Supporting Information

General and Mild Cobalt-Catalyzed C-Alkylation of Unactivated Amides and Esters with Alcohols

Nicklas Deibl and Rhett Kempe*

kempe@uni-bayreuth.de
Anorganische Chemie II−Katalysatordesign, Universität Bayreuth, 95440 Bayreuth, Germany

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1 General Methods

Air- and moisture sensitive reactions were carried out under nitrogen or argon atmosphere using standard Schlenk techniques or a glove box. Dry solvents were obtained from a solvent purification system (activated alumina cartridges) or purchased from Acros. Chemicals were purchased from commercial vendors and used without purification if not noted otherwise. NMR-Spectra were collected at ambient temperature (23 °C) on Varian INOVA 300 (300 MHz for ^{1}H, 75 MHz for ^{13}C) or Bruker Avance III HD 500 (500 MHz for ^{1}H, 126 (125.76) MHz for ^{13}C) instruments. Chemical shifts are reported in ppm relative to the residual solvent signal ($CDCl_3$: 7.26 ppm (^{1}H), 77.16 ppm (^{13}C)). Coupling constants (*J*) are reported in Hz (coupling patterns: d = doublet, t = triplet, q = quartet, sxt = sextet, spt = septet, m = multiplet). GC analyses were carried out on an Agilent 6890N Network GC system equipped with a HP-5 column (30 m x 0.32 mm x 0.25 μm) or on an Agilent 6850 GC system equipped with a Optima17 column (30 m x 0.32mm x 25μm). GC-MS analyses were carried out on an Agilent 7890A GC system equipped with a HP-5MS column (30 m x 0.32 mm x 0.25 μm) and a 5975C inert MSD detector. Flash column chromatography was conducted on Macherey-Nagel silica gel 60 (40–63 μm particle size). Elemental analysis was performed on an Elementar Vario El *III* Instrument. High resolution mass spectra (HRMS) were obtained from a Thermo Fisher Scientific Q-Exactive (Orbitrap) instrument in ESI+ mode.

MTBE = Methyl *tert*-butyl ether.
DIBAL-H = Diisopropylaluminum hydride.

t-BuOK was dried under high vacuum at 70 °C and stored in a glove box.

The identity and purity of all compounds was characterized by ^{1}H and ^{13}C NMR spectroscopy and GC-MS. Unknown compounds were further characterized by HRMS or elemental analysis. Ambiguous NMR spectra were confirmed by two-dimensional methods.
Compounds **5i, 5m, 5v, 6e, 6g, 7a, 7c, 7d** were previously not described in the literature.

Ligands[1] and Co-complexes[2] were prepared according to methods previously reported by our group. Representative procedures are also given below.

2 General procedures

Typical procedure for ligand preparation: Under inert gas atmosphere a round-bottom flask with gas inlet was charged with a magnetic stirring bar and a solution of the

corresponding triazine or pyridine diamine (1 eq) in abs. THF (~0.1 M). The solution was cooled to 0 °C and the corresponding chlorophosphine (2.1 eq) was added dropwise by syringe through a septum maintaining a positive inert gas pressure. Afterwards triethylamine (4 eq) was added dropwise by syringe. The flask was sealed and the reaction was warmed to room temperature and then heated to 60 °C overnight. After cooling, triethyl ammoniumchloride was allowed to settle and the organic phase was isolated by filtration. The salt cake was washed with THF once and the combined organic phases were concentrated and dried under high vacuum giving the PNP ligand. In most cases no further purification was required. Otherwise, the ligands can be recrystallized in a small amount of hot toluene.

Co-complex preparation. Under inert gas atmosphere (glove box) a Schlenk tube was charged with a magnetic stirring bar and a suspension of $CoCl_2$ (1 eq) in THF (~0.12 M). The PNP-ligand (1 eq) was dissolved in THF (~0.12 M) and added to the stirred suspension of $CoCl_2$ in one portion leading to an instant color change. The Schlenk tube was sealed, removed from the glove box and heated to 60 °C overnight.
Complexes **1e, 1f** were isolated upon concentration in vacuo. Complex **1d** precipitated from the reaction mixture and the solvent was concentrated to half volume, the organic phase was removed and the remainder was dried under high vacuum.

Amide alkylation (1 mmol scale). Using a glove box (dry N_2 atmosphere), an oven dried 10 mL top screw vial was charged with a magnetic stirring bar, *t*-BuOK (1.2 mmol, 134.4 mg, 1.2 eq), alcohol (1 mmol, 1.0 eq), catalyst **1e** (1 mL from a 0.025 M stock solution in THF, 0.025 mmol, 2.5 mol%), amide (2 mmol, 2.0 eq) and THF (3.0 mL). The vial was sealed, removed from the glove box and the reaction mixture was heated to 100 °C (oil bath temperature) for 24 h. The reaction mixture was quenched with water (1 mL) and extracted with diethyl ether (3x 10 mL). The organic phase was analyzed with GC and GC-MS to monitor consumption of alcohol and product formation. The combined organic phases were dried over Na_2SO_4, evaporated and the amide product was purified using a small column of silica gel and pentane/ethyl acetate as the eluent.

As shown for product **5t**, the reaction gives the same yields when run on higher scale (10 mmol).

Version without pre-synthesized complex (1 mmol scale reaction): In an analogous manner as described above, a 10 mL top screw vial was charged with a magnetic stirring bar and $CoCl_2$ (0.025 mmol, 3.25 mg, 2.5 mol%). A solution of the corresponding ligand (0.025 mmol, 9.96 mg) in THF (1 mL) was added. After stirring for 2 min, a deep purple solution was obtained. Afterwards, the remaining components were added and the reaction was conducted and

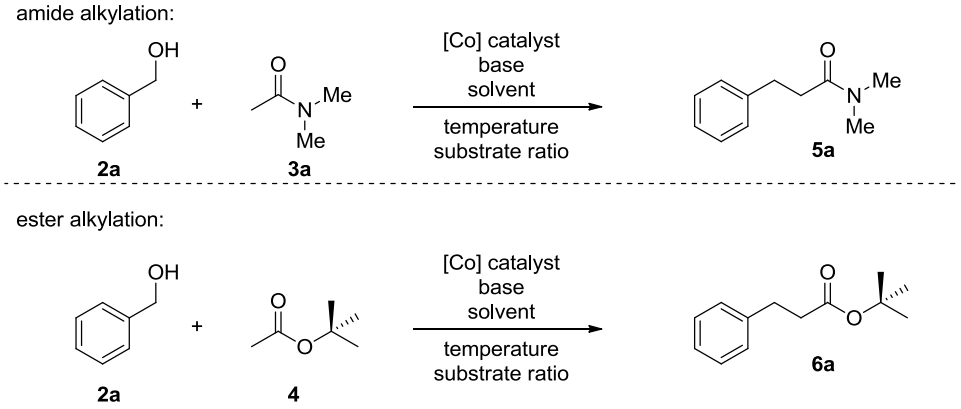
subjected to work up as described above. Amide **5a** was isolated in 81 % yield (143 mg, 0.808 mmol).

Ester alkylation. Using a glove box (dry N_2 atmosphere), an oven dried glass tube (38 mL volume) was charged with a magnetic stirring bar, *t*-BuOK (1.5 mmol, 168 mg, 1.5 eq), alcohol (1 mmol, 1.0 eq), catalyst **1d** (31 mg, 0.05 mmol, 5 mol%), *tert*-butyl acetate (4 mmol, 4.0 eq) and toluene (1 mL). The tube was sealed with a teflon cap, removed from the glove box and the reaction mixture was heated to 80 °C (oil bath temperature) for 4 h. The reaction mixture was quenched with water (1 mL) and extracted with diethyl ether (3x 10 mL). The organic phase was analyzed with GC and GC-MS to monitor consumption of alcohol and product formation. The combined organic phases were dried over Na_2SO_4, evaporated and the ester product was purified using flash column chromatography.

Note: Since the reaction mixture gets viscous during the reaction, efficient stirring is necessary. Therefore, a reaction tube with higher diameter is beneficial.

3 Screening reactions

In order to find the optimal reaction conditions for ester and amide alkylation, the following reactions were investigated.



Typical screening procedure: Using a nitrogen-filled glove box, a 10 mL top-screw vial was charged with a magnetic stirring bar, the corresponding starting materials, base, catalyst and solvent. The vial was sealed, removed from the glove box and the reaction mixture was immersed into a pre-heated oil bath. Afterwards, the reaction was cooled, water (1 mL), diethyl ether (5 mL) and dodecane (GC-standard) were added. After shaking, an aliquot of the organic phase was analyzed by GC-FID to determine the yield based on the internal standard method. For further details, see the table footnotes.
For catalyst screening, see article.

3.1 Amide alkylation

Table S 1. Solvent Screening

Entry	Solvent	Yield (GC)
1	**THF**	**71 %**
2	1,4-dioxane	58 %
3	toluene	52 %
4	*tert*-amyl alcohol	48 %
5	Diglyme	57 %

Reaction Conditions: *N*,*N*′-Dimethylacetamide (2 mmol), benzyl alcohol (1 mmol), precatalyst **1c** (0.05 mmol, 5 mol%), *t*-BuOK (1.0 mmol), solvent (2 mL), pressure tube, 100 °C oil bath, 19 h reaction time.

Table S 2. Base Screening

Entry	Base	Yield (GC)
1	*t*-BuOLi	28 %
2	*t*-BuONa	63 %
3	***t*-BuOK**	**65 %**
4	KOH	0 %
5	KH	45 %
6	Cs_2CO_3	0 %
7	KHMDS	23 %

Reaction Conditions: *N*,*N*′-Dimethylacetamide (2 mmol), benzyl alcohol (1 mmol), precatalyst **1c** (0.05 mmol, 5 mol%), base (1.0 mmol), THF (2 mL), pressure tube, 100 °C oil bath, 19 h reaction time.

Table S 3. Base Amount Screening

Entry	Base amount [eq.]	Yield (GC)
1	0.1	0 %
2	0.2	0 %
3	0.5	25 %
4	1.0	55 %
5	**1.2**	**66 %**
6	1.5	65 %
7	1.7	69 %
8	2.0	69 %

Reaction Conditions: *N,N'*-Dimethylacetamide (2 mmol), benzyl alcohol (1 mmol), precatalyst **1c** (0.05 mmol, 5 mol%), *t*-BuOK (0.1-2.0 mmol), THF (3 mL), pressure tube, 100 °C oil bath, 19 h reaction time.

Table S 4. Screening of substrate ratio

Entry	Me_2NAc : BnOH ratio	Yield (GC)
1	1.0 : 1.0	58 %
2	1.5 : 1.0	64 %
3	**2.0 : 1.0**	**68 %**
4	1.0 : 1.5	39 %
5	1.0 : 2.0	35 %

Reaction Conditions: *N,N'*-Dimethylacetamide (1-2 mmol), benzyl alcohol (1-2 mmol), precatalyst **1c** (0.05 mmol, 5 mol%), *t*-BuOK (1.2 mmol), THF (2 mL), pressure tube, 100 °C oil bath, 19 h reaction time.

Table S 5. Temperature Screening

Entry	Temperature	Yield (GC)
1	60 °C	40 %
2	80 °C	65 %
3	**100 °C**	**67 %**

Reaction Conditions: N,N'-Dimethylacetamide (2 mmol), benzyl alcohol (1 mmol), precatalyst **1c** (0.05 mmol, 5 mol%), *t*-BuOK (1.2 mmol), THF (2 mL), pressure tube, 100 °C oil bath, 19 h reaction time.

3.2 Ester Alkylation

Table S 6. Solvent Screening

Entry	Solvent	Yield (GC)
1	THF	24 %
2	**Toluene**	**40 %**
3	*tert*-amyl alcohol	8 %
4	1,4-dioxane	27 %
5	Diglyme	13 %

Reaction Conditions: tert-butyl acetate (2.0 mmol), benzyl alcohol (1.0 mmol), solvent (2 mL), *t*-BuOK (1 mmol), precatalyst **1c** (0.05 mmol, 5 mol%), 80 °C oil bath, sealed tube, 20 h

Table S 7. Base Screening

Entry	Base (1.0 eq.)	Yield (GC)
1	*t*-BuOLi	*n/d*
2	*t*-BuONa	37 %
3	***t*-BuOK**	**38 %**
4	KOH	*n/d*
5	KH	18 %
6	Cs_2CO_3	*n/d*
7	KHMDS	15 %

Reaction Conditions: tert-butyl acetate (2.0 mmol), benzyl alcohol (1.0 mmol), toluene (2 mL), base (1 mmol), precatalyst **1c** (0.05 mmol, 5 mol%), 70 °C, sealed tube, 20 h
n/d = not detected

Table S 8. Base Amount Screening

Entry	Base amount (eq)	Yield (GC)
1	0.10	*n/d*
2	0.20	*n/d*
3	0.50	15 %
4	1.00	43 %
5	1.20	53 %
6	**1.50**	**60 %**
7	1.70	57 %
8	2.00	53 %

Reaction Conditions: tert-butyl acetate (2.0 mmol), benzyl alcohol (1.0 mmol), toluene (2 mL), t-BuOK (0.1-2.0 mmol), precatalyst **1c** (0.05 mmol, 5 mol%), 70 °C, sealed tube, 20 h
n/d = not detected

Table S 9. Screening of substrate ratio

Entry	*t*-BuOAc/BnOH ratio	Yield (GC)
1	2.0 : 1.0	55 %
2	**4.0 : 1.0**	**90 %**
3	6.0 : 1.0	90 %
4	Neat ester (1.5 mL)	52 %

Reaction Conditions: *tert*-butyl acetate (2.0-1.0 mmol), benzyl alcohol (1.5-1.0 mmol), toluene (2 mL), t-BuOK (1.5 mmol), precatalyst **1d** (0.05 mmol, 5 mol%), 70 °C, sealed tube, 20 h.
(Screening with optimized catalyst **1d**)

The reaction can be run within a temperature range of 70-100 °C without high variations in yield (Table S 10). 80 °C was chosen eventually to account for a broad scope.

Table S 10. Screening of temperature

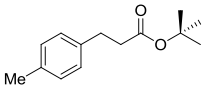
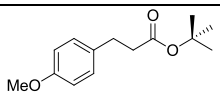
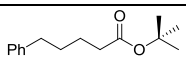
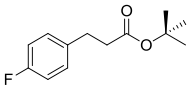
Entry	Temperature	Isolated yield of **6a**
1	70 °C	70 %
2	100 °C	71 %

Reaction Conditions: *tert*-butyl acetate (4 mmol), benzyl alcohol (1 mmol), toluene (1 mL), *t*-BuOK (1.5 mmol), precatalyst **1d** (0.05 mmol, 5 mol%), 70 °C, sealed tube, 4 h.

The reaction was found to be complete in 4 hours. For the following products, the isolated yields were compared for different reaction times (4 h vs. 12 h) and catalyst loadings (3 mol%

vs. 5 mol%,). No significant variations were detected and 4 h reaction time was chosen eventually (Table S 11).

Table S 11. Comparison of reaction conditions.

Entry	Product	Conditions	Isolated yield
1		cat. **1d** (5 mol%), 4 h	68 %
2		cat. **1d** (3 mol%), 12 h	69 %
3		cat. **1d** (5 mol%), 4 h	77 %
4		cat. **1d** (3 mol%), 12 h	68 %
5		cat**. 1d** (5 mol%), 4 h	58 %
6		cat. **1d** (3 mol%), 12 h	56 %
7		cat. **1d** (5 mol%), 4 h	82 %
8		cat. **1d** (3 mol%), 12 h	75 %

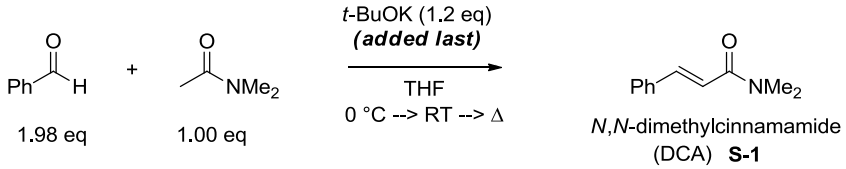
Reaction Conditions: *tert*-butyl acetate (4 mmol), alcohol (1 mmol), toluene (1 mL), *t*-BuOK (1.5 mmol), precatalyst **1d** (3 or 5 mol%), 80 °C oil bath, sealed tube, 4 or 12 h.

3.3 Mechanistic Investigations

3.3.1 Amide alkylation

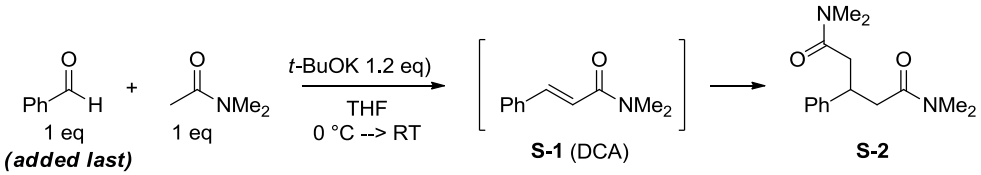
3.3.1.1 Synthesis of *N,N*-dimethylcinnamamide

In order to obtain deeper mechanistic insight into the alkylation reaction, we first prepared *N,N*-dimethylcinnamamide (**S-1**, Scheme S 1, see also synthesis section) which is believed to be a central intermediate in the catalytic cycle.



Scheme S 1. Preparation of N,N-dimethylcinnamamide.

During preparation, we noticed formation of the di-amide **S-2** (Scheme S 2), which is derived from 1,4-addition of *N,N*-dimethylacetamide to DCA. **S-2** was obtained exclusively when benzaldehyde was added dropwise to the anion of *N,N*-dimethylacetamide (prepared from *N,N*-dimethylacetamide and *t*-BuOK in THF, Scheme S 2).



Scheme S 2. Attempted synthesis of N,N-dimethylcinnamamide.

The crude reaction mixture of all prepared amide substrates was analyzed by GC and in general only low amounts of side-products occurred. This result suggested that the concentration of unsaturated intermediate [DCA (**S-1**) for the model reaction] in the reaction mixture must be low (see also Figure S 2 for a typical gas-chromatogram after reaction end).

3.3.1.2 Time-conversion-plot for the model reaction (amide alkylation)

The time-conversion-plot of the model-reaction of the amide alkylation reaction is depicted in Figure S 1. Yields and conversions were obtained by reaction monitoring by GC with dodecane as internal standard.

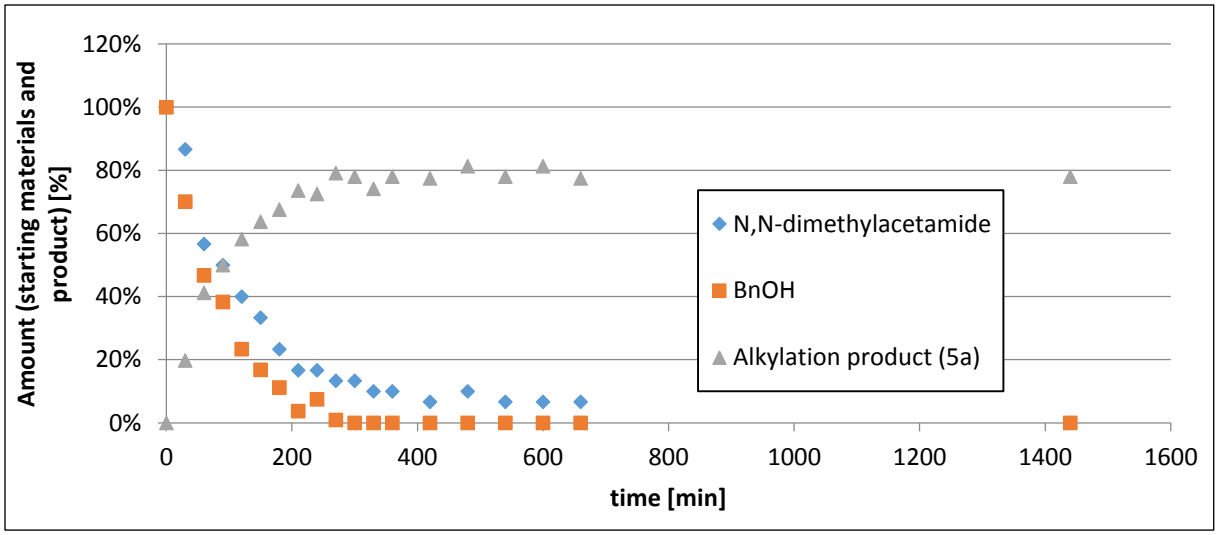
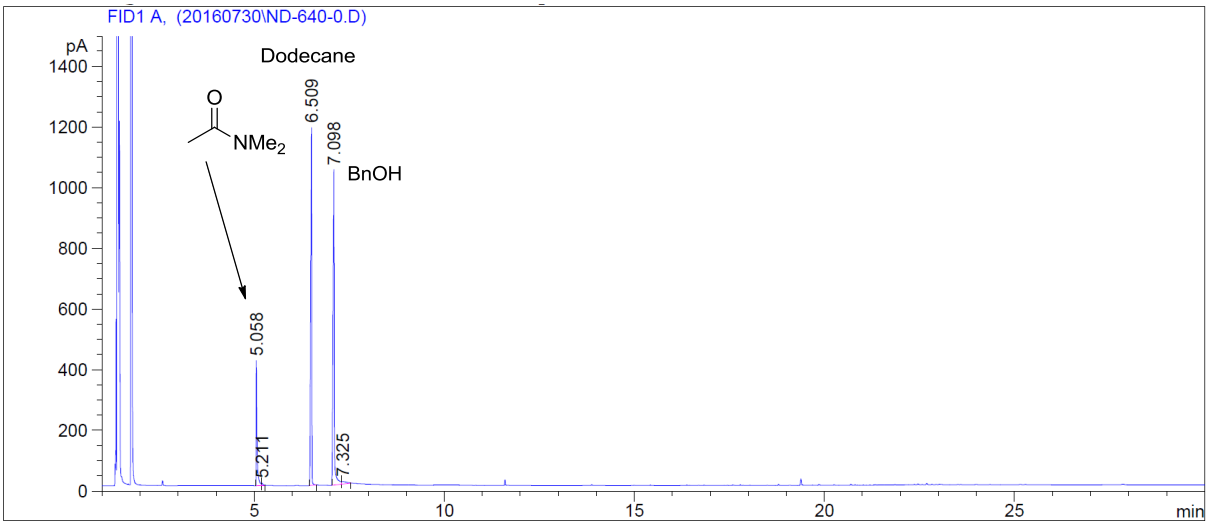


Figure S 1. Time-conversion plot of the amide alkylation reaction.

Reaction start



Reaction end (24 h)

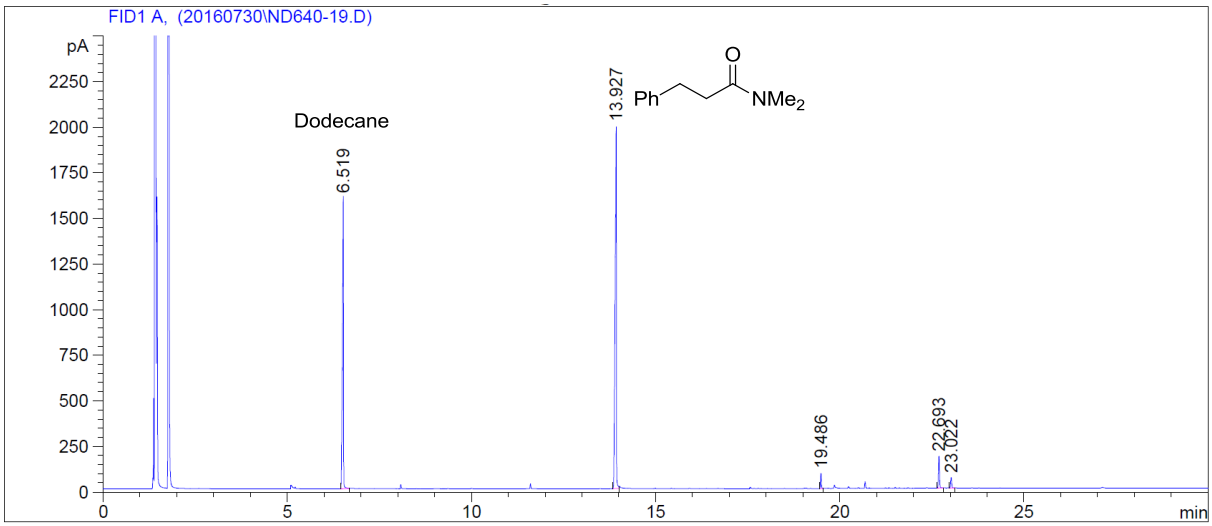


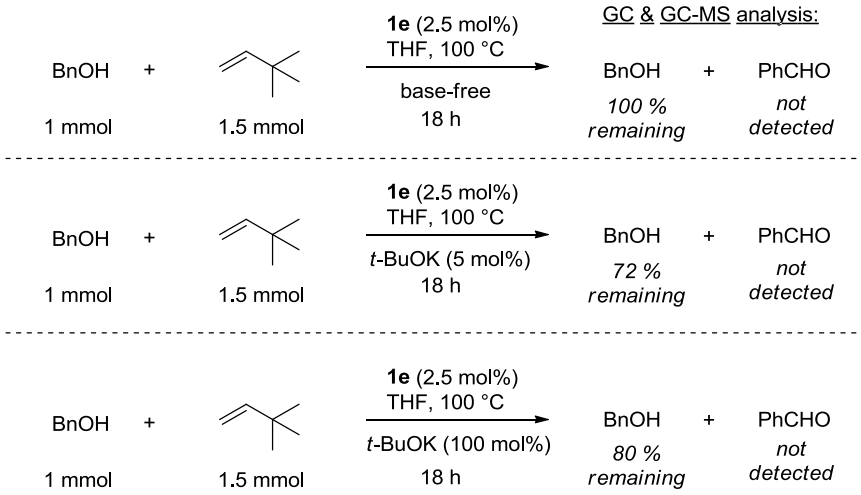
Figure S 2. Gas-chromatograms of the model reaction at reaction start and reaction end.

The following conclusions were drawn:

- No induction period was observed
- No *N*,*N*-dimethylcinnamamide intermediate was detected during the reaction which means the oxidation of alcohol is rate-determining and reduction proceeds relatively fast.
- No significant amount of side-products was observed.
- Alcohol conversion and product formation correlate.

3.3.1.3 Investigation of the oxidation step

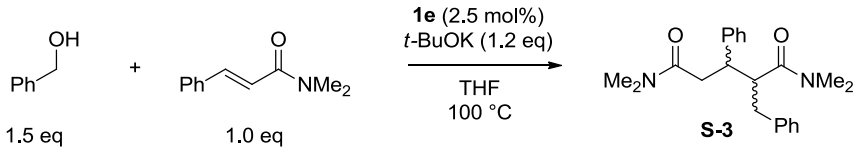
For an Ir-catalyst, the transfer hydrogenation between benzyl alcohol and 3,3-dimethylbut-1-ene is described in the literature as the only mechanistic work. When this reaction was conducted with the cobalt catalyst, no significant conversion of benzyl alcohol was observed with or without base (Scheme S 3).



Scheme S 3. Investigation of transfer hydrogenation.

3.3.1.4 Concerted oxidation/reduction

When the reaction between the proposed intermediate *N*,*N*-dimethylcinnamamide and benzyl alcohol under catalytic conditions was monitored, another side-product accumulated in significant amount. The product was identified by GC-MS as the 1,4-addition product between the intermediate *N*,*N*-dimethylcinnamamide and the hydrogenation product. This observation further supports the assumption that the reduction of the α,β-unsaturated intermediate proceeds before competition reactions take place since only very low amounts of this side-product are seen in the catalytic reaction (cf. the gas-chromatogram in Figure S 3 with Figure S 4).



Scheme S 4. Attempted transfer hydrogenation between benzyl alcohol and intermediate.

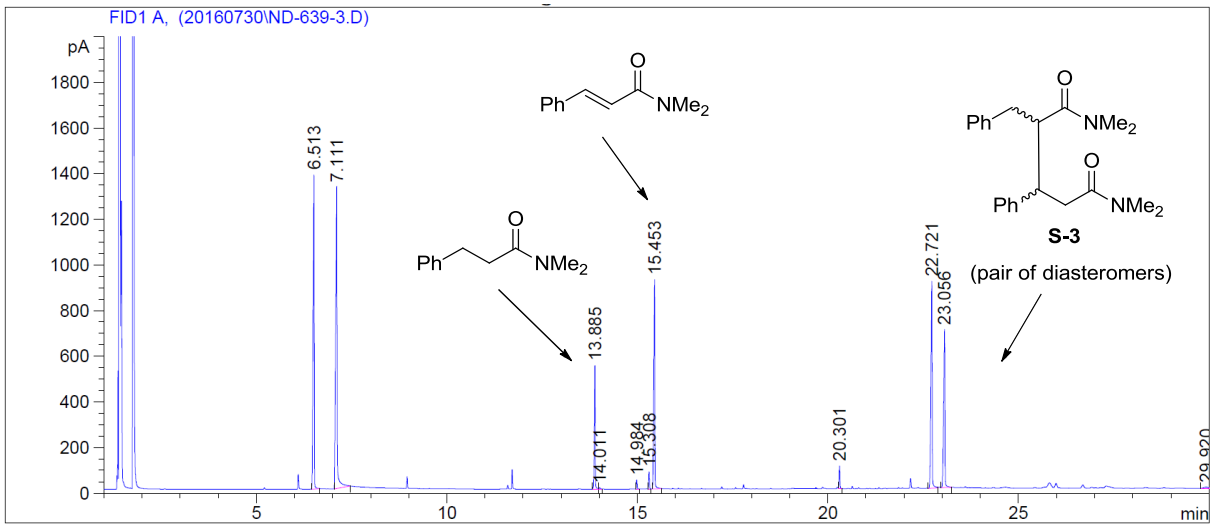


Figure S 3. Gas-chromatogram of the reaction depicted in Scheme S 4 after 1.5 h.

Comparison with catalytic reaction:

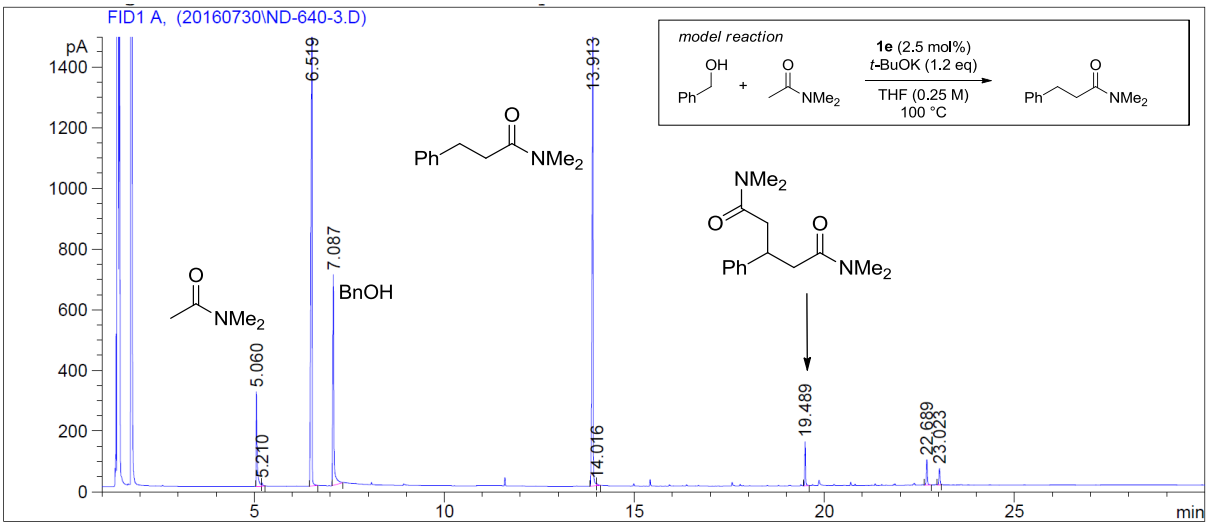
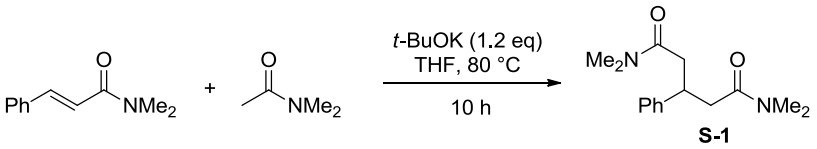
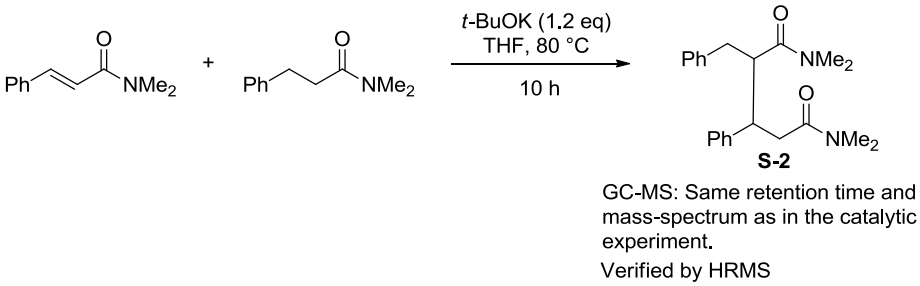


Figure S 4. Gas-chromatogram of the model reaction after 1.5 h.

Possible 1,4-addition products were prepared independently to verify GC-measurements (Scheme S 5).

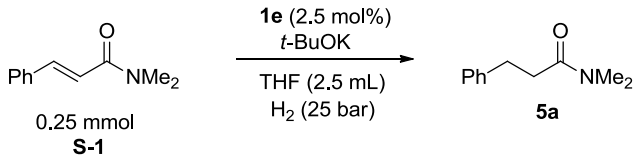




Scheme S 5. Control experiments to verify possible 1,4-addition side-products.

3.3.1.5 Hydrogenation experiments

DCA (**S-1**) was subjected to hydrogenation under catalytic conditions. If hydrogen equivalents are not obtained from the rate-limiting alcohol oxidation, but from molecular hydrogen, it was envisioned that fast reduction would limit 1,4-addition side-reactions.



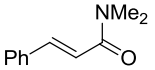
Conditions:	(1) 80 °C, 5 mol% *t*-BuOK, 4 h:	30 % conversion, 20 % yield
	(2) 80 °C, 120 mol% *t*-BuOK, 4 h:	100 % conversion, 41 % yield
	(3) 80 °C, 50 mol% *t*-BuOK, 4 h:	100 % conversion, 61 % yield
	(4) 40 °C, 50 mol% *t*-BuOK, 4 h:	100 % conversion, 42 % yield
	(5) 80 °C, 50 mol% *t*-BuOK, 1 h:	100 % conversion, 60 % yield
	(6) 80 °C, 50 mol% *t*-BuOK, 0.5 h:	100 % conversion, 57 % yield
		(determined by GC with dodecane as internal standard)

Scheme S 6. Hydrogenation experiments.

Hydrogenation proceeded even within 30 min (entry 6 in Scheme S 6) and the 1,4-addition product was not obtained.

3.3.1.6 Syntheses

*N,N-dimethylcinnamamide (**S-1**)*



To a stirred solution of benzaldehyde (98.9 mmol, 10 mL, 1.98 eq) and *N,N*-dimethylacetamide (50.0 mmol, 4.65 mL, 1.00 eq) in THF (200 mL) was added *t*-BuOK (60 mmol, 6.72 g, 1.2 eq) in portions at 0 °C. The reaction mixture was warmed to rt and heated

to reflux for 1 hour. After cooling, water was added until a clear solution was obtained. The reaction mixture was then concentrated and partitioned between water (50 mL) and CH_2Cl_2 (100 mL). After separation of the phases, the aqueous phase was extracted with CH_2Cl_2 (2x 100 mL). The combined organic phase was dried over Na_2SO_4, concentrated and purified by column chromatography (silica gel, pentane/ethyl acetate 1:1 → 1:2) to give the title compound as a crystalline white solid (2.98 g, 17.0 mmol, 34 %).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.67 (d, *J*=15.26 Hz, 1 H), 7.50 - 7.55 (m, 2 H), 7.31 - 7.40 (m, 3 H), 6.89 (d, *J*=15.26 Hz, 1 H), 3.17 (s, 3 H), 3.07 (s, 3 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 166.8, 142.5, 135.5, 129.7, 128.9, 127.9, 117.5, 37.6, 36.1 ppm.

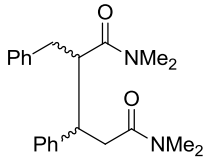
MS (EI, 70 eV) *m/z*: 175.1 (M^+), 131.1, 103.1, 77.1, 51.1.

The spectroscopic data correspond with those reported in the literature.[3]

Note: When the reactants were added in a different order (*N*,*N*-dimethylacetamide, *t*-BuOK, then dropwise addition of benzaldehyde (1 eq)), the corresponding 1,4-addition product **S-2** was obtained as monitored by GC-MS (*m/z* 262.1).

Confirmation of 1,4-addition products:

2-benzyl-N^1,N^1,N^5,N^5-tetramethyl-3-phenylpentanediamide

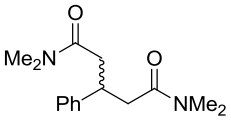


Under nitrogen atmosphere (glove box), *N*,*N*-dimethylcinnamamide (0.5 mmol, 87.5 mg, 1 eq), *N*,*N*-dimethyl-3-phenylpropanamide (0.75 mmol, 133 mg, 1.5 eq), *t*-BuOK (67 mg, 0.6 mmol, 1.2 eq) and THF (3 mL) were mixed in a 10 mL vial. The vial was sealed and the reaction mixture was heated with a 80 °C oil bath for 10.5 h. The reaction was quenched with water (2 mL) and extracted with ethyl acetate (3x 10 mL) and concentrated. The crude product was analyzed by GC-MS and LC-HRMS. The above 1,4-addition product was observed at the same retention time as in the catalytic reaction and the identity was further confirmed by HRMS.

GC-MS (EI, 70 eV) *m/z*: 352.2 (M^+), 308.2, 266.1, 216.1, 176.1, 131.1, 115.1, 103.1, 91.1, 72.1.

HRMS (ESI+): *m/z* calcd. for $[C_{22}H_{28}N_2O_2 + H]^+$ 353.22235; found: 353.22134.

N^1,N^1,N^5,N^5-tetramethyl-3-phenylpentanediamide



Under nitrogen atmosphere (glove box), *N*,*N*-dimethylcinnamamide (0.5 mmol, 87.5 mg, 1 eq), *N*,*N*-dimethylacetamide (1 mmol, 93 µL, 2 eq), *t*-BuOK (67 mg, 0.6 mmol, 1.2 eq) and THF (3 mL) were mixed in a 10 mL vial. The vial was sealed and the reaction mixture was heated with a 80 °C oil bath for 10.5 h. The reaction was quenched with water (2 mL) and extracted with ethyl acetate (3x 10 mL) and concentrated. The crude product was analyzed by GC-MS and LC-HRMS. The above 1,4-addition product was observed at the same retention time as in the catalytic reaction and the identity was further confirmed by HRMS.

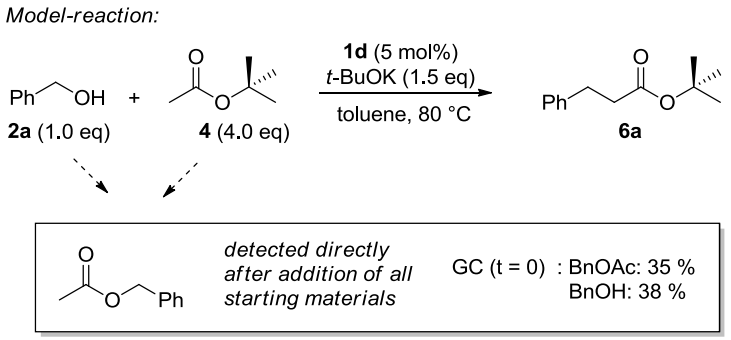
GC-MS (EI, 70 eV) *m/z*: 262.1 (M^+), 218.1, 190.1, 176.1, 131.0, 103.0, 87.1, 72.0.

HRMS (ESI+): *m/z* calcd. for $[C_{15}H_{22}N_2O_2 + H]^+$ 263.17540; found: 263.17462.

3.3.2 Ester alkylation

3.3.2.1 Reaction monitoring

The reaction of the ester alkylation (model reaction) was monitored by GC with dodecane as internal standard (Scheme S 7 and Figure S 5).



Scheme S 7. Model reaction for ester alkylation and outcome of analysis of the reaction directly after addition of starting materials.

An aliquot (500 µL from a 2 mmol scale reaction) was removed from the reaction mixture immediately after addition of *tert*-butyl acetate. The aliquot was quenched with water and extracted with diethyl ether.

GC-FID and GC-MS analysis of the t = 0 min reaction sample showed a significant amount of benzyl acetate which was confirmed by GC-MS and by comparison of the retention time of an authentic sample.

This result indicates that transesterification products undergo resolution by alcohol exchange with *t*-BuOH followed by consumption of the primary alcohol in the catalytic alkylation reaction. The catalytic reaction gives one single product after 1-4 h.

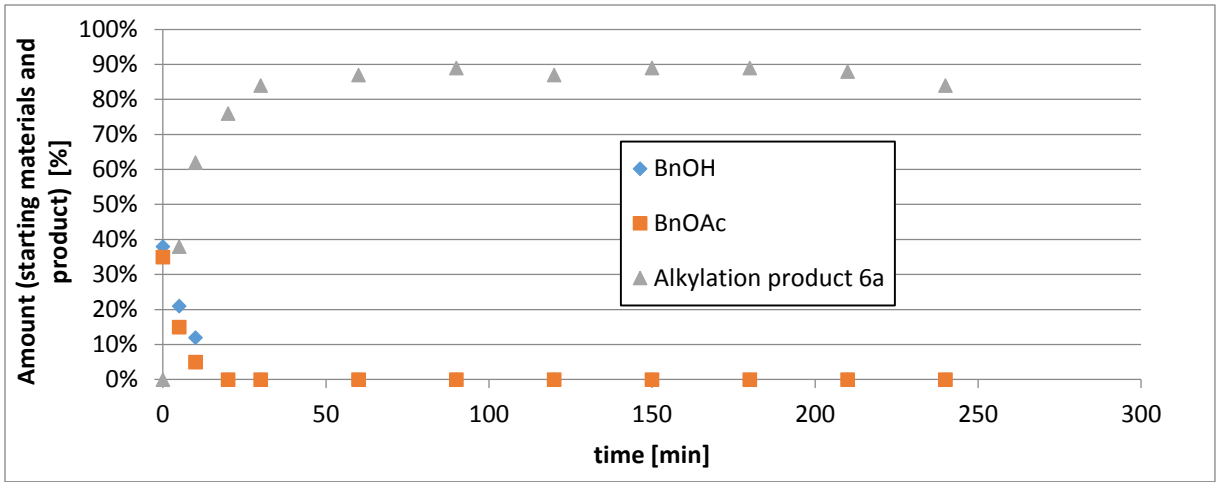
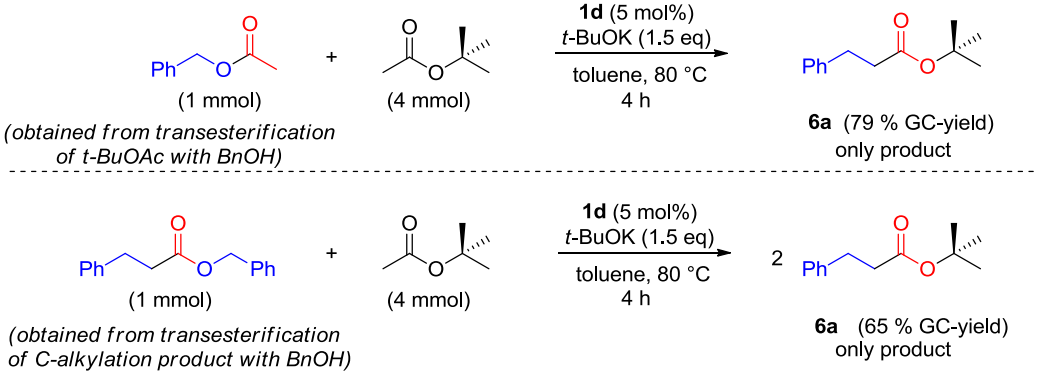


Figure S 5. Time-conversion plot for the catalytic ester alkylation (model reaction).

3.3.2.2 Control reactions

The corresponding transesterification products were subjected to the reaction conditions to prove the shift towards the *tert*-butyl ester.



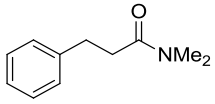
Scheme S 8. Control reactions of transesterification products under catalytic conditions.

Both benzyl acetate and benzyl 3-phenylpropanoate were converted into the alkylated *tert*-butyl ester **6a** under catalytic conditions (Scheme S 8). Conversion was quantitative and no other side-products were observed by GC analysis.

4 Characterization data

4.1 Amide alkylation products

*N,N-dimethyl-3-phenylpropanamide (**5a**)*



Purification by column chromatography (silica gel, pentane/ethyl acetate, 1:1.5). Yield: 147 mg (0.830 mmol, 83 %) colorless oil.

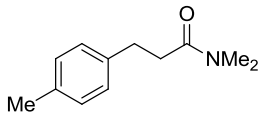
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.25 - 7.31 (m, 2 H), 7.17 - 7.24 (m, 3 H), 3.00-2.94 (m, 8 H, overlapping signals of NMe_2 and CH_2), 2.58 - 2.64 (m, 2 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 172.3, 141.6, 128.5, 126.2, 37.2, 35.4, 31.5 ppm.

MS (EI, 70 eV) *m/z*: 177.2 (M^+), 131.1, 105.1, 91.1, 72.1.

The spectroscopic data correspond to those reported in the literature.[4]

*N,N-dimethyl-3-(p-tolyl)propanamide (**5b**)*



Purification by column chromatography (silica gel, pentane/ethyl acetate, 1:1). Yield: 163 mg (0.853 mmol, 85 %) colorless oil.

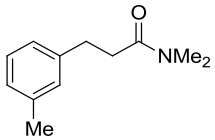
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.05 - 7.16 (m, 4 H), 2.87 - 2.98 (m, 8 H, overlapping signals of NMe_2 and CH_2), 2.54 - 2.64 (m, 2 H), 2.31 (s, 3 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 172.3, 138.5, 135.6, 129.2, 128.4, 37.2, 35.6, 35.5, 31.0, 21.1 ppm.

MS (EI, 70 eV) *m/z*: 191.1 (M^+), 147.1, 131.0, 118.1, 105.1, 91.1, 72.1.

The spectroscopic data correspond to those reported in the literature.[4]

*N,N-dimethyl-3-(m-tolyl)propanamide (**5c**)*



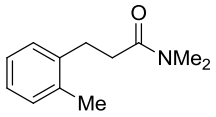
Purification by column chromatography (silica gel, pentane/ethyl acetate, 1:1). Yield: 154 mg (0.806 mmol, 81 %) colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.13 - 7.21 (m, 1 H), 6.99 - 7.07 (m, 3 H), 2.89 - 2.99 (m, 8 H overlapping signals of NMe_2 and CH_2), 2.56 - 2.65 (m, 2 H), 2.33 (s, 3 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 172.3, 141.5, 138.1, 129.3, 128.5, 126.9, 125.5, 37.2, 35.5, 31.4, 21.5 ppm.

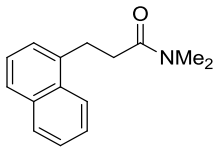
MS (EI, 70 eV) *m/z*: 191.2 (M^+), 147.1, 131.1, 119.1, 105.1, 91.1, 72.1.
The spectroscopic data correspond to those reported in the literature.[4]

*N,N-dimethyl-3-(o-tolyl)propanamide (**5d**)*



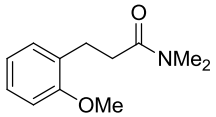
Purification by column chromatography (silica gel, pentane/ethyl acetate, 1:1). Yield: 153 mg (0.801 mmol, 80 %) colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.06 - 7.21 (m, 5 H), 2.89 - 3.00 (m, 8 H, overlapping signals of NMe_2 and CH_2), 2.53 - 2.60 (m, 2 H), 2.33 (s, 3 H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ = 172.4, 140.0, 136.1, 130.4, 128.9, 126.4, 126.2, 37.2, 35.5, 34.0, 28.8, 19.4 ppm.
MS (EI, 70 eV) *m/z*: 191.1 (M^+), 176.1, 162.1, 147.1, 119.1, 105.1, 91.1, 72.0.
The spectroscopic data correspond to those reported in the literature.[4]

*N,N-dimethyl-3-(naphthalen-1-yl)propanamide (**5e**)*



Purification by column chromatography (silica gel, pentane/ethyl acetate, 1:1). Yield: 176 mg (0.775 mmol, 78 %) colorless viscous oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.03 - 8.09 (m, 1 H), 7.86 (dd, *J*=8.39, 1.07 Hz, 1 H), 7.73 (d, *J*=7.63 Hz, 1 H), 7.45 - 7.55 (m, 2 H), 7.35 - 7.43 (m, 2 H), 3.42 - 3.48 (m, 2 H), 2.96 (s, 3 H), 2.85 (s, 3 H), 2.70 - 2.77 (m, 2 H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ = 172.4, 137.8, 134.0, 131.8, 129.0, 127.1, 126.3, 126.2, 125.8, 123.7, 37.2, 35.6, 34.7, 28.6 ppm.
MS (EI, 70 eV) m/z: 227.1 (M^+), 183.1, 154.1, 141.1, 128.1, 115.1, 86.0, 72.0.
HRMS (ESI+) *m/z* $[C_{15}H_{17}NO + H]^+$ calcd. 228.13829, found 228.13771
The spectroscopic data correspond to those reported in the literature.[6]

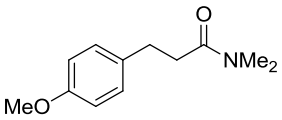
*3-(2-methoxyphenyl)-N,N-dimethylpropanamide (**5f**)*



Purification by column chromatography (silica gel, pentane/ethyl acetate, 1:1.5). Yield: 184 mg (0.889 mmol, 89 %) colorless oil.

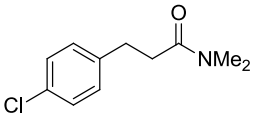
^{1}H NMR (500 MHz, $CDCl_3$) δ =7.15 - 7.22 (m, 2 H), 6.87 (td, *J*=7.40, 1.07 Hz, 1 H), 6.84 (d, *J*=8.24 Hz, 1 H), 3.82 (s, 3 H), 2.90 - 2.97 (m, 8 H, overlapping signals of NMe_2 and CH_2), 2.54 - 2.61 (m, 2 H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ = 172.9, 157.6, 130.3, 129.8, 127.5, 120.6, 110.3, 55.3, 37.2, 35.4, 33.8, 26.8 ppm.
MS (EI, 70 eV) *m/z*: 207.1 (M^+), 192.1, 176.1, 161.1, 150.1, 134.1, 121.1, 105.1, 91.1, 72.1, 65.1.
The spectroscopic data correspond to those reported in the literature.[4]

*3-(4-methoxyphenyl)-N,N-dimethylpropanamide (**5g**)*



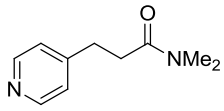
Purification by column chromatography (silica gel, pentane/ethyl acetate, 1:1→1:1.5). Yield: 177 mg (0.855 mmol, 86 %) colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.07 - 7.17 (m, 2 H), 6.76 - 6.85 (m, 2 H), 3.76 (s, 3 H), 2.91-2.88 (m, 8 H, overlapping signals of NMe_2 and CH_2), 2.50 - 2.62 (m, 2 H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ =172.3, 158.0, 133.6, 129.4, 113.9, 55.3, 37.2, 36.0, 35.4, 30.5 ppm.
MS (EI, 70 eV) *m/z*: 224.1 (M^+), 183.2, 154.2, 140.1, 121.1, 100.1, 87.1, 79.1, 72.1, 55.1.
The spectroscopic data correspond to those reported in the literature.[4]

*3-(4-chlorophenyl)-N,N-dimethylpropanamide (**5h**)*



Variation from the general procedure: t-BuONa (1.2 mmol) was used as base instead of *t*-BuOK. Purification by column chromatography (silica gel, pentane/ethyl acetate, 1:1 → 1:2). Yield: 160 mg (0.758 mmol, 76 %) colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.20 - 7.25 (m, 2 H), 7.12 - 7.16 (m, 2 H), 2.89 - 2.96 (m, 8 H, overlapping signals of CH_2 and NMe_2), 2.54 - 2.60 (m, 2 H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ = 171.9, 140.1, 131.9, 129.9, 128.6, 37.2, 35.5, 35.1, 30.7 ppm.
MS (EI, 70 eV) *m/z*: 211.1 (M^+), 167.0, 138.0, 131.0, 125.0, 103.0, 86.1, 72.0, 58.0.
The spectroscopic data correspond to those reported in the literature.[4]

*N,N-dimethyl-3-(pyridin-4-yl)propanamide (**5i**)*



Variation from the general procedure: Catalyst **1f** (5 mol%) was used. Purification by column chromatography (silica gel, CH_2Cl_2/MeOH, 100:5). Yield: 125 mg (0.702 mmol, 70 %) yellow oil.

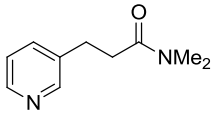
^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.46 (d, *J*=4.88 Hz, 2 H), 7.13 (d, *J*=5.80 Hz, 2 H), 2.96-2.91 (m, 8 H, overlapping signals of NMe_2 and CH_2), 2.60 (t, *J*=7.78 Hz, 2 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 171.3, 150.7, 149.8, 124.0, 37.2, 35.6, 33.8, 30.5 ppm.

MS (EI, 70 eV) *m/z*: 178.1 (M^+), 134.4, 106.1, 72.1.

HRMS (ESI+) *m/z* $[C_{10}H_{14}N_2O + H]^+$ calcd. 179.11789, found 179.11739

*N,N-dimethyl-3-(pyridin-3-yl)propanamide (**5j**)*



Variation from the general procedure: Catalyst **1f** (5 mol%) was used. Purification by column chromatography (silica gel, CH_2Cl_2/MeOH, 100:5). Yield: 144 mg (0.809 mmol, 81 %) colorless oil.

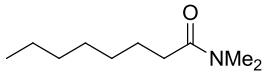
^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.46 (s, 1 H), 8.42 (d, *J*=4.27 Hz, 1 H), 7.54 (d, *J*=7.93 Hz, 1 H), 7.18 (dd, *J*=7.93, 4.88 Hz, 1 H), 2.98-2.91 (m, 8 H, overlapping signals of NMe_2 and CH_2), 2.59 (t, *J*=7.63 Hz, 2 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 171.5, 150.0, 147.7, 136.9, 136.2, 123.4, 37.2, 35.6, 34.7, 28.4 ppm.

MS (EI, 70 eV) *m/z*: 177.1 (M^+), 135.1, 106.1, 92.0, 72.0.

The spectroscopic data correspond to those reported in the literature.[5]

*N,N-dimethyloctanamide (**5k**)*



Purification by column chromatography (silica gel, pentane/ethyl acetate, 1:1). Yield: 156 mg (0.912 mmol, 91 %) colorless oil.

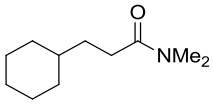
^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.00 (s, 3 H), 2.94 (s, 3 H), 2.26 - 2.34 (m, 2 H), 1.57 - 1.67 (m, 2 H), 1.20 - 1.38 (m, 8 H), 0.82 - 0.91 (m, 3 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 173.4, 37.4, 35.5, 33.6, 31.9, 29.6, 29.3, 25.4, 22.8, 14.2 ppm.

MS (EI): *m/z* 171.2 (M^+), 142.1, 128.1, 114.1, 100.1, 87.1, 72.1, 57.1.

The spectroscopic data correspond to those reported in the literature.[6]

*3-cyclohexyl-N,N-dimethylpropanamide (**5l**)*



Purification by column chromatography (silica gel, pentane/ethyl acetate, 1:1). Yield: 170 mg (0.929 mmol, 93 %) colorless oil.

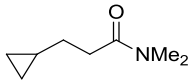
^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.98 (s, 3 H), 2.91 (s, 3 H), 2.25 - 2.32 (m, 2 H), 1.57 - 1.74 (m, 5 H), 1.44 - 1.54 (m, 2 H), 1.04 - 1.29 (m, 4 H), 0.81 - 0.95 (m, 2 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 173.6, 37.6, 37.4, 35.5, 33.2, 32.7, 31.0, 26.7, 26.4 ppm.

MS (EI, 70 eV): *m/z* 183.2 (M^+), 154.2, 140.1, 121.1, 100.1, 87.1, 72.1, 55.1.

The spectroscopic data correspond to those reported in the literature.[4]

*3-cyclopropyl-N,N-dimethylpropanamide (**5m**)*



Purification by column chromatography (silica gel, pentane/ethyl acetate, 1:1). Yield: 114 mg (0.809 mmol, 81 %) colorless oil.

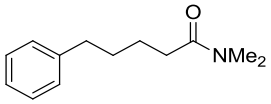
^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.00 (s, 3 H), 2.92 (s, 3 H), 2.35 - 2.44 (m, 2 H), 1.48 - 1.54 (m, 2 H), 0.66 - 0.75 (m, 1 H), 0.37 - 0.42 (m, 2 H), 0.00 - 0.05 (m, 2 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 173.2, 37.4, 35.4, 33.5, 10.8, 4.6 ppm.

MS (EI, 70 eV) *m/z* 141.2 (M^+), 126.1, 113.1, 98.1, 87.1, 72.1, 55.1.

HRMS (ESI+) *m/z* $[C_8H_{15}NO + H]^+$ calcd. 142.12264, found 142.12217.

*N,N-dimethyl-5-phenylpentanamide (**5n**)*



Purification by column chromatography (silica gel, pentane/ethyl acetate, 1:1→1:1.5). Yield: 176 mg (0.857 mmol, 86 %) colorless oil.

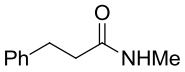
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.24 - 7.30 (m, 2 H), 7.14 - 7.21 (m, 3 H), 2.98 (s, 3 H), 2.94 (s, 3 H), 2.65 (t, *J*=7.02 Hz, 2 H), 2.30 - 2.36 (m, 2 H), 1.63 - 1.74 (m, 4 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 173.0, 142.5, 128.5, 128.4, 125.8, 37.4, 35.9, 35.5, 33.3, 31.4, 25.0 ppm.

MS (EI, 70 eV) *m/z*: 205.2 (M^+), 117.1, 100.1, 87.1, 72.1.

The spectroscopic data correspond to those reported in the literature.[4]

*N-methyl-3-phenylpropanamide (**5o**)*



Purification by column chromatography (pentane/ethyl acetate, 1:2 → 1:3). Yield: 89 mg (0.546 mmol, 55 %) crystalline white solid.

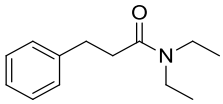
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.27 - 7.31 (m, 2 H), 7.17 - 7.23 (m, 3 H), 5.40 (br. s., 1 H), 2.97 (t, *J*=7.32 Hz, 2 H), 2.77 (d, *J*=4.88 Hz, 3 H), 2.47 (t, *J*=7.93 Hz, 2 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 172.8, 141.1, 128.7, 128.5, 126.4, 38.6, 31.9, 26.4 ppm.

MS (EI, 70 eV) *m/z*: 163.1 (M^+), 133.1, 105.1, 91.1, 77.1, 65.1, 58.1, 51.1.

The spectroscopic data correspond to those reported in the literature.[4]

*N,N-diethyl-3-phenylpropanamide (**5p**)*



Variation from the general procedure: 5 mol% of catalyst **1d** was used. Purification by column chromatography (pentane/ethyl acetate, 1:1.5). Yield: 156 mg (0.761 mmol, 76 %) colorless oil.

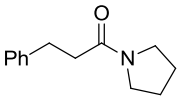
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.15 - 7.32 (m, 5 H), 3.38 (q, *J*=7.12 Hz, 2 H), 3.22 (q, *J*=7.02 Hz, 2 H), 2.96 - 3.01 (m, 2 H), 2.56 - 2.62 (m, 2 H), 1.10 (td, *J*=7.17, 4.58 Hz, 6 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 171.4, 141.8, 128.60, 128.59, 126.2, 42.0, 40.3, 35.3, 31.8, 14.4, 13.2 ppm.

MS (EI, 70 eV) m/z: 205.2 (M^+), 176.1, 133.1, 120.1, 105.1, 91.1, 72.1, 58.1.

The spectroscopic data correspond to those reported in the literature.[4]

*3-phenyl-1-(pyrrolidin-1-yl)propan-1-one (**5q**)*



Purification by column chromatography (pentane/ethyl acetate, 1:2). Yield: 133 mg (0.655 mmol, 66 %) colorless oil.

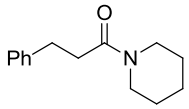
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.27 - 7.31 (m, 2 H), 7.17 - 7.25 (m, 3 H), 3.47 (t, *J*=6.87 Hz, 2 H), 3.29 (t, *J*=6.71 Hz, 2 H), 2.96 - 3.02 (m, 2 H), 2.54 - 2.59 (m, 2 H), 1.85 - 1.92 (m, 2 H), 1.79 - 1.85 (m, 2 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.9, 141.6, 128.5, 126.1, 46.6, 45.7, 36.8, 31.3, 26.1, 24.4 ppm.

MS (EI, 70 eV) m/z: 203.2 (M^+), 112.1, 91.1, 70.1, 55.1.

The spectroscopic data correspond to those reported in the literature.[7]

*3-phenyl-1-(piperidin-1-yl)propan-1-one (**5r**)*



Purification by column chromatography (pentane/ethyl acetate, 1:1). Yield: 167 mg (0.770 mmol, 77 %) colorless oil.

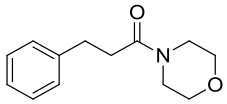
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.27 - 7.34 (m, 2 H), 7.18 - 7.27 (m, 3 H), 3.57 (t, *J*=5.80 Hz, 2 H), 3.34 (t, *J*=5.49 Hz, 2 H), 2.98 (t, *J*=7.63 Hz, 2 H), 2.63 (t, *J*=8.24 Hz, 2 H), 1.59 - 1.66 (m, 2 H), 1.50 - 1.58 (m, 2 H), 1.43 - 1.50 (m, 2 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.5, 141.5, 128.53, 128.50, 126.1, 46.7, 42.8, 35.3, 31.7, 26.4, 25.6, 24.6 ppm.

MS (EI, 70 eV) m/z: 217.2 (M^+), 126.1, 112.1, 105.1, 91.1, 84.1, 77.1, 69.1, 56.1.

The spectroscopic data correspond to those reported in the literature.[4]

*1-morpholino-3-phenylpropan-1-one (**5s**)*



Purification by column chromatography (silica gel, pentane/ethyl acetate, 1:1→1:3). Yield: 183 mg (0.836 mmol, 84 %) colorless oil which solidified upon standing (pale yellow solid).

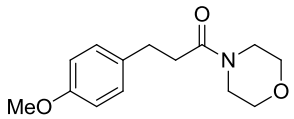
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.25 - 7.31 (m, 2 H), 7.17 - 7.22 (m, 3 H), 3.57 - 3.64 (m, 4 H), 3.47 - 3.53 (m, 2 H), 3.31 - 3.38 (m, 2 H), 2.94 - 3.00 (m, 2 H), 2.57 - 2.64 (m, 2 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.9, 141.1, 128.6, 128.5, 126.4, 126.3, 67.0, 66.5, 46.0, 42.0, 34.9, 31.5 ppm.

MS (EI, 70 eV) m/z: 219.2 (M^+), 128.1, 105.1, 91.1, 77.1, 57.1.

The spectroscopic data correspond to those reported in the literature.[4]

*3-(4-methoxyphenyl)-1-morpholinopropan-1-one (**5t**)*



Representative procedure for 10 mmol scale reaction: Using a glove box, a pressure tube (Ace pressure tube, 38 mL volume) was charged with a magnetic stirring bar, 4-acetyl morpholine (20 mmol, 2.30 mL, 2.0 eq), *t*-BuOK (12.0 mmol, 1.34 g, 1.2 eq), 4-methoxybenzyl alcohol (10 mmol, 1.24 mL, 1.0 eq), catalyst **1d** (0.250 mmol, 132 mg, 2.5 mol%) and THF (10 mL). The tube was sealed with a Teflon cap and immersed into a 100 °C oil bath outside the glove box for 24 hours. After cooling, the reaction mixture was quenched with half-saturated aqueous NaCl solution (10 mL) and extracted with diethyl ether (3x 100 mL). The combined organic phase was dried over Na_2SO_4 and concentrated. The crude product was nearby pure as judged by ^{1}H NMR analysis and was purified using a small pad (5

cm height) of silica gel eluting with pentane/ethyl acetate, 1:2 to give the product as a colorless oil (2.01 g, 8.06 mmol, 81 %).

The reaction gave the same yields on a 1 and 5 mmol scale.

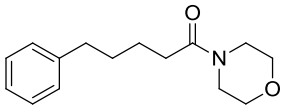
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.08 - 7.17 (m, 2 H), 6.79 - 6.87 (m, 2 H), 3.78 (s, 3 H), 3.58 - 3.67 (m, 4 H), 3.50 - 3.57 (m, 2 H), 3.31 - 3.40 (m, 2 H), 2.87 - 2.95 (m, 2 H), 2.53 - 2.62 (m, 2 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 171.1, 158.2, 133.2, 129.5, 114.1, 67.0, 66.6, 55.4, 46.1, 42.0, 35.2, 30.7 ppm.

MS (EI, 70 eV) *m/z*: 249.2 (M^+), 161.1, 134.1, 121.1, 108.1, 86.1, 70.1, 57.1.

The spectroscopic data correspond to those reported in the literature.[7]

*1-morpholino-5-phenylpentan-1-one (**5u**)*



10 mmol scale. Purification by column chromatography (pentane/ethyl acetate, 6:4 → 1:1). Yield: 2.02 g (8.17 mmol, 82 %) colorless oil.

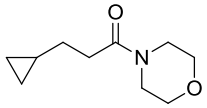
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.21 - 7.25 (m, 2 H), 7.12 - 7.19 (m, 3 H), 3.55 - 3.66 (m, 6 H), 3.35 - 3.42 (m, 2 H), 2.58 - 2.67 (m, 2 H), 2.24 - 2.34 (m, 2 H), 1.60 - 1.71 (m, 4 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ =171.7, 142.3, 128.5, 125.9, 67.1, 66.8, 46.1, 42.0, 35.8, 33.1, 31.2, 25.0 ppm.

MS (EI, 70 eV) *m/z*: 247.2 (M^+), 156.1, 142.1, 129.1, 117.1, 104.1, 91.1, 70.1, 57.2.

The spectroscopic data correspond to those reported in the literature.[8]

*3-cyclopropyl-1-morpholinopropan-1-one (**5v**)*



5 mmol scale. Purification by column chromatography (pentane/ethyl acetate, 1:1). Yield: 780 mg (4.26 mmol, 85 %) colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.64 - 3.70 (m, 1 H), 3.58 - 3.63 (m, 1 H), 3.46 - 3.52 (m, 1 H), 2.38 - 2.45 (m, 1 H), 1.49 - 1.57 (m, 1 H), 0.67 - 0.77 (m, 1 H), 0.41 - 0.46 (m, 1 H), 0.03 - 0.08 (m, 2 H) ppm.

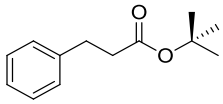
^{13}C NMR (126 MHz, $CDCl_3$) δ = 171.9, 67.1, 66.8, 46.2, 42.0, 33.2, 30.6, 10.8, 4.7 ppm.

MS (EI, 70 eV) *m/z*: 183.1 (M^+), 168.1, 154.1, 140.1, 129.1, 114.1, 97.1, 86.1, 70.1, 57.1.

HRMS (ESI+): *m/z* $[C_{10}H_{17}NO_2 + H]^+$ calcd. 184.13321, found 184.13268.

4.2 Ester alkylation products

*tert-butyl 3-phenylpropanoate (**6a**)*



Purification by column chromatography (silica gel, pentane/diethyl ether, 50:1). Yield: 145 mg (0.704 mmol, 70 %) colorless oil.

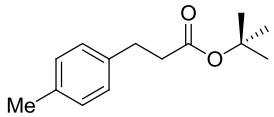
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.16 - 7.23 (m, 2 H), 7.08 - 7.15 (m, 3 H), 2.83 (t, *J*=7.78 Hz, 2 H), 2.43 - 2.49 (m, 2 H), 1.34 (s, 9 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 172.4, 140.9, 128.50, 128.45, 126.2, 80.4, 37.2, 31.3, 28.2 ppm.

MS (EI, 70 eV) *m/z*: 206.1 (M^+), 150.1, 133.1, 104.1, 91.1, 77.1, 57.1.

The spectroscopic data correspond to those reported in the literature.[9]

*tert-butyl 3-(p-tolyl)propanoate (**6b**)*



Purification by column chromatography (silica gel, pentane/diethyl ether, 50:1). Yield: 149 mg (0.677 mmol, 68 %) colorless oil.

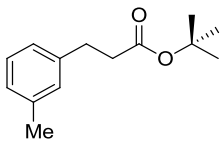
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.11 (s, 4 H), 2.89 (t, *J*=7.63 Hz, 2 H), 2.53 (t, *J*=8.24 Hz, 2 H), 2.33 (s, 3 H), 1.44 (s, 9 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 172.5, 137.8, 135.6, 129.2, 128.3, 80.4, 37.4, 30.8, 28.2, 21.1 ppm.

MS (EI, 70 eV) *m/z*: 220.2 (M^+), 164.1, 147.1, 118.1, 105.1, 91.1, 77.1, 65.1, 57.1

The spectroscopic data correspond to those reported in the literature.[9]

*tert-butyl 3-(m-tolyl)propanoate (**6c**)*



Purification by column chromatography (silica gel, pentane/diethyl ether, 50:1). Yield: 168 mg (0.764 mmol, 76 %) colorless oil.

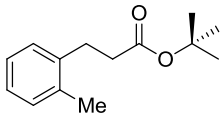
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.19 (t, J=7.48 Hz, 1 H), 6.99 - 7.06 (m, 3 H), 2.90 (t, *J*=7.93 Hz, 2 H), 2.52 - 2.58 (m, 2 H), 2.34 (s, 3 H), 1.45 (s, 9 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 172.4, 140.8, 138.0, 129.3, 128.4, 126.9, 125.4, 80.4, 37.2, 31.2, 28.2, 21.5 ppm.

MS (EI, 70 eV) *m/z*: 220.2 (M^+), 164.1, 147.1, 118.1, 105.1, 91.1, 77.1, 65.1, 57.2.

The spectroscopic data correspond to those reported in the literature.[9]

*tert-butyl 3-(o-tolyl)propanoate (**6d**)*



Purification by column chromatography (silica gel, pentane/diethyl ether, 50:1). Yield: 138 mg (0.626 mmol, 63 %) colorless oil.

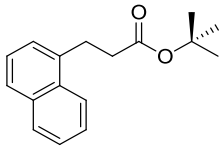
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.06 - 7.19 (m, 4 H), 2.86 - 2.96 (m, 3 H), 2.48 - 2.55 (m, 2 H), 2.34 (s, 3 H), 1.45 (s, 9 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 172.56, 139.0, 136.1, 130.3, 128.6, 126.4, 126.1, 80.5, 35.9, 28.6, 28.2, 19.4 ppm.

MS (EI, 70 eV) *m/z*: 220.2 (M^+), 164.1, 147.1, 119.1, 105.1, 91.1, 77.1, 65.1, 57.1.

The spectroscopic data correspond to those reported in the literature.[9]

*tert-butyl 3-(naphthalen-1-yl)propanoate (**6e**)*



Purification by column chromatography (silica gel, pentane/diethyl ether, 50:1). Yield: 161 mg (0.629 mmol, 63 %) colorless oil.

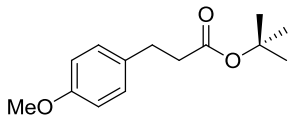
^{1}H NMR (500 MHz, $CDCl_3$) δ =8.06 (d, J=8.54 Hz, 1 H), 7.87 (d, J=7.93 Hz, 1 H), 7.74 (d, J=7.93 Hz, 1 H), 7.46 - 7.57 (m, 2 H), 7.34 - 7.44 (m, 2 H), 3.35 - 3.44 (m, 2 H), 2.65 - 2.73 (m, 2 H), 1.42 - 1.51 (m, 9 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 172.5, 136.9, 134.0, 131.8, 128.9, 127.1, 126.1, 126.0, 125.7, 123.6, 80.6, 36.5, 28.4, 28.2 ppm.

MS (EI, 70 eV) *m/z*: 256.1 (M^+), 200.1, 183.1, 153.1, 141.1, 128.1, 115.0, 77.0, 57.1.

Elemental analysis (%) for $C_{17}H_{20}O_2$ calcd. C 79.65, H 7.86; found: C 79.55, H 7.68.

*tert-butyl 3-(4-methoxyphenyl)propanoate (**6f**)*



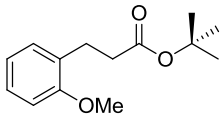
Purification by column chromatography (silica gel, pentane/diethyl ether, 30:1). Yield: 181 mg (0.767 mmol, 77 %) colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ =7.12 (d, *J*=8.20 Hz, 2 H), 6.82 (d, *J*=8.20 Hz, 2 H), 3.78 (s, 3 H), 2.85 (t, *J*=8.20 Hz, 2 H), 2.50 (t, *J*=7.61 Hz, 2 H), 1.42 (s, 9 H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ = 172.5, 133.0, 129.4, 113.9, 80.4, 55.4, 37.5, 30.4, 28.2 ppm.

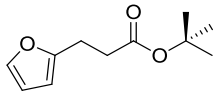
MS (EI, 70 eV) *m/z*: 236.1 (M^+), 180.1, 163.1, 137.0, 121.1, 91.1, 77.0, 57.1.
The spectroscopic data correspond to those reported in the literature.[10]

*tert-butyl 3-(2-methoxyphenyl)propanoate (**6g**)*



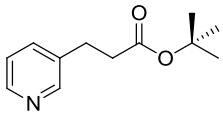
Purification by column chromatography (silica gel, pentane/diethyl ether, 40:1). Yield: 165 mg (0.699 mmol, 70 %) colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.10 - 7.24 (m, 2 H), 6.78 - 6.93 (m, 2 H), 3.83 (s, 3 H), 2.84 - 2.96 (m, 2 H), 2.46 - 2.58 (m, 2 H), 1.43 (s, 9 H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ = 172.9, 157.6, 130.0, 129.2, 127.5, 120.4, 110.3, 80.1, 55.3, 35.5, 28.2, 26.3 ppm.
MS (EI, 70 eV) *m/z*: 236.1 (M^+), 180.1, 163.0, 134.1, 121.1, 105.1, 91.1, 77.0, 65.1, 57.1.
Elemental analysis (%) for $C_{14}H_{20}O_3$ calcd. C 71.16, H 8.53; found: C 71.08, H 8.82.
Due to low polarity of the compound, no ESI+ HRMS could be obtained.

*tert-butyl 3-(furan-2-yl)propanoate (**6h**)*



Purification by column chromatography (silica gel, pentane/diethyl ether, 50:1). Yield: 107 mg (0.546 mmol, 55 %) colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.29 (dd, *J*=1.83, 0.92 Hz, 1 H), 6.27 (dd, *J*=3.05, 1.83 Hz, 1 H), 6.00 (dd, *J*=3.36, 0.92 Hz, 1 H), 2.92 (t, *J*=7.63 Hz, 1 H), 2.53 - 2.59 (m, 2 H), 1.43 (s, 9 H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ = 172.0, 154.6, 141.2, 110.3, 105.3, 80.6, 34.0, 28.2, 23.8 ppm.
MS (EI, 70 eV) *m/z*: 196.1 (M^+), 140.0, 123.0, 94.0, 81.0, 65.1, 57.1.
The spectroscopic data correspond to those reported in the literature.[9]

*tert-butyl 3-(pyridin-3-yl)propanoate (**6i**)*



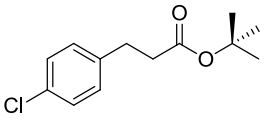
Purification by column chromatography (silica gel, pentane/diethyl ether, 50:1). Yield: 100 mg (0.483 mmol, 48 %) colorless oil.
^{1}H NMR (500 MHz, $CDCl^3$) δ = 8.35 - 8.53 (m, 2 H), 7.50 (dt, *J*=7.63, 1.83 Hz, 1 H), 7.18 (dd, *J*=7.78, 4.73 Hz, 1 H), 2.88 (t, *J*=7.63 Hz, 2 H), 2.53 (t, *J*=7.48 Hz, 2 H), 1.38 (s, 9 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 171.8, 150.0, 147.8, 136.1, 136.0, 123.4, 80.8, 36.6, 28.3, 28.1 ppm.

MS (EI, 70 eV) *m/z*: 207.1 (M^+), 192.1, 162.1, 151.0, 134.0, 106.1, 92.0, 78.0, 65.1, 57.1.

The spectroscopic data correspond to those reported in the literature.[11]

*tert-butyl 3-(4-chlorophenyl)propanoate (**6j**)*



Variation from the general procedure: *t*-BuONa (1.5 equiv) was used as the base. Purification by column chromatography (pentane/diethyl ether, 50:1). Yield: 174 mg (0.723 mmol, 72 %) colorless oil.

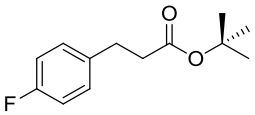
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.21 - 7.31 (m, 2 H), 7.08 - 7.20 (m, 2 H), 2.78 - 2.96 (m, 2 H), 2.46 - 2.62 (m, 2 H), 1.43 (s, 9 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 172.1, 139.4, 132.0, 129.8, 128.6, 80.6, 37.0, 30.6, 28.2 ppm.

MS (EI, 70 eV) *m/z*: 240.1 (M^+), 225.0, 207.0, 184.0, 167.0, 149.0, 138.0, 125.0, 112.0, 103.1, 89.0, 77.0, 57.1

The spectroscopic data correspond to those reported in the literature.[9]

*tert-butyl 3-(4-fluorophenyl)propanoate (**6k**)*



2 mL toluene were used. Purification by column chromatography (silica gel, pentane/diethyl ether, 50:1). Yield: 184 mg (0.821 mmol, 82 %) colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.15 (dd, *J*=8.39, 5.34 Hz, 2 H), 6.96 (t, *J*=8.70 Hz, 2 H), 2.88 (t, *J*=7.63 Hz, 2 H), 2.51 (t, *J*=7.78 Hz, 2 H), 1.41 (s, 9 H) ppm.

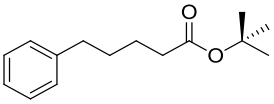
^{13}C NMR (126 MHz, $CDCl_3$) δ = 172.2, 162.5, 160.6, 136.54*, 136.51*, 129.9*, 129.8*, 115.3*, 115.2*, 80.6, 37.3, 30.5, 28.2 ppm.

*^{13}C-^{19}F coupling is observed.

MS (EI, 70 eV) *m/z*: 224.1 (M^+), 168.1, 151.1, 122.1, 109.1, 103.1, 96.1, 83.1, 77.1, 57.1.

The spectroscopic data correspond to those reported in the literature.[9]

*tert-butyl 5-phenylpentanoate (**6l**)*

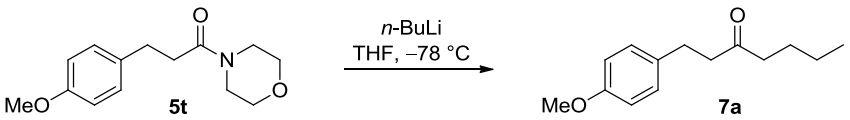


Purification by column chromatography (silica gel, pentane/diethyl ether, 50:1). Yield: 135 mg (0.576 mmol, 58 %) colorless oil.

When conducted at 100 °C (oil bath), the reaction gave the same isolated yield.
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.15 - 7.25 (m, 10 H), 7.05 - 7.14 (m, 3 H), 2.50 - 2.59 (m, 2 H), 2.12 - 2.20 (m, 2 H), 1.56 (dt, *J*=7.32, 3.66 Hz, 4 H), 1.36 (s, 9 H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$) δ = 173.2, 142.2, 128.5, 128.4, 125.9, 80.1, 35.8, 35.5, 31.0, 28.2, 24.9 ppm.
MS (EI, 70 eV) *m/z*: 234.1 (M^+), 178.1, 161.1, 117.1, 104.1, 91.1, 77.1, 65.0, 57.1.
The spectroscopic data correspond to those reported in the literature.[9]

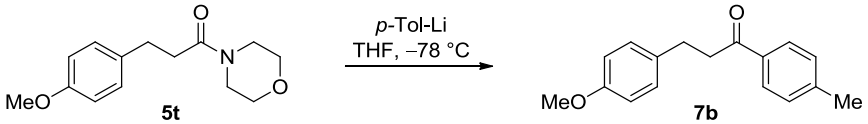
4.3 Follow-up products

*1-(4-methoxyphenyl)heptan-3-one (**7a**)*



To a solution of amide **5t** (255 mg, 1.02 mmol, 1 eq) in abs. THF (5 mL) was added *n*-BuLi (1.6 M in hexane, 3 mmol, 3 equiv, 1.88 mL) dropwise at –78 °C. After 3 h and 3 h 40 min aliquots of *n*-BuLi (0.5 mmol and 0.3 mmol, respectively) were added in addition. After 4 h 20 min overall reaction time the reaction was quenched with aqueous acetic acid (30 %, 5 mL), warmed to rt and extracted with diethyl ether (3x 30 mL). The combined organic phase was dried over Na_2SO_4 and concentrated. Purification by column chromatography (silica gel, pentane/diethyl ether, 6:1) gave ketone **7a** as a colorless oil (207 mg, 0.941 mmol, 92 %).
^{1}H NMR (300 MHz, $CDCl_3$) δ =7.03 - 7.15 (m, 2 H), 6.76 - 6.89 (m, 2 H), 3.78 (s, 3 H), 2.78 - 2.90 (m, 2 H), 2.63 - 2.76 (m, 2 H), 2.37 (t, *J*=7.32 Hz, 2 H), 1.44 - 1.61 (m, 2 H), 1.28 (dq, *J*=14.86, 7.35 Hz, 2 H), 0.88 (t, *J*=7.32 Hz, 3 H) ppm.
^{13}C NMR (75 MHz, $CDCl_3$) δ = 210.7, 158.0, 133.3, 129.3, 114.0, 55.4, 44.7, 42.9, 29.1, 26.0, 22.4, 14.0 ppm
MS (EI, 70 eV) *m/z*: 220.1 (M^+), 163.1, 135.1, 121.0, 108.0, 91.1, 85.0, 77.0, 57.1.
HRMS (ESI+): *m/z* $[C_{14}H_{20}O_2 + H]^+$ calcd. 221.15361, found 221.15303.

*3-(4-methoxyphenyl)-1-(pyridin-2-yl)propan-1-one (**7b**)*



To a solution of *para*-tolyl lithium (241 mg, 2.46 mmol, 3 eq.) in abs. THF (8 mL) was added a solution of 3-(4-methoxyphenyl)-1-morpholinopropan-1-one (204 mg, 0.819 mmol, 1 eq.) in abs. THF (3 mL) dropwise by syringe at –78 °C. The reaction mixture was stirred for 1 hour and was then quenched by the addition of aqueous acetic acid (30%, 5 mL). The reaction mixture was warmed to rt and extracted with MTBE (3x 30 mL). The combined organic phase was dried over Na_2SO_4 and concentrated. Column chromatography (pentane/diethyl ether,

9:1) gave the title compound as a colorless oil which solidified upon standing (187 mg, 0.736 mmol, 90 %).

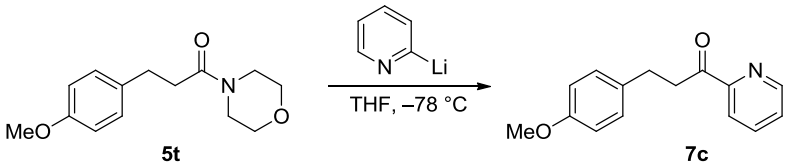
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.79 (d, *J*=8.24 Hz, 2 H), 7.14 - 7.23 (m, 2 H), 7.05 - 7.13 (m, 2 H), 6.72 - 6.81 (m, 2 H), 3.71 (s, 3 H), 3.11 - 3.23 (m, 2 H), 2.89 - 2.97 (m, 2 H), 2.33 (s, 3 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 199.1, 158.0, 143.9, 134.5, 133.5, 129.4, 128.3, 114.0, 55.3, 40.7, 29.4, 21.7 ppm.

MS (EI, 70 eV) *m/z*: 254.1 (M^+), 239.1, 135.0, 121.1, 108.1, 91.1, 77.0, 65.1, 51.0.

The spectroscopic data correspond to those reported in the literature.[12]

*3-(4-methoxyphenyl)-1-(pyridin-2-yl)propan-1-one (**7c**)*



5t **7c**

To a solution of 2-bromopyridine (438 mg, 264 µL, 2.77 mmol, 3.0 eq) in abs. THF (4 mL) was added *n*-butyl lithium (1.6 M in hexane, 1.44 mL, 2.30 mmol, 2.5 eq) dropwise at –78 °C and the resulting dark-orange solution was stirred for 1 hour at this temperature. Then a solution of the amide **5t** (230 mg, 0.924 mmol, 1.0 eq) in THF (3 mL) was added dropwise. After one hour the reaction was quenched by the addition of hydrochloric acid (1 M, 5 mL), diluted with MTBE and warmed to rt. The aqueous phase was extracted with MTBE (3x 30 mL) and the combined organic phase was dried over Na_2SO_4 and concentrated. Column chromatography (silica gel, pentane/diethyl ether, 5:1) gave the ketone as a colorless oil (180 mg, 0.747 mmol, 81 %).

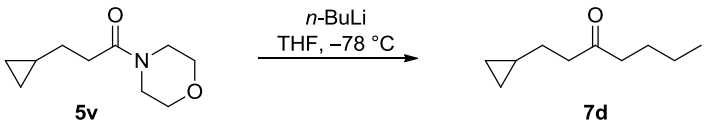
^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.58 - 8.73 (m, 1 H), 8.03 (dt, *J*=7.78, 1.14 Hz, 1 H), 7.82 (td, *J*=7.71, 1.68 Hz, 1 H), 7.45 (ddd, *J*=7.63, 4.88, 1.22 Hz, 1 H), 7.12 - 7.24 (m, 2 H), 6.76 - 6.89 (m, 2 H), 3.77 (s, 3 H), 3.54 (t, *J*=7.63 Hz, 2 H), 3.01 (t, *J*=7.63 Hz, 2 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 201.2, 158.0, 153.4, 149.1, 137.0, 133.6, 129.5, 127.2, 121.9, 113.9, 55.3, 39.8, 29.1 ppm.

MS (EI, 70 eV) *m/z*: 241.1 (M^+), 212.1, 121.1, 107.0, 91.1, 79.0, 65.1, 51.0.

HRMS (ESI+): *m/z* $[C_{10}H_{14}N_2O + H]^+$ calcd. 242.11756, found 242.11702

*1-cyclopropylheptan-3-one (**7d**)*



5v **7d**

To a solution of amide **5v** (267 mg, 1.46 mmol, 1 eq) in abs. THF (5 mL) was added *n*-butyl lithium (1.6 M in hexane, 2.73 mL, 4.38 mmol, 3 eq) dropwise at –78 °C. The reaction mixture was stirred at this temperature for 1 hour and was then quenched with hydrochloric

acid (1 M, 5 mL) and diluted with diethyl ether (10 mL). After warming to rt, the reaction mixture was extracted with diethyl ether (3x 10 mL), the combined phase was dried over Na_2SO_4 and concentrated. Column chromatography (pentane/diethyl ether, 15:1, 1st eluting fraction) gave ketone **7d** as a colorless oil (203 mg, 1.32 mmol, 90 %).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.50 (t, *J*=7.32 Hz, 2 H), 2.41 (t, *J*=7.48 Hz, 2 H), 1.55 (dt, *J*=15.18, 7.51 Hz, 2 H), 1.46 (q, *J*=7.12 Hz, 2 H), 1.31 (dq, *J*=15.03, 7.40 Hz, 2 H), 0.90 (t, *J*=7.32 Hz, 3 H), 0.61 - 0.71 (m, 1 H), 0.35 - 0.46 (m, 2 H), -0.01 - 0.05 (m, 2 H) ppm.

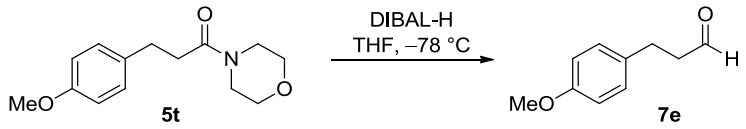
^{13}C NMR (126 MHz, $CDCl_3$) δ = 211.8, 42.9, 29.2, 26.1, 22.5, 14.0, 10.7, 4.6 ppm.

MS (EI, 70 eV) *m/z*: 154.1 (M^+), 139.1, 125.1, 112.1, 97.1, 83.1, 69.1, 57.1.

Elemental analysis (%) for $C_{10}H_{18}O$: calcd. C 77.87, H 11.76; found: C 77.76, H 12.03.

Due to low molecular weight and polarity, no ESI+ HRMS could be obtained.

*3-(4-methoxyphenyl)propanal (**7e**)*



To a solution of amide **5t** (130 mg, 0.522 mmol, 1 eq) in abs. THF (3 mL) was added DIBAL-H (1 M in hexane, 0.6 mL, 0.600 mmol, 1.15 eq) at –78 °C. The reaction was stirred for 50 min and was then quenched by the addition of an aqueous solution of Na/K tartrate and diluted with diethyl ether. The reaction was warmed to rt, the phases were separated and the aqueous phase was extracted with diethyl ether (4x 20 mL). The combined organic phase was dried over Na_2SO_4 and concentrated. Column chromatography (pentane/diethyl ether, 1:1) gave the aldehyde as a colorless oil (81 mg, 0.494 mmol, 95 %).

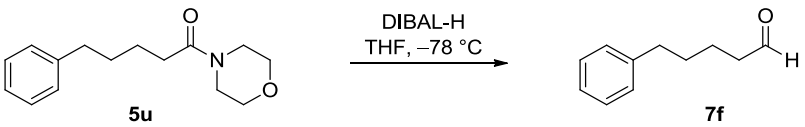
^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.81 (t, *J*=1.46 Hz, 1 H), 7.03 - 7.18 (m, 2 H), 6.75 - 6.94 (m, 2 H), 3.78 (s, 3 H), 2.86 - 2.95 (m, 2 H), 2.69 - 2.78 (m, 2 H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ = 201.9, 158.2, 129.3, 114.1, 55.4, 45.7, 27.4 ppm.

MS (EI, 70 eV) *m/z*: 164.1 (M^+), 121.1, 108.1, 91.1, 77.1, 65.1.

The spectroscopic data correspond to those reported in the literature.[13]

5-phenylpentanal (**7f**)



To a solution of amide **5u** (245 mg, 0.991 mmol, 1 eq) in abs. THF (5 mL) was added DIBAL-H (1 M in hexane, 1.09 mL, 1.09 mmol, 1.1 eq) dropwise at –78 °C. After 1 hour the reaction was monitored by TLC and another aliquot of DIBAL-H (300 µL, 300 µmol) was added. After further 20 min the reaction mixture was quenched with an aqueous solution of citric acid (33 wt-%, 6 mL), diluted with diethyl ether (10 mL), warmed to rt and stirred for

30 min. The phases were separated and the aqueous phase was extracted with diethyl ether (3x 10 mL). The combined organic phase was dried over Na_2SO_4 and concentrated. Column chromatography (pentane/diethyl ether, 15:1) gave the aldehyde **7f** as a colorless oil (117 mg, 0.722 mmol, 73 %).

The ^{1}H NMR spectrum was referenced using dichloromethane (δ = 5.30 ppm) because compound- and $CDCl_3$ signals overlapped.

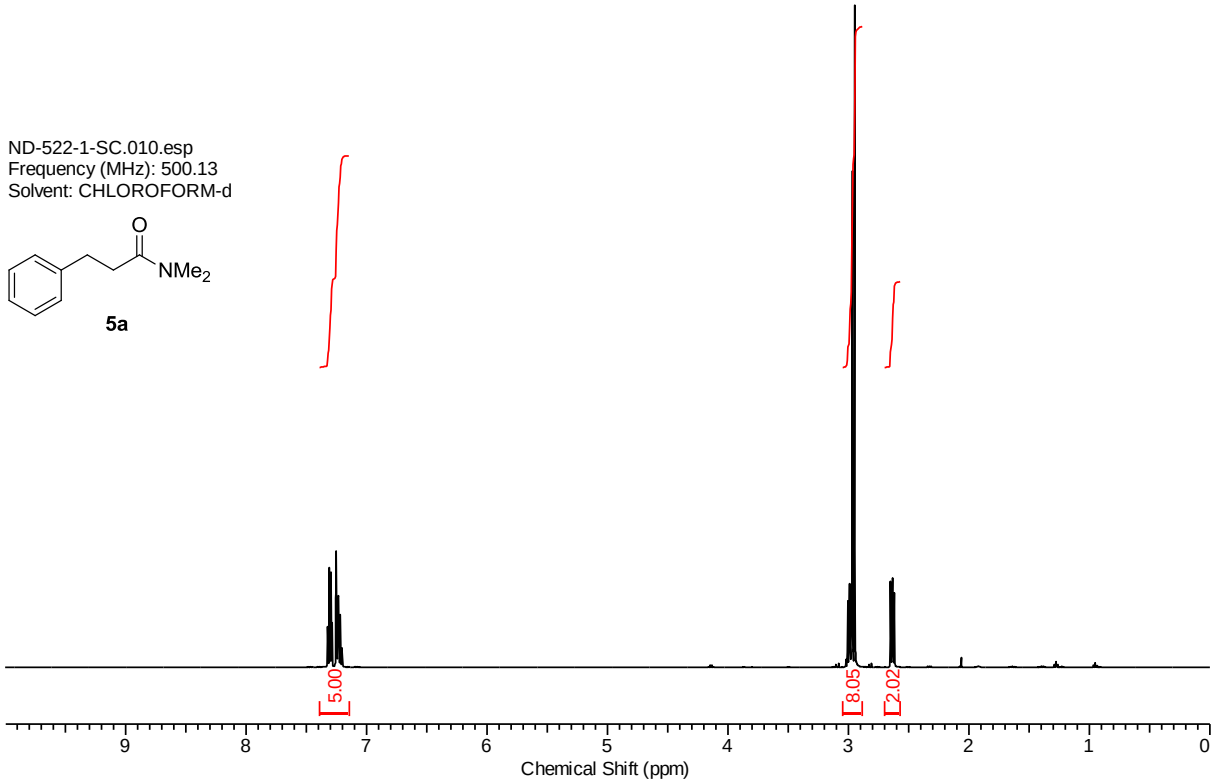
^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.76 (t, *J*=1.83 Hz, 1 H), 7.24 - 7.33 (m, 2 H), 7.13 - 7.24 (m, 3 H), 2.57 - 2.70 (m, 2 H), 2.46 (dtd, *J*=7.06, 3.57, 3.57, 1.68 Hz, 2 H), 1.62 - 1.75 (m, 4 H) ppm.

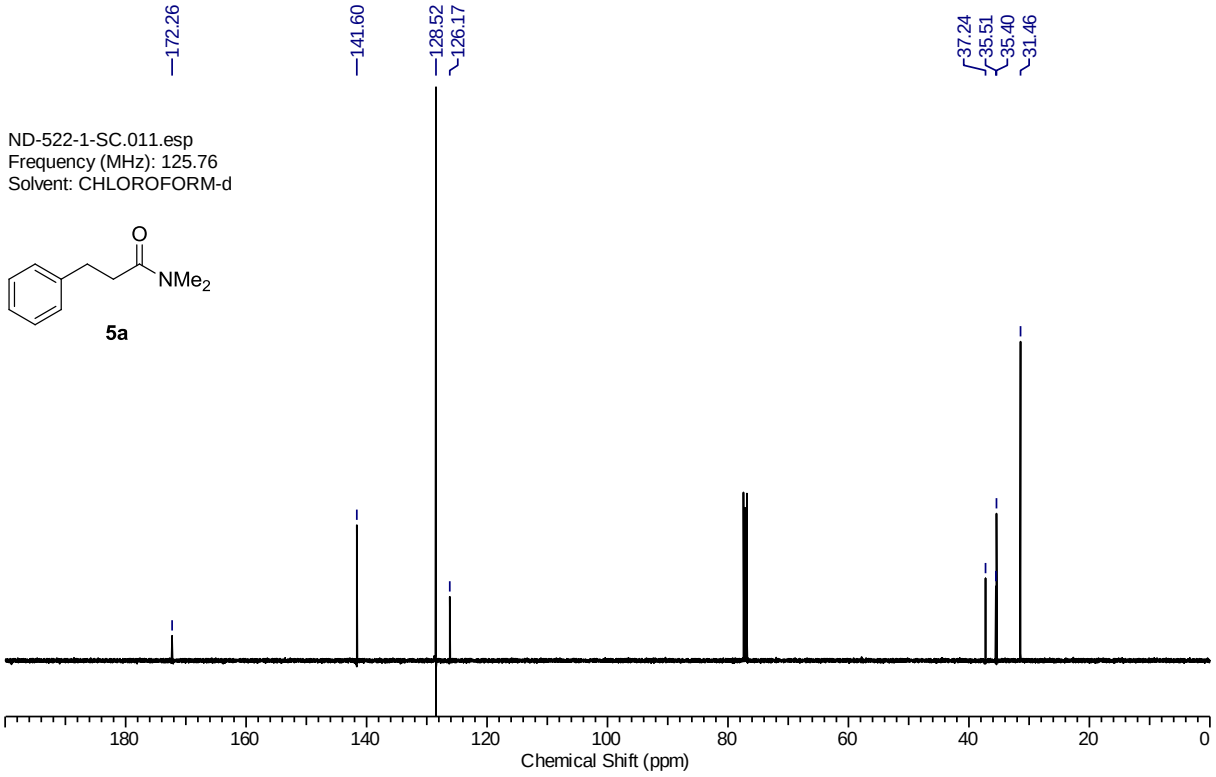
^{13}C NMR (126 MHz, $CDCl_3$) δ = 202.7, 142.1, 128.5, 126.0, 43.9, 35.8, 31.0, 21.8 ppm.

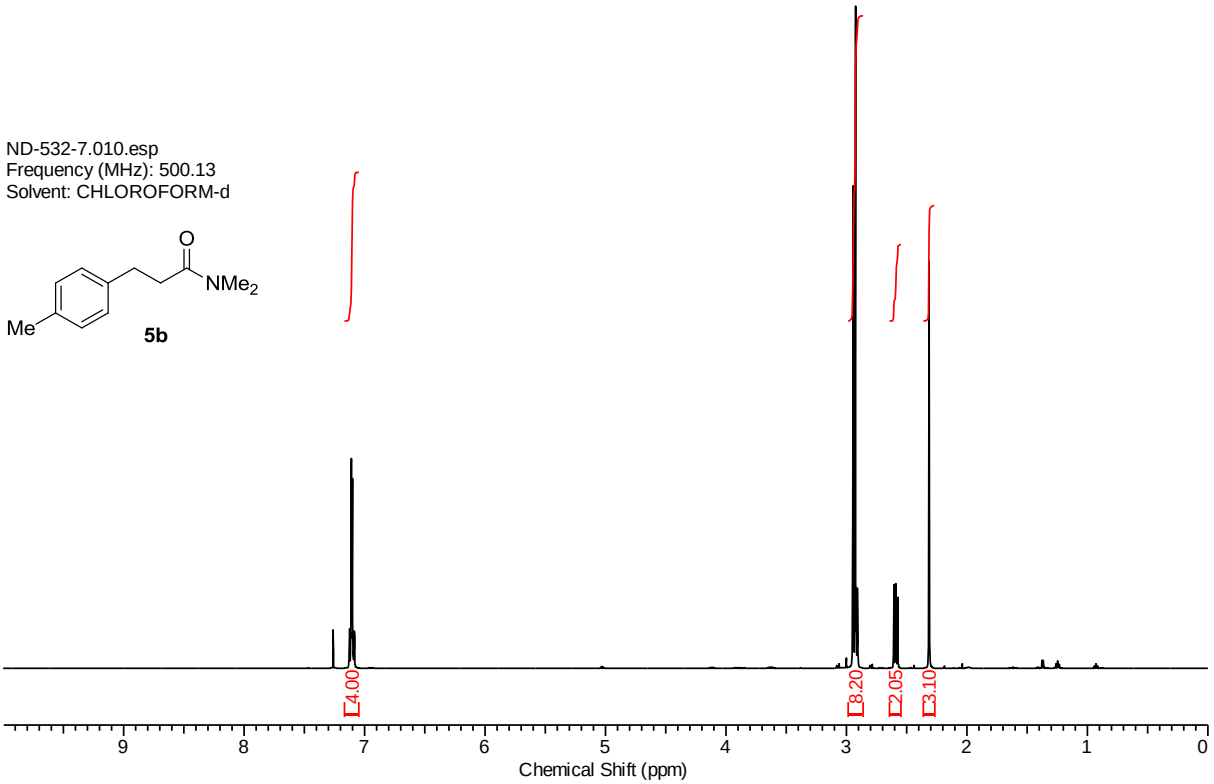
MS (EI, 70 eV) *m/z*: 162.1 (M^+), 144.1, 129.1, 117.1, 105.1, 91.1, 84.1, 77.1, 71.1, 65.1, 57.1, 51.1.

The spectroscopic data correspond to those reported in the literature.[14]

5 NMR-Spectra



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3.10
9
8
7
6
5
4
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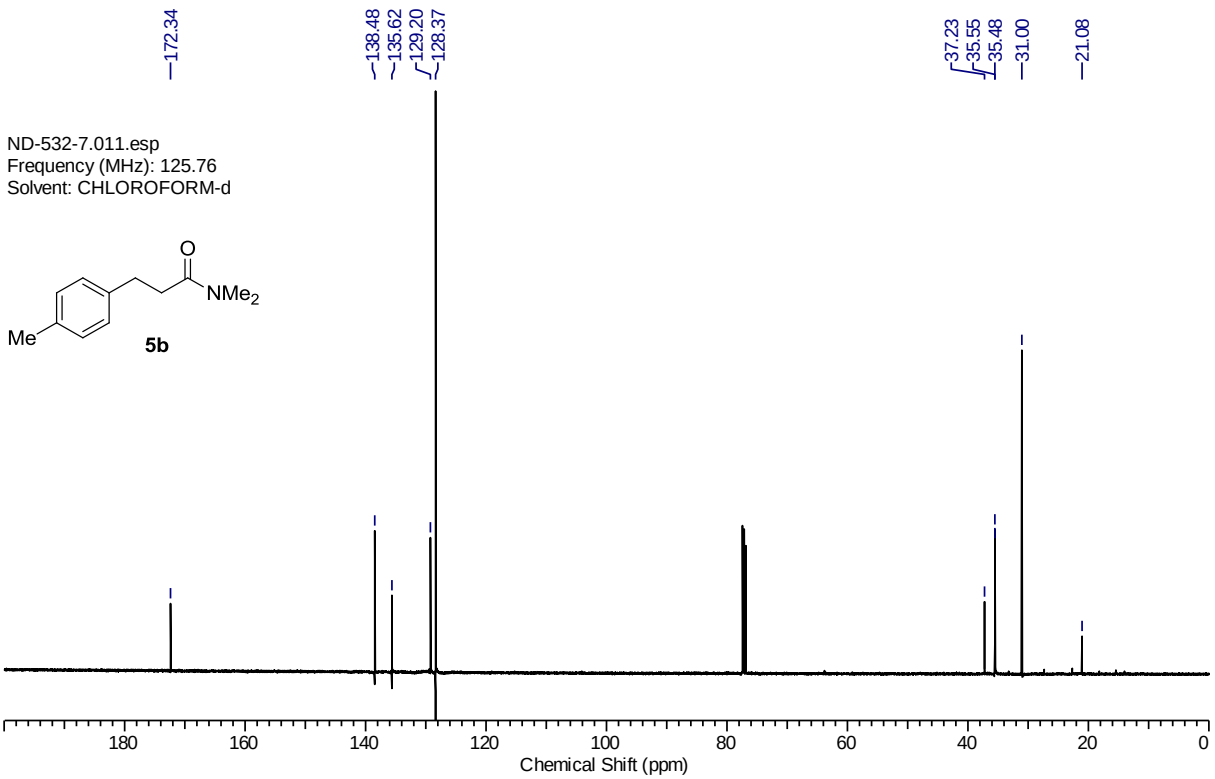
2
1
0
Chemical Shift (ppm)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5b
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140
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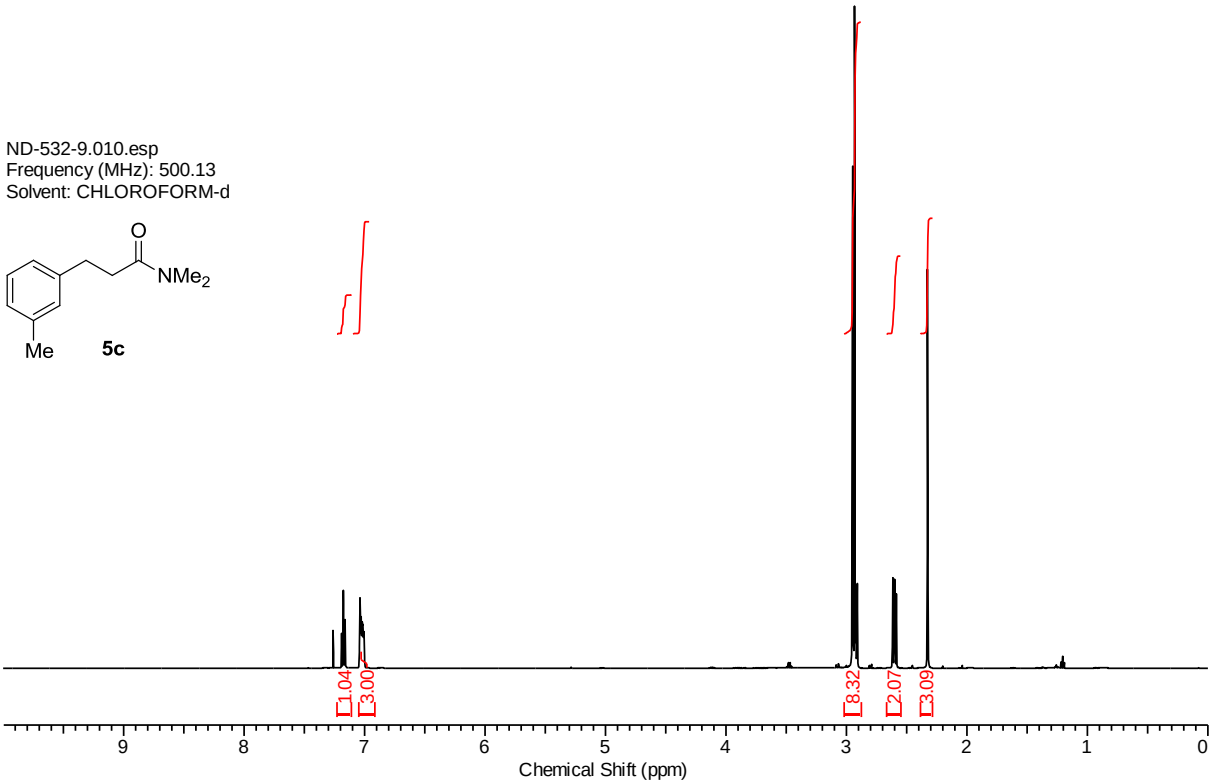
Chemical Shift (ppm)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7
6
5
4
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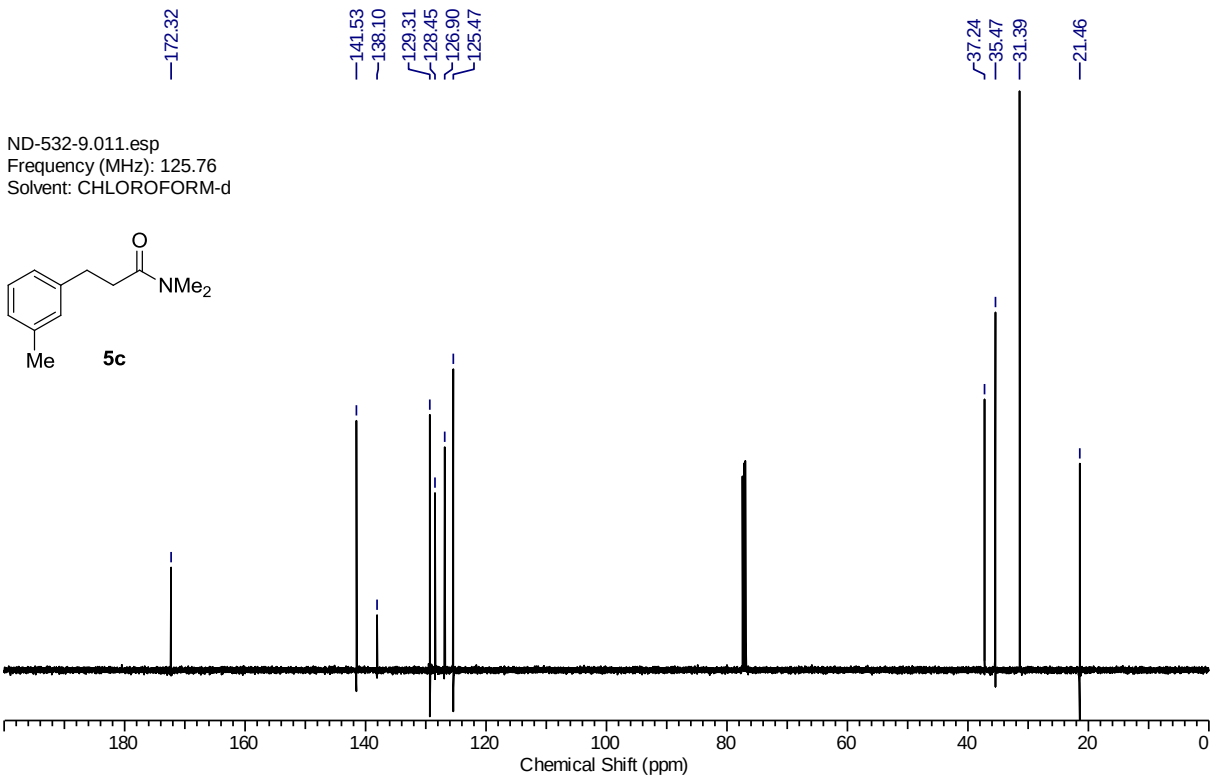
Chemical Shift (ppm)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128.45
126.90
125.47
37.24
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31.39
21.46
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Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
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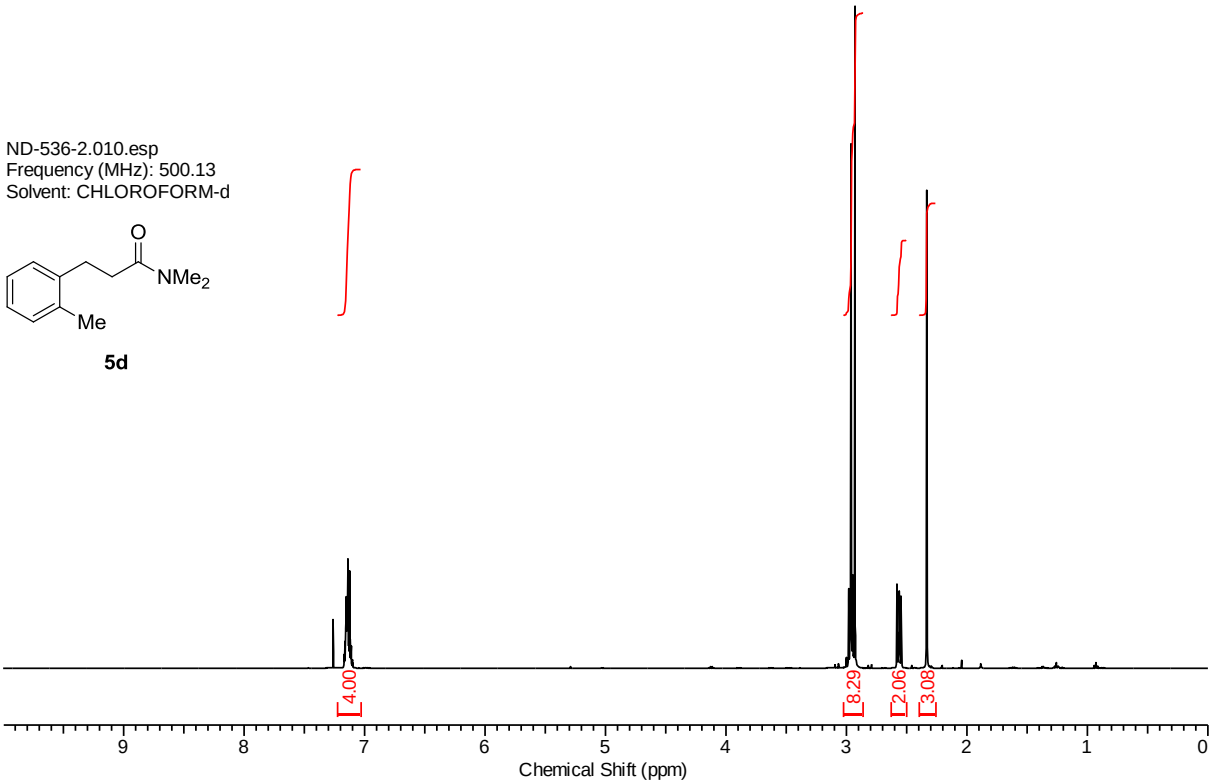
NMe2
Me
5c
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)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2
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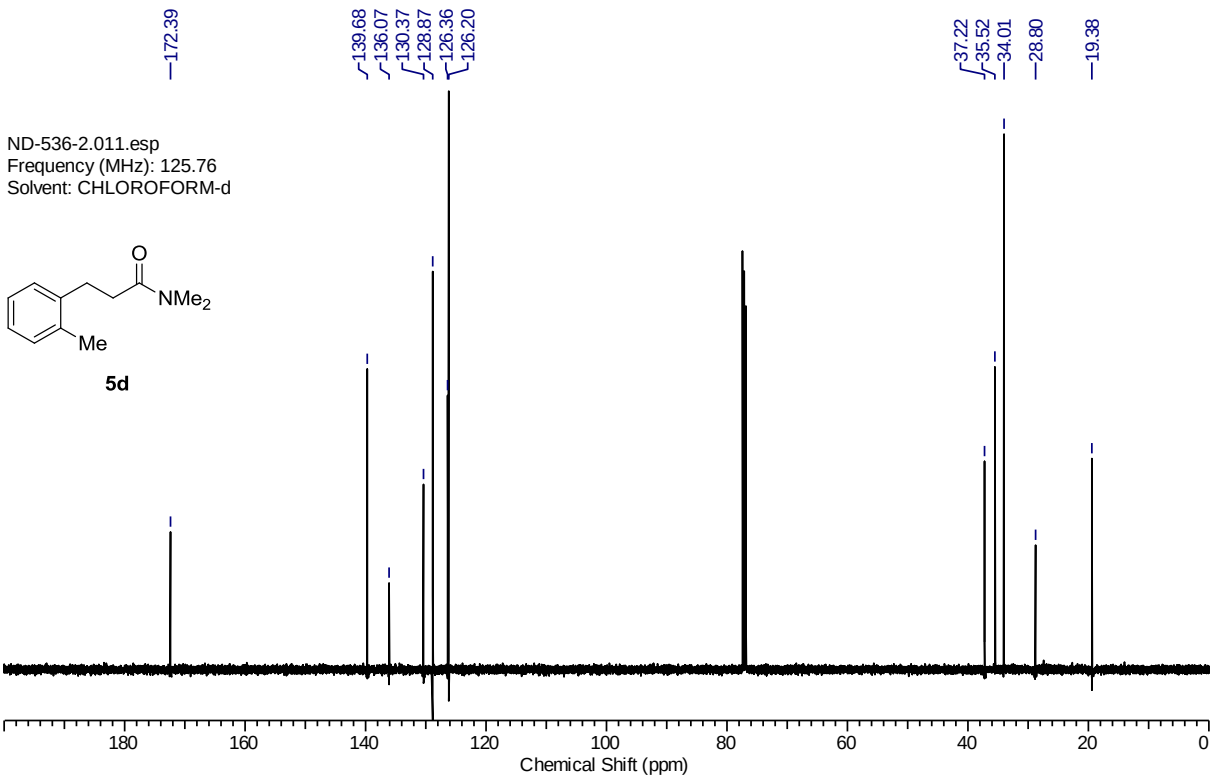
Chemical Shift (ppm)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28.80
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100
80
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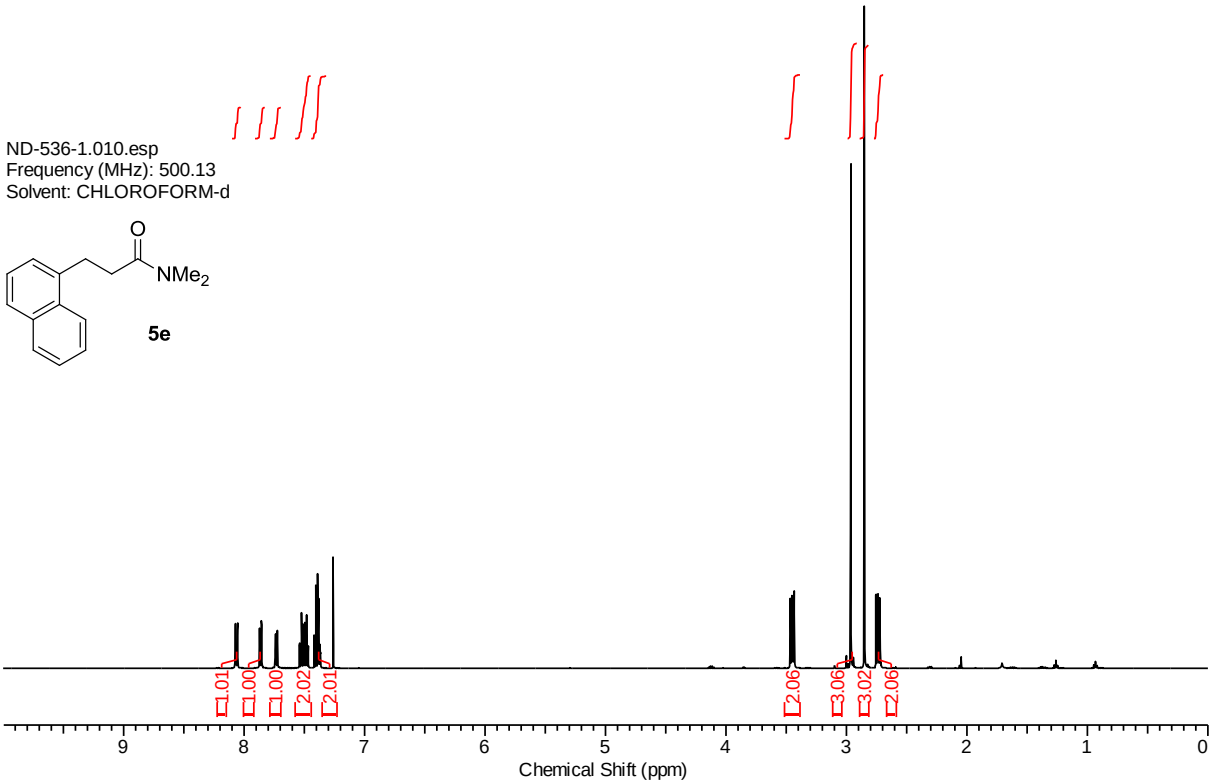
Chemical Shift (ppm)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3.02
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9
8
7
6
5
4
3
2
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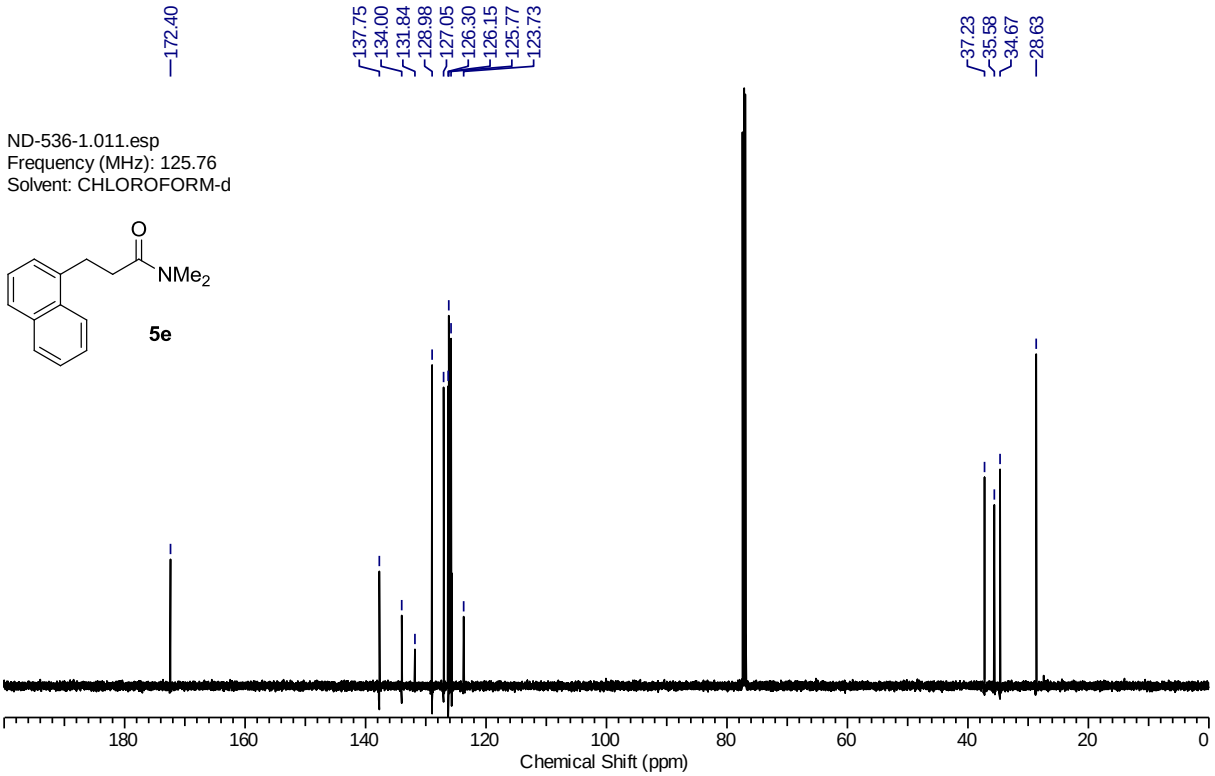
0
Chemical Shift (ppm)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123.73
37.23
35.58
34.67
28.63
ND-536-1.011.esp
Frequency (MHz): 125.76
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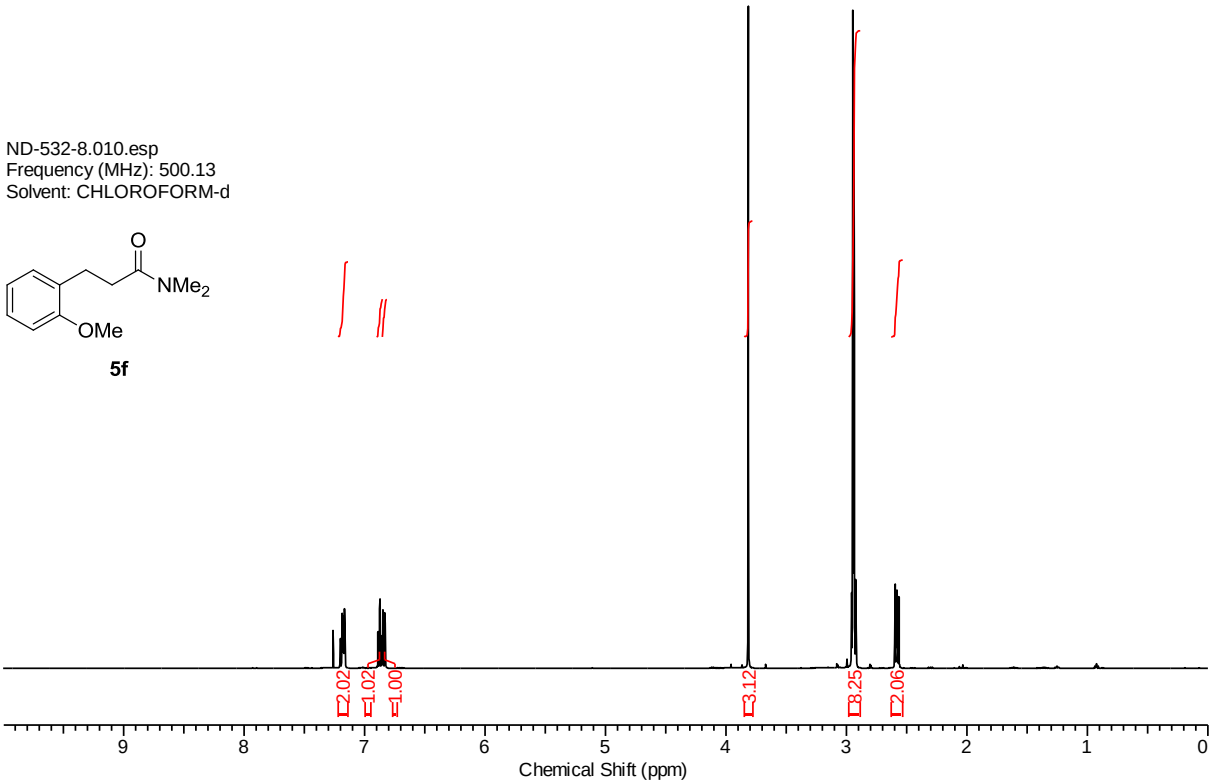
NMe2
5e
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)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9
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7
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4
3
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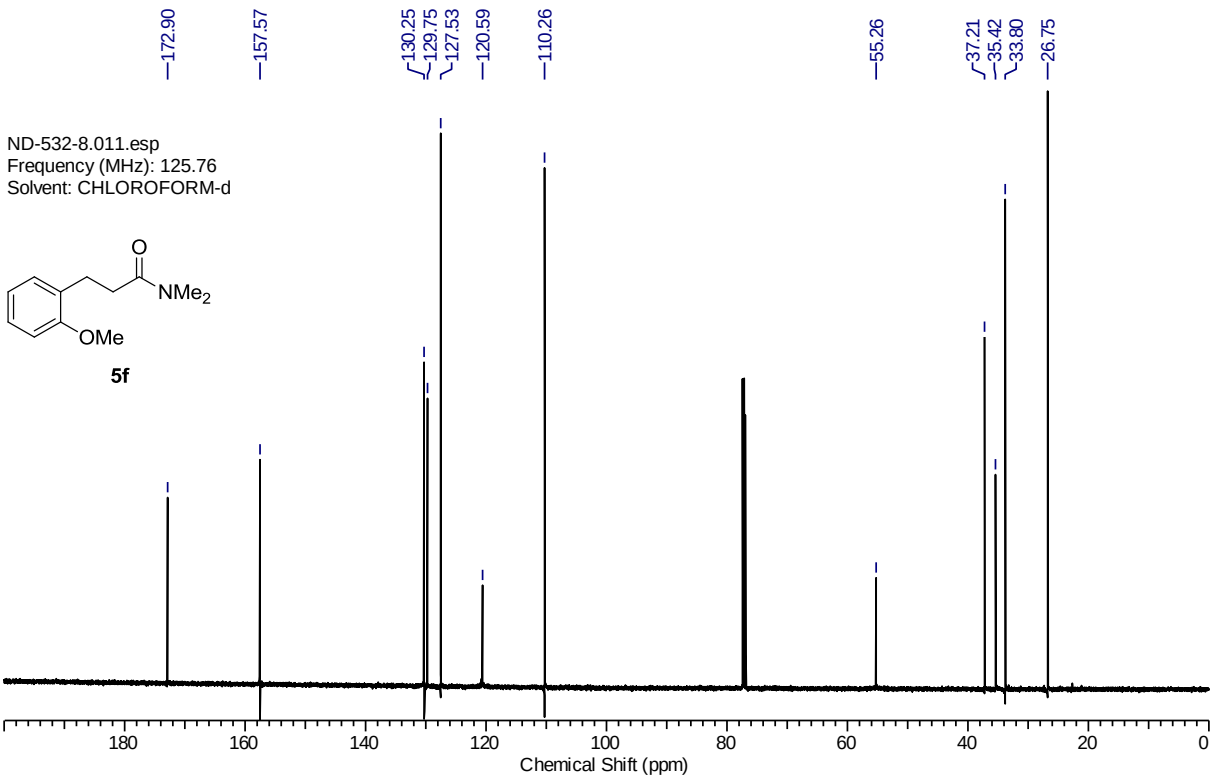
Chemical Shift (ppm)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127.53
120.59
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55.26
37.21
35.42
33.80
26.75
ND-532-8.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
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OMe
5f
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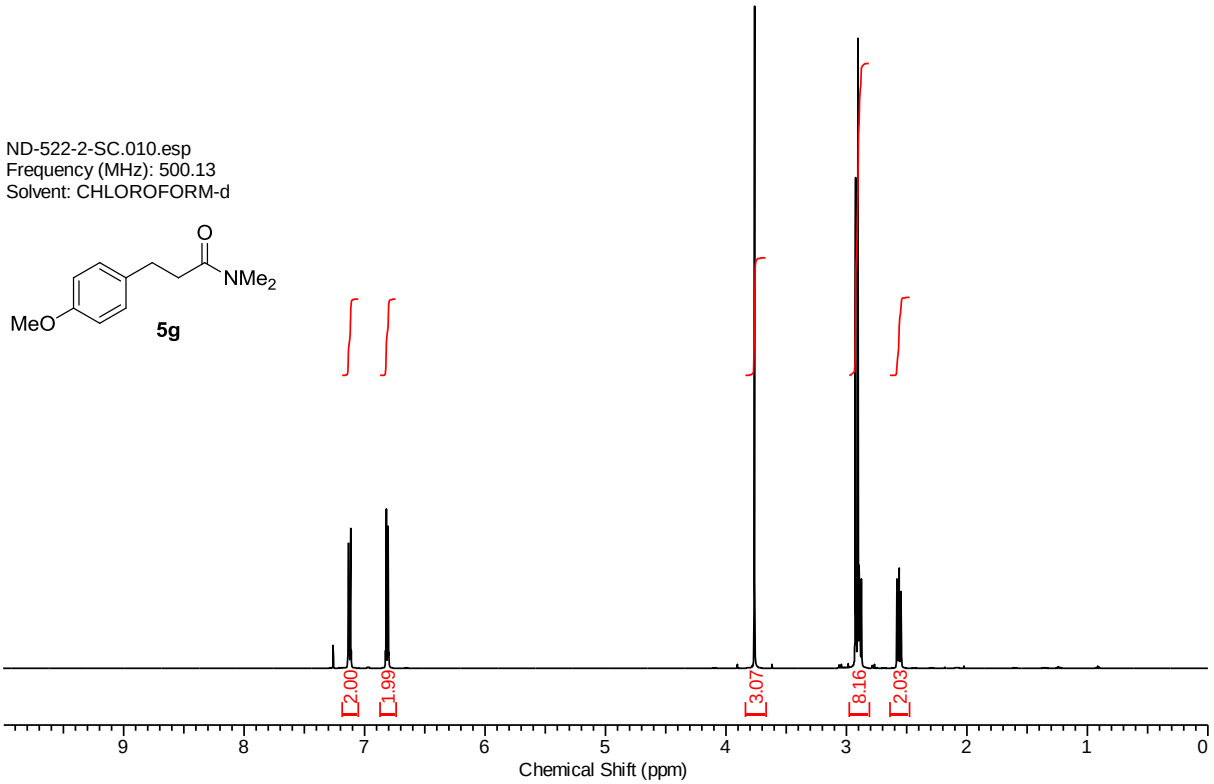
140
120
100
80
60
40
20
0
Chemical Shift (ppm)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9
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7
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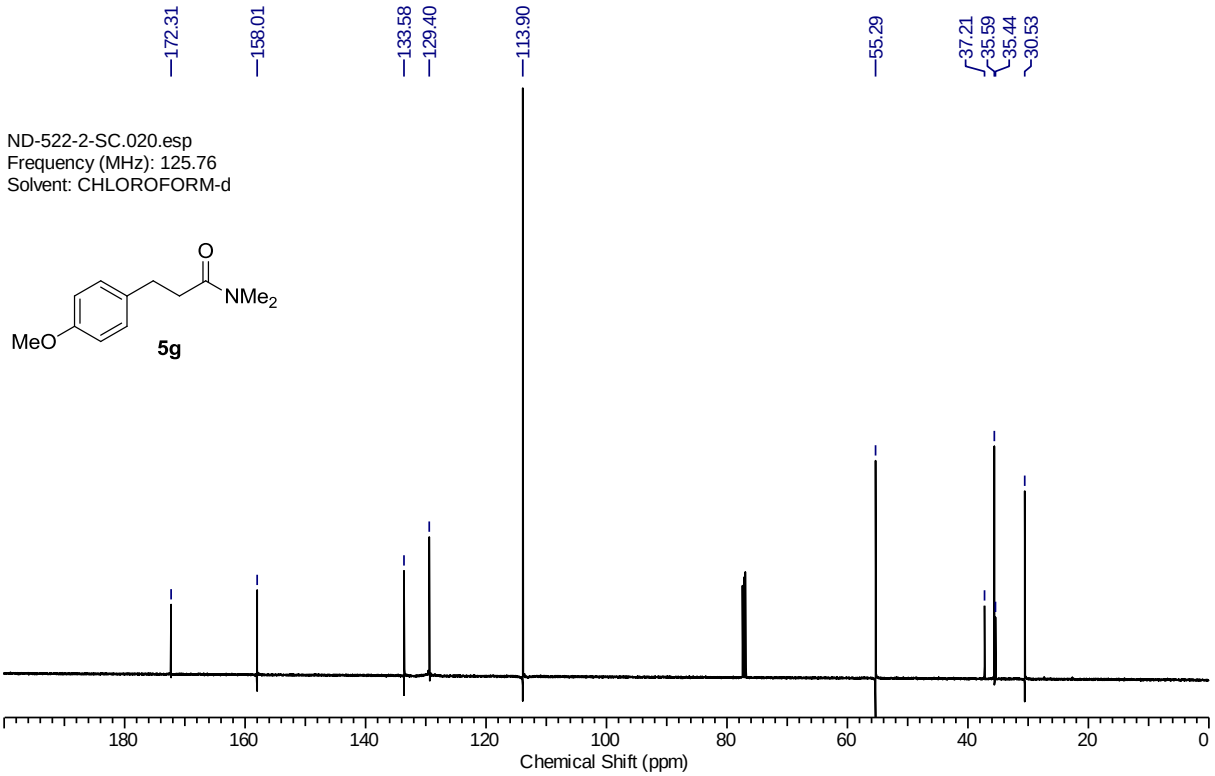
5
4
3
2
1
0
Chemical Shift (ppm)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129.40
113.90
55.29
37.21
35.59
35.44
30.53
ND-522-2-SC.020.esp
Frequency (MHz): 125.76
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5g
180
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100
80
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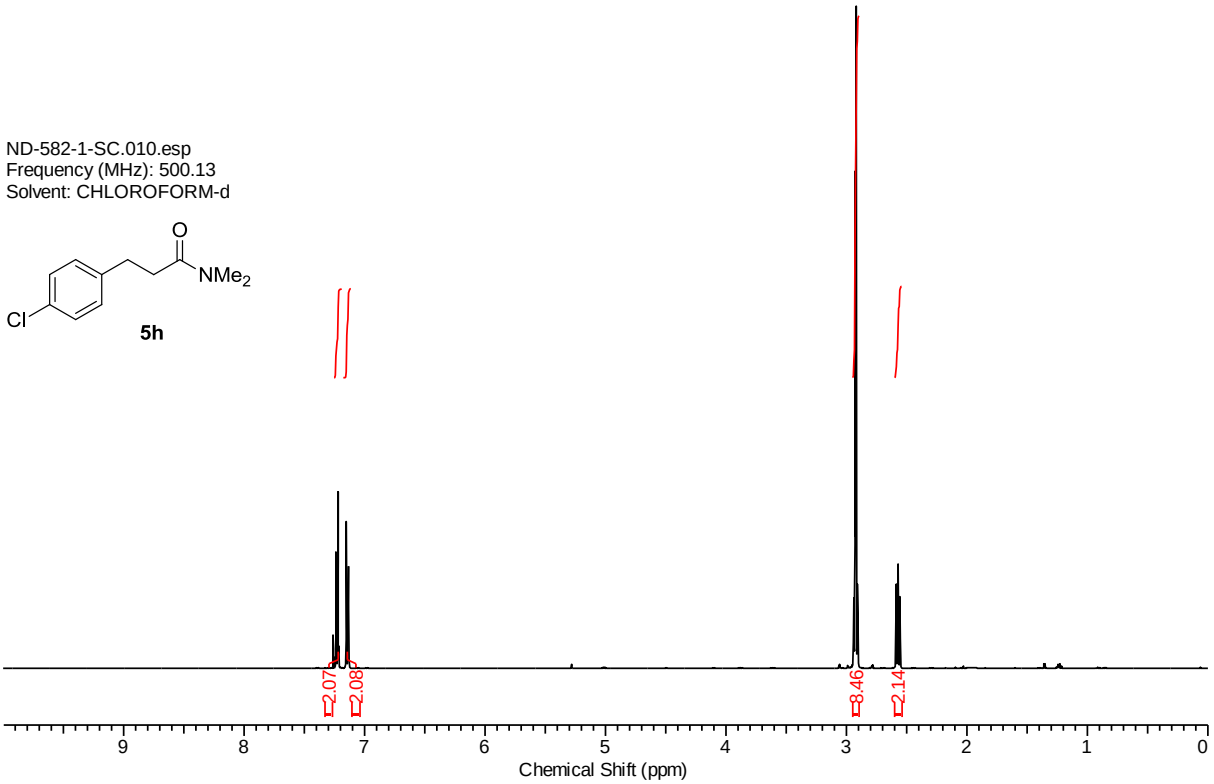
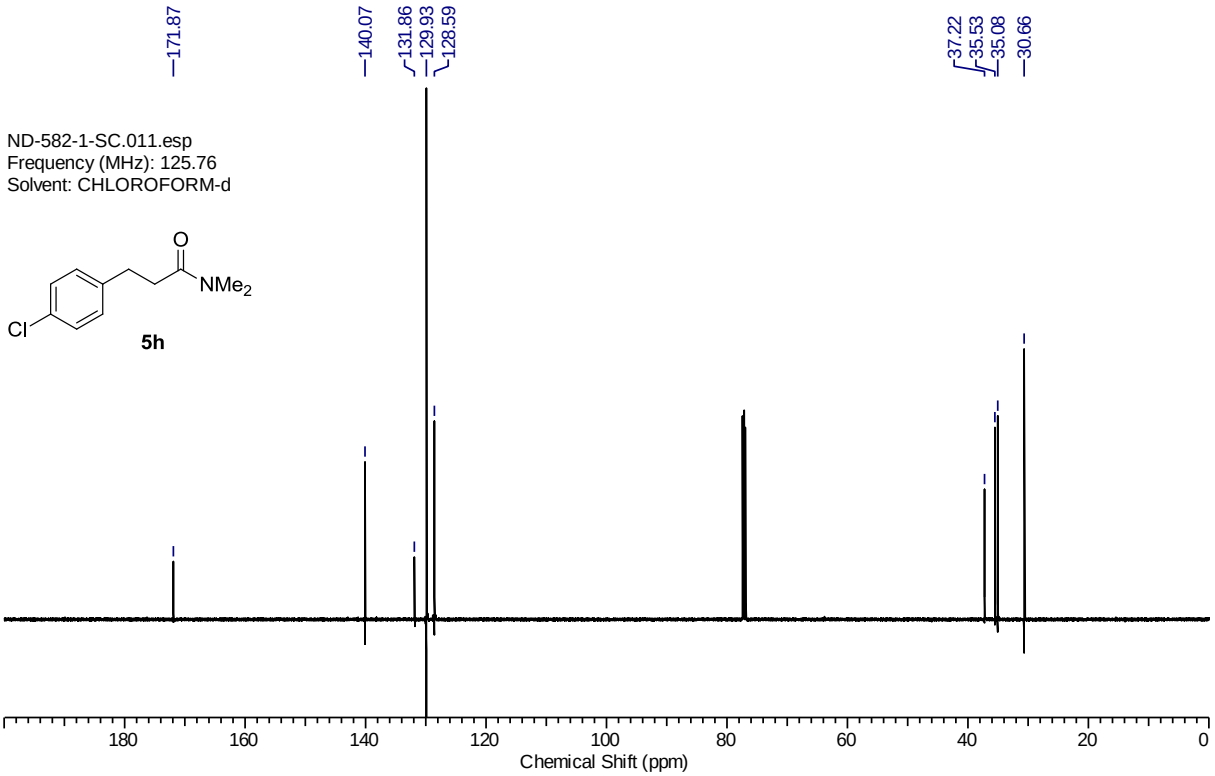
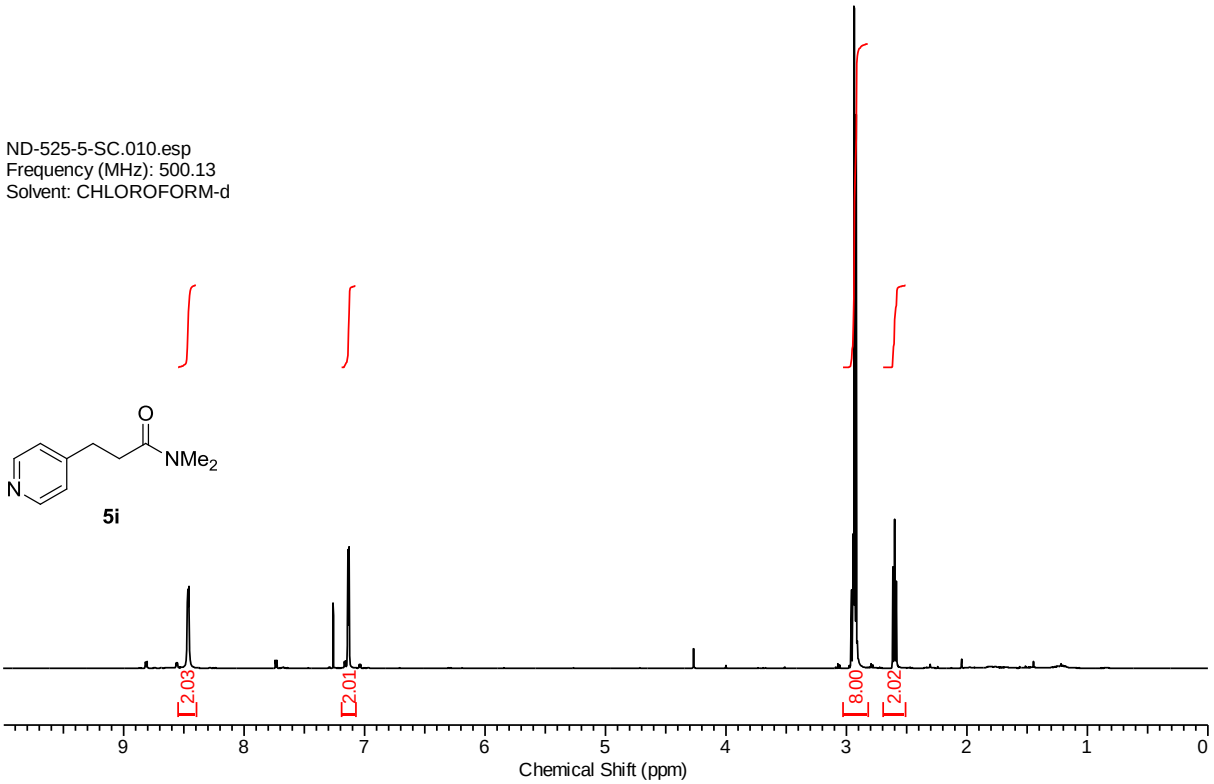
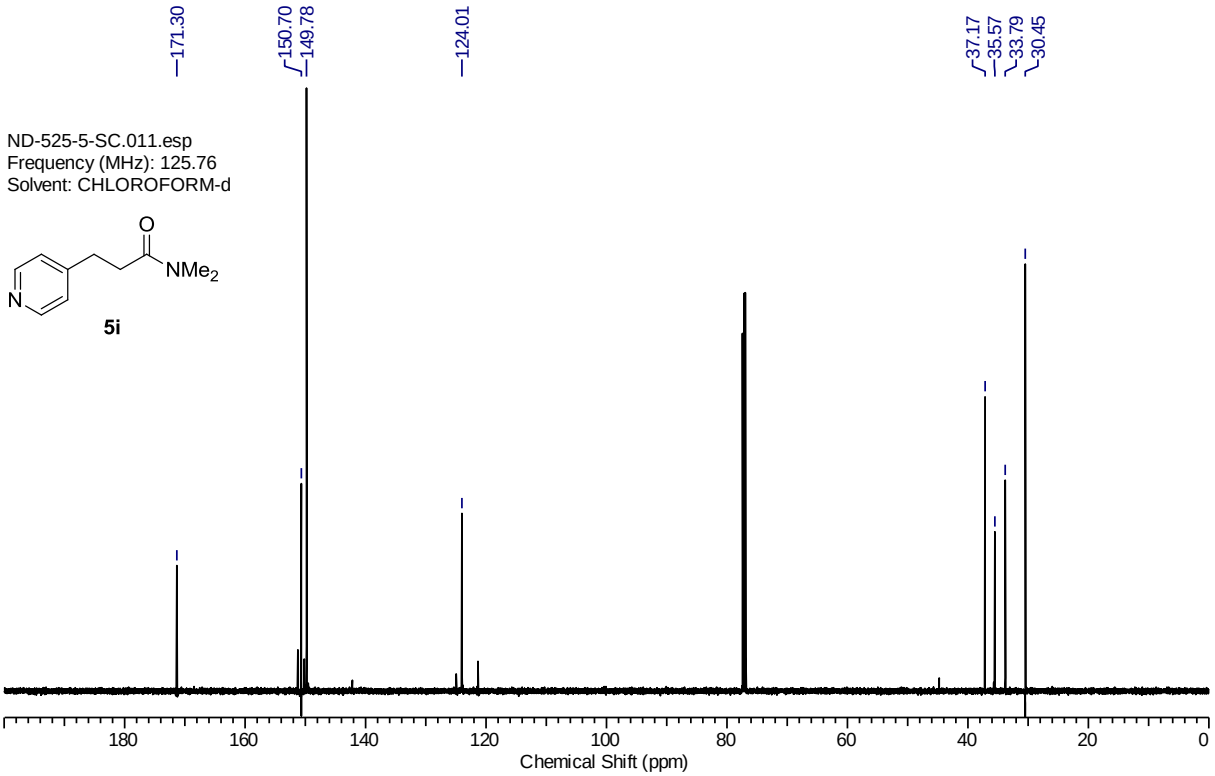
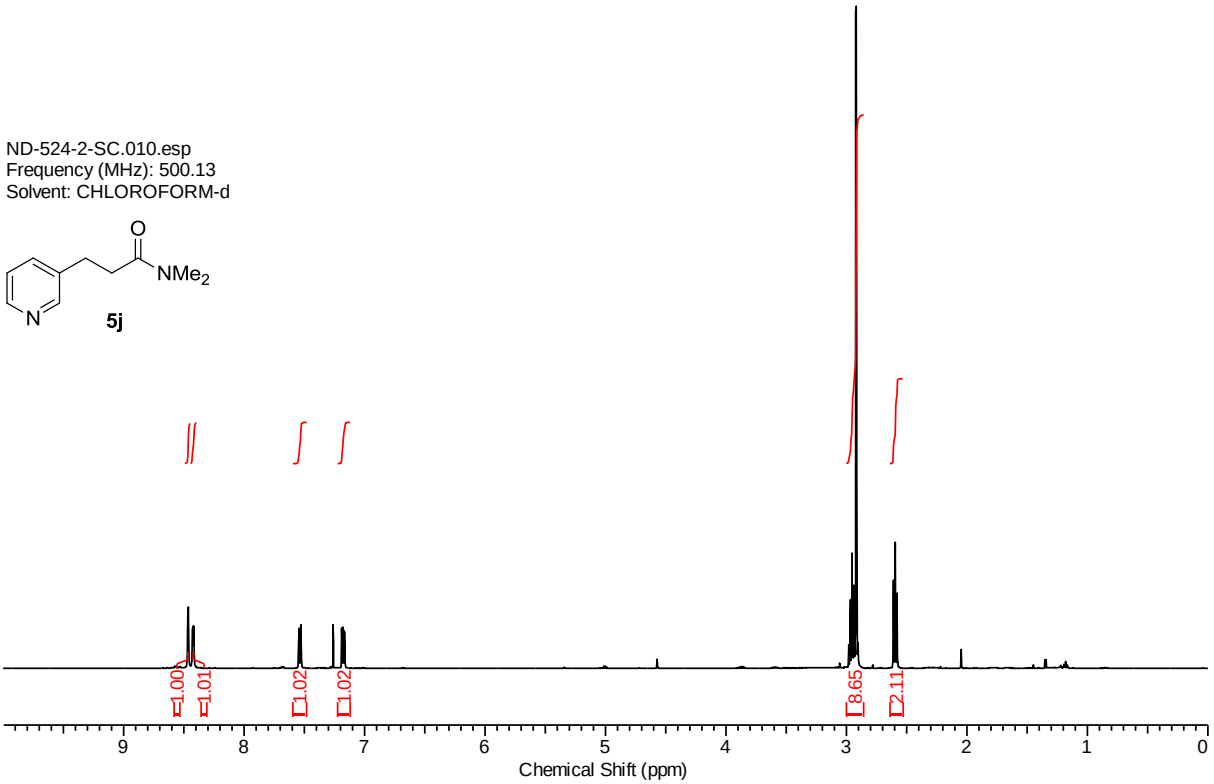
20
0
Chemical Shift (ppm)

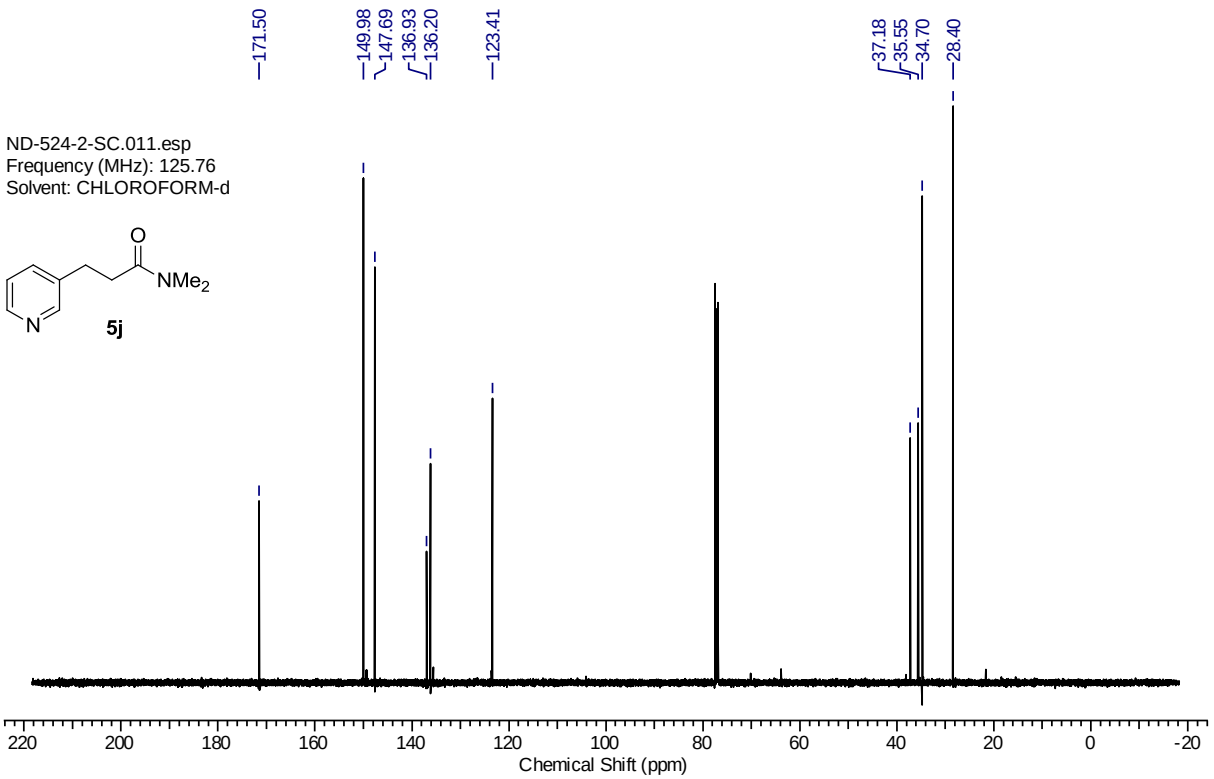

ND-582-1-SC.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
O
NMe2
Cl
5h
2.07
2.08
3.46
2.14
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

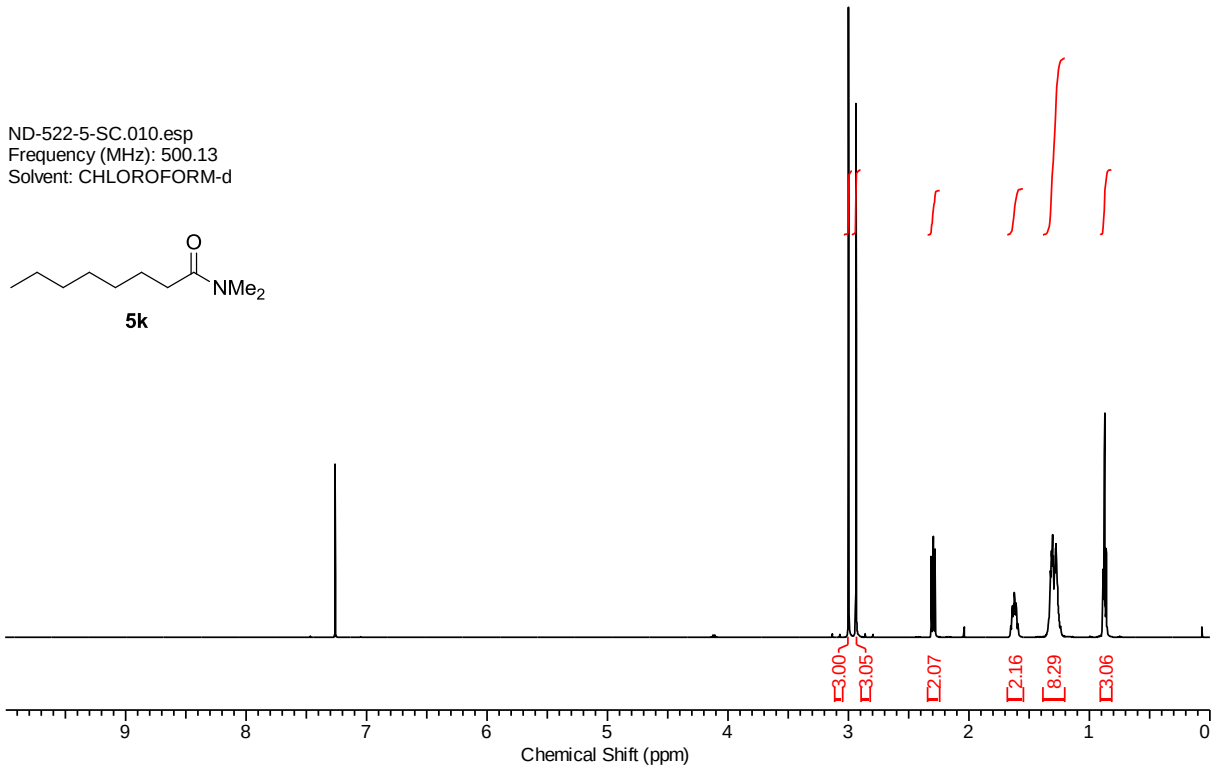

171.87
140.07
131.86
129.93
128.59
37.22
35.53
35.08
30.66
ND-582-1-SC.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
O
NMe2
Cl
5h
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

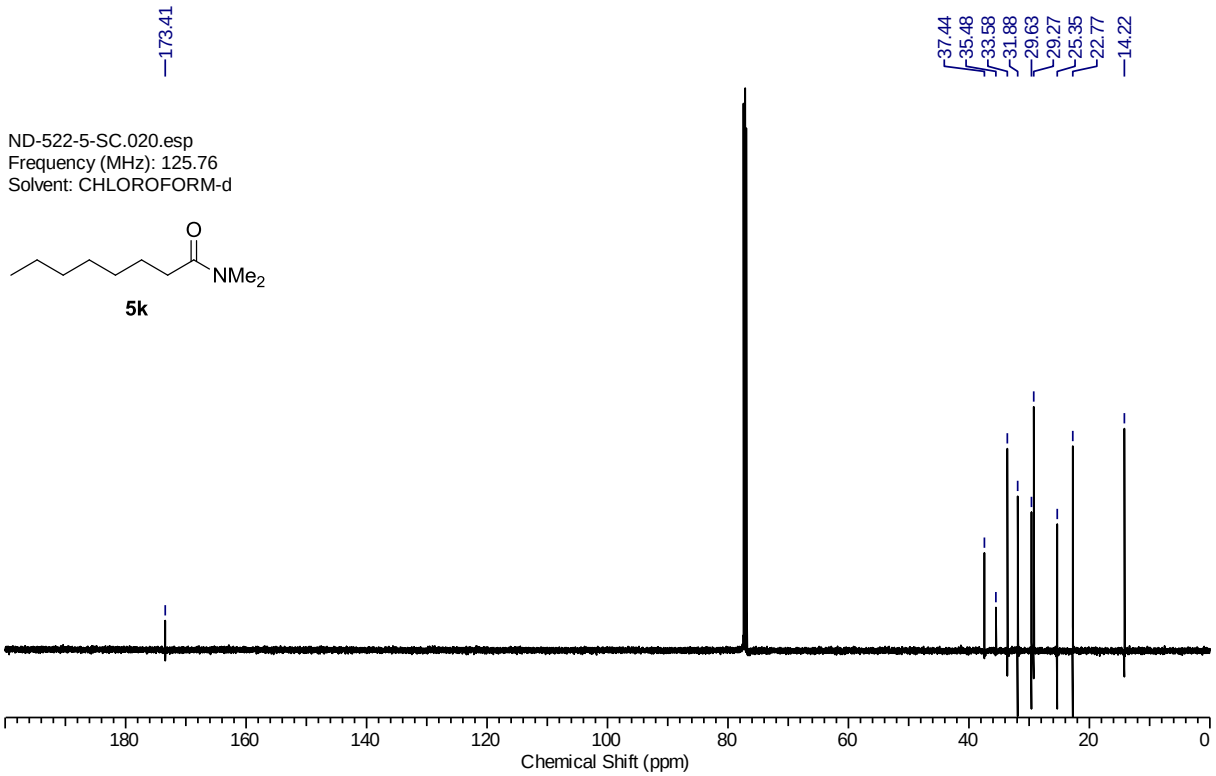

ND-525-5-SC.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
O
NMe2
N
5i
2.03
2.01
8.00
2.02
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

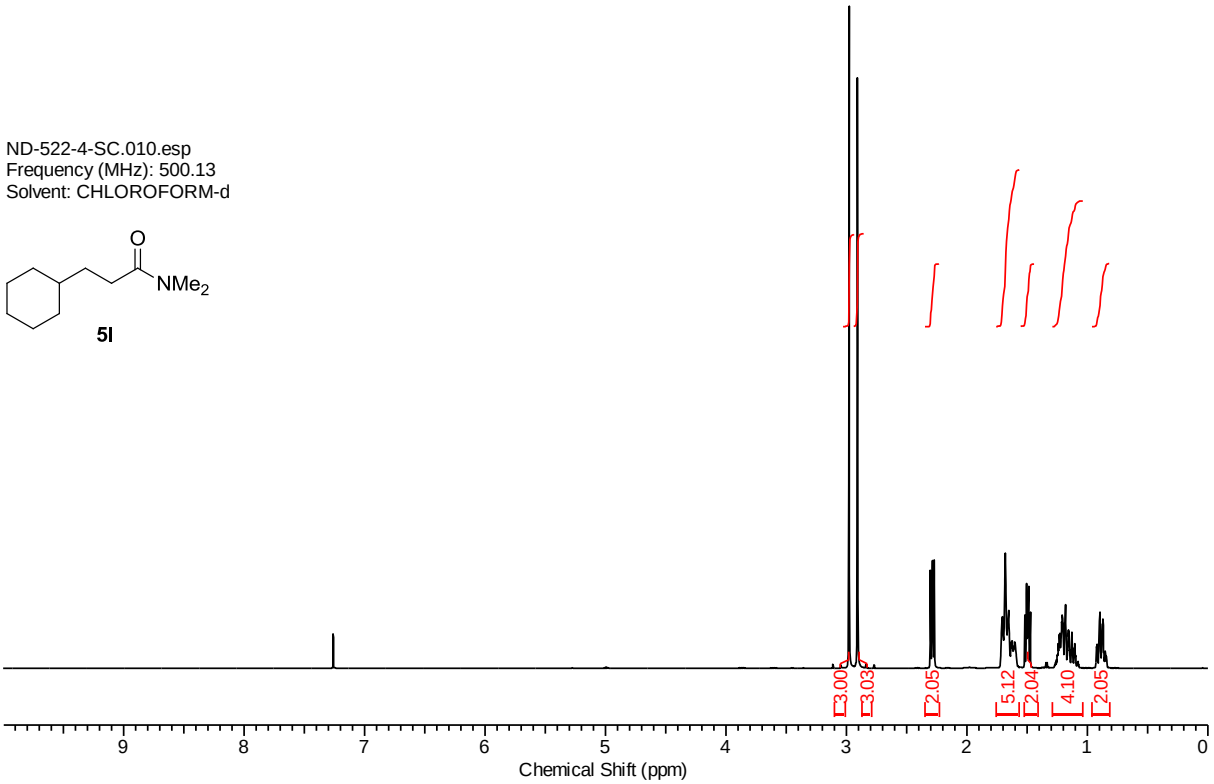

171.30
150.70
149.78
124.01
37.17
35.57
33.79
30.45
ND-525-5-SC.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
O
NMe2
N
5i
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

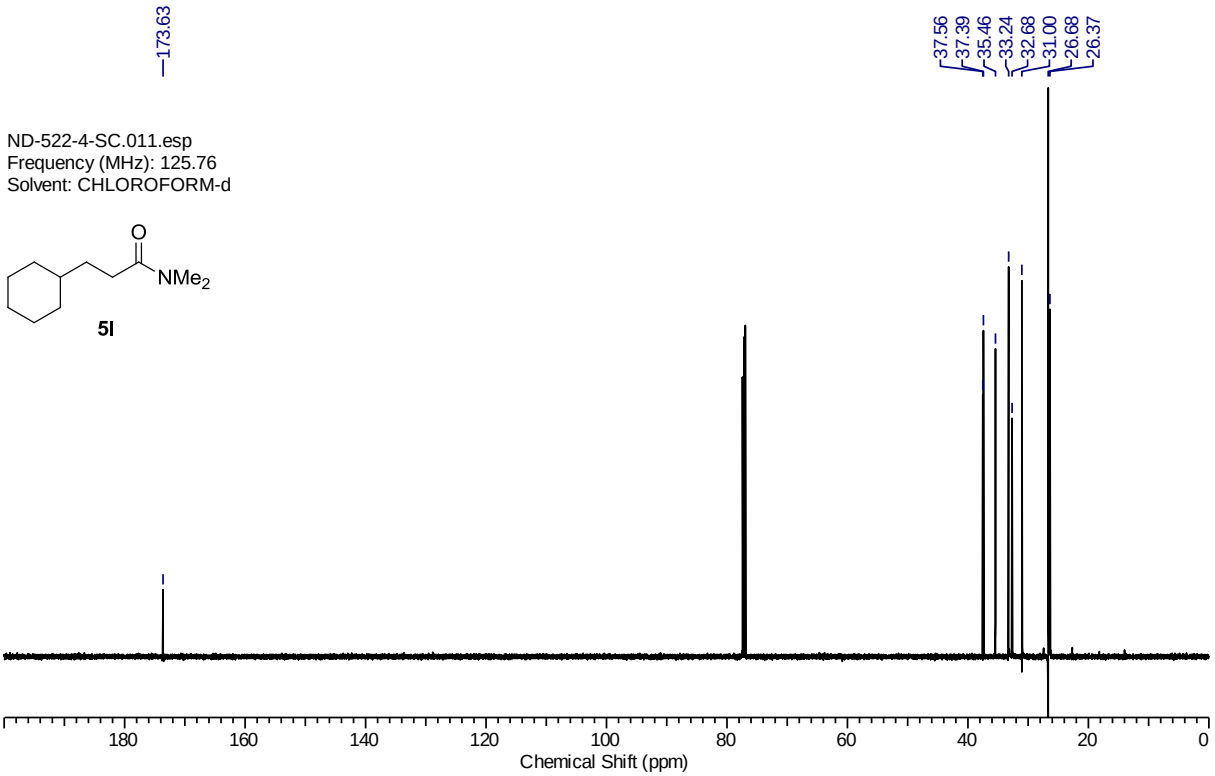

ND-524-2-SC.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
O
NMe2
N
5j
1.00
1.01
1.02
1.02
8.65
2.11
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

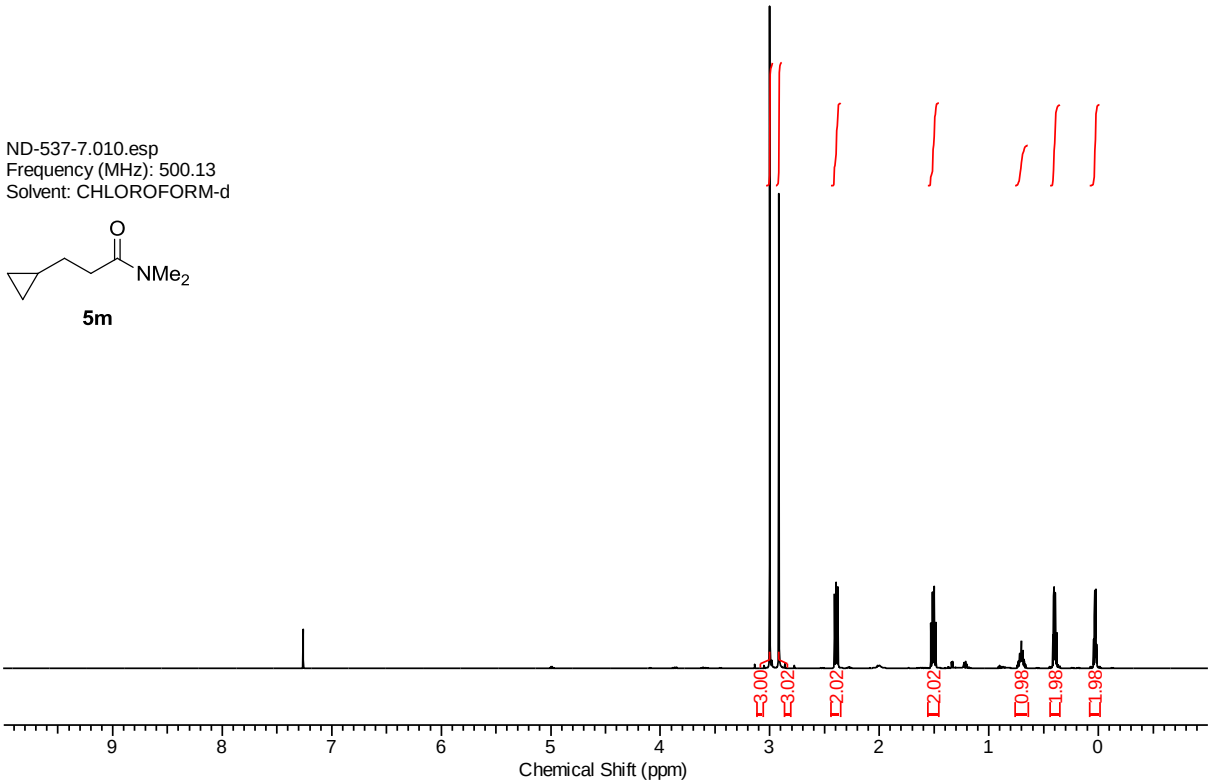

171.50
149.98
147.69
136.93
136.20
123.41
37.18
35.55
34.70
28.40
ND-524-2-SC.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
O
NMe2
N
5j
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

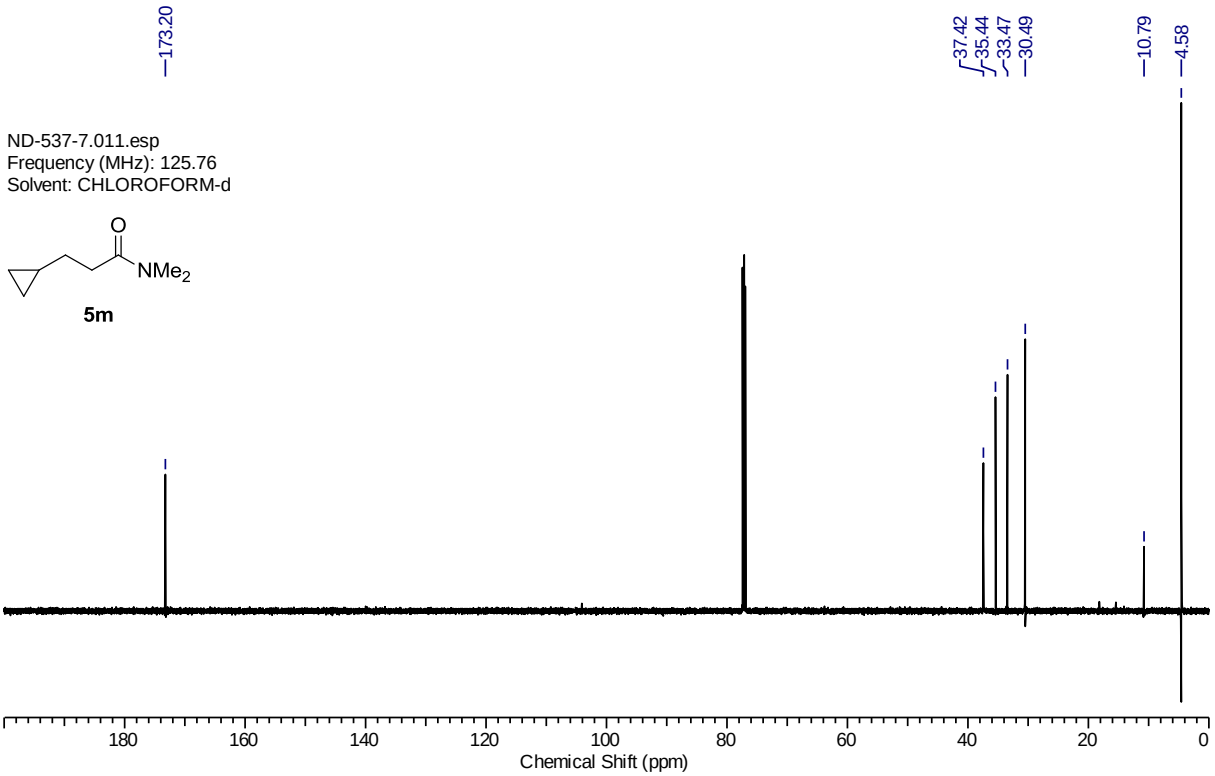

ND-522-5-SC.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
O
NMe2
5k
3.00
3.05
2.07
2.16
8.29
3.06
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

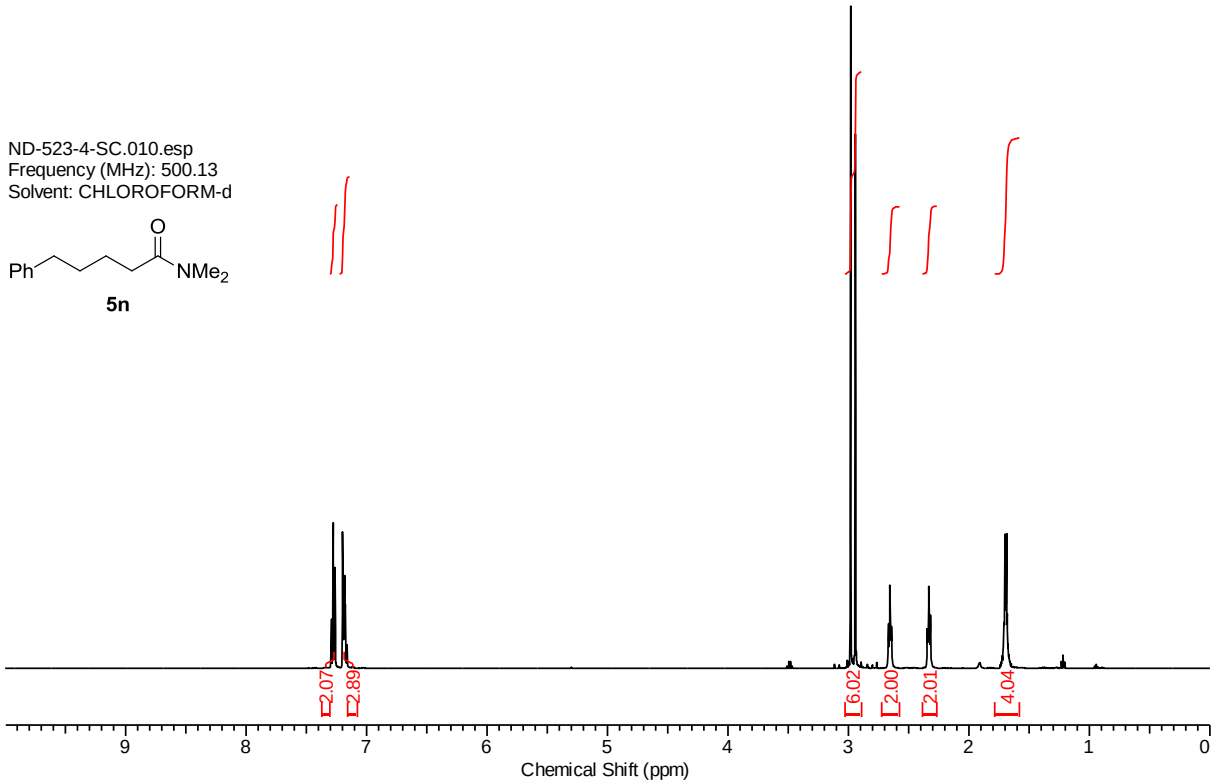

173.41
37.44
35.48
33.58
31.88
29.63
29.27
25.35
22.77
14.22
ND-522-5-SC.020.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
O
NMe2
5k
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

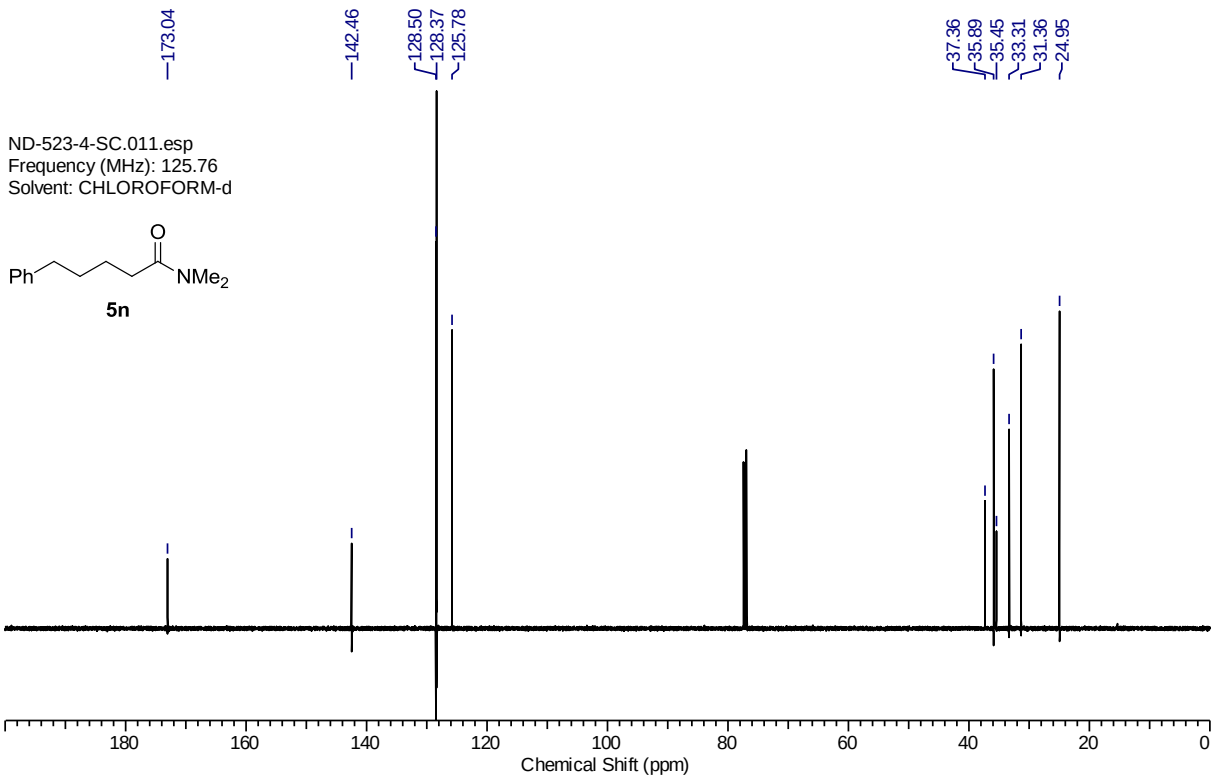

ND-522-4-SC.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
O
NMe2
5l
3.00
3.03
2.05
5.12
2.04
4.10
2.05
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

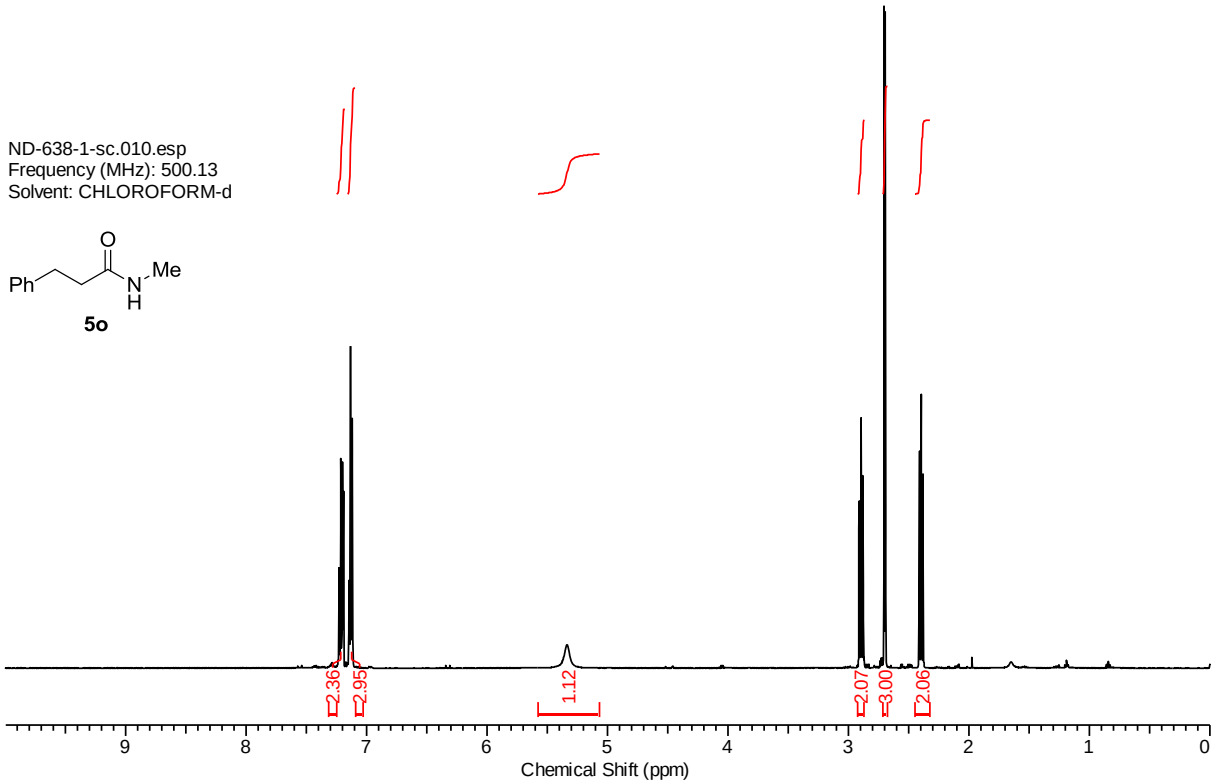

173.63
37.56
37.39
35.46
33.24
32.68
31.00
26.68
26.37
ND-522-4-SC.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
O
NMe2
5l
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

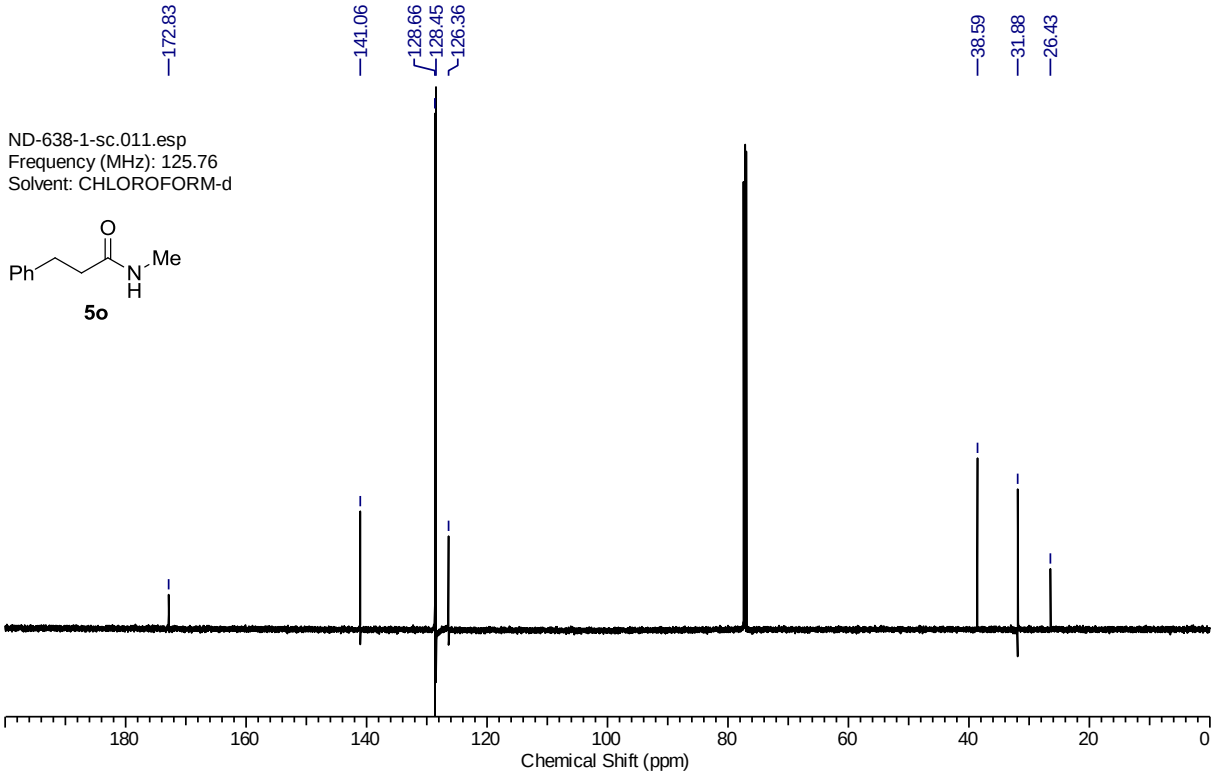

ND-537-7.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
O
NMe2
5m
3.00
3.02
2.02
2.02
0.98
1.98
1.98
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

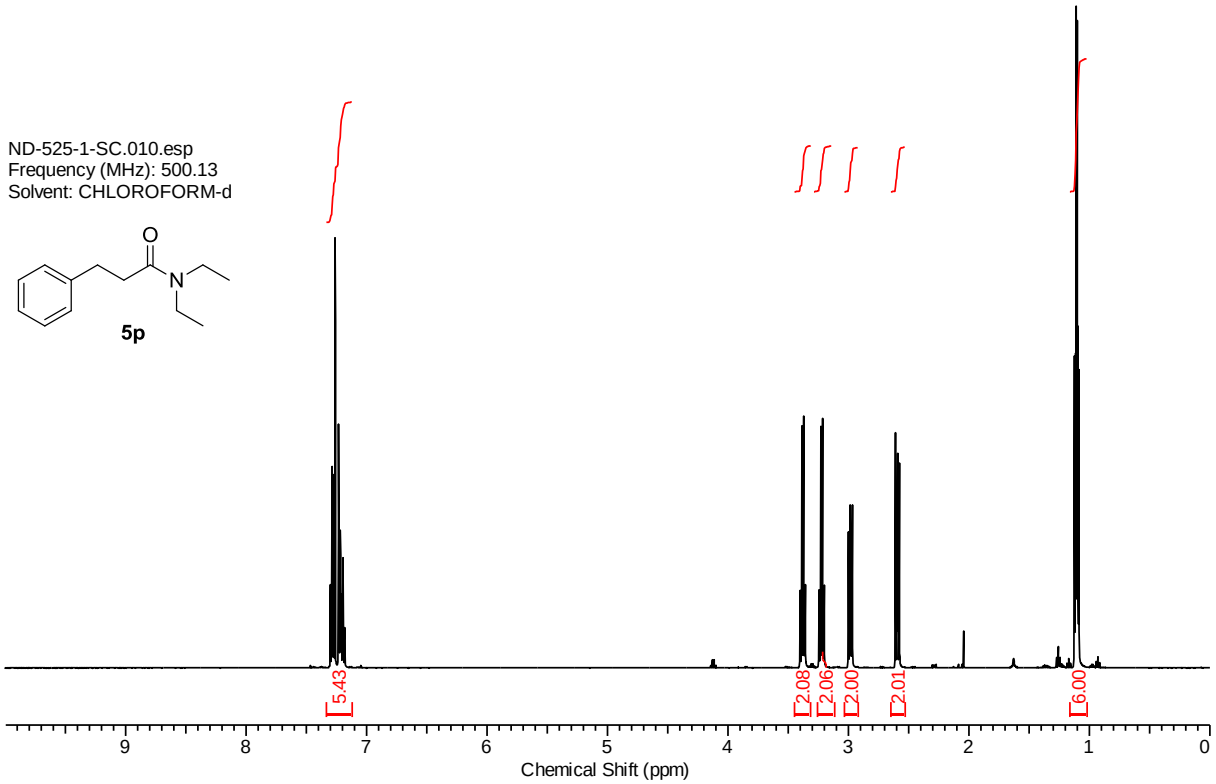

173.20
37.42
35.44
33.47
30.49
10.79
4.58
ND-537-7.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
O
NMe2
5m
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

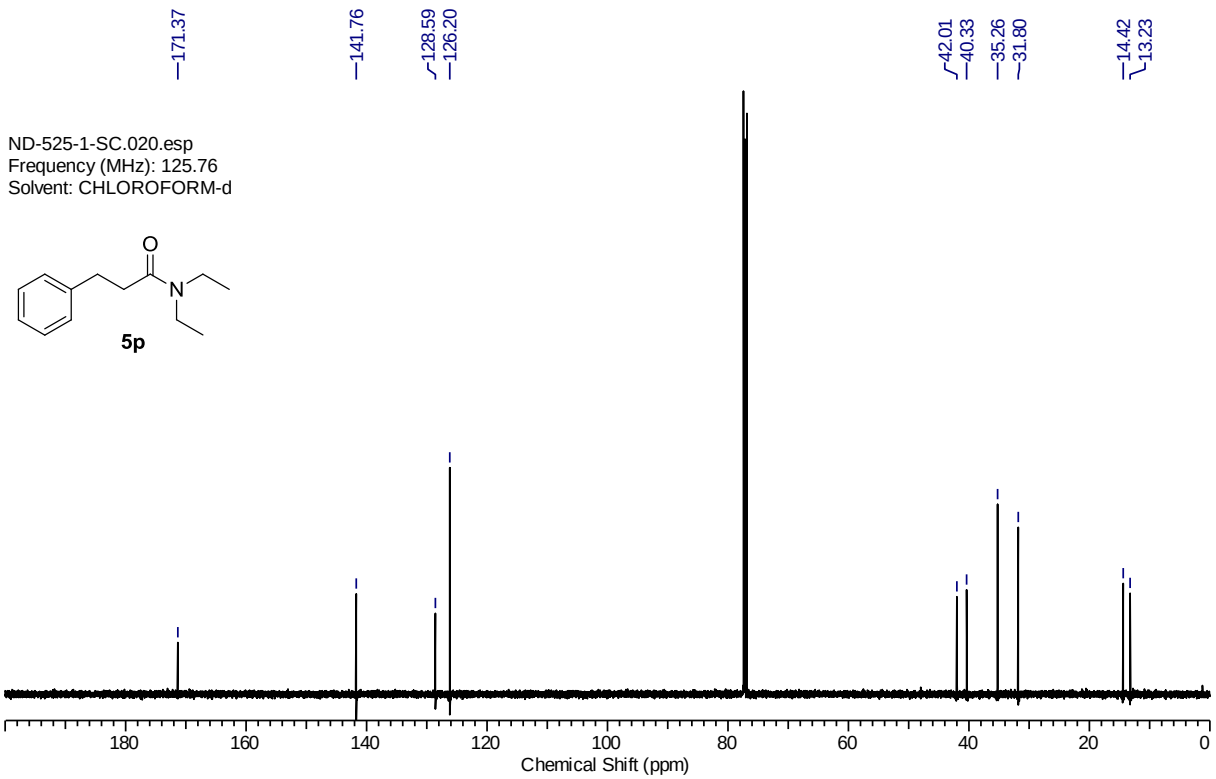

ND-523-4-SC.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
Ph
O
NMe2
5n
2.07
2.89
6.02
2.00
2.01
4.04
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

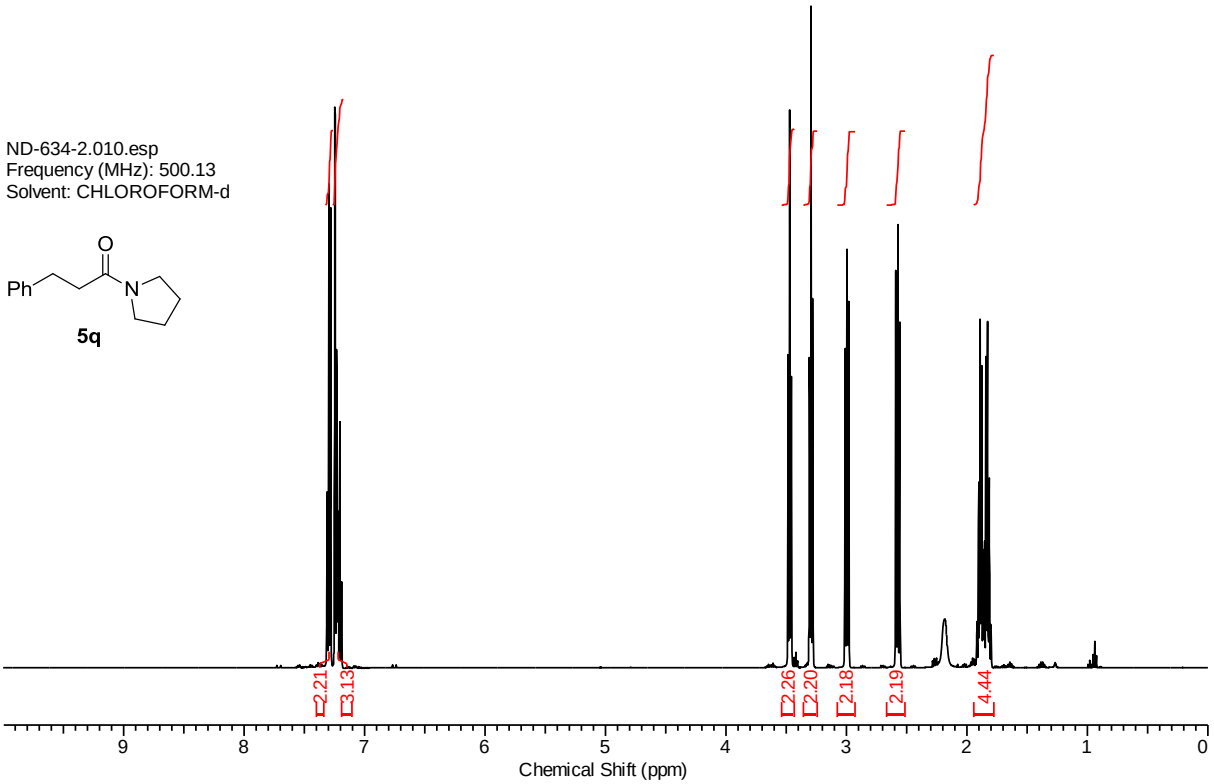

173.04
142.46
128.50
128.37
125.78
37.36
35.89
35.45
33.31
31.36
24.95
ND-523-4-SC.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
Ph
O
NMe2
5n
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

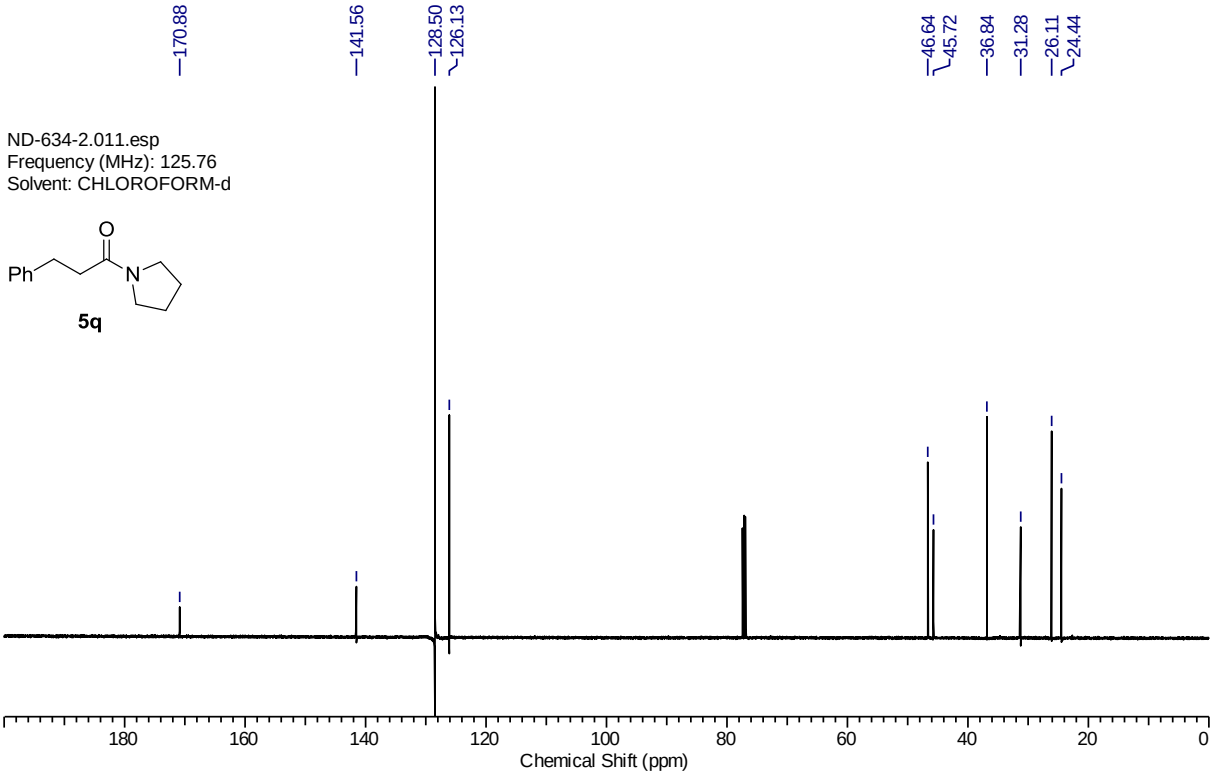

ND-638-1-sc.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
Ph
O
N
H
Me
5o
2.36
2.95
1.12
2.07
3.00
2.06
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

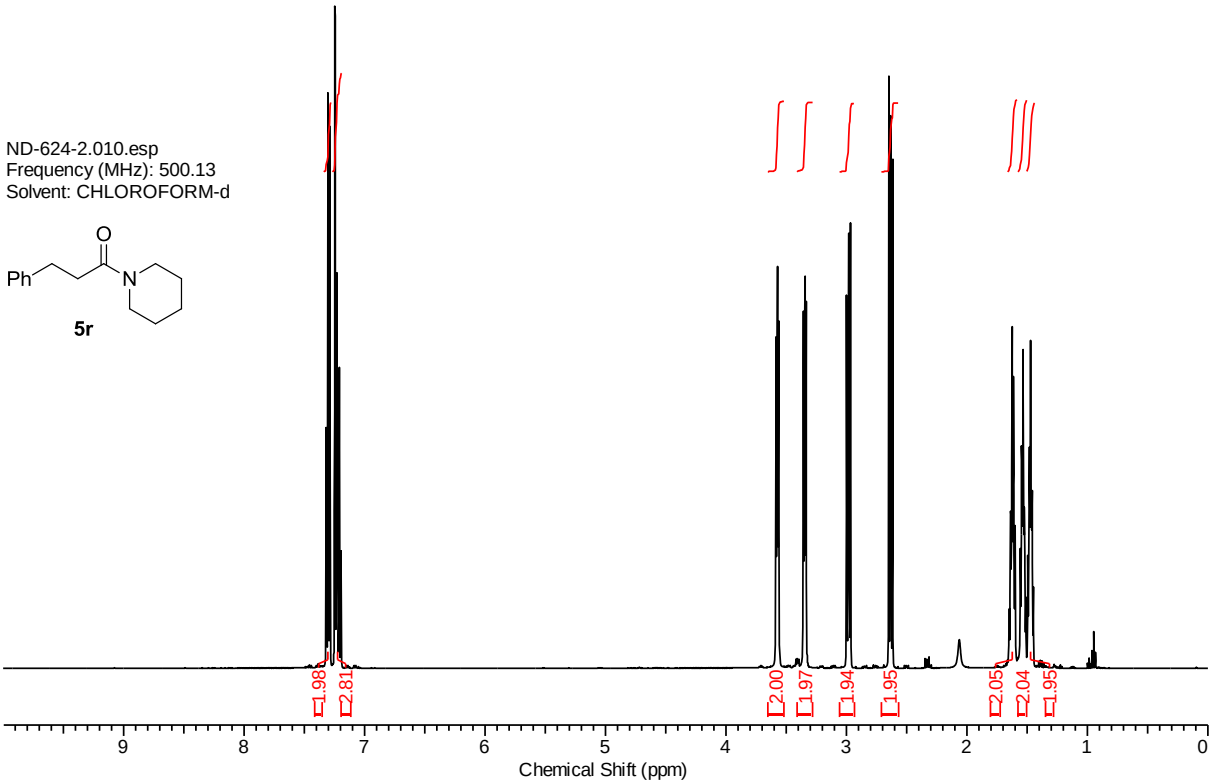

172.83
141.06
128.66
128.45
126.36
38.59
31.88
26.43
ND-638-1-sc.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
Ph
O
N
H
Me
5o
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

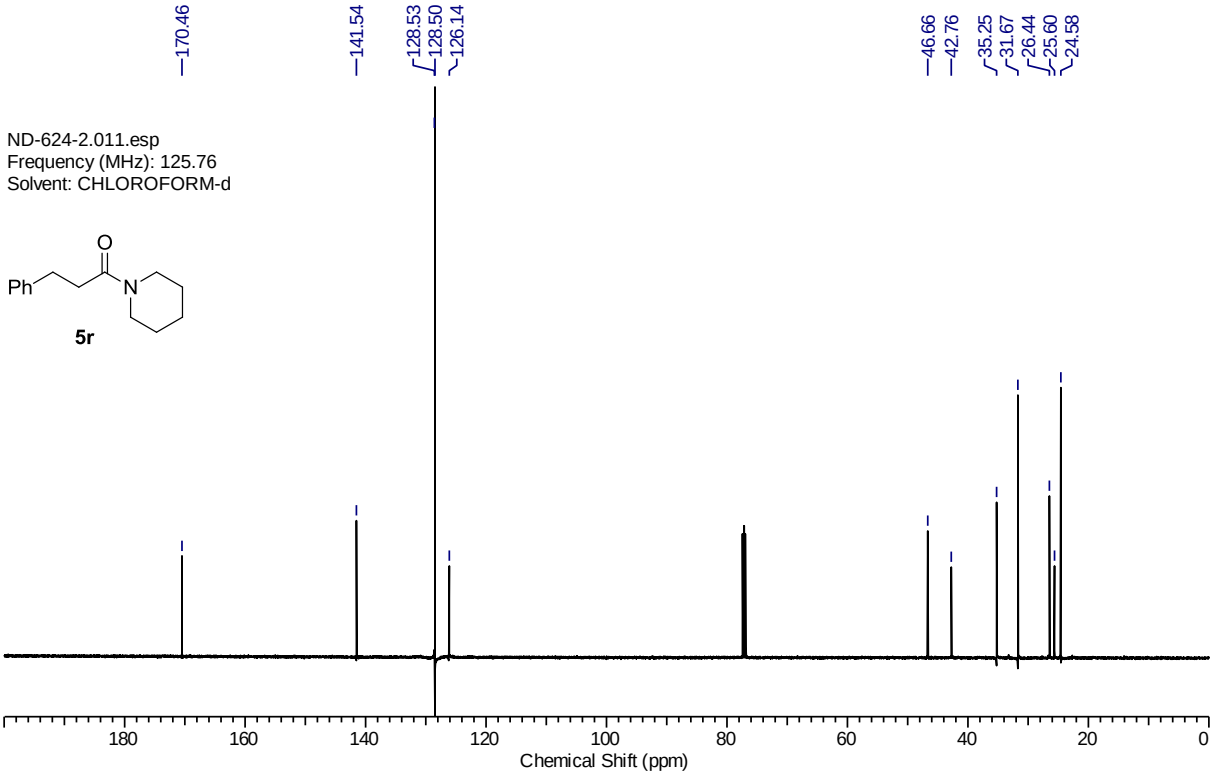

ND-525-1-SC.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
O
N
5p
5.43
2.08
2.06
2.00
2.01
6.00
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

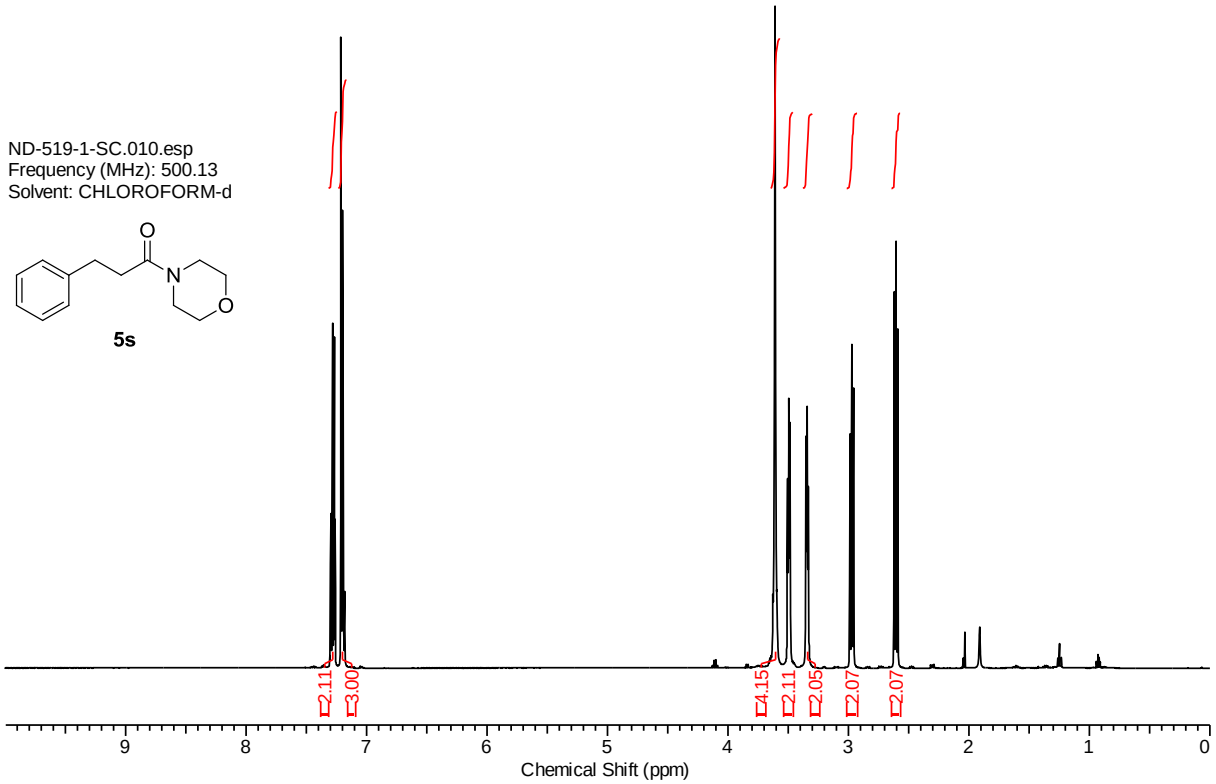

171.37
141.76
128.59
126.20
42.01
40.33
35.26
31.80
14.42
13.23
ND-525-1-SC.020.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
O
N
5p
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

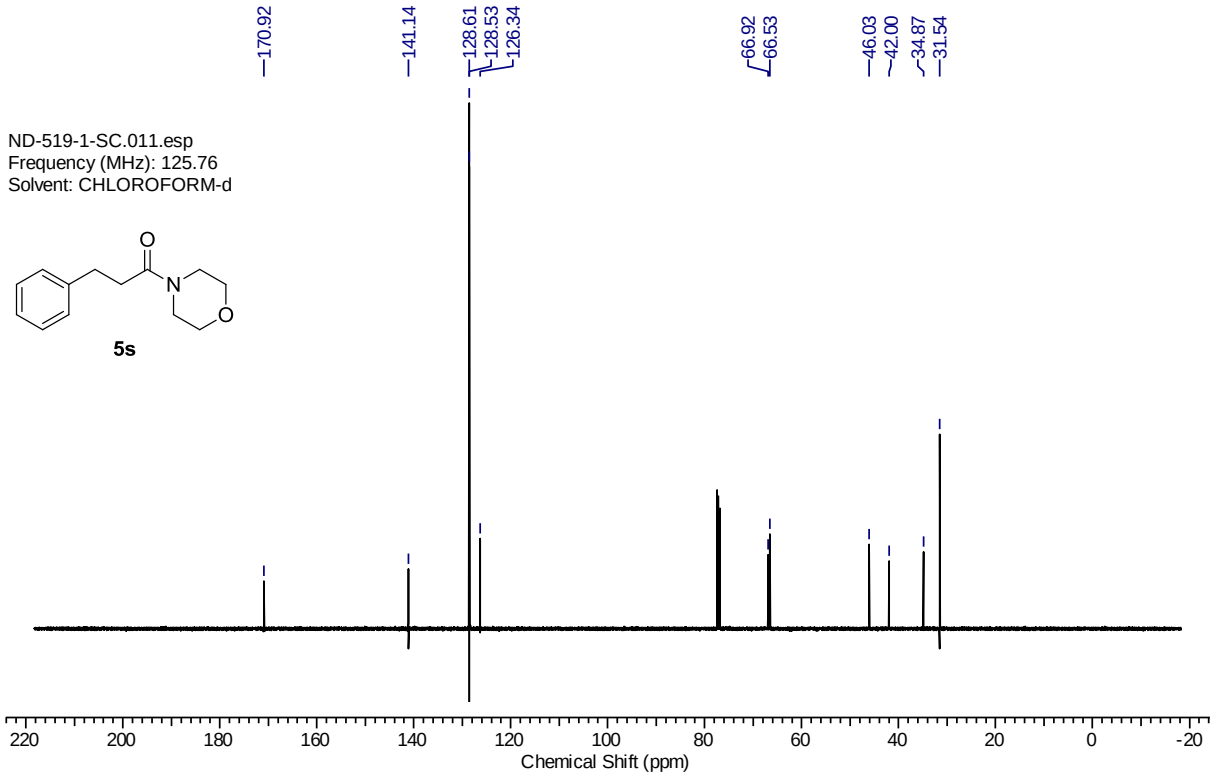

ND-634-2.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
Ph
N
O
5q
2.21
3.13
2.26
2.20
2.18
2.19
4.44
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

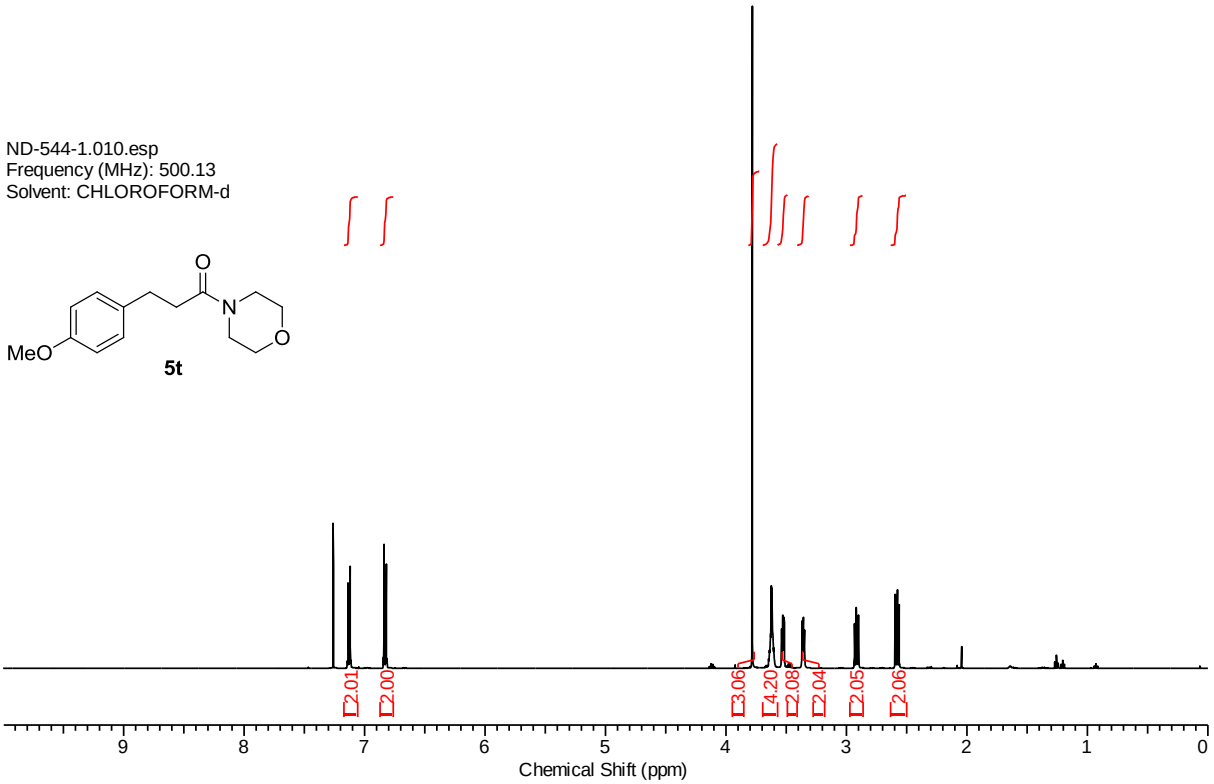

170.88
141.56
128.50
126.13
46.64
45.72
36.84
31.28
26.11
24.44
ND-634-2.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
Ph
N
O
5q
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

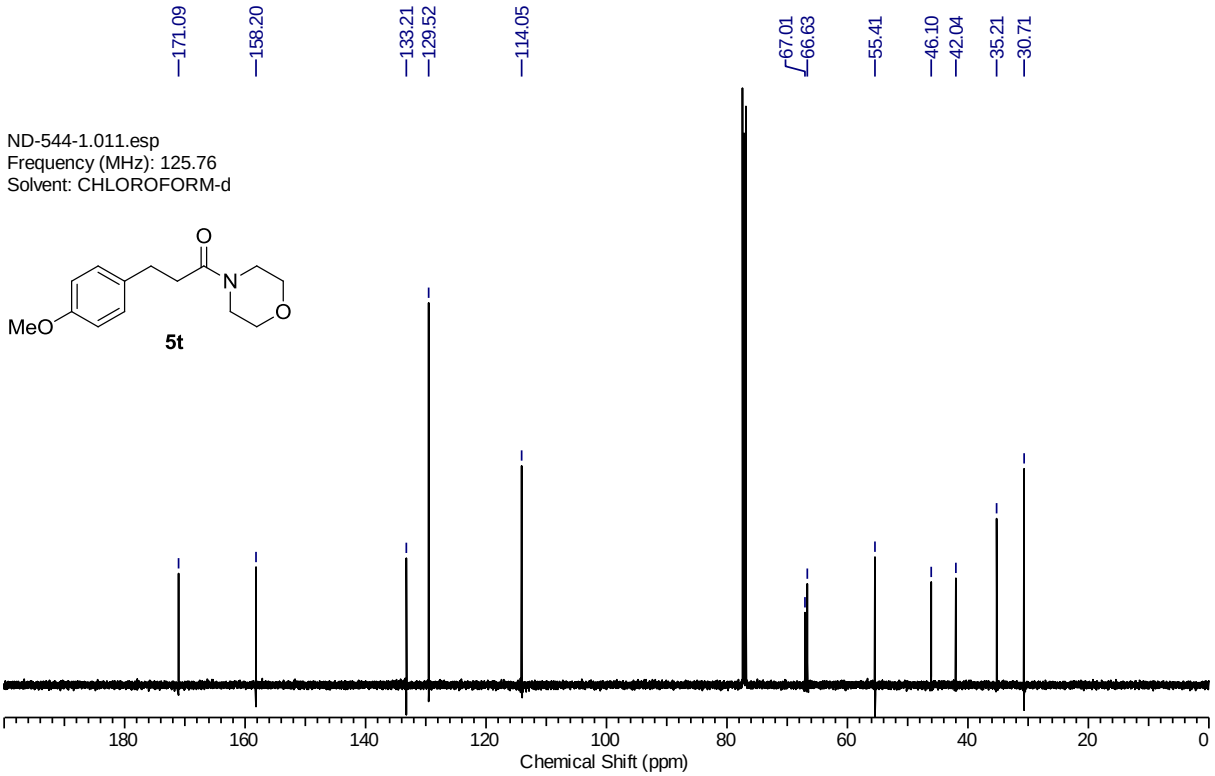

ND-624-2.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
Ph
O
N
5r
1.98
2.81
2.00
1.97
1.94
1.95
2.05
2.04
1.95
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

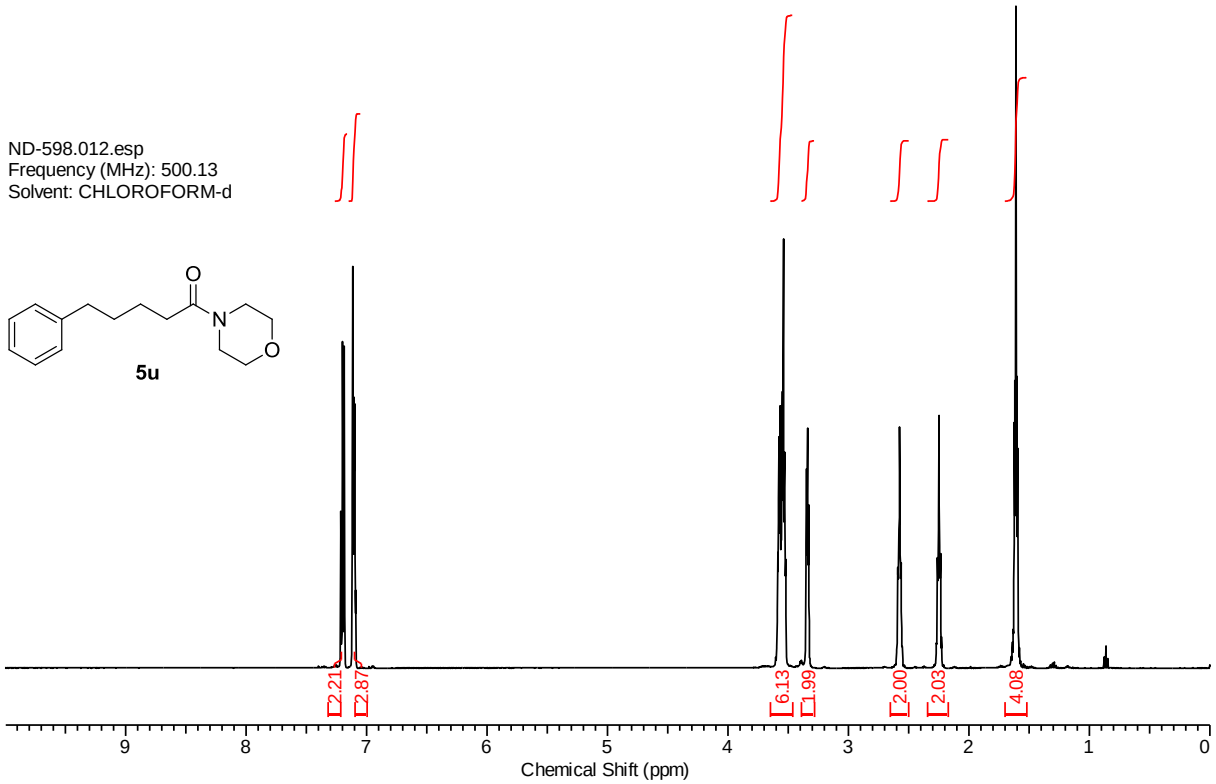

170.46
141.54
128.53
128.50
126.14
46.66
42.76
35.25
31.67
26.44
25.60
24.58
ND-624-2.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
Ph
O
N
5r
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

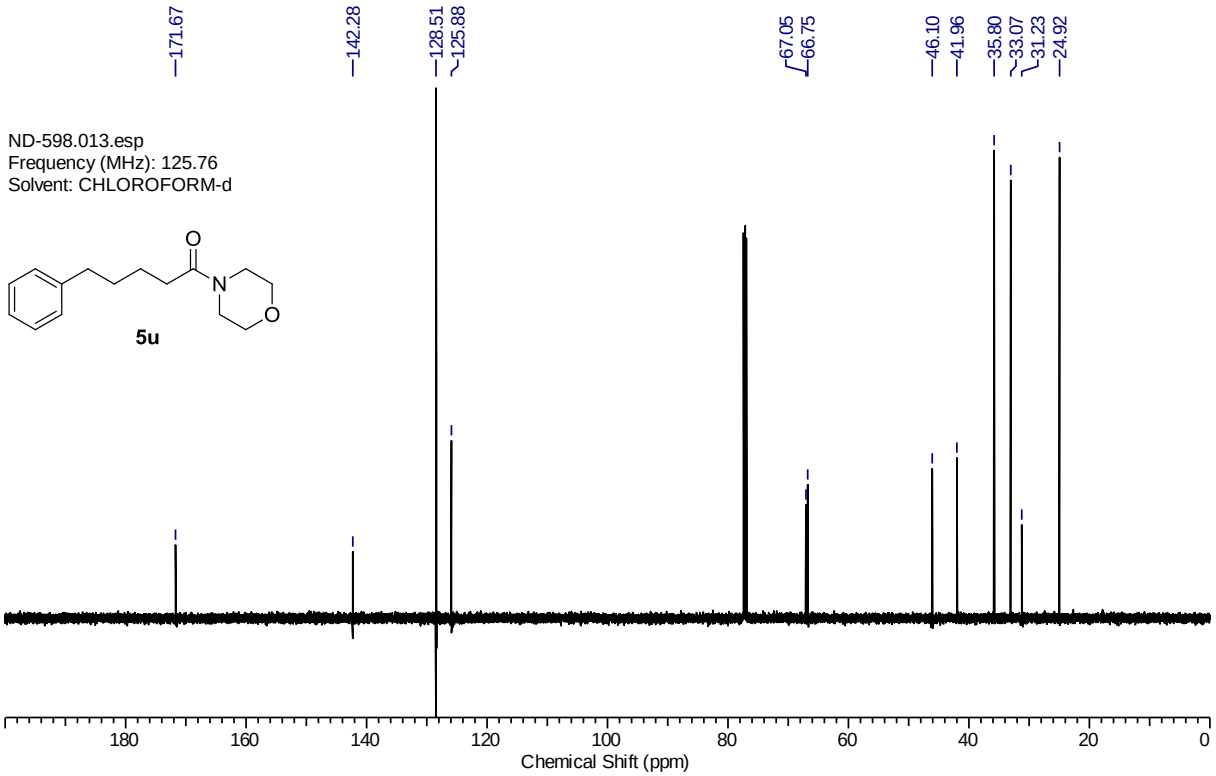

ND-519-1-SC.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
5s
2.11
3.00
4.15
2.11
2.05
2.07
2.07
Chemical Shift (ppm)

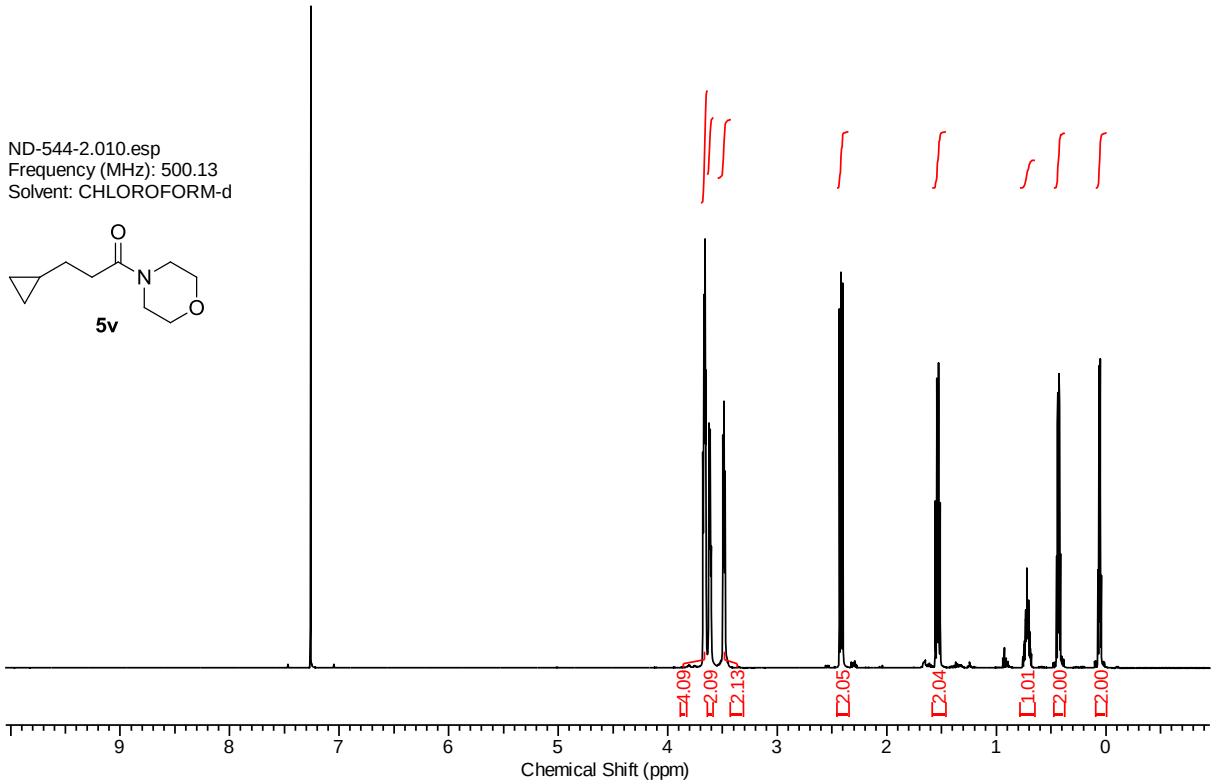

170.92
141.14
128.61
128.53
126.34
66.92
66.53
46.03
42.00
34.87
31.54
ND-519-1-SC.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
5s
Chemical Shift (ppm)

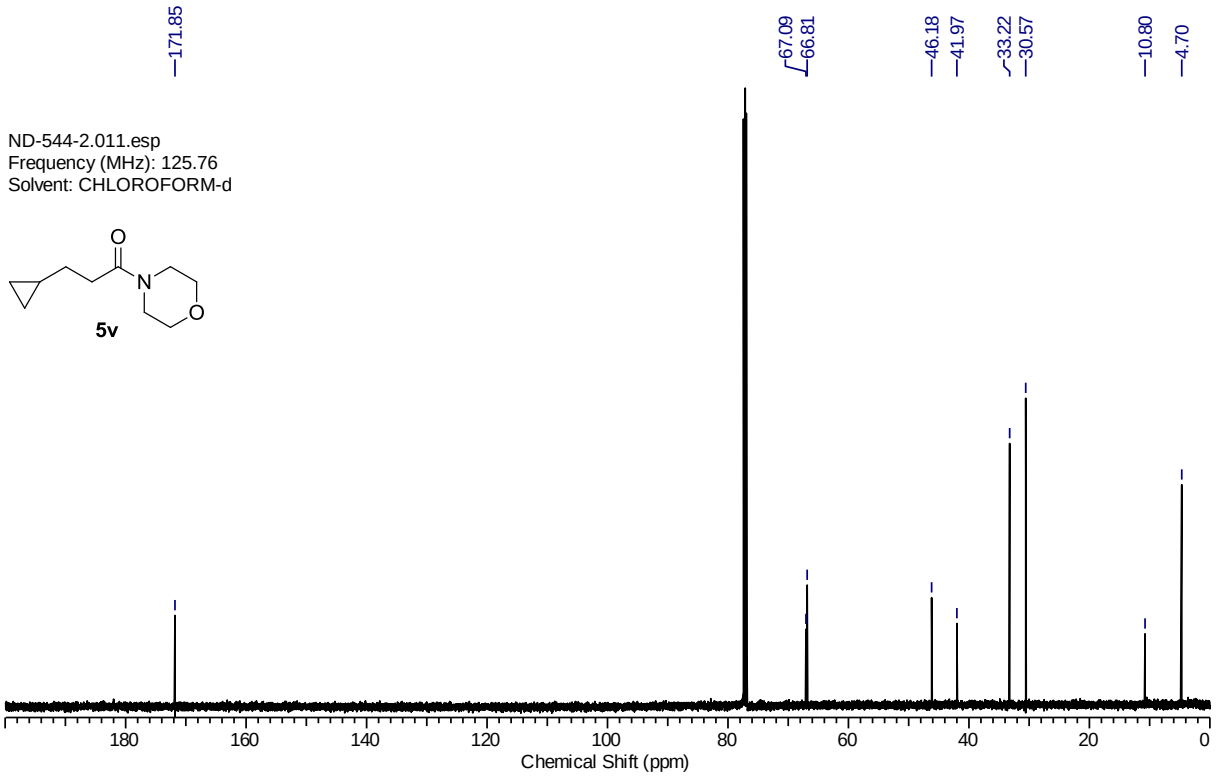

ND-544-1.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
MeO
O
N
O
5t
2.01
2.00
3.06
4.20
2.08
2.04
2.05
2.06
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

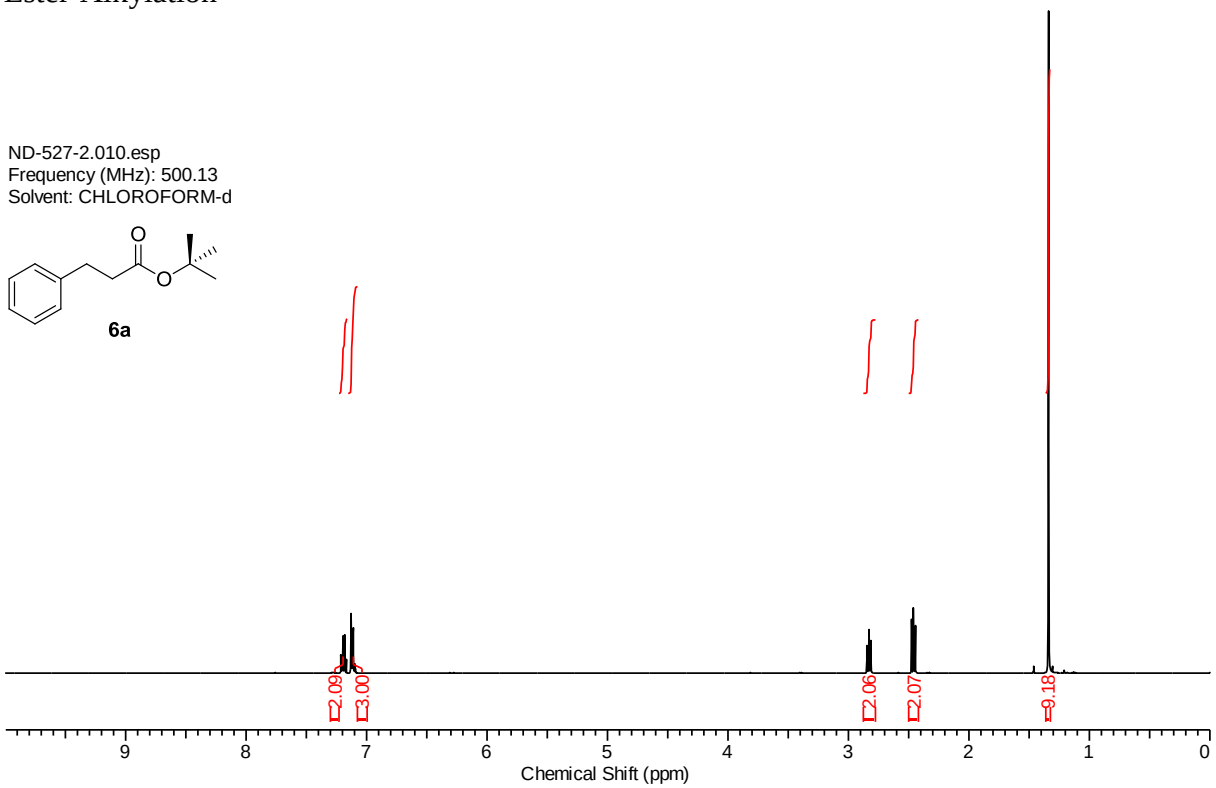

171.09
158.20
133.21
129.52
114.05
67.01
66.63
55.41
46.10
42.04
35.21
30.71
ND-544-1.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
MeO
O
N
O
5t
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

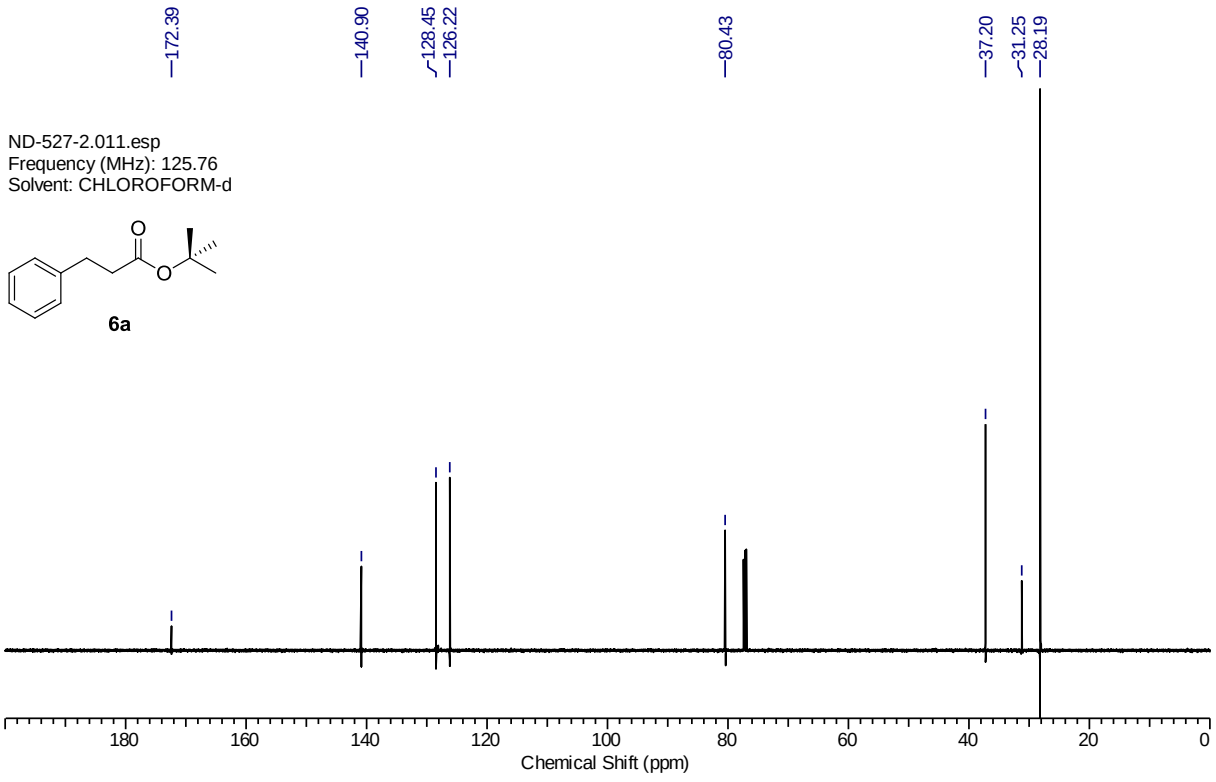

ND-598.012.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
5u
2.21
2.87
6.13
1.99
2.00
2.03
4.08
Chemical Shift (ppm)

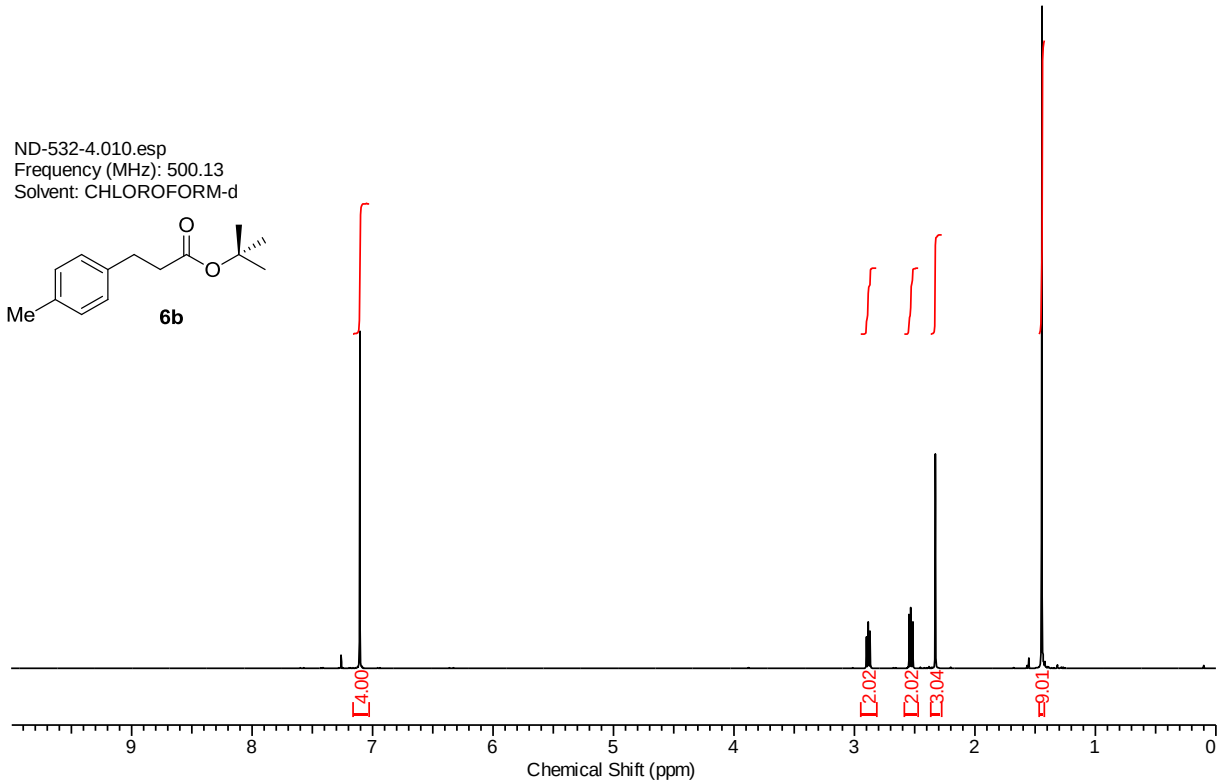

171.67
142.28
128.51
125.88
67.05
66.75
46.10
41.96
35.80
33.07
31.23
24.92
ND-598.013.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
5u
Chemical Shift (ppm)

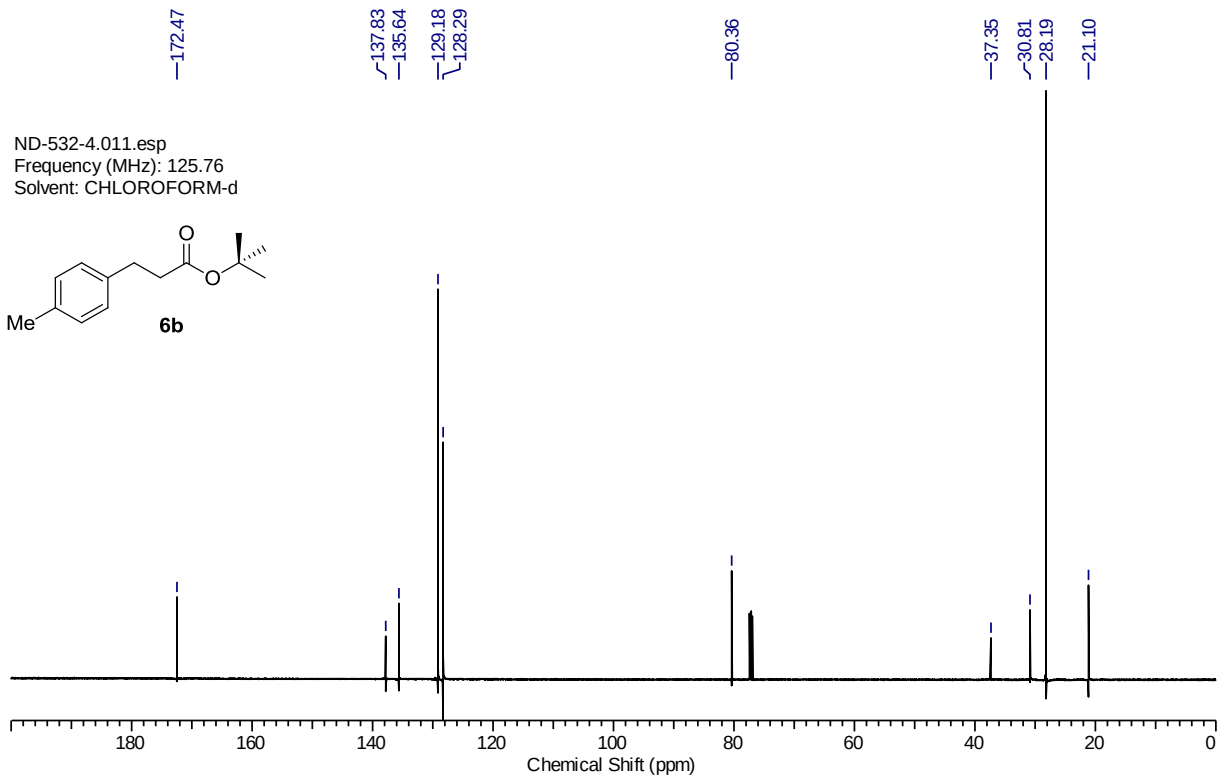

ND-544-2.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
5v
4.09
2.09
2.13
2.05
2.04
1.01
2.00
2.00
Chemical Shift (ppm)

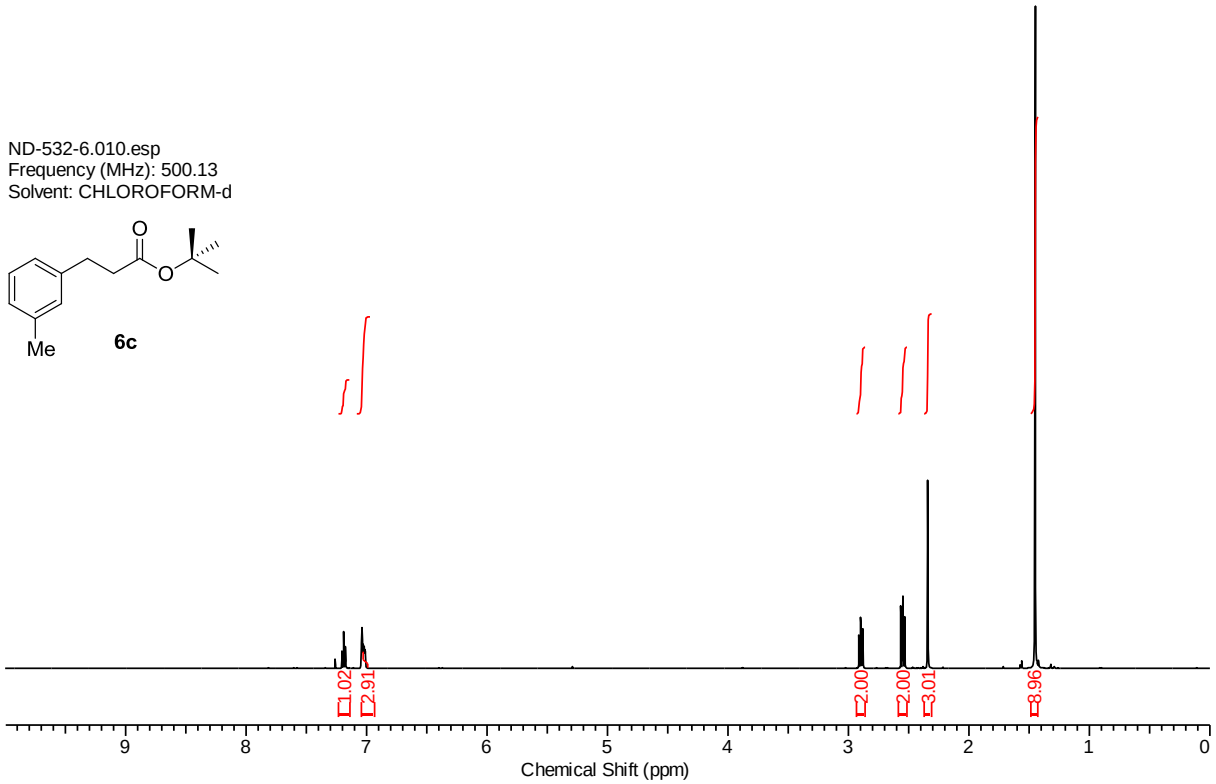

171.85
67.09
66.81
46.18
41.97
33.22
30.57
10.80
4.70
ND-544-2.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
5v
Chemical Shift (ppm)

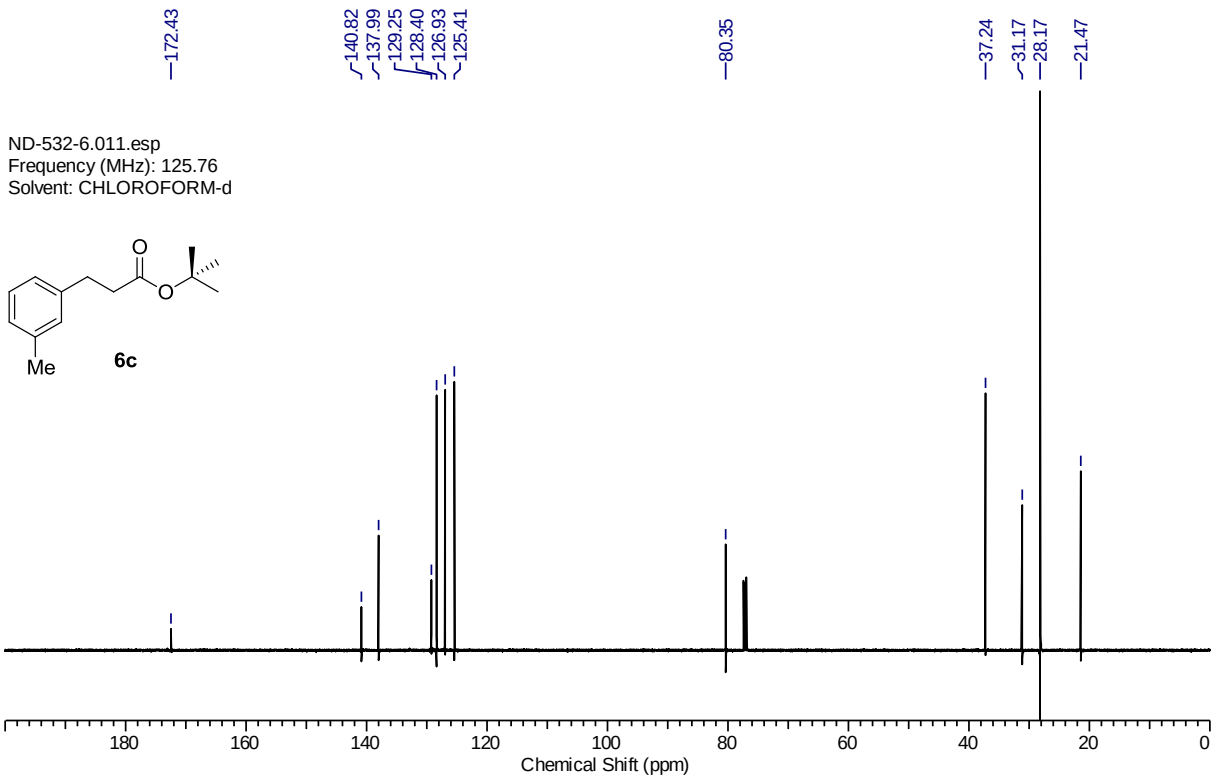

ND-527-2.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
6a
2.09
3.00
2.06
2.07
9.18
Chemical Shift (ppm)

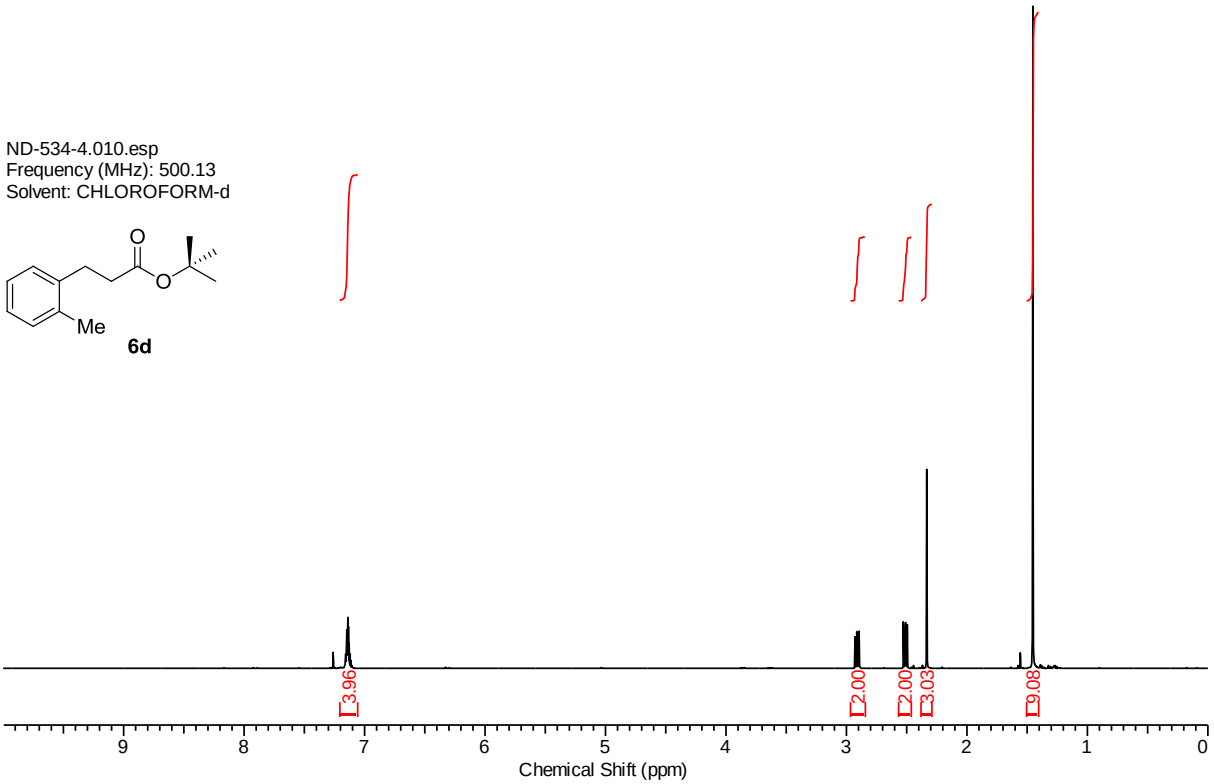

172.39
140.90
128.45
126.22
80.43
37.20
31.25
28.19
ND-527-2.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
6a
Chemical Shift (ppm)

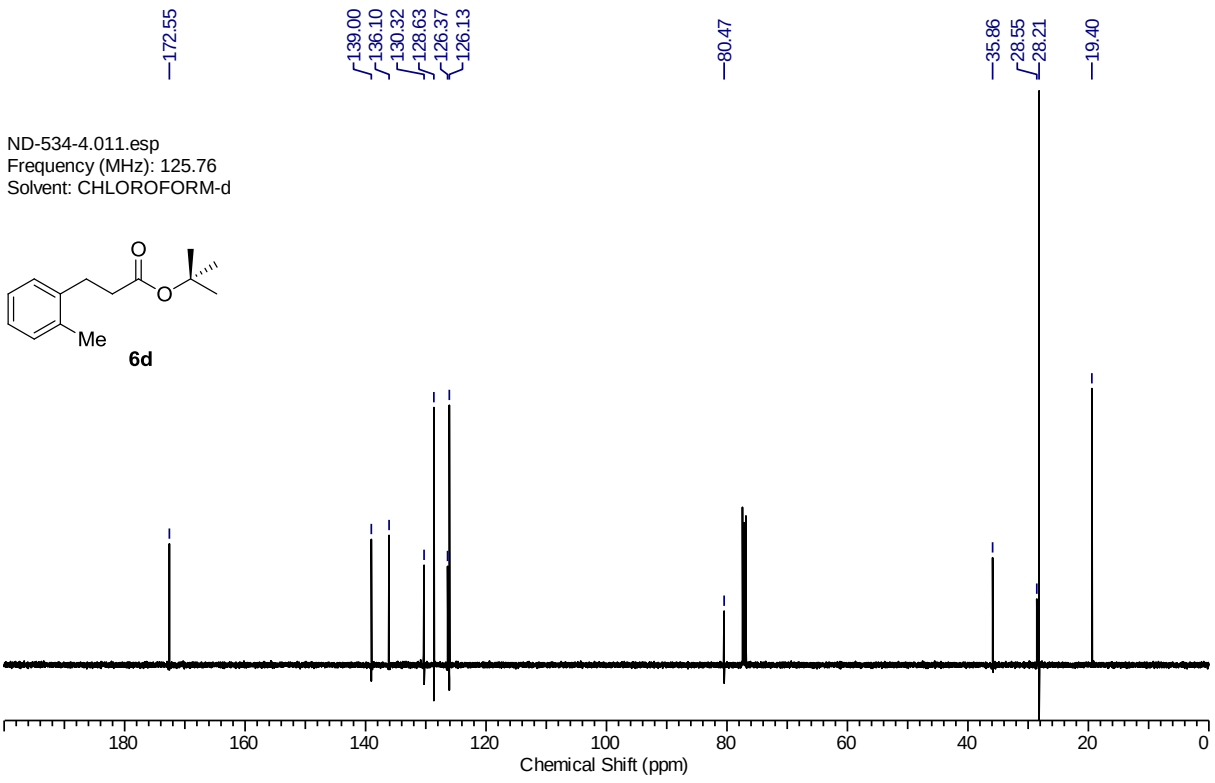

ND-532-4.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
Me
O
O
6b
4.00
2.02
2.02
3.04
9.01
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

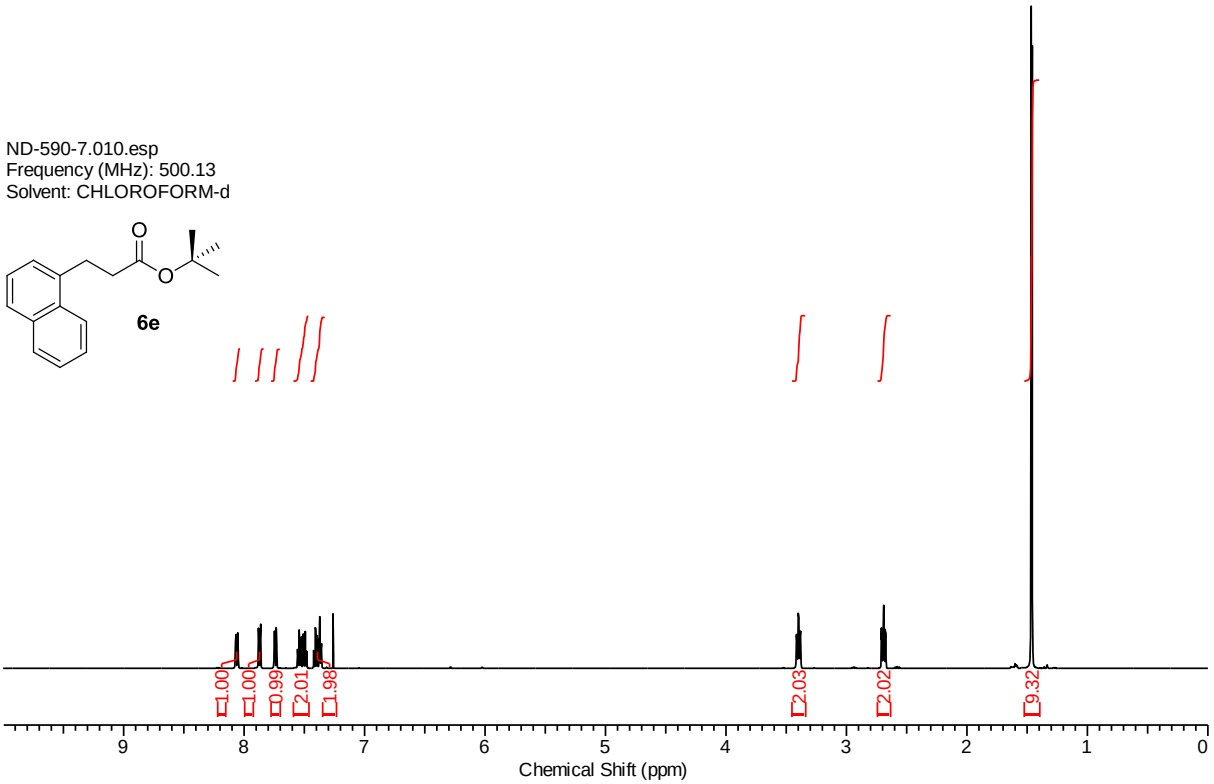

172.47
137.83
135.64
129.18
128.29
80.36
37.35
30.81
28.19
21.10
ND-532-4.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
Me
O
O
6b
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

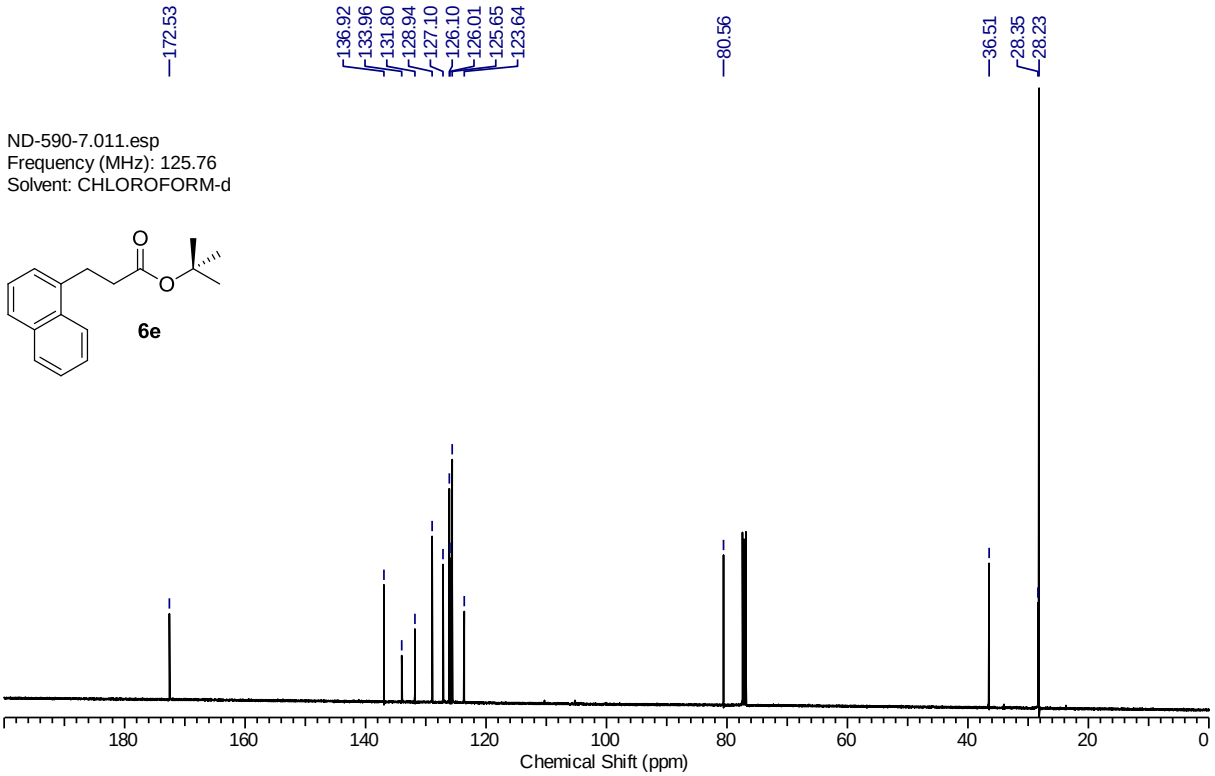

ND-532-6.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
O
O
Me
6c
1.02
2.91
2.00
2.00
3.01
8.96
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

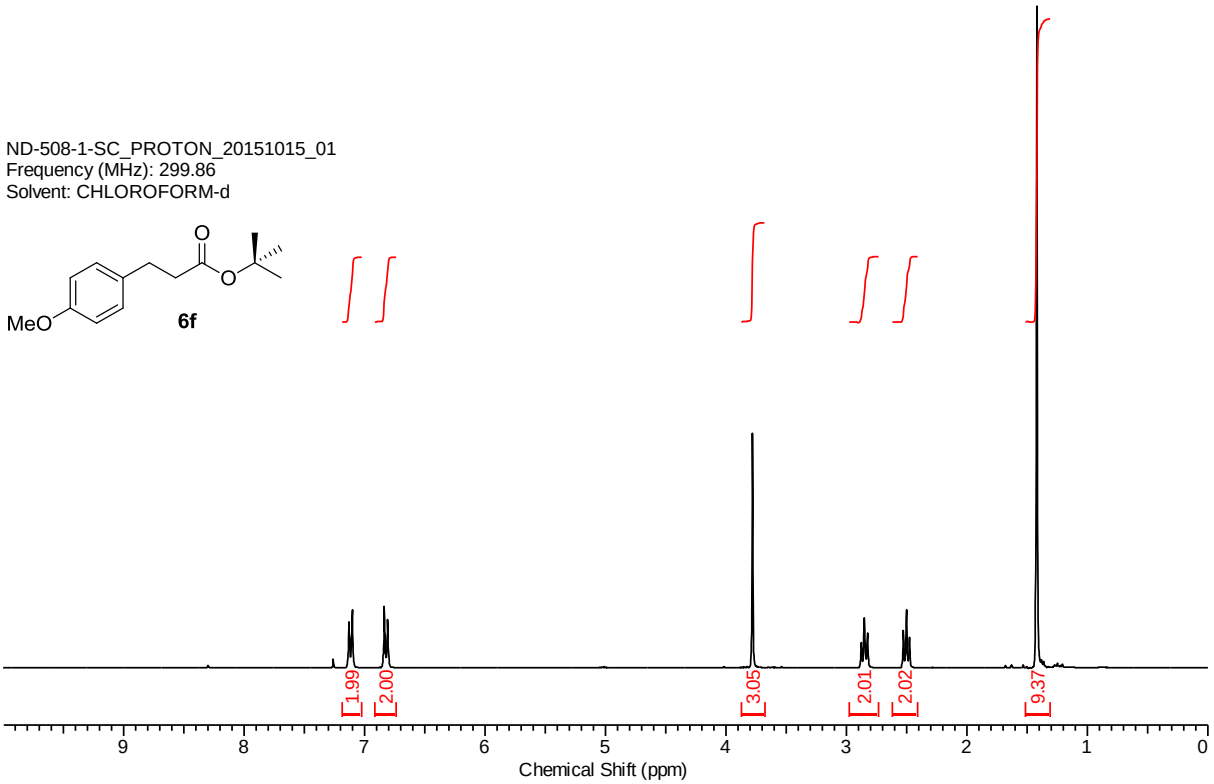

172.43
140.82
137.99
129.25
128.40
126.93
125.41
80.35
37.24
31.17
28.17
21.47
ND-532-6.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
O
O
Me
6c
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

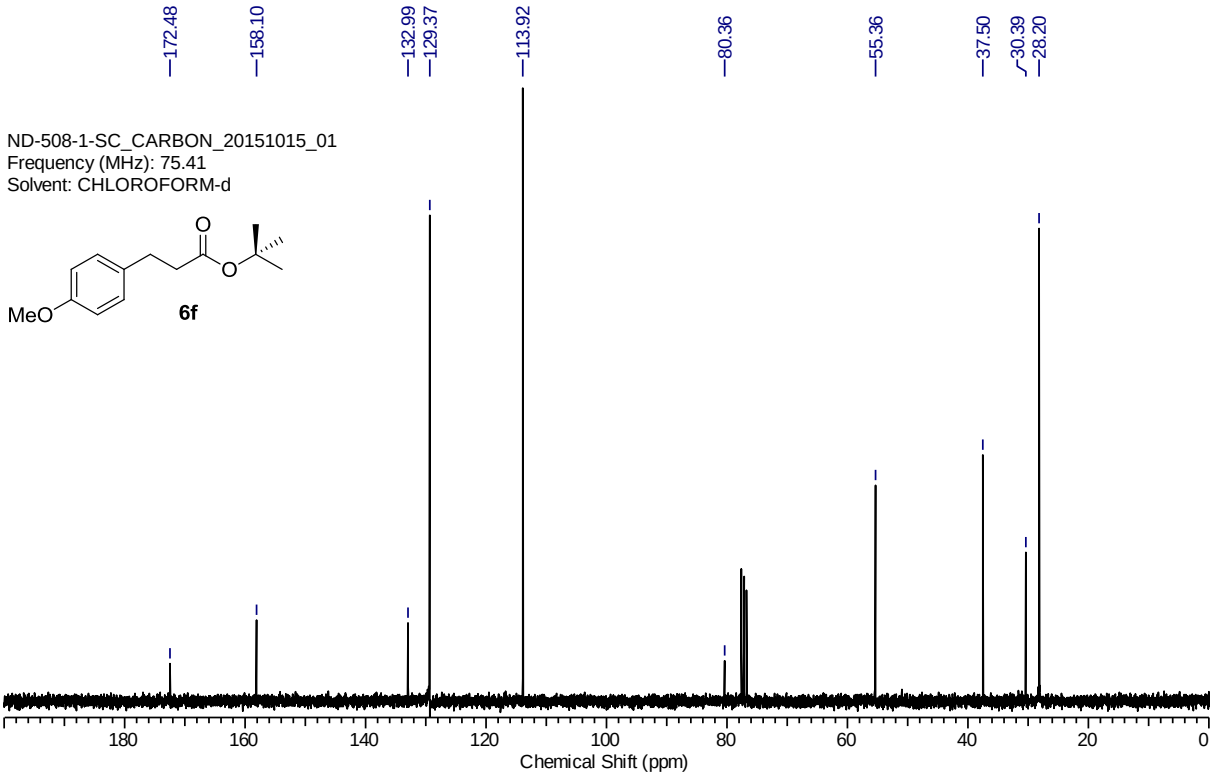

ND-534-4.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
O
O
Me
6d
3.96
2.00
2.00
3.03
9.08
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

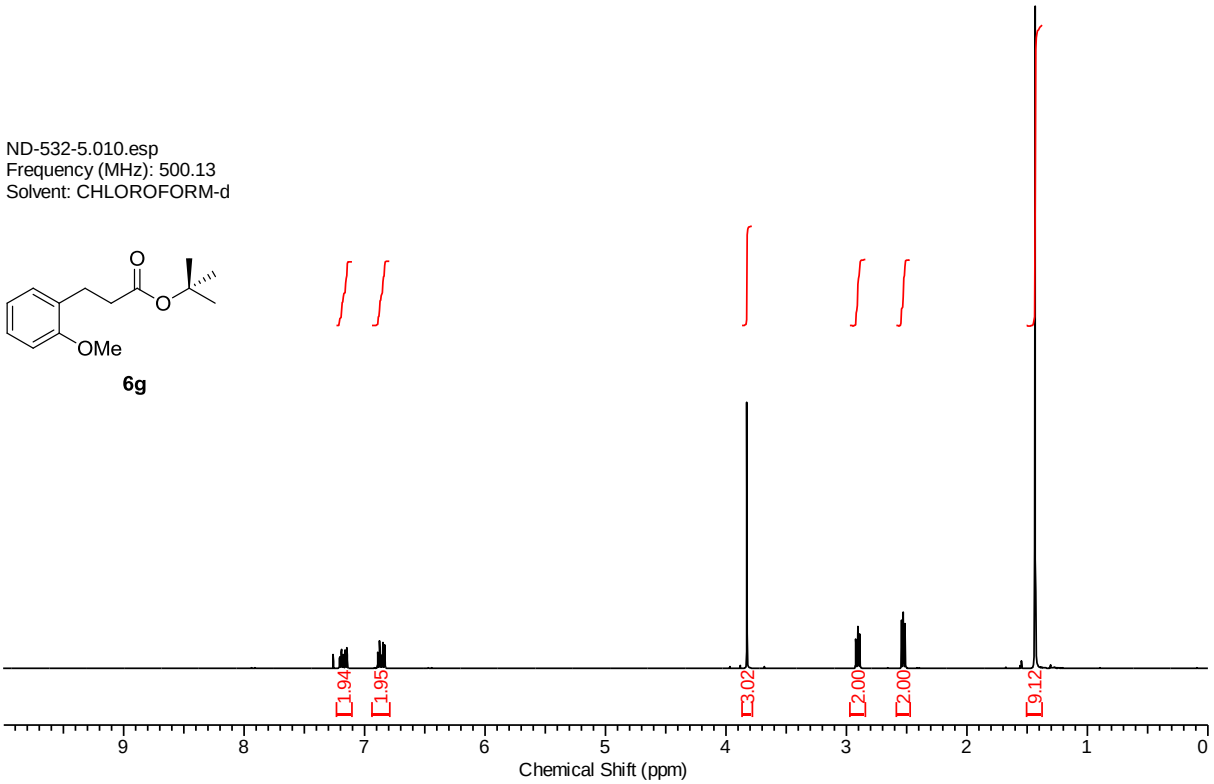

172.55
139.00
136.10
130.32
128.63
126.37
126.13
80.47
35.86
28.55
28.21
19.40
ND-534-4.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
O
O
Me
6d
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

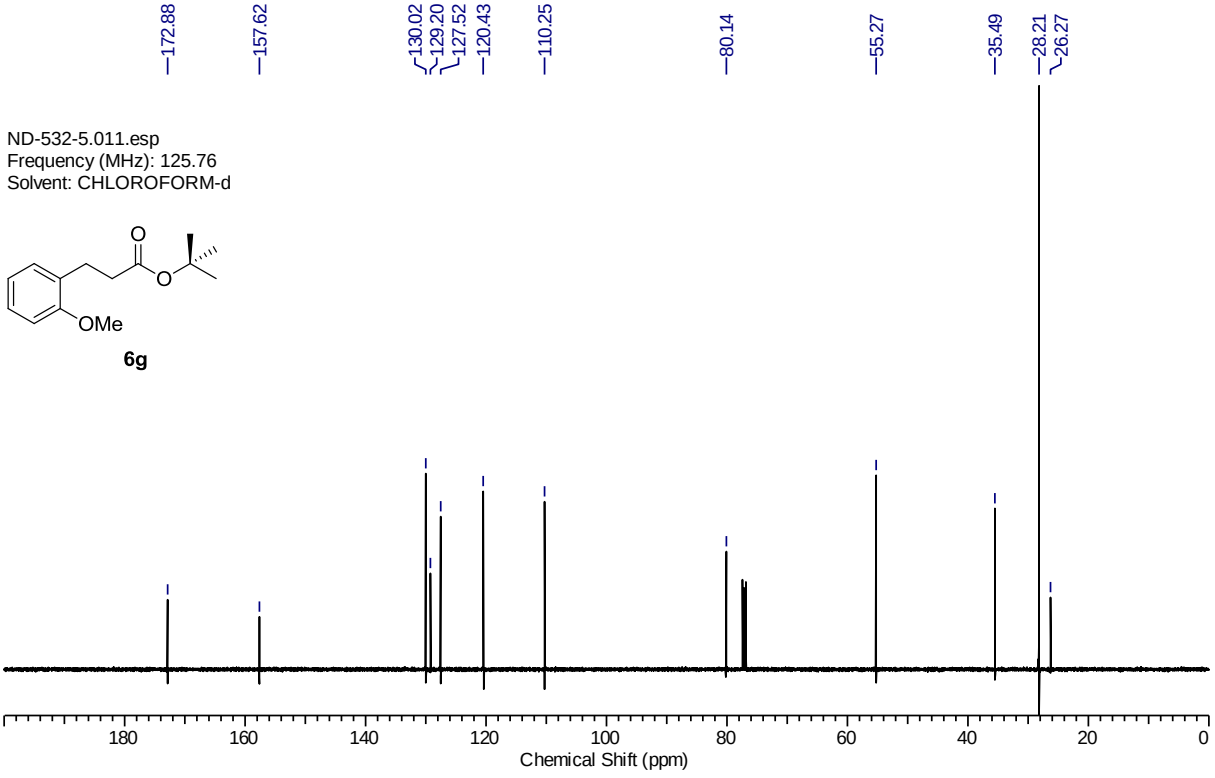

ND-590-7.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
6e
1.00
1.00
0.99
2.01
1.98
2.03
2.02
9.32
Chemical Shift (ppm)

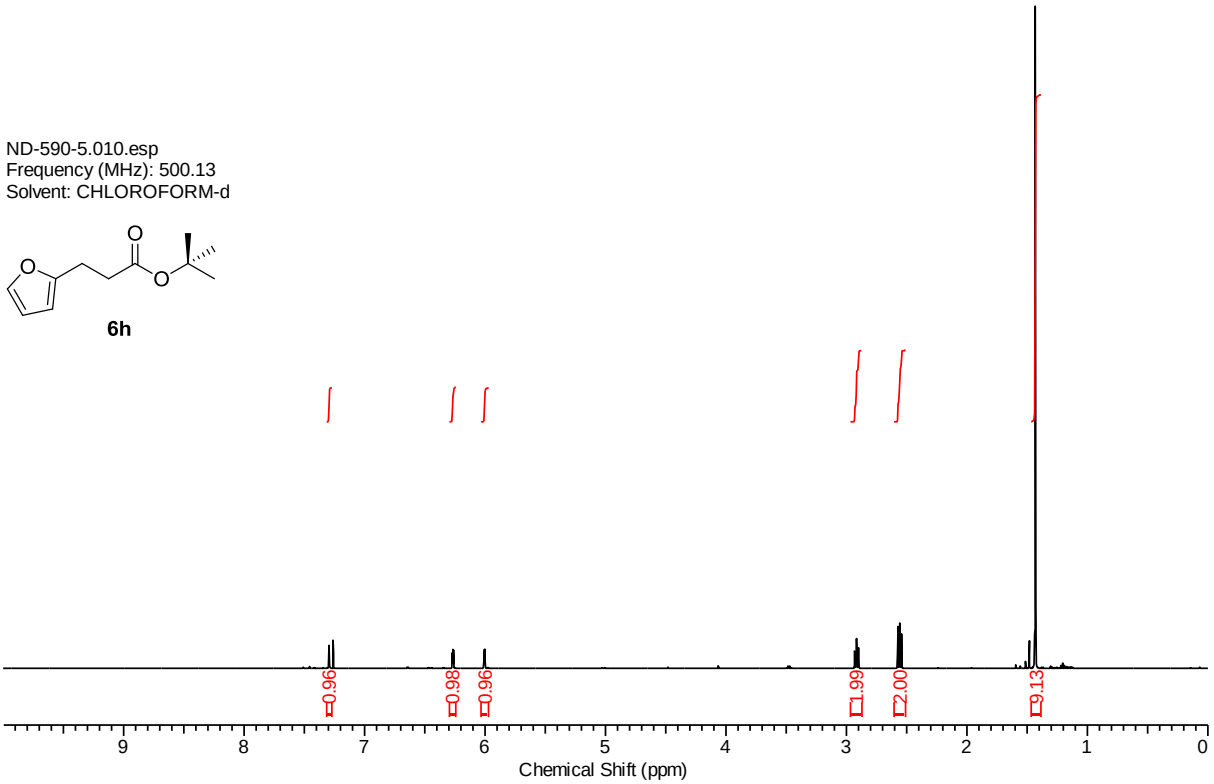

172.53
136.92
133.96
131.80
128.94
127.10
126.10
126.01
125.65
123.64
80.56
36.51
28.35
28.23
ND-590-7.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
6e
Chemical Shift (ppm)

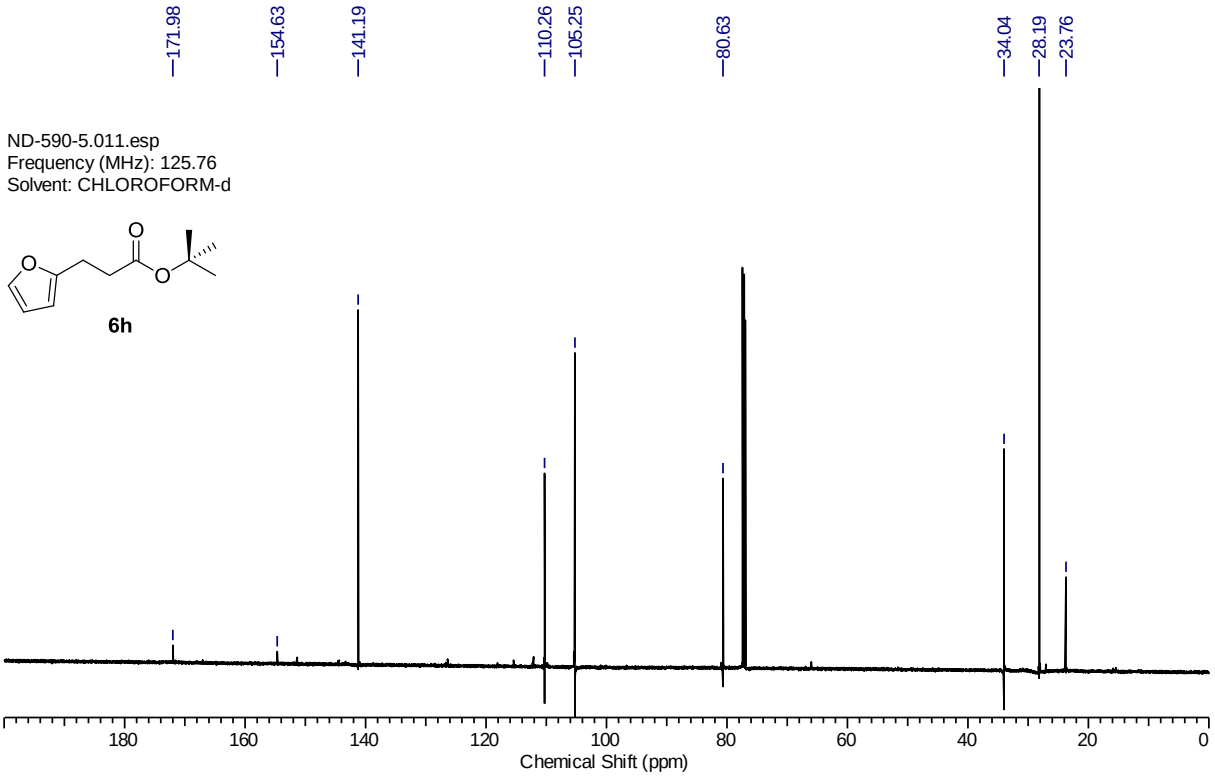

ND-508-1-SC_PROTON_20151015_01
Frequency (MHz): 299.86
Solvent: CHLOROFORM-d
MeO
6f
1.99
2.00
3.05
2.01
2.02
9.37
Chemical Shift (ppm)


172.48
158.10
132.99
129.37
113.92
80.36
55.36
37.50
30.39
28.20
ND-508-1-SC_CARBON_20151015_01
Frequency (MHz): 75.41
Solvent: CHLOROFORM-d
MeO
6f
Chemical Shift (ppm)

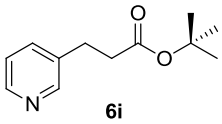

ND-532-5.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
O
O
OMe
6g
1.94
1.95
3.02
2.00
2.00
9.12
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


172.88
157.62
130.02
129.20
127.52
120.43
110.25
80.14
55.27
35.49
28.21
26.27
ND-532-5.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
O
O
OMe
6g
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


ND-590-5.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
6h
0.96
0.98
0.96
1.99
2.00
9.13
Chemical Shift (ppm)

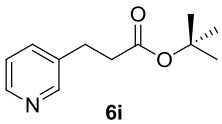

171.98
154.63
141.19
110.26
105.25
80.63
34.04
28.19
23.76
ND-590-5.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
6h
Chemical Shift (ppm)

ND-590-2.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d

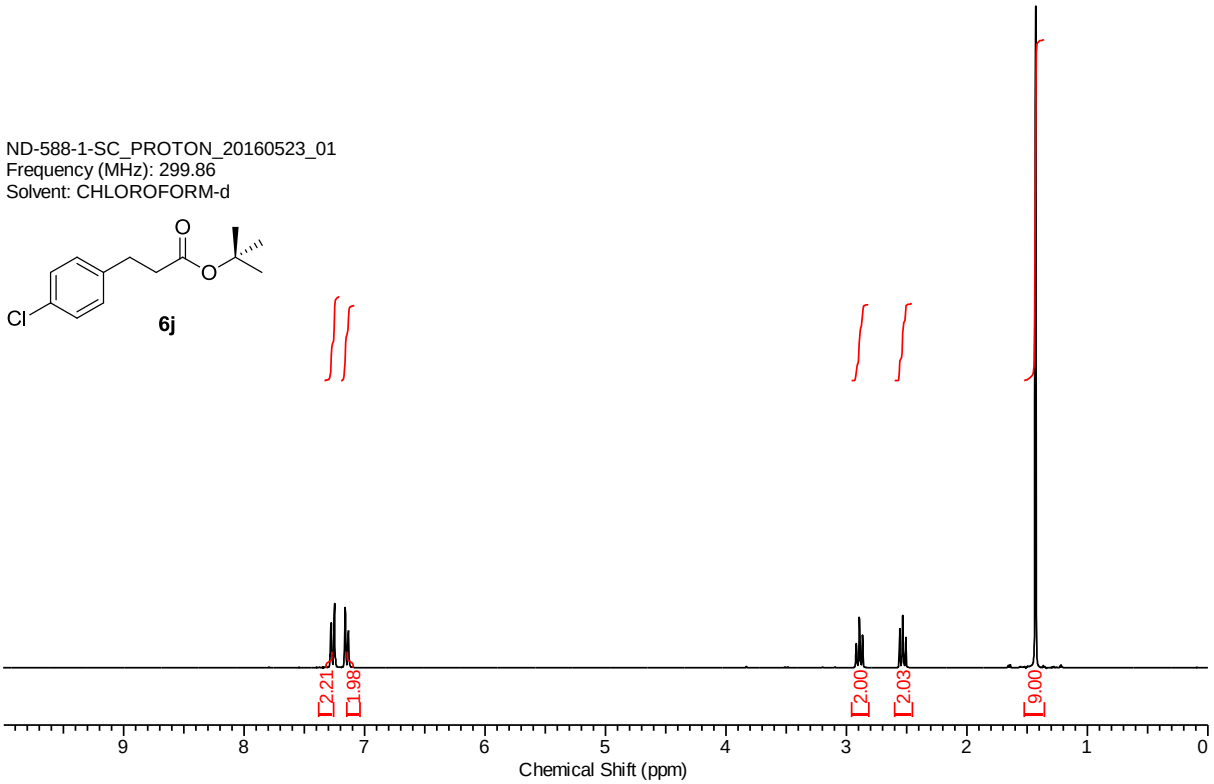


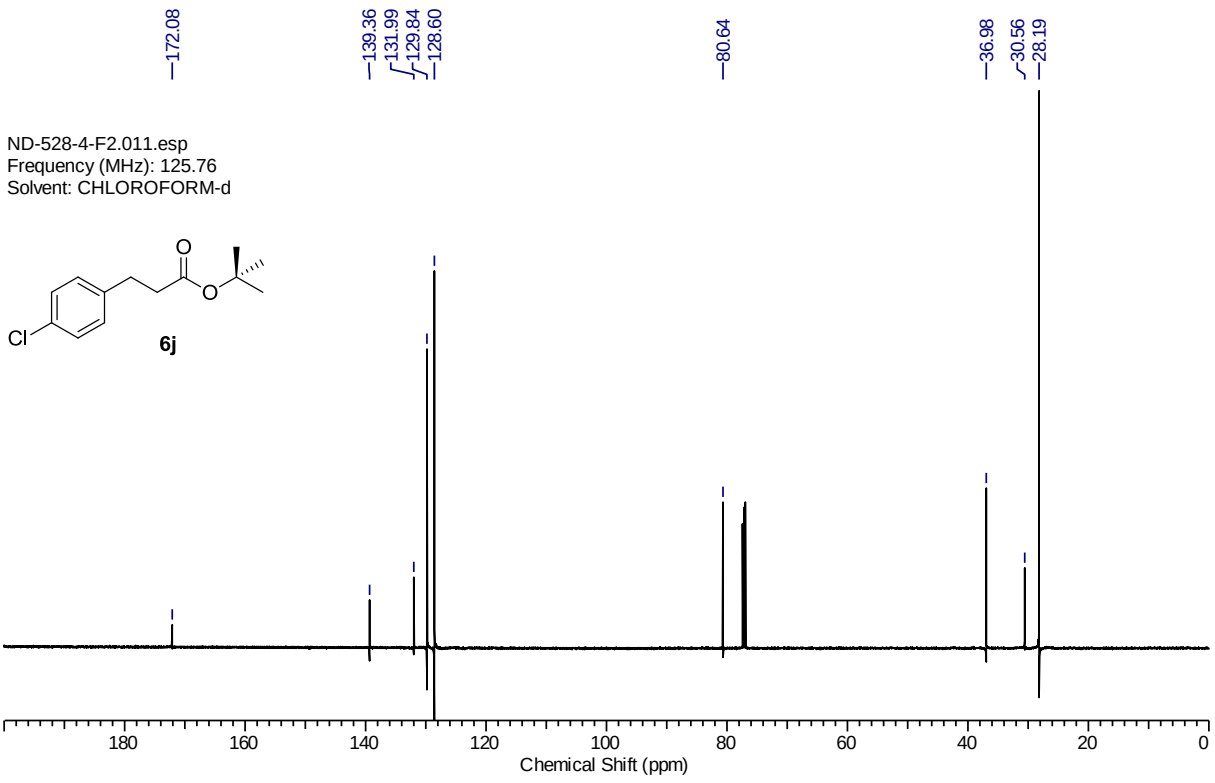
6i

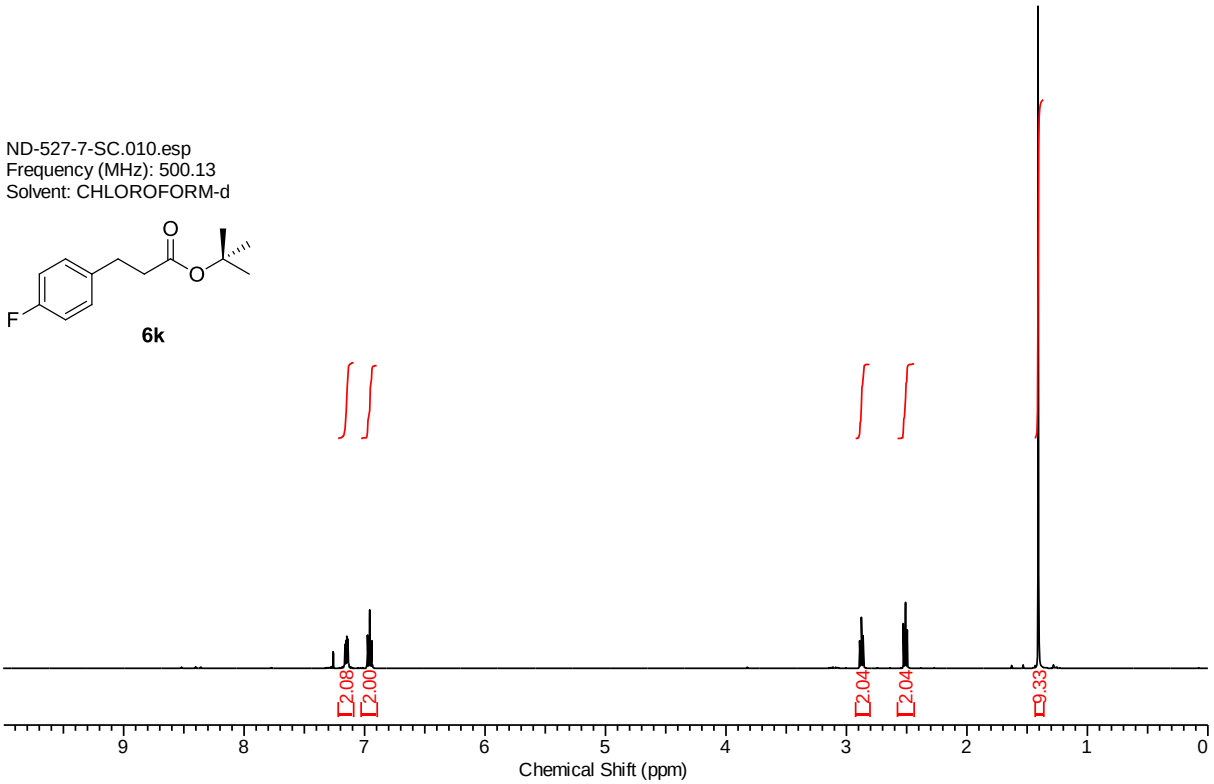
ND-590-2.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d

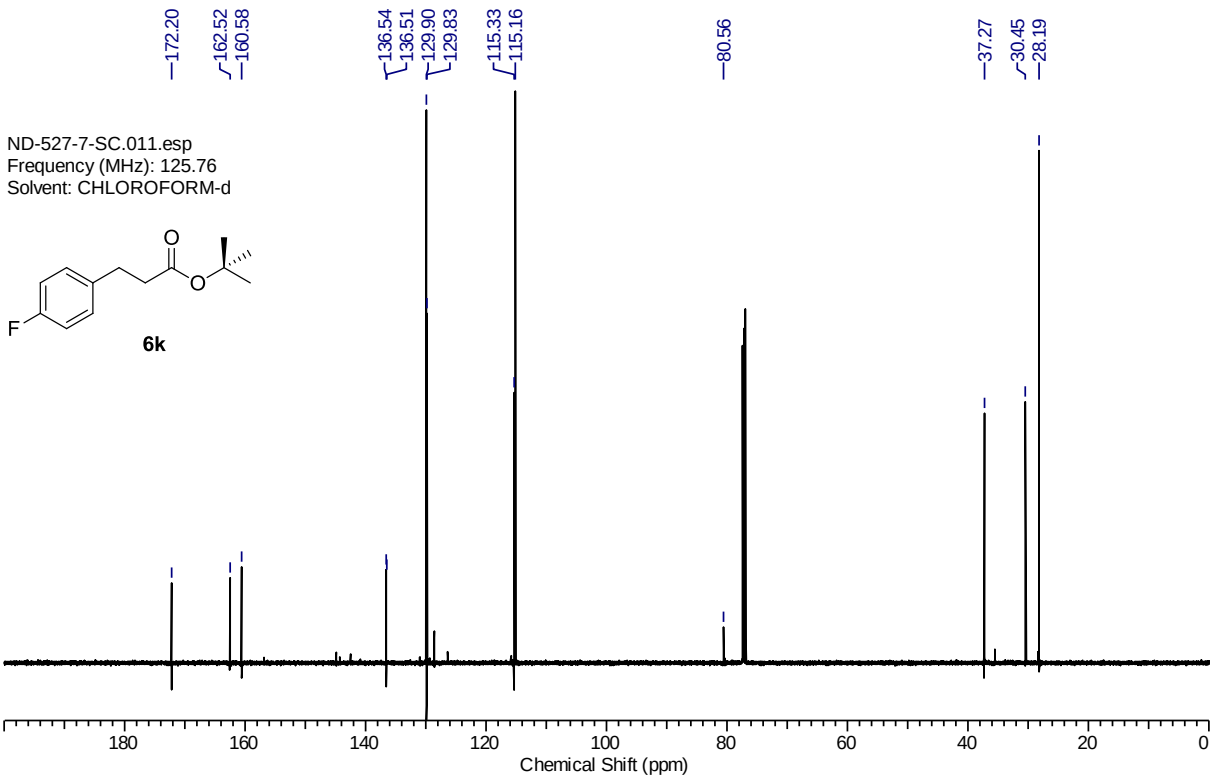


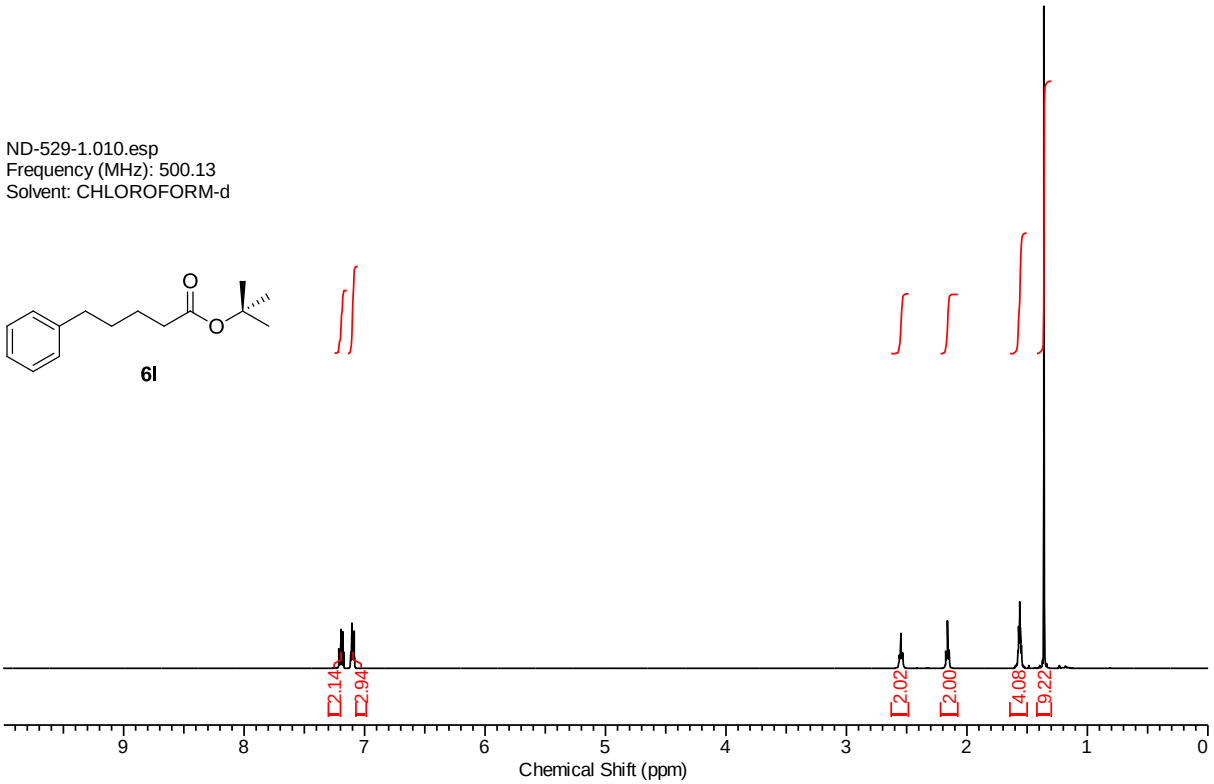
6i

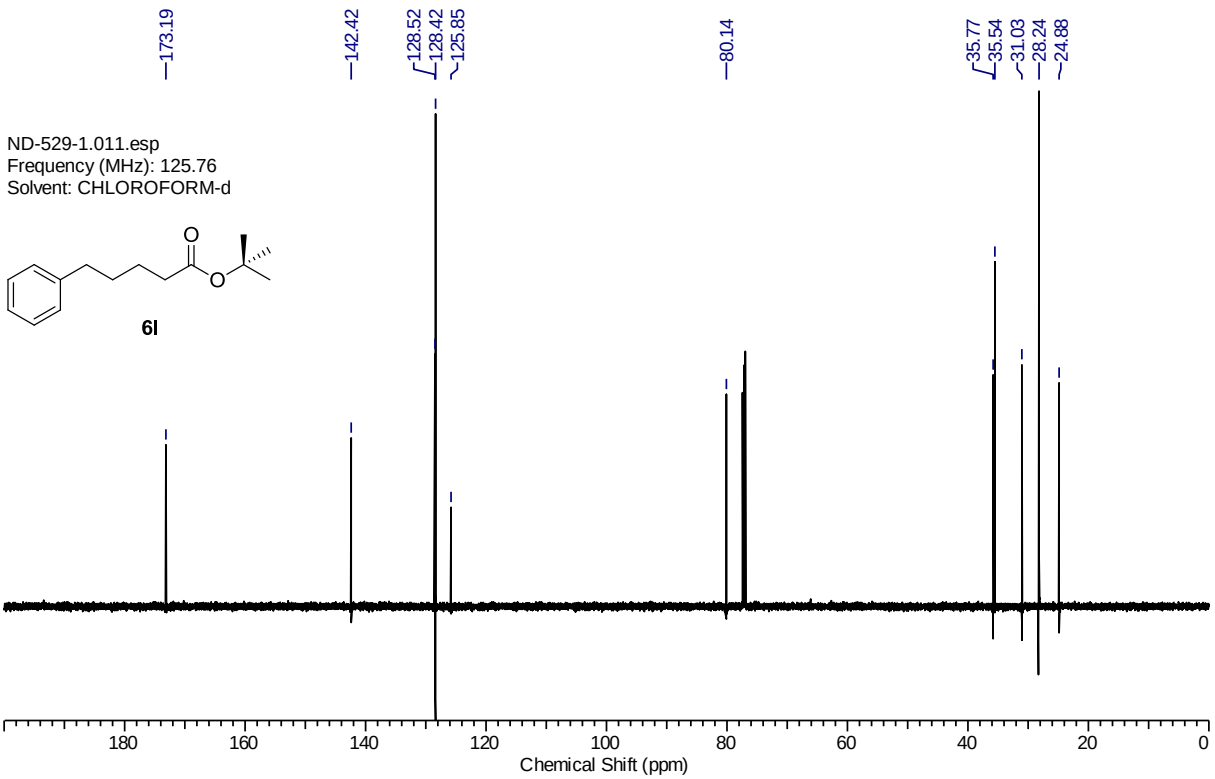

ND-588-1-SC_PROTON_20160523_01
Frequency (MHz): 299.86
Solvent: CHLOROFORM-d
O
O
Cl
6j
2.21
1.98
2.00
2.03
9.00
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


172.08
139.36
131.99
129.84
128.60
80.64
36.98
30.56
28.19
ND-528-4-F2.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
O
O
Cl
6j
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

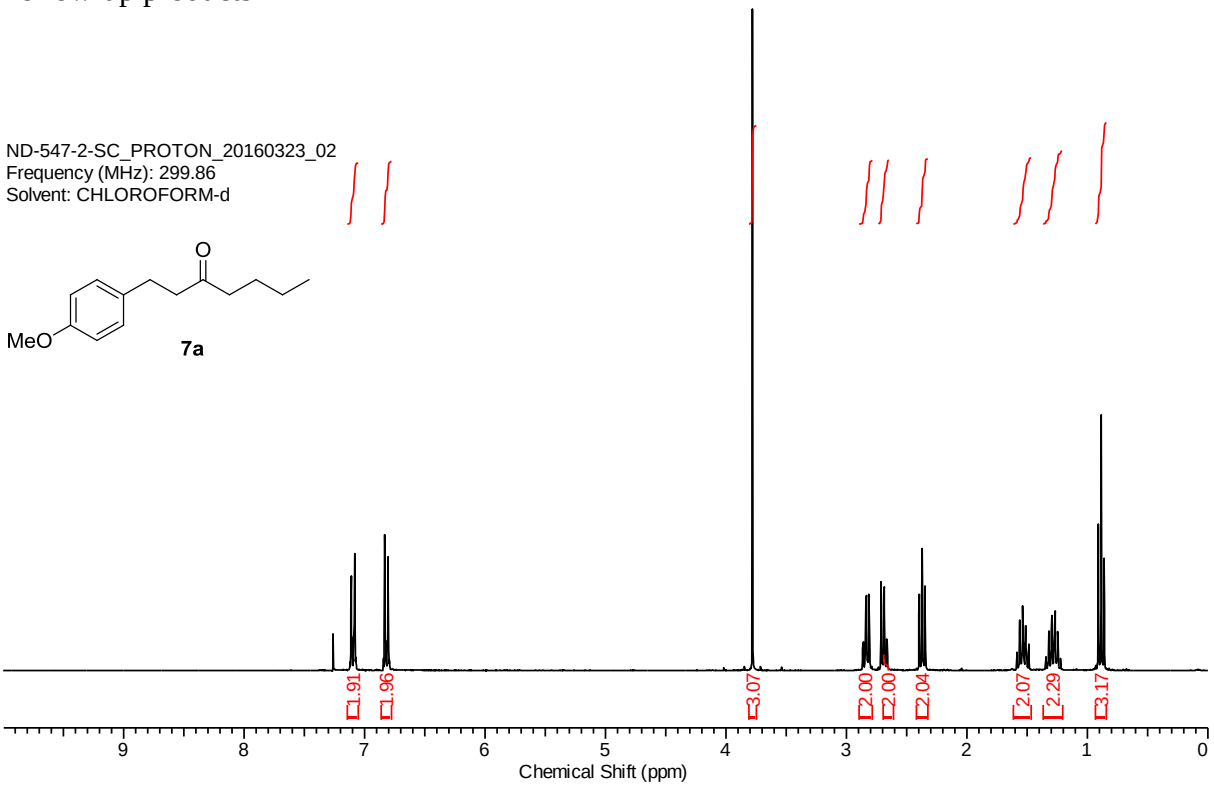

ND-527-7-SC.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
O
O
F
6k
2.08
2.00
2.04
2.04
9.33
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

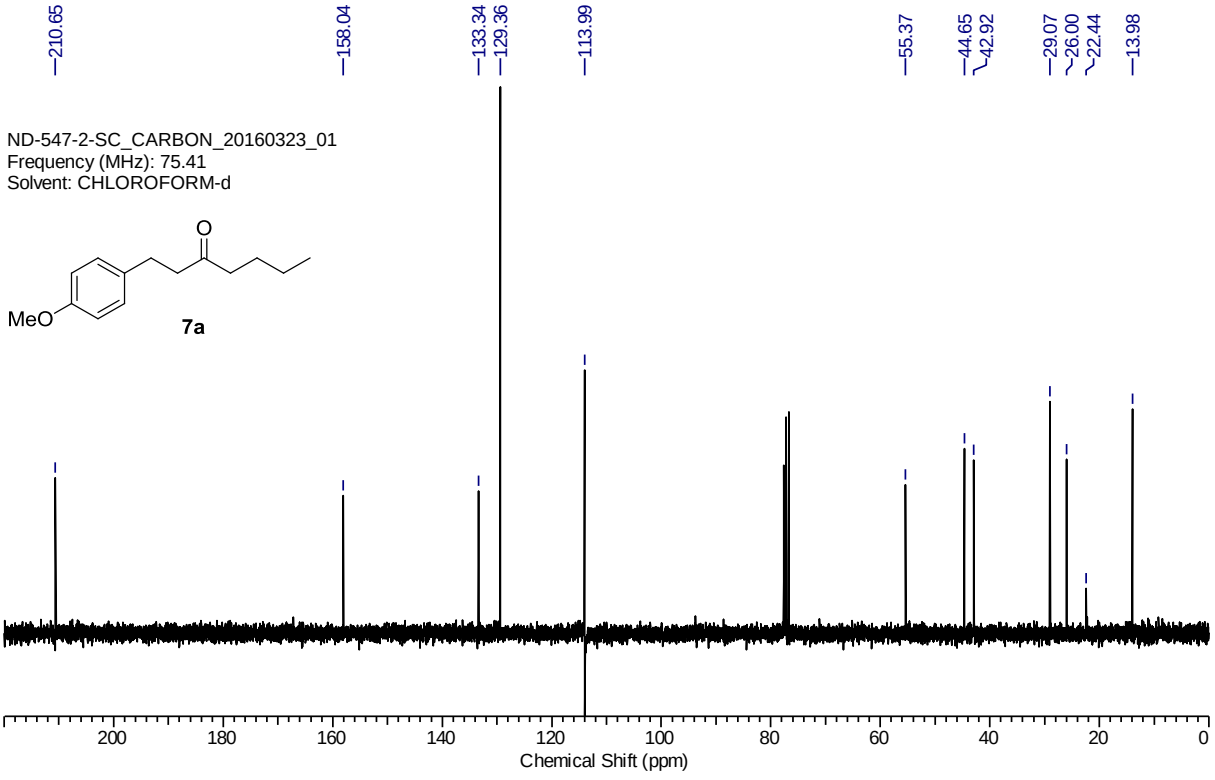

172.20
162.52
160.58
136.54
136.51
129.90
129.83
115.33
115.16
80.56
37.27
30.45
28.19
ND-527-7-SC.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
O
O
F
6k
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

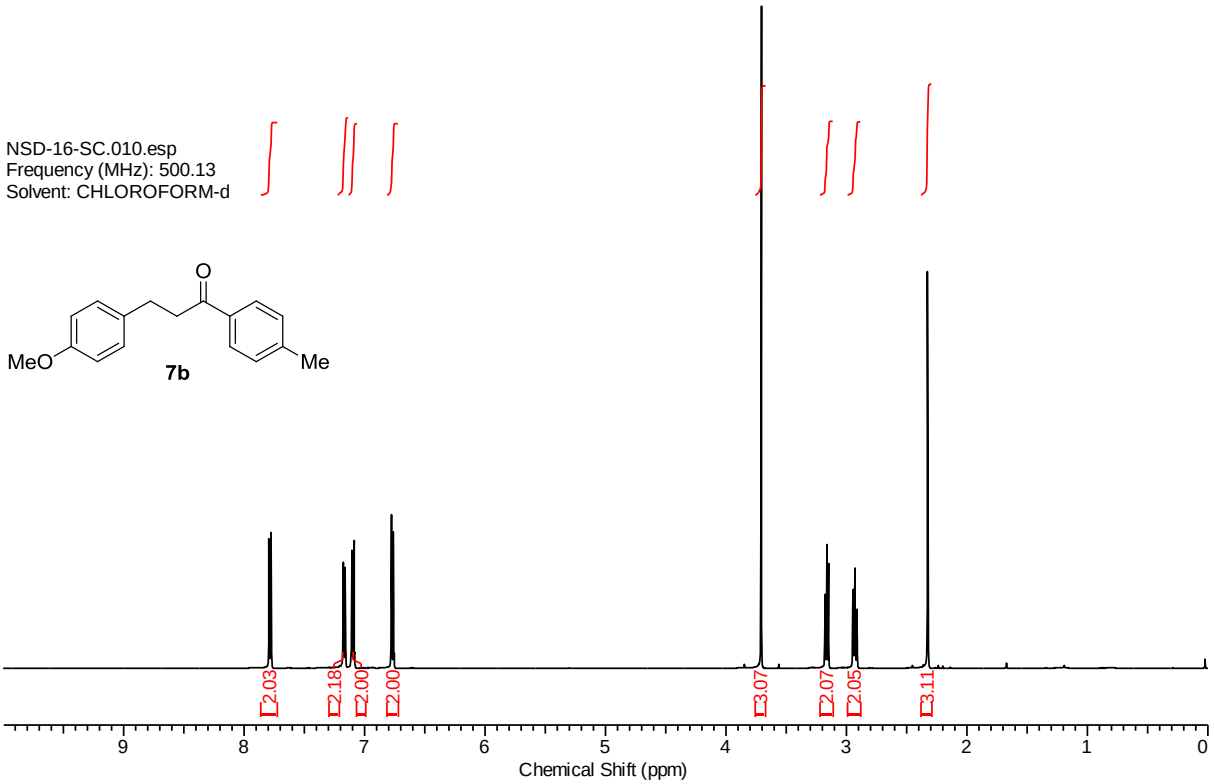

ND-529-1.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
6l
2.14
2.94
2.02
2.00
4.08
9.22
Chemical Shift (ppm)

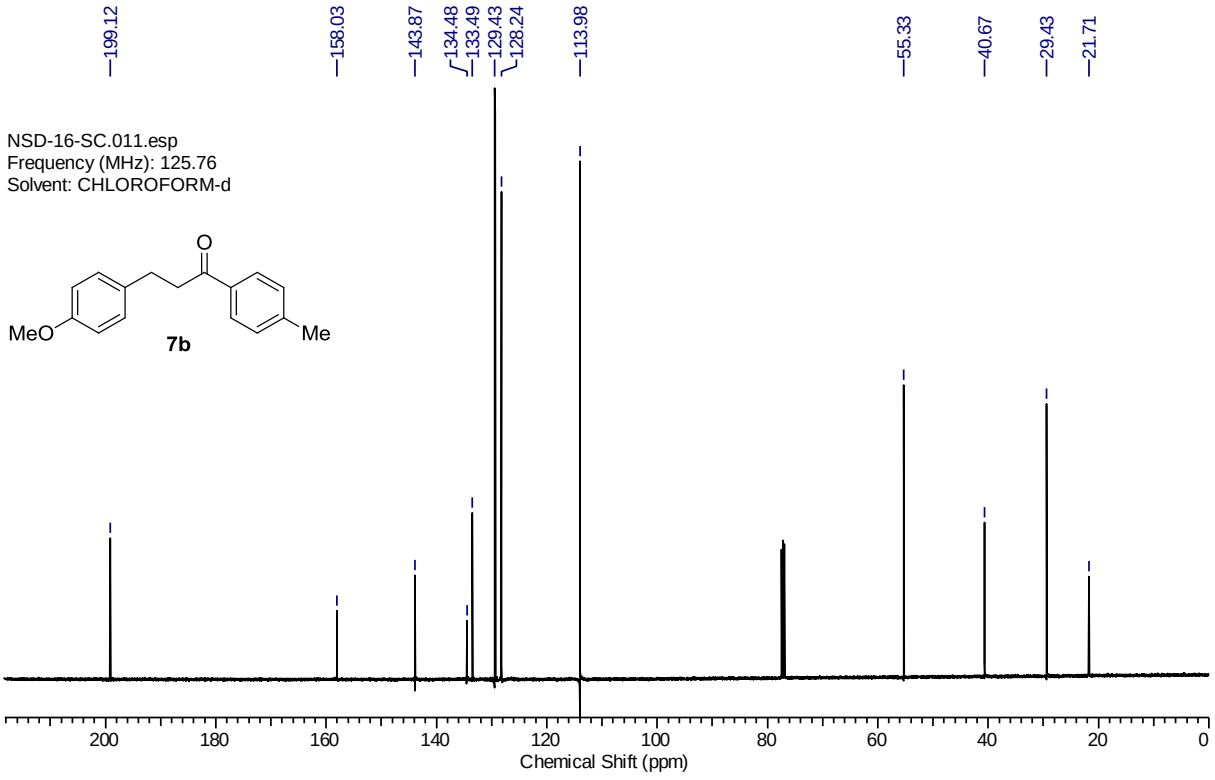

173.19
142.42
128.52
128.42
125.85
80.14
35.77
35.54
31.03
28.24
24.88
ND-529-1.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
6l
Chemical Shift (ppm)

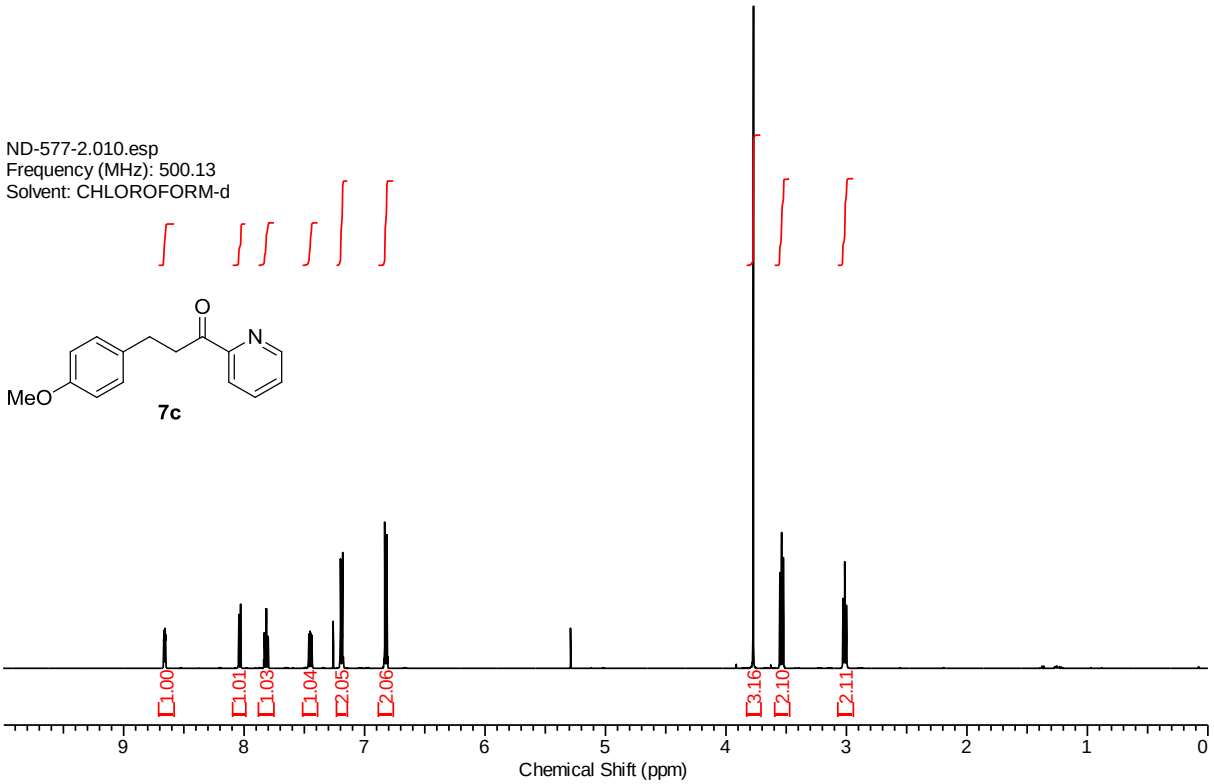
Follow-up products

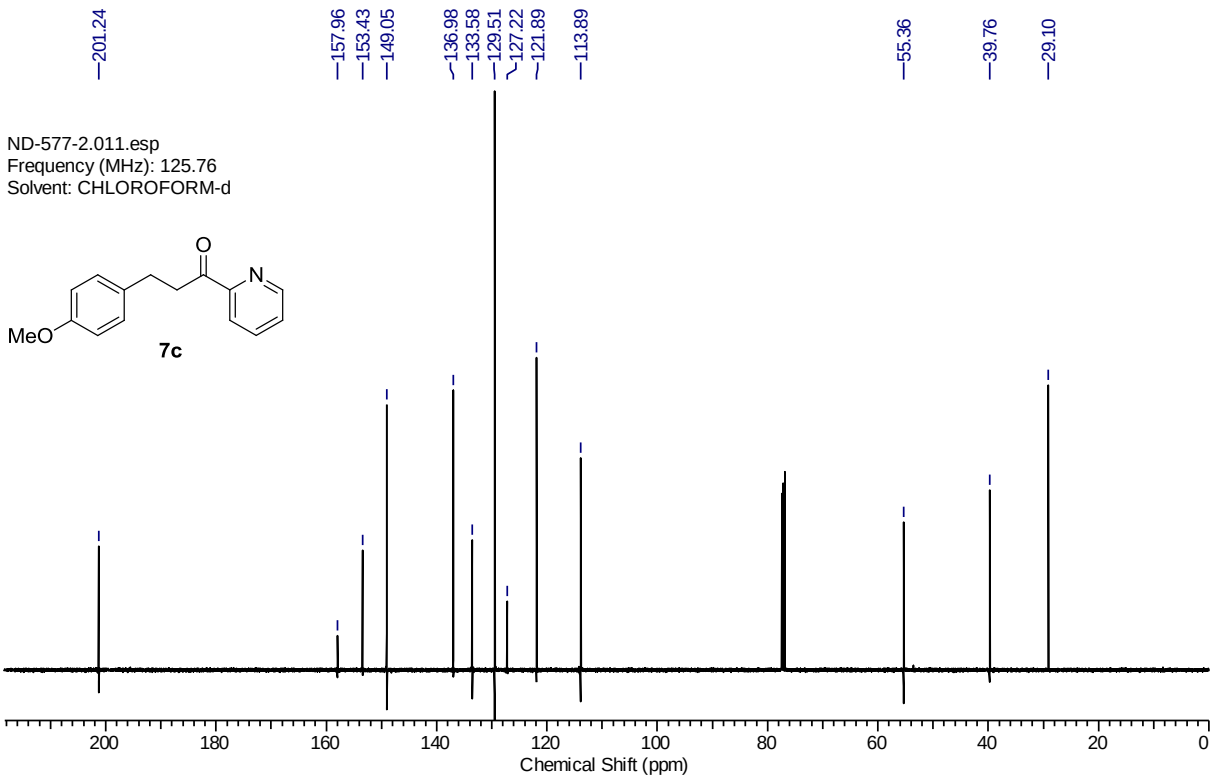


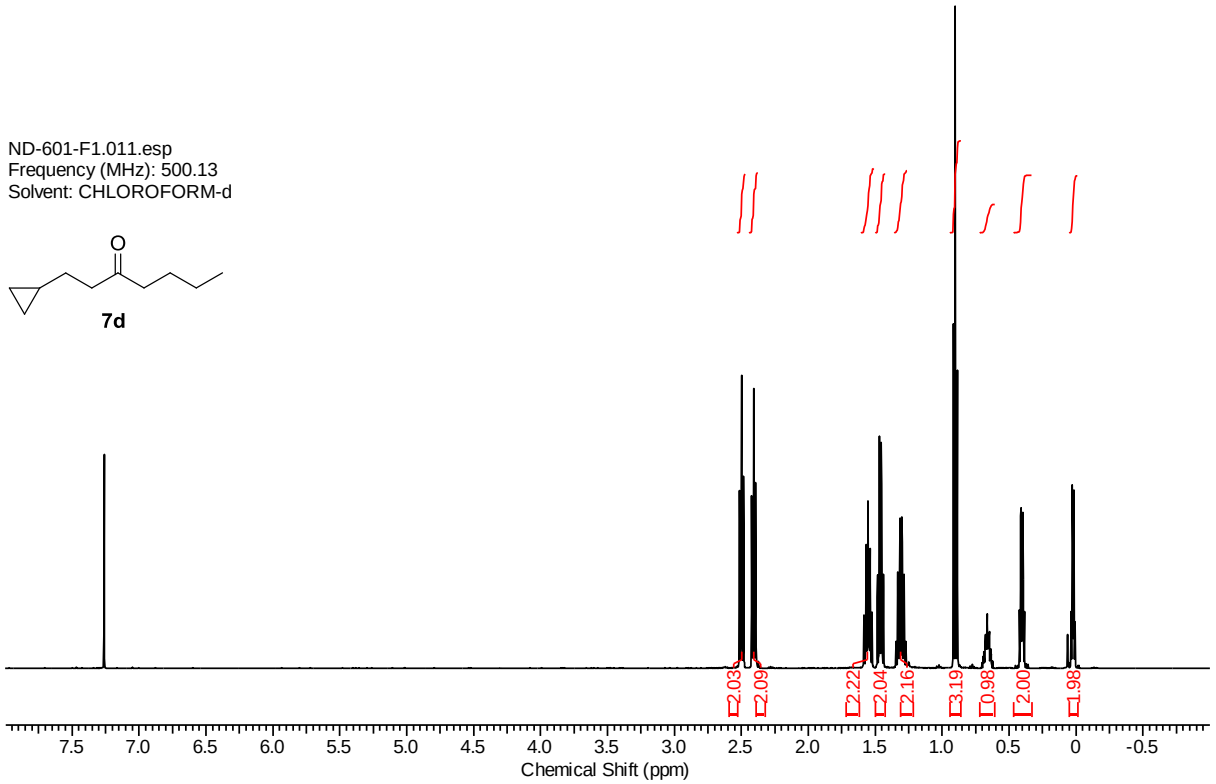


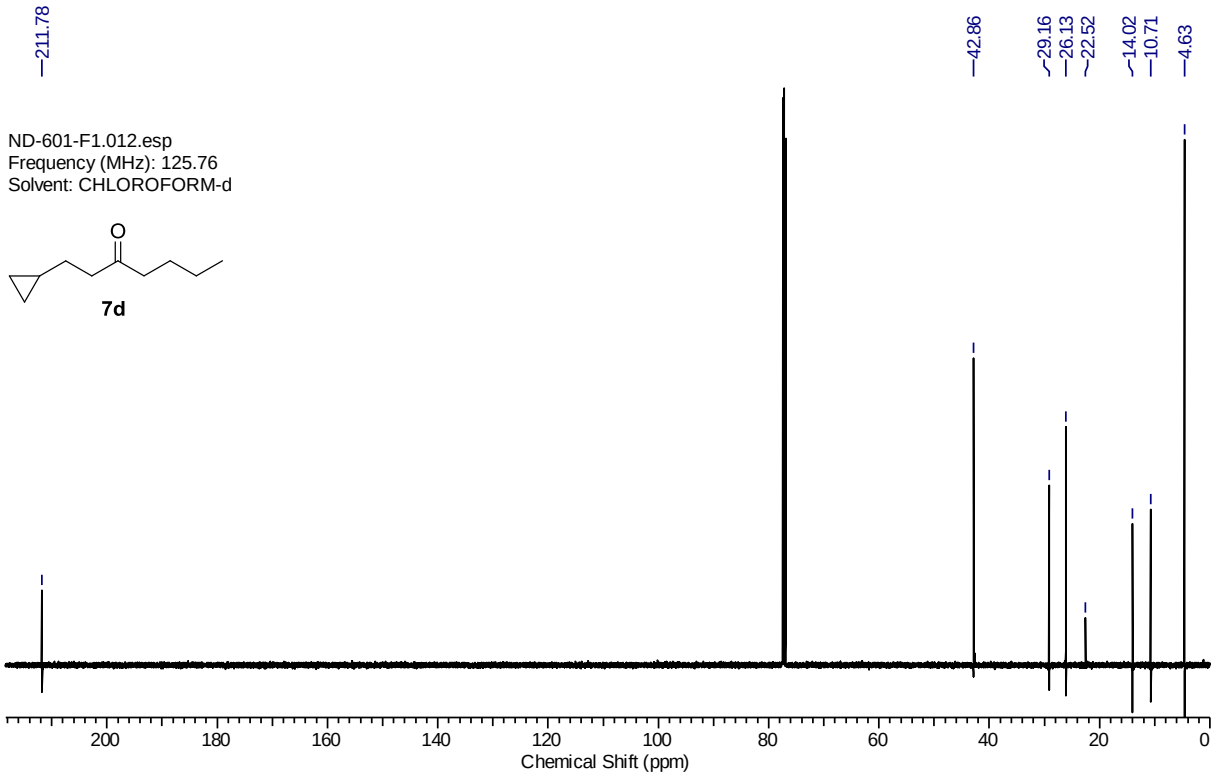

NSD-16-SC.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
O
MeO
Me
7b
2.03
2.18
2.00
2.00
3.07
2.07
2.05
3.11
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

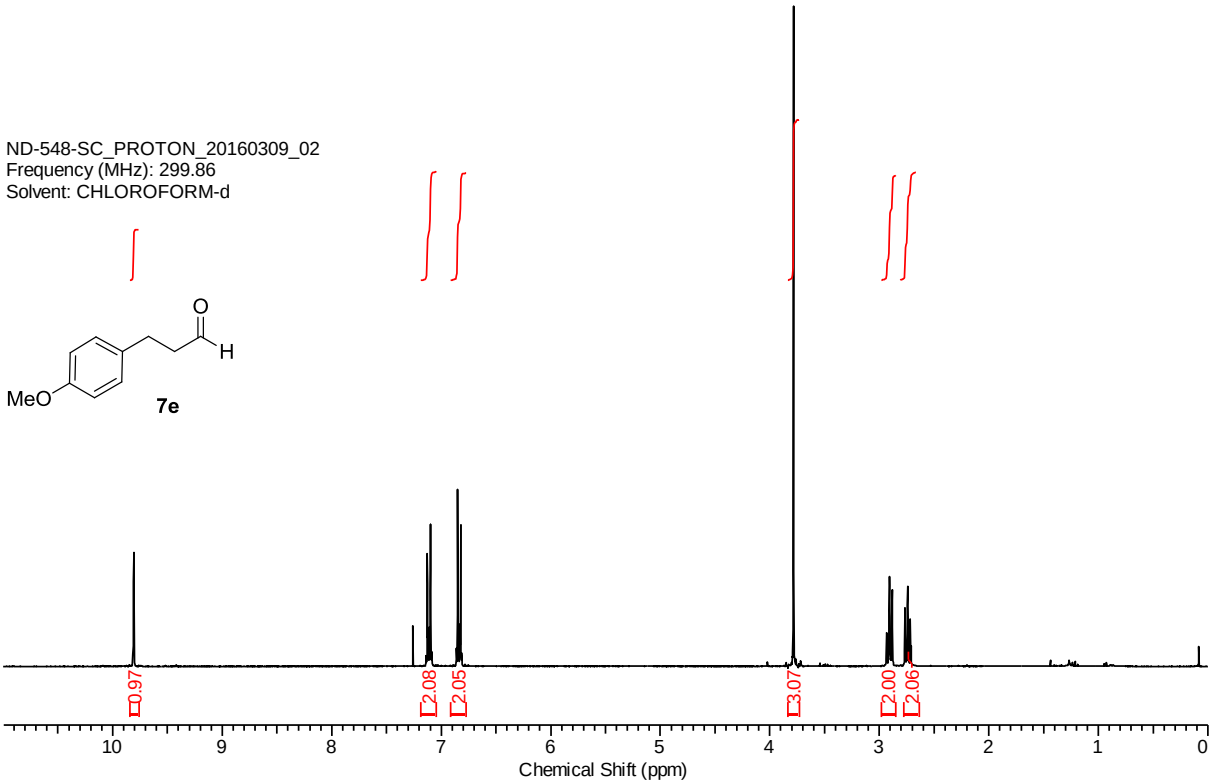

199.12
158.03
143.87
134.48
133.49
129.43
128.24
113.98
55.33
40.67
29.43
21.71
NSD-16-SC.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
O
MeO
Me
7b
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

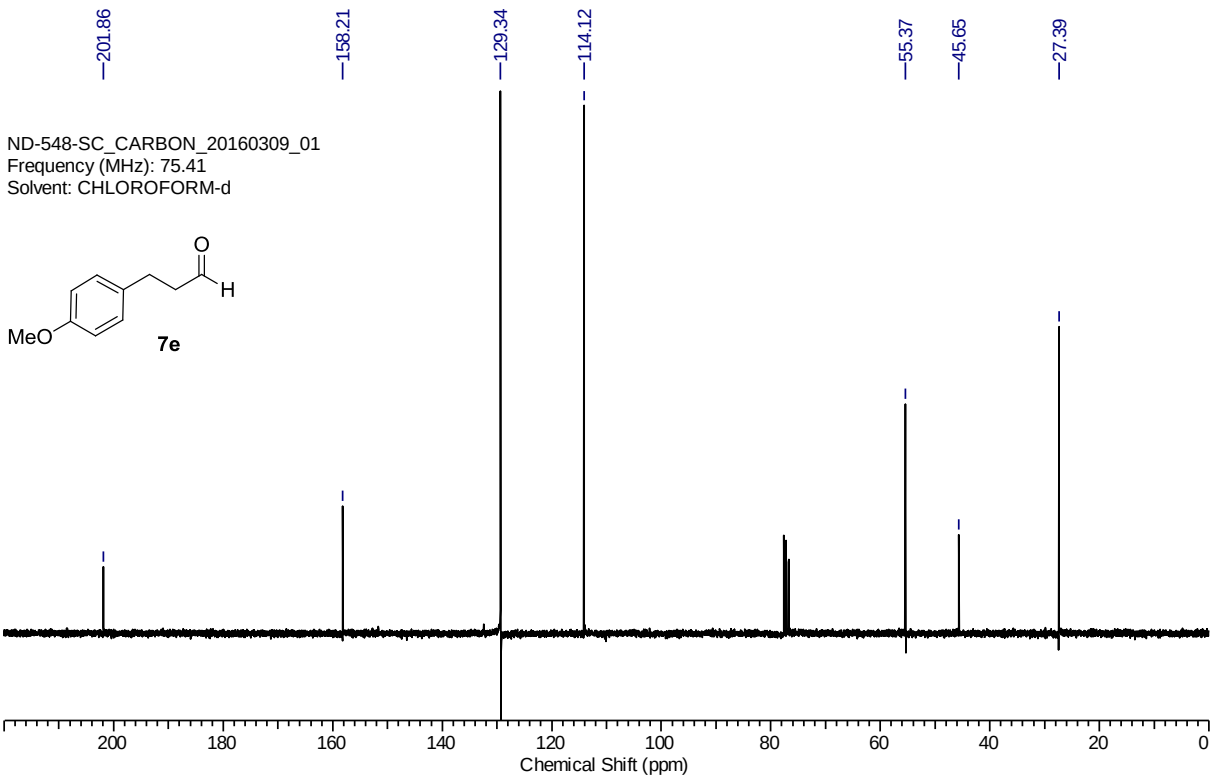

ND-577-2.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
O
N
MeO
7c
1.00
1.01
1.03
1.04
2.05
2.06
3.16
2.10
2.11
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

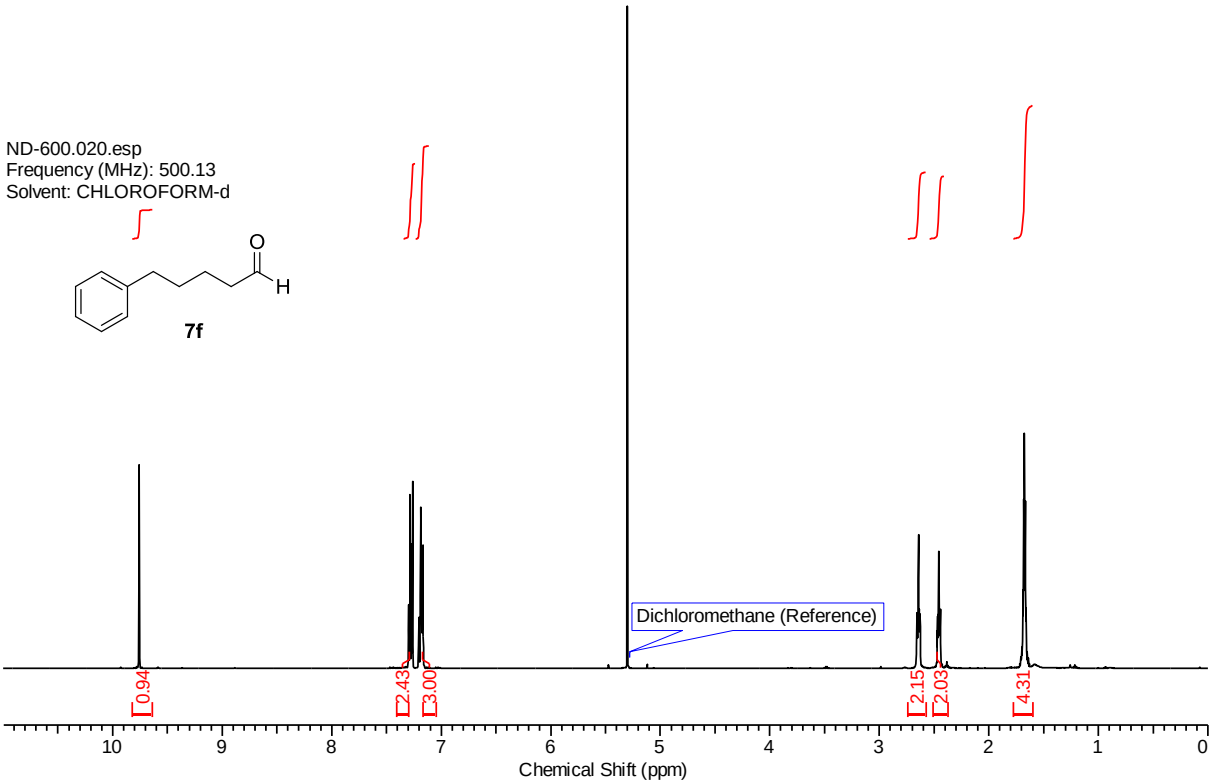

201.24
157.96
153.43
149.05
136.98
133.58
129.51
127.22
121.89
113.89
55.36
39.76
29.10
ND-577-2.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
O
N
MeO
7c
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

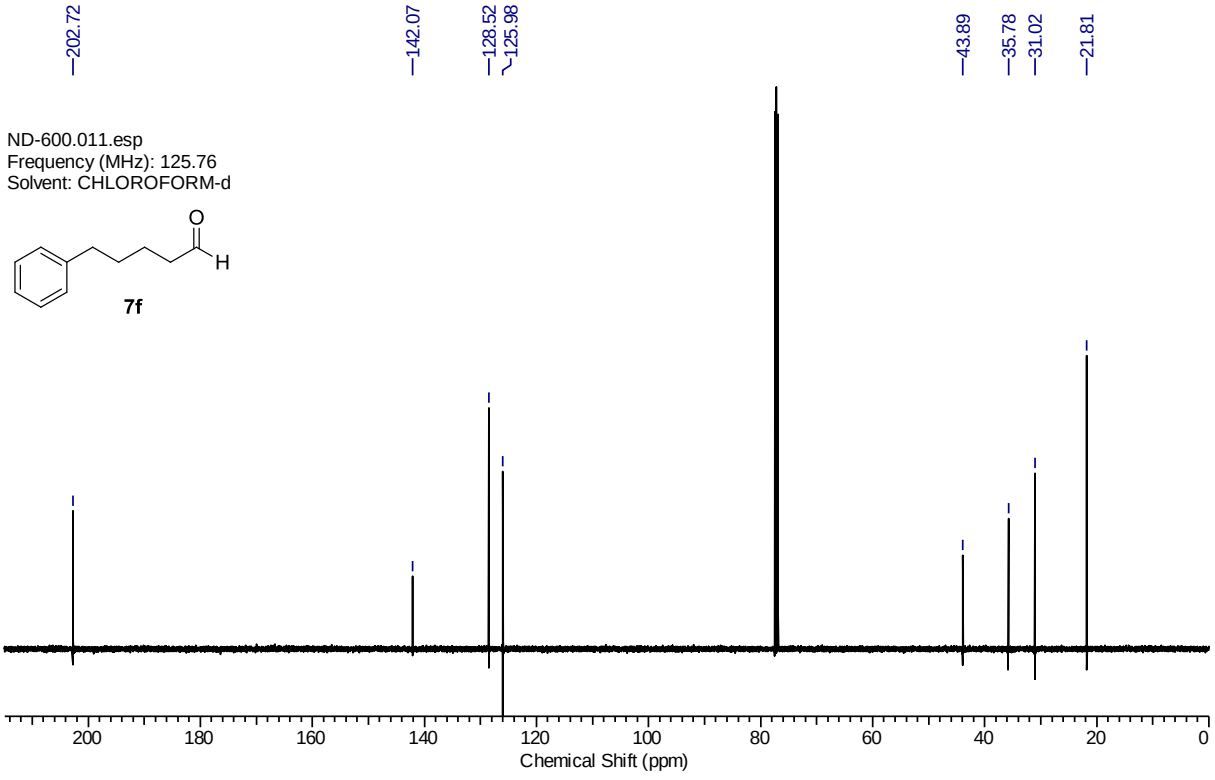

ND-601-F1.011.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
O
7d
2.03
2.09
2.22
2.04
2.16
3.19
0.98
2.00
1.98
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0 -0.5
Chemical Shift (ppm)

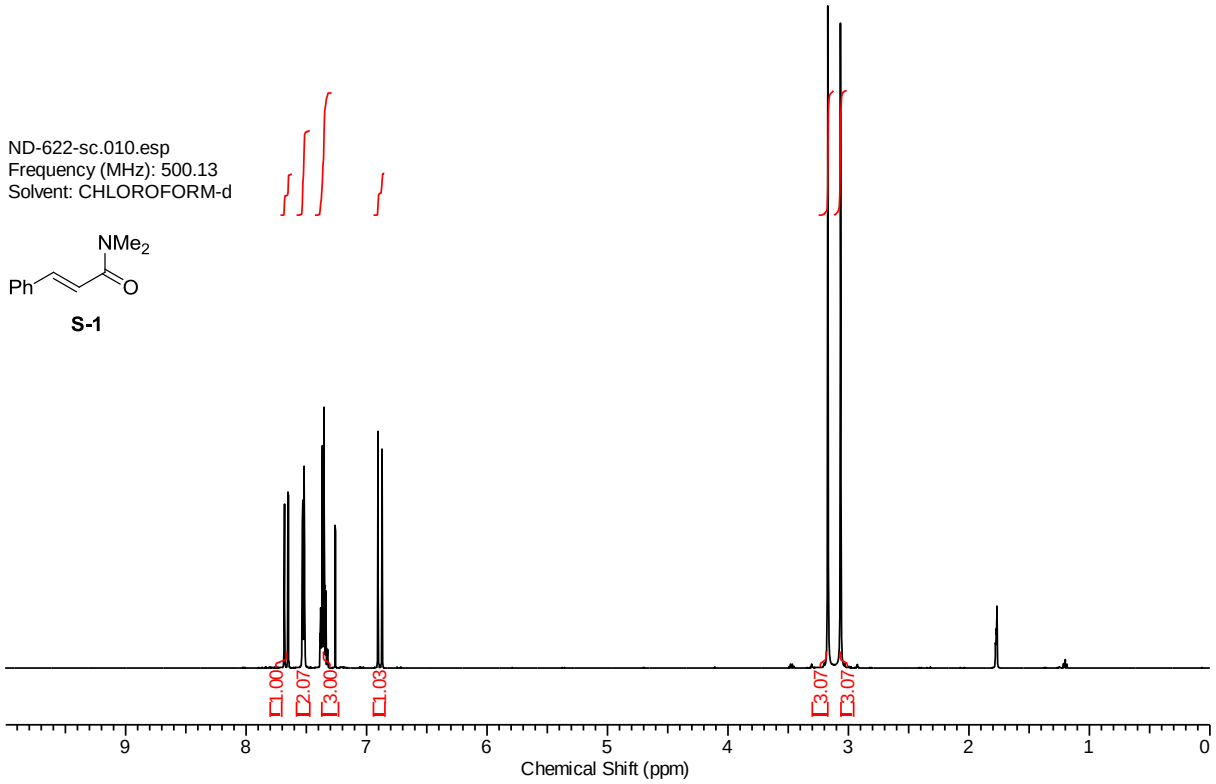

211.78
42.86
29.16
26.13
22.52
14.02
10.71
4.63
ND-601-F1.012.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
O
7d
200 180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)

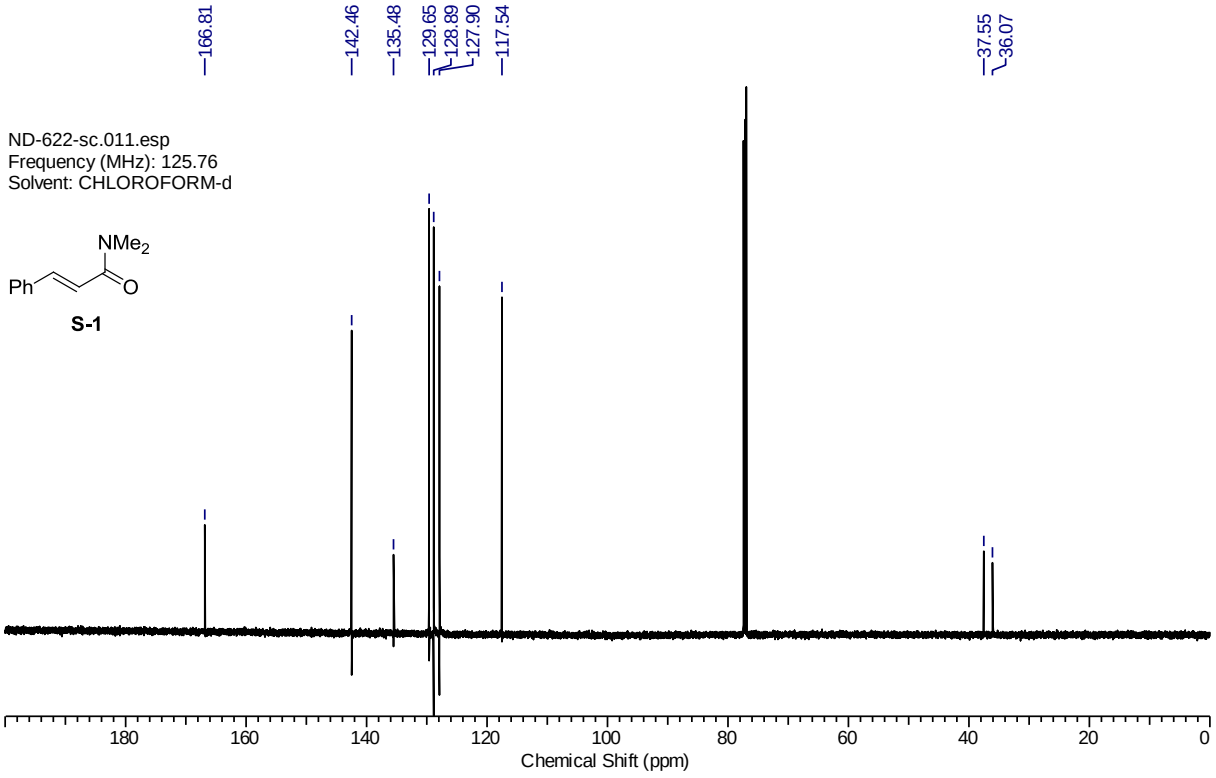

ND-548-SC_PROTON_20160309_02
Frequency (MHz): 299.86
Solvent: CHLOROFORM-d
O
H
MeO
7e
0.97
2.08
2.05
3.07
2.00
2.06
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


201.86
158.21
129.34
114.12
55.37
45.65
27.39
ND-548-SC_CARBON_20160309_01
Frequency (MHz): 75.41
Solvent: CHLOROFORM-d
O
H
MeO
7e
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


ND-600.020.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
O
H
7f
Dichloromethane (Reference)
0.94
2.43
3.00
2.15
2.03
4.31
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


202.72
142.07
128.52
125.98
43.89
35.78
31.02
21.81
ND-600.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
O
H
7f
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


ND-622-sc.010.esp
Frequency (MHz): 500.13
Solvent: CHLOROFORM-d
NMe2
Ph
O
S-1
1.00
2.07
3.00
1.03
3.07
3.07
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


166.81
142.46
135.48
129.65
128.89
127.90
117.54
37.55
36.07
ND-622-sc.011.esp
Frequency (MHz): 125.76
Solvent: CHLOROFORM-d
NMe2
Ph
O
S-1
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

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