Contents

Materials and experimental details

Materials: Acridines **A1** and **A2**,[1] as well as acid **S1**,[2] were prepared as previously described. Commercial anhydrous Cu(hfac)$_2$, and the corresponding hydrated form were used without any detriment to the reaction performance. All other chemicals were used as commercially available.

Experimental equipment: The photoinduced reactions were conducted in borosilicate glass test-tubes (9 and 10 mL capacity) fitted with GL14 and GL18 screw-caps placed in a test-tube rack on a magnetic stirplate that was flanked by two 400 nm 36W LED lights. The temperature in the test-tube rack was 35 °C. Eight parallel reactions arranged in two rows of four tubes were typically carried out in one test-tube rack.

Glovebox work was carried out in a nitrogen-filled LC Technology Solutions LCPW-220 glovebox.

Purification: Column chromatography was performed using CombiFlash Rf-200 (Teledyne-Isco) automated flash chromatography system, as well as manually. Thin layer chromatography was carried out on silica gel-coated glass plates (Merck Kieselgel 60 F254). Plates were visualized under ultraviolet light (254 nm) and using a potassium permanganate stain.

Characterization: ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectra were recorded at 500 MHz (^{1}H), 125 MHz (^{13}C), 202 MHz (^{31}P), 470 MHz (^{19}F), and 160 MHz (^{11}B) on Bruker AVANCE III 500 instruments in $CDCl_3$ or other specified deuterated solvents with and without tetramethylsilane (TMS) as an internal standard at 25 °C, unless specified otherwise. Chemical shifts (δ) are reported in parts per million (ppm) from tetramethylsilane (^{1}H and ^{13}C), $BF_3{\cdot}OEt_2$ (^{11}B), and $CFCl_3$ (^{19}F). Coupling constants (*J*) are in Hz. Proton multiplicity is assigned using the following abbreviations: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint.), septet (sept.), multiplet (m), broad (br).

Infrared measurements were carried out neat on a Bruker Vector 22 FT-IR spectrometer fitted with a Specac diamond attenuated total reflectance (ATR) module.

UV/Vis spectra were recorded on a Cary 5000 UV/Vis/NIR spectrophotometer. EPR spectra were collected at room temperature on a Bruker EMX X-band EPR spectrometer.

General Procedures

General procedure using excess amount of acid (GP1, Method A and Schemes 2–5)

To a 10 mL test-tube equipped with a stirbar, aniline (0.3 mmol), carboxylic acid (0.6−1.5 mmol, 2−5 equiv.), acridine **A1** or **A2** (0.03 mmol, 10 mol%), Cu catalyst (anhydrous or hydrated $Cu(hfac)_2$ or $Cu(acac)_2$) (0.03 mmol, 10 mol%), and oxidant (DTBP or DCP) (0.45−0.6 mmol, 1.5−2 equiv.) were added. An organic solvent (ethyl acetate or trifluorotoluene or chlorobenzene) (1.5−4.5 mL) was then added and the reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light ($\lambda = 400$ nm) while stirring for 12−36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel to give the amine product.

General procedure using excess amount of aniline (GP2, Method B and Schemes 2–5)

To a 10 mL test-tube equipped with a stirbar, aniline (0.75 mmol, 2.5 equiv.), carboxylic acid (0.3 mmol), acridine **A1** or **A2** (0.03 mmol, 10 mol%), Cu catalyst (anhydrous or hydrated $Cu(hfac)_2$ or $Cu(acac)_2$) (0.03 mmol, 10 mol%), and oxidant (DTBP or DCP) (0.45−0.6 mmol, 1.5−2 equiv.) were added. An organic solvent (ethyl acetate, trifluorotoluene or chlorobenzene) (1.5−4.5 mL) was then added and the reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light ($\lambda = 400$ nm) while stirring for 12−36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted

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with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel to give the amine product.

Mechanistic studies

Cyclic voltammetry measurements

Cyclic voltammetry was carried out on a BASi Epsilon potentiostat using a three-electrode cell with a glassy carbon working electrode, a 1M KCl Ag|AgCl reference electrode, and a platinum counter electrode at a 50 mV·s^{-1} scan rate. with a degassed 50mM solution of *N*-methyl-*p*-anisidine or tetrabutylammonium cyclohexanecarboxylate in acetonitrile with tetrabutylammonium hexafluorophosphate (0.15M) as an electrolyte. The half-wave potential for the Fc^+|Fc redox couple was determined to be 0.39 V vs SCE. The reported oxidation potential (E_{ox} = 0.52 V vs SCE in MeCN) is the inflection point potential, since inflection point potentials were shown to provide optimal estimates of half-wave potentials for quasireversible and irreversible redox systems.[3]

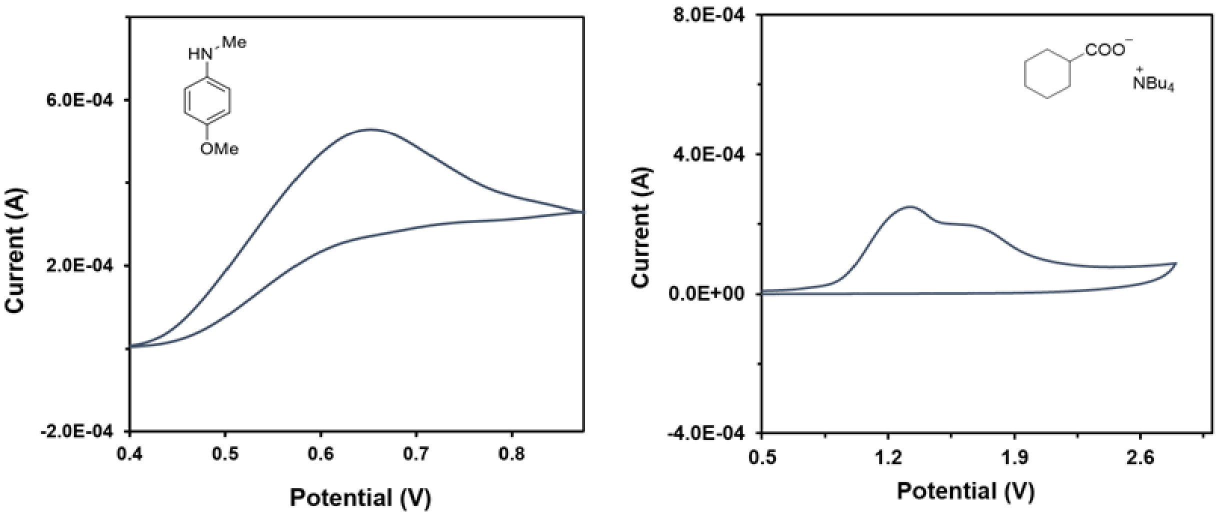

Figure S1. Cyclic voltammograms of *N*-methyl-*p*-anisidine and tetrabutylammonium cyclohexanecarboxylate.

Job plot analysis of $Cu(hfac)_2$–aniline binding stoichiometry

The binding stoichiometry of $Cu(hfac)_2$ and aniline was determined by a Job plot analysis constructed from the relative absorbance of the complex at 374 nm in UV-Vis spectra. Solutions with varied ratios of $Cu(hfac)_2$ and aniline were prepared in degassed ethyl acetate, and their total concentration was kept constant at 5mM. The relative absorbance of the mixture was calculated by subtracting the absorbances of $Cu(hfac)_2$ and aniline from those of the mixtures.[4] Maximum of ΔA at $\chi(Cu(hfac)_2) = 0.5$ indicates a 1 : 1 stoichiometry of the $Cu(hfac)_2$–aniline complex in the solution. This conclusion is independently corroborated by the Job plot analysis of EPR data for the $Cu(hfac)_2$–aniline system.

Table S1. Measured absorbance and relative absorbance values for the Job plot analysis.

$\chi(Cu(hfac)_2)$	A	ΔA
0	0.00654	0
0.1	0.28723	0.20296
0.2	0.46188	0.29988
0.3	0.63774	0.3980
0.4	0.78975	0.47229
0.5	0.93858	0.54339
0.6	0.93359	0.46067
0.7	0.88320	0.33255
0.8	0.86047	0.23208
0.9	0.80837	0.10226
1	0.78384	0

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Cu(hfac)$_2$–Aniline association constant determination by nonlinear regression analysis

The Cu(hfac)$_2$–aniline association constant was determined by means of UV-Vis spectroscopy. 0.2mM Solutions of Cu(hfac)$_2$ with varied amounts of aniline (1, 3, 5, 10, 20, 30, 50, 70, 80, 100 equiv.) in degassed ethyl acetate were prepared. The difference UV-Vis absorption spectra were obtained by subtracting the absorbances of Cu(hfac)$_2$ and aniline from those of the mixtures. Changes in absorbance at 384 nm were used to determine the equilibrium constant according to a nonlinear modified Benesi–Hildebrand equilibrium model,[5] giving the association constant of 54 M^{-1}.

Table S2. Relative absorbance values for the nonlinear regression analysis.

Equiv. of aniline	[aniline], M	ΔA
1	0.0002	0.00034
3	0.0006	0.01846
5	0.001	0.01508
10	0.002	0.02482
20	0.004	0.06438
30	0.006	0.08701
50	0.01	0.12438
70	0.014	0.15181
80	0.016	0.16593
100	0.02	0.17975

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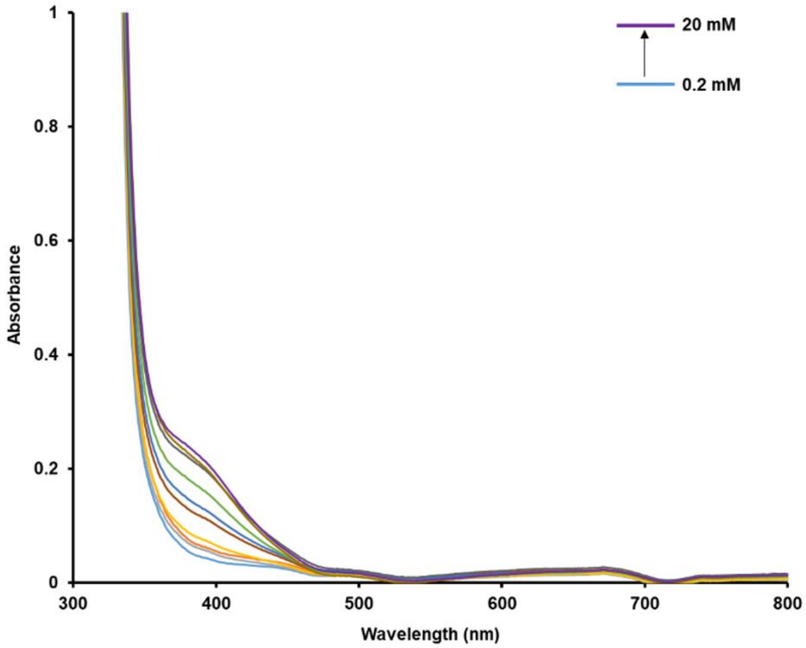

Figure S2. UV-Vis spectra of 0.2mM solutions of Cu(hfac)$_2$ in EtOAc in the presence of varied amounts of aniline (0.2–20mM).

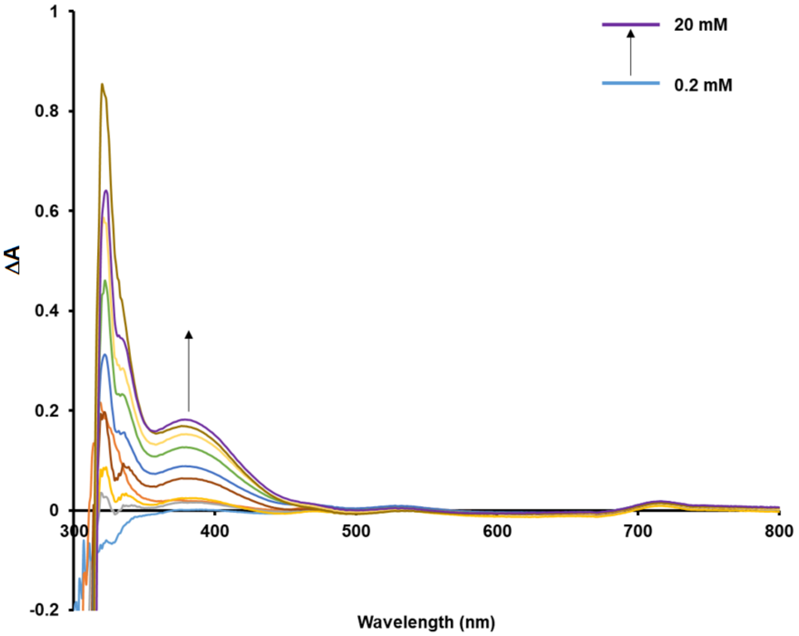

Figure S3. Difference UV-Vis spectra of 0.2mM solutions of Cu(hfac)$_2$ in EtOAc in the presence of varied amounts of aniline (0.2–20mM).

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EPR Investigation of $Cu(hfac)_2$–aniline complexation

In order to independently corroborate the 1 : 1 stoichiometry of the $Cu(hfac)_2$–aniline complex in solution, EPR spectra were collected in benzene solutions with varied molar fractions of $Cu(hfac)_2$ and a total concentration of $Cu(hfac)_2$ and aniline of 50mM (Figure S4). The Job plot was then constructed (Figure S5) as described for the UV-Vis study. With the ΔA maximum at $\chi(Cu(hfac)_2) = 0.5$, the EPR studies confirmed the 1 : 1 stoichiometry of the $Cu(hfac)_2$–aniline complex.

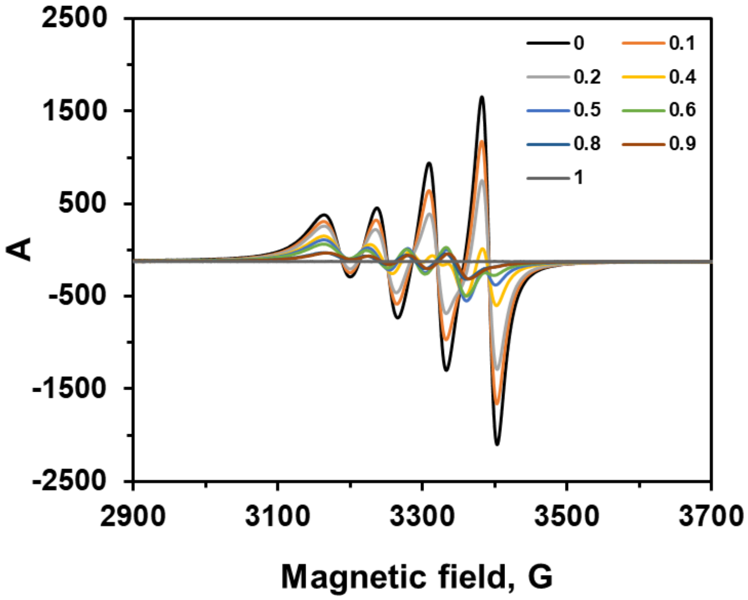

Figure S4. EPR spectra of $Cu(hfac)_2$ in the presence of aniline with combined total concentration of 10 mM in benzene at room temperature. The molar fractions of $Cu(hfac)_2$ are color-coded in the upper right quadrant of the plot.

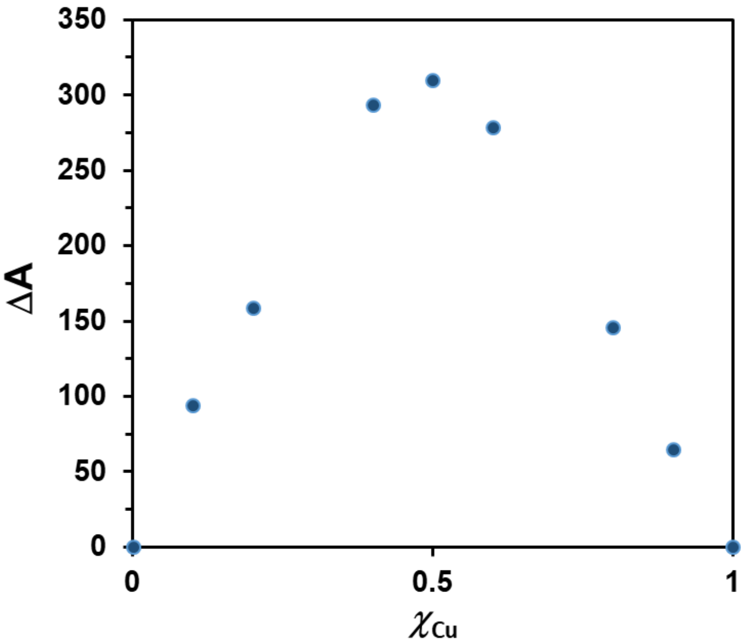

Figure S5. Job plot of the Cu(hfac)$_2$–aniline system at 3265.94 G.

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Hammett plot analysis of the direct decarboxylative *N*-alkylation

Reactions were carried out as described in GP1 with 1,4-dimethoxybenzene as an internal standard and aliquots were taken and analyzed by means of ^{1}H NMR spectroscopy at 30, 60, 120, 180, 240, and 300 min (Figure S6 and Table S3).

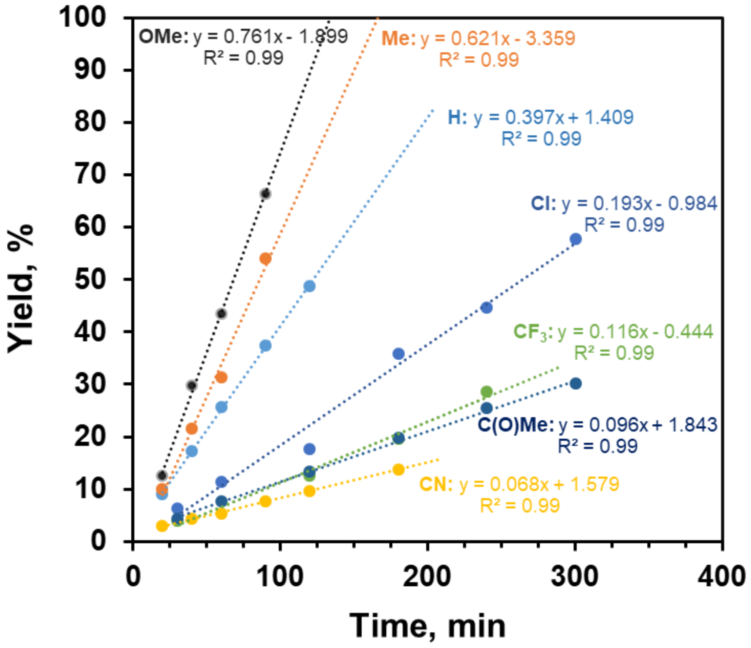
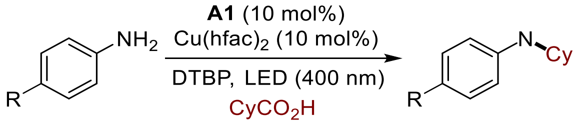


Figure S6. Time course plot of the DDA reaction of *para*-substituted anilines with cycloxexanecarboxylic acid.

Table S3. Experimental kinetic data for the Hammett plot analysis of the DDA reaction of *para*-substituted anilines with cyclohexanecarboxylic acid.

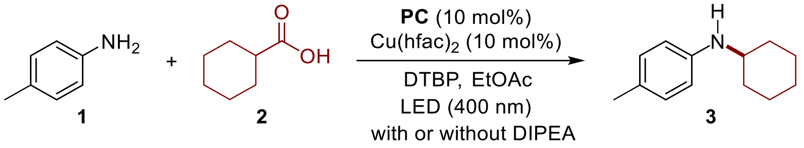


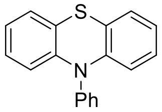
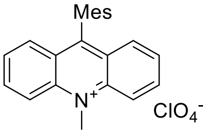
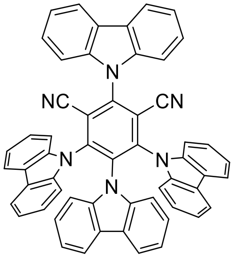
Substituent	**σ**[6]	**log(k_R/k_H)**
H	0	0
Me	–0.17	0.194
OMe	–0.27	0.282
Cl	0.23	–0.314
CF_3	0.54	–0.533
C(O)Me	0.50	–0.615
CN	0.66	–0.769

Additional discussion of the DDA reaction mechanism

Other photocatalysts: Replacement of acridine photocatalysts **A1** and **A2** with other types of photocatalysts (Table S4), including organic photocatalysts (entries 1–3), as well as ruthenium and iridium photocatalysts (entries 4–9) in the presence and in the absence of DIPEA, did not lead to formation of product **3**. These results are in in line with the prior detailed experimental and computational studies of the visible light-driven acridine photocatalysis that point to the importance of the directional character of the acridine–carboxylic acid interaction for a successful merger of the direct photocatalytic decarboxylation with other catalytic processes.[1]

Table S4. DDA reaction performance with other photocatalysts with and without added DIPEA.[a]



Entry	Photocatalyst (**PC**)	Yield, %[b]
1		0
2		0
3		0
4	$[Ru(bpy)_3](BF_4)_2$	0
5	$[Ru(p\text{-}CF_3\text{-}bpy)_3](BF_4)_2$	0
6	$[Ru(bpm)_3](BF_4)_2$	0
7	$Ir(p\text{-}CF_3ppy)_3$	0
8	$Ir(dFppy)_3$	0
9	$[Ir\{dF(CF_3)ppy\}_2(dtbpy)]PF_6$	0

[a] Reaction conditions: aniline **1** (0.3 mmol), carboxylic acid **2** (0.75 mmol), photocatalyst (10 mol%), $Cu(hfac)_2$ (10 mol%), DTBP (0.6 mmol), with or without DIPEA (2 equiv.), EtOAc (4.5 mL), LED (400 nm), 12 h. [b] Determined by ^1H NMR with 1,4-dimethoxybenzene as an internal standard.

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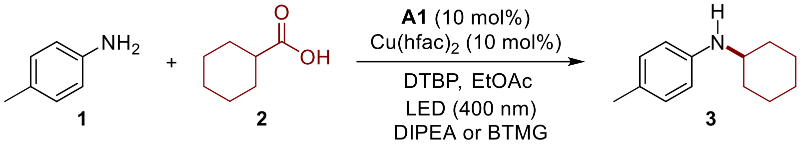
Influence of added base: Additionally, the acridine-catalyzed DDA reaction was carried out in the presence of DIPEA and BTMG that were expected to inhibit the reaction, due to the interference with the acridine–carboxylic acid interaction (Table S5). Indeed, addition of the bases led to inhibition of the DDA reaction, further supporting the proposed mechanism.

Table S5. DDA reaction performance in the presence of added base.[a]



Entry	Bases	Yield, %[b]
1	No base	99
2	DIPEA	15
3	BTMG	17

[a] Reaction conditions: aniline **1** (0.3 mmol), carboxylic acid **2** (0.75 mmol), photocatalyst (10 mol%), Cu(hfac)$_2$ (10 mol%), DTBP (0.6 mmol), EtOAc (4.5 mL), LED (400 nm), base (0.3 mmol), 12 h. [b] Determined by ^{1}H NMR with 1,4-dimethoxybenzene as an internal standard. DIPEA = *N,N*-diisopropylethylamine, BTMG = 2-*tert*-Butyl-1,1,3,3-tetramethylguanidine.

Cu(hfac)$_2$–aniline complexation in the presence of acid and DTBP: In order to confirm that Cu(hfac)$_2$–aniline complex **B** is also formed in the presence of acetic acid and DTBP, the EPR spectra of Cu(hfac)$_2$ in the presence of the additives were recorded (Figure S7). The studies confirmed that complexation between Cu(hfac)$_2$ and aniline indeed took place and no additional new signals were observed.

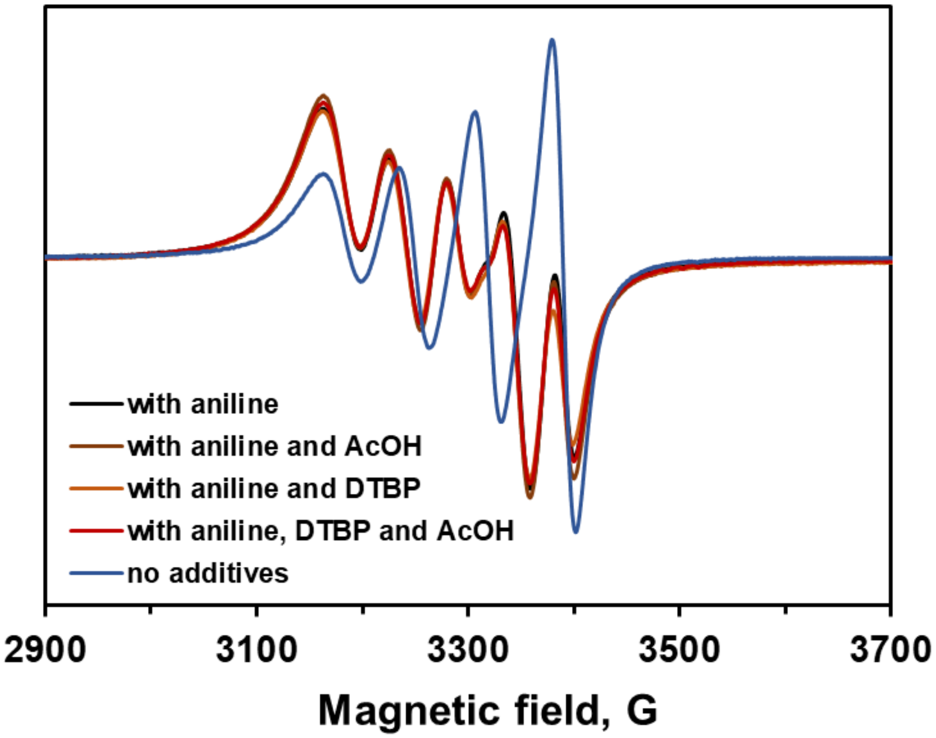


Figure S7. EPR spectra of Cu(hfac)$_2$ in the presence of aniline, acetic acid and TBHP (1 equiv.) in benzene at 10mM at room temperature.

Radical trapping with TEMPO was previously performed to ascertain alkyl radical production in acridine-photocatalyzed direct decarboxylation reactions.[1] In order to confirm that alkyl radical intermediates are produced and involved in the DDA reaction, it was carried out in the presence of TEMPO (Figure S8). Inhibition of the reaction was observed, and the corresponding radical trapping product **S2** was produced, supporting the radical pathway.

Additionally, the DDA reaction was carried out with cyclopropylacetic acid that produced the ring-opening product **S6**, as expected for the radical pathway. Similarly, the cyclized **S7** product was formed in addition to the uncyclized product **S8** with 6-heptenoic acid, supporting the radical mechanism.

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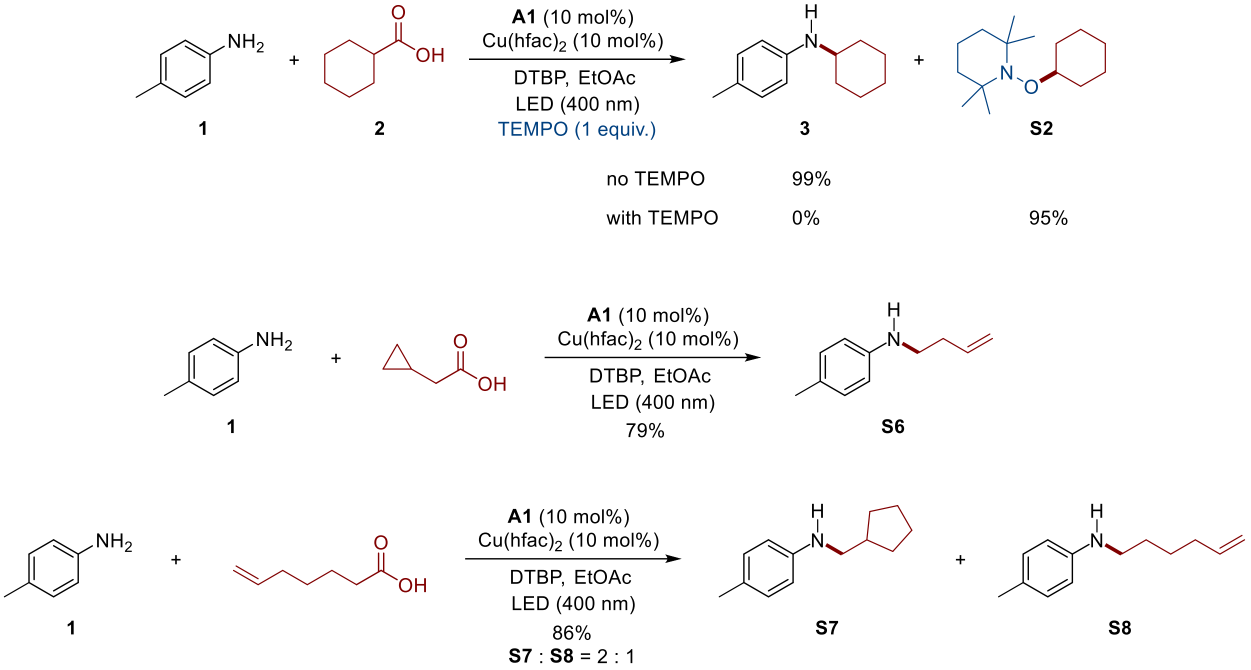


Figure S8. Radical trapping experiments with TEMPO as well as radical ring-opening and ring-closing experiments with cyclopropylacetic acid and 6-heptenoic acid.

Evaluation of involvement of alkyl carbocations: Rearrangement products due to 1,2-hydride shifts were not observed for carboxylic acids that would be expected to produce rearrangement products, if the DDA reaction involved a carbocation intermediate (Figure S9). 1,2-Hydride shifts occur with rates that exceed the diffusion limit ($k_{1,2\text{-H}} > 2{\cdot}10^{10}\ \text{s}^{-1}$),[7] and the absence of the rearrangement products indicates that the DDA reaction does not involve alkyl carbocation intermediates.[8]

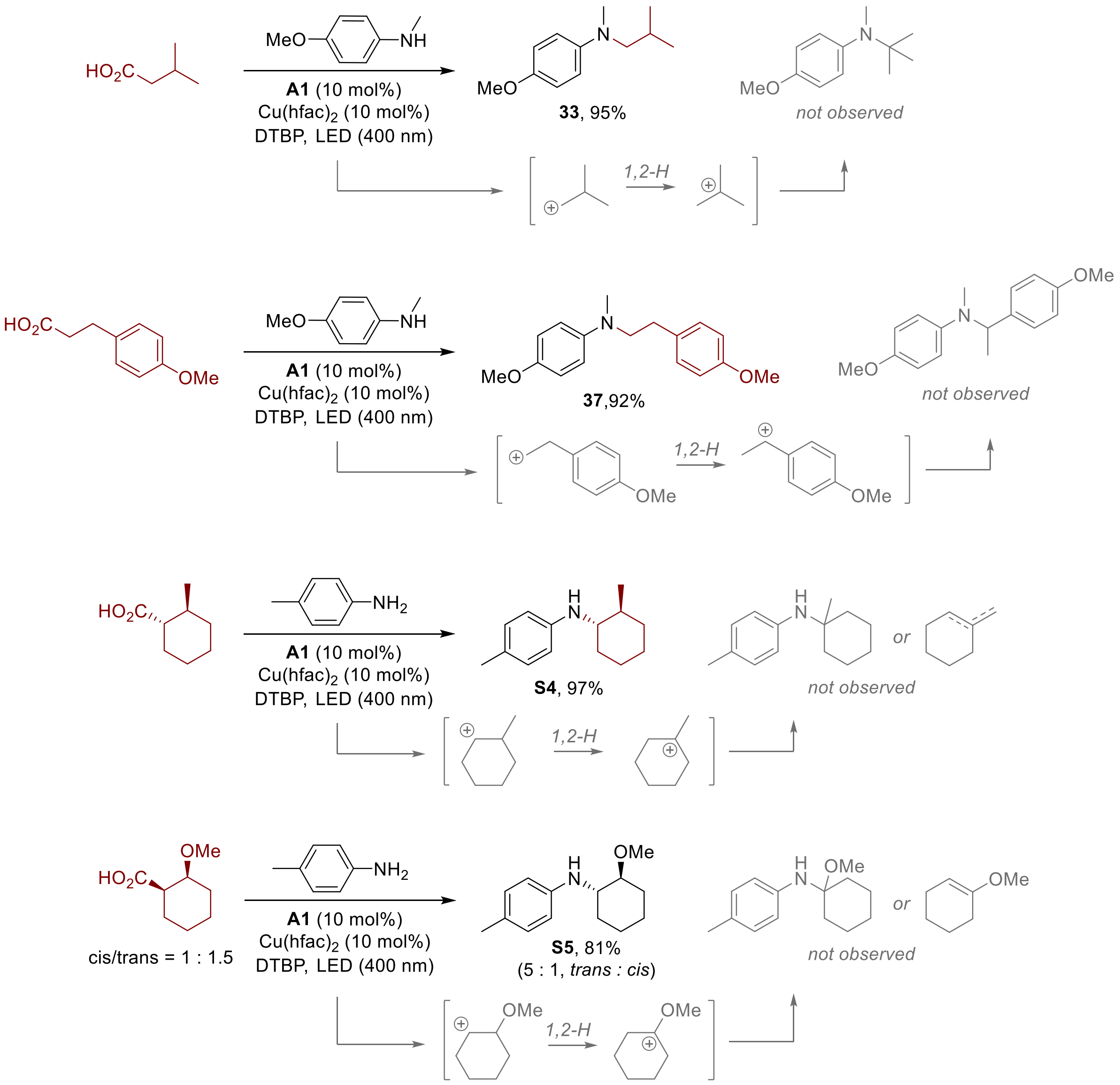


Figure S9. Evaluation of involvement of alkyl carbocations in the DDA reaction.

Evaluation of the direct reductive elimination and the base-assisted process: The mechanisms of C–N bond-forming Cu^{III}–N reductive elimination processes remain poorly understood. Additional calculations were carried out in order to compare the direct unimolecular reductive elimination (**C** → **D** + **E**, Figure 2) with the net bimolecular base-mediated pathways with aniline and acridine catalyst **A1** as bases (Figure S10). The deprotonation of intermediate **C** was highly thermodynamically unfavorable in both cases. The thermodynamically unfavorable deprotonation resulted in the total barrier of 30.4 kcal/mol for aniline, making the pathway highly kinetically unfavorable. The total barrier was 19.6 kcal/mol for acridine **A1**. Since the base-mediated pathways are net bimolecular and dependent on the concentration of the base in the solution, the base concentration has to be factored in to compare the relative rates of the unimolecular direct reductive elimination and the bimolecular base-mediated elimination process ($v_u/v_b = k_u/k_b c_{A1} = e^{-\Delta\Delta G\neq/RT}/c_{A1}$; where v_u, k_u and v_b, k_b are the rates and rate constants of the direct unimolecular and the base-mediated bimolecular reductive eliminations, c_{A1} is the concentration of acridine **A1**.).

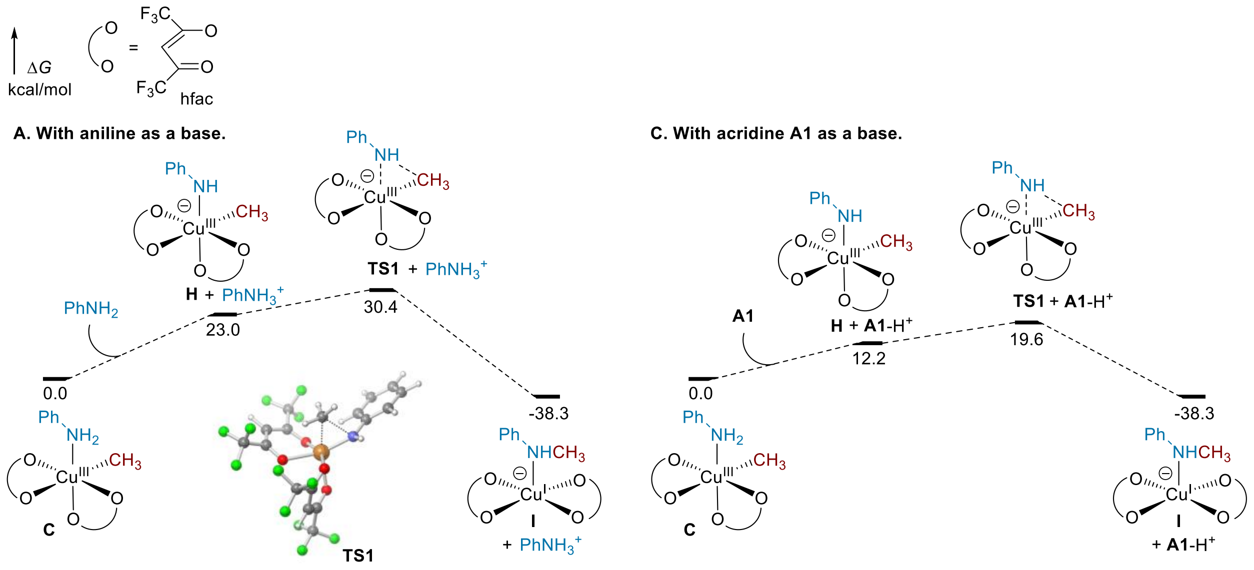


Figure S10. Computational studies of the base-mediated reductive elimination pathways with aniline and acridine **A1** as bases.

Given that c_{A1} cannot exceed the initial **A1** concentration of 0.02M, the calculations indicate that the unimolecular direct reductive elimination is >7.8 times faster than the acridine **A1**-mediated reductive elimination process. This result is in line with the moderately negative Hammett reaction constant ρ = –1.1 observed for the DDA reaction, and with prior computational studies that demonstrated that base-mediated reductive elimination processes become highly disfavored with weak organic bases.[9]

Additionally, further computational studies showed that deprotonation of complex **B** ($Cu^{II}(PhNH_2)(hfac)_2$) is highly thermodynamically disfavored by 31.4 and 20.5 kcal/mol with aniline and acridine **A1**, indicating that intermediate **J** is not present in sufficient concentrations to compete with complex **B** in the cross-termination with the alkyl radical.

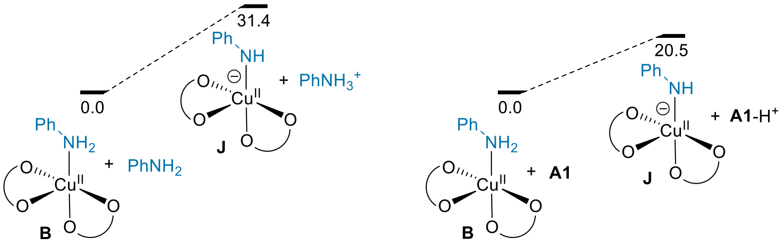
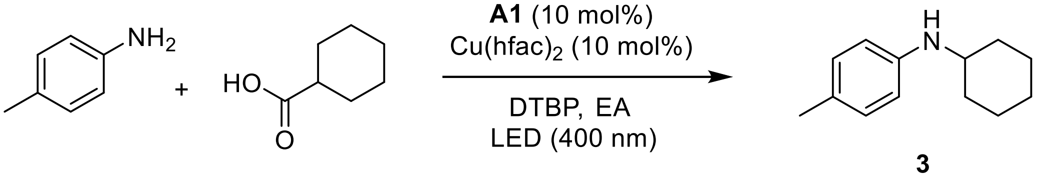


Figure S11. Computational studies of the deprotonation of complex **B** with aniline and acridine **A1**.

These computational results suggest that the direct C–N bond-forming reductive elimination from the Cu^{III} center is operative under the condition of the DDA reaction. Although C–N bond-forming reductive elimination processes from high-valent Cu^{III} complexes remain poorly understood from the experimental and theoretical perspectives, analogous direct C–N and C–P bond-forming reductive eliminations are known to readily take place from isoelectronic Au^{III} complexes.[10]

Amine products

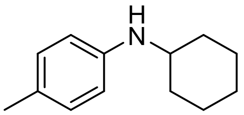
N-Cyclohexyl-4-methylaniline (3)[11]



3

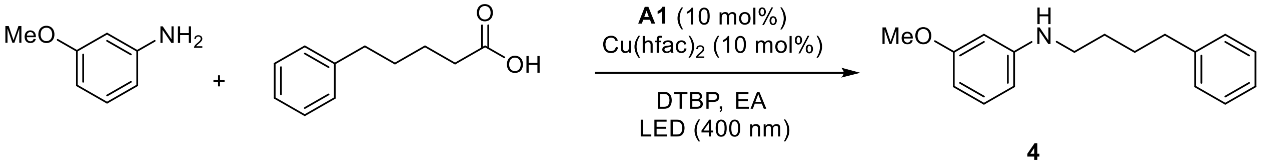
According to **GP1**, the reaction was carried out with *p*-toluidine (32 mg, 0.3 mmol), cyclohexanecarboxylic acid (96 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 35 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **3** (55 mg, 97%) as a brown solid.

Gram scale for compound 3: According to **GP1**, the reaction was carried out with *p*-toluidine (1.28 g, 12 mmol), cyclohexanecarboxylic acid (3.84 g, 30 mmol, 2.5 equiv.), acridine **A1** (176 mg, 0.6 mmol, 5 mol%), Cu(hfac)$_2$ (280 mg, 0.6 mmol, 5 mol%), and DTBP (3.52 g, 24 mmol, 2 equiv.) in ethyl acetate (80 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 5 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (50 mL), extracted with a saturated solution of EDTA (30 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **3** (2.12 g, 94%) as a brown solid.



m.p.: 38–40 ˚C. – ^{1}H NMR (500 MHz, $CDCl_3$): 6.97 (2 H, d, *J* = 8.1 Hz), 6.53 (2 H, d, *J* = 8.4 Hz), 3.22 (1 H, tt, *J* = 10.1, 3.6 Hz), 2.23 (3 H, s), 2.10–1.99 (2 H, m), 1.76 (2 H, dt, *J* = 13.2, 3.7 Hz), 1.65 (1 H, dt, *J* = 12.4, 3.5 Hz), 1.46–1.31 (2 H, m), 1.23 (1 H, ddd, *J* = 15.6, 9.7, 3.3 Hz), 1.18–1.08 (2 H, m) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 145.2, 129.9, 126.3, 113.7, 52.2, 33.7, 26.1, 25.2, 20.5 ppm. – IR: 3393, 3074, 3019, 2923, 2850, 1617, 1516, 1481, 1448, 1317, 1300, 1146,1125, 1101, 805 cm^{-1}.

3-Methoxy-*N*-(4-phenylbutyl)aniline (4)



4

According to **GP1**, the reaction was carried out with *m*-anisidine (37 mg, 0.3 mmol), 5-phenylpentanoic acid (133 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), $Cu(hfac)_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 9 : 1 v/v) to give the amine product **4** (69 mg, 89%) as a colorless liquid.

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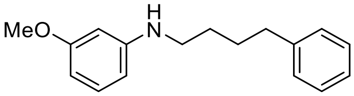
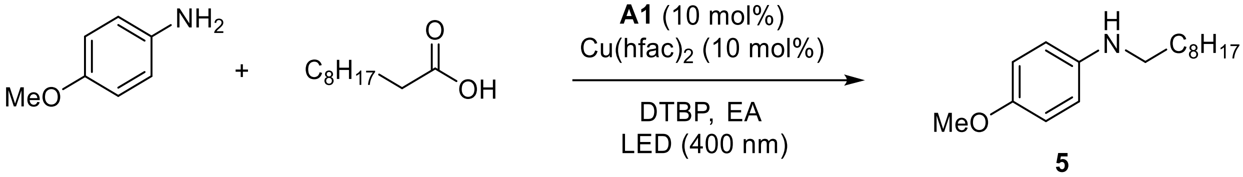
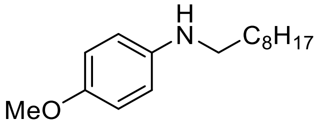


^{1}H NMR (500 MHz, $CDCl_3$): 7.33 (2 H, t, *J* = 6.9 Hz), 7.28–7.19 (3 H, m), 7.12 (1 H, t, *J* = 8.1 Hz), 6.31 (1 H, d, *J* = 8.5 Hz), 6.25 (1 H, d, *J* = 8.0 Hz), 6.19 (1 H, s), 3.81 (3 H, d, *J* = 1.8 Hz), 3.64 (1 H, s), 3.15 (2 H, t, *J* = 6.9 Hz), 2.70 (2 H, t, *J* = 7.5 Hz), 1.78 (2 H, quint., *J* = 7.4 Hz), 1.69 (2 H, quint., *J* = 7.0 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 161.0, 149.9, 142.3, 130.0, 128.5, 128.4, 125.9, 106.0, 102.3, 98.7, 55.2, 43.9, 35.8, 29.2, 29.0 ppm. – IR: 3400, 3092, 3024, 2930, 2855, 2844, 1614. 1509, 1452, 1341, 1301, 1210, 1161, 1120, 1046, 699 cm^{-1}. – HRMS: calcd for $C_{17}H_{22}NO$: 256.1696, found 256.1696 [M+H$^+$].

4-Methoxy-*N*-nonylaniline (5)

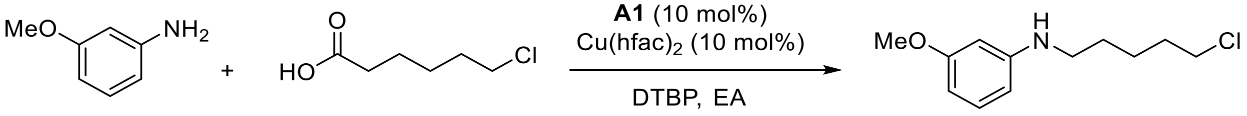


According to **GP1**, the reaction was carried out with *p*-anisidine (37 mg, 0.3 mmol), decanoic acid (129 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 9 : 1 v/v) to give the amine product **5** (55 mg, 74%) as a dark yellow liquid.



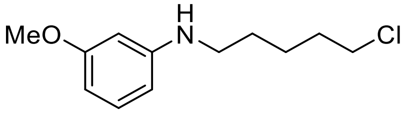
^{1}H NMR (500 MHz, $CDCl_3$): 6.79 (2 H, d, *J* = 8.8 Hz), 6.59 (2 H, d, *J* = 8.9 Hz), 3.76 (3 H, s), 3.07 (2 H, t, *J* = 7.2 Hz), 1.61 (2 H, quint., *J* = 7.2 Hz), 1.48–1.19 (12 H, m), 0.91 (3 H, t, *J* = 6.8 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 152.0, 143.0, 115.0, 114.1, 55.9, 45.1, 32.0, 29.8, 29.7, 29.6, 29.4, 27.3, 22.8, 14.2 ppm. – IR: 3387, 3056, 2959, 2922, 2852, 2834, 1619, 1512, 1464, 1437, 1377, 1234, 1179, ,1110, 1039, 817, 767 cm^{-1}. – HRMS: calcd for $C_{16}H_{28}NO$: 250.2165, found 250.2168 [M+H$^+$].

N-(5-Chloropentyl)-3-methoxyaniline (6)



6

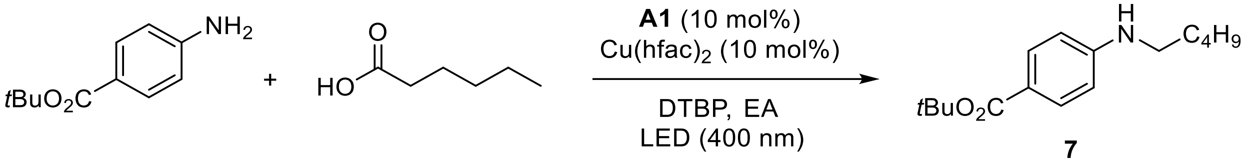
According to **GP1**, the reaction was carried out with *m*-anisidine (37 mg, 0.3 mmol), 6-chlorohexanoic acid (112 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 9 : 1 v/v) to give the amine product **6** (36 mg, 53%) as a colorless liquid.



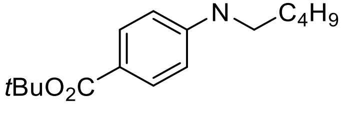
^{1}H NMR (500 MHz, $CDCl_3$): 7.08 (1 H, t, *J* = 8.1 Hz), 6.28 (1 H, dd, *J* = 8.2, 2.4 Hz), 6.23 (1 H, dd, *J* = 8.0, 2.2 Hz), 6.16 (1 H, d, *J* = 2.4 Hz), 3.78 (3 H, s), 3.68 (1 H, brs), 3.56 (2 H, t, *J* = 6.6 Hz), 3.12 (2 H, t, *J* = 7.0

Hz), 1.83 (2 H, quint., *J* = 6.9 Hz), 1.65 (2 H, quint., *J* = 7.1 Hz), 1.56 (2 H, q, *J* = 8.1 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 161.0, 149.8, 130.1, 106.0, 102.4, 98.8, 55.2, 45.0, 43.8, 32.4, 28.9, 24.6 ppm. – IR: 3303, 3066, 2998, 2934, 2859, 2838, 1614, 1601, 1497, 1453, 1342, 1268, 1210, 1161, 1057, 997, 770, 694 cm^{-1}. – HRMS: calcd for $C_{12}H_{19}ClNO$: 228.1150, found 228.1150 [M+H$^+$].

tert-Butyl 4-(pentylamino)benzoate (7)



According to **GP1**, the reaction was carried out with *tert*-butyl 4-aminobenzoate (58 mg, 0.3 mmol), hexanoic acid (87 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **7** (64 mg, 81%) as a colorless liquid.



^{1}H NMR (500 MHz, CDCl$_3$): 7.81 (2 H, d, *J* = 8.8 Hz), 6.52 (2 H, d, *J* = 8.7 Hz), 4.66 (1 H, brs), 3.14 (2 H, t, *J* = 7.2 Hz), 1.76–1.58 (11 H, m), 1.45–1.31 (4 H, m, *J* = 7.3, 6.3 Hz), 0.92 (3 H, t, *J* = 7.0 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 166.3, 151.9, 131.4, 120.0, 111.3, 79.8, 43.5, 29.3, 29.1, 28.4, 22.6, 14.1 ppm. – IR: 3376, 3000, 2956, 2928, 2859, 1711, 1681, 1602, 1526, 1475,

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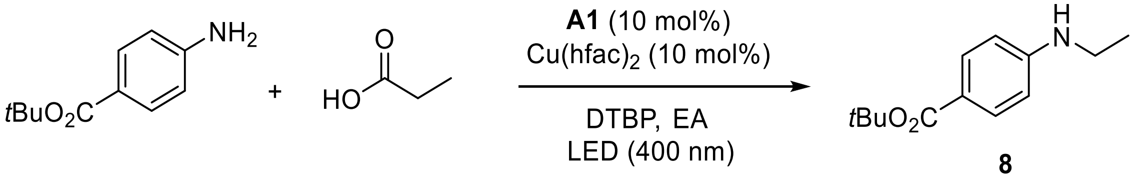
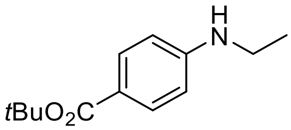
1366, 1309, 1290, 1157, 1106, 868, 835, 771, 700 cm^{-1}. – HRMS: calcd for $C_{16}H_{26}NO_2$: 264.1958, found 264.1960 [M+H$^+$].

tert-Butyl 4-(pentylamino)benzoate (8)[12]



According to **GP1**, the reaction was carried out with *tert*-butyl 4-aminobenzoate (58 mg, 0.3 mmol), propanoic acid (56 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), $Cu(hfac)_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 9 : 1 v/v) to give the amine product **8** (46 mg, 69%) as a colorless liquid.



^{1}H NMR (500 MHz, $CDCl_3$): 7.81 (2 H, d, *J* = 8.9 Hz), 6.52 (2 H, d, *J* = 8.9 Hz), 4.01 (1 H, s), 3.20 (2 H, q, *J* = 7.1 Hz), 1.57 (9 H, s), 1.26 (3 H, t, *J* = 7.2 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 166.3, 151.8, 131.4, 120.2, 111.4, 79.9, 38.1, 28.5, 14.8 ppm. – IR: 3362, 3063, 2973, 2931, 2909, 2878, 1693, 1605, 1522, 1492, 1400, 1315, 1297, 1267, 1167, 1153, 1113, 1073, 1010, 838, 780, 741 cm^{-1}.

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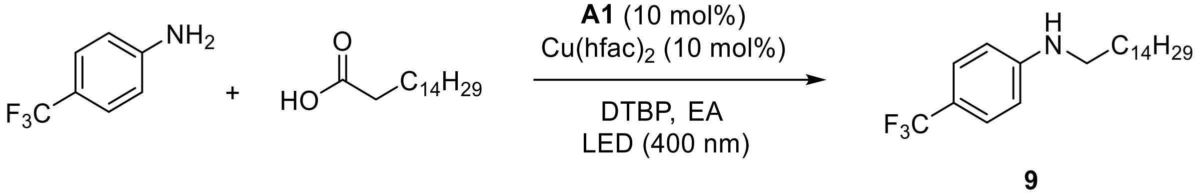
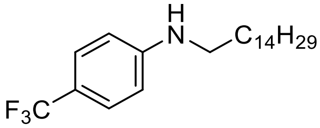
N-Pentadecyl-4-(trifluoromethyl)aniline (9)



9

According to **GP1**, the reaction was carried out with 4-(trifluoromethyl)aniline (48 mg, 0.3 mmol), palmitic acid (192 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **9** (99 mg, 89%) as a brown solid



m.p.: 37–39 ˚C. – ^{1}H NMR (500 MHz, CDCl$_3$): 7.36 (2 H, d, *J* = 8.4 Hz), 6.55 (2 H, d, *J* = 8.4 Hz), 3.91 (1 H, s), 3.10 (2 H, t, *J* = 7.2 Hz), 1.59 (2 H, quint., *J* = 7.2 Hz), 1.41–1.12 (24 H, m), 0.87 (3 H, t, *J* = 6.8 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 150.9, 126.5 (q, $^3J_{C\text{-}F}$ = 3.5 Hz), 122.9 (q, $^1J_{C\text{-}F}$ = 270.0 Hz), 118.1 (q, $^2J_{C\text{-}F}$ = 32.2 Hz), 111.6, 43.5, 32.0, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 27.1, 22.7, 14.1 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): – 60.9 ppm. – IR: 3439, 3063, 2915, 2848, 1620, 1585, 1532, 1480, 1464, 1187, 1271, 1120, 1104, 1093, 1057, 1005, 938, 907, 821 cm^{-1}. – HRMS: calcd for $C_{22}H_{37}F_3N$: 372.2873, found 372.2871 [M+H$^+$].

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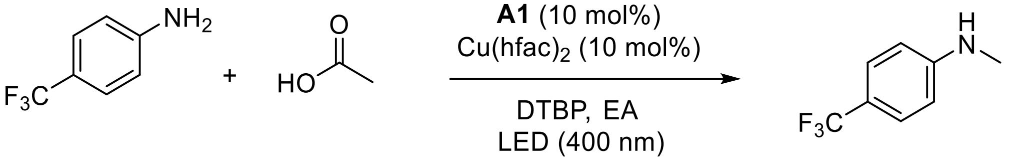
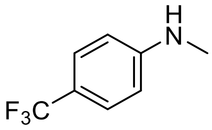
N-Methyl-4-(trifluoromethyl)aniline (10)[13]



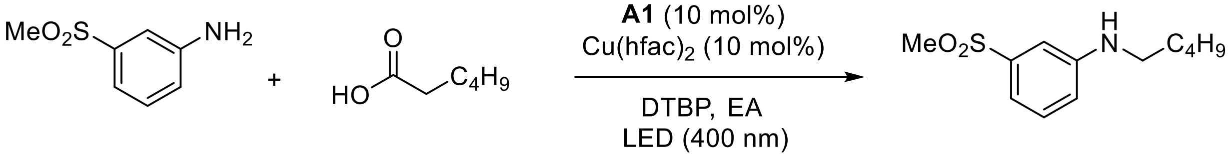
10

According to **GP1**, the reaction was carried out with 4-(trifluoromethyl)aniline (48 mg, 0.3 mmol), acetic acid (90 mg, 1.5 mmol, 5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **10** (28 mg, 53%) as a colorless liquid.



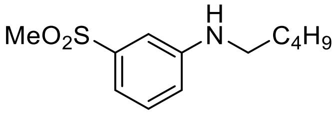
^{1}H NMR (500 MHz, CDCl$_3$): 7.41 (2 H, d, *J* = 8.4 Hz), 6.60 (2 H, d, *J* = 8.4 Hz), 4.05 (1 H, brs), 2.87 (3 H, s) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 151.8, 126.7 (q, $^3J_{C\text{-}F}$ = 3.5 Hz), 125.2 (q, $^1J_{C\text{-}F}$ = 270.4 Hz), 118.8 (q, $^2J_{C\text{-}F}$ = 32.5 Hz), 111.6, 30.4 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): –61.0 ppm. – IR: 3454, 2932, 2253, 1795, 1652, 1617, 1536, 1474, 1381, 1327, 1274, 1188, 1156, 1106, 1074 cm^{-1}.

3-(Methylsulfonyl)-*N*-pentylaniline (11)



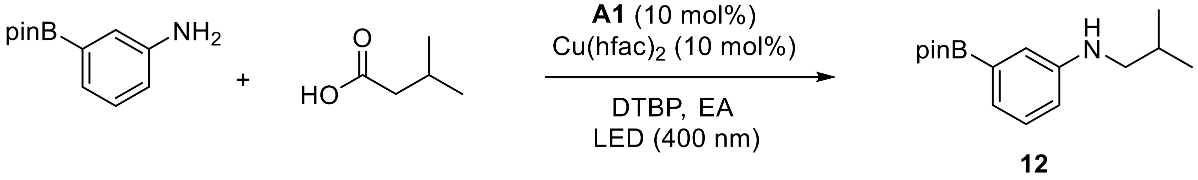
11

According to **GP1**, the reaction was carried out with 3-(methylsulfonyl)aniline (51 mg, 0.3 mmol), hexanoic acid (87 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 4 : 1 v/v) to give the amine product **11** (63 mg, 87%) as a colorless liquid.

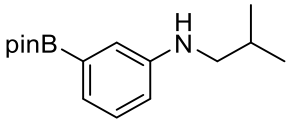


^{1}H NMR (500 MHz, CDCl$_3$): 7.30 (1 H, t, *J* = 8.0 Hz), 7.17 (1 H, dt, *J* = 7.8, 1.3 Hz), 7.09 (1 H, t, *J* = 2.1 Hz), 6.80 (1 H, ddd, *J* = 8.2, 2.5, 0.9 Hz), 3.13 (2 H, t, *J* = 7.2 Hz), 3.03 (3 H, s), 1.72–1.57 (2 H, m), 1.48–1.31 (4 H, m), 1.07–0.80 (3 H, m,) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 149.2, 141.3, 130.1, 117.4, 114.9, 110.0, 44.5, 43.7, 29.3, 28.9, 22.5, 14.1 ppm. – IR: 3390, 3054, 2955, 2927, 2858, 2255, 1736, 1600, 1513, 1473, 1424, 1377, 1155, 1081, 986, 908, 856 cm^{-1}. – HRMS: calcd for $C_{12}H_{20}NO_2S$: 242.1209, found 242.1207 [M+H$^+$].

N-Isobutyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (12)



According to **GP1**, the reaction was carried out with 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (66 mg, 0.3 mmol), isovaleric acid (77 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **12** (51 mg, 59%) as a colorless liquid.



^{1}H NMR (500 MHz, CDCl$_3$): 7.20 (1 H, t, *J* = 7.6 Hz), 7.15 (1 H, d, *J* = 7.0 Hz), 7.07 (1 H, d, *J* = 2.0 Hz), 6.80–6.67 (1 H, m), 3.68 (1 H, brs), 2.97 (2 H, d, *J* = 6.7 Hz), 1.89 (1 H, dp, *J* = 13.3, 6.7 Hz), 1.35 (12 H, s), 0.99 (6 H, d, *J* = 6.7 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 148.1, 128.8, 123.6, 119.2, 115.4, 83.7, 51.8, 28.2, 25.0, 20.6 ppm. – ^{11}B NMR (160 MHz, CDCl$_3$): 31.0 ppm. – IR: 3406, 3055, 2975, 2961, 1935. 1868. 1737. 1603, 1581, 1511, 1469, 1428, 1353, 1317, 1274, 1237, 1144, 1075, 990, 872, 751, 707 cm^{-1}. – HRMS: calcd for C$_{17}$H$_{29}$BNO$_2$: 290.2286, found 290.2283 [M+H$^+$].

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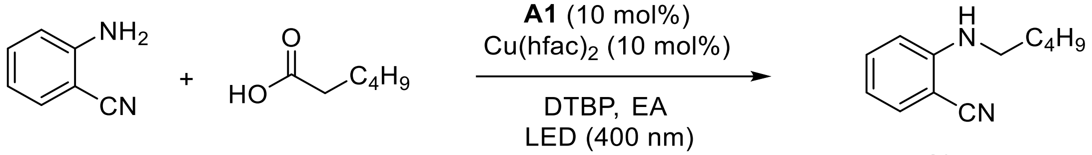
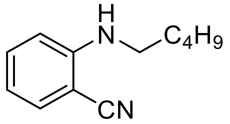
2-(Pentylamino)benzonitrile (13)[14]



13

According to **GP1**, the reaction was carried out with 2-aminobenzonitrile (35 mg, 0.3 mmol), hexanoic acid (87 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **13** (45 mg, 80%) as a colorless liquid.



^{1}H NMR (500 MHz, CDCl$_3$): 7.41–7.35 (2 H, m), 6.68–6.58 (2 H, m), 4.54 (1 H, brs), 3.18 (2 H, td, *J* = 7.2, 5.1 Hz), 1.66 (2 H, quint., *J* = 7.2 Hz), 1.43– 1.34 (4 H, dquint., *J* = 7.4, 3.5 Hz), 0.93 (3 H, t, *J* = 6.9 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 150.5, 134.3, 132.8, 118.1, 116.2, 110.6, 95.5, 43.4, 29.2, 28.9, 22.5, 14.1 ppm. – IR: 3380, 3054, 2964, 2930, 2859, 2211, 1694, 1606, 1577, 1515, 1460, 1326, 1264, 1166, 736, 704 cm^{-1}.

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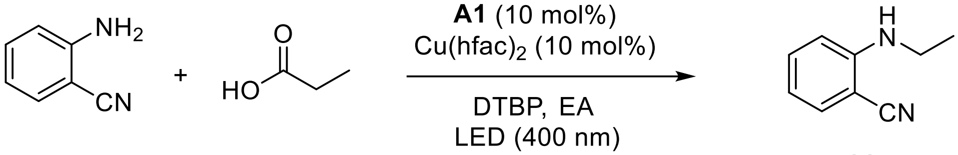
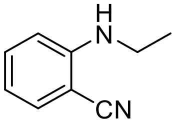
2-(Ethylamino)benzonitrile (14)[15]



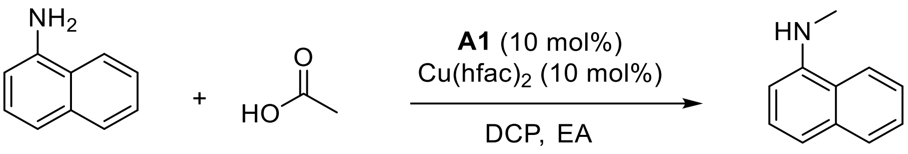
14

According to **GP1**, the reaction was carried out with 2-aminobenzonitrile (35 mg, 0.3 mmol), propanoic acid (56 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **14** (33 mg, 75%) as a pale yellow solid.



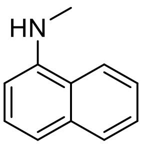
m.p.: 62–65 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 7.40–7.35 (m, 2H), 6.68–6.63 (m, 2H), 4.47 (brs, 1H), 3.48–3.10 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 150.4, 134.4, 132.9, 118.1, 116.4, 110.6, 95.6, 38.1, 14.6 ppm. – IR: 3427, 3061, 2977, 2213, 1606, 1582, 1526, 1421, 1264, 1178, 908, 733, 704 cm^{-1}.

N-methylnaphthalen-1-amine (15)[13]



15

According to **GP1**, the reaction was carried out with naphthalen-1-amine (43 mg, 0.3 mmol), acetic acid (90 mg, 1.5 mmol, 5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DCP (120 mg, 0.45 mmol, 1.5 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 24 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **15** (35 mg, 97%) as a colorless liquid.



^{1}H NMR (500 MHz, CDCl$_3$): 7.88–7.75 (2 H, m), 7.45 (2 H, pd, *J* = 6.8, 1.4 Hz), 7.39 (1 H, t, *J* = 7.9 Hz), 7.26 (1 H, d, *J* = 8.2 Hz), 6.62 (1 H, d, *J* = 7.5 Hz), 4.44 (1 H, brs), 3.03 (3 H, s) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 144.6, 134.3, 128.8, 126.8, 125.8, 124.8, 123.6, 119.9, 117.4, 103.9, 31.2 ppm. – IR: 3438, 3048, 2983, 2922, 2845, 2812, 1622, 1581, 1527, 1486, 1403, 1370, 1342, 1286, 1253, 1171, 1150, 1113, 1064 cm^{-1}.

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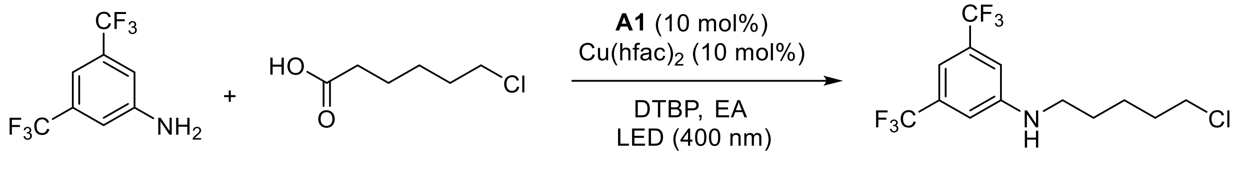
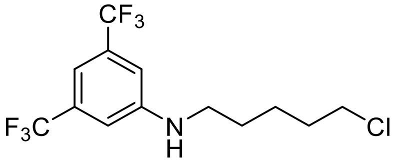
N-(5-Chloropentyl)-3,5-bis(trifluoromethyl)aniline (16)



16

According to **GP1**, the reaction was carried out with 3,5-bis(trifluoromethyl)aniline (69 mg, 0.3 mmol), 6-chlorohexanoic acid (113 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product 16 (80 mg, 80%) as a colorless liquid.



^{1}H NMR (500 MHz, CDCl$_3$): 7.21 (1 H, s), 7.03 (2 H, s), 3.54 (2 H, t, *J* = 6.6 Hz), 2.39 (2 H, t, *J* = 7.5 Hz), 1.80 (2 H, dt, *J* = 14.1, 6.8 Hz), 1.68 (2 H, quint., *J* = 7.2 Hz), 1.59–1.42 (2 H, m) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 148.9, 132.5 (q, $^2J_{\text{C-F}}$ = 32.6 Hz), 123.7 (q, $^1J_{\text{C-F}}$ = 273.0 Hz), 111.8, 110.1 (q, $^3J_{\text{C-F}}$ = 4.3 Hz), 44.9, 43.5, 32.3, 28.5, 24.4 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): –63.2 ppm. – IR: 3428, 2917, 2849, 1731, 1621, 1472, 1432, 1399, 1275, 1170, 1126, 1104, 995, 908, 861, 732, 701 cm^{-1}. – HRMS: calcd for $C_{13}H_{15}ClF_6N$: 334.0792, found 334.0792 [M+H$^+$].

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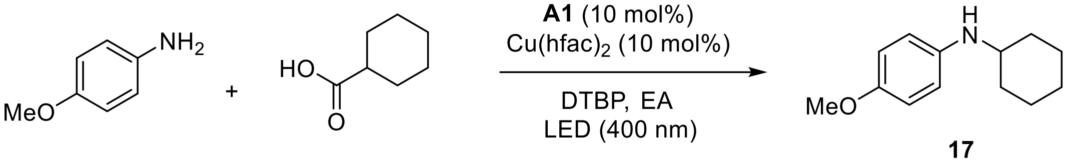
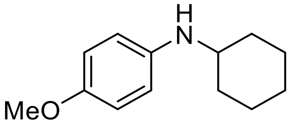
N-Cyclohexyl-4-methoxyaniline (17)[16]

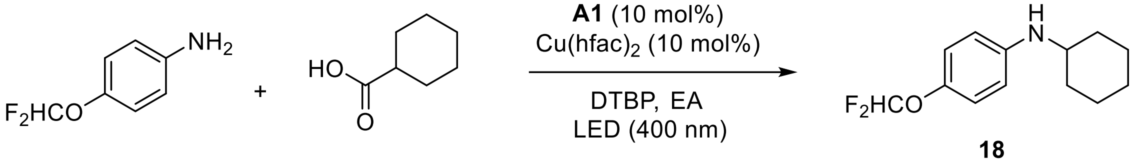


According to **GP1**, the reaction was carried out with *p*-anisidine (37 mg, 0.3 mmol), cyclohexanecarboxylic acid (96 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 9 : 1 v/v) to give the amine product **17** (47 mg, 76%) as a colorless liquid.

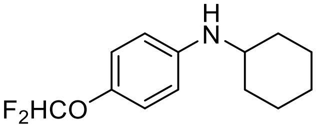


^{1}H NMR (500 MHz, $CDCl_3$): 6.90–6.70 (2 H, m), 6.64–6.42 (2 H, m), 3.74 (3 H, s), 3.17 (1 H, tt, *J* = 10.2, 3.7 Hz), 2.76 (1 H, brs), 2.21–1.94 (2 H, m), 1.76 (2 H, dt, *J* = 13.9, 3.9 Hz), 1.69–1.56 (1 H, m), 1.44–1.29 (2 H, m), 1.28–1.18 (1 H, m), 1.16–1.01 (2 H, m) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 152.0, 141.7, 115.0, 115..0, 56.0, 52.9, 33.8, 26.1, 25.2 ppm. – IR: 3041, 2958, 2912, 2854, 2214, 1762, 1742, 1511, 1277, 1284, 1205, 1140, 1045 cm^{-1}.

N-Cyclohexyl-4-(difluoromethoxy)aniline (18)



According to **GP1**, the reaction was carried out with 4-(difluoromethoxy)aniline (48 mg, 0.3 mmol), cyclohexanecarboxylic acid (96 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 14 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **18** (52 mg, 72%) as a yellow liquid.



^{1}H NMR (500 MHz, CDCl$_3$): 6.95 (2 H d, *J* = 8.9 Hz), 6.53 (2 H, d, *J* = 8.9 Hz), 6.37 (1 H, t, *J* = 75.1 Hz), 3.51 (1 H, brs), 3.21 (1 H, tt, *J* = 10.2, 3.8 Hz), 2.14–2.00 (2 H, m), 1.77 (2 H, dt, *J* = 13.2, 3.6 Hz), 1.66 (1 H, dt, *J* = 12.7, 3.6 Hz), 1.43–1.32 (2 H, m), 1.30–1.04 (1 H, m) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 145.5, 142.1, 121.6, 116.8 (t, $^1J_{C\text{-}F}$ = 258.5 Hz), 113.7, 52.2, 33.5, 26.0, 25.1 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): –79.9 ppm. – IR: 3396, 3030, 2930, 2856, 1753, 1710, 1614, 1513, 1418, 1360, 1220, 1176, 1122, 1097, 1037, 822 cm^{-1}. – HRMS: calcd for $C_{13}H_{18}F_2NO$: 242.1351, found 242.1351 [M+H$^+$].

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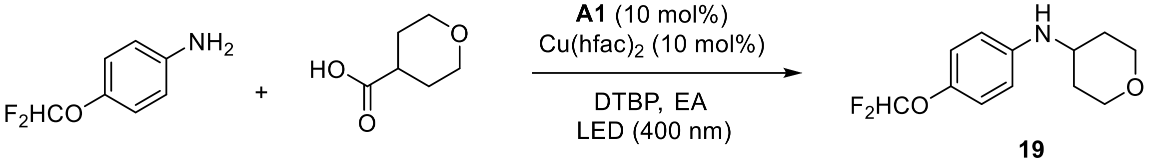
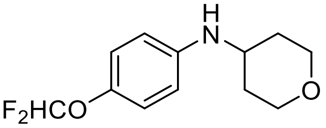
N-(4-(Difluoromethoxy)phenyl)tetrahydro-2*H*-pyran-4-amine (19)



According to **GP1**, the reaction was carried out with 4-(difluoromethoxy)aniline (48 mg, 0.3 mmol), tetrahydro-2*H*-pyran-4-carboxylic acid (98 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 4 : 1 v/v) to give the amine product **19** (40 mg, 55%) as a light brown solid.



^{1}H NMR (500 MHz, CDCl$_3$): 6.96 (2 H, d, *J* = 8.8 Hz), 6.56 (2 H, d, *J* = 8.9 Hz), 6.37 (1 H, t, *J* = 74.9 Hz), 4.00 (2 H, dt, *J* = 11.8, 3.5 Hz), 3.63–3.26 (3 H, m), 2.02 (2 H, dd, *J* = 12.5, 2.3 Hz), 1.46 (2 H, qd, *J* = 11.1, 4.3 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 144.8, 142.5, 121.7,116.6 (t, $^1J_{C\text{-}F}$ = 258.9 Hz), 114.0, 67.0, 49.6, 33.6 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): –80.1 (d, *J* = 74.8 Hz) ppm. – IR: 2969, 2935, 2859, 2253, 1750, 1743, 1511, 1377, 1353, 1288, 1209, 1130, 1045, 909 cm^{-1}. – HRMS: calcd for $C_{12}H_{16}F_2NO_2$: 244.1144, found 244.1148 [M+H$^+$].

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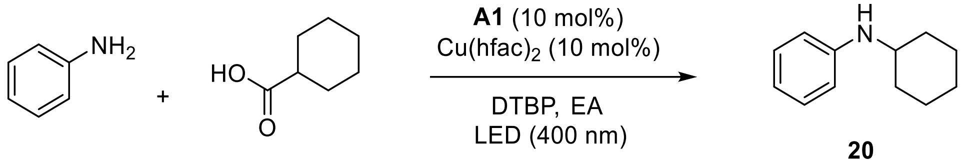
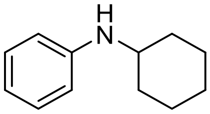
N-Cyclohexylaniline (20)[11]



According to **GP2**, the reaction was carried out with aniline (70 mg, 0.75 mmol, 2.5 equiv.), cyclohexanecarboxylic acid (38 mg, 0.3 mmol), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **20** (39 mg, 74%) as a colorless liquid.



^{1}H NMR (500 MHz, CDCl$_3$): 7.16 (2 H, t, *J* = 7.8 Hz), 6.67 (1 H, t, *J* = 7.3 Hz), 6.60 (2 H, d, *J* = 7.9 Hz), 3.51 (1 H, brs), 3.26 (1 H, tt, *J* = 10.2, 3.8 Hz), 2.07 (2 H, dd, *J* = 13.0, 4.1 Hz), 1.87–1.72 (2 H, m), 1.71–1.60 (1 H, m), 1.49–1.33 (2 H, m), 1.31–1.09 (3 H, m) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 147.5, 129.4, 117.0, 113.3, 51.8, 33.6, 26.1, 25.2 ppm. – IR: 3401, 2925, 2852, 1617, 1504, 1463, 1448, 1406, 1318, 1303, 1233, 1129, 1107 cm^{-1}.

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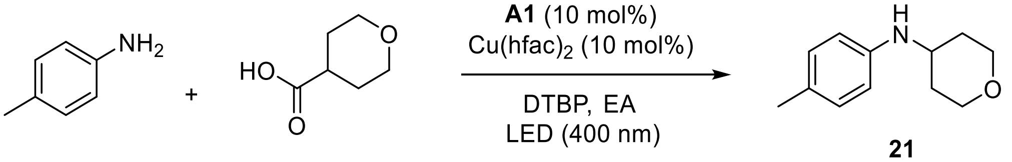
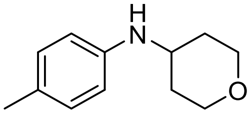
N-(*p*-Tolyl)tetrahydro-2*H*-pyran-4-amine (21)



According to **GP1**, the reaction was carried out with *p*-toluidine (32 mg, 0.3 mmol), tetrahydro-2*H*-pyran-4-carboxylic acid (98 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 14 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **21** (51 mg, 89%) as a colorless liquid.



^{1}H NMR (500 MHz, CDCl$_3$): 7.00 (2 H, d, *J* = 8.1 Hz), 6.56 (2 H, d, *J* = 8.1 Hz), 4.01 (2 H, dt, *J* = 11.7, 3.2 Hz), 3.50 (3H, dtd, *J* = 17.8, 11.0, 10.4, 4.1 Hz), 2.25 (3 H, s), 2.04 (2 H, dd, *J* = 12.7, 2.3 Hz), 1.46 (2 H, qd, *J* = 11.0, 4.3 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 144.5, 129.9, 126.9, 113.8, 67.2, 49.6, 33.8, 20.5 ppm. – IR: 3350, 3024, 2953, 2917, 2845, 1735, 1616, 1584, 1536, 1466, 1380, 1317, 1280, 1260, 1168, 1085, 1043, 1010, 981, 868 cm^{-1}. – HRMS: calcd for C$_{12}$H$_{18}$NO: 192.1383, found 192.1384 [M+H$^+$].

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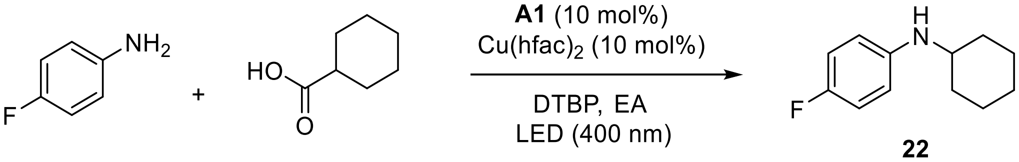
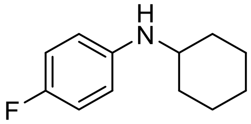
N-Cyclohexyl-4-fluoroaniline (22)[11]

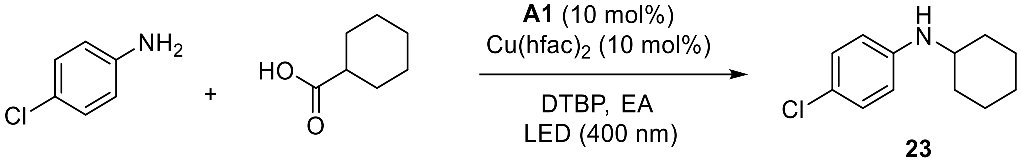


According to **GP1**, the reaction was carried out with 4-fluoroaniline (33 mg, 0.3 mmol), cyclohexanecarboxylic acid (96 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), $Cu(hfac)_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 24 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 :95 v/v) to give the amine product **22** (45 mg, 78%) as a colorless liquid.



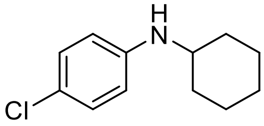
^{1}H NMR (500 MHz, $CDCl_3$): 7.16–6.80 (2 H, m), 6.73–6.43 (2 H, m), 3.39 (1 H, brs), 3.17 (1 H, tt, J = 10.2, 3.7 Hz), 2.04 (2 H, dd, J = 13.0, 3.6 Hz), 1.76 (2 H, dt, J = 13.5, 3.9 Hz), 1.65 (1 H, dt, J = 12.7, 3.7 Hz), 1.44–1.31 (2 H, m), 1.29–1.05 (3 H, m) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 155.7 (d, $^1J_{C\text{-}F}$ = 234.4 Hz), 143.8, 115.8 (d, $^2J_{C\text{-}F}$ = 22.0 Hz), 114.2 (d, $^3J_{C\text{-}F}$ = 7.3 Hz), 52.6, 33.6, 26.1, 25.2 ppm. – ^{19}F NMR (471 MHz, $CDCl_3$): –128.7 (t, J = 4.8 Hz) ppm. – IR: 3409, 2926, 2951, 1613, 1507, 1450, 1402, 1305, 1254, 1218, 1155, 1116, 1091 cm^{-1}.

4-Chloro-*N*-cyclohexylaniline (23)[11]



23

According to **GP1**, the reaction was carried out with 4-chloroaniline (38 mg, 0.3 mmol), cyclohexanecarboxylic acid (96 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 24 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **23** (45 mg, 72%) as a colorless solid.



m.p.: 47–50 ˚C. – ^{1}H NMR (500 MHz, CDCl$_3$): 7.22–6.75 (2 H, m), 6.64–6.16 (2 H, m), 3.52 (1 H, brs), 3.20 (1 H, tt, *J* = 10.2, 3.7 Hz), 2.03 (2 H, dd, *J* = 12.8, 3.1 Hz), 1.76 (2 H, dt, *J* = 13.3, 3.7 Hz), 1.66 (1 H, dt, *J* = 12.8, 3.7 Hz), 1.45–1.30 (2 H, m), 1.29–1.05 (3 H, m) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 146.0, 129.2, 121.4, 114.3, 52.0, 33.440, 26.0, 25.1 ppm. – IR: 3415, 3068, 3034, 2935, 2857, 2660, 1869, 1598, 1500, 1454, 1400, 1387, 1294, 1262, 1255, 1229, 1174, 1092, 1027 cm^{-1}.

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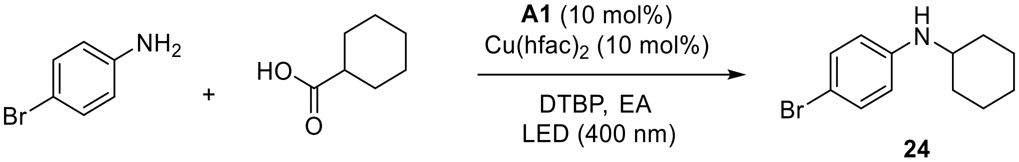
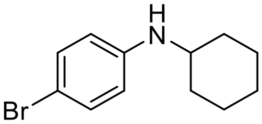
4-Bromo-*N*-cyclohexylaniline (24)[11]

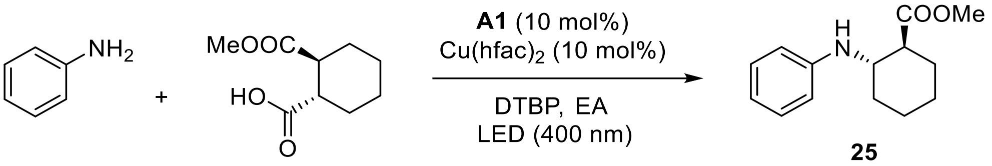


According to **GP1**, the reaction was carried out with 4-bromoaniline (51 mg, 0.3 mmol), cyclohexanecarboxylic acid (96 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 24 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **24** (53 mg, 69%) as a colorless solid.

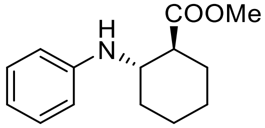


m.p.: 50–52 ˚C. – ^{1}H NMR (500 MHz, CDCl$_3$): 7.32–6.82 (2 H, m), 6.68–6.24 (2 H, m), 3.57 (1 H, brs), 3.20 (1 H, tt, *J* = 10.2, 3.7 Hz), 2.03 (2 H, dd, *J* = 13.2, 4.0 Hz), 1.76 (2 H, dt, *J* = 13.6, 3.8 Hz), 1.65 (1 H, dt, *J* = 12.8, 3.7 Hz), 1.48–1.30 (2 H, m), 1.29–1.03 (3 H, m) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 146.4, 132.0, 114.8, 108.3, 51.9, 33.4, 25.0, 25.1 ppm. – IR: 3413, 3011, 2928, 2853, 1592, 1493, 1462, 1449, 1397, 1367, 1314, 1254, 1214, 1106 cm^{-1}.

Methyl (1*S**,2*S**)-2-(phenylamino)cyclohexane-1-carboxylate (25)[17]



According to **GP2**, the reaction was carried out with aniline (70 mg, 0.75 mmol, 2.5 equiv.), (1*S**,2*S**)-2-(methoxycarbonyl)cyclohexane-1-carboxylic acid (56 mg, 0.3 mmol), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **25** (42 mg, 60%) as a colorless liquid.



^{1}H NMR (500 MHz, CDCl$_3$): 7.14 (2 H, t, *J* = 7.6 Hz), 6.68 (1 H, t, *J* = 7.4 Hz), 6.62 (2 H, d, *J* = 7.9 Hz), 3.72–3.37 (5 H, m), 2.30 (1 H, t, *J* = 12.0 Hz), 2.21 (1 H, d, *J* = 11.3 Hz), 1.96 (1 H, d, *J* = 13.0 Hz), 1.77 (2 H, d, *J* = 12.3 Hz), 1.66 (1 H, q, *J* = 12.4, 12.0 Hz), 1.39 (1 H, q, *J* = 12.7 Hz), 1.32–1.20 (1 H, m), 1.07 (1 H, q, *J* = 11.4 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 175.4, 147.2, 129.3, 117.7, 113.9, 54.2, 51.8, 51.0, 33.0, 29.1, 24.9, 24.8 ppm. – IR: 3365, 3058, 3021, 2933, 2856, 1730, 1601, 1497, 1448, 1434, 1322, 1262, 1192, 1169, 1031, 867, 749, 693 cm^{-1}.

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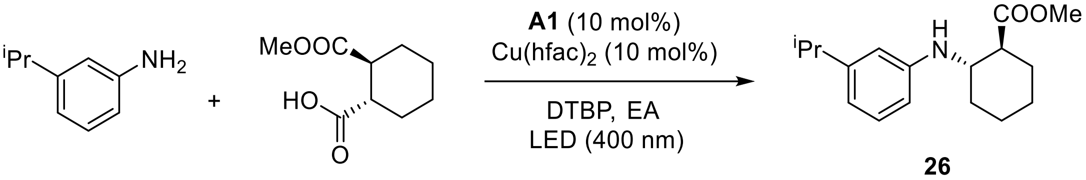
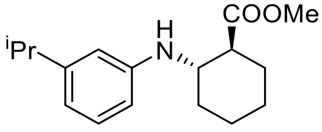
Methyl (1*S**,2*S**)-2-((3-isopropylphenyl)amino)cyclohexane-1-carboxylate (26)



According to **GP2**, the reaction was carried out with 3-isopropylaniline (101 mg, 0.75 mmol, 2.5 equiv.), (1*S**,2*S**)-2-(methoxycarbonyl)cyclohexane-1-carboxylic acid (56 mg, 0.3 mmol), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **26** (50 mg, 61%) as a brown solid.



^{1}H NMR (500 MHz, CDCl$_3$): 7.08 (1 H, t, *J* = 7.7 Hz), 6.58 (1 H, d, *J* = 7.5 Hz), 6.52–6.44 (2 H, m), 3.60 (3 H, s), 3.57 (1 H, dd, *J* = 10.3, 3.8 Hz), 3.43 (1 H, brs), 2.81 (1 H, hept, *J* = 6.7 Hz), 2.31 (1 H, ddd, *J* = 13.8, 10.3, 3.7 Hz), 2.23 (1 H, dd, *J* = 13.4, 3.9 Hz), 2.03–1.91 (1 H, m), 1.78 (2 H, d, *J* = 12.7 Hz), 1.68 (2 H q, *J* = 12.4, 12.0 Hz), 1.40 (1 H, q, *J* = 12.8 Hz), 1.32–1.26 (1 H, m), 1.23 (6 H, d, *J* = 7.0 Hz), 1.07 (1 H, q, *J* = 12.9 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 175.4, 150.1, 147.2, 129.2, 115.9, 112.4, 111.2, 54.2, 51.8, 50.9, 34.3, 33.0, 29.0, 24.8, 24.1 ppm. – IR: 3366, 3035, 2967, 2931, 2856, 1728, 1604, 1587, 1514, 1485, 1448, 1321, 1269, 1251, 1192, 1167, 1027, 855, 777, 700 cm^{-1}. – HRMS: calcd for C$_{17}$H$_{26}$NO$_2$: 276.1958, found 276.1958 [M+H$^+$].

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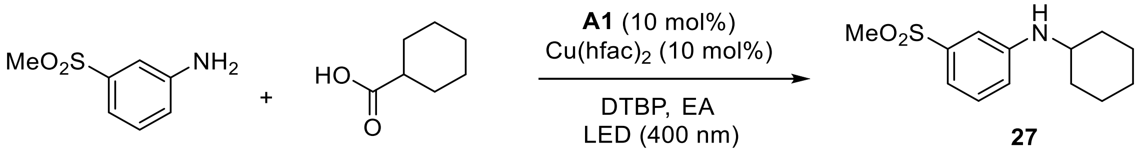
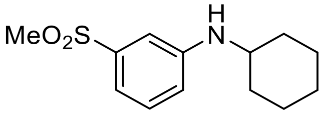
N-Cyclohexyl-3-(methylsulfonyl)aniline (27)

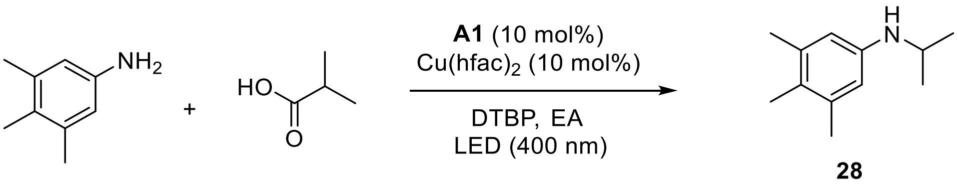


According to **GP1**, the reaction was carried out with 3-(methylsulfonyl)aniline (51 mg, 0.3 mmol), cyclohexanecarboxylic acid (96 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 4 : 1 v/v) to give the amine product **27** (53 mg, 71%) as a colorless liquid.

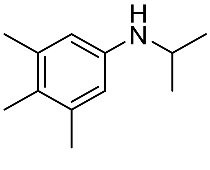


^{1}H NMR (500 MHz, $CDCl_3$): 7.28 (1 H, t, *J* = 7.9 Hz), 7.13 (1 H, d, *J* = 7.6 Hz), 7.06 (1 H, t, *J* = 1.9 Hz), 6.76 (1 H, dd, *J* = 8.2, 1.8 Hz), 4.16 (1 H, brs), 3.29 (1 H, td, *J* = 10.0, 4.9 Hz), 3.02 (3 H, s), 2.02 (2 H, d, *J* = 9.6 Hz), 1.75 (2 H, dt, *J* = 12.9, 3.2 Hz), 1.65 (1 H, d, *J* = 12.9 Hz), 1.38 (2 H, q, *J* = 12.1 Hz), 1.19 (3 H, dq, *J* = 25.0, 12.6 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 148.1, 141.4, 130.3, 117.7, 114.8, 110.5, 51.6, 44.5, 3.20, 25.8, 24.9 ppm. – IR: 3384, 1084, 3033, 2928, 2853, 2255, 1737, 1599, 1515, 1486, 1449, 1370, 1297, 126, 1231, 1150, 1088, 991, 858 cm^{-1}. – HRMS: calcd for $C_{13}H_{20}NO_2S$: 254.1209, found 254.1204 [M+H$^+$].

N-Isopropyl-3,4,5-trimethylaniline (28)[18]



According to **GP1**, the reaction was carried out with 3,4,5-trimethylaniline (41 mg, 0.3 mmol), isobutyric acid (66 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 14 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **28** (35 mg, 66%) as a yellow liquid.



^{1}H NMR (500 MHz, CDCl$_3$): 6.31 (2 H, s), 3.60 (1 H, hept, *J* = 6.3 Hz), 2.22 (6 H, s), 2.07 (3 H, s), 1.19 (6 H, d, *J* = 6.3 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 145.1, 137.3, 123.7, 113.2, 44.5, 23.3, 21.0, 14.5 ppm. – IR: 3323, 3003, 2948, 2885, 2854, 1743, 1709, 1667, 1546, 1484, 1514, 1484, 1440, 1388, 1221, 1194, 1148, 1091, 1013 cm^{-1}.

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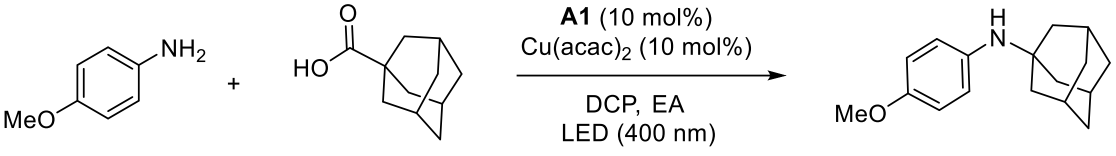
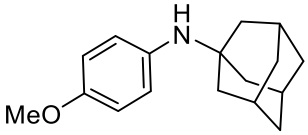
N-(4-Methoxyphenyl)adamantan-1-amine (29)[19]



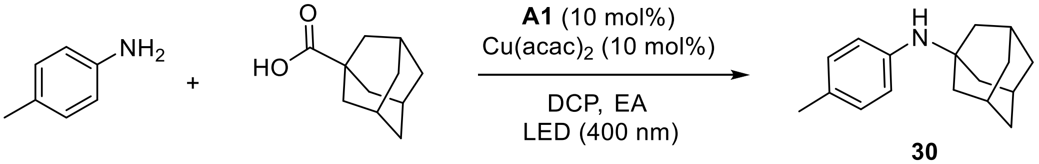
29

According to **GP2**, the reaction was carried out with *p*-anisidine (92 mg, 0.75 mmol, 2.5 equiv.), adamantane-1-carboxylic acid (54 mg, 0.3 mmol), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(acac)$_2$ (8 mg, 0.03 mmol, 10 mol%), and DCP (120 mg, 0.45 mmol, 1.5 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then extracted with concentrated HCl (2 x 10 mL), neutralized the aqueous phase with solid sodium carbonate, and back extracted with ethyl acetate (3x 15 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 4 : 1 v/v) to give the amine product **29** (40 mg, 51%) as a pale brown solid.

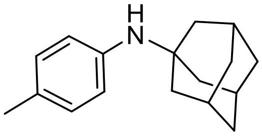


m.p.: 49–52˚C. –^{1}H NMR (300 MHz, CDCl$_3$): 6.82 (2 H, d, *J* = 8.7 Hz), 6.75 (2 H, d, *J* = 8.7 Hz), 3.76 (3 H, s), 2.62 (1 H, s), 2.08 (3H, s), 1.75 (6H, s), 1.63 (6 H, q, *J* = 10.8 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 155.0, 138.4, 124.4, 114.0, 55.69, 52.8, 43.9, 36.6, 29.9 ppm. – IR: 2903, 2848, 2255, 1609, 1506, 1468, 1356, 1308, 1233, 1078, 1038, 906, 833, 729 cm^{-1}.

N-(*p*-Tolyl)adamantan-1-amine (30)[19]



According to **GP2**, the reaction was carried out with *p*-toluidine (80 mg, 0.75 mmol, 2.5 equiv.), adamantane-1-carboxylic acid (54 mg, 0.3 mmol), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(acac)$_2$ (8 mg, 0.03 mmol, 10 mol%), and DCP (120 mg, 0.45 mmol, 1.5 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then extracted with concentrated HCl (2 x 10 mL), neutralized the aqueous phase with solid sodium carbonate, and back extracted with ethyl acetate (3x 15 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **30** (59 mg, 81%) as a pale brown solid.



m.p.: 60–62°C. –^{1}H NMR (500 MHz, CDCl$_3$): 6.98 (2 H, d, *J* = 7.9 Hz), 6.75 (2 H, d, *J* = 7.9 Hz), 2.71 (1 H, brs), 2.26 (3 H, s), 2.09 (3 H, s), 1.82 (6 H, s), 1.66 (6 H, q, *J* = 12.5 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 143.2, 129.6, 129.3, 121.0, 52.5, 43.8, 36.6, 29.9, 20.7 ppm. – IR: 3063, 2977, 2945, 2908, 2854, 1756, 1743, 1625, 1510, 1450, 1264, 1256, 907, 731, 705 cm^{-1}.

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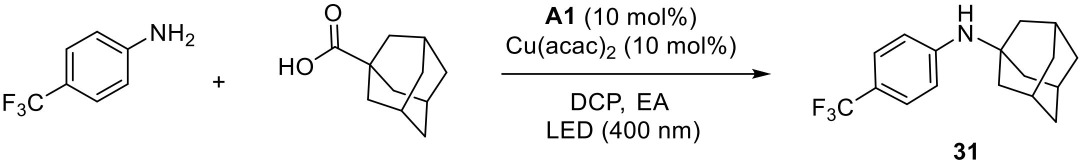
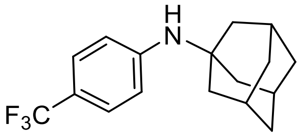
N-(4-(Trifluoromethyl)phenyl)adamantan-1-amine (31)[20]



According to **GP2**, the reaction was carried out with 4-(trifluoromethyl)aniline (121 mg, 0.75 mmol, 2.5 equiv.), adamantane-1-carboxylic acid (54 mg, 0.3 mmol), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(acac)$_2$ (8 mg, 0.03 mmol, 10 mol%), and DCP (120 mg, 0.45 mmol, 1.5 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then extracted with concentrated HCl (2 x 10 mL), neutralized the aqueous phase with solid sodium carbonate, and back extracted with ethyl acetate (3x 15 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **31** (50 mg, 56%) as a colorless solid.



m.p.: 68–71˚C. –^{1}H NMR (500 MHz, CDCl$_3$): 7.34 (2 H, d, *J* = 8.4 Hz), 6.74 (2 H, d, *J* = 8.3 H), 2.14 (3 H, s), 1.95 (6 H, s), 1.78 – 1.64 (6H, m) ppm– ^{13}C NMR (125 MHz, CDCl$_3$): 149.2 (q, $^2J_{C\text{-}F}$ = 7.8 Hz), 146.3, 126.8 (q, $^1J_{C\text{-}F}$ = 273.5 Hz), 126.3 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 115.5, 42.9, 36.5, 29.8 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): –61.1 ppm. – IR: 3429, 2908, 2852, 1615, 1528, 1505, 1460, 1327, 1308, 1289, 1187, 1162, 1112, 1066, 905, 826, 730 cm^{-1}.

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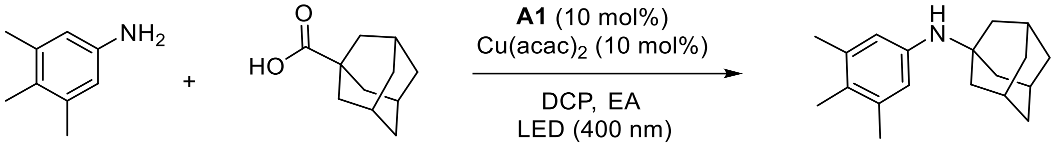
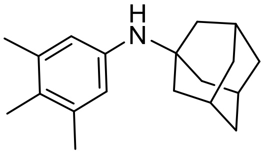
N-(3,4,5-Trimethylphenyl)adamantan-1-amine (32)



32

According to **GP2**, the reaction was carried out with 3,4,5-trimethylaniline (101 mg, 0.75 mmol, 2.5 equiv.), adamantane-1-carboxylic acid (54 mg, 0.3 mmol), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(acac)$_2$ (8 mg, 0.03 mmol, 10 mol%), and DCP (120 mg, 0.45 mmol, 1.5 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then extracted with concentrated HCl (2 x 10 mL), neutralized the aqueous phase with solid sodium carbonate, and back extracted with ethyl acetate (3x 15 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **32** (59 mg, 74%) as a yellow solid.



m.p.: 68–71˚C. – ^{1}H NMR (500 MHz, CDCl$_3$): 6.54 (2 H, s), 2.23 (6 H, s), 2.10 (6 H, s), 1.84 (6 H, s), 1.66 (6 H, q, *J* = 10.7 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 142.9, 136.6, 126.9, 120.4, 43.8, 36.6, 29.9, 20.9, 14.7 ppm. – IR: 3066, 3006, 2961, 2906, 2854, 1608, 1492, 1369, 1059, 893, 809 cm^{-1}. – HRMS: calcd for C$_{19}$H$_{28}$N: 270.2216, found 270.2219 [M+H$^+$].

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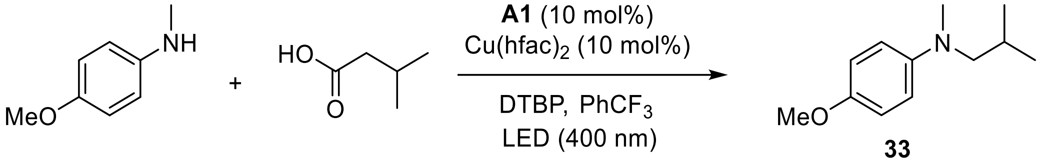
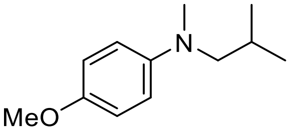
N-Isobutyl-4-methoxy-*N*-methylaniline (33)

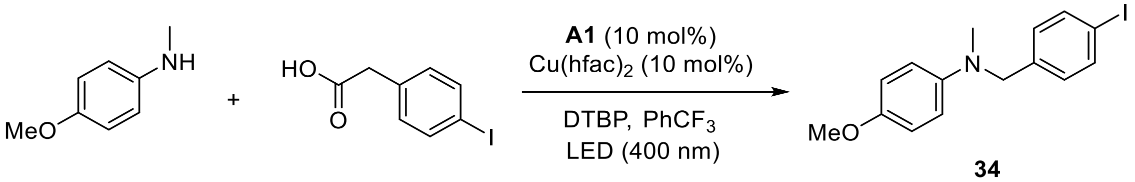


According to **GP2**, the reaction was carried out with 4-methoxy-*N*-methylaniline (103 mg, 0.75 mmol, 2.5 equiv.), isovaleric acid (31 mg, 0.3 mmol), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in trifluorotoluene (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 9 : 1 v/v) to give the amine product **33** (55 mg, 95%) as a yellow liquid.

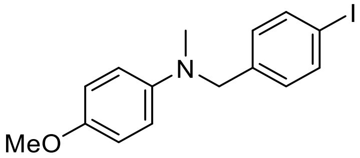


^{1}H NMR (500 MHz, CDCl$_3$): 6.85 (2 H, d, *J* = 8.9 Hz), 6.69 (2 H, d, *J* = 8.9 Hz), 3.78 (3 H, s), 3.02 (2 H, d, *J* = 7.3 Hz), 2.91 (3 H, s), 2.03 (1 H, dp, *J* = 13.4, 6.3 Hz), 0.94 (6 H, d, *J* = 6.8 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 151.2, 145.1, 114.9, 113.8, 62.2, 56.0, 39.9, 27.5, 20.6 ppm. – IR: 3063, 2952, 2875, 2831, 1753, 1713, 1511, 1464, 1363, 1240, 1218, 1180, 1039, 978, 814, 700 cm^{-1}. – HRMS: calcd for $C_{12}H_{20}NO$: 194.1539, found 194.1540 [M+H$^+$].

N-(4-Iodobenzyl)-4-methoxy-*N*-methylaniline (34)



According to **GP2**, the reaction was carried out with 4-methoxy-*N*-methylaniline (103 mg, 0.75 mmol, 2.5 equiv.), 2-(4-iodophenyl)acetic acid (79 mg, 0.3 mmol), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in trifluorotoluene (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 9 : 1 v/v) to give the amine product **34** (74 mg, 70%) as a brown liquid.



^{1}H NMR (500 MHz, CDCl$_3$): 7.64 (2 H, d, *J* = 8.1 Hz), 7.01 (2 H, d, *J* = 8.0 Hz), 6.83 (2 H, d, *J* = 9.0 Hz), 6.72 (2 H, d, *J* = 9.1 Hz), 4.36 (2 H, s), 3.77 (3 H, s), 2.91 (3 H, s) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 152.1, 144.6, 139.1, 137.6, 129.3, 114.9, 114.8, 92.1, 57.7, 55.9, 39.3 ppm. – IR: 3399, 2987, 2932, 2829, 1738, 1583, 1510, 1482, 1366, 1241, 1212, 1039, 1005, 950, 812, 716 cm^{-1}. – HRMS: calcd for $C_{15}H_{16}INO$: 354.0349, found 354.0352 [M+H$^+$].

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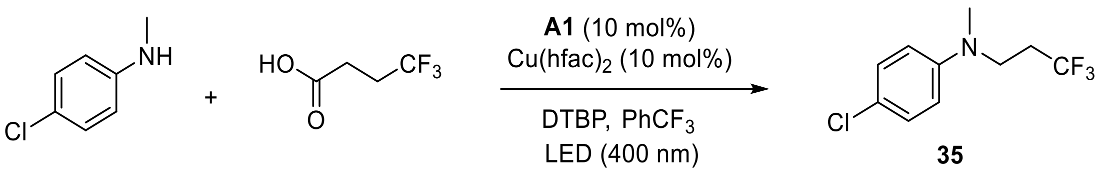
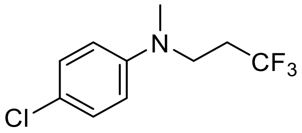
4-Chloro-*N*-methyl-*N*-(3,3,3-trifluoropropyl)aniline (35)



According to **GP2**, the reaction was carried out with 4-chloro-*N*-methylaniline (106 mg, 0.75 mmol, 2.5 equiv.), 4,4,4-trifluorobutanoic acid (43mg, 0.3 mmol), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in trifluorotoluene (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **35** (48mg, 67%) as a colorless liquid.



^{1}H NMR (500 MHz, CDCl$_3$): 7.20 (d, *J* = 9.0 Hz, 2H), 6.61 (d, *J* = 9.0 Hz, 2H), 4.05–3.19 (m, 2H), 2.93 (s, 3H), 2.52–2.20 (m, 2H) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 146.8, 129.4, 126.5 (q, $^1J_{C\text{-}F}$ = 276.9 Hz), 122.2, 113.6, 46.1 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 38.6, 30.7 (q, $^2J_{C\text{-}F}$ = 27.3 Hz) ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): –65.2 (t, *J* = 10.9 Hz) ppm. – IR: 3440, 2985, 2918, 2891, 2823, 1745, 1598, 1500, 1440, 1376, 1336, 1316, 1246, 1142, 1101, 1000, 954, 811 cm^{-1}. – HRMS: calcd for $C_{10}H_{12}ClF_3N$: 238.0605, found 238.0605 [M+H$^+$].

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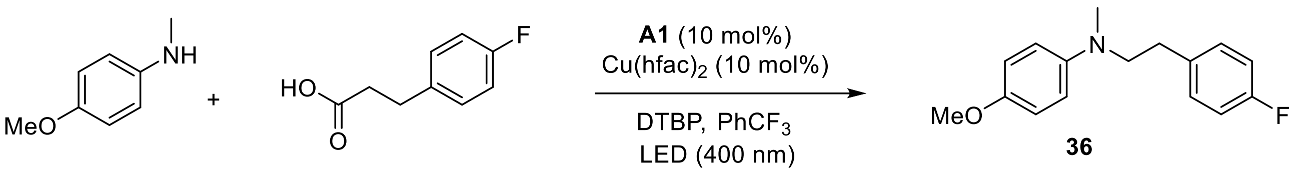
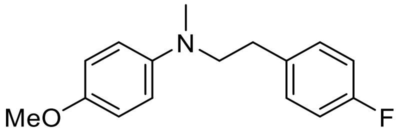
N-(4-Fluorophenethyl)-4-methoxy-*N*-methylaniline (36)



According to **GP2**, the reaction was carried out with 4-methoxy-*N*-methylaniline (103 mg, 0.75 mmol, 2.5 equiv.), 3-(4-fluorophenyl)propanoic acid (50 mg, 0.3 mmol), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in trifluorotoluene (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 9 : 1 v/v) to give the amine product **36** (44 mg, 57%) as a dark yellow liquid.



^{1}H NMR (500 MHz, CDCl$_3$): 7.15 (2 H, d, *J* = 8.3, 5.6 Hz), 6.99 (2 H, t, *J* = 8.7 Hz), 6.87 (2 H, d, *J* = 9.0 Hz), 6.73 (2 H, d, *J* = 9.0 Hz), 3.78 (3 H, s), 3.47 (2 H, dd, *J* = 8.9, 6.5 Hz), 2.85 (3 H, s), 2.80 (2 H, dd, *J* = 8.8, 6.5 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 161.6 (d, $^1J_{C\text{-}F}$ = 243.7 Hz), 151.8, 143.9, 135.8 (d, $^4J_{C\text{-}F}$ = 3.8 Hz), 130.3 (d, $^3J_{C\text{-}F}$ = 7.6 Hz), 115.4 (d, $^2J_{C\text{-}F}$ = 21.4 Hz), 115.0, 114.6, 56.1, 55.9, 39.3, 32.2 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): –117.2 (ddd, *J* = 14.1, 8.8, 5.4 Hz) ppm. – IR: 3061, 3001, 2934, 2875, 2841, 1737, 1701, 1600, 1508, 1464, 1256, 1243, 1220, 1181, 1157, 1037, 821 cm^{-1}. – HRMS: calcd for C$_{16}$H$_{18}$FNO: 260.1445, found 260.1447 [M+H$^+$].

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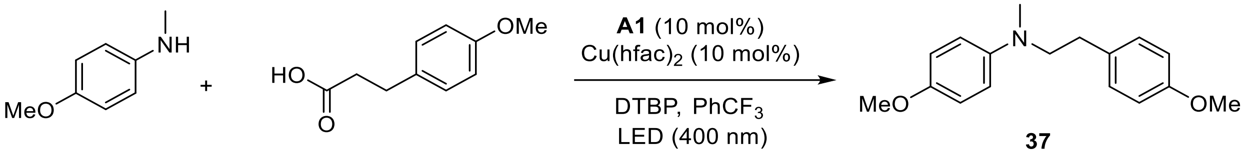
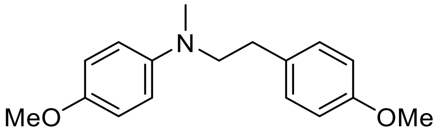
4-Methoxy-*N*-(4-methoxyphenethyl)-*N*-methylaniline (37)



According to **GP2**, the reaction was carried out with 4-methoxy-*N*-methylaniline (103 mg, 0.75 mmol, 2.5 equiv.), 3-(4-methoxyphenyl)propanoic acid (54 mg, 0.3 mmol), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in trifluorotoluene (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 9 : 1 v/v) to give the amine product **37** (75 mg, 92%) as a yellow liquid.



^{1}H NMR (500 MHz, $CDCl_3$): 7.13 (2 H, d, *J* = 8.6 Hz), 6.87 (4 H, t, *J* = 8.2 Hz), 6.74 (2 H, d, *J* = 9.0 Hz), 3.81 (3 H, s), 3.79 (3 H, s), 3.55–3.38 (2 H, m), 2.87 (3H, s), 2.82–2.69 (2 H, m) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 158.1, 151.7, 144.0, 132.1, 129.8, 115.0, 114.5, 114.0, 56.1, 55.9, 55.4, 39.2, 31.9 ppm. – IR: 3069, 2998, 2937, 2841, 1745, 1712, 1611, 1510, 1473, 1440, 1361, 1219, 1178, 1036, 910, 820, 732 cm^{-1}. – HRMS: calcd for $C_{17}H_{22}NO_2$: 272.1645, found 272.1649 [M+H$^+$].

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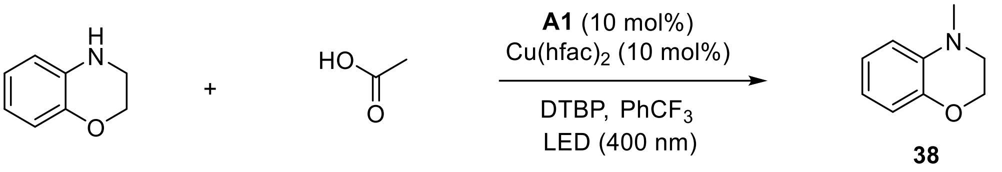
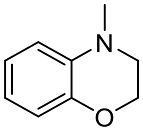
4-Methyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazine (38)[21]



According to **GP1**, the reaction was carried out with 3,4-dihydro-2*H*-benzo[*b*][1,4]oxazine (41 mg, 0.3 mmol), acetic acid (90 mg, 1.5 mmol, 5 .0 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in trifluorotoluene (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 24 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 9 : 1 v/v) to give the amine product **38** (28 mg, 62%) as a colorless liquid.



^{1}H NMR (500 MHz, $CDCl_3$): 6.84 (1 H, t, *J* = 7.6 Hz), 6.77 (1 H, d, *J* = 7.8 Hz), 6.73–6.61 (2 H, m), 4.36–4.26 (2 H, m), 3.34–3.19 (2 H, m), 2.88 (3 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 144.4, 136.7, 121.6, 118.4, 116.0, 112.7, 65.0, 49.4, 38.9 ppm. – IR: 2873, 2816, 1682, 1606, 1502, 1476, 1457, 1332, 1307, 1255, 1224, 1208, 1128, 1056 cm^{-1}.

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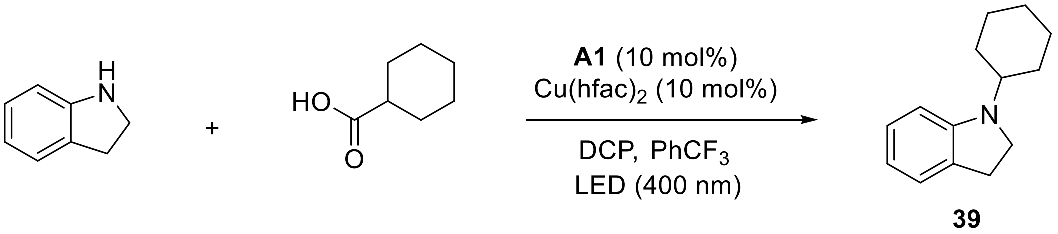
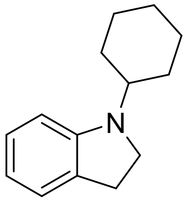
1-Cyclohexylindoline (39)[22]



According to **GP2**, the reaction was carried out with indoline (89 mg, 0.75 mmol, 2.5 equiv.), cyclohexanecarboxylic acid (38 mg, 0.3 mmol), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DCP (120 mg, 0.45 mmol, 1.5 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then extracted with concentrated HCl (2 x 10 mL), neutralized the aqueous phase with solid sodium carbonate, and back extracted with ethyl acetate (3x 15 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **39** (51 mg, 85%) as a dark yellow liquid.



^{1}H NMR (500 MHz, CDCl$_3$): 7.10 – 7.04 (2 H, m), 6.60 (1 H, t, *J* = 7.3 Hz), 6.43 (1 H, d, *J* = 7.8 Hz), 3.44 – 3.29 (3 H, m), 2.96 (2 H, t, *J* = 8.4 Hz), 1.91 – 1.83 (4 H, m), 1.80 – 1.67 (1 H, m), 1.45 – 1.32 (4 H, m), 1.23 – 1.09 (1 H, m) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 151.3, 130.2, 127.3, 124.5, 116.7, 106.9, 54.7, 46.8, 28.8, 28.4, 26.2, 26.1 ppm. – IR: 3350, 3049, 2930, 2854, 1709, 1651, 1609, 1578, 1508, 1478, 1460, 1311, 1264, 1211, 1184, 1019, 892, 736, 702 cm^{-1}.

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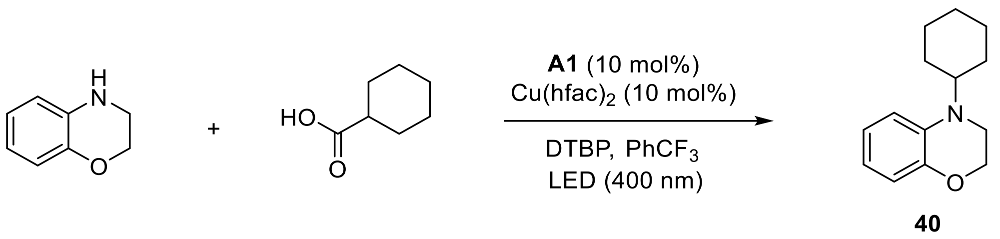
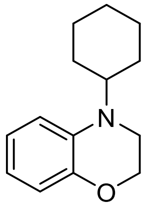
4-Cyclohexyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazine (40)

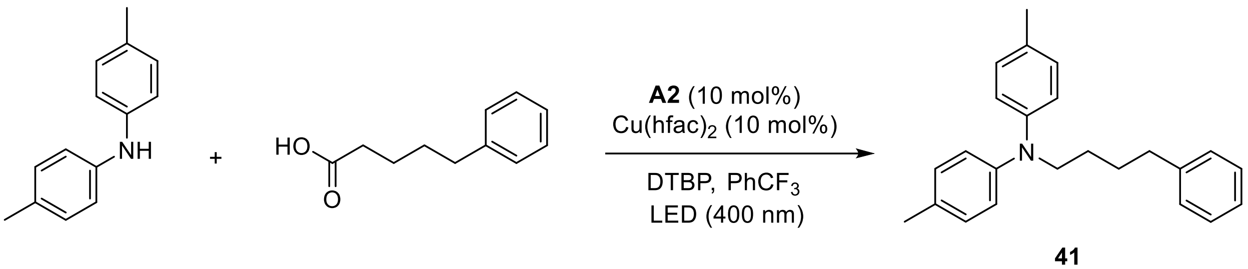


According to **GP2**, the reaction was carried out with 3,4-dihydro-2*H*-benzo[*b*][1,4]oxazine (101 mg, 0.75 mmol, 2.5 equiv.), cyclohexanecarboxylic acid (38 mg, 0.3 mmol), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in trifluorotoluene (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 5 : 95 v/v) to give the amine product **40** (56 mg, 86%) as a dark yellow liquid.



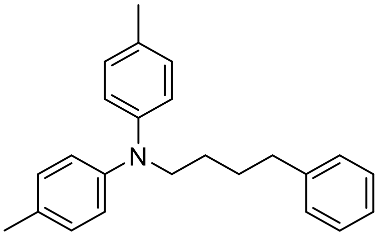
^{1}H NMR (500 MHz, $CDCl_3$): 6.84 (1 H, td, *J* = 8.0, 7.5, 1.5 Hz), 6.80 (1 H, dd, *J* = 7.9, 1.5 Hz), 6.75 (1 H, d, *J* = 8.0 Hz), 6.60 (1 H, td, *J* = 7.8, 1.4 Hz), 4.26–4.14 (2 H, m), 3.58 (1 H, ddt, *J* = 11.1, 6.9, 3.4 Hz), 3.40–3.19 (2 H, m), 2.00–1.81 (4 H, m), 1.73 (1 H, d, *J* = 13.0 Hz), 1.42 (4 H, quint., *J* = 10.8, 9.6 Hz), 1.22–1.09 (1 H, m) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 144.4, 135.1, 121.6, 116.9, 116.6, 112.1, 65.2, 55.9, 40.2, 29.2, 26.2, 26.1 ppm. – IR: 3074, 3054, 2995, 2943, 1614, 1502, 1458, 1431, 1264, 1212, 895, 734, 704 cm^{-1}. – HRMS: calcd for $C_{14}H_{20}NO$: 218.1539, found 218.1542 [M+H$^+$].

4-Methyl-*N*-(4-phenylbutyl)-*N*-(*p*-tolyl)aniline (41)



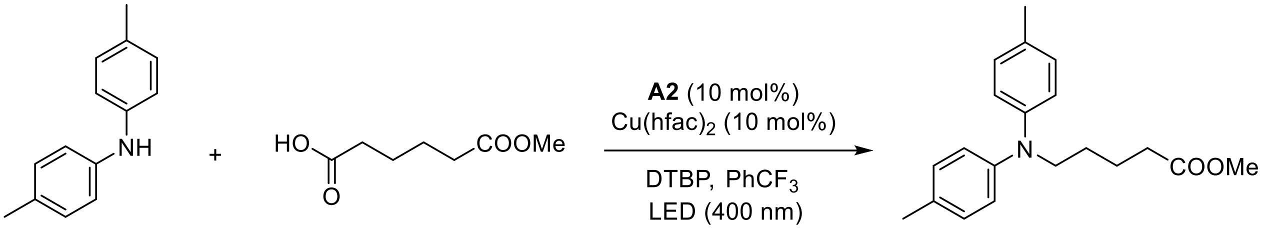
41

According to **GP1**, the reaction was carried out with di-*p*-tolylamine (59 mg, 0.3 mmol) 5-phenylpentanoic acid (133.5 mg, 0.75 mmol, 2.5 equiv.), acridine **A2** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in trifluorotoluene (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 24 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **41** (71 mg, 72%) as a colorless liquid.



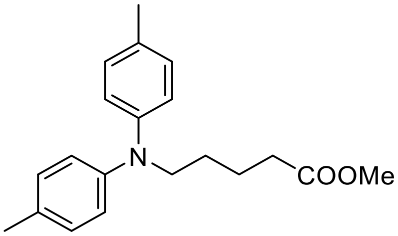
^{1}H NMR (500 MHz, $CDCl_3$): 7.36–7.24 (2 H, m), 7.26–7.13 (3 H, m), 7.08 (4 H, d, *J* = 8.2 Hz), 6.88 (4 H, d, *J* = 8.5 Hz), 3.68 (2 H, t, *J* = 7.0 Hz), 2.64 (2 H, t, *J* = 7.1 Hz), 2.33 (6 H, s), 1.85–1.58 (4 H, m) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 146.1, 142.5, 130.4, 129.9, 128.5, 128.4, 125.8, 121.0, 52.4, 35.8, 29.1, 27.3, 20.8 ppm. – IR: 3023, 2919, 2856, 1607, 1568, 1508, 1452, 1364, 1285, 1245, 1161, 1110, 1029 cm^{-1}. – HRMS: calcd for $C_{24}H_{28}N$: 330.2216, found 330.2214 [M+H$^+$].

Methyl 5-(di-*p*-tolylamino)pentanoate (42)



42

According to **GP1**, the reaction was carried out with di-*p*-tolylamine (59 mg, 0.3 mmol) 6-methoxy-6-oxohexanoic acid (120 mg, 0.75 mmol, 2.5 equiv.), acridine **A2** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in trifluorotoluene (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 24 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **42** (69 mg, 74%) as a colorless liquid.



^{1}H NMR (500 MHz, CDCl$_3$): 7.08 (4 H, d, *J* = 8.2 Hz), 6.98–6.80 (4 H, m), 3.68 (5 H, s), 2.35 (2 H, t, *J* = 6.1 Hz), 2.32 (6 H, s), 1.75–1.65 (4 H, m) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 174.0, 146.0, 130.5, 129.9, 121.0, 120.9, 52.1, 51.6, 34.0, 27.2, 22.6, 20.7 ppm. – IR: 3023, 2918, 2859, 1736, 1608, 1568, 1507, 1436, 1364, 1317, 1289, 1245, 1160, 1094, 1017 cm^{-1}. – HRMS: calcd for $C_{20}H_{26}NO_2$: 312.1958, found 312.1956 [M+H$^+$].

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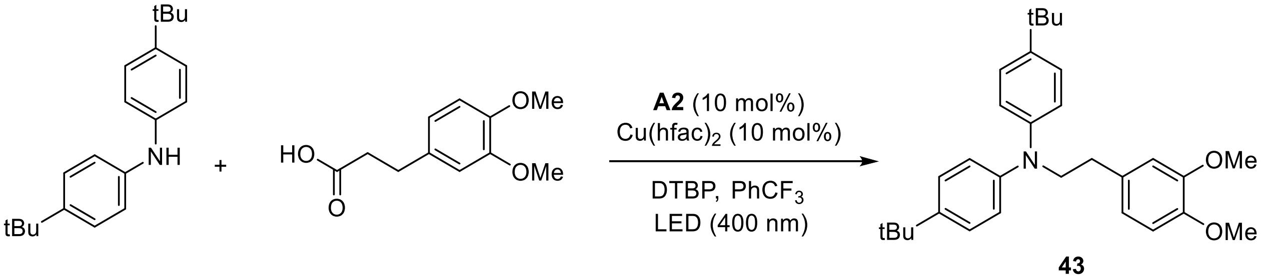
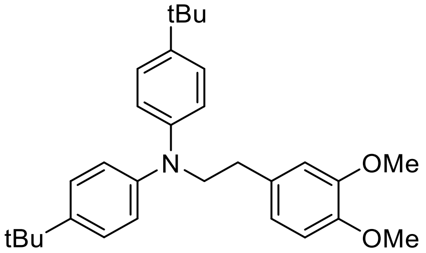
4-(*tert*-Butyl)-*N*-(4-(*tert*-butyl)phenyl)-*N*-(3,4-dimethoxyphenethyl)aniline (43)



According to **GP1**, the reaction was carried out with bis(4-(*tert*-butyl)phenyl)amine (84 mg, 0.3 mmol), 3-(3,4-dimethoxyphenyl)propanoic acid (158 mg, 0.75 mmol, 2.5 equiv.), acridine **A2** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in trifluorotoluene (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 24 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 9 : 1 v/v) to give the amine product **43** (92 mg, 69%) as a colorless solid.



m.p.: 93–95 ˚C. – ^{1}H NMR (500 MHz, CDCl$_3$): 7.28 (4 H, d, *J* = 8.7 Hz), 6.91 (4 H, d, *J* = 8.8 Hz), 6.81 (1 H, d, *J* = 8.1 Hz), 6.76 (1 H, d, *J* = 8.0 Hz), 6.69 (1 H, s), 3.89 (2 H, q, *J* = 7.6 Hz), 3.87 (3 H, s), 3.84 (3 H, s), 2.91 (2 H, t, *J* = 7.8 Hz), 1.32 (18 H, s) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 149.0, 147.6, 145.4, 144.0, 132.2, 126.2, 120.8, 120.5, 112.3, 111.5, 56.1, 56.0, 54.2, 34.3, 33.5, 31.6 ppm. – IR: 2958, 2864, 1606, 1510, 1462, 1417, 1392, 1363, 1282, 1234, 1176, 1156, 1138, 1071, 1029 cm^{-1}. – HRMS: calcd for C$_{30}$H$_{40}$NO$_2$: 446.3054, found 446.3049 [M+H$^+$].

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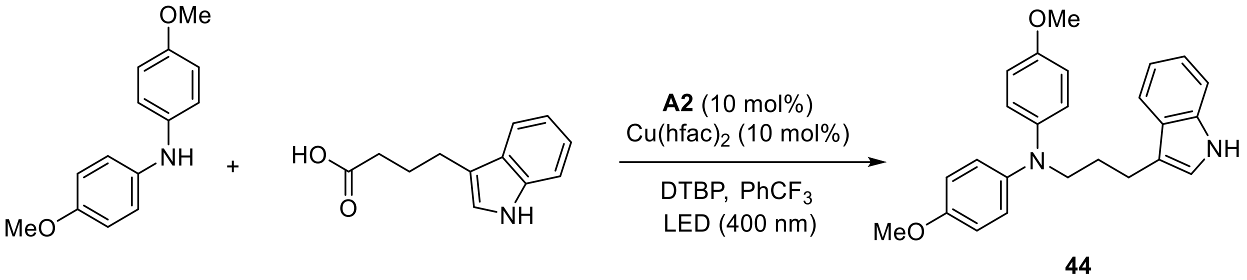
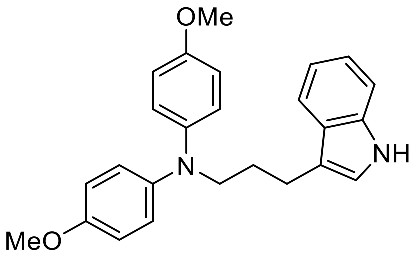
N-(3-(1*H*-Indol-3-yl)propyl)-4-methoxy-*N*-(4-methoxyphenyl)aniline (44)

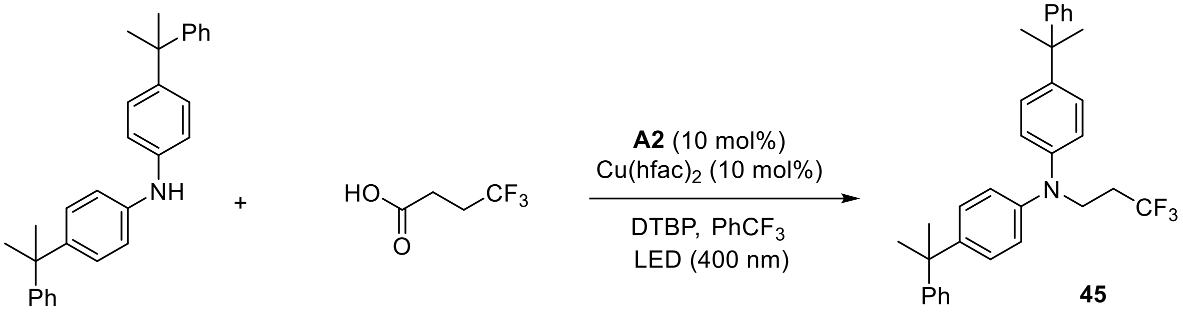


According to **GP1**, the reaction was carried out with bis(4-methoxyphenyl)amine (69 mg, 0.3 mmol), 4-(1*H*-indol-3-yl)butanoic acid (152 mg, 0.75 mmol, 2.5 equiv.), acridine **A2** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in trifluorotoluene (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 24 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 4 : 1 v/v) to give the amine product **44** (59 mg, 51%) as a brown liquid.

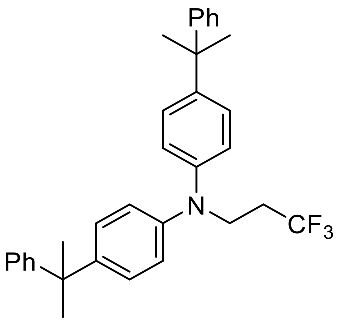


^{1}H NMR (500 MHz, CDCl$_3$): 7.91 (1 H, s), 7.56 (1 H, d, *J* = 7.9 Hz), 7.36 (1 H, s), 7.20 (1 H, t, *J* = 7.5 Hz), 7.12 (1 H, t, *J* = 7.5 Hz), 6.89 (4 H, d, *J* = 9.0 Hz), 6.82 (4 H, d, *J* = 8.9 Hz), 3.79 (6 H, s), 3.69 (2 H, t, *J* = 7.5 Hz), 2.84 (2 H, t, *J* = 7.6 Hz), 2.07 (2 H, quint., *J* = 7.6 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 154.3, 142.7, 136.5, 127.6, 122.3, 122.0, 121.3, 119.3, 119.0, 116.1, 114.8, 111.2, 55.7, 52.6, 27.9, 22.7 ppm. – IR: 3410, 3038, 2930, 2831, 1616, 1501, 1455, 1440, 1418, 1337, 1237, 1177, 1080, 1033 cm^{-1}. – HRMS: calcd for $C_{25}H_{27}N_2O_2$: 387.2067, found 387.2066 [M+H$^+$].

4-(2-Phenylpropan-2-yl)-*N*-(4-(2-phenylpropan-2-yl)phenyl)-*N*-(3,3,3-trifluoropropyl)aniline (45)

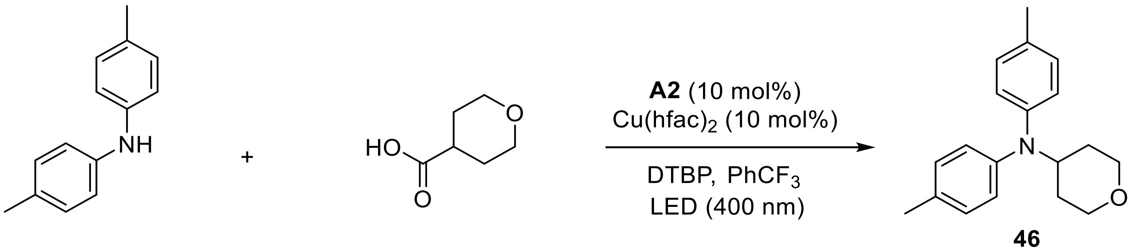


According to **GP1**, the reaction was carried out with bis(4-(2-phenylpropan-2-yl)phenyl)amine (121 mg, 0.3 mmol), 4,4,4-trifluorobutanoic acid (107 mg, 0.75 mmol, 2.5 equiv.), acridine **A2** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in trifluorotoluene (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light ($\lambda = 400$ nm) while stirring for 24 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **45** (77 mg, 51%) as a colorless liquid.



^{1}H NMR (500 MHz, CDCl$_3$): 7.35–7.29 (8 H, m), 7.24–7.15 (6 H, m), 6.98–6.87 (4 H, m), 4.09–3.88 (2 H, m), 2.65–2.33 (2 H, m), 1.71 (12 H, s) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 150.8, 144.8, 144.3, 128.1, 127.9, 126.9, 125.7, 124.3 (d, $^1J_{C\text{-}F}$ = 277.4 Hz), 120.3, 45.3 (q, $^3J_{C\text{-}F}$ = 4.1 Hz), 42.5, 31.9 (q, $^2J_{C\text{-}F}$ = 27.0 Hz), 30.9 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): –65.1 (td, J = 10.8, 3.3 Hz) ppm. – IR: 3029, 2966, 1602, 1507, 1494, 1464, 1445, 1384, 1334, 1289, 1234, 1200, 1145, 1089, 1029, 1003 cm^{-1}. – HRMS: calcd for $C_{33}H_{35}F_3N$: 502.2716, found 502.2716 [M+H$^+$].

***N*,*N*-Di-*p*-tolyltetrahydro-2*H*-pyran-4-amine (46)**



According to **GP1**, the reaction was carried out with di-*p*-tolylamine (59 mg, 0.3 mmol), tetrahydro-2*H*-pyran-4-carboxylic acid (98 mg, 0.75 mmol, 2.5 equiv.), acridine **A2** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in trifluorotoluene (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 24 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 4 : 1 v/v) to give the amine product **46** (57 mg, 68%) as a colorless liquid.

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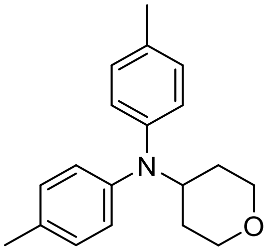
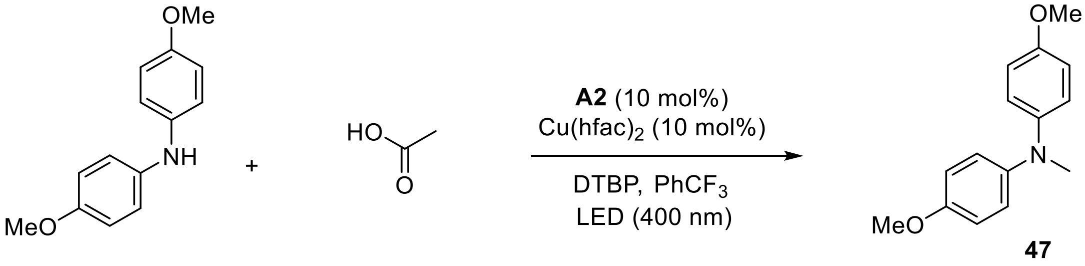


^{1}H NMR (500 MHz, CDCl$_3$): 7.08 (4 H, d, *J* = 7.9 Hz), 6.75 (4 H, d, *J* = 8.8 Hz), 4.02 (3 H, dd, *J* = 16.7, 8.4 Hz), 3.52 (2 H, t, *J* = 11.9 Hz), 2.31 (6 H, s), 1.90 (2 H, d, *J* = 12.6 Hz), 1.57 (2 H, ddq, *J* = 24.7, 12.4, 8.1, 6.4 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 143.9, 131.4, 129.9, 122.8, 67.9, 54.2, 31.9, 20.8 ppm. – IR: 3023, 2950, 2920, 2837, 1737, 1617, 1568, 1505, 1446, 1381, 1305, 1278, 1250, 1233, 1145, 1128, 1105, 1083 cm^{-1}. – HRMS: calcd for $C_{19}H_{24}NO$: 282.1852, found 282.1856 [M+H$^+$].

4-Methoxy-*N*-(4-methoxyphenyl)-*N*-methylaniline (47)[23]



According to **GP1**, the reaction was carried out with bis(4-methoxyphenyl)amine (69 mg, 0.3 mmol), acetic acid (90 mg, 1.5 mmol, 5.0 equiv.), acridine **A2** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in trifluorotoluene (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 24 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 9 : 1 v/v) to give the amine product **47** (49 mg, 67%) as a colorless liquid.

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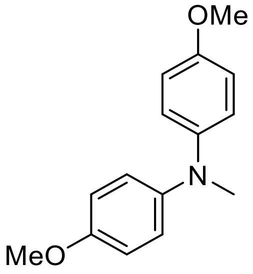
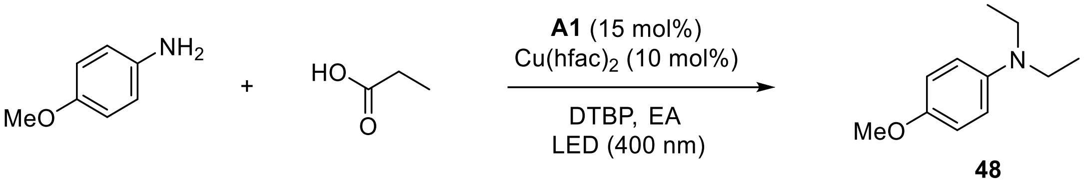


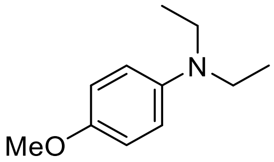
m.p.: 102–104 ˚C. –^{1}H NMR (500 MHz, $CDCl_3$): 6.91 (4 H, d, *J* = 8.9 Hz), 6.83 (4 H, d, *J* = 8.9 Hz), 3.78 (6 H, s), 3.21 (3 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 154.5, 143.8, 121.7, 114.7, 55.8, 41.2 ppm. – IR: 3014, 2950, 2909, 1834, 1880, 1609, 1509, 1457, 1442, 1336, 1283, 1241, 1180, 1135, 1123, 1108, 1029 cm^{-1}.

***N,N*-Diethyl-4-methoxyaniline (48)**[19]



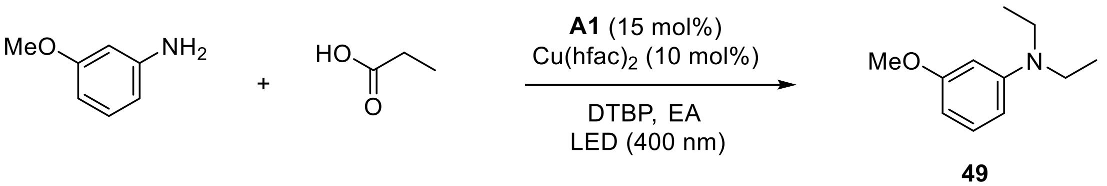
48

According to **GP1**, the reaction was carried out with 4-methoxyaniline (37 mg, 0.3 mmol), propionic acid (111 mg, 1.5 mmol, 5 equiv.), acridine **A1** (13 mg, 0.045 mmol, 15 mol%), $Cu(hfac)_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (1.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **48** (26 mg, 48%) as a yellow liquid.



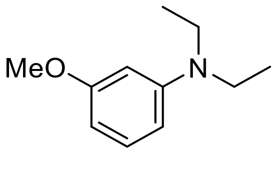
^{1}H NMR (500 MHz, $CDCl_3$): 6.84 (2 H, d, *J* = 8.9 Hz), 6.72 (2 H, d, *J* = 8.5 Hz), 3.77 (3 H, s), 3.27 (4 H, q, *J* = 6.9 Hz), 1.11 (6 H, t, *J* = 7.0 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 151.6, 143.0, 115.4, 114.9, 55.9, 45.3, 12.6 ppm. – IR: 3058, 2968, 2938, 2878, 2833, 1512, 1464, 1372, 1242, 1181, 1040, 813 cm^{-1}.

N,N-Diethyl-3-methoxyaniline (49)[24]



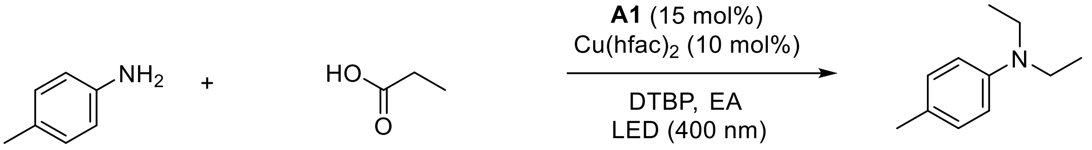
49

According to **GP1**, the reaction was carried out with 3-methoxyaniline (37 mg, 0.3 mmol), propionic acid (111 mg, 1.5 mmol, 5 equiv.), acridine **A1** (13 mg, 0.045 mmol, 15 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (1.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **49** (32 mg, 60%) as a colorless liquid.



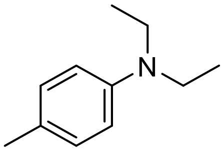
^{1}H NMR (500 MHz, CDCl$_3$): 7.12 (1 H, t, *J* = 8.5 Hz), 6.32 (1 H, d, *J* = 9.8 Hz), 6.23 (2 H, dd, *J* = 5.0, 2.6 Hz), 3.79 (3 H, s), 3.34 (4 H, q, *J* = 7.1 Hz,), 1.16 (6 H, t, *J* = 7.1 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 161.1, 149.3, 130.0, 105.2, 100.1, 98.5, 55.2, 44.6, 12.8 ppm. – IR: 2967, 2930, 2899, 2885, 2832, 1608, 1572, 1498, 1485, 1455, 1392, 1356, 1327, 1220, 1139, 1055, 1019, 824, 746, 687 cm^{-1}.

N,N-Diethyl-4-methylaniline (50)[25]



50

According to **GP1**, the reaction was carried out with 4-methylaniline (32 mg, 0.3 mmol), propionic acid (111 mg, 1.5 mmol, 5 equiv.), acridine **A1** (13 mg, 0.045 mmol, 15 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (1.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light ($\lambda = 400$ nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 98 : 2 v/v) to give the amine product **50** (32 mg, 65%) as a colorless liquid.



^{1}H NMR (500 MHz, CDCl$_3$): 7.03 (2 H, d, *J* = 8.5 Hz), 6.63 (2 H, d, *J* = 8.5 Hz), 3.32 (4 H, q, *J* = 7.0 Hz), 2.24 (3 H, s), 1.14 (6 H, t, *J* = 7.0 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 146.0, 129.9, 124.9, 112.7, 44.7, 20.3, 12.7 ppm. – IR: 3055, 2968, 2928, 2857, 1735, 1617, 1580, 1519, 1484, 1455, 1374, 1264, 1194, 803, 737, 704 cm^{-1}.

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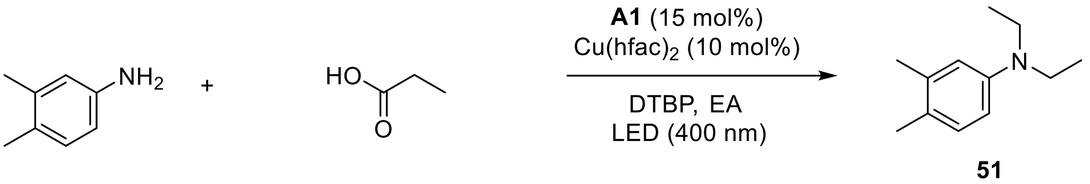
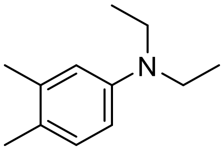
N,N-Diethyl-3,4-dimethylaniline (51)[26]

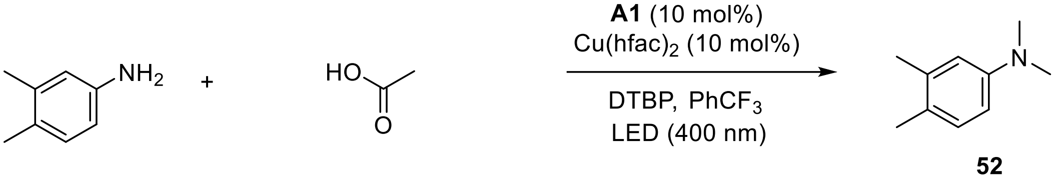


According to **GP1**, the reaction was carried out with 3,4-dimethylaniline (36 mg, 0.3 mmol), propionic acid (111 mg, 1.5 mmol, 5 equiv.), acridine **A1** (13 mg, 0.045 mmol, 15 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (1.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 98 : 2 v/v) to give the amine product **51** (31 mg, 58%) as a colorless liquid.

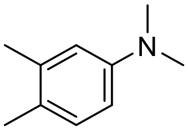


^{1}H NMR (500 MHz, CDCl$_3$): 6.98 (1 H, d, *J* = 8.2 Hz), 6.54 (1 H, s), 6.48 (1 H, dd, *J* = 8.3, 2.7 Hz), 3.32 (4 H, q, *J* = 7.0 Hz), 2.24 (3 H, s), 2.17 (3 H, s), 1.14 (6 H, t, *J* = 7.0 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 146.4, 137.3, 130.5, 123.8, 114.2, 110.2, 44.6, 20.6, 18.6, 12.7 ppm. – IR: 3061, 2968, 2929, 2893, 2875, 2244, 2614, 1509, 1485, 1374, 1265, 1198, 1024, 908, 732, 704 cm^{-1}.

N,N-Dimethyl-3,4-dimethylaniline (52)

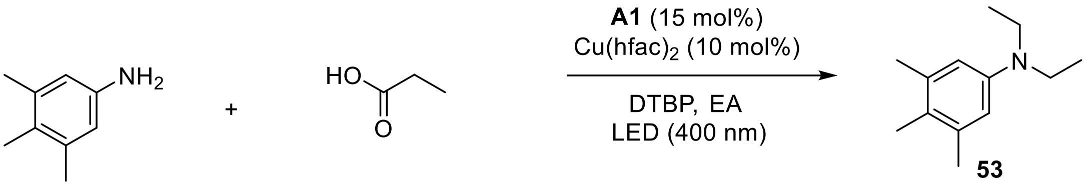


According to **GP1**, the reaction was carried out with 3,4-dimethylaniline (36 mg, 0.3 mmol), acetic acid (108 mg, 1.8 mmol, 6 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (1.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 98 : 2 v/v) to give the amine product **52** (22 mg, 49%) as a colorless liquid.

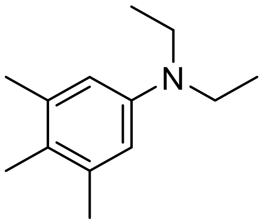


^{1}H NMR (500 MHz, $CDCl_3$): 7.00 (1 H, d, *J* = 8.3 Hz), 6.60 (1 H, s), 6.54 (1 H, dd, *J* = 8.2, 2.7 Hz), 2.89 (6 H, s), 2.24 (3 H, s), 2.18 (3 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 149.5, 137.1, 130.3, 125.1, 115.0, 110.9, 41.3, 20.5, 18.7 ppm. – IR: 3022, 2966, 2852, 1990, 1736, 1615, 1593, 1543, 1499, 1451, 1398, 1332, 1288, 1257, 1199, 1121, 1020 cm^{-1}. – HRMS: calcd for $C_{10}H_{16}N$: 150.1277, found 150.1279 [M+H$^+$].

N,N-Diethyl-3,4,5-trimethylaniline (53)

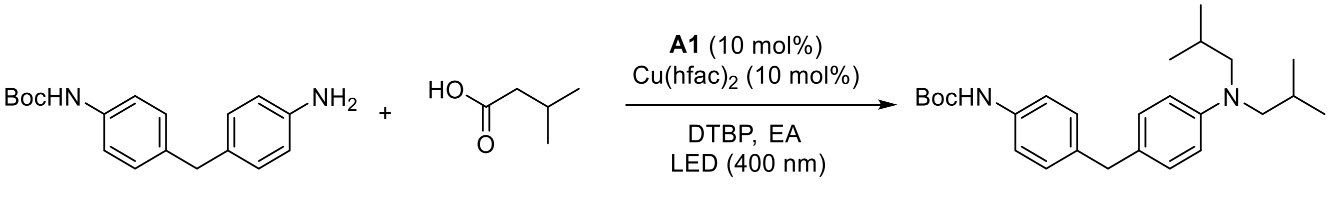


According to **GP1**, the reaction was carried out with 3,4,5-trimethylaniline (41 mg, 0.3 mmol), propionic acid (111 mg, 1.5 mmol, 5 equiv.), acridine **A1** (13 mg, 0.045 mmol, 15 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (1.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 98 : 2 v/v) to give the amine product **53** (39 mg, 68%) as a colorless liquid.



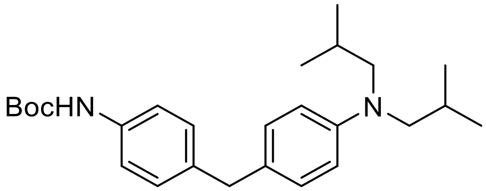
^{1}H NMR (500 MHz, CDCl$_3$): 6.81 (2 H, s), 3.05 (4 H, q, *J* = 7.1 Hz), 2.24 (9 H, s), 0.99 (6 H, t, *J* = 7.1 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 145.2, 138.2, 134.3, 129.4, 47.6, 20.9, 19.6, 15.0 ppm. – IR: 3061, 2968, 2927, 2869, 1771, 1735, 1606, 1586, 1497, 1445, 1398, 1289, 1234, 1201, 1126, 1043, 827, 780 cm^{-1}. – HRMS: calcd for C$_{13}$H$_{22}$N: 192.1747, found 192.1746 [M+H$^+$].

tert-Butyl (4-(4-(diisobutylamino)benzyl)phenyl)carbamate (54)



54

According to **GP1**, the reaction was carried out with tert-butyl (4-(4-aminobenzyl)phenyl)carbamate (89 mg, 0.3 mmol), isovaleric acid (77 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **54** (77mg, 63%) as a colorless liquid.



^{1}H NMR (500 MHz, CDCl$_3$): 7.29 (2 H, d, *J* = 7.8 Hz), 7.16 (2 H, s), 7.02 (2 H, d, *J* = 8.5 Hz), 6.61 (2 H, d, *J* = 8.6 Hz), 6.50 (1 H, s), 3.85 (2 H, s), 3.14 (4 H, d, *J* = 7.2 Hz), 2.09 (2 H, dp, *J* = 13.5, 6.7 Hz), 1.55 (9 H, s), 0.92 (12 H, d, *J* = 6.9 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 153.0, 146.7, 137.0, 136.2, 129.5, 129.4, 127.9, 118.9, 112.7, 80.4, 60.7, 40.3, 28.5, 26.5, 20.6 ppm. – IR: 3335, 3009, 2954, 2927, 2867, 1723, 1709, 1613, 1515, 1466, 1410, 1380, 1365, 1316, 1240, 1157, 1100, 1052, 1017, 906, 809, 747 cm^{-1}. – HRMS: calcd for C$_{26}$H$_{38}$N$_2$O$_2$: 411.3006, found 411.3011 [M+H$^+$].

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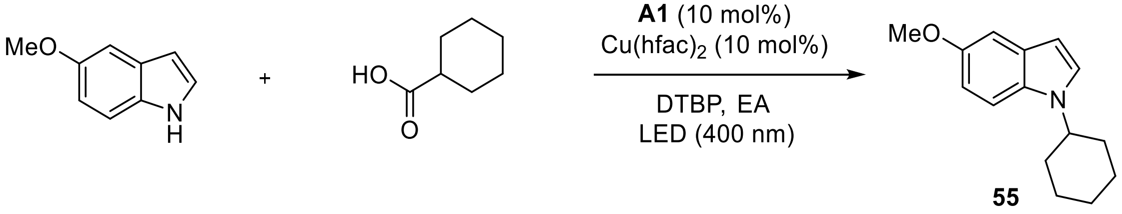
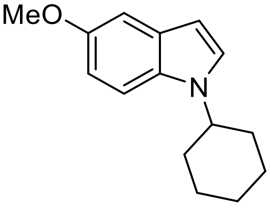
1-Cyclohexyl-5-methoxy-1*H*-indole (55)[27]

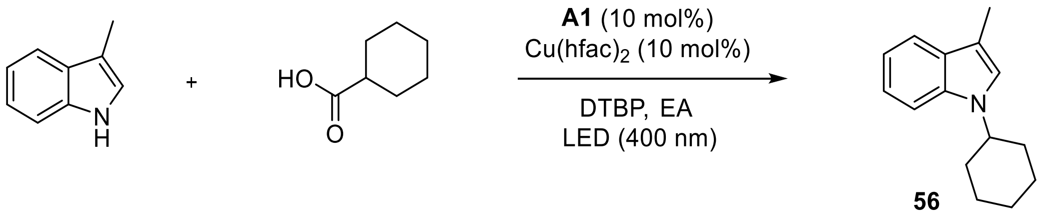


According to **GP2**, the reaction was carried out with 5-methoxy-1*H*-indole (110 mg, 0.75 mmol, 2.5 equiv.), cyclohexanecarboxylic acid (38 mg, 0.3 mmol), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **55** (39 mg, 57%) as a colorless liquid.

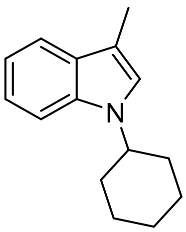


^{1}H NMR (500 MHz, CDCl$_3$): 7.28 (1 H, d, *J* = 8.9 Hz), 7.20 (1 H, d, *J* = 3.1 Hz), 7.11 (1 H, d, *J* = 2.4 Hz), 6.88 (1 H, dd, *J* = 8.9, 2.4 Hz), 6.43 (1 H d, *J* = 3.1 Hz), 4.17 (1 H, tt, *J* = 11.9, 3.8 Hz), 3.86 (3 H, s), 2.14 (2 H, d, *J* = 12.8 Hz), 1.94 (2 H, d, *J* = 13.8 Hz), 1.80 (1 H, d, *J* = 13.2 Hz), 1.70 (2 H qd, *J* = 12.6, 3.5 Hz), 1.50 (2 H, qt, *J* = 13.1, 3.5 Hz), 1.37–1.18 (1 H, m) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 154.0, 131.0, 128.8, 124.7, 111.6, 110.3, 102.6, 100.6, 56.0, 55.4, 33.7, 26.1, 25.8 ppm. – IR: 3006, 2931, 2854, 2833, 1748, 1713, 1618, 1575, 1480, 1449, 1352, 1234, 1211, 1189, 1150, 1034, 908, 810 cm^{-1}.

1-Cyclohexyl-3-methyl-1*H*-indole (56)[27]

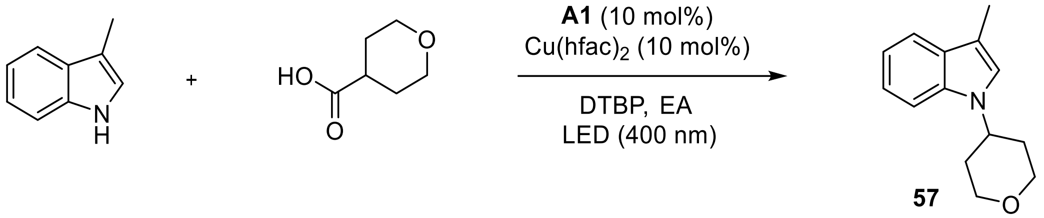


According to **GP2**, the reaction was carried out with 3-methyl-1*H*-indole (98 mg, 0.75 mmol, 2.5 equiv.), cyclohexanecarboxylic acid (38 mg, 0.3 mmol), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **56** (34 mg, 53%) as a brown liquid.

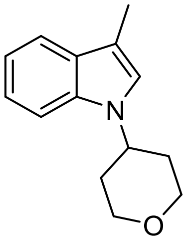


^{1}H NMR (500 MHz, $CDCl_3$): 7.59 (1 H, d, *J* = 7.9 Hz), 7.36 (1 H, d, *J* = 8.3 Hz), 7.26–7.19 (1 H, m), 7.11 (1 H, t, *J* = 7.8 Hz), 7.02 (1 H, s), 4.19 (1 H, tt, *J* = 11.9, 3.8 Hz), 2.36 (3 H, d, *J* = 1.2 Hz), 2.13 (2 H, d, *J* = 13.1 Hz), 1.95 (2 H, d, *J* = 13.5 Hz), 1.81 (1 H, d, *J* = 13.2 Hz), 1.71 (2 H, qd, *J* = 12.6, 3.3 Hz), 1.55–1.45 (2 H, m), 1.30 (1 H, qt, *J* = 13.0, 3.7 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 135.9, 128.6, 121.9, 121.2, 119.1, 118.6, 110.2, 109.3, 54.9, 33.7, 26.2, 25.8, 9.8 ppm. – IR: 3006, 2935, 2858, 1717, 1614, 1461, 1424, 1359, 1220, 1091, 1014, 907 cm^{-1}.

3-Methyl-1-(tetrahydro-2*H*-pyran-4-yl)-1*H*-indole (57)



According to **GP2**, the reaction was carried out with 3-methyl-1*H*-indole (98 mg, 0.75 mmol, 2.5 equiv.), tetrahydro-2*H*-pyran-4-carboxylic acid (39 mg, 0.3 mmol), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **57** (56 mg, 87%) as a brown liquid.



^{1}H NMR (500 MHz, CDCl$_3$): 7.60 (1 H, d, *J* = 7.8 Hz), 7.37 (1 H, d, *J* = 8.2 Hz), 7.29–7.19 (1 H, m), 7.13 (1 H, td, *J* = 7.7, 2.8 Hz), 7.01 (1 H, s), 4.43 (1 H, tt, *J* = 11.6, 4.4 Hz), 4.16 (2 H, dd, *J* = 11.8, 4.4 Hz), 3.62 (2 H, td, *J* = 11.9, 2.1 Hz), 2.36 (3 H, s), 2.10 (2 H, qd, *J* = 12.2, 4.5 Hz), 2.02 (2 H, dd, *J* = 12.6, 2.5 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 135.8, 128.8, 121.6, 121.5, 119.3, 118.9, 110.9, 109.1, 67.7, 52.2, 33.6, 9.8 ppm. – IR: 3087, 3047, 3024, 2953, 2923, 2846, 2763, 1737, 1462, 1384, 1357, 1238, 1224, 1144, 1087, 1009, 981, 877, 827 cm^{-1}. – HRMS: calcd for $C_{14}H_{18}NO$: 216.1383, found 216.1387 [M+H$^+$].

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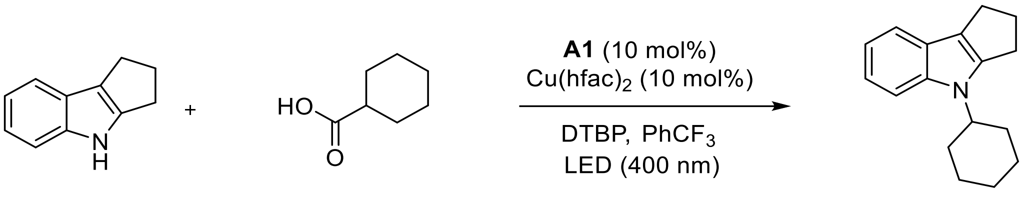
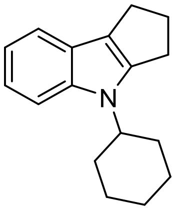
4-Cyclohexyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (58)



58

According to **GP1**, the reaction was carried out with 1,2,3,4-tetrahydrocyclopenta[*b*]indole (47 mg, 0.3 mmol), cyclohexanecarboxylic acid (98 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in trifluorotoluene (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **58** (37mg, 52%) as a yellow liquid.



^{1}H NMR (500 MHz, CDCl$_3$): 7.45 (1 H, d, *J* = 7.7 Hz), 7.35 (1 H, d, *J* = 8.2 Hz), 7.12 (1 H, t, *J* = 7.2 Hz), 7.07 (1 H t, *J* = 7.4 Hz), 4.20 (1 H tt, *J* = 12.1, 3.8 Hz), 2.99 (2 H, t, *J* = 7.1 Hz), 2.83 (2 H, t, *J* = 7.0 Hz), 2.54 (2 H p, *J* = 7.1 Hz), 2.03 (2 H, d, *J* = 12.6 Hz), 1.94 (2 H, d, *J* = 13.6 Hz), 1.81 (3 H, qd, *J* = 12.4, 3.4 Hz), 1.49 (2 H, tdd, *J* = 13.2, 8.3, 3.3 Hz), 1.28 (1 H, qt, *J* = 13.2, 3.7 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 144.5, 140.5, 124.3, 119.9, 119.0, 118.8, 118.6, 109.9, 55.6, 33.1, 28.9, 28.0, 26.4, 25.8, 24.0 ppm. – IR: 3394, 3050, 2982, 2932, 2852, 1620, 1562, 1453, 1367, 1336, 1168, 736 cm^{-1}. – HRMS: calcd for $C_{17}H_{21}N$: 239.1674, found 239.1678 [M$^+$].

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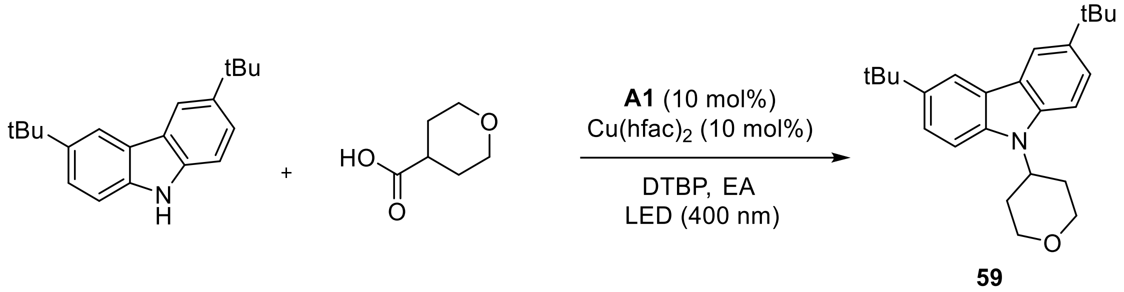
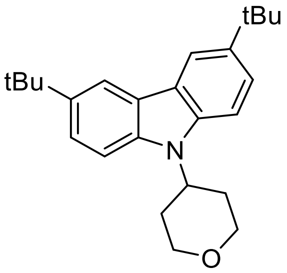
3,6-Di-*tert*-butyl-9-(tetrahydro-2*H*-pyran-4-yl)-9*H*-carbazole (59)



According to **GP2**, the reaction was carried out with 3,6-di-tert-butyl-9*H*-carbazole (209 mg, 0.75 mmol, 2.5 equiv.), tetrahydro-2*H*-pyran-4-carboxylic acid (39 mg, 0.3 mmol), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 9 : 1 v/v) to give the amine product **59** (80 mg, 73%) as a colorless solid.



m.p.: 243–245˚C. – ^{1}H NMR (500 MHz, CDCl$_3$): 8.14 (2 H, s), 7.78–7.41 (4 H, m), 4.69 (1 H, tt, *J* = 12.3, 4.4 Hz), 4.25 (2 H, dd, *J* = 11.7, 4.6 Hz), 3.67 (2 H, t, *J* = 11.3 Hz), 2.79 (2 H, qd, *J* = 12.6, 4.7 Hz), 1.99–1.79 (2 H, m), 1.49 (18 H, s) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 141.8, 138.1, 123.4, 123.2, 116.4, 109.4, 68.2, 52.4, 34.7, 32.2, 30.9 ppm. – IR: 3056, 2954, 2902, 2862, 2836, 2754, 1737, 1606, 1578, 1489, 1474, 1363, 1296, 1232, 1145, 1108, 1007, 907, 878 cm^{-1}. – HRMS: calcd for $C_{25}H_{34}NO$: 364.2635, found 364.2641 [M+H$^+$].

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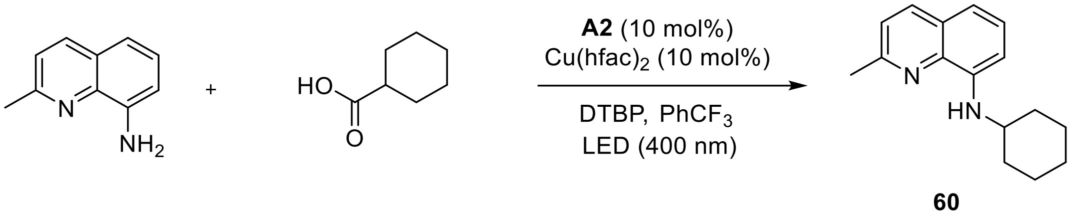
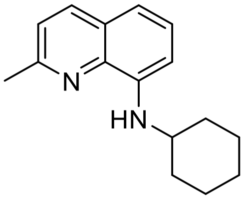
N-Cyclohexyl-2-methylquinolin-8-amine (60)

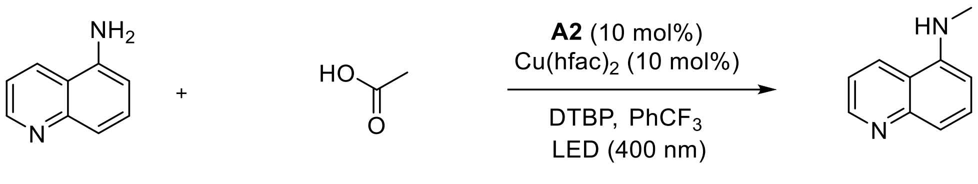


According to **GP1**, the reaction was carried out with 2-methylquinolin-8-amine (47 mg, 0.3 mmol), cyclohexanecarboxylic acid (98 mg, 0.75 mmol, 2.5 equiv.), acridine **A2** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 24 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **60** (43 mg, 60%) as a brown solid.



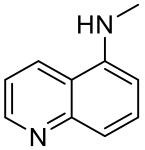
m.p.: 35–37 ˚C. – ^{1}H NMR (500 MHz, CDCl$_3$): 7.91 (1 H, d, *J* = 8.3 Hz), 7.29 (1 H, t, *J* = 7.9 Hz), 7.22 (1 H, d, *J* = 8.3 Hz), 6.95 (1 H, d, *J* = 8.1 Hz), 6.66 (1 H, d, *J* = 7.6 Hz), 6.16 (1 H, brs), 3.45 (1 H, s), 2.69 (3 H, s), 2.18 (2 H, d, *J* = 11.6 Hz), 1.84 (2 H, d, *J* = 13.0 Hz), 1.70 (1 H, d, *J* = 13.1 Hz), 1.60–1.21 (7 H, m) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 155.5, 143.4, 137.6, 136.2, 126.9, 126.8, 122.1, 113.1, 105.0, 51.4, 33.2, 26.2, 25.3 ppm. – IR: 3385, 3017, 2930, 2854, 2399, 1711, 1614, 1595, 1589, 1519, 1487, 1463, 1450, 1434, 1344, 1303, 1246, 1213, 1125 cm^{-1}. – HRMS: calcd for $C_{16}H_{12}N_2$: 241.1699, found 241.1701 [M+H$^+$].

N-Methylquinolin-5-amine (61)[28]



61

According to **GP1**, the reaction was carried out with quinolin-5-amine (43 mg, 0.3 mmol), acetic acid (90 mg, 1.5 mmol, 5.0 equiv.), acridine **A2** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light ($\lambda = 400$ nm) while stirring for 24 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **61** (25 mg, 52%) as a yellow liquid.



^{1}H NMR (500 MHz, $CDCl_3$): 8.71 (1 H, dd, *J* = 4.3, 1.7 Hz), 8.05 (1 H, d, *J* = 1.5 Hz), 7.41 (1 H, t, *J* = 7.9 Hz), 7.37 (1 H, dd, *J* = 8.2, 4.2 Hz), 7.05 (1 H, d, *J* = 8.1 Hz), 6.65 (1 H, d, *J* = 7.6 Hz), 6.13 (1 H, brs), 3.05 (3 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 146.9, 146.0, 138.4, 136.1, 128.7, 128.0, 121.5, 113.8, 104.3, 30.2 ppm. – IR: 3438, 3048, 2921, 2844, 1621, 1581, 1517, 1403, 1370, 2395, 1251, 1151, 1062 cm^{-1}.

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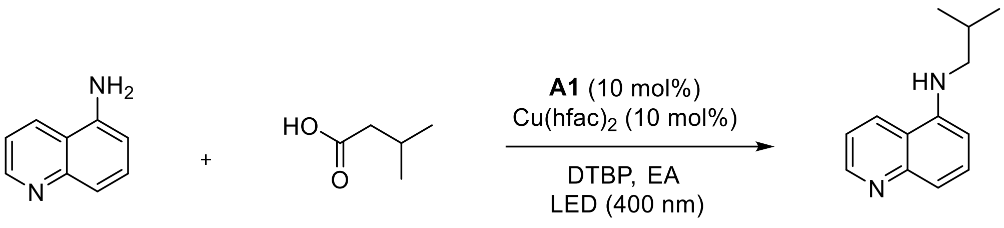
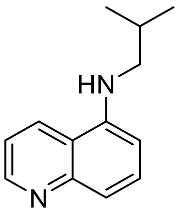
N-Isobutylquinolin-5-amine (62)[29]



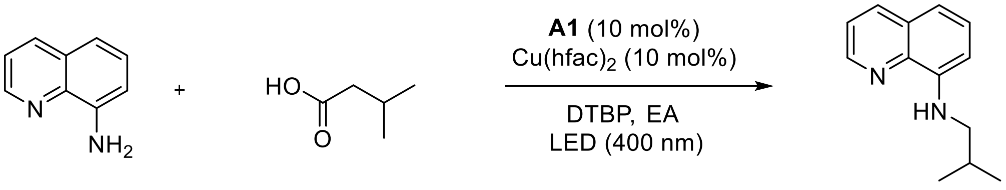
62

According to **GP1**, the reaction was carried out with quinolin-5-amine (43 mg, 0.3 mmol), isovaleric acid (77 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **62** (44 mg, 73%) as a colorless liquid.



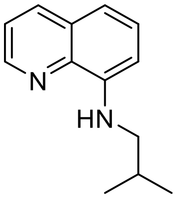
^{1}H NMR (500 MHz, CDCl$_3$): 8.84 (1 H, d, *J* = 4.0 Hz), 8.16 (1 H, d, *J* = 8.5 Hz), 7.54 (1 H, t, *J* = 8.1 Hz), 7.46 (1 H, d, *J* = 8.4 Hz), 7.28 (1 H, dd, *J* = 8.5, 4.2 Hz), 6.60 (1 H, d, *J* = 7.6 Hz), 4.45 (1 H, brs), 3.08 (2 H, d, *J* = 6.7 Hz), 2.03 (1 H, dquint., *J* = 13.4, 6.7 Hz), 1.06 (6 H, d, *J* = 6.7 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 149.9, 149.2, 144.0, 130.6, 128.8, 119.2, 118.4, 118.0, 104.6, 52.0, 28.0, 20.8 ppm. – IR: 3321, 3070, 2956, 2933, 2868, 1756, 1732, 1611, 1586, 1577, 1532, 1480, 1465, 1385, 1366, 1146. 1107, 788, 739 cm^{-1}.

N-Isobutylquinolin-8-amine (63)[29]



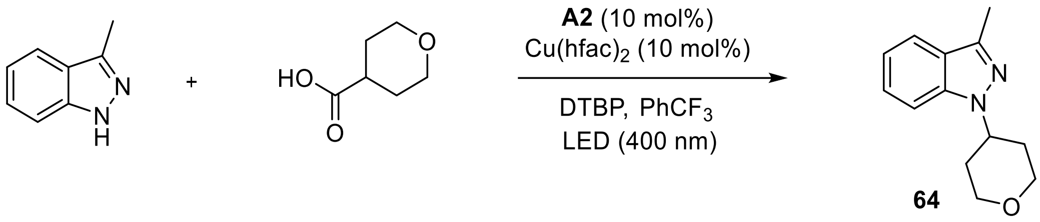
63

According to **GP1**, the reaction was carried out with quinolin-8-amine (43 mg, 0.3 mmol), isovaleric acid (77 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), $Cu(hfac)_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light ($\lambda = 400$ nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **63** (51 mg, 85%) as a colorless liquid.

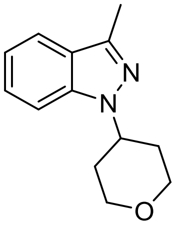


^{1}H NMR (500 MHz, $CDCl_3$): 8.73 (1 H, d, *J* = 5.5 Hz), 8.05 (1 H, d, *J* = 8.2 Hz), 7.40 (1 H, d, *J* = 7.9 Hz), 7.39–7.33 (1 H, m), 7.07–6.99 (1 H, m), 6.74–6.55 (1 H, m), 6.31 (1 H, brs), 3.16 (2 H, d, *J* = 6.8 Hz), 2.10 (1 H, dq, *J* = 13.4, 6.7 Hz), 1.09 (6 H, d, *J* = 6.7 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 146.8, 145.2, 138.3, 136.1, 128.8, 127.9, 121.4, 113.4, 104.5, 51.4, 28.1, 20.8 ppm. – IR: 3411, 3055, 3048, 2956, 2933, 2865, 1611, 1575, 1522, 1481, 1452, 1381, 1337, 1264, 1152, 907 cm^{-1}.

3-Methyl-1-(tetrahydro-2*H*-pyran-4-yl)-1*H*-indazole (64)



According to **GP1**, the reaction was carried out with 3-methyl-1*H*-indazole (40 mg, 0.3 mmol), tetrahydro-2*H*-pyran-4-carboxylic acid (98 mg, 0.75 mmol, 2.5 equiv.), acridine **A2** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl trifluorotoluene (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 4 : 1 v/v) to give the amine product **64** (54 mg, 83%) as a colorless solid.



m.p.: 59–62 ˚C. – ^{1}H NMR (500 MHz, CDCl$_3$): 7.66 (1 H, d, *J* = 8.1 Hz), 7.41 (1 H, d, *J* = 8.4 Hz), 7.38–7.32 (1 H, m), 7.12 (1 H, t, *J* = 7.4 Hz), 4.57 (1 H, tt, *J* = 11.7, 4.2 Hz), 4.16 (2 H, dd, *J* = 11.8, 4.6 Hz), 3.60 (2 H, t, *J* = 11.9 Hz), 2.58 (3 H, s), 2.41 (2 H, qd, *J* = 12.2, 4.5 Hz), 1.95 (2 H, dd, *J* = 12.8, 2.3 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 141.4, 139.6, 126.1, 123.7, 120.7, 119.8, 108.9, 67.5, 55.1, 32.5, 12.0 ppm. – IR: 3058, 2958, 2923, 2845, 2768. 1736, 1722, 1613, 1505, 1448, 1324, 1295, 1203, 1145 ,1089, 1012, 981, 879, 775, 760 cm^{-1}. – HRMS: calcd for C$_{13}$H$_{17}$N$_2$O: 217.1335, found 217.1335 [M+H$^+$].

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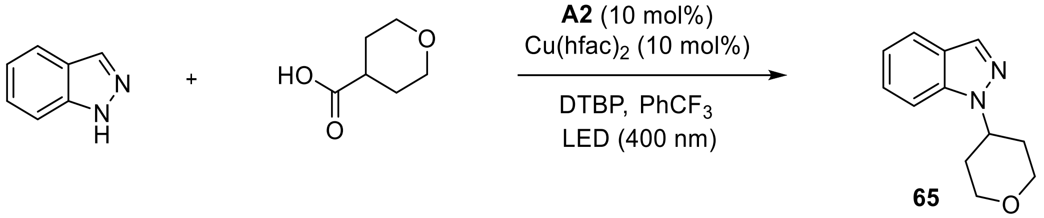
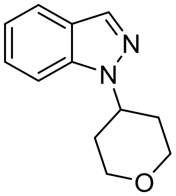
1-(Tetrahydro-2*H*-pyran-4-yl)-1*H*-indazole (65)



According to **GP1**, the reaction was carried out with 1*H*-indazole (35 mg, 0.3 mmol), tetrahydro-2*H*-pyran-4-carboxylic acid (98 mg, 0.75 mmol, 2.5 equiv.), acridine **A2** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in trifluorotoluene (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 4 : 1 v/v) to give the amine product **65** (58 mg, 95%) as a colorless solid.



m.p.: 62–65 °C. –^{1}H NMR (500 MHz, $CDCl_3$): 8.02 (1 H, s), 7.75 (1 H, d, *J* = 8.1 Hz), 7.47 (1 H, d, *J* = 8.5 Hz), 7.38 (1 H, t, *J* = 7.6 Hz), 7.15 (1 H, t, *J* = 7.5 Hz), 4.65 (1 H, tt, *J* = 11.6, 4.2 Hz), 4.18 (2 H, dd, *J* = 11.1, 3.9 Hz), 3.63 (2 H, t, *J* = 11.9 Hz), 2.42 (2 H, qd, *J* = 12.2, 4.5 Hz), 1.99 (2 H, d, *J* = 14.9 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 138.7, 133.0, 126.2, 124.4, 121.4, 120.7, 109.0, 67.4, 55.3, 32.5 ppm. – IR: 3063, 2960, 2930, 2846, 1745, 1644, 1463, 1425, 1363, 1233, 1194, 1145, 1090, 1145, 1015, 827 cm^{-1}. – HRMS: calcd for $C_{12}H_{15}N_2O$: 203.1179, found 203.1179 [M+H$^+$].

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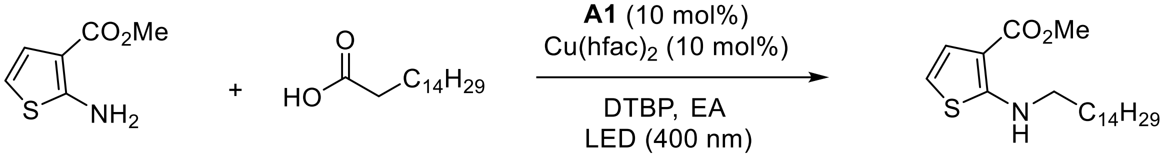
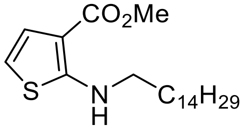
Methyl 2-(pentadecylamino)thiophene-3-carboxylate (66)



66

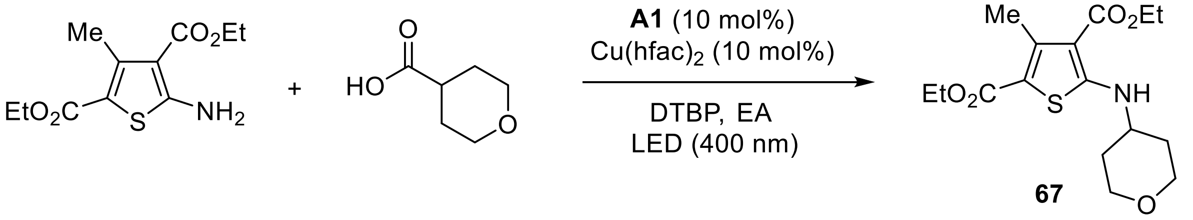
According to **GP1**, the reaction was carried out with methyl 2-aminothiophene-3-carboxylate (47 mg, 0.3 mmol), palmitic acid (192 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 9 v/v) to give the amine product **66** (101 mg, 92%) as a brown liquid that glassified upon standing.

Gram scale for compound 66: According to **GP1**, the reaction was carried out with methyl 2-aminothiophene-3-carboxylate (0.79 g, 5 mmol), palmitic acid (3.2 g, 12.5 mmol, 2.5 equiv.), acridine **A1** (147 mg, 0.5 mmol, 10 mol%), Cu(hfac)$_2$ (233 mg, 0.5 mmol, 10 mol%), and DTBP (1.46 mg, 10 mmol, 2 equiv.) in ethyl acetate (75 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (100 mL), extracted with a saturated solution of EDTA (30 mL). The organic layer was collected, washed with saturated sodium carbonate (3x10 mL), dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **66** (1.2 g, 63 %) as a brown liquid that glassified upon standing.



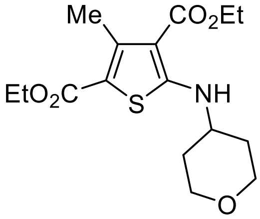
^{1}H NMR (500 MHz, $CDCl_3$): 7.40 (1 H, s), 7.01 (1 H, d, *J* = 5.7 Hz), 6.14 (1 H, d, *J* = 5.7 Hz), 3.79 (3 H, s), 3.21 (2 H, td, *J* = 7.0, 5.5 Hz), 1.69 (2 H, quint., *J* = 7.1 Hz), 1.47–1.36 (2 H, m), 1.36–1.27 (22 H, m), 0.88 (3 H, t, *J* = 6.9 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 166.2, 166.0, 126.2, 105.4, 103.1, 5.79, 47.8, 31.9, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 26.9, 22.7, 14.1 ppm. – IR: 3331, 3121, 2922, 2852, 2251, 1669, 1547, 1513, 1440, 1387, 1341, 1302, 1241, 1192, 1105 cm^{-1}. – HRMS: calcd for $C_{22}H_{38}NO_2S$: 368.2618, found 368.2614 [M+H$^+$].

Diethyl 3-methyl-5-((tetrahydro-2*H*-pyran-4-yl)amino)thiophene-2,4-dicarboxylate (67)



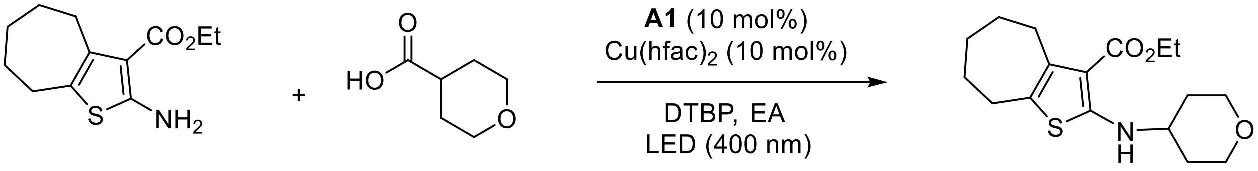
67

According to **GP1**, the reaction was carried out with diethyl 5-amino-3-methylthiophene-2,4-dicarboxylate (79 mg, 0.3 mmol), tetrahydro-2*H*-pyran-4-carboxylic acid (98 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 1 : 9 v/v) to give the amine product **67** (79 mg, 77%) as a yellow liquid.



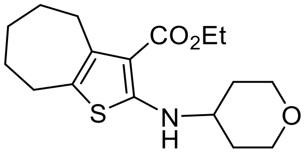
^{1}H NMR (500 MHz, $CDCl_3$) 8.38 (1 H, d, *J* = 8.1 Hz), 4.26 (4 H, dq, *J* = 13.9, 7.2 Hz), 3.98 (2 H, dt, *J* = 12.4, 3.9 Hz), 3.58 – 3.25 (3 H, m), 2.69 (3 H, s), 2.07 (2 H, dd, *J* = 13.1, 3.8 Hz), 1.67 – 1.54 (2 H, m), 1.33 (6 H, dt, *J* = 14.8, 7.1 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 166.9, 166.5, 163.0, 148.9, 107.7, 106.6, 66.4, 60.4, 60.1, 53.4, 32.5, 16.1, 14.5, 14.4 ppm. – IR: 3419, 3315, 3016, 2982, 2943, 2252, 1709, 1666, 1587, 1531, 1497, 1417, 1363, 1230, 1096, 1055, 908, 730 cm^{-1}. – HRMS: calcd for $C_{16}H_{24}NO_5S$: 342.1370, found 342.1370 [M+H$^+$].

Ethyl 2-((tetrahydro-2*H*-pyran-4-yl)amino)-5,6,7,8-tetrahydro-4*H*-cyclohepta[*b*]thiophene-3-carboxylate (68)



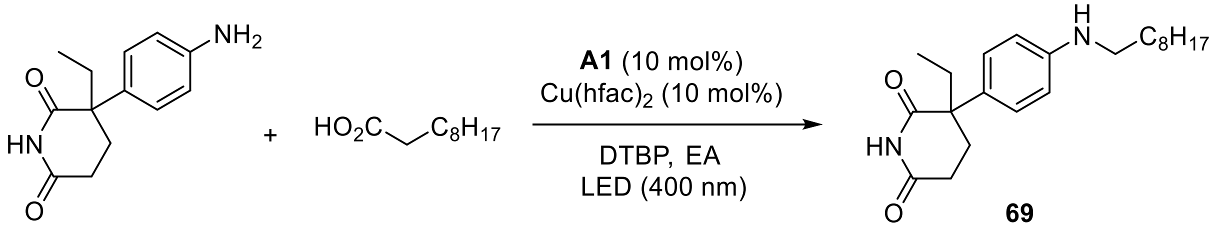
68

According to **GP1**, the reaction was carried out with ethyl 2-amino-5,6,7,8-tetrahydro-4*H*-cyclohepta[*b*]thiophene-3-carboxylate (72 mg, 0.3 mmol), tetrahydro-2*H*-pyran-4-carboxylic acid (98 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 1 : 4 v/v) to give the amine product **68** (69 mg, 71%) as a yellow liquid.

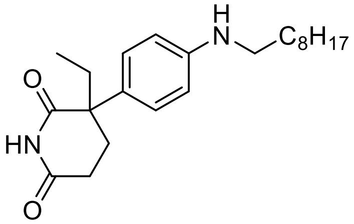


^{1}H NMR (500 MHz, $CDCl_3$): 7.70 (1 H, d, *J* = 8.0 Hz), 4.24 (2 H, q, *J* = 7.1 Hz), 3.96 (2 H, dt, *J* = 11.9, 4.0 Hz), 3.48 (2 H, td, *J* = 11.3, 2.5 Hz), 3.33 (1 H, brs), 3.12–2.91 (2 H, m), 2.59–2.56 (2 H, m), 2.05 (2 H, d, *J* = 12.8 Hz), 1.79 (2 H, dt, *J* = 11.7, 5.9 Hz), 1.69–1.54 (6 H, m), 1.32 (3 H, t, *J* = 7.1 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 166.7, 161.9, 138.3, 120.0, 104.5, 66.6, 59.5, 53.2, 33.0, 32.1, 28.8, 28.7, 28.0, 26.9, 14.5 ppm. – IR: 3312, 3066. 2985, 2922, 2848, 2252, 2750, 2693, 1644, 1529, 1445, 1410, 1383, 1263, 1210, 1135, 1088, 1030, 906 cm^{-1}. – HRMS: calcd for $C_{17}H_{25}NO_3S$: 324.1628, found 324.1627 [M+H$^+$].

3-Ethyl-3-(4-(nonylamino)phenyl)piperidine-2,6-dione (69)

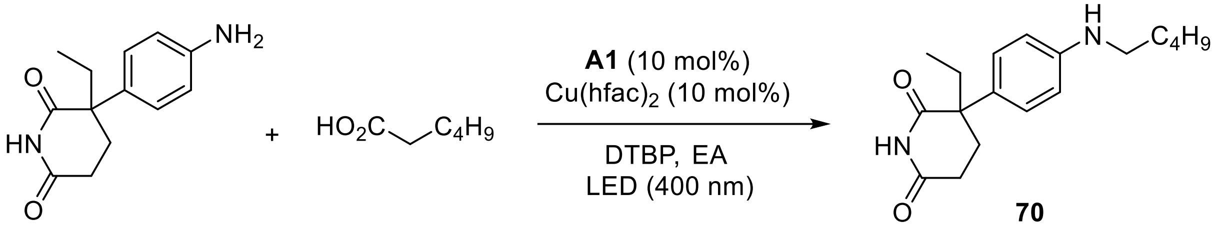


According to **GP1**, the reaction was carried out with 3-(4-aminophenyl)-3-ethylpiperidine-2,6-dione (70 mg, 0.3 mmol), decanoic acid (129 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 7 : 3 v/v) to give the amine product **69** (61 mg, 57%) as a pale yellow solid.

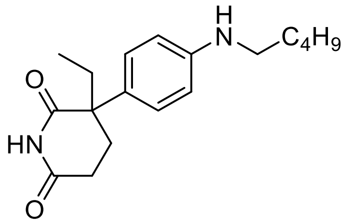


m.p.: 40–42°C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.26 (1 H, s), 7.04 (2 H, d, *J* = 8.3 Hz), 6.56 (2 H, d, *J* = 8.3 Hz), 4.17 (1 H, s), 3.08 (2 H, t, *J* = 7.1 Hz), 2.56 (1 H, dt, *J* = 18.0, 3.7 Hz), 2.46 (1 H, ddd, *J* = 17.9, 13.2, 4.9 Hz), 2.36–2.24 (1 H, m), 2.15 (1 H, td, *J* = 13.7, 4.7 Hz), 1.99 (1 H, dq, *J* = 14.6, 7.4 Hz), 1.87 (1 H, dq, *J* = 14.5, 7.4 Hz), 1.60 (2 H, p, *J* = 7.1 Hz), 1.45–1.19 (12 H, m), 0.86 (6 H, dt, *J* = 17.5, 7.0 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 175.9, 173.0, 147.8, 127.2, 126.5, 113.0, 50.3, 44.0, 34.0, 33.1, 32.0, 29.7, 29.6, 29.5, 29.5, 29.4, 27.3, 27.1, 24.9, 22.8, 14.2, 9.1 ppm. – IR: 3056, 2961, 2926, 2859, 1701, 1670, 1613, 1519, 1463, 1340, 1264, 1209, 1187, 1147, 1099, 895, 704 cm^{-1}. – HRMS: calcd for $C_{22}H_{35}N_2O_2$: 359.2693, found 359.2690 [M+H$^+$].

3-Ethyl-3-(4-(pentylamino)phenyl)piperidine-2,6-dione (70)

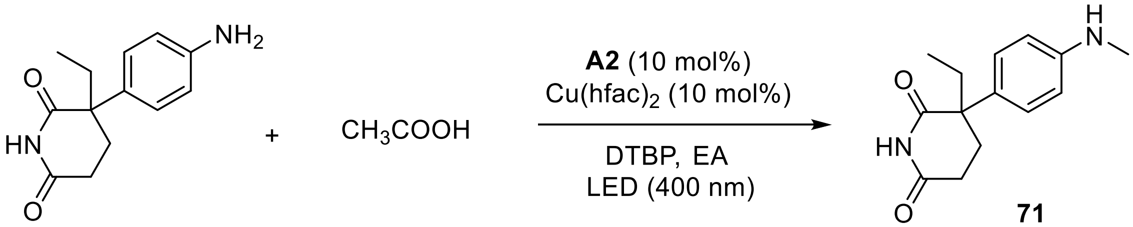


According to **GP1**, the reaction was carried out with 3-(4-aminophenyl)-3-ethylpiperidine-2,6-dione (70 mg, 0.3 mmol), hexanoic acid (87 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 7 : 3 v/v) to give the amine product **70** (69 mg, 76%) as a pale yellow solid.

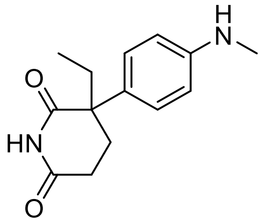


m.p.: 59–62˚C. – ^{1}H NMR (500 MHz, $CDCl_3$): 8.48 (1 H, s), 7.04 (2 H, d, *J* = 8.7 Hz), 6.56 (2 H, d, *J* = 8.7 Hz), 4.24 (1 H, s), 3.07 (2 H, t, *J* = 7.1 Hz), 2.56 (1 H, ddd, *J* = 17.8, 4.7, 2.7 Hz), 2.45 (1 H, ddd, *J* = 18.0, 13.2, 4.9 Hz), 2.30 (1 H, ddd, *J* = 17.0, 5.2, 2.7 Hz), 2.14 (1 H, td, *J* = 13.7, 4.7 Hz), 1.98 (1 H, dq, *J* = 14.7, 7.4 Hz), 1.86 (1 H, dq, *J* = 14.6, 7.4 Hz), 1.61 (2 H, m), 0.91 (3 H, t, *J* = 7.0 Hz), 0.84 (3 H, t, *J* = 7.4 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 176.1, 173.2, 147.8, 127.1, 126.5, 113.0, 50.2, 43.9, 33.0, 29.4, 29.4, 29.3, 27.0, 22.6, 14.1, 9.1 ppm. – IR: 3500, 2962, 2156, 2004, 1724, 1696, 1612, 1520, 1345, 1261, 1187, 1047, 10078, 974 cm^{-1}. – HRMS: calcd for $C_{18}H_{27}N_2O_2$: 303.2067, found 303.2077 [M+H$^+$].

3-Ethyl-3-(4-(methylamino)phenyl)piperidine-2,6-dione (71)[30]

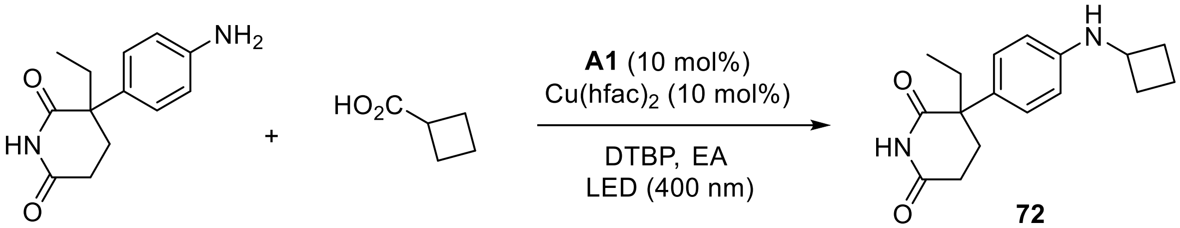


According to **GP1**, the reaction was carried out with 3-(4-aminophenyl)-3-ethylpiperidine-2,6-dione (70 mg, 0.3 mmol), acetic acid (90 mg, 1.5 mmol, 5.0 equiv.), acridine **A2** (9 mg, 0.03 mmol, 10 mol%), $Cu(hfac)_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (1.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 24 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 7:3 v/v) to give the amine product **71** (52 mg, 68%) as a colorless liquid.

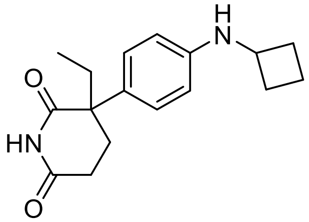


^{1}H NMR (500 MHz, $CDCl_3$): 7.89 (1 H, d, *J* = 18.0 Hz), 7.13–7.05 (2 H, m), 6.65–6.55 (2 H, m), 2.63–2.55 (1 H, m), 2.49 (1 H, ddd, *J* = 17.9, 13.3, 5.0 Hz), 2.34 (1 H, ddd, *J* = 14.2, 5.0, 2.7 Hz), 2.18 (1 H, ddd, *J* = 14.2, 13.3, 4.6 Hz), 2.02 (1 H, dq, *J* = 14.8, 7.4 Hz), 1.90 (1 H, dq, *J* = 14.6, 7.4 Hz), 0.88 (3 H, t, *J* = 7.4 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 175.8, 172.7, 148.6, 127.2, 126.8, 112.8, 50.4, 33.1, 30.8, 29.5, 27.1, 9.2 ppm. – IR: 3413, 3208, 3093, 2970, 2933, 2882, 2816, 2254, 1697, 1614, 1522, 1484, 1457, 1348, 1308, 1264, 1201, 1186, 1158, 1111, 1048 cm^{-1}.

3-(4-(Cyclobutylamino)phenyl)-3-ethylpiperidine-2,6-dione (72)

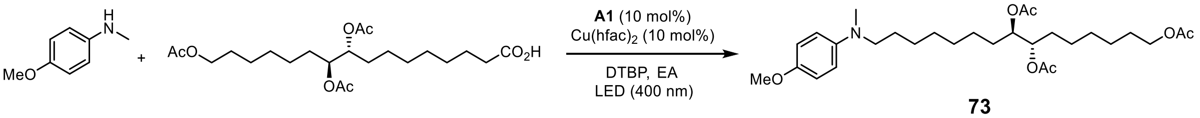


According to **GP1**, the reaction was carried out with -(4-aminophenyl)-3-ethylpiperidine-2,6-dione (70 mg, 0.3 mmol), cyclobutanecarboxylic acid (75 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 7:3 v/v) to give the amine product **72** (46 mg, 54%) as a colorless liquid.



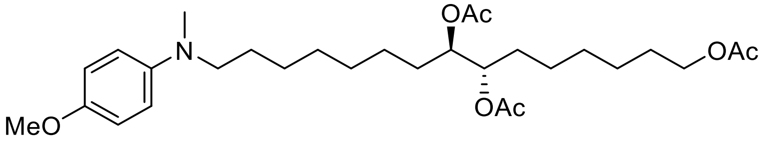
^{1}H NMR (500 MHz, $CDCl_3$): 8.30–7.99 (1 H, m), 7.02 (2 H, d, *J* = 8.4 Hz), 6.50 (2 H, d, *J* = 8.3 Hz), 3.88 (2 H, p, *J* = 7.4 Hz), 2.56 (1 H, dt, *J* = 17.9, 3.6 Hz), 2.51–2.35 (3 H, m), 2.29 (1 H, ddd, *J* = 14.2, 5.0, 2.8 Hz), 2.14 (1 H, td, *J* = 13.8, 4.6 Hz), 1.98 (1 H, dq, *J* = 14.7, 7.4 Hz), 1.90–1.72 (5 H, m), 0.84 (3 H, t, *J* = 7.4 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 176.0, 173.1, 146.6, 127.2, 126.7, 113.3, 50.3, 49.0, 33.1, 31.3, 29.5, 27.1, 15.4, 9.1 ppm. – IR: 3383, 3212, 2967, 2922, 2878, 1693, 1611, 1516, 1457, 1348. 1306, 1255, 1190, 1145, 1047, 959 cm^{-1}. – HRMS: calcd for $C_{17}H_{23}N_2O_2$: 287.1754, found 287.1760 [M+H$^+$].

(7*S**,8*R**)-15-((4-methoxyphenyl)(methyl)amino)pentadecane-1,7,8-triyl triacetate (73)



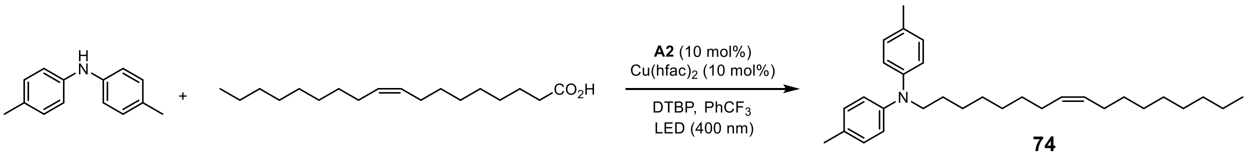
73

According to **GP1**, the reaction was carried out with 4-methoxy-*N*-methylaniline (57 mg, 0.375 mmol, 2.5 equiv.), (9*R**,10*S**)-9,10,16-triacetoxyhexadecanoic acid (65 mg, 0.15 mmol), acridine **A1** (5 mg, 0.015 mmol, 10 mol%), Cu(hfac)$_2$ (7 mg, 0.015 mmol, 10 mol%), and DTBP (44 mg, 0.3 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 9 : 1 v/v) to give the amine product **73** (55 mg, 70%) as a yellow liquid.

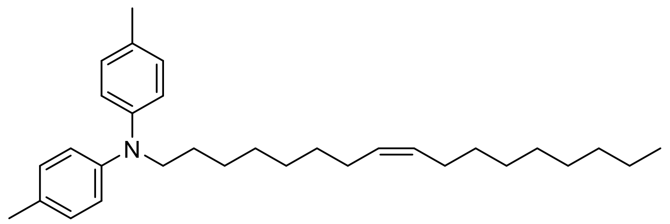


^{1}H NMR (500 MHz, CDCl$_3$): 6.87–6.79 (2 H, m), 6.73–6.66 (2 H, m), 4.98 (2 H, p, *J* = 3.9 Hz), 4.03 (2 H, t, *J* = 6.7 Hz), 3.75 (32 H, s), 3.18 (2 H, t, *J* = 7.6 Hz), 2.83 (3 H, s), 2.06 (9 H, d, *J* = 19.3 Hz), 1.54 (8 H, dq, *J* = 45.6, 7.0 Hz), 1.38–1.19 (14 H, m) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 171.3, 170.8, 151.6, 144.6, 114.9, 114.6, 73.9, 73.9, 64.6, 55.9, 54.1, 39.1, 30.9, 30.8, 29.5, 29.5, 29.1, 28.6, 27.2, 26.6, 25.9, 25.3, 25.2, 21.1, 21.1 ppm. – IR: 2931, 2856, 2836, 2802, 1734, 1512, 1369, 1226, 1201, 1038, 951, 814 cm^{-1}. – HRMS: calcd for $C_{29}H_{48}NO_7$: 522.3425, found 522.3428 [M+H$^+$].

(*Z*)-*N*-(Heptadec-8-en-1-yl)-4-methyl-*N*-(*p*-tolyl)aniline (74)

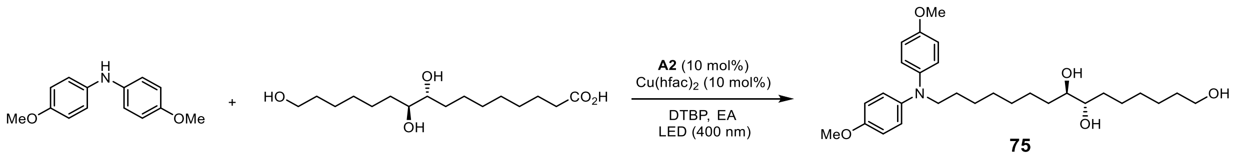


According to **GP2**, the reaction was carried out with di-*p*-tolylamine (148 mg, 0.75 mmol, 2.5 equiv.), oleic acid (85 mg, 0.3 mmol), acridine **A2** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in PhCF$_3$ (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 24 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **74** (101 mg, 78%) as a colorless liquid.



^{1}H NMR (500 MHz, $CDCl_3$): 7.16–7.02 (4 H, m), 6.90 (4 H, dd, *J* = 8.4, 2.2 Hz), 5.38 (2 H, dt, *J* = 7.5, 4.8 Hz), 3.70–3.59 (2 H, m), 2.32 (6 H, s), 2.04 (4 H, p, *J* = 5.2, 4.2 Hz), 1.67 (2 H, t, *J* = 7.4 Hz), 1.46–1.19 (20 H, m), 0.92 (3 H, td, *J* = 6.8, 2.1 Hz) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 146.2, 130.3, 130.1, 129.9, 129.9, 120.9, 52.6, 32.1, 29.9, 29.8, 29.8, 29.7, 29.51, 29.48, 29.4, 27.6, 27.4, 27.3, 27.2, 22.8, 20.8, 14.3 ppm. – IR: 3005, 2921, 2851, 1727, 1609, 1568, 1508, 1463, 1376, 1308, 1248, 1018 cm^{-1}. – HRMS: calcd for $C_{31}H_{48}N$: 434.3781, found 434.3789 [M+H^{+}].

(7*S**,8*R**)-15-(Bis(4-methoxyphenyl)amino)pentadecane-1,7,8-triol (75)



According to **GP2**, the reaction was carried out with bis(4-methoxyphenyl)amine (172 mg, 0.75 mmol, 2.5 equiv.), (+/-)-erythro-aleuritic acid (91 mg, 0.3 mmol), acridine **A2** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash

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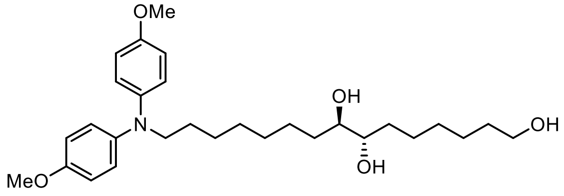
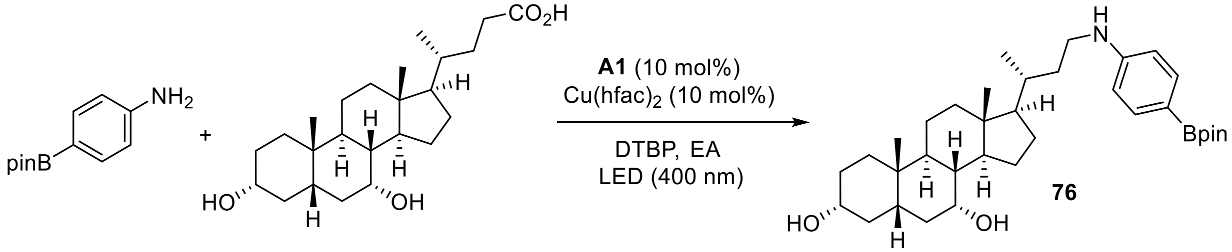
chromatography on silica gel (hexane/ ethyl acetate 1:9 v/v) to give the amine product **75** (79 mg, 54%) as a red liquid.

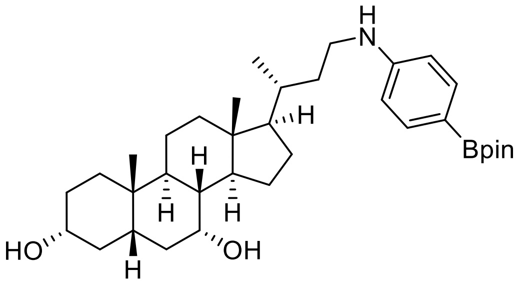


^{1}H NMR (500 MHz, CDCl$_3$): 6.86 (4 H, d, *J* = 9.0 Hz), 6.81 (4 H, d, *J* = 9.0 Hz), 3.77 (6 H, s), 3.63 (2 H, t, *J* = 6.5 Hz), 3.54 (2 H, t, *J* = 7.6 Hz), 3.47–3.31 (2 H, m), 2.51–1.86 (3 H, m), 1.66–1.08 (22 H, m) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 154.3, 142.7, 122.2, 114.7, 74.63, 74.59, 63.1, 55.8, 53.0, 33.7, 33.6, 32.8, 29.8, 29.6, 29.5, 27.7, 27.2, 25.8, 25.7, 25.6 ppm. – IR: 3332, 2927, 2852, 1729, 1504, 1463, 1239, 1179, 1036 cm^{-1}. – HRMS: calcd for $C_{29}H_{46}NO_5$: 488.3371, found 488.3371 [M+H$^+$].

(3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-4-((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amino)butan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,7-diol (76)

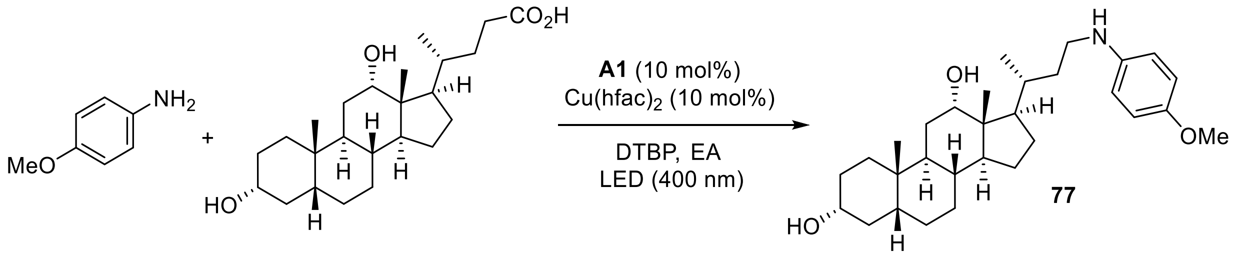


According to **GP2**, the reaction was carried out with 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (82 mg, 0.375 mmol, 2.5 mmol), chenodeoxycholic acid (60 mg, 0.15 mmol), acridine **A1** (5 mg, 0.015 mmol, 10 mol%), Cu(hfac)$_2$ (7 mg, 0.015 mmol, 10 mol%), and DTBP (44 mg, 0.3 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 3 : 2 v/v) to give the amine product **76** (55 mg, 71%) as a colorless solid .



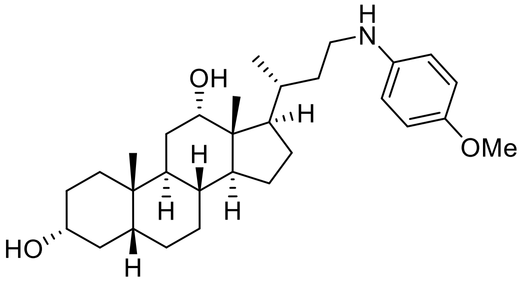
m.p.: 88–90˚C. – $[\alpha]_D^{23}$ = + 12.6 (c 0.23, $CHCl_3$). – ^1H NMR (500 MHz, $CDCl_3$): 7.62 (2 H, d, *J* = 8.0 Hz), 6.56 (2 H, d, *J* = 8.0 Hz), 3.85 (1 H, d, *J* = 3.6 Hz), 3.46 (1 H, tt, *J* = 11.3, 4.5 Hz), 3.19 (1 H, ddd, *J* = 12.0, 9.5, 4.9 Hz), 3.06 (1 H, ddd, *J* = 12.0, 9.1, 6.6 Hz), 2.20 (1 H, q, *J* = 12.4 Hz), 2.03–1.77 (5 H, m), 1.77–1.58 (4 H, m), 1.57–1.45 (3 H, m), 1.44–1.08 (23 H, m), 1.05–0.81 (9 H, m), 0.67 (3 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 151.1, 136.5, 111.8, 83.3, 72.2, 68.7, 56.3, 50.6, 42.9, 41.6, 41.1, 40.0, 39.8, 39.6, 35.8, 35.5, 35.2, 34.8, 34.8, 34.7, 34.3, 33.0, 31.7, 30.8, 28.6, 25.4, 25.0, 23.9, 22.9, 22.8, 20.8, 20.7, 19.0, 14.3, 11.9 ppm. – ^{11}B NMR (160 MHz, $CDCl_3$): 31.1 ppm. – IR: 3069, 2985. 2931. 2868, 1605, 1484, 1400, 1359, 1327, 1264, 1199, 1143, 1077, 896, 736 cm^{-1}. – HRMS: calcd for $C_{35}H_{56}BNO_4K$: 604.3934, found 604.3923 [M+K$^+$].

(3*R*,5*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-17-((*R*)-4-((4-Methoxyphenyl)amino)butan-2-yl)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,12-diol (77)



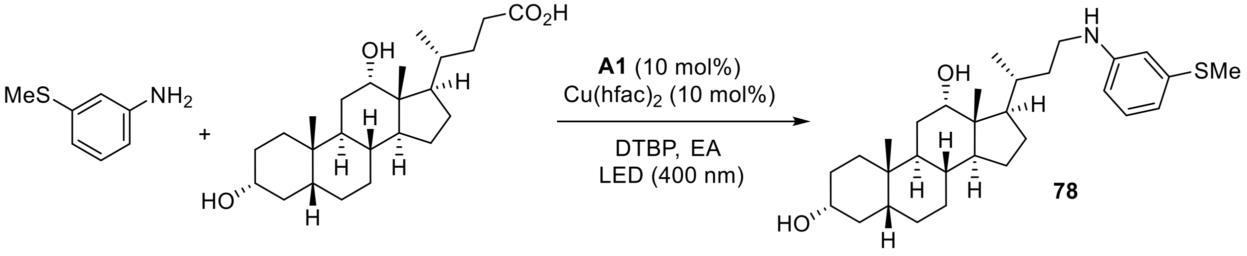
According to **GP2**, the reaction was carried out with *p*-anisidine (46 mg, 0.375 mmol, 2.5 mmol), deoxycholic acid (60 mg, 0.15 mmol), acridine **A1** (5 mg, 0.015 mmol, 10 mol%),

$Cu(hfac)_2$ (7 mg, 0.015 mmol, 10 mol%), and DTBP (44 mg, 0.3 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 2 : 3 v/v) to give the amine product **77** (54 mg, 75%) as a brown liquid.

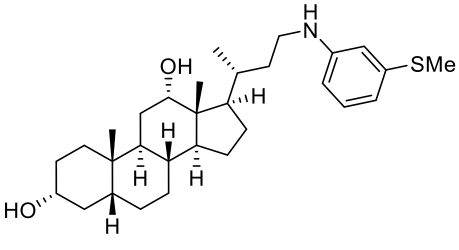


$[\alpha]_D^{23}$ = + 9.4 (c 0.16, $CHCl_3$). – ^1H NMR (500 MHz, $CDCl_3$): 6.78 (2 H, d, *J* = 8.8 Hz), 6.64–6.52 (2 H, m), 3.84 (1 H, d, *J* = 3.3 Hz), 3.74 (3 H, s), 3.52–3.37 (1 H, m), 3.11 (1 H, td, *J* = 10.6, 10.0, 4.8 Hz), 2.99 (1 H, ddd, *J* = 11.7, 9.2, 6.5 Hz), 2.49–1.77 (8 H, m), 1.77–1.58 (4 H, m), 1.58–1.44 (4 H, m), 1.44–1.05 (10 H, m), 1.04–0.93 (3 H, m), 0.89 (4 H, d, *J* = 11.4 Hz), 0.67 (3 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 152.1, 143.0, 115.0, 114.2, 72.1, 68.6, 56.3, 56.2, 56.0, 50.6, 42.9, 42.6, 41.6, 40.0, 39.8, 39.5, 36.1, 35.5, 35.2, 34.8, 34.7, 34.3, 33.0, 31.7, 30.8, 28.5, 25.4, 23.8, 22.9, 22.8, 20.7, 19.0, 14.3, 11.9 ppm. – IR: 3392, 2985, 2926, 2863, 2833, 1748, 1715, 1512, 1464, 1336, 1233, 1175, 1078, 1039, 977, 774 cm^{-1}. – HRMS: calcd for $C_{30}H_{48}NO_3$: 470.3629, found 470.3621 $[M+H^+]$.

(3*R*,5*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-4-((3-(methylthio)phenyl)amino)butan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,12-diol (78)

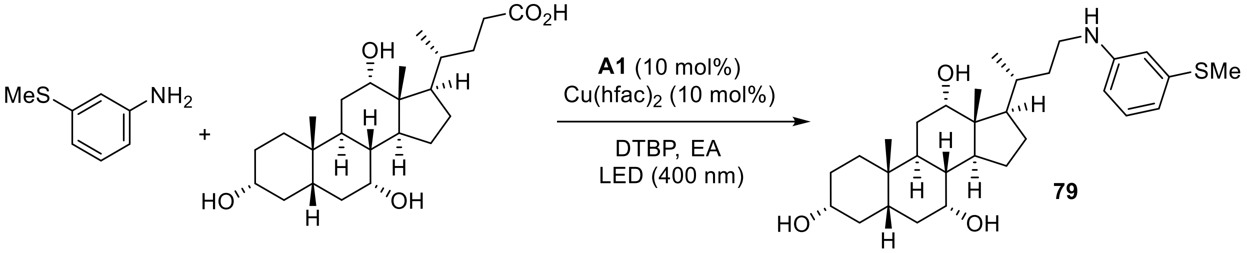


According to **GP2**, the reaction was carried out with 3-(methylthio)aniline (52 mg, 0.375 mmol, 2.5 mmol), deoxycholic acid (60 mg, 0.15 mmol), acridine **A1** (5 mg, 0.015 mmol, 10 mol%), Cu(hfac)$_2$ (7 mg, 0.015 mmol, 10 mol%), and DTBP (44 mg, 0.3 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 7 : 3 v/v) to give the amine product **78** (49 mg, 68%) as a yellow solid.

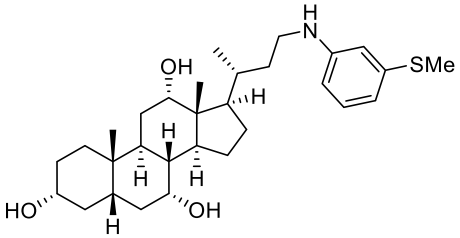


m.p.: 78– 80˚C. – $[\alpha]_D^{23}$ = + 21.7 (c 0.28, CHCl$_3$). – ^{1}H NMR (500 MHz, CDCl$_3$): 7.08 (1 H, t, *J* = 7.8 Hz), 6.59 (1 H, d, *J* = 7.8 Hz), 6.50 (1 H, s), 6.38 (1 H, d, *J* = 8.2 Hz), 4.01 (1 H, s), 3.62 (1 H, dq, *J* = 12.0, 6.9, 5.8 Hz), 3.16 (1 H, ddd, *J* = 13.8, 10.0, 4.6 Hz), 3.11–2.96 (1 H, m), 2.46 (3 H, s), 1.98–0.78 (32 H, m), 0.70 (3 H, s) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 149.0, 139.3, 129.7, 115.4, 110.8, 110.1, 73.3, 72.0, 48.5, 47.9, 46.7, 42.2, 41.5, 36.6, 36.2, 35.8, 35.3, 34.3, 34.0, 33.8, 30.7, 28.9, 27.9, 27.3, 26.3, 23.8, 23.3, 18.1, 16.0, 12.9 ppm. – IR: 3037, 2987, 2936, 2870, 1737, 1732, 1590, 1499, 1458, 1365, 1216, 1204, 1089, 1040, 1016 cm^{-1}. – HRMS: calcd for $C_{30}H_{48}NSO_2$: 486.3390, found 486.3393 [M+H$^+$].

(3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-4-((3-(methylthio)phenyl)amino)butan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,7,12-triol (79)

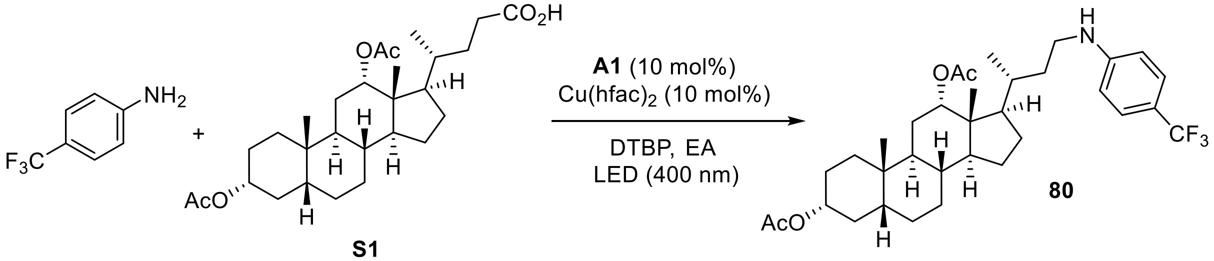


According to **GP2**, the reaction was carried out with 3-(methylthio)aniline (52 mg, 0.375 mmol, 2.5 mmol), cholic acid (61 mg, 0.15 mmol), acridine **A1** (5 mg, 0.015 mmol, 10 mol%), Cu(hfac)$_2$ (7 mg, 0.015 mmol, 10 mol%), and DTBP (44 mg, 0.3 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 7 : 3 v/v) to give the amine product **79** (41 mg, 55%) as a colorless liquid.

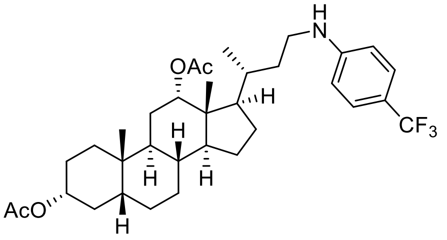


$[\alpha]_D^{23}$ = + 39.1 (c 0.1, CHCl$_3$). – ^{1}H NMR (500 MHz, CDCl$_3$): 7.06 (1 H, t, *J* = 7.9 Hz), 6.57 (1 H, d, *J* = 7.7 Hz), 6.49 (1 H, t, *J* = 2.1 Hz), 6.38 (1 H, dd, *J* = 8.1, 2.2 Hz), 3.97 (1 H, d, *J* = 3.1 Hz), 3.88–3.77 (1 H, m), 3.61–2.96 (6 H, m), 2.44 (3 H, s), 2.28–2.12 (2 H, m), 1.98–1.18 (19 H, m), 1.06 (3 H, t, *J* = 10.5 Hz), 1.00–0.79 (5 H, m), 0.68 (3 H, s) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 149.0, 139.2, 129.7, 115.4, 110.8, 110.1, 73.2, 72.0, 68.6, 47.5, 46.6, 41.8, 41.6, 39.7, 39.6, 35.8, 35.4, 34.9, 34.8, 34.2, 31.7, 30.5, 28.3, 27.9, 26.5, 23.4, 22.8, 22.6, 18.1, 15.9, 14.3, 14.3, 12.6 ppm. – IR: 3390, 2972, 2924, 2864, 1591, 1510, 1478, 1437, 1264, 1077, 1041, 980, 908 cm^{-1}. – HRMS: calcd for $C_{30}H_{48}NO_3S$: 502.3349, found 502.3346 [M+H$^+$].

(3*R*,5*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-4-((4-(trifluoromethyl)phenyl)amino)butan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,12-diyl diacetate (80)

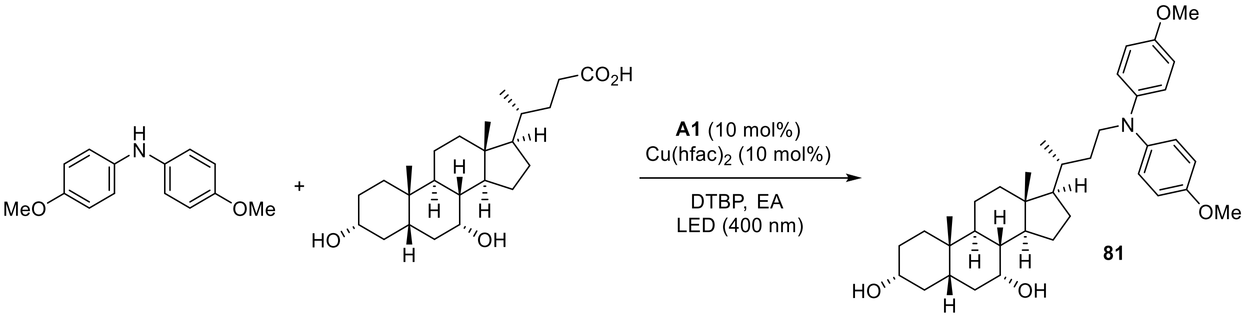


According to **GP2**, the reaction was carried out with 4-(trifluoromethyl)aniline (60 mg, 0.375 mmol, 2.5 mmol), acid **S1** (71 mg, 0.15 mmol), acridine **A1** (5 mg, 0.015 mmol, 10 mol%), Cu(hfac)$_2$ (7 mg, 0.015 mmol, 10 mol%), and DTBP (44 mg, 0.3 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 1 : 4 v/v) to give the amine product **80** (67 mg, 76%) as a colorless liquid.



$[\alpha]_D^{23}$ = + 7.1 (c 0.3, $CHCl_3$). – ^1H NMR (500 MHz, $CDCl_3$): 7.38 (2 H, d, *J* = 8.4 Hz), 6.57 (2 H, d, *J* = 8.4 Hz), 5.15–5.05 (1 H, m), 4.70 (1 H, tt, *J* = 11.4, 4.7 Hz), 3.88 (1 H, s), 3.19 (1 H, td, *J* = 10.8, 9.5, 4.6 Hz), 3.11–2.98 (1 H, m), 2.10 (3 H, s), 2.03 (3 H, s), 1.94–0.94 (24 H, m), 0.94–0.81 (6 H, m), 0.74 (3 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 170.7, 170.6, 150.9,126.6 (q, $^3J_{C-F}$ = 3.9 Hz), 125.0 (q, $^1J_{C-F}$ = 270.5 Hz), 118.5 (q, $^2J_{C-F}$ = 32.6 Hz), 111.8, 76.0, 74.3, 49.6, 48.1, 45.2, 42.0, 41.2, 35.8, 35.6, 34.9, 34.8, 34.7, 34.6, 34.2, 33.6, 32.4, 31.7, 27.7, 27.0, 26.8, 26.0, 25.8, 25.4, 23.6, 23.2, 22.8, 21.62, 21.55, 18.3, 14.3, 12.6 ppm. – ^{19}F NMR (471 MHz, $CDCl_3$): -60.95 (s) ppm. – IR: 3608, 3410, 3003, 2963, 2924, 1752, 1617, 1564, 1419, 1358, 1327, 1219, 1159, 1063, 1028 cm^{-1}. – HRMS: calcd for $C_{34}H_{49}F_3NO_4$: 592.3608, found 592.3625 [M+H$^+$].

(3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-17-((*R*)-4-(Bis(4-methoxyphenyl)amino)butan-2-yl)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,7-diol (81)



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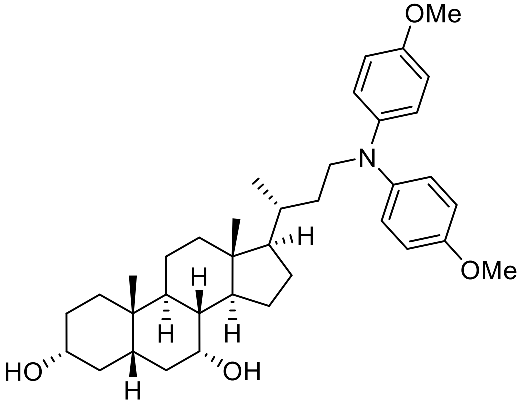
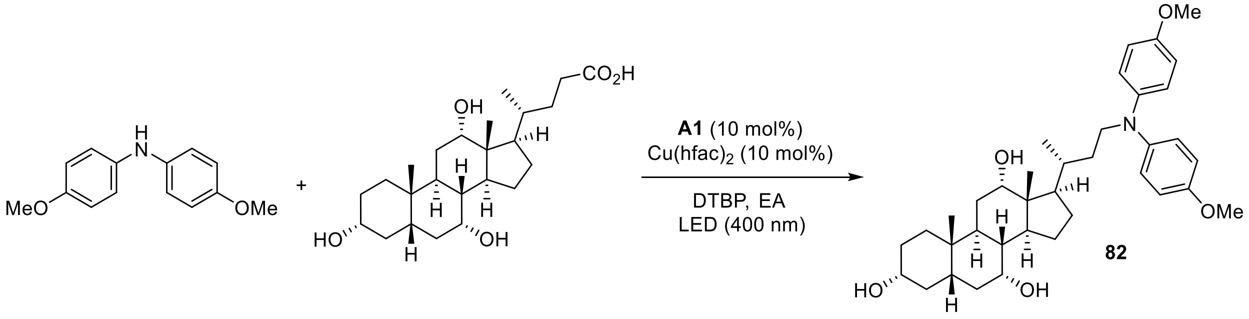
According to **GP2**, the reaction was carried out with bis(4-methoxyphenyl)amine (86 mg, 0.375 mmol, 2.5 equiv.), chenodeoxycholic acid (44 mg, 0.15 mmol), acridine **A1** (4 mg, 0.02 mmol, 10 mol%), Cu(hfac)$_2$ (7 mg, 0.02 mmol, 10 mol%), and DTBP (44 mg, 0.3 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 24 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 1 : 9 v/v) to give the amine product **81** (85 mg, 99%) as a brown liquid.

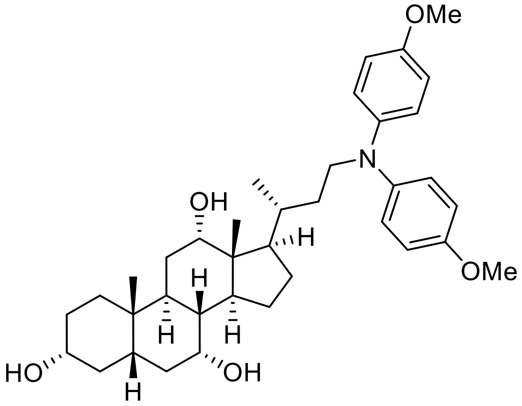


$[\alpha]_D^{23}$ = + 6.2 (c 0.4, CHCl$_3$). – ^{1}H NMR (500 MHz, CDCl$_3$): 6.96–6.70 (8 H, m), 3.90–3.72 (7 H, m), 3.55 (3 H, dtdd, *J* = 36.0, 15.9, 10.7, 5.6 Hz), 2.20 (1 H, q, *J* = 12.6 Hz), 2.08–0.73 (31 H, m), 0.65 (3 H, s) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 154.2, 142.6, 122.1, 114.7, 72.1, 68.6, 56.1, 55.7, 50.6, 50.5, 42.8, 41.6, 39.9, 39.8, 39.7, 39.5, 35.5, 35.2, 34.8, 34.7, 34.6, 34.4, 34.3, 33.4, 32.9, 31.7, 30.8, 29.8, 28.4, 25.4, 23.8, 22.9, 22.8, 20.8, 20.7, 20.3, 19.1, 18.7, 14.2, 11.8 ppm. – IR: 3408, 2926, 2863, 1504, 1463, 1375, 1238, 1179, 1115, 1077, 1037, 1000, 977 cm^{-1}. – HRMS: calcd for $C_{37}H_{54}NO_4$: 576.4047, found 576.4045 [M+H$^+$].

(3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-17-((*R*)-4-(Bis(4-methoxyphenyl)amino)butan-2-yl)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,7,12-triol (82)

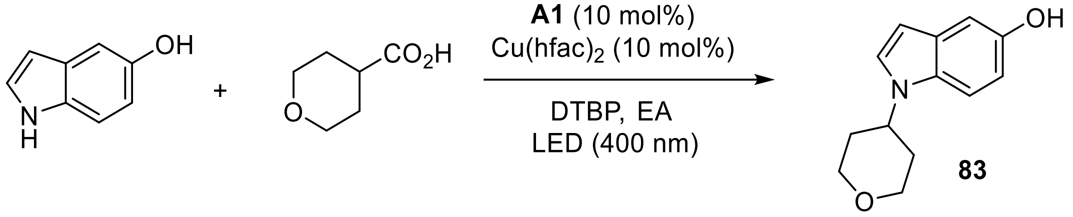


According to **GP2**, the reaction was carried out with bis(4-methoxyphenyl)amine (86 mg, 0.375 mmol, 2.5 equiv.), cholic acid (61 mg, 0.15 mmol), acridine **A1** (4 mg, 0.02 mmol, 10 mol%), Cu(hfac)$_2$ (7 mg, 0.02 mmol, 10 mol%), and DTBP (44 mg, 0.3 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 24 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 1:9 v/v) to give the amine product **82** (74 mg, 83%) as a brown liquid.

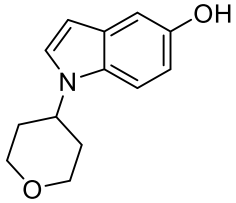


$[\alpha]_D^{23}$ = + 10.4 (c 0.4, CHCl$_3$). – ^{1}H NMR (500 MHz, CDCl$_3$): 6.95–6.71 (8 H, m), 3.95 (1 H, s), 3.77 (1 H, s), 3.70–3.60 (7 H, m), 3.58–3.47 (1 H, m), 3.41 (2 H, d, *J* = 11.2 Hz), 2.95 (3 H, s), 2.27–2.12 (2 H, m), 1.97–0.77 (26 H, m), 0.65 (3 H, s) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 154.2, 142.7, 122.1, 114.7, 73.2, 72.0, 68.6, 55.7, 50.7, 47.4, 46.6, 41.8, 41.6, 39.6, 35.4, 34.9, 34.8, 34.3, 33.4, 30.5, 29.8, 28.3, 27.7, 26.5, 23.4, 22.6, 18.1, 12.5 ppm. – IR: 3383, 2925, 2857, 1615, 1504, 1463, 1375, 1239, 1179, 1076, 1037, 980 cm^{-1}. – HRMS: calcd for $C_{37}H_{54}NO_5$: 592.3997, found 592.3997 [M+H$^+$].

1-(Tetrahydro-2*H*-pyran-4-yl)-1*H*-indol-5-ol (83)

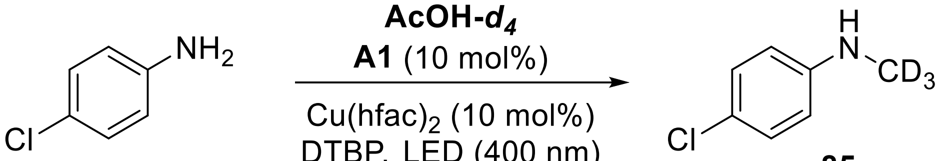


According to **GP1**, the reaction was carried out with 1*H*-indol-5-ol (20 mg, 0.15 mmol), tetrahydro-2*H*-pyran-4-carboxylic acid (59 mg, 0.45 mmol, 3 equiv.), acridine **A1** (4 mg, 0.02 mmol, 10 mol%), Cu(hfac)$_2$ (7 mg, 0.02 mmol, 10 mol%), and DTBP (44 mg, 0.3 mmol, 2 equiv.) in chlorobenzene (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 24 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 4:1 v/v) to give the amine product 8**3** (20 mg, 61%) as a colorless solid.



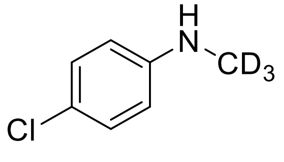
m.p.: 90–95˚C. – ^{1}H NMR (500 MHz, CD_3OD): 7.36–7.18 (2 H, m), 6.95 (1 H, d, *J* = 2.0 Hz), 6.74 (1 H, dd, *J* = 8.8, 2.1 Hz), 6.36–6.24 (1 H, m), 4.48 (1 H, td, *J* = 11.7, 5.4 Hz), 4.09 (2 H, d, *J* = 11.7 Hz), 3.65 (2 H, ddd, *J* = 14.7, 8.5, 2.8 Hz), 2.16–1.87 (4 H, m) ppm. – ^{13}C NMR (125 MHz, CD_3OD): 151.6, 132.1, 130.8, 125.5, 112.2, 110.8, 105.83, 105.75, 101.5, 68.4, 53.3, 34.5 ppm. – IR: 3326, 2874, 2498, 1666, 1606, 1503, 1478, 1456, 1385, 1332, 1308, 1258, 1230, 1210, 1151, 1130, 1088, 1055, 1008, 913 cm^{-1}. – HRMS: calcd for $C_{13}H_{16}NO_2$: 218.1176, found 218.1179 [M+H$^+$].

4-Chloro-*N*-(methyl-d_3)aniline (85)[31]



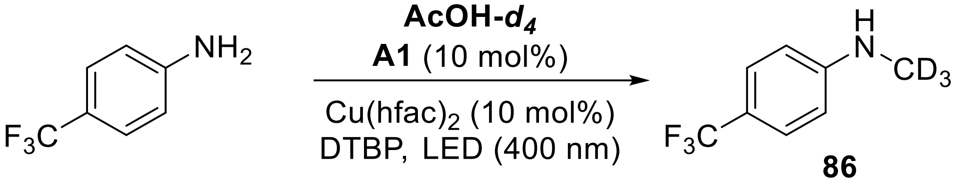
85

According to **GP1**, the reaction was carried out with 4-chloroaniline (38 mg, 0.3 mmol), acetic acid-d_4 (96 mg, 1.5 mmol, 5.0 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (1.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **85** (31 mg, 72%) as a colorless liquid.

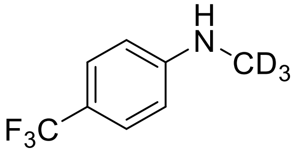


^{1}H NMR (500 MHz, $CDCl_3$): 7.17–7.09 (2 H, m), 6.58–6.46 (2 H, m), 3.67 (1 H, brs) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 148.0, 129.1, 121.9, 113.6 ppm. – ^{2}H NMR (77 MHz, $CDCl_3$): 2.79 (3 H, s) ppm. – IR: 3418, 2810, 2153, 1620, 1520, 1416, 1403, 1357, 1326, 1102, 997 cm^{-1}.

N-(Methyl-d_3)-4-(trifluoromethyl)aniline (86)



According to **GP1**, the reaction was carried out with 4-(trifluoromethyl)aniline (48 mg, 0.3 mmol), acetic acid-d_4 (96 mg, 1.5 mmol, 5.0 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (1.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **86** (33 mg, 62%) as a colorless liquid.



^{1}H NMR (500 MHz, CDCl$_3$): 7.41 (2 H, d, *J* = 8.4 Hz), 6.60 (2 H, d, *J* = 8.5 Hz), 3.99 (1 H, brs) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 126.7 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 125.2 (q, $^1J_{C\text{-}F}$ = 269.9 Hz), 118.8 (q, $^2J_{C\text{-}F}$ = 32.6 Hz), 111.6, 29.9 ppm. – ^{2}H NMR (77 MHz, CDCl$_3$): 2.85 (3 H, s) ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -61.0 (s) ppm. – IR: 3420, 2919, 2201, 2069, 1730, 1617, 1535, 1509, 1432, 1410, 1327, 1188, 1159, 1113, 1085, 938 cm^{-1}. – HRMS: calcd for $C_8H_6D_3F_3N$: 179.0870, found 179.0877 [M+H$^+$].

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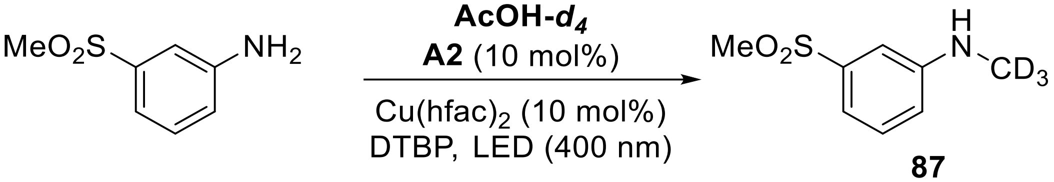
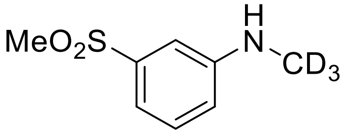
N-(Methyl-d_3)-3-(methylsulfonyl)aniline (87)

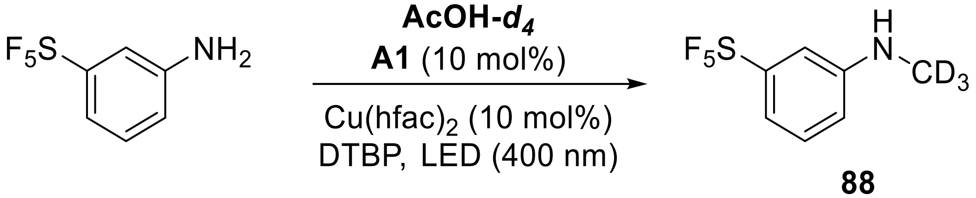


According to **GP1**, the reaction was carried out with 3-(methylsulfonyl)aniline (51 mg, 0.3 mmol), acetic acid-d_4 (96 mg, 1.5 mmol, 5.0 equiv.), acridine **A2** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (1.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 1:9 v/v) to give the amine product **87** (36 mg, 64%) as a colorless liquid.



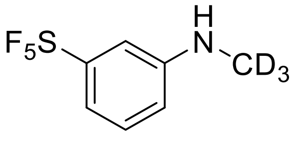
^{1}H NMR (500 MHz, CDCl$_3$): 7.35–7.29 (1 H, m), 7.20 (1 H, d, *J* = 7.7 Hz), 7.08 (1 H, t, *J* = 2.1 Hz), 6.80 (1 H, ddd, *J* = 8.2, 2.5, 1.0 Hz), 4.08 (1 H, brs), 3.03 (3 H, s) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 150.0, 141.5, 130.2, 117.4, 115.3, 109.8, 44.6 ppm. – ^{2}H NMR (77 MHz, CDCl$_3$): 2.85 (3 H, s) ppm. – IR: 3403, 3067, 2925, 2198, 2069, 1600, 1509, 1475, 1420, 1292, 1171, 1079, 1051, 1024, 959 cm^{-1}. – HRMS: calcd for $C_8H_8D_3NO_2S$: 189.0772, found 189.0778 [M+H$^+$].

N-(Methyl-*d*3)-3-(pentafluoro-λ6-sulfaneyl)aniline (88)



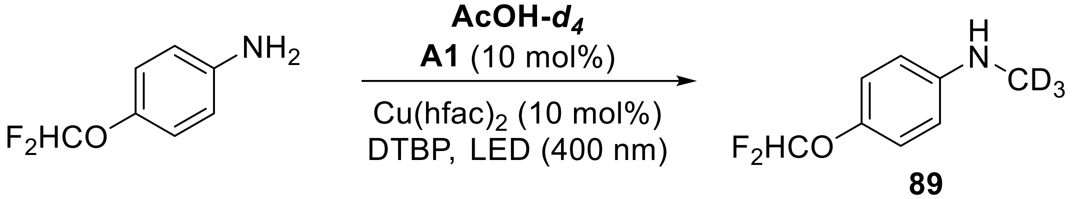
88

According to **GP1**, the reaction was carried out with 3-(pentafluoro-λ6-sulfaneyl)aniline (66 mg, 0.3 mmol), acetic acid-*d*4 (96 mg, 1.5 mmol, 5.0 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (1.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **88** (52 mg, 73%) as a colorless liquid.

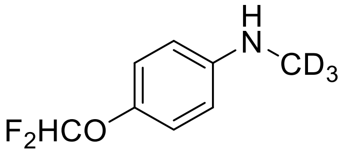


^{1}H NMR (500 MHz, CDCl$_3$): 7.23 (1 H, t, *J* = 8.2 Hz), 7.06 (1 H, dd, *J* = 8.2, 2.1 Hz), 6.93 (1 H, d, *J* = 2.3 Hz), 6.69 (1 H, dd, *J* = 8.2, 2.2 Hz), 3.93 (1 H, brs) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 155.3 (p, $^2J_{\text{C-F=}}$ = 16.1 Hz), 149.5, 129.3, 115.2, 114.4 (p, $^3J_{\text{C-F=}}$ = 4.9 Hz), 109.6 (p, $^3J_{\text{C-F=}}$ = 5.1 Hz), 29.9 ppm. – ^{2}H NMR (77 MHz, CDCl$_3$): 2.84 (3 H, s) ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -75.68 (s) ppm. – IR: 3436, 2074, 1608, 1511, 1496, 1331, 1305, 1262, 1178, 1114, 976 cm^{-1}. – HRMS: calcd for $C_7H_6D_3F_5NS$: 237.0559, found 237.0569 [M+H$^+$].

4-(Difluoromethoxy)-*N*-(methyl-*d*$_3$)aniline (89)



According to **GP1**, the reaction was carried out with 4-(difluoromethoxy)aniline (48 mg, 0.3 mmol), acetic acid-*d*$_4$ (96 mg, 1.5 mmol, 5.0 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (1.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **89** (25 mg, 48%) as a colorless liquid.



^{1}H NMR (500 MHz, $CDCl_3$): 6.98 (2 H, d, *J* = 8.8 Hz), 6.56 (2 H, d, *J* = 8.9 Hz), 6.37 (1 H, t, *J* = 74.9 Hz), 3.68 (1 H, brs) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 147.4, 142.5, 121.6, 116.7 (t, $^1J_{C\text{-}F}$ = 258.8 Hz), 113.0 ppm. – ^{2}H NMR (77 MHz, $CDCl_3$): 2.80 (3 H, s) ppm. – ^{19}F NMR (471 MHz, $CDCl_3$): -79.99 (d, *J* = 74.9 Hz) ppm. – IR: 2748, 2194, 2059, 1609, 1512, 1484, 1454, 1396, 1381, 1331, 1290, 1227, 1127, 1041 cm^{-1}. – HRMS: calcd for $C_{20}H_{18}FP$: 309.1203, found 309.1196 [M+H$^+$].

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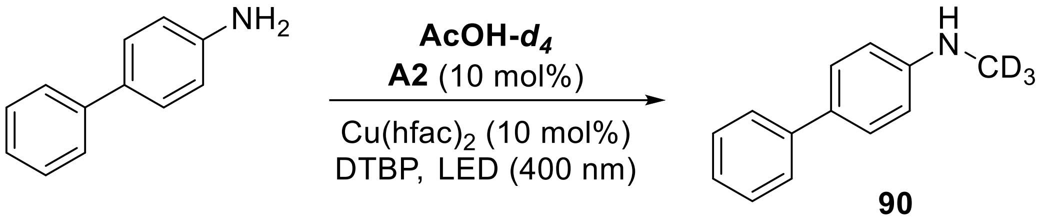
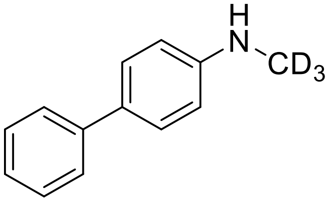
N-(Methyl-*d*$_3$)-[1,1'-biphenyl]-4-amine (90)

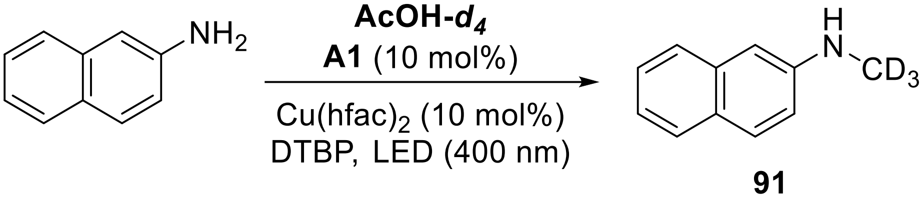


According to **GP1**, the reaction was carried out with [1,1'-biphenyl]-4-amine (51 mg, 0.3 mmol), acetic acid-*d*$_4$ (96 mg, 1.5 mmol, 5.0 equiv.), acridine **A2** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (1.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **90** (32 mg, 58%) as a colorless liquid.



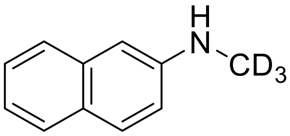
^{1}H NMR (500 MHz, $CDCl_3$): 7.56 (2 H, d, *J* = 7.7 Hz), 7.48 (2 H, d, *J* = 8.3 Hz), 7.41 (2 H, t, *J* = 7.6 Hz), 7.32–7.19 (1 H, m), 6.70 (2 H, d, *J* = 8.5 Hz), 3.79 (1 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 148.9, 141.5, 130.3, 128.8, 128.0, 126.4, 126.2, 112.8 ppm. – ^{2}H NMR (77 MHz, $CDCl_3$): 2.87 (3 H, s) ppm. – IR: 3418, 3023, 2192, 2063, 1613, 1599, 1525, 1442, 1403, 1324, 1273, 1253, 1190, 1150, 1120, 1041 cm^{-1}. – HRMS: calcd for $C_{13}H_{11}D_3N$: 187.1309, found 187.1317 [M+H$^+$].

N-(Methyl-d_3)naphthalen-2-amine (91)



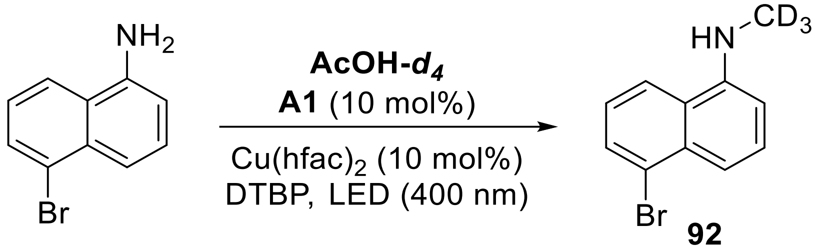
91

According to **GP1**, the reaction was carried out with naphthalen-2-amine (43 mg, 0.3 mmol), acetic acid-d_4 (96 mg, 1.5 mmol, 5.0 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (1.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **91** (71 mg, 64%) as a colorless liquid.

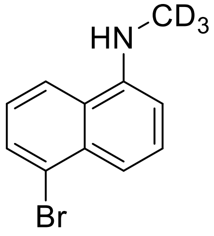


^{1}H NMR (500 MHz, $CDCl_3$): 7.72–7.59 (3 H, m), 7.37 (1 H, t, *J* = 7.5 Hz), 7.20 (1 H, t, *J* = 7.5 Hz), 6.89 (1 H, dd, *J* = 8.7, 2.2 Hz), 6.81 (1 H, d, *J* = 2.3 Hz), 3.88 (1 H, brs) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 147.1, 135.4, 129.0, 127.8, 127.6, 126.4, 126.1, 122.0, 118.0, 103.9 ppm. – ^{2}H NMR (77 MHz, $CDCl_3$): 2.93 (3 H, s) ppm. – IR: 3418, 3044, 2927, 2539, 2188, 2064, 1631, 1603, 1522, 1481, 1398, 1273, 1227, 1189, 1144, 1020 cm^{-1}. – HRMS: calcd for $C_{11}H_9D_3N$: 161.1153, found 161.1154 [M+H$^+$].

5-Bromo-*N*-(methyl-*d*$_3$)naphthalen-1-amine (92)



According to **GP1**, the reaction was carried out with 5-bromonaphthalen-1-amine (67mg, 0.3 mmol), acetic acid-*d*$_4$ (96 mg, 1.5 mmol, 5.0 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (1.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **92** (34 mg, 47%) as a yellow liquid.



^{1}H NMR (500 MHz, CDCl$_3$): 7.76 (2 H, dd, *J* = 7.9, 5.0 Hz), 7.65 (1 H, d, *J* = 8.5 Hz), 7.48 (1 H, t, *J* = 8.1 Hz), 7.29–7.20 (1 H, m), 6.65 (1 H, d, *J* = 7.6 Hz), 4.43 (1 H, brs) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 144.90, 132.9, 130.1, 128.3, 124.8, 124.7, 123.9, 119.9, 116.4, 104.8 ppm. – ^{2}H NMR (77 MHz, CDCl$_3$): 3.00 (3 H, s) ppm. – IR: 3444, 3072, 2916, 2192, 2064, 1973, 1614, 1587, 1567, 1518, 1470, 1399, 1326, 1287, 1201, 1104, 1063, 997 cm^{-1}. – HRMS: calcd for C$_{11}$H$_8$D$_3$BrN: 239.0258, found 239.0268 [M+H$^+$].

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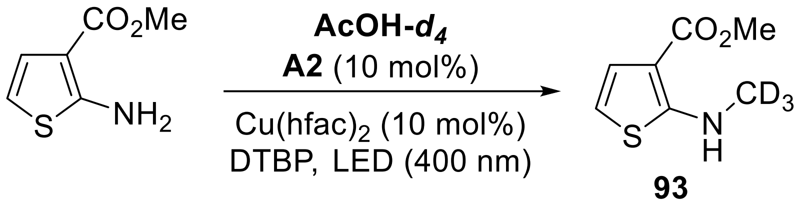
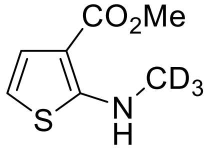
Methyl 2-((methyl-*d*$_3$)amino)thiophene-3-carboxylate (93)



According to **GP1**, the reaction was carried out with methyl 2-aminothiophene-3-carboxylate (47 mg, 0.3 mmol), acetic acid-*d*$_4$ (96 mg, 1.5 mmol, 5.0 equiv.), acridine **A2** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (1.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **93** (37 mg, 71%) as a red liquid.



^{1}H NMR (500 MHz, $CDCl_3$): 7.29 (1 H, brs), 7.03 (1 H, d, *J* = 5.7 Hz), 6.18 (1 H, d, *J* = 5.7 Hz), 3.79 (3 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 167.1, 166.3, 126.5, 105.8, 103.5, 51.0 ppm. – ^{2}H NMR (77 MHz, $CDCl_3$): 2.98 (3 H, s) ppm. – IR: 3349, 2947, 2195, 2064, 1667, 1549, 1512, 1381, 1317, 1242, 1192, 1165 cm^{-1}. – HRMS: calcd for $C_7H_7D_3NO_2S$: 175.0615, found 175.0622 [M+H$^+$].

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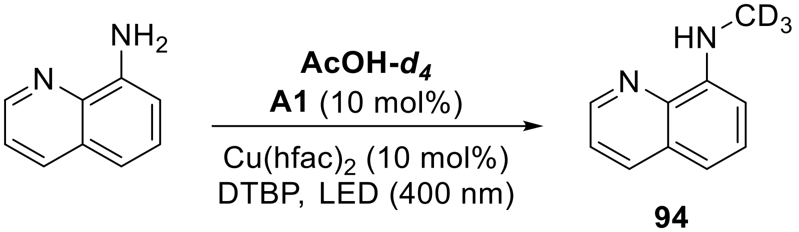
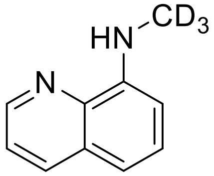
N-(Methyl-*d*$_3$)quinolin-8-amine (94)



94

According to **GP1**, the reaction was carried out with quinolin-8-amine (43 mg, 0.3 mmol), acetic acid-*d*$_4$ (96 mg, 1.5 mmol, 5.0 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (1.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **94** (26 mg, 52%) as a yellow liquid.



^{1}H NMR (500 MHz, CDCl$_3$): 8.71 (1 H, dd, *J* = 4.2, 1.7 Hz), 8.06 (1 H, dd, *J* = 8.3, 1.7 Hz), 7.51–7.32 (2 H, m), 7.05 (dd, *J* = 8.2, 1.2 Hz), 6.65 (1 H, dd, *J* = 7.6, 1.2 Hz), 6.11 (1 H, brs) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 146.9, 146.0, 138.4, 136.1, 128.7, 128.0, 121.5, 113.8, 104.3 ppm. – ^{2}H NMR (77 MHz, CDCl$_3$): 3.03 (3 H, s) ppm. – IR: 3411, 3032, 2965, 2185, 2056, 1599, 1574, 1519, 1478, 1444, 1380, 1341, 1233, 1200, 1149, 1090 cm^{-1}. – HRMS: calcd for $C_{10}H_8D_3N_2$: 162.1105, found 162.1110 [M+H$^+$].

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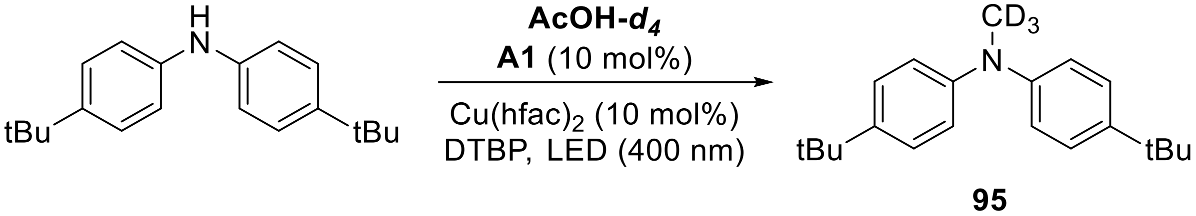
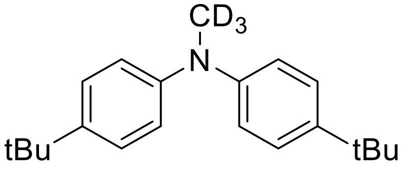
4-(Tert-butyl)-*N*-(4-(tert-butyl)phenyl)-*N*-(methyl-*d*3)aniline (95)



According to **GP1**, the reaction was carried out with bis(4-(*tert*-butyl)phenyl)amine (84 mg, 0.3 mmol), acetic acid-d_4 (96 mg, 1.5 mmol, 5.0 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (1.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **95** (61 mg, 68%) as a colorless solid.



m.p.: 90–93 °C. – ^{1}H NMR (500 MHz, CDCl$_3$): 7.31 (4 H, d, *J* = 8.3 Hz), 6.98 (4 H, d, *J* = 8.3 Hz), 1.34 (18 H, s) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 146.7, 143.8, 126.1, 119.9, 34.3, 31.6 ppm. – ^{2}H NMR (77 MHz, CDCl$_3$): 3.29 (3 H, s) ppm. – IR: 3034, 2957, 2901, 2194, 2062, 1605, 1508, 1463, 1362, 1331, 1305, 1266, 1201 cm^{-1}. – HRMS: calcd for $C_{21}H_{27}D_3N$: 299.2561, found 299.2562 [M+H$^+$].

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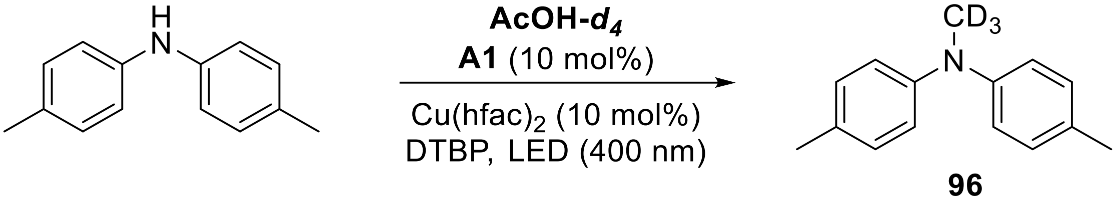
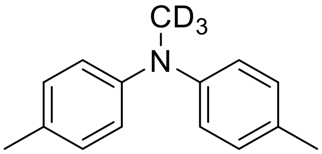
4-Methyl-*N*-(methyl-d_3)-*N*-(*p*-tolyl)aniline (96)

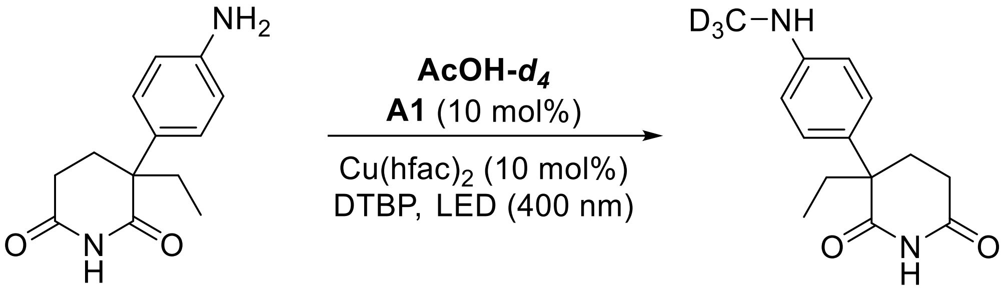


According to **GP1**, the reaction was carried out with di-*p*-tolylamine (59 mg, 0.3 mmol), acetic acid-d_4 (96 mg, 1.5 mmol, 5.0 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (1.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **96** (47 mg, 73%) as a colorless liquid.



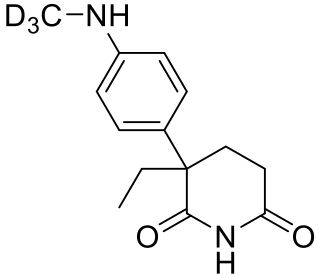
^{1}H NMR (500 MHz, $CDCl_3$): 7.09 (4 H, d, *J* = 7.9 Hz), 6.93 (4 H, d, *J* = 8.0 Hz), 2.32 (6 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 147.2, 130.6, 129.8, 120.5, 29.9, 20.8 ppm. – ^{2}H NMR (77 MHz, $CDCl_3$): 3.26 (3 H, s) ppm. – IR: 3024, 2919, 2853, 2062, 1608, 1587, 1507, 1462, 1327, 1241, 1180, 1130, 1038 cm^{-1}. – HRMS: calcd for $C_{15}H_{15}D_3N$: 215.1622, found 215.1624 [M+H$^+$].

3-Ethyl-3-(4-((methyl-*d*$_3$)amino)phenyl)piperidine-2,6-dione (97)



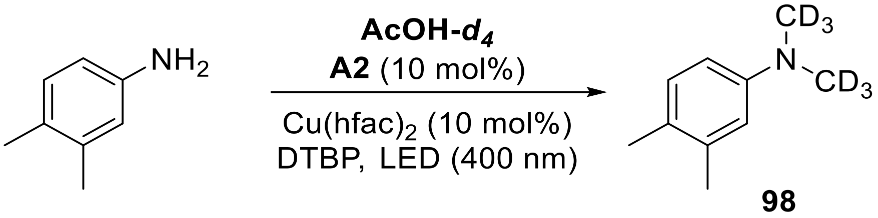
97

According to **GP1**, the reaction was carried out with 3-(4-aminophenyl)-3-ethylpiperidine-2,6-dione (70 mg, 0.3 mmol), acetic acid-*d*$_4$ (96 mg, 1.5 mmol, 5.0 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (1.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 3:7 v/v) to give the amine product **97** (46 mg, 62%) as a colorless liquid.

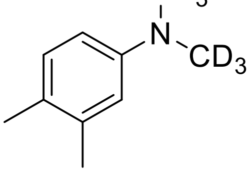


^{1}H NMR (500 MHz, CDCl$_3$): 8.14 (1 H, brs), 7.07 (2 H, d, *J* = 8.8 Hz), 6.57 (2 H, d, *J* = 8.7 Hz), 3.78 (1 H, s), 2.56 (1 H, ddd, *J* = 17.8, 4.7, 2.8 Hz), 2.46 (1 H, ddd, *J* = 18.0, 13.3, 5.0 Hz), 2.31 (1 H, ddd, *J* = 14.2, 5.0, 2.7 Hz), 2.15 (1 H, td, *J* = 13.8, 4.6 Hz), 2.00 (1 H, ddd, *J* = 21.7, 14.0, 6.6 Hz), 1.87 (1 H, dq, *J* = 14.6, 7.4 Hz), 0.85 (3 H, t, *J* = 7.5 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 175.9, 172.9, 148.7, 127.2, 126.7, 112.8, 50.3, 33.1, 29.5, 27.1, 9.1 ppm. – ^{2}H NMR (77 MHz, $CDCl_3$): 2.80 (3 H, s) ppm. – IR: 3370, 3019, 2253, 2055, 1698, 1614, 1463, 1327, 1215, 1184, 904 cm^{-1}. – HRMS: calcd for $C_{14}H_{16}D_3N_2O_2$: 250.1629, found 250.1640 [M+H$^+$].

3,4-Dimethyl-*N*,*N*-bis(methyl-*d*$_3$)aniline (98)



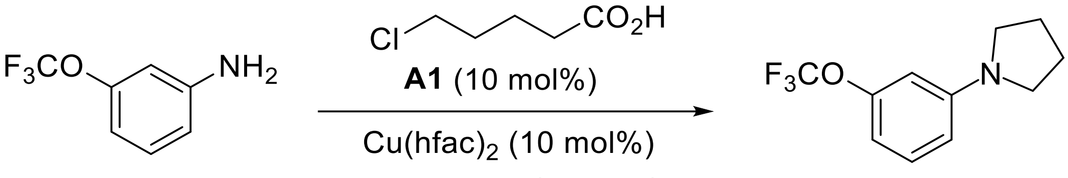
According to **GP1**, the reaction was carried out with 3,4-dimethylaniline (36 mg, 0.3 mmol), acetic acid-*d*$_4$ (115 mg, 1.8 mmol, 6.0 equiv.), acridine **A2** (9 mg, 0.03 mmol, 10 mol%), $Cu(hfac)_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (1.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 3:7 v/v) to give the amine product **98** (24 mg, 52%) as a colorless liquid.



^{1}H NMR (500 MHz, $CDCl_3$): 7.00 (1 H, d, *J* = 8.4 Hz), 6.59 (1 H, d, *J* = 2.7 Hz), 6.54 (1 H, dd, *J* = 8.3, 2.7 Hz), 2.24 (3 H, s), 2.18 (3 H, s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 149.5, 137.1, 130.3, 125.1, 115.0, 110.9, 20.5, 18.7 ppm. – ^{2}H NMR (77 MHz, $CDCl_3$): 2.87 (3 H, s) ppm. – IR:

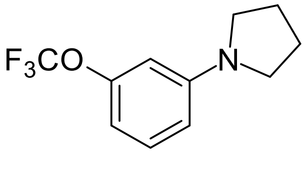
3017, 2919, 2857, 2193, 2051, 1738, 1613, 1567, 1510, 1454, 1335, 1290, 1200, 1159, 1136 1065 cm^{-1}. – HRMS: calcd for $C_{10}H_{10}D_6N$: 156.1654, found 156.1656 [M+H$^+$].

1-(3-(trifluoromethyl)phenyl)pyrrolidine (100)



100

According to **GP1**, the reaction was carried out with 3-(trifluoromethoxy)aniline (53 mg, 0.3 mmol), 5-chlorovaleric acid (102 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 98 : 2 v/v) to give the amine product **100** (43 mg, 63%) as a pale brown liquid.



^{1}H NMR (500 MHz, CDCl$_3$): 7.18 (1 H, t, *J* = 8.2 Hz), 6.52–6.47 (1 H, m), 6.45 (1 H, dd, *J* = 8.4, 2.3 Hz), 6.36 (1 H, d, *J* = 2.3 Hz), 3.31–3.24 (4 H, m), 2.06–1.95 (4 H, m) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 150.6, 149.2, 130.1, 120.7 (q, $^1J_{C\text{-}F}$ = 256.1 Hz), 110.0, 107.2, 104.1, 47.8, 25.6 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -57.42 (s) ppm. – IR: 2972, 2943, 2922, 2844, 1614, 1574, 1504, 1487, 1461, 1376, 1253, 1219, 1158, 1017, 934 cm^{-1}. – HRMS: calcd for $C_{11}H_{13}F_3NO$: 232.0944, found 232.0945 [M+H$^+$].

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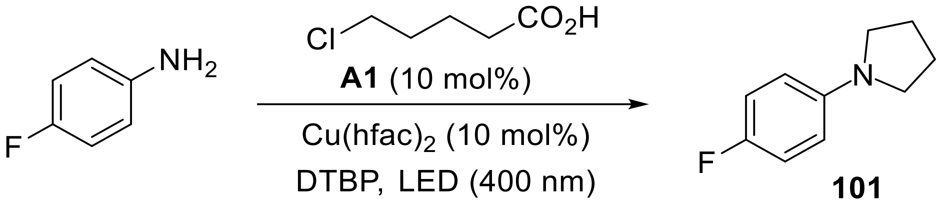
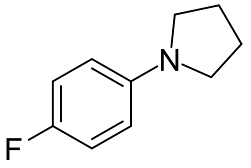
1-(4-Fluorophenyl)pyrrolidine (101)[32]

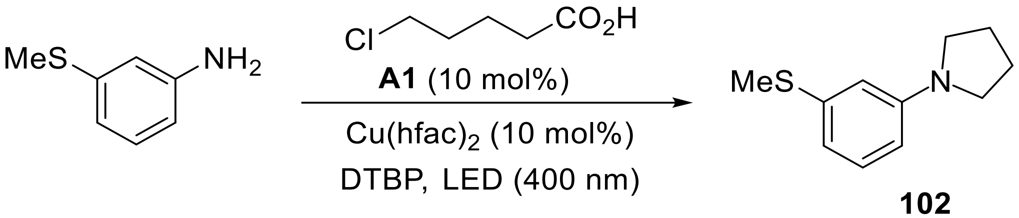


According to **GP1**, the reaction was carried out with 4-fluoroaniline (33 mg, 0.3 mmol), 5-chlorovaleric acid (102 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 98 : 2 v/v) to give the amine product **101** (32 mg, 65%) as an orange liquid.



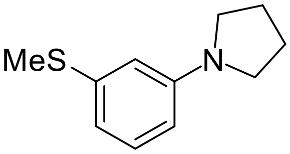
^{1}H NMR (500 MHz, CDCl$_3$): 6.94 (1 H, t, *J* = 8.8 Hz), 6.48 (1 H, dd, *J* = 9.0, 4.3 Hz), 3.30–3.12 (2 H, m), 2.06–1.90 (2 H, m) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 154.9 (d, $^1J_{C\text{-}F}$ = 232.8 Hz), 145.0, 115.59 (d, $^2J_{C\text{-}F}$ = 21.9 Hz), 112.2 (d, $^3J_{C\text{-}F}$ = 7.2 Hz), 48.2, 25.6 ppm. – ^{19}F NMR (471 MHz, CDCl$_3$): -130.82–131.08 (m) ppm. – IR: 3056, 2970. 2951, 2912, 2844, 1738, 1610, 1518, 1488, 1462, 1370, 1264, 1223, 1206, 1157, 908, 813 cm^{-1}.

1-(3-(Methylthio)phenyl)pyrrolidine (102)[33]



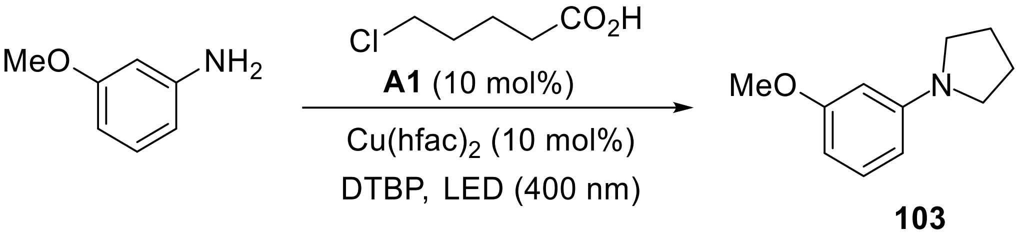
102

According to **GP1**, the reaction was carried out with 3-(methylthio)aniline (42 mg, 0.3 mmol), 5-chlorovaleric acid (102 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 98 : 2 v/v) to give the amine product **102** (31 mg, 53%) as a brown liquid.

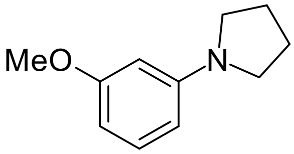


^{1}H NMR (500 MHz, CDCl$_3$): 7.15 (1 H, t, *J* = 7.9 Hz), 6.58 (1 H, dd, *J* = 7.7, 1.7 Hz), 6.49 (1 H, t, *J* = 2.1 Hz), 6.37 (1 H, dd, *J* = 8.2, 2.4 Hz), 3.39–3.15 (4 H, m), 2.49 (3 H, s), 2.11–1.89 (4 H, m) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 148.3, 139.0, 129.6, 113.8, 110.0, 109.1, 47.7, 25.6, 16.2 ppm. – IR: 3040, 2964, 2919, 2893, 2835, 1588, 1562, 1486, 1463, 1360, 1277, 1196, 1170, 1102, 764, 694 cm^{-1}.

1-(3-Methoxyphenyl)pyrrolidine (103)[34]

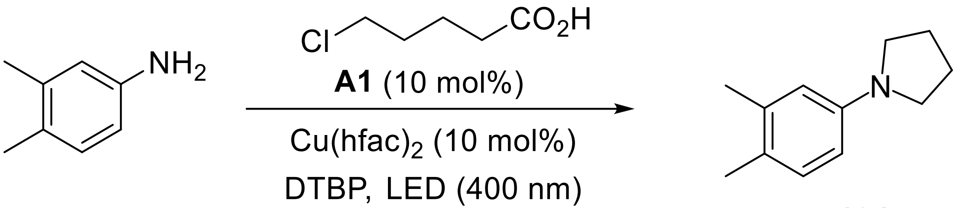


According to **GP1**, the reaction was carried out with *m*-anisidine (37 mg, 0.3 mmol), 5-chlorovaleric acid (102 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 98 : 2 v/v) to give the amine product **103** (39 mg, 73%) as a brown liquid.



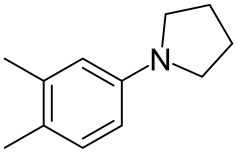
^{1}H NMR (500 MHz, CDCl$_3$): 7.14 (1 H, t, *J* = 8.1 Hz), 6.25 (1 H, dd, *J* = 8.1, 2.4 Hz), 6.21 (1 H, dd, *J* = 8.2, 2.3 Hz), 6.13 (1 H, t, *J* = 2.4 Hz), 3.81 (3 H, s), 3.32–3.22 (4 H, m), 2.06–1.94 (4 H, m) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 160.9, 149.4, 129.9, 105.1, 100.6, 98.0, 55.2, 47.8, 25.6 ppm. – IR: 3055. 2970, 2917, 2847, 1736, 1606, 1573, 1502, 1458, 1372, 1264, 1219, 1167, 1053, 908, 704 cm^{-1}.

1-(3,4-Dimethylphenyl)pyrrolidine (104)[35]



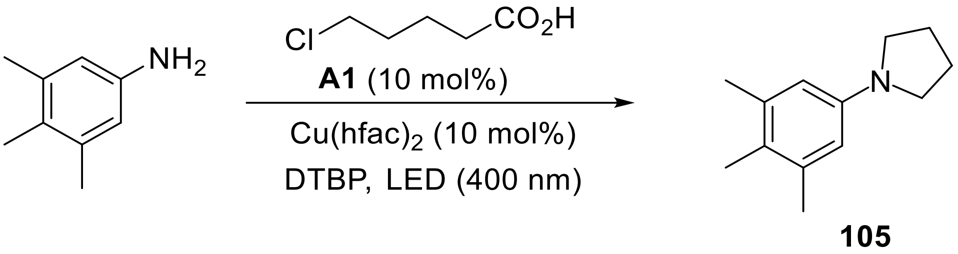
104

According to **GP1**, the reaction was carried out with 3,4-dimethylaniline (36 mg, 0.3 mmol), 5-chlorovaleric acid (102 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 98 : 2 v/v) to give the amine product **104** (37 mg, 70%) as a brown liquid.

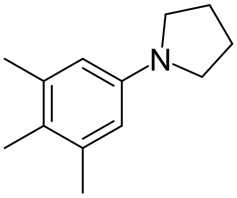


^{1}H NMR (500 MHz, CDCl$_3$): 6.99 (1 H, d, *J* = 8.1 Hz), 6.42 (1 H, d, *J* = 2.6 Hz), 6.36 (1 H, dd, *J* = 8.2, 2.6 Hz), 3.33–3.20 (4 H, m), 2.25 (3 H, s), 2.18 (3 H, s), 2.05–1.94 (4 H, m) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 146.8, 137.2, 130.4, 130.3, 123.4, 113.5, 109.4, 48.0, 25.5, 20.4, 18.7 ppm. – IR: 3066, 2974, 2922, 2867, 1745, 1612, 1511, 1488, 1264, 1200, 1159, 1119, 1102, 1019, 735, 704 cm^{-1}.

1-(3,4,5-Trimethylphenyl)pyrrolidine (105)

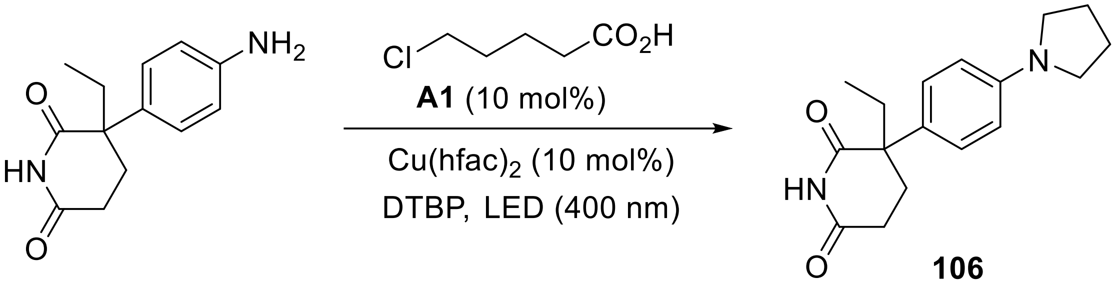


According to **GP1**, the reaction was carried out with 3,4,5-trimethylaniline (41 mg, 0.3 mmol), 5-chlorovaleric acid (102 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 36 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 98 : 2 v/v) to give the amine product **105** (30 mg, 53%) as a brown liquid.

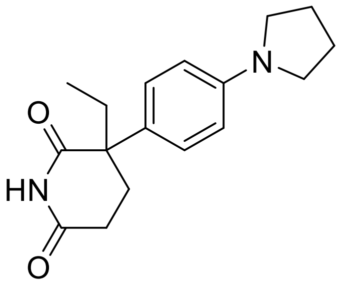


^{1}H NMR (500 MHz, $CDCl_3$): 6.30 (2 H, s), 3.36–3.19 (2 H, m), 2.27 (3 H, s), 2.10 (1 H, s), 2.05–1.85 (2 H, m) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 146.2, 137.1, 122.1, 111.5, 47.9, 25.5, 21.2, 14.4 ppm. – IR: 3058, 2969, 2930, 2883, 2849, 1737, 1498, 1486, 1383, 1364, 1264, 1160, 907, 829, 703 cm^{-1}. – HRMS: calcd for $C_{13}H_{19}N$: 190.1590, found 190.1589 [M+H$^+$].

3-Ethyl-3-(4-(pyrrolidin-1-yl)phenyl)piperidine-2,6-dione (106)

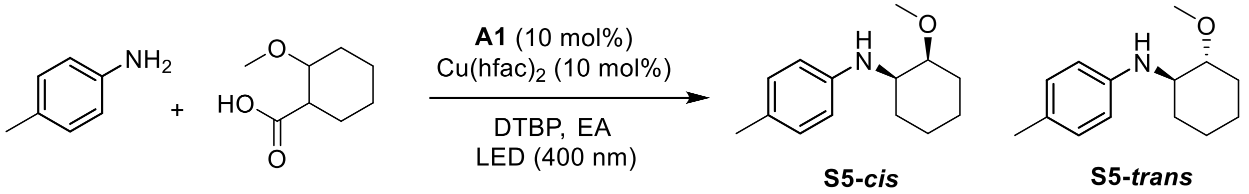


According to **GP1**, the reaction was carried out with 3-(4-aminophenyl)-3-ethylpiperidine-2,6-dione (70 mg, 0.3 mmol), 5-chlorovaleric acid (102 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na$_2$SO$_4$, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 98 : 2 v/v) to give the amine product **106** (43 mg, 50%) as a colorless liquid.

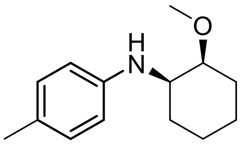


^{1}H NMR (500 MHz, CDCl$_3$): 8.09 (1 H, s), 7.10 (2 H, d, *J* = 8.3 Hz), 6.53 (2 H, d, *J* = 8.3 Hz), 3.26 (4 H, d, *J* = 6.3 Hz), 2.62–2.41 (2 H, m), 2.33 (1 H, dt, *J* = 14.3, 3.7 Hz), 2.16 (1 H, td, *J* = 13.8, 4.8 Hz), 1.94 (6 H, dt, *J* = 49.7, 6.8 Hz), 0.85 (3 H, t, *J* = 7.5 Hz) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 175.9, 172.9, 147.1, 127.1, 124.6, 111.9, 50.2, 47.7, 33.1, 29.5, 27.1, 25.6, 9.2 ppm. – IR: 3212, 3092, 3055, 2966, 2951, 2878, 2844, 1694, 1610, 1520, 1565, 1520, 1487, 1460, 1352, 1266, 1189, 1048, 814, 733, 702 cm^{-1}. – HRMS: calcd for $C_{17}H_{23}N_2O_2$: 287.1754, found 287.1754 [M+H$^+$].

N-(-2-Methoxycyclohexyl)-4-methylaniline (S5)



According to **GP1**, the reaction was carried out with *p*-toluidine (32 mg, 0.3 mmol), 2-methoxycyclohexane-1-carboxylic acid (cis/trans = 1 : 1.5) (96 mg, 0.75 mmol, 2.5 equiv.), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), $Cu(hfac)_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2 equiv.) in ethyl acetate (3 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at 35 °C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL), extracted with a saturated solution of EDTA (3 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **S5-*cis*** (9 mg, 14%) and **S5-*trans*** (44 mg, 67%) as a colorless liquid.



^{1}H NMR (500 MHz, $CDCl_3$): 6.97 (2 H, d, *J* = 8.0 Hz), 6.55 (2 H, d, *J* = 8.4 Hz), 3.92 (1 H, brs), 3.51 (1 H, dt, *J* = 5.0, 2.6 Hz), 3.36 (1 H, dt, *J* = 10.6, 3.4 Hz), 3.32 (3 H, s), 2.23 (3 H, s), 2.06 – 1.98 (1 H, m), 1.79 – 1.65 (2 H, m), 1.57–1.45 (2 H, m), 1.43 – 1.22 (3 H, m) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 145.3, 129.9, 126.5, 114.1, 77.8, 56.4, 54.2, 27.6, 27.5, 24.3, 20.5, 20.3 ppm. – IR: 3386, 3024, 2977, 2930, 2861, 1616, 1517, 1458, 1371, 1310, 1297, 1197, 1085, 908, 855, 805, 731 cm^{-1}. – HRMS: calcd for $C_{14}H_{22}NO$: 220.1696, found 220.1694 [M+H$^+$].

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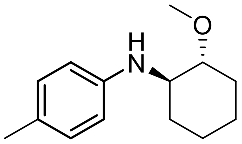
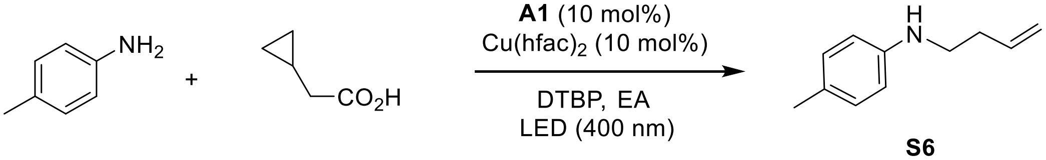
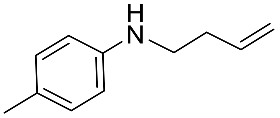


^{1}H NMR (500 MHz, CDCl$_3$): 6.98 (2 H, d, *J* = 8.0 Hz), 6.62 (2 H, d, *J* = 8.4 Hz), 3.39 (3 H, s), 3.19 (1 H, td, *J* = 8.9, 3.8 Hz), 3.13 (1 H, td, *J* = 8.7, 3.5 Hz), 2.24 (3 H, s), 2.23 – 2.15 (1 H, m), 2.08 (1 H, dd, *J* = 10.6, 5.7 Hz), 1.80 – 1.73 (1 H, m), 1.69 – 1.62 (1 H, m), 1.42 – 1.26 (3 H, m), 1.24 – 1.15 (1 H, m) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$): 145.8, 129.7, 126.9, 114.4, 82.2, 57.0, 56.3, 31.3, 29.1, 23.9, 23.8, 20.5 ppm. – IR: 3401, 3016, 2987, 2866, 2821, 1617, 1573, 1517, 1315, 1251, 1098, 1039, 909, 805, 780 cm^{-1}. – HRMS: calcd for $C_{14}H_{22}NO$: 220.1696, found 220.1696 [M+H$^+$].

N-(But-3-en-1-yl)-4-methylaniline (S6)[36]

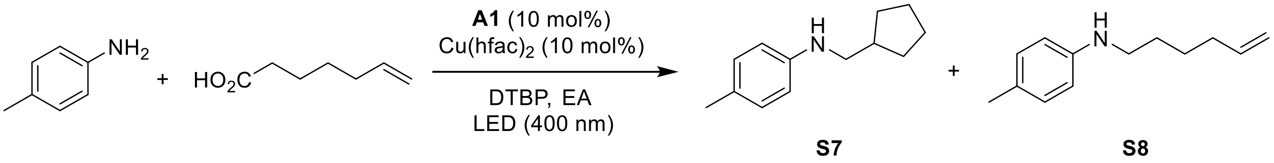


According to **GP2**, the reaction was carried out with *p*-toluidine (80 mg, 0.75 mmol, 2.5 equiv.), 2-cyclopropylacetic acid (30 mg, 0.3 mmol), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2.0 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was extracted with ethyl acetate (3x 15 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the amine product **S6** (38 mg, 79%) as a yellow oil.

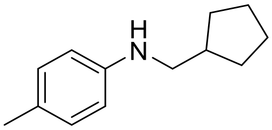


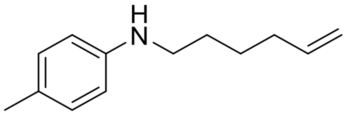
^{1}H NMR (500 MHz, $CDCl_3$): 6.98 (2 H, d, *J* = 7.9 Hz), 6.53 (2 H, d, *J* = 7.9 Hz), 5.81 (1 H, ddt, *J* = 17.0, 9.8, 6.9 Hz), 5.11 (2 H, dd, *J* = 18.4, 13.8 Hz), 3.15 (2 H, t, *J* = 6.7 Hz), 2.36 (2 H, q, *J* = 6.7 Hz), 2.23 (3 H s) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): 146.1, 136.0, 129.9, 126.7, 117.1, 113.3, 43.4, 33.8, 20.5 ppm. – IR: 3406, 3082, 3018, 2980, 2922, 2875, 1646, 1622, 1521, 1484, 1316, 1269, 1152, 997 cm^{-1}.

***N*-(Cyclopentylmethyl)-4-methylaniline (S7) and *N*-(hex-5-en-1-yl)-4-methylaniline (S8)** [36]



According to **GP2**, the reaction was carried out with *p*-toluidine (80 mg, 0.75 mmol, 2.5 equiv.), hept-6-enoic acid (38 mg, 0.3 mmol), acridine **A1** (9 mg, 0.03 mmol, 10 mol%), Cu(hfac)$_2$ (14 mg, 0.03 mmol, 10 mol%), and DTBP (88 mg, 0.6 mmol, 2.0 equiv.) in ethyl acetate (4.5 mL). The reaction mixture was degassed using a stream of argon bubbled through a glass pipet reaching the bottom of the test-tube, while vigorous stirring was maintained for 3 min. The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring for 12 h. The reaction mixture was extracted with ethyl acetate (3x 15 mL). The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography on silica gel (hexane/ ethyl acetate 95 : 5 v/v) to give the inseparable mixture of amine products **S7** and **S8** (49 mg, 86%, 2 : 1 ratio) as a yellow oil.





***N*-(Cyclopentylmethyl)-4-methylaniline (S7):** ^{1}H NMR (500 MHz, $CDCl_3$): 6.96 (2 H, d, *J* = 7.9 Hz), 6.52 (2 H, dd, *J* = 8.4, 3.1 Hz), 3.47 (1 H, brs), 2.99 (2 H, d, *J* = 7.2 Hz), 2.22 (3 H, s), 2.11 (1 H, m), 1.61 (4 H, m), 1.24 (4 H, m) ppm.

***N*-(Hex-5-en-1-yl)-4-methylaniline (S8):** ^{1}H NMR (500 MHz, CDCl$_3$): 6.96 (2 H, d, *J* = 7.9 Hz), 6.52 (2 H, dd, *J* = 8.4, 3.1 Hz), 5.80 (1 H, ddt, *J* = 16.9, 9.7, 6.7 Hz), 4.98 (2 H, dd, *J* = 28.0, 13.6 Hz), 3.47 (1 H, brs), 3.08 (2 H, t, *J* = 7.1 Hz), 2.22 (3 H, s), 2.11 (2 H, m), 1.80 (2 H, m), 1.61 (2 H, m) ppm. – ^{13}C NMR (125 MHz, CDCl$_3$) mixture: 146.5, 146.4, 138.7, 130.0, 129.8, 129.8, 127.6, 126.4, 126.3, 114.8, 113.0, 50.0, 44.3, 39.6, 33.6, 30.8, 29.2, 26.5, 25.4, 20.5 ppm.

– IR (mixture): 3416, 3079, 3016, 2940, 2861, 1646, 1625, 1520, 1478, 1322, 1264, 1204, 1128, 1097, 989, 916 cm^{-1}.

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X-Ray Crystallographic Data

4-Chloro-*N*-cyclohexylaniline (23)

CCDC 1967998

Bond precision: C–C = 0.0023 Å Wavelength = 1.54184

Cell:	a = 11.2673(2)	b = 6.0662(1)	c = 16.0679(3)
	α = 90	β = 100.025(2)	γ = 90

Temperature: 100 K

	Calculated	Reported
Volume	1081.47(3)	1081.47(3)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{12}H_{16}ClN$	$C_{12}H_{16}ClN$
Sum formula	$C_{12}H_{16}ClN$	$C_{12}H_{16}ClN$
Mr	209.71	209.71
D_x, g cm^{-3}	1.288	1.288
Z	4	4
Mu (mm^{-1})	2.775	2.775
F000	448.0	448.0
F000'	450.40	
h,k,l_{max}	14,7,20	14,7,20
N_{ref}	2283	2206
T_{min},T_{max}	0.753,0.920	0.310,1.000
T_{min}'	0.628	

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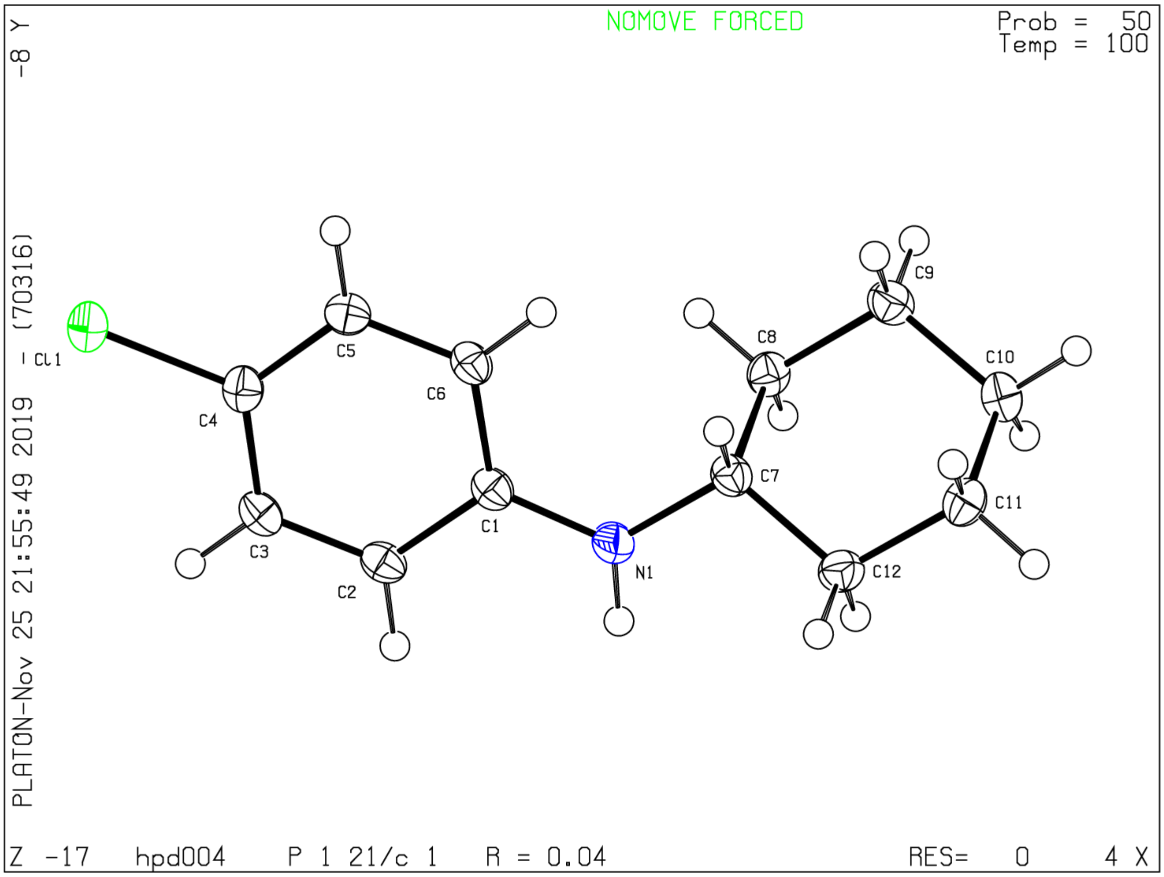
Correction method = # Reported T Limits: T_{min} =0.310 T_{max} =1.000

AbsCorr = MULTI-SCAN

Data completeness = 0.966 Theta(max) = 76.599

R(reflections) = 0.0396 (1977) wR2(reflections) = 0.1022 (2206)

S = 1.008 N_{par}= 127



4-Bromo-*N*-cyclohexylaniline (24)

CCDC 1967999

Bond precision:	C–C = 0.0030 Å		Wavelength = 1.54184
Cell:	a = 11.5286(2)	b = 6.0765(1)	c = 16.0680(3)
	α = 90	β = 101.200(2)	γ = 90
Temperature:	100 K		

	Calculated	Reported
Volume	1104.18(3)	1104.18(3)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{12}H_{16}BrN$	$C_{12}H_{16}BrN$
Sum formula	$C_{12}H_{16}BrN$	$C_{12}H_{16}BrN$
Mr	254.16	254.17
$D_{x,}$ g cm^{-3}	1.529	1.529
Z	4	4
Mu (mm^{-1})	4.732	4.732
F000	520.0	520.0
F000'	518.23	
h,k,l_{max}	14,7,20	14,7,20
N_{ref}	2314	2230
T_{min},T_{max}	0.306,0.868	0.270,1.000
T_{min}'	0.231	

Correction method = # Reported T Limits: T_{min} = 0.270 T_{max} = 1.000

AbsCorr = MULTI-SCAN

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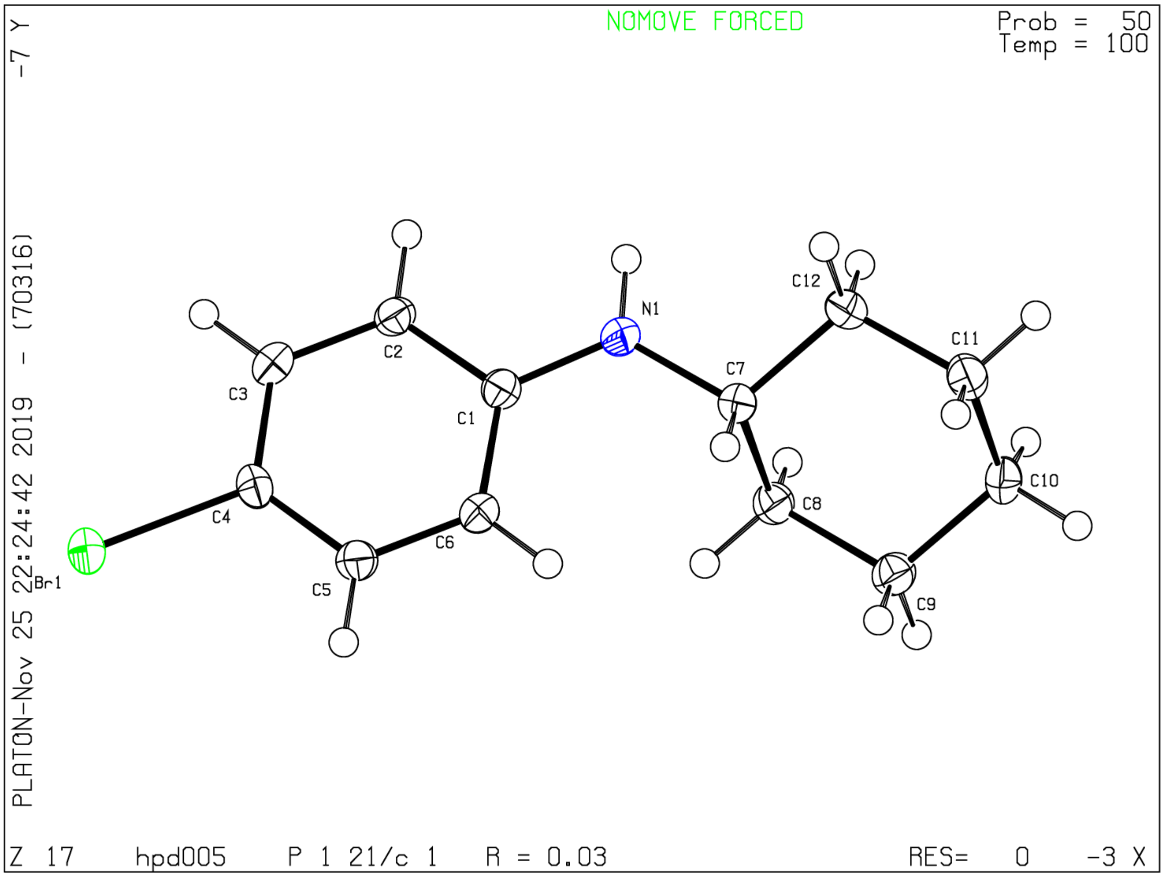
Data completeness = 0.964 Theta(max) = 76.322

R(reflections) = 0.0329 (2051) wR2(reflections) = 0.0929 (2230)

S = 1.091 N_{par}= 127



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N-Cyclohexyl-2-methylquinolin-8-amine (60)

CCDC 1967993

Bond precision: C–C = 0.0018 Å Wavelength = 0.71073

Cell: a = 13.1241(4) b = 5.2605(1) c = 19.2284(5)

α = 90 β = 91.801(3) γ = 90

Temperature: 100 K

	Calculated	Reported
Volume	1326.86(6)	1326.86(6)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{16}H_{20}N_2$	$C_{16}H_{20}N_2$
Sum formula	$C_{16}H_{20}N_2$	$C_{16}H_{20}N_2$
M_r	240.34	240.34
D_x, g cm^{-3}	1.203	1.203
Z	4	4
Mu (mm^{-1})	0.071	0.071
F000	520.0	520.0
F000'	520.16	
h,k,l_{max}	15,6,23	15,6,23
N_{ref}	2479	2477
T_{min},T_{max}	0.992,0.995	0.985,1.000
T_{min}'	0.965	

Correction method = # Reported T Limits: T_{min} = 0.985 T_{max} = 1.000

AbsCorr = MULTI-SCAN

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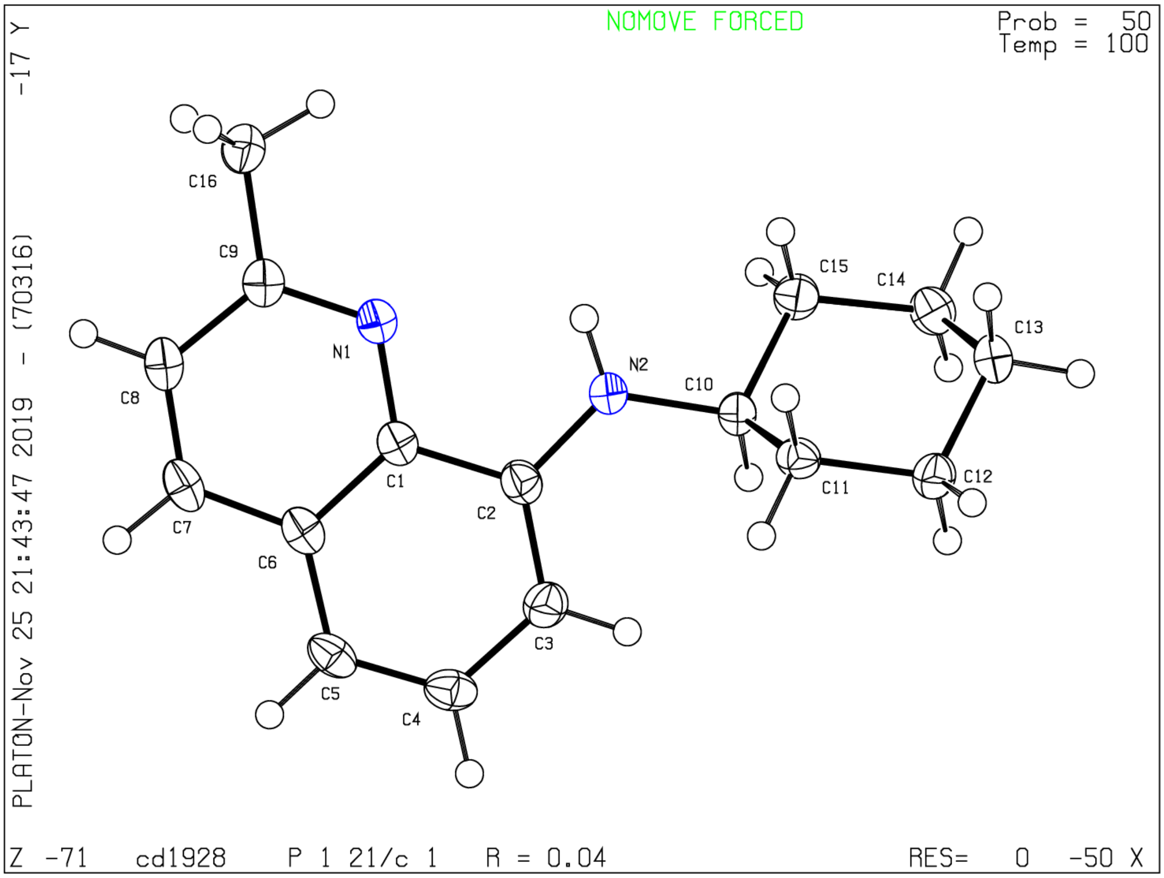
Data completeness = 0.999 Theta(max) = 25.498

R(reflections) = 0.0412 (2373) wR2(reflections)= 0.0985 (2477)

S = 1.020 N_{par}= 172



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1-(Tetrahydro-2*H*-pyran-4-yl)-1*H*-indol-5-ol (83)

CCDC 1972876

Bond precision: C–C = 0.0020 A Wavelength = 1.54184

Cell: a = 7.8676(1) b = 16.1982(2) c = 10.7102(1)

α = 90 β = 104.304(1) γ = 90

Temperature: 100 K

	Calculated	Reported
Volume	1322.60(3)	1322.60(3)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{27}H_3N_2O_4Cl_3$	$C_{27}H_3N_2O_4Cl_3$
Sum formula	$C_{27}H_3N_2O_4Cl_3$	$C_{27}H_3N_2O_4Cl_3$
Mr	553.89	553.89
D_x, g cm^{-3}	1.391	1.391
Z	2	2
Mu (mm^{-1})	3.437	3.437
F000	580.0	580.0
F000'	583.63	
h,k,l_{max}	9,20,13	9,20,13
N_{ref}	2789	2654
T_{min},T_{max}	0.814,0.851	0.749,1.000
T_{min}'	0.579	

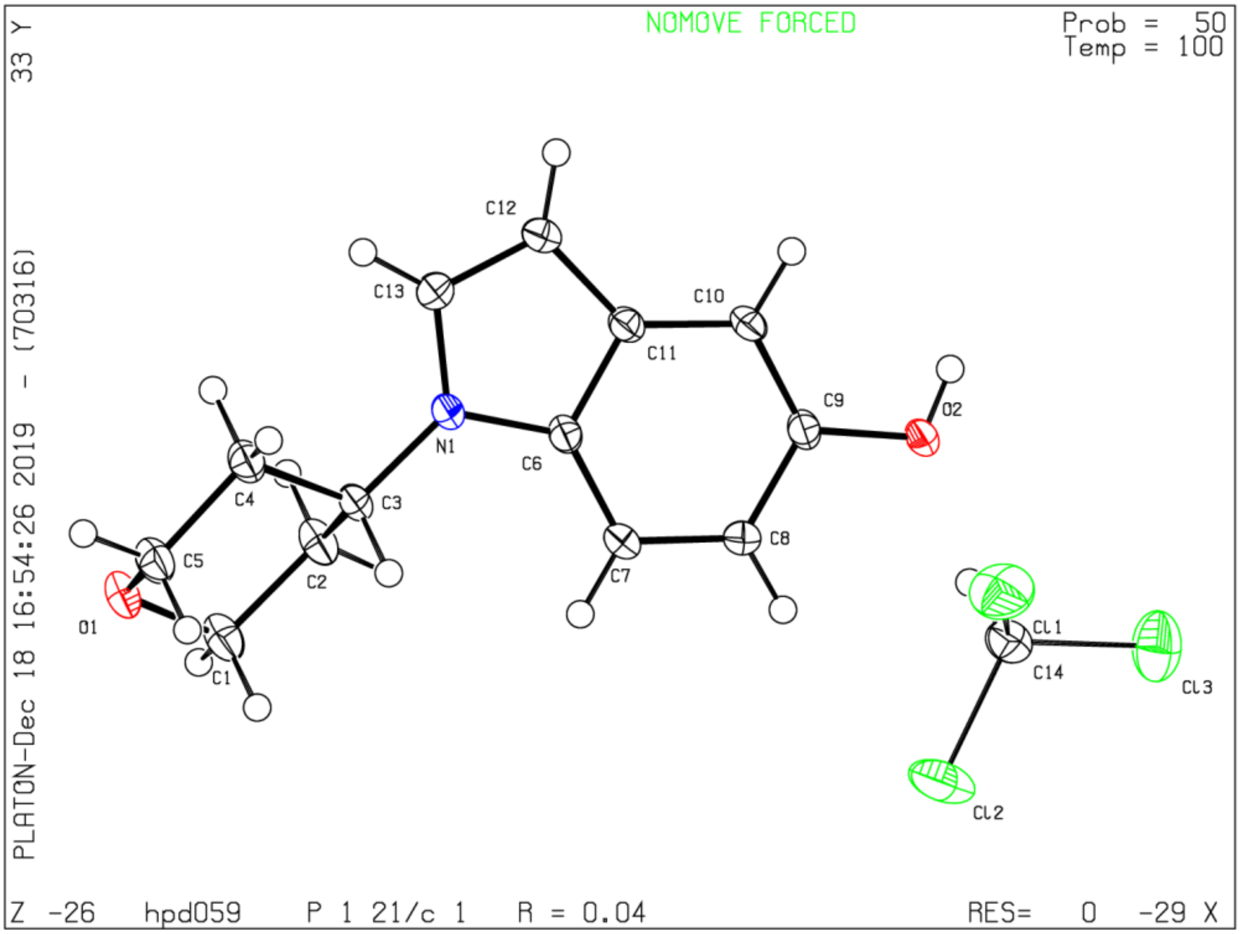
Correction method = # Reported T Limits: T_{min} = 0.749 T_{max} = 1.000

AbsCorr = GAUSSIAN

Data completeness = 0.952 Theta(max) = 76.532

R(reflections) = 0.0413 (2425) wR2(reflections) = 0.0989 (2654)

S = 1.000 N_{par}= 184



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Computational Data

All geometry optimizations, vibrational frequency calculations, and IRCs were conducted using the Gaussian 16 program.[37] Calculations were performed using the Stampede2 supercomputer at the Texas Advanced Computing Center (TACC) hosted by the University of Texas in Austin, Texas.[38] General day-to-day visualization and monitoring of calculations was performed with Chemcraft.[39] Final images of minima and transition state geometries were rendered using CYLview.[40] Geometries of ground state minima and transition states were optimized without constraints using the M06-L functional[41] with the def2-SVP[42,43] basis set in the SMD solvation model,[44] based on their demonstrated performance with copper complexes.[45] Convergence criteria for these calculations was set to "tight" and an ultrafine grid was selected. Frequency calculations were performed on the resultant geometries to verify the nature of the isolated stationary points. Geometries with zero imaginary frequencies were deemed minima whereas those with exactly one imaginary frequency along the chemical path of interest were deemed transition states. IRC calculations were performed to further corroborate that the located transition states connected reactants to products.

Marcus theory-based estimation of activation barrier for the anilinium E-assisted proton-coupled electron transfer

The activation barrier for the proton coupled electron transfer (PCET) process were calculated using Marcus-Hush theory[46] in conjunction with the Savéant model:[47,48]

$$\Delta G_{PCET}{}^{\ddagger} = \Delta G_0{}^{\ddagger}\left(1 + \frac{\Delta G_r}{4\Delta G_0{}^{\ddagger}}\right)^2 \tag{1}$$

The intrinsic barrier, $\Delta G_0{}^{\ddagger}$, is estimated by calculating λ_{PCET}, the sum of internal and solvent reorganization energies:

$$\Delta G_0{}^{\ddagger} = \frac{\lambda_{PCET}}{4} = \frac{\lambda_i + \lambda_0}{4} = \frac{\lambda_i + (\lambda_0^{ET} + \lambda_0^{PT})}{4} \tag{2}$$

The internal reorganization energy, λ_i, is calculated using the Savéant model as:

$$\lambda_i = \frac{\lambda_i^R + \lambda_i^P}{2} \tag{3}$$

Where λ_i^R and λ_i^P are the difference between distorted and equilibrium geometries for reactants and products, respectively.

The solvent reorganization energy, λ_0, is separated into two components, one related to electron transfer (4) and the other related to proton transfer (5):

$$\lambda_s^{ET} = \left(332\frac{kcal}{mol}\right)\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R_{12}}\right)\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right) \tag{4}$$

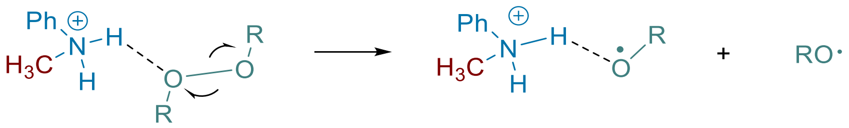
$$\lambda_s^{PT} = \frac{1}{4\pi\varepsilon_0}\left(\frac{\varepsilon_s - 1}{2\varepsilon_s + 1} - \frac{\varepsilon_{op} - 1}{\varepsilon_{op} + 1}\right)\frac{(\mu_R - \mu_P)^2}{a^3} \tag{5}$$

Where a_1 and a_2 are the radii of the donor and acceptor species and R_{12} is the inter-center distance. ε_{op} is the square of the refractive index and ε_s the dielectric constant; a^3 is the total radius of the encounter complex. $\mu_R - \mu_P$ is the difference between reactant and product dipole moments.

The intrinsic barrier also contains a contribution from the bond dissociation free energy of the acceptor species:

$$\Delta G_0{}^{\ddagger} = \frac{\lambda_{PCET}}{4} = \frac{\lambda_i + (\lambda_0^{ET} + \lambda_0^{PT}) + BDFE}{4} \tag{6}$$

The BDFE is calculated for:



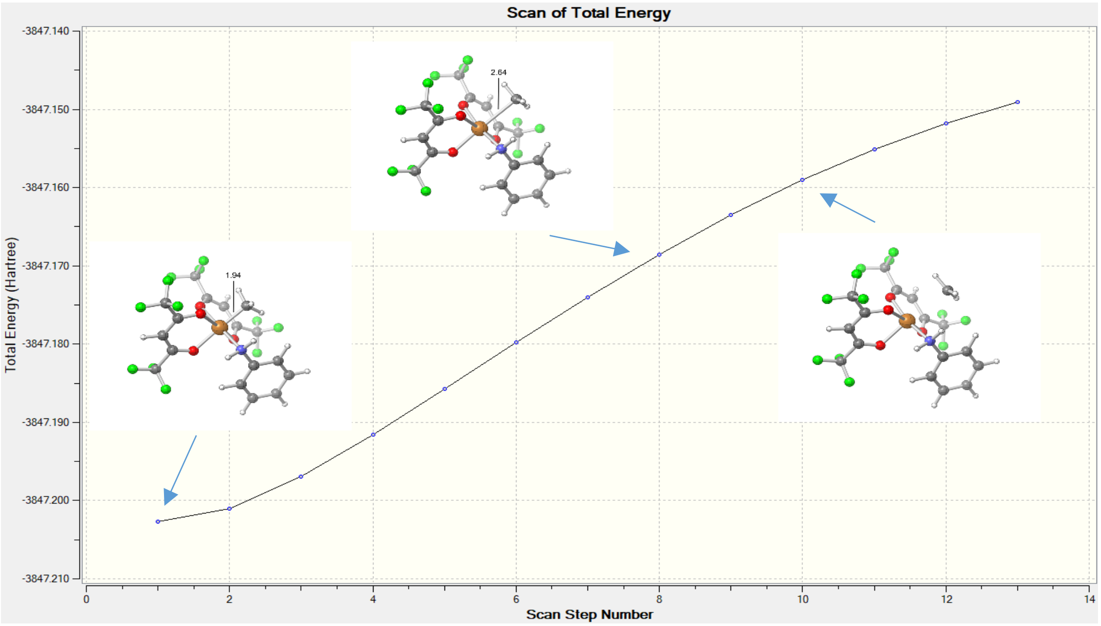
(7)

Table S4. PCET values [a]

a1 / Å	a2/ Å	λ_i	λ_s	Sum ($\lambda_i + \lambda_s$)	λ_{PT}	BDFE	ΔG_{rxn}	$\Delta G_{PCET}^{\ddagger}$
5.38	5.72	59.40	11.42	70.81	1.22	14.44	-38.15	6.67

[a] a1 is the radius of the donor species, a2 the radius of the acceptor species, λ_i is the internal reorganization energy, λ_0 is the solvent reorganization energy, BDFE is the O–O bond dissociation free energy of the $PhCH_3NH_2^+$–DTBP complex, ΔG_{rxn} the Gibbs free energy of the concerted DET process, and $\Delta G_{ET}^{\ddagger}$ is the calculated activation barrier of the electron transfer processes. Reorganization and free energy entries are expressed in kcal/mol.

Relaxed PES scan of the Cu–CH_3 bond in complex C



A relaxed scan of the Cu–CH_3 bond length was conducted at the uM06-L / def2-SVP / SMD level of theory to probe for the presence of a barrier to the addition of methyl radical. Scanning began from the optimized bond distance from Cu(III)-NH_2Ph (1.94442 Å). An interval of 0.1 Å was selected for the scan, and 13 geometries were obtained. The final Cu–C bond distance was 3.14442 Å. Cleavage of the bond occurred between points 9 and 10, corresponding to distances of 2.74442 Å and 2.84442 Å, respectively. The scan indicated that the addition proceeds without a barrier.

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Optimized Geometries

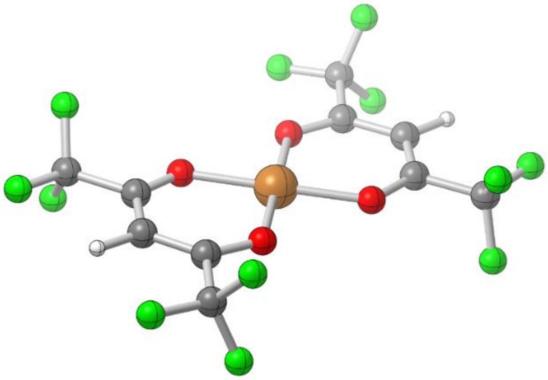
Cu(hfac)$_2$

E(UM06L) = -3519.97640884

Zero-point correction= 0.134866 (Hartree/Particle)
Thermal correction to Energy= 0.160248
Thermal correction to Enthalpy= 0.161193
Thermal correction to Gibbs Free Energy= 0.073568
Sum of electronic and ZPE= -3519.841543
Sum of electronic and thermal Energies= -3519.816160
Sum of electronic and thermal Enthalpies= -3519.815216
Sum of electronic and thermal Free Energies= -3519.902841

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	100.557	88.795	184.421

Cu,0,-0.0357414503,0.8439909431,-0.059591722
C,0,-0.5608407008,3.6655565391,-0.222437761
C,0,-1.8947525767,3.5447247842,0.1852083553
C,0,-2.442323333,2.3038579357,0.5097184037
H,0,-2.5121649637,4.4391859229,0.2519426902
O,0,0.2965592745,2.75915581,-0.3503128308
O,0,-1.8854951638,1.1741741439,0.4816861618
C,0,-0.0781939539,5.0808014522,-0.5786534937
C,0,-3.898067019,2.2342629783,0.9841838972
F,0,1.2246622026,5.1080713097,-0.8237678928
F,0,-0.7187580986,5.5241115475,-1.6687143815
F,0,-0.3367463032,5.9375997005,0.4159972895
F,0,-4.5843113927,1.3603138377,0.2442994861
F,0,-4.5231157361,3.4109015826,0.9172071136
F,0,-3.9418252745,1.8170402759,2.2542111879
C,0,0.4797065307,-1.9849100638,0.0327000926
C,0,1.7899494085,-1.871142121,-0.4390935266
C,0,2.3433378758,-0.6217187885,-0.730482901
H,0,2.3898500573,-2.7676602676,-0.5759785404
O,0,-0.36023587,-1.0687272784,0.224377695
O,0,1.8114244449,0.5125690814,-0.61408053



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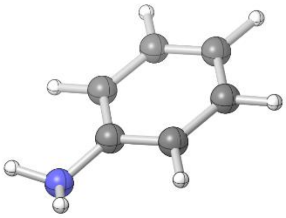
C,0,-0.0677481116,-3.3715205567,0.3913966996
C,0,3.7835488392,-0.5476355423,-1.2519198149
F,0,-1.1833764507,-3.619639016,-0.2988754734
F,0,0.7989567975,-4.3542918976,0.1433849744
F,0,-0.3749153664,-3.4117073077,1.6919498456
F,0,3.8177983598,0.1324964226,-2.4004437624
F,0,4.321913853,-1.7486094929,-1.4680688118
F,0,4.5551530711,0.0979060454,-0.3714682101

Aniline

E(RM06L) = -287.374709231



Zero-point correction= 0.117119 (Hartree/Particle)
Thermal correction to Energy= 0.122853
Thermal correction to Enthalpy= 0.123797
Thermal correction to Gibbs Free Energy= 0.088050
Sum of electronic and ZPE= -287.257590
Sum of electronic and thermal Energies= -287.251856
Sum of electronic and thermal Enthalpies= -287.250912
Sum of electronic and thermal Free Energies= -287.286659

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	77.091	23.153	75.236

C,0,-0.688483039,1.1776204614,-0.0775262461
C,0,0.7139596408,1.2073520477,0.0603926811
C,0,1.344361984,2.4645268021,0.1550003163
C,0,0.5975255747,3.6382919046,0.1172143717
C,0,-0.7924542924,3.6012297442,-0.0168969896
C,0,-1.4237069537,2.3588017844,-0.1141561907
H,0,-1.1933879597,0.2104113069,-0.1551275583
H,0,2.4323727106,2.5059171128,0.2598937774
H,0,1.1138002601,4.5995375925,0.1911686594
H,0,-1.3739136288,4.5252023301,-0.0479055378
H,0,-2.5104741937,2.3052931671,-0.2242271697
N,0,1.441348315,0.0410090963,0.1578199117
H,0,1.0089959113,-0.7874300273,-0.2355160692
H,0,2.4261950428,0.1094861482,-0.0729130671

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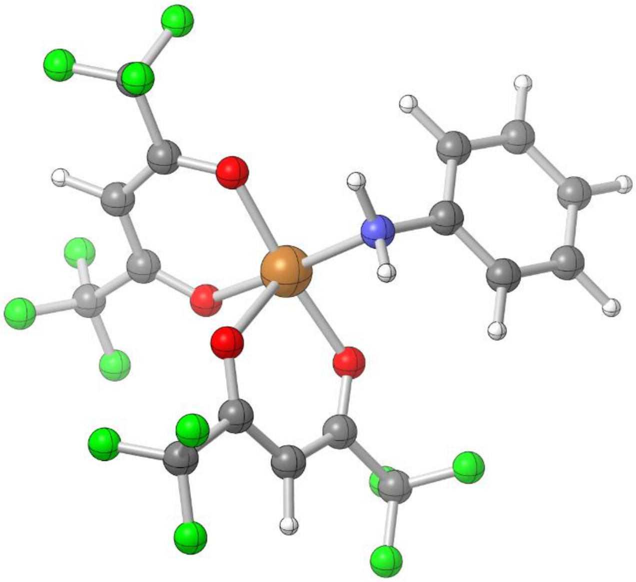
Complex B

E(UM06L) = -3807.37553291

Zero-point correction= 0.254315 (Hartree/Particle)
Thermal correction to Energy= 0.287170
Thermal correction to Enthalpy= 0.288114
Thermal correction to Gibbs Free Energy= 0.181893
Sum of electronic and ZPE= -3807.121218
Sum of electronic and thermal Energies= -3807.088363
Sum of electronic and thermal Enthalpies= -3807.087419
Sum of electronic and thermal Free Energies= -3807.193639

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	180.202	116.465	223.56

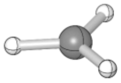


Cu,0,0.1661212962,0.5947301035,-0.6598318539
C,0,-0.3259356915,3.4320554977,-0.4349760549
C,0,-1.6788285644,3.2505342114,-0.1033199373
C,0,-2.2208478379,1.989361173,0.1350323963
H,0,-2.3100691671,4.1298340372,0.0158038187
O,0,0.5529334811,2.5632197707,-0.6219708513
O,0,-1.658203123,0.864550193,0.0515791473
C,0,0.1432934799,4.8909719802,-0.5549245303
C,0,-3.6790764031,1.8835320105,0.59077909
F,0,1.4007456709,4.9724988242,-0.9712228578
F,0,-0.6265391024,5.5714458527,-1.4141581912
F,0,0.0575379405,5.5070942949,0.6332637305
F,0,-4.3554997815,1.0515088076,-0.2074174679
F,0,-4.3171759768,3.0552041046,0.596580325
F,0,-3.7315374892,1.3831515133,1.8321194823
C,0,0.457199434,0.7443435705,-3.6854522458
C,0,1.8513730804,0.5452800556,-3.5814269605
C,0,2.5021630019,0.2897415907,-2.3756107221
H,0,2.4511478251,0.5806245518,-4.48792976
O,0,-0.3970653774,0.7229996526,-2.7828565842
O,0,2.0372195384,0.2184762888,-1.2065876588
C,0,-0.1220324579,1.0145347076,-5.0839644483

C,0,4.0120396467,0.0228641256,-2.4031464935
F,0,-0.746668986,2.1990825808,-5.101873708
F,0,0.7940561892,1.026535255,-6.058652074
F,0,-1.0294604208,0.07864087,-5.3945824893
F,0,4.6534949879,0.8847129502,-1.6069598647
F,0,4.5520567691,0.1157045419,-3.6215260557
F,0,4.2649619873,-1.2116615043,-1.9424478106
N,0,-0.1690818162,-1.4416428915,-0.4389403278
H,0,-0.0488650684,-1.8648265796,-1.3611185811
H,0,-1.1571687717,-1.5040300529,-0.185497915
C,0,0.6799616429,-2.0259029112,0.5343521127
C,0,1.8771977928,-2.6370910807,0.1457596188
C,0,0.3496642098,-1.9267395226,1.8912688164
C,0,2.7343466459,-3.1530058722,1.1136522669
H,0,2.1290289116,-2.7027604778,-0.9151853188
C,0,1.2124263046,-2.4489555896,2.8506665691
H,0,-0.5837355807,-1.4372269589,2.1828104464
C,0,2.4073013392,-3.0621248953,2.4677710434
H,0,3.666887154,-3.6308905056,0.804475036
H,0,0.9481311896,-2.3749874162,3.908018238
H,0,3.0823425573,-3.4686761275,3.2238734548

Methyl Radical

E(UM06L) = -39.7948461124



Zero-point correction= 0.028577 (Hartree/Particle)
Thermal correction to Energy= 0.031974
Thermal correction to Enthalpy= 0.032918
Thermal correction to Gibbs Free Energy= 0.008417
Sum of electronic and ZPE= -39.766269
Sum of electronic and thermal Energies= -39.762872
Sum of electronic and thermal Enthalpies= -39.761928
Sum of electronic and thermal Free Energies= -39.786429

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	20.064	8.06	51.567

C,0,-1.3230997557,1.2857142677,0.0

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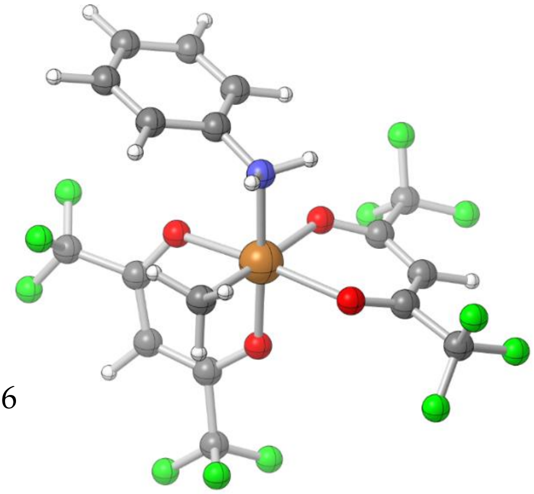
H,0,-2.4137566334,1.2857142688,0.0
H,0,-0.7776660837,2.2301594816,0.0
H,0,-0.7776660872,0.3412690518,0.0

Complex C

E(RM06L) = -3847.20267479



Zero-point correction= 0.290147 (Hartree/Particle)
Thermal correction to Energy= 0.325205
Thermal correction to Enthalpy= 0.326149
Thermal correction to Gibbs Free Energy= 0.218788
Sum of electronic and ZPE= -3846.912528
Sum of electronic and thermal Energies= -3846.877470
Sum of electronic and thermal Enthalpies= -3846.876526
Sum of electronic and thermal Free Energies= -3846.983886

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	204.069	125.599	225.96

C,0,1.6435326579,3.0109243654,-0.4247730906
C,0,0.6535732462,3.224816089,0.5336219326
C,0,-0.3112261141,2.2495888317,0.8588298904
H,0,0.5981193495,4.1994775704,1.0128997939
C,0,3.6806270622,-1.5641200976,-1.1130123543
C,0,3.0747531579,-0.9583625723,1.1795001186
C,0,3.8125124934,-1.730078037,0.2839158025
H,0,4.4652343585,-2.5095708708,0.6720694165
Cu,0,1.1752490651,0.1525819575,-0.7678148774
O,0,3.012836947,-0.7040666774,-1.7067655835
O,0,2.230896197,-0.0521683407,0.9358525866
O,0,-0.4352569043,1.0990586763,0.4021062104
O,0,1.9144159574,1.9702725471,-1.0795004426
C,0,2.5578729469,4.1798846022,-0.8066073565
C,0,-1.3973283592,2.6265640098,1.8792815577
C,0,4.3583358597,-2.5871854899,-2.0352397579
C,0,3.1995667701,-1.2593508198,2.6758400316
F,0,3.8402288896,3.8528550923,-0.6158253183

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F,0,2.4067492588,4.4667546111,-2.1093406596
F,0,2.3158338332,5.2981168564,-0.1179870816
F,0,-2.6035851877,2.5921680837,1.2937211985
F,0,-1.4152321075,1.7430241984,2.8837332635
F,0,-1.2443123485,3.8432674219,2.4125140264
F,0,4.9286495927,-1.9884088153,-3.0827720361
F,0,3.4223858536,-3.428821489,-2.5151397258
F,0,5.2909489988,-3.3297660283,-1.4286792241
F,0,2.0640333774,-1.830290942,3.111977337
F,0,4.2053714885,-2.0879062835,2.9719713709
F,0,3.3770377843,-0.1364963103,3.3781690401
N,0,0.1313058407,0.3069570522,-2.5448220822
H,0,-0.1604709441,1.2869242168,-2.5224008737
C,0,0.9486910124,0.0117588317,-3.6651051229
C,0,1.8006466696,0.9935323284,-4.182361318
C,0,0.9671632269,-1.2875075331,-4.1843137568
C,0,2.6747971284,0.6660223084,-5.2135326964
H,0,1.7895461271,1.9993028382,-3.7563117795
C,0,1.8460150423,-1.6034822245,-5.2151127577
H,0,0.2958245139,-2.0445839096,-3.7700299699
C,0,2.7073870592,-0.6318194646,-5.7280536534
H,0,3.3420727617,1.4315738741,-5.6156122745
H,0,1.8627880557,-2.6194471153,-5.6161218924
H,0,3.4021652909,-0.8850874494,-6.5317134336
C,0,0.4127174106,-1.622457823,-0.547444911
H,0,-0.671104998,-1.4994690627,-0.6521724973
H,0,0.8752278679,-2.2330847212,-1.3332933208
H,0,0.7012069783,-1.9053572411,0.4706099535
H,0,-0.7109922476,-0.2700764258,-2.514445958

TS$_{Cu}$

E(RM06L) = -3847.17146115

Zero-point correction= 0.289406 (Hartree/Particle)
Thermal correction to Energy= 0.324011
Thermal correction to Enthalpy= 0.324955
Thermal correction to Gibbs Free Energy= 0.220636
Sum of electronic and ZPE= -3846.882056
Sum of electronic and thermal Energies= -3846.847450

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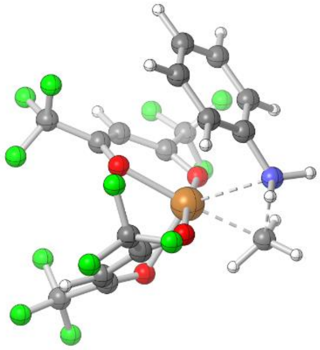
Sum of electronic and thermal Enthalpies= -3846.846506
Sum of electronic and thermal Free Energies= -3846.950825

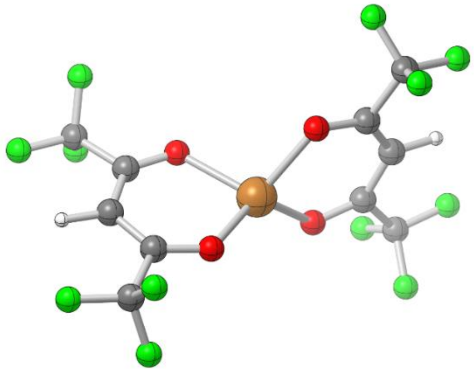
	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	203.32	124.389	219.559



C,0,2.137960561,2.636960166,-0.113785922
C,0,0.968407187,3.133002903,0.490871257
C,0,-0.253740298,2.454602865,0.459334423
H,0,1.00522054,4.108381159,0.970992471
C,0,3.231366658,-1.282312541,-1.46533955
C,0,2.879349195,-0.946073141,0.931851523
C,0,3.724792307,-1.23074732,-0.16080013
H,0,4.799836566,-1.294196177,-0.001767589
Cu,0,0.809707923,0.135601534,-0.886712671
O,0,2.036182922,-1.177047516,-1.854611396
O,0,1.636819674,-0.854789083,0.930730499
O,0,-0.525837161,1.317890194,-0.005622918
O,0,2.29997842,1.564932783,-0.730865385
C,0,3.406018434,3.49887283,-0.066008665
C,0,-1.492025114,3.173612597,1.001949949
C,0,4.241180397,-1.364881235,-2.610441383
C,0,3.534471262,-0.603858406,2.274915442
F,0,4.422351918,2.797850407,0.451015206
F,0,3.76085321,3.861312166,-1.30859248
F,0,3.276207425,4.61735135,0.656576386
F,0,-2.301049763,3.502195052,-0.02247113
F,0,-2.189697943,2.377073036,1.817489515
F,0,-1.216626423,4.297493638,1.669789965
F,0,4.427346943,-0.137301783,-3.134141772
F,0,3.789925997,-2.146147269,-3.600025228
F,0,5.441225275,-1.827835248,-2.245074637
F,0,2.939627365,-1.254182897,3.282541715
F,0,4.843038599,-0.882873822,2.334044116
F,0,3.394075591,0.71277988,2.514829203
N,0,-0.428180759,-0.48012616,-3.05429974
H,0,-1.382988033,-0.635941846,-3.381894457
C,0,0.028143354,0.847000143,-3.281000282
C,0,-0.796607658,1.927586775,-2.942634009

C,0,1.317321431,1.064528222,-3.782724145
C,0,-0.315163564,3.22464603,-3.086972763
H,0,-1.796180538,1.740931559,-2.542903546
C,0,1.785863623,2.367043701,-3.921880438
H,0,1.943088874,0.21042035,-4.045489608
C,0,0.977389041,3.448360827,-3.568502461
H,0,-0.951970081,4.067682763,-2.807889107
H,0,2.797299798,2.53489028,-4.299410187
H,0,1.356450729,4.468366866,-3.663616135
C,0,-0.846615677,-1.331354921,-1.207374952
H,0,-1.670802063,-0.68934646,-0.891747485
H,0,-1.149235417,-2.188219511,-1.810987044
H,0,-0.139942625,-1.644434953,-0.42424869
H,0,0.19435052,-1.18778035,-3.449144256

Complex D



E(RM06L) = -3520.11571658

Zero-point correction= 0.131913 (Hartree/Particle)
Thermal correction to Energy= 0.158602
Thermal correction to Enthalpy= 0.159546
Thermal correction to Gibbs Free Energy= 0.068087
Sum of electronic and ZPE= -3519.983804
Sum of electronic and thermal Energies= -3519.957115
Sum of electronic and thermal Enthalpies= -3519.956170
Sum of electronic and thermal Free Energies= -3520.047630

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	99.524	90.696	192.492

Cu,0,0.1214960064,0.9326048226,0.1349631401
C,0,-0.5082532807,3.7078156773,0.6905058586
C,0,-1.8048131333,3.6431069342,0.1549832207
C,0,-2.3448899536,2.4780455972,-0.4196003175
H,0,-2.4341316864,4.528308,0.2184557044
O,0,0.3676563186,2.8116011386,0.7456261849
O,0,-1.8042014248,1.3672383942,-0.6057887246
C,0,-0.0547198637,5.0258380301,1.3207876937
C,0,-3.8084094368,2.5237168541,-0.875126341

F,0,0.2854909231,4.8430202335,2.6070426455
F,0,1.0346204883,5.5005590927,0.6940039662
F,0,-0.9807898272,5.9946308104,1.2910791152
F,0,-3.9166647221,2.1634621552,-2.1632076461
F,0,-4.3901952951,3.7261359031,-0.750792337
F,0,-4.5442942296,1.6537932239,-0.1625750795
C,0,0.9849737239,-1.7694297547,0.7678036472
C,0,1.6433720548,-1.9614656119,-0.4581623366
C,0,1.6992968583,-0.9792112723,-1.4629227667
H,0,2.1556254384,-2.9061148563,-0.6281712853
O,0,0.3447539748,-0.7694710167,1.1695083218
O,0,1.1876249602,0.1613354619,-1.4791729096
C,0,1.0398812511,-2.8991768169,1.7988617358
C,0,2.5051281361,-1.2984085072,-2.727278478
F,0,-0.197737083,-3.2798663889,2.1521920175
F,0,1.6850997657,-3.9960584347,1.37693175
F,0,1.6547308608,-2.4839039506,2.9191224851
F,0,1.7464040467,-1.1444182183,-3.8233547295
F,0,3.0050709323,-2.542394506,-2.7644048835
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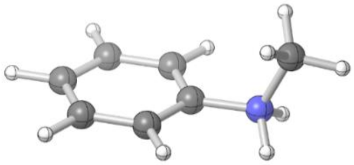
Product E

E(RM06L) = -327.086825318



Zero-point correction= 0.160456 (Hartree/Particle)
Thermal correction to Energy= 0.167609
Thermal correction to Enthalpy= 0.168554
Thermal correction to Gibbs Free Energy= 0.128961
Sum of electronic and ZPE= -326.926369
Sum of electronic and thermal Energies= -326.919216
Sum of electronic and thermal Enthalpies= -326.918272
Sum of electronic and thermal Free Energies= -326.957865

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	105.177	27.592	83.33

C,0,-0.4280382114,1.2331028551,-0.4004308334
C,0,0.7875810403,1.3566117094,0.2634497083

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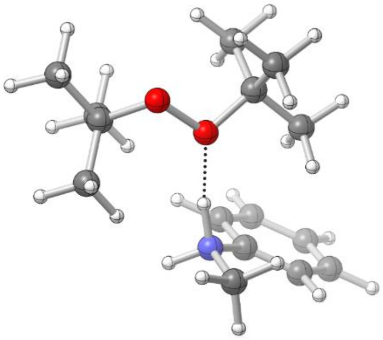
C,0,1.2479735644,2.5764973663,0.7458751104
C,0,0.4552154095,3.7081909031,0.5638901541
C,0,-0.7702609203,3.6066335439,-0.0946771458
C,0,-1.2105295442,2.3730667965,-0.5750884071
H,0,-0.7585635482,0.2598403144,-0.7702362861
H,0,2.208557018,2.6372882718,1.2630381143
H,0,0.7988362966,4.672293301,0.9432239998
H,0,-1.3886459322,4.4958962709,-0.2323885943
H,0,-2.1709167239,2.2927107922,-1.0876835368
N,0,1.6319497525,0.1681970373,0.4235943915
H,0,1.036065062,-0.6579247855,0.5633857177
C,0,2.5594665837,-0.0890126419,-0.7104249682
H,0,3.2192872045,0.775616407,-0.8220793991
H,0,3.1414207171,-0.9880674047,-0.4895643896
H,0,1.9673622001,-0.2318114661,-1.6183273112
H,0,2.1764278625,0.2510674275,1.2918272635

Ph $CH_3NH_2^+$–DTBP complex

E(RM06L) = -792.760945916



Zero-point correction= 0.412631 (Hartree/Particle)
Thermal correction to Energy= 0.433922
Thermal correction to Enthalpy= 0.434866
Thermal correction to Gibbs Free Energy= 0.363702
Sum of electronic and ZPE= -792.348315
Sum of electronic and thermal Energies= -792.327024
Sum of electronic and thermal Enthalpies= -792.326080
Sum of electronic and thermal Free Energies= -792.397244

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	272.29	82.461	149.778

C,0,3.4049661534,4.4118550299,-5.753288197
C,0,2.8529133563,4.7640636819,-4.5234480601
C,0,2.6101165273,6.0884136949,-4.1828801607
C,0,2.9299579881,7.0847075138,-5.1071798425
C,0,3.4796340468,6.752723578,-6.3433184951
C,0,3.7195169208,5.4156573798,-6.6646630245

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H,0,3.5809162363,3.3605061949,-5.9944872385
H,0,2.1730281172,6.3576862853,-3.2210825248
H,0,2.742838116,8.1294079936,-4.8514252037
H,0,3.7244582277,7.5387781979,-7.0604201258
H,0,4.152819918,5.1494767348,-7.6306404293
N,0,2.4869808077,3.6645750316,-3.6174132618
H,0,3.3054752419,3.050083113,-3.5144486533
C,0,1.9819497133,4.0149773009,-2.2743875027
H,0,1.061934065,4.5977495282,-2.3745898402
H,0,1.7687981134,3.0850355705,-1.7392577616
H,0,2.740081499,4.5915617531,-1.7364430129
H,0,1.7636603579,3.0695109316,-4.0853311264
C,0,1.0871582305,-0.0189388498,-4.5318965012
C,0,1.8165540922,0.1045363639,-3.2050206964
H,0,2.2253164946,1.1113715585,-3.0530698537
H,0,1.1429398783,-0.1168651755,-2.3659045199
H,0,2.6619765434,-0.5958368818,-3.1583092137
C,0,1.9770623468,0.3450632478,-5.7052442221
H,0,1.436437682,0.2609206607,-6.6575801727
H,0,2.367778435,1.3687691791,-5.6212537075
H,0,2.8392956683,-0.3349651886,-5.745989837
O,0,-0.1171653571,0.7781047,-4.5090364164
O,0,0.1996251022,2.2058885327,-4.5410047338
C,0,-0.810426712,2.8486385023,-5.3764501899
C,0,-0.7219896119,2.3297274115,-6.7985283122
H,0,-0.9554530214,1.258404705,-6.8494223379
H,0,-1.4404855992,2.8611522559,-7.4380920206
H,0,0.2822387999,2.4905681039,-7.2166769018
C,0,-2.1806954008,2.612754513,-4.7680386964
H,0,-2.2140833999,2.9668126097,-3.7281518144
H,0,-2.9465619049,3.1565762017,-5.3377443749
H,0,-2.4460995098,1.548576933,-4.77852427
C,0,-0.4273487046,4.3149146808,-5.3057693113
H,0,0.5218069439,4.5149277355,-5.8228962474
H,0,-1.1995430229,4.9195200654,-5.7996873529
H,0,-0.3528872088,4.6617699326,-4.264429353
C,0,0.5065762695,-1.4137654069,-4.6963311489
H,0,-0.0254640436,-1.5117159656,-5.652245958
H,0,1.3125947981,-2.1590560212,-4.6735274427
H,0,-0.1943557741,-1.6474415571,-3.8835668026
```

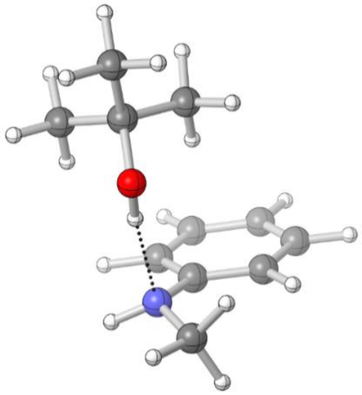
Ph $CH_3NH_2^+$–*t*BuOH complex

E(RM06L) = -560.128810652

Zero-point correction= 0.281943 (Hartree/Particle)
Thermal correction to Energy= 0.297434
Thermal correction to Enthalpy= 0.298378
Thermal correction to Gibbs Free Energy= 0.236890
Sum of electronic and ZPE= -559.846868
Sum of electronic and thermal Energies= -559.831376
Sum of electronic and thermal Enthalpies= -559.830432
Sum of electronic and thermal Free Energies= -559.891921

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	186.643	57.556	129.414

C,0,0.2150995169,1.183552392,-0.4757014854
C,0,1.0908899255,1.622584622,0.6915264826
H,0,2.1295379292,1.2846945933,0.5461806723
H,0,1.1023725647,2.7188505234,0.7804872162
H,0,0.7411557997,1.2066226965,1.6482391554
C,0,0.2285982246,-0.3353606268,-0.604158858
H,0,-0.3405579577,-0.6547746921,-1.489873318
H,0,1.2569924752,-0.7144725259,-0.7096303781
H,0,-0.2121661755,-0.8237505917,0.2780353762
O,0,0.6935851685,1.7785937049,-1.6815883936
H,0,1.6259751733,1.516824227,-1.791131268
C,0,4.2605167592,-0.5482924279,-0.8736258235
C,0,3.6444476609,-0.2878253278,-2.114185187
C,0,3.1962798004,-1.3783095098,-2.8818525561
C,0,3.3418969362,-2.6806160182,-2.4042177523
C,0,3.9404178666,-2.932179599,-1.1701398899
C,0,4.4029507344,-1.8516565551,-0.4125222608
H,0,4.6225959716,0.2927647349,-0.2749321937
H,0,2.724424387,-1.2086853468,-3.8517422278
H,0,2.9819996718,-3.5123924113,-3.0158849404
H,0,4.0524337703,-3.9551477899,-0.8044613493
H,0,4.8844976898,-2.0263408865,0.553402017



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N,0,3.4411894406,1.0244958879,-2.517516179
H,0,4.0790248868,1.6856374837,-2.0841753786
C,0,3.1092191016,1.3318605603,-3.8878714539
H,0,2.1144995383,0.9392361335,-4.1454682714
H,0,3.0687266541,2.4202601071,-4.0103474297
H,0,3.8332671672,0.928045708,-4.618178122
C,0,-1.2046894064,1.692877622,-0.3056864836
H,0,-1.8277980893,1.3976340555,-1.162373547
H,0,-1.6687651377,1.2933301953,0.6068780885
H,0,-1.2186009383,2.7907192414,-0.2442199012

Radical F

E(UM06L) = -232.802974025

Zero-point correction= 0.121527 (Hartree/Particle)
Thermal correction to Energy= 0.128021
Thermal correction to Enthalpy= 0.128966
Thermal correction to Gibbs Free Energy= 0.092060
Sum of electronic and ZPE= -232.681447
Sum of electronic and thermal Energies= -232.674953
Sum of electronic and thermal Enthalpies= -232.674008
Sum of electronic and thermal Free Energies= -232.710914

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	80.335	23.834	77.675

C,0,0.4014713626,1.6330242175,0.02628622
C,0,0.9245796523,2.7556355868,0.9210271936
H,0,2.0239083707,2.7522589976,0.9339571796
H,0,0.5922794149,3.7354039536,0.5515034515
H,0,0.5753327163,2.6377779616,1.9567207802
C,0,0.8350309447,0.257261954,0.530045578
H,0,0.4389081114,-0.5373445971,-0.1169392833
H,0,1.9316920225,0.1796597013,0.5309214097
H,0,0.4840289247,0.0778767257,1.5562524148
O,0,0.7687714601,1.8236718692,-1.2784433077
C,0,-1.1448709865,1.6996877037,-0.0452054385
H,0,-1.5398145543,1.5564464583,0.9704907502

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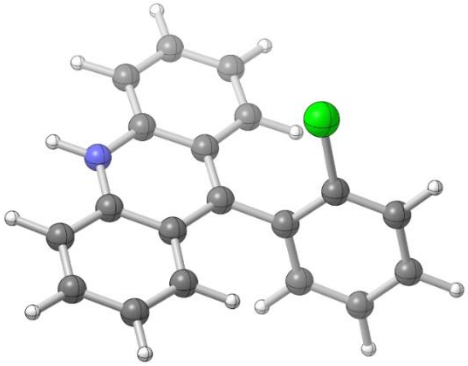
H,0,-1.4782119479,2.6747459223,-0.4224327934
H,0,-1.5418559515,0.9104804355,-0.6961262246

Radical G



E(UM06L) = -1246.04552669

Zero-point correction= 0.264576 (Hartree/Particle)
Thermal correction to Energy= 0.280344
Thermal correction to Enthalpy= 0.281288
Thermal correction to Gibbs Free Energy= 0.219964
Sum of electronic and ZPE= -1245.780951
Sum of electronic and thermal Energies= -1245.765183
Sum of electronic and thermal Enthalpies= -1245.764239
Sum of electronic and thermal Free Energies= -1245.825563

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	175.918	64.763	129.066

C,0,-8.0271837927,-1.3302826638,-0.750385807
C,0,-6.8573195506,-1.7900396631,-0.1497602337
C,0,-5.7912808257,-0.9135172136,0.0825812919
C,0,-5.8826129272,0.4656393487,-0.2807814758
C,0,-7.0831613527,0.8902499606,-0.9011827729
C,0,-8.1353534104,0.0128508455,-1.1295997402
C,0,-4.7689176357,1.3284061881,-0.0284346976
C,0,-3.585138379,0.8050613387,0.5831725201
C,0,-3.5325756397,-0.5800935745,0.9265068951
C,0,-2.3934124741,-1.1293321068,1.5268637537
H,0,-2.3887807104,-2.1944231365,1.7728489557
C,0,-1.2902579478,-0.3257192448,1.8046953164
C,0,-1.3222433312,1.0378412114,1.4882439001
C,0,-2.448041417,1.5898969293,0.8916961381
H,0,-8.8526500418,-2.0233852779,-0.9272888099
H,0,-6.7528759426,-2.8371998492,0.1456291423
H,0,-7.1730350187,1.9343417011,-1.2098143094
H,0,-9.0468420441,0.3743890008,-1.6110373906
H,0,-0.4061770543,-0.7638356038,2.2732702853
H,0,-0.4616145376,1.6721996643,1.7122590934
H,0,-2.4664255622,2.656361201,0.6537353374

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N,0,-4.6299044168,-1.3660433314,0.6626415423
C,0,-4.8619794665,2.7669698455,-0.3618599471
C,0,-4.1326516206,3.3590481956,-1.4079018671
C,0,-5.7095396514,3.6127184982,0.3741815916
C,0,-4.2234307858,4.7197419623,-1.7004712315
C,0,-5.8147447512,4.972358916,0.0952950363
H,0,-6.2922416226,3.1760014839,1.1899491154
C,0,-5.0670593803,5.528039806,-0.9429837799
H,0,-3.6387034739,5.1352282797,-2.5225910728
H,0,-6.4792085729,5.6002564798,0.6928298267
H,0,-5.1391747338,6.5937212602,-1.1712911391
Cl,0,-3.0875908475,2.3696268702,-2.401967816
H,0,-4.5785575823,-2.3490448874,0.9129566696

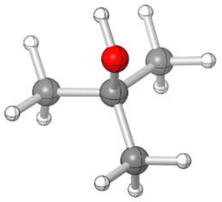
*t*BuOH

E(RM06L) = -233.474454117

Zero-point correction= 0.135054 (Hartree/Particle)
Thermal correction to Energy= 0.141723
Thermal correction to Enthalpy= 0.142667
Thermal correction to Gibbs Free Energy= 0.106170
Sum of electronic and ZPE= -233.339400
Sum of electronic and thermal Energies= -233.332731
Sum of electronic and thermal Enthalpies= -233.331787
Sum of electronic and thermal Free Energies= -233.368284

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	88.932	24.948	76.814

C,0,0.3628547434,1.6398067455,0.0308469202
C,0,0.9192479126,2.748646679,0.9137909615
H,0,2.0202014157,2.7302914058,0.9199283681
H,0,0.6015276085,3.7351318198,0.5464281624
H,0,0.5825300841,2.6487473574,1.9562289847
C,0,0.8373347102,0.2771038693,0.5170462875
H,0,0.4614140516,-0.5224757115,-0.1374684102
H,0,1.9370731647,0.2217998027,0.5186535562
H,0,0.4961454185,0.0674150187,1.5415426595
O,0,0.7932397806,1.8426868943,-1.3205083954



H,0,1.7589459577,1.8021501604,-1.31716399
C,0,-1.1521902231,1.6979597258,-0.0200474456
H,0,-1.5897033825,1.553558219,0.9773812356
H,0,-1.4913471686,2.670498641,-0.4044979087
H,0,-1.5493267934,0.9167664526,-0.6839375258

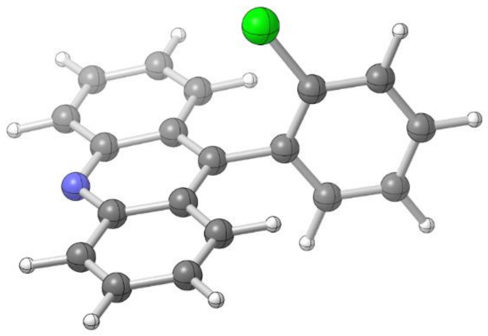
Catalyst A1

E(RM06L) = -1245.44846717

Zero-point correction= 0.253739 (Hartree/Particle)
Thermal correction to Energy= 0.269076
Thermal correction to Enthalpy= 0.270020
Thermal correction to Gibbs Free Energy= 0.210130
Sum of electronic and ZPE= -1245.194728
Sum of electronic and thermal Energies= -1245.179391
Sum of electronic and thermal Enthalpies= -1245.178447
Sum of electronic and thermal Free Energies= -1245.238337

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	168.848	62.633	126.05

C,0,-7.9557301532,-1.3464882494,-0.7783762211
C,0,-6.8137700263,-1.7981990275,-0.1683907141
C,0,-5.7244688855,-0.9149596827,0.0954880398
C,0,-5.8535427183,0.4730882134,-0.2854784617
C,0,-7.0540525582,0.8994692007,-0.9267389737
C,0,-8.0757404721,0.0148540974,-1.1654681063
C,0,-4.7749444938,1.3389772112,-0.0166247957
C,0,-3.6203273781,0.8158399143,0.5990975161
C,0,-3.6010264161,-0.5901317817,0.9291762808
C,0,-2.4346842702,-1.1284548252,1.5507776811
H,0,-2.4397119087,-2.1937597142,1.792014206
C,0,-1.3539691987,-0.3320526923,1.8298459856
C,0,-1.3759988567,1.0514277314,1.50847163
C,0,-2.478355459,1.6099493916,0.9120775136
H,0,-8.7804171352,-2.0358626639,-0.9746473685
H,0,-6.6984006638,-2.8422034941,0.1313095802
H,0,-7.1502474229,1.9442128696,-1.2322253197



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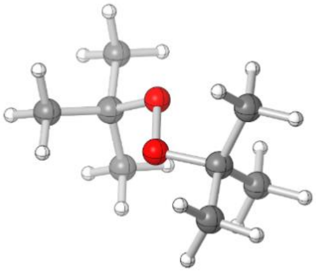
H,0,-8.9881617814,0.3559580099,-1.6596636652
H,0,-0.4676827772,-0.7593191357,2.3050419592
H,0,-0.5080015274,1.6722556803,1.7413278749
H,0,-2.4906284275,2.6759906694,0.670787924
N,0,-4.6288537815,-1.4133032502,0.682758876
C,0,-4.867390327,2.7819649485,-0.3530962865
C,0,-4.2130302087,3.3399181939,-1.4615567087
C,0,-5.6324344731,3.6434550804,0.4466915843
C,0,-4.3055328704,4.6979149273,-1.7639517177
C,0,-5.7324054325,5.0022045439,0.1596900168
H,0,-6.1532192418,3.2255562887,1.312220585
C,0,-5.0671960429,5.5291679518,-0.9466711254
H,0,-3.7842833691,5.0935600735,-2.6367810865
H,0,-6.3321870972,5.6500442591,0.8021491154
H,0,-5.1396556628,6.5932002497,-1.1819381085
Cl,0,-3.2633032975,2.3133392319,-2.5095333205

Related Structures

DTBP

E(RM06L) = -465.664913470



Zero-point correction= 0.249541 (Hartree/Particle)
Thermal correction to Energy= 0.262665
Thermal correction to Enthalpy= 0.263609
Thermal correction to Gibbs Free Energy= 0.211763
Sum of electronic and ZPE= -465.415373
Sum of electronic and thermal Energies= -465.402249
Sum of electronic and thermal Enthalpies= -465.401305
Sum of electronic and thermal Free Energies= -465.453151

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	164.825	50.166	109.119

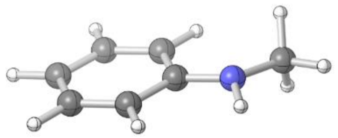
C,0,0.355023671,1.6210093094,0.0536265903
C,0,0.9098911784,2.7693746421,0.8811512047
H,0,2.0075205681,2.7548171838,0.8947172767
H,0,0.585948072,3.7369007398,0.4720622299

H,0,0.5591762952,2.7041717907,1.9209507578
C,0,0.8390935374,0.2783991182,0.574569881
H,0,0.4268516706,-0.5500758509,-0.0188614087
H,0,1.9347936648,0.2151415571,0.5432032138
H,0,0.5237908044,0.1347605004,1.617982464
O,0,0.7109054779,1.7941730139,-1.33143693
O,0,2.171765664,1.8005363278,-1.4251769795
C,0,2.5410264848,1.1579404708,-2.660378831
C,0,2.1015866855,-0.2965242156,-2.6680516069
H,0,1.0081254013,-0.3784007031,-2.6110884347
H,0,2.4279254114,-0.7915413663,-3.5939199659
H,0,2.5353931254,-0.8471581399,-1.8212236187
C,0,1.9554811502,1.9198863382,-3.8385198101
H,0,2.2475748311,2.9789989176,-3.8019272619
H,0,2.3127911239,1.5000400426,-4.7895539674
H,0,0.8588995775,1.8680621726,-3.8385765013
C,0,4.0552414465,1.2738312742,-2.6299297706
H,0,4.4743932928,0.7549411323,-1.7564821659
H,0,4.4870522481,0.822288408,-3.5333518095
H,0,4.3711384336,2.3254411058,-2.5897127708
C,0,-1.1619036909,1.6720261204,-0.0069167806
H,0,-1.5843923715,1.5588963646,1.0006598019
H,0,-1.5095761418,2.6302254721,-0.4171171094
H,0,-1.5605029017,0.8636073134,-0.6357328571

PhNHCH$_3$

E(RM06L) = -326.645312608

Zero-point correction= 0.144909 (Hartree/Particle)
Thermal correction to Energy= 0.152251
Thermal correction to Enthalpy= 0.153195
Thermal correction to Gibbs Free Energy= 0.113507
Sum of electronic and ZPE= -326.500404
Sum of electronic and thermal Energies= -326.493062
Sum of electronic and thermal Enthalpies= -326.492118
Sum of electronic and thermal Free Energies= -326.531806



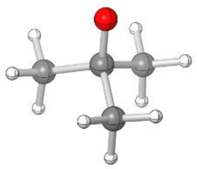
	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)

Total	95.539	28.181	83.53

C,0,-0.688566426,1.1982599254,-0.092675824
C,0,0.7226440872,1.2533092348,-0.0328535354
C,0,1.3329879597,2.5232511616,0.054055427
C,0,0.5545224289,3.6791055575,0.0923954201
C,0,-0.8380448557,3.6161007056,0.0381468195
C,0,-1.4481022633,2.360403724,-0.0568376646
H,0,-1.1755123941,0.2214949641,-0.1673580091
H,0,2.4215005416,2.603027636,0.092797172
H,0,1.0538789574,4.6497457461,0.1619073091
H,0,-1.4395266325,4.5272209029,0.0660800166
H,0,-2.5380883692,2.2846437889,-0.1053661525
N,0,1.4574271277,0.0967443268,-0.0398882269
H,0,0.9617714935,-0.7457571163,-0.3032401428
C,0,2.8850305998,0.0799443642,-0.1732718826
H,0,3.3804101694,0.5727739213,0.678682702
H,0,3.2336573881,-0.9584582095,-0.1940906023
H,0,3.2459806276,0.5753355667,-1.093975066

*t*BuO$^-$

E(RM06L) = -232.922493087



Zero-point correction= 0.119673 (Hartree/Particle)
Thermal correction to Energy= 0.126043
Thermal correction to Enthalpy= 0.126988
Thermal correction to Gibbs Free Energy= 0.091043
Sum of electronic and ZPE= -232.802820
Sum of electronic and thermal Energies= -232.796450
Sum of electronic and thermal Enthalpies= -232.795506
Sum of electronic and thermal Free Energies= -232.831450

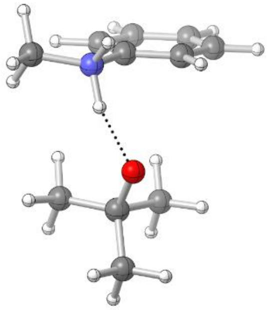
	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	79.093	23.908	75.651

C,0,0.399068477,1.6563814024,-0.0755474781
C,0,0.9149898635,2.7475134459,0.9151920021
H,0,2.0188782424,2.734737357,0.9272074578

H,0,0.615279596,3.7439718819,0.5464321547
H,0,0.5645243034,2.6540828104,1.9622495615
C,0,0.8333069064,0.2792476068,0.5187778472
H,0,0.4642305416,-0.5311058658,-0.1338054501
H,0,1.9351284547,0.212055053,0.513060514
H,0,0.4861906783,0.0678729733,1.5496545384
O,0,0.8514826832,1.8397902062,-1.305732973
C,0,-1.1602812012,1.6945443558,-0.0035594415
H,0,-1.6014912485,1.5440820692,1.0016375018
H,0,-1.5194550234,2.6653682021,-0.3873030144
H,0,-1.5728509534,0.9193954318,-0.6728757705

PhCH$_3$NH$_2^+$–*t*BuO radical complex

E(UM06L) = -559.904783054



Zero-point correction= 0.283767 (Hartree/Particle)
Thermal correction to Energy= 0.298557
Thermal correction to Enthalpy= 0.299501
Thermal correction to Gibbs Free Energy= 0.241459
Sum of electronic and ZPE= -559.621016
Sum of electronic and thermal Energies= -559.606226
Sum of electronic and thermal Enthalpies= -559.605282
Sum of electronic and thermal Free Energies= -559.663324

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	187.347	56.293	122.16

C,0,3.3007305709,3.9658008285,-5.7341745014
C,0,2.7940349648,4.5861010782,-4.5923908992
C,0,2.585896448,5.9594493231,-4.5400888189
C,0,2.9018618116,6.7269175417,-5.6628807419
C,0,3.4122931737,6.1245250661,-6.8112646914
C,0,3.6128832347,4.7438420542,-6.84531282
H,0,3.4456409307,2.8825026927,-5.7498710471
H,0,2.1878053902,6.439113975,-3.6453090444
H,0,2.7457452535,7.8069934682,-5.6319271245
H,0,3.6575900472,6.7333596547,-7.6838337883
H,0,4.0132457987,4.266063006,-7.7416118707
N,0,2.4223169937,3.712986358,-3.4728559938

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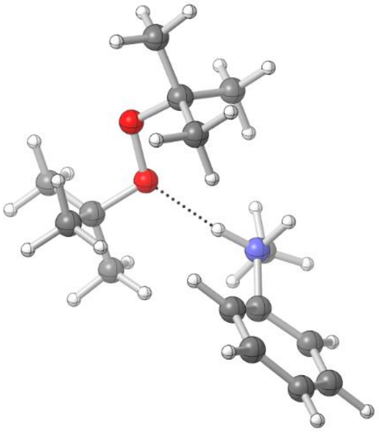
H,0,3.178994424,3.0349573707,-3.3205693589
C,0,2.072090933,4.3415316592,-2.1857628571
H,0,1.1753591237,4.9548178892,-2.3087038936
H,0,1.8706512552,3.5447663989,-1.4646222777
H,0,2.9065541634,4.9567395153,-1.836299515
H,0,1.6132457684,3.138120374,-3.8322962105
O,0,0.5188221375,2.4262489182,-4.9958935044
C,0,-0.6406660191,3.0770035226,-5.340034594
C,0,-0.2618907829,3.7688262041,-6.6833904048
H,0,0.0818560101,3.0352141458,-7.4225172841
H,0,-1.171179391,4.2612304162,-7.0558293838
H,0,0.5184482547,4.5240746703,-6.5255679858
C,0,-1.7491948547,2.0571906154,-5.5958099445
H,0,-1.992653957,1.5220389486,-4.6678009998
H,0,-2.657930712,2.5621815521,-5.9494981813
H,0,-1.4394361197,1.3212444753,-6.3487462157
C,0,-1.0367864146,4.1291703106,-4.3128074706
H,0,-0.2479597345,4.8885402423,-4.2020196675
H,0,-1.9586114849,4.6462665639,-4.6115273576
H,0,-1.2147702172,3.6631191608,-3.3327025516

PhCH$_3$NH$_2^+$–DTBP radical complex

E(UM06L) = -792.815715987



Zero-point correction= 0.405895 (Hartree/Particle)
Thermal correction to Energy= 0.428341
Thermal correction to Enthalpy= 0.429286
Thermal correction to Gibbs Free Energy= 0.354227
Sum of electronic and ZPE= -792.409821
Sum of electronic and thermal Energies= -792.387375
Sum of electronic and thermal Enthalpies= -792.386430
Sum of electronic and thermal Free Energies= -792.461489

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	268.788	85.454	157.973

C,0,2.864431818,4.7162174035,-5.9440418881
C,0,2.7245730407,5.1227909663,-4.5674068446
C,0,3.6800958348,6.0828616922,-4.0694571042

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C,0,4.5585771376,6.7061099163,-4.9332861131
C,0,4.6115185891,6.3820456549,-6.3141467556
C,0,3.7508464947,5.3560601247,-6.7857703303
H,0,2.197991245,3.9374962627,-6.3370111044
H,0,3.6587852132,6.3822384054,-3.0157969539
H,0,5.2223684053,7.4834686034,-4.5380506236
H,0,5.3185291079,6.877673243,-6.9830212921
H,0,3.7754023568,5.0724939299,-7.8438343659
N,0,2.3366042767,4.0172074681,-3.6365127445
H,0,3.1345393625,3.3864751548,-3.4309116991
C,0,1.7454019999,4.4364431305,-2.3530258297
H,0,0.9356463641,5.1452485353,-2.55770263
H,0,1.3583139352,3.5583395644,-1.8239647292
H,0,2.5083743195,4.9219137362,-1.737152183
H,0,1.6539239626,3.408798144,-4.1206994317
C,0,1.3400267916,0.1653644875,-4.5357966115
C,0,1.8935343987,0.369292239,-3.1353840175
H,0,2.0653507758,1.4311430647,-2.9136281418
H,0,1.1984179636,-0.0234663721,-2.3802239979
H,0,2.8550146453,-0.1499461711,-3.0181572421
C,0,2.2646996683,0.7260593244,-5.6014014117
H,0,1.8382547873,0.5928288372,-6.6055315413
H,0,2.4636446453,1.7964849659,-5.4564379887
H,0,3.2336774663,0.2080419102,-5.575252292
O,0,0.0199469524,0.7314200227,-4.6372061108
O,0,0.0821999801,2.1837167377,-4.4402747101
C,0,-0.9790136373,2.7662174616,-5.2424172543
C,0,-0.6959111505,2.5563150139,-6.7184867763
H,0,-0.6668548371,1.4869945493,-6.9655998216
H,0,-1.482247137,3.0218773823,-7.3291036048
H,0,0.2640470909,3.0076405083,-7.0082770219
C,0,-2.3154835174,2.1681322458,-4.8373411127
H,0,-2.4709795927,2.2574268087,-3.753035489
H,0,-3.1349355772,2.6971664784,-5.3434290941
H,0,-2.3817864695,1.1071265698,-5.1081124223
C,0,-0.9113576824,4.2343154201,-4.86204678
H,0,0.0676130503,4.6825311017,-5.0962918508
H,0,-1.6686146611,4.7962226034,-5.4251574697
H,0,-1.1154352154,4.3761058401,-3.7913820767
C,0,1.0488163261,-1.3047000779,-4.7912106575

H,0,0.6260995249,-1.4558333955,-5.7939004739
H,0,1.976577413,-1.8878346754,-4.7201059346
H,0,0.3387893071,-1.7013457142,-4.0528467443

Complex H

cu3-nha-def2-m06l.log
m06l/def2svp
E(RM06L) = -3846.72496152

Zero-point correction= 0.275852 (Hartree/Particle)
Thermal correction to Energy= 0.310955
Thermal correction to Enthalpy= 0.311899
Thermal correction to Gibbs Free Energy= 0.203950
Sum of electronic and ZPE= -3846.449109
Sum of electronic and thermal Energies= -3846.414006
Sum of electronic and thermal Enthalpies= -3846.413062
Sum of electronic and thermal Free Energies= -3846.521012

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	195.127	125.149	227.199

C,0,1.7410393447,3.2221809597,0.0404249793
C,0,0.6030161251,3.1569500047,0.8544041307
C,0,-0.357805414,2.131602511,0.7388824396
H,0,0.4353306858,3.9528860058,1.5766989658
C,0,4.3836058342,-0.9471428108,-0.8264686721
C,0,3.0855352741,-0.6907160595,1.2335765737
C,0,4.1094851647,-1.3065412564,0.5127134381
H,0,4.6991535993,-2.0859571645,0.9913028069
Cu,0,1.5960067881,0.4389802486,-1.0509335152
O,0,3.8581231618,-0.0396183037,-1.4860637896
O,0,2.2491869727,0.1655066485,0.8484337028
O,0,-0.3749284202,1.166859264,-0.0409814821
O,0,2.1585639167,2.4175255771,-0.8208449959
C,0,2.6357446505,4.4626260329,0.1683462529
C,0,-1.585835871,2.2064389865,1.6610098176
C,0,5.4171712153,-1.7781277193,-1.6012996354

```
C,0,2.8556518229,-1.1302814238,2.6818381147
F,0,3.9033390236,4.1080199923,0.4231605533
F,0,2.6429526824,5.1507312718,-0.9850566415
F,0,2.2611470182,5.3141352106,1.133682277
F,0,-2.7034463508,2.3678935417,0.931107691
F,0,-1.7291180791,1.0635610355,2.3479634261
F,0,-1.5526743921,3.2051075343,2.5560163186
F,0,6.3509538508,-0.9906615762,-2.1501119376
F,0,4.8055710159,-2.4268726139,-2.610464707
F,0,6.0516679162,-2.6997549129,-0.8637793884
F,0,1.7165315714,-1.8405973051,2.7686193217
F,0,3.8370372445,-1.8929623578,3.1811216645
F,0,2.7222065263,-0.0707220628,3.4880147884
N,0,0.8383691713,0.6512176143,-2.7974273685
C,0,0.9797415319,-0.1803613375,-3.8754486158
C,0,2.2619220841,-0.649262862,-4.2582713609
C,0,-0.1235823071,-0.561132273,-4.6785979356
C,0,2.4235516357,-1.433891868,-5.3912797103
H,0,3.1165277548,-0.3907314424,-3.6278294307
C,0,0.0553124493,-1.3242229024,-5.8283057764
H,0,-1.1245968795,-0.22702197,-4.3879532794
C,0,1.3268551337,-1.7720900897,-6.1945431243
H,0,3.4239127877,-1.7880189903,-5.6574500909
H,0,-0.813467422,-1.5872468697,-6.4384101761
H,0,1.4624425916,-2.3837761555,-7.0895091042
C,0,0.997732405,-1.4129564559,-1.1949428899
H,0,-0.0077055346,-1.4867115712,-1.623491032
H,0,1.7500650591,-1.9123056716,-1.8217878311
H,0,1.009990157,-1.7465280394,-0.1482244998
H,0,-0.1568951707,0.8121802779,-2.6196758517
```

Complex J

cu2nh2-anion-m06l.log
m06l/def2svp
E(UM06L) = -3806.88527572

Zero-point correction= 0.239366 (Hartree/Particle)
Thermal correction to Energy= 0.272266
Thermal correction to Enthalpy= 0.273211

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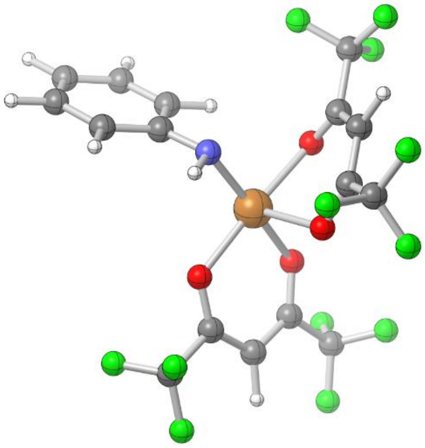
Thermal correction to Gibbs Free Energy= 0.167822
Sum of electronic and ZPE= -3806.645909
Sum of electronic and thermal Energies= -3806.613009
Sum of electronic and thermal Enthalpies= -3806.612065
Sum of electronic and thermal Free Energies= -3806.717453

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	170.85	116.384	221.808

Cu,0,0.5543953718,0.900522425,-0.7045263914
C,0,-0.1449933661,3.6838566358,-0.1317947211
C,0,-1.4822050839,3.3904835703,0.1745138971
C,0,-1.9356853238,2.071290322,0.3050793652
H,0,-2.1784045458,4.2082754159,0.3448178347
O,0,0.7933840751,2.8919505773,-0.3680005189
O,0,-1.2968099813,1.005037661,0.1533617657
C,0,0.2781072976,5.1562115978,-0.1990815099
C,0,-3.3991075066,1.8385585484,0.6976320402
F,0,0.7160273785,5.4568868536,-1.4294533352
F,0,-0.7055531956,6.0147032591,0.0974656667
F,0,1.2863137952,5.3920496746,0.6508881946
F,0,-4.0202150066,1.1081090488,-0.2380084904
F,0,-4.1022483307,2.9658552814,0.8597212515
F,0,-3.4673011725,1.1533736083,1.8477468103
C,0,0.3898436846,0.6585936281,-3.7104475017
C,0,1.7228723128,0.2018266431,-3.7661693262
C,0,2.6262451168,0.3702622298,-2.7087330933
H,0,2.0620054559,-0.3117047957,-4.6634543965
O,0,-0.1940075295,1.2482418144,-2.7844904823
O,0,2.4518144428,0.9292069188,-1.6028417211
C,0,-0.5014928849,0.3900015281,-4.9329617099
C,0,4.0260075903,-0.2335771761,-2.8633513336
F,0,-1.0763185385,1.5254202099,-5.356223269
F,0,0.141053144,-0.1430783194,-5.9822552138
F,0,-1.4942205973,-0.454952821,-4.605570845
F,0,4.9738316616,0.6597842261,-2.5474002858
F,0,4.3007824769,-0.6846532246,-4.0955888261
F,0,4.167157056,-1.2724110237,-2.0203169148
N,0,0.4551366893,-1.0591180209,-0.8121167307



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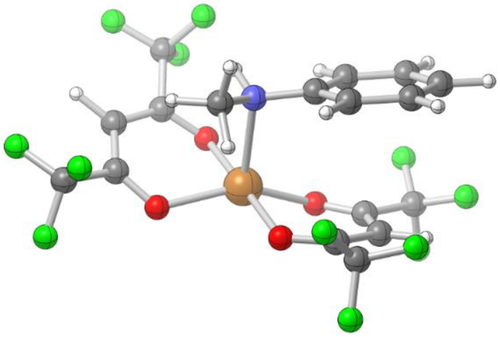
H,0,-0.5051510509,-1.3350641331,-1.0329338206
C,0,0.8524486071,-1.6963823631,0.3219616956
C,0,2.1043677681,-1.362899287,0.9156271881
C,0,0.0929529402,-2.7177921059,0.9584971527
C,0,2.5557055221,-2.011250114,2.0562493923
H,0,2.7049258618,-0.580220526,0.4409115088
C,0,0.5654147264,-3.3699780433,2.0907742035
H,0,-0.8791953324,-2.9865643302,0.5327904815
C,0,1.7981834029,-3.0257718067,2.6565525432
H,0,3.5203825929,-1.7266030333,2.4869723231
H,0,-0.0431261672,-4.1551873106,2.549669677
H,0,2.161379643,-3.5357592429,3.5518304454

Complex I

cu1-nhme-def2-m06l.log
m06l/def2svp
E(RM06L) = -3846.79105061



Zero-point correction= 0.279029 (Hartree/Particle)
Thermal correction to Energy= 0.313709
Thermal correction to Enthalpy= 0.314653
Thermal correction to Gibbs Free Energy= 0.208943
Sum of electronic and ZPE= -3846.512021
Sum of electronic and thermal Energies= -3846.477341
Sum of electronic and thermal Enthalpies= -3846.476397
Sum of electronic and thermal Free Energies= -3846.582108

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	196.856	123.608	222.486

Cu,0,0.2622779733,0.8018462365,0.302787145
C,0,-0.3407724705,3.675434463,0.4557446112
C,0,-1.7300976035,3.474915506,0.3838984111
C,0,-2.2806750754,2.1883994035,0.5218754181
H,0,-2.3738981816,4.3053227028,0.0980503419
O,0,0.549983456,2.8209880663,0.6881541636
O,0,-1.6954970089,1.1386500524,0.8894370862
C,0,0.2038146098,5.0645541163,0.1315512873
C,0,-3.7233478564,1.9685935304,0.0799096669

```
F,0,1.0880659825,5.4631574836,1.059003208
F,0,0.8604773969,5.0652486412,-1.0469355772
F,0,-0.7402299205,6.0158643405,0.0536232688
F,0,-3.7478444467,1.2475081499,-1.0683361755
F,0,-4.4077618703,3.097042112,-0.1562462572
F,0,-4.4186638752,1.2641846149,0.9828930394
C,0,0.9059773514,-2.0514159132,0.5361438746
C,0,2.104785637,-1.9419454166,-0.1862254371
C,0,2.633560813,-0.6902383215,-0.5435191938
H,0,2.5761821938,-2.8449126908,-0.5713692791
O,0,0.1981794281,-1.1293731775,1.0038644458
O,0,2.2296756661,0.4482733651,-0.2078934245
C,0,0.3758796807,-3.4578233596,0.8295657058
C,0,3.8868302305,-0.6743649495,-1.4233690348
F,0,-0.959624649,-3.5054567888,0.7515341162
F,0,0.8585983523,-4.4054794359,0.0093194985
F,0,0.7049869972,-3.8267286486,2.084487854
F,0,3.8409688136,0.3125278139,-2.3294038121
F,0,4.0986178804,-1.8189453414,-2.0926634157
F,0,4.9828329532,-0.4569902824,-0.6692863956
N,0,-0.4074582225,0.950805449,-1.9818212609
H,0,-1.3945355201,1.1490554455,-1.8350395097
C,0,-0.2003659823,-0.3530006596,-2.4403554626
C,0,0.8623563971,-0.6840213976,-3.2978493675
C,0,-1.0478907222,-1.3793771949,-1.9807759987
C,0,1.0781505194,-2.0130928876,-3.6661519735
H,0,1.5302956639,0.0944820037,-3.6694322754
C,0,-0.8257098437,-2.6963145741,-2.3622046319
H,0,-1.8619844195,-1.1244100958,-1.2944908424
C,0,0.2435343751,-3.0279359068,-3.2025656833
H,0,1.9201990682,-2.2520851606,-4.3218192939
H,0,-1.4885004903,-3.4802361009,-1.9868040297
H,0,0.4204225783,-4.0675671822,-3.4878284051
C,0,0.3046102664,2.047071377,-2.6001116796
H,0,1.3709675182,2.0163245691,-2.3303729979
H,0,0.2261490639,2.0513488715,-3.7020208077
H,0,-0.1054637007,2.9921689761,-2.2288636905
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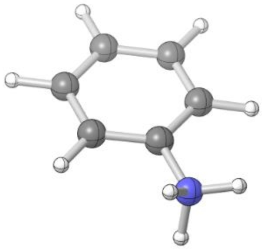
Anilium Cation

anilp-def2-m06l.log
m06l/def2svp
E(RM06L) = -287.815535884



Zero-point correction= 0.132141 (Hartree/Particle)
Thermal correction to Energy= 0.138019
Thermal correction to Enthalpy= 0.138963
Thermal correction to Gibbs Free Energy= 0.102707
Sum of electronic and ZPE= -287.683395
Sum of electronic and thermal Energies= -287.677517
Sum of electronic and thermal Enthalpies= -287.676573
Sum of electronic and thermal Free Energies= -287.712829

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	86.608	22.901	76.307

C,0,-0.7700128297,1.1702450386,-0.0333344819
C,0,0.6169513503,1.2079957411,0.0646267464
C,0,1.3231639812,2.4036965079,0.1185534042
C,0,0.611610938,3.6019446655,0.0731477143
C,0,-0.7789300223,3.5880224022,-0.0256236217
C,0,-1.4674234047,2.375260449,-0.0781305517
H,0,-1.2952373555,0.2133888421,-0.0709093766
H,0,2.4127442121,2.3985415318,0.1958866238
H,0,1.152208418,4.5492056862,0.1168875316
H,0,-1.3317047463,4.5289579161,-0.0595288362
H,0,-2.5563863495,2.3632258946,-0.1528044744
N,0,1.3542073961,-0.0557126551,0.0958454988
H,0,1.3712952664,-0.5164193269,-0.8246565235
H,0,2.3327564843,0.0741554386,0.3782218189
H,0,0.9404364316,-0.7317479117,0.7503958102

A1-H$^+$

anthcl-cat-def2-m06l.log
m06l/def2svp
E(RM06L) = -1245.90593618

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Zero-point correction= 0.267654 (Hartree/Particle)
Thermal correction to Energy= 0.283122
Thermal correction to Enthalpy= 0.284066
Thermal correction to Gibbs Free Energy= 0.224107
Sum of electronic and ZPE= -1245.638282
Sum of electronic and thermal Energies= -1245.622814
Sum of electronic and thermal Enthalpies= -1245.621870
Sum of electronic and thermal Free Energies= -1245.681829

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	177.662	63.46	126.194

C,0,-7.9802923439,-1.3252527026,-0.7686242483
C,0,-6.8406657534,-1.7976218523,-0.159449571
C,0,-5.7727131987,-0.9109997642,0.084796266
C,0,-5.8657175817,0.4706516375,-0.2833491874
C,0,-7.0606623347,0.9083635006,-0.9224930926
C,0,-8.0907032629,0.0316603201,-1.1572077711
C,0,-4.772460137,1.3261767554,-0.0184425502
C,0,-3.604668674,0.8118464966,0.5904338014
C,0,-3.5547207996,-0.5775771637,0.9339974245
C,0,-2.4100093583,-1.1316677995,1.5426103871
H,0,-2.4017255744,-2.1946791105,1.7907311108
C,0,-1.3314306772,-0.3200455284,1.8075669762
C,0,-1.3588485456,1.0583738393,1.4841348036
C,0,-2.466895429,1.6121417091,0.8928513814
H,0,-8.8087325326,-2.0097511343,-0.9609815466
H,0,-6.7429225614,-2.8436149987,0.1362112193
H,0,-7.1422454783,1.9519436765,-1.230151224
H,0,-9.0000118063,0.3776887388,-1.6510233829
H,0,-0.4427291183,-0.7448481219,2.2782682663
H,0,-0.4923840948,1.6812742805,1.7113955036
H,0,-2.4892434462,2.6760841009,0.6499732324
N,0,-4.6337523587,-1.3538065211,0.6695580893
C,0,-4.8672906645,2.7669588843,-0.352310829
C,0,-4.1754527121,3.3293556109,-1.4353756543
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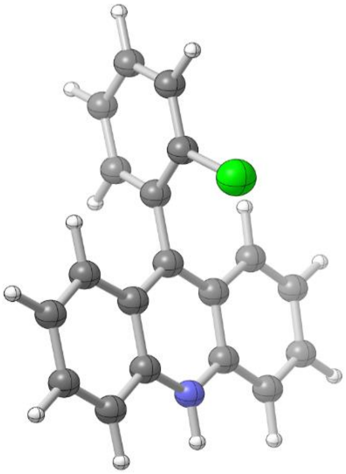
C,0,-4.2698804537,4.6873020979,-1.7327852477



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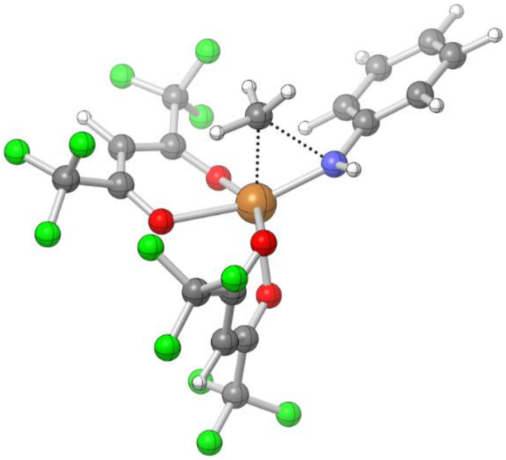
H,0,-6.2188997354,3.1847815273,1.2702761555
C,0,-5.0636781243,5.5073583508,-0.9349668167
H,0,-3.7258088787,5.0917673305,-2.587164937
H,0,-6.3890397106,5.6120863527,0.7696794582
H,0,-5.1353437372,6.5720286183,-1.1664143995
Cl,0,-3.1947717848,2.3081145436,-2.4557924089
H,0,-4.5826689626,-2.3415293118,0.9238156705

TS1



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m06l/def2svp
E(RM06L) = -3846.71444978

Zero-point correction= 0.275575 (Hartree/Particle)
Thermal correction to Energy= 0.310093
Thermal correction to Enthalpy= 0.311037
Thermal correction to Gibbs Free Energy= 0.205166
Sum of electronic and ZPE= -3846.438875
Sum of electronic and thermal Energies= -3846.404357
Sum of electronic and thermal Enthalpies= -3846.403413
Sum of electronic and thermal Free Energies= -3846.509284

	E, kcal/mol	CV, cal/(mol·K)	S, cal/(mol·K)
Total	194.586	123.394	222.825

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C,0,2.703290848,-0.577285789,0.91528604
C,0,3.517752013,-1.362465233,0.085187441
H,0,3.940928439,-2.29062588,0.466263694
Cu,0,1.324996516,0.850908876,-1.325084284
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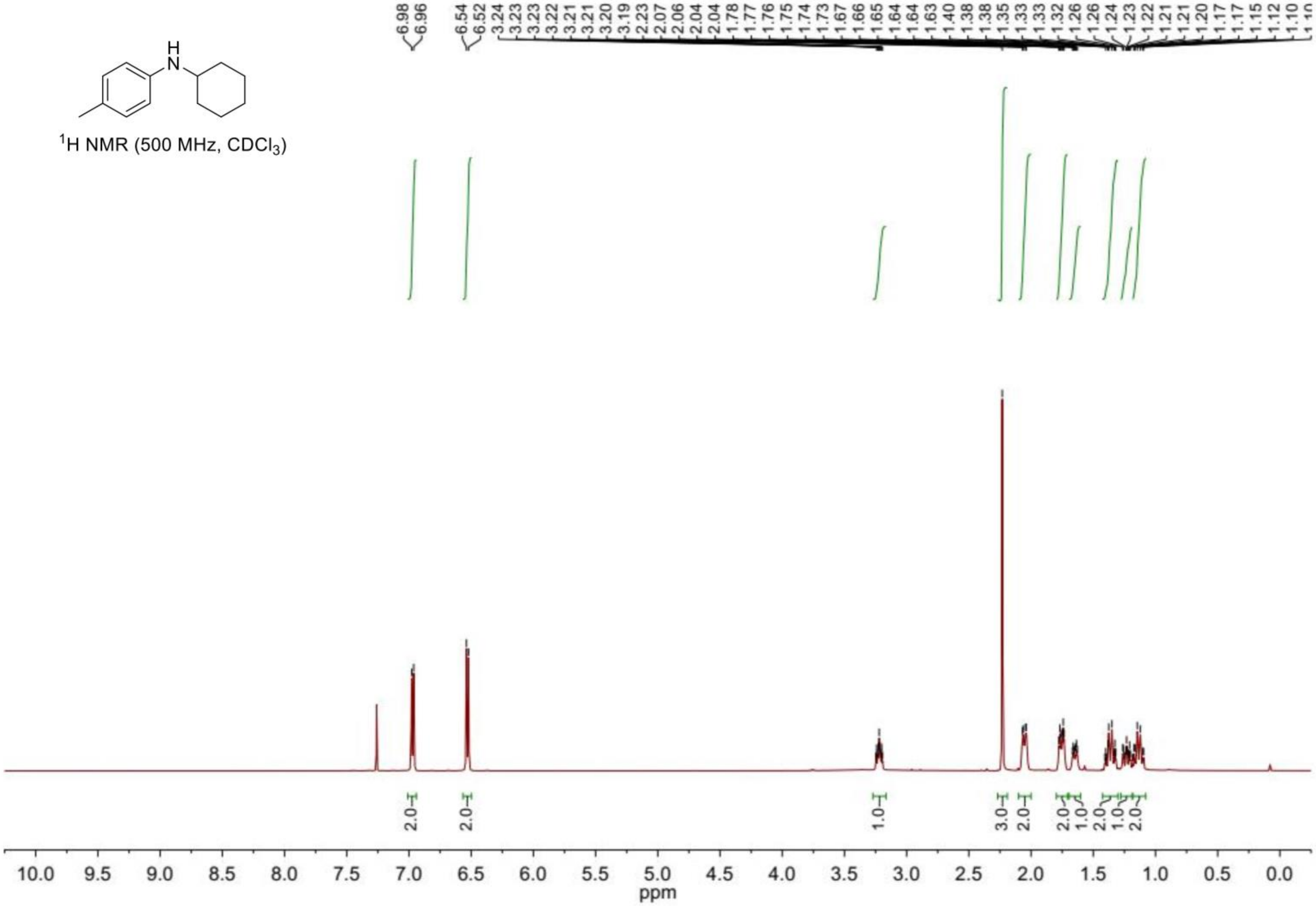
NMR Spectroscopic data

N-Cyclohexyl-4-methylaniline (3)



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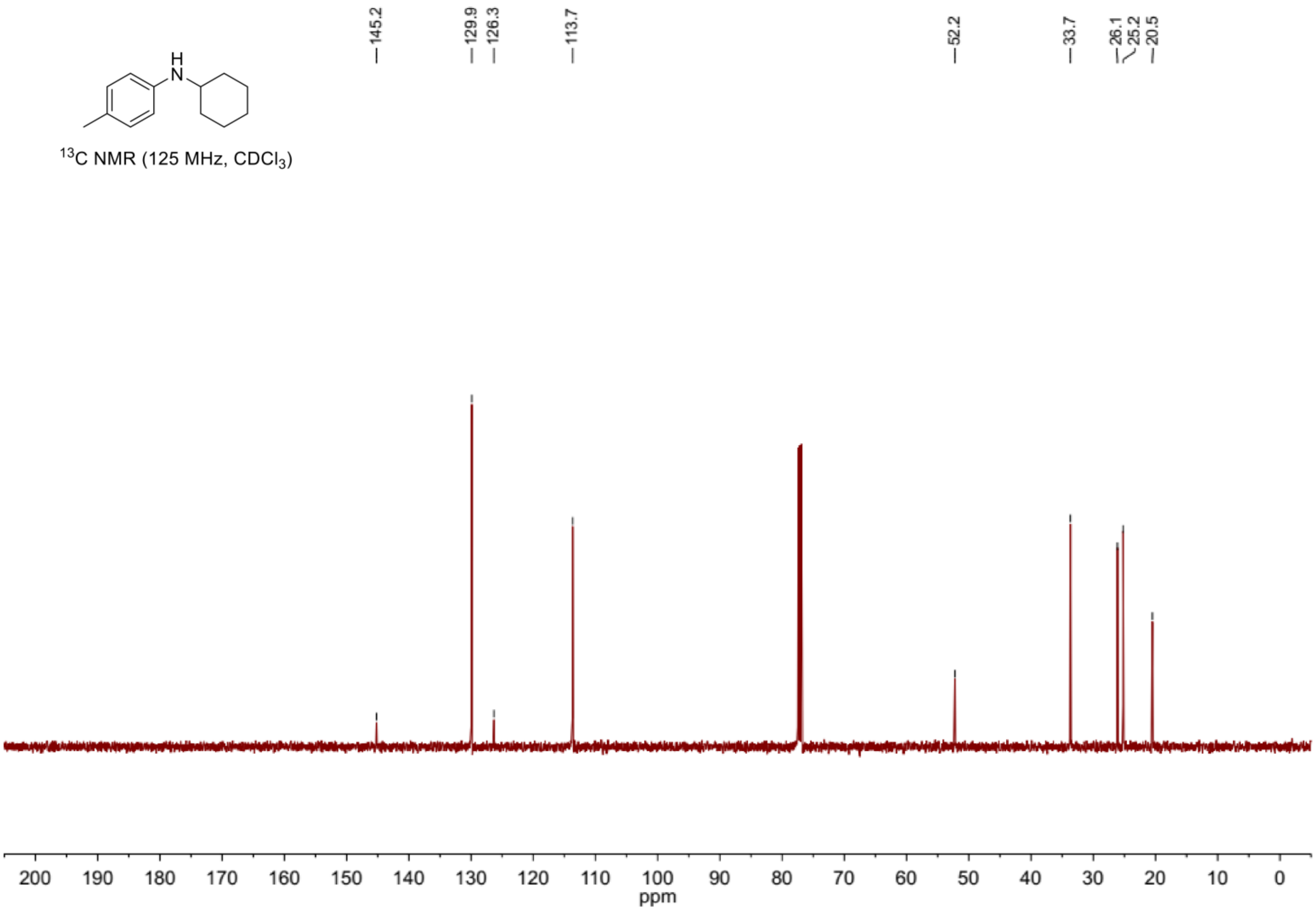
N-Cyclohexyl-4-methylaniline (3)


^{13}C NMR (125 MHz, $CDCl_3$)

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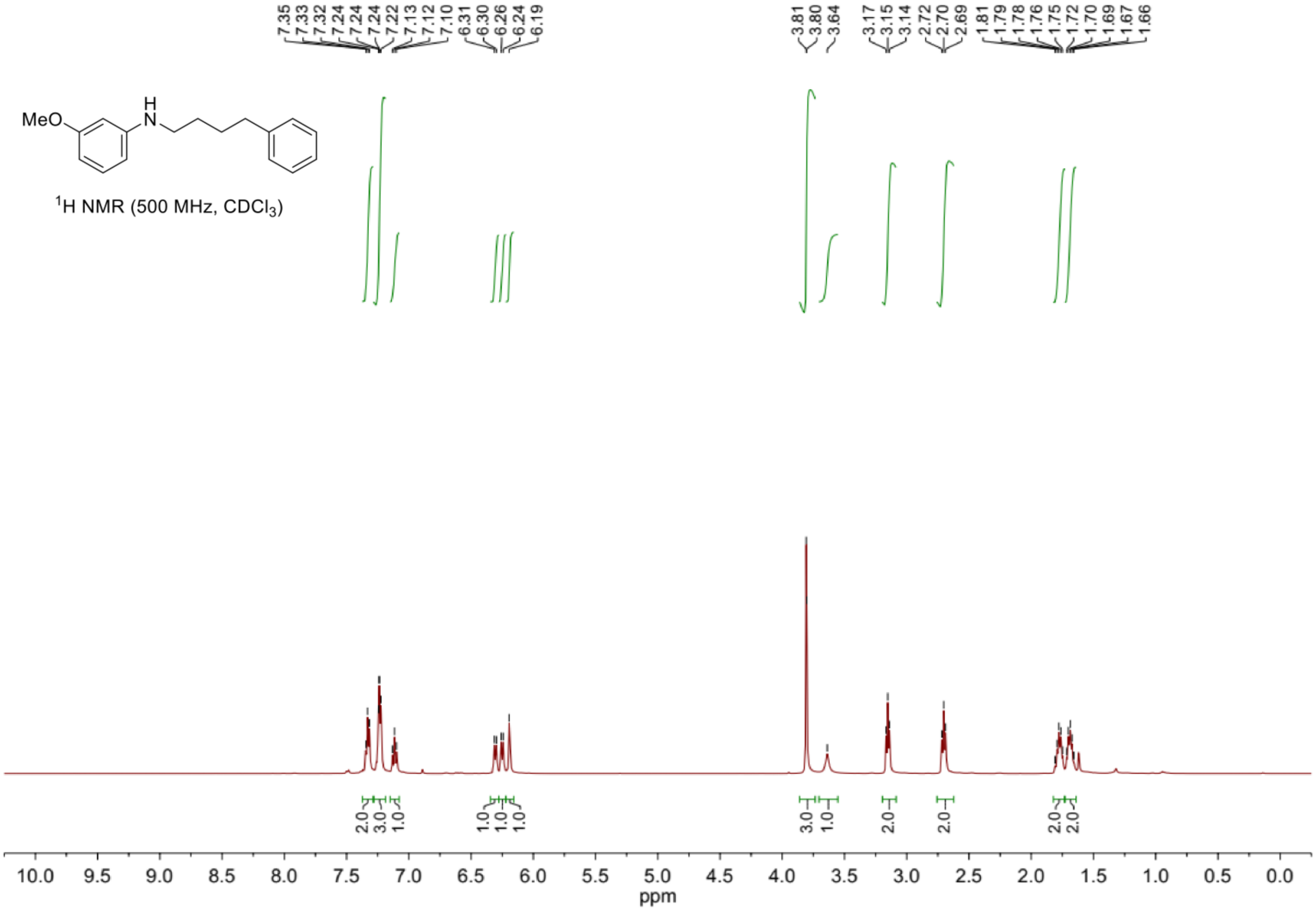
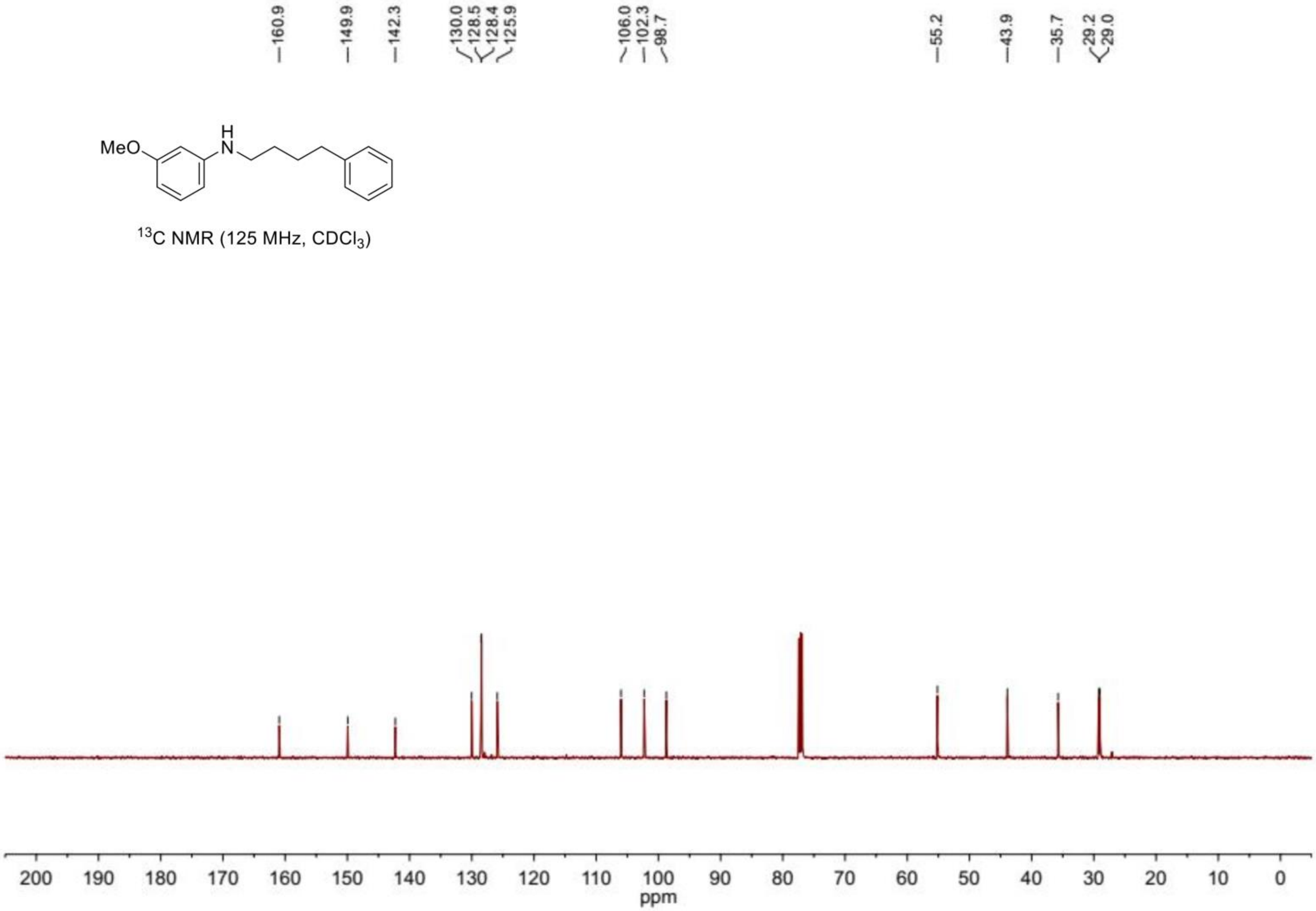
3-Methoxy-*N*-(4-phenylbutyl)aniline (4)



^{1}H NMR (500 MHz, $CDCl_3$)

Go back to table of contents

3-Methoxy-*N*-(4-phenylbutyl)aniline (4)



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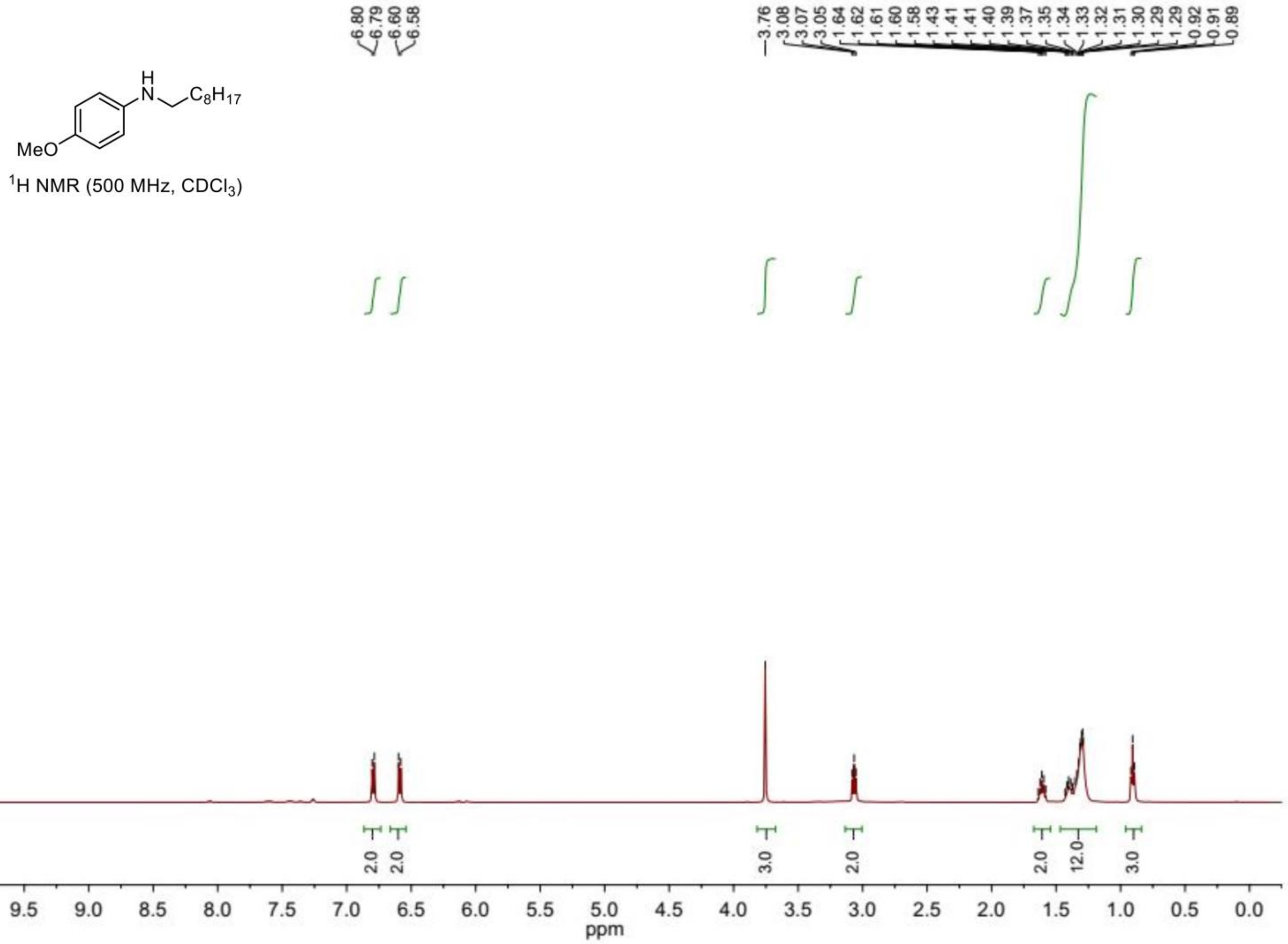
4-Methoxy-*N*-nonylaniline (5)



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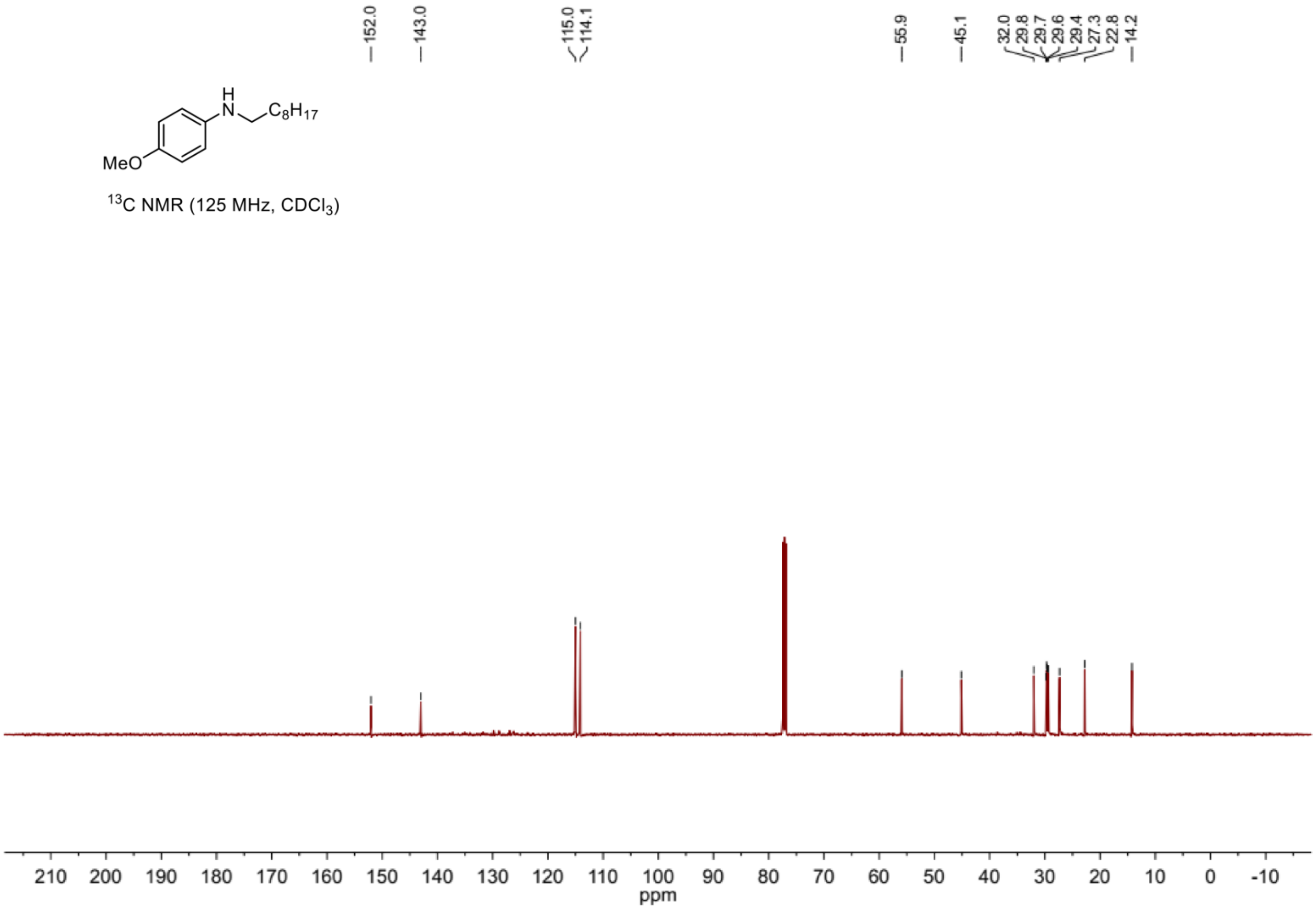
4-Methoxy-*N*-nonylaniline (5)



^{13}C NMR (125 MHz, $CDCl_3$)

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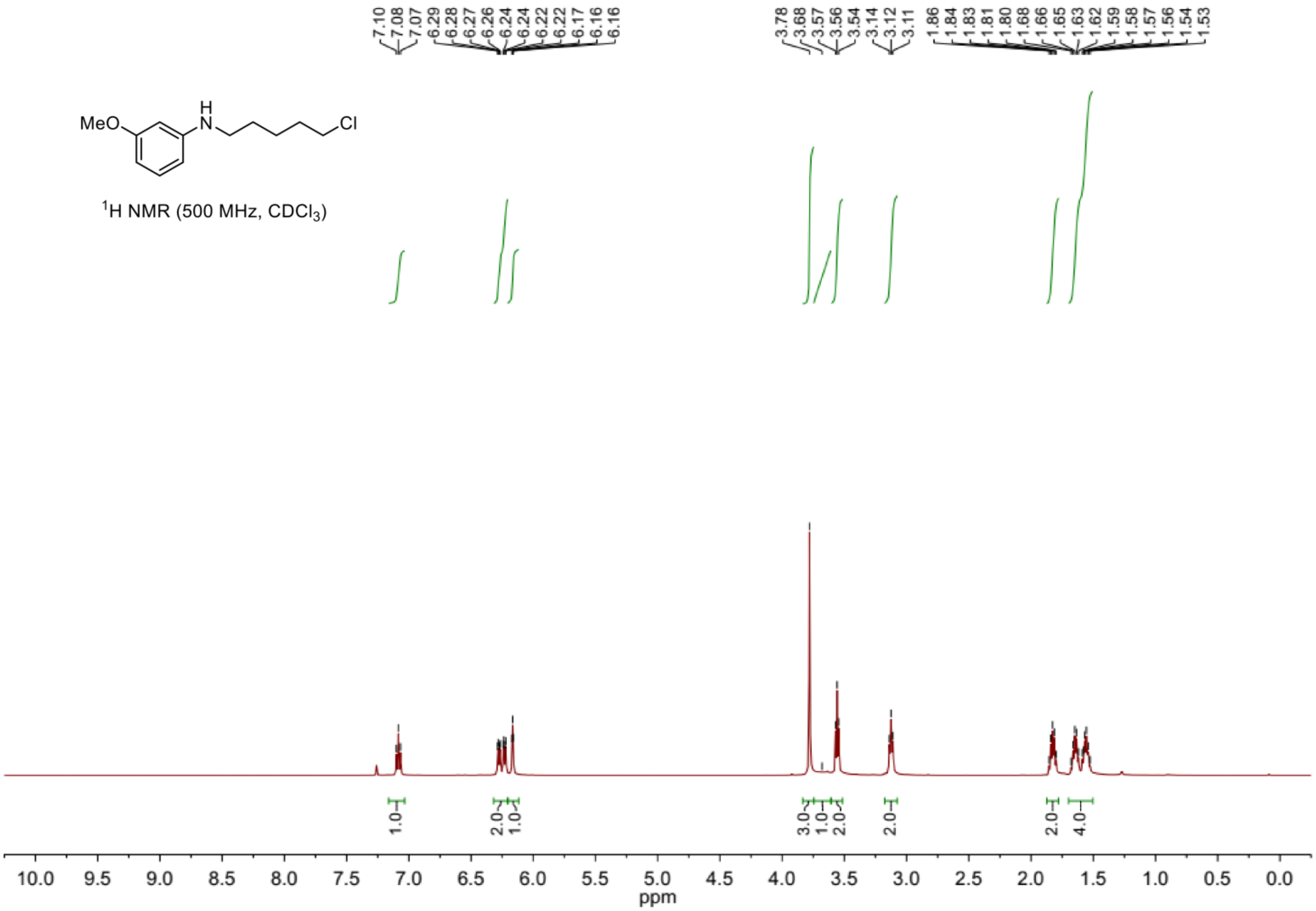
N-(5-Chloropentyl)-3-methoxyaniline (6)



^{1}H NMR (500 MHz, $CDCl_3$)

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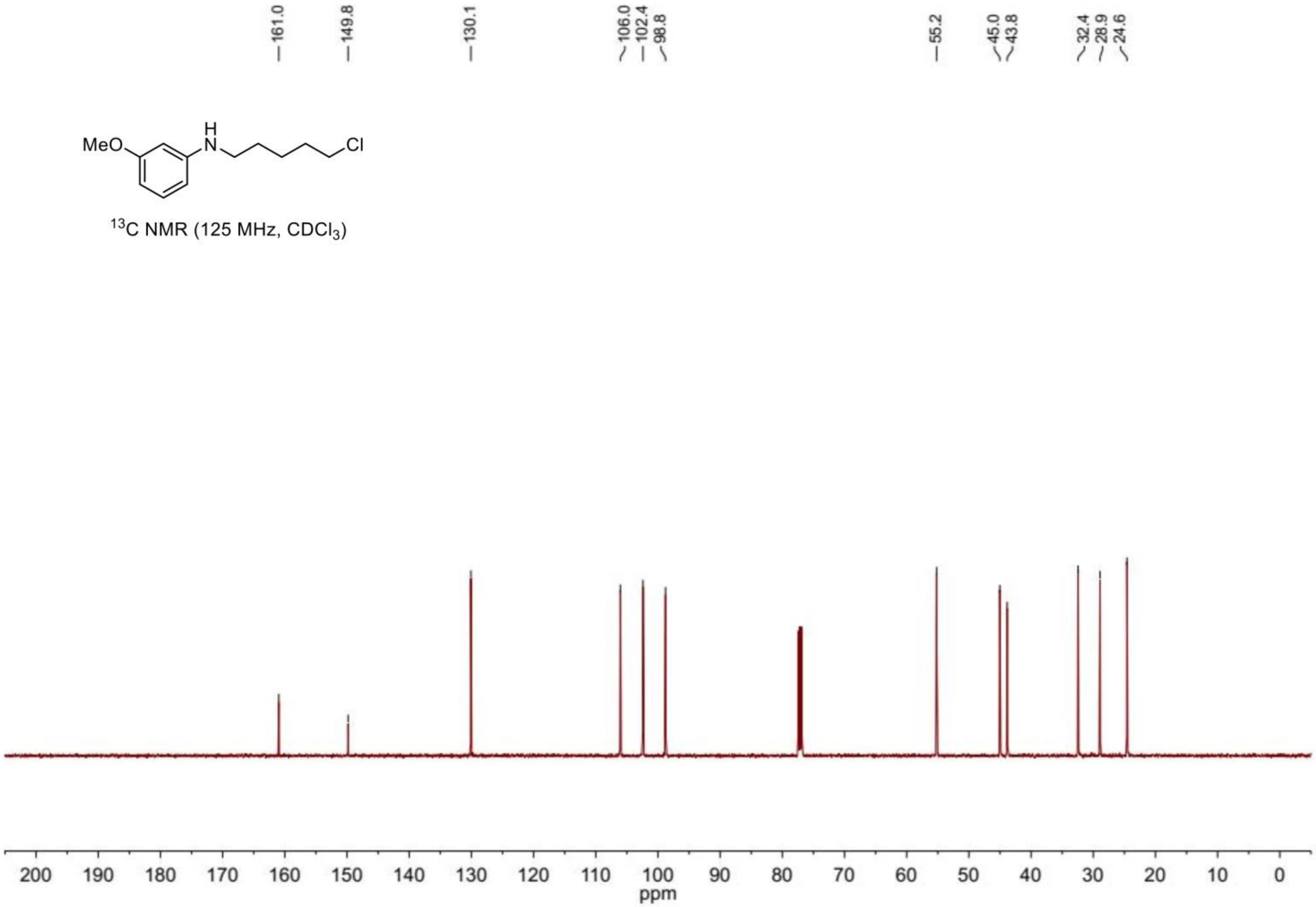
N-(5-Chloropentyl)-3-methoxyaniline (6)



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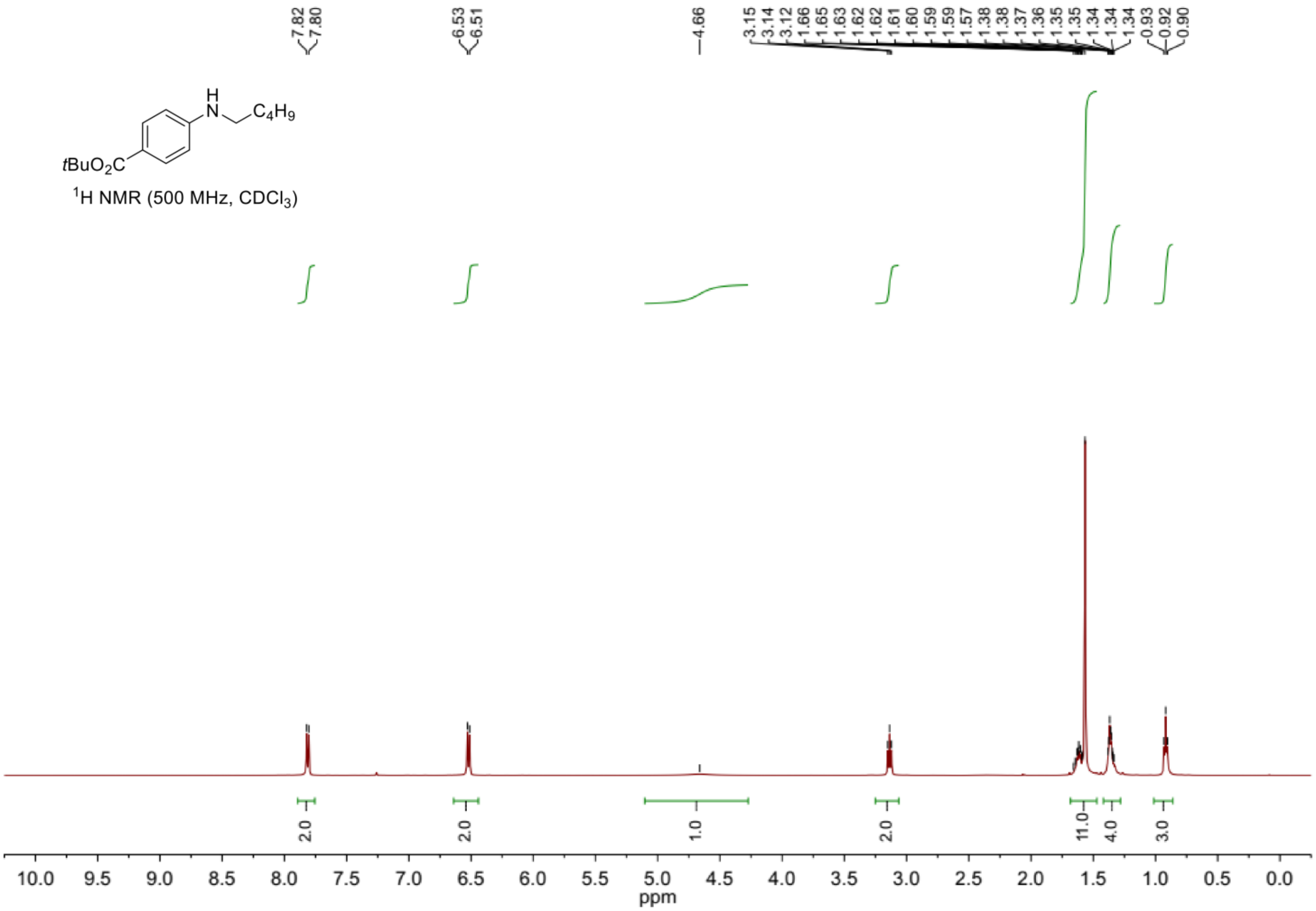
tert-Butyl 4-(pentylamino)benzoate (7)



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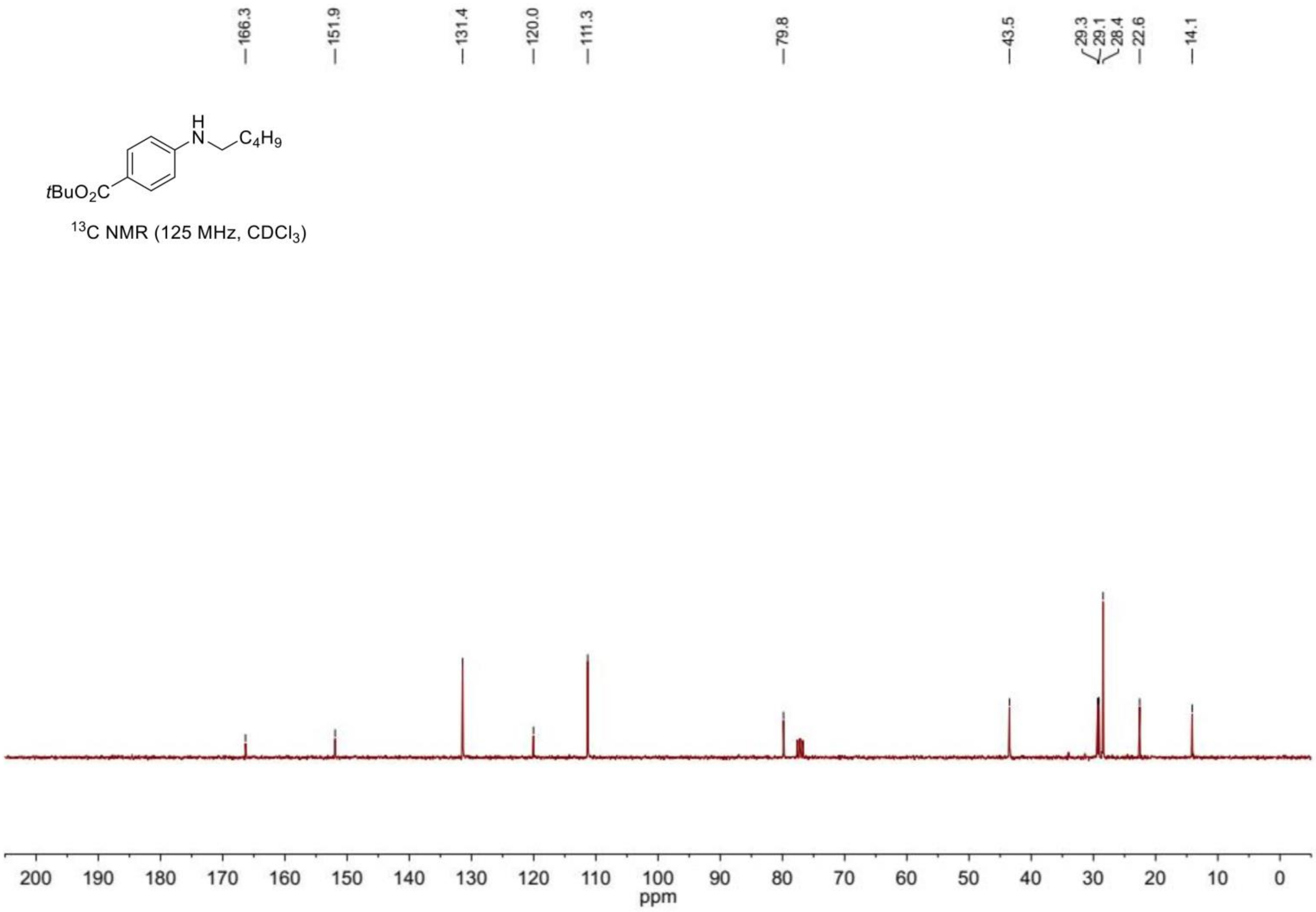
tert-Butyl 4-(pentylamino)benzoate (7)



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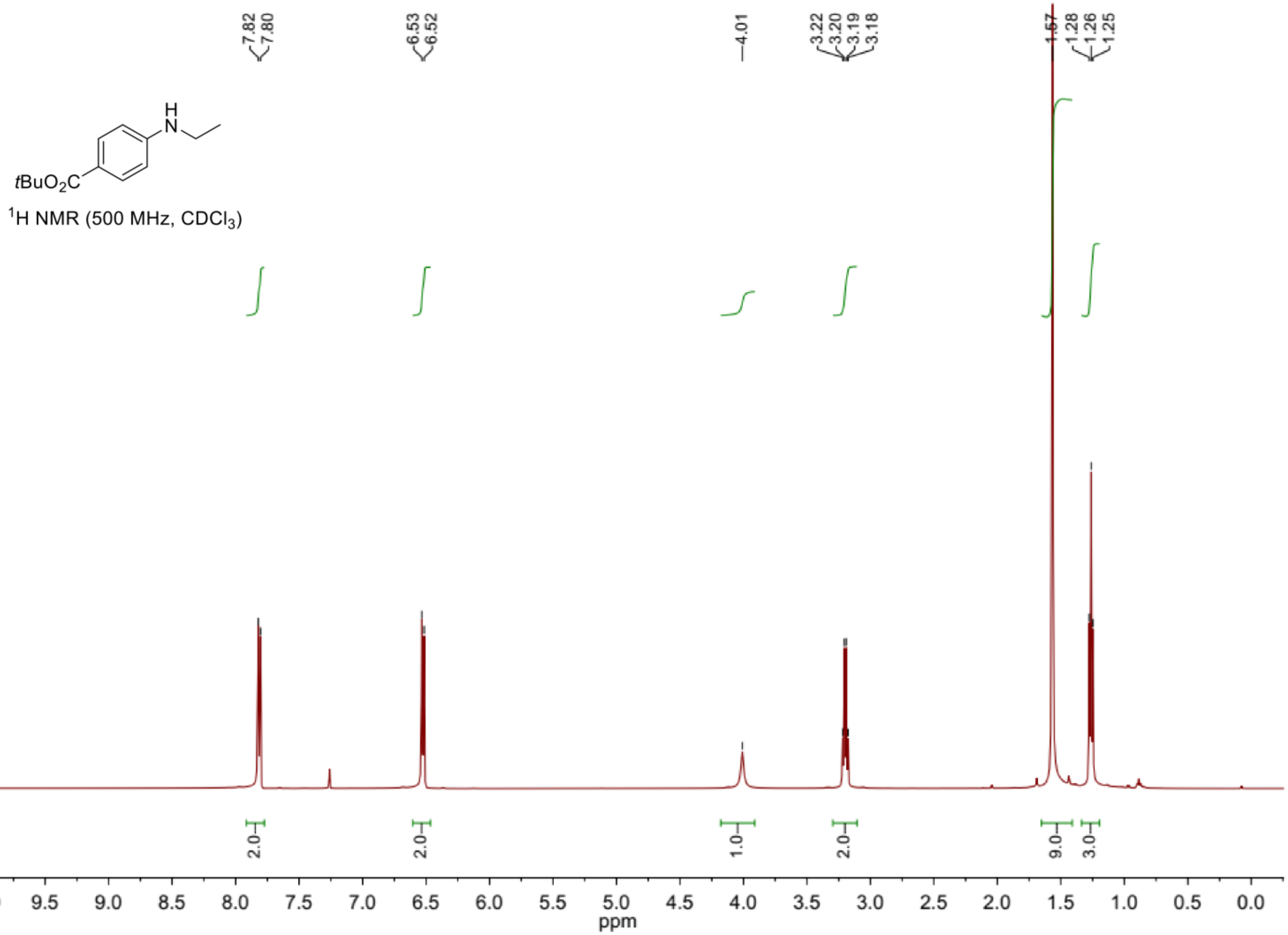
tert-Butyl 4-(pentylamino)benzoate (8)



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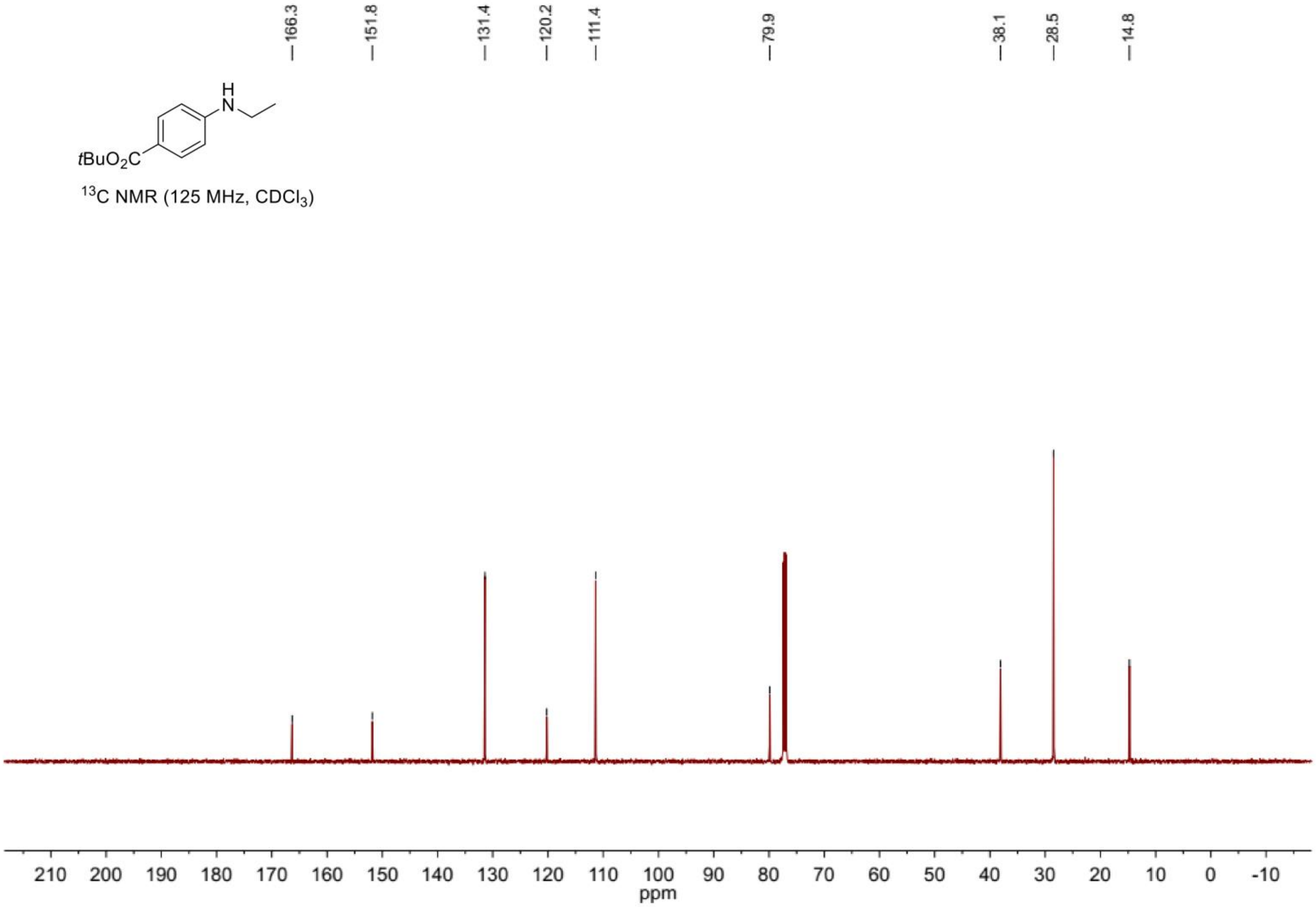
tert-Butyl 4-(pentylamino)benzoate (8)



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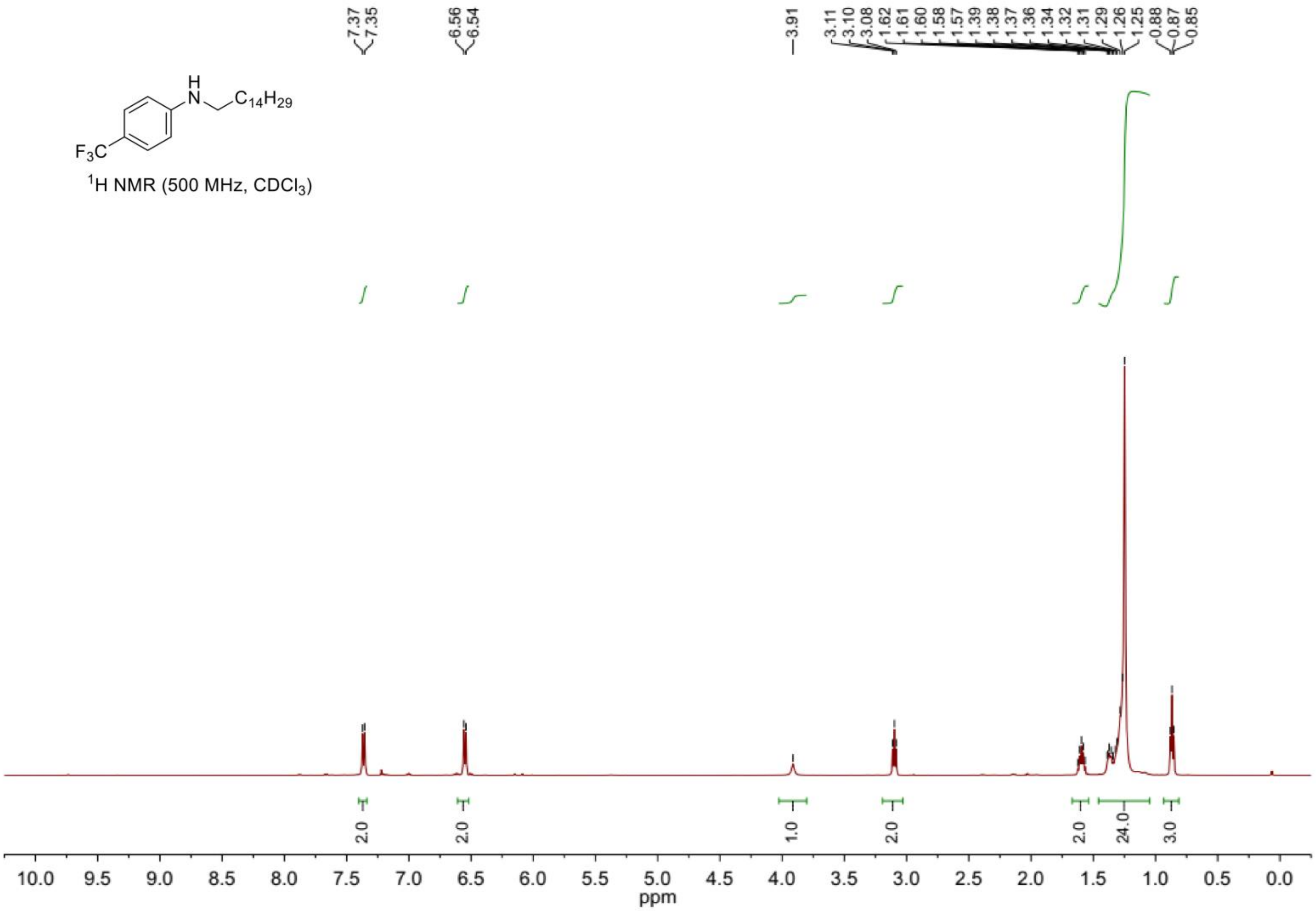
N-Pentadecyl-4-(trifluoromethyl)aniline (9)



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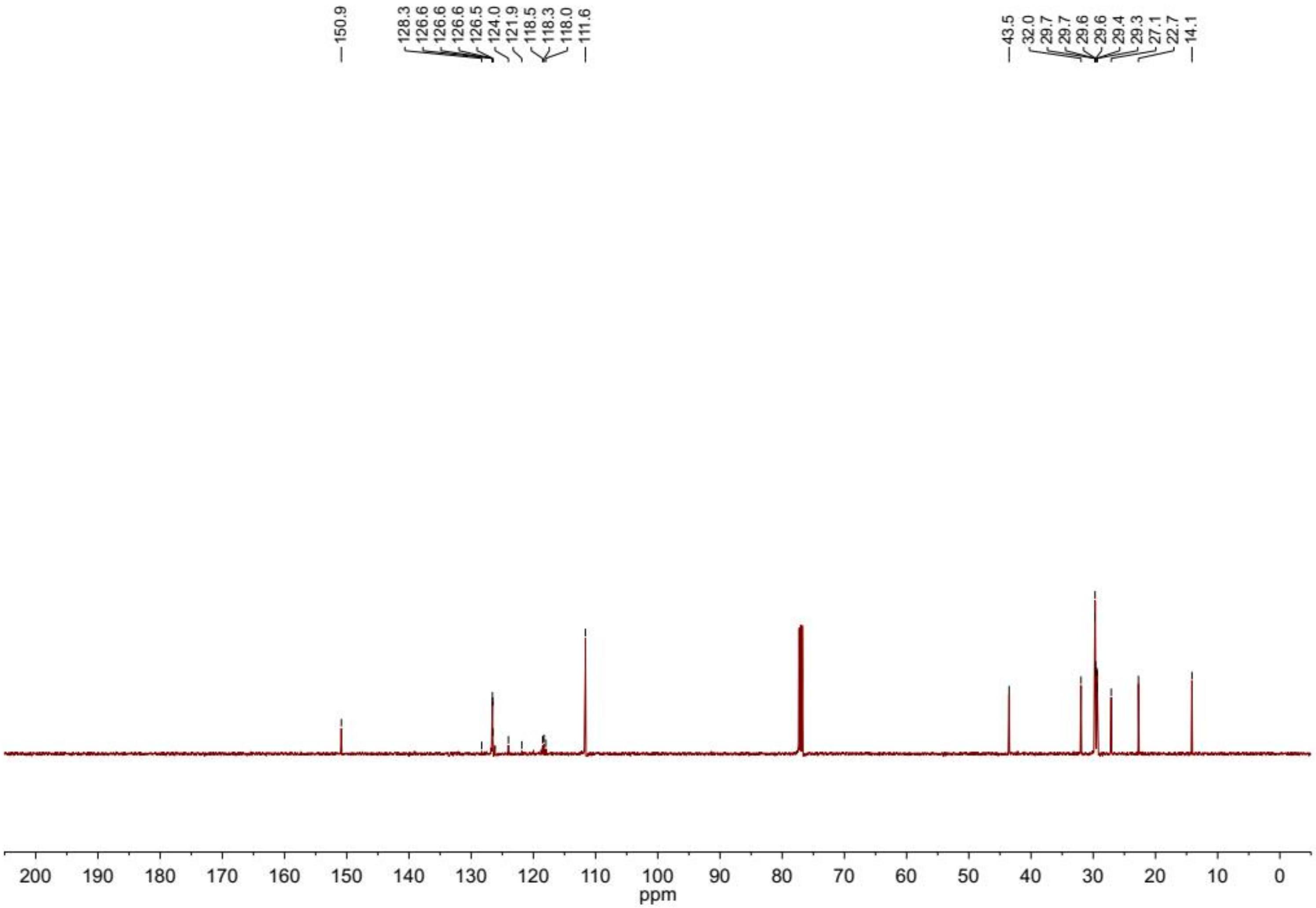
N-Pentadecyl-4-(trifluoromethyl)aniline (9)



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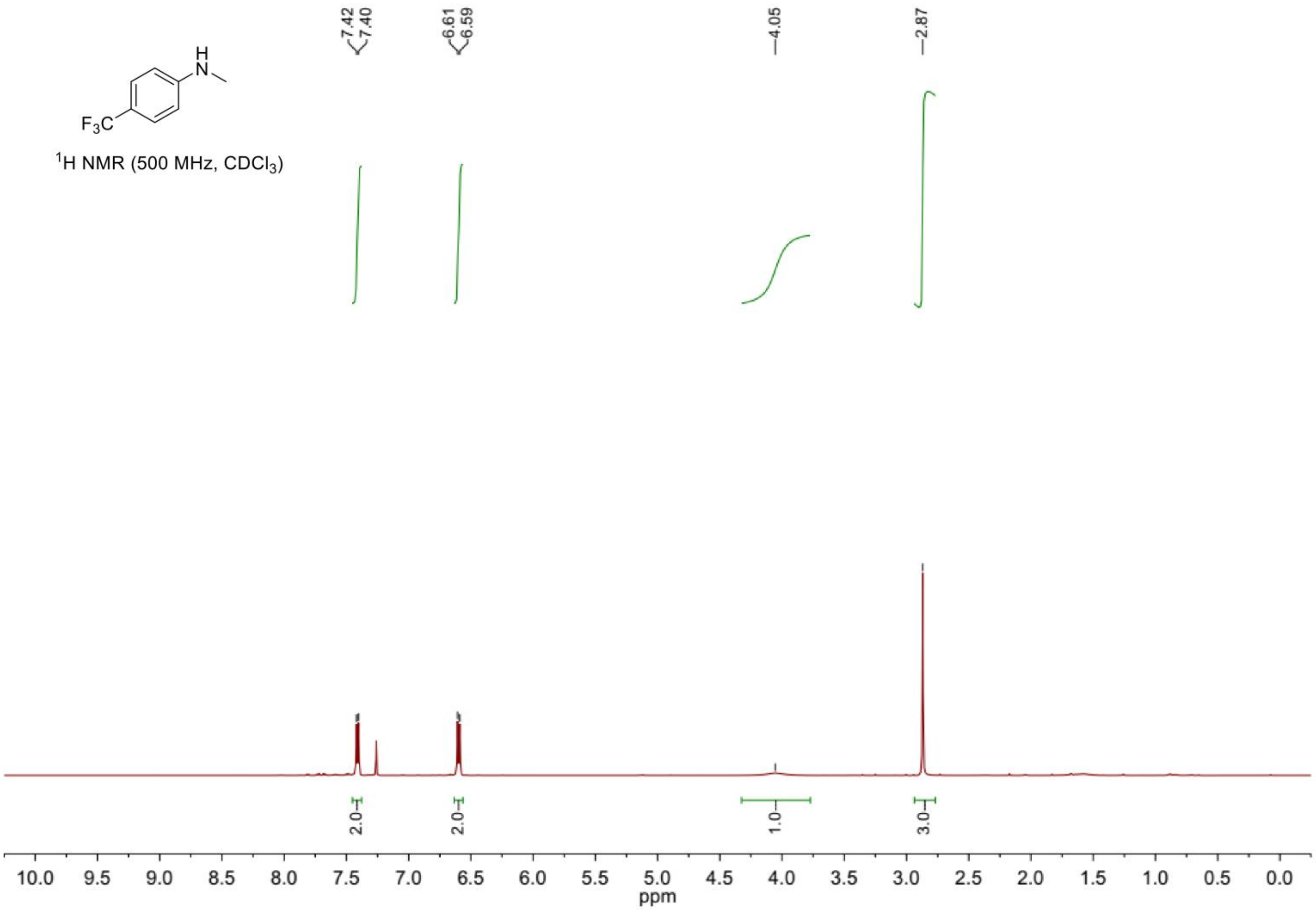
N-Methyl-4-(trifluoromethyl)aniline (10)



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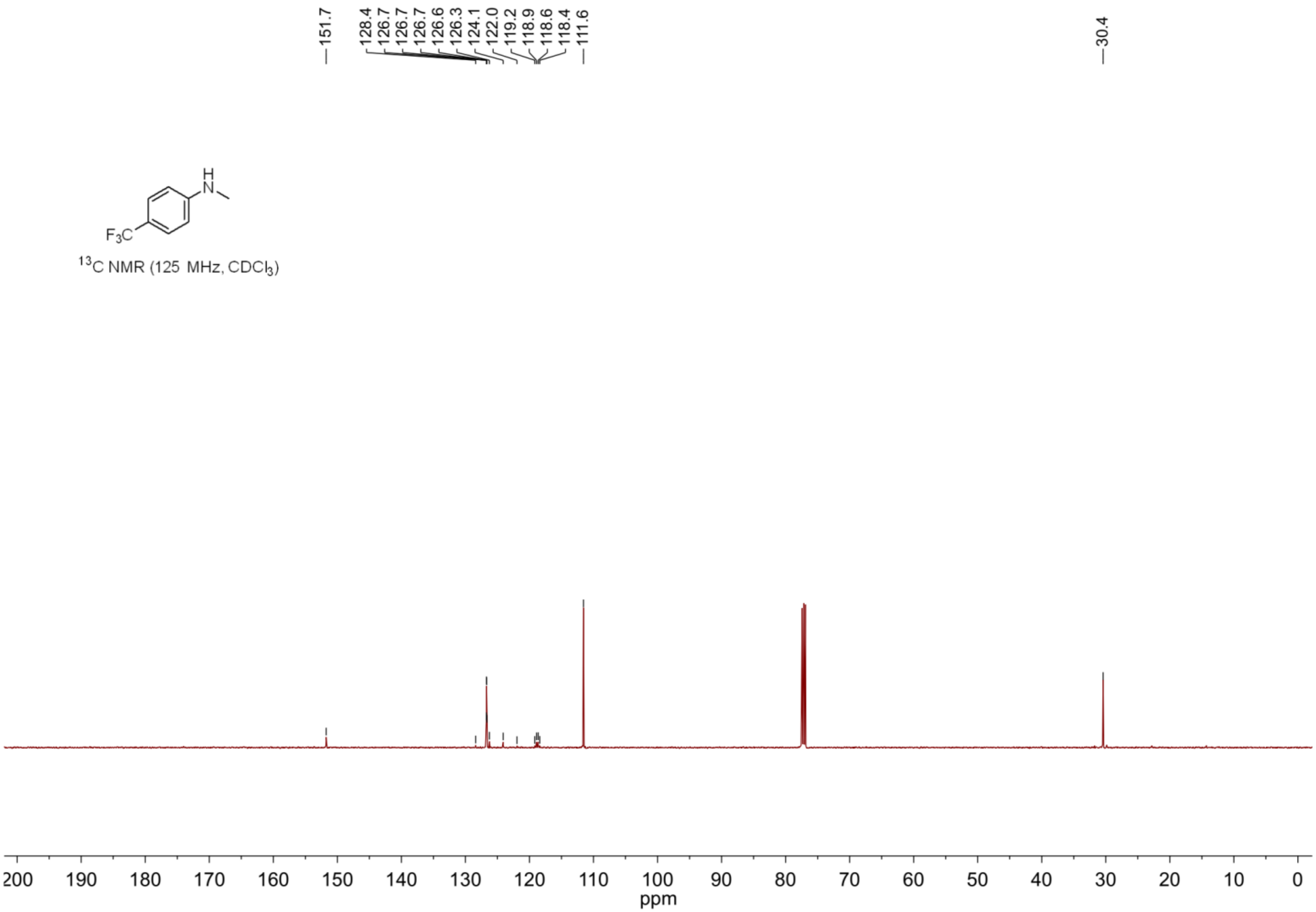
N-Methyl-4-(trifluoromethyl)aniline (10)



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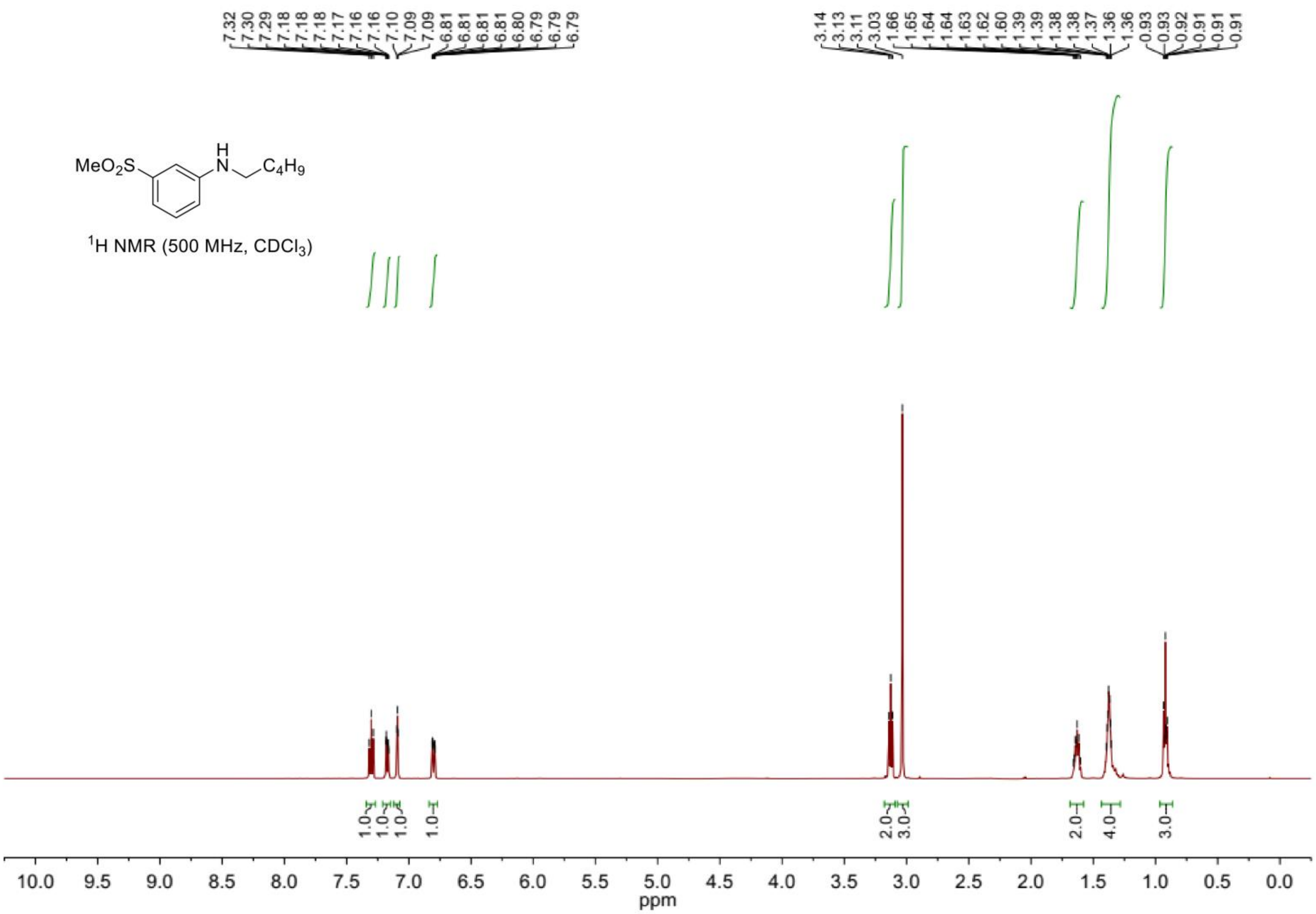
3-(Methylsulfonyl)-*N*-pentylaniline (11)



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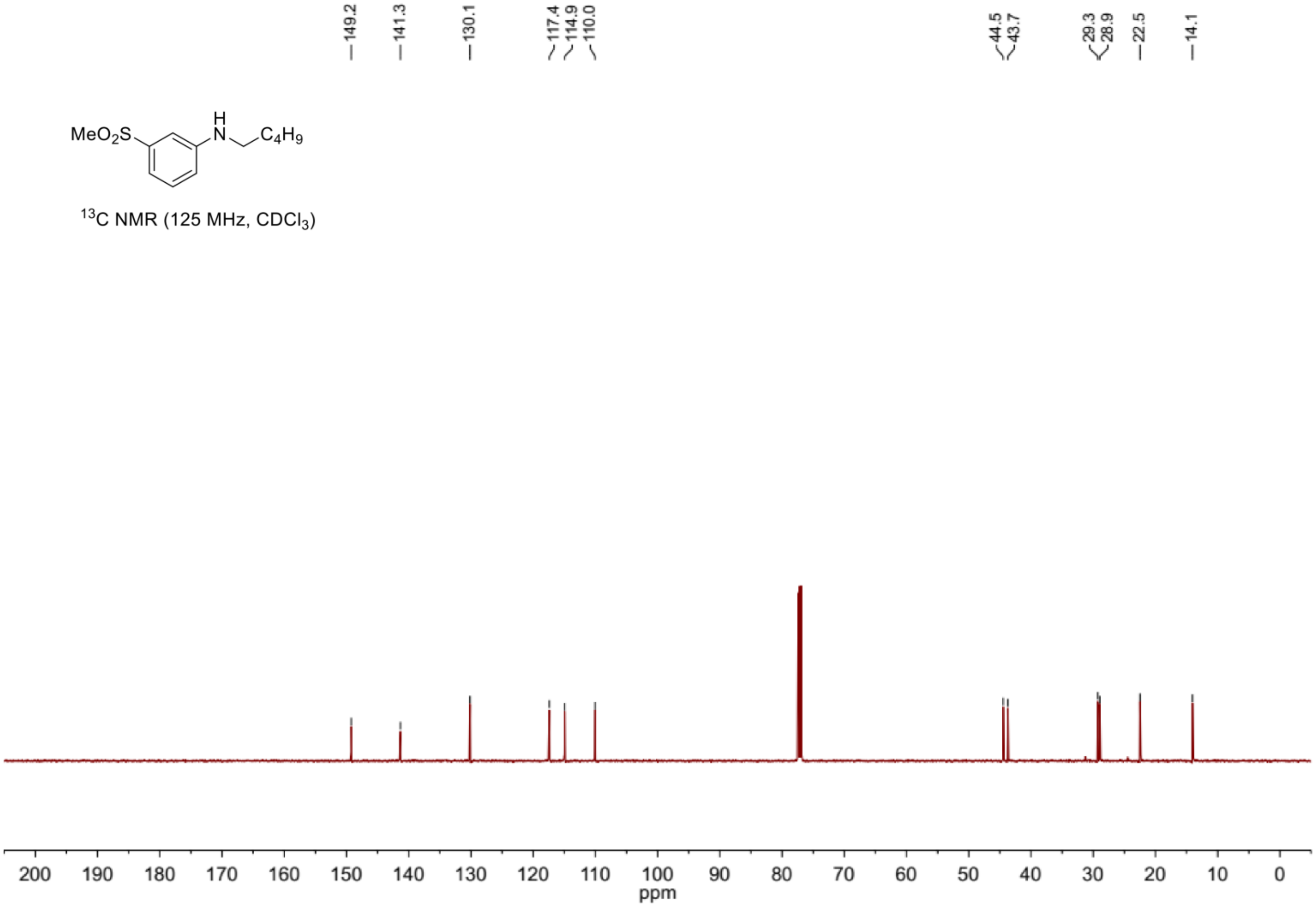
3-(Methylsulfonyl)-*N*-pentylaniline (11)



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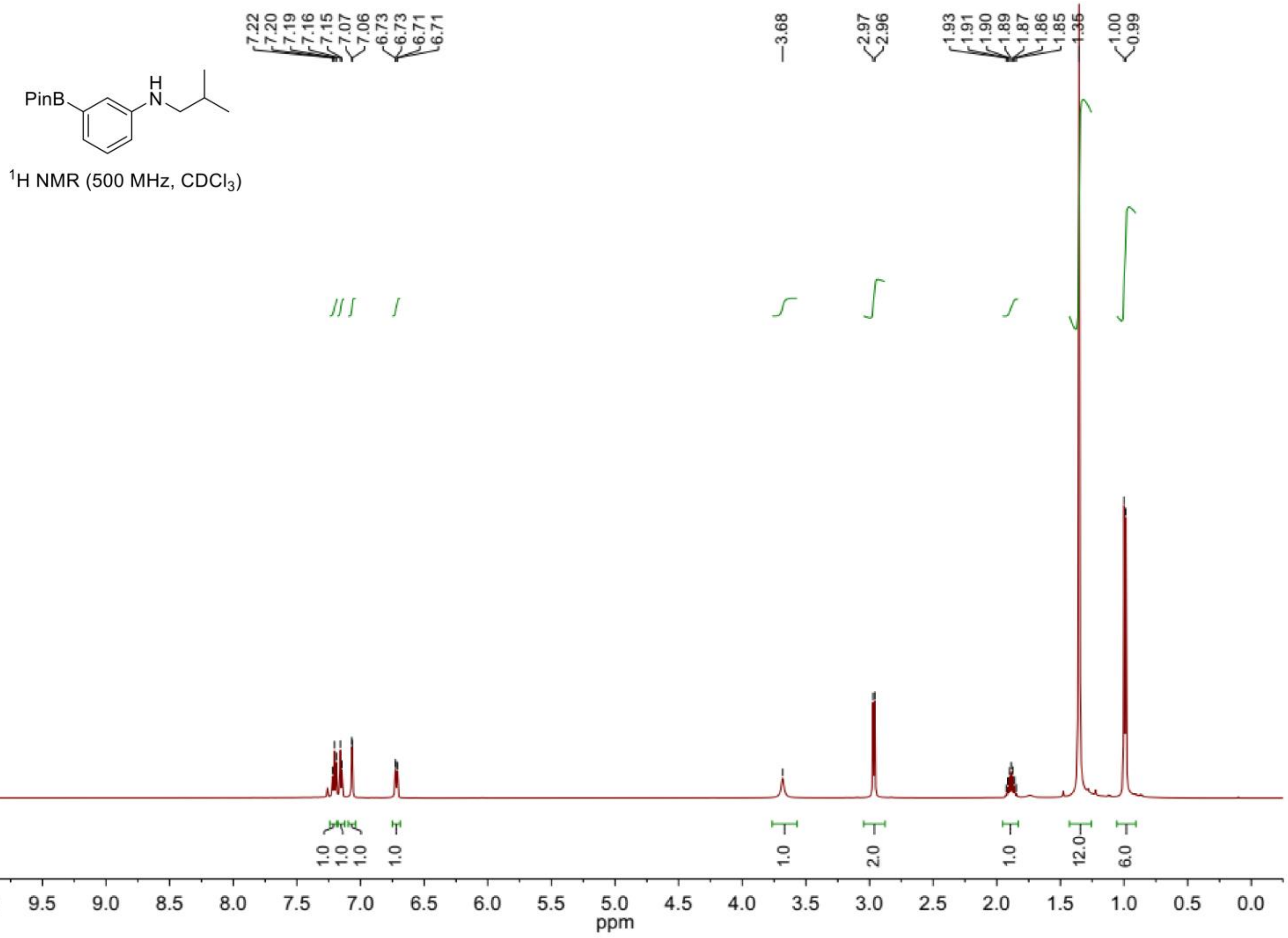
N-Isobutyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (12)



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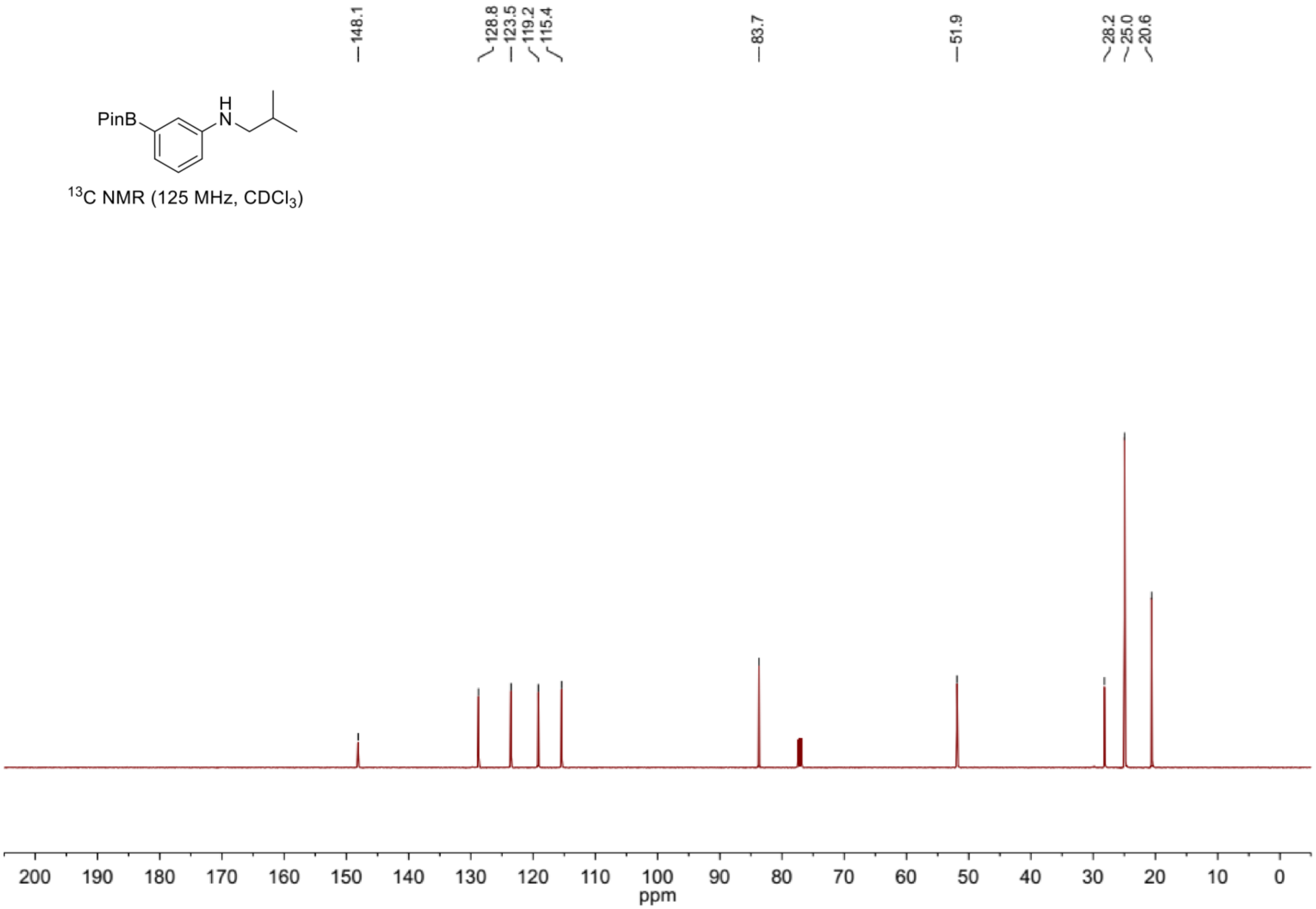
N-Isobutyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (12)



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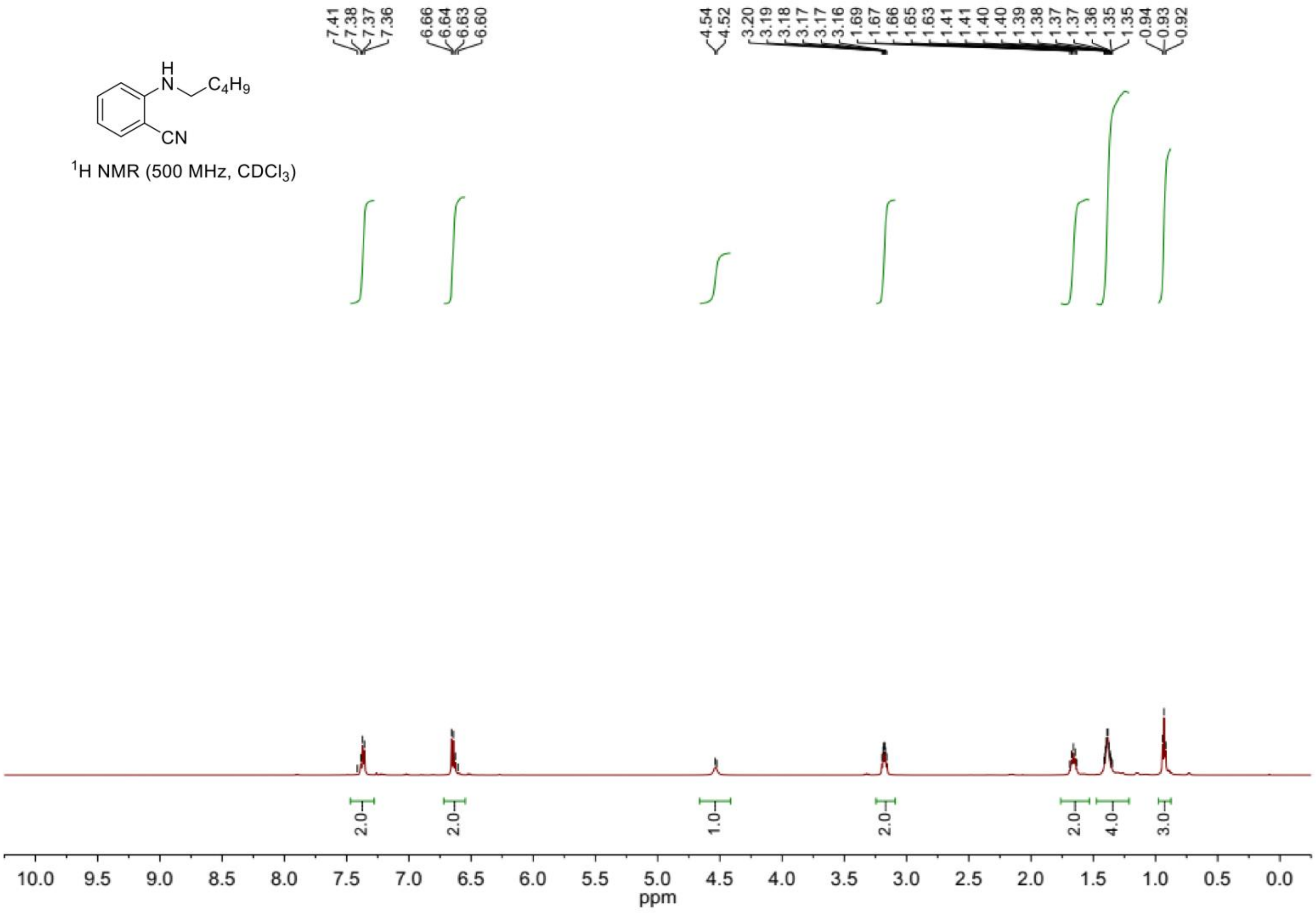
2-(Pentylamino)benzonitrile (13)



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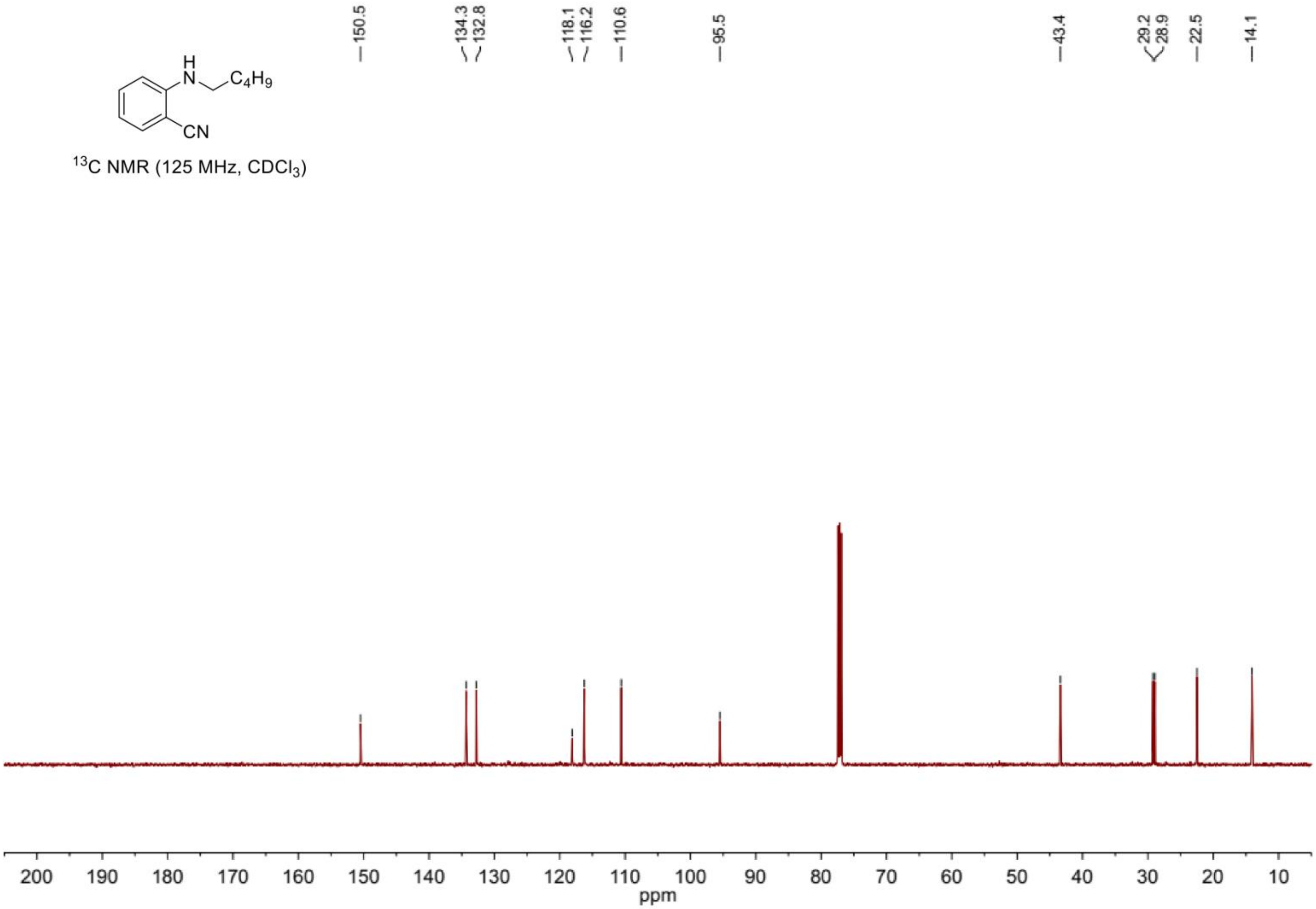
2-(Pentylamino)benzonitrile (13)



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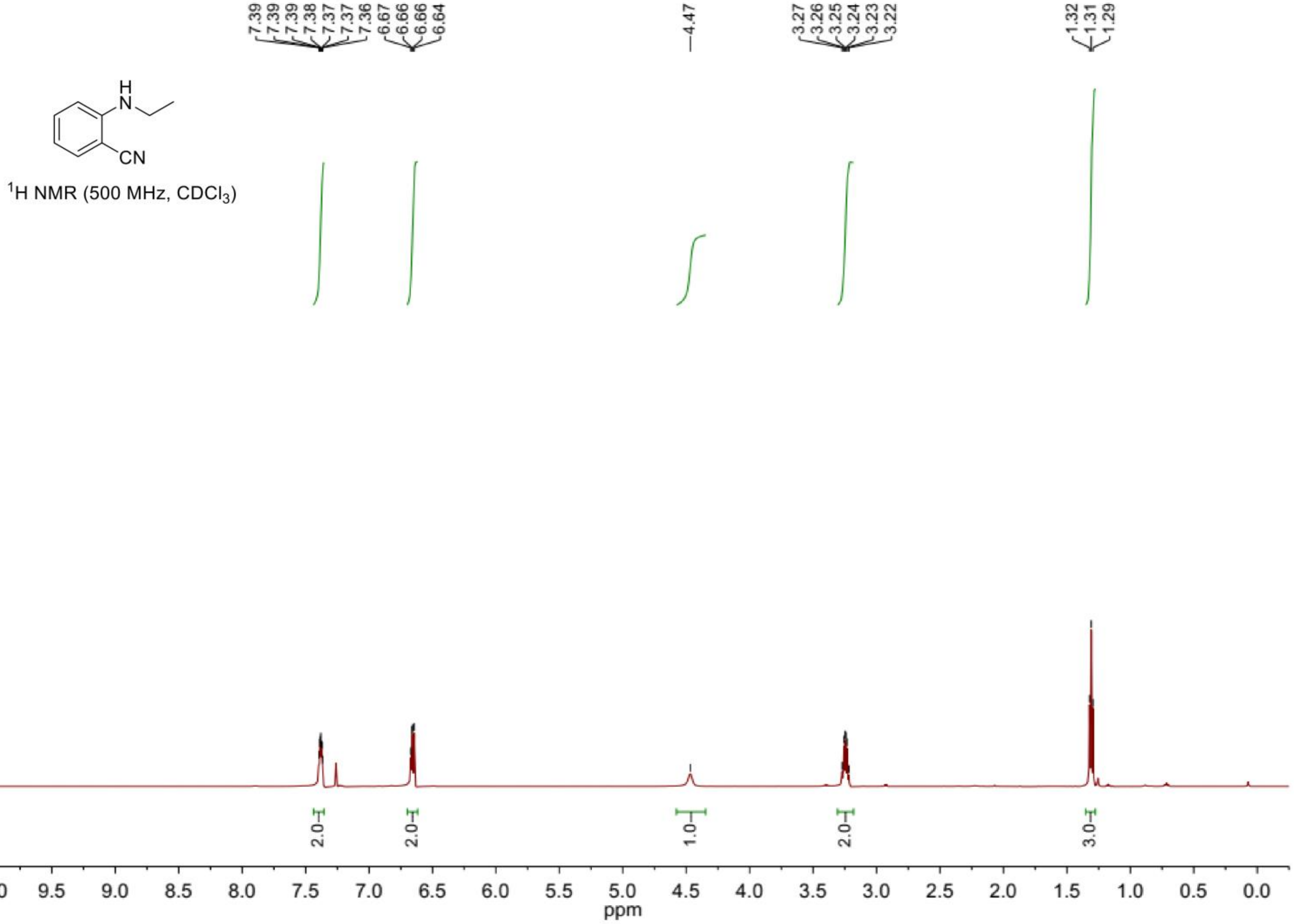
2-(Ethylamino)benzonitrile (14)



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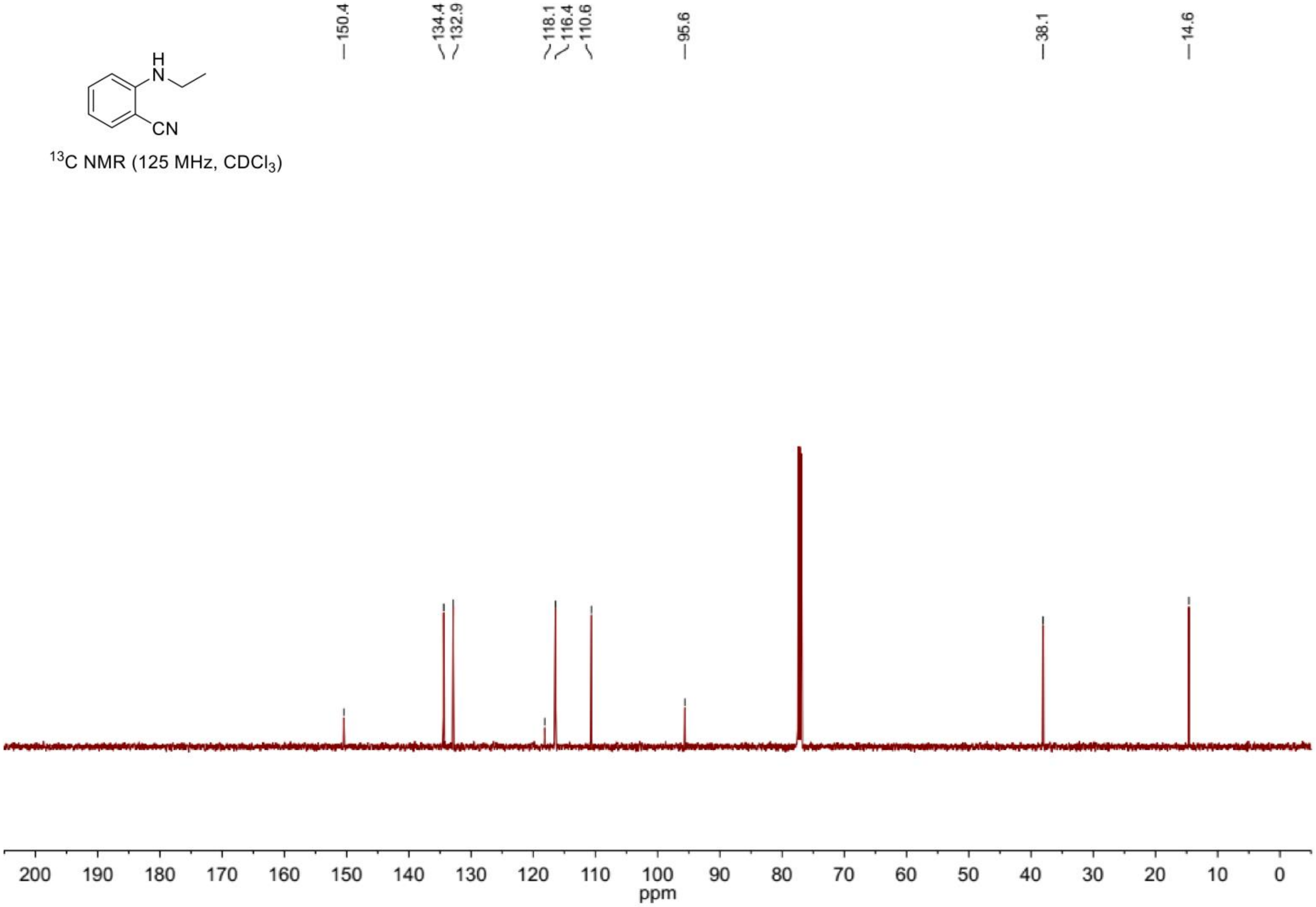
2-(Ethylamino)benzonitrile (14)



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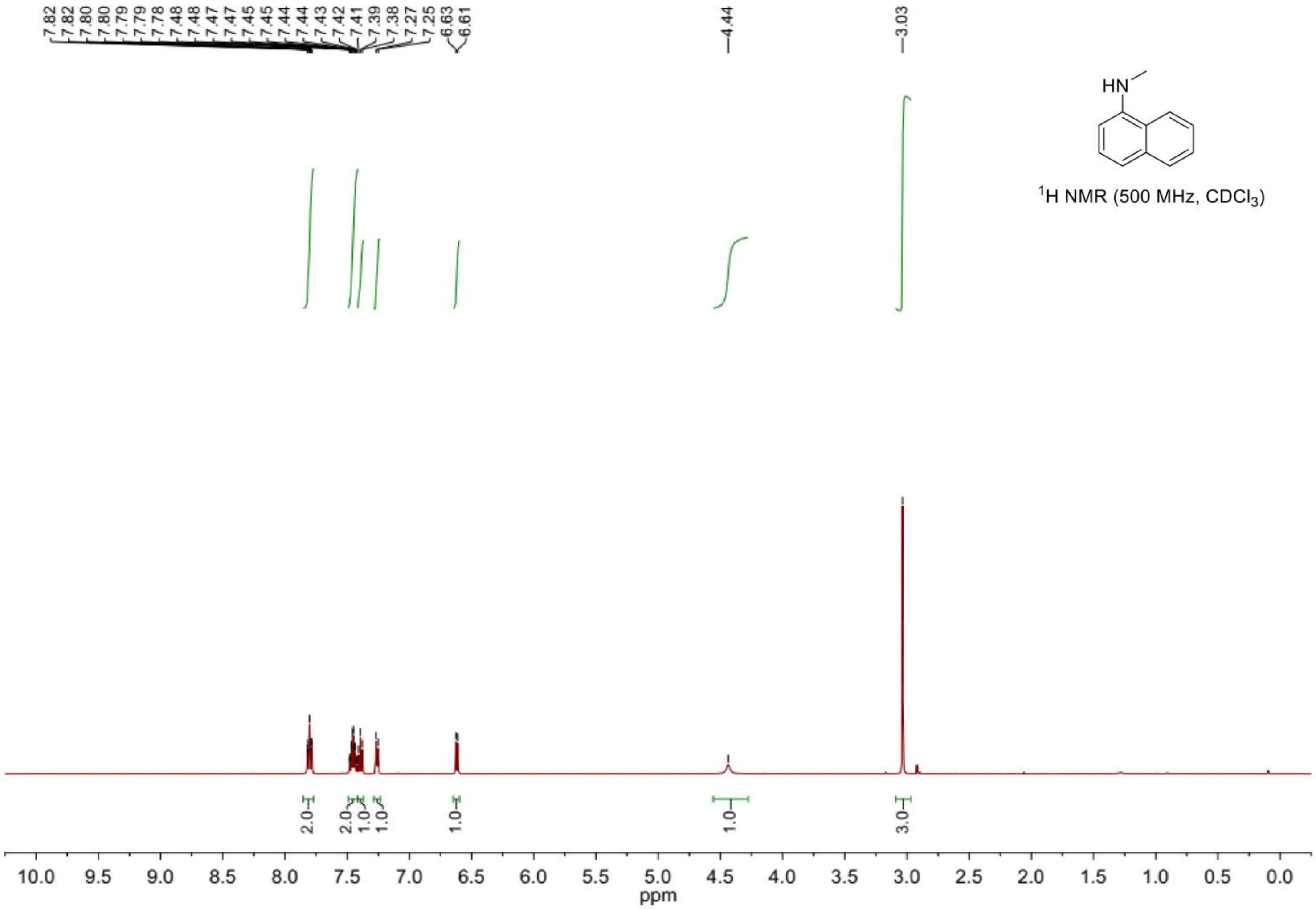
N-methylnaphthalen-1-amine (15)



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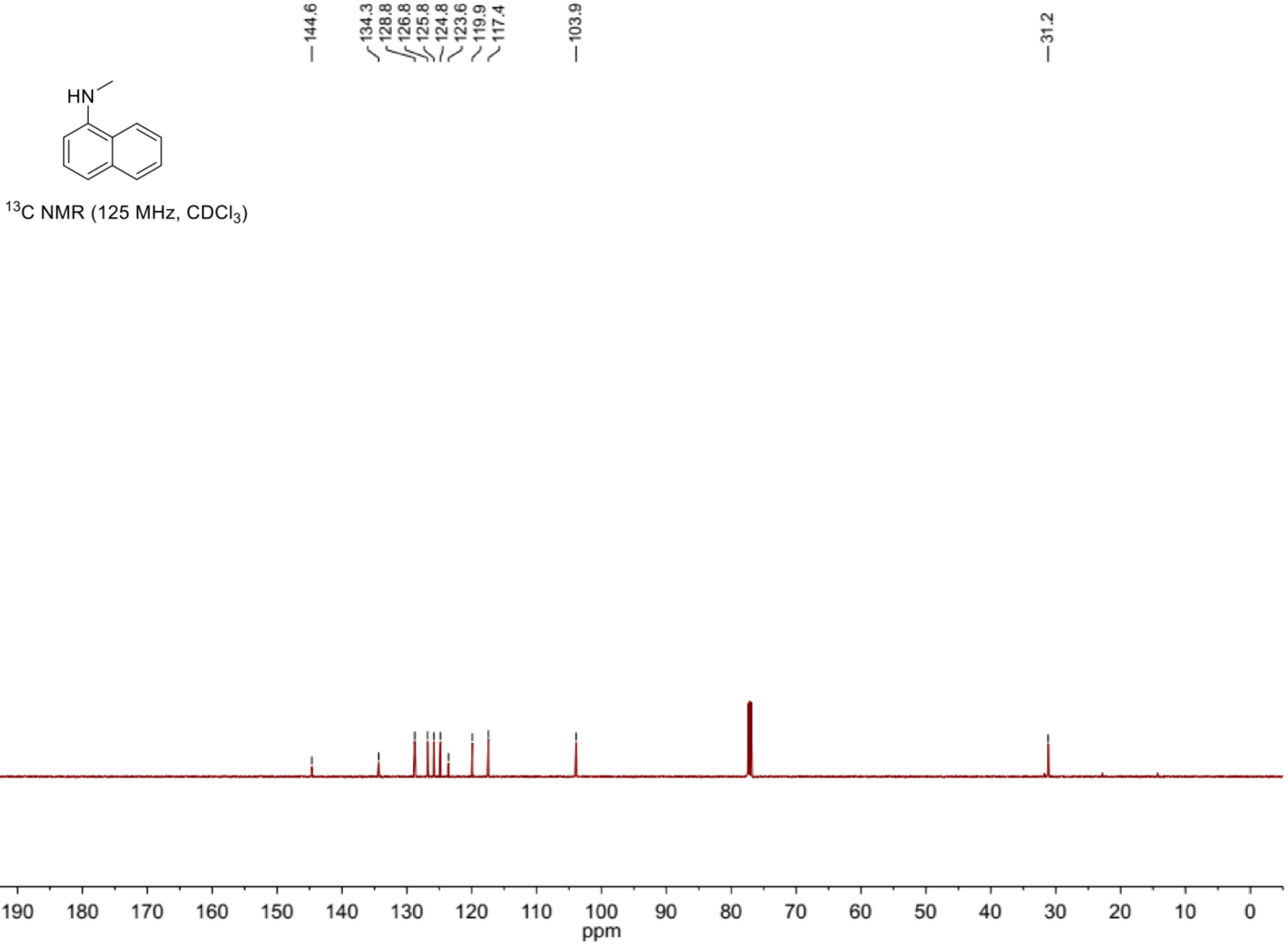
N-methylnaphthalen-1-amine (15)



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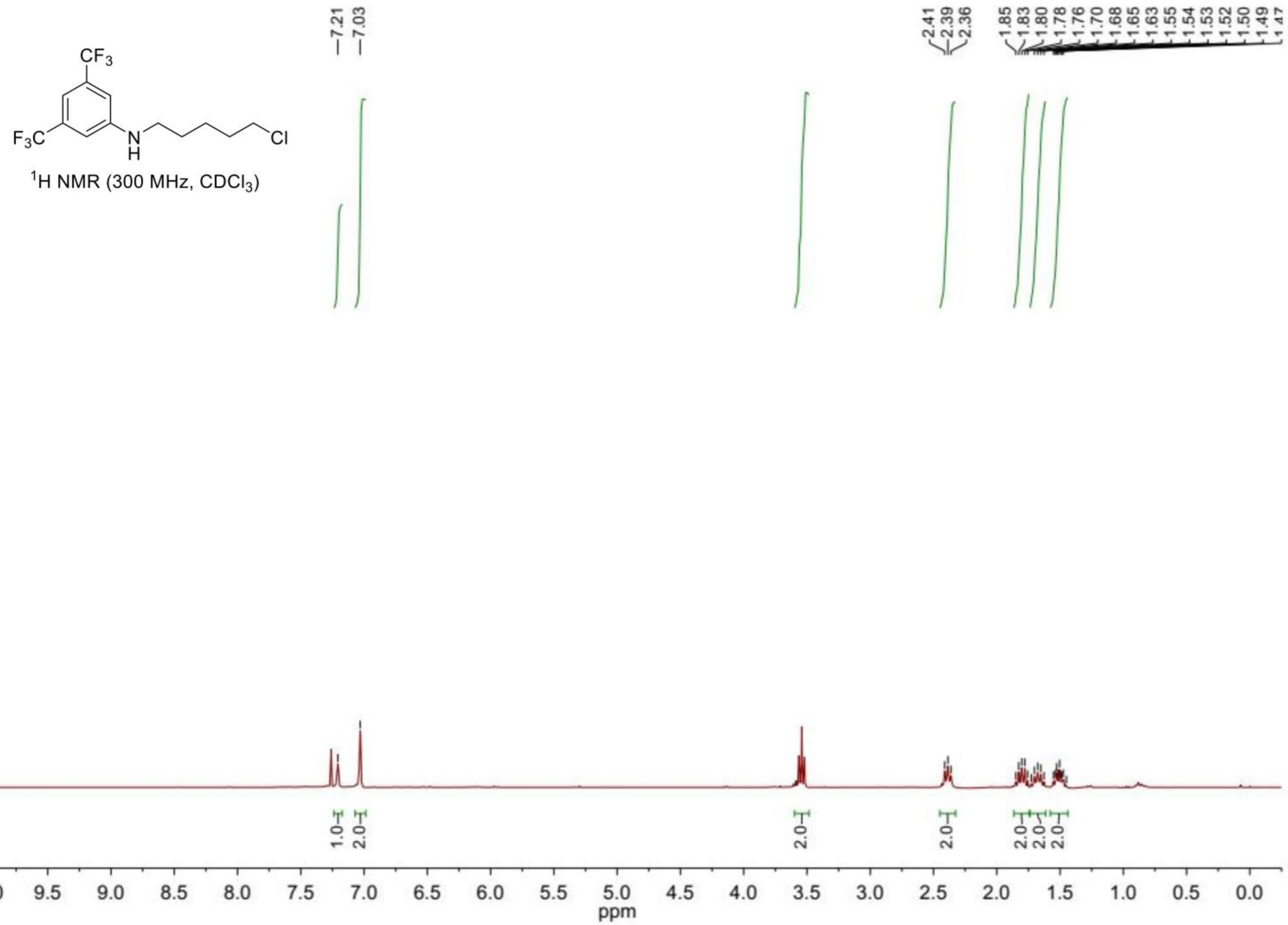
N-(5-Chloropentyl)-3,5-bis(trifluoromethyl)aniline (16)



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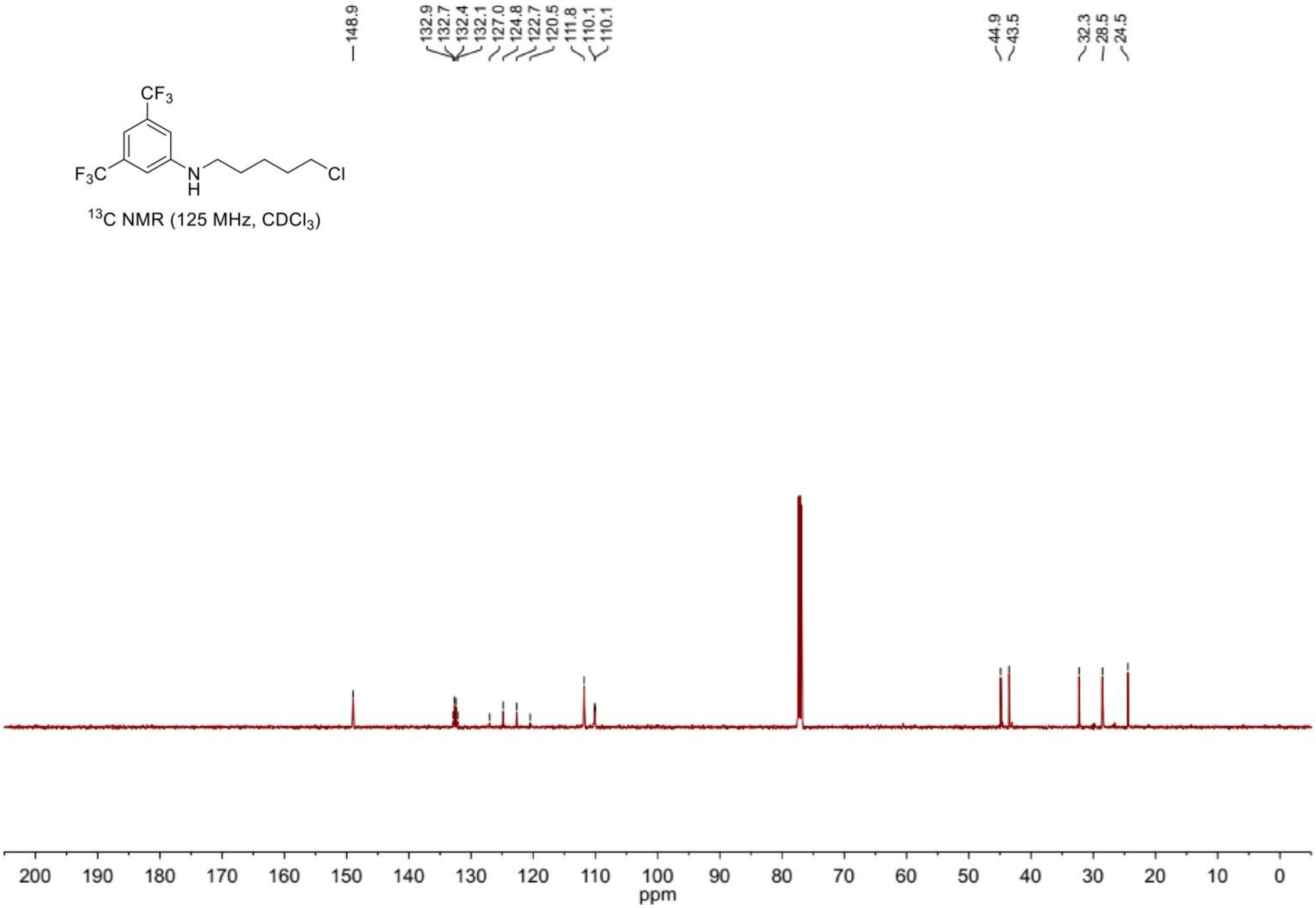
N-(5-Chloropentyl)-3,5-bis(trifluoromethyl)aniline (16)



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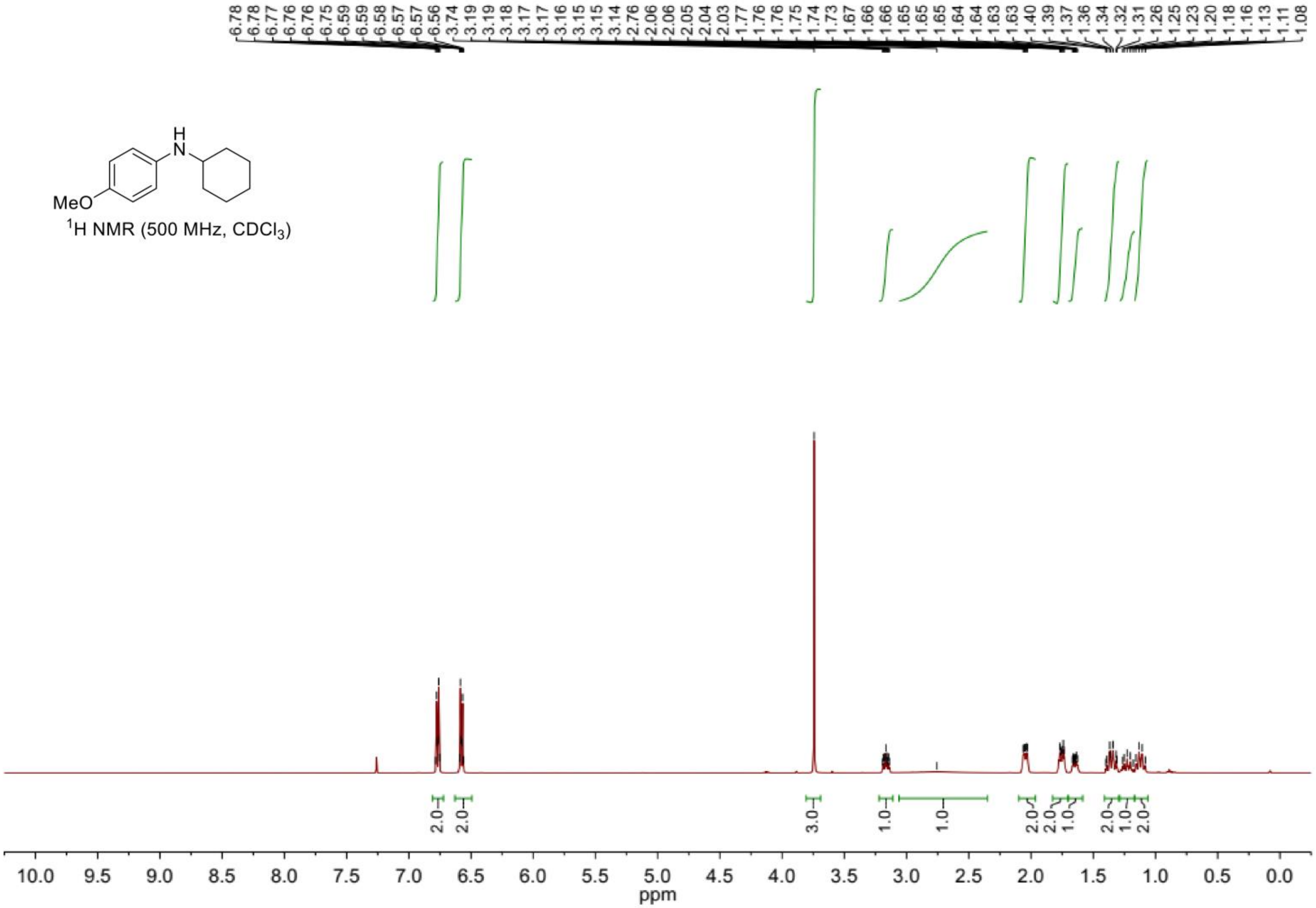
N-Cyclohexyl-4-methoxyaniline (17)



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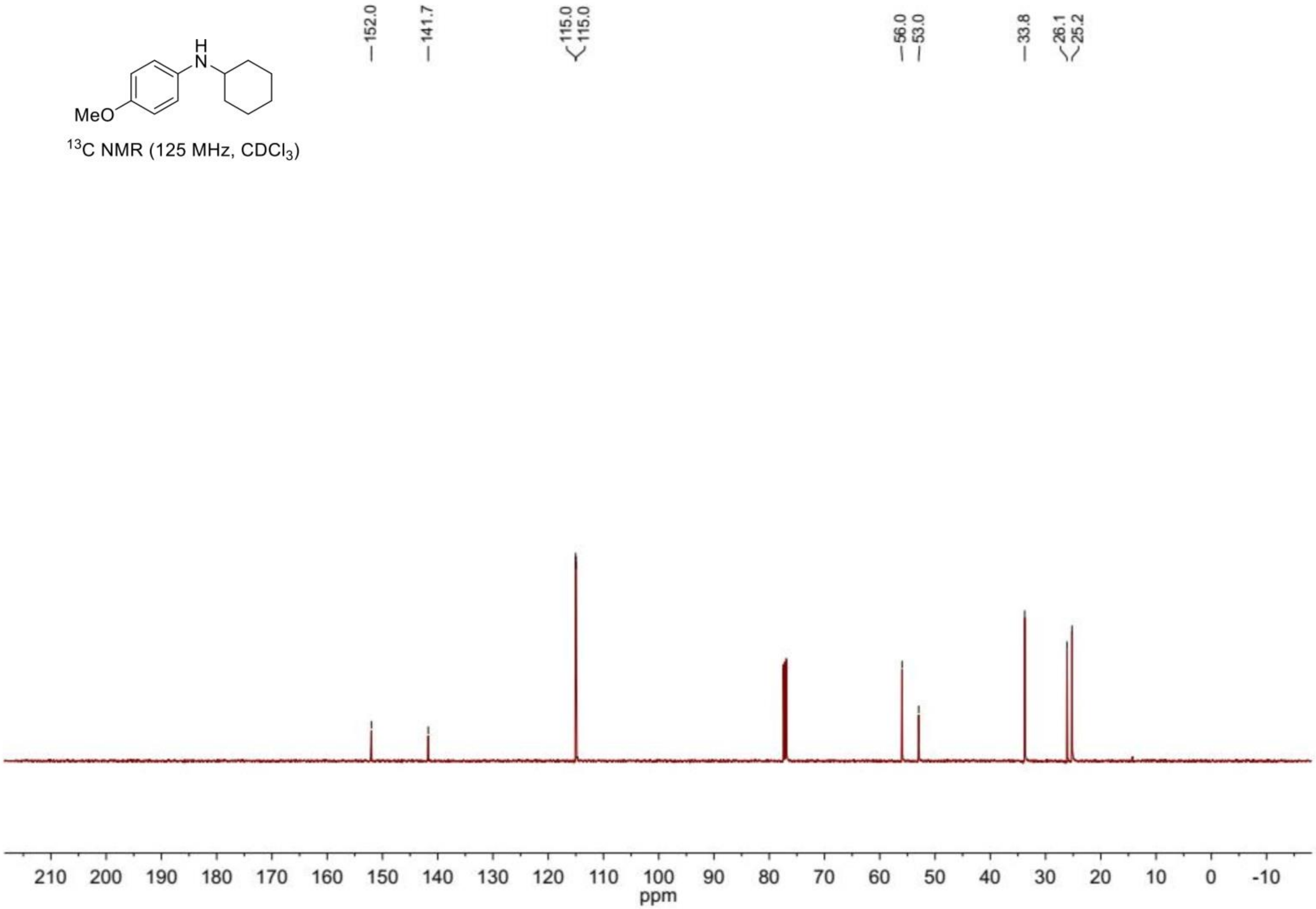
N-Cyclohexyl-4-methoxyaniline (17)



^{13}C NMR (125 MHz, CDCl$_3$)

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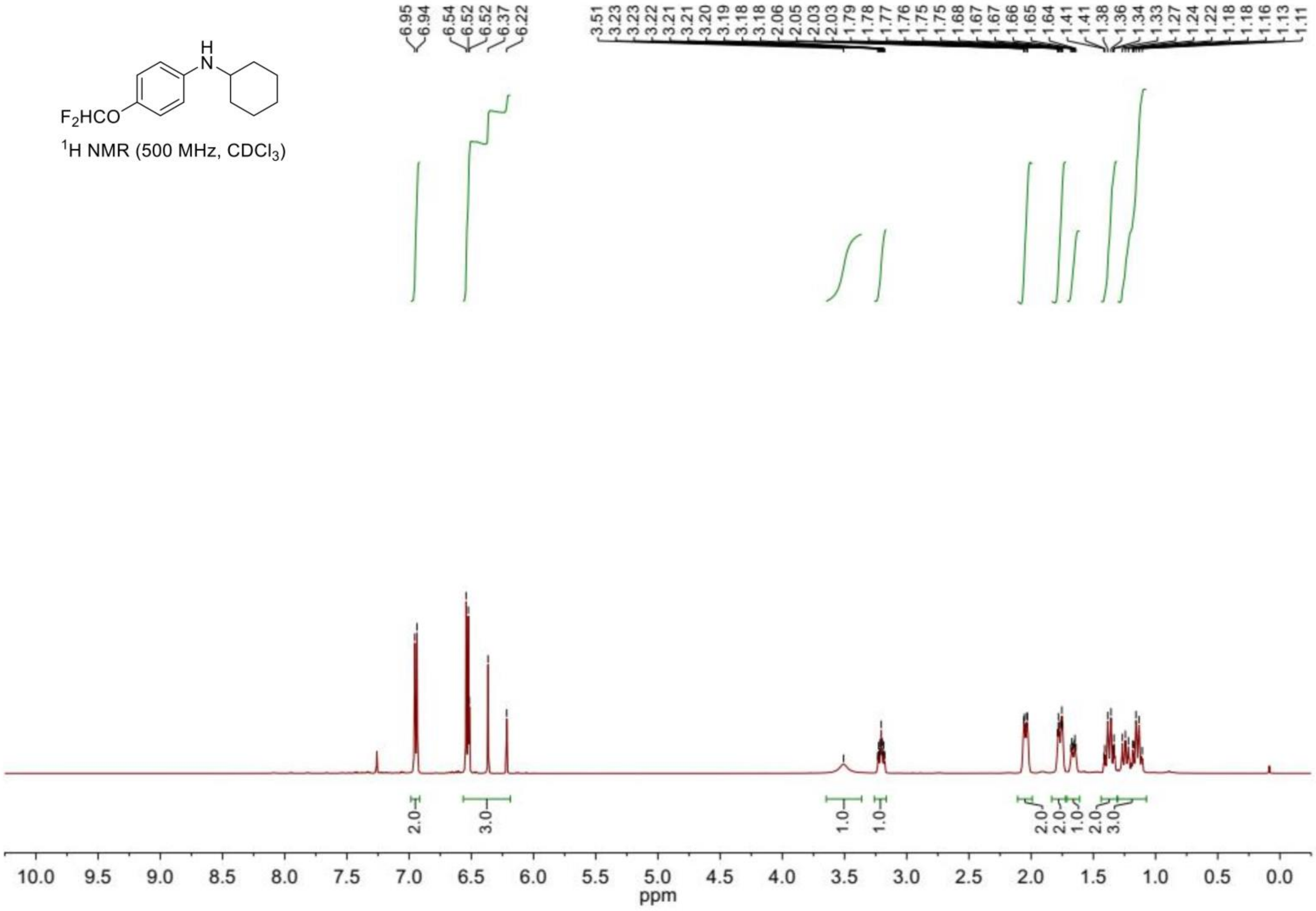
N-Cyclohexyl-4-(difluoromethoxy)aniline (18)



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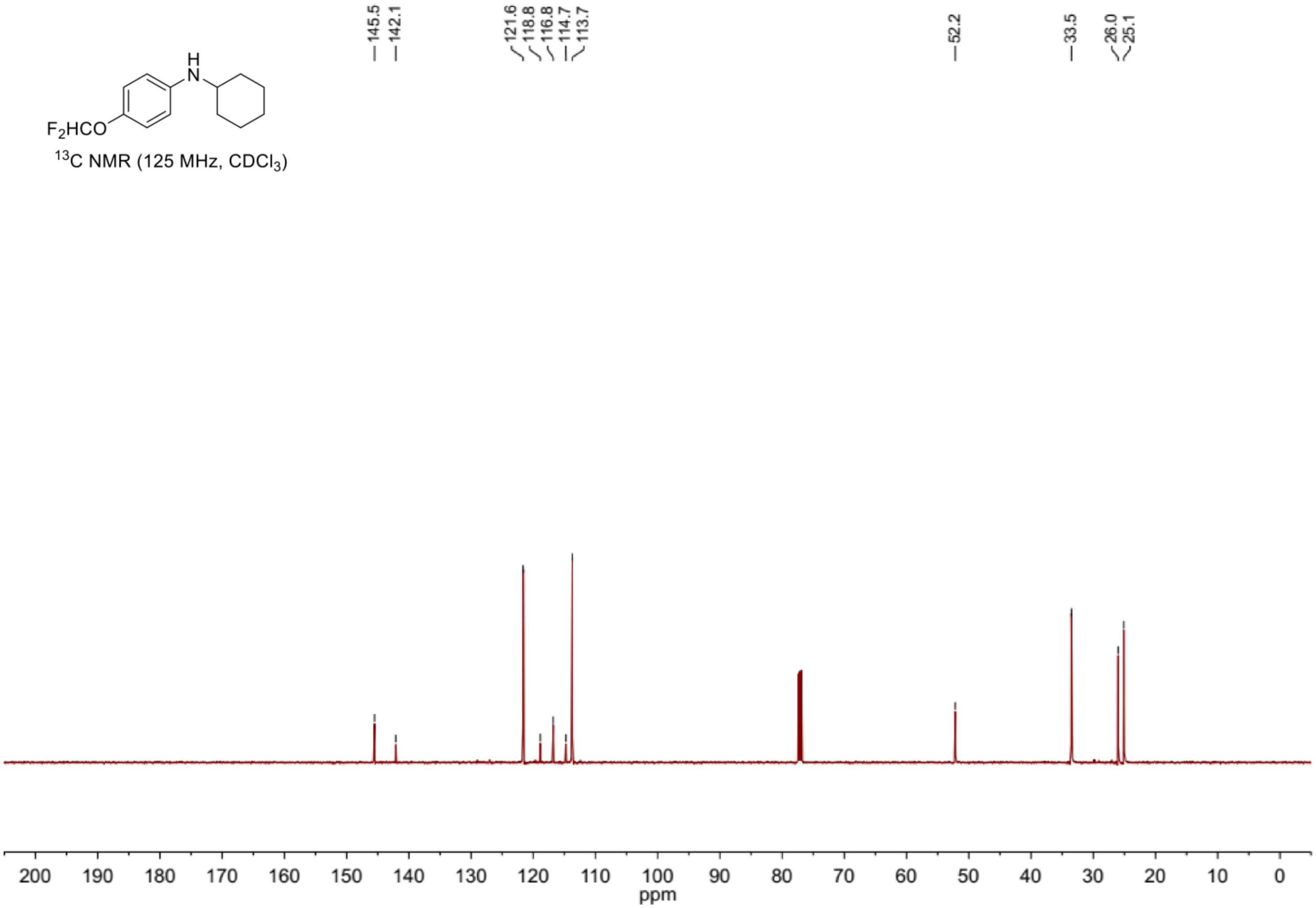
N-Cyclohexyl-4-(difluoromethoxy)aniline (18)



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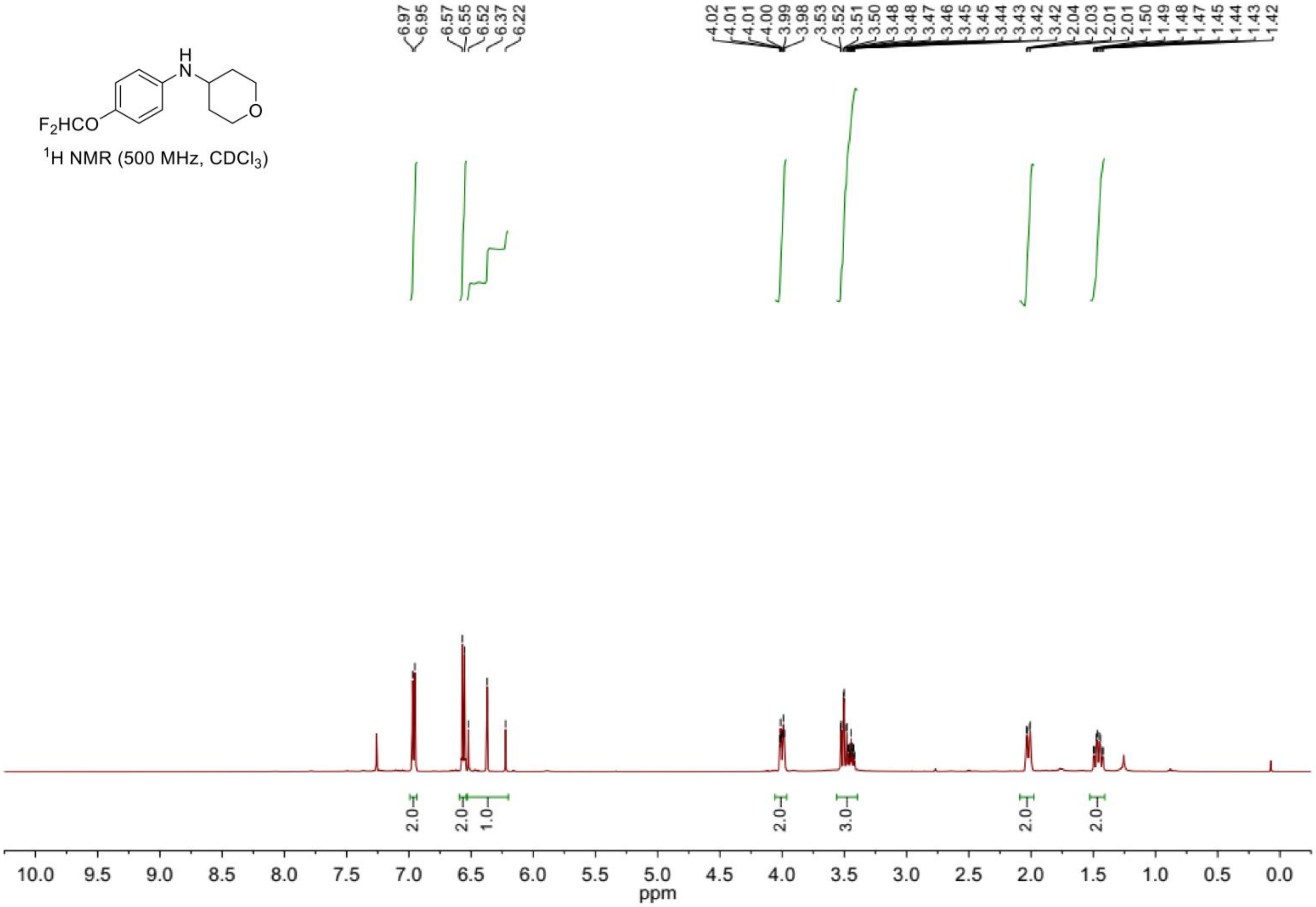
N-(4-(Difluoromethoxy)phenyl)tetrahydro-2*H*-pyran-4-amine (19)



^{1}H NMR (500 MHz, CDCl$_3$)

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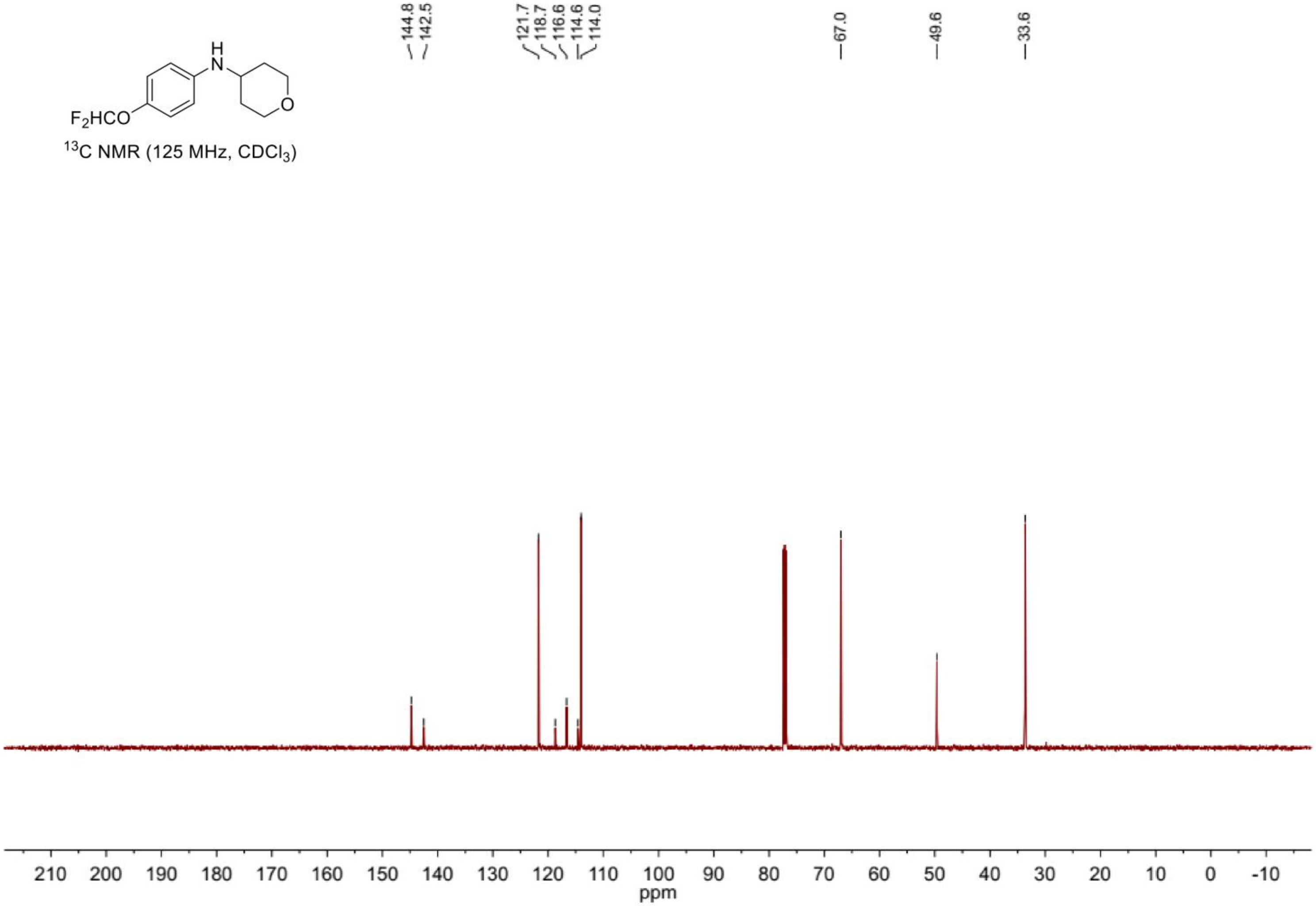
N-(4-(Difluoromethoxy)phenyl)tetrahydro-2*H*-pyran-4-amine (19)



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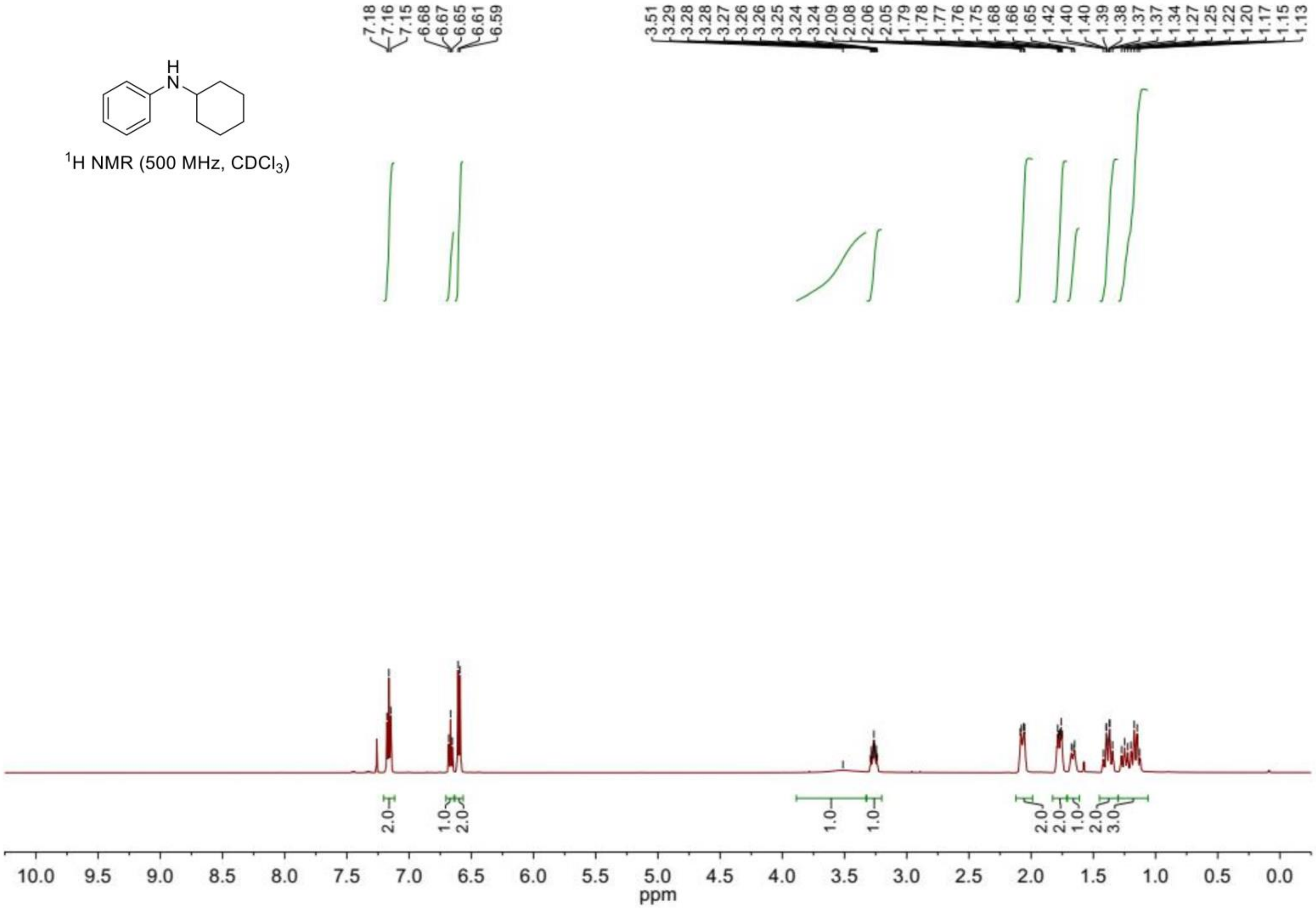
N-Cyclohexylaniline (20)



^{1}H NMR (500 MHz, CDCl$_3$)

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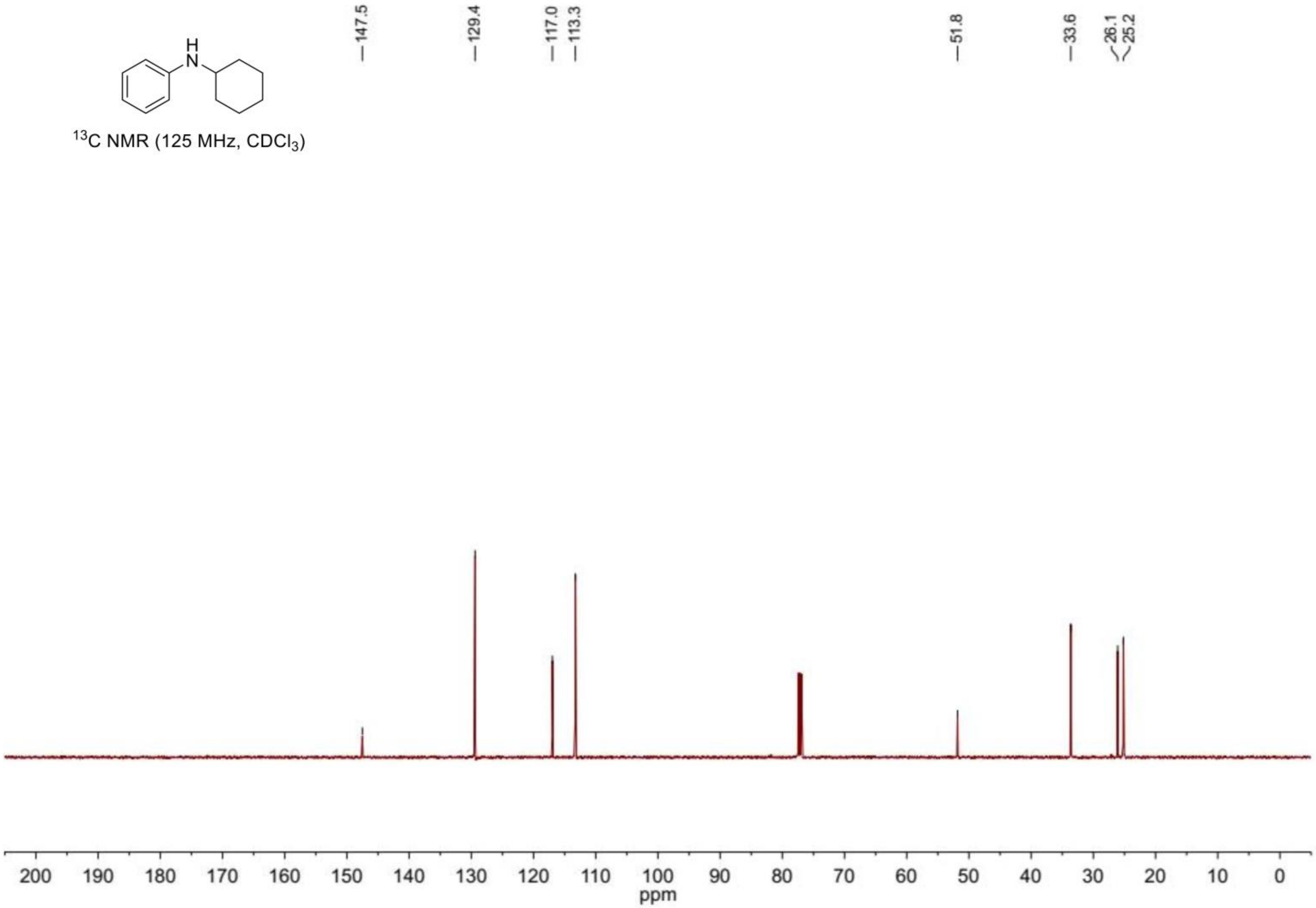
N-Cyclohexylaniline (20)



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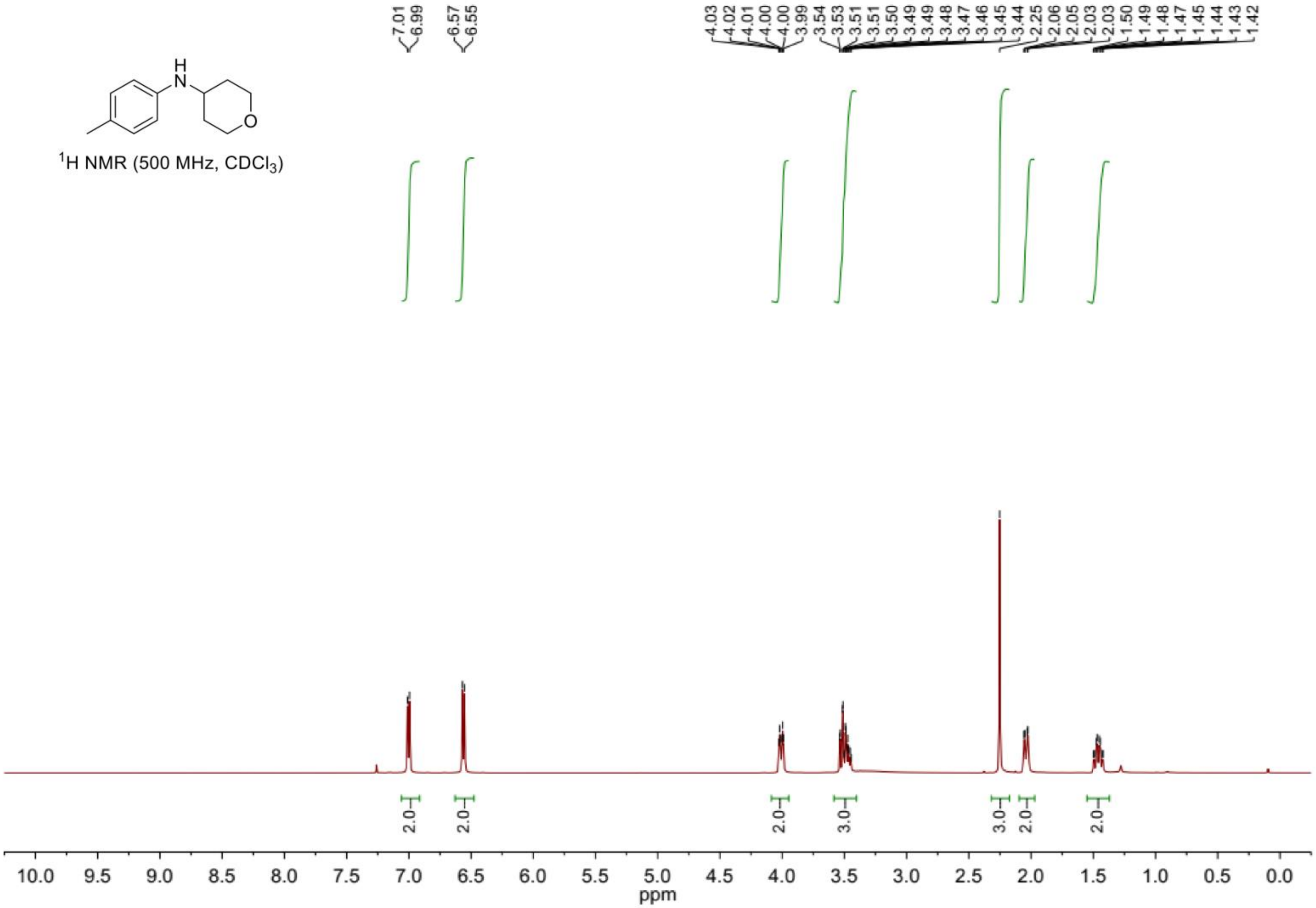
N-(*p*-Tolyl)tetrahydro-2*H*-pyran-4-amine (21)



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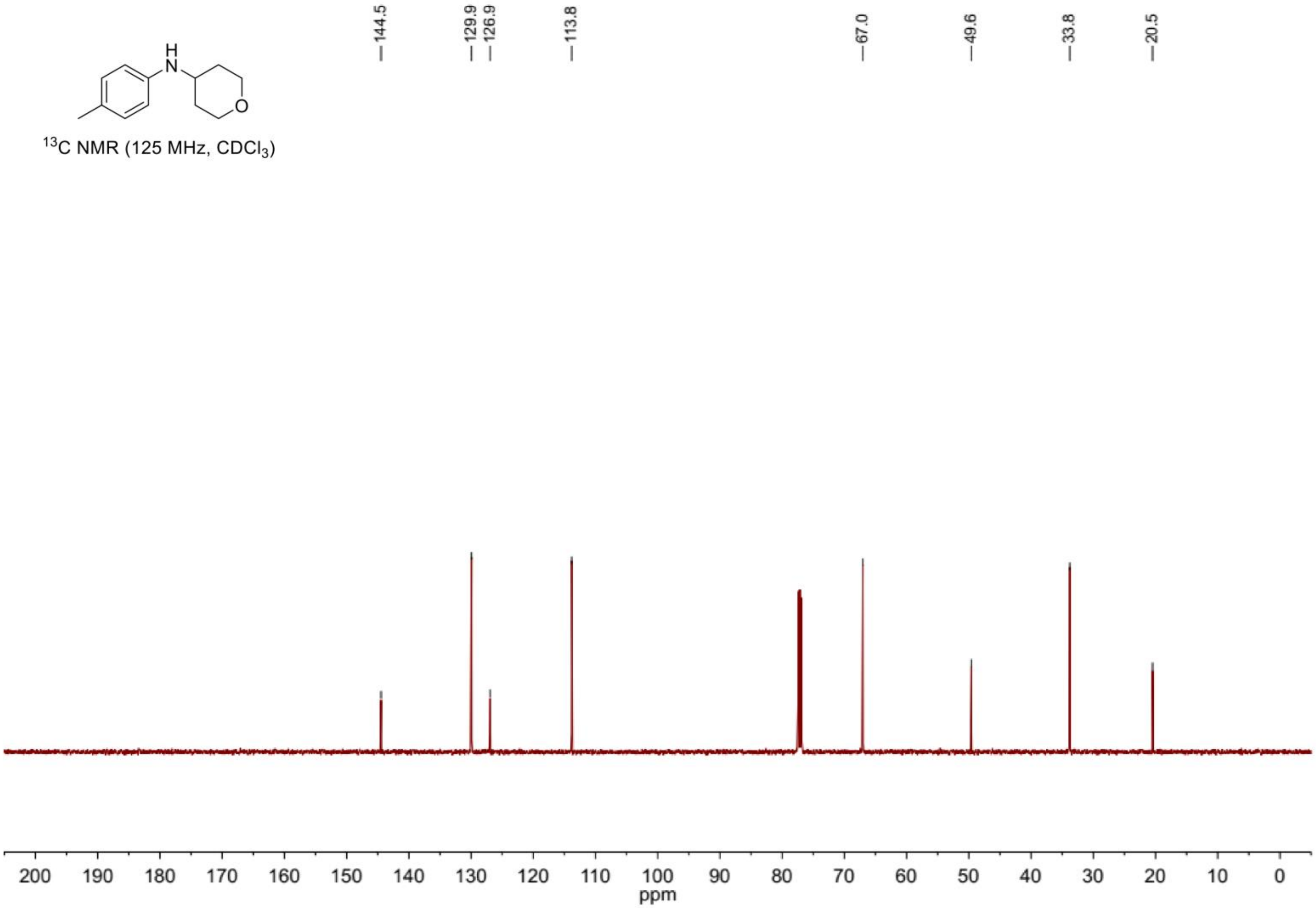
N-(*p*-Tolyl)tetrahydro-2*H*-pyran-4-amine (21)

^{13}C NMR (125 MHz, CDCl$_3$)



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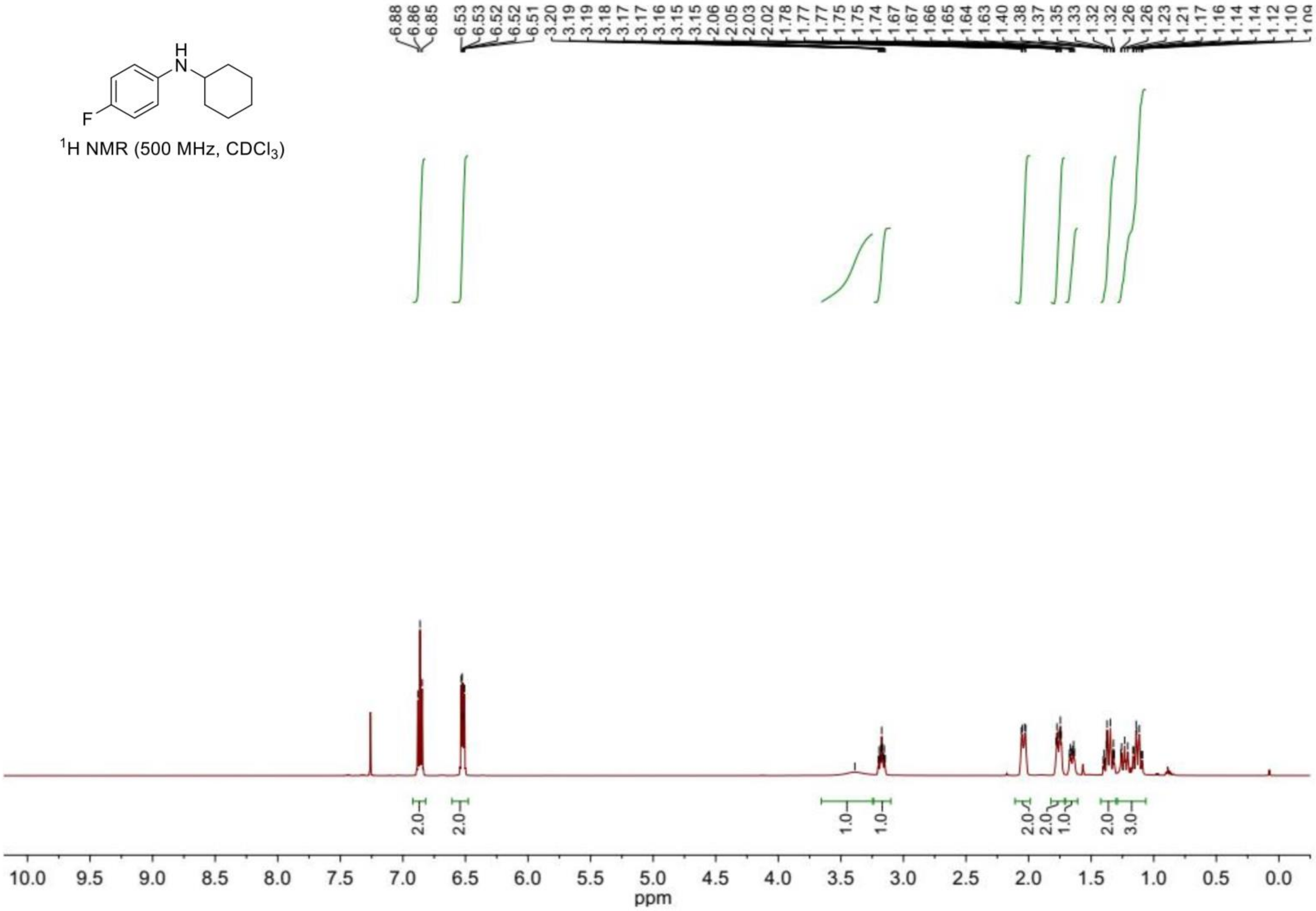
N-Cyclohexyl-4-fluoroaniline (22)



^{1}H NMR (500 MHz, CDCl$_3$)

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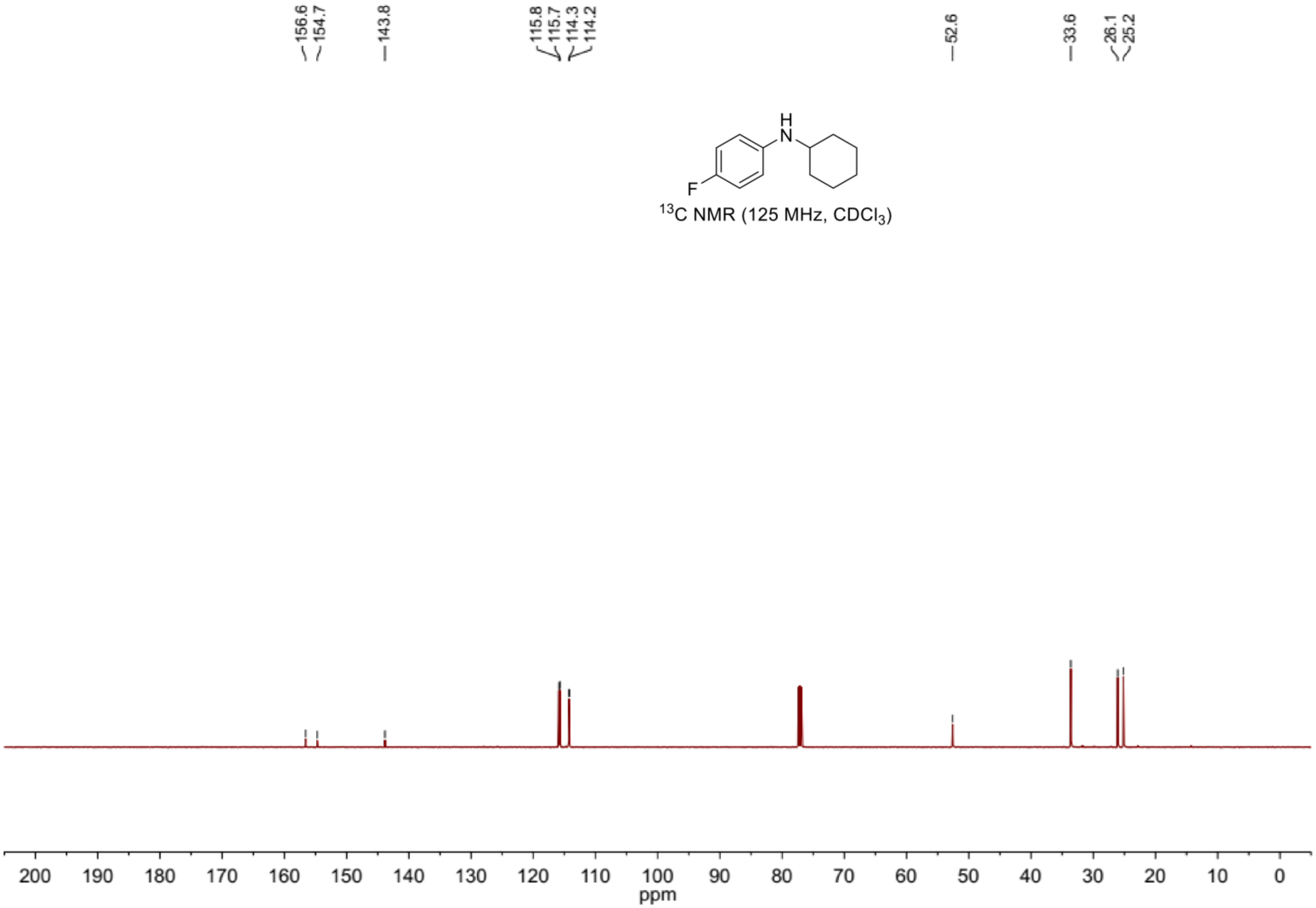
N-Cyclohexyl-4-fluoroaniline (22)



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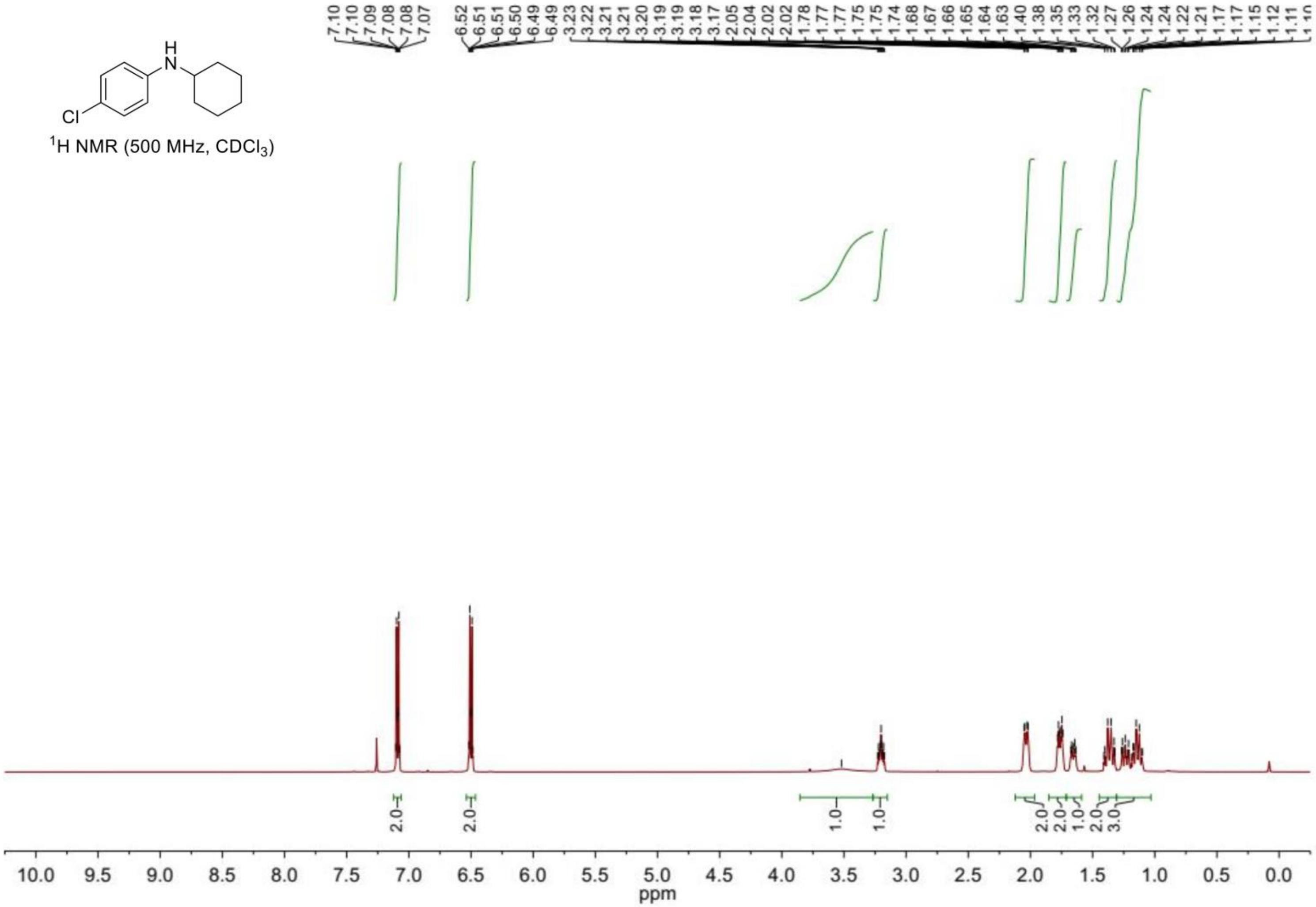
4-Chloro-*N*-cyclohexylaniline (23)



^{1}H NMR (500 MHz, CDCl$_3$)

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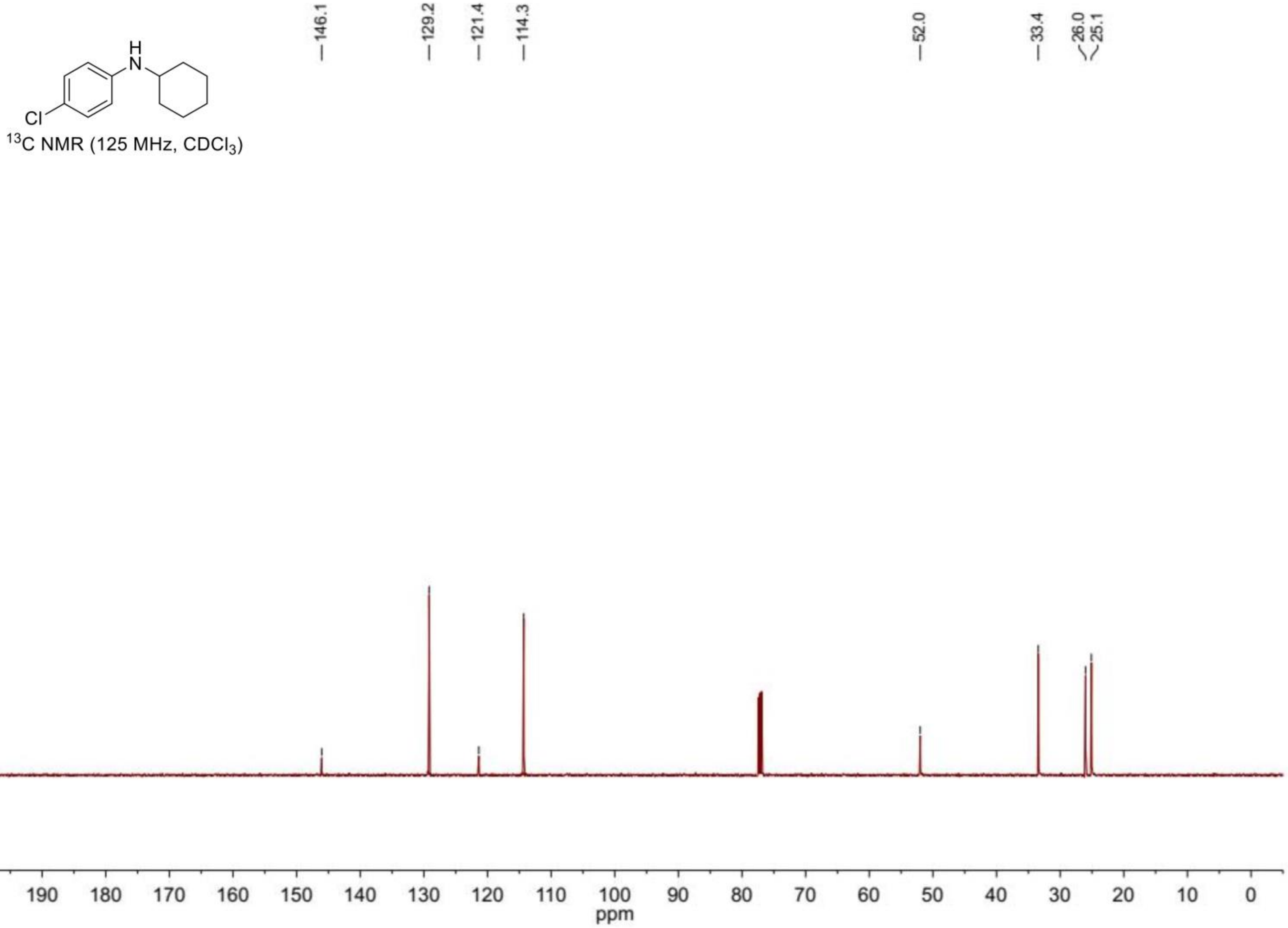
4-Chloro-*N*-cyclohexylaniline (23)



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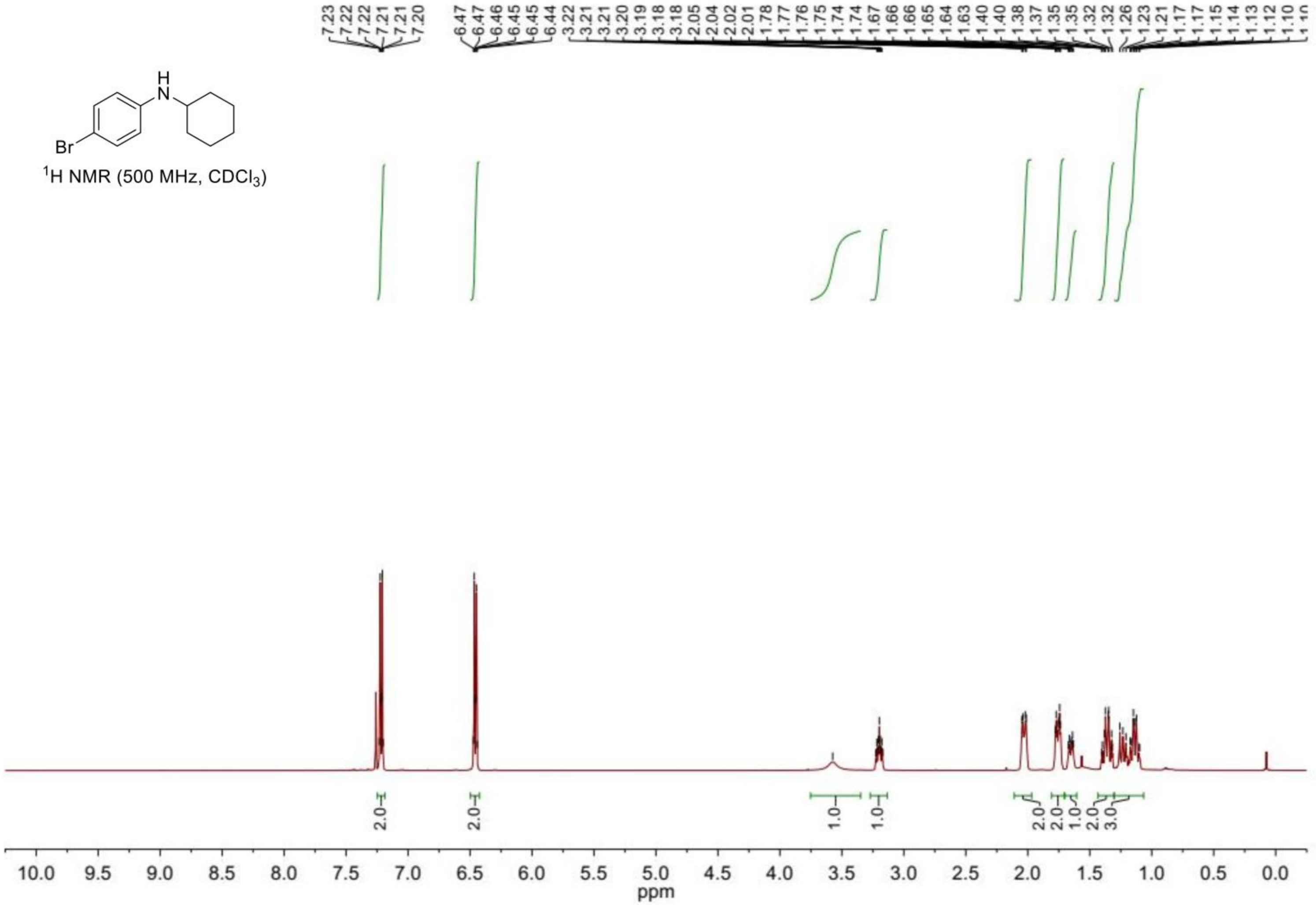
4-Bromo-*N*-cyclohexylaniline (24)



^{1}H NMR (500 MHz, CDCl$_3$)

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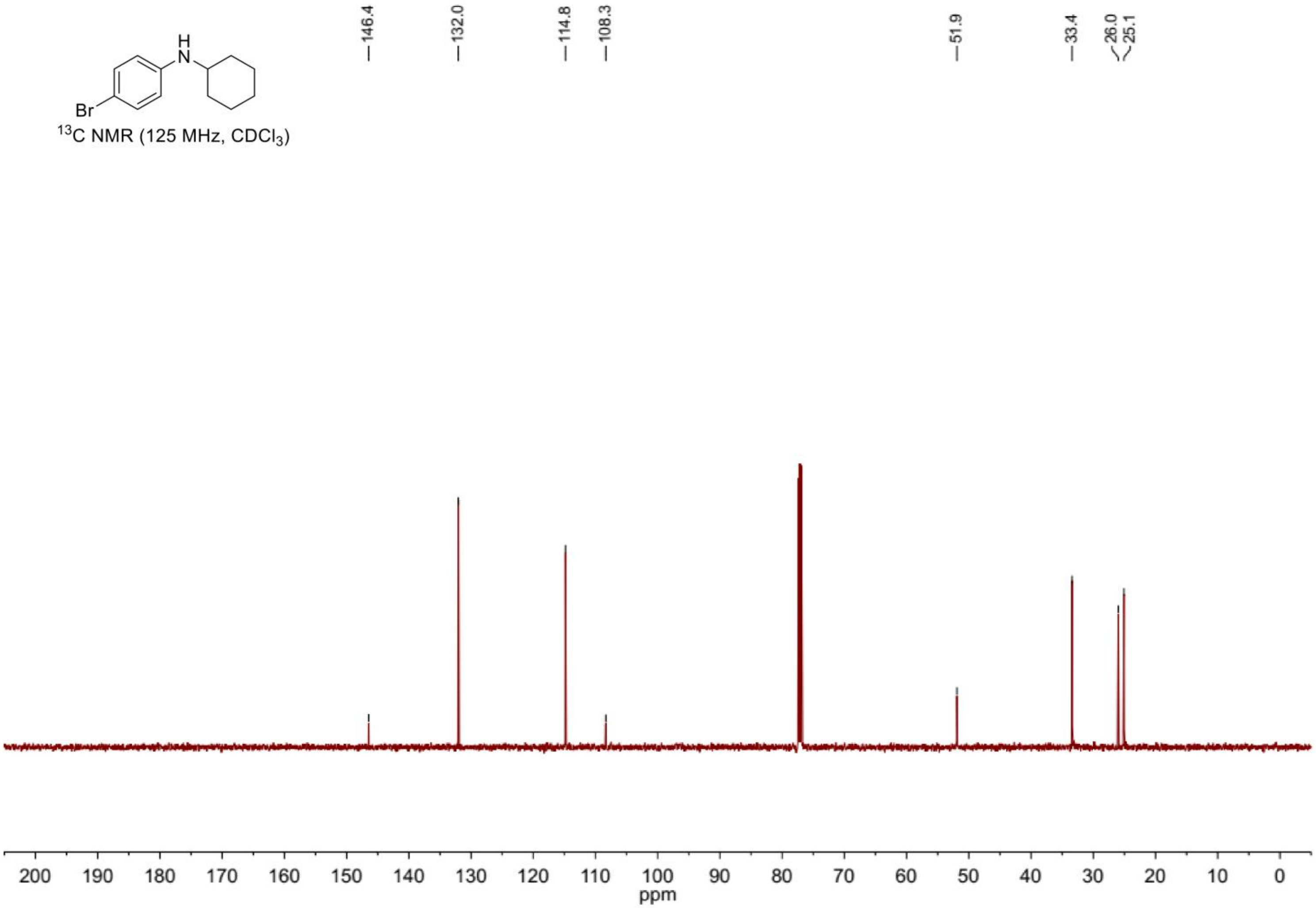
4-Bromo-*N*-cyclohexylaniline (24)



^{13}C NMR (125 MHz, $CDCl_3$)

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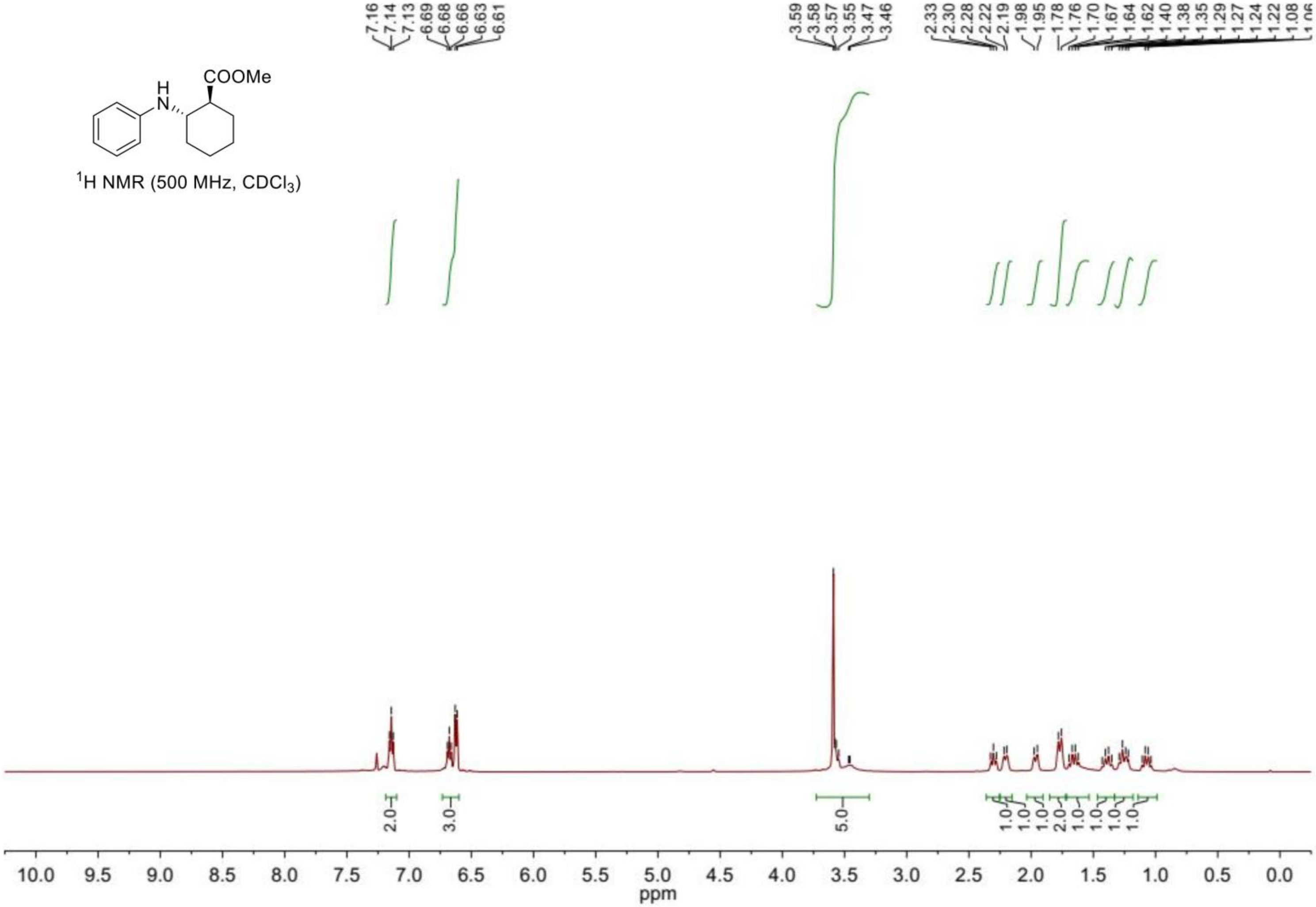
Methyl (1*S**,2*S**)-2-(phenylamino)cyclohexane-1-carboxylate (25)

^{1}H NMR (500 MHz, $CDCl_3$)



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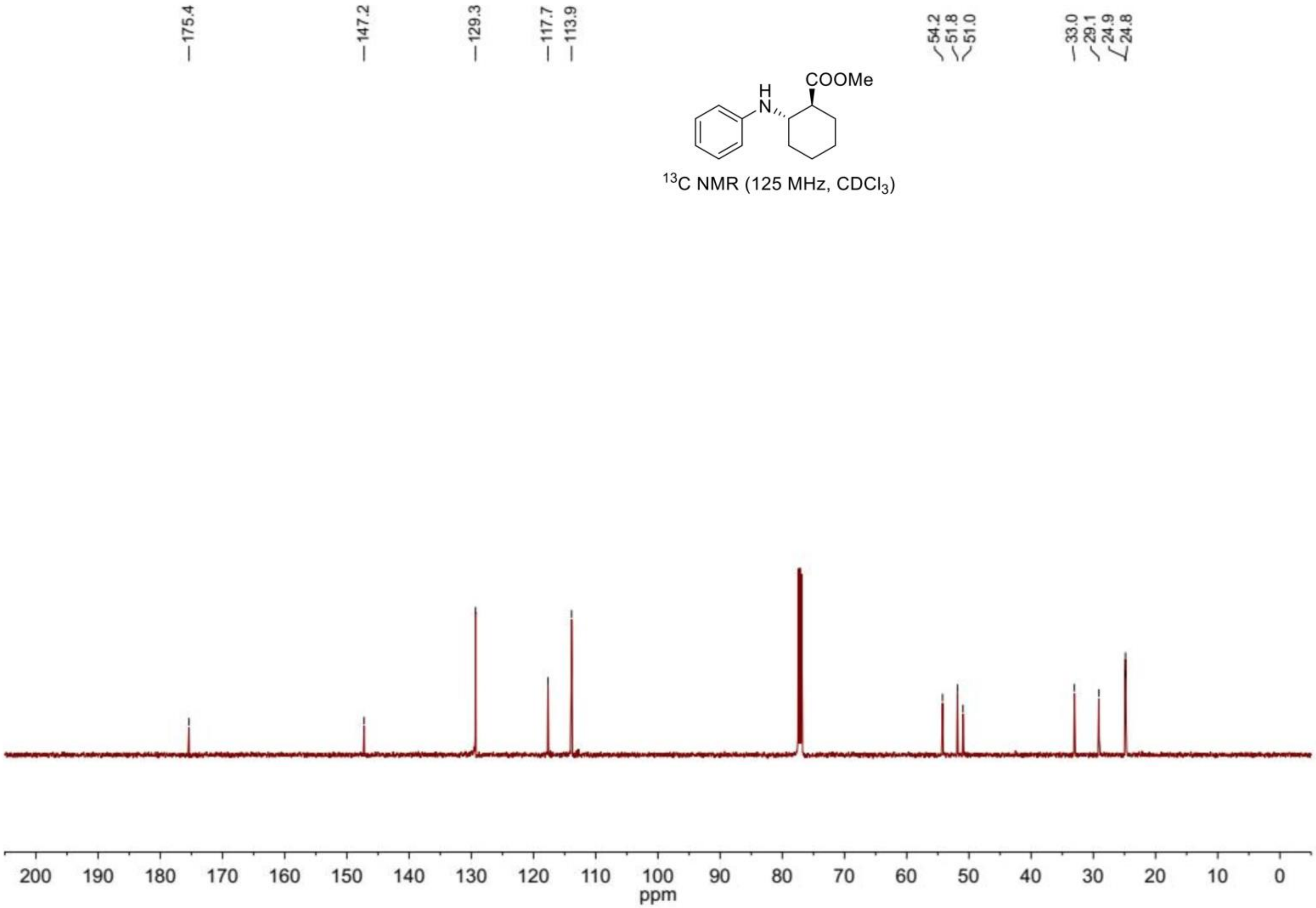
Methyl (1*S**,2*S**)-2-(phenylamino)cyclohexane-1-carboxylate (25)



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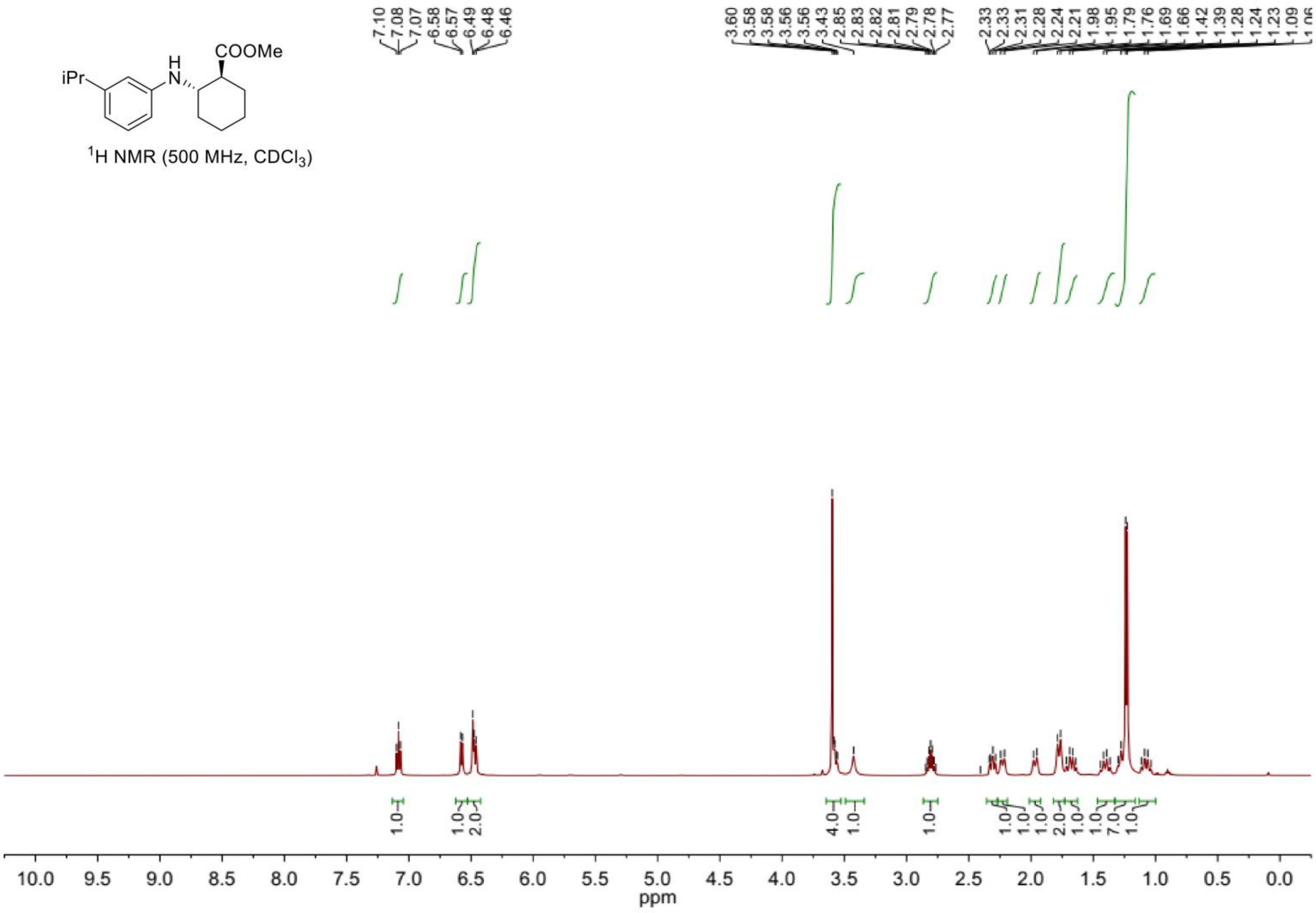
Methyl (1*S**,2*S**)-2-((3-isopropylphenyl)amino)cyclohexane-1-carboxylate (26)



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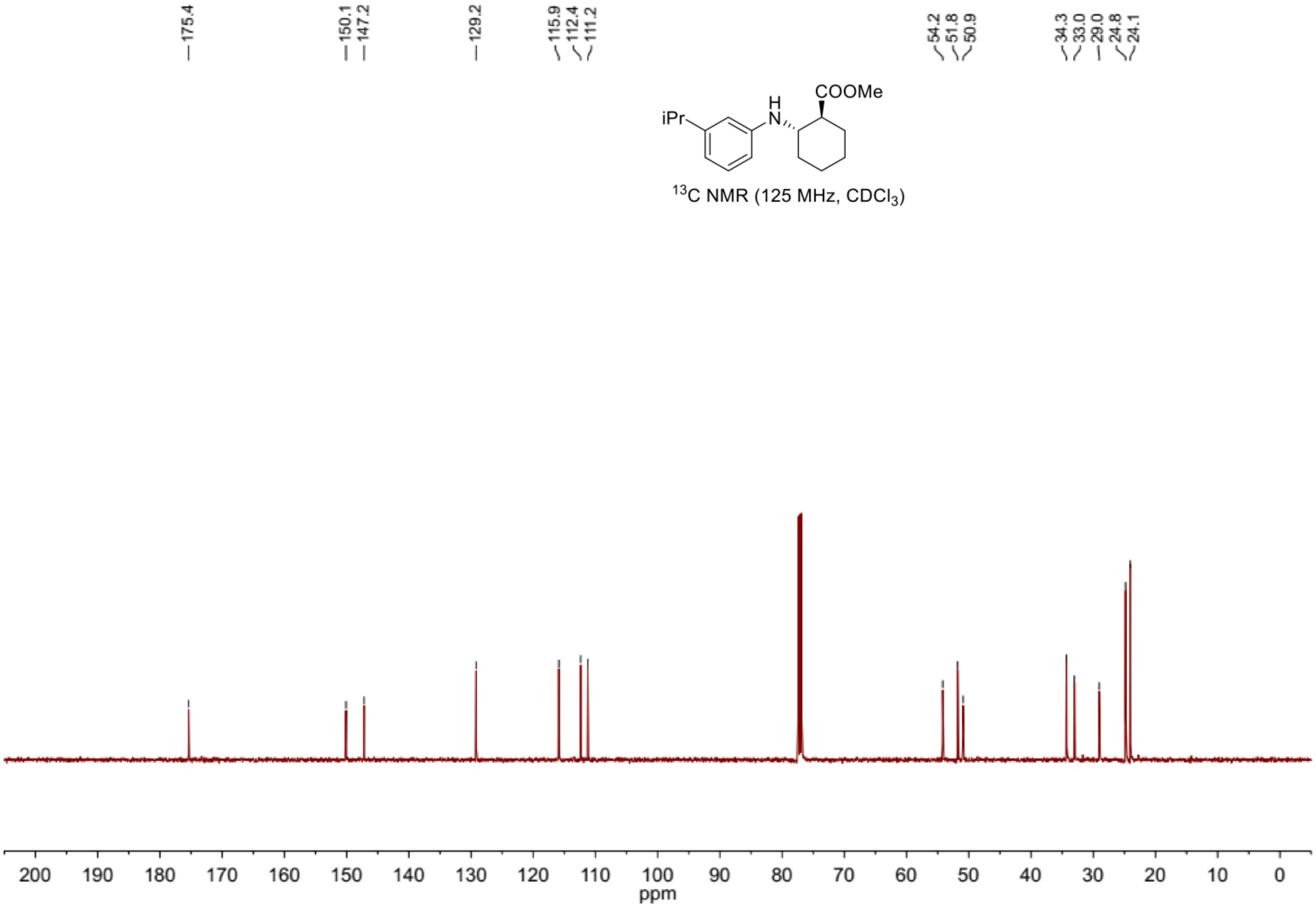
Methyl (1*S**,2*S**)-2-((3-isopropylphenyl)amino)cyclohexane-1-carboxylate (26)



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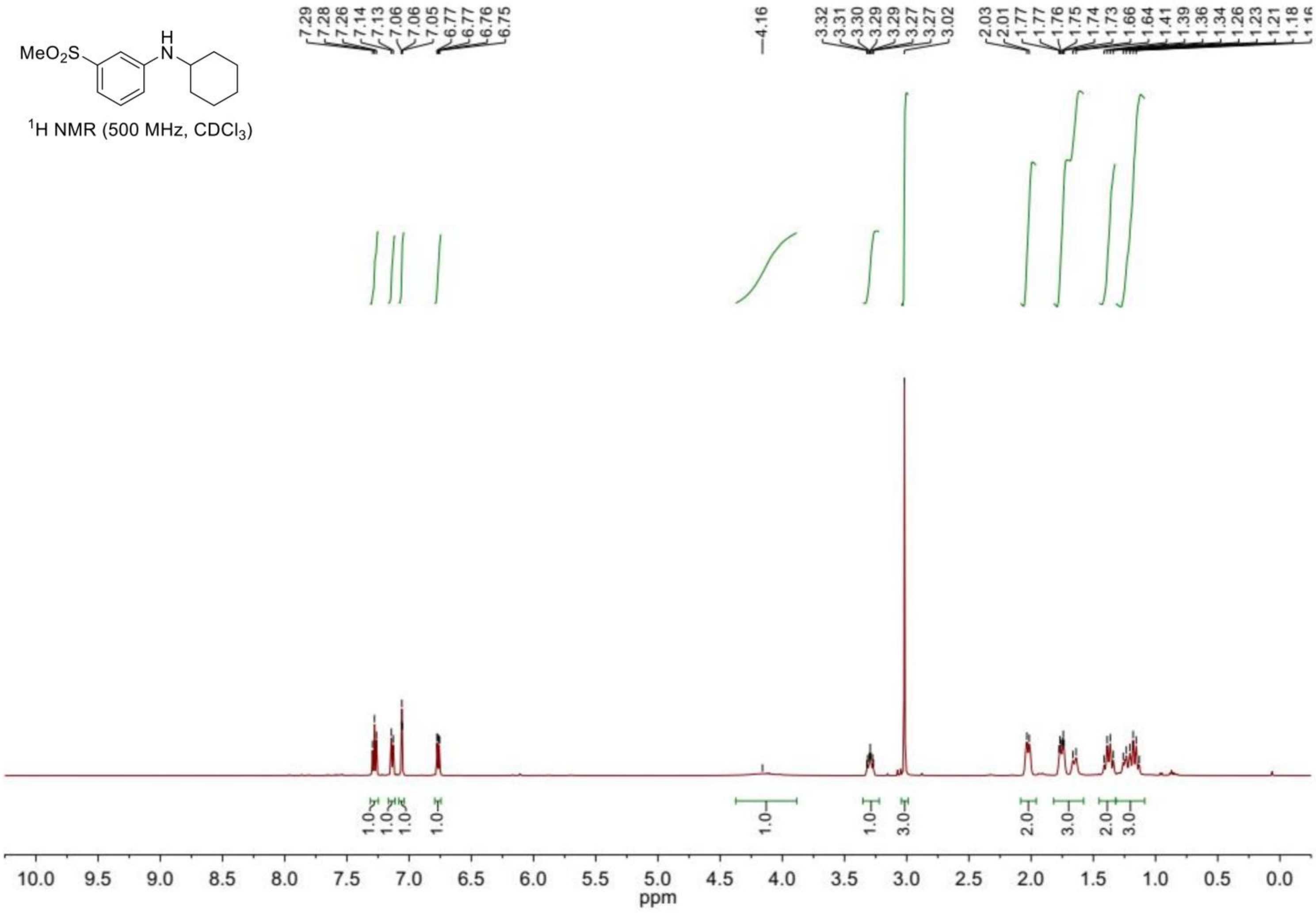
N-Cyclohexyl-3-(methylsulfonyl)aniline (27)



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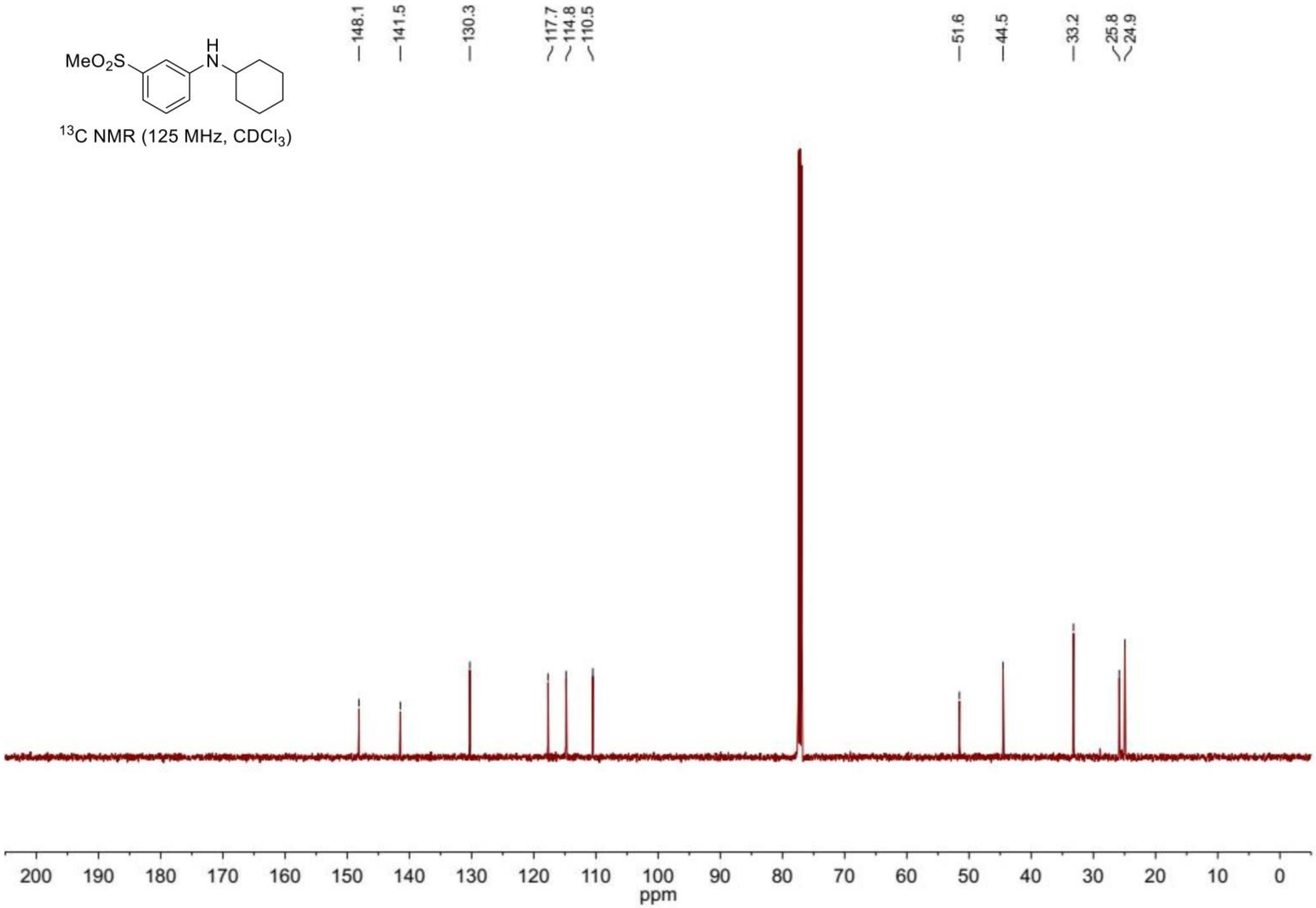
N-Cyclohexyl-3-(methylsulfonyl)aniline (27)



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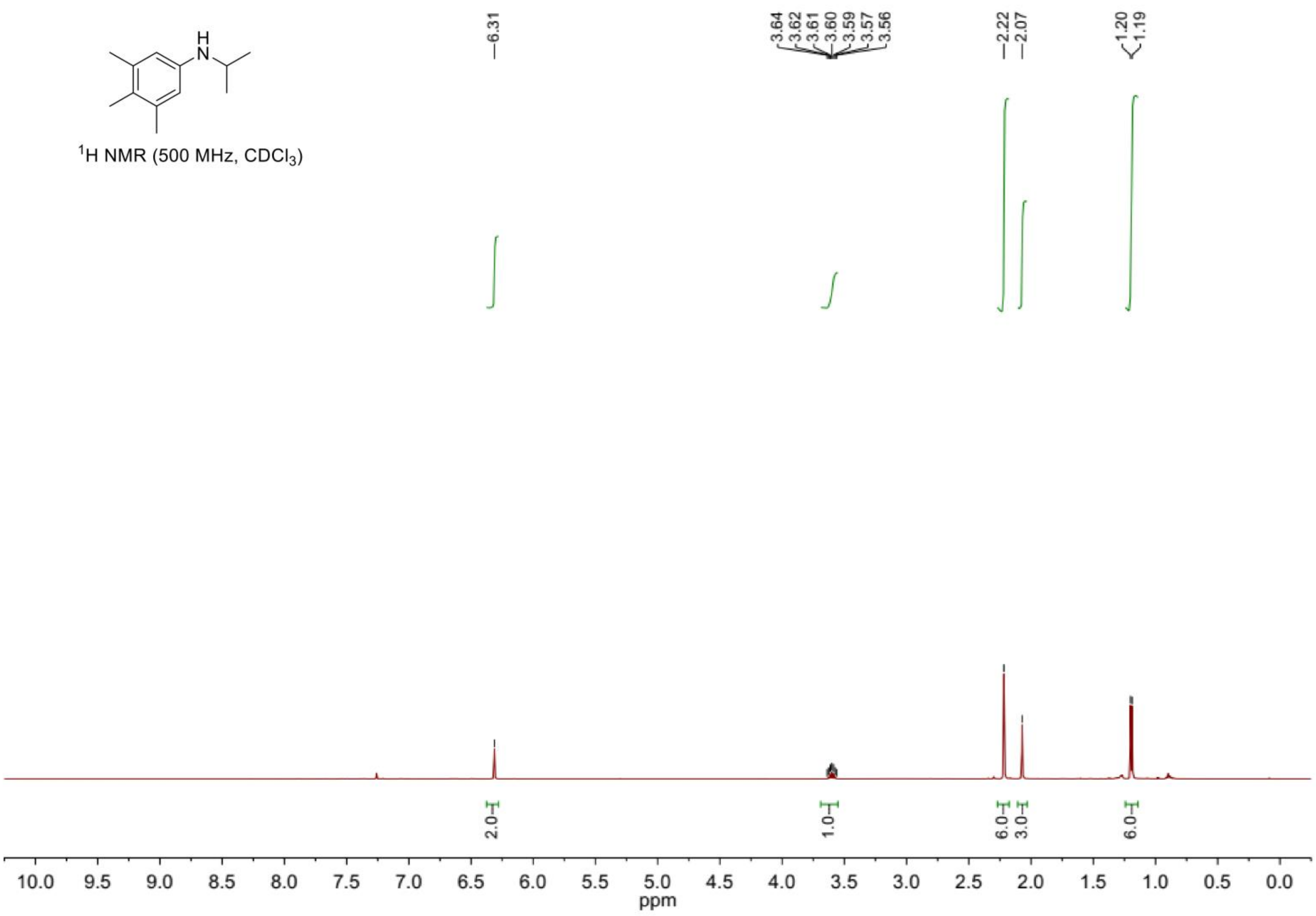
N-Isopropyl-3,4,5-trimethylaniline (28)



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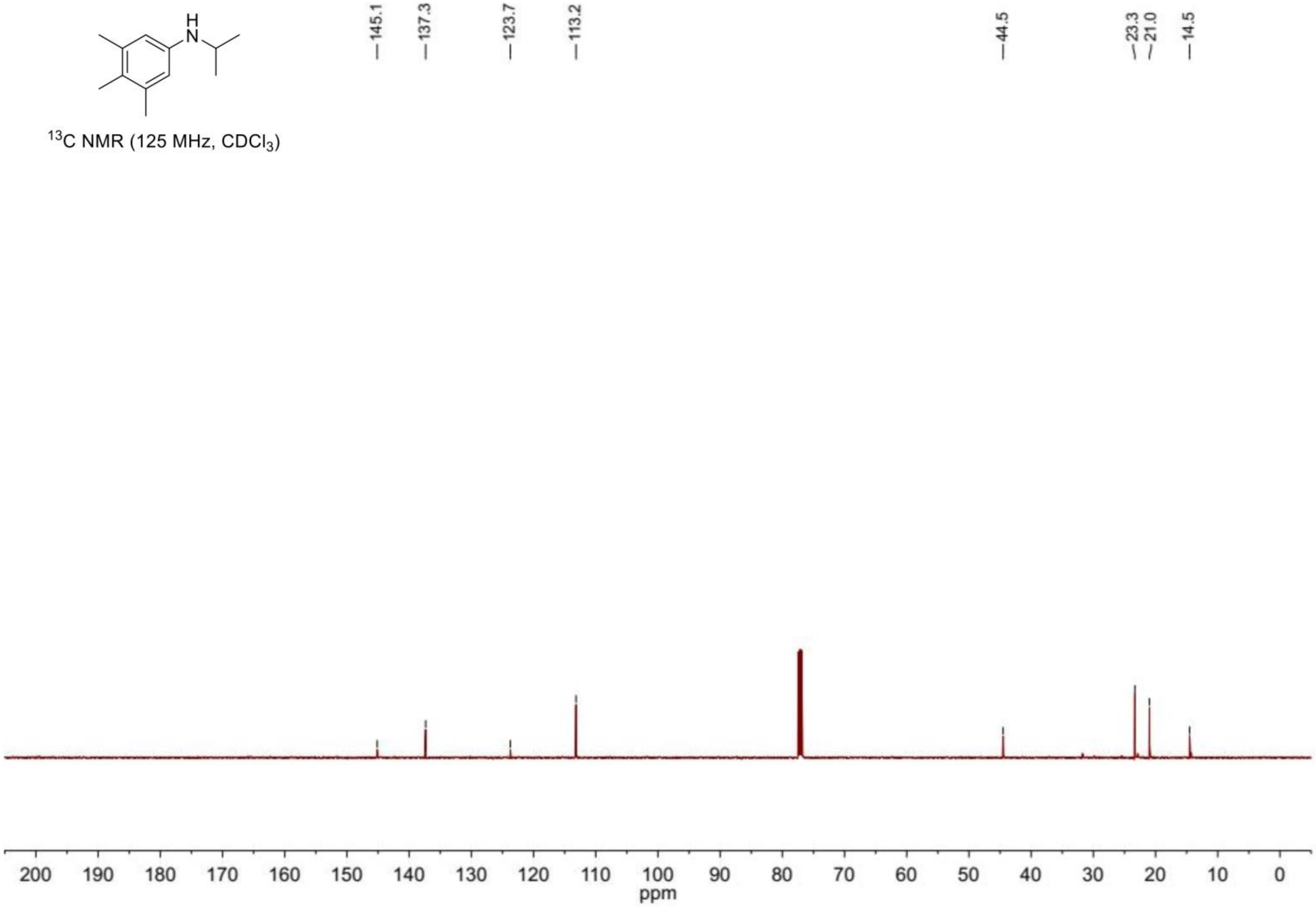
N-Isopropyl-3,4,5-trimethylaniline (28)



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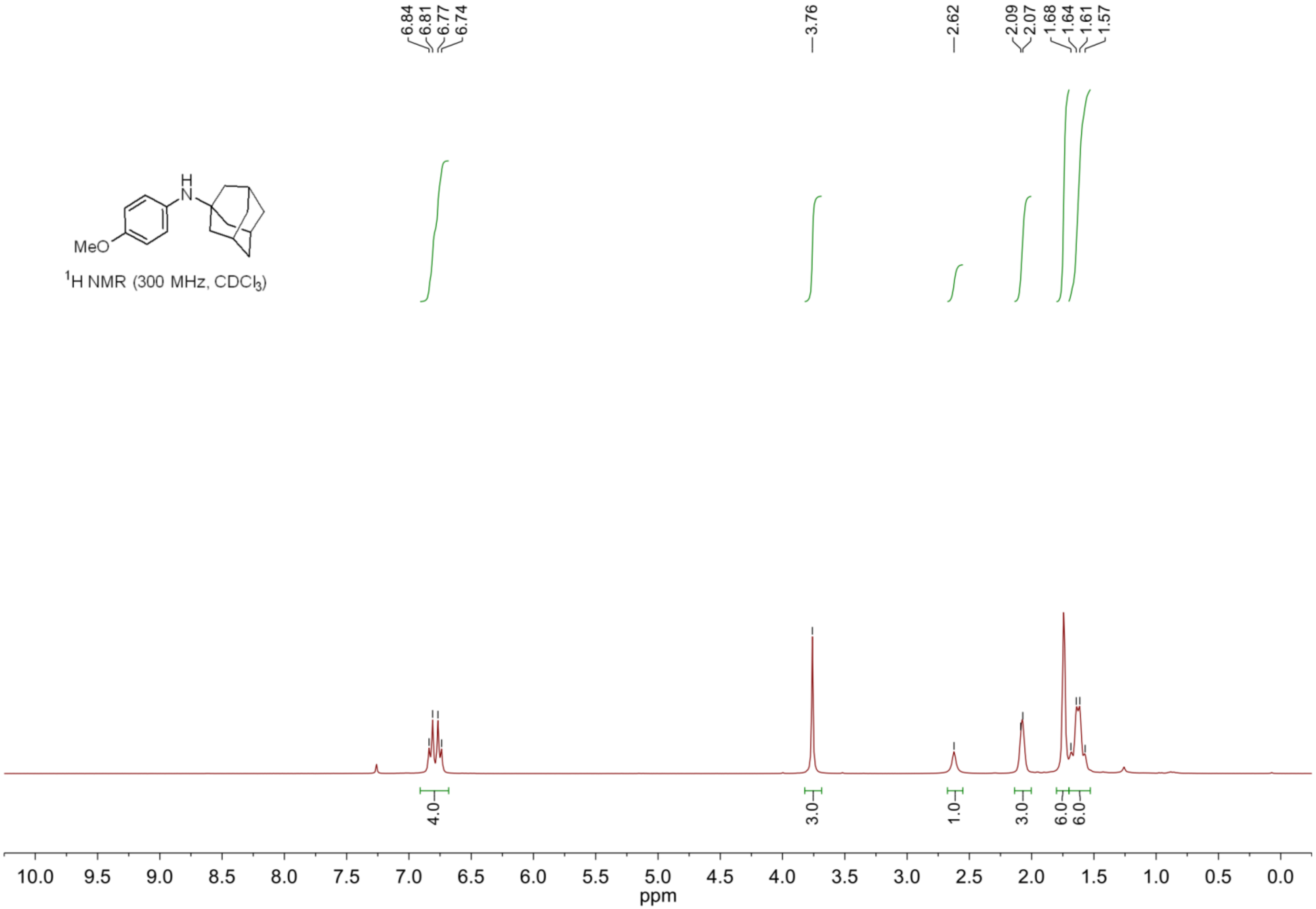
N-(4-Methoxyphenyl)adamantan-1-amine (29)



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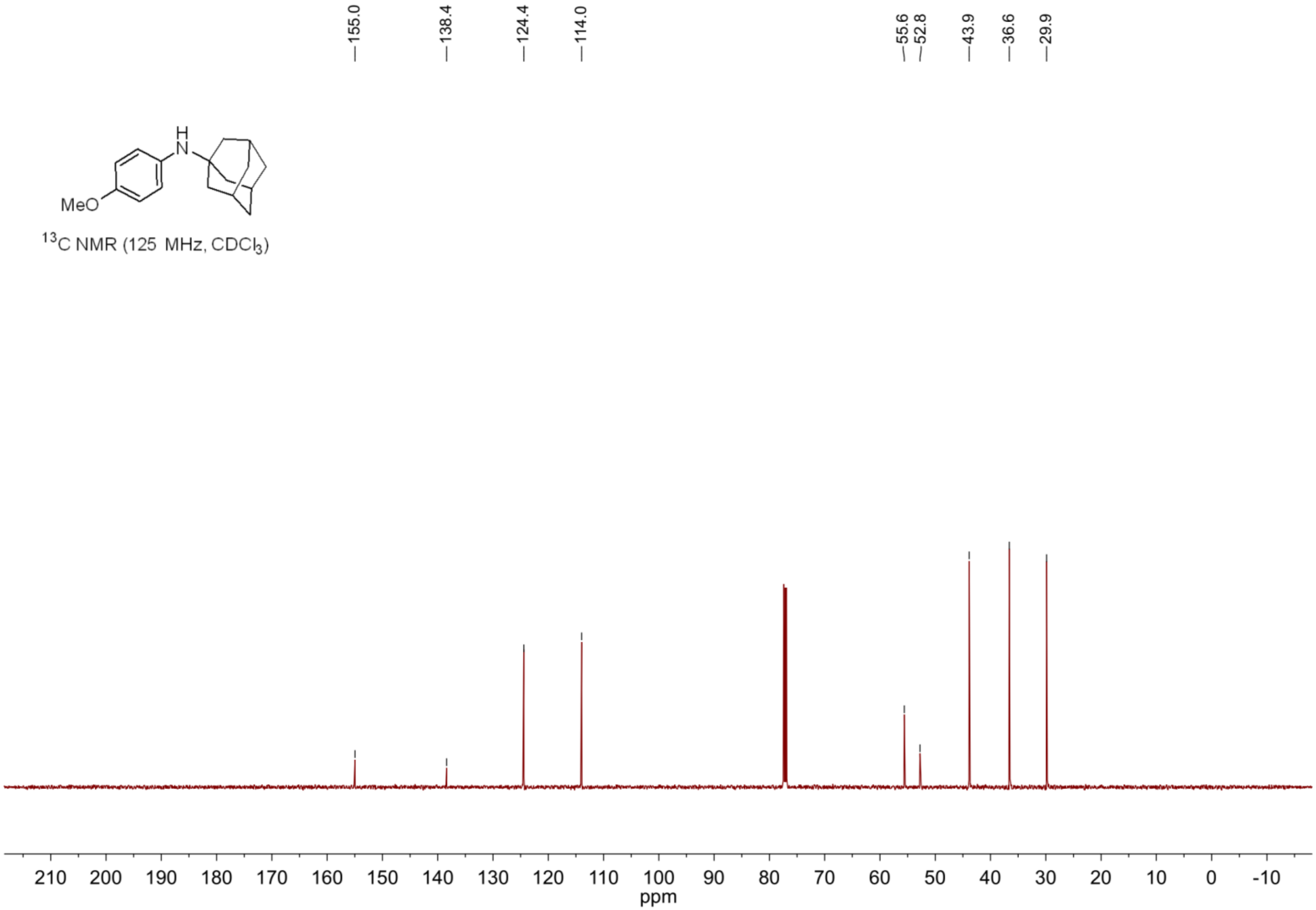
N-(4-Methoxyphenyl)adamantan-1-amine (29)



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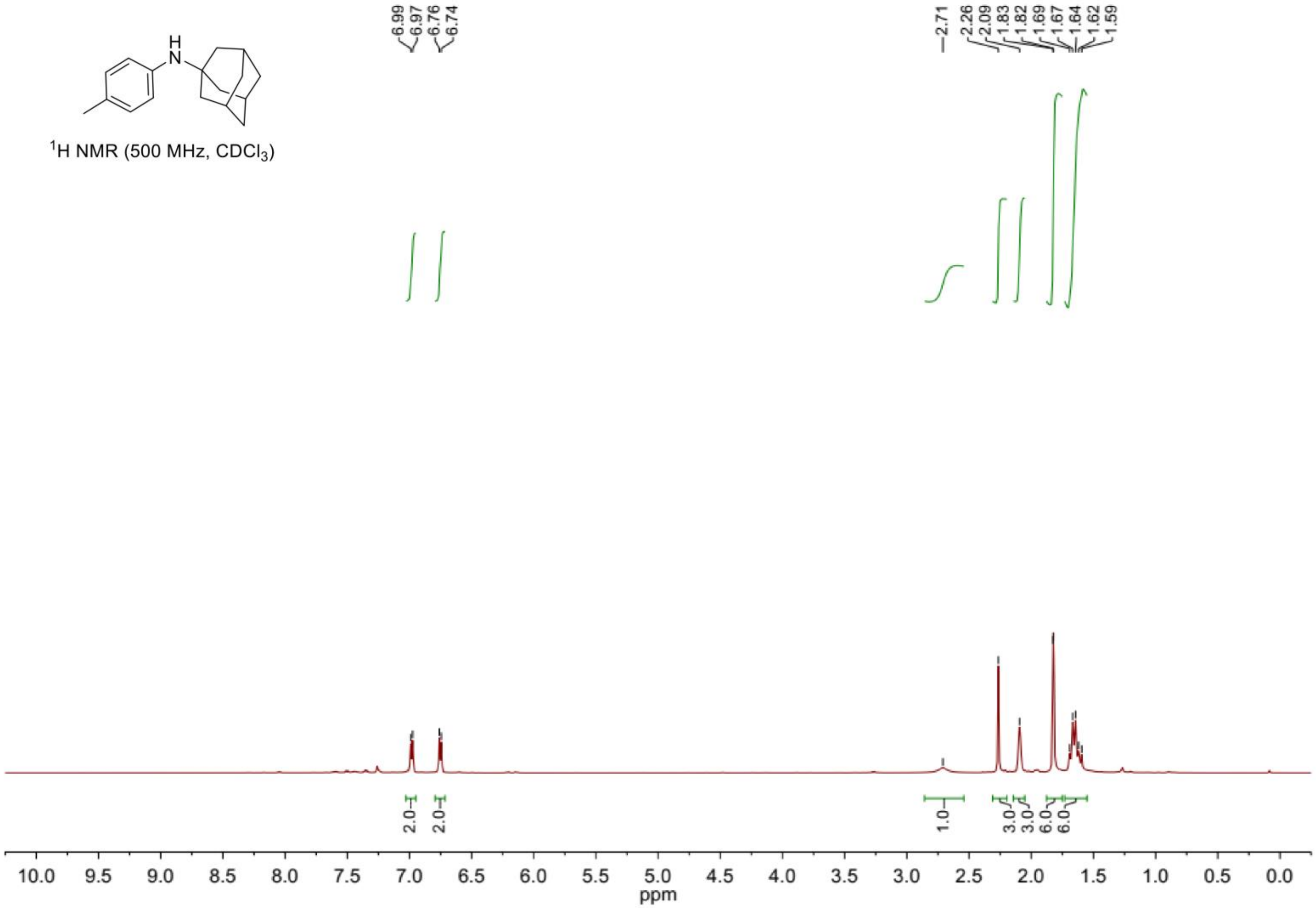
N-(*p*-Tolyl)adamantan-1-amine (30)



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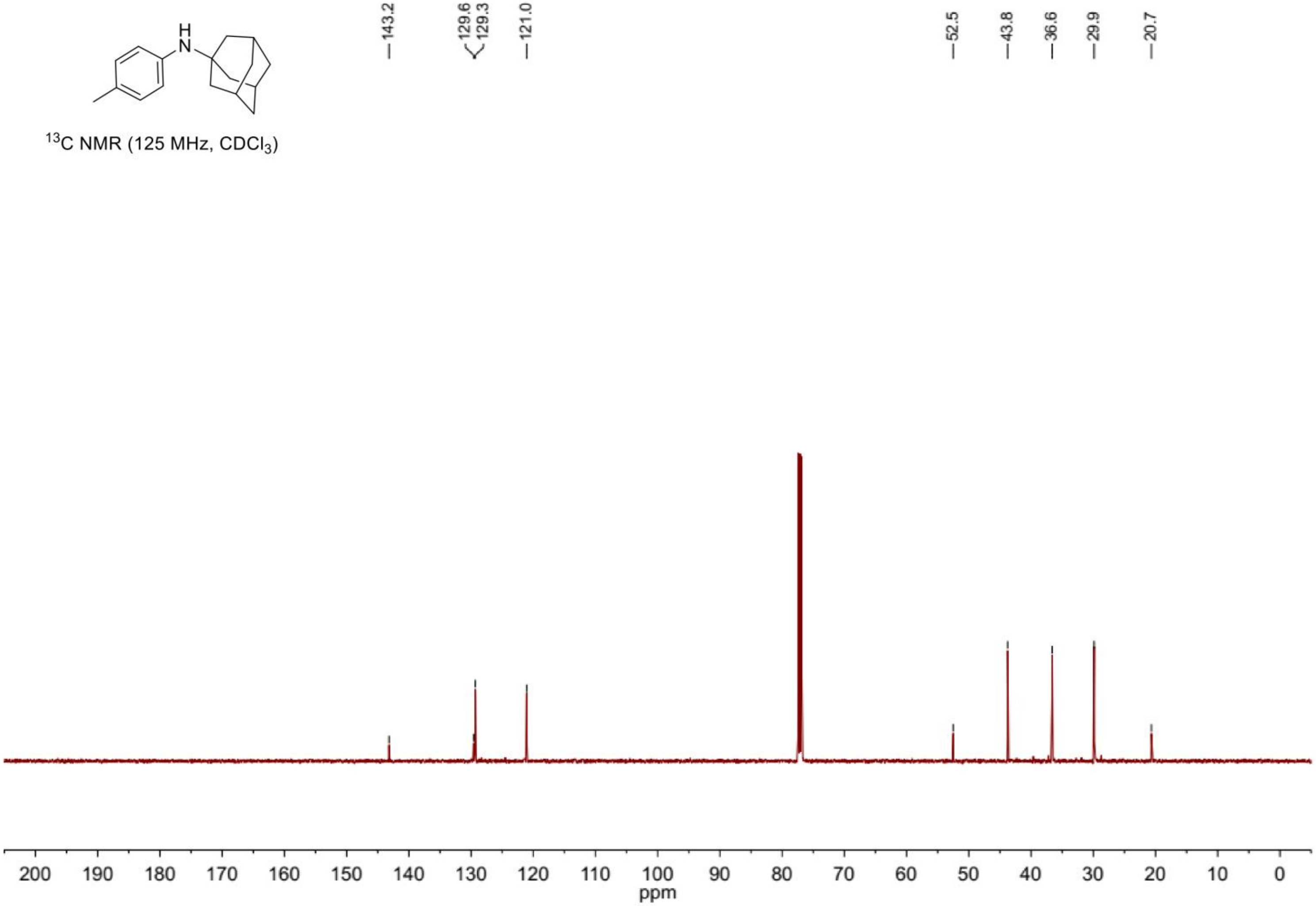
N-(*p*-Tolyl)adamantan-1-amine (30)



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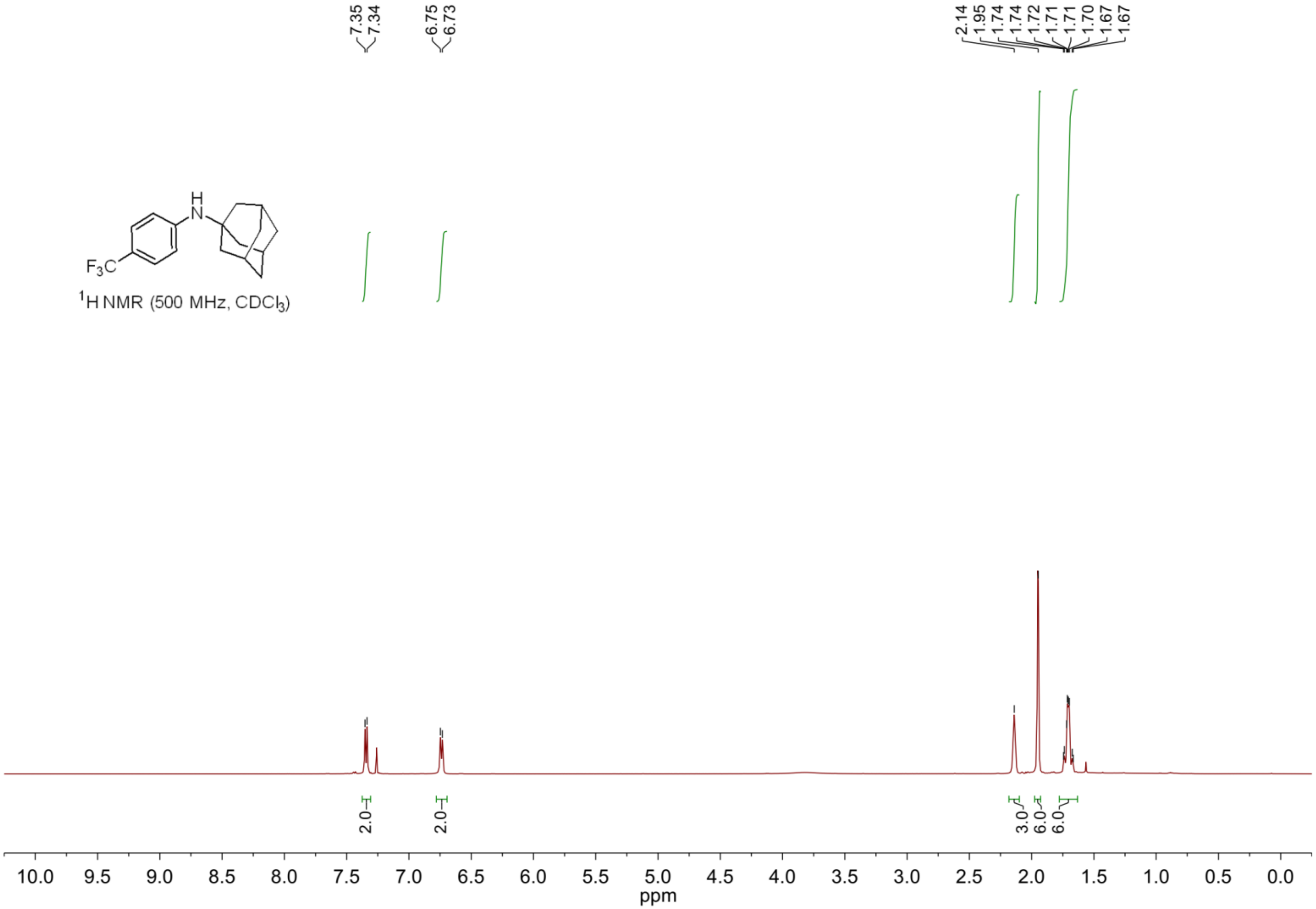
N-(4-(Trifluoromethyl)phenyl)adamantan-1-amine (31)



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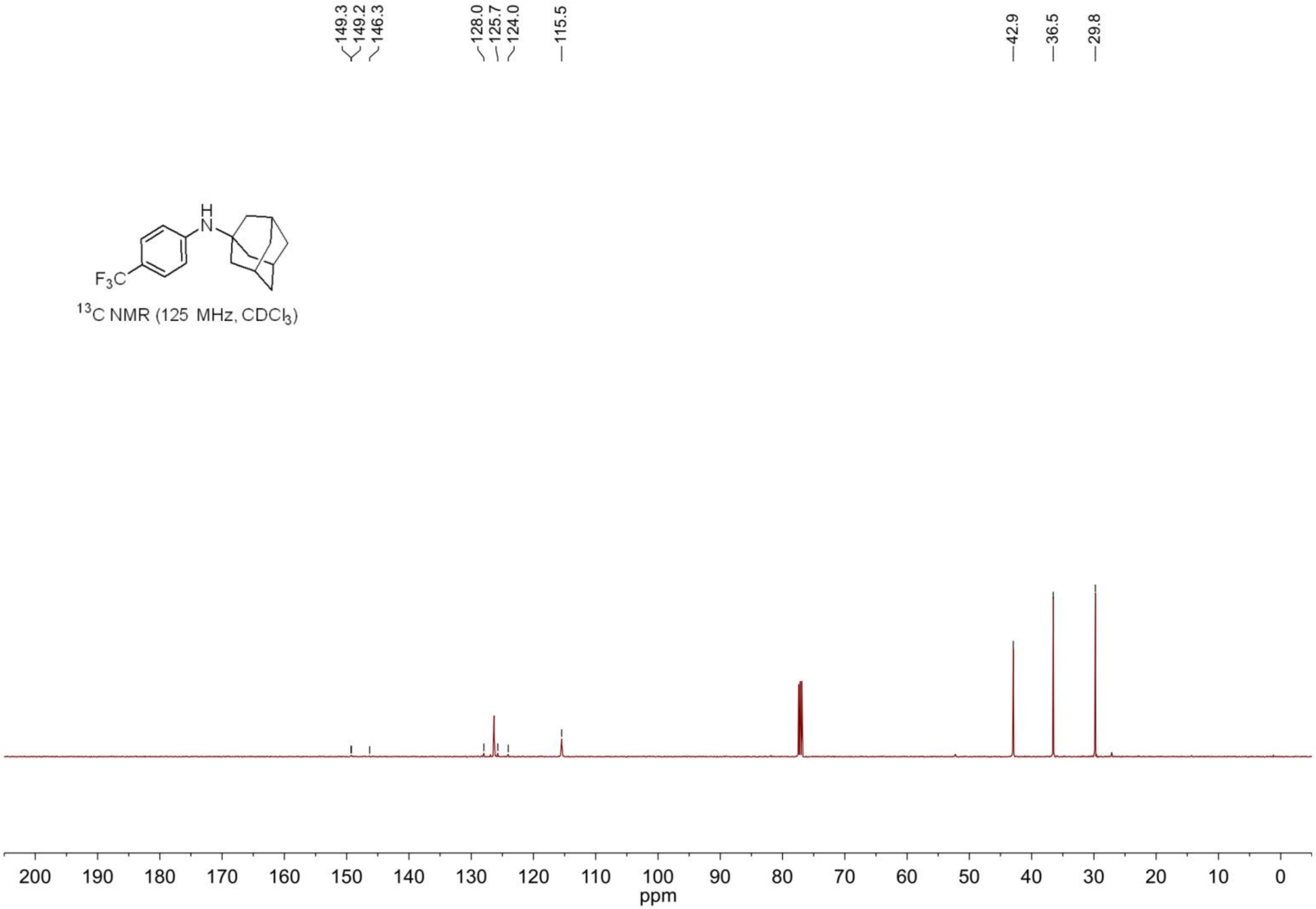
N-(4-(Trifluoromethyl)phenyl)adamantan-1-amine (31)



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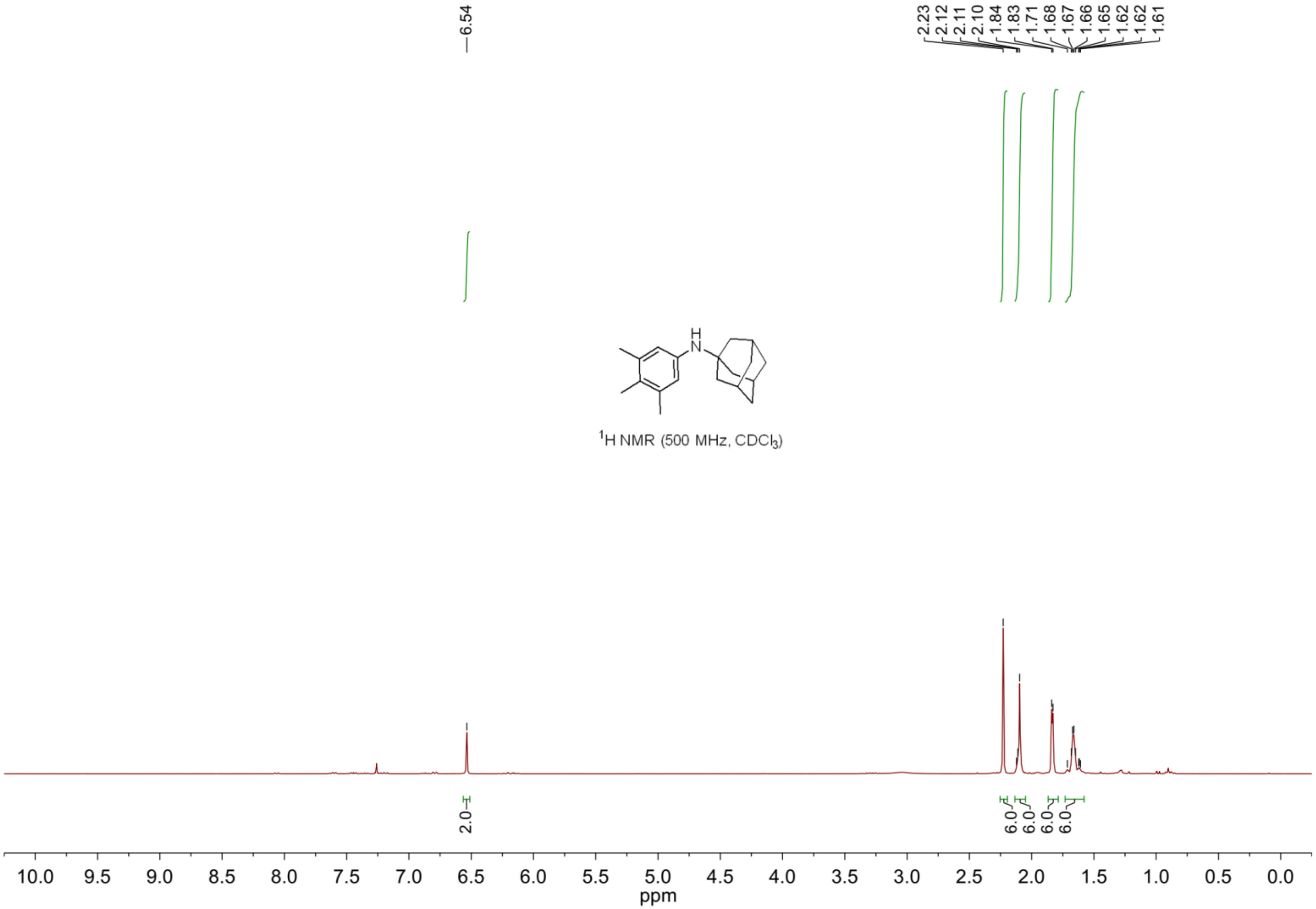
N-(3,4,5-Trimethylphenyl)adamantan-1-amine (32)



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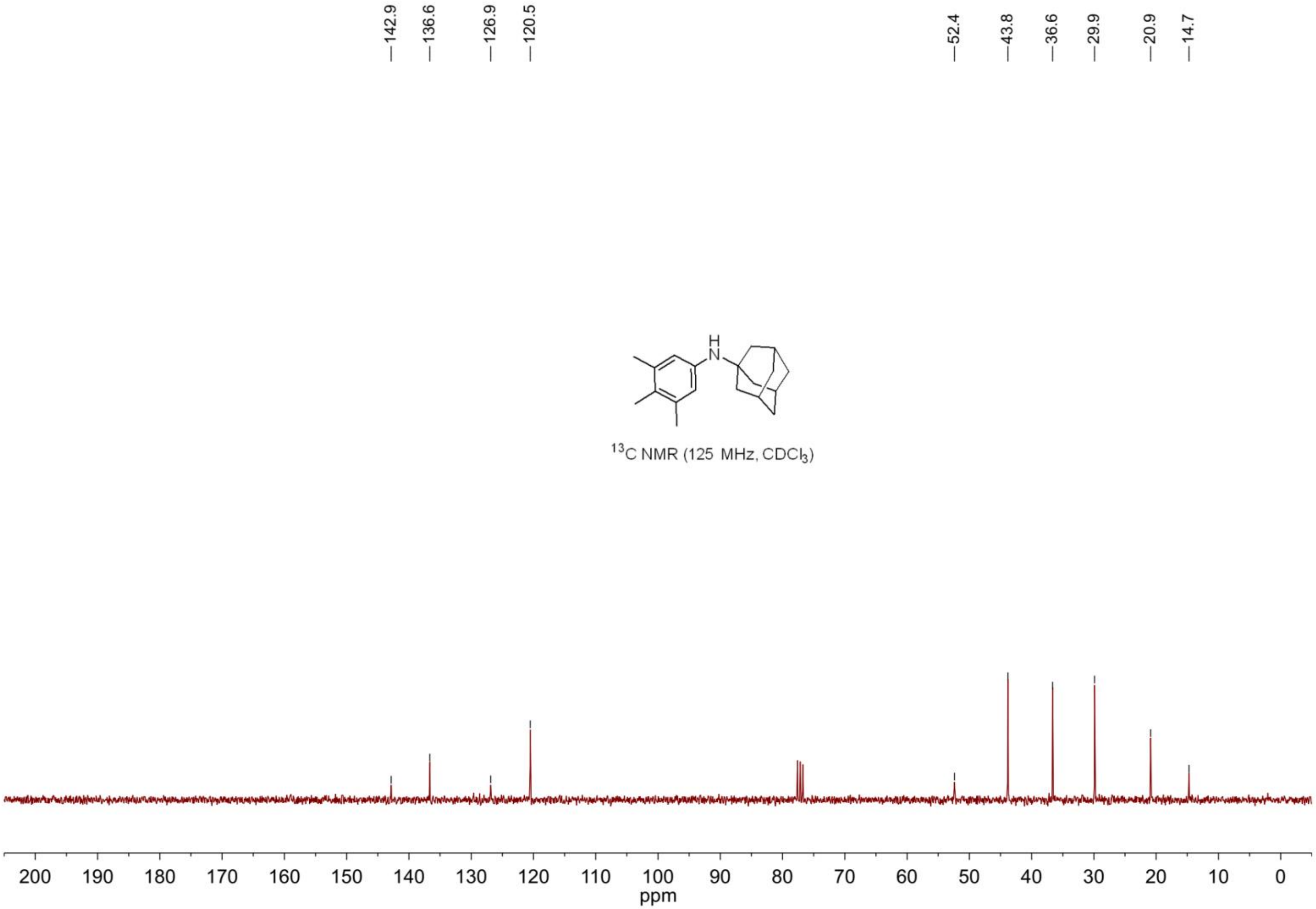
N-(3,4,5-Trimethylphenyl)adamantan-1-amine (32)



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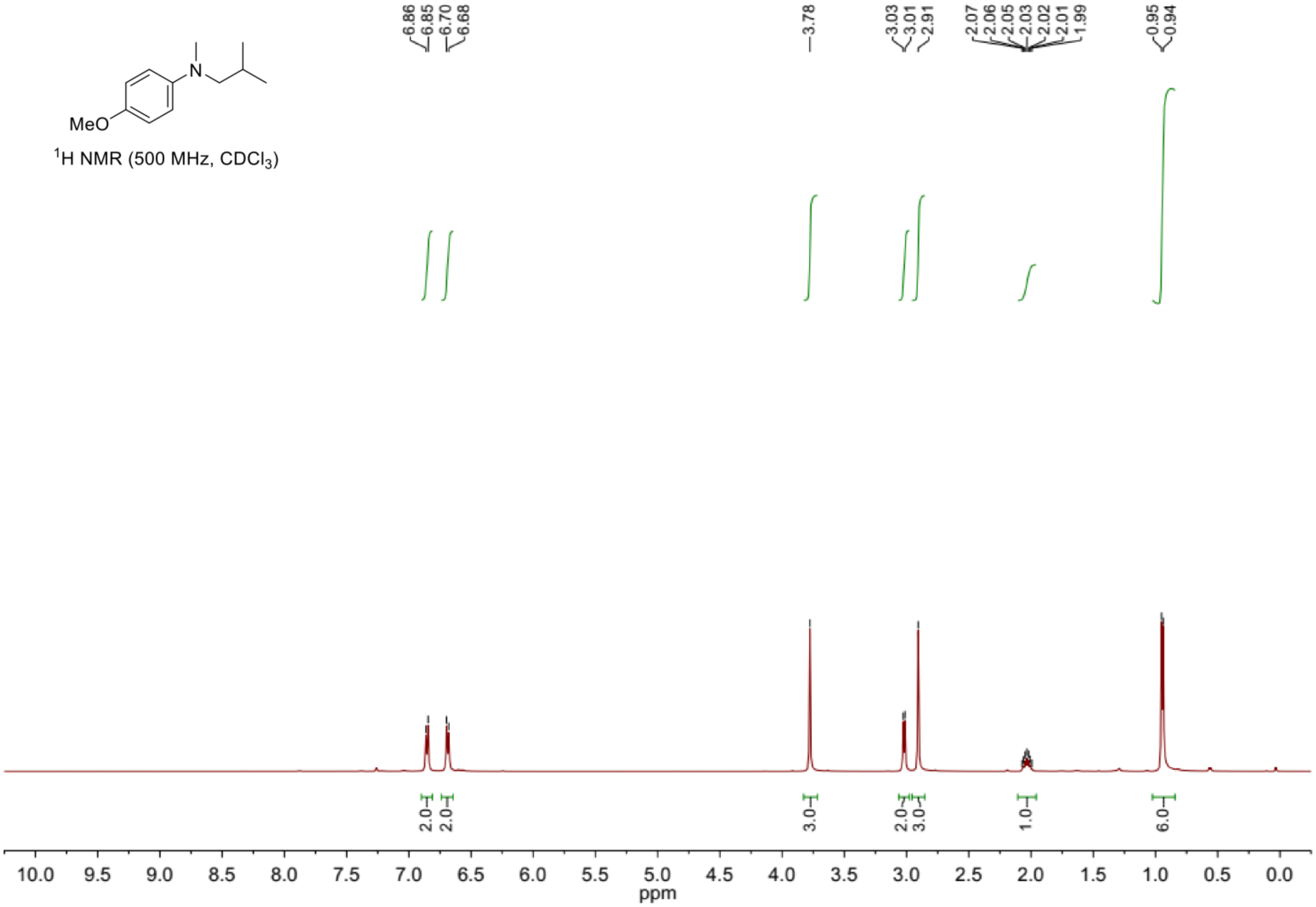
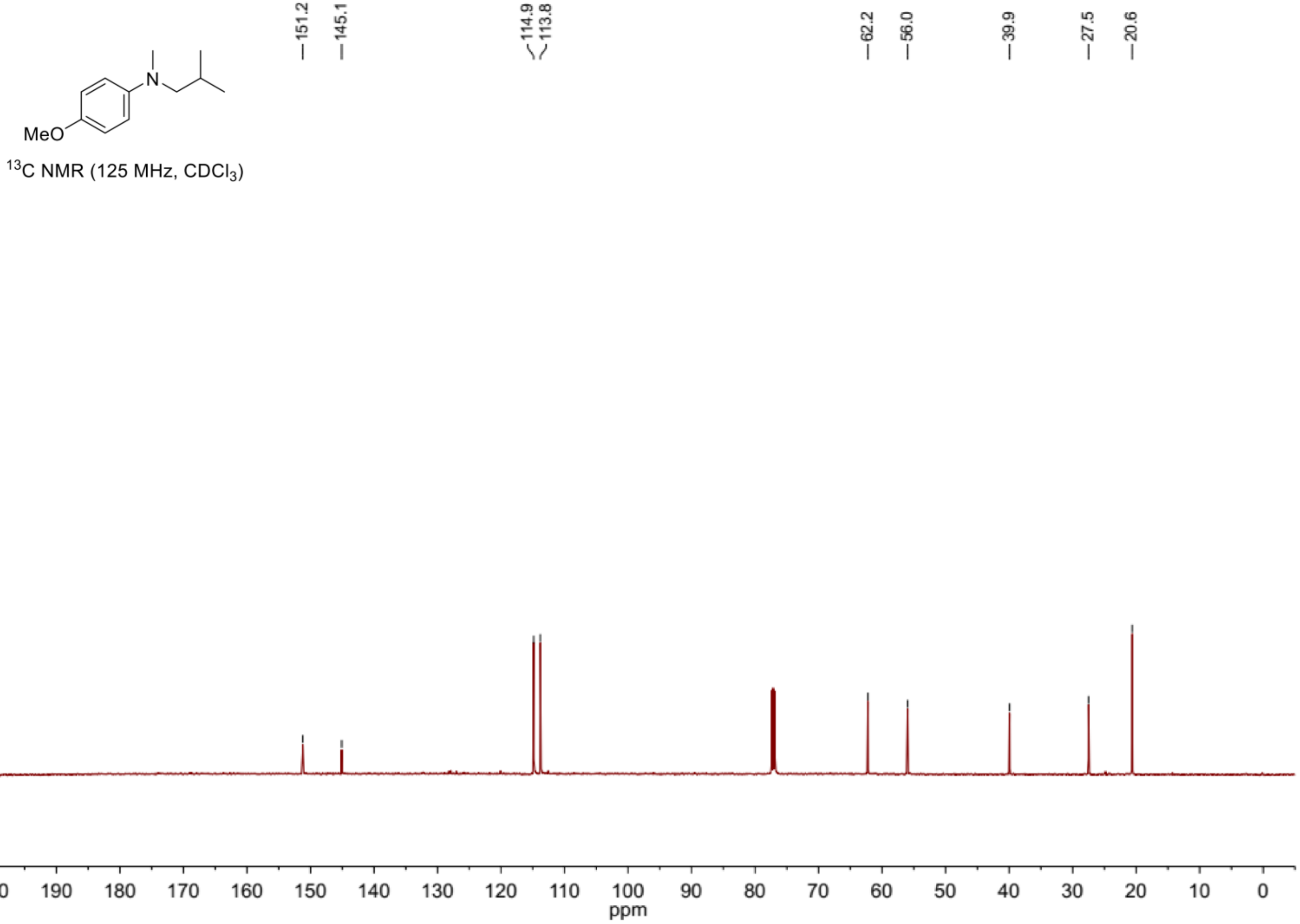
N-Isobutyl-4-methoxy-*N*-methylaniline (33)



N-Isobutyl-4-methoxy-*N*-methylaniline (33)



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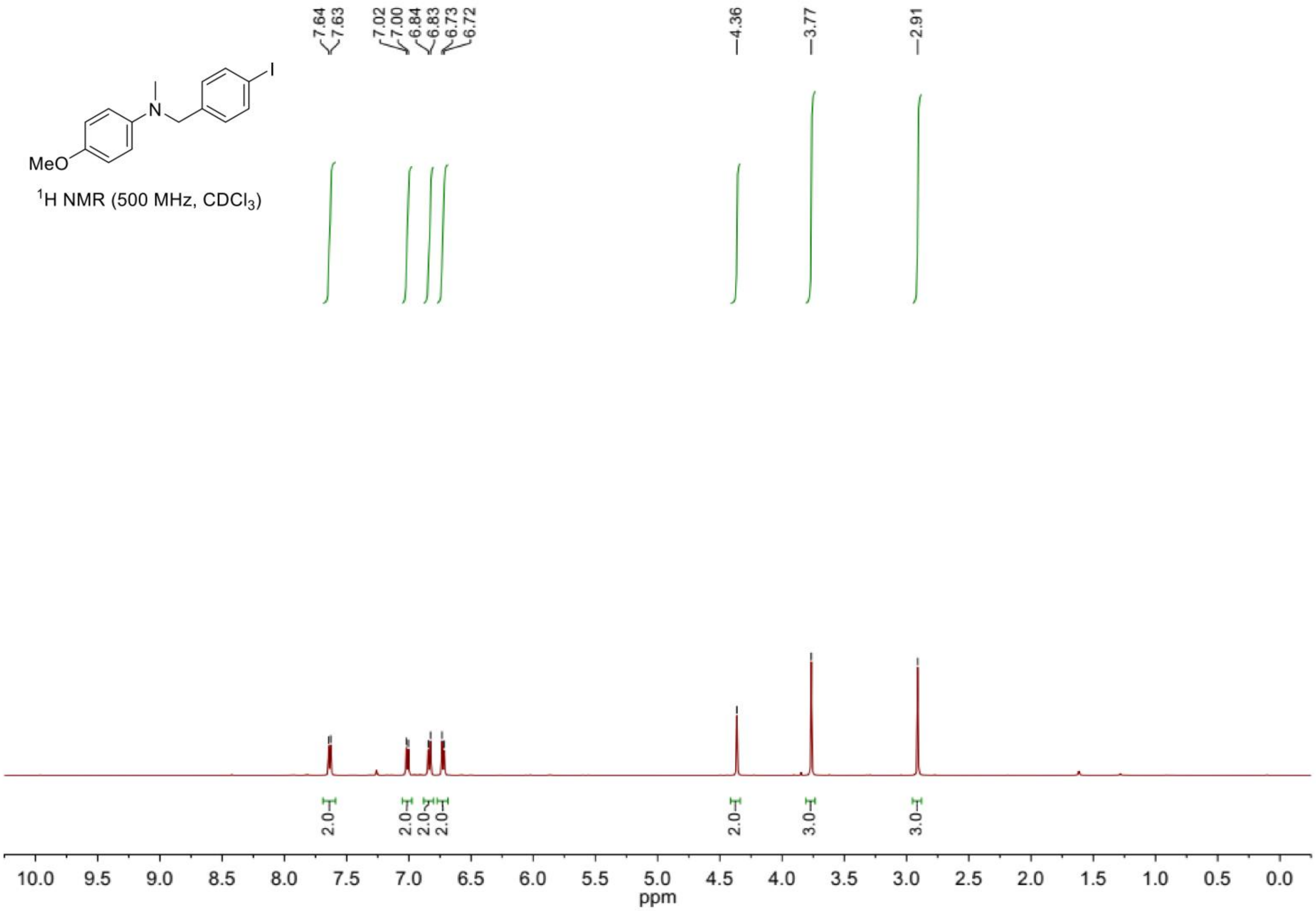
N-(4-Iodobenzyl)-4-methoxy-*N*-methylaniline (34)



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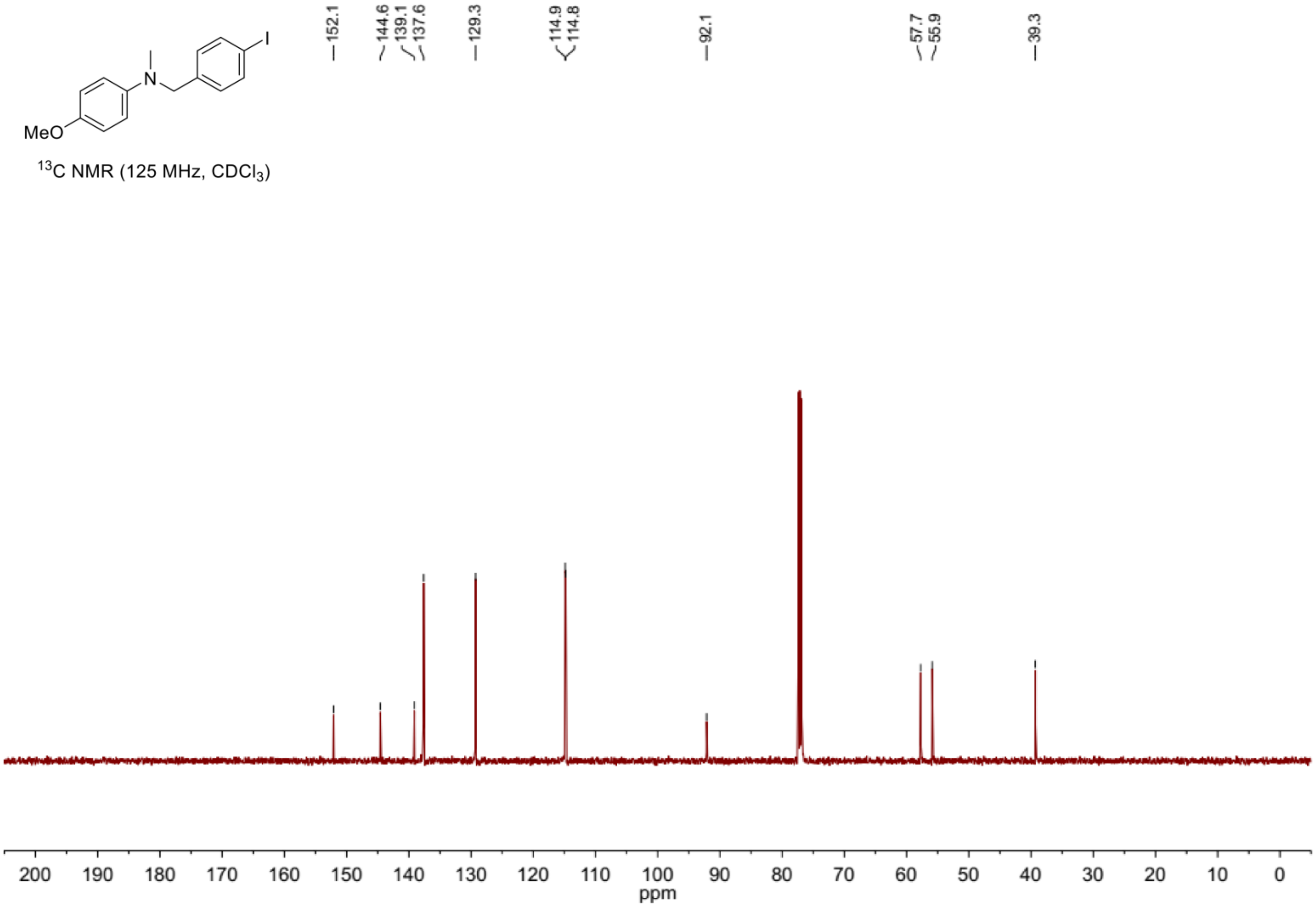
N-(4-Iodobenzyl)-4-methoxy-*N*-methylaniline (34)



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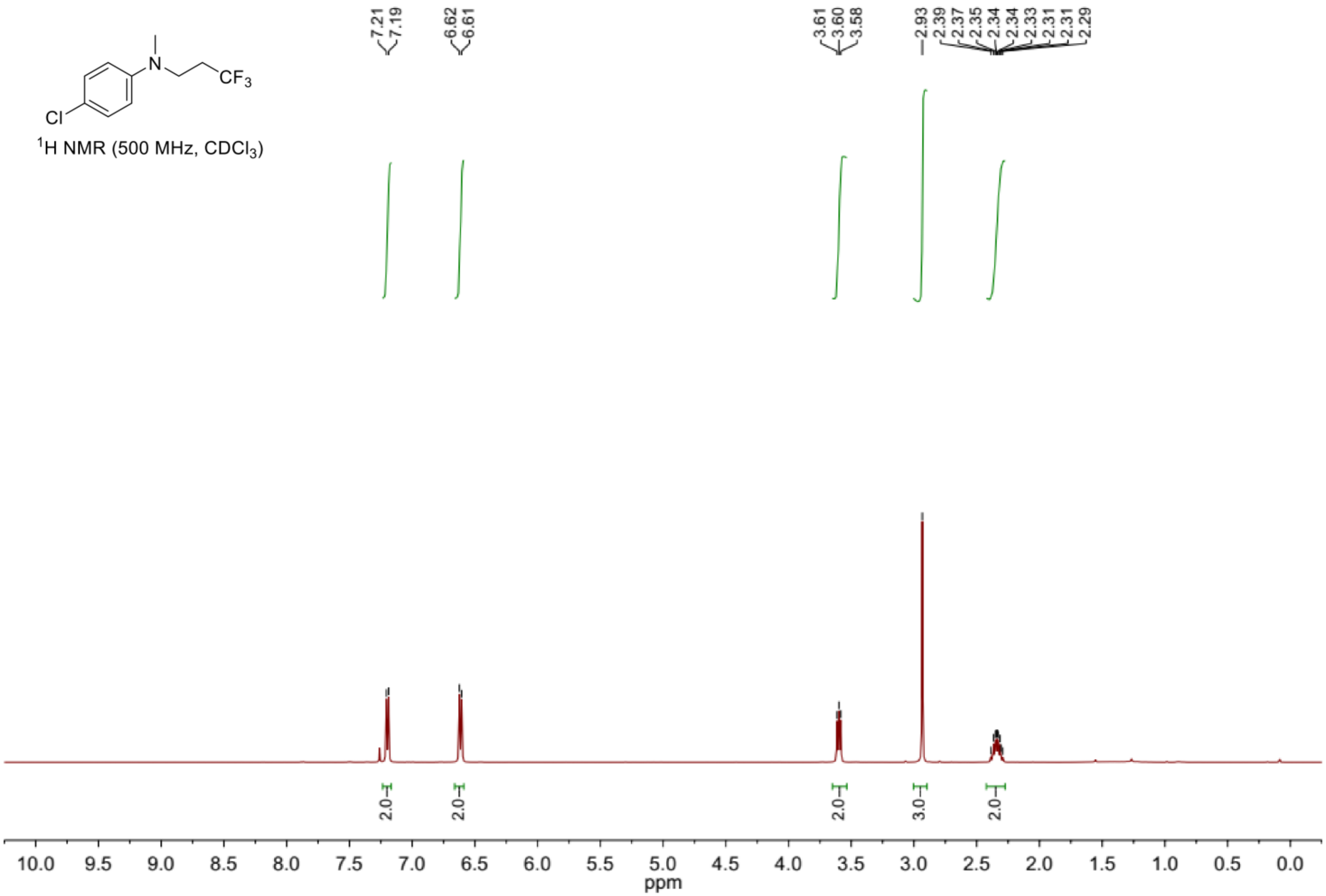
4-Chloro-*N*-methyl-*N*-(3,3,3-trifluoropropyl)aniline (35)



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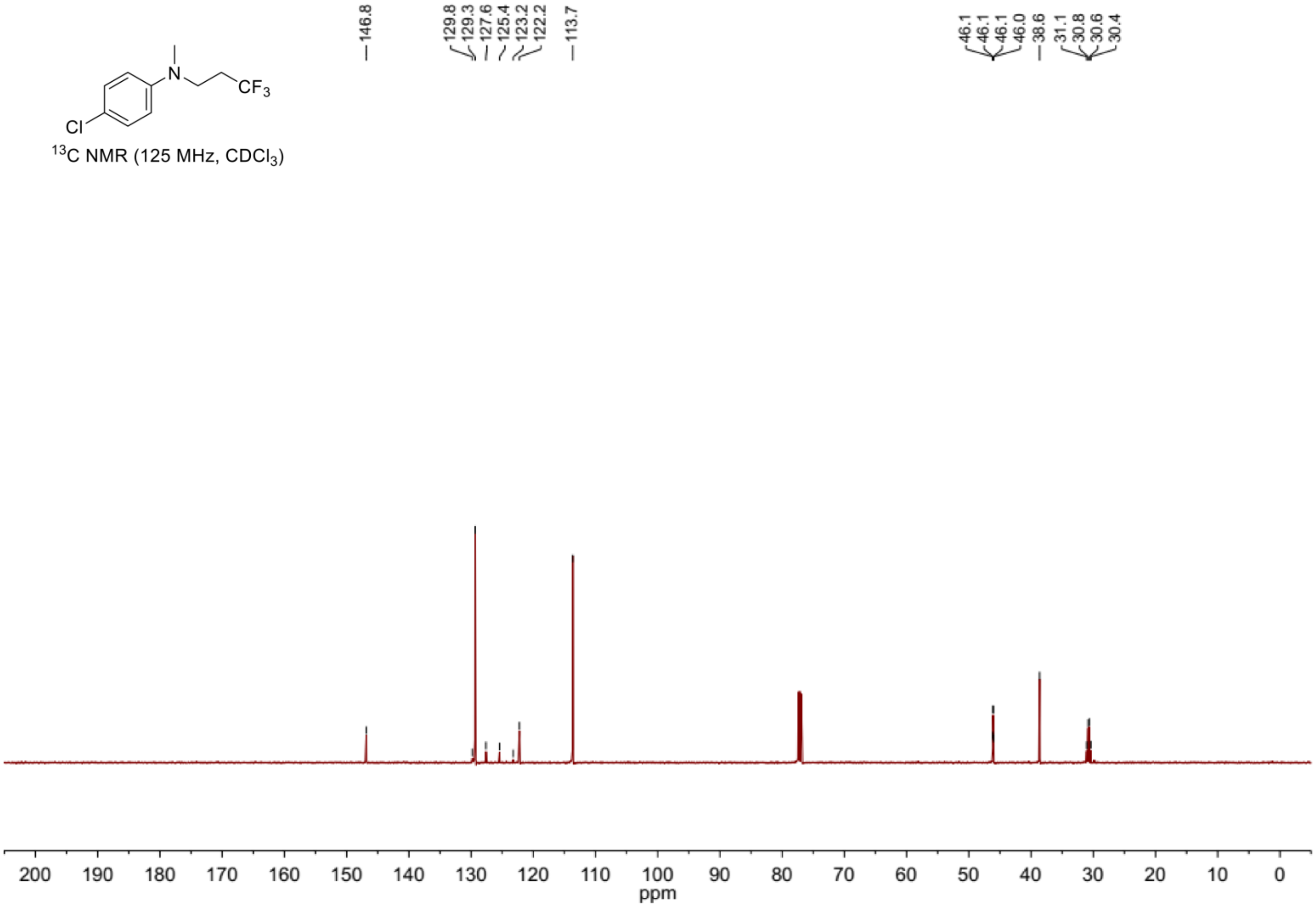
4-Chloro-*N*-methyl-*N*-(3,3,3-trifluoropropyl)aniline (35)



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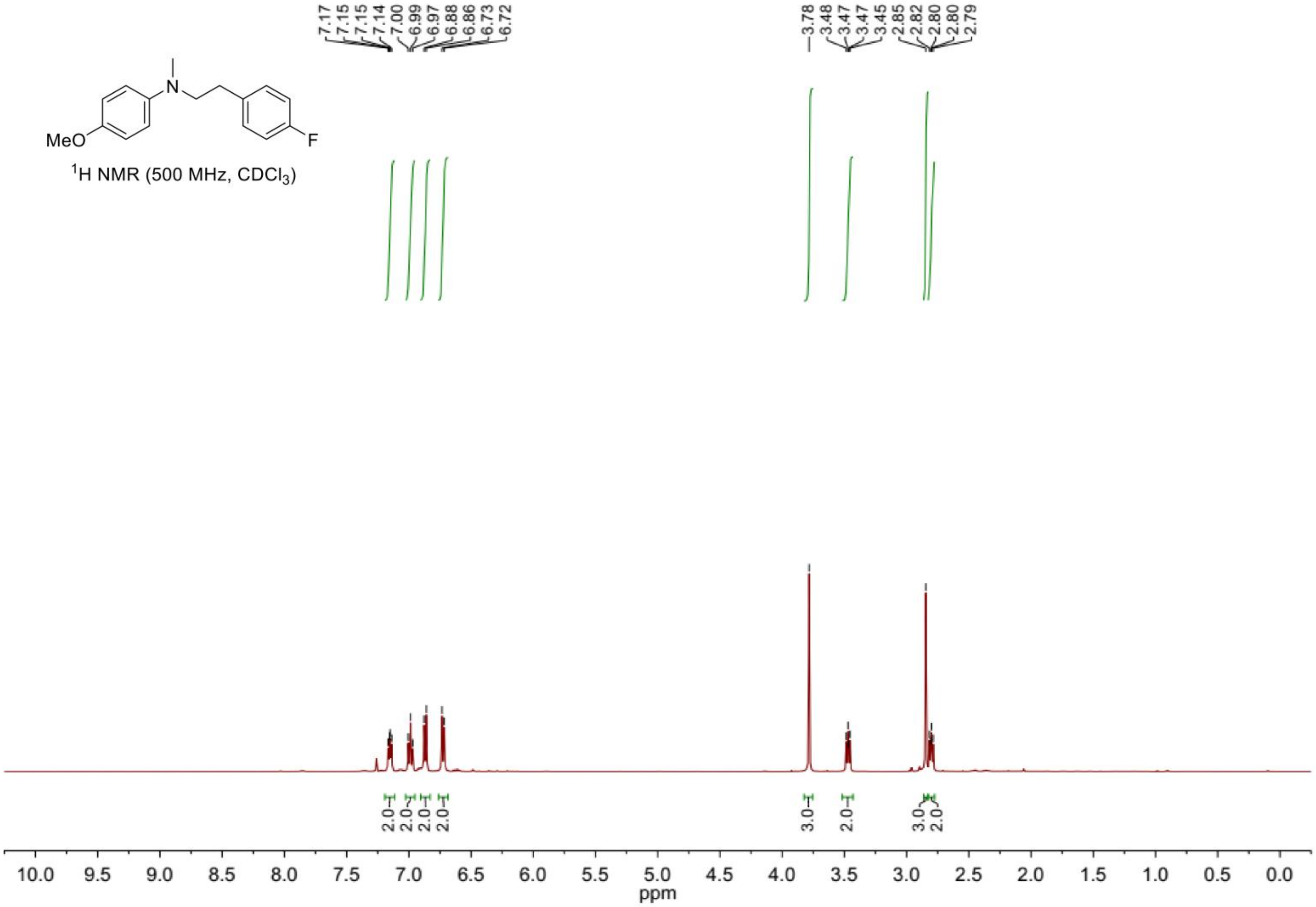
N-(4-Fluorophenethyl)-4-methoxy-*N*-methylaniline (36)



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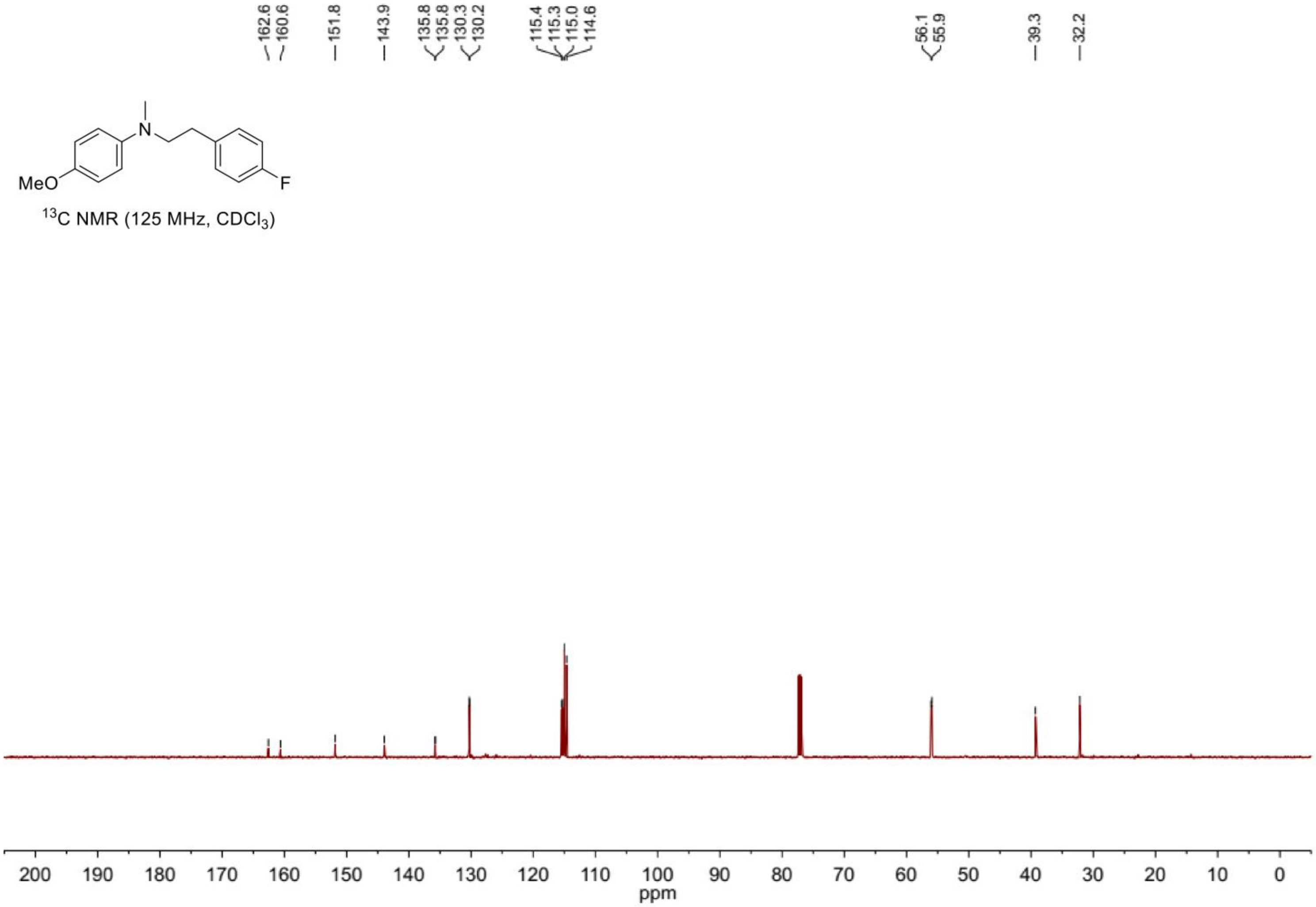
N-(4-Fluorophenethyl)-4-methoxy-*N*-methylaniline (36)



^{13}C NMR (125 MHz, $CDCl_3$)

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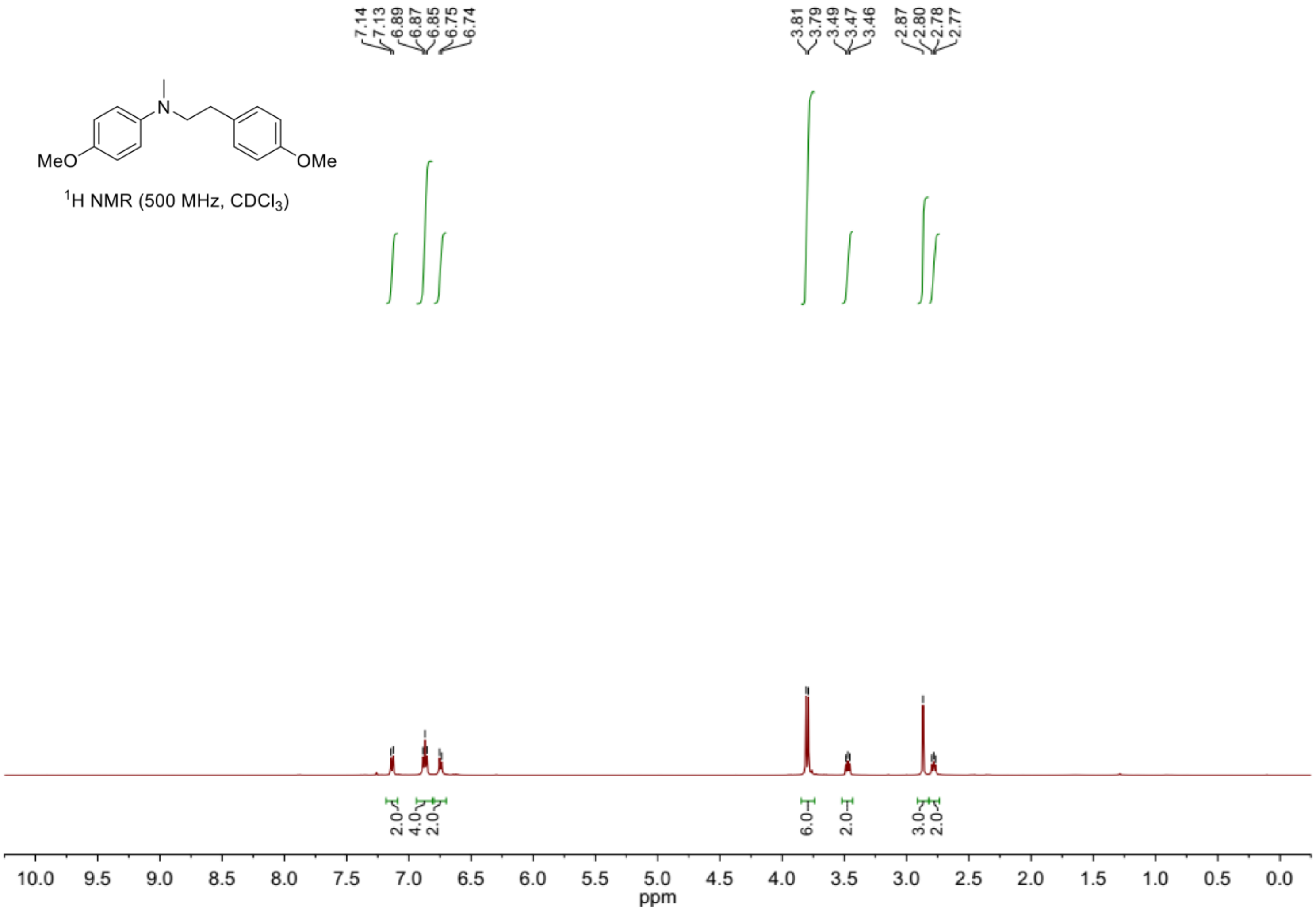
4-Methoxy-*N*-(4-methoxyphenethyl)-*N*-methylaniline (37)



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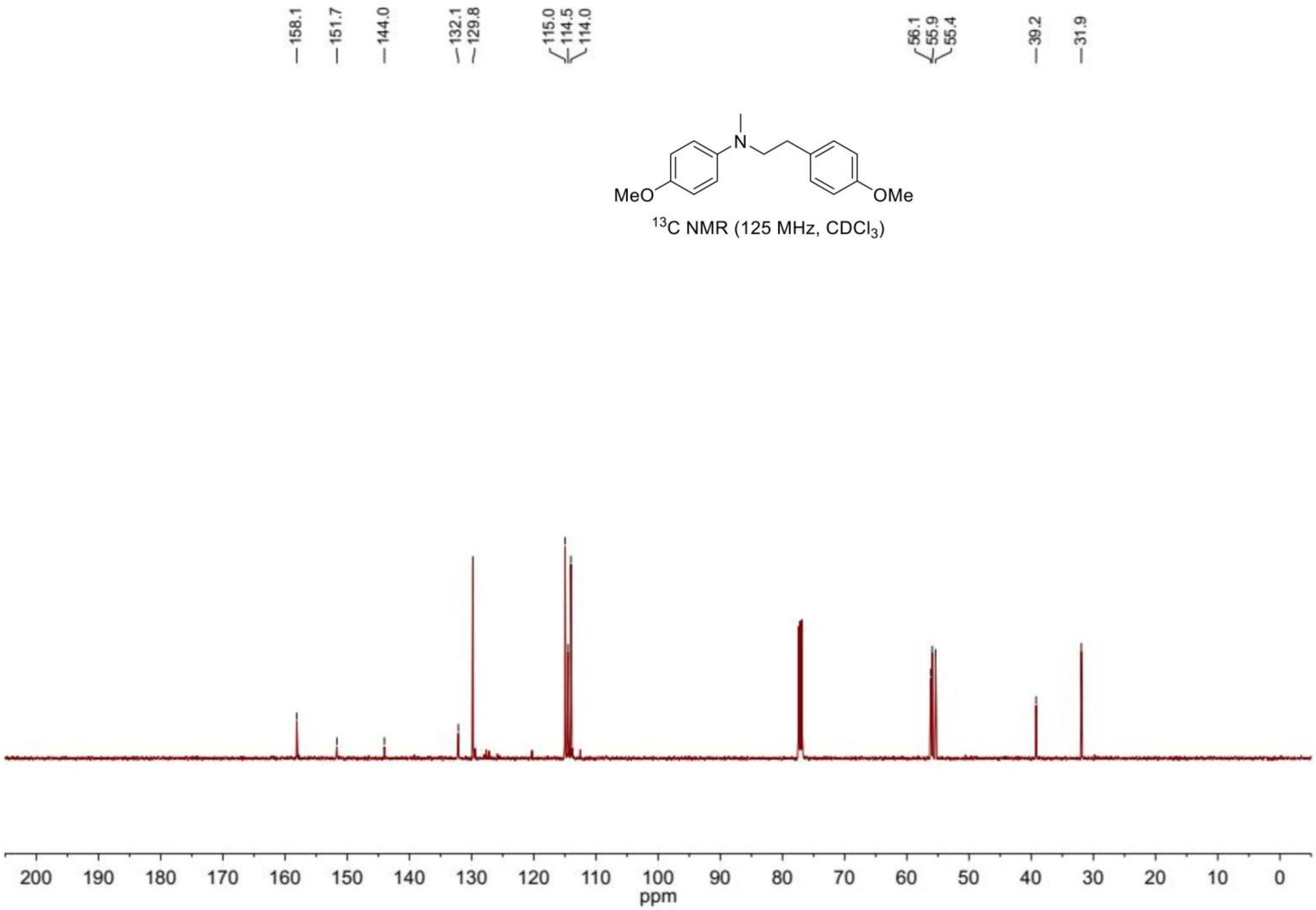
4-Methoxy-*N*-(4-methoxyphenethyl)-*N*-methylaniline (37)



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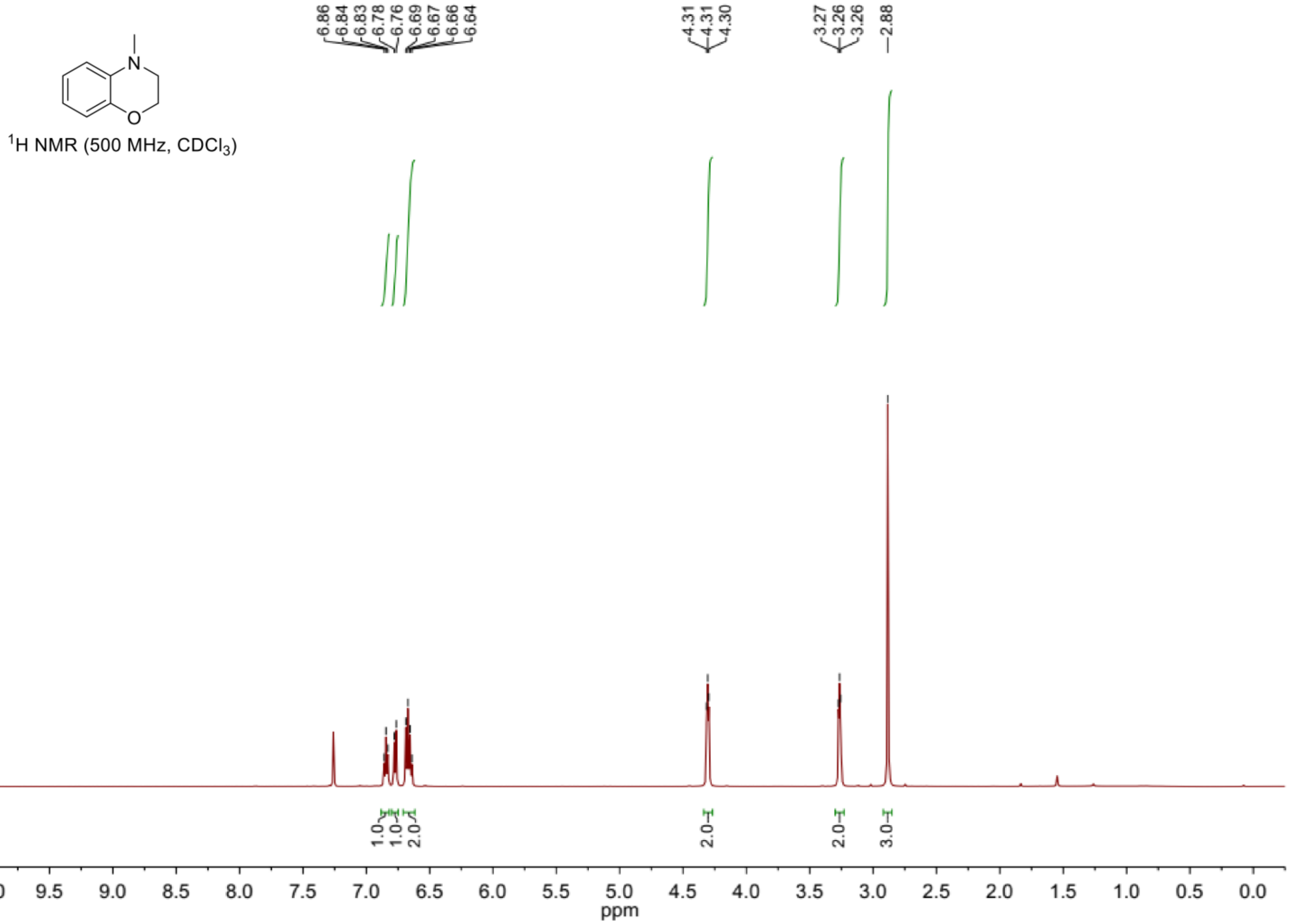
4-Methyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazine (38)



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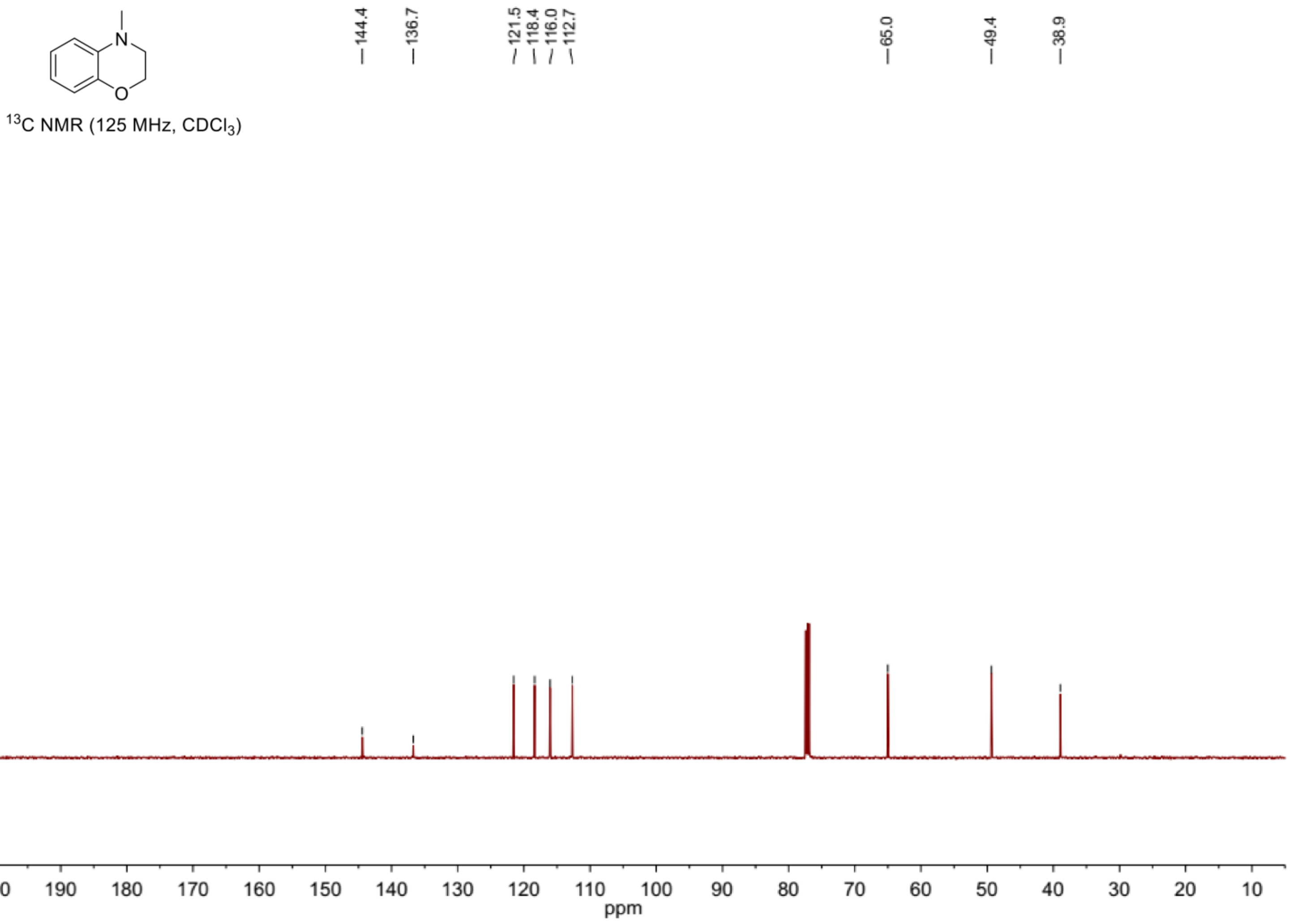
4-Methyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazine (38)



^{13}C NMR (125 MHz, CDCl$_3$)

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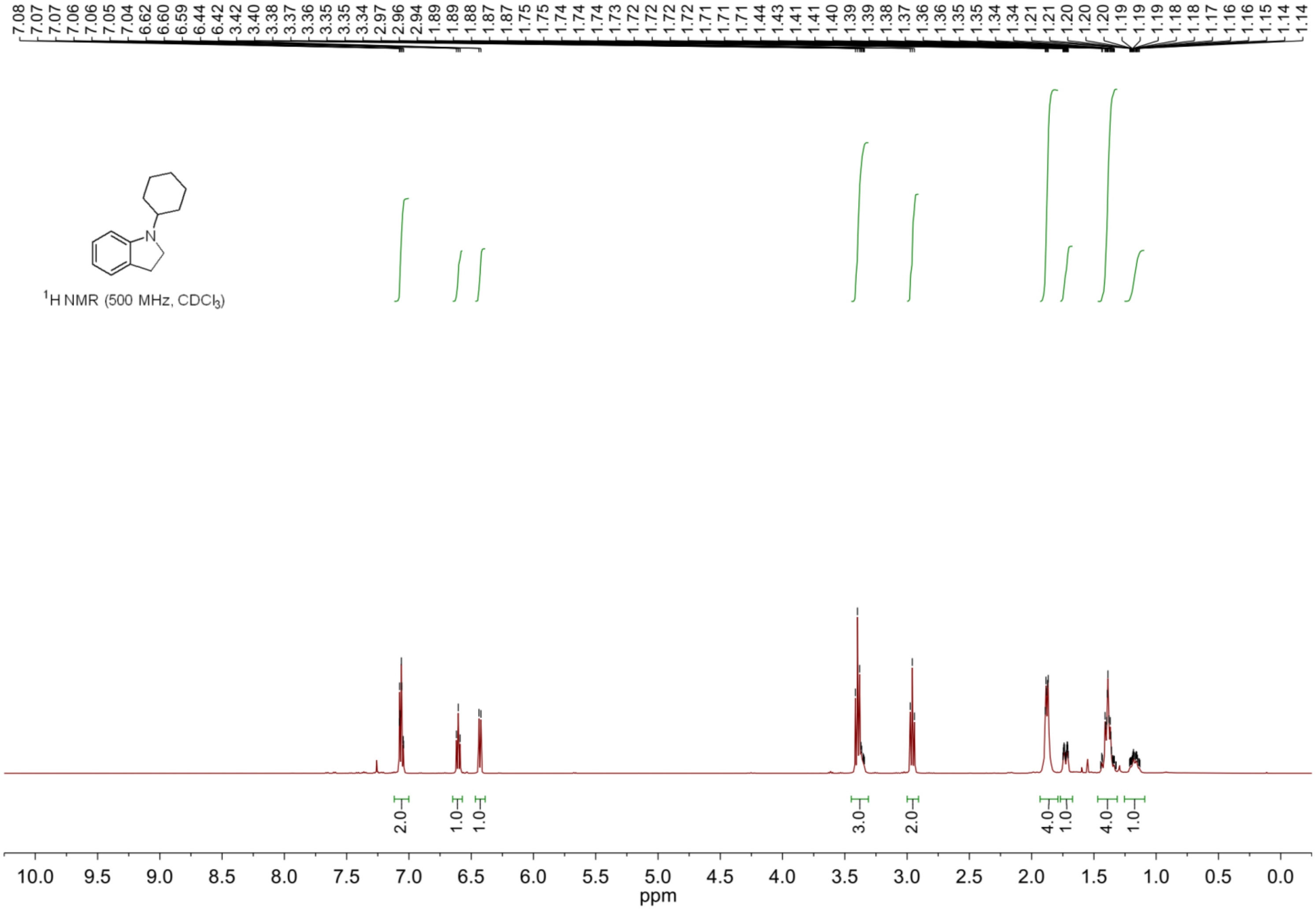
1-Cyclohexylindoline (39)



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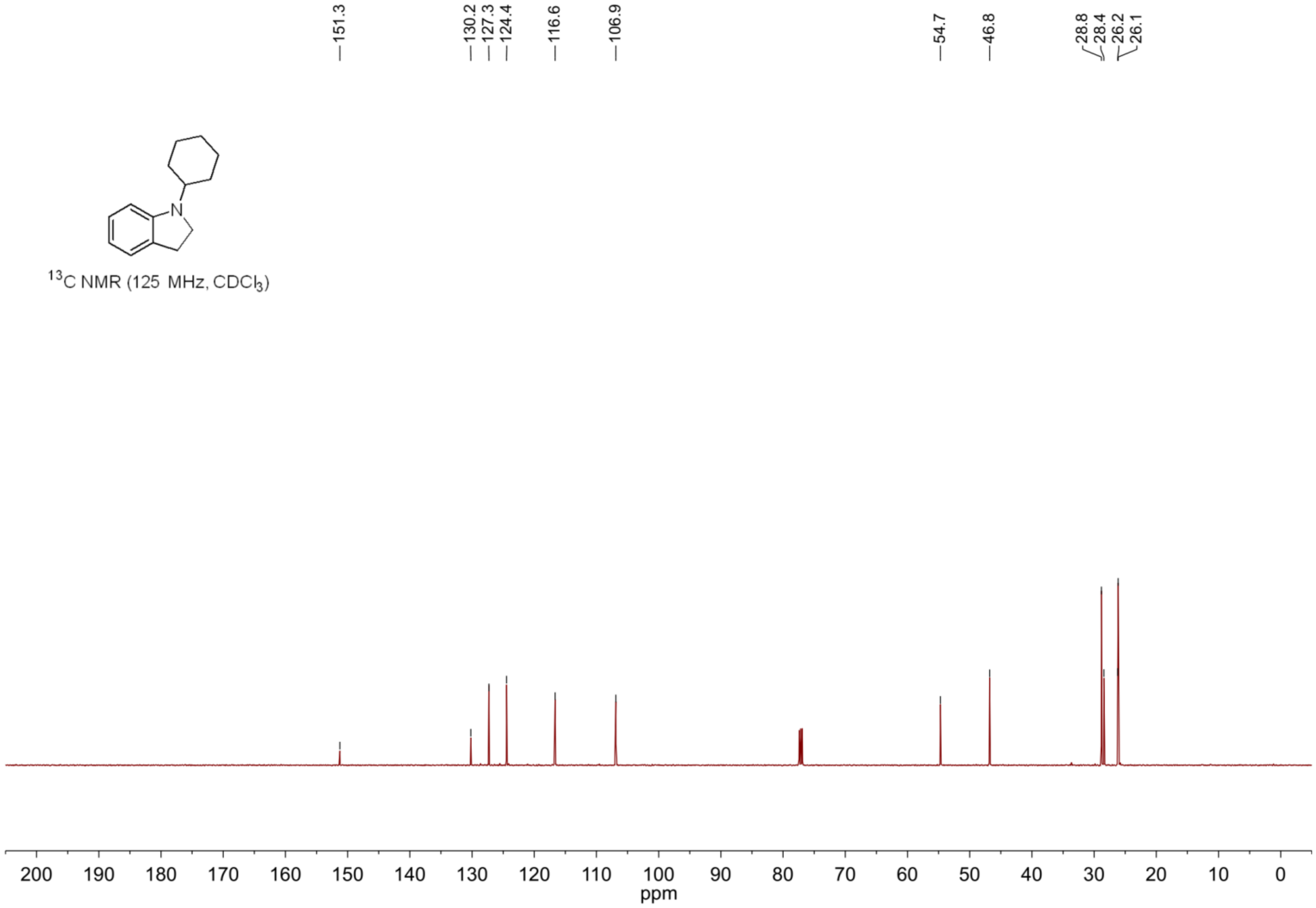
1-Cyclohexylindoline (39)



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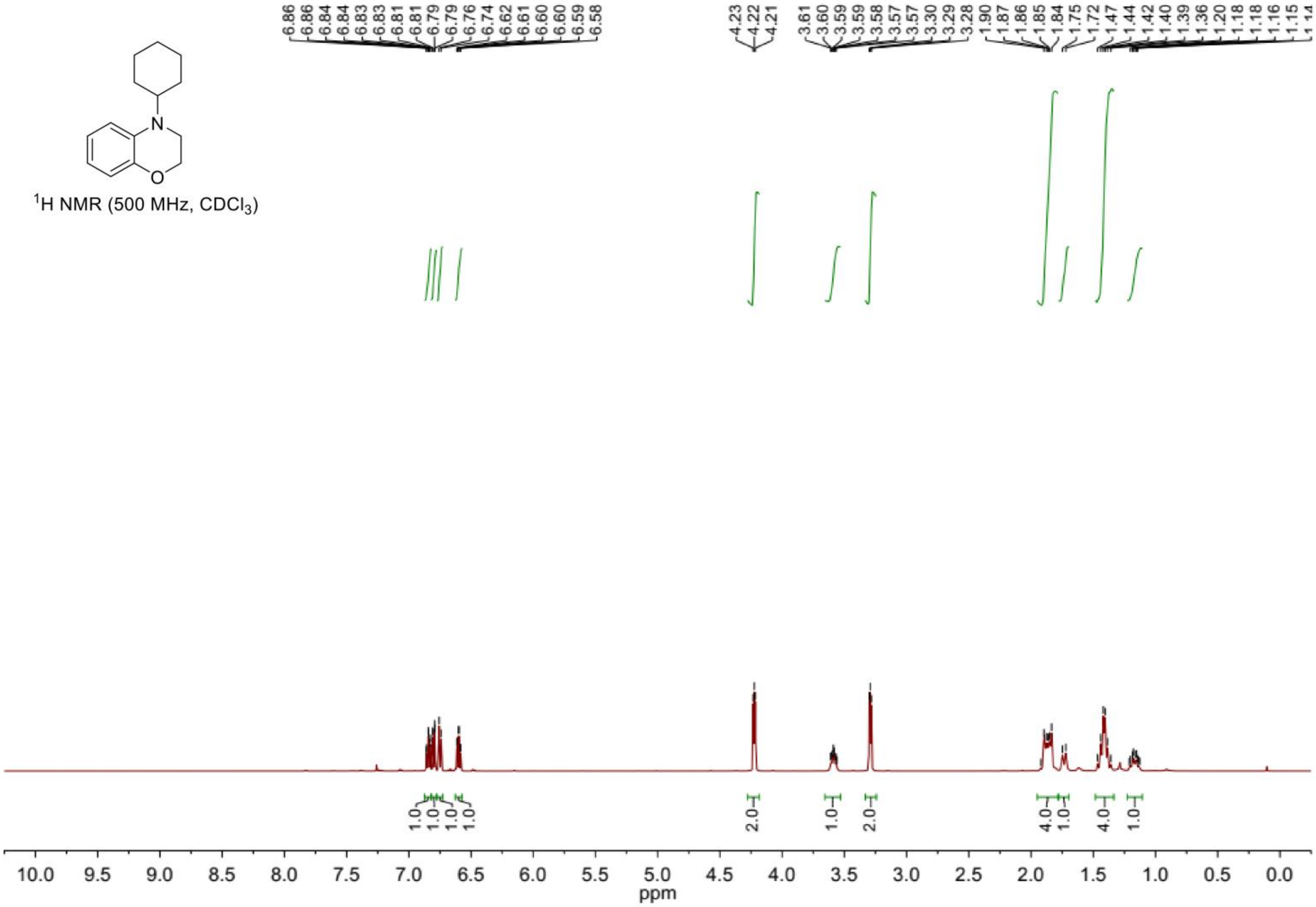
4-Cyclohexyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazine (40)



^{1}H NMR (500 MHz, CDCl$_3$)

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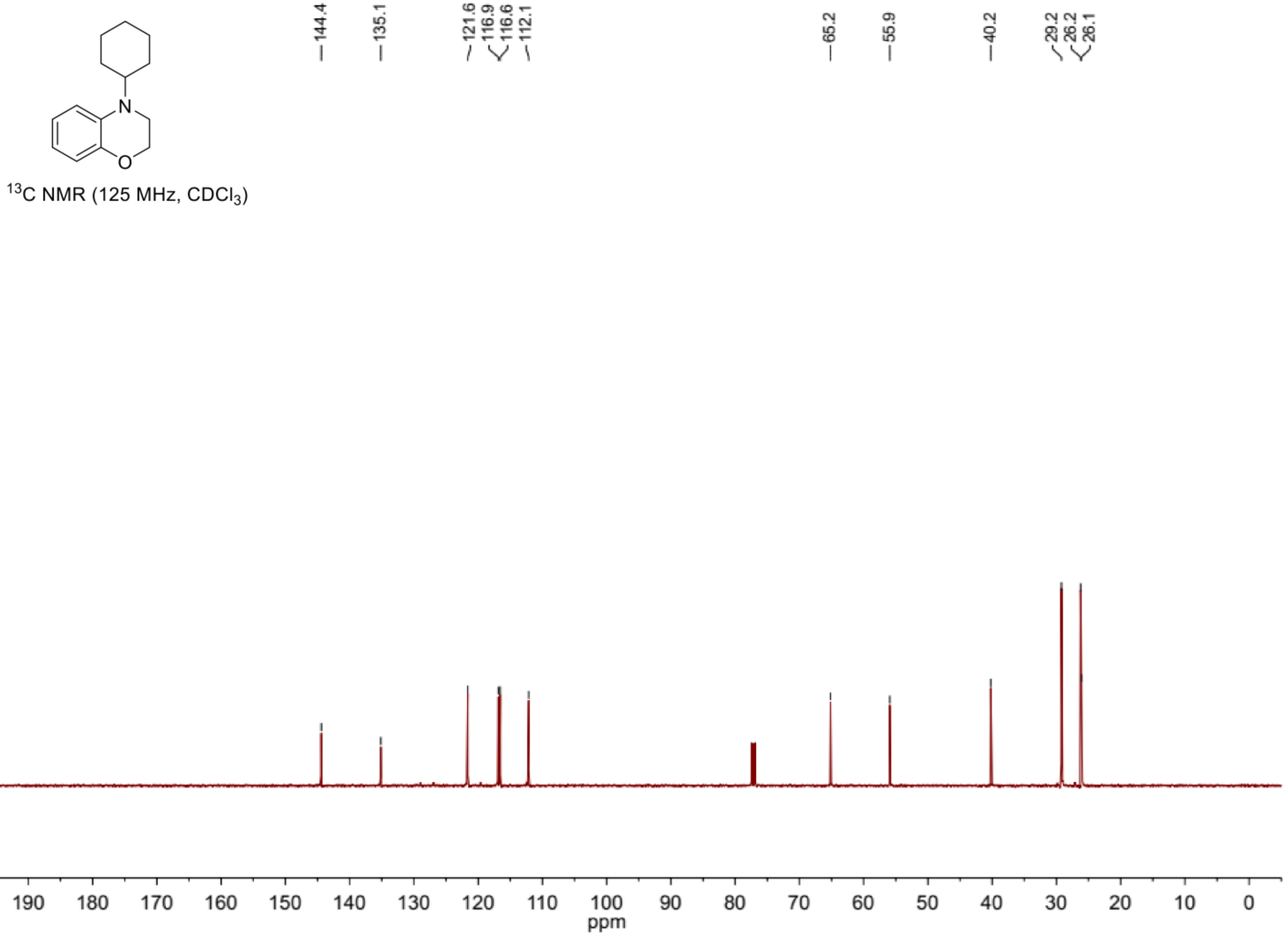
4-Cyclohexyl-3,4-dihydro-2*H*-benzo[*b*][1,4]oxazine (40)



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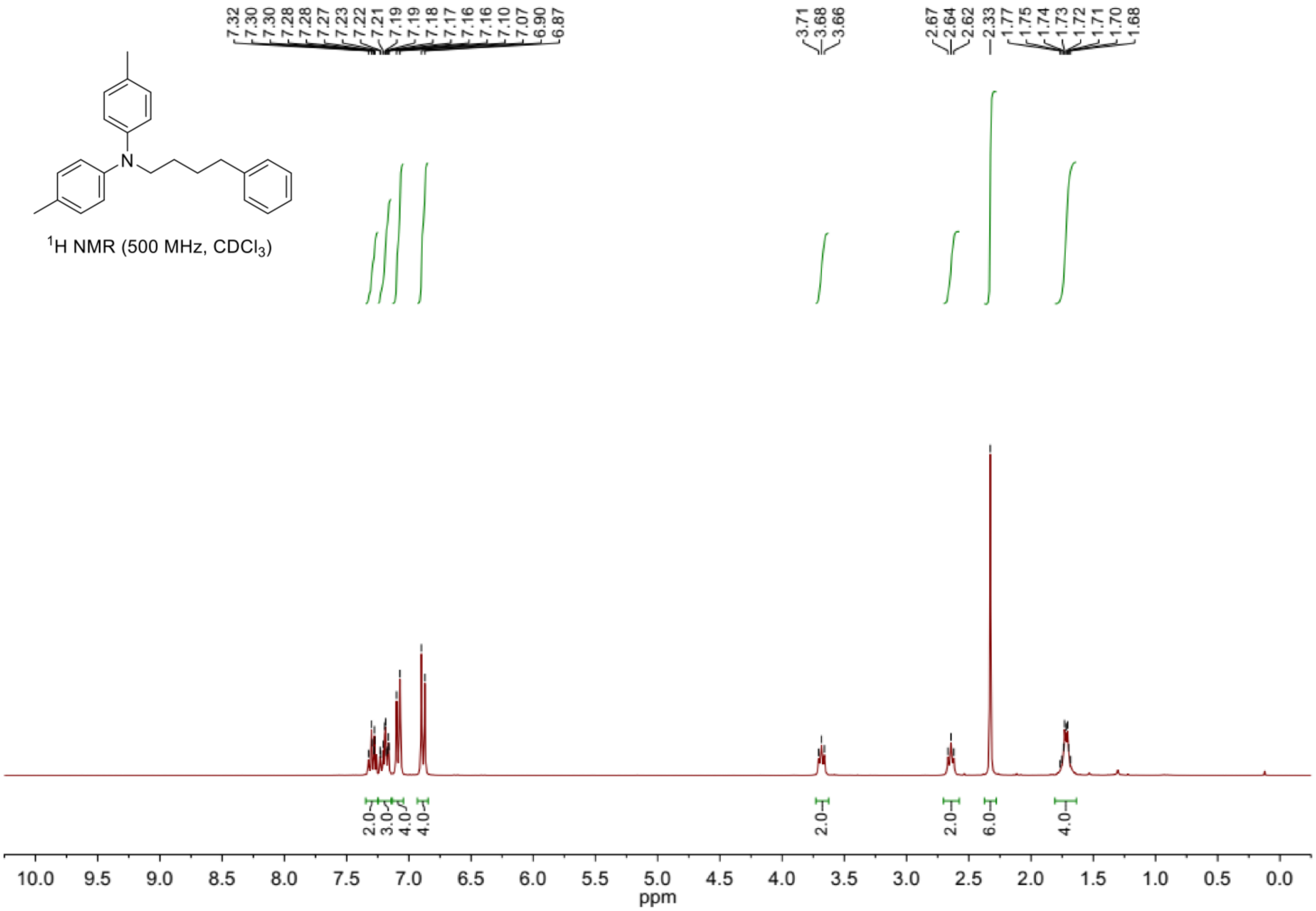
4-Methyl-*N*-(4-phenylbutyl)-*N*-(*p*-tolyl)aniline (41)



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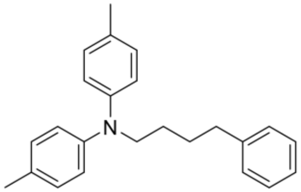
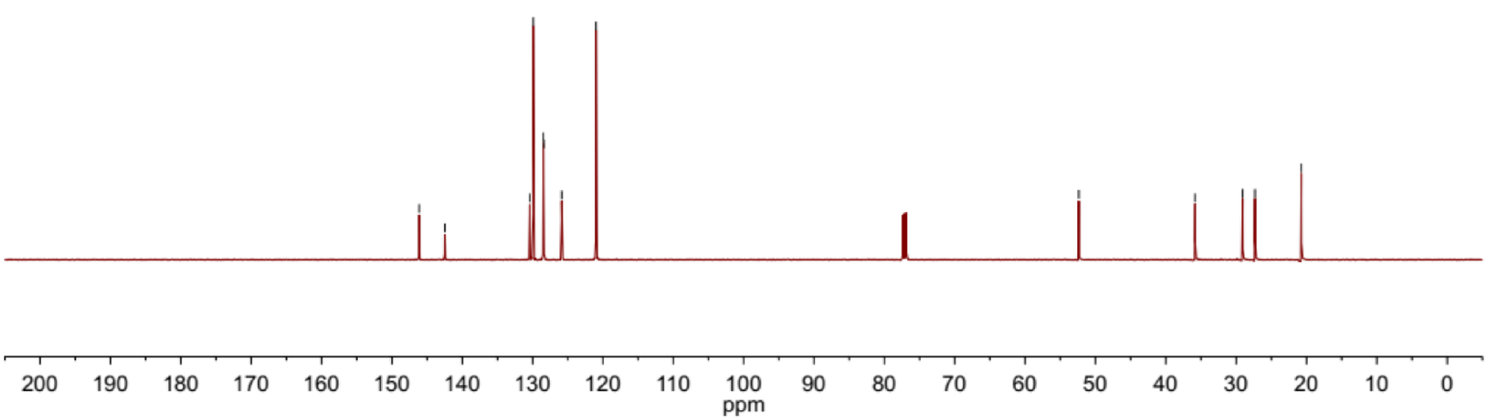
4-Methyl-*N*-(4-phenylbutyl)-*N*-(*p*-tolyl)aniline (41)



^{13}C NMR (125 MHz, CDCl$_3$)



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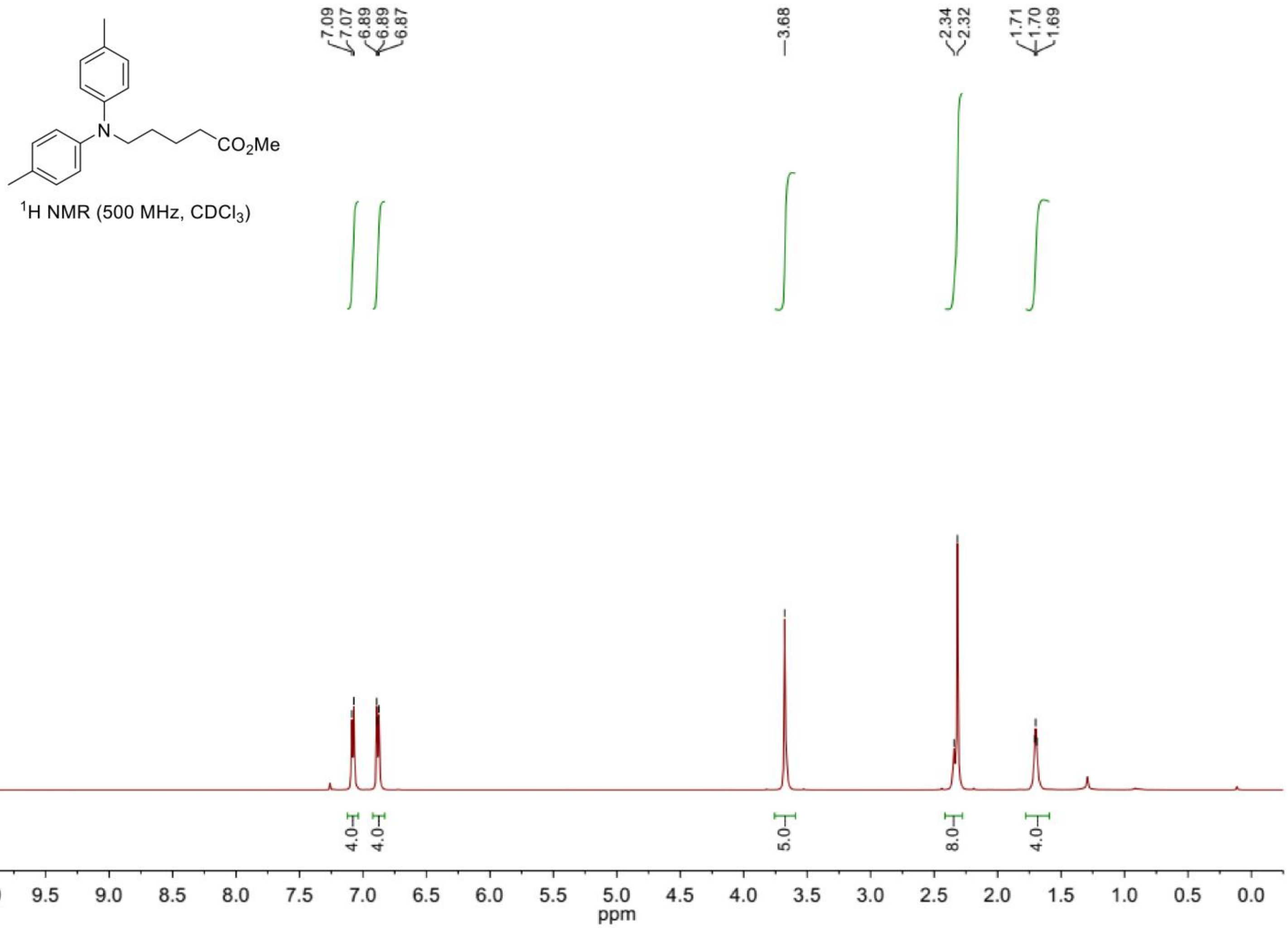
Methyl 5-(di-*p*-tolylamino)pentanoate (42)



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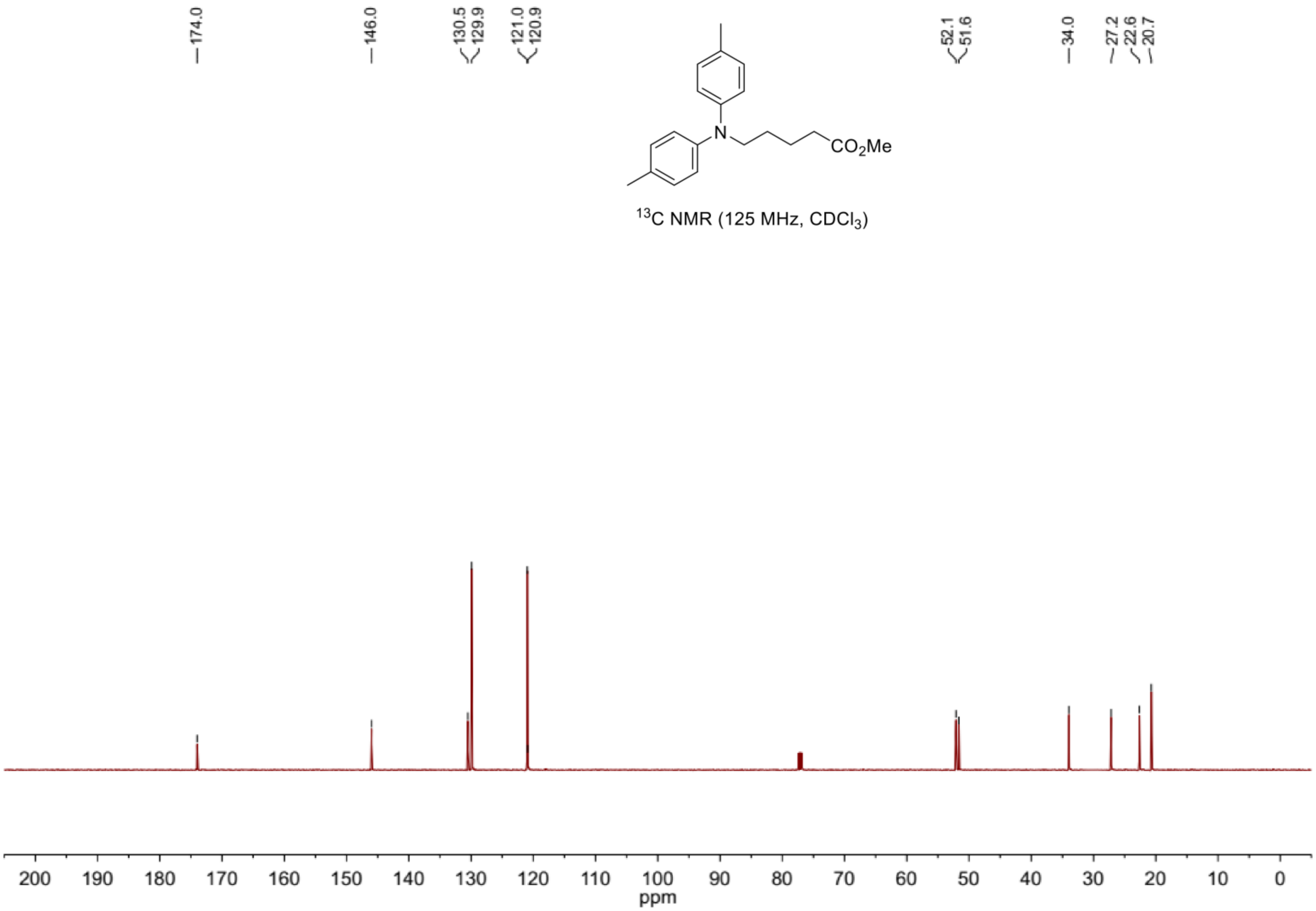
Methyl 5-(di-*p*-tolylamino)pentanoate (42)



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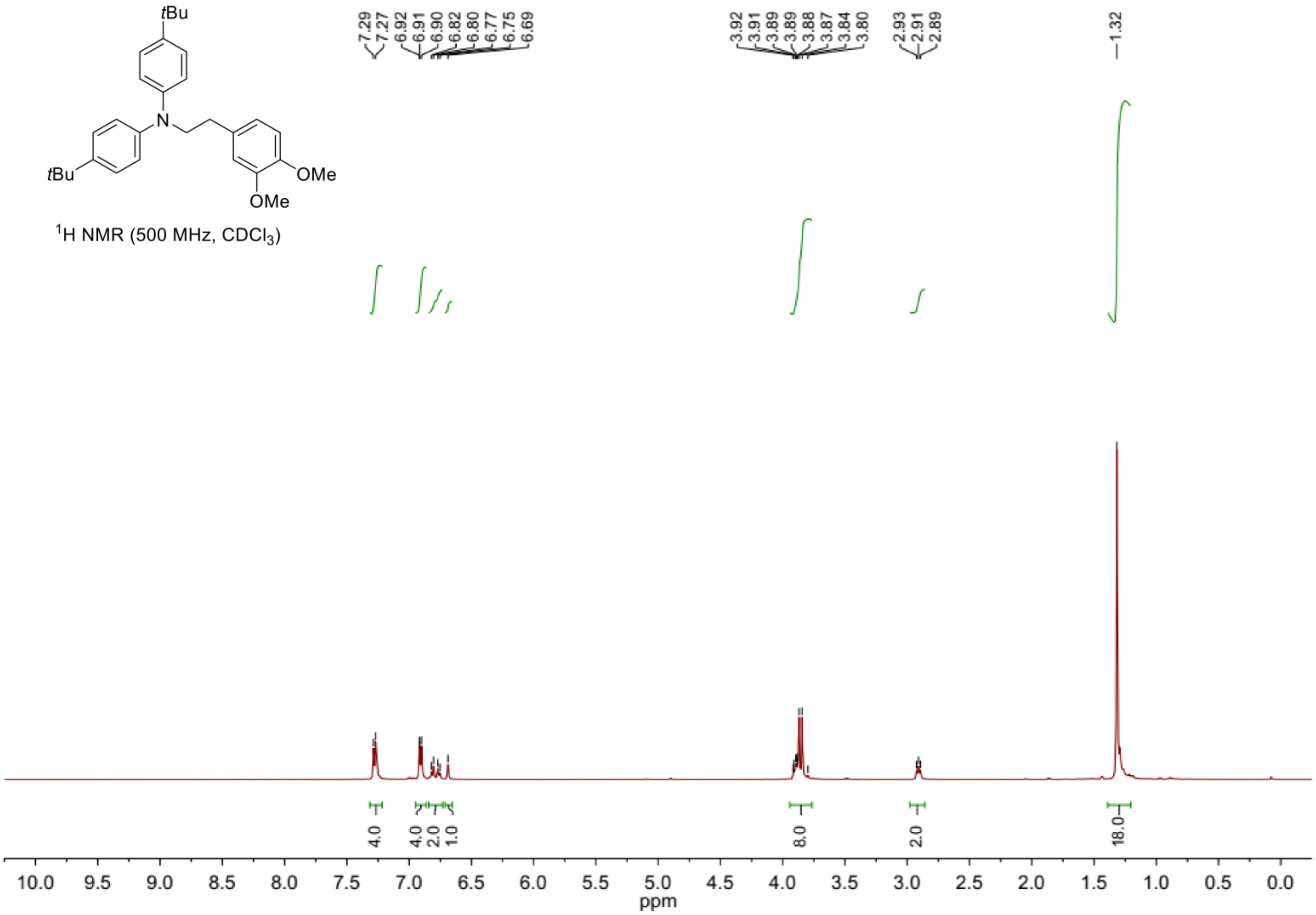
4-(*tert*-Butyl)-*N*-(4-(*tert*-butyl)phenyl)-*N*-(3,4-dimethoxyphenethyl)aniline (43)


^{1}H NMR (500 MHz, CDCl$_3$)

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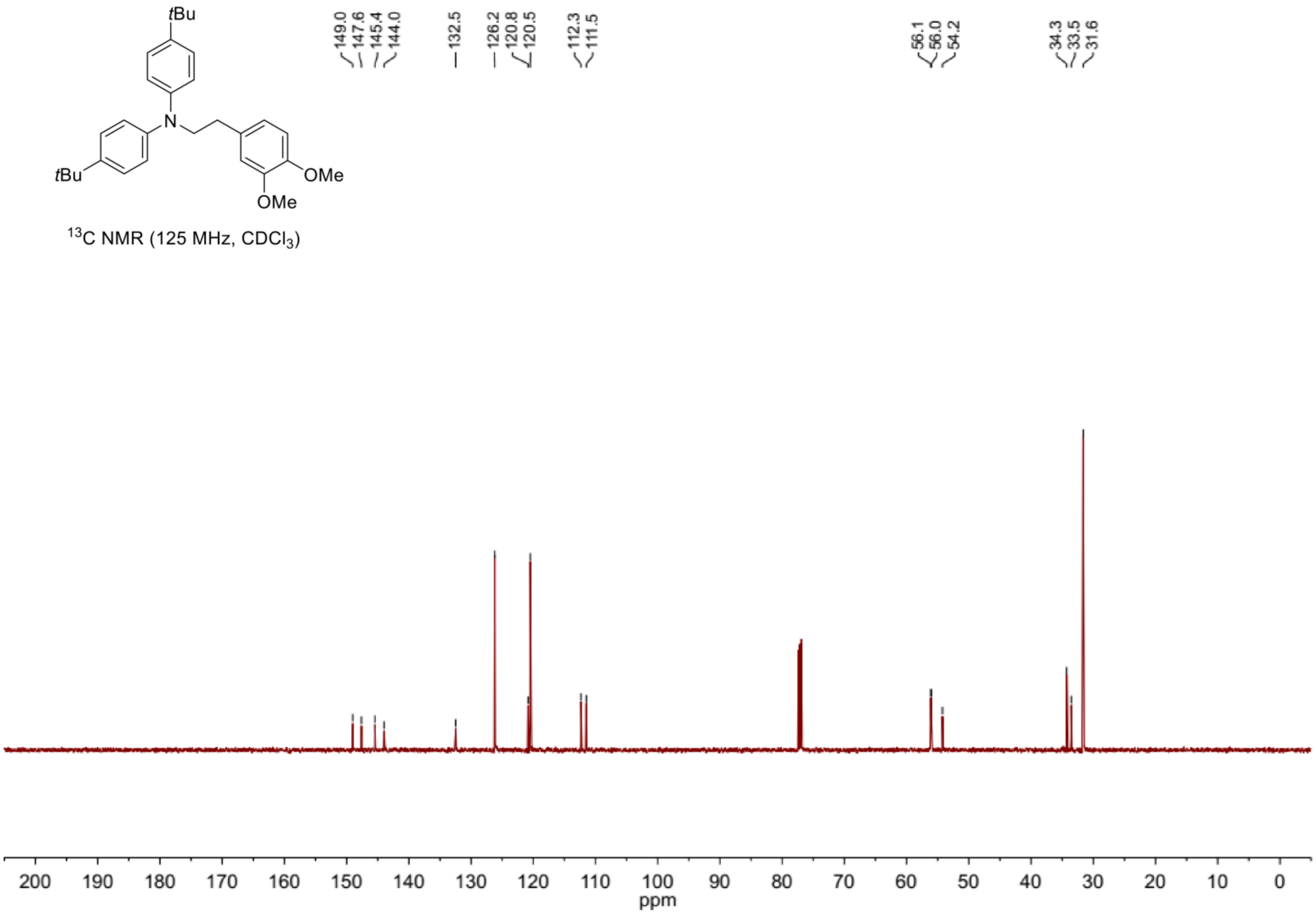
4-(*tert*-Butyl)-*N*-(4-(*tert*-butyl)phenyl)-*N*-(3,4-dimethoxyphenethyl)aniline (43)



^{13}C NMR (125 MHz, $CDCl_3$)

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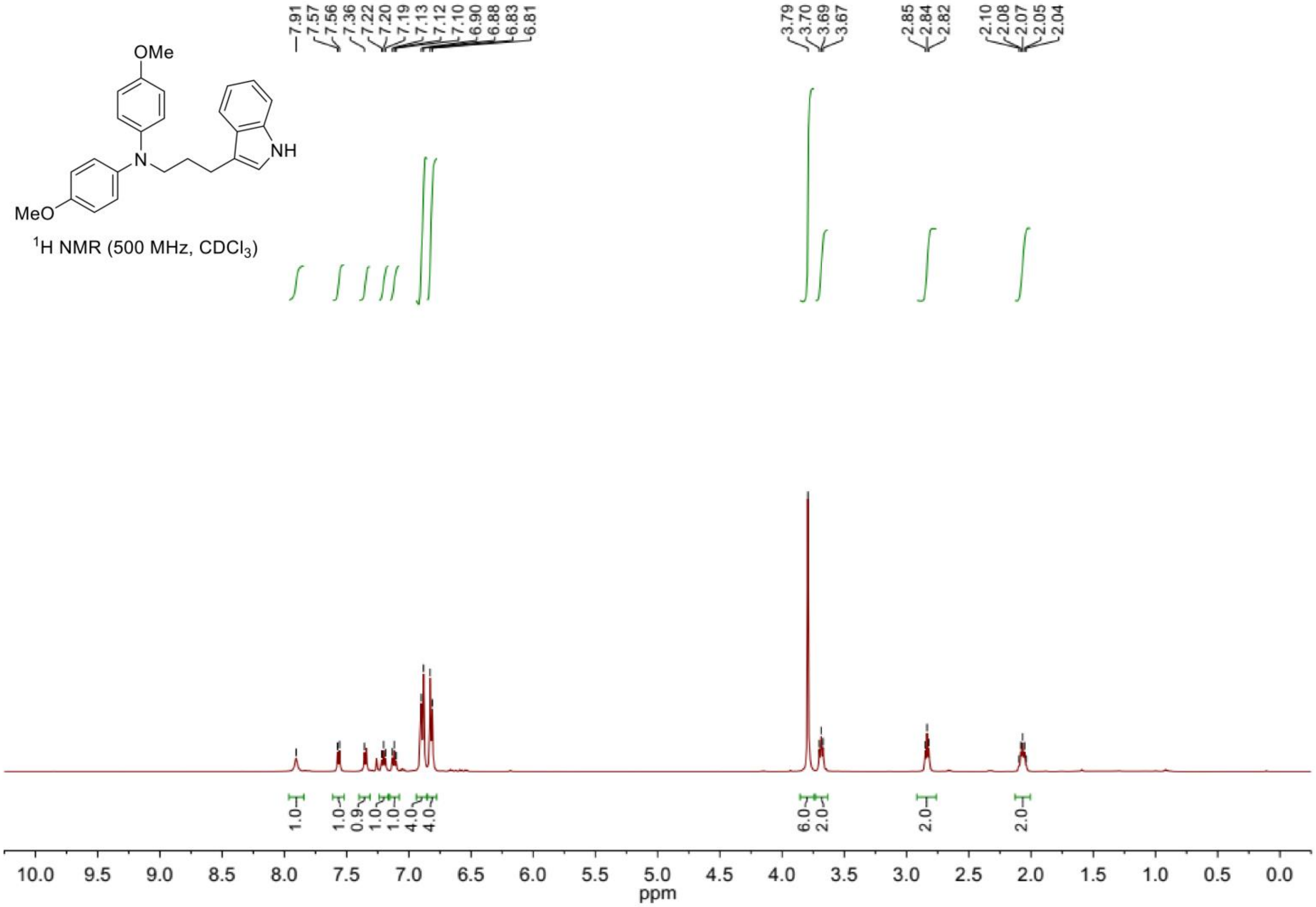
N-(3-(1*H*-Indol-3-yl)propyl)-4-methoxy-*N*-(4-methoxyphenyl)aniline (44)



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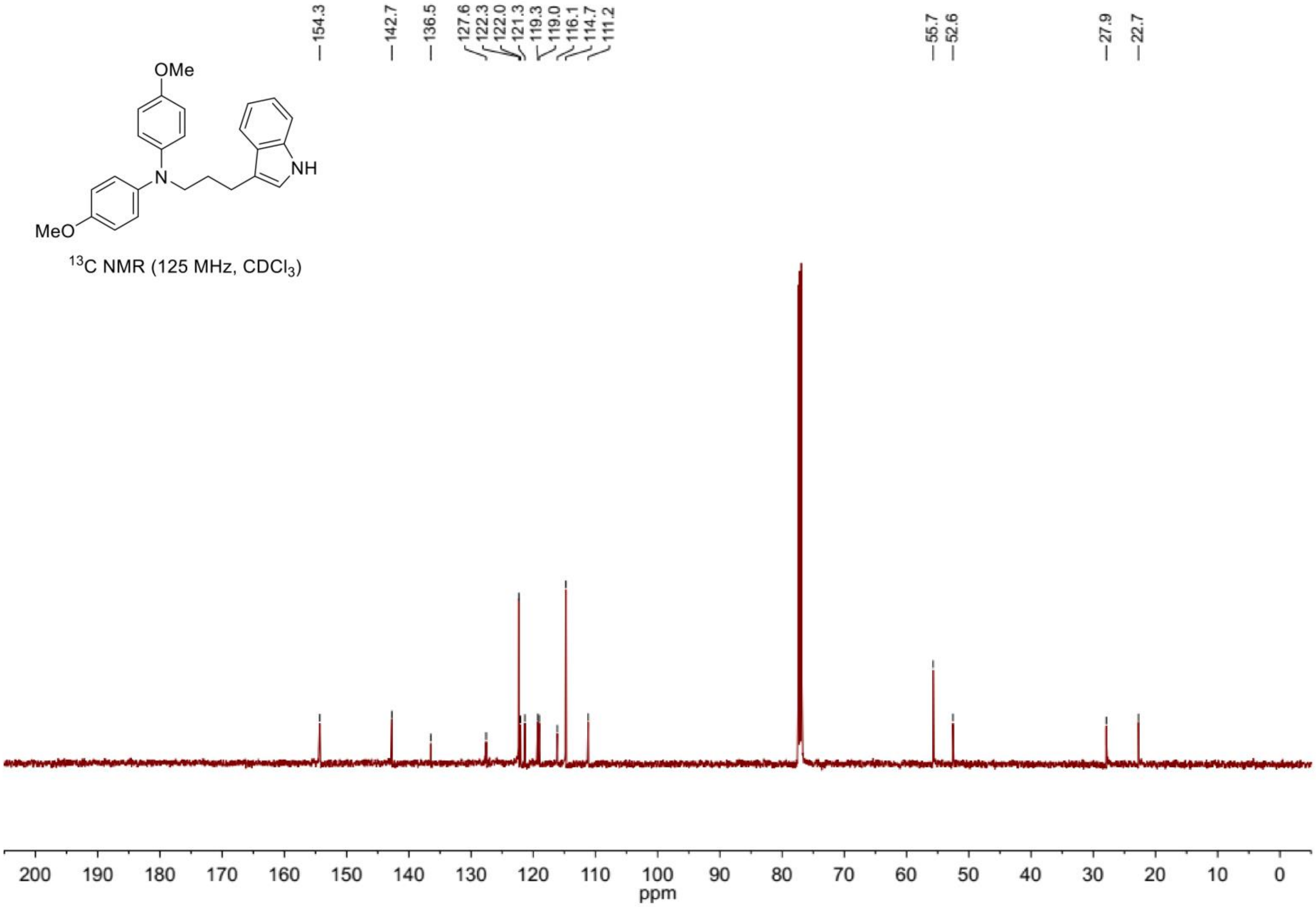
N-(3-(1*H*-Indol-3-yl)propyl)-4-methoxy-*N*-(4-methoxyphenyl)aniline (44)



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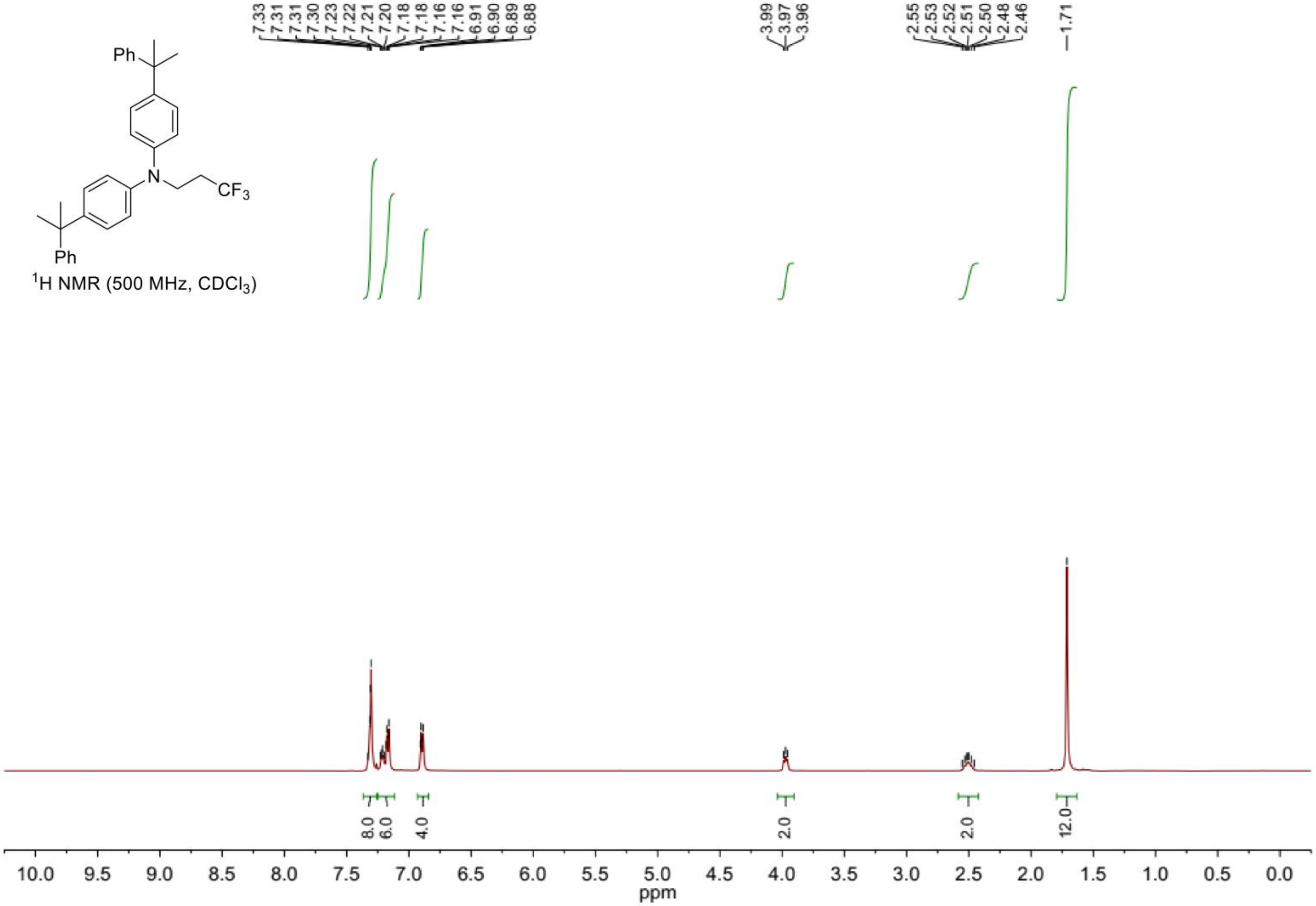
4-(2-Phenylpropan-2-yl)-*N*-(4-(2-phenylpropan-2-yl)phenyl)-*N*-(3,3,3-trifluoropropyl)aniline (45)



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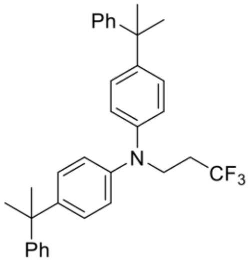
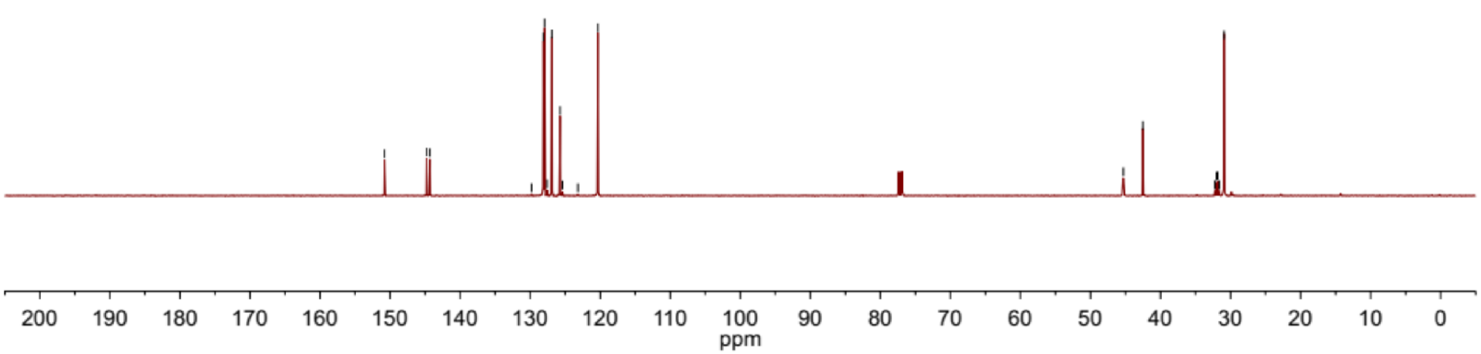
4-(2-Phenylpropan-2-yl)-*N*-(4-(2-phenylpropan-2-yl)phenyl)-*N*-(3,3,3-trifluoropropyl)aniline (45)



^{13}C NMR (125 MHz, CDCl$_3$)



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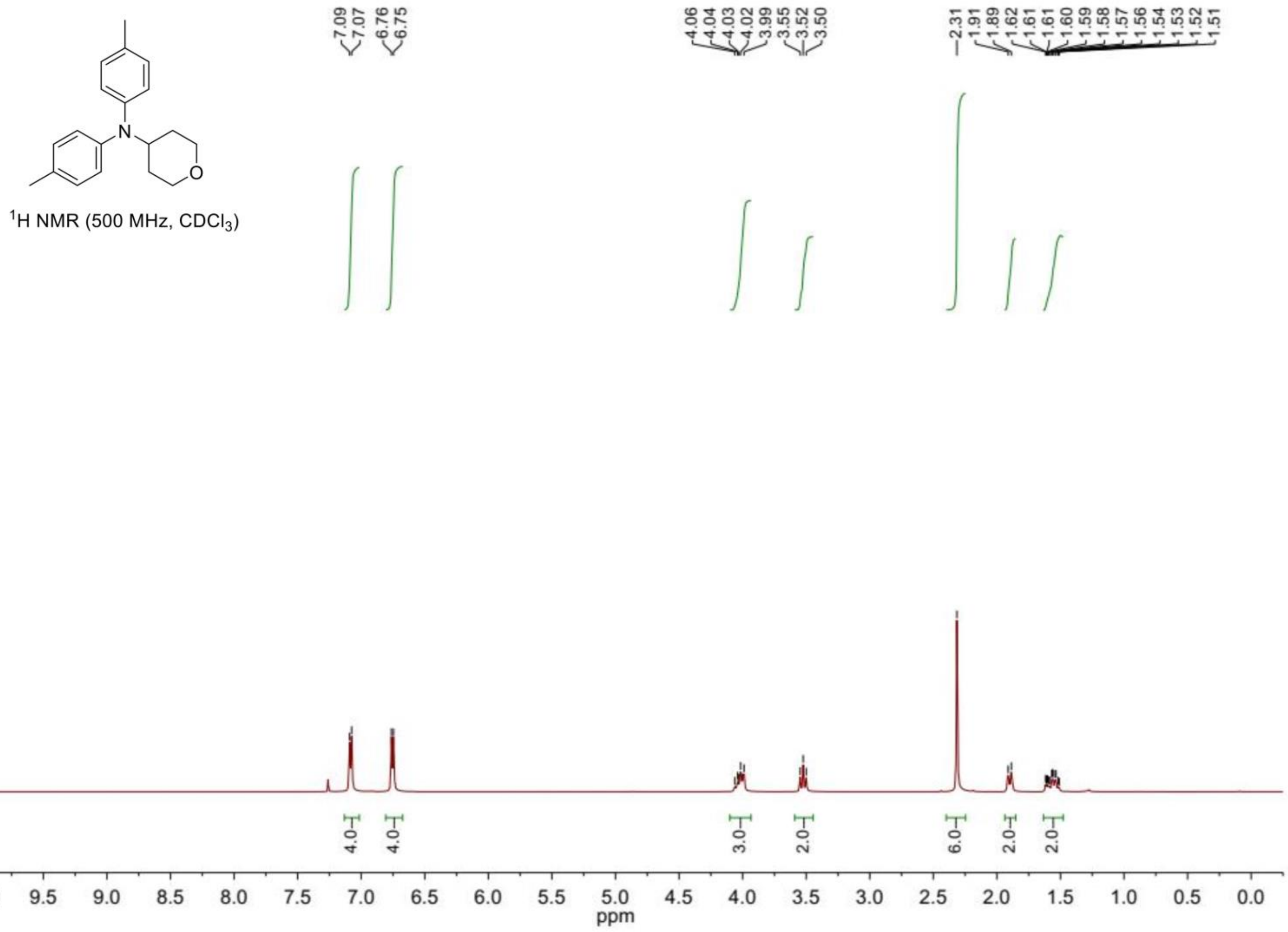
N,*N*-Di-*p*-tolyltetrahydro-2*H*-pyran-4-amine (46)



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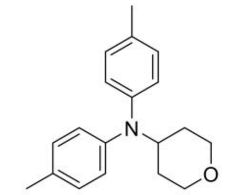
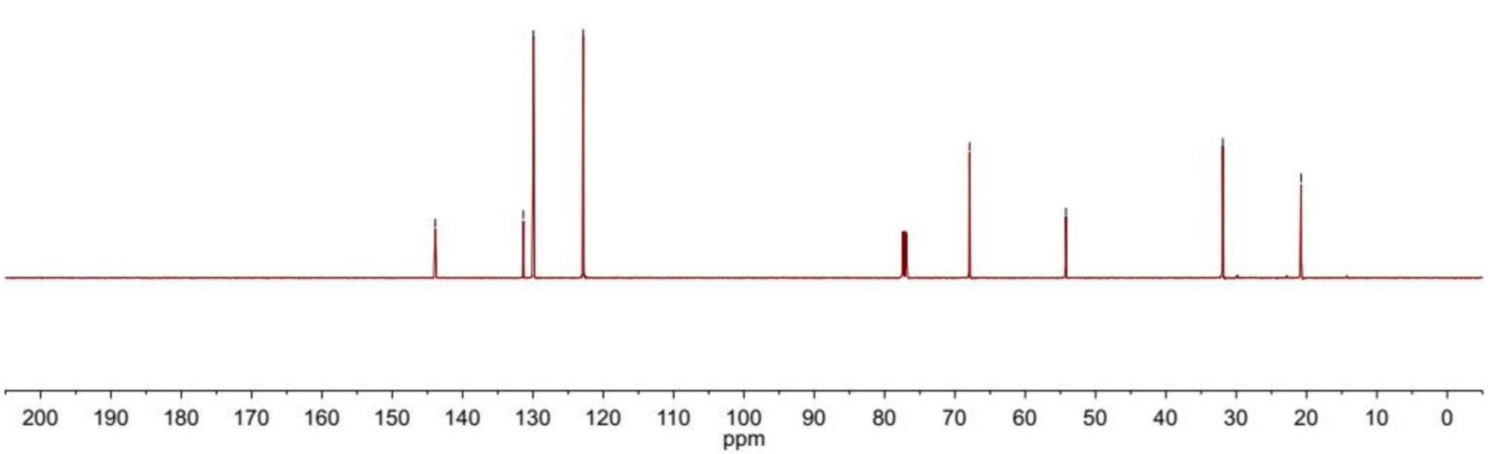
N,N-Di-*p*-tolyltetrahydro-2*H*-pyran-4-amine (46)



^{13}C NMR (125 MHz, CDCl$_3$)



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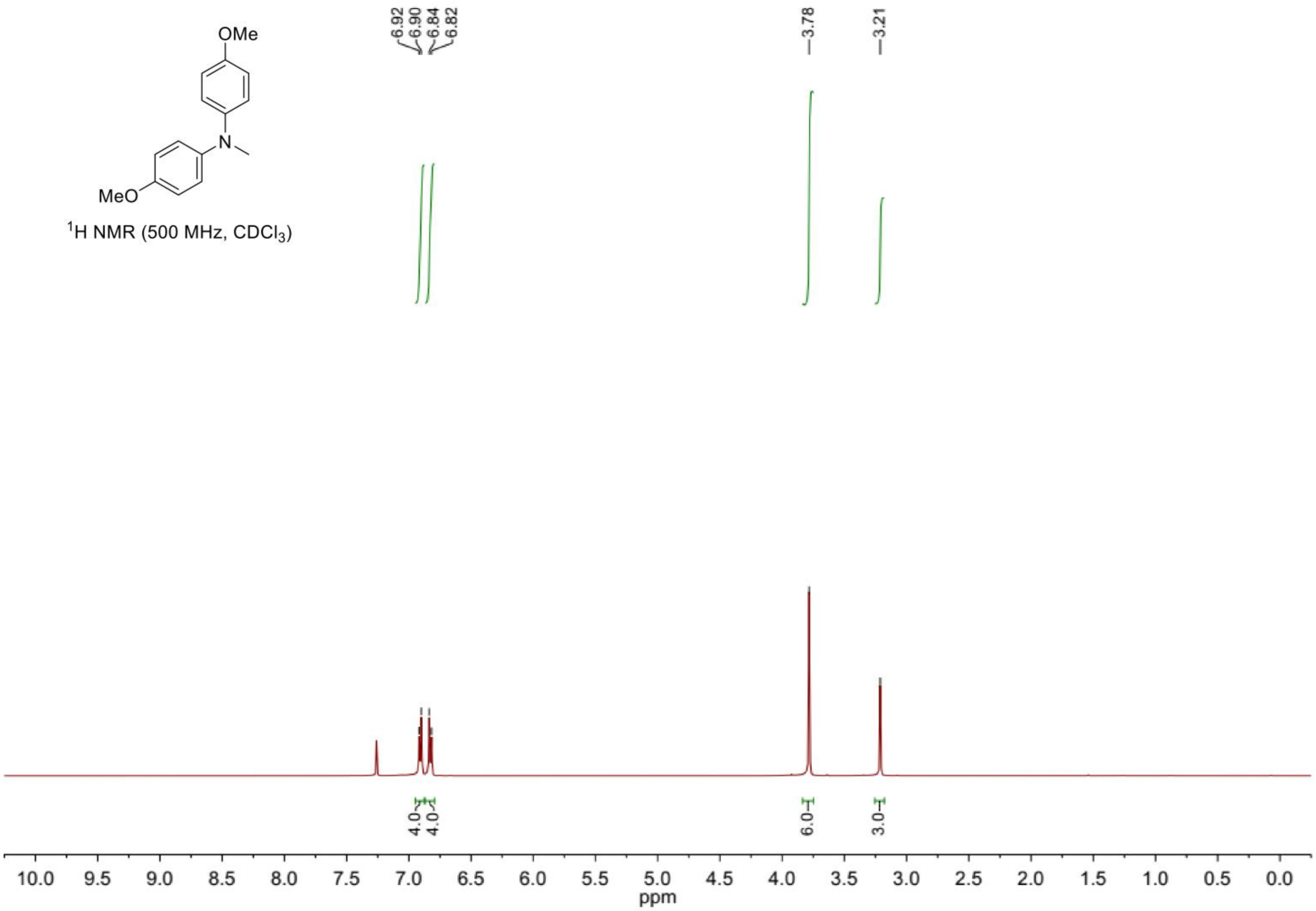
4-Methoxy-*N*-(4-methoxyphenyl)-*N*-methylaniline (47)



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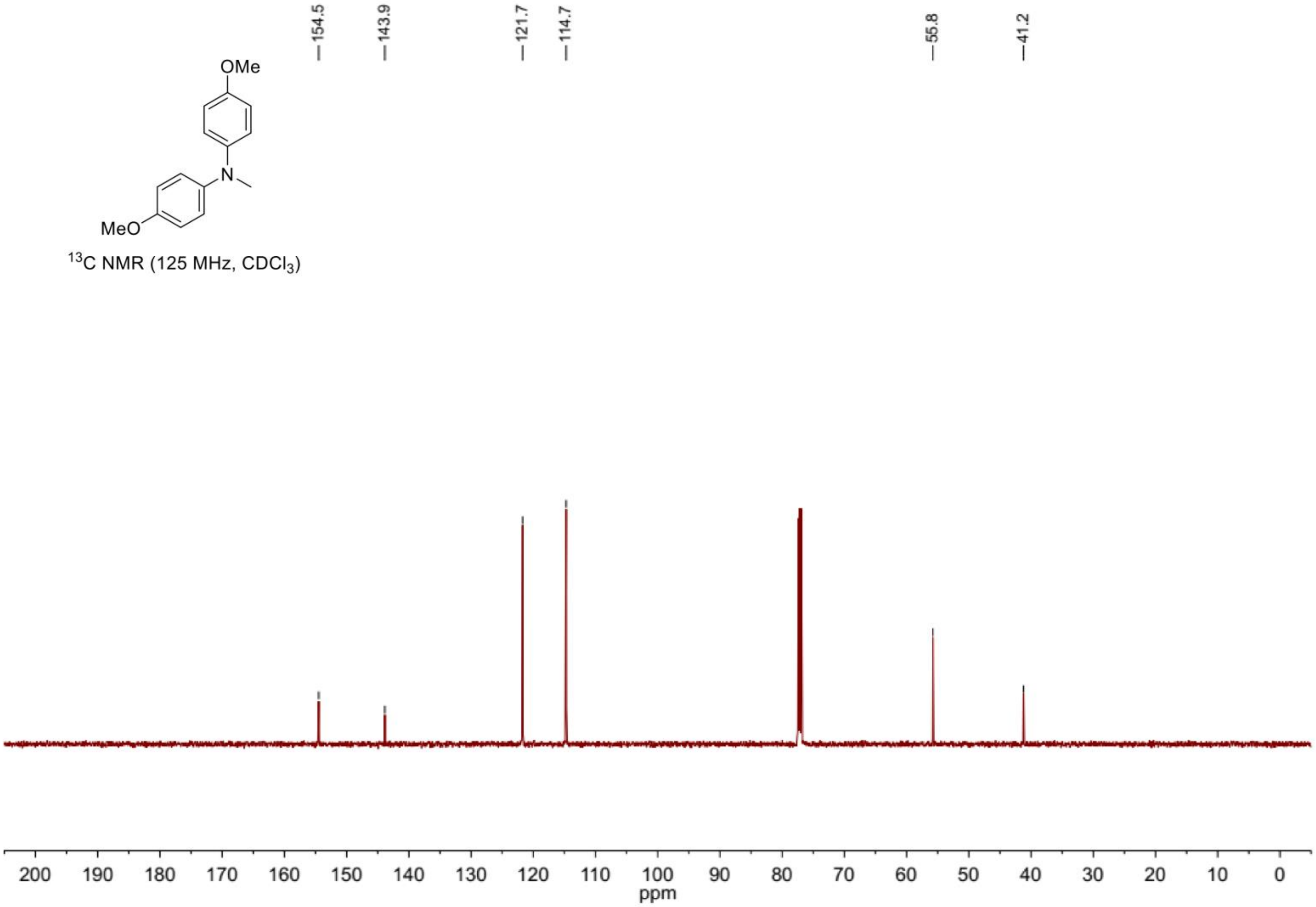
4-Methoxy-*N*-(4-methoxyphenyl)-*N*-methylaniline (47)



^{13}C NMR (125 MHz, $CDCl_3$)

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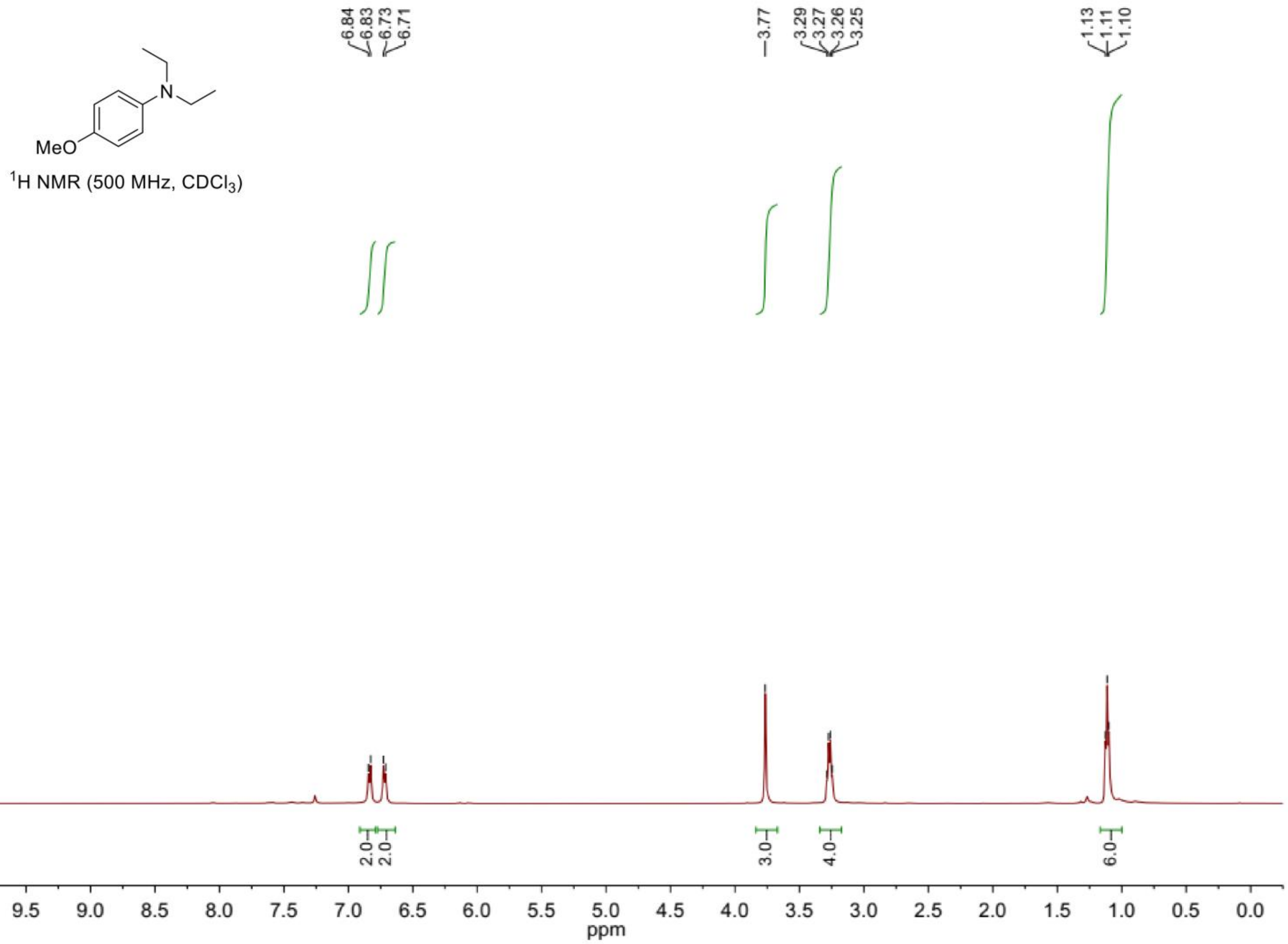
N,*N*-Diethyl-4-methoxyaniline (48)



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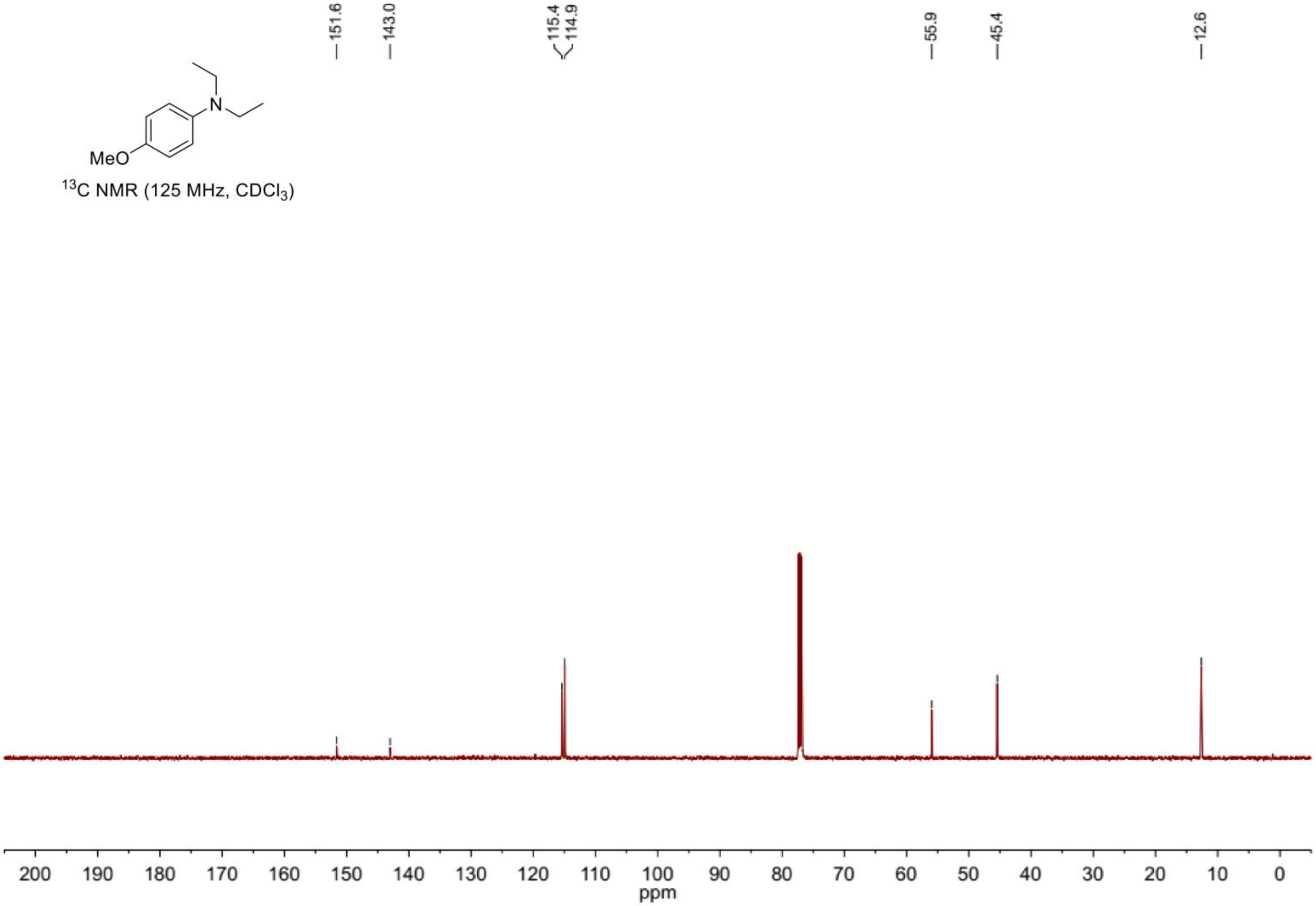
N,*N*-Diethyl-4-methoxyaniline (48)



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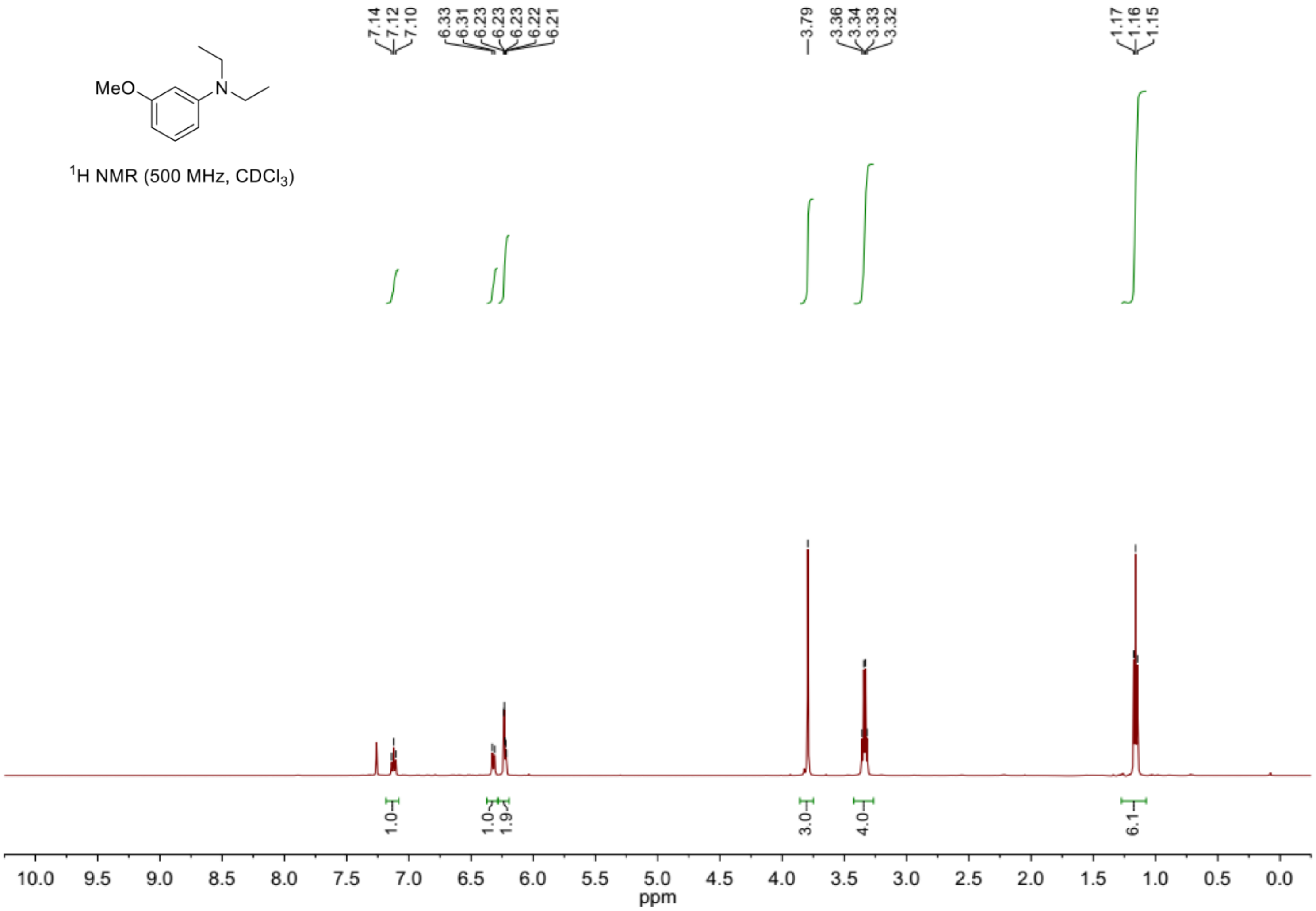
N,*N*-Diethyl-3-methoxyaniline (49)



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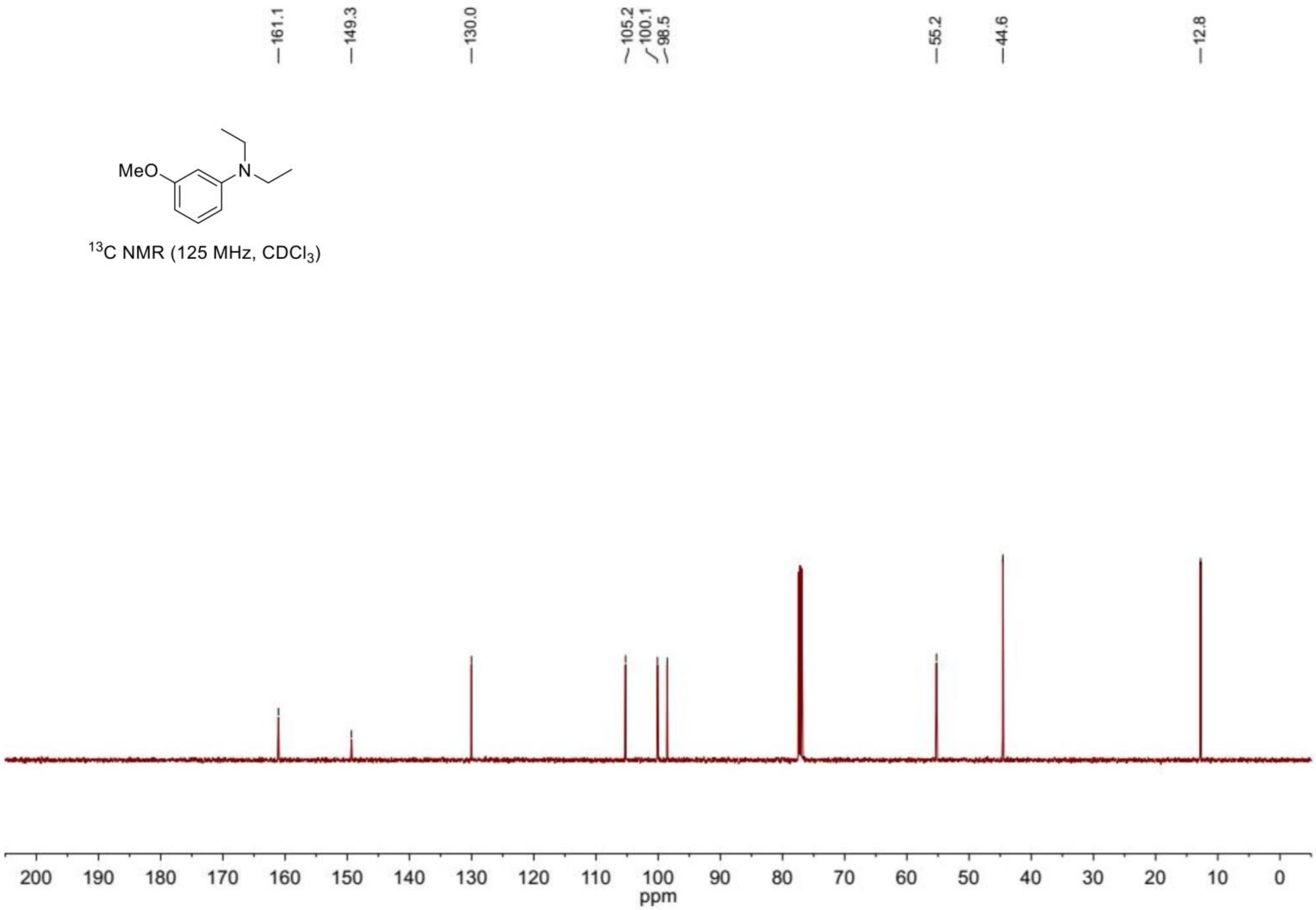
N,*N*-Diethyl-3-methoxyaniline (49)



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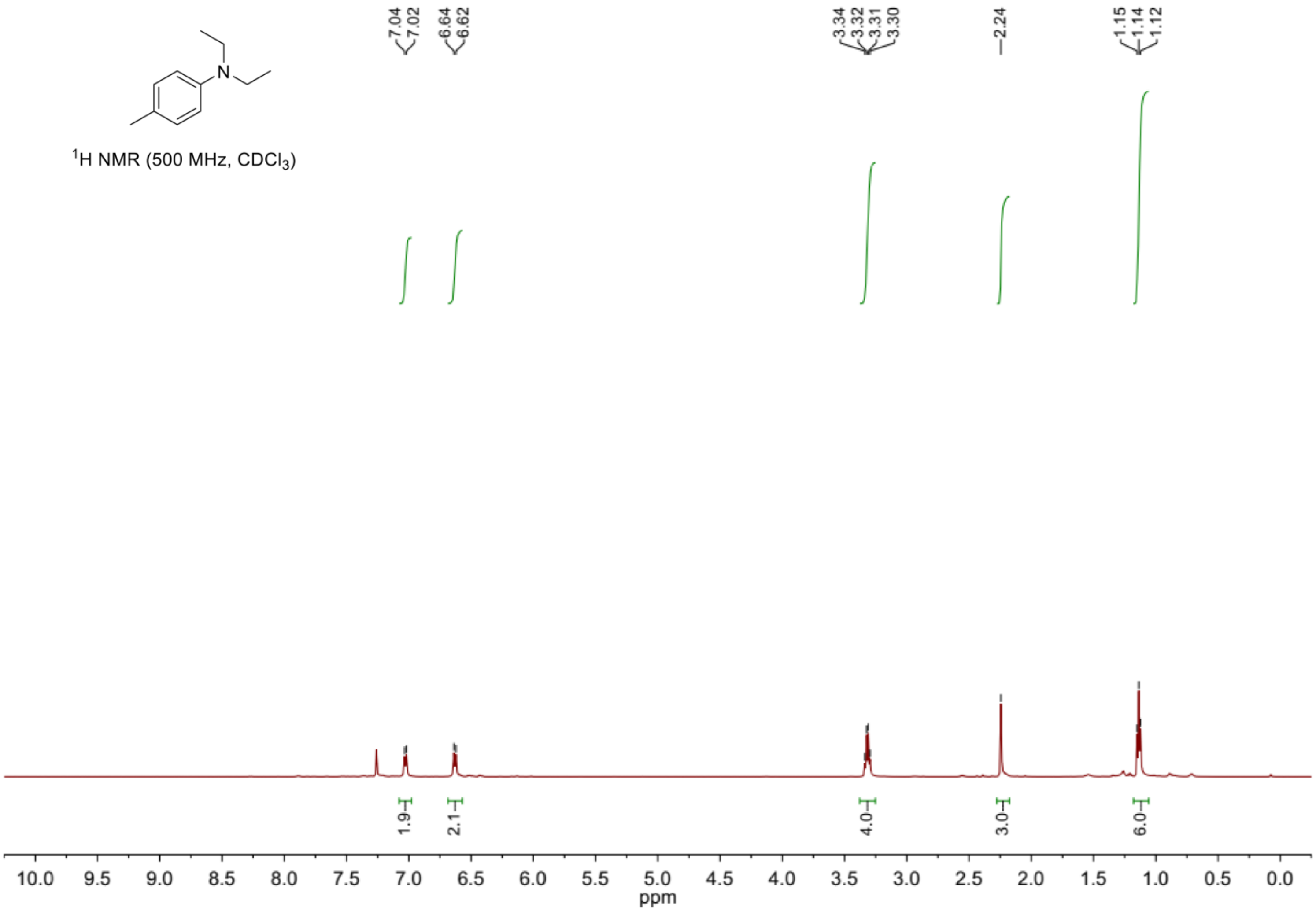
N,N-Diethyl-4-methylaniline (50)



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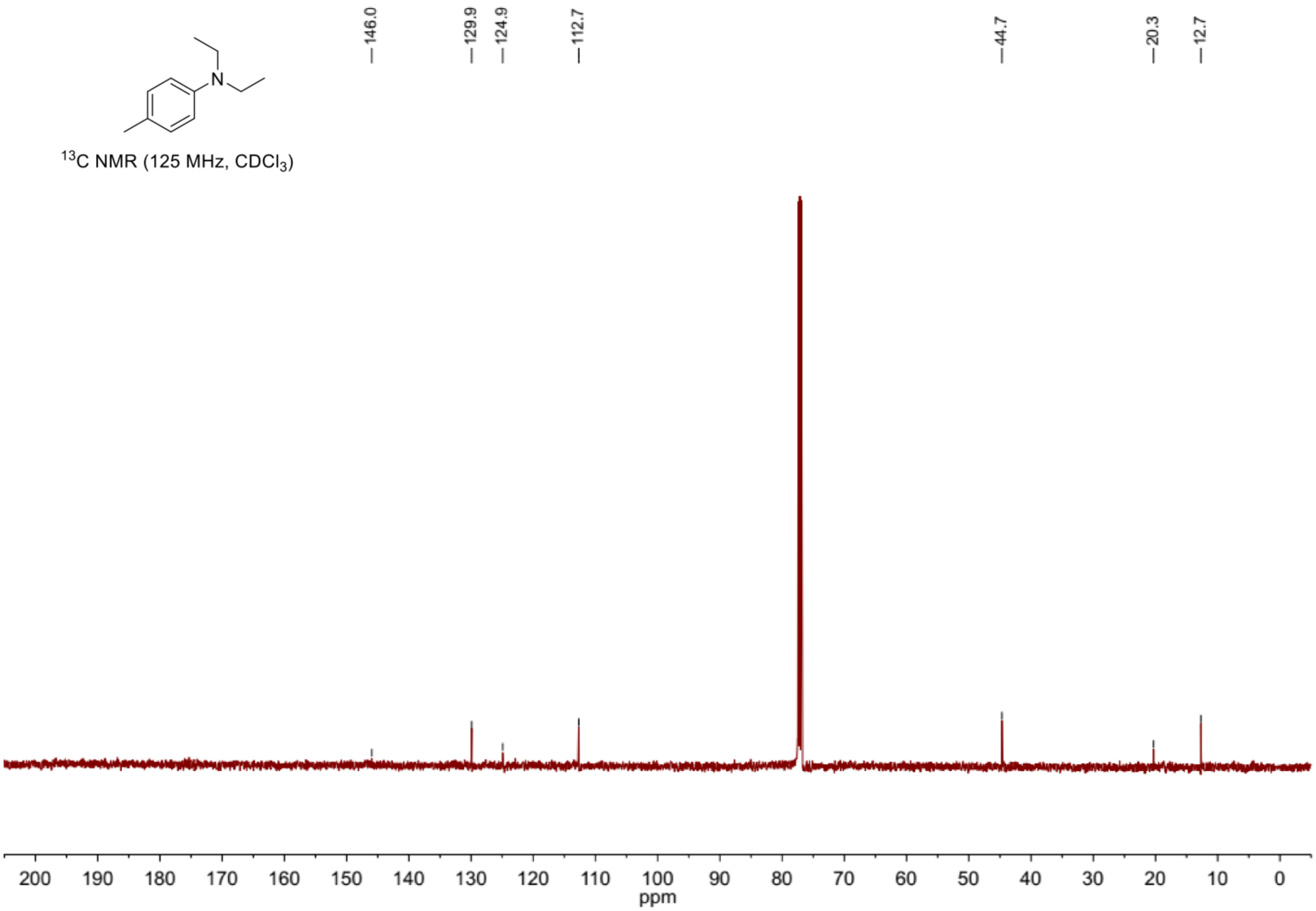
N,N-Diethyl-4-methylaniline (50)



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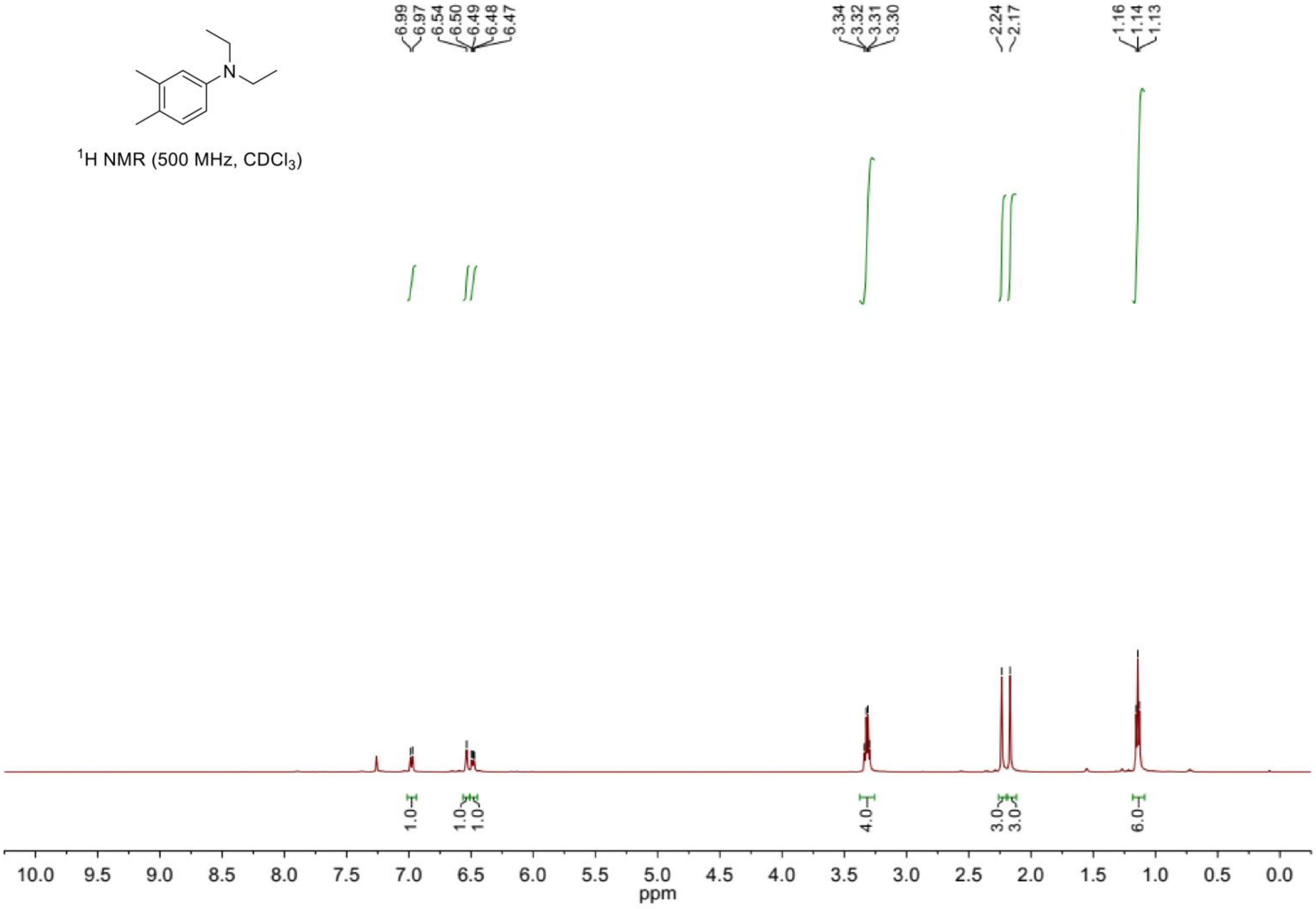
N,N-Diethyl-3,4-dimethylaniline (51)



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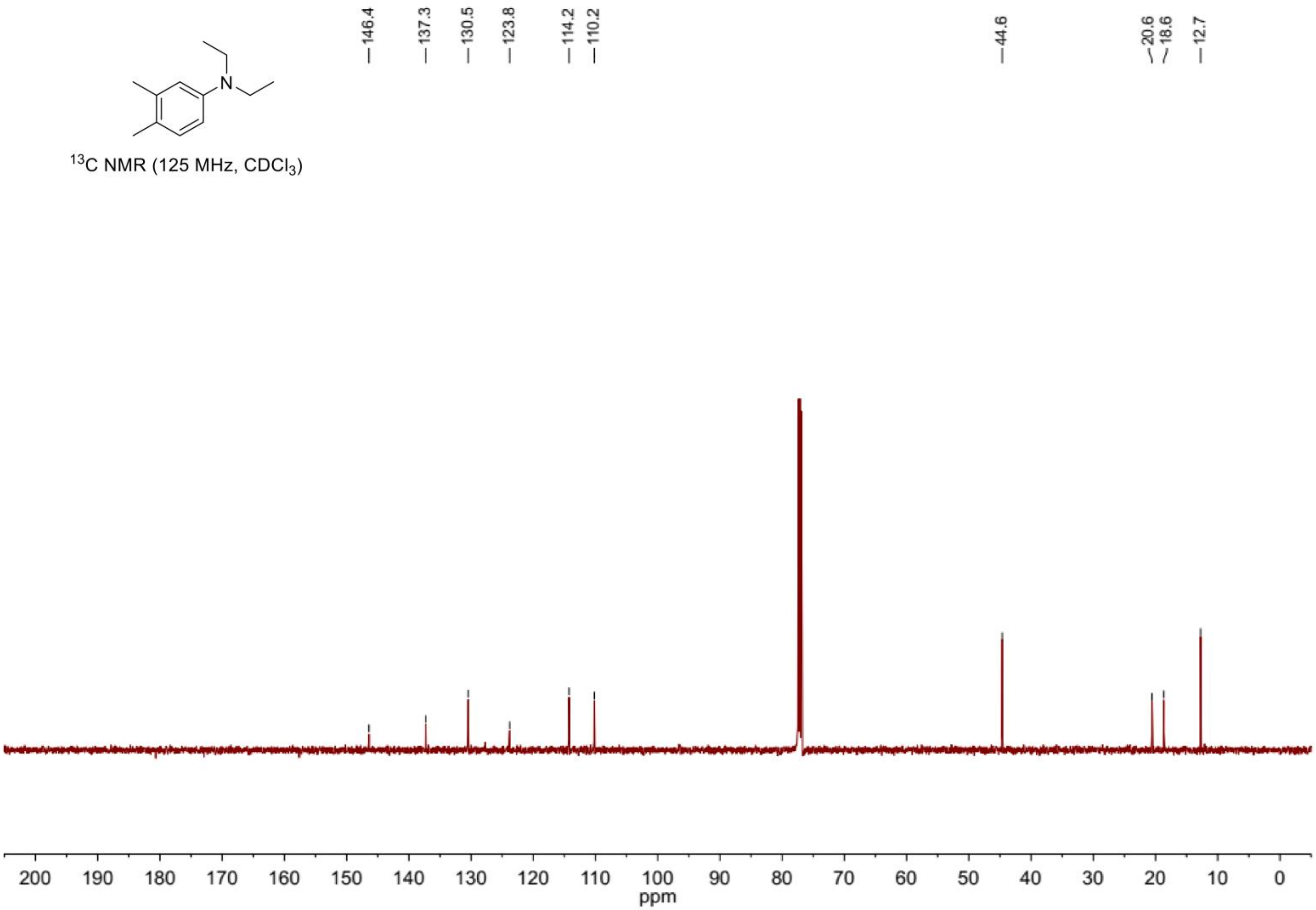
N,N-Diethyl-3,4-dimethylaniline (51)



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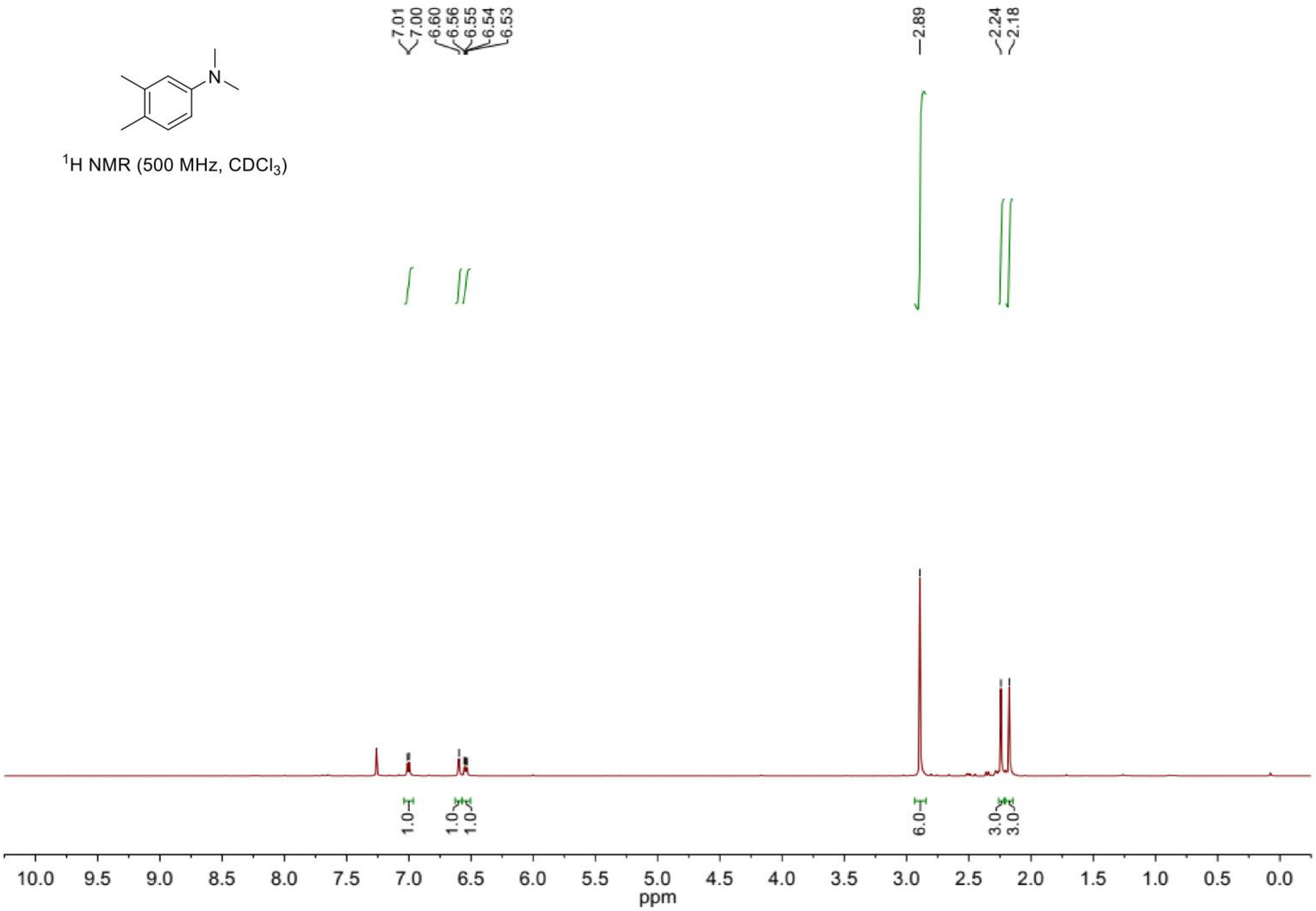
N,N-Dimethyl-3,4-dimethylaniline (52)



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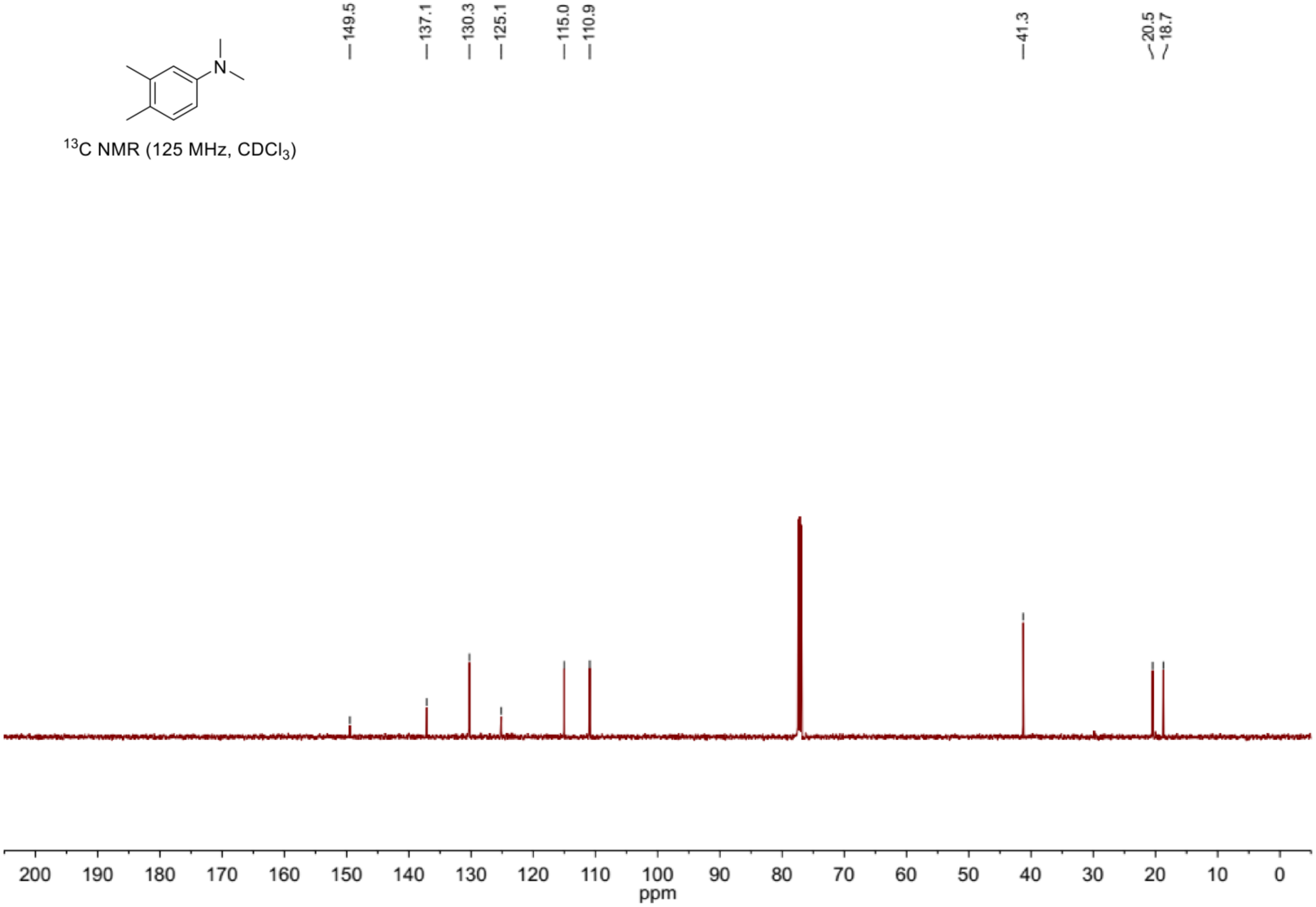
N,N-Dimethyl-3,4-dimethylaniline (52)



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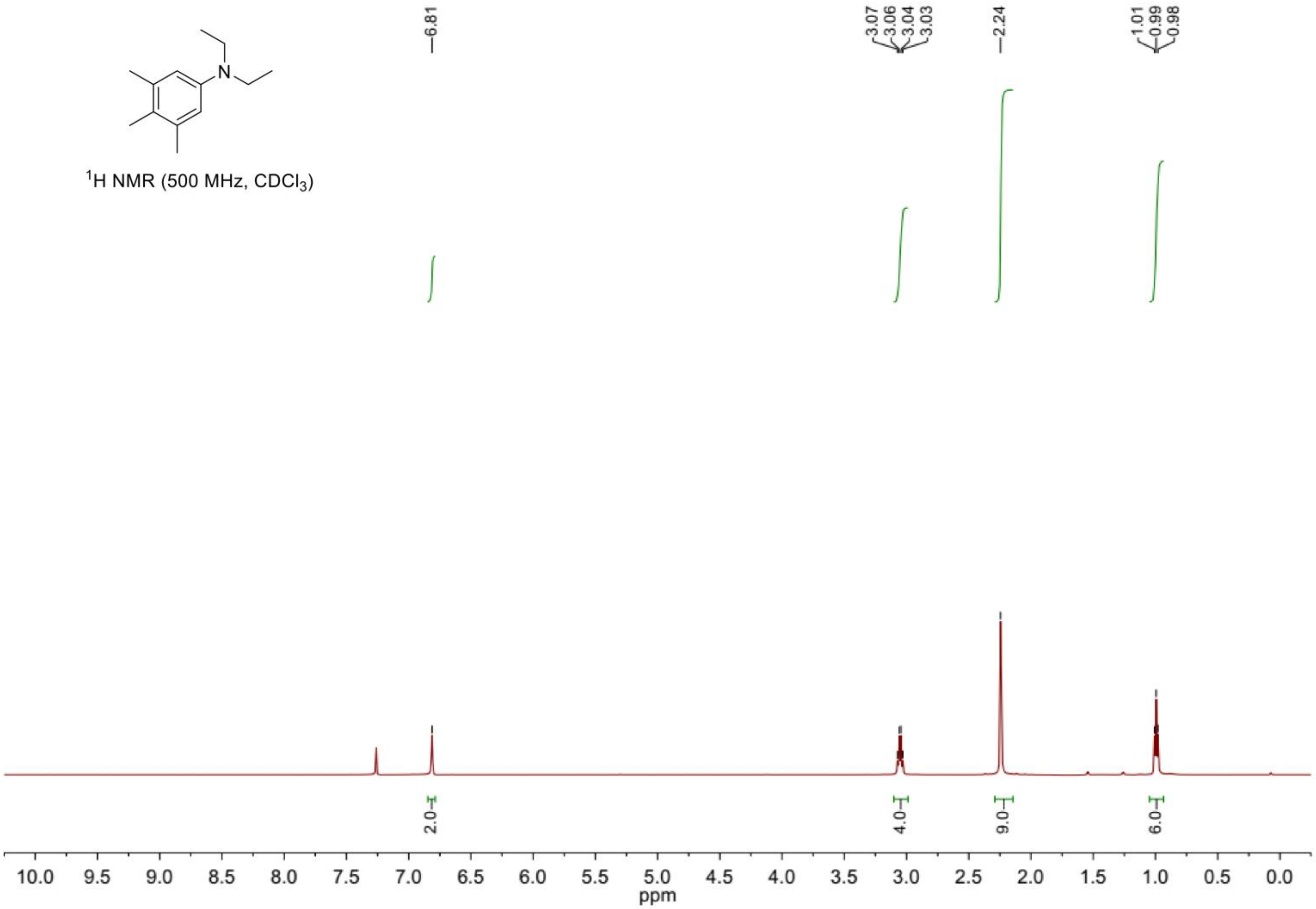
N,N-Diethyl-3,4,5-trimethylaniline (53)



^{1}H NMR (500 MHz, $CDCl_3$)

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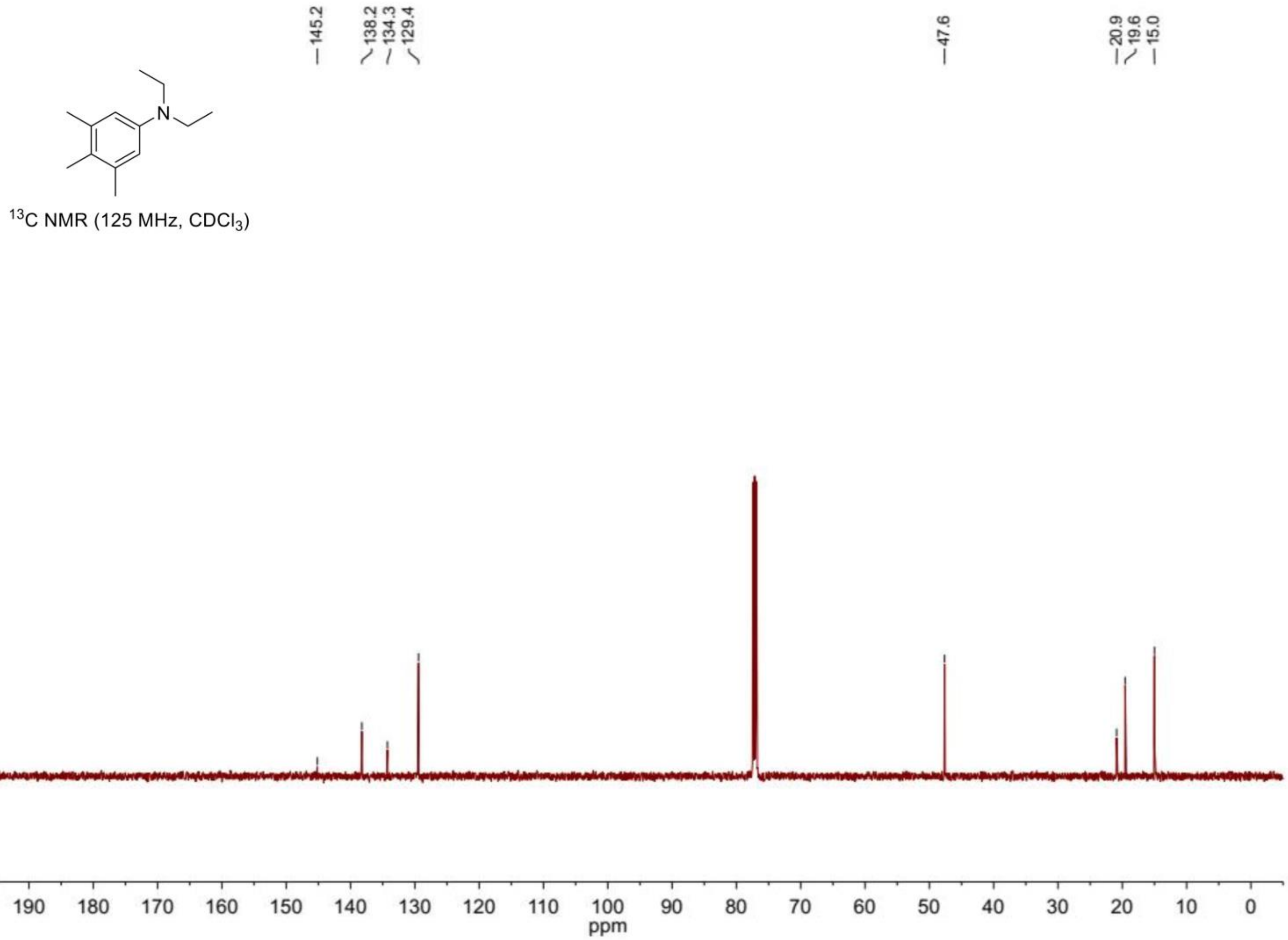
N,N-Diethyl-3,4,5-trimethylaniline (53)



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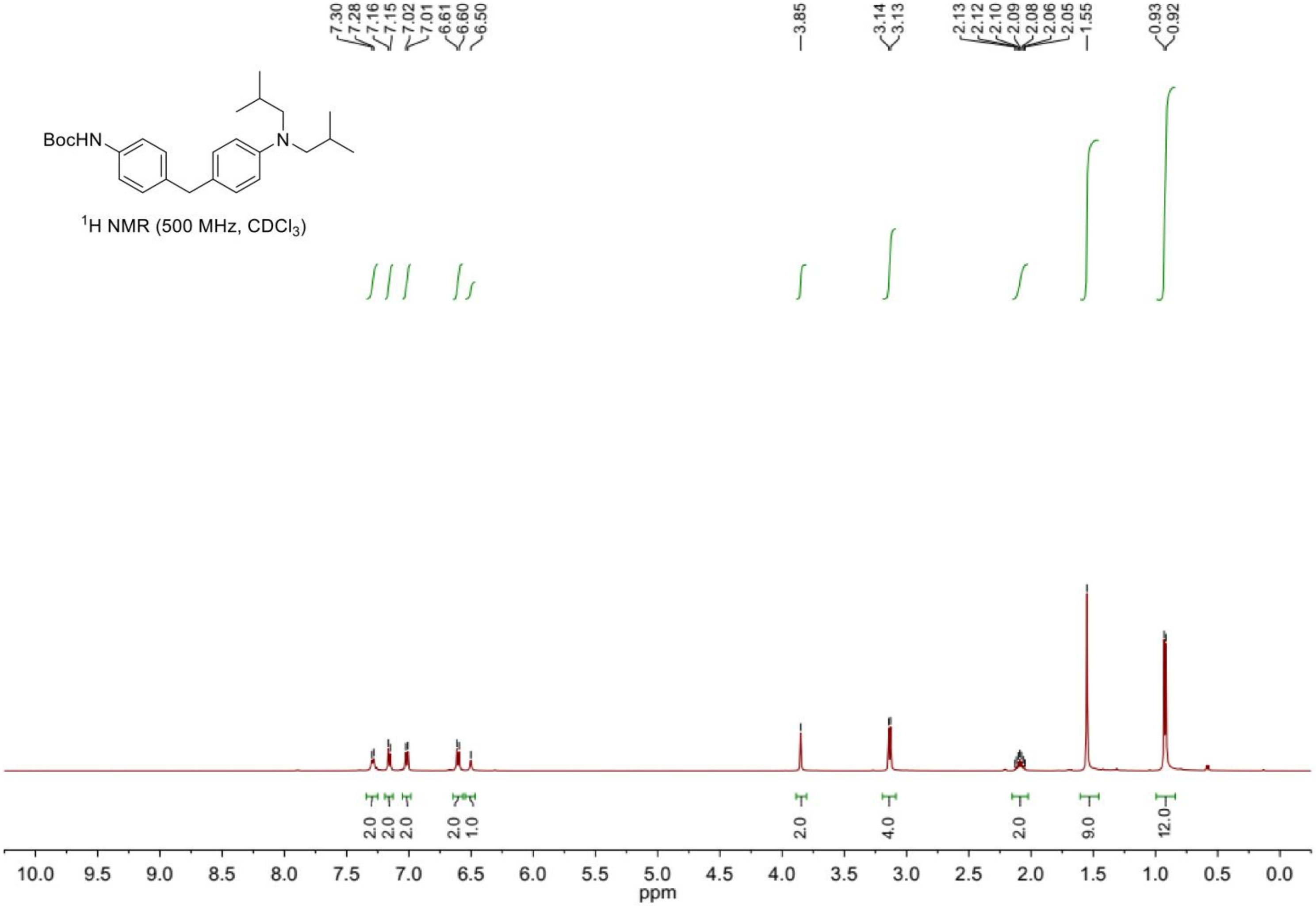
tert-Butyl (4-(4-(diisobutylamino)benzyl)phenyl)carbamate (54)



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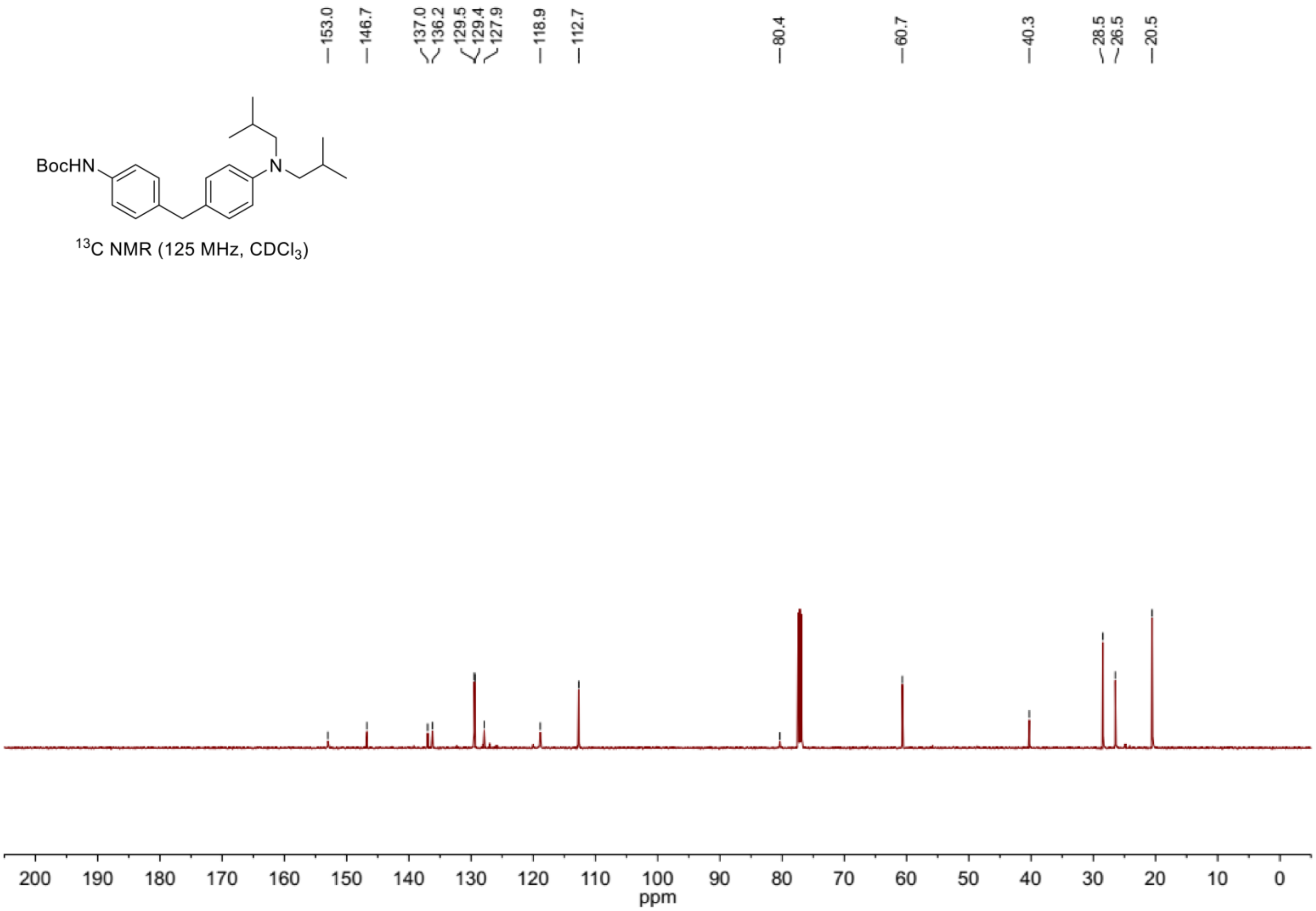
tert-Butyl (4-(4-(diisobutylamino)benzyl)phenyl)carbamate (54)



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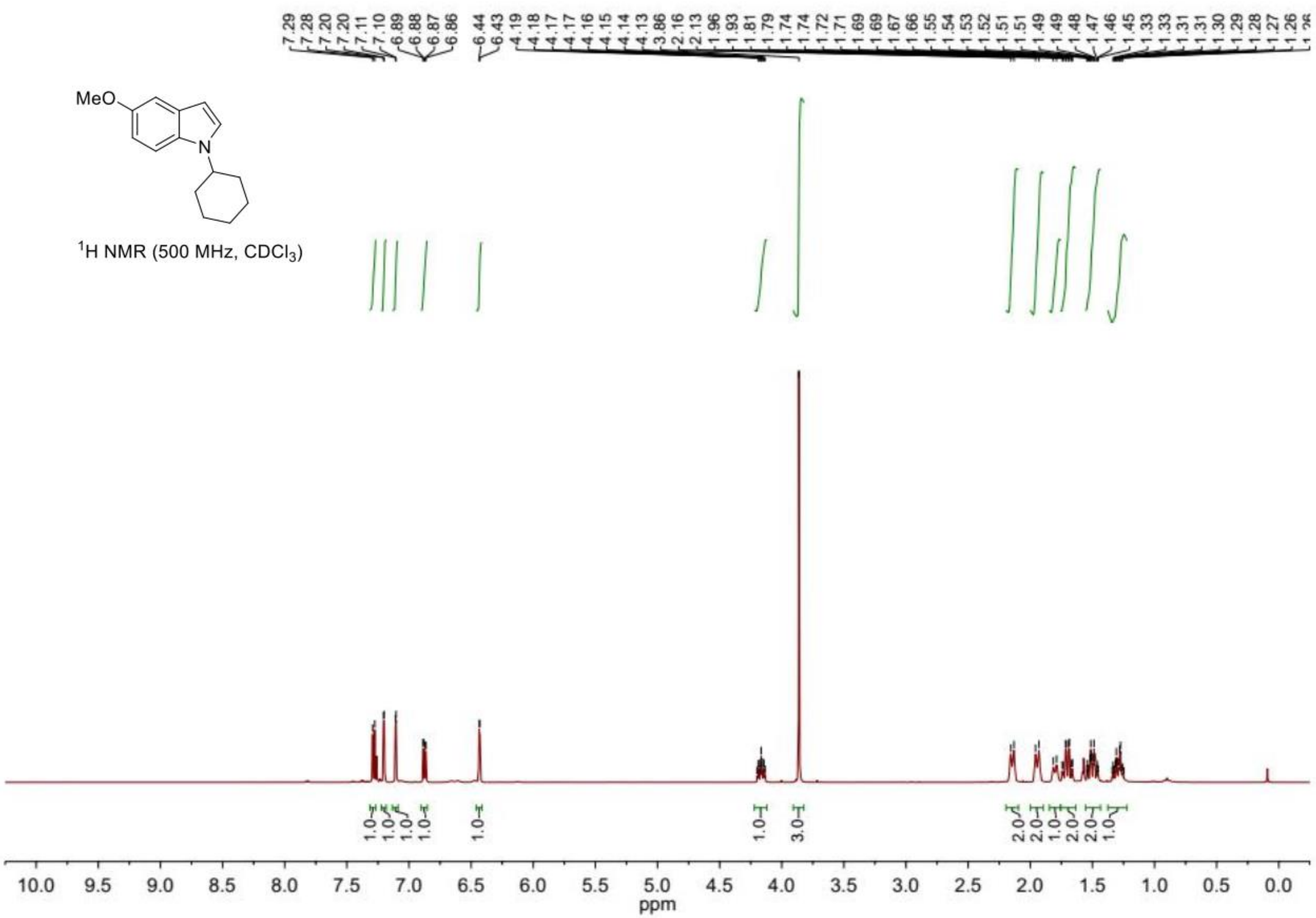
1-Cyclohexyl-5-methoxy-1*H*-indole (55)



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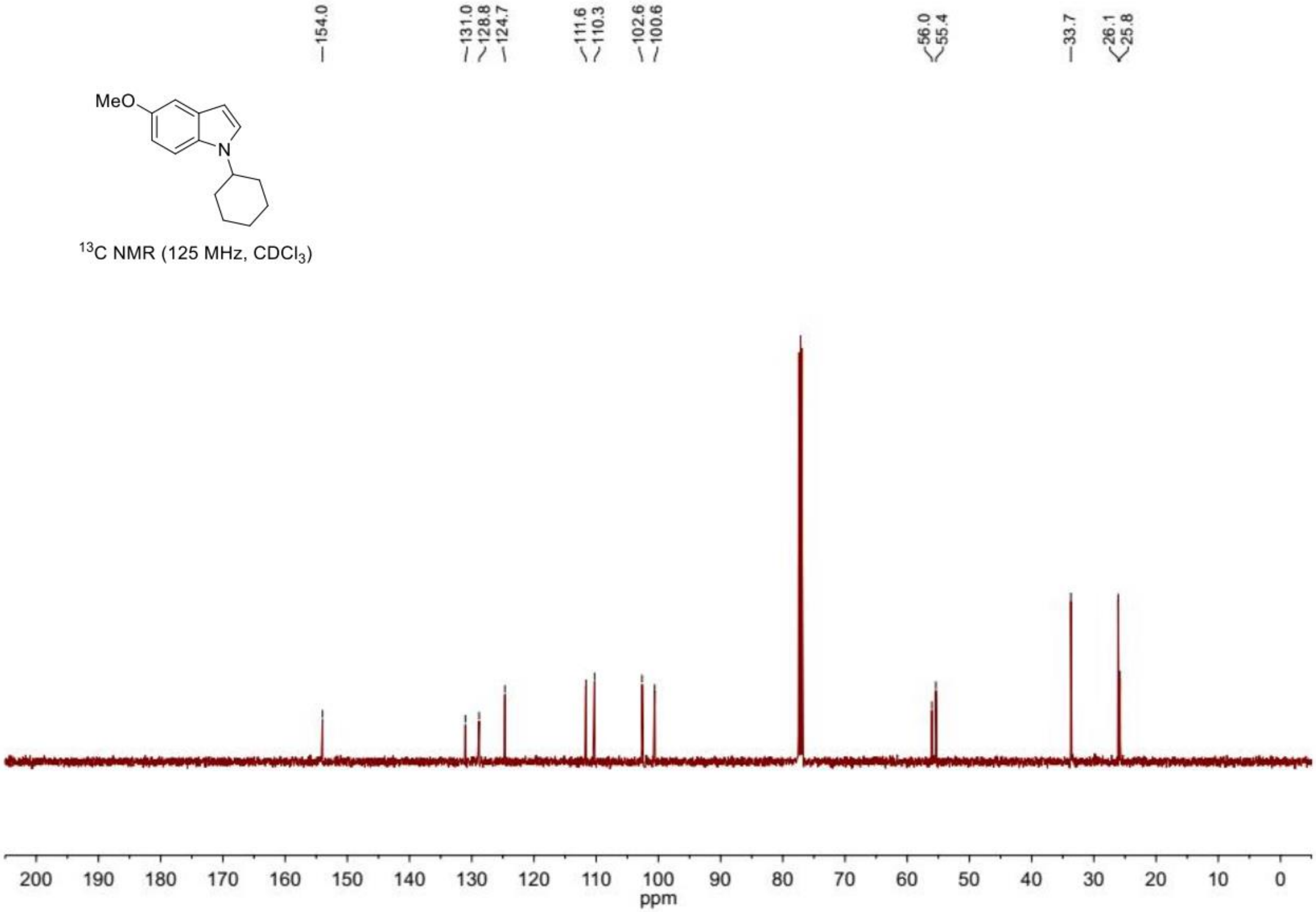
1-Cyclohexyl-5-methoxy-1*H*-indole (55)



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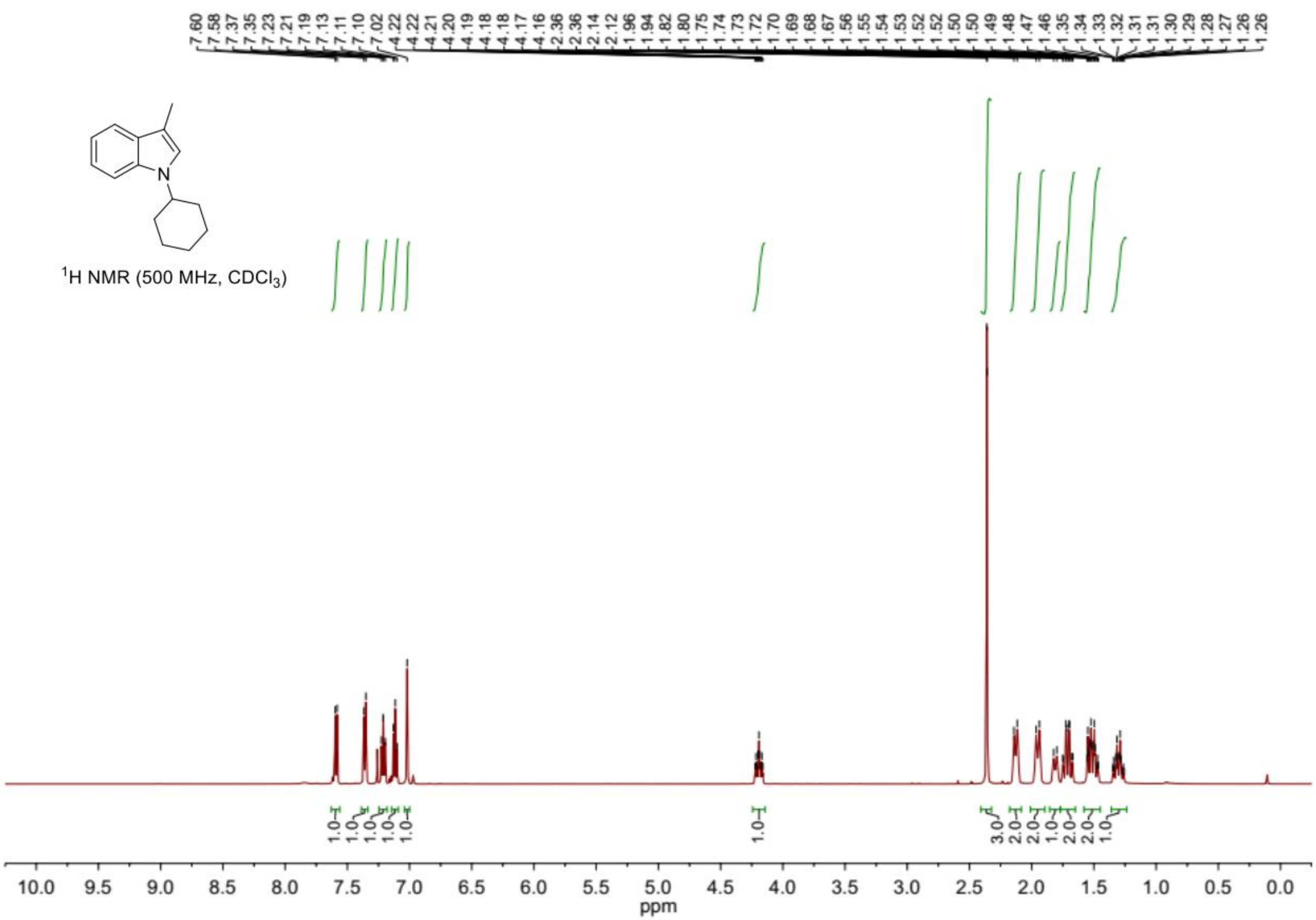
1-Cyclohexyl-3-methyl-1*H*-indole (56)



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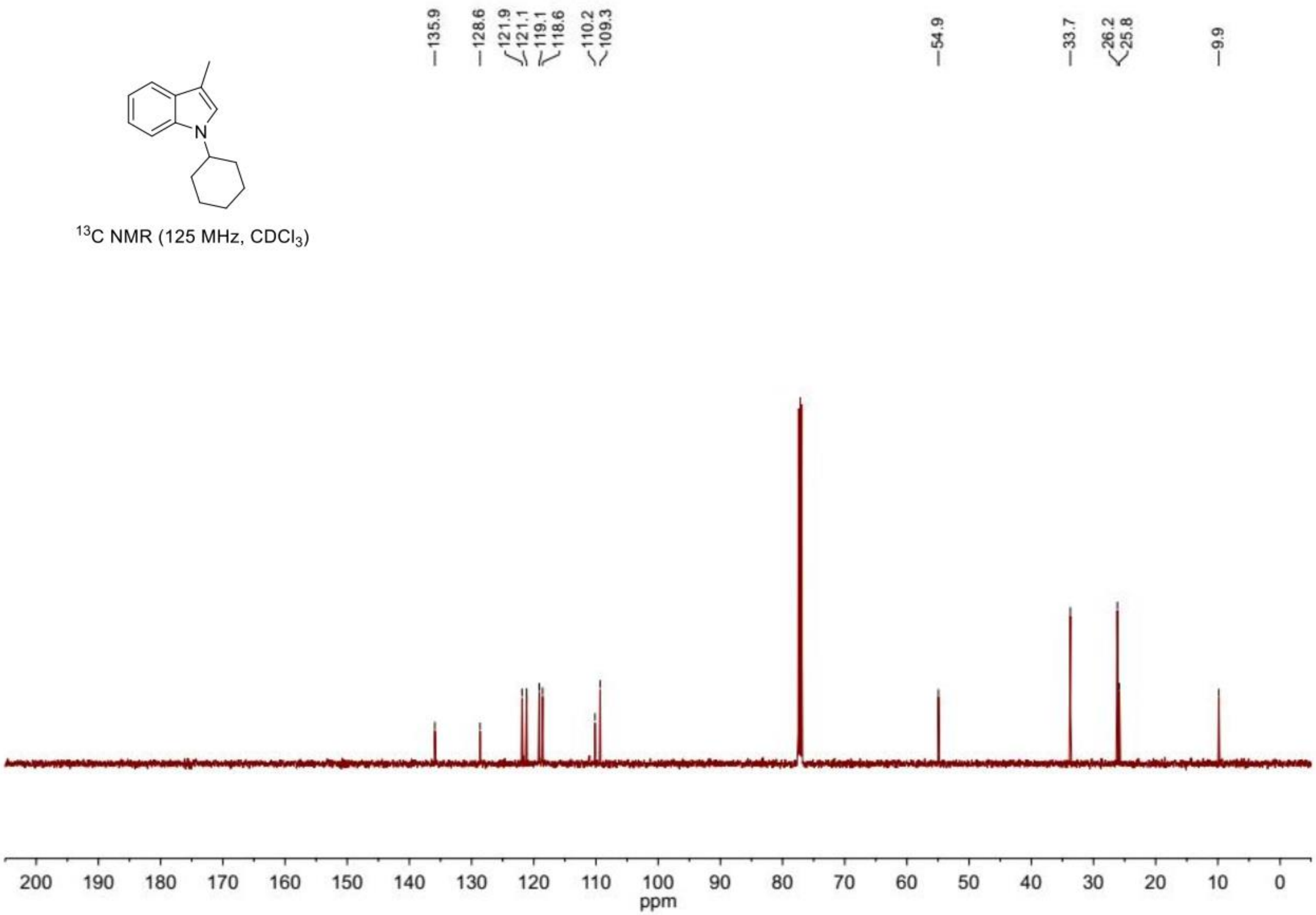
1-Cyclohexyl-3-methyl-1*H*-indole (56)



^{13}C NMR (125 MHz, $CDCl_3$)

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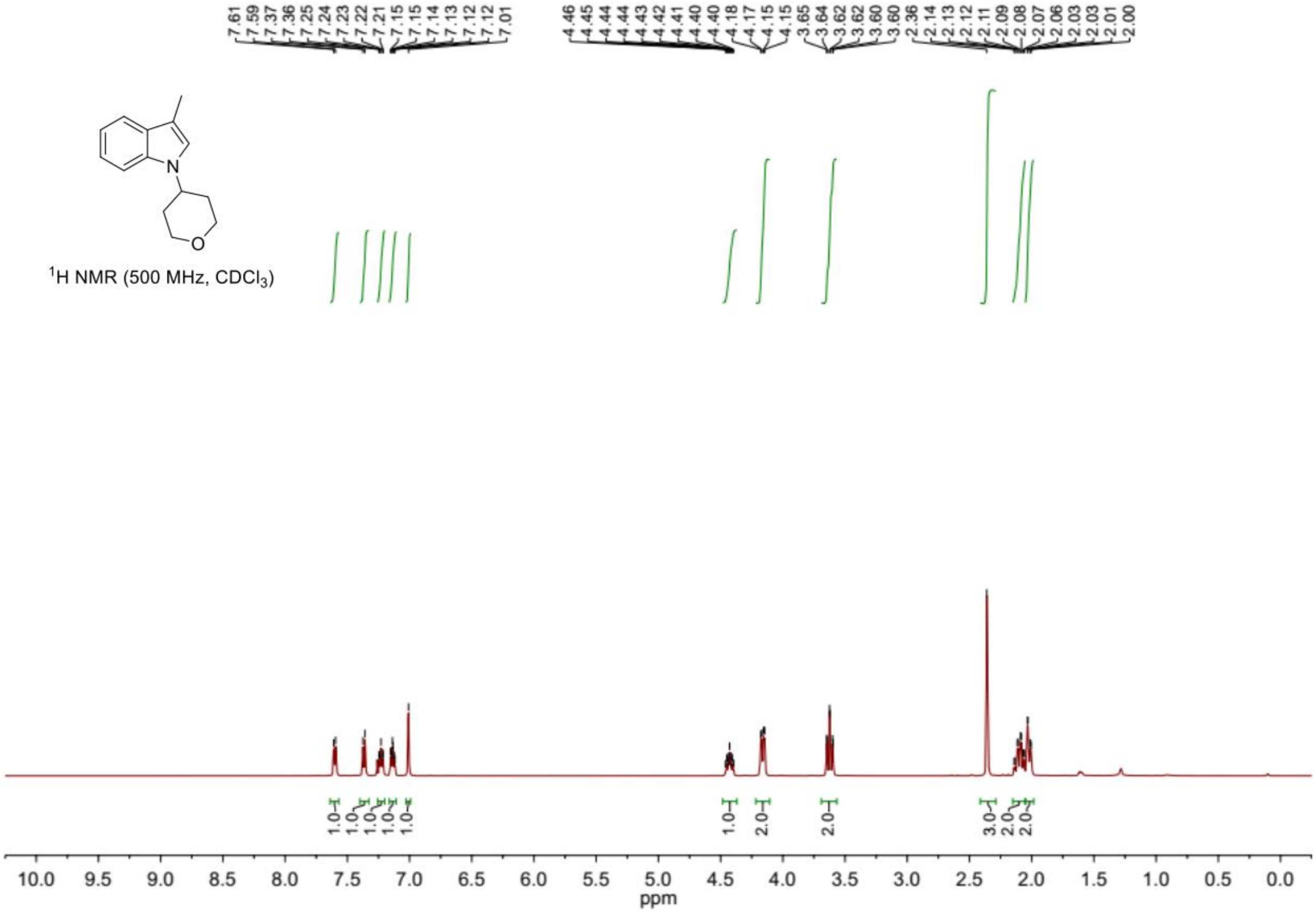
3-Methyl-1-(tetrahydro-2*H*-pyran-4-yl)-1*H*-indole (57)



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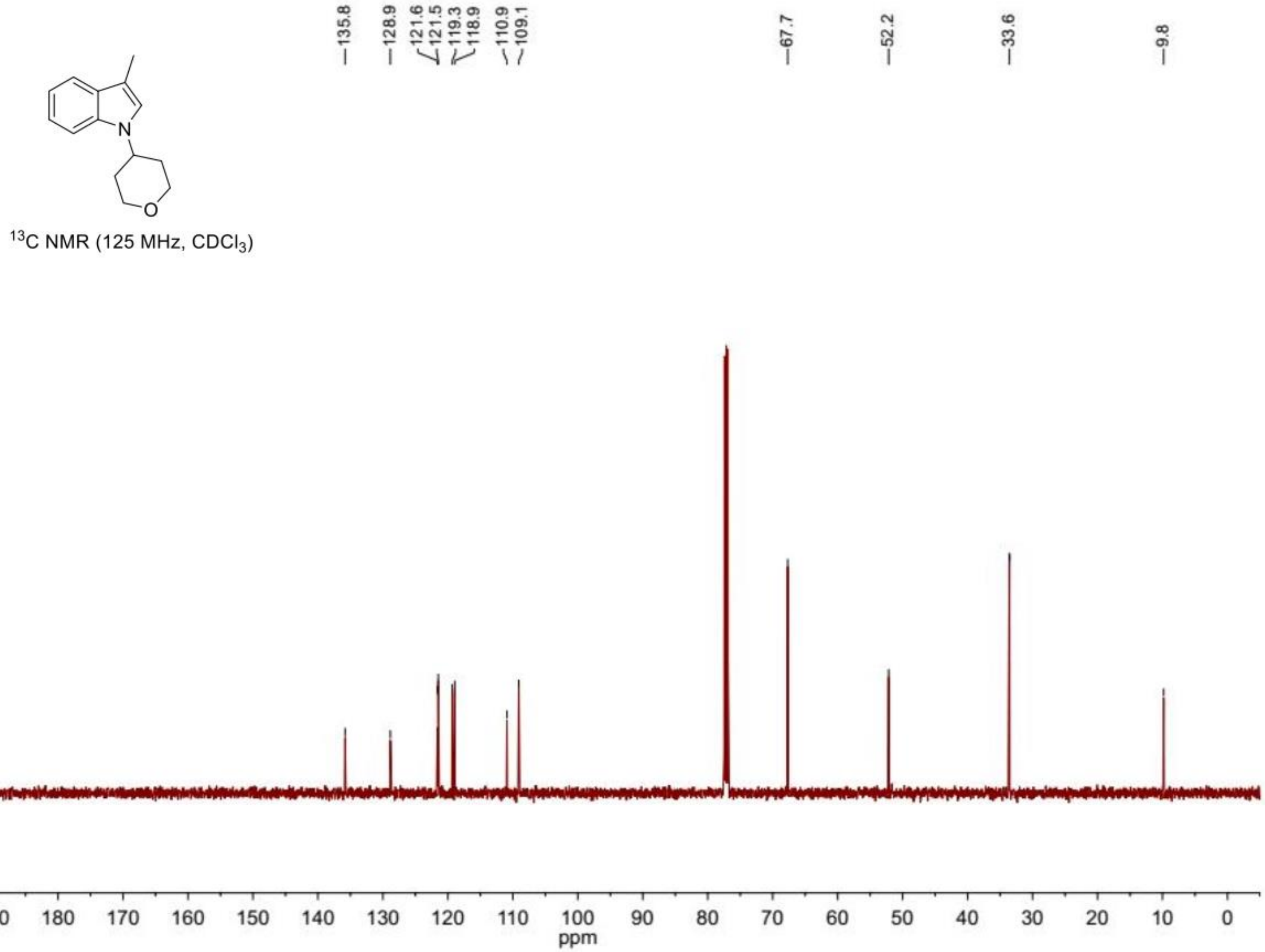
3-Methyl-1-(tetrahydro-2*H*-pyran-4-yl)-1*H*-indole (57)



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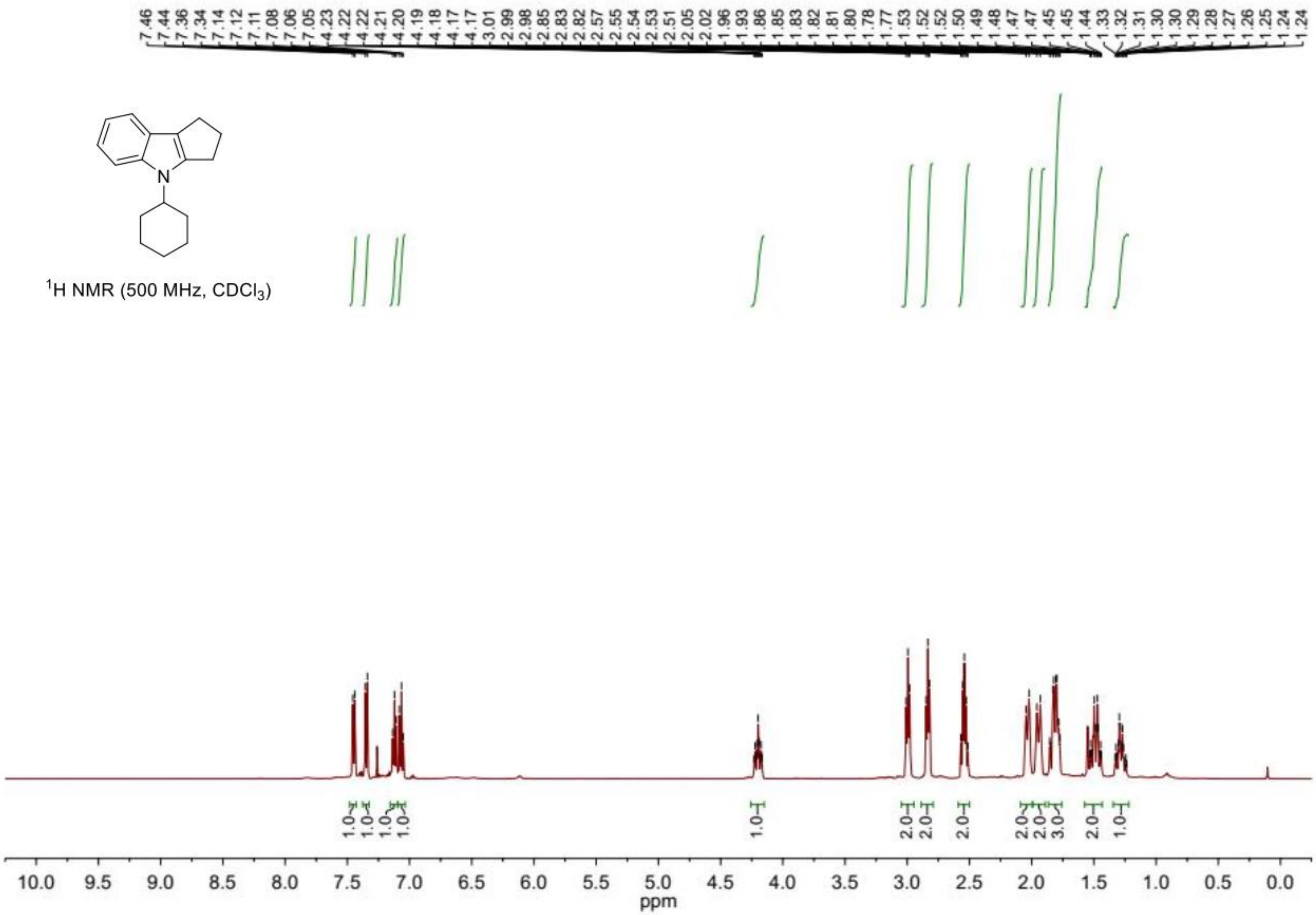
4-Cyclohexyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (58)



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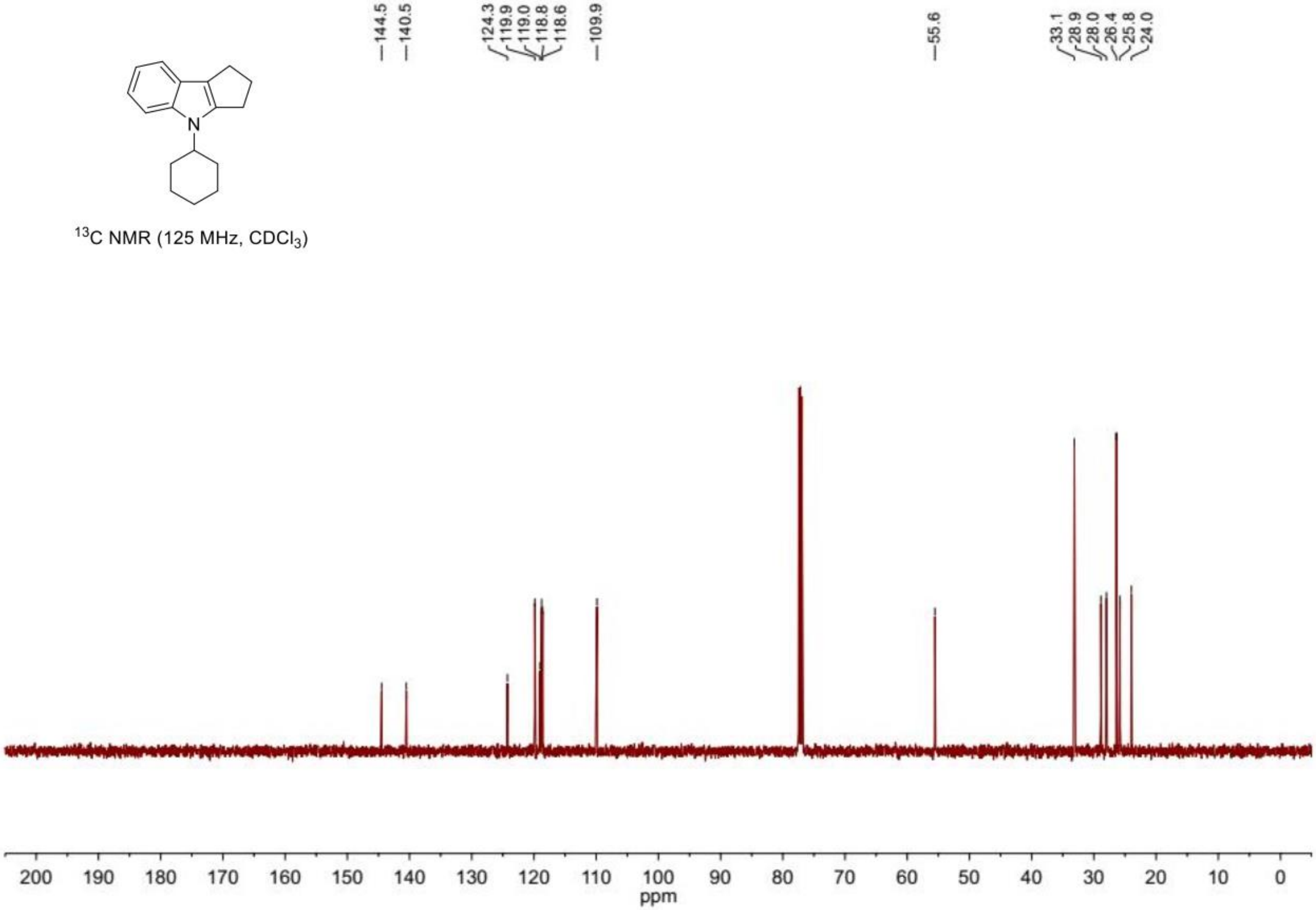
4-Cyclohexyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (58)



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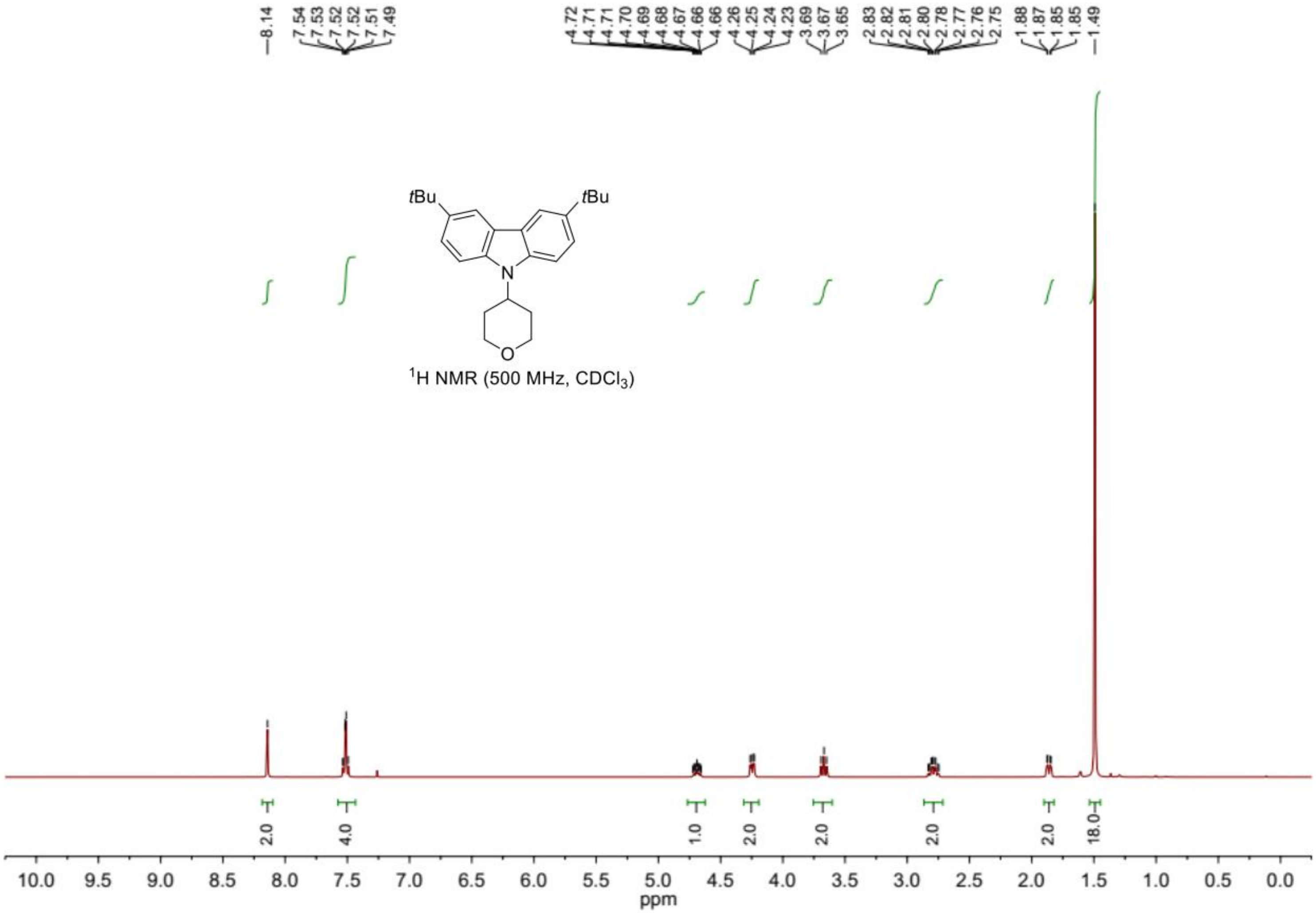
3,6-Di-*tert*-butyl-9-(tetrahydro-2*H*-pyran-4-yl)-9*H*-carbazole (59)



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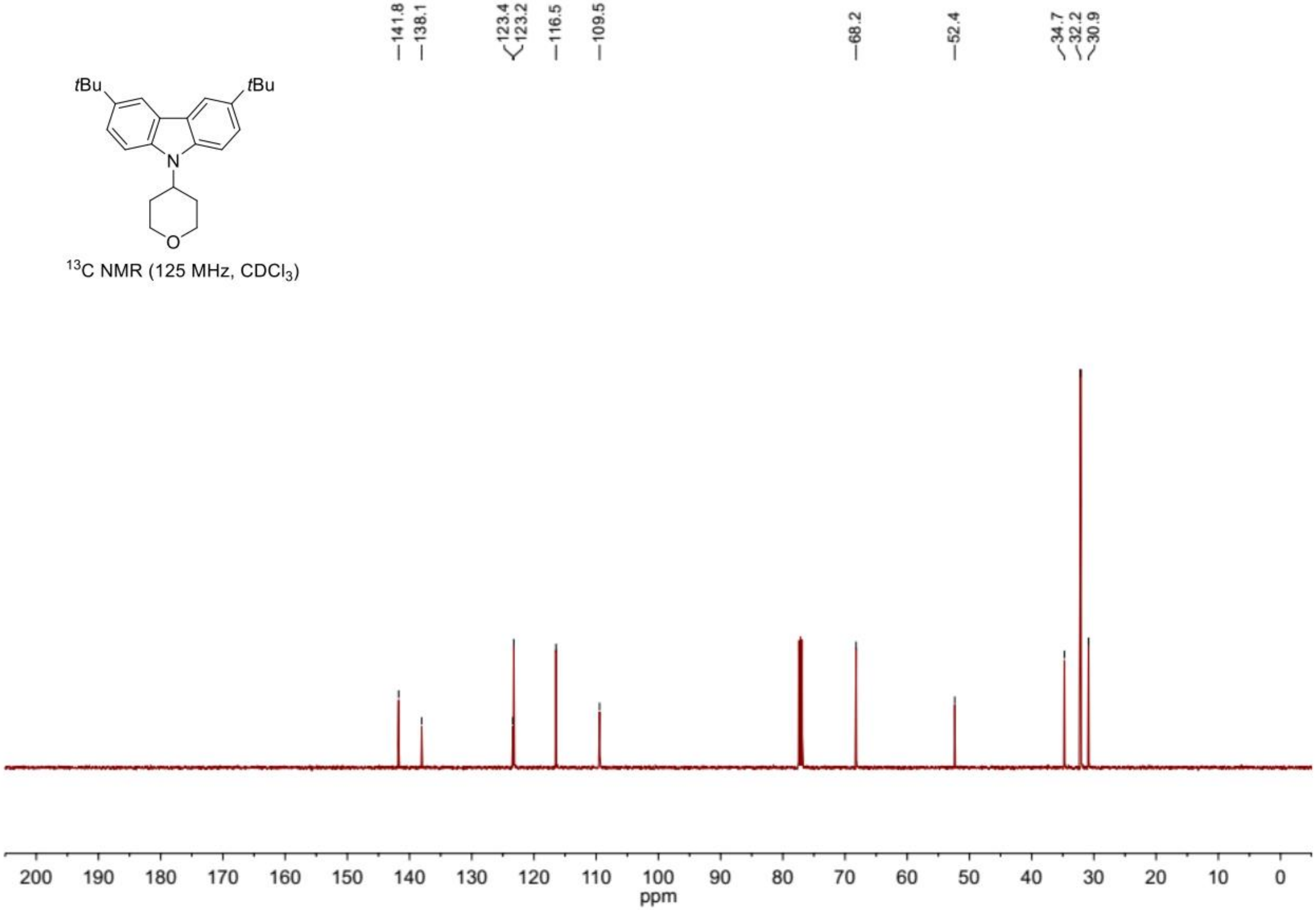
3,6-Di-*tert*-butyl-9-(tetrahydro-2*H*-pyran-4-yl)-9*H*-carbazole (59)



^{13}C NMR (125 MHz, CDCl$_3$)

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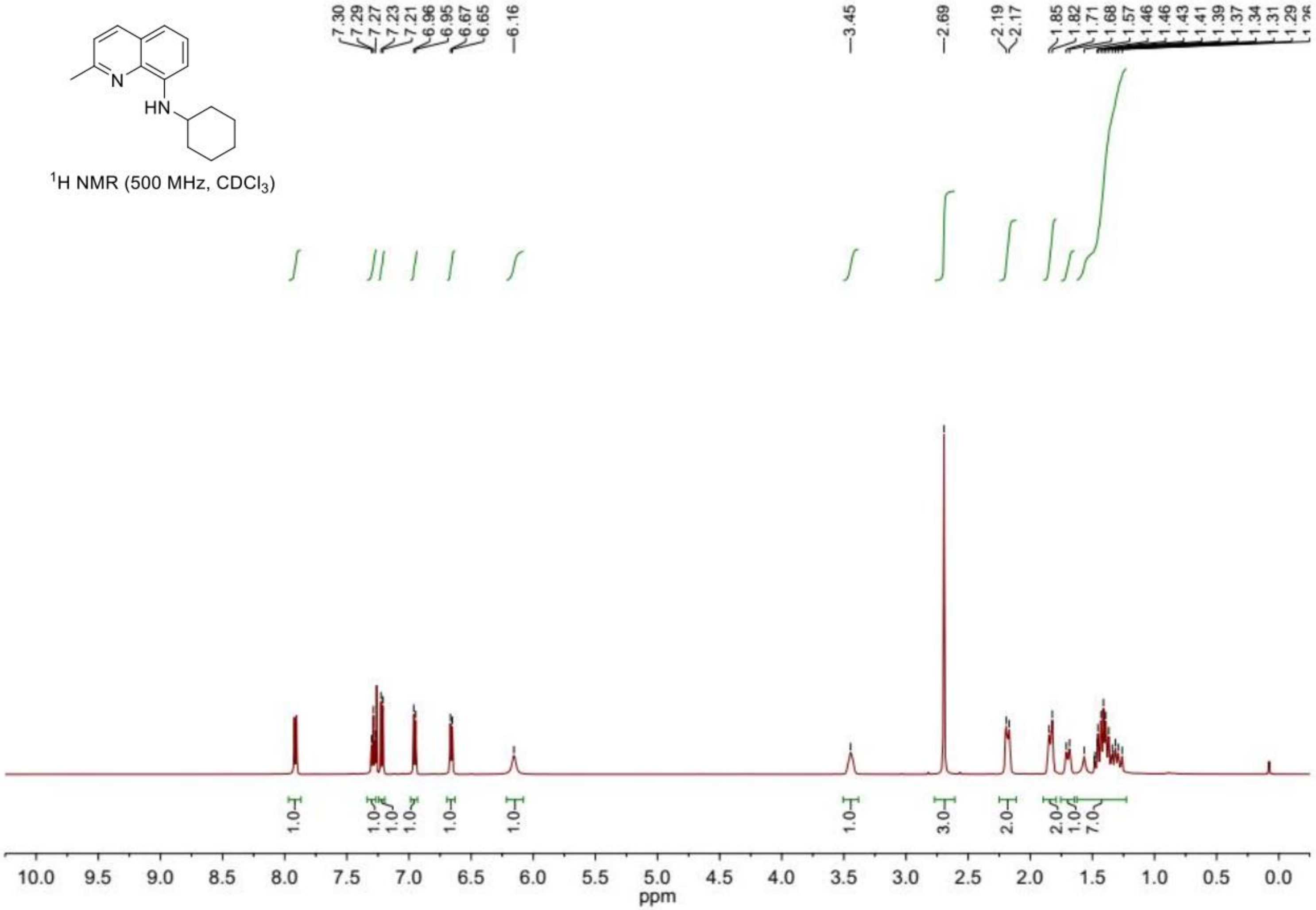
N-Cyclohexyl-2-methylquinolin-8-amine (60)



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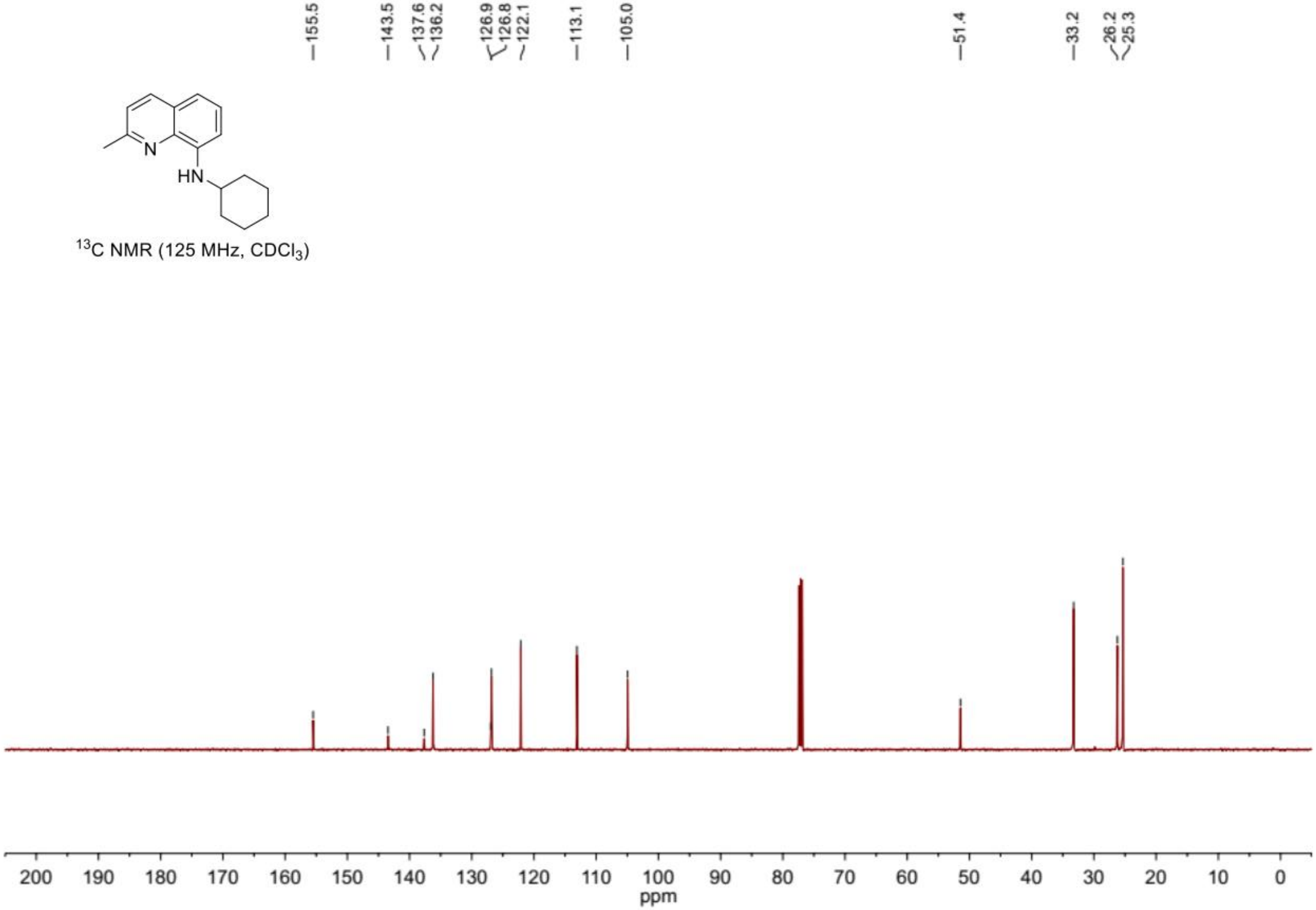
N-Cyclohexyl-2-methylquinolin-8-amine (60)



^{13}C NMR (125 MHz, CDCl$_3$)

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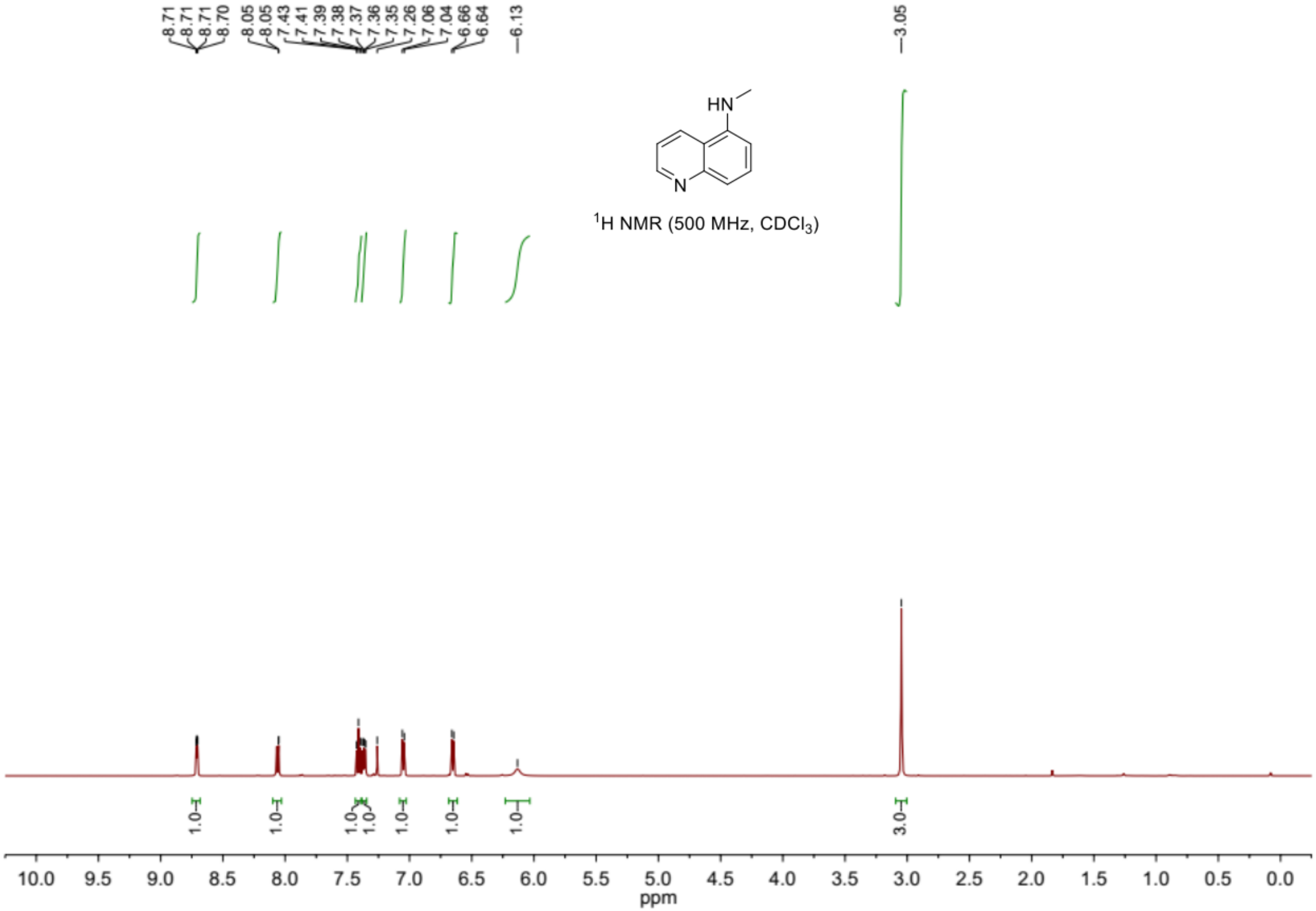
N-Methylquinolin-5-amine (61)



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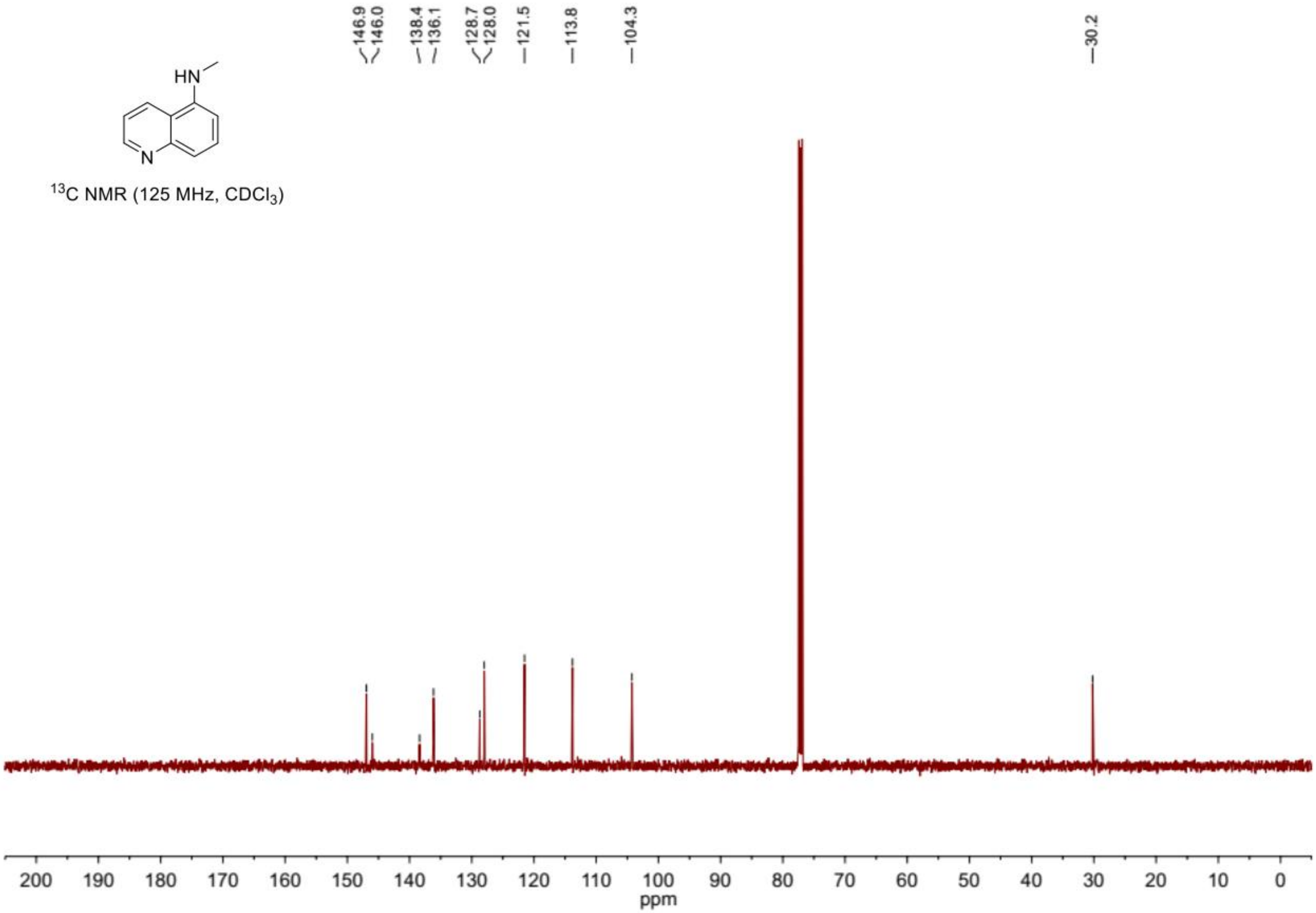
N-Methylquinolin-5-amine (61)



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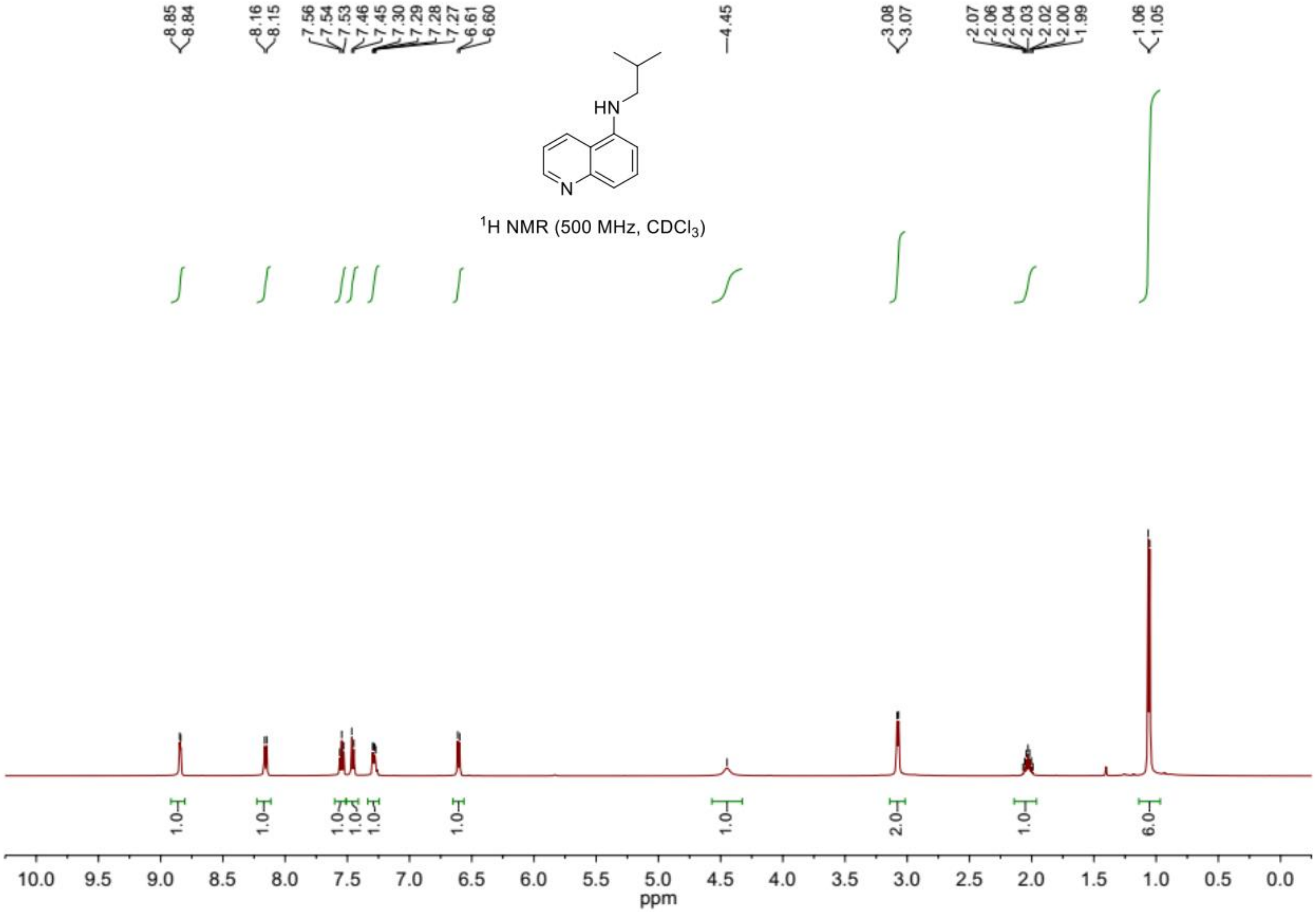
N-Isobutylquinolin-5-amine (62)



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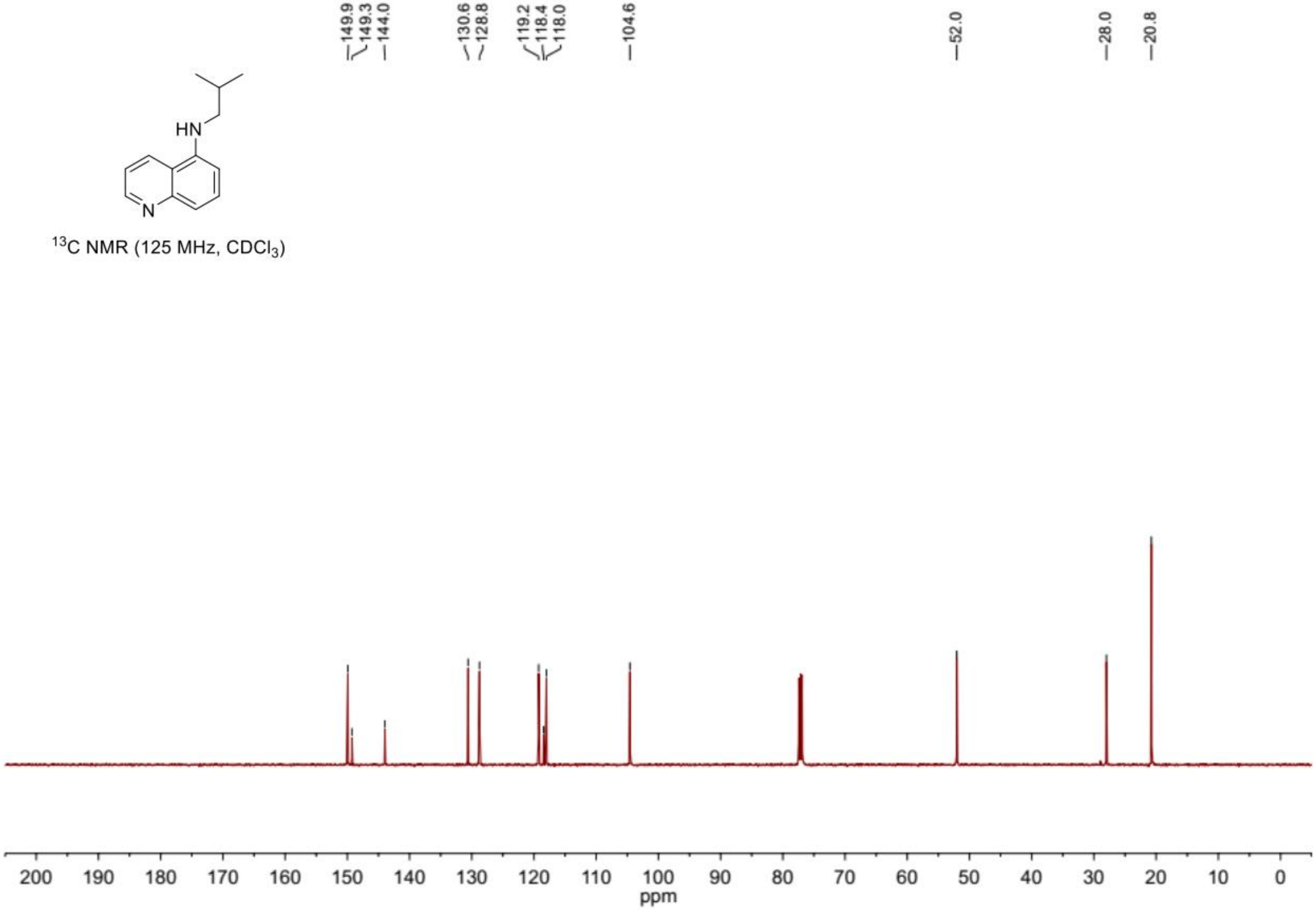
N-Isobutylquinolin-5-amine (62)

^{13}C NMR (125 MHz, $CDCl_3$)



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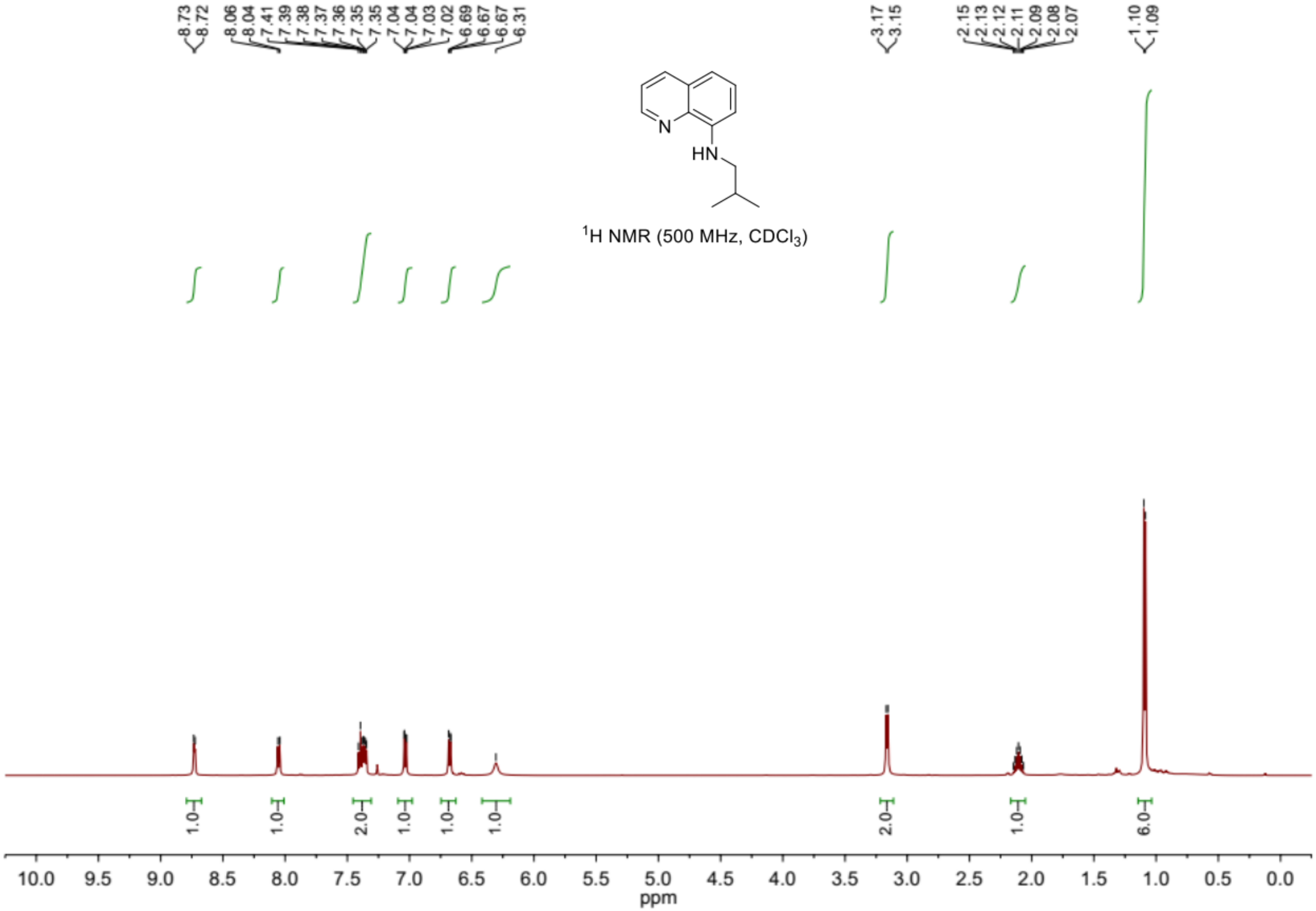
N-Isobutylquinolin-8-amine (63)



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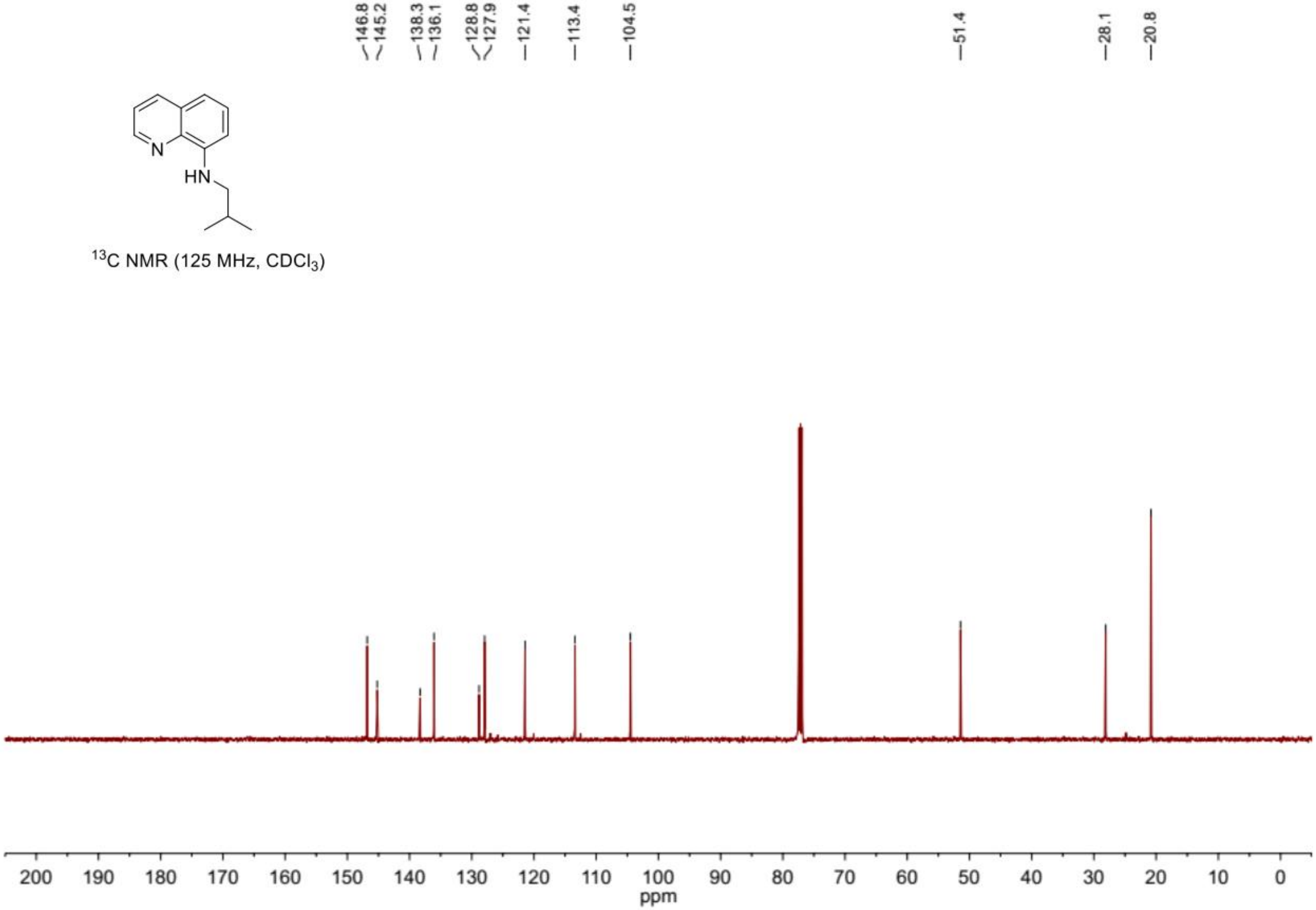
N-Isobutylquinolin-8-amine (63)



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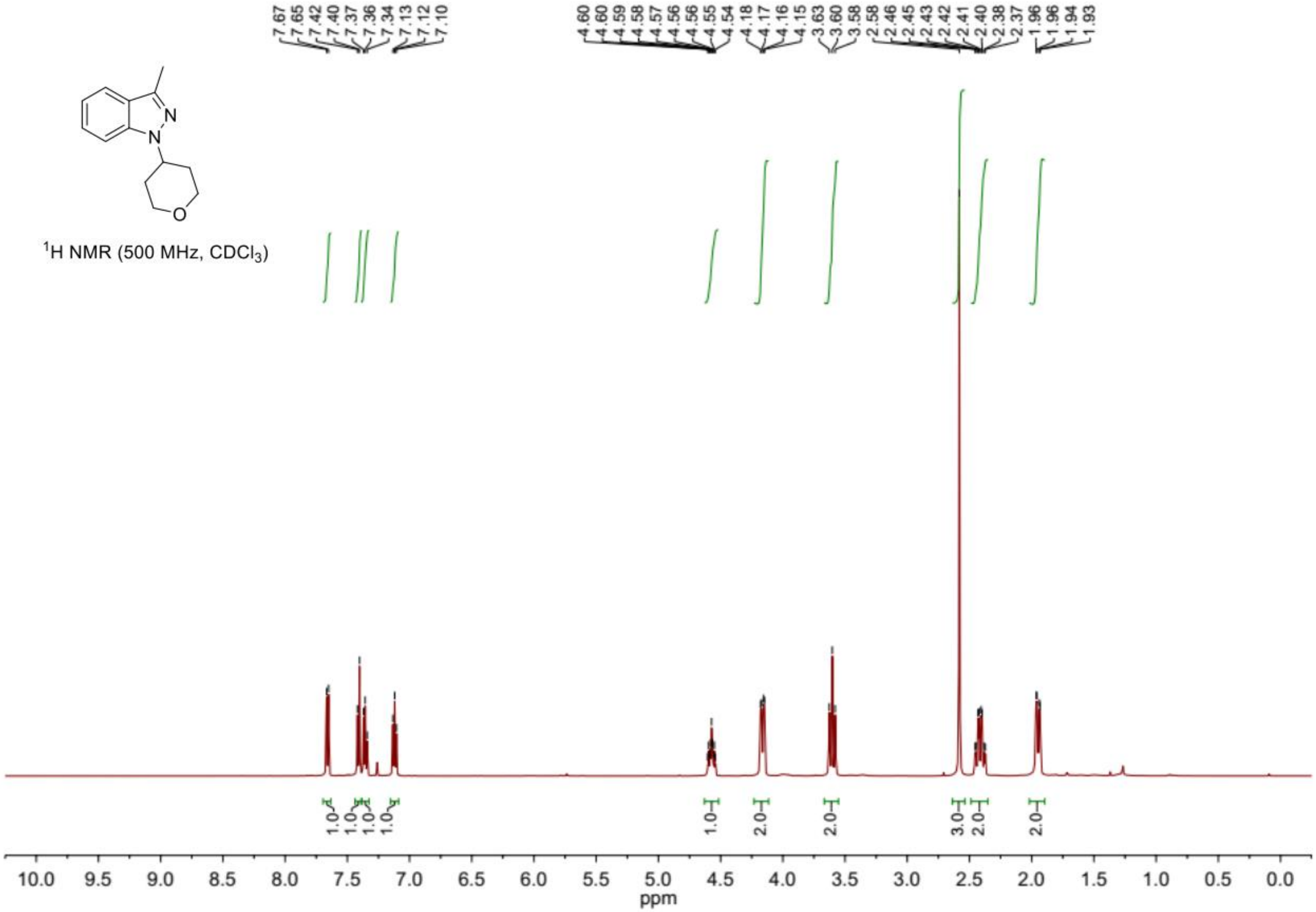
3-Methyl-1-(tetrahydro-2*H*-pyran-4-yl)-1*H*-indazole (64)



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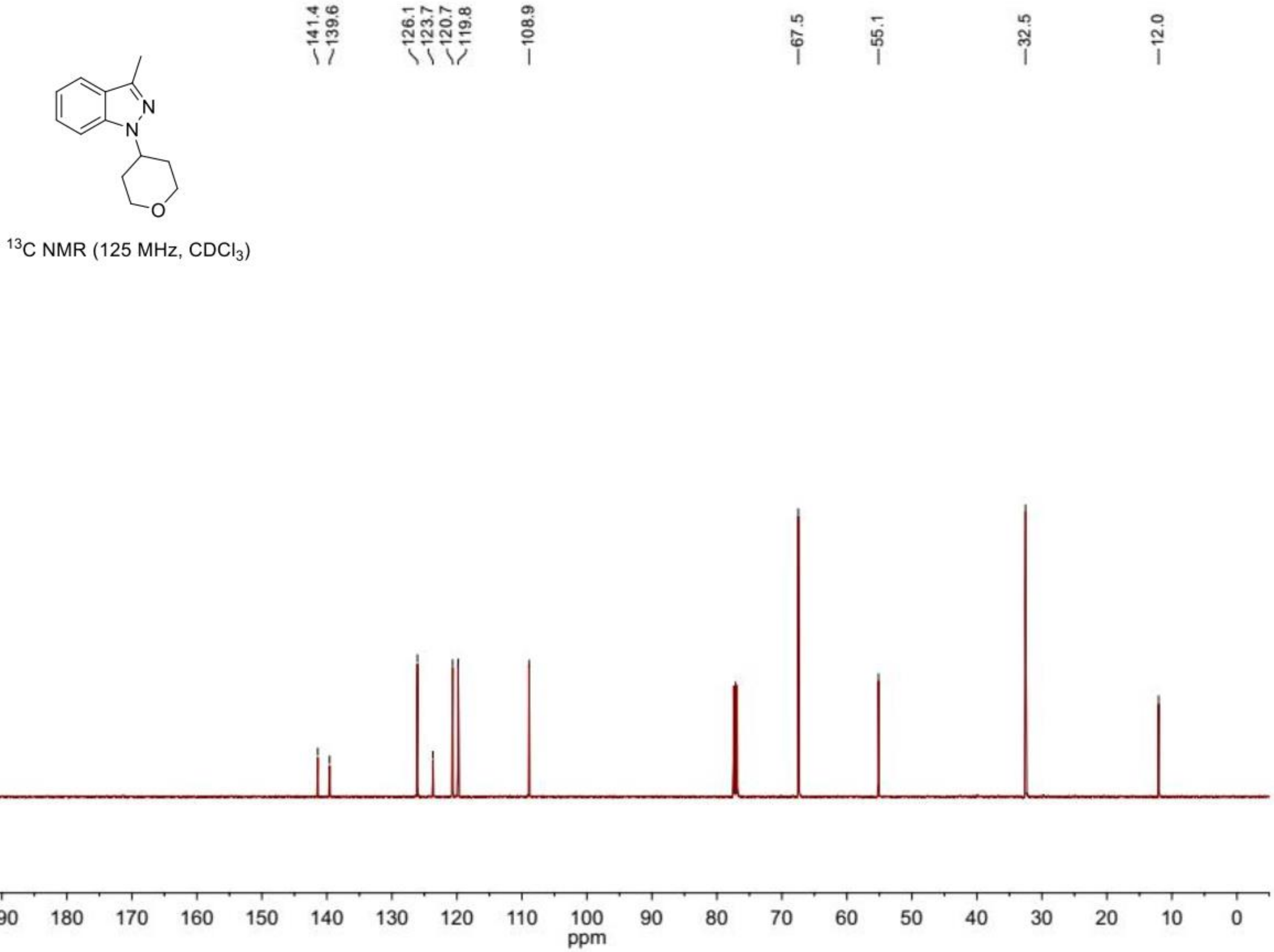
3-Methyl-1-(tetrahydro-2*H*-pyran-4-yl)-1*H*-indazole (64)



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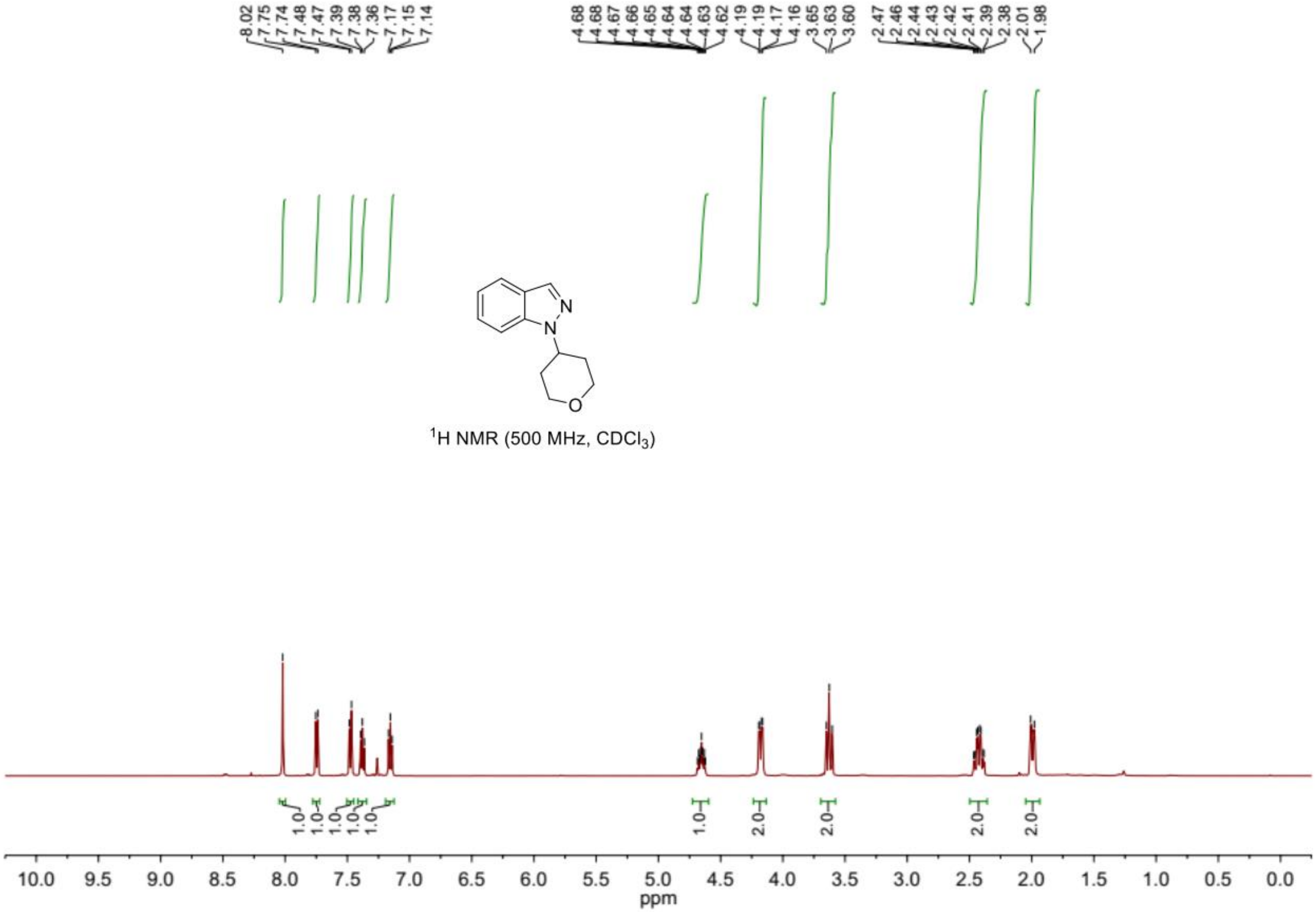
1-(Tetrahydro-2*H*-pyran-4-yl)-1*H*-indazole (65)



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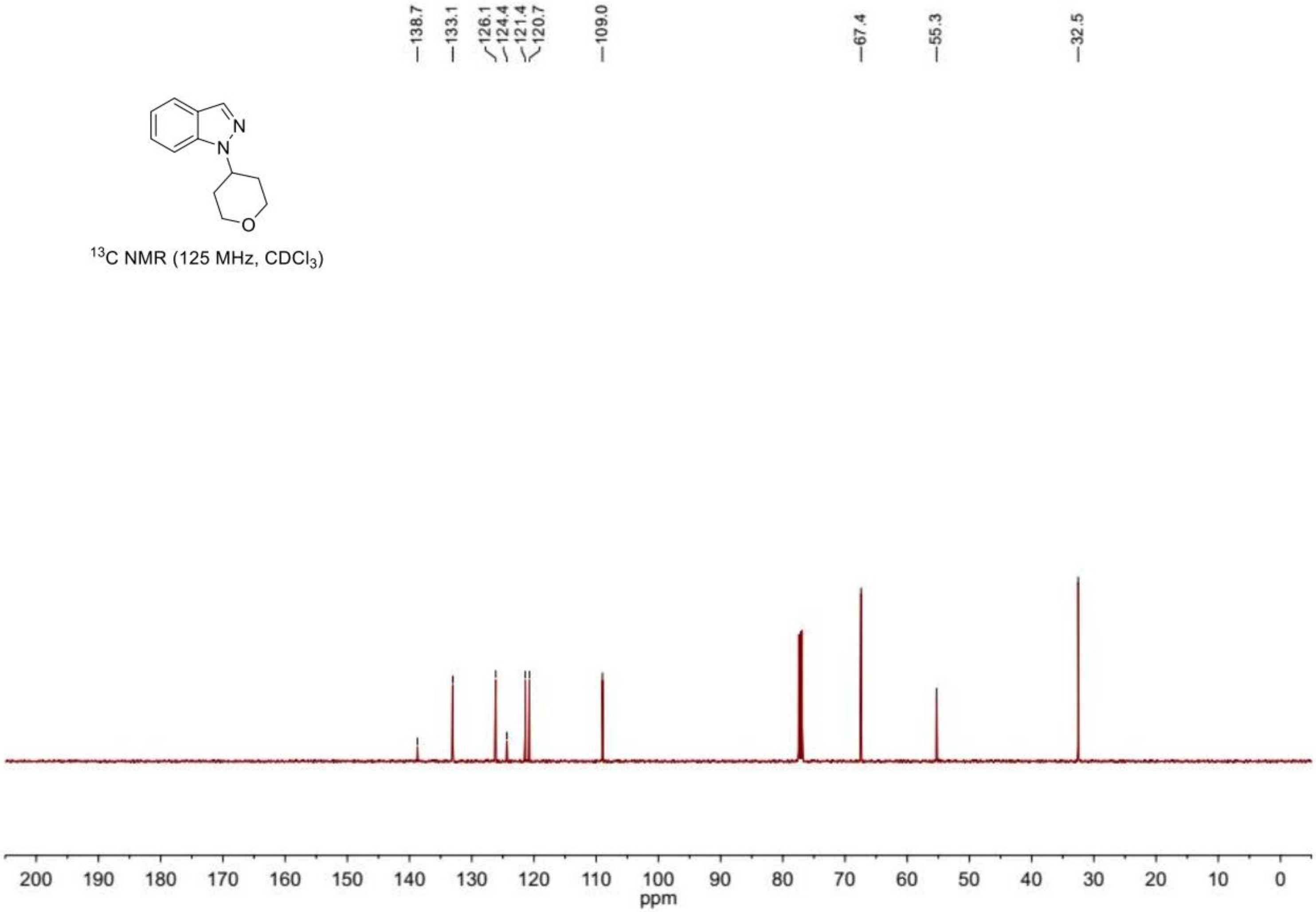
1-(Tetrahydro-2*H*-pyran-4-yl)-1*H*-indazole (65)



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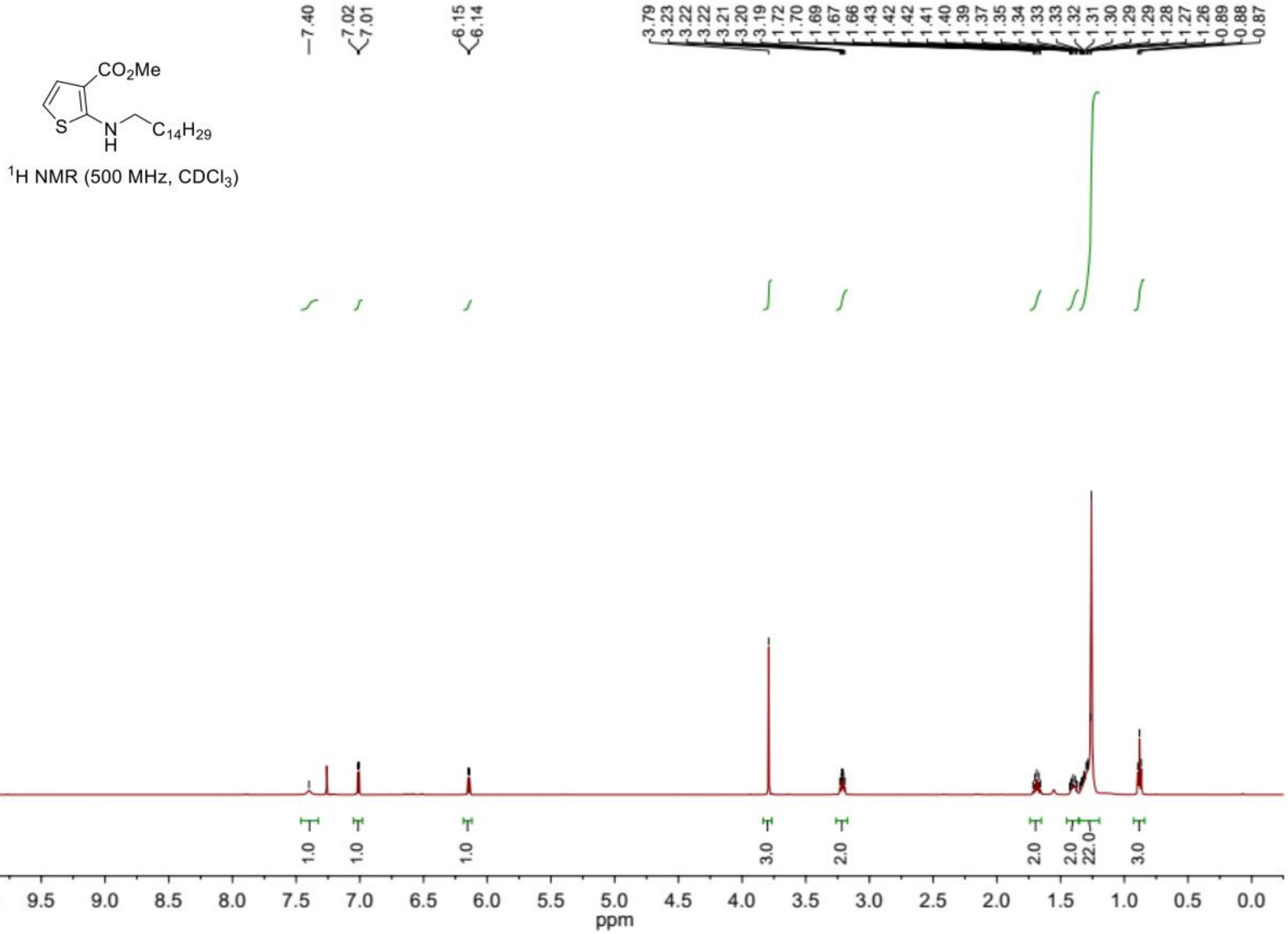
Methyl 2-(pentadecylamino)thiophene-3-carboxylate (66)



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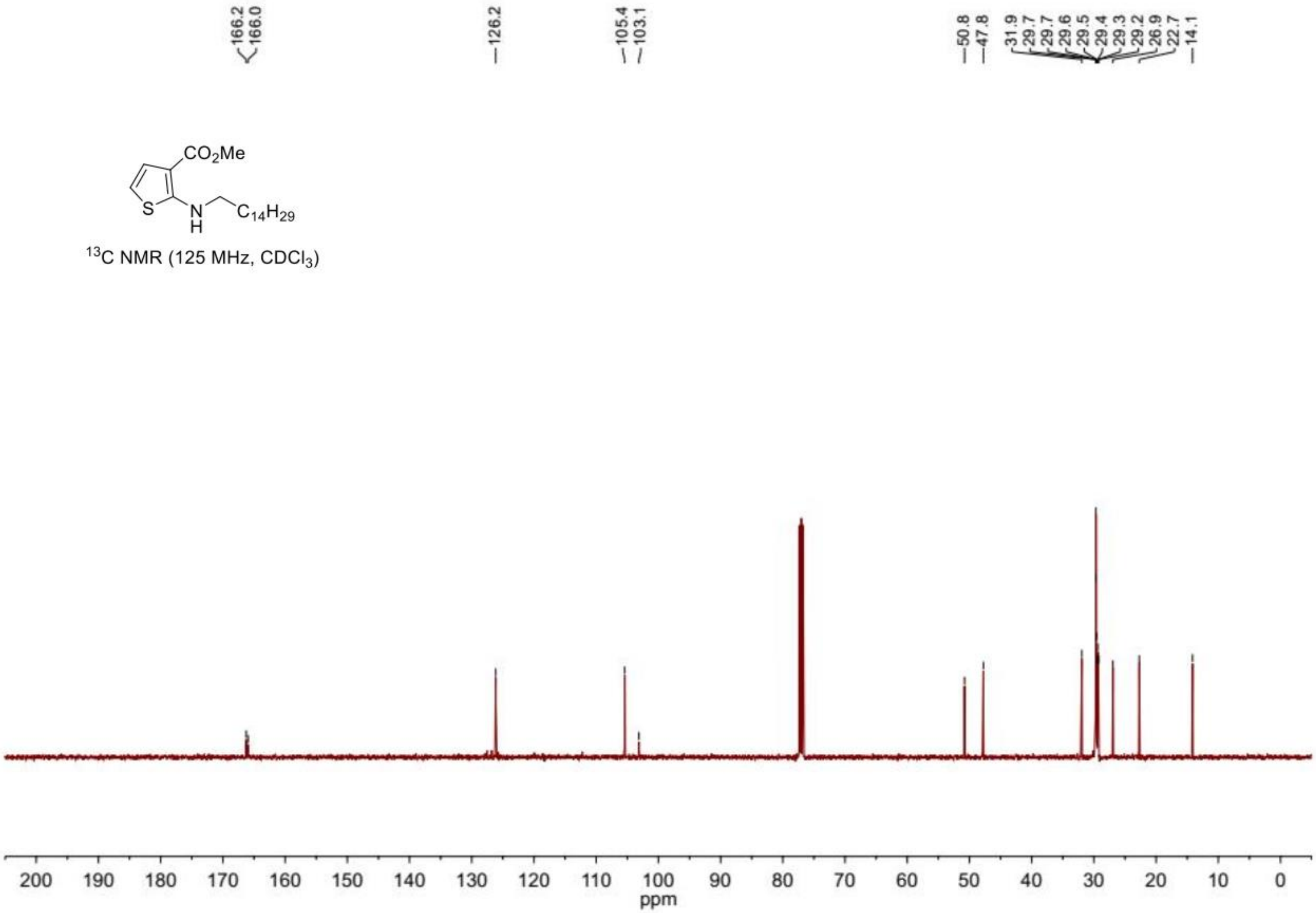
Methyl 2-(pentadecylamino)thiophene-3-carboxylate (66)



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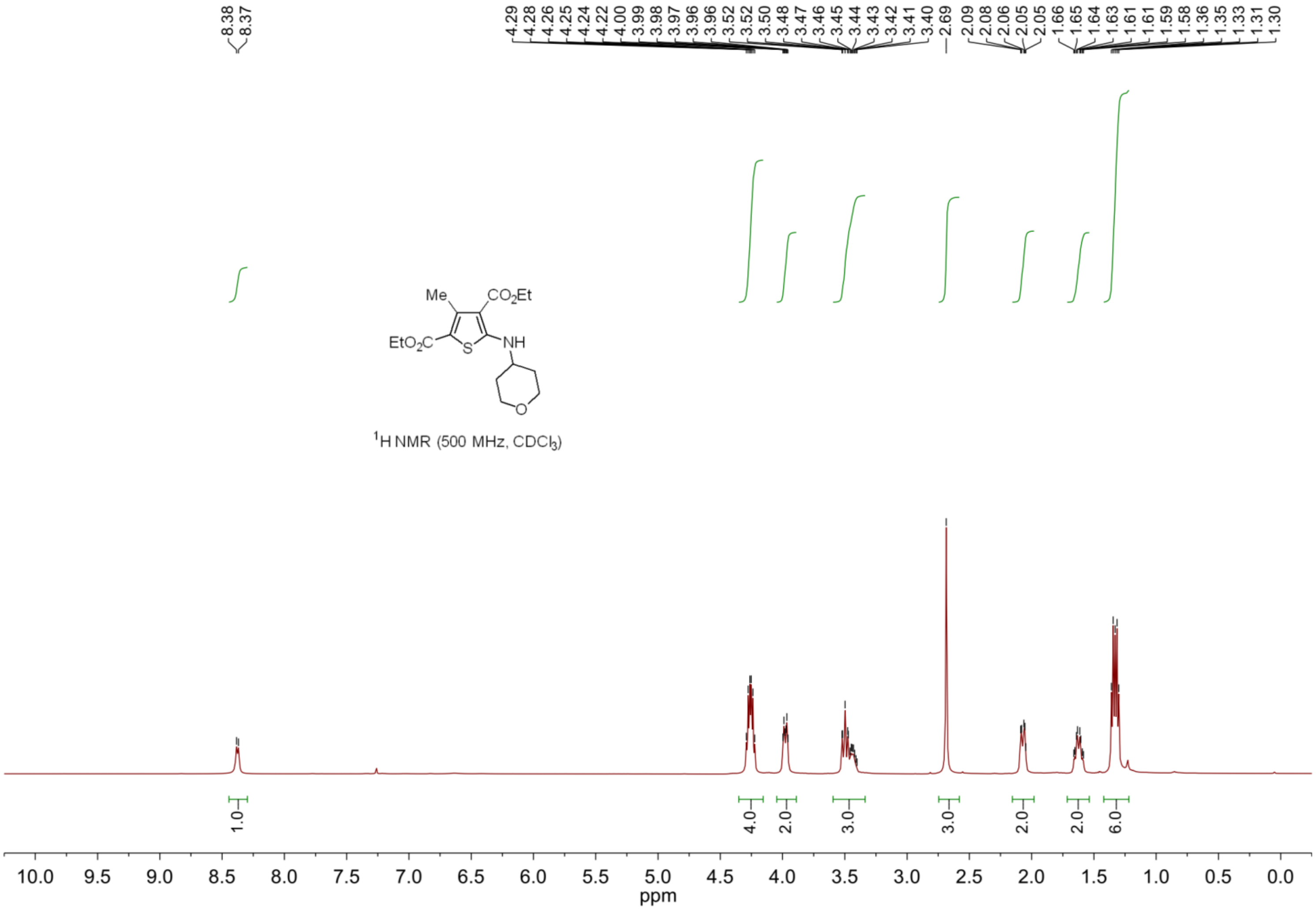
Diethyl 3-methyl-5-((tetrahydro-2*H*-pyran-4-yl)amino)thiophene-2,4-dicarboxylate (67)



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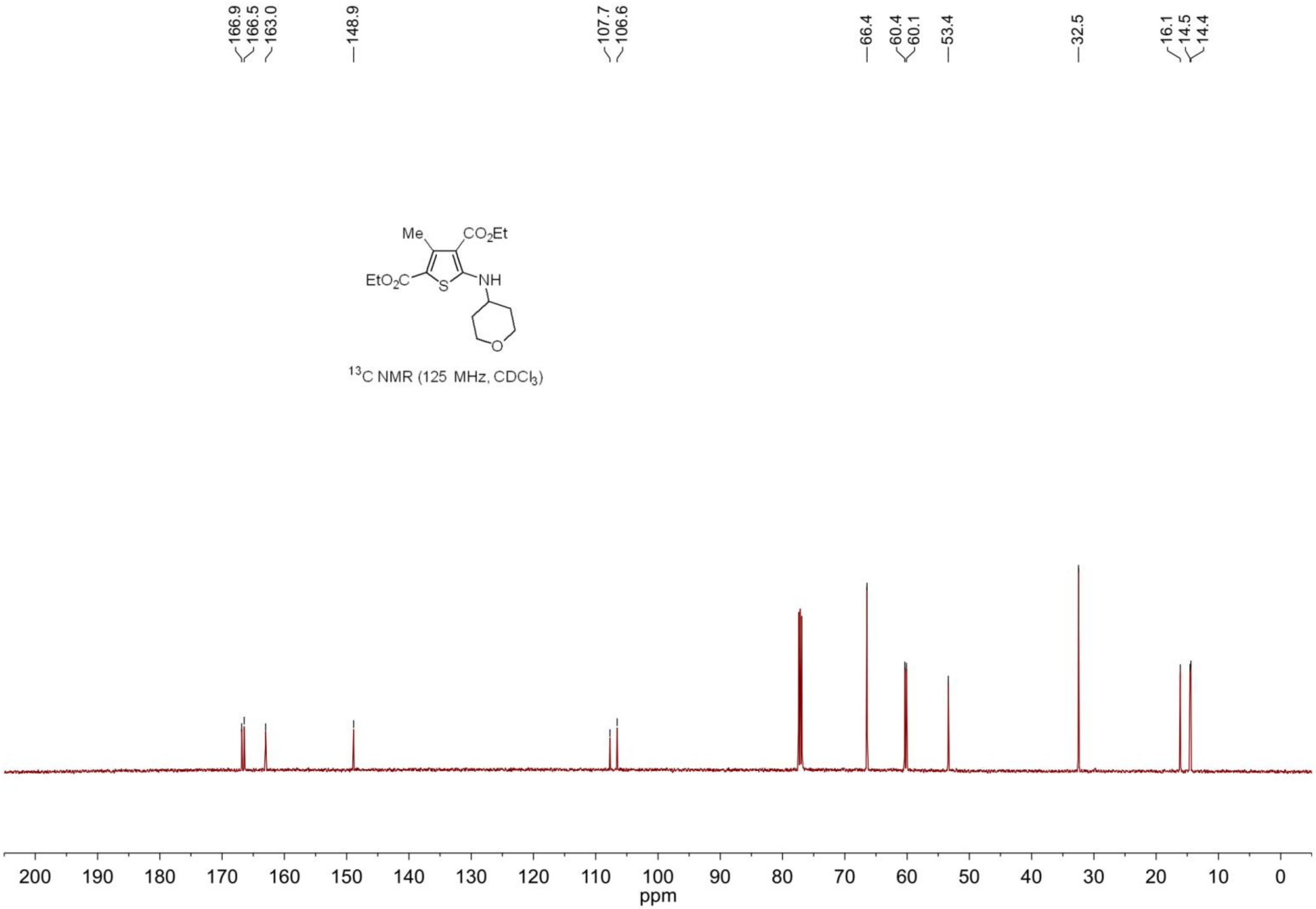
Diethyl 3-methyl-5-((tetrahydro-2*H*-pyran-4-yl)amino)thiophene-2,4-dicarboxylate (67)



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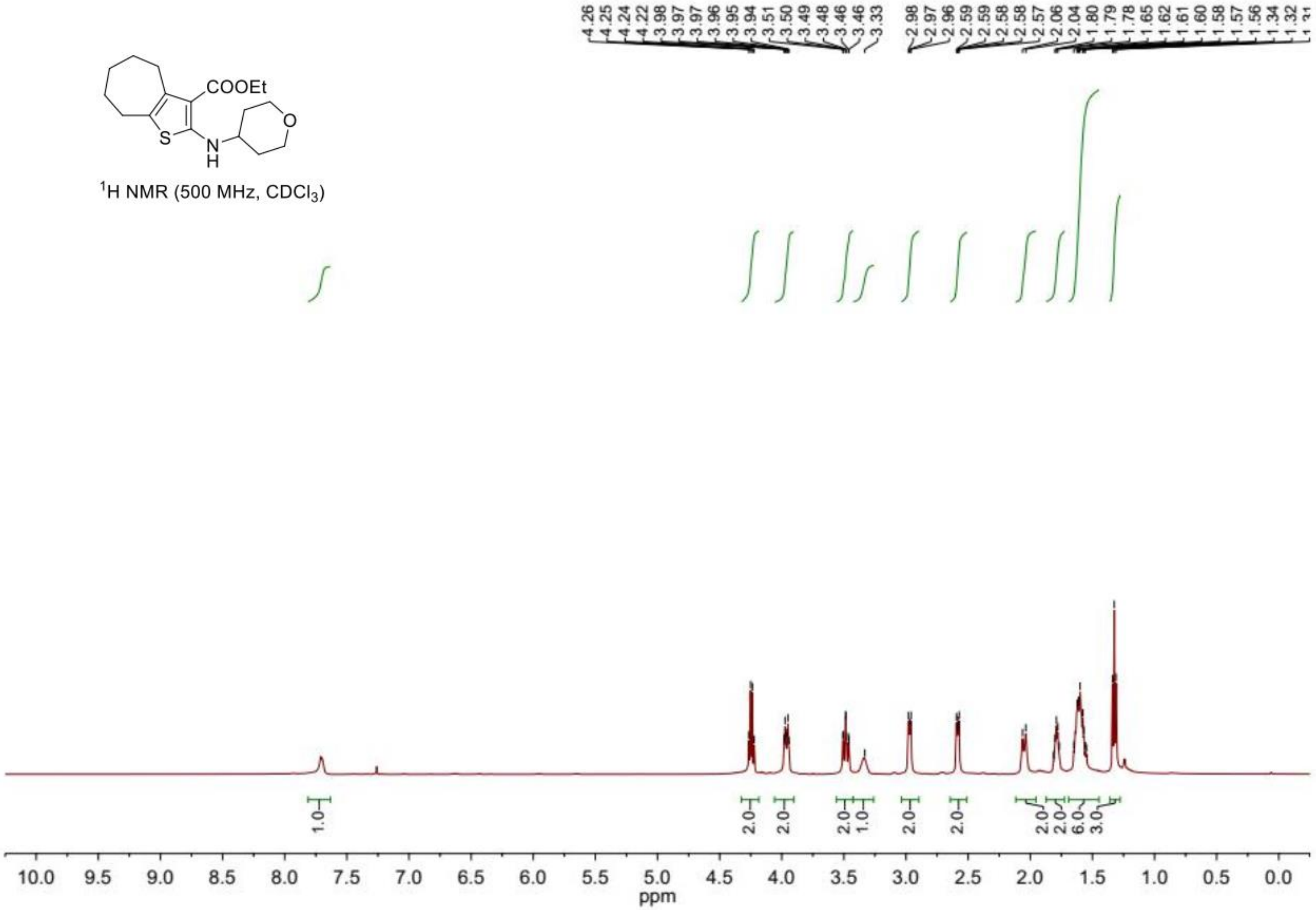
Ethyl 2-((tetrahydro-2*H*-pyran-4-yl)amino)-5,6,7,8-tetrahydro-4*H*-cyclohepta[*b*]thiophene-3-carboxylate (68)



^{1}H NMR (500 MHz, CDCl$_3$)

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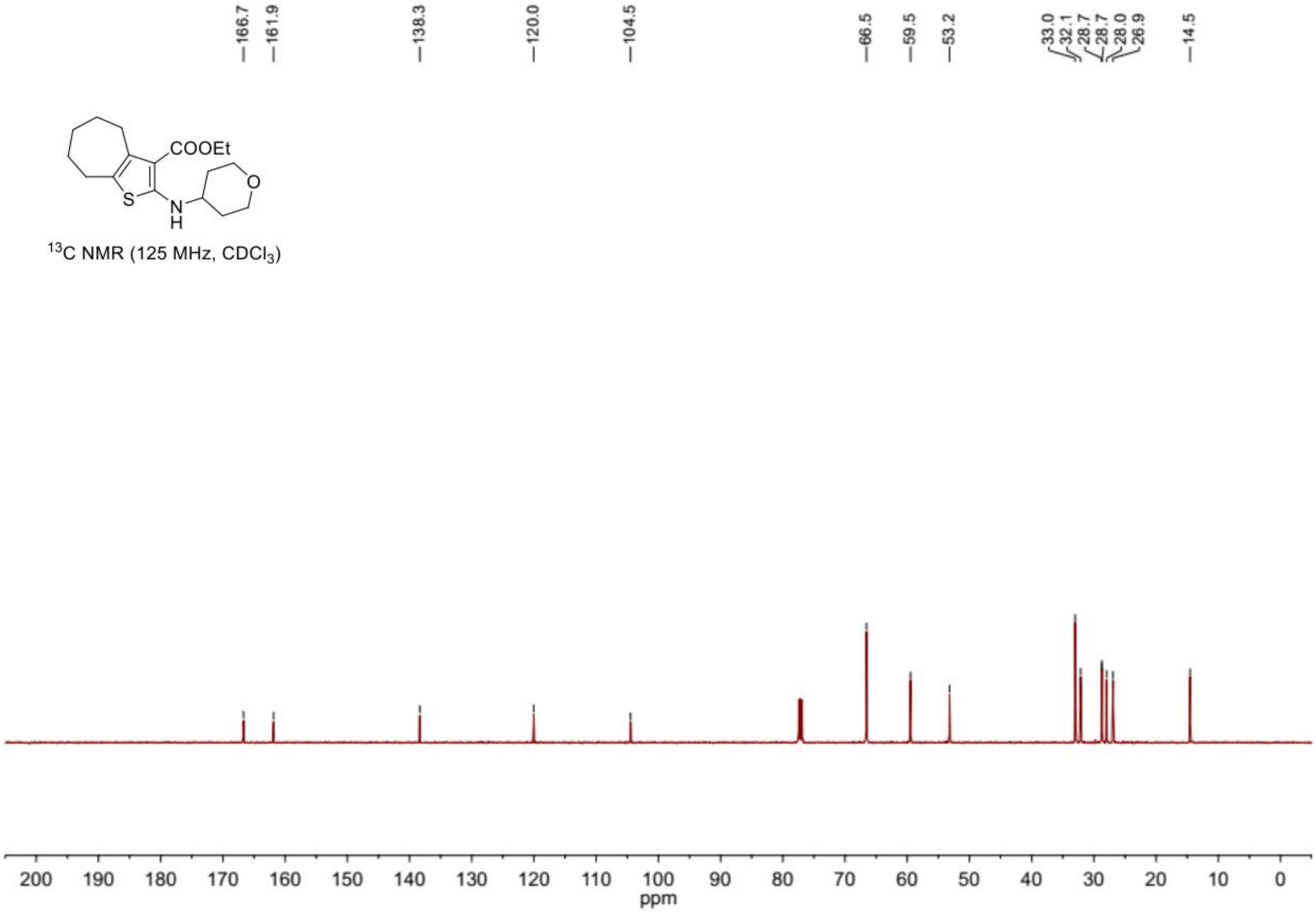
Ethyl 2-((tetrahydro-2*H*-pyran-4-yl)amino)-5,6,7,8-tetrahydro-4*H*-cyclohepta[*b*]thiophene-3-carboxylate (68)



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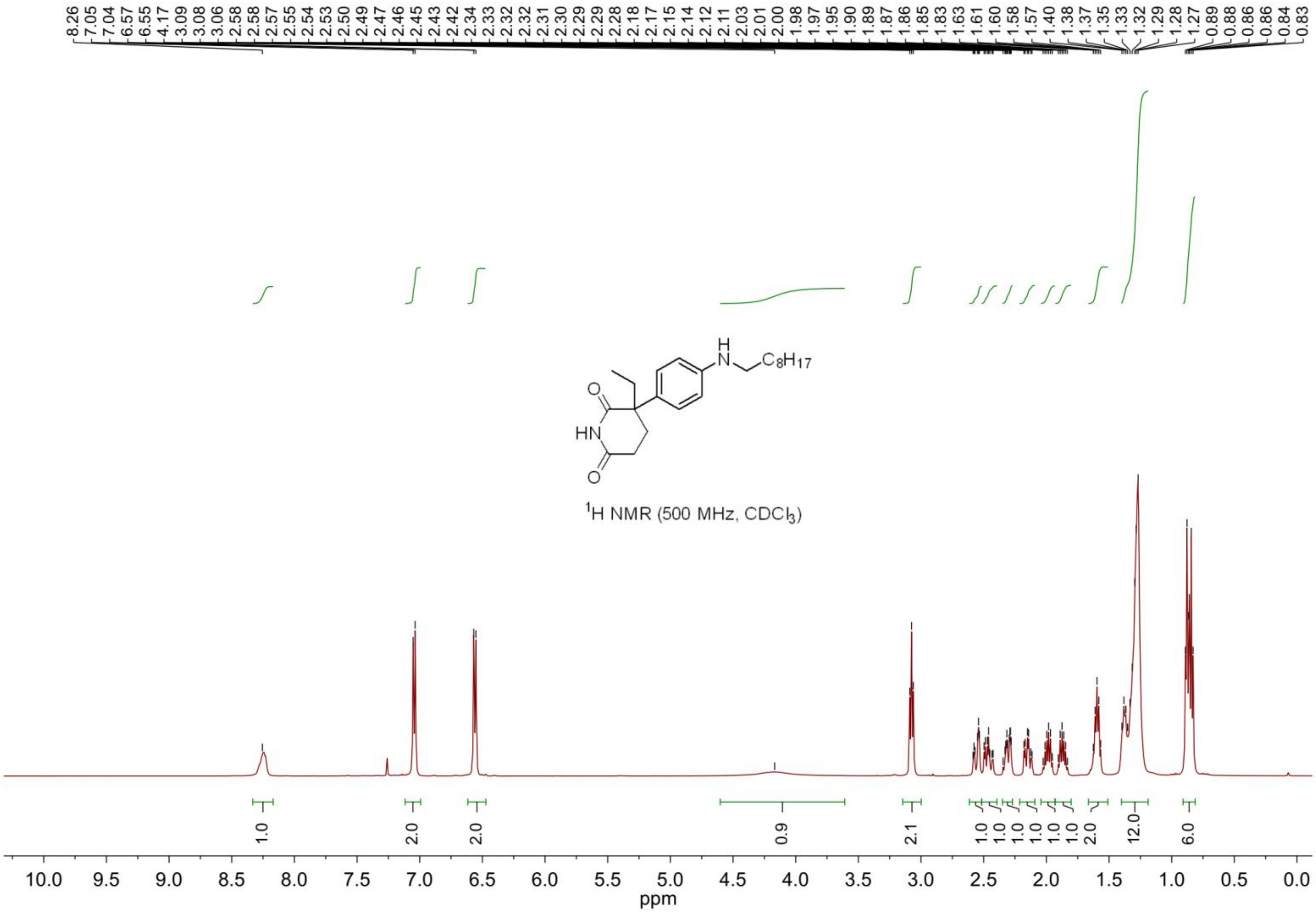
3-Ethyl-3-(4-(nonylamino)phenyl)piperidine-2,6-dione (69)



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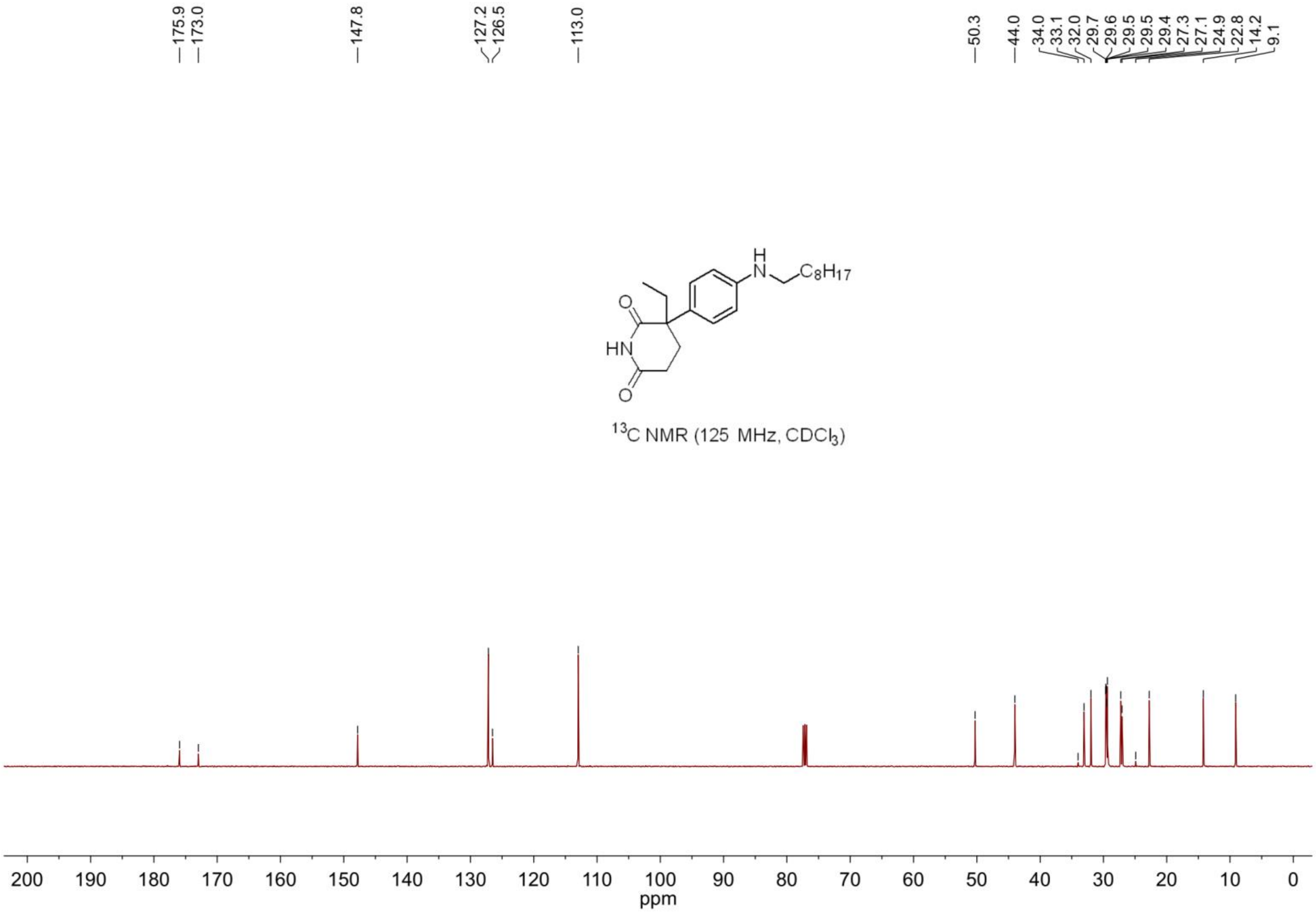
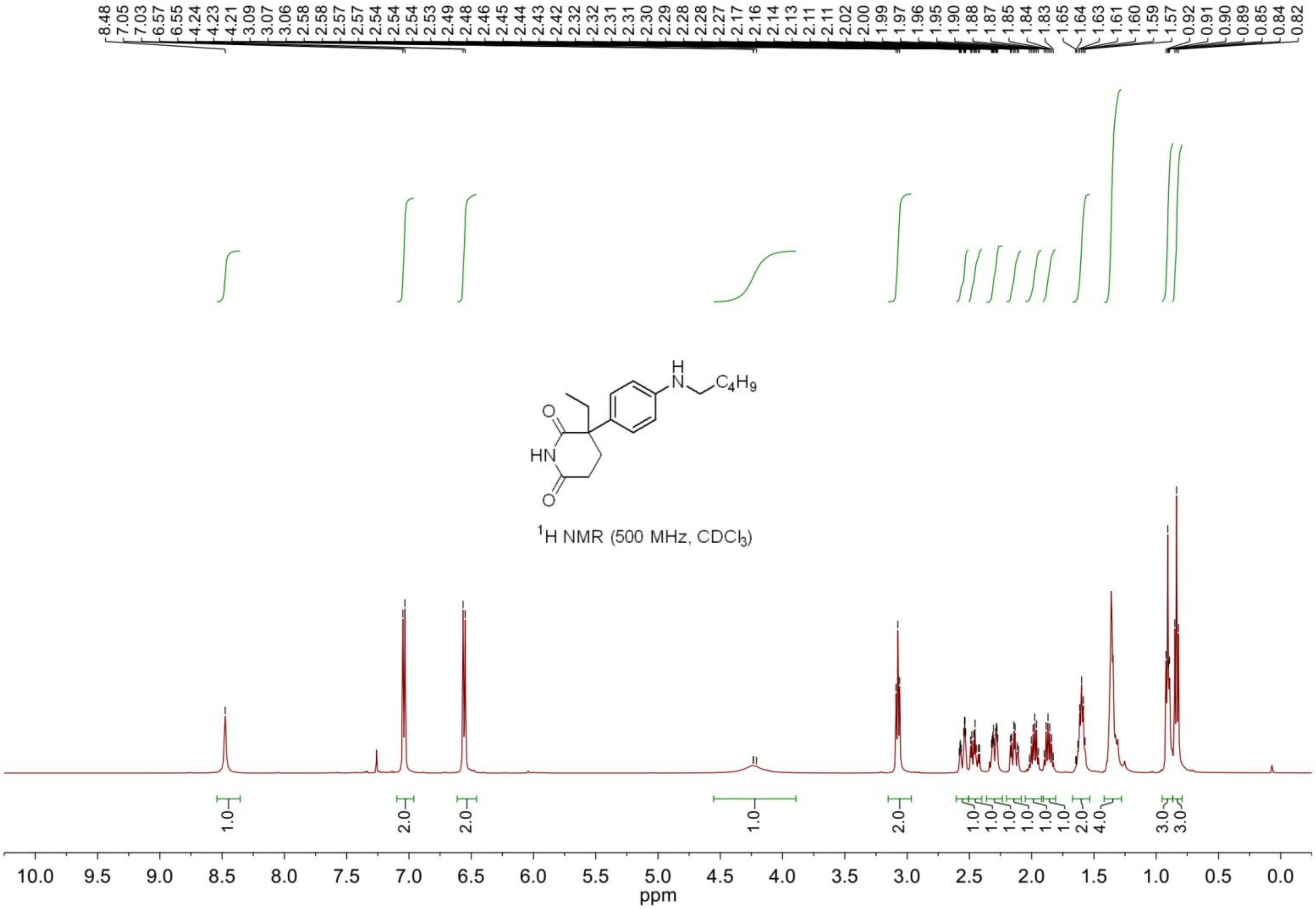
3-Ethyl-3-(4-(nonylamino)phenyl)piperidine-2,6-dione (69)



3-Ethyl-3-(4-(pentylamino)phenyl)piperidine-2,6-dione (70)



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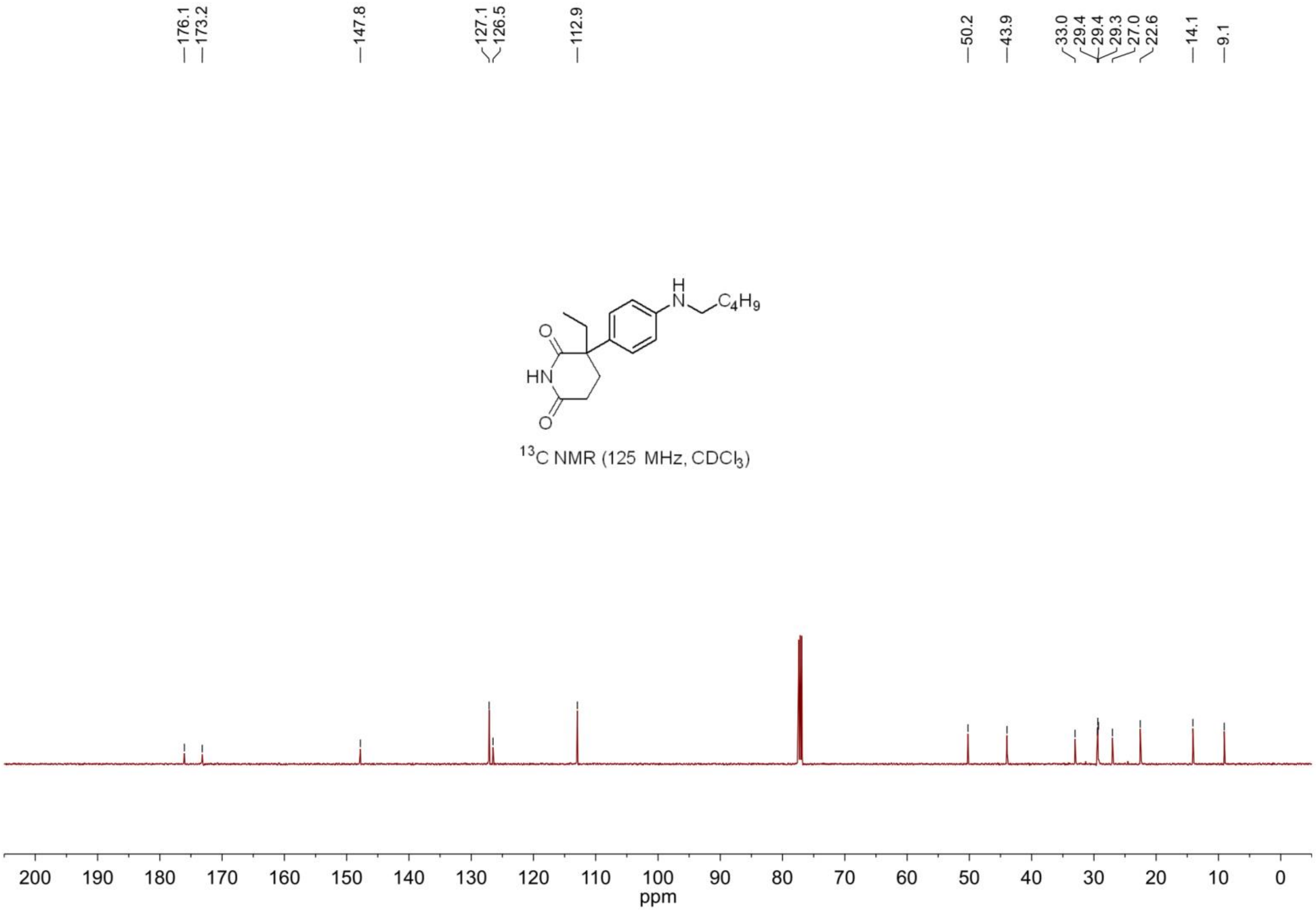
3-Ethyl-3-(4-(pentylamino)phenyl)piperidine-2,6-dione (70)



^{13}C NMR (125 MHz, $CDCl_3$)

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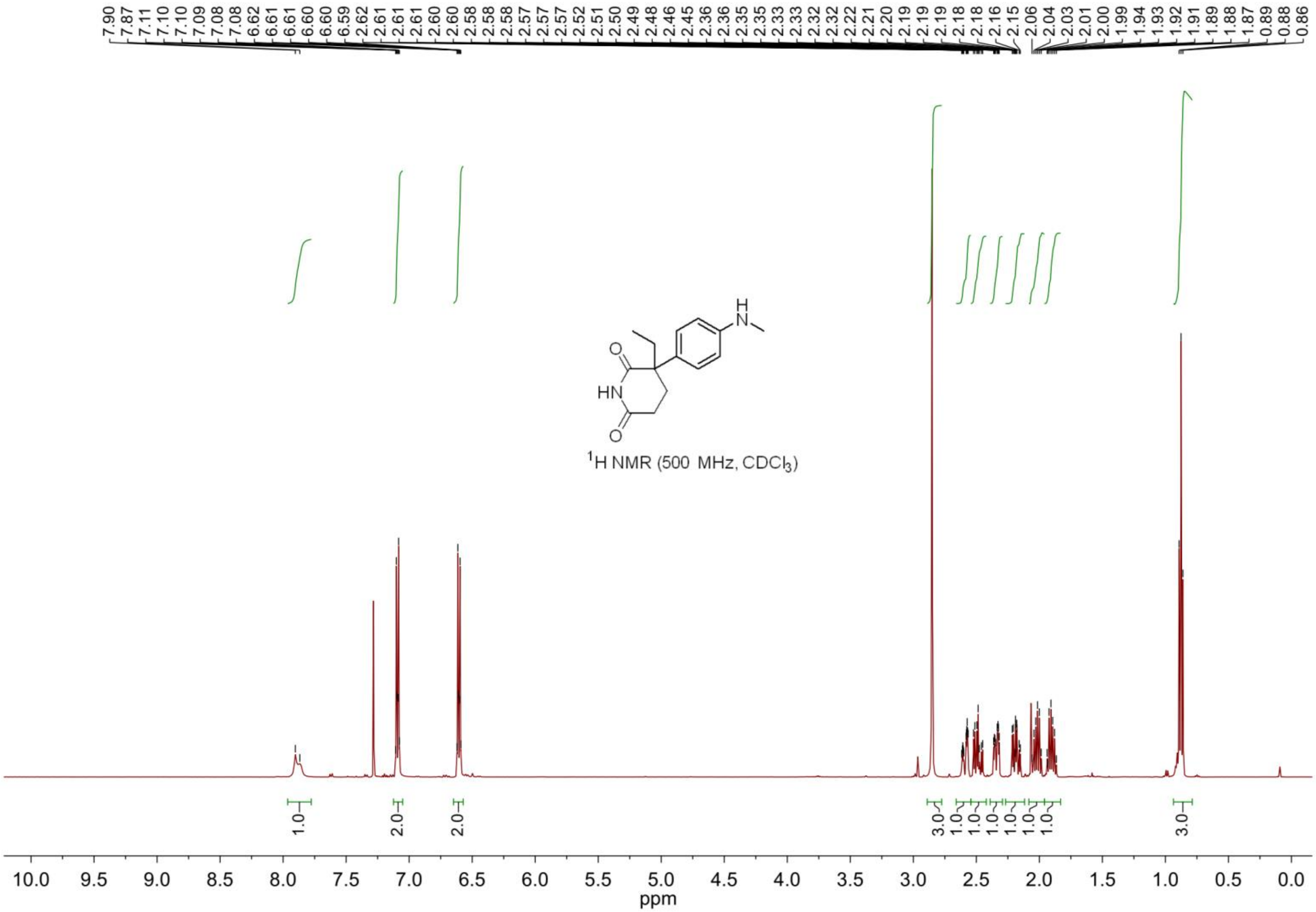
3-Ethyl-3-(4-(methylamino)phenyl)piperidine-2,6-dione (71)



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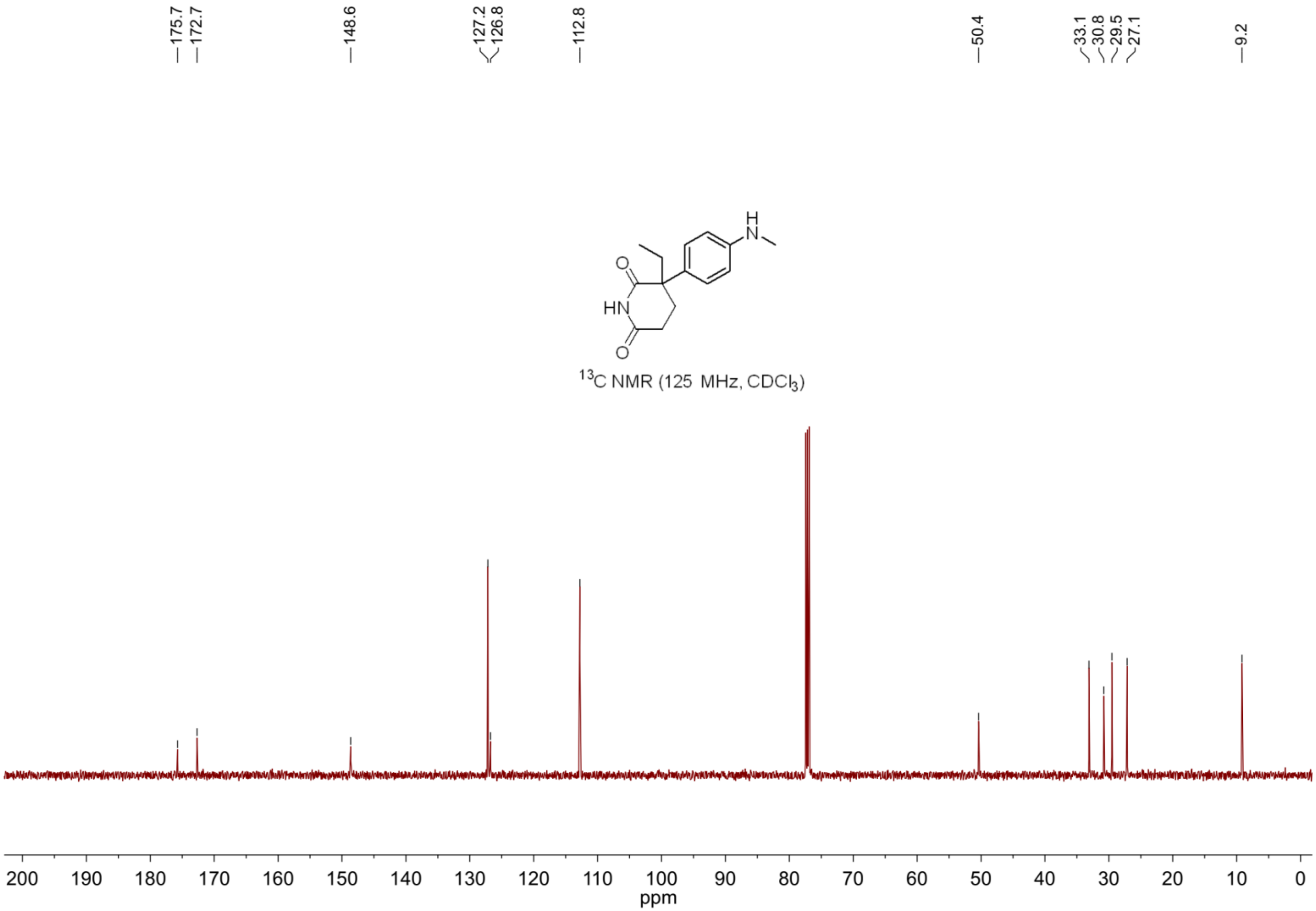
3-Ethyl-3-(4-(methylamino)phenyl)piperidine-2,6-dione (71)



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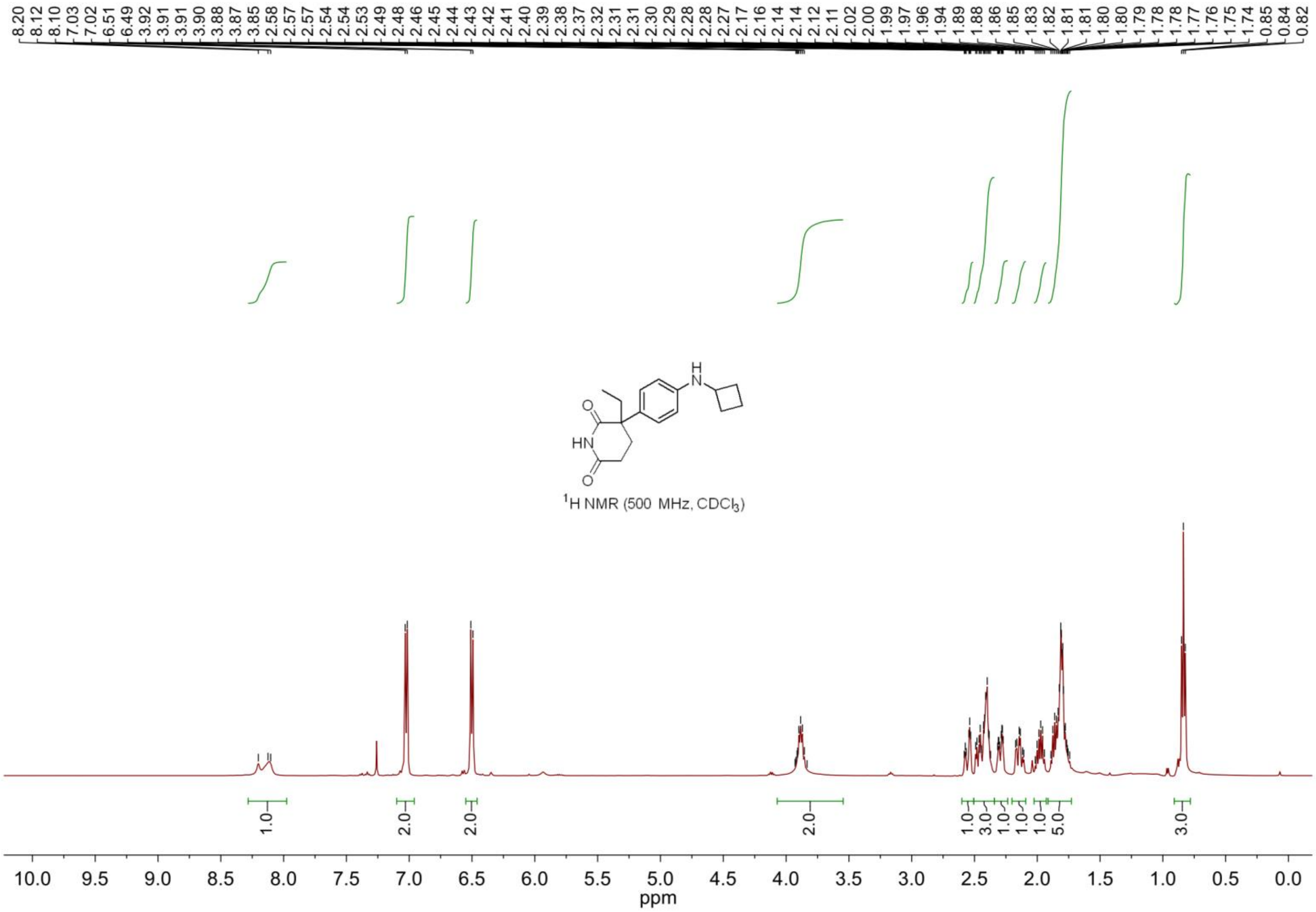
3-(4-(Cyclobutylamino)phenyl)-3-ethylpiperidine-2,6-dione (72)



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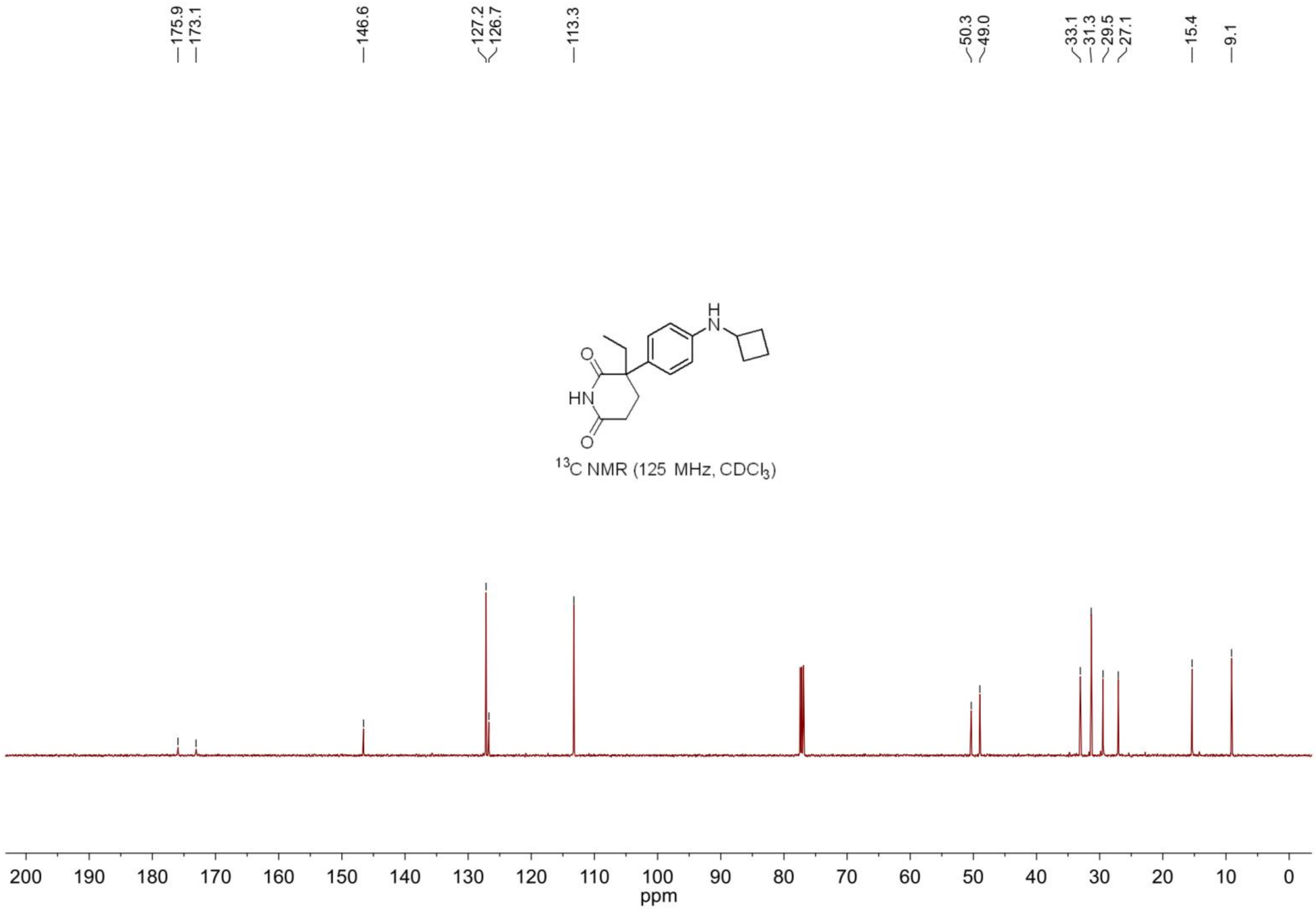
3-(4-(Cyclobutylamino)phenyl)-3-ethylpiperidine-2,6-dione (72)



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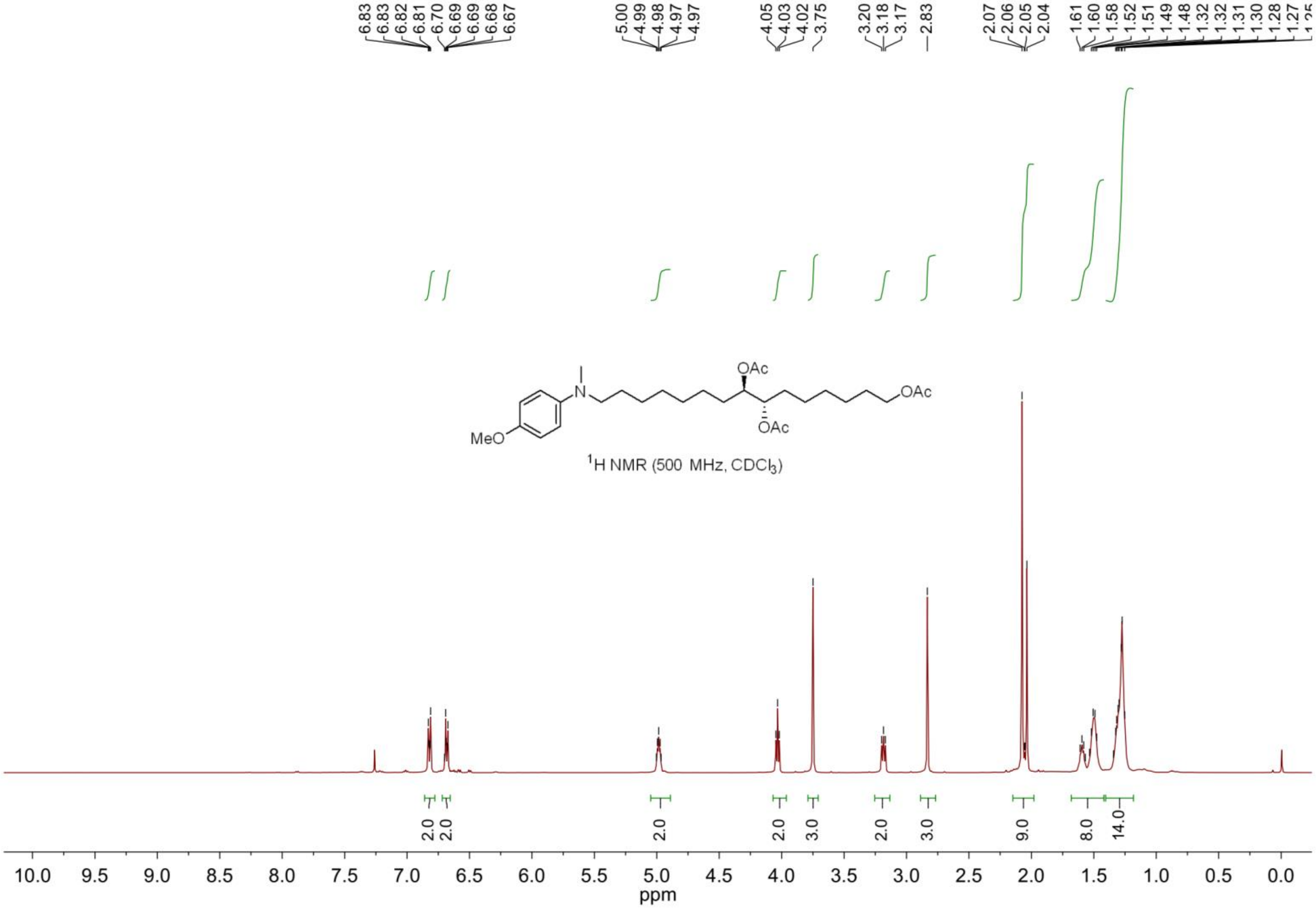
(7*S**,8*R**)-15-((4-methoxyphenyl)(methyl)amino)pentadecane-1,7,8-triyl triacetate (73)



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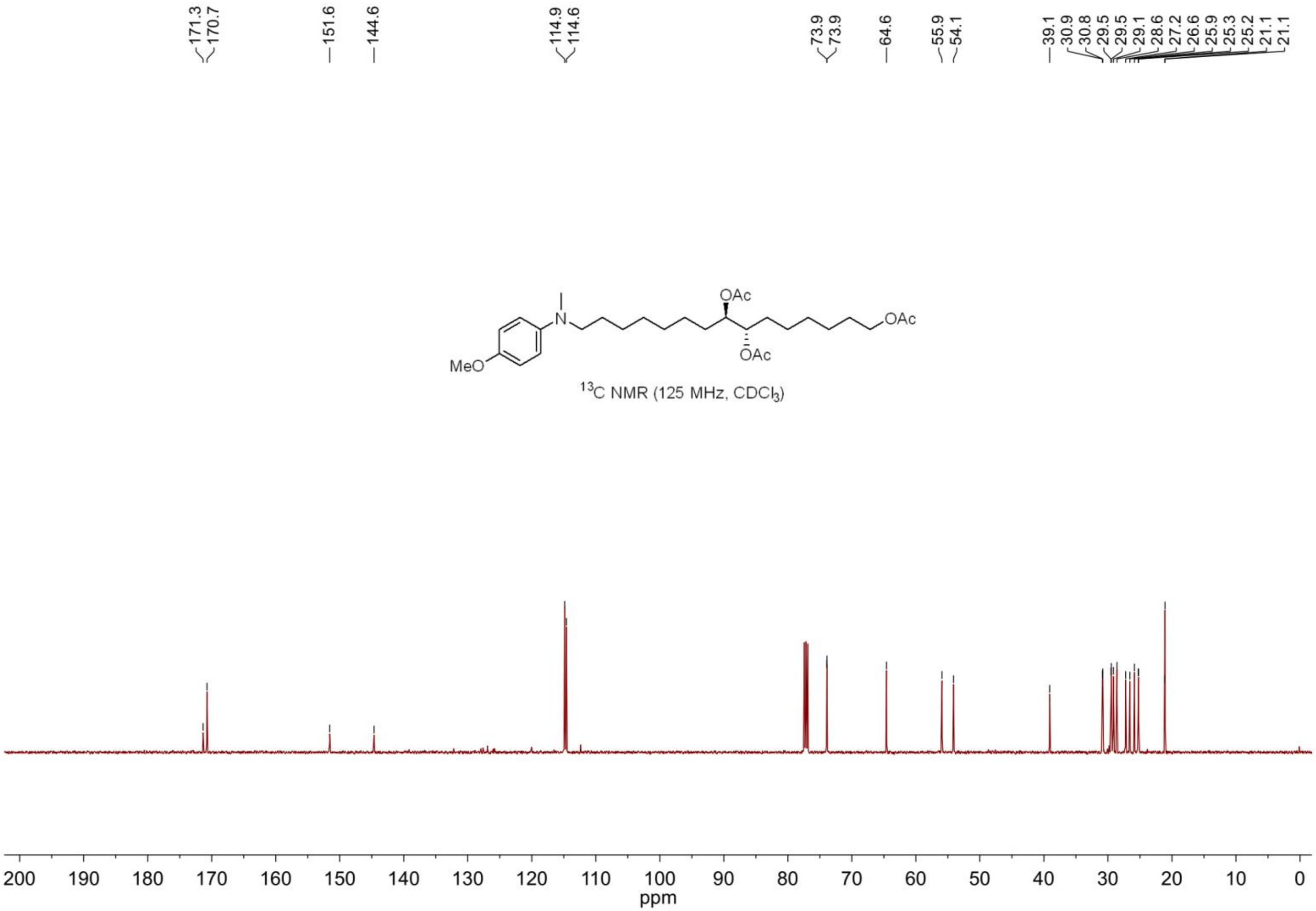
(7*S**,8*R**)-15-((4-methoxyphenyl)(methyl)amino)pentadecane-1,7,8-triyl triacetate (73)



^{13}C NMR (125 MHz, $CDCl_3$)

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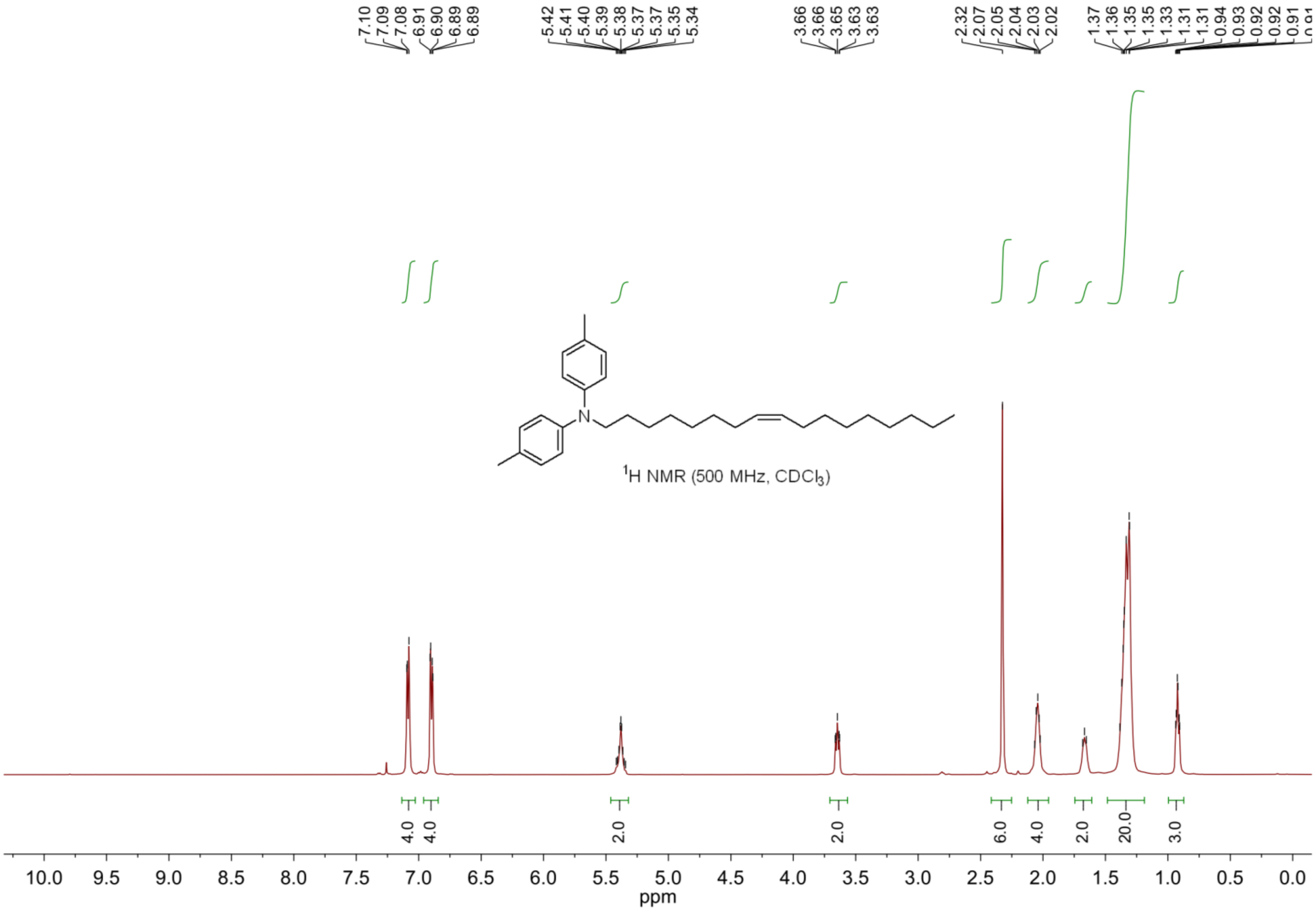
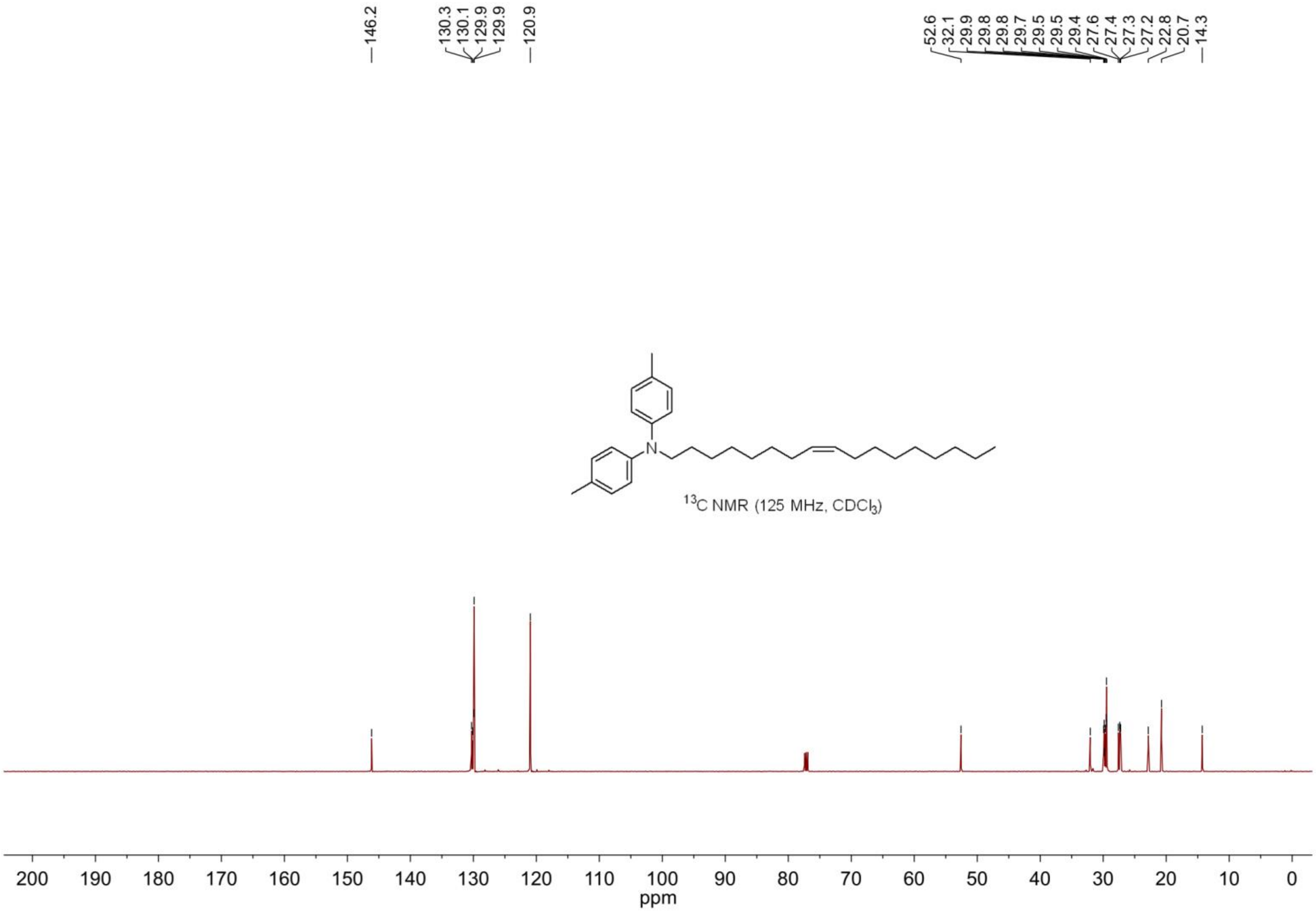
(*Z*)-*N*-(Heptadec-8-en-1-yl)-4-methyl-*N*-(*p*-tolyl)aniline (74)



(*Z*)-*N*-(Heptadec-8-en-1-yl)-4-methyl-*N*-(*p*-tolyl)aniline (74)



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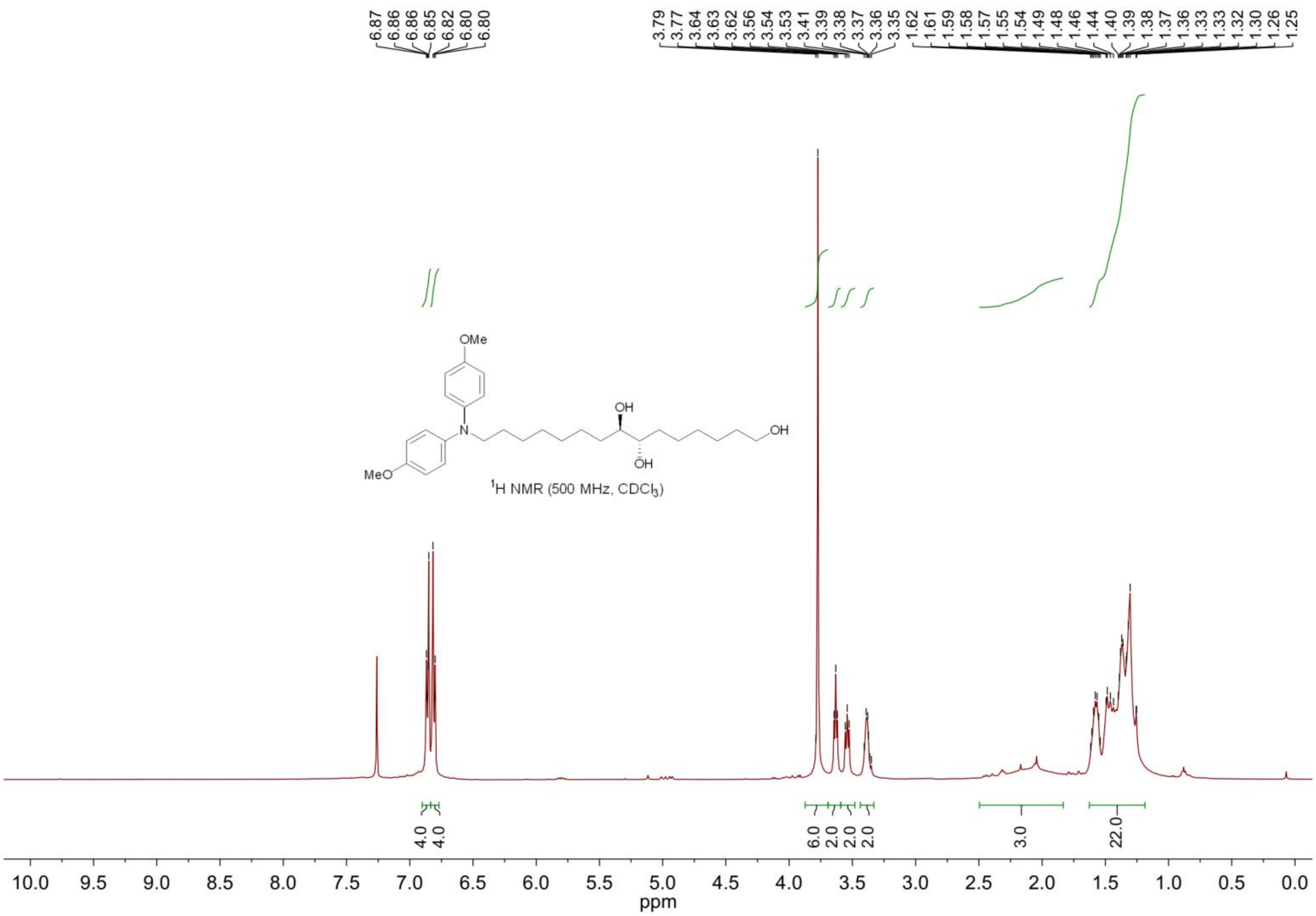
(7*S**,8*R**)-15-(Bis(4-methoxyphenyl)amino)pentadecane-1,7,8-triol (75)



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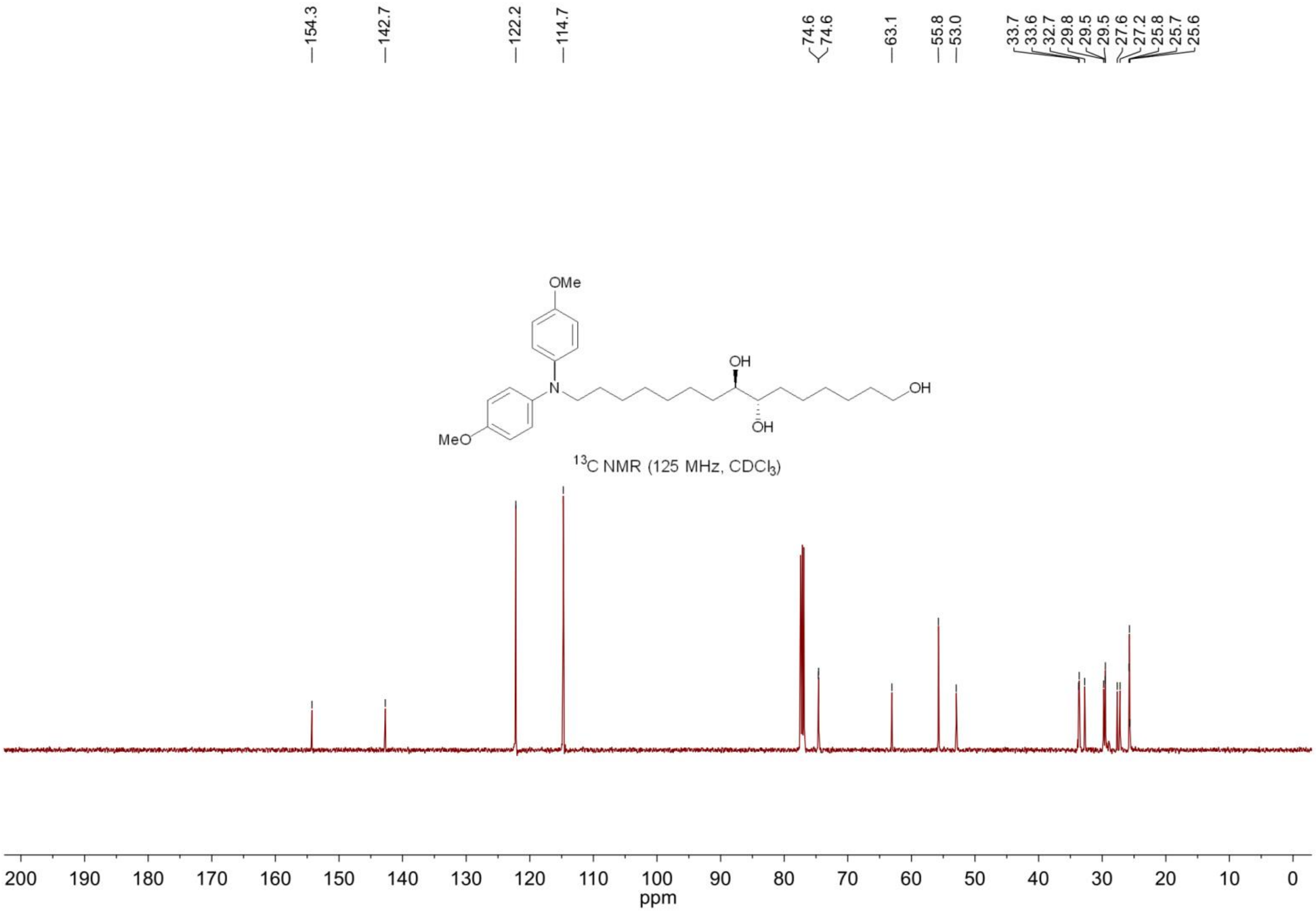
(7*S**,8*R**)-15-(Bis(4-methoxyphenyl)amino)pentadecane-1,7,8-triol (75)



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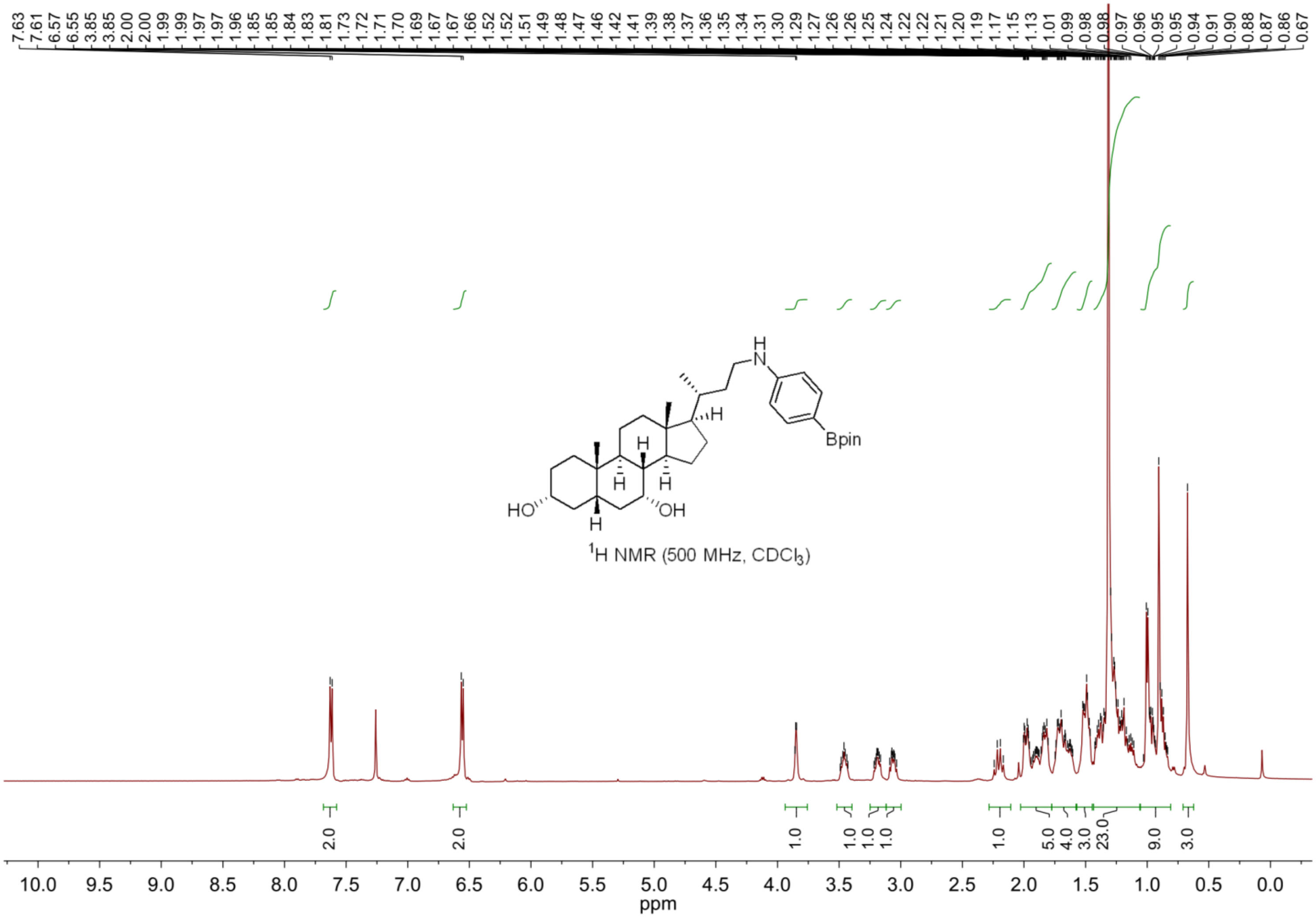
(3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-4-((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amino)butan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,7-diol (76)



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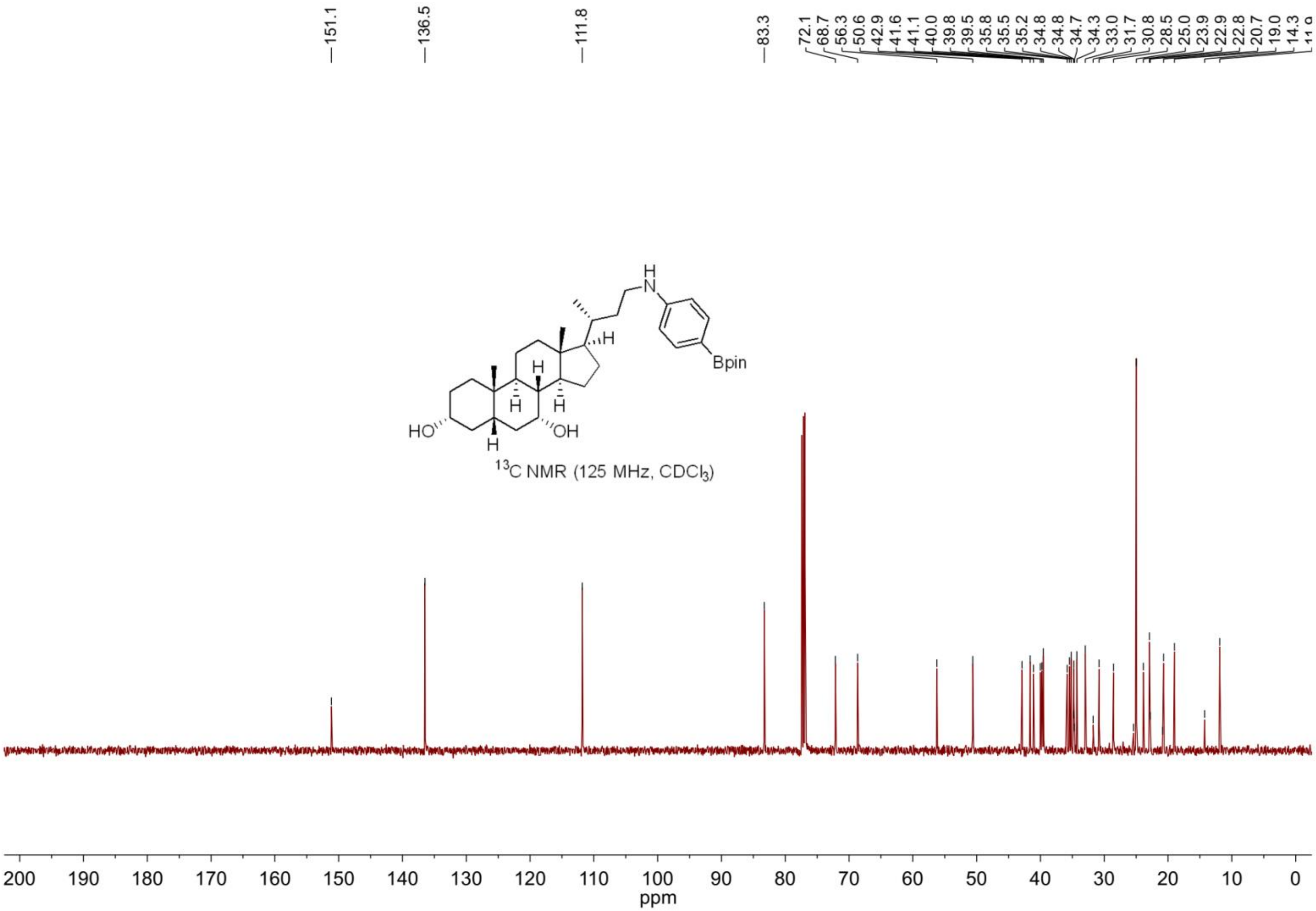
(3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-4-((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amino)butan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,7-diol (76)



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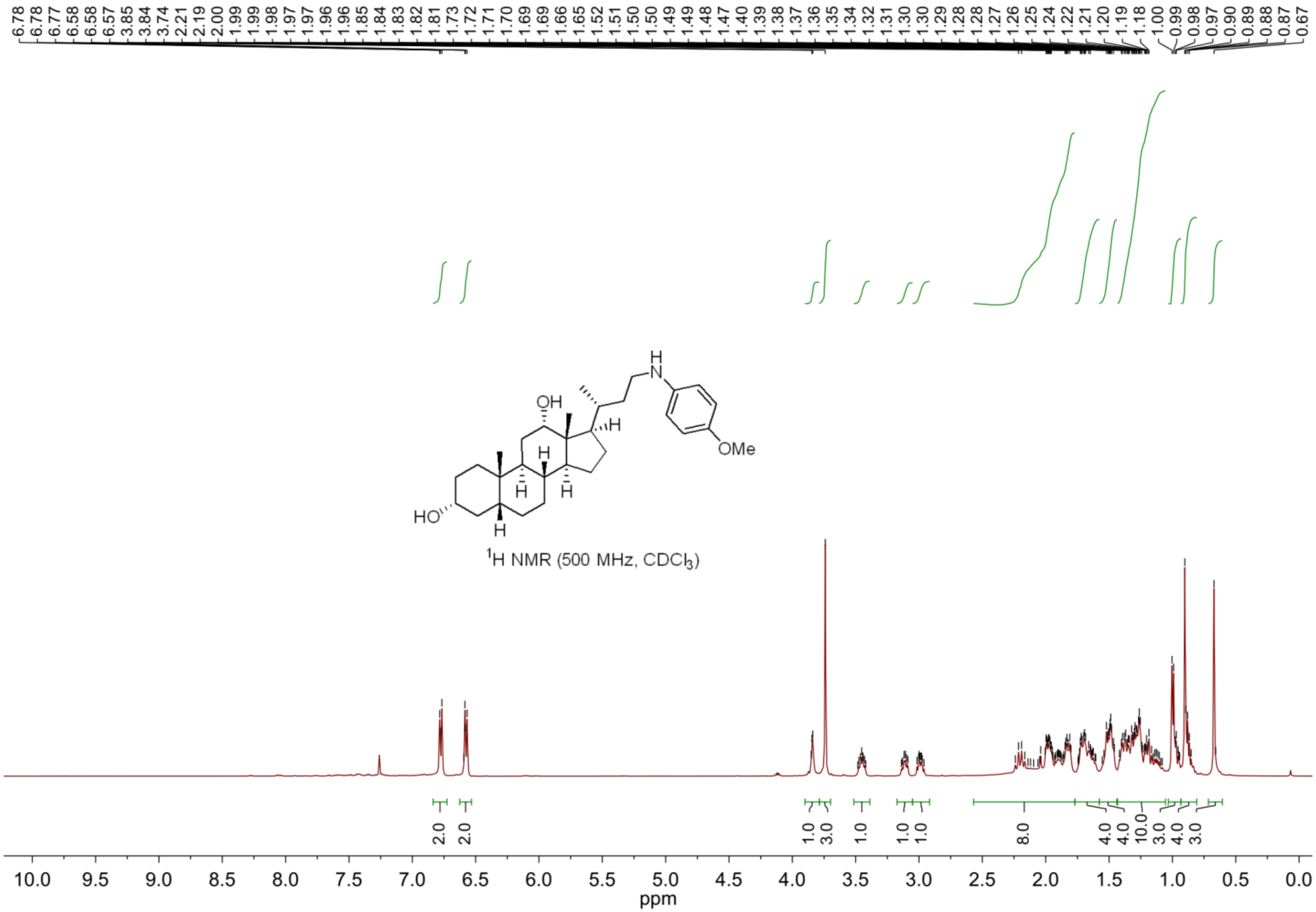
(3*R*,5*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-17-((*R*)-4-((4-Methoxyphenyl)amino)butan-2-yl)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,12-diol (77)



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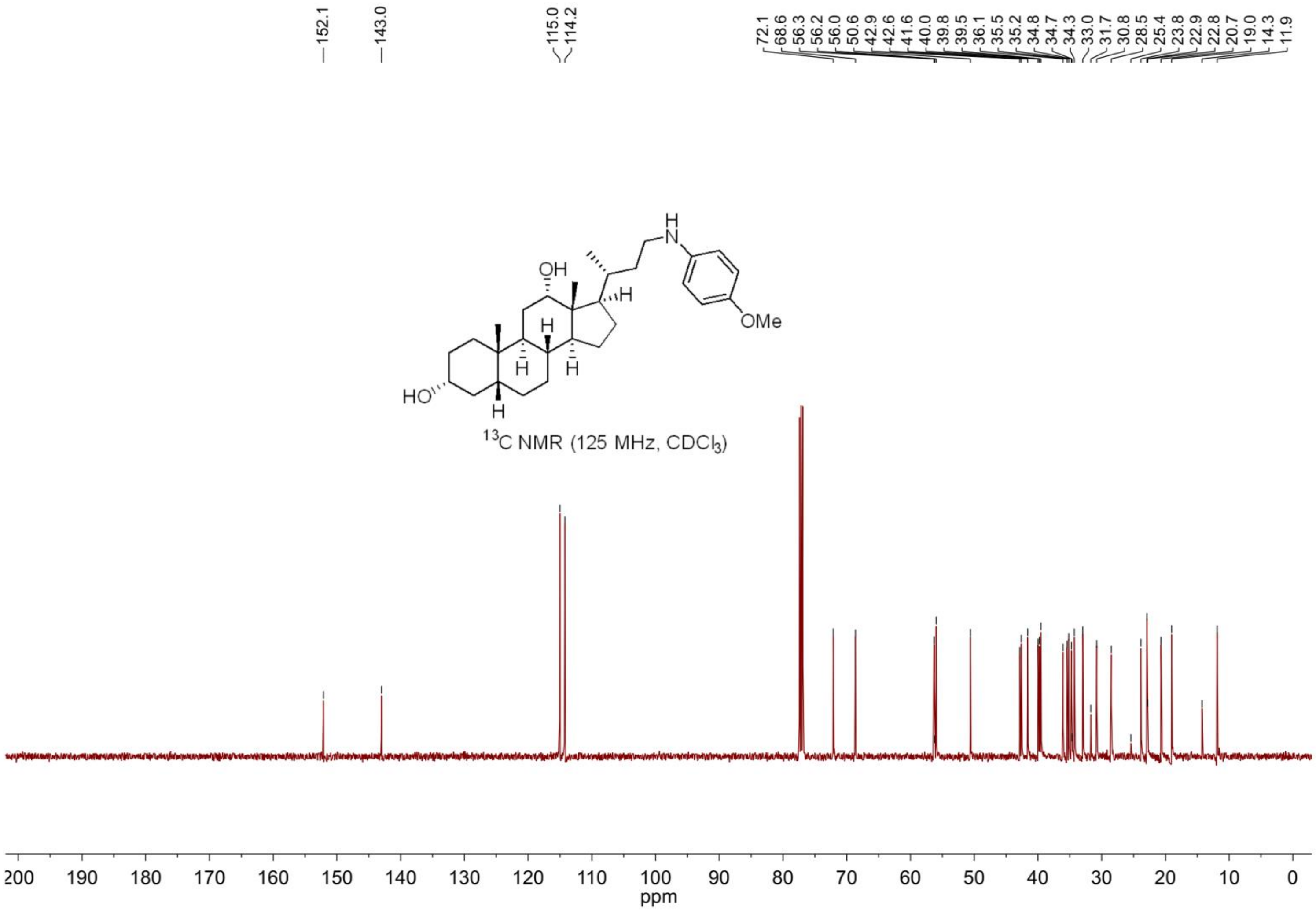
(3*R*,5*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-17-((*R*)-4-((4-Methoxyphenyl)amino)butan-2-yl)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,12-diol (77)



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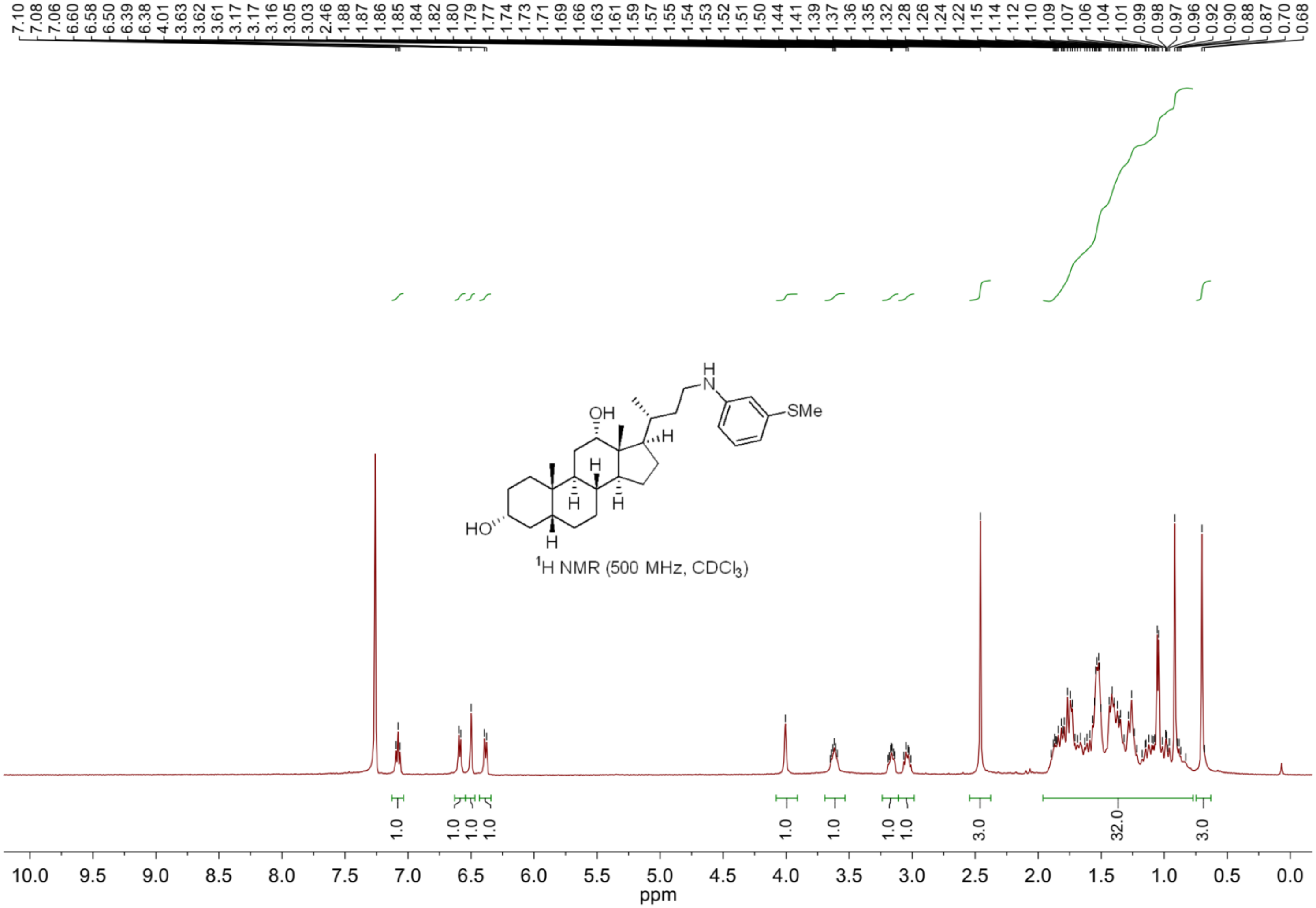
(3*R*,5*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-4-((3-(methylthio)phenyl)amino)butan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,12-diol (78)



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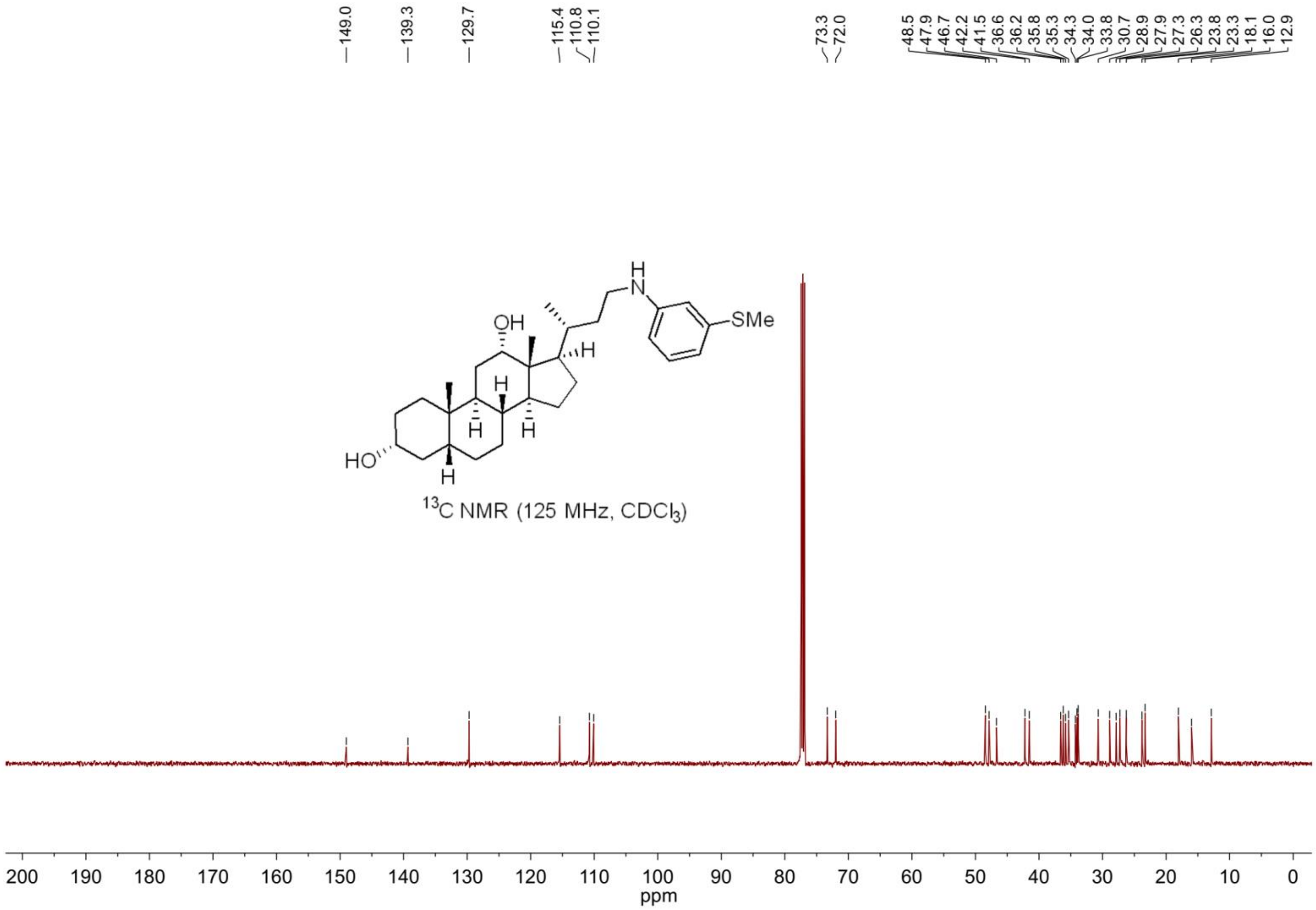
(3*R*,5*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-4-((3-(methylthio)phenyl)amino)butan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,12-diol (78)



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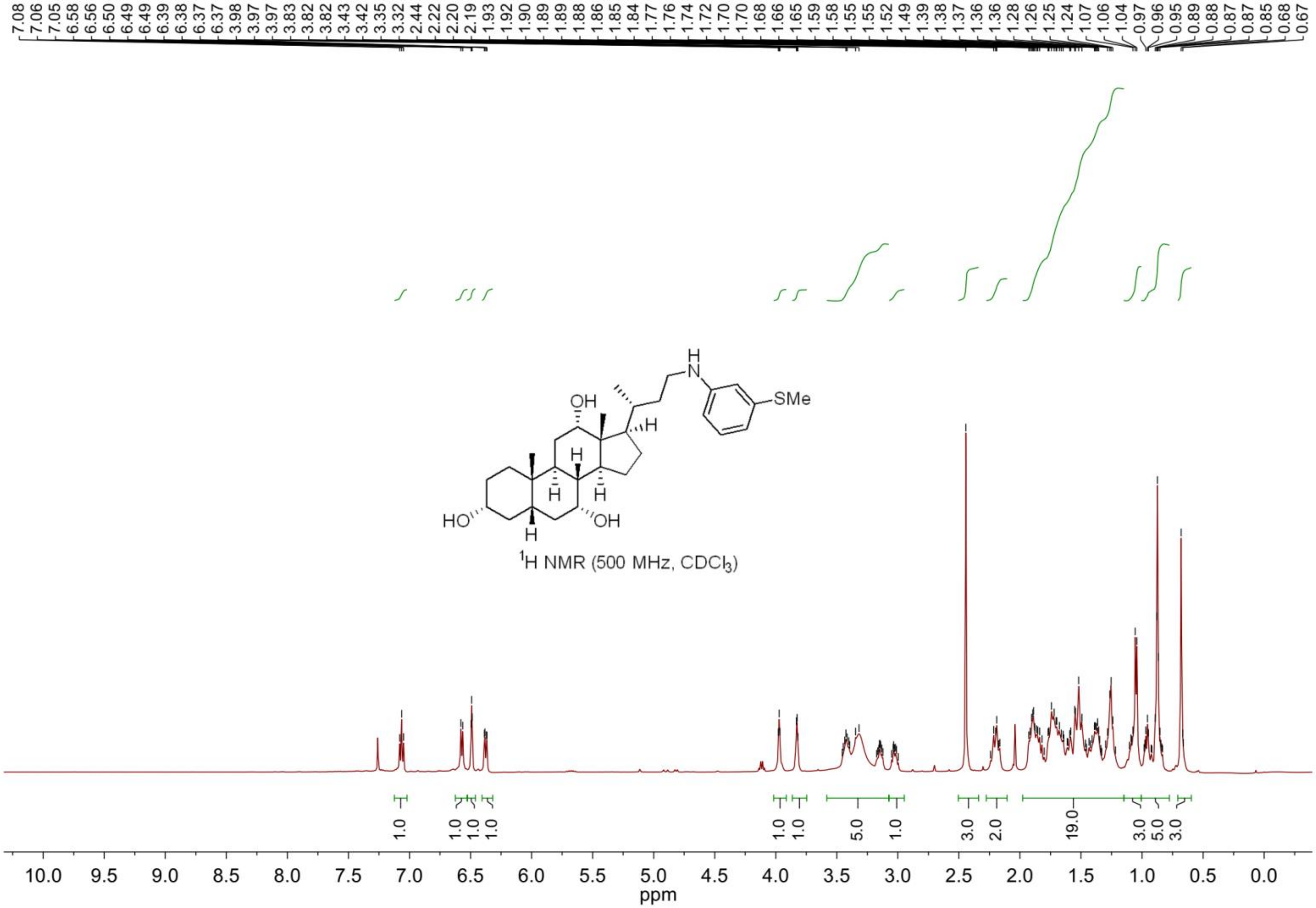
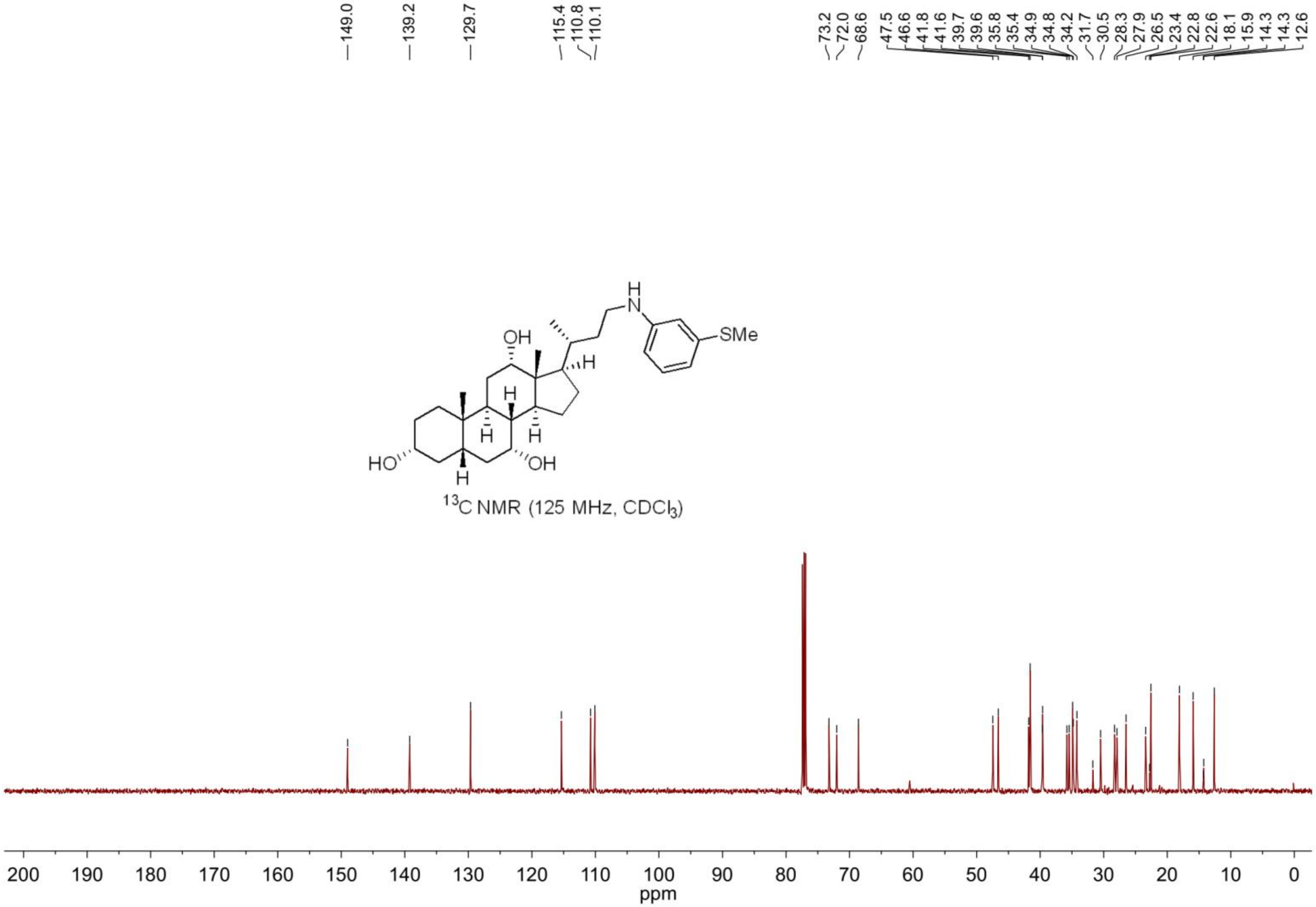
(3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-4-((3-(methylthio)phenyl)amino)butan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,7,12-triol (79)



^{1}H NMR (500 MHz, CDCl$_3$)

(3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-4-((3-(methylthio)phenyl)amino)butan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,7,12-triol (79)



^{13}C NMR (125 MHz, CDCl$_3$)

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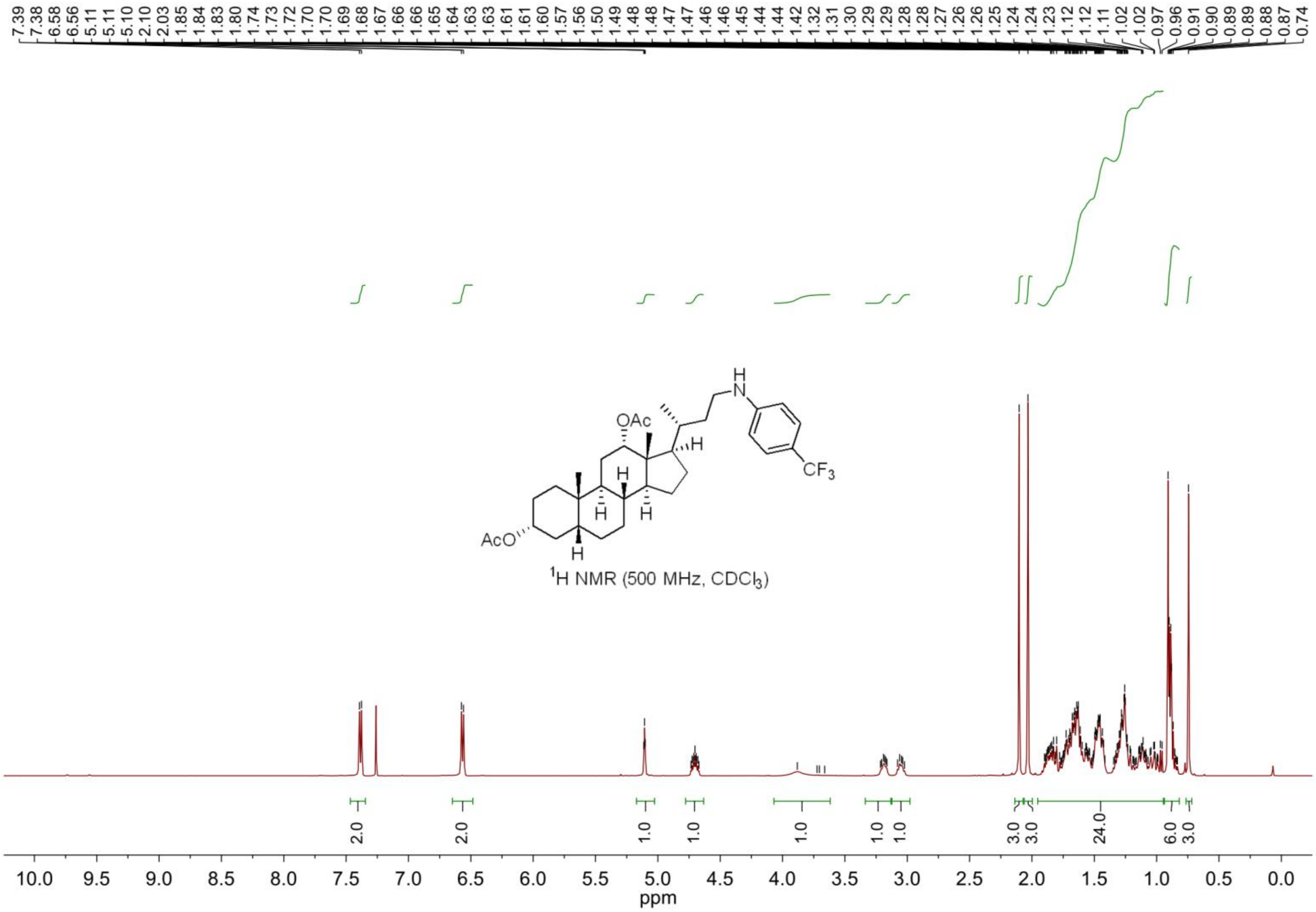
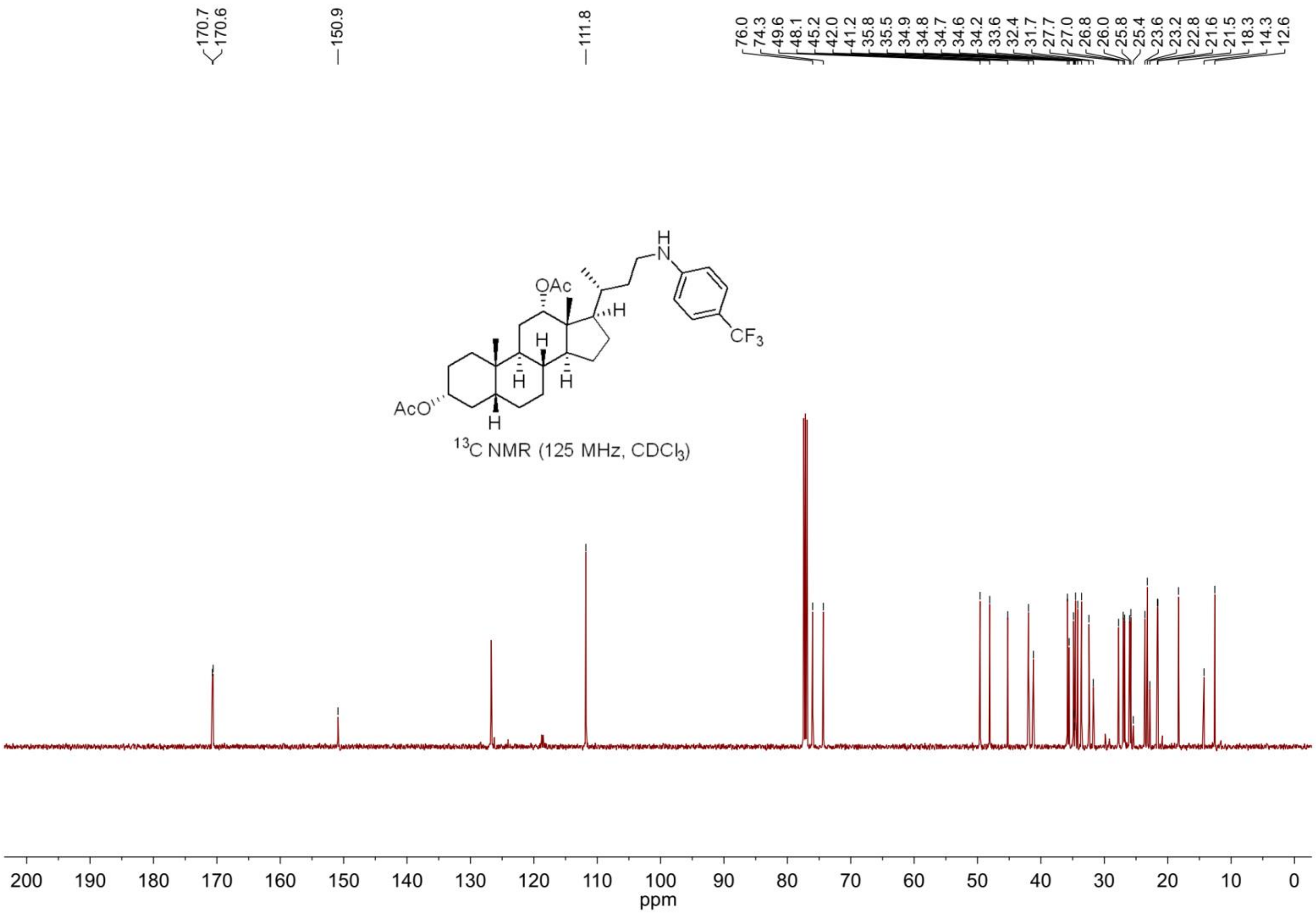
(3*R*,5*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-4-((4-(trifluoromethyl)phenyl)amino)butan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,12-diyl diacetate (80)



^{1}H NMR (500 MHz, CDCl$_3$)

(3*R*,5*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-4-((4-(trifluoromethyl)phenyl)amino)butan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,12-diyl diacetate (80)



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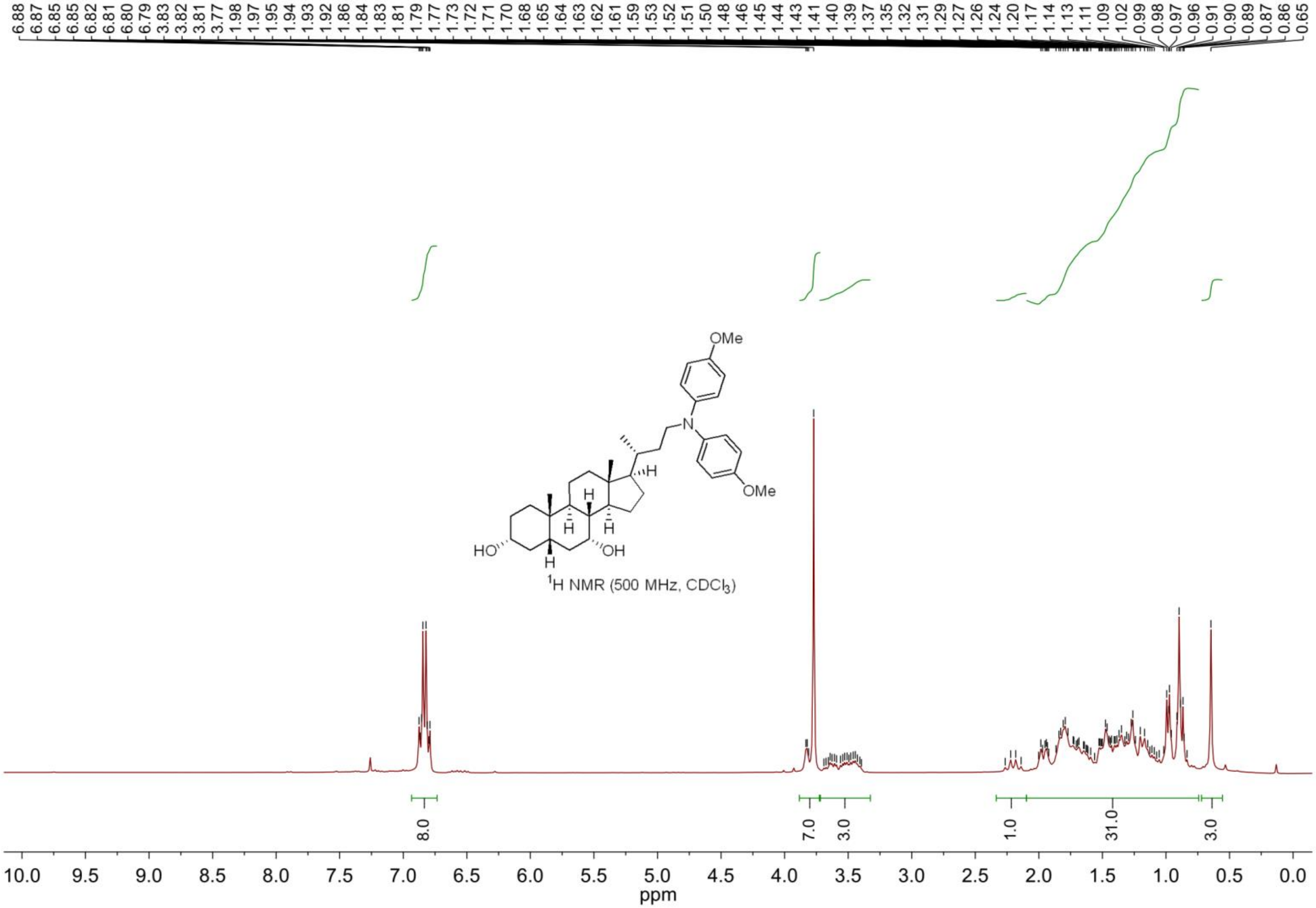
(3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-17-((*R*)-4-(Bis(4-methoxyphenyl)amino)butan-2-yl)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,7-diol (81)



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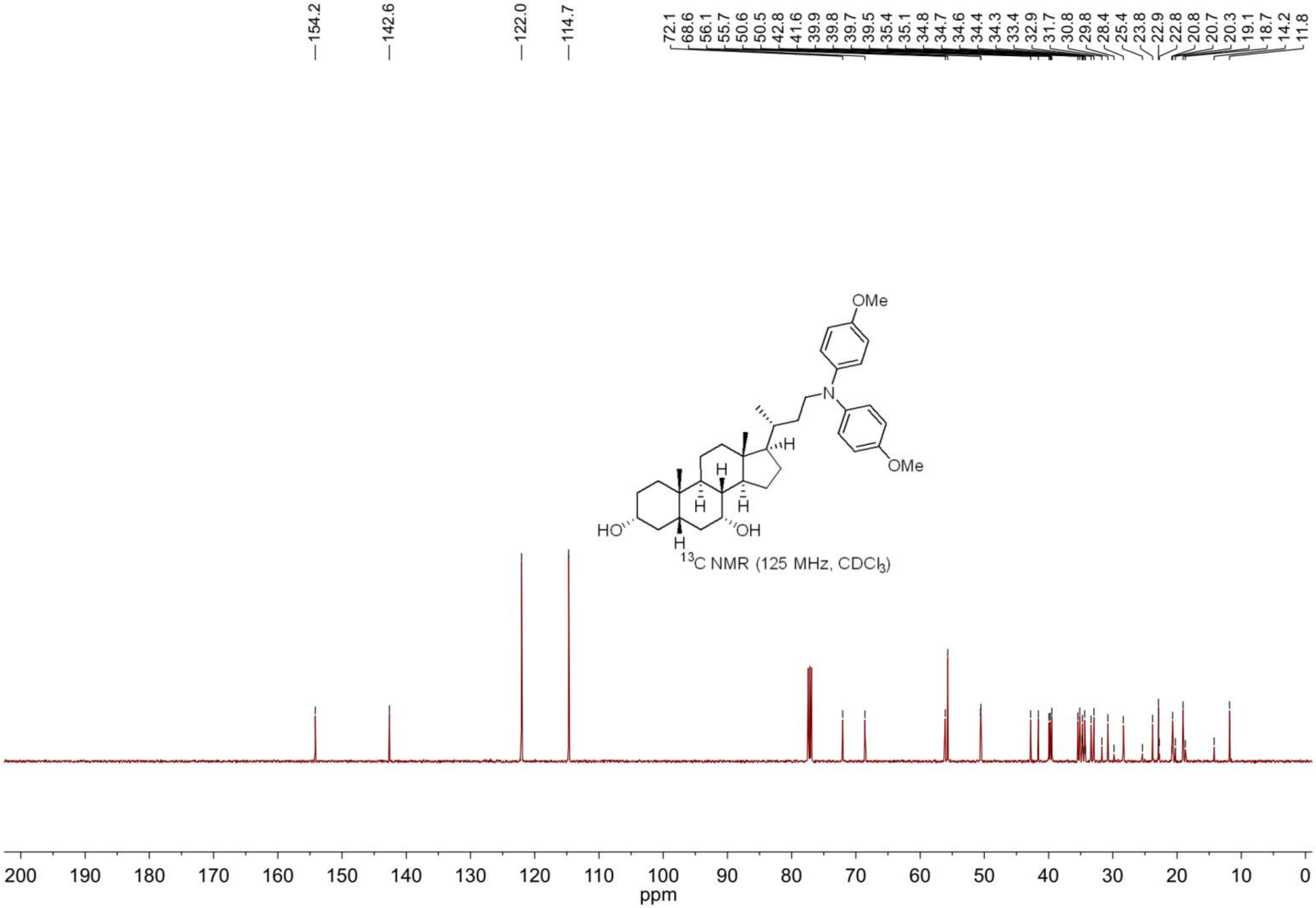
(3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-17-((*R*)-4-(Bis(4-methoxyphenyl)amino)butan-2-yl)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,7-diol (81)



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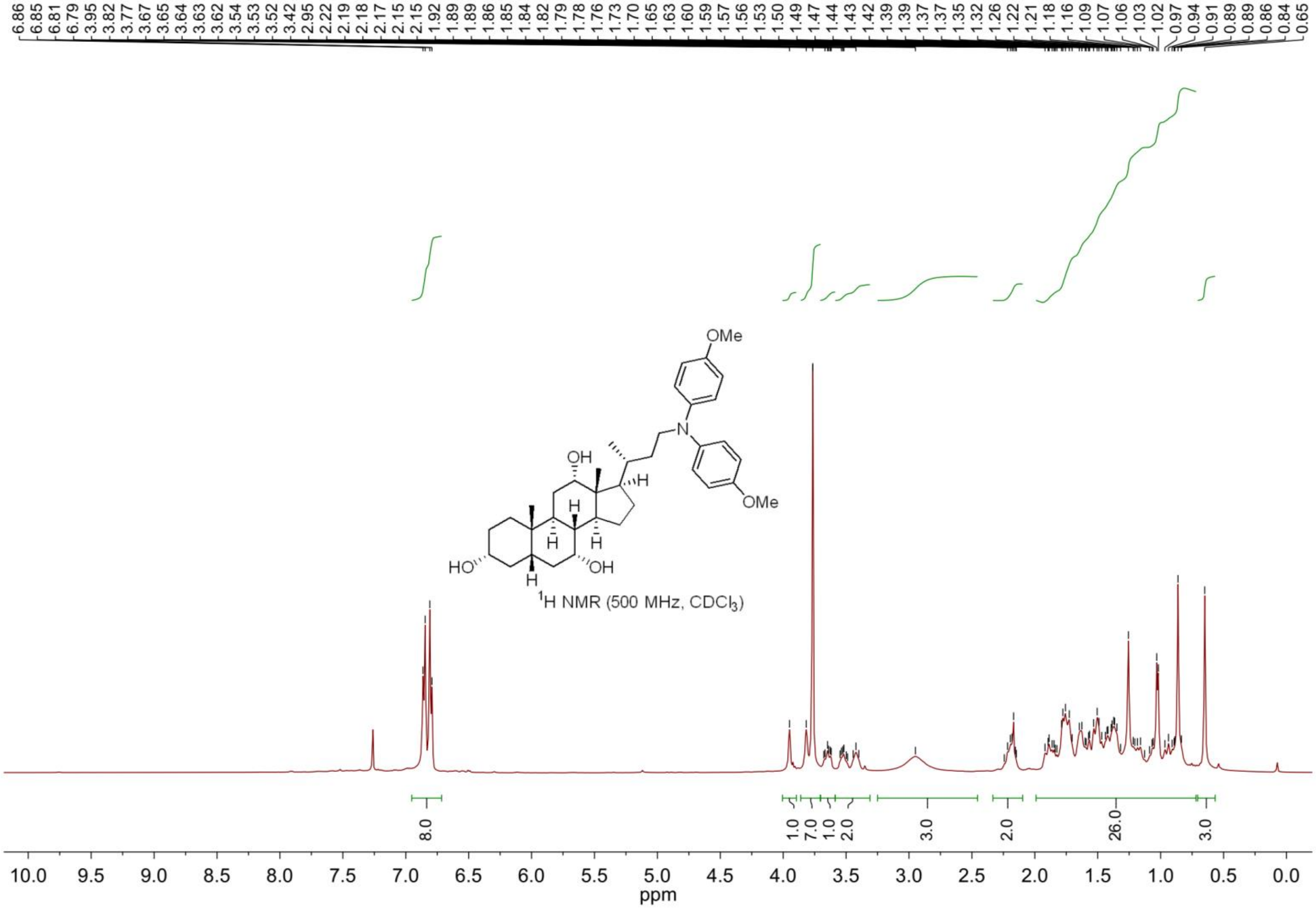
(3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-17-((*R*)-4-(Bis(4-methoxyphenyl)amino)butan-2-yl)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,7,12-triol (82)



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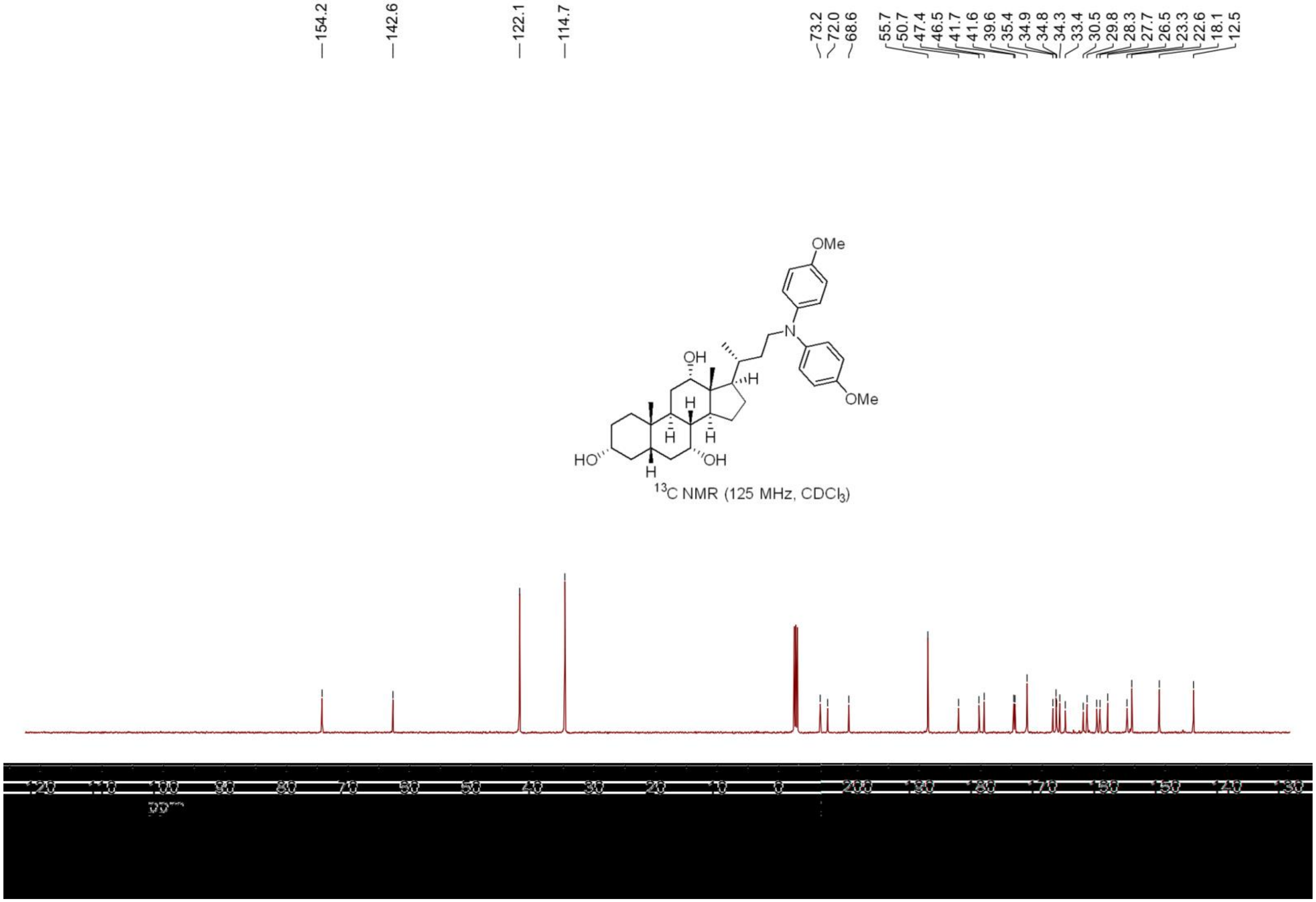
(3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-17-((*R*)-4-(Bis(4-methoxyphenyl)amino)butan-2-yl)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthrene-3,7,12-triol (82)



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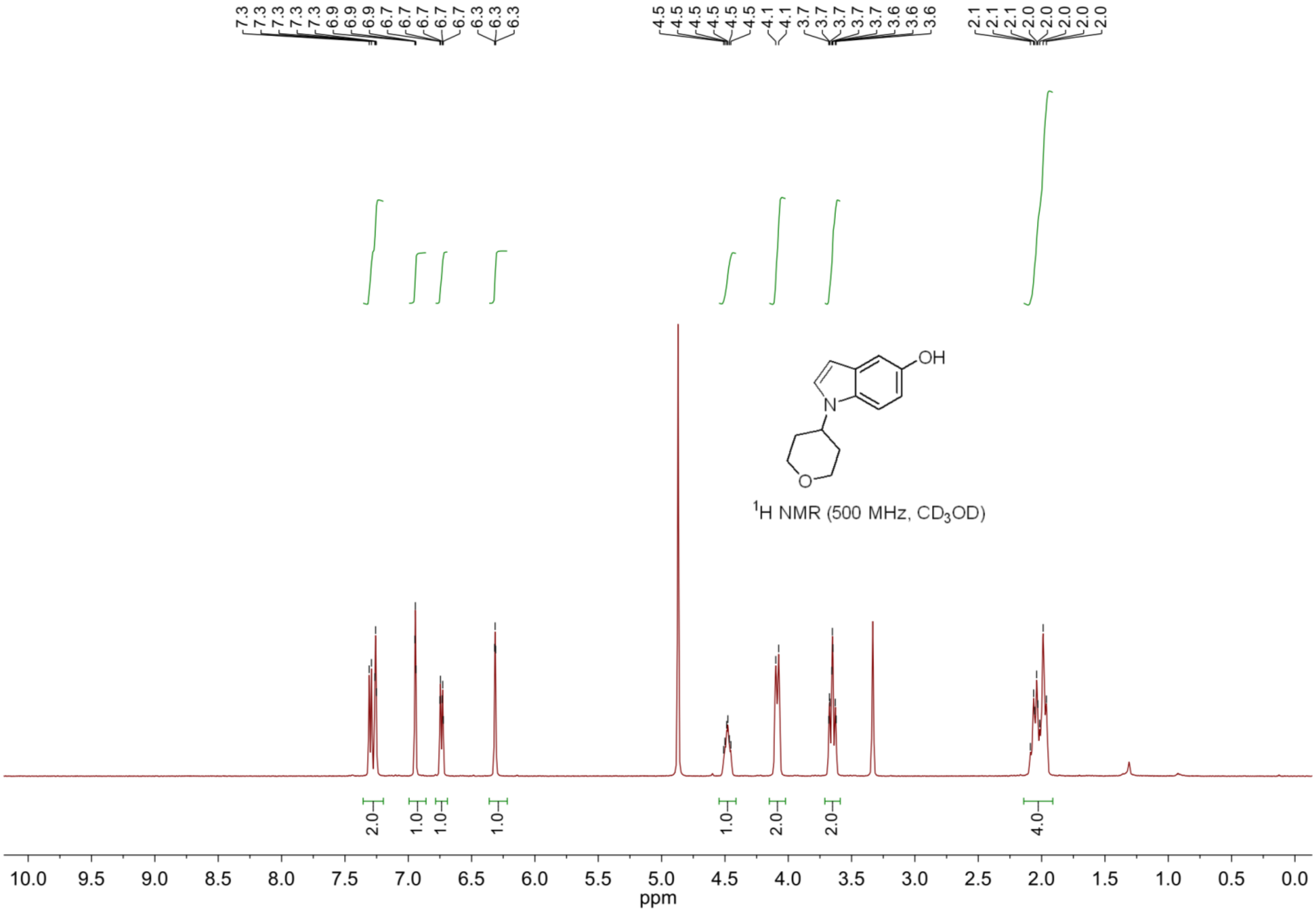
1-(Tetrahydro-2*H*-pyran-4-yl)-1*H*-indol-5-ol (83)



^{1}H NMR (500 MHz, CD$_3$OD)

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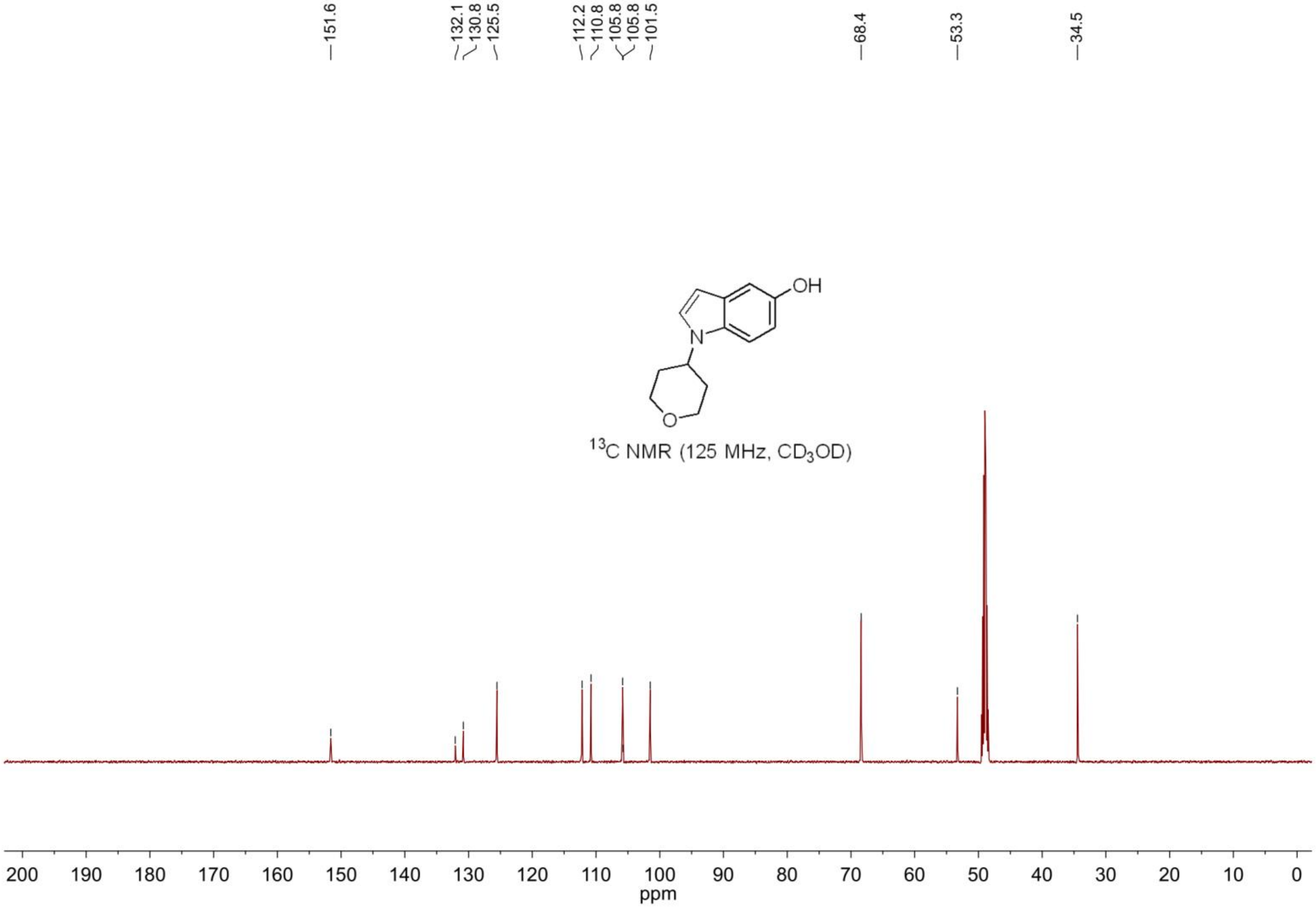
1-(Tetrahydro-2*H*-pyran-4-yl)-1*H*-indol-5-ol (83)



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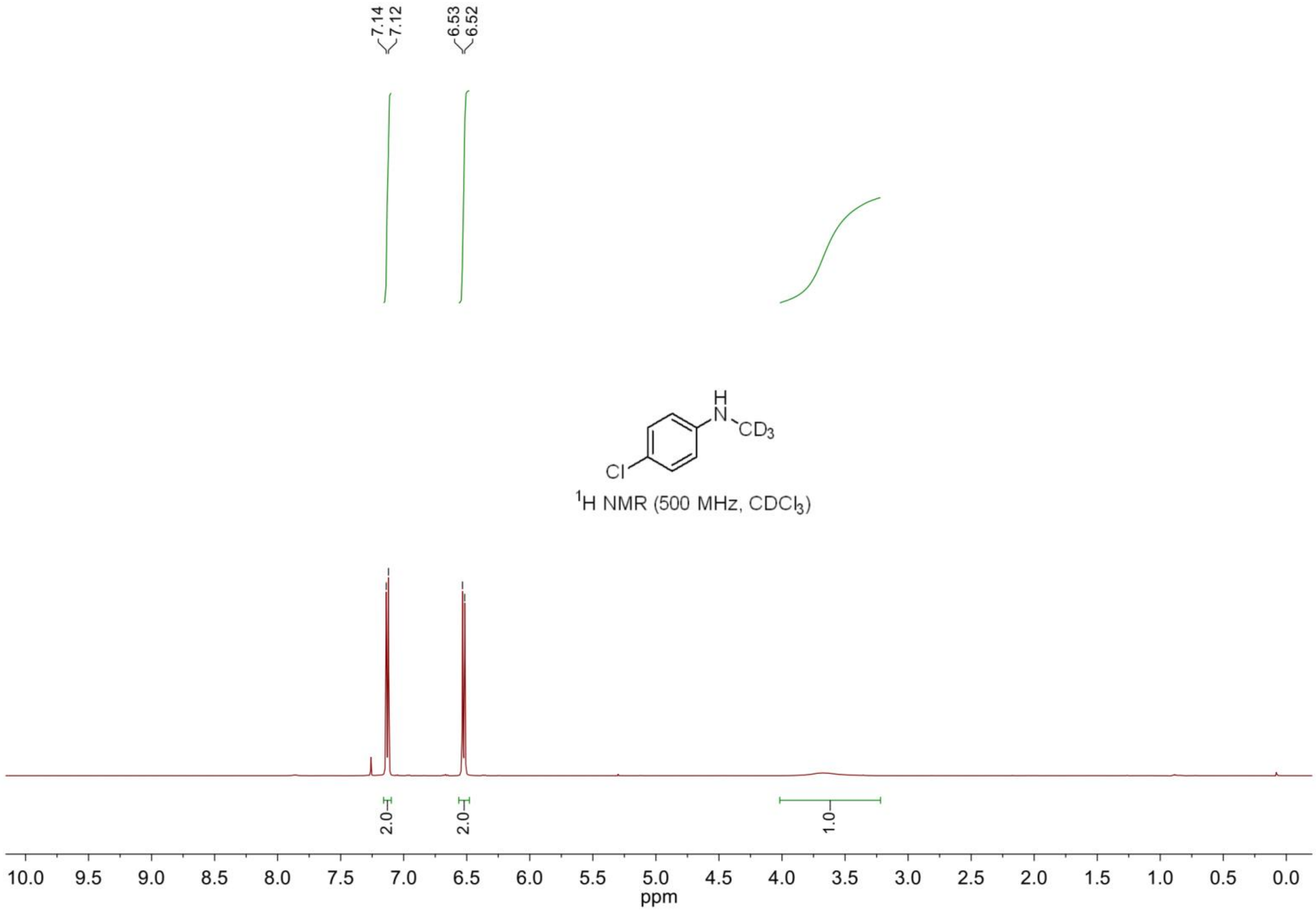
4-Chloro-*N*-(methyl-d_3)aniline (85)



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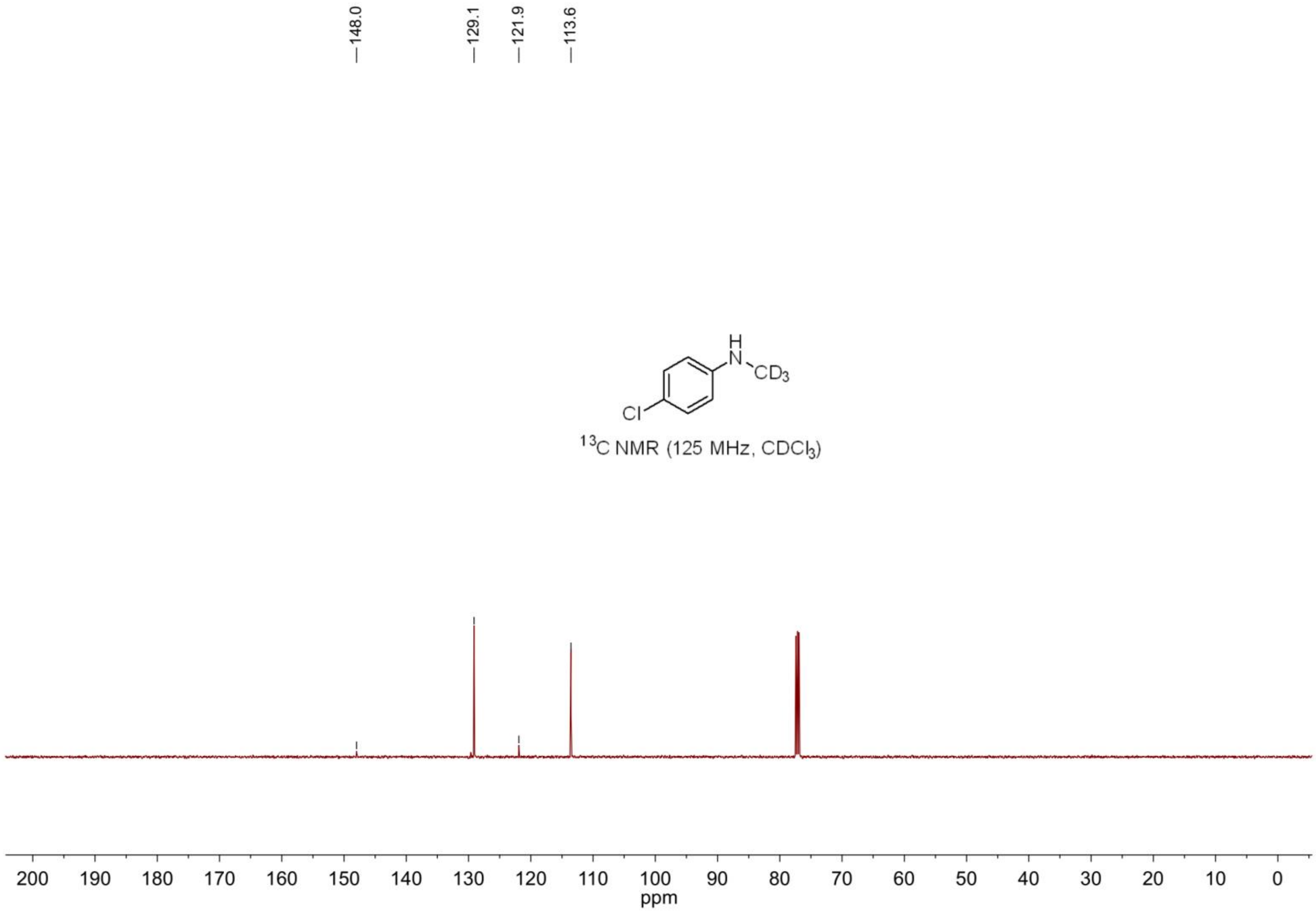
4-Chloro-*N*-(methyl-*d*$_3$)aniline (85)



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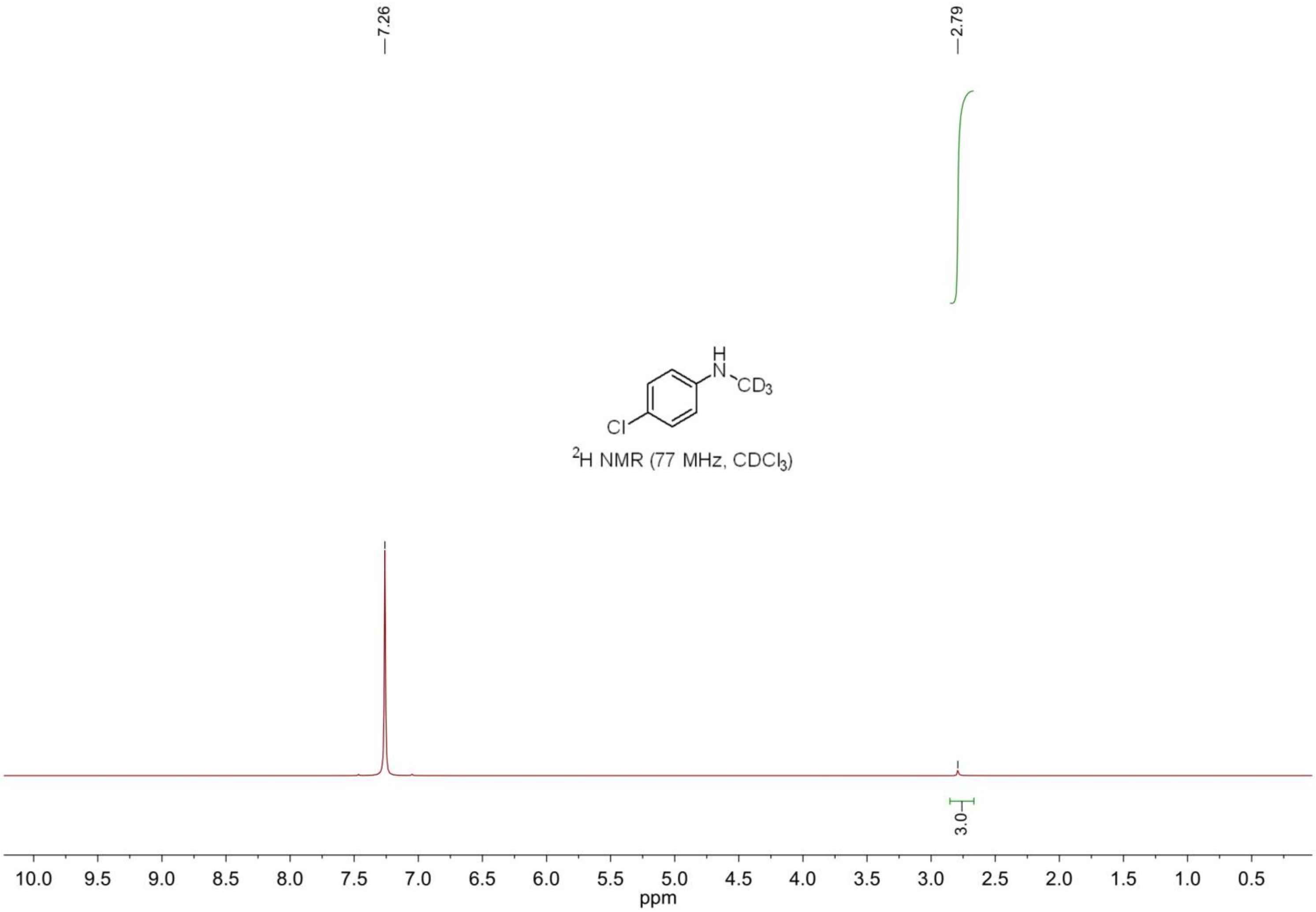
4-Chloro-*N*-(methyl-*d*3)aniline (85)



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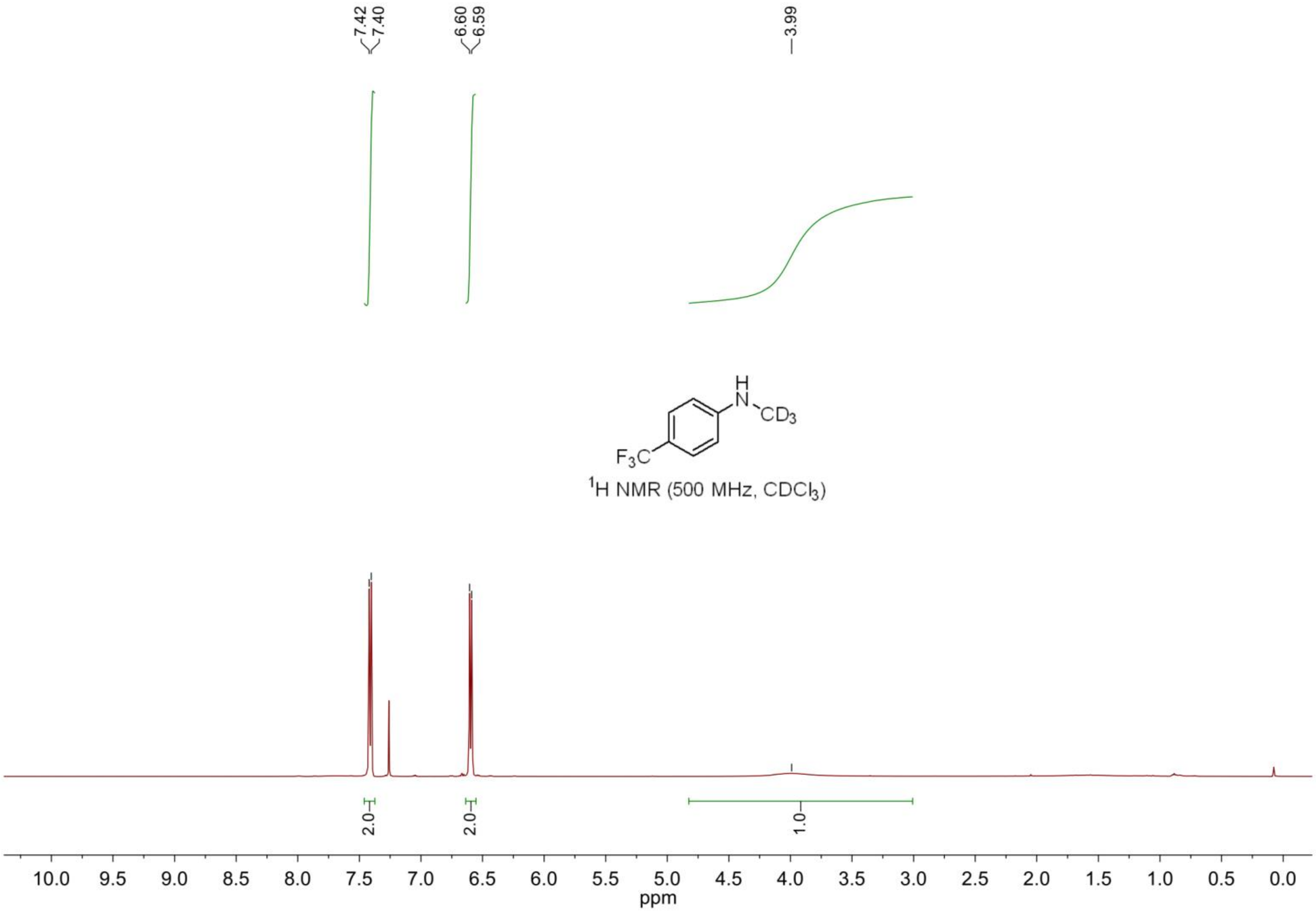
N-(Methyl-*d*₃)-4-(trifluoromethyl)aniline (86)



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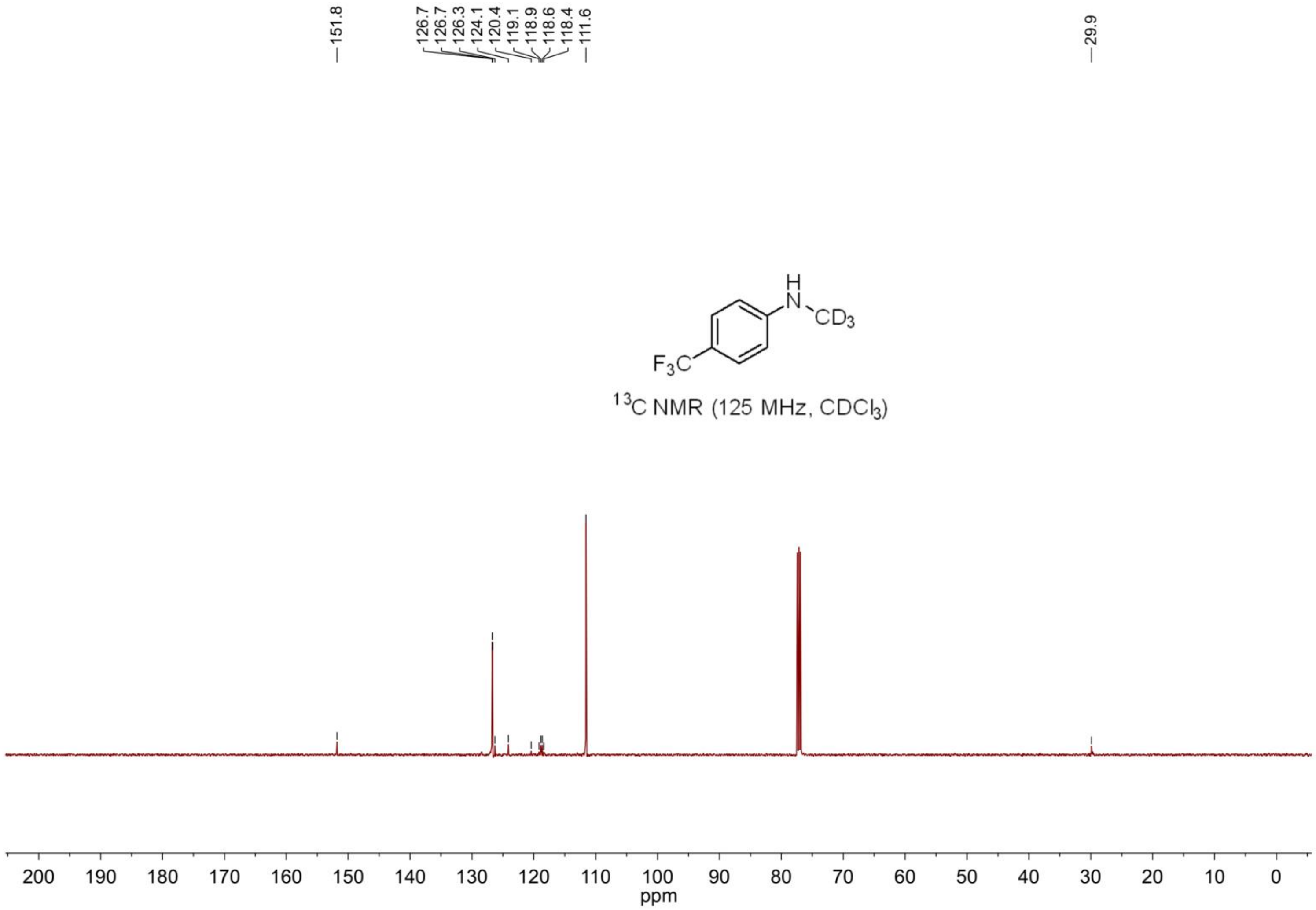
N-(Methyl-*d*₃)-4-(trifluoromethyl)aniline (86)



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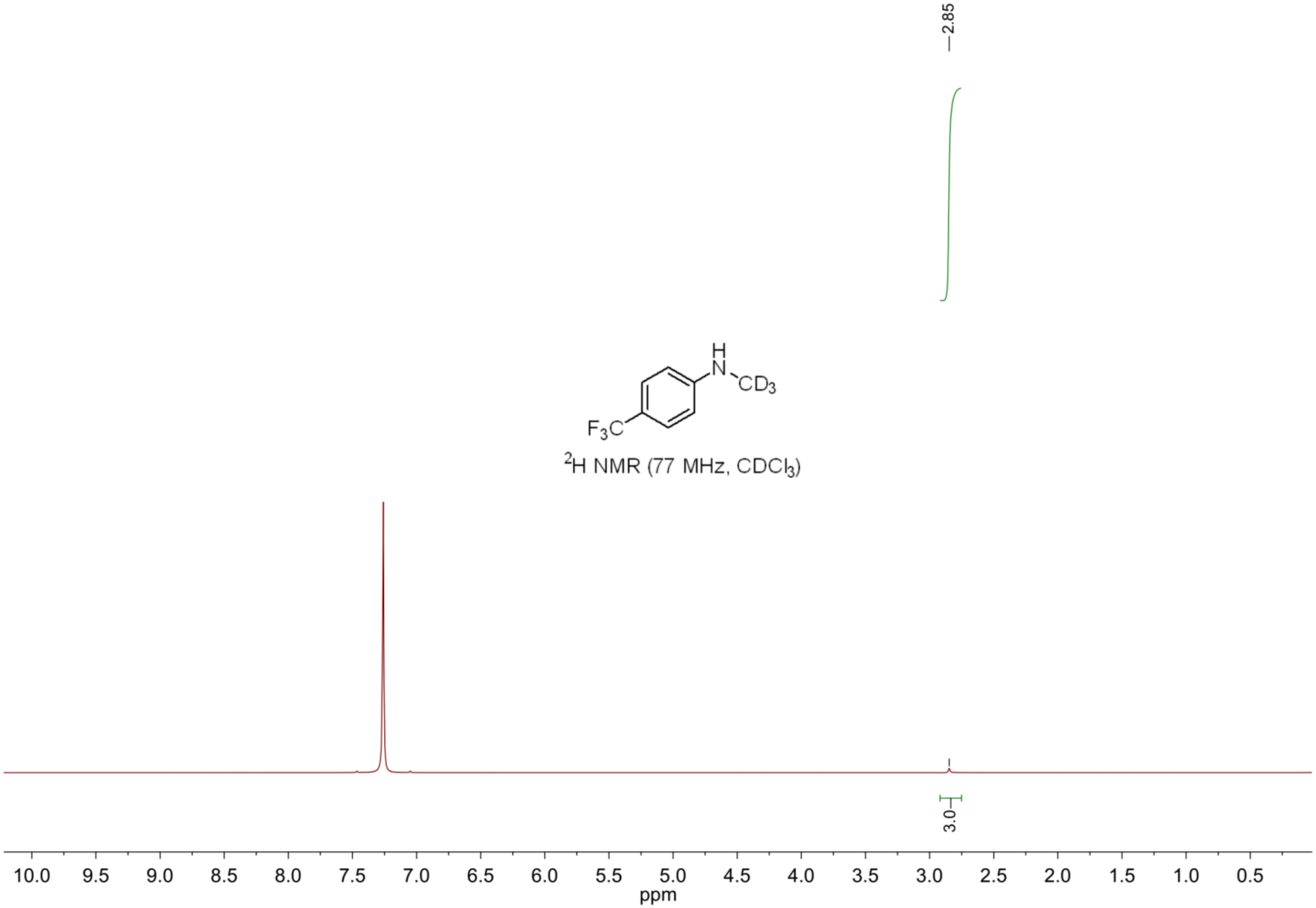
N-(Methyl-d_3)-4-(trifluoromethyl)aniline (86)



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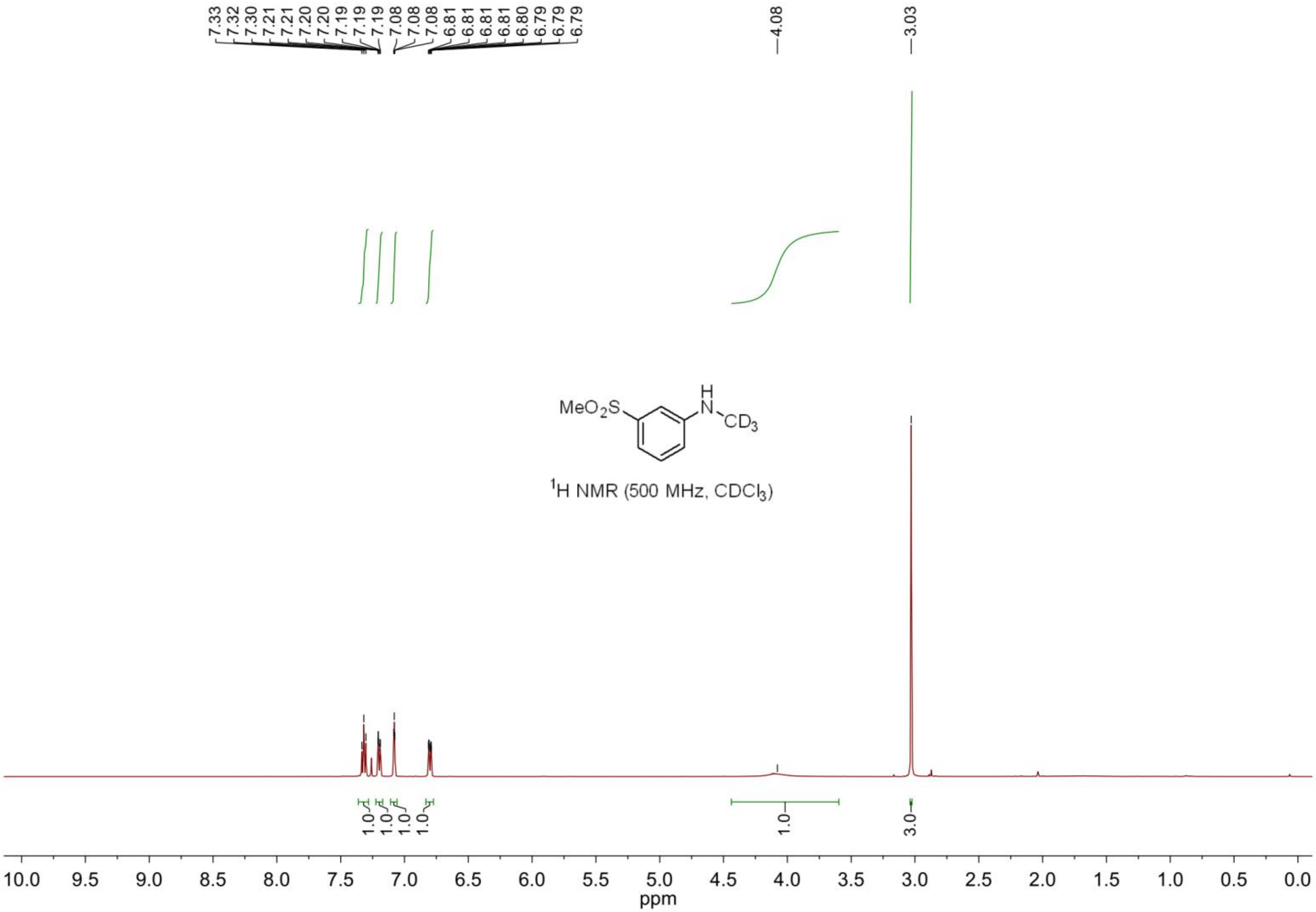
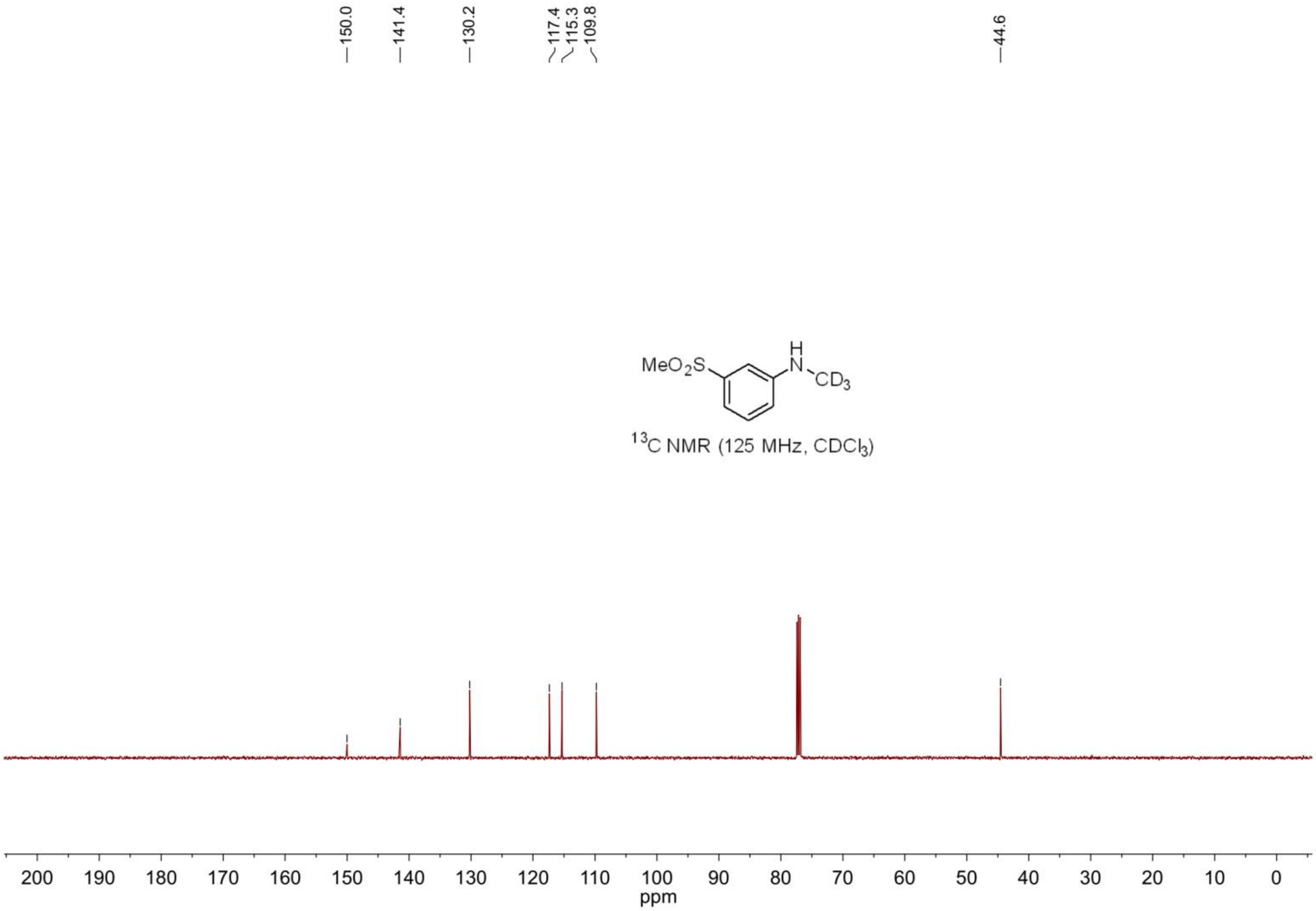
N-(Methyl-*d*$_3$)-3-(methylsulfonyl)aniline (87)



N-(Methyl-*d*$_3$)-3-(methylsulfonyl)aniline (87)



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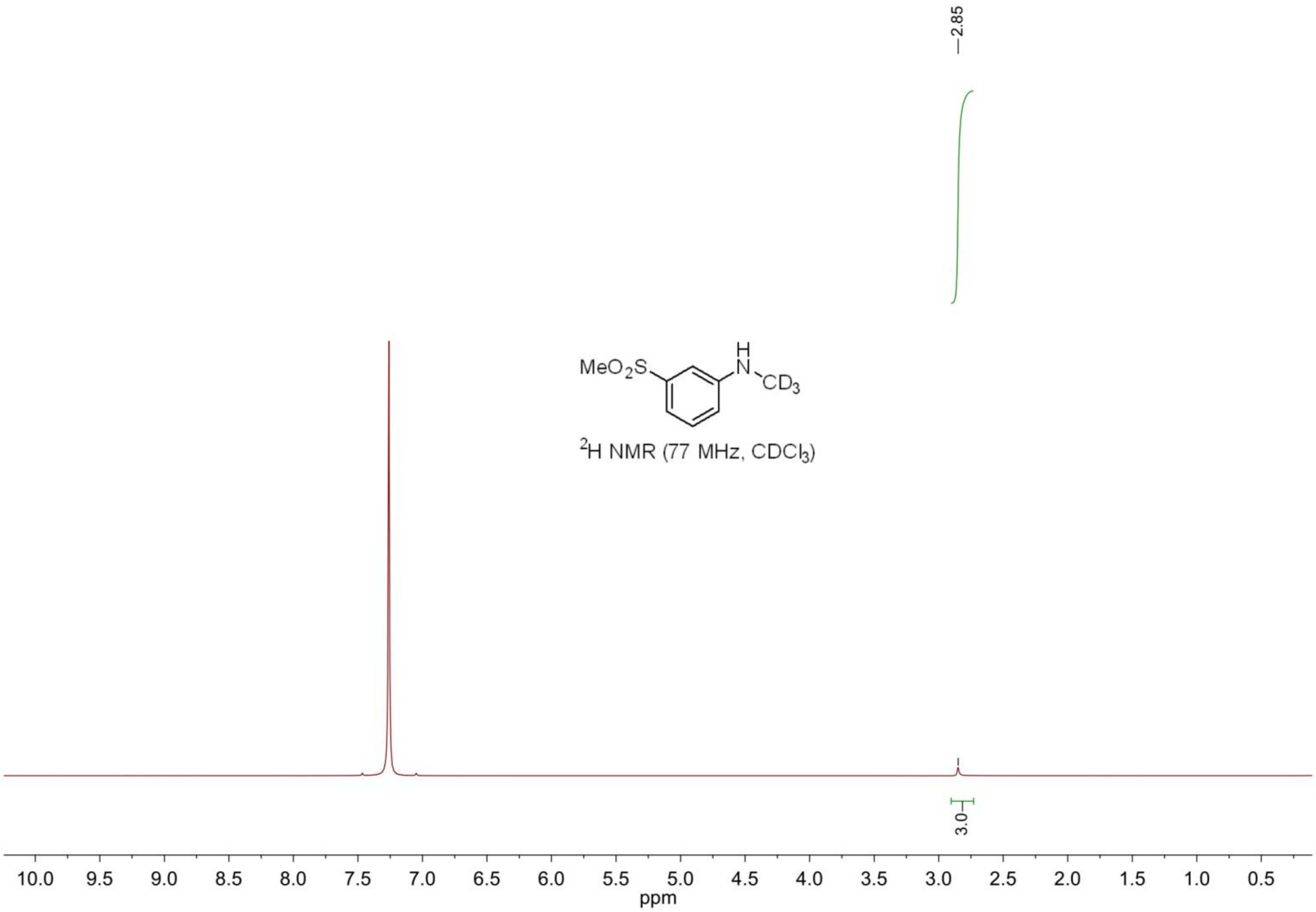
N-(Methyl-*d*3)-3-(methylsulfonyl)aniline (87)



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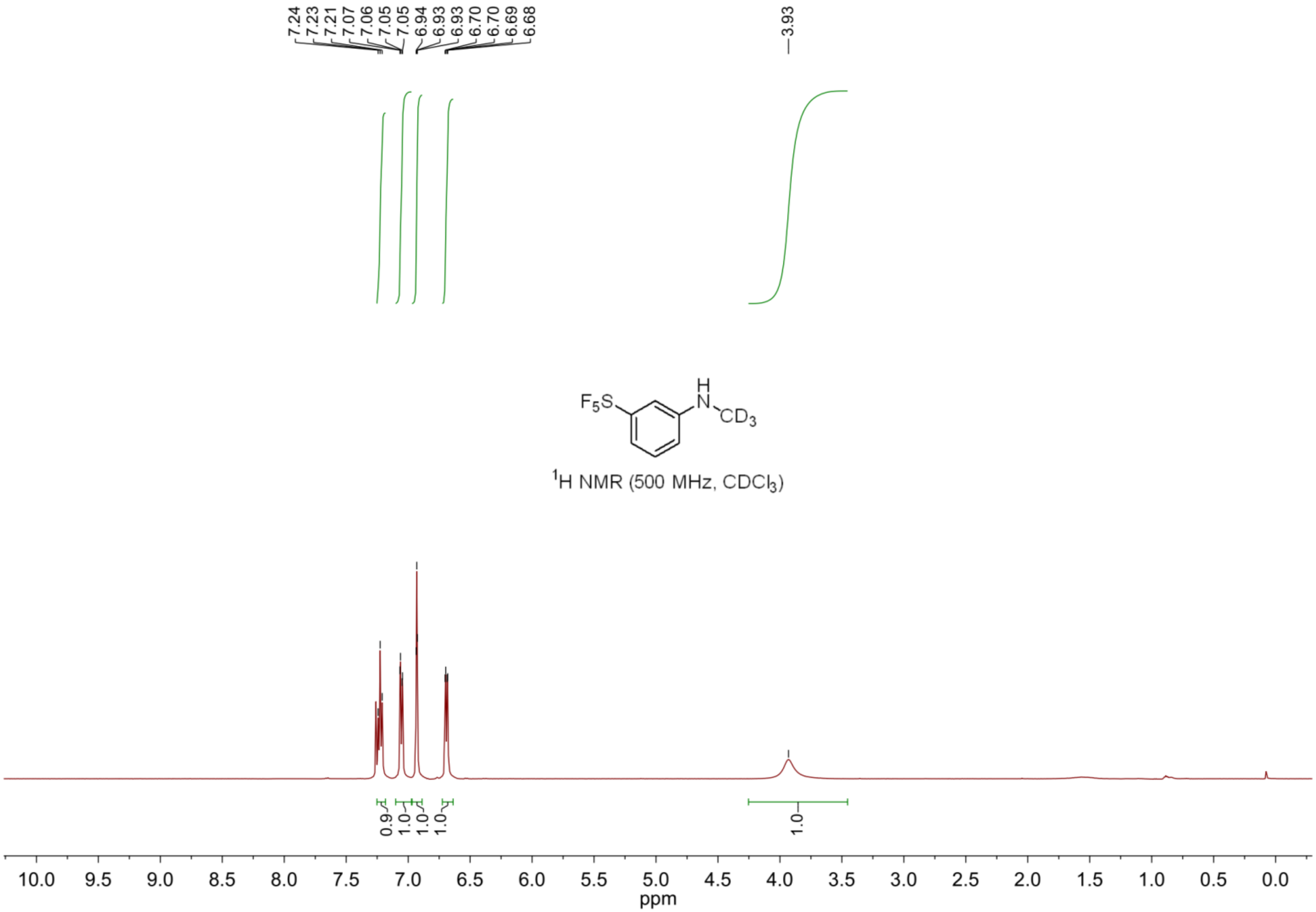
N-(Methyl-*d*₃)-3-(pentafluoro-λ⁶-sulfaneyl)aniline (88)



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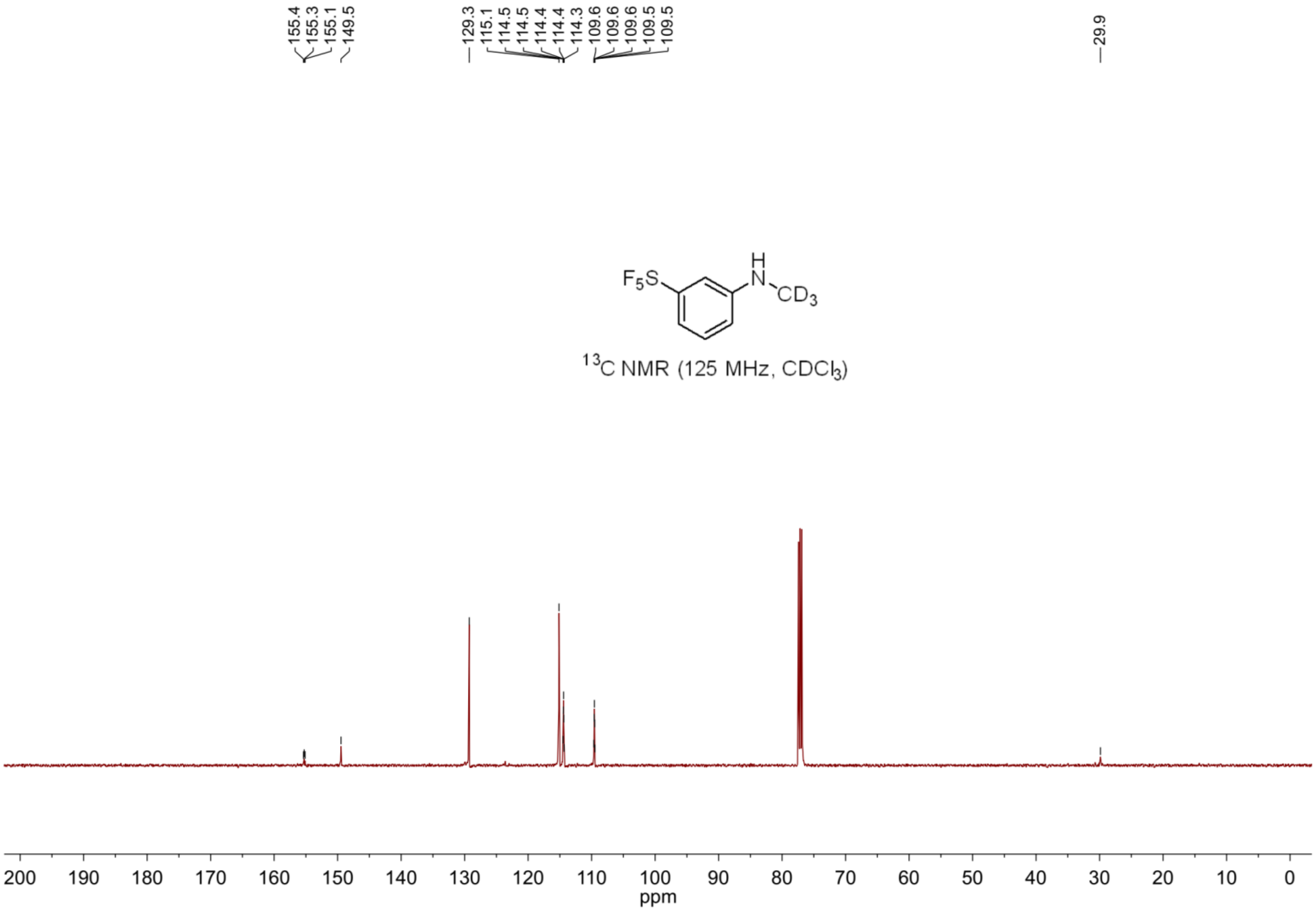
N-(Methyl-*d*$_3$)-3-(pentafluoro-λ^6-sulfaneyl)aniline (88)



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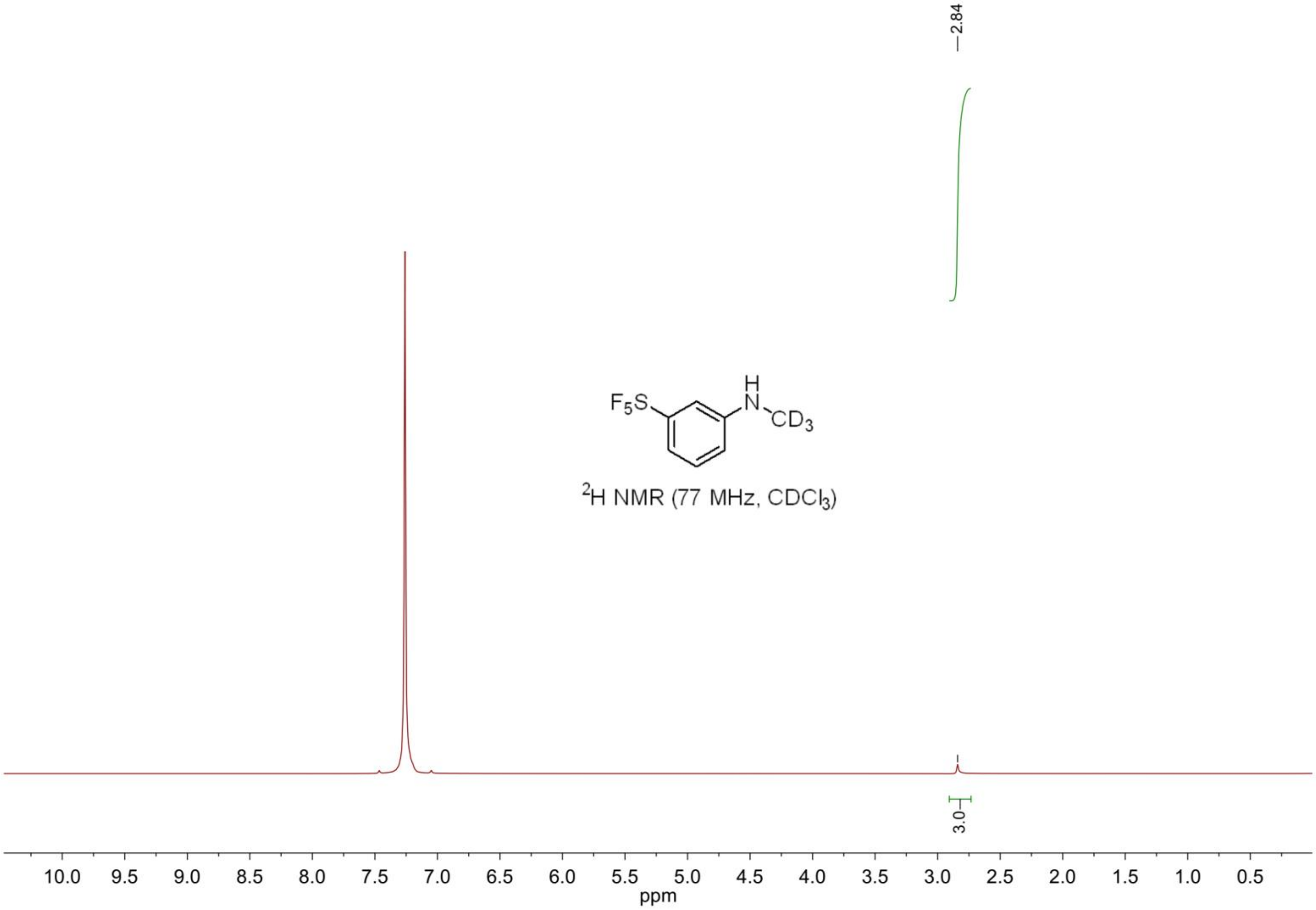
N-(Methyl-*d*3)-3-(pentafluoro-λ6-sulfaneyl)aniline (88)



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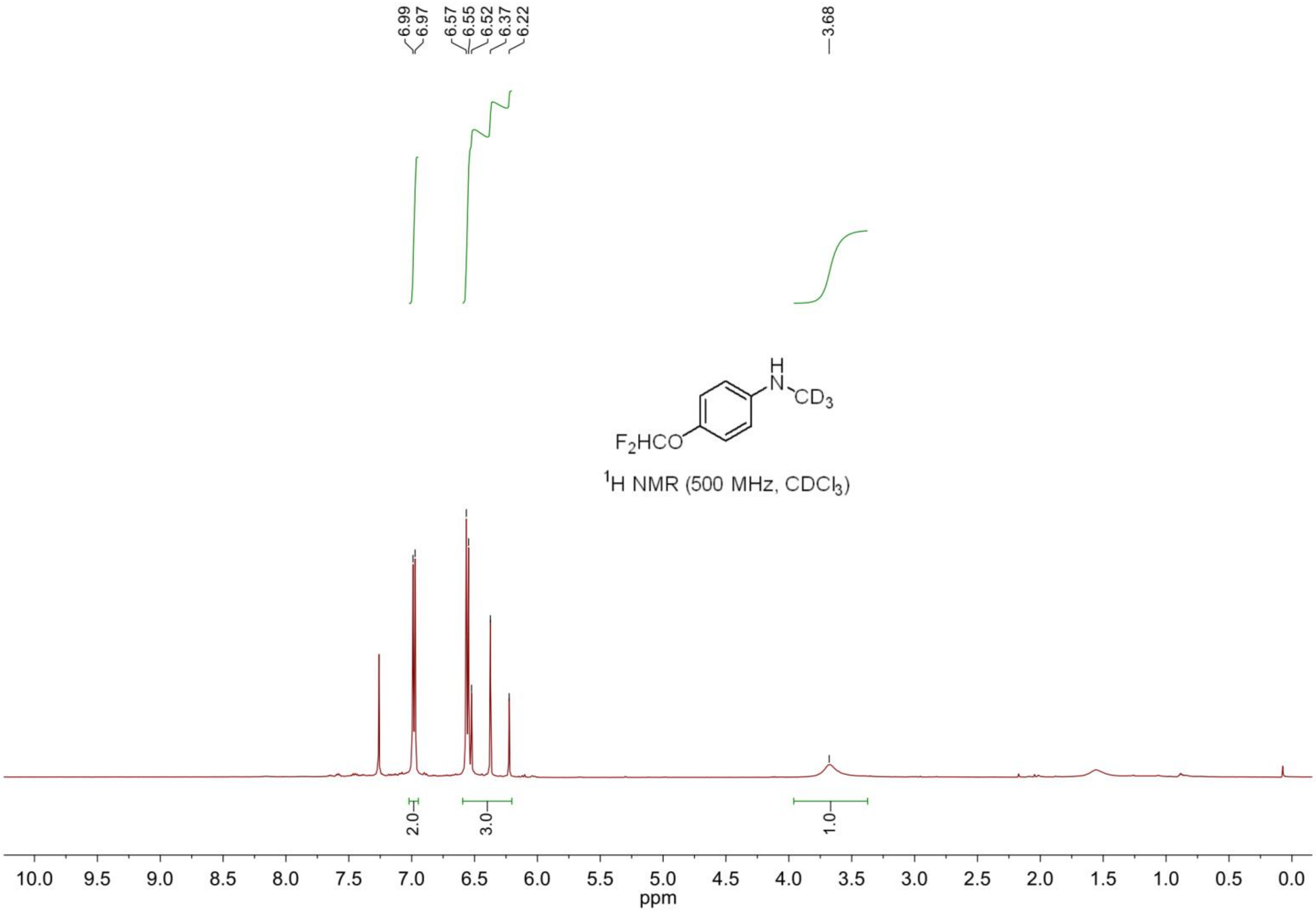
4-(Difluoromethoxy)-*N*-(methyl-*d*3)aniline (89)



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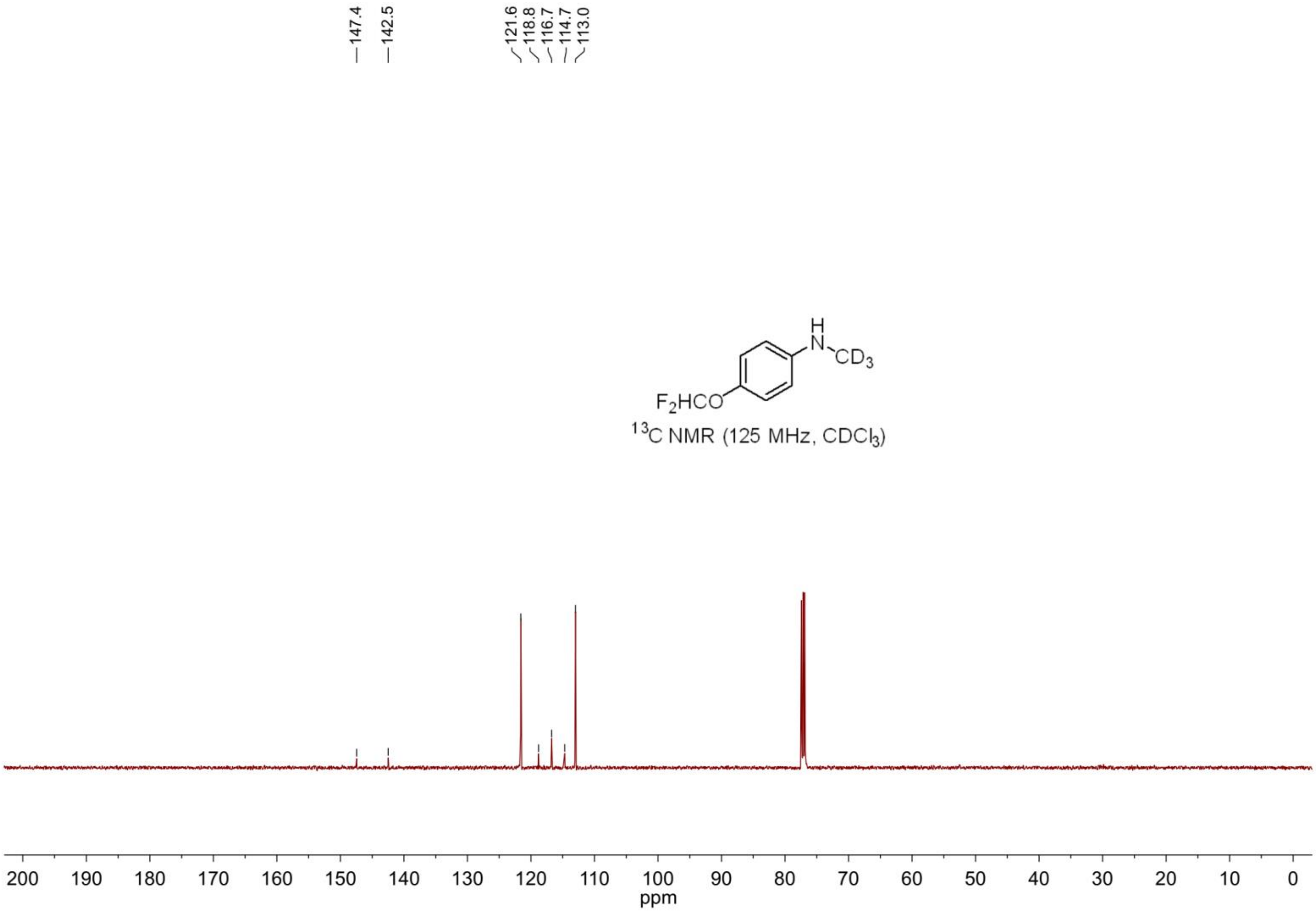
4-(Difluoromethoxy)-*N*-(methyl-*d*₃)aniline (89)



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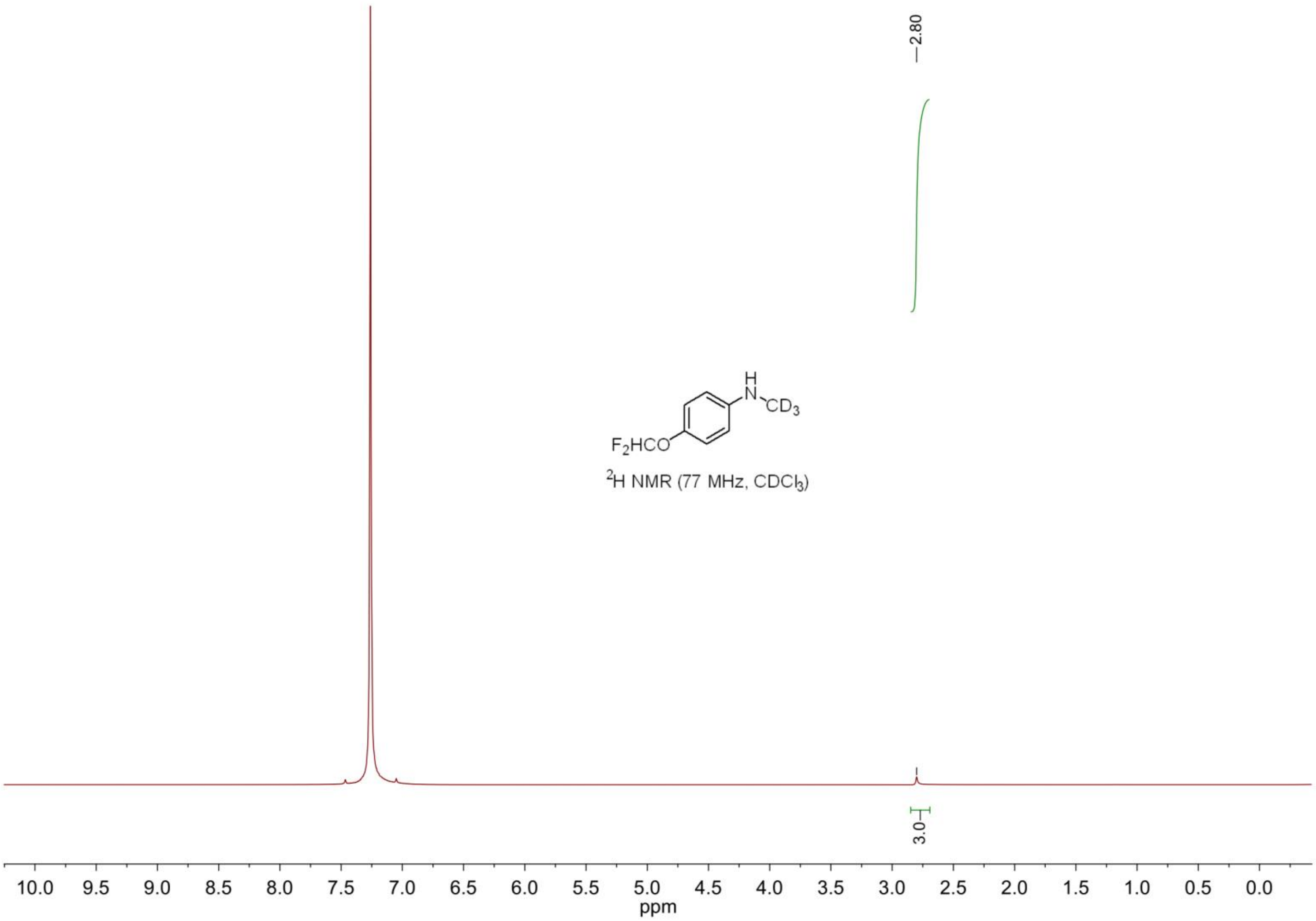
4-(Difluoromethoxy)-*N*-(methyl-*d*3)aniline (89)



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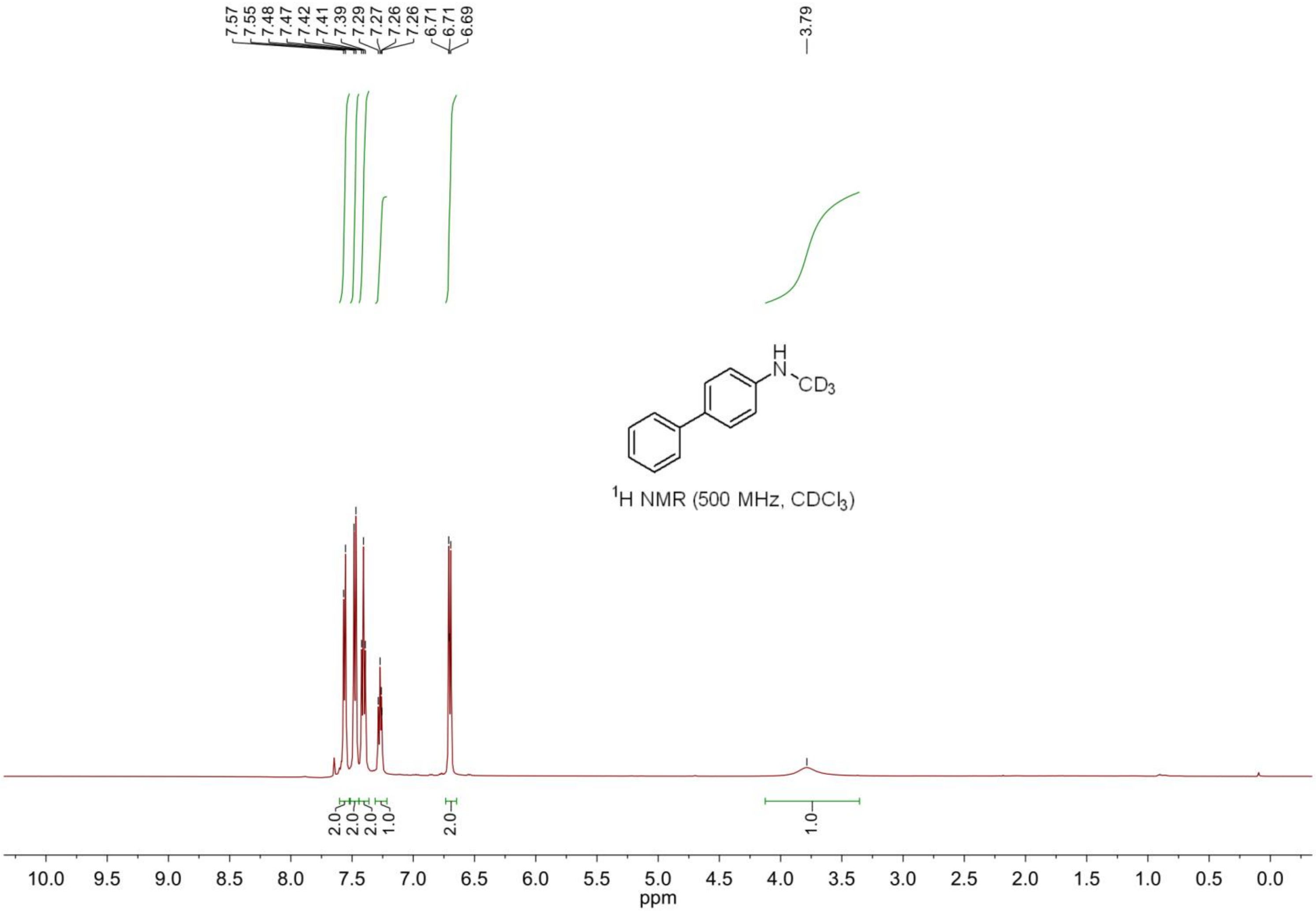
N-(Methyl-*d*3)-[1,1'-biphenyl]-4-amine (90)



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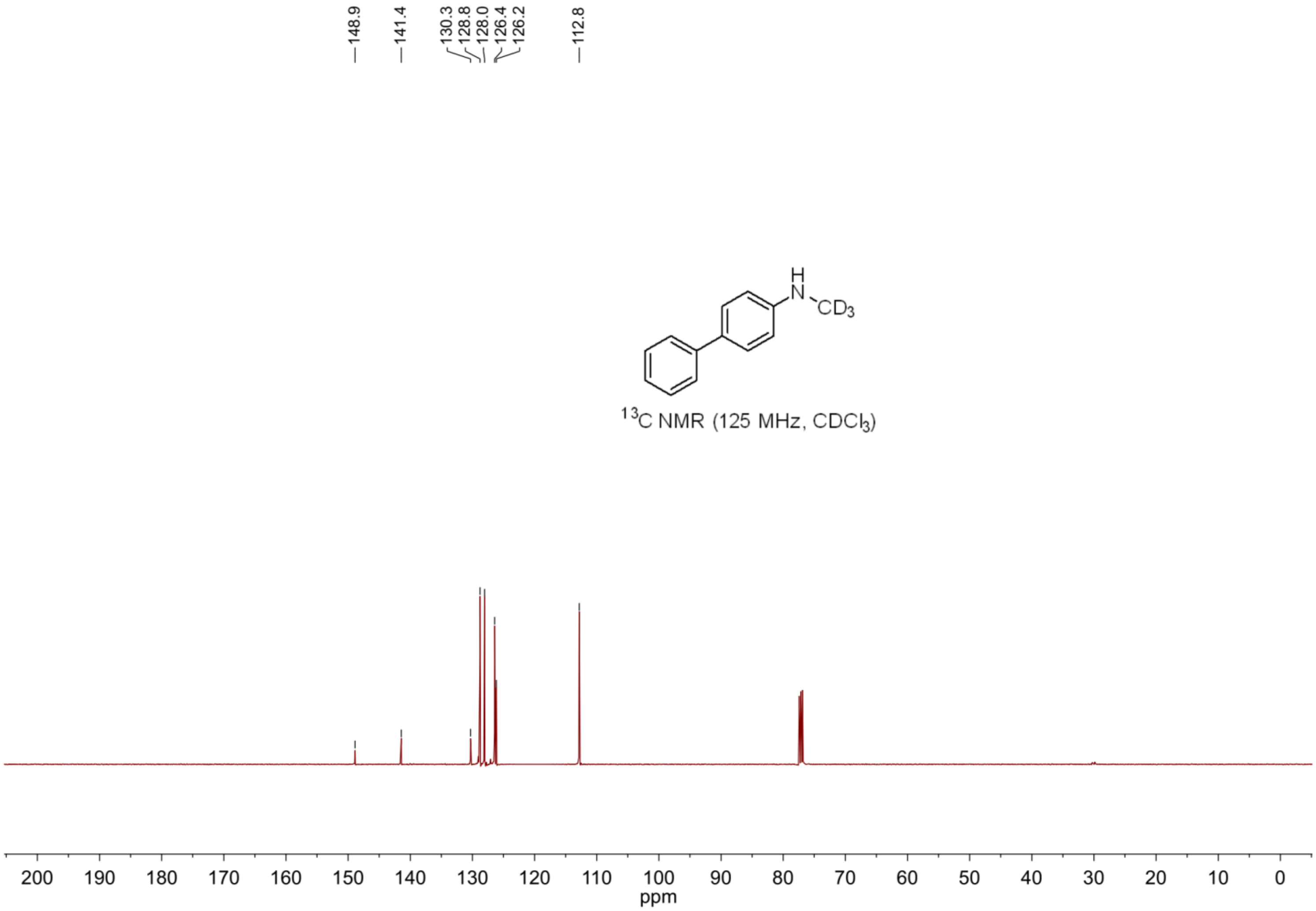
N-(Methyl-*d*3)-[1,1'-biphenyl]-4-amine (90)



^{13}C NMR (125 MHz, $CDCl_3$)

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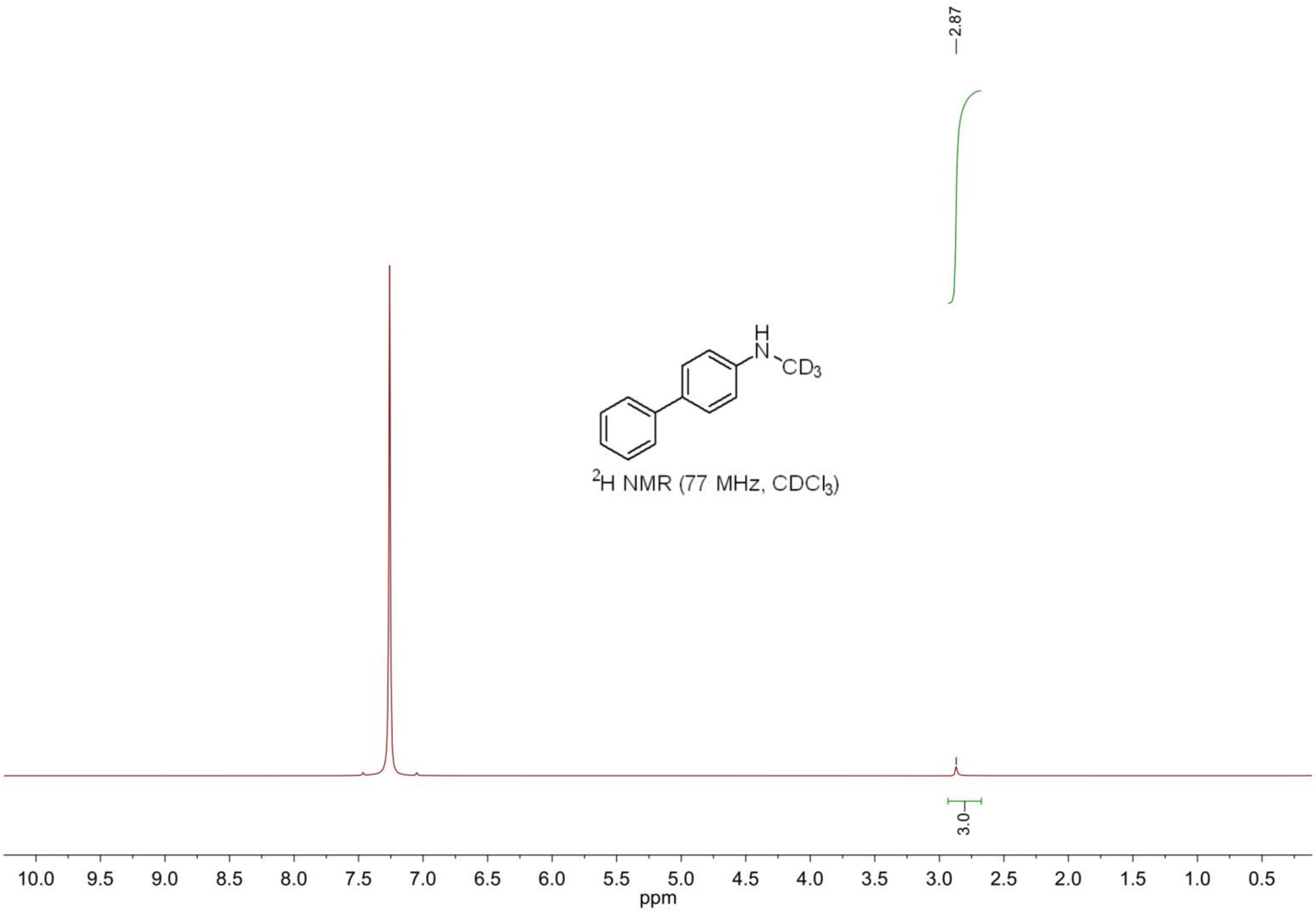
N-(Methyl-d_3)-[1,1'-biphenyl]-4-amine (90)



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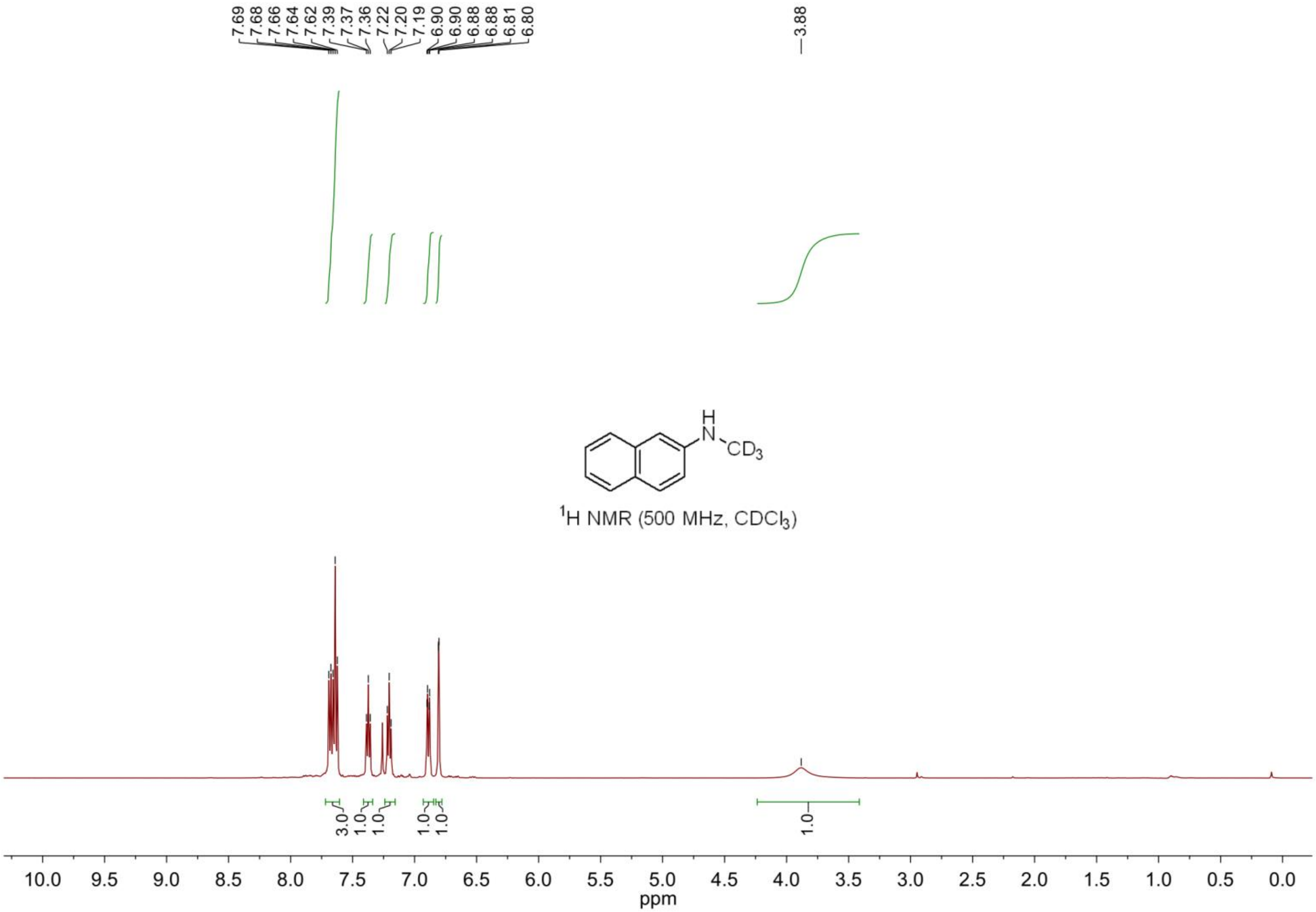
N-(Methyl-d_3)naphthalen-2-amine (91)



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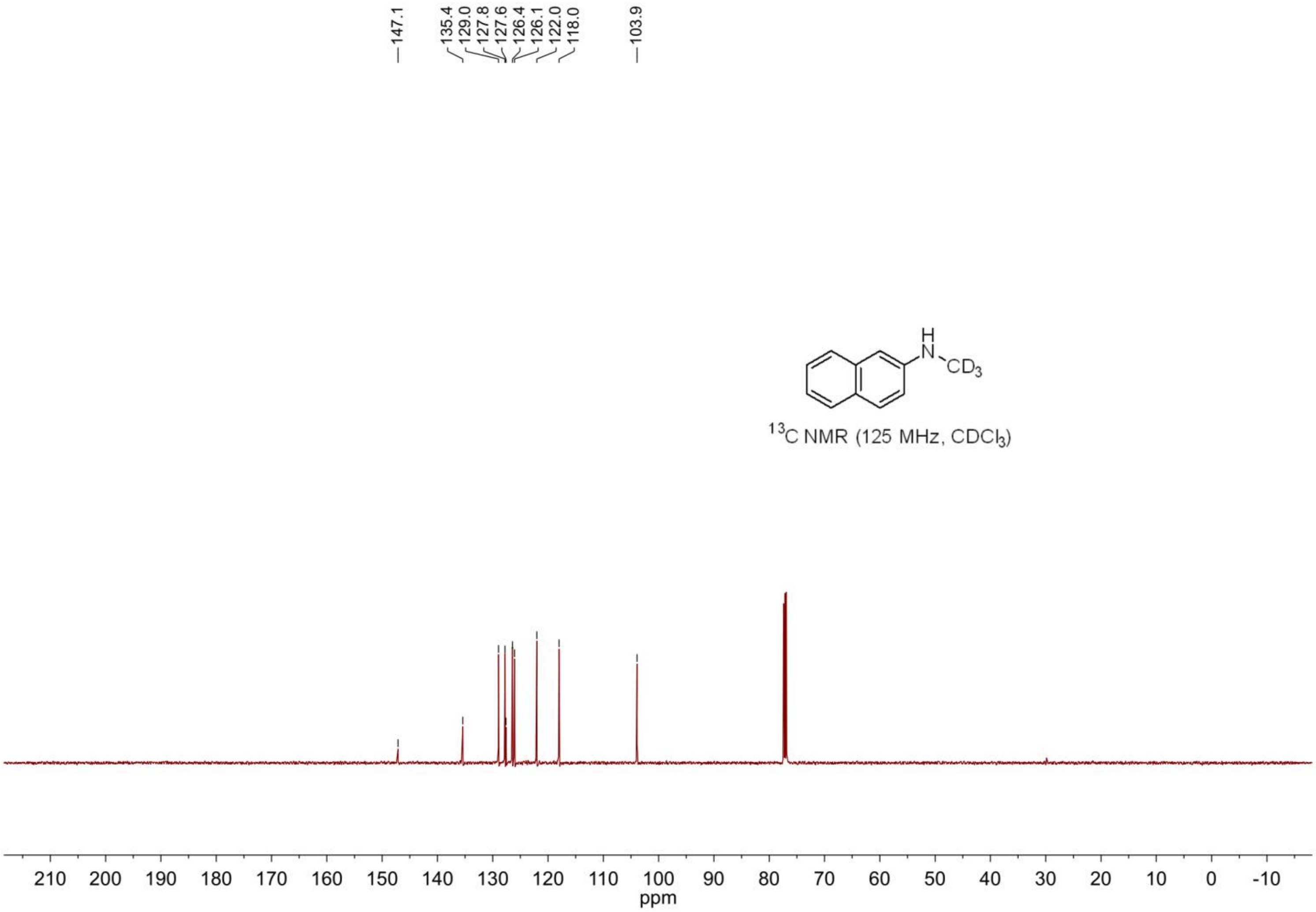
N-(Methyl-*d*₃)naphthalen-2-amine (91)



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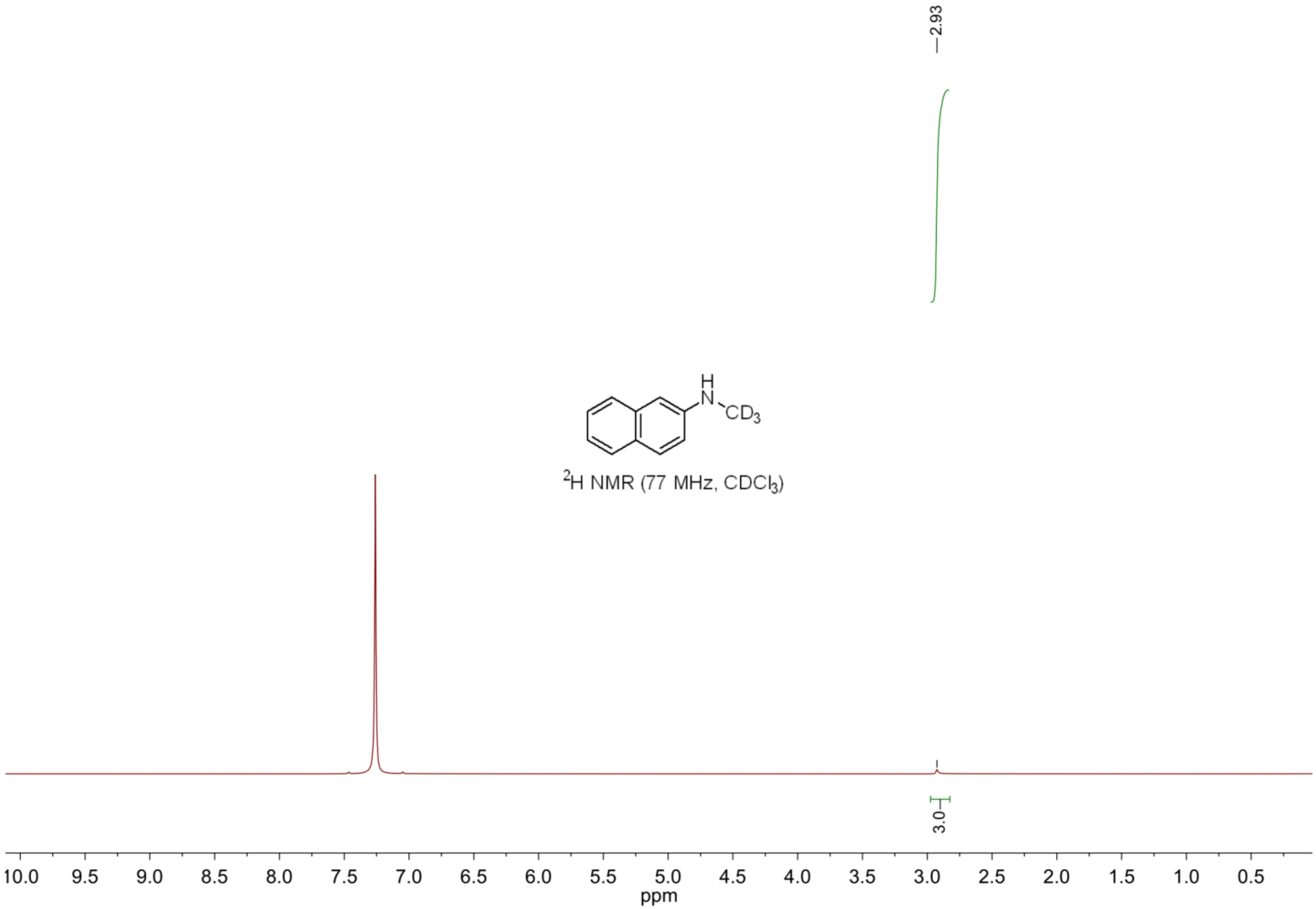
N-(Methyl-d_3)naphthalen-2-amine (91)



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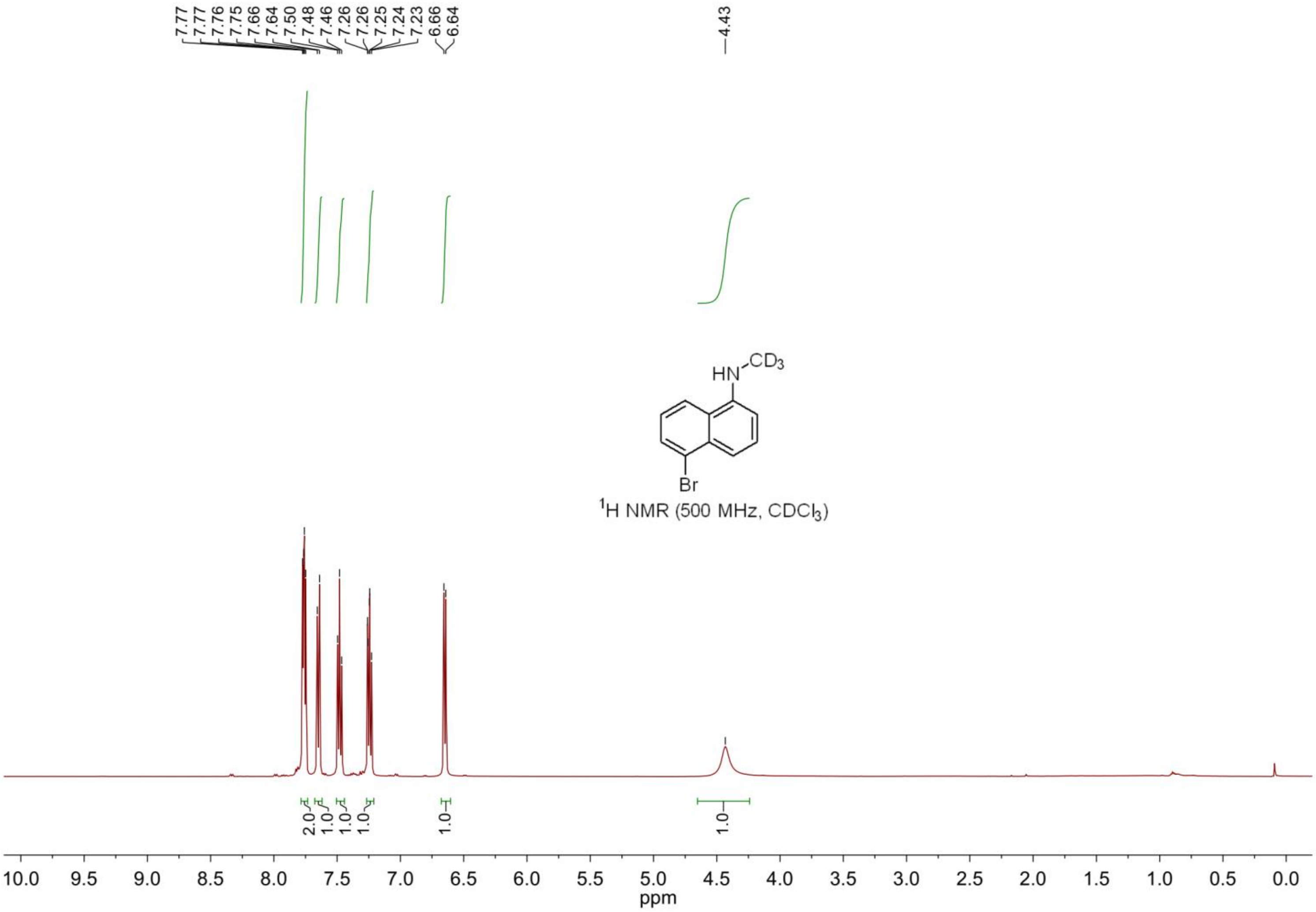
5-Bromo-*N*-(methyl-*d*$_3$)naphthalen-1-amine (92)



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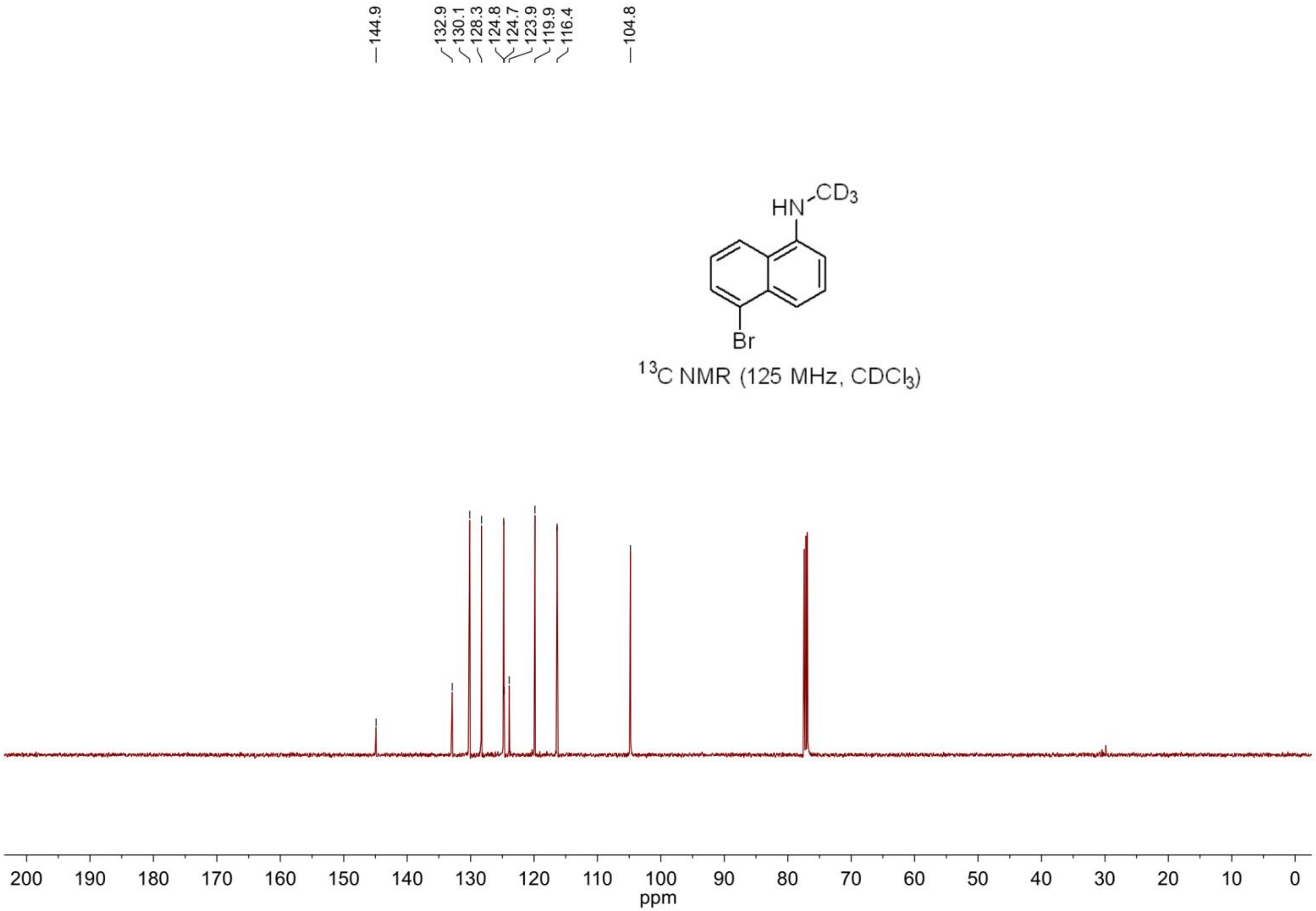
5-Bromo-*N*-(methyl-d_3)naphthalen-1-amine (92)



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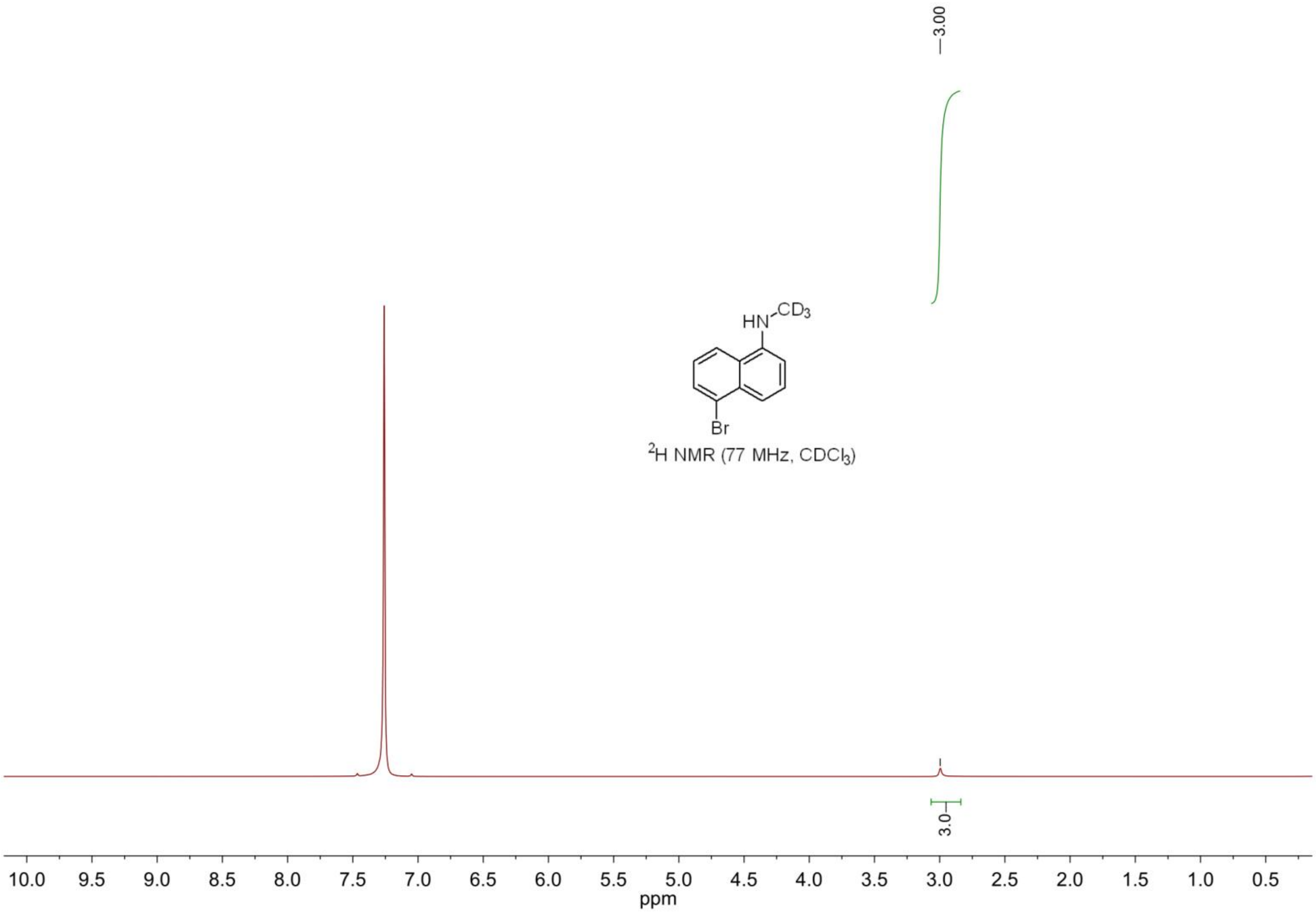
5-Bromo-*N*-(methyl-d_3)naphthalen-1-amine (92)



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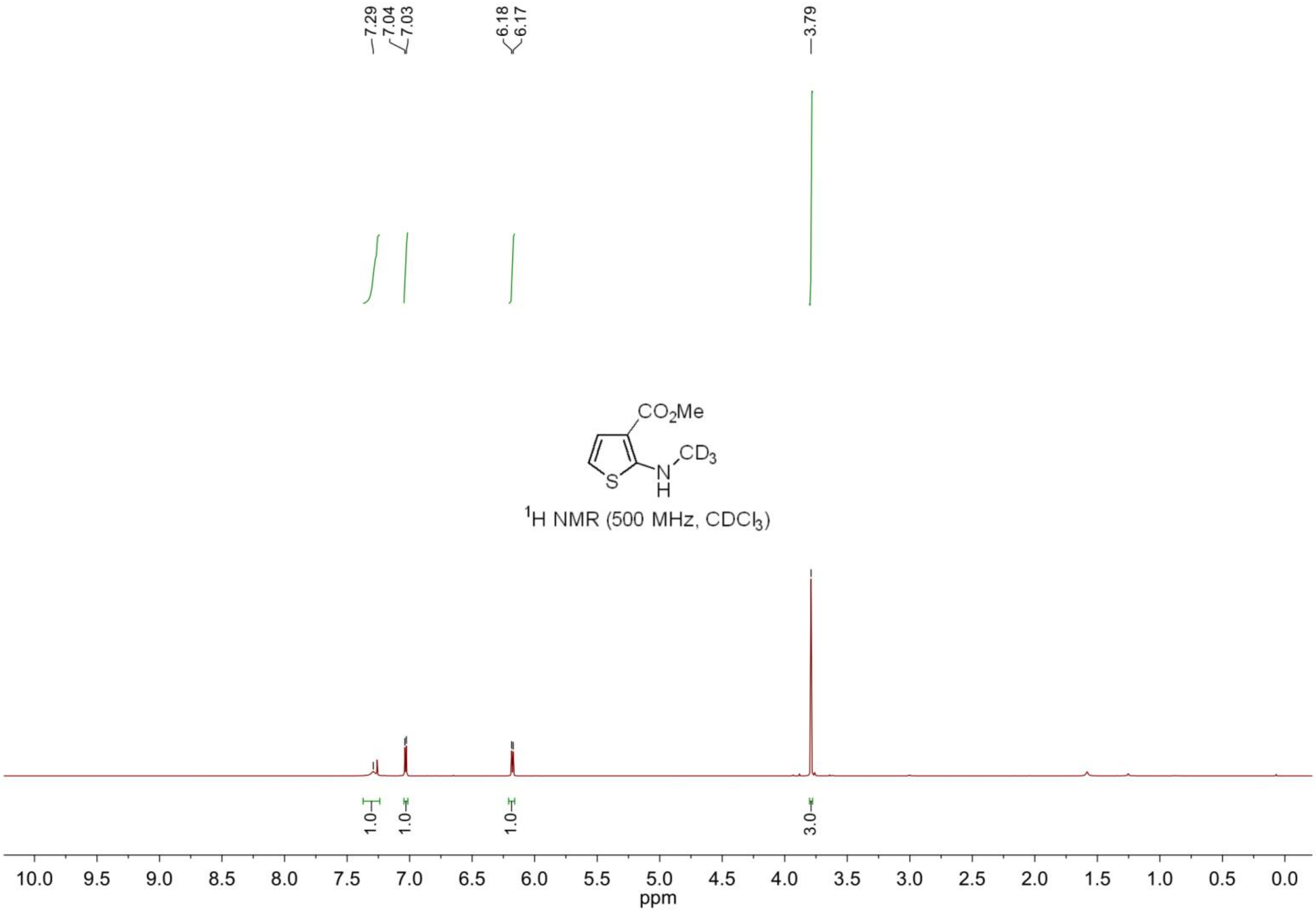
Methyl 2-((methyl-*d*$_3$)amino)thiophene-3-carboxylate (93)



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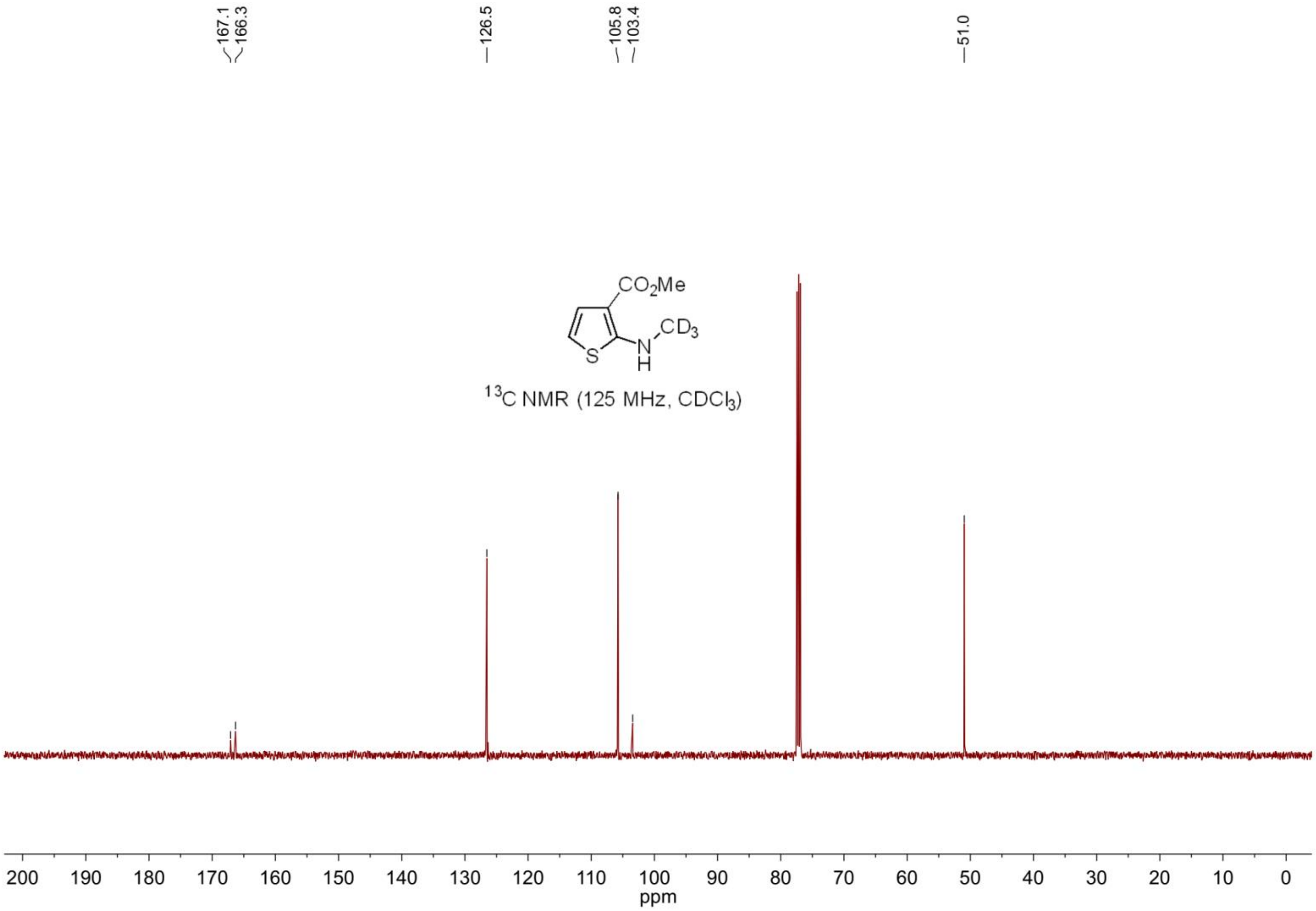
Methyl 2-((methyl-d_3)amino)thiophene-3-carboxylate (93)



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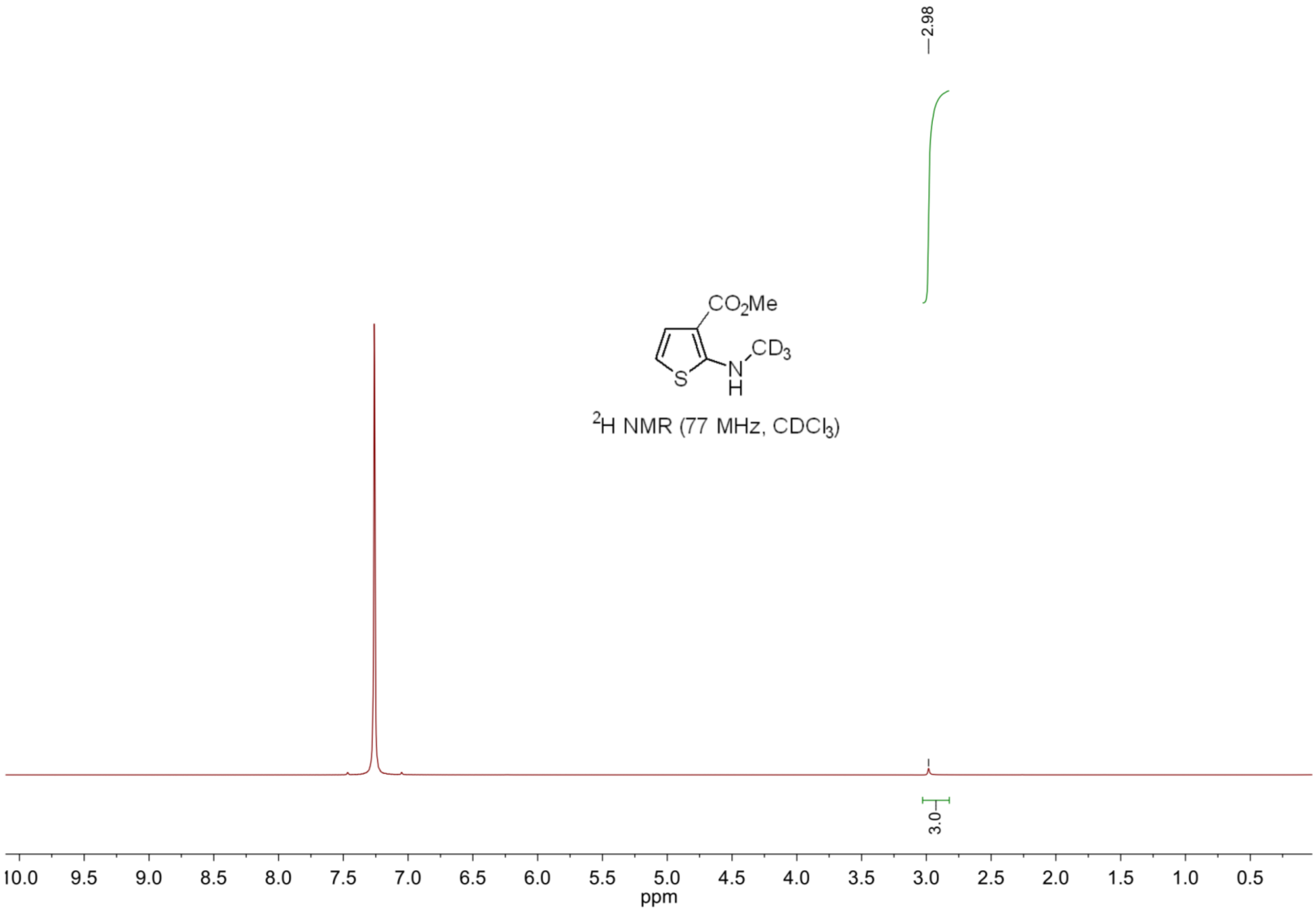
Methyl 2-((methyl-*d*$_3$)amino)thiophene-3-carboxylate (93)



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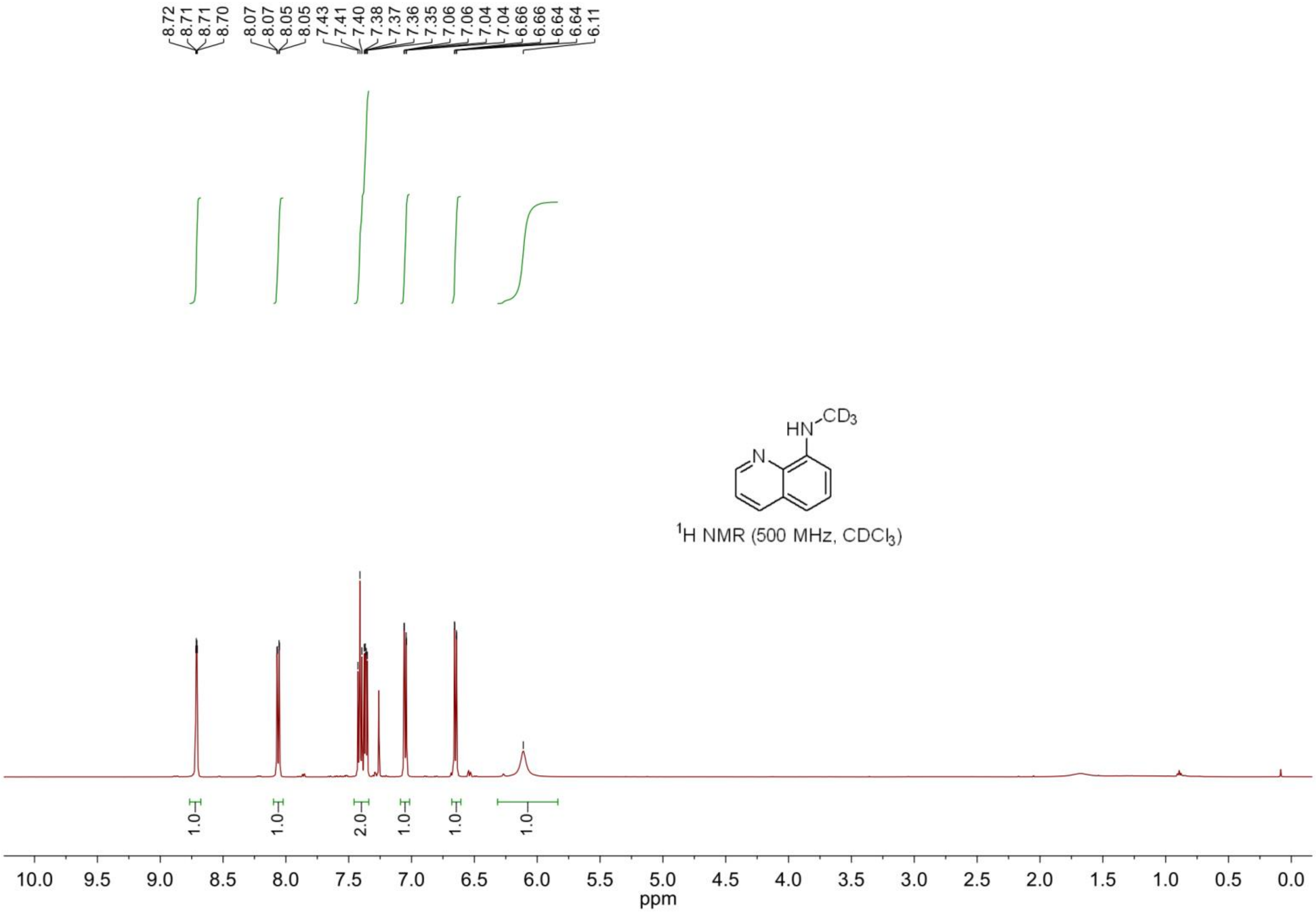
N-(Methyl-*d*₃)quinolin-8-amine (94)



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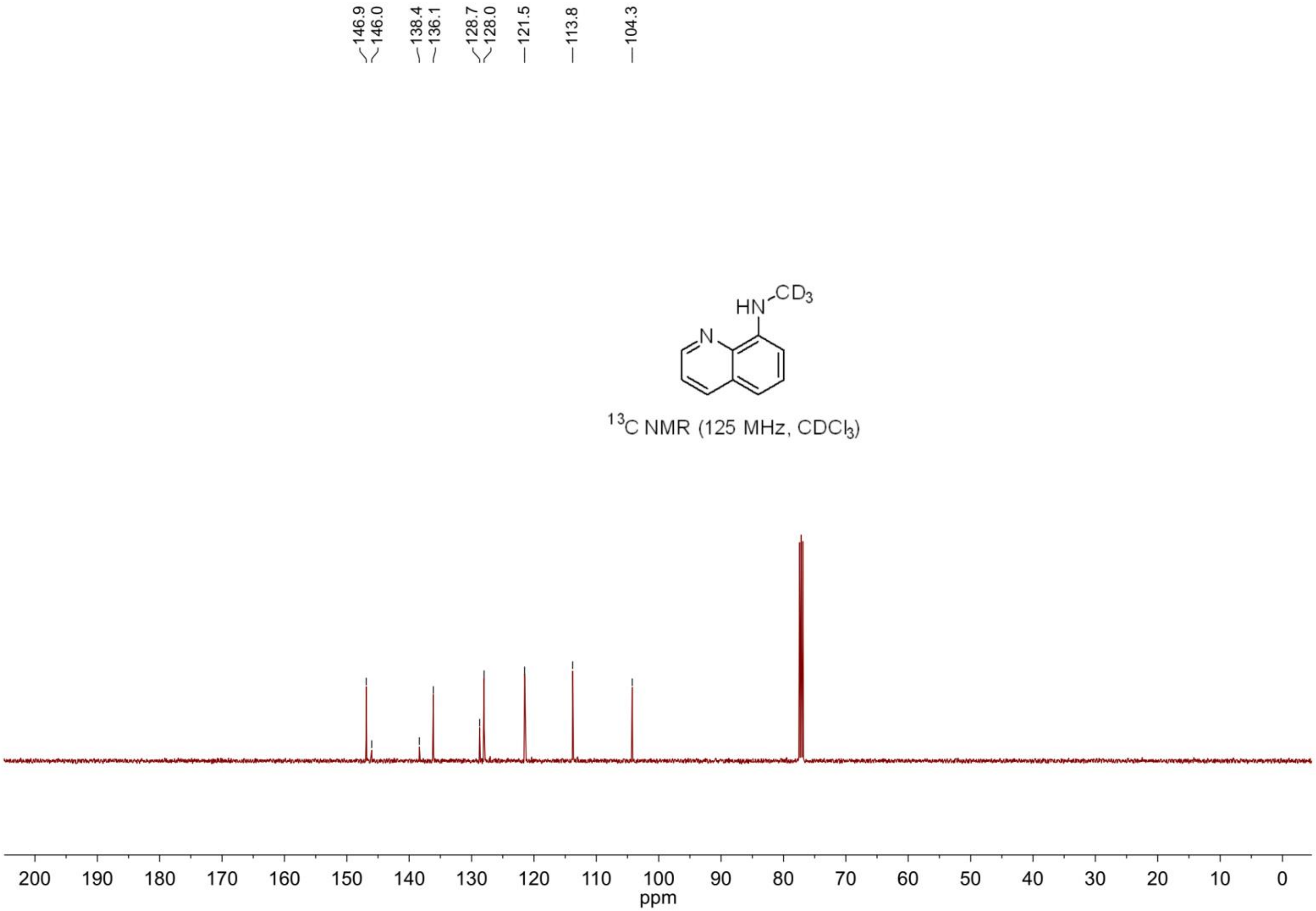
N-(Methyl-*d*₃)quinolin-8-amine (94)



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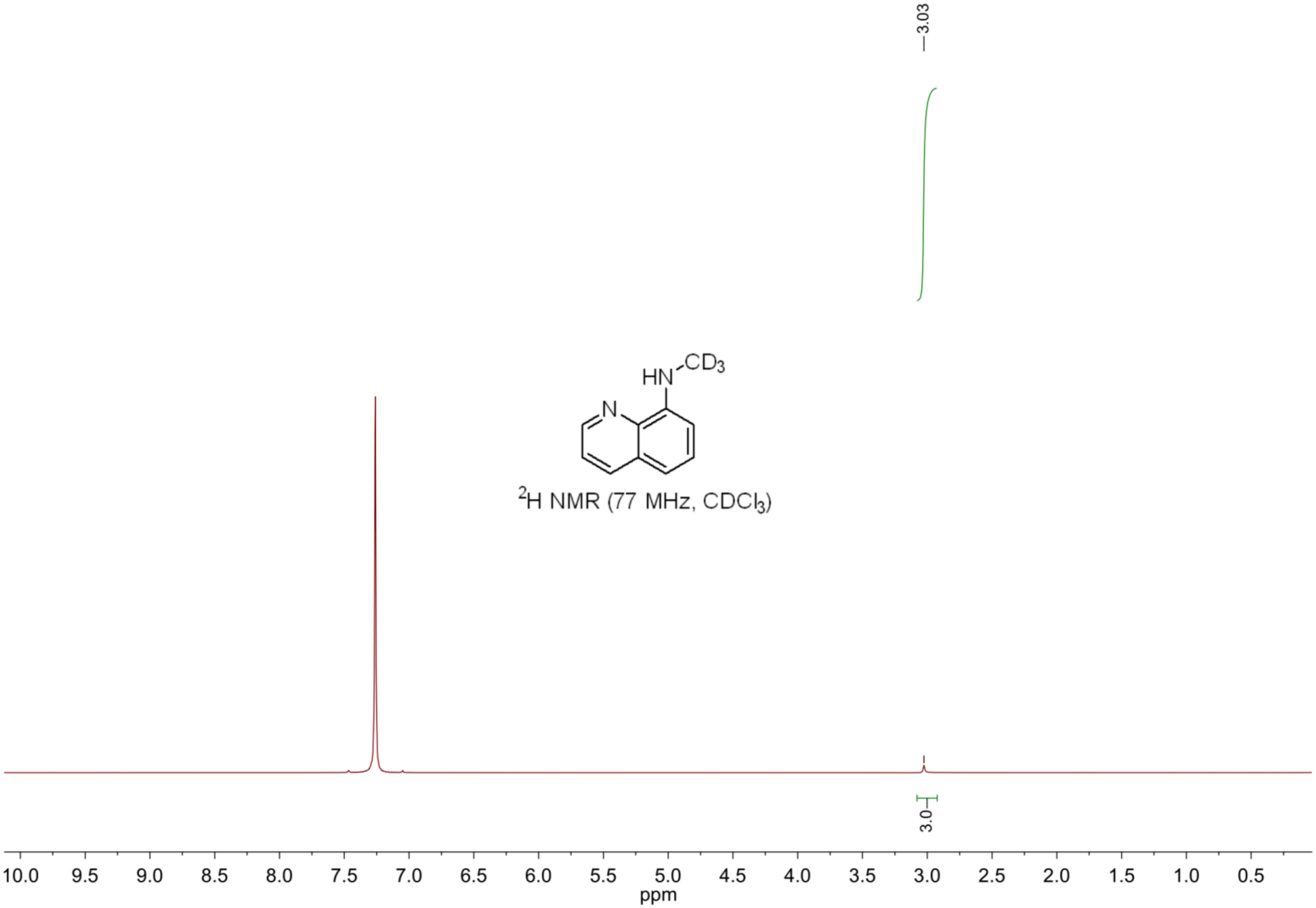
N-(Methyl-d_3)quinolin-8-amine (94)



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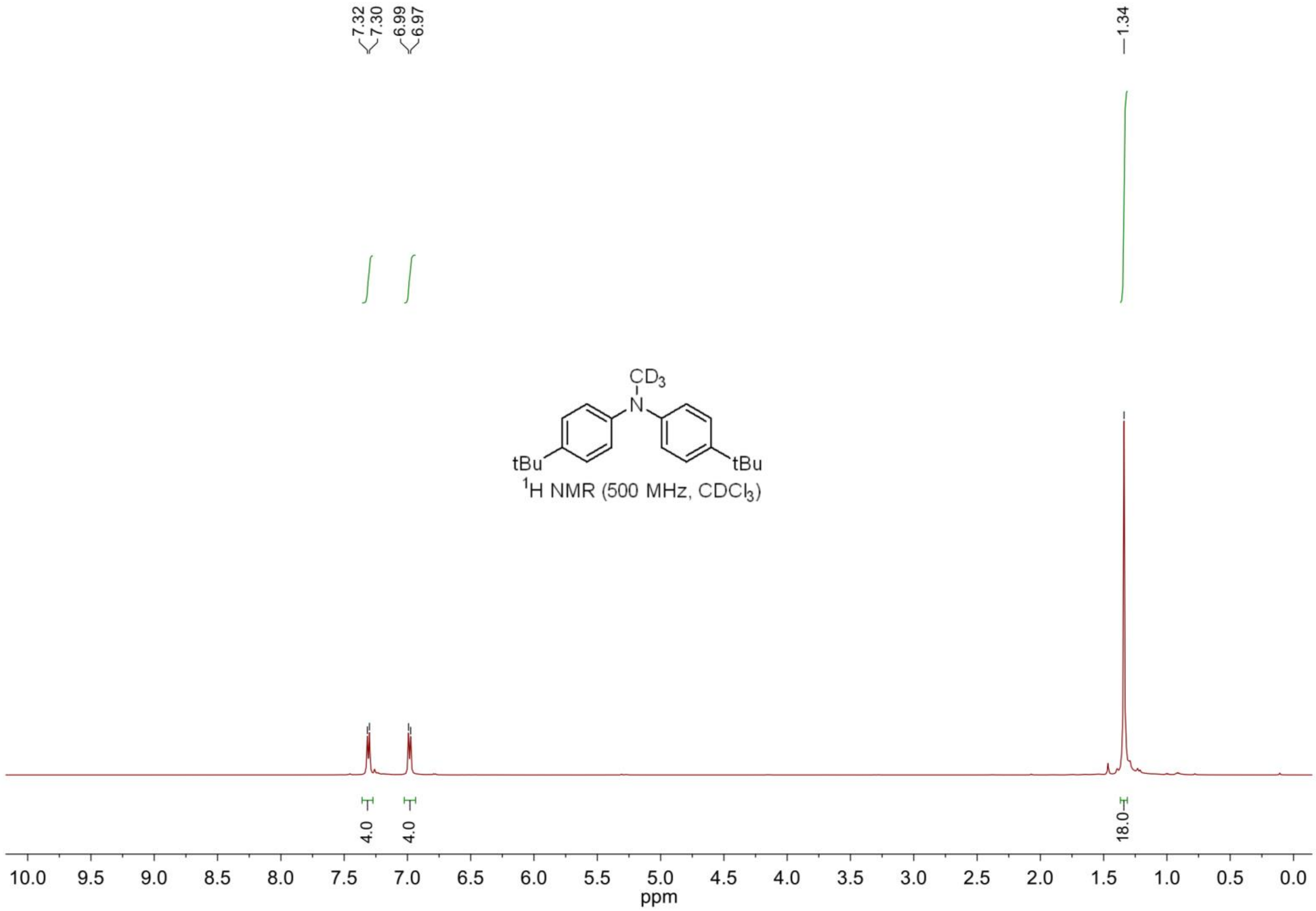
4-(Tert-butyl)-*N*-(4-(tert-butyl)phenyl)-*N*-(methyl-d_3)aniline (95)



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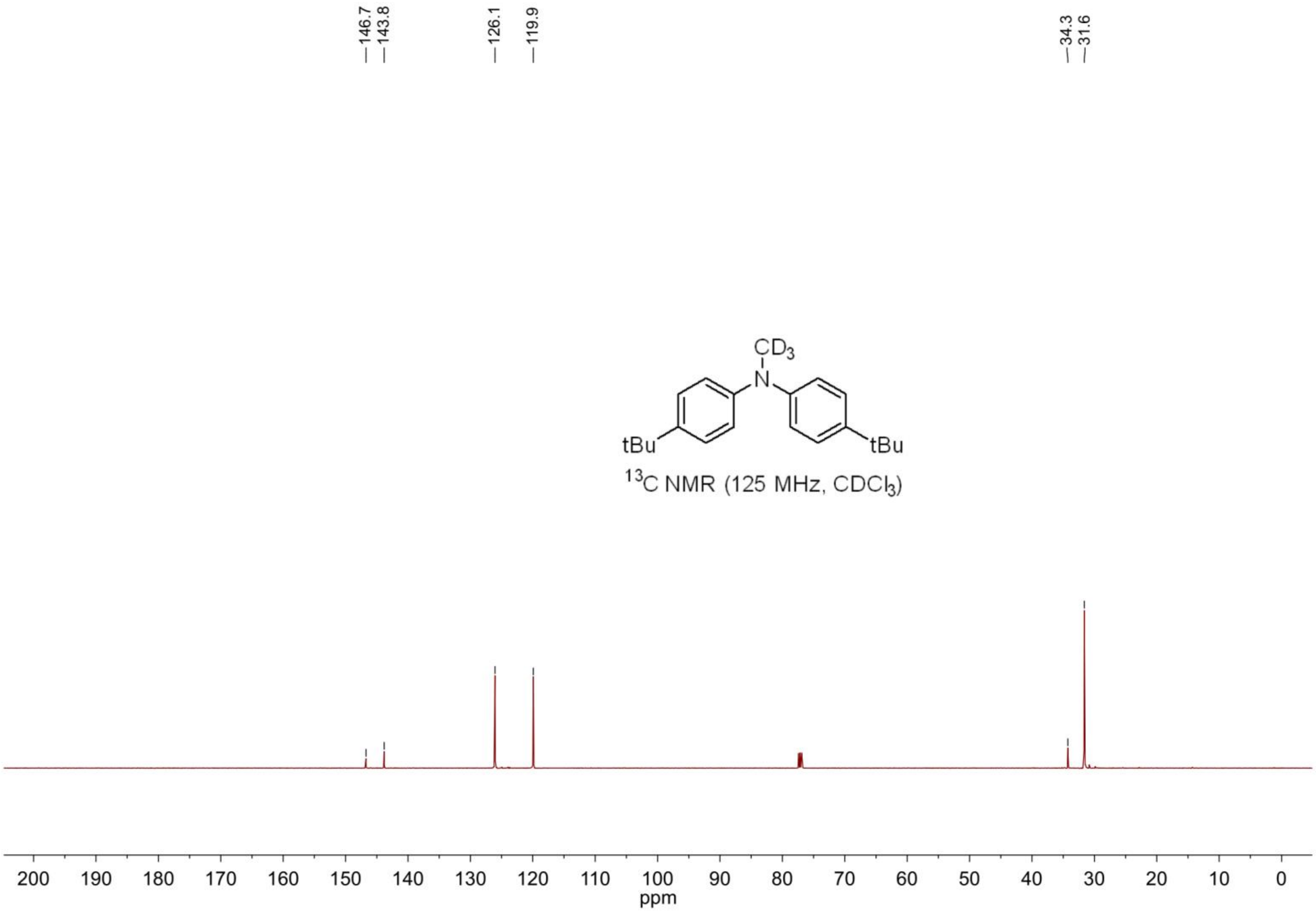
4-(Tert-butyl)-*N*-(4-(tert-butyl)phenyl)-*N*-(methyl-*d*₃)aniline (95)



^{13}C NMR (125 MHz, $CDCl_3$)

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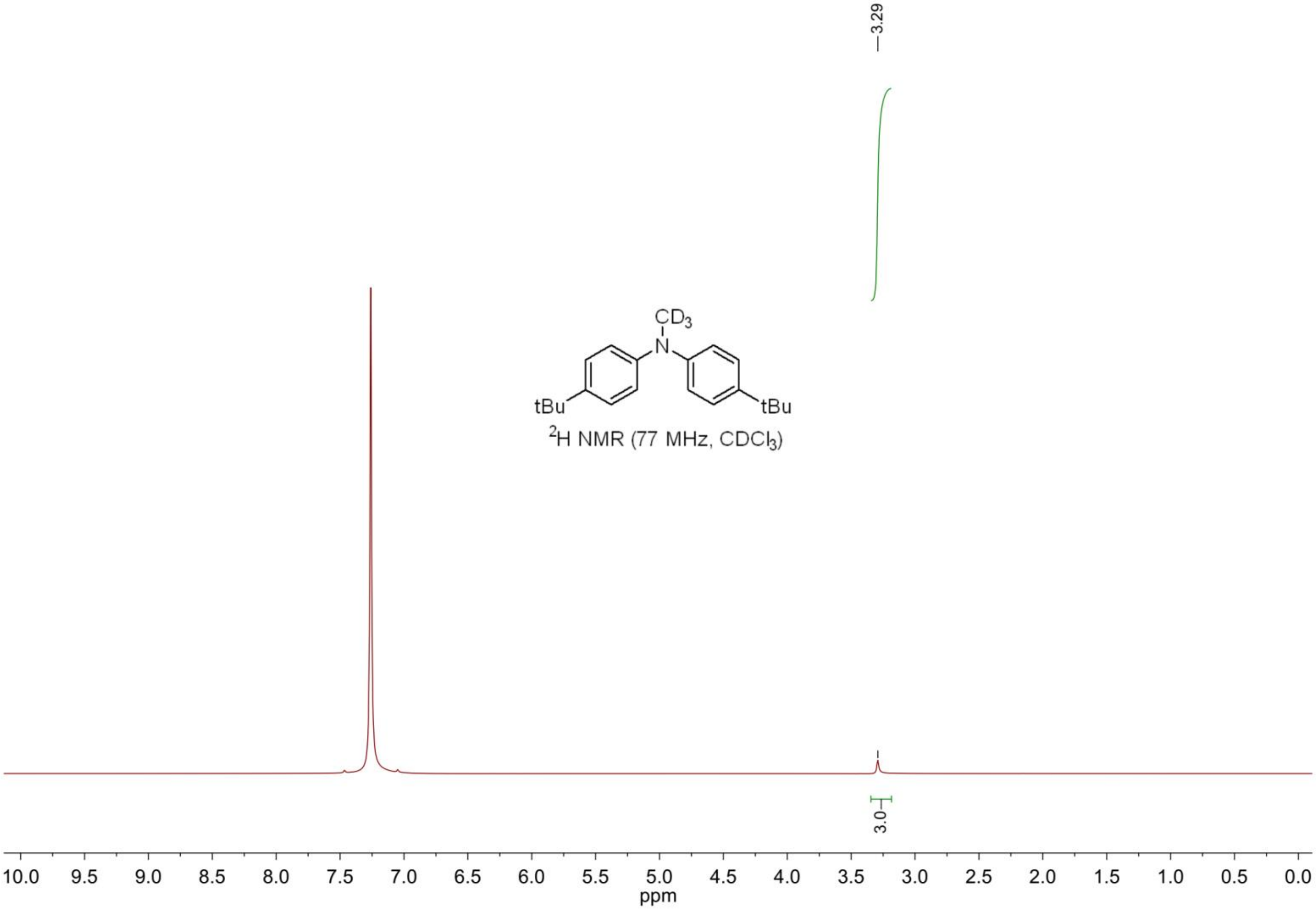
4-(Tert-butyl)-*N*-(4-(tert-butyl)phenyl)-*N*-(methyl-*d*3)aniline (95)



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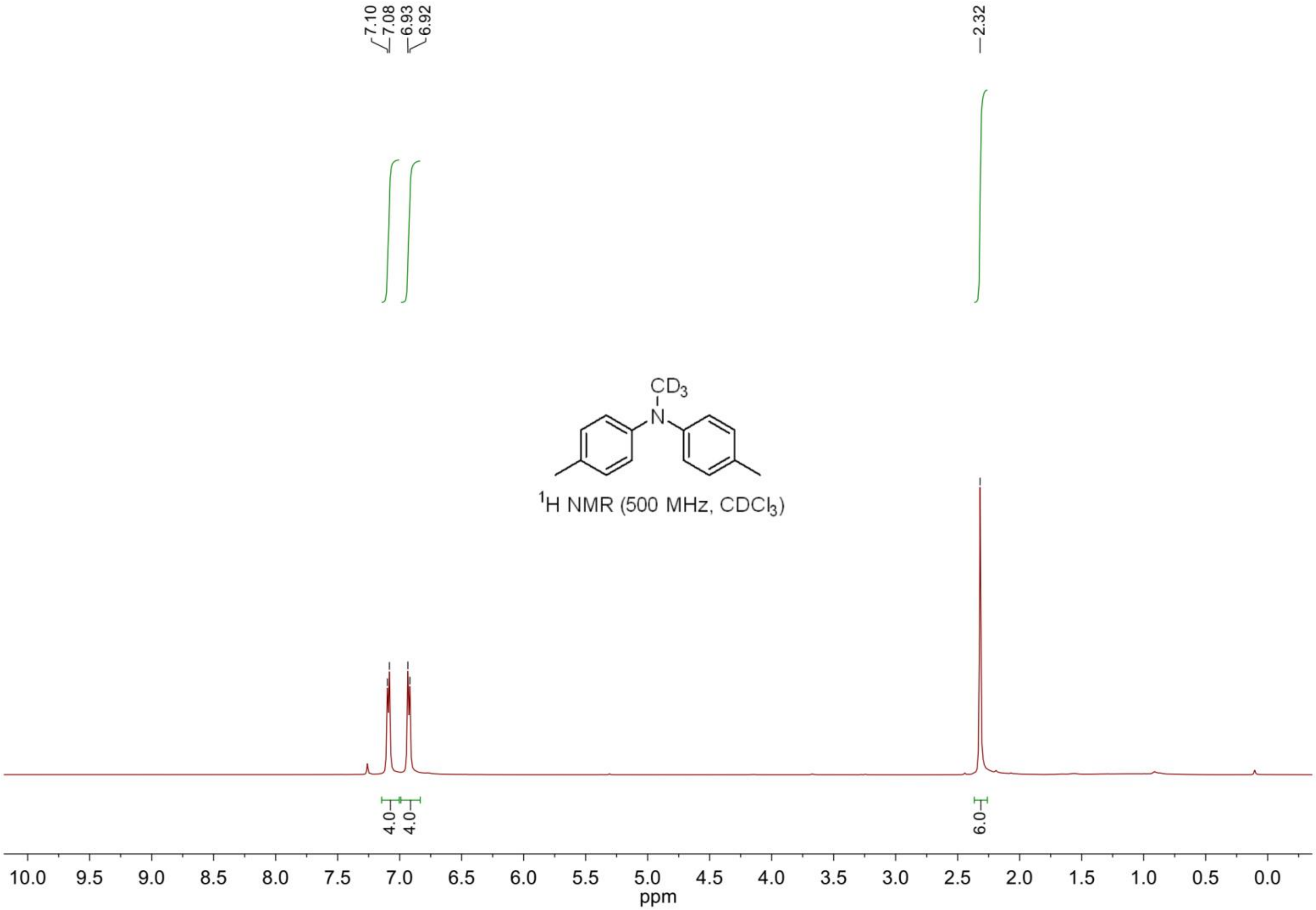
4-Methyl-*N*-(methyl-*d*₃)-*N*-(*p*-tolyl)aniline (96)



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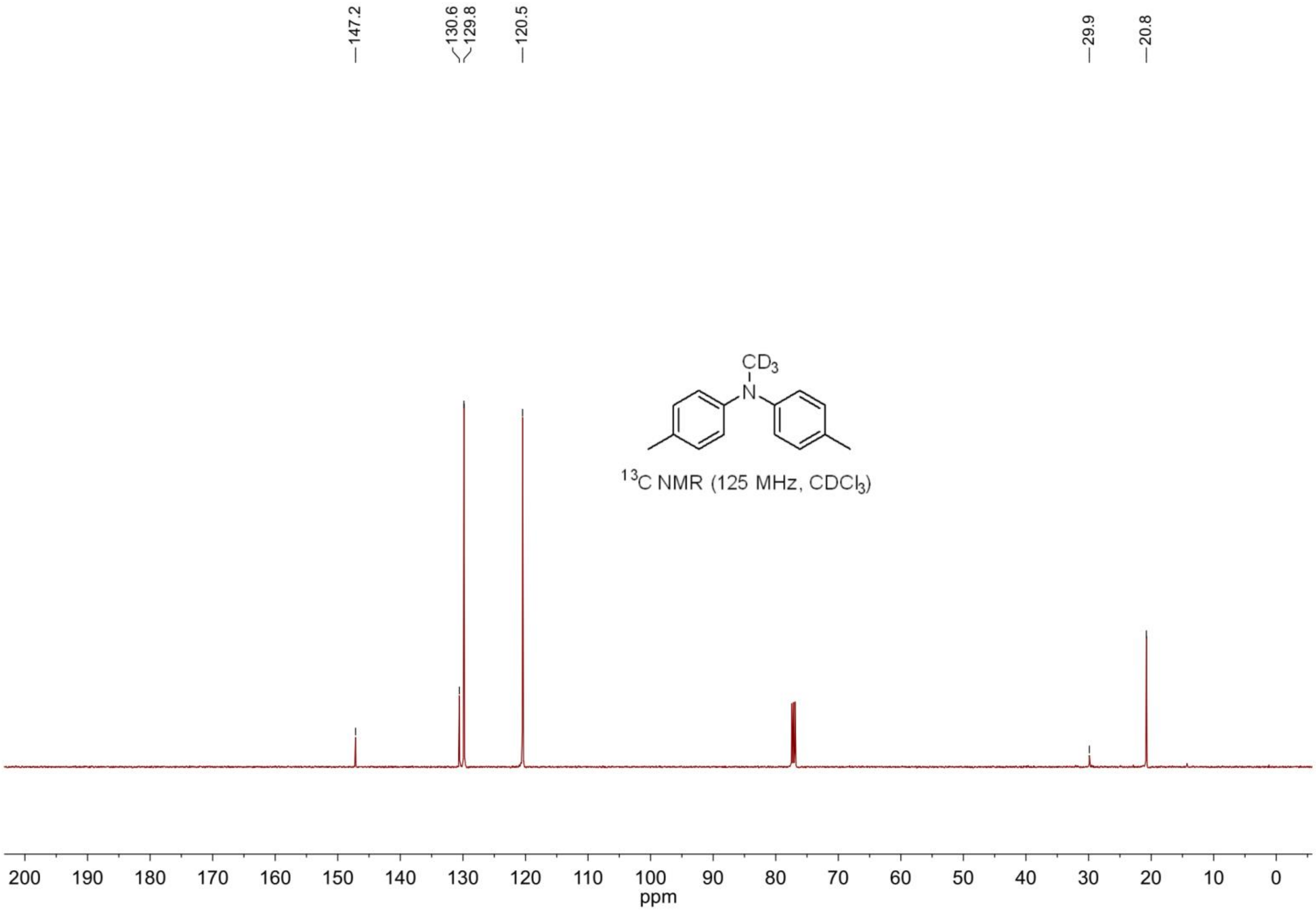
4-Methyl-*N*-(methyl-*d*₃)-*N*-(*p*-tolyl)aniline (96)



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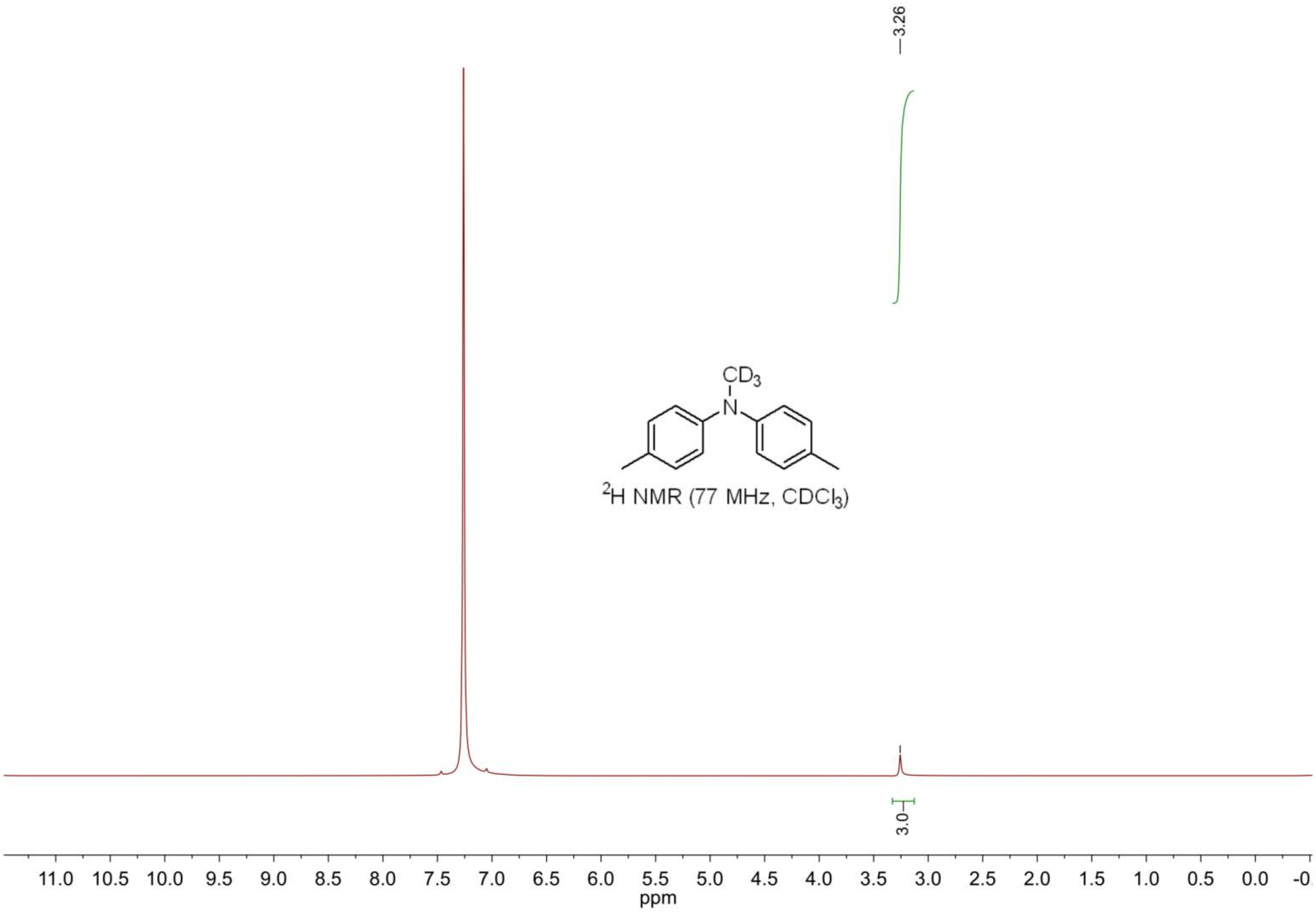
4-Methyl-*N*-(methyl-*d*$_3$)-*N*-(*p*-tolyl)aniline (96)



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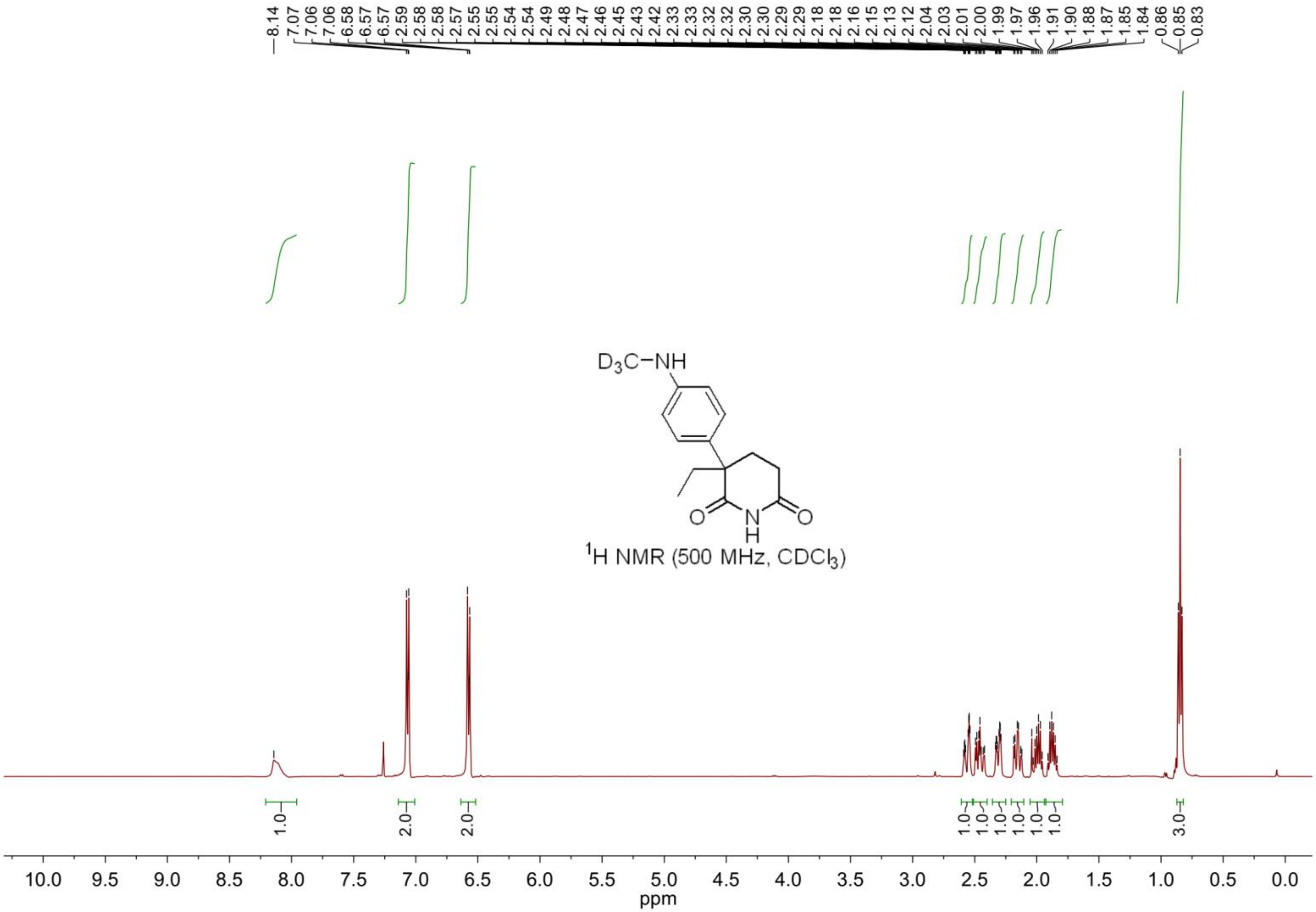
3-Ethyl-3-(4-((methyl-*d*₃)amino)phenyl)piperidine-2,6-dione (97)



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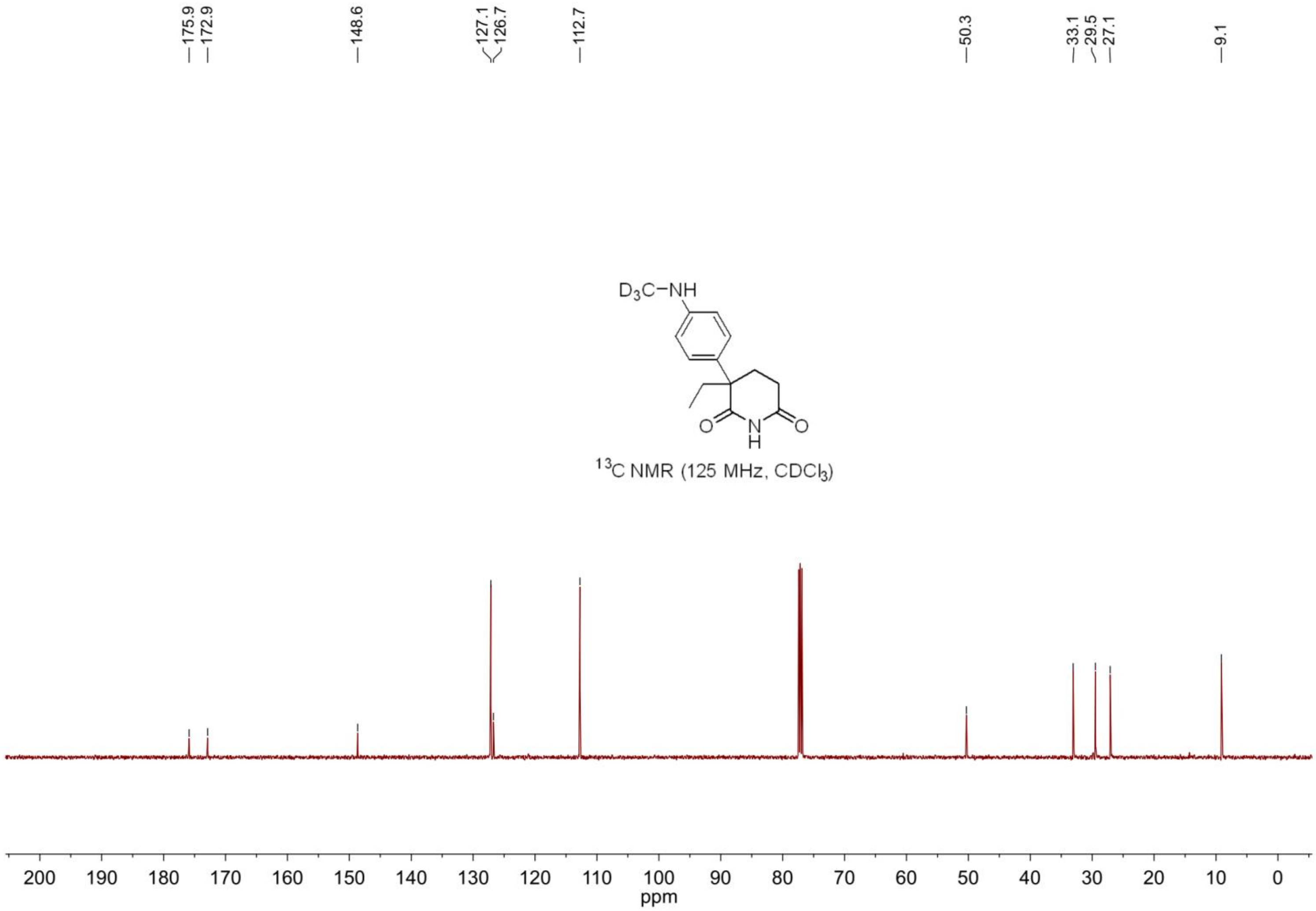
3-Ethyl-3-(4-((methyl-*d*3)amino)phenyl)piperidine-2,6-dione (97)



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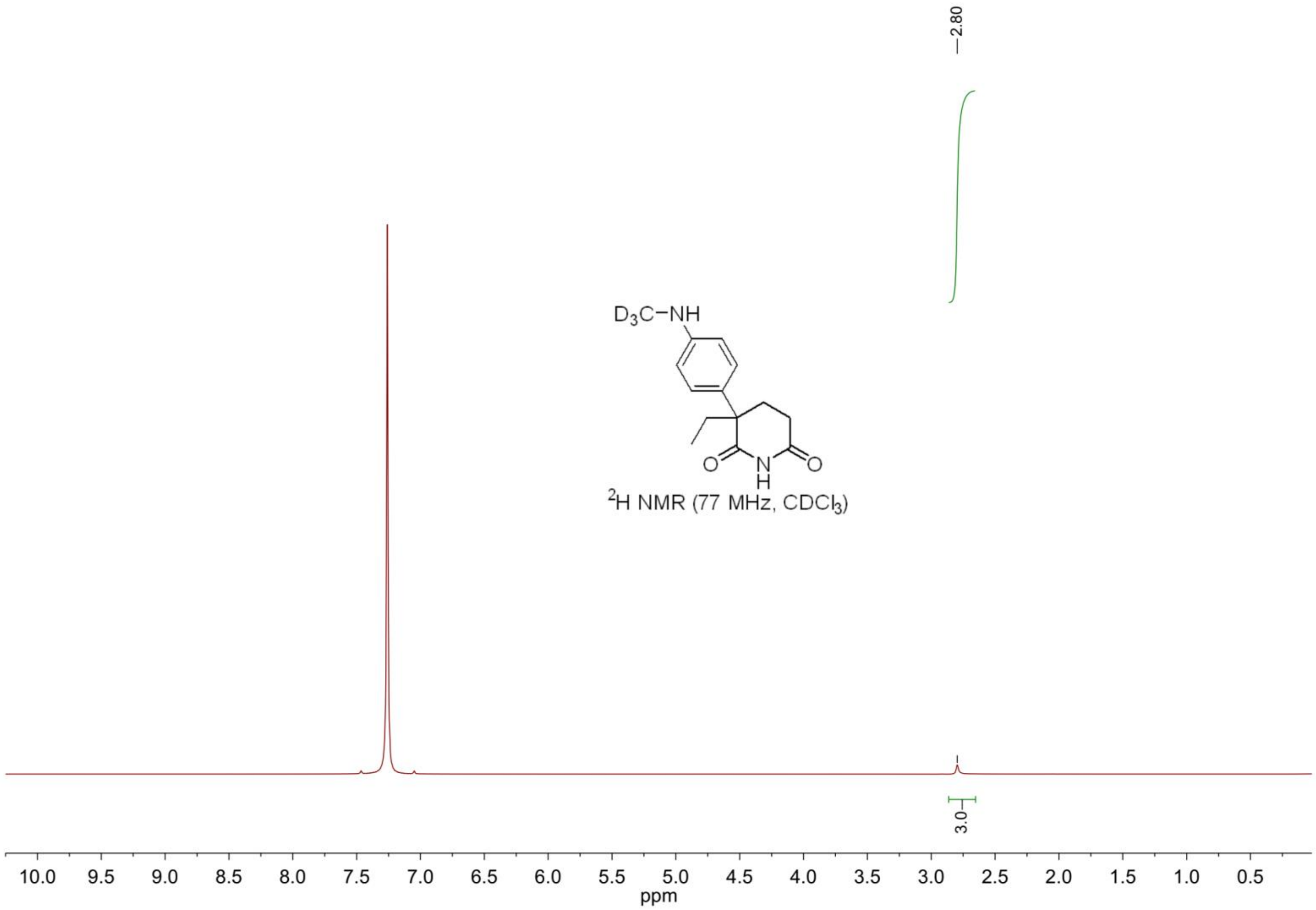
3-Ethyl-3-(4-((methyl-*d*3)amino)phenyl)piperidine-2,6-dione (97)



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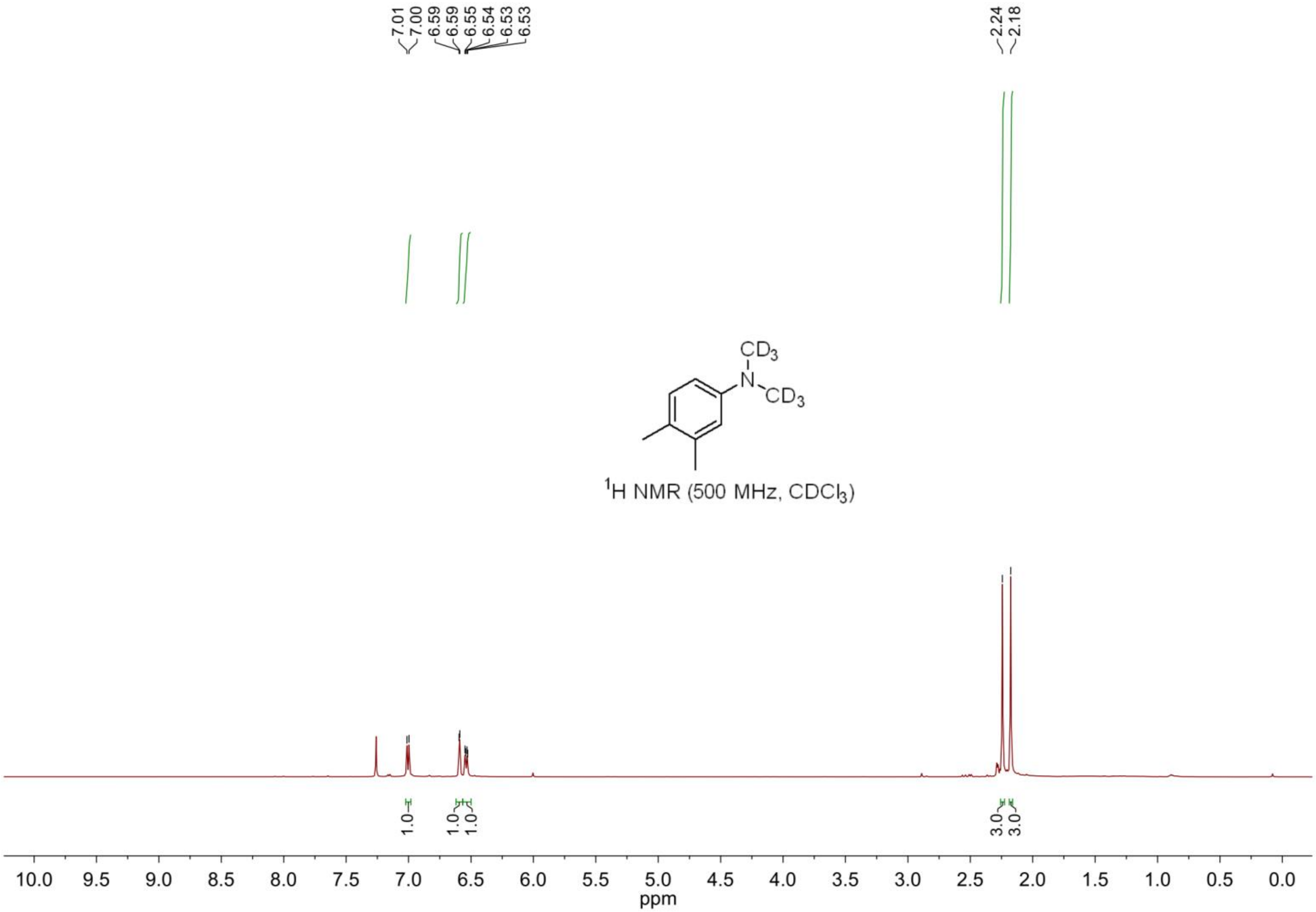
3,4-Dimethyl-*N*,*N*-bis(methyl-*d*₃)aniline (98)



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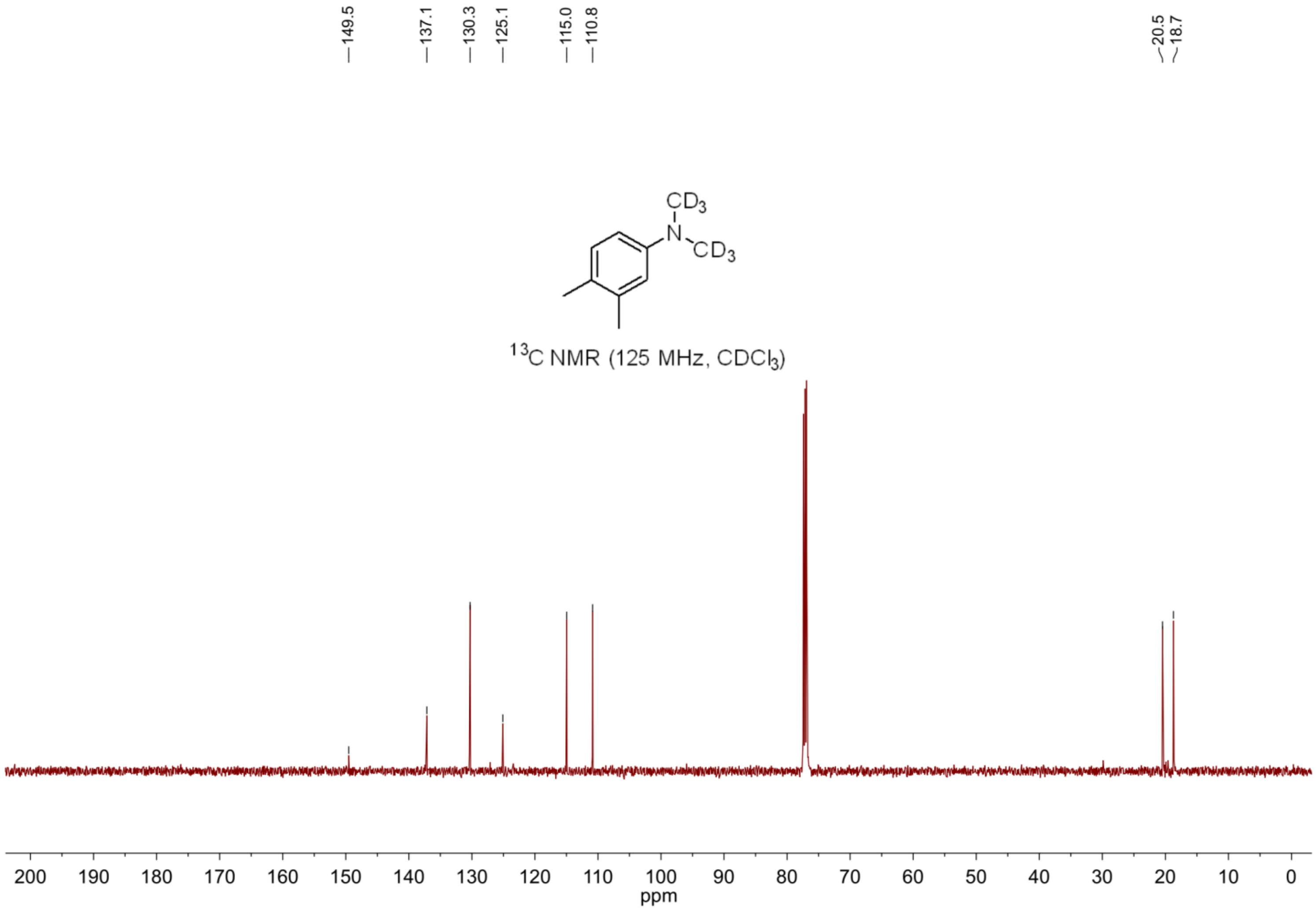
3,4-Dimethyl-*N*,*N*-bis(methyl-*d*$_3$)aniline (98)



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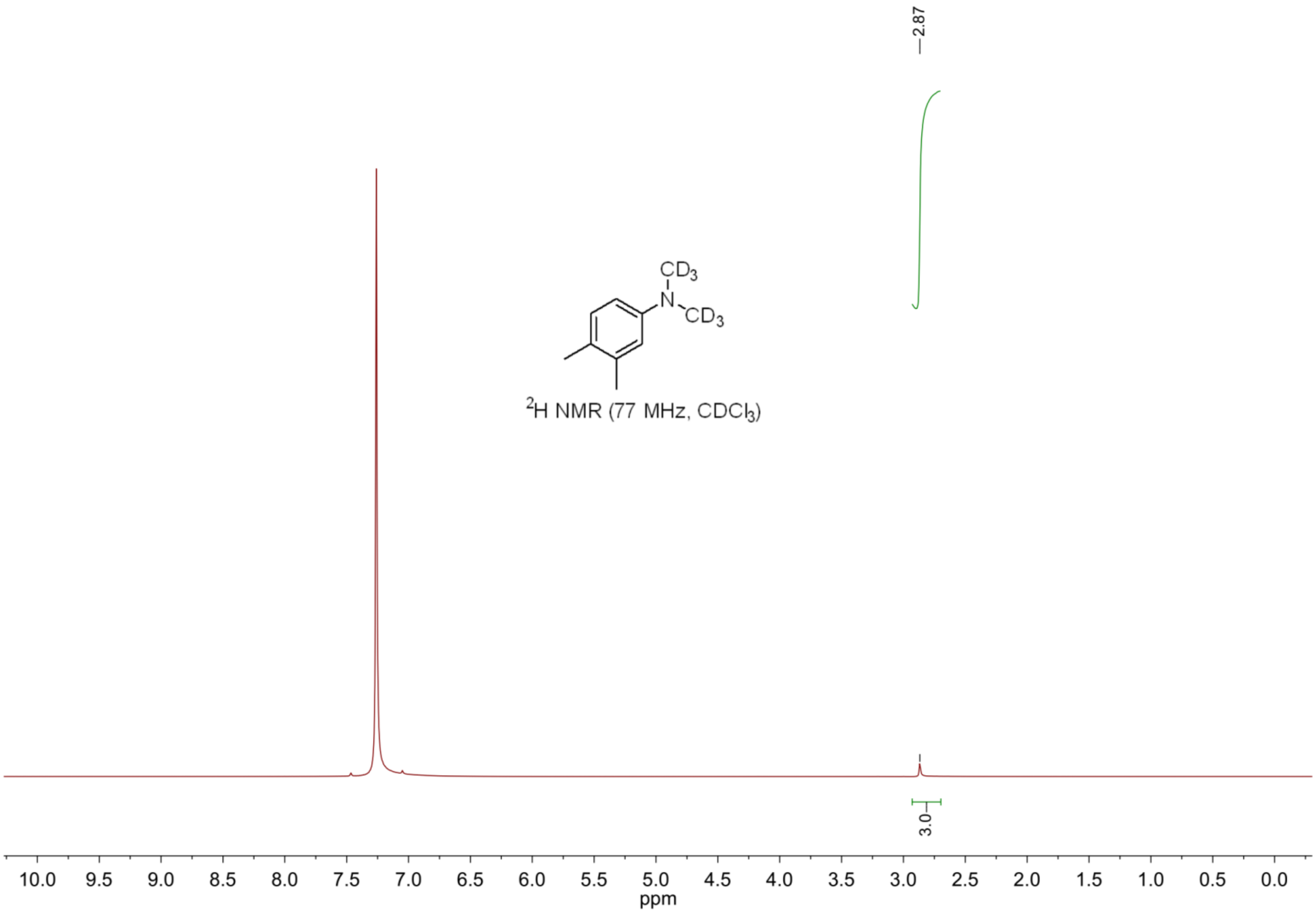
3,4-Dimethyl-*N*,*N*-bis(methyl-d_3)aniline (98)



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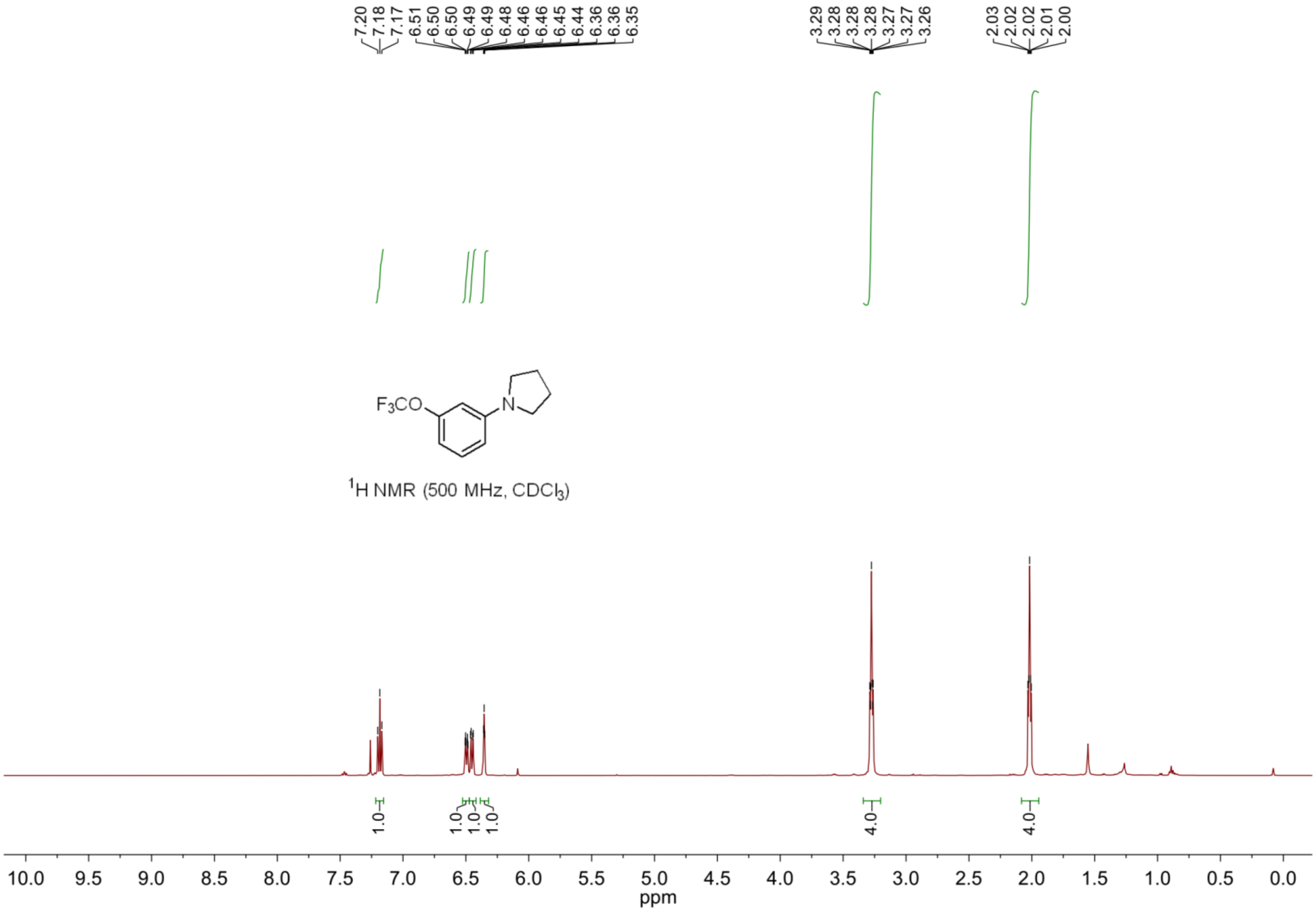
1-(3-(trifluoromethyl)phenyl)pyrrolidine (100)



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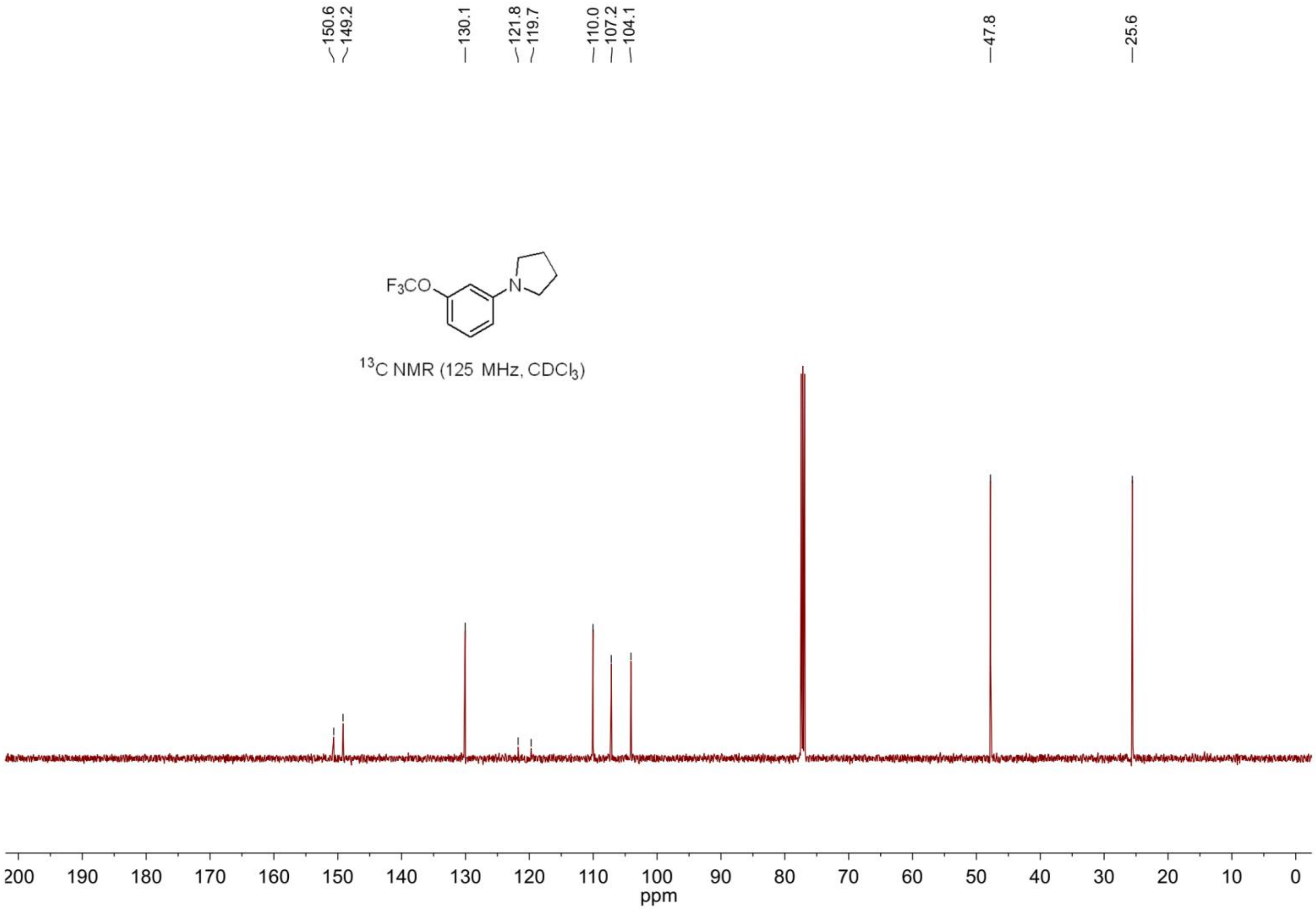

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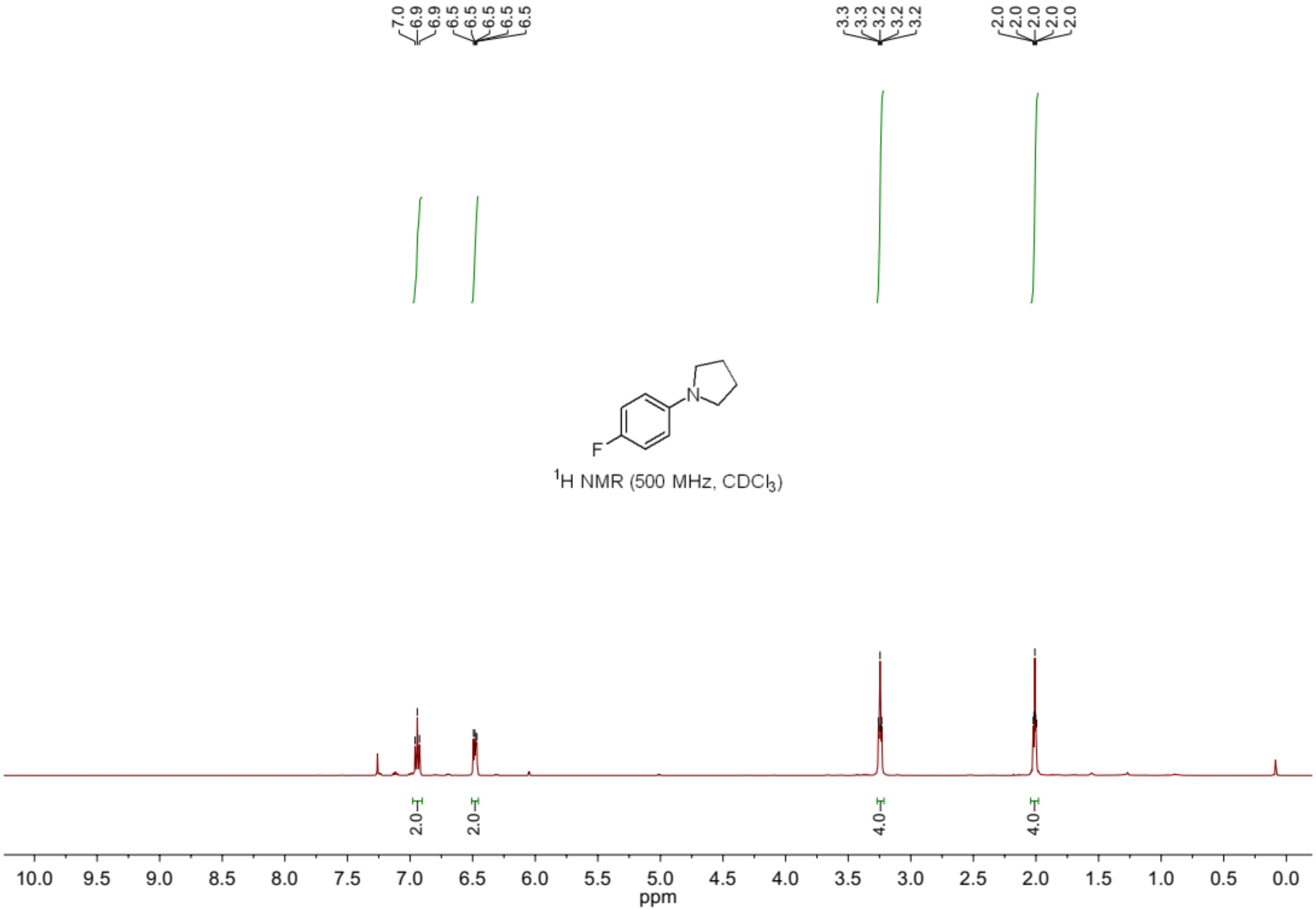

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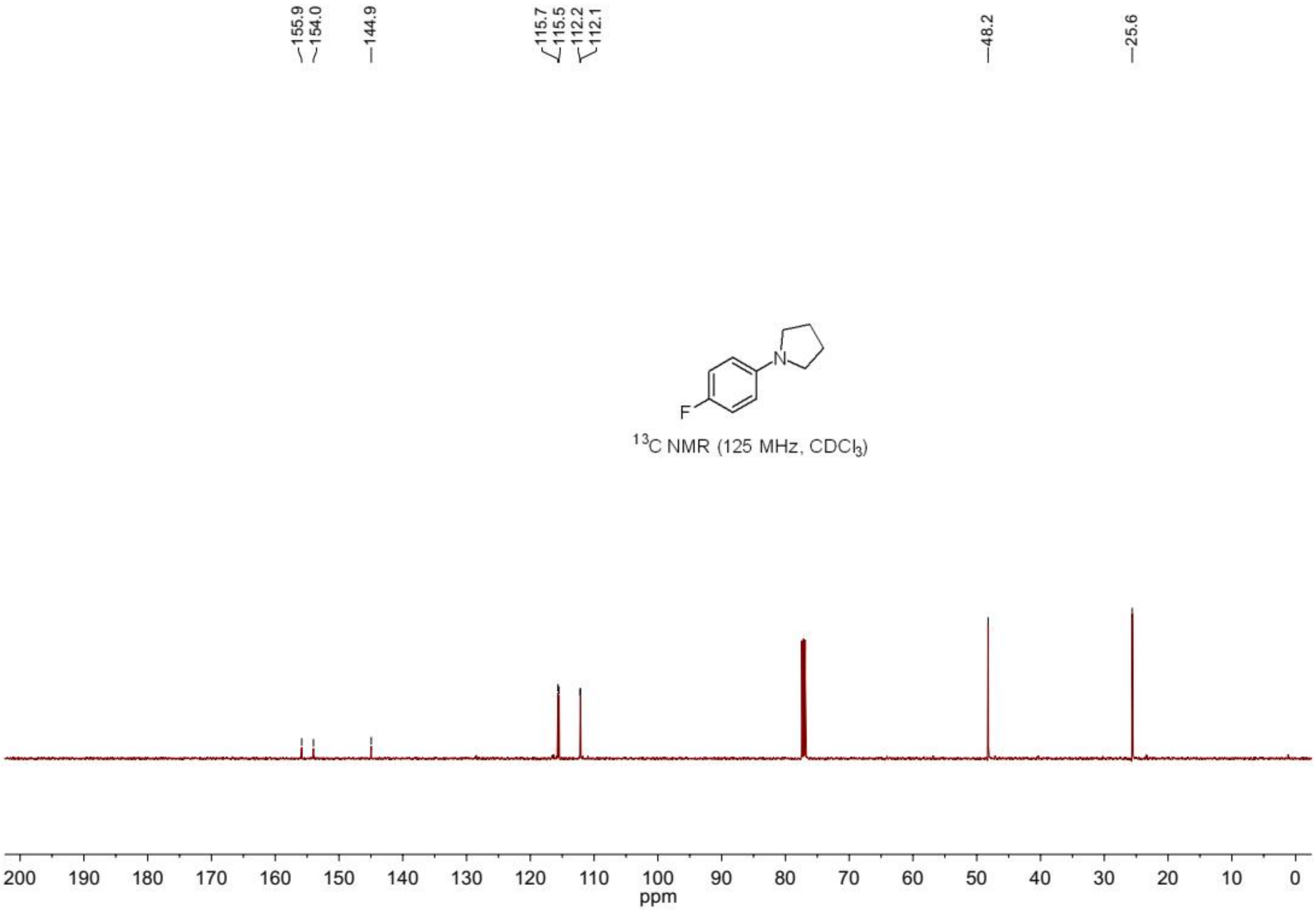

^{13}C NMR (125 MHz, CDCl$_3$)

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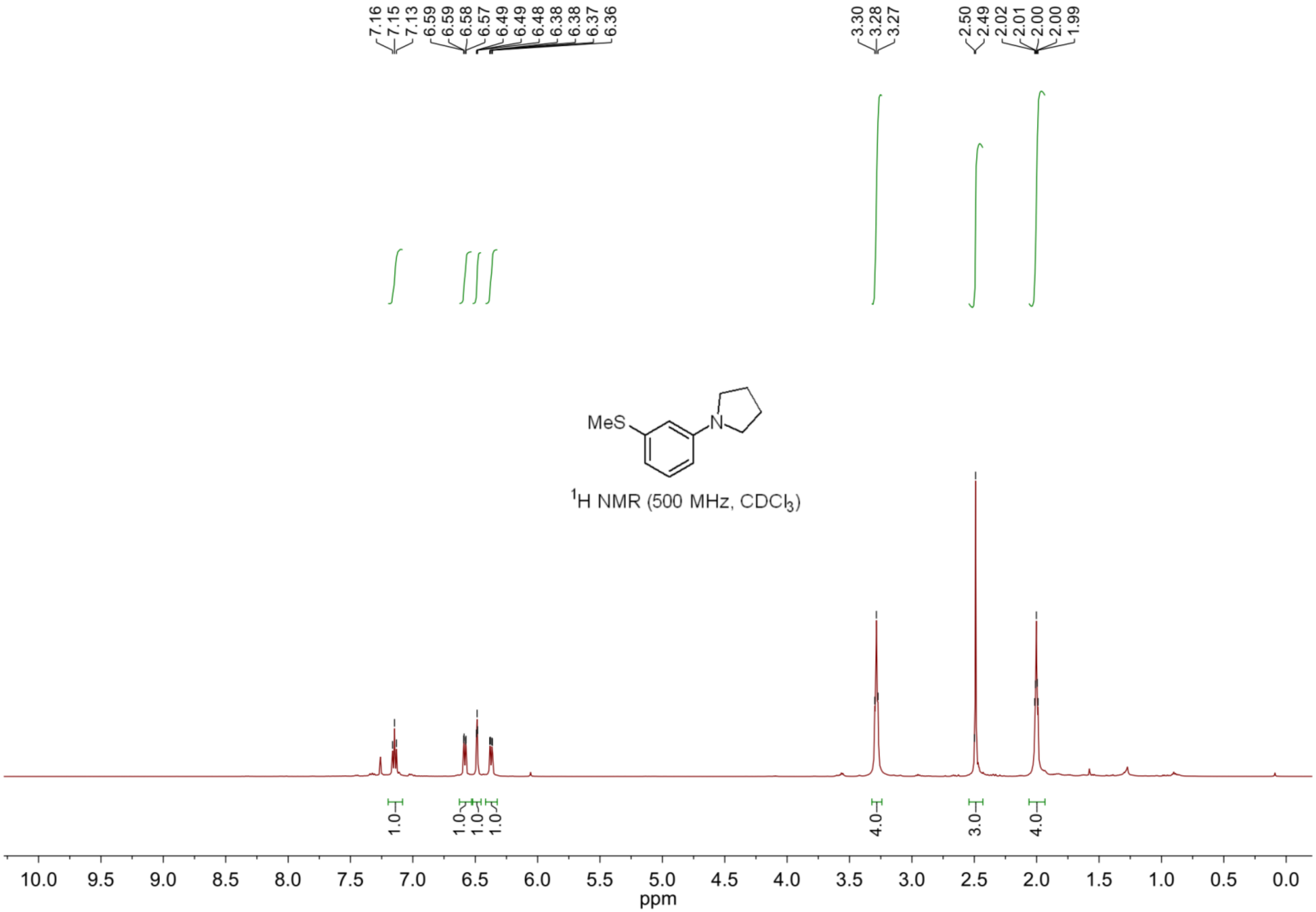
1-(3-(Methylthio)phenyl)pyrrolidine (102)



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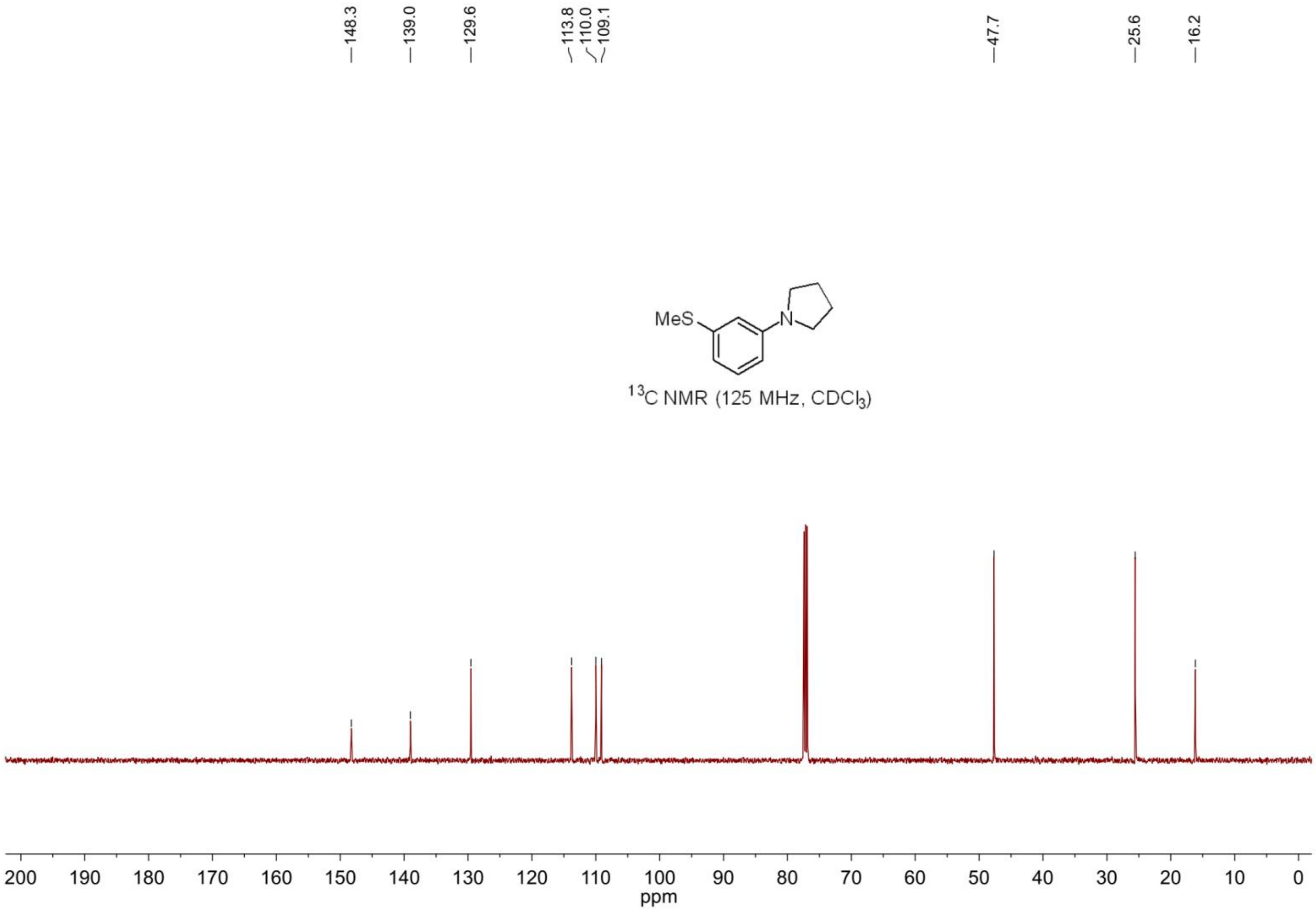

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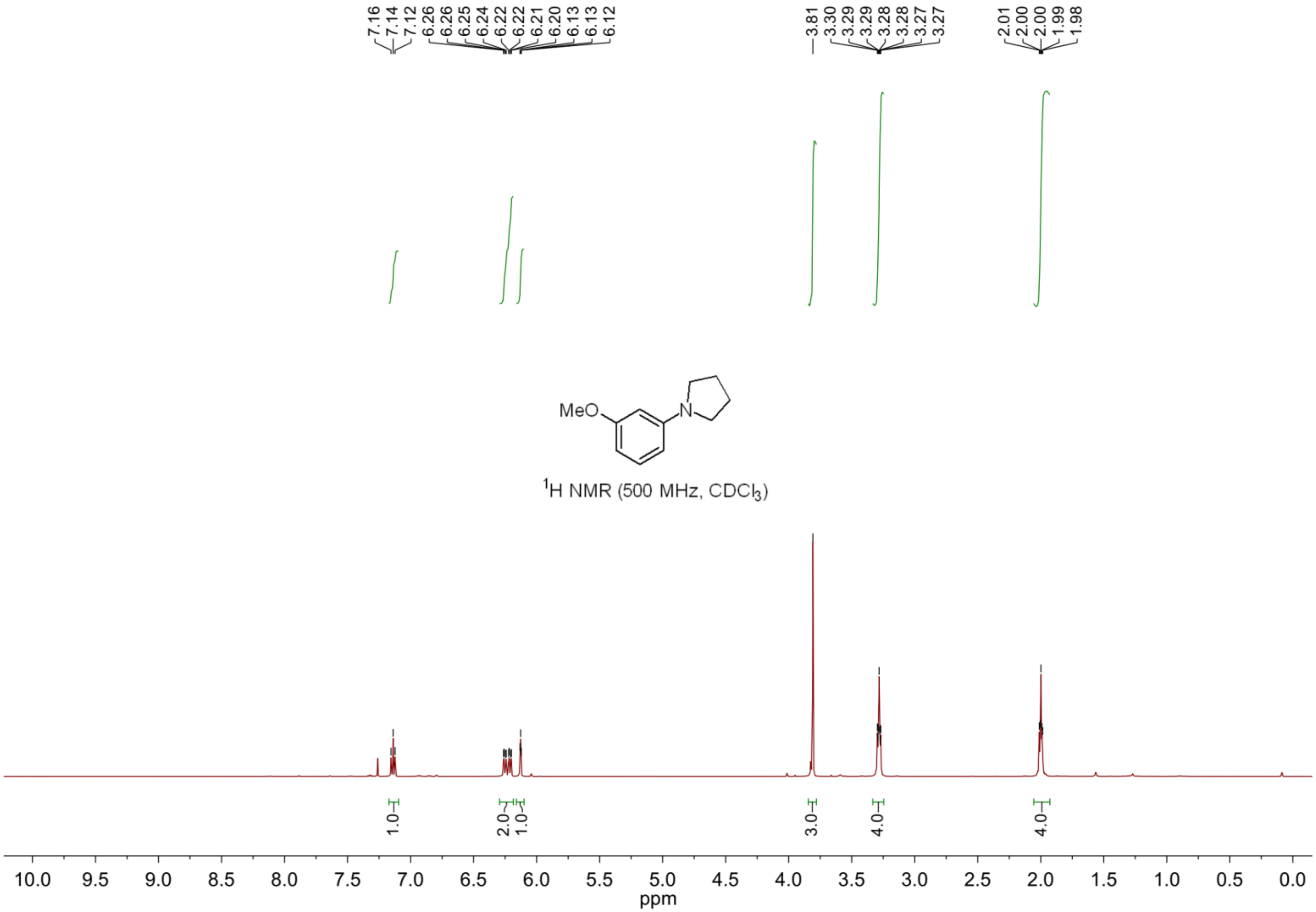
1-(3-Methoxyphenyl)pyrrolidine (103)



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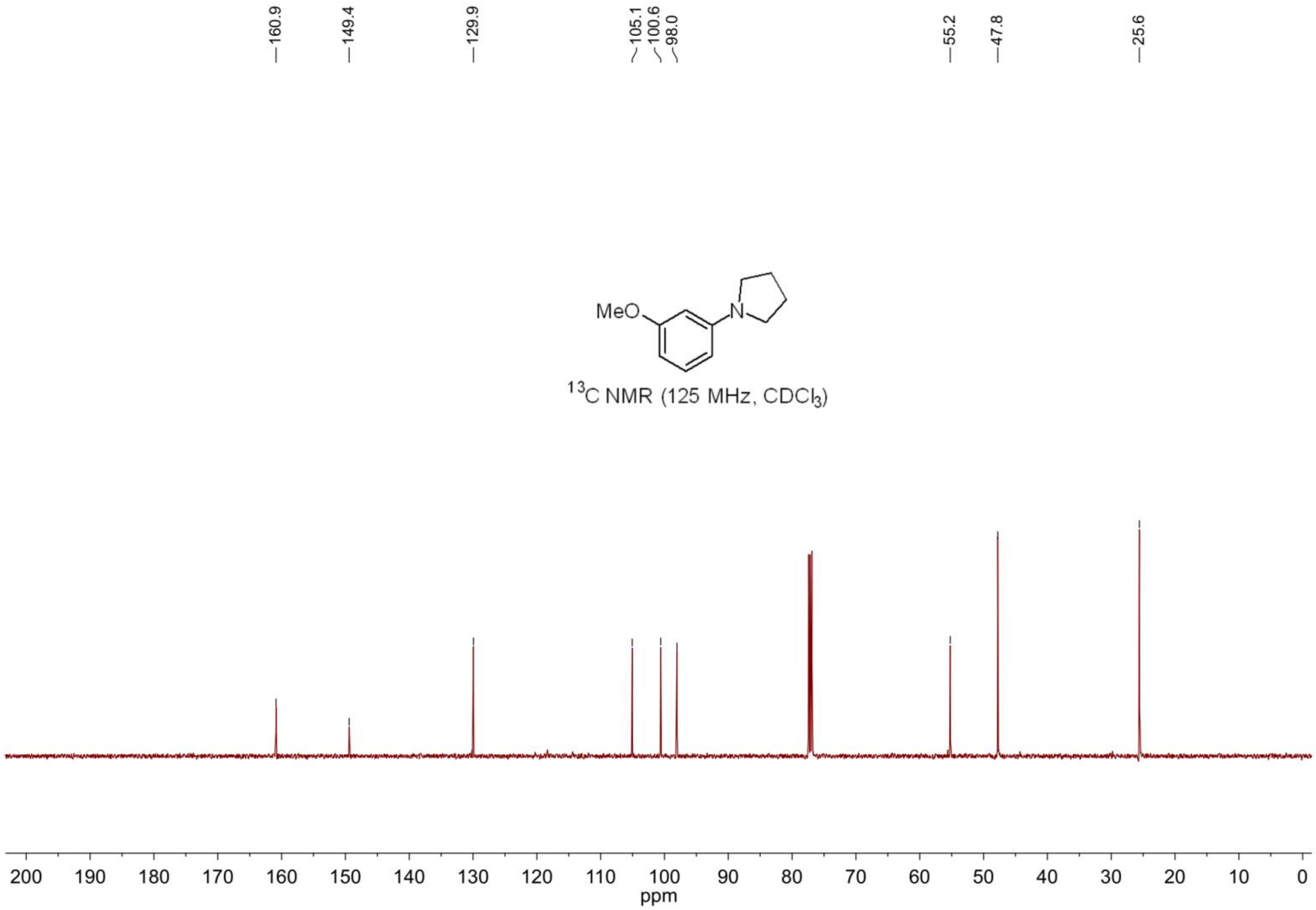

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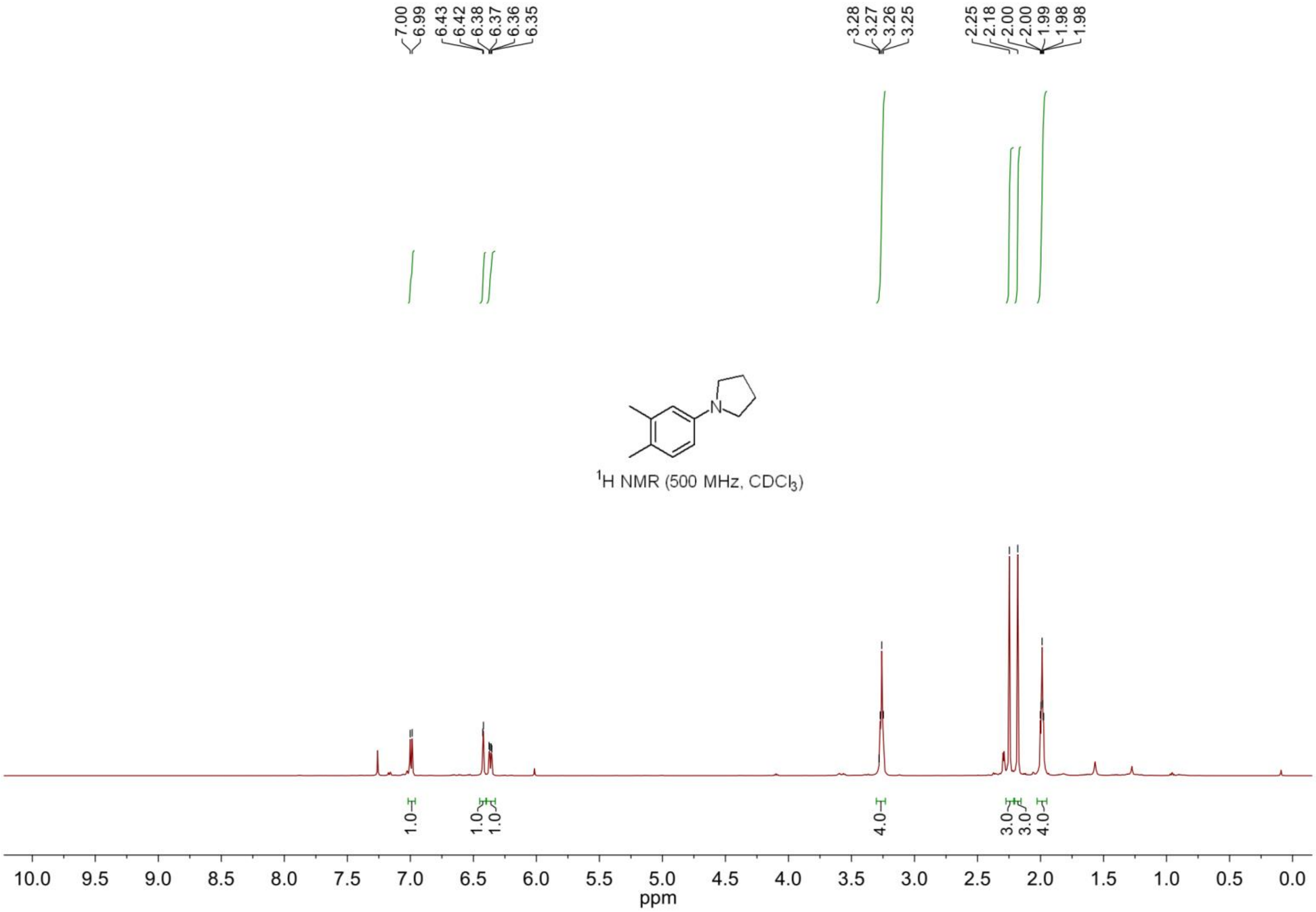

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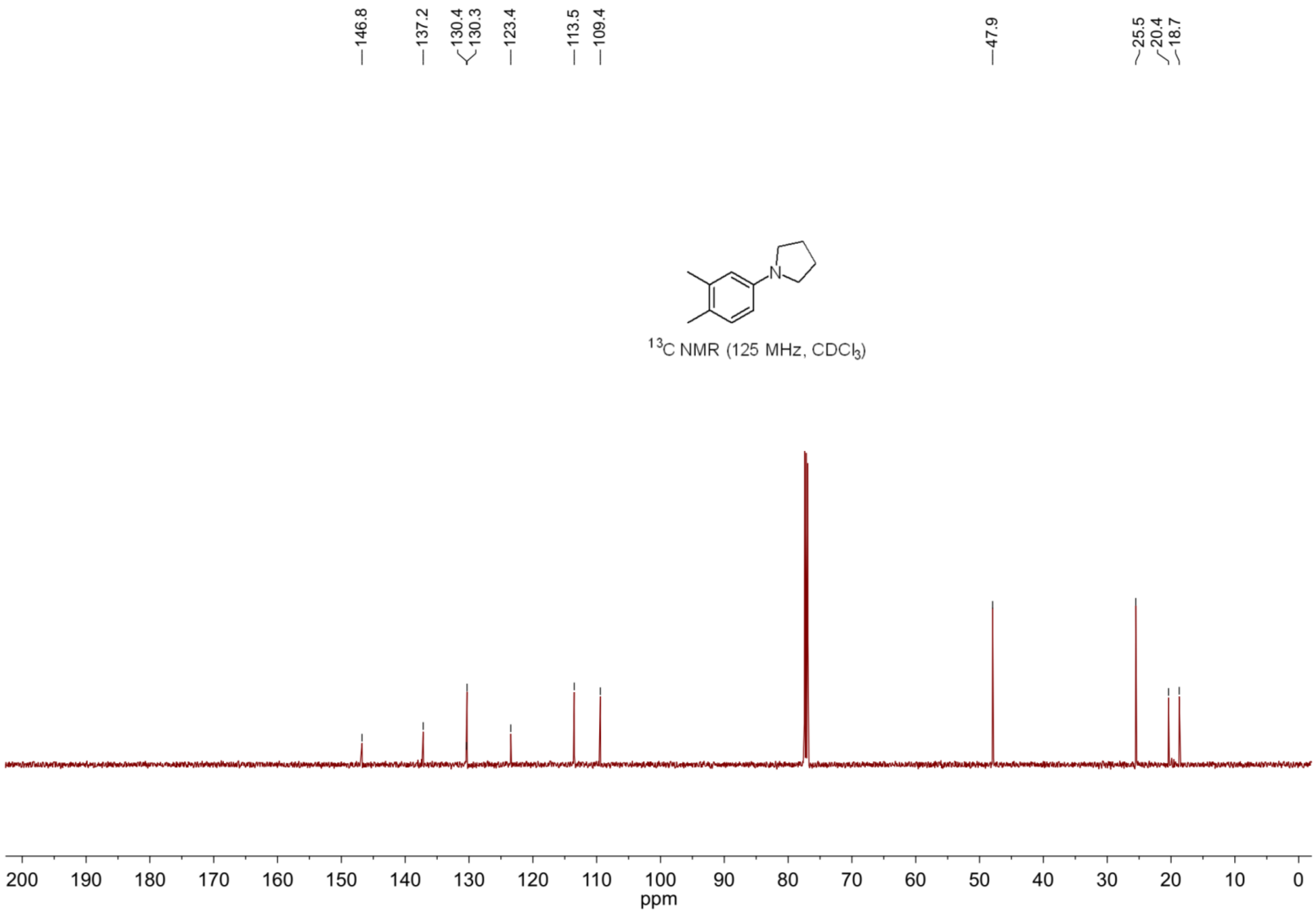

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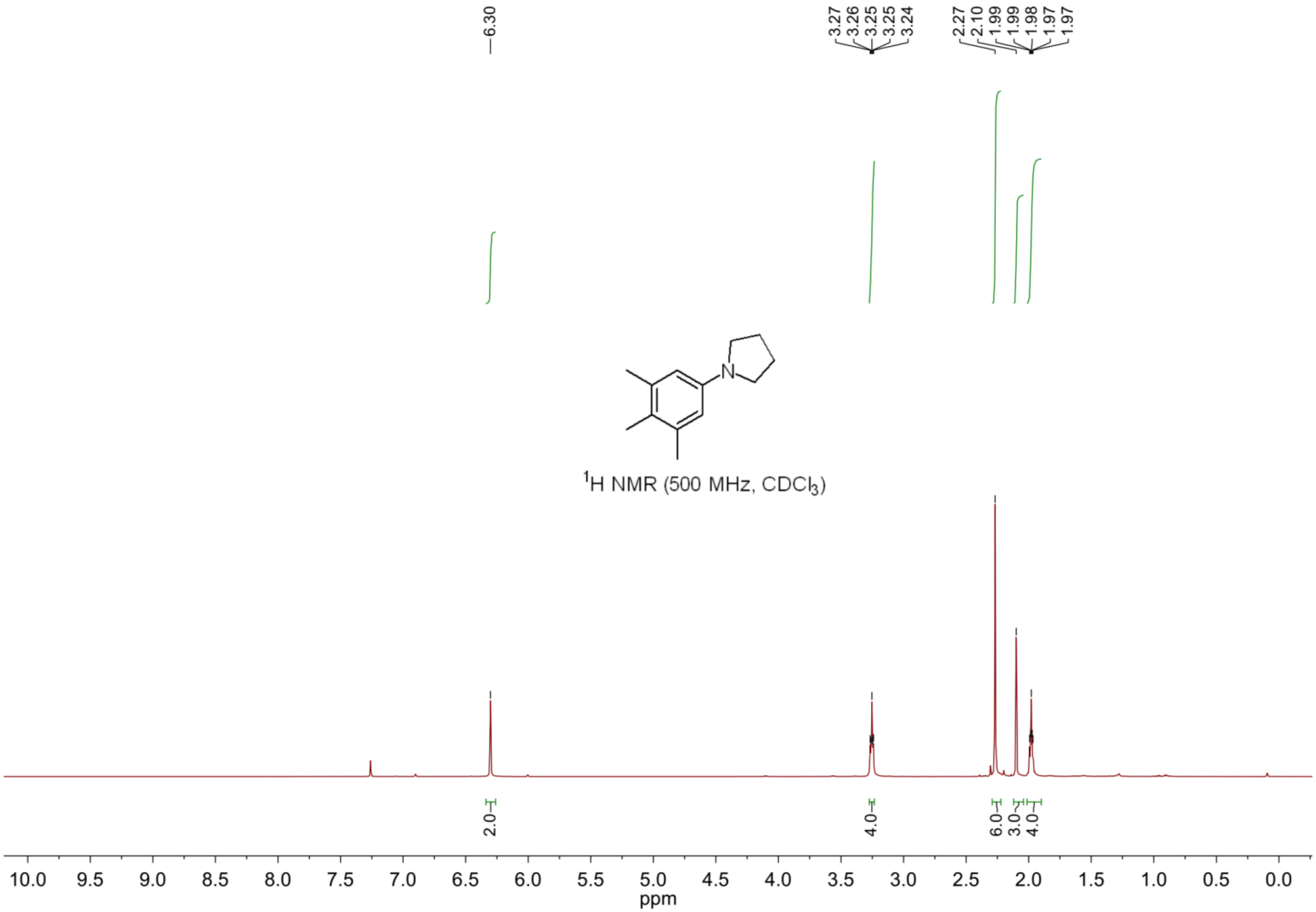

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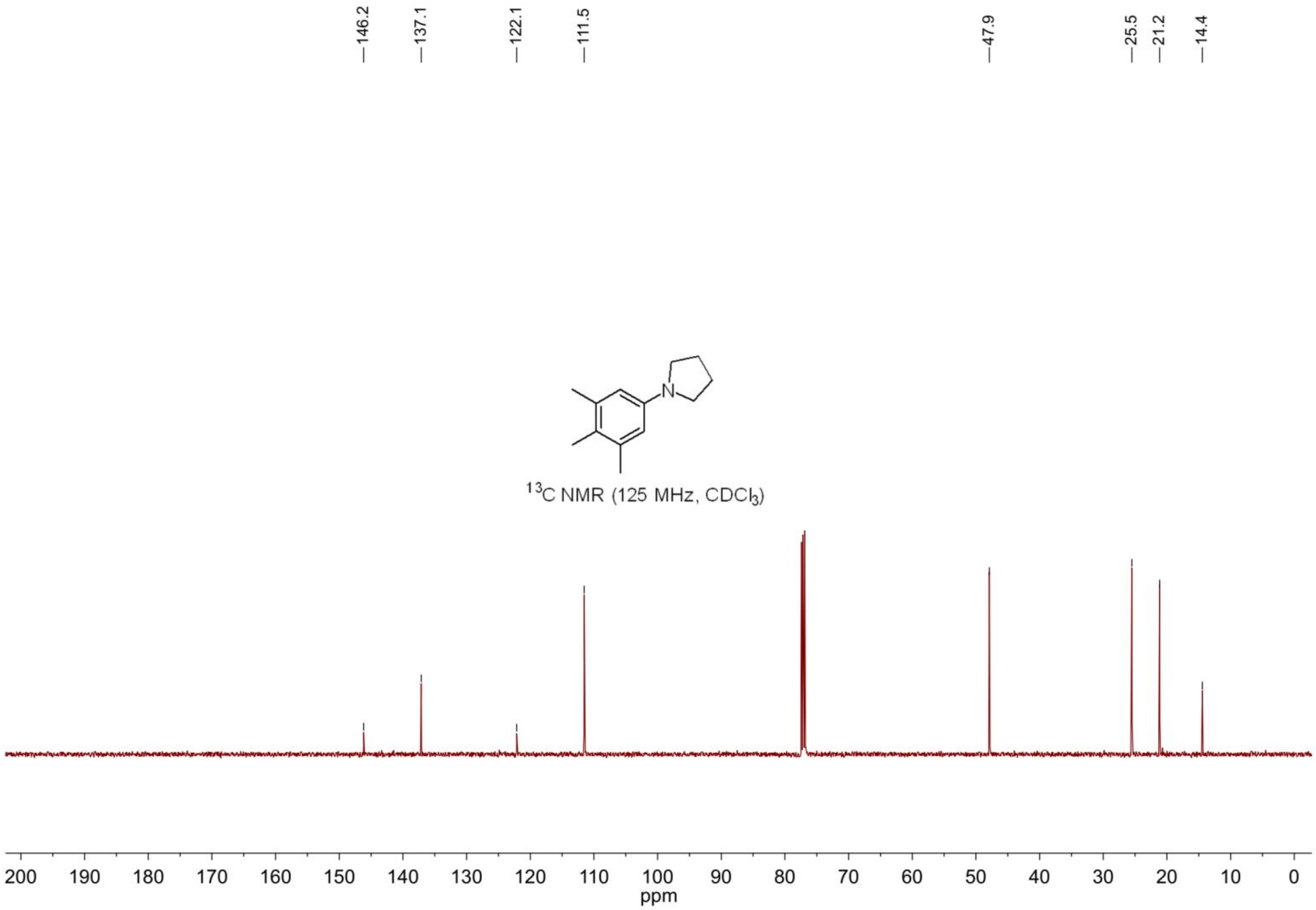
1-(3,4,5-Trimethylphenyl)pyrrolidine (105)



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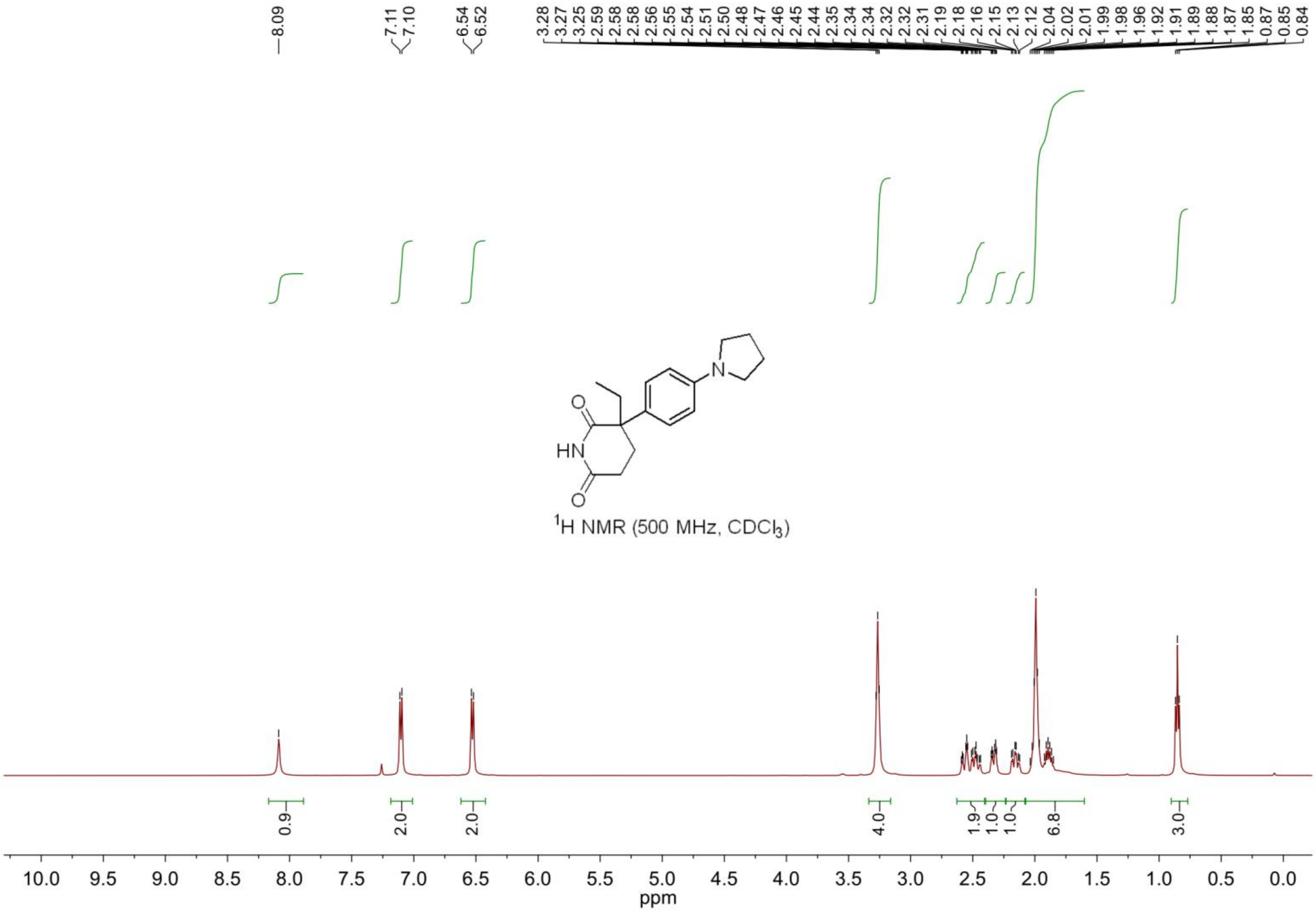
3-Ethyl-3-(4-(pyrrolidin-1-yl)phenyl)piperidine-2,6-dione (106)



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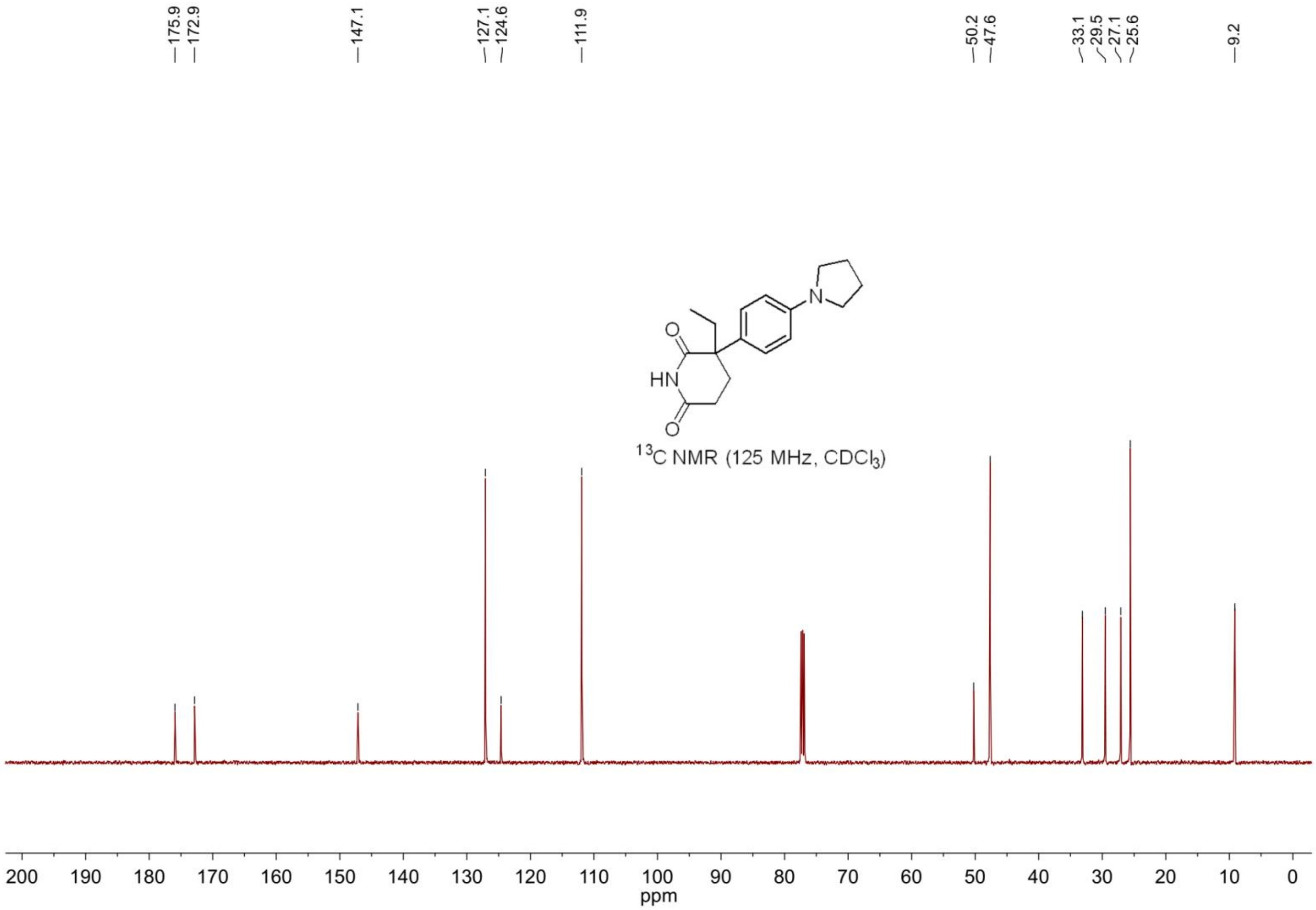
3-Ethyl-3-(4-(pyrrolidin-1-yl)phenyl)piperidine-2,6-dione (106)



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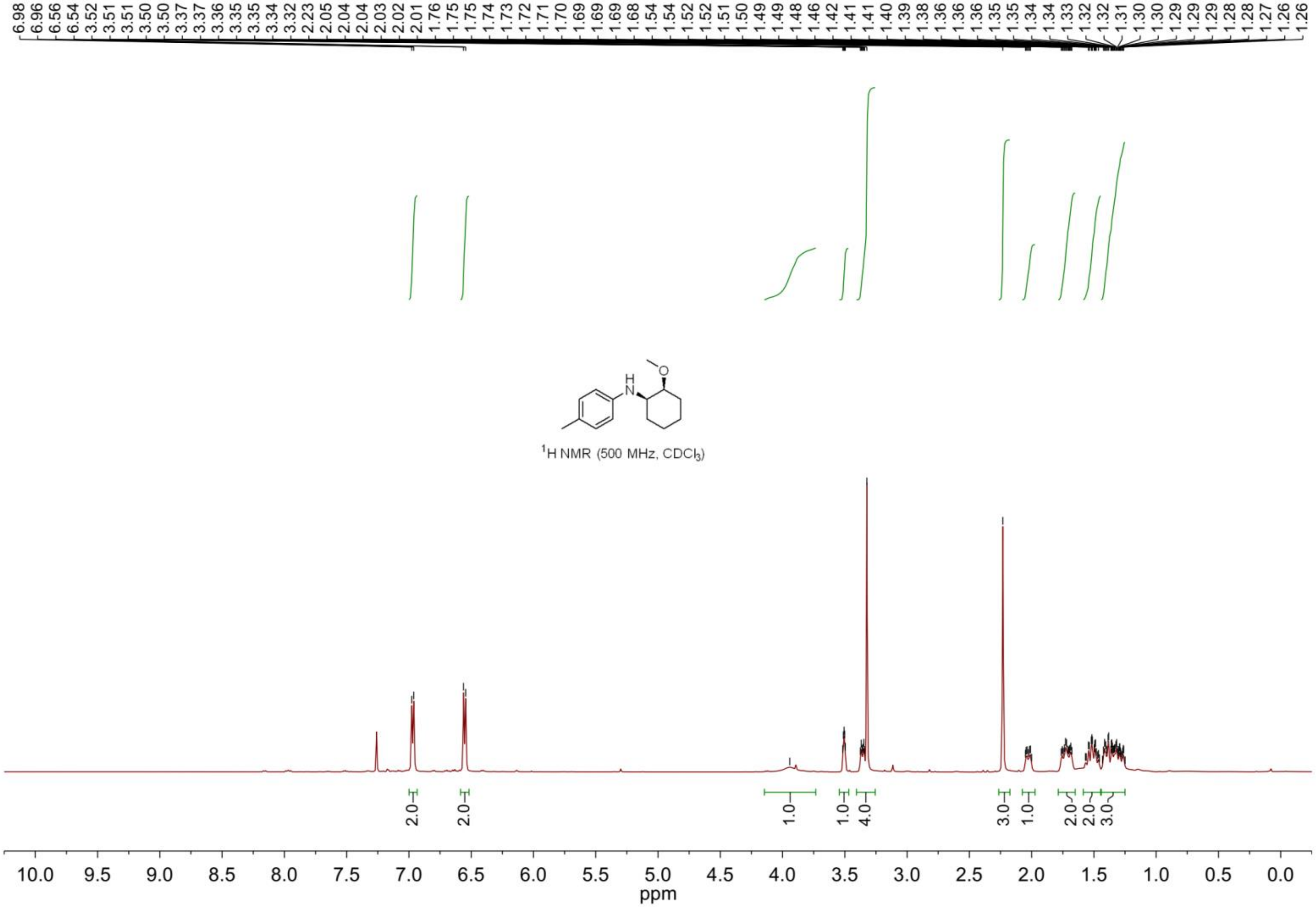
N-(-2-Methoxycyclohexyl)-4-methylaniline (S5)



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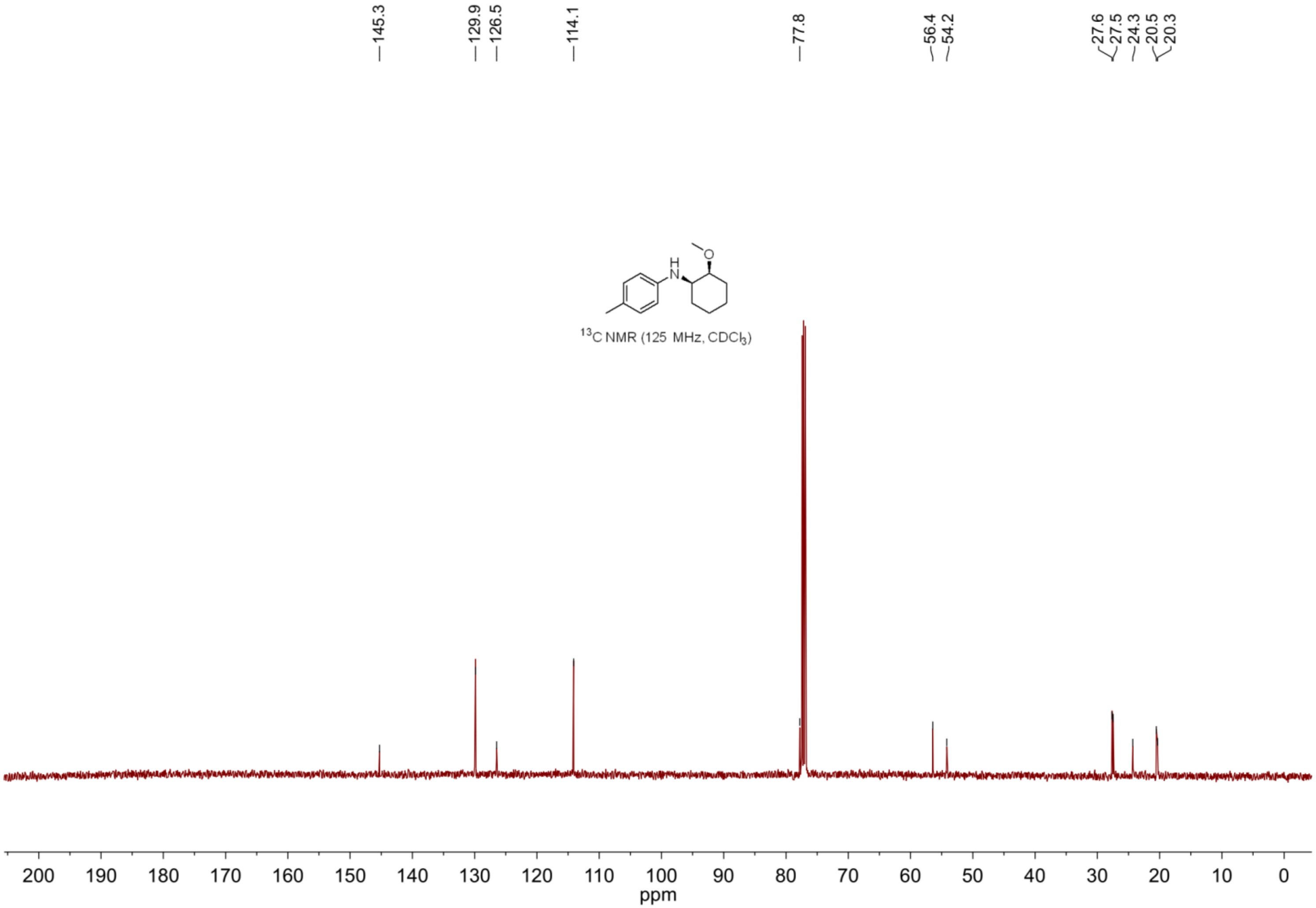
4-Methyl-*N*-((1*S**,2*S**)-2-methylcyclohexyl)aniline (S5)



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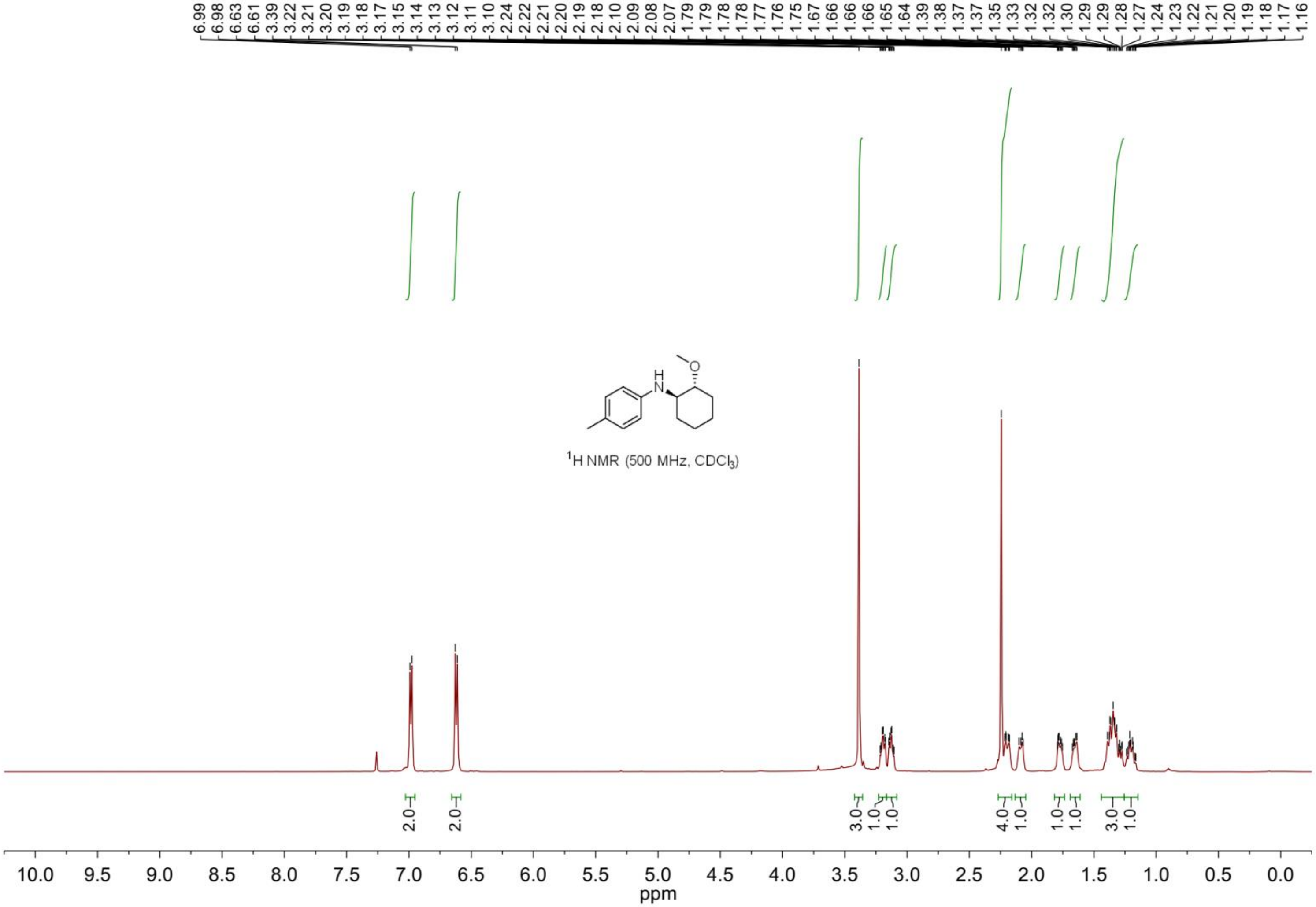
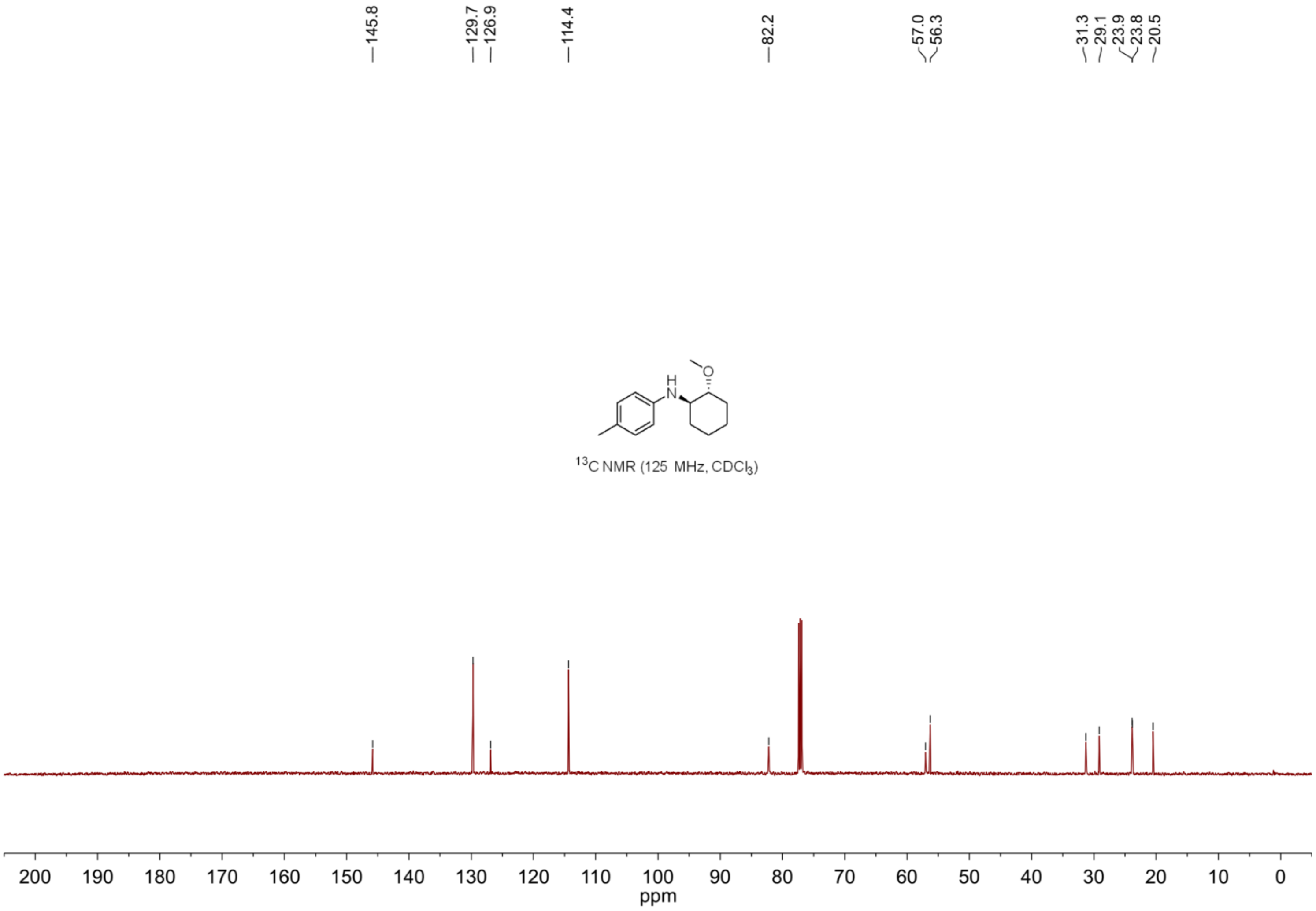


4-Methyl-*N*-((1*S**,2*S**)-2-methylcyclohexyl)aniline (S5)



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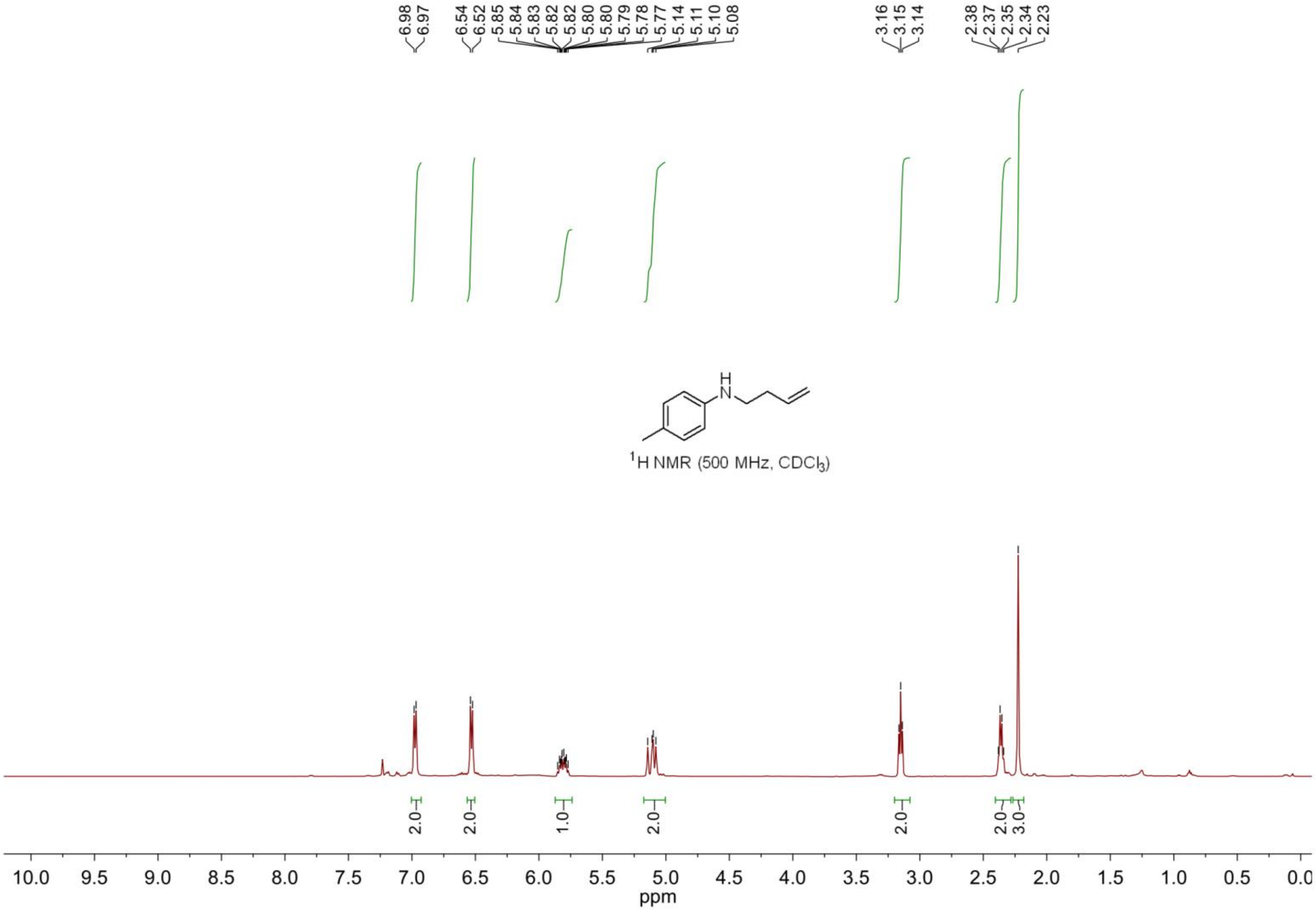
N-(But-3-en-1-yl)-4-methylaniline (S6)



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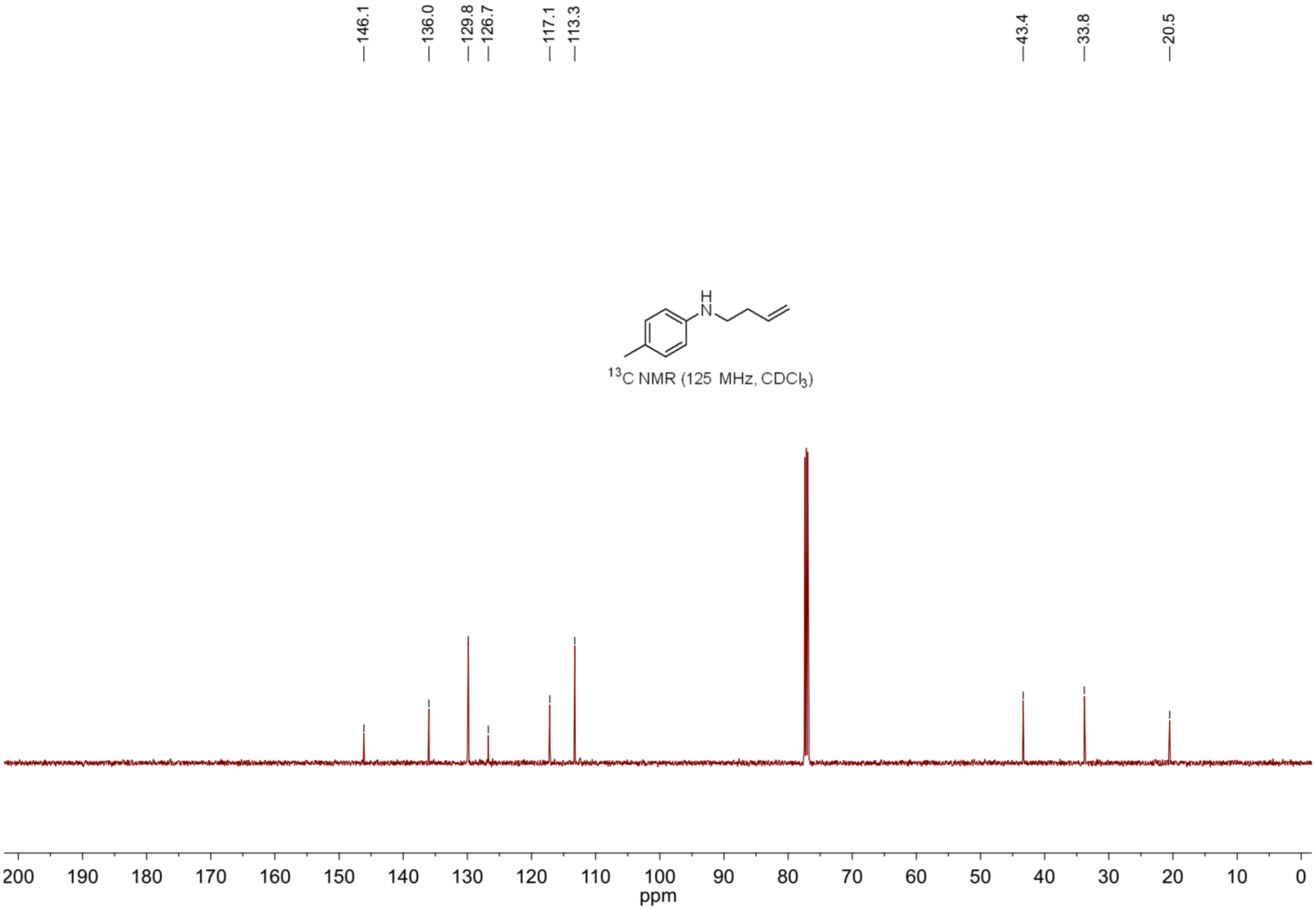
N-(But-3-en-1-yl)-4-methylaniline (S6)



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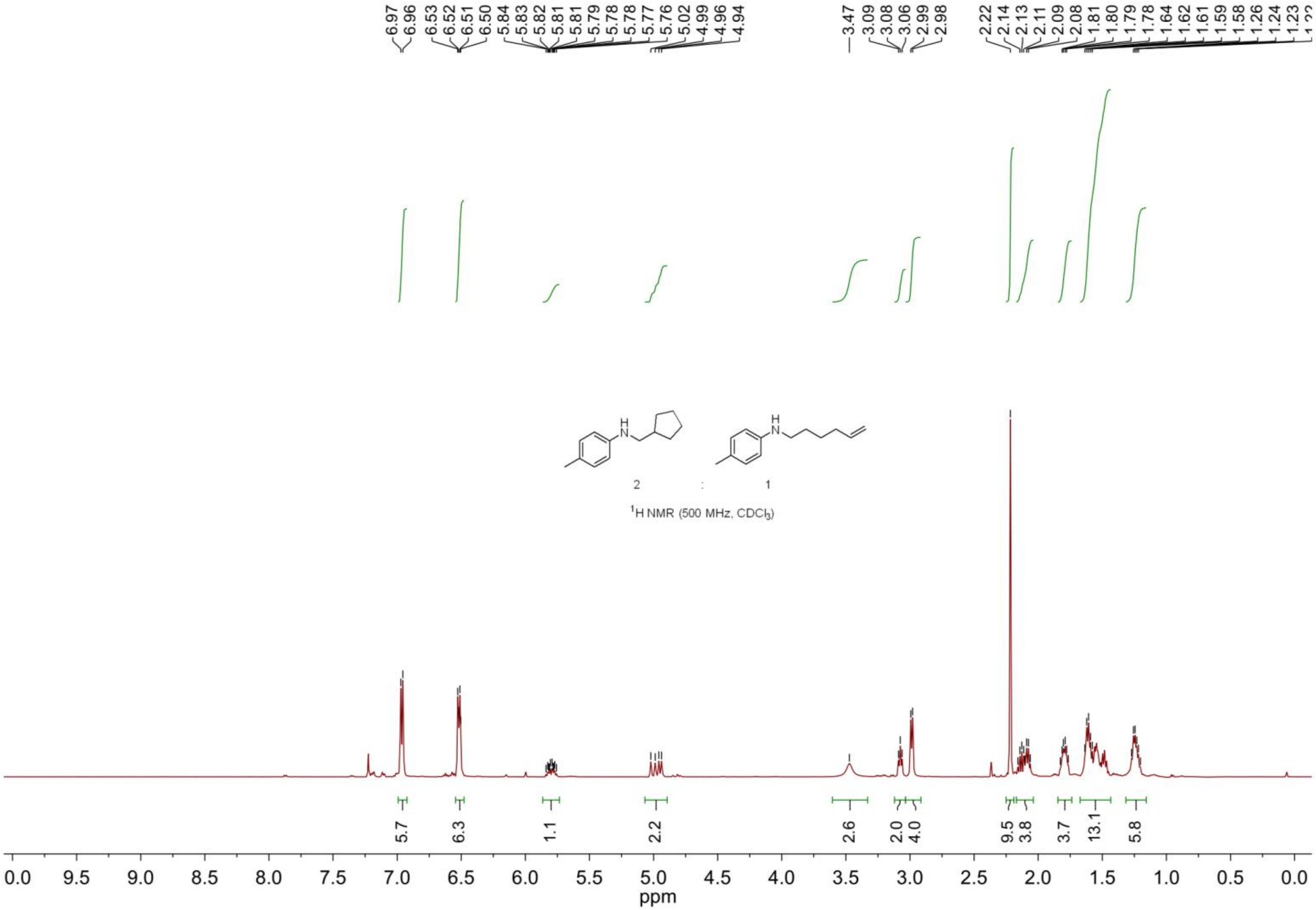
N-(Cyclopentylmethyl)-4-methylaniline (S7) and *N*-(hex-5-en-1-yl)-4-methylaniline (S8)



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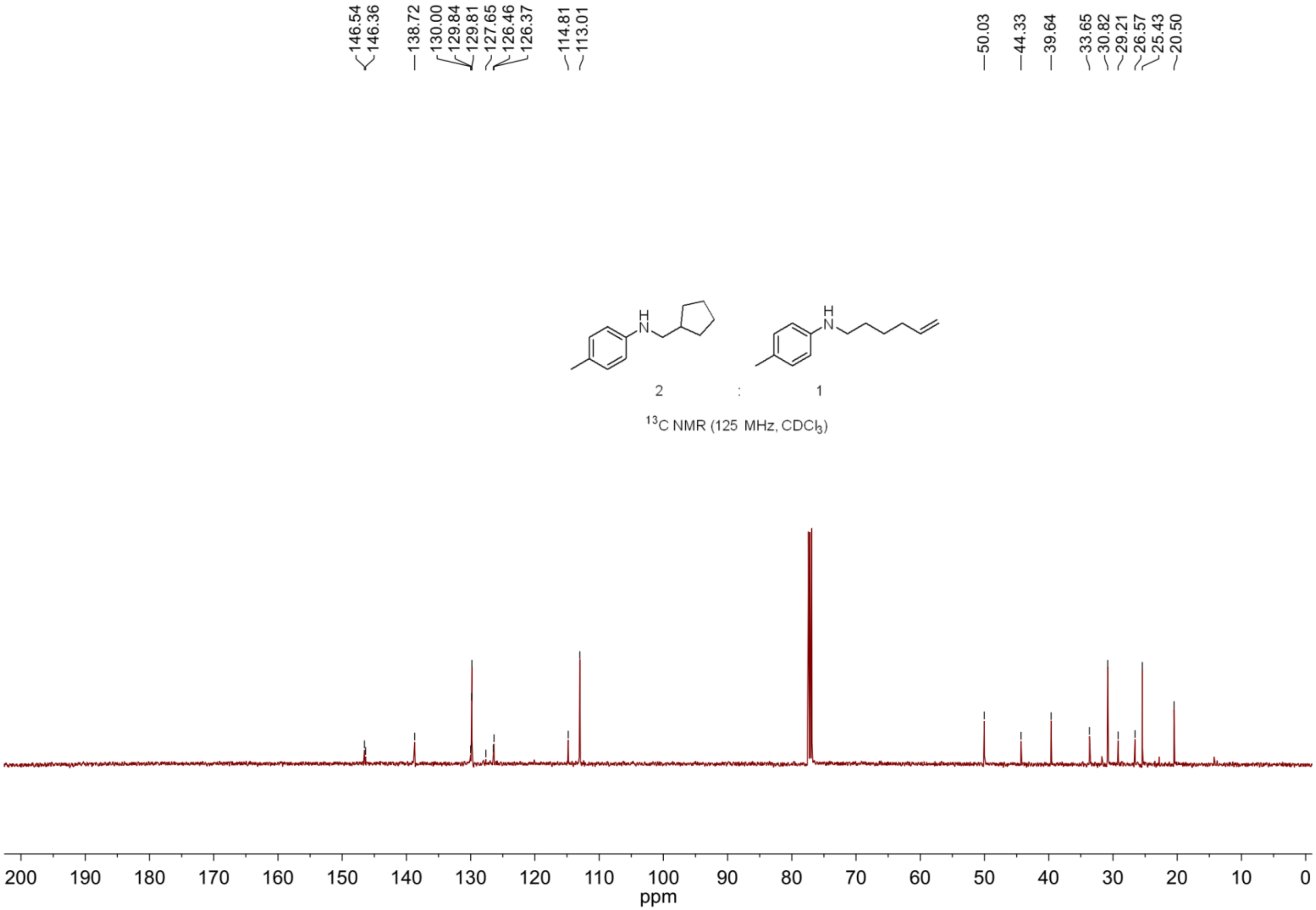
N-(Cyclopentylmethyl)-4-methylaniline (S7) and *N*-(hex-5-en-1-yl)-4-methylaniline (S8)



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References

[1] V. T. Nguyen, V. D. Nguyen, G. C. Haug, H. T. Dang, S. Jin, Z. Li, C. Flores-Hansen, B. S. Benavides, H. D. Arman, O. V. Larionov, *ACS Catal.* **2019**, *9*, 9485–9498.

[2] G. G. Liñares, M. A. Zígolo, L. Simonetti, S. A. Longhi, A. Baldessari, *Bioorg. Med. Chem.* **2015**, *23*, 4804–4814.

[3] E. M. Espinoza, J. A. Clark, J. Soliman, J. B. Derr, M. Morales, V. I. Vullev. *J. Electrochem. Soc.* **2019**, *166*, H3175–H3187.

[4] M. Neus Piña, B. Soberats, C. Rotger, P. Ballester, P. M. Deyà, A. Costa, *New J. Chem.* **2008**, *32*, 1919–1923.

[5] M. Agorrody, *Can. J. Chem.* **1987**, *65*, 694–700.

[6] C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, *91*, 165–195.

[7] O. Kronja, M. Biruš, M. Saunders, *J. Chem. Soc.*, *Perkin Trans. 2*, **1999**, 1375–1379.

[8] For a similar approach to the analysis of the carbocationic and radical pathways of decarboxylative functionalization, see: S. Shibutani, T. Kodo, M. Takeda, K. Nagao, N. Tokunaga, Y. Sasaki, H. Ohmiya, *J. Am. Chem. Soc.* **2020**, *142*, 1211–1216.

[9] Y. Sunesson, E. Limé, S. O. Nilsson Lill, R. E. Meadows, P.-O. Norrby, *J. Org. Chem.* **2014**, *79*, 11961**–**11969.

[10] (a) H. Kawai, W. J. Wolf, A. G. DiPasquale, M. S. Winston, F. D. Toste, *J. Am. Chem. Soc.* **2016**, *138*, 587–593. (b) J. H. Kim, R. T. Mertens, A. Agarwal, S. Parkin, G. Berger, S. G. Awuah, *Dalton Trans.* **2019**, *48*, 6273–6282.

[11] R. Mao, A. Frey, J. Balon, X. Hu, *Nat. Catal.* **2018**, *1*, 120–126.

[12] G. M. Bisset, V. Bavetsias, T. J. Thornton, K. Pawelczak, A. H. Calvert, L. R. Hughes, A. L. Jackman, *J. Med. Chem.* **1994**, *37*, 3294–3302.

[13] W. Yao, L. He, D. Han, A. Zhong, *J. Org. Chem.* **2019**, *84*, 14627–14635.

Go back to table of contents

[14] R. Arundhathi, D. C. Kumar, B. Sreedhar, *Eur. J. Org. Chem.* **2010**, *19*, 3621–3630.

[15] J. Dong, Z. Wu, Z. Liu, P. Liu, P. Sun, *J. Org. Chem.* **2015**, *80*, 12588–12593.

[16] W. Yamakoshi, M. Arisawa, K. Murai, *Org. Lett.* **2019**, *21*, 3023–3027.

[17] I. I. Jevtić, L. Došen-Mićović, E. R. Ivanović, M. D. Ivanović, *Synthesis* **2016**, *48*, 1550–1560.

[18] C. Uncuta, T. S. Balaban, A. Petride, F. Chiraleu, A. T. Balaban, *Rev. Roum. Chim.* **1989**, *34*, 1425–1437.

[19] X. Ding, M. Huang, Z. Yi, D. Du, X. Zhu, Y. Wan, *J. Org. Chem.* **2017**, *82*, 5416–5423.

[20] C. Li, Y. Kawamata, H. Nakamura, J. C. Vantourout, Z. Liu, Q. Hou, D. Bao, J. T. Starr, J. Chen, M. Yan, P. S. Baran, *Angew. Chem., Int. Ed.* **2017**, *56*, 13088–13093.

[21] C. L. Bailey, A. Y. Joh, Z. Q. Hurley, C. L. Anderson, B. Singaram, *J. Org. Chem.* **2016**, *81*, 3619–3628.

[22] S. Bayindir, E. Erdogan, H. Kilic, O. Aydin, N. Saracoglu, *J. Heterocycl. Chem.* **2015**, *52*, 1589–1594.

[23] J. Cheng, X. Deng, G. Wang, Y. Li, X. Cheng, G. Li, *Org. Lett.* **2016**, *18*, 4538–4541.

[24] I. Sorribes, J. R. Cabrero–Antonino, C. Vicent, K. Junge, M. Beller, *J. Am. Chem. Soc.* **2015**, *137*, 13580–13587.

[25] P. Weber, T. Scherpf, I. Rodstein, D. Lichte, L. T. Scharf, L. J. Gooßen, V. H. Gessner, *Angew. Chem., Int. Ed.* **2019**, *58*, 3203–3207.

[26] E. R. Biehl, A. Razzuk, M. V. Jovanovic, S. P. Khanapure, *J. Org. Chem.* **1986**, *51*, 5157–5160.

[27] Z. Qiu, J. S. Li, C. J. Li, *Chem. Sci.* **2017**, *8*, 6954–6958.

[28] S. Huang, X. Hong, H. Z. Cui, Q. Zhou, Y. J. Lin, X. F. Hou, *Dalton Trans.* **2019**, *48*, 5072–5082.

Go back to table of contents

[29] F. Hollywood, B. Nay, E. F. Scriven, H. Suschitzky, Z. U. Khan, R. Hull, *J. Chem. Soc., Perkin Trans. 1* **1982**, 421–429.

[30] V. I. Uzgiris, P. E. Graves, H. A. Salhanick, *Biochemistry* **1977**, *16*, 593–600.

[31] J. P. Dinnocenzo, S. B. Karki, J. P. Jones, *J. Am. Chem. Soc.* **1993**, *115*, 7111–7116.

[32] Y. Ma, X. Yao, L. Zhang, P. Ni, R. Cheng, J. Ye, *Angew. Chem., Int. Ed. Engl.* **2019**, *58*, 16548–16552.

[33] H. L. Li, Y. Kuninobu, M. Kanai, *Angew. Chem., Int. Ed.* **2017**, *56*, 1495–1499.

[34] V. H. Tran, M. T. La, H. K. Kim, *Tetrahedron Lett.* **2019,** *60*, 1860–1863.

[35] K. Matsumoto, S. Takeda, T. Hirokane, M. Yoshida, *Org. Lett.* **2019**, *21*, 7279–7283.

[36] Y. Feng, M. I. Hussain, X. Zhang, J. Shi, W. Hu, Y. Xiong, *Tetrahedron* **2018**, *74*, 2669–2676.

[37] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, Jr. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, in *Gaussian 16*, Revision B.01, Gaussian, Inc., Wallingford CT, **2016**.

Go back to table of contents

[38] Texas Advanced Computing Center (TACC), The University of Texas at Austin.

[39] Chemcraft – graphical software for visualization of quantum chemistry computations. https://www.chemcraftprog.com.

[40] C. Y. Legault in *CYLview*, 1.0b Université de Sherbrooke, **2009** (http://www.cylview.org).

[41] Y. Zhao, D. G. Truhlar, *J. Chem. Phys.* **2006**, *125*, 194101–194118.

[42] K. Eichkorn, F. Weigend, O. Truetler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119–124.

[43] F. Weigend, *Phys. Chem. Chem. Phys*. **2006**, *8*, 1057–1065.

[44] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B.* **2009**, *113*, 6378–6396.

[45] (a) S. Niu, D. L. Huang, P. D. Dau, H. T. Liu, L. S. Wang, T. Ichiye, *J Chem Theory Comput.* **2014**, *10*, 1283–1291. (b) J. Jover, *Phys.Chem.Chem.Phys.* **2017**, *19*, 29344–29353.

[46] (a) R. A. Marcus, *J. Chem. Phys.* **1956**, *24*, 966–978. (b) R. A. Marcus, *J. Chem. Phys.* **1956**, *24*, 962–972. (c) R. A. Marcus, *J. Chem. Phys.* **1957**, *26*, 872–877. (d) N. S. Hush, *J. Chem. Phys.* **1958**, *28*, 962–972. (e) R. A. Marcus, *Can. J. Chem.* **1959**, *37*, 155–163. (f) N. S. Hush, *Trans. Faraday Soc.* **1961**, *57*, 557–580. (g) Marcus, R. A.; *Faraday Discuss. Chem. Soc.* **1982**, *74*, 7–15. (h) R. A. Marcus, N. Sutin, *Biochim. Biophys. Acta, Rev. Bioenerg.* **1985**, *811*, 265–322.

[47] C, Costentin, M. Robert, J.-M. Savéant, *J. Electroanal. Chem*. **2006**, *2*, 197–206.

[48] C. Costentin, M. Robert, J.-M. Saveant, C. Tard, *Phys. Chem. Chem. Phys.* **2011**, *13*, 5353–5358.

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