$B(C_6F_5)_3$-Catalyzed C–H Alkylation of *N*-Alkylamines Using Silicon Enolates without External Oxidant

*Jessica Z. Chan,‡ Yejin Chang,‡ and Masayuki Wasa**

Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467, United States

Table of Contents

1. Procedures, Materials and Instrumentation

General experimental procedures. All reactions were performed in standard, dry glassware fitted with rubber septa under an inert atmosphere of nitrogen unless otherwise described. Stainless steel syringes or cannulae were used to transfer air- and moisture-sensitive liquids. Reported concentrations refer to solution volumes at room temperature. Evaporation and concentration *in vacuo* were performed using house vacuum (ca. 40 mm Hg). Column chromatography was performed with SiliaFlash® 60 (40–63 micron) silica gel from Silicycle. Thin layer chromatography (TLC) was used for reaction monitoring and product detection

using pre-coated glass plates covered with 0.20 mm silica gel with fluorescent indicator; visualization by UV light (λ_{ex} = 254 nm) or $KMnO_4$ stain.

Materials. Reagents were purchased in reagent grade from commercial suppliers and used without further purification, unless otherwise described. Amines and silicon enolates were prepared according to the procedures reported previously.[1-22] Tris(pentafluorophenyl)borane and ((1-methoxy-2-methylprop-1-en-1-yl)oxy)trimethylsilane were purchased from TCI and used without further purification. H_2O, in synthetic procedures, refers to distilled water.

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra and proton-decoupled carbon nuclear magnetic resonance (^{13}C {^{1}H} NMR) spectra were recorded at 25 °C (unless stated otherwise) on Inova 600 (600 MHz), Varian Unity/Inova 500 (500 MHz) or Oxford AS400 (400 MHz) spectrometers at the Boston College nuclear magnetic resonance facility. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to 0 ppm. Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent. The solvent peak was referenced to 77.0 ppm for ^{13}C for $CDCl_3$. Benzotrifluoride was used as an external standard for ^{19}F NMR and referenced to –63.7 ppm. Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz).

Infrared spectra were recorded on a Bruker FT-IR Alpha (ATR mode) spectrophotometer. Data are represented as follows: frequency of absorption (cm^{-1}).

High-resolution mass spectrometry was performed on a JEOL AccuTOF-DART (positive mode) at the Mass Spectrometry Facility, Boston College.

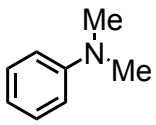
Abbreviations used. Bn = benzyl, Boc = *tert*-butoxycarbonyl, DART = direct analysis in real time, DCE = 1,2-dichloroethane, DCM = dichloromethane, DIPEA = diisopropylethylamine, DMF = *N,N*-dimethylformamide, ESI = electrospray ionization, Et_2O = diethyl ether, EtOAc = ethyl acetate, HR = high-resolution, KOH = potassium hydroxide, LC = liquid chromatography, $MgSO_4$ = magnesium sulfate, MS = mass spectrometry, PTLC = preparatory thin-layer chromatography, TBME = *tert*-butyl methyl ether, THF =

tetrahydrofuran, TLC = thin-layer chromatography, TMS = trimethylsilane, TOF = time-of-flight.

2. Experimental Section

2.1 Substrate Preparation

Table S1. List of Amine Substrates



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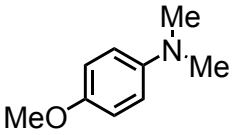

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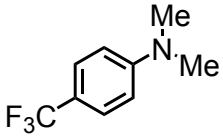

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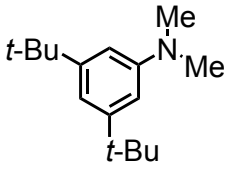

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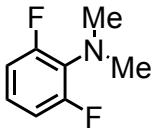

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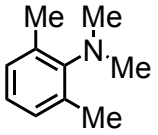

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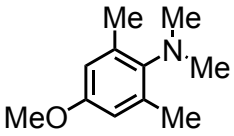

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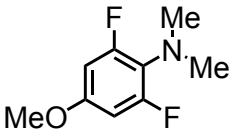

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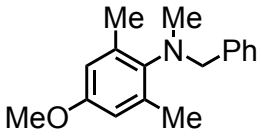

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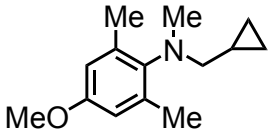

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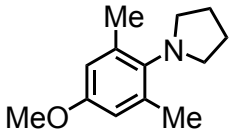

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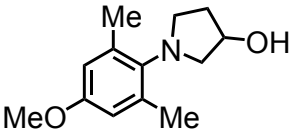

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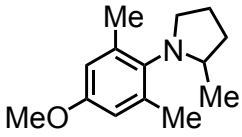

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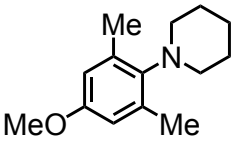

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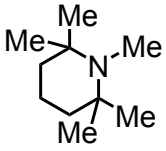

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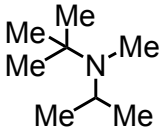

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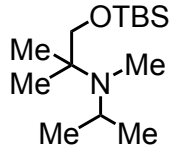
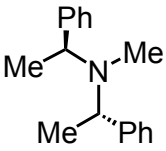


1r



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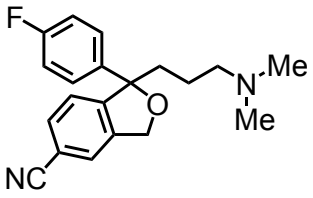
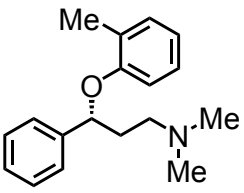


7a



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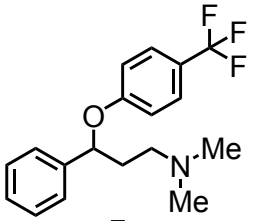


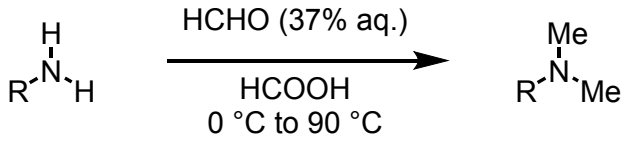
7c

Amines **1a**, **1p** and **1q** were obtained from commercial sources. Substrates **1b-1f**,[1] **1g**,[2-7] **1h**[1], **1i**,[7] **1j**,[8] **1k**,[9] **1l**,[10-12] **1n**,[13] **1o**,[9] **1r**,[14-16] and **1s**,[17-18] were prepared accordingly to the literature procedures. Amine **7a** was obtained commercially as the HBr salt and was treated with

NaOH (1M aqueous solution) before use. Amines **7b**[1] and **7c**[1] were prepared accordingly to the literature procedures. The spectroscopic data for the newly synthesized molecules (**1e**, **1g**, **1h**, **1i, 1j**, **1k**, **1l**, **1n**, **1o**, **1r**, **1s**, **7b**, and **7c**) are described as the following.

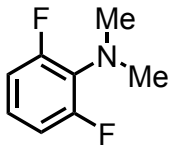
Preparation of Amine Substrates

General Procedure for the Methylation of Amines



1b-1f, 1h, **7b, 7c**

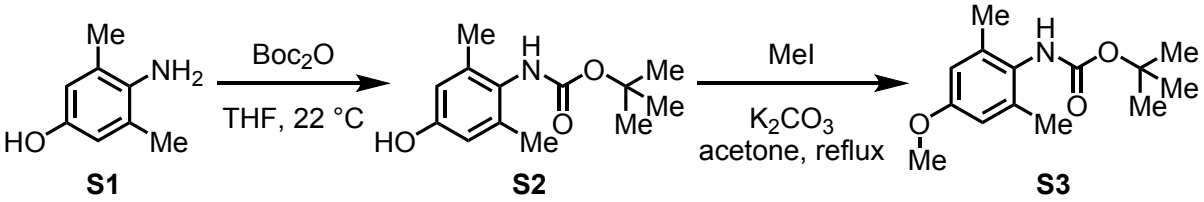
Amines **1b-1f**, **1h**, **7b** and **7c** were prepared following a known procedure.[1] A solution of amine and formaldehyde (37% aq. solution, 6.0 equiv.) was cooled to 0 °C. To the reaction mixture, formic acid (10 equiv.) was added dropwise. The reaction mixture was then warmed to 90 °C for 2 hours. Upon completion, NaOH (1M aq. solution) was added at 0 °C until the pH of the aqueous layer was 12. The organic material was then extracted with Et_2O (3 x 15 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The unpurified product mixture was subjected to silica gel chromatography.



1e

2,6-Difluoro-*N*,*N*-dimethylaniline (1e)

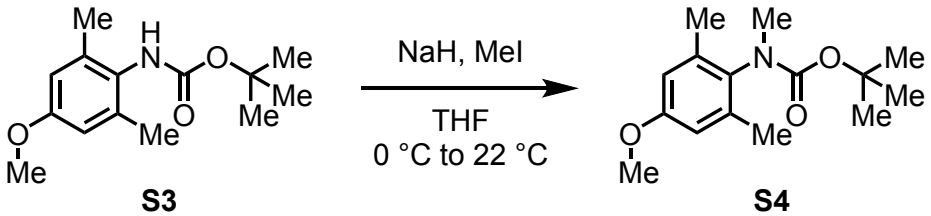
2,6-Difluoro-*N,N*-dimethylaniline was prepared on a 5.0 mmol scale using the General Procedure for the Methylation of Amines to afford a colorless liquid (560 mg, 71%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.91 (ddt, *J* = 9.1, 7.5, 5.9 Hz, 1H), 6.82 (ddd, *J* = 9.8, 8.2, 1.1 Hz, 2H), 2.88 (t, *J* = 1.7 Hz, 6H).



S1 **S2** **S3**

***tert*-Butyl (4-hydroxy-2,6-dimethylphenyl)carbamate (S2)**: *tert*-Butyl (4-hydroxy-2,6-dimethylphenyl)carbamate was prepared following a known procedure.[2] To a solution of 4-amino-3,5-dimethylphenol (**S1**, 10.0 g, 72.9 mmol) in THF (200 mL), was added di-*tert*-butyl dicarbonate (16.7 mL, 72.9 mmol) in a dropwise manner. The reaction mixture was allowed to stir at 22 °C for 12 hours. Upon completion, the reaction mixture was concentrated and used without further purification. The spectroscopic data of **S2** matched those reported by Nam.[3]

***tert*-Butyl (4-methoxy-2,6-dimethylphenyl)carbamate (S3)**: *tert*-Butyl (4-methoxy-2,6-dimethylphenyl)carbamate was prepared following a known procedure.[4] Carbamate **S2** (8.6 g, 36.4 mmol) was dissolved in acetone (50 mL). To the solution was added potassium carbonate (6.1 g, 54.6 mmol) and iodomethane (2.3 mL, 36.4 mmol), dropwise. The reaction mixture was heated to reflux and allowed to stir for 12 hours. Upon completion (monitored by TLC), the reaction was quenched with a saturated aqueous solution of KOH (50 mL), extracted with Et_2O (3 x 50 mL), dried ($MgSO_4$), and concentrated *in vacuo*. The unpurified product mixture was subjected to silica gel chromatography to afford a colorless solid (5.9 g, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.60 (s, 2H), 3.76 (s, 3H), 2.24 (s, 6H), 1.49 (s, 9H).

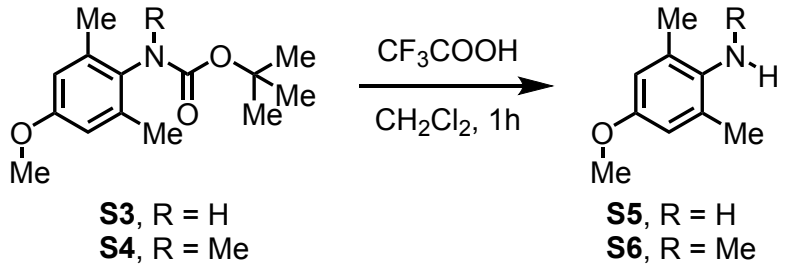


S3 **S4**

***tert*-Butyl (4-methoxy-2,6-dimethylphenyl)(methyl)carbamate (S4):** *tert*-Butyl (4-methoxy-2,6-dimethylphenyl)(methyl)carbamate was prepared following a known procedure.[5] Carbamate **S3** (8.5 g, 33.9 mmol) was dissolved in THF (30 mL). The solution was cooled to 0 °C, sodium hydride (60% oil dispersion, 1.6 g, 40.7 mmol) was added and allowed to stir for 10 minutes. Subsequently, iodomethane (2.5 mL, 40.7 mmol) was added

dropwise at 0 °C. The reaction mixture was allowed to stir at 22 °C for 2 hours. Upon completion of the reaction (monitored by TLC), water was slowly added to the reaction mixture, extracted with EtOAc (3 x 20 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The unpurified product mixture was subjected to silica gel chromatography (5% EtOAc/hexanes) to give the product as a colorless solid (8.5 g, 95%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.59–6.57 (m, 2H), 3.77–3.75 (m, 3H), 3.04 (s, 3H), 2.17– 2.15 (m, 6H), 1.32 (s, 9H).

General Procedure for the Removal of *N*-Boc Protection Group[5]



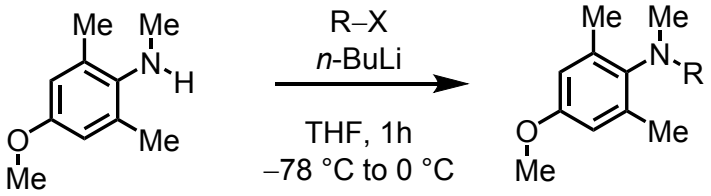
S3, R = H
S4, R = Me

S5, R = H
S6, R = Me

To a solution of carbamate **S3** or **S4** in DCM (0.3 M), CF_3COOH (5.0 equiv.) was added dropwise at 22 °C. The reaction mixture was allowed to stir for 1 hour. Upon completion of the reaction (monitored by TLC), aqueous $NaHCO_3$ was added until the solution was alkaline, extracted with DCM, dried ($MgSO_4$), filtered, and concentrated. The unpurified product mixture was subjected to silica gel chromatography (5% EtOAc/hexanes) to give the product as a yellow liquid. The spectroscopic data of **S5** matched those reported by Organ.[6]

4-Methoxy-*N*,2,6-trimethylaniline (**S6**)**: ^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.58 (s, 2H), 3.74 (s, 3H), 2.72 (s, 1H), 2.68 (s, 3H), 2.29 (s, 6H).

General Procedure A for the Alkylation of Amine S6



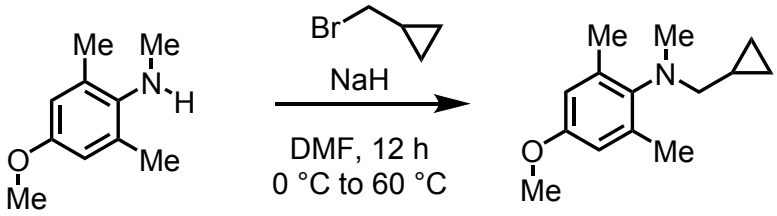
S6

1g, R = Me
1i, R = Bn

Amines **1g** and **1i** were prepared following a known procedure.[7] To a solution of 4-methoxy-*N*,2,6-trimethylaniline (**S6)** in THF (0.5 M) at –78 °C, was added *n*-BuLi (2.5 M, 1.0 equiv.),

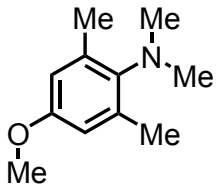
dropwise. The reaction mixture was allowed to stir for 10 minutes, whereupon the respective alkylhalide (1.0 equiv.) was added dropwise at −78 °C. The reaction mixture was then allowed to warm to 0 °C. Upon completion of the reaction (monitored by TLC), the unpurified product mixture was concentrated *in vacuo* and purified by silica gel chromatography (2% EtOAc/hexanes).

General Procedure B for the Alkylation of Amine S6



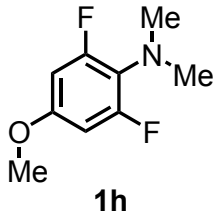
S6 **1j**

Amine **1j** was prepared following a known procedure.[8] To a solution of 4-methoxy-*N*,2,6-trimethylaniline (**S6)** in DMF (1 M) at 0 °C, was added sodium hydride (1.2 equiv.). The mixture was warmed to 60 °C to stir for 15 minutes then allowed to cool to 0 °C, whereupon the alkylhalide (1.2 equiv.) was added dropwise. The reaction mixture was warmed to 60 °C and stirred for 12 hours. The unpurified product mixture was then cooled to 0 °C, water was added slowly, extracted with EtOAc, dried ($MgSO_4$), concentrated *in vacuo*, and was purified by silica gel chromatography (2% EtOAc/hexanes).



4-Methoxy-*N,N*,2,6-tetramethylaniline (1g)

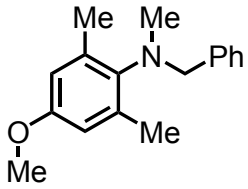
4-Methoxy-*N,N*,2,6-tetramethylaniline was synthesized using General Procedure A on a 10.0 mmol scale to afford a colorless liquid (765 mg, 43%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.54 (s, 2H), 3.75 (s, 3H), 2.79 (s, 6H), 2.28 (s, 6H).



1h

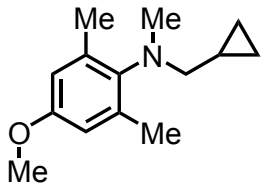
2,6-Difluoro-4-methoxy-*N*,*N*-dimethylaniline (1h)

2,6-Difluoro-4-methoxy-*N*,*N*-dimethylaniline was prepared on a 5.0 mmol scale following the General Procedure for the Methylation of Amines to afford a colorless liquid (860 mg, 92%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.46 – 6.37 (m, 2H), 3.74 (s, 3H), 2.81 (t, *J* = 1.3 Hz, 6H).



***N*-Benzyl-4-methoxy-*N*,2,6-trimethylaniline (1i)**

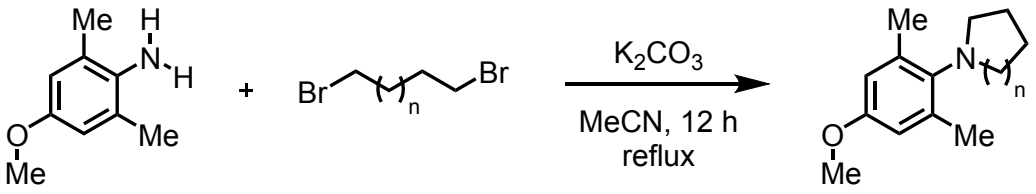
N-Benzyl-4-methoxy-*N*,2,6-trimethylaniline was synthesized using General Procedure A on a 3.1 mmol scale to afford a colorless oil (408 mg, 52%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.25 (m, 1H), 6.56 (s, 2H), 4.14 (s, 3H), 3.76 (s, 3H), 2.65 (s, 2H), 2.35 (s, 6H).



***N*-(Cyclopropylmethyl)-4-methoxy-*N*,2,6-trimethylaniline (1j)**

N-(Cyclopropylmethyl)-4-methoxy-*N*,2,6-trimethylaniline was synthesized using General Procedure B on a 3.0 mmol scale to give the product as a colorless liquid (346 mg, 53%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.54 (s, 2H), 3.75 (s, 3H), 2.81 (m, 5H), 2.27 (s, 6H), 0.95 – 0.82 (m, 1H), 0.45 – 0.39 (m, 2H), 0.11 – 0.02 (m, 2H).

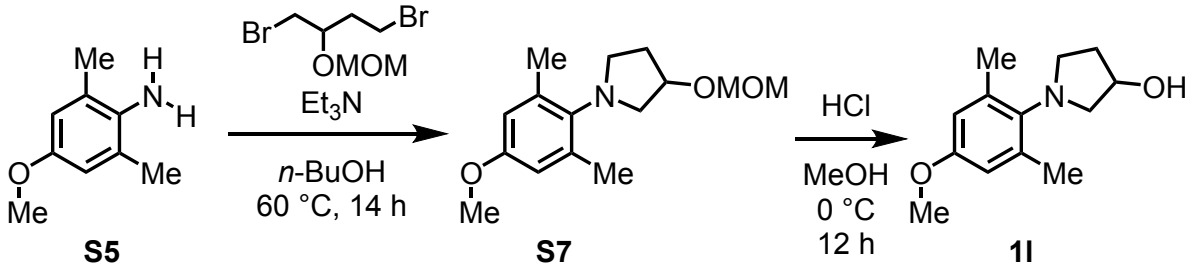
Procedure for Synthesizing Amine 1k and 1o



S5 n = 1 or 2 **1k**, n = 1 **1o**, n = 2

1-(4-Methoxy-2,6-dimethylphenyl)pyrrolidine (1k)

1-(4-Methoxy-2,6-dimethylphenyl)pyrrolidine was prepared using a known procedure.[9] A mixture of aniline **S5** (1.0 g, 6.6 mmol), K_2CO_3 (2.7 g, 19.8 mmol), and 1,4-dibromobutane (1.2 mL, 9.9 mmol) in acetonitrile (10 mL) was heated to reflux for 12 hours. Upon completion, the reaction mixture was quenched with H_2O, extracted with EtOAc (3 x 25 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The unpurified product mixture was subjected to silica gel chromatography (3% EtOAc/hexanes) to give the product as a yellow liquid (1.1 g, 82%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.58 (s, 2H), 3.75 (s, 3H), 3.20 – 3.08 (m, 4H), 2.23 (s, 6H), 1.99 – 1.90 (m, 4H).



S5 **S7** **1l**

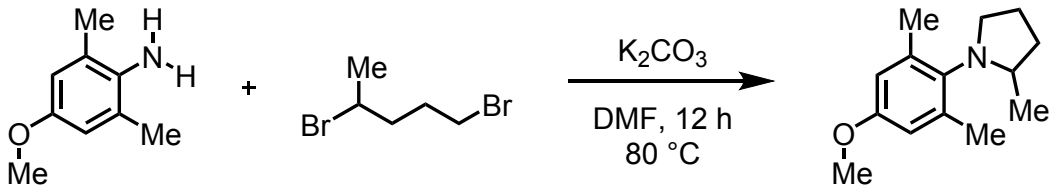
1-(4-Methoxy-2,6-dimethylphenyl)-3-(methoxymethoxy)pyrrolidine (S7)

1-(4-Methoxy-2,6-dimethylphenyl)-3-(methoxymethoxy)pyrrolidine was synthesized using a known procedure.[10] 1,4-dibromo-2-(methoxymethoxy)butane was prepared following the literature procedure using chloromethyl methyl ether.[11] To a solution of aniline **S5** (500 mg, 3.3 mmol) in *n*-butanol (5 mL) was added 1,4-dibromo-2-(methoxymethoxy)butane (1.0 g, 3.63 mmol) and triethylamine (1.4 mL, 9.9 mmol). The solution was then allowed to heat at 80 °C for 14 hours. The reaction mixture was diluted with H_2O (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic layer was washed with brine (1 x 20 mL), dried ($MgSO_4$), and concentrated *in vacuo*. The unpurified product mixture was subjected to silica gel chromatography to afford **S7** as a colorless liquid (263 mg, 30%). **^{1}H NMR** (500 MHz,

$CDCl_3$) δ 6.57 (s, 2H), 4.75 – 4.69 (m, 2H), 4.44 – 4.36 (m, 1H), 3.75 (s, 3H), 3.47 – 3.39 (m, 2H), 3.39 (s, 3H), 3.21 – 3.09 (m, 2H), 2.25 (s, 6H), 2.24 – 2.12 (m, 1H), 2.11 – 2.00 (m, 1H).

1-(4-Methoxy-2,6-dimethylphenyl)pyrrolidin-3-ol (1l)

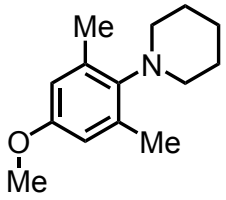
1-(4-Methoxy-2,6-dimethylphenyl)pyrrolidin-3-ol was obtained by the deprotection of the MOM protecting group of **S7** following the literature procedure.[12] To a solution of amine **S7** (100 mg, 0.4 mmol) in MeOH (1 mL) at 0 °C was added 10 M HCl (0.8 mL), dropwise. The reaction was allowed to stir for 12 hours at room temperature, whereupon the reaction mixture was concentrated *in vacuo*. The resulting residue was basified with saturated aqueous solution of K_2CO_3 until alkaline. The solution was then extracted with EtOAc (3 x 15 mL) and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo.* The unpurified product mixture was subjected to silica gel chromatography (15% EtOAc/hexanes) to afford the product as a colorless liquid (70 mg, 78%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.52 (s, 2H), 4.45 (s, 1H), 3.70 (s, 3H), 3.43 – 3.39 (m, 1H), 3.11 – 3.06 (m, 1H), 3.01 – 2.97 (m, 1H), 2.20 (s, 6H), 2.18 – 2.10 (m, 1H), 1.94 – 1.87 (m, 1H), 1.76 (s, 1H).



1-(4-Methoxy-2,6-dimethylphenyl)-2-methylpyrrolidine (1n)

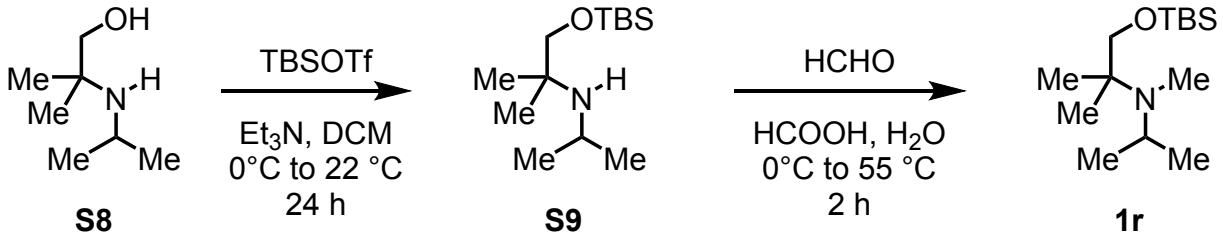
1-(4-Methoxy-2,6-dimethylphenyl)-2-methylpyrrolidine was prepared using a known procedure.[13] To a solution of aniline **S5** (650 mg, 4.3 mmol) in DMF (5 mL) was added K_2CO_3 (654 mg, 4.7 mmol) and 1,4-dibromopentane (0.6 mL, 4.7 mmol). The reaction mixture was stirred under reflux for 12 hours. After cooling the reaction mixture to room temperature, the mixture was quenched with H_2O (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The unpurified product mixture was subjected to silica gel chromatography (2% EtOAc/hexanes) to afford **1n** as a colorless liquid (593 mg, 63%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.57 (s, 2H), 3.75 (s, 3H), 3.59 – 3.51 (m, 1H), 3.27 (td, *J* = 7.9, 5.0 Hz, 1H), 3.05

(td, J = 8.1, 6.2 Hz, 1H), 2.24 (s, 6H), 2.14 – 2.03 (m, 1H), 2.02 – 1.81 (m, 2H), 1.59 – 1.46 (m, 1H), 0.91 (d, J = 6.0 Hz, 3H).



1-(4-Methoxy-2,6-dimethylphenyl)piperidine (1o)

1-(4-Methoxy-2,6-dimethylphenyl)piperidine was prepared using a known procedure[9] on 1.0 mmol scale, using 1,5-dibromopentane. The product was obtained as a white solid (165 mg, 75%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.52 (s, 2H), 3.74 (s, 3H), 2.98 (t, J = 5.1 Hz, 4H), 2.29 (s, 6H), 1.65 – 1.58 (m, 4H), 1.58 – 1.51 (m, 2H).

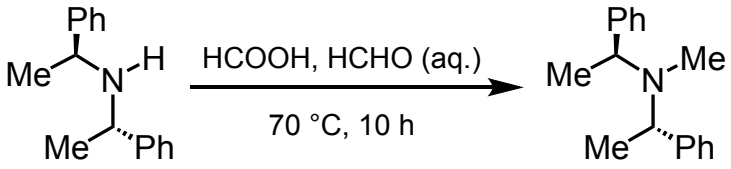


1-((*tert*-Butyldimethylsilyl)oxy)-*N*-isopropyl-2-methylpropan-2-amine (S8) 1-((*tert*-Butyldimethylsilyl)oxy)-*N*-isopropyl-2-methylpropan-2-amine was prepared following a known procedure.[14] To a solution of 2-(isopropylamino)-2-methylpropan-1-ol[15] (20 mmol), and triethylamine (26 mmol) in DCM (50 mL) at 0 °C was added *tert*-butyldimethylsilyl trifluoromethanesulfonate (26 mmol) dropwise. The reaction mixture was allowed to stir at 22 °C for 24 hours. Upon completion, the reaction was quenched with H_2O (20 mL), the organic phase was separated and the aqueous phase was extracted with DCM (3 × 50 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The unpurified product mixture was subjected to silica gel chromatography (5% Et_3N/hexanes) to afford **S9** as a colorless oil (4.68 g, 19.08 mmol, 95%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.32 (s, 2H), 2.87 (m, 1H), 1.04 (d, J = 6.3 Hz, 6H), 1.01 (s, 6H), 0.89 (s, 9H), 0.04 (s, 6H).

1-((*tert*-Butyldimethylsilyl)oxy)-*N*-isopropyl-*N*,2-dimethylpropan-2-amine (1r)

1-((*tert*-Butyldimethylsilyl)oxy)-*N*-isopropyl-*N*,2-dimethylpropan-2-amine was prepared following a known procedure.[16] A 37% aq. solution of formaldehyde (1.6 g, 22 mmol) was

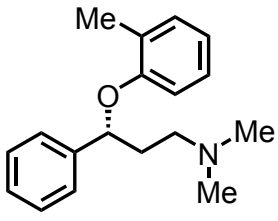
added to a mixture of 1-((*tert*-butyldimethylsilyl)oxy)-*N*-isopropyl-2-methylpropan-2-amine **S9** (4.43 g, 18.1 mmol) and 88% formic acid (1.8 g, 39 mmol) at 0 °C. The reaction mixture was kept at 55 °C for 2 hours. Upon completion (monitored by TLC), the reaction was quenched with 8.0 M KOH (10 mL), extracted with Et_2O (3 x 50 mL), dried ($MgSO_4$), and concentrated *in vacuo*. The unpurified product mixture was subjected to silica gel chromatography (2% Et_3N/hexanes) to afford **1r** as a colorless oil (3.2 g, 68% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 3.43 (s, 2H), 3.31 (hept, J = 6.6 Hz, 1H), 2.21 (s, 3H), 1.05 (s, 6H), 1.00 (d, J = 6.8 Hz, 6H), 0.89 (s, 9H), 0.03 (s, 6H).



S10 **1s**

(*S*)-*N*-Methyl-1-phenyl-*N*-((*S*)-1-phenylethyl)ethan-1-amine (1s)

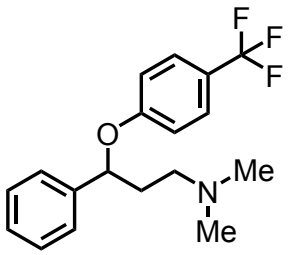
(*S*)-*N*-Methyl-1-phenyl-*N*-((*S*)-1-phenylethyl)ethan-1-amine was prepared following a known procedure.[17] A 37% aq. solution of formaldehyde (17.6 mmol) was added to a mixture of (*S*)-bis((*S*)-1-phenylethyl)amine **S10** (1.0 g, 4.4 mmol) and 88% formic acid (8.8 mmol) at 0 °C. The reaction mixture was kept at 70 °C for 10 hours. Upon completion (monitored by TLC), the reaction was basified with 1 M NaOH, extracted with EtOAc (3 x 40 mL), dried ($MgSO_4$), and concentrated *in vacuo*. The unpurified product mixture was subjected to silica gel chromatography (2% Et_3N/hexanes) to afford **1s** as a colorless oil (0.9 g, 94% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 7H), 7.26 – 7.21 (m, 2H), 3.82 (q, J = 6.8 Hz, 2H), 2.00 (s, 3H), 1.33 (d, J = 6.8 Hz, 6H).[18]



(*R*)-*N,N*-Dimethyl-3-phenyl-3-(*o*-tolyloxy)propan-1-amine (7b)

(*R*)-*N,N*-Dimethyl-3-phenyl-3-(*o*-tolyloxy)propan-1-amine was prepared following the General Procedure for Methylation of Amines on a 8.8 mmol scale. The unpurified product

mixture was subjected to silica gel chromatography (4% MeOH/DCM) and was obtained as a colorless liquid (2.3 g, 97% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 4H), 7.28 – 7.19 (m, 1H), 7.13 – 7.06 (m, 1H), 6.99 – 6.90 (m, 1H), 6.76 (td, *J* = 7.4, 1.1 Hz, 1H), 6.62 (d, *J* = 8.2 Hz, 1H), 5.22 (dd, *J* = 8.2, 4.7 Hz, 1H), 2.45 (t, *J* = 7.3 Hz, 2H), 2.31 (s, 3H), 2.23 (s, 6H), 2.21 – 2.12 (m, 1H), 2.05 – 1.92 (m, 1H).

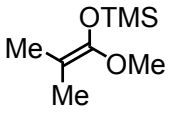
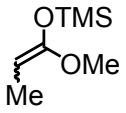
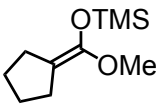
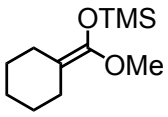
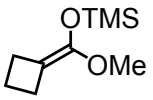
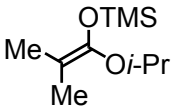
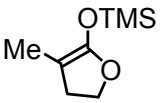
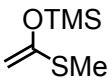


***N,N*-Dimethyl-3-phenyl-3-(4-(trifluoromethyl)phenoxy)propan-1-amine (7c)**

N,N-Dimethyl-3-phenyl-3-(4-(trifluoromethyl)phenoxy)propan-1-amine was prepared following the General Procedure for Methylation of Amines on a 7.3 mmol scale. The unpurified product mixture was subjected to silica gel chromatography (2% MeOH/DCM) and was obtained as a colorless liquid (2.2 g, 95% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.6 Hz, 2H), 7.37 – 7.30 (m, 4H), 7.29 – 7.25 (m, 1H), 6.91 (d, *J* = 8.6 Hz, 2H), 5.28 (dd, *J* = 8.2, 5.0 Hz, 1H), 2.50 – 2.37 (m, 2H), 2.24 (s, 6H), 2.22 – 2.14 (m, 1H), 1.98 (tt, *J* = 13.9, 5.7 Hz, 1H).

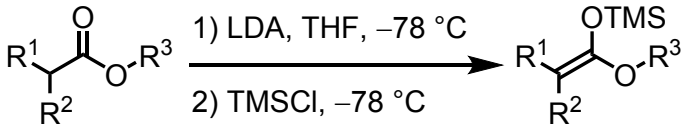
Preparation of Silicon Enolate Substrates

Table S2. Silicon Enolate Substrates

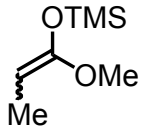
			
2a	**2b**	**2c**	**2d**
			
2e	**2f**	**2g**	**2h**

Silicon enolate molecule **2a** was obtained from commercial sources. Substrates **2b**,[19] **2c**,[20] **2d**,[20] **2e**,[20] **2f**,[21] **2g**,[22] and **2h** were prepared accordingly to the procedures previously reported in the literatures.

General Procedure for Preparation of Silicon Enolates

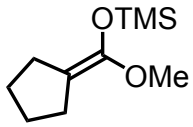


To a solution of diisopropylamine (1.25 equiv.) in THF, *n*-BuLi (2.5 M in hexanes, 1.2 equiv.) was added dropwise at −78 °C and the solution was stirred for 15 minutes. A solution of ester in THF was added dropwise at −78 °C and the solution was stirred for 1 hour. Subsequently, TMSCl (1.2 equiv.) was added slowly at −78 °C, the reaction mixture was warmed up to 22 °C and was stirred until the completion of the reaction (monitored by ^{1}H NMR). The reaction mixture was diluted with ice-cold pentane and the resulting suspension was filtered through a pad of Celite. The filtrate was concentrated under vacuum and the resulting crude mixture was purified by distillation under reduced pressure to give the corresponding silicon enolate.



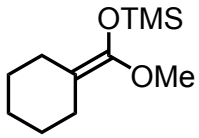
((1-Methoxyprop-1-en-1-yl)oxy)trimethylsilane (2b)

((1-Methoxyprop-1-en-1-yl)oxy)trimethylsilane was synthesized following the general procedure at 20.0 mmol scale and was kept at −78 °C until the reaction was complete. The product was obtained as colorless liquid (*E*/*Z* = 7:1). The NMR spectroscopic data were in agreement with those reported in the literature.[19]



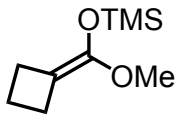
(Cyclopentylidene(methoxy)methoxy)trimethylsilane (2c)

(Cyclopentylidene(methoxy)methoxy)trimethylsilane was synthesized following the general procedure on 7.7 mmol scale. The product was obtained as colorless liquid. The NMR spectroscopic data were in agreement with those reported in the literature.[20]



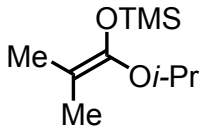
(Cyclohexylidene(methoxy)methoxy)trimethylsilane (2d)

(Cyclohexylidene(methoxy)methoxy)trimethylsilane was synthesized following the general procedure at 10.0 mmol scale. The product was obtained as colorless liquid. The NMR spectroscopic data were in agreement with those reported in the literature.[20]



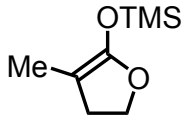
(Cyclobutylidene(methoxy)methoxy)trimethylsilane (2e)

(Cyclobutylidene(methoxy)methoxy)trimethylsilane was synthesized following the general procedure at 8.7 mmol scale. The product was obtained as colorless liquid (OSi/CSi=6:1). The NMR spectroscopic data were in agreement with those reported in the literature.[20]



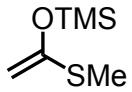
((1-Isopropoxy-2-methylprop-1-en-1-yl)oxy)trimethylsilane (2f)

((1-Isopropoxy-2-methylprop-1-en-1-yl)oxy)trimethylsilane was synthesized following the general procedure at 60.0 mmol scale. The product was obtained as colorless liquid. The NMR spectroscopic data were in agreement with those reported in the literature.[21]



Trimethyl((3-methyl-4,5-dihydrofuran-2-yl)oxy)silane (2g)

Trimethyl((3-methyl-4,5-dihydrofuran-2-yl)oxy)silane was synthesized following the general procedure at 10.0 mmol scale. The product was obtained as colorless liquid. The NMR spectroscopic data were in agreement with those reported in the literature.[22]



Trimethyl((1-(methylthio)vinyl)oxy)silane (2h)

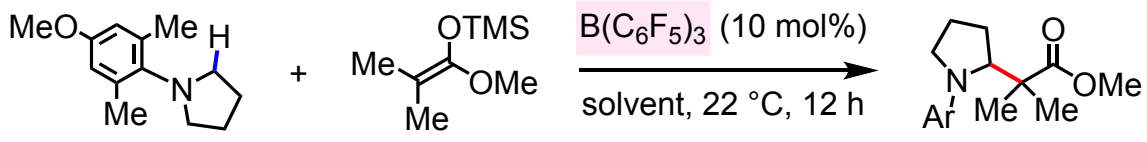
Trimethyl((1-(methylthio)vinyl)oxy)silane was synthesized following the general procedure at 10.0 mmol scale and was kept at −78 °C until the reaction was complete (1 hour). The filtrate was concentrated under vacuum and the resulting crude oil was purified by distillation under reduced pressure (40 °C, 40 mmHg), to give trimethyl((1-(methylthio)vinyl)oxy)silane as colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.39 (d, J = 2.2 Hz, 1H), 4.22 (d, J = 2.2 Hz, 1H), 2.22 (s, 3H), 0.26 (s, 9H).

2.2 $B(C_6F_5)_3$-Catalyzed Mannich-type Reaction

Experimental Procedure for the Optimization of Solvent (see Table S3 in SI)

To a 15 mL oven-dried sealed tube equipped with a magnetic stir bar was added amine **1k** (0.1 mmol), $B(C_6F_5)_3$ (0.01 mmol), ((1-methoxy-2-methylprop-1-en-1-yl)oxy)trimethylsilane **2a** (0.2 mmol), and solvent (0.25 mL) under a nitrogen atmosphere. The reaction mixture was stirred for 12 hours at 22 °C. Upon completion, the reaction mixture was concentrated *in vacuo*. The product yield was determined by the ^1H NMR analysis of the unpurified product mixtures using mesitylene as the internal standard. The unpurified product mixture was subjected to PTLC using 20% EtOAc in hexanes as the eluent to give **3k**.

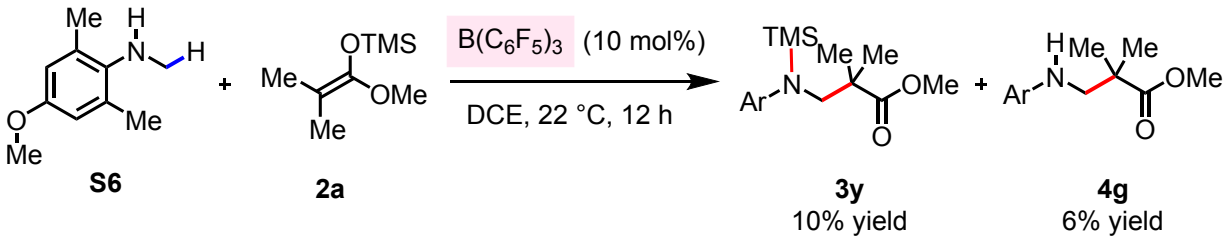
Table S3. Evaluation of Solvents for Cyclic Amine Substrate **1k**



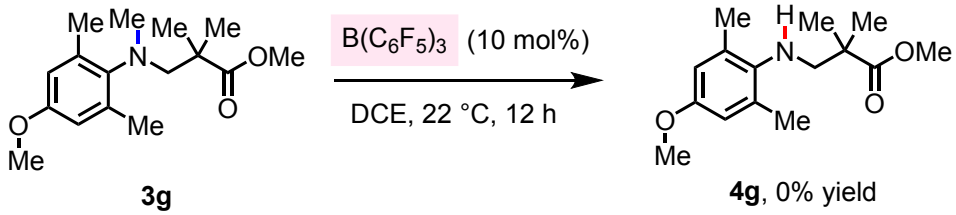
1k **2a** **3k**

Entry	Solvent	yield (%)
1	CH_2Cl_2	46
2	Toluene	76
3	Benzene	78
4	TBME	90
5	THF	93

Control Experiments for the Formation of 4g

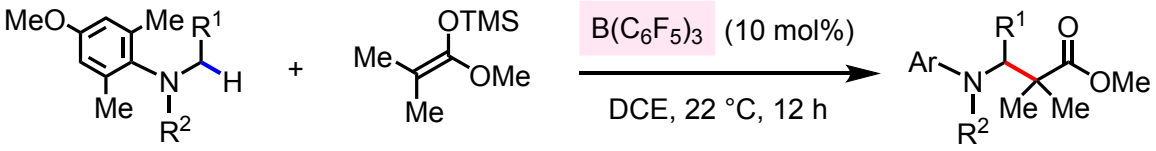


To a 15 mL oven-dried sealed tube equipped with a magnetic stir bar was added amine **S6** (0.4 mmol), $B(C_6F_5)_3$ (0.04 mmol), ((1-methoxy-2-methylprop-1-en-1-yl)oxy)trimethylsilane **2a** (0.8 mmol), and DCE (1.0 mL) under a nitrogen atmosphere. The reaction mixture was allowed to stir for 12 hours at 22 °C. Upon completion, the reaction mixture was concentrated *in vacuo*. The unpurified product mixture was subjected to silica gel chromatography (3% Et_2O/hexanes) to give the product as a mixture of **3y** (13.5 mg, 10%) and desilylated product **4g** (6.7 mg, 6%).

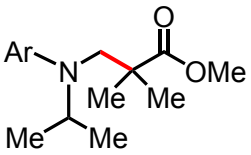
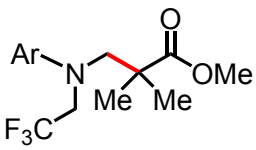
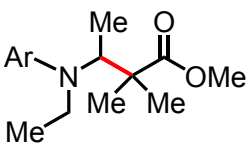
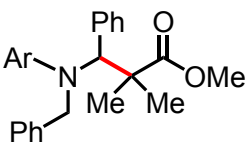


To a 15 mL oven-dried sealed tube equipped with a magnetic stir bar was added amine **3g** (0.1 mmol), $B(C_6F_5)_3$ (0.01 mmol), and DCE (0.25 mL) under a nitrogen atmosphere. The reaction mixture was allowed to stir for 12 hours at 22 °C. Upon completion, the reaction mixture was concentrated *in vacuo*. The ^1H NMR analysis of the unpurified product mixture revealed that there was no product formation and >90% of **3g** was observed using mesitylene as the internal standard.

Reaction of Different *N,N*-Dialkylanilines with Silicon Enolate 2a

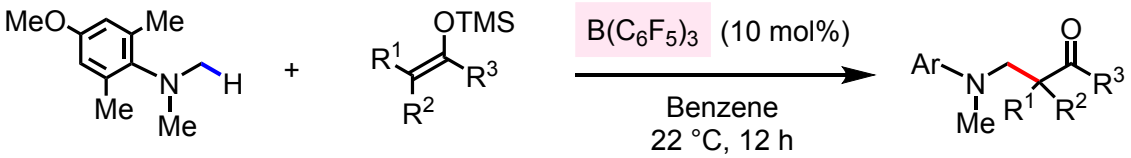


1 **2a** **4**

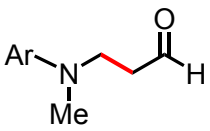
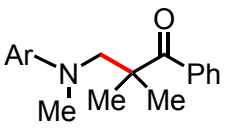
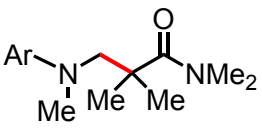
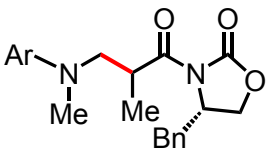
			
4a, 10% yield	**4b** 0% yield	**4c**, 0% yield	**4d**, 0% yield

To a 15 mL oven-dried sealed tube equipped with a magnetic stir bar was added *N,N*-dialkylaniline (0.2 mmol), $B(C_6F_5)_3$ (0.02 mmol), ((1-methoxy-2-methylprop-1-en-1-yl)oxy)trimethylsilane **2a** (0.4 mmol), and DCE (0.5 mL) under a nitrogen atmosphere. The reaction mixture was allowed to stir for 12 hours at 22 °C. Upon completion, the reaction mixture was concentrated *in vacuo*. The ^{1}H NMR analysis of the unpurified product mixtures revealed that there was no product formation and >90% of the starting amine was observed using mesitylene as the internal standard.

Reaction of *N,N*-Dimethylaniline with Different Silicon Enolates



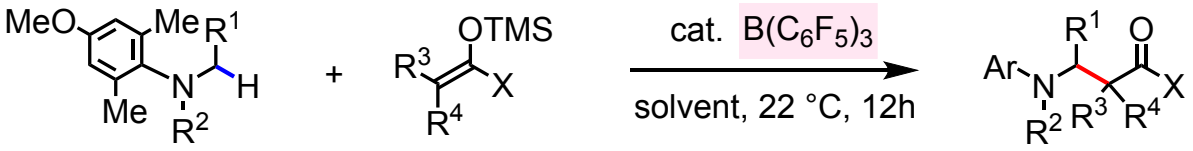
1g **2** **4**

			
4e, 0% yield	**4f**, 0% yield	**4h**, 0% yield	**4i**, 0% yield

To a 15 mL oven-dried sealed tube equipped with a magnetic stir bar was added *N,N*-methylaniline (0.2 mmol), $B(C_6F_5)_3$ (0.02 mmol), silicon enolate **2** (0.4 mmol), and benzene (0.5 mL) under a nitrogen atmosphere. The reaction mixture was allowed to stir for 12 hours at 22 °C. Upon completion, the reaction mixture was concentrated *in vacuo*. The ^{1}H NMR

analysis of the unpurified product mixtures revealed that there was no product formation and >90% of **1g** was observed using mesitylene as the internal standard.

General Procedure for the Mannich Reaction (See Tables 3-4 in Manuscript)



1 **2** **3**

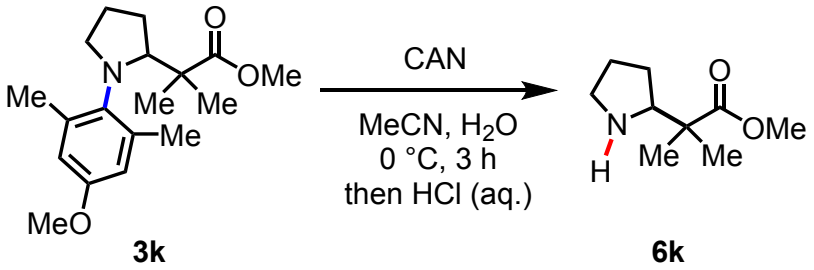
An oven-dried sealed tube equipped with a magnetic stir bar was used. To this tube were added amine (0.2 mmol), $B(C_6F_5)_3$ (0.01 mmol or 0.02 mmol), silicon enolate **2** (0.4 mmol), and solvent (0.5 mL) under nitrogen atmosphere. The reaction mixture was allowed to stir for 12 hours at 22 °C. Upon completion, the reaction mixture was diluted with DCM, concentrated *in vacuo* and purified by silica gel column chromatography, typically using ethyl ether in hexanes as the eluent.

Products **3g**, **3i**, **3j**, and **3p-3r** were obtained using benzene as the solvent. For products **3k**, **3l**, **3m**, **3n**, **3o**, **3s-3x**, and **5a-5d**, THF was used as the solvent. Product **8a** was obtained using benzene as the solvent at 70 °C. For products **8b** and **8c**, DCM was used as the solvent.

2.3 Reaction Procedure for a 1.0 mmol Scale Reaction

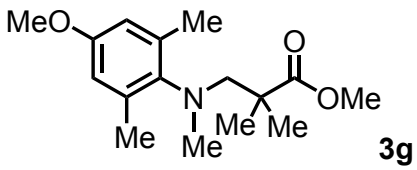
An oven-dried sealed tube equipped with a magnetic stir bar was used. To this tube were added amine **1k** (0.2 g, 1.0 mmol), $B(C_6F_5)_3$ (26 mg, 0.05 mmol), ((1-methoxy-2-methylprop-1-en-1-yl)oxy)trimethylsilane **2a** (0.3 g, 2.0 mmol), and THF (2.5 mL) under nitrogen atmosphere. The reaction mixture was allowed to stir for 12 hours at 22 °C. The unpurified product mixture was subjected to silica gel chromatography (3% Et_2O/hexanes) to afford **3k** as a colorless liquid (0.3 g, 97%).

2.4 Deprotection of *N*-Aryl Group



The deprotection of *N*-aryl group was performed following the literature procedure.[23] To a solution of **3k** (61 mg, 0.2 mmol) in MeCN (2.0 mL) at 0 °C was added a solution of ceric ammonium nitrate (548 mg, 1.0 mmol) in H_2O (3.3 mL), dropwise. The reaction mixture was allowed to stir at 0 °C for 1 hour, whereupon the mixture was cooled to 22 °C and stirred for 3 hours. Upon completion (monitored by TLC), the reaction mixture was quenched with 1 M NaOH until the pH of the solution was 10; and the crude product was extracted with DCM (3 x 15 mL). The combined organic layers were concentrated *in vacuo*, whereupon the resulting oil was acidified with 4 N HCl (4 mL) and extracted again with DCM (3 x 5 mL). The *aqueous* layer was then concentrated *in vacuo* to obtain a solid residue. To the unpurified product mixture was added DCM, and the resulting suspension was filtered through Celite and concentrated to afford a brown residue which was characterized as the HCl salt of **6k** (40 mg, 97%). Upon treatment of the salt with K_2CO_3 (aqueous) and extraction with DCM (3 x 10 mL), the free base **6k** was obtained as a brown oil (27 mg, 79% yield from **6k**). The spectroscopic data of **6k** matched those reported by Sekiya.[24]

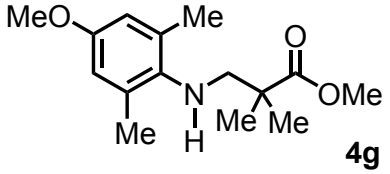
3. Analytical Data



3g

Methyl 3-((4-methoxy-2,6-dimethylphenyl)(methyl)amino)-2,2-dimethylpropanoate (3g)

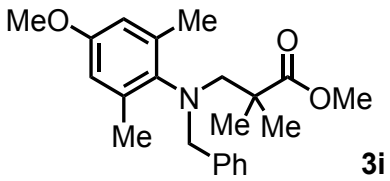
Substrate **1g** was reacted with ((1-methoxy-2-methylprop-1-en-1-yl)oxy)trimethylsilane **2a** following the general procedure using benzene as the solvent and 5 mol% $B(C_6F_5)_3$. After purification by column chromatography (3% ethyl ether in hexanes), **3g** was obtained as a colorless liquid (44.7 mg, 80%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.53 (s, 2H), 3.73 (s, 3H), 3.52 (s, 3H), 3.17 (s, 2H), 2.69 (s, 3H), 2.26 (s, 6H), 1.16 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 178.07, 156.15, 144.23, 137.54, 113.69, 67.21, 55.15, 51.36, 45.32, 43.85, 23.66, 19.34; **IR** (neat) ν 2948, 2837, 2790, 1729, 1602, 1484, 1468, 1433, 1286, 1192, 1154, 1140, 1063, 983, 855 cm^{-1}; **HRMS** (DART) Calcd for $C_{16}H_{26}NO_3$ (MH^+): 280.1913; found: 280.1902.



4g

Methyl 3-((4-methoxy-2,6-dimethylphenyl)amino)-2,2-dimethylpropanoate (4g)

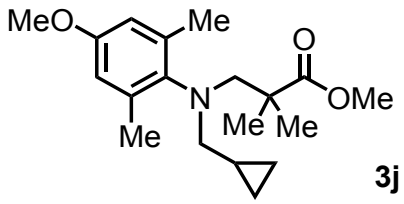
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.45 (s, 2H), 4.39 (s, 1H), 3.52 (s, 3H), 3.16 (s, 2H), 2.69 (s, 3H), 2.23 (s, 6H), 1.16 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.18, 152.13, 144.24, 137.83, 115.10, 67.20, 51.40, 45.36, 43.90, 23.65, 19.14; **IR** (neat) ν 3402, 2949, 2927, 2792, 1707, 1609, 1592, 1467, 1390, 1289, 1239, 1196, 1163, 1095, 1026, 856 cm^{-1}; **HRMS** (DART) Calcd for $C_{15}H_{24}NO_3$ (MH^+): 266.1756; found: 266.1744.



3i

Methyl 3-(benzyl(4-methoxy-2,6-dimethylphenyl)amino)-2,2-dimethylpropanoate (3i)

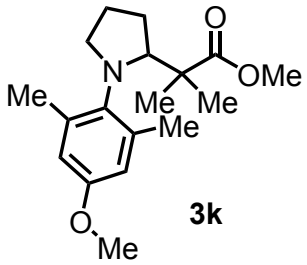
Substrate **1i** was reacted with ((1-methoxy-2-methylprop-1-en-1-yl)oxy)trimethylsilane **2a** following the general procedure using benzene as the solvent. After purification by column chromatography (2% ethyl ether in hexanes), **3i** was obtained as a colorless liquid (45.5 mg, 64%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.23 – 7.19 (m, 3H), 7.06 – 7.00 (m, 2H), 6.48 (s, 2H), 4.00 (s, 2H), 3.73 (s, 3H), 3.42 (s, 3H), 3.25 (s, 2H), 2.05 (s, 6H), 1.12 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.88, 156.09, 141.13, 138.72, 138.05, 129.91, 127.92, 126.96, 113.83, 63.34, 60.35, 55.07, 51.33, 44.94, 23.88, 19.83; **IR** (neat) ν 3027, 2948, 2837, 1732, 1602, 1470, 1455, 1314, 1261, 1194, 1152, 1069, 861, 701 cm^{-1}; **HRMS** (DART) Calcd for $C_{22}H_{30}NO_3$ (MH^+): 356.2226; found: 356.2238.



3j

Methyl 3-((cyclopropylmethyl)(4-methoxy-2,6-dimethylphenyl)amino)-2,2-dimethylpropanoate (3j)

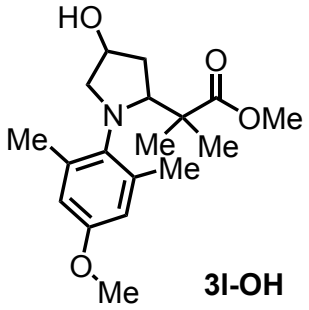
Substrate **1j** was reacted with ((1-methoxy-2-methylprop-1-en-1-yl)oxy)trimethylsilane **2a** following the general procedure using benzene as the solvent. After purification by column chromatography (3% ethyl ether in hexanes), **3j** was obtained as a colorless liquid (35.8 mg, 56%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.52 (s, 2H), 3.73 (s, 3H), 3.42 (s, 3H), 3.27 (s, 2H), 2.79 (d, J = 6.9 Hz, 2H), 2.31 (s, 6H), 1.15 (s, 6H), 0.85 – 0.77 (m, 1H), 0.35 – 0.31 (m, 2H), -0.06 – -0.10 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 178.00, 156.05, 142.21, 138.13, 113.65, 65.09, 62.03, 55.09, 51.25, 45.12, 23.78, 23.65, 19.90, 10.49, 3.67; **IR** (neat) ν 2947, 2837, 1730, 1602, 1468, 1389, 1314, 1259, 1192, 1153, 1069, 855 cm^{-1}; **HRMS** (DART) Calcd for $C_{19}H_{30}NO_3$ (MH^+): 320.2226; found: 320.2236.



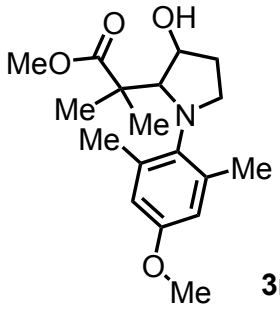
3k

Methyl 2-(1-(4-methoxy-2,6-dimethylphenyl)pyrrolidin-2-yl)-2-methylpropanoate (3k)

Substrate **1k** was reacted with ((1-methoxy-2-methylprop-1-en-1-yl)oxy)trimethylsilane **2a** following the general procedure, using THF as the solvent. After purification by column chromatography (5% ethyl ether in hexanes) **3k** was obtained as a colorless liquid (55.0 mg, 90%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.56 – 6.51 (m, 2H), 4.05 (dd, J_1 = 9.4 Hz, J_2 = 2.0 Hz, 1H), 3.73 (s, 3H), 3.30 – 3.28 (m, 1H), 3.07 (s, 3H), 2.92 – 2.88 (m, 1H), 2.29 (s, 3H), 2.25 (s, 3H), 2.13 – 2.05 (m, 1H), 1.91 – 1.81 (m, 3H), 1.11 (s, 3H), 1.08 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.75, 156.09, 139.88, 139.75, 136.75, 114.62, 112.92, 66.82, 55.14, 54.48, 50.89, 47.67, 27.60, 25.61, 23.22, 19.66, 19.60, 19.38; **IR** (neat) ν 2948, 2836, 1732, 1603, 1466, 1315, 1253, 1192, 1129, 1070, 839 cm^{-1}; **HRMS** (DART) Calcd for $C_{18}H_{28}NO_3$ (MH^+): 306.2069; found: 306.2067.



3l-OH



3m-OH

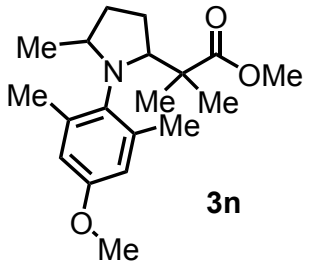
Methyl 2-(hydroxy-1-(4-methoxy-2,6-dimethylphenyl)pyrrolidin-2-yl)-2-methylpropanoate (3l-OH, 3m-OH)

Substrate **1l** was reacted with ((1-methoxy-2-methylprop-1-en-1-yl)oxy)trimethylsilane **2a** following the general procedure using THF as the solvent. ^{1}H NMR analysis of the unpurified reaction mixture revealed that **3l** and **3m** were obtained in the ratio of 2.5 : 1. The diastereomeric ratio (dr) of **3l** was 4 : 1 and the dr of **3m** was >20 : 1. After purification by column chromatography (3% ethyl ether in hexanes), **3l** and **3m** were separated to give pure **3l** (24.2 mg, 31% yield) and **3m** (18.3 mg, 23% yield). The isolated and purified products were treated with 4 N HCl for 24 hours to give the desilylated products that are characterized as below. The relative configuration of the pyrrolidine substituents for **3l-OH** and **3m-OH** was assigned *anti* based on NOESY experiments (See SI Section 5 for NOE spectra).

Major regioisomer (3l-OH): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.57 – 6.48 (m, 2H), 4.55 – 4.35 (m, 1H), 4.34 – 4.05 (m, 1H), 3.77 – 3.68 (m, 3H), 3.64 – 3.57 (m, 1H), 3.28 – 3.01 (m, 3H), 2.88 – 2.80 (m, 1H), 2.40 – 2.19 (m, 6H), 2.14 – 1.93 (m, 2H), 1.70 – 1.54 (m, 1H), 1.13 – 0.93 (m, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.76, 177.30, 156.49, 156.28, 139.87, 139.57, 138.41, 138.35, 137.32, 136.90, 114.87, 114.69, 113.15, 112.98, 70.74, 70.53, 66.76, 65.93, 63.29, 62.04, 55.17, 51.35, 51.08, 46.91, 46.67, 36.70, 36.61, 24.17, 23.50, 21.01, 20.04, 19.50, 19.46; **IR** (neat) ν 3418, 2947, 2837, 1730, 1602, 1469, 1315, 1267, 1193, 1134, 1069, 990, 854 cm^{-1}; **HRMS** (DART) Calcd for $C_{18}H_{28}NO_4$ (MH^+): 322.2018; found: 322.2024.

Minor regioisomer (3m-OH): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.57 – 6.49 (m, 2H), 4.31 (d, J = 5.1 Hz, 1H), 4.05 (s, 1H), 3.73 (s, 3H), 3.32 – 3.20 (m, 2H), 3.14 (s, 3H), 2.40 (s, 3H), 2.29 (s, 3H), 2.06 – 1.97 (m, 1H), 1.81 (dd, J = 13.2, 5.5 Hz, 1H), 1.69 (br, 1H), 1.18 (s, 3H), 1.05 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ177.44, 156.34, 139.82, 138.09, 137.43, 114.72, 113.12, 75.75, 75.30, 55.15, 52.15, 51.20, 46.06, 34.01, 22.62, 20.80, 19.74, 19.46; **IR**

(neat) ν 3485, 2948, 2835, 1732, 1603, 1469, 1314, 1256, 1192, 1154, 1131, 1071, 991, 856 cm^{-1}; **HRMS** (DART) Calcd for $C_{18}H_{28}NO_4$ (MH^+): 322.2018; found: 322.2016.

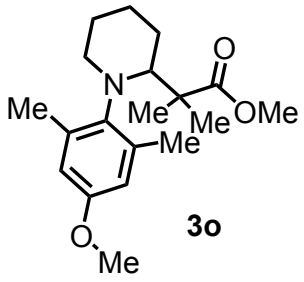


3n

Methyl 2-(-1-(4-methoxy-2,6-dimethylphenyl)-5-methylpyrrolidin-2-yl)-2-methylpropanoate (3n)

Substrate **1n** was reacted with ((1-methoxy-2-methylprop-1-en-1-yl)oxy)trimethylsilane **2a** following the general procedure, using THF as the solvent. ^{1}H NMR analysis of the crude material revealed that the diastereomeric ratio was 7 : 1. After purification by column chromatography (4% ethyl ether in hexanes) **3n** was obtained as a colorless liquid (44.7 mg, 70%) as a mixture of diastereomers. The relative configuration of the pyrrolidine substituents was assigned *anti* based on NOESY experiments (See SI Section 5 for NOE spectra).

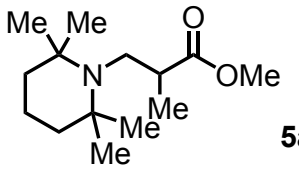
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.51 (d, J = 6.1 Hz, 2H), 4.20 – 4.14 (m, 1H), 3.76 – 3.70 (m, 4H), 3.05 (s, 3H), 2.26 (s, 3H), 2.24 (s, 3H), 2.16 – 2.05 (m, 2H), 1.80 – 1.70 (m, 1H), 1.55 – 1.46 (m, 1H), 1.09 (s, 3H), 1.04 (s, 3H), 0.71 (d, J = 6.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.68, 155.64, 139.44, 137.79, 136.78, 113.89, 112.94, 67.34, 57.52, 55.11, 50.98, 47.84, 33.80, 25.49, 23.27, 20.64, 20.04, 19.65, 19.50; **IR** (neat) ν 2956, 2873, 2836, 1731, 1602, 1467, 1371, 1303, 1256, 1192, 1155, 1131, 1070, 854 cm^{-1}; **HRMS** (DART) Calcd for $C_{19}H_{30}NO_3$ (MH^+): 320.2226; found: 320.2236.



3o

Methyl -2-(1-(4-methoxy-2,6-dimethylphenyl)piperidin-2-yl)-2-methylpropanoate (3o)

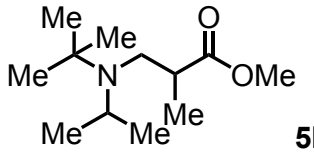
Substrate **1o** was reacted with ((1-methoxy-2-methylprop-1-en-1-yl)oxy)trimethylsilane **2a** following the general procedure using benzene as the solvent; the reaction mixture was heated at 50 °C. After purification by column chromatography (5% ethyl ether in hexanes), **3o** was obtained as a colorless liquid (24.3 mg, 38%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.55 (d, *J* = 3.1 Hz, 1H), 6.44 (d, *J* = 3.1 Hz, 1H), 3.81 – 3.76 (m, 1H), 3.73 (s, 3H), 3.23 (s, 3H), 3.07 – 2.99 (m, 1H), 2.99 – 2.91 (m, 1H), 2.35 (s, 3H), 2.32 (s, 3H), 1.82 – 1.72 (m, 2H), 1.59 – 1.47 (m, 4H), 1.06 (m, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.94, 155.90, 142.39, 138.55, 137.91, 114.45, 113.37, 61.44, 55.14, 52.18, 51.29, 48.30, 26.22, 25.68, 24.44, 22.94, 20.89, 20.62, 19.70; **IR** (neat) ν 2934, 2854, 2836, 1731, 1601, 1466, 1388, 1255, 1233, 1171, 1133, 1069, 917, 854 cm^{-1}; **HRMS** (ESI) Calcd for $C_{19}H_{30}NO_3$ (MH^+): 320.2226; found: 320.2228.



5a

Methyl 2-methyl-3-(2,2,6,6-tetramethylpiperidin-1-yl)propanoate (5a)

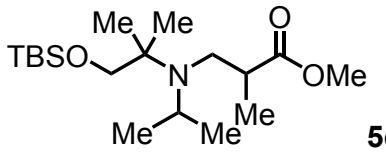
Substrate **1p** was reacted with ((1-methoxyprop-1-en-1-yl)oxy)trimethylsilane **2b** following the general procedure using THF as the solvent at 70 °C. After purification by column chromatography (2.5% triethylamine in hexanes), **5a** was obtained as a colorless liquid (45.8 mg, 95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 3.65 (s, 3H), 2.86 (dd, *J* = 15.4, 7.4 Hz, 1H), 2.57 (h, *J* = 7.1 Hz, 1H), 2.45 (dd, *J* = 15.5, 5.4 Hz, 1H), 1.52 (br, 2H), 1.44 – 1.36 (m, 4H), 1.11 (d, *J* = 7.3 Hz, 3H), 1.01 (s, 6H), 0.95 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.77, 54.60, 51.23, 48.93, 44.22, 41.30, 17.80, 16.09; **IR** (neat) ν 2966, 2927, 2874, 1736, 1464, 1434, 1379, 1365, 1256, 1168 cm^{-1}; **HRMS** (ESI) Calcd for $C_{14}H_{28}NO_2$ (MH^+): 242.2042; found: 242.2117.



5b

Methyl 3-(*tert*-butyl(isopropyl)amino)-2-methylpropanoate (5b)

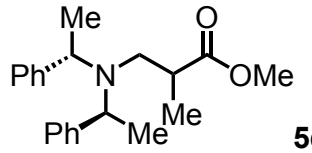
Substrate **1q** was reacted with ((1-methoxyprop-1-en-1-yl)oxy)trimethylsilane **2b** following the general procedure using THF as the solvent at 70 °C. After purification by column chromatography (2.5% triethylamine in hexanes), **5b** was obtained as a colorless liquid (40.1 mg, 93%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 3.66 (s, 3H), 3.29 – 3.19 (m, 1H), 2.84 (dd, *J* = 14.5, 7.7 Hz, 1H), 2.65 – 2.52 (m, 1H), 2.49 (dd, *J* = 14.4, 6.8 Hz, 1H), 1.10 (d, *J* = 6.9 Hz, 3H), 1.07 (s, 9H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.36, 55.63, 51.16, 46.96, 46.58, 42.97, 28.61, 22.72, 15.23; **IR** (neat) ν 2959, 2928, 2864, 2178, 1738, 1707, 1457, 1387, 1376, 1249, 1168, 1138, 1112 cm^{-1}; **HRMS** (ESI) Calcd for $C_{12}H_{26}NO_2$ (MH^+): 216.1885; found: 216.1961.



5c

Methyl 3-((1-((*tert*-butyldimethylsilyl)oxy)-2-methylpropan-2-yl)(isopropyl)amino)-2-methylpropanoate (5c)

Substrate **1r** was reacted with ((1-methoxyprop-1-en-1-yl)oxy)trimethylsilane **2b** following the general procedure using THF as the solvent at 70 °C. After purification by column chromatography (2% triethylamine in hexanes), **5c** was obtained as a colorless liquid (64.9 mg, 94%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 3.65 (s, 3H), 3.40 – 3.34 (m, 2H), 3.26 (dt, *J* = 12.8, 7.0 Hz, 1H), 2.96 (dd, *J* = 14.6, 7.8 Hz, 1H), 2.65 (dd, *J* = 15.0, 7.2 Hz, 1H), 2.57 (h, *J* = 7.0 Hz, 1H), 1.08 (d, *J* = 7.0 Hz, 3H), 1.05 (s, 6H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.96 (d, *J* = 6.7 Hz, 3H), 0.89 (s, 9H), 0.03 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.31, 69.59, 59.26, 51.10, 47.33, 46.40, 42.91, 25.82, 24.27, 22.84, 18.15, 15.12, -5.60; **IR** (neat) ν 2954, 2929, 2884, 2857, 1737, 1462, 1360, 1250, 1197, 1165, 1086, 835, 774 cm^{-1}; **HRMS** (ESI) Calcd for $C_{18}H_{40}NO_3Si$ (MH^+): 346.2699; found: 346.2778.



5d

Methyl 3-(bis((*S*)-1-phenylethyl)amino)-2-methylpropanoate (5d)

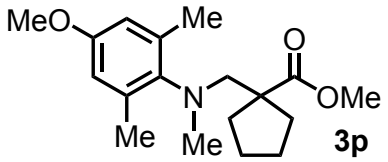
Substrate **1s** was reacted with ((1-methoxyprop-1-en-1-yl)oxy)trimethylsilane **2b** following the general procedure using THF as the solvent at 70 °C. By ^{1}H NMR analysis of the unpurified reaction mixture, the diastereomeric ratio was determined to be 1.6 : 1. After purification by column chromatography (2% triethylamine in hexanes), **5d** was obtained as a colorless liquid (57.3 mg, 88%). Diastereomers were separated chromatographically: **5d-(*S,S,R*)** (35.3 mg, 54%) and **5d-(*S,S,S*)** (22.0 mg, 34%).[25]

5d-(*S*, *S*, *R*):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.24 (m, 8H), 7.24 – 7.18 (m, 2H), 3.86 (q, *J* = 6.9 Hz, 2H), 3.68 (s, 3H), 3.06 (ddd, *J* = 13.9, 8.2, 1.4 Hz, 1H), 2.53 – 2.41 (m, 1H), 2.36 (ddd, *J* = 13.8, 6.4, 1.5 Hz, 1H), 1.35 (dd, *J* = 6.9, 1.5 Hz, 6H), 0.87 (dd, *J* = 6.9, 1.5 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.93, 144.44, 127.98, 127.92, 126.62, 58.35, 51.32, 50.07, 41.39, 18.76, 15.10; **IR** (neat) ν 2969, 2934, 1736, 1452, 1371, 1196, 1177, 1150, 758, 700 cm^{-1}; **HRMS** (ESI) Calcd for $C_{21}H_{28}NO_2$ (MH^+): 326.4240; found: 326.2121; $[\alpha]^{25}_D$ = –33.5° (c = 0.4, EtOH).

5d-(*S*, *S*, *S*):

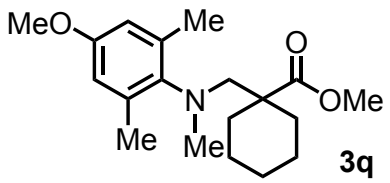
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 8H), 7.23 – 7.17 (m, 2H), 3.95 (q, *J* = 6.9 Hz, 2H), 3.46 (s, 3H), 2.76 (dd, *J* = 7.5, 2.4 Hz, 2H), 2.59 (q, *J* = 7.1 Hz, 1H), 1.44 – 1.33 (m, 6H), 1.11 (dd, *J* = 6.9, 0.8 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.31, 144.40, 127.94, 127.90, 126.53, 57.45, 51.30, 49.53, 40.54, 17.81, 15.37; **IR** (neat) ν 2968, 2946, 1735, 1493, 1451, 1196, 1180, 1152, 699 cm^{-1}; **HRMS** (ESI) Calcd for $C_{21}H_{28}NO_2$ (MH^+): 326.4240; found: 326.2120; $[\alpha]^{25}_D$ = –2.1° (c = 0.3, EtOH).



3p

Methyl 1-(((4-methoxy-2,6-dimethylphenyl)(methyl)amino)methyl)cyclopentane-1-carboxylate (3p)

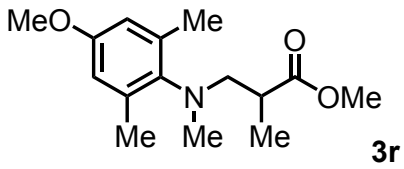
Substrate **1g** was reacted with (cyclopentylidene(methoxy)methoxy)trimethylsilane **2c** following the general procedure using benzene as the solvent. After purification by column chromatography (3% ethyl ether in hexanes), **3p** was obtained as a colorless liquid (44.6 mg, 73%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.52 (s, 2H), 3.73 (s, 3H), 3.55 (s, 3H), 3.26 (s, 2H), 2.69 (s, 3H), 2.25 (s, 6H), 2.16 – 2.04 (m, 2H), 1.67 – 1.46 (m, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 178.02, 156.20, 143.82, 137.80, 113.65, 65.05, 56.69, 55.15, 51.44, 43.15, 34.37, 25.03, 19.30; **IR** (neat) ν 2948, 2870, 2837, 2794, 1729, 1602, 1484, 1434, 1272, 1192, 1154, 1063, 854 cm^{-1}; **HRMS** (DART) Calcd for $C_{18}H_{28}NO_3$ (MH^+): 306.2069; found: 306.2076.



3q

Methyl 1-(((4-methoxy-2,6-dimethylphenyl)(methyl)amino)methyl)cyclohexane-1-carboxylate (3q)

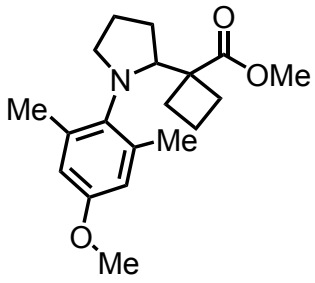
Substrate **1g** was reacted with (cyclohexylidene(methoxy)methoxy)trimethylsilane **2d** following the general procedure using benzene as the solvent. After purification by column chromatography (4% ethyl ether in hexanes), **3q** was obtained as a colorless liquid (50.5 mg, 79%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.52 (s, 2H), 3.73 (s, 3H), 3.55 (s, 3H), 3.17 (s, 2H), 2.65 (s, 3H), 2.27 (s, 6H), 2.13 – 2.04 (m, 2H), 1.59 – 1.49 (m, 3H), 1.40 – 1.28 (m, 2H), 1.24 – 1.15 (m, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.93, 156.10, 144.40, 137.44, 113.70, 67.68, 55.12, 51.18, 49.94, 43.82, 32.56, 25.97, 23.04, 19.40; **IR** (neat) ν 2934, 2853, 2792, 1730, 1602, 1451, 1372, 1298, 1156, 1133, 1095, 1064, 1035, 988, 854, 832 cm^{-1}; **HRMS** (DART) Calcd for $C_{19}H_{30}NO_3$ (MH^+): 320.2226; found: 320.2221.



3r

Methyl 3-((4-methoxy-2,6-dimethylphenyl)(methyl)amino)-2-methylpropanoate (3r)

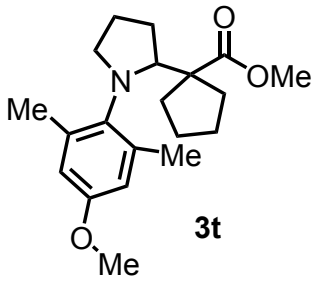
Substrate **1g** was reacted with ((1-methoxyprop-1-en-1-yl)oxy)trimethylsilane **2b** following the general procedure using benzene as the solvent. After purification by column chromatography (5% ethyl acetate in hexanes), **3r** was obtained as a colorless liquid (35.0 mg, 66%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.52 (s, 2H), 3.74 (s, 3H), 3.65 (s, 3H), 3.32 – 3.25 (m, 1H), 3.07 – 3.00 (m, 1H), 2.74 – 2.65 (m, 4H), 2.25 (s, 3H), 2.21 (s, 3H), 1.13 (d, J = 7.0 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.72, 156.40, 142.51, 138.28, 138.23, 113.76, 113.62, 60.09, 55.15, 51.45, 41.04, 40.31, 19.41, 19.12, 15.40; **IR** (neat) ν 2949, 2838, 2799, 1736, 1602, 1485, 1458, 1435, 1379, 1304, 1254, 1194, 1155, 1063, 987, 854, 834 cm^{-1}; **HRMS** (DART) Calcd for $C_{15}H_{24}NO_3$ (MH^+): 266.1756; found: 266.1755.



3s

Methyl 1-(1-(4-methoxy-2,6-dimethylphenyl)pyrrolidin-2-yl)cyclobutane-1-carboxylate (3s)

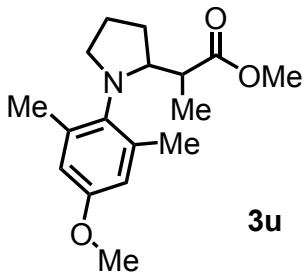
Substrate **1k** was reacted with (cyclobutylidene(methoxy)methoxy)trimethylsilane **2e** following the general procedure using THF as the solvent. After purification by column chromatography (5% ethyl ether in hexanes), **3s** was obtained as a colorless liquid (48.9 mg, 77%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.56 – 6.50 (m, 2H), 4.07 (dd, J_1 = 8.6 Hz, J_2 = 3.8 Hz, 1H), 3.73 (s, 3H), 3.33 – 3.24 (m, 4H), 2.94 (q, J = 7.8 Hz, 1H), 2.41 – 2.29 (m, 1H), 2.26 (s, 3H), 2.24 (s, 3H), 2.21 – 1.98 (m, 5H), 1.93 – 1.67 (m, 4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.22, 156.36, 140.79, 139.02, 137.42, 114.43, 112.76, 64.82, 55.13, 54.07, 52.44, 51.25, 28.41, 28.14, 25.62, 25.21, 19.45, 18.97, 15.68; **IR** (neat) ν 2947, 2836, 1727, 1602, 1481, 1464, 1434, 1316, 1266, 1209, 1193, 1153, 1116, 1069, 854 cm^{-1}; **HRMS** (DART) Calcd for $C_{19}H_{28}NO_3$ (MH^+): 318.2069; found: 318.2080.



3t

Methyl 1-(1-(4-methoxy-2,6-dimethylphenyl)pyrrolidin-2-yl)cyclopentane-1-carboxylate (3t)

Substrate **1k** was reacted with (cyclopentylidene(methoxy)methoxy)trimethylsilane **2c** following the general procedure using THF as the solvent. After purification by column chromatography (5% ethyl ether in hexanes), **3t** was obtained as a colorless liquid (66.0 mg, >95%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.58 – 6.50 (m, 2H), 4.13 (dd, J_1 = 9.2 Hz, J_2 = 2.6 Hz, 1H), 3.73 (s, 3H), 3.32 – 3.18 (m, 4H), 2.90 (q, J = 7.4 Hz, 1H), 2.29 (s, 3H), 2.23 (s, 3H), 2.19 – 2.09 (m, 2H), 1.93 – 1.81 (m, 4H), 1.60 – 1.48 (m, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.61, 156.17, 140.22, 139.46, 136.99, 114.52, 112.82, 65.95, 60.47, 55.10, 54.38, 51.19, 34.14, 31.38, 28.78, 25.30, 25.23, 25.12, 19.57, 19.07; **IR** (neat) ν 2947, 2872, 2835, 1726, 1602, 1463, 1433, 1370, 1316, 1255, 1228, 1192, 1151, 1121, 1068, 853, 834 cm^{-1}; **HRMS** (DART) Calcd for $C_{20}H_{30}NO_3$ (MH^+): 332.2226; found: 332.2222.



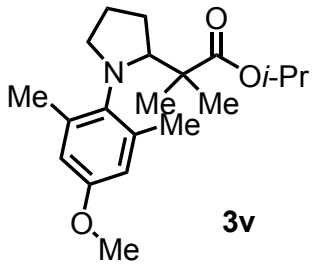
3u

Methyl 2-(1-(4-methoxy-2,6-dimethylphenyl)pyrrolidin-2-yl)propanoate (3u)

Substrate **1k** was reacted with ((1-methoxyprop-1-en-1-yl)oxy)trimethylsilane **2b** following the general procedure using THF as the solvent. ^{1}H NMR analysis of the unpurified reaction mixture revealed that the diastereomeric ratio was 2.5 : 1. After purification by column chromatography (5% ethyl ether in hexanes), **3u** was obtained as a colorless liquid (34.9 mg, 60%) as a mixture of diastereomers. The diastereomers were isolated by PTLC (10% ether in hexanes): major diastereomer (16.0 mg, 27% yield), minor diastereomer (12.2 mg, 21% yield).[25]

3u-major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 – 6.50 (m, 2H), 3.92 – 3.84 (m, 1H), 3.74 (s, 3H), 3.34 – 3.24 (m, 4H), 3.02 – 2.94 (m, 1H), 2.40 – 2.31 (m, 1H), 2.27 (s, 3H), 2.24 (s, 3H), 2.12 – 2.02 (m, 1H), 1.97 – 1.86 (m, 2H), 1.82 – 1.72 (m, 1H), 1.11 (d, J = 7.0 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.13, 156.55, 140.65, 138.49, 137.43, 114.37, 112.89, 62.72, 55.16, 52.68, 51.07, 45.21, 29.04, 24.99, 19.47, 19.21, 13.45; **IR** (neat) ν 2948, 2838, 1733, 1602, 1484, 1465, 1374, 1318, 1273, 1194, 1154, 1117, 1067, 855 cm^{-1}; **HRMS** (ESI) Calcd for $C_{17}H_{26}NO_3$ (MH^+): 292.1912; found: 292.1908.

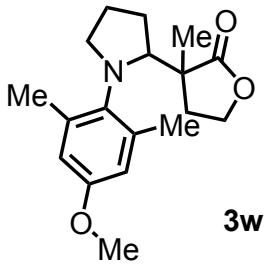
3u-minor: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.59 – 6.52 (m, 2H), 3.87 – 3.81 (m, 1H), 3.74 (s, 3H), 3.44 (s, 3H), 3.30 – 3.24 (m, 1H), 2.96 – 2.88 (m, 1H), 2.49 – 2.41 (m, 1H), 2.29 (s, 3H), 2.23 (s, 3H), 2.17 – 2.08 (m, 1H), 1.96 – 1.84 (m, 3H), 1.01 (d, J = 7.0 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.93, 156.37, 140.28, 138.84, 137.22, 114.45, 112.99, 63.56, 55.15, 53.36, 51.07, 45.87, 29.79, 25.10, 19.42, 19.07, 13.78; **HRMS** (ESI) Calcd for $C_{17}H_{26}NO_3$ (MH^+): 292.1912; found: 292.1911.



3v

Isopropyl 2-(1-(4-methoxy-2,6-dimethylphenyl)pyrrolidin-2-yl)-2-methylpropanoate (3v)

Substrate **1k** was reacted with ((1-isopropoxy-2-methylprop-1-en-1-yl)oxy)trimethylsilane **2f** following the general procedure using THF as the solvent. After purification by column chromatography (6% ethyl ether in hexanes), **3v** was obtained as a colorless liquid (60.0 mg, 90%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.56 – 6.50 (m, 2H), 4.53 (h, J = 6.2 Hz, 1H), 4.02 (dd, J_1 = 9.4 Hz, J_2 = 2.1 Hz, 1H), 3.73 (s, 3H), 3.33 – 3.27 (m, 1H), 2.91 – 2.84 (m, 1H), 2.32 (s, 3H), 2.25 (s, 3H), 2.15 – 2.06 (m, 1H), 1.95 – 1.78 (m, 3H), 1.11 – 1.07 (m, 6H), 1.03 (s, 3H), 0.90 (d, J = 6.3 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.93, 156.17, 140.72, 139.83, 136.50, 114.75, 113.17, 67.15, 66.89, 55.18, 54.74, 48.33, 28.03, 25.82, 22.08, 21.61, 21.25, 19.61, 19.59; **IR** (neat) ν 2973, 2937, 2836, 1722, 1603, 1468, 1386, 1372, 1316, 1254, 1154, 1132, 1106, 1070, 935, 855 cm^{-1}; **HRMS** (DART) Calcd for $C_{20}H_{32}NO_3$ (MH^+): 334.2382; found: 334.2379.



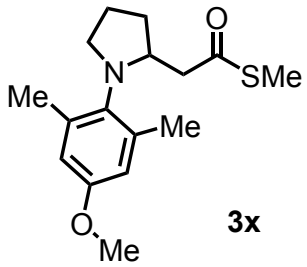
3w

3-(1-(4-Methoxy-2,6-dimethylphenyl)pyrrolidin-2-yl)-3-methyldihydrofuran-2(3*H*)-one (3w)

Substrate **1k** was reacted with trimethyl((3-methyl-4,5-dihydrofuran-2-yl)oxy)silane **2g** following the general procedure using THF as the solvent. ^{1}H NMR analysis of the unpurified reaction mixture revealed that the diastereomeric ratio was 1.3 : 1. After purification by column chromatography (10% ethyl ether in hexanes), **3w** was obtained as a colorless liquid (42.8 mg, 70%). Diastereomers were separated chromatographically; major diastereomer (23.9 mg, 39%) and minor diastereomer (18.9 mg, 31%).

3w-major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (s, 2H), 4.12 – 4.04 (m, 2H), 3.87 (t, J = 6.1 Hz, 1H), 3.74 (s, 3H), 3.39 – 3.31 (m, 1H), 3.00 – 2.91 (m, 1H), 2.38 – 2.27 (m, 4H), 2.25 (s, 3H), 2.20 – 2.13 (m, 2H), 2.00 – 1.88 (m, 2H), 1.78 – 1.69 (m, 1H), 1.26 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 180.82, 156.47, 139.89, 139.18, 136.52, 114.90, 113.30, 64.68, 64.04, 55.08, 54.52, 48.20, 32.05, 27.62, 25.75, 19.53, 19.25, 19.06; **IR** (neat) ν 2962, 2912, 2836, 1767, 1603, 1482, 1466, 1371, 1317, 1255, 1193, 1154, 1070, 1031, 854 cm^{-1}; **HRMS** (DART) Calcd for $C_{18}H_{26}NO_3$ (MH^+): 304.1913; found: 304.1924.

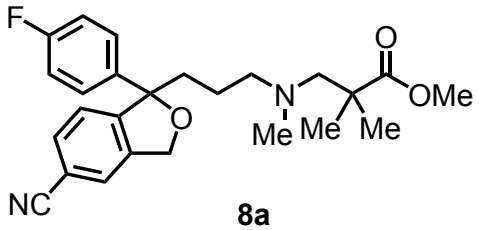
3w-minor: ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.60 – 6.53 (m, 2H), 4.27 – 4.16 (m, 2H), 3.94 (dd, J_1 = 8.8 Hz, J_2 = 3.9 Hz, 1H), 3.75 (s, 3H), 3.37 – 3.32 (m, 1H), 2.99 – 2.93 (m, 1H), 2.55 – 2.48 (m, 1H), 2.30 (s, 3H), 2.29 – 2.22 (m, 4H), 2.00 – 1.89 (m, 3H), 1.79 – 1.73 (m, 1H), 0.94 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 181.24, 156.48, 140.35, 139.10, 136.41, 114.76, 113.38, 65.49, 65.20, 55.14, 54.69, 48.88, 31.22, 29.49, 25.56, 22.55, 19.78, 19.15; **HRMS** (ESI) Calcd for $C_{18}H_{26}NO_3$ (MH^+): 304.1913; found: 304.1915.



3x

***S*-Methyl 2-(1-(4-methoxy-2,6-dimethylphenyl)pyrrolidin-2-yl)ethanethioate (3x)**

Substrate **1k** was reacted with trimethyl((1-(methylthio)vinyl)oxy)silane **2h** following the general procedure using THF as the solvent. After purification by column chromatography (5% ethyl acetate in hexanes), **3x** was obtained as a colorless liquid (30.5 mg, 52%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.57 (br, 2H), 3.95 – 3.88 (m, 1H), 3.75 (s, 3H), 3.28 – 3.22 (m, 1H), 3.06 – 2.99 (m, 1H), 2.58 (dd, J_1 = 14.3 Hz, J_2 = 4.4 Hz, 1H), 2.48 (dd, J_1 = 14.3, J_2 = 9.2 Hz, 1H), 2.24 (s, 6H), 2.23 – 2.13 (m, 4H), 2.03 – 1.86 (m, 2H), 1.79 – 1.70 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 198.42, 156.84, 140.67, 138.92, 136.39, 114.33, 113.03, 58.65, 55.19, 51.43, 50.56, 31.92, 24.46, 19.15, 11.51; **IR** (neat) ν 2953, 2872, 2836, 1685, 1603, 1483, 1370, 1319, 1269, 1193, 1154, 1069, 1018, 855 cm^{-1}; **HRMS** (ESI) Calcd for $C_{16}H_{24}NO_2S$ (MH^+): 294.1527; found: 294.1530.

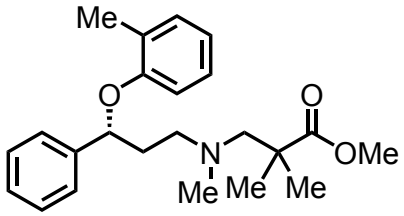


8a

Methyl 3-((3-(5-cyano-1-(4-fluorophenyl)-1,3-dihydroisobenzofuran-1-yl)propyl) (methyl)amino)-2,2-dimethylpropanoate (8a)

Substrate **7a** was reacted with ((1-methoxy-2-methylprop-1-en-1-yl)oxy)trimethylsilane **2a** following the general procedure on a 3.0 mmol scale using benzene as the solvent at 70 °C. After purification by column chromatography (20% ethyl acetate in hexanes), **8a** was obtained as a colorless liquid (301.9 mg, 23%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 1H), 7.50 (s, 1H), 7.46 – 7.34 (m, 3H), 7.01 (t, J = 8.7 Hz, 2H), 5.17 (q, J = 12.9 Hz, 2H), 3.59 (s, 3H), 2.44 (s, 2H), 2.34 (t, J = 7.0 Hz, 2H), 2.18 (ddd, J = 14.2, 11.4, 4.7 Hz, 1H), 2.08 (s, 4H), 1.45 – 1.32 (m, 1H), 1.29 – 1.18 (m, 1H), 1.12 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.07, 161.97 (d, $J_{C\text{-}F}$ = 246.1 Hz), 149.61, 140.30, 139.68 (d, $J_{C\text{-}F}$ = 3.1 Hz), 131.82, 126.73 (d, $J_{C\text{-}F}$ = 8.0 Hz), 125.15, 122.74, 118.63, 115.27 (d, $J_{C\text{-}F}$ = 21.1 Hz), 111.64, 91.22, 71.25, 67.39, 59.50, 51.48, 44.09, 43.61, 38.70, 23.86, 23.84, 22.02; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -116.48 (tt, J = 8.4, 5.0 Hz); **IR** (neat) ν 2950, 2847, 2788, 2229, 1725, 1506, 1460, 1271, 1224, 1193, 1149, 1049, 1033, 834 cm^{-1}; **HRMS** (ESI) Calcd for $C_{25}H_{30}FN_2O_3$ (MH^+): 425.2235; found: 425.2232.

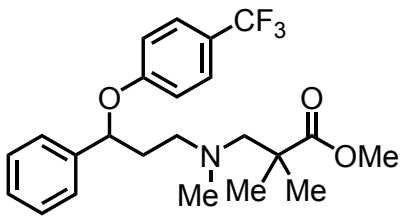


8b

Methyl (*R*)-2,2-dimethyl-3-(methyl(3-phenyl-3-(o-tolyloxy)propyl)amino)propanoate (8b)

Substrate **7b** was reacted with ((1-methoxy-2-methylprop-1-en-1-yl)oxy)trimethylsilane **2a** following the general procedure on a 1.0 mmol scale using DCM as the solvent. After purification by column chromatography (15% ethyl acetate in hexanes), **8b** was obtained as a colorless liquid (91.9 mg, 25%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 4H), 7.26 – 7.19 (m, 1H), 7.09 (d, *J* = 7.3 Hz, 1H), 6.94 (t, *J* = 7.9 Hz, 1H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.59 (d, *J* = 8.2 Hz, 1H), 5.19 (dd, *J* = 8.5, 4.3 Hz, 1H), 3.58 (s, 3H), 2.59 (t, *J* = 7.3 Hz, 2H), 2.51 (t, *J* = 1.8 Hz, 2H), 2.31 (s, 3H), 2.21 (s, 3H), 2.11 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.00 – 1.88 (m, 1H), 1.18 – 1.07 (m, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 180.79, 158.73, 145.01, 133.12, 131.18, 129.99, 129.59, 129.14, 128.41, 122.71, 115.38, 80.35, 69.68, 58.85, 54.20, 54.16, 46.61, 39.53, 26.55, 26.47, 19.16; **IR** (neat) ν 2949, 2847, 1727, 1601, 1491, 1453, 1305, 1270, 1237, 1192, 1149, 1119, 1047, 747, 700 cm^{-1}; **HRMS** (ESI) Calcd for $C_{23}H_{32}NO_3$ (MH^+): 370.2383; found: 370.2372; $[\alpha]^{25}_D$ = –4.6° (c = 1.0, $CHCl_3$).



8c

Methyl 2,2-dimethyl-3-(methyl(3-phenyl-3-(4-(trifluoromethyl)phenoxy)propyl) amino)propanoate (8c)

Substrate **7c** was reacted with ((1-methoxy-2-methylprop-1-en-1-yl)oxy)trimethylsilane **2a** following the general procedure on 1.0 mmol scale using DCM as the solvent. After purification by column chromatography (15% ethyl acetate in hexanes), **8c** was obtained as a colorless liquid (113 mg, 27%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 4.3 Hz, 4H), 7.25 (d, J = 3.4 Hz, 1H), 6.89 (d, J = 8.5 Hz, 2H), 5.25 (dd, J = 8.5, 4.4 Hz, 1H), 3.59 (d, J = 1.1 Hz, 3H), 2.67 – 2.45 (m, 4H), 2.21 (s, 3H), 2.16 – 2.01 (m, 1H), 2.01 – 1.86 (m, 1H), 1.12 (d, J = 7.4 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 178.09, 160.66, 141.35, 128.72, 127.72, 125.80, 126.67 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.39 (q, $J_{C\text{-}F}$ = 271.1 Hz), 122.64 (q, $J_{C\text{-}F}$ = 32.7 Hz), 115.74, 78.26, 67.14, 55.84, 51.55, 43.92, 43.91, 36.86, 23.96, 23.84; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -62.53; **IR** (neat) ν 2970, 1727, 1614, 1517, 1455, 1325, 1250, 1177, 1158, 1110, 1067, 1044, 835, 701 cm^{-1}; **HRMS** (ESI) Calcd for $C_{23}H_{29}F_3NO_3$ (MH^+): 424.2100; found: 424.2092.

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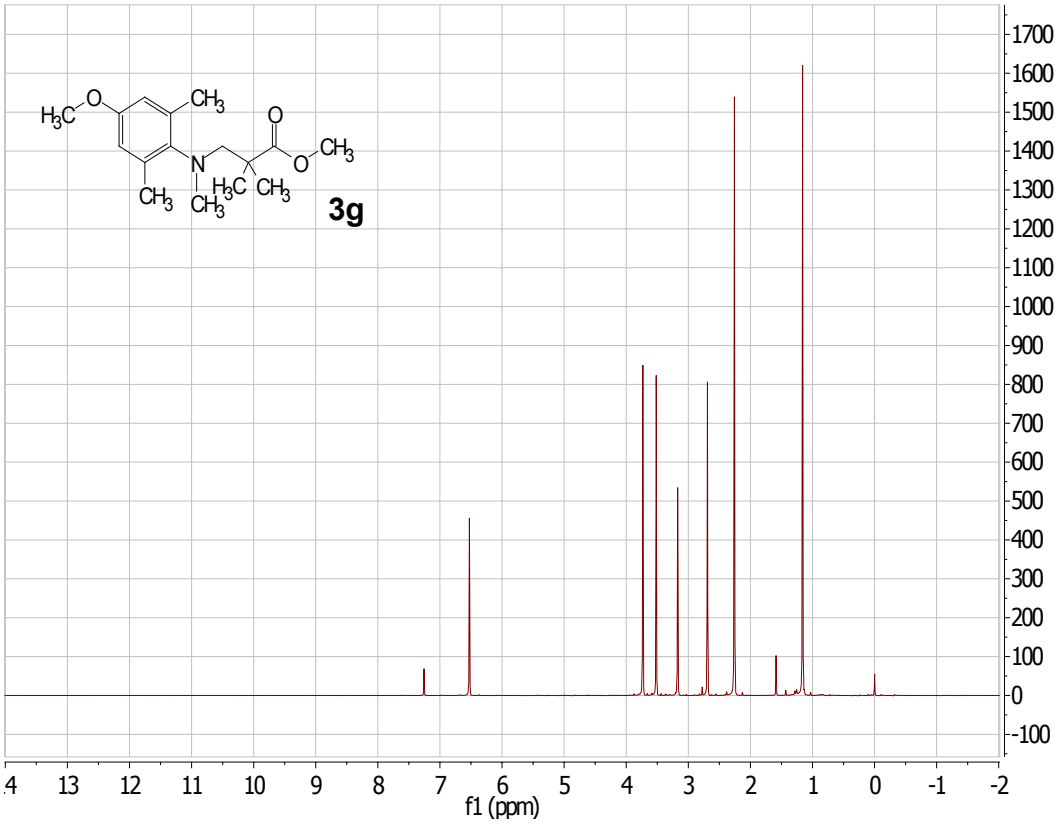
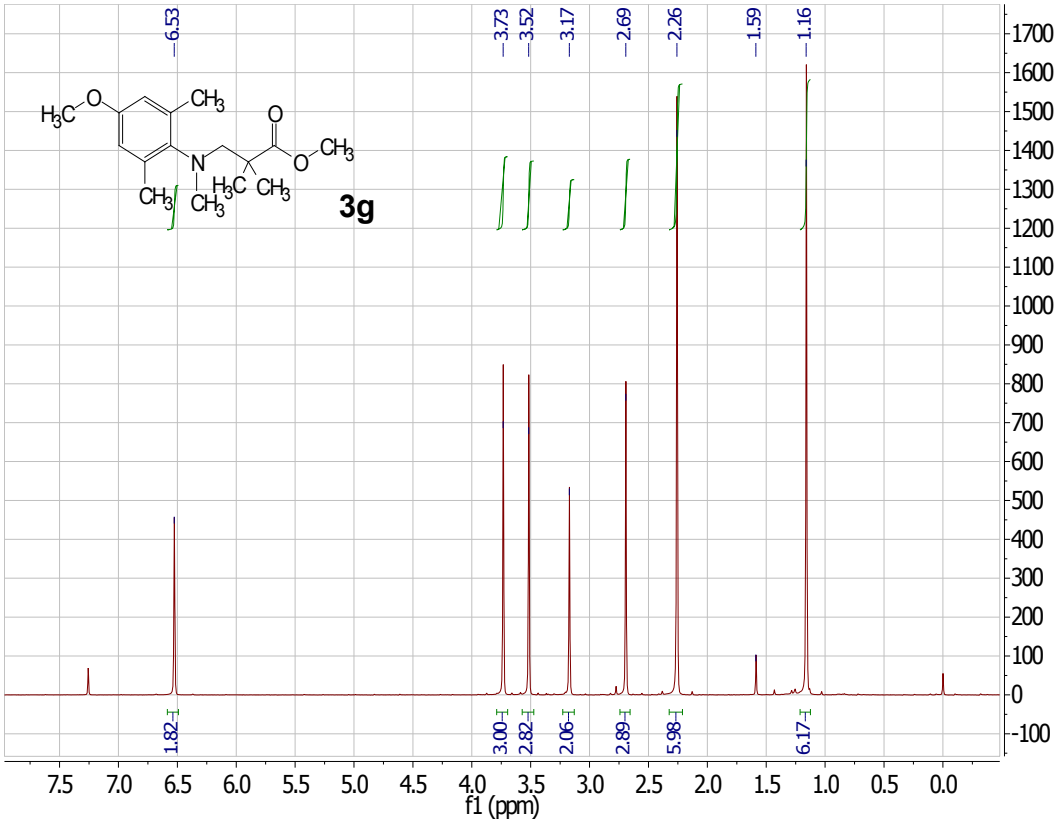
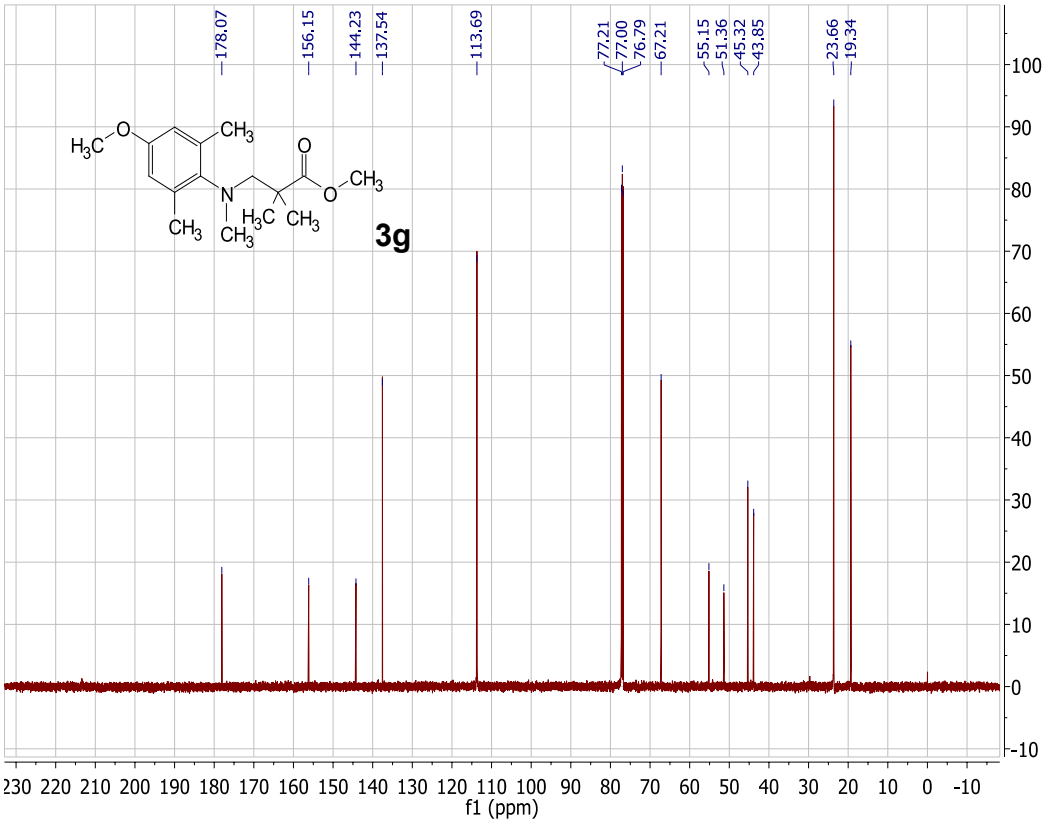
5. NMR Spectra



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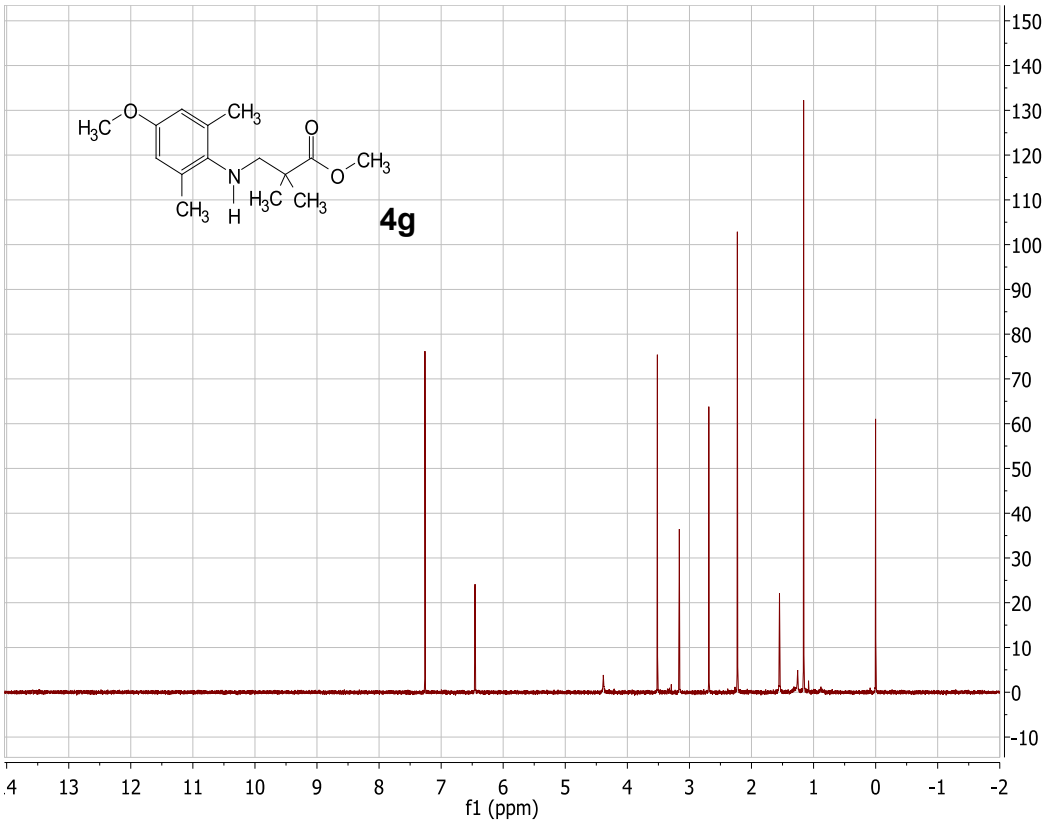
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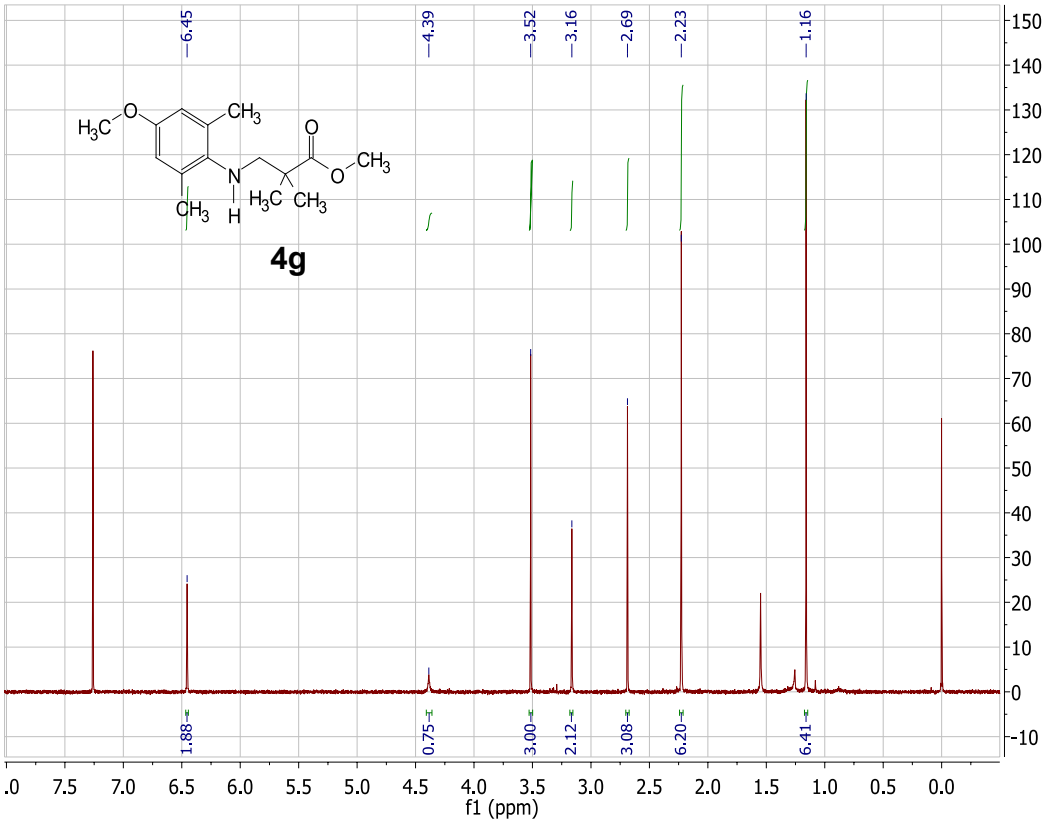
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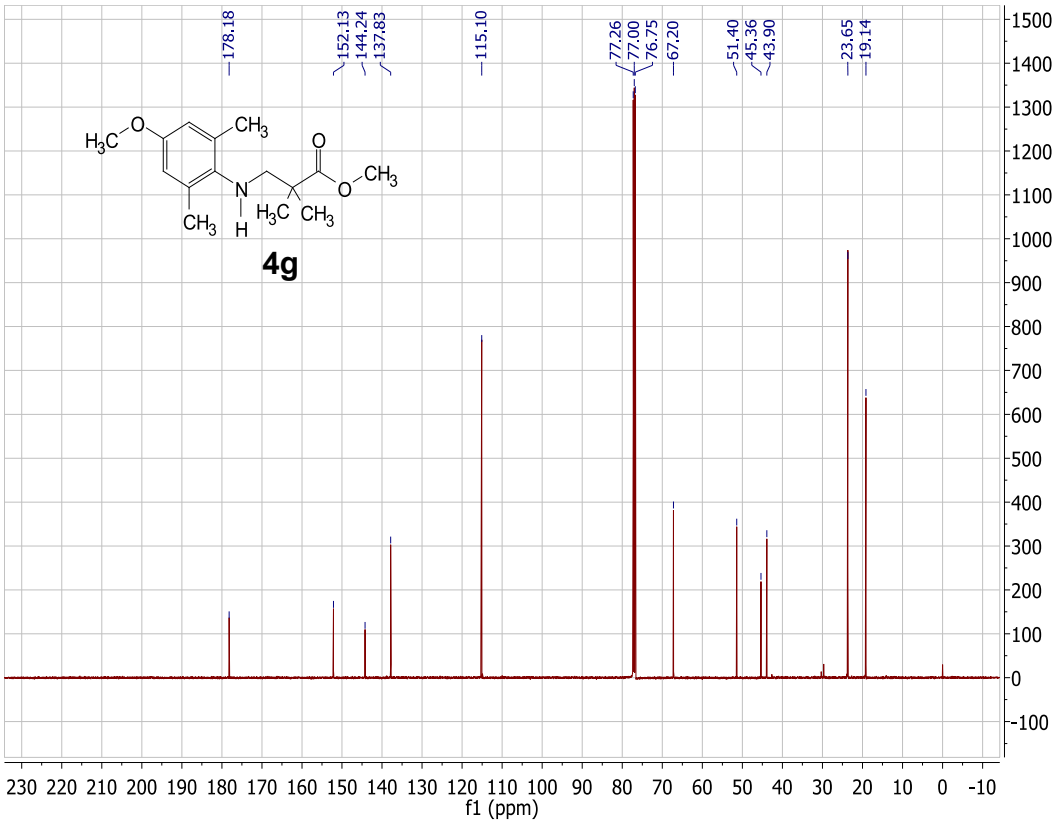
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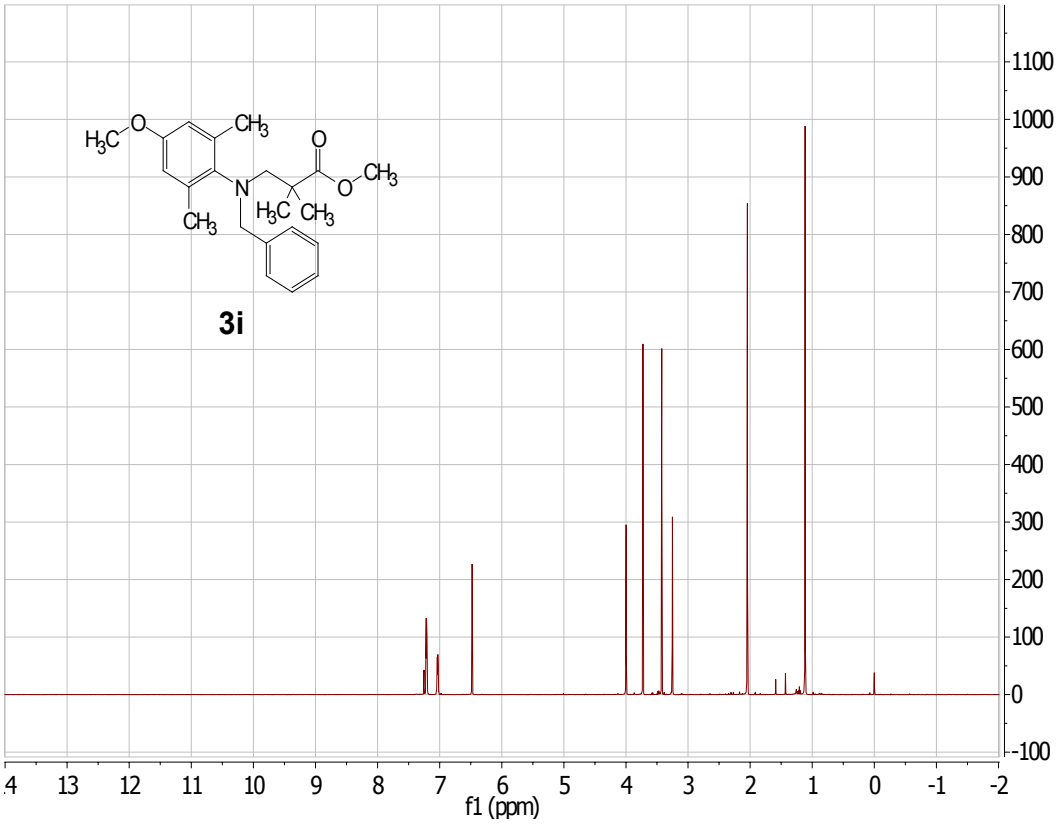
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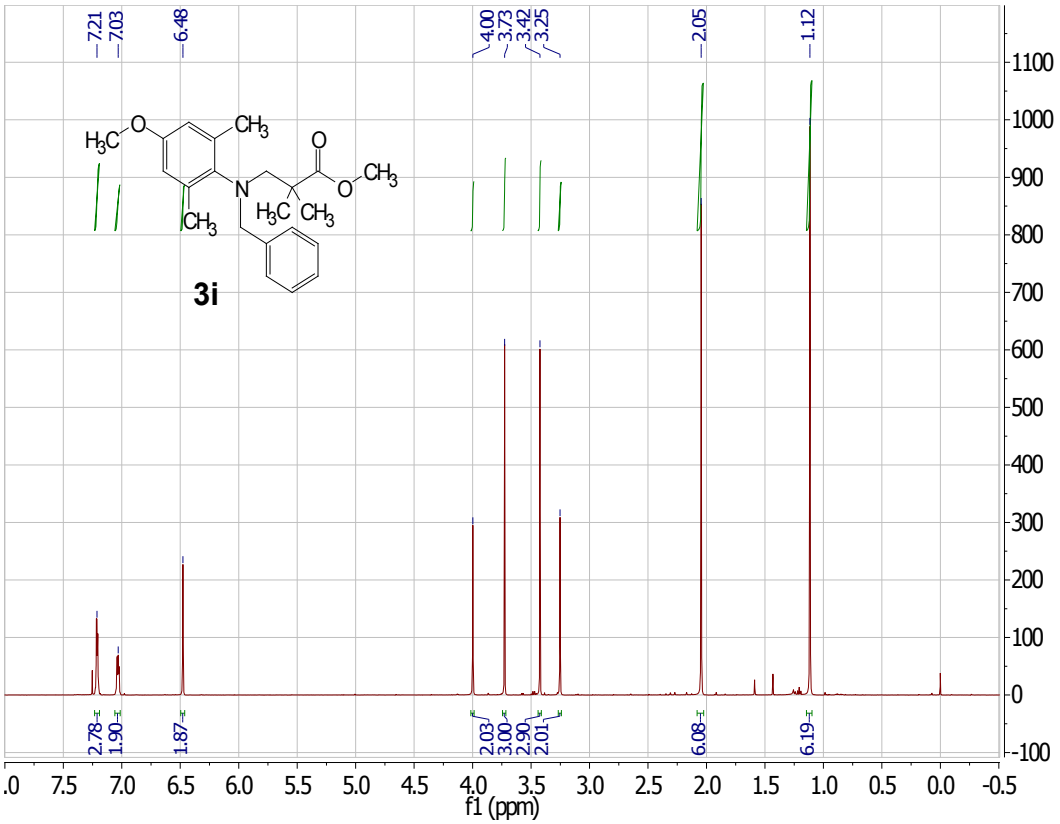
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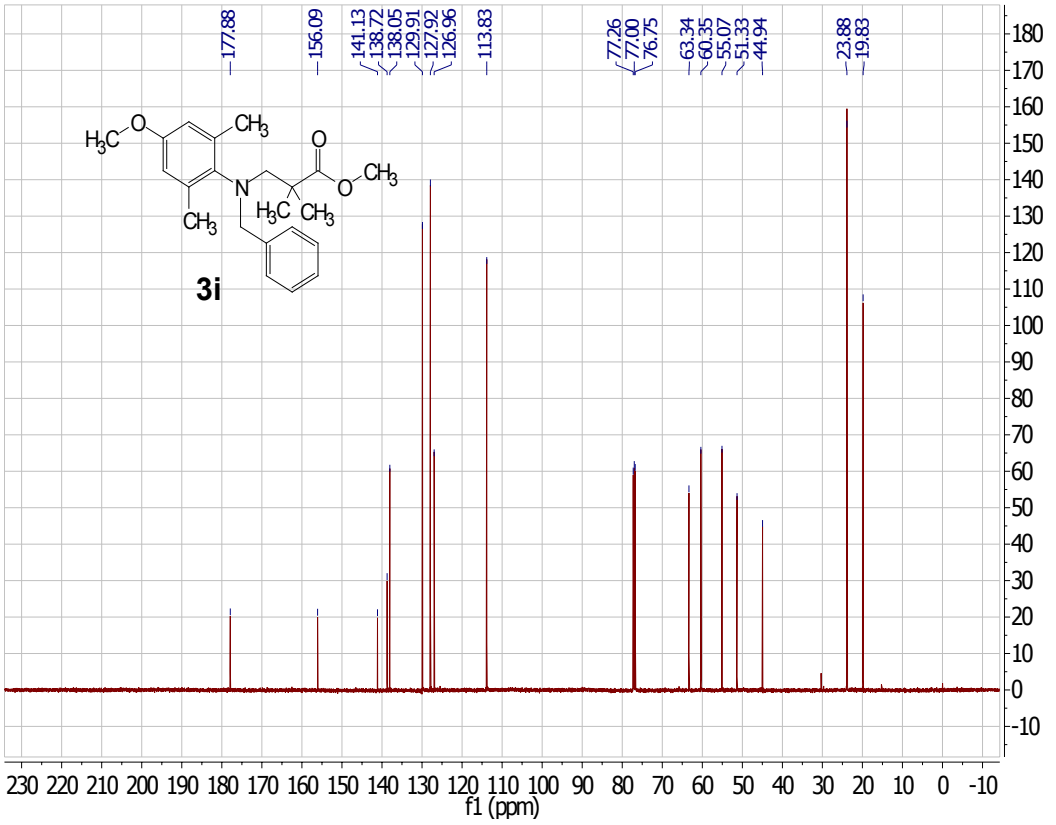
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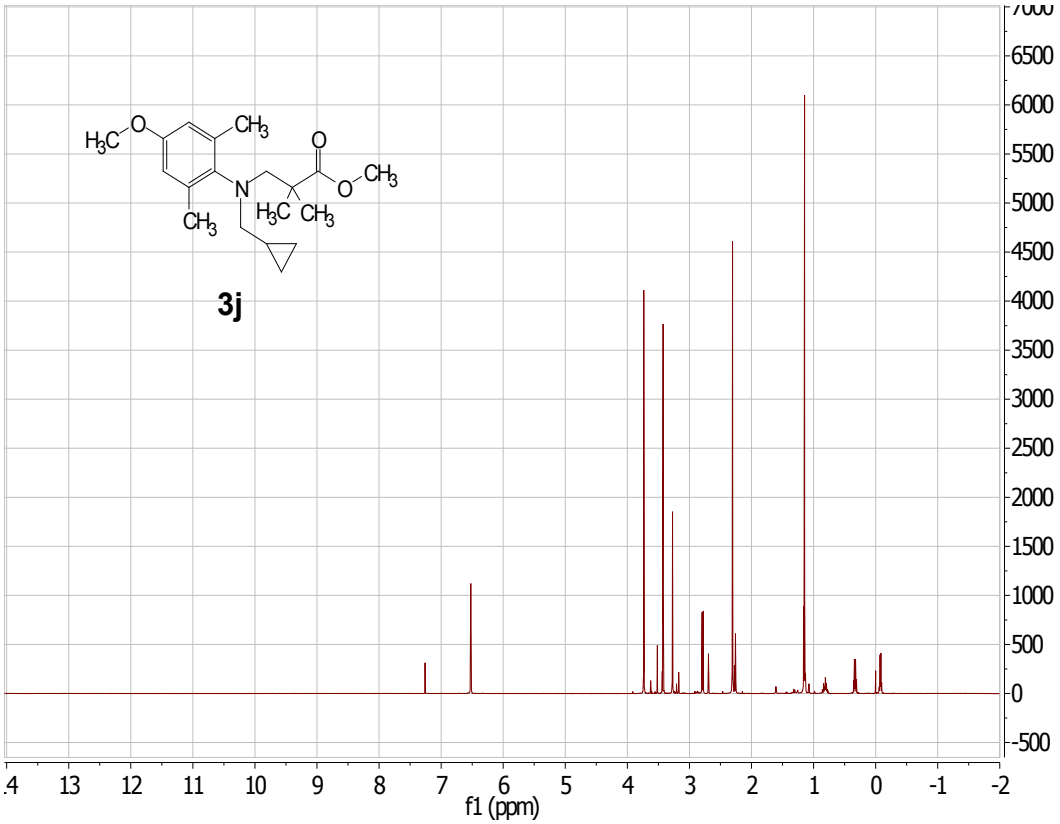
f1 (ppm)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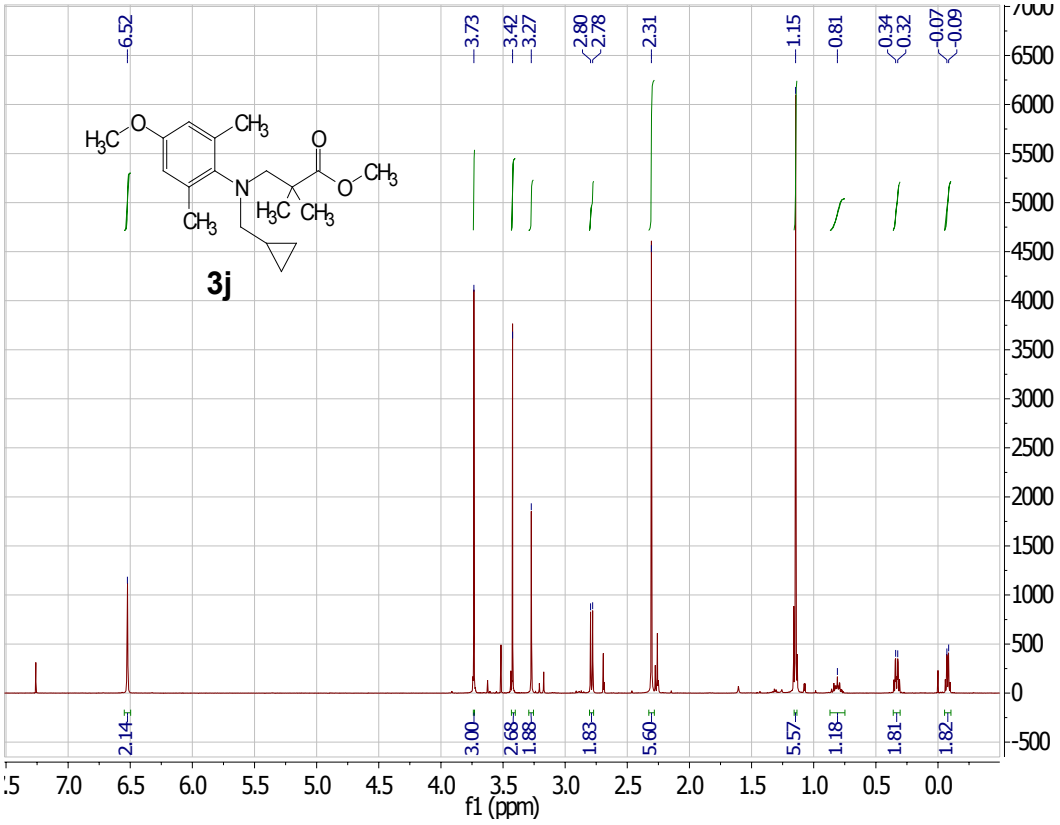
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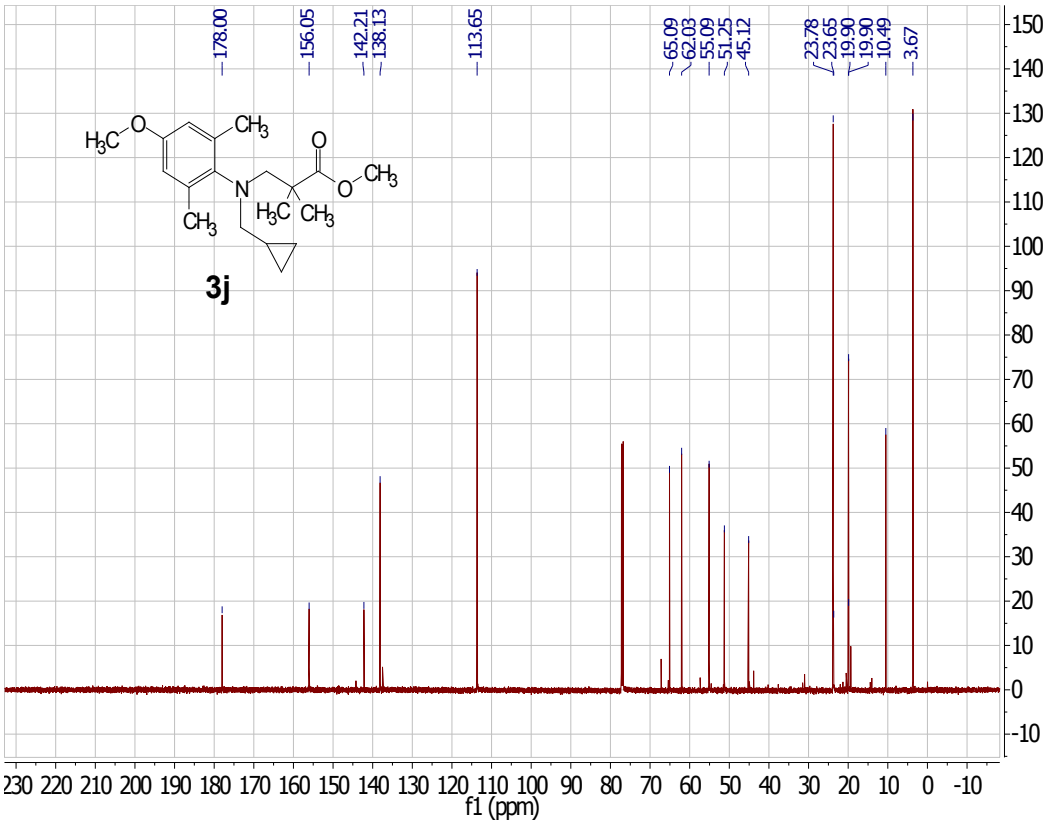
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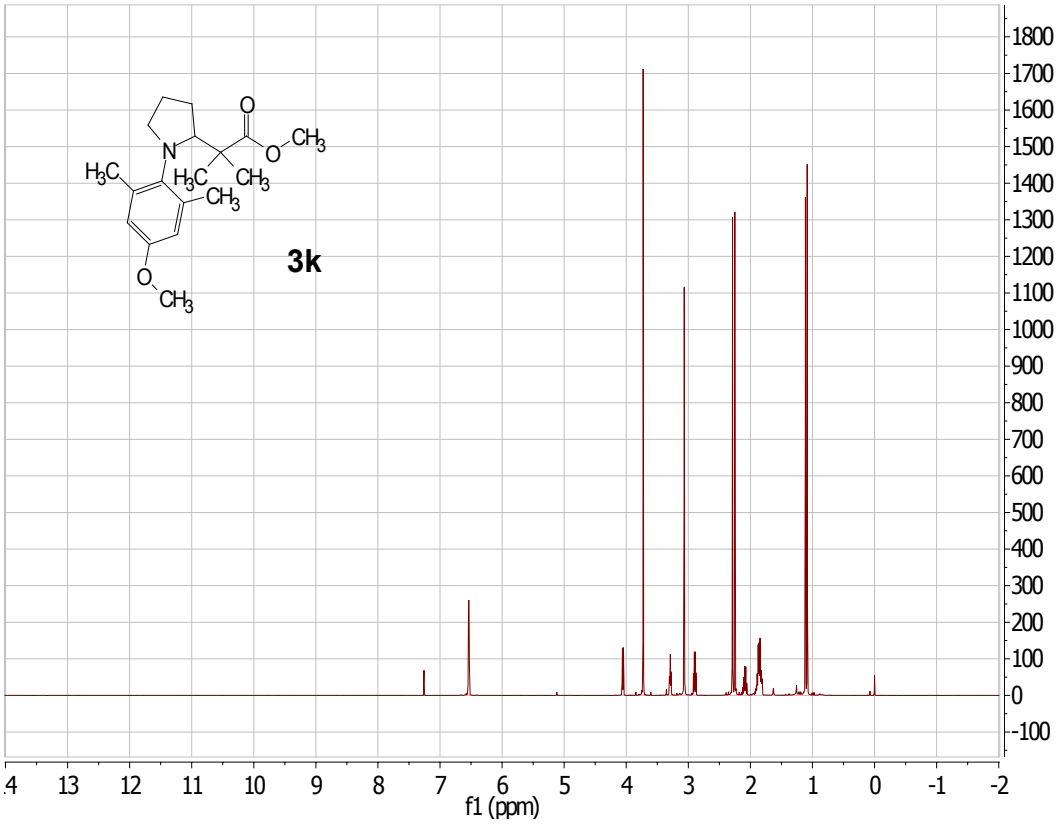
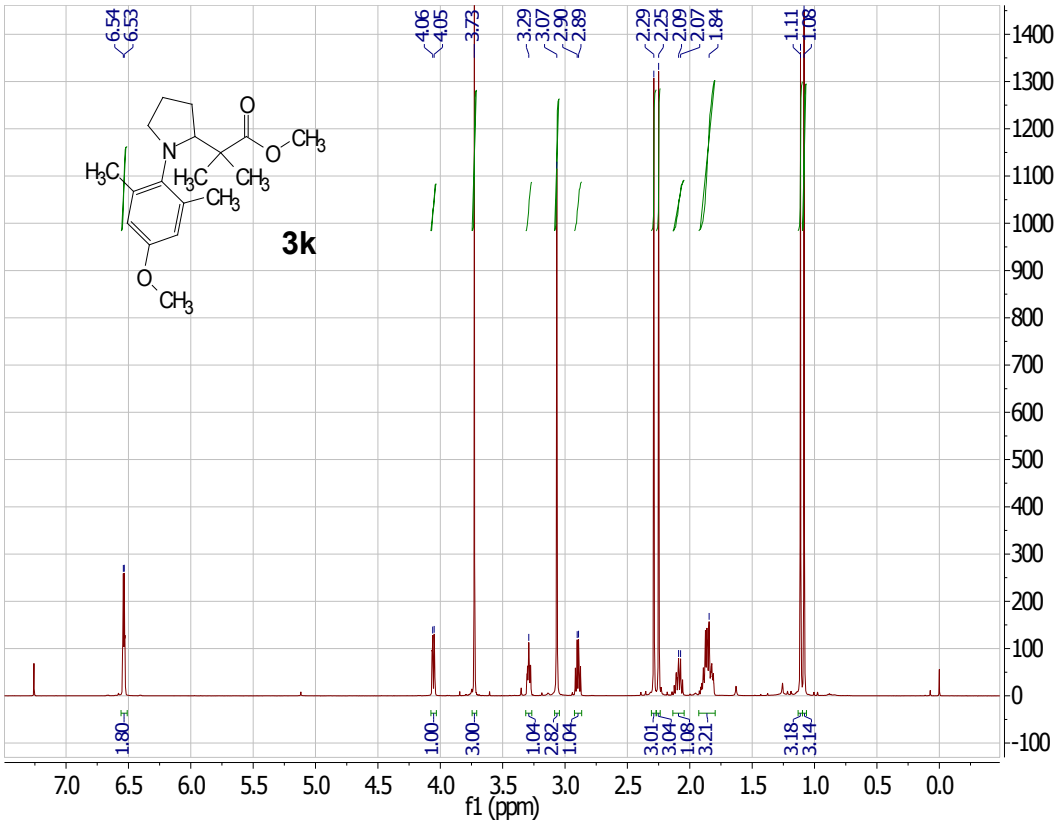
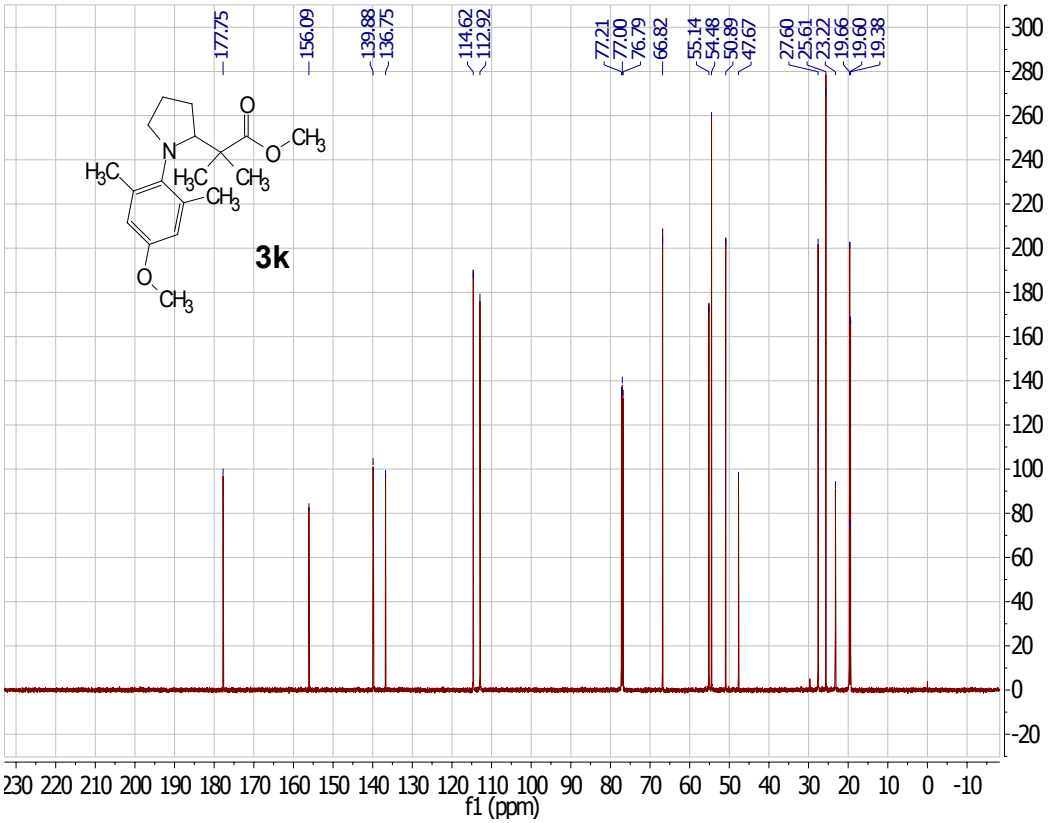
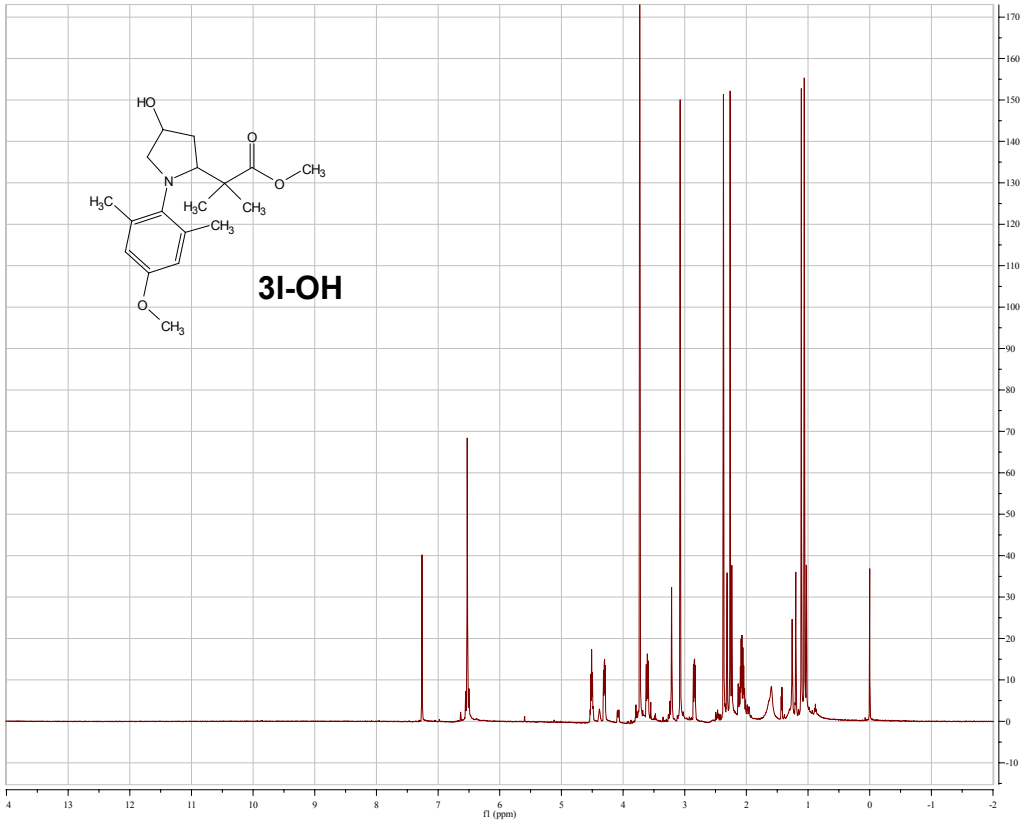
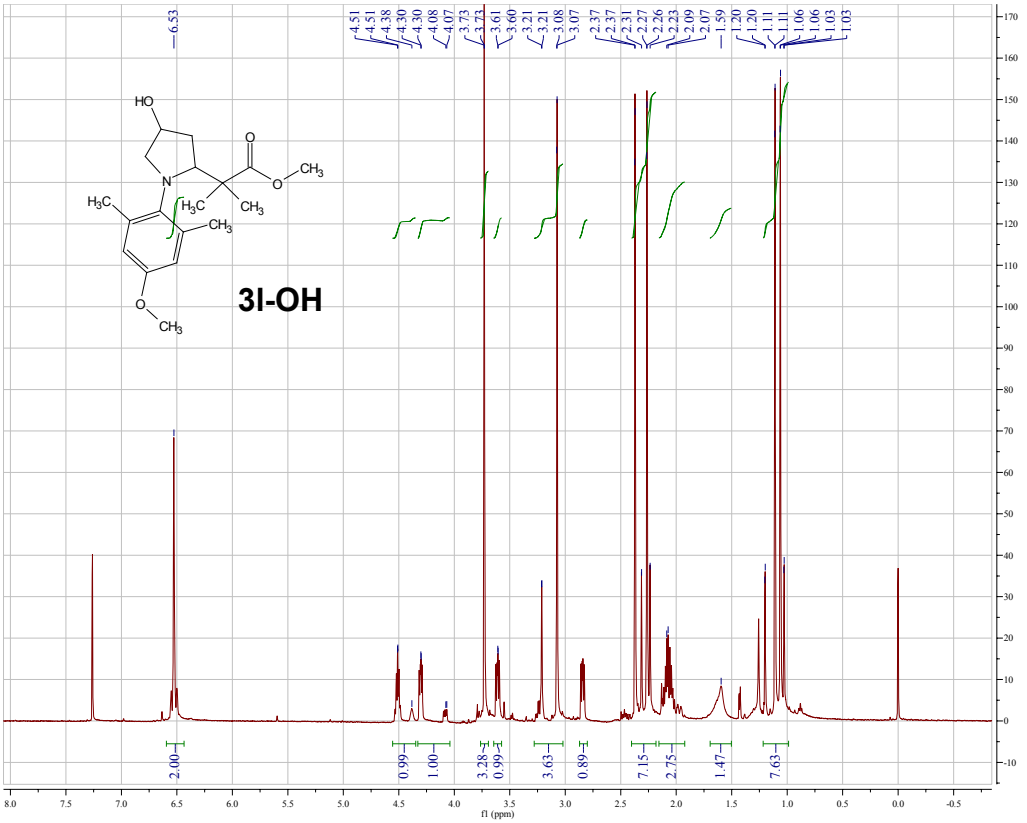
3j
f1 (ppm)

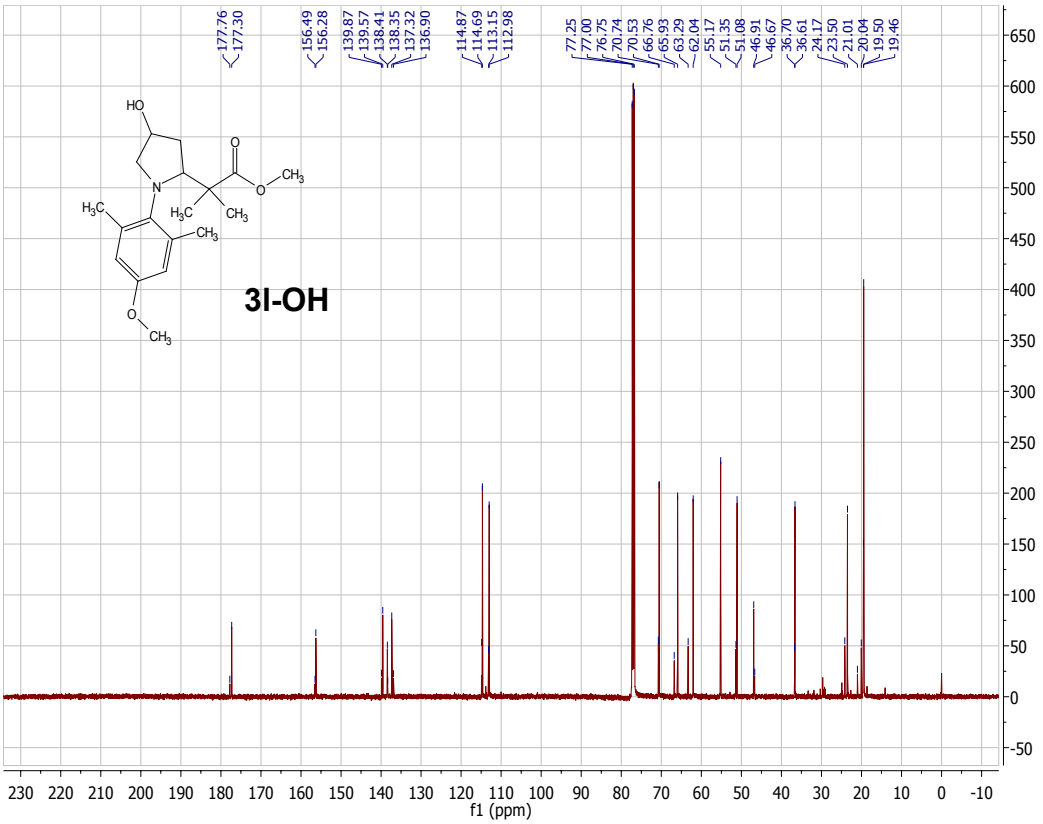

3k
f1 (ppm)

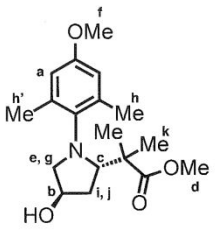

6.54
6.53
4.06
4.05
3.73
3.29
3.07
2.90
2.89
2.29
2.25
2.09
2.07
1.84
1.11
1.08
3k
1.80
1.00
3.00
1.04
2.82
1.04
3.01
3.04
1.08
3.21
3.18
3.14
f1 (ppm)


177.75
156.09
139.88
136.75
114.62
112.92
77.21
77.00
76.79
66.82
55.14
54.48
50.89
47.67
27.60
25.61
23.22
19.66
19.60
19.38
3k
f1 (ppm)

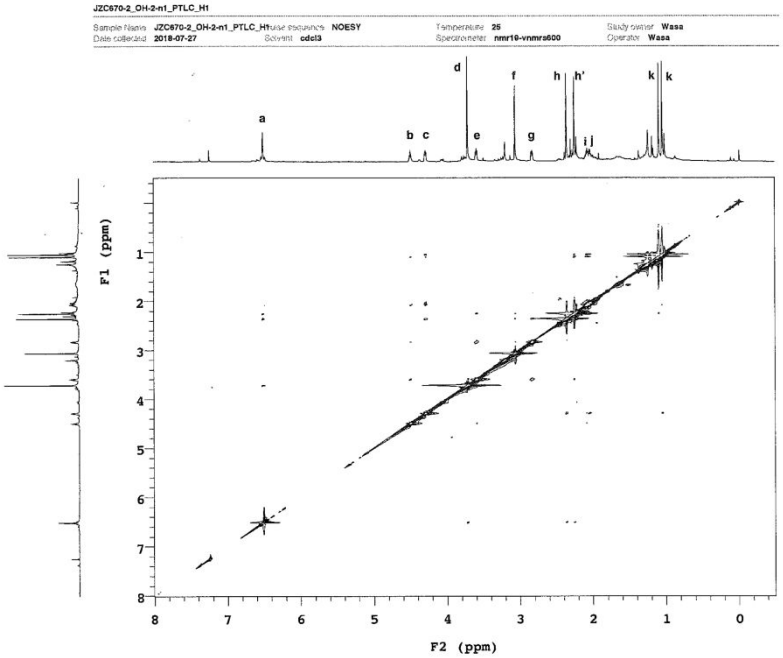

3l-OH
f1 (ppm)

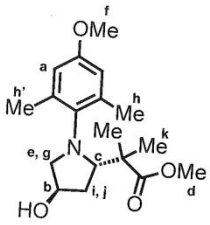

3l-OH


3l-OH
f1 (ppm)

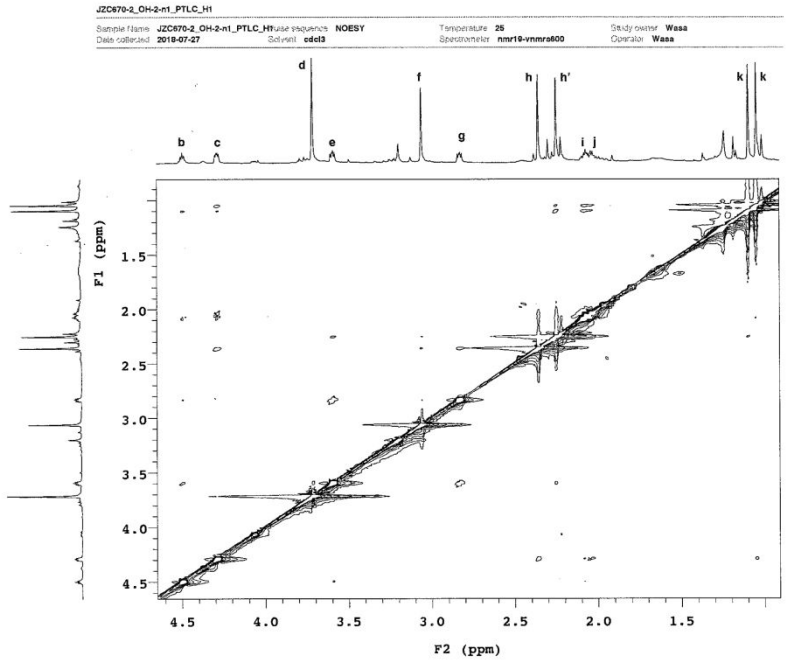

f
OMe
a
h'
Me
h
Me
Me
k
Me
e, g
N
c
OMe
b
i, j
d
HO
O

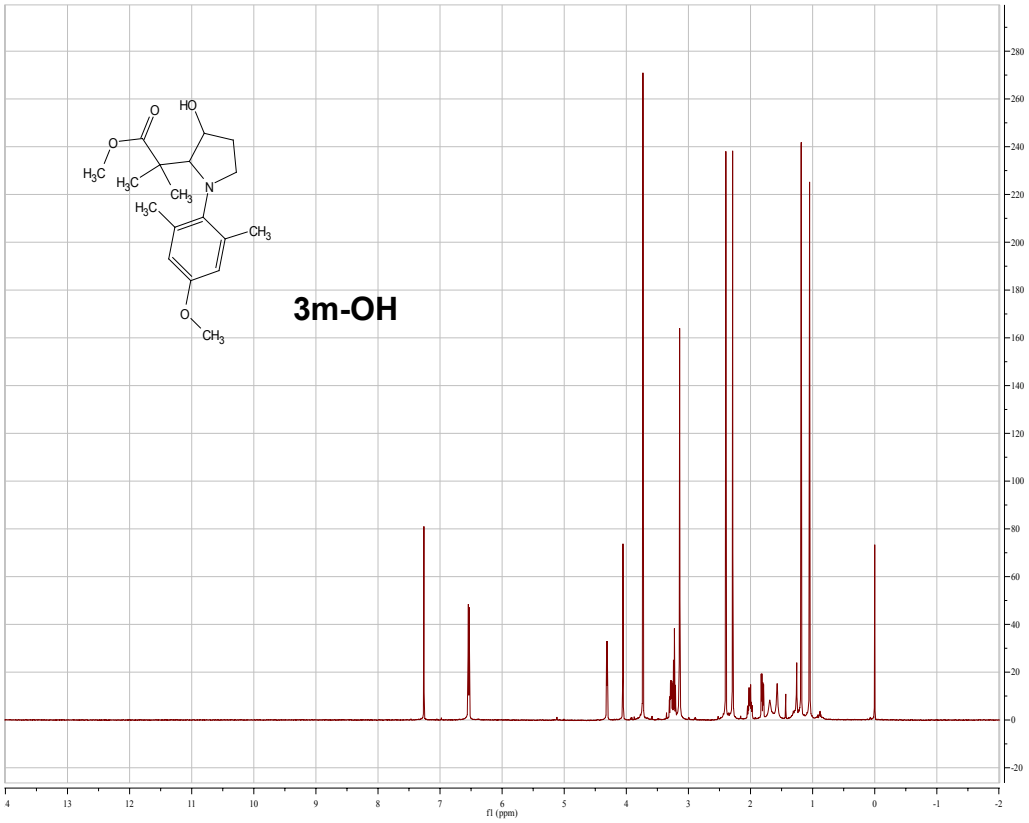
3l-OH

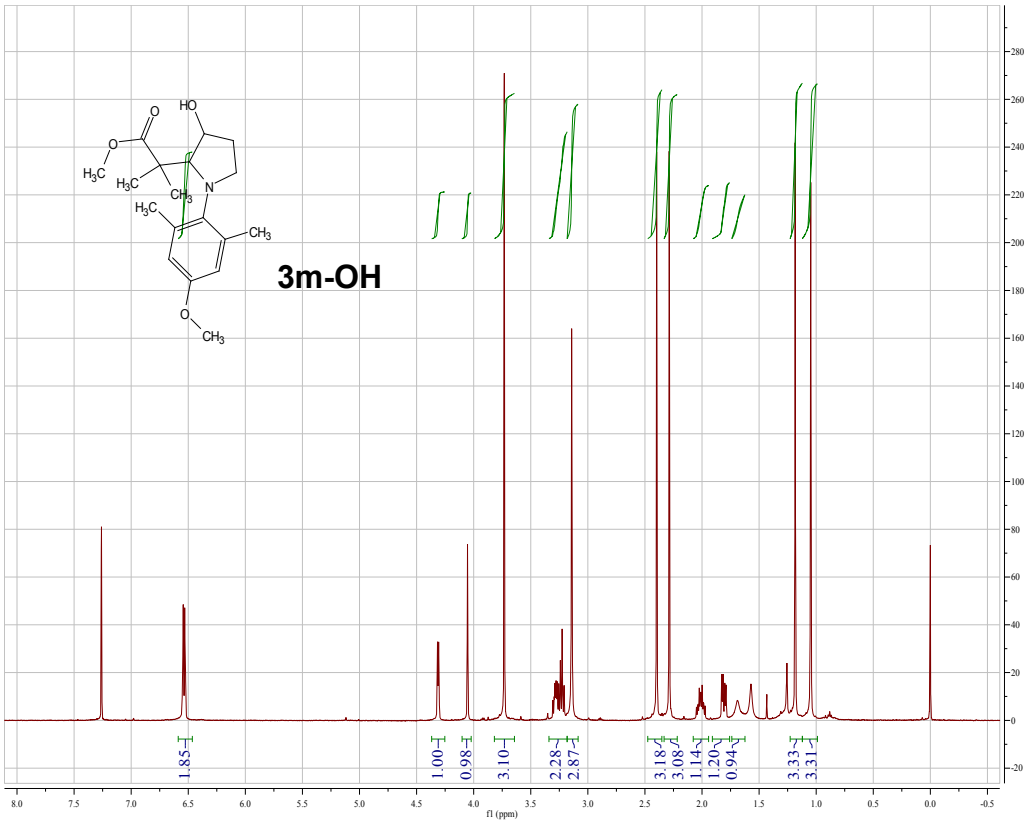

JZC670-2_OH-2-n1_PTLC_H1
Sample Name JZC670-2_OH-2-n1_PTLC_H1
Pulse sequence NOESY
Temperature 25
Study owner Wasa
Date collected 2018-07-27
Solvent cdcl3
Spectrometer nmr19-vnmrs600
Operator Wasa
a
b c
d
e
f
g
h
h'
i j
k
k
F1 (ppm)
F2 (ppm)
Data file
Plot date 2018-07-26

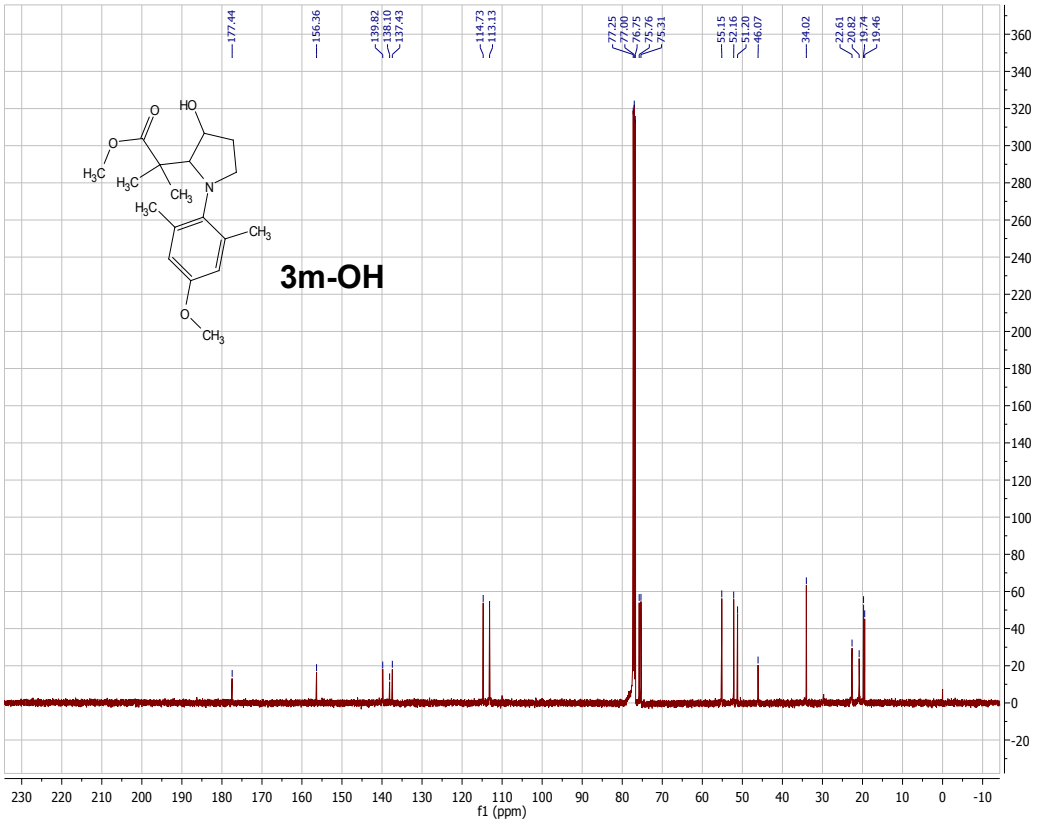

f
OMe
a
h'
Me
h
Me
Me
k
Me
e, g
N
c
OMe
b
i, j
d
HO
O

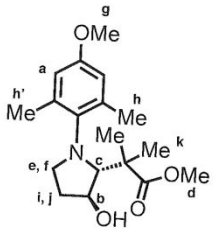
3l-OH

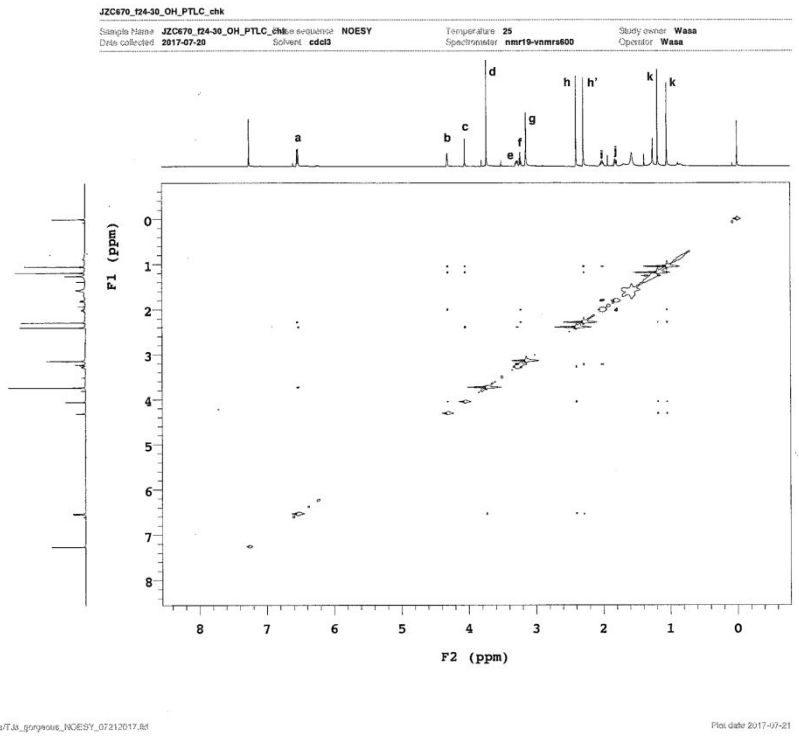

JZC670-2_OH-2-n1_PTLC_H1
Sample Name JZC670-2_OH-2-n1_PTLC_H1
Pulse sequence NOESY
Temperature 25
Study owner Wasa
Date collected 2018-07-27
Solvent cdcl3
Spectrometer nmr19-vnmrs600
Operator Wasa
b
c
d
e
f
g
h
h'
i j
k
k
F1 (ppm)
F2 (ppm)
Data file
Plot date 2018-07-26

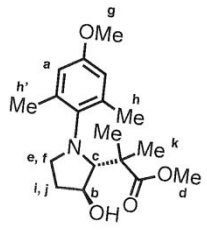

3m-OH
f1 (ppm)


3m-OH
1.85
1.00
0.98
3.10
2.28
2.87
3.18
3.08
1.14
1.20
0.94
3.33
3.31
f1 (ppm)

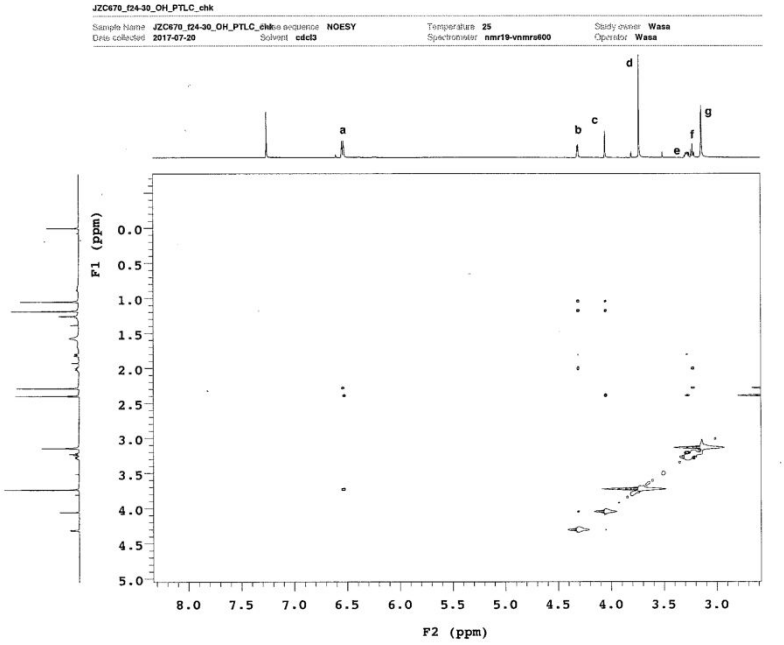

177.44
156.36
139.82
138.10
137.43
114.73
113.13
77.25
77.00
76.75
75.76
75.31
55.15
52.16
51.70
46.07
34.02
22.61
20.82
19.74
19.46
3m-OH
f1 (ppm)

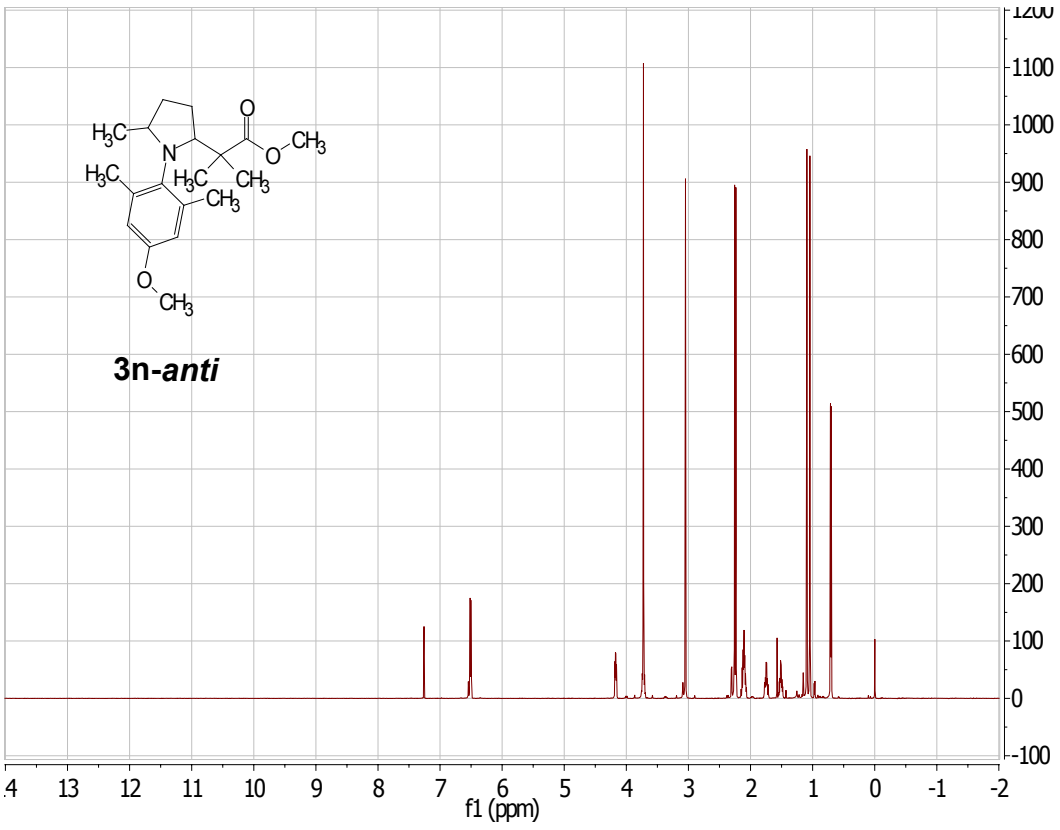

3m-OH


JZC670_f24-30_OH_PTLC_chk
F1 (ppm)
F2 (ppm)

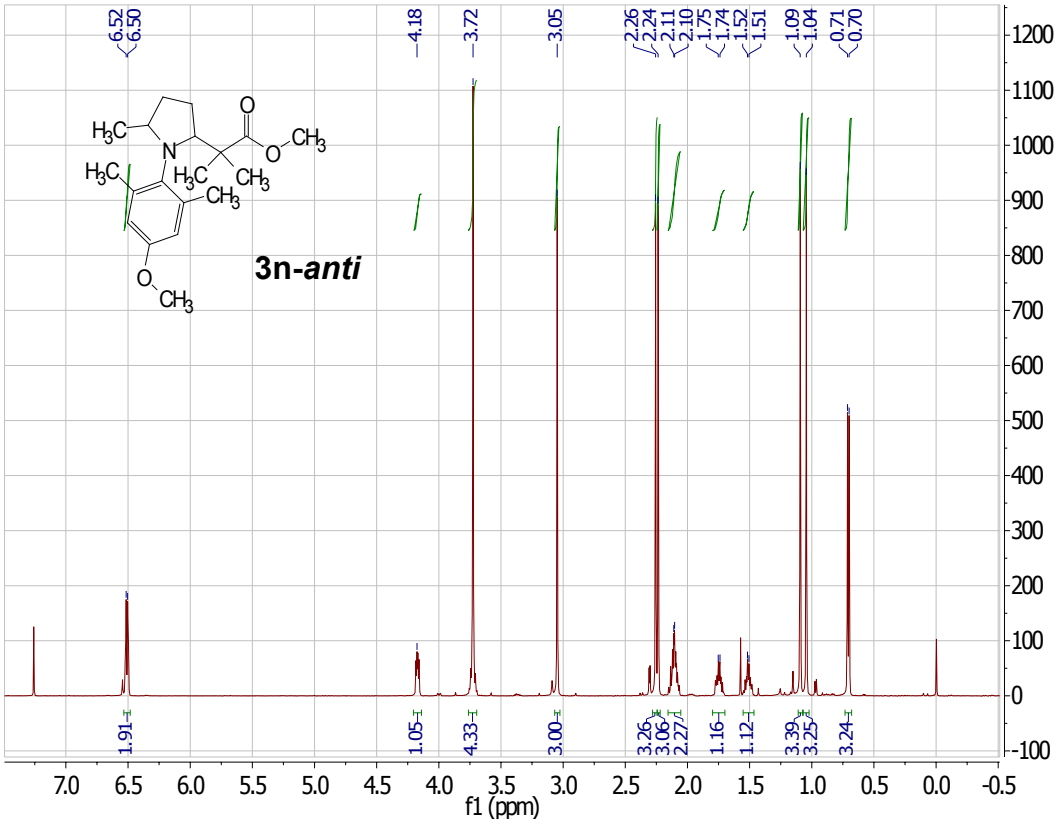

g
OMe
a
h'
Me
h
Me
Me
N
e, f
c
Me
k
OMe
d
i, j
b
OH
O

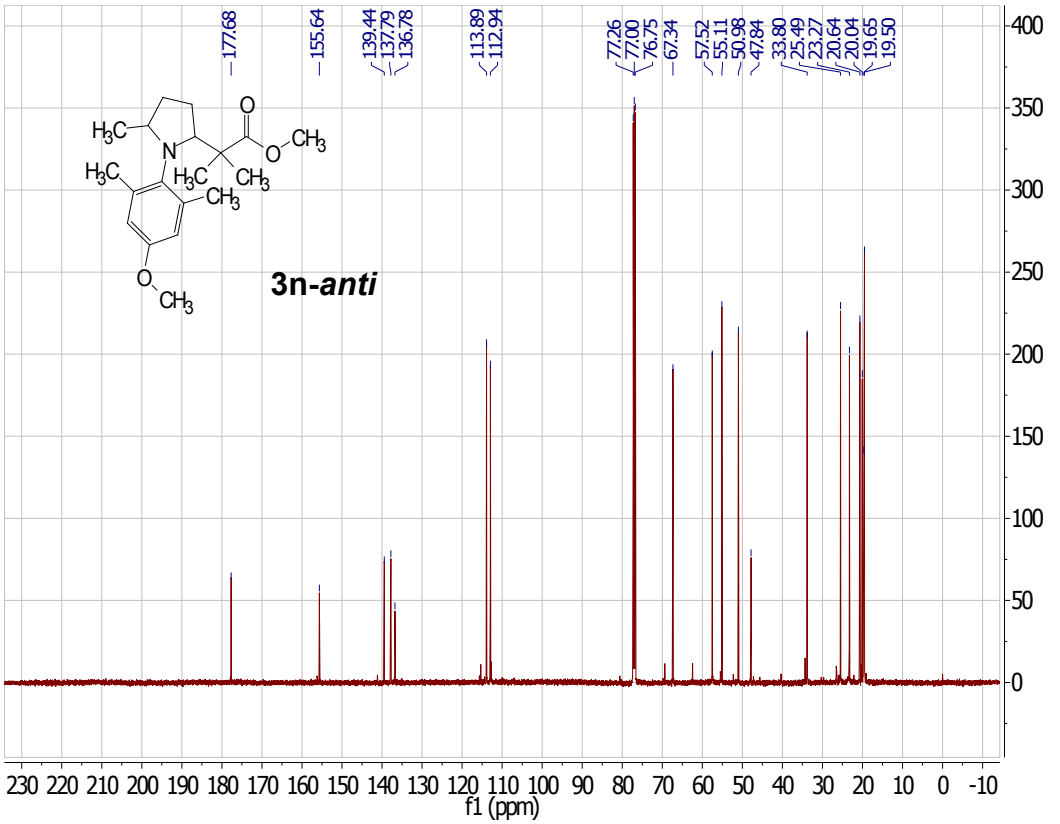
3m-OH


JZC670_f24-30_OH_PTLC_chk
Sample Name JZC670_f24-30_OH_PTLC_chk
Pulse sequence NOESY
Temperature 25
Study owner Wasa
Data collected 2017-07-20
Solvent cdcl3
Spectrometer nmr19-vnmrs600
Operator Wasa
a
b
c
d
e
f
g
F1 (ppm)
F2 (ppm)
Data file /home/ALL/Wasa/Jaetica/TJs_gorgeous_NOESY_07212017.fid
Plot date 2017-07-21


H3C
N
O
O
CH3
H3C
H3C
CH3
CH3
O
CH3
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

3n-*anti*


6.52
6.50
4.18
3.72
3.05
2.26
2.24
2.11
2.10
1.75
1.74
1.52
1.51
1.09
1.04
0.71
0.70
3n-anti
1.91
1.05
4.33
3.00
3.26
3.06
2.27
1.16
1.12
3.39
3.25
3.24
f1 (ppm)


177.68
155.64
139.44
137.79
136.78
113.89
112.94
77.26
77.00
76.75
67.34
57.52
55.11
50.98
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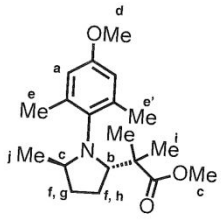
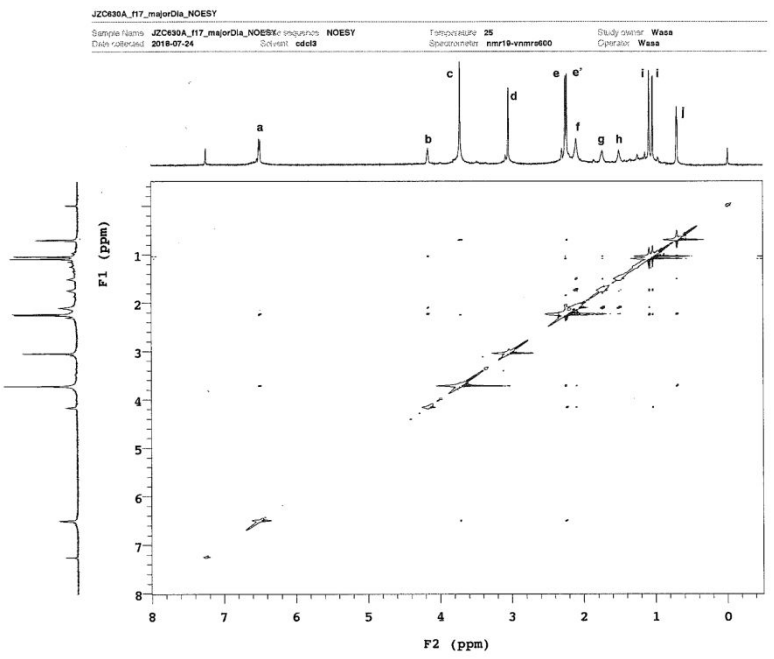
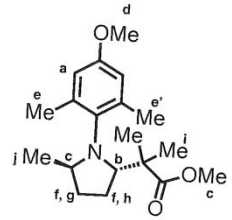
33.80
25.49
23.27
20.64
20.04
19.65
19.50
3n-anti
f1 (ppm)

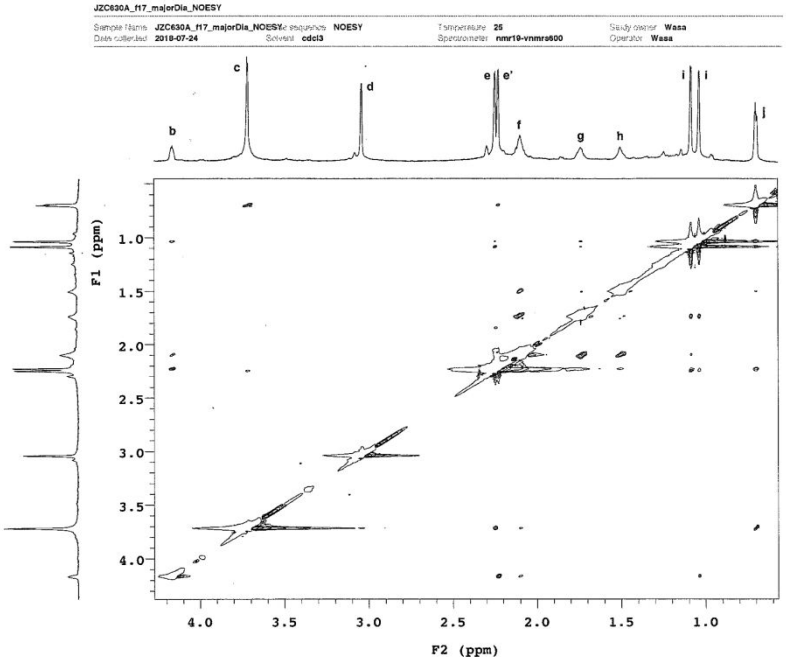


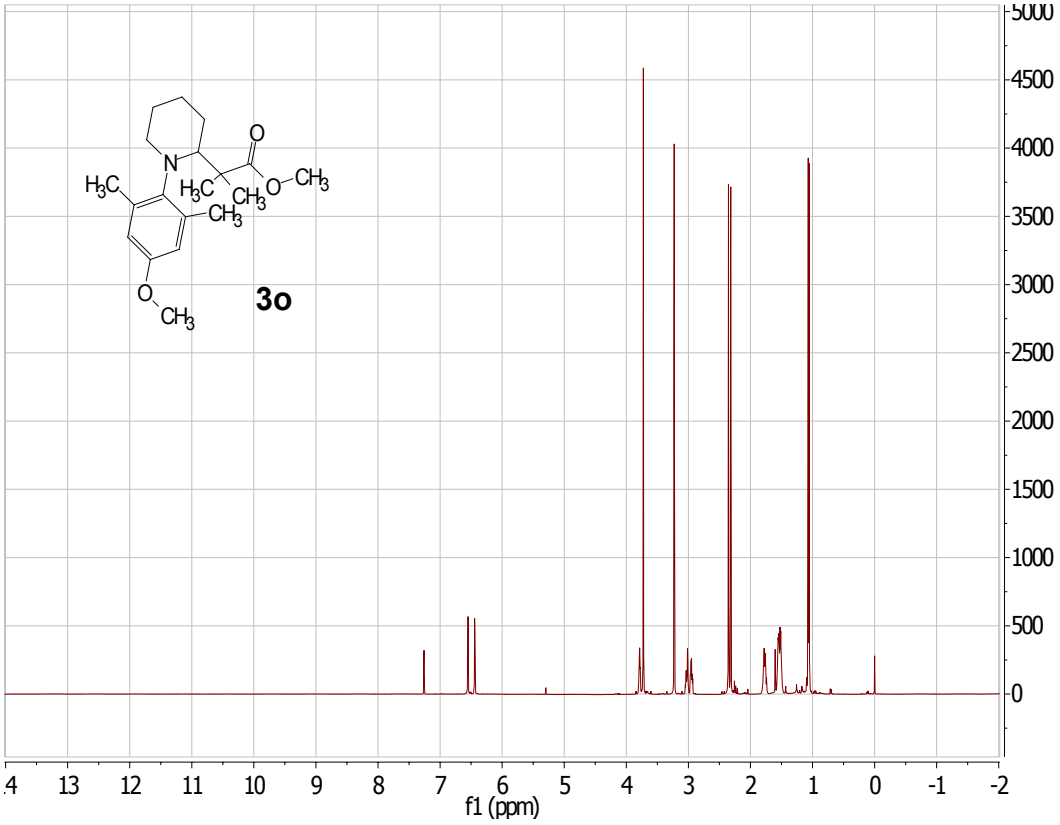
3n-*anti*

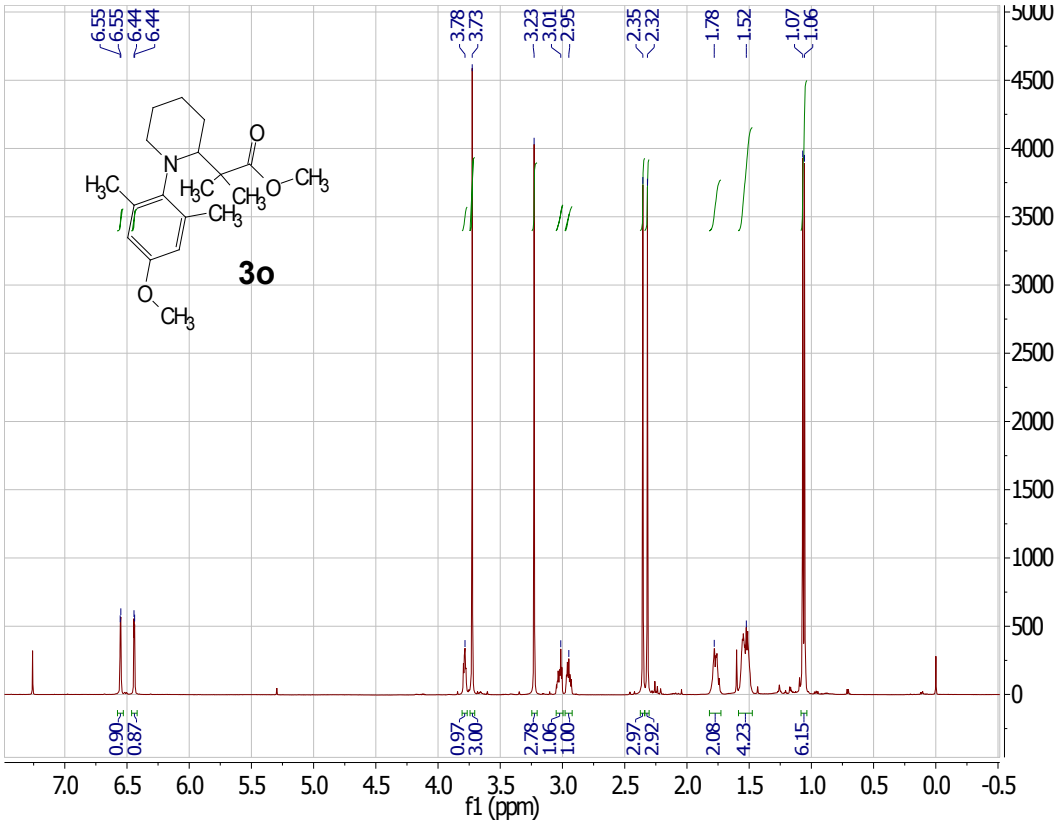


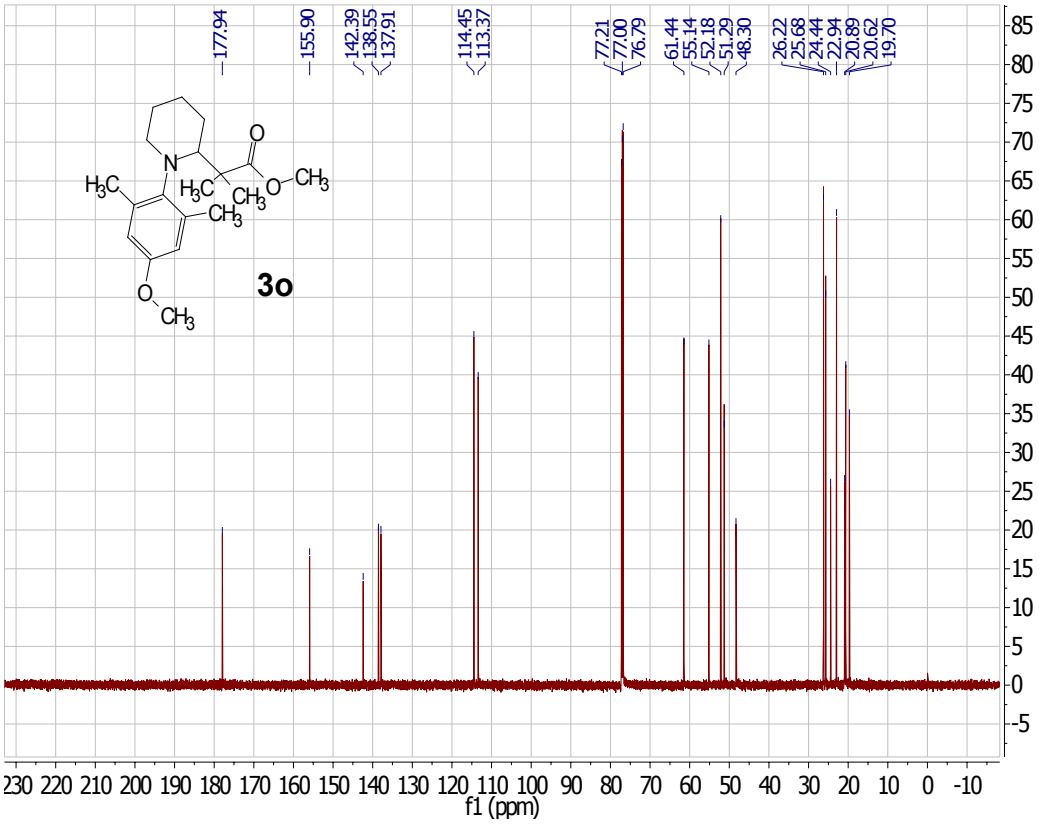


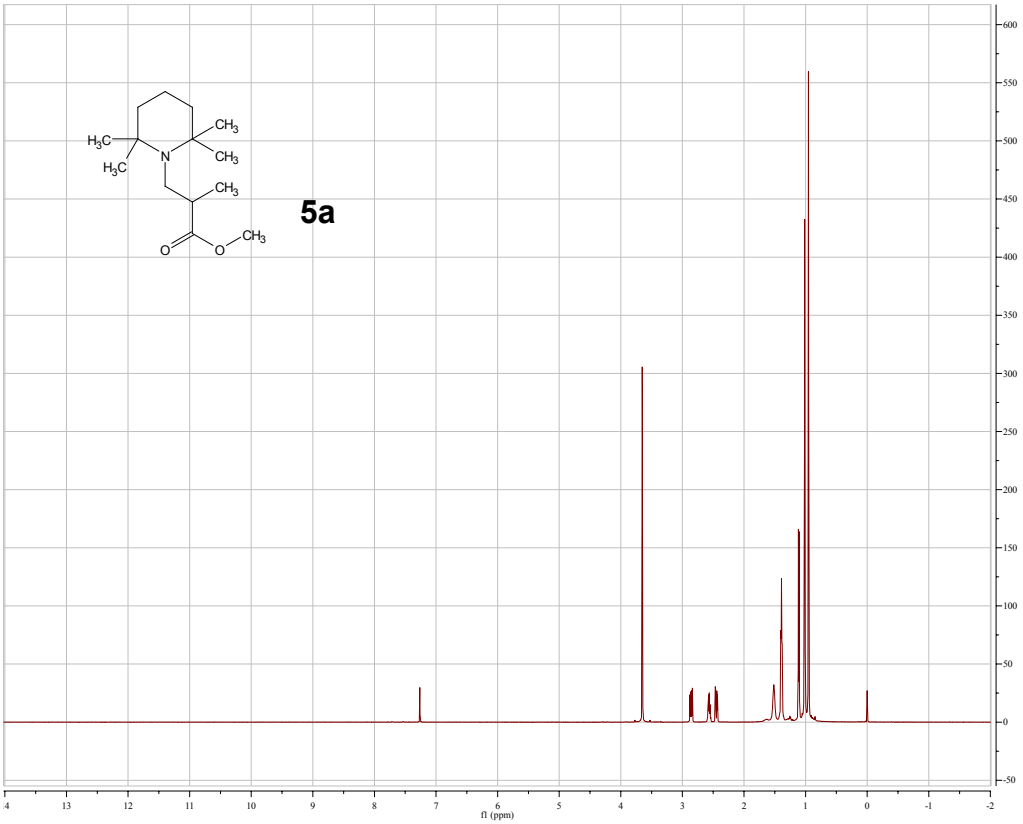
3n-*anti*

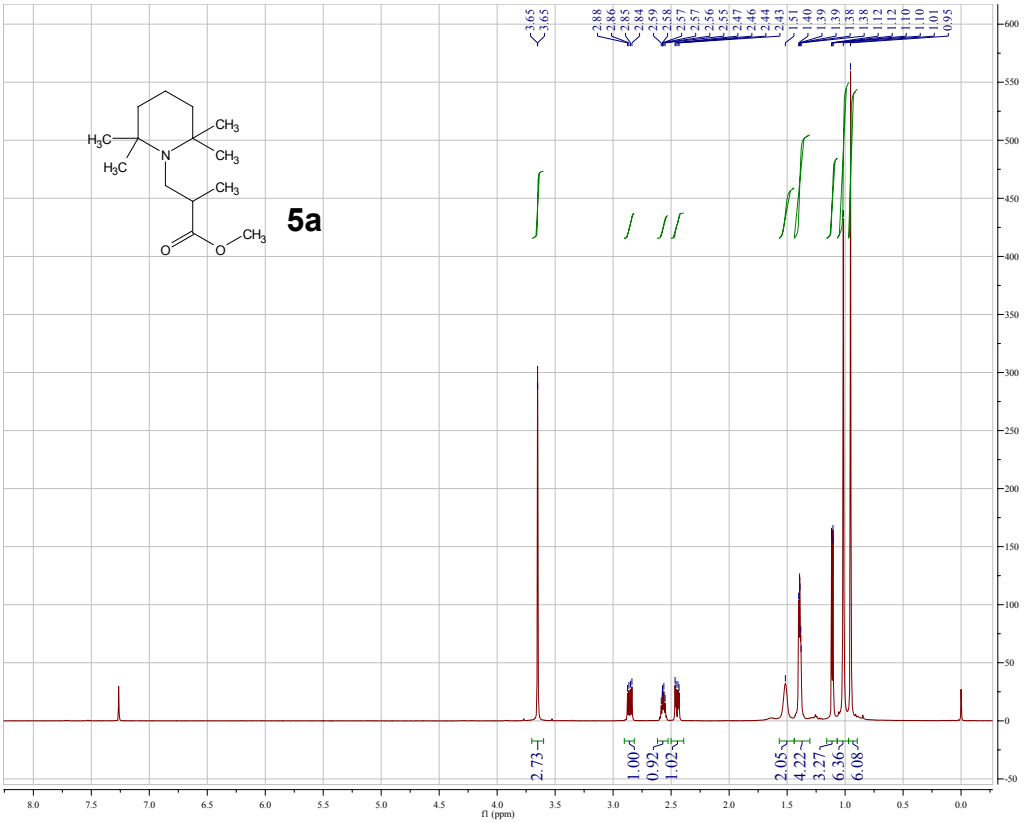


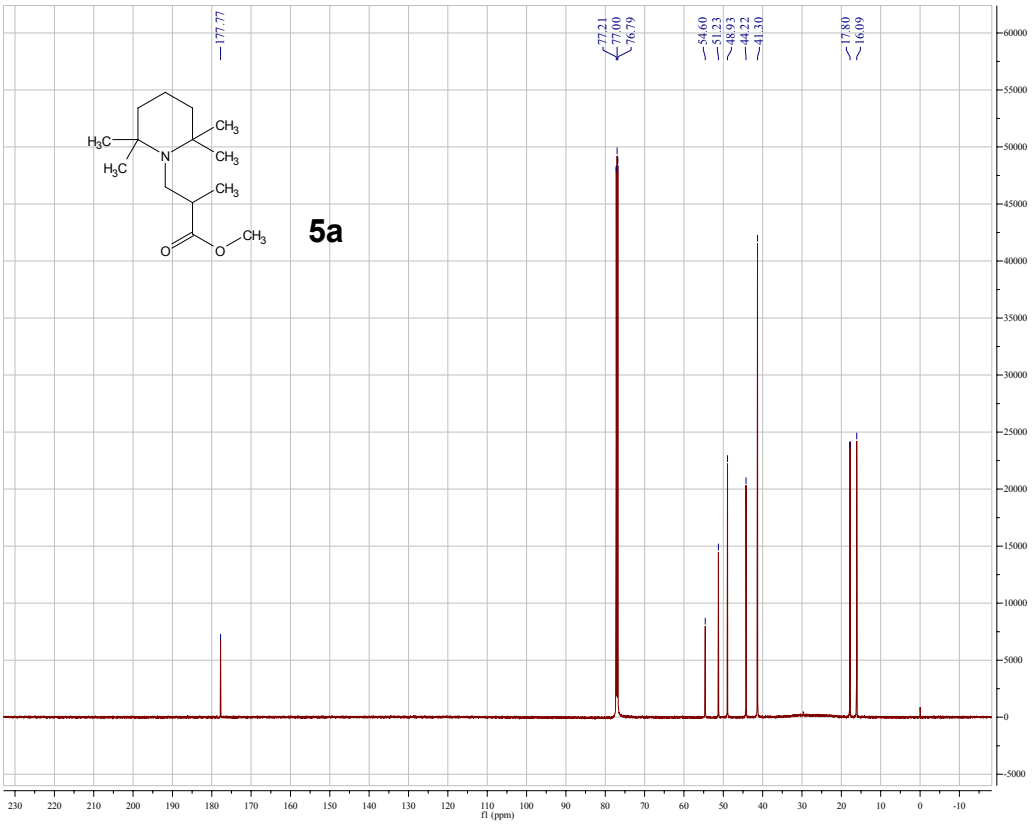

3o
f1 (ppm)

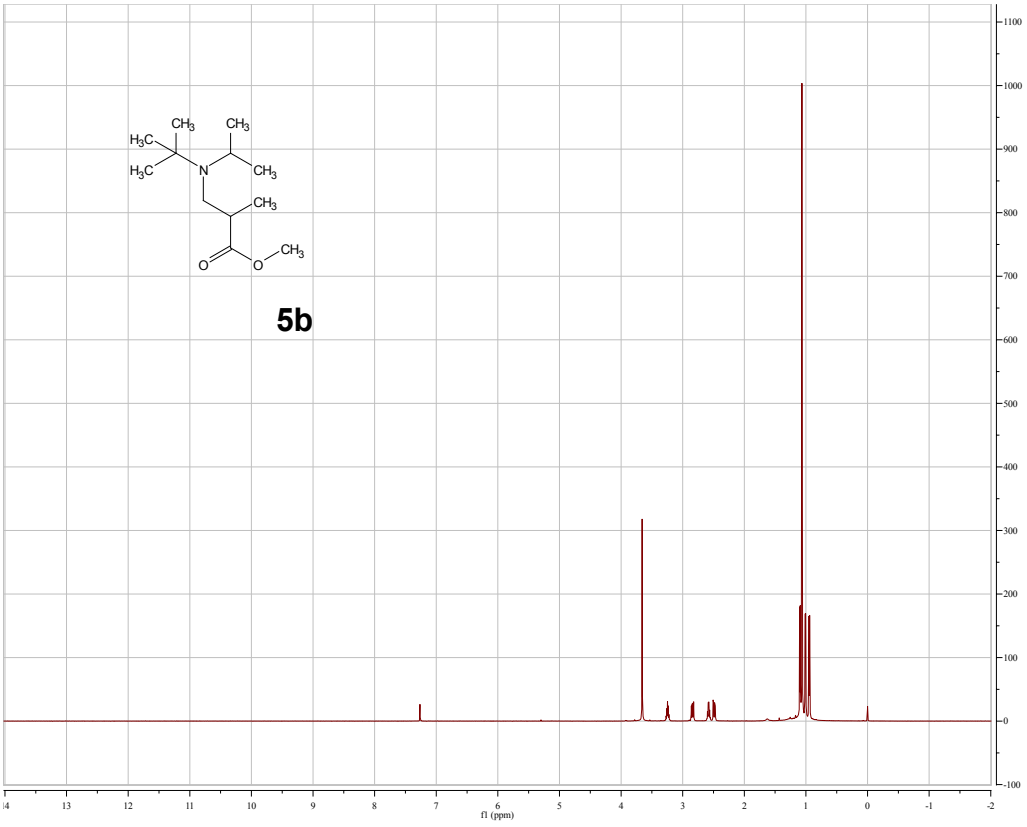

6.55
6.55
6.44
6.44
3.78
3.73
3.23
3.01
2.95
2.35
2.32
1.78
1.52
1.07
1.06
3o
0.90
0.87
0.97
3.00
2.78
1.06
1.00
2.97
2.92
2.08
4.23
6.15
f1 (ppm)

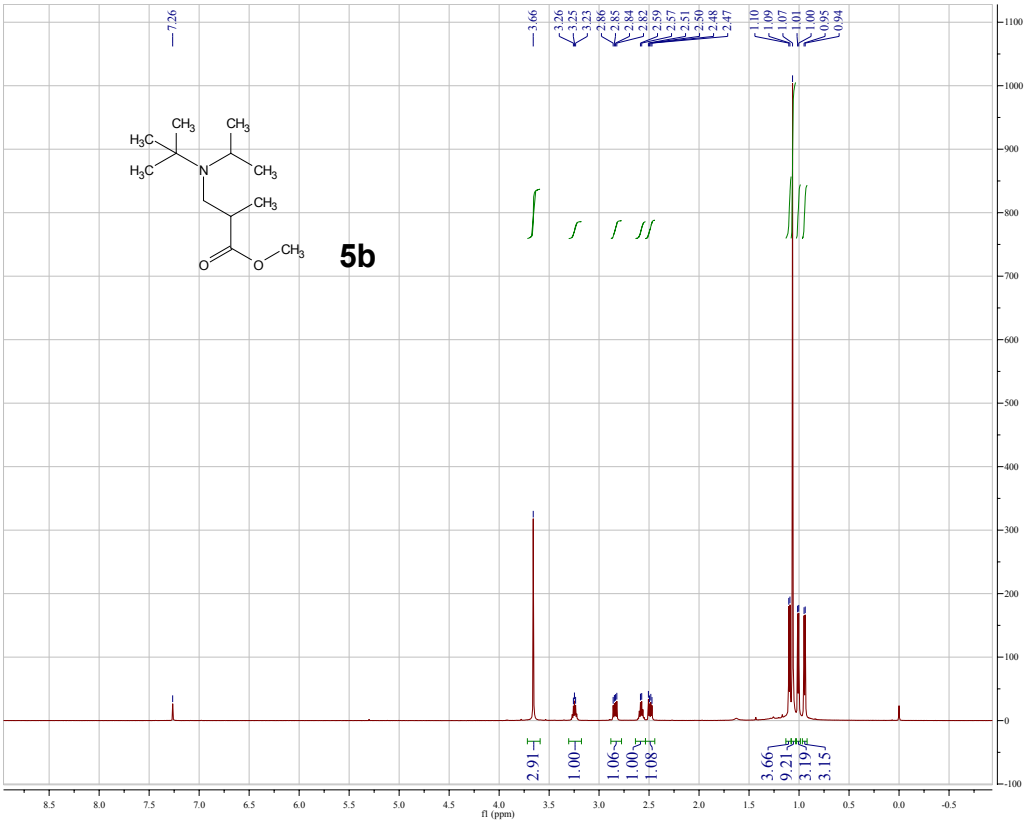

177.94
155.90
142.39
138.55
137.91
114.45
113.37
77.21
77.00
76.79
61.44
55.14
52.18
51.29
48.30
26.22
25.68
24.44
22.94
20.89
20.62
19.70
3o
f1 (ppm)

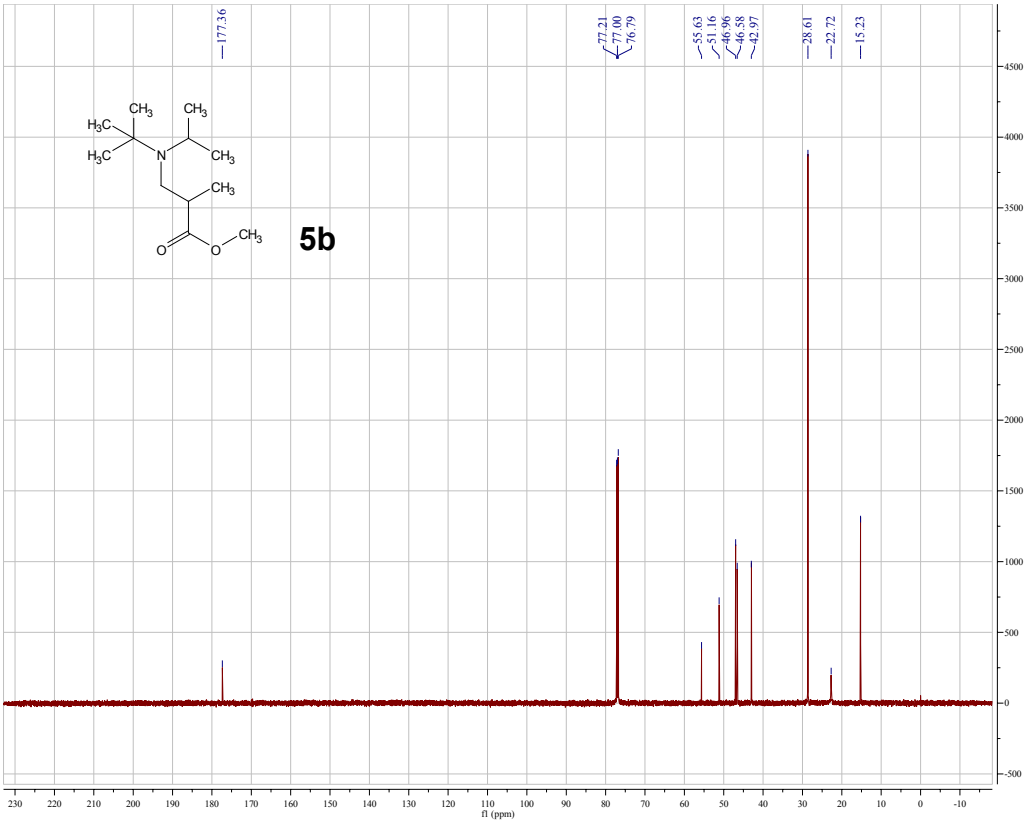

5a
f1 (ppm)

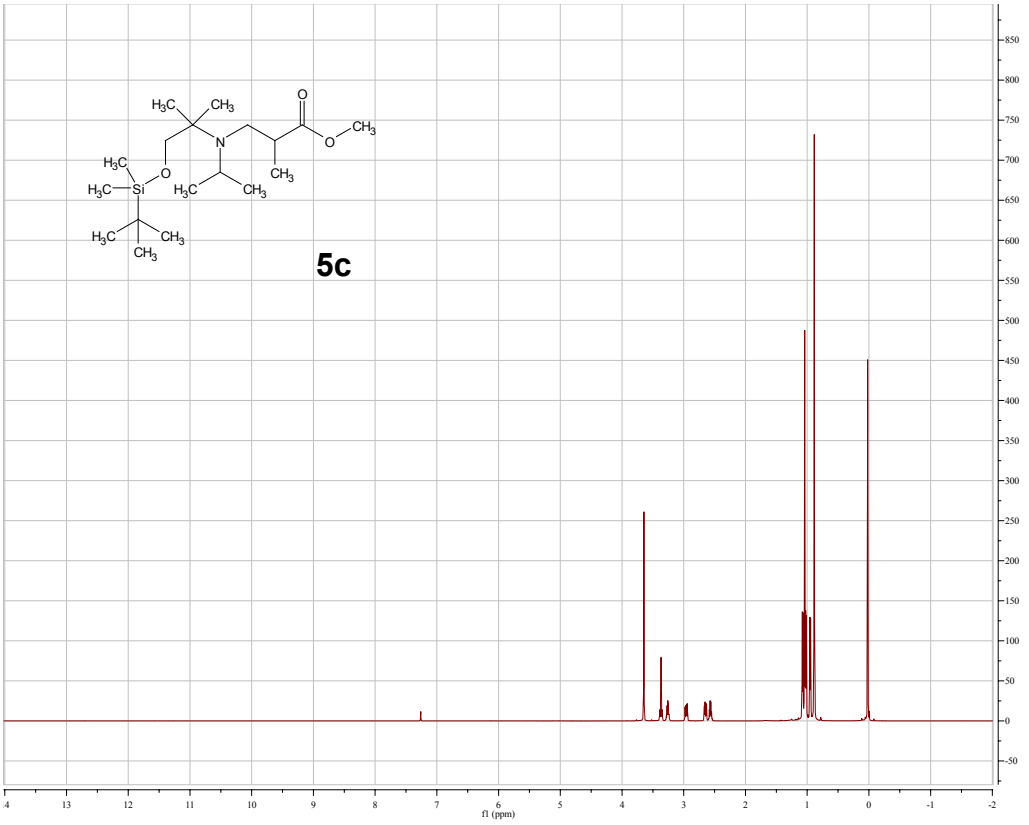

5a
3.65
3.65
2.88
2.86
2.85
2.84
2.59
2.58
2.57
2.57
2.56
2.55
2.47
2.46
2.44
2.43
1.51
1.40
1.39
1.39
1.38
1.38
1.12
1.12
1.10
1.10
1.01
0.95
2.73
1.00
0.92
1.02
2.05
4.22
3.27
6.36
6.08
f1 (ppm)

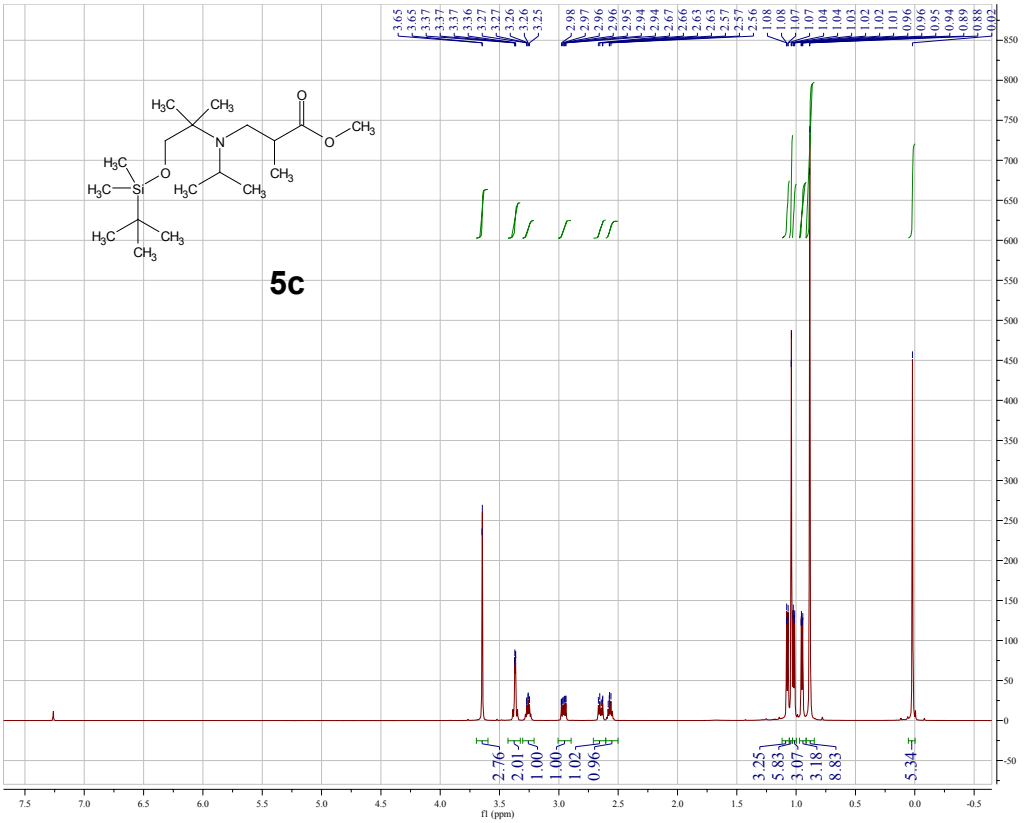

5a
177.77
77.21
77.00
76.79
54.60
51.23
48.93
44.22
41.30
17.80
16.09
f1 (ppm)

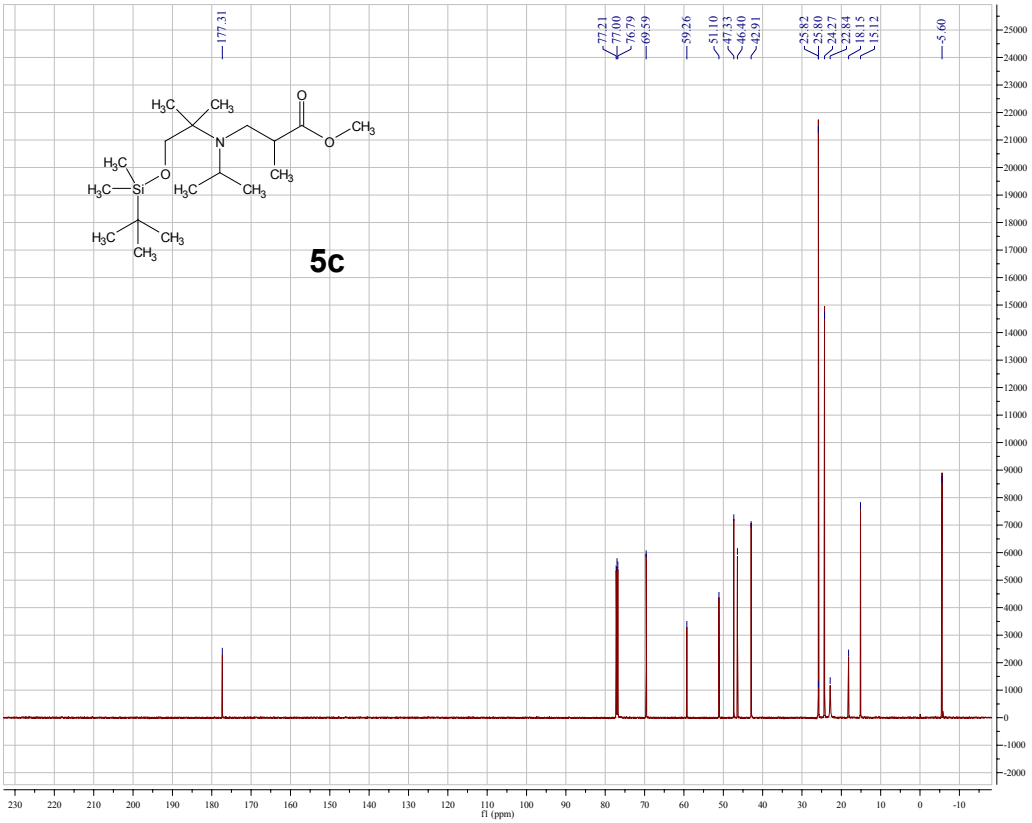

5b
f1 (ppm)

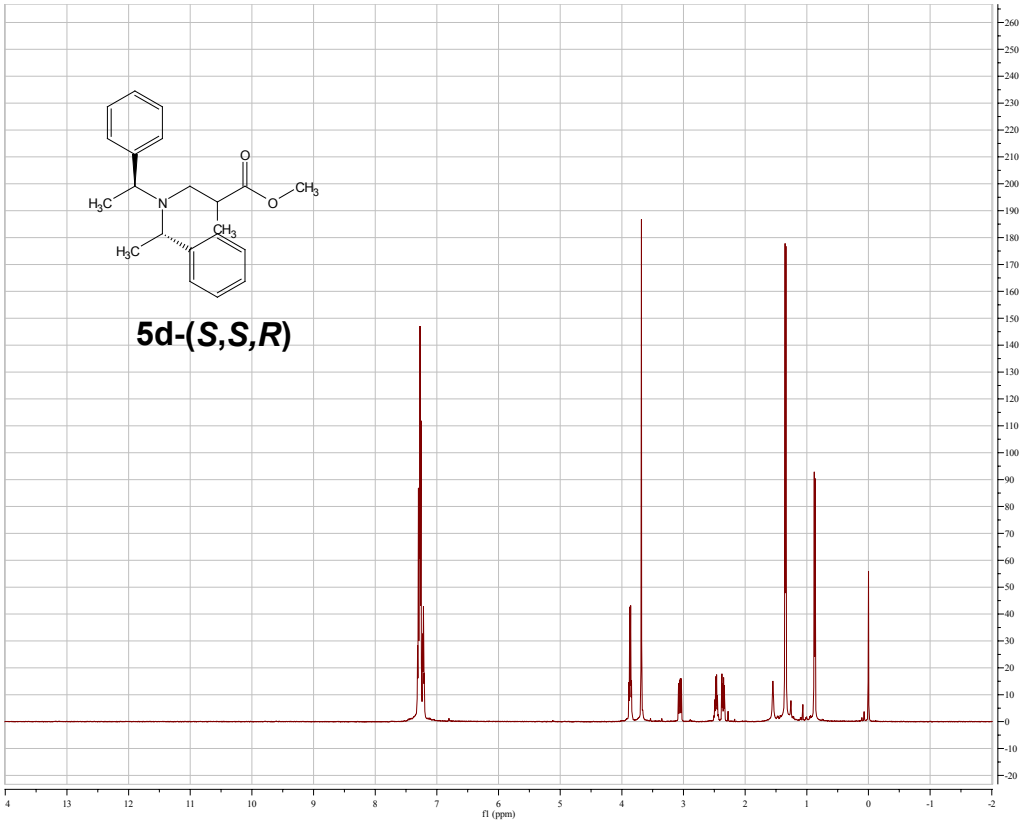

7.26
3.66
3.26
3.25
3.23
2.86
2.85
2.84
2.82
2.59
2.57
2.51
2.50
2.48
2.47
1.10
1.09
1.07
1.01
1.00
0.95
0.94
5b
2.91
1.00
1.06
1.00
1.08
3.66
9.21
3.19
3.15
f1 (ppm)

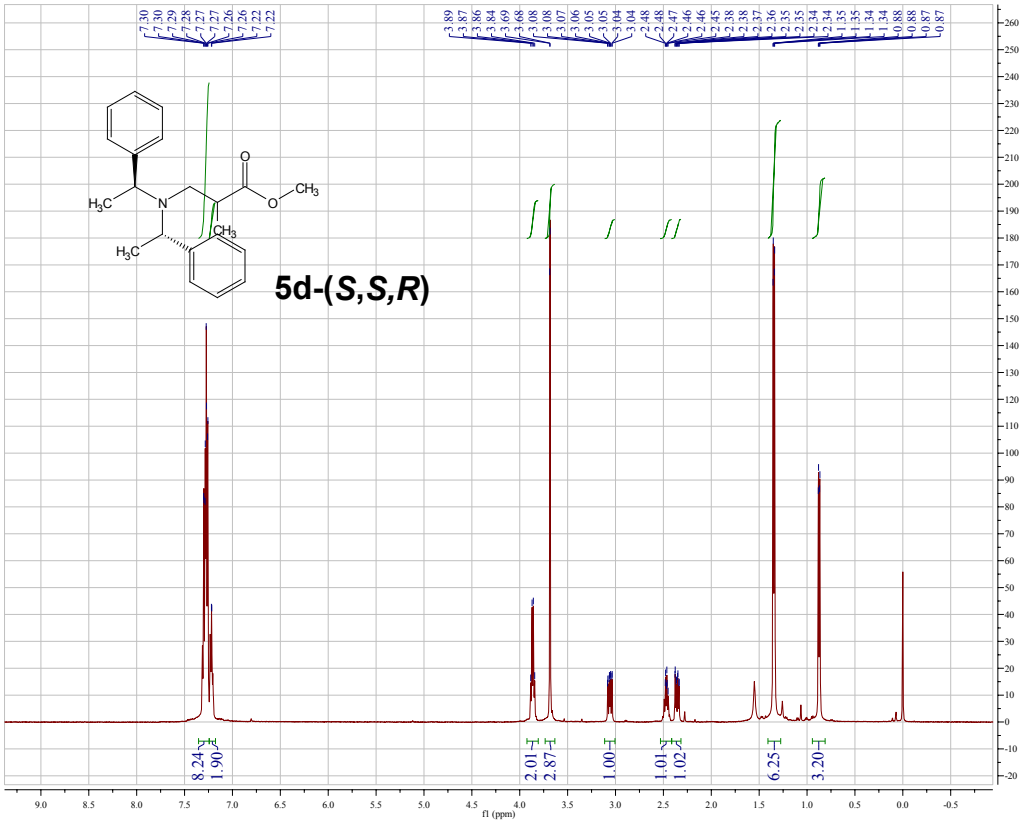

177.36
77.21
77.00
76.79
55.63
51.16
46.96
46.58
42.97
28.61
22.72
15.23
5b
f1 (ppm)

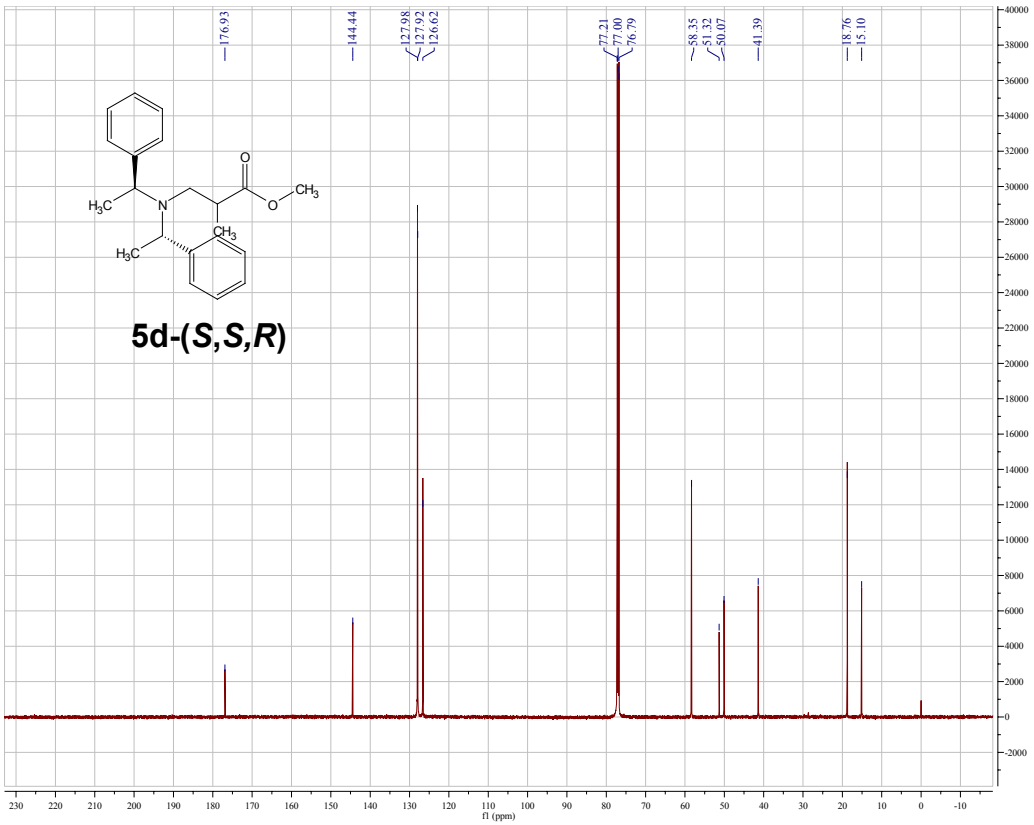

5c
f1 (ppm)

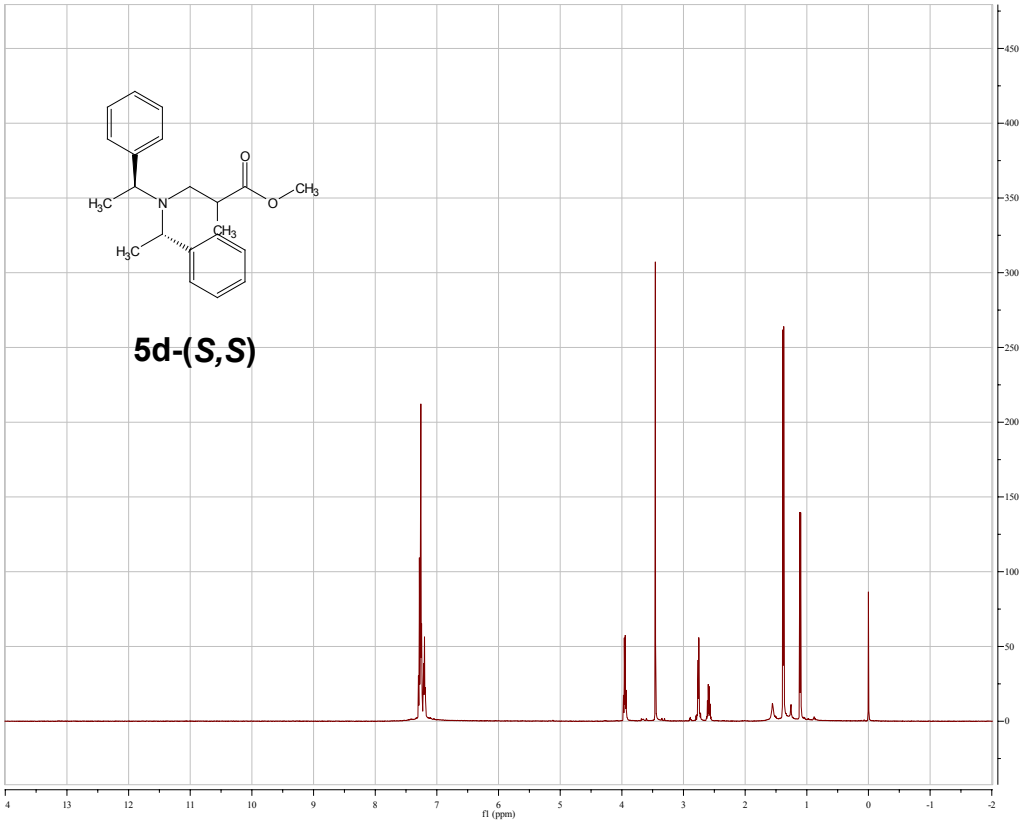

5c
f1 (ppm)

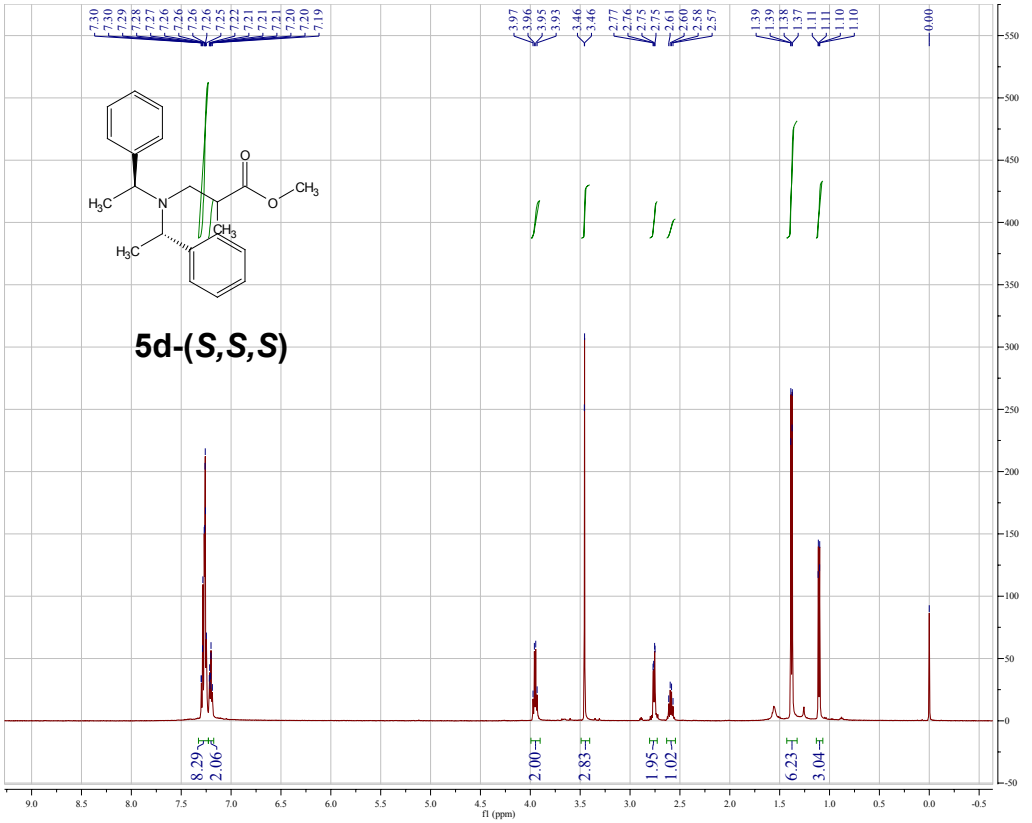

5c
f1 (ppm)

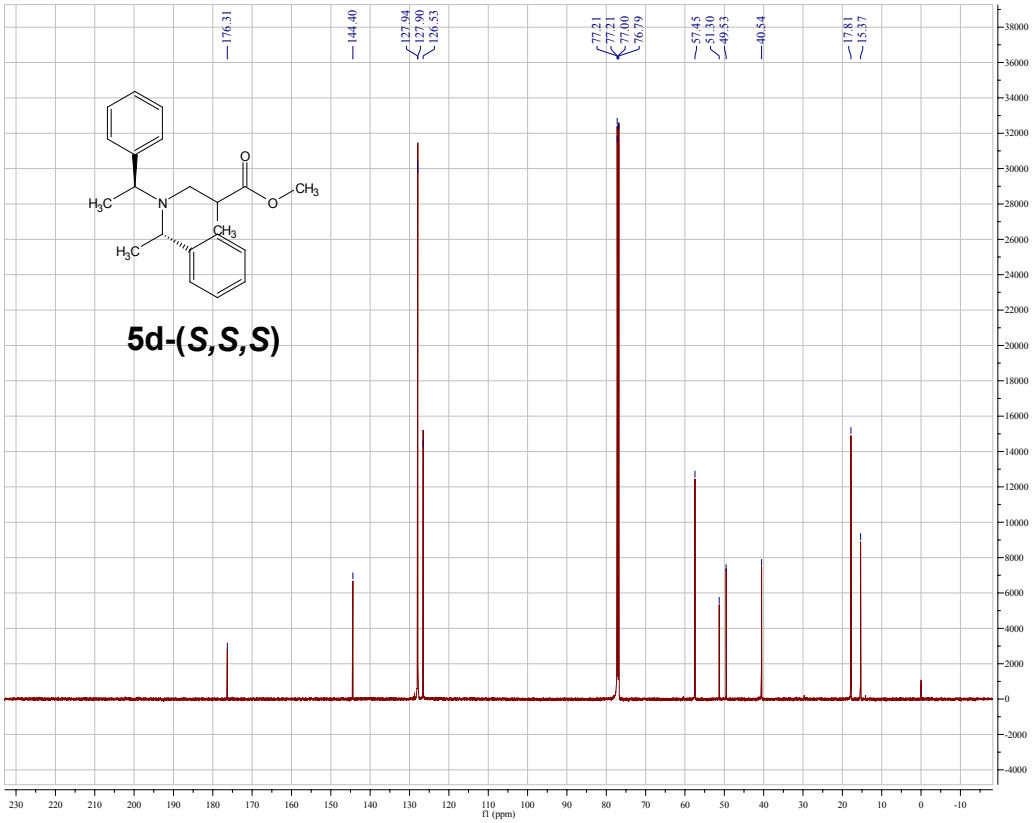

5d-(S,S,R)
f1 (ppm)


5d-(S,S,R)
8.24
1.90
2.01
2.87
1.00
1.01
1.02
6.25
3.20
f1 (ppm)


176.93
144.44
127.98
127.92
126.62
77.21
77.00
76.79
58.35
51.32
50.07
41.39
18.76
15.10
5d-(S,S,R)
f1 (ppm)


5d-(S,S)
f1 (ppm)


7.30
7.30
7.29
7.28
7.27
7.26
7.26
7.26
7.26
7.25
7.22
7.21
7.21
7.21
7.20
7.20
7.19
3.97
3.96
3.95
3.93
3.46
3.46
2.77
2.76
2.75
2.75
2.61
2.60
2.58
2.57
1.39
1.39
1.38
1.37
1.11
1.11
1.10
1.10
0.00
O
CH3
H3C
N
CH3
H3C
5d-(S,S,S)
8.29
2.06
2.00
2.83
1.95
1.02
6.23
3.04
f1 (ppm)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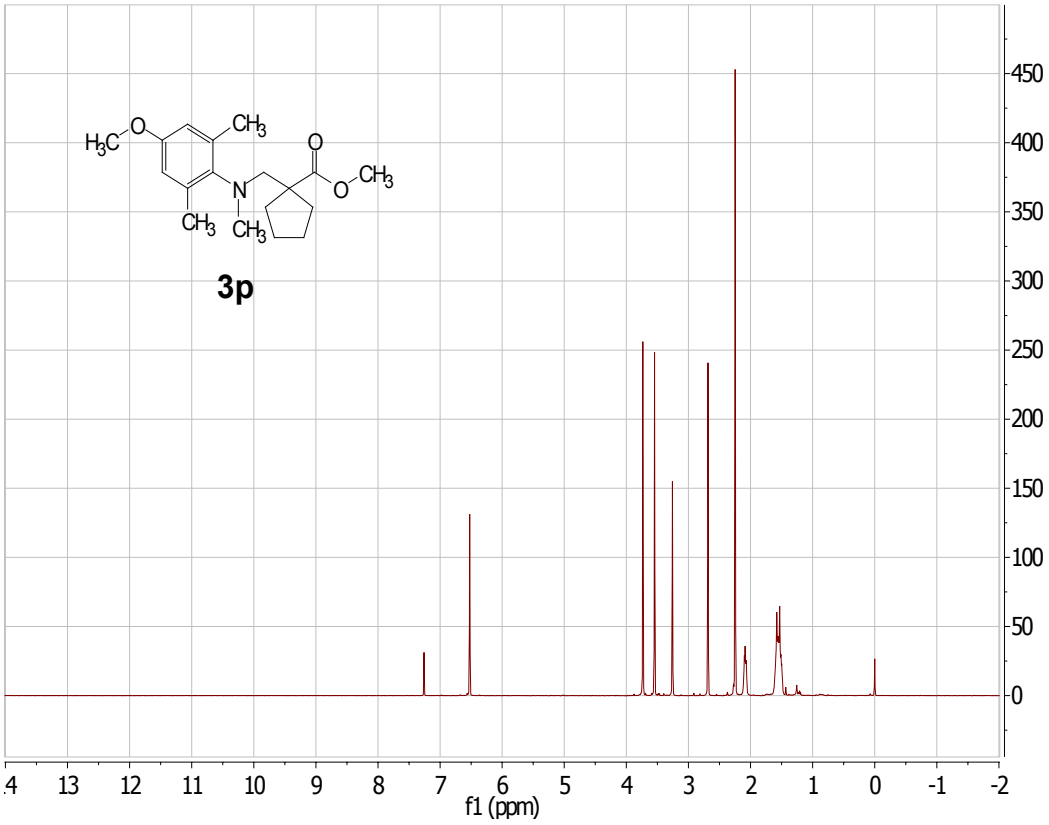
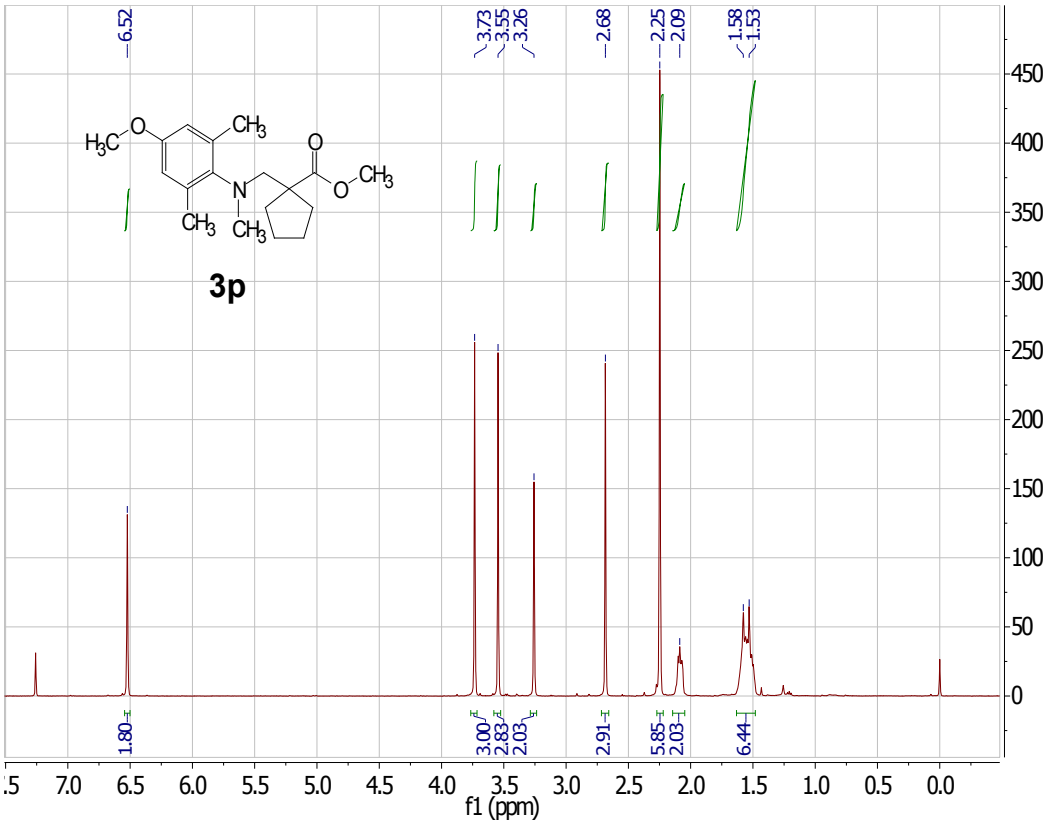
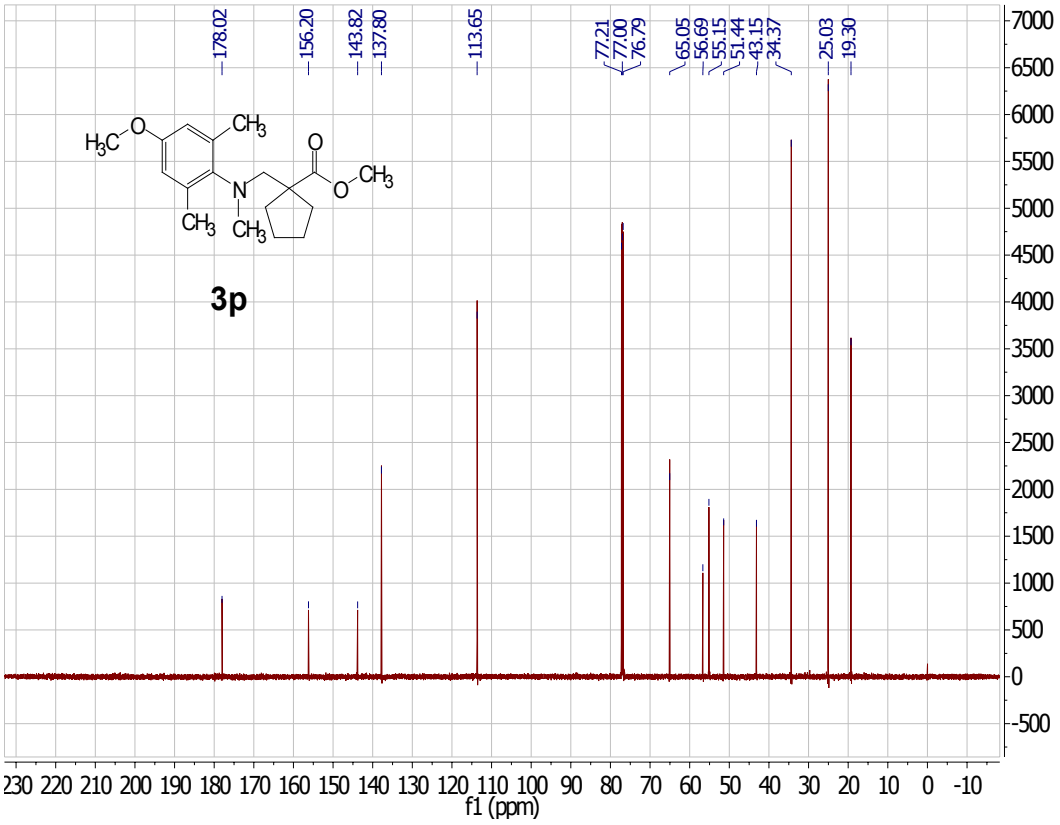
144.40
127.94
127.90
126.53
77.21
77.21
77.00
76.79
57.45
53.30
49.53
40.54
17.81
15.37
O
CH3
H3C
N
CH3
H3C
5d-(S,S,S)
f1 (ppm)


3p
f1 (ppm)


6.52
3.73
3.55
3.26
2.68
2.25
2.09
1.58
1.53
3p
1.80
3.00
2.83
2.03
2.91
5.85
2.03
6.44
f1 (ppm)


178.02
156.20
143.82
137.80
113.65
77.21
77.00
76.79
65.05
56.69
55.15
51.44
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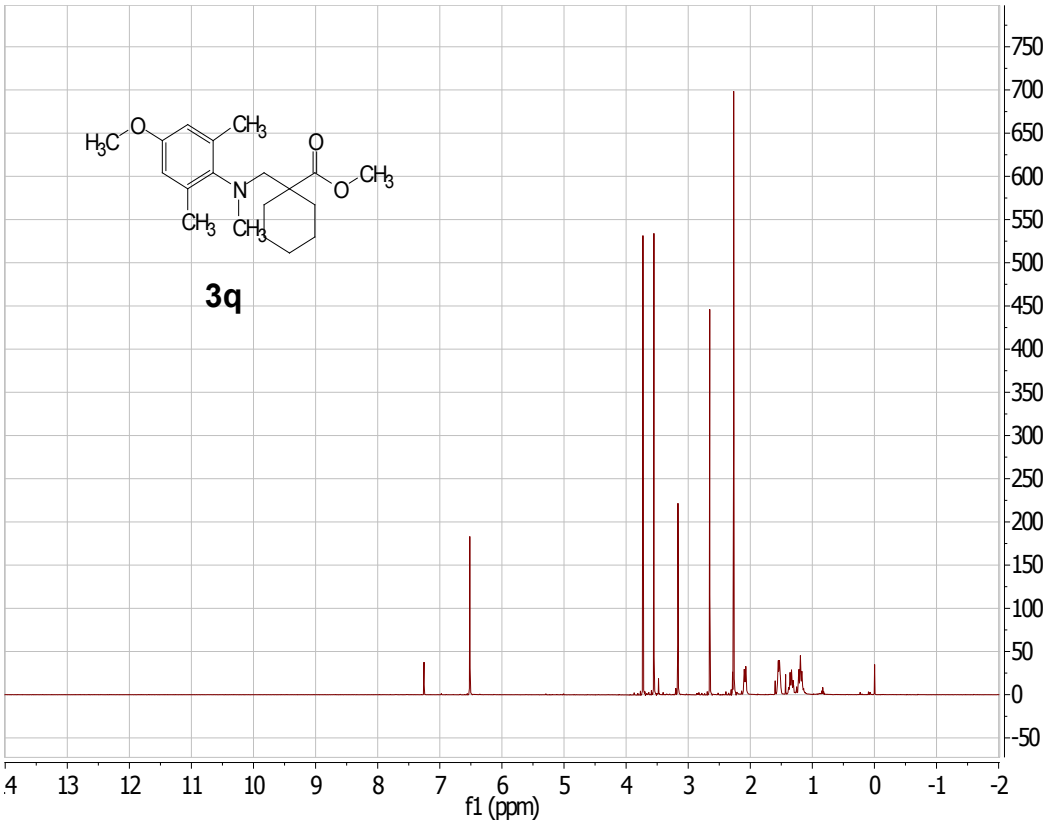
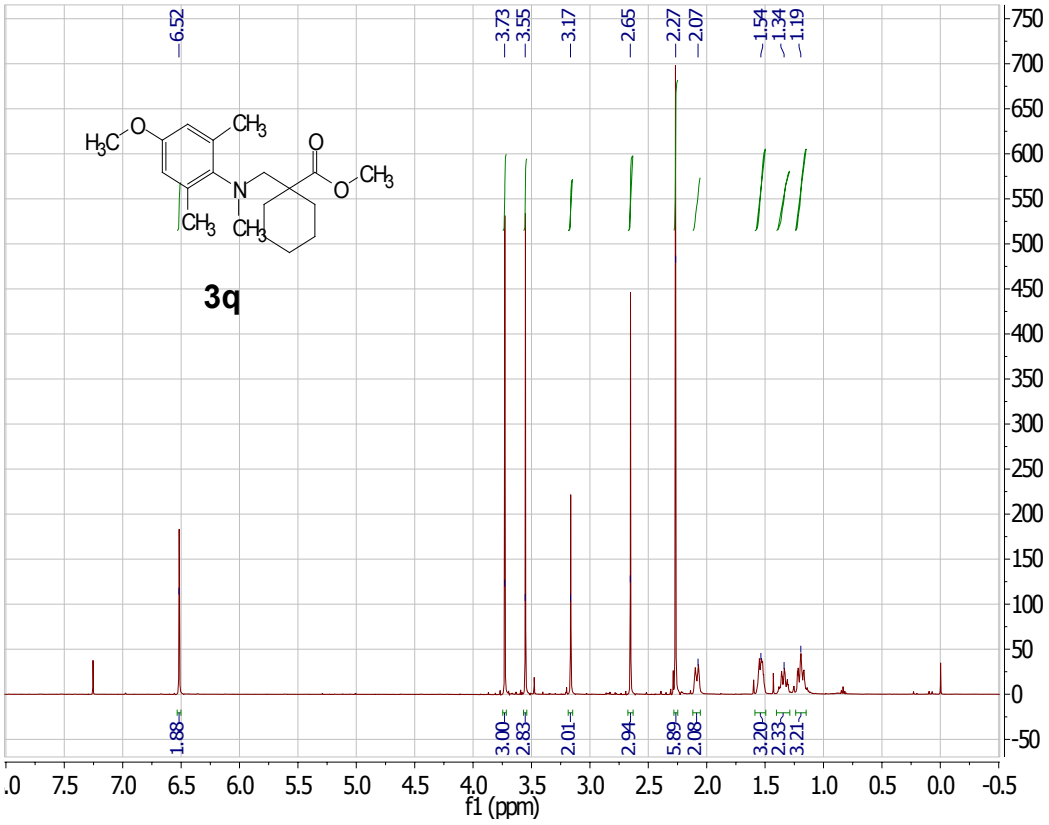
34.37
25.03
19.30
3p
f1 (ppm)


3q
f1 (ppm)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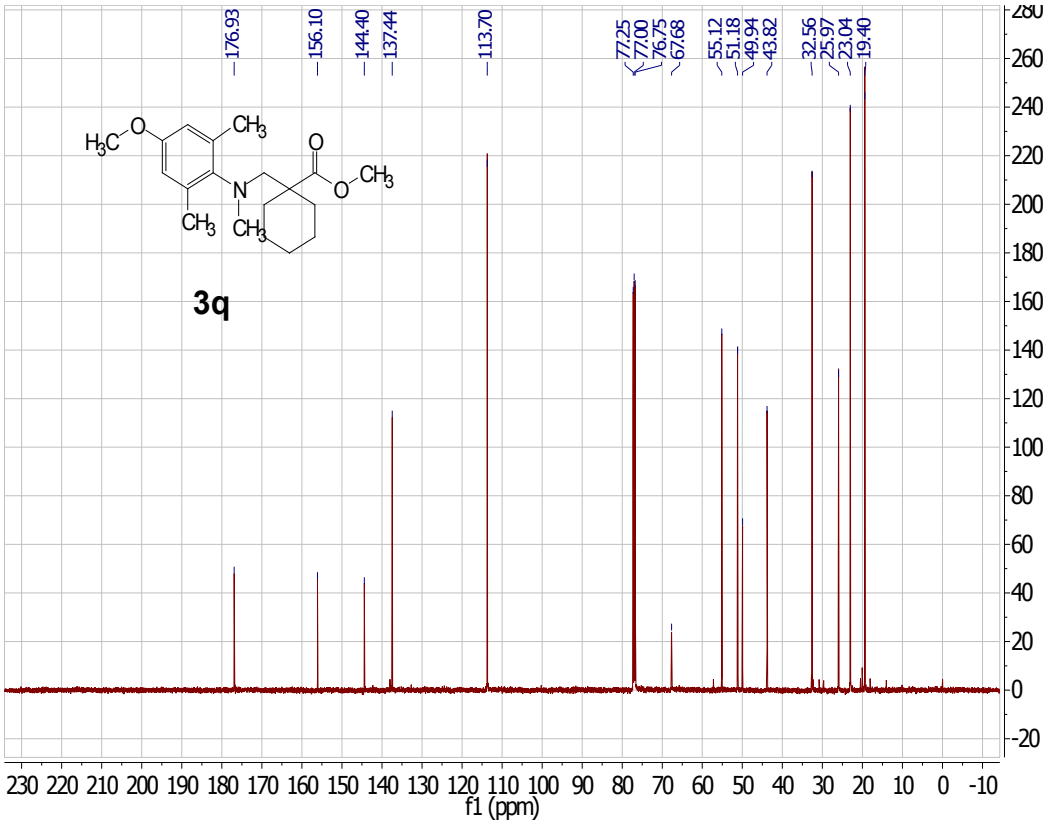
3.55
3.17
2.65
2.27
2.07
1.54
1.34
1.19
3q
1.88
3.00
2.83
2.01
2.94
5.89
2.08
3.20
2.33
3.21
f1 (ppm)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156.10
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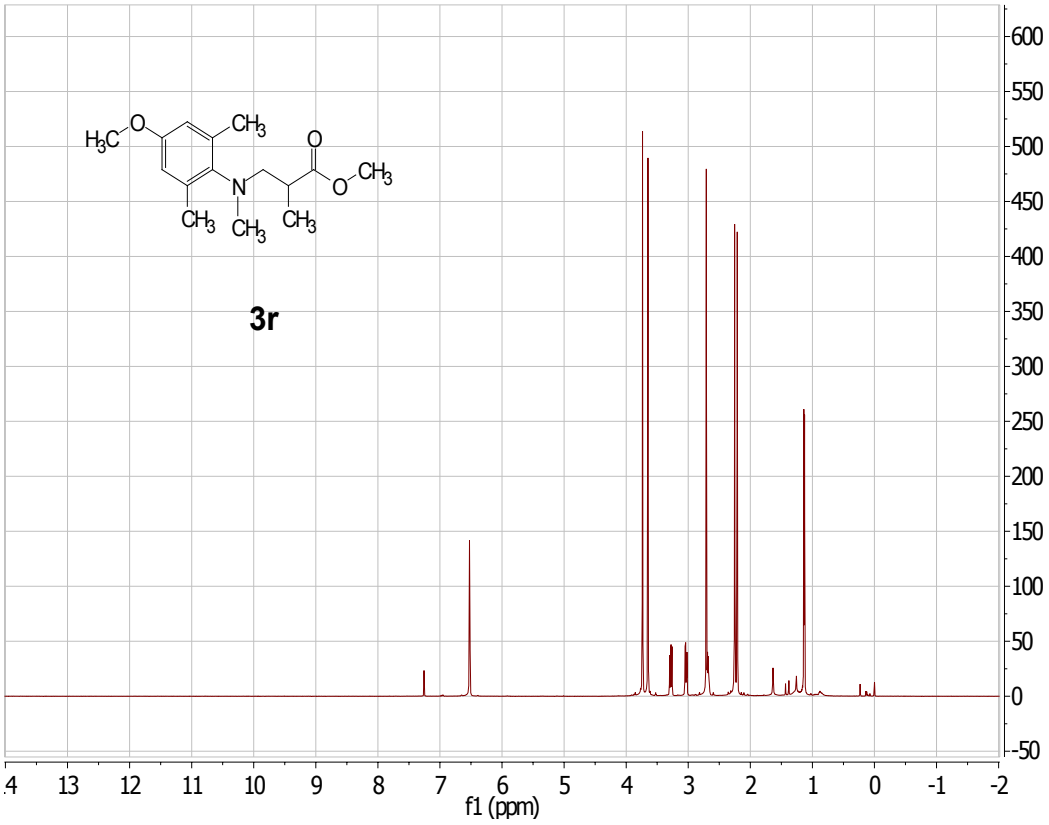
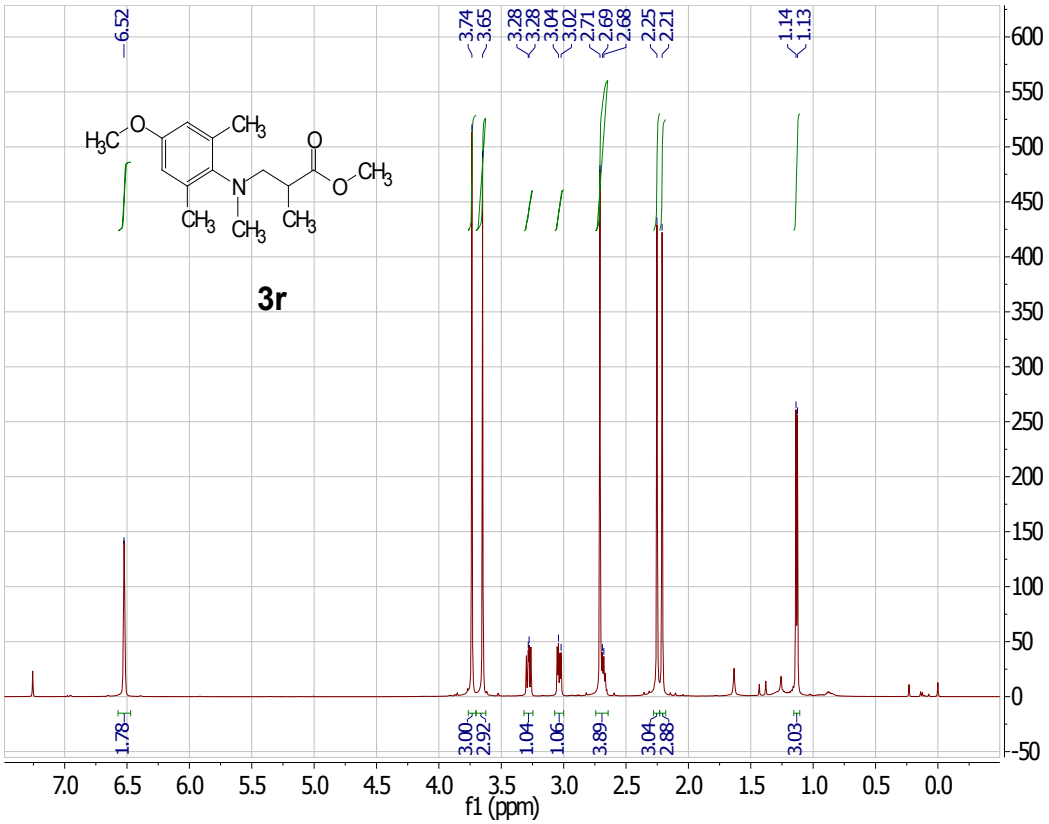
137.44
113.70
77.25
77.00
76.75
67.68
55.12
51.18
49.94
43.82
32.56
25.97
23.04
19.40
3q
f1 (ppm)


3r
f1 (ppm)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3.74
3.65
3.28
3.28
3.04
3.02
2.71
2.69
2.68
2.25
2.21
1.14
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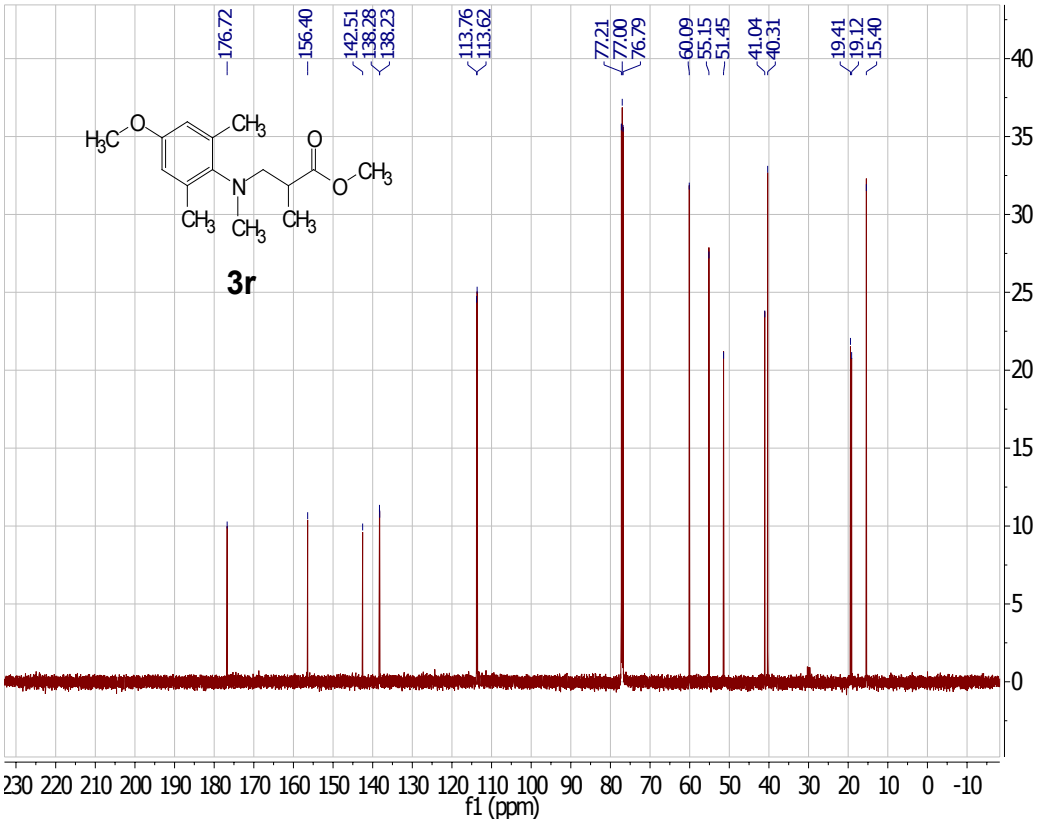
3.00
2.92
1.04
1.06
3.89
3.04
2.88
3.03
f1 (ppm)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142.51
138.28
138.23
113.76
113.62
77.21
77.00
76.79
60.09
55.15
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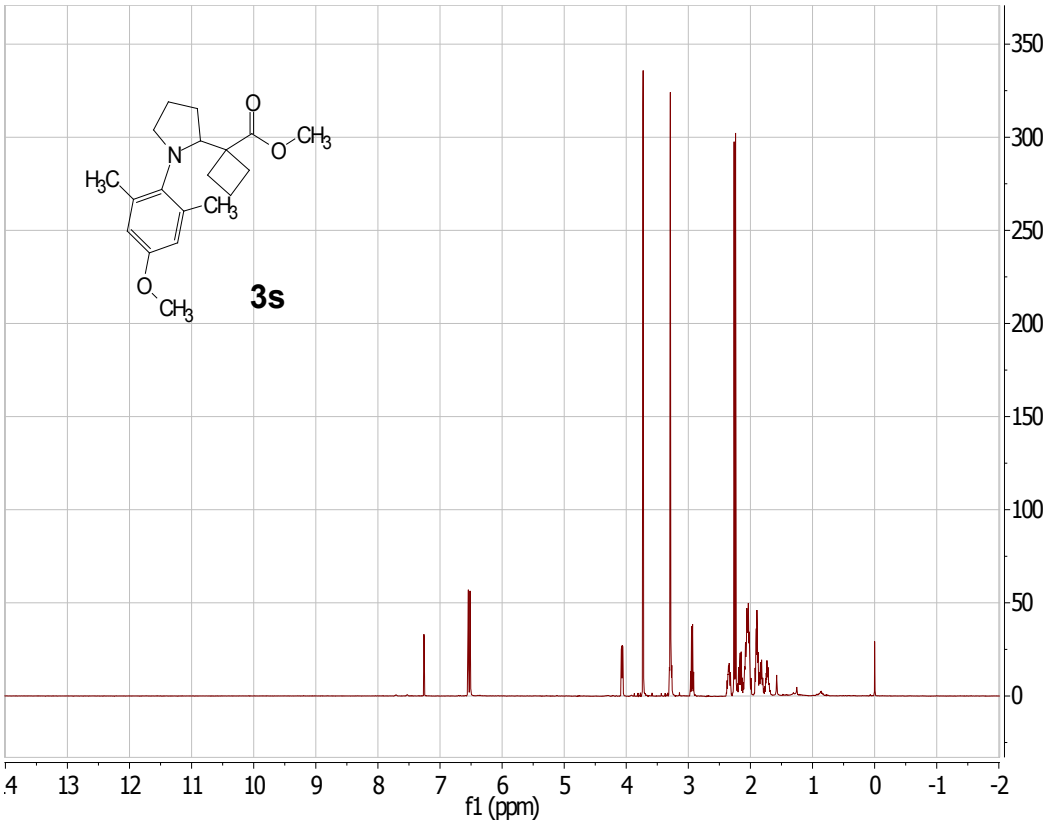
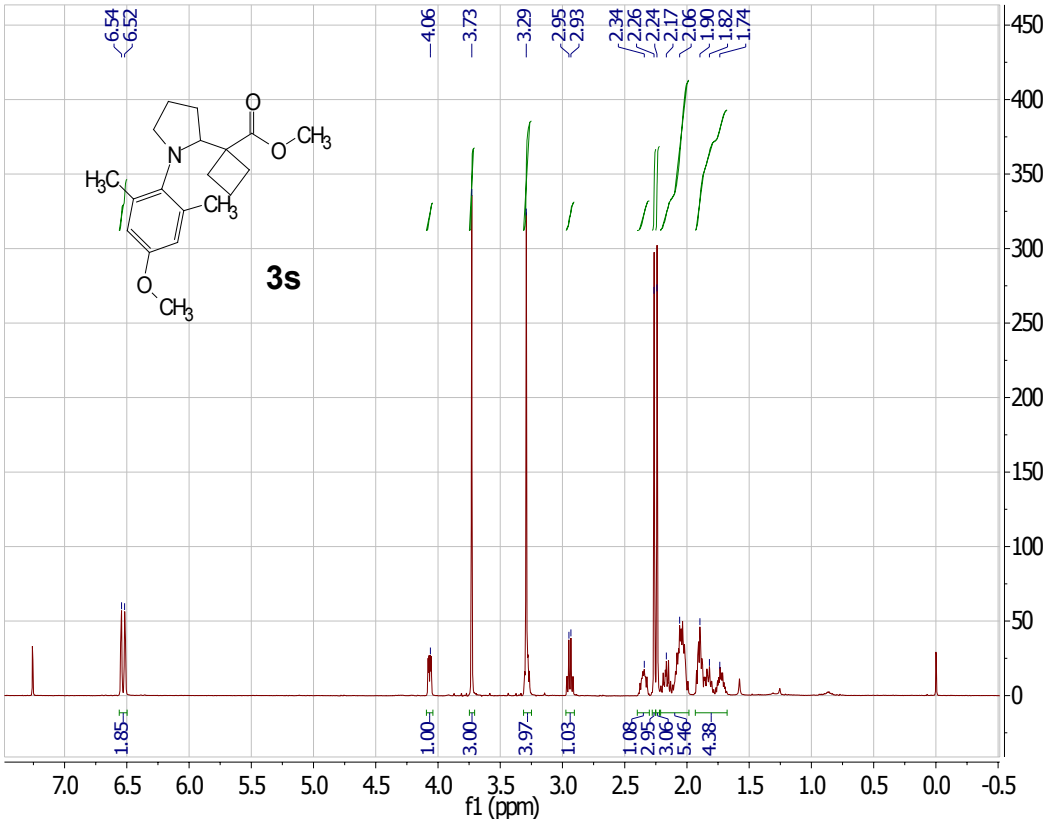
41.04
40.31
19.41
19.12
15.40
3r
f1 (ppm)


3s
f1 (ppm)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6.52
4.06
3.73
3.29
2.95
2.93
2.34
2.26
2.24
2.17
2.06
1.90
1.82
1.74
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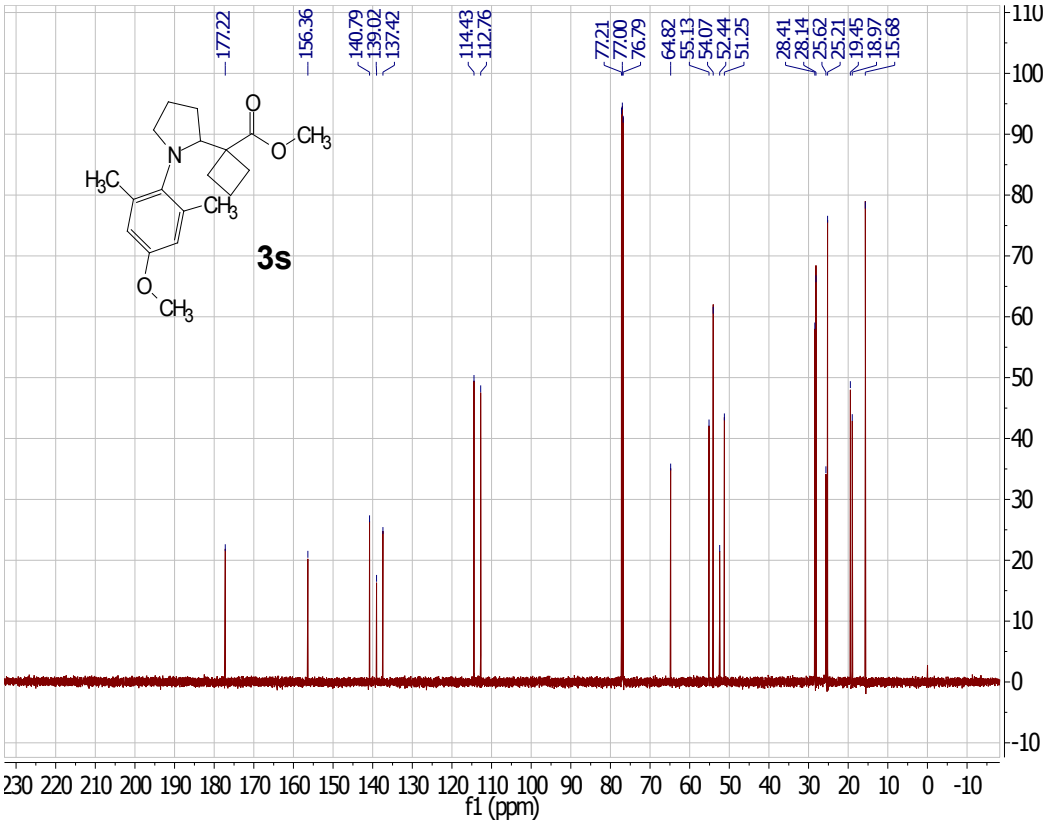
2.95
3.06
5.46
4.38
f1 (ppm)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114.43
112.76
77.21
77.00
76.79
64.82
55.13
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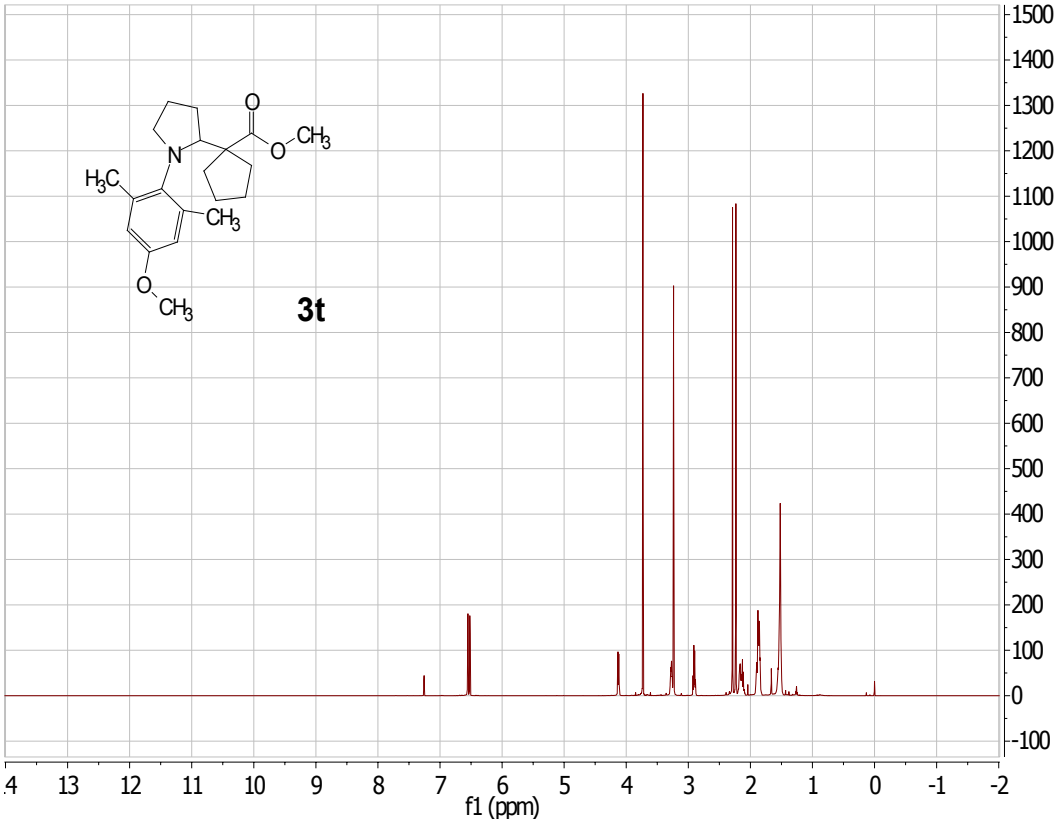
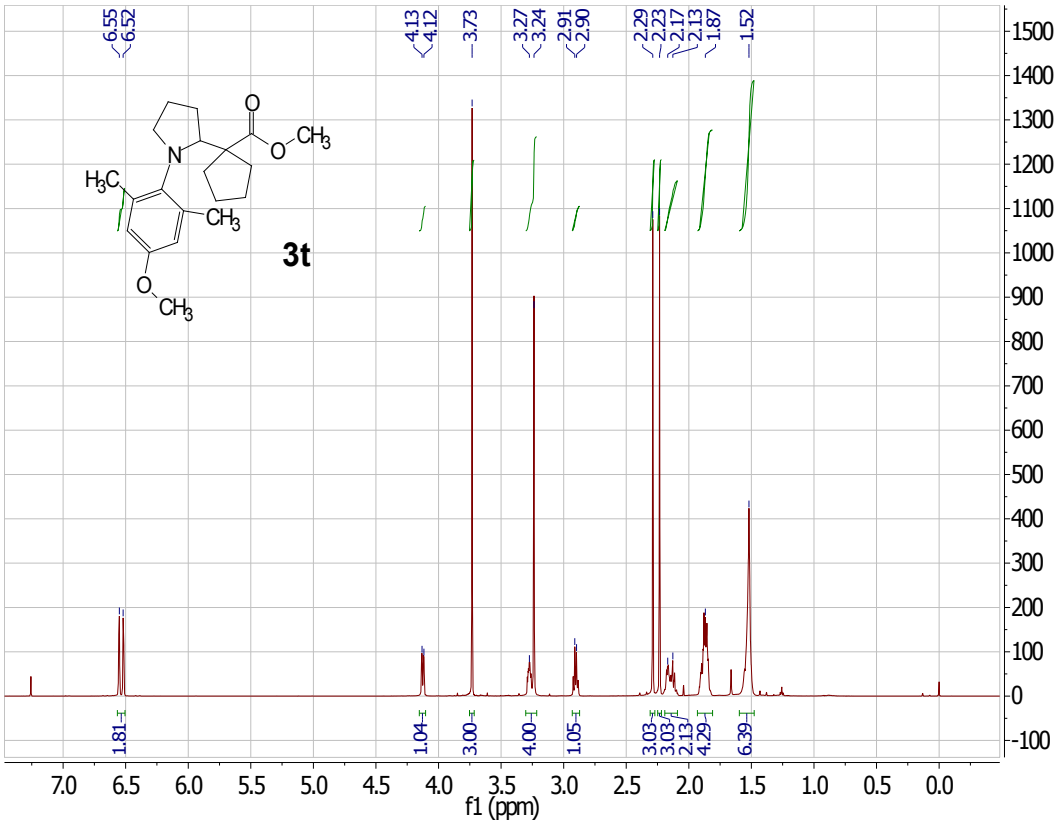
19.45
18.97
15.68
3s
f1 (ppm)


3t
f1 (ppm)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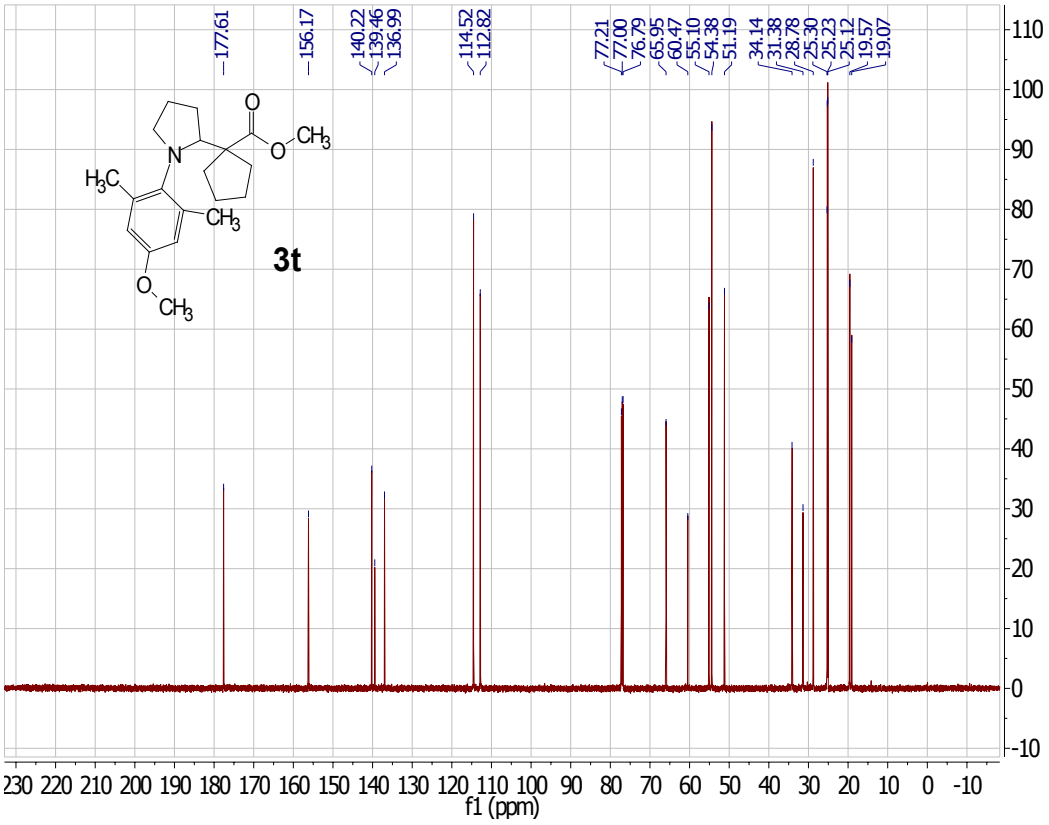
6.52
4.13
4.12
3.73
3.27
3.24
2.91
2.90
2.29
2.23
2.17
2.13
1.87
1.52
3t
1.81
1.04
3.00
4.00
1.05
3.03
3.03
2.13
4.29
6.39
f1 (ppm)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114.52
112.82
77.21
77.00
76.79
65.95
60.47
55.10
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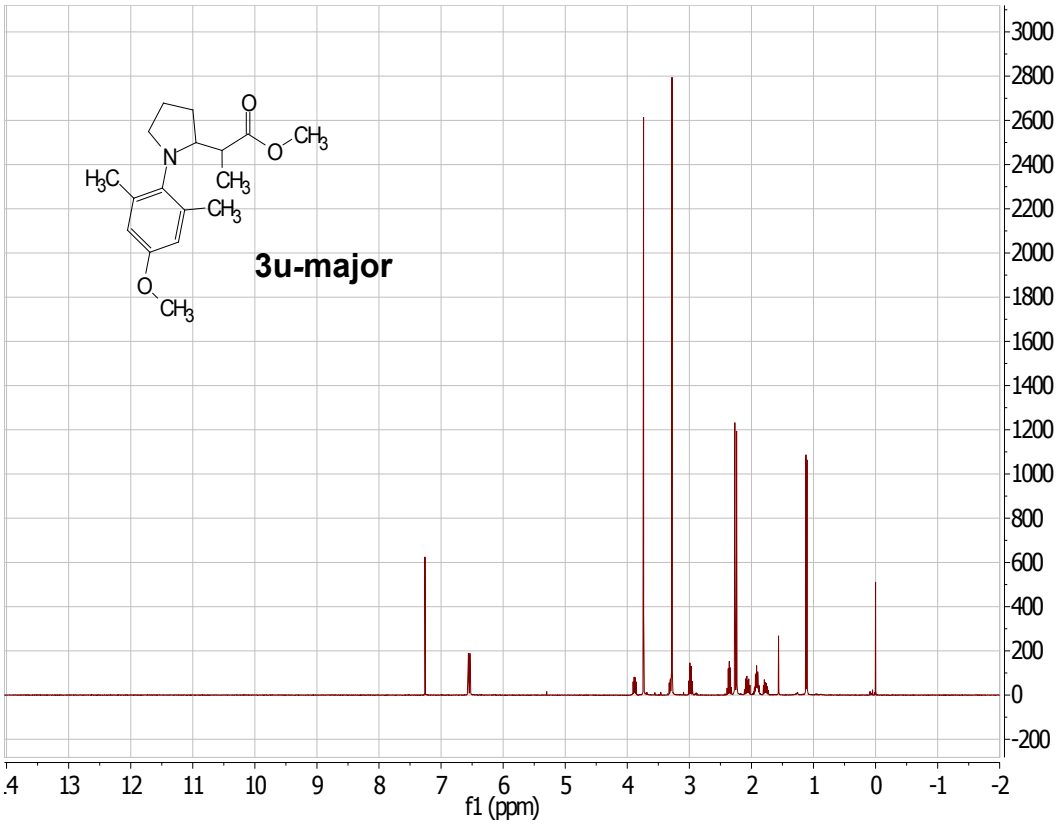
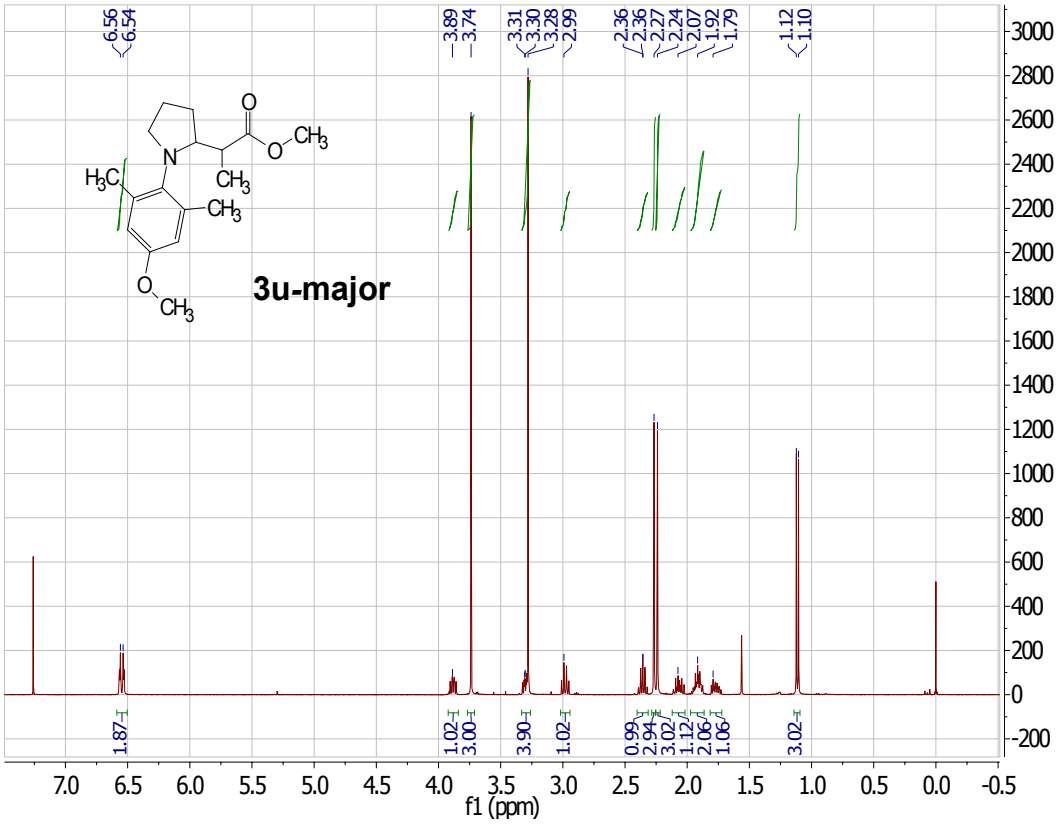
51.19
34.14
31.38
28.78
25.30
25.23
25.12
19.57
19.07
3t
f1 (ppm)


3u-major
f1 (ppm)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6.54
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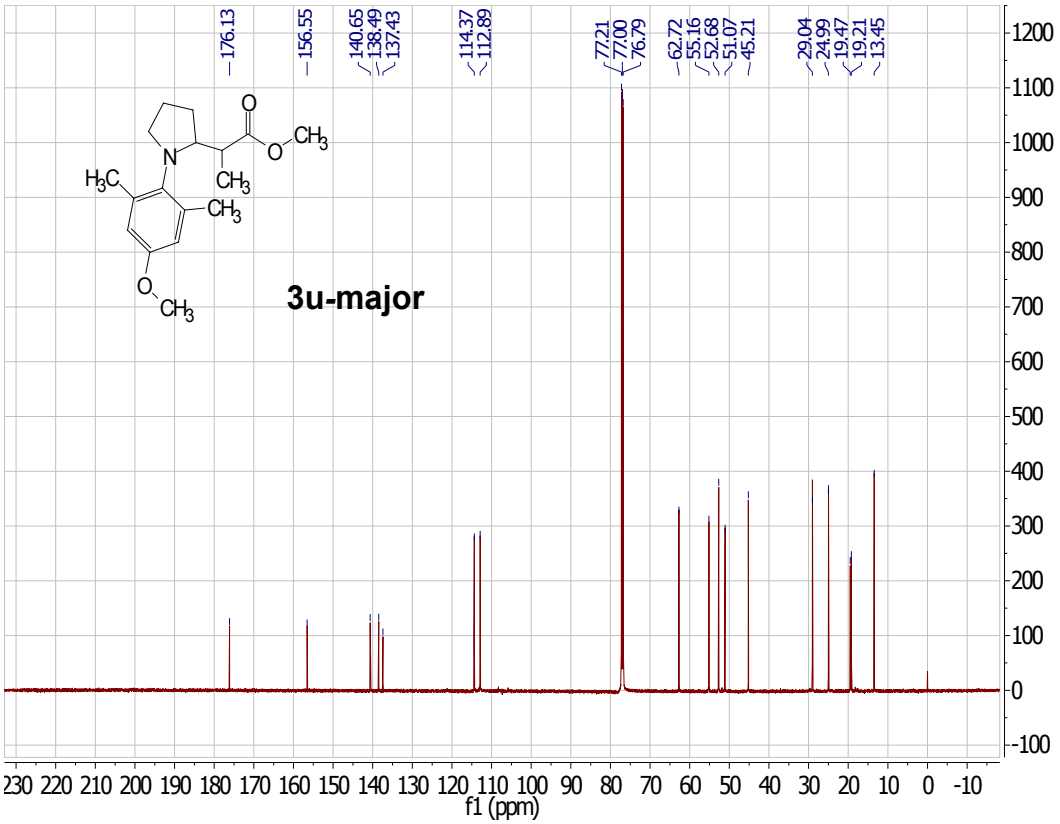
3.31
3.30
3.28
2.99
2.36
2.36
2.27
2.24
2.07
1.92
1.79
1.12
1.10
3u-major
1.87
1.02
3.00
3.90
1.02
0.99
2.94
3.02
1.12
2.06
1.06
3.02
f1 (ppm)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137.43
114.37
112.89
77.21
77.00
76.79
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51.07
45.21
29.04
24.99
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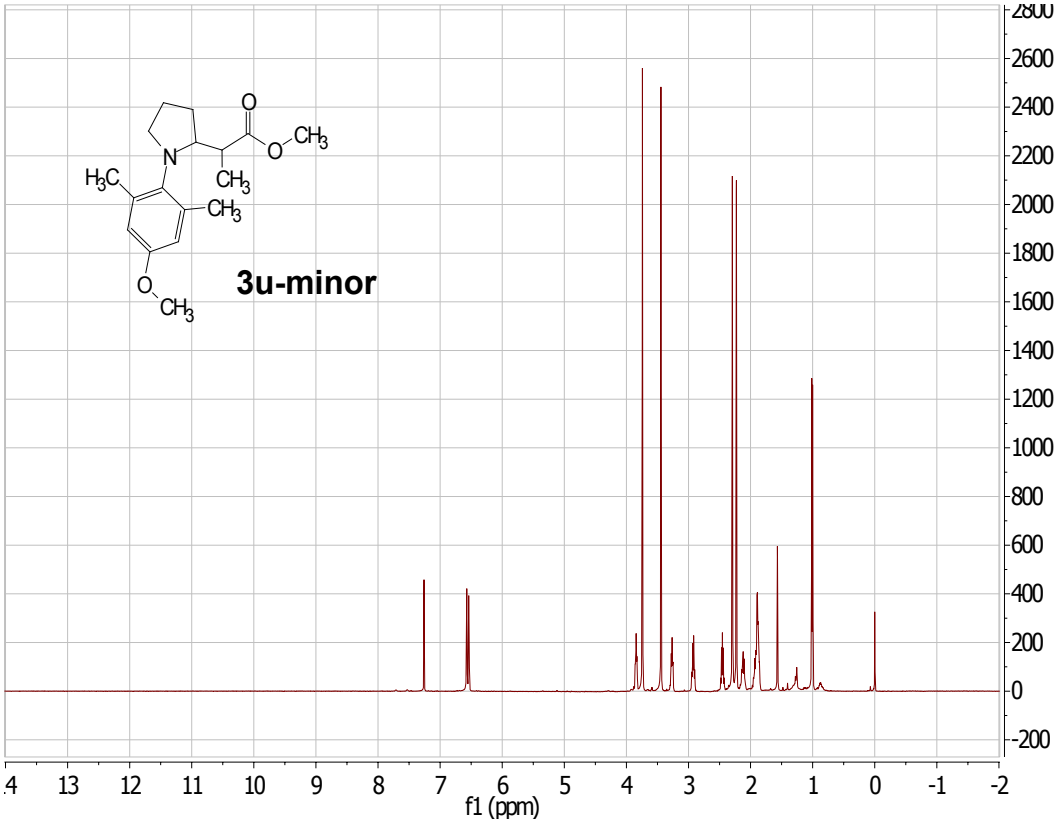
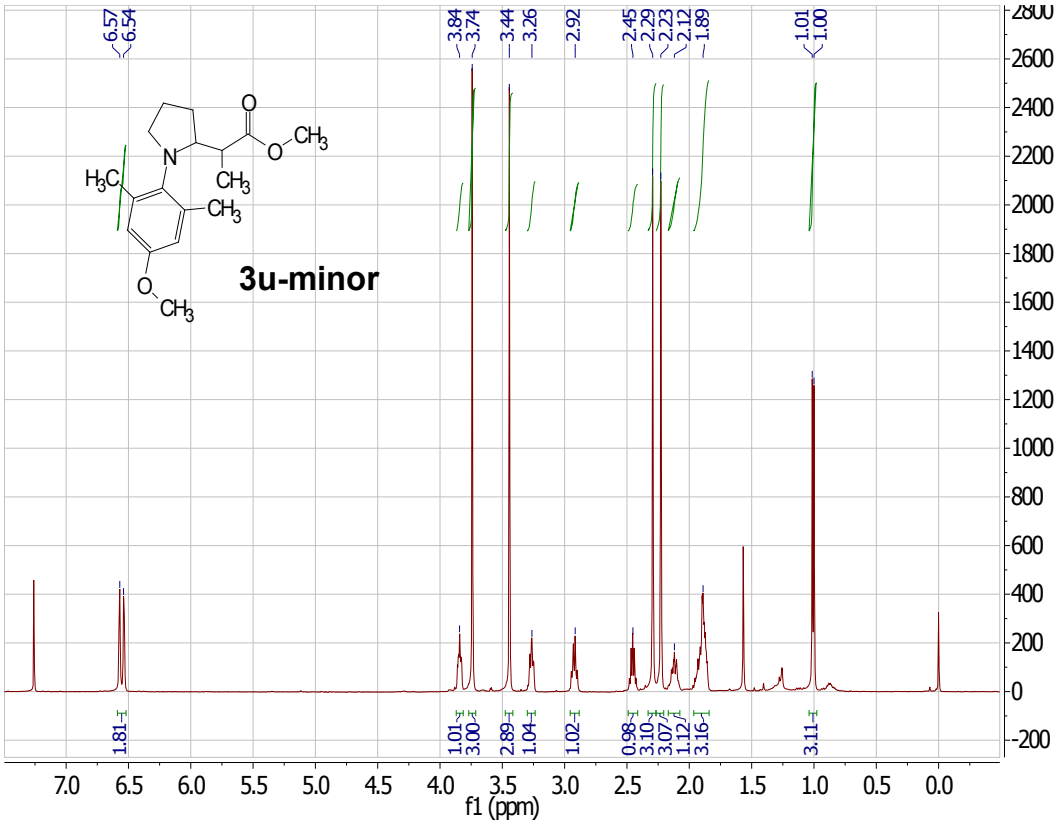
19.21
13.45
3u-major
f1 (ppm)


3u-minor
f1 (ppm)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3.84
3.74
3.44
3.26
2.92
2.45
2.29
2.23
2.12
1.89
1.01
1.00
3u-minor
1.81
1.01
3.00
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1.04
1.02
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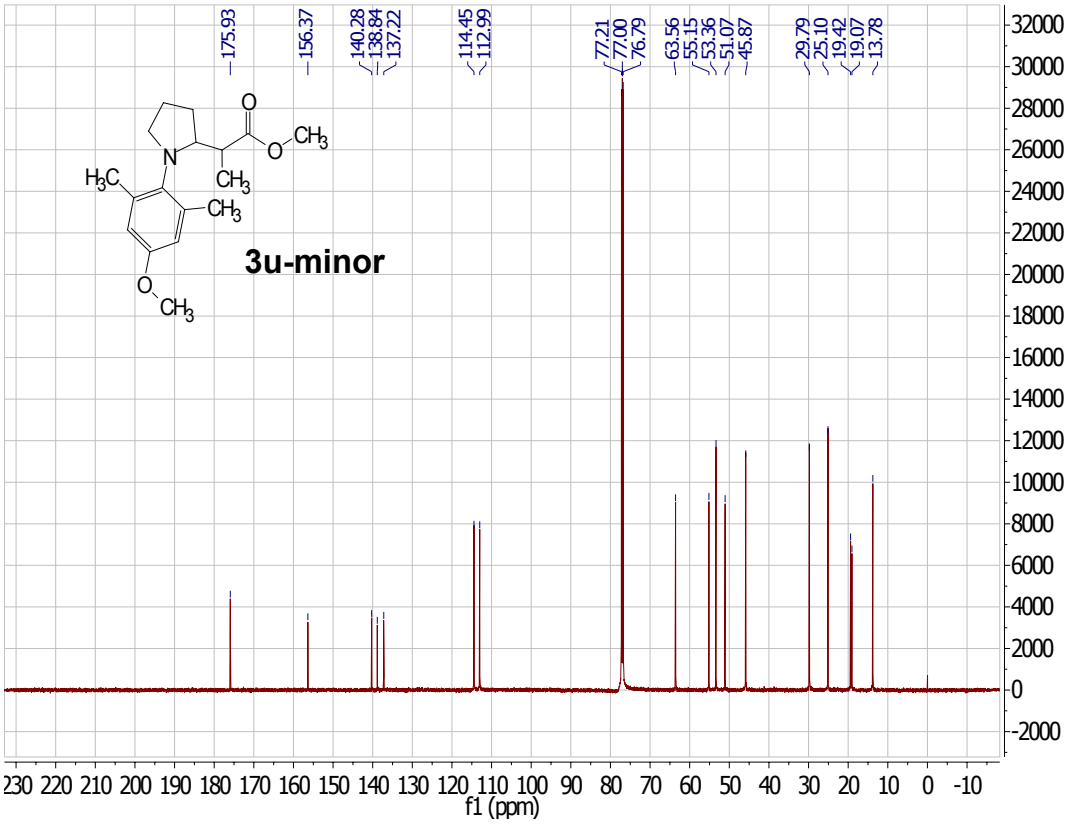
1.12
3.16
3.11
f1 (ppm)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114.45
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77.21
77.00
76.79
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19.07
13.78
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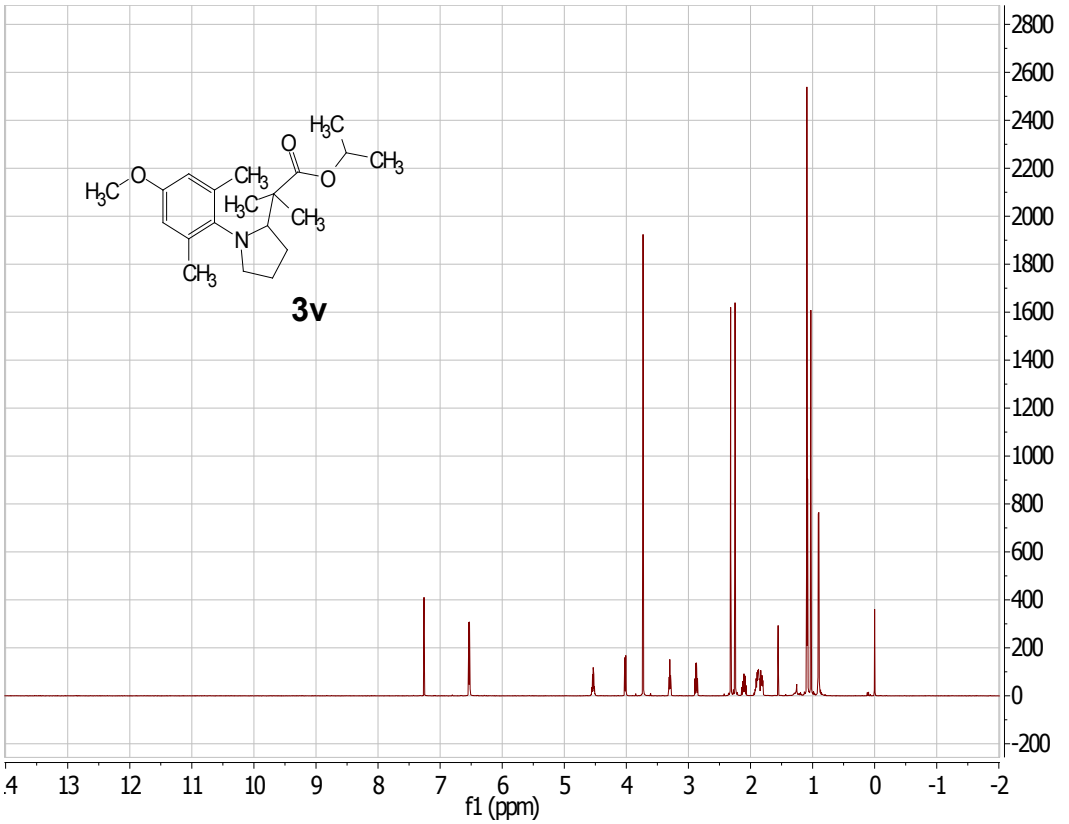
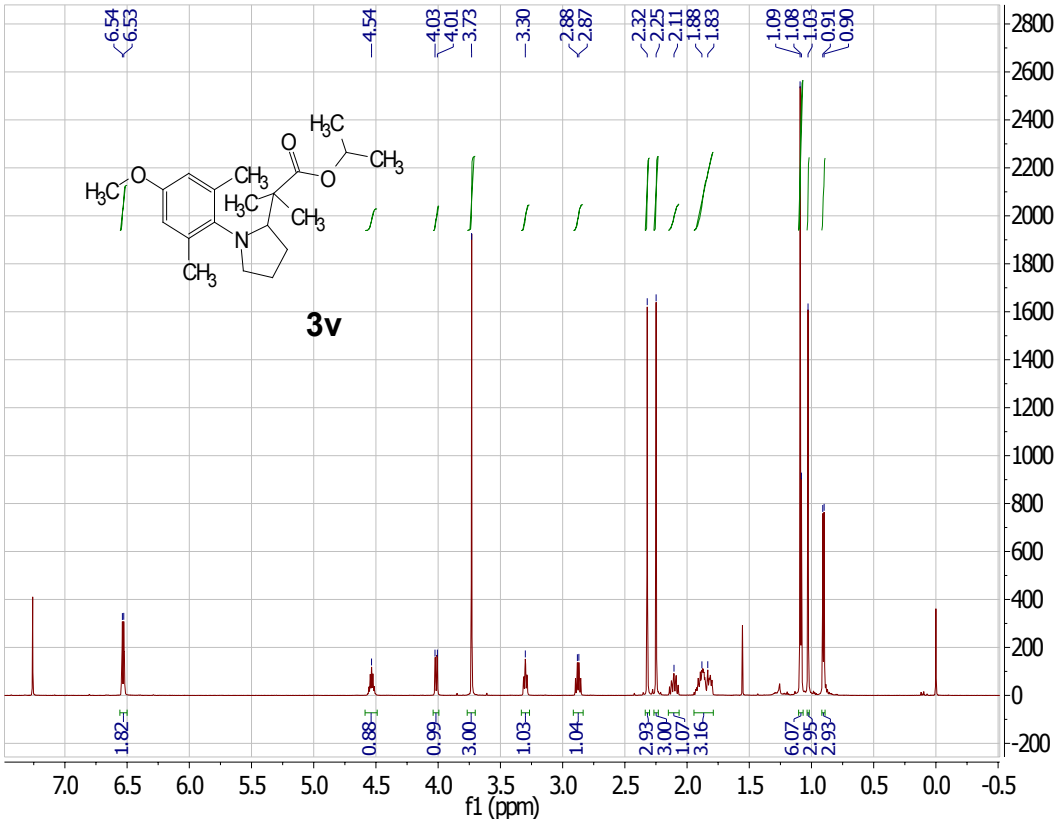
f1 (ppm)


3v
f1 (ppm)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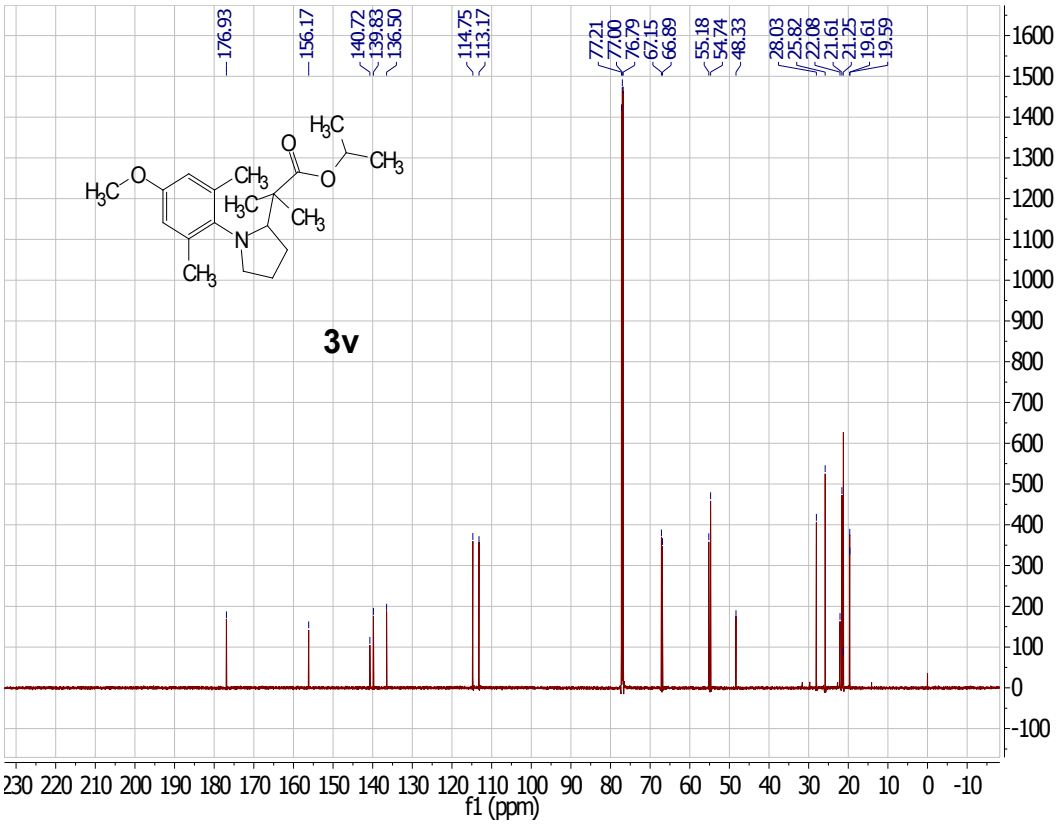
4.01
3.73
3.30
2.88
2.87
2.32
2.25
2.11
1.88
1.83
1.09
1.08
1.03
0.91
0.90
3v
1.82
0.88
0.99
3.00
1.03
1.04
2.93
3.00
1.07
3.16
6.07
2.95
2.93
f1 (ppm)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113.17
77.21
77.00
76.79
67.15
66.89
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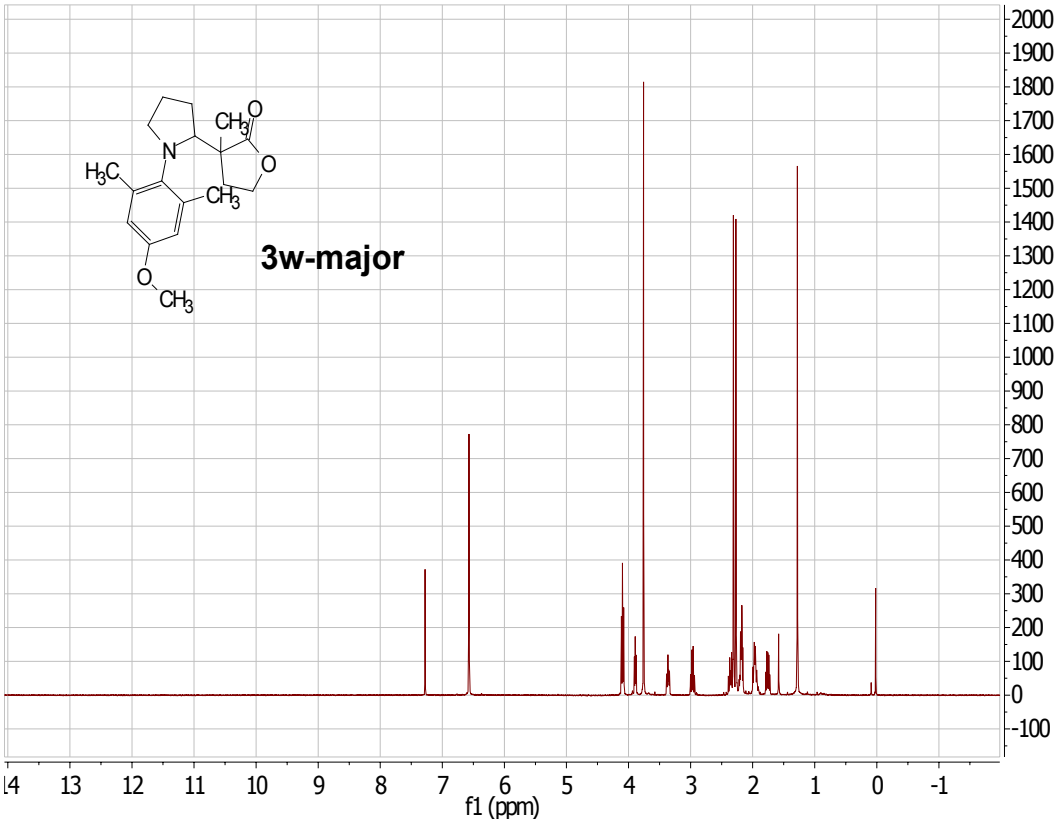
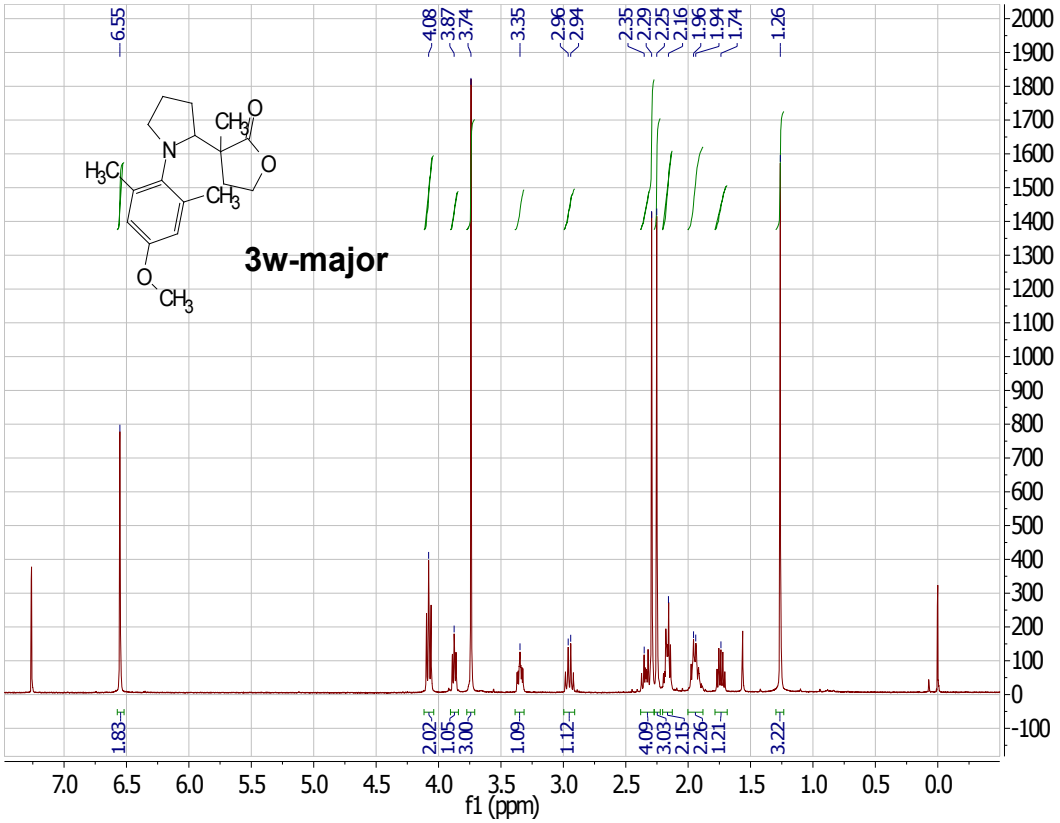
54.74
48.33
28.03
25.82
22.08
21.61
21.25
19.61
19.59
3v
f1 (ppm)


3w-major
f1 (ppm)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3.74
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2.96
2.94
2.35
2.29
2.25
2.16
1.96
1.94
1.74
1.26
3w-major
1.83
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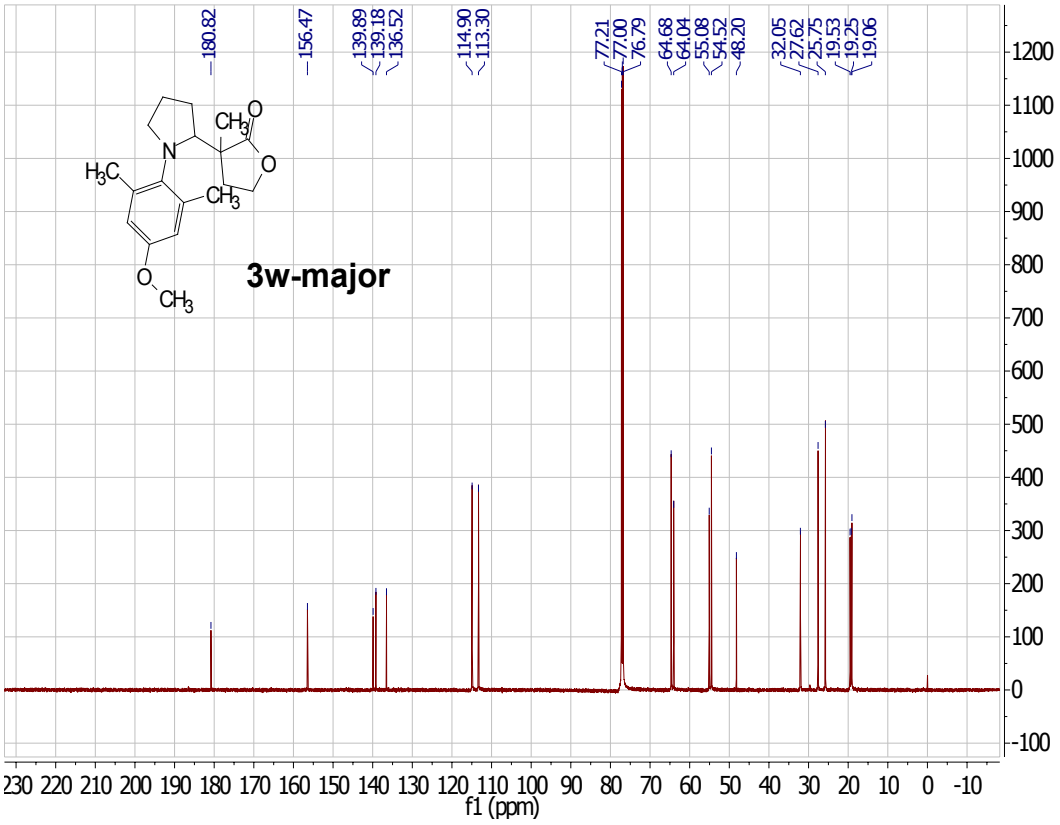
1.09
1.12
4.09
3.03
2.15
2.26
1.21
3.22
f1 (ppm)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136.52
114.90
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77.21
77.00
76.79
64.68
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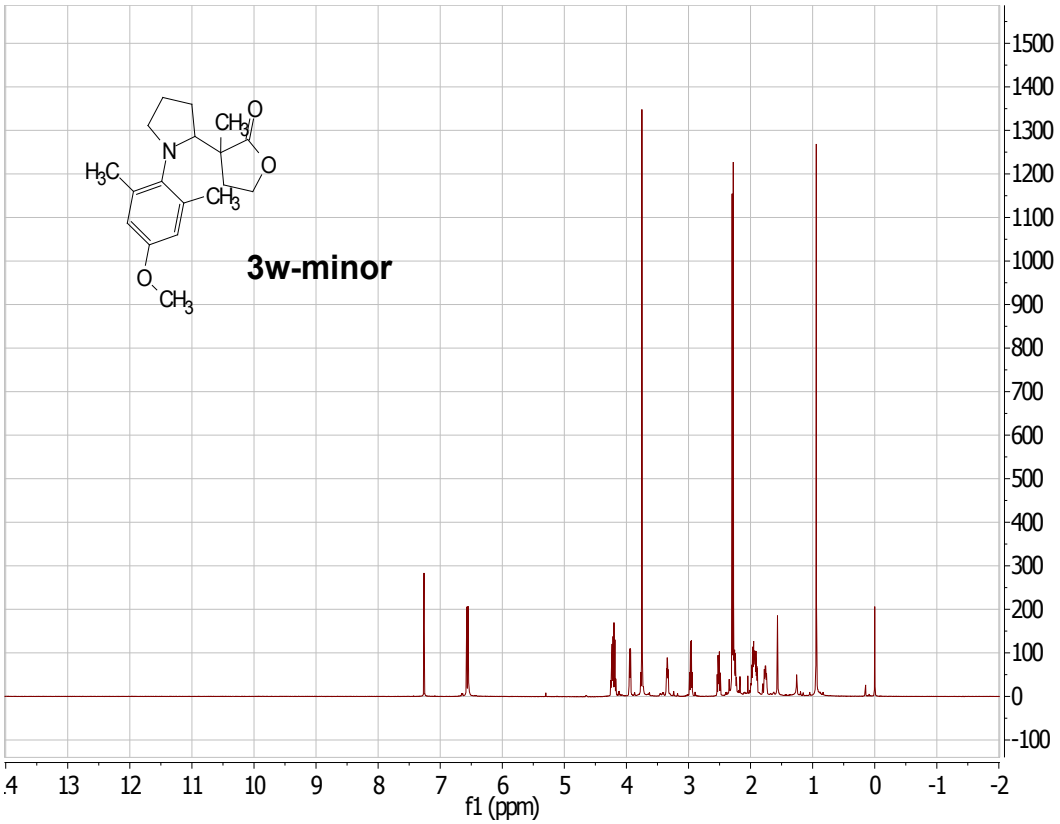
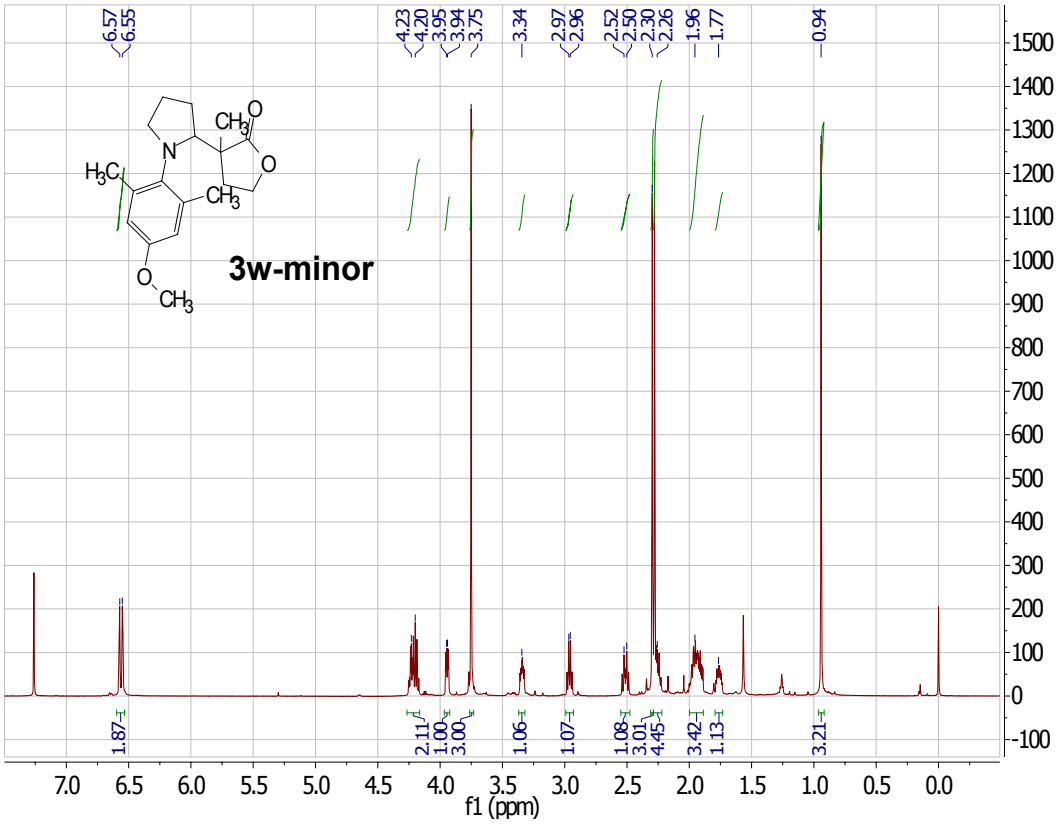
48.20
32.05
27.62
25.75
19.53
19.25
19.06
3w-major
f1 (ppm)


3w-minor
f1 (ppm)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3.94
3.75
3.34
2.97
2.96
2.52
2.50
2.30
2.26
1.96
1.77
0.94
3w-minor
1.87
2.11
1.00
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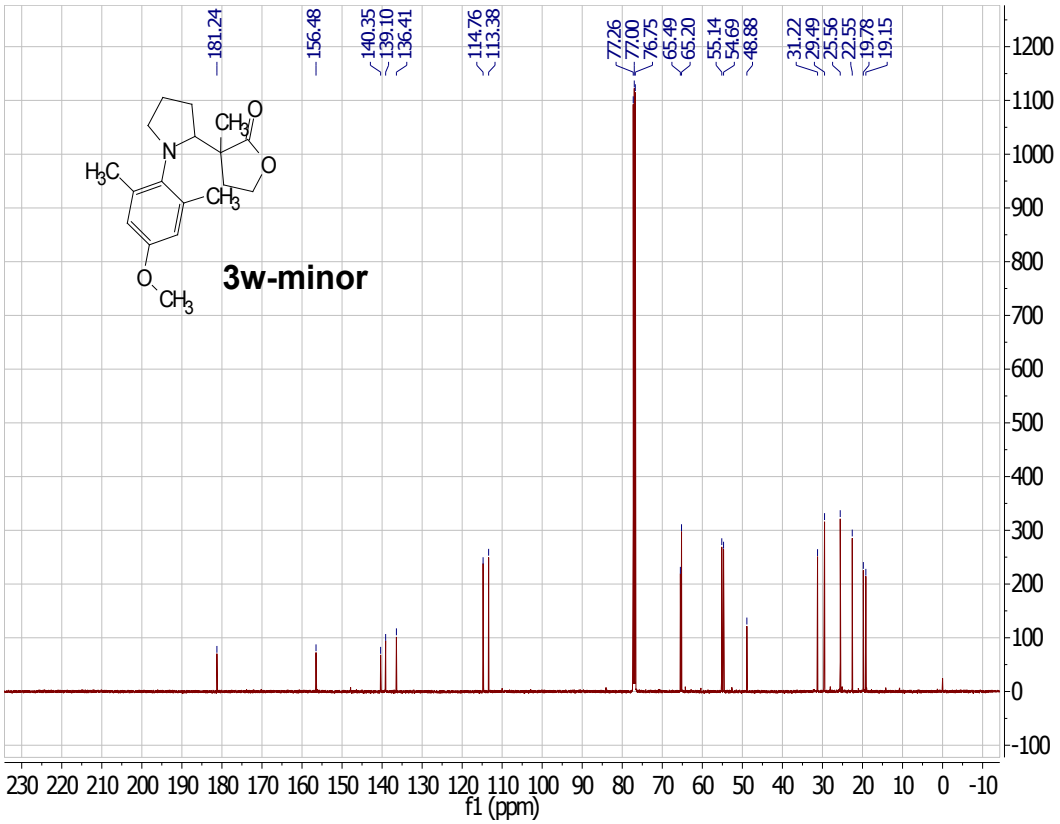
1.06
1.07
1.08
3.01
4.45
3.42
1.13
3.21
f1 (ppm)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77.00
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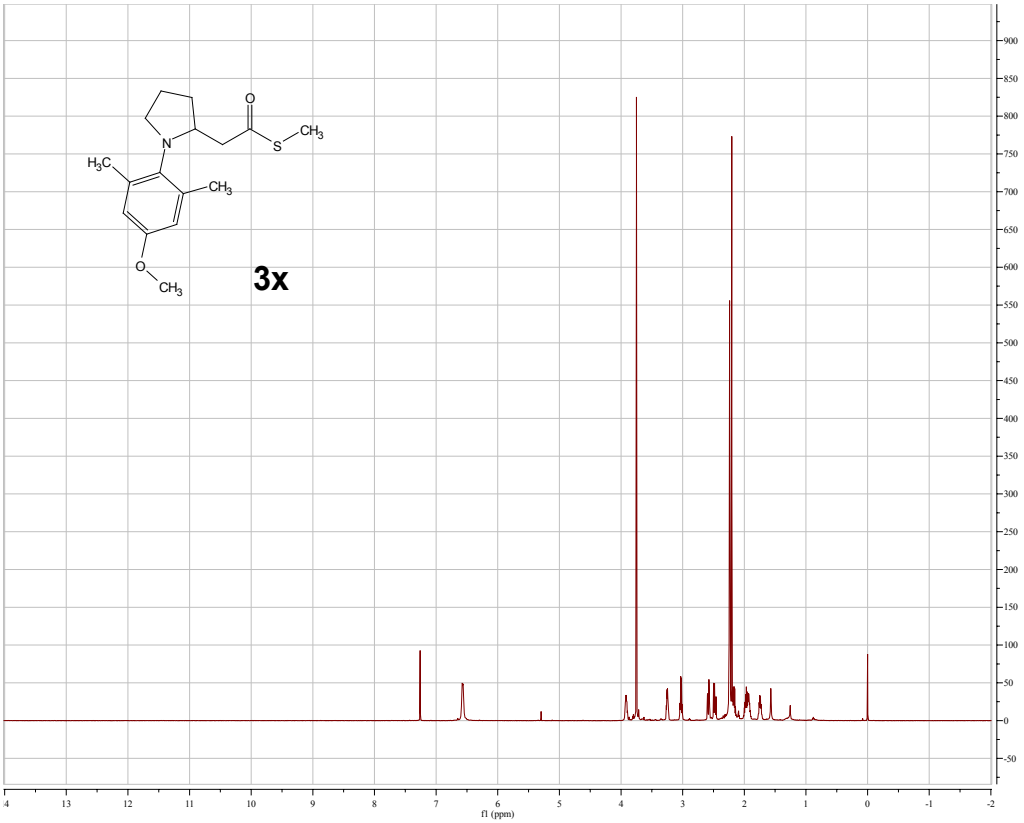
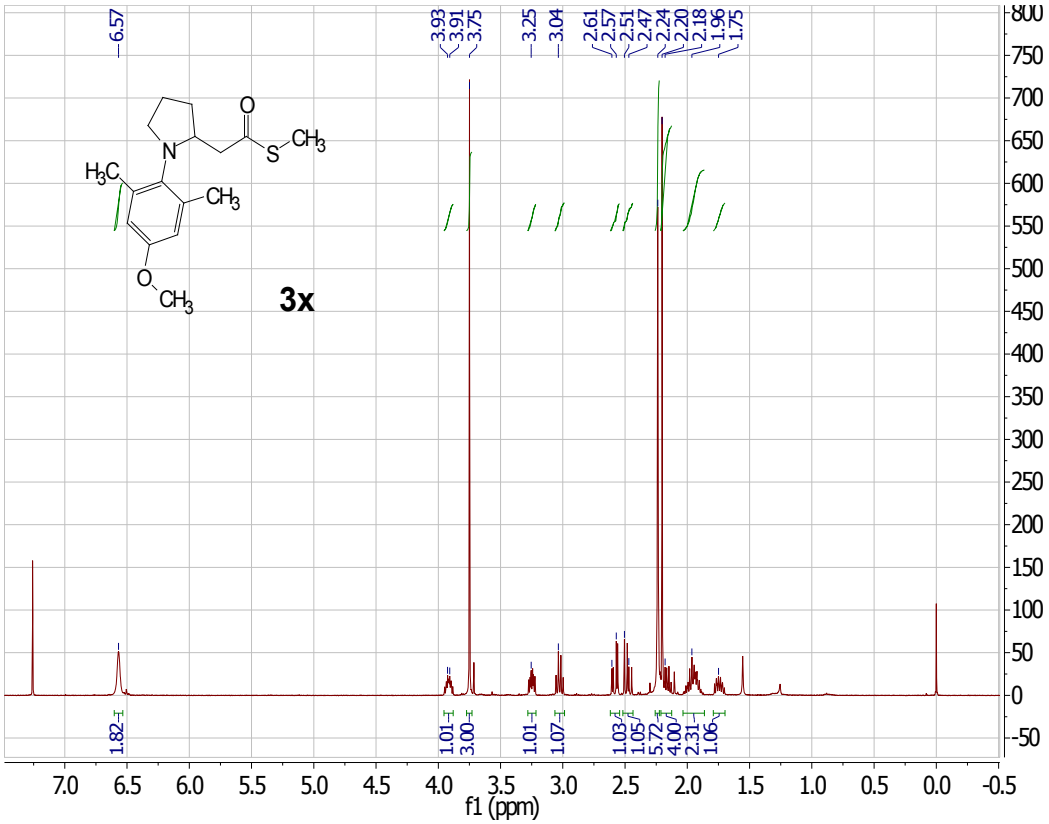
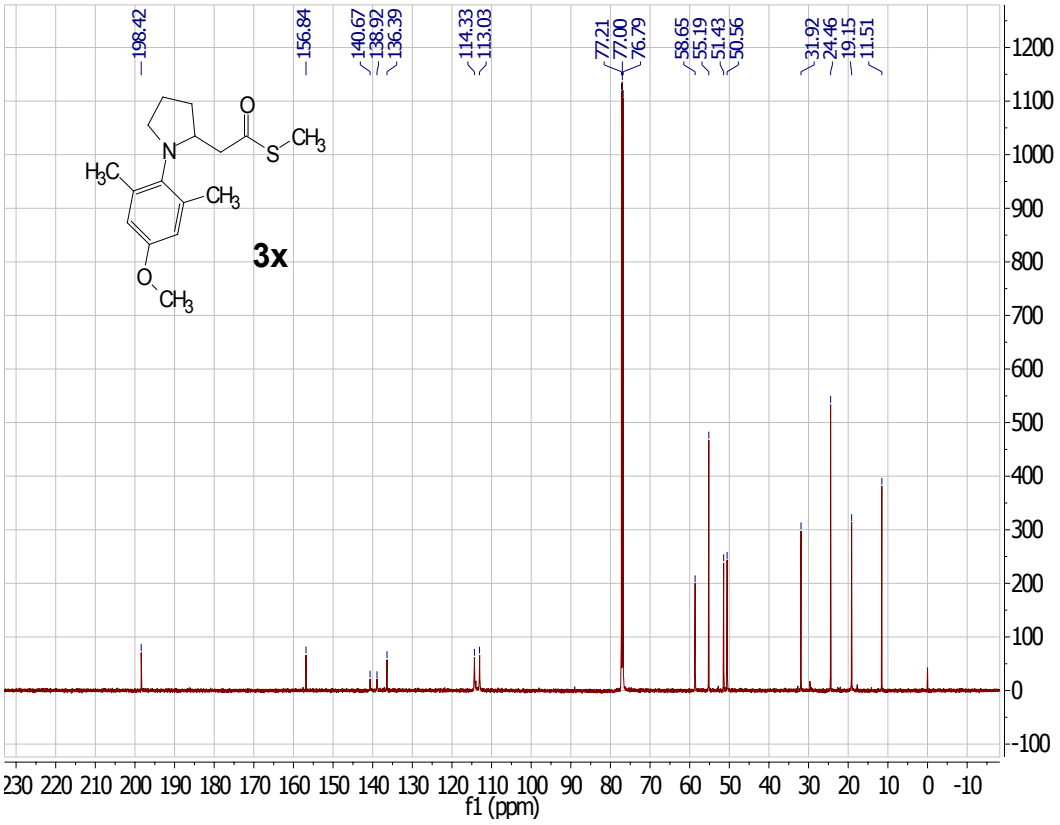
31.22
29.49
25.56
22.55
19.78
19.15
3w-minor
f1 (ppm)


3x


6.57
3.93
3.91
3.75
3.25
3.04
2.61
2.57
2.51
2.47
2.24
2.20
2.18
1.96
1.75
3x
1.82
1.01
3.00
1.01
1.07
1.03
1.05
5.72
4.00
2.31
1.06
f1 (ppm)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136.39
114.33
113.03
77.21
77.00
76.79
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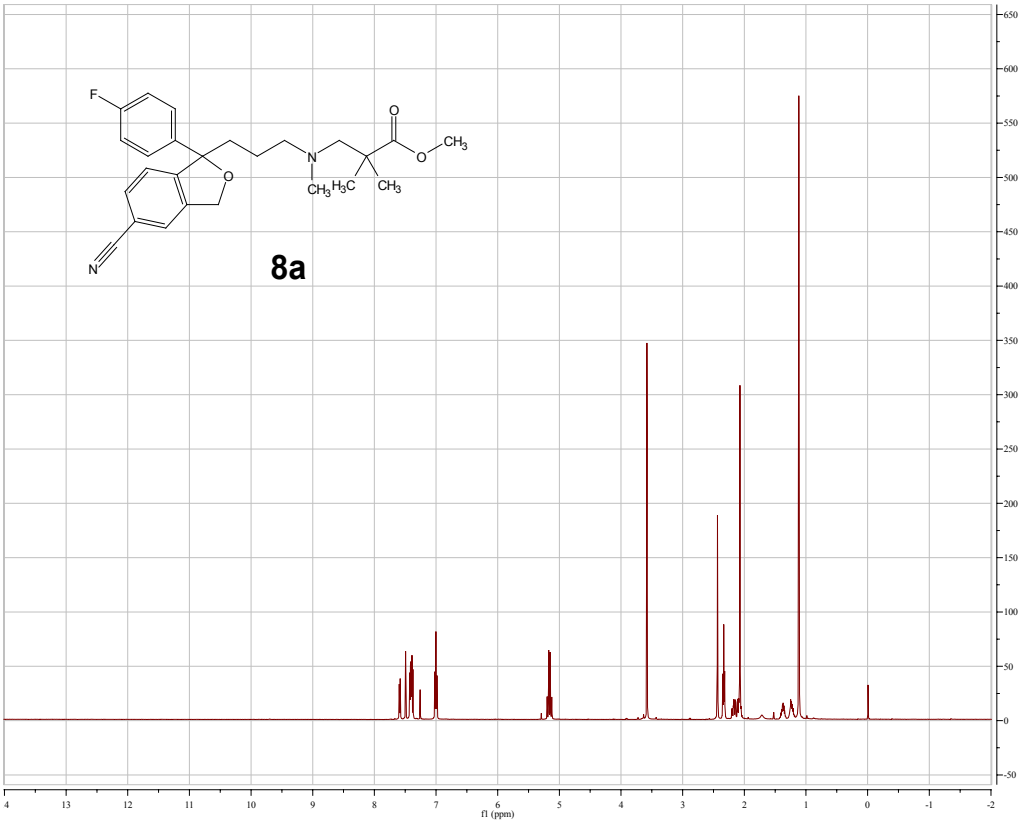
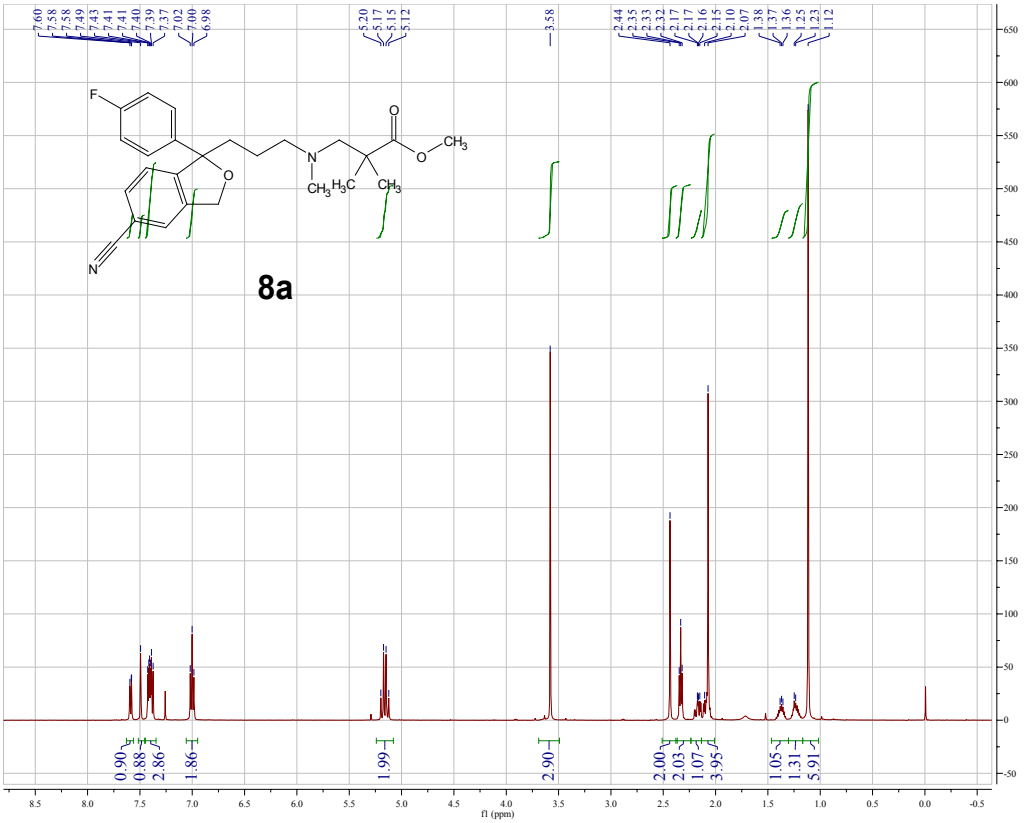
24.46
19.15
11.51
3x
f1 (ppm)


8a
f1 (ppm)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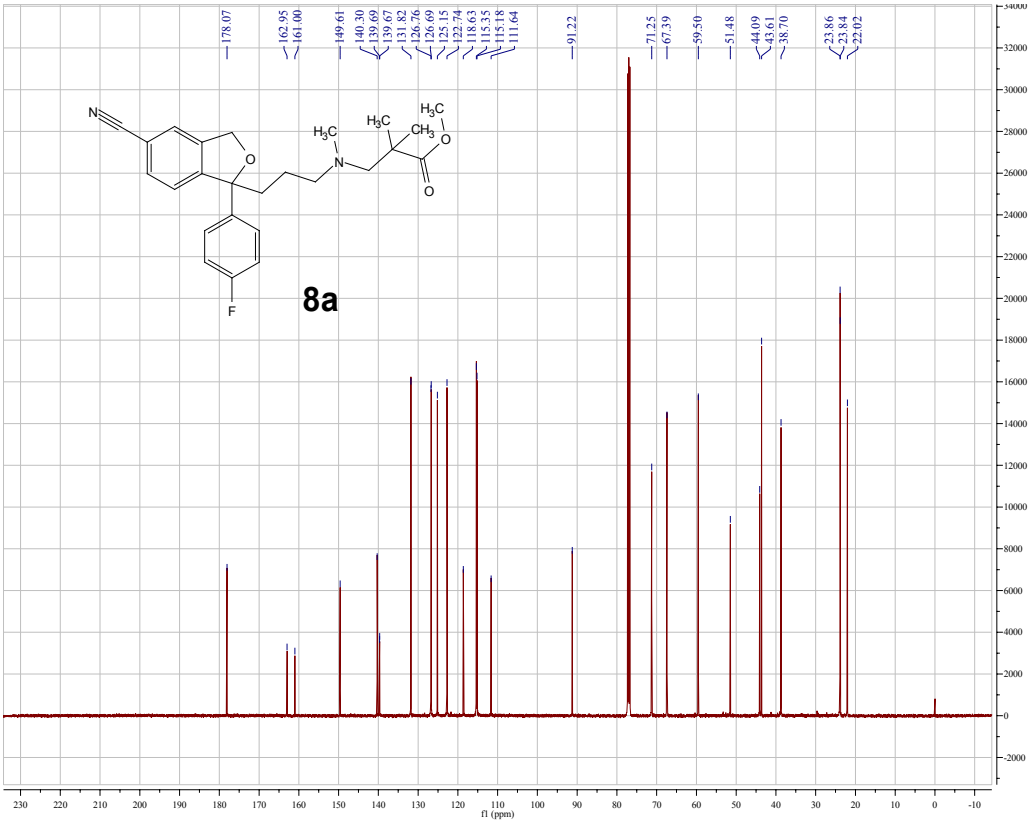
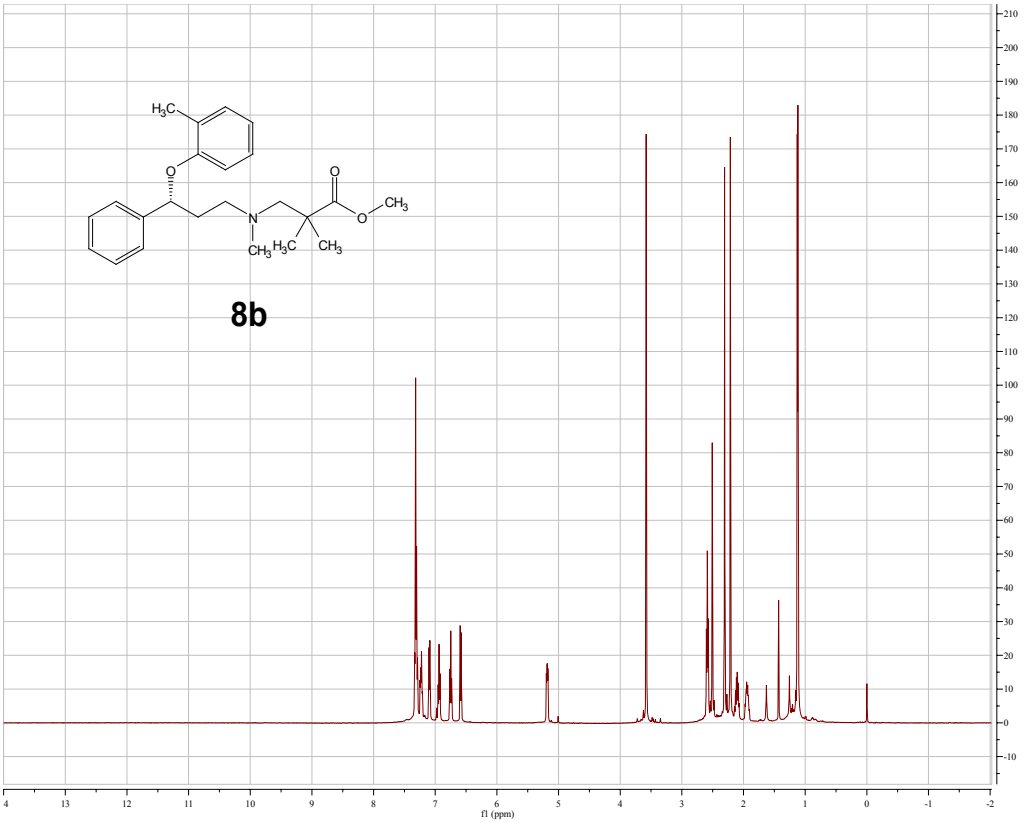
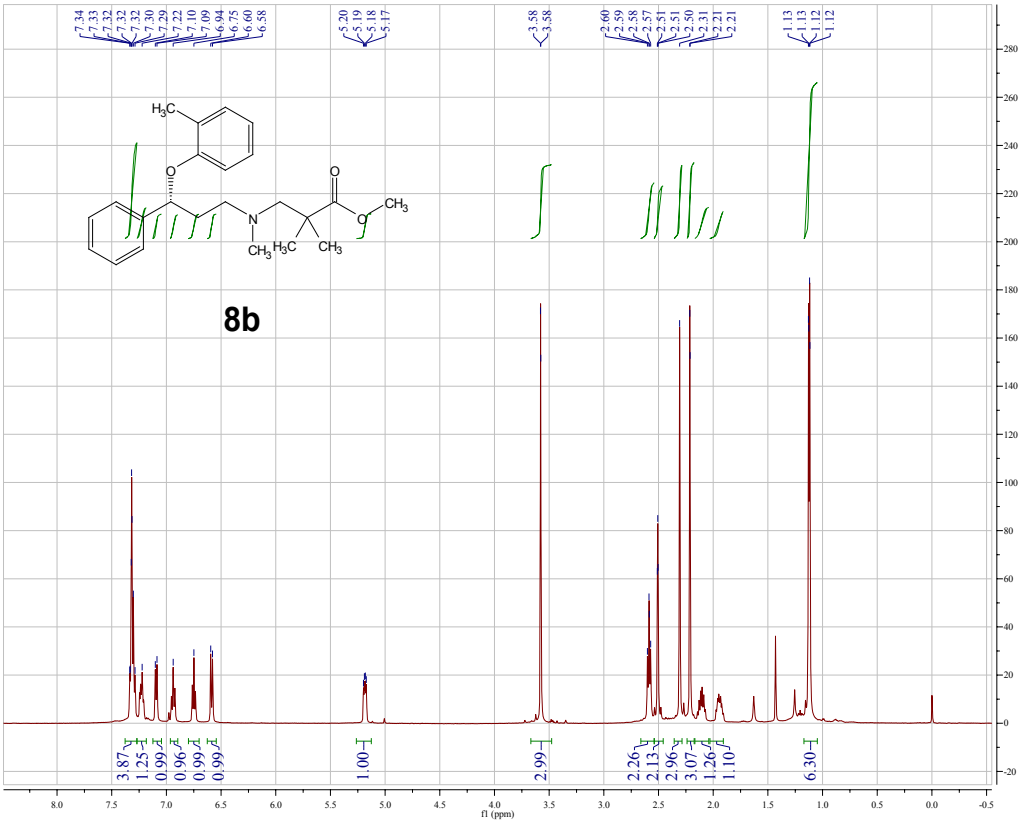
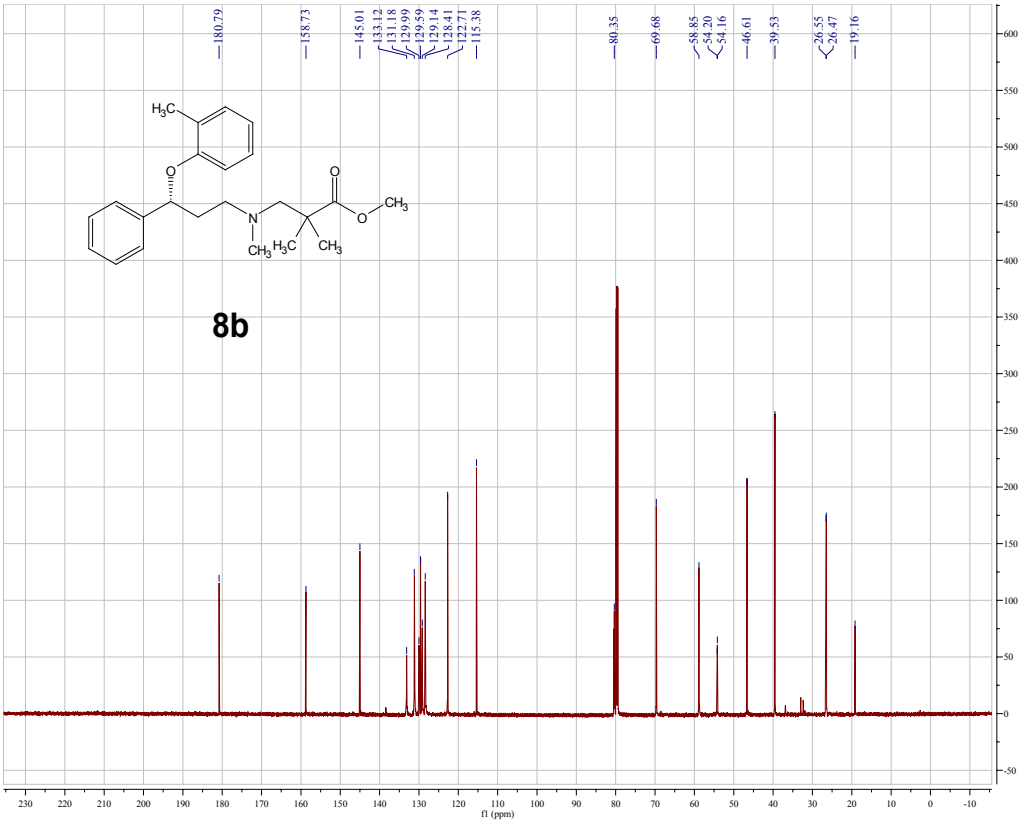
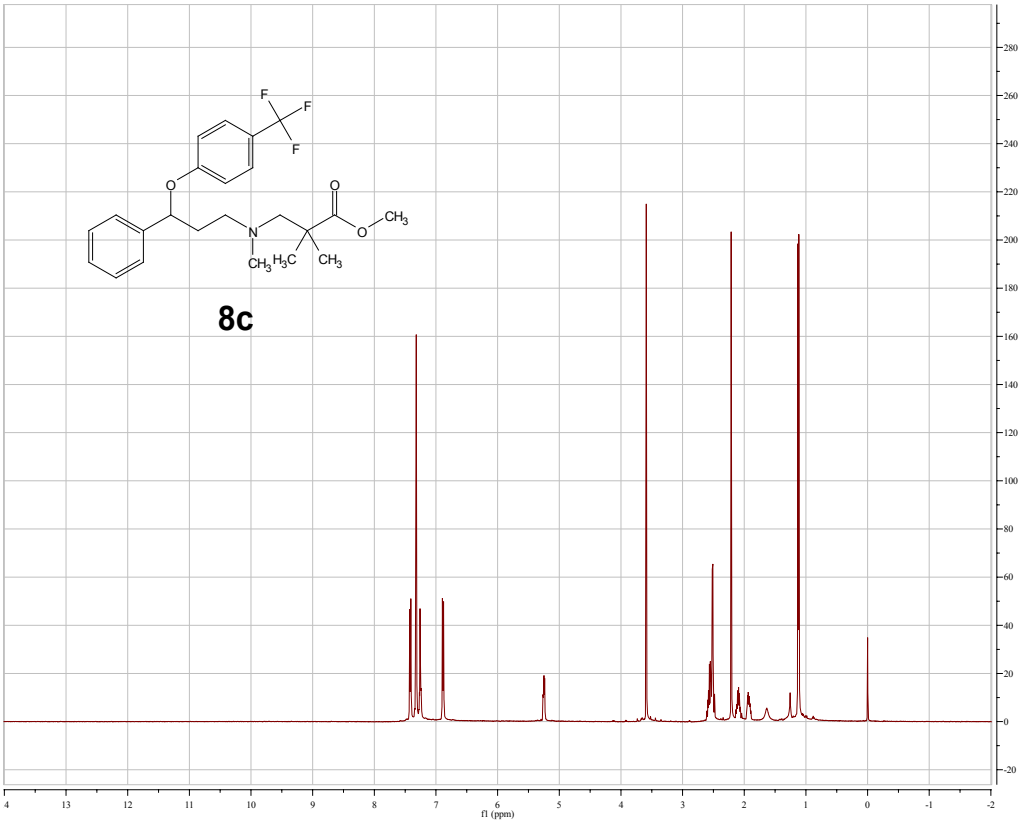
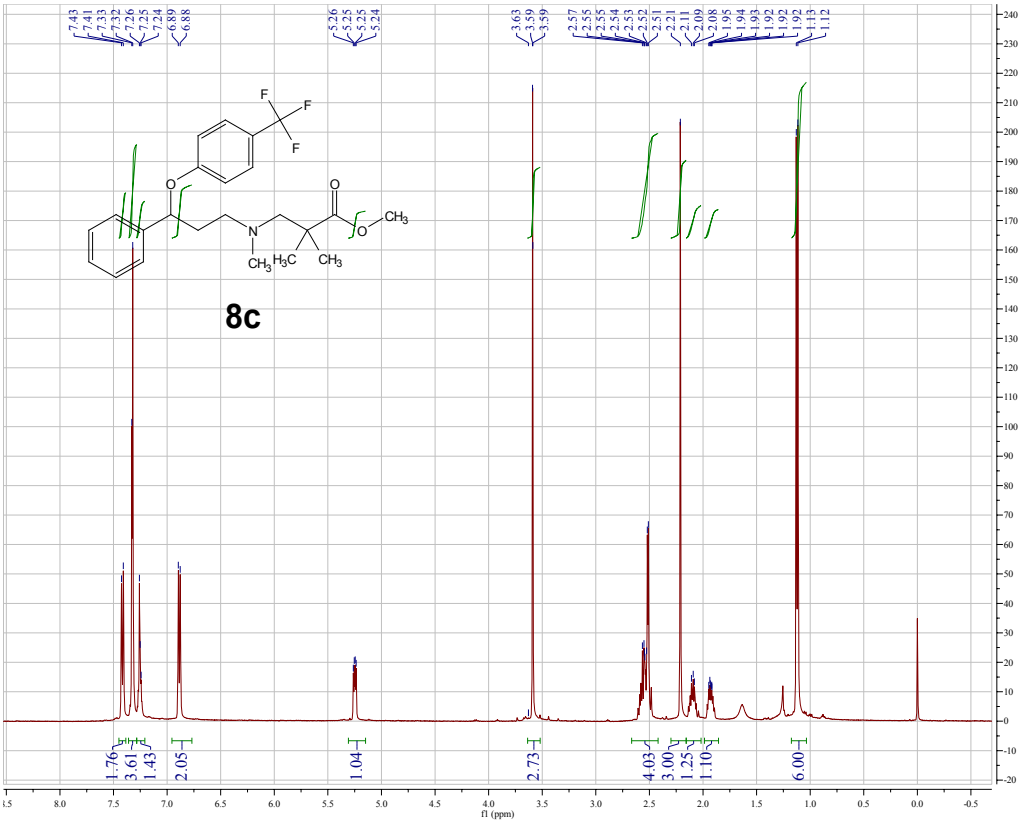

8a

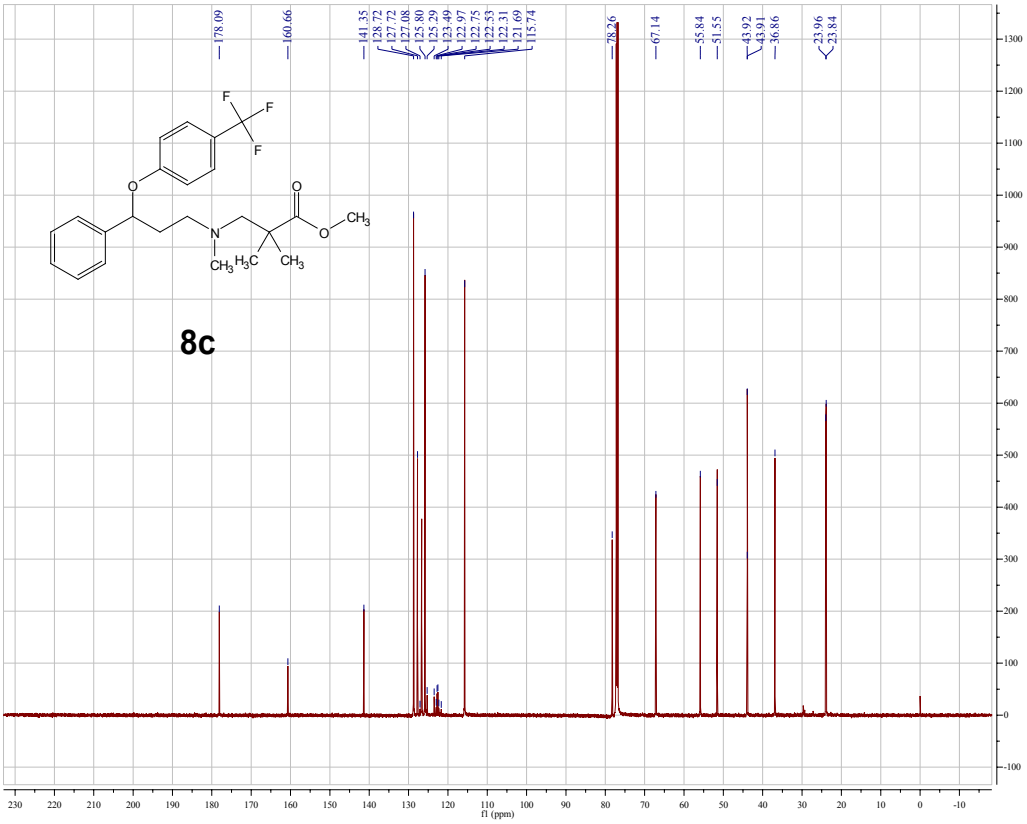

8b
f1 (ppm)

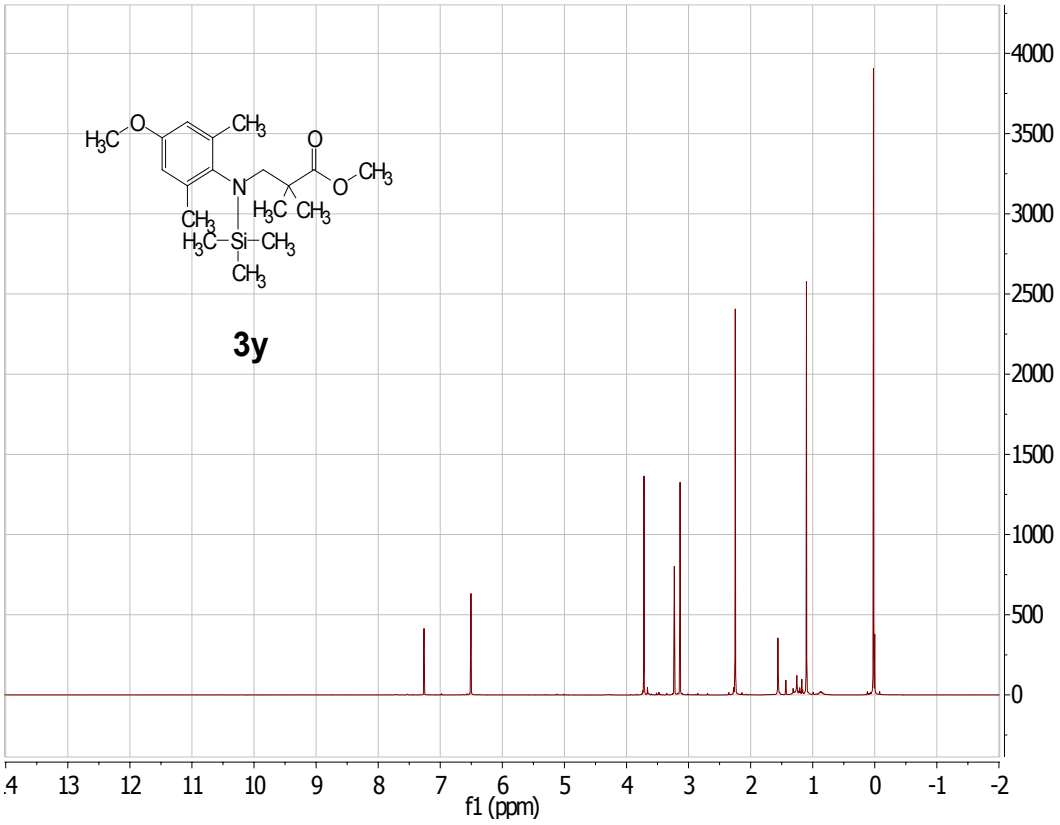

8b
7.34
7.33
7.32
7.32
7.32
7.30
7.29
7.22
7.10
7.09
6.94
6.75
6.60
6.58
5.20
5.19
5.18
5.17
3.58
3.58
2.60
2.59
2.58
2.57
2.51
2.51
2.50
2.31
2.21
2.21
1.13
1.13
1.12
1.12
3.87
1.25
0.99
0.96
0.99
0.99
1.00
2.99
2.26
2.13
2.96
3.07
1.26
1.10
6.30
f1 (ppm)

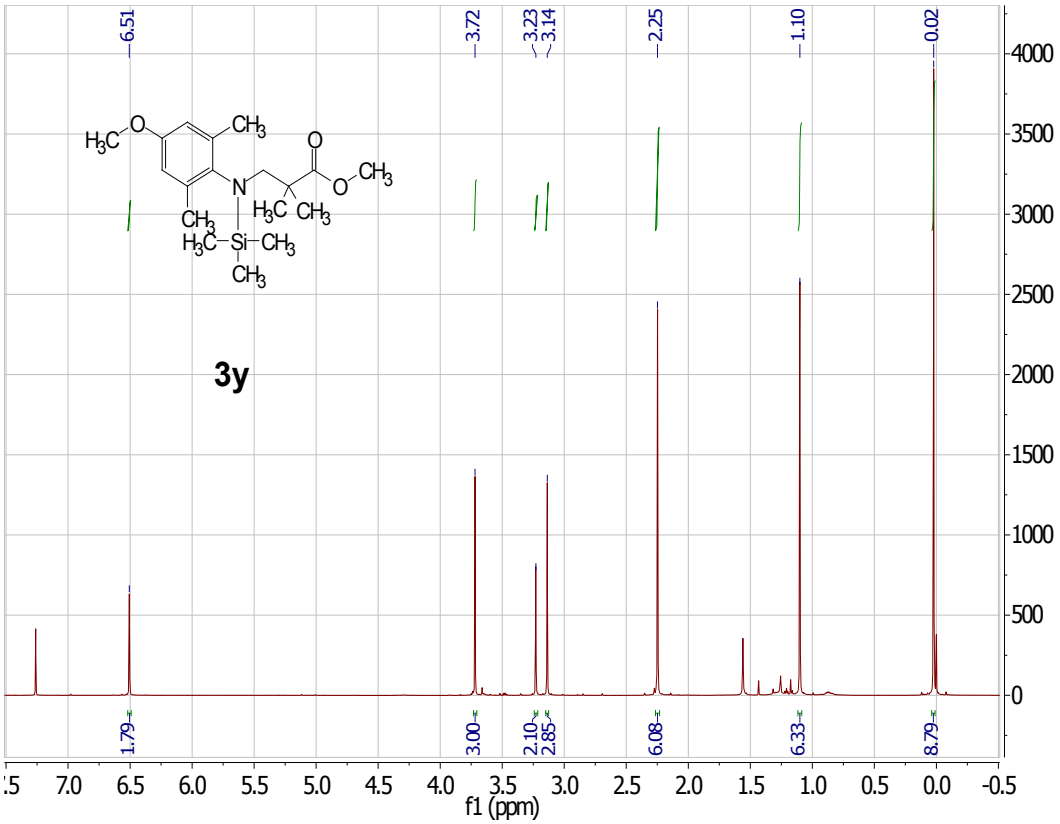

180.79
158.73
145.01
133.12
131.18
129.99
129.59
129.14
128.41
122.71
115.38
80.35
69.68
58.85
54.20
54.16
46.61
39.53
26.55
26.47
19.16
8b
f1 (ppm)

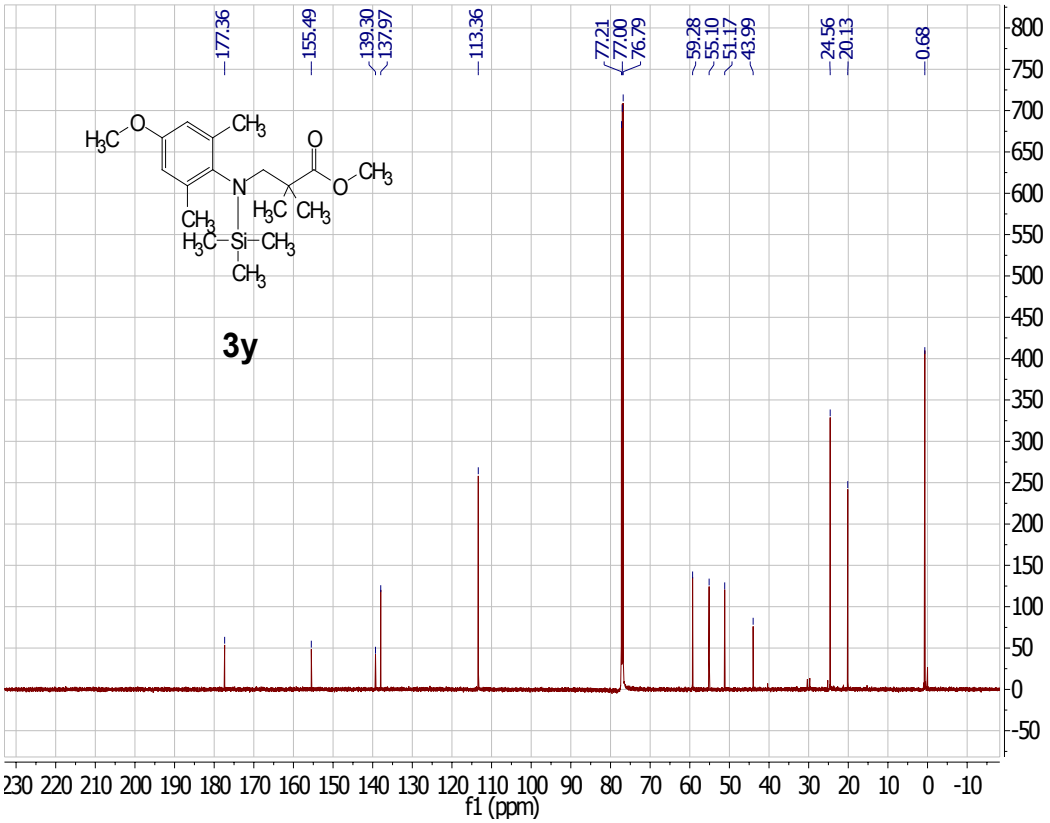

8c
f1 (ppm)


8c
1.76
3.61
1.43
2.05
1.04
2.73
4.03
3.00
1.25
1.10
6.00
f1 (ppm)


8c
f1 (ppm)


3y
f1 (ppm)


6.51
3.72
3.23
3.14
2.25
1.10
0.02
1.79
3.00
2.10
2.85
6.08
6.33
8.79
3y
f1 (ppm)


177.36
155.49
139.30
137.97
113.36
77.21
77.00
76.79
59.28
55.10
51.17
43.99
24.56
20.13
0.68
3y
f1 (ppm)