Supplementary Information

for

Photocatalytic (Hetero)Arylation of C(sp^3)–H Bonds with Carbon Nitride

Saikat Das, Kathiravan Murugesan, Gonzalo J. Villegas Rodríguez, Jaspreet Kaur, Joshua. P. Barham, Aleksandr Savateev, Markus Antonietti and Burkhard König*

*Correspondence: burkhard.koenig@ur.de

Table of Contents

1.		**General Information**	S1
2.		**Characterization of fresh mpg-CN photocatalyst**	S3
3.		**Description of general synthetic procedures**	S9
	3.1	Synthesis of mpg-CN photocatalyst	S9
	3.2	General procedure 1 (GP1) for Aryl Bromides	S9
	3.3	General procedure 2 (GP2) for Aryl Chlorides	S10
	3.4	General procedure 3 (GP3) for Heteroaryl Halides	S10
	3.5	General Procedure 4 (GP4) for C(sp3)−H arylation of amides	S11
	3.6	General Procedure 5 (GP5) for gram scale synthesis	S12
4.		**Optimization Studies**	S13
5.		**Scope and analytical data**	S16
6.		**Characterization of recovered mpg-CN photocatalyst**	S55
7.		**Mechanistic Considerations**	S64
8.		**Investigation of scalability in Continuous Flow reactors**	S66
9.		**Supplementary references**	S79
10.		**NMR Spectra**	S81

1. General information

All reactions were carried out with dry solvents unless otherwise stated. Dry nitrogen was used as inert gas atmosphere. All solvents and commercially available reagents were purchased as reagent grade or at the highest commercial quality and used without further purification, unless otherwise stated. Thin-layer chromatography was performed using silica gel plates 60 F254: Visualization was accomplished with short wavelength UV light (254 nm) and near UV light (366 nm) sources. Standard flash chromatography was performed on a Biotage® Isolera™ Spektra system automated with high performance flash purification system using either a pre-packed Biotage® SNAP Ultra HP-Sphere™ silica gel of particle size 25 μm or silica gel 60 M (particle size 40–63 μm, 230–440 mesh, Merck). Photocatalytic reactions were performed using TAK 120 photoreactor equipped with blue LEDs (OSRAM OSLON® SSL 80 GD CS8PM1.14 LEDs (λ= 451 nm (± 15 nm), 5 W optical power), unless stated otherwise. The optical power of LEDs was determined using FieldMaxII-TOTM laser power meter equipped with PM3 sensor. GC measurements were performed on a GC 7890 from Agilent Technologies. Data acquisition and evaluation was done with Agilent Chem Station Rev.C.01.04. GC–MS measurements were performed on a 7890A GC system from Agilent Technologies with an Agilent 5975 MSD Detector. Data acquisition and evaluation was done with MSD Chem Station E.02.02.1431. A capillary column HP-5MS/30 m x 0.25 mm/0.25 μM film and helium as carrier gas (flow rate of 1 mL/min) were used. The injector temperature (split injection: 40:1 split) was 280 °C, detection temperature 300 °C (FID). GC measurements were made and investigated via integration of the signal obtained. The GC oven temperature program was adjusted as follows: initial temperature 40 °C was kept for 3 minutes, the temperature was increased at a rate of 15 °C/min over a period of 16 minutes until 280 °C was reached and kept for 5 minutes, the temperature was again increased at a rate of 25 °C/min over a period of 48 seconds until the final temperature (300 °C) was reached and kept for 5 minutes. 1,4-dimethoxy benzene was used as an internal standard. All NMR spectra were measured at room temperature using a Bruker Avance 300 (300 MHz for ^{1}H, 75 MHz for ^{13}C, 282 MHz for ^{19}F) or a Bruker Avance 400 (400 MHz for ^{1}H, 101 MHz for ^{13}C, 376 MHz for ^{19}F) NMR spectrometer in $CDCl_3$, DMSO-*d6*, and MeOH-*d4* solutions with internal solvent signals (for ^{1}H and ^{13}C) as reference (7.26, 77.2 for $CDCl_3$, 2.50 and 39.5 for DMSO-*d6*, and 3.31, 49.0 for MeOH-*d4*). All chemical shifts are reported in δ-scale as parts per million [ppm] (multiplicity, coupling constant J, number of protons) relative to the solvent residual peaks as the internal standard. Coupling constants J are given in Hertz [Hz]. Abbreviations used for signal multiplicity: ^{1}H-NMR: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet dd = doublet of

doublets, dt = doublet of triplets, dq = doublet of quartets, and m = multiplet; ^{13}C-NMR: (+) = primary/tertiary, (–) = secondary, (Cq) = quaternary carbon. *Most of the characterized compounds gave double signals in ^{1}H ,^{13}C NMR and ^{19}F NMR, this is due to the rotamer nature of the amide compounds*. HRMS (high resolution mass spectra) and LRMS (low resolution mass spectra) were measured at the Central Analytical Laboratory of the University of Regensburg. These mass spectra were recorded on a Finnigan MAT 95, Thermo Quest Finnigan TSQ 7000, Finnigan MAT SSQ 710 A or an Agilent Q-TOF 6540 UHD instrument. Powder X-Ray diffraction (PXRD) patterns have been acquired using Bruker D8 diffractometer using radiation from Cu Kα (λ = 1.54060 nm) equipped with scintillation counter detector in the range of 2θ 3-60° with step size 0.05° and time per step 4 s. Scanning electron microscopy (SEM) and Energy Dispersive X-Ray Analysis (EDX) have been performed using JSM-7500F (JEOL) scanning electron microscope at accelerating voltage 3 kV. Inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima 8000; Perkin Elmer) was used to analyze Ni content in the samples. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Thermo Fisher Scientific ESCALAB spectrometer with aluminum Kα radiation. Data was processed using Origin 2020b. Shirley's background has been subtracted prior deconvolution of the peaks. Fourier-transform infrared spectra (ATR FT-IR) have been acquired in the range of wavelengths 550-4000 cm^{-1} using Nicolet iS5 equipped with attenuated total reflectance module iD5. Nitrogen sorption by the materials has been conducted at 77K using Quantasorb SI station. Prior measurements samples were degassed at 150ºC in vacuum (<0.2 mbar) for 15 h. Relative pressure range (P/P0) from 0.05 to 0.3 was used to calculate surface area of the materials employing Brunauer–Emmett–Teller (BET) theory model in Quantachrome ® QuadraWin™ v.5.11 software. N2 at 77K on carbon (slit/cylindric/sphere pores, quenched solid density functional theory (QSDFT), adsorption branch kernel) has been chosen to analyze pore diameter distribution. Diffuse-reflectance UV-vis (DRUV-vis) absorption spectra of the samples in solid state has been acquired using Shimadzu UV-2600 equipped with integrating sphere. Room temperature steady-state photoluminescence spectra of the samples upon excitation with 365 nm, have been acquired using Jasco FP-8300 spectrometer. Transmission electron microscopy (TEM) images were obtained on a double-corrected JEOL ARM200 at an acceleration voltage of 80 kV and an emission of 10 μA.

2. Characterization of fresh mpg-CN photocatalyst

The structure of the prepared mpg-CN has been confirmed by a series techniques and characterization results are in agreement with the reported earlier data.[1] EDX elemental composition revealed C/N ratio of 0.58 (**Table S1**), which is lower than expected for melon (i.e. 0.75) and is explained by the presence of terminal amino groups in the structure of mpg-CN due to incomplete condensation of the precursor and partially hydroxylated surface. In agreement with this conclusion is FT-IR spectrum (**Fig. S1**). A broad peak with maximum at 3180 cm^{-1} was assigned to N–H and hydrogen-bonded O–H stretch; a peak at 2180 cm^{-1} to nitrile stretch; a broad band between 1000-1650 cm^{-1} is assigned to vibrations of CN heterocycles. The peak at 805 cm^{-1} is assigned to deformation vibration of tri-*s*-triazine system. In addition, a peak at 1628 cm^{-1} was assigned to primary amine N–H bend; a peak at 1561 cm^{-1} to secondary amine N–H bend; and peaks at 1230, 1308, 1398 cm^{-1} to C-O stretch.

Table S1 | EDX elemental analysis

C wt. %	N wt. %	O wt. %
36±1.3	62±1.2	2±0.4

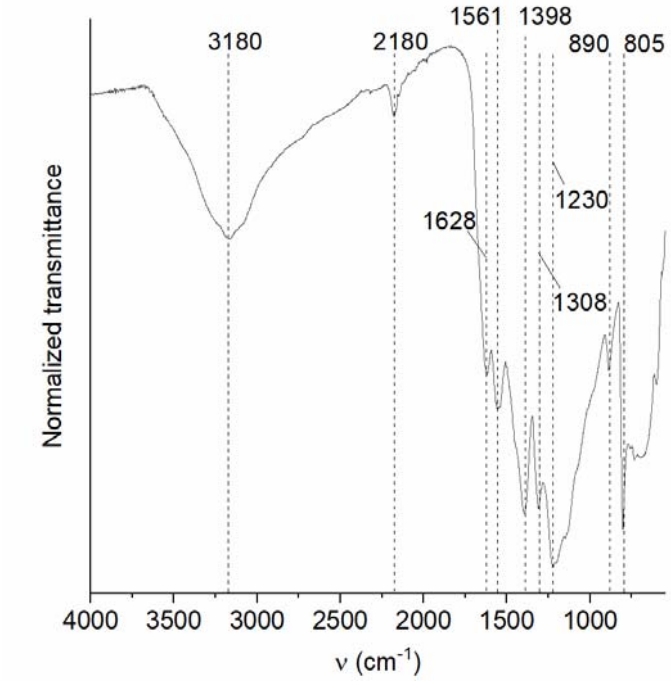


Fig. S1 | FT-IR spectrum of mpg-CN

Given that penetration depth in XPS is limited to ~5 nm, higher oxygen content (8.3 at. %) determined by this technique compared to EDX (2±0.4%), confirmed that oxygen is located mainly on the surface of the material (**Table S2**). Deconvolution of high-resolution X-Ray photoelectron spectrum of C 1s confirmed existence of this element in three chemical states (**Fig. S2**). The peak with maximum at 288.3 eV was assigned to carbon coordinated to nitrogen (CN_3) (**Fig. S2 and S3**),[2,3] peak at 286.2 eV to carbon bound to oxygen[4,5] and peak at 284.7 eV to adventitious carbon.[2,4,3] Deconvolution of high-resolution X-Ray photoelectron spectrum of N 1s revealed the following chemical states: peak at 398.8 eV was assigned to di-coordinated nitrogen of C=N-C moieties in tri-s-triazine (**Fig. S3 and S4**),[2,5,6] peak at 400.1 eV to the central nitrogen atom of tri-s-triazine,[2,6,3] peak at 401.3 eV to secondary and primary amino-groups in mpg-CN due to incomplete condensation,[2,7,3] and a broad peak of low intensity at 404.8 eV to π-π* satellite or π-excitation that is indicative for conjugated aromatic structures.[8,9] Deconvolution of high-resolution X-Ray photoelectron spectrum of O 1s revealed oxygen in two chemical states: the peak at 532.0 eV is assigned to oxygen bound to carbon (**Fig. S5**),[2] while the peak at 533.4 eV to water absorbed in mpg-CN.[2]

Table S2 | XPS elemental analysis

C at. %	N at. %	O at. %
29.1	64.8	6.1

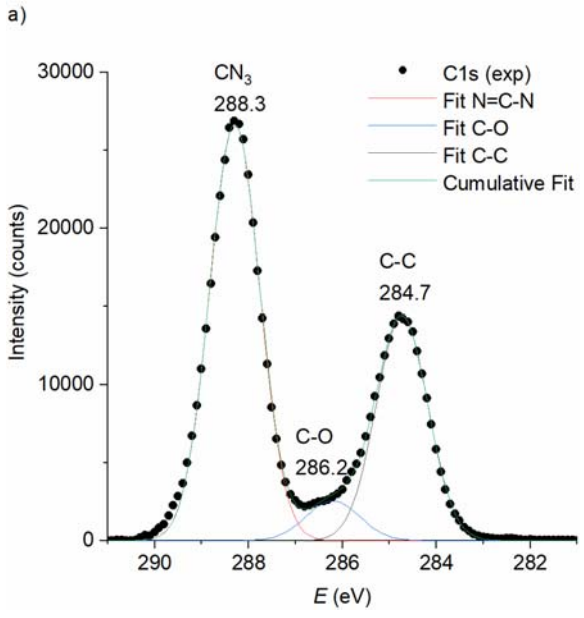


Fig. S2 | C 1s XPS of mpg-CN

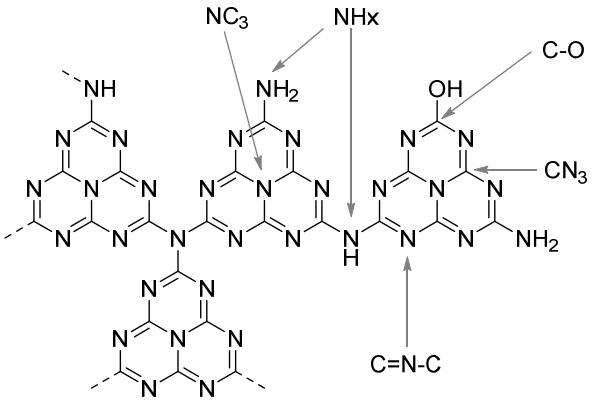


Fig. S3 | A fragment of mpg-CN structure based on characterization data

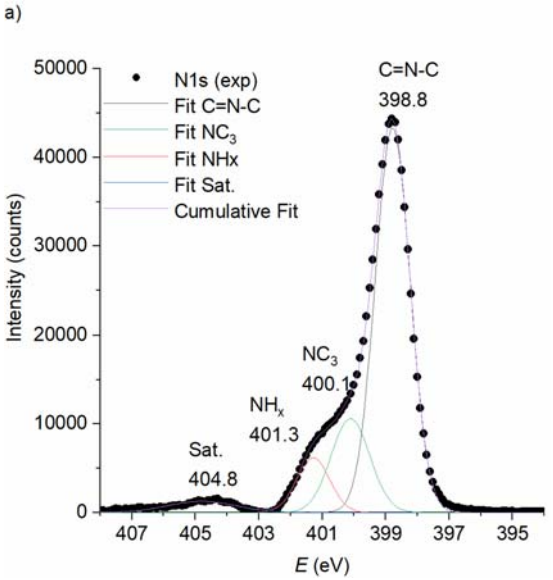


Fig. S4 | N 1s XPS of mpg-CN

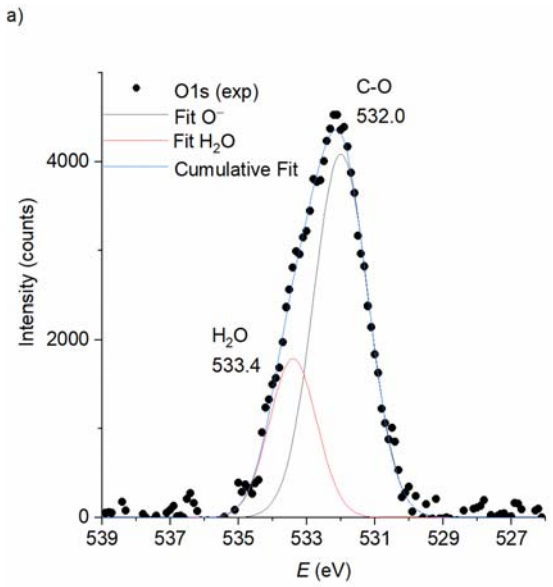


Fig. S5 | O 1s XPS of mpg-CN

Surface area of mpg-CN was determined from N_2 absorption isotherm to be 186 m^2g^{-1} (**Fig. S6a**). Mpg-CN features pores in the range from 5 to 44 nm and maximum at 13 nm (**Fig. S6b**). As evidenced by PXRD, mpg-CN is amorphous material (**Fig. S7**). The diffraction pattern features a peak at ~ 27° that is related to interplanar periodicity in the material with the distance between layers of ~0.326 nm.[10,11] Less pronounced peak at ~13° is assigned to intraplanar periodicity in the material with the corresponding distance of ~0.68 nm.

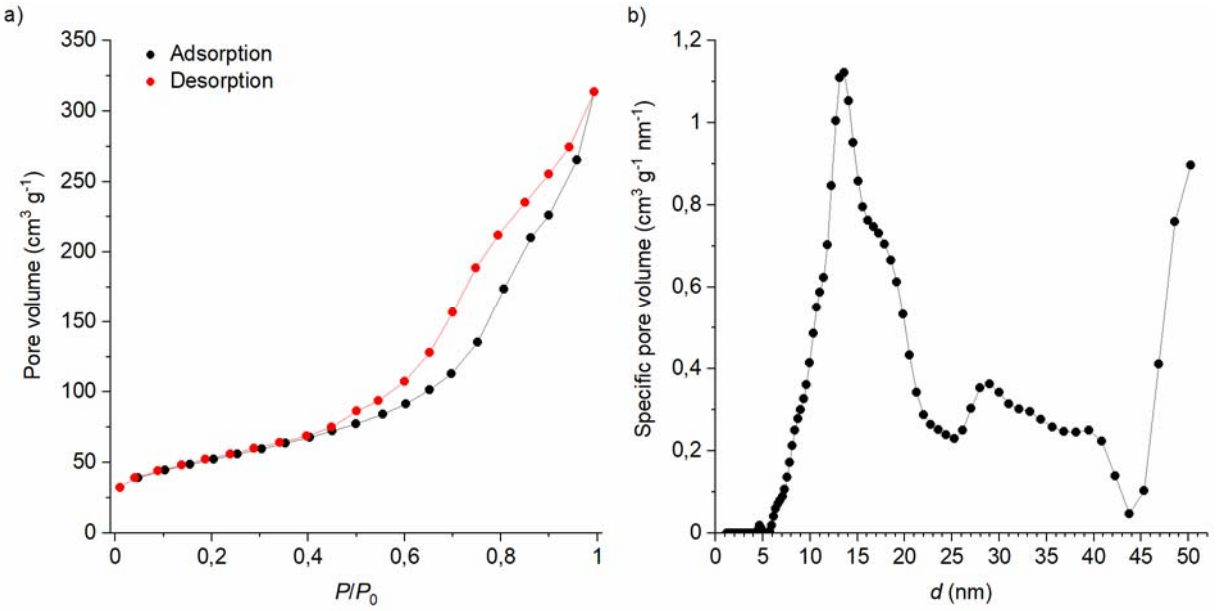


Fig. S6 | (a) N_2 sorption isotherm recorded at 77K and (b) pore size distribution in mpg-CN

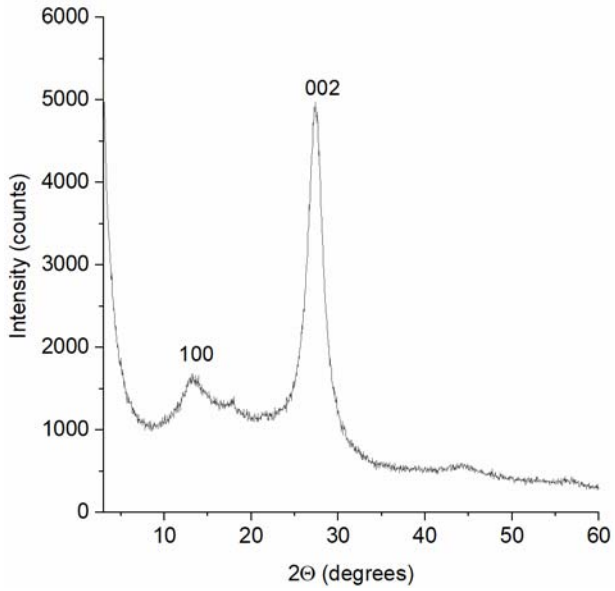


Fig. S7 | PXRD pattern of mpg-CN

DRUV-vis spectrum of mpg-CN features steep onset of absorption at ~460 nm that is related to electron transition between conduction and valence band, also known in literature as π-π* transitions, (**Fig. S8a**).[11] The optical band gap calculated from Tauc plot assuming that mpg-CN is a direct semiconductor is 2.7 eV (**Fig. S8b**).[11] A band at ~650 nm of lower intensity is assigned to n-π* transitions that involve N- and O-electron pairs (**Fig. S8a**).[12,13] mpg-CN features broad fluorescence signal with maximum at 508 nm related radiative recombination of photogenerated electrons and holes (**Fig. S9**).

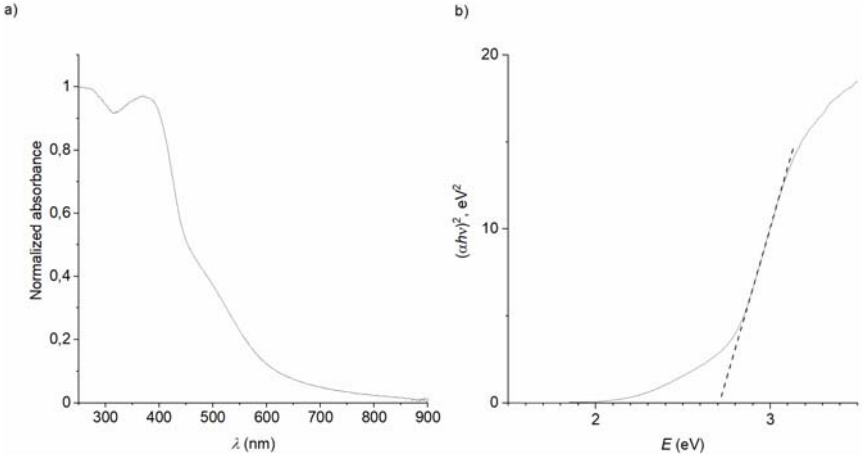


Fig. S8 | (a) DRUV-vis absorption spectrum and (b) Tauc plot of mpg-CN

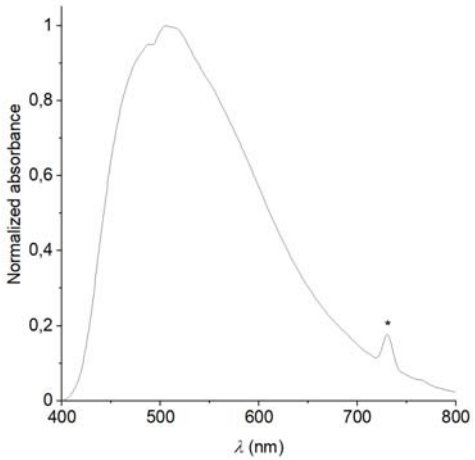


Fig. S9 | Steady state PL spectrum of mpg-CN. The sample was excited with λ = 365 nm. Asterisk denotes 2nd order excitation light diffraction.

Morphology of mpg-CN is represented by agglomerated particles with the dimeter ranging from few hundred nanometers to few micrometers (**Figure S10**). TEM image revealed mesoporous structure of the material with pores ranging from <10 nm up to ~25 nm (**Figure S11a**) that is consistent with the results of pore-size distribution analysis derived from N_2 sorption (**Figure S6b**). HR-TEM image and the results of the corresponding FFT analysis (**Figure S11b**)

confirmed PXRD data that mpg-CN is amorphous material, albeit possessing layered structure with the distance between layers of ~0.352 nm as seen from the profile analysis (**Figure S11c**).

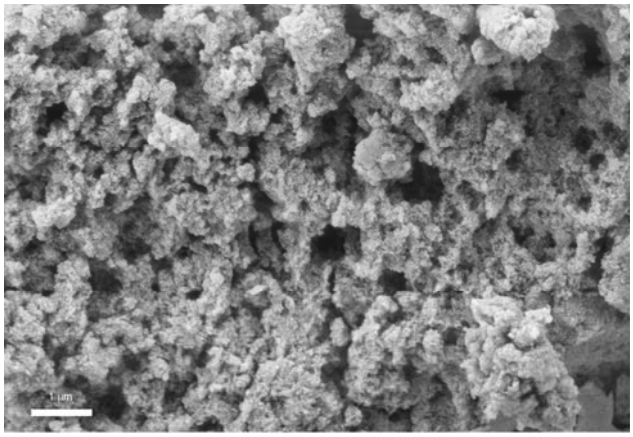


Fig. S10 | SEM image of mpg-CN

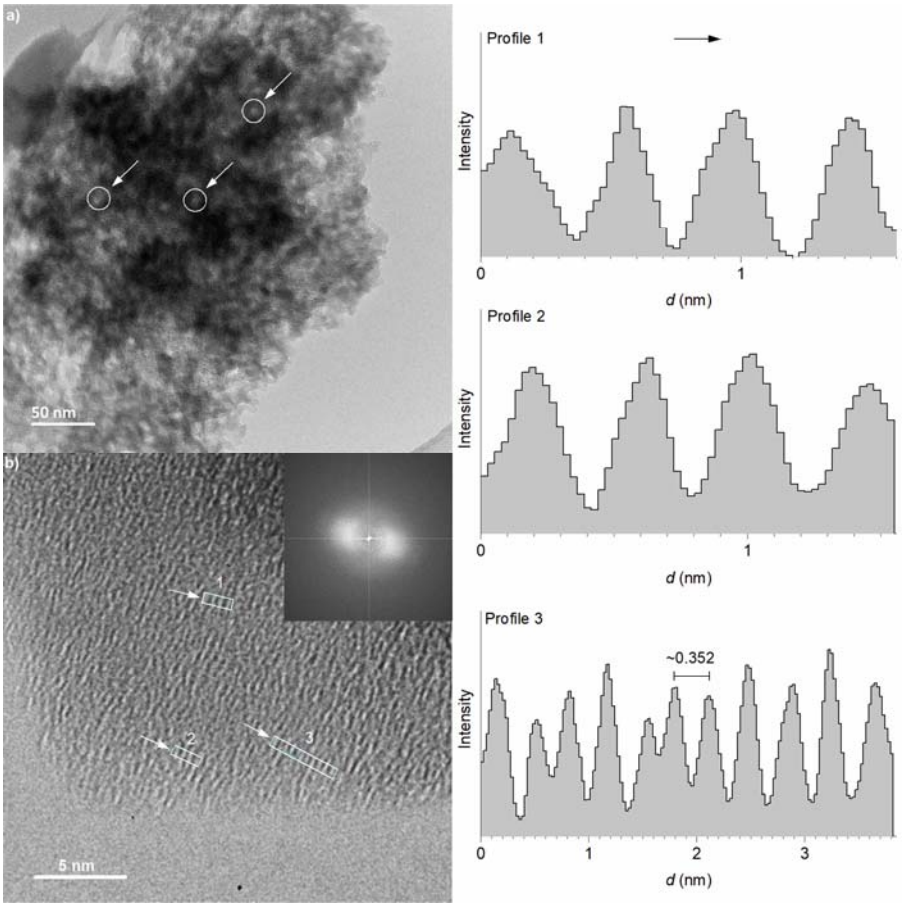


Fig. S11 | TEM image of mpg-CN. (a) Overview image. Circles mark pores in the structure of the material. (b) HR-TEM image of mpg-CN with Fast Fourier Transform (FFT) in inset. **Arrows** denote directions of view in profile analysis. (c) Profiles of the corresponding areas of HR-TEM image

3. Description of general synthetic procedures

3.1 Synthesis of mpg-CN photocatalyst

mpg-CN has been synthesized according to the reported literature procedure.[1]

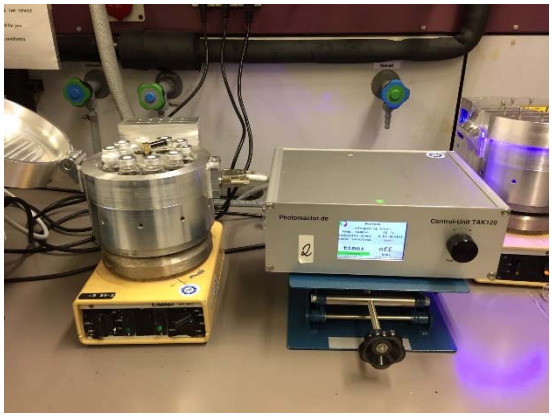
3.2 General procedure 1 (GP1) for Aryl Bromides

A 5 mL crimp vial equipped with a magnetic stirring bar was charged with, bromo arene (0.2 mmol, 1.0 equiv), mpg-CN (10.0 mg), $NiBr_2$•glyme (0.01 mmol, 5 mol%.) and 2,2′-bipyridine (0.01 mmol, 5 mol%). Subsequently, 1.0 mL of *N*,*N*-dimethylacetamide (DMA) was added followed by addition of 2,6-lutidine (0.6 mmol, 3.0 equiv). The vial was sealed, and the reaction mixture was then introduced to a nitrogen atmosphere via "*freeze-pump-thaw*" cycles (×3) with a syringe needle, keeping the vacuum approx. 5 mbar. After that the reaction mixture was irradiated with 5 W 455 (± 15) nm LEDs through the plane bottom side of the crimp vial (see **Fig. S12a** for the reaction set up) and stirred intensely. The temperature was maintained at 30 °C by cooling with built-in cooling fan. The reaction progress was monitored by GC or TLC analysis. After completion (approx. 48 h), the reaction mixture was transferred to a centrifuge tube (approx. 3 x 3 mL of ethyl acetate was used in order to transfer the reaction mixture completely), and the mixture was centrifuged at 4000 rpm (time approx. 1–10 minutes) until the heterogeneous photocatalyst mpg-CN precipitates. The supernatant liquid was collected in a separating funnel, and the solid in the centrifuge tube was washed three times using approx. 10 mL of ethyl acetate and added to the same separating funnel. Then, the mixture was washed with approx. 10 mL of distilled water and 5 mL of brine solution the organic layer was collected. The water layer was extracted again with ethyl acetate (2 x 10 mL). The combined organic layers were washed with 5 mL of 0.1N HCl solution and the organic layer was collected. The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuum. Purification of the crude product was achieved by flash column chromatography.

3.3 General procedure 2 (GP2) for Aryl Chlorides

A 5 mL crimp vial equipped with a magnetic stirring bar was charged with, chloro arene (0.2 mmol, 1.0 equiv), mpg-CN (10.0 mg), $NiCl_2$•glyme (0.01 mmol, 5 mol%.) and 2,2′-bipyridine (0.01 mmol, 5 mol%). Subsequently, 1.0 mL of *N*,*N*-dimethylacetamide (DMA) was added followed by addition of 2,6-lutidine (0.6 mmol, 3.0 equiv). The vial was sealed, and the reaction mixture was then introduced to a nitrogen atmosphere via "*freeze-pump-thaw*" cycles (×3) with a syringe needle, keeping the vacuum approx. 5 mbar. After that the reaction mixture was

irradiated with 5 W 455 (± 15) nm LEDs through the plane bottom side of the crimp vial (**Fig. S12a**) and stirred intensely. The temperature was maintained at 30 °C by cooling with built-in cooling fan. The reaction progress was monitored by GC or TLC analysis. After completion (approx. 72h), the reaction mixture was transferred to a centrifuge tube (approx. 3 x 3 mL of ethyl acetate was used in order to transfer the reaction mixture completely), and the mixture was centrifuged at 4000 rpm (time approx. 1–10 minutes) until the heterogeneous photocatalyst mpg-CN precipitates. The supernatant liquid was collected in a separating funnel, and the solid in the centrifuge tube was washed three times using approx. 10 mL of ethyl acetate and added to the same separating funnel. Then, the mixture was washed with approx. 10 mL of distilled water and 5 mL of brine solution the organic layer was collected. The water layer was extracted again with ethyl acetate (2 x 10 mL). The combined organic layers were washed with 5 mL of 0.1N HCl solution and the organic layer was collected. The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuum. Purification of the crude product was achieved by flash column chromatography.



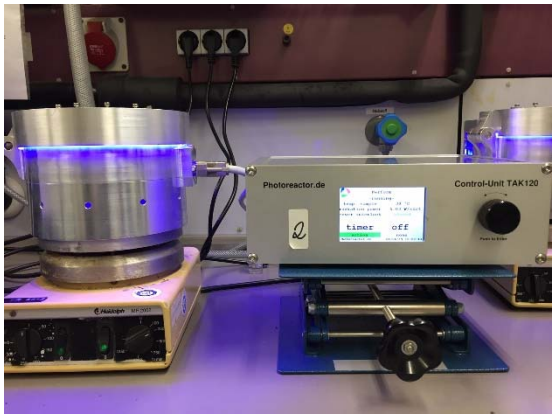


Fig. S12a | Photograph for the photochemical reaction set-up

3.4 General procedure 3 (GP3) for Heteroaryl Halides

A 5 mL crimp vial equipped with a magnetic stirring bar was charged with, halo (het)arene (0.2 mmol, 1.0 equiv), mpg-CN (10.0 mg), NiX_2•glyme (0.01 mmol, 5 mol%.) (in case of bromoarene $NiBr_2$•glyme and in case of chloro (het)arene $NiCl_2$•glyme) and 2,2′-bipyridine (0.01 mmol, 5 mol%). Subsequently, 1.0 mL of *N*,*N*-dimethylacetamide (DMA) was added followed by addition of 2,6-lutidine (0.6 mmol, 3.0 equiv). The vial was sealed, and the reaction mixture was then introduced to a nitrogen atmosphere via "*freeze-pump-thaw*" cycles (×3) with a syringe needle, keeping the vacuum approx. 5 mbar. After that the reaction mixture was irradiated with 5 W 455 (± 15) nm LEDs through the plane bottom side of the crimp vial (**Fig. 12a**) and stirred intensely. The temperature was maintained at 30 °C by cooling with built-in

cooling fan. The reaction progress was monitored by GC or TLC analysis. After completion (approx. 48-72h), the reaction mixture was transferred to a centrifuge tube (approx. 3 x 3 mL of ethyl acetate was used in order to transfer the reaction mixture completely), and the mixture was centrifuged at 4000 rpm (time approx. 1–10 minutes) until the heterogeneous photocatalyst mpg-CN precipitates. The supernatant liquid was collected in a round bottom flask, and the solid in the centrifuge tube was washed three times using approx. 10 mL of ethyl acetate and added to the same round bottom flask. The combined organic layers were directly concentrated under reduced pressure. Purification of the crude product was achieved by flash column chromatography.

3.5 General Procedure 4 (GP4) for C(sp^3)−H arylation of amides

A 5 mL crimp vial equipped with a magnetic stirring bar was charged with, chloro (het)arene (0.2 mmol, 1.0 equiv), mpg-CN (10.0 mg), $NiCl_2$•glyme (0.01 mmol, 5 mol%.) and 2,2′-bipyridine (0.01 mmol, 5 mol%). Subsequently, 1.0 mL of C-H precursors (for those which can be used as solvents, otherwise, 2.0 mmol, 10 equiv. of C-H precursors in combination with 0.8 mL of CH_3CN as solvent and 10 mol% tetrabutylammonium chloride as an additive) was added followed by addition of 2,6-lutidine (0.6 mmol, 3.0 equiv). The vial was sealed, and the reaction mixture was then introduced to a nitrogen atmosphere via "*freeze-pump-thaw*" cycles (×3) with a syringe needle, keeping the vacuum approx. 5 mbar. After that the reaction mixture was irradiated with 5 W 455 (± 15) nm LEDs through the plane bottom side of the crimp vial (**Fig. S12a**) and stirred intensely. The temperature was maintained at 30 °C by cooling with built-in cooling fan. The reaction progress was monitored by GC or TLC analysis. After completion (approx. 72h), the reaction mixture was transferred to a centrifuge tube (approx. 3 x 3 mL of ethyl acetate was used in order to transfer the reaction mixture completely), and the mixture was centrifuged at 4000 rpm (time approx. 1–10 minutes) until the heterogeneous photocatalyst mpg-CN precipitates. The supernatant liquid was collected in a separating funnel, and the solid in the centrifuge tube was washed three times using approx. 10 mL of ethyl acetate and added to the same separating funnel. Then, the mixture was washed with approx. 10 mL of distilled water and 5 mL of brine solution the organic layer was collected. The water layer was extracted again with ethyl acetate (2 x 10 mL). The combined organic layers were washed with 5 mL of 0.1N HCl solution and the organic layer was collected. The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuum. Purification of the crude product was achieved by flash column chromatography.

3.6 General Procedure 5 (GP5) for gram scale synthesis

A custom-made glass-photoreactor (“Tauchschachtreaktor”) was charged with a magnetic stirring bar, the bromoarene (6.0 mmol, 1.0 equiv.), mpg-CN (150.0 mg), and $NiBr_2$•glyme (0.3 mmol, 5 mol%.) and 2,2′-bipyridine (0.3 mmol, 5 mol%). Subsequently, 60 mL of *N*,*N*-dimethylacetamide (DMA) (c = 0.1 M) was added followed by addition of 2,6-lutidine (12 mmol, 2.0 equiv). The reaction mixture was placed in a nitrogen atmosphere via "*freeze-pump-thaw*" cycles (×3). The reaction mixture was then irradiated at 25 °C under nitrogen atmosphere using blue LED arrays (OSRAM Oslon SSL 80 LT-2010, λ = 451 nm, 700 mA) generating a total radiant flux of 12 W (**Fig. 12b**) and stirred intensely. After completion (approx. 60h), the reaction mixture was transferred to a centrifuge tube (approx. 5 X 15 mL of ethyl acetate was used in order to transfer the reaction mixture completely), and the mixture was centrifuged until the mpg-CN precipitates. The supernatant liquid was then collected in a separating funnel, and the solid in the centrifuge tube was washed 5 times using approx. 15 mL ethyl acetate and the solvent added to the same separating funnel. Then, approx. 60 mL of brine solution was added, shaken, and the organic layer was collected. The water layer was extracted with ethyl acetate (3 X 15 mL). The combined organic layers were washed with 60 mL of 0.1 N HCl solution, the organic layer was collected and dried over $MgSO_4$, filtered and concentrated in vacuum. Purification of the crude product by column chromatography.

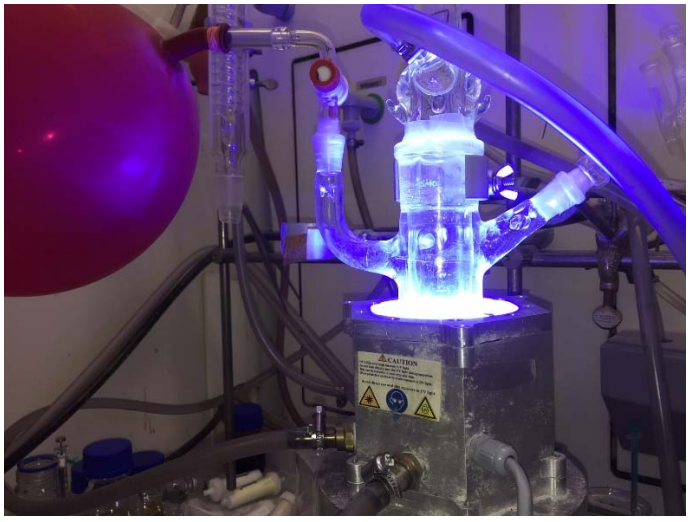
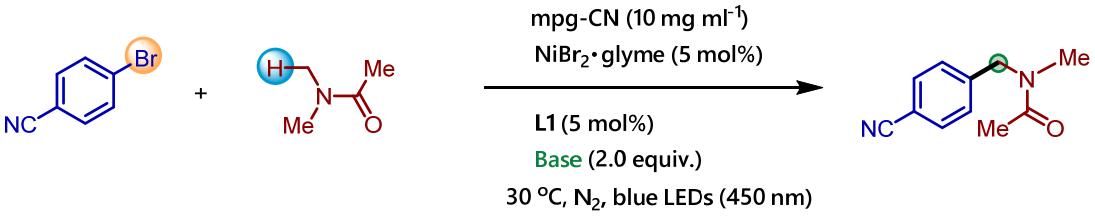


Fig. S12b | Photograph for the large-scale photochemical reaction set-up (‘‘Tauchschacht Photoreactor’’)

4. Optimization Studies

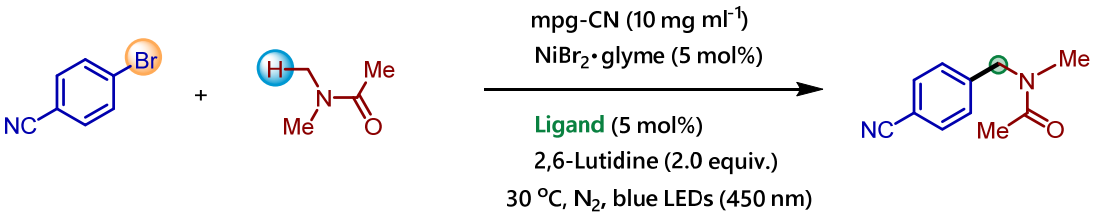
Table S3 | Screening of Bases



Entry[a]	Base	Yield[b]
1.	K_2CO_3	11%
2.	K_3PO_4	13%
3.	K_2HPO_4	16%
4.	DABCO	12%
5.	DBU	15%
6.	DBN	<5%
7.	2,6-Lutidine	52%
8.	2,4,6-Collindine	34%
9.	Pyridine	28%
10.	DMAP	18%

[a]Reaction Condition: 4-bromobenzonitrile (0.2 mmol, 36.4 mg), mpg-CN (10 mg), $NiBr_2$·glyme (5 mol%, 3.2 mg), **L1** (5 mol%, 2.7 mg), Base (2.0 equiv.), DMA (1 mL) under nitrogen atmosphere and blue light irradiation for 48 h. [b]Yields were determined by GC-FID using 1,4-dimethoxybenzene as internal standard.

Table S4 | Screening of Ligands



Entry[a]	Ligand	Yield[b]
1.	**L1**	52%
2.	**L2**	43%
3.	**L3**	54%
4.	**L4**	28%
5.	**L5**	65%
6.	**L6**	74%
7.	**L7**	22%
8.	**L8**	72%
9.	**L9**	13%

[a]Reaction Condition: 4-bromobenzonitrile (0.2 mmol, 36.4 mg), mpg-CN (10 mg), $NiBr_2$·glyme (5 mol%, 3.2 mg), **Ligand** (5 mol%), 2,6-lutidine (48 µL, 2.0 equiv.), DMA (1 mL) under nitrogen atmosphere and blue light irradiation for 48 h. [b]Yields were determined by GC-FID using 1,4-dimethoxybenzene as internal standard.

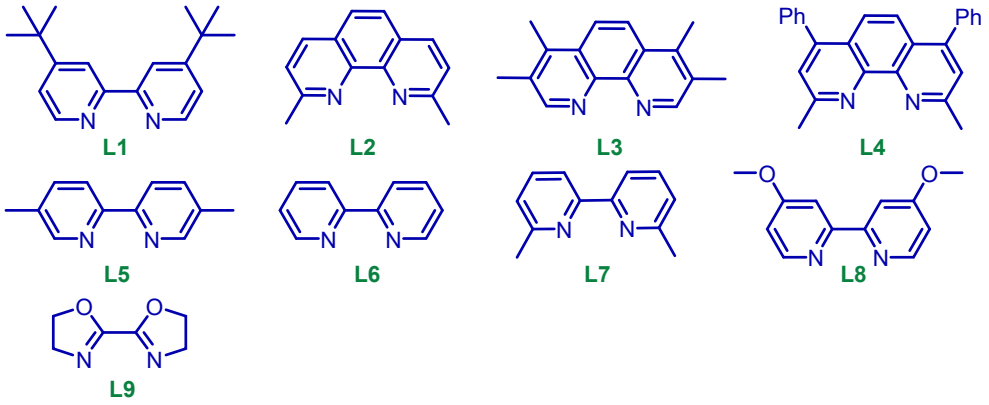
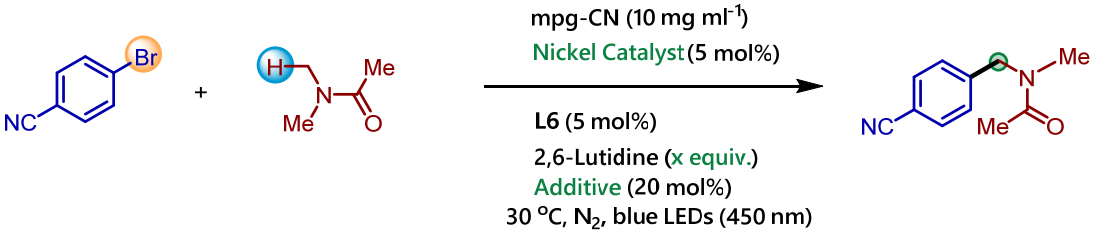


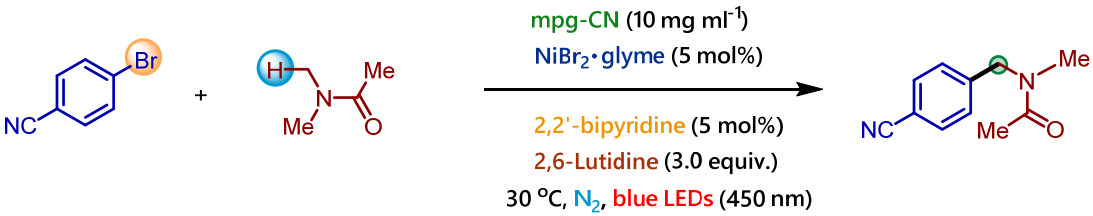
Table S5 | Screening of Additives and other variables



Entry[a]	Nickel source	Base	Additive	Yield[b]
1.	$NiBr_2$·glyme	2,6-Lutidine	NaBr	48%
2.	$NiBr_2$·glyme	2,6-Lutidine	CBr_4	<5%
3.	$NiBr_2$·glyme	2,6-Lutidine	TBAB[c]	7%
4.	$NiBr_2$·glyme	2,6-Lutidine (1.2 equiv.)	-	62%
5.	$NiBr_2$·glyme	2,6-Lutidine (3.0 equiv.)	-	90% (85%)[d]
6.	$NiBr_2$	2,6-Lutidine (3.0 equiv.)	-	18%
7.	$NiBr_2 \cdot 3H_2O$	2,6-Lutidine (3.0 equiv.)	-	72%
8.	$Ni(bpy)_3Br_2$	2,6-Lutidine (3.0 equiv.)	-	46%

[a]Reaction Condition: 4-bromobenzonitrile (0.2 mmol, 36.4 mg), mpg-CN (10 mg), Nickel catalyst (5 mol%), **L6** (5 mol%, 1.6 mg), 2,6-lutidine, DMA (1 mL) under nitrogen atmosphere and blue light irradiation for 48 h. [b]Yields were determined by GC-FID using 1,4-dimethoxybenzene as internal standard. [c]TBAB = Tetrabutyl ammonium bromide. [d]Yield of the isolated product.

Table S6 | Control Experiments

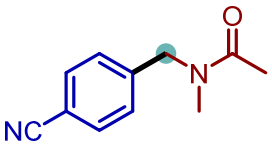


Entry[a]	Conditions	Yield[b]
1.	Without mpg-CN	ND
2.	Without $NiBr_2$·glyme	ND
3.	Without 2,2'-bipyridine	<5%
4.	Without 2,6-Lutidine	11%
5.	Without Light	ND
6.	Without degassing & N_2	74%
7.	Under air	60%

[a]Reaction Condition: 4-bromobenzonitrile (0.2 mmol, 36.4 mg), mpg-CN (10 mg), Nickel catalyst (5 mol%), 2,2'-bipyridine (5 mol%, 1.6 mg), 2,6-lutidine, DMA (1 mL) under nitrogen atmosphere and blue light irradiation for 48 h. [b]Yields were determined by GC-FID using 1,4-dimethoxybenzene as internal standard. ND, Not detected.

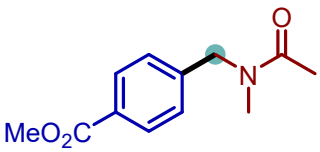
5. Scope and analytical data

_N_-(4-cyanobenzyl)-_N_-methylacetamide (1)



The compound was prepared according to the **General Procedure 1** using 4-bromobenzonitrile (36.4 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 85% yield (31.9 mg). Following the **General Procedure 2** the same compound was synthesized from 4-chlorobenzonitrile (27.4 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiCl_2$•glyme (2.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol) with an isolated yield of 89% (33.4 mg). Following the **General Procedure 5** the same compound was synthesized from 4-bromobenzonitrile (1.1 g, 6.0 mmol) with an isolated yield of 83% (936 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, J = 8.2 Hz) & 7.61 (d, J = 8.2 Hz, 2H combined), 7.34 (d, J = 8.1 Hz) & 7.29 (d, J = 8.1 Hz, 2H combined), 4.62 (s) & 4.59 (s, 2H combined), 2.96 (s) & 2.94 (s, 3H combined), 2.17 (s) & 2.12 (s, 3H combined). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0 & 170.9, 142.9 &142.1, 132.8 & 132.4, 128.4 &126.9, 118.7 & 118.4, 111.3 & 111.2, 53.9 & 50.6, 35.9 & 33.9, 21.7 & 21.4. HRMS (APCI): *m/z* calculated. for $C_{11}H_{13}N_2O$ $[M+H]^+$: 189.1022; found 189.1024.

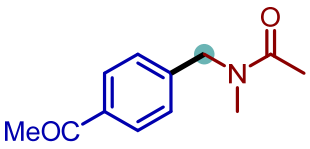
Methyl 4-((*N*-methylacetamido)methyl)benzoate (2)



The compound was prepared according to the **General Procedure 1** using ethyl 4-bromobenzoate (45.8 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 73% yield (32.2 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 – 7.98 (m) & 7.98 – 7.92 (m, 2H combined), 7.29 – 7.23 (m) & 7.24 – 7.18 (m, 2H combined), 4.60 (s) & 4.55 (s, 2H combined), 3.88 (s), 3.86 (s,

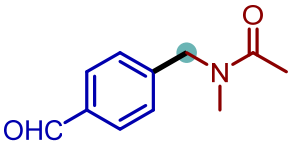
3H combined), 2.91 (s) & 2.90 (s, 3H combined), 2.14 (s) & 2.10 (s, 3H combined). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0 & 170.9, 166.8 & 166.6, 142.6 & 141.8, 130.3 & 129.9, 129.6 &129.2, 127.82 &126.2, 54.0 & 50.4, 52.2 & 52.1, 35.7 & 33.9, 21.8 & 21.4. HRMS (ESI): *m/z* calculated. for $C_{12}H_{16}NO_3$ $[M+H]^+$: 222.1125; found 222.1128.

_N_-(4-acetylbenzyl)-_N_-methylacetamide (3)



The compound was prepared according to the **General Procedure 1** using 1-(4-bromophenyl)ethan-1-one (39.8 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N,N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 82% yield (33.6 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 – 7.90 (m) & 7.89 – 7.85 (m, 2H combined), 7.31 – 7.26 (m) & 7.26 – 7.21 (m, 2H combined), 4.60 (s) & 4.55 (s, 2H combined), 2.91 (s, 3H), 2.56 (s) & 2.55 (s, 3H combined), 2.14 (s) & 2.10 (s, 3H combined). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.7 &197.5, 171.0 & 170.9, 142.9 & 142.0, 136.6 & 136.2, 129.0 & 128.7, 128.0 & 126.4, 54.0 & 50.4, 35.8 & 33.9, 26.6, 21.8 & 21.4. HRMS (APCI): *m/z* calculated. for $C_{12}H_{16}NO_2$ $[M+H]^+$: 206.1176; found 206.1177.

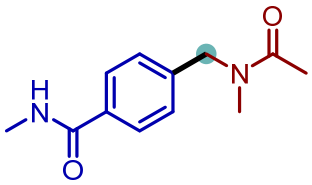
_N_-(4-formylbenzyl)-_N_-methylacetamide (4)



The compound was prepared according to the **General Procedure 1** using 4-bromobenzaldehyde (37.0 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N,N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 70% yield (27.6 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.99 (s) & 9.96 (s, 1H combined), 7.87 (d, J = 8.2 Hz) & 7.81 (d, J = 8.2 Hz, 2H combined), 7.37 (d, J = 8.1 Hz) & 7.32 (d, J = 8.1 Hz, 2H), 4.63 (s) & 4.59 (s, 2H), 2.94 (s) & 2.94 (s, 3H), 2.16 (s) & 2.11 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.9 & 191.6, 171.1 & 171.0, 144.5 & 143.6, 136.0 & 135.6, 130.4 & 130.1, 128.4 & 126.8,

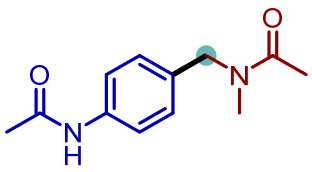
54.1 & 50.6, 35.9 & 34.0, 21.8 & 21.5. HRMS (ESI): *m/z* calculated. for $C_{12}H_{14}NO_2$ $[M+H]^+$: 192.1019; found 192.1022.

_N_-methyl-4-((_N_-methylacetamido)methyl)benzamide (5)



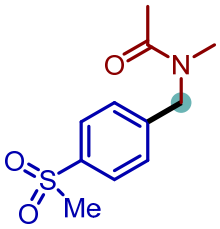
The compound was prepared according to the **General Procedure 1** using 4-bromo-*N*-methylbenzamide (42.8 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using DCM/MeOH solvent mixture as eluent to provide the title compound in 74% yield (32.6 mg). ^{1}H NMR (300 MHz, CDCl3) δ 7.84 – 7.74 (m) & 7.77 – 7.67 (m, 2H combined), 7.29 – 7.23 (m) & 7.22 – 7.16 (m, 2H combined), 6.49 (s, 1H), 4.60 (s) & 4.55 (s, 2H), 3.00 (d, *J* = 4.8 Hz) & 2.99 (d, *J* = 4.8 Hz, 3H combined), 2.92 (s, 3H), 2.16 (s) & 2.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1 & 171.0, 168.0 & 167.7, 140.9 & 140.1, 134.2 & 133.9, 128.1 & 127.7, 127.3 & 126.4, 54.1 & 50.53, 35.83 & 33.97, 26.9, 21.89 & 21.54. HRMS (ESI): *m/z* calculated. for $C_{12}H_{17}N_2O_2$ $[M+H]^+$: 221.1285; found 222.1286.

_N_-(4-acetamidobenzyl)-_N_-methylacetamide (6)



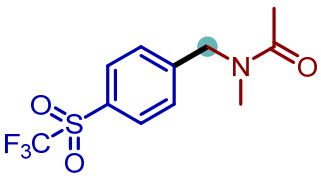
The compound was prepared according to the **General Procedure 1** using *N*-(4-bromophenyl)acetamide (42.8 mg, 0.2 mmol), mpg CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using DCM/MeOH solvent mixture as eluent to provide the title compound in 63% yield (27.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.3 Hz) & 7.44 (d, *J* = 8.3 Hz, 2H combined), 7.19 (d, *J* = 8.3 Hz) & 7.11 (d, *J* = 8.3 Hz, 2H combined), 4.54 (s) & 4.48 (s, 2H combined), 2.92 (s) & 2.91 (s, 3H combined), 2.18 (s) & 2.17 (s, 3H combined), 2.15 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3 & 171.0, 169.0 & 168.9, 138.0 & 137.6, 132.8 & 131.8, 128.5 & 126.9, 120.4 & 120.3, 54.0 & 50.3, 35.7 & 33.8, 24.4, 21.9 & 21.61. HRMS (APCI): *m/z* calculated. for $C_{12}H_{17}N_2O_2$ $[M+H]^+$: 221.1285; found 222.1286.

_N_-methyl-_N_-(4-(methylsulfonyl)benzyl)acetamide (7)



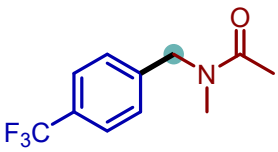
The compound was prepared according to the **General Procedure 1** using 1-bromo-4-(methylsulfonyl)benzene (47.0 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using DCM/MeOH solvent mixture as eluent to provide the title compound in 78% yield (37.6 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz) &, 7.86 (d, *J* = 8.3 Hz, 2H combined), 7.40 (d, *J* = 8.3 Hz) & 7.35 (d, *J* = 8.3 Hz, 2H combined), 4.63 (s) & 4.60 (s, 2H combined), 3.03 (s) & 3.01 (s, 3H combined), 2.95 (s) & 2.92 (s, 3H combined), 2.15 (s) & 2.10 (s, 3H combined). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0 & 170.9, 144.0 & 143.2, 140.1 & 139.6, 128.6 & 128.2, 127.7 & 127.2, 53.9 & 50.5, 44.6 & 44.5, 36.0 & 33.9, 21.7 & 21.4. HRMS (ESI): *m/z* calculated. for $C_{11}H_{16}NO_3S$ $[M+H]^+$: 242.0845; found 242.0848.

_N_-methyl-_N_-(4-((trifluoromethyl)sulfonyl)benzyl)acetamide (8)



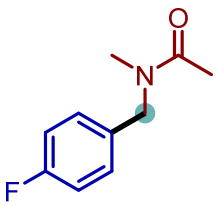
The compound was prepared according to the **General Procedure 1** using 1-bromo-4-((trifluoromethyl)sulfonyl)benzene (57.8 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using DCM/MeOH solvent mixture as eluent to provide the title compound in 64% yield (37.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz) & 7.98 (d, *J* = 8.3 Hz, 2H combined), 7.52 (d, *J* = 8.4 Hz) & 7.48 (d, *J* = 8.4 Hz, 2H combined), 4.70 (s) & 4.67 (s, 2H combined), 3.01 (s) & 2.97 (s, 3H combined), 2.19 (s) & 2.12 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2 & 171.0, 147.5 & 146.8, 131.6 & 131.2, 130.2 & 130.2, 129.1 & 127.67, 119.1 (q, *J* = 325 Hz) & 119.0 (q, *J* = 325 Hz), 54.0 & 50.7, 36.3 & 34.1, 21.7 & 21.4. HRMS (APCI): *m/z* calculated. for $C_{11}H_{13}F_3NO_3S$ $[M+H]^+$: 296.0563; found 293.0564.

***N*-methyl-*N*-(4-(trifluoromethyl)benzyl)acetamide (9)**



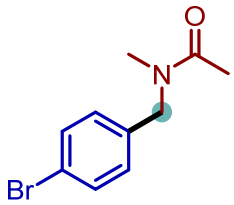
The compound was prepared according to the **General Procedure 1** using 1-bromo-4-(trifluoromethyl)benzene (45.0 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 84% yield (38.8 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz) & 7.55 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz) & 7.28 (d, *J* = 8.0 Hz, 2H), 4.62 (s) & 4.57 (s, 2H), 2.93 (s, 3H), 2.16 (s) & 2.12 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1 & 171.0, 141.6 (q, *J* = 1.3 Hz) & 140.8 (q, *J* = 1.3 Hz), 130.0 (q, *J* = 32.7 Hz) & 129.9 (q, *J* = 32.7 Hz), 128.2 & 127.9, 126.0 (q, *J* = 3.6 Hz) & 125.6 (q, *J* = 3.6 Hz), 122.5 (q, *J* = 270.1 Hz) & 122.4 (q, *J* = 270.1 Hz), 53.9 & 50.4, 35.8 & 33.9, 21.8 & 21.4. HRMS (ESI): *m/z* calculated. for $C_{11}H_{13}F_3NO$ $[M+H]^+$: 232.0944; found 232.0947.

***N*-(4-fluorobenzyl)-*N*-methylacetamide (10)**



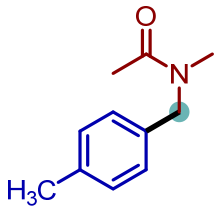
The compound was prepared according to the **General Procedure 1** using 1-bromo-4-fluorobenzene (35.0 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 76% yield (27.5 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 – 7.09 (m, 2H combined), 7.07 – 6.87 (m, 2H, combined), 4.52 (s) & 4.47 (s, 2H combined), 2.90 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9 & 170.7, 162.3 (d, *J* = 245.4 Hz) & 162.2 (d, *J* = 245.4 Hz), 133.3 (d, *J* = 3.5 Hz) & 132.3 (d, *J* = 3.5 Hz), 129.8 (d, *J* = 8.0 Hz) & 128.08 (d, *J* = 8.0 Hz), 115.9 (d, *J* = 21.6 Hz) & 115.48 (d, *J* = 21.6 Hz). 53.6 & 50.0, 35.5 & 33.6, 21.8 & 21.48. HRMS (ESI): *m/z* calculated. for $C_{10}H_{13}FNO$ $[M+H]^+$: 182.0976; found 182.0977.

***N*-(4-bromobenzyl)-*N*-methylacetamide (11)**



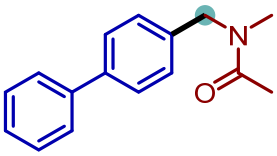
The compound was prepared according to the **General Procedure 1** using 1,4-dibromobenzene (47.0 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 72% yield (34.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.3 Hz) & 7.43 (d, *J* = 8.3 Hz, 2H combined), 7.12 (d, *J* = 8.3 Hz) & 7.04 (d, *J* = 8.3 Hz, 2H combined), 4.52 (s) & 4.47 (s, 2H combined), 2.92 (s) & 2.91 (s, 3H combined), 2.14 (s) & 2.13 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0 & 170.8, 136.5 & 135.7, 132.2 & 131.8, 129.9 & 128.1, 121.6 & 121.3, 53.8 & 50.2, 35.6 & 33.8, 21.9 & 21.5. HRMS (APCI): *m/z* calculated. for $C_{10}H_{13}BrNO$ $[M+H]^+$: 242.0175; found 242.0174.

***N*-methyl-*N*-(4-methylbenzyl)acetamide (12)**



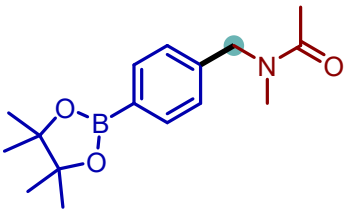
The compound was prepared according to the **General Procedure 1** using 1-bromo-4-methylbenzene (34.2 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 67% yield (23.7 mg). Following the **General Procedure 2** the same compound was synthesized from 1-chloro-4-methylbenzene (25.2 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiCl_2$•glyme (2.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol) with an isolated yield of 84% (29.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s) & 7.26 (s, 2H combined), 7.30 (d, *J* = 8.0 Hz) & 7.19 (d, *J* = 8.0 Hz, 2H combined), 4.67 (s) & 4.61 (s, 2H combined), 3.05 (s) & 3.03 (s, 3H combined), 2.48 (s) & 2.46 (s, 3H combined), 2.28 (s), 2.27 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1 & 170.7, 137.5 & 137.1, 134.4 & 133.6, 129.7 & 129.3, 128.2 & 126.4, 54.1 & 50.4, 35.5 & 33.7, 22.0 & 21.6, 21.2 & 21.1. EI−MS: *m/z* calculated. for $C_{11}H_{15}NO$ $[M]^+$: 177.11482; found 177.11474.

***N*-([1,1'-biphenyl]-4-ylmethyl)-*N*-methylacetamide (13)**



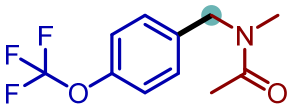
The compound was prepared according to the **General Procedure 1** using 4-bromo-1,1'-biphenyl (46.6 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 77% yield (36.8 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.51 (m, 4H combined), 7.49 – 7.39 (m, 2H combined), 7.39 – 7.20 (m, 3H combined), 4.63 (s) & 4.56 (s, 2H combined), 2.98 (s) & 2.96 (s, 3H combined), 2.18 (s) & 2.17 (s, 3H combined). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0 & 170.7, 140.8 & 140.7, 140.5 & 140.4, 136.5 & 135.6, 128.9 & 128.8, 128.5, 127.74 & 127.5, 127.3 & 127.3, 127.1 & 126.8, 54.0 & 50.4, 35.6 & 33.8, 21.9 & 21.5. HRMS (ESI): *m/z* calculated. for $C_{16}H_{18}NO$ $[M+H]^+$: 240.1383; found 240.1386.

***N*-methyl-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)acetamide (14)**



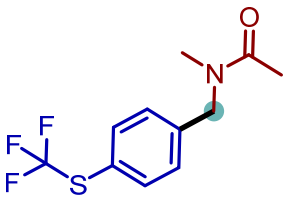
The compound was prepared according to the **General Procedure 1** using 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (56.4 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 75% yield (43.3 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz) & 7.75 (d, *J* = 8.0 Hz, 2H combined), 7.22 (d, *J* = 8.0 Hz) & 7.16 (d, *J* = 8.0 Hz, 2H combined), 4.58 (s) & 4.52 (s, 2H), 2.92 (s) & 2.88 (s, 3H combined), 2.14 (s) & 2.12 (s, 3H combined), 1.33 (s) & 1.32 (s, 12H combined). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1 & 170.7, 140.6 & 139.8, 135.5 & 135.1, 127.4 & 125.7, 83.9 & 83.8, 54.4 & 50.7, 35.5 & 33.8, 24.9, 21.8 & 21.4. HRMS (ESI): *m/z* calculated. for $C_{16}H_{25}BNO_3$ $[M+H]^+$: 289.1958; found 289.1962.

***N*-methyl-*N*-(4-(trifluoromethoxy)benzyl)acetamide (15)**



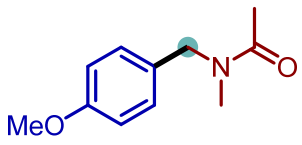
The compound was prepared according to the **General Procedure 1** using 1-bromo-4-(trifluoromethoxy)benzene (48.2 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 68% yield (38.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 6.32 (m, 4H), 4.56 (s) & 4.51 (s, 2H combined), 2.92 (s, 3H), 2.14 (s) & 2.13 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0 & 170.9, 148.7 & 148.5, 136.3 & 135.4, 129.4 & 127.7, 121.6 & 121.2, 120.5 (q, J = 256.9 Hz), 53.6 & 50.1, 35.7 & 33.7, 21.8 & 21.4. HRMS (APCI): *m/z* calculated. for $C_{11}H_{13}F_3NO_2$ $[M+H]^+$: 248.0893; found 248.0898.

***N*-methyl-*N*-(4-((trifluoromethyl)thio)benzyl)acetamide (16)**



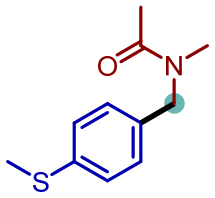
The compound was prepared according to the **General Procedure 1** using (4-bromophenyl)(trifluoromethyl)sulfane (51.4 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 83% yield (43.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.1 Hz) & 7.57 (d, J = 8.1 Hz, 2H combined), 7.26 (d, J = 8.1 Hz) & 7.21 (d, J = 8.1 Hz, 2H combined), 4.58 (s) & 4.54 (s, 2H combined), 2.93 (s) & 2.92 (s, 3H combined), 2.14 (s) & 2.11 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0 & 170.9, 140.7 & 140.0, 136.9 & 136.6, 129.6 (q, J = 308.1 Hz) & 129.5 (q, J = 308.1 Hz), 128.9 & 128.1, 123.72 (q, J = 4.2 Hz) & 123.2 (d, J = 4.2 Hz) 53.8 & 50.3, 35.9 & 33.9, 21.7 &, 21.4. HRMS (APCI): *m/z* calculated. for $C_{11}H_{13}F_3NOS$ $[M+H]^+$: 264.0664; found 264.0666.

***N*-(4-methoxybenzyl)-*N*-methylacetamide (17)**



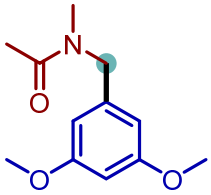
The compound was prepared according to the **General Procedure 1** using 1-bromo-4-methoxybenzene (37.4 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 84% yield (32.4 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.5 Hz) & 7.08 (d, *J* = 8.5 Hz, 2H combined), 6.88 (d, *J* = 8.5 Hz) & 6.84 (d, *J* = 8.5 Hz, 2H combined), 4.51 (s) & 4.44 (s, 2H combined), 3.80 (s) & 3.78 (s, 3H combined), 2.90 (s) & 2.89 (s, 3H combined), 2.15 (s) & 2.12 (s, 3H combined). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9 & 170.6, 159.3 & 159.1, 129.6 & 129.5, 128.6 & 127.7, 114.4 & 114.1, 55.3, 53.8 & 50.1, 35.4 & 33.5, 21.95 & 21.5. HRMS (ESI): *m/z* calculated. for $C_{11}H_{16}NO_2$ $[M+H]^+$: 194.1176; found 194.1179.

***N*-methyl-*N*-(4-(methylthio)benzyl)acetamide (18)**



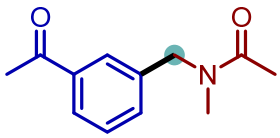
The compound was prepared according to the **General Procedure 1** using (4-bromophenyl)(methyl)sulfane (40.6 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 66% yield (27.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.08 (m, 4H), 4.57 (s) & 4.52 (s, 2H combined), 2.96 (s) & 2.95 (s, 3H combined), 2.52 (s) & 2.50 (s, 3H combined), 2.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0 & 170.7, 138.0 & 137.5, 134.3 & 133.4, 128.7 & 127.1, 126.9 & 126.9, 53.9 & 50.2, 35.5 & 33.7, 21.8 & 21.5, 16.0 & 15.9. HRMS (ESI): *m/z* calculated. for $C_{11}H_{16}NOS$ $[M+H]^+$: 210.0947; found 210.0948.

***N*-(3,5-dimethoxybenzyl)-*N*-methylacetamide (19)**



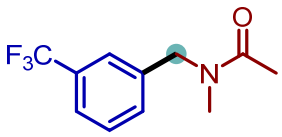
The compound was prepared according to the **General Procedure 1** using 1-bromo-3,5-dimethoxybenzene (43.4 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 81% yield (36.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 – 6.20 (m, 3H), 4.48 (s) & 4.42 (s, 2H combined), 3.75 (s) & 3.73 (s, 6H combined), 2.91 (s) & 2.89 (s, 3H combined), 2.12 (s) & 2.10 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1 & 170.7, 161.4 & 161.0, 139.8 & 139.2, 105.9 & 104.2, 99.2 & 99.1, 55.4 & 55.3, 54.3 & 50.6, 35.5 & 33.8, 21.8 & 21.4. HRMS (APCI): *m/z* calculated. for $C_{12}H_{17}NO_3$ $[M+H]^+$: 224.1281; found 224.1283.

***N*-(3-acetylbenzyl)-*N*-methylacetamide (20)**



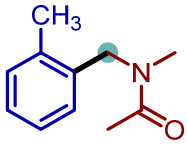
The compound was prepared according to the **General Procedure 1** using 1-(3-bromophenyl)ethan-1-one (39.8 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 79% yield (32.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.69 (m, 2H), 7.50 – 7.31 (m, 2H), 4.60 (s) & 4.55 (s, 2H combined), 2.92 (s) & 2.91 (s, 3H combined), 2.57 (s) & 2.56 (s, 3H combined), 2.14 (s) & 2.12 (s, 3H combined). ^{13}C NMR (101 MHz, CDCl3) δ 198.0 & 197.7, 171.0 & 170.9, 138.1 & 137.8, 137.5 & 137.4, 132.7 & 130.8, 129.3 & 129.0, 127.8 & 127.6, 127.5 & 126.1, 54.0 & 50.5, 35.7 & 33.7, 26.7, 21.8 & 21.5. EI-MS: *m/z* calculated. for $C_{12}H_{15}NO_2$ $[M]^+$: 205.10973; found 205.11.013.

***N*-methyl-*N*-(3-(trifluoromethyl)benzyl)acetamide (21)**



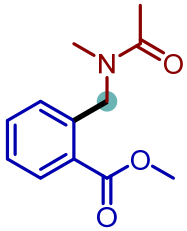
The compound was prepared according to the **General Procedure 1** using 1-bromo-3-(trifluoromethyl)benzene (45.0 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 82% yield (37.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.33 (m, 4H), 4.63 (s) & 4.58 (s, 2H combined), 2.95 (s, 3H), 2.17 (s) & 2.15 (s, 3H combined). ^{13}C NMR (101 MHz, CDCl3) δ 171.0 & 171.9, 138.4 & 137.7, 131.1 (q, *J* = 32.1 Hz) & 131.0 (q, *J* = 32.1 Hz), 131.3 & 129.1, 129.6 & 129.5, 124.6 (q, *J* = 3.5 Hz), 124.3 (q, *J* = 3.5 Hz), 123.2 (q, J = 270.1 Hz), 53.9 & 50.4, 35.7 & 33.8, 21.8 & 21.4. EI-MS: *m/z* calculated. for $C_{11}H_{12}NOF_3$ $[M]^+$: 231.08655; found 231.08620.

***N*-methyl-*N*-(2-methylbenzyl)acetamide (22)**



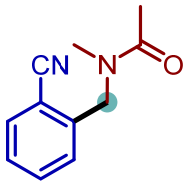
The compound was prepared according to the **General Procedure 1** using 1-bromo-2-methylbenzene (34.2 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 73% yield (25.8 mg). Following the **General Procedure 2** the same compound was synthesized from 1-chloro-2-methylbenzene (25.2 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiCl_2$•glyme (2.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol) with an isolated yield of 81% (28.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.01 (m, 4H), 4.61 (s) & 4.47 (s, 2H combined), 2.96 (s) & 2.88 (s, 3H combined), 2.28 (s, 3H), 2.17 (s) & 2.09 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4 & 170.7, 136.6 & 135.3, 134.9 & 134.3, 130.7 & 130.6, 128.0 & 127.5, 127.4 & 126.6, 126.1 & 125.1, 52.2 & 48.4, 35.4 & 34.0, 21.9 & 21.4, 19.2 & 19.0. EI-MS: *m/z* calculated. for $C_{11}H_{15}NO$ $[M]^+$: 177.11482; found 177.11500.

Methyl 2-((*N*-methylacetamido)methyl)benzoate (23)



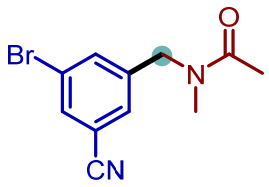
The compound was prepared according to the **General Procedure 1** using methyl 2-bromobenzoate (43.0 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 46% yield (20.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.8, 1.0 Hz) & 7.92 (dd, *J* = 7.8, 1.0 Hz 1H combined), 7.54 (td, *J* = 7.6, 1.2 Hz) & 7.47 (td, *J* = 7.6, 1.2 Hz, 1H combined), 7.36 (td, *J* = 7.6, 1.2 Hz) & 7.30 (td, *J* = 7.6, 1.2 Hz, 1H combined), 5.00 (s) & 4.94 (s, 2H combined), 3.90 (s) & 3.88 (s, 3H), 2.98 (s) & 2.97 (s, 3H combined), 2.19 (s) & 2.04 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8 & 171.1, 167.8 & 167.3, 139.1 & 139.0, 133.20 & 132.5, 131.6 & 130.9, 129.3 & 128.2, 127.6 & 127.3, 126.9 & 125.8, 53.3 & 49.0, 52.2 & 52.1, 36.3 & 34.3, 21.9 & 21.3. EI-MS: *m/z* calculated. for $C_{12}H_{15}NO_3$ $[M]^+$: 221.10464; found 221.10447.

***N*-(2-cyanobenzyl)-*N*-methylacetamide (24)**



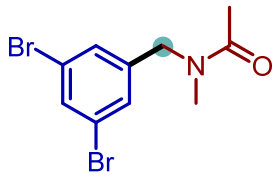
The compound was prepared according to the **General Procedure 1** using methyl 2-bromobenzonitrile (36.4 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 69% yield (25.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.49 (m, 2H), 7.44 – 7.20 (m, 2H), 4.79 (s) & 4.73 (s, 2H combined), 3.00 (s) & 2.94 (s, 3H combined), 2.16 (s) & 2.11 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2 & 171.1, 141.3 & 140.4, 133.6 & 133.4, 133.31 & 132.8, 128.8 & 128.3, 127.9 & 126.4, 117.6 & 116.9, 111.8 & 111.1, 52.5 & 48.9, 36.2 & 33.9, 21.7 & 21.4 EI-MS: *m/z* calculated. for $C_{11}H_{12}N_2O$ $[M]^+$: 188.09441; found 188.09437.

***N*-(3-bromo-5-cyanobenzyl)-*N*-methylacetamide (25)**



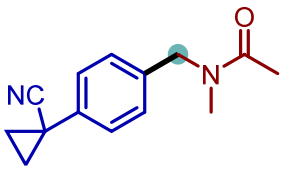
The compound was prepared according to the **General Procedure 1** using 3,5-dibromobenzonitrile (52.0 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 67% yield (35.7 mg).). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s) & 7.67 (s, 1H combined), 7.61 (s) & 7.54 (s, 1H combined), 7.45 (s) & 7.40 (s, 1H combined), 4.55 (s) & 4.53 (s, 2H combined), 2.97 (s) & 2.93 (s, 3H combined), 2.17 (s) & 2.12 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1 & 170.8, 141.3 & 140.6, 135.5 & 134.1, 133.8 & 133.7, 130.0 & 128.5, 123.8 & 123.2, 117.2, & 116.9, 114.9 & 114.4, 53.22 & 49.9, 36.1 & 33.9, 21.7 & 21.5. HRMS (APCI): *m/z* calculated. for $C_{11}H_{12}BrN_2O$ $[M+H]^+$: 267.0128; found 267.0128.

***N*-(3,5-dibromobenzyl)-*N*-methylacetamide (26)**



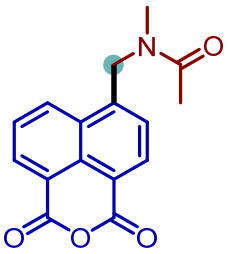
The compound was prepared according to the **General Procedure 1** using 1,3,5-tribromobenzene (62.8 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 63% yield (40.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 1H), 7.34 – 7.20 (m, 2H), 4.52 (s), 4.47 (s, 2H combined), 2.95 (s), 2.94 (s, 3H combined), 2.17 (s) & 2.13 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0 & 170.9, 141.6 & 140.8, 133.6 & 133.2, 129.8 & 128.2, 123.8 & 123.3, 53.3 & 49.9, 35.9 & 34.0, 21.8 & 21.5. HRMS (APCI): *m/z* calculated. for $C_{10}H_{12}Br_2NO$ $[M+H]^+$: 319. 928; found 319.928.

***N*-(4-(1-cyanocyclopropyl)benzyl)-*N*-methylacetamide (27)**



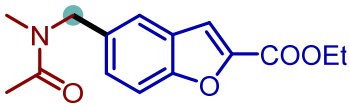
The compound was prepared according to the **General Procedure 1** using 1-(4-bromophenyl)cyclopropane-1-carbonitrile (44.4 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 82% yield (37.3 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.12 (m, 4H), 4.58 (s) & 4.54 (s, 2H combined), 2.95 (s, 3H), 2.18 (s) & 2.16 (s, 3H combined), 1.82 – 1.65 (m, 2H), 1.48 – 1.34 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9 & 170.8, 137.0 & 136.2, 135.6 & 135.1, 128.5 & 126.9, 126.4 & 126.0, 122.5 & 122.4, 53.8 & 50.1, 35.6 & 33.7, 21.8 & 21.4, 18.2, 18.1, 13.5. HRMS (APCI): *m/z* calculated. for $C_{14}H_{17}N_2O$ $[M+H]^+$: 229.1335; found 229.1343.

***N*-((1,3-dioxo-1*H*,3*H*-benzo[*de*]isochromen-6-yl)methyl)-*N*-methylacetamide (28)**



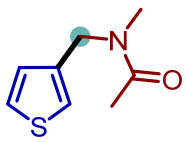
The compound was prepared according to the **General Procedure 1** using 6-bromo-1*H*,3*H*-benzo[*de*]isochromene-1,3-dione (55.4 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 61% yield (34.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 – 8.33 (m, 3H), 7.99 – 7.75 (m, 1H), 7.74 – 7.53 (m, 1H), 5.18 (s) & 5.15 (s, 2H combined), 3.10 (s) & 2.99 (s, 3H combined) 2.23 (s) & 2.14 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4 & 171.0, 160.6 & 160.4, 142.5 (x2), 133.6 & 133.5, 133.5 & 133.1, 132.0 (x2), 130.8 & 130.4, 129.7 & 129.4, 128.1 & 123.9, 128.0 & 127.6, 119.3 & 118.7, 52.1 & 48.6, 35.7 & 34.6, 22.0 & 21.4. HRMS (APCI): *m/z* calculated. for $C_{16}H_{14}NO_4$ $[M+H]^+$: 284.0917; found 284.0923.

Ethyl 5-((*N*-methylacetamido)methyl)benzofuran-2-carboxylate (29)



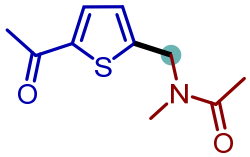
The compound was prepared according to the **General Procedure 3** using ethyl 5-bromobenzofuran-2-carboxylate (53.8 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 3**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 86% yield (47.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 3H), 7.14 (dd, *J* = 8.6, 1.6 Hz) & 7.04 (dd, *J* = 8.6, 1.6 Hz, 1H combined), 4.45 (s) & 4.41 (s, 2H combined), 4.23 (q, *J* = 7.1 Hz) & 4.22 (q, *J* = 7.1 Hz, 2H combined), 2.74 (s) & 2.73 (s, 3H combined), 1.97 (s) & 1.96 (s, 3H combined), 1.22 (t, *J* = 7.1 Hz), 1.21 (t, *J* = 7.1 Hz, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0 & 170.8, 159.5 & 159.4 & 155.1, 146.5 & 146.2, 133.3 & 132.3, 128.0 & 127.5, 127.2 & 126.1, 122.2 & 120.2, 113.6 & 113.5, 112.9 & 112.5, 61.7 & 61.6, 54.1 & 50.5, 35.6 & 33.7, 21.9 & 21.5, 14.3. HRMS (APCI): *m/z* calculated. for $C_{15}H_{17}NO_4$ $[M+H]^+$: 276.1230; found 276.1236.

***N*-methyl-*N*-(thiophen-3-ylmethyl)acetamide (30)**



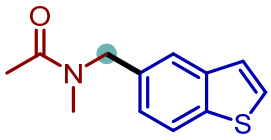
The compound was prepared according to the **General Procedure 3** using 3-bromothiophene (32.6 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 3**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 60% yield (20.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 5.0, 3.0 Hz) & 7.25 (dd, *J* = 5.0, 3.0 Hz, 1H combined), 7.10 (dd, *J* = 2.8, 1.2 Hz) & 7.04 (dd, *J* = 2.8, 1.2 Hz, 1H combined), 6.99 (dd, *J* = 4.9, 1.1 Hz) & 6.91 (dd, *J* = 5.0, 1.2 Hz, 1H combined), 4.53 (s) & 4.48 (s, 3H combined), 2.94 (s) & 2.92 (s, 3H combined), 2.14 (s) & 2.10 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8 & 170.5, 138.2 & 137.8, 127.8 & 127.0, 126.2 & 126.1, 122.7 & 121.5, 50.3 & 45.9, 35.5 & 33.7, 21.9 & 21.4. HRMS (APCI): *m/z* calculated. for $C_8H_{11}NOS$ $[M+H]^+$: 170.0634; found 170.0635.

***N*-((5-acetylthiophen-2-yl)methyl)-*N*-methylacetamide (31)**



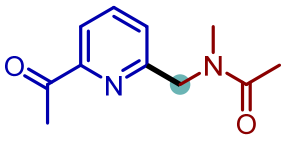
The compound was prepared according to the **General Procedure 3** using 1-(5-bromothiophen-2-yl)ethan-1-one (41.0 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 3**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 63% yield (26.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 3.8 Hz) & 7.52 (d, *J* = 3.8 Hz, 1H combined), 6.95 (d, *J* = 3.8 Hz) & 6.91 (d, *J* = 3.8 Hz, 1H combined), 4.67 (s) & 4.63 (s, 2H combined), 2.99 (s) & 2.95 (s, 3H combined), 2.50 (s) & 2.48 (s, 3H combined), 2.15 (s) & 2.09 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.59 & 190.4, 170.6 & 170.4, 149.3 & 149.1 & 144.0 & 143.7, 132.6 & 132.5, 127.2 & 126.0, 50.0 & 46.1, 35.9 & 33.7, 26.6 & 26.6, 21.7 & 21.4. HRMS (APCI): *m/z* calculated. for $C_{10}H_{14}NO_2S$ $[M+H]^+$: 212.0740; found 212.0742.

***N*-(benzo[*b*]thiophen-5-ylmethyl)-*N*-methylacetamide (32)**



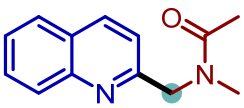
The compound was prepared according to the **General Procedure 3** using 5-bromobenzo[*b*]thiophene (42.6 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 3**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 82% yield (35.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz) & 7.65 (d, *J* = 8.3 Hz, 1H combined), 7.53 (s) & 7.43 (s, 1H combined), 7.31 (d, *J* = 5.4 Hz) & 7.27 (d, *J* = 5.4 Hz, 1H combined), 7.16 – 7.09 (m, 1H), 7.08 (dd, *J* = 8.3, 1.3 Hz) & 6.98 (dd, *J* = 8.3, 1.3 Hz, 1H combined), 4.52 (s) & 4.46 (s, 2H combined), 2.80 (s) & 2.75 (s, 3H combined), 2.02 (s) & 2.00 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1 & 170.8, 140.1 & 139.9, 139.0 & 138.8, 133.7 & 132.8, 127.5 & 127.0, 124.6, 123.7 & 123.7, 123.1 & 123.1, 122.8 & 122.7, 121.0, 54.3 & 50.6, 35.5 & 33.8, 21.9 & 21.5. HRMS (APCI): *m/z* calculated. for $C_{12}H_{13}NOS$ $[M+H]^+$: 220.0791; found 212.0793.

***N*-((6-acetylpyridin-2-yl)methyl)-*N*-methylacetamide (33)**



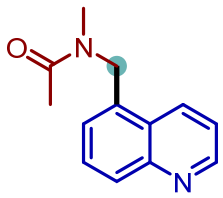
The compound was prepared according to the **General Procedure 3** using 1-(6-bromopyridin-2-yl)ethan-1-one (40.0 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 3**. Purification was performed using flash chromatography on silica gel using DCM/MeOH solvent mixture as eluent to provide the title compound in 52% yield (21.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz) & 7.92 (d, *J* = 7.9 Hz, 1H combined), 7.85 (dd, $J_1 = J_2$ =7.7 Hz) & 7.78 (dd, $J_1 = J_2$ =7.7 Hz, 1H combined), 7.44 (d, *J* = 7.6 Hz) & 7.34 (d, *J* = 7.6 Hz, 1H combined), 4.75 (s) & 4.67 (s, 2H combined), 3.14 (s) & 3.01 (s, 3H combined), 2.71 (s) & 2.70 (s, 3H combined), 2.21 (s) & 2.19 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.3 & 200.0, 171.5 & 171.1, 157.0 & 156.2, 153.8 & 153.1, 138.0 & 137.7, 125.7 & 124.2, 120.5 & 120.2, 56.0 & 52.8, 36.9 & 34.3 25.8(x2), 21.8 & 21.6. EI-MS: *m/z* calculated. for $C_{11}H_{14}N_2O_2$ $[M]^+$: 206.10498; found 206.10478.

***N*-methyl-*N*-(quinolin-2-ylmethyl)acetamide (34)**



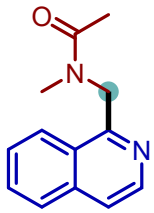
The compound was prepared according to the **General Procedure 3** using 2-chloroquinoline (32.6 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiCl_2$•glyme (2.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 3**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 83% yield (35.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.5 Hz) & 8.10 (d, *J* = 8.5 Hz, 1H combined), 8.04 (d, *J* = 8.5 Hz) & 8.03 (d, *J* = 8.5 Hz, 1H combined), 7.84 – 7.64 (m, 2H), 7.56 – 7.46 (m, 1H), 7.38 (d, *J* = 8.5 Hz) & 7.27 (d, *J* = 8.5 Hz, 1H combined), 4.88 (s) & 4.78 (s, 2H combined), 3.04 (s) & 3.03 (s, 3H combined), 2.18 (s) & 2.17 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5 & 171.1, 158.0 & 157.1, 148.0 & 147.5, 137.5 & 137.1, 130.1 & 129.7, 129.1 & 129.0, 127.7 & 127.6, 127.5 & 127.4, 126.7 & 126.4, 120.2 & 118.1, 56.9 & 53.3, 36.3 & 34.4, 21.8 & 21.7. EI-MS: *m/z* calculated. for $C_{13}H_{14}N_2O$ $[M]^+$: 214.11006; found 214.11012.

***N*-methyl-*N*-(quinolin-5-ylmethyl)acetamide (35)**



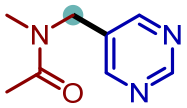
The compound was prepared according to the **General Procedure 3** using 5-bromoquinoline (41.2 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 3**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 61% yield (26.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.5 Hz) & 8.14 (d, *J* = 8.5 Hz, 1H combined), 8.10 – 8.02 (m, 1H), 7.85 – 7.79 (m, 1H), 7.77 – 7.68 (m, 1H), 7.58 – 7.50 (m, 1H), 7.42 (d, *J* = 8.5 Hz) & 7.29 (d, *J* = 8.5 Hz, 1H combined), 4.91 (s) & 4.80 (s, 2H combined), 3.07 (s) & 3.05 (s, 3H combined), 2.20 (s) & 2.19 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5 & 171.0, 157.9 & 157.1, 147.9 & 147.8, 137.5 & 137.4, 130.1 & 129.9, 129.0 & 128.6, 127.7 & 127.6, 127.4 & 127.3, 126.7 & 126.6, 120.3 & 118.1, 56.9 & 53.0, 36.3 & 34.4, 21.8 & 21.6. EI-MS: *m/z* calculated. for $C_{13}H_{14}N_2O$ $[M]^+$: 214.11006; found 214.11069.

***N*-(isoquinolin-1-ylmethyl)-*N*-methylacetamide (36)**



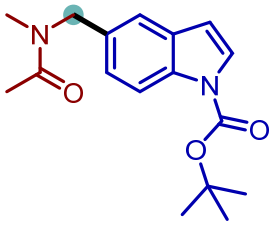
The compound was prepared according to the **General Procedure 3** using 1-chloroisoquinoline (32.6 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiCl_2$•glyme (2.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 3**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 86% yield (36.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 5.7 Hz) & 8.44 (d, *J* = 5.7 Hz, 1H combined), 8.35 (d, *J* = 8.5 Hz) & 8.02 (d, *J* = 8.5 Hz, 1H combined), 7.87 (d, *J* = 8.1 Hz) & 7.82 (d, *J* = 8.1 Hz, 1H combined) 7.73 – 7.55 (m, 3H), 5.23 (s) & 5.11 (s, 2H combined), 3.00 (s) & 2.96 (s, 3H combined), 2.15 (s) & 2.14 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2 & 170.6, 156.6 & 154.4, 142.2 & 141.2, 136.5 & 136.2, 130.5 & 130.2, 127.9 & 127.8, 127.7 & 127.2, 126.9 & 126.2, 125.6 & 123.2, 121.0 & 120.5, 53.4 & 50.3, 35.6 & 34.6, 21.9 & 21.7. EI-MS: *m/z* calculated. for $C_{13}H_{14}N_2O$ $[M]^+$: 214.11006; found 214.11034.

***N*-methyl-*N*-(pyrimidin-5-ylmethyl)acetamide (37)**



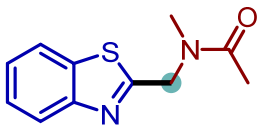
The compound was prepared according to the **General Procedure 3** using 5-bromopyrimidine (31.6 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 3**. Purification was performed using flash chromatography on silica gel using DCM/MeOH solvent mixture as eluent to provide the title compound in 74% yield (24.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (s) & 9.12 (s, 1H combined), 8.65 (s) & 8.60 (s, 2H combined), 4.63 (s) & 4.54 (s, 2H combined), 2.99 (s) & 2.93 (s, 3H combined), 2.16 (s) & 2.13 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1 & 170.6, 158.5 & 158.1, 156.7 & 155.5, 131.0 & 130.2, 49.9 & 46.5, 36.0 & 33.7, 21.7 & 21.5. EI-MS: *m/z* calculated. for $C_8H_{11}N_3O$ $[M]^+$: 165.08966; found 165.08986.

***tert*-Butyl 5-((*N*-methylacetamido)methyl)-1*H*-indole-1-carboxylate (38)**



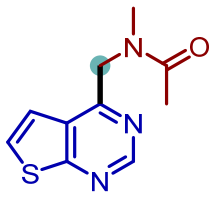
The compound was prepared according to the **General Procedure 3** using *tert*-butyl 5-bromo-1*H*-indole-1-carboxylate (59.2 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 3**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 74% yield (24.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 3.7 Hz) & 7.57 (d, *J* = 3.6 Hz, 1H combined), 7.33 – 7.19 (m, 1H), 7.07 (d, *J* = 7.3 Hz) & 6.99 (d, *J* = 7.4 Hz, 1H combined), 6.71 (d, *J* = 3.7 Hz) & 6.53 (d, *J* = 3.7 Hz, 1H combined), 4.83 (s) & 4.75 (s, 2H combined), 2.96 (s) & 2.83 (s, 3H combined), 2.15 (s) & 2.13 (s, 3H combined), 1.66 (s) & 1.65 (s, 9H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3 & 170.5, 149.7 & 149.6, 135.5 & 135.4, 129.7 & 129.3, 128.4 & 128.3, 126.4 & 126.0, 124.6 & 124.1, 123.1 & 119.6, 114.7 & 114.6, 105.8 & 104.2, 84.1 & 83.8, 52.1 & 48.1, 35.0 & 33.9, 28.2, 21.9 & 21.5. HRMS (ESI): *m/z* calculated. for $C_{17}H_{22}N_2O_3$ $[M+H]^+$: 303.1703; found 303.1707.

***N*-(benzo[*d*]thiazol-2-ylmethyl)-*N*-methylacetamide (39)**



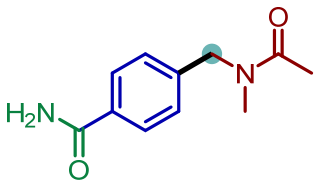
The compound was prepared according to the **General Procedure 3** using 2-bromobenzo[*d*]thiazole (42.8 mg, 0.2 mmol), tetrabutylammonium chloride (66.7 mg, 0.24 mmol), mpg-CN (10.0 mg), $NiCl_2$•glyme (2.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 3**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 66% yield (29.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.9 Hz) & 7.98 (d, *J* = 7.9 Hz, 1H combined), 7.87 (d, *J* = 7.8 Hz) & 7.84 (d, *J* = 7.8 Hz, 1H combined), 7.53 – 7.32 (m, 2H), 4.96 (s) & 4.87 (s, 1H combined), 3.11 (s) & 3.08 (s, 3H combined), 2.22 (s) & 2.17 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1 & 171.0, 168.2 & 167.9, 153.3 & 152.7, 135.7 & 134.9, 126.5 & 126.1, 125.6 & 125.3, 123.2 & 123.0, 121.9 & 121.8, 53.2 & 49.4, 36.5 & 34.5, 21.7 & 21.6. EI-MS: *m/z* calculated. for $C_{11}H_{12}N_2OS$ $[M]^+$: 220.06649; found 220.06674.

***N*-methyl-*N*-(thieno[2,3-d]pyrimidin-4-ylmethyl)acetamide (40)**



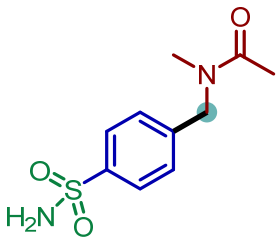
The compound was prepared according to the **General Procedure 3** using 4-bromothieno[2,3-*d*]pyrimidine (43.0 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiCl_2$•glyme (2.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 3**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 81% yield (35.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s) & 8.99 (s, 1H combined), 7.62 (d, *J* = 6.1 Hz) & 7.58 (d, *J* = 6.1 Hz, 1H combined), 7.52 (d, *J* = 6.1 Hz) & 7.35 (d, *J* = 6.1 Hz, 1H combined), 4.99 (s) & 4.92 (s, 2H combined), 3.08 (s) & 2.99 (s, 3H combined), 2.16 (s) & 2.15 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6 & 170.9, 169.4 & 169.2, 159.8 & 159.2, 153.4 & 152.9, 129.0 & 128.5, 127.9 & 127.5, 120.1 & 118.0, 54.2 & 50.5, 36.5 & 34.6, 21.7. EI-MS: *m/z* calculated. for $C_{10}H_{11}N_3OS$ $[M]^+$: 221.06173; found 221.06156.

4-((*N*-methylacetamido)methyl)benzamide (41)



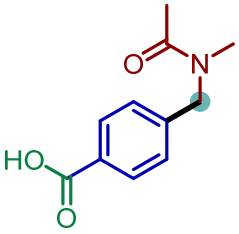
The compound was prepared according to the **General Procedure 1** using 4-bromobenzamide (40.0 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 85% yield (35.0 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.00 (s) & 7.97 (s, 1H combined), 7.90 (d, J = 8.2 Hz) & 7.85 (d, J = 8.2 Hz, 2H combined), 7.39 (s) & 7.36 (s, 1H combined), 7.27 (d, J = 8.2 Hz, 2H), 4.59 (s) & 4.52 (s, 2H combined), 2.91 (s) & 2.79 (s, 3H combined), 2.07 (s) & 2.03 (s, 3H combined). ^{13}C NMR (101 MHz, DMSO-d_6) δ 170.2 & 170.1, 167.8 & 167.7, 141.3 & 140.9, 133.3 & 133.0, 128.0 & 127.7, 127.2 & 126.4, 53.1 & 49.5, 35.6 & 33.2, 21.5 & 21.3. HRMS (ESI): *m/z* calculated. for $C_{11}H_{15}N_2O_2$ $[M+H]^+$: 207.1128; found 207.1130.

***N*-methyl-*N*-(4-sulfamoylbenzyl)acetamide (42)**



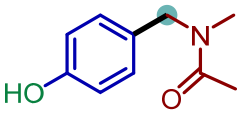
The compound was prepared according to the **General Procedure 1** using 4-bromobenzenesulfonamide (47.2 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 87% yield (42.2 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.83 (d, J = 8.3 Hz) & 7.78 (d, J = 8.3 Hz, 2H combined), 7.39 (d, J = 8.3 Hz, 2H), 7.35 (s) & 7.33 (s, 1H combined), 4.64 (s) & 4.55 (s, 2H combined), 2.93 (s) & 2.80 (s, 3H combined), 2.08 (s) & 2.03 (s, 3H combined). ^{13}C NMR (101 MHz, DMSO-d_6) δ 170.2 & 170.0, 143.1 & 142.8, 142.1 & 141.7, 127.8 & 127.0, 126.1 & 125.8, 52.9 & 49.4, 35.7 & 33.2, 21.5 & 21.2. HRMS (ESI): *m/z* calculated. for $C_{10}H_{15}N_2O_3S$ $[M+H]^+$: 243.0798; found 243.0806.

4-((*N*-methylacetamido)methyl)benzoic acid (43)



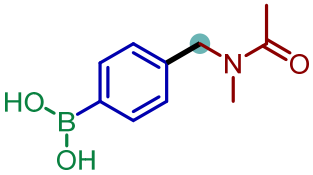
The compound was prepared according to the **General Procedure 1** using 4-bromobenzoic acid (40.2 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 68% yield (28.2 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.92 (d, J = 8.1 Hz) & 7.88 (d, J = 8.1 Hz, 2H combined), 7.24 (d, J = 8.1 Hz) & 7.23 (d, J = 8.1 Hz, 2H combined), 4.60 (s) & 4.53 (s, 2H combined), 2.91 (s) & 2.79 (s, 3H combined), 2.07 (s) & 2.03 (s, 3H combined). ^{13}C NMR (101 MHz, DMSO-d_6) δ 170.2 & 170.1, 167.9, 142.3 & 141.8, 131.2 & 131.0, 129.8 & 129.5, 127.3 & 126.4, 53.2 & 49.6, 35.7 & 33.3, 21.6 & 21.3. HRMS (ESI): *m/z* calculated. for $C_{11}H_{14}NO_3$ $[M+H]^+$: 208.0968; found 208.0973.

***N*-(4-hydroxybenzyl)-N-methylacetamide (44)**



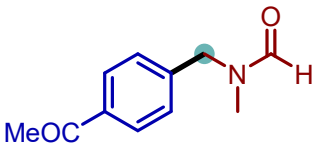
The compound was prepared according to the **General Procedure 1** using 4-bromophenol (34.6 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 63% yield (22.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.07 (d, J = 8.5 Hz) & 6.97 (d, J = 8.5 Hz, 2H combined), 6.87 (d, J = 8.5 Hz) & 6.82 (d, J = 8.5 Hz, 2H combined), 4.50 (s) & 4.42 (s, 2H combined), 2.92 (s, 1H) & 2.91 (s, 3H combined), 2.18 (s) & 2.14 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9 &171.5, 156.7 & 156.4, 129.5 & 127.8, 127.9 & 126.8, 116.1 & 115.7, 54.06 & 50.4, 35.5 & 33.8, 21.7 & 21.4. EI-MS: *m/z* calculated. for $C_{10}H_{13}NO_2$ $[M]^+$: 179.09408; found 179.09440.

(4-((*N*-methylacetamido)methyl)phenyl)boronic acid (45)



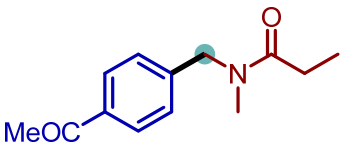
The compound was prepared according to the **General Procedure 1** using (4-bromophenyl)boronic acid (40.0 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 82% yield (33.9 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.98 (s) & 7.94 (s, 2H combined), 7.78 (d, J = 7.9 Hz) & 7.73 (d, J = 7.9 Hz, 2H combined), 7.14 (d, J = 7.9 Hz, 2H), 4.54 (s) & 4.47 (s, 2H combined), 2.88 (s) & 2.77 (s, 3H combined), 2.05 (s) & 2.01 (s, 3H combined). ^{13}C NMR (101 MHz, DMSO-d_6) δ 170.0, 139.72 & 139.3, 134.6 & 134.3, 126.4 & 125.5, 53.3 & 49.6, 35.5 & 33.2, 21.6 & 21.3. HRMS (ESI): *m/z* calculated. for $C_{10}H_{15}BNO_3$ $[M+H]^+$: 2081140; found 208.1143.

***N*-(4-acetylbenzyl)-*N*-methylformamide (46)**



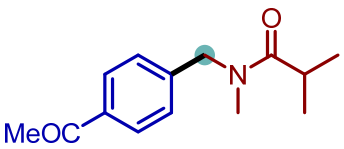
The compound was prepared according to the **General Procedure 4** using 1-(4-bromophenyl)ethan-1-one (39.8 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylformamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 4**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 64% yield (24.4 mg). The same compound was synthesized from 1-(4-chlorophenyl)ethan-1-one (30.8 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiCl_2$•glyme (2.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylformamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol) with an isolated yield of 73% (27.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s) & 8.18 (s, 1H combined), 7.95 (d, J = 8.3 Hz) & 7.92 (d, J = 8.3 Hz, 2H combined), 7.33 (d, J = 8.3 Hz) & 7.30 (d, J = 8.3 Hz, 2H combined), 4.57 (s) & 4.45 (s, 2H combined), 2.87 (s) & 2.79 (s, 3H combined), 2.60 (s) & 2.58 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7 & 197.5, 162.8 & 162.7, 141.5 & 141.2, 137.1 & 136.6, 129.1 & 128.9, 128.3 & 127.6, 53.2 & 47.6, 34.3 & 29.7, 26.7 & 26.7. HRMS (APCI): *m/z* calculated. for $C_{11}H_{14}NO_2$ $[M+H]^+$:192.1019; found192.1023.

***N*-(4-acetylbenzyl)-*N*-methylpropionamide (47)**



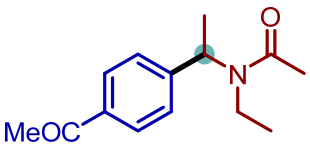
The compound was prepared according to the **General Procedure 4** using 1-(4-chlorophenyl)ethan-1-one (30.8 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiCl_2$•glyme (2.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylpropionamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 4**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 84% yield (36.8 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz) & 7.88 (d, *J* = 8.3 Hz, 2H combined), 7.29 (d, *J* = 8.3 Hz) & 7.23 (d, *J* = 8.3 Hz, 2H combined), 4.62 (s) & 4.57 (s, 2H combined), 2.94 (s) & 2.91 (s, 3H combined), 2.58 (s) & 2.56 (s, 3H combined), 2.40 (q, *J* = 7.4 Hz) & 2.35 (q, *J* = 7.4 Hz, 2H combined) 1.17 (t, *J* = 7.4 Hz) & 1.13 (t, *J* = 7.4 Hz, 3H combined). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.82 & 197.6, 174.3 & 174.1, 143.2 & 142.3, 136.6 & 136.2, 129.0 & 128.7, 128.0 & 126.4, 53.1 & 50.7, 35.0 & 34.2, 26.8 & 26.7, 26.3, 9.6 & 9.3. HRMS (APCI): *m/z* calculated. for $C_{13}H_{18}NO_2$ $[M+H]^+$: 220.1332; found 220.1337.

***N*-(4-acetylbenzyl)-*N*-methylisobutyramide (48)**



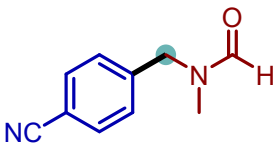
The compound was prepared according to the **General Procedure 4** using 1-(4-chlorophenyl)ethan-1-one (30.8 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiCl_2$•glyme (2.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), tetrabutylammonium chloride (5.6 mg, 10 mol%), *N*,*N*-dimethylisobutyramide (230.4 mg, 2.0 mmol), 2,6-lutidine (70 µL 0.6 mmol) and CH_3CN (0.8 mL). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 4**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 81% yield (37.7 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz) & 7.85 (d, *J* = 8.2 Hz, 2H combined), 7.25 (d, *J* = 8.2 Hz) & 7.20 (d, *J* = 8.2 Hz, 2H combined), 2.93 (s) & 2.90 (s, 2H combined), 2.81 (h, *J* = 6.7 Hz) & 2.71 (h, *J* = 6.7 Hz, 1H combined), 2.55 (s) & 2.53 (s, 3H combined), 1.12 (d, *J* = 6.7 Hz) & 1.08 (d, *J* = 6.7 Hz, 6H combined). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.8 & 197.5, 177.7 & 177.3, 143.3 & 142.5, 136.5 & 136.2, 129.0 & 128.7, 127.9 & 126.3, 53.0 & 50.8, 34.9 & 34.3, 30.4, 26.6, 19.8 & 19.3. HRMS (APCI): *m/z* calculated. for $C_{14}H_{20}NO_2$ $[M+H]^+$: 234.1489; found 234.1493.

***N*-(1-(4-acetylphenyl)ethyl)-*N*-ethylacetamide (49)**



The compound was prepared according to the **General Procedure 4** using 1-(4-chlorophenyl)ethan-1-one (30.8 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiCl_2$•glyme (2.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), tetrabutylammonium chloride (5.6 mg, 10 mol%), *N*,*N*-diethylacetamide (230.4 mg, 2.0 mmol), 2,6-lutidine (70 µL 0.6 mmol) and CH_3CN (0.8 mL). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 4**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 59% yield (27.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz), &7.91 (d, *J* = 8.2 Hz, 2H combined), 7.40 (d, *J* = 8.2 Hz) & 7.35 (d, *J* = 8.2 Hz, 2H combined), 6.03 (q, *J* = 7.0 Hz), 5.09 (q, *J* = 7.0 Hz, 1H combined), 3.42 (dq, *J* = 14.3, 7.1 Hz) & 3.18 (dq, *J* = 14.3, 7.1 Hz, 1H combined), 3.05 (dq, *J* = 14.3, 7.1 Hz) & 2.94 (dq, *J* = 14.3, 7.1 Hz, 1H combined), 2.60 (s) & 2.59 (s, 3H combined), 2.19 (s) & 2.17 (s, 3H combined), 1.67 (d, *J* = 6.9 Hz) & 1.55 (d, *J* = 6.9 Hz, 3H combined), 1.01 (dt, *J* = 14.3, 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8 & 197.6, 170.8 & 170.8, 147.0 & 146.3, 136.3 & 136.2, 128.8 & 128.6, 127.7 & 126.9, 56.3 & 50.9, 39.3 & 38.1, 26.7, 22.4 & 21.9, 18.6 & 16.9, 16.2 & 14.6. HRMS (APCI): *m/z* calculated. for $C_{14}H_{20}NO_2$ $[M+H]^+$: 234.1489; found 234.1486.

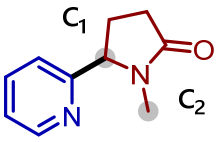
***N*-(4-cyanobenzyl)-*N*-methylformamide (50)**



The compound was prepared according to the **General Procedure 4** using 4-bromobenzonitrile (36.4 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylformamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 4**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 62% yield (21.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s) & 8.18 (s, 1H combined), 7.68 (d, *J* = 8.3 Hz) & 7.63 (d, *J* = 8.3 Hz, 2H combined), 7.35 (d, *J* = 8.3 Hz) & 7.32 (d, *J* = 8.3 Hz, 2H combined), 4.56 (s) & 4.46 (s, 2H combined), 2.88 (s) & 2.79 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 & 162.8, 141.6 & 141.4, 132.9 & 132.6, 128.8 & 128.0, 118.6 & 118.4, 112.3 & 111.8, 53.1 &

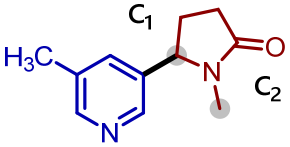
47.7, 34.3 & 29.8 HRMS (APCI): *m/z* calculated. for $C_{10}H_{11}N_2O$ $[M+H]^+$: 175.0866; found 175.0868.

1-methyl-5-(pyridin-2-yl)pyrrolidin-2-one (51)



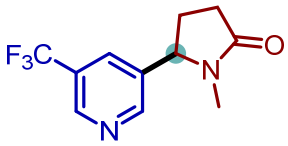
The compound was prepared according to the **General Procedure 4** using 2-chloropyridine (22.6 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiCl_2$•glyme (2.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), 1-methylpyrrolidin-2-one (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 4**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 71% yield (25.0 mg, C_1:C_2 = 8:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57 (ddd, *J* = 4.9, 1.7, 0.9 Hz, 1H), 7.68 (td, *J* = 7.7, 1.7 Hz, 1H), 7.20 (ddd, *J* = 7.7, 4.9, 0.9 Hz, 1H), 7.12 (dt, *J* = 7.7, 0.9 Hz, 1H), 4.65 – 4.58 (m, 1H), 2.68 (s, 3H), 2.57 – 2.34 (m, 3H), 2.04 – 1.91 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.8, 160.4, 150.1, 137.2, 122.9, 120.5, 65.8, 29.9, 28.4, 26.5 HRMS (APCI): *m/z* calculated. for $C_{10}H_{13}N_2O$ $[M+H]^+$: 177.1022; found 177.1023.

1-methyl-5-(5-methylpyridin-3-yl)pyrrolidin-2-one (52)



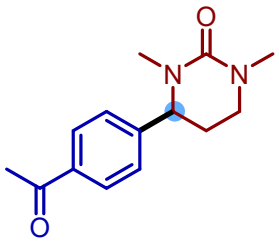
The compound was prepared according to the **General Procedure 4** using 3-chloro-5-methylpyridine (25.4 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiCl_2$•glyme (2.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), 1-methylpyrrolidin-2-one (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 4**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 63% yield (23.9 mg, C_1:C_2 = 2.7:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.28 (s, 1H), 7.29 (s, 1H), 4.54 – 4.47 (m, 1H), 2.65 (s, 3H), 2.62 – 2.37 (m, 3H), 2.34 (s, 3H), 1.93 – 1.79 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 150.4, 145.6, 136.2, 134.1, 131.8, 62.1, 30.0, 28.3, 28.2, 18.5. EI-MS: *m/z* calculated. for $C_{11}H_{14}N_2O$ $[M]^+$: 190.11006; found 190.11019.

1-methyl-5-(5-(trifluoromethyl)pyridin-3-yl)pyrrolidin-2-one (53)



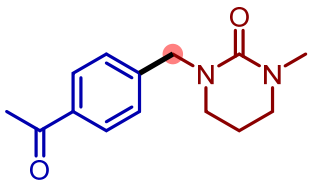
The compound was prepared according to the **General Procedure 4** using 3-chloro-5-(trifluoromethyl)pyridine (36.2 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiCl_2$•glyme (2.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), 1-methylpyrrolidin-2-one (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 4**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 69% yield (33.6 mg, C_1:C_2 = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.70 (s, 1H), 7.74 (s, 1H), 4.73 – 4.58 (m, 1H), 2.70 (s, 3H), 2.66 – 2.37 (m, 3H), 1.95 – 1.81 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 175.4, 152.7, 151.6,146.7 (q, *J* = 4.7 Hz), 146.6 (q, *J* = 4.1 Hz), 137.3, 132.9, 130.9 (q, *J* = 3.5 Hz), 127.5, 124.7 (q, *J* = 264.1 Hz), 124.6 (q, *J* = 272.9 Hz), 62.0, 46.8, 43.9, 30.6, 29.8, 28.5, 28.4, 17.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.92. EI-MS: *m/z* calculated. for $C_{11}H_{11}F_3N_2O$ $[M]^+$: 244.08180; found 244.08172.

4-(4-acetylphenyl)-1,3-dimethyltetrahydropyrimidin-2(1*H*)-one (54)



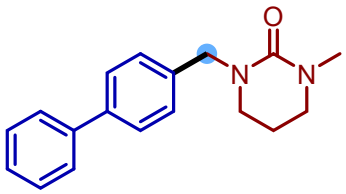
The compound was prepared according to the **General Procedure 4** using 1-(4-bromophenyl)ethan-1-one (39.8 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), 1,3-dimethyltetrahydropyrimidin-2(1*H*)-one (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 4**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 63% yield (31.0 mg, C_1:C_2 = 8:1 from crude NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 4.55 – 4.49 (m, 1H), 3.13 – 3.04 (m, 2H), 2.98 (s, 3H), 2.88 (s, 3H), 2.59 (s, 3H), 2.45 – 2.33 (m, 1H), 1.98 – 1.82 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 156.7, 147.1, 136.6, 129.0, 126.5, 61.3, 44.0, 36.0, 35.0, 29.6, 26.7 EI-MS: *m/z* calculated. for $C_{14}H_{18}N_2O_2$ $[M]^+$: 246.13628; found 246.13626.

1-(4-acetylbenzyl)-3-methyltetrahydropyrimidin-2(1*H*)-one (55)



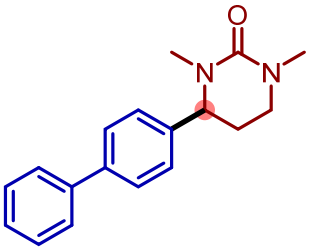
The compound was prepared according to the **General Procedure 4** using 1-(4-chlorophenyl)ethan-1-one (30.8 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiCl_2$•glyme (2.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), 1,3-dimethyltetrahydropyrimidin-2(1*H*)-one (256.4 mg, 2.0 mmol), 2,6-lutidine (70 µL 0.6 mmol) and CH_3CN (0.8 mL). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 4**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 67% yield (32.9 mg, C_1:C_2 = >20:1 from crude NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 4.60 (s, 2H), 3.28 (t, *J* = 6.0 Hz, 2H), 3.18 (t, *J* = 6.0 Hz, 2H), 2.98 (s, 3H), 2.58 (s, 3H), 1.94 (p, *J* = 6.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 156.6, 144.5, 136.2, 128.7, 127.9, 51.3, 48.0, 45.7, 36.0, 26.7, 22.4. EI-MS: *m/z* calculated. for $C_{14}H_{18}N_2O_2$ $[M]^+$: 246.13628; found 246.13679.

1-([1,1'-biphenyl]-4-ylmethyl)-3-methyltetrahydropyrimidin-2(1*H*)-one (56)



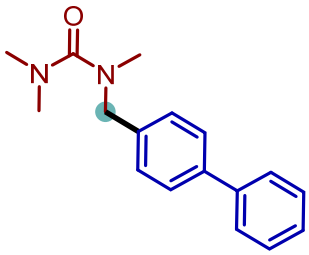
The compound was prepared according to the **General Procedure 4** using 4-chloro-1,1'-biphenyl (37.6 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiCl_2$•glyme (2.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), 1,3-dimethyltetrahydropyrimidin-2(1*H*)-one (256.4 mg, 2.0 mmol), 2,6-lutidine (70 µL 0.6 mmol) and CH_3CN (0.8 mL). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 4**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 66% yield (37.0 mg, C_1:C_2 = >20:1 from crude NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 4H), 7.48 – 7.39 (m, 2H), 7.38 – 7.31 (m, 3H), 4.60 (s, 2H), 3.28 (t, *J* = 6.0 Hz, 2H), 3.22 (t, *J* = 6.0 Hz, 2H), 3.00 (s, 3H), 1.95 (p, *J* = 5.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 141.1, 140.1, 137.8, 128.8, 128.4, 127.3, 127.3, 127.2, 51.1, 48.0, 45.4, 36.0, 22.4. EI-MS: *m/z* calculated. for $C_{18}H_{20}N_2O$ $[M]^+$: 280.15701; found 280.15639.

4-([1,1'-biphenyl]-4-yl)-1,3-dimethyltetrahydropyrimidin-2(1*H*)-one (57)



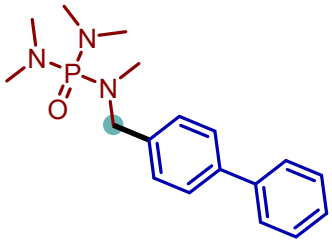
The compound was prepared according to the **General Procedure 4** using 4-bromo-1,1'-biphenyl (46.6 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), 1,3-dimethyltetrahydropyrimidin-2(1*H*)-one (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 4**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 61% yield (34.2 mg, C_1:C_2 = 7.9:1 from crude NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 4H), 7.47 – 7.41 (m, 2H), 7.37 – 7.31 (m, 1H), 7.27 – 7.20 (m, 2H), 4.51 (t, *J* = 4.4 Hz, 1H), 3.18 (td, *J* = 11.5, 3.8 Hz, 1H), 3.10 – 3.04 (m, 1H), 2.39 (ddt, *J* = 13.2, 10.6, 5.1 Hz, 1H), 1.92 (dq, *J* = 13.2, 3.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 140.7, 140.6, 140.5, 128.8, 127.5, 127.4, 127.1, 126.7, 61.14, 44.1, 35.9, 34.9, 29.9. EI-MS: *m/z* calculated. for $C_{18}H_{20}N_2O$ $[M]^+$: 280.15701; found 280.15667.

1-([1,1'-biphenyl]-4-ylmethyl)-1,3,3-trimethylurea (58)



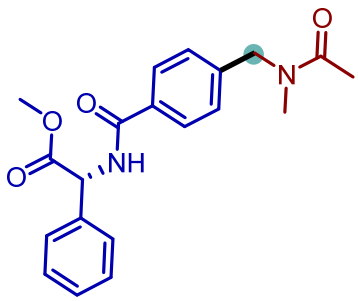
The compound was prepared according to the **General Procedure 4** using 4-bromo-1,1'-biphenyl (46.6 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), 1,1,3,3-tetramethylurea (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 4**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 73% yield (39.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 4H), 7.46 – 7.41 (m, 2H), 7.37 – 7.31 (m, 3H), 4.42 (s, 2H), 2.87 (s, 6H), 2.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 140.9, 140.1, 137.2, 128.8, 128.1, 127.4, 127.3, 127.1, 53.9, 38.8, 36.7. HRMS (ESI): *m/z* calculated. for $C_{17}H_{21}N_2O$ $[M+H]^+$: 269.1648; found 269.1653.

Hexamethylphosphoramide derivative (59)



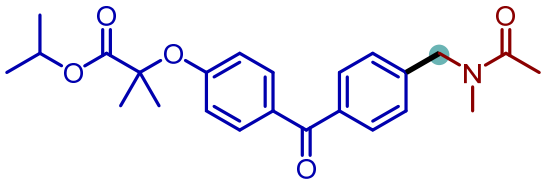
The compound was prepared according to the **General Procedure 4** using 4-bromo-1,1'-biphenyl (46.6 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), hexamethylphosphoramide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 4**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 43% yield (28.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 4H), 7.46 – 7.39 (m, 4H), 7.36 – 7.31 (m, 1H), 4.19 (d, *J* = 9.1 Hz, 2H), 2.71 (s, 6H), 2.69 (s, 6H), 2.58 (d, *J* = 9.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 140.2, 137.7, 137.6, 128.9, 128.6, 127.3, 127.2, 127.1, 53.0, 52.9, 37.1, 37.0, 34.2, 34.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ -62.92. HRMS (ESI): *m/z* calculated. for $C_{18}H_{27}N_3OP$ $[M+H]^+$: 332.1886; found 332.1890.

Methyl (*R*)-2-(4-((N-methylacetamido)methyl)benzamido)-2-phenylacetate (70)



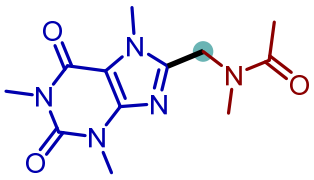
The compound was prepared according to the **General Procedure 1** methyl (*R*)-2-(4-bromobenzamido)-2-phenylacetate[14] (69.6 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 91% yield (64.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz) & 7.75 (d, *J* = 8.2 Hz, 2H combined), 7.44 – 7.27 (m, 6H), 7.23 (d, *J* = 8.2 Hz) & 7.17 (d, *J* = 8.2 Hz, 2H combined), 5.74 (d, *J* = 6.9 Hz) & 5.73 (d, *J* = 6.9 Hz, 1H combined), 4.55 (s) & 4.50 (s, 2H combined), 3.71 (s, 2H), 2.87 (s) & 2.86 (s, 3H combined), 2.09 (s) & 2.06 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4 (x2), 170.9 & 170.8, 166.3 & 166.1, 141.4 & 140.6, 136.4 & 136.3, 133.0 & 132.6, 129.0 & 128.9, 128.5 & 128.5, 127.9 (x2), 127.5 & 127.4, 126.3 (x2), 56.8, 52.8, 53.9 & 50.3, 35.6 & 33.7, 21.6 & 21.3. HRMS (ESI): *m/z* calculated. for $C_{20}H_{23}N_2O_4$ $[M+H]^+$: 355.1652; found 355.1659.

Isopropyl 2-methyl-2-(4-(4-((*N*-methylacetamido)methyl)benzoyl)phenoxy)propanoate (71)



The compound was prepared according to the **General Procedure 2** using fenofibrate (72.0 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiCl_2$•glyme (2.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 2**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 83% yield (68.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 1H) & 7.69 (d, *J* = 8.1 Hz, 2H combined), 7.73 (d, *J* = 8.8 Hz) & 7.72 (d, *J* = 8.8 Hz, 2H combined), 7.31 (d, *J* = 8.1 Hz) & 7.26 (d, *J* = 8.1 Hz, 2H combined), 6.85 (d, *J* = 8.8 Hz) & 6.84 (d, *J* = 8.8 Hz, 2H combined), 5.06 (hept, *J* = 6.3 Hz, 1H), 4.64 (s) & 4.59 (s, 2H combined), 2.95 (s, 3H), 2.16 (s) & 2.14 (s, 3H combined), 1.64 (s, 6H), 1.18 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.2 & 194.8, 173.2 & 173.1, 171.0 & 170.9, 159.7 & 159.6, 141.7 & 140.8, 137.7 & 137.3, 132.1, 130.6 & 130.4, 130.5 & 130.2, 127.7 & 126.1, 117.3 & 117.2, 79.4 & 79.4, 69.3, 54.1 & 50.6, 35.9 & 34.0, 25.4, 21.6, 21.8 & 21.5. HRMS (ESI): *m/z* calculated. for $C_{24}H_{30}NO_5$ $[M+H]^+$: 412.2118; found 412.2124.

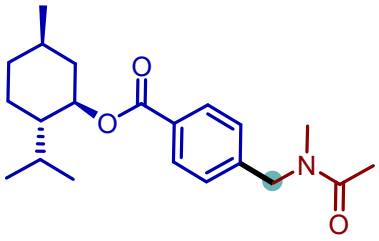
***N*-methyl-*N*-((1,3,7-trimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1*H*-purin-8-yl)methyl)acetamide (72)**



The compound was prepared according to the **General Procedure 2** methyl 8-bromo caffeine (54.6 mg, 0.2 mmol), tetrabutylammonium chloride (66.7 mg, 0.24 mmol), mpg-CN (10.0 mg), $NiCl_2$•glyme (2.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 2**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 72% yield (40.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.67 (s) & 4.57 (s, 2H combined), 3.99 (s) & 3.96 (s, 3H combined), 3.54 (s) & 3.53 (s, 3H combined), 3.37 (s, 3H) 3.10 (s) & 3.00 (s, 3H combined), 2.12 (s) & 2.09 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 155.5, 151.7, 149.2, 147.7, 108.2,

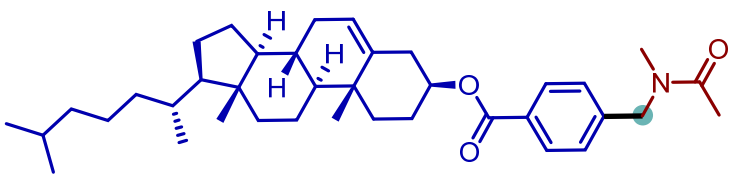
42.2, 36.1, 32.4, 29.8, 28.0, 21.6. HRMS (ESI): *m/z* calculated. for $C_{12}H_{18}N_5O_3$ $[M+H]^+$: 280.1404; found 280.1409.

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-((*N*-methylacetamido)methyl)benzoate (73)



The compound was prepared according to the **General Procedure 1** (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-bromobenzoate[14] (67.8 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 79% yield (54.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz) & 7.96 (d, *J* = 8.2 Hz, 2H combined), 7.26 (d, *J* = 8.2 Hz) & 7.21 (d, *J* = 8.2 Hz, 2H combined), 4.96 – 4.77 (m, 1H), 4.67 – 4.51 (m, 2H), 2.91 (s) & 2.90 (s, 3H combined), 2.12 (s) & 2.09 (s, 3H combined), 2.08 – 2.02 (m, 1H), 1.97 – 1.84 (m, 1H), 1.75 – 1.61 (m, 2H), 1.58 – 1.41 (m, 2H), 1.15 – 0.97 (m, 2H), 0.91 – 0.84 (m, 7H), 0.75 (d, *J* = 6.9 Hz) & 0.74 (d, *J* = 6.9 Hz, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9 & 170.7, 165.8 & 165.6, 142.4 & 141.6, 130.4 & 130.2, 130.0 & 129.9, 127.8 & 126.2, 74.9 & 74.8, 54.1 & 50.4, 47.2, 40.9, 34.3, 35.72 & 33.8, 31.4, 26.6, 26.5, 23.6, 22.0, 21.7 & 21.4, 20.7, 16.5. HRMS (ESI): *m/z* calculated. for $C_{21}H_{32}NO_3$ $[M+H]^+$: 346.2377; found 346.2381.

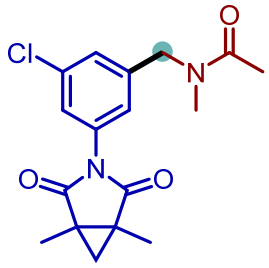
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 4-((*N*-methylacetamido)methyl)benzoate (74)



The compound was prepared according to the **General Procedure 1** (3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-bromobenzoate[14] (113.8 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was

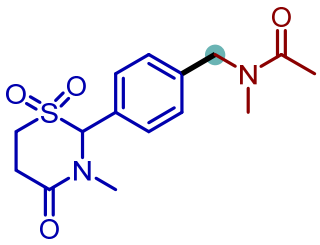
irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 71% yield (81.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.2 Hz) & 7.99 (d, *J* = 8.2 Hz, 2H combined), 7.29 (d, *J* = 8.2 Hz) & 7.23 (d, *J* = 8.2 Hz, 2H combined), 5.41 (dd, *J* = 4.9, 2.4 Hz, 1H), 4.92 – 4.76 (m, 1H), 4.63 (s) & 4.57 (s, 2H combined), 2.94 (s) & 2.92 (s, 3H combined), 2.45 (d, *J* = 7.6 Hz, 2H), 2.17 (s) & 2.13 (s, 3H combined), 2.08 – 1.67 (m, 6H), 1.62 – 1.08 (m, 17H), 1.06 (s, 3H), 1.05 – 0.96 (m, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.86 (dd, *J* = 6.6, 1.7 Hz, 6H), 0.68 (s, 3H). ^{3}C NMR (101 MHz, $CDCl_3$) δ 171.1 & 170.9, 165.8 & 165.6, 142.5 & 141.7, 139.8 & 139.7, 130.5 &, 130.4, 130.1 & 130.0, 127.9 & 126.2, 123.0 & 122.9, 74.8, 74.7, 56.8, 56.3, 54.2 & 50.6, 50.2, 42.4, 39.8, 39.6, 38.3, 37.2, 36.8, 36.3, 35.9, 35.7 & 34.0, 32.1, 32.0, 28.3, 28.1, 28.0, 24.4, 23.9, 22.9, 22.7, 21.9 & 21.5, 21.2, 19.5, 18.8, 12.0. HRMS (ESI): *m/z* calculated. for $C_{38}H_{58}NO_3$ $[M+H]^+$: 576.4411; found 576.4407.

_N_-(3-chloro-5-(1,5-dimethyl-2,4-dioxo-3-azabicyclo[3.1.0]hexan-3-yl)benzyl)-_N_-methylacetamide (75)



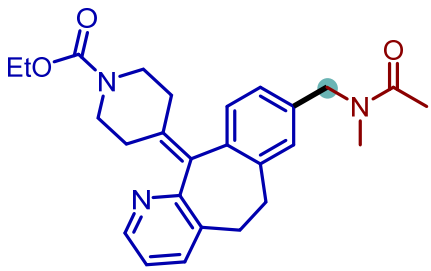
The compound was prepared according to the **General Procedure 2** using procymidone (56.8 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiCl_2$•glyme (2.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 2**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 67% yield (44.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.09 (m, 2H), 7.02 (s) & 6.94 (s, 1H combined), 4.53 (s) & 4.49 (s, 2H combined), 2.92 (s) & 2.92 (s, 3H combined), 2.13 (s) & 2.11 (s, 3H combined), 1.74 (dd, *J* = 9.6, 4.7 Hz, 1H), 1.49 (s) & 1.47 (s, 6H combined), 1.18 (dd, *J* = 9.6, 4.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.3 & 176.2, 171.1 & 170.9, 140.1 & 139.4, 135.3 & 134.7, 133.6 & 133.2, 127.7 & 125.9, 125.7 & 125.5, 124.3 & 122.4, 53.6 & 50.0, 35.7 & 33.9, 33.0 & 32.9, 30.2 & 30.1, 21.8 & 21.5, 10.0. HRMS (ESI): *m/z* calculated. for $C_{17}H_{19}ClN_2O_3$ $[M+H]^+$: 335.1157; found 335.1162.

***N*-methyl-*N*-(4-(3-methyl-1,1-dioxido-4-oxo-1,3-thiazinan-2-yl)benzyl)acetamide (76)**



The compound was prepared according to the **General Procedure 2** using chlormezanone (54.6 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiCl_2$•glyme (2.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 2**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 76% yield (49.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.16 (m, 4H), 5.24 – 5.18 (m, 1H), 4.63 – 4.36 (m, 2H), 3.34 – 2.97 (m, 4H), 2.90 (s) & 2.87 (s, 3H combined), 2.87 (s) & 2.86 (s, 3H combined), 2.09 (s) & 2.06 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1 & 171.0, 166.2, 140.2 & 139.5, 129.6 & 129.1, 128.9 & 128.7, 128.5 & 127.2, 80.5 & 80.4, 53.4 & 50.5, 43.7 & 43.5, 36.3 & 36.2, 36.2 & 34.0, 30.6, 21.8 & 21.5. HRMS (ESI): *m/z* calculated. for $C_{15}H_{21}N_2O_4S$ $[M+H]^+$: 325.1217; found 325.1219.

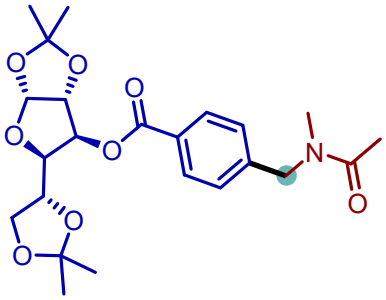
Ethyl 4-(8-((*N*-methylacetamido)methyl)-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidine-1-carboxylate (77)



The compound was prepared according to the **General Procedure 2** using loratadine (76.4 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiCl_2$•glyme (2.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 2**. Purification was performed using flash chromatography on silica gel using PE/EtOAc/Et_3N solvent mixture as eluent to provide the title compound in 63% yield (54.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 7.44 (dd, $J_1 = J_2 = 6.4$ Hz, 1H), 7.22 – 6.90 (m, 4H), 4.51 (s) & 4.47 (s, 2H combined), 4.13 (q, $J = 7.1$ Hz, 2H), 3.94 – 3.67 (m, 2H), 3.47 – 3.25 (m, 2H), 3.20 – 3.05 (m, 2H), 2.92 (s, 3H), 2.90 – 2.72 (m, 2H), 2.58 – 2.20 (m, 4H), 2.14 (s) & 2.13 (s, 3H combined), 1.24 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0 & 170.7, 157.6 & 157.5, 155.5, 146.7 & 146.6, 138.6 & 138.4, 138.3 & 138.0, 137.5 & 137.4, 137.1 & 136.8, 136.6 & 135.7, 135.10 & 134.8, 133.7 & 133.6, 129.9 & 129.5, 128.7 & 126.8, 125.6 & 124.1, 122.2 & 122.1, 61.3, 54.0 & 50.4, 44.9 & 44.8, 35.81 & 33.8,

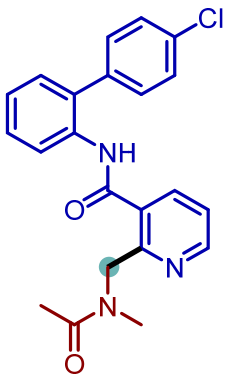
32.0 & 31.9, 31.7 & 31.6, 30.8 & 30.6, 21.9 & 21.5, 14.7. HRMS (ESI): *m/z* calculated. for $C_{26}H_{32}N_3O_3$ $[M+H]^+$: 434.2438; found 434.2444.

(3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 4-((*N*-methylacetamido)methyl)benzoate (78)



The compound was prepared according to the **General Procedure 1** (3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 4-bromobenzoate[14] (88.6 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 48h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 74% yield (66.4 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz) & 7.95 (d, *J* = 8.4 Hz, 2H combined), 7.29 (d, *J* = 8.4 Hz) & 7.24 (d, *J* = 8.4 Hz, 2H combined), 5.92 (d, *J* = 3.6 Hz, 0H), 5.91 (d, *J* = 3.6 Hz, 1H combined), 5.48 – 5.43 (m, 1H), 4.61(s) & 4.57 (s, 2H combined), 4.60(s) & 4.58 (s, 1H combined), 4.37 – 4.25 (m, 2H), 4.13 – 3.99 (m, 2H), 2.92 (s, 3H), 2.15 (s) & 2.10 (s, 3H combined), 1.52 (s, 3H), 1.38 (s, 3H), 1.29 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.00 & 170.9, 164.9 & 164.8, 143.4 & 142.6, 130.4 & 130.1, 129.1 & 128.6, 127.9 & 126.4, 112.5 & 112.4, 109.4 & 109.4, 105.2, 83.4, 79.9, 76.8 & 76.6, 72.6, 67.3 & 67.2, 54.1 & 50.5, 35.8 & 33.9, 26.8 & 26.7, 26.2 & 25.2, 21.7 & 21.4. HRMS (ESI): *m/z* calculated. for $C_{23}H_{32}N_3O_8$ $[M+H]^+$: 450.2122; found 450.2115.

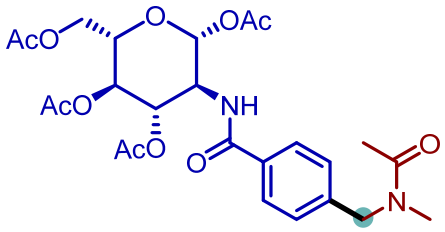
***N*-(4'-chloro-[1,1'-biphenyl]-2-yl)-2-((*N*-methylacetamido)methyl)nicotinamide (79)**



The compound was prepared according to the **General Procedure 2** using boscalid (68.6 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiCl_2$•glyme (2.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 2**. Purification was performed using flash chromatography on silica gel using PE/EtOAc/Et_3N solvent mixture as eluent to provide

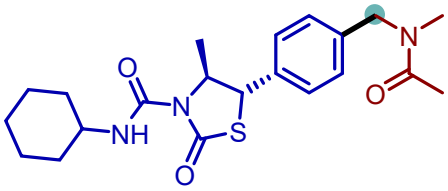
the title compound in 61% yield (47.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 8.54 (d, *J* = 3.8 Hz) & 8.45 (d, *J* = 3.8 Hz, 1H combined), 7.77 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.41 – 7.29 (m, 2H), 7.24 – 7.04 (m, 6H), 4.72 (s), 4.19 (s, 2H combined), 3.26 (s) & 2.76 (s, 3H combined), 2.01 (s) & 1.87 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5 & 171.3, 167.2 & 167.0, 155.6 & 153.6, 151.2 & 150.6, 139.7 & 138.3, 137.4, 135.8, 134.9, 134.2 & 133.4, 132.1 & 130.9, 130.6 & 130.4, 129.4 & 128.4, 129.1 & 128.62, 126.1 & 126.0, 125.9 & 125.8, 122.6 & 122.4, 53.8 & 52.7, 40.5 & 34.1, 22.4 & 21.7. HRMS (ESI): *m/z* calculated. for $C_{22}H_{21}ClN_3O_2$ $[M+H]^+$: 394.1317; found 394.1321.

(2*R*,3*S*,4*S*,5*R*,6*S*)-6-(acetoxymethyl)-3-(4-((*N*-methylacetamido)methyl)benzamido)tetrahydro-2*H*-pyran-2,4,5-triyl triacetate (80)



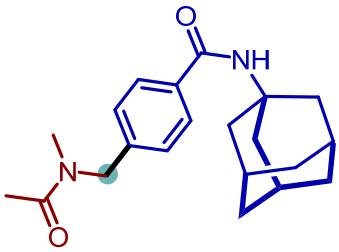
The compound was prepared according to the **General Procedure 1** (2*R*,3*S*,4*S*,5*R*,6*S*)-6-(acetoxymethyl)-3-(4-bromobenzamido)tetrahydro-2*H*-pyran-2,4,5-triyl triacetate (106 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 74% yield (79.3 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz) & 7.66 (d, *J* = 8.3 Hz, 2H combined), 7.49 (d, *J* = 9.5 Hz) & 7.45 (d, *J* = 9.5 Hz, 1H combined), 7.18 (d, *J* = 8.3 Hz) & 7.14 (d, *J* = 8.3 Hz, 2H combined), 5.87 (d, *J* = 8.8 Hz, 1H), 5.39 (ddd, *J* = 10.6, 9.5, 5.1 Hz, 1H), 5.15 (t, *J* = 9.5 Hz, 1H), 4.65 – 4.46 (m, 3H), 4.28 (d, *J* = 4.8 Hz) & 4.24 (d, *J* = 4.8 Hz, 1H combined), 4.14 (d, *J* = 2.0 Hz) & 4.09 (d, *J* = 2.0 Hz, 1H combined), 3.89 – 3.74 (m, 1H), 2.90 (s) & 2.89 (s, 3H combined), 2.15 (s, 2H), 2.08 (s) & 2.07 (s, 3H combined), 2.02 (s) & 2.01 (s, 3H combined), 1.94 (s) & 1.93 (s, 3H combined). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 171.1 & 170.8, 169.5 & 169.4, 167.2 & 166.8, 141.3 & 140.5, 133.3 & 133.1, 128.0 & 127.6, 126.25, 92.7, 72.8, 68.2, 61.8, 53.9 & 50.4, 53.2 & 53.12, 35.8 & 34.0, 21.8 & 21.4, 20.9 & 20.8, 20.7 & 20.6. HRMS (ESI): *m/z* calculated. for $C_{25}H_{33}N_2O_{11}$ $[M+H]^+$: 537.2079; found 537.2090.

(±)-*N*-cyclohexyl-4-methyl-5-(4-((*N*-methylacetamido)methyl)phenyl)-2-oxothiazolidine-3-carboxamide (81)



The compound was prepared according to the **General Procedure 2** using hexythiazox (70.4 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiCl_2$•glyme (2.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 2**. Purification was performed using flash chromatography on silica gel using PE/EtOAc/Et_3N solvent mixture as eluent to provide the title compound in 68% yield (54.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.11 (m, 4H), 4.88 – 4.81 (m, 1H), 4.55 (s) & 4.51 (s, 2H), 4.20 (s) & 4.18 (s, 1H combined), 3.75 – 3.62 (m, 1H), 2.92 (s, 3H), 2.15 (s) & 2.13 (s, 3H combined), 1.98 – 1.86 (m, 2H), 1.75 – 1.65 (m, 2H), 1.63 – 1.53 (m, 4H), 1.43 – 1.18 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1 & 172.9, 171.1 & 170.9, 150.4, 140.6 & 140.2, 137.8 & 137.0, 128.9 & 127.3, 127.1 & 126.9, 62.1, 53.9 & 50.3, 50.7 & 50.6, 49.2, 35.8 & 33.9, 33.1 & 33.0, 25.6, 24.7, 21.9 & 21.5, 20.5. HRMS (ESI): *m/z* calculated. for $C_{21}H_{30}N_3O_3S$ $[M+H]^+$: 404.2002; found 404.2011.

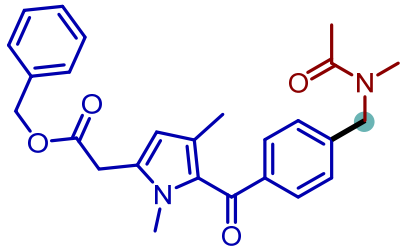
***N*-(adamantan-1-yl)-4-((*N*-methylacetamido)methyl)benzamide (82)**



The compound was prepared according to the **General Procedure 1** *N*-(adamantan-1-yl)-4-bromobenzamide (66.8 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title compound in 64% yield (43.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz) & 7.63 (d, *J* = 8.3 Hz, 2H combined), 7.22 (d, *J* = 8.3 Hz) & 7.15 (d, *J* = 8.3 Hz, 2H combined), 5.90 (s) & 5.88 (s, 1H combined), 4.55 (s) & 4.51 (s, 2H combined), 2.88 (s) & 2.87 (s, 3H combined), 2.11 (s) & 2.08 (s, 12H combined), 1.67 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9 & 170.8, 166.3 & 166.0, 140.5 & 139.6, 135.5 & 135.2,

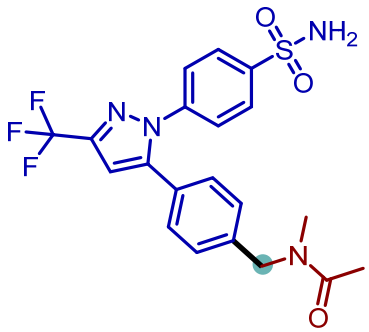
127.9 & 127.5, 127.1 & 126.3, 53.4 & 50.3, 52.4 & 52.3, , 41.6, 36.4, 35.6 & 33.8, 29.5, 21.7 & 21.4. HRMS (ESI): *m/z* calculated. for $C_{21}H_{29}N_2O_2$ $[M+H]^+$: 341.2224; found 341.2231.

Benzyl 2-(1,4-dimethyl-5-(4-((*N*-methylacetamido)methyl)benzoyl)-1*H*-pyrrol-2-yl)acetate (83)



The compound was prepared according to the **General Procedure 2** using benzyl ester of zomepirac[15] (69.4 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiCl_2$•glyme (2.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 2**. Purification was performed using flash chromatography on silica gel using PE/EtOAc/Et_3N solvent mixture as eluent to provide the title compound in 58% yield (50.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz) & 7.57 (d, *J* = 8.2 Hz, 2H combined), 7.32 – 7.12 (m, 7H), 5.85 (s) & 5.84 (s, 1H combined), 5.09 (s, 2H), 4.56 (s) & 4.50 (s, 2H combined), 3.62 (s) & 3.61 (s, 5H combined), 2.87 (s) & 2.84 (s, 3H combined), 2.09 (s) & 2.06 (s, 3H combined), 1.64 (s) & 1.62 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.6 & 187.2, 171.1 & 170.9, 169.5 & 169.4, 141.35 & 140.6, 140.4 & 140.2, 135.6 & 135.5, 132.9 & 132.6, 130.1 & 130.0, 129.9 & 129.6, 129.1 & 129.0, 128.7 & 128.4, 128.61, 127.9, 126.4, 112.6 & 112.5, 67.3 & 67.2, 54.2 & 50.5, 35.7 & 33.9, 33.2, 32.92, 21.9 & 21.6, 14.5 & 14.4. HRMS (ESI): *m/z* calculated. for $C_{26}H_{29}N_2O_4$ $[M+H]^+$: 433.2122; found 433.2128.

***N*-methyl-*N*-(4-(1-(4-sulfamoylphenyl)-3-(trifluoromethyl)-1*H*-pyrazol-5-yl)benzyl)acetamide (84)**



The compound was prepared according to the **General Procedure 1** Br-celecoxib (89.2 mg, 0.2 mmol), mpg-CN (10.0 mg), $NiBr_2$•glyme (3.2 mg, 5 mol%), 2,2′-bipyridine (1.6 mg 5 mol%), *N*,*N*-dimethylacetamide (1.0 mL) and 2,6-lutidine (70 µL 0.6 mmol). The reaction mixture was irradiated under nitrogen atmosphere for 72h using blue LED (455 (± 15) nm). The reaction mixture was then subjected to the work-up procedure as described in the **General Procedure 1**. Purification was performed using flash chromatography on silica gel using PE/EtOAc solvent mixture as eluent to provide the title

compound in 77% yield (69.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.78 (m, 2H), 7.41 – 7.33 (m, 2H), 7.24 – 7.11 (m, 4H), 6.76 (s) & 6.73 (s, 1H combined), 5.71 (s, 2H), 4.55 (s) & 4.53 (s, 2H combined), 2.96 (s) & 2.90 (s, 3H combined), 2.14 (s) & 2.11 (s, 3H combined). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 144.8 & 144.5, 144.4 & 144.3,144.0 & 143.9, 142.3 & 142.2, 138.9 & 138.3, 129.5 & 129.2, 128.3 & 128.1, 127.7 & 127.6, 127.5 & 127.1, 125.6 & 125.5, 123.8 (q, J = 269.2 Hz) & 122.4 (q, J = 269.2 Hz), 106.7 & 106.5, 54.0 & 50.6, 36.2 & 34.1, 21.8 & 21.5. HRMS (ESI): *m/z* calculated. for $C_{20}H_{20}F_3N_4O_3S[M+H]^+$: 453.1203; found 453.1212.

6. Characterization of recovered mpg-CN photocatalyst

After the photocatalytic tests, mpg-CN was washed with a series of solvents and 1M HCl solution to prepare the catalyst for post characterization. The material was characterized by the same set of techniques used for fresh mpg-CN. Position and intensity of all peaks observed in FT-IR spectrum of mpg-CN revealed that bulk chemical structure of the photocatalyst has not changed (**Fig. S13**). EDX and XPS revealed enhanced oxygen content on the surface of the photocatalyst (**Table S8**, **S9** and **Fig. S14b**). Additionally, ICP-OES revealed that mpg-CN after the photocatalytic tests contained 0.0709±0.0131 wt. % of Ni (**Table S10**, entry 2). Detection limit of Ni by ICP-OES was determined to be >0.0013±0.00001 wt. % (**Table S10**, entry 1). However, Ni 2p XPS did not show a distinct signal of nickel (**Fig. S23b**). Given that XPS is surface-sensitive technique, such result confirmed that Ni in the sample is located mainly in the bulk of the material and it was completely removed from the surface upon washing with HCl acid solution. Similarly, no signal was observed in Br 3d XPS (**Fig. S24b**), which potentially could be related to using $NiBr_2$ as metal precursor. HR-TEM of the recovered mpg-CN revealed that mesoporous structure has retained (**Fig. S22d**). In HR-TEM images we observed dark spots with diameter of 2-6 nm that could be ascribed to Ni(0) nanoparticles. Indeed, deposition of Ni(0) nanoparticles, albeit significantly larger amount (1.4-12.6 wt.%) of Ni black, compared to ~0.071 wt.% in this work, has been reported earlier by Pieber et al. in dual Ni/carbon nitride photocatalysis in C–N coupling.[16,17] Despite reaction conditions in earlier reports and herein, strictly speaking, are different, they could not account completely for 20 to 180 times larger difference in Ni content in recovered photocatalysts. The reason for such discrepancy, in our opinion, lies mainly in different chemical structures of carbon nitride photocatalysts. Thus, in the present work mpg-CN belongs to covalent carbon nitrides, while carbon nitride used by Pieber et al., CN-OA-m[18] – to ionic carbon nitrides.[19] Due to abundant nitrogen atoms, carbon nitrides can serve as polydentate ligands to coordinate Ni species. However, taking into account differences in their structures, purely covalent structure (in mpg-CN) and ionic represented by N–K bonds (in CN-OA-m), the coordination mode of $NiBr_2$ is different as shown in **Fig. S25**. In covalent carbon nitrides, such as mpg-CN, Ni precursor coordinated by the carbon nitride scaffold and gives 16e Ni(II) chelate complex (**Fig. S25a**). In ionic carbon nitrides, such as CN-OA-m, more reactive 14e Ni(II)-amide complex is formed (**Fig. S25b**). Our results demonstrate that the problem of Ni black formation in dual Ni/photoredox catalysis, in addition to adjusting rates of oxidative addition and reductive elimination by tuning energy of incident light and concentration of reagents,[17] could be also eliminated by selecting robust carbon nitride photocatalyst able to stabilize Ni species and does

not compromise rate of the entire process. Modification of mpg-CN surface also results in slight shift of absorption onset in DRUV-vis spectrum (**Fig. S19a**) and expansion of optical band gap by ~0.05 eV (**Fig. S19b**). In steady-state PL such surface modification of mpg-CN is observed as blue shift of fluorescence by ~0.1 eV (**Fig. S20**). Morphology of recovered mpg-CN particles adopted rounded shape compared to more rough surface of fresh mpg-CN (**Fig. S21b**). Overall, post characterization of mpg-CN clearly shows robustness and stability of this photocatalyst.

Table S8 | EDX elemental analysis.

Sample	C wt. %	N wt. %	O wt. %
Fresh mpg-CN	36±1.3	62±1.2	2±0.4
Recovered mpg-CN	35±0.6	61±0.7	4±0.3

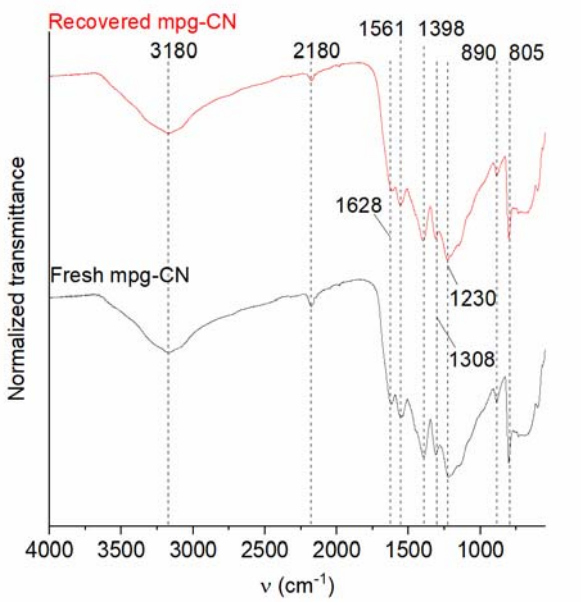


Fig. S13 | FT-IR spectra of fresh and recovered mpg-CN

Table S9 | XPS elemental analysis.

Sample	C at. %	N at. %	O at. %
Fresh mpg-CN	29.1	64.8	6.1
Recovered mpg-CN	30.7	70.2	9.6

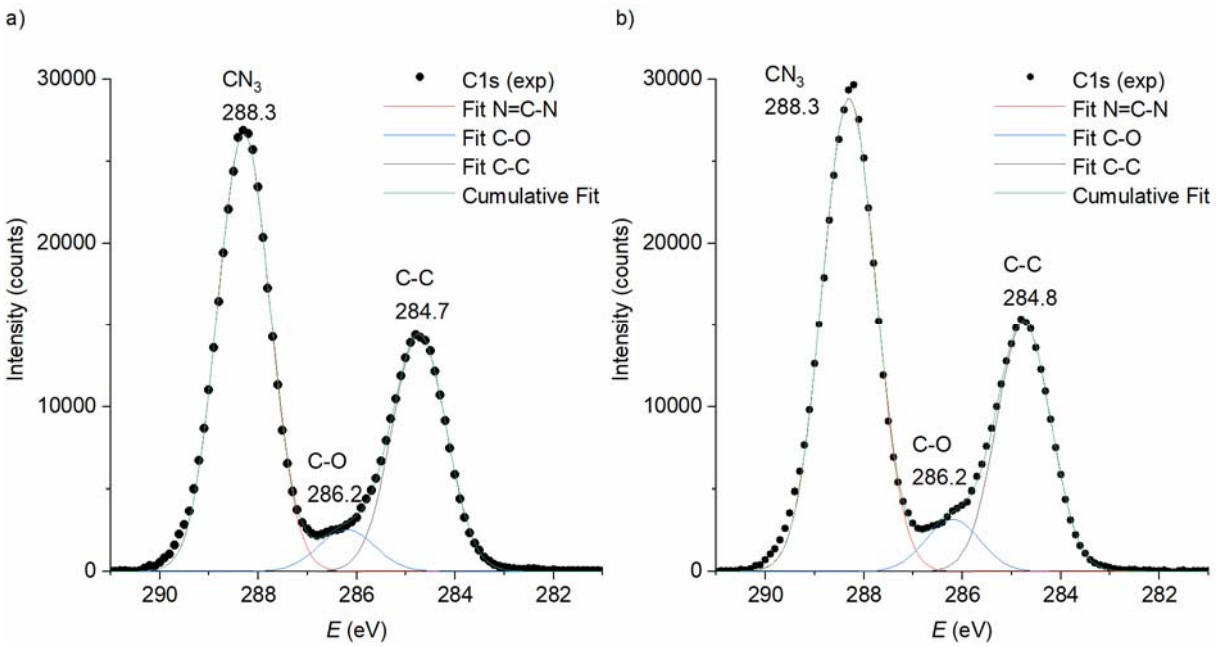


Fig. S14 | C 1s XPS of (a) fresh and recovered (b) mpg-CN.

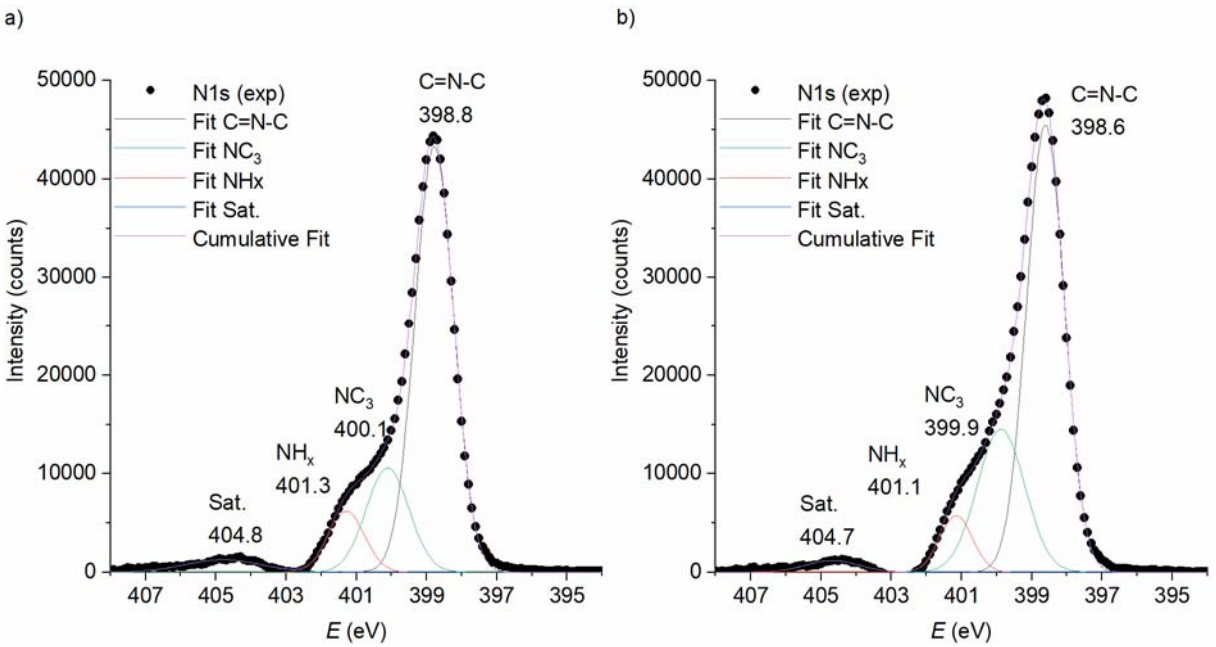


Fig. S15 | N 1s XPS of (a) fresh and (b)recovered mpg-CN.

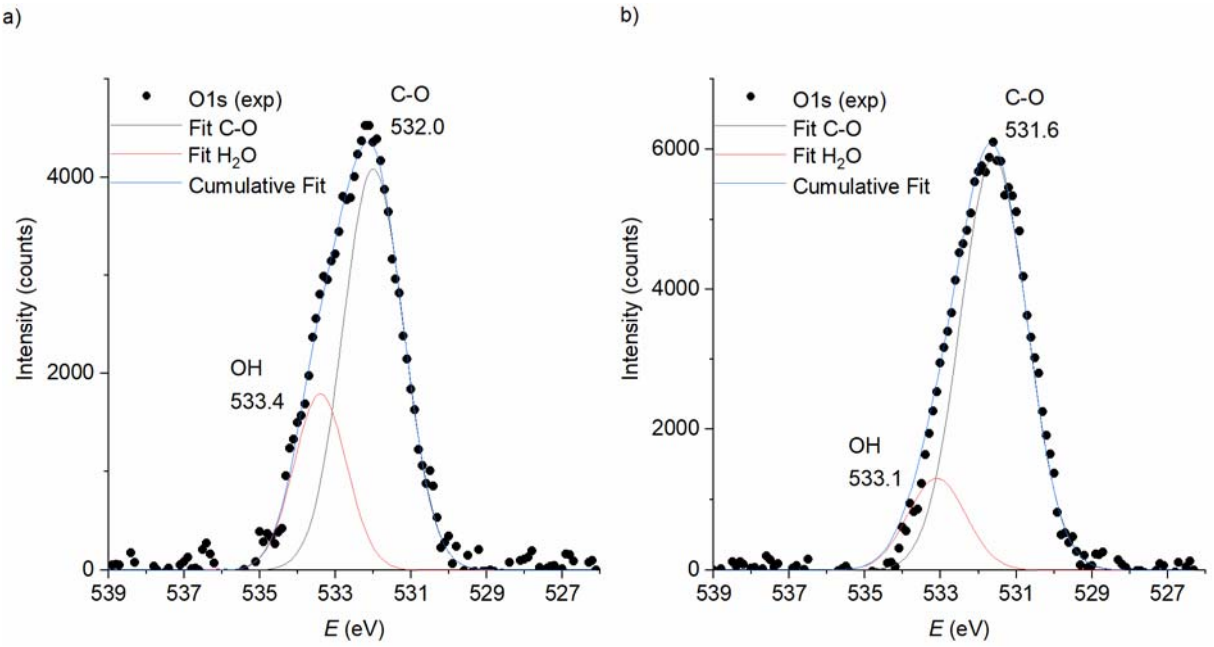


Fig. S16 | O 1s XPS of (a) fresh and (b)recovered mpg-CN.

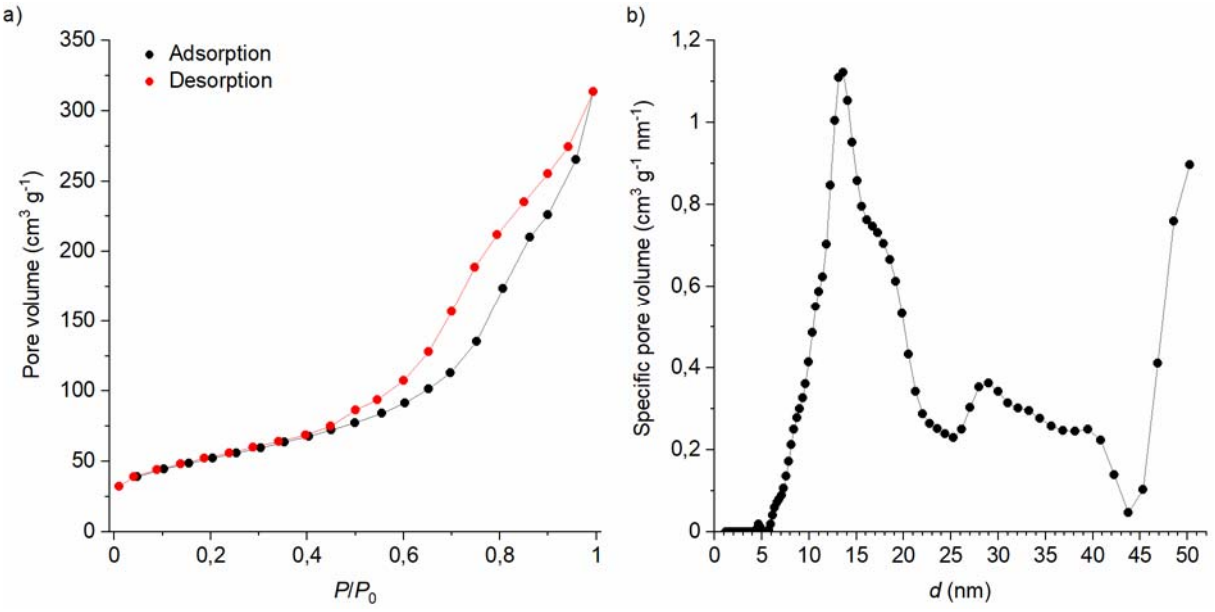


Fig. S17 | (a) N_2 sorption isotherm recorded at 77K and (b)pore size distribution in mpg-CN.

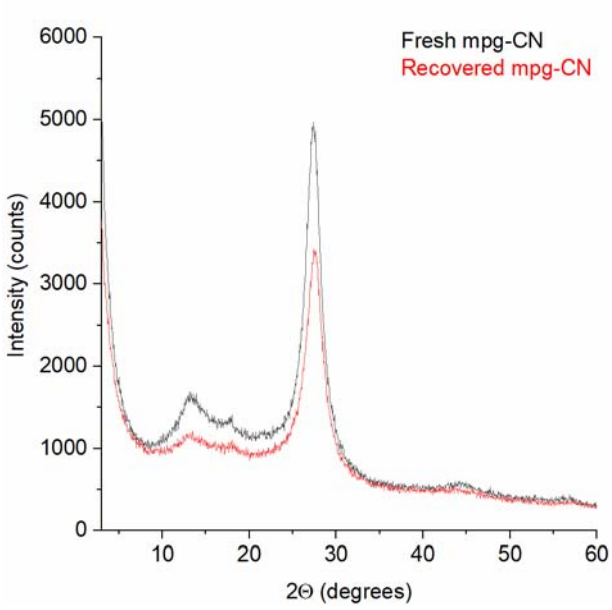


Fig. S18 | PXRD pattern of fresh and recovered mpg-CN.

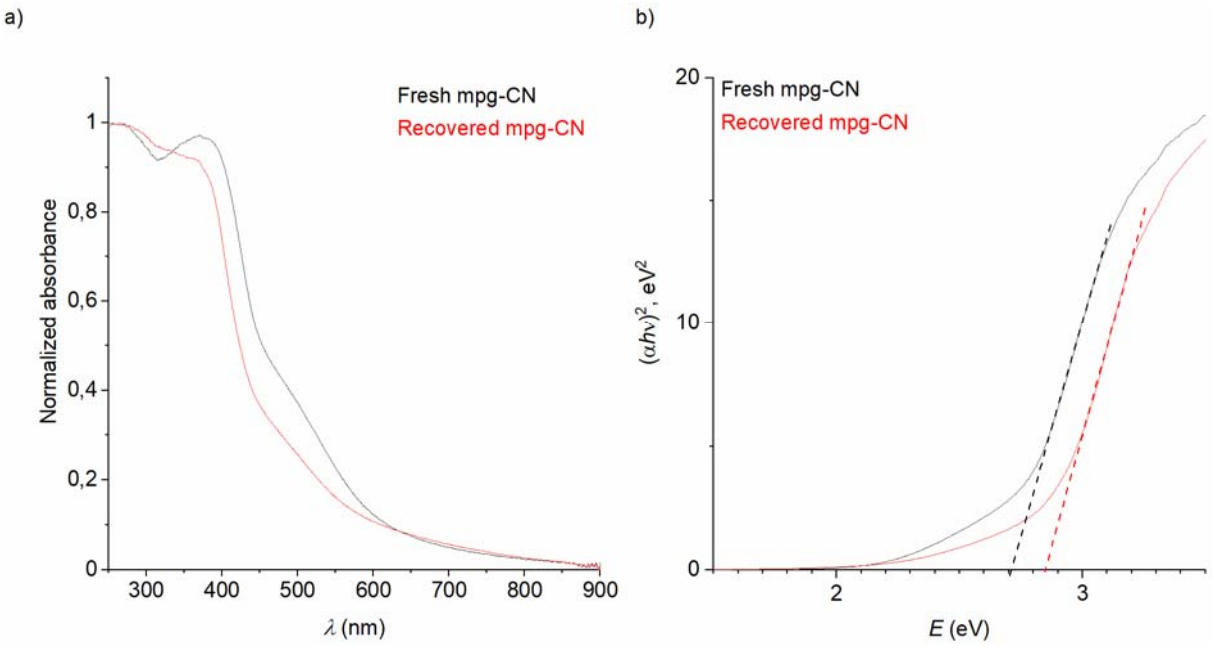


Fig. S19 | (a) DRUV-vis absorption spectra and (b)Tauc plots of fresh and recovered mpg-CN

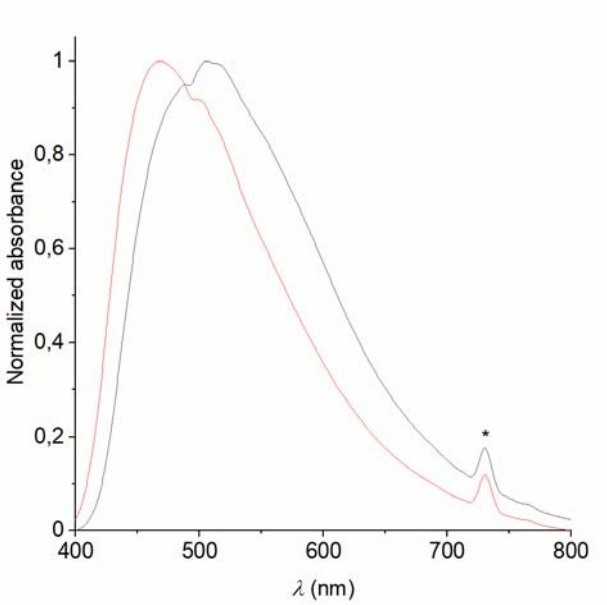


Fig. 20 | Steady state PL of fresh mpg-CN and recovered after the photocatalytic experiment. Samples were excited with λ = 365 nm. Asterisk denotes 2nd order excitation light diffraction.

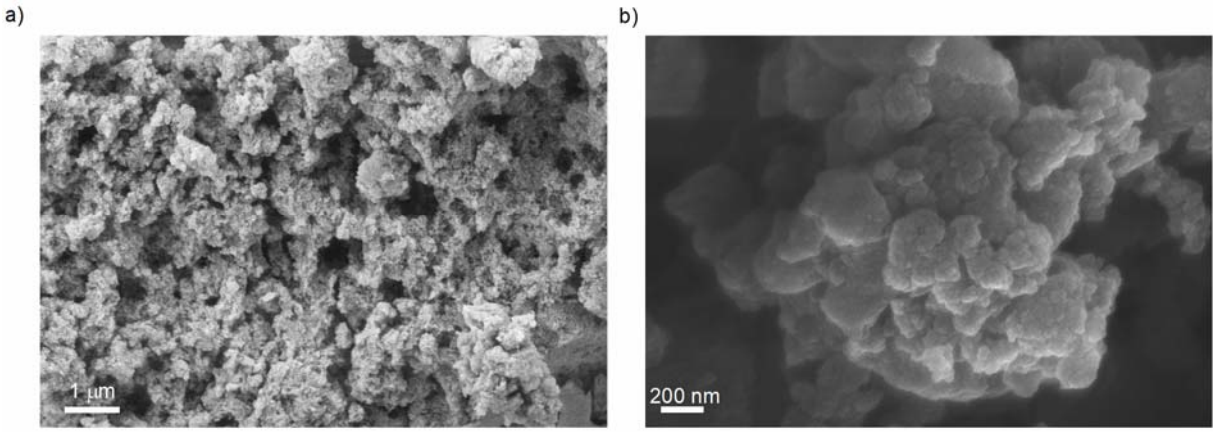


Fig. S21 | SEM (a) fresh mpg-CN. (b) recovered mpg-CN.

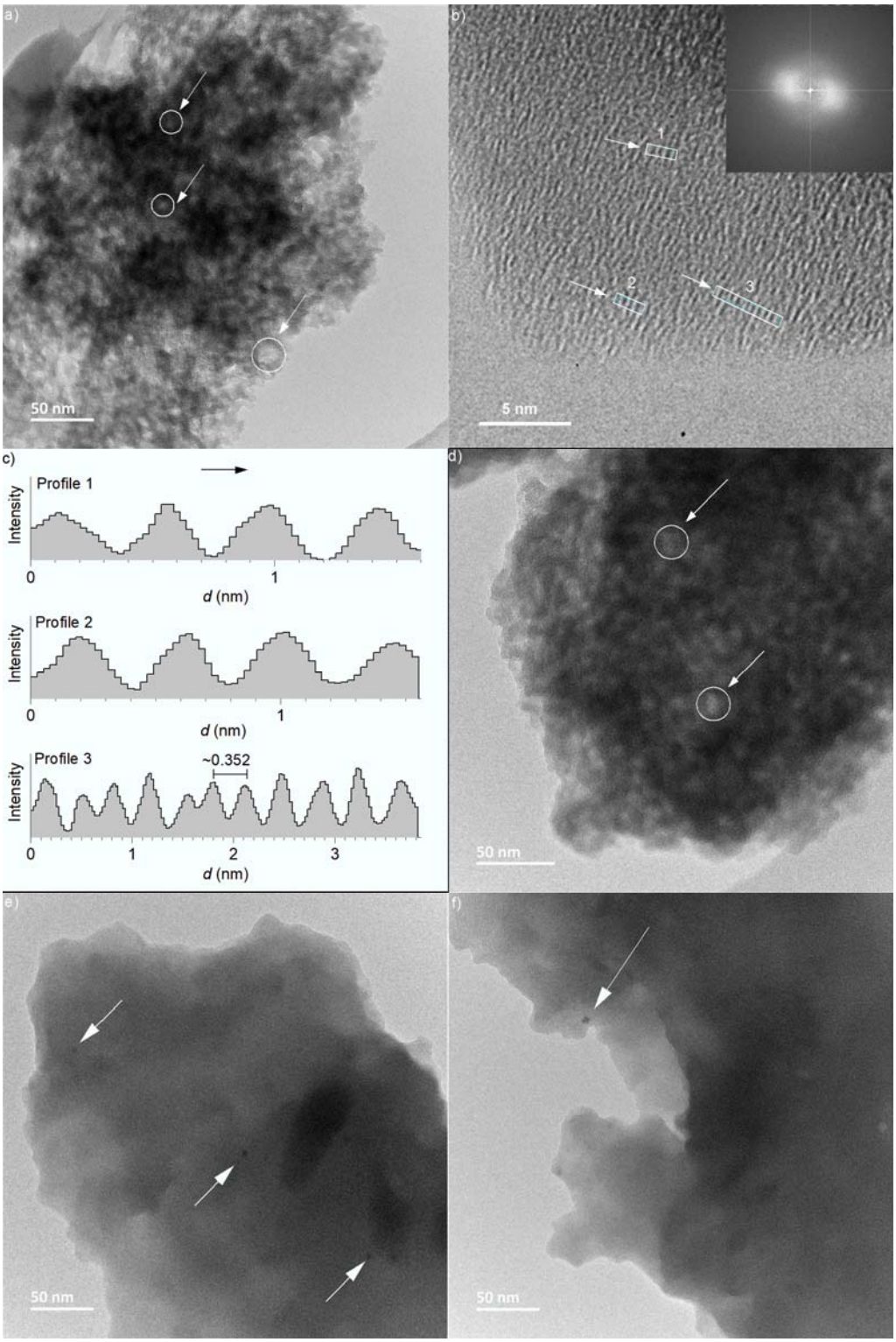


Fig. S22 | TEM images of mpg-CN. (a) overview image of fresh mpg-CN. Circles mark mesopores. (b) HR-TEM image of fresh mpg-CN with FFT in inset. (c) Profile analysis of the corresponding areas marked in the panel. (b) & (d) Overview image of recovered mpg-CN. (e) & (f) TEM images of recovered mpg-CN. Arrows mark Ni(0) nanoparticles.

Table S10 | ICP-OES elemental analysis.

Sample	Ni wt. %
Fresh mpg-CN	0.0013±0.00001
Recovered mpg-CN	0.0709±0.0131

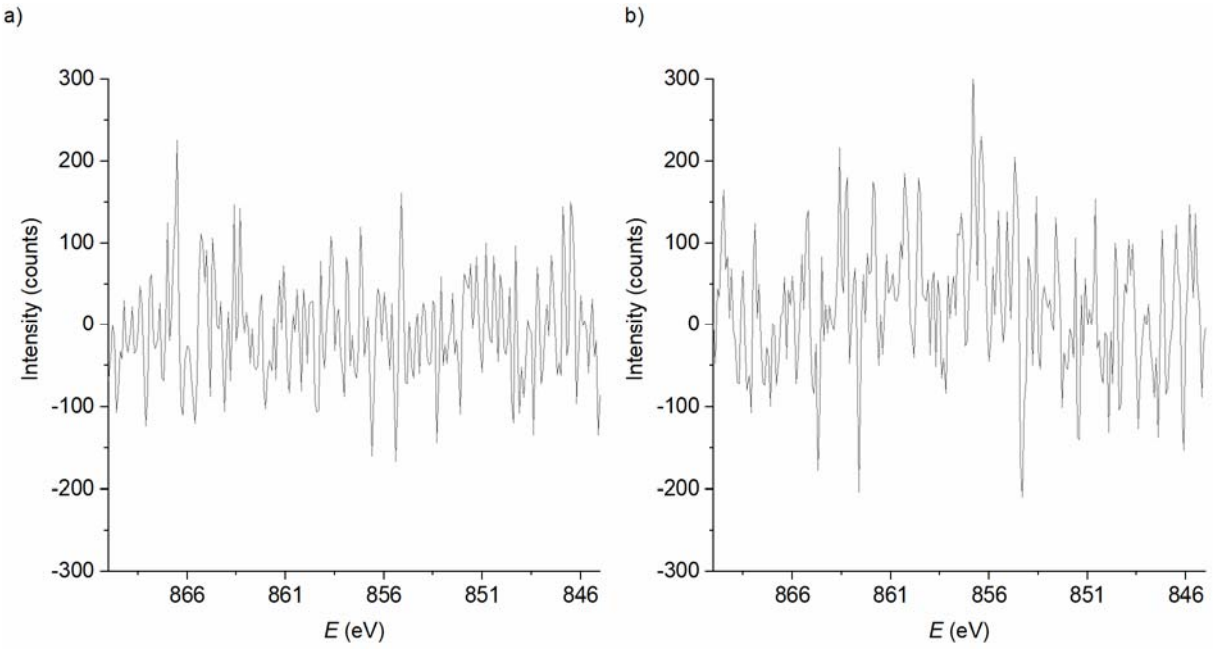


Fig. S23 | Ni 2p XPS of (a) fresh and (b)recovered mpg-CN.

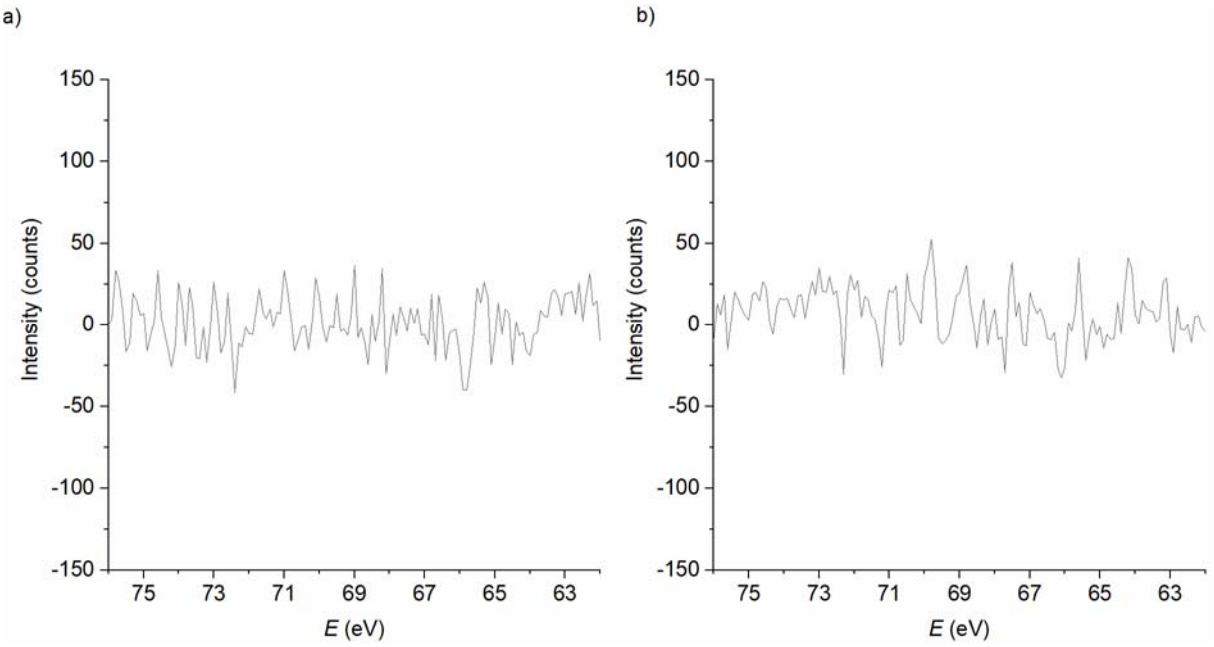


Fig. S24 | Br 3d XPS of (a) fresh and (b) recovered mpg-CN.

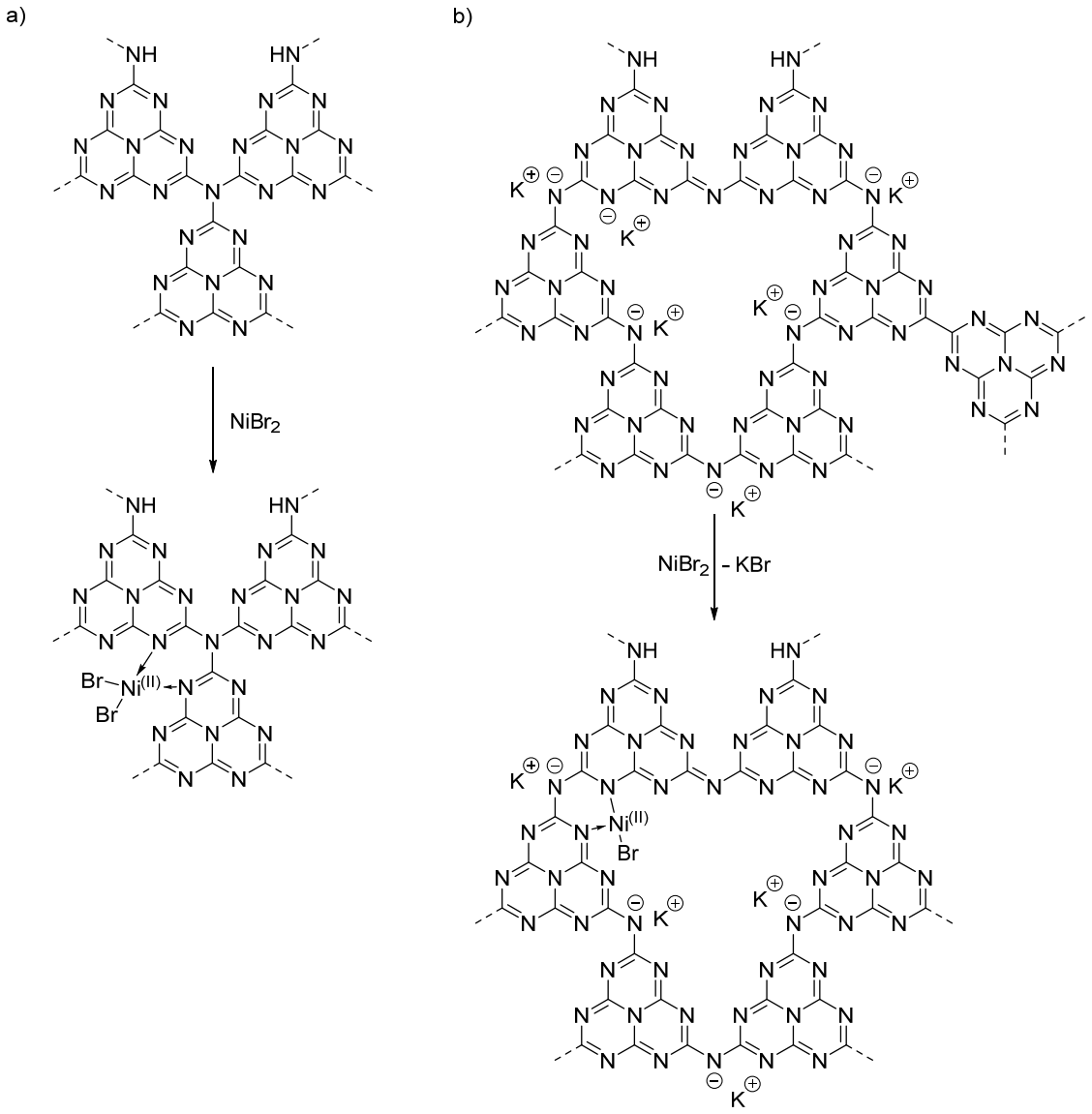


Fig. S25 | Schematic representation of Ni salt coordination. (a) Covalent carbon nitride, such as mpg-CN, and (b) ionic carbon nitride, such as CN-OA-m.

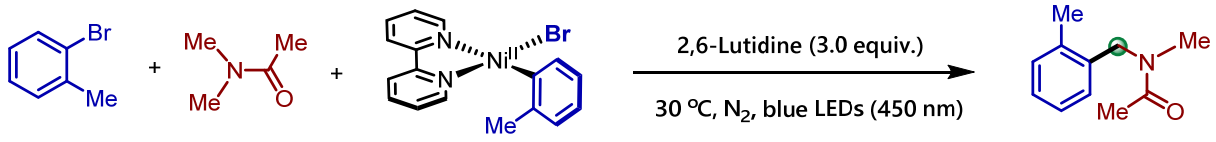
6. Mechanistic Experiments

[(bpy)Ni^{II}(*o*-tolyl)Br] (**B**) was synthesized following the literature procedure.[20,21]

*Representative Procedure for experiments with catalytic[(bpy)Ni^{II}(o-tolyl)Br] complex **II**:*

A 5 mL crimp vial equipped with a magnetic stirring bar was charged with, 1-bromo-2-methylbenzene (34.2 mg, 0.2 mmol), mpg-CN (10.0 mg), [(bpy)Ni^{II}(o-tolyl)Br] (3.9 mg, 5 mol%). Subsequently, 1.0 mL of *N*,*N*-dimethylacetamide (DMA) was added followed by addition of 2,6-lutidine (70 µL, 0.6 mmol). The vial was sealed, and the reaction mixture was then introduced to a nitrogen atmosphere via "*freeze-pump-thaw*" cycles (×3) with a syringe needle, keeping the vacuum approx. 5 mbar. It was irradiated with 5 W 455 (± 15) nm LEDs through the plane bottom side of the crimp vial and stirred intensely. The temperature was maintained at 30 °C by cooling with built-in cooling fan. After 48 h, the crude product was analyzed by GC-FID using1,4-dimethoxybenzene as an external standard.

Table S11 | Catalytic experiments with preformed [(bpy)Ni^{II}(*o*-tolyl)Br] complex II



II

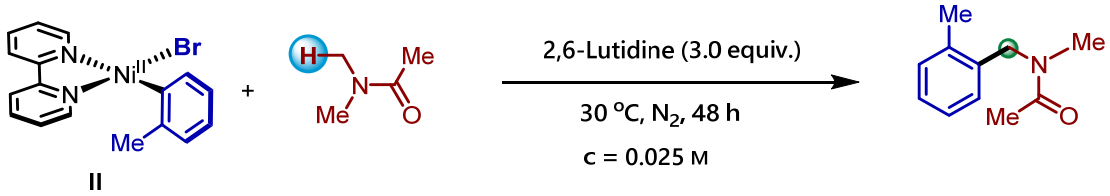
Entry	Deviation from the above condition	Yield
1.	none	5%
2.	With mpg-CN (10 mg mL^{-1})	56%

*Representative Procedure for experiments with stoichiometric [(bpy)Ni^{II}(o-tolyl)Br] complex **II**:*

A 5 mL crimp vial equipped with a magnetic stirring bar was charged with, [(bpy)Ni^{II}(*o*-tolyl)Br] (9.64 mg, 5 mol%). Subsequently, 1.0 mL of *N*,*N*-dimethylacetamide (DMA) was added followed by addition of 2,6-lutidine (8.8 µL, 0.075 mmol). The vial was sealed, and the reaction mixture was then introduced to a nitrogen atmosphere via "*freeze-pump-thaw*" cycles (×3) with a syringe needle, keeping the vacuum approx. 5 mbar. It was irradiated with indicated light source through the plane bottom side of the crimp vial and stirred intensely. The

temperature was maintained at 30 °C by cooling with built-in cooling fan. After 48 h, the crude product was analyzed by GC-FID using1,4-dimethoxybenzene as an external standard.

Table S12 | Stoichiometric experiments with preformed [(bpy)Ni^{II}(*o*-tolyl)Br] complex II



Entry	Photocatalyst	Light source	Yield
1.	-	340 nm	17%
2.	-	450 nm	20%
3.	-	Dark	ND
4.[a]	$Ru(bpz)_3PF_6$ (E_{M^*/M^-} = + 1.45 VEm λ = 591 nm)	450 nm	22%
5.[a]	$(9\text{-MesAcr})ClO_4$ (E_{M^*/M^-} = + 2.05 V Em λ = 590 nm)	450 nm	24%

[a]10 mol% photocatalyst was used.

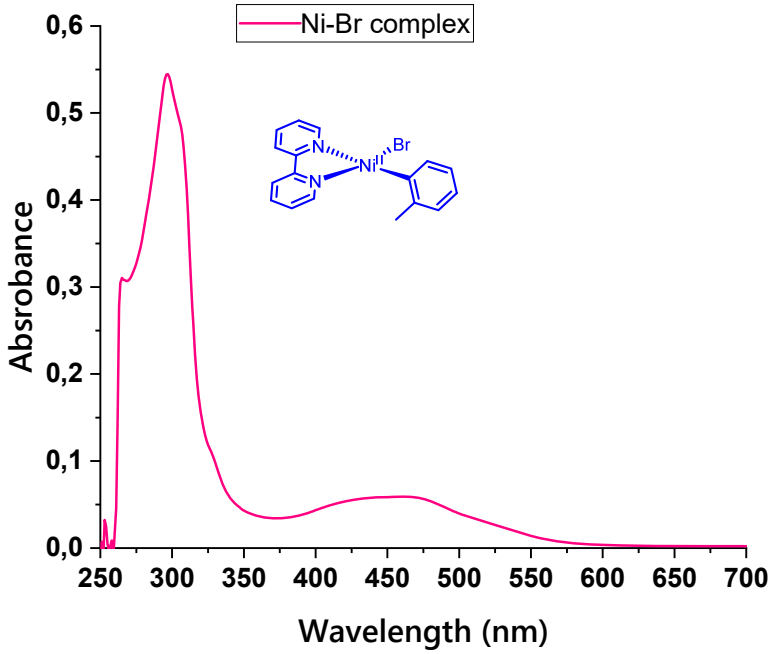


Fig. S26 | UV-Visible spectra of [(bpy)Ni^{II}(*o*-tolyl)Br] complex B in DMA.

8. Investigation of scalability in Continuous Flow reactors

8.1 Representative Procedure for Continuous Flow Investigations

Flow reactions were conducted within a "Vapourtec reactor" **(Fig. S27a-c)**, fitted with a pulsator unit (ProMinent (beta/4) pulsator unit with stainless steel 316 pump head) between a Vapourtec V3 slurry-handling pump and a 10 mL PTFE reactor coil housed within the Vapourtec UV-150 mirrored photochemical reactor cavity[22]. The blue LED manifold was positioned at the center of the coil resulting in a fully closed system. The flow path was first flushed clean with DMA degassed via Ar bubbling (30 min). A 50 mL crimp cap vial equipped with a stir bar was dried overnight and charged with 4-bromobenzonitrile (4.6 mmol, 1.0 equiv.), mpg-CN (10 mg mL^{-1}), $NiBr_2$•glyme (5 mol%) and 2,2′-bipyridine (5 mol%) before placing under a nitrogen atmosphere. Afterwards, 2,6-lutidine (3.0 eq.) and DMA (23 mL) were added under nitrogen via a syringe. The reaction mixture was degassed via "*freeze-pump-thaw*" cycles (×3), backfilled with N_2 and stirred intensely under N_2 protection. Then, blue LEDs (60 W input power, 24 W radiant power at 450 nm) and the pulsator (20% amplitude and 50% frequency) were switched on and the degassed reaction mixture was introduced via an inlet directly from the crimp cap vial through the slurry-handling V3 pump, through the pulsator and into the "Vapourtec reactor" with a 0.50 mL min^{-1} flow rate. An adjustable BPR was set for a back pressure between 2-3 bar. First combined 20 mL of solvent (*ca.* 19 mL total reactor volume) and diluted reaction mixture was discarded. A 1 mL of sample was then collected for analysis of a 'single pass' reaction. After collecting the sample, the flow rate was stopped, and the outlet was connected directly to the reaction vial for recirculation. Argon was introduced via a syringe and the flow rate was returned. The argon protection needle was removed after a further 10 minutes. Temperature of the coil reactor was maintained at *ca.* 25 °C by a nitrogen flow through a canister filled with dry ice chips.

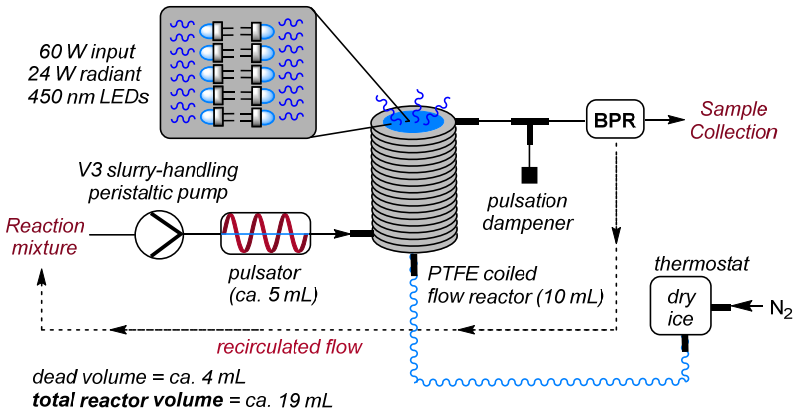


Fig. S27a | Schematic representation of "Vapourtec reactor" continuous flow setup.

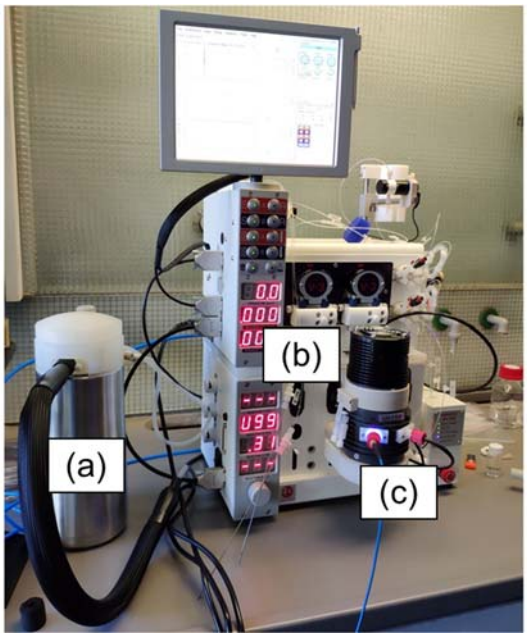


Fig. S27b | Representative Photograph of the continuous flow setup photochemical reaction set-up ("Vapourtec reactor"). (a) Temperature control unit utilizing a flow of N_2 over dry ice chips. (b) Vapourtec R-Series V3 peristaltic pumps. (c) Vapourtec UV-150 module consisting of a 10 mL PFA reaction coil and a Vapourtec LED module, λ_{max} = 450 nm, up to 60 W input power, 24 W radiant power at maximum current.

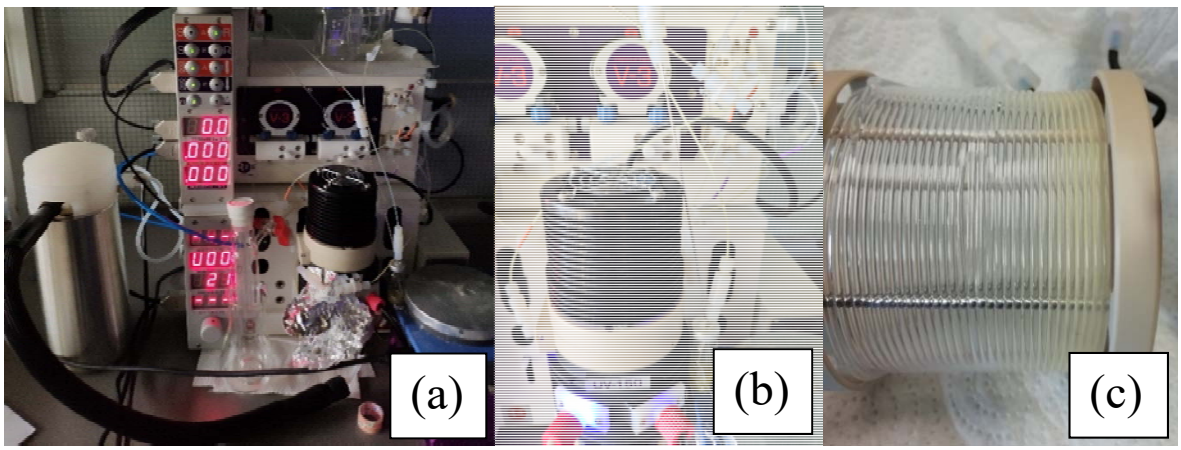


Fig. S27c | Photograph of the continuous flow setup photochemical reaction set-up ("Vapourtec reactor"). (a) Connection of the cooling unit to the UV-150 module prior to operation, temperature was set to 50 °C (external temperature). (b) Visually-even dispersion of mpg-CN photocatalyst across the laminar-type flow path (coiled tube reactor) before entry to the coil. (c) Sedimentation of mpg-CN within the laminar-type flow path (10 mL PFA reactor coil).

8.2 Representative Procedure for Continuous Flow Investigations

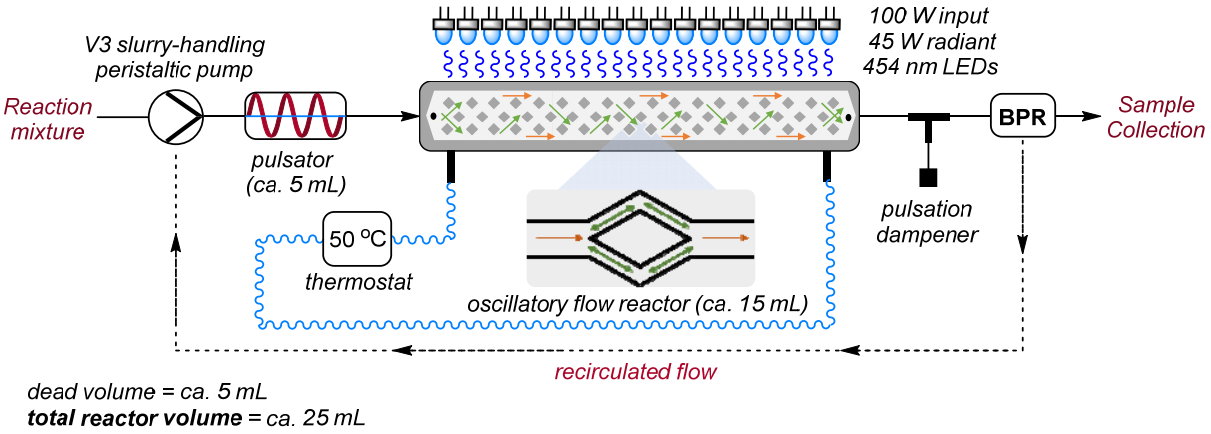


Fig. S27d | Schematic representation of "HANU reactor" continuous flow setup.

Flow reactions were conducted within a "HANU reactor" **(Fig. S27d-f)**, fitted with a pulsator unit (ProMinent (beta/4) pulsator unit with stainless steel 316 pump head) between a Vapourtec V3 slurry-handling pump and the 15 mL HANU reactor. The water-cooled blue LED manifold was positioned on top of the HANU reactor as a fully enclosed system. The flow path was first flushed clean with DMA degassed via Ar bubbling (30 min). A 50 mL crimp cap vial equipped with a stir bar was dried overnight and charged with 4-bromobenzonitrile (6.0 mmol, 1.0 equiv.), mpg-CN (10 mg mL^{-1}), $NiBr_2$•glyme (5 mol%) and 2,2′-bipyridine (5 mol%) before placing under a nitrogen atmosphere. Afterwards, 2,6-lutidine (3.0 eq.) and DMA (30 mL) were added under nitrogen via a syringe. The reaction mixture was degassed via "*freeze-pump-thaw*" cycles (×3), backfilled with N_2 and stirred intensely under N_2 protection. Then, blue LEDs (100 W input power, 45 W radiant power at 454 nm) and the pulsator (20% amplitude and 50% frequency) were switched on and the degassed reaction mixture was introduced via an inlet directly from the crimp cap vial through the slurry-handling V3 pump, through the pulsator and into the "Vapourtec reactor" with a 0.75 mL min^{-1} flow rate. An adjustable BPR was set for a back pressure between 2-3 bar. First combined 25 mL of solvent and diluted reaction mixture (*ca.* 26 mL total reactor volume) was discarded. A 1 mL of sample was then collected for analysis of a 'single pass' reaction. After collecting the sample, the flow rate was stopped, and the outlet was connected directly to the reaction vial for recirculation. Argon was introduced via a syringe and the flow rate was returned. The argon protection needle was removed after a further 10 minutes. Temperature of the ''HANU'' reactor block was maintained at *ca.* 25 °C or *ca.* 50 °C by a thermostat recirculating heated distilled water.

Alternatively, a customized PTFE-base oscillatory flow reactor[23] (**Fig. 27e**) was employed to confirm if a material incompatibility issue of stainless steel 316 with the reaction mixture was responsible for poor conversion. Since the Teflon material is a strong thermal insulator, the heat generated by the LED manifold could not be removed and the flow path temperature could not be precisely controlled but was measured at *ca.* 33-43 °C (external temperature).

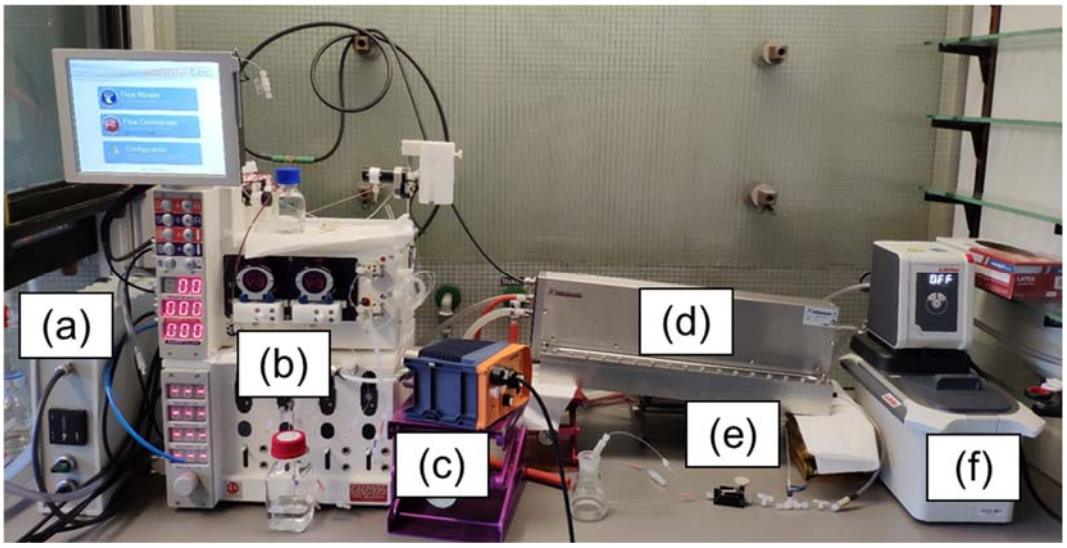


Fig. S27e | Photograph of the continuous flow setup photochemical reaction set-up (''HANU^{TM} reactor''). (a) Peschl Ultraviolet LED light intensity regulator. (b) Vapourtec R-Series V3 peristaltic pumps. (c) CreaFlow customized ProMinent (beta/4) pulsator unit with stainless steel 316 pump head (positioned as in **Fig. S27e** during operation). (d) reactor module consisting of i) a water-cooled stainless steel 316 microstructured oscillatory baffled flow reactor (HANU^{TM} reactor, 15 mL internal volume) and ii) a water-cooled Peschl Ultraviolet LED module, λ_{max} = 454 nm, up to 100 W input power, 45 W radiant power (F_e) at maximum current. (e) Adjustable backpressure regulator (Vapourtec) following a pulsation dampener. (f) Thermostat for temperature control of the HANU^{TM} flow path set at 25 or 50 °C (external temperature).

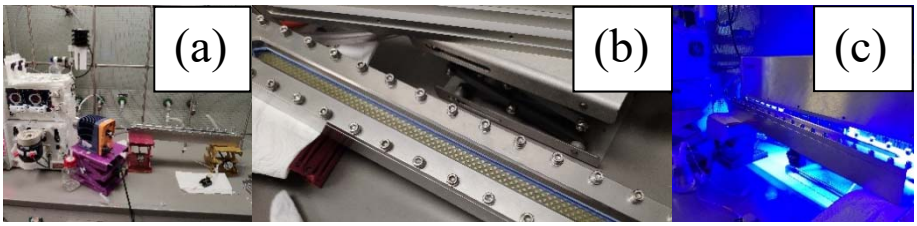


Fig. S27f | Photograph of the continuous flow setup photochemical reaction set-up (''HANU^{TM} reactor''). (a) Vertical positioning of pulsator unit. (b) Visually-even dispersion of mpg-CN photocatalyst across the turbulent-type flow path before irradiation. (c)

Representative picture of the operating Peschl LED module (during operation, the LED module was placed directly atop the HANU^{TM} reactor).

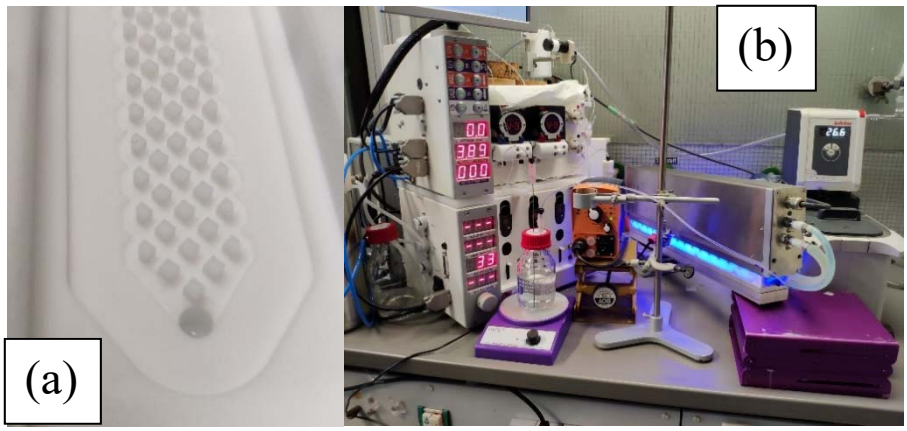
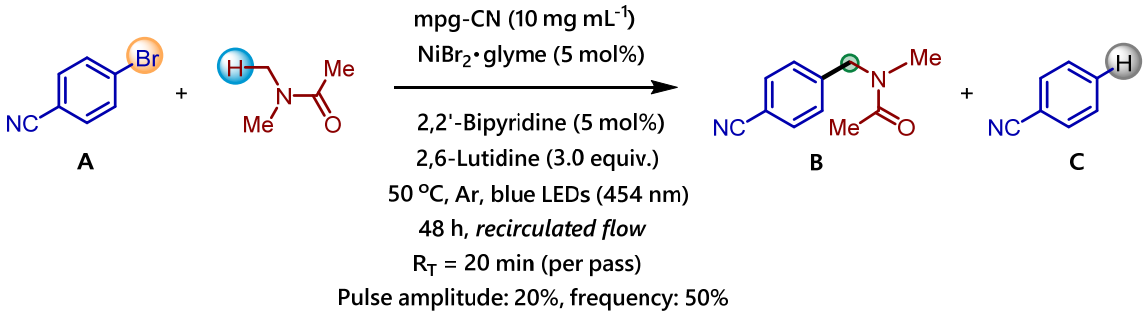


Fig. S27g | Photograph of the continuous flow setup photochemical reaction set-up (Teflon-modified oscillatory flow reactor). (a) PTFE-modified flow oscillatory flow path; (b) Assembled system as per **Fig. S12g-h** including a ProMinent (beta 4-BT4b) pulsator unit with a PTFE pump head. External temperature of the flow path varied from 33-43 ºC.

The model reaction of 4-bromobenzonitrile (**A**) with DMA was chosen for scalability evaluation in continuous flow reactors. We first examined the use of a commercially-available microstructured oscillatory flow reactor (HANU^{TM} reactor, CreaFlow), in combination with a pulsator unit, whose synergy is a state-of-the-art technology for processing heterogeneous photocatalytic reactions in a continuous flowing suspension/slurry.[23] The microstructured cubic static mixing elements are especially designed, in tandem with pulsation, to ensure homogeneity in the suspension of carbon nitride particles and to prevent settling and flow channel fouling at any given flow rate. Initial conditions mirrored a previous report employing a different carbon nitride catalyst ("CN-OA-m", reported particle size distribution 0.45-875 mm) which afforded the optimal residence time distribution and yield for a photocatalytic Buchwald-Hartwig-type amination.[24] Namely, 0.2 M concentration of **A**, 3.33 mg mL^{-1} mpg-CN loading, 5 mol% loading of both nickel catalyst and ligand, temperature of 50 ºC, pulsation amplitude of 20% and frequency of 50% and residence time of 20 minutes. LED manifold input and radiant power employed (λ_{max} = 454 nm, 45 W radiant power at maximum current) were very similar to this report (λ_{max} = 460 nm, 34 W radiant power at maximum current were reported). Given the proximity of the LEDs to the flow channel occupying a thin film (HANU channel depth = *ca.* 2.0 mm) of 15 mL and assuming an ideal system in which no optical power is lost from the reactor, one can estimate a 'radiant power density' of 3.0 W mL^{-1}. However, we were surprised

to find absolutely no conversion of **A** under these conditions after a single pass through the reactor (**Table S13**, entry 1). Recirculating for 16 h afforded *ca.* 6% conversion (entry 2).

Table S13 | Investigation of scalability in Continuous Flow reactors



Entry[a]	Reactor System	Deviation from Conditions	Ratio **A**:**B**:**C**[b]
1.	HANU^{TM} SS 316 OFR	3.33 mg/mL mpg-CN, 'single pass' , R_T = 20 min	n.r.
2.	HANU^{TM} SS 316 OFR	3.33 mg/mL mpg-CN, 16 h	94:5:1
3.	HANU^{TM} SS 316 OFR	'single pass', R_T = 20 min	n.r.
4.	HANU^{TM} SS 316 OFR	15 h	88: 10: 2
5.	HANU^{TM} SS 316 OFR	48h	65:27:8
6.	HANU^{TM} SS 316 OFR	110 h	39:45:16
7.	HANU^{TM} SS 316 OFR	3-acetoxyquinuclidine (1.5 eq.) instead of 2,6-lutidine	74:17:9
8.	Teflon OFR	(different reactor material)	79:9:12
9.	HANU^{TM} SS 316 OFR	'pulsated batch'	66:30:4
10.	HANU^{TM} SS 316 OFR	'pulsated batch', 25 °C	77:14:9
11.	HANU^{TM} SS 316 OFR	30% light intensity	89:7:4
12[c].	Vapourtec UV-150	- (39 h)	58:28:14
13[c].	Vapourtec UV-150	- (110 h)	42:34:24

[a]Reaction Condition: 4-bromobenzonitrile '**A**' (6 mmol), mpg-CN (10 mg mL^{-1}), $NiBr_2$·glyme (5 mol%), 2,2'-bipyridine (5 mol%), 2,6-lutidine (3.0 equiv.), DMA (0.2 M with respect to **A**). [b]Reaction component ratios were determined by GC-FID and are expressed as a relative ratio of their total peak areas (i.e. do not account for other products).[c]4.6 mmol of '**A**' was used in DMA (0.2 M with respect to **A**). n.r., no reaction.

Increasing mpg-CN loading to 10 mg mL^{-1} still gave no conversion after a single pass through the reactor (entry 3), while recirculation for 15 h gave *ca.* 12% conversion, double that of the 3.33 mg mL^{-1} loading (entry 4). Further recirculation of this reaction for 48 h and 110 h (almost 5 days!) increased conversion to *ca.* 35% and *ca.* 61%, respectively (entries 5-6). Suspecting that the herein-proposed bromine radicals as HAT agents may be interacting with the stainless steel (SS 316) material of the reactor, we substituted 2,6-Lutidine base with 3-acetoxyquinuclidine whose radical cation is a HAT agent known to engage α-amido C-H bonds.[25] However, conversion did not improve (*ca.* 25% after 48 h, entry 7). We also performed the reaction in a modified oscillatory flow reactor path made from Teflon, and employed a

pulsator with a PTFE pump head, removing all contact of the reaction mixture with SS 316. However, conversion did not improve (*ca.* 21% after 48 h, entry 8). In light of these results, a material compatibility issue with SS 316 can be ruled out. Next, we operated the HANU reactor in a 'batch-type' mode, filling the 15 mL reactor with reaction mixture, ceasing the flow and pulsating within the illuminated reactor. After 48 h (entry 9), the result was almost identical to result of recirculated flow with a 0.75 mL min^{-1} flow rate, indicating that a flowing stream of reaction mixture offers no benefit to conversion. Decreasing light intensity to 30% of the maximum value (*ca.* 13.5 W radiant power) gave 30% of the combined relative amounts of products as was provided by the 100% intensity (entry 10 vs entry 5). Conversion may therefore be photon-limited, but on the assumption of the aforementioned direct proportionality between intensity and conversion, one would require ca. 135 W of radiant power across the flow path for full conversion and 48 h of reaction time at 50 °C. Since 50 °C is a sub-optimal temperature for the reaction described herein (as it provides increased amounts of reduced product), the corresponding reaction at rt would require an even longer reaction time. We then attempted to process the reaction mixture within another commercial photochemical flow reactor; a Vapourtec UV-150 photochemical reactor equipped with a 10 mL PTFE coil placed within a mirrored cavity and surrounding an LED manifold (λ_{max} = 450 nm, 60 W input power. Interestingly, under the same conditions (10 mg/mL^{-1} mpg-CN, 5 mol% nickel catalyst and ligand, 50 °C) we observed 42% conversion after 39 h of recirculating (no products were detected upon a single pass through the reactor), which was at a first glance superior to the result after 48 h of recirculating in the HANU reactor (entry 12 vs entry 5). However, over extended periods of operation we observed accumulation of mpg-CN due to sedimentation in the PTFE coil, leading to a blockage and loss of detected pressure after 40 h. When the reaction was restarted, the rate of conversion was noticeably lower (see **Fig. S27h**, final graph and entry 12) ultimately resulting in a similar conversion after 110 h as the HANU reactor with its superior mixing properties (see **Fig. S27h**, first graph and entry 5). Due to the different mixing properties of the reactors, it is inappropriate to make comparisons of the kinetic profiles shown in **Fig. S27h** at this stage. Given the proximity of the LEDs to the PTFE coil reactor which provides a thin film (o.d. = 1.6 mm, i.d. = 1.0 mm) of 10 mL and assuming an ideal system in which no optical power is lost from the reactor, one can estimate a 'radiant power density' of 2.4 W mL^{-1}. This 'radiant power density' is 0.8x that of the 3.0 W mL^{-1} estimated from the HANU reactor. Given that the Vapourtec UV-150 total reactor volume requires 0.8x that of the HANU reactor and reactions are compared at identical concentration, we are confident in the

comparability of results between Vapourtec UV-150 reactor and HANU reactor systems in this study.

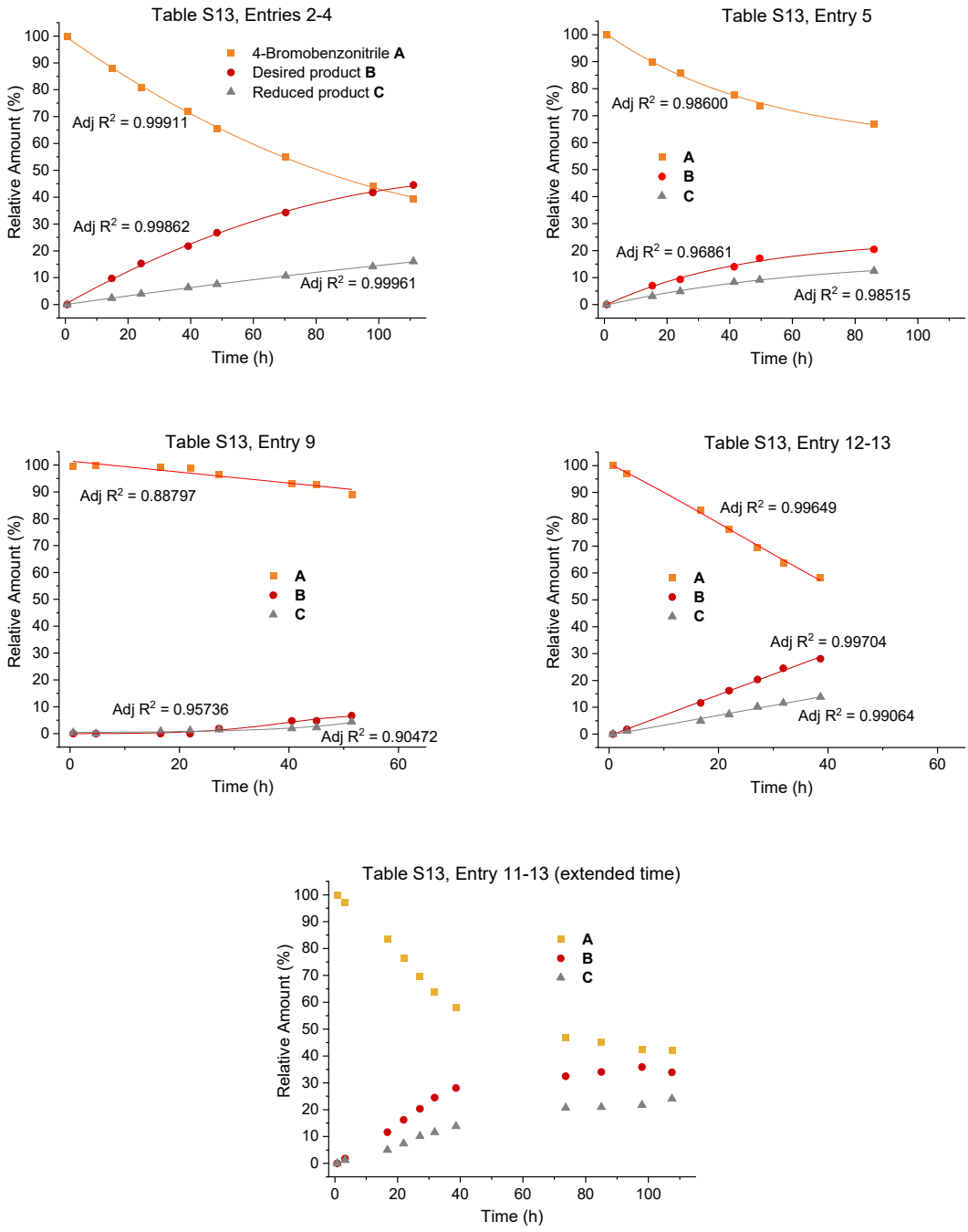
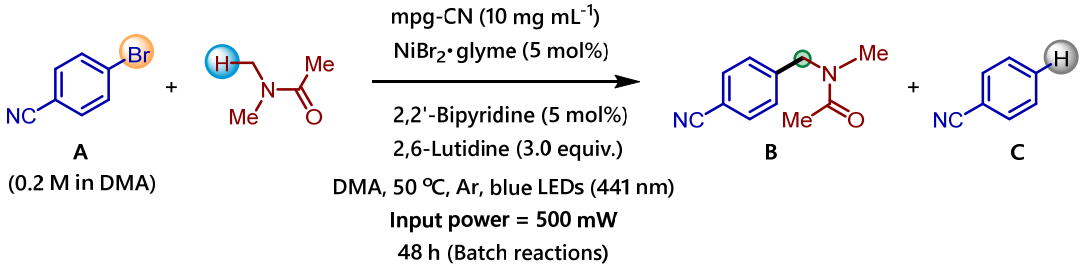


Fig. S27h | Time-course profiles for Continuous Flow reaction investigations in Table S13.

We investigated increasing the nickel and bipyridine catalyst loadings to elucidate their impact in batch mode, in search of more suitable reaction conditions for continuous flow processing (**Table S14**). We note that (unless otherwise stated) reactions performed in **Table S14** used OSRAM Oslon SSL 80 LDCQ7P-2U3U LT1960 LEDs (λ= 440 nm (± 15 nm), 1.5 W LEDs

(optical power 500 mW), which are weaker in optical power than the LEDs used generally in the study but nonetheless afforded full conversion after 105 h at rt and after 85 h at 50 °C under the reaction conditions described in **General Procedures 8.1** and **8.2** (0.2 M **A** in DMA, 10 mg mL^{-1} mpg-CN, 5 mol% nickel and bipyridine catalyst, 3.0 eq. 2,6-Lutidine). Different reaction conditions are compared with these LEDs in **Table S14**.

Table S14 | Investigation of reaction kinetics in batch mode.



Entry[a]	Deviation from Conditions	Ratio **A**:**B**:**C**[b]	Rate constant *k* of consumption of **A** ($M\ s^{-1}$)
1.	-	24:49:27 (48 h) <1:61:39 (85 h)	-9.68×10^{-7} [c]
2.	r.t.	53:43:4 (48 h) 4:87:9 (105 h)	-4.86×10^{-7}
3.	15 mol% $NiBr_2$•glyme **and** 2,2'-Bipyridine	64:10:26 (48 h) 26:21:53 (105 h)	-4.28×10^{-7}
4.	15 mol% $NiBr_2$•glyme **and** 2,2'-Bipyridine, r.t.	83:13:4 (48 h) 57:36:7 (105 h)	-2.31×10^{-7}
5[d].	**A** = 0.6 M, 15 mol% $NiBr_2$•glyme **and** 2,2'-Bipyridine	86:4:10 (48 h) 66:10:24 (105 h)	-1.80×10^{-7}
6[d].	**A** = 0.6 M, 15 mol% $NiBr_2$•glyme **and** 2,2'-Bipyridine, r.t.	91:7:2 (48 h) 80:16:4 (105 h)	-1.08×10^{-7}
7.	3-acetoxyquinuclidine (1.5 eq.), no 2,4-lutidine	<1:60:40[e] (48 h)	n.d.

[a]Reaction Condition: 4-bromobenzonitrile '**A**' (0.2 mmol), mpg-CN (10 mg mL^{-1}), $NiBr_2$·glyme (5 mol%), 2,2'-bipyridine (5 mol%), 2,6-lutidine (3.0 equiv.), DMA (0.2 M with respect to **A**). [b]Reaction component ratios were determined by GC-FID and are expressed as a relative ratio of their total peak areas (i.e. do not account for other products). [c]Pseudo-zero-order rate constants were obtained by fitting the first five datapoints (to 10,000 s). [d]1.2 mmol of '**A**' was used in DMA (0.2 M with respect to **A**). [e]Reaction performed using OSRAM OSLON® SSL 80 GD CS8PM1.14 LEDs (λ= 451 nm (± 15 nm), 5 W optical power). n.d. not determined

Clearly, the reaction is operating under a photon-limited regime, given the comparison of different LED intensities (**Table S13**, entries 5 vs 11 and the fact that reactions took >80 h to complete using 500 mW optical power LEDs compared to the 'standard' 5 W optical power LEDs used for the substrate scope and optimization studies). Reaction rates also show a

temperature dependence; reactions proceed faster at 50 °C but lead to more debromination product (**Table S14**, entry 1 vs 2). We were intrigued to observe an apparent change in reaction kinetic profile from pseudo-zero-order behaviour to zero-order behaviour in the consumption

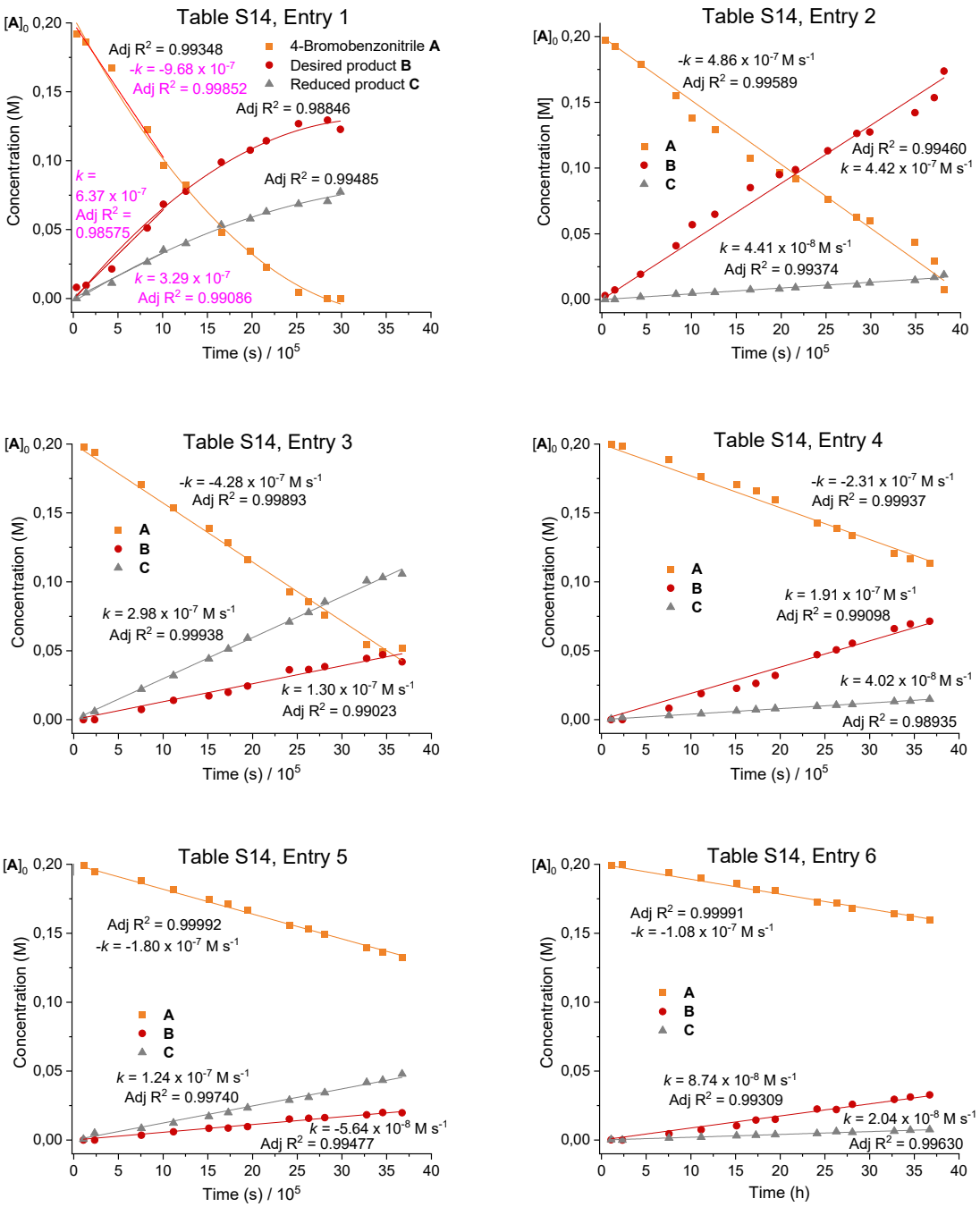


Fig. S27i | Time-course profiles for batch reaction investigations in Table S4.

of **A** and formation of **B** and **C** from 25 °C to 50 °C (see **Fig. S27i**, first and second graph, entry 2 and entry 1 of **Table S14**). Given these that temperature is the only different factor, the zero-order dependence observed at 25 °C is not related to the abundance of light (both reactions are likely photon-limited in regime). Zero-order kinetic behaviour is typical of heterogeneous

catalytic reactions[26] in which active sites are saturated by absorbed reactant molecules and has been reported elsewhere for mpg-CN in both non-photocatalytic and dual-photocatalytic chemistry.[27,28] As the reaction reaches full conversion, active sites become more available on the mpg-CN surface resulting in a final curvature of the kinetic behaviour. Zero-order behaviour in heterogeneous catalysis is well-known to result from the existence of an absorption equilibrium (equation 1) which is followed by a single, slow surface reaction step that is rate-determining (equation 2)[29]

$[Ni]_{liquid} \leftrightarrows [Ni]_{adsorbed}$ **(1)**;*equilibrium* $[Ni]_{adsorbed} \rightarrow products$ **(2)**; *rate-determining*

In this case, the rate law can be defined for consumption of 4-bromobenzonitrile **A** as equation 3. Integration from $t = 0$ ($[\mathbf{A}]_0$) to time $t = t$ ($[\mathbf{A}]_t$) as per equation 4 leads to equation 5 which is a straight-line plot whose gradient = $-k$. The rate constant was thereby calculated for all plots in **Table S14**.

$$-\frac{d[\boldsymbol{A}]}{dt} = -k[\boldsymbol{A}] \quad \textbf{(3)} \qquad -\int_{t=0}^{t=t} d[\boldsymbol{A}] = -k\int_{t=0}^{t=t} dt \quad \textbf{(4)} \qquad [\boldsymbol{A}]_t = [\boldsymbol{A}]_0 - kt \quad \textbf{(5)}$$

At higher temperatures, we tentatively ascribe the shift in zero-order kinetic behaviour to pseudo-zero-order kinetic behaviour as one of three possibilities: (1) the activation energy of the surface-based rate-determining slow process (presumably involving adsorbed [Ni] complexes) is overcome, promoting desorption of 'products' from the mpg-CN surface and freeing up active sites of the mpg-CN catalyst; (2) a shift in the equilibrium of adsorption at the heterogeneous surface allowing more [Ni] complex whose reaction is rate-determining to engage with the active site; (3) An off-cycle direct reduction of **A** by a photoactive species is increased, providing a radical anion that traps the nickel as reported by Pieber, Seeberger et al.[28] Proposal (3) is consistent with: i) the increase in abundance of dehydrohalogenated product **C** at 50 °C, ii) the fractional rate dependence of aryl halide on the heterogeneous rate law (entries 5,6 vs entries 3,4) discussed below and iii) the redox potential of **A** (E^{p}_{red} = -1.75 V vs. SCE in DMF/0.1 M $^{n}Bu_4N{\cdot}BF_4$)[30] being within almost within reach of photoexcited mpg-CN (up to -1.5 V vs. SCE), albeit a slightly endergonic SET process that may be accessible at 50 °C[31]. Interestingly, increasing the [Ni] catalyst (+ ligand) loading by 3x (at the same concentration of **A**) increased the relative amount of debromination product and halved the reaction rate (**Table S14**, entries 3,4 vs entries 1,2). This contrasts to Pieber and Seeberger's previous study involving decarboxylative arylation of *N*-Boc-protected pyrrole with 4-iodomethylbenzoate, which found that increasing [Ni] catalyst (+ ligand) increased the rate of reaction in a photon-unlimited regime of mpg-CN photocatalysis or had no impact on the rate

of reaction when in a photon-limited regime.[28] In moving from 5 mol% to 15 mol% of the [Ni] catalyst, the pseudo-zero-order behaviour also shifted to represent zero-order behaviour. One could rationalize this with a (Le Chatelier's principle) shift in the equilibrium to remove liquid-phase [Ni] complexes in preference of adsorbed [Ni] complexes, saturating the mpg-CN active sites. If the [Ni] complex whose reaction is rate-determining has to compete with other off-cycle or non-rate-determining on-cycle [Ni] complexes for mpg-CN active sites, the overall rate would slow. Increasing concentration of 4-bromobenzonitrile **A** to 0.6 M further slowed reaction conversion (entries 5,6 vs entries 3,4). The fractional dependence on haloarene concentration is consistent with that reported by Pieber, Seeberger et al.[28]

Whether the reaction mechanism proceeds via Pathway **A** or Pathway **B** (see main manuscript and **Section 7** for experiments supporting Pathway **B**), both mechanisms contain two steps where an [Ni] complex engages with the mpg-CN surface either in SET or EnT. In particular, we note that EnT processes are reported to be extremely efficient at very short distances[32] and so effective adsorption to the mpg-CN surface may be crucial. While further investigations are underway in our laboratories, we tentatively propose that continuous flow results in (a) faster moving liquid phase and (b) a slower-moving mpg-CN solid particles. The asynchrous/divorced flow rates of (a) and (b) are unsupportive of adsorption of [Ni] complexes onto the mpg-CN surface. Pulsated flow and efficient mixing may also be disruptive to the adsorption processes on this particular morphology (mpg-CN) of carbon nitride photocatalyst. In batch mode, [Ni] complexes and mpg-CN are confined in space, resulting in a more uniform and constant flux of [Ni] complexes to mpg-CN.

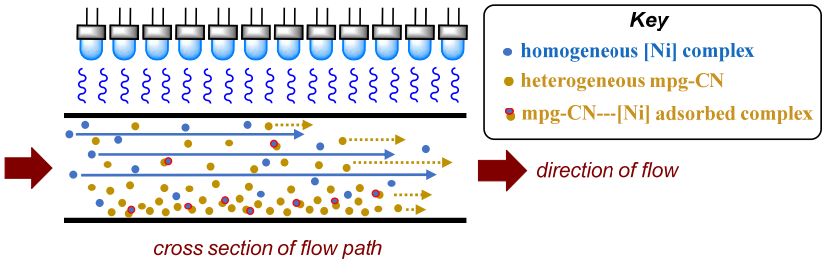


Fig. S27j | Pictorial representation of the divorced time-domains resulting from different flow rates of homogeneous [Ni] complexes and heterogeneous mpg-CN.

In conclusion, this study presents a rare example of how continuous flow is a not a viable solution for scale-up of a heterogeneous photocatalytic reaction. Two different commercially-available photochemical flow reactors especially designed to handle and irradiate suspensions were compared (**Table S15**) and neither outcompeted the actual gram h^{-1} productivity of a batch reaction in the ''Tauchschacht Photoreactor'' on a *ca.* 6 mmol scale (83% of **B** after 60 h, a

concentration of 0.1 M was required by the Tauchschacht reactor compared to standard small-scale batch experiments and flow experiments in to maintain efficient reactor cooling). Even if one were to assume the relative amount (%) of product (**Fig. S27h**) tracks with the yield, the maximum productivities at 0.2 M of **A** in both flow systems would be *ca.* 6.3 mg h^{-1} **B** (**Table S15**). Since 'single-pass' conditions do not afford any conversion, further optimization is unlikely to remedy this to a level where it could be synthetically useful. Recirculated flow is fundamentally limited in scale-up and would be too time-consuming to be synthetically useful. Finally, while energy efficiency is not usually critically discussed in reports scaling-up photochemical reactions in continuous flow, we highlight the difference in LED input power required by the three systems (not taking into consideration the additional demand for resources, such as electrical, water, and N_2 in cooling the hi-power LEDs). We note that while the benefits of continuous flow are usually obvious in scale-up of photochemical processes, this is not always the case[33] and batch chemistry can be a viable scale-up option for certain chemistries.

Table S15 | Actual productivity, yield and LED input power comparison of batch and flow systems.

Reactor	Tauchshacht[a]	Vapourtec UV-150[b,c]	HANU SS 316[b,c]
Processing mode	Batch	Pulsated Flow, laminar-type	Pulsated Flow, oscillatory baffled
Conversion (%)[d]	100%	35[e]	42[f]
Yield (%)	83	28[e]	27[f]
Productivity of B (mg h^{-1})	15.6	6.2	6.3
Productivity of B (mg day^{-1})	374.5	148.8	151.2
Input LED power	12 W	60 W	100 W

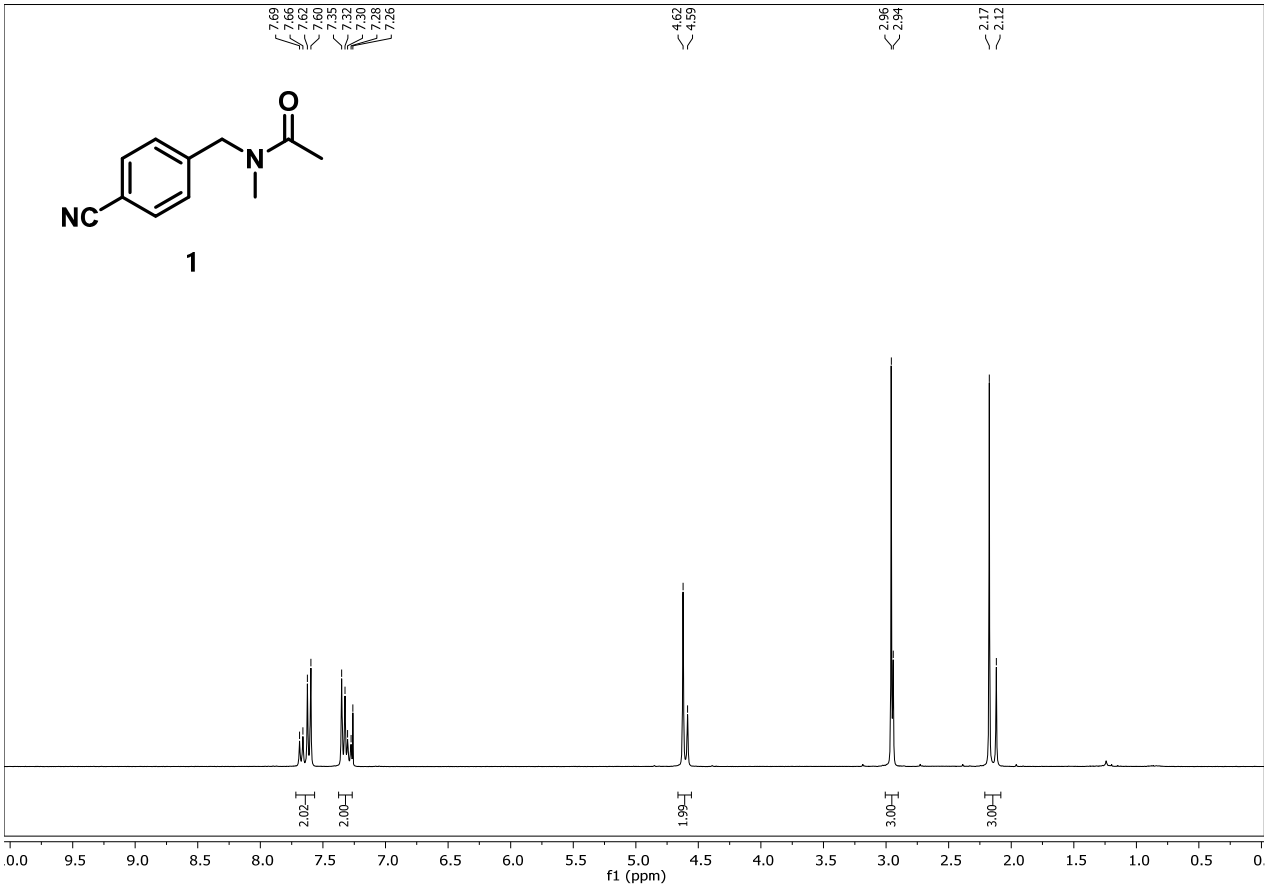
[a]Based on isolated yield after 60 h. [b]Assuming yield tracks with relative amount (%**B**) detected by the calibrated GC FID method as an estimation. [c]Reactions conducted at 50 °C, reactions at rt provided poorer conversion. [d]Based on the relative amount of starting material left (100 - %**A**) determined by the calibrated GC FID method. [e]39 h. [f]48 h.

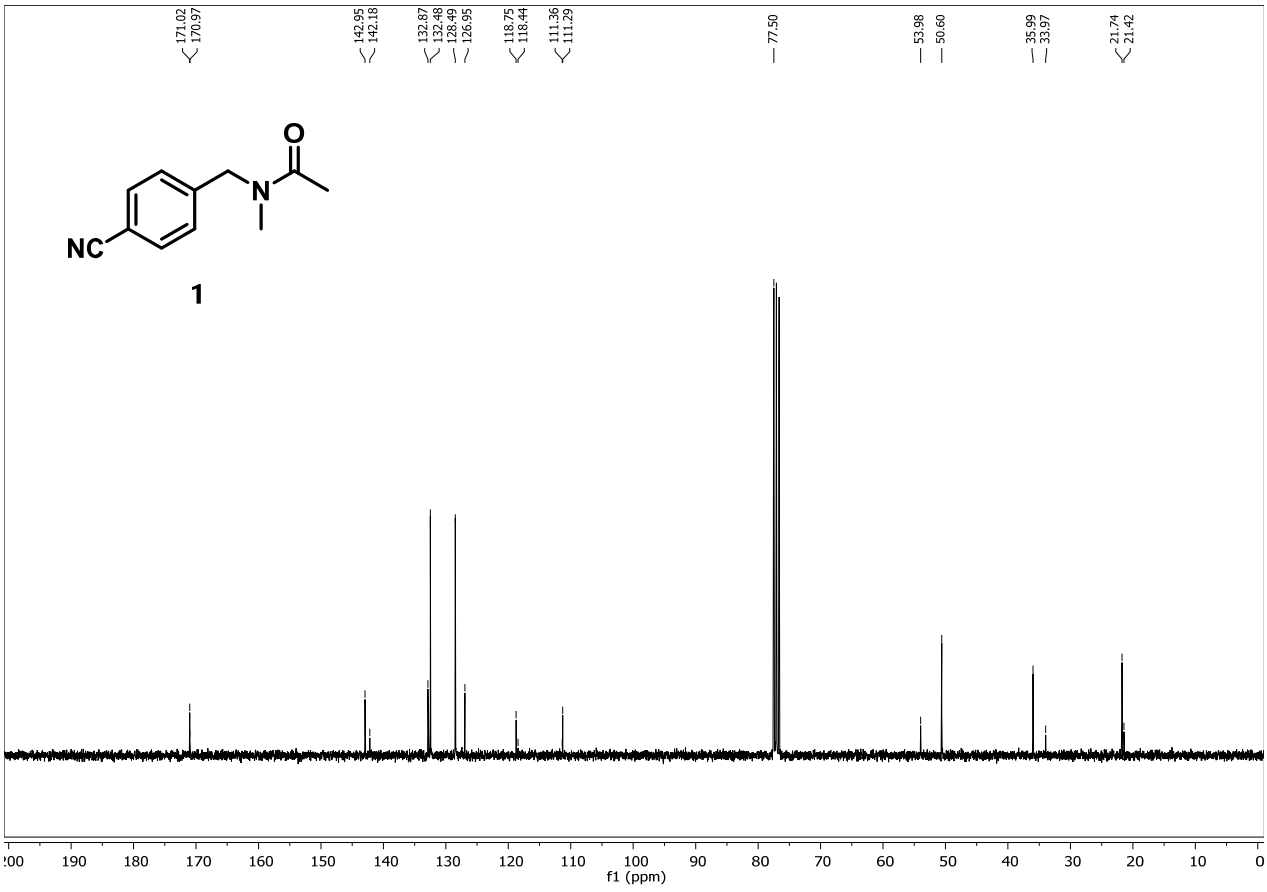
9. Supplementary references

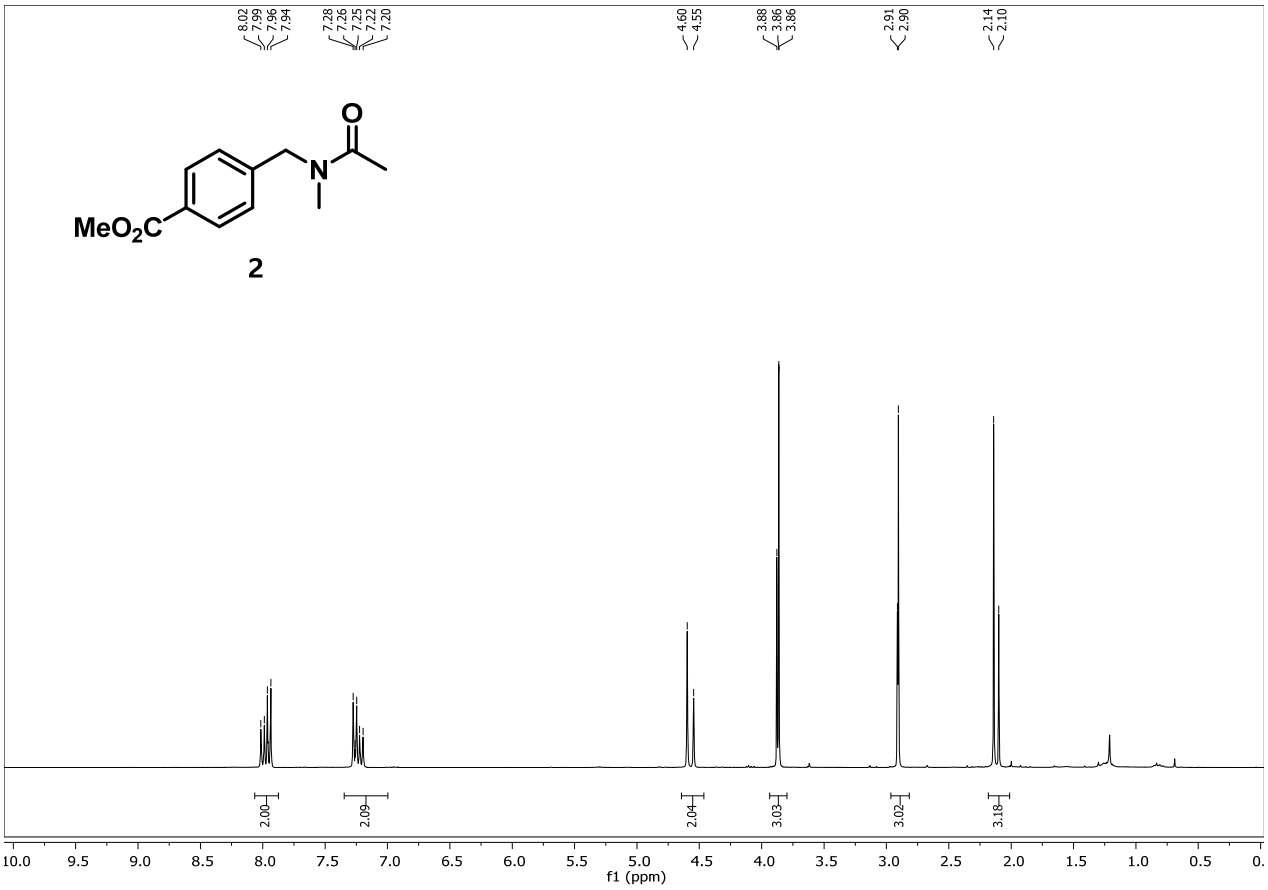
1. Ghosh, I. *et al.* Organic semiconductor photocatalyst can bifunctionalize arenes and heteroarenes. *Science* **365**, 360 (2019).
2. Thurston, J. H., Hunter, N. M. & Cornell, K. A. Preparation and characterization of photoactive antimicrobial graphitic carbon nitride (g-C_3N_4) films. *RSC Advances* **6**, 42240-42248 (2016).
3. Gao, D., Liu, Y., Liu, P., Si, M. & Xue, D. Atomically Thin B doped g-C_3N_4 Nanosheets: High-Temperature Ferromagnetism and calculated Half-Metallicity. *Sci. Rep.* **6**, 35768 (2016).
4. Wang, Y. *et al.* Linker-controlled polymeric photocatalyst for highly efficient hydrogen evolution from water. *Energy Environ. Sci.* **10**, 1643-1651 (2017).
5. Chang, F. *et al.* Enhanced visible-light-driven photocatalytic performance of porous graphitic carbon nitride. *Appl. Surf. Sci.* **358**, 270-277 (2015).
6. Dontsova, D. *et al.* Triazoles: A New Class of Precursors for the Synthesis of Negatively Charged Carbon Nitride Derivatives. *Chem. Mater.* **27**, 5170-5179 (2015).
7. Dai, H. *et al.* Synthesis and characterization of graphitic carbon nitride sub-microspheres using microwave method under mild condition. *Diam. Relat. Mater.* **38**, 109-117 (2013).
8. Zhu, B., Xia, P., Li, Y., Ho, W. & Yu, J. Fabrication and photocatalytic activity enhanced mechanism of direct Z-scheme g-C_3N_4/Ag_2WO_4 photocatalyst. *Appl. Surf. Sci.* **391**, 175-183 (2017).
9. Zhang, H. *et al.* Flower-like Cobalt Hydroxide/Oxide on Graphitic Carbon Nitride for Visible-Light-Driven Water Oxidation. *ACS Appl. Mater. Interfaces* **8**, 35203-35212 (2016).
10. Cao, S., Low, J., Yu, J. & Jaroniec, M. Polymeric Photocatalysts Based on Graphitic Carbon Nitride. *Adv. Mater.* **27**, 2150-2176 (2015).
11. Wang, X. *et al.* A metal-free polymeric photocatalyst for hydrogen production from water under visible light. *Nat. Mater.* **8**, 76-80 (2009).
12. Jorge, A. B. *et al.* H_2 and O_2 Evolution from Water Half-Splitting Reactions by Graphitic Carbon Nitride Materials. *J. Phys. Chem. C* **117**, 7178-7185 (2013).
13. Savateev, A. *et al.* Potassium Poly(Heptazine Imide): Transition Metal-Free Solid-State Triplet Sensitizer in Cascade Energy Transfer and [3+2]-cycloadditions. *Angew. Chem. Int. Ed.* **59**, 15061-15068 (2020).
14. Shen, Y., Gu, Y. & Martin, R. sp^3 C–H Arylation and Alkylation Enabled by the Synergy of Triplet Excited Ketones and Nickel Catalysts. *J. Am. Chem. Soc.* **140**, 12200-12209 (2018).
15. Shields, B. J. & Doyle, A. G. Direct C(sp^3)–H Cross Coupling Enabled by Catalytic Generation of Chlorine Radicals. *J. Am. Chem. Soc.* **138**, 12719-12722 (2016).
16. Pieber, B. *et al.* Semi-heterogeneous Dual Nickel/Photocatalysis using Carbon Nitrides: Esterification of Carboxylic Acids with Aryl Halides. *Angew. Chem. Int. Ed.* **58**, 9575-9580 (2019).
17. Gisbertz, S., Reischauer, S. & Pieber, B. Overcoming limitations in dual photoredox/nickel-catalysed C–N cross-couplings due to catalyst deactivation. *Nat. Catal.* **3**, 611-620 (2020).
18. Zhang, G. *et al.* Optimizing Optical Absorption, Exciton Dissociation, and Charge Transfer of a Polymeric Carbon Nitride with Ultrahigh Solar Hydrogen Production Activity. *Angew. Chem. Int. Ed.* **56**, 13445-13449 (2017).
19. Savateev, A. & Antonietti, M. Ionic Carbon Nitrides in Solar Hydrogen Production and Organic Synthesis: Exciting Chemistry and Economic Advantages. *ChemCatChem* **11**, 6166-6176 (2019).

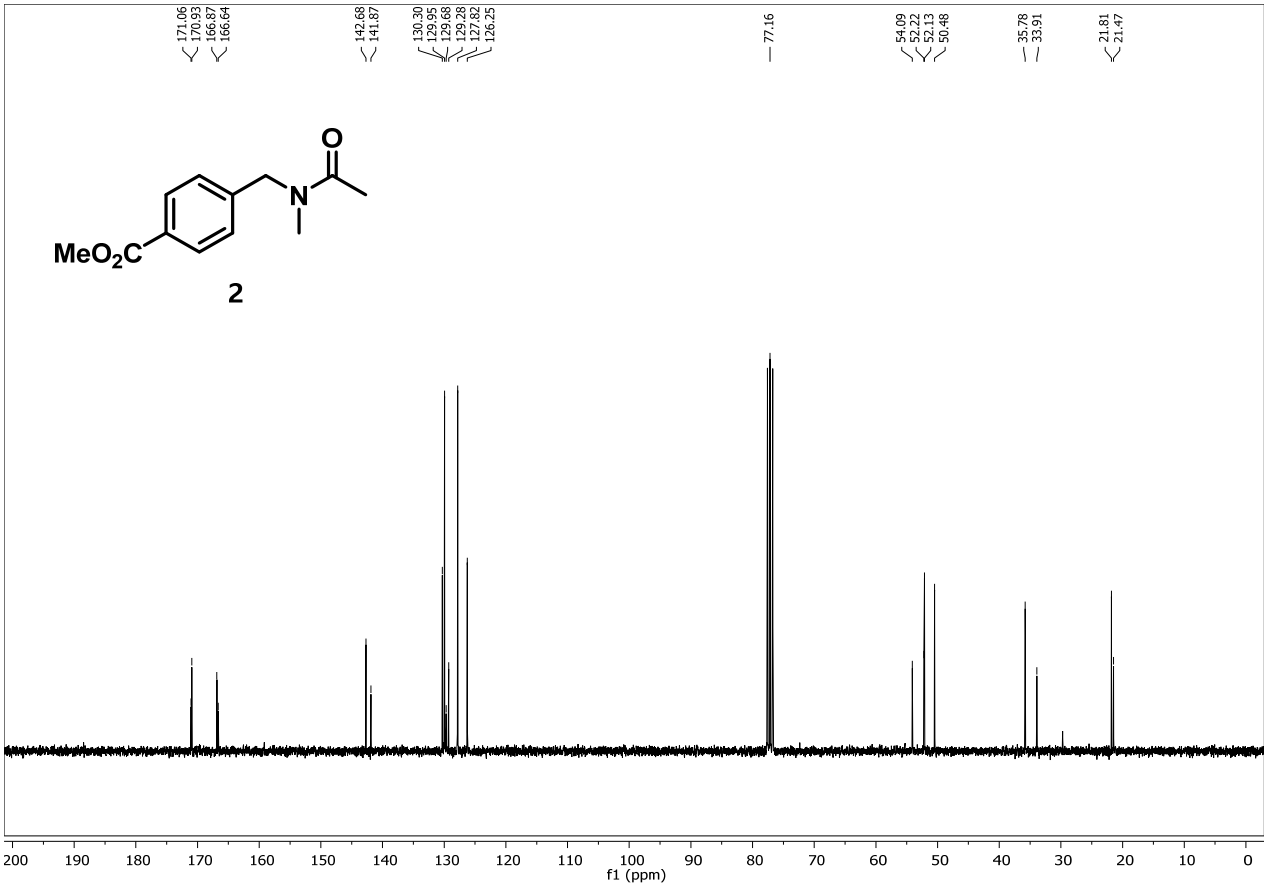
20. Ting, S. I. *et al.* 3d-d Excited States of Ni(II) Complexes Relevant to Photoredox Catalysis: Spectroscopic Identification and Mechanistic Implications. *J. Am. Chem. Soc.* **142**, 5800-5810 (2020).
21. Standley, E. A., Smith, S. J., Müller, P. & Jamison, T. F. A Broadly Applicable Strategy for Entry into Homogeneous Nickel(0) Catalysts from Air-Stable Nickel(II) Complexes. *Organometallics* **33**, 2012-2018 (2014).
22. https://www.vapourtec.com/products/flow-reactors/.
23. http://www.creaflow.be/products.
24. Rosso, C. *et al.* An oscillatory plug flow photoreactor facilitates semi-heterogeneous dual nickel/carbon nitride photocatalytic C–N couplings. *React. Chem. Eng.* **5**, 597-604 (2020).
25. Shaw, M. H., Shurtleff, V. W., Terrett, J. A., Cuthbertson, J. D. & MacMillan, D. W. C. Native functionality in triple catalytic cross-coupling: sp^3 C–H bonds as latent nucleophiles. *Science* **352**, 1304-1308 (2016).
26. Gaya, U. *Heterogeneous photocatalysis using inorganic semiconductor solids*. (SPRINGER, 2016).
27. Ayán-Varela, M. *et al.* Investigating the Dispersion Behavior in Solvents, Biocompatibility, and Use as Support for Highly Efficient Metal Catalysts of Exfoliated Graphitic Carbon Nitride. *ACS Appl. Mater. Interfaces* **7**, 24032-24045 (2015).
28. Malik, J. A., Madani, A., Pieber, B. & Seeberger, P. H. Evidence for Photocatalyst Involvement in Oxidative Additions of Nickel-Catalyzed Carboxylate *O*-Arylations. *J. Am. Chem. Soc.* **142**, 11042-11049 (2020).
29. Murzin, D. Y. On Langmuir kinetics and zero order reactions. *Catal. Commun.* **9**, 1815-1816 (2008).
30. Reche, I., Mena, S., Gallardo, I. & Guirado, G. Electrocarboxylation of halobenzonitriles: An environmentally friendly synthesis of phthalate derivatives. *Electrochim. Acta* **320**, 134576 (2019).
31. Vogt, D. B., Seath, C. P., Wang, H. & Jui, N. T. Selective C–F Functionalization of Unactivated Trifluoromethylarenes. *J. Am. Chem. Soc.* **141**, 13203-13211 (2019).
32. Welin, E. R., Le, C., Arias-Rotondo, D. M., McCusker, J. K. & MacMillan, D. W. C. Photosensitized, energy transfer-mediated organometallic catalysis through electronically excited nickel(II). *Science* **355**, 380-385 (2017).
33. Elliott, L. D. *et al.* Batch versus Flow Photochemistry: A Revealing Comparison of Yield and Productivity. *Chem. Eur. J.* **20**, 15226-15232 (2014).

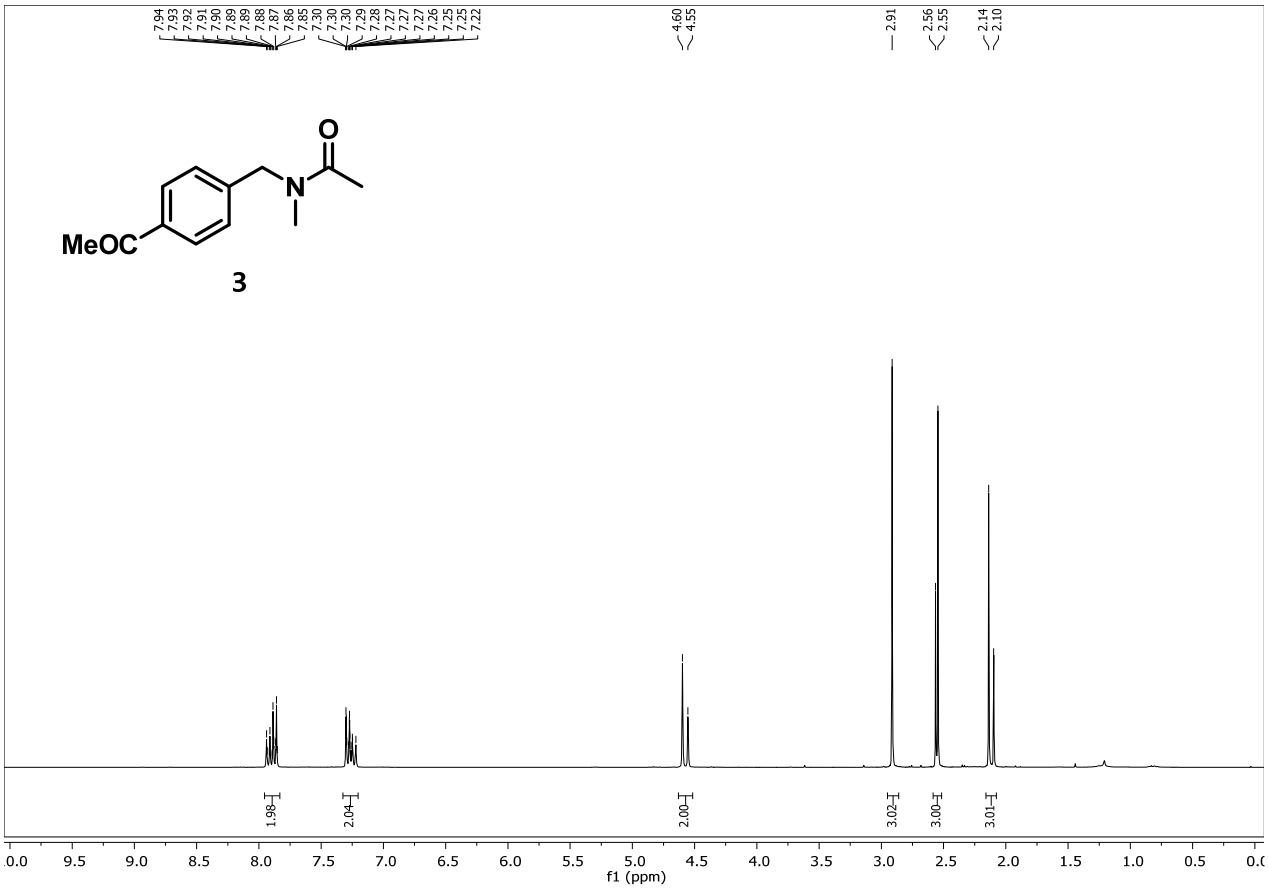
^{1}H and ^{13}C Spectra

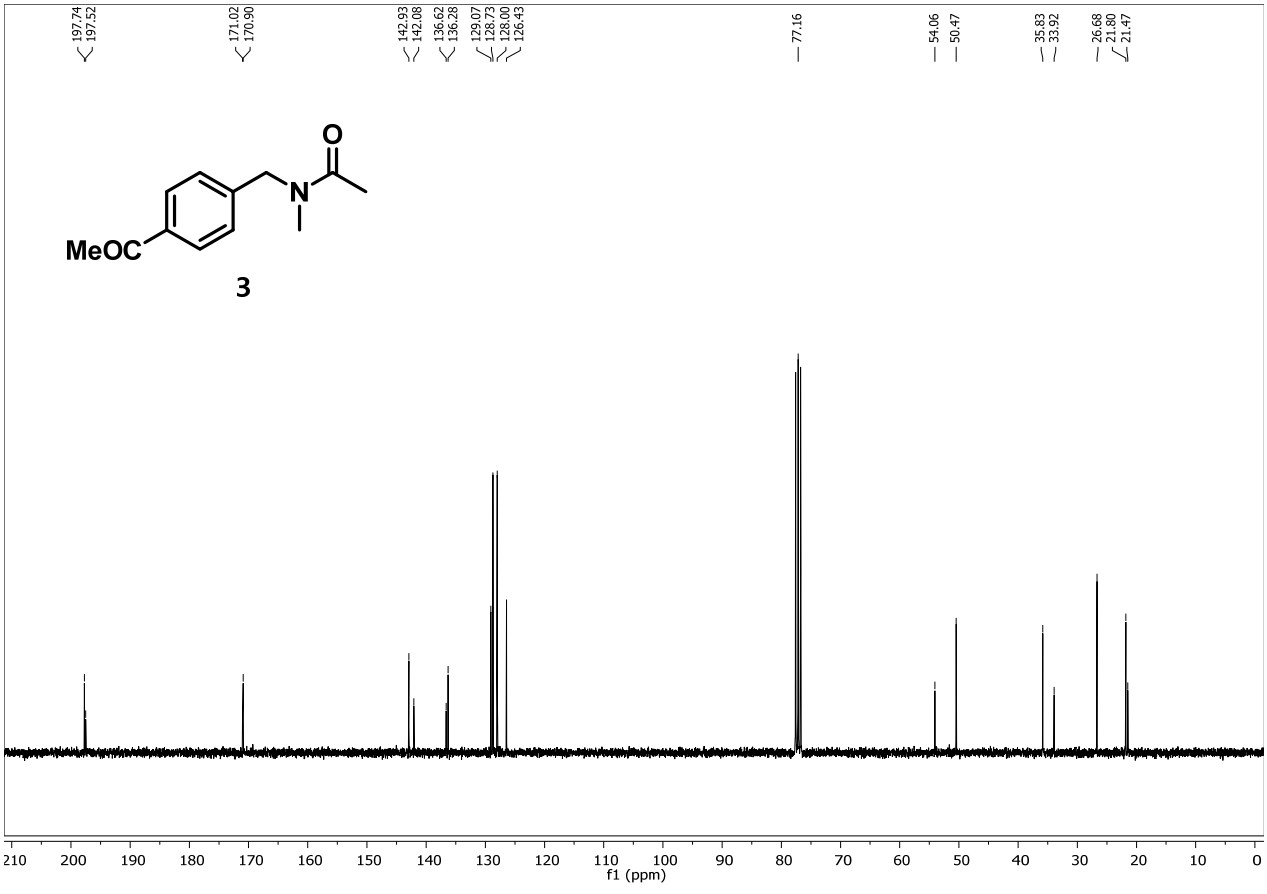


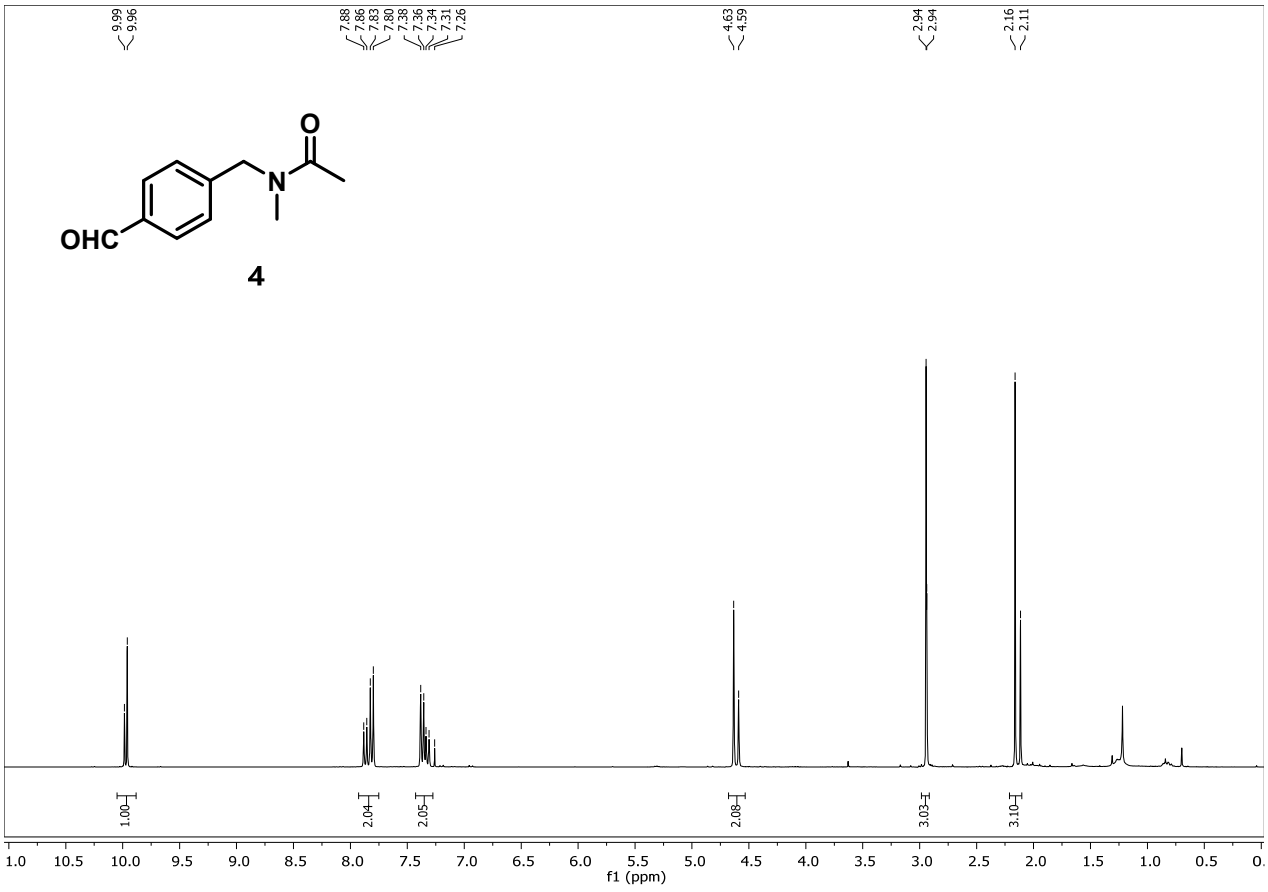


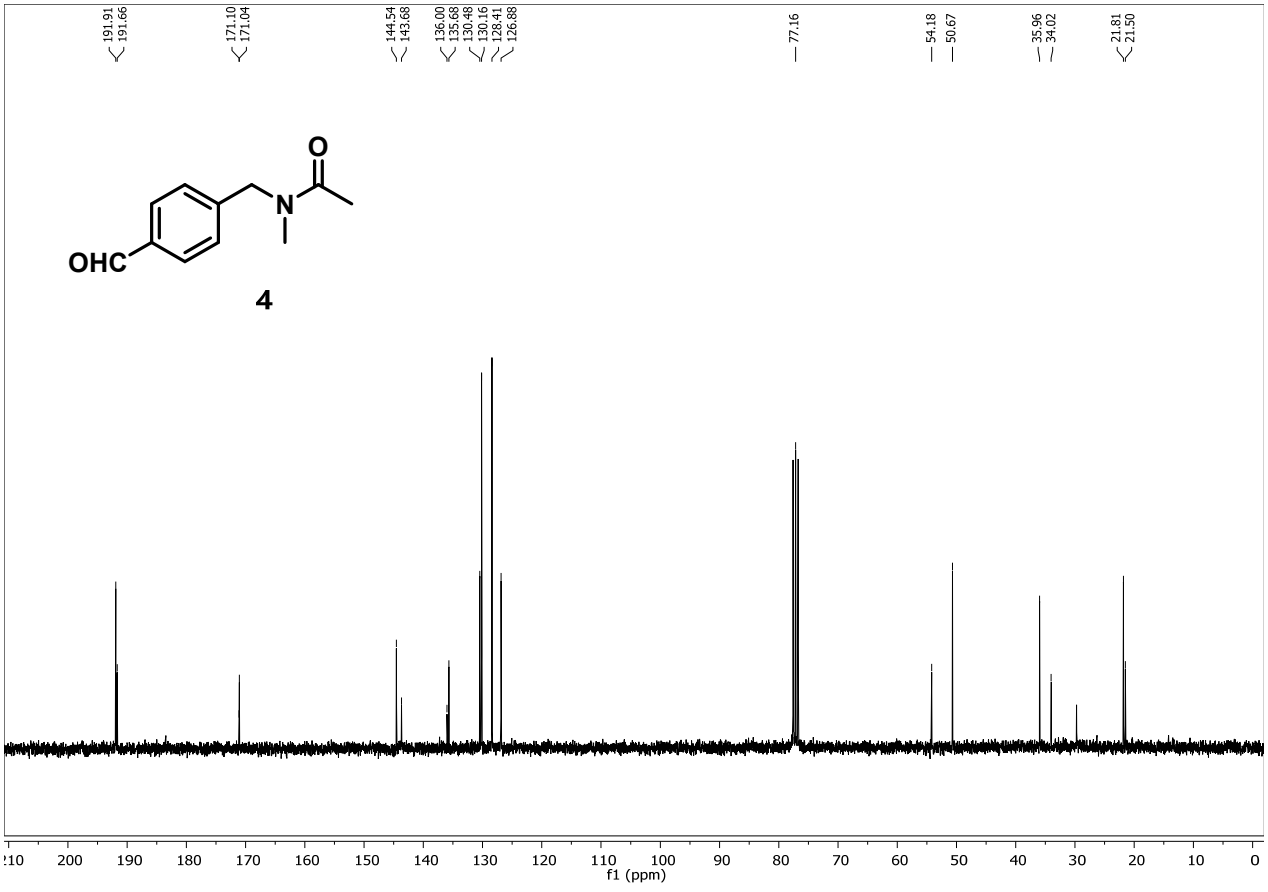

8.02
7.99
7.96
7.94
7.28
7.26
7.25
7.22
7.20
4.60
4.55
3.88
3.86
3.86
2.91
2.90
2.14
2.10
O
N
MeO2C
2
2.00
2.09
2.04
3.03
3.02
3.18
f1 (ppm)

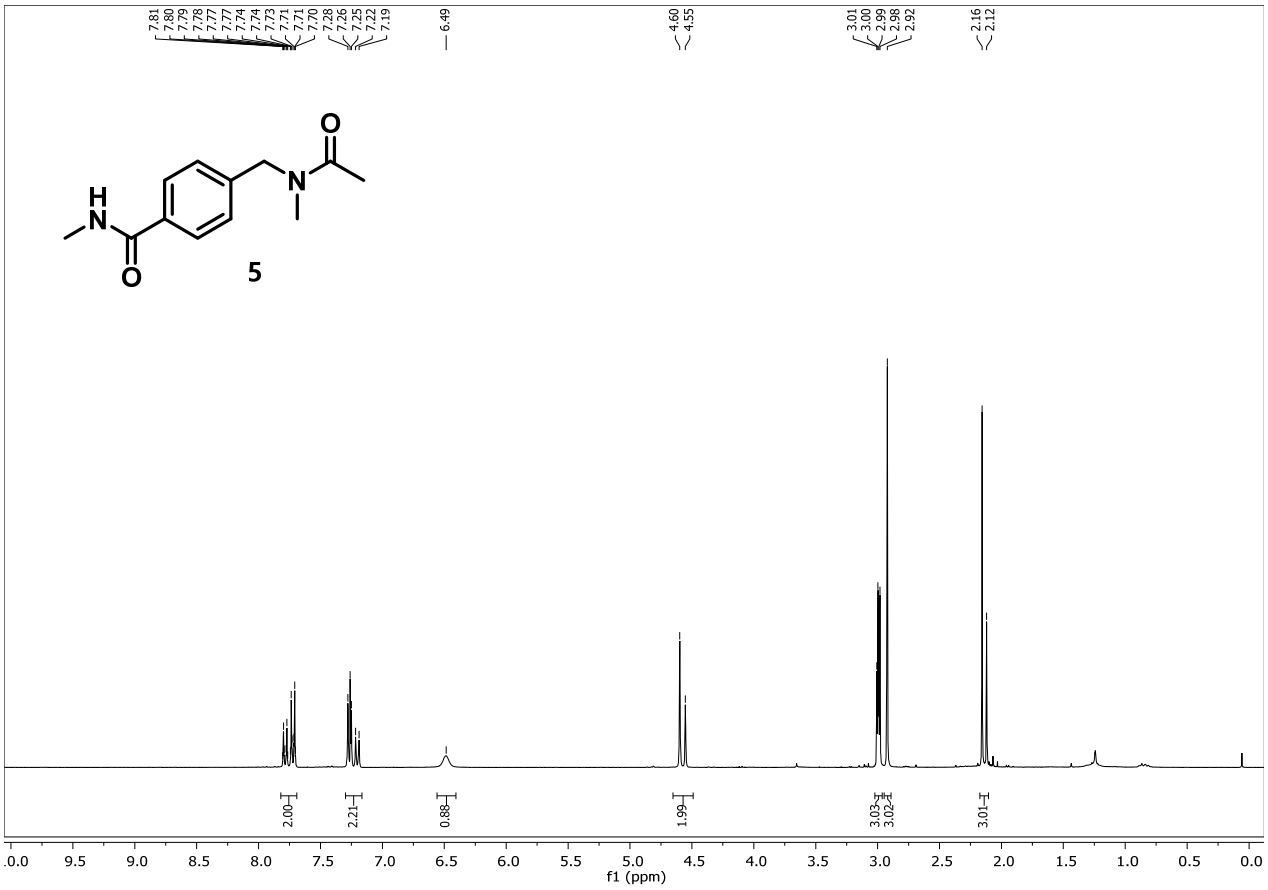

171.06
170.93
166.87
166.64
142.68
141.87
130.30
129.95
129.68
129.28
127.82
126.25
77.16
54.09
52.22
52.13
50.48
35.78
33.91
21.81
21.47
O
N
MeO2C
2
f1 (ppm)

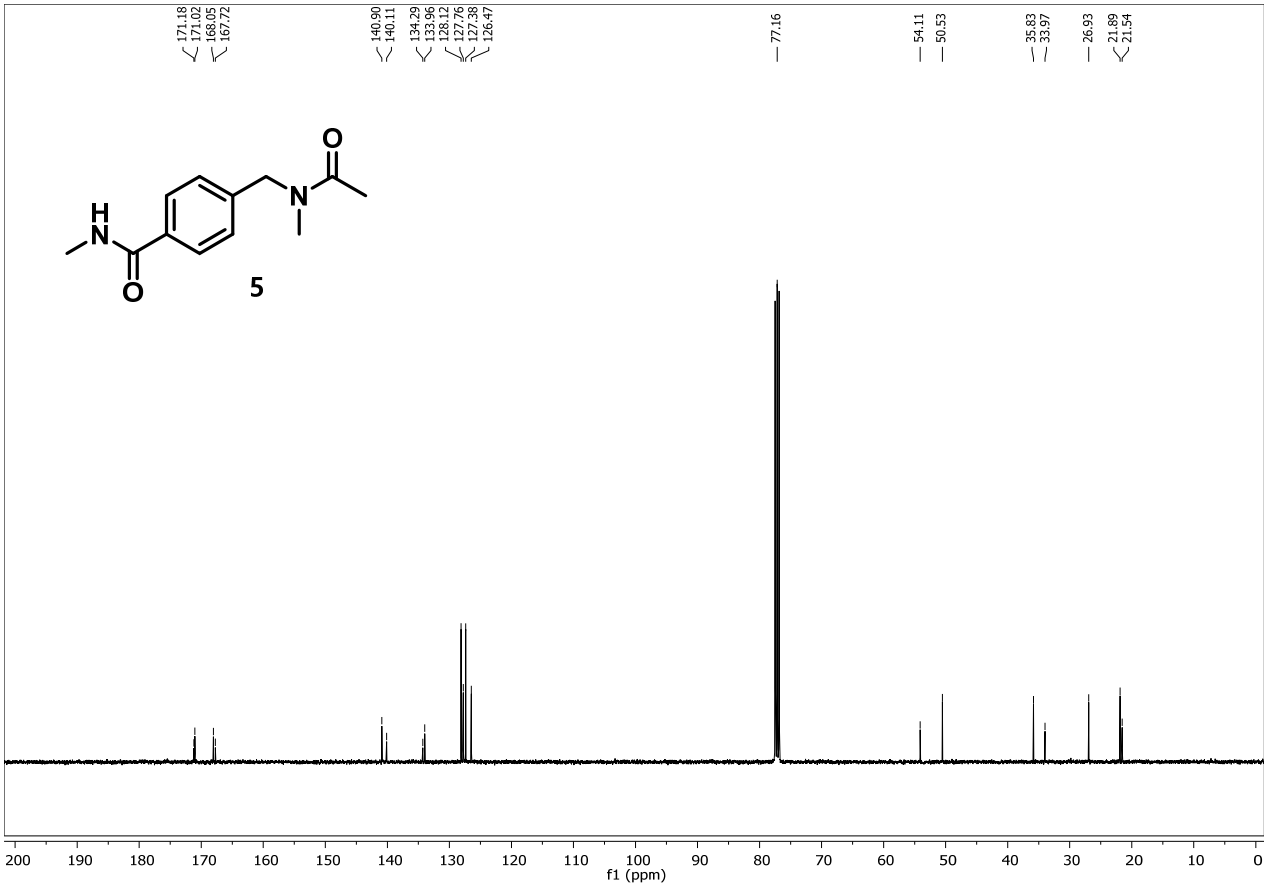

7.94
7.93
7.92
7.91
7.90
7.89
7.89
7.88
7.87
7.86
7.85
7.30
7.30
7.30
7.29
7.28
7.27
7.27
7.27
7.26
7.25
7.25
7.22
4.60
4.55
2.91
2.56
2.55
2.14
2.10
O
N
MeOC
3
1.98
2.04
2.00
3.02
3.00
3.01
f1 (ppm)

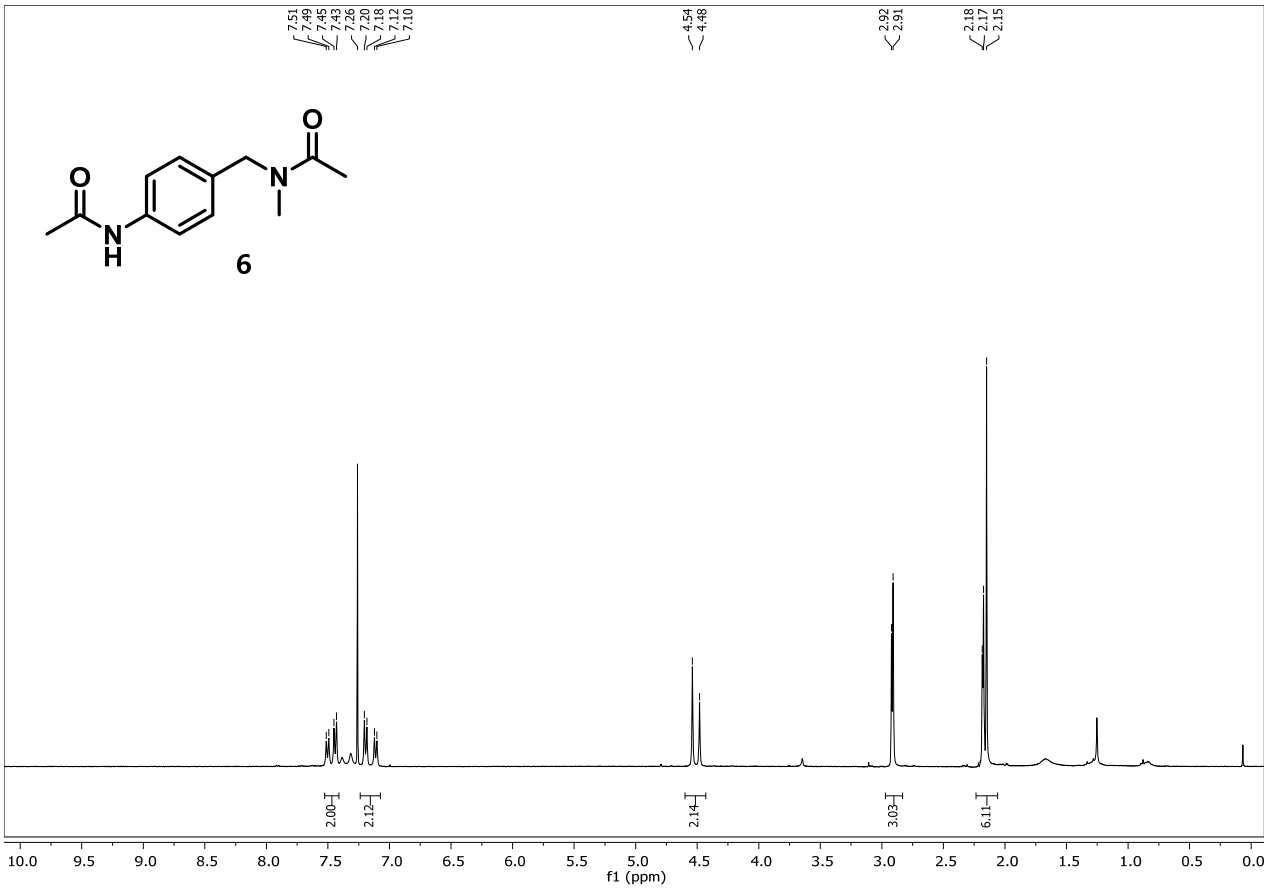

197.74
197.52
171.02
170.90
142.93
142.08
136.62
136.28
129.07
128.73
128.00
126.43
77.16
54.06
50.47
35.83
33.92
26.68
21.80
21.47
O
N
MeOC
3
f1 (ppm)

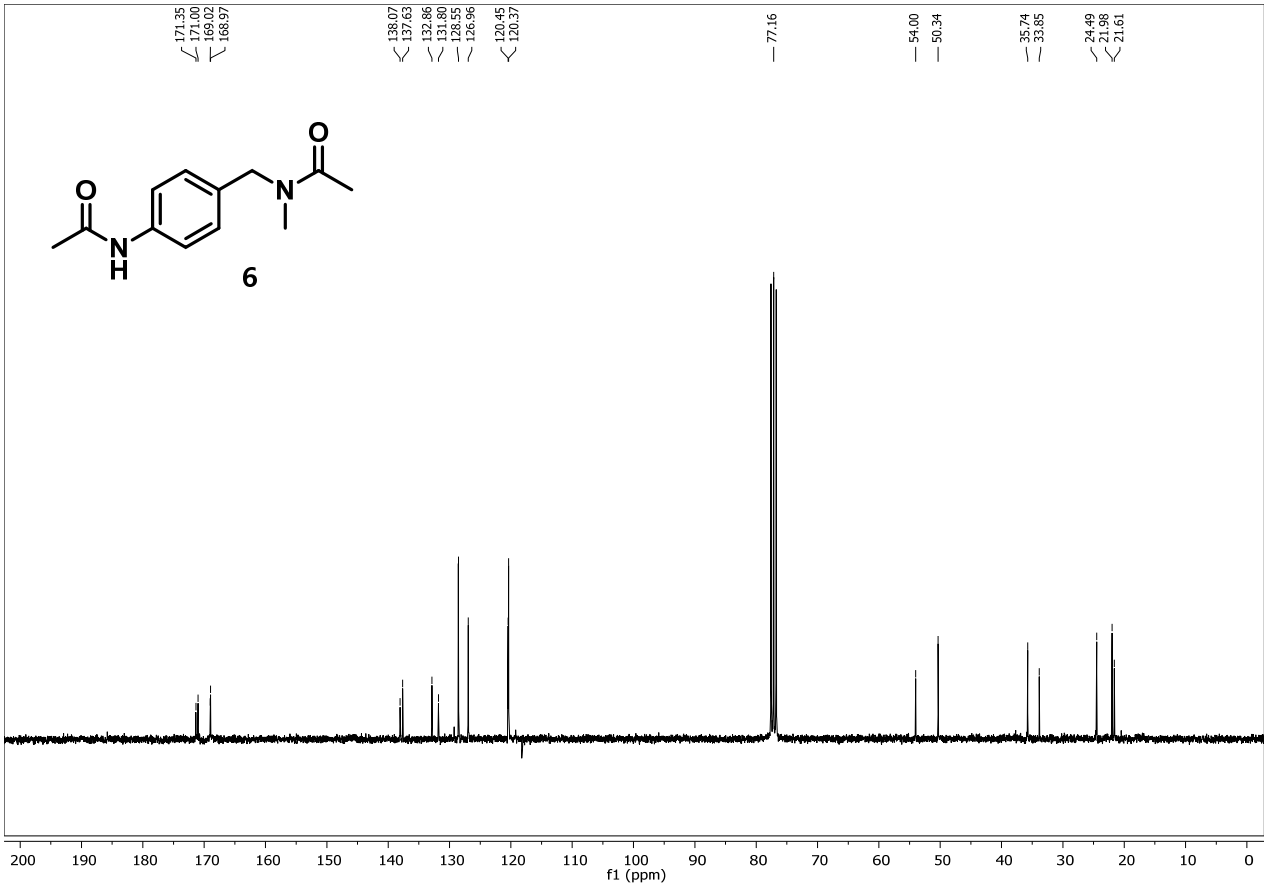

9.99
9.96
7.88
7.86
7.83
7.80
7.38
7.36
7.34
7.31
7.26
4.63
4.59
2.94
2.94
2.16
2.11
O
N
OHC
4
1.00
2.04
2.05
2.08
3.03
3.10
f1 (ppm)

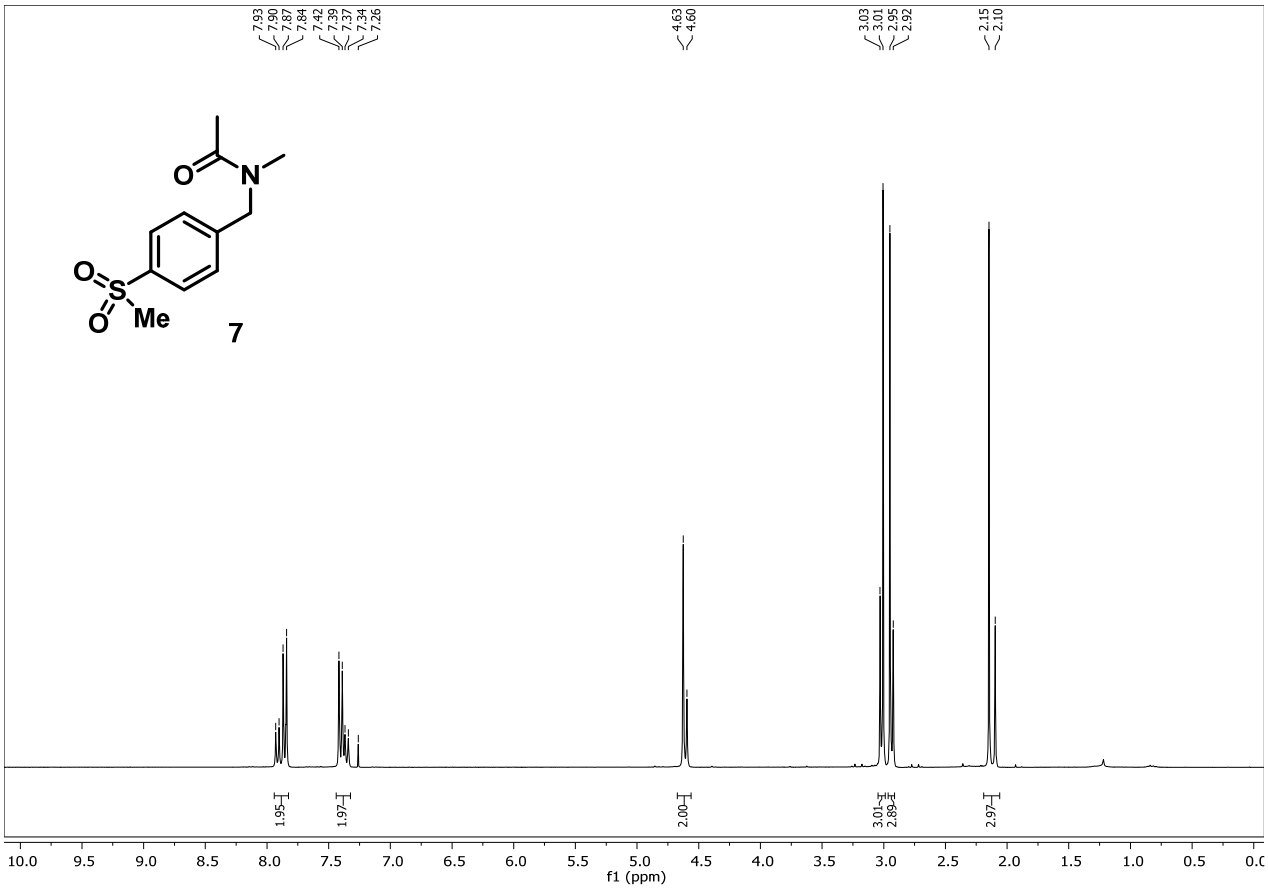

191.91
191.66
171.10
171.04
144.54
143.68
136.00
135.68
130.48
130.16
128.41
126.88
77.16
54.18
50.67
35.96
34.02
21.81
21.50
O
N
OHC
4
f1 (ppm)

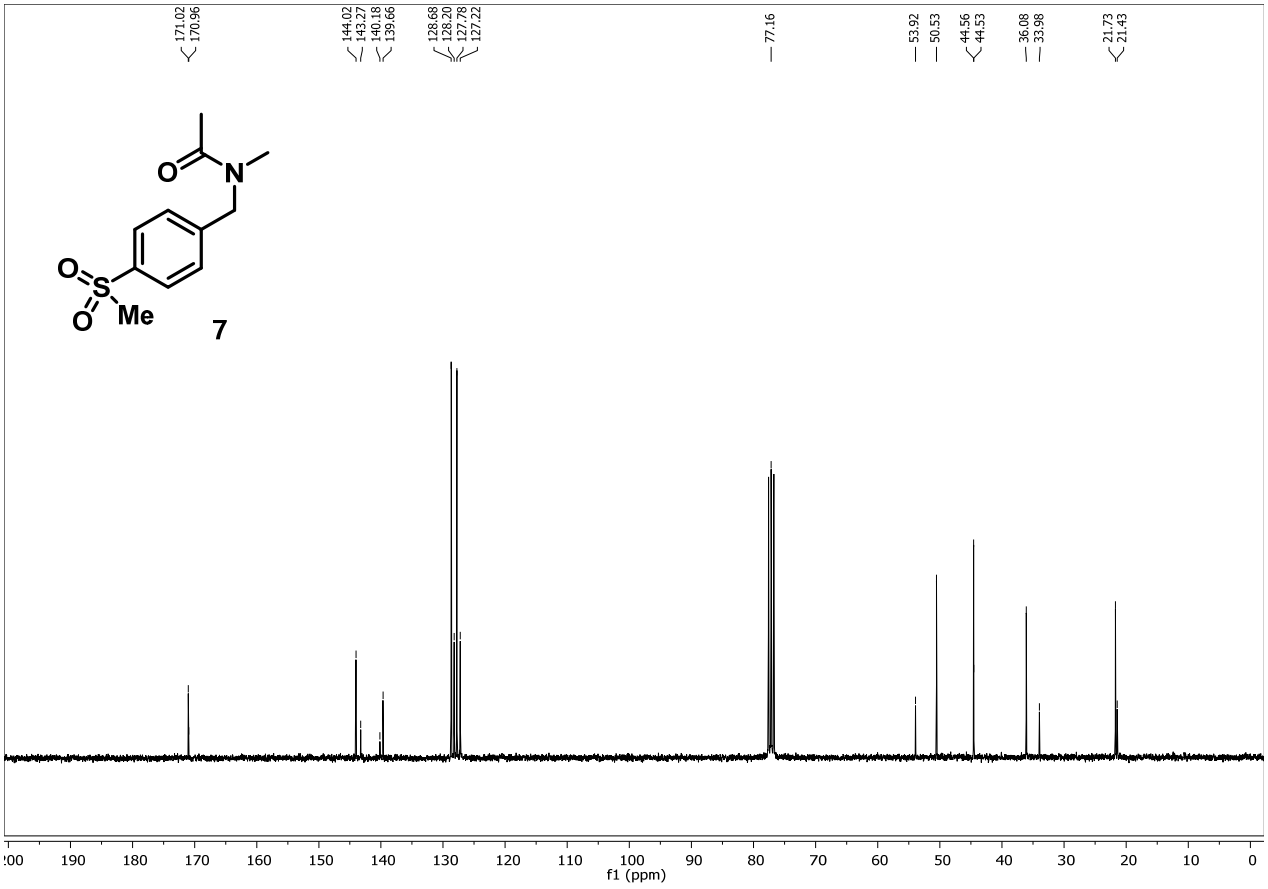

7.81
7.80
7.79
7.78
7.77
7.77
7.74
7.74
7.73
7.71
7.71
7.70
7.28
7.26
7.25
7.22
7.19
6.49
4.60
4.55
3.01
3.00
2.99
2.98
2.92
2.16
2.12
5
2.00
2.21
0.88
1.99
3.03
3.02
3.01
f1 (ppm)

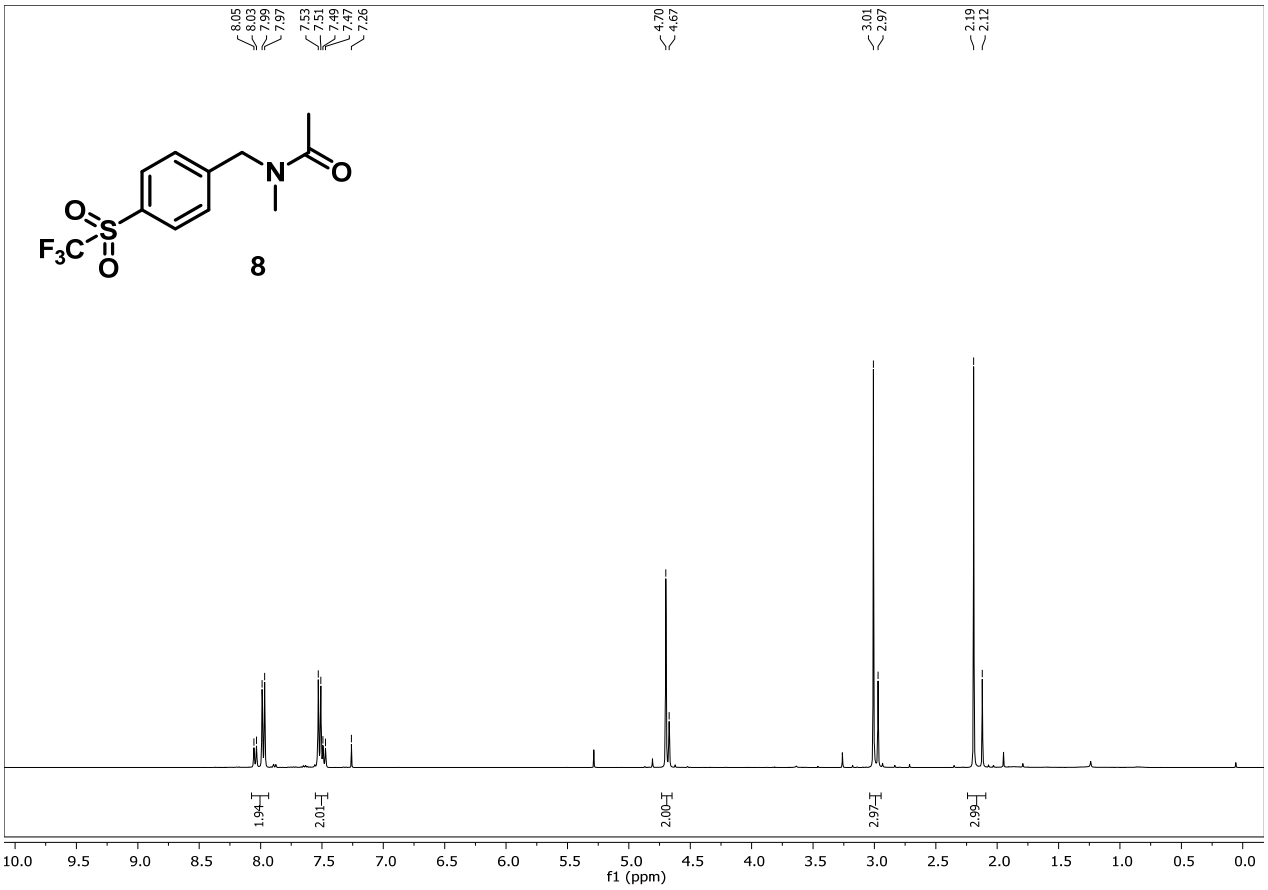

171.18
171.02
168.05
167.72
140.90
140.11
134.29
133.96
128.12
127.76
127.38
126.47
77.16
54.11
50.53
35.83
33.97
26.93
21.89
21.54
5
f1 (ppm)

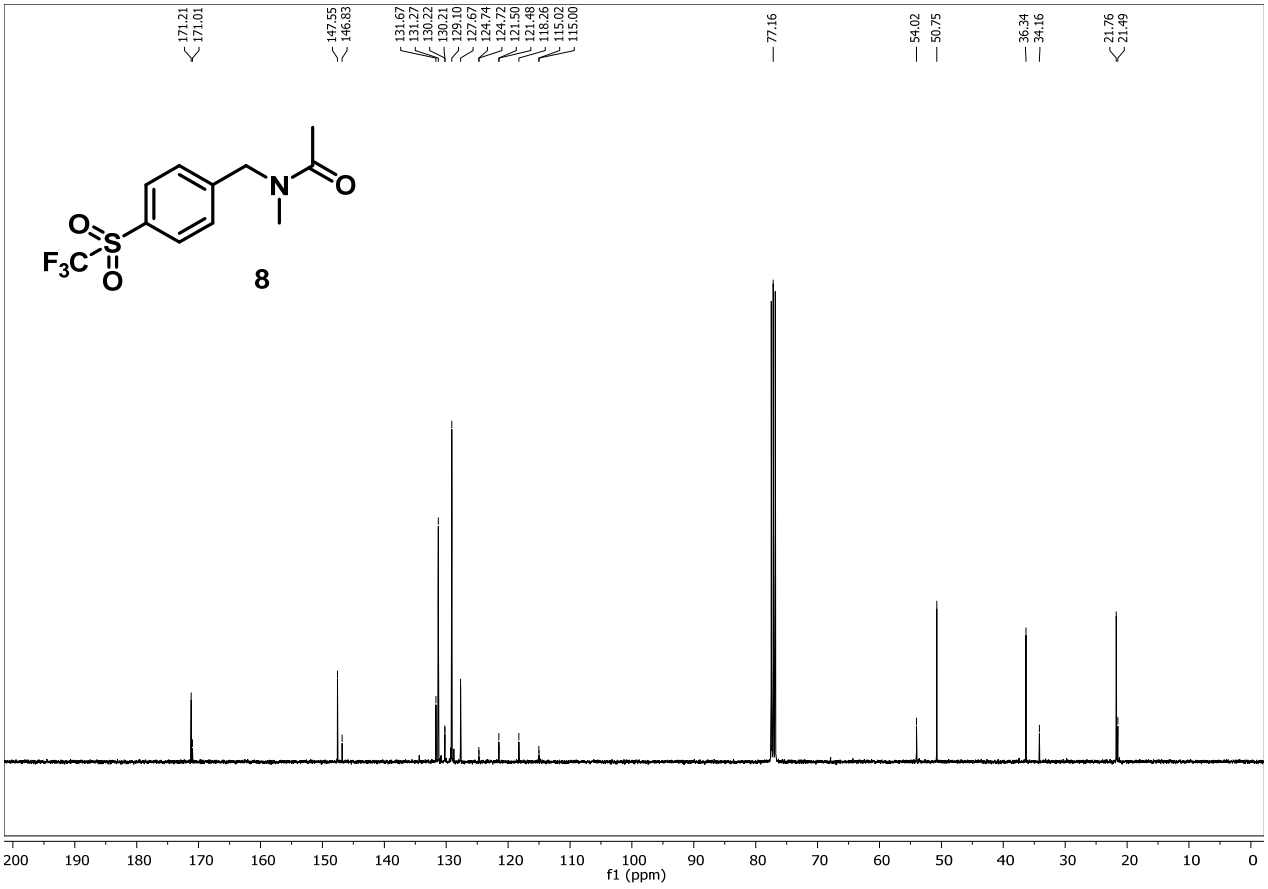

7.51
7.49
7.45
7.43
7.26
7.20
7.18
7.12
7.10
4.54
4.48
2.92
2.91
2.18
2.17
2.15
O
N
H
O
N
O
6
2.00
2.12
2.14
3.03
6.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

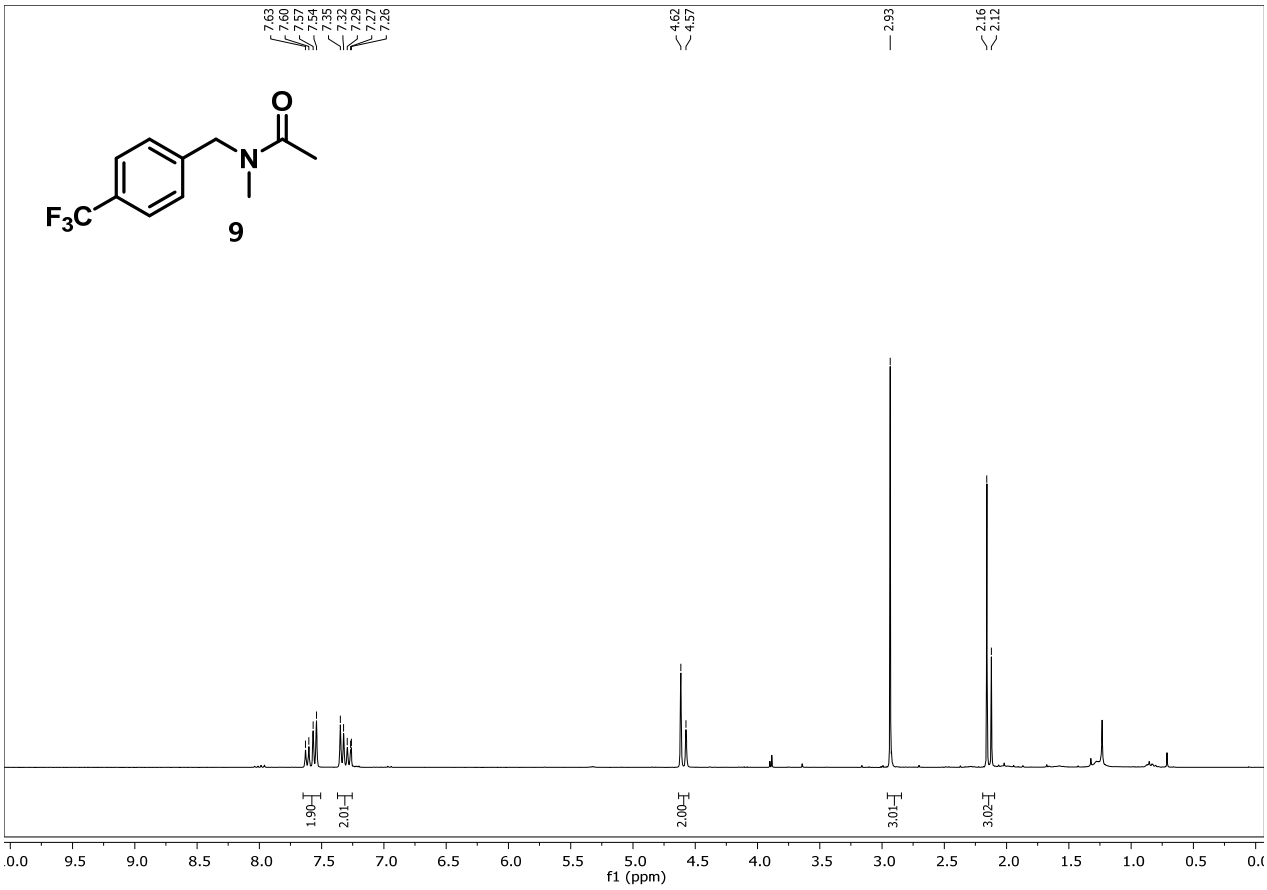

171.35
171.00
169.02
168.97
138.07
137.63
132.86
131.80
128.55
126.96
120.45
120.37
77.16
54.00
50.34
35.74
33.85
24.49
21.98
21.61
O
N
H
O
N
O
6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

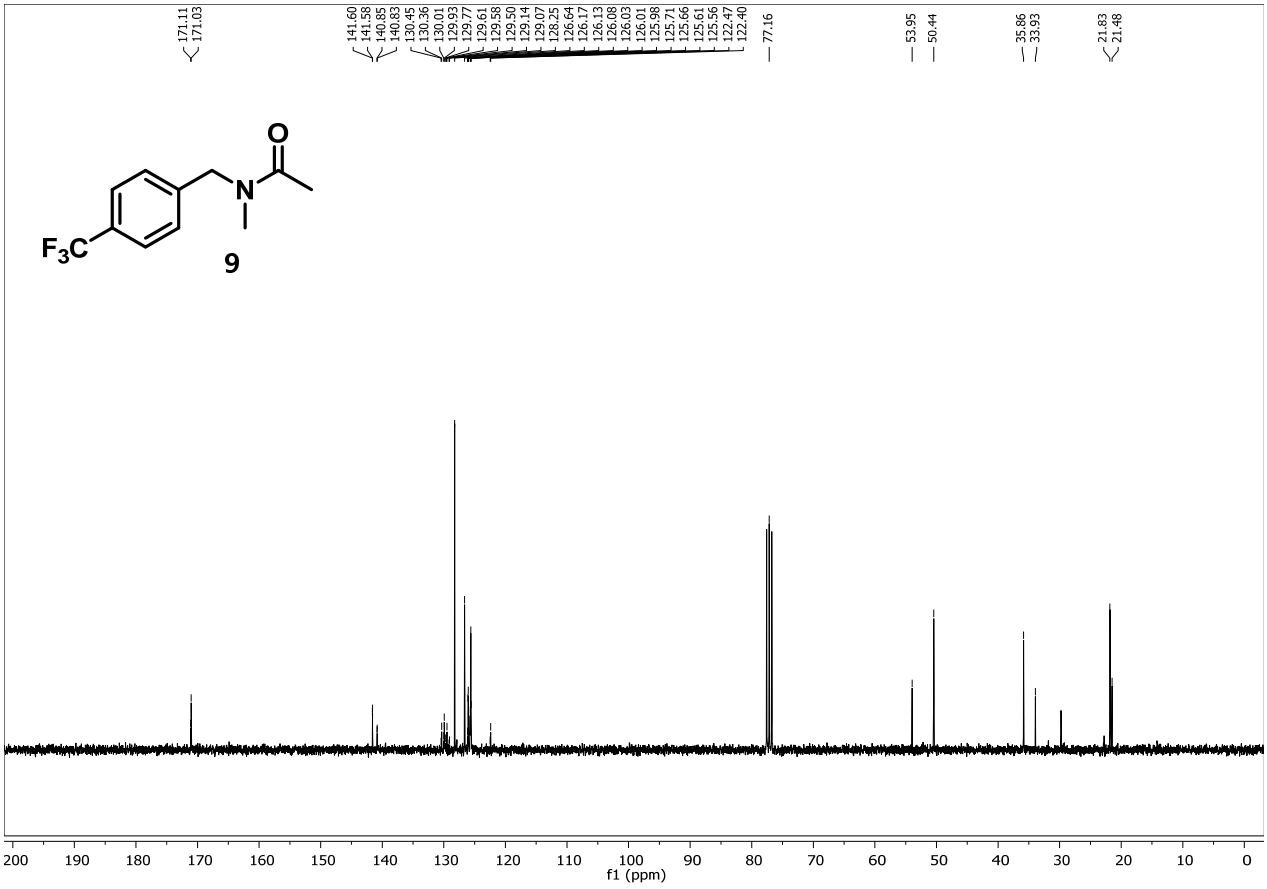

7.93
7.90
7.87
7.84
7.42
7.39
7.37
7.34
7.26
4.63
4.60
3.03
3.01
2.95
2.92
2.15
2.10
O
N
O
S
O
Me
7
1.95
1.97
2.00
3.01
2.89
2.97
f1 (ppm)

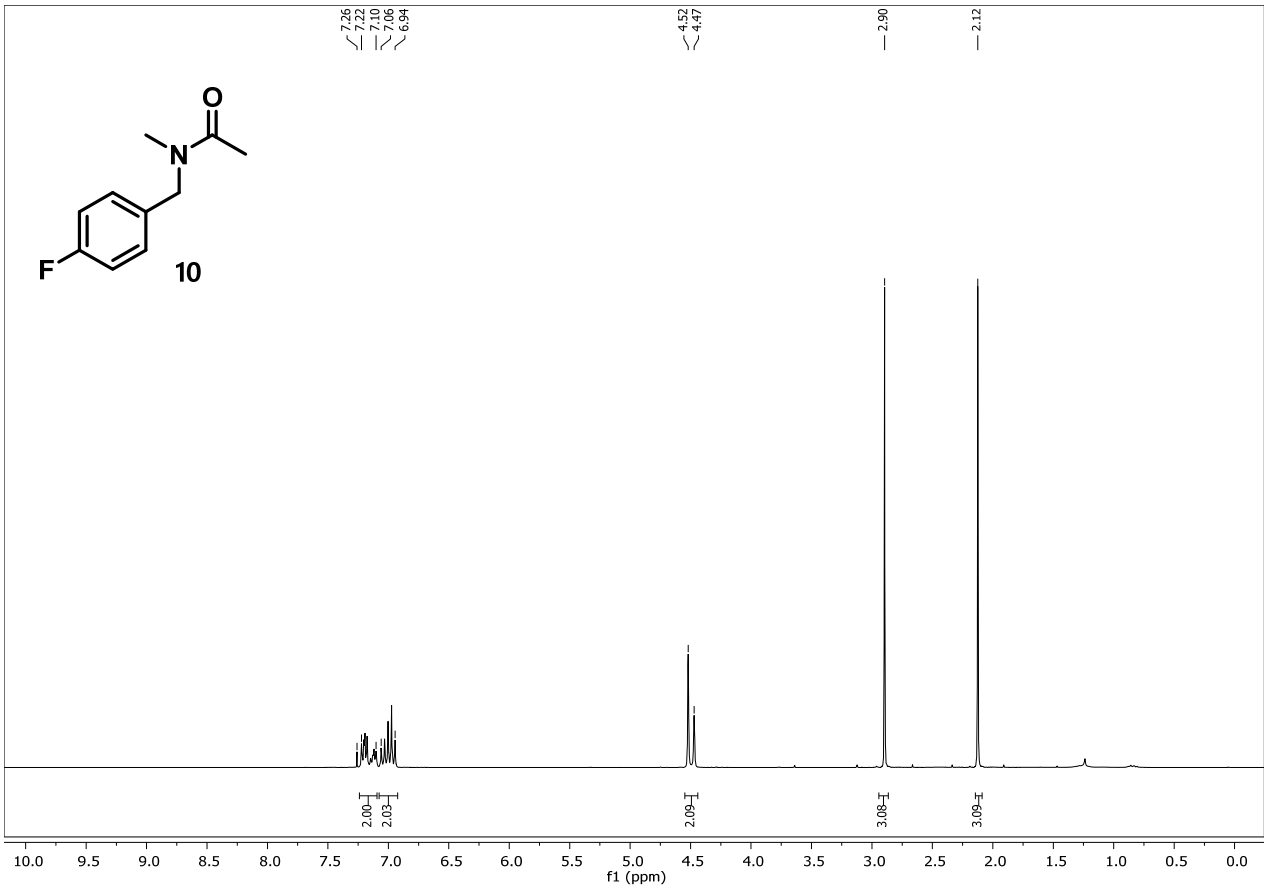

171.02
170.96
144.02
143.27
140.18
139.66
128.68
128.20
127.78
127.22
77.16
53.92
50.53
44.56
44.53
36.08
33.98
21.73
21.43
O
N
O
S
O
Me
7
f1 (ppm)

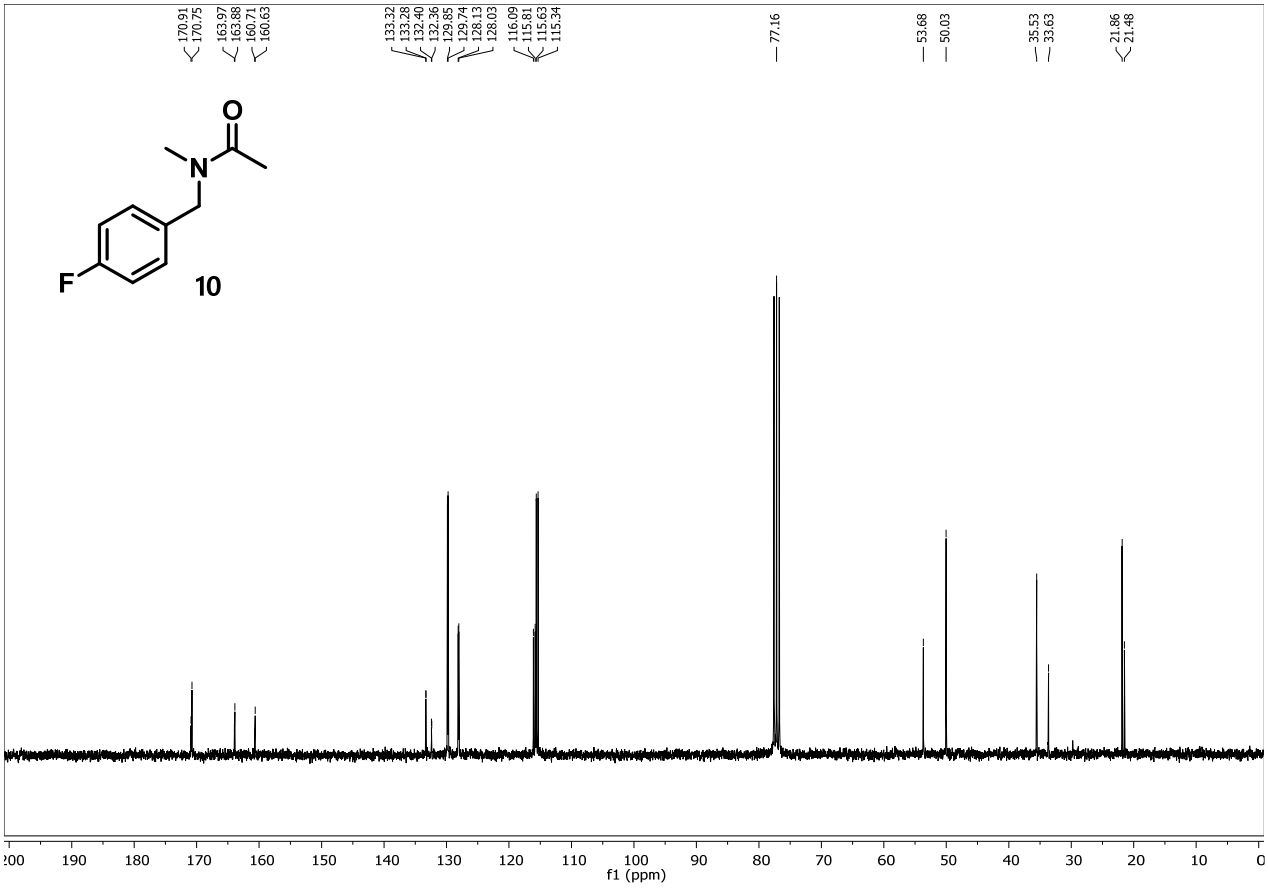

8.05
8.03
7.99
7.97
7.53
7.51
7.49
7.47
7.26
4.70
4.67
3.01
2.97
2.19
2.12
8
1.94
2.01
2.00
2.97
2.99
f1 (ppm)

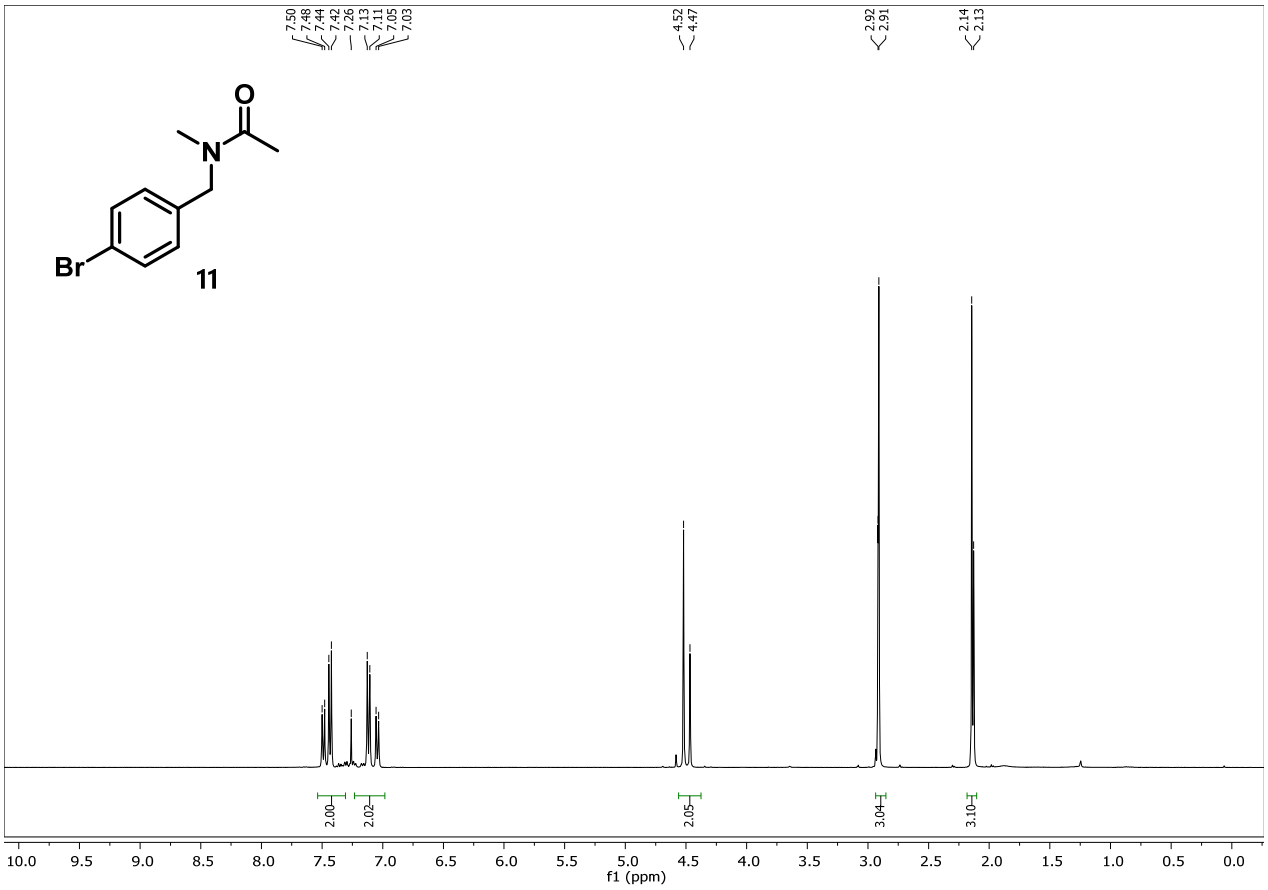

171.21
171.01
147.55
146.83
131.67
131.27
130.22
130.21
129.10
127.67
124.74
124.72
121.50
121.48
118.26
115.02
115.00
77.16
54.02
50.75
36.34
34.16
21.76
21.49
8
f1 (ppm)

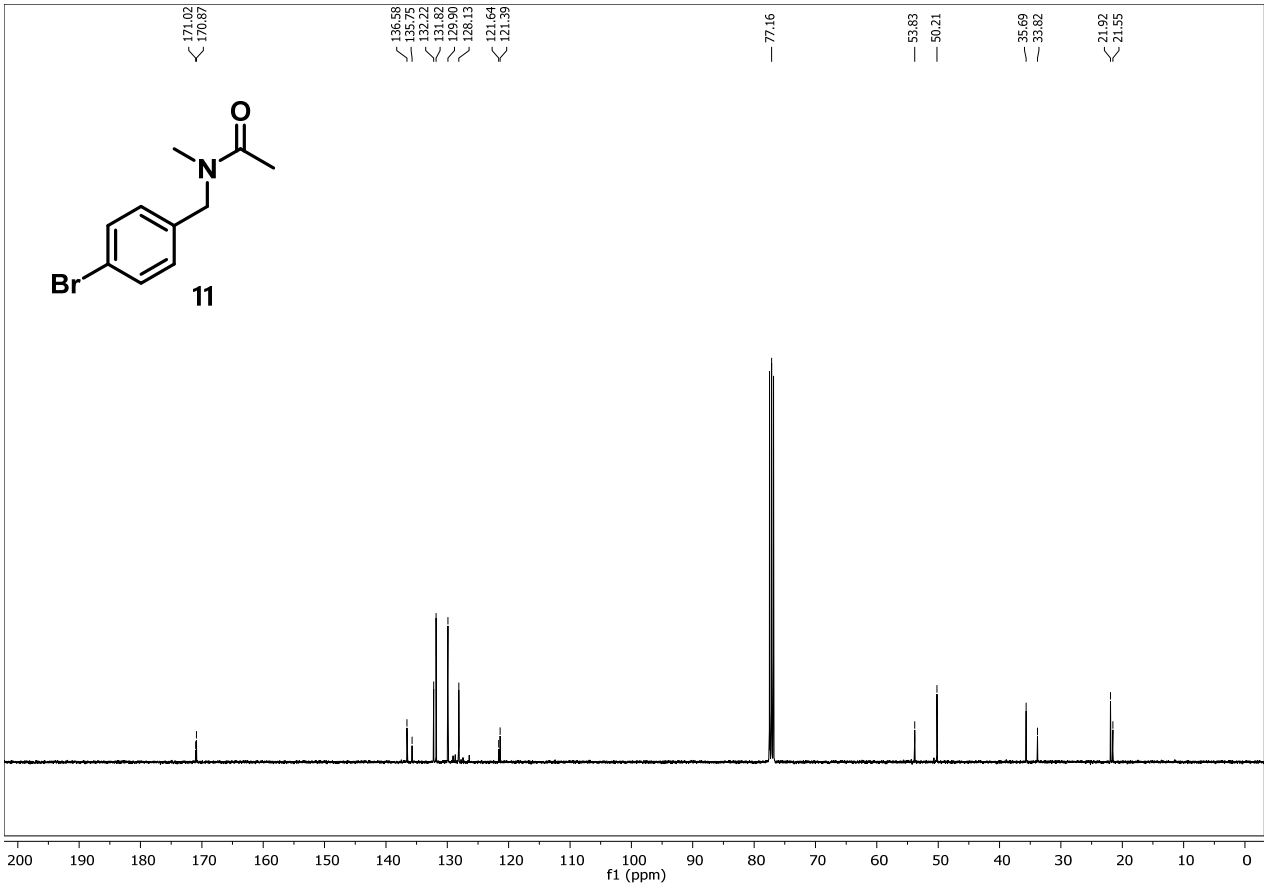

7.63
7.60
7.57
7.54
7.35
7.32
7.29
7.27
7.26
4.62
4.57
2.93
2.16
2.12
O
N
F3C
9
1.90
2.01
2.00
3.01
3.02
f1 (ppm)

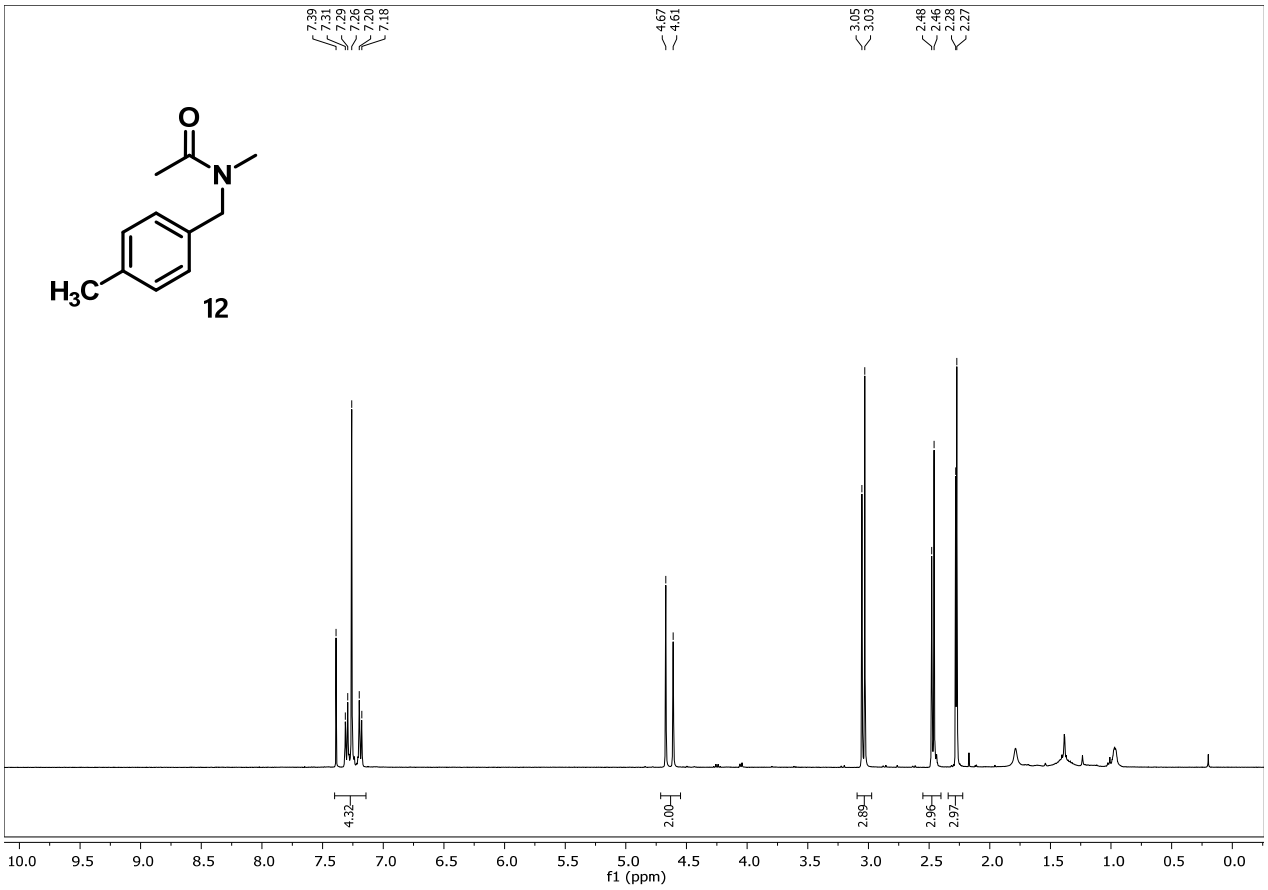

171.11
171.03
141.60
141.58
140.85
140.83
130.45
130.36
130.01
129.93
129.77
129.61
129.58
129.50
129.14
129.07
128.25
126.64
126.17
126.13
126.08
126.03
126.01
125.98
125.71
125.66
125.61
125.56
122.47
122.40
77.16
53.95
50.44
35.86
33.93
21.83
21.48
O
N
F3C
9
f1 (ppm)

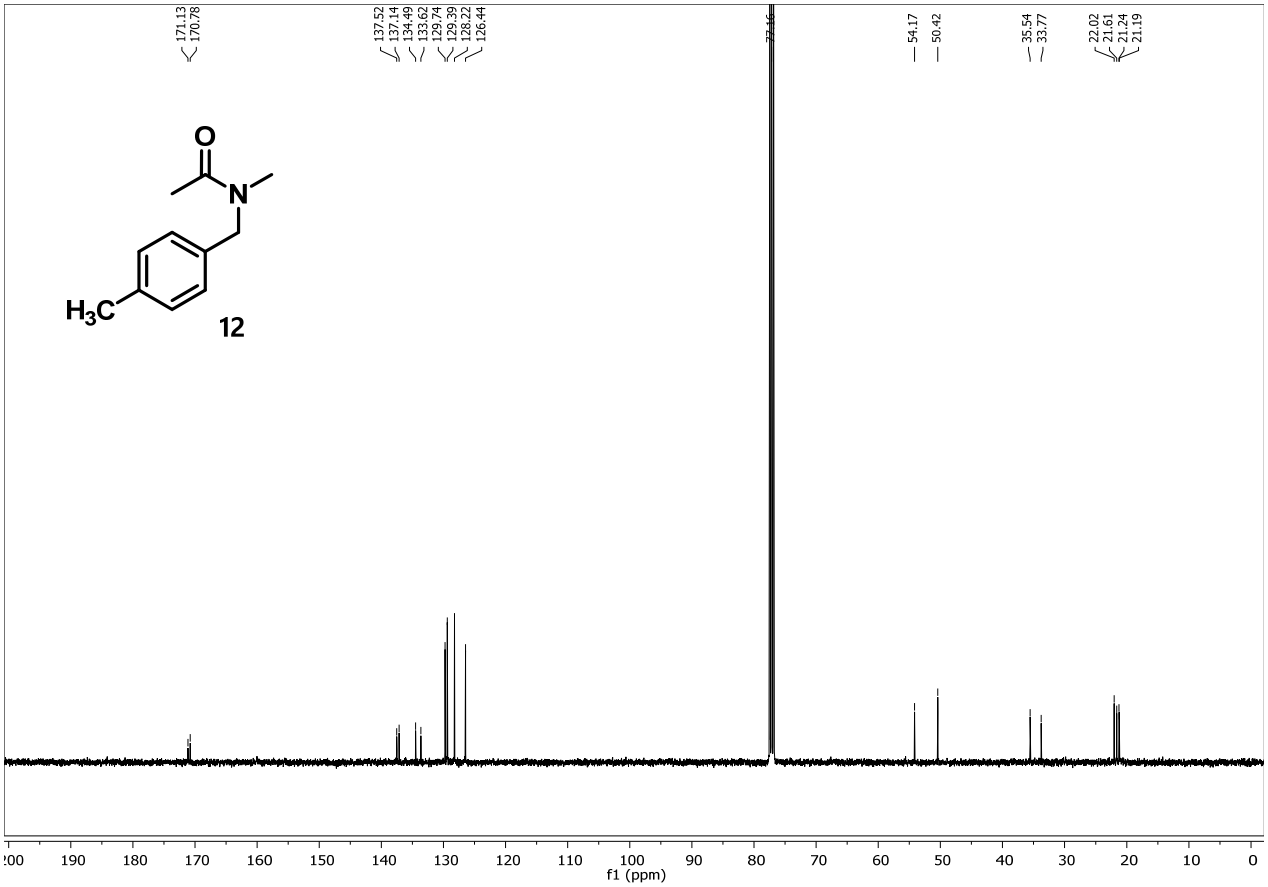

7.26
7.22
7.10
7.06
6.94
4.52
4.47
2.90
2.12
O
N
F
10
2.00
2.03
2.09
3.08
3.09
f1 (ppm)

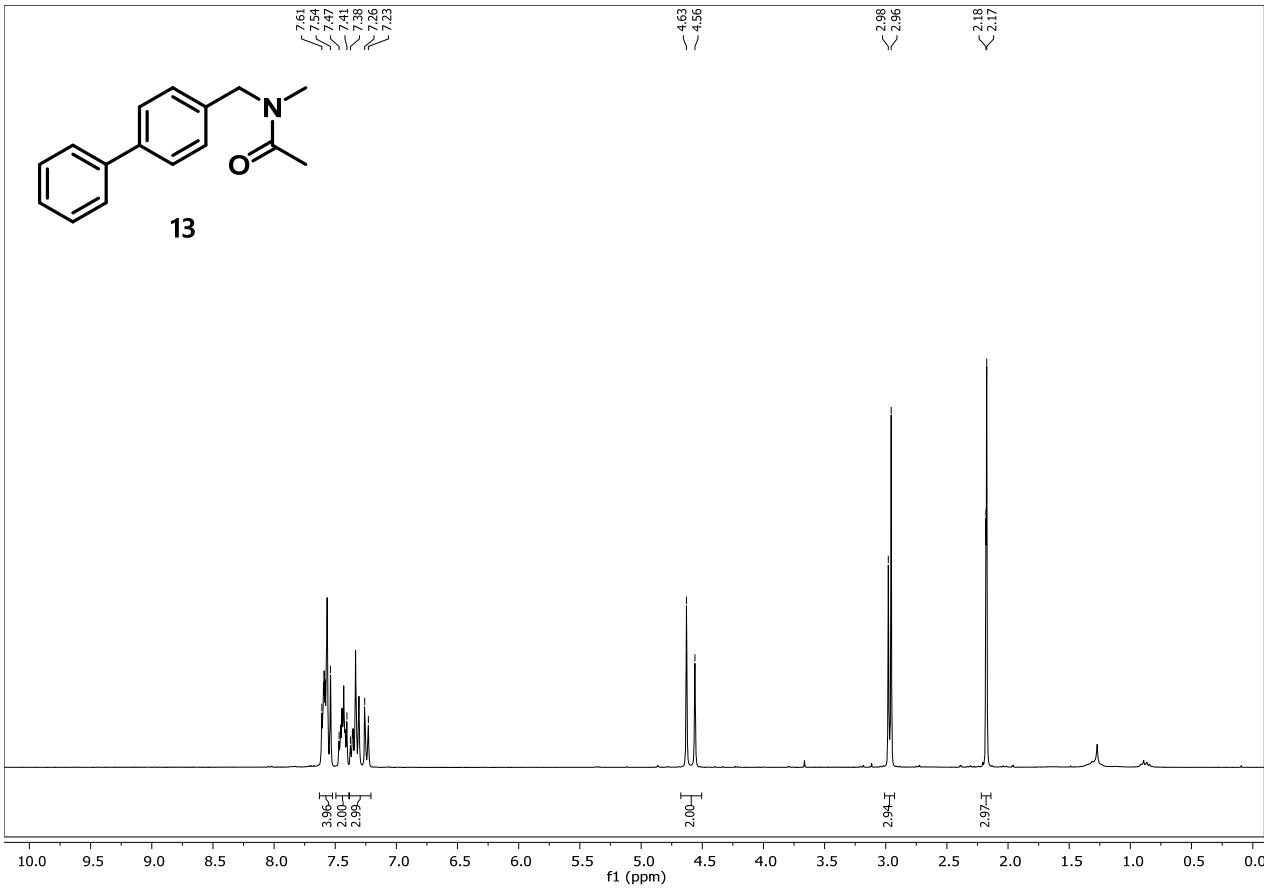

170.91
170.75
163.97
163.88
160.71
160.63
133.32
133.28
132.40
132.36
129.85
129.74
128.13
128.03
116.09
115.81
115.63
115.34
77.16
53.68
50.03
35.53
33.63
21.86
21.48
O
N
F
10
f1 (ppm)

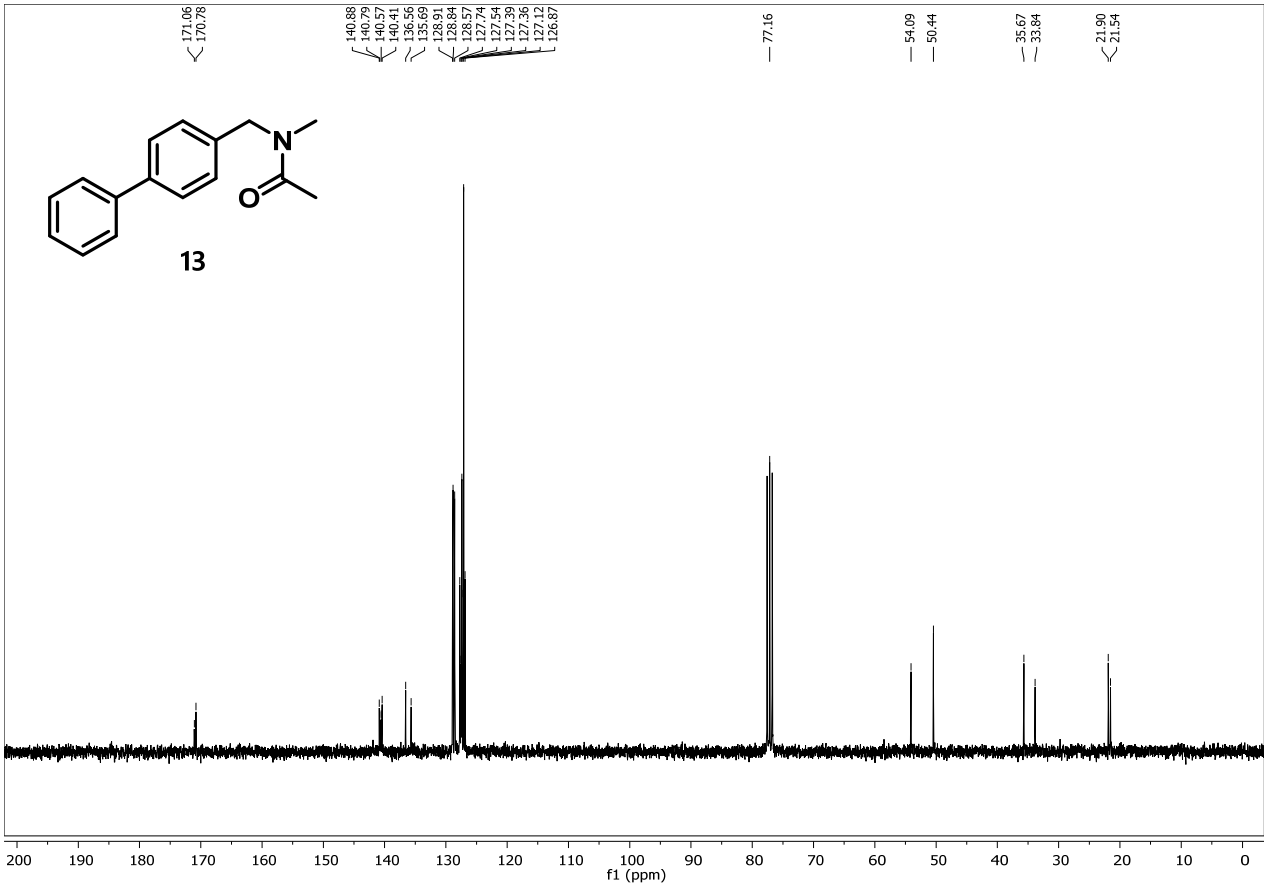

7.50
7.48
7.44
7.42
7.26
7.13
7.11
7.05
7.03
4.52
4.47
2.92
2.91
2.14
2.13
O
N
Br
11
2.00
2.02
2.05
3.04
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

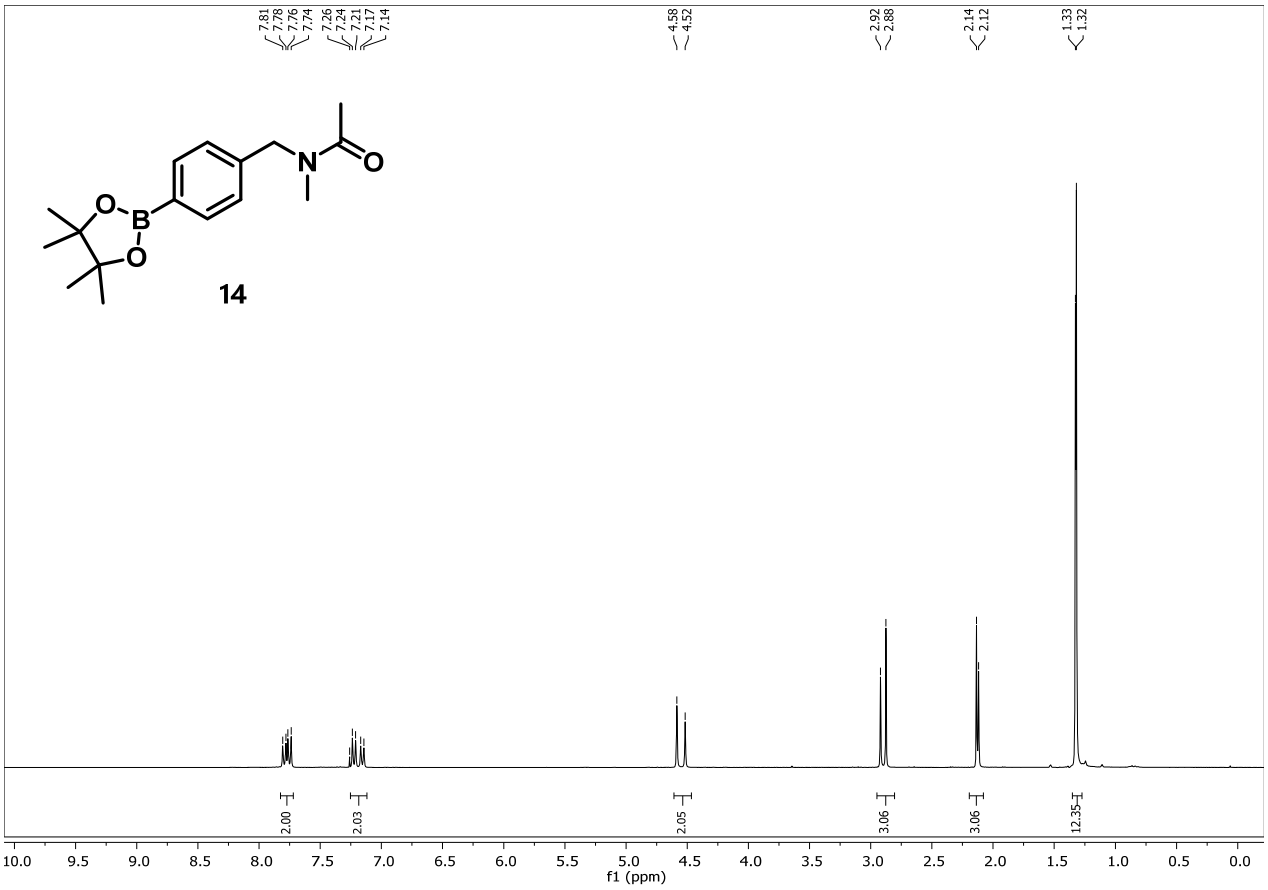

171.02
170.87
136.58
135.75
132.22
131.82
129.90
128.13
121.64
121.39
77.16
53.83
50.21
35.69
33.82
21.92
21.55
O
N
Br
11
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

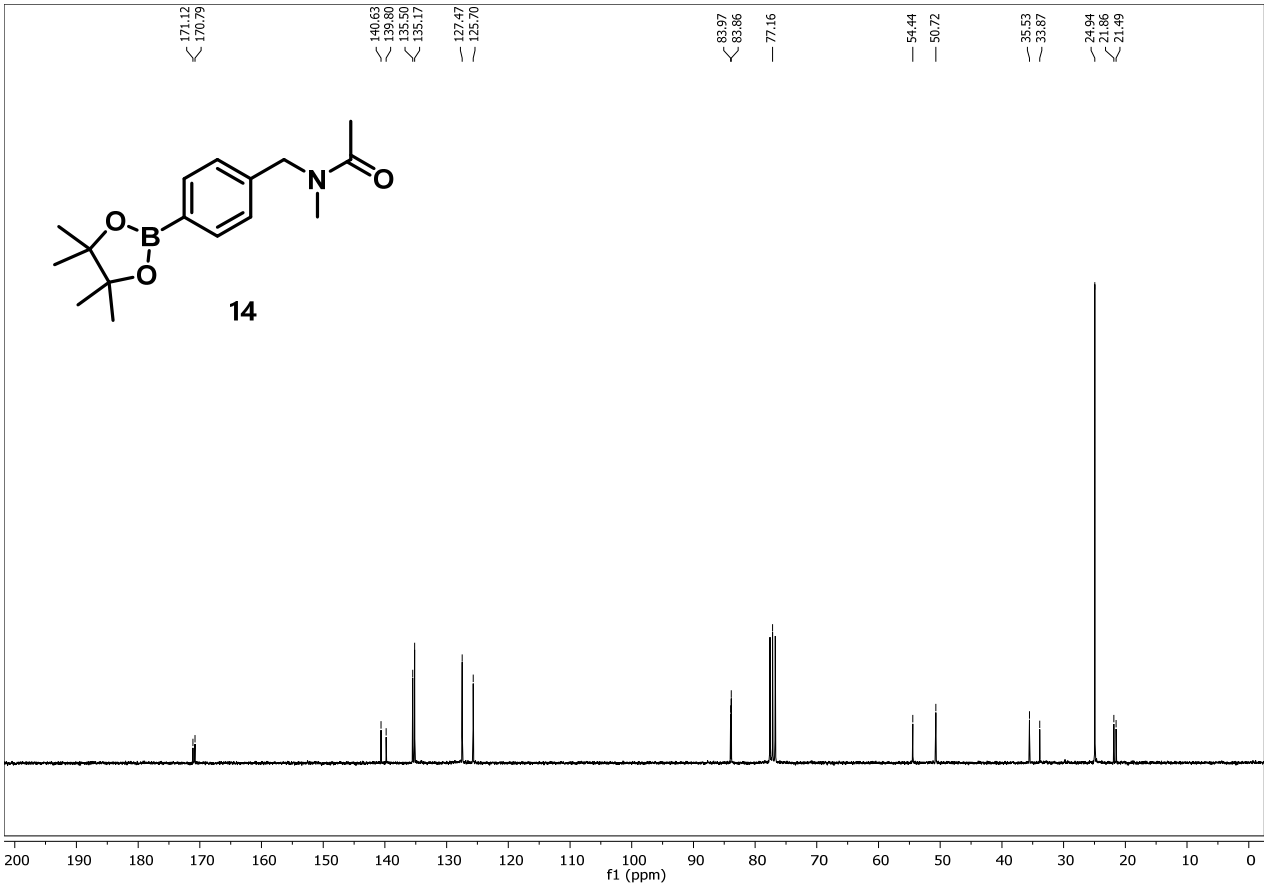

7.39
7.31
7.29
7.26
7.20
7.18
4.67
4.61
3.05
3.03
2.48
2.46
2.28
2.27
O
N
H3C
12
4.32
2.00
2.89
2.96
2.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

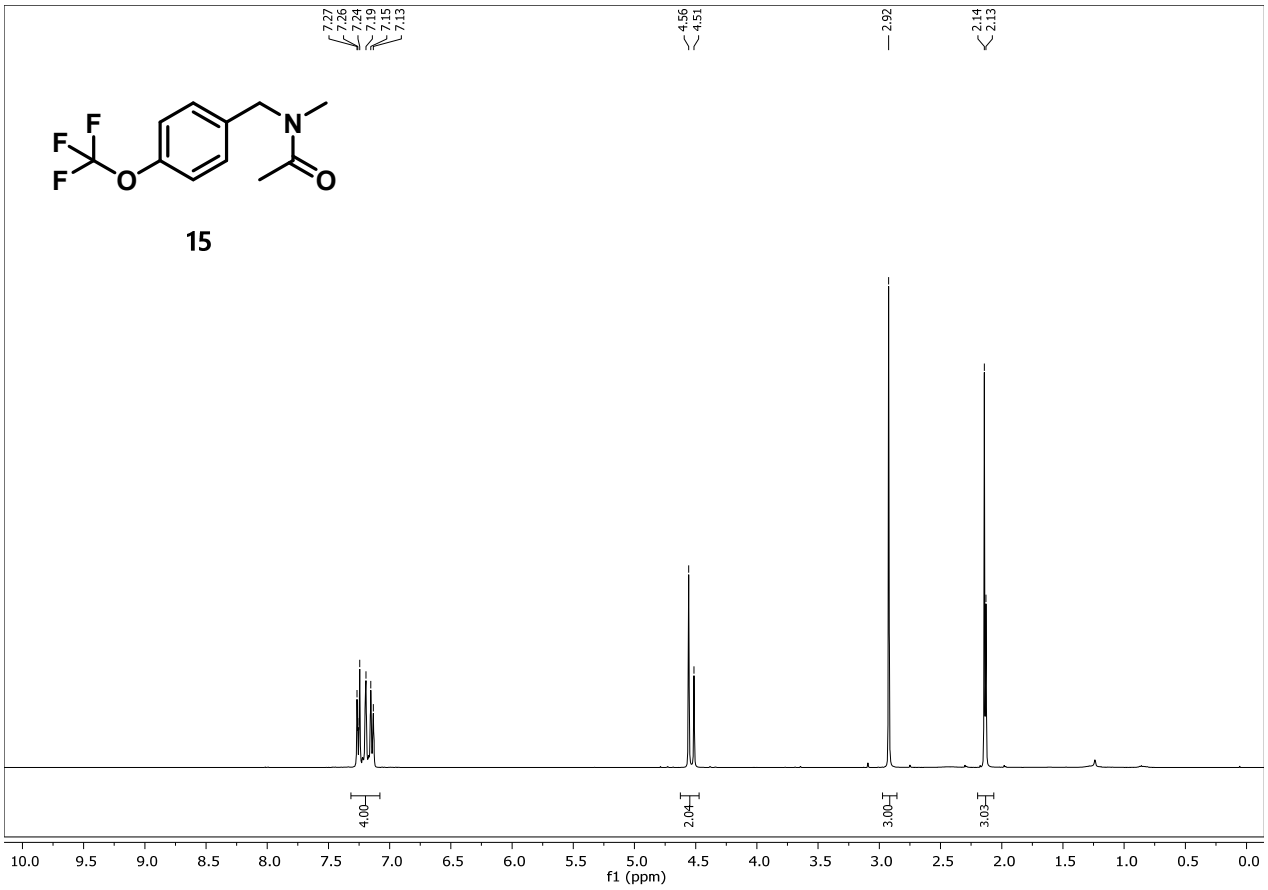

171.13
170.78
137.52
137.14
134.49
133.62
129.74
129.39
128.22
126.44
77.16
54.17
50.42
35.54
33.77
22.02
21.61
21.24
21.19
O
N
H3C
12
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

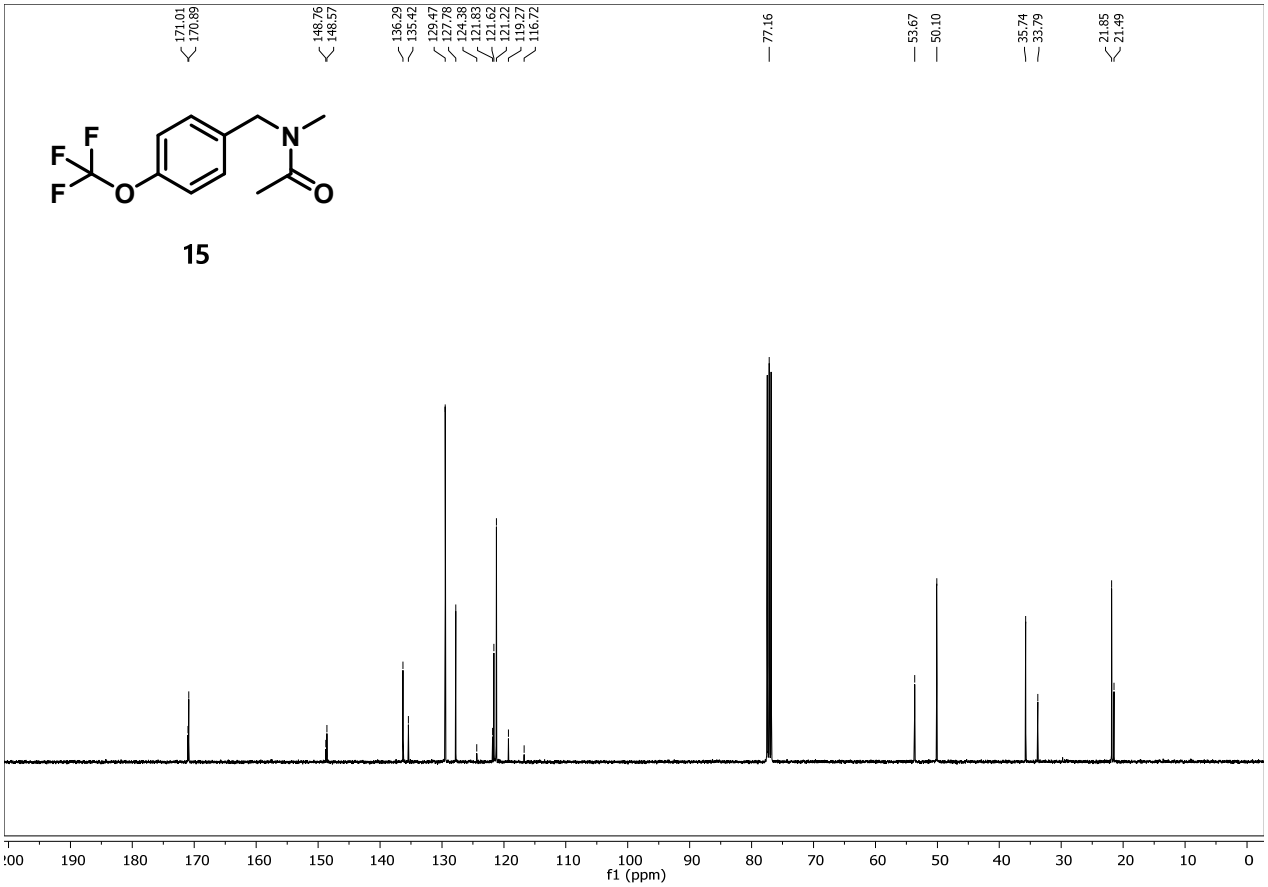

7.61
7.54
7.47
7.41
7.38
7.26
7.23
4.63
4.56
2.98
2.96
2.18
2.17
N
O
13
3.96
2.00
2.99
2.00
2.94
2.97
f1 (ppm)

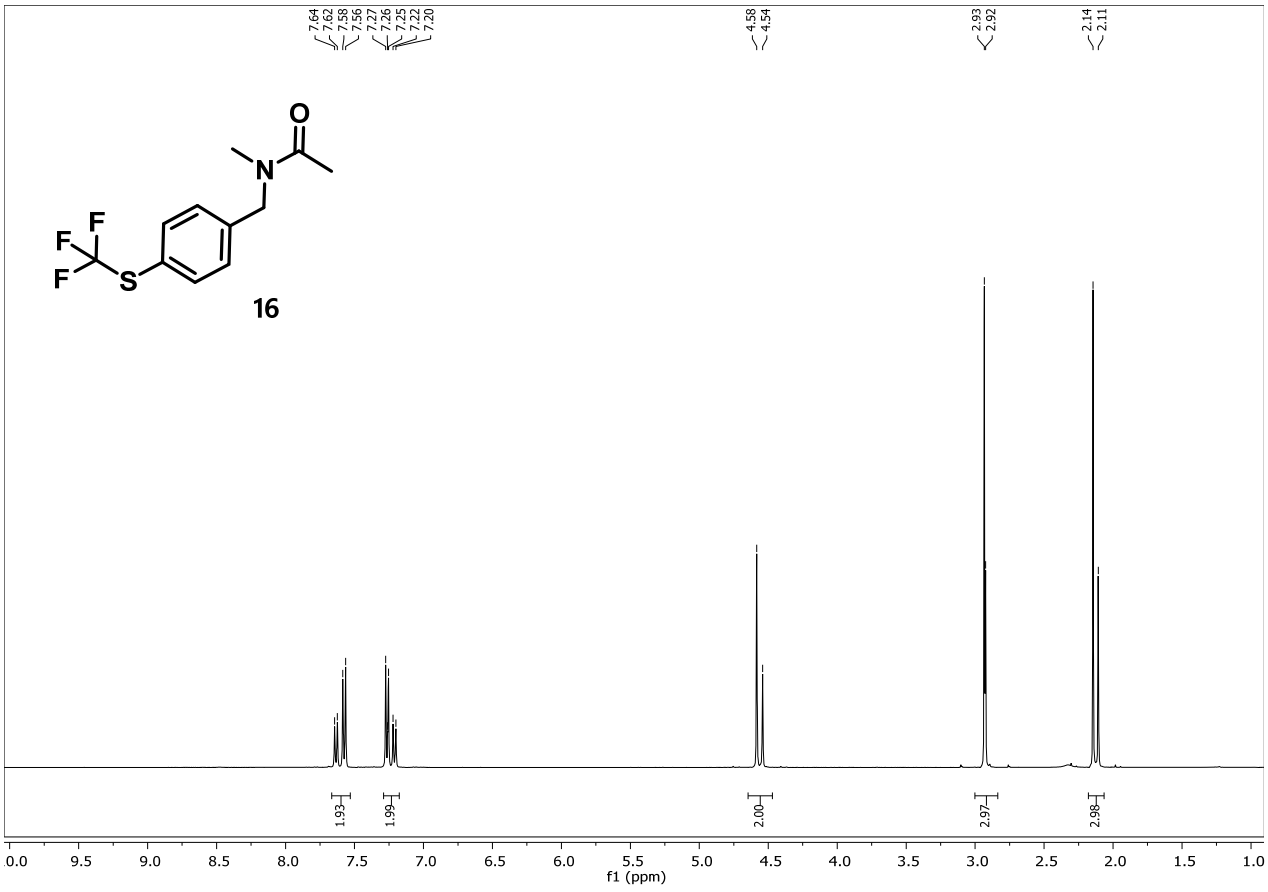

171.06
170.78
140.88
140.79
140.57
140.41
136.56
135.69
128.91
128.84
128.57
127.74
127.54
127.39
127.36
127.12
126.87
77.16
54.09
50.44
35.67
33.84
21.90
21.54
N
O
13
f1 (ppm)

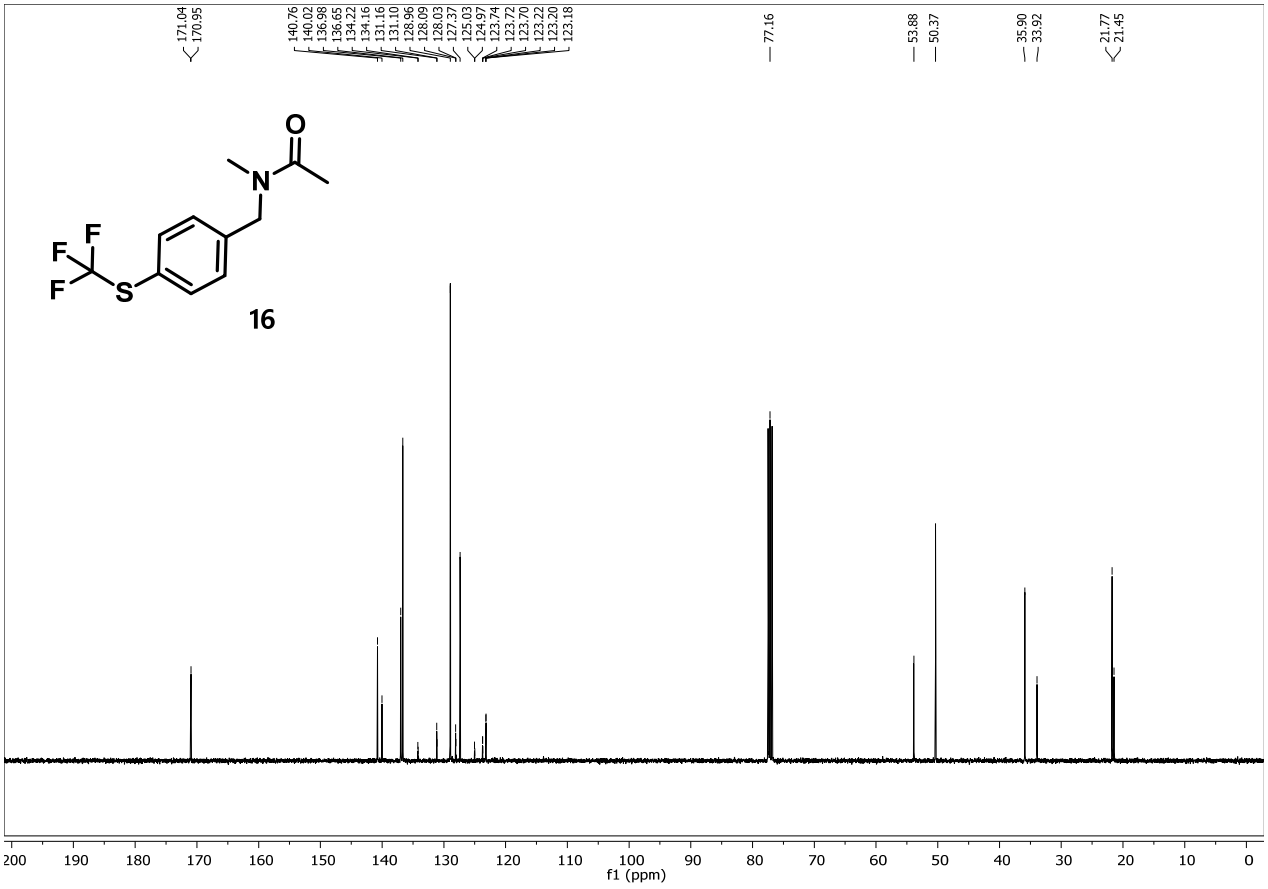

7.81
7.78
7.76
7.74
7.26
7.24
7.21
7.17
7.14
4.58
4.52
2.92
2.88
2.14
2.12
1.33
1.32
14
2.00
2.03
2.05
3.06
3.06
12.35
f1 (ppm)

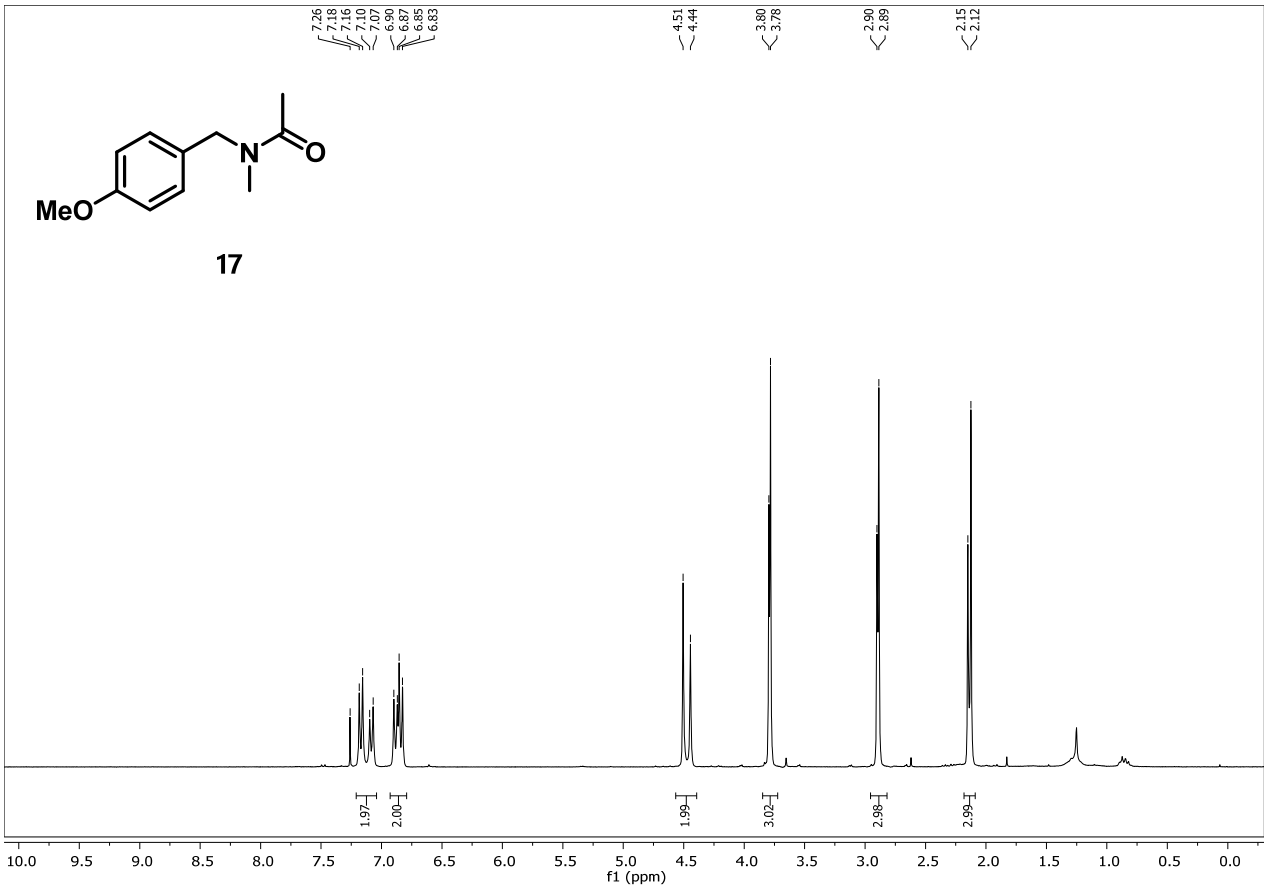

171.12
170.79
140.63
139.80
135.50
135.17
127.47
125.70
83.97
83.86
77.16
54.44
50.72
35.53
33.87
24.94
21.86
21.49
14
f1 (ppm)

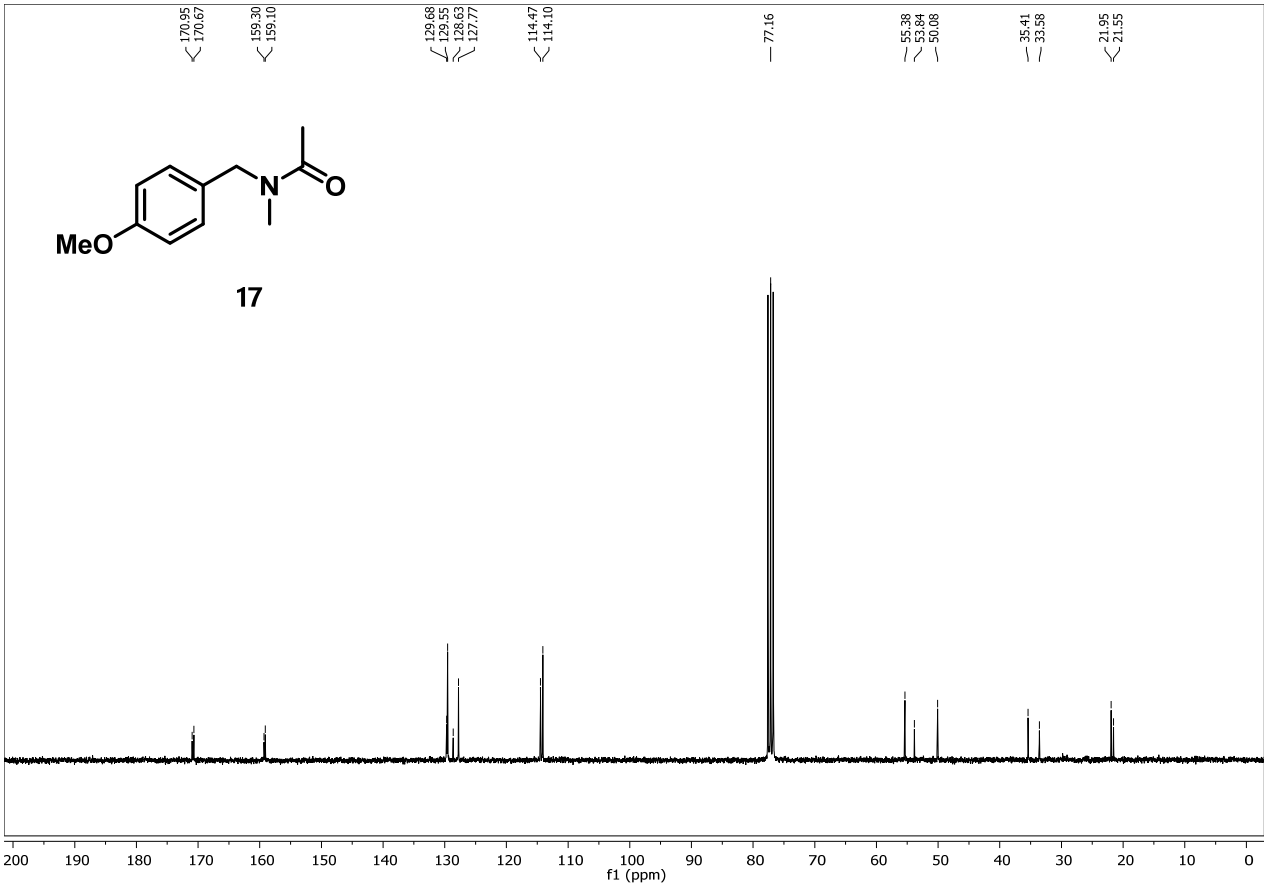

7.27
7.26
7.24
7.19
7.15
7.13
4.56
4.51
2.92
2.14
2.13
F
F
F
O
N
O
15
4.00
2.04
3.00
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

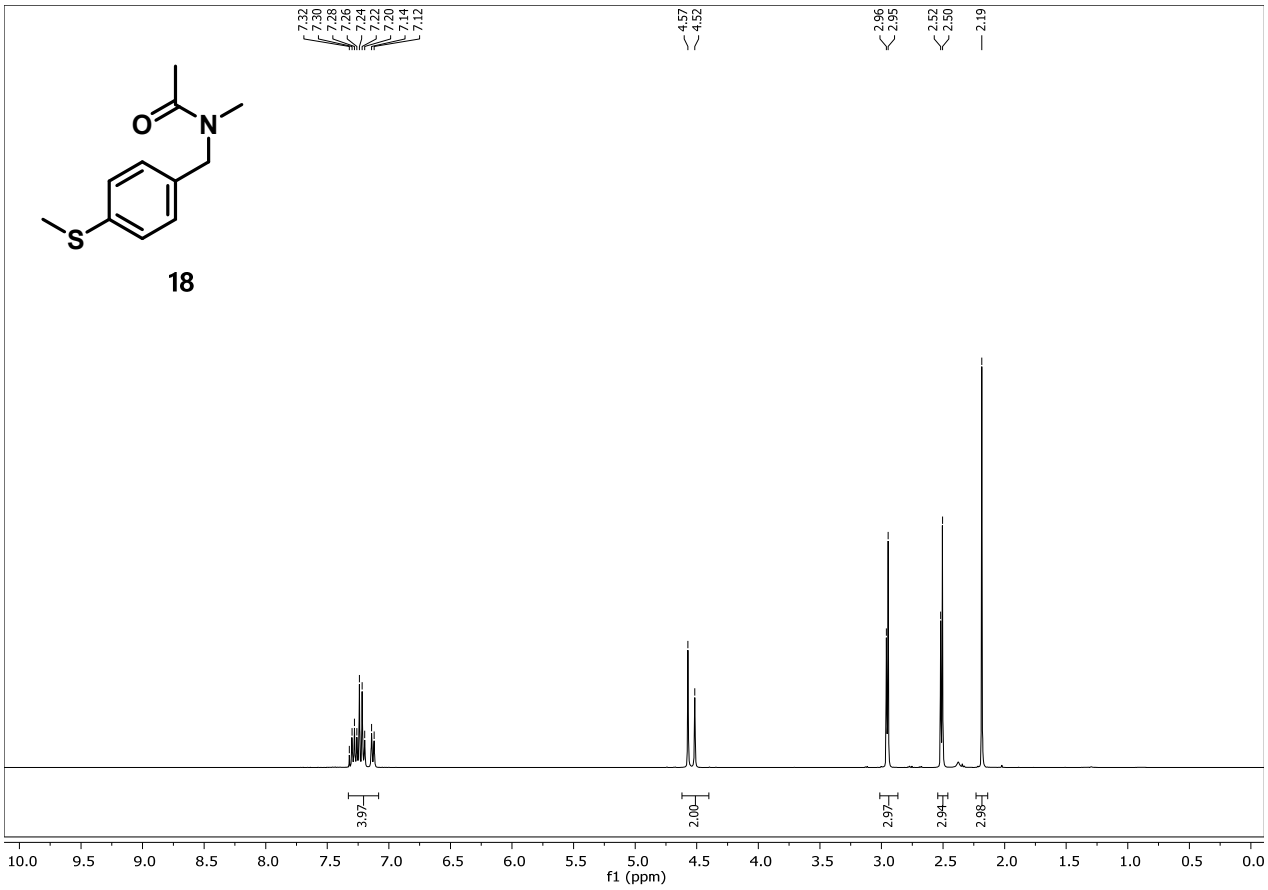

171.01
170.89
148.76
148.57
136.29
135.42
129.47
127.78
124.38
121.83
121.62
121.22
119.27
116.72
77.16
53.67
50.10
35.74
33.79
21.85
21.49
F
F
F
O
N
O
15
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

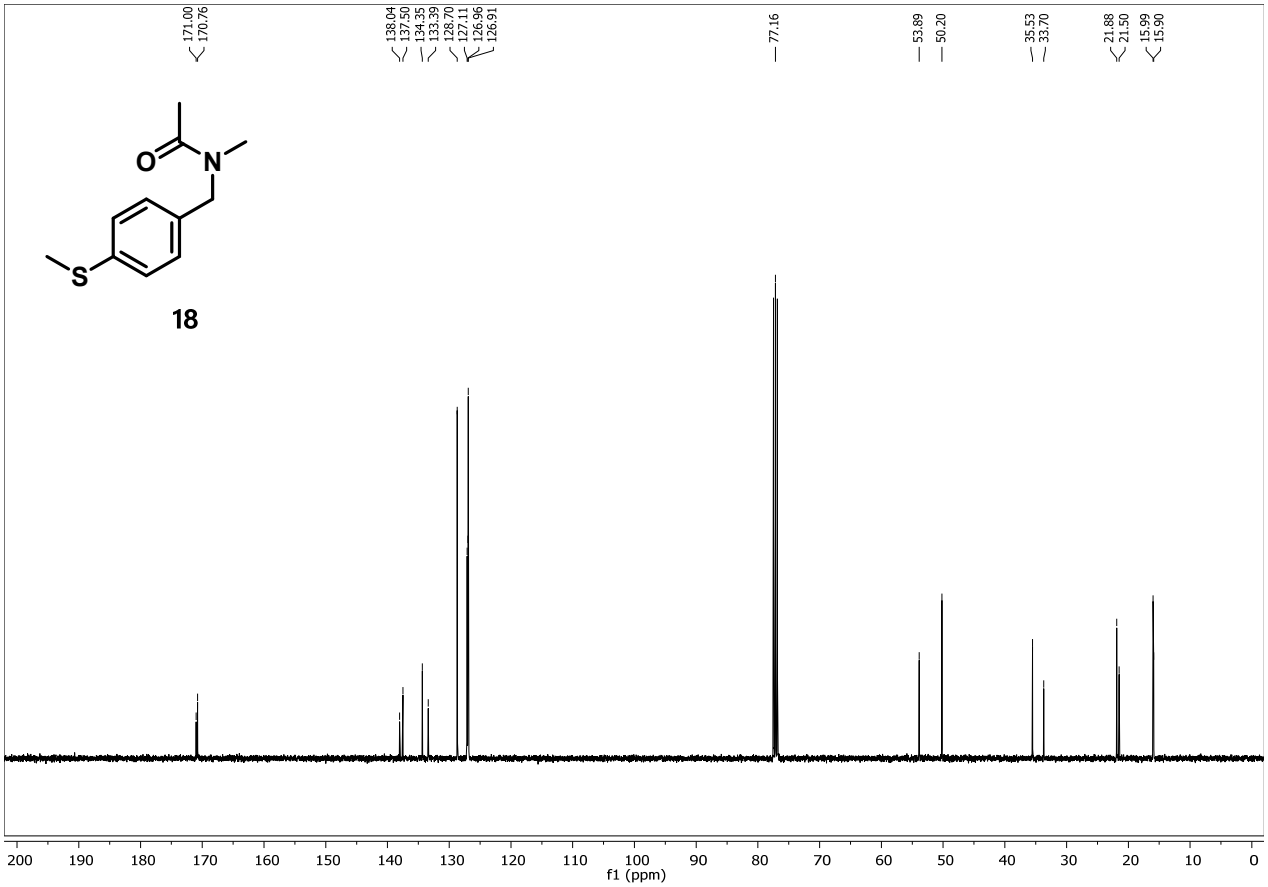

7.64
7.62
7.58
7.56
7.27
7.26
7.25
7.22
7.20
4.58
4.54
2.93
2.92
2.14
2.11
O
N
F
F
F
S
16
1.93
1.99
2.00
2.97
2.98
f1 (ppm)

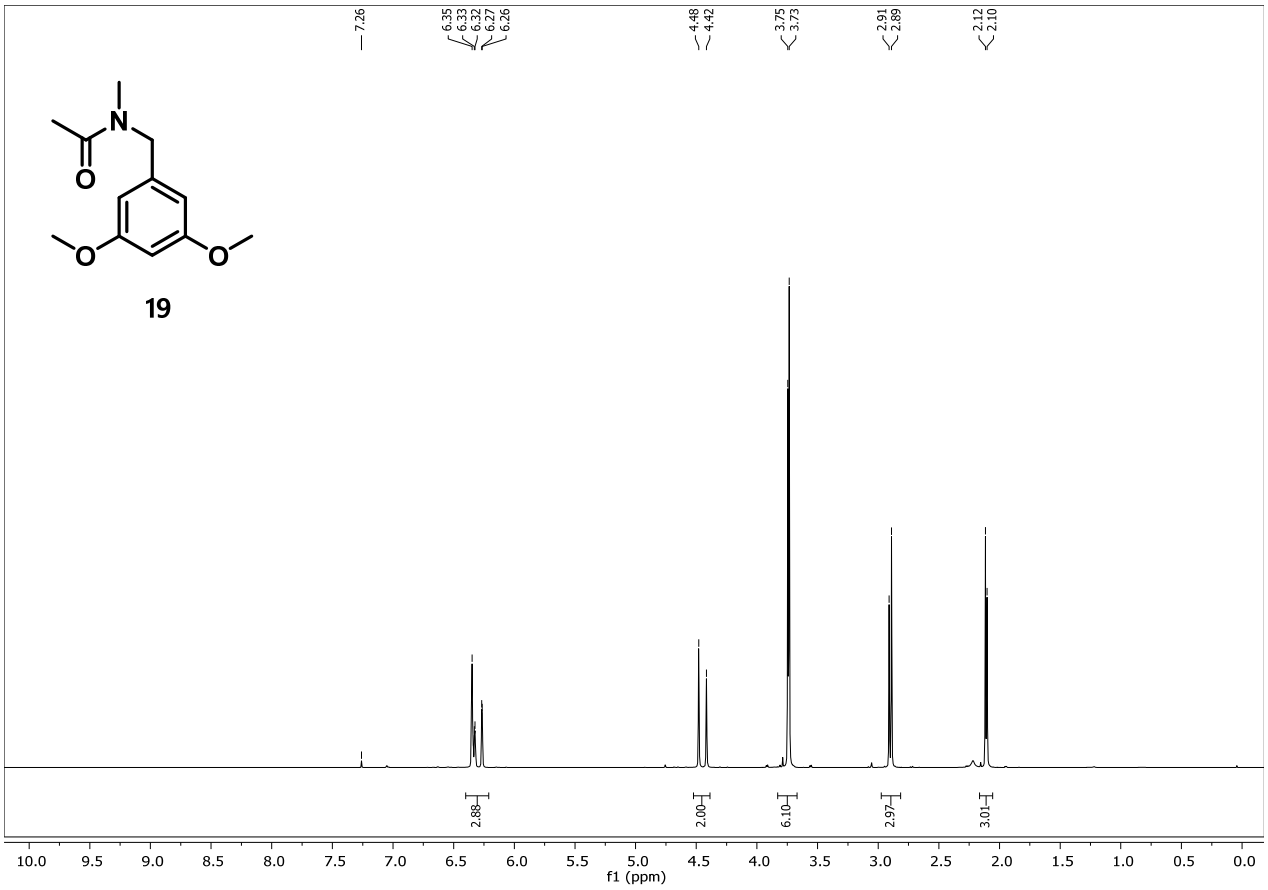

171.04
170.95
140.76
140.02
136.98
136.65
134.22
134.16
131.16
131.10
128.96
128.09
128.03
127.37
125.03
124.97
123.74
123.72
123.70
123.22
123.20
123.18
77.16
53.88
50.37
35.90
33.92
21.77
21.45
O
N
F
F
F
S
16
f1 (ppm)


7.26
7.18
7.16
7.10
7.07
6.90
6.87
6.85
6.83
4.51
4.44
3.80
3.78
2.90
2.89
2.15
2.12
MeO
N
O
17
1.97
2.00
1.99
3.02
2.98
2.99
f1 (ppm)

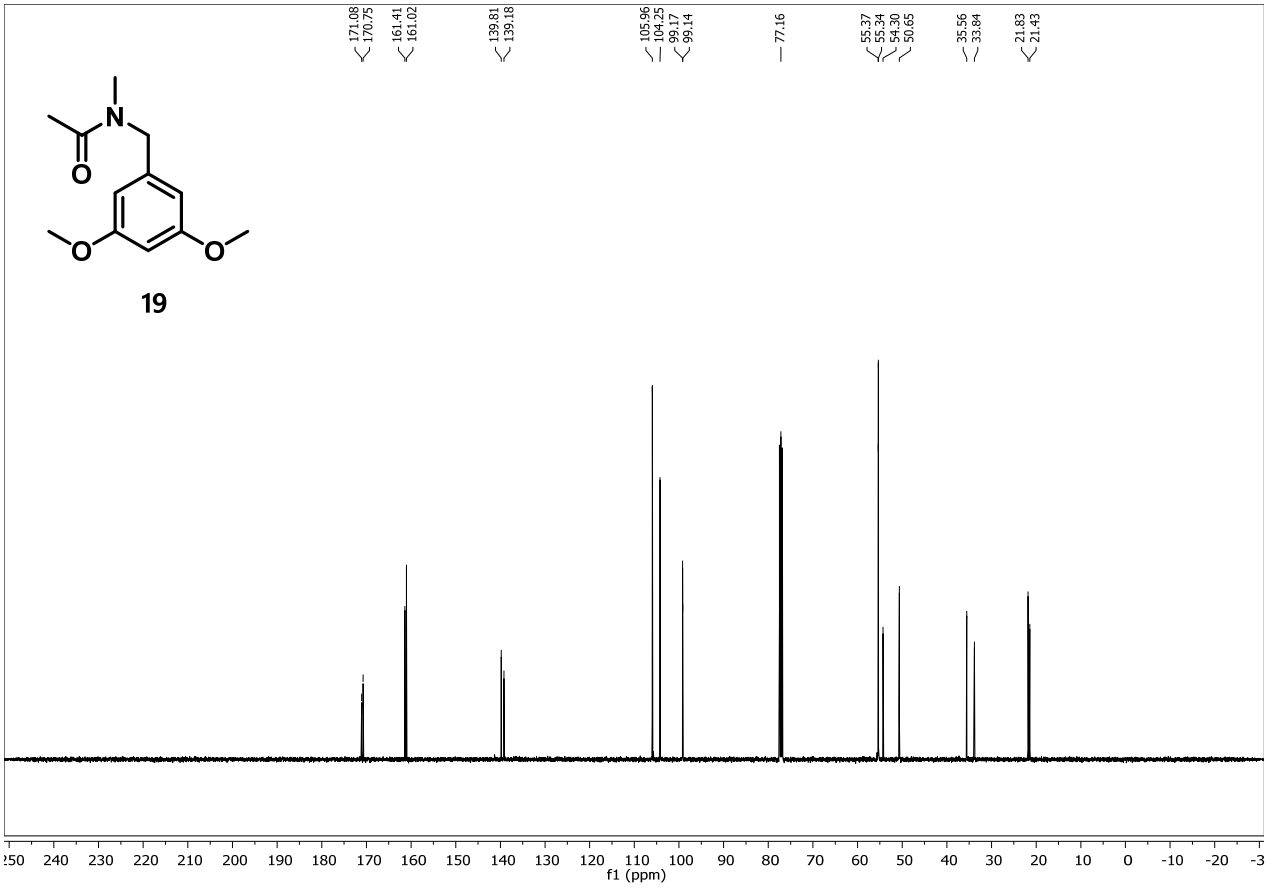

170.95
170.67
159.30
159.10
129.68
129.55
128.63
127.77
114.47
114.10
77.16
55.38
53.84
50.08
35.41
33.58
21.95
21.55
MeO
N
O
17
f1 (ppm)


7.32
7.30
7.28
7.26
7.24
7.22
7.20
7.14
7.12
4.57
4.52
2.96
2.95
2.52
2.50
2.19
O
N
S
18
3.97
2.00
2.97
2.94
2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

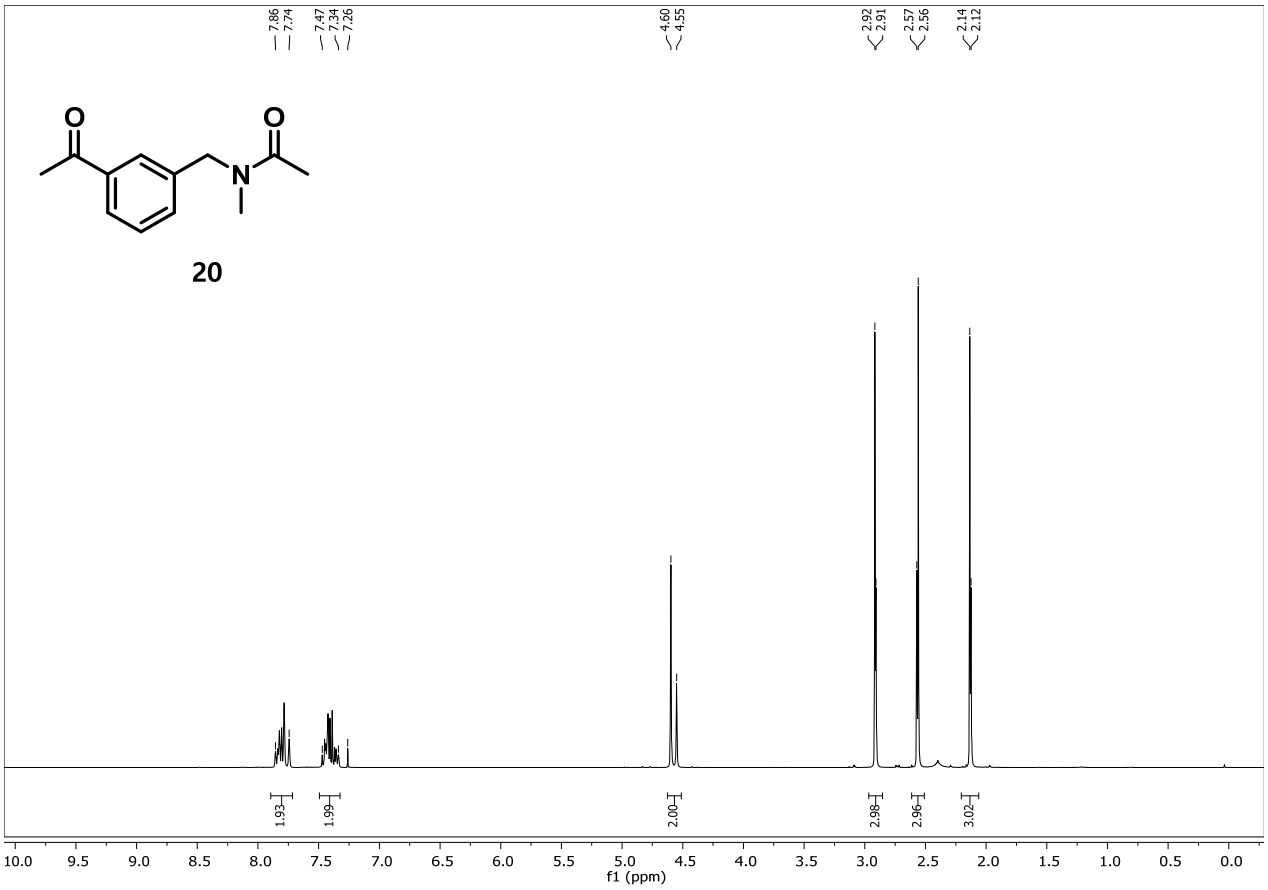

171.00
170.76
138.04
137.50
134.35
133.39
128.70
127.11
126.96
126.91
77.16
53.89
50.20
35.53
33.70
21.88
21.50
15.99
15.90
O
N
S
18
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

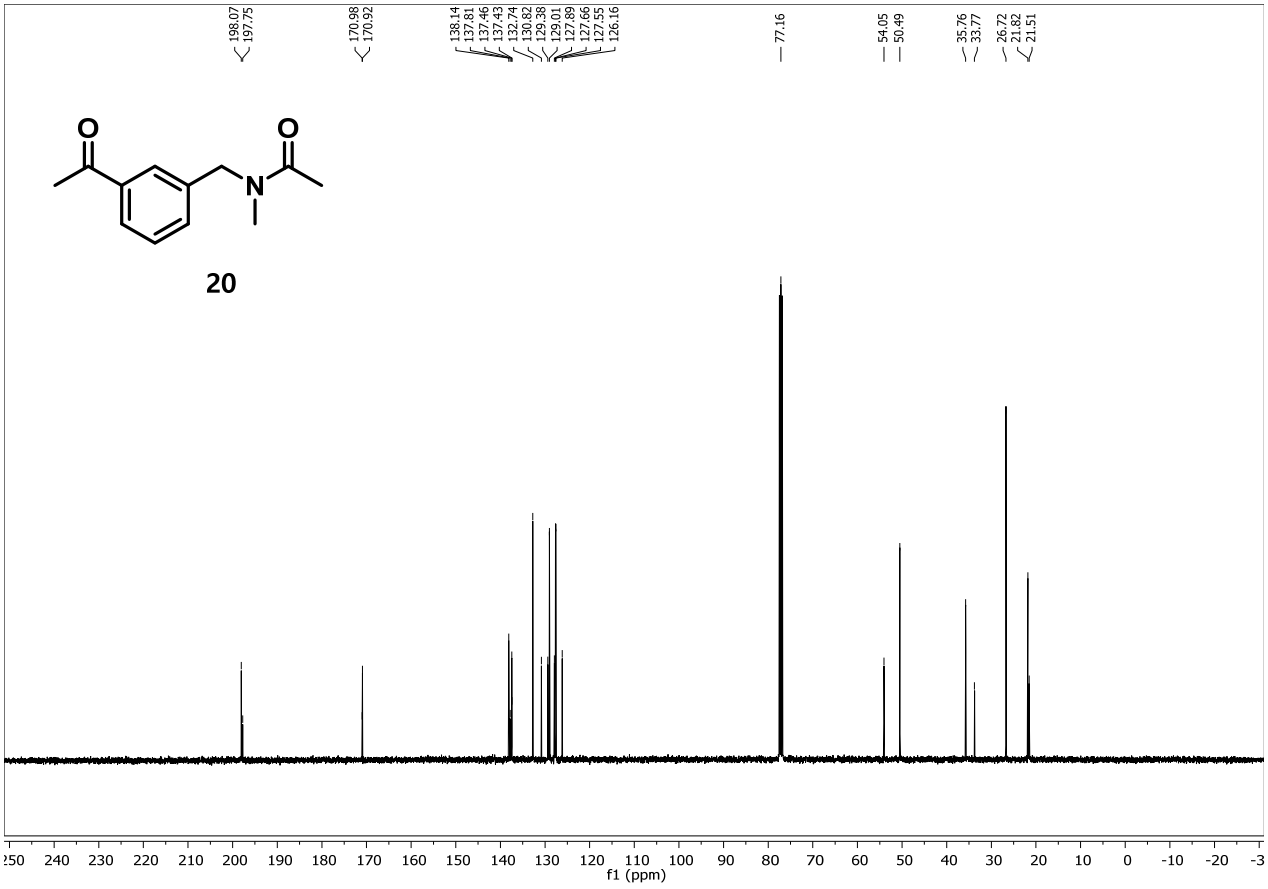

7.26
6.35
6.33
6.32
6.27
6.26
4.48
4.42
3.75
3.73
2.91
2.89
2.12
2.10
2.88
2.00
6.10
2.97
3.01
f1 (ppm)

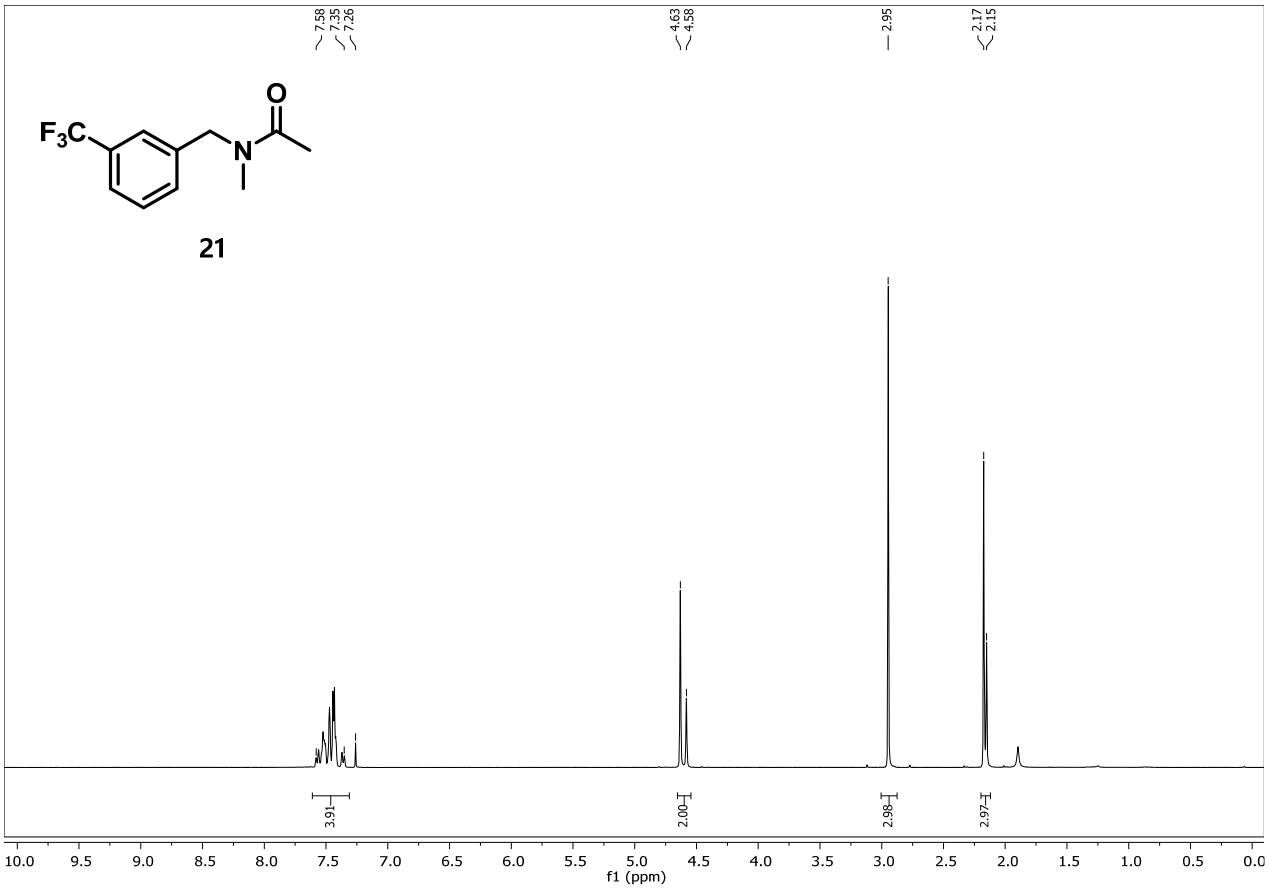
19

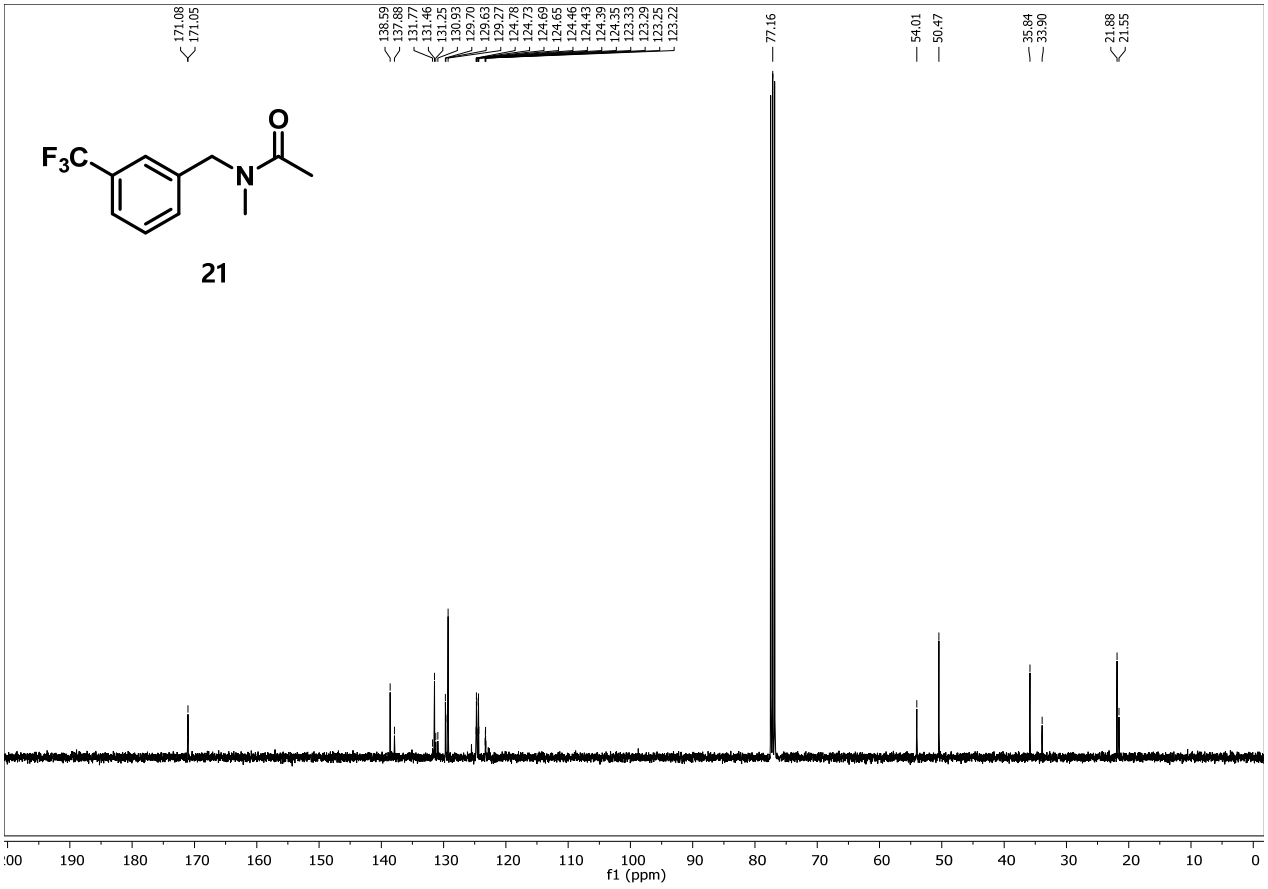

171.08
170.75
161.41
161.02
139.81
139.18
105.96
104.25
99.17
99.14
77.16
55.37
55.34
54.30
50.65
35.56
33.84
21.83
21.43
f1 (ppm)

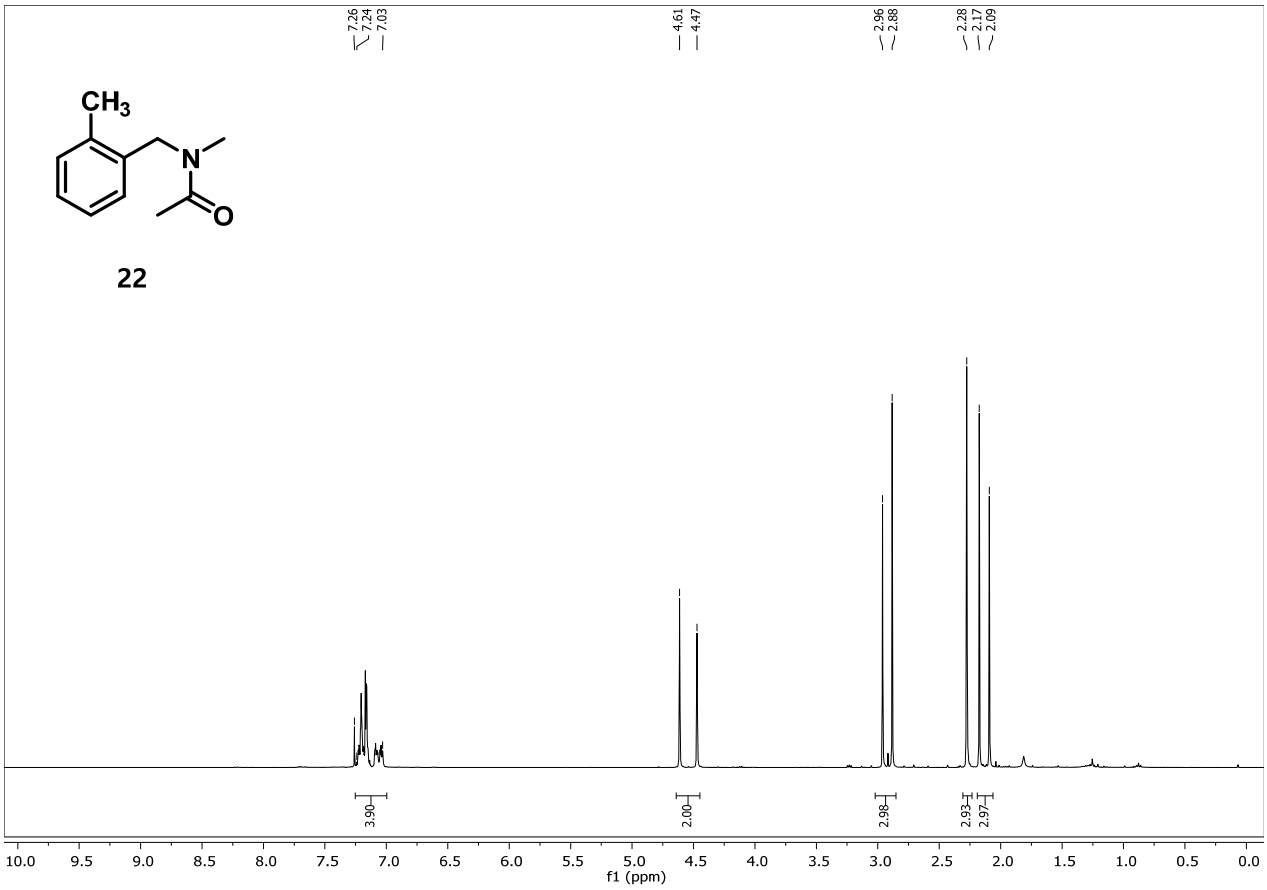
19

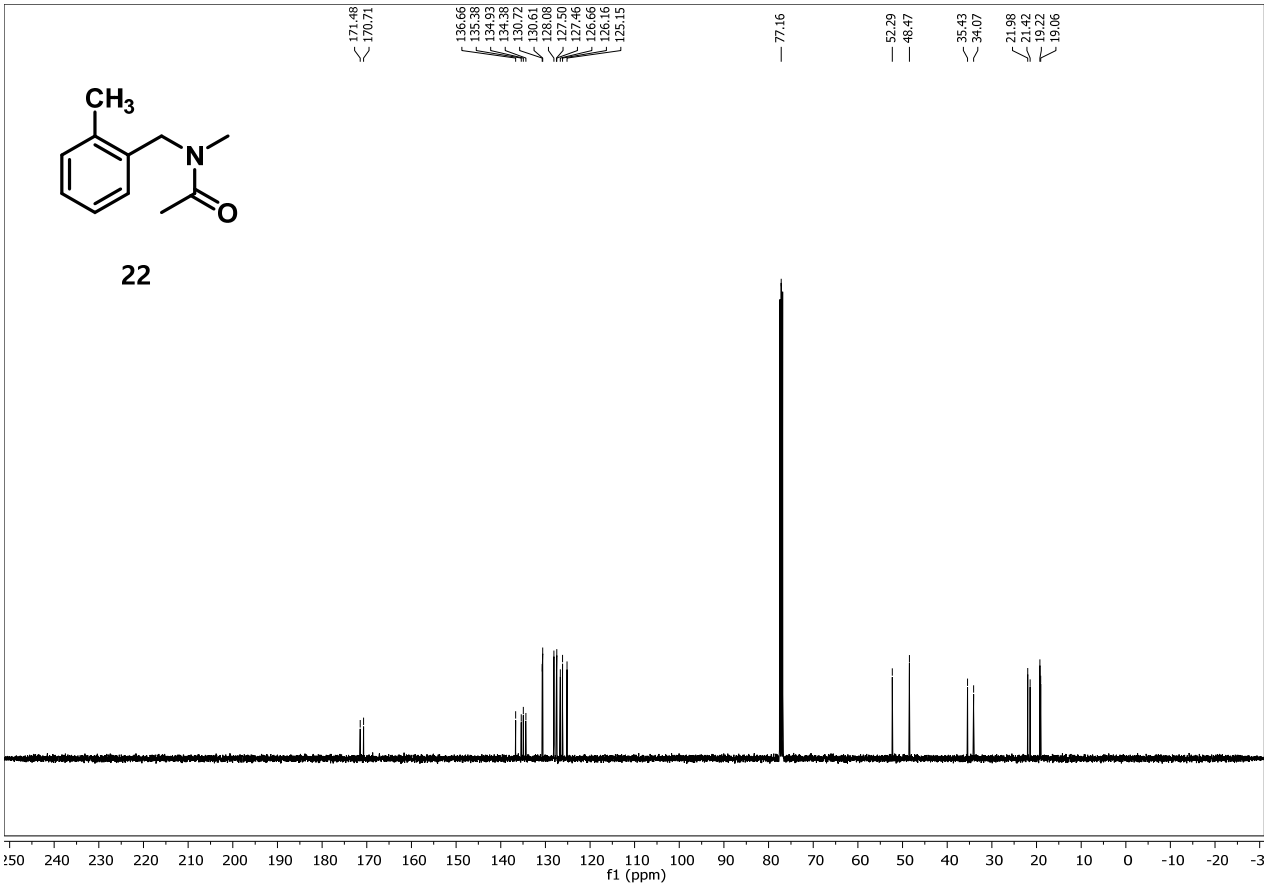

7.86
7.74
7.47
7.34
7.26
4.60
4.55
2.92
2.91
2.57
2.56
2.14
2.12
20
1.93
1.99
2.00
2.98
2.96
3.02
f1 (ppm)

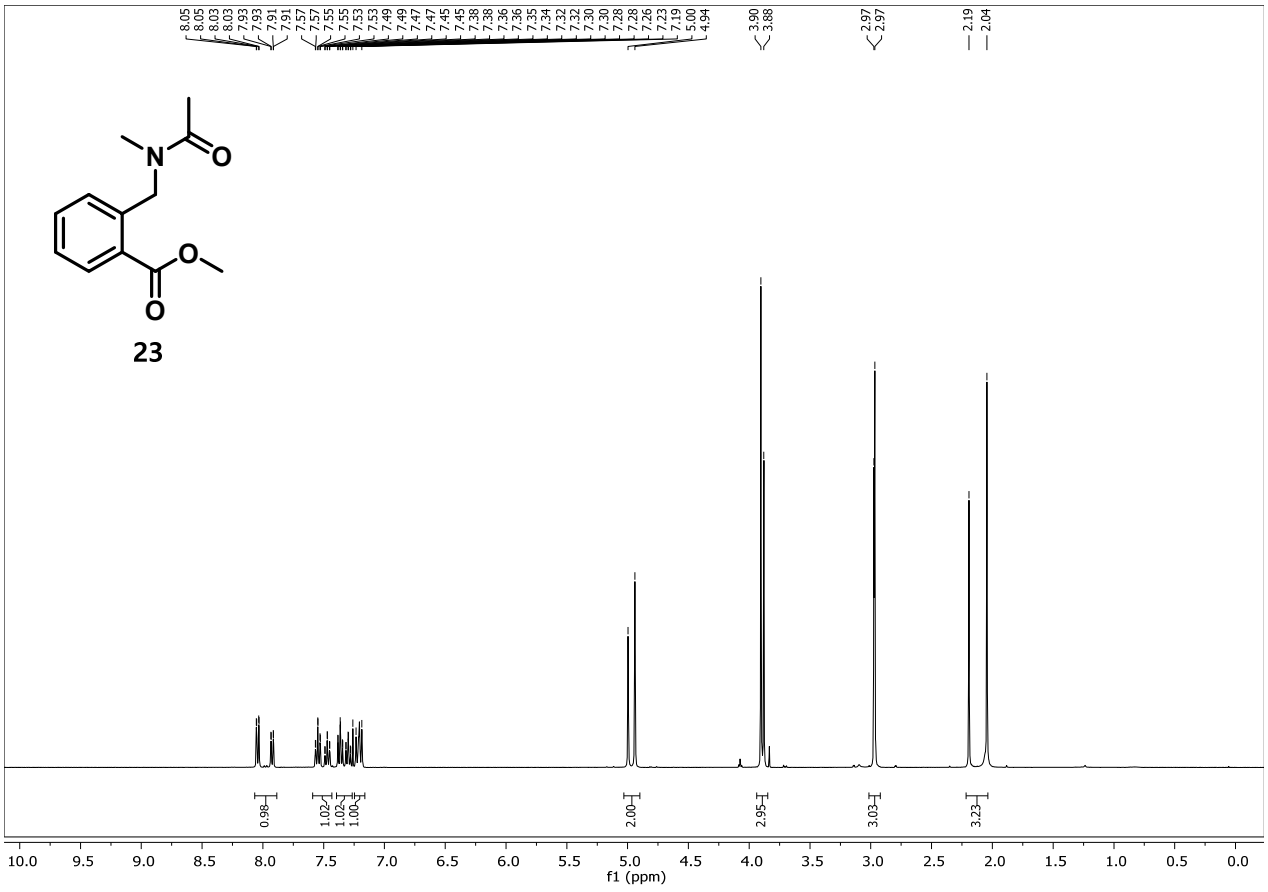

198.07
197.75
170.98
170.92
138.14
137.81
137.46
137.43
132.74
130.82
129.38
129.01
127.89
127.66
127.55
126.16
77.16
54.05
50.49
35.76
33.77
26.72
21.82
21.51
20
f1 (ppm)

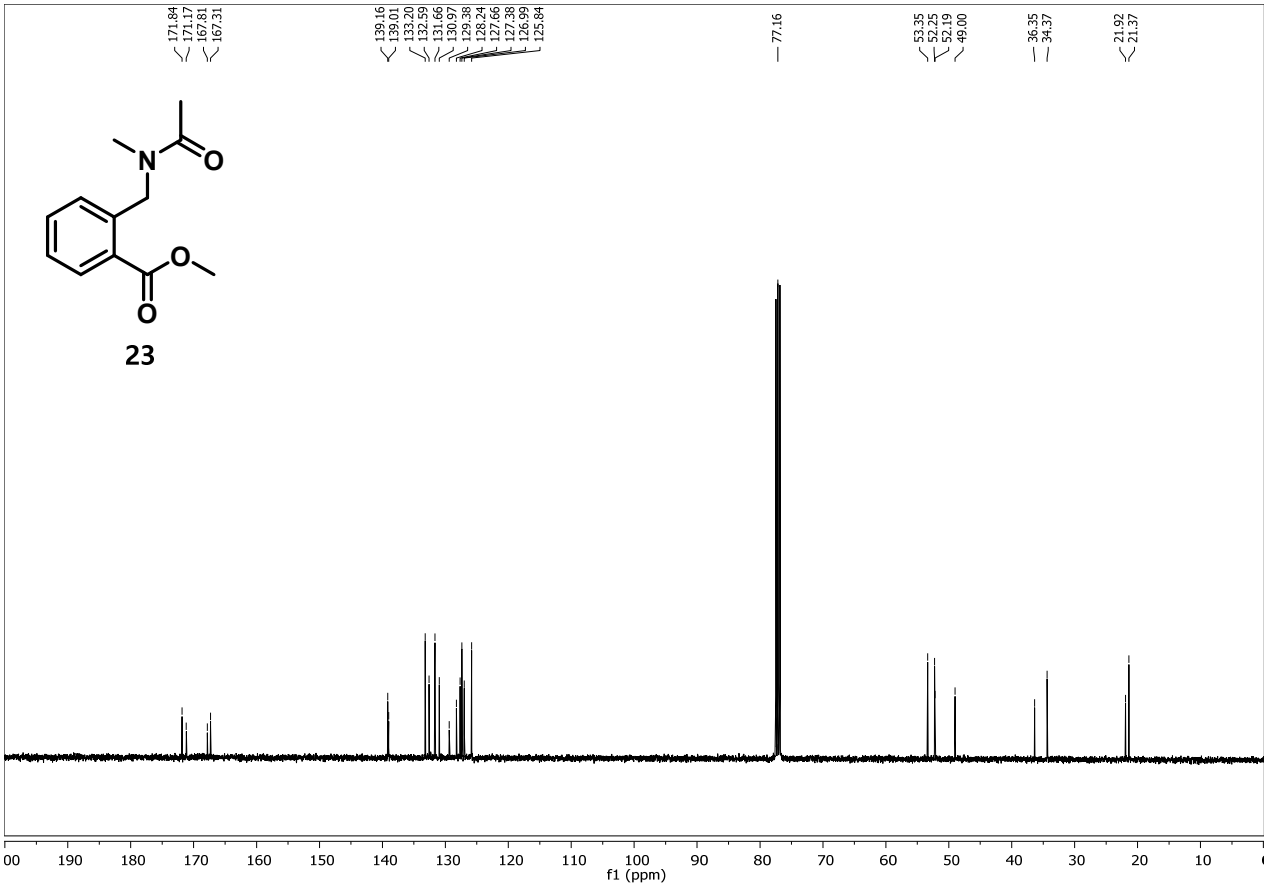

7.58
7.35
7.26
4.63
4.58
2.95
2.17
2.15
F3C
N
O
21
3.91
2.00
2.98
2.97
f1 (ppm)

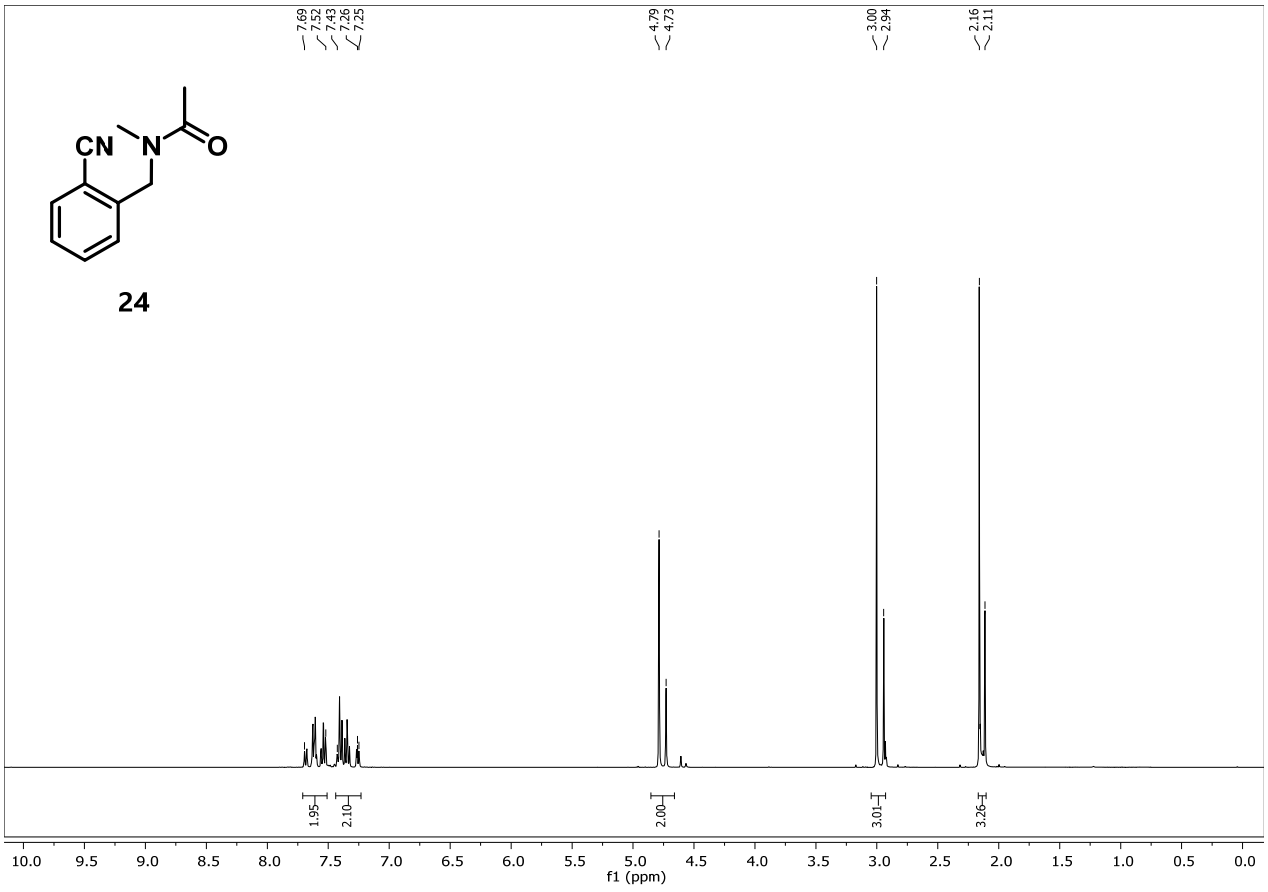

171.08
171.05
138.59
137.88
131.77
131.46
131.25
130.93
129.70
129.63
129.27
124.78
124.73
124.69
124.65
124.46
124.43
124.39
124.35
123.33
123.29
123.25
123.22
77.16
54.01
50.47
35.84
33.90
21.88
21.55
F3C
N
O
21
f1 (ppm)

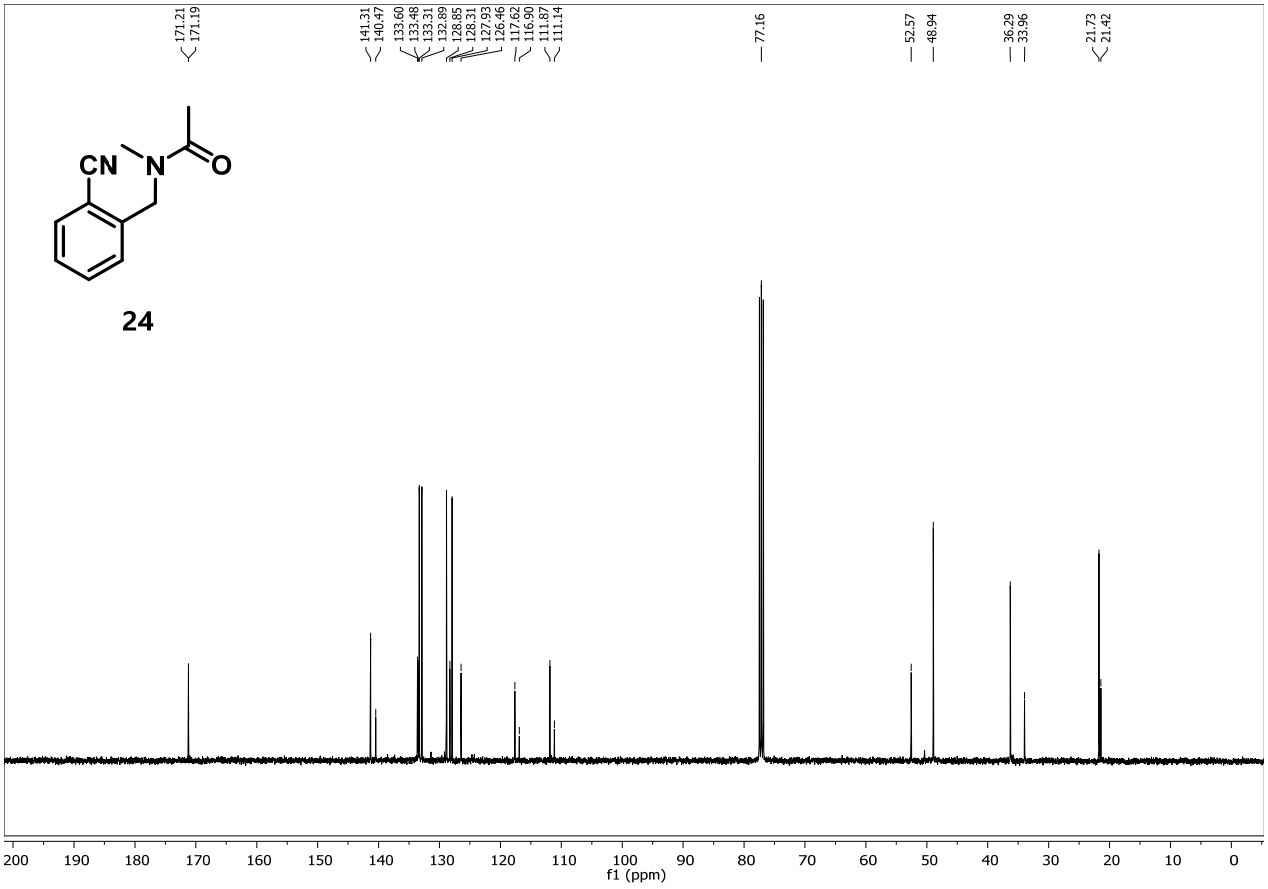

7.26
7.24
7.03
4.61
4.47
2.96
2.88
2.28
2.17
2.09
CH3
N
O
22
3.90
2.00
2.98
2.93
2.97
f1 (ppm)

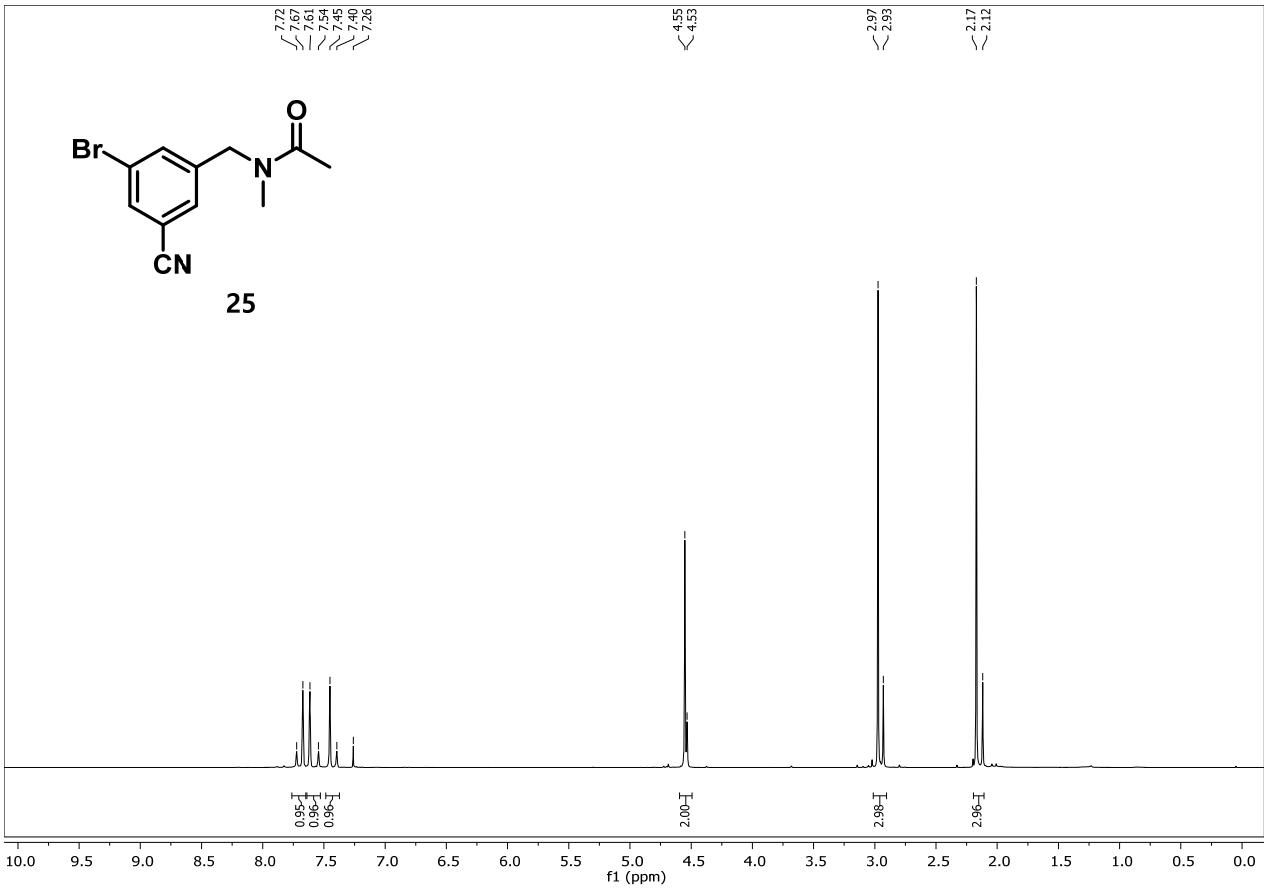

171.48
170.71
136.66
135.38
134.93
134.38
130.72
130.61
128.08
127.50
127.46
126.66
126.16
125.15
77.16
52.29
48.47
35.43
34.07
21.98
21.42
19.22
19.06
CH3
N
O
22
f1 (ppm)

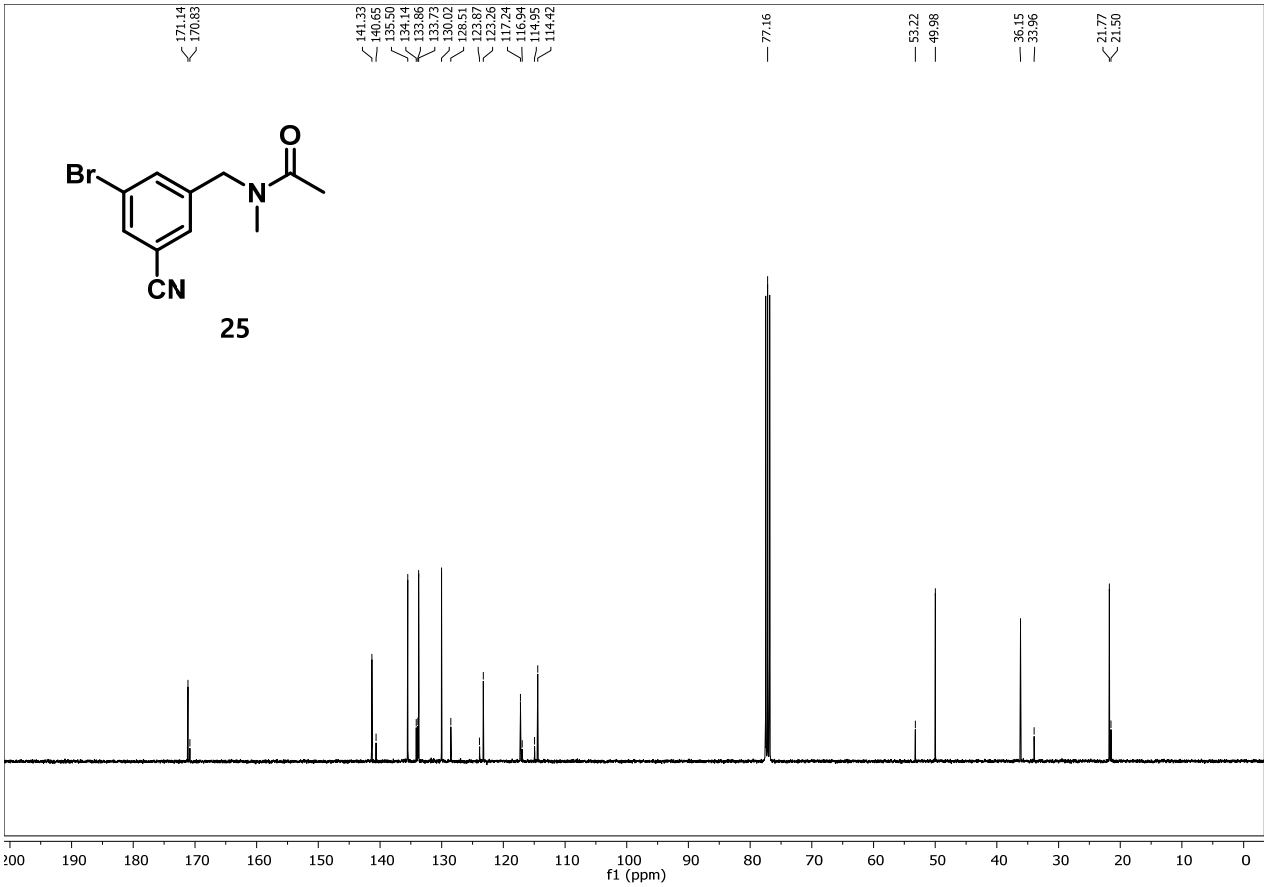

8.05
8.05
8.03
8.03
7.93
7.93
7.91
7.91
7.57
7.57
7.55
7.55
7.53
7.53
7.49
7.49
7.47
7.47
7.45
7.45
7.38
7.38
7.36
7.36
7.35
7.34
7.32
7.32
7.30
7.30
7.28
7.28
7.26
7.23
7.19
5.00
4.94
3.90
3.88
2.97
2.97
2.19
2.04
N
O
O
O
23
0.98
1.02
1.02
1.00
2.00
2.95
3.03
3.23
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

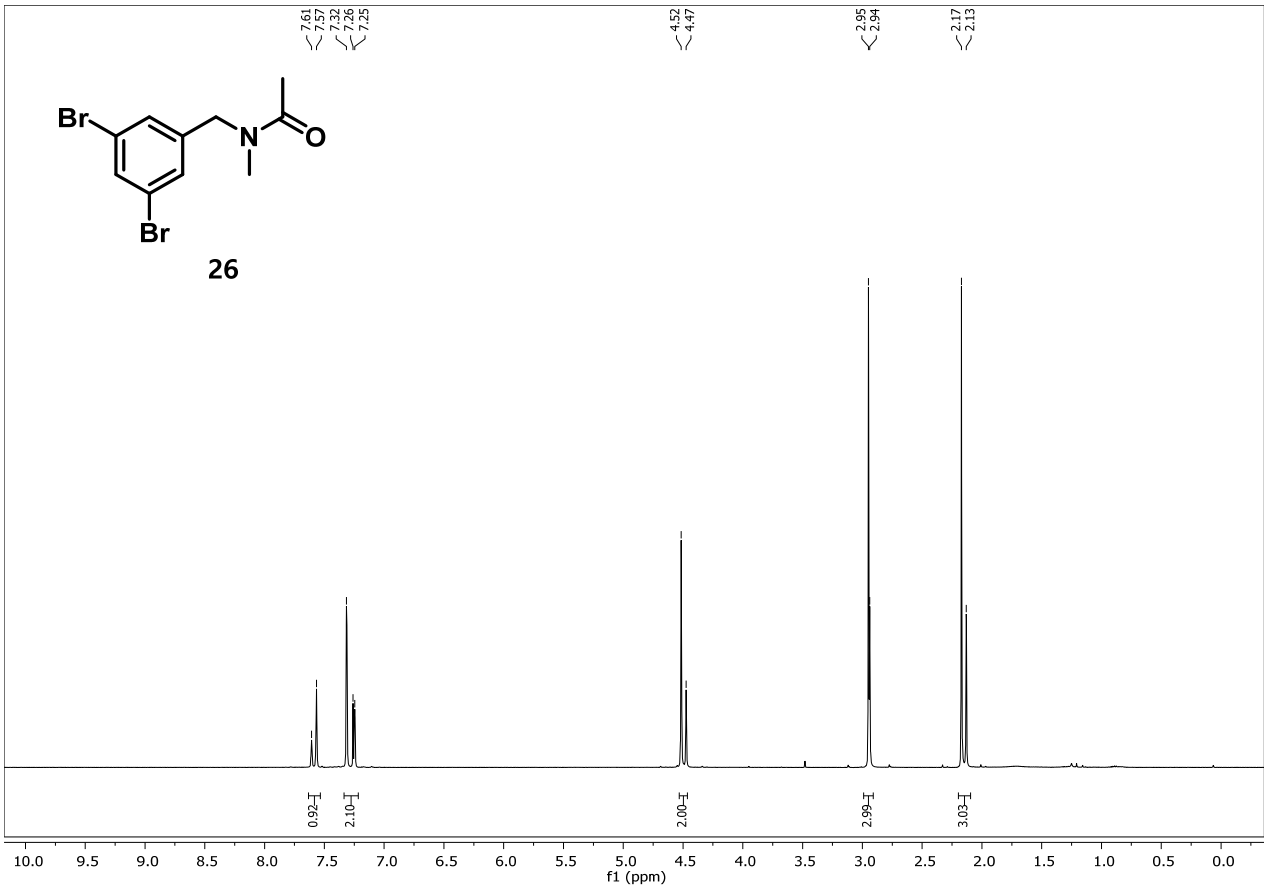

171.84
171.17
167.81
167.31
139.16
139.01
133.20
132.59
131.66
130.97
129.38
128.24
127.66
127.38
126.99
125.84
77.16
53.35
52.25
52.19
49.00
36.35
34.37
21.92
21.37
N
O
O
O
23
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

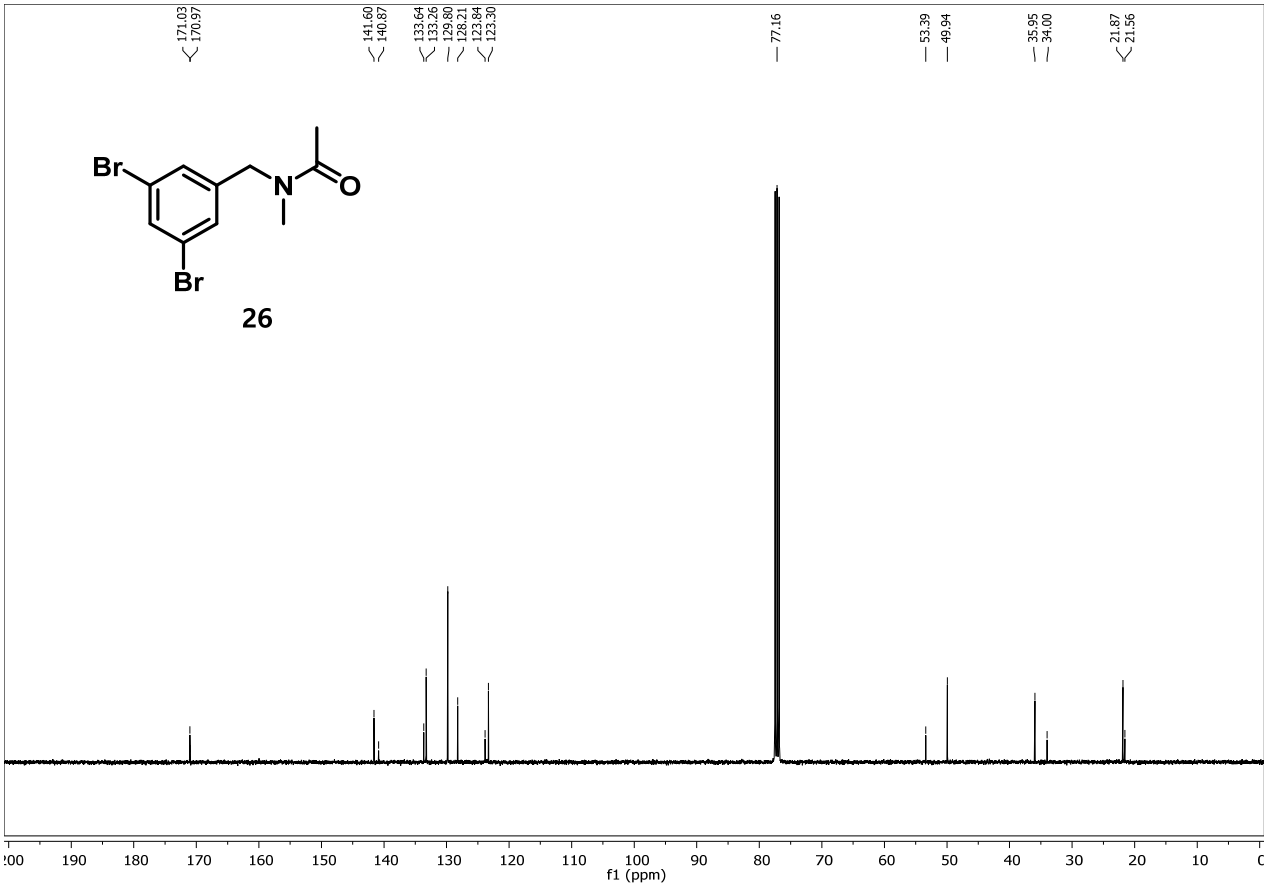

7.69
7.52
7.43
7.26
7.25
4.79
4.73
3.00
2.94
2.16
2.11
CN
N
O
24
1.95
2.10
2.00
3.01
3.26
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

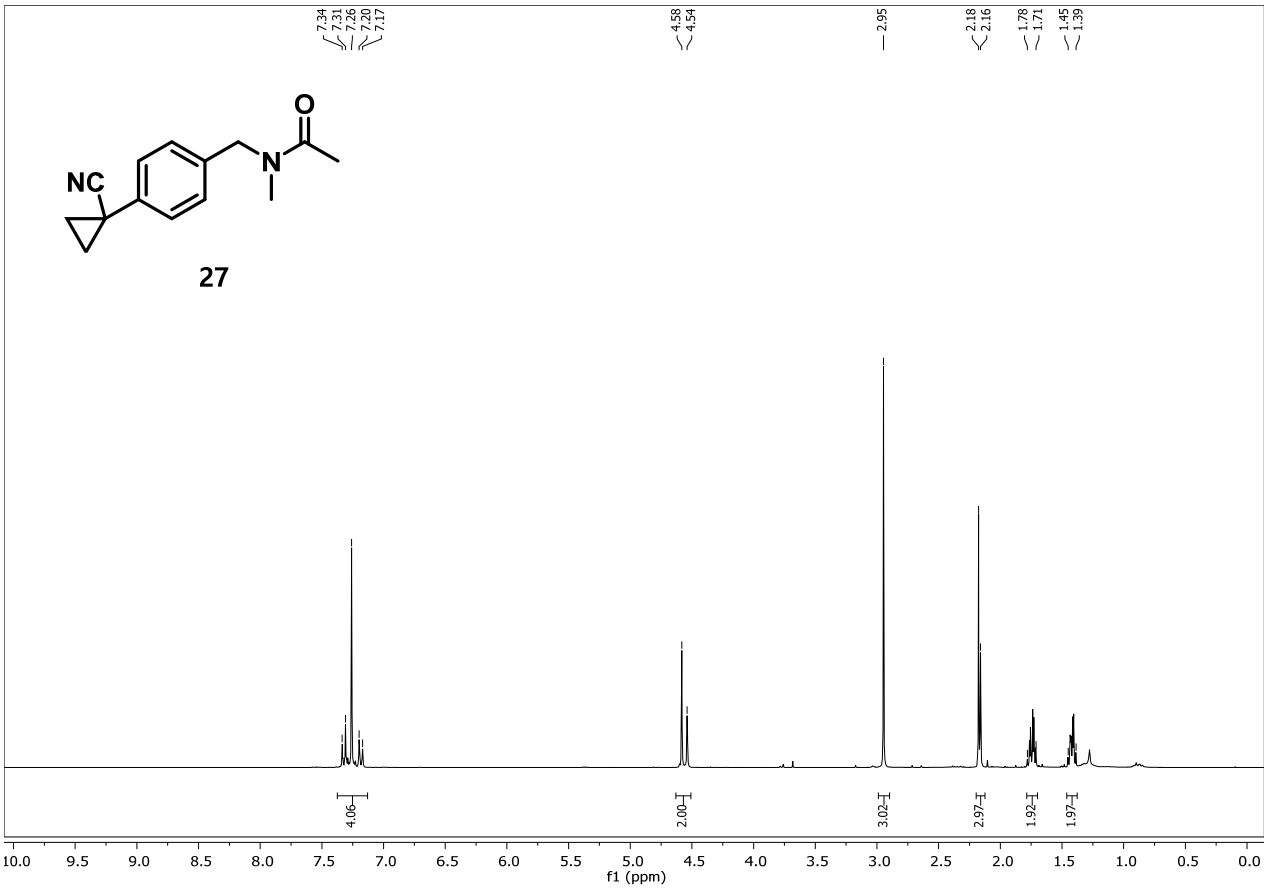

171.21
171.19
141.31
140.47
133.60
133.48
133.31
132.89
128.85
128.31
127.93
126.46
117.62
116.90
111.87
111.14
77.16
52.57
48.94
36.29
33.96
21.73
21.42
CN
N
O
24
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

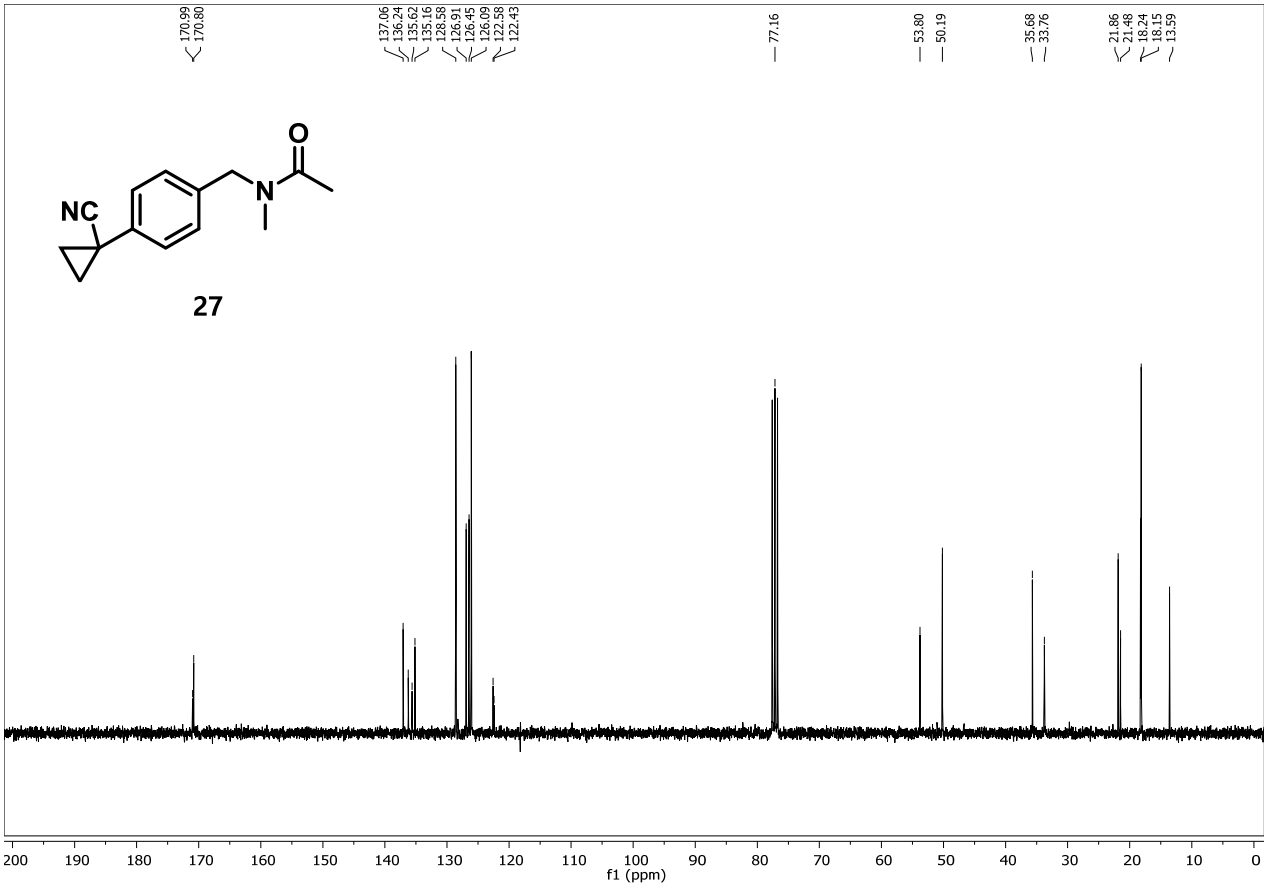

7.72
7.67
7.61
7.54
7.45
7.40
7.26
4.55
4.53
2.97
2.93
2.17
2.12
Br
N
O
CN
25
0.95
0.96
0.96
2.00
2.98
2.96
f1 (ppm)

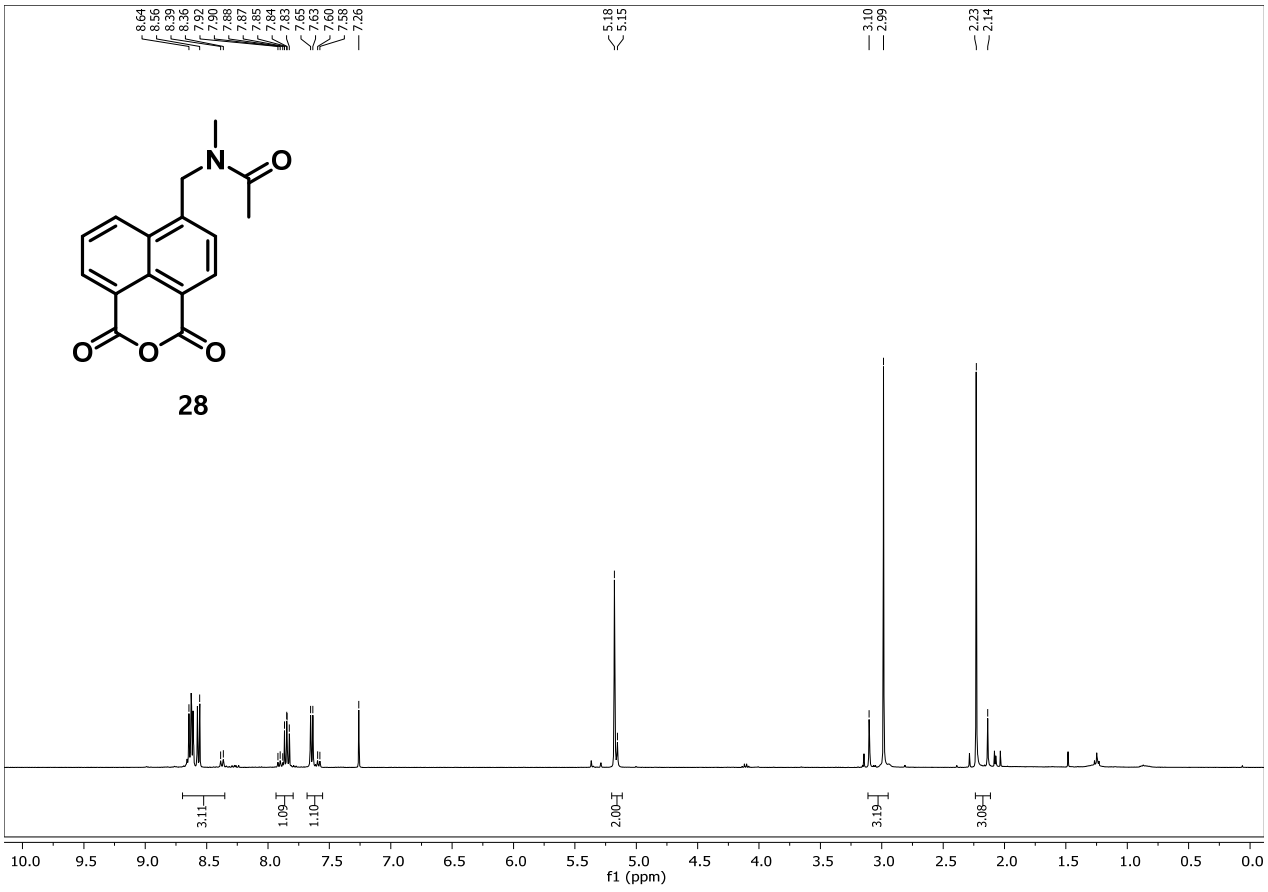

171.14
170.83
141.33
140.65
135.50
134.14
133.86
133.73
130.02
128.51
123.87
123.26
117.24
116.94
114.95
114.42
77.16
53.22
49.98
36.15
33.96
21.77
21.50
Br
N
O
CN
25
f1 (ppm)

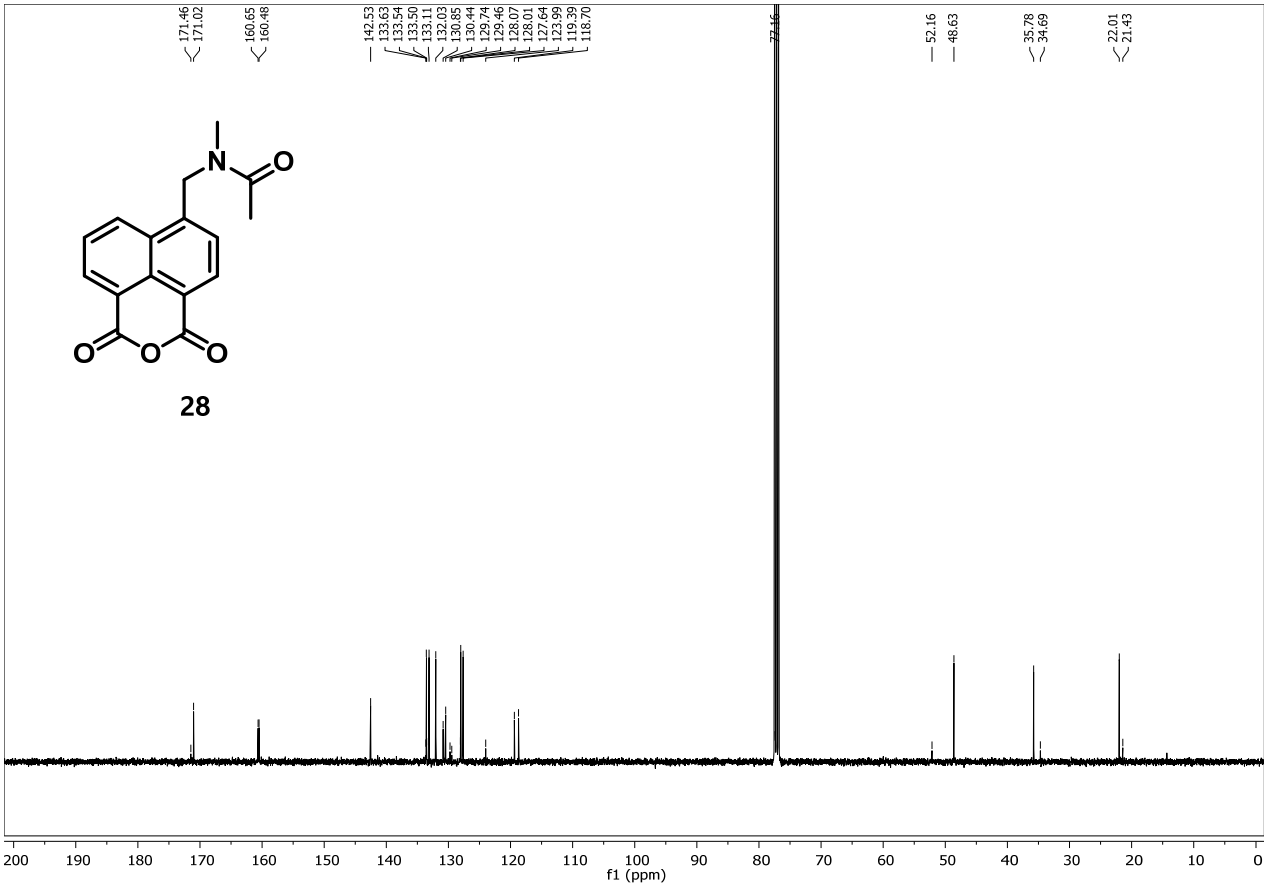

7.61
7.57
7.32
7.26
7.25
4.52
4.47
2.95
2.94
2.17
2.13
Br
N
O
Br
26
0.92
2.10
2.00
2.99
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

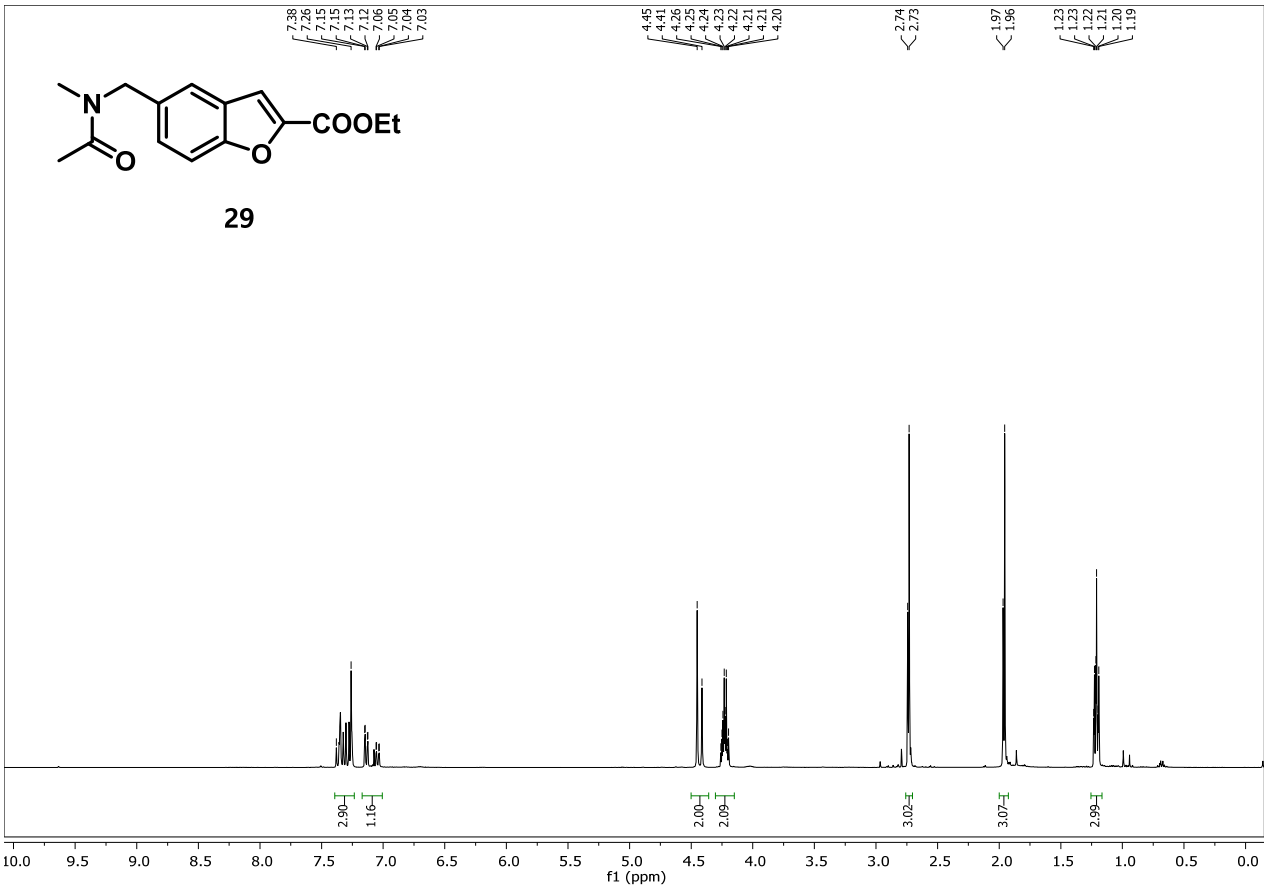

171.03
170.97
141.60
140.87
133.64
133.26
129.80
128.21
123.84
123.30
77.16
53.39
49.94
35.95
34.00
21.87
21.56
Br
N
O
Br
26
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

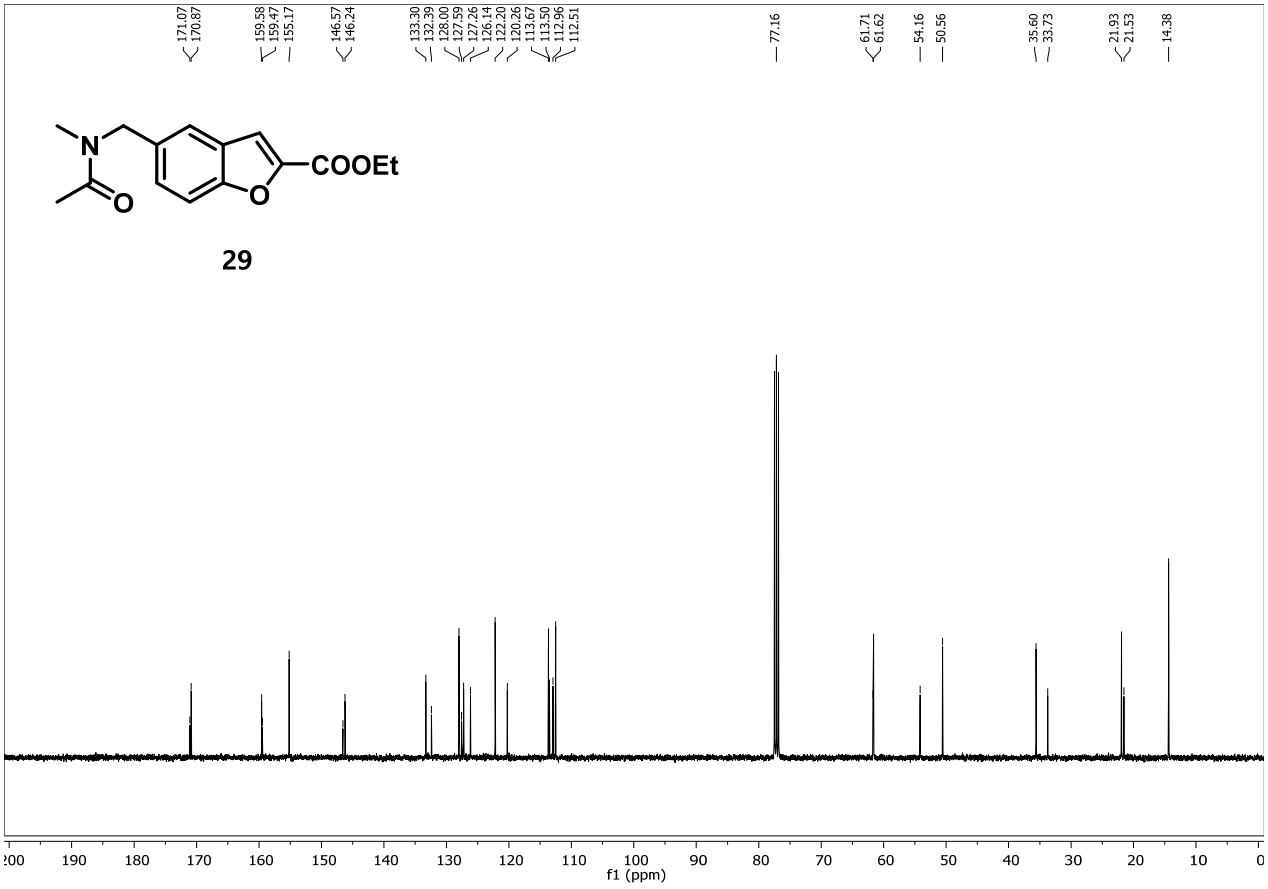

7.34
7.31
7.26
7.20
7.17
4.58
4.54
2.95
2.18
2.16
1.78
1.71
1.45
1.39
NC
O
N
27
4.06
2.00
3.02
2.97
1.92
1.97
f1 (ppm)

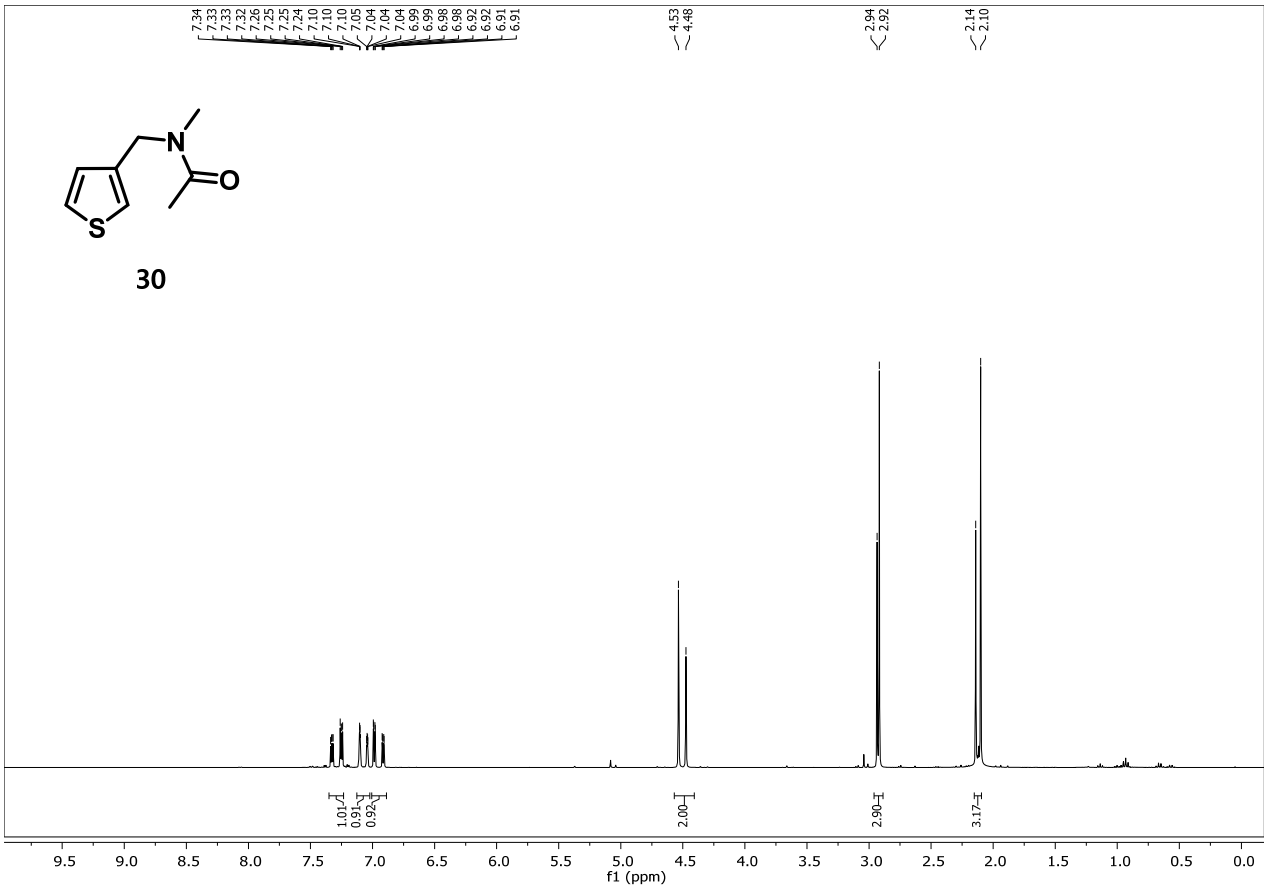

170.99
170.80
137.06
136.24
135.62
135.16
128.58
126.91
126.45
126.09
122.58
122.43
77.16
53.80
50.19
35.68
33.76
21.86
21.48
18.24
18.15
13.59
NC
O
N
27
f1 (ppm)

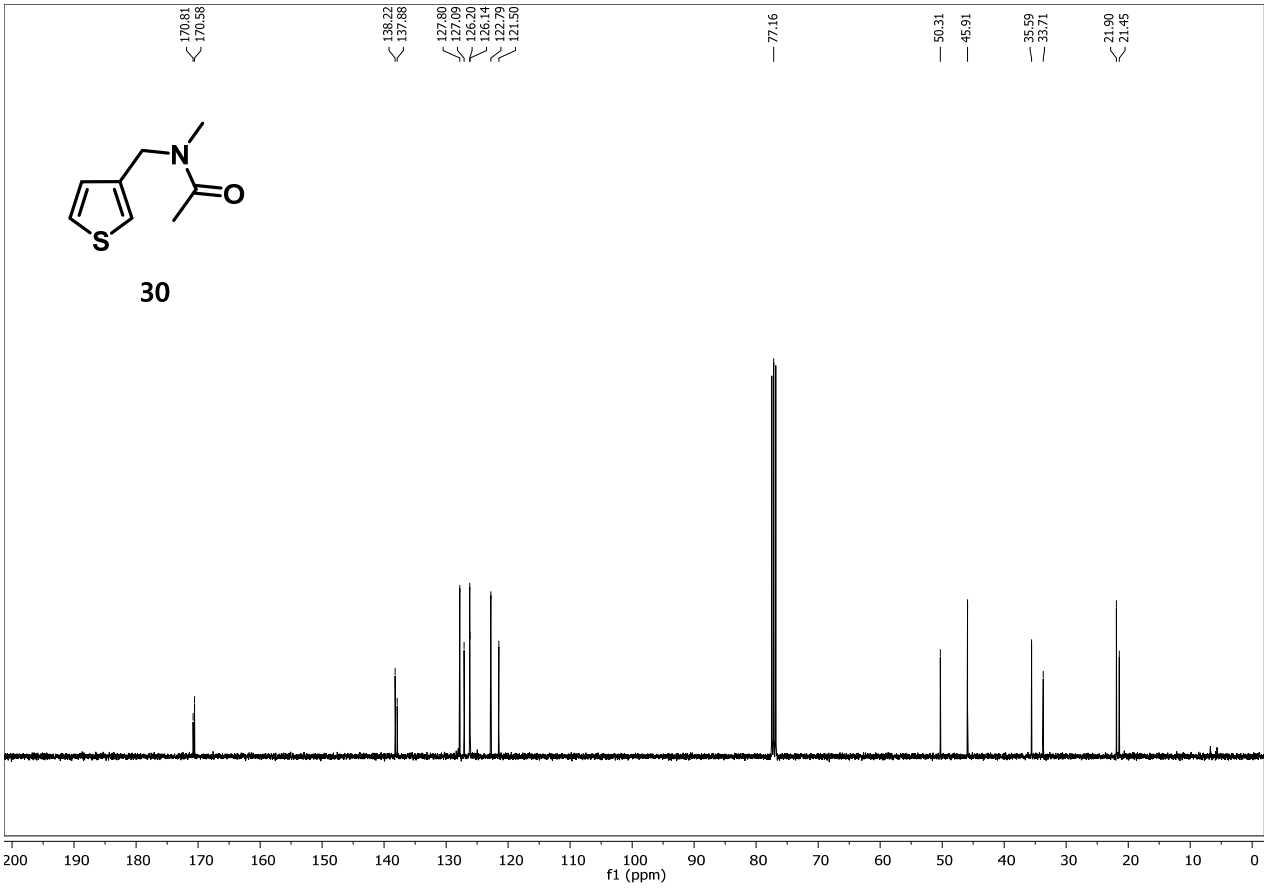

8.64
8.56
8.39
8.36
7.92
7.90
7.88
7.87
7.85
7.84
7.83
7.65
7.63
7.60
7.58
7.26
5.18
5.15
3.10
2.99
2.23
2.14
N
O
O
O
O
O
28
3.11
1.09
1.10
2.00
3.19
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

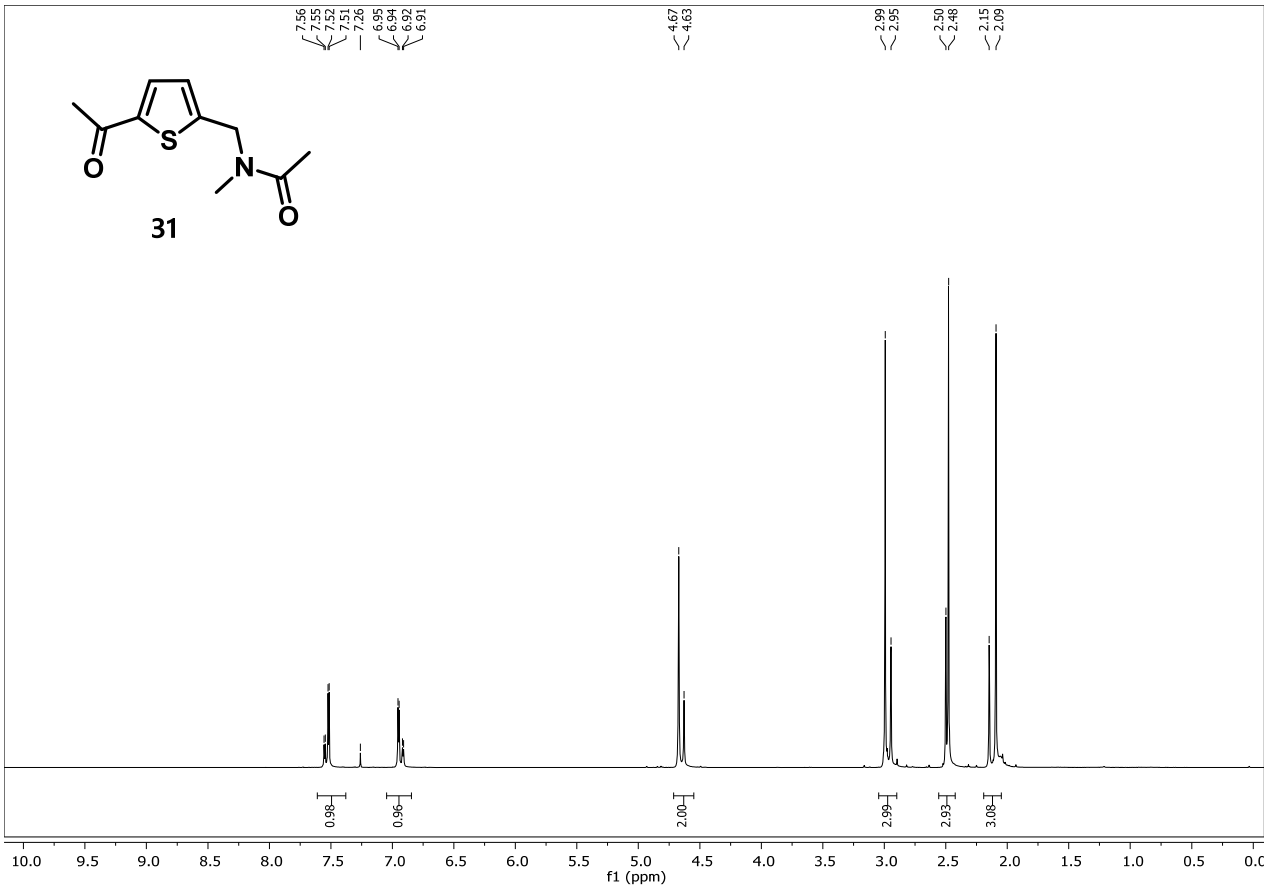

171.46
171.02
160.65
160.48
142.53
133.63
133.54
133.50
133.11
132.03
130.85
130.44
129.74
129.46
128.07
128.01
127.64
123.99
119.39
118.70
77.16
52.16
48.63
35.78
34.69
22.01
21.43
N
O
O
O
O
O
28
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

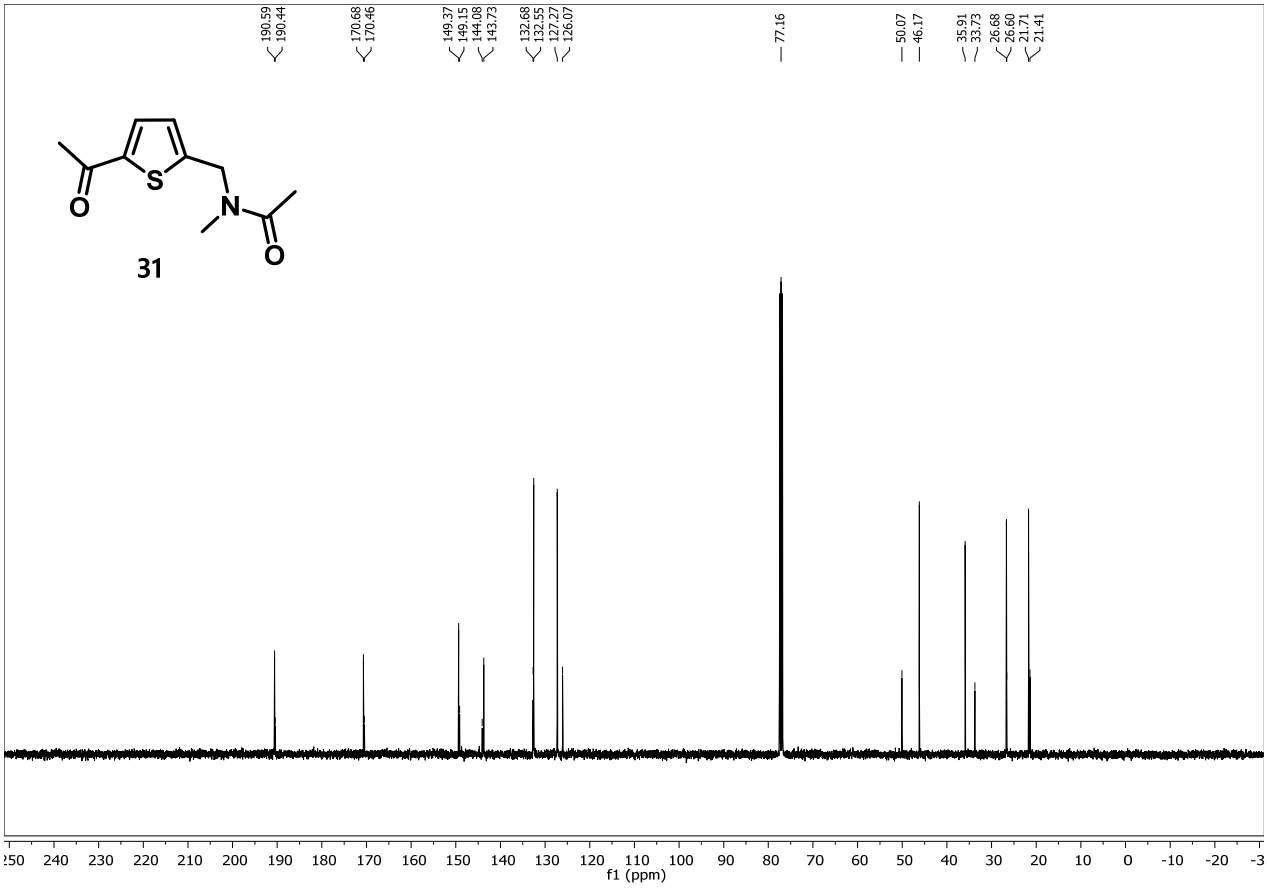

7.38
7.26
7.15
7.15
7.13
7.12
7.06
7.05
7.04
7.03
4.45
4.41
4.26
4.25
4.24
4.23
4.22
4.21
4.21
4.20
2.74
2.73
1.97
1.96
1.23
1.23
1.22
1.21
1.20
1.19
N
O
O
COOEt
29
2.90
1.16
2.00
2.09
3.02
3.07
2.99
f1 (ppm)

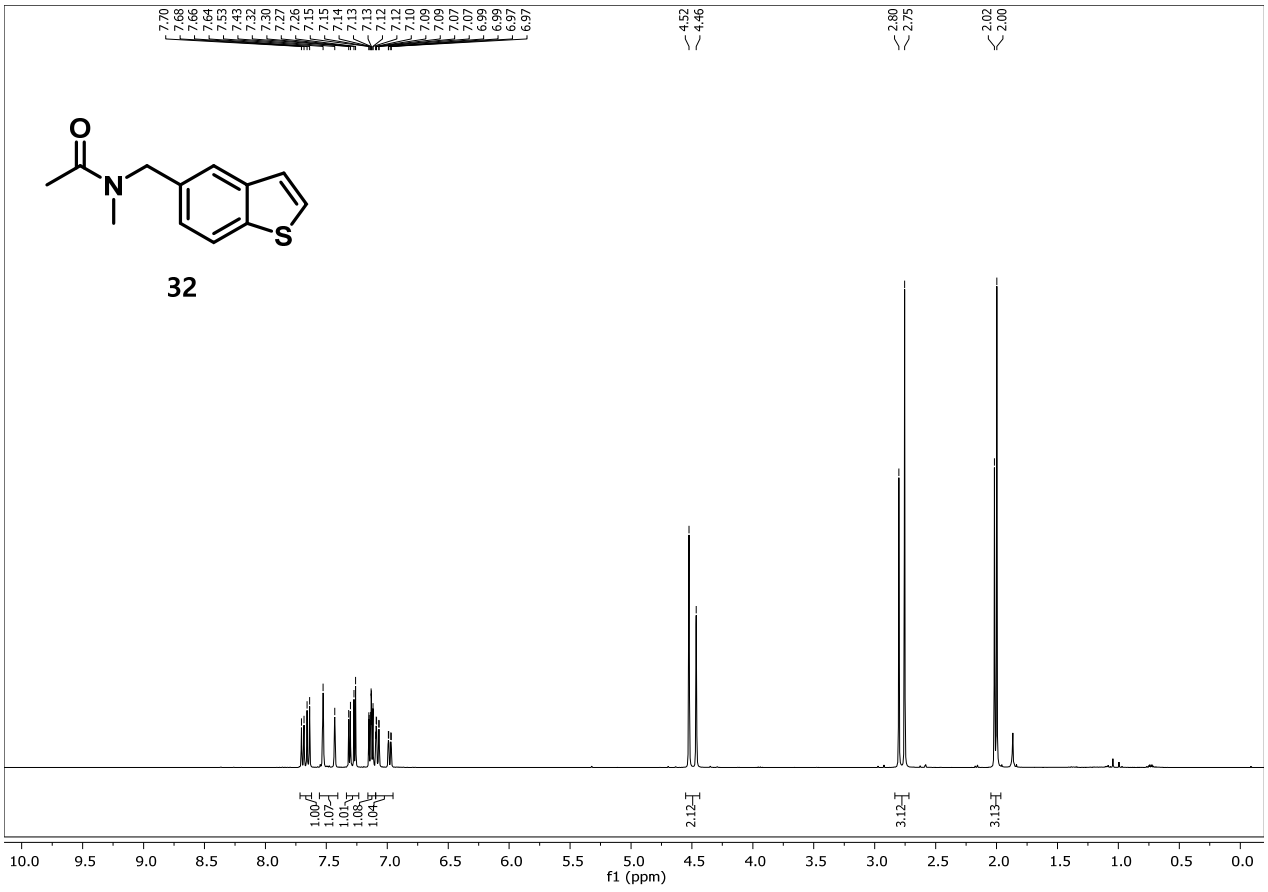

171.07
170.87
159.58
159.47
155.17
146.57
146.24
133.30
132.39
128.00
127.59
127.26
126.14
122.20
120.26
113.67
113.50
112.96
112.51
77.16
61.71
61.62
54.16
50.56
35.60
33.73
21.93
21.53
14.38
N
O
O
COOEt
29
f1 (ppm)

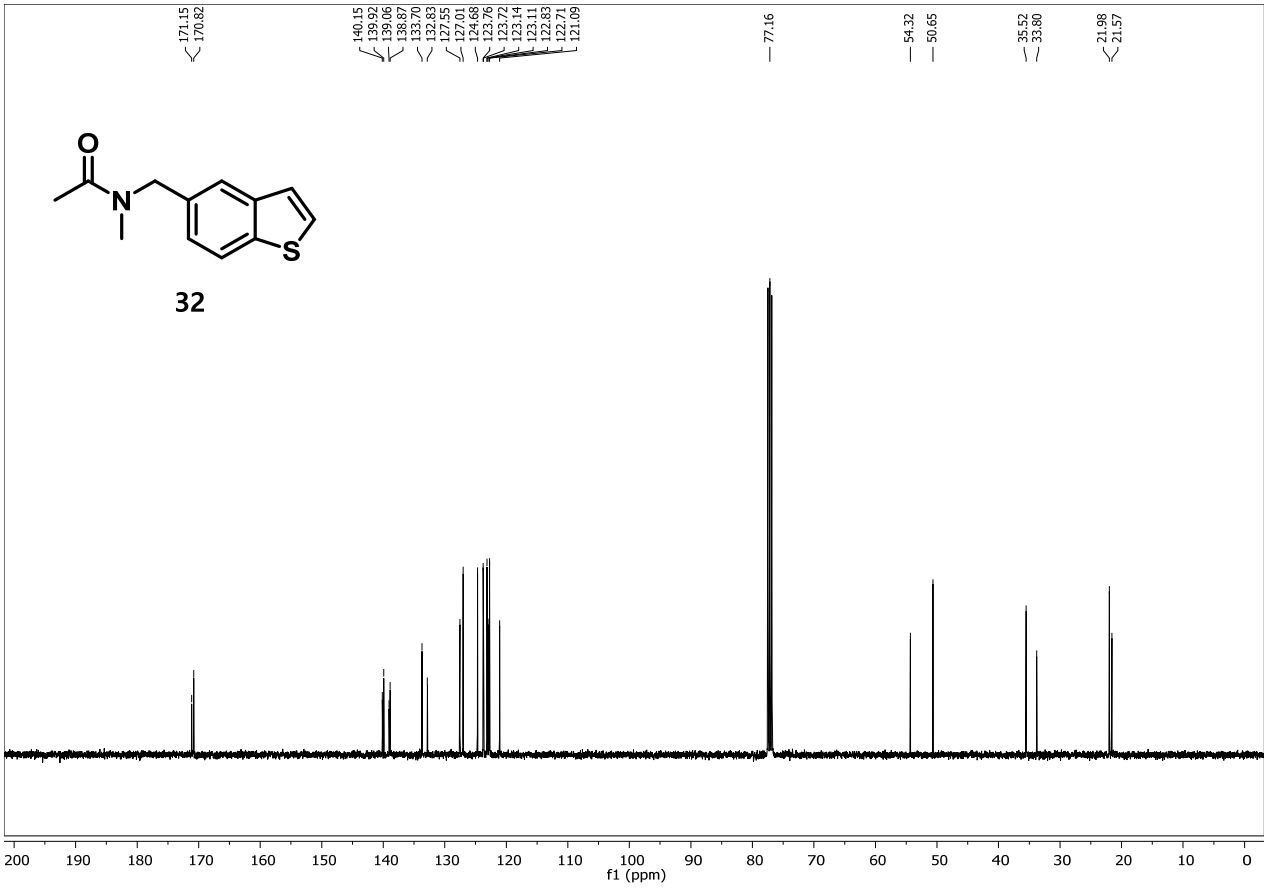

7.34
7.33
7.33
7.32
7.26
7.25
7.25
7.24
7.10
7.10
7.05
7.04
7.04
7.04
6.99
6.99
6.98
6.98
6.92
6.92
6.91
6.91
4.53
4.48
2.94
2.92
2.14
2.10
N
O
S
30
1.01
0.91
0.92
2.00
2.90
3.17
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

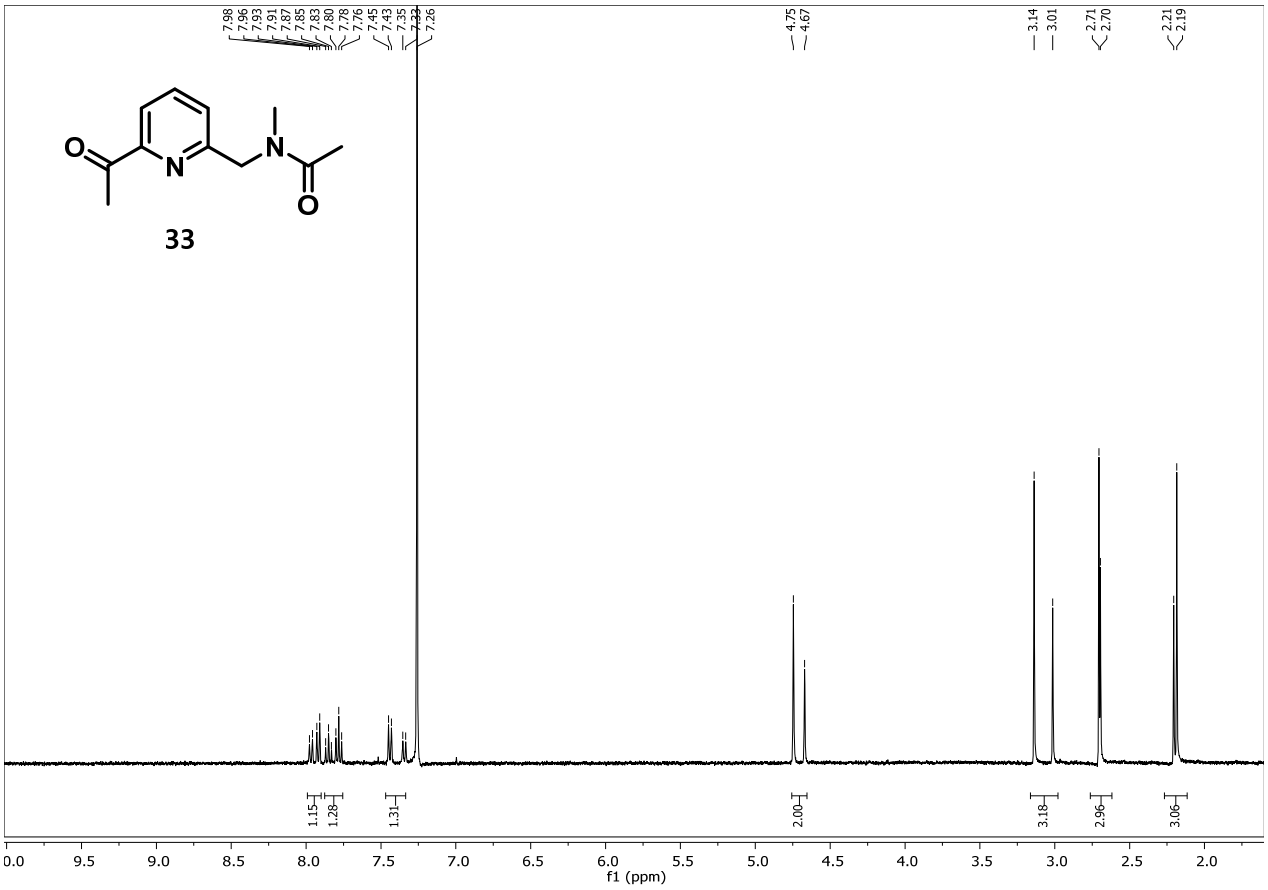

170.81
170.58
138.22
137.88
127.80
127.09
126.20
126.14
122.79
121.50
77.16
50.31
45.91
35.59
33.71
21.90
21.45
N
O
S
30
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.56
7.55
7.52
7.51
7.26
6.95
6.94
6.92
6.91
4.67
4.63
2.99
2.95
2.50
2.48
2.15
2.09
O
S
N
O
31
0.98
0.96
2.00
2.99
2.93
3.08
f1 (ppm)

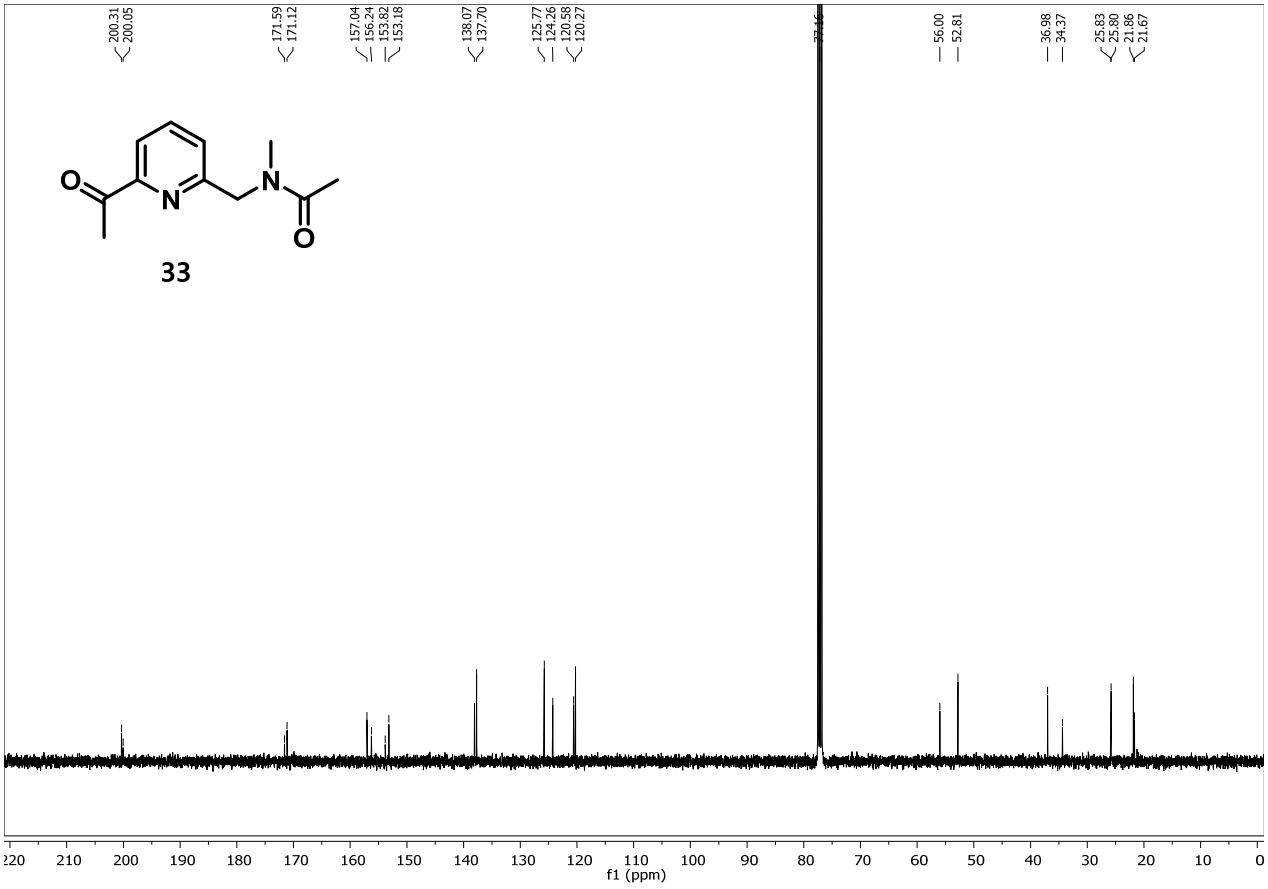

190.59
190.44
170.68
170.46
149.37
149.15
144.08
143.73
132.68
132.55
127.27
126.07
77.16
50.07
46.17
35.91
33.73
26.68
26.60
21.71
21.41
O
S
N
O
31
f1 (ppm)


7.70
7.68
7.66
7.64
7.53
7.43
7.32
7.30
7.27
7.26
7.15
7.15
7.14
7.13
7.13
7.12
7.12
7.10
7.09
7.09
7.07
7.07
6.99
6.99
6.97
6.97
4.52
4.46
2.80
2.75
2.02
2.00
O
N
S
32
1.00
1.07
1.01
1.08
1.04
2.12
3.12
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

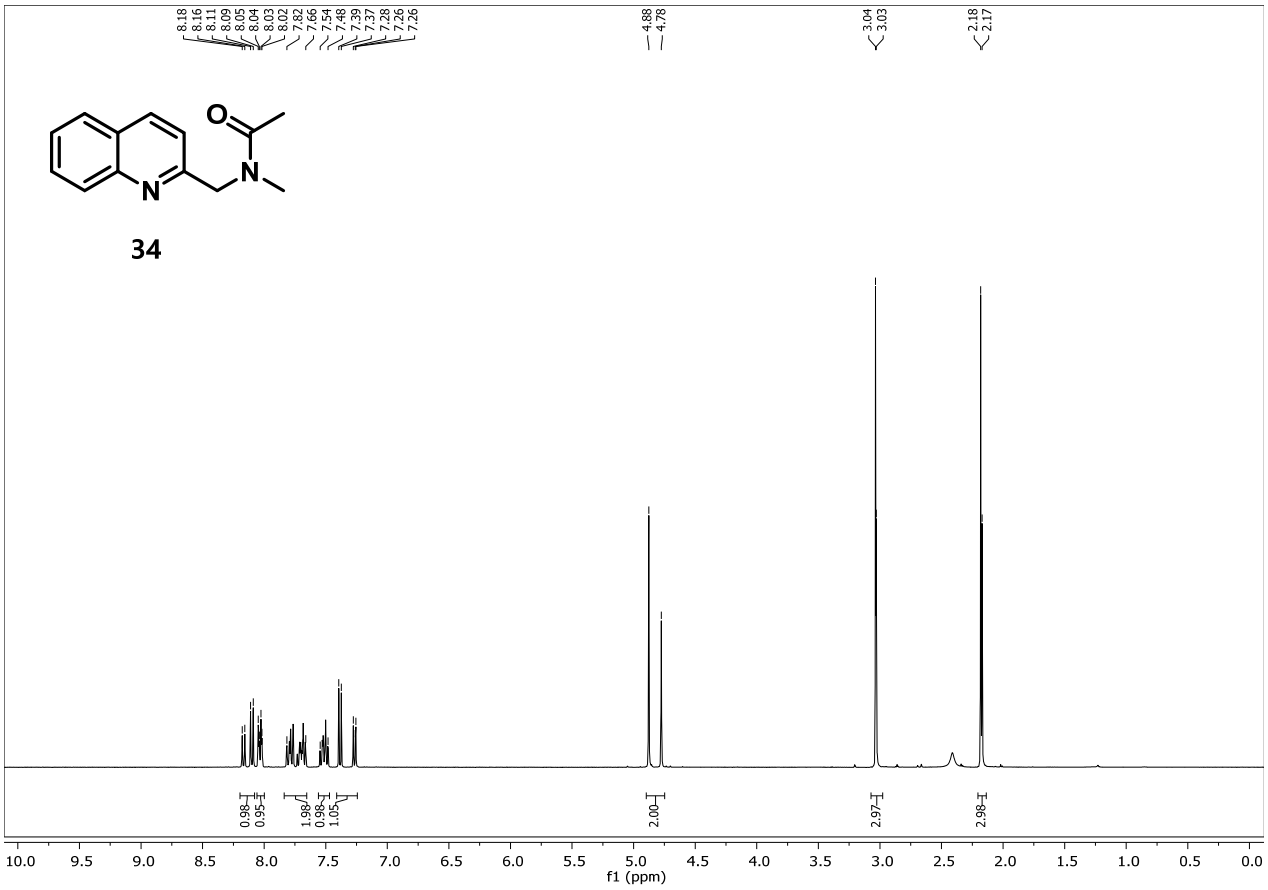

171.15
170.82
140.15
139.92
139.06
138.87
133.70
132.83
127.55
127.01
124.68
123.76
123.72
123.14
123.11
122.83
122.71
121.09
77.16
54.32
50.65
35.52
33.80
21.98
21.57
O
N
S
32
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

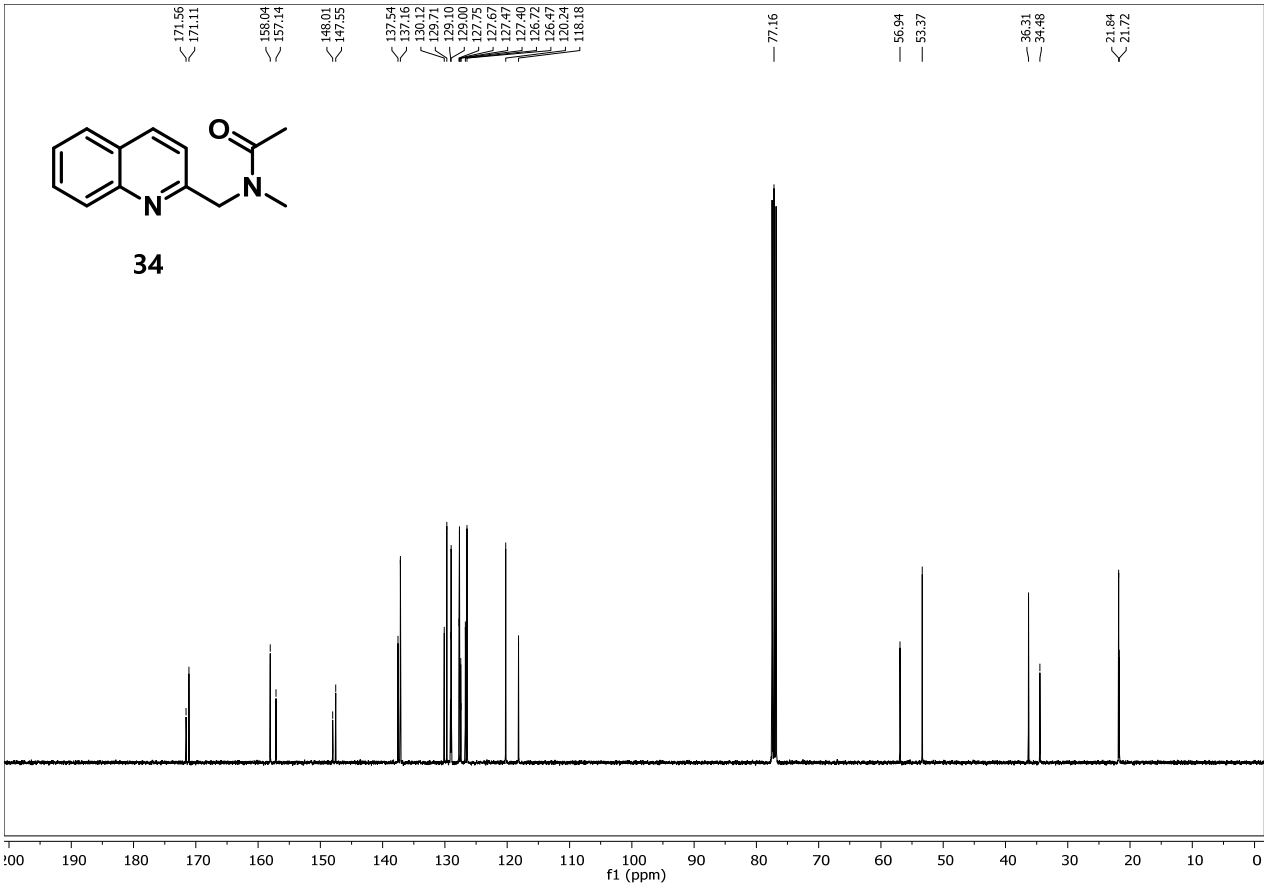

7.98
7.96
7.93
7.91
7.87
7.85
7.83
7.80
7.78
7.76
7.45
7.43
7.35
7.33
7.26
4.75
4.67
3.14
3.01
2.71
2.70
2.21
2.19
1.15
1.28
1.31
2.00
3.18
2.96
3.06
f1 (ppm)

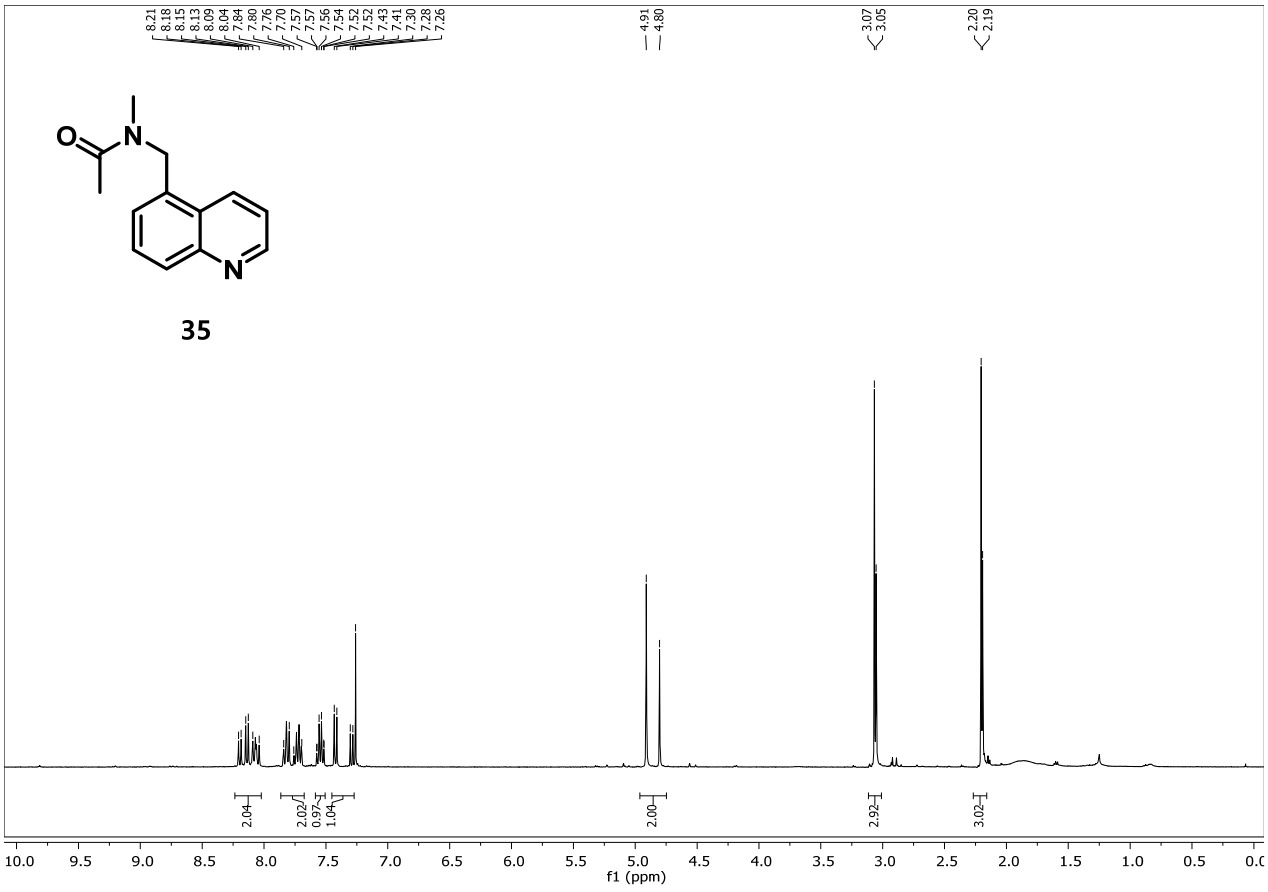
33

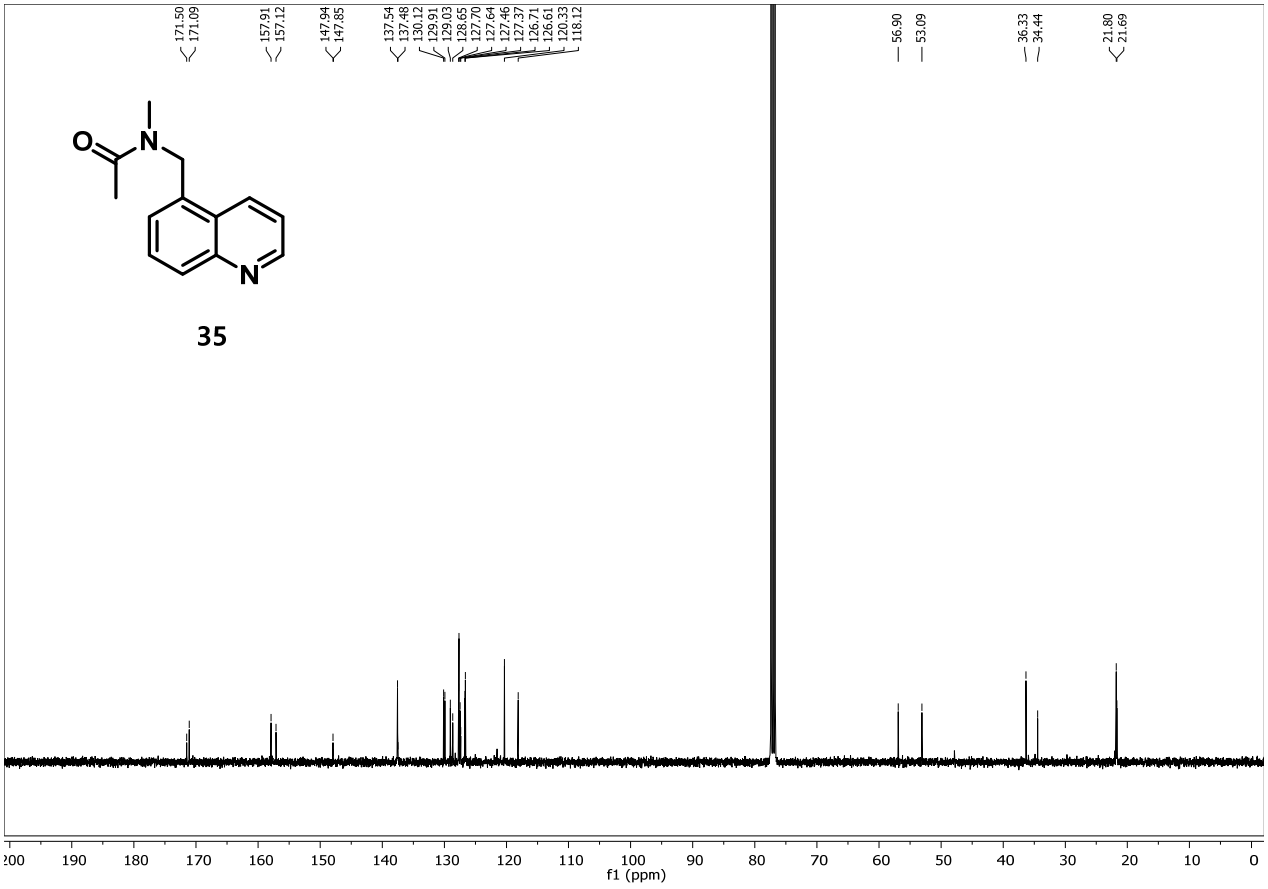

200.31
200.05
171.59
171.12
157.04
156.24
153.82
153.18
138.07
137.70
125.77
124.26
120.58
120.27
77.46
56.00
52.81
36.98
34.37
25.83
25.80
21.86
21.67
f1 (ppm)

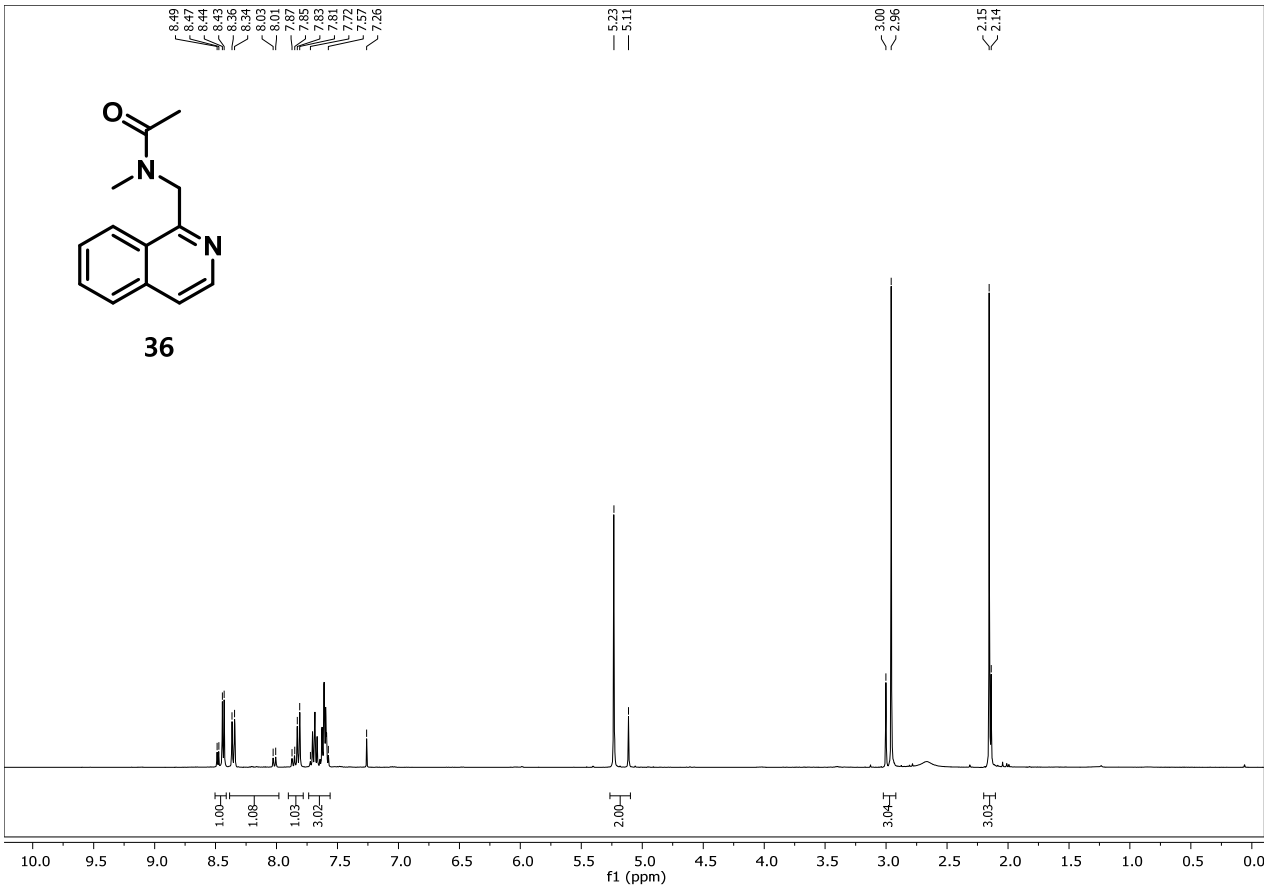
33

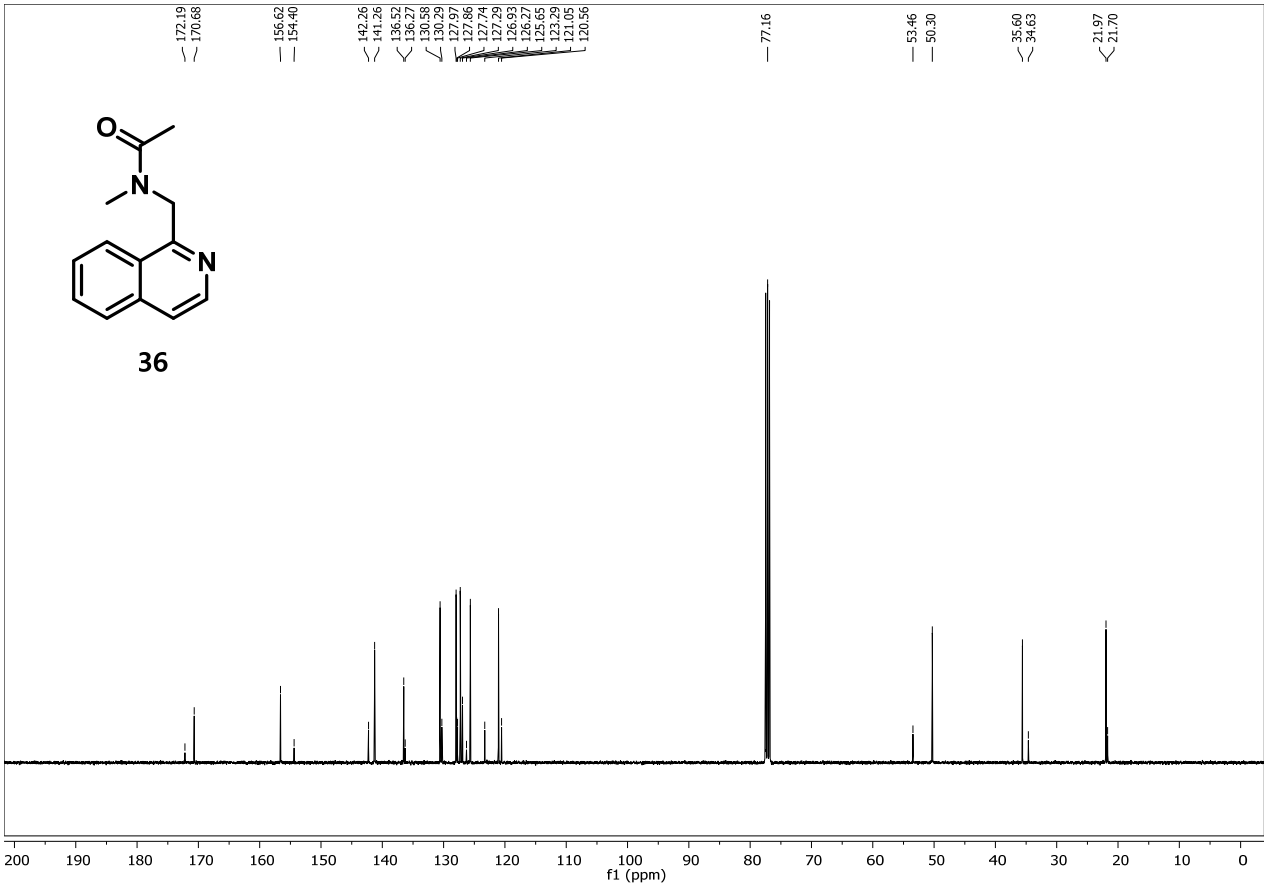

8.18
8.16
8.11
8.09
8.05
8.04
8.03
8.02
7.82
7.66
7.54
7.48
7.39
7.37
7.28
7.26
7.26
4.88
4.78
3.04
3.03
2.18
2.17
O
N
N
34
0.98
0.95
1.98
0.98
1.05
2.00
2.97
2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

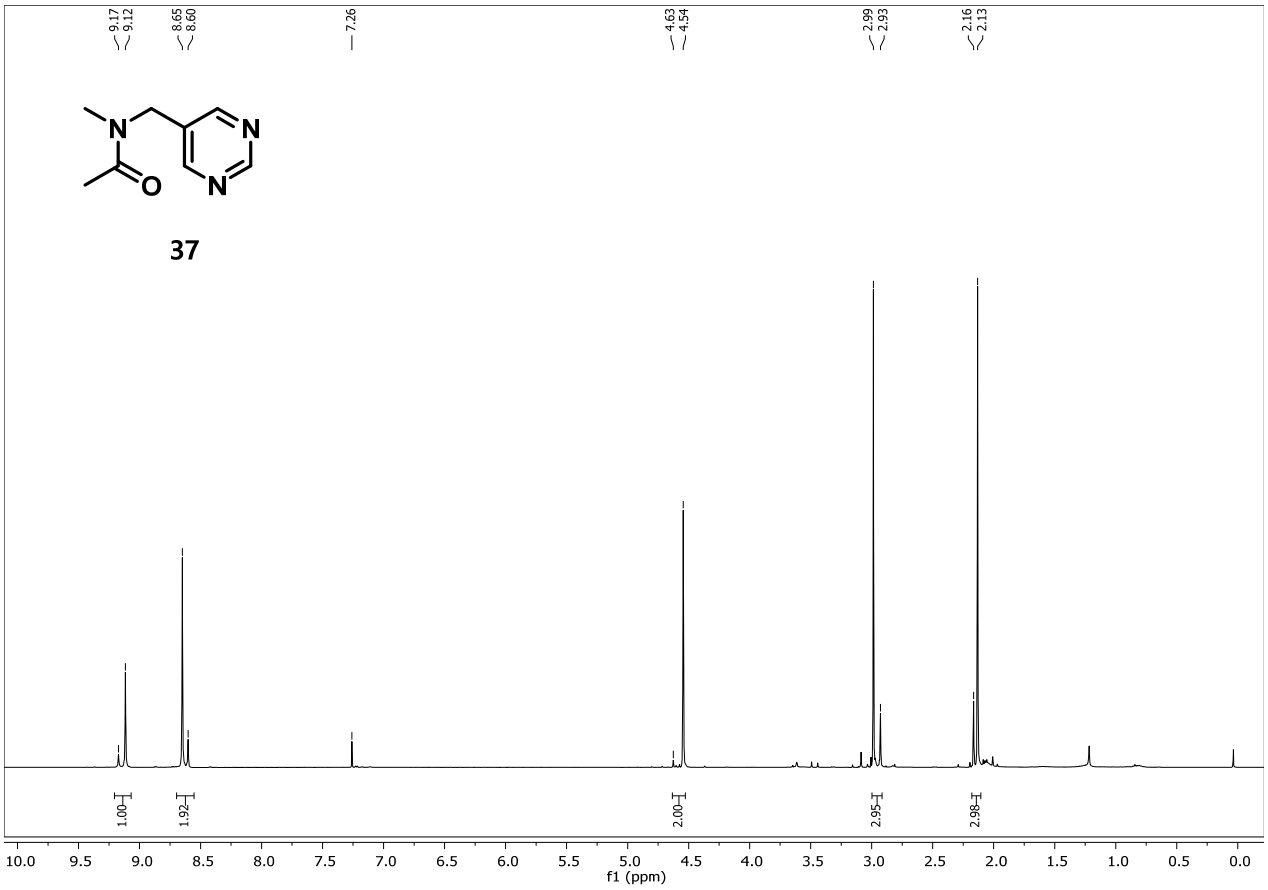

171.56
171.11
158.04
157.14
148.01
147.55
137.54
137.16
130.12
129.71
129.10
129.00
127.75
127.67
127.47
127.40
126.72
126.47
120.24
118.18
77.16
56.94
53.37
36.31
34.48
21.84
21.72
O
N
N
34
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

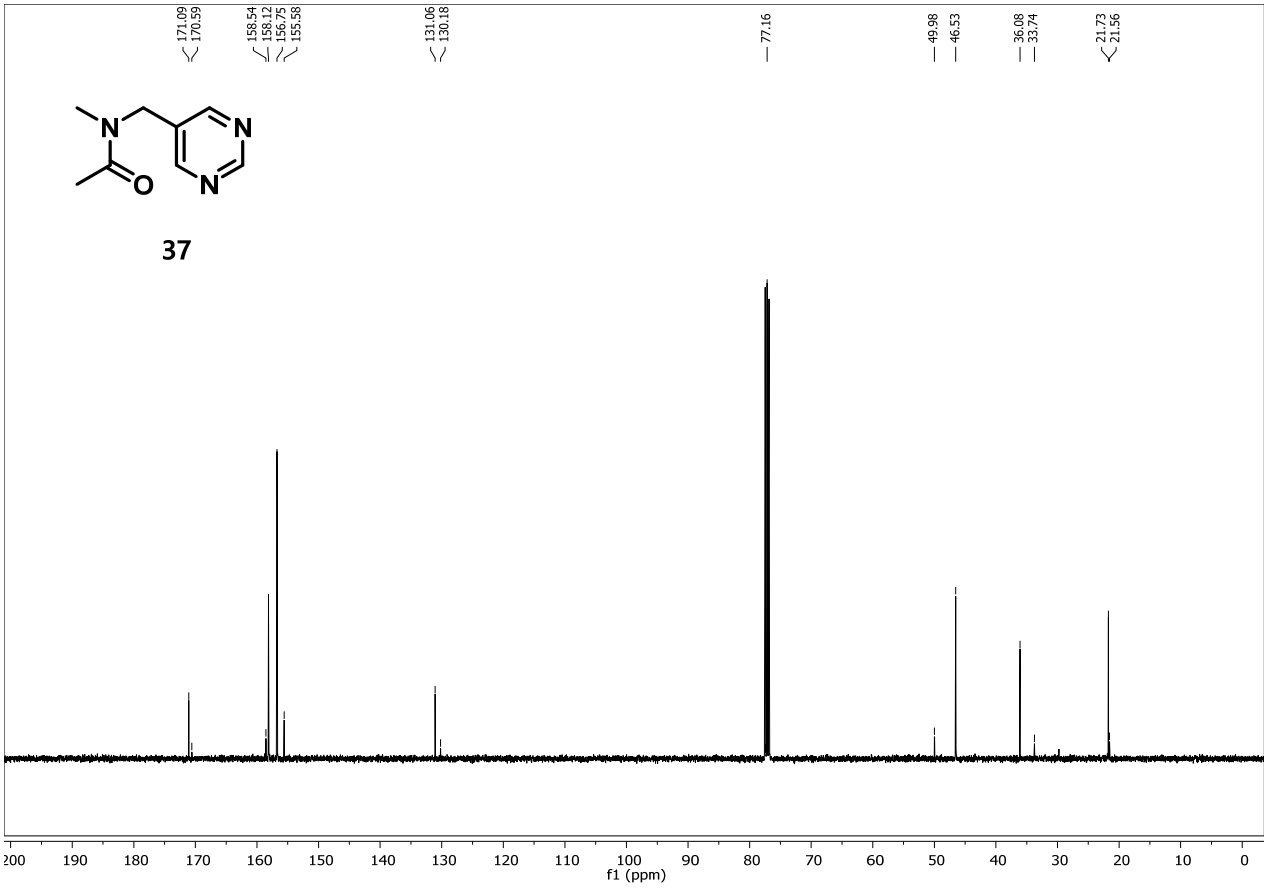

8.21
8.18
8.15
8.13
8.09
8.04
7.84
7.80
7.76
7.70
7.57
7.57
7.56
7.54
7.52
7.52
7.43
7.41
7.30
7.28
7.26
4.91
4.80
3.07
3.05
2.20
2.19
O
N
N
35
2.04
2.02
0.97
1.04
2.00
2.92
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

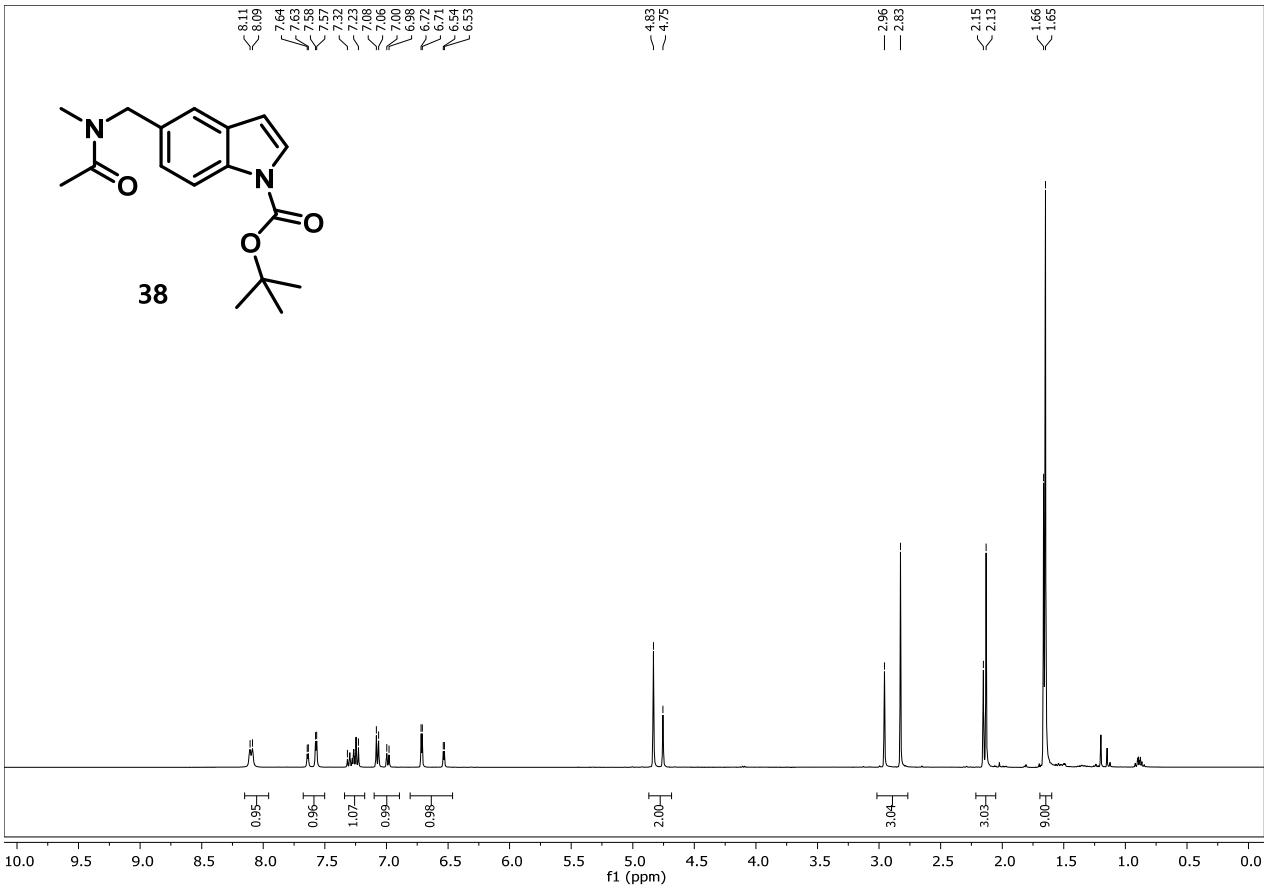

171.50
171.09
157.91
157.12
147.94
147.85
137.54
137.48
130.12
129.91
129.03
128.65
127.70
127.64
127.46
127.37
126.71
126.61
120.33
118.12
56.90
53.09
36.33
34.44
21.80
21.69
O
N
N
35
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

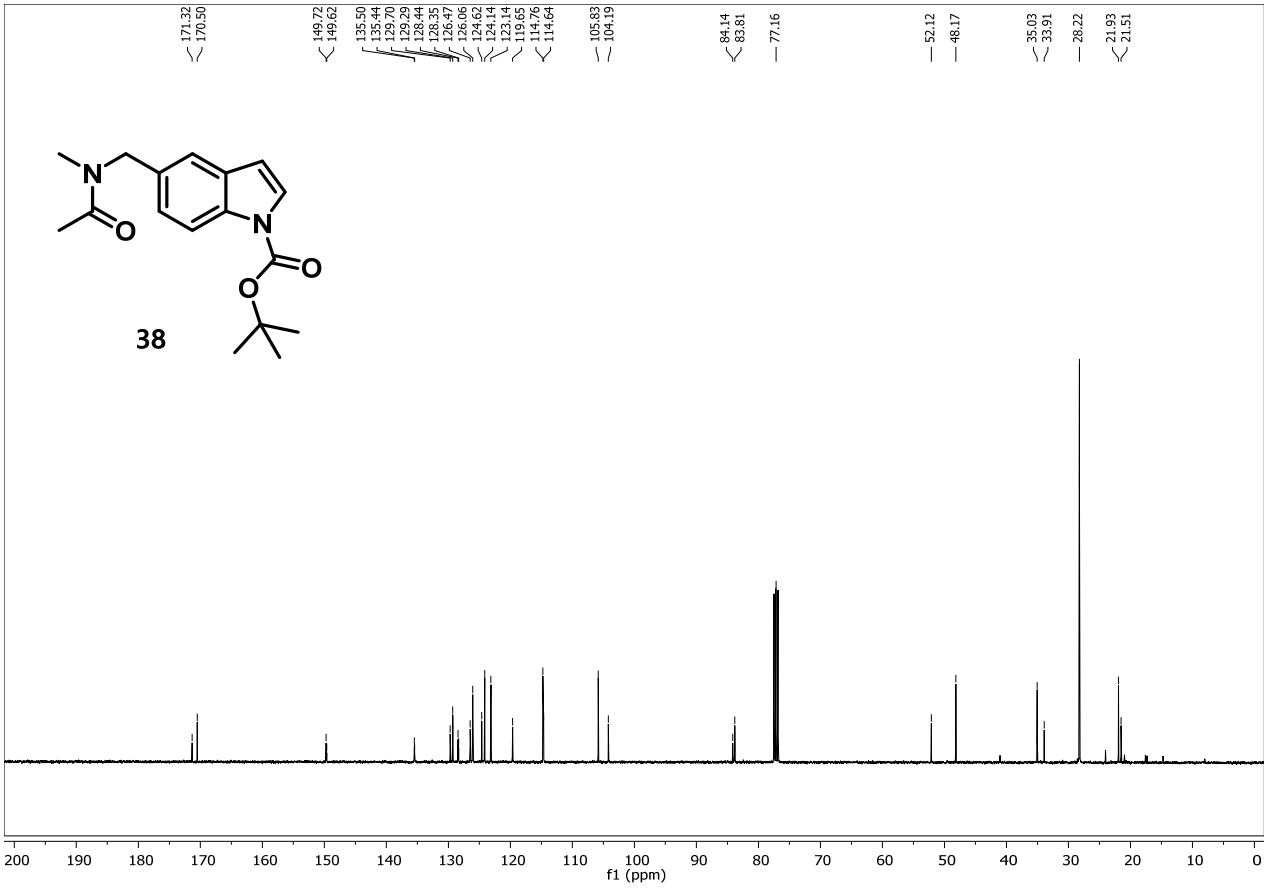

8.49
8.47
8.44
8.43
8.36
8.34
8.03
8.01
7.87
7.85
7.83
7.81
7.72
7.57
7.26
5.23
5.11
3.00
2.96
2.15
2.14
O
N
N
36
1.00
1.08
1.03
3.02
2.00
3.04
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

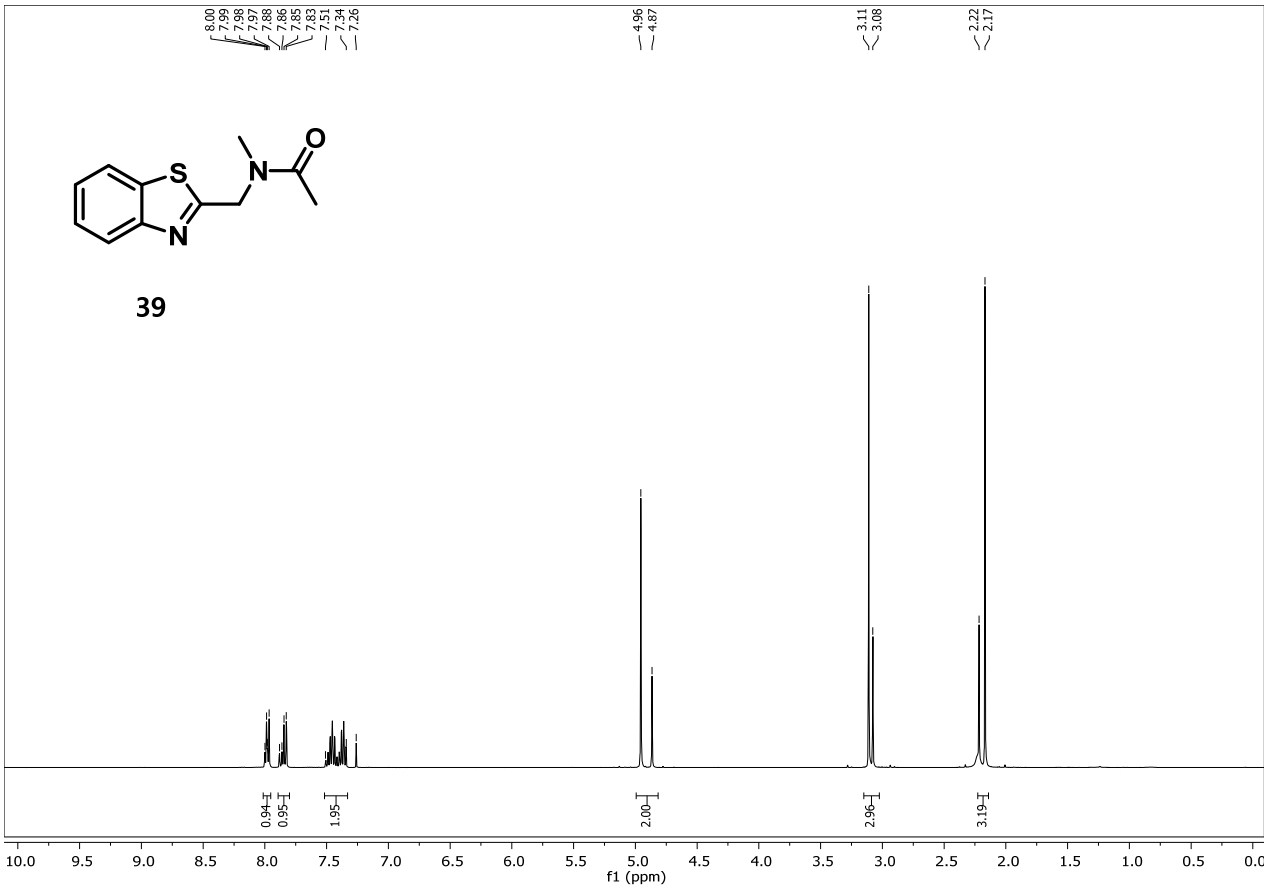

172.19
170.68
156.62
154.40
142.26
141.26
136.52
136.27
130.58
130.29
127.97
127.86
127.74
127.29
126.93
126.27
125.65
123.29
121.05
120.56
77.16
53.46
50.30
35.60
34.63
21.97
21.70
O
N
N
36
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

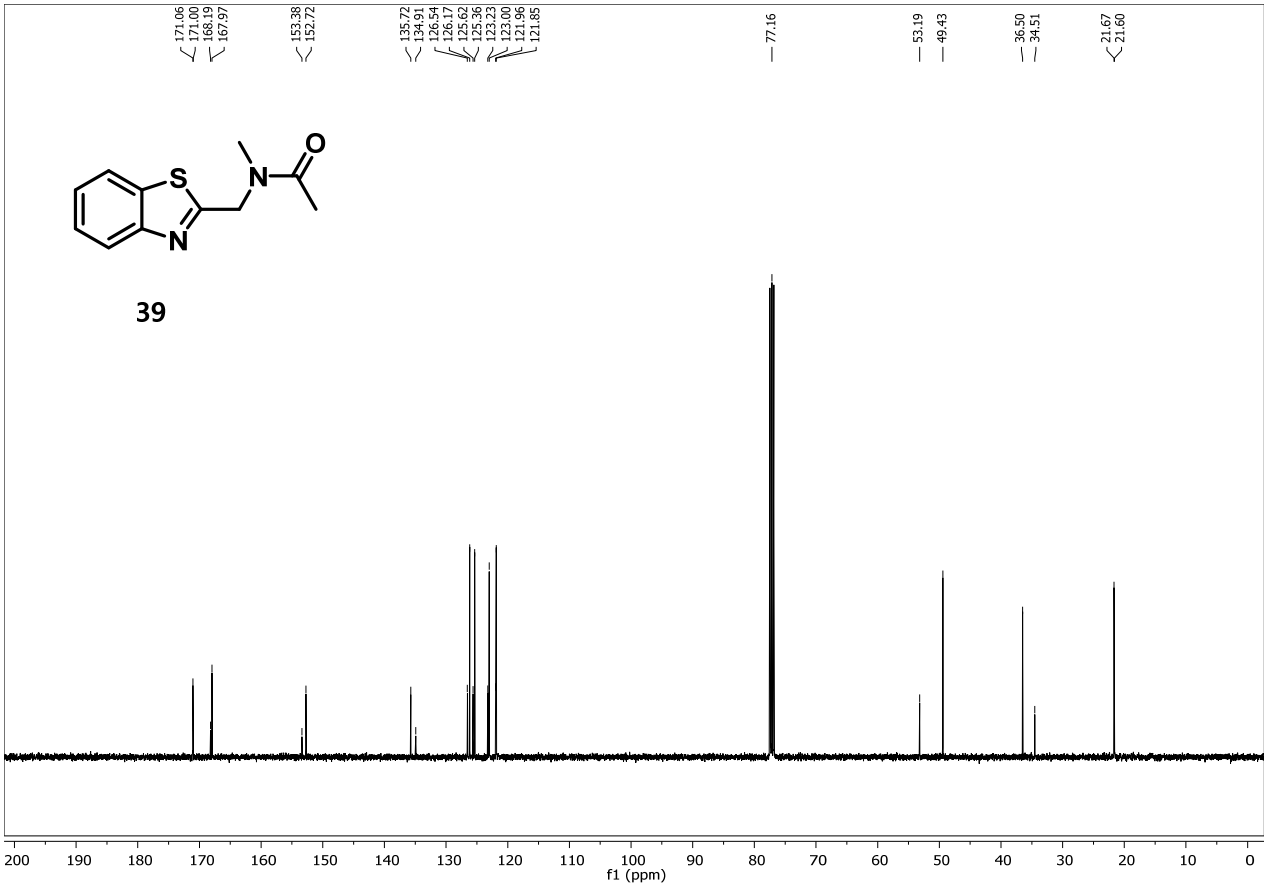

9.17
9.12
8.65
8.60
7.26
4.63
4.54
2.99
2.93
2.16
2.13
N
N
N
O
37
1.00
1.92
2.00
2.95
2.98
f1 (ppm)

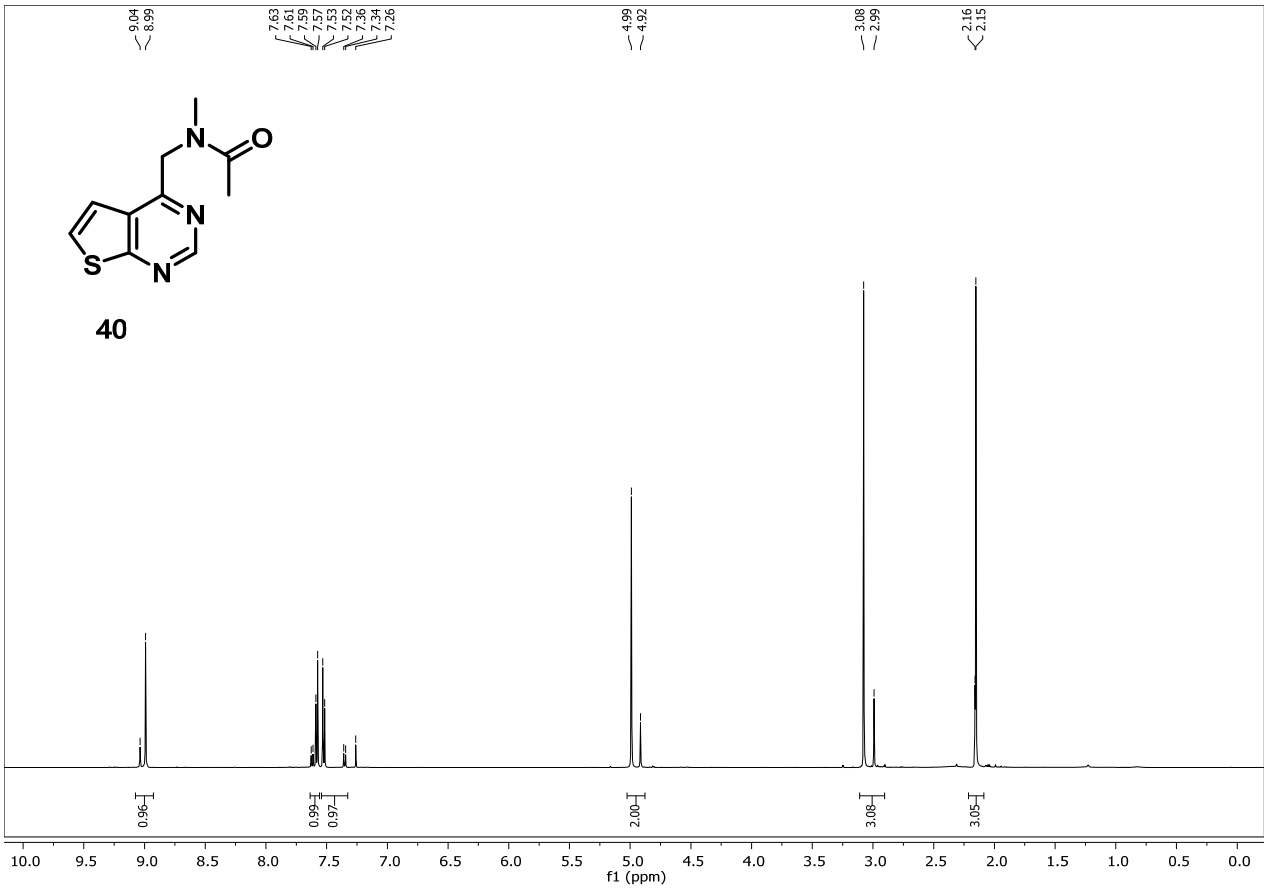

171.09
170.59
158.54
158.12
156.75
155.58
131.06
130.18
77.16
49.98
46.53
36.08
33.74
21.73
21.56
N
N
N
O
37
f1 (ppm)

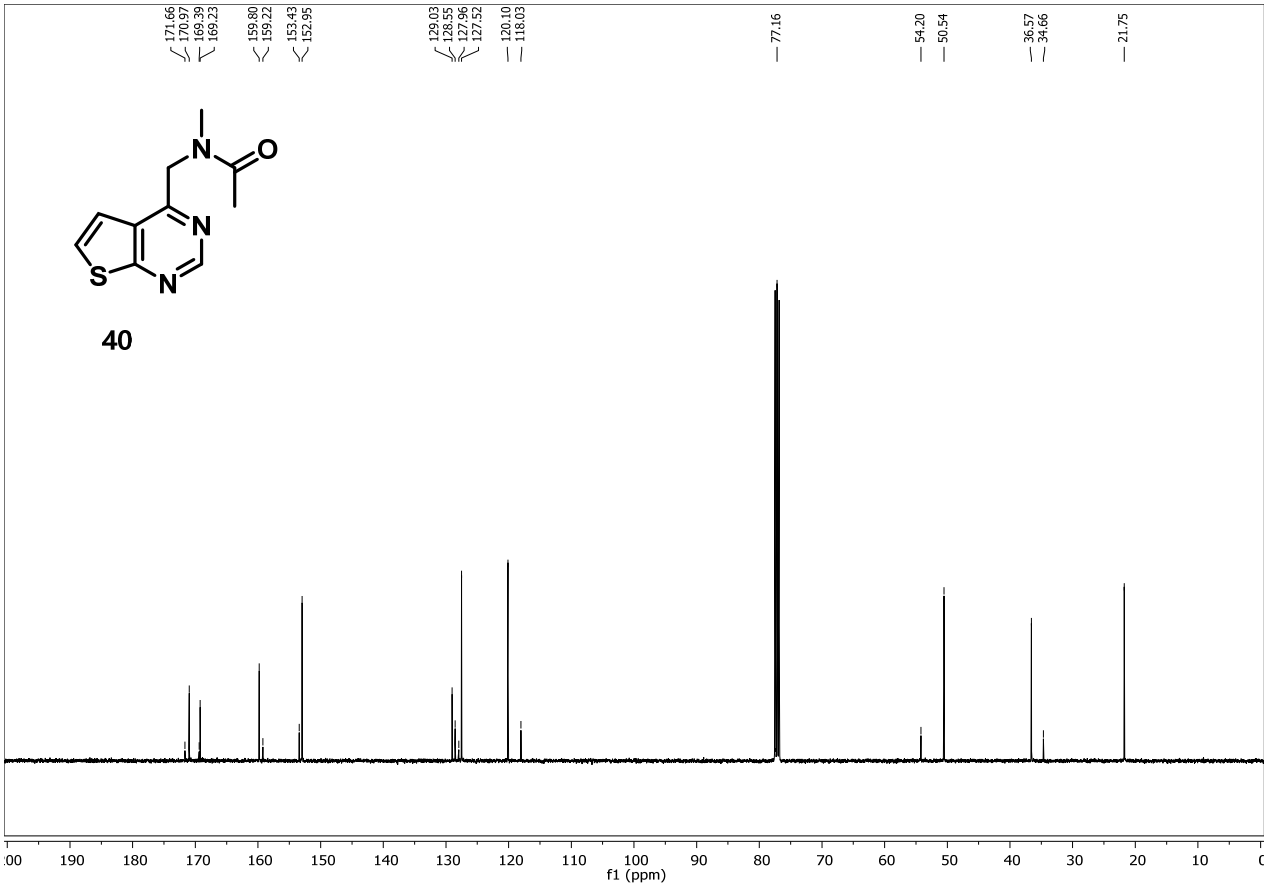

8.11
8.09
7.64
7.63
7.58
7.57
7.32
7.23
7.08
7.06
7.00
6.98
6.72
6.71
6.54
6.53
4.83
4.75
2.96
2.83
2.15
2.13
1.66
1.65
38
0.95
0.96
1.07
0.99
0.98
2.00
3.04
3.03
9.00
f1 (ppm)

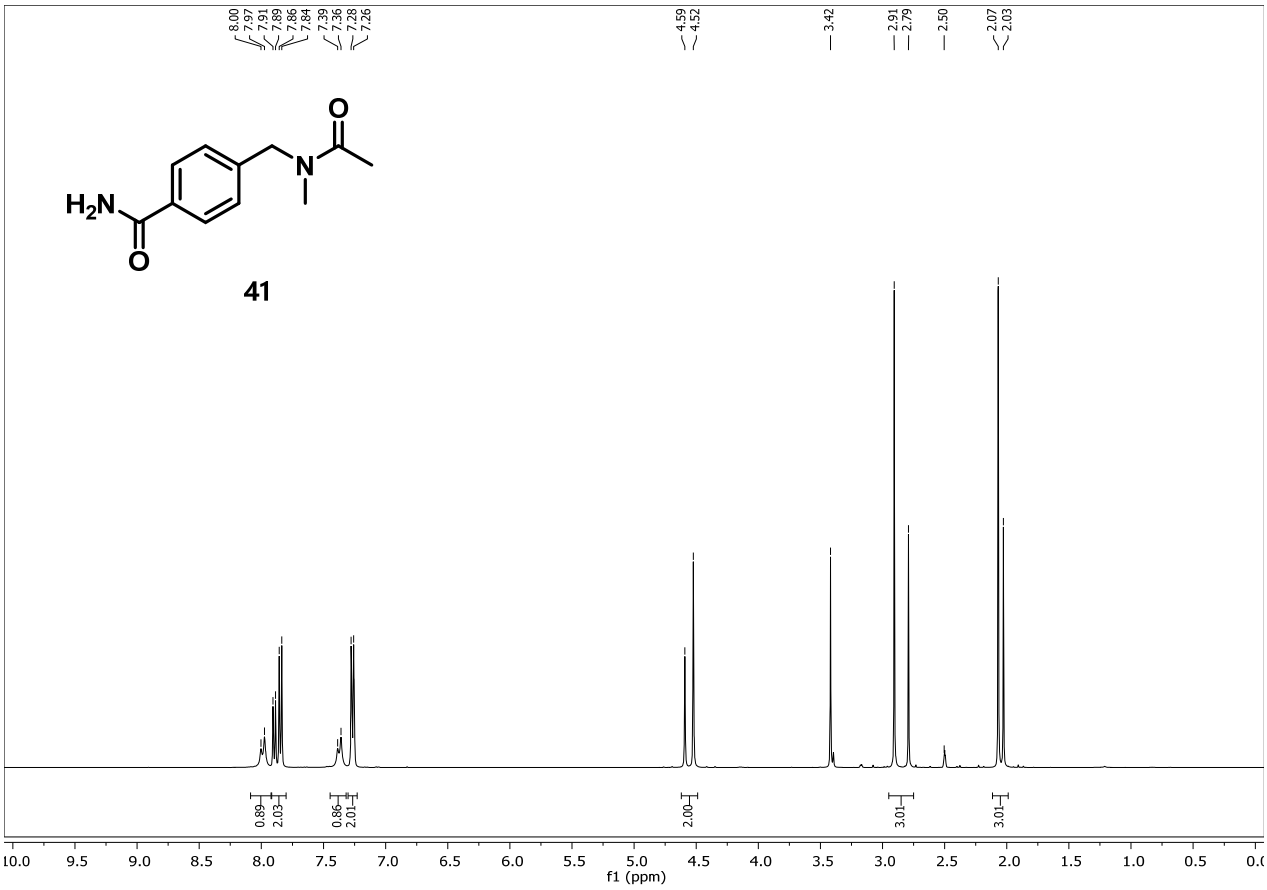

171.32
170.50
149.72
149.62
135.50
135.44
129.70
129.29
128.44
128.35
126.47
126.06
124.62
124.14
123.14
119.65
114.76
114.64
105.83
104.19
84.14
83.81
77.16
52.12
48.17
35.03
33.91
28.22
21.93
21.51
38
f1 (ppm)

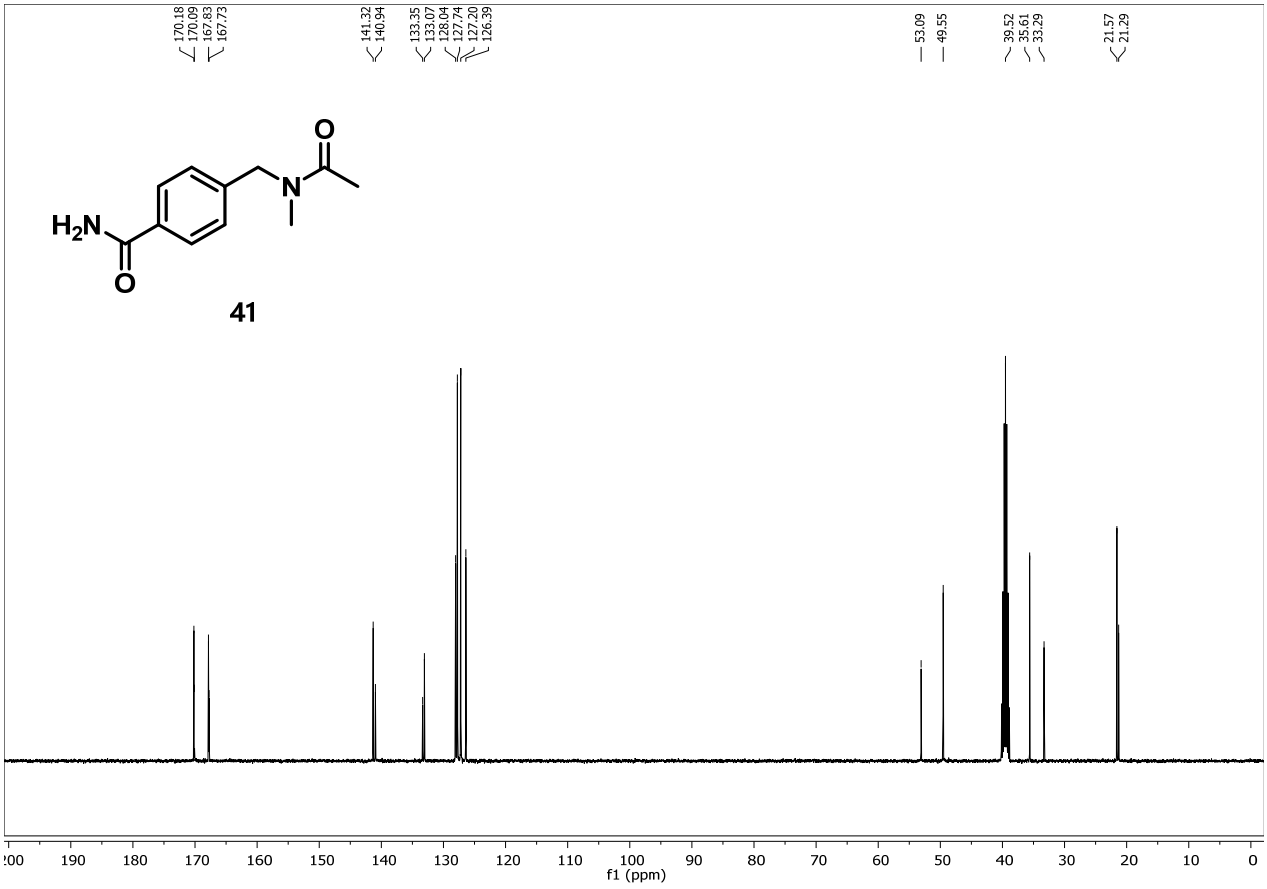

8.00
7.99
7.98
7.97
7.88
7.86
7.85
7.83
7.51
7.34
7.26
4.96
4.87
3.11
3.08
2.22
2.17
S
N
O
N
39
0.94
0.95
1.95
2.00
2.96
3.19
f1 (ppm)

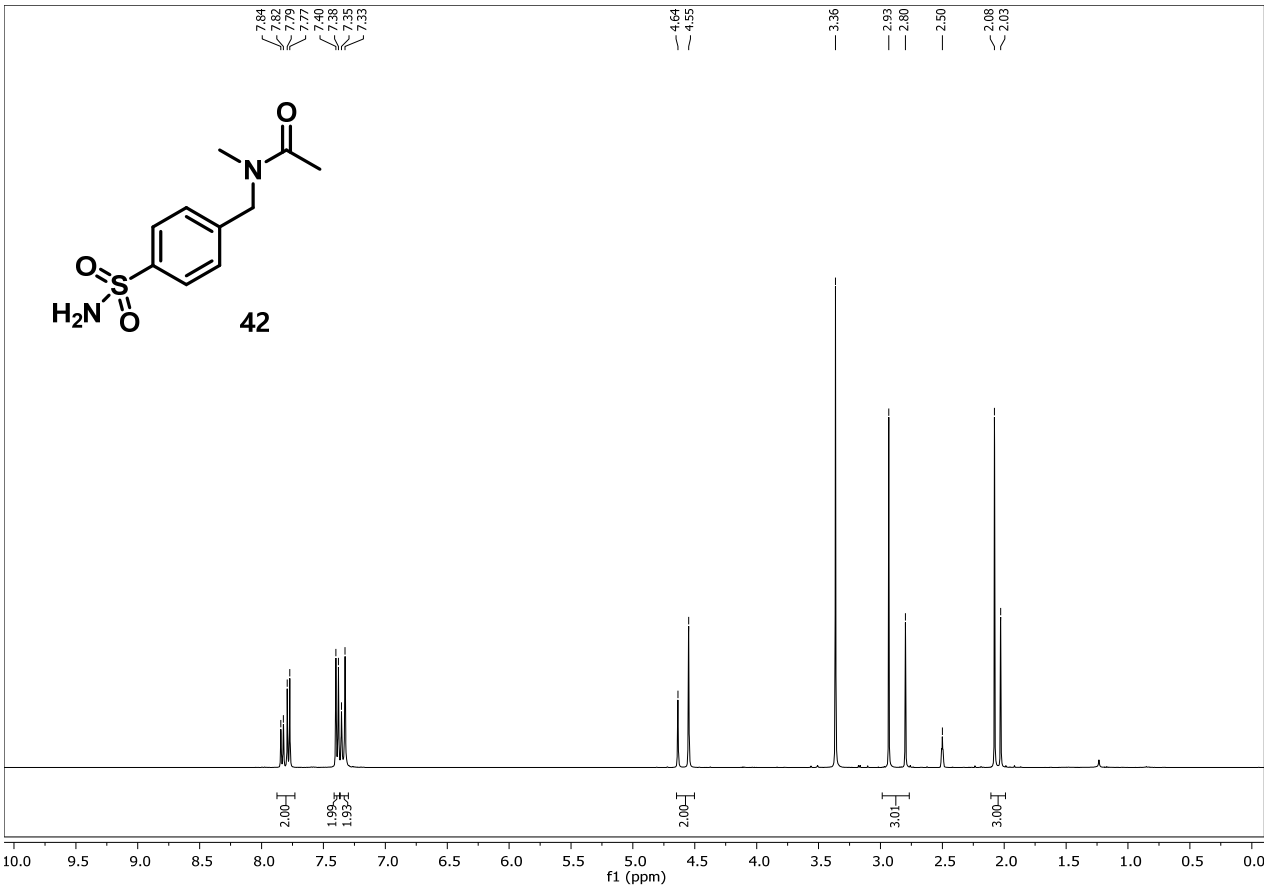

171.06
171.00
168.19
167.97
153.38
152.72
135.72
134.91
126.54
126.17
125.62
125.36
123.23
123.00
121.96
121.85
77.16
53.19
49.43
36.50
34.51
21.67
21.60
S
N
O
N
39
f1 (ppm)

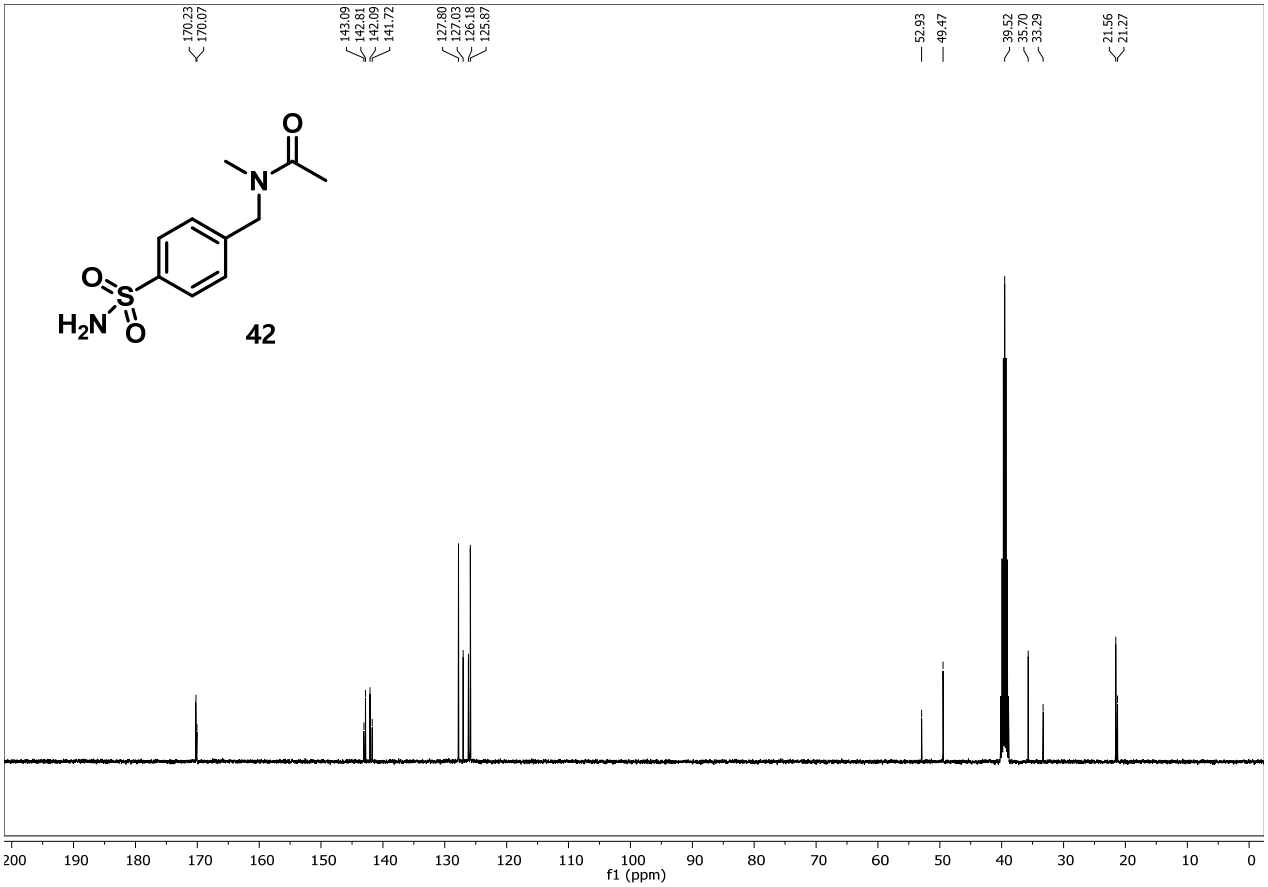

9.04
8.99
7.63
7.61
7.59
7.57
7.53
7.52
7.36
7.34
7.26
4.99
4.92
3.08
2.99
2.16
2.15
N
O
N
S
N
40
0.96
0.99
0.97
2.00
3.08
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

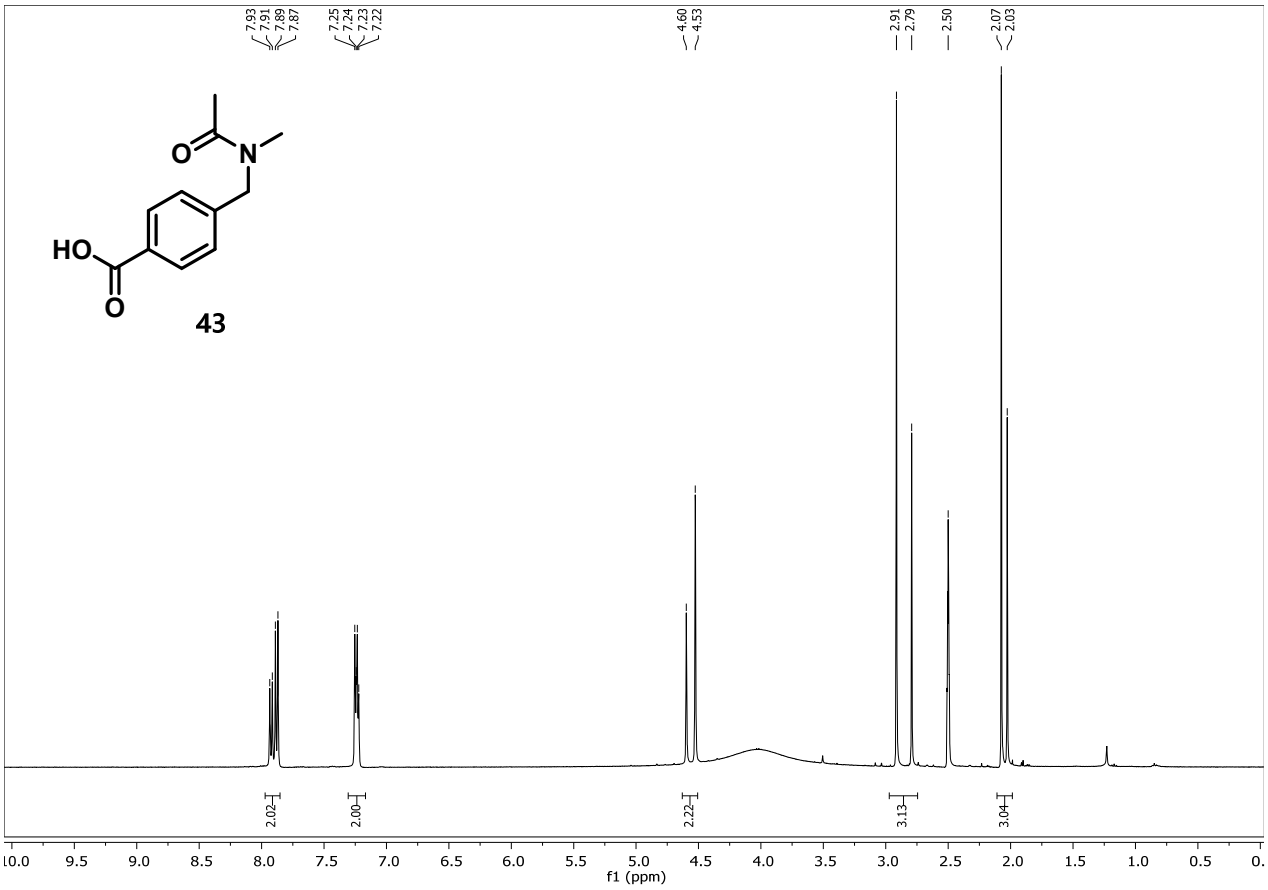

171.66
170.97
169.39
169.23
159.80
159.22
153.43
152.95
129.03
128.55
127.96
127.52
120.10
118.03
77.16
54.20
50.54
36.57
34.66
21.75
N
O
N
S
N
40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

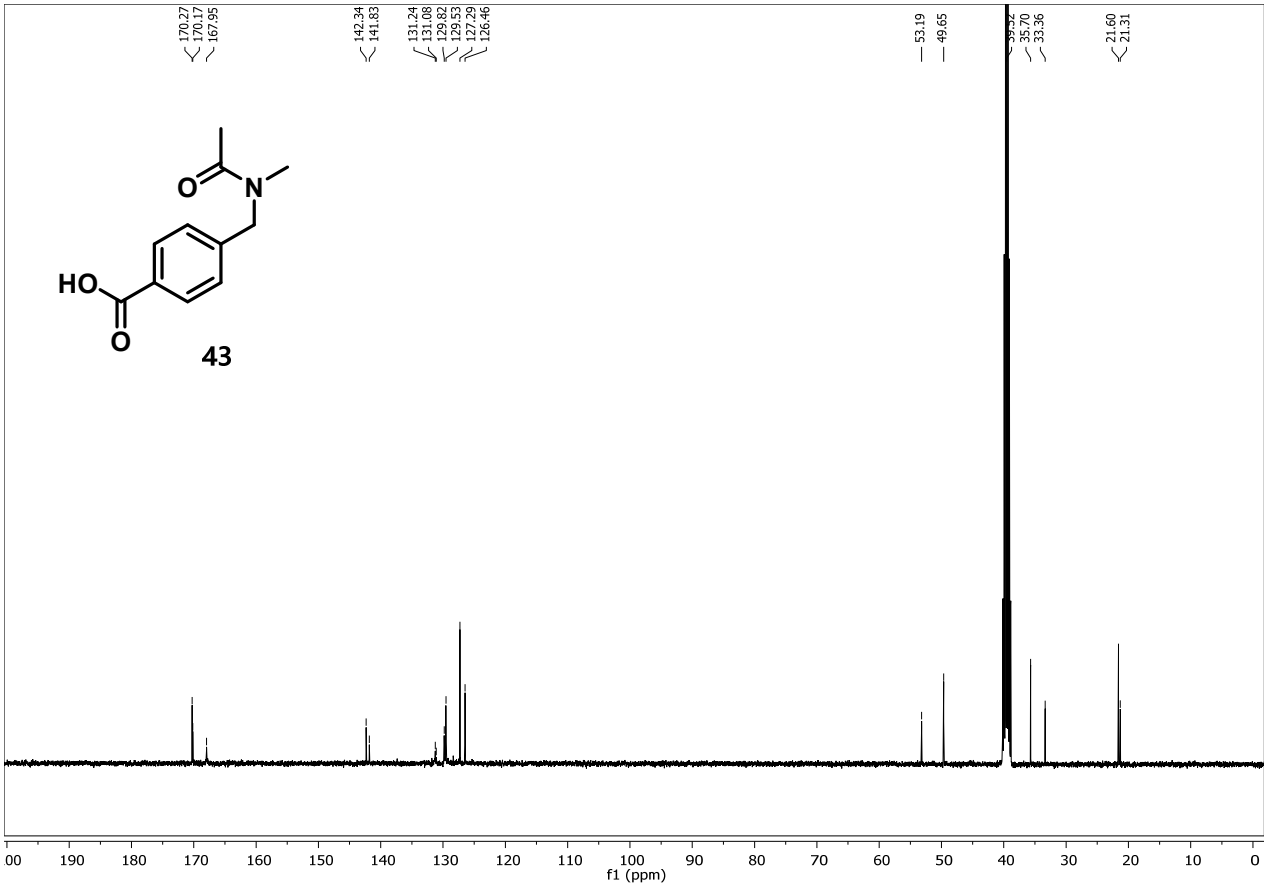

8.00
7.97
7.91
7.89
7.86
7.84
7.39
7.36
7.28
7.26
4.59
4.52
3.42
2.91
2.79
2.50
2.07
2.03
O
N
H2N
O
41
0.89
2.03
0.86
2.01
2.00
3.01
3.01
f1 (ppm)

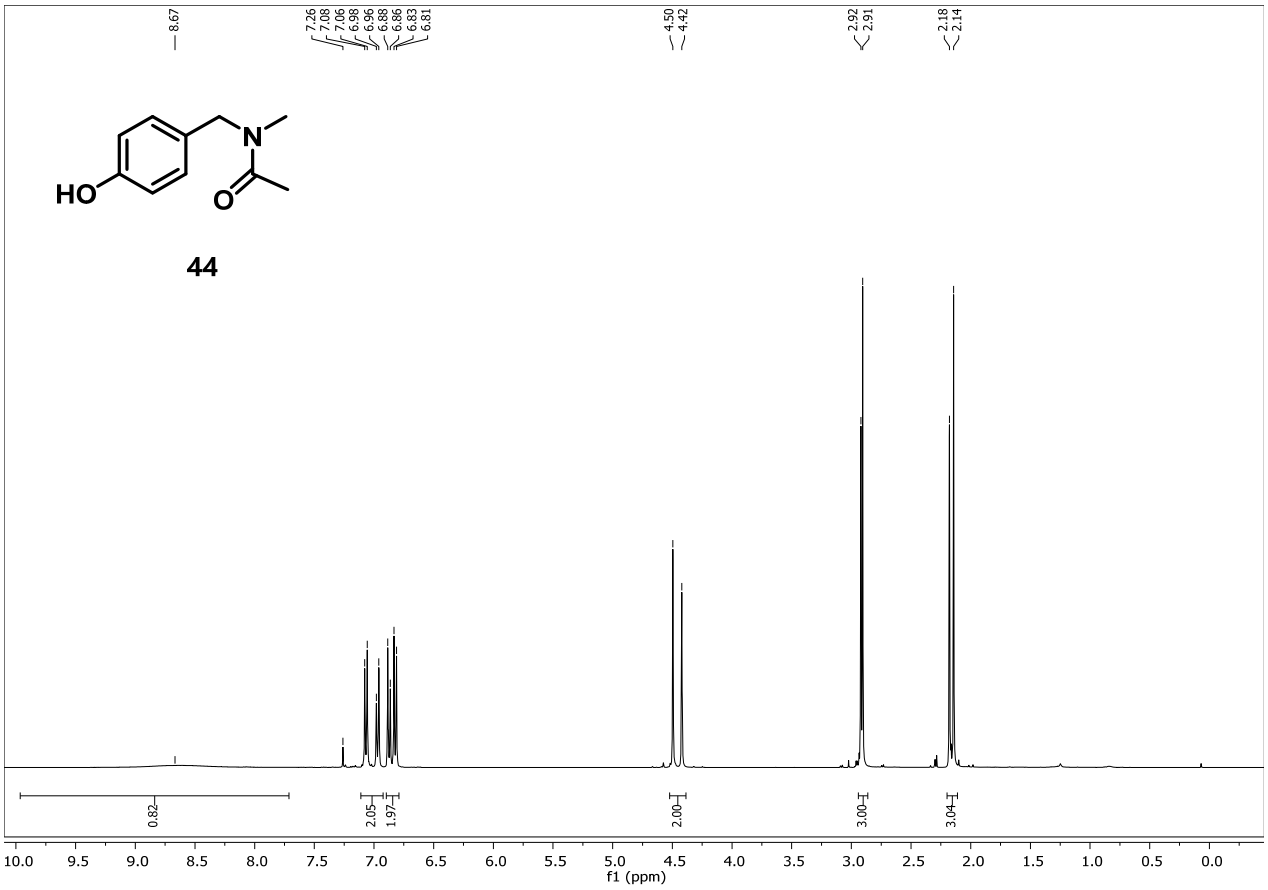

170.18
170.09
167.83
167.73
141.32
140.94
133.35
133.07
128.04
127.74
127.20
126.39
53.09
49.55
39.52
35.61
33.29
21.57
21.29
O
N
H2N
O
41
f1 (ppm)

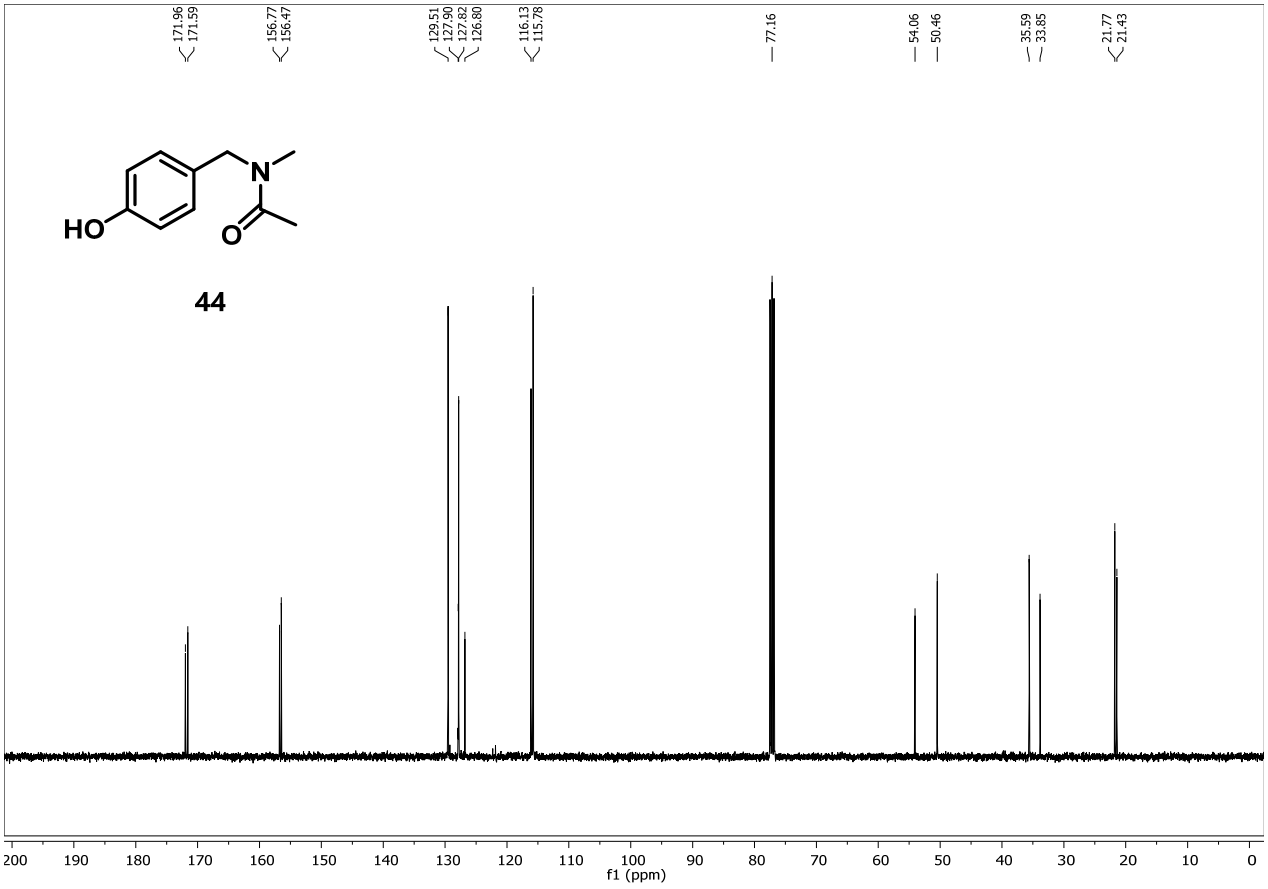

7.84
7.82
7.79
7.77
7.40
7.38
7.35
7.33
4.64
4.55
3.36
2.93
2.80
2.50
2.08
2.03
42
2.00
1.99
1.93
2.00
3.01
3.00
f1 (ppm)

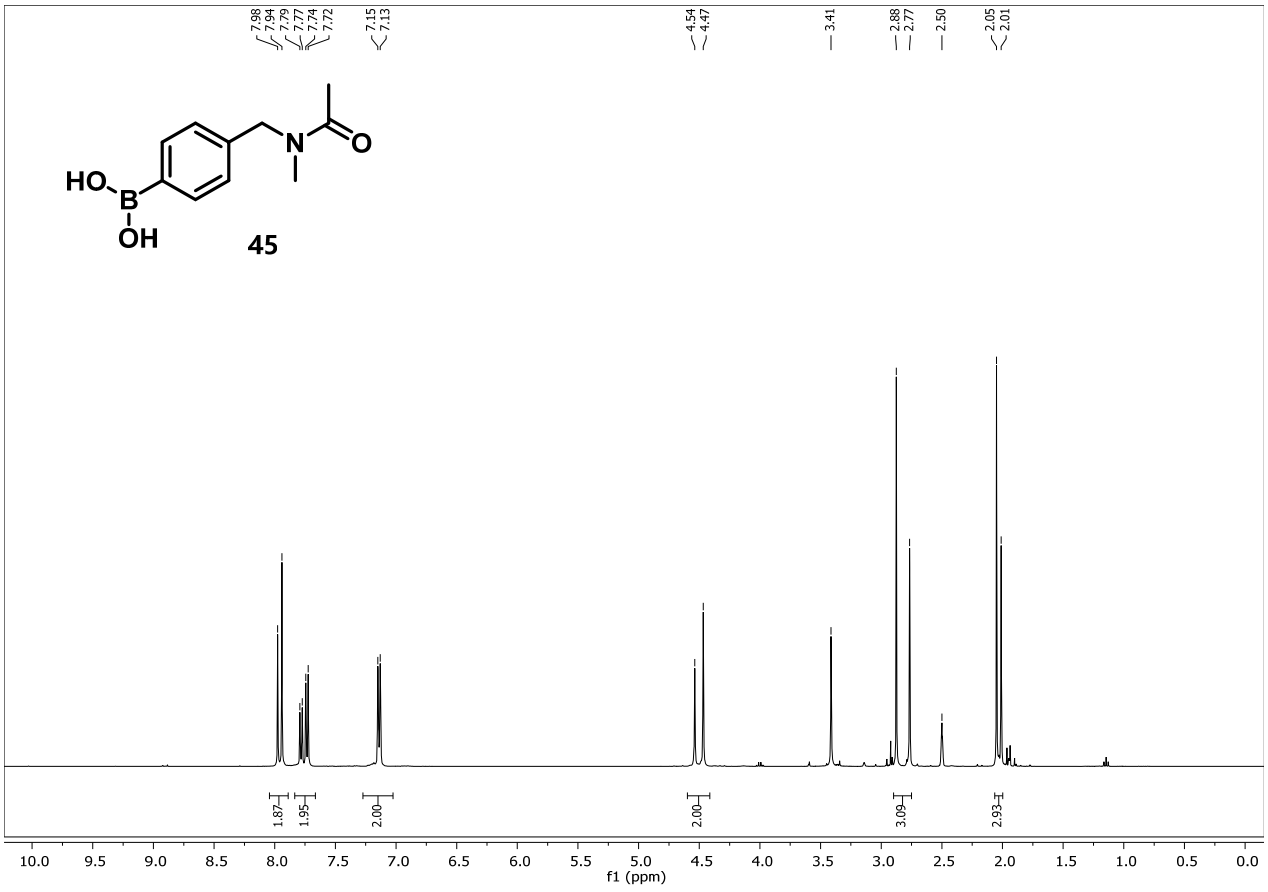

170.23
170.07
143.09
142.81
142.09
141.72
127.80
127.03
126.18
125.87
52.93
49.47
39.52
35.70
33.29
21.56
21.27
42
f1 (ppm)

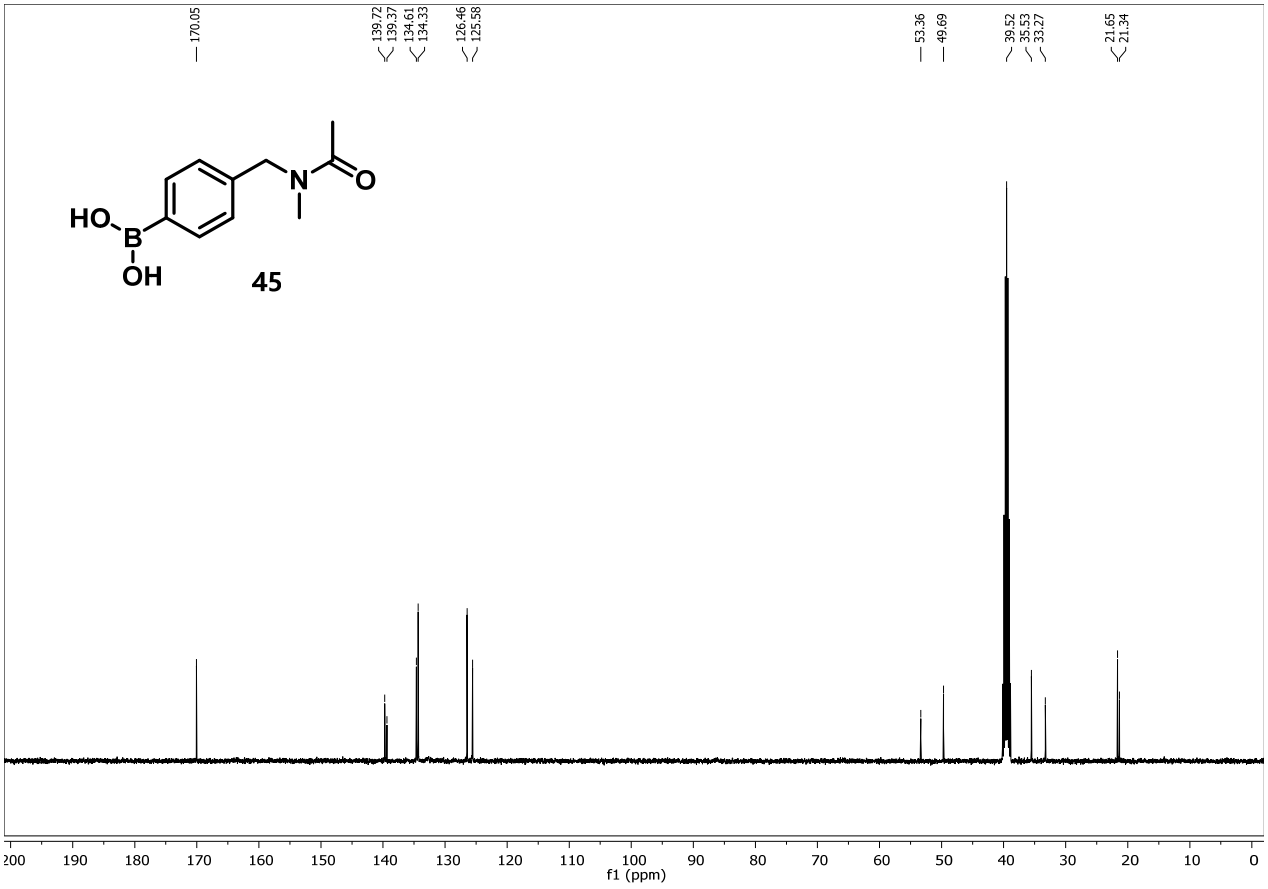

7.93
7.91
7.89
7.87
7.25
7.24
7.23
7.22
4.60
4.53
2.91
2.79
2.50
2.07
2.03
O
N
HO
O
43
2.02
2.00
2.22
3.13
3.04
f1 (ppm)

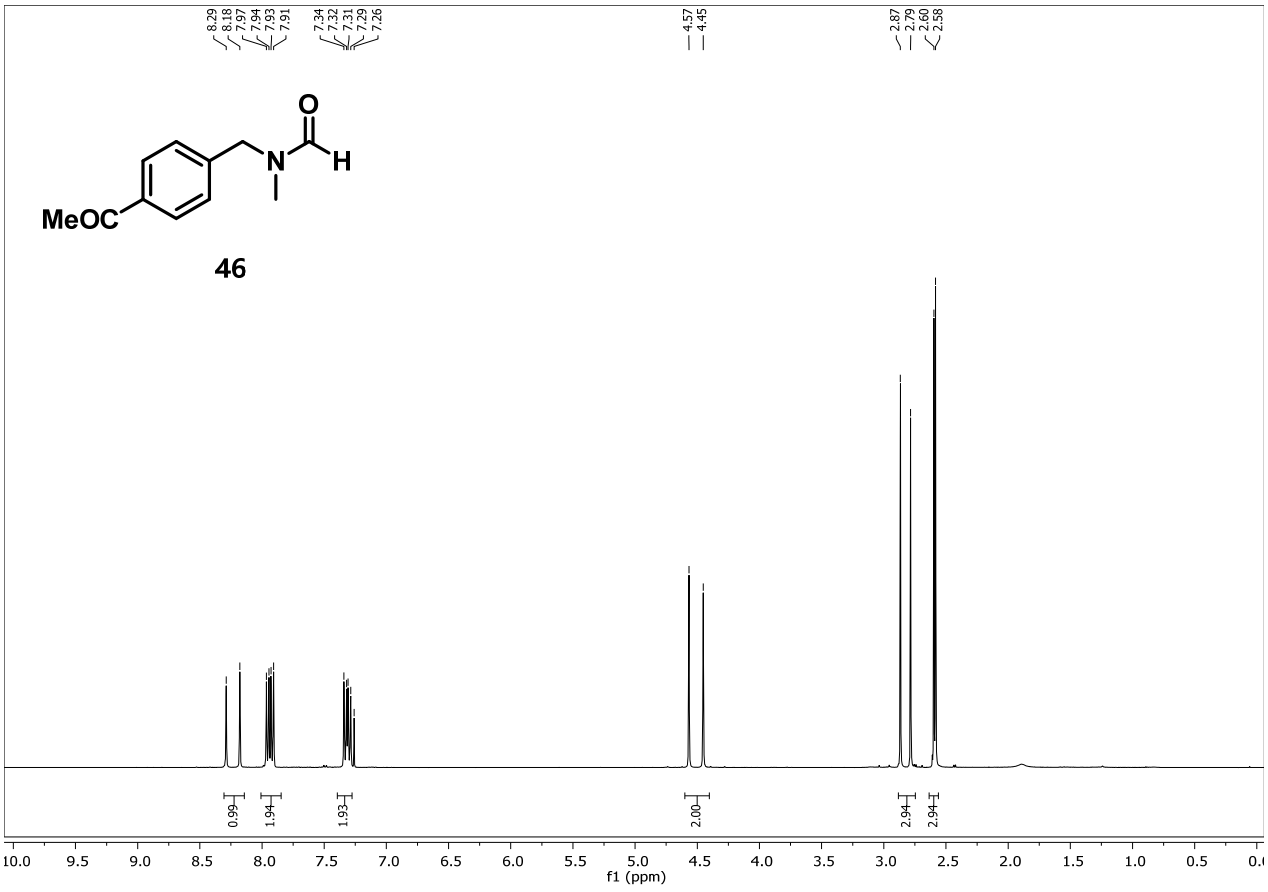

170.27
170.17
167.95
142.34
141.83
131.24
131.08
129.82
129.53
127.29
126.46
53.19
49.65
39.52
35.70
33.36
21.60
21.31
O
N
HO
O
43
f1 (ppm)

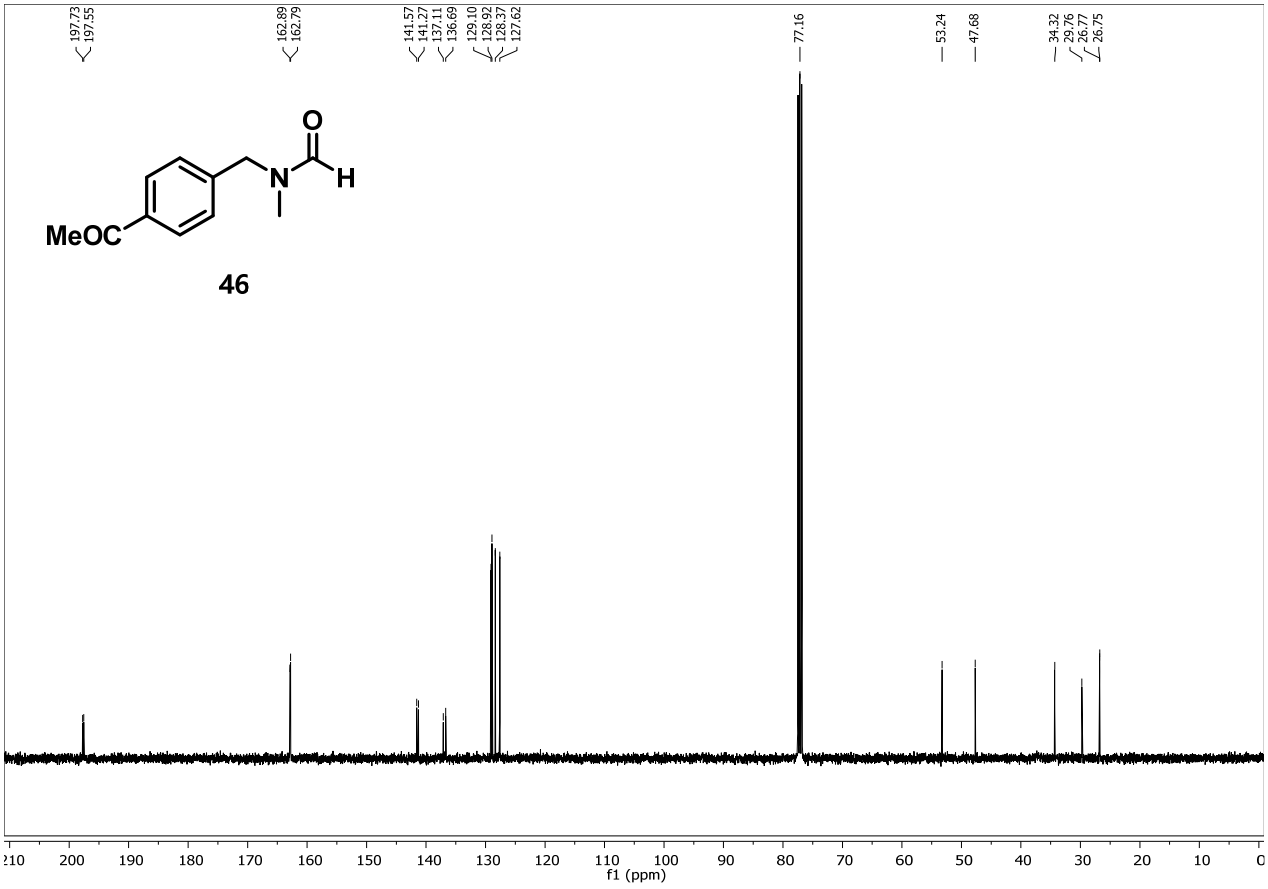

8.67
7.26
7.08
7.06
6.98
6.96
6.88
6.86
6.83
6.81
4.50
4.42
2.92
2.91
2.18
2.14
HO
N
O
44
0.82
2.05
1.97
2.00
3.00
3.04
f1 (ppm)

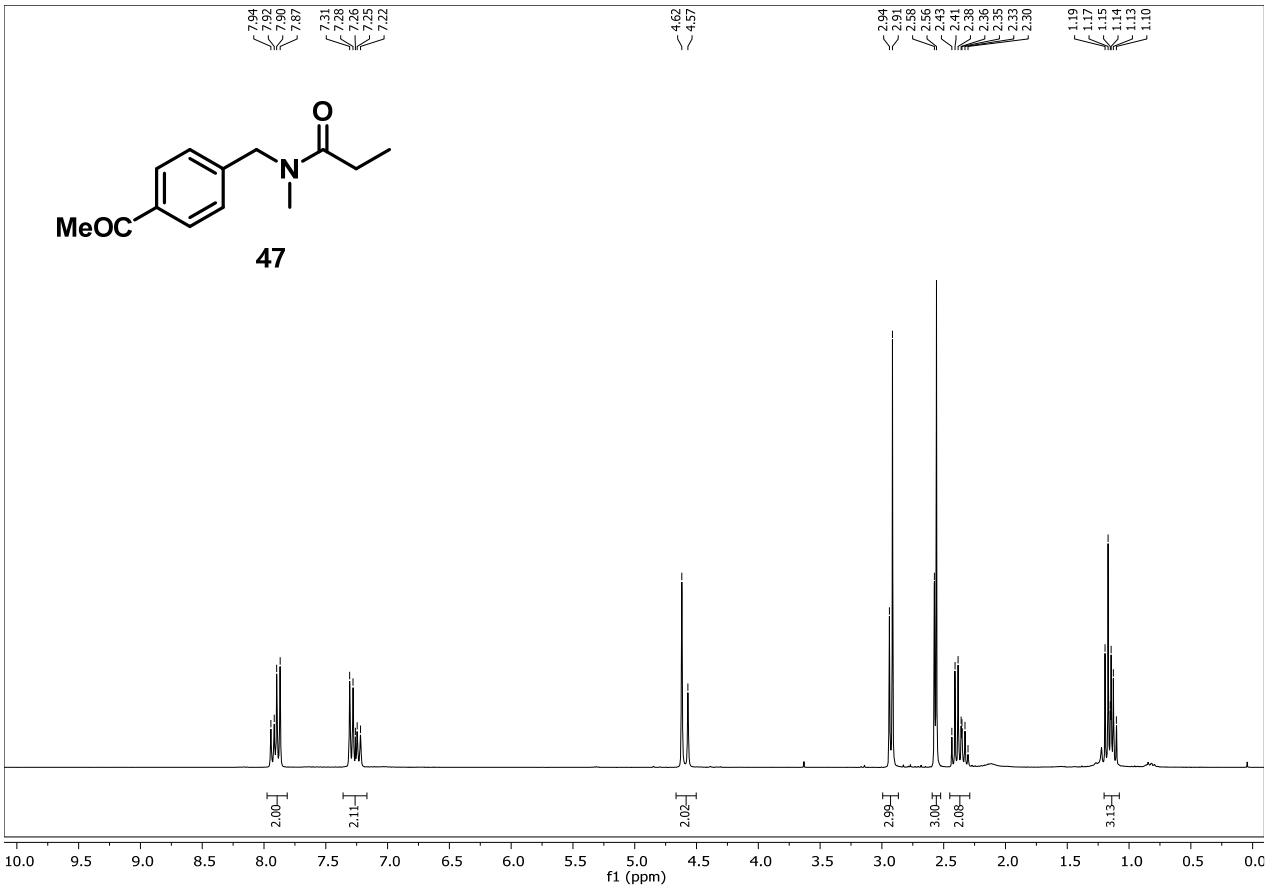

171.96
171.59
156.77
156.47
129.51
127.90
127.82
126.80
116.13
115.78
77.16
54.06
50.46
35.59
33.85
21.77
21.43
HO
N
O
44
f1 (ppm)

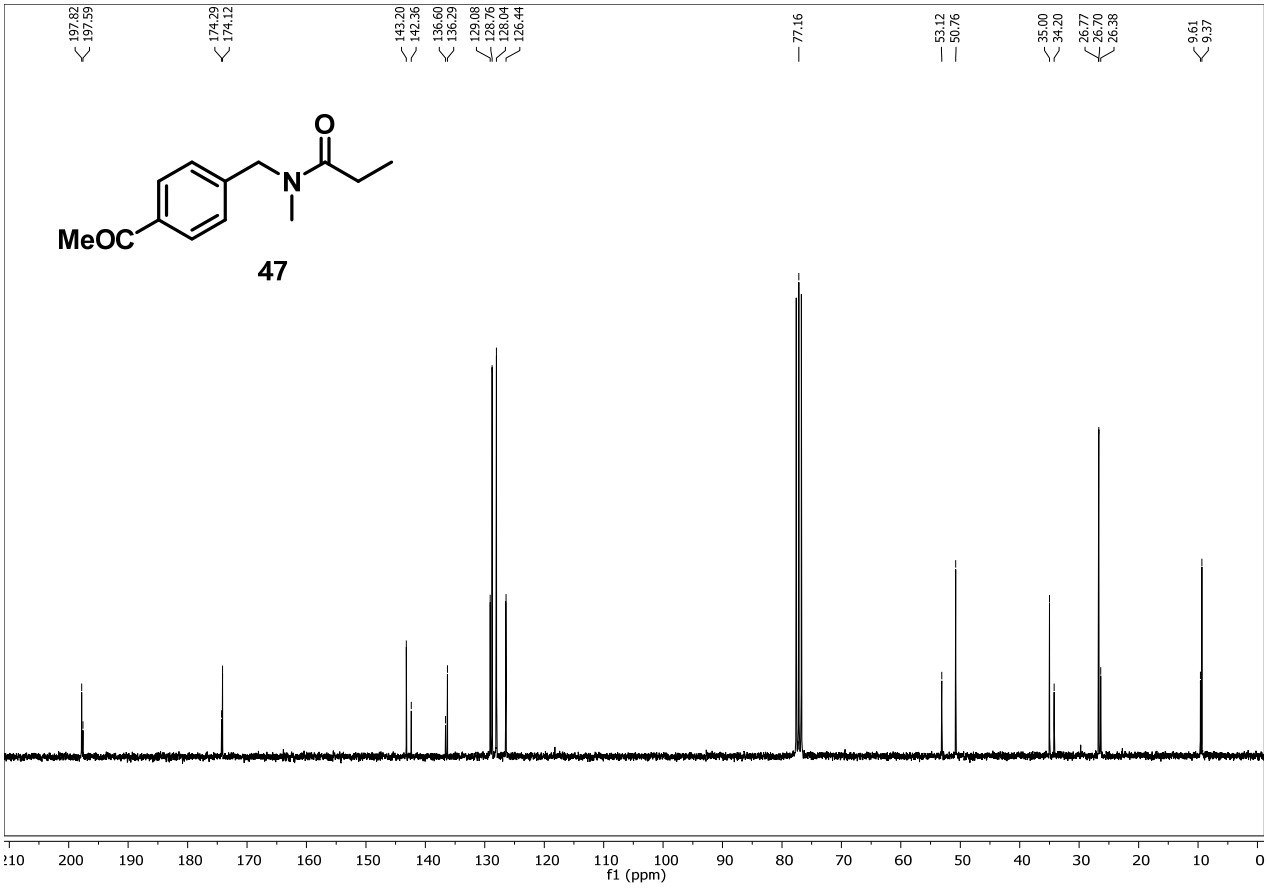

7.98
7.94
7.79
7.77
7.74
7.72
7.15
7.13
4.54
4.47
3.41
2.88
2.77
2.50
2.05
2.01
HO
B
OH
N
O
45
1.87
1.95
2.00
2.00
3.09
2.93
f1 (ppm)

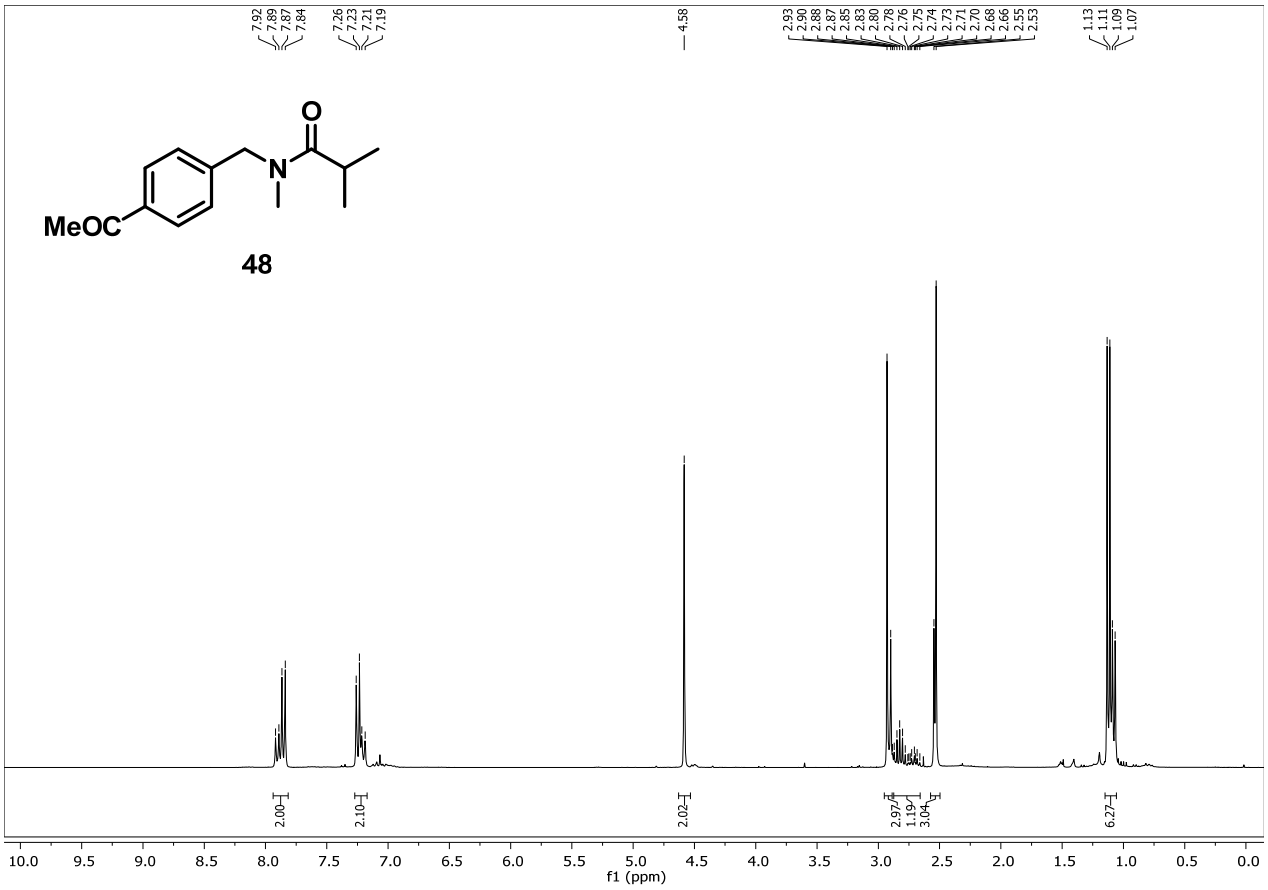

170.05
139.72
139.37
134.61
134.33
126.46
125.58
53.36
49.69
39.52
35.53
33.27
21.65
21.34
HO
B
OH
N
O
45
f1 (ppm)

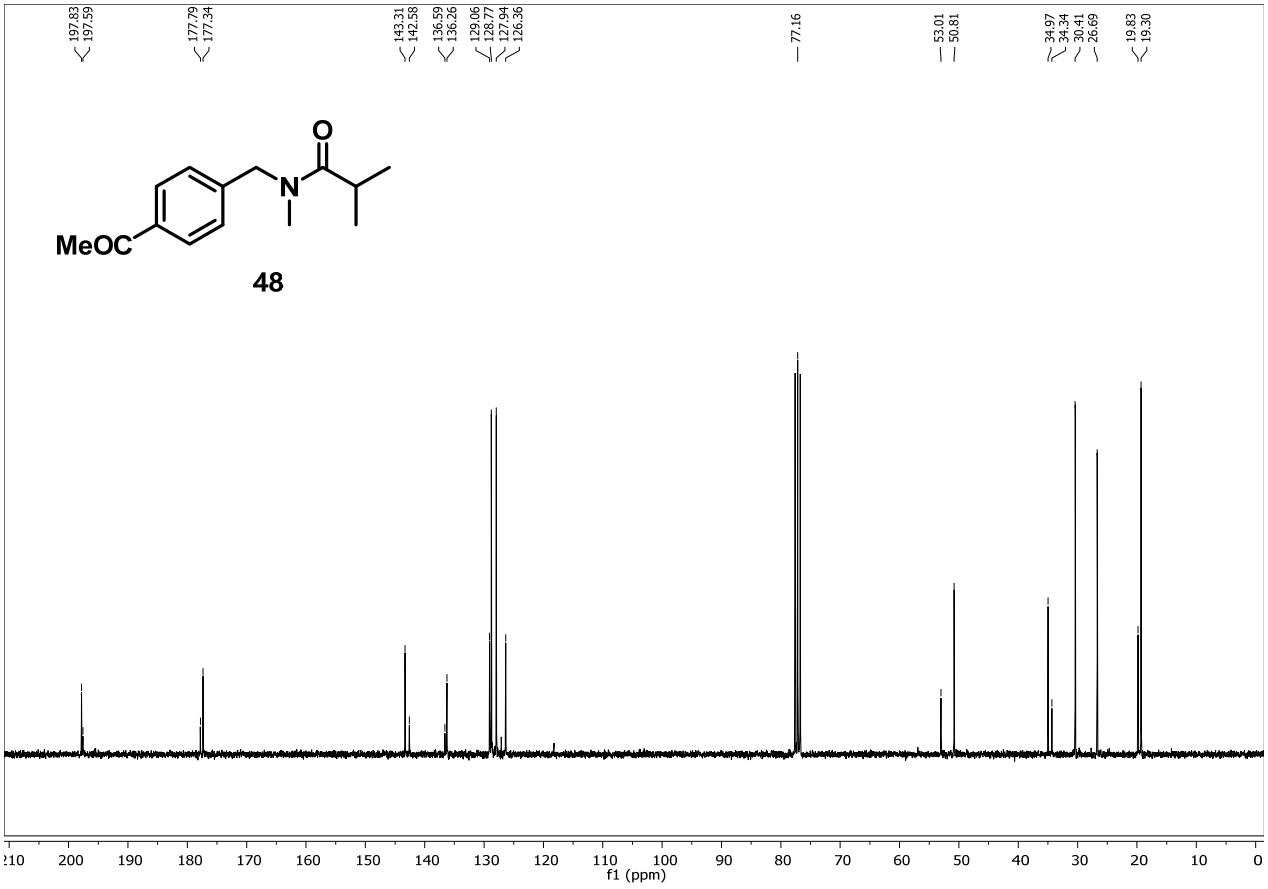

8.29
8.18
7.97
7.94
7.93
7.91
7.34
7.32
7.31
7.29
7.26
4.57
4.45
2.87
2.79
2.60
2.58
O
N
H
MeOC
46
0.99
1.94
1.93
2.00
2.94
2.94
f1 (ppm)

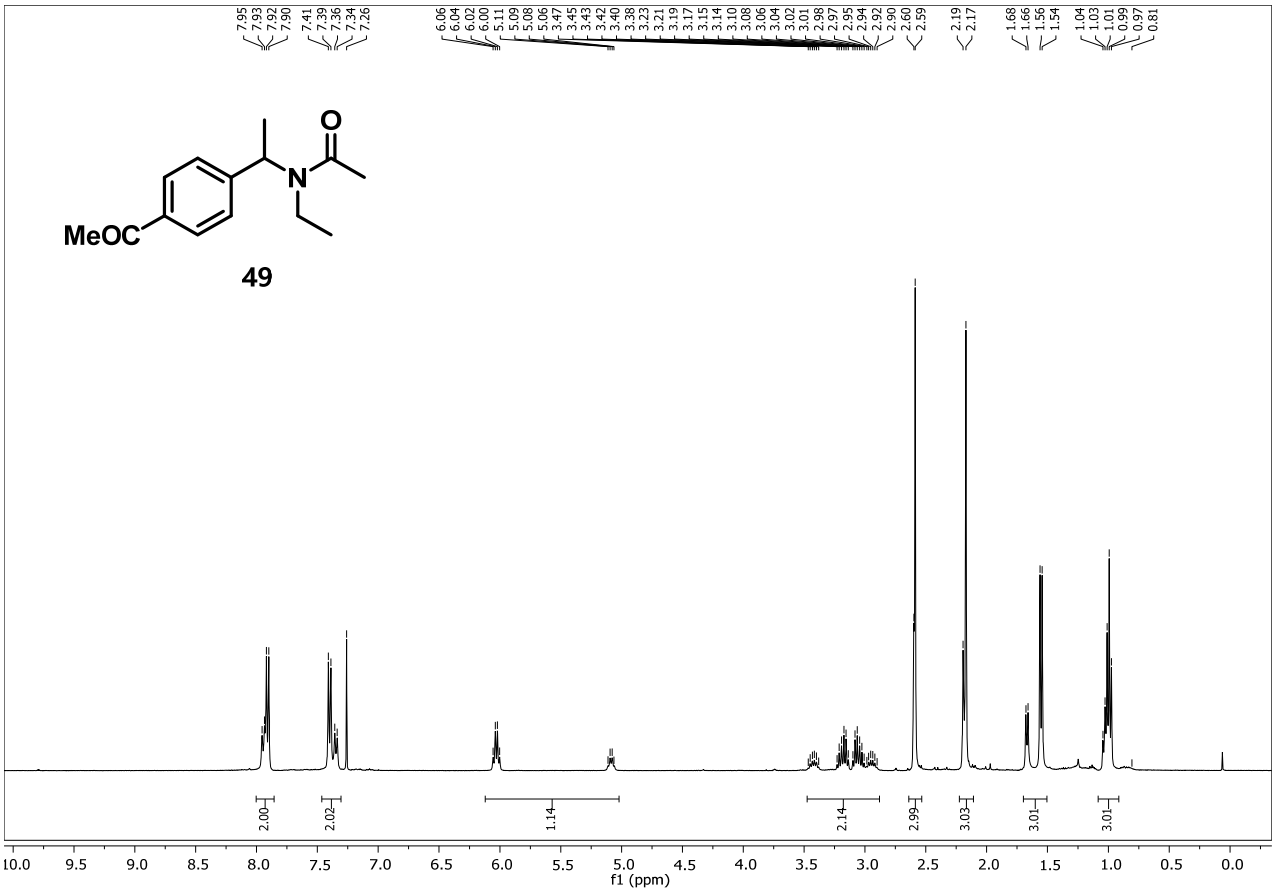

197.73
197.55
162.89
162.79
141.57
141.27
137.11
136.69
129.10
128.92
128.37
127.62
77.16
53.24
47.68
34.32
29.76
26.77
26.75
O
N
H
MeOC
46
f1 (ppm)

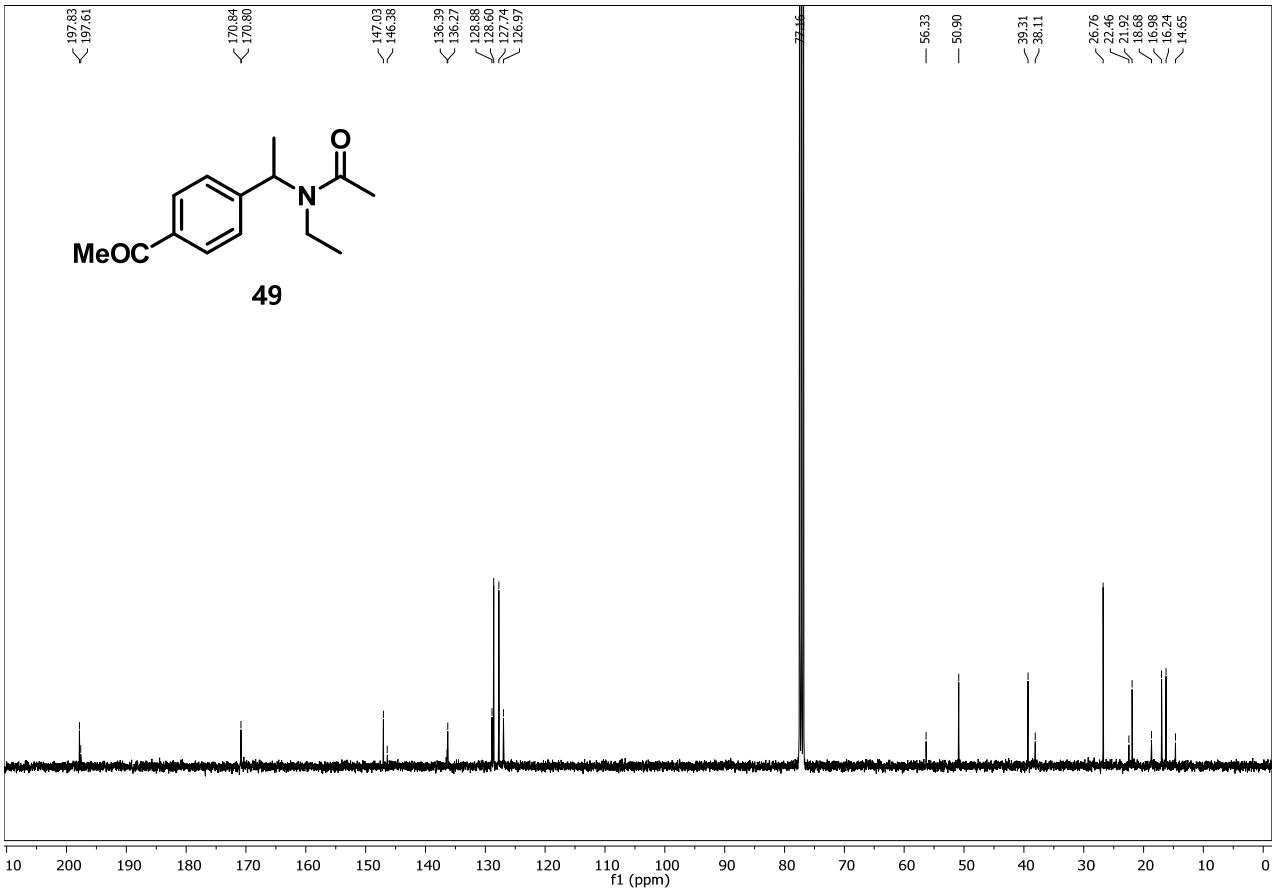

MeOC
47
f1 (ppm)

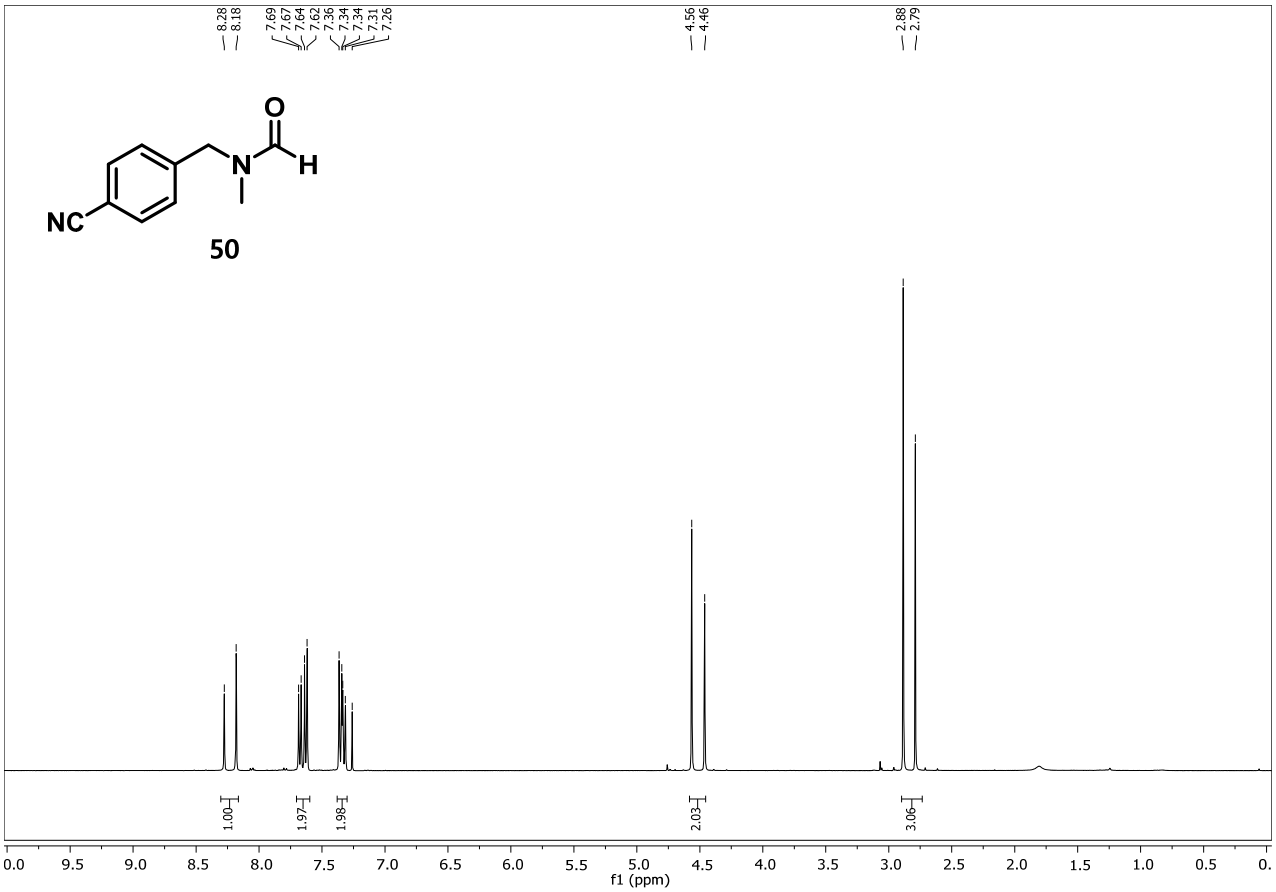

MeOC
47
f1 (ppm)

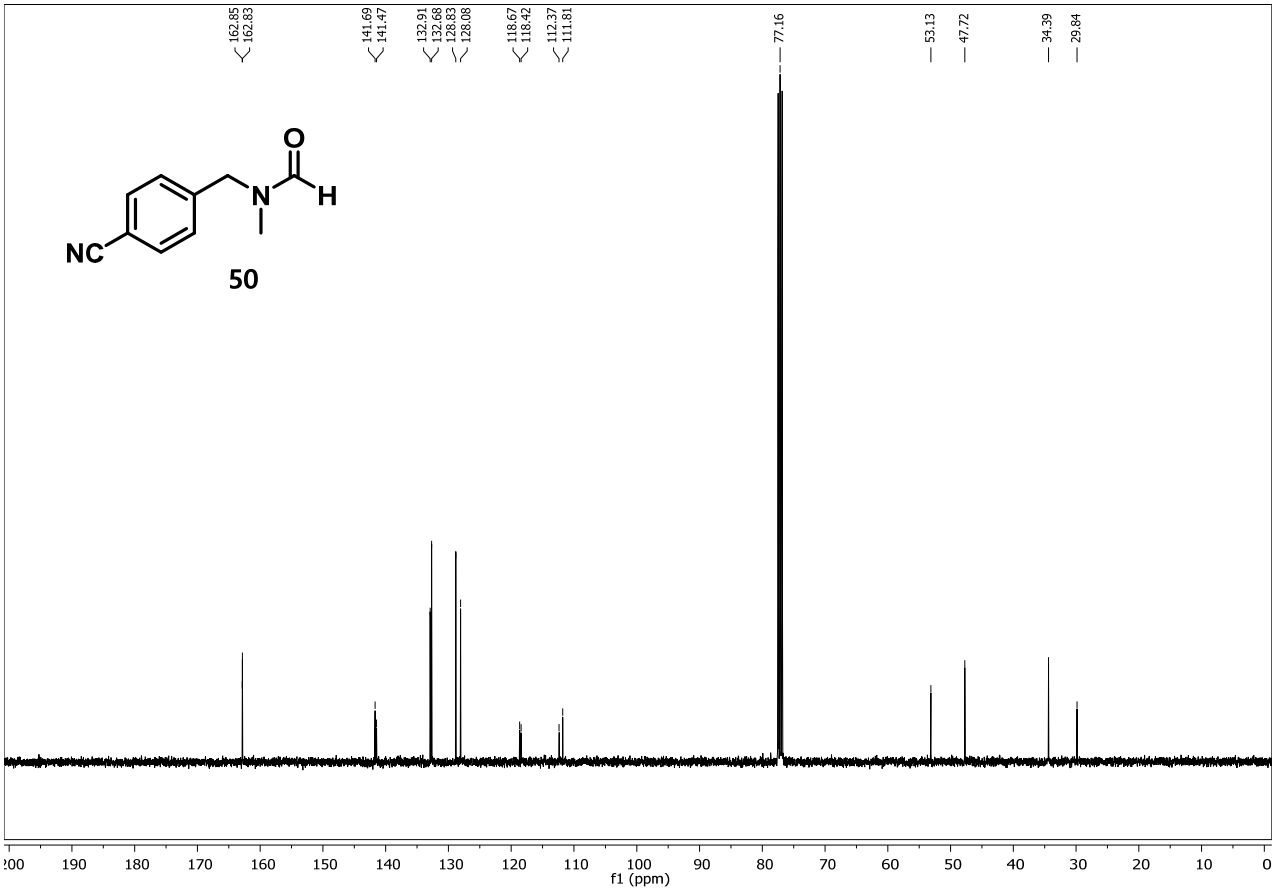

7.92
7.89
7.87
7.84
7.26
7.23
7.21
7.19
4.58
2.93
2.90
2.88
2.87
2.85
2.83
2.80
2.78
2.76
2.75
2.74
2.73
2.71
2.70
2.68
2.66
2.55
2.53
1.13
1.11
1.09
1.07
O
N
MeOC
48
2.00
2.10
2.02
2.97
1.19
3.04
6.27
f1 (ppm)

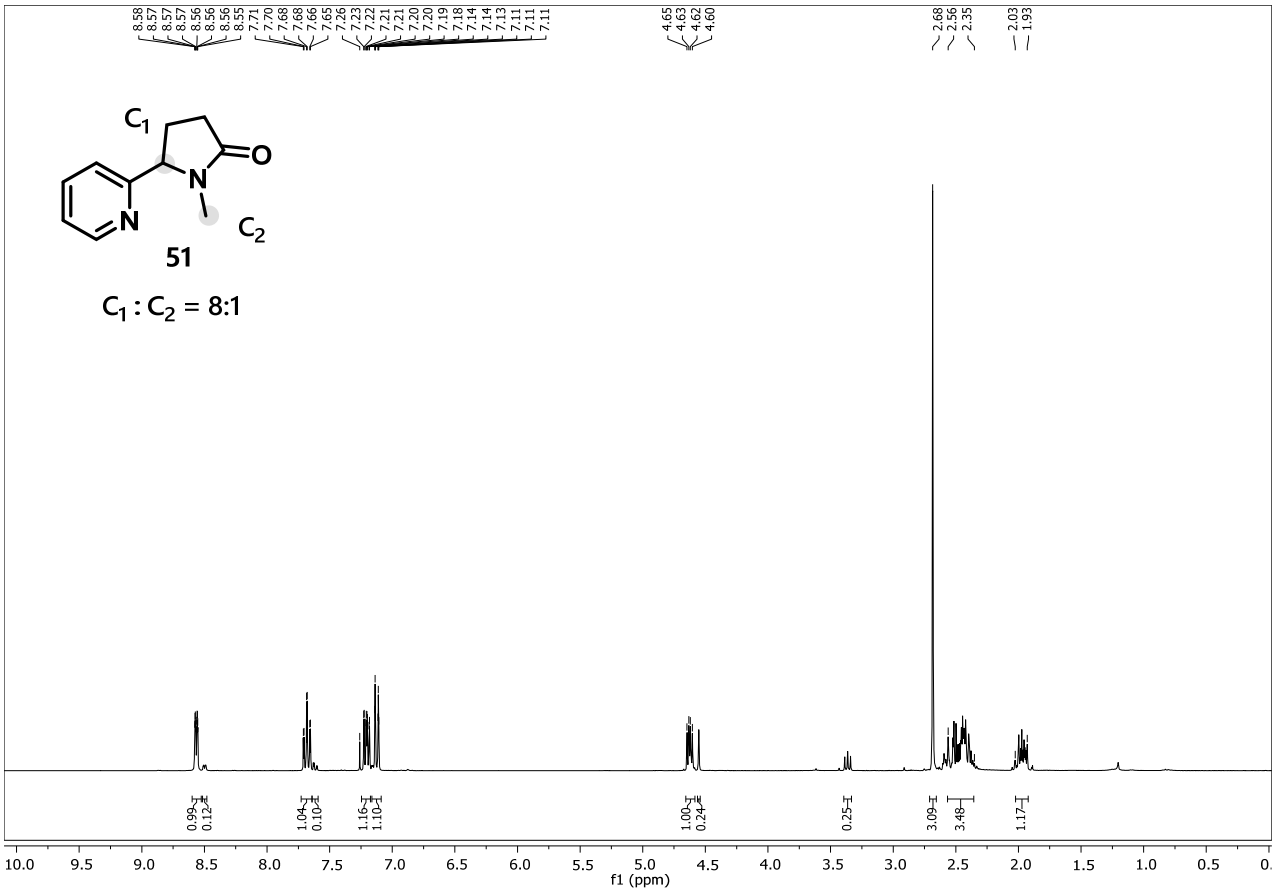

197.83
197.59
177.79
177.34
143.31
142.58
136.59
136.26
129.06
128.77
127.94
126.36
77.16
53.01
50.81
34.97
34.34
30.41
26.69
19.83
19.30
O
N
MeOC
48
f1 (ppm)

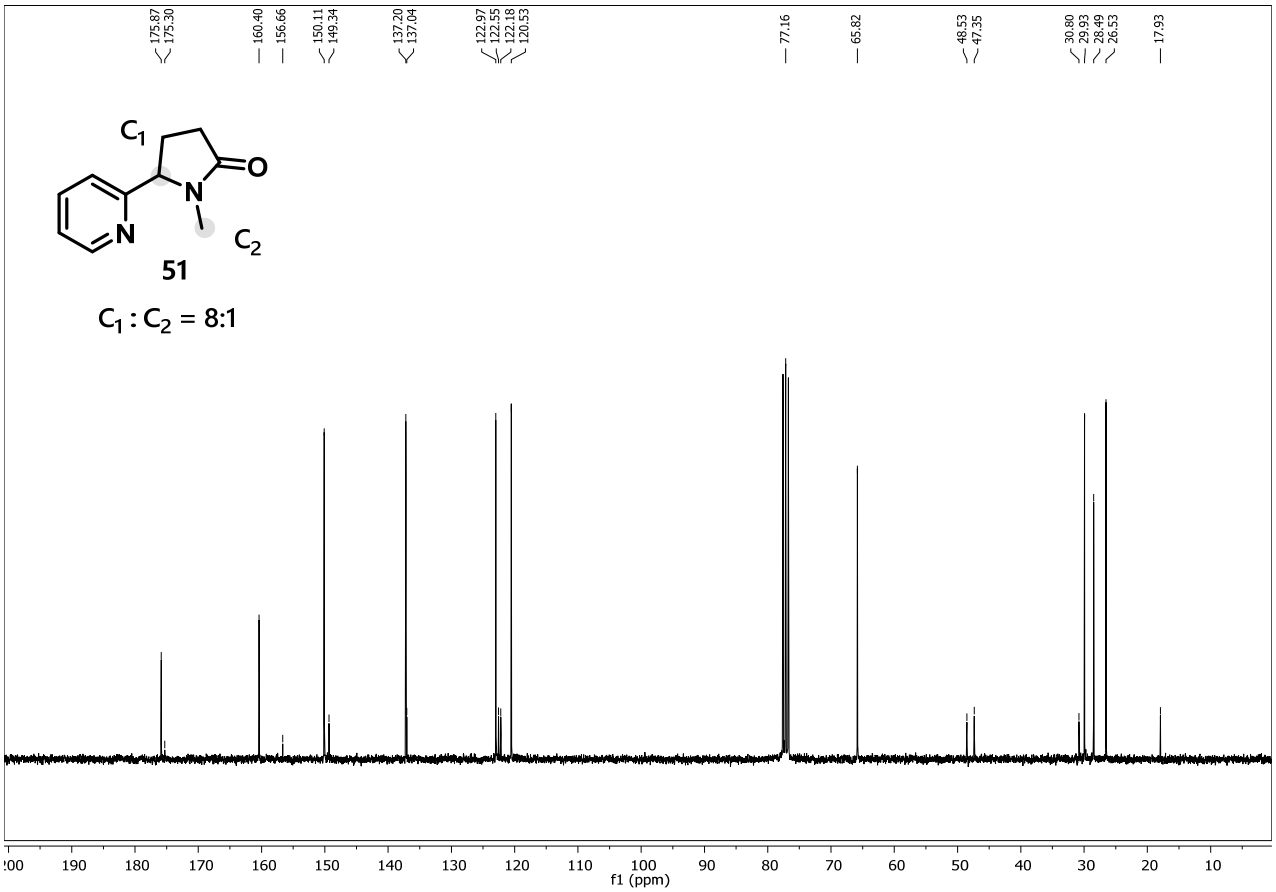

MeOC
N
O
49
f1 (ppm)

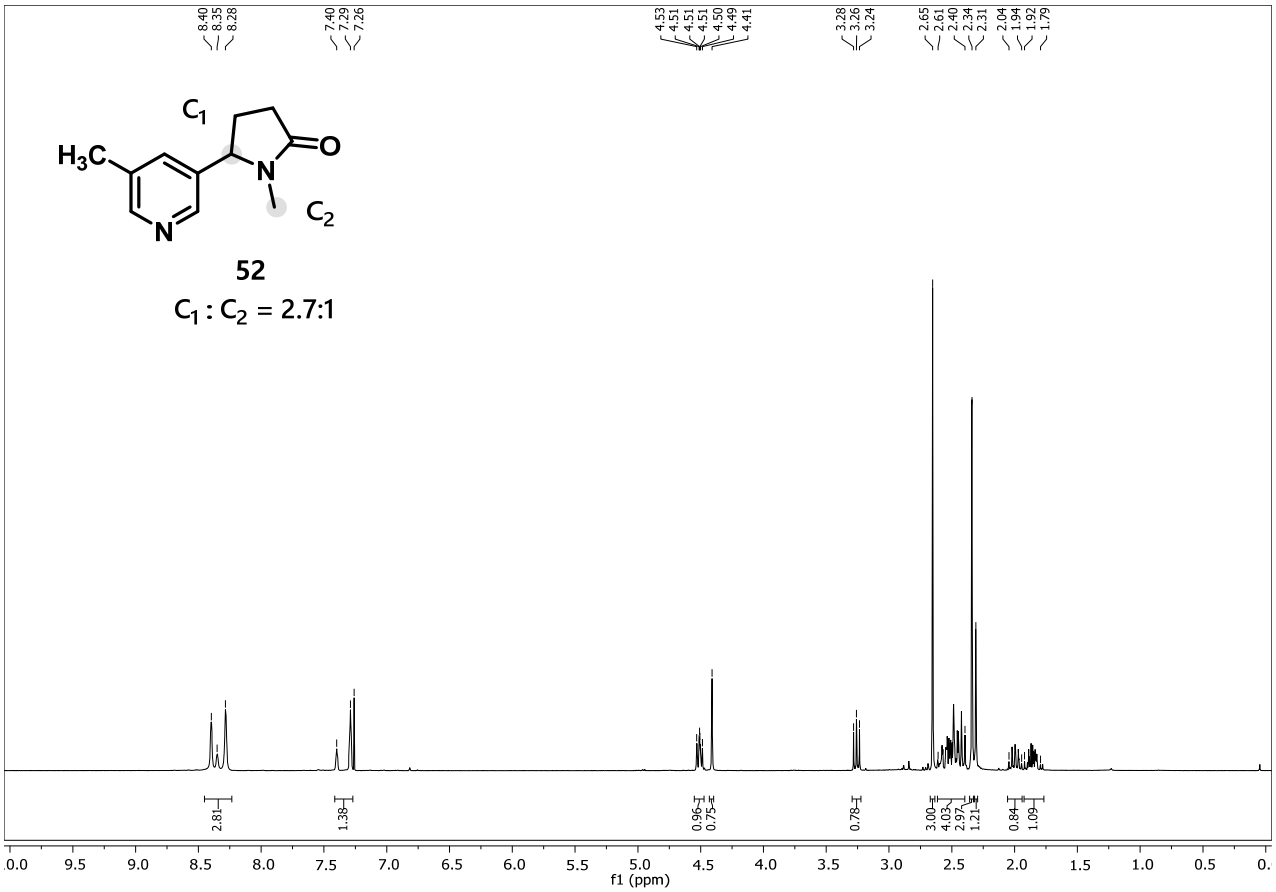

MeOC
N
O
49
f1 (ppm)

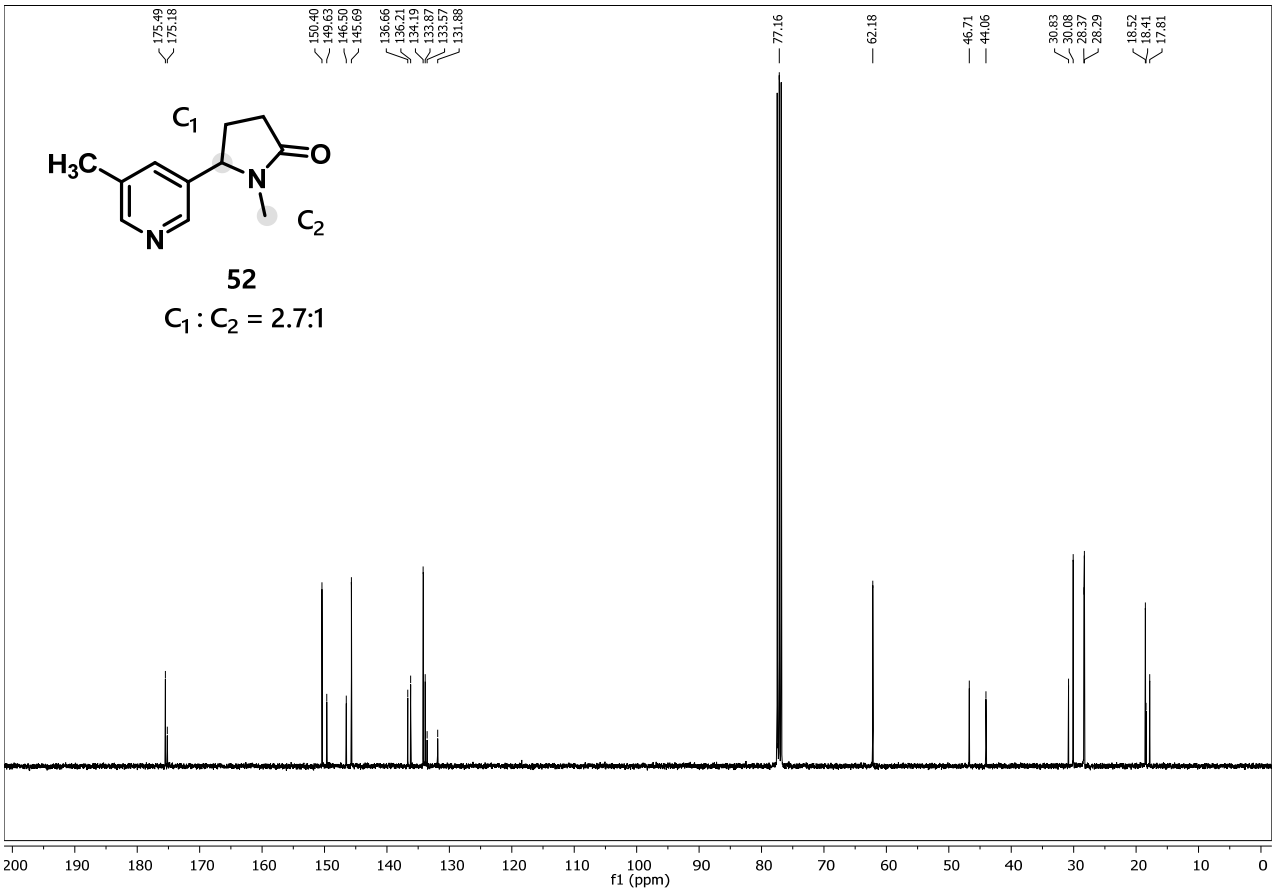

8.28
8.18
7.69
7.67
7.64
7.62
7.36
7.34
7.34
7.31
7.26
4.56
4.46
2.88
2.79
O
N
H
NC
50
1.00
1.97
1.98
2.03
3.06
f1 (ppm)

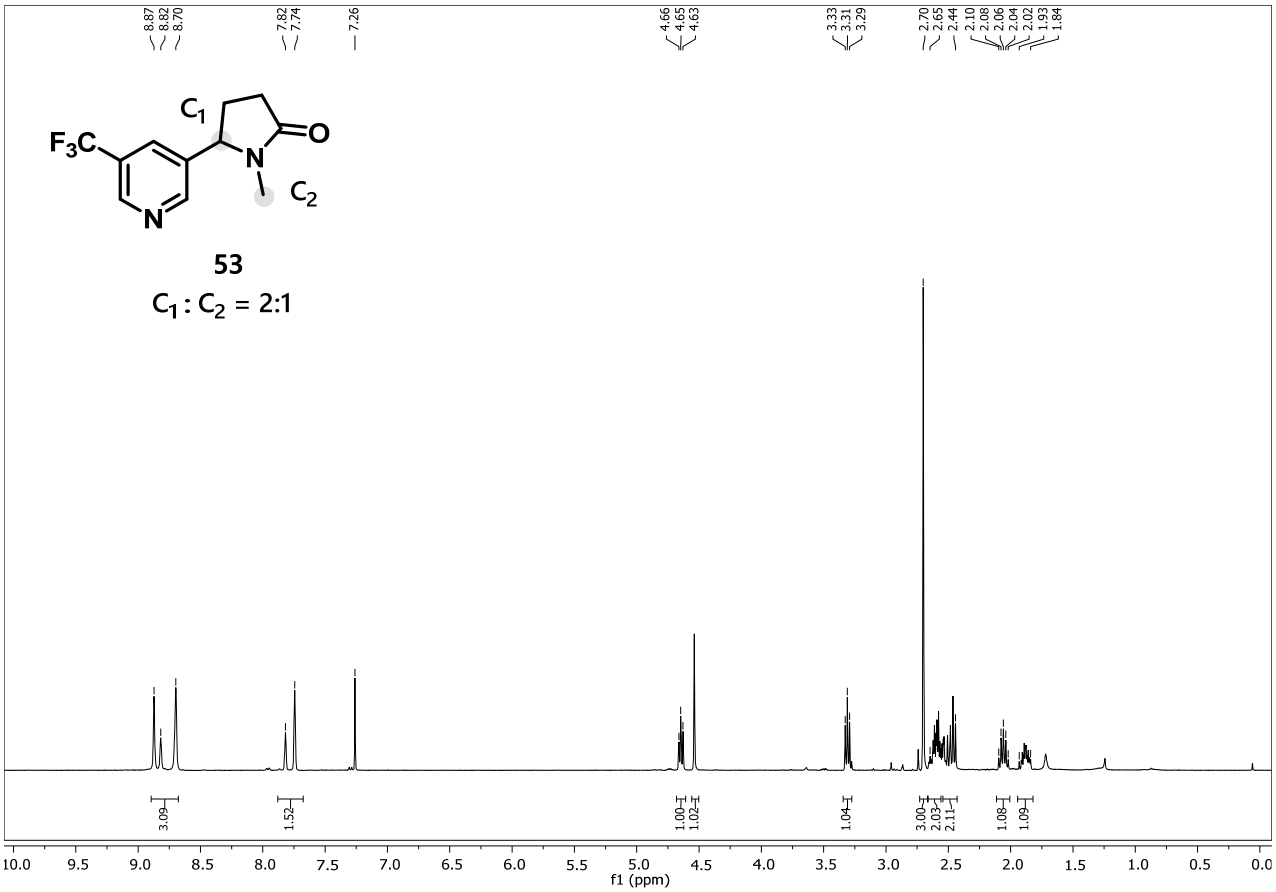

162.85
162.83
141.69
141.47
132.91
132.68
128.83
128.08
118.67
118.42
112.37
111.81
77.16
53.13
47.72
34.39
29.84
O
N
H
NC
50
f1 (ppm)

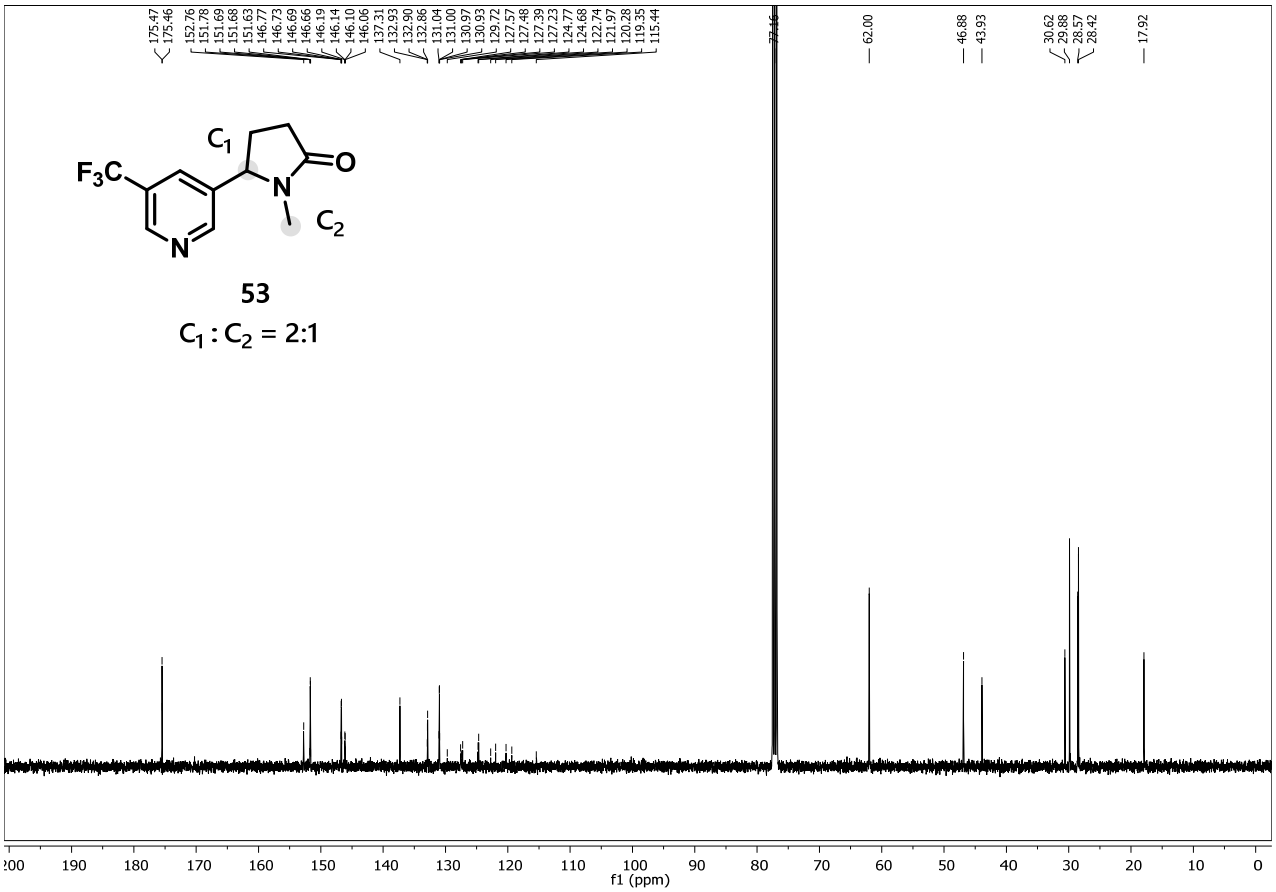

8.58
8.57
8.57
8.57
8.56
8.56
8.56
8.55
7.71
7.70
7.68
7.68
7.66
7.65
7.26
7.23
7.22
7.21
7.21
7.20
7.20
7.19
7.18
7.14
7.13
7.11
7.11
7.11
4.65
4.63
4.62
4.60
2.68
2.56
2.35
2.03
1.93
C1
O
N
N
C2
51
C1 : C2 = 8:1
0.99
0.12
1.04
0.10
1.16
1.10
1.00
0.24
0.25
3.09
3.48
1.17
f1 (ppm)

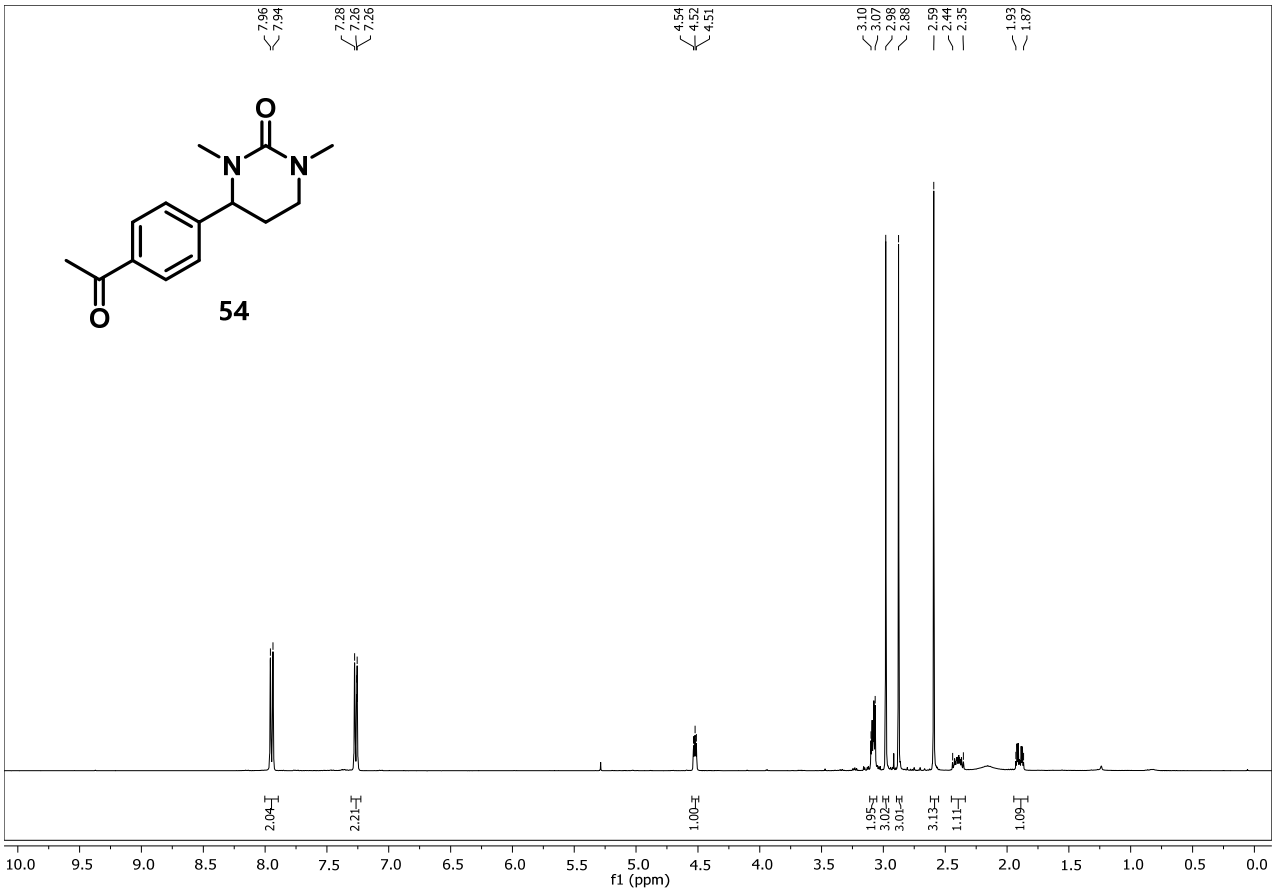

175.87
175.30
160.40
156.66
150.11
149.34
137.20
137.04
122.97
122.55
122.18
120.53
77.16
65.82
48.53
47.35
30.80
29.93
28.49
26.53
17.93
C1
O
N
N
C2
51
C1 : C2 = 8:1
f1 (ppm)

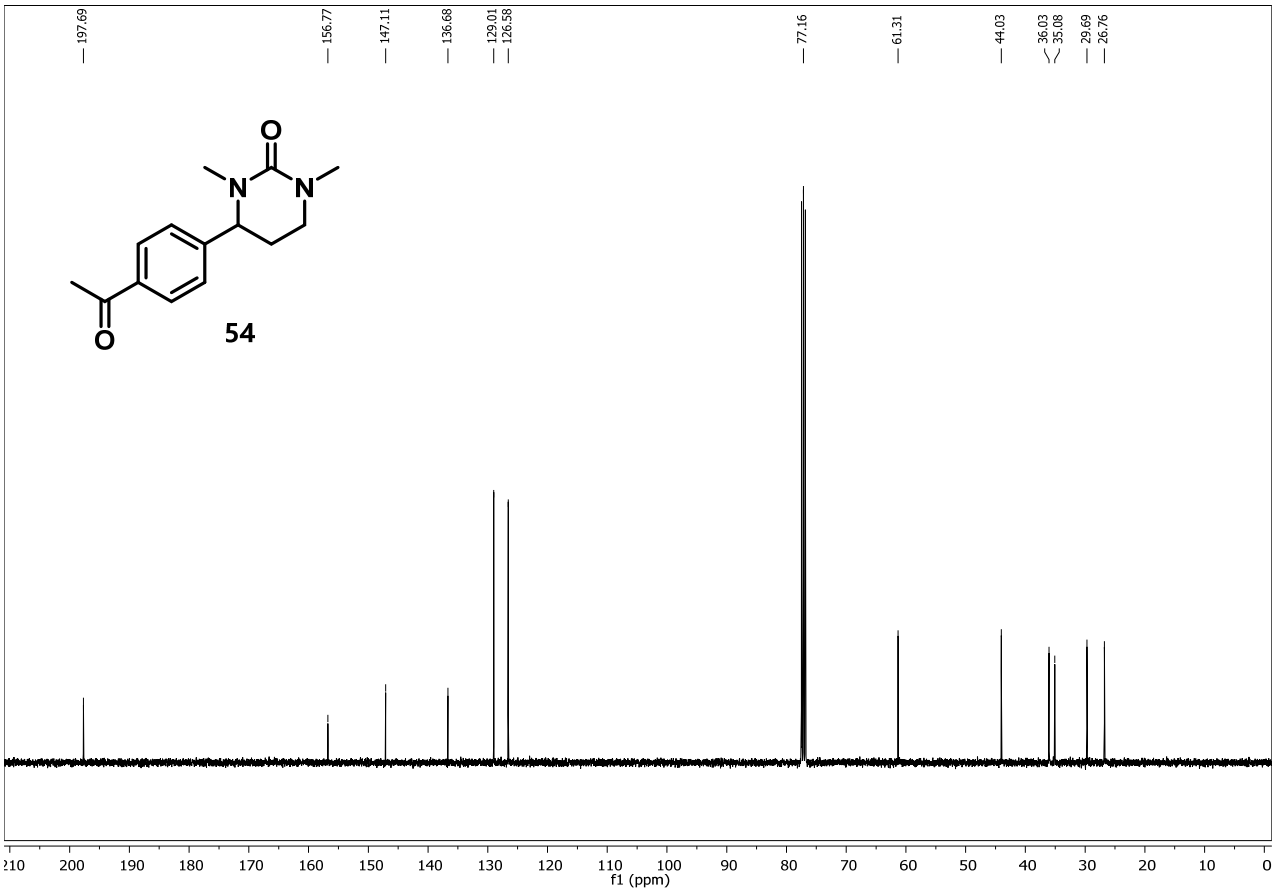

8.40
8.35
8.28
7.40
7.29
7.26
4.53
4.51
4.51
4.51
4.50
4.49
4.41
3.28
3.26
3.24
2.65
2.61
2.40
2.34
2.31
2.04
1.94
1.92
1.79
C1
H3C
O
N
C2
N
52
C1 : C2 = 2.7:1
2.81
1.38
0.96
0.75
0.78
3.00
4.03
2.97
1.21
0.84
1.09
f1 (ppm)

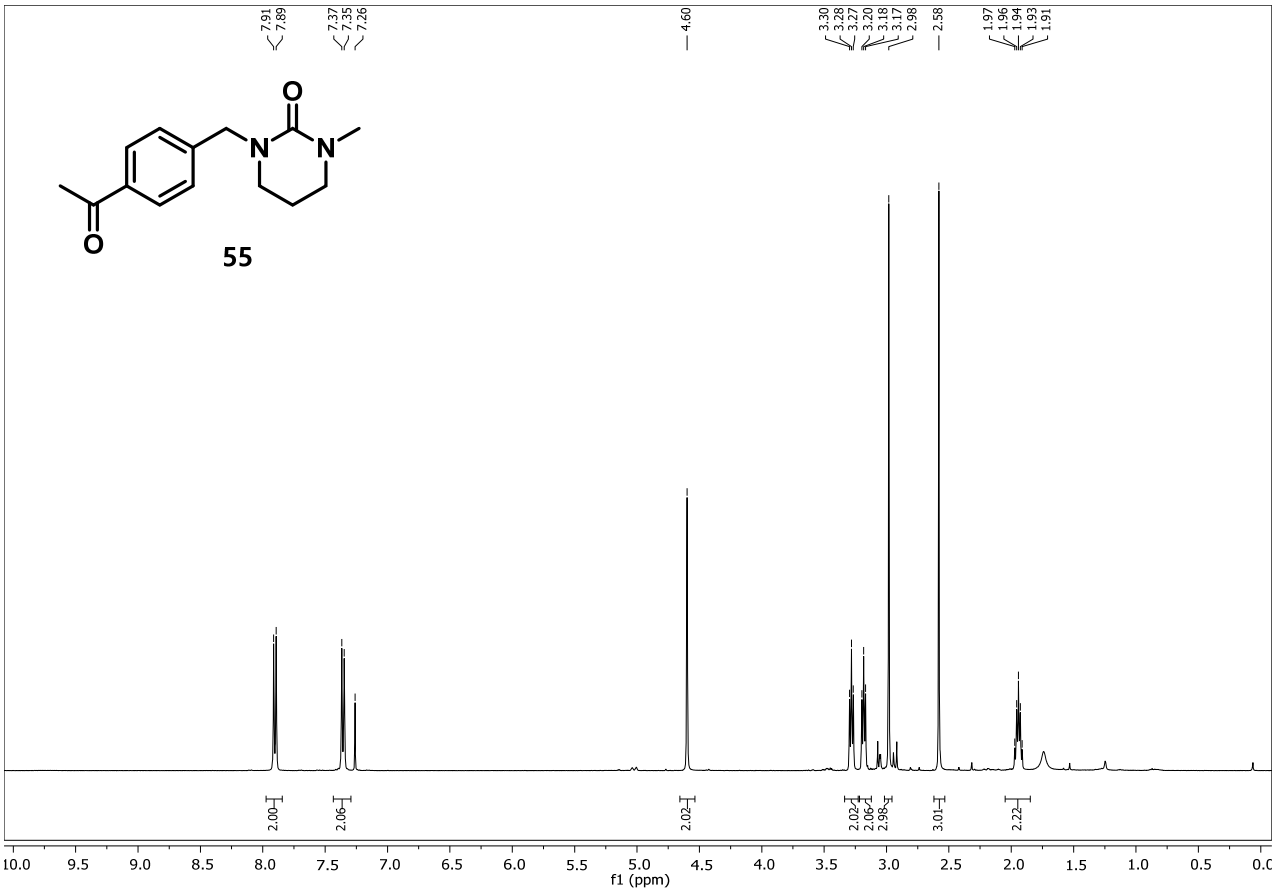

175.49
175.18
150.40
149.63
146.50
145.69
136.66
136.21
134.19
133.87
133.57
131.88
77.16
62.18
46.71
44.06
30.83
30.08
28.37
28.29
18.52
18.41
17.81
C1
H3C
O
N
C2
N
52
C1 : C2 = 2.7:1
f1 (ppm)

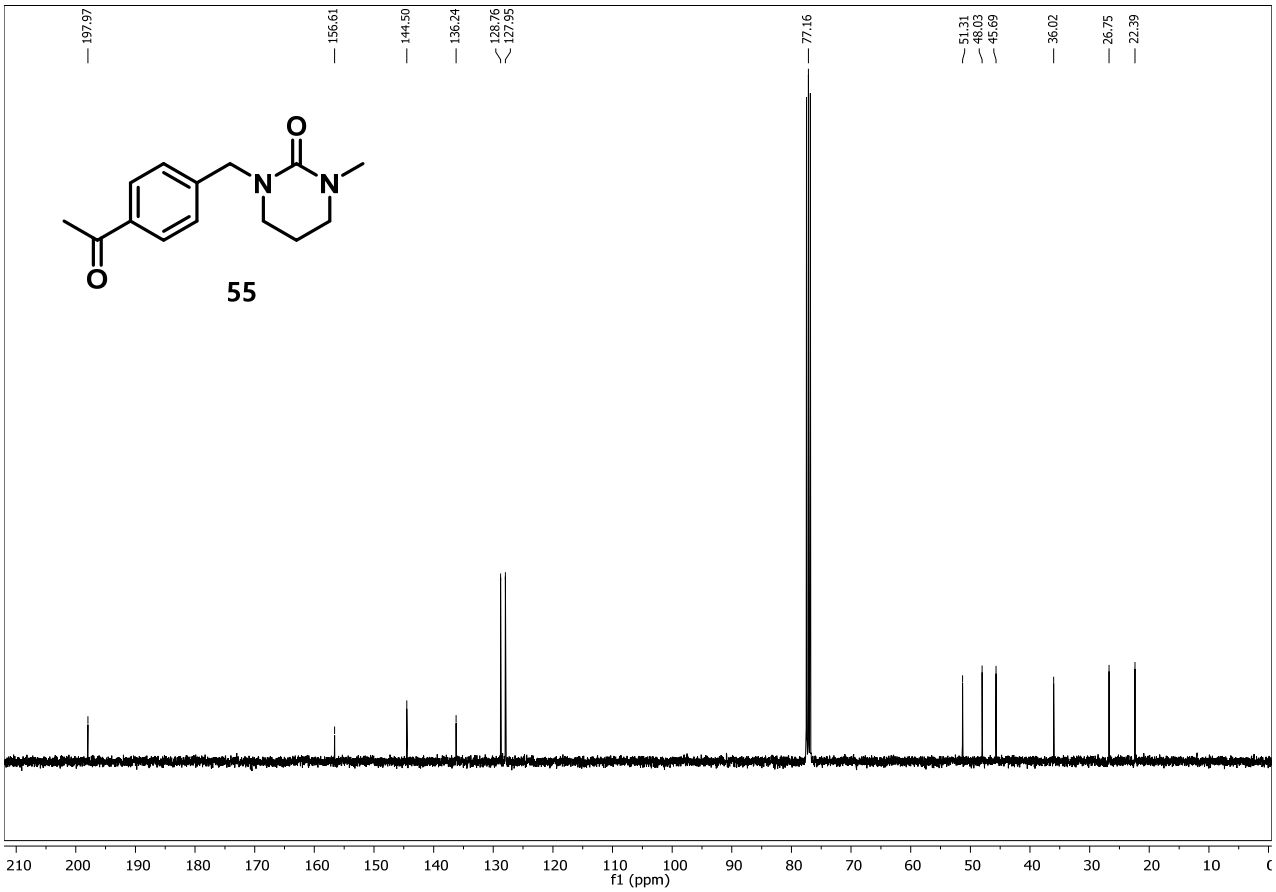

8.87
8.82
8.70
7.82
7.74
7.26
4.66
4.65
4.63
3.33
3.31
3.29
2.70
2.65
2.44
2.10
2.08
2.06
2.04
2.02
1.93
1.84
C1
F3C
O
N
C2
N
53
C1 : C2 = 2:1
3.09
1.52
1.00
1.02
1.04
3.00
2.03
2.11
1.08
1.09
f1 (ppm)

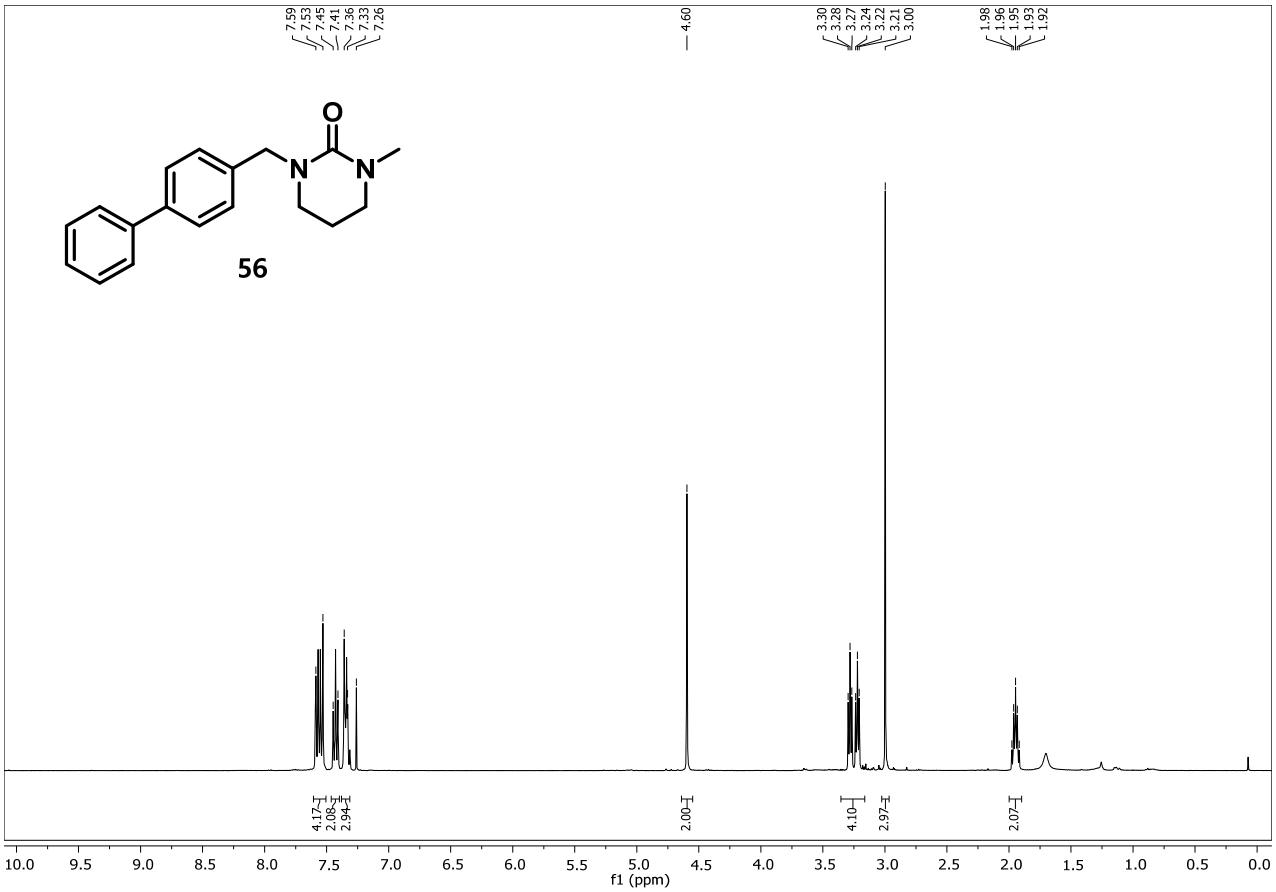

175.47
175.46
152.76
151.78
151.69
151.68
151.63
146.77
146.73
146.69
146.66
146.19
146.14
146.10
146.06
137.31
132.93
132.90
132.86
131.04
131.00
130.97
130.93
129.72
127.57
127.48
127.39
127.23
124.77
124.68
122.74
121.97
120.28
119.35
115.44
77.16
62.00
46.88
43.93
30.62
29.88
28.57
28.42
17.92
C1
F3C
O
N
C2
N
53
C1 : C2 = 2:1
f1 (ppm)

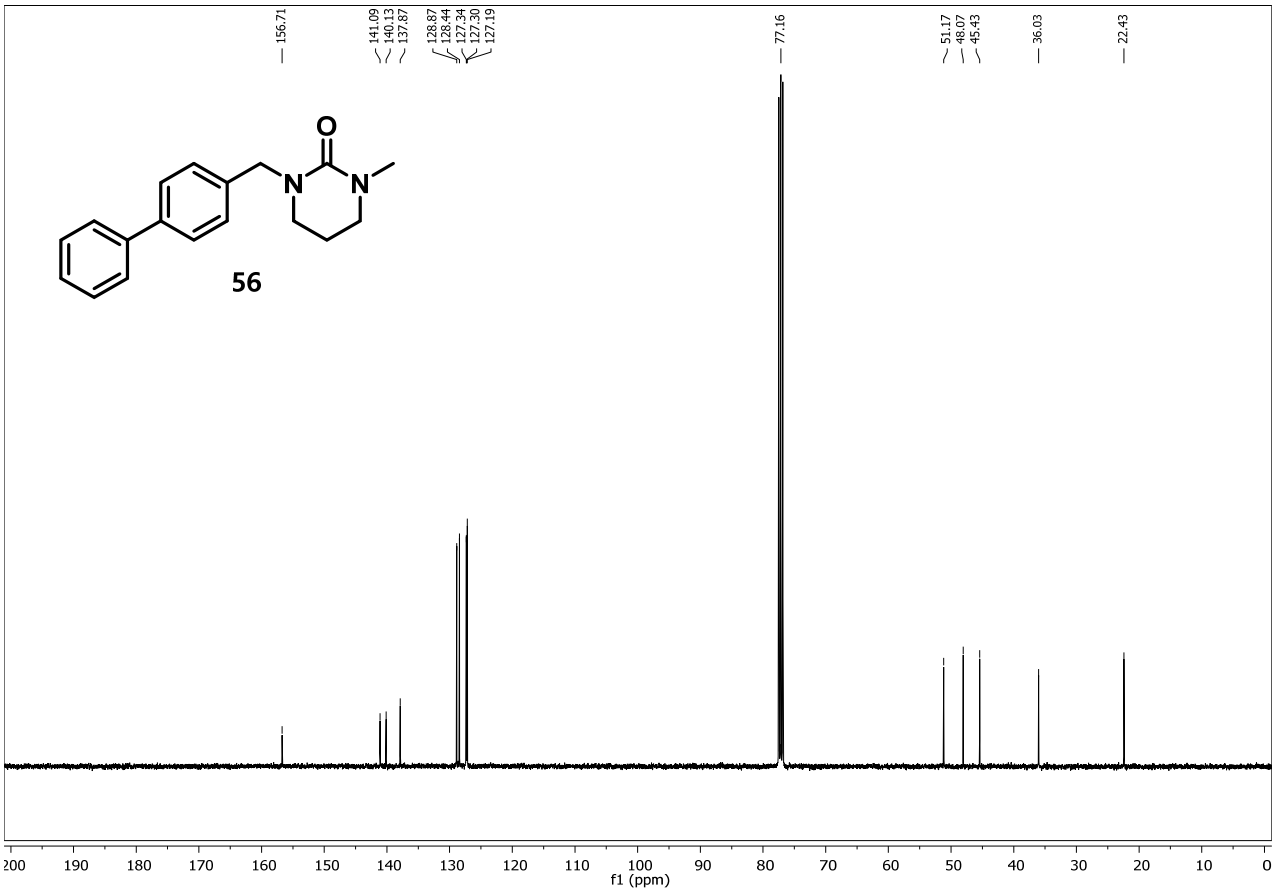

7.96
7.94
7.28
7.26
7.26
4.54
4.52
4.51
3.10
3.07
2.98
2.88
2.59
2.44
2.35
1.93
1.87
O
N
N
O
54
2.04
2.21
1.00
1.95
3.02
3.01
3.13
1.11
1.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

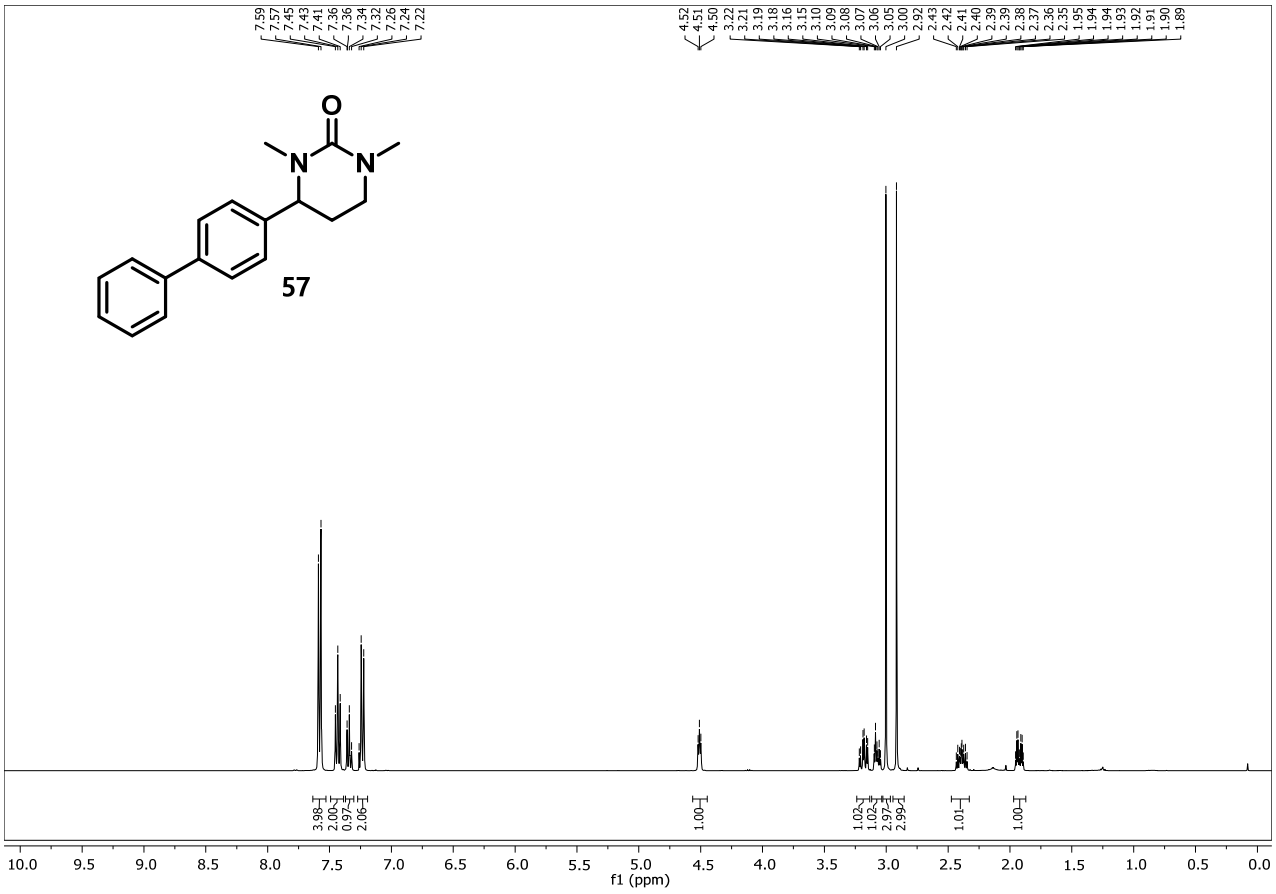

197.69
156.77
147.11
136.68
129.01
126.58
77.16
61.31
44.03
36.03
35.08
29.69
26.76
O
N
N
O
54
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

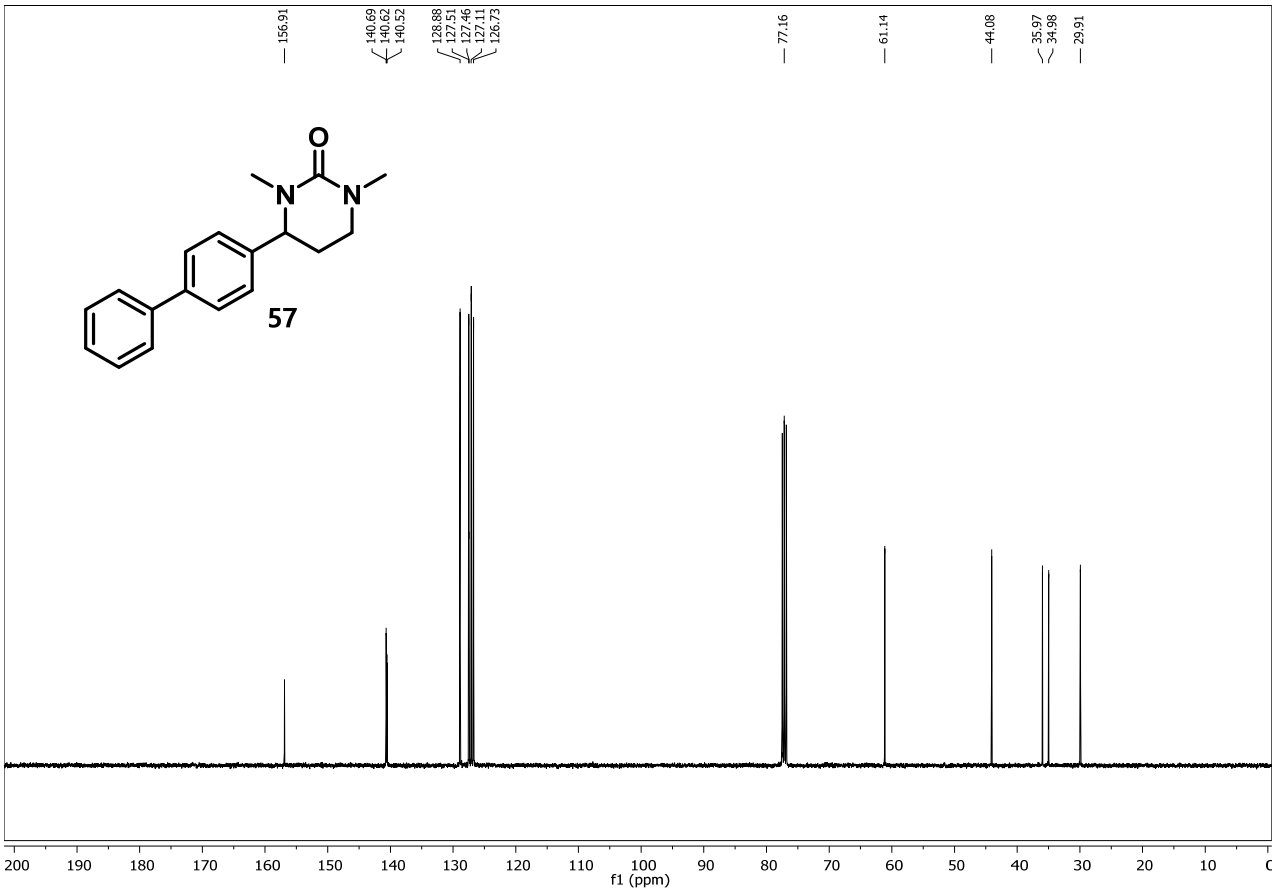

7.91
7.89
7.37
7.35
7.26
4.60
3.30
3.28
3.27
3.20
3.18
3.17
2.98
2.58
1.97
1.96
1.94
1.93
1.91
55
2.00
2.06
2.02
2.02
2.06
2.98
3.01
2.22
f1 (ppm)

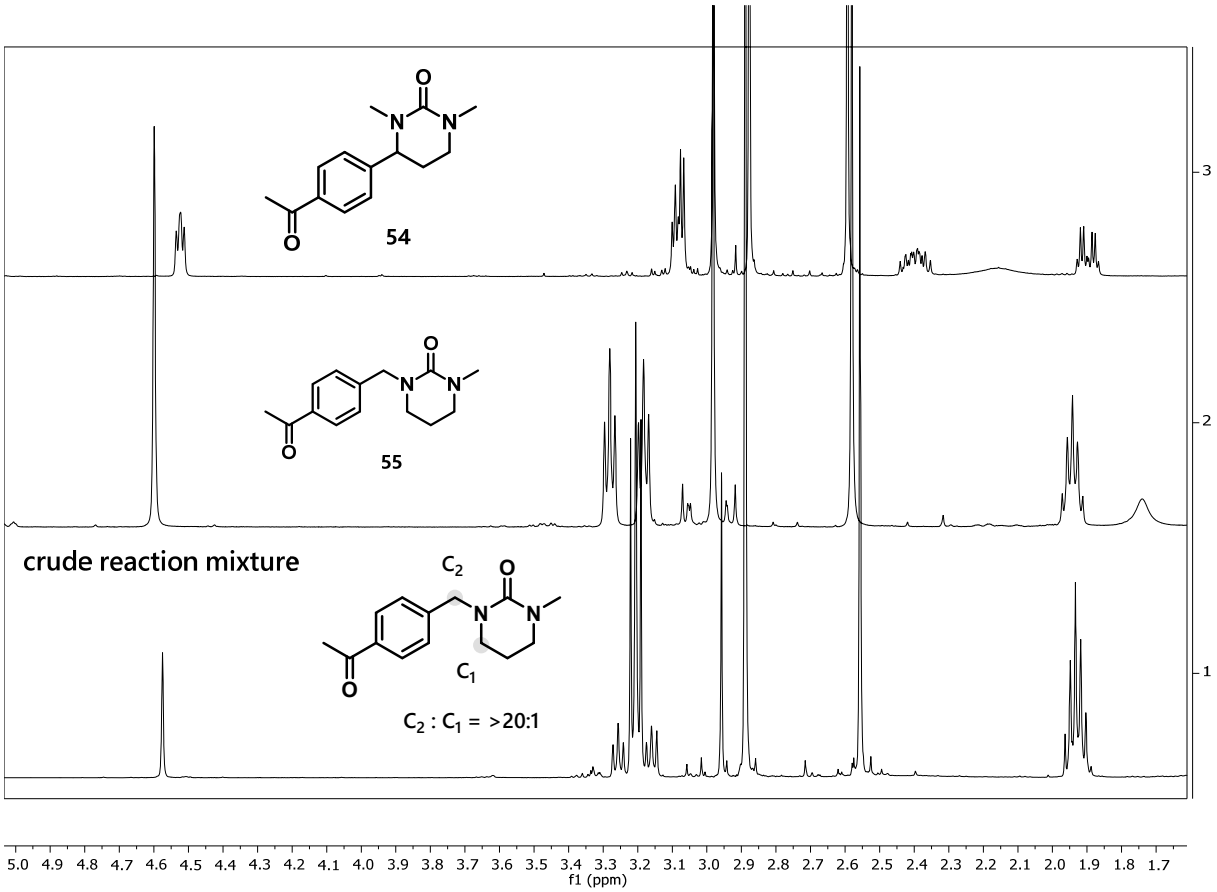

197.97
156.61
144.50
136.24
128.76
127.95
77.16
51.31
48.03
45.69
36.02
26.75
22.39
55
f1 (ppm)

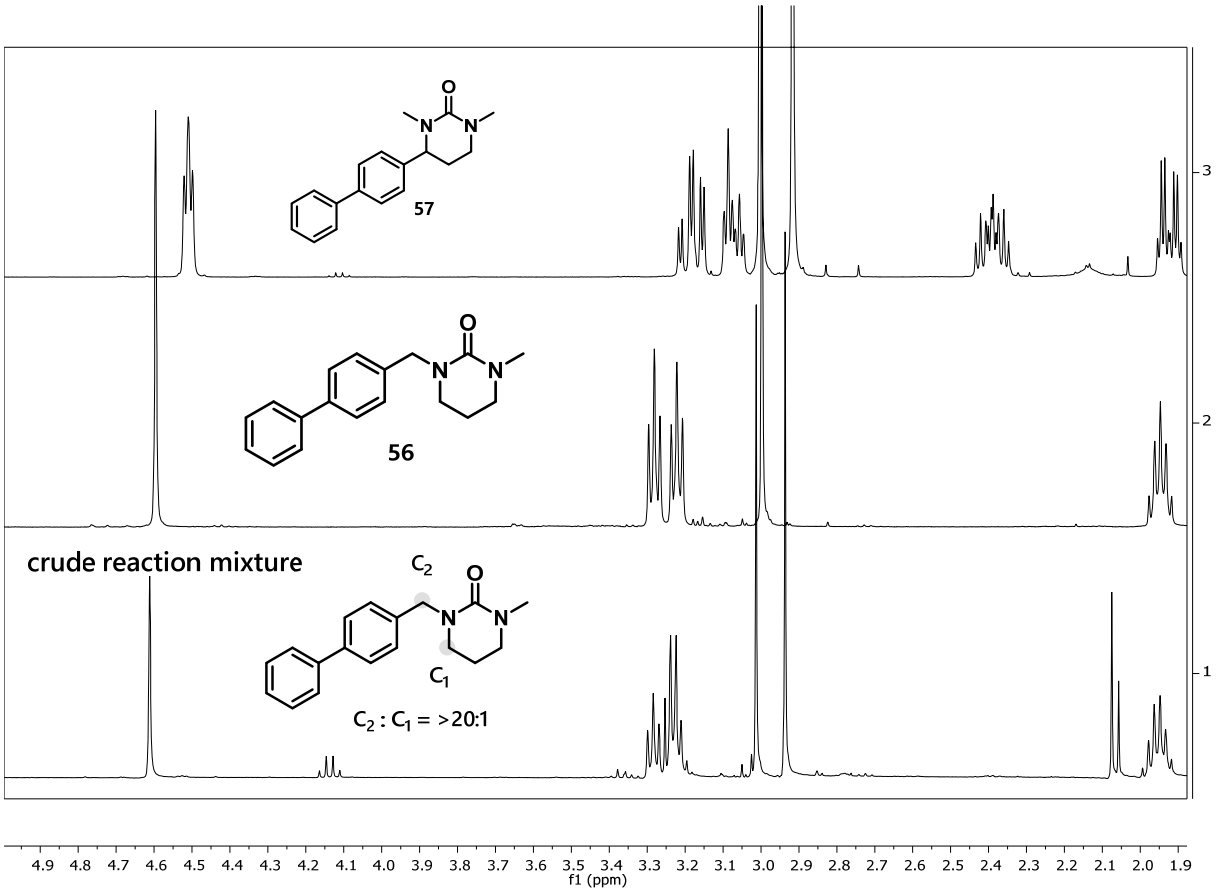

7.59
7.53
7.45
7.41
7.36
7.33
7.26
4.60
3.30
3.28
3.27
3.24
3.22
3.21
3.00
1.98
1.96
1.95
1.93
1.92
O
N
N
56
4.17
2.08
2.94
2.00
4.10
2.97
2.07
f1 (ppm)

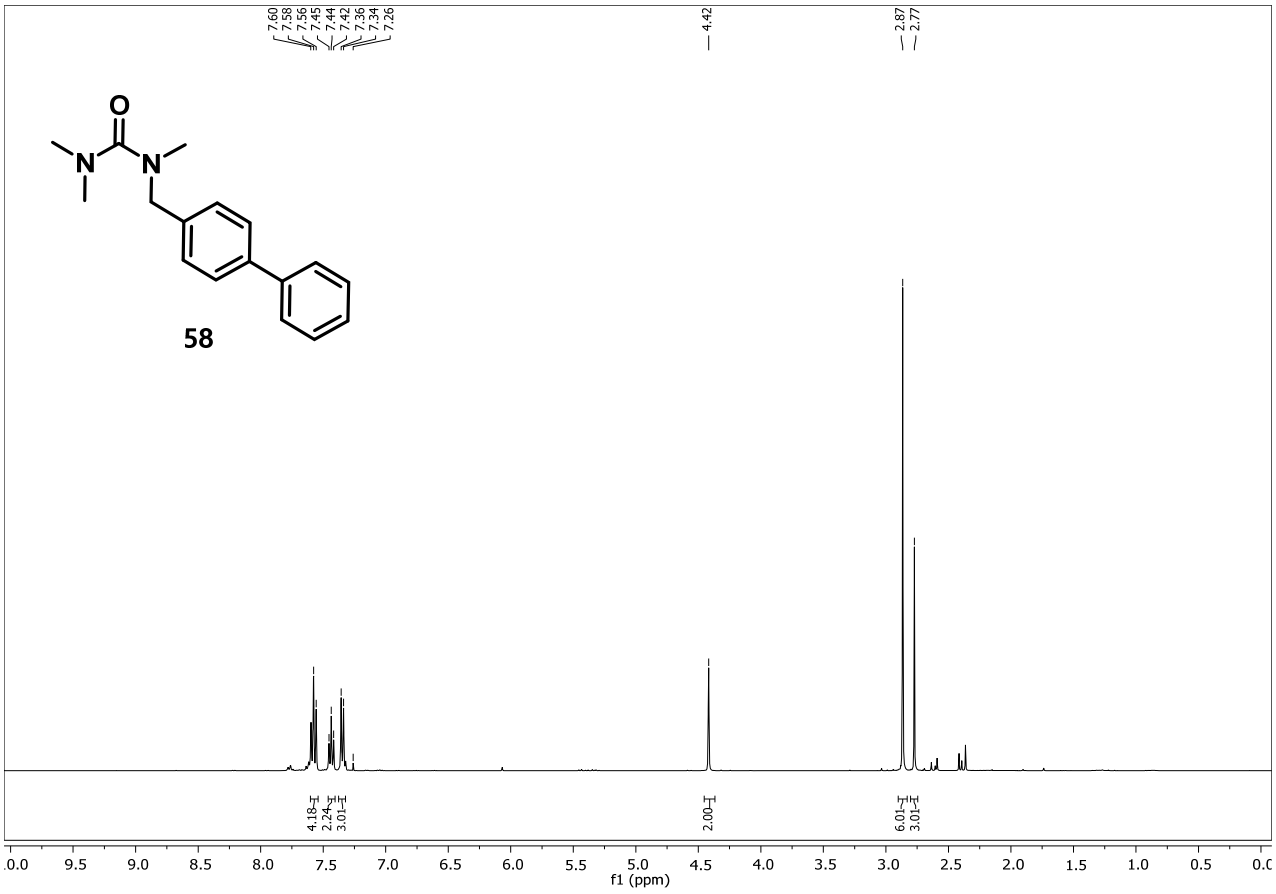

156.71
141.09
140.13
137.87
128.87
128.44
127.34
127.30
127.19
77.16
51.17
48.07
45.43
36.03
22.43
O
N
N
56
f1 (ppm)

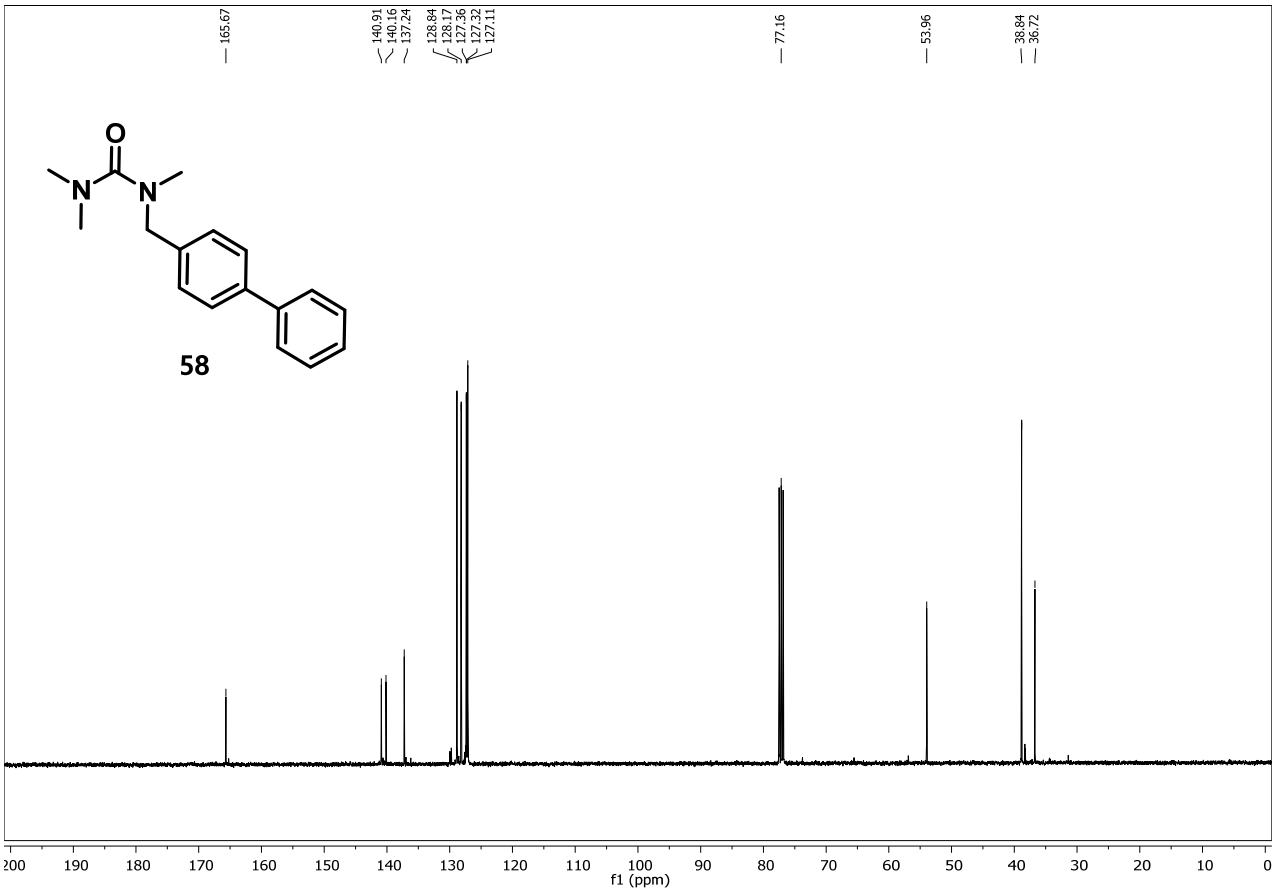

7.59
7.57
7.45
7.43
7.41
7.36
7.36
7.34
7.32
7.26
7.24
7.22
4.52
4.51
4.50
3.22
3.21
3.19
3.18
3.16
3.15
3.10
3.09
3.08
3.07
3.06
3.05
3.00
2.92
2.43
2.42
2.41
2.40
2.39
2.39
2.38
2.37
2.36
2.35
1.95
1.94
1.94
1.93
1.92
1.91
1.90
1.89
O
N
N
57
3.98
2.00
0.97
2.06
1.00
1.02
1.02
2.97
2.99
1.01
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

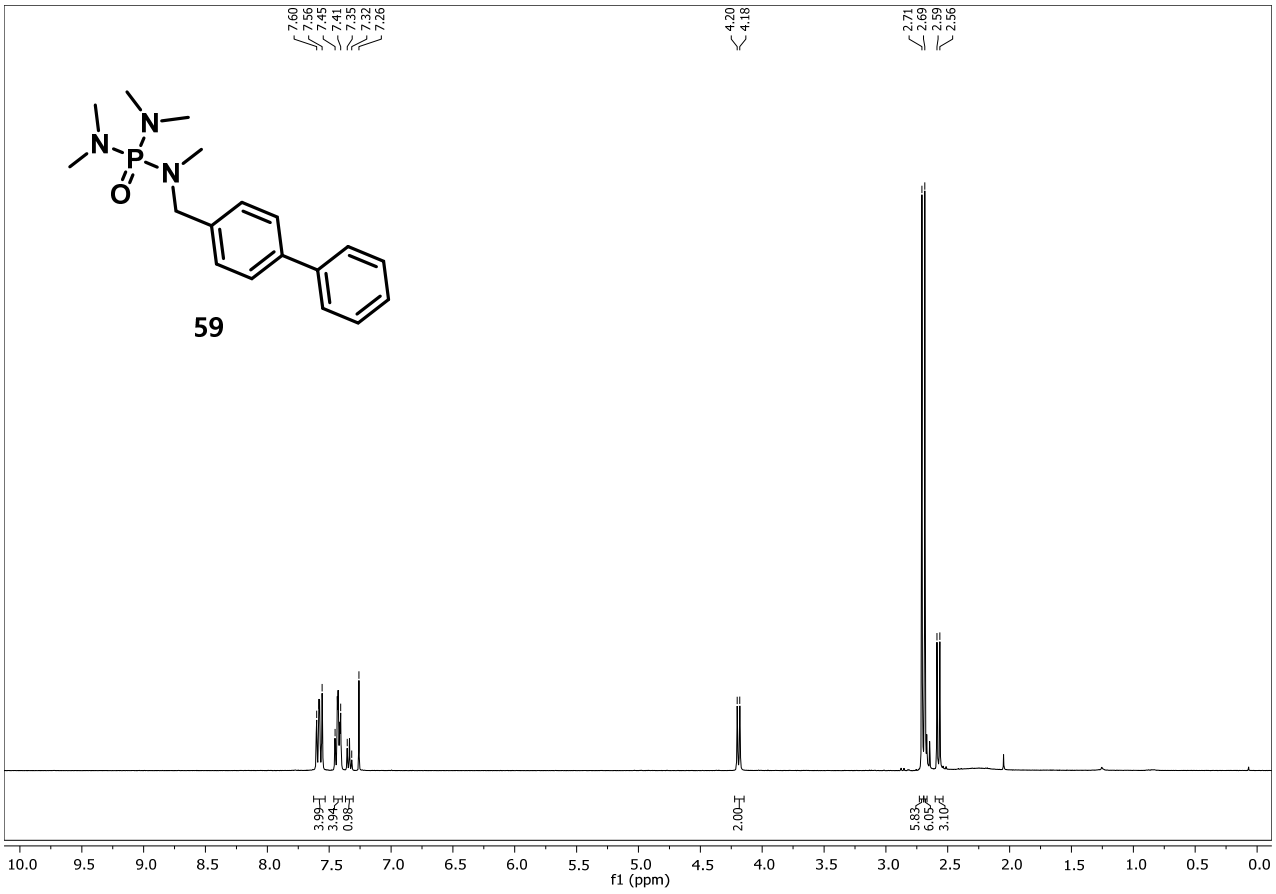

156.91
140.69
140.62
140.52
128.88
127.51
127.46
127.11
126.73
77.16
61.14
44.08
35.97
34.98
29.91
O
N
N
57
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

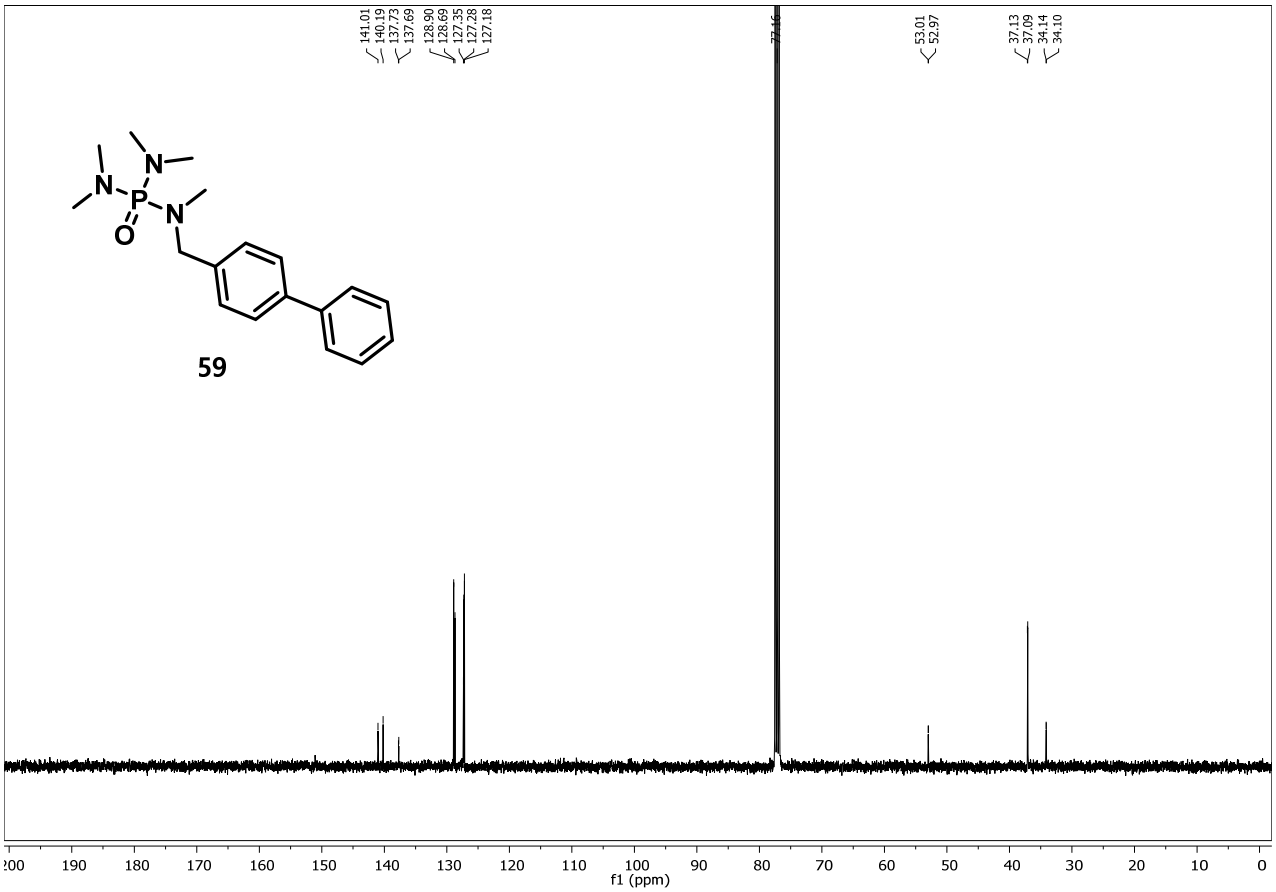

54
55
crude reaction mixture
C2
C1
C2 : C1 = >20:1
3
2
1
5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7
f1 (ppm)

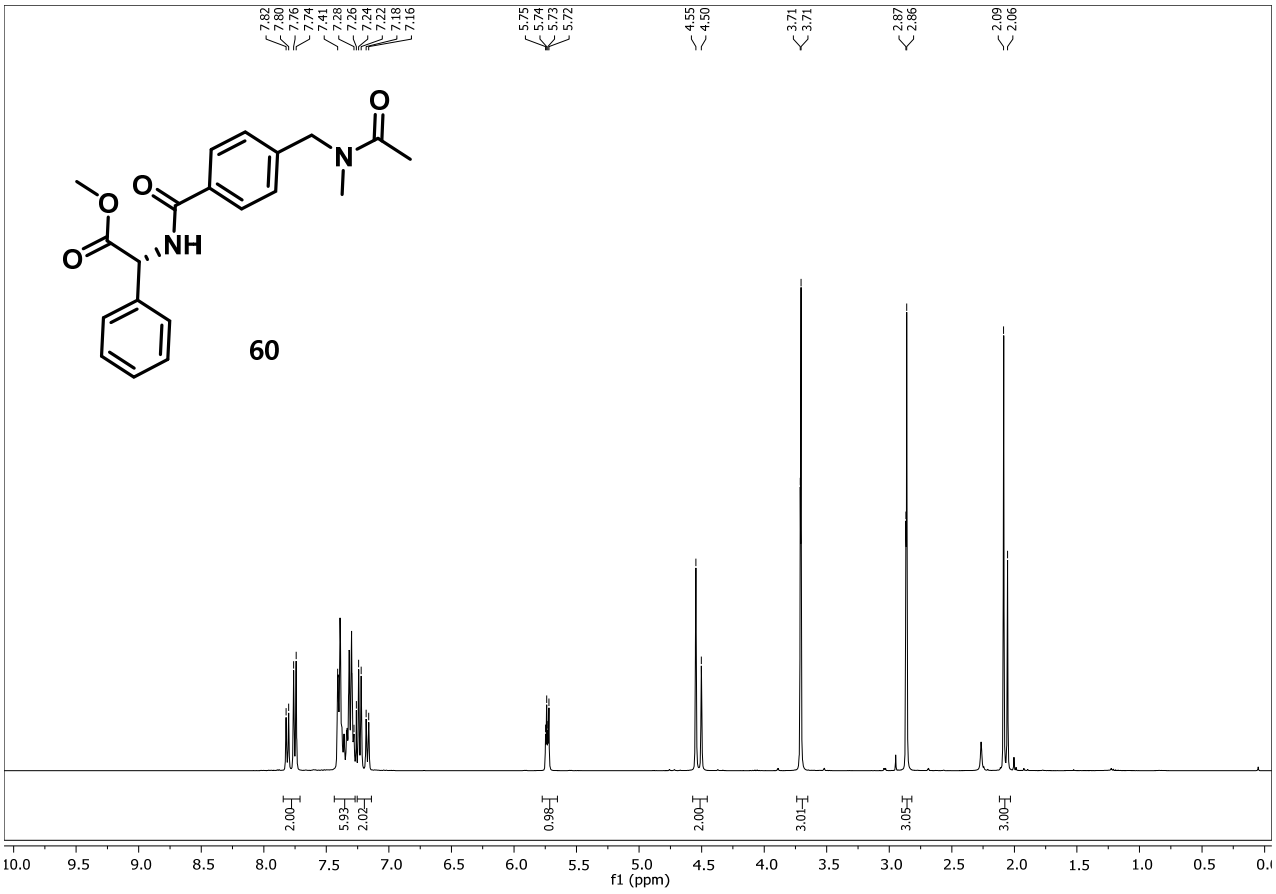

57
56
crude reaction mixture
C2
C1
C2 : C1 = >20:1
3
2
1
4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9
f1 (ppm)

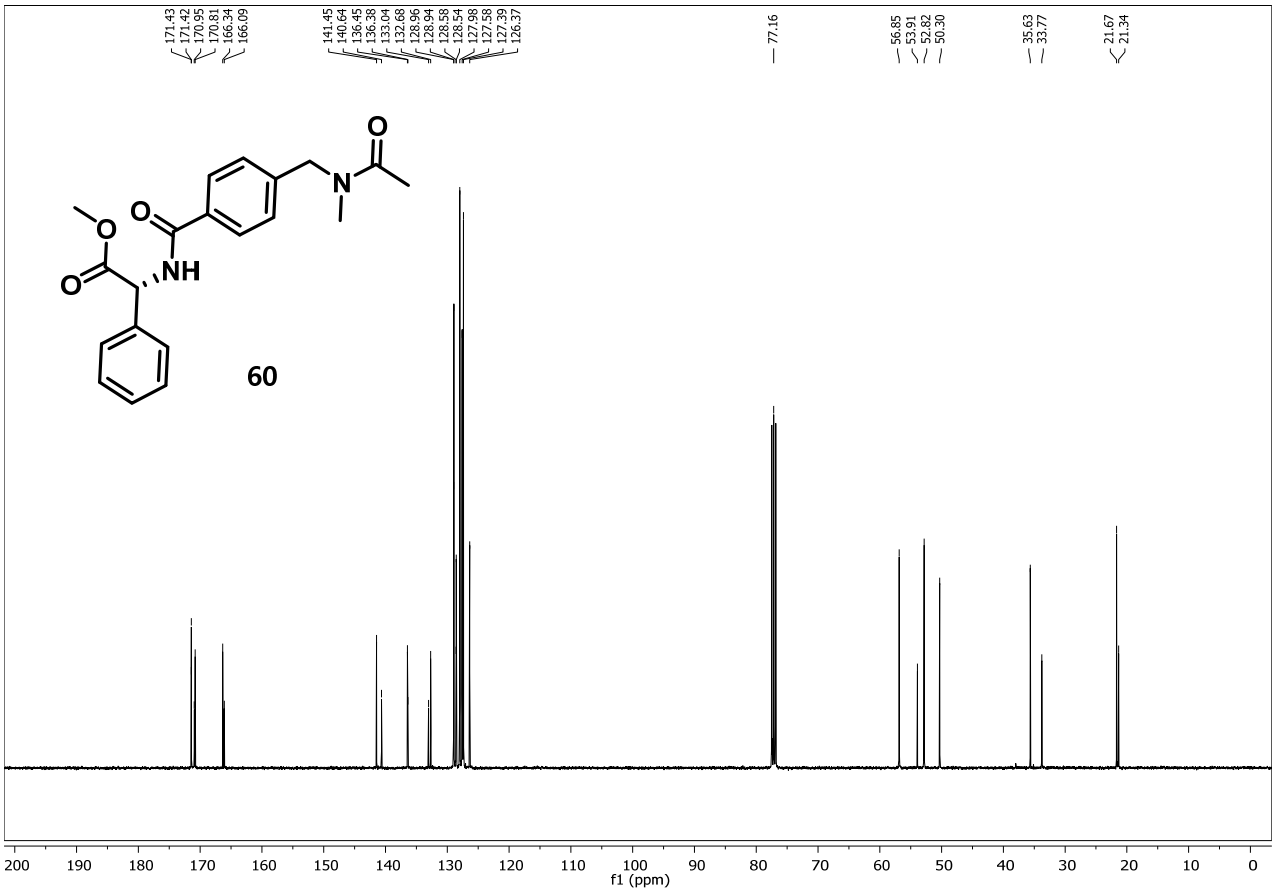

7.60
7.58
7.56
7.45
7.44
7.42
7.36
7.34
7.26
4.42
2.87
2.77
58
4.18
2.24
3.01
2.00
6.01
3.01
f1 (ppm)

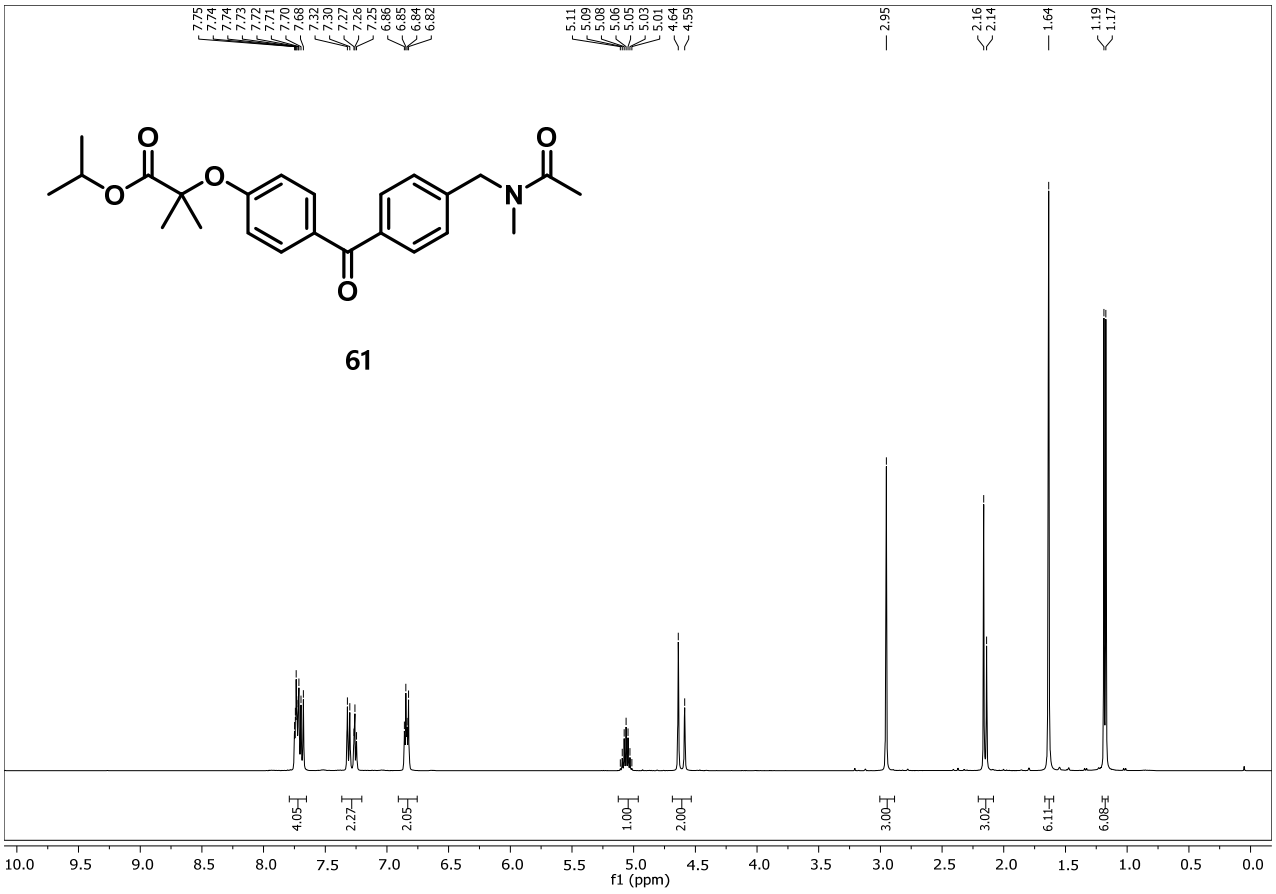

165.67
140.91
140.16
137.24
128.84
128.17
127.36
127.32
127.11
77.16
53.96
38.84
36.72
58
f1 (ppm)

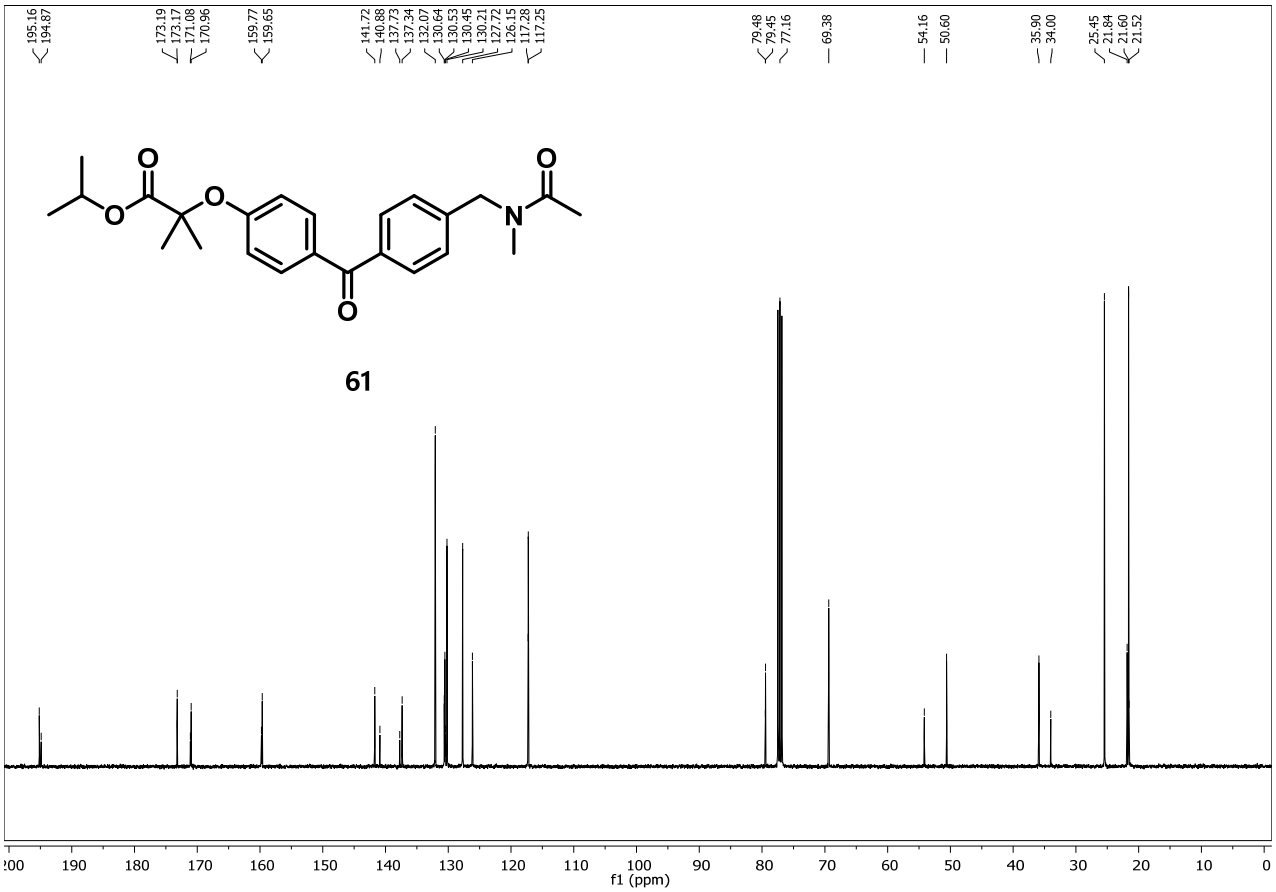

7.60
7.56
7.45
7.41
7.35
7.32
7.26
4.20
4.18
2.71
2.69
2.59
2.56
59
3.99
3.94
0.98
2.00
5.83
6.05
3.10
f1 (ppm)

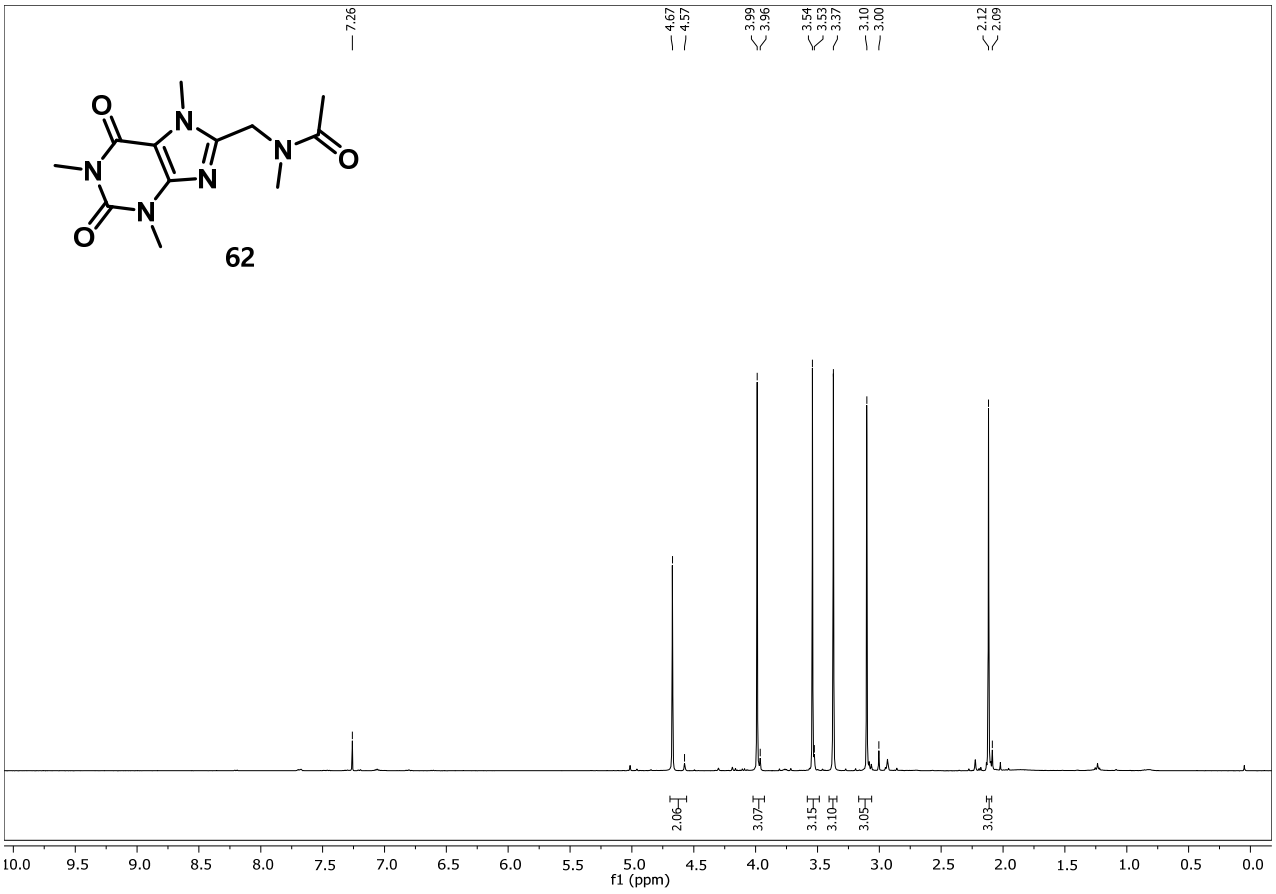

141.01
140.19
137.73
137.69
128.90
128.69
127.35
127.28
127.18
77.16
53.01
52.97
37.13
37.09
34.14
34.10
59
f1 (ppm)

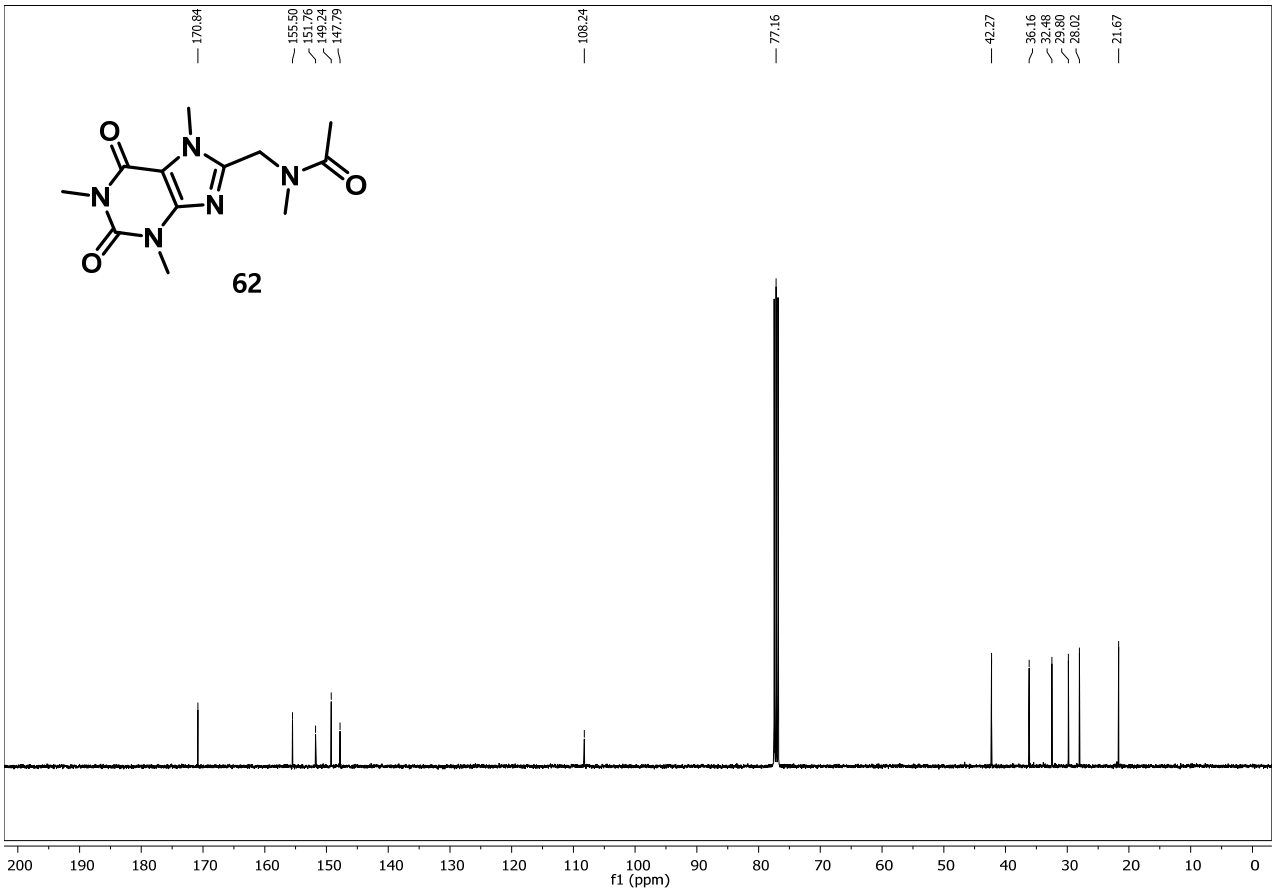

7.82
7.80
7.76
7.74
7.41
7.28
7.26
7.24
7.22
7.18
7.16
5.75
5.74
5.73
5.72
4.55
4.50
3.71
3.71
2.87
2.86
2.09
2.06
O
N
O
O
O
NH
60
2.00
5.93
2.02
0.98
2.00
3.01
3.05
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

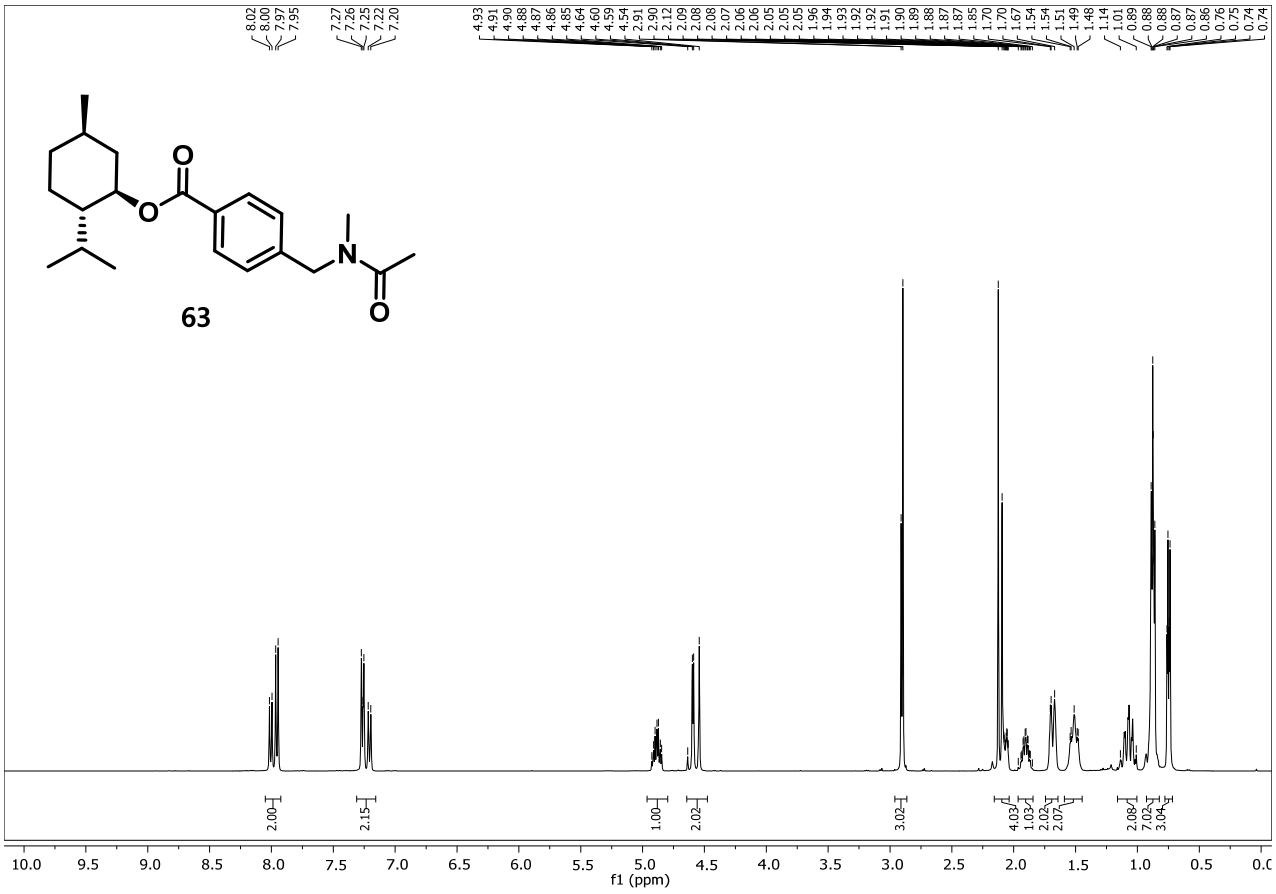

171.43
171.42
170.95
170.81
166.34
166.09
141.45
140.64
136.45
136.38
133.04
132.68
128.96
128.94
128.58
128.54
127.98
127.58
127.39
126.37
77.16
56.85
53.91
52.82
50.30
35.63
33.77
21.67
21.34
O
N
O
O
O
NH
60
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

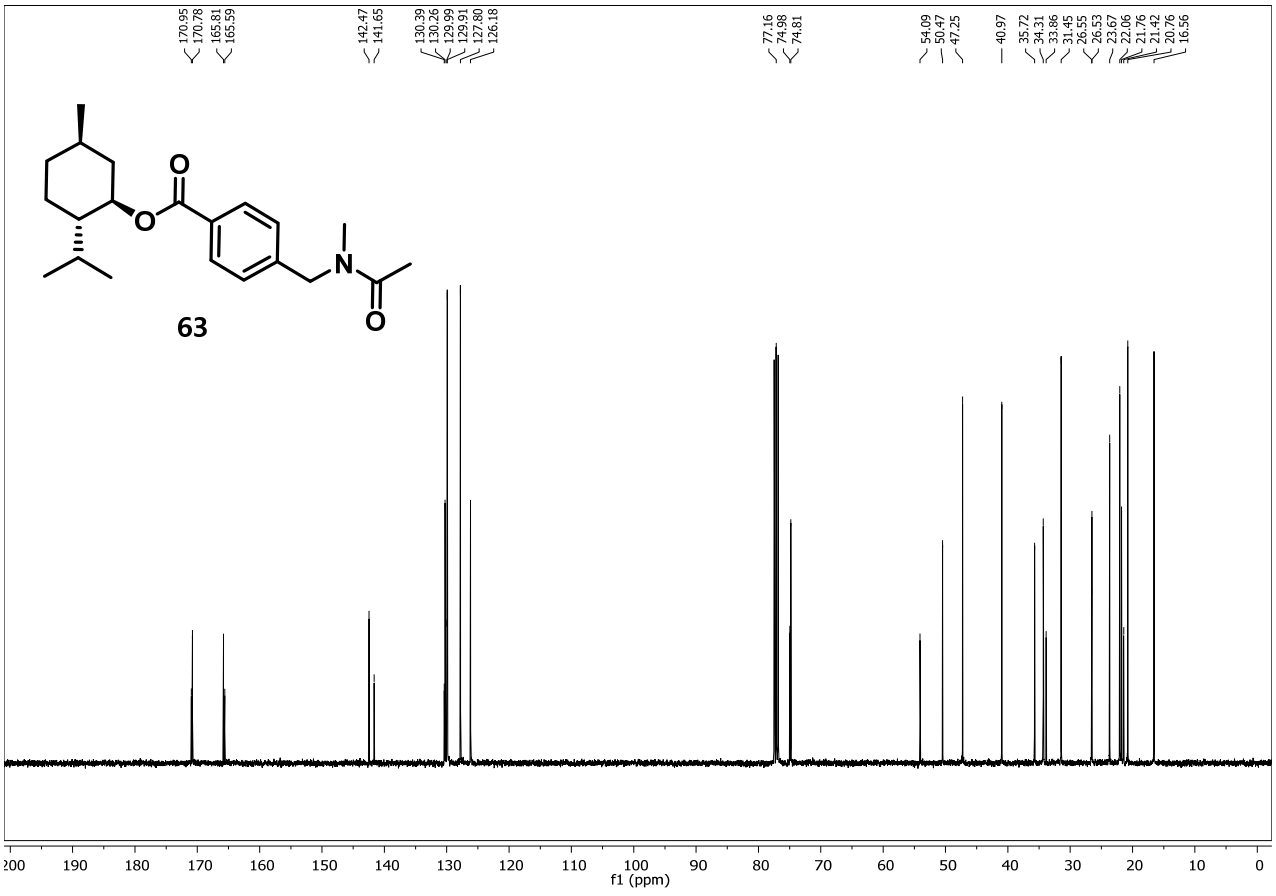

7.75
7.74
7.74
7.73
7.72
7.71
7.70
7.68
7.32
7.30
7.27
7.26
7.25
6.86
6.85
6.84
6.82
5.11
5.09
5.08
5.06
5.05
5.03
5.01
4.64
4.59
2.95
2.16
2.14
1.64
1.19
1.17
O
O
O
O
N
O
61
4.05
2.27
2.05
1.00
2.00
3.00
3.02
6.11
6.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

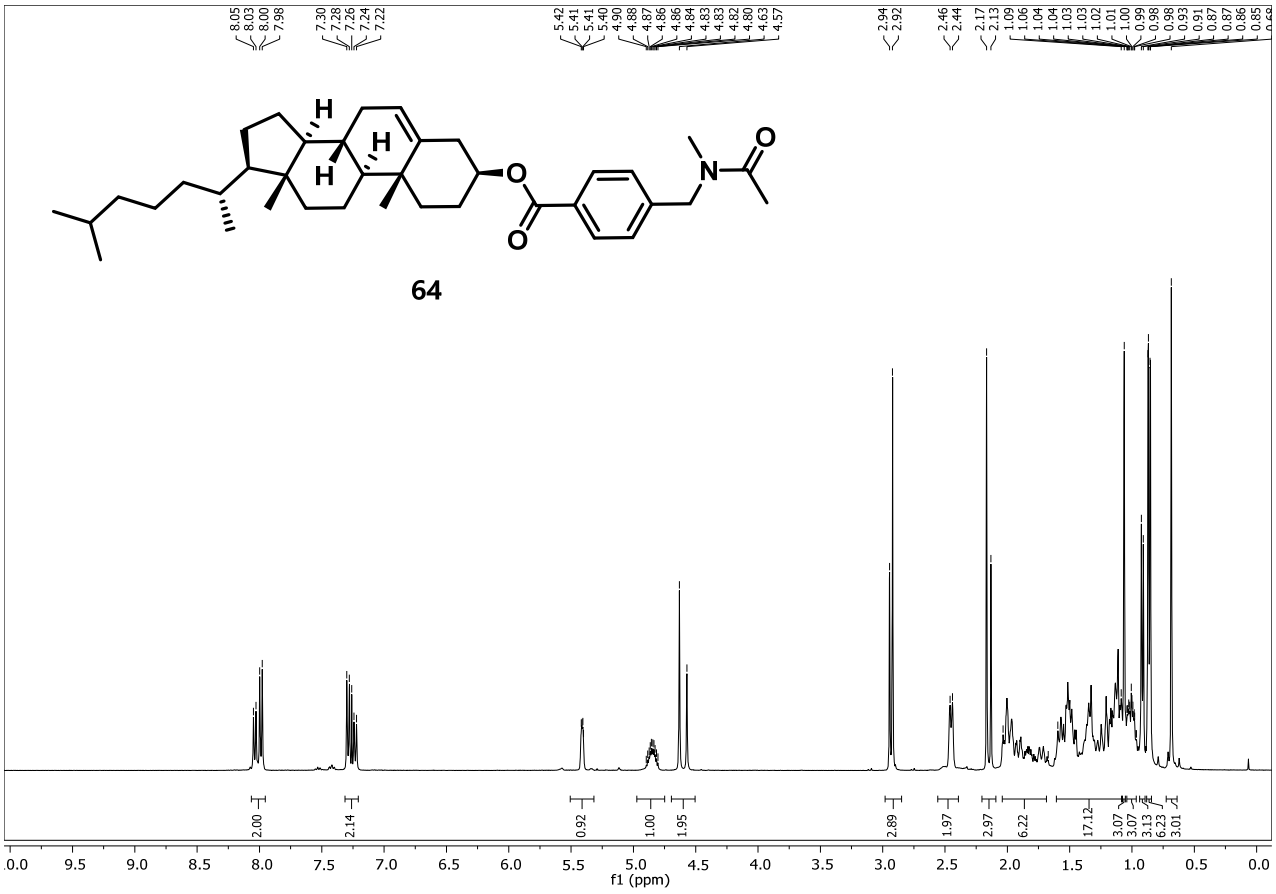

195.16
194.87
173.19
173.17
171.08
170.96
159.77
159.65
141.72
140.88
137.73
137.34
132.07
130.64
130.53
130.45
130.21
127.72
126.15
117.28
117.25
79.48
79.45
77.16
69.38
54.16
50.60
35.90
34.00
25.45
21.84
21.60
21.52
O
O
O
O
N
O
61
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

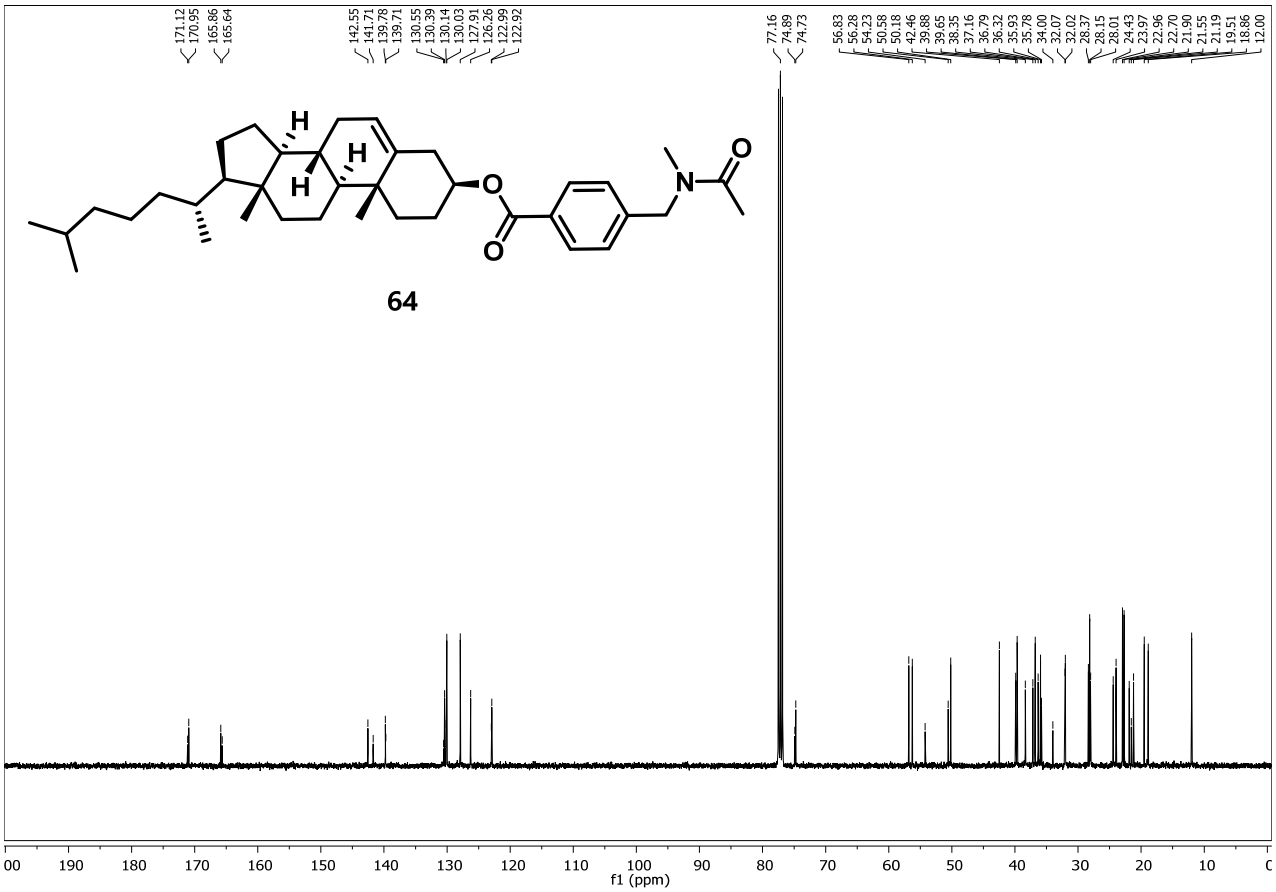

7.26
4.67
4.57
3.99
3.96
3.54
3.53
3.37
3.10
3.00
2.12
2.09
62
2.06
3.07
3.15
3.10
3.05
3.03
f1 (ppm)

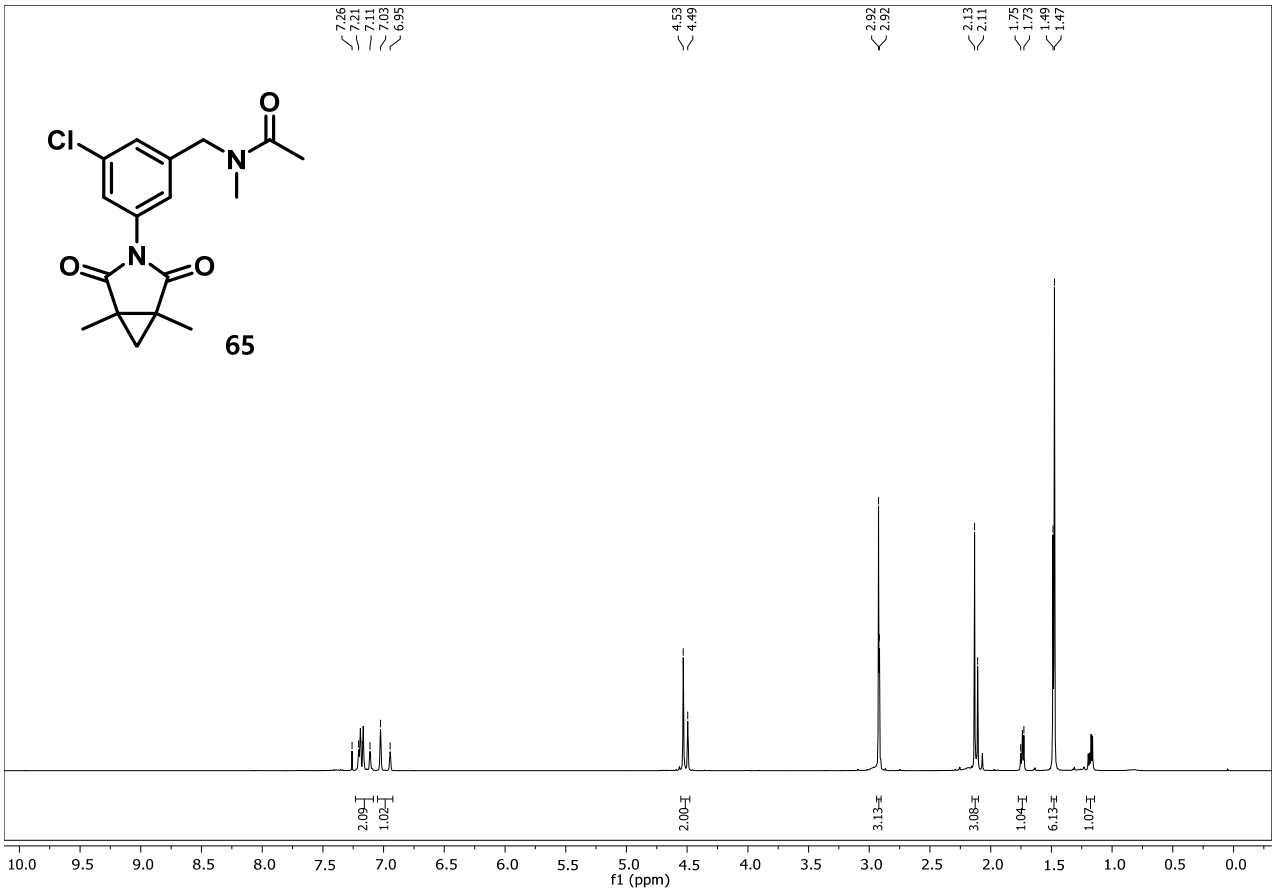

170.84
155.50
151.76
149.24
147.79
108.24
77.16
42.27
36.16
32.48
29.80
28.02
21.67
62
f1 (ppm)

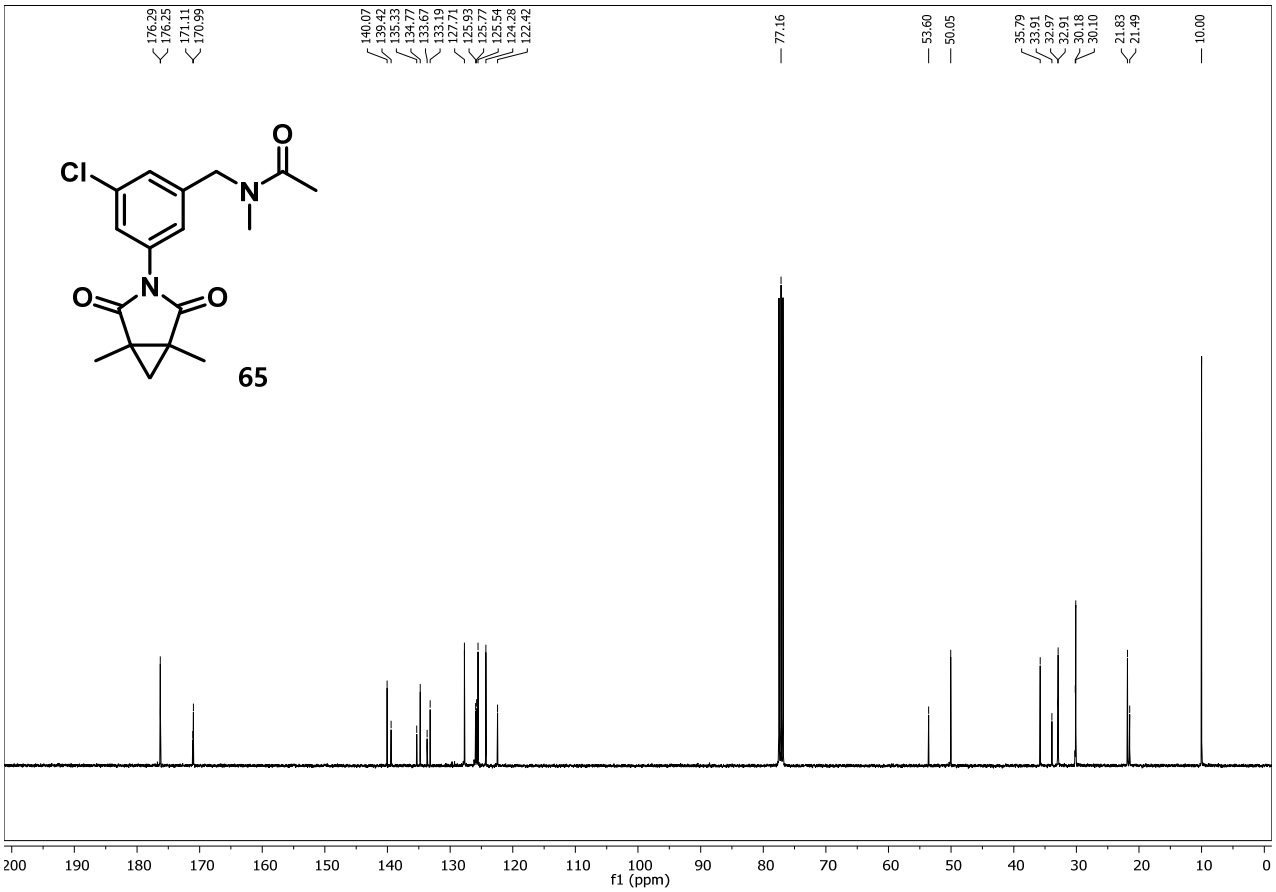

63
f1 (ppm)

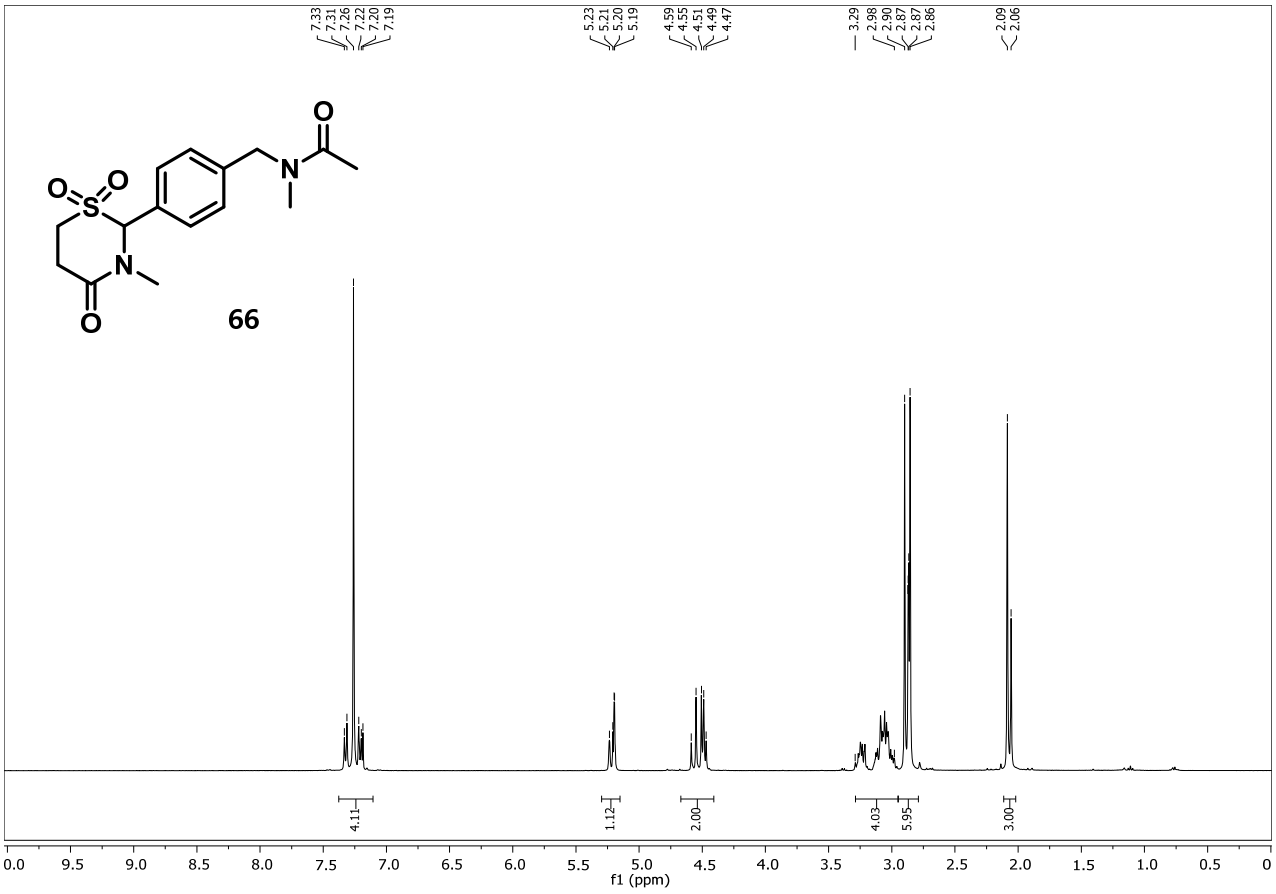

63
f1 (ppm)

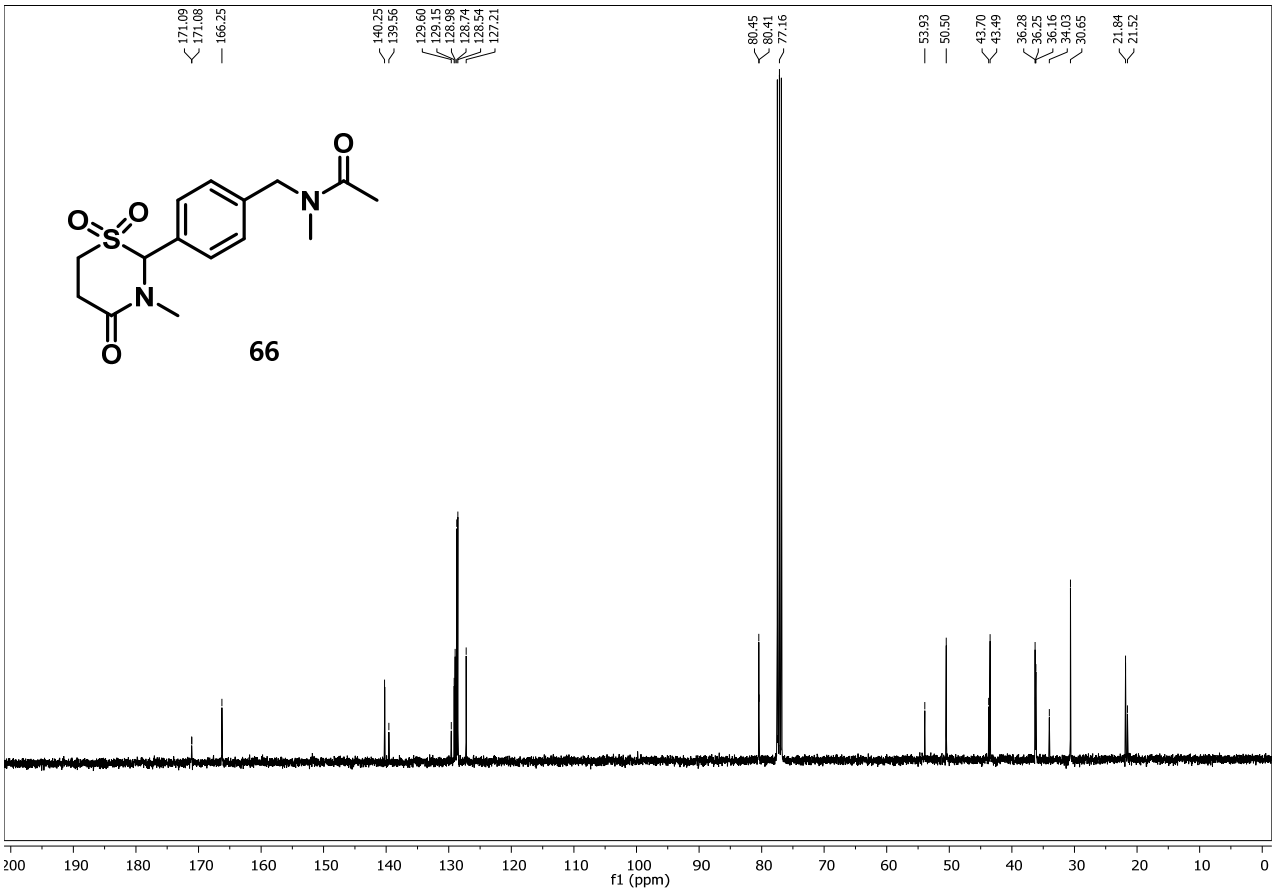

64
f1 (ppm)

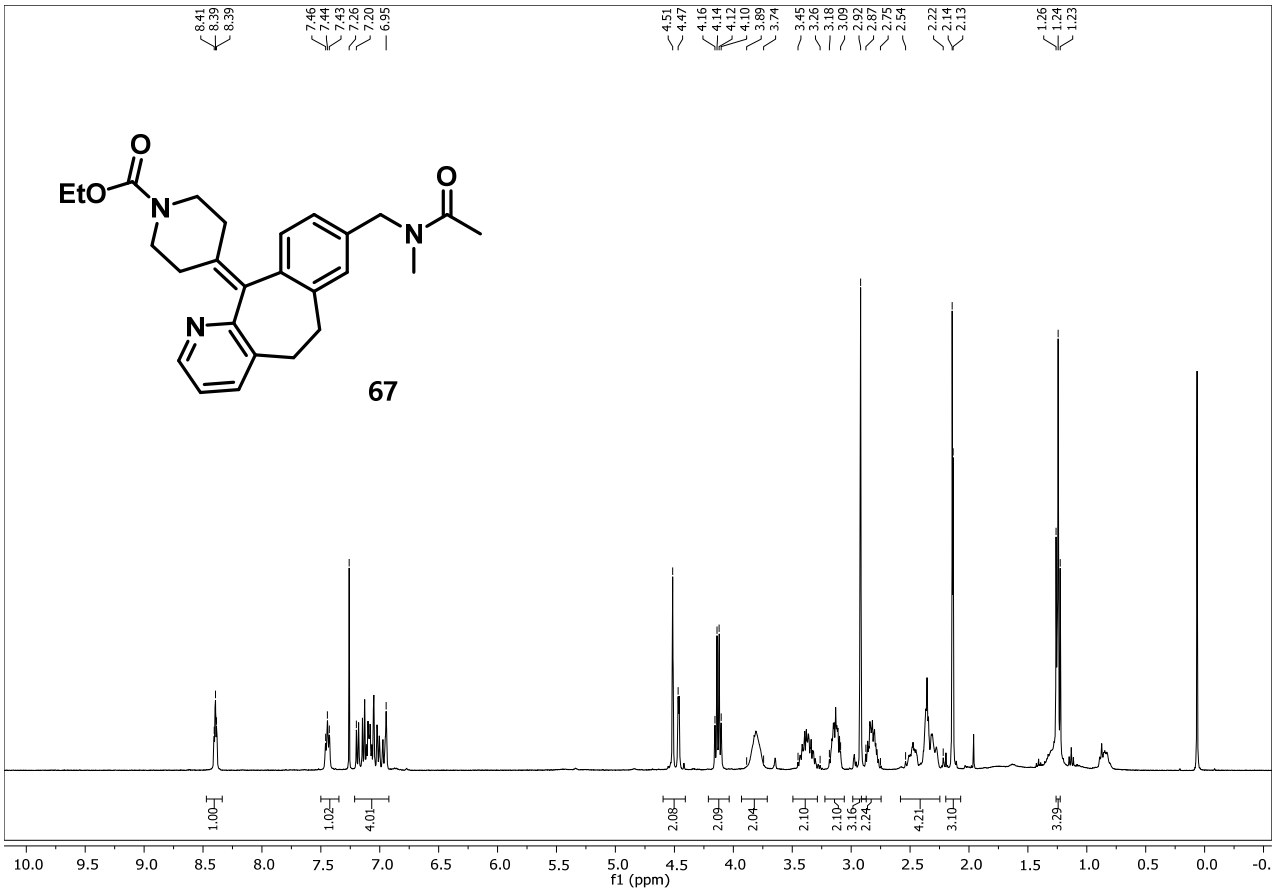

64
f1 (ppm)

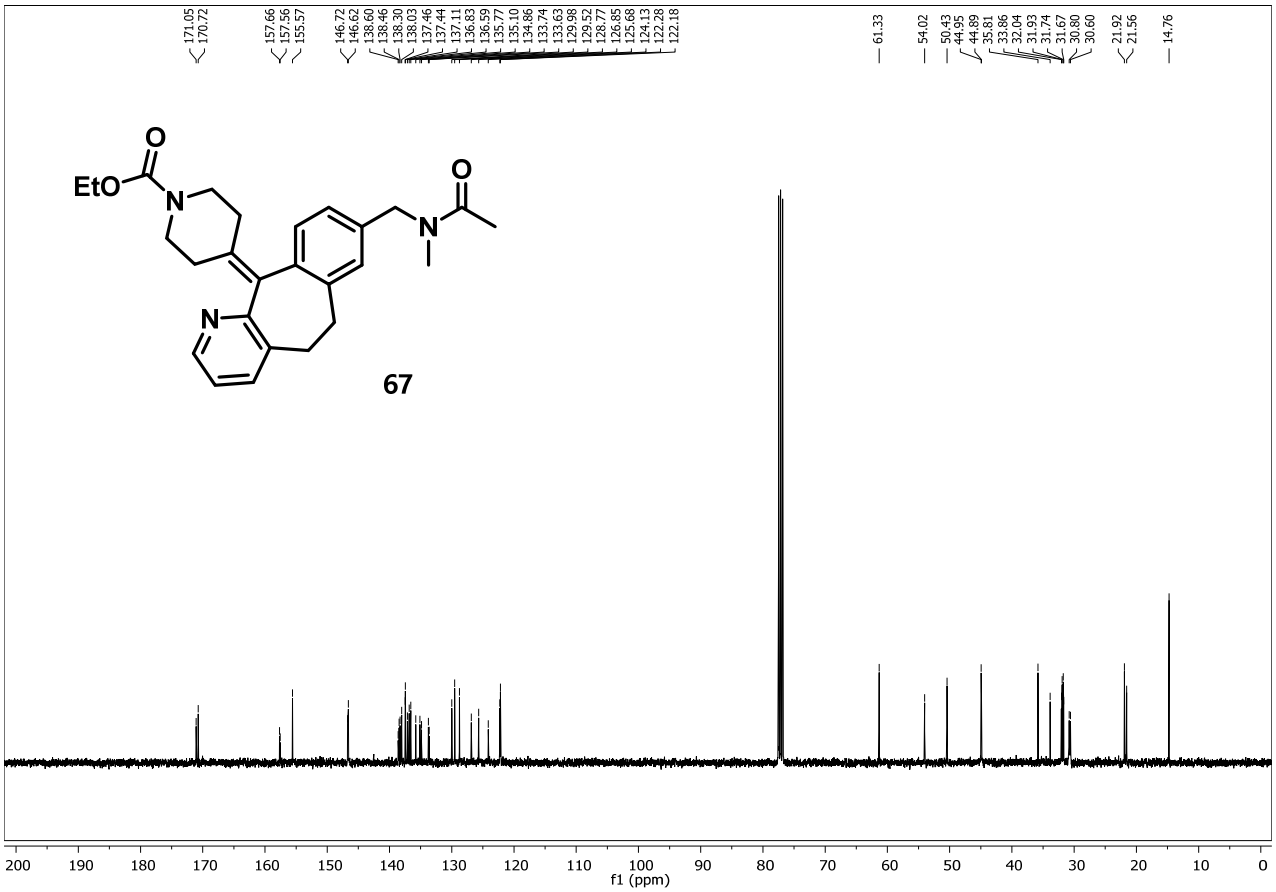

7.26
7.21
7.11
7.03
6.95
4.53
4.49
2.92
2.92
2.13
2.11
1.75
1.73
1.49
1.47
Cl
N
O
O
N
O
O
65
2.09
1.02
2.00
3.13
3.08
1.04
6.13
1.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

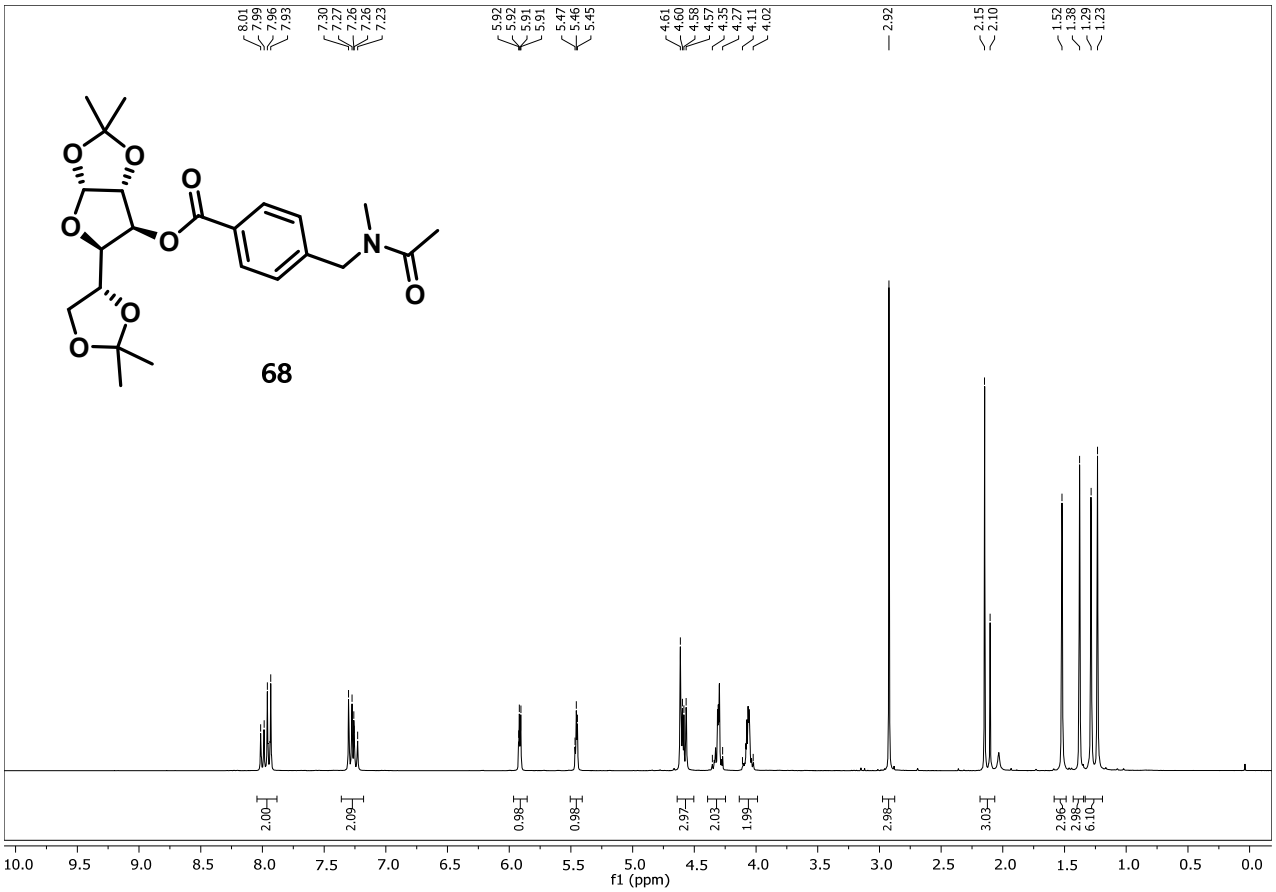

176.29
176.25
171.11
170.99
140.07
139.42
135.33
134.77
133.67
133.19
127.71
125.93
125.77
125.54
124.28
122.42
77.16
53.60
50.05
35.79
33.91
32.97
32.91
30.18
30.10
21.83
21.49
10.00
Cl
N
O
O
N
O
O
65
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

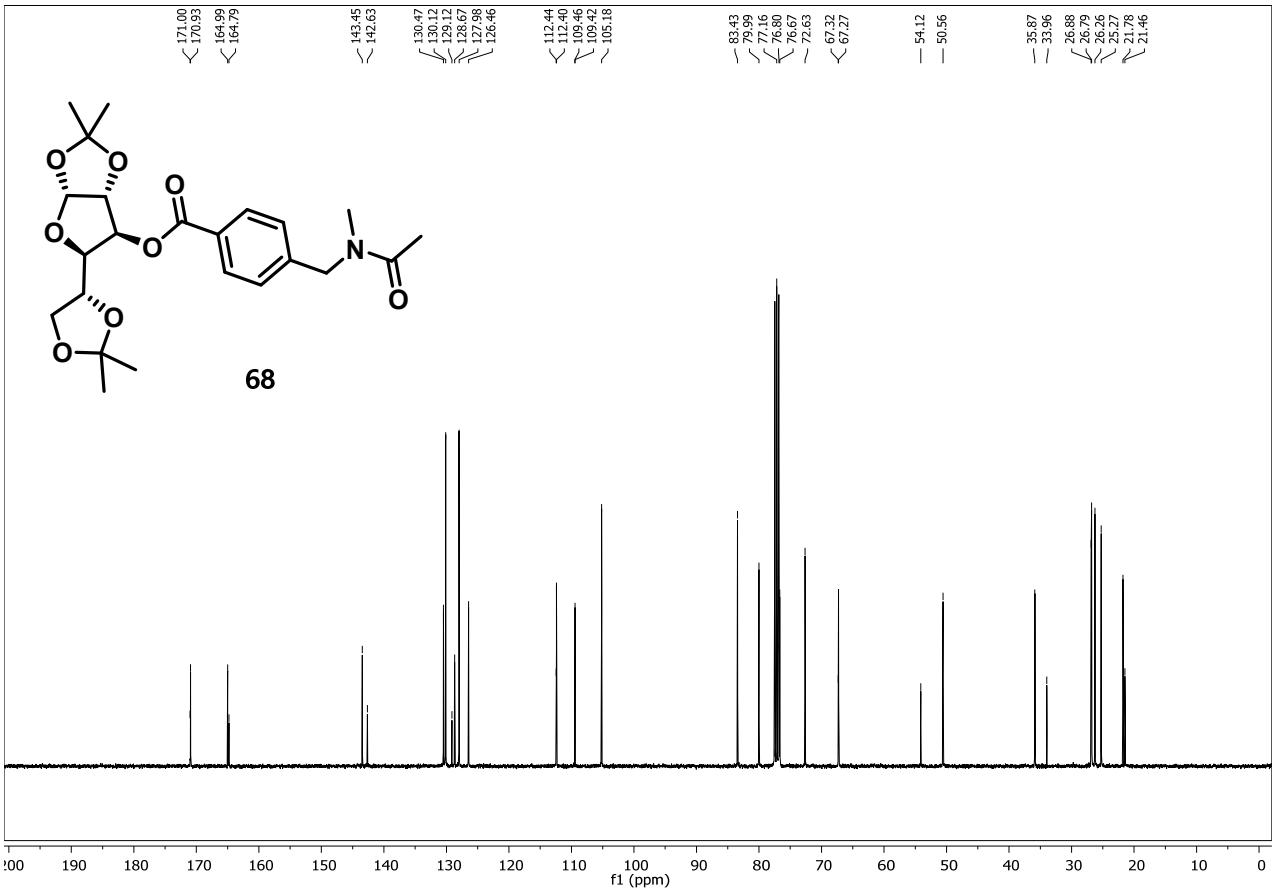

7.33
7.31
7.26
7.22
7.20
7.19
5.23
5.21
5.20
5.19
4.59
4.55
4.51
4.49
4.47
3.29
2.98
2.90
2.87
2.87
2.86
2.09
2.06
O
O
S
O
N
N
O
66
4.11
1.12
2.00
4.03
5.95
3.00
f1 (ppm)

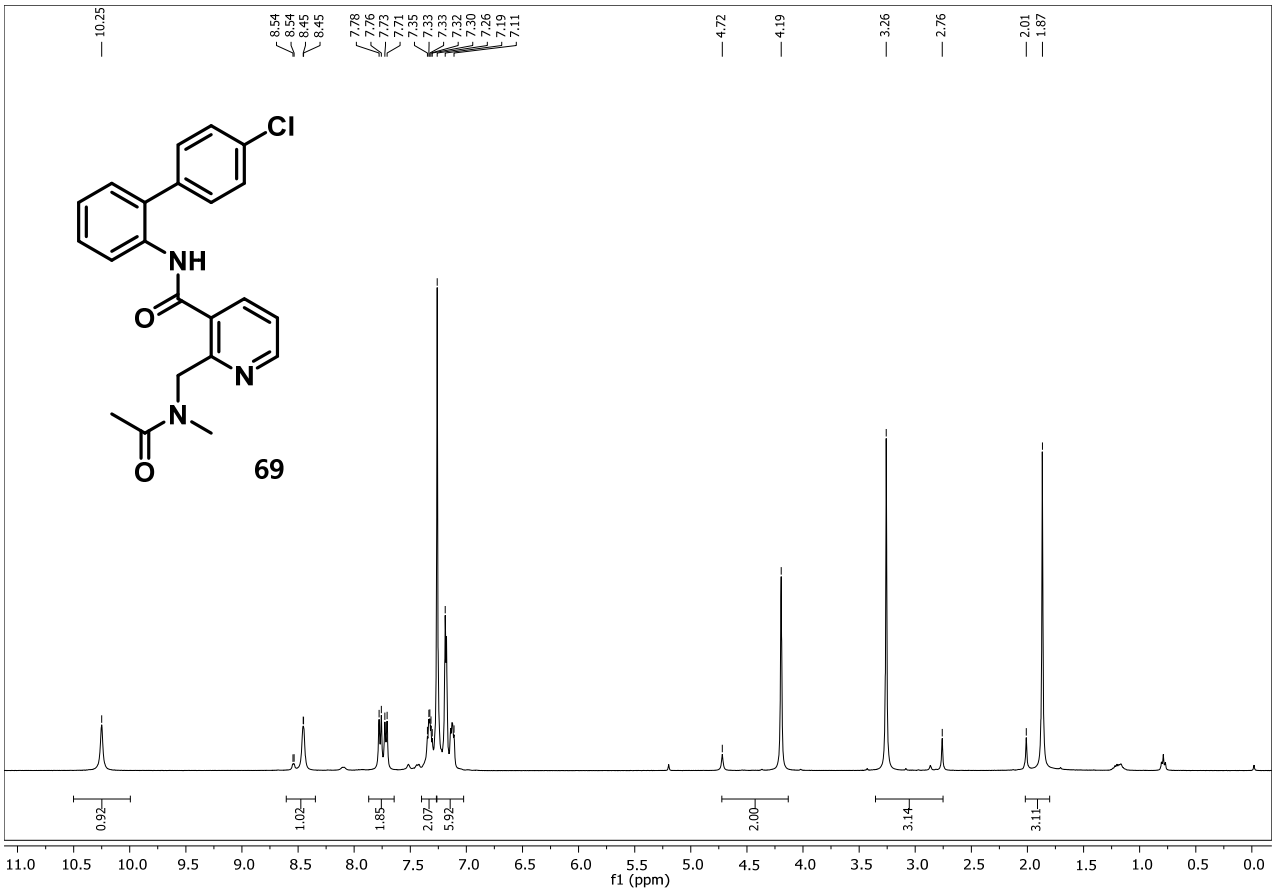

171.09
171.08
166.25
140.25
139.56
129.60
129.15
128.98
128.74
128.54
127.21
80.45
80.41
77.16
53.93
50.50
43.70
43.49
36.28
36.25
36.16
34.03
30.65
21.84
21.52
O
O
S
O
N
N
O
66
f1 (ppm)

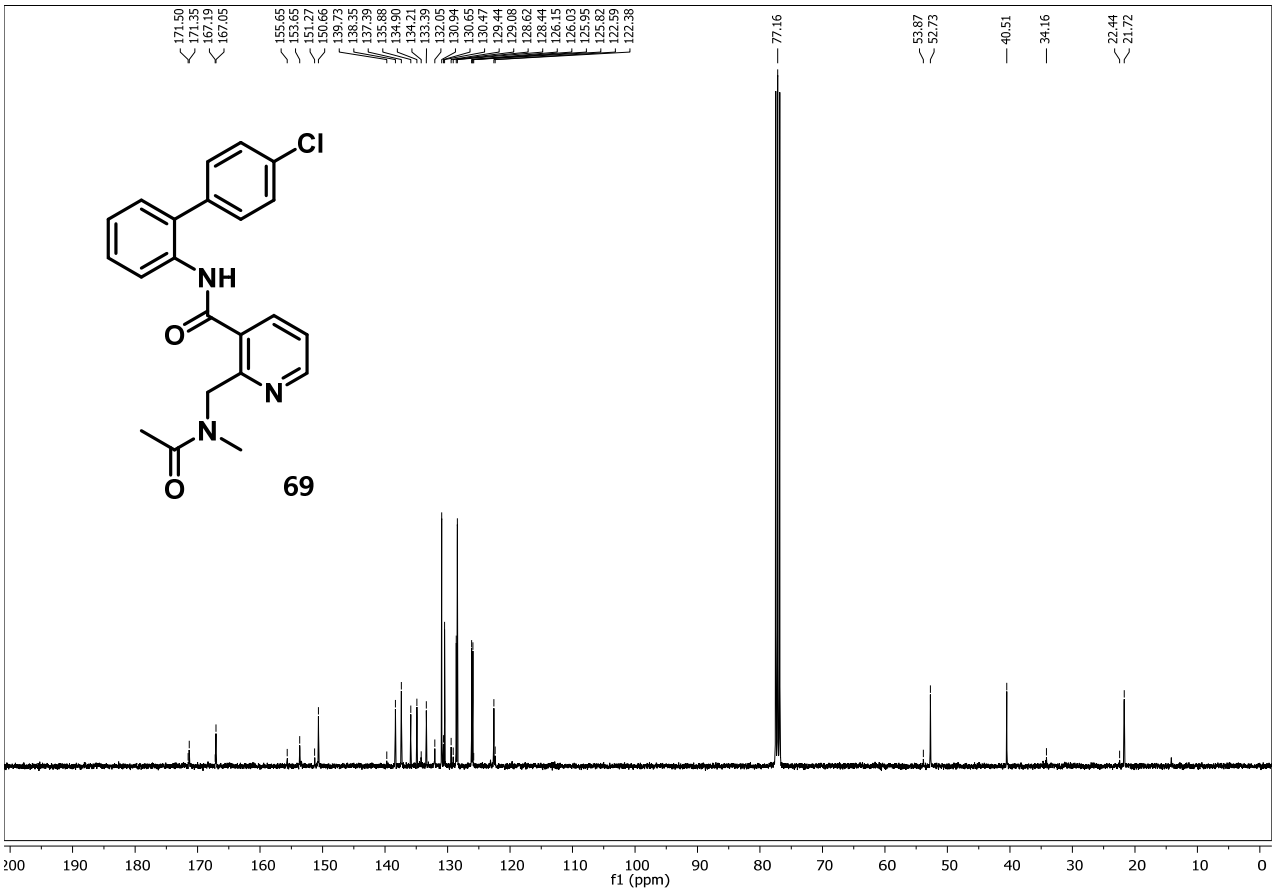

8.41
8.39
8.39
7.46
7.44
7.43
7.26
7.20
6.95
4.51
4.47
4.16
4.14
4.12
4.10
3.89
3.74
3.45
3.26
3.18
3.09
2.92
2.87
2.75
2.54
2.22
2.14
2.13
1.26
1.24
1.23
EtO
O
N
O
N
N
67
1.00
1.02
4.01
2.08
2.09
2.04
2.10
2.10
3.16
2.24
4.21
3.10
3.29
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

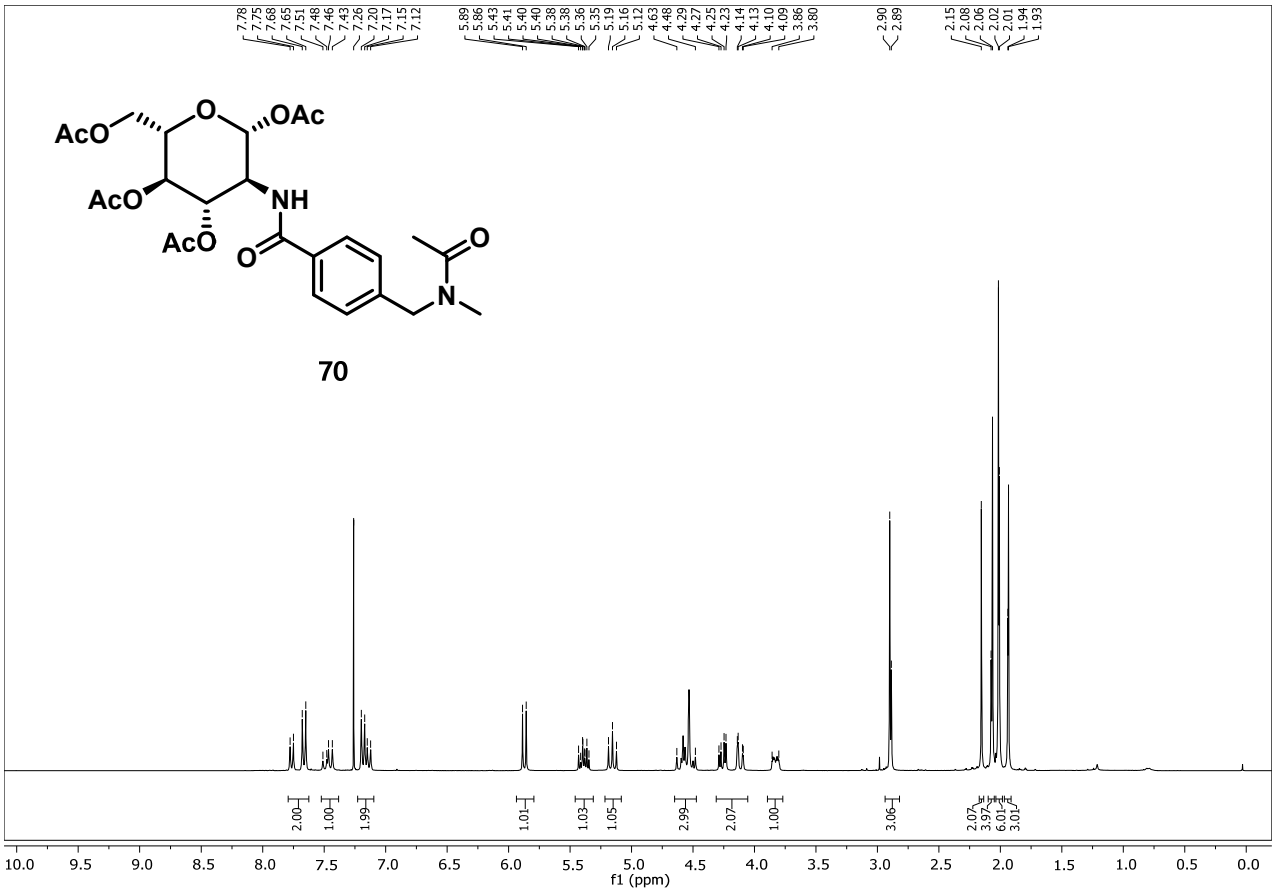

171.05
170.72
157.66
157.56
155.57
146.72
146.62
138.60
138.46
138.30
138.03
137.46
137.44
137.11
136.83
136.59
135.77
135.10
134.86
133.74
133.63
129.98
129.52
128.77
126.85
125.68
124.13
122.28
122.18
61.33
54.02
50.43
44.95
44.89
35.81
33.86
32.04
31.93
31.74
31.67
30.80
30.60
21.92
21.56
14.76
EtO
O
N
O
N
N
67
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

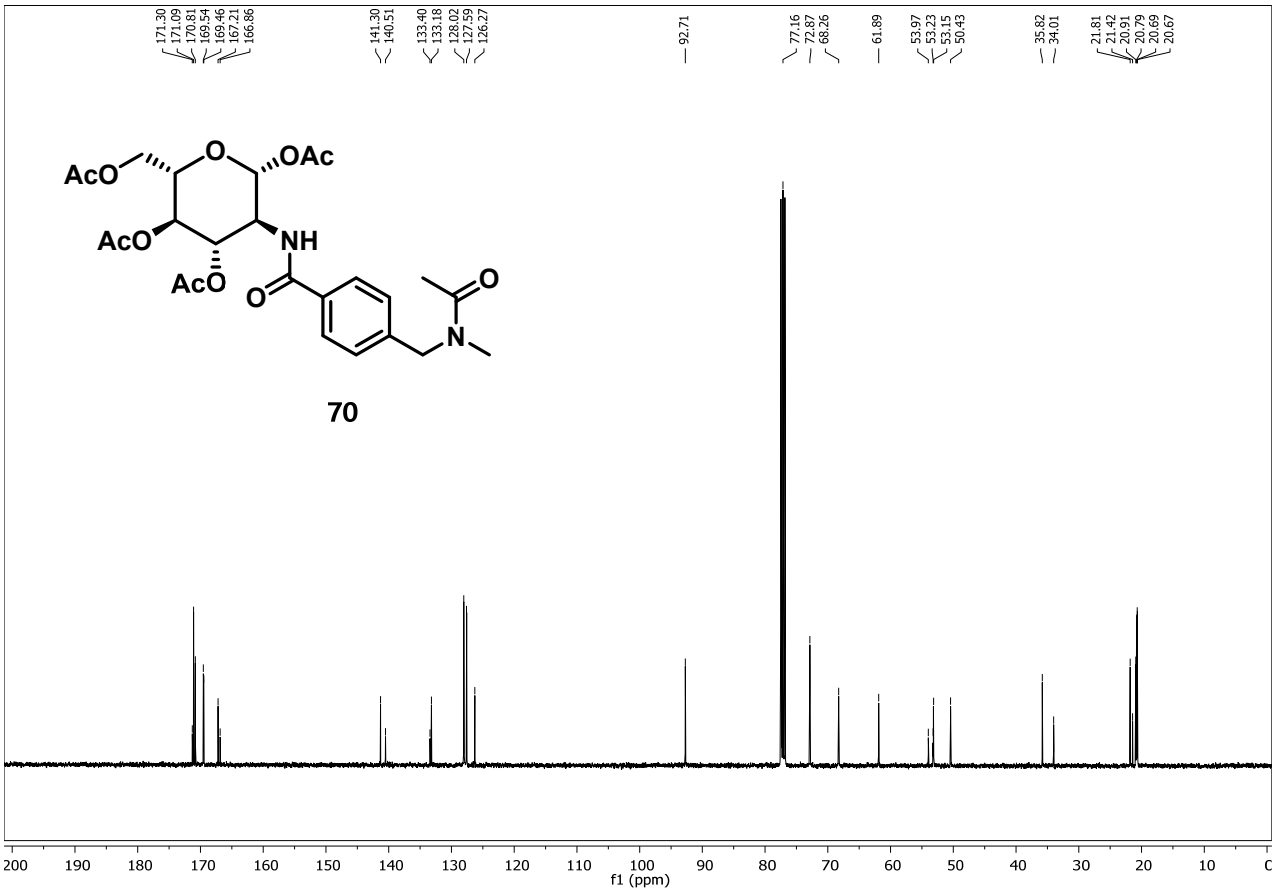

8.01
7.99
7.96
7.93
7.30
7.27
7.26
7.26
7.23
5.92
5.92
5.91
5.91
5.47
5.46
5.45
4.61
4.60
4.58
4.57
4.35
4.27
4.11
4.02
2.92
2.15
2.10
1.52
1.38
1.29
1.23
68
2.00
2.09
0.98
0.98
2.97
2.03
1.99
2.98
3.03
2.96
2.98
6.10
f1 (ppm)

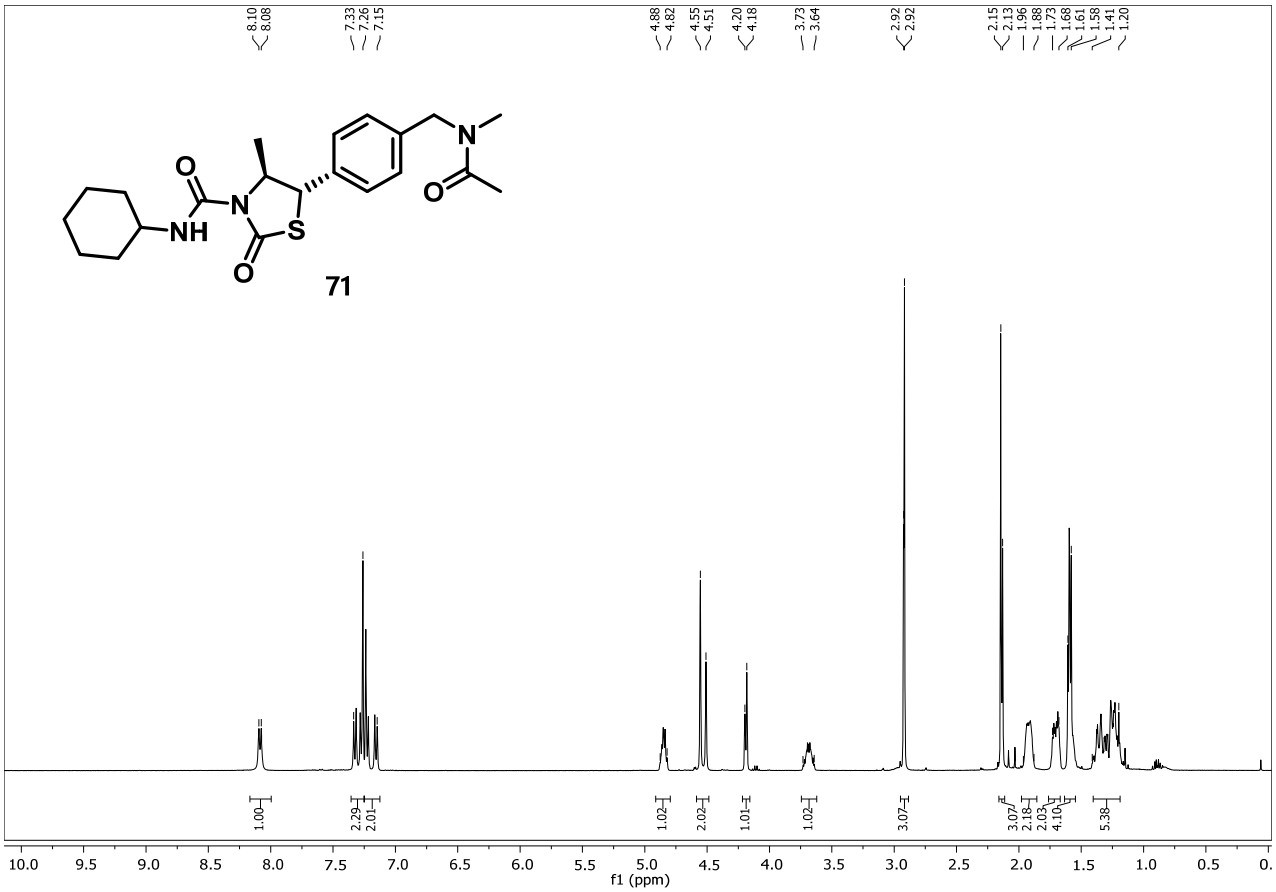

171.00
170.93
164.99
164.79
143.45
142.63
130.47
130.12
129.12
128.67
127.98
126.46
112.44
112.40
109.46
109.42
105.18
83.43
79.99
77.16
76.80
76.67
72.63
67.32
67.27
54.12
50.56
35.87
33.96
26.88
26.79
26.26
25.27
21.78
21.46
68
f1 (ppm)

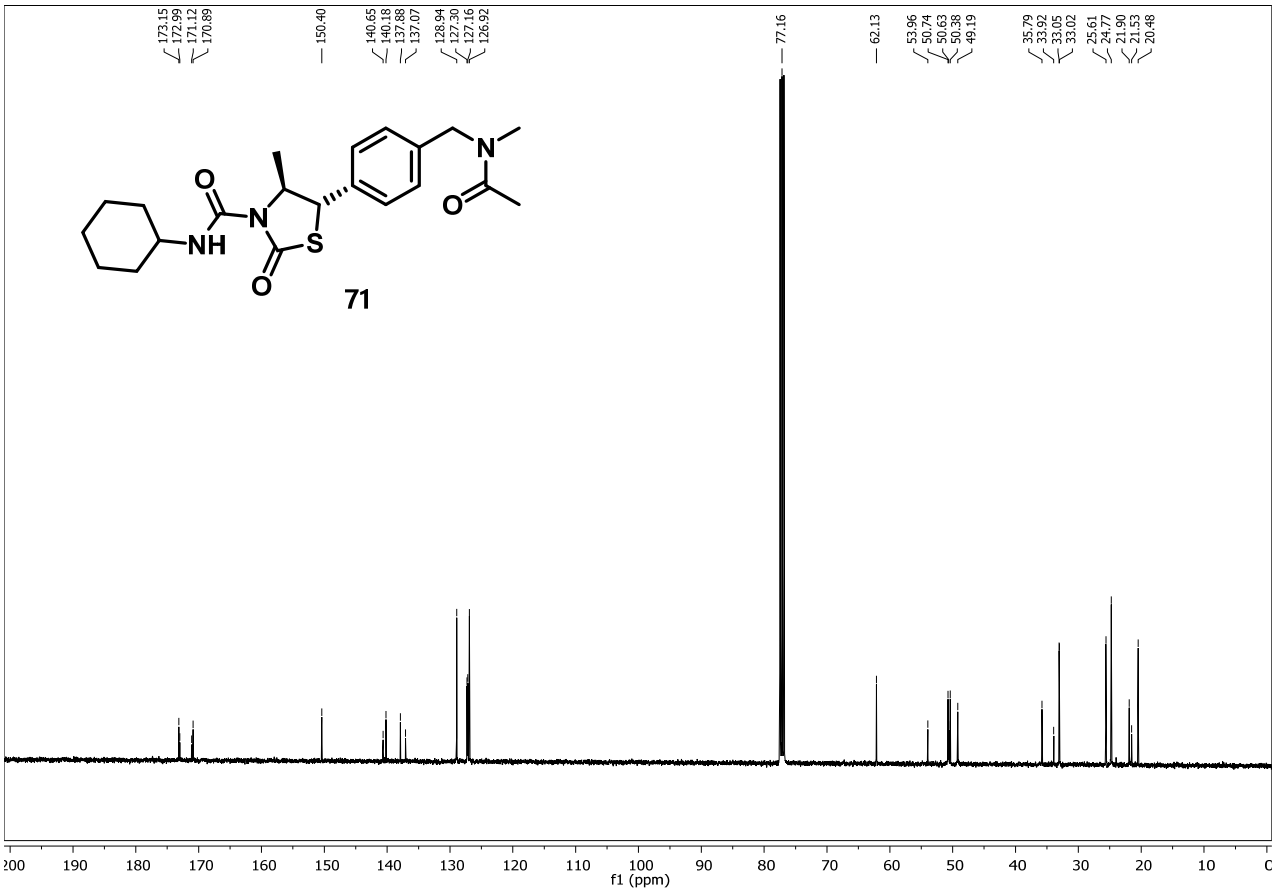

10.25
8.54
8.54
8.45
8.45
7.78
7.76
7.73
7.71
7.35
7.33
7.33
7.32
7.30
7.26
7.19
7.11
4.72
4.19
3.26
2.76
2.01
1.87
Cl
NH
O
N
N
O
69
0.92
1.02
1.85
2.07
5.92
2.00
3.14
3.11
f1 (ppm)

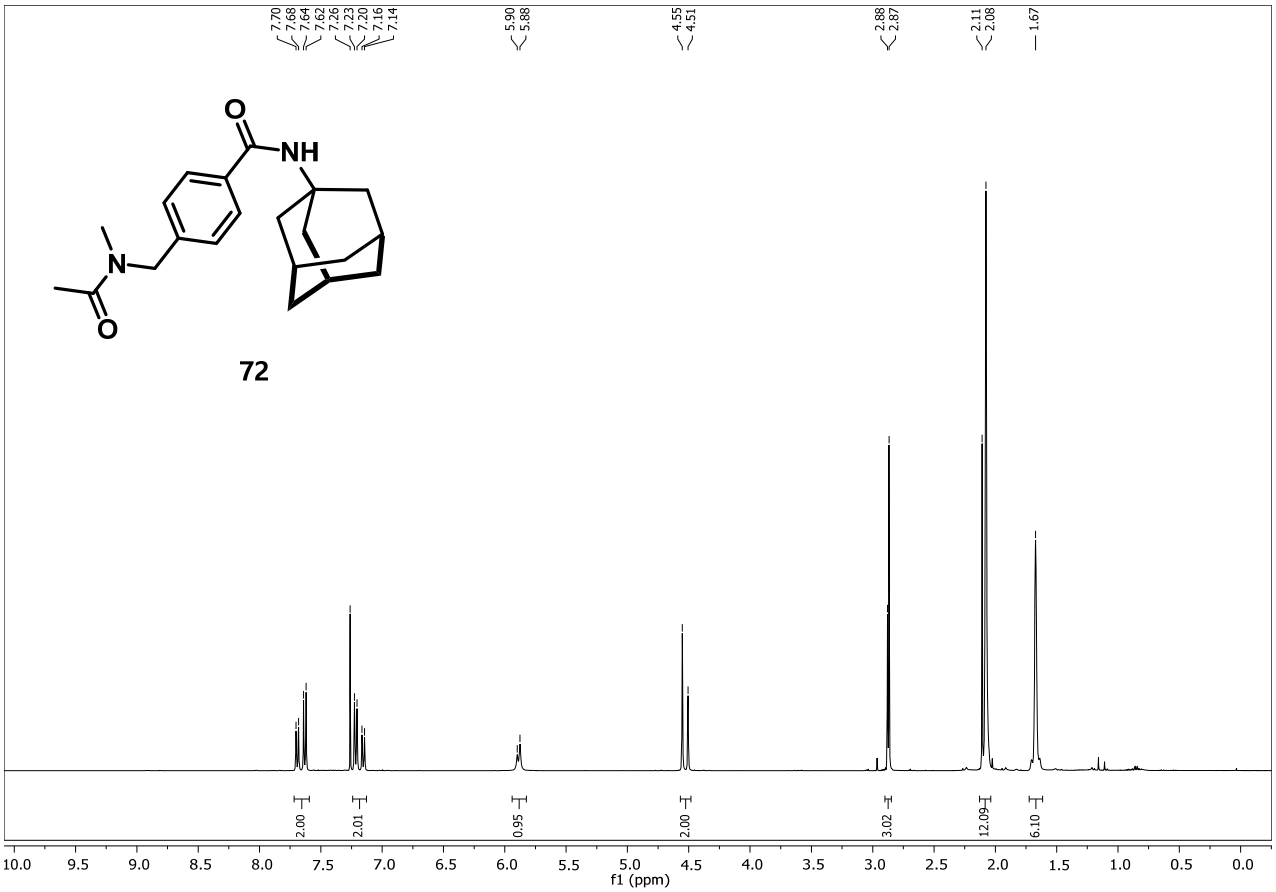

171.50
171.35
167.19
167.05
155.65
153.65
151.27
150.66
139.73
138.35
137.39
135.88
134.90
134.21
133.39
132.05
130.94
130.65
130.47
129.44
129.08
128.62
128.44
126.15
126.03
125.95
125.82
122.59
122.38
77.16
53.87
52.73
40.51
34.16
22.44
21.72
Cl
NH
O
N
N
O
69
f1 (ppm)

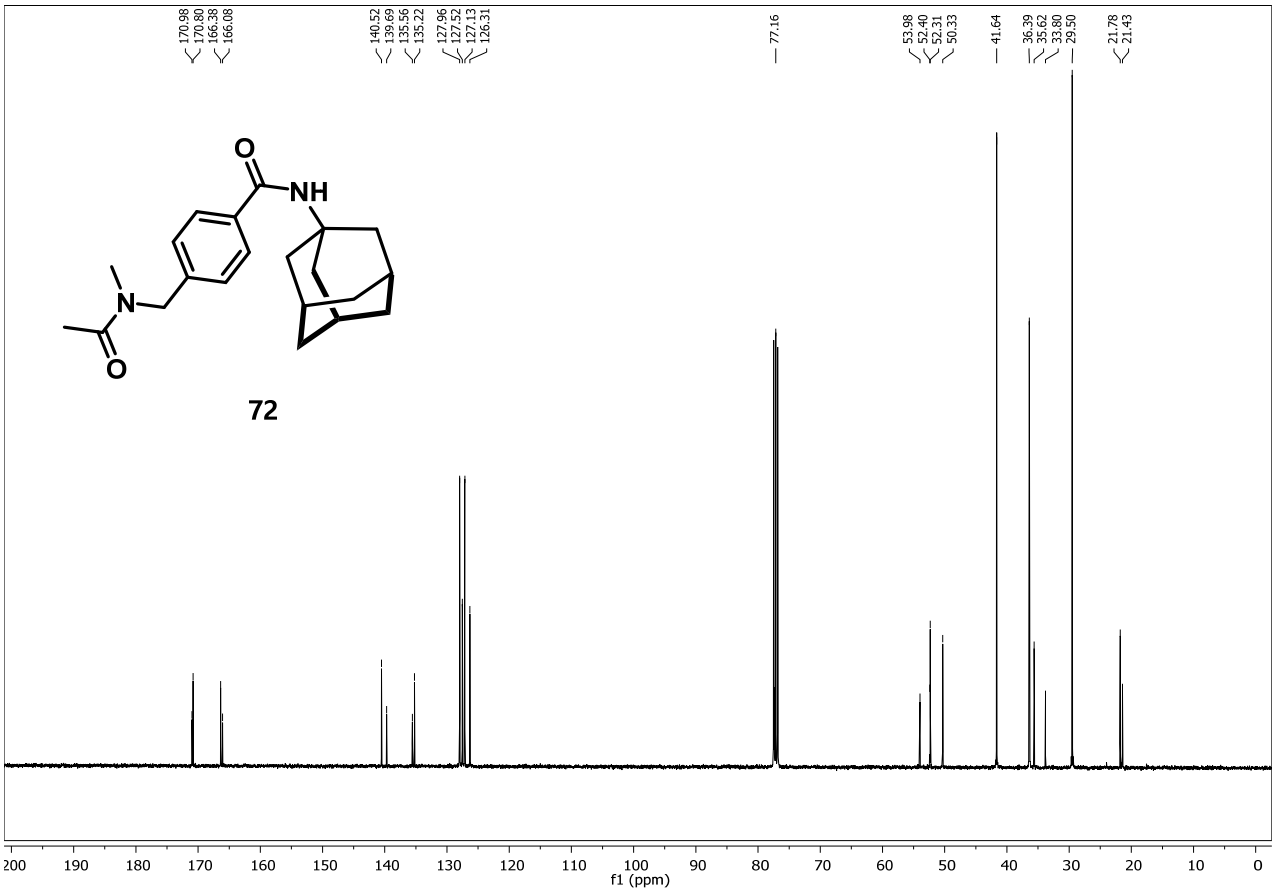

AcO
OAc
AcO
NH
AcO
O
O
N
70
f1 (ppm)

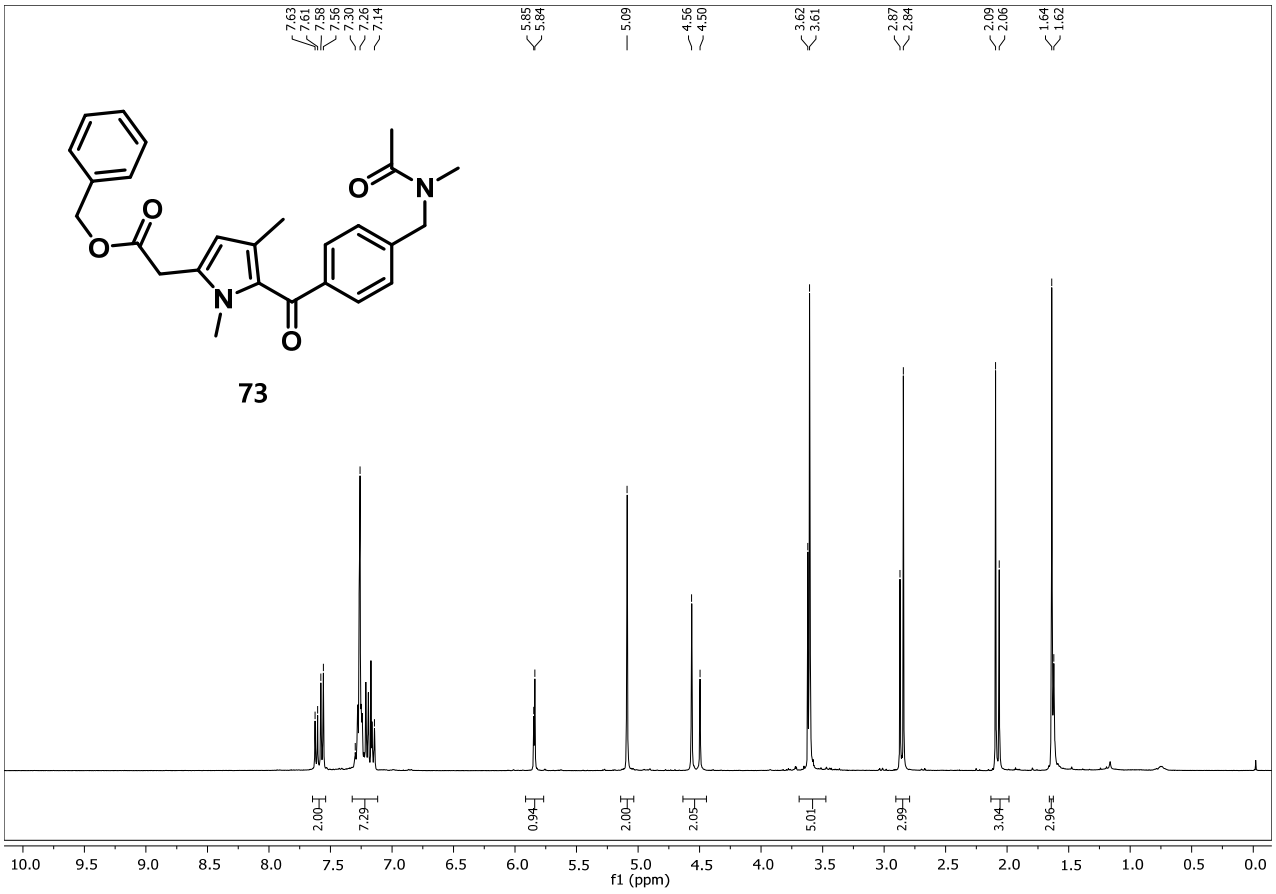

AcO
OAc
AcO
NH
AcO
O
O
N
70
f1 (ppm)


8.10
8.08
7.33
7.26
7.15
4.88
4.82
4.55
4.51
4.20
4.18
3.73
3.64
2.92
2.92
2.15
2.13
1.96
1.88
1.73
1.68
1.61
1.58
1.41
1.20
O
N
NH
S
O
O
N
71
1.00
2.29
2.01
1.02
2.02
1.01
1.02
3.07
3.07
2.18
2.03
4.10
5.38
f1 (ppm)

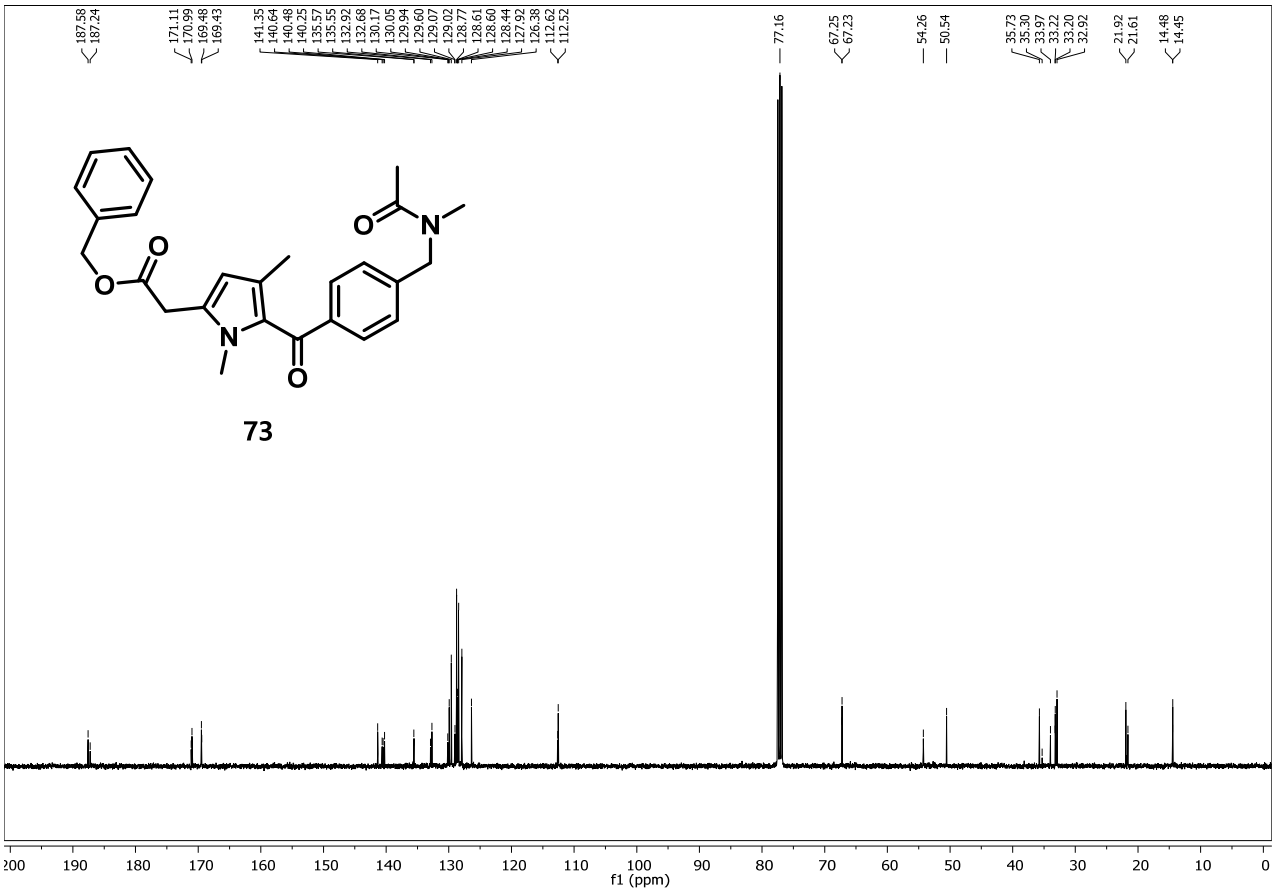

173.15
172.99
171.12
170.89
150.40
140.65
140.18
137.88
137.07
128.94
127.30
127.16
126.92
77.16
62.13
53.96
50.74
50.63
50.38
49.19
35.79
33.92
33.05
33.02
25.61
24.77
21.90
21.53
20.48
O
N
NH
S
O
O
N
71
f1 (ppm)


7.70
7.68
7.64
7.62
7.26
7.23
7.20
7.16
7.14
5.90
5.88
4.55
4.51
2.88
2.87
2.11
2.08
1.67
O
NH
N
O
72
2.00
2.01
0.95
2.00
3.02
12.09
6.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

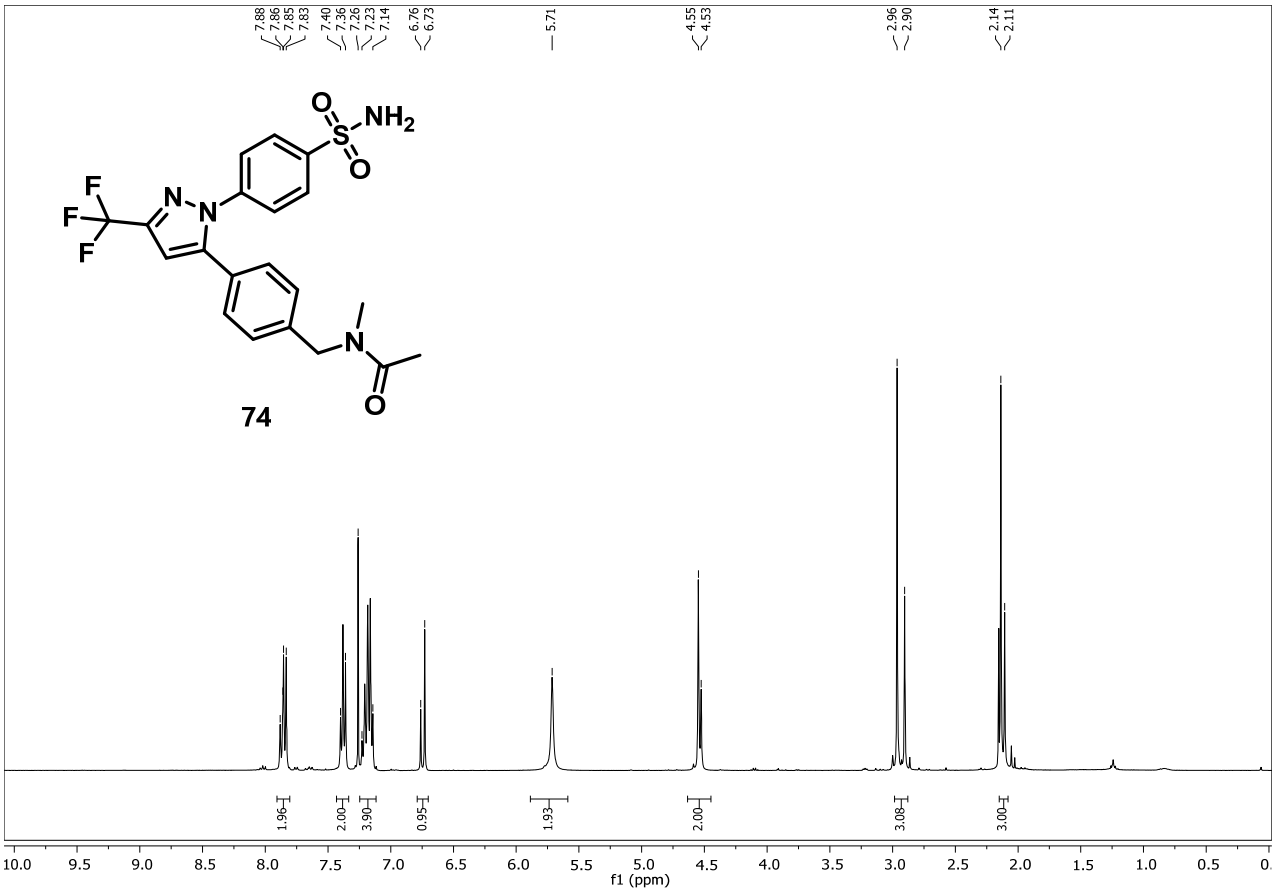

170.98
170.80
166.38
166.08
140.52
139.69
135.56
135.22
127.96
127.52
127.13
126.31
77.16
53.98
52.40
52.31
50.33
41.64
36.39
35.62
33.80
29.50
21.78
21.43
O
NH
N
O
72
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

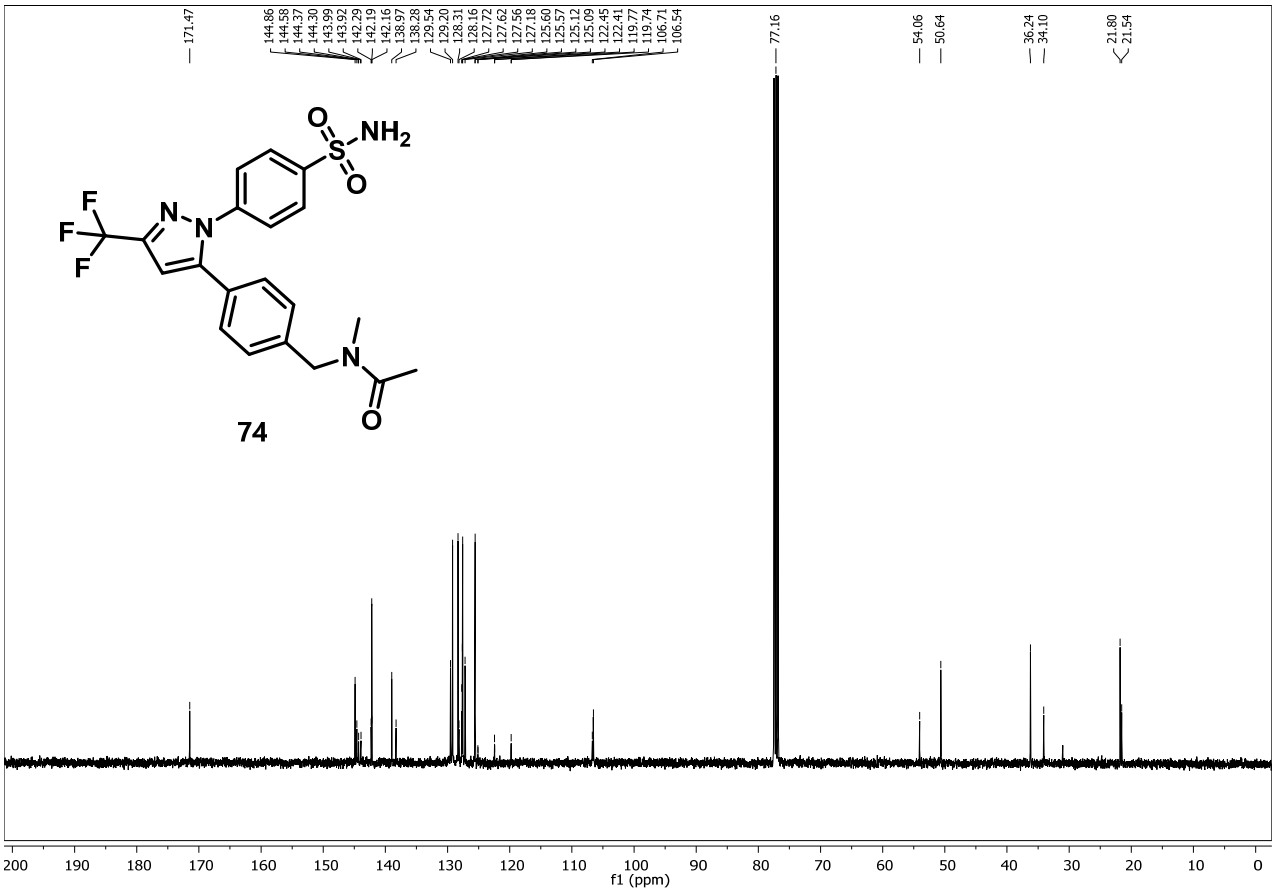

7.63
7.61
7.58
7.56
7.30
7.26
7.14
5.85
5.84
5.09
4.56
4.50
3.62
3.61
2.87
2.84
2.09
2.06
1.64
1.62
O
N
O
O
N
O
2.00
7.29
0.94
2.00
2.05
5.01
2.99
3.04
2.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

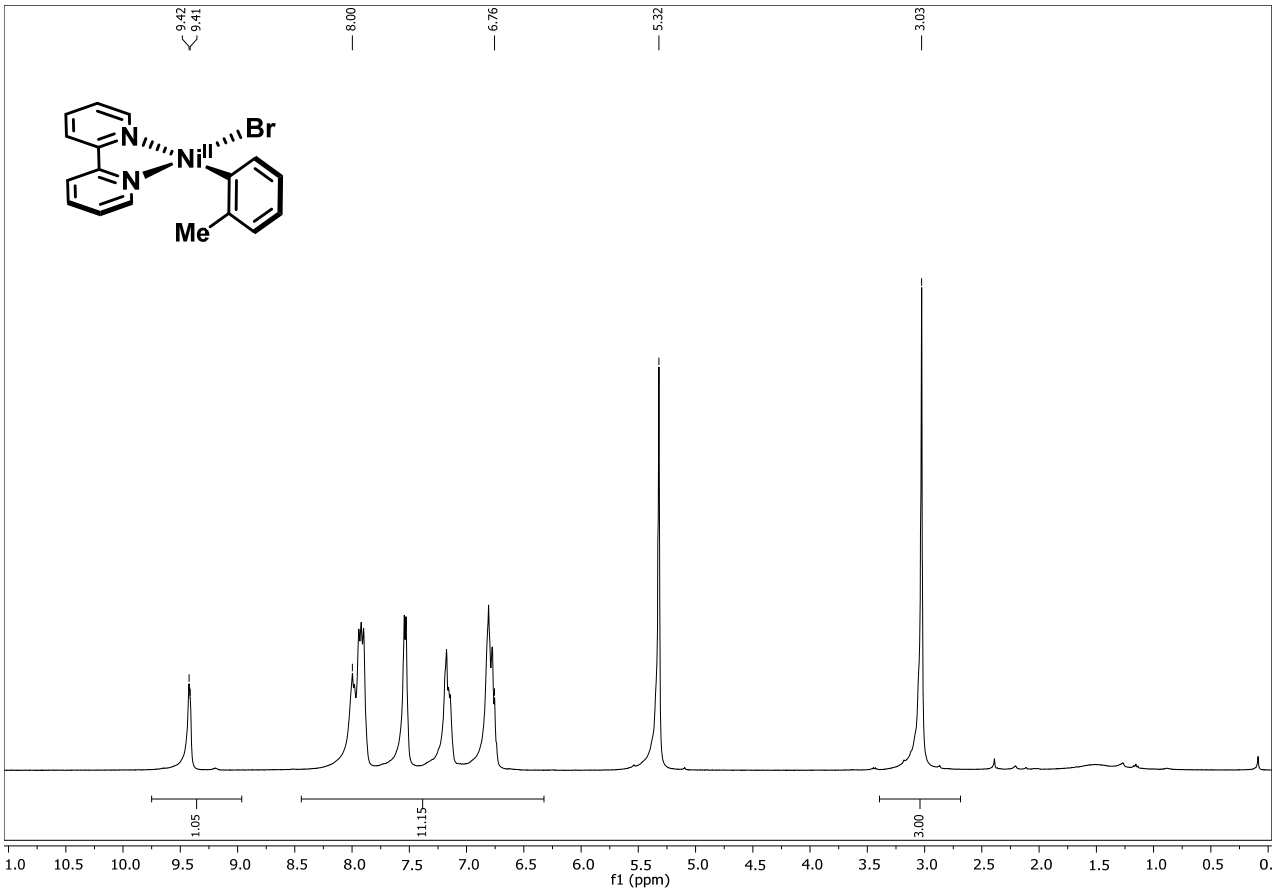
73

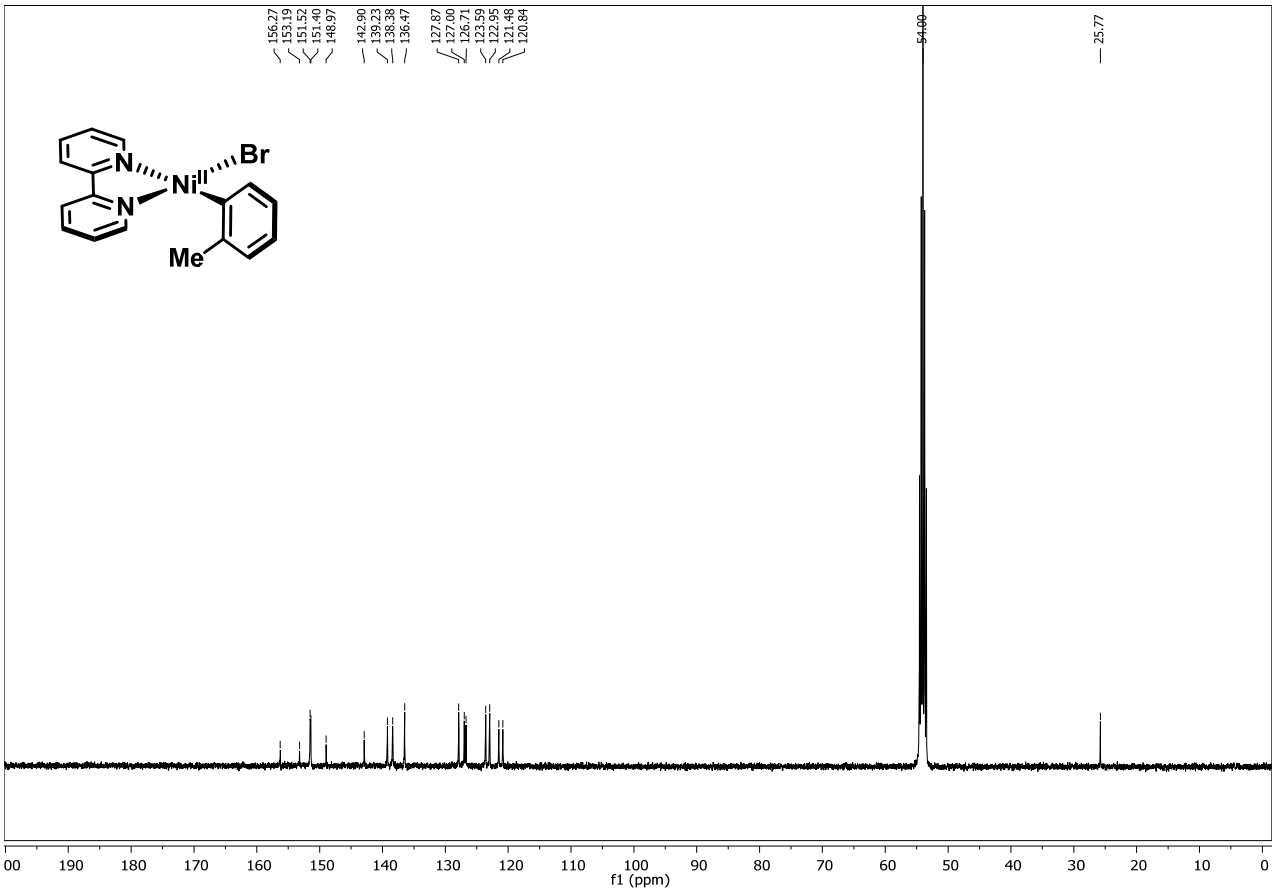

187.58
187.24
171.11
170.99
169.48
169.43
141.35
140.64
140.48
140.25
135.57
135.55
132.92
132.68
130.17
130.05
129.94
129.60
129.07
129.02
128.77
128.61
128.60
128.44
127.92
126.38
112.62
112.52
77.16
67.25
67.23
54.26
50.54
35.73
35.30
33.97
33.22
33.20
32.92
21.92
21.61
14.48
14.45
O
N
O
O
N
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

73


7.88
7.86
7.85
7.83
7.40
7.36
7.26
7.23
7.14
6.76
6.73
5.71
4.55
4.53
2.96
2.90
2.14
2.11
O
NH2
S
O
F
F
F
N
N
N
O
74
1.96
2.00
3.90
0.95
1.93
2.00
3.08
3.00
f1 (ppm)


171.47
144.86
144.58
144.37
144.30
143.99
143.92
142.29
142.19
142.16
138.97
138.28
129.54
129.20
128.31
128.16
127.72
127.62
127.56
127.18
125.60
125.57
125.12
125.09
122.45
122.41
119.77
119.74
106.71
106.54
77.16
54.06
50.64
36.24
34.10
21.80
21.54
O
NH2
S
O
F
F
F
N
N
N
O
74
f1 (ppm)


9.42
9.41
8.00
6.76
5.32
3.03
N
Ni
II
Br
N
Me
1.05
11.15
3.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)


156.27
153.19
151.52
151.40
148.97
142.90
139.23
138.38
136.47
127.87
127.00
126.71
123.59
122.95
121.48
120.84
54.00
25.77
N
Ni
II
Br
N
Me
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)