Supporting Information

Intermolecular oxidative amination of unactivated alkenes by dual photoredox and copper catalysis

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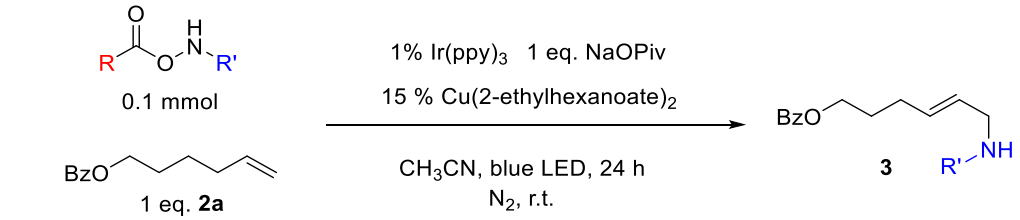
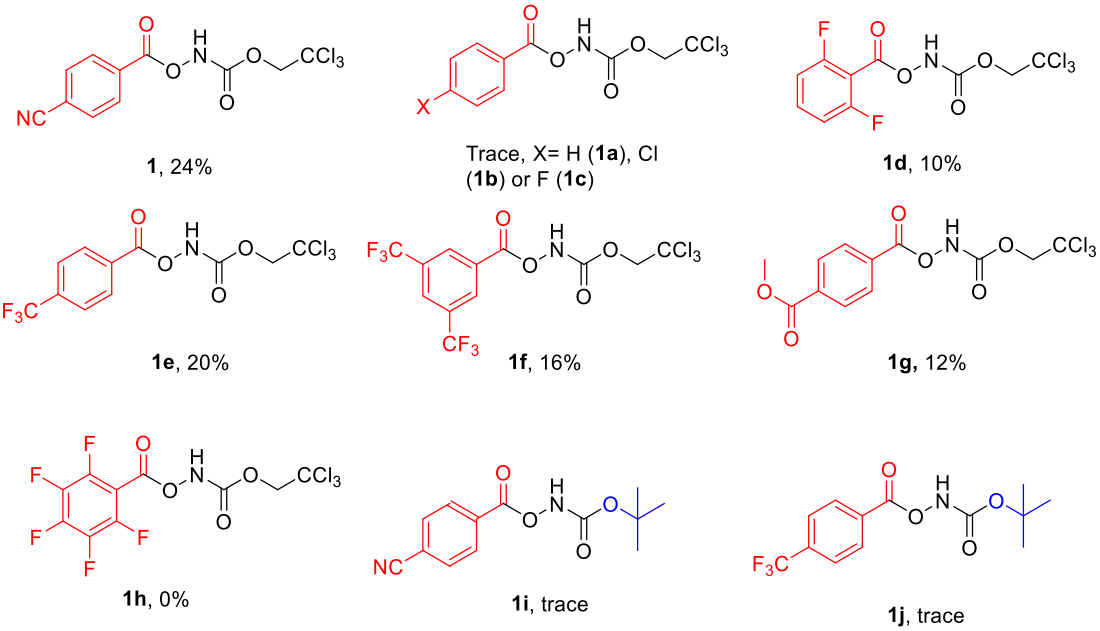
1. General information

Solvents (dichloromethane (DCM), anhydrous acetonitrile and DMSO) and commercially available reagents were used without purification. H_2O was purged with N_2 for 2 h to remove oxygen before use. 15 mL Teflon-screw capped vials (d = 2 cm) were used for the setup of oxidative amination reaction. Blue LEDs (From Kessil Co., Ltd., 40 W max., wavelength centered at 460 nm, product No. A160WE) was used as the radiation source and a cooling fan was used to keep the reaction temperature from going up during photolysis. After the reaction workup, ^{1}H- NMR spectra of crude products were recorded with 1,3,5-trimethylbenzene as an internal standard to determine the NMR yields. Silica gel columns were used for reaction separation, with hexane- ethyl acetate (EA) as eluent unless otherwise noted. NMR spectra were recorded with a Bruker Avance 400 MHz instrument. Chemical shifts are reported in ppm after being referenced to residual signal of $CHCl_3$ for ^{1}H (7.26 ppm) and $CDCl_3$ for ^{13}C (77.16 ppm). Descriptions of multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. Determinations of high resolution mass spectra (HRMS) of unknown compounds by electrospray ionization (ESI) were performed with a Micro Mass QTOF Ultima spectrometer at the EPFL Mass Spectrometry Center. Fluorescence quenching were examined with a Varian Cary Eclipse fluorescence spectrophotometer. Cyclic voltammograms (CV) were recorded on a BIO-LOGIC VSP.

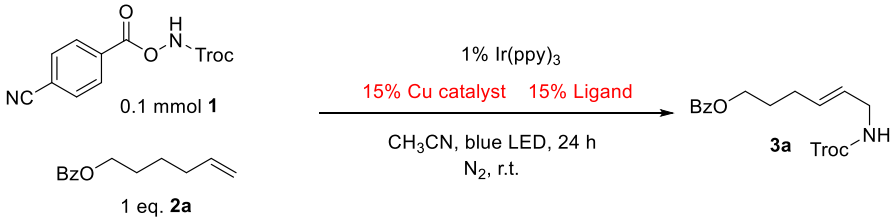
2. Detailed optimizations of reaction

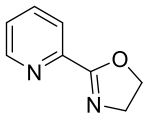




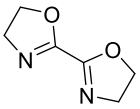
Scheme S1. Screening of amidyl radical sources. Conditions: All reagents of indicated amount dissolved in 1 mL CH_3CN in a glass vial (d=2 cm), blue LED radiation for 24 h.

Table S1. Screening of Cu catalysts.





L1

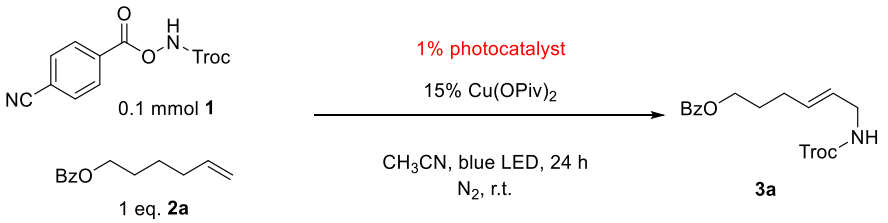


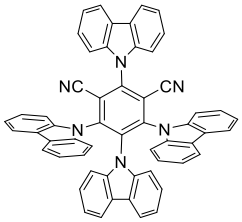
L2

Entry	Cu catalyst	ligand	Yield/ %
1	-	-	7
2	Cu(2-Ethyl hexanoate)$_2$	-	38
3	Cu(OTf)$_2$	-	0
4	Cu(OPiv)$_2$	-	42
5	Cu(OAc)	-	21
6	Cu(2-Ethyl hexanoate)$_2$	bipyridine	0
7	Cu(2-Ethyl hexanoate)$_2$	1,10-phenanthroline	0
8	Cu(2-Ethyl hexanoate)$_2$	L1	10
9	Cu(2-Ethyl hexanoate)$_2$	L2	39

Conditions: All reagents of indicated amount dissolved in 1 mL CH_3CN in a glass vial (d=2 cm), blue LED radiation for 24 h.

Table S2. Screening of photocatalysts.

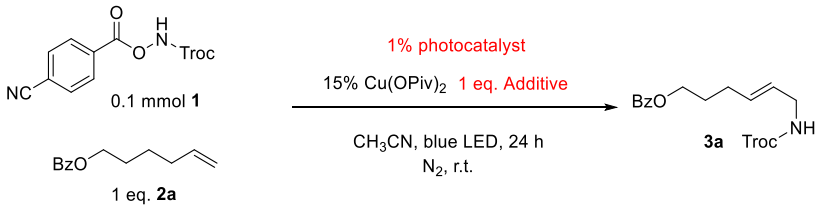


CzIPN= 

Entry	Photocatalyst	Yield/ %
1	$Ir(ppy)_2(dbbpy)\ BF_4$	trace
2	CzIPN	trace
3	$Ru(bpy)_3\ (BF_4)_2$	0
4	$Ir(dfppy)\ (ppy)_2$	40
5	$Ir(dfppy)_2(ppy)$	39
6	$Ir(ppy)_3$	42
7	$Ir(dfppy)_3$	41

Conditions: All reagents of indicated amount dissolved in 1 mL CH_3CN in a glass vial (d=2 cm), blue LED radiation for 24 h.

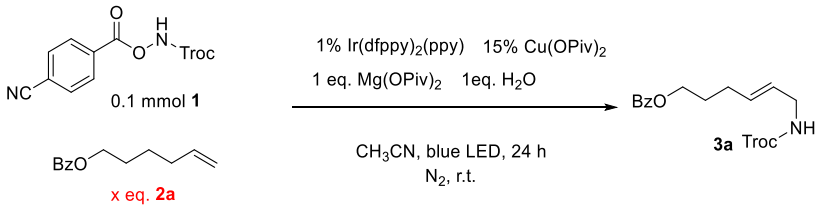
Table S3. Screening of additives.



Entry	photocatalyst	additive	Yield/ %
1	$Ir(ppy)_3$	NEt_3	0
2	$Ir(ppy)_3$	pyridine	27
3	$Ir(ppy)_3$	2,6-dimethylpyridine	35
4	$Ir(ppy)_3$	NaOPiv	24
5	$Ir(ppy)_3$	$Zn(OPiv)_2$	21
6	$Ir(ppy)_3$	$Mg(OPiv)_2$	38
7	$Ir(ppy)_3$	LiOPiv	34
8	$Ir(ppy)_3$	$Al(OPiv)_3$	30
9	$Ir(ppy)_3$	$Mg(OPiv)_2$, H_2O	44
10	$Ir(dfppy)_2(ppy)$	$Mg(OPiv)_2$, H_2O	49

Conditions: All reagents of indicated amount dissolved in 1 mL CH_3CN in a glass vial (d=2 cm), blue LED radiation for 24 h.

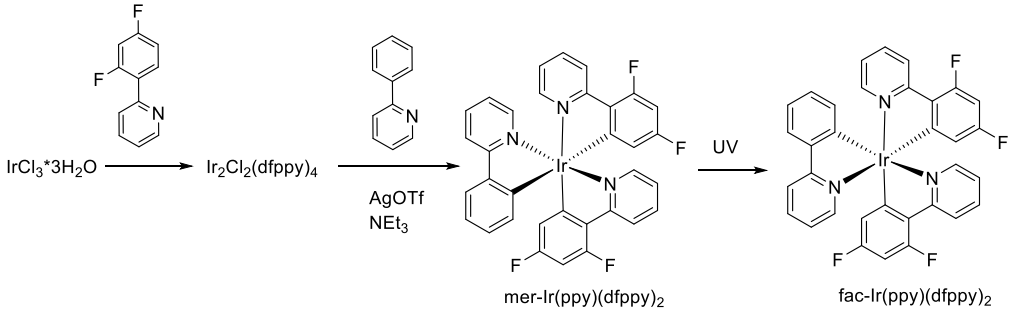
Table S4. Optimization of the amount of alkene and addition procedure.



Entry	Amount of alkene	Variations	Yield/ %
1	1 equiv.	-	49
2	2 equiv.	-	59
3	3 equiv.	-	64
4[a]	2 equiv.	Slow addition of **1**	67
5[a]	3 equiv.	Slow addition of **1**	76
6[a]	3 equiv.	10% $Cu(OPiv)_2$, Slow addition of **1**	77

Conditions: All reagents of indicated amount dissolved in 1 mL CH_3CN in a glass vial (d=2 cm), blue LED radiation for 24 h. [a] Slow addition procedure: 0.02 mmol **1** and all other reagents were dissolved in 0.2 mL CH_3CN; the rest of **1** (0.08 mmol) was dissolved in 0.4 mL CH_3CN; the latter was added at 1.2 uL/min to the former after reaction starts.

3. Synthesis of catalysts, additives and substrates.



fac-Ir(ppy)(dfppy)$_2$: 0.5 mmol $IrCl_3$*3H_2O and 1.75 mmol 2-(2,4-difluorophenyl)pyridine were added to a 50 mL flask containing 15 mL 2-ethoxylethanol and 5 mL H_2O. The mixture was heated to 135 °C under nitrogen for 24 h, and then the reaction was quenched by addition of 20 mL H_2O. Filtration and subsequent wash with EtOH and Et_2O gave chloride-bridged iridium dimer $IrCl_2(dfppy)_4$ as a bright yellow powder in 66% yield.

0.04 mmol $IrCl_2(dfppy)_4$, 0.2 mmol AgOTf, 0.16 mmol 2-phenylpyridine, 0.16 mmol NEt_3 were added to 6 mL DCE.[1] The mixture was refluxed under nitrogen for 6 h. mer-Ir(dfppy)$_2$(ppy) was obtained by chromatography on silica gel with DCM-hexane as eluent, as a yellow powder in 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, J = 15.0, 8.6 Hz, 2H), 8.09 (d, J = 5.9 Hz, 1H), 7.94 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 5.6 Hz, 1H), 7.78 – 7.74 (m, 1H), 7.65 (td, J = 7.6, 1.8 Hz, 1H), 7.61 – 7.51 (m, 2H), 7.50 (t, J = 7.9 Hz, 1H), 7.07 – 6.96 (m, 2H), 6.99 – 6.87 (m, 2H), 6.79 – 6.69 (m, 2H), 6.50 – 6.35 (m, 2H), 6.08 – 6.00 (m, 1H), 5.84 (dd, J = 9.2, 2.4 Hz, 1H).

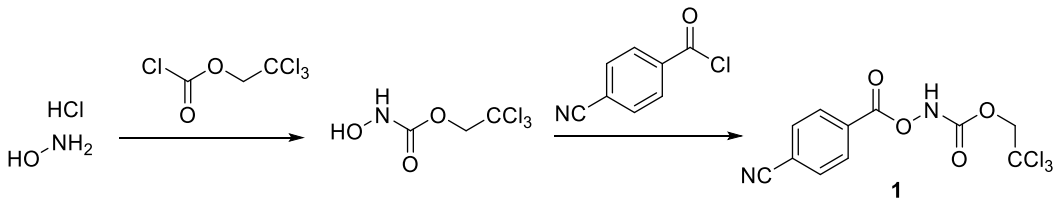
0.04 mmol mer-Ir(dfppy)$_2$(ppy) was dissolved in 3 mL DMSO and radiated by UV (254 nm) overnight under nitrogen.[2] A precipitate was formed. The solution was diluted by DCM until the precipitate was dissolved. The solution mixture was washed with water to remove DMSO. Evaporation of the organic phase afforded a yellow solid, which was then washed twice by DCM-hexane (1:10). fac-Ir(dfppy)$_2$(ppy) was obtained in 88% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.32 – 8.18 (m, 3H), 7.99 – 7.79 (m, 4H), 7.63 – 7.53 (m, 2H), 7.47 – 7.41 (m, 1H), 7.32 – 7.16 (m, 3H), 6.89 (td, J = 7.5, 1.5 Hz, 1H), 6.80 (td, J = 7.3, 1.4 Hz, 1H), 6.71 – 6.60 (m, 2H), 6.55 (dd, J = 7.5, 1.4 Hz, 1H), 6.15 – 6.05 (m, 2H).

Cu(OPiv)$_2$

3 mmol $Cu_2(OH)_2CO_3$ and 12 mmol pivalic acid were suspended in 5 mL CH_3CN-H_2O (4:1). The mixture was stirred overnight at room temperature. Then, filtration, evaporation and subsequent drying under vacuum gave Cu(OPiv)$_2$ as blue particles, which are soluble in organic solvents

Mg(OPiv)$_2$

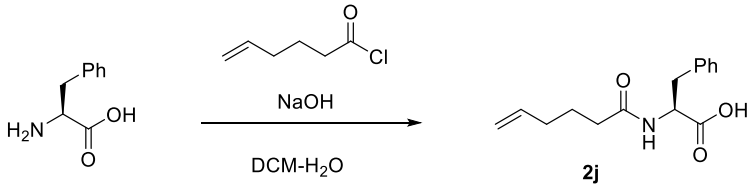
5 mmol $Mg(OH)_2$ and 10 mmol pivalic acid were added to 8 mL CH_3CN-H_2O (1:1). Stirring overnight led to the disappearance of the solid. Evaporation and then drying at 60 °C under vacuum for 12 h gave a fine white powder as product.



1

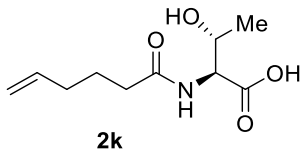
The synthesis of **1** and the analogous amidyl radical sources followed the procedure reported in literature, with minor modifications.[3] NEt_3 (2.8 mL, 20 mmol) and hydroxylamine hydrochloride (0.77g, 11 mmol) were added into 10 mL DCM, and the reaction mixture was stirred at room temperature for 5 min. Then, the suspension was cooled to 0 °C, and Troc-Cl (10 mmol, in 20 mL DCM) was added over 30 min by a syringe pump. The mixture was stirred at room temperature for 30 min and 1.4 mL NEt_3 (10 mmol) was added. Next, the suspension was cooled again to 0 °C , followed by the addition of 4-cyanobenzoyl chloride (7 mmol, in 10 mL of DCM) over 30 min. The mixture was then warmed to room temperature and left for 30 min. The product was separated by chromatography on silica gel to afford **1** as a white solid in 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 – 8.59 (s, 1H), 8.25 – 8.17 (m, 2H), 7.85 – 7.77 (m, 2H), 4.84 (s, 2H).

The series of amidyl radical sources **1a-1h** were synthesized following the same procedure.



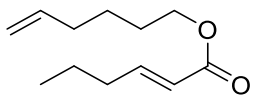
2j

6 mmol phenylalanine and 12 mmol NaOH were dissolved in 5 mL water, then the solution was cooled to 0 °C. 3 mmol acid chloride dissolved in 5 mL DCM was added, and the reaction was vigorously stirred for 1 h at 0 °C and was then allowed to warm to room temperature and was left overnight. The solution was acidified with hydrochloric acid and extracted with ethyl acetate. The organic phase was separated by chromatography on silica gel, yielding a yellowish solid as product, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.13 (m, 5H), 6.25 – 6.13 (m, 1H), 5.80 – 5.61 (m, 1H), 5.02 – 4.87 (m, 3H), 3.24 (dd, J = 14.0, 5.6 Hz, 1H), 3.12 (dd, J = 14.0, 6.1 Hz, 1H), 2.19 (t, J = 7.6 Hz, 2H), 2.02 (q, J = 7.2 Hz, 2H), 1.67 (p, J = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 173.9, 137.7, 135.9, 129.5, 128.7, 127.3, 115.6, 53.2, 37.4, 35.6, 33.0, 24.7.



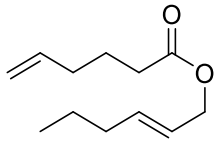
2k

Synthesied via the same procedure as **2j**, sticky gel, 47 % yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (b, 1H), 6.96 – 6.78 (m, 1H), 5.77 (ddt, J = 16.9, 10.1, 6.7 Hz, 1H), 5.16 – 4.87 (m, 2H), 4.54 (dd, J = 8.4, 2.5 Hz, 1H), 4.47 – 4.29 (m, 1H), 2.32 (t, J = 7.6 Hz, 2H), 2.09 (q, J = 6.5, 2H), 1.74 (p, J = 7.4 Hz, 2H), 1.21 (d, J = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.3, 173.6, 137.7, 115.7, 67.6, 57.6, 35.6, 33.2, 24.9, 19.5.



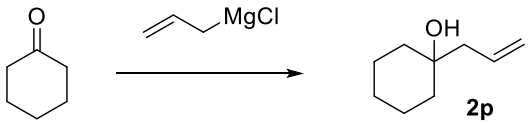
2l

3.5 mmol 5-hexen-1-ol and 1 mL pyridine were added to 5 mL DCM. 3 mmol hex-2-enoyl chloride in 3 mL DCM was added slowly to the above solution under stirring at room temperature. The reaction was maintained overnight. Separation by chromatography on silica gel gave a colorless liquid **2l** as product in 82% yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (dt, *J* = 15.5, 7.0 Hz, 1H), 5.86 – 5.72 (m, 2H), 5.06 – 4.91 (m, 2H), 4.12 (t, *J* = 6.6 Hz, 2H), 2.22 – 2.03 (m, 4H), 1.72 – 1.61 (m, 2H), 1.48 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 149.4, 138.5, 121.5, 114.9, 64.2, 34.3, 33.4, 28.3, 25.4, 21.4, 13.8.



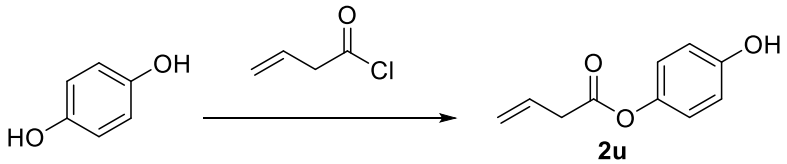
2m

Following the same procedure of **2l**. **2m** was obtained in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 – 5.70 (m, 2H), 5.62 – 5.49 (m, 1H), 5.07 – 4.93 (m, 2H), 4.51 (dd, *J* = 6.4, 1.2 Hz, 2H), 2.32 (t, *J* = 7.5 Hz, 2H), 2.14 – 2.00 (m, 4H), 1.73 (p, *J* = 7.5 Hz, 2H), 1.41 (q, *J* = 7.4 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).



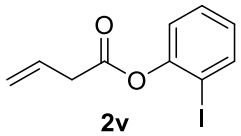
2p

3 mmol cyclohexanone was dissolved in 3 mL THF in a Schlenk tube. 3 mL allyl magnesium chloride (1 M in THF) was added dropwise at 0 °C. The reaction mixture was maintained at 0 °C for 1 h, and was then naturally warmed to room temperature during 2 h. Subsequent quenching with a ammonium chloride solution, extraction and separation afforded **2p** in 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 (ddt, *J* = 17.6, 10.2, 7.5 Hz, 1H), 5.16 – 4.97 (m, 2H), 2.15 (d, *J* = 7.5 Hz, 2H), 1.55 – 1.32 (m, 10H), 1.25 – 1.13 (m, 1H).



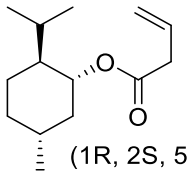
2u

9 mmol 1,4-Dihydroxylbenzene and 1 mL pyridine were added to 10 mL DCM. 3 mmol acid chloride in 3 mL DCM was added slowly to the above solution under stirring at room temperature. The reaction was maintained overnight. Separation by chromatography on silica gel gave a yellowish oil **2s** as product in 70% yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 – 6.89 (m, 2H), 6.77 (m, 2H), 6.09 – 5.95 (m, 1H), 5.32 – 5.20 (m, 2H), 5.06 (b, 1H), 3.33 (dt, *J* = 6.9, 1.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 153.5, 144.2, 129.8, 122.5, 119.4, 116.2, 39.2.



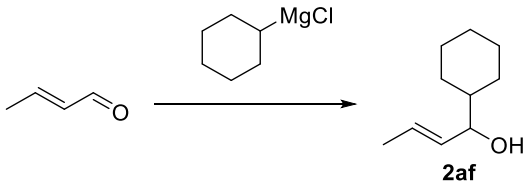
2v

4.5 mmol 2-iodophenol and 1 mL pyridine were added to 5 mL DCM. 3 mmol acid chloride in 3 mL DCM was added slowly to the above solution under stirring at room temperature. The reaction was maintained overnight. Separation by chromatography on silica gel gave a colorless oil **2v** as product in 78% yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.36 (ddd, *J* = 8.0, 7.4, 1.5 Hz, 1H), 7.11 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.98 (td, *J* = 7.7, 1.5 Hz, 1H), 6.09 (ddt, *J* = 17.1, 10.1, 6.9 Hz, 1H), 5.37 – 5.25 (m, 2H), 3.42 (dt, *J* = 6.9, 1.4 Hz, 2H).



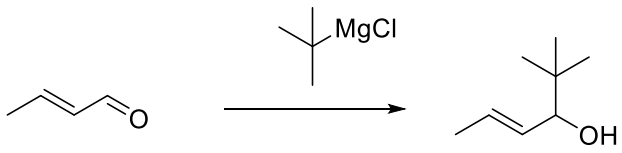
(1R, 2S, 5R) **2y**

Following the same procedure of **2l**. **2y** was obtained in 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (ddt, *J* = 16.5, 10.9, 6.9 Hz, 1H), 5.25 – 5.06 (m, 2H), 4.69 (td, *J* = 10.9, 4.4 Hz, 1H), 3.07 (dt, *J* = 6.9, 1.5 Hz, 2H), 2.03 – 1.95 (m, 1H), 1.93 – 1.78 (m, 1H), 1.72 – 1.63 (m, 2H), 1.55 – 1.43 (m, 1H), 1.44 – 1.31 (m, 1H), 1.12 – 1.02 (m, 1H), 0.99 – 0.86 (m, 8H), 0.75 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 130.7, 118.4, 74.6, 47.1, 41.0, 39.7, 34.4, 31.5, 26.4, 23.6, 22.2, 20.9, 16.5.



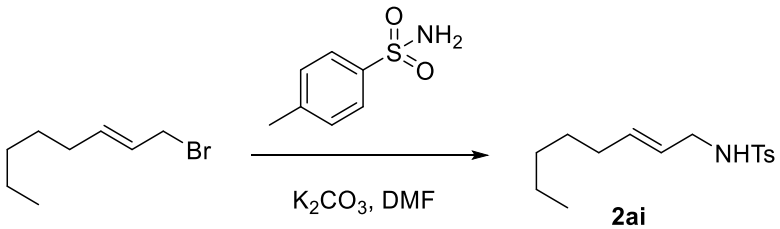
2af

Following the same procedure of **2p**. **2af** was obtained in 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.69 – 5.58 (m, 1H), 5.48 (ddq, *J* = 15.2, 7.5, 1.5 Hz, 1H), 3.76 (t, *J* = 7.0 Hz, 1H), 1.94 – 1.81 (m, 1H), 1.80 – 1.60 (m, 6H), 1.45 – 1.04 (m, 5H), 1.04 – 0.81 (m, 2H).



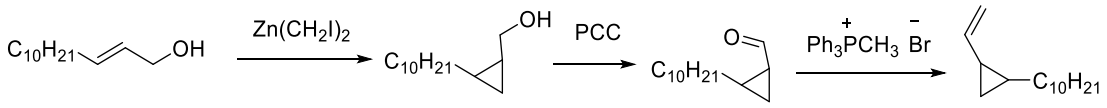
2ag

Following the same procedure of **2p**. **2ag** was obtained in 21% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 – 5.59 (m, 1H), 5.53 (ddq, *J* = 15.2, 7.6, 1.4 Hz, 1H), 3.68 (d, *J* = 7.5 Hz, 1H), 1.71 (d, *J* = 6.7 Hz, 3H), 0.89 (s, 9H).



2ai

3 mmol 1-bromo-2-octene, 6 mmol *p*-toluenesulfonamide and 6 mmol K_2CO_3 were added to 6 mL acetone. The reaction mixture was heated at 60 °C overnight. Separation by chromatography on silica gel gave a white solid **2af** as product in 62% yield.[1]H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 2H), 7.34 – 7.27 (m, 2H), 5.54 (dtt, *J* = 14.9, 6.7, 1.4 Hz, 1H), 5.30 (dtt, *J* = 15.4, 6.4, 1.5 Hz, 1H), 4.37 (s, 1H), 3.52 (td, *J* = 6.2, 1.4 Hz, 2H), 2.43 (s, 3H), 1.97 – 1.87 (m, 2H), 1.34 – 1.13 (m, 6H), 0.86 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 137.3, 135.4, 129.8, 127.3, 124.4, 45.5, 32.2, 31.4, 28.7, 22.6, 21.7, 14.1.



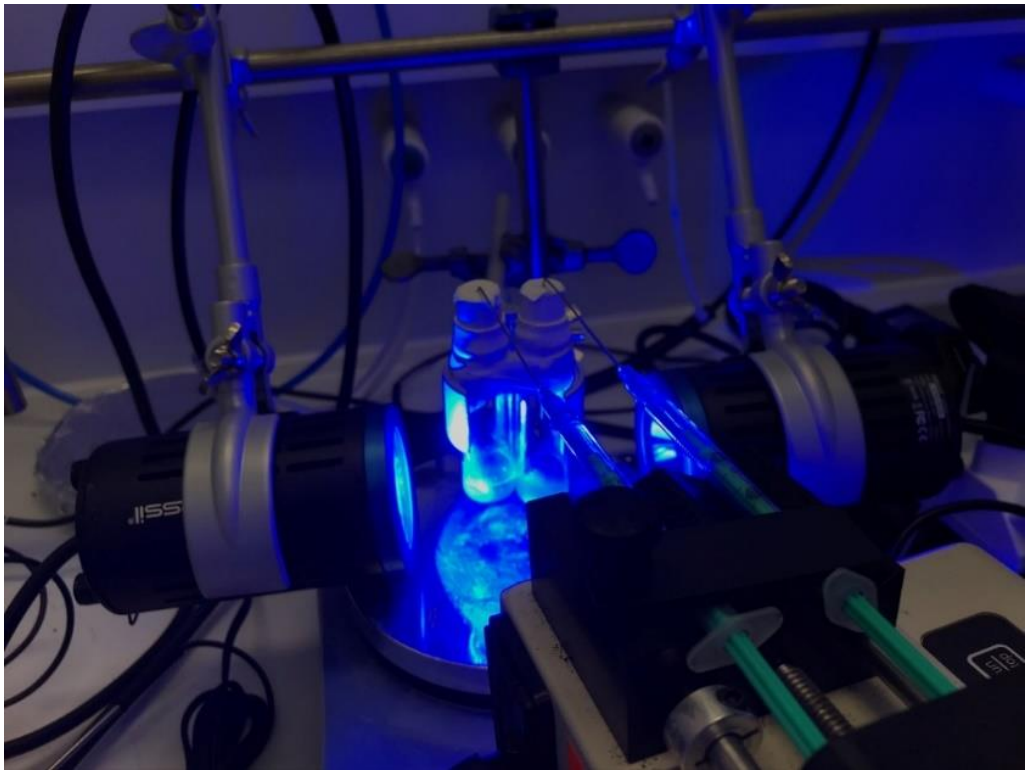
2al

A solution of $ZnEt_2$ (6 mL, 1 M in hexane) was added to 10 mL DCM at -10 °C under nitrogen. Then, 12 mmol CH_2I_2 (0.97 mL) was slowly added.[4] After stirring for 15 min, a suspension was formed. A solution of 2-tridecen-1ol (5 mmol) in dry DCM (5 mL) was added dropwise, followed by addition of $Ti(OiPr_4)$ (0.3 mmol, 75 uL). The mixture was stirred overnight while the temperature raised to room temperature. The reaction was quenched with a saturated aqueous NH_4Cl solution (6 mL). Separation by chromatography on silica gel gave (2-decylcyclopropyl)methanol in 72% yield. Subsequent oxidation by pyridinium chlorochromate (PCC) and Wittig reaction were conducted following reported procedures.[5,6] The overall yield for the final product was 56% ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (ddd, *J* = 17.0, 10.3, 8.7 Hz, 1H), 5.01 (dd, *J* = 17.1, 2.0 Hz, 1H), 4.80 (dd, *J* = 10.3, 2.0 Hz, 1H), 1.44 – 1.20 (m, 18H), 1.19 – 1.04 (m, 1H), 0.88 (t, *J* = 6.9 Hz, 3H), 0.78 – 0.68 (m, 1H), 0.61 – 0.50 (m, 1H), 0.53 – 0.44 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 111.0, 34.0, 32.1, 29.8, 29.8, 29.6, 29.5, 22.8, 22.7, 21.3, 14.3, 14.1.

4. Synthesis and characterizations of products.

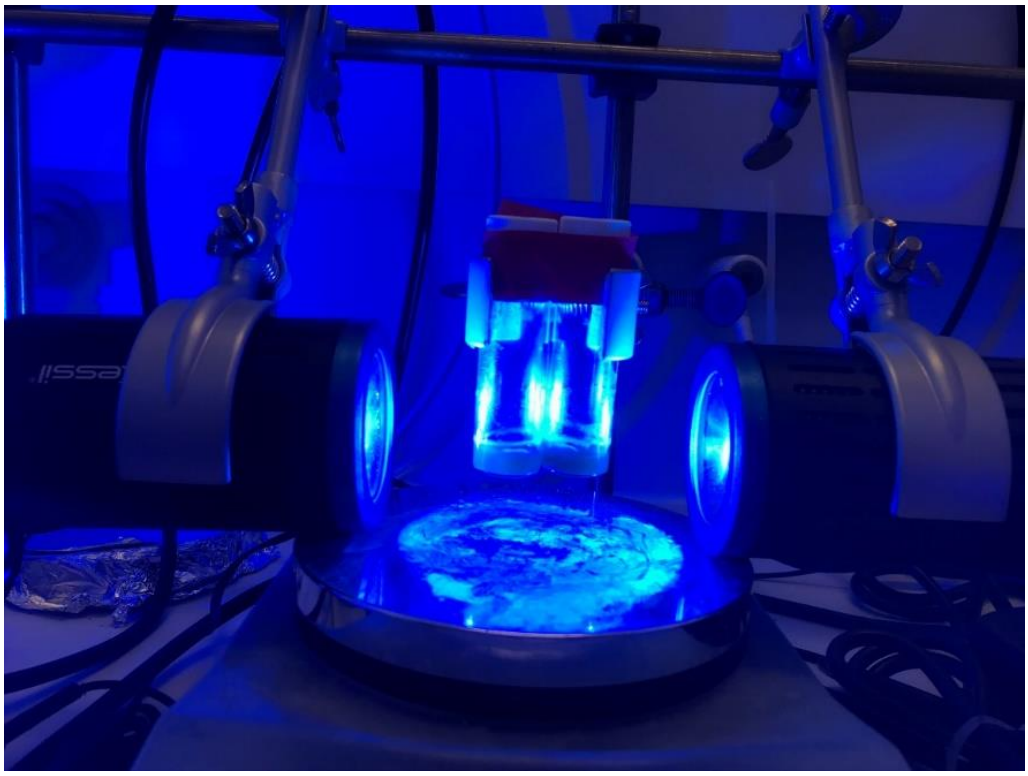
General procedure 1 (GP1):

0.01 mmol $Cu(OPiv)_2$ and 0.001 mmol Ir $(dfppy)_2(ppy)$ were added to a glass vial (d=2 cm), which was then transferred to the glovebox. 0.1 mmol $Mg(OPiv)_2$, 0.3 mmol alkene **2**(3 equiv.), 0.1 mL acetonitrile solution of water (1 M H_2O) and 0.1 mL acetonitrile solution of **1** (0.2 M, 20% of the total amount) were added to the vial. The vial was sealed with a rubber septum and placed under blue LED radiation. The rest solution of **1** (0.4 mL, 0.2 M) was added to the vial at a rate of 1.2 μL/min by a syringe pump. The setup is illustrated in the picture below. After 24 h, the reaction was stopped. To the reaction solution were added 4 mL ethyl acetate, 1mL water and 2 drops of 15% ammonia solution, and then the organic phase was collected after sufficient mixing. The organic phase was concentrated. The residue was subsequently analyzed by NMR to obtain the NMR yield and was separated on silica gel column to give the final product.



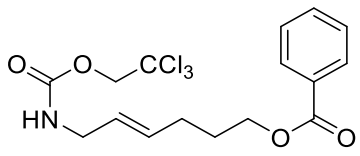
General procedure 2 (GP2):

0.01 mmol $Cu(OPiv)_2$, 0.001 mmol Ir $(dfppy)_2(ppy)$ and 0.1 mmol **1** were added to a glass vial (d=2 cm), which was then transferred to the glovebox. 0.1 mmol $Mg(OPiv)_2$, 0.3 mmol alkene **2** (3 equiv.), 0.1 mL acetonitrile solution of water (1 M H_2O) and 0.9 mL acetonitrile were added to the vial. The vial was sealed with a plastic cap and placed under blue LED radiation for 24 h. The setup is illustrated in the picture below. When the reaction completed, to the reaction solution were added 4 mL ethyl acetate, 1mL water and 2 drops of 15% ammonia solution, and then the organic phase was collected after sufficient mixing. The organic phase was concentrated. The residue subsequently was analyzed by NMR to obtain the NMR yield and was separated on silica gel column to give the final product.



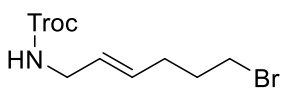
General procedure 3 (GP3):

0.01 mmol $Cu(OPiv)_2$, 0.001 mmol Ir $(dfppy)_2(ppy)$ and 0.1 mmol **1** were added to a glass vial (d=2 cm), which was then transferred to the glovebox. 0.3 mmol alkene **1** (3 equiv.), 1 mL acetonitrile were added to the vial. The vial was sealed with a plastic cap and placed under blue LED radiation for 24 h (the setup is the same as in GP2). When the reaction completed, 0.6 mmol MeI and 1 mmol K_2CO_3 were added to the reaction, and the vial was heated for 12 h at 60 °C. To the reaction solution were added 4 mL ethyl acetate, 1 mL water and 2 drops of 15% ammonia solution, and then the organic phase was collected after sufficient mixing. The organic phase was concentrated. The residue was subsequently analyzed by NMR to obtain the NMR yield and was separated on silica gel column to give the final product.



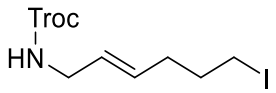
3a

(E)-6-((Troc-amino)hex-4-en-1-yl benzoate, synthesized via GP1, colorless oil, 27.4 mg (Yield = 70%), trans: cis = 9:1. For trans-isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.8 Hz, 2H), 7.55 (t, J = 6.9 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 5.77 – 5.62 (m, 1H), 5.59 – 5.44 (m, 1H), 5.13 (b, 1H), 4.72 (s, 2H), 4.32 (td, J = 6.5, 2.5 Hz, 2H), 3.79 (t, J = 6.7 Hz, 2H), 2.29 – 2.09 (m, 2H), 1.93 – 1.79 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 154.5 133.0, 132.4, 130.4, 129.6, 128.5, 126.5, 95.7, 74.6, 64.3, 43.2, 28.7, 28.1. HRMS (ESI/QTOF) m/z: $[M + Na]^+$Calcd for $C_{16}H_{18}Cl_3NNaO_4^+$ 416.0194; Found 416.0193.



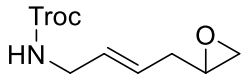
3b

2,2,2-Trichloroethyl (E)-(6-bromohex-2-en-1-yl)carbamate, synthesized via GP1, colorless oil, 23.0 mg (Yield = 65%), trans: cis = 9:1. For trans-isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68 – 5.49 (m, 2H), 5.01 (b, 1H), 4.73 (s, 2H), 3.81 (t, J = 5.7 Hz, 2H), 3.39 (t, J = 6.6 Hz, 3H), 2.20 (q, J = 6.9 Hz, 2H), 1.98 – 1.88 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 131.7, 127.1, 95.7, 74.7, 43.2, 33.1, 32.0, 30.6. HRMS (ESI/QTOF) m/z: [M + Na]$^+$Calcd for $C_9H_{13}BrCl_3NNaO_2^+$ 373.9087; Found 373.9081.



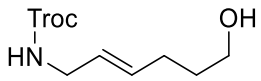
3c

2,2,2-Trichloroethyl (E)- (6-iodohex-2-en-1-yl)carbamate, synthesized via GP1, colorless oil, 24.0 mg (Yield = 60%), trans: cis = 10:1. For trans-isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67 – 5.48 (m, 2H), 5.01 (b, 1H), 4.73 (s, 2H), 3.80 (t, J = 5.5 Hz, 2H), 3.17 (t, J = 6.8 Hz, 3H), 2.15 (q, J = 6.6 Hz, 2H), 1.89 (p, J = 6.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 131.5, 127.1, 95.7, 74.7, 43.2, 32.8, 32.6, 6.3. HRMS (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_9H_{13}Cl_3INNaO_2^+$ 421.8949; Found 421.8958.



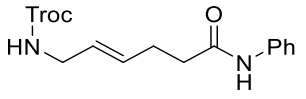
3d

2,2,2-Trichloroethyl (E)-(4-(oxiran-2-yl)but-2-en-1-yl)carbamate, synthesized via GP1, colorless oil, 18.5 mg (Yield = 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 – 5.58 (m, 2H), 5.07 (b, 1H), 4.73 (s, 2H), 3.83 (t, J = 5.5 Hz, 2H), 3.02 – 2.92 (m, 1H), 2.81 – 2.71 (t, J = 4.4 Hz, 1H), 2.50 (dd, J = 4.9, 2.7 Hz, 1H), 2.42 – 2.22 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 128.7, 127.8, 95.7, 74.7, 51.3, 46.7, 43.1, 35.1. HRMS (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_9H_{12}Cl_3NNaO_3^+$ 309.9775; Found 309.9781.



3e

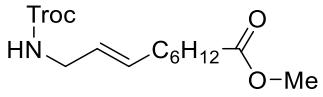
2,2,2-Trichloroethyl (E)-(6-hydroxyhex-2-en-1-yl)carbamate, synthesized via GP2, colorless oil, 17.7 mg (Yield = 61%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67 (dtt, *J* = 14.7, 6.6, 1.4 Hz, 1H), 5.50 (dtt, *J* = 15.3, 6.1, 1.5 Hz, 1H), 5.08 (b, 1H), 4.72 (s, 2H), 3.79 (td, *J* = 5.9, 1.1 Hz, 2H), 3.64 (t, *J* = 6.5 Hz, 2H), 2.13 (q, *J* = 6.7 Hz, 2H), 1.68 – 1.61 (m, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 133.3, 126.1, 95.7, 74.7, 62.4, 43.3, 32.1, 28.6. HRMS (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_9H_{14}Cl_3NNaO_3^+$ 311.9931; Found 311.9935.



3f

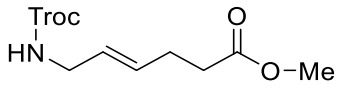
2,2,2-Trichloroethyl (E)-(6-oxo-6-(phenylamino)hex-2-en-1-yl)carbamate, synthesized via GP1, white solid, 20.4 mg (Yield = 54%). trans: cis = 12:1. For trans-isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.9 Hz, 2H), 7.31 (m, 3H), 7.10 (t, J = 7.4 Hz, 1H), 5.71 (dt, J = 15.8, 6.0 Hz, 1H), 5.56 (dt, J = 15.8, 6.0 Hz, 1H), 5.08 (b, 1H), 4.69 (s, 2H), 3.79 (t, J = 6.0 Hz, 2H), 2.56 – 2.35 (m,

4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 154.6, 137.9, 131.7, 129.2, 127.1, 124.5, 120.0, 95.7, 74.6, 43.1, 37.2, 28.0. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{17}Cl_3N_2NaO_3^+$ 401.0197; Found 401.0202.



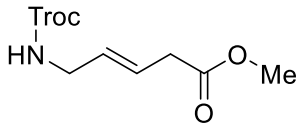
3g-Me

(E)-Methyl 10-(Troc-amino)dec-8-enoate, synthesized via GP3, isolated as methylated product, colorless oil, 19.4 mg (Yield = 52%), trans: cis = 7:1. For trans-isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63 (dt, J = 14.1, 6.8 Hz, 1H), 5.45 (dt, J = 14.1, 6.2 Hz, 1H), 5.04 (b, 1H), 4.72 (s, 2H), 3.78 (t, J = 6.1 Hz, 2H), 3.66 (s, 3H), 2.29 (t, J = 7.5 Hz, 2H), 2.01 (m, 2H), 1.60 (m, 2H), 1.43 – 1.18 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 154.5, 134.1, 125.4, 95.8, 74.6, 51.6, 43.3, 34.2, 32.2, 29.0, 28.9, 28.8, 25.0. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{22}Cl_3NNaO_4^+$ 396.0507; Found 396.0501.



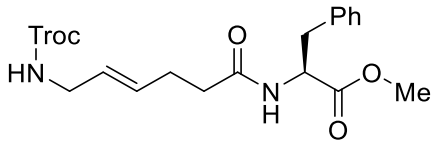
3h-Me

(E)-Methyl 6-(Troc-amino)hex-4-enoate, synthesized via GP3, isolated as methylated product, colorless oil, 15.8 mg (Yield = 50%), trans: cis = 9:1. For trans-isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.70 – 5.59 (m, 1H), 5.57 – 5.45 (m, 1H), 5.02 (b, 1H), 4.72 (s, 2H), 3.79 (t, J = 5.6 Hz, 2H), 3.67 (s, 3H), 2.44 – 2.29 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 154.5, 131.6, 126.8, 95.7, 74.7, 51.8, 43.1, 33.6, 27.5. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{14}Cl_3NNaO_4^+$ 339.9881; Found 339.9877.



3i-Me

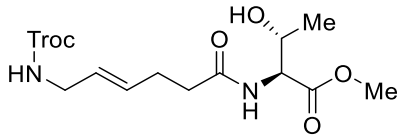
(E)-Methyl 5-(Troc-amino)pent-3-enoate, synthesized via GP3, isolated as methylated product, colorless oil, 16.1 mg (Yield = 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (dt, J = 15.2, 6.8 Hz, 1H), 5.62 (dt, J = 15.4, 5.9, 1H), 5.10 (b, 1H), 4.72 (s, 2H), 3.85 (t, J = 5.4 Hz, 2H), 3.68 (s, 3H), 3.09 (d, J = 6.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 154.5, 129.8, 124.9, 95.7, 74.7, 52.1, 42.9, 37.4. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_9H_{12}Cl_3NNaO_4^+$ 325.9724; Found 325.9731.



3j-Me

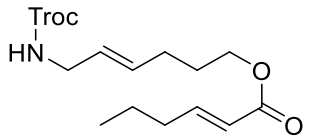
Methyl (S,E)-3-phenyl-2-(6-(Troc-amino)hex-4-enamido)propanoate, synthesized via GP3, isolated as methylated product, sticky gel, 20.9 mg (Yield = 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.23 (m, 3H), 7.12 – 7.04 (m, 2H), 5.95 (d, J = 7.9 Hz, 1H), 5.64 – 5.54 (m, 1H), 5.44 (dt, J = 15.2, 6.1 Hz, 1H), 5.23 (b, 1H), 4.95 – 4.83 (m, 1H), 4.80 – 4.66 (m, 2H), 3.75 (m, 5H), 3.16 (dd, J = 13.9, 5.8 Hz, 1H), 3.08 (dd, J = 13.9, 5.8 Hz, 1H), 2.42 – 2.21 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 171.8, 154.5, 135.9, 131.8, 129.4, 128.7, 128.7, 127.3, 95.8, 74.7, 53.1, 52.6, 43.2, 37.9, 35.7, 28.0. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{23}Cl_3N_2NaO_5^+$ 487.0565; Found

487.0578.



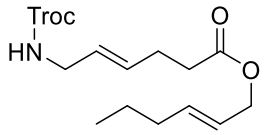
3k-Me

Methyl ((E)-6-(Troc-amino)hex-4-enoyl)-L-threoninate, synthesized via GP3, isolated as methylated product, sticky gel, 13.5 mg (Yield = 32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.35 (d, *J* = 9.0 Hz, 1H), 5.75 – 5.63 (m, 1H), 5.57 (dt, *J* = 15.4, 5.8 Hz, 1H), 5.46 (s, 1H), 4.71 (s, 2H), 4.59 (dd, *J* = 8.8, 2.5 Hz, 1H), 4.35 (qd, *J* = 6.4, 2.5 Hz, 1H), 3.86 – 3.75 (m, 5H), 2.49 – 2.35 (m, 4H), 2.19 (m, 1H), 1.23 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 171.8, 154.6, 131.7, 127.4, 95.8, 74.7, 68.2, 57.3, 52.8, 43.2, 36.0, 28.2, 20.3. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{21}Cl_3N_2NaO_6^+$ 441.0357; Found 441.0352.



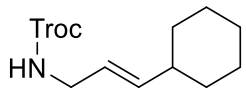
3l

(E)-(E)-6-(Troc-amino)hex-4-en-1-yl hex-2-enoate, synthesized via GP2, colorless oil, 19.7 mg (Yield = 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (dt, J = 15.5, 6.9 Hz, 1H), 5.81 (dt, J = 15.6, 1.7 Hz, 1H), 5.65 (dt, J = 14.8, 6.6 Hz, 1H), 5.50 (dt, J = 15.1, 6.1 Hz, 1H), 5.02 (b, 1H), 4.72 (s, 2H), 4.12 (t, J = 6.5 Hz, 2H), 3.80 (t, J = 6.0 Hz, 2H), 2.25 – 2.07 (m, 4H), 1.74 (p, J = 6.8 Hz, 2H), 1.57 – 1.46 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 154.5, 149.6, 132.6, 126.4, 121.4, 95.7, 74.7, 63.5, 43.2, 34.4, 28.7, 28.2, 21.4, 13.8. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{22}Cl_3NNaO_4^+$ 408.0507; Found 408.0507.



3m

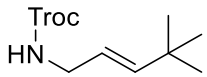
(E)-Hex-2-en-1-yl (E)-6-(Troc-amino)hex-4-enoate, synthesized via GP1, colorless oil, 17.4 mg (Yield = 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 – 5.71 (m, 1H), 5.70 – 5.61 (m, 1H), 5.60 – 5.46 (m, 2H), 5.00 (s, 1H), 4.72 (s, 2H), 4.51 (dq, *J* = 6.4, 1.1 Hz, 2H), 3.79 (t, *J* = 6.0, 2H), 2.42 – 2.29 (m, 4H), 2.03 (qt, *J* = 6.7, 1.4 Hz, 2H), 1.48 – 1.34 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 154.5, 136.7, 131.7, 126.8, 124.0, 95.7, 74.7, 65.5, 43.1, 34.4, 33.8, 27.5, 22.2, 13.8. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{22}Cl_3NNaO_4^+$ 408.0507; Found 408.0505.



3n

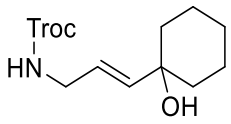
2,2,2-Trichloroethyl (E)- (3-cyclohexylallyl)carbamate, synthesized via GP1, colorless oil, 17.0 mg (Yield = 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.59 (dd, J = 15.5, 6.6 Hz, 1H), 5.41 (dt, J = 15.5, 5.9 Hz, 1H), 4.98 (b, 1H), 4.72 (s, 2H), 3.79 (t, J = 6.0 Hz, 2H), 1.98 – 1.88 (m, 1H), 1.80 – 1.59 (m, 5H), 1.34 – 0.97 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 140.0, 122.8, 95.8, 74.7, 43.5,

40.4, 32.9, 26.2, 26.1. HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{19}Cl_3NO_2^+$ 314.0476; Found 314.0475.



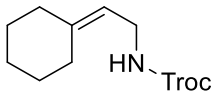
3o

2,2,2-Trichloroethyl (E)- (4,4-dimethylpent-2-en-1-yl)carbamate, synthesized via GP1, white solid, 16.5 mg (Yield = 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 (dt, J = 15.7, 1.4 Hz, 1H), 5.37 (dt, J = 15.6, 6.2 Hz, 1H), 4.96 (b, 1H), 4.73 (s, 2H), 3.80 (td, J = 6.0, 1.4 Hz, 2H), 1.00 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 145.1, 120.2, 95.8, 74.7, 43.6, 33.1, 29.6. HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{10}H_{17}Cl_3NO_2^+$ 288.0319; Found 288.0313.



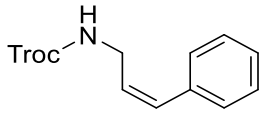
3p

2,2,2-Trichloroethyl (E)-(3-(1-hydroxycyclohexyl)allyl)carbamate, synthesized via GP1, colorless liquid, 22.4 mg (Yield = 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 – 5.64 (m, 2H), 5.10 (s, 1H), 4.73 (s, 2H), 3.85 (t, *J* = 5.6 Hz, 2H), 1.69 – 1.44 (m, 10H), 1.33 – 1.22 (m, 1H). ^{13}C NMR ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 140.6, 123.2, 95.7, 74.7, 71.3, 43.0, 37.9, 25.5, 22.1. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{18}NCl_3NaO_3^+$ 352.0244; Found 352.0249.



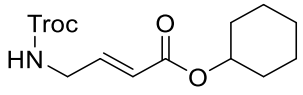
3q

2,2,2-Trichloroethyl (2-cyclohexylideneethyl)carbamate, synthesized via GP2, colorless oil, 6.0 mg (Yield = 20%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.16 (t, J = 7.2 Hz, 1H), 4.87 (b, 1H), 4.72 (s, 2H), 3.83 (t, J = 6.3 Hz, 2H), 2.17 (m,2H), 2.09 (m, 2H), 1.61 – 1.40 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 145.1, 116.5, 95.8, 74.7, 38.4, 37.1, 29.0, 28.5, 27.9, 26.8. HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{17}Cl_3NO_2^+$ 300.0319; Found 300.0319.



3r

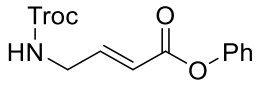
2,2,2-Trichloroethyl (Z)-(3-phenylallyl)carbamate, synthesized via GP2, colorless oil, 8.9 mg (Yield = 29%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, J = 7.4 Hz, 2H), 7.32 – 7.26 (m, 1H), 7.22 (d, J = 7.3 Hz, 2H), 6.61 (d, J = 11.6 Hz, 1H), 5.77 – 5.59 (m, 1H), 5.07 (b, 1H), 4.74 (s, 2H), 4.15 (t, J = 6.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 136.2, 132.2, 128.8, 128.5, 127.7, 127.6, 95.7, 74.7, 39.7. HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{13}Cl_3NO_2^+$ 308.0006; Found 308.0005.



3s

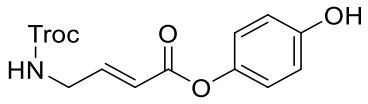
Cyclohexyl 4- (E)-(Troc-amino)but-2-enoate, synthesized via GP1, colorless liquid, 21.9 mg (Yield

= 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (dt, J = 15.8, 4.9 Hz, 1H), 5.90 (d, J = 15.6 Hz, 1H), 5.17 (b, 1H), 4.81 – 4.71 (m, 1H), 4.70 (s, 2H), 3.96 (m, 2H), 1.85 – 1.74 (m, 2H), 1.66 (m, , 2H), 1.51 – 1.11 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 154.6, 142.9, 122.7, 95.5, 74.8, 73.1, 42.0, 31.7, 25.5, 23.9. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{18}Cl_3NNaO_4^+$ 380.0194; Found 380.0195.



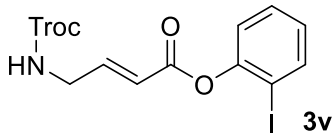
3t

(E)-Phenyl 4-(Troc-amino)but-2-enoate, synthesized via GP1, colorless oil, 18.0 mg (Yield = 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 2H), 7.27 – 7.22 (m, 1H), 7.16 – 7.07 (m, 3H), 6.19 (dt, *J* = 15.8, 2.1 Hz, 1H), 5.28 (s, 1H), 4.78 (s, 2H), 4.15 – 4.06 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 154.6, 150.7, 145.7, 129.6, 126.1, 121.6, 121.3, 95.5, 74.9, 42.1. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{12}Cl_3NNaO_4^+$ 373.9724; Found 373.9728.



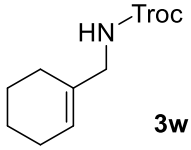
3u

(E)-4-Hydroxyphenyl 4-(Troc-amino)but-2-enoate, synthesized via GP1, sticky gel, 14.0 mg (Yield = 38%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (dt, *J* = 15.7, 4.8 Hz, 1H), 7.00 – 6.89 (m, 2H), 6.82 – 6.73 (m, 2H), 6.16 (dt, *J* = 15.7, 1.9 Hz, 1H), 5.42 (s, 1H), 5.33 (t, *J* = 6.3 Hz, 1H), 4.77 (s, 2H), 4.14 – 4.06 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 154.7, 153.7, 145.7, 144.0, 122.5, 121.3, 116.2, 95.4, 74.9, 42.1. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{12}Cl_3NNaO_5^+$ 389.9673; Found 389.9679.



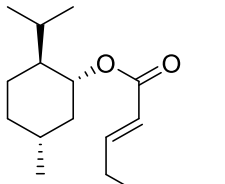
3v

(E)-2-Iodophenyl 4-(Troc-amino)but-2-enoate, synthesized via GP1, colorless oil, 24.4 mg (Yield =51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.37 (ddd, *J* = 8.9, 6.2, 1.5 Hz, 1H), 7.20 (dt, *J* = 15.7, 4.8 Hz, 1H), 7.14 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.98 (td, *J* = 7.6, 1.5 Hz, 1H), 6.23 (dt, *J* = 15.8, 2.0 Hz, 1H), 5.27 (s, 1H), 4.79 (s, 2H), 4.14 (ddd, *J* = 6.6, 4.9, 2.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 154.6, 151.2, 146.5, 139.6, 129.6, 127.8, 123.1, 121.1, 95.6, 90.4, 75.0, 42.2. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{11}Cl_3INNaO_4^+$ 499.8691; Found 499.8693.



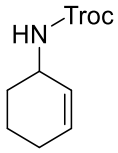
3w

2,2,2-trichloroethyl (cyclohex-1-en-1-ylmethyl)carbamate, synthesized via modified GP2 (acetone as solvent) , white solid, 12.1 mg (Yield =43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.61 (m, 1H), 4.98 (b, 1H), 4.73 (s, 2H), 3.72 (d, *J* = 6.1 Hz, 2H), 2.05 – 1.92 (m, 4H), 1.71 – 1.52 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 134.2, 123.8, 95.8, 74.6, 47.6, 26.4, 25.1, 22.6, 22.4.. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{14}Cl_3NNaO_2^+$ 307.9982; Found 307.9983.



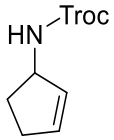
3y

(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl (E)-4-(Troc-amino)but-2-enoate, synthesized via scale-up procedure (section 4), sticky gel, 0.632 g (Yield =61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (dt, *J* = 15.7, 4.9 Hz, 1H), 5.94 (dq, *J* = 15.8, 1.9 Hz, 1H), 5.45 (s, 1H), 4.78 – 4.61 (m, 3H), 4.01 (td, *J* = 6.5, 1.7 Hz, 2H), 2.00 – 1.93 (m, 1H), 1.82 (m, 1H), 1.72 – 1.62 (m, 2H), 1.47 (m, 1H), 1.41 – 1.33 (m, 1H), 1.11 – 0.95 (m, 2H), 0.89 – 0.83 (m, 7H), 0.72 (dd, *J* = 6.9, 1.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 154.6, 143.1, 122.5, 95.5, 74.8, 74.6, 47.2, 42.0, 41.0, 34.3, 31.5, 27.2, 26.4, 23.5, 22.1, 20.8, 16.4. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{26}Cl_3NNaO_4^+$ 436.0820; Found 436.0821.



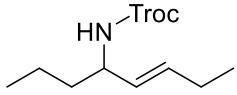
3z

2,2,2-Trichloroethyl cyclohex-2-en-1-ylcarbamate, synthesized via GP1, white solid, 12.0 mg (Yield =44%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94 – 5.80 (m, 1H), 5.69 – 5.57 (m, 1H), 4.97 (b, 1H), 4.72 (s, 2H), 4.29 – 4.15 (m, 1H), 2.10 – 1.88 (m, 3H), 1.81 – 1.54 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 131.5, 127.3, 95.8, 74.6, 46.8, 29.7, 24.9, 19.7. HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_9H_{13}Cl_3NO_2^+$ 272.0006; Found 272.0012.



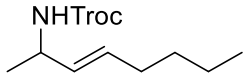
3aa

2,2,2-Trichloroethyl cyclopent-2-en-1-ylcarbamate, synthesized via GP1, white solid, 13.9 mg (Yield =54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 – 5.93 (m, 1H), 5.75 – 5.67 (m, 1H), 4.95 (b, 1H), 4.85 – 4.75 (m, 1H), 4.73 (s, 2H), 2.51 – 2.27 (m, 3H), 1.69 – 1.57 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 135.3, 130.7, 95.8, 74.6, 57.8, 31.5, 31.2. HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_8H_{11}Cl_3NO_2^+$ 257.9850; Found 257.9849.

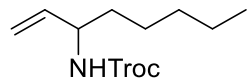


3ab

(E)-2,2,2-Trichloroethyl oct-5-en-4-ylcarbamate, synthesized via GP2, colorless oil, 15.1 mg (Yield =50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.60 (dt, J = 15.3, 6.3 Hz, 1H), 5.26 (dd, J = 15.5, 6.5 Hz, 1H), 4.78 (d, J = 8.6 Hz, 1H), 4.65 (m, 2H), 4.06 (p, J = 7.2 Hz, 1H), 1.97 (p, J = 7.1 Hz, 2H), 1.44 (m, 2H), 1.36 – 1.24 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H), 0.86 (t, J = 7.3 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 133.6, 128.9, 95.9, 74.6, 53.2, 37.8, 25.4, 19.1, 14.0, 13.6. HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{18}Cl_3NNaO_2^+$ 324.0295; Found 324.0299.

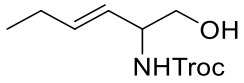


3ac-1



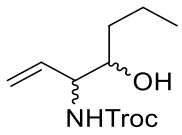
3ac-2

(E)-2,2,2-Trichloroethyl oct-3-en-2-ylcarbamate+ 2,2,2-trichloroethyl oct-1-en-3-ylcarbamate , synthesized via GP2, colorless oil, 16.6 mg (Yield =55%), **3aa-1**:**3aa-2** = 1.4:1.For alkenyl hydrogen of **3aa-1**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68 – 5.58 (m, 1H), 5.41 (dd, J = 15.5, 5.8 Hz, 1H). For alkenyl hydrogen of **3aa-2**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 – 5.71 (m, 1H), 5.20 (d, J = 17.1 Hz, 1H), 5.13 (d, J = 10.4 Hz, 1H). For the details of ^{1}H NMR, Please refer to the attached spectrum. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 153.8, 138.3, 131.6, 130.8, 115.1, 95.8, 74.6, 53.8, 48.8, 35.1, 32.0, 31.6, 31.4, 25.4, 22.7, 22.3, 21.2, 14.1, 14.1. HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{19}Cl_3NO_2^+$ 302.0476; Found 302.0484.



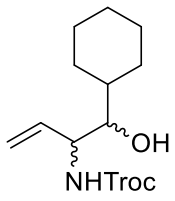
3ad

(E)-2,2,2-Trichloroethyl (1-hydroxyhex-3-en-2-yl)carbamate, synthesized via GP1, white solid, 14.9 mg (Yield =51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 (dt, J = 15.6, 6.3 Hz, 1H), 5.41 (dd, J = 15.5, 6.1 Hz, 1H), 5.32 (b, 1H), 4.73 (s, 2H), 4.29 (m, 1H), 3.70 (m, 2H), 2.08 (p, J = 7.4, 2H), 1.84 (b, 1H), 1.00 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 136.0, 125.0, 95.7, 74.8, 65.3, 54.9, 25.5, 13.5. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_9H_{14}Cl_3NNaO_3^+$ 311.9931; Found 311.9935.



3ae

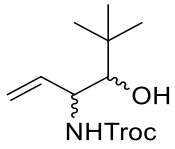
2,2,2-Trichloroethyl (4-hydroxyhept-1-en-3-yl)carbamate, synthesized via GP1, colorless liquid, 16.1 mg (Yield =53%), dr= 2.0:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 – 5.72 (m, 1H), 5.70-5.30(d, *J* =9.0 Hz, 1H), 5.30 – 5.10 (m, 2H), 4.68 (d, *J* = 7.8 Hz, 2H), 4.32 – 4.09 (m, 1H), 3.69 (m, 1H), 1.70 (s, 1H), 1.52 – 1.27 (m, 4H), 0.87 (td, *J* = 6.8, 3.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 154.3, 136.3, 132.8, 118.6, 116.8, 91.7, 74.7, 74.6, 73.4, 72.7, 57.9, 57.2, 36.4, 35.8, 19.1, 19.0, 14.1, 14.1. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{16}Cl_3NNaO_3^+$ 326.0088; Found 326.0086.



3af

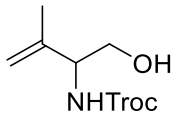
2,2,2-Trichloroethyl (1-cyclohexyl-1-hydroxybut-3-en-2-yl)carbamate, synthesized via GP1, colorless liquid, 11.6 mg (Yield =34%), dr= 2.6:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (m, 1H), 5.70 – 5.44 (m, 1H), 5.38 – 5.23 (m, 2H), 4.83 – 4.62 (m, 2H), 4.49 – 4.35 (m, 1H), 3.38 (m, 1H), 1.99

(m, 1H), 1.85 – 1.09 (m,9H), 0.98 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 154.1, 136.9, 132.5, 118.5, 116.6, 95.9, 78.1, 77.4, 74.7, 74.6, 55.1, 54.5, 40.9, 40.0, 29.4, 29.0, 28.7, 26.4, 26.3, 26.1, 25.9, 25.9, 25.8. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{20}Cl_3NNaO_3^+$ 366.0401; Found 366.0402.



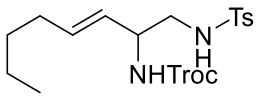
3ag

2,2,2-Trichloroethyl (1-^{t}butyl-1-hydroxybut-3-en-2-yl)carbamate, synthesized via GP1, colorless liquid, 11.4 mg (Yield =36%), dr= 2.2:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 – 5.80 (m, 1H), 5.61 (m, 1H), 5.39 – 5.15 (m, 2H), 4.88 – 4.61 (m, 2H), 4.52 – 4.36 (m, 1H), 3.30-3.50 (s, 1H), 1.83 (s, 1H), 0.99 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 153.8, 138.4, 134.0, 118.4, 115.5, 95.8, 81.5, 79.7, 74.7, 74.6, 55.6, 53.3, 35.2, 34.9, 26.7, 26.5. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{18}Cl_3NNaO_3^+$ 340.0244; Found 340.0240.



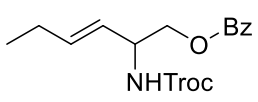
3ah

2,2,2-trichloroethyl (1-hydroxy-3-methylbut-3-en-2-yl)carbamate, synthesized via modified GP2 (acetone as solvent), white solid, 13.0 mg (Yield =47%).^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65 – 5.43 (m, 1H), 5.06 – 5.02 (s, 1H), 5.01 – 4.96 (s, 1H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.70 (d, *J* = 12.1 Hz, 1H), 4.21 (m, 1H), 3.77 (m, 2H), 1.82 (s, 3H), 1.73 (b, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 141.9, 113.0, 95.6, 74.7, 63.1, 57.9, 20.5. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_8H_{12}Cl_3NNaO_3^+$ 297.9775; Found 297.9779.



3ai

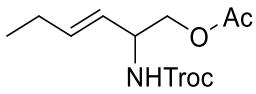
2,2,2-Trichloroethyl (E)-(1-((4-methylphenyl)sulfonamido)oct-3-en-2-yl)carbamate, synthesized via GP1, yellowish oil, 22.2 mg (Yield = 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 5.66 (dtd, *J* = 15.1, 6.7, 1.4 Hz, 1H), 5.34 – 5.22 (m, 2H), 4.95 – 4.83 (m, 1H), 4.80 – 4.56 (m, 2H), 4.26 – 4.18 (m, 1H), 3.15 (ddd, *J* = 11.7, 7.0, 4.8 Hz, 1H), 3.05 (dt, *J* = 12.9, 6.3 Hz, 1H), 2.43 (s, 3H), 2.00 (q, *J* = 6.8 Hz, 2H), 1.38 – 1.20 (m, 4H), 0.91 – 0.83 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 143.8, 136.9, 135.2, 130.0, 127.2, 125.7, 95.6, 74.7, 52.6, 47.0, 32.0, 31.1, 22.3, 21.7, 14.0. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{25}Cl_3N_2NaSO_4^+$ 493.0493; Found 493.0499.



3aj

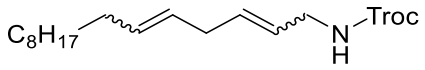
(E)-2-(Troc-amino)hex-3-en-1-yl benzoate, synthesized via GP2, colorless oil, 11.4 mg (Yield =29%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 5.94 – 5.78 (m, 1H), 5.46 (dd, J = 15.5, 6.2, 1H), 5.25 (s, 1H), 4.82 – 4.59 (m, 3H), 4.39 (d, J = 5.8 Hz, 2H), 2.08 (p, J = 7.1 Hz, 2H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 154.0, 136.1, 133.3, 129.7, 128.5, 124.3, 95.5, 74.5, 66.2, 52.4, 25.4, 13.3. HRMS

(ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{18}Cl_3NNaO_4^+$ 416.0194; Found 416.0194.



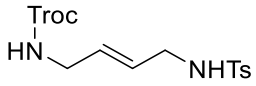
3ak

(E)-2-(Troc-amino)hex-3-en-1-yl acetate, synthesized via GP2, colorless oil, 8.7 mg (Yield =26%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (dt, *J* = 16.5, 6.5 Hz, 1H), 5.37 (dd, *J* = 15.6, 6.2 Hz, 1H), 5.21 – 5.12 (m, 1H), 4.73 (s, 2H), 4.45 (m, 1H), 4.13 (d, *J* = 5.4 Hz, 2H), 2.07 (m, 5H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 154.1, 136.0, 124.4, 95.7, 74.7, 65.9, 52.4, 25.4, 20.9, 13.4. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{16}Cl_3NNaO_4^+$ 354.0037; Found 354.0039.



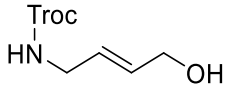
3al

2,2,2-Trichloroethyl pentadeca-2,5-dien-1-ylcarbamate, synthesized via GP2, colorless oil, 16.1 mg (Yield =40%), as mixture of stereoisomers 3.7:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 – 5.55 (m, 1H), 5.53 – 5.31 (m, 3H), 4.97 (s, 1H), 4.73 (s, 2H), 3.93 – 3.77 (m, 2H), 2.82 – 2.68 (m, 2H), 1.98 (m, 2H), 1.38 – 1.24 (m, 14H), 0.92 – 0.84 (m, 3H). For the major isomer, ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 132.7, 132.3, 127.3, 125.8, 95.8, 74.7, 43.3, 35.3, 32.7, 32.1, 29.7, 29.7, 29.7, 29.6, 29.5, 29.4, 22.8, 14.3. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{30}Cl_3NNaO_2^+$ 420.1234; Found 420.1244.



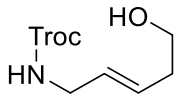
3an

2,2,2-Trichloroethyl (E)-(4-((4-methylphenyl)sulfonamido)but-2-en-1-yl)carbamate, synthesized via GP2, colorless oil, 11.6 mg (Yield = 28%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 2H), 7.35 – 7.28 (m, 2H), 5.67 – 5.49 (m, 2H), 5.01 (s, 1H), 4.71 (s, 2H), 4.61 (s, 1H), 3.76 (t, *J* = 5.6 Hz, 2H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 143.8, 137.1, 129.9, 129.4, 127.6, 127.3, 95.6, 74.7, 44.7, 42.5, 21.7. HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{18}Cl_3N_2O_4S^+$ 415.0047; Found 415.0052.



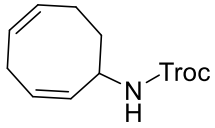
3aq

2,2,2-Trichloroethyl (E)-(4-hydroxybut-2-en-1-yl)carbamate, synthesized via GP2, colorless oil, 18.5 mg (Yield = 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (dt, *J* = 15.8, 5.1 Hz, 1H), 5.74 (dt, *J* = 15.6, 5.5 Hz, 1H), 5.22 (s, 1H), 4.72 (s, 2H), 4.15 (d, *J* = 5.0 Hz, 2H), 3.85 (d, *J* = 5.8 Hz, 2H), 1.83 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 131.6, 127.1, 95.7, 74.7, 62.8, 42.7. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_7H_{10}Cl_3NNaO_3^+$ 283.9618; Found 283.9628.



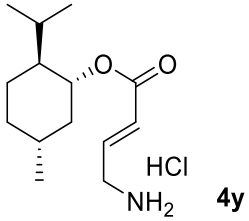
3ar

2,2,2-Trichloroethyl (E)-(5-hydroxypent-2-en-1-yl)carbamate, synthesized via GP2, colorless oil, 4.0 mg (Yield = 14%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63 (m, 2H), 5.09 (s, 1H), 4.73 (s, 2H), 3.83 (t, *J* = 5.7 Hz, 2H), 3.67 (t, *J* = 6.2 Hz, 2H), 2.31 (q, *J* = 6.3 Hz, 2H), 1.57 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 129.8, 128.6, 95.7, 74.7, 61.9, 43.2, 35.7. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_8H_{12}Cl_3NNaO_3^+$ 297.9775; Found 297.9784.



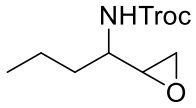
3as

2,2,2-Trichloroethyl (E)-(5-hydroxypent-2-en-1-yl)carbamate, synthesized via GP1, colorless oil, 3.2 mg (Yield = 11%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 – 5.64 (m, 2H), 5.59 – 5.43 (m, 1H), 5.22 – 5.12 (m, 1H), 5.00 (s, 1H), 4.88 (m, 1H), 4.71 (s, 2H), 3.04 – 2.78 (m, 2H), 2.66 – 2.52 (m, 1H), 2.06 (m, 1H), 1.85 (m, 1H), 1.40 – 1.28 (m, 1H). HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{15}Cl_3NO_2^+$ 298.0163; Found 298.0168.



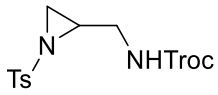
4y

(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl (E)-4-aminobut-2-enoate hydrochloride. 0.2 mmol **3w** and 2 mmol Zn powder were added to 2 mL acetic acid. The reaction was stirred for 24 h at room temperature. The reaction solution was filtered on a thin paddle of celite, which was then washed with MeOH. The collected filtrate was evaporated, redissolved with Et_2O and washed with a K_2CO_3 aqueous solution. The organic phase was dried and evaporated to 2 mL, and then 0.2 mL HCl (4 M in dioxane) was added. **4w** was obtained as a white solid, 46.8 mg, 85%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 – 8.47 (b, 3H), 7.01 (dt, *J* = 15.8, 5.9 Hz, 1H), 6.20 (d, *J* = 15.8 Hz, 1H), 4.78 – 4.67 (m, 1H), 3.89 (m, 2H), 2.02 – 1.93 (m, 1H), 1.84 (pd, *J* = 7.1, 2.7 Hz, 1H), 1.73 – 1.61 (m, 2H), 1.53 – 1.33 (m, 2H), 1.12 – 0.96 (m, 2H), 0.92 – 0.84 (m, 7H), 0.73 (dd, *J* = 7.0, 2.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 138.0, 126.4, 75.2, 47.1, 41.0, 40.5, 34.3, 31.5, 26.3, 23.5, 22.2, 20.9, 16.5. HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{26}NO_2^+$ 240.1958; Found 240.1955.



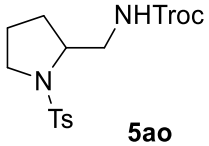
5ad

2,2,2-Trichloroethyl (1-(oxiran-2-yl)butyl)carbamate, synthesized via GP1, colorless oil, dr= 1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.05 – 4.81 (m, 1H), 4.80 – 4.59 (m, 2H), 1.77 – 1.58 (m, 2H), 1.47 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H). For the details of hydrogens on epoxy group please see the attached spectrum. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 154.5, 95.7, 74.7, 74.6, 53.9, 53.5, 52.8, 50.0, 46.0, 44.4, 35.6, 33.7, 19.1, 18.9, 14.0, 13.9. HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_9H_{14}Cl_3NNaO_3^+$ 311.9931; Found 311.9928.



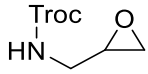
5am

2,2,2-Trichloroethyl ((1-tosylaziridin-2-yl)methyl)carbamate, synthesized via GP2, colorless oil, 18.0 mg (Yield = 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 5.00 (t, *J* = 6.2 Hz, 1H), 4.68 (m, 2H), 3.60 (ddd, *J* = 14.7, 6.4, 3.6 Hz, 1H), 3.18 (dt, *J* = 14.6, 6.1 Hz, 1H), 2.96 (tt, *J* = 7.0, 4.0 Hz, 1H), 2.66 (d, *J* = 7.0 Hz, 1H), 2.45 (s, 3H), 2.21 (d, *J* = 4.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 145.1, 134.6, 130.0, 128.1, 95.5, 74.7, 41.5, 38.4, 31.7, 21.8. HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{16}Cl_3N_2O_4S^+$ 400.9891; Found 400.9889.



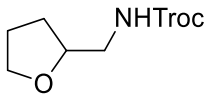
5ao

2,2,2-Trichloroethyl ((1-tosylpyrrolidin-2-yl)methyl)carbamate, synthesized via GP2, colorless oil, 28.0 mg (Yield = 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 8.3, 2.0 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 5.79 (t, *J* = 6.0 Hz, 1H), 4.84 – 4.67 (m, 2H), 3.74 – 3.63 (m, 1H), 3.51 – 3.32 (m, 3H), 3.27 – 3.08 (m, 1H), 2.43 (s, 3H), 1.86 – 1.57 (m, 3H), 1.47 (dt, *J* = 12.4, 6.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 144.0, 133.9, 130.0, 127.8, 95.8, 74.6, 59.8, 49.9, 45.6, 29.7, 24.2, 21.7. HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{20}Cl_3N_2O_4S^+$ 429.0204; Found 429.0205.



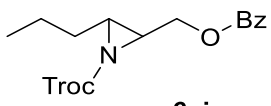
5ap

2,2,2-Trichloroethyl (oxiran-2-ylmethyl)carbamate, synthesized via GP2, colorless oil, 12.7 mg (Yield = 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.20 (s, 1H), 4.83 – 4.66 (m, 2H), 3.67 (ddd, *J* = 14.8, 6.1, 3.0 Hz, 1H), 3.33 (ddd, *J* = 14.7, 6.3, 5.1 Hz, 1H), 3.14 (ddt, *J* = 5.4, 3.8, 2.8 Hz, 1H), 2.82 (t, *J* = 4.3 Hz, 1H), 2.64 (dd, *J* = 4.6, 2.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 95.6, 74.8, 50.5, 45.1, 42.4. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_6H_8Cl_3NNaO_3^+$ 269.9462; Found 269.9463.



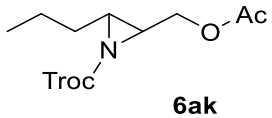
5ar

2,2,2-Trichloroethyl ((tetrahydrofuran-2-yl)methyl)carbamate, synthesized via GP2, colorless oil, 17.2mg (Yield = 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 (s, 1H), 4.81 – 4.62 (m, 2H), 3.99 (qd, *J* = 6.9, 3.3 Hz, 1H), 3.92 – 3.82 (m, 1H), 3.80 – 3.70 (m, 1H), 3.48 (ddd, *J* = 13.9, 6.7, 3.4 Hz, 1H), 3.18 (ddd, *J* = 13.1, 7.1, 5.3 Hz, 1H), 2.11 – 1.83 (m, 3H), 1.64 – 1.49 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 95.7, 77.7, 74.7, 68.3, 45.1, 28.6, 26.0. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_8H_{12}Cl_3NNaO_3^+$ 297.9775; Found 297.9783.



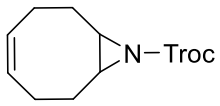
6aj

2,2,2-Trichloroethyl 2-((benzoyloxy)methyl)-3-propylaziridine-1-carboxylate, synthesized via GP2, colorless oil, 13.7mg (Yield = 35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 7.99 (m, 2H), 7.62 – 7.53 (m, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 4.78 – 4.65 (m, 2H), 4.61 – 4.44 (m, 2H), 2.78 (q, *J* = 4.5 Hz, 1H), 2.68 (td, *J* = 6.3, 3.3 Hz, 1H), 1.82 (ddt, *J* = 14.3, 8.9, 5.6 Hz, 1H), 1.61 – 1.49 (m, 2H), 1.42 – 1.31 (m, 1H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 159.6, 133.5, 129.9, 129.6, 128.6, 94.9, 63.0, 42.2, 41.9, 33.0, 20.3, 13.8. HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{19}Cl_3NO_4^+$ 394.0374; Found 394.0373.



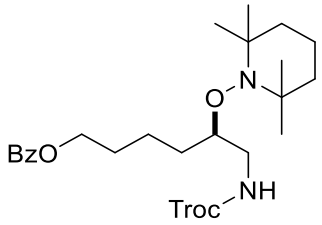
6ak

2,2,2-Trichloroethyl 2-(acetoxymethyl)-3-propylaziridine-1-carboxylate, synthesized via GP2, colorless oil, 10.6 mg (Yield = 32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.74 (s, 2H), 4.33 – 4.16 (m, 2H), 2.64 (td, *J* = 5.0, 3.3 Hz, 1H), 2.54 (ddd, *J* = 6.9, 5.6, 3.3 Hz, 1H), 2.07 (s, 3H), 1.79 (ddt, *J* = 14.4, 8.8, 5.6 Hz, 1H), 1.60 – 1.43 (m, 2H), 1.35 – 1.24 (m, 1H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 159.6, 94.9, 75.7, 63.0, 42.5, 41.6, 32.9, 20.9, 20.3, 13.8. HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{16}Cl_3NNaO_4^+$ 354.0037; Found 354.0039.



6as

2,2,2-Trichloroethyl 2-(acetoxymethyl)-3-propylaziridine-1-carboxylate, synthesized via GP1, colorless oil, 17.0 mg (Yield = 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 – 5.67 (m, 2H), 4.82 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 11.9 Hz, 1H), 2.42 – 2.15 (m, 8H), 1.20 – 1.06 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 130.6, 95.2, 75.4, 45.0, 27.9, 25.8. HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{15}Cl_3NO_2^+$ 298.0163; Found 298.0167.



7a

(R)-5-TEMPO-6-(Troc-amino)hexyl benzoate, synthesized via GP2 (with addition of 1 equiv. of TEMPO), colorless oil, 9.3 mg (Yield = 17%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dt, *J* = 7.0, 1.5 Hz, 2H), 7.60 – 7.51 (m, 1H), 6.98 – 6.81 (m, 1H), 4.80 – 4.65 (m, 2H), 4.33 (t, *J* = 6.5 Hz, 2H), 4.13 – 4.03 (m, 1H), 3.50 (ddd, *J* = 14.1, 7.8, 3.1 Hz, 1H), 3.36 (ddd, *J* = 14.1, 8.2, 3.1 Hz, 1H), 1.86 – 1.66 (m, 4H), 1.52 – 1.02 (m, 20H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 154.6, 133.0, 130.6, 129.7, 128.5, 96.0, 79.8, 74.5, 64.9, 61.1, 60.0, 46.1, 40.7, 40.3, 34.6, 33.2, 32.0, 29.1, 22.5, 20.7, 17.3. HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{38}Cl_3N_2O_5^+$ 551.1841; Found 551.1849

5. Scale-up reaction and separation

10% $Cu(OPiv)_2$ (67.5 mg), 0.5% $Ir(dfppy)_2(ppy)$ (10 mg), 1equiv. $Mg(OPiv)_2$ (0.58 g) and 3 equiv. alkene **2y** (1.70 g) were added to a 50 mL Schlenk tube, in which the atmosphere was then changed to nitrogen. Next, 3 mL CH_3CN, 45 μL H_2O and 2 mL solution of **1** (0.25 M in CH_3CN) was added and the reaction vessel was placed under radiation of blue LED. 8 mL of solution of **1** (0.25 M in CH_3CN) was added at a rate of 0.01 mL/min by a syringe pump. After the addition, the reaction was maintained for another 20 h for completion. A substantial amount of precipitate was obtained.

Filtering the reaction mixture gave a white solid, which was then washed twice with diethyl ether. Drying under vacuum led to 0.328 g white powder, which was further analyzed in section 6.3.

To the filtrate were added 30 mL ethyl acetate, 2 mL water and 1 mL 15% ammonia solution, and then the organic phase was collected after sufficient mixing. The organic phase was concentrated. The residue was separated on silica gel column to recover the alkene (1.232 g, 2.20 equiv.) and give the final product (0.632 g, 61%).

6. Mechanistic studies

6.1. Fluorescence quenching

Procedure: All solutions and samples were prepared under nitrogen. Stock solutions of $Ir(dfppy)_2(bpy)$ (2.9 mg in 20.0 mL CH_3CN, 2.0×10^{-4} M), $Cu(OPiv)_2$ (10.6 mg in 20.0 mL CH_3CN, 2.0×10^{-3} M), CuOAc (2.5 mg in 10.0 mL CH_3CN, 2.0×10^{-3} M) $Mg(OPiv)_2*H_2O$ (45.3 mg $Mg(OPiv)_2$ and 3.6 μL H_2O in 20.0 mL CH_3CN, 1.0×10^{-2} M), **2a** (81.6 mg in 20.0 mL CH_3CN, 2.0×10^{-2} M), **1** (135 mg in 20.0 mL CH_3CN, 2.0×10^{-2} M) and **1a** (62.5 mg in 10.0 mL CH_3CN, 2.0×10^{-2} M) were prepared. The sample solutions were prepared by mixing given amounts of certain stock solutions, and then diluted to 5.0 mL in a volumetric flask under nitrogen. The sample solution was transfer to a cuvette with screw cap for further measurements on a fluorescence spectrometer. Parameters: exciting (420 nm, slit 2.5 nm), emission measurement (430 nm-700 nm).

1 could effectively quench the excited $Ir(dfppy)_2(ppy)$ while **1a** (without electron-withdrawing cyano group) couldn't (Figure S1 left). On the other hand, the excited $Ir(dfppy)_2(dtbbpy)$ PF_6 couldn't be quenched by **1** (Figure S1 right). These results are consistent with the fact that neither **1a** or $Ir(ppy)_2(dtbbpy)$ PF_6 were suitable for the reaction (Scheme. S1, Table. S2).

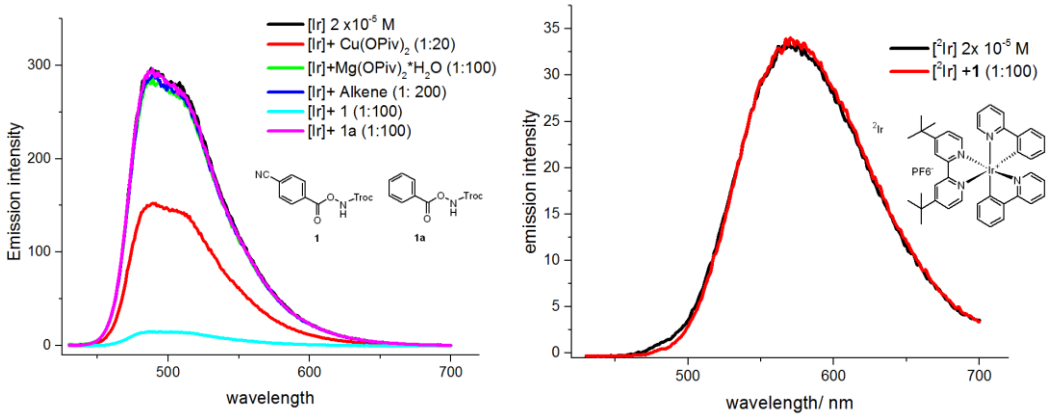


Figure S1. Fluorescence quenching of two different photocatalysts.

The slopes (which are proportional to the corresponding quenching coefficients k_q) for Stern-Volmer plots are 9955 M^{-1}, 2348 M^{-1} and 1397 M^{-1} for 1, $Cu(OPiv)_2$ and CuOAc, respectively, suggesting that **1** is more efficient in quenching the excited photocatalyst than the copper species.

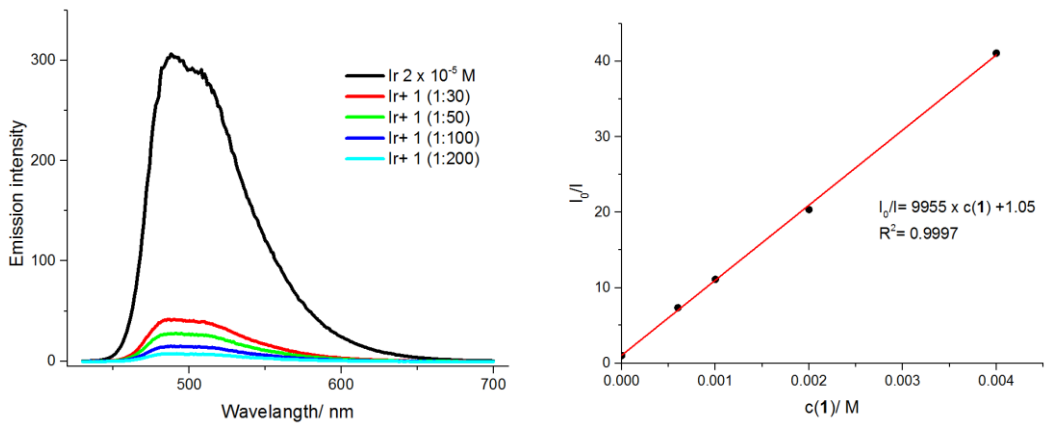


Figure S2. Fluorescence quenching by **1** at different concentrations and the corresponding Stern-Volmer Plot.

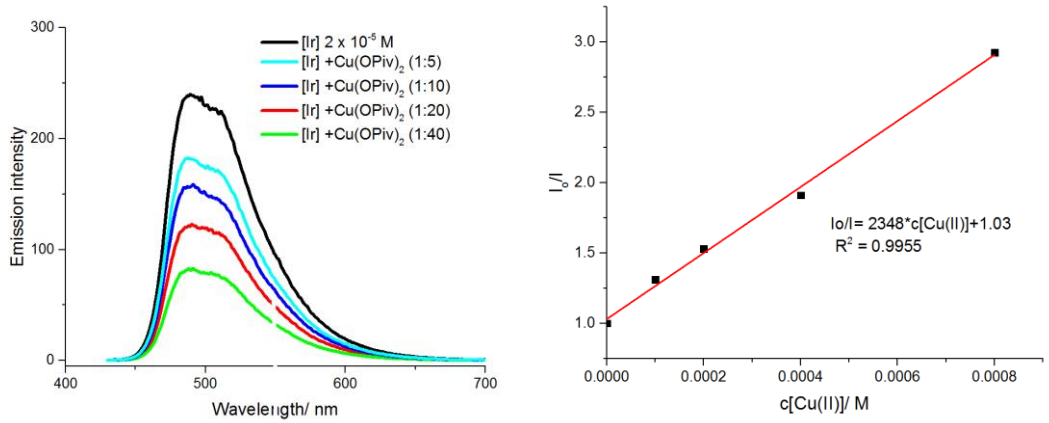


Figure S3. Fluorescence quenching by $Cu(OPiv)_2$ at different concentrations and the corresponding Stern-Volmer Plot.

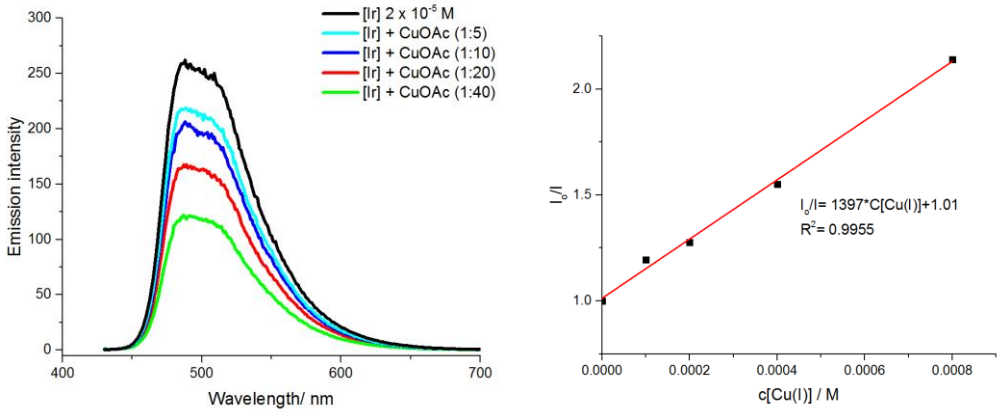


Figure S4. Fluorescence quenching by CuOAc at different concentrations and the corresponding Stern-Volmer Plot.

6.2 Measurement of redox potentials of reagents in the reaction.

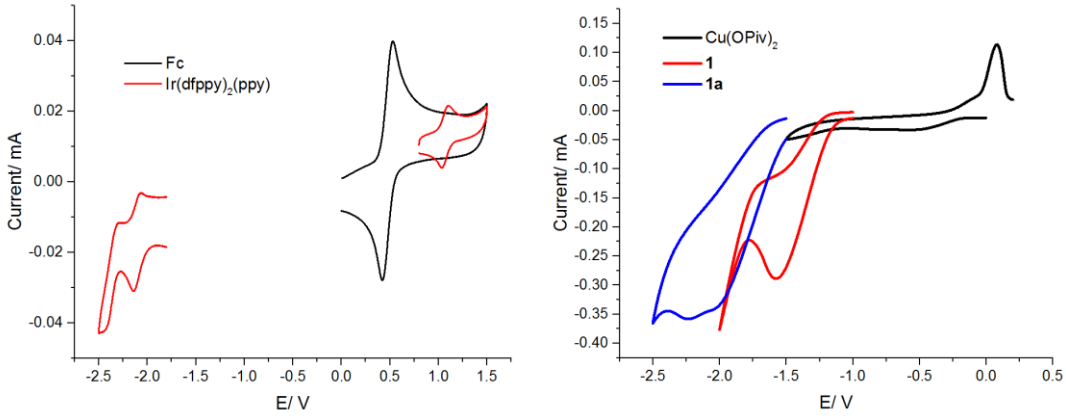


Figure S5. CVs of reaction reagents. The CVs were recorded in CH_3CN, with Bu_4NBF_4 (0.05 M) as electrolyte, glassy carbon disk as working electrode (diameter, 3 mm), Pt wire as counter electrode, Ag|AgCl, as reference electrode. The scan rate was 100 mV/s. Concentration of reagents (if applicable): 0.0001 M Fc, 0.0001 M $Ir(dfppy)_2(ppy)$, 0.001 M $Cu(OPiv)_2$, 0.01 M **1**, 0.01 M **1a**.

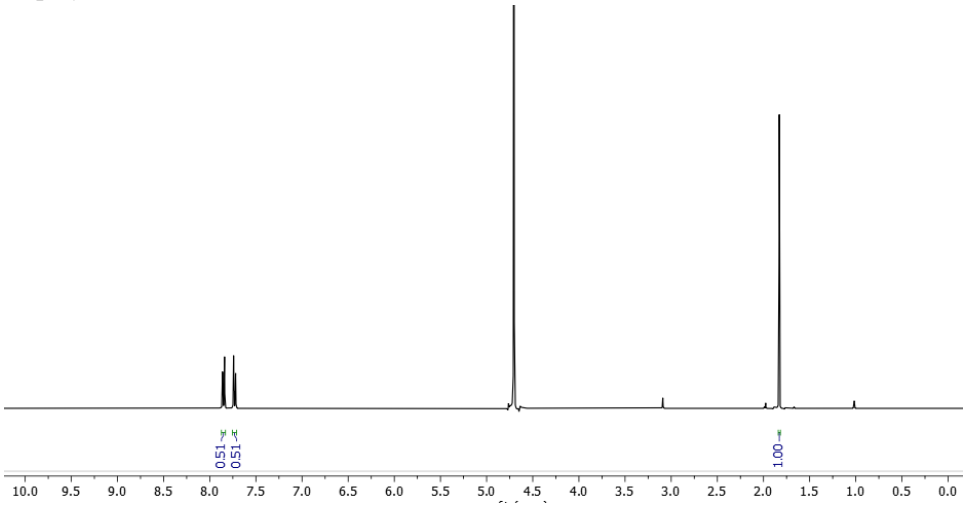
$E(Fc^+/Fc)$ is 0.477 V vs. the reference electrode in our system. $E(Fc^+/Fc)$ in CH_3CN is 0.380 V

vs. SCE.[7] The potentials vs $E(Fc^{+}/Fc)$ above are converted to potentials vs SCE: $E(Ir^{III}/Ir^{II})$ = -2.22 V, $E(Ir^{IV}/Ir^{III})$ = 0.97 V, $E_{ox}(Cu^{I})$ = -0.10 V, E_{red}(**1**) = -1.43 V, E_{red}(**1a**) = -1.82 V.

Based on the emission spectrum (Figure S1), λ_{max} = 490 nm, which corresponds to an emission energy E_0 = 2.53 eV. The oxidation potential of the excited state can be estimated[8, 9]: $E(Ir^{*}/Ir^{IV})$= $E(Ir^{III}/Ir^{IV})$- E_0= -1.56 V. This value is lower than the reduction potential of **1** yet higher than the reduction potential of **1a**, which is consistent with the fluorescence quenching results (Figure S1)

6.3 Analysis of the precipitate from the scale-up reaction

5.0 mg solid and 3.3 mg NaOAc were dissolved in deuterated water. The NMR spectrum is displayed below.

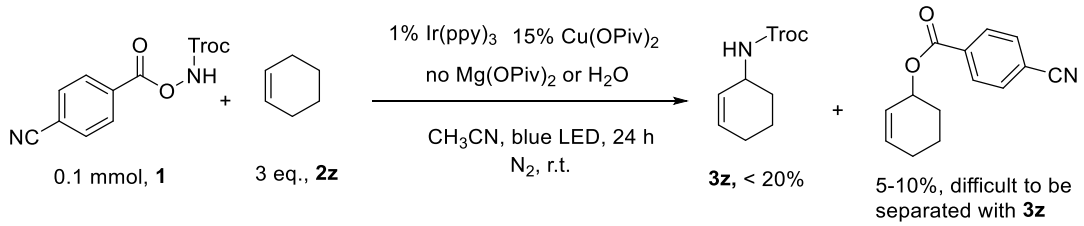


The two sets of peak at 7.73 ppm and 7.85 ppm could be assigned to 4-cyanobenzoate, and no pivalate was present. With NaOAc as an internal standard, the quantity can be calculated:

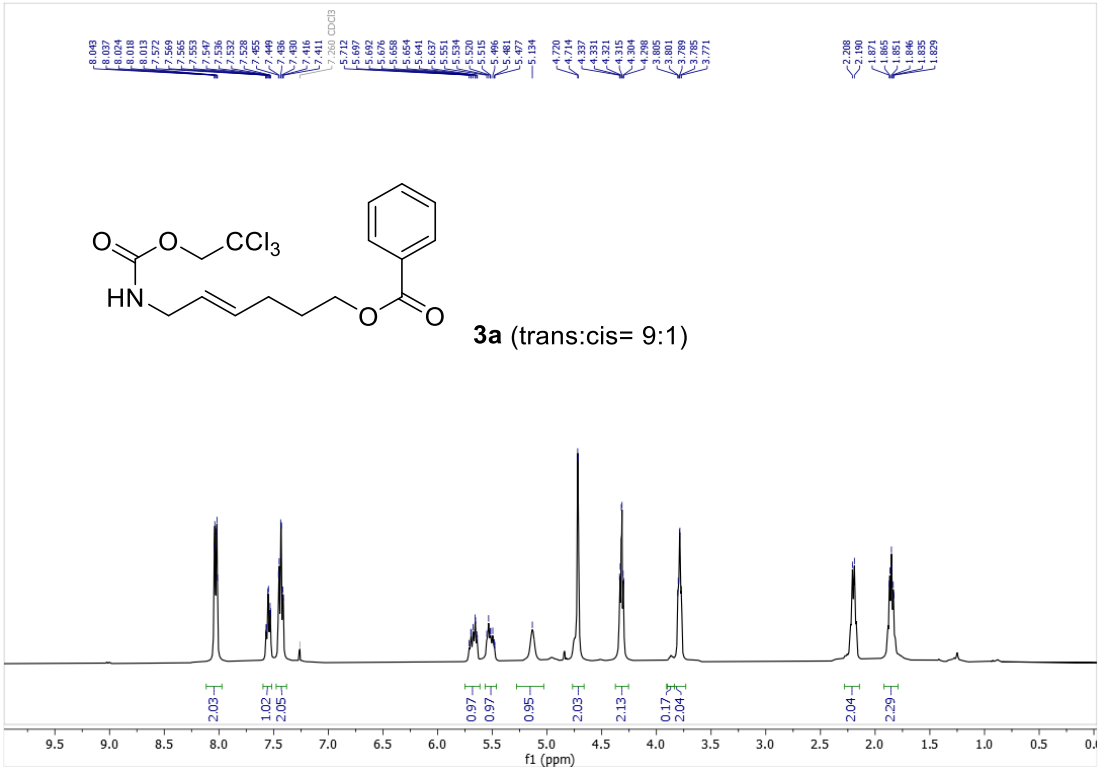
n(4-cyanobenzoate)= n(NaOAc) x $\frac{3}{2}$ x 0.51 =0.031 mmol,

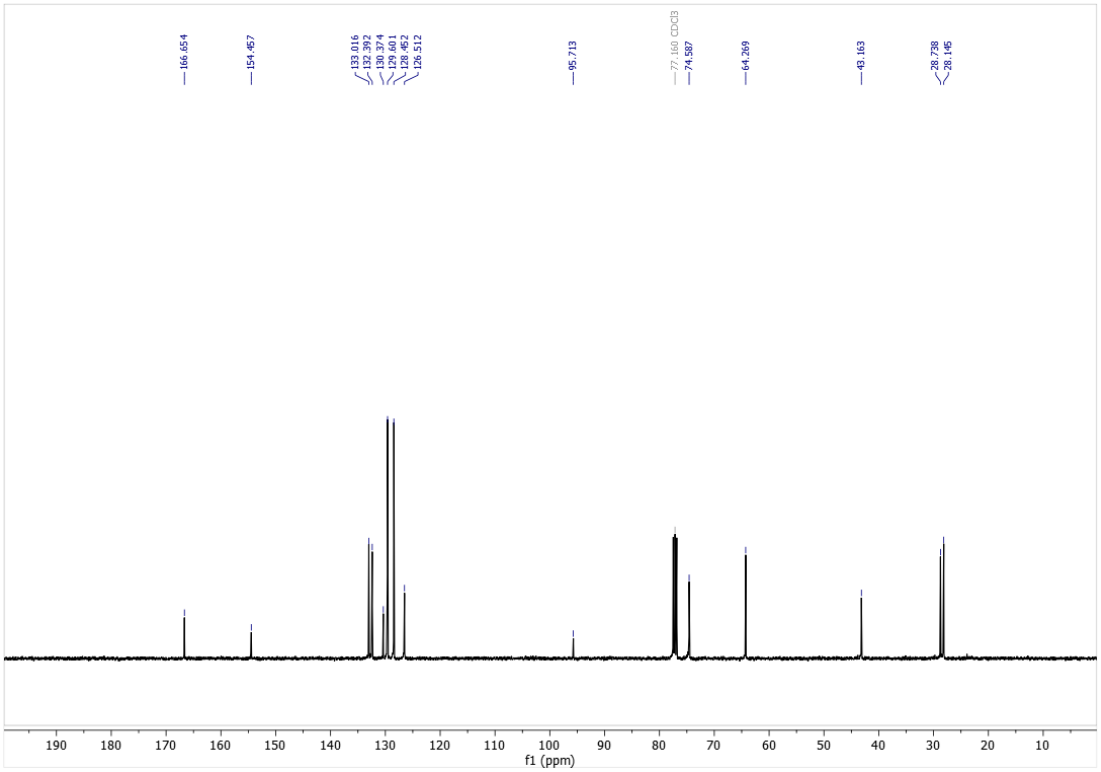
Based on the formula of Mg(4-cyanobenzoate)$_2$, the weight should be $\frac{0.031}{2}$ x 316 mg =4.9 mg, which is only slightly lower than the weight measurement at the beginning (5.0 mg). The rest part of the weight could have been contributed by H_2O.

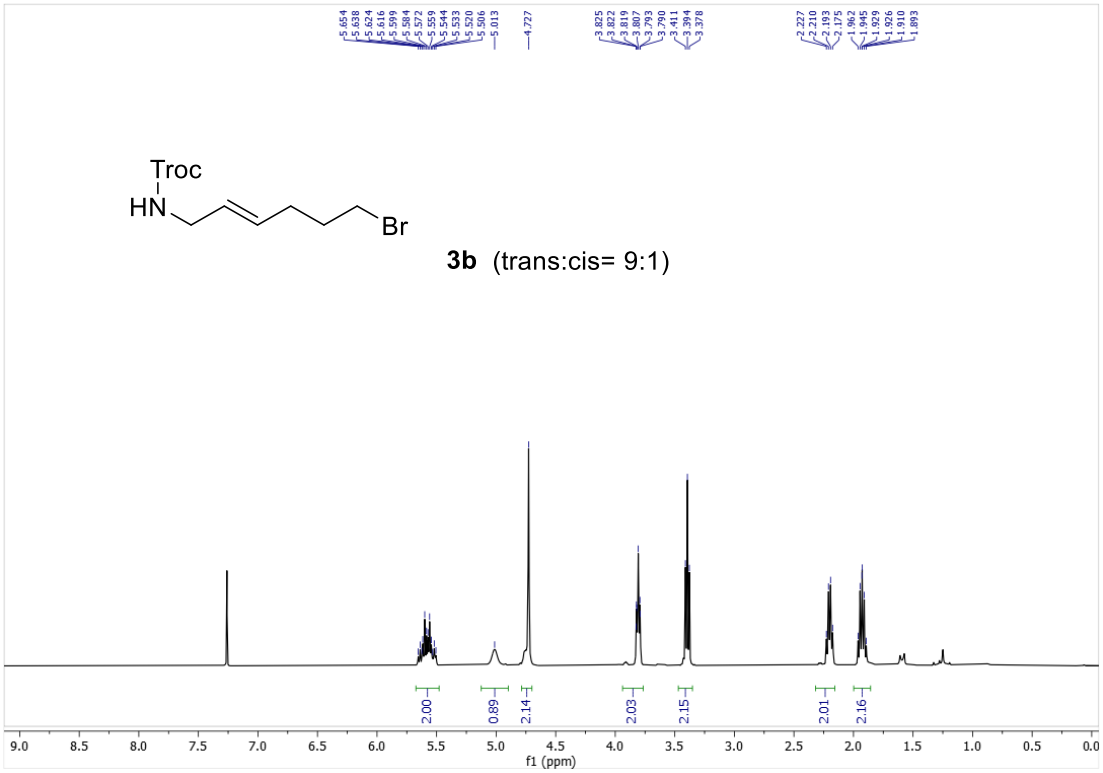
Notably, addition of 1 equiv. of H_2O was indispensable for the formation of the precipitate. $Mg(OPiv)_2$ and H_2O together can remove 4-cyanobenzoate out of the reaction solution. In the model reaction, they could improve the yield by about 10%. For some substrates (eg. **3z**), they could avoid the side product from addition of 4-cyanobenzoate to the **2z**.



7. NMR spectra of products



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Br
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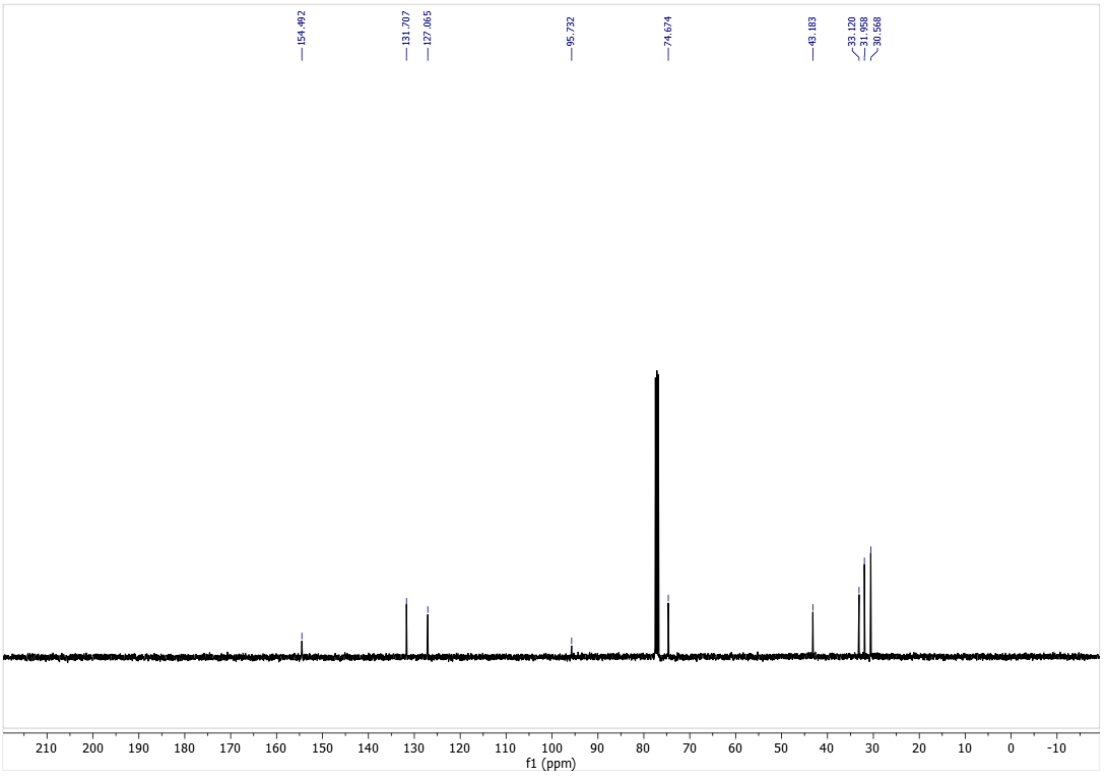
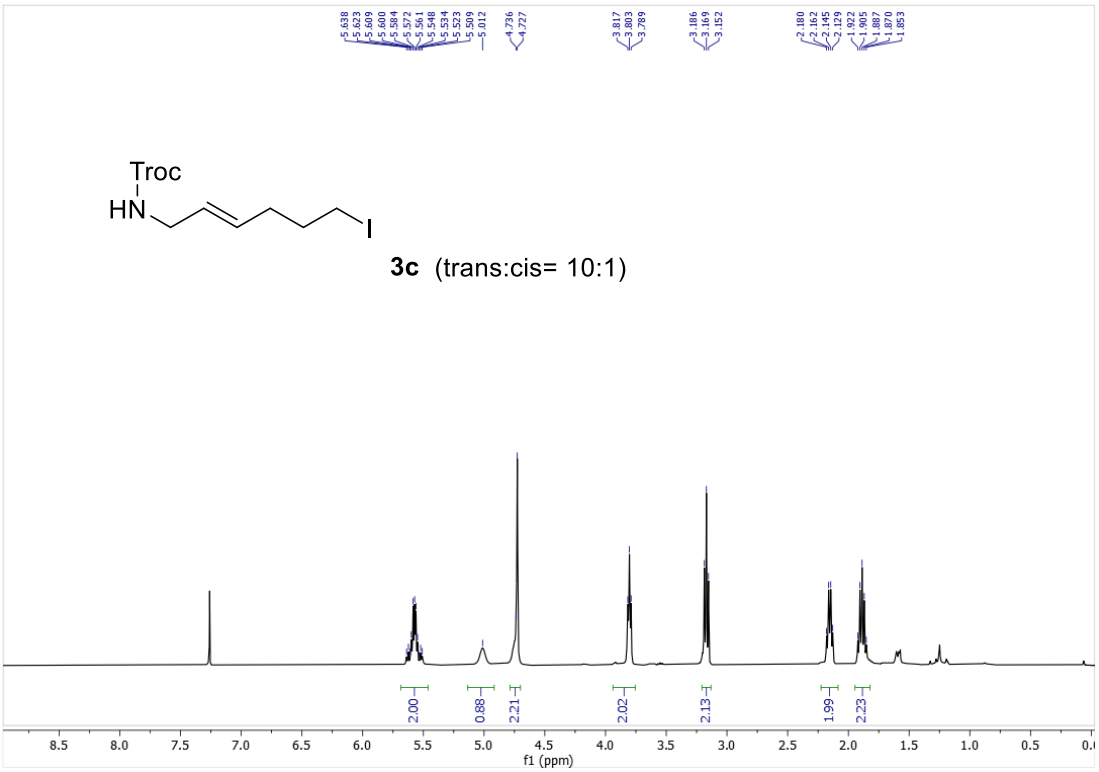
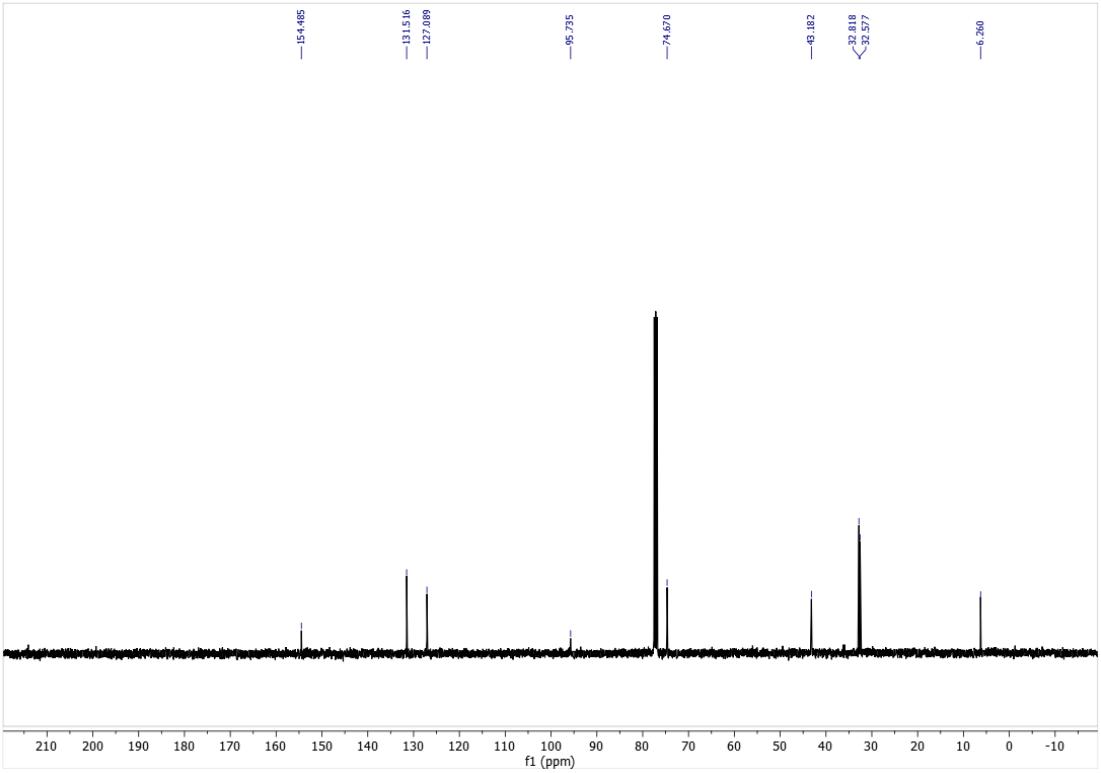
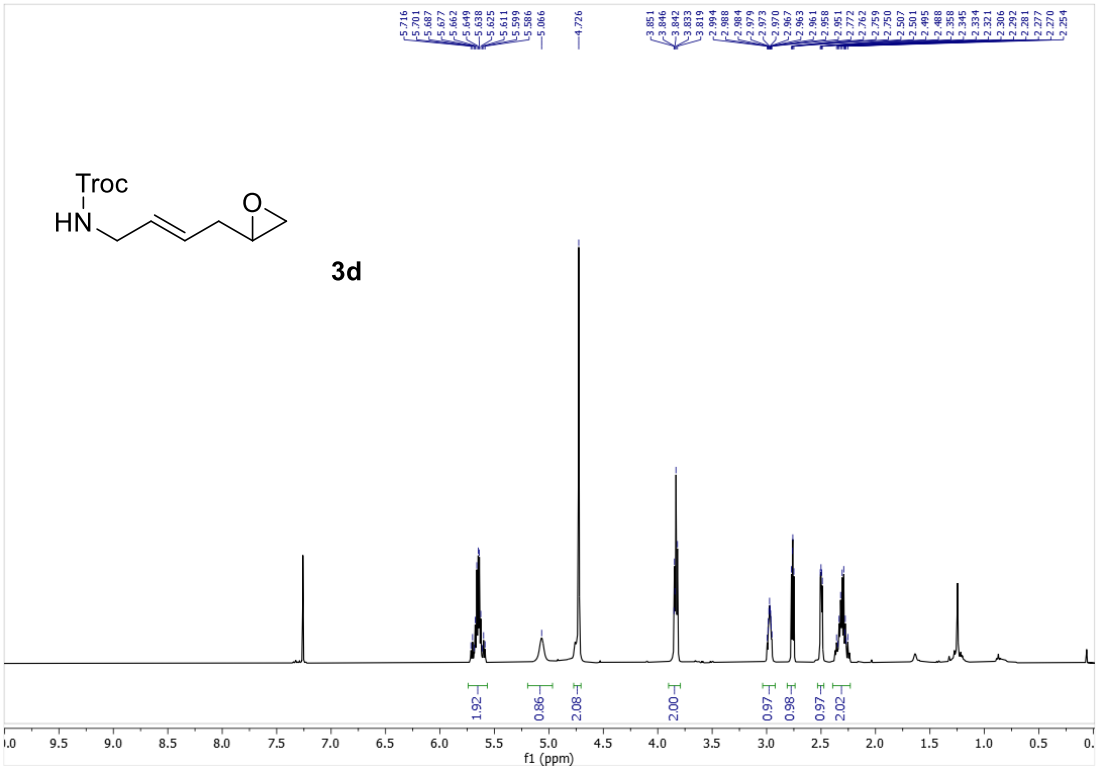
f1 (ppm)


f1 (ppm)


Troc
HN
I
3c (trans:cis= 10:1)
f1 (ppm)


f1 (ppm)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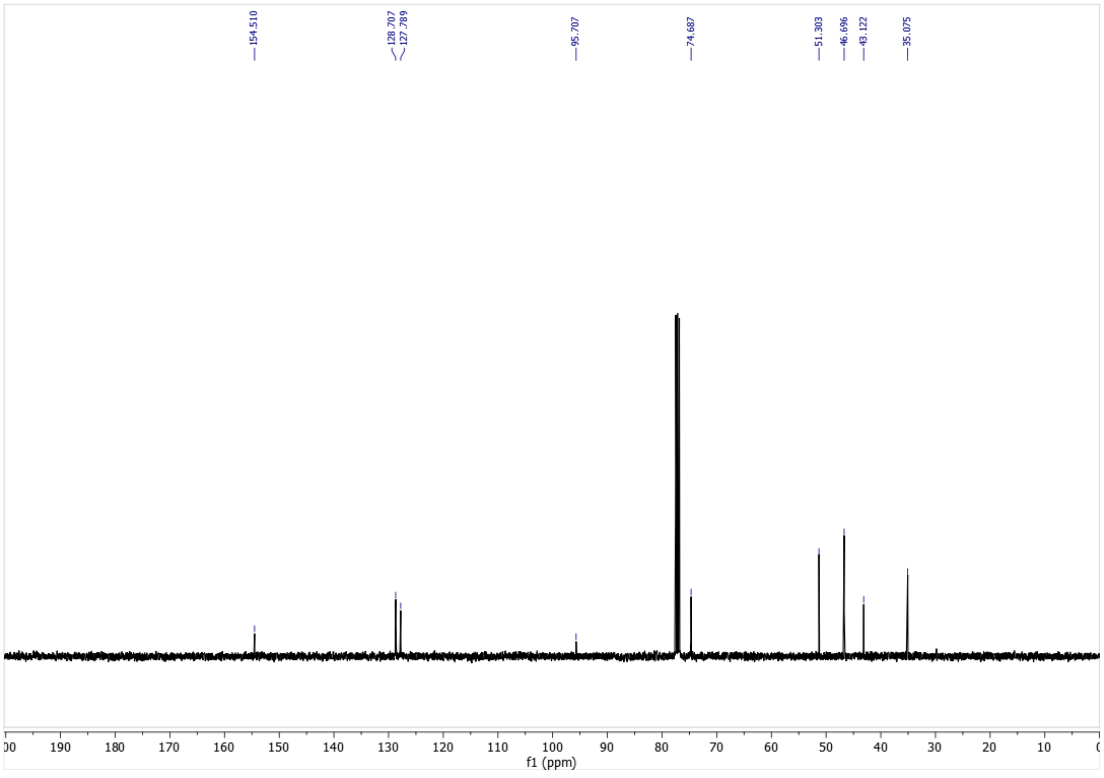
HN
O
3d
f1 (ppm)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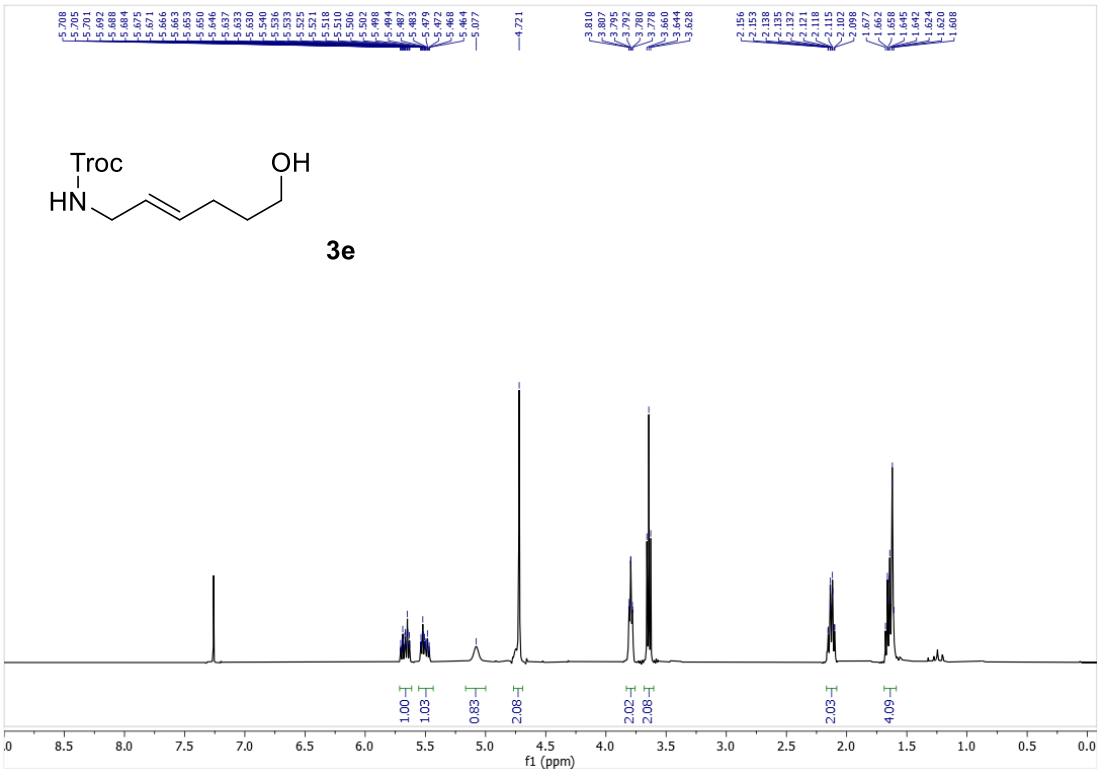
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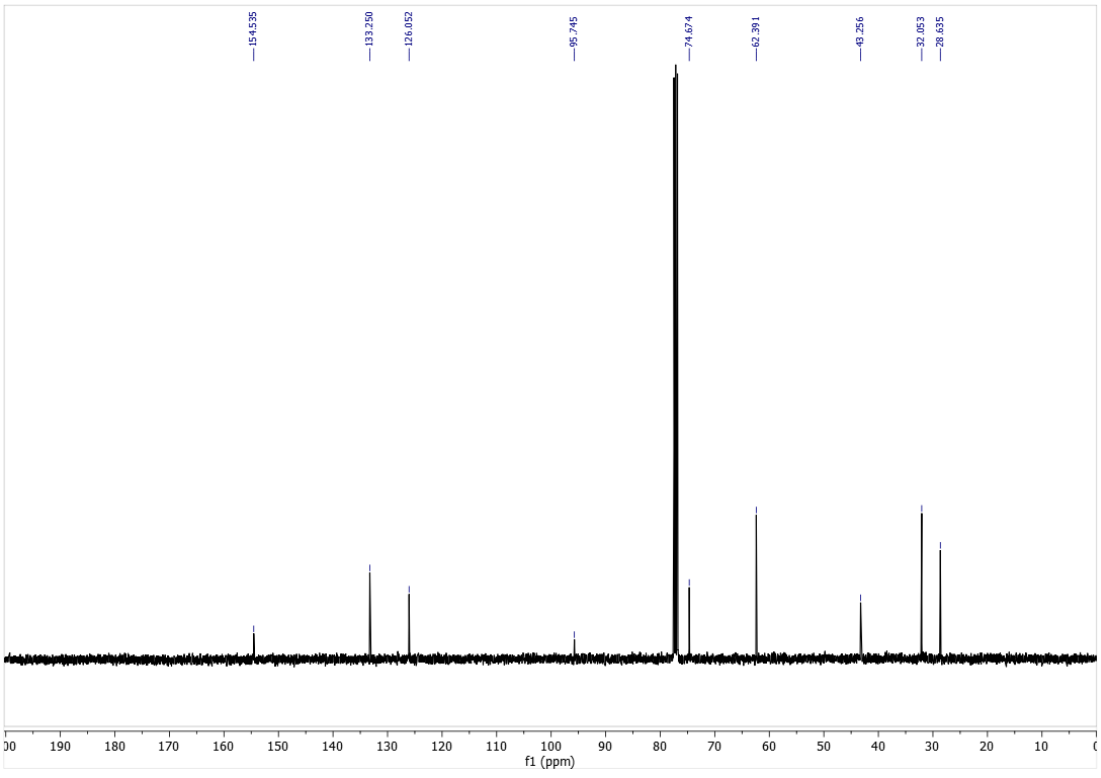
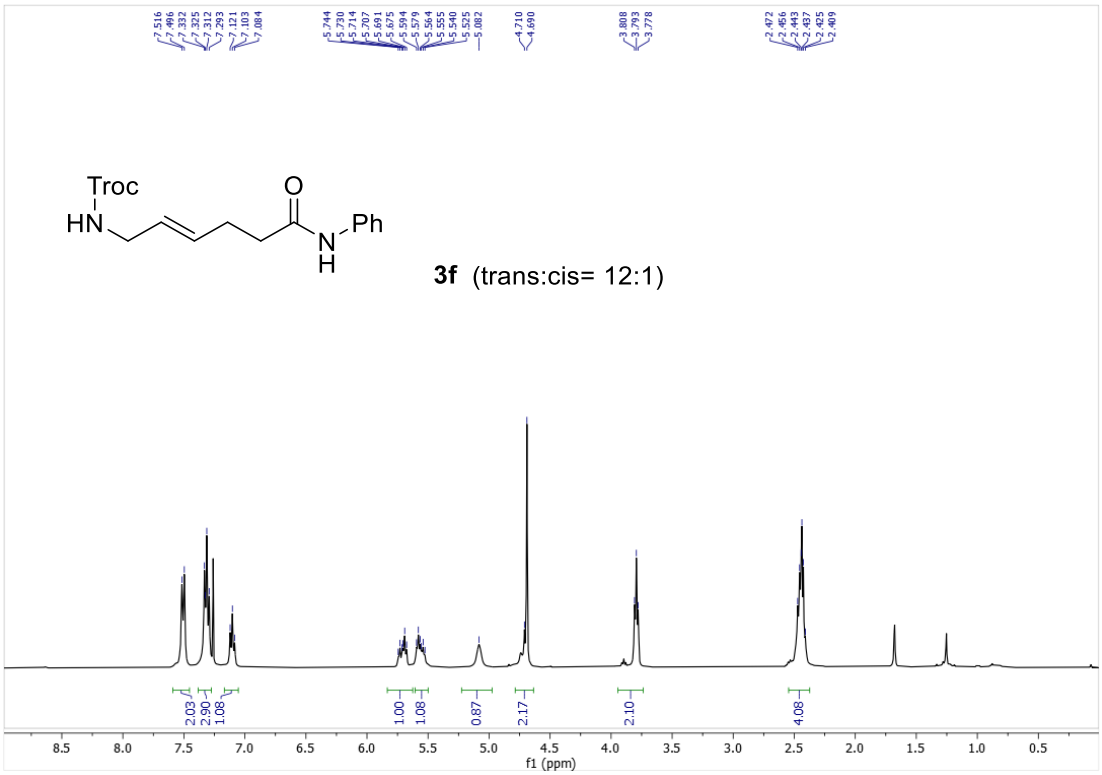
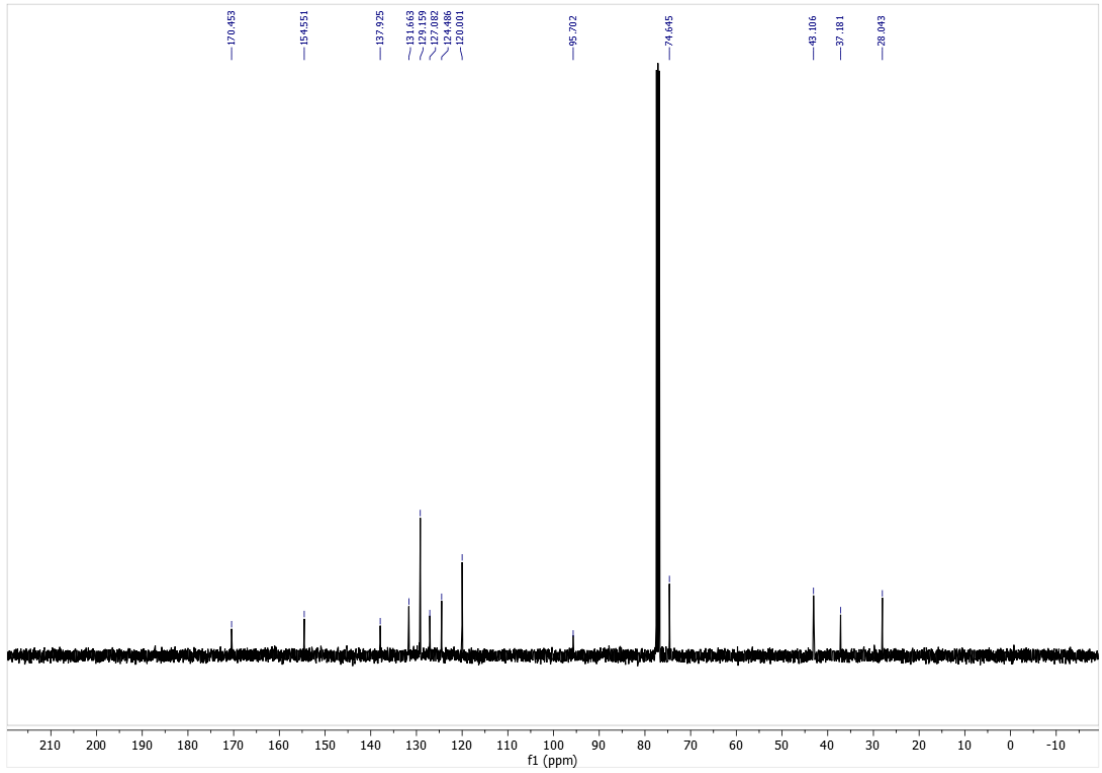
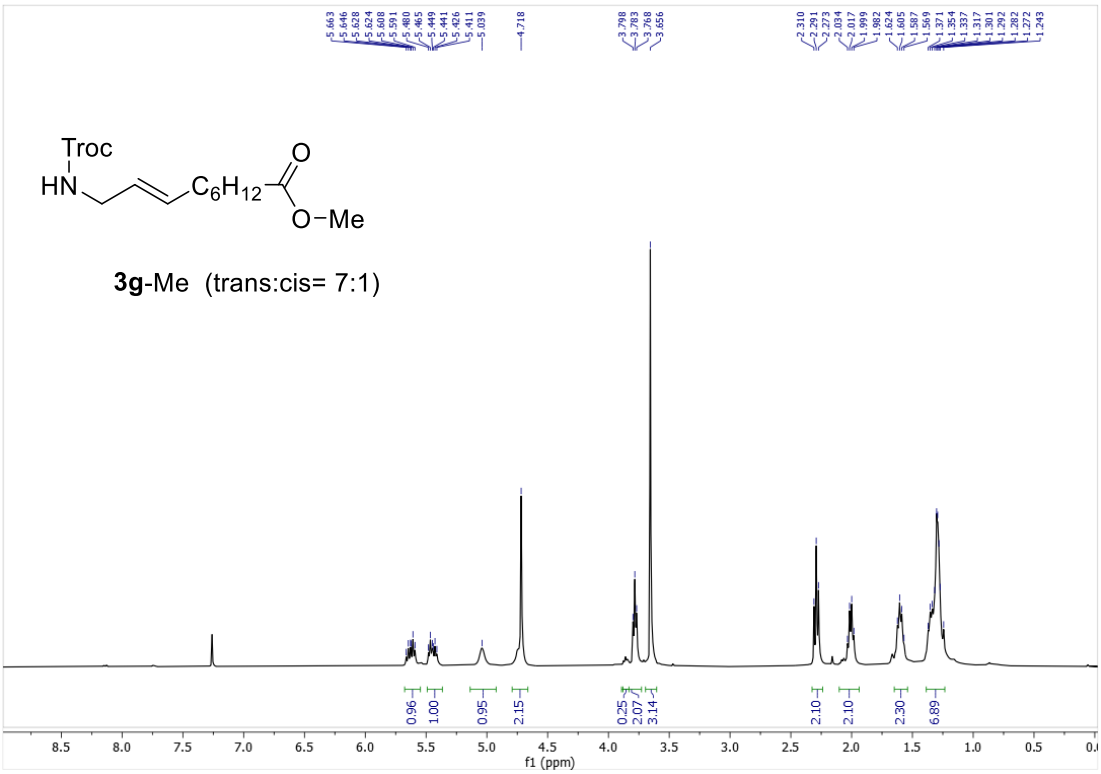
OH
3e
f1 (ppm)

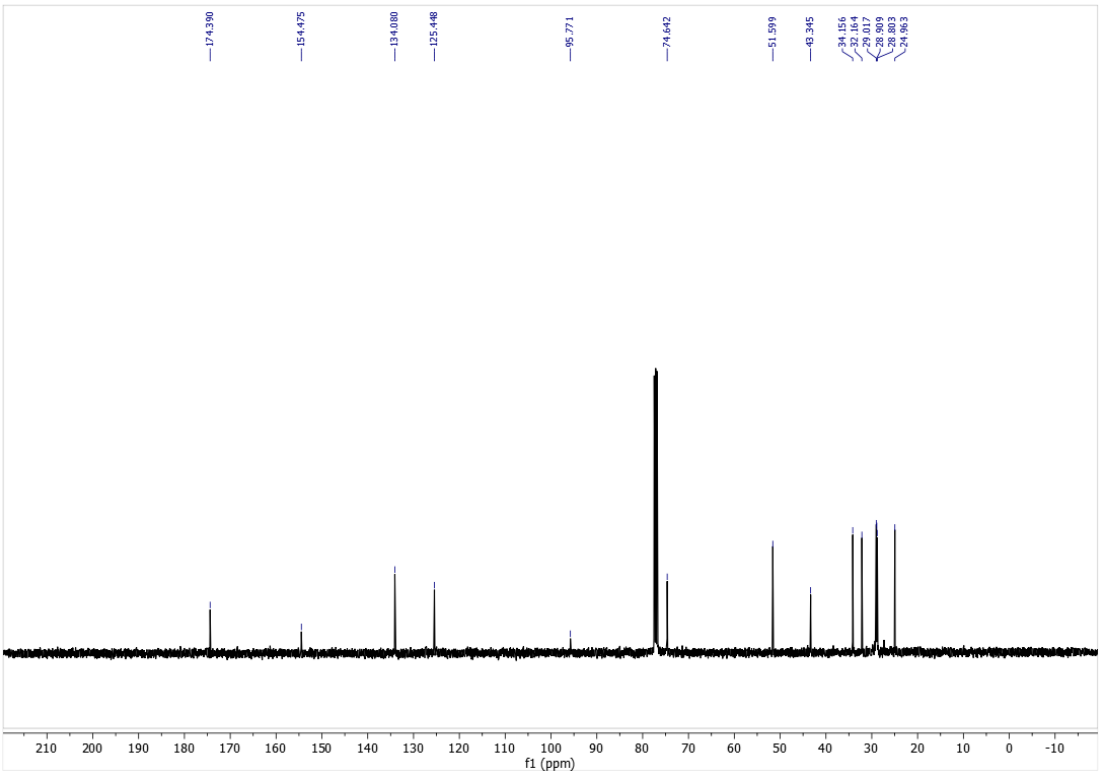

f1 (ppm)

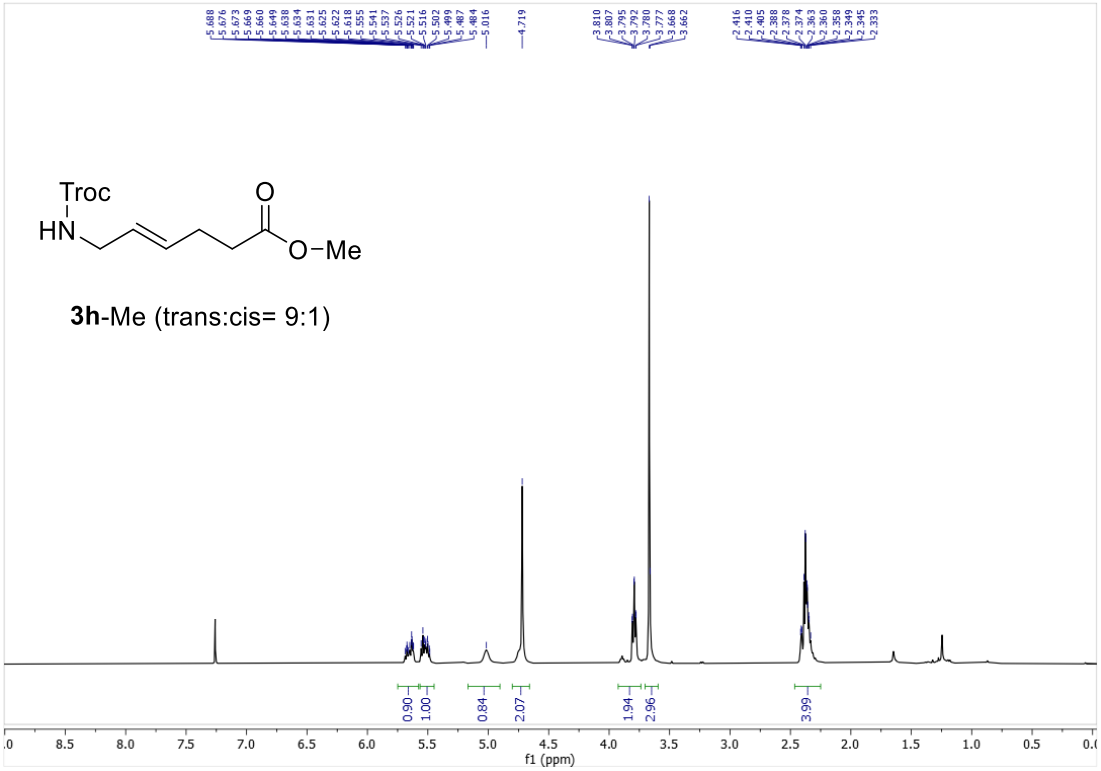


3f (trans:cis= 12:1)




Troc
HN
C_6H_{12}
O
O−Me
3g-Me (trans:cis= 7:1)
f1 (ppm)


f1 (ppm)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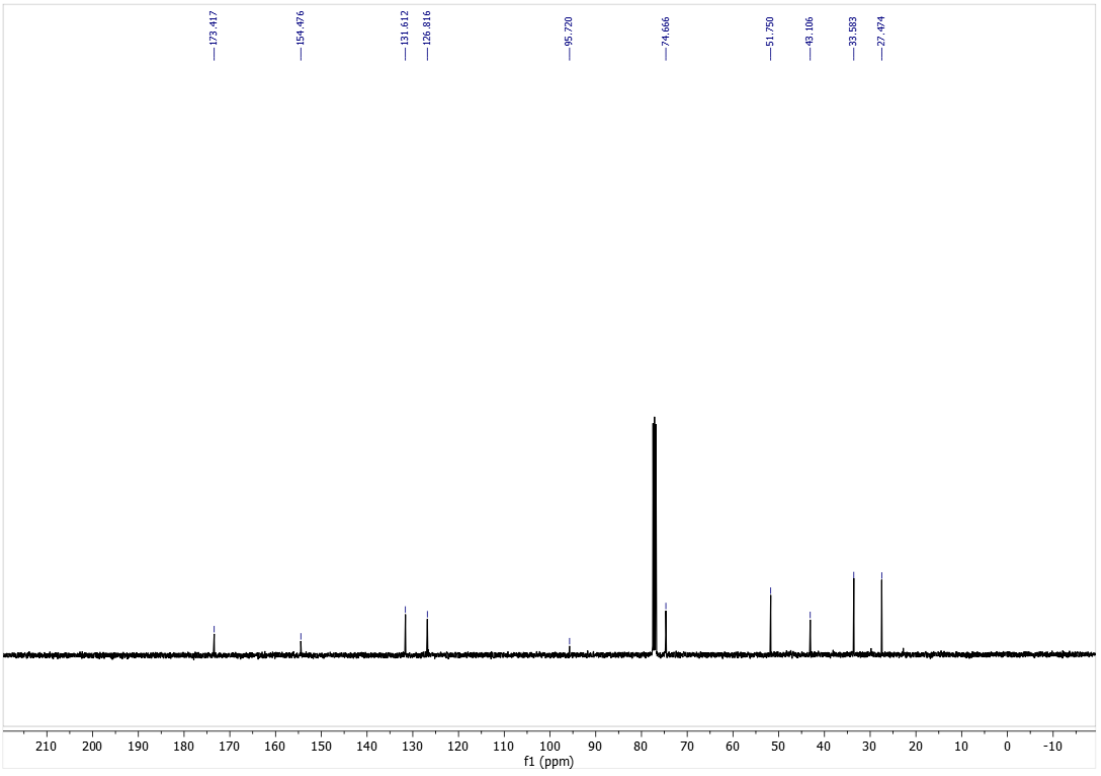
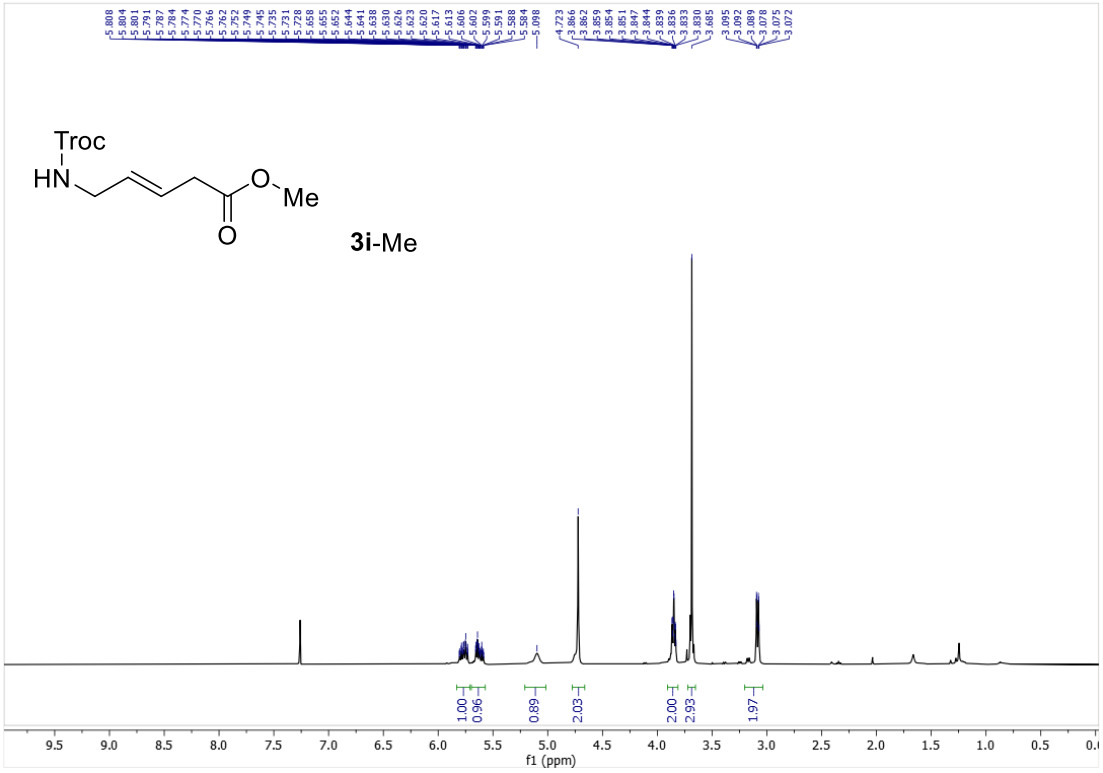
HN
O
O−Me
3h-Me (trans:cis= 9:1)
f1 (ppm)


f1 (ppm)


Troc
HN
O
Me
O
3i-Me
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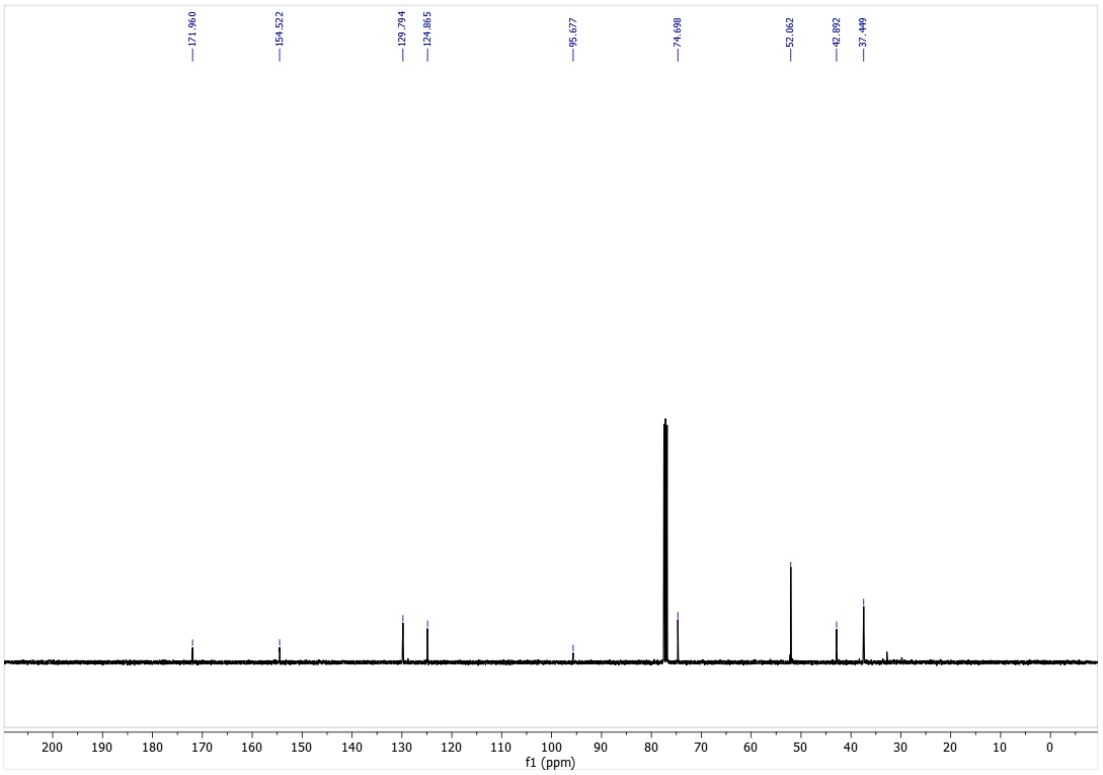
0.89
2.03
2.00
2.93
1.97
f1 (ppm)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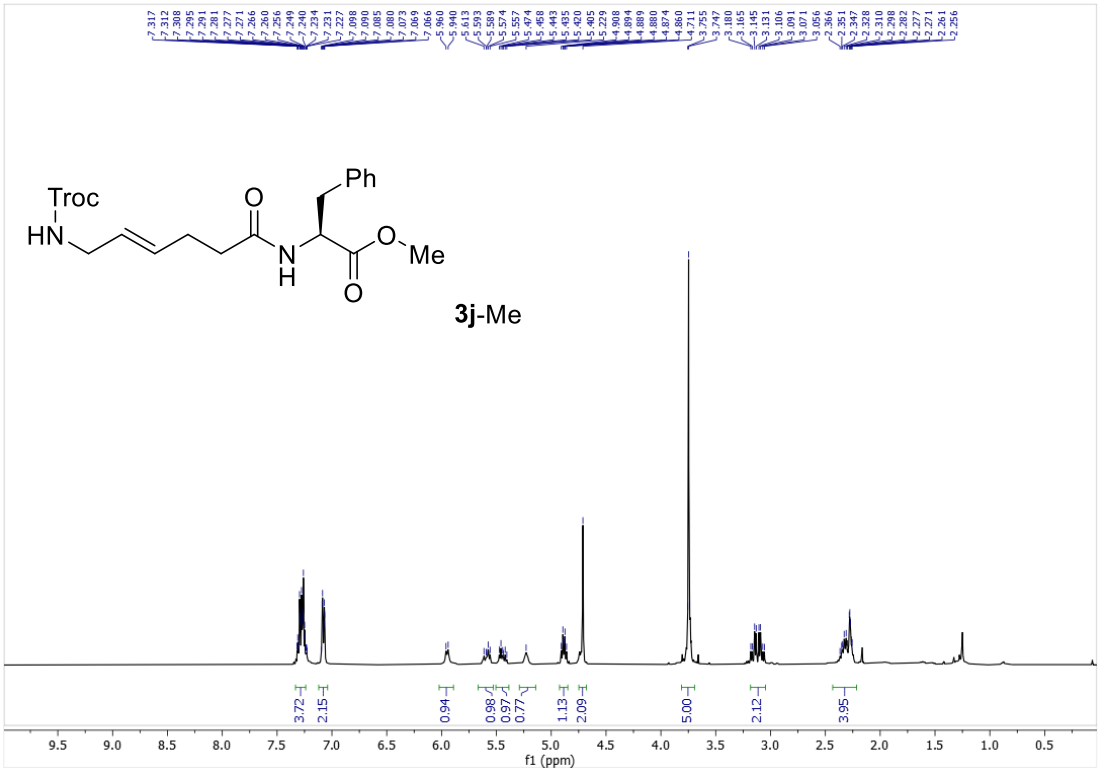
37.449
f1 (ppm)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HN
O
N
H
Ph
O
O
Me
3j-Me
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0.77
1.13
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5.00
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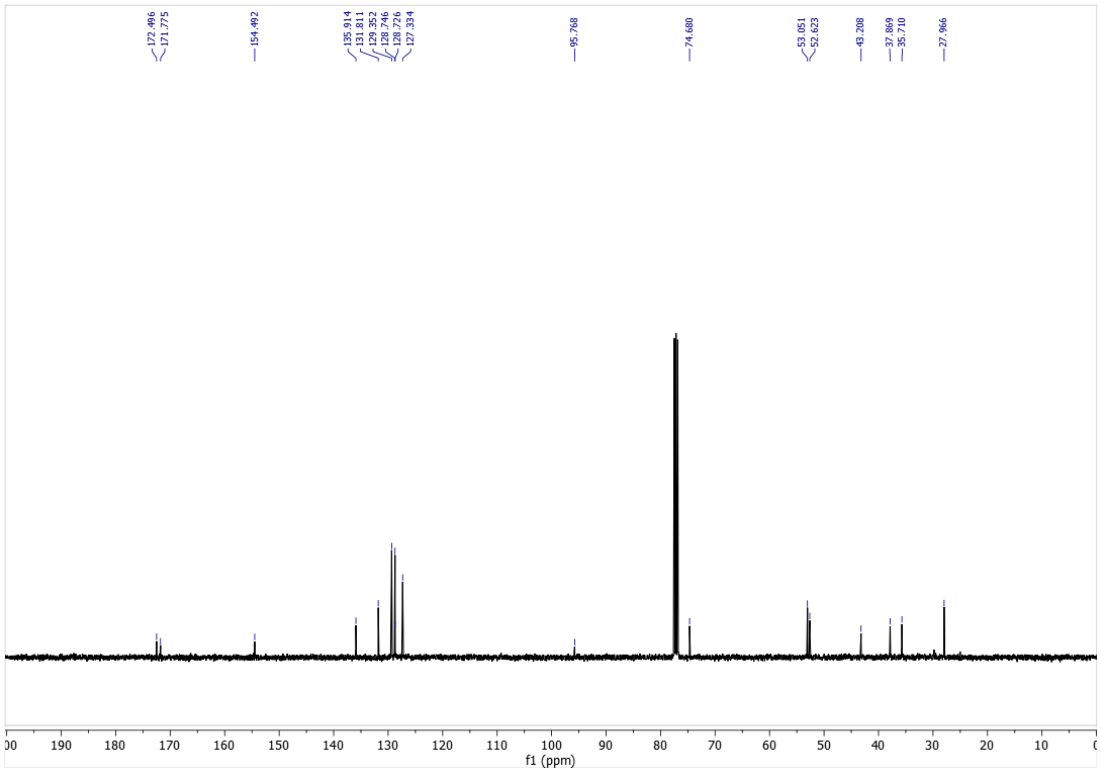
3.95
f1 (ppm)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37.869
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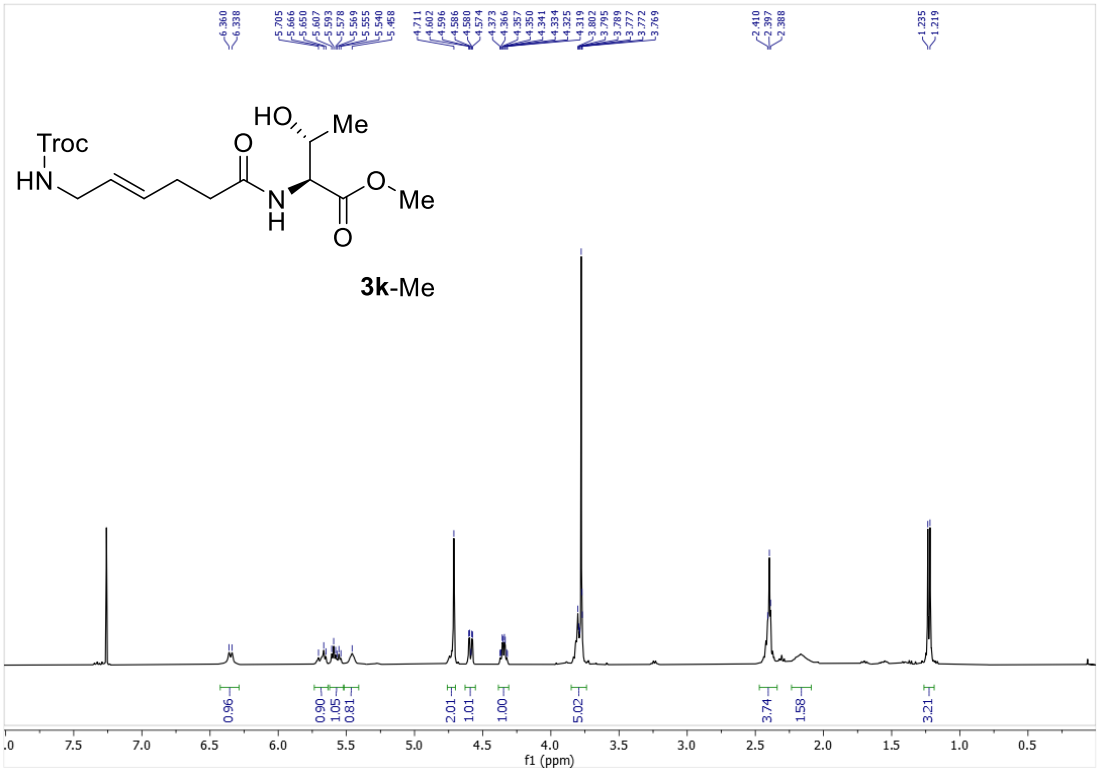
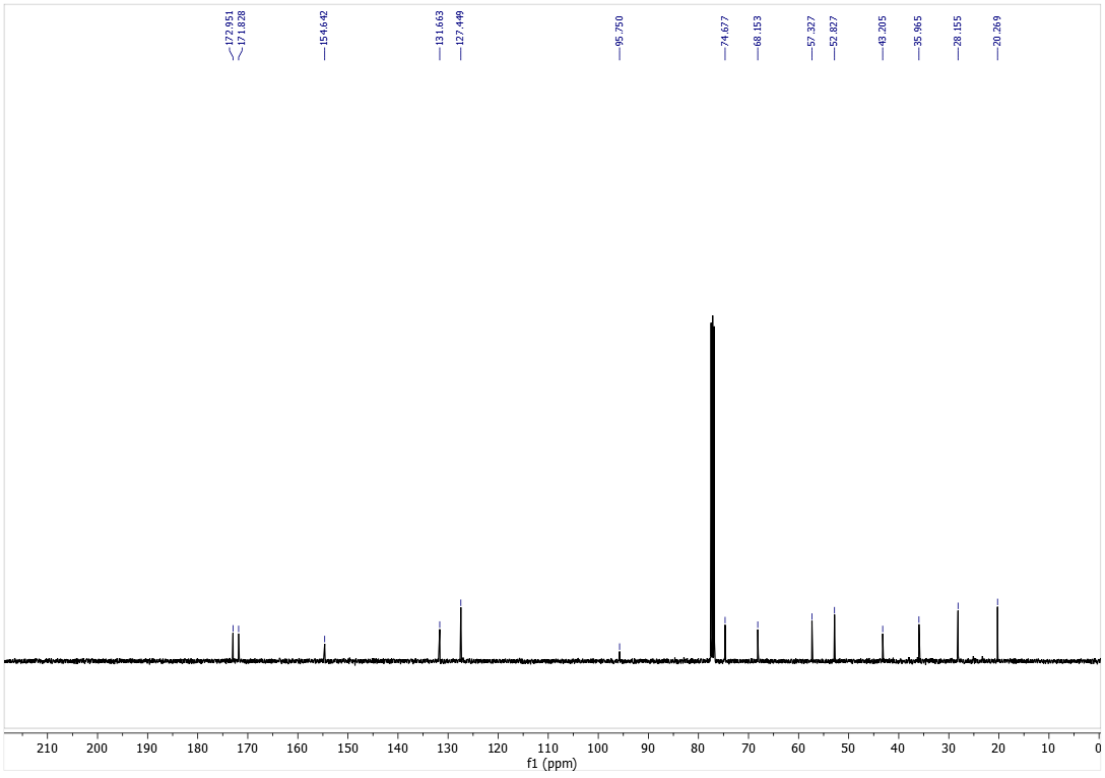
27.966
f1 (ppm)


Troc
HN
O
HO
Me
N
H
O
O
Me
3k-Me
f1 (ppm)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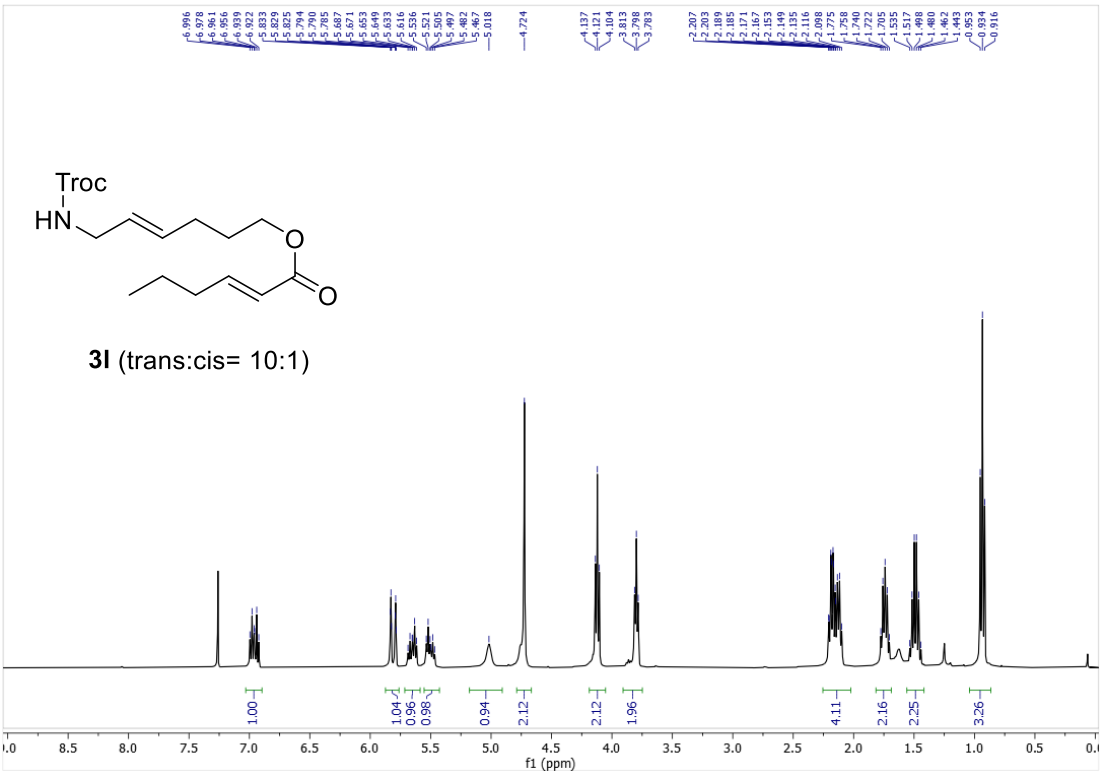
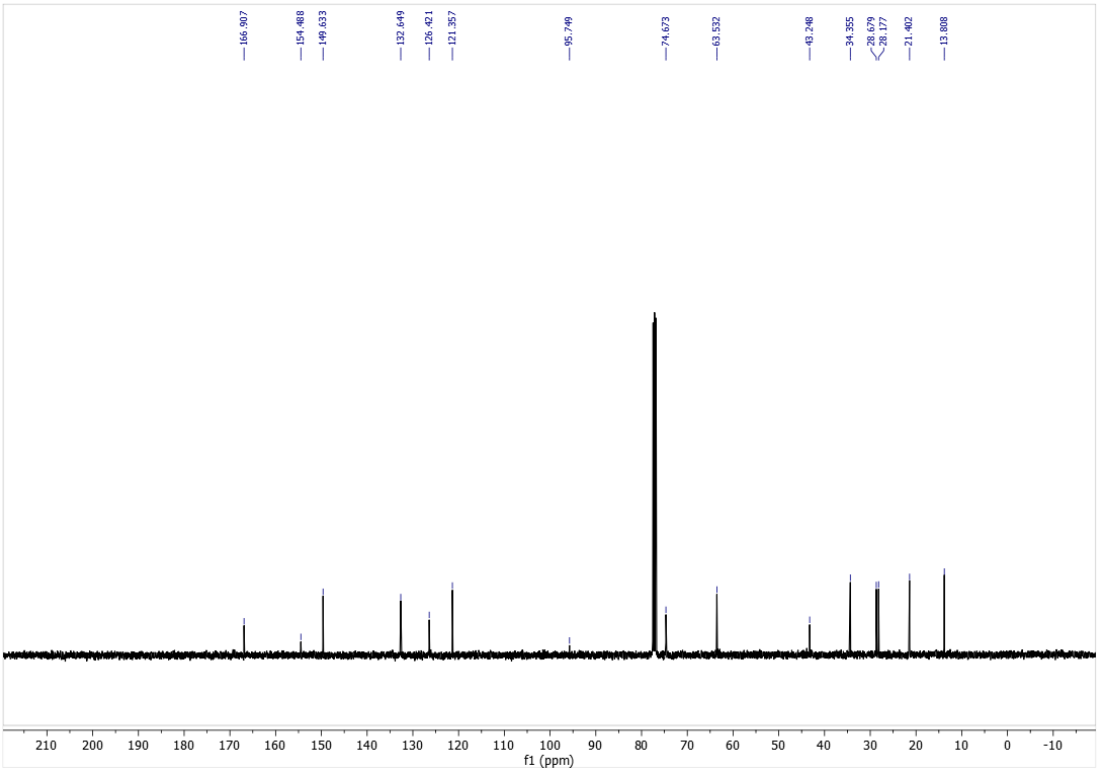
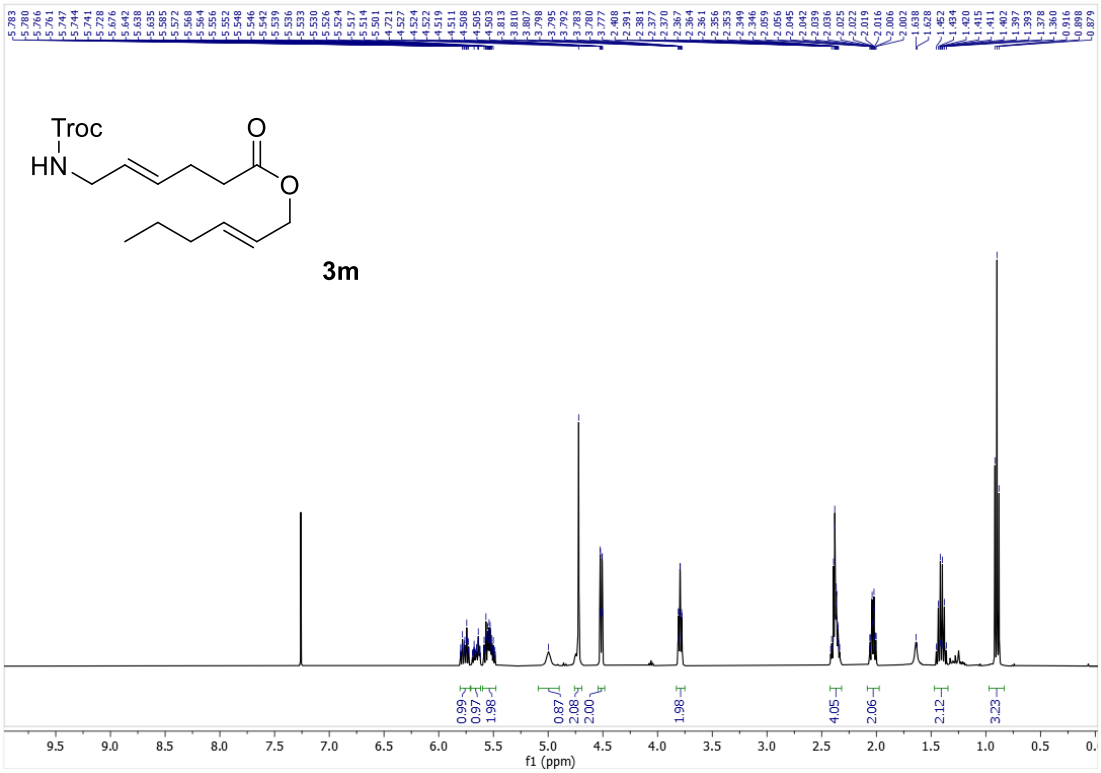

Troc
HN
O
O
3l (trans:cis= 10:1)
f1 (ppm)


f1 (ppm)


Troc
HN
O
O
3m
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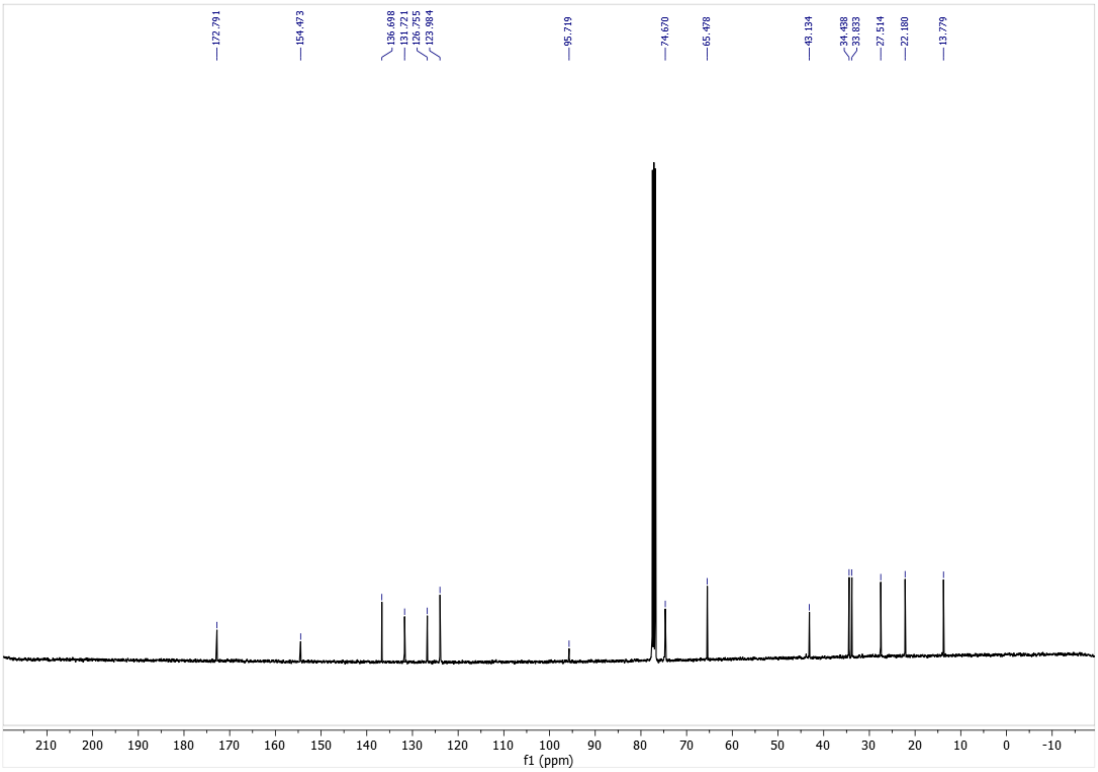
0.97
1.98
0.87
2.08
2.00
1.98
4.05
2.06
2.12
3.23
f1 (ppm)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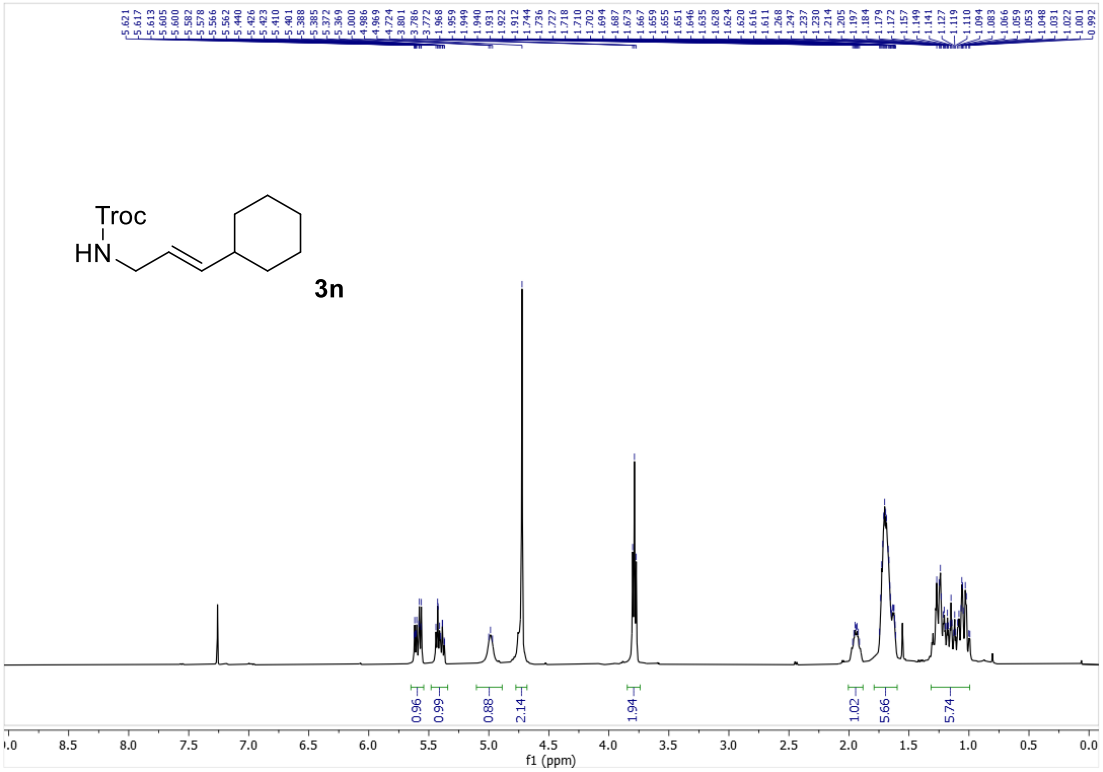
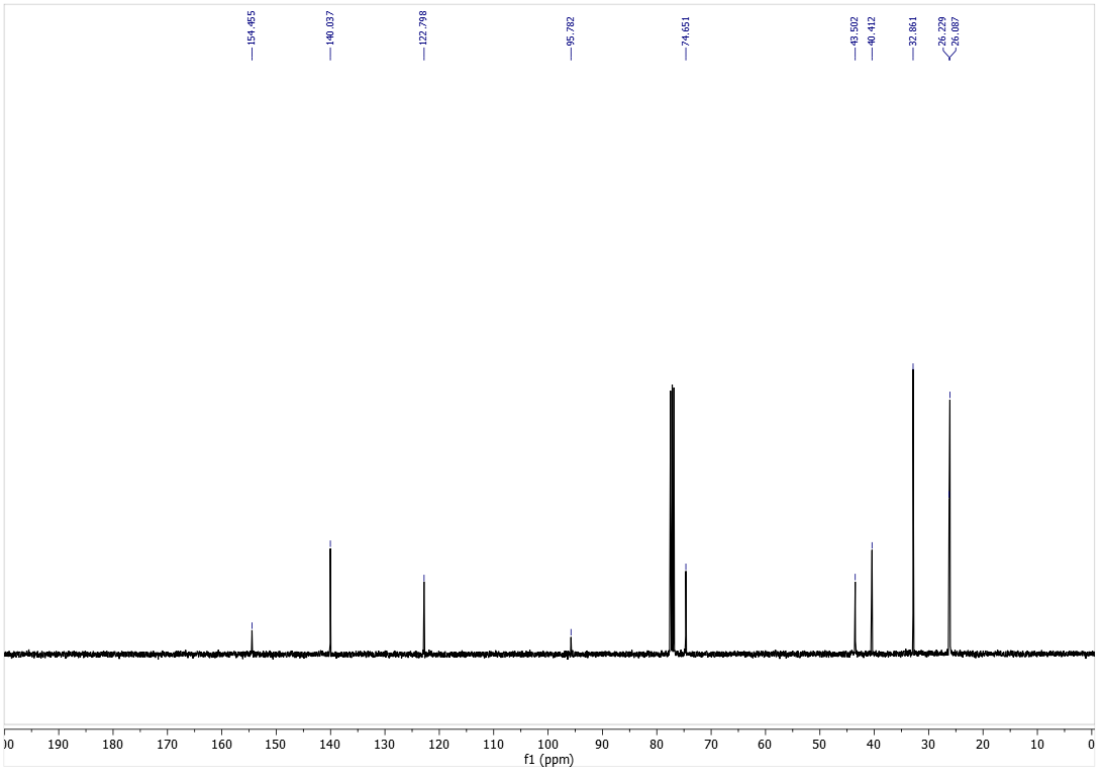
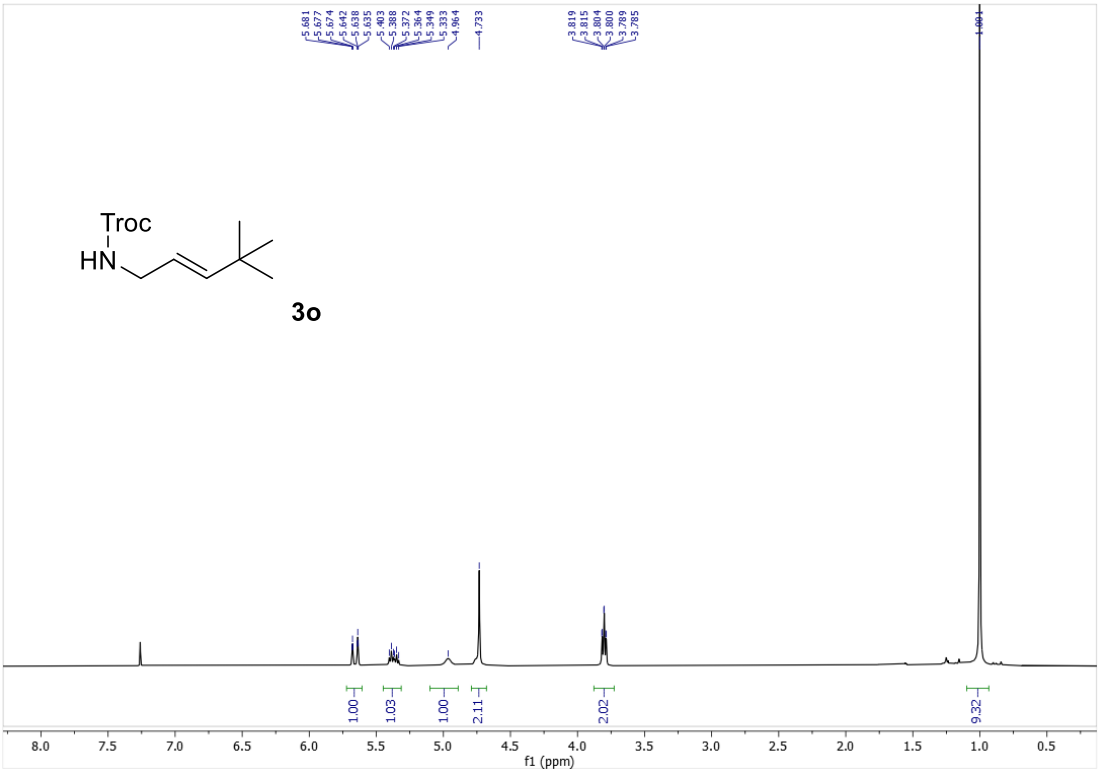
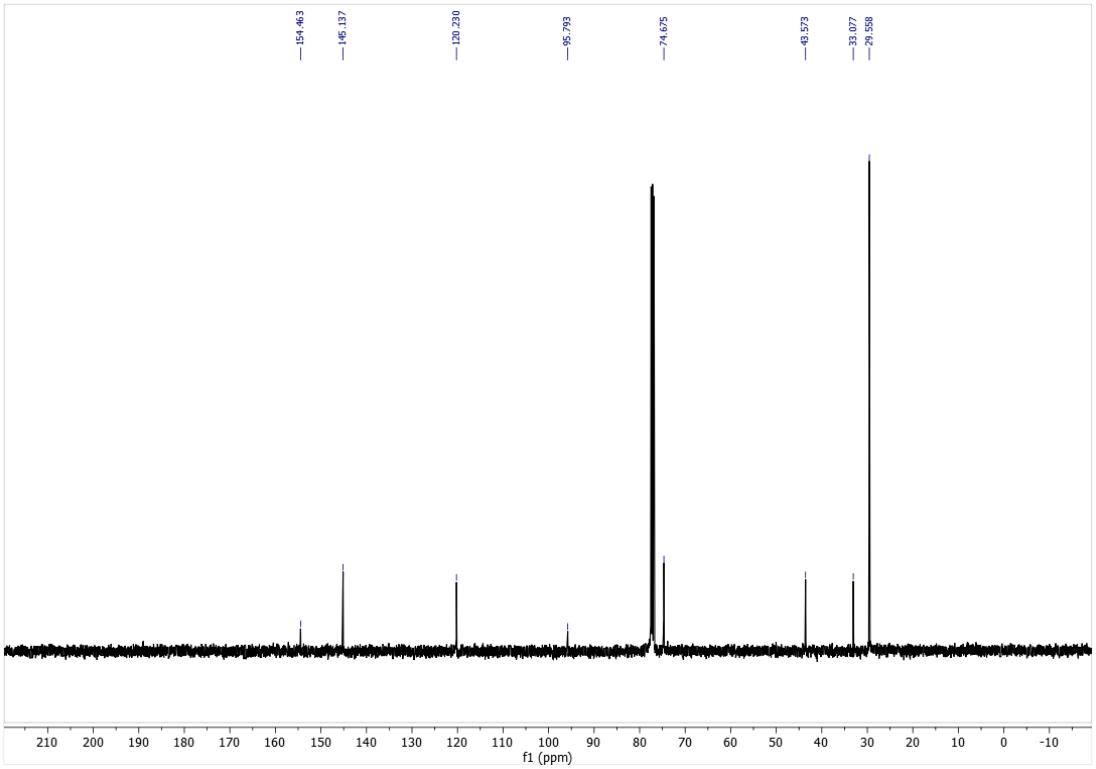
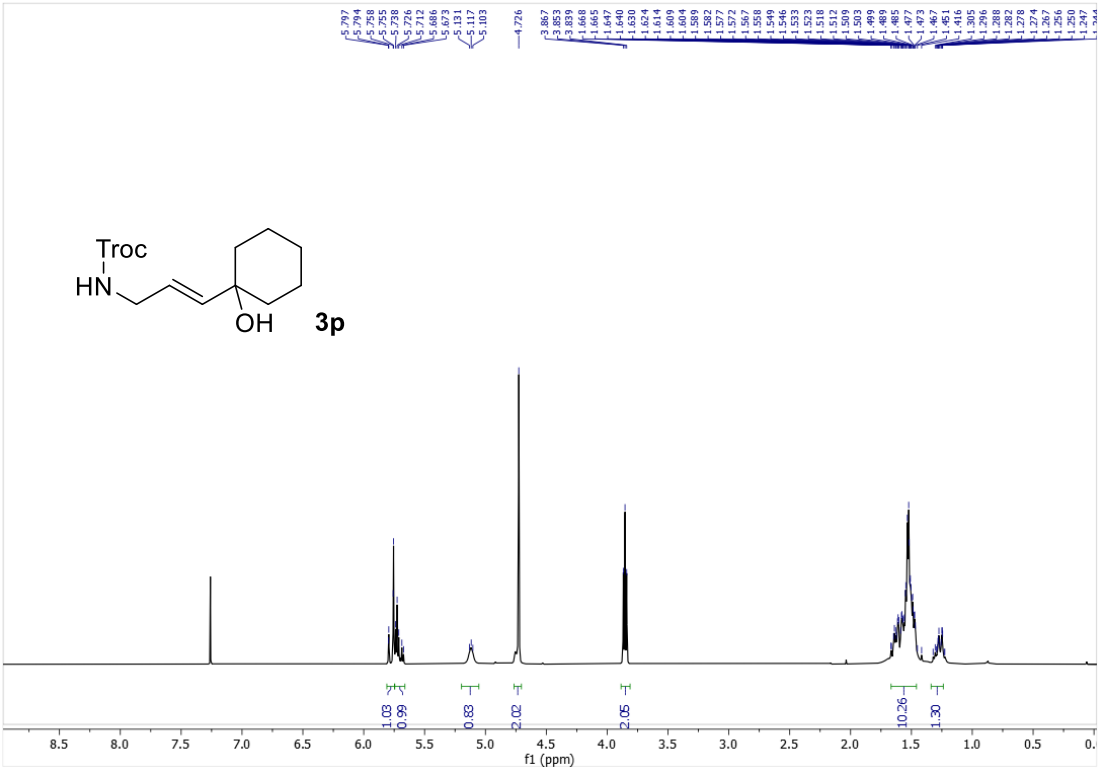
126.755
123.984
95.719
74.670
65.478
43.134
34.438
33.833
27.514
22.180
13.779
f1 (ppm)

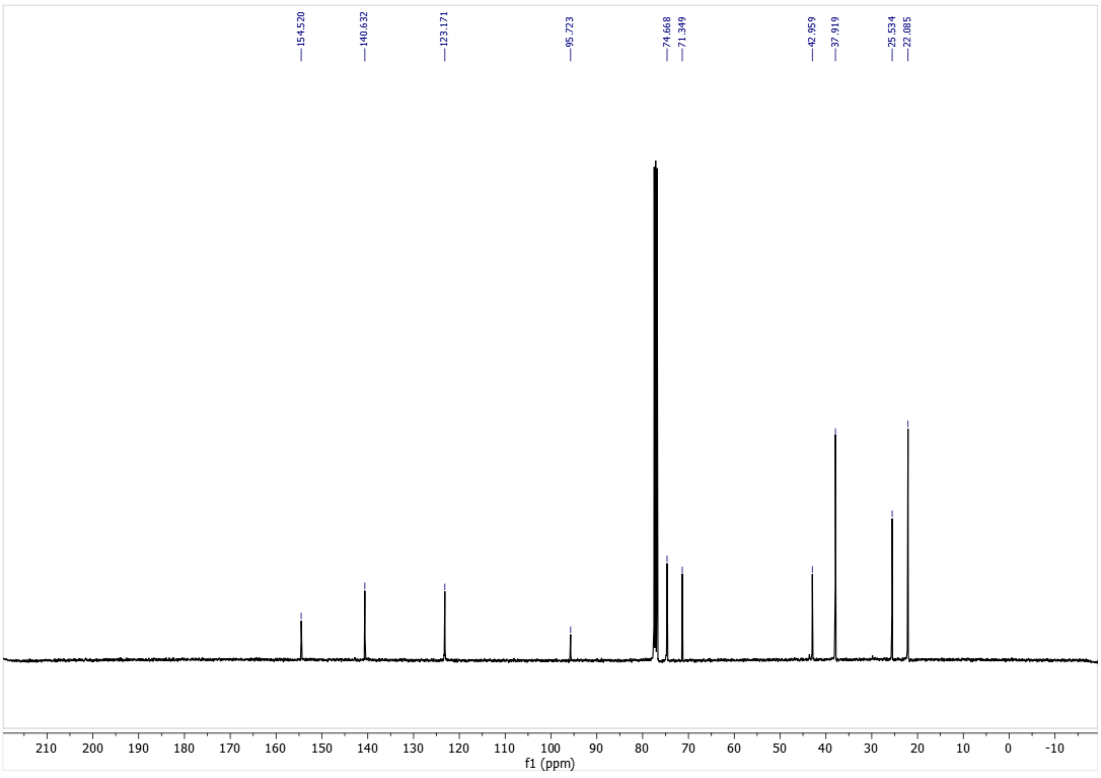

Troc
HN
3n
0.96
0.99
0.88
2.14
1.94
1.02
5.66
5.74
f1 (ppm)

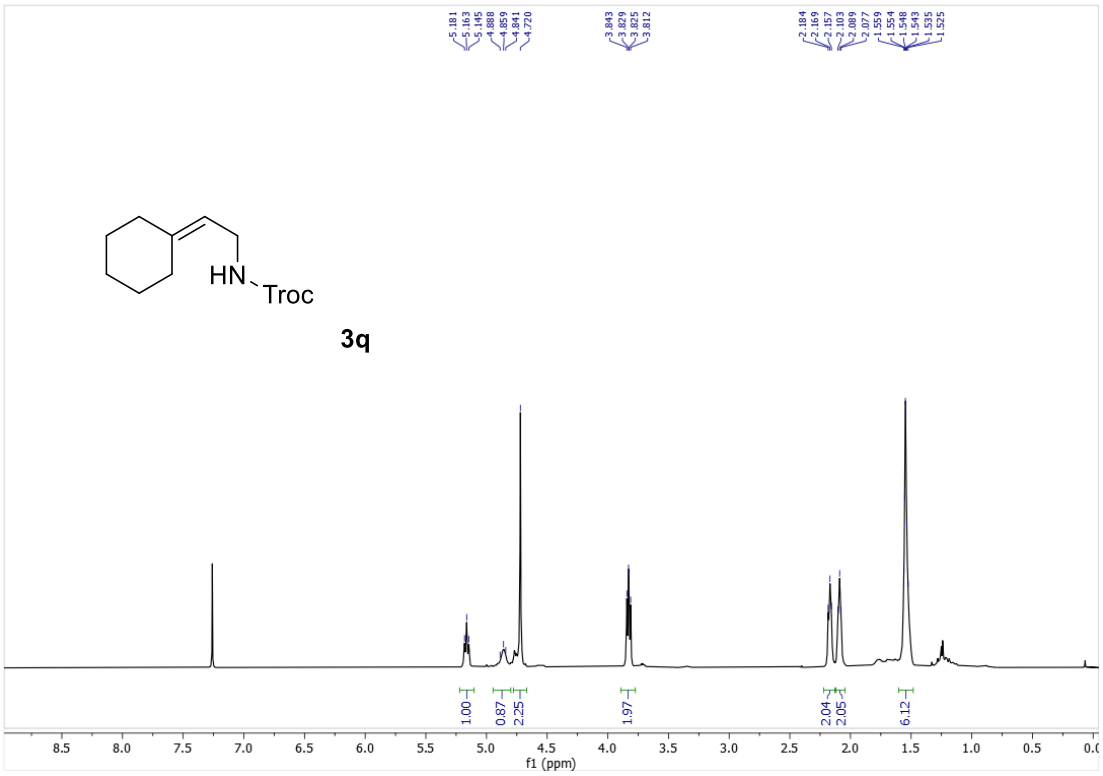

154.455
140.037
122.798
95.782
74.651
43.502
40.412
32.861
26.229
26.087
f1 (ppm)


Troc
HN
3o
5.681
5.677
5.674
5.642
5.638
5.635
5.403
5.388
5.372
5.344
5.340
5.333
4.964
4.733
3.819
3.815
3.804
3.800
3.789
3.785
1.001
1.00
1.03
1.00
2.11
2.02
9.32
f1 (ppm)

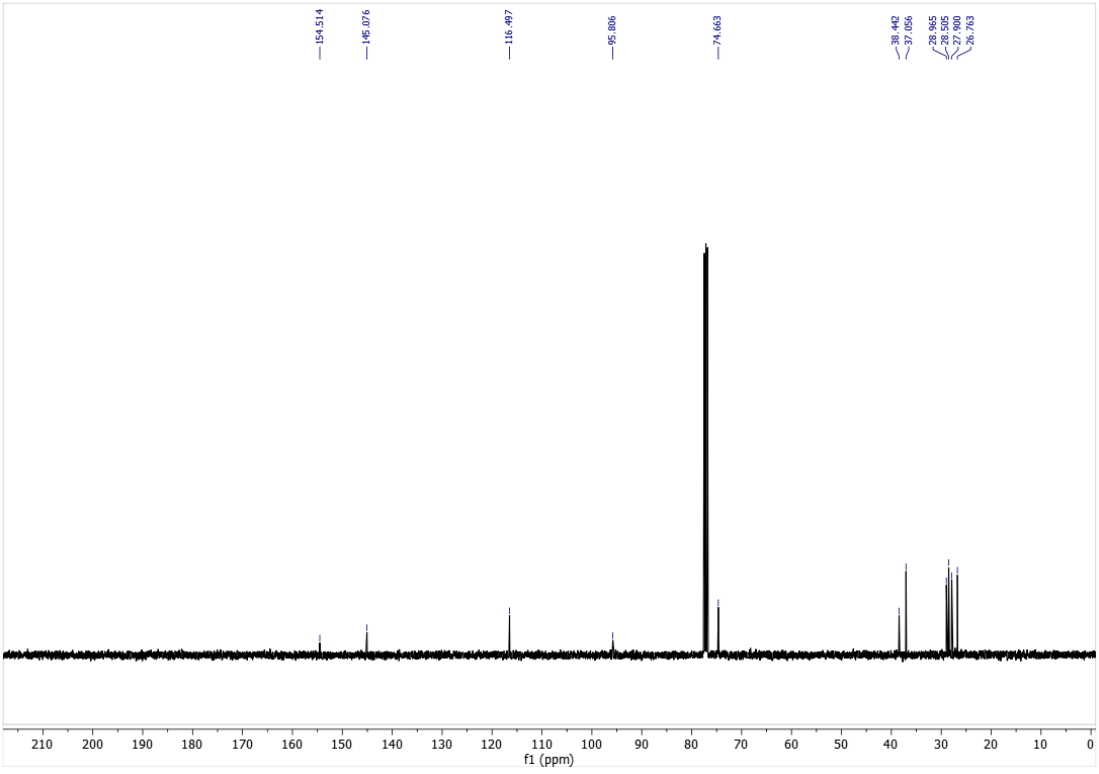

154.463
146.137
120.230
95.793
74.675
43.573
33.077
29.558
f1 (ppm)

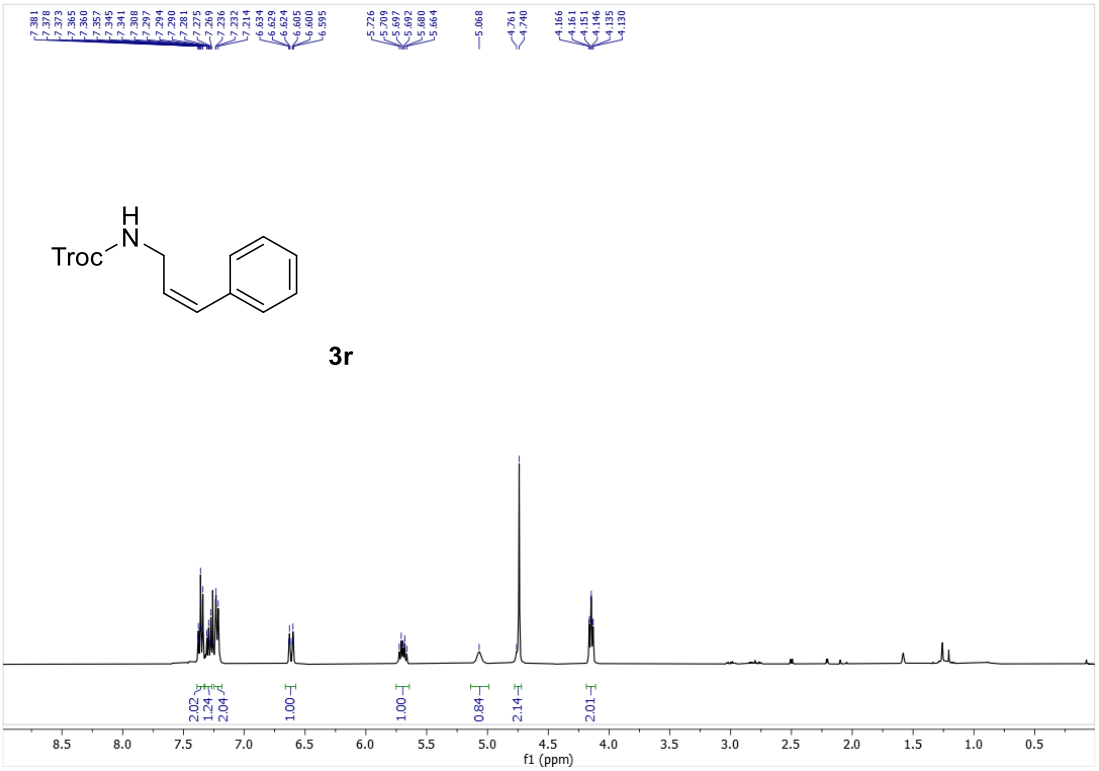

Troc
HN
OH
3p
f1 (ppm)


f1 (ppm)

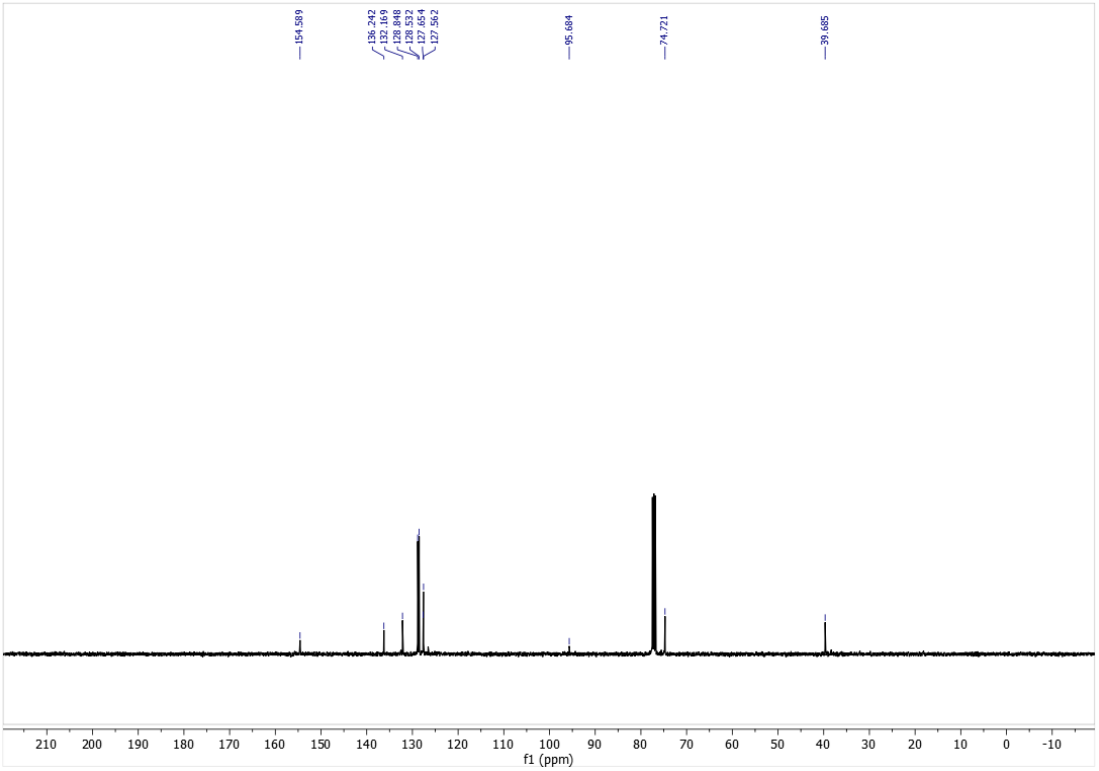

HN
Troc
5.181
5.163
5.145
4.888
4.859
4.841
4.720
3.843
3.829
3.825
3.812
2.184
2.169
2.157
2.103
2.089
2.077
1.559
1.554
1.548
1.543
1.535
1.525
1.00
0.87
2.25
1.97
2.04
2.05
6.12
f1 (ppm)

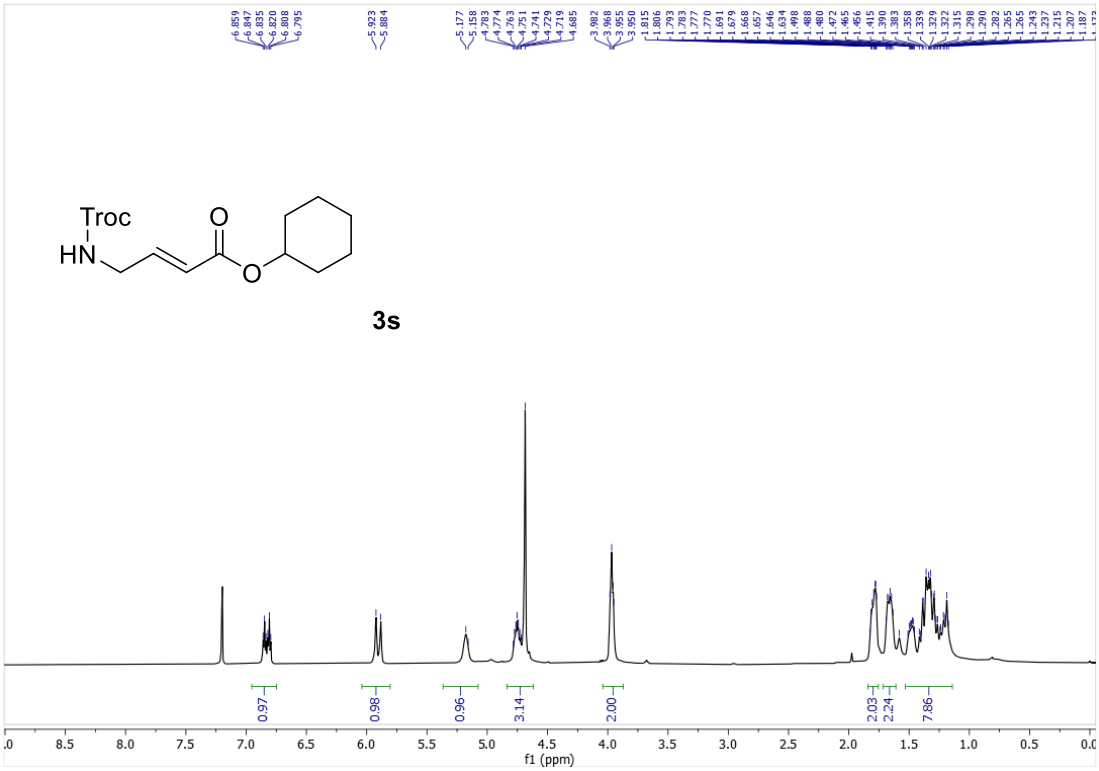
3q

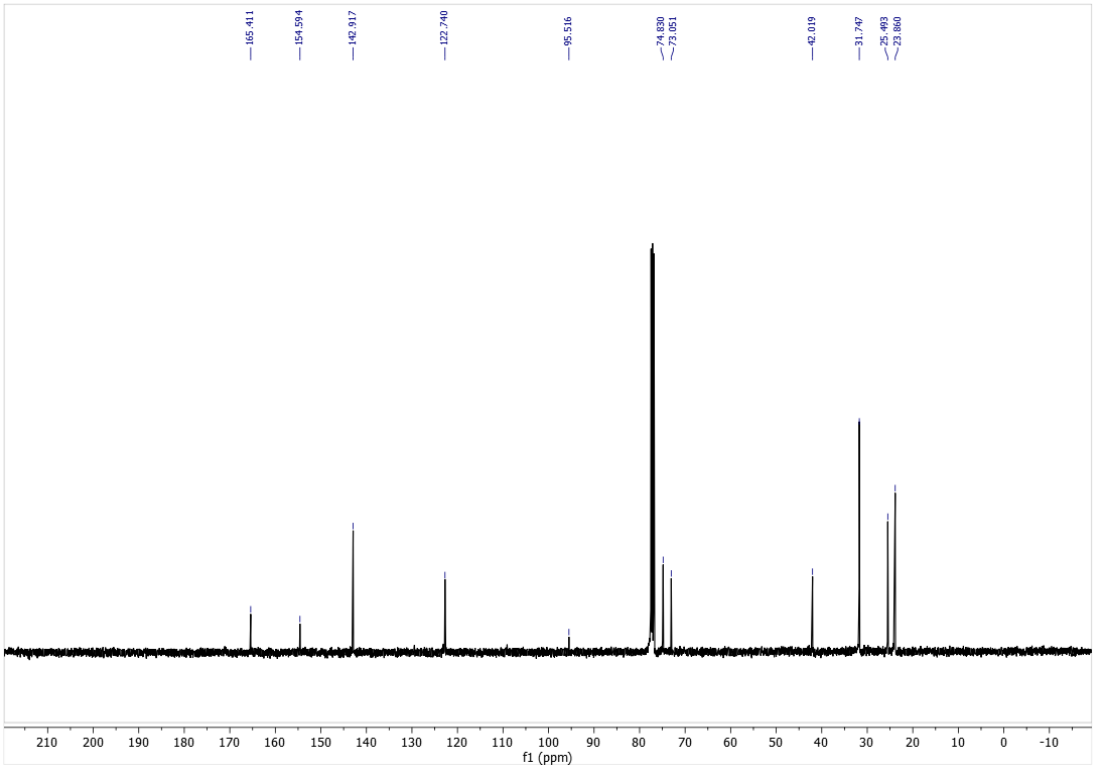

154.514
145.076
116.497
95.806
74.663
38.442
37.056
28.965
28.595
27.900
26.763
f1 (ppm)

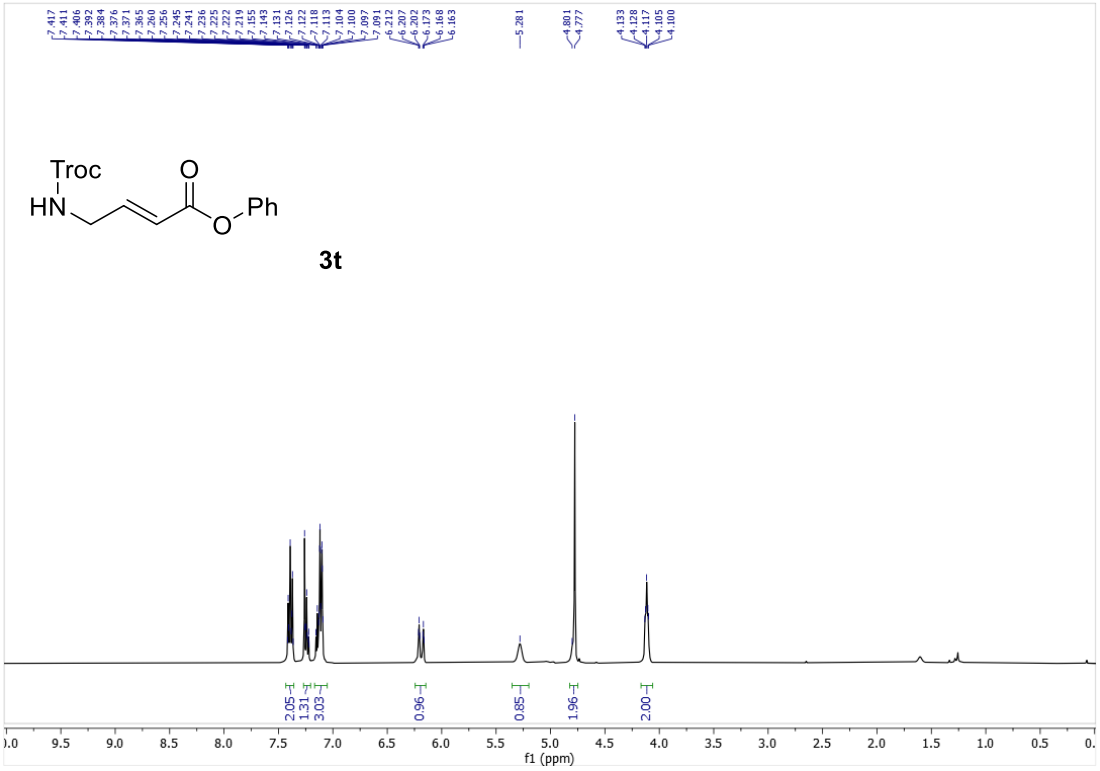

7.381
7.378
7.373
7.365
7.360
7.357
7.345
7.341
7.308
7.297
7.294
7.290
7.281
7.275
7.269
7.236
7.232
7.214
6.634
6.629
6.624
6.605
6.600
6.595
5.726
5.709
5.697
5.692
5.680
5.664
5.068
4.761
4.740
4.166
4.161
4.151
4.146
4.135
4.130
H
N
Troc
2.02
1.24
2.04
1.00
1.00
0.84
2.14
2.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

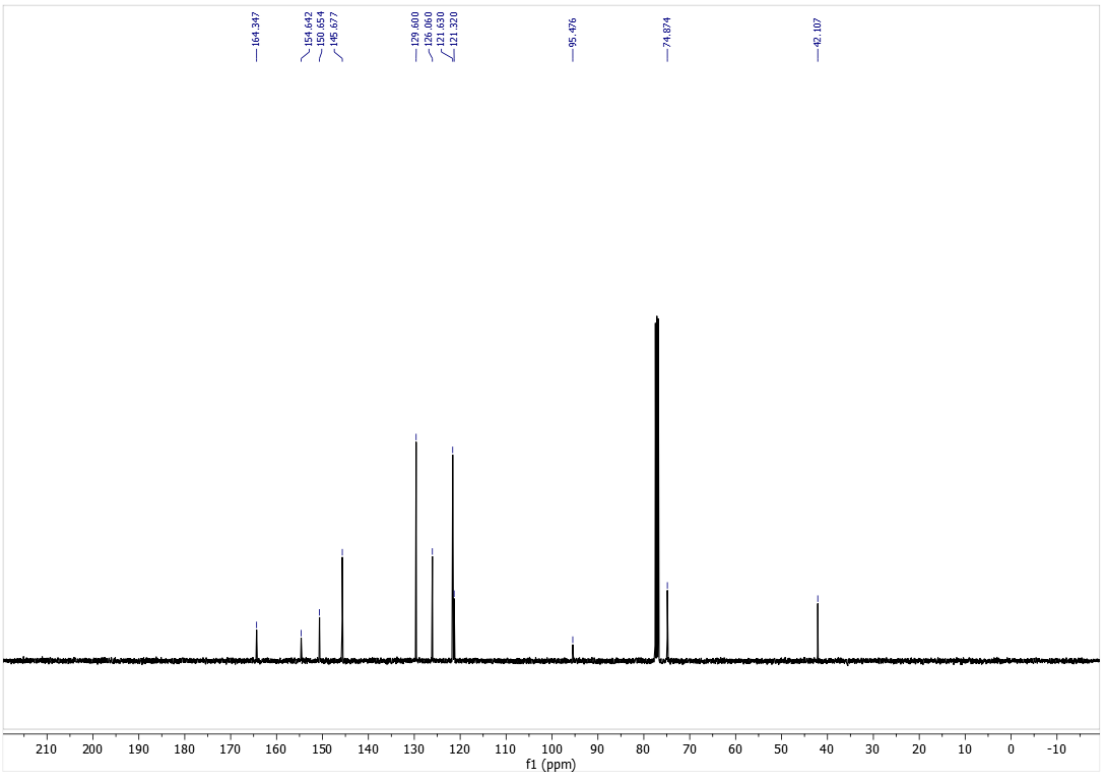
3r

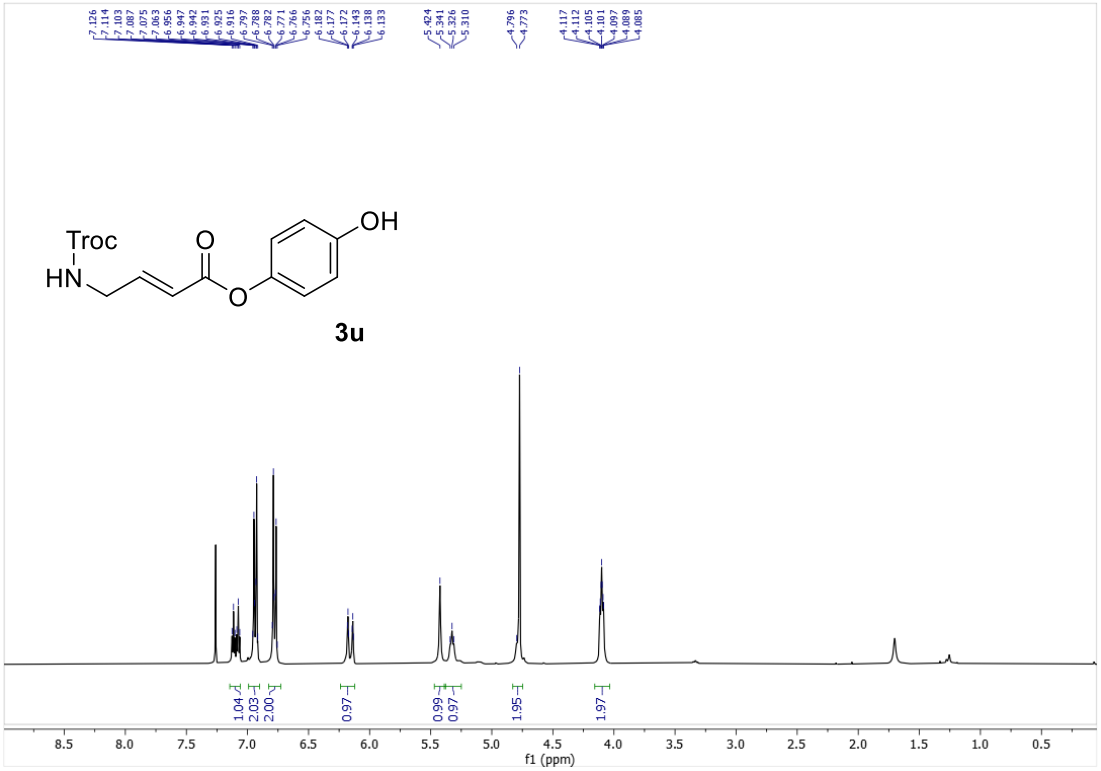

154.589
136.242
132.169
128.848
128.532
127.654
127.562
95.684
74.721
39.685
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

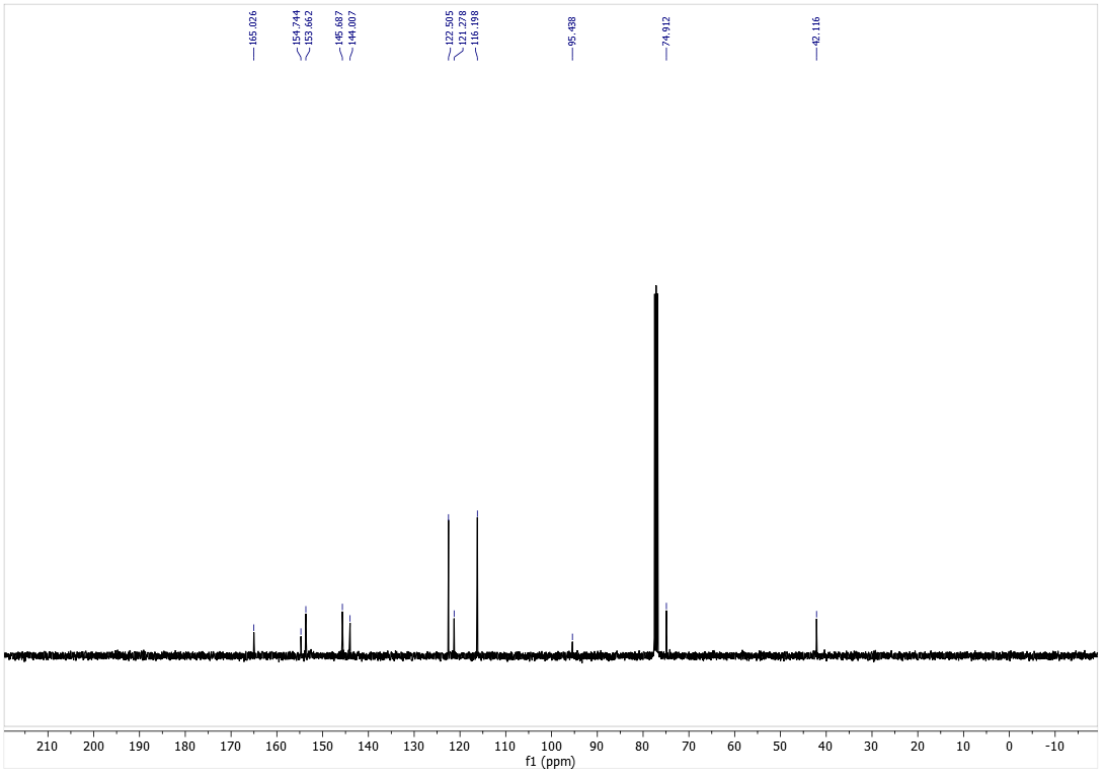

Troc
HN
O
O
3s
0.97
0.98
0.96
3.14
2.00
2.03
2.24
7.86
f1 (ppm)

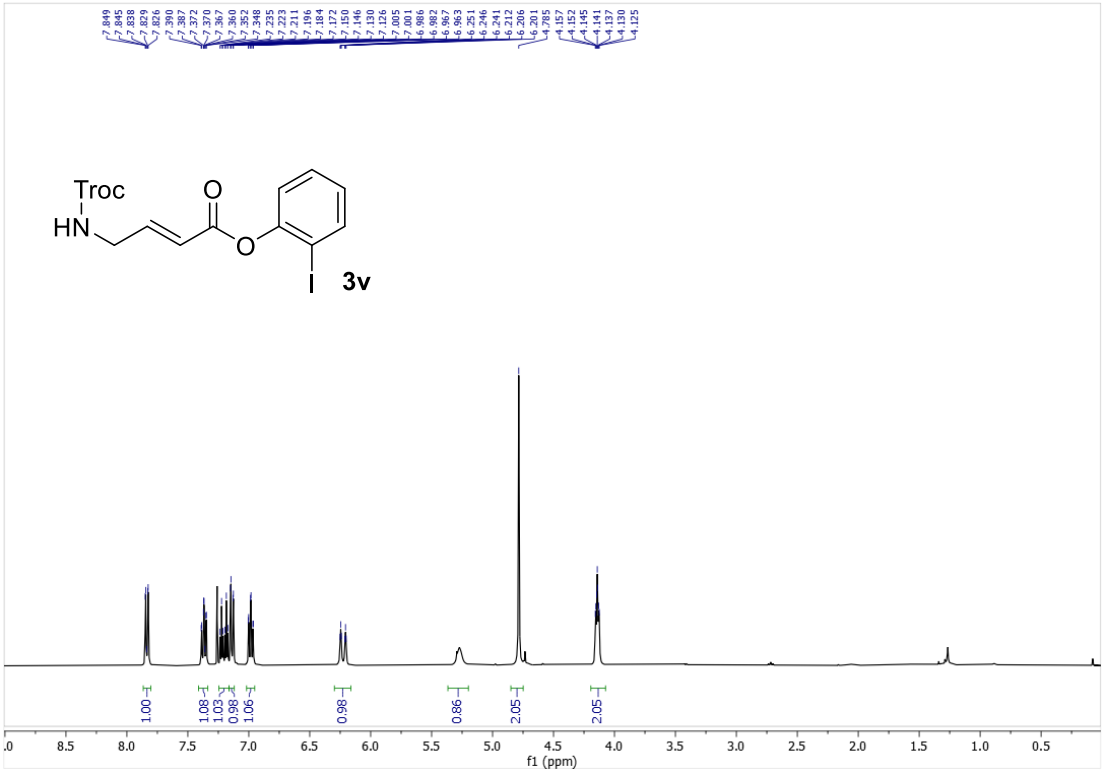

165.411
154.594
142.917
122.740
95.516
74.830
73.051
42.019
31.747
25.493
23.860
f1 (ppm)

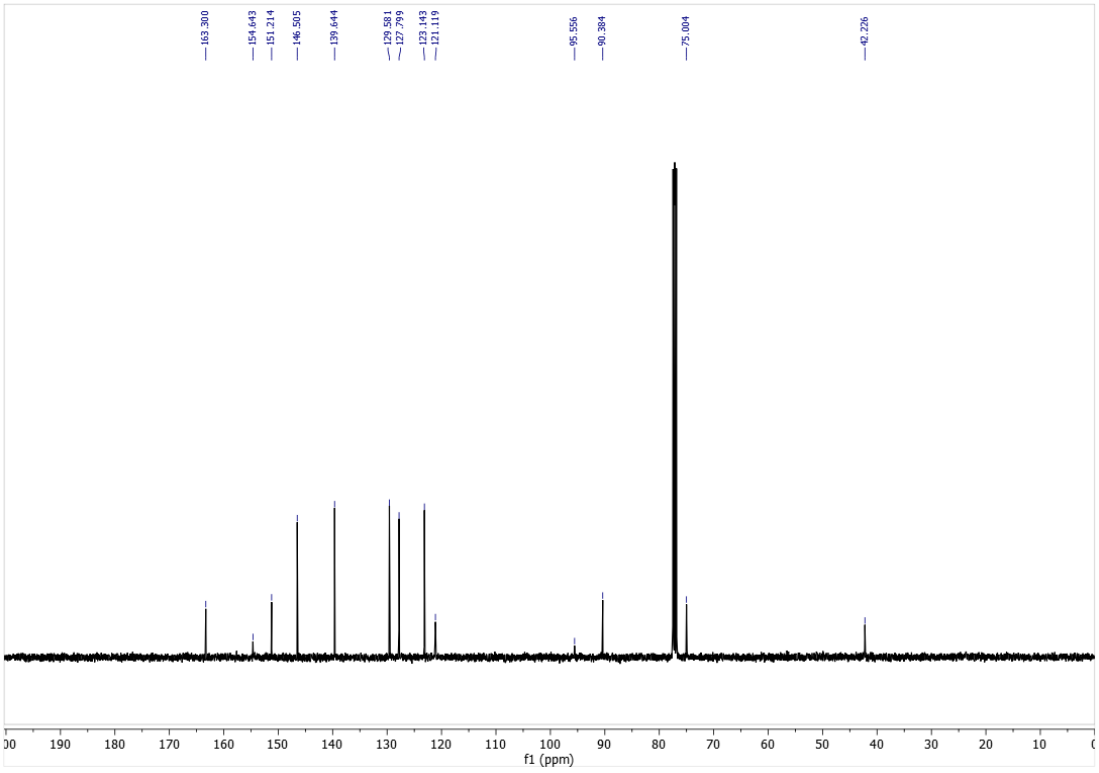

7.417
7.411
7.406
7.392
7.384
7.376
7.371
7.365
7.260
7.256
7.245
7.241
7.236
7.225
7.222
7.219
7.155
7.143
7.131
7.126
7.122
7.118
7.113
7.104
7.100
7.097
7.091
6.212
6.207
6.202
6.173
6.168
6.163
5.281
4.801
4.777
4.133
4.128
4.117
4.105
4.100
Troc
HN
O
O
Ph
3t
2.05
1.31
3.03
0.96
0.85
1.96
2.00
f1 (ppm)

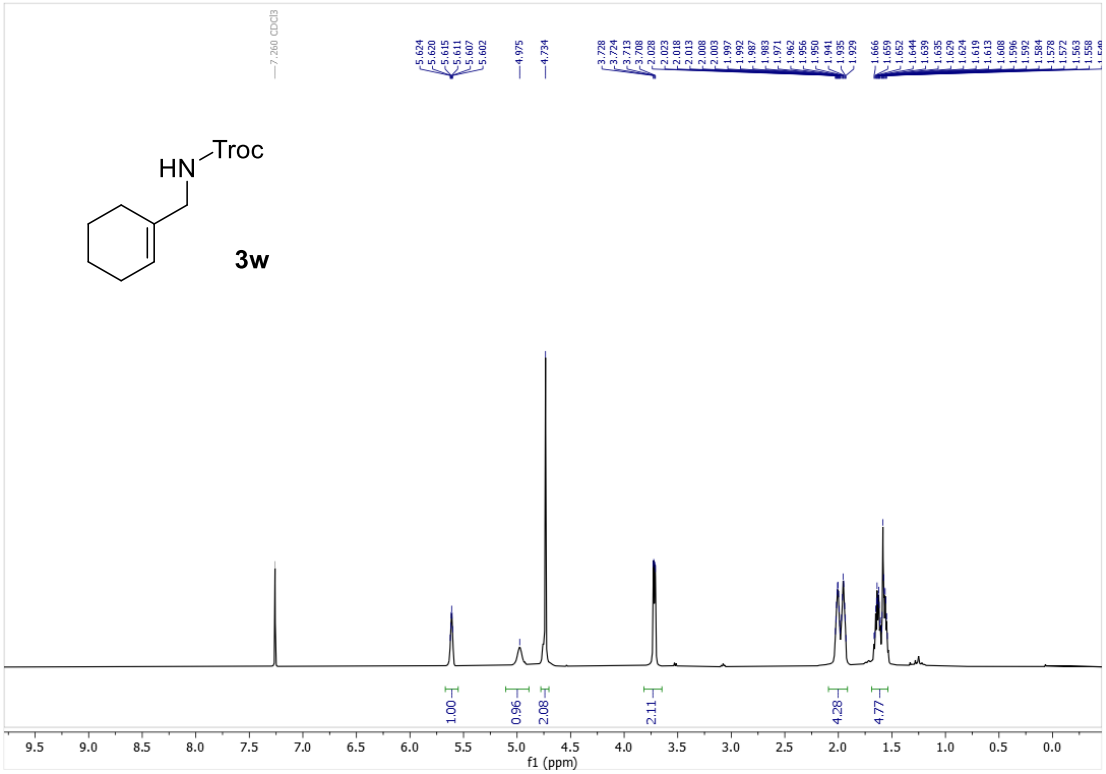

164.347
154.642
150.654
146.877
129.600
126.060
121.630
121.320
95.476
74.874
42.107
f1 (ppm)

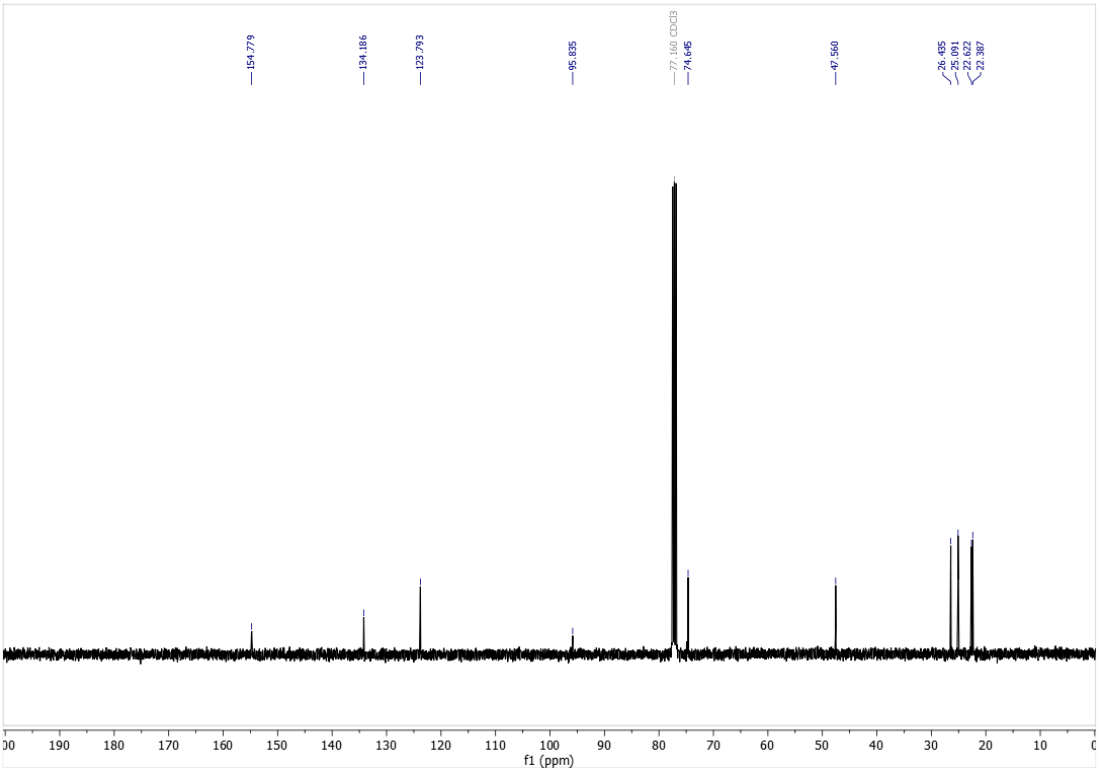

Troc
HN
O
O
OH
3u
f1 (ppm)

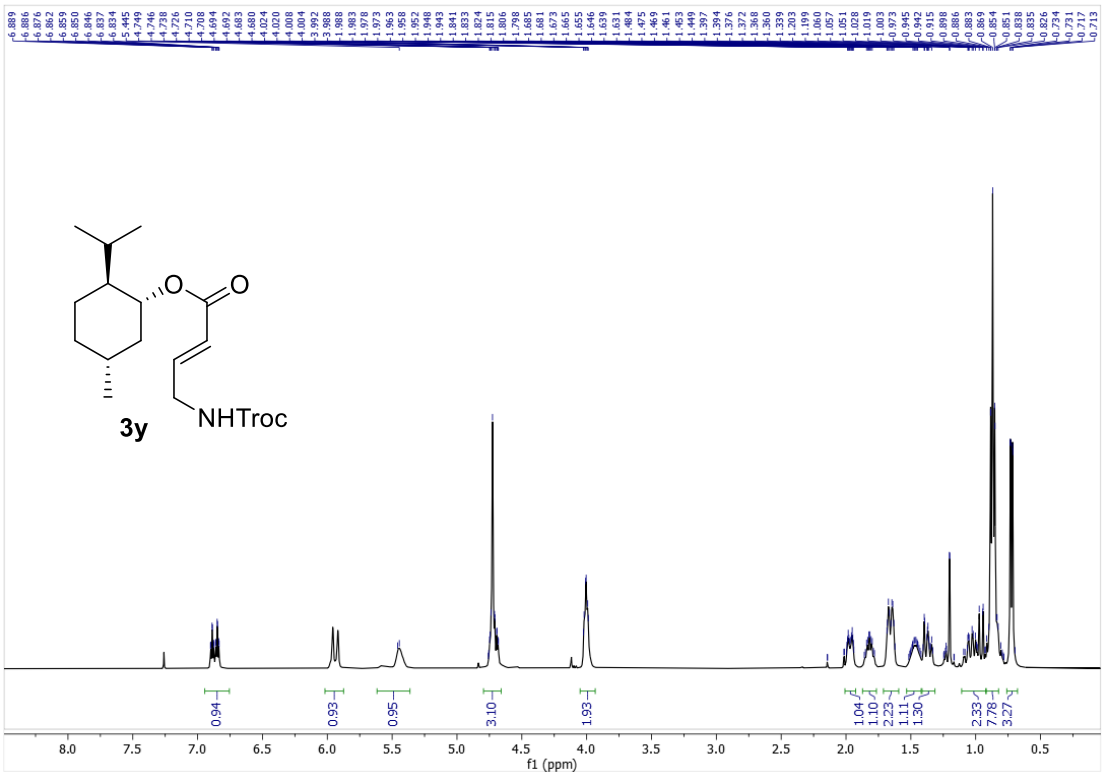

f1 (ppm)

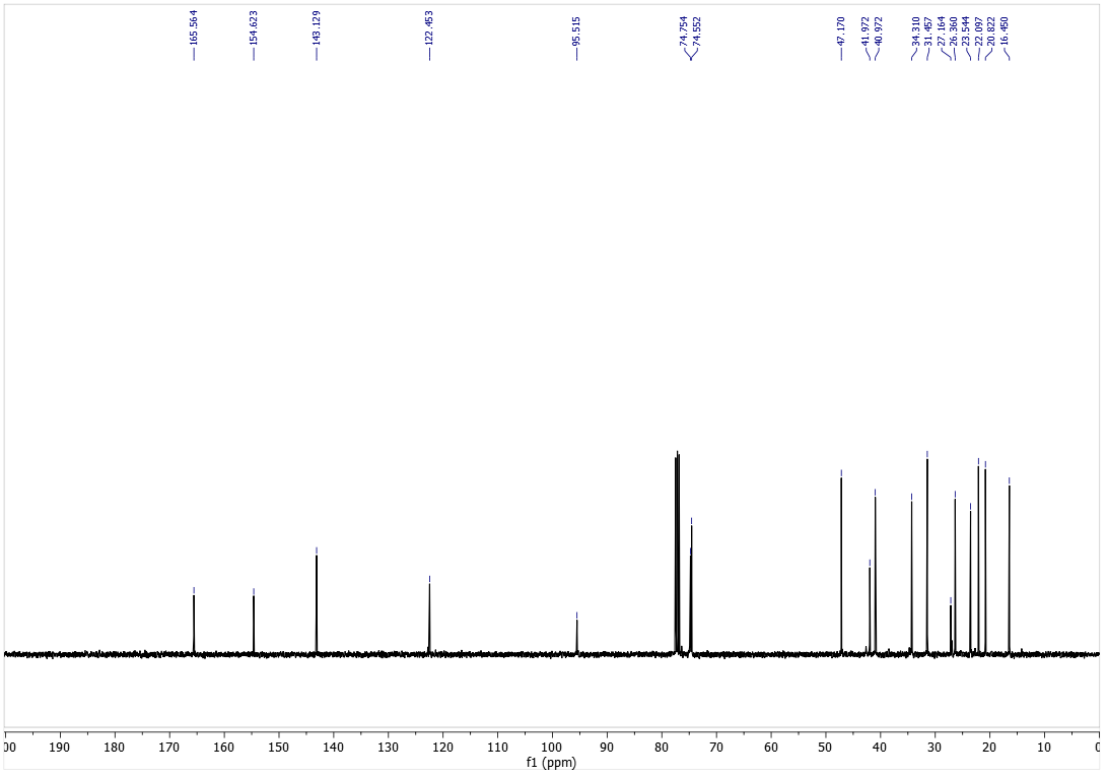

Troc
HN
O
O
I
3v
f1 (ppm)

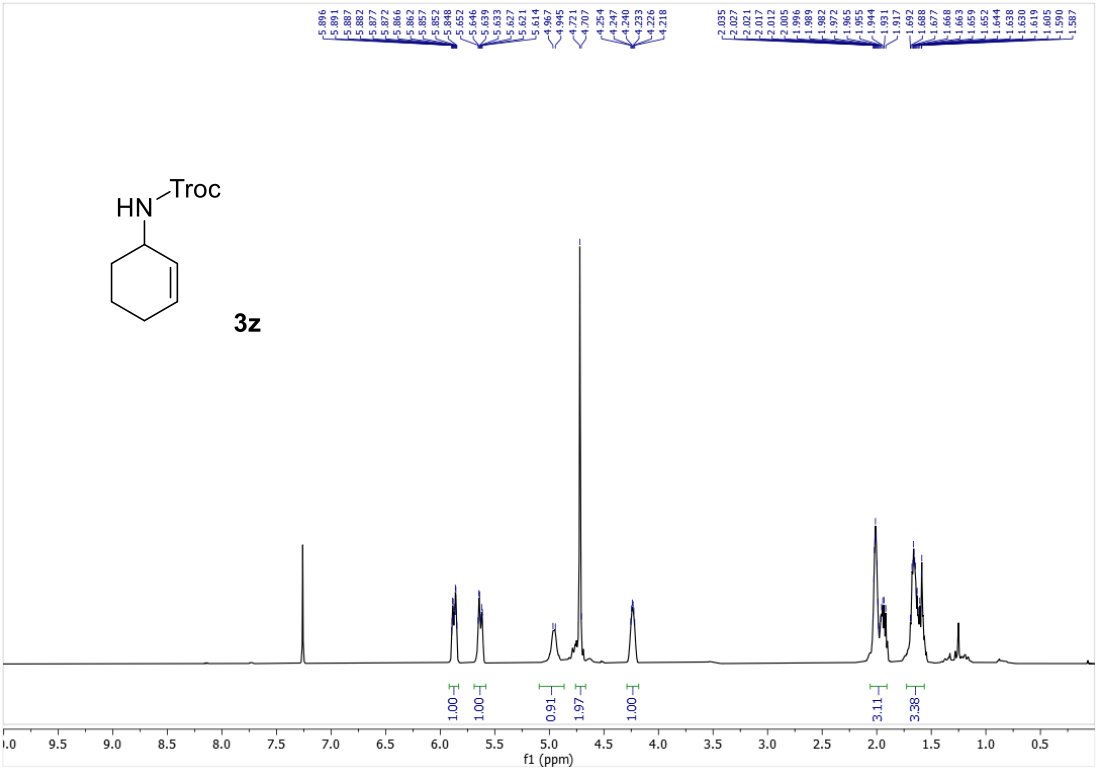

163.300
154.643
151.214
146.505
139.644
129.581
127.799
123.143
121.119
95.556
90.384
75.004
42.226
f1 (ppm)

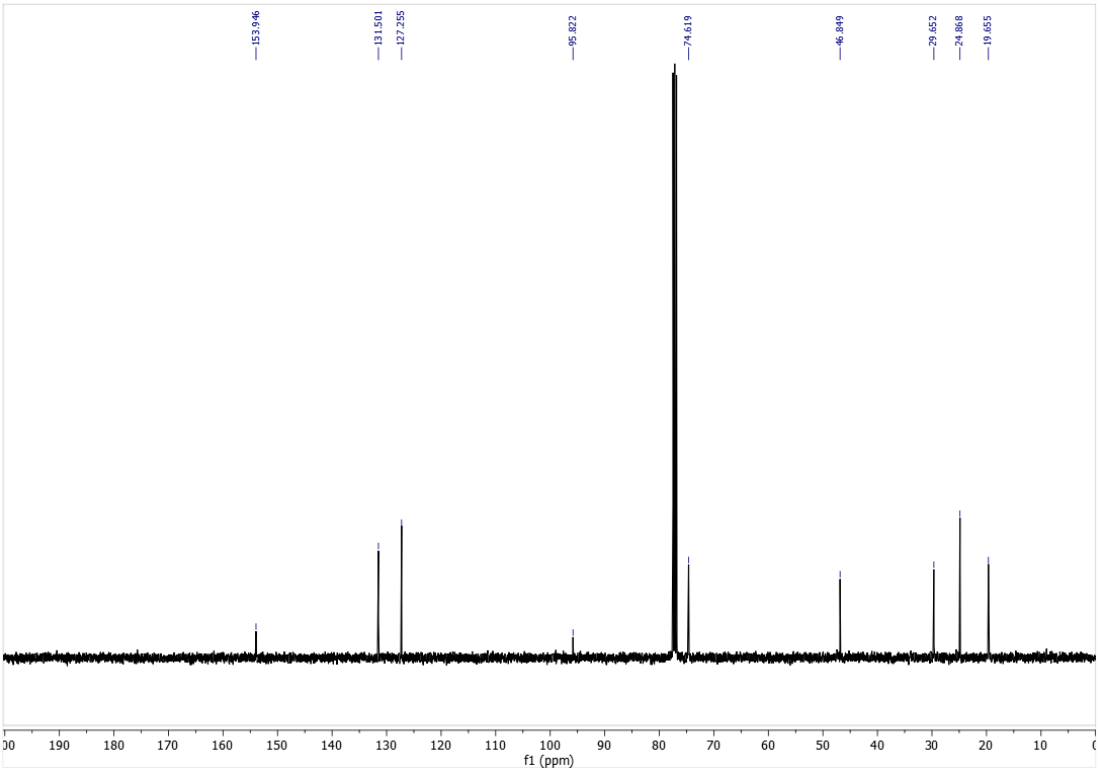

HN
Troc
3w
1.00
0.96
2.08
2.11
4.28
4.77
f1 (ppm)

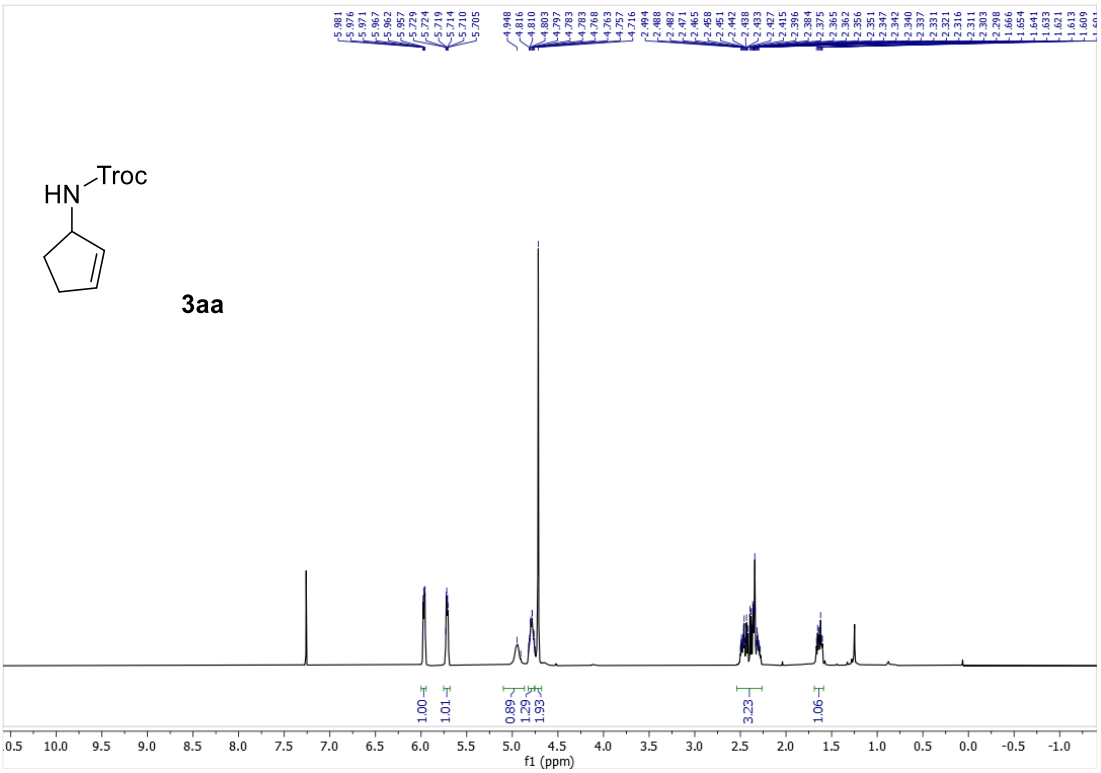

154.779
134.186
123.793
95.835
77.160 CDCl3
74.645
47.560
26.435
25.091
22.622
22.387
f1 (ppm)

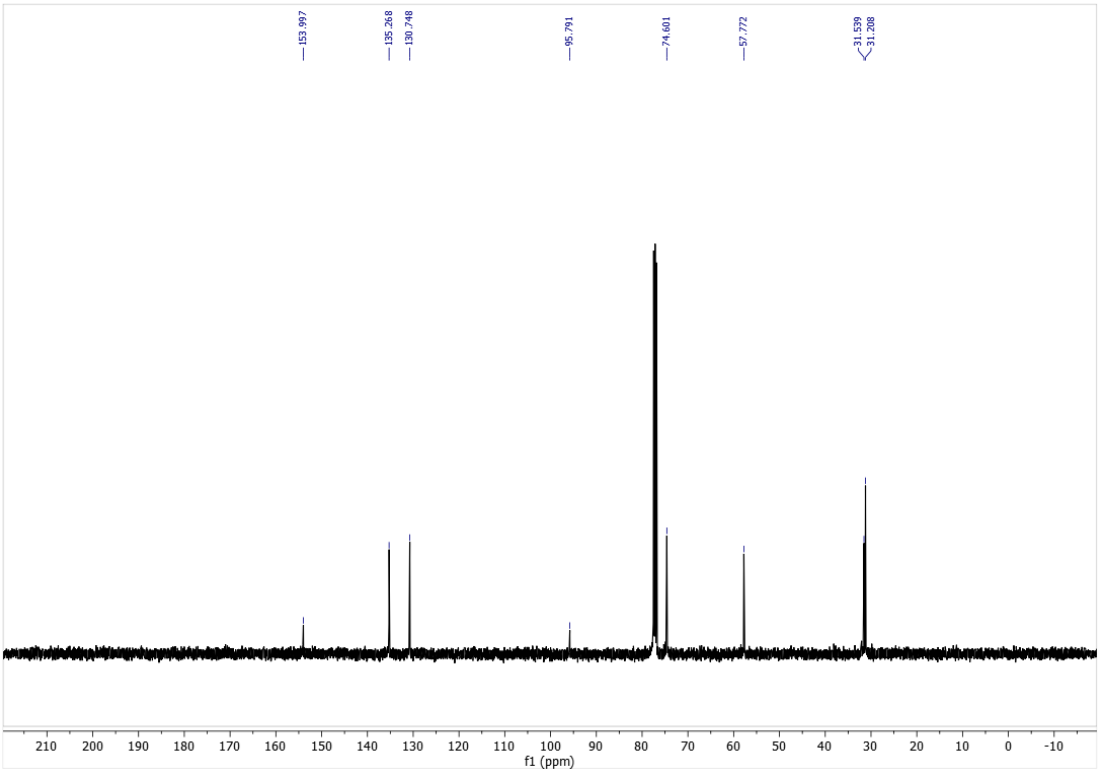

O
O
NHTroc
3y
0.94
0.93
0.95
3.10
1.93
1.04
1.10
2.23
1.11
1.30
2.33
7.78
3.27
f1 (ppm)

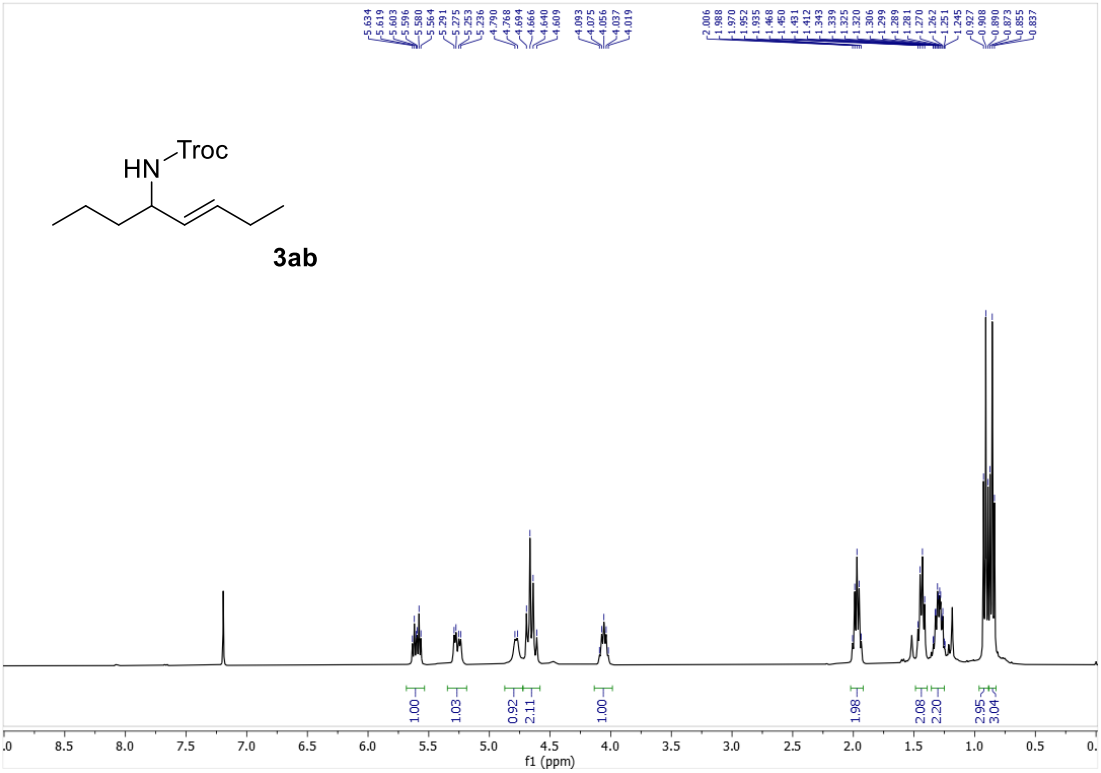

165.564
154.623
143.129
122.453
95.515
74.754
74.552
47.170
41.972
40.972
34.310
31.457
27.164
26.360
23.544
22.697
20.822
16.460
f1 (ppm)

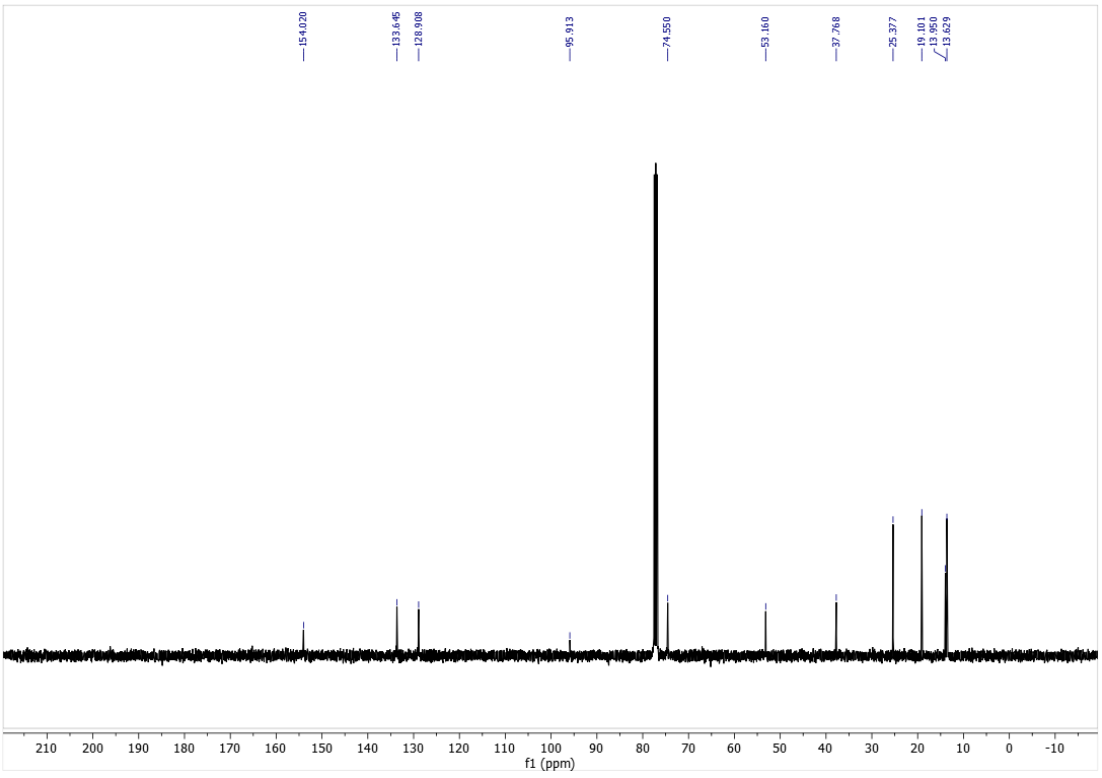

HN
Troc
3z
1.00
1.00
0.91
1.97
1.00
3.11
3.38
f1 (ppm)

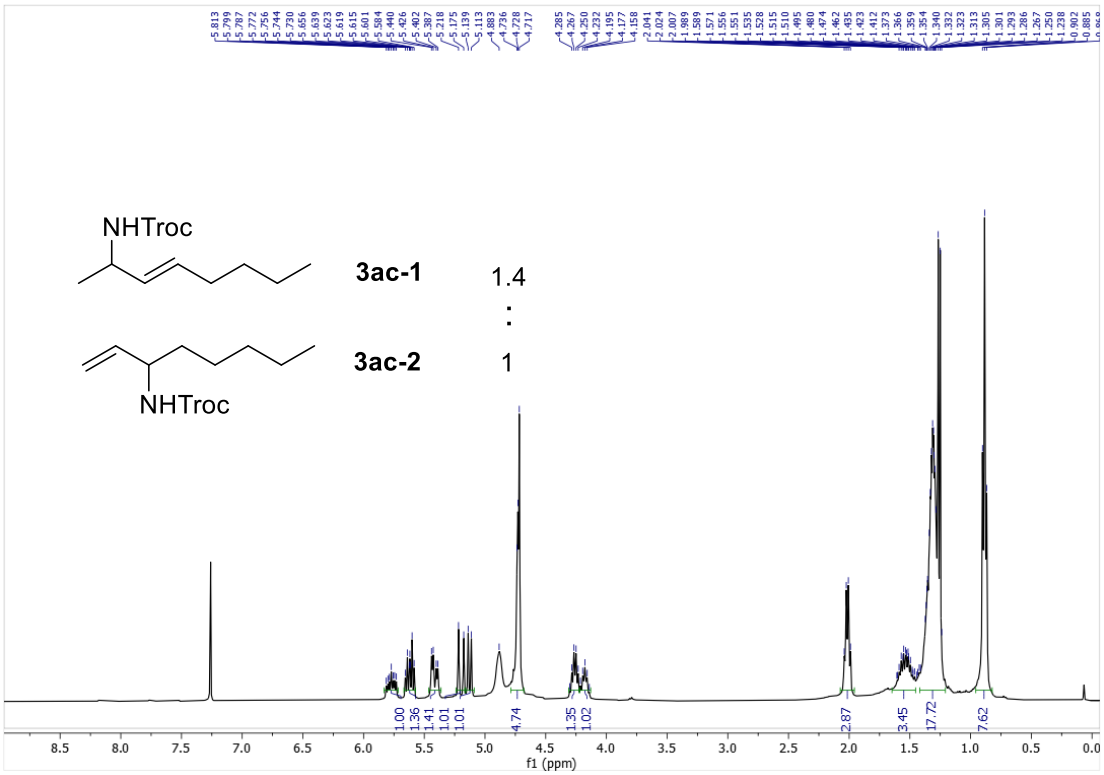

153.946
131.501
127.255
95.822
74.619
46.849
29.652
24.868
19.655
f1 (ppm)

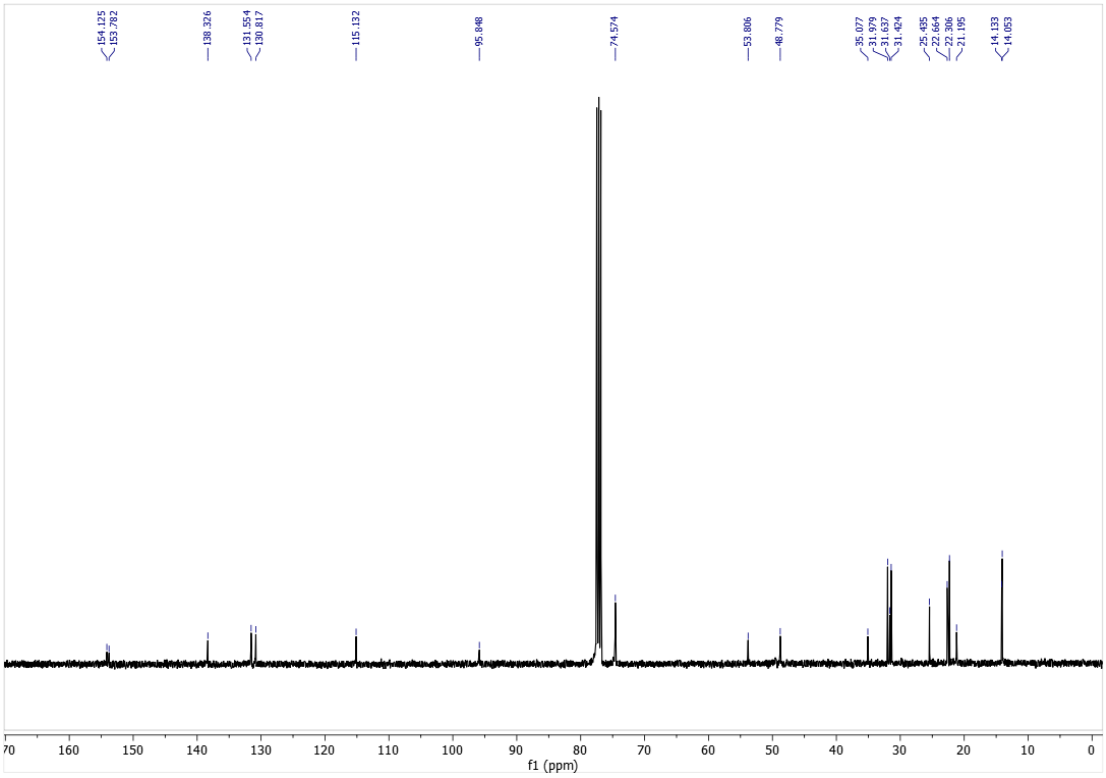

HN
Troc
3aa
1.00
1.01
0.89
1.29
1.93
3.23
1.06
f1 (ppm)

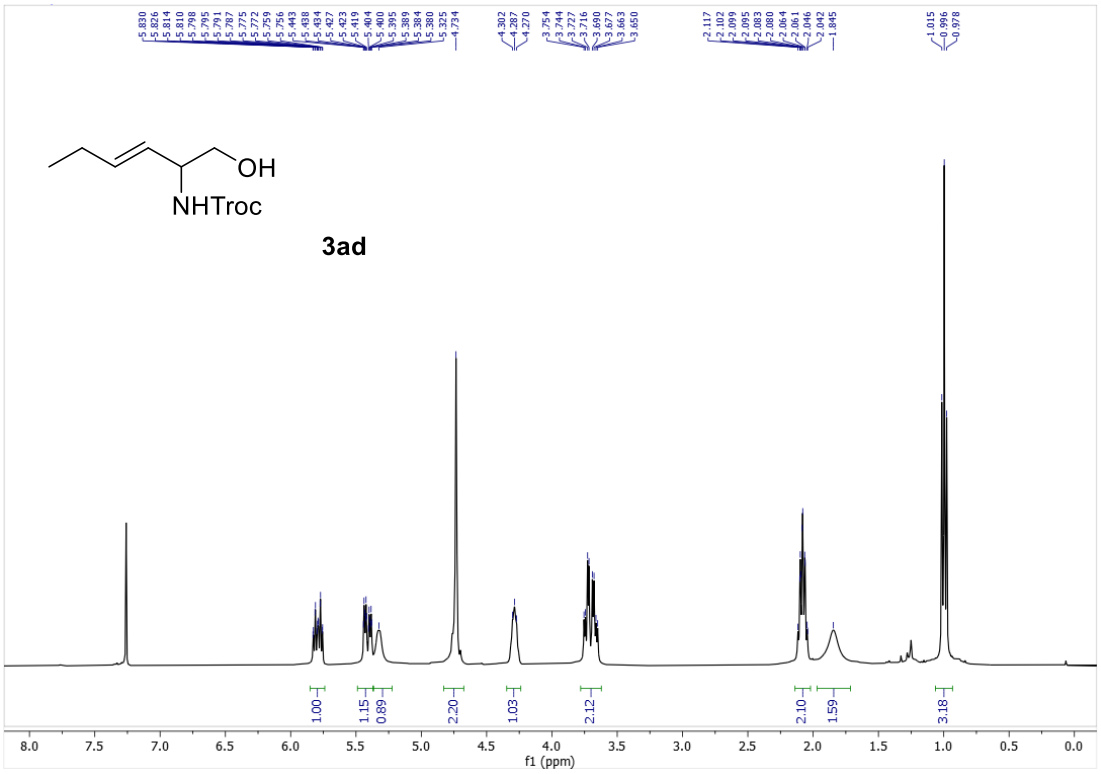

153.997
135.268
130.748
95.791
74.601
57.772
31.539
31.208
f1 (ppm)

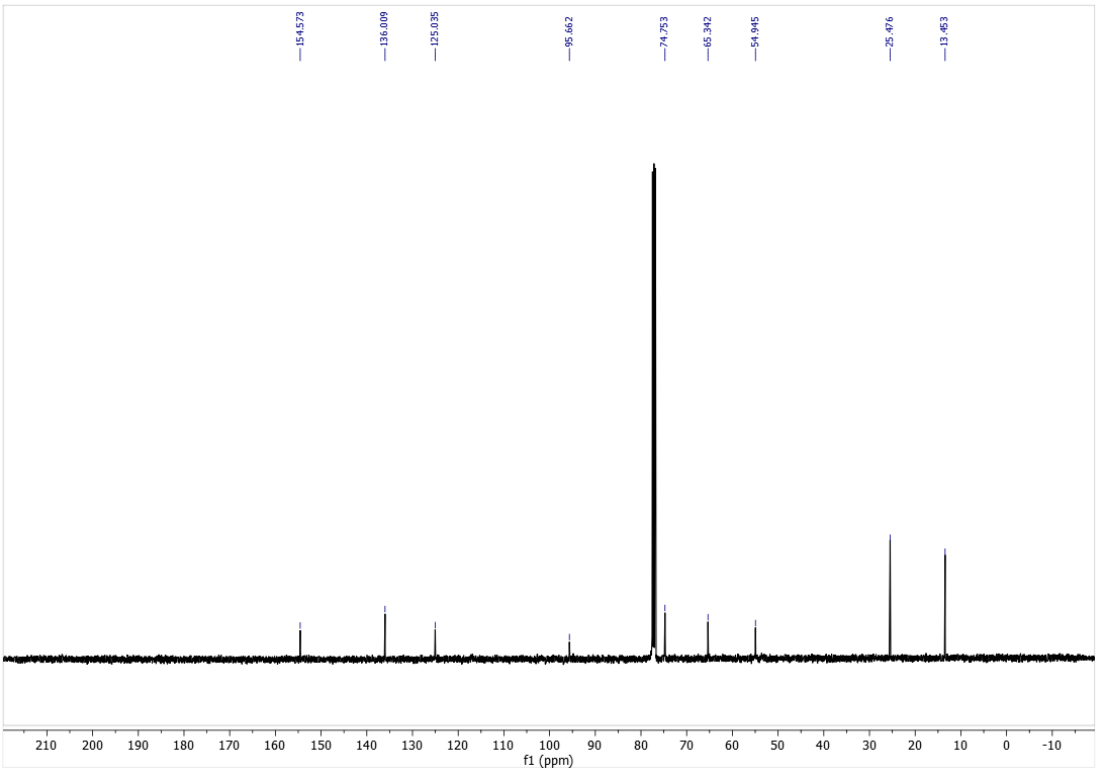

HN
Troc
3ab
f1 (ppm)

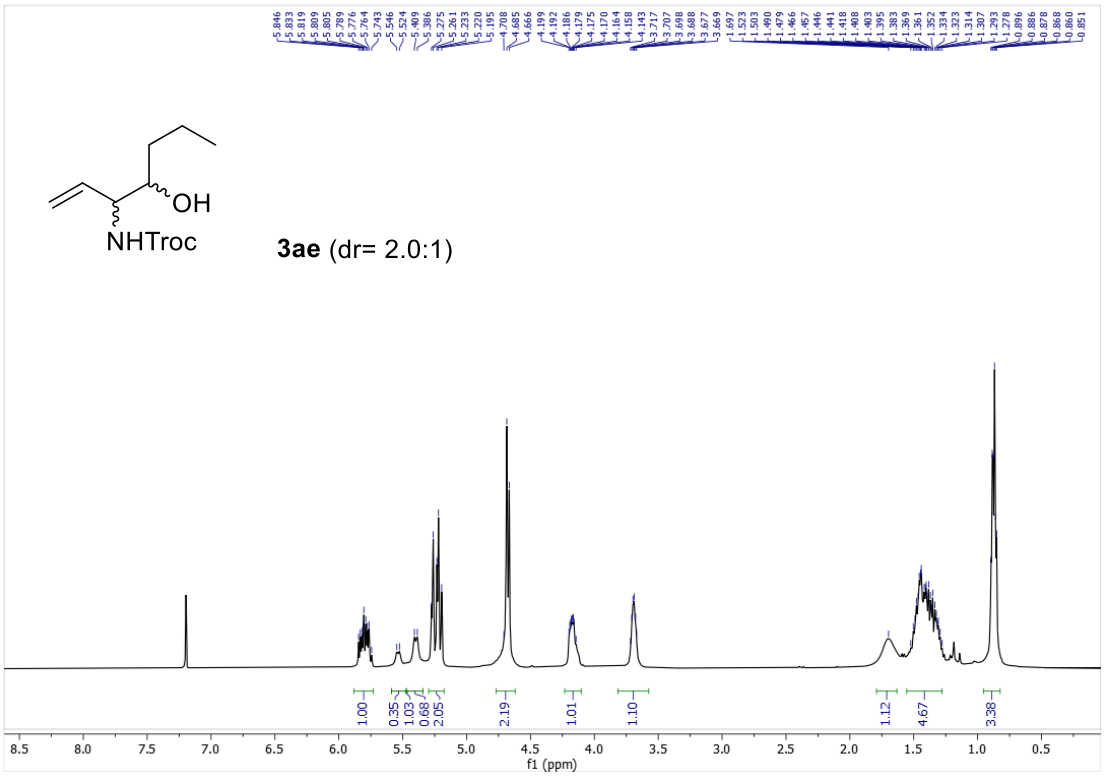

f1 (ppm)

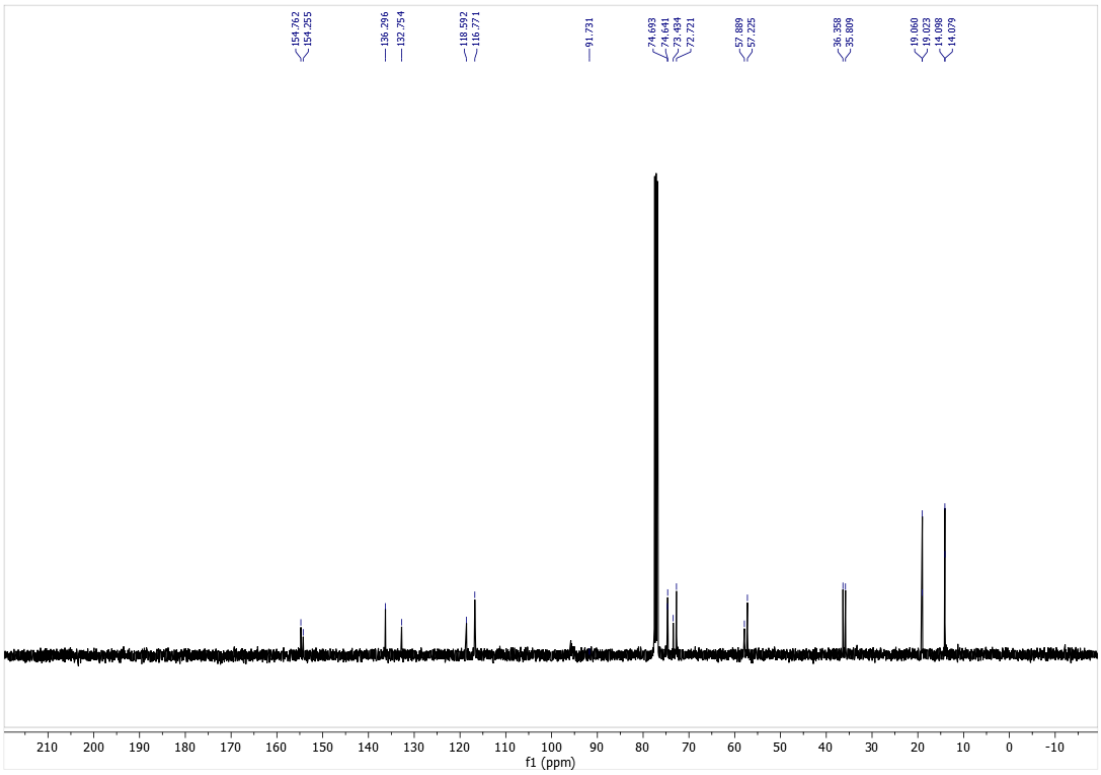

NHTroc
3ac-1
1.4
:
3ac-2
1
NHTroc
f1 (ppm)

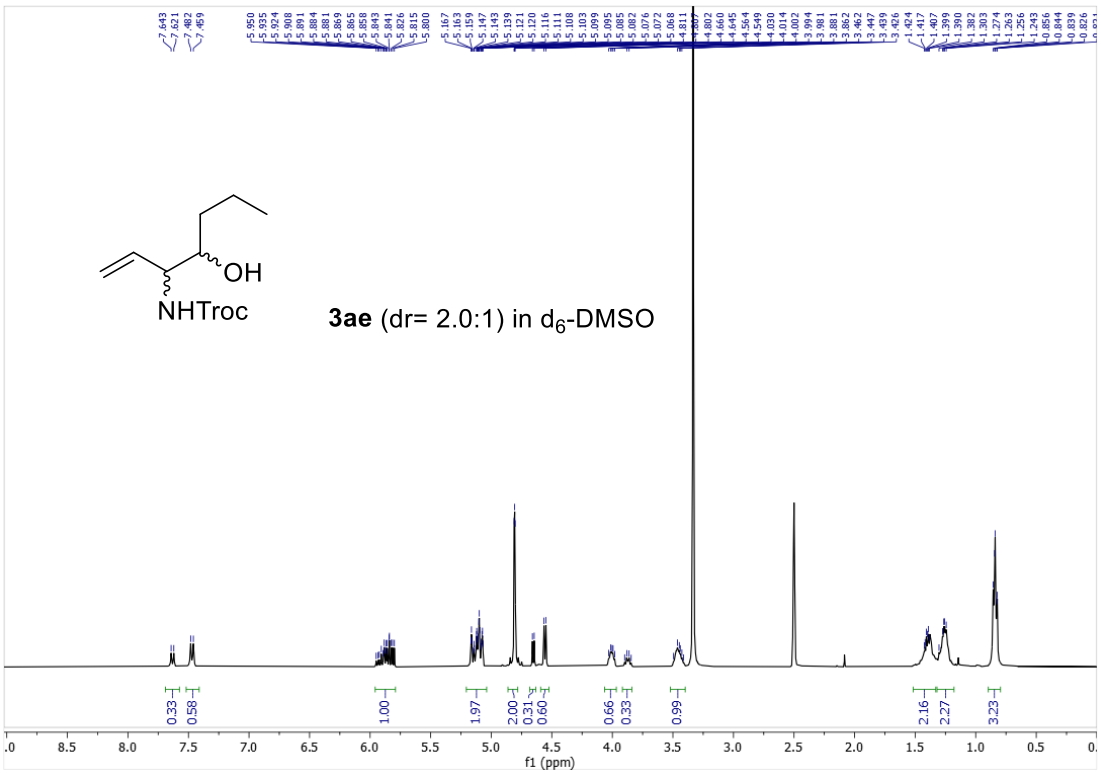

f1 (ppm)

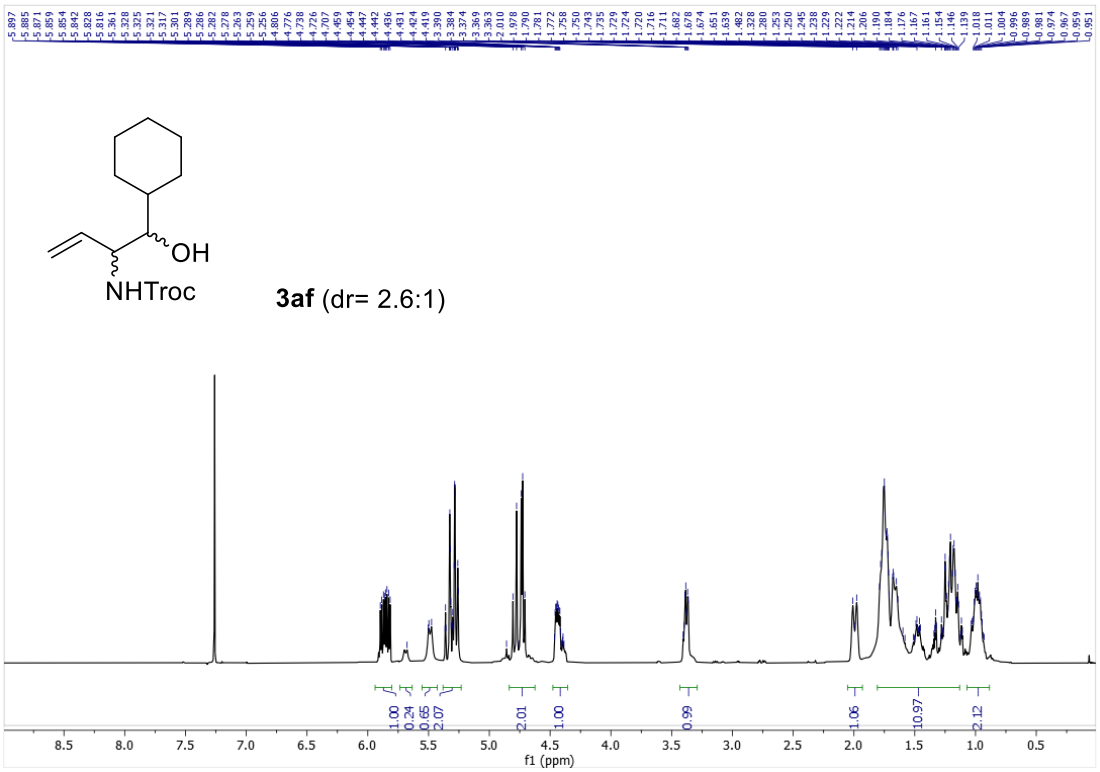

OH
NHTroc
3ad
f1 (ppm)

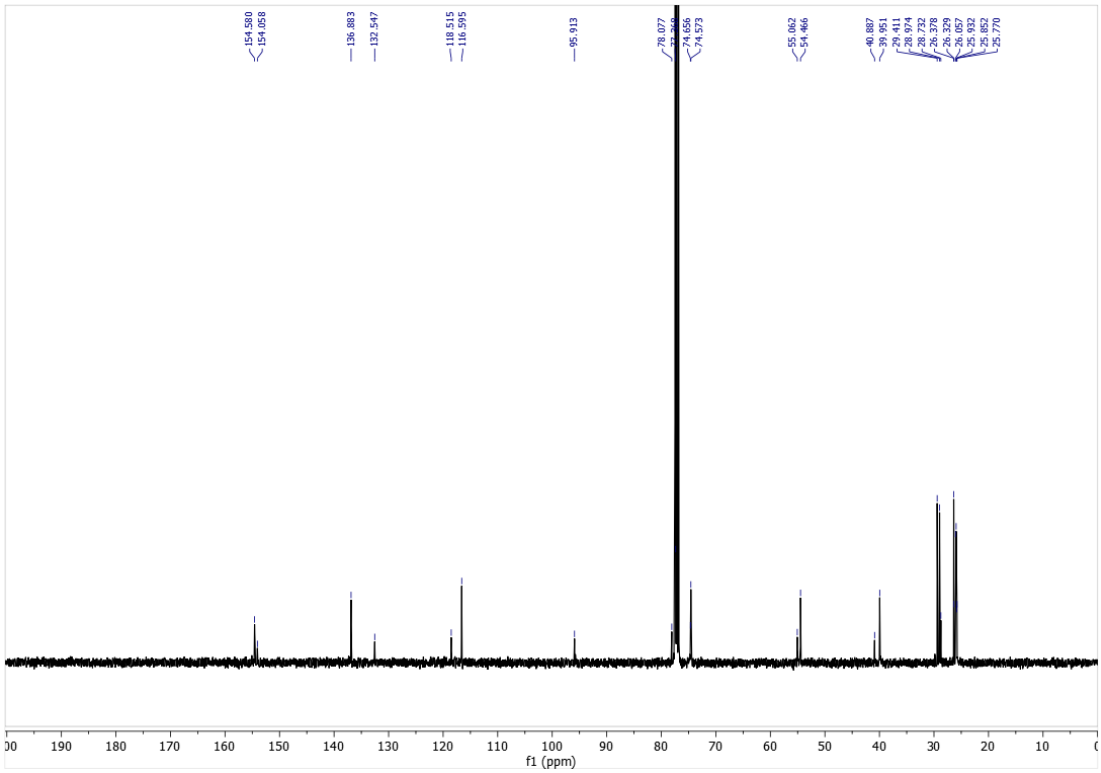

f1 (ppm)

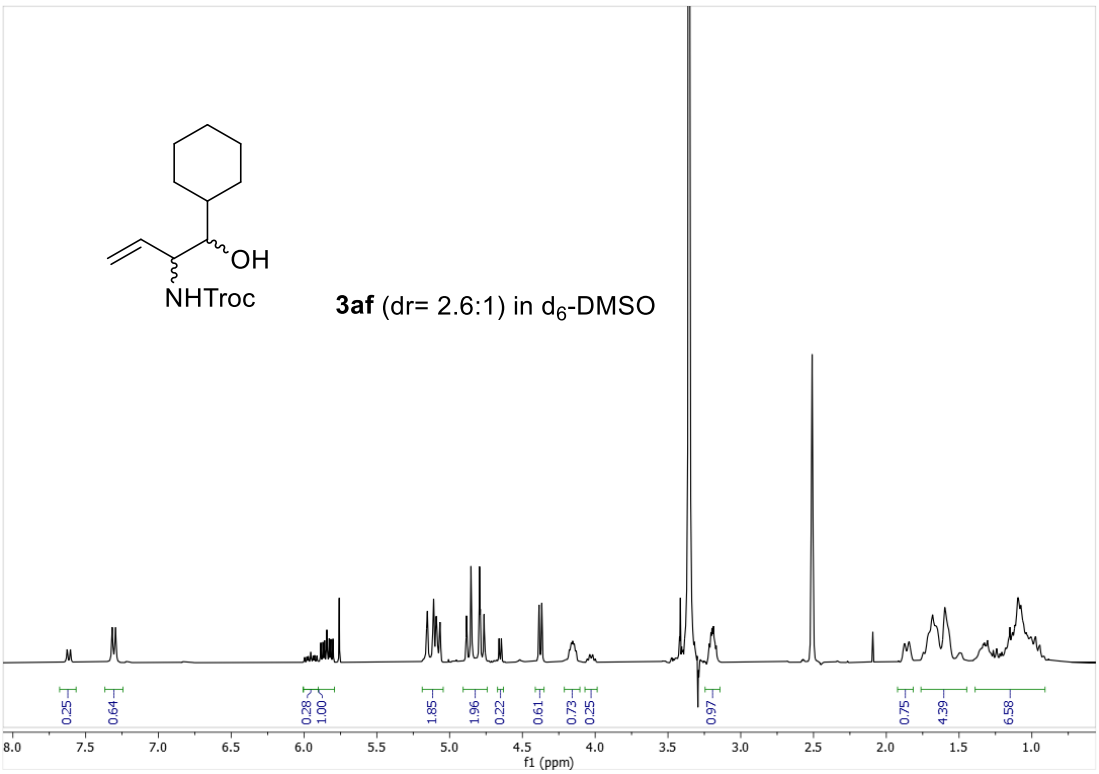

OH
NHTroc
3ae (dr= 2.0:1)
1.00
0.35
1.03
0.68
2.05
2.19
1.01
1.10
1.12
4.67
3.38
f1 (ppm)

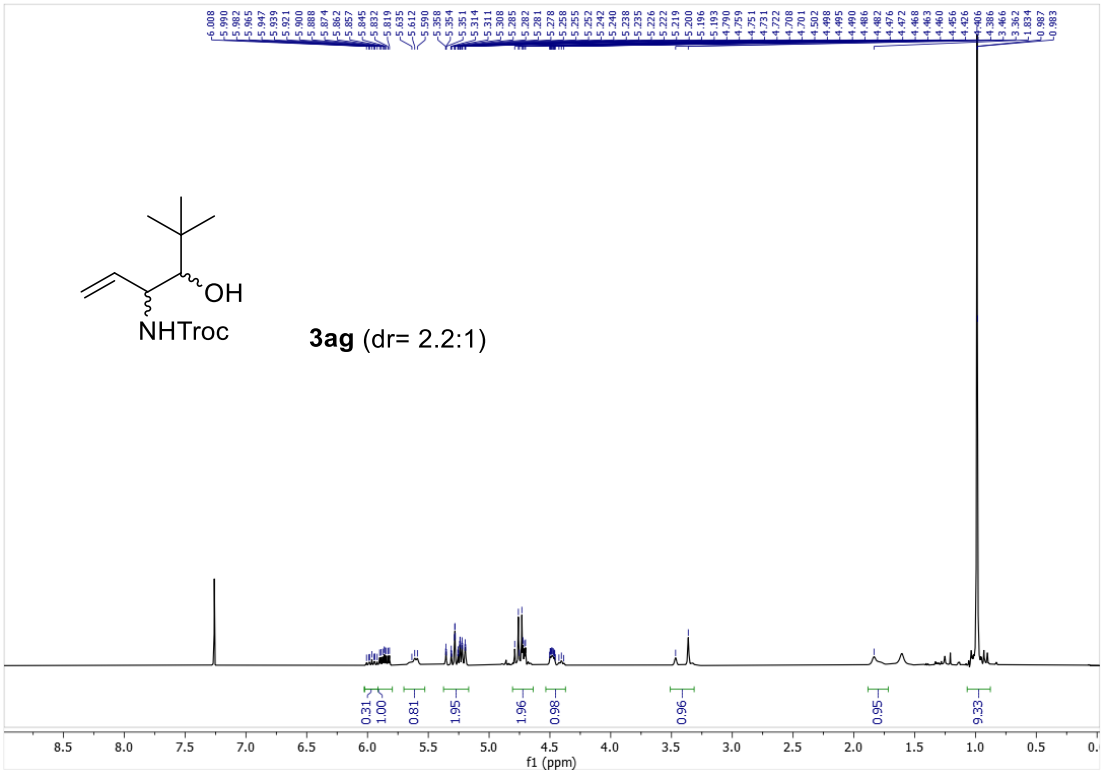

154.762
154.255
136.296
132.754
118.592
116.771
91.731
74.693
74.441
73.434
72.721
57.889
57.225
36.358
35.809
19.060
19.023
14.098
14.079
f1 (ppm)

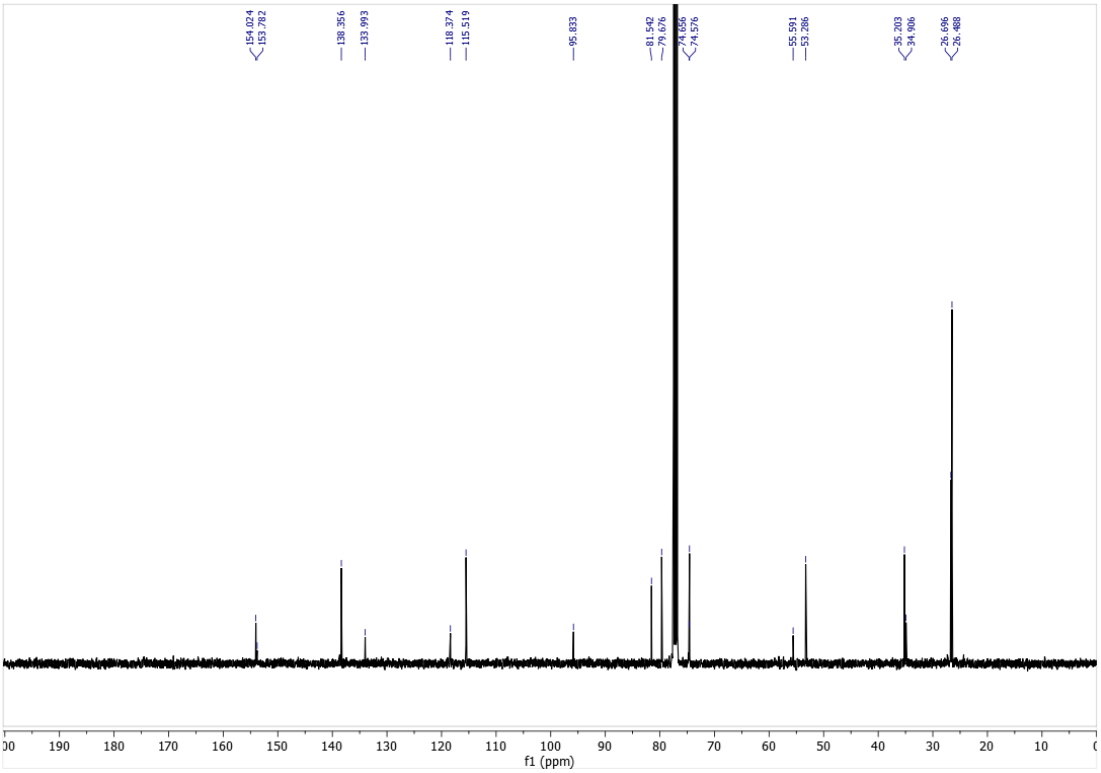

OH
NHTroc
3ae (dr= 2.0:1) in d6-DMSO
f1 (ppm)

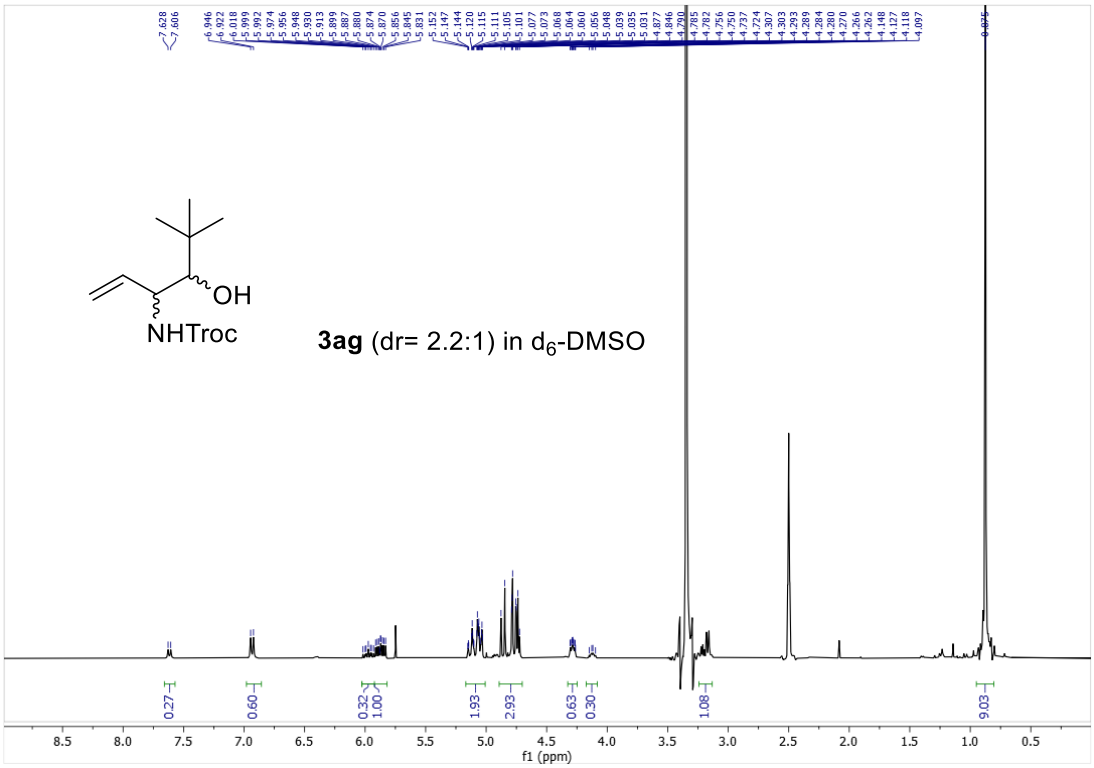

OH
NHTroc
3af (dr= 2.6:1)
1.00
0.24
0.65
2.07
2.01
1.00
0.99
1.06
10.97
2.12
f1 (ppm)

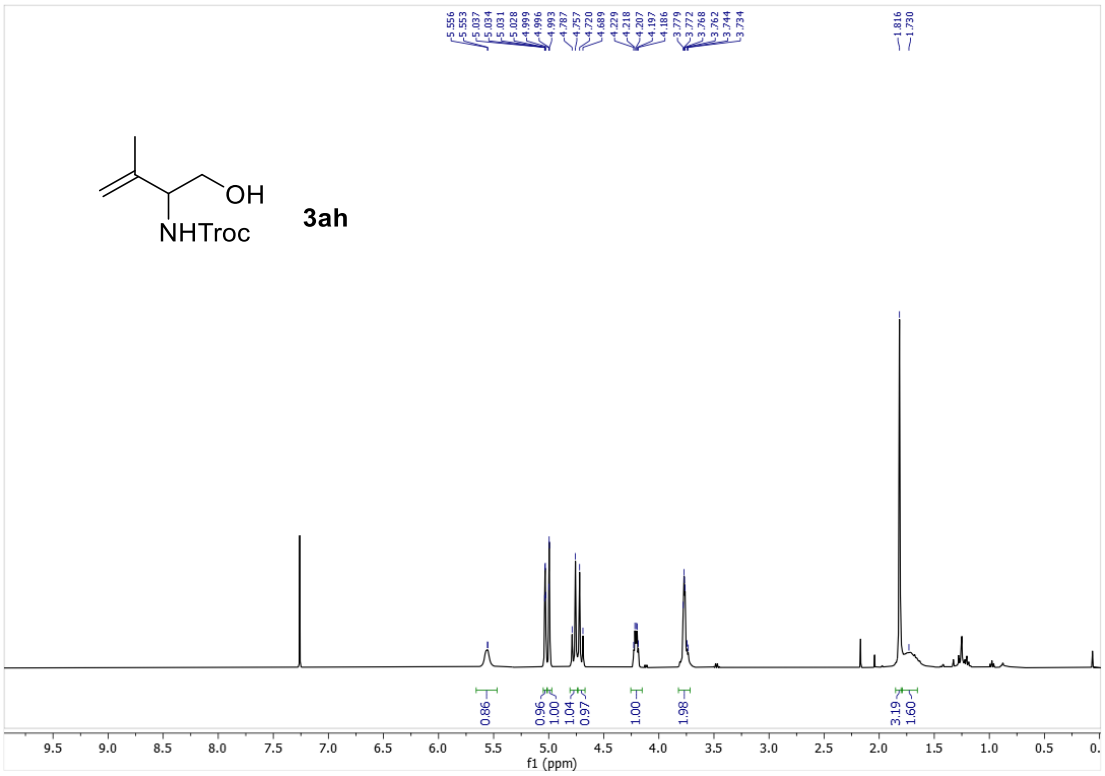

f1 (ppm)

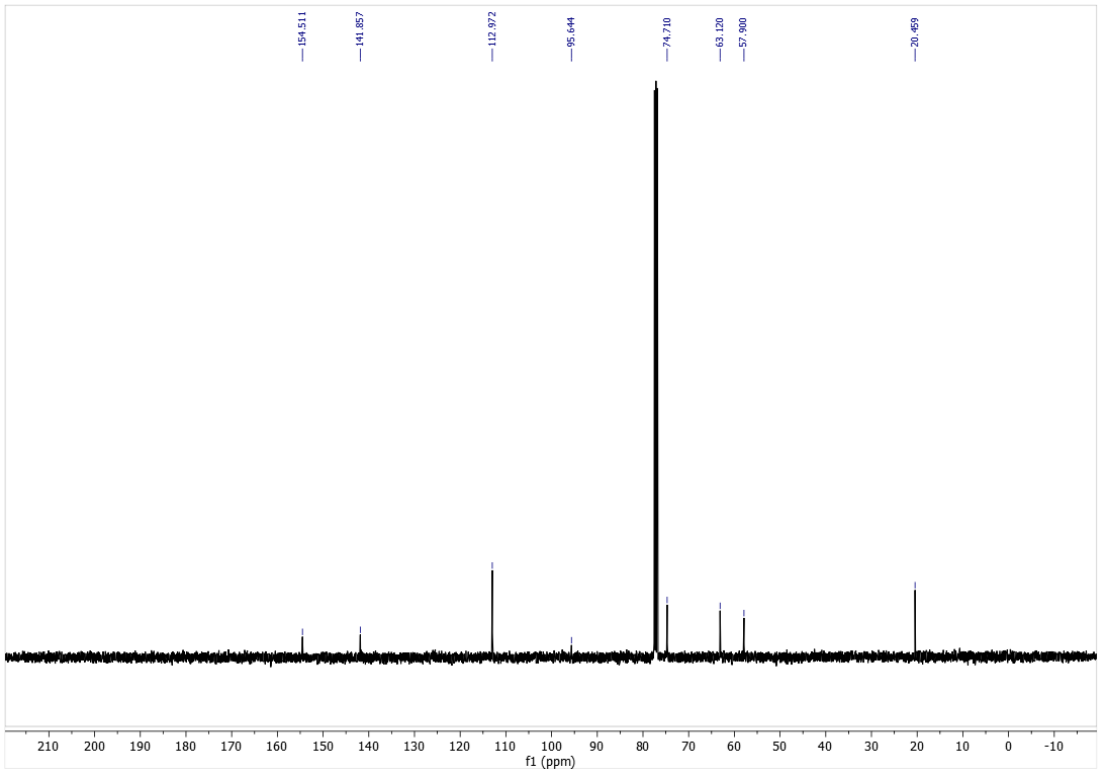

OH
NHTroc
3af (dr= 2.6:1) in d6-DMSO
0.25
0.64
0.28
1.00
1.85
1.96
0.22
0.61
0.73
0.25
0.97
0.75
4.39
6.58
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

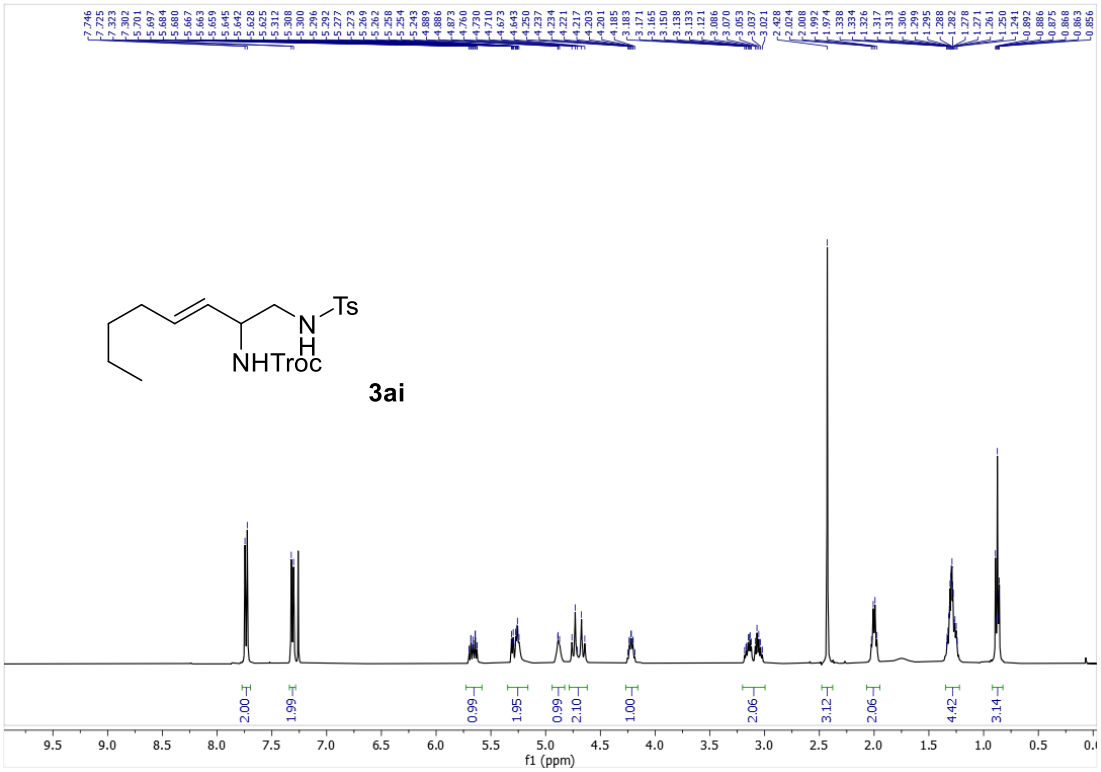

OH
NHTroc
3ag (dr= 2.2:1)
0.31
1.00
0.81
1.95
1.96
0.98
0.96
0.95
9.33
f1 (ppm)

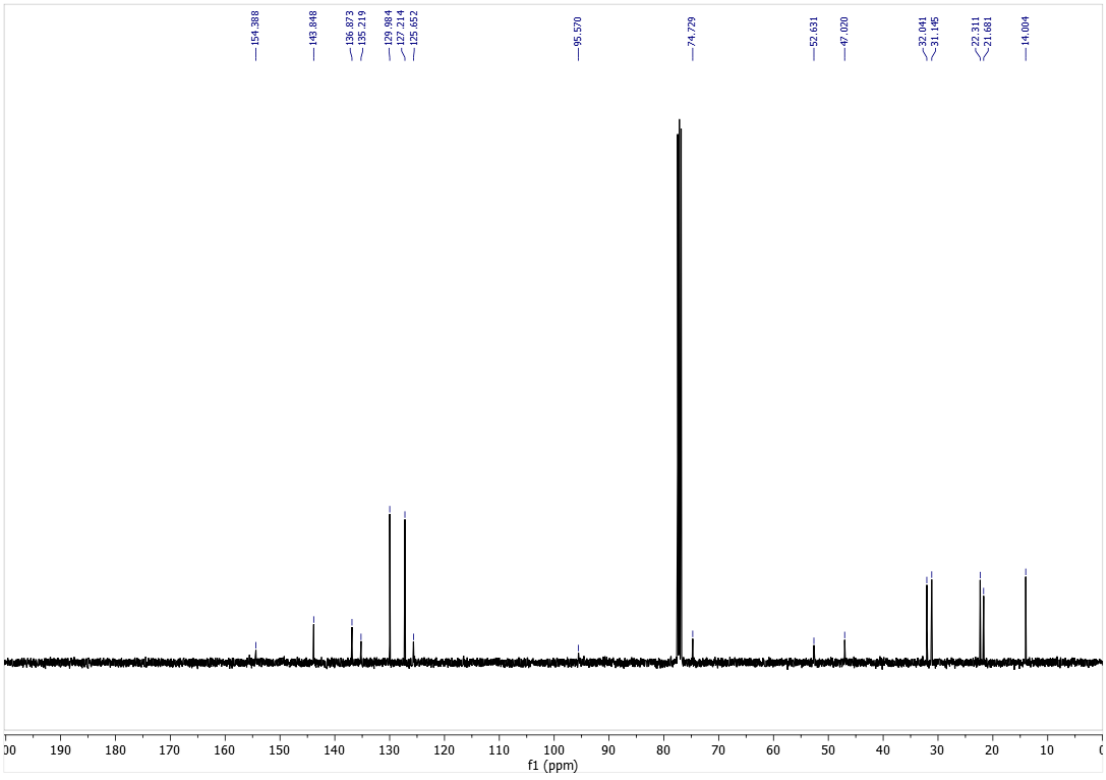

154.024
153.702
138.356
133.993
118.374
115.519
95.833
81.542
79.676
74.656
74.576
55.591
53.286
35.203
34.906
26.696
26.488
f1 (ppm)

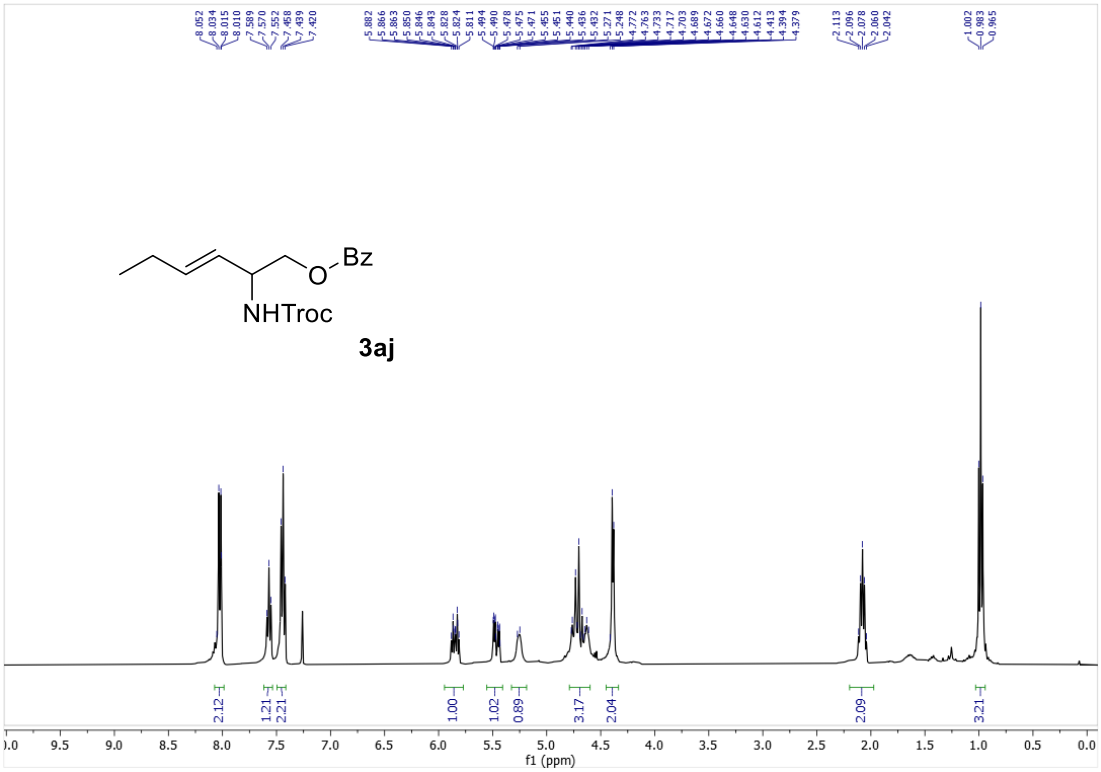

OH
NHTroc
3ag (dr= 2.2:1) in d6-DMSO
0.27
0.60
0.32
1.00
1.93
2.93
0.63
0.30
1.08
9.03
f1 (ppm)

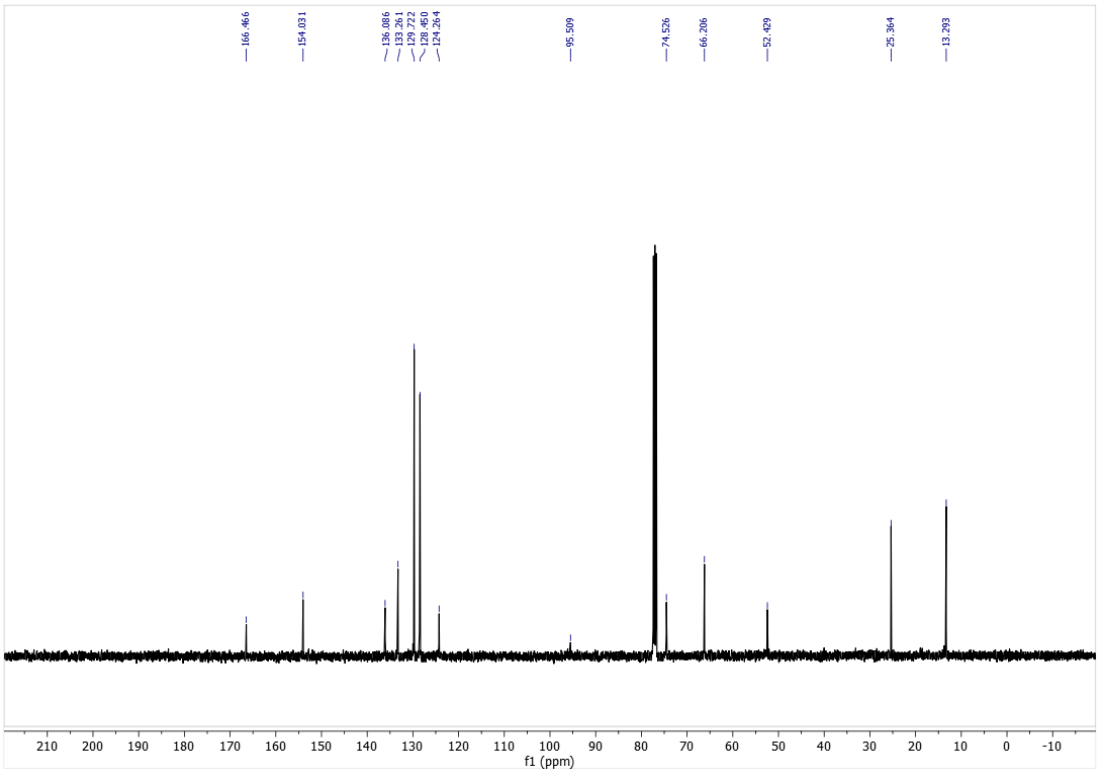

OH
NHTroc
3ah
f1 (ppm)

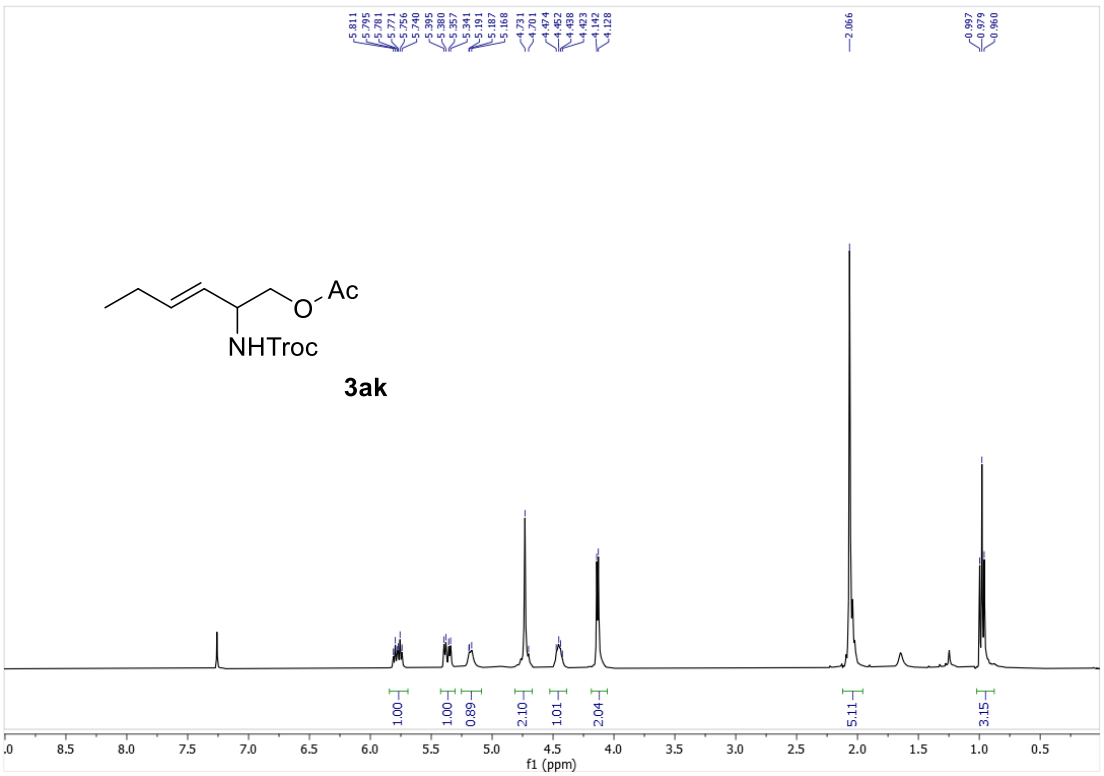

f1 (ppm)

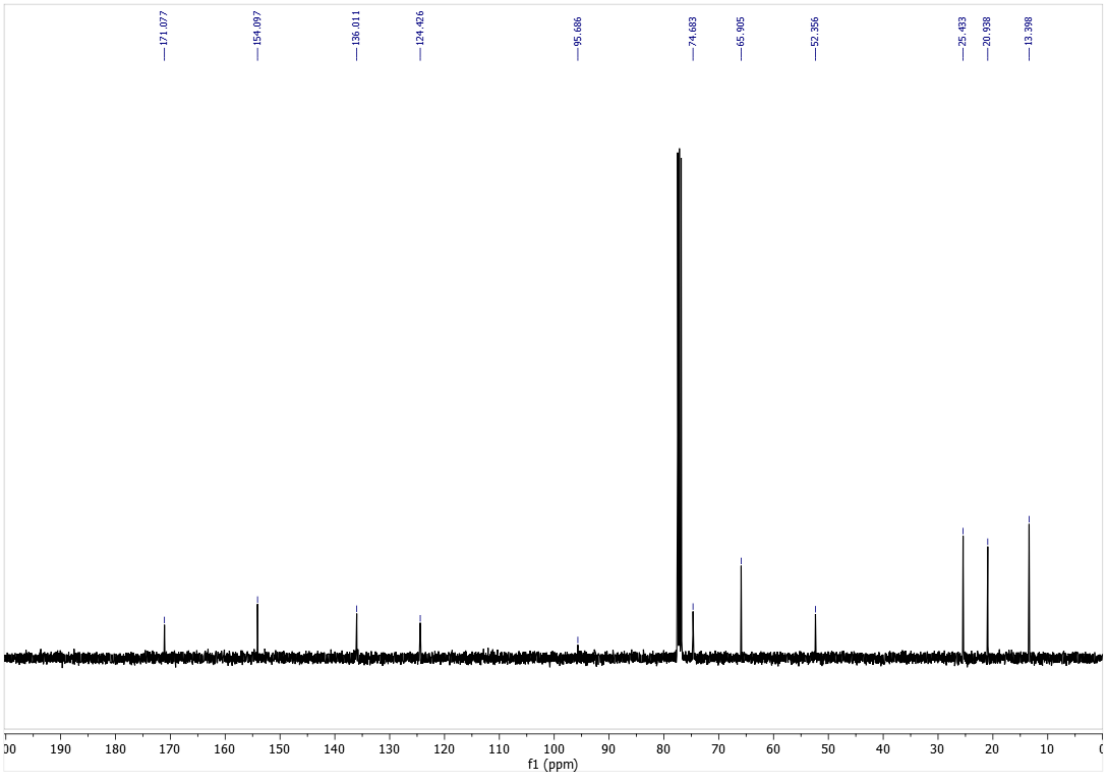

Ts
N
H
NHTroc
3ai
f1 (ppm)

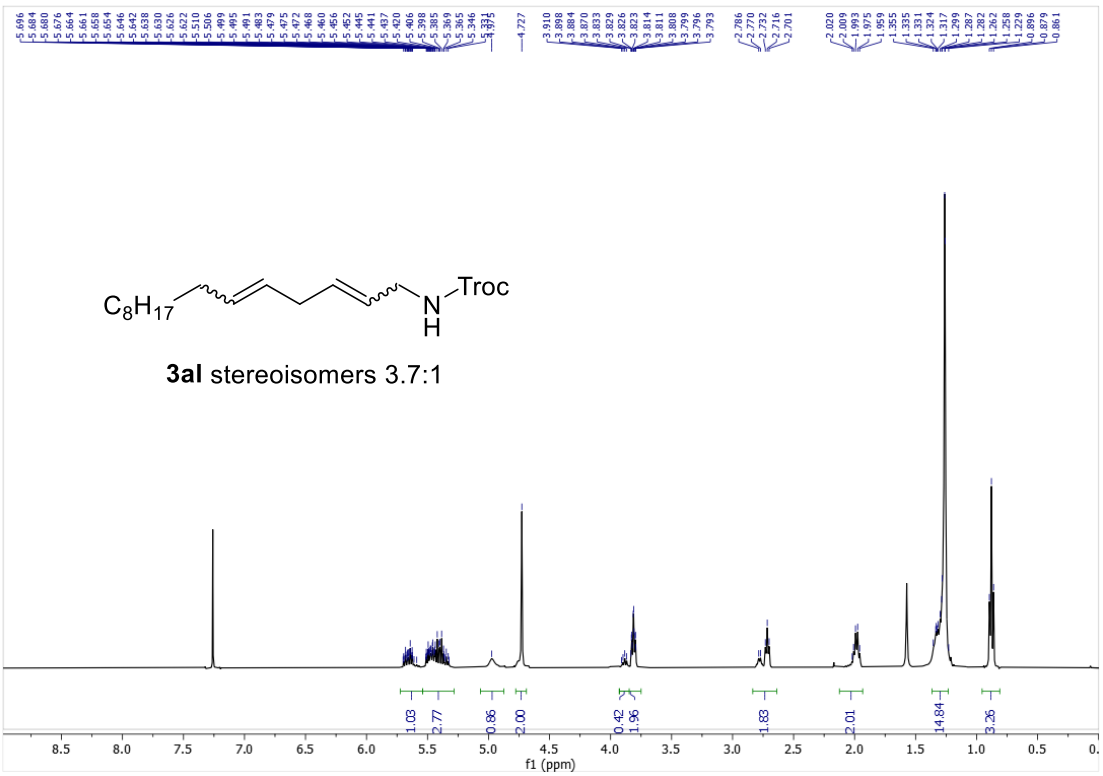

f1 (ppm)

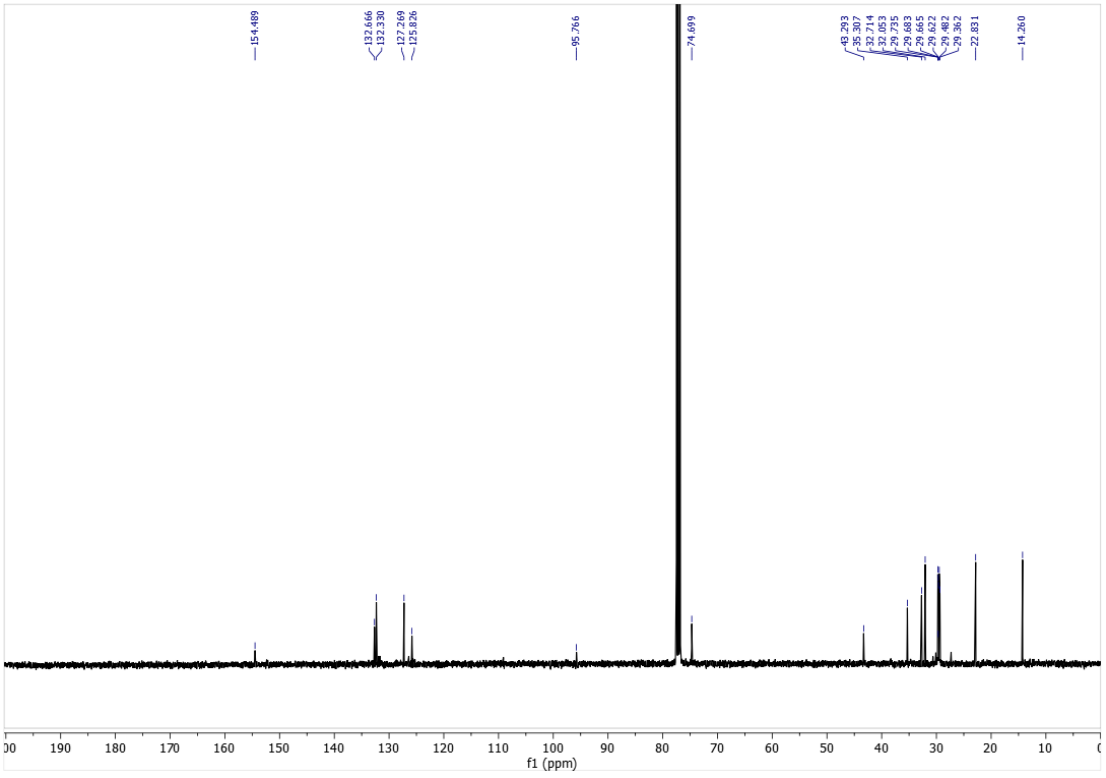

Bz
O
NHTroc
3aj
f1 (ppm)

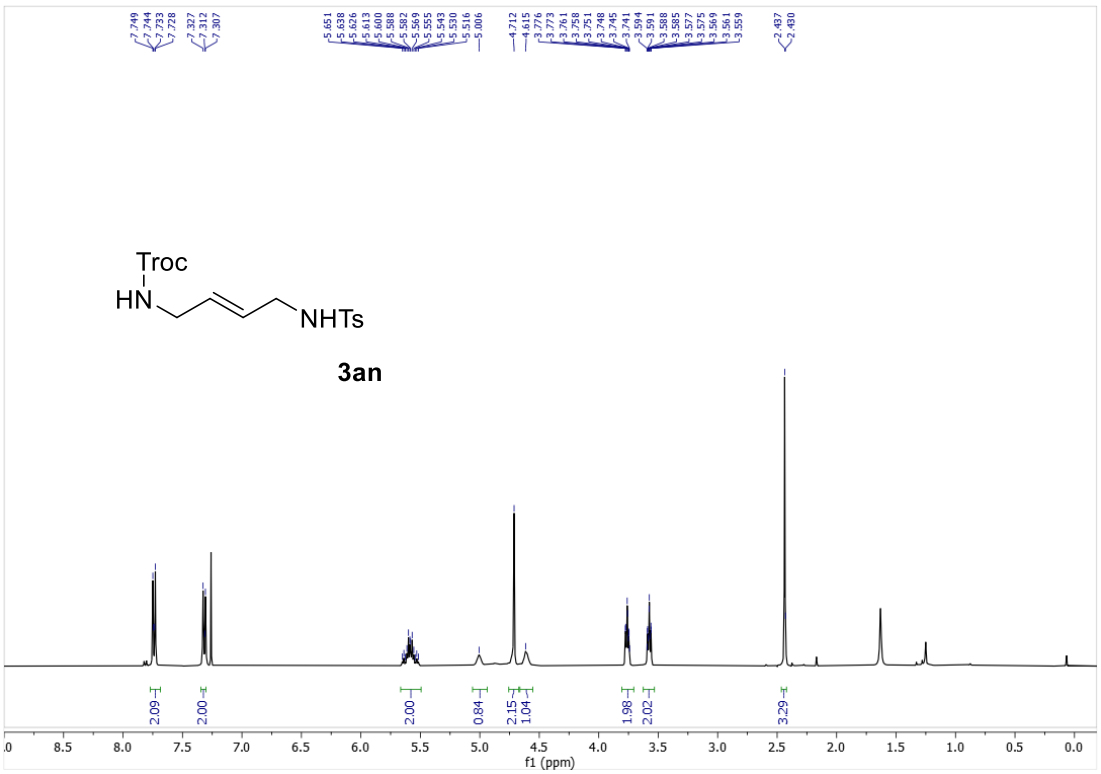

f1 (ppm)

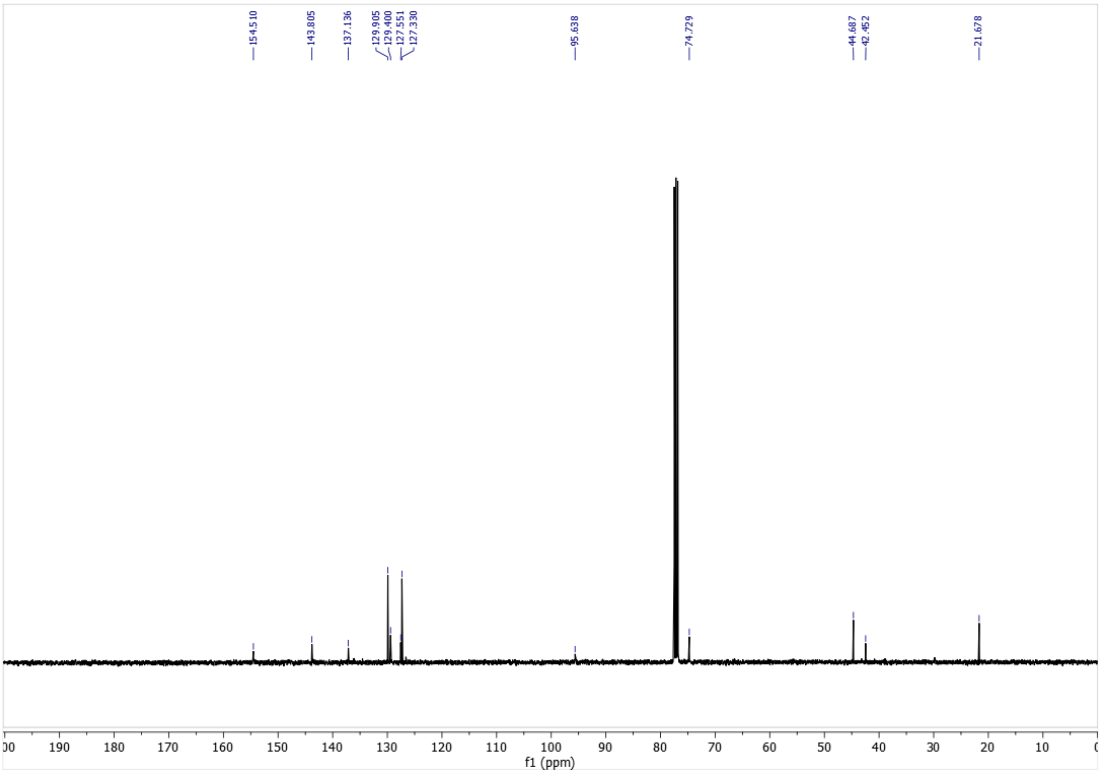

Ac
O
NHTroc
3ak
f1 (ppm)

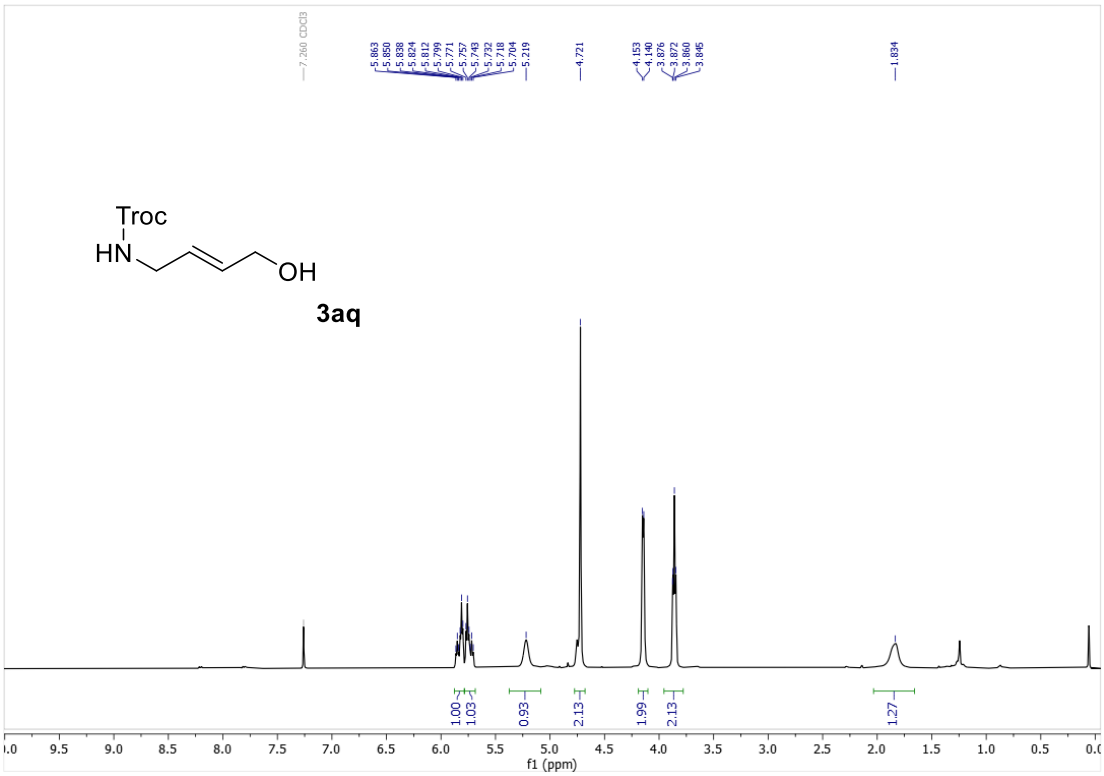

f1 (ppm)

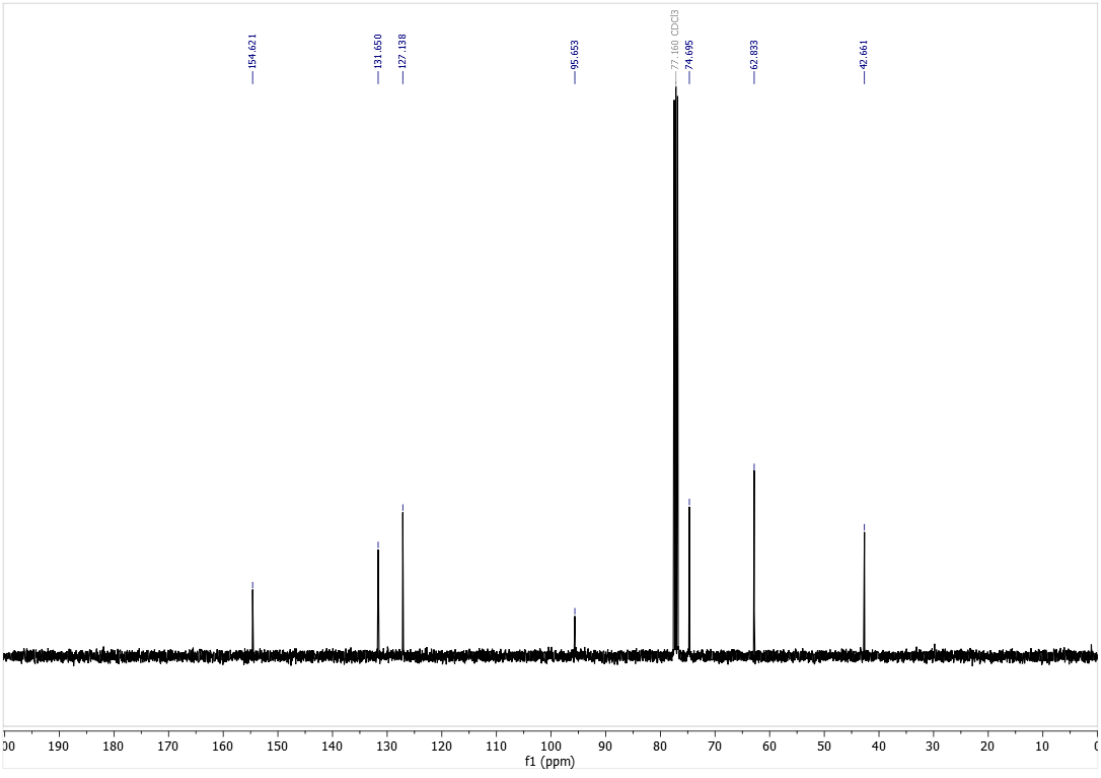

C8H17
N
H
Troc
3aI stereoisomers 3.7:1
f1 (ppm)

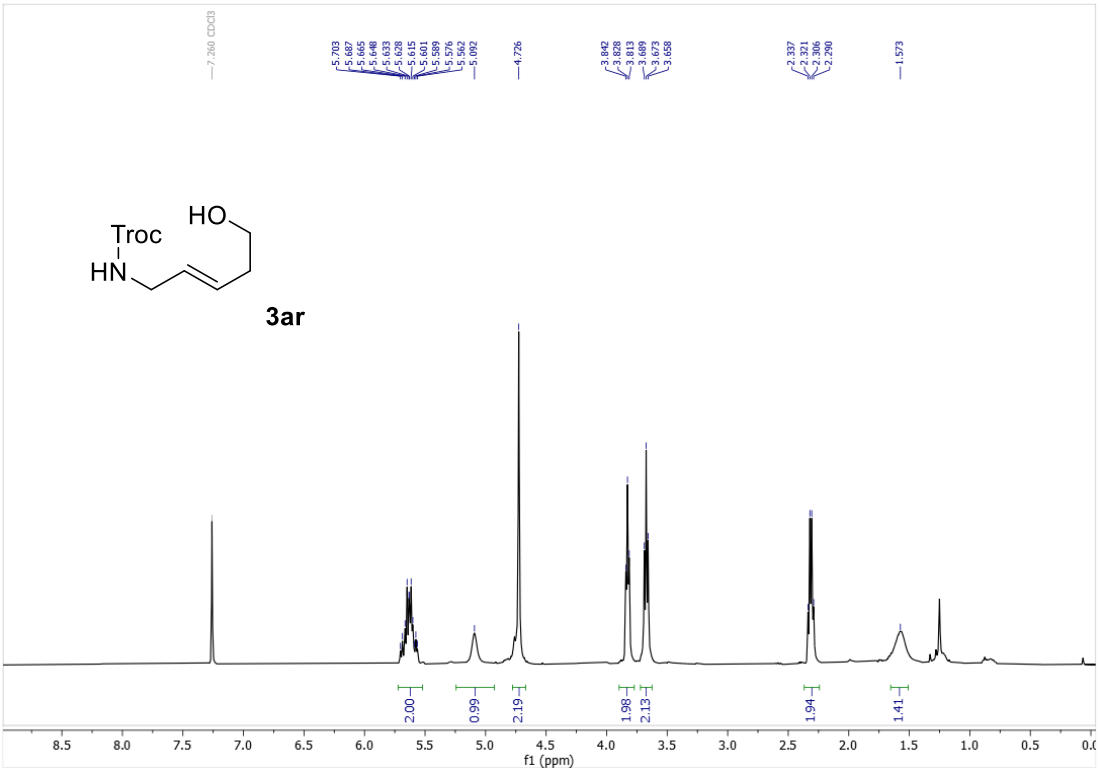

f1 (ppm)

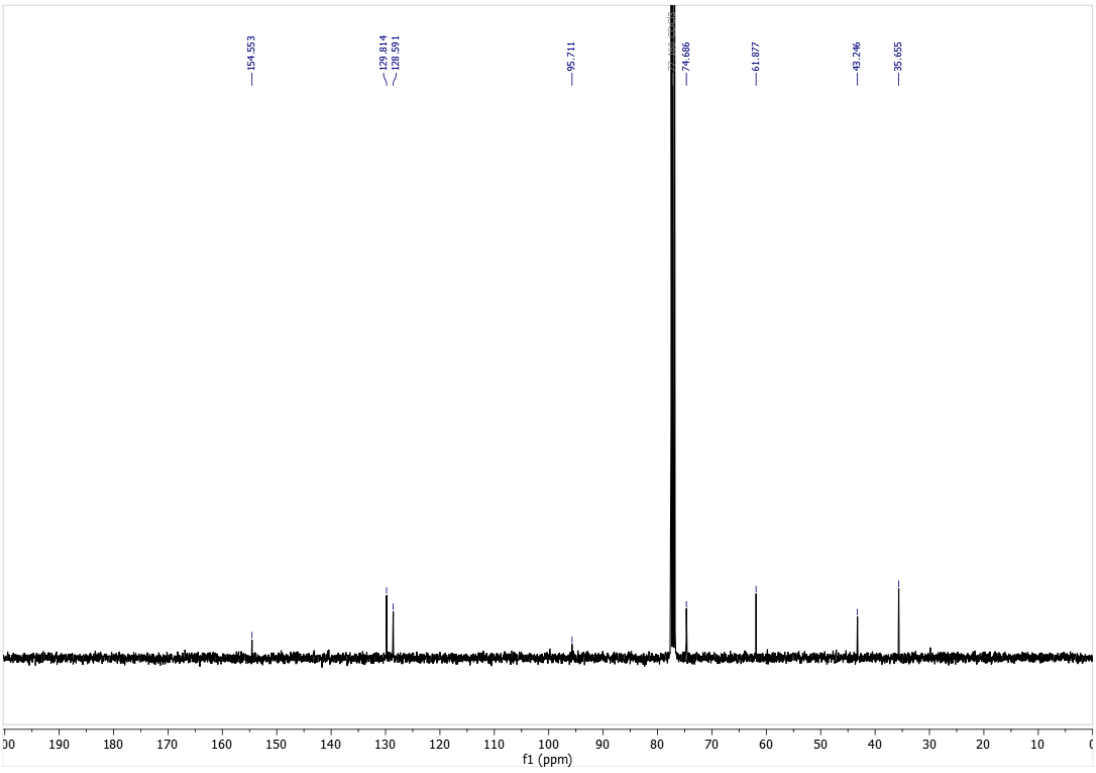

Troc
HN
NHTs
3an
f1 (ppm)

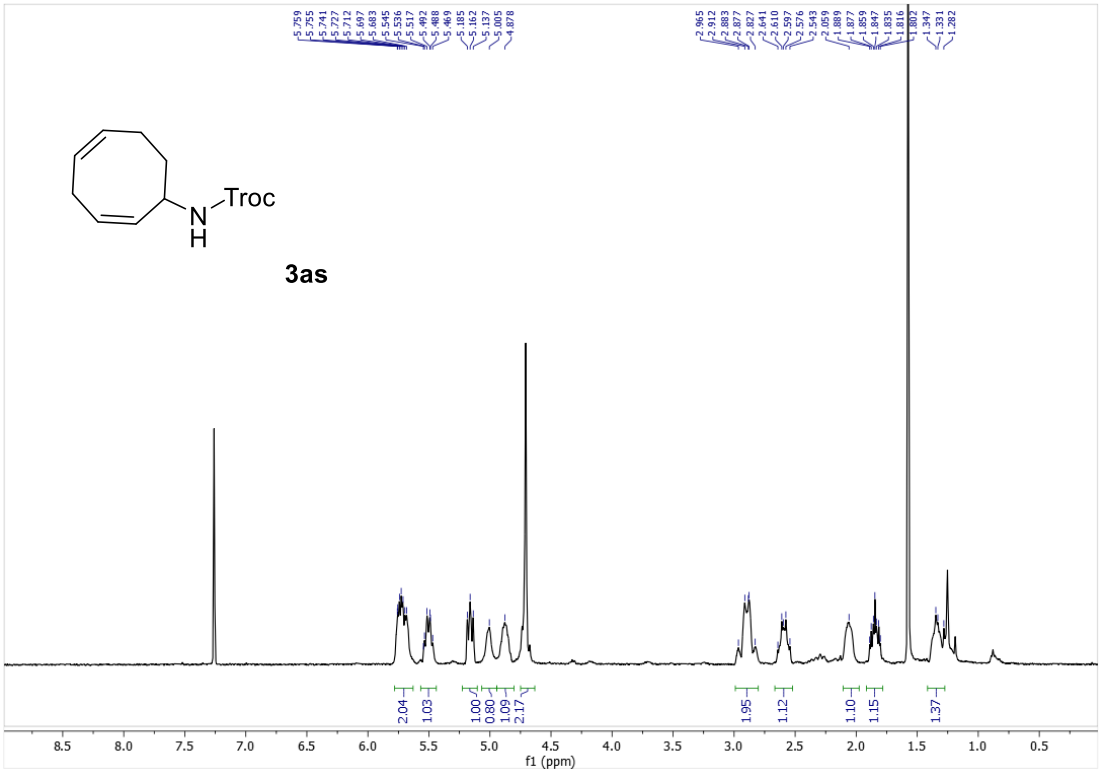

f1 (ppm)

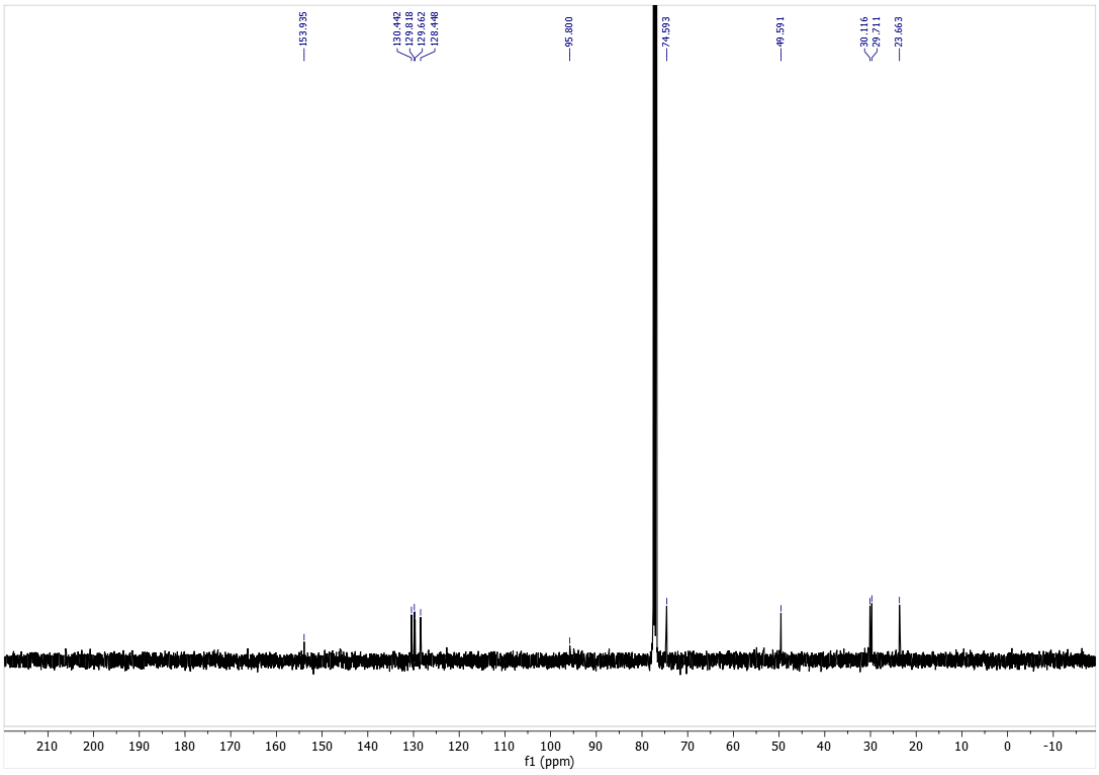

7.260 CDCl3
5.863
5.850
5.838
5.824
5.812
5.799
5.771
5.757
5.745
5.732
5.718
5.704
5.219
4.721
4.153
4.140
3.876
3.872
3.860
3.845
1.834
Troc
HN
OH
3aq
1.00
1.03
0.93
2.13
1.99
2.13
1.27
f1 (ppm)

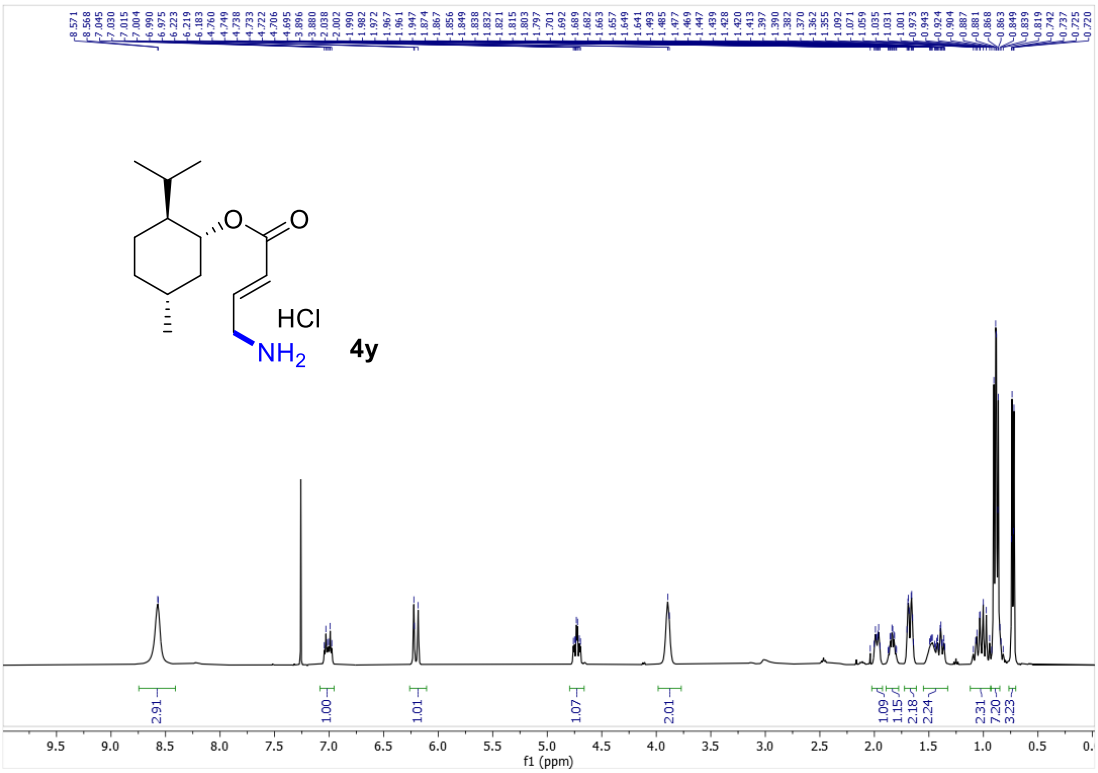

154.621
131.650
127.138
95.653
77.160 CDCl3
74.695
62.833
42.661
f1 (ppm)

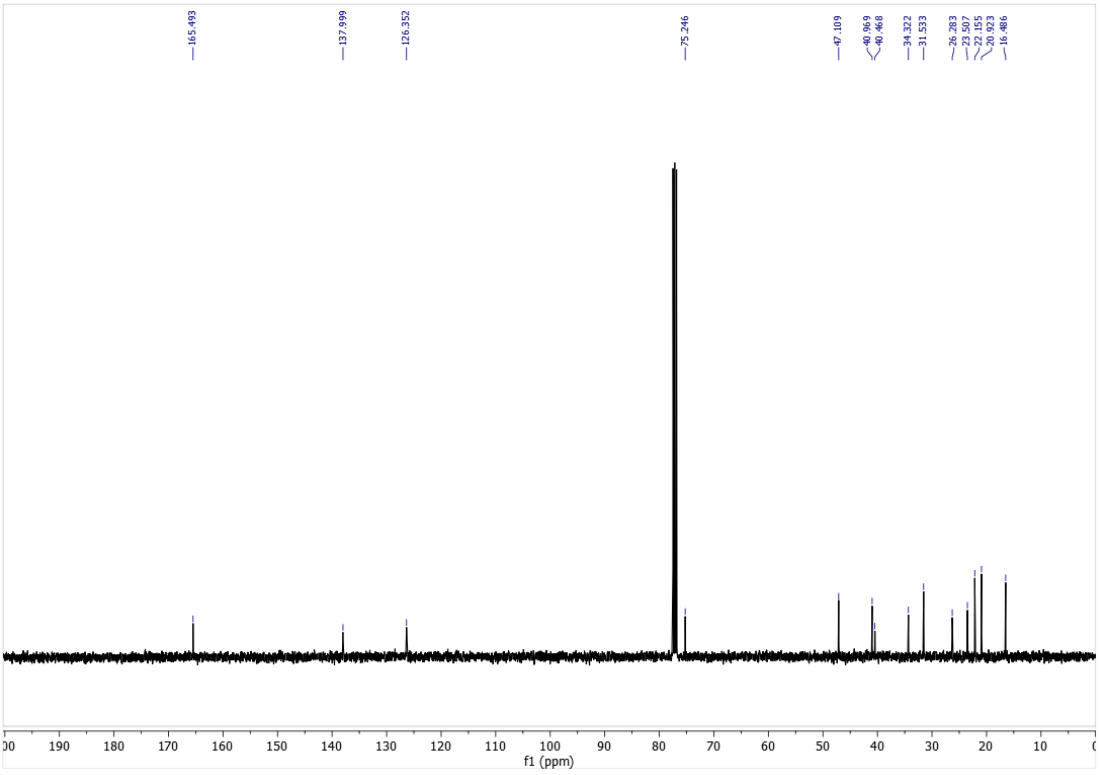

HO
Troc
HN
3ar
f1 (ppm)

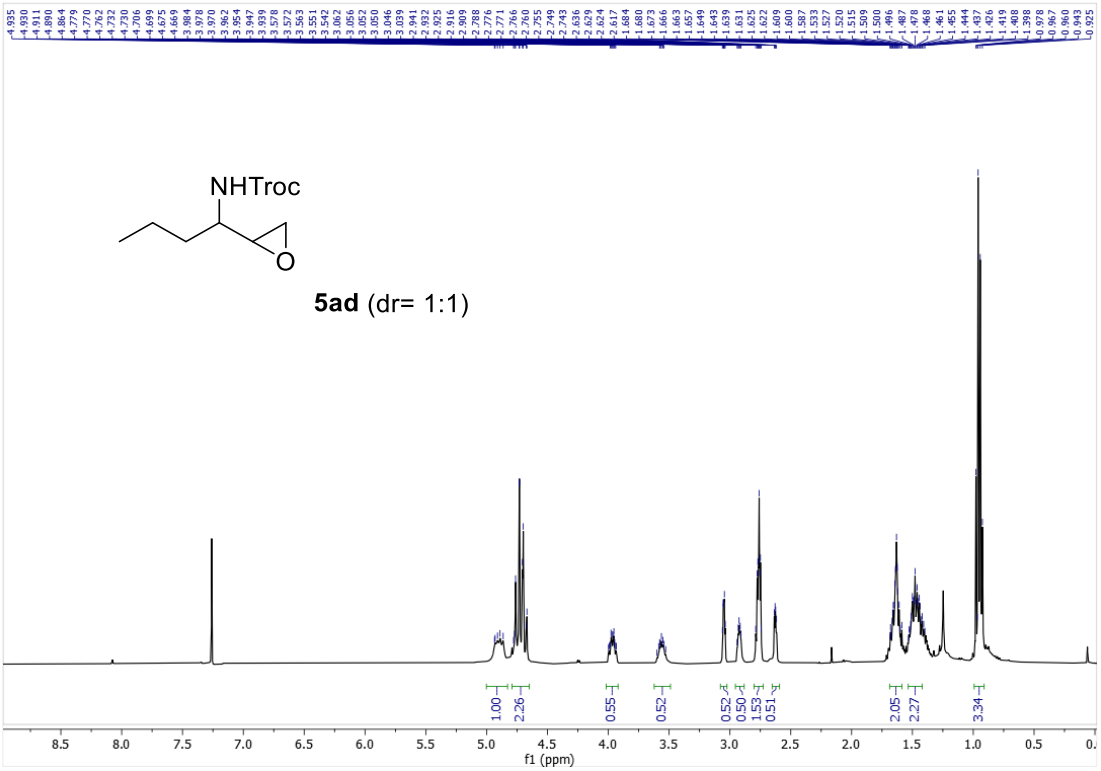

f1 (ppm)

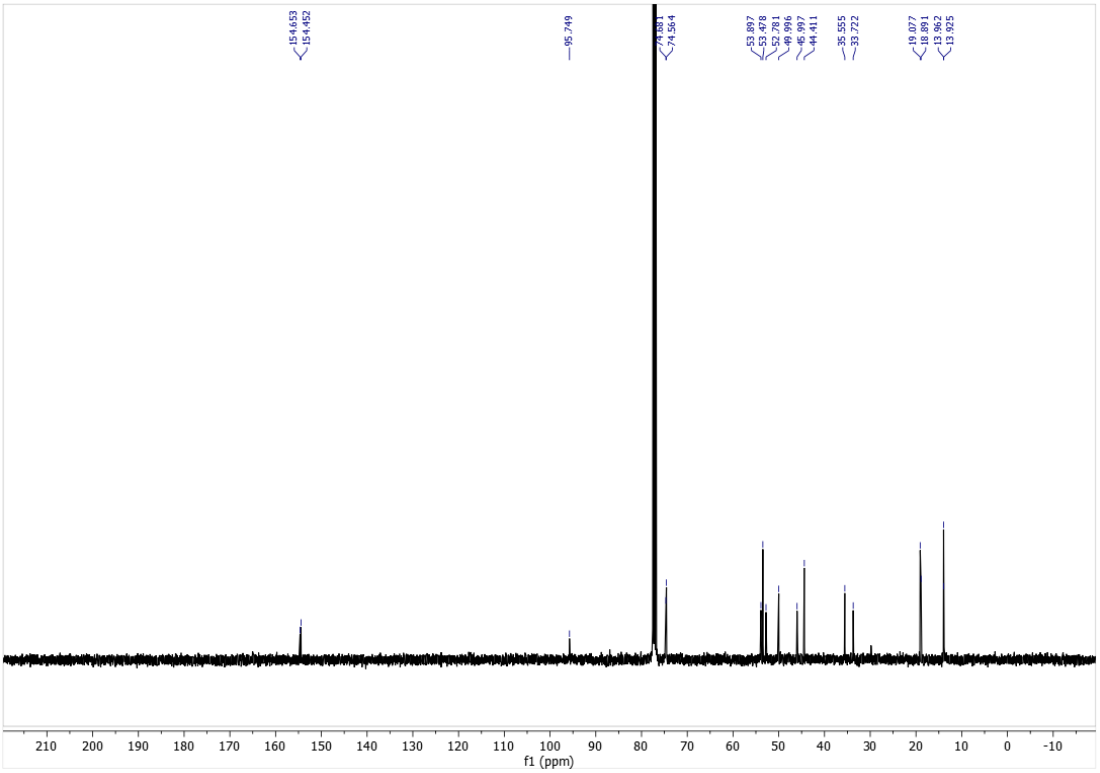

Troc
N
H
3as
f1 (ppm)

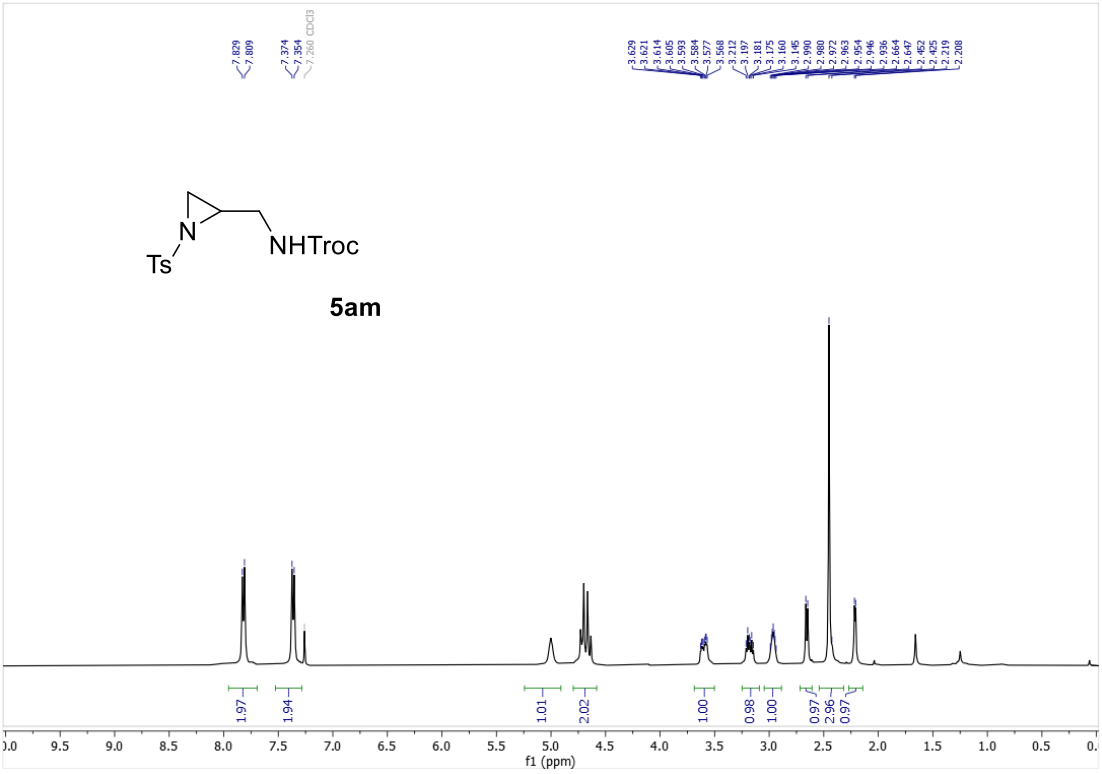

f1 (ppm)

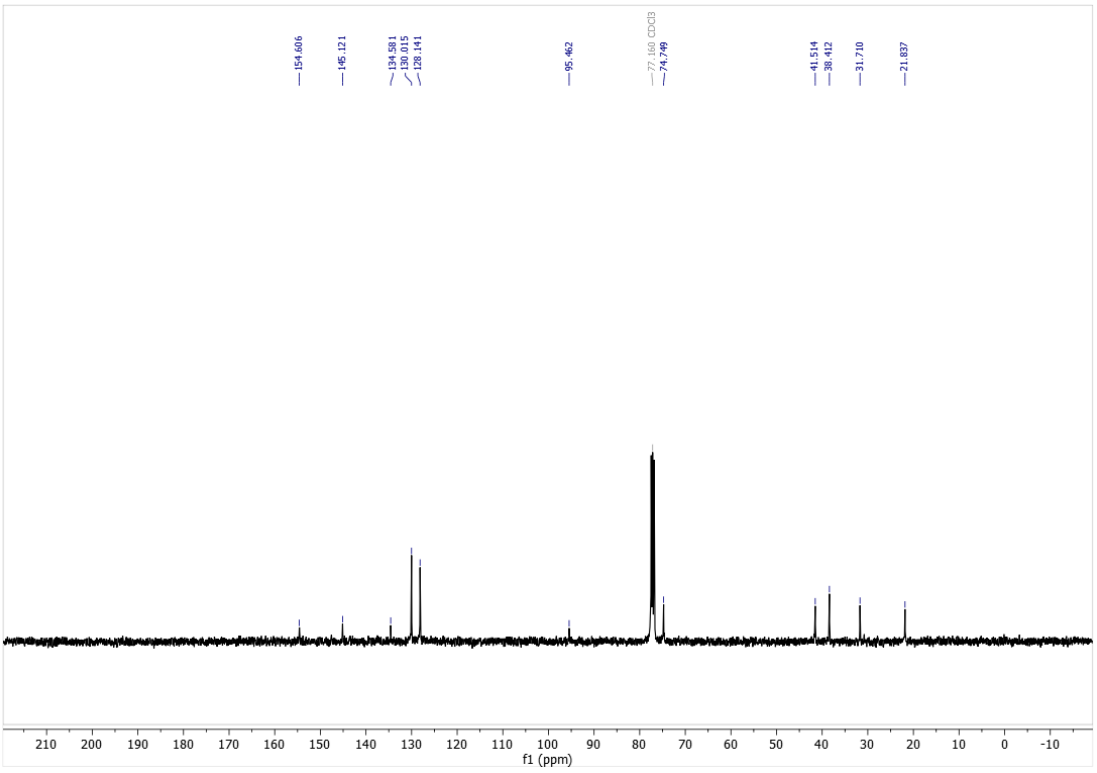

HCl
NH2
4y
f1 (ppm)

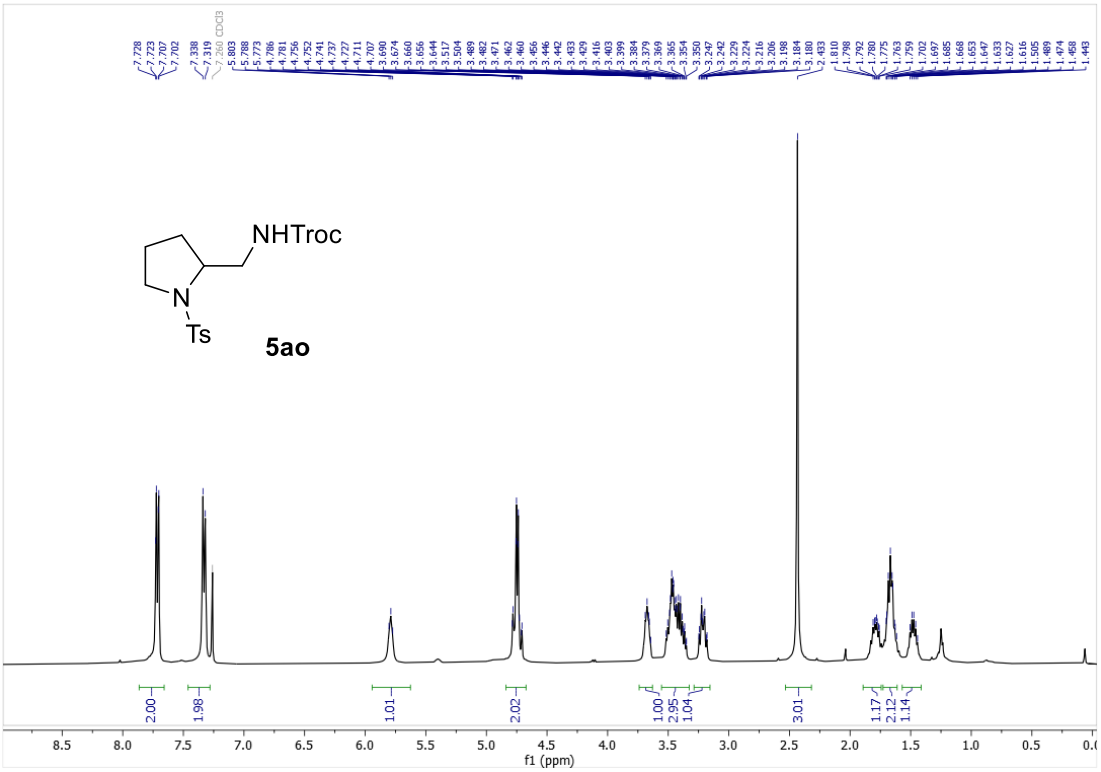

f1 (ppm)

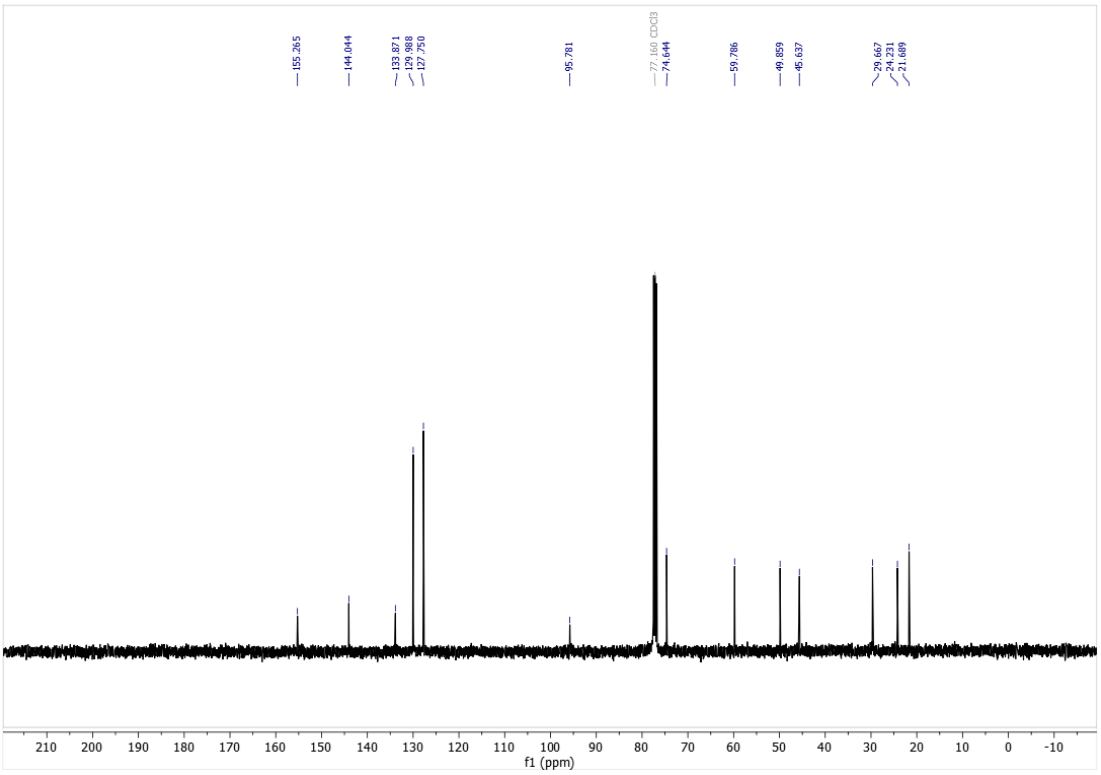

NHTroc
O
5ad (dr= 1:1)
1.00
2.26
0.55
0.52
0.52
0.50
1.53
0.51
2.05
2.27
3.34
f1 (ppm)

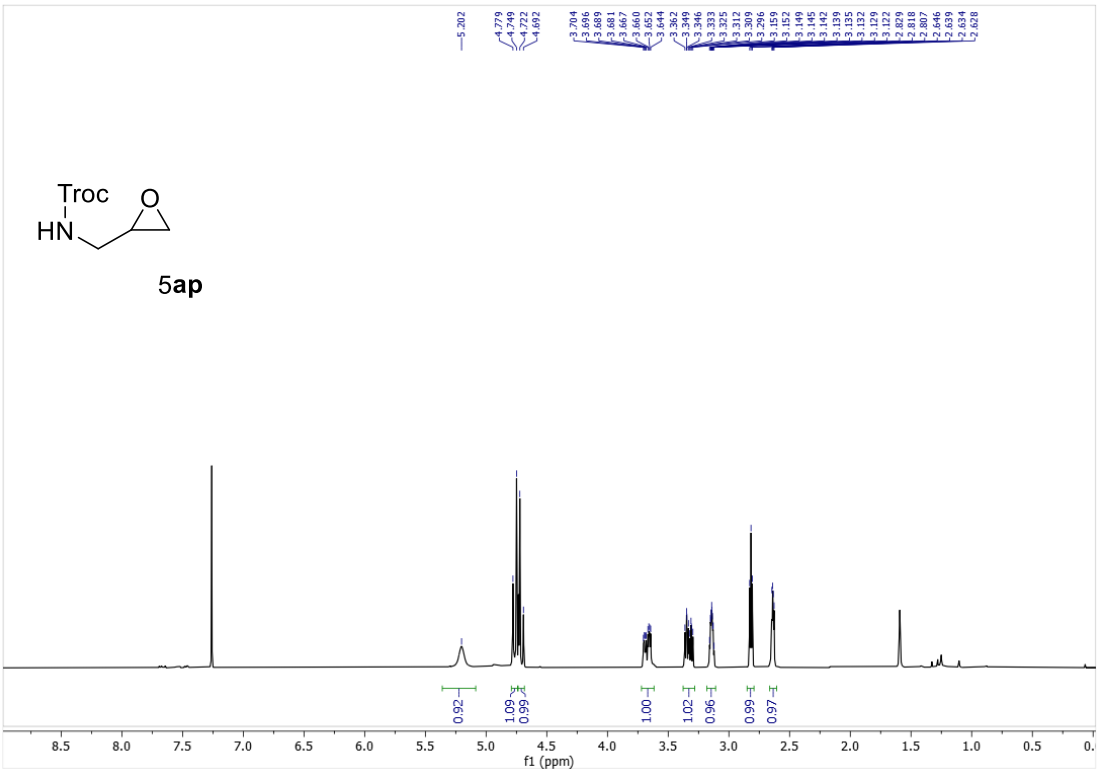

154.653
154.452
95.749
74.881
74.564
53.897
53.478
52.781
49.996
45.997
44.411
35.555
33.722
19.077
18.891
13.962
13.925
f1 (ppm)

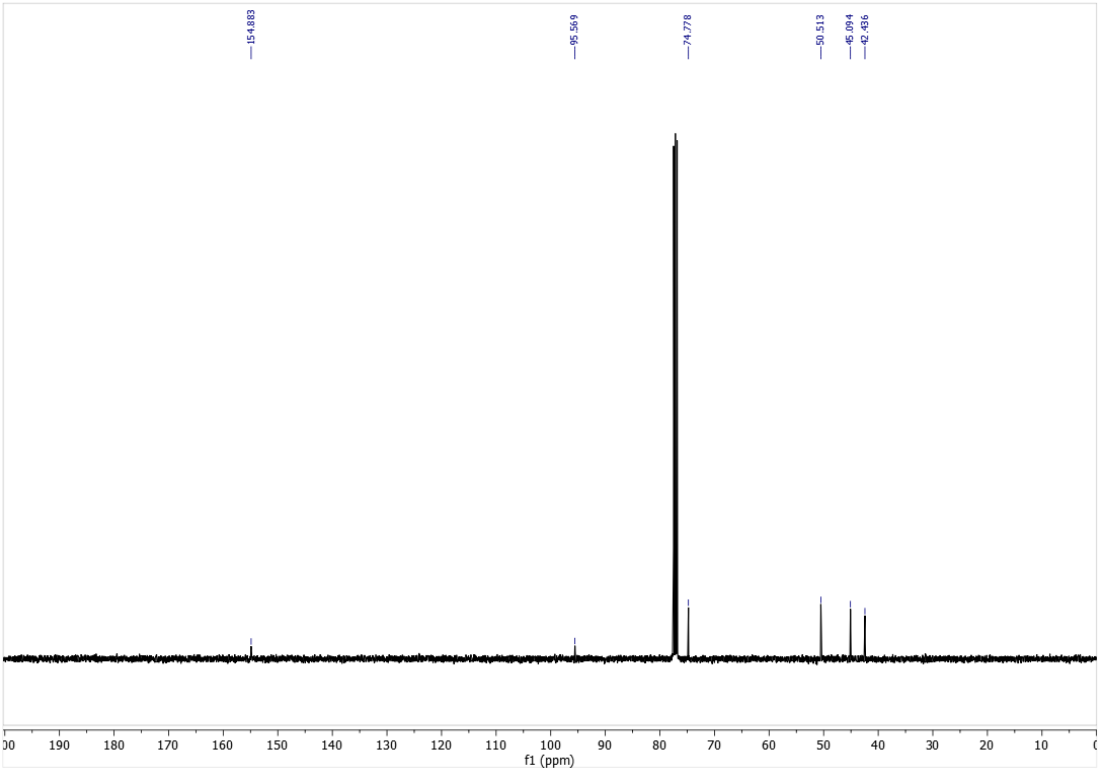

7.829
7.809
7.374
7.354
7.260 CDCl3
3.629
3.621
3.614
3.605
3.593
3.584
3.577
3.568
3.212
3.197
3.181
3.175
3.166
3.145
3.490
2.980
2.972
2.963
2.954
2.946
2.936
2.664
2.647
2.425
2.425
2.219
2.208
N
Ts
NHTroc
5am
1.97
1.94
1.01
2.02
1.00
0.98
1.00
0.97
2.96
0.97
f1 (ppm)

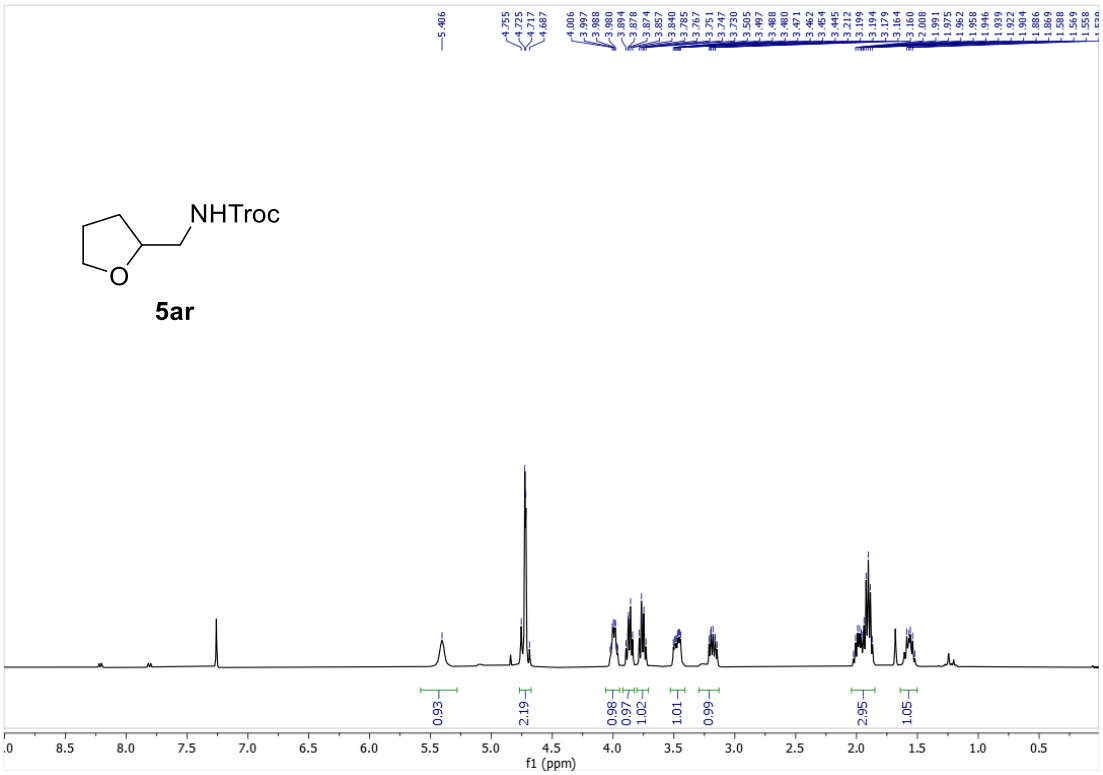

154.606
145.121
134.581
130.015
128.141
95.462
77.160 CDCl3
74.749
41.514
38.412
31.710
21.837
f1 (ppm)

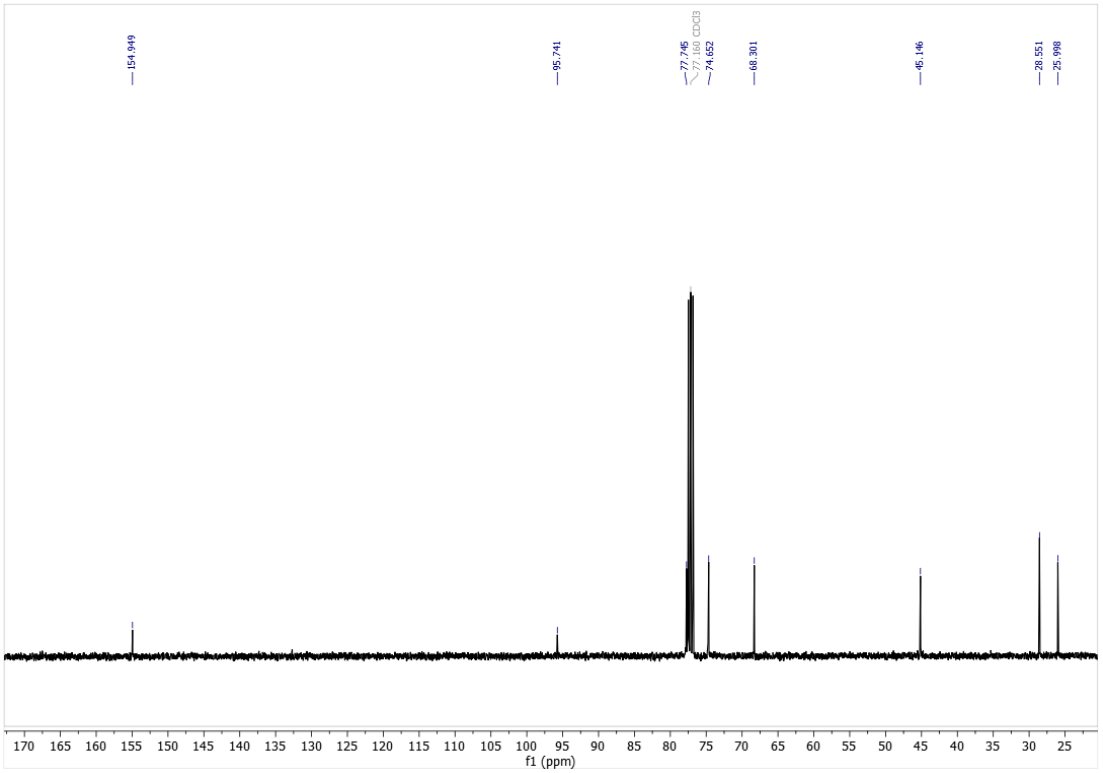

NHTroc
N
Ts
5ao
f1 (ppm)

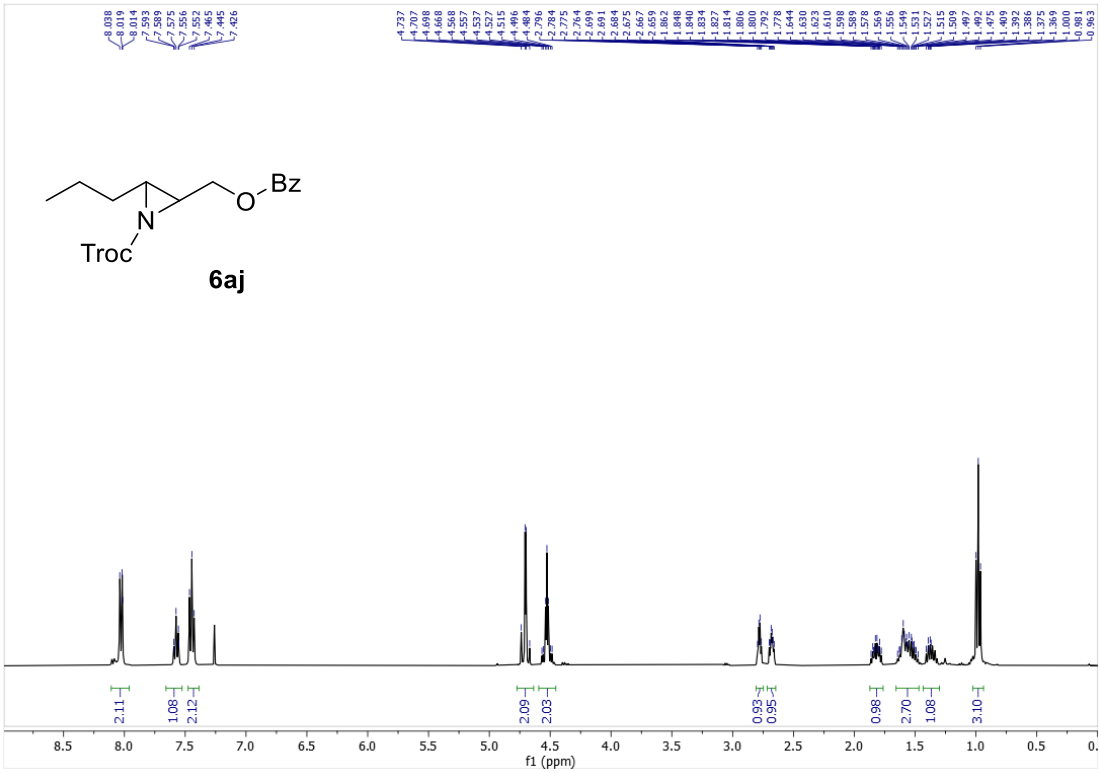

f1 (ppm)

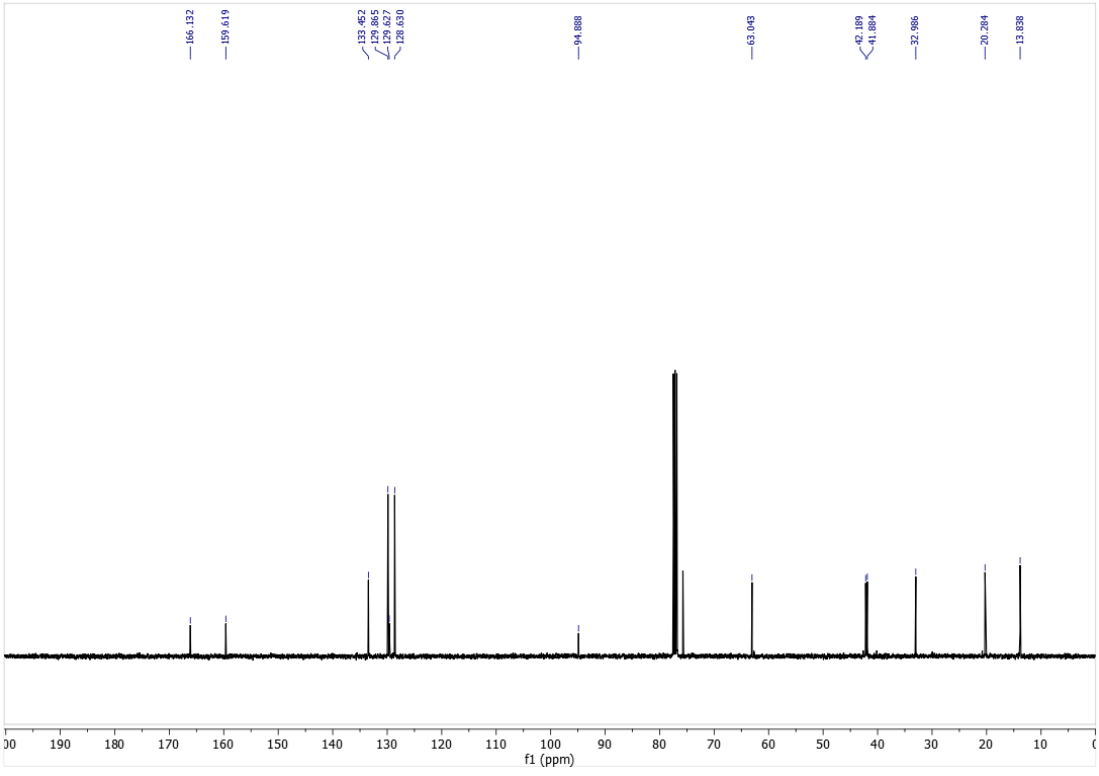

Troc
HN
O
5ap
f1 (ppm)

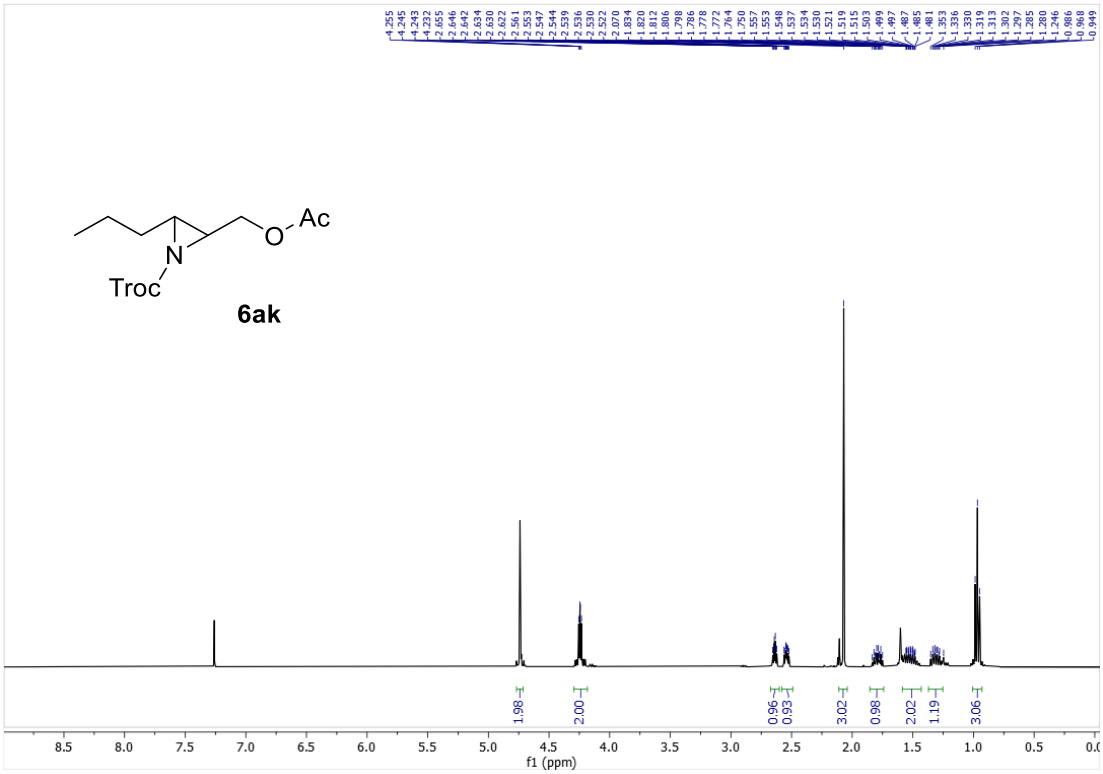

154.883
95.569
74.778
50.513
45.094
42.436
f1 (ppm)

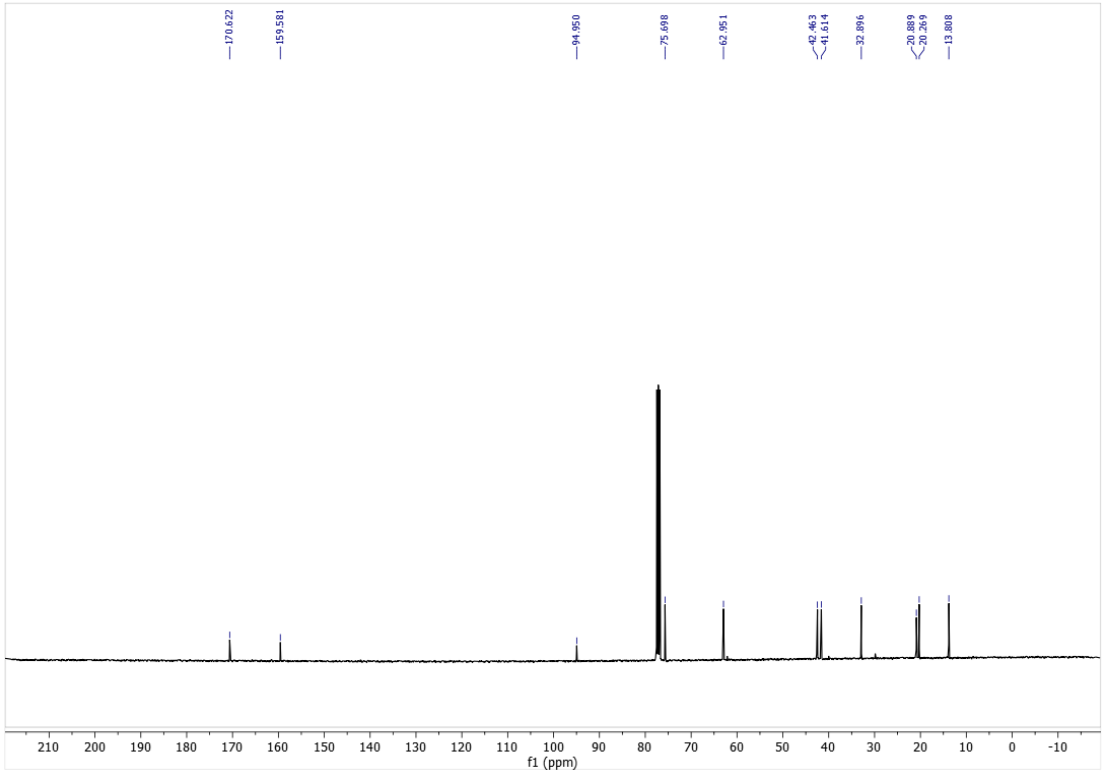

NHTroc
O
5ar
f1 (ppm)

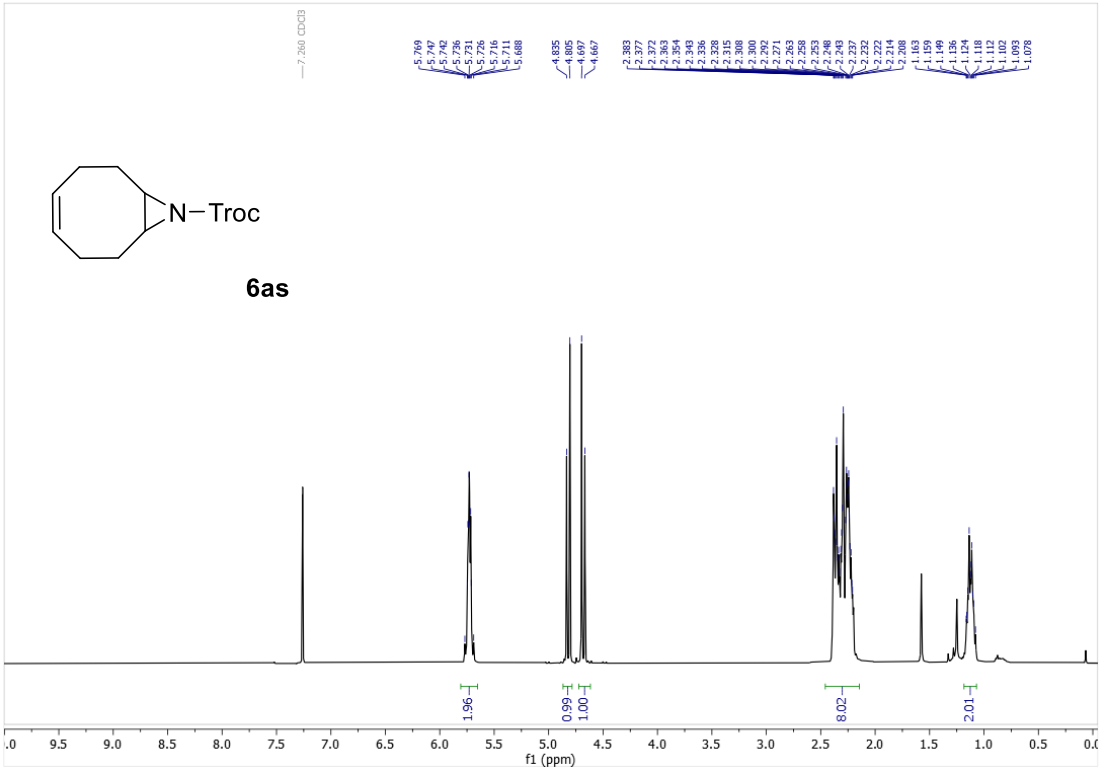

f1 (ppm)

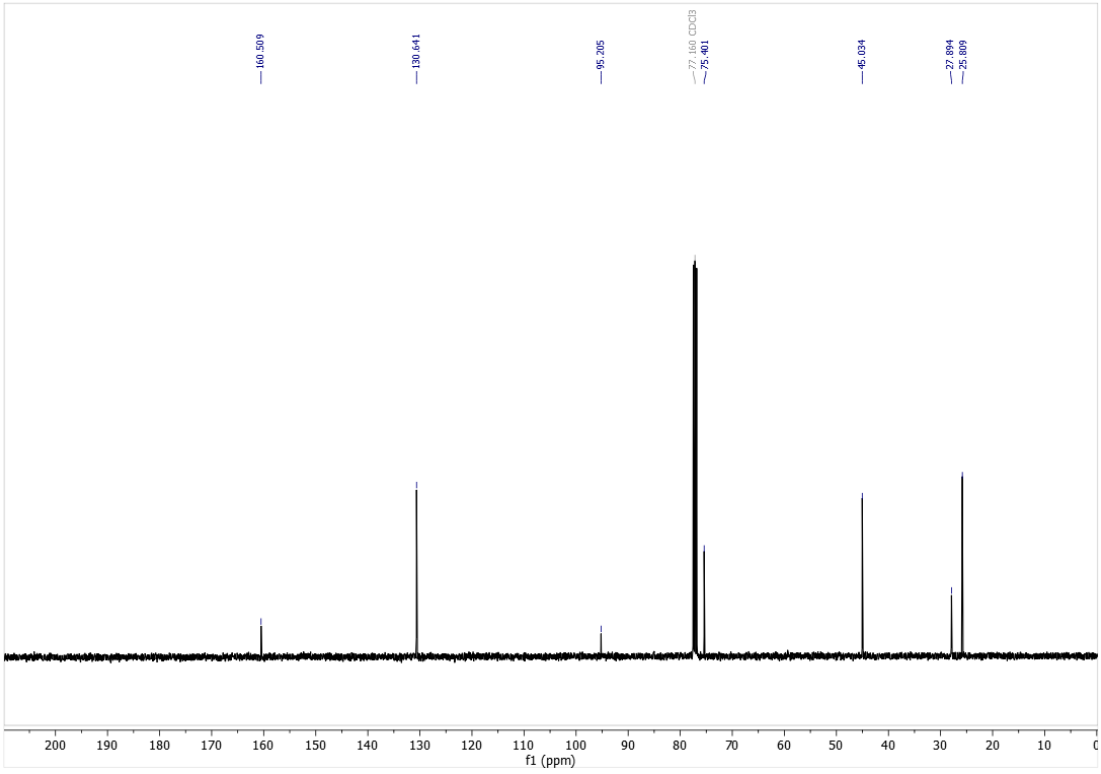

Bz
O
N
Troc
6aj
f1 (ppm)

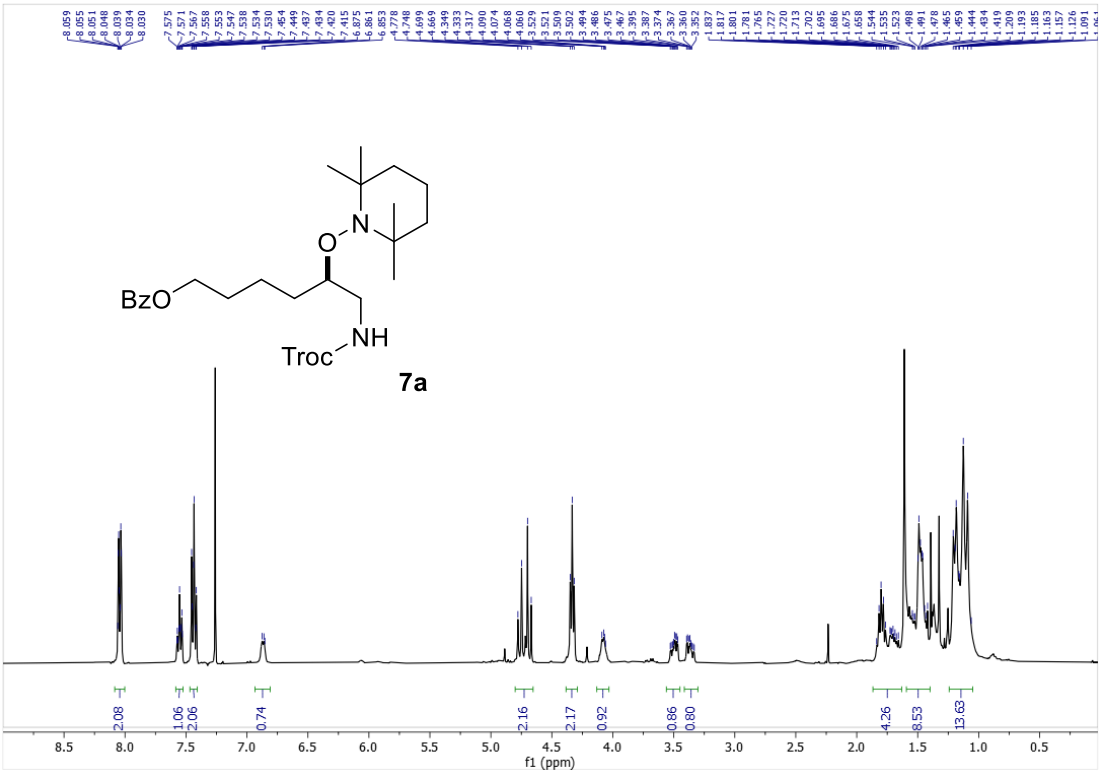

f1 (ppm)

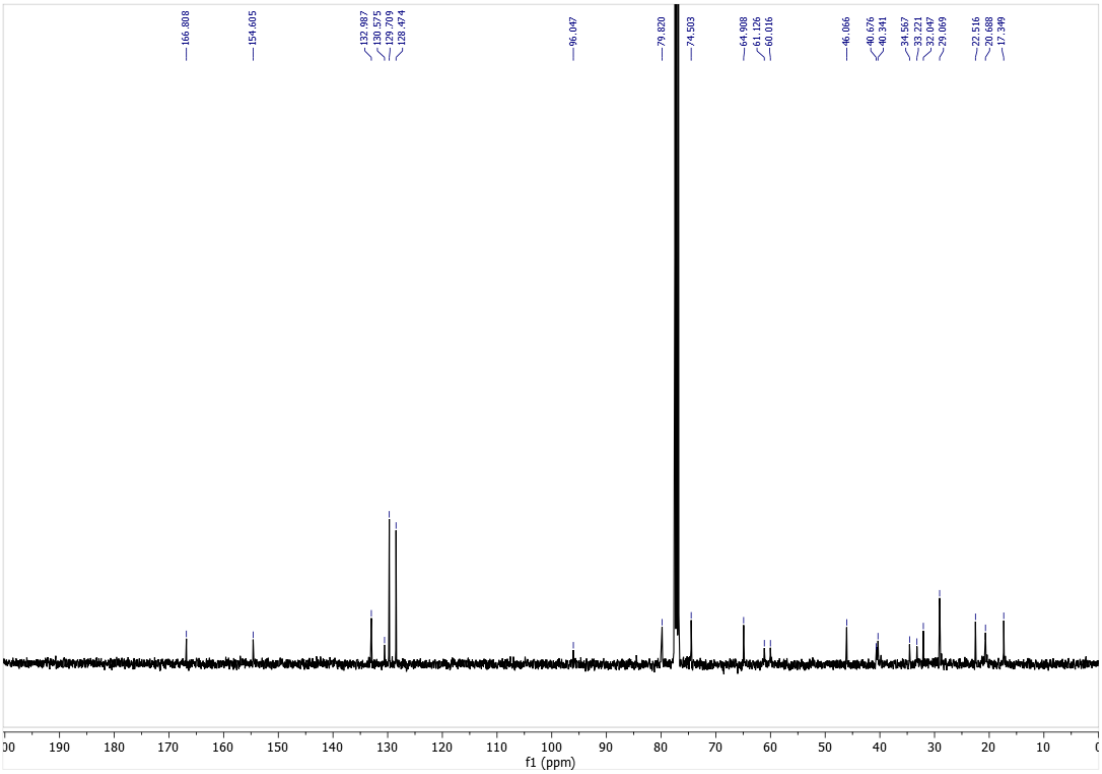

Ac
O
N
Troc
6ak
1.98
2.00
0.96
0.93
3.02
0.98
2.02
1.19
3.06
f1 (ppm)


170.622
159.581
94.950
75.698
62.951
42.463
41.614
32.896
20.889
20.269
13.808
f1 (ppm)


N–Troc
6as
f1 (ppm)


f1 (ppm)


BzO
O
N
NH
Troc
7a
f1 (ppm)


f1 (ppm)

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