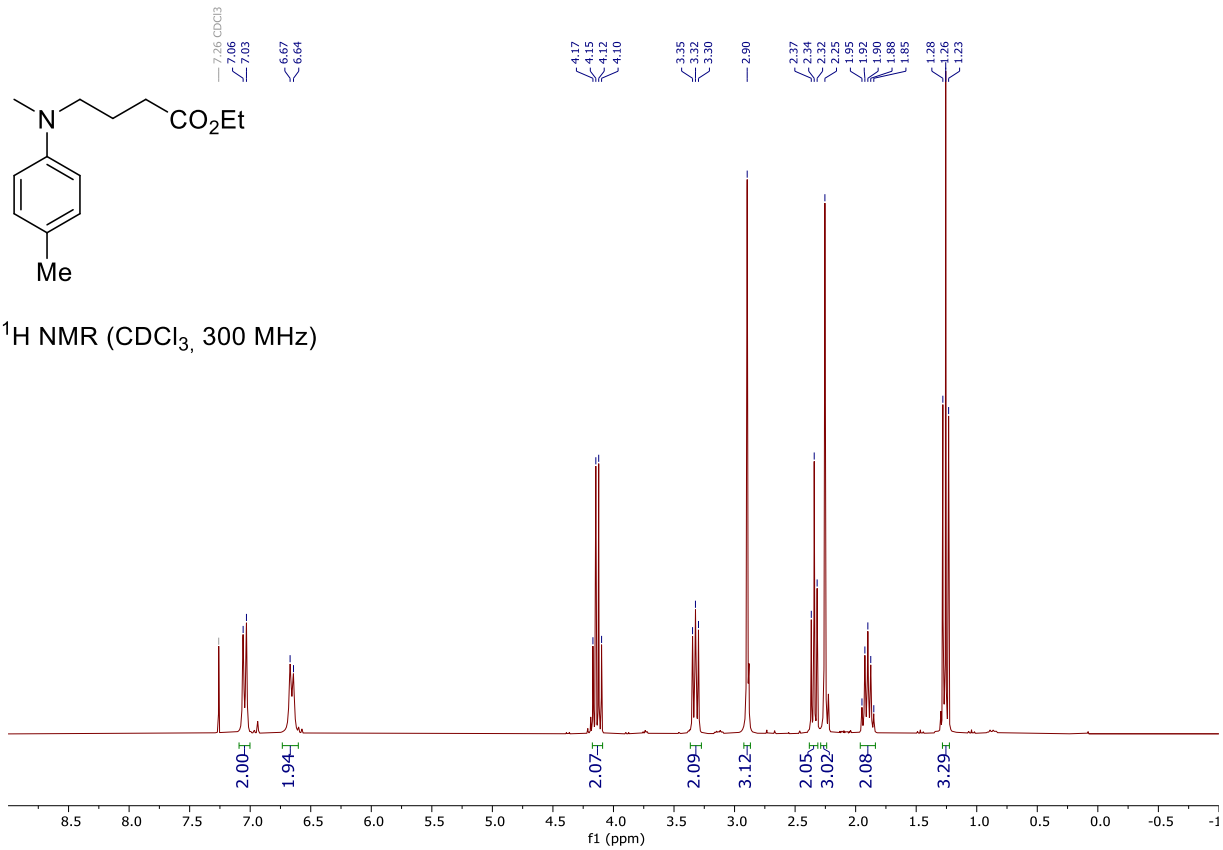
18, ^{13}C NMR ($CDCl_3$, 75 MHz)



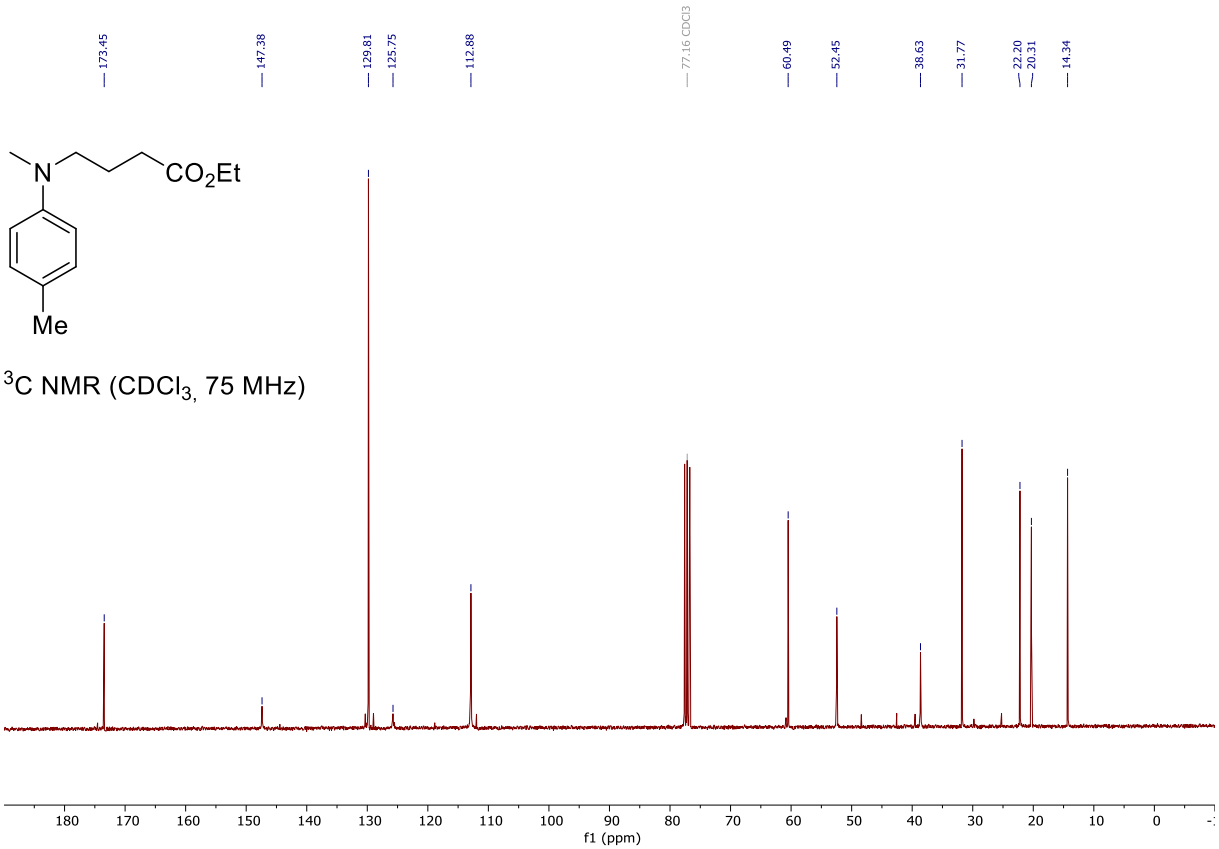
19, ^{1}H NMR ($CDCl_3$, 300 MHz)



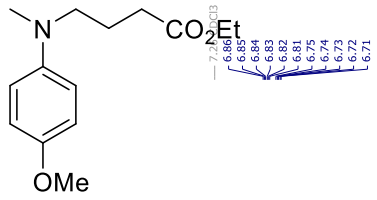
19, ^{13}C NMR ($CDCl_3$, 75 MHz)



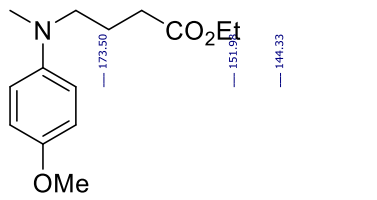
20, ^{1}H NMR ($CDCl_3$, 300 MHz)



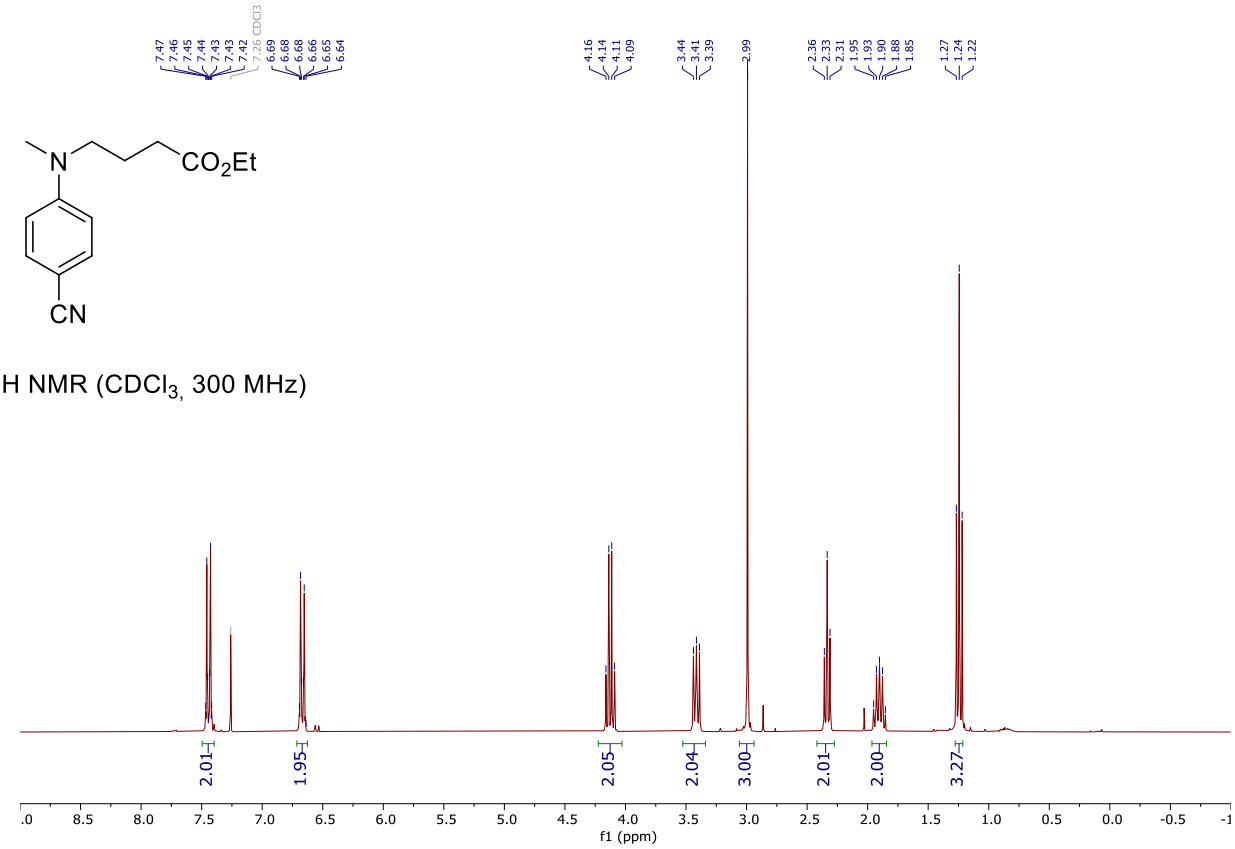
20, ^{13}C NMR ($CDCl_3$, 75 MHz)



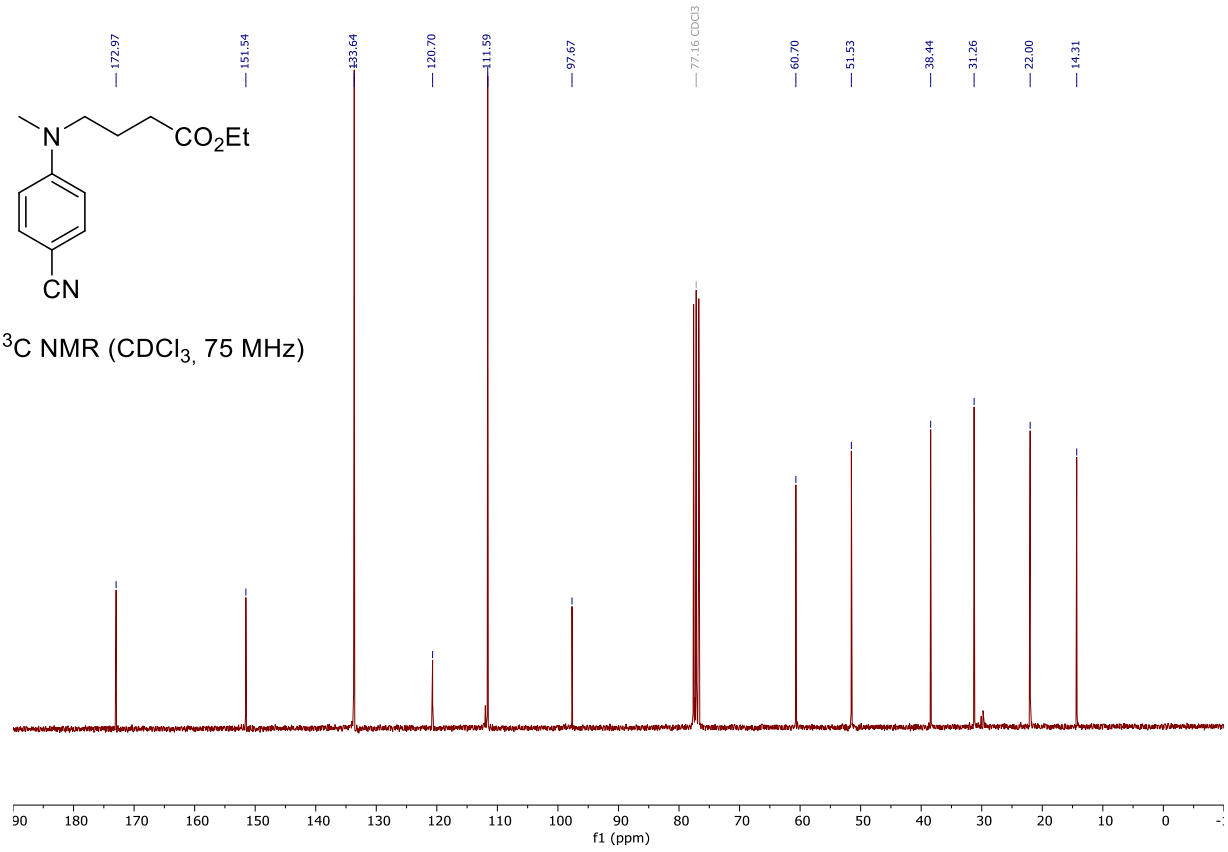
21, ^{1}H NMR ($CDCl_3$, 300 MHz)



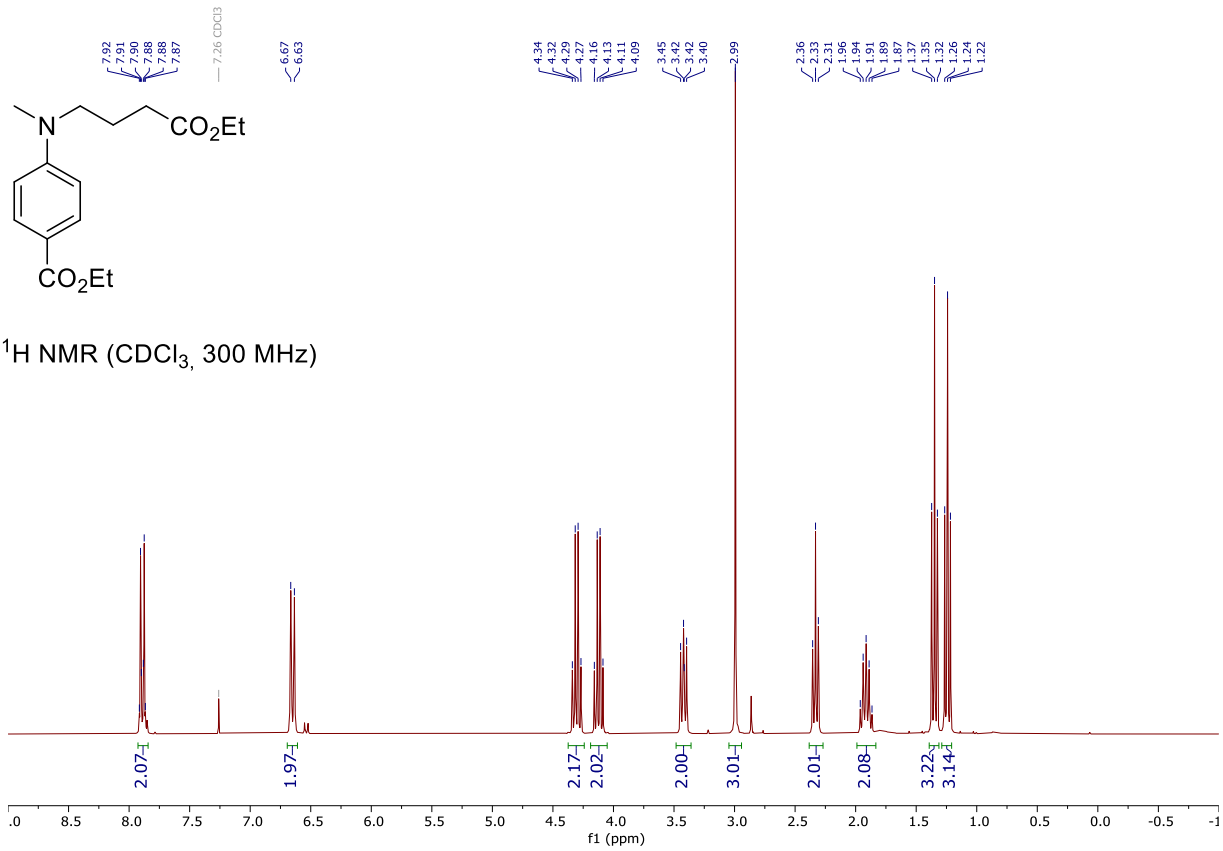
21, ^{13}C NMR ($CDCl_3$, 75 MHz)



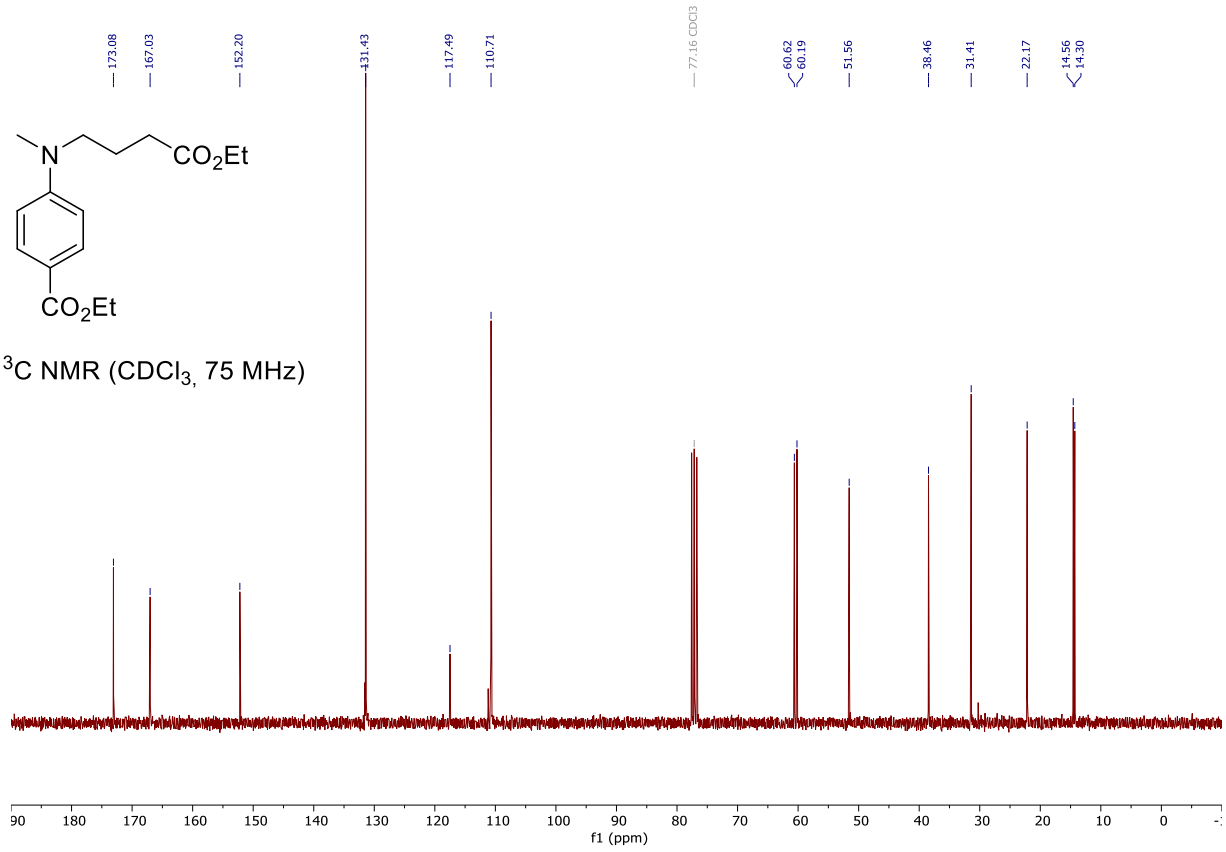
22, ^{1}H NMR ($CDCl_3$, 300 MHz)



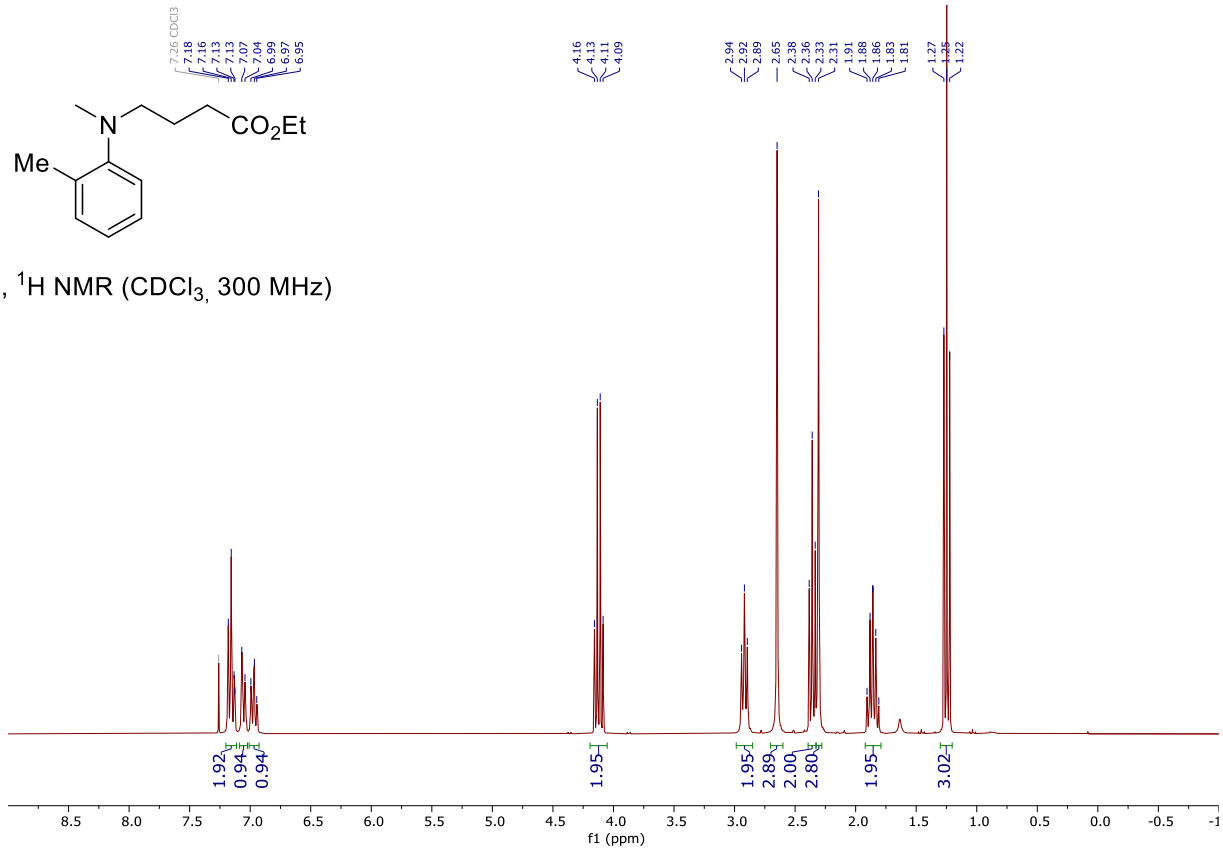
22, ^{13}C NMR ($CDCl_3$, 75 MHz)



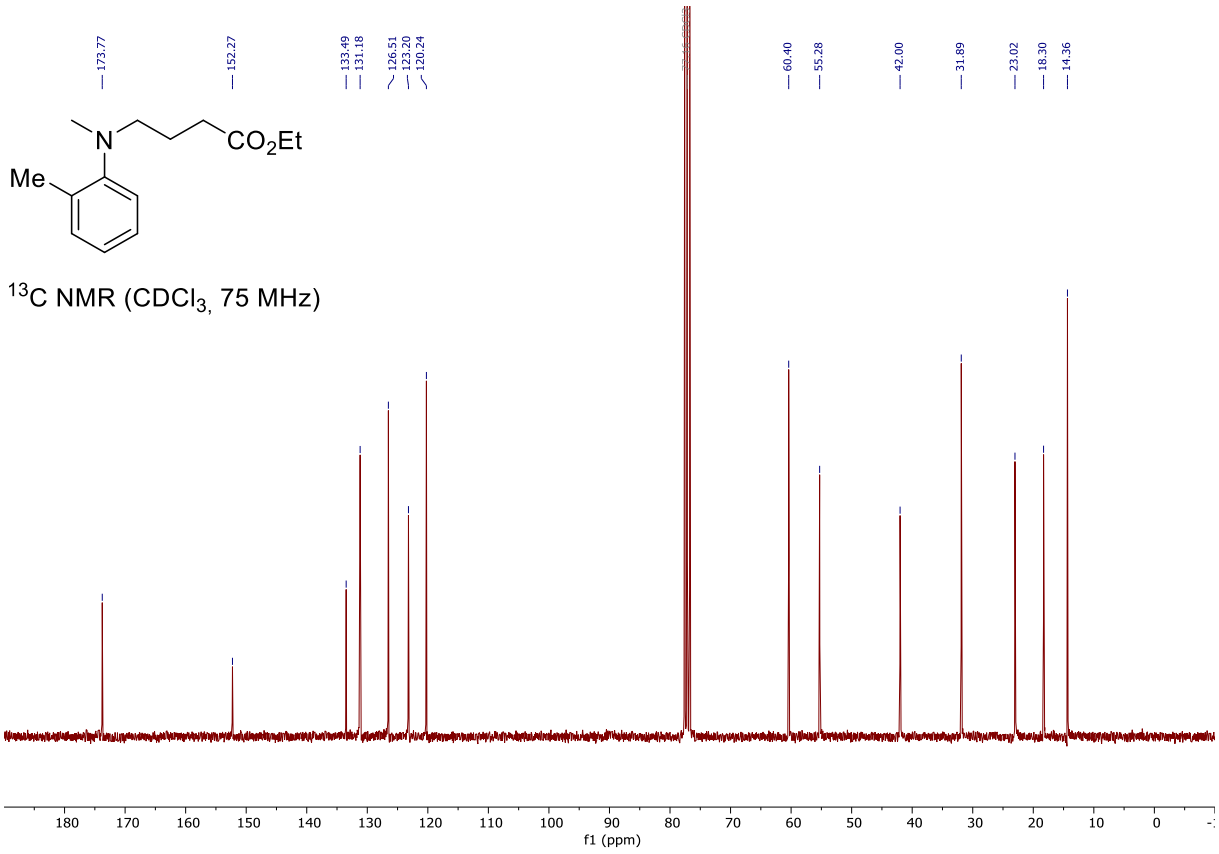
23, ^{1}H NMR ($CDCl_3$, 300 MHz)



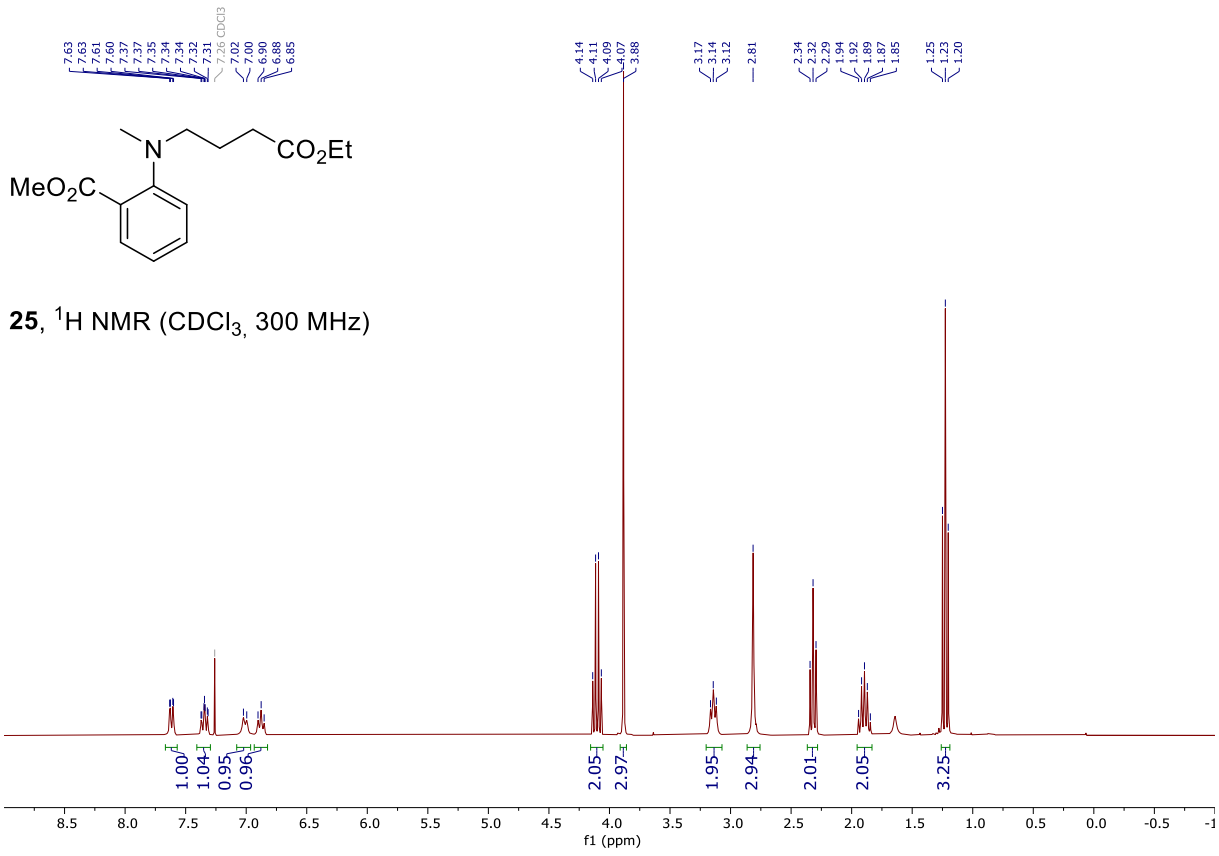
23, ^{13}C NMR ($CDCl_3$, 75 MHz)



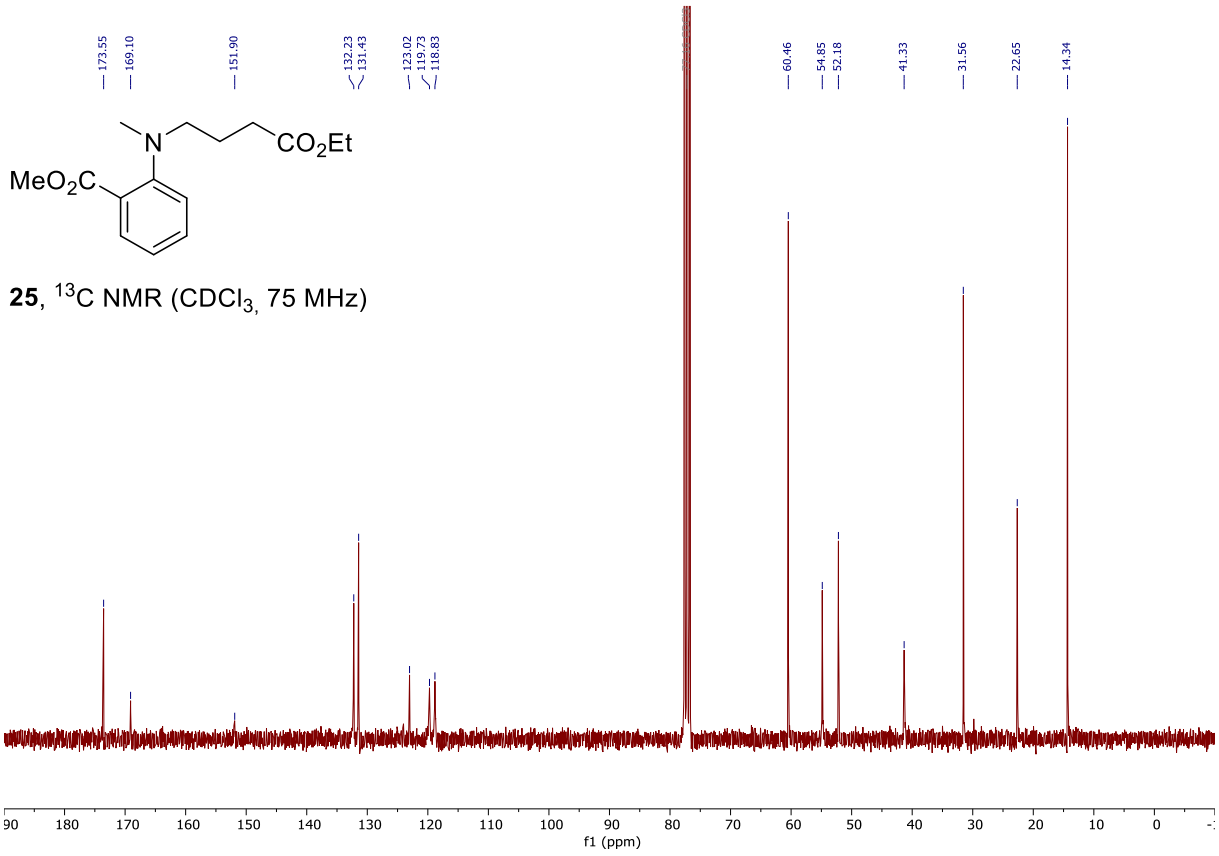
24, ^{1}H NMR ($CDCl_3$, 300 MHz)



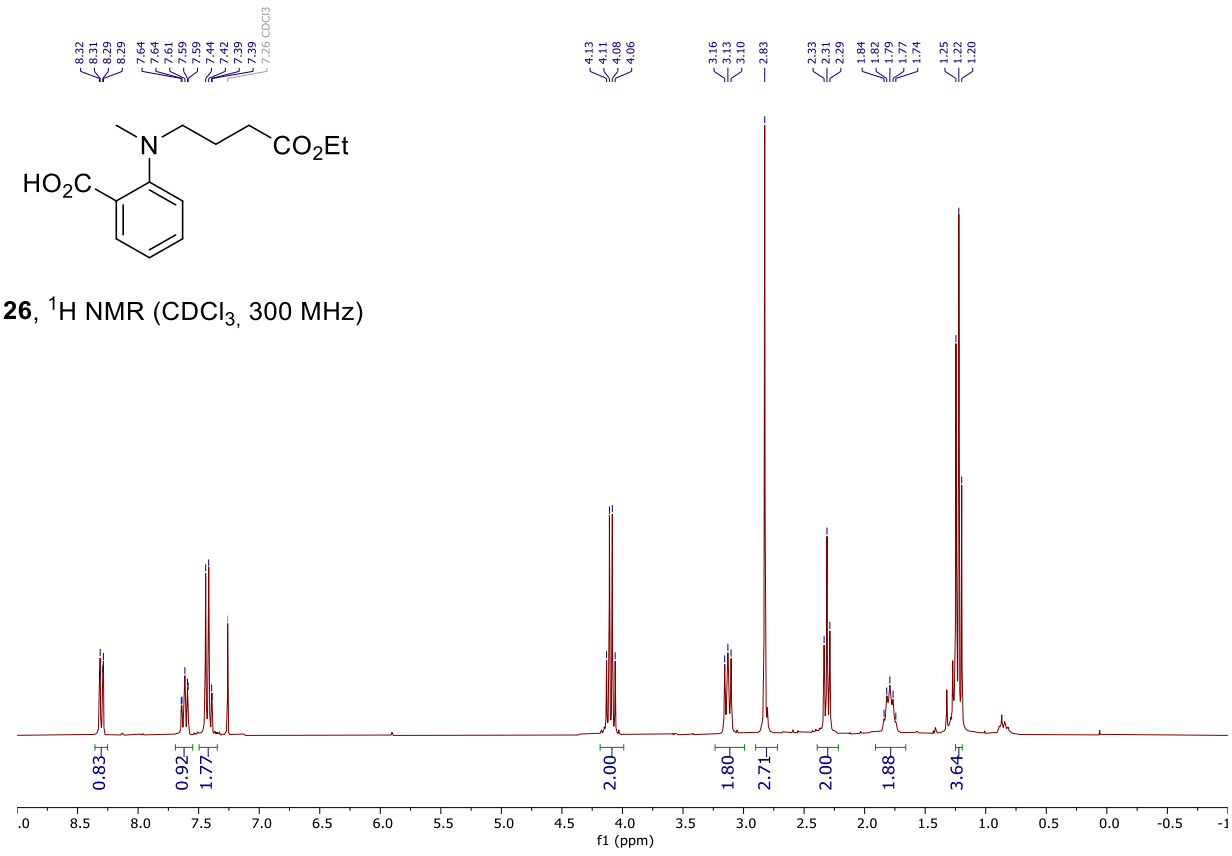
24, ^{13}C NMR ($CDCl_3$, 75 MHz)



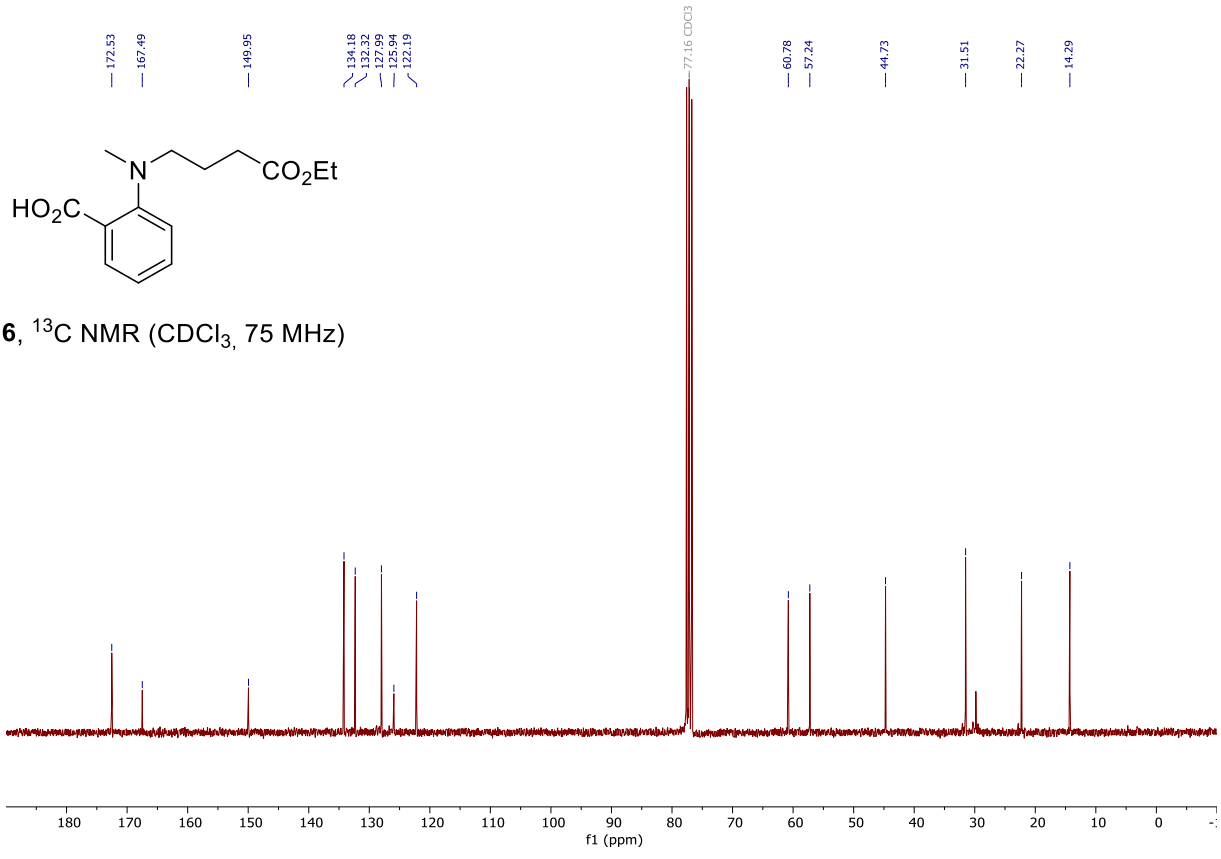
25, ^{1}H NMR ($CDCl_3$, 300 MHz)



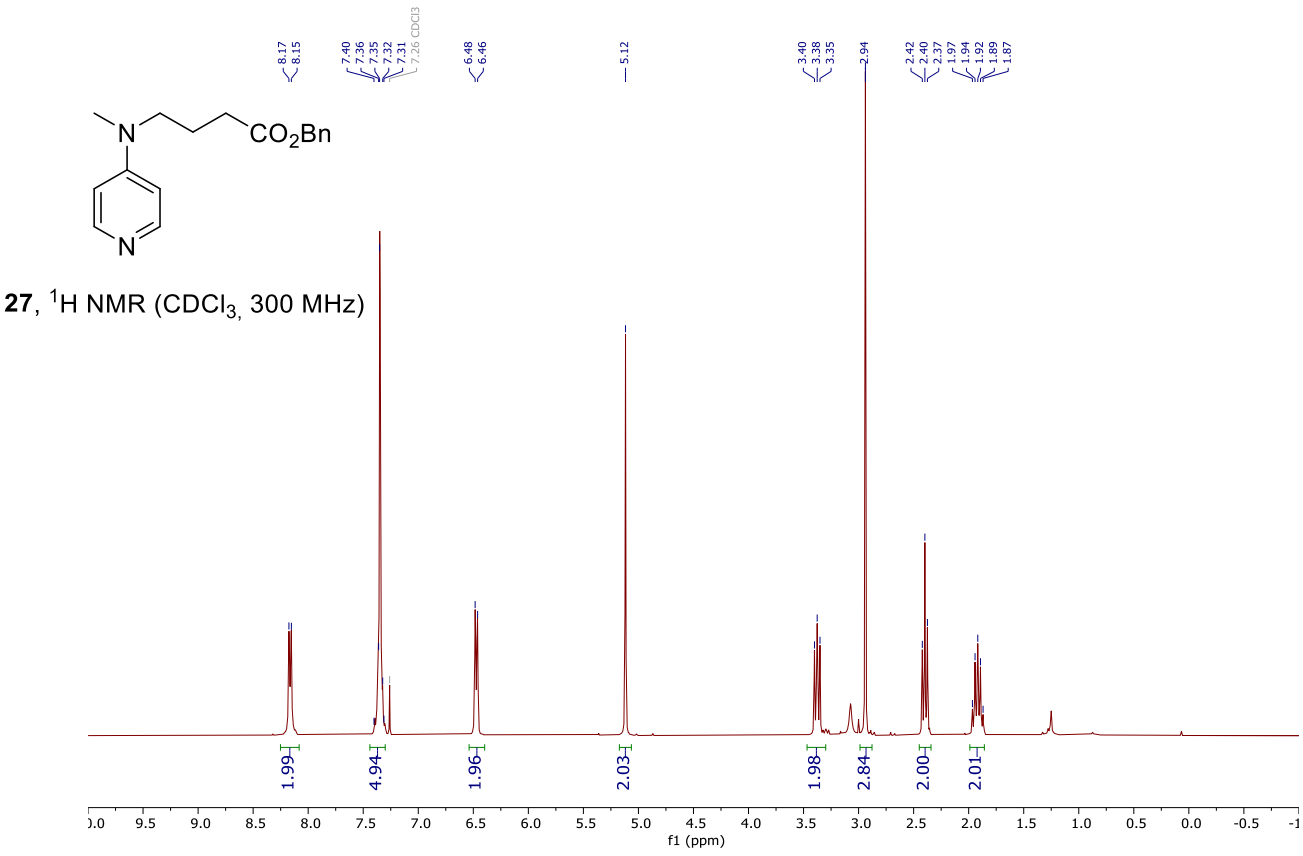
25, ^{13}C NMR ($CDCl_3$, 75 MHz)



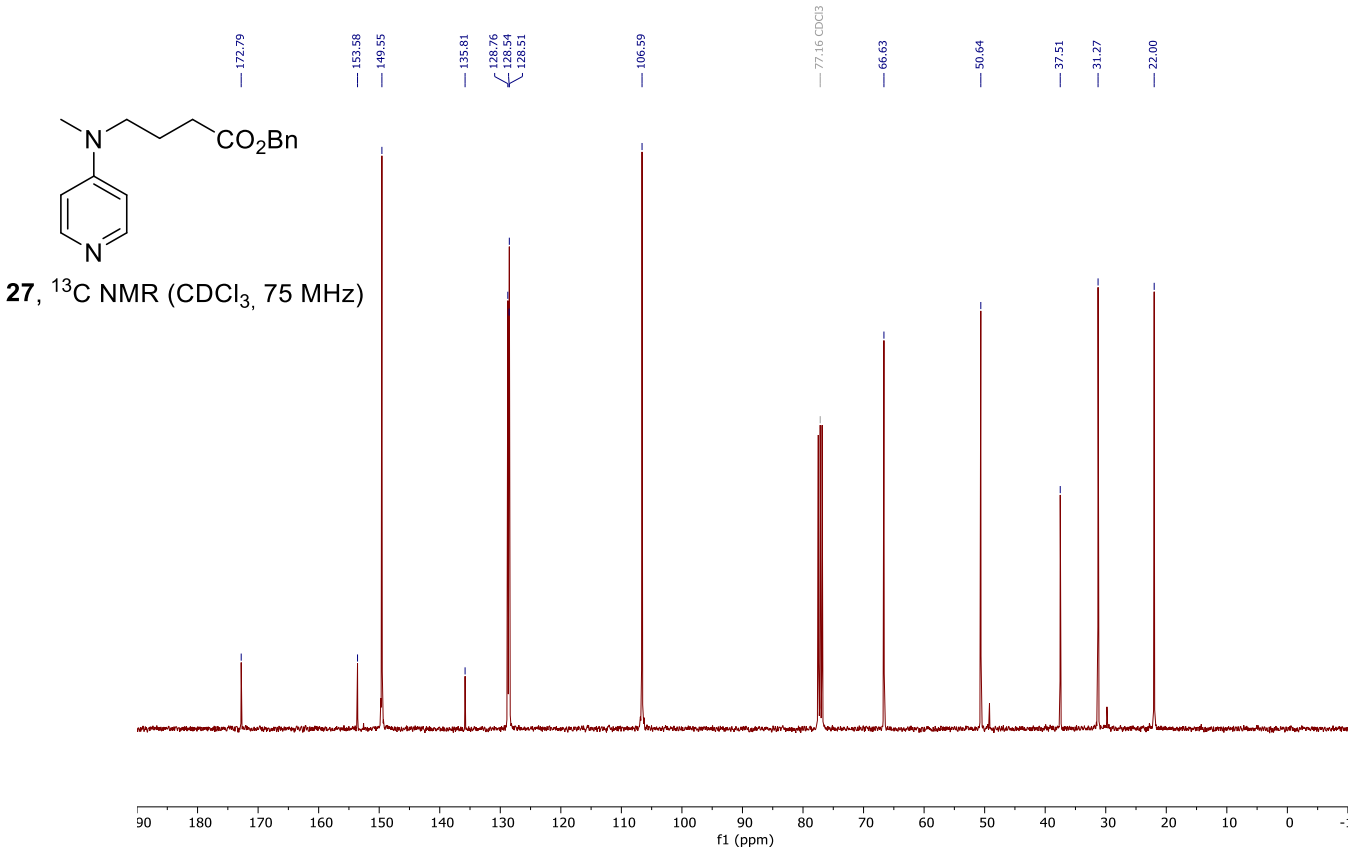
26, ^{1}H NMR ($CDCl_3$, 300 MHz)



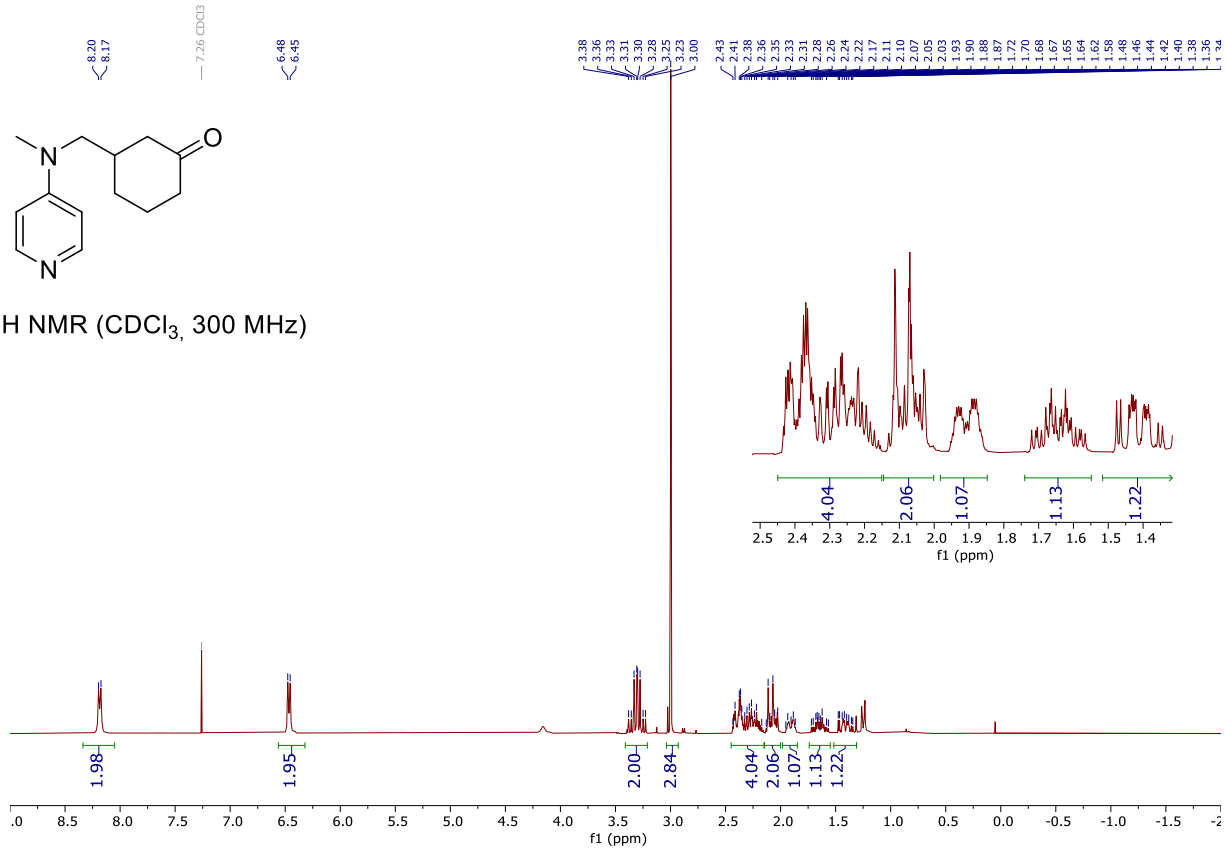
26, ^{13}C NMR ($CDCl_3$, 75 MHz)



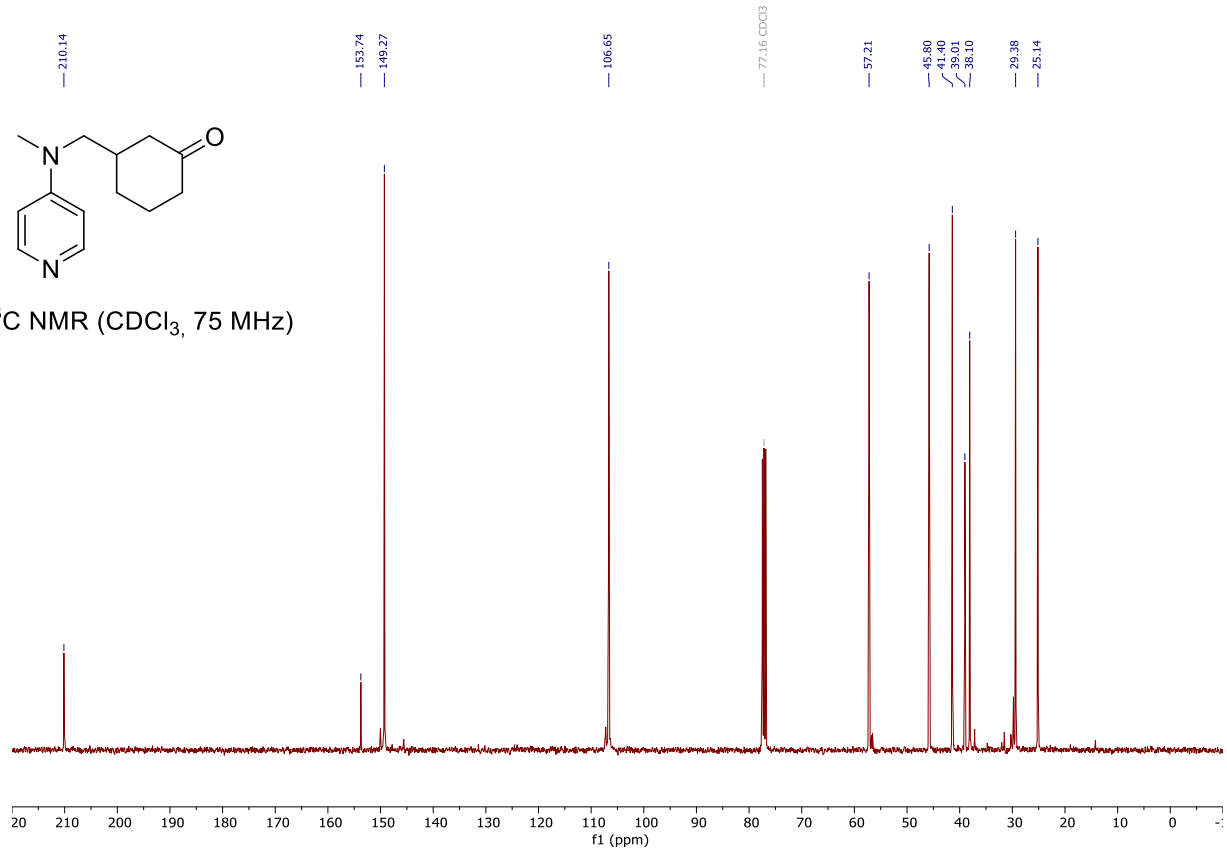
27, ^{1}H NMR ($CDCl_3$, 300 MHz)



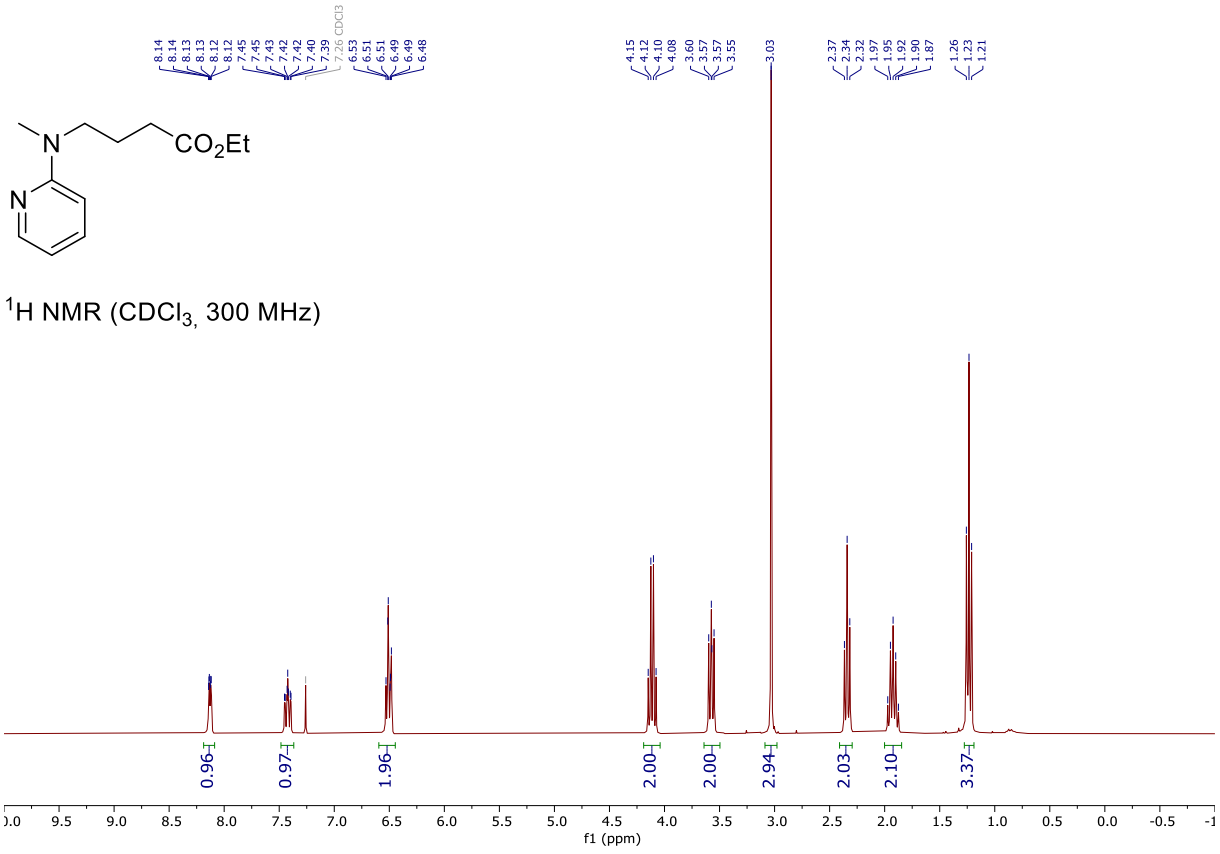
27, ^{13}C NMR ($CDCl_3$, 75 MHz)



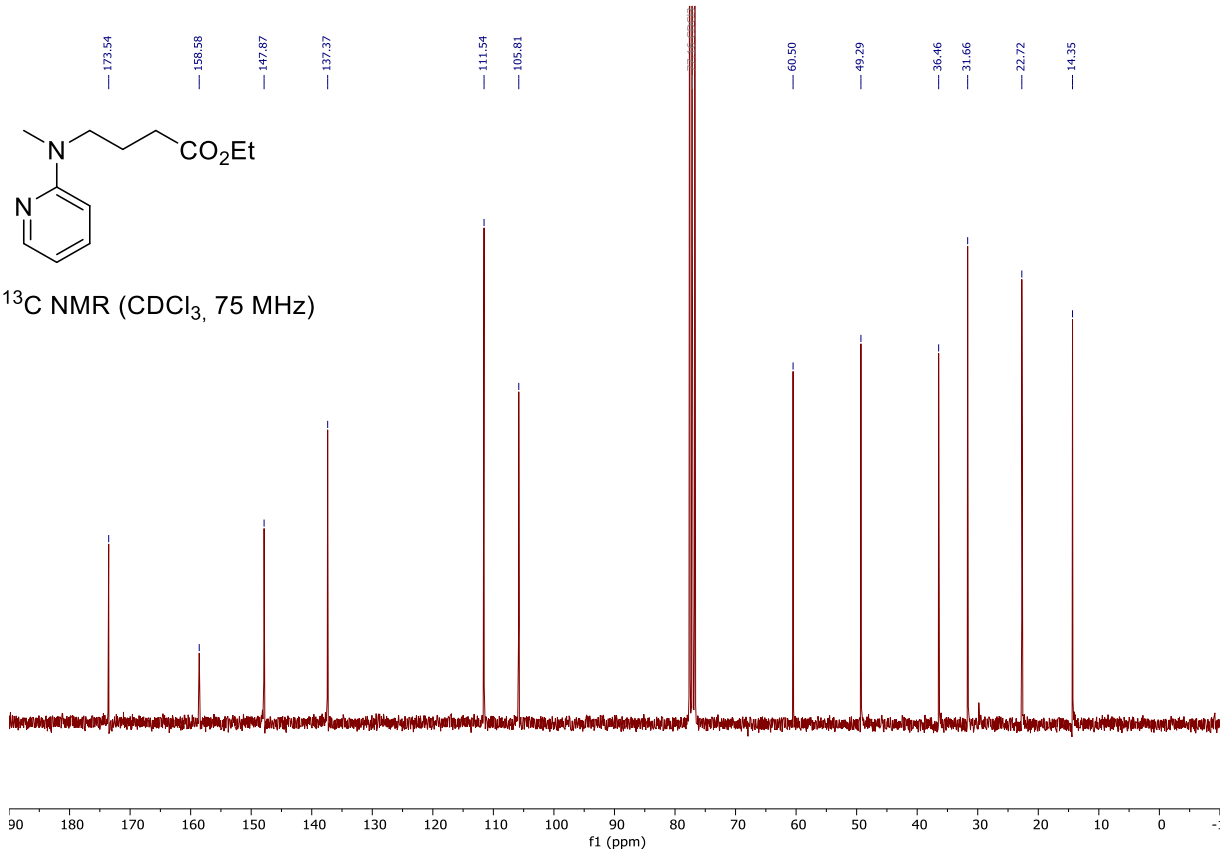
28, ^{1}H NMR ($CDCl_3$, 300 MHz)



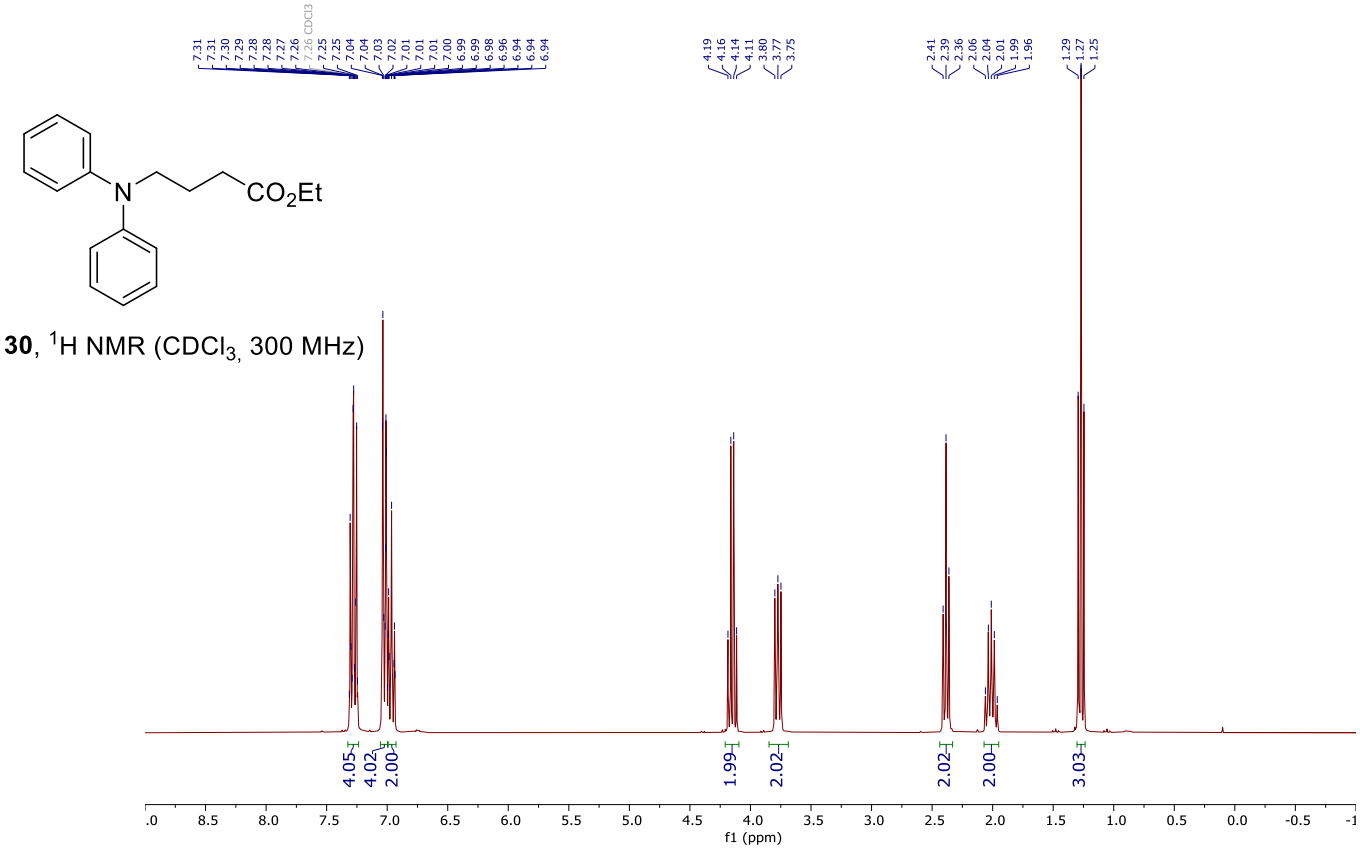
28, ^{13}C NMR ($CDCl_3$, 75 MHz)



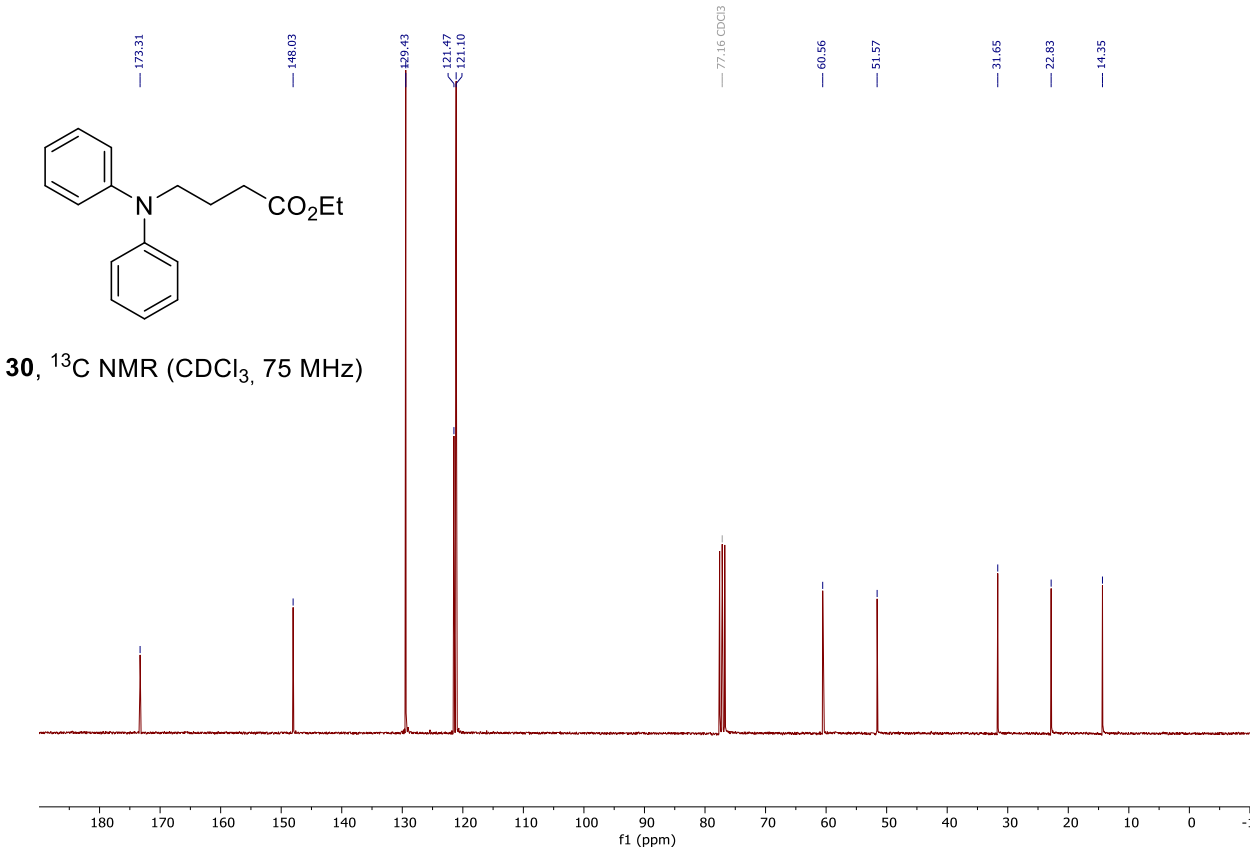
29, ^{1}H NMR ($CDCl_3$, 300 MHz)



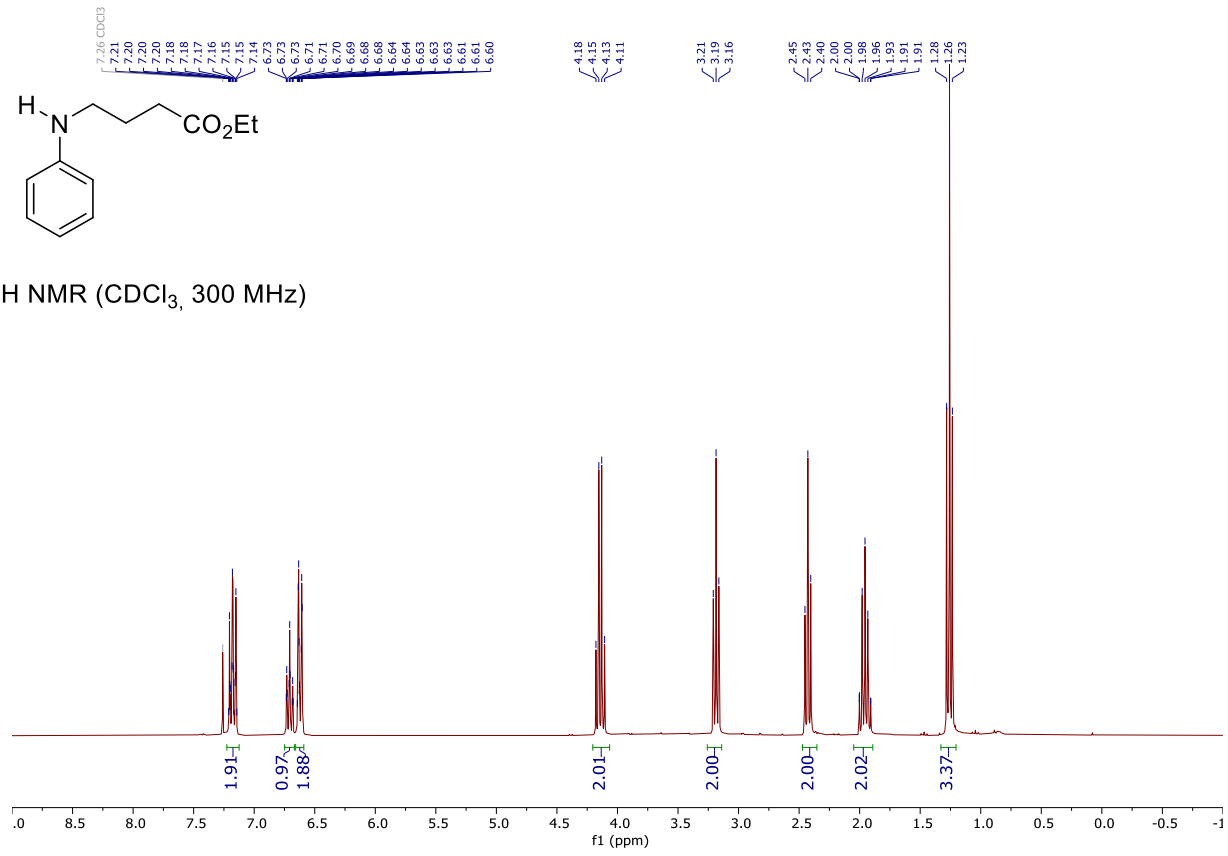
29, ^{13}C NMR ($CDCl_3$, 75 MHz)



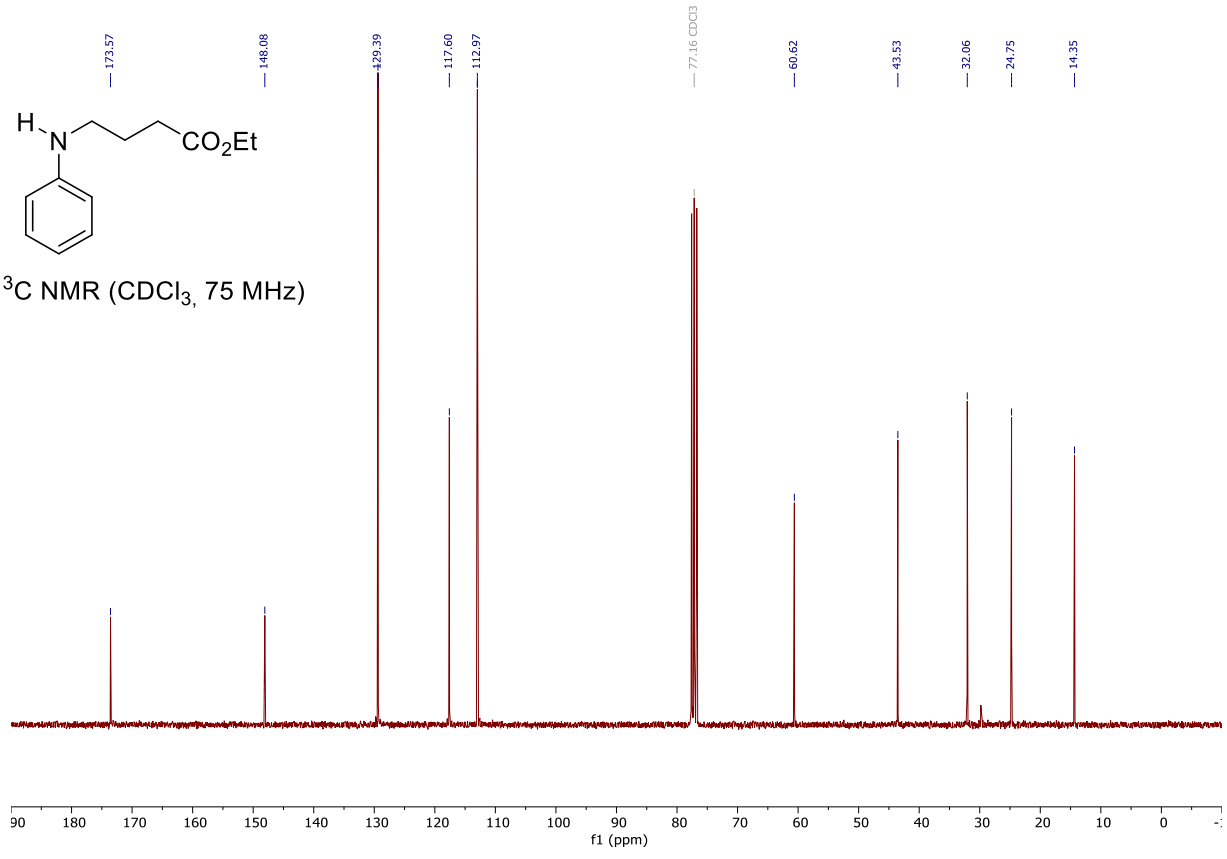
30, ^{1}H NMR ($CDCl_3$, 300 MHz)



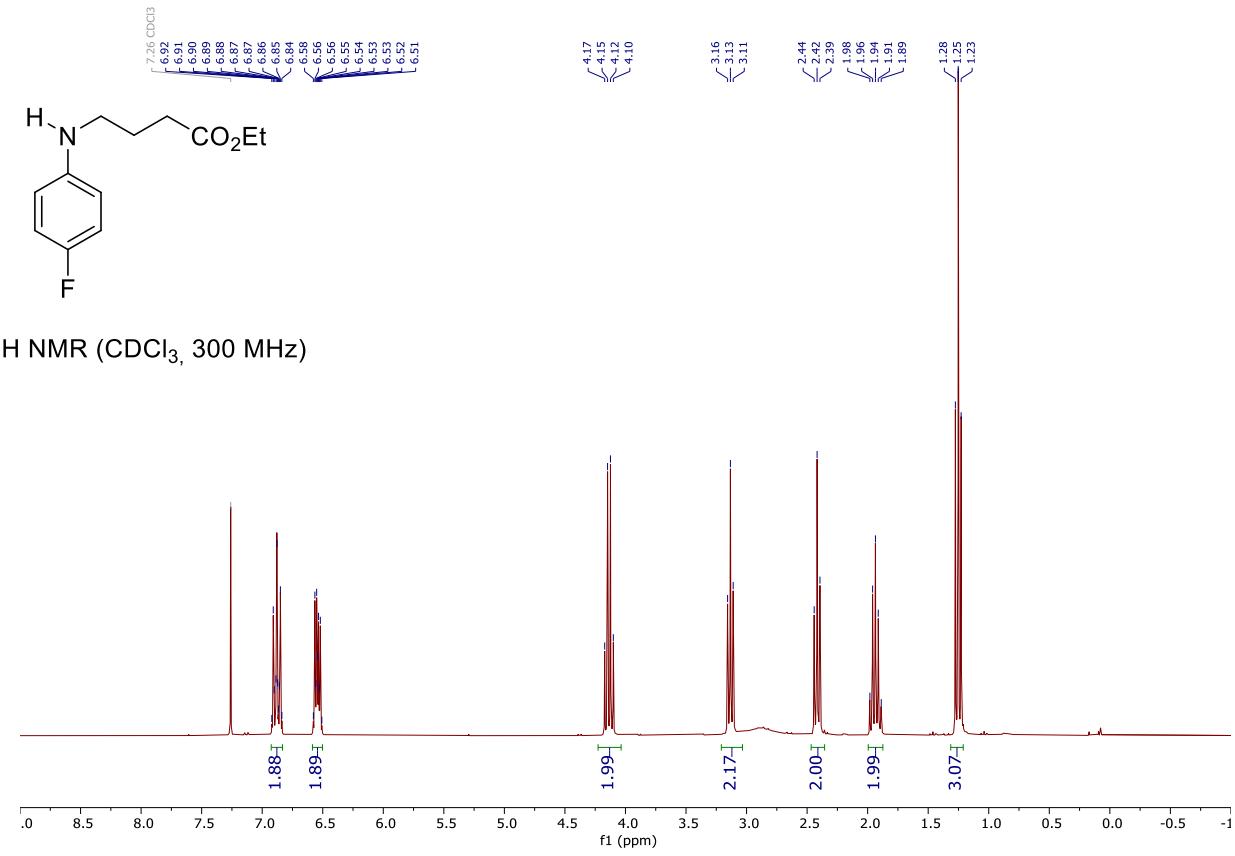
30, ^{13}C NMR ($CDCl_3$, 75 MHz)



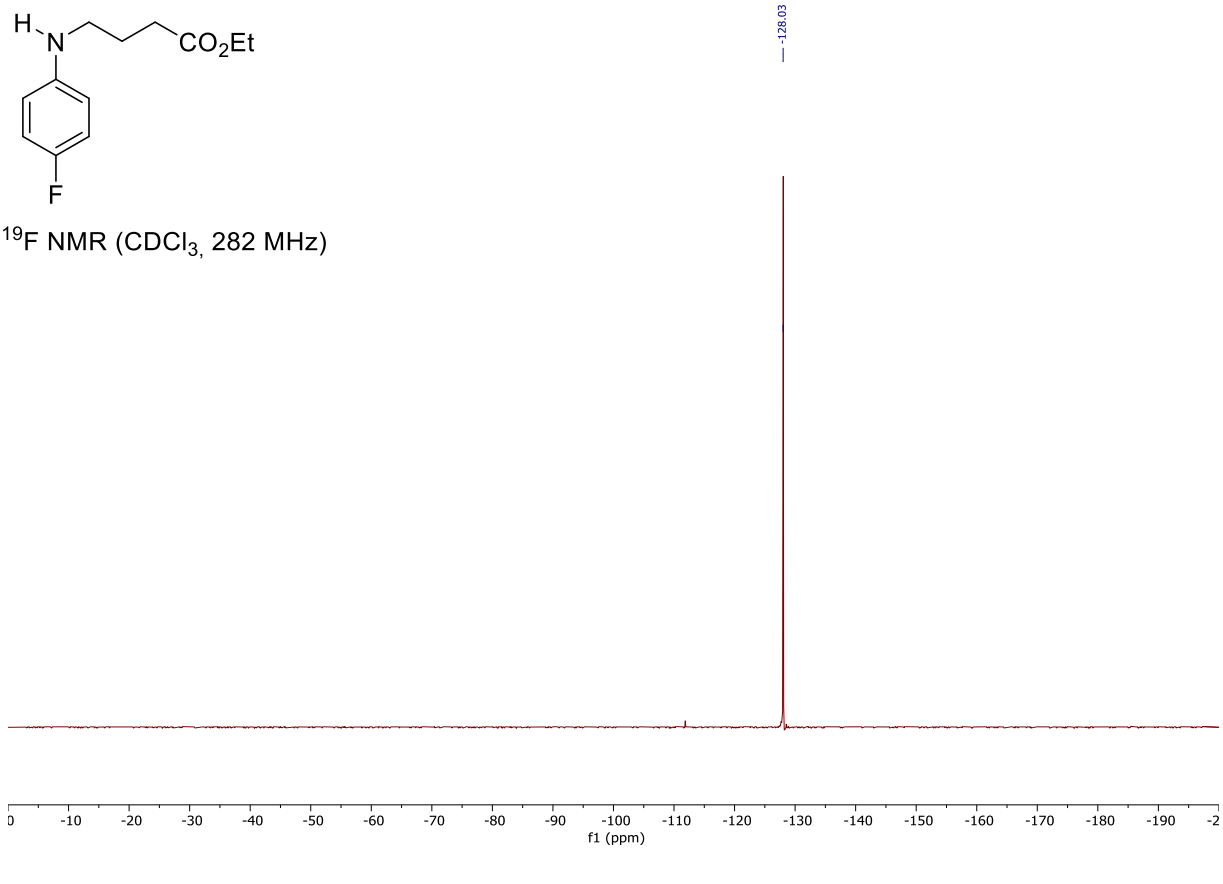
31, ^{1}H NMR ($CDCl_3$, 300 MHz)



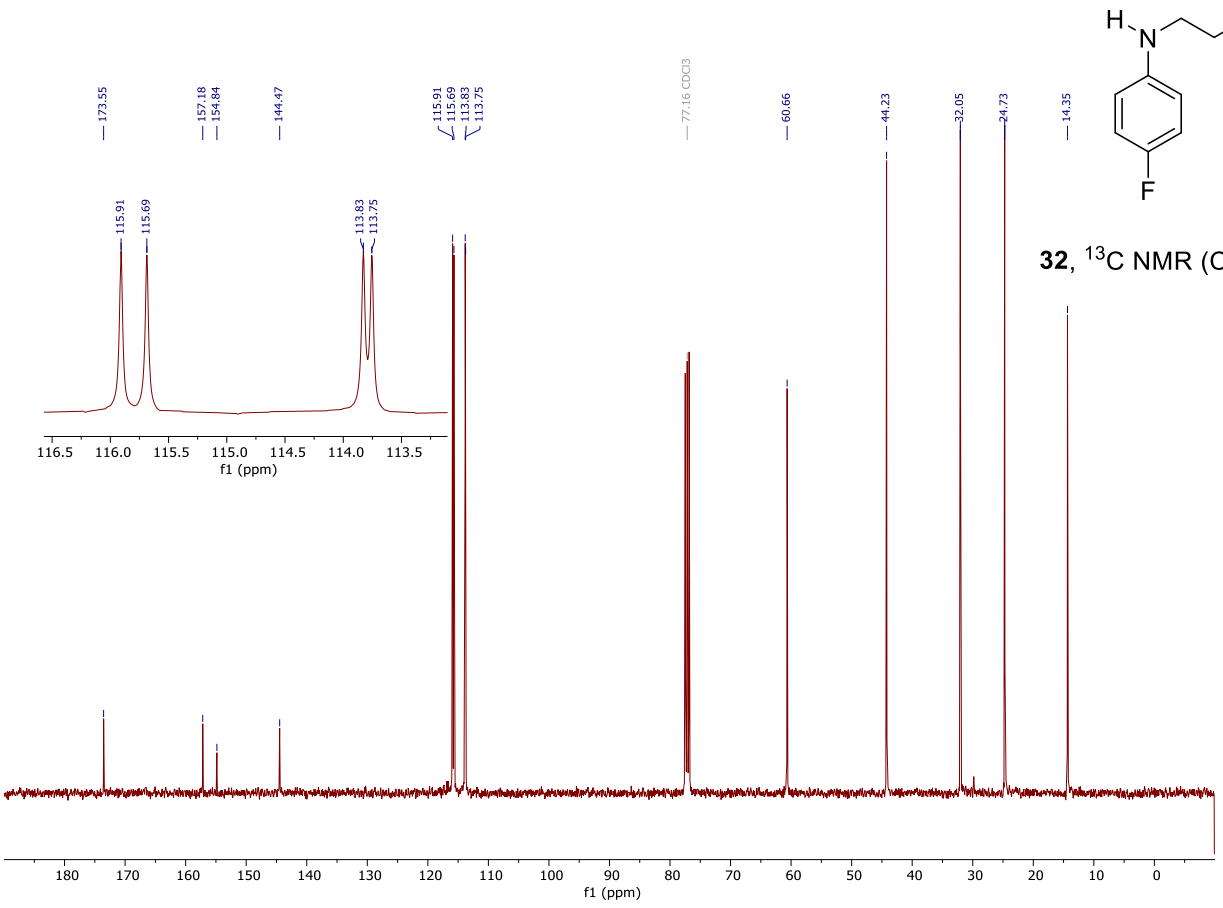
31, ^{13}C NMR ($CDCl_3$, 75 MHz)



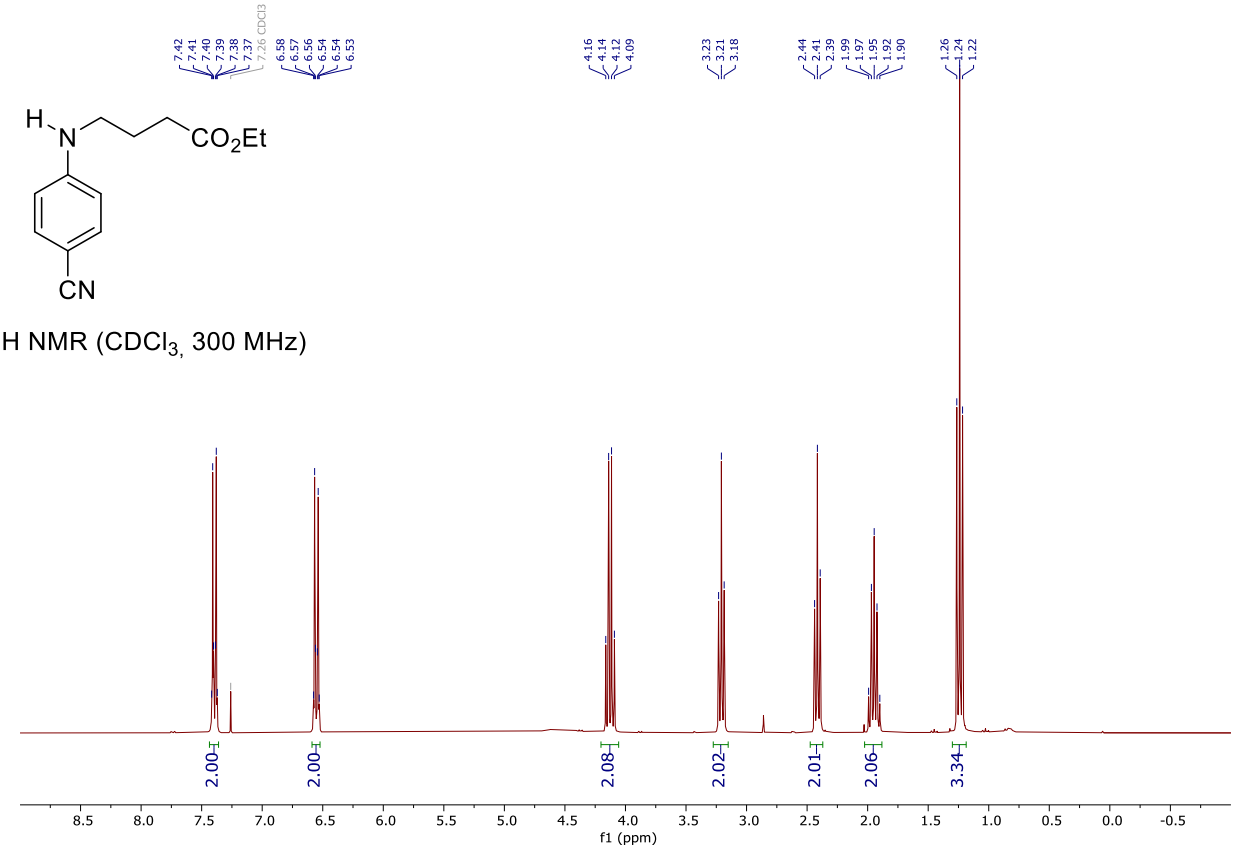
32, ^{1}H NMR ($CDCl_3$, 300 MHz)



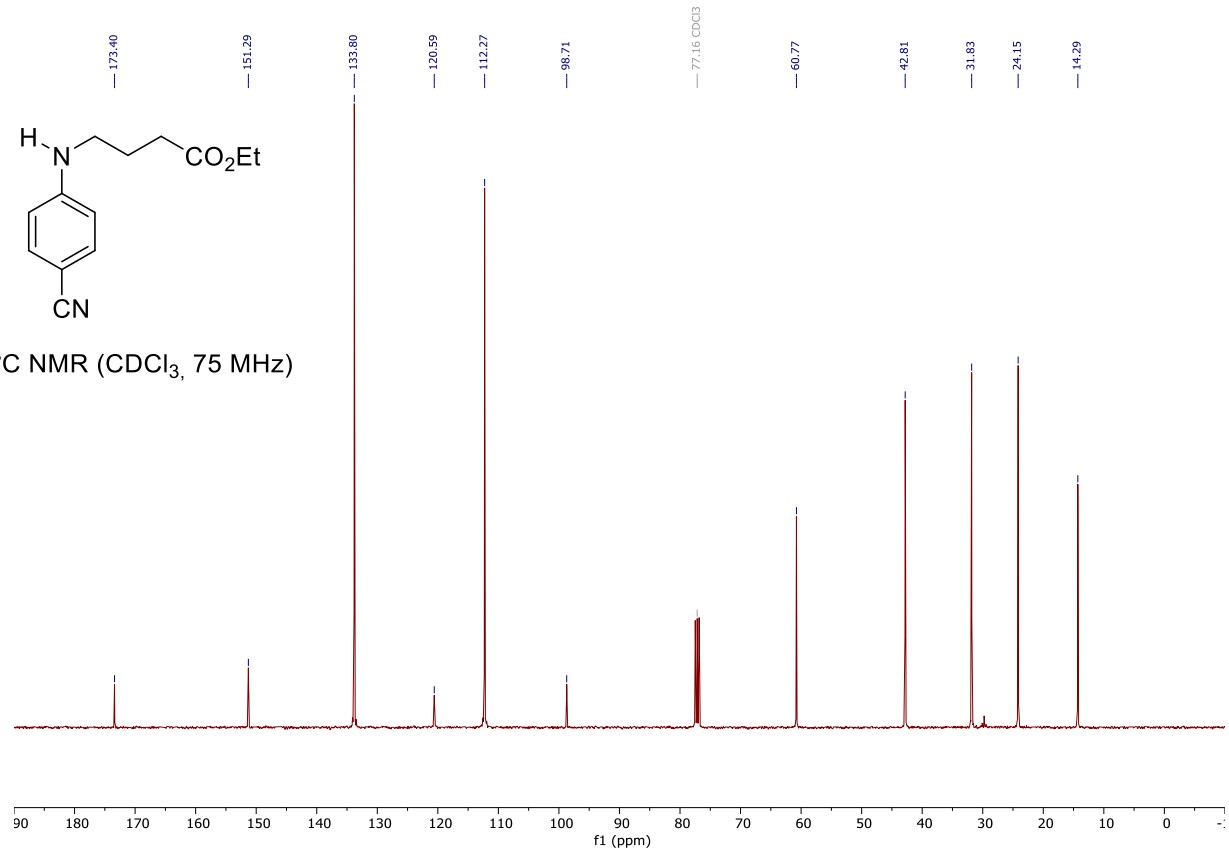
32, ^{19}F NMR ($CDCl_3$, 282 MHz)



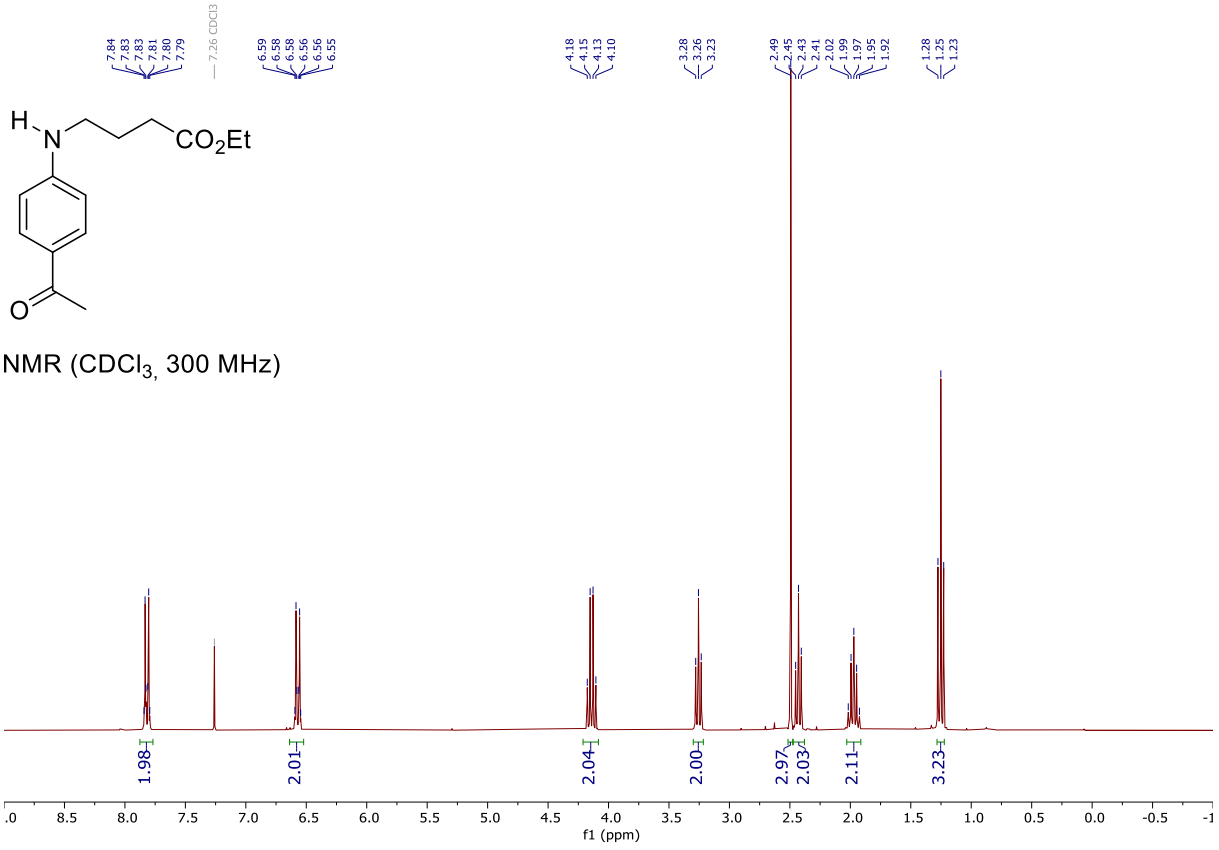
32, ^{13}C NMR ($CDCl_3$, 75 MHz)



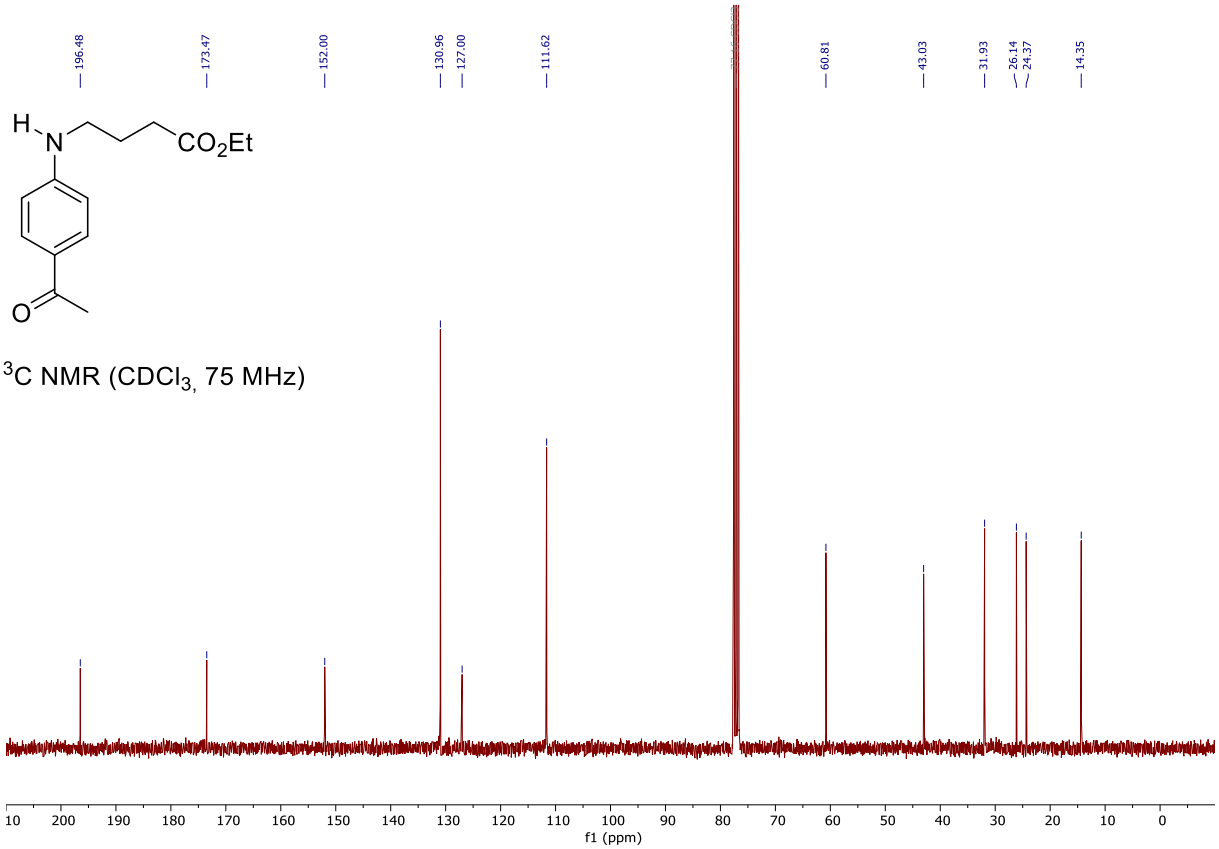
33, ^{1}H NMR ($CDCl_3$, 300 MHz)



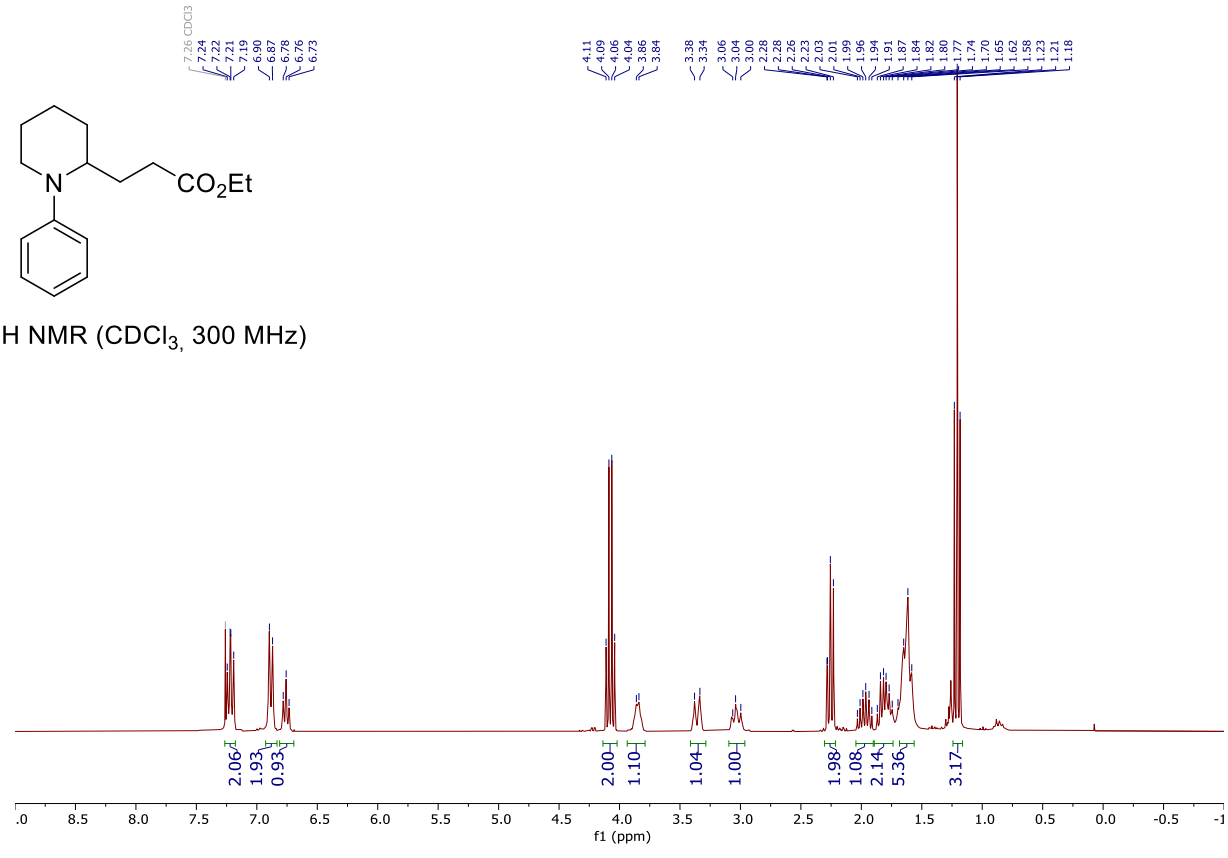
33, ^{13}C NMR ($CDCl_3$, 75 MHz)



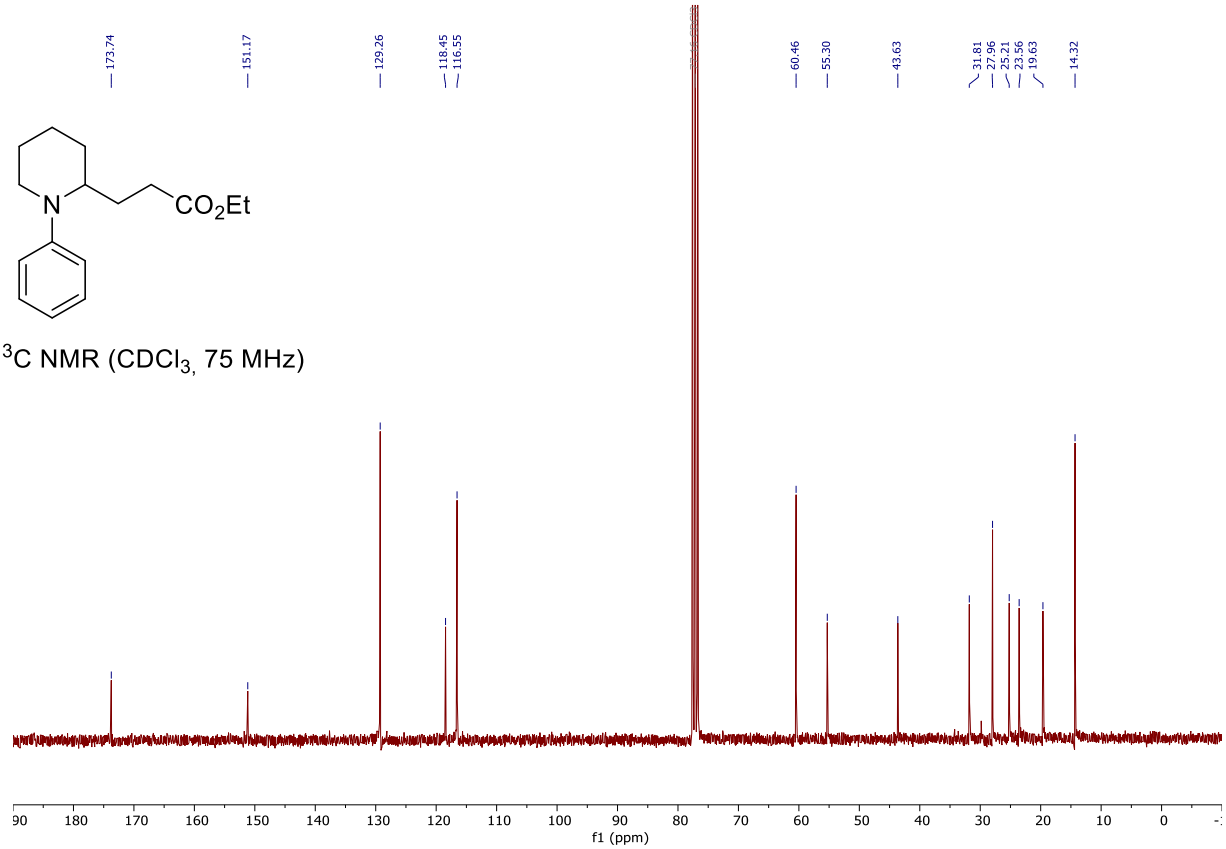
34, ^{1}H NMR ($CDCl_3$, 300 MHz)



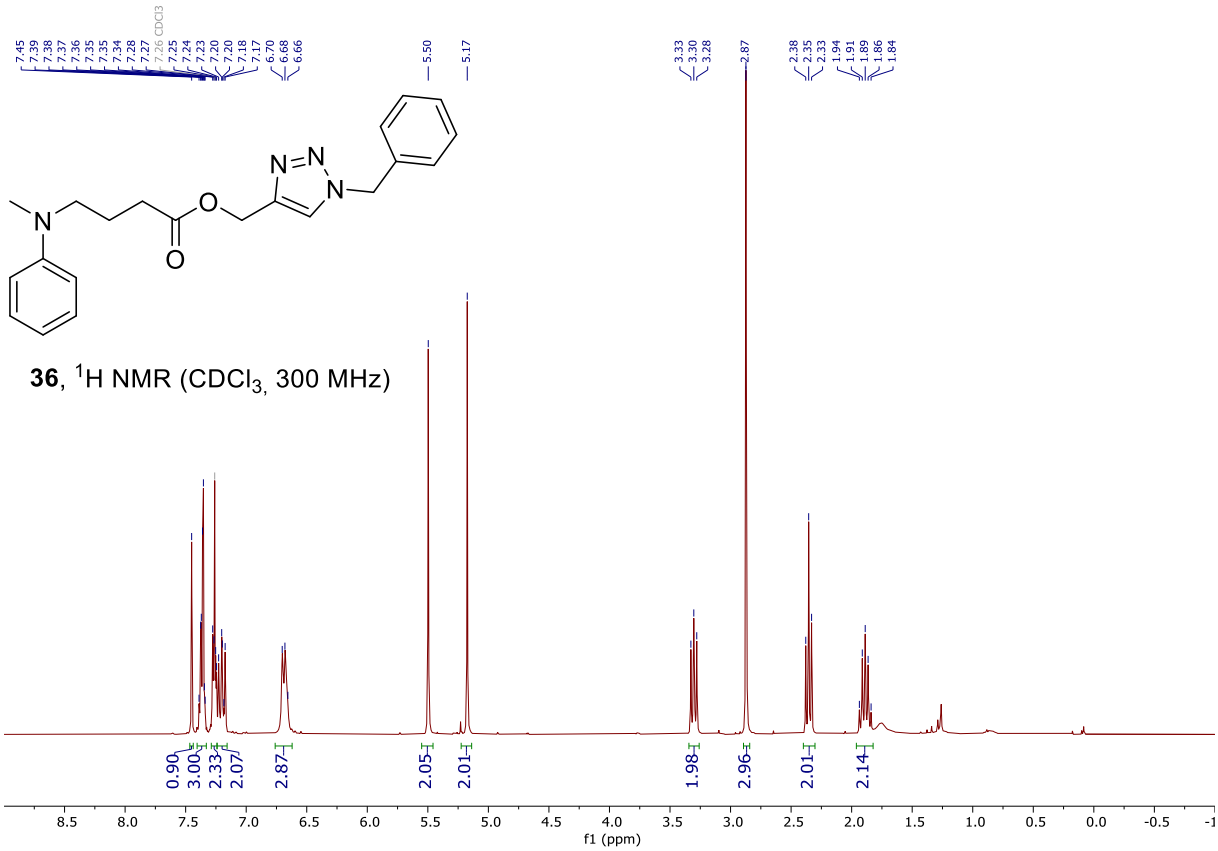
34, ^{13}C NMR ($CDCl_3$, 75 MHz)



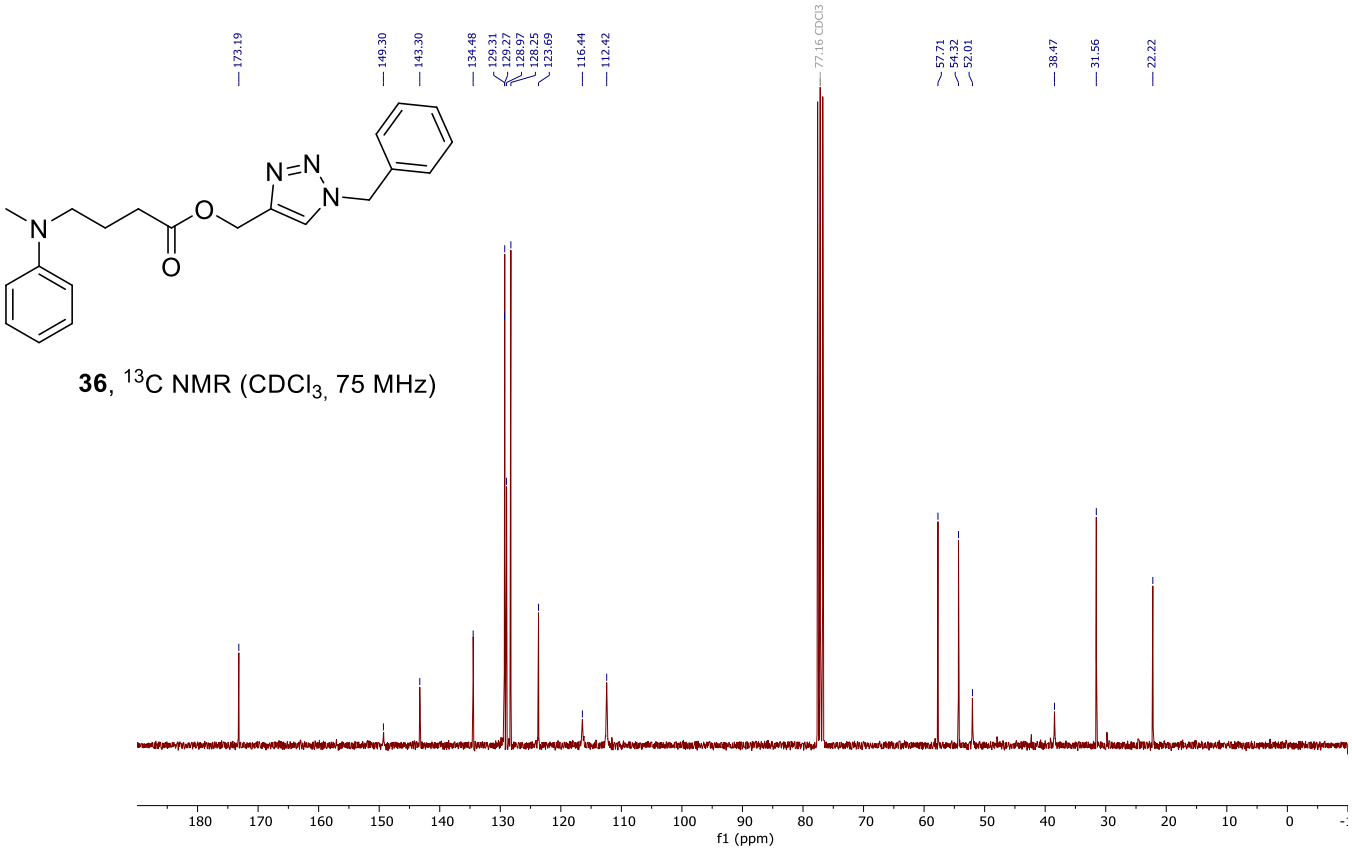
35, ^{1}H NMR ($CDCl_3$, 300 MHz)



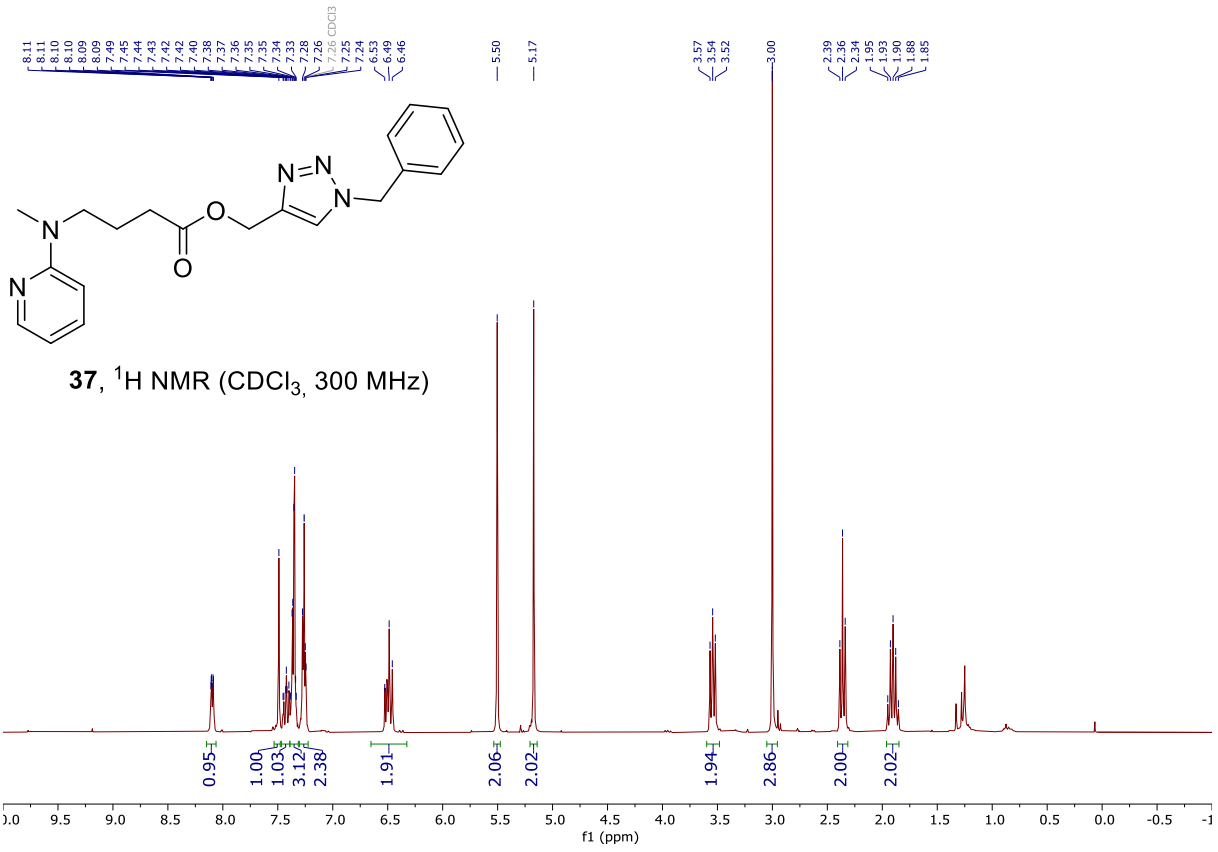
35, ^{13}C NMR ($CDCl_3$, 75 MHz)



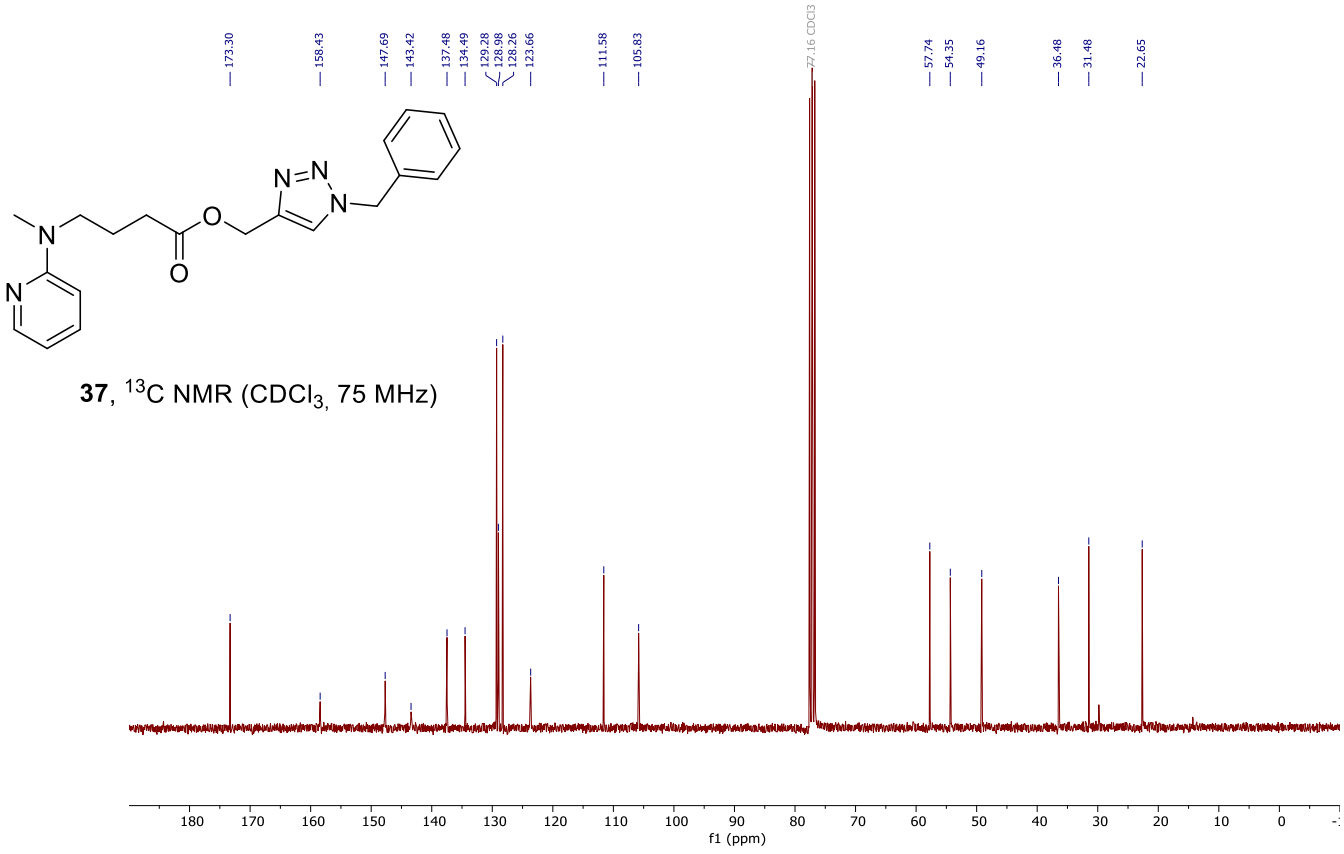
36, ^{1}H NMR ($CDCl_3$, 300 MHz)



36, ^{13}C NMR ($CDCl_3$, 75 MHz)



37, ^{1}H NMR ($CDCl_3$, 300 MHz)



37, ^{13}C NMR ($CDCl_3$, 75 MHz)