Cross-coupling of Amines via Photocatalytic Denitrogenation of In Situ-Generated Diazenes.

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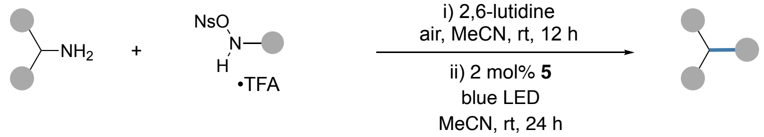
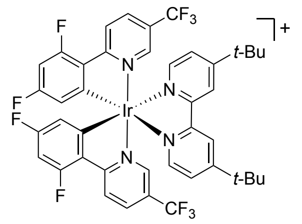
1. General Information

All reactions were conducted under a nitrogen atmosphere, unless otherwise noted. Commercial reagents were purchased from Sigma Aldrich, Matrix Chemical, AKSci, Alfa Aesar, Oakwood chemical or TCI and used without purification. Flash chromatography was performed using silica gel 60 (230-400 mesh) from SilicaFlash on a Biotage Isolera One system. Thin layer chromatography was performed using EMD Silica Gel 60 F254 plates under UV light (254 nm) or visualized with potassium permanganate stain. Solvents were dried using a JC Meyer solvent purification system. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Inova-400 (400 MHz) and Bruker-AV (500 MHz). Chemical shifts for proton are referenced to residual proton in the NMR solvent ($CHCl_3$ = δ 7.26, CD_3OD = δ 3.10). Chemical shifts for carbon are referenced to the carbon resonances of the solvent ($CDCl_3$ = δ 77.0, CD_3OD = δ 49.0). Data are represented as follows: chemical shift, multiplicity (br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublet of doublets, m = multiplet), (J=Hz), integration. Yields determined with ^{1}H NMR used mesitylene as internal standard. Mass spectral data were obtained using a Thermo Fisher Scientific Exactive series DART Mass Spectrometer. Infrared (IR) spectra were obtained using a Bruker Tensor II Infrared Spectrometer and are reported in cm^{-1}. Optical rotations were measured on a Rudolph Research Analytical Autopol I Automatic Polarimeter and are reported in degrees.

2. General Procedures





Ir(dFCF$_3$ppy)$_2$(dtbbpy)$^+$ (5)

Note: General Procedure A was used for simple substrates. For substrates with lower solubility and/or acid-sensitive functionality, modified General Procedure B was used.

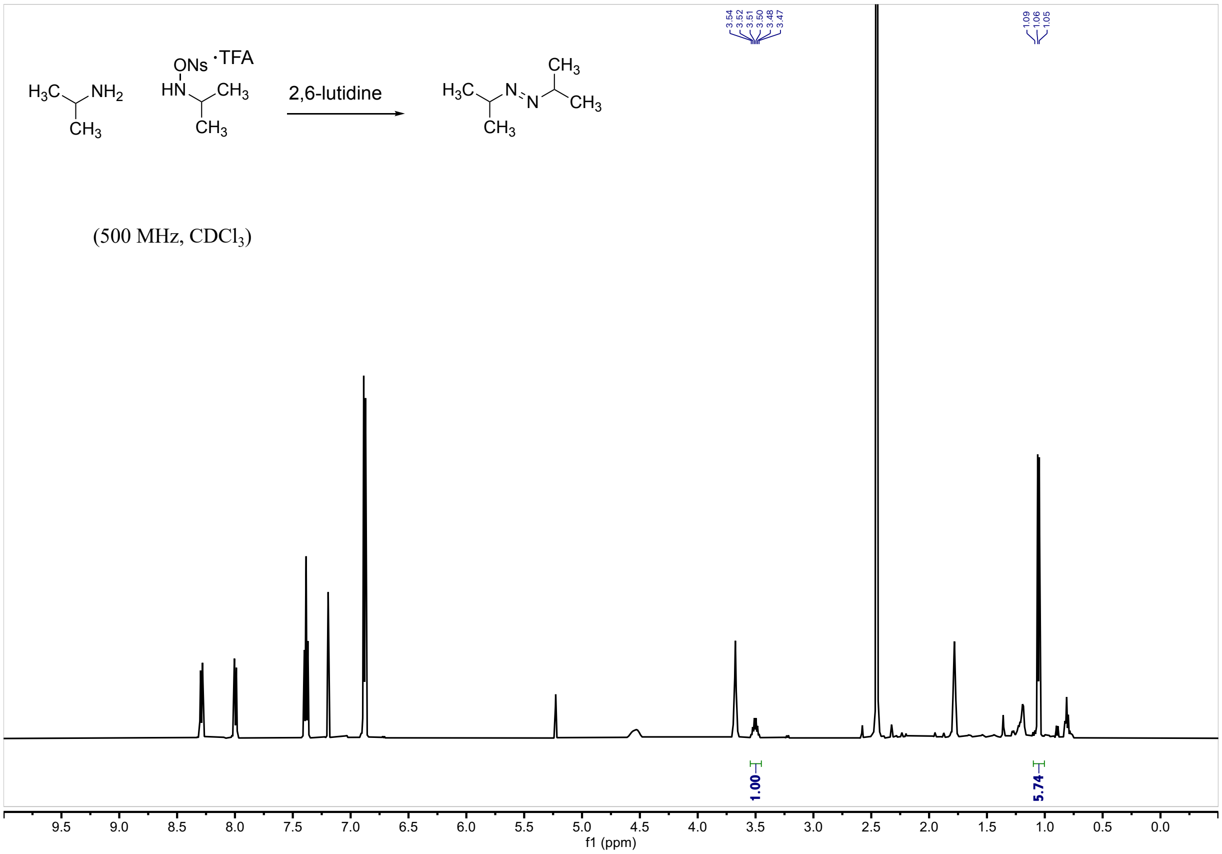
General Procedure A [Simple substrates]

To a 20 mL scintillation vial was added the O-nosylhydroxylamine salt (38 mg, 0.10 mmol), the amine (0.10 mmol, 1.0 eq), and a magnetic stir bar. Dry MeCN (1 mL, 0.1 M) and 2,6-lutidine (22 mg, 0.20 mmol, 2.0 eq) were added by syringe, and the reaction mixture was stirred under open to air for 12 h. Reaction progress can be monitored by ^{1}H NMR or TLC. The reaction mixture was filtered over a short plug of Celite® and washed with dry MeCN. (Ir[dF(CF$_3$)ppy]$_2$(dtbpy))PF$_6$ (2.3 mg, 0.02 mmol, 2 mol%) was added and the reaction mixture was degassed by sparging with nitrogen gas for 15 minutes. The reaction mixture was sealed and irradiated with blue LEDs while being cooled with an oscillating fan for the duration of the reaction. After 16 h, the reaction mixture was quenched with 1M HCl and extracted with ethyl acetate, dried over sodium sulfate, and concentrated. The crude reaction mixture was purified by column chromatography on silica gel using the indicated solvent system.

General Procedure B [More complex substrates bearing acid sensitivity/less soluble]

To a 20 mL scintillation vial was added the O-nosylhydroxylamine salt (38 mg, 0.10 mmol), the amine (0.10 mmol, 1.0 eq), and a magnetic stir bar. Dry MeCN (1 mL, 0.1 M) and 2,6-lutidine (22 mg, 0.20 mmol, 2.0 eq) were added by syringe, and the reaction mixture was stirred open to air for 12 h. Reaction progress can be monitored by ^{1}H NMR or TLC. (Ir[dF(CF$_3$)ppy]$_2$(dtbpy))PF$_6$ (2.3 mg, 0.02 mmol, 2 mol%) was added and the reaction mixture was degassed by sparging with nitrogen gas for 15 minutes. The reaction mixture was sealed and irradiated with blue LEDs while cooling with an oscillating fan for the duration of the reaction. After 16 h, the reaction mixture was concentrated, and the crude residue was purified by column chromatography on silica gel using the indicated solvent system.

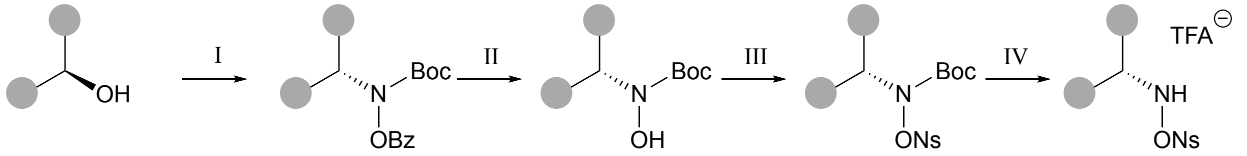
In-situ formed diazene can be monitored by ^{1}H NMR:



^{1}H NMR (500 MHz, $CDCl_3$) δ 3.50 (h, *J* = 6.5 Hz, 1H, -N=NC**H**-), 1.05 (d, *J* = 6.5 Hz, 6H, -(C**H$_3$)$_2$**).

3. Starting Material Synthesis

tert-butyl(benzoyloxy)carbamate[1] and *tert*-butylhydroxy(isopropyl)carbamate[2] were prepared according to the literature procedures.



General Procedure I: Mitsunobu Alkylation of Hydroxylamine
As adapted from a reported procedure,[3] to a stirring solution of triphenylphosphine (PPh_3) (1.2 eq) in dry THF (0.12 M) at 0 °C under a nitrogen atmosphere was added diisopropylazodicarboxylate (DIAD) (1.2 eq). After 30 min, the alcohol substrate (1.0 eq) and *tert*-butyl(benzoyloxy)carbamate (BzONHBoc) (1.2 eq) were added successively. After 1 h, the ice bath was removed. The reaction mixture was subsequently stirred at room temperature overnight, after which the volatiles were removed *in vacuo* and the residue was purified via column chromatography on silica gel using the indicated solvent system to yield the product.

General Procedure II: Benzoyl Deprotection
As adapted from a reported procedure,[4] to a stirred solution of the product (1.0 eq) from General Procedure I in MeOH (0.2 M) was added K_2CO_3 (1.0 eq). After completion as determined by TLC (~1-5 h), the mixture was concentrated *in vacuo*, diluted with water, and extracted with ethyl acetate (3x). The combined organic phases were washed with brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The residue was purified via column chromatography on silica gel using the indicated solvent system to yield the deprotected product.

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(1) Jeon, J.; Lee, C.; Seo, H.; Hong, S. NiH-Catalyzed Proximal-Selective Hydroamination of Unactivated Alkenes. *J. Am. Chem. Soc.* **2020**, *142*, 20470–20480.

(2) Tamura, Y.; Ikeda, H.; Morita, I.; Tsubouchi, H.; Ikeda, M. O-Arenesulfonyl-N-Alkylhydroxylamines as Aminating Reagents. *Chemical & Pharmaceutical Bulletin* **1982**, *30*, 1221–1224.

(3) Munnuri, S.; Adebesin, A. M.; Paudyal, M. P.; Yousufuddin, M.; Dalipe, A.; Falck, J. R. Catalyst-Controlled Diastereoselective Synthesis of Cyclic Amines via C–H Functionalization. *J. Am. Chem. Soc.* **2017**, *139*, 18288–18294.

(4) Liu, Y.; Ao, J.; Paladhi, S.; Song, C. E.; Yan, H. Organocatalytic Asymmetric Synthesis of Chiral Dioxazinanes and Dioxazepanes with in Situ Generated Nitrones via a Tandem Reaction Pathway Using a Cooperative Cation Binding Catalyst. *J. Am. Chem. Soc.* **2016**, *138*, 16486–16492.

General Procedure III: Nosyl Protection

As adapted from a reported procedure,[5] to a stirred solution of the product from General Procedure II (1.0 eq) in CH_2Cl_2 (0.65 M) at 0 °C was added triethylamine (1.1 eq) and nosyl chloride (1.1 eq). The reaction mixture was allowed to warm to room temperature and was subsequently allowed to stir overnight, after which the mixture was washed with aqueous saturated sodium bicarbonate (2x). The organic layer was washed with brine and dried over anhydrous sodium sulfate. Volatiles were removed *in vacuo* and the residue was purified via column chromatography on silica gel using the indicated solvent system to yield the product.

General Procedure IV: Boc Deprotection

As adapted from a reported procedure,[6] to a stirred solution of the product from General Procedure III (1.0 eq) in CH_2Cl_2 (0.4 M) was added trifluoroacetic acid (10 eq). The reaction mixture was allowed to warm to room temperature and stirred overnight, after which the volatiles were removed *in vacuo*. The crude product was recrystallized from dichloromethane layered with ether to yield the ONHA•TFA salt, which was used directly in the reaction. Consistent with the precedent by tosyl salts[6,7] and previous reports,[8] salts were unstable in solution, but stable in solid phase when stored in the freezer. Hydrolysis in NMR solvents was observed, which precluded further characterization.

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(5) Paudyal, M. P.; Wang, M.; Siitonen, J. H.; Hu, Y.; Yousufuddin, M.; Shen, H. C.; Falck, J. R.; Kürti, L. Intramolecular N–Me and N–H Aminoetherification for the Synthesis of N-Unprotected 3-Amino-O-Heterocycles. *Org. Biomol. Chem.* **2021**, *19*, 557–560.

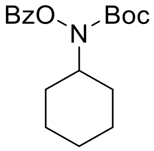
(6) Paudyal, M. P.; Adebesin, A. M.; Burt, S. R.; Ess, D. H.; Ma, Z.; Kürti, L.; Falck, J. R. Dirhodium-Catalyzed C-H Arene Amination Using Hydroxylamines. *Science* **2016**, *353*, 1144–1147.

(7) Munnuri, S.; Adebesin, A. M.; Paudyal, M. P.; Yousufuddin, M.; Dalipe, A.; Falck, J. R. Catalyst-Controlled Diastereoselective Synthesis of Cyclic Amines via C–H Functionalization. *J. Am. Chem. Soc.* **2017**, *139*, 18288–18294.

(8) (a) Hoffman, R. V.; Belfoure, E. L. The Preparation of N-Alkyl-O-Arenesulfonylhydroxylamines. *Synthesis* **1983**, *1983*, 34–35. (b) Dannley, R. L.; Gagen, J. E.; Stewart, O. J. Arylsulfonoxylation of Aromatic Compounds. II. Partial Rate Factors for the Nitrophenylsulfonoxylation of Alkylbenzenes. *J. Org. Chem.* **1970**, *35*, 3076–3079.

4. Starting Material Characterization

tert-butyl (benzoyloxy)(cyclohexyl)carbamate (S1)



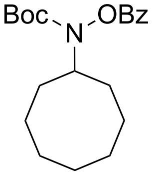
Prepared according to general procedure I using cyclohexanol (800 mg, 7.99 mmol), DIAD (1.94 g, 9.59 mmol), PPh_3 (2.51 g, 9.59 mmol), and BzONHBoc (2.27 g, 9.59 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate afforded **S1** in 37% yield (952 mg, 2.98 mmol).

^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.07 (m, 2H, C**H**$_{Ar}$), 7.64 – 7.58 (m, 1H, C**H**$_{Ar}$), 7.48 (m, 2H, C**H**$_{Ar}$), 4.07 (m, 1H, -NC**H**-), 1.95 (br s, 2H, -C**H**$_2$-), 1.80 (br s, 2H, -C**H**$_2$-), 1.68 – 1.56 (m, 2H, -C**H**$_2$-), 1.46 (s, 9H, -C**H**$_3$), 1.34 (m, 3H, -C**H**$_2$-), 1.08 (m, 1H, -C**H**$_2$-).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 165.0, 154.8, 133.8, 130.0, 128.7, 128.0, 82.4, 59.5, 29.8, 28.3, 25.7, 25.5.

HRMS (DART-MS): m/z $[M + H]^+$ calcd for $C_{18}H_{26}NO_4$: 320.1856 found 320.18927.

tert-butyl (benzoyloxy)(cyclooctyl)carbamate (S2)



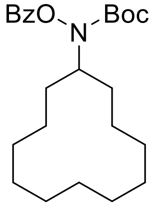
Prepared according to general procedure I using cyclooctanol (1.00 g, 7.80 mmol), DIAD (1.89 g, 9.36 mmol), PPh_3 (2.46 g, 9.36 mmol), and BzONHBoc (2.22 g, 9.36 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate afforded **S2** in 39% yield (1.04 g, 3.00 mmol).

^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.06 (m, 2H, C**H**$_{Ar}$), 7.64 – 7.57 (m, 1H, C**H**$_{Ar}$), 7.47 (m, 2H, C**H**$_{Ar}$), 4.35 (m, 1H, -NC**H**-), 1.97 – 1.87 (m, 2H, -C**H**$_2$-), 1.72 (m, 3H, -C**H**$_2$-), 1.63 – 1.49 (m, 8H, -C**H**$_2$-), 1.47 (m, 10H, -C**H**$_2$-, -C**H**$_3$).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 164.9, 155.1, 133.7, 130.0, 129.5, 128.7, 128.1, 82.4, 60.3, 30.9, 29.1, 28.3, 27.4, 26.6, 26.5, 24.9, 22.8.

HRMS (DART-MS): m/z $[M + H]^+$ calcd for $C_{20}H_{30}NO_4$: 348.2169 found 348.2202.

tert-butyl (benzoyloxy)(cyclododecyl)carbamate (S3)



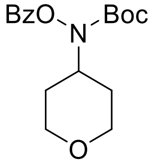
Prepared according to general procedure I using cyclododecanol (1.00 g, 5.43 mmol), DIAD (1.32 g, 6.51 mmol), PPh_3 (1.71 g, 6.51 mmol), and BzONHBoc (1.55 g, 6.51 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate afforded **S3** in 32% yield (692 mg, 1.72 mmol).

^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.06 (m, 2H, C**H$_{Ar}$**), 7.63 – 7.56 (m, 1H, C**H$_{Ar}$**), 7.46 (m, 2H, C**H$_{Ar}$**), 4.42 (m, 1H, -NC**H**-), 1.83 – 1.72 (m, 1H, -C**H$_2$**-), 1.61 (m, 3H, -C**H$_2$**-), 1.48 (m, 11H, -C**H$_2$**-, -C**H$_3$**), 1.45 – 1.24 (m, 16H, -C**H$_2$**-).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 164.7, 155.1, 133.7, 130.0, 128.7, 128.0, 82.3, 55.5, 29.1, 28.3, 24.5, 23.9, 23.0, 23.0, 22.5.

HRMS (DART-MS): m/z $[M + H]^+$ calcd for $C_{24}H_{38}NO_4$: 404.2795 found 404.2756.

tert-butyl (benzoyloxy)(tetrahydro-2H-pyran-4-yl)carbamate (S4)



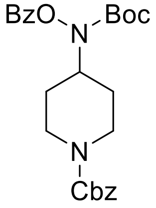
Prepared according to general procedure I using tetrahydro-2H-pyran-4-ol (500 mg, 4.90 mmol), DIAD (1.19 g, 5.88 mmol), PPh_3 (1.54 g, 5.88 mmol), and BzONHBoc (1.39 g, 5.88 mmol). Purification by column chromatography on silica gel using 85:15 hexanes: ethyl acetate afforded **S4** in 70% yield (1.10 g, 3.42 mmol).

^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.09 – 8.03 (m, 2H, C**H$_{Ar}$**), 7.66 – 7.57 (m, 1H, C**H$_{Ar}$**), 7.48 (m, 2H, C**H$_{Ar}$**), 4.33 (m, 1H, -NC**H**-), 4.01 (br s, 2H, -OC**H$_2$**-), 3.44 (m, 2H, -OC**H$_2$**-), 1.99 (br s, 1H, -C**H$_2$**-), 1.84 (m, 2H, -C**H$_2$**-), 1.70 (br s, 1H, -C**H$_2$**-), 1.45 (s, 9H, -C**H$_3$**).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 164.9, 154.6, 134.0, 130.0, 128.8, 127.6, 82.8, 67.3, 56.3, 30.0, 29.5, 28.2.

HRMS (DART-MS): m/z $[M + H]^+$ calcd for $C_{17}H_{24}NO_5$: 322.1649 found 322.1684.

benzyl 4-((benzoyloxy)(tert-butoxycarbonyl)amino)piperidine-1-carboxylate (S5)



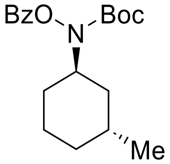
To a dry 100 mL round bottom flask was added a stir bar and benzyl 4-hydroxypiperidine-1-carboxylate (1.48 g, 6.27 mmol), tetramethylazodicarboxamide (1.40 g, 8.16 mmol), and BzONHBoc (2.98 g, 12.55 mmol). The flask was purged with nitrogen, charged with dry THF (35 mL), and cooled to 0 °C. Tributylphosphine (2.54 g, 12.55 mmol) was added, and the reaction mixture was allowed to warm to room temperature and stir overnight. Volatiles were removed *in vacuo*. Purification via column chromatography on silica gel using 80:20 hexanes: ethyl acetate afforded **S5** in 60% yield (1.72 g, 3.78 mmol).

^{1}H NMR: (500 MHz, CDCl$_3$) δ 8.07 – 8.01 (m, 2H, C$\mathbf{H}_{\mathbf{Ar}}$), 7.67 – 7.59 (m, 1H, C$\mathbf{H}_{\mathbf{Ar}}$), 7.48 (m, 2H, C$\mathbf{H}_{\mathbf{Ar}}$), 7.31 (m, 5H, C$\mathbf{H}_{\mathbf{Ar}}$), 5.09 (br s, 2H, PhC$\mathbf{H_2}$O-), 4.28 (m, 3H, -NC**H**-, -NC$\mathbf{H_2}$-), 2.85 (br s, 2H, -NC$\mathbf{H_2}$-), 1.86 (m, 3H, -C$\mathbf{H_2}$-), 1.45 (m, 10H, -C$\mathbf{H_3}$, -C$\mathbf{H_2}$-).

^{13}C NMR: (126 MHz, CDCl$_3$) δ 164.9, 155.2, 154.4, 136.8, 134.0, 130.0, 128.8, 128.6, 128.1, 128.0, 127.5, 82.9, 67.3, 57.2, 43.4, 28.3.

HRMS (DART-MS): m/z [M + H]$^+$ calcd for $C_{25}H_{31}N_2O_6$: 455.2177 found 455.2228.

tert-butyl (benzoyloxy)((1R,3R)-3-methylcyclohexyl)carbamate (S6)



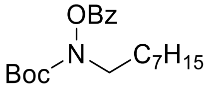
Prepared according to general procedure I using cis-3-methylcyclohexanol (750 mg, 6.57 mmol), DIAD (1.59 g, 7.88 mmol), PPh$_3$ (2.07 g, 7.88 mmol), and BzONHBoc (1.87 g, 7.88 mmol). Purification by column chromatography on silica gel using 95:5 hexanes: ethyl acetate afforded **S6** in 24% yield (520 mg, 1.56 mmol).

^{1}H NMR: (500 MHz, CDCl$_3$) δ 8.11 – 8.03 (m, 2H, C$\mathbf{H}_{\mathbf{Ar}}$), 7.64 – 7.57 (m, 1H, C$\mathbf{H}_{\mathbf{Ar}}$), 7.47 (m, 2H, C$\mathbf{H}_{\mathbf{Ar}}$), 4.34 (m, 1H, -NC**H**-), 2.10 (br s, 1H, -C**H**CH$_3$), 1.88 (br s, 2H, -C$\mathbf{H_2}$-), 1.73 – 1.53 (m, 4H, -C$\mathbf{H_2}$-), 1.46 (s, 11H, -C$\mathbf{H_2}$-, -C$\mathbf{H_3}$), 1.01 (m, 3H, -C$\mathbf{H_3}$).

^{13}C NMR (126 MHz, CDCl$_3$) δ 165.0, 154.9, 133.8, 130.0, 128.7, 128.0, 82.3, 55.0, 35.4, 31.2, 29.9, 28.3, 28.0, 20.4, 18.5.

HRMS (DART-MS): m/z [M + H]$^+$ calcd for $C_{19}H_{28}NO_4$: 334.2013 found 334.2028.

tert-butyl (benzoyloxy)(octyl)carbamate (S7)



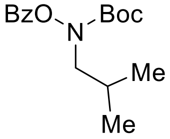
Prepared according to general procedure I using octanol (1.00 g, 7.68 mmol), DIAD (1.86 g, 9.21 mmol), PPh_3 (2.42 g, 9.21 mmol), and BzONHBoc (2.19 g, 9.21 mmol). Purification by column chromatography on silica gel using 95:5 hexanes: ethyl acetate afforded **S7** in 99% yield (2.65 g, 7.59 mmol).

^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 2H, C$\mathbf{H}_{\mathbf{Ar}}$), 7.57 – 7.50 (m, 1H, C$\mathbf{H}_{\mathbf{Ar}}$), 7.40 (m, 2H, C$\mathbf{H}_{\mathbf{Ar}}$), 3.61 (m, 2H, -NC$\mathbf{H_2}$-), 1.57 (m, 2H, -C$\mathbf{H_2}$-), 1.39 (s, 9H, -C$\mathbf{H_3}$), 1.34 – 1.11 (m, 10H, -C$\mathbf{H_2}$-), 0.79 (m, 3H, -C$\mathbf{H_3}$).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 164.8, 155.0, 133.9, 130.0, 128.7, 127.9, 82.3, 50.8, 31.9, 29.3, 28.3, 27.3, 26.7, 22.7, 14.2.

HRMS (DART-MS): m/z $[M + H]^+$ calcd for $C_{20}H_{32}NO_4$: 350.2326 found 350.2342.

tert-butyl (benzoyloxy)(isobutyl)carbamate (S8)



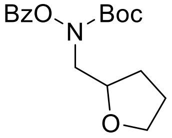
Prepared according to general procedure I using isobutanol (550 mg, 7.42 mmol), DIAD (1.80 g, 8.91 mmol), PPh_3 (2.34 g, 8.91 mmol), and BzONHBoc (2.11 g, 8.91 mmol). Purification by column chromatography on silica gel using 95:5 hexanes: ethyl acetate afforded **S8** in 98% yield (2.12 g, 7.24 mmol).

^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.09 – 8.03 (m, 2H, C$\mathbf{H}_{\mathbf{Ar}}$), 7.63 – 7.56 (m, 1H, C$\mathbf{H}_{\mathbf{Ar}}$), 7.46 (m, 2H, C$\mathbf{H}_{\mathbf{Ar}}$), 3.51 (m, 2H, -NC$\mathbf{H_2}$-), 1.97 (m, 1H, -C**H**-), 1.45 (s, 9H, -C$\mathbf{H_3}$), 0.98 (d, J = 6.7 Hz, 6H, -C$\mathbf{H_3}$).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 164.7, 154.9, 133.9, 129.9, 128.7, 127.8, 82.1, 58.0, 28.2, 27.1, 20.1.

HRMS (DART-MS): m/z $[M + H]^+$ calcd for $C_{16}H_{24}NO_4$: 294.1700 found 294.1730.

tert-butyl (benzoyloxy)((tetrahydrofuran-2-yl)methyl)carbamate (S9)



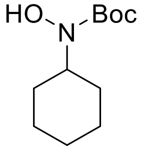
Prepared according to general procedure I using tetrahydrofurfuryl alcohol (800 mg, 7.83 mmol), DIAD (1.90 g, 9.40 mmol), PPh_3 (2.47 g, 9.40 mmol), and BzONHBoc (2.23 g, 9.40 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate afforded **S9** in 61% yield (1.53 g, 4.76 mmol).

^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 2H, C**H**$_{\mathbf{Ar}}$), 7.63 – 7.56 (m, 1H, C**H**$_{\mathbf{Ar}}$), 7.50 – 7.41 (m, 2H, C**H**$_{\mathbf{Ar}}$), 4.17 (m, 1H, -OC**H**-), 3.93 – 3.77 (m, 2H, -OC**H**$_{\mathbf{2}}$-), 3.77 – 3.64 (m, 2H, -NC**H**$_{\mathbf{2}}$-), 2.03 (m, 1H, -C**H**$_{\mathbf{2}}$-), 1.98 – 1.81 (m, 2H, -C**H**$_{\mathbf{2}}$-), 1.69 (m, 1H, -C**H**$_{\mathbf{2}}$-), 1.45 (s, 9H, -C**H**$_{\mathbf{3}}$).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 164.8, 155.0, 133.9, 130.0, 128.7, 127.8, 82.5, 76.2, 68.2, 54.3, 29.4, 28.2, 25.6, 21.8.

HRMS (DART-MS): m/z $[M + H]^+$ calcd for $C_{17}H_{24}NO_5$: 322.1649 found 322.1684.

tert-butyl cyclohexyl(hydroxy)carbamate (S10)



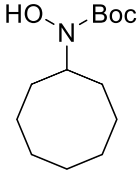
Prepared according to general procedure II using tert-butyl (benzoyloxy)(cyclohexyl)carbamate **S1** (900 mg, 2.82 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate afforded **S10** in 82% yield (496 mg, 2.30 mmol).

^{1}H NMR: (500 MHz, $CDCl_3$) δ 6.52 (s, 1H, -O**H**), 3.73 (m, 1H, -NC**H**-), 1.81 (m, 2H, -C**H**$_{\mathbf{2}}$-), 1.75 – 1.57 (m, 5H, -C**H**$_{\mathbf{2}}$-), 1.48 (s, 9H, -C**H**$_{\mathbf{3}}$), 1.28 (qt, *J* = 13.1, 3.7 Hz, 2H, -C**H**$_{\mathbf{2}}$-), 1.11 (qt, *J* = 13.0, 3.6 Hz, 1H, -C**H**$_{\mathbf{2}}$-).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 157.1, 81.7, 58.5, 29.3, 28.5, 25.8, 25.5.

HRMS (DART-MS): m/z $[M + H]^+$ calcd for $C_{11}H_{22}NO_3$: 216.1594 found 216.1619.

tert-butyl cyclooctyl(hydroxy)carbamate (S11)



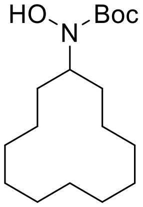
Prepared according to general procedure II using tert-butyl (benzoyloxy)(cyclooctyl)carbamate **S2** (1.20 g, 3.45 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate afforded **S11** in 88% yield (742 mg, 3.05 mmol).

^{1}H NMR: (500 MHz, $CDCl_3$) δ 6.47 (s, 1H, -O**H**), 4.09 – 4.00 (m, 1H, -NC**H**-), 1.94 – 1.81 (m, 2H, -C**H₂**-), 1.78 – 1.67 (m, 4H, -C**H₂**-), 1.65 – 1.50 (m, 7H, -C**H₂**-), 1.48 (m, 10H, -C**H₂**-, -C**H₃**).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 157.1, 81.7, 59.2, 30.7, 28.5, 26.7, 26.5, 25.1.

HRMS (DART-MS): m/z $[M + H]^+$ calcd for $C_{13}H_{26}NO_3$: 244.1907 found 244.1934.

tert-butyl cyclododecyl(hydroxy)carbamate (S12)



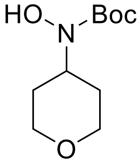
Prepared according to general procedure II using tert-butyl (benzoyloxy)(cyclododecyl)carbamate **S3** (1.20 g, 2.96 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate afforded **S12** in 74% yield (656 mg, 2.19 mmol).

^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.24 (s, 1H, -O**H**), 4.12 (m, 1H, -NC**H**-), 1.73 – 1.63 (m, 2H, -C**H₂**-), 1.56 (m, 2H, -C**H₂**-), 1.47 (s, 9H, -C**H₃**), 1.45 – 1.22 (m, 18H, -C**H₂**-).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 157.0, 81.4, 53.7, 28.5, 27.7, 24.5, 24.1, 22.8, 22.5, 22.3.

HRMS (DART-MS): m/z $[M + H]^+$ calcd for $C_{17}H_{34}NO_3$: 300.2533 found 300.2567.

tert-butyl hydroxy(tetrahydro-2H-pyran-4-yl)carbamate (S13)



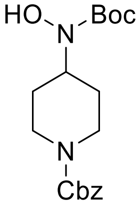
Prepared according to general procedure II using tert-butyl (benzoyloxy)(tetrahydro-2H-pyran-4-yl)carbamate **S4** (800 mg, 2.49 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate afforded **S13** in 69% yield (378 mg, 1.74 mmol).

^{1}H NMR: (500 MHz, CDCl$_3$) δ 6.99 (br s, 1H, -O**H**), 4.09 – 3.89 (m, 3H, -NC**H**-, -OC**H$_2$**-), 3.41 (m, 2H, -OC**H$_2$**-), 2.03 (m, 2H, -C**H$_2$**-), 1.60 (m, 2H, -C**H$_2$**-), 1.47 (s, 9H, -C**H$_3$**).

^{13}C NMR: (126 MHz, CDCl$_3$) δ 157.0, 82.1, 67.4, 55.5, 29.2, 28.5.

HRMS (DART-MS): m/z [M + H]$^+$ calcd for $C_{10}H_{20}NO_4$: 218.1387 found 218.1412.

benzyl 4-((tert-butoxycarbonyl)(hydroxy)amino)piperidine-1-carboxylate (S14)



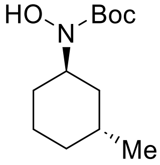
Prepared according to general procedure II using benzyl 4-((benzoyloxy)(tert-butoxycarbonyl)amino)piperidine-1-carboxylate **S5** (1.50 g, 3.30 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate afforded **S14** in 94% yield (1.09 g, 3.11 mmol).

^{1}H NMR: (500 MHz, CDCl$_3$) δ 7.40 – 7.29 (m, 5H, C**H$_{Ar}$**), 6.37 (br s, 1H, -O**H**), 5.12 (br s, 2H, PhC**H$_2$**O-), 4.27 (m, 2H, -NC**H$_2$**-), 3.98 – 3.88 (m, 1H, -NC**H**-), 2.81 (br s, 2H, -NC**H$_2$**-), 1.87 (m, 2H, -C**H$_2$**-), 1.69 (m, 2H, -C**H$_2$**-), 1.49 (s, 9H, -C**H$_3$**).

^{13}C NMR: (126 MHz, CDCl$_3$) δ 156.8, 155.3, 136.9, 128.6, 128.2, 128.0, 82.4, 67.3, 56.3, 43.4, 28.5.

HRMS (DART-MS): m/z [M + H]$^+$ calcd for $C_{18}H_{27}N_2O_5$: 351.1914 found 351.1953.

tert-butyl hydroxy((1R,3R)-3-methylcyclohexyl)carbamate (S15)



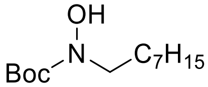
Prepared according to general procedure II using tert-butyl (benzoyloxy)((1R,3R)-3-methylcyclohexyl)carbamate **S6** (330 mg, 0.990 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate afforded **S15** in 82% yield (185 mg, 0.807 mmol).

^{1}H NMR: (500 MHz, $CDCl_3$) δ 6.27 – 6.12 (br s, 1H, -O**H**), 4.00 (m, 1H, -NC**H**-), 2.14 (m, 1H, -C**H₂**-), 1.88 (m, 1H, -C**H₂**-), 1.74 – 1.60 (m, 3H, -C**H₂**-, -C**H**CH₃), 1.49 (m, 12H, -C**H₂**- -C**H₃**), 1.39 – 1.30 (m, 1H, -C**H₂**-), 0.99 (d, *J* = 7.2 Hz, 3H, -C**H₃**).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 157.1, 81.8, 53.8, 35.0, 31.1, 29.5, 28.5, 28.0, 20.5, 18.5.

HRMS (DART-MS): m/z $[M + H]^+$ calcd for $C_{12}H_{24}NO_3$: 230.1751 found 230.1762.

tert-butyl hydroxy(octyl)carbamate (S16)



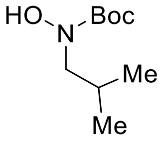
Prepared according to general procedure II using tert-butyl (benzoyloxy)(octyl)carbamate **S7** (1.80 g, 5.15 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate afforded **S16** in 65% yield (827 mg, 3.37 mmol).

^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.52 (br s, 1H, -O**H**), 3.45 (t, *J* = 7.0 Hz, 2H, -NC**H₂**-), 1.61 (m, 2H, -C**H₂**-), 1.46 (s, 9H, -C**H₃**), 1.34 – 1.20 (m, 10H, -C**H₂**-), 0.87 (m, 3H, -C**H₃**).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 157.2, 81.6, 50.2, 32.0, 29.4, 29.3, 28.5, 27.1, 26.7, 22.8, 14.2.

HRMS (DART-MS): m/z $[M + H]^+$ calcd for $C_{13}H_{28}NO_3$: 246.2064 found 246.2075.

tert-butyl hydroxy(isobutyl)carbamate (S17)



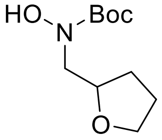
Prepared according to general procedure II using tert-butyl (benzoyloxy)(isobutyl)carbamate **S8** (1.80 g, 6.14 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate afforded **(S17)** in 59% yield (686 mg, 3.63 mmol).

^{1}H NMR: (500 MHz, CDCl$_3$) δ 7.85 (br s, 1H, -O**H**), 3.28 (d, *J* = 7.1 Hz, 2H, -NC**H$_2$**-), 2.05 (m, 1H, -C**H**-), 1.45 (s, 9H, -C**H$_3$**), 0.90 (d, *J* = 6.7 Hz, 6H, -C**H$_3$**).

^{13}C NMR: (126 MHz, CDCl$_3$) δ 157.1, 81.5, 57.6, 28.5, 26.7, 20.1.

HRMS (DART-MS): m/z [M + H]$^+$ calcd for $C_9H_{20}NO_3$: 190.1438 found 190.1459.

tert-butyl hydroxy((tetrahydrofuran-2-yl)methyl)carbamate (S18)



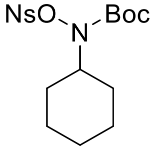
Prepared according to general procedure II using tert-butyl (benzoyloxy)((tetrahydrofuran-2-yl)methyl)carbamate **S9** (1.20 g, 3.73 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate afforded **S18** in 85% yield (689 mg, 3.17 mmol).

^{1}H NMR: (500 MHz, CDCl$_3$) δ 7.49 (s, 1H, -O**H**), 4.19 (m, 1H, -OC**H**-), 3.85 (m, 1H, -OC**H$_2$**-), 3.75 (m, 1H, -OC**H$_2$**-), 3.56 (dd, *J* = 14.4, 7.1 Hz, 1H, -NC**H$_2$**-), 3.49 (dd, *J* = 14.5, 5.0 Hz, 1H, -NC**H$_2$**-), 1.98 (m, 1H, -C**H$_2$**-), 1.88 (m, 2H, -C**H$_2$**-), 1.60 (m, 1H, -C**H$_2$**-), 1.45 (s, 9H, -C**H$_3$**).

^{13}C NMR: (126 MHz, CDCl$_3$) δ 156.8, 81.6, 76.7, 68.1, 54.0, 29.1, 28.4, 25.5.

HRMS (DART-MS): m/z [M + H]$^+$ calcd for $C_{10}H_{20}NO_4$: 218.1387 found 218.1409.

tert-butyl cyclohexyl(((4-nitrophenyl)sulfonyl)oxy)carbamate (S19)



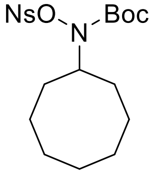
Prepared according to general procedure III using tert-butyl cyclohexyl(hydroxy)carbamate **S10** (496 mg, 2.30 mmol), triethylamine (256 mg, 2.53 mmol), and nosyl chloride (561 mg, 2.53 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate afforded **S19** in 66% yield (606 mg, 1.51 mmol).

^{1}H NMR: (400 MHz, CDCl$_3$) δ 8.37 (m, 2H, C**H**$_{Ar}$), 8.18 (m, 2H, C**H**$_{Ar}$), 3.76 (m, 1H, -NC**H**-), 1.82 (m, 4H, -C**H**$_2$-), 1.68 – 1.47 (m, 3H, -C**H**$_2$-), 1.28 (m, 11H, -C**H**$_2$-, -C**H**$_3$), 1.09 (m, 1H, -C**H**$_2$-).

^{13}C NMR: (101 MHz, CDCl$_3$) δ 156.1, 151.1, 140.8, 131.1, 124.0, 84.2, 64.5, 29.6, 27.9, 25.9, 25.3.

HRMS (DART-MS): m/z [M + H]$^+$ calcd for $C_{17}H_{25}N_2O_7S$: 401.1377 found 401.1423.

tert-butyl cyclooctyl(((4-nitrophenyl)sulfonyl)oxy)carbamate (S20)



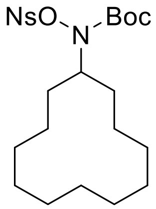
Prepared according to general procedure III using tert-butyl cyclohexyl(hydroxy)carbamate **S11** (550 mg, 2.26 mmol), triethylamine (274 mg, 2.71 mmol), and nosyl chloride (551 mg, 2.49 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate afforded **S20** in 64% yield (621 mg, 1.45 mmol).

^{1}H NMR: (500 MHz, CDCl$_3$) δ 8.37 (m, 2H, C**H**$_{Ar}$), 8.18 (m, 2H, C**H**$_{Ar}$), 3.97 (m, 1H, -NC**H**-), 1.83 (m, 4H, -C**H**$_2$-), 1.72 (m, 2H, -C**H**$_2$-), 1.59 (m, 1H, -C**H**$_2$-), 1.52 (m, 6H, -C**H**$_2$-), 1.46 – 1.38 (m, 1H, -C**H**$_2$-), 1.28 (s, 9H, -C**H**$_3$).

^{13}C NMR: (126 MHz, CDCl$_3$) δ 156.0, 151.1, 140.8, 131.1, 124.0, 84.1, 66.1, 31.2, 27.9, 26.4, 26.3.

HRMS (DART-MS): m/z [M + H]$^+$ calcd for $C_{19}H_{29}N_2O_7S$: 429.169 found 429.1732.

tert-butyl cyclododecyl(((4-nitrophenyl)sulfonyl)oxy)carbamate (S21)



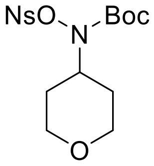
Prepared according to general procedure III using tert-butyl cyclododecyl(hydroxy)carbamate **S12** (500 mg, 1.67 mmol), triethylamine (186 mg, 1.84 mmol), and nosyl chloride (407 mg, 1.84 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate afforded **S22** in 40% yield (324 mg, 0.669 mmol).

^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.37 (m, 2H, C**H$_{Ar}$**), 8.22 – 8.15 (m, 2H, C**H$_{Ar}$**), 4.12 (m, 1H, -NC**H**-), 1.75 – 1.65 (m, 2H, -C**H$_2$**-), 1.62 – 1.43 (m, 4H, -C**H$_2$**-), 1.30 (m, 25H, -C**H$_2$**-, -C**H$_3$**).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 156.5, 151.1, 140.9, 131.0, 124.0, 84.1, 60.1, 27.9, 24.0, 22.8, 22.4, 22.2.

HRMS (DART-MS): m/z $[M + H]^+$ calcd for $C_{23}H_{37}N_2O_7S$: 485.2316 found 485.2375.

tert-butyl (((4-nitrophenyl)sulfonyl)oxy)(tetrahydro-2H-pyran-4-yl)carbamate (S22)



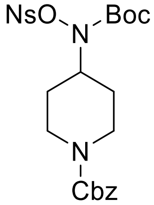
Prepared according to general procedure III using tert-butyl hydroxy(tetrahydro-2H-pyran-4-yl)carbamate **S13** (330 mg, 1.52 mmol), triethylamine (169 mg, 1.67 mmol), and nosyl chloride (370 mg, 1.67 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate afforded **S22** in 42% yield (257 mg, 0.639 mmol).

^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.38 (m, 2H, C**H$_{Ar}$**), 8.17 (m, 2H, C**H$_{Ar}$**), 4.07 – 3.96 (m, 3H, -NC**H**-, -OC**H$_2$**-), 3.37 (m, 2H, -OC**H$_2$**-), 1.91 (m, 2H, -C**H$_2$**-), 1.70 (m, 2H, -C**H$_2$**-), 1.28 (s, 9H, -C**H$_3$**).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 155.6, 151.2, 140.5, 131.1, 124.1, 84.7, 67.3, 61.2, 29.7, 27.8.

HRMS (DART-MS): m/z $[M + H]^+$ calcd for $C_{16}H_{23}N_2O_8S$: 403.1170 found 403.1125.

benzyl 4-((tert-butoxycarbonyl)(((4-nitrophenyl)sulfonyl)oxy)amino)piperidine-1-carboxylate (S23)



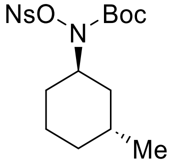
Prepared according to general procedure III using benzyl 4-((tert-butoxycarbonyl)(hydroxy)amino)piperidine-1-carboxylate **S14** (600 mg, 1.71 mmol), triethylamine (191 mg, 1.88 mmol), and nosyl chloride (417 mg, 1.88 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate afforded **S23** in 53% yield (486 mg, 0.907 mmol).

^{1}H NMR: (500 MHz, CDCl$_3$) δ 8.38 (m, 2H, C**H$_{\mathbf{Ar}}$**), 8.17 (m, 2H, C**H$_{\mathbf{Ar}}$**), 7.50 – 7.29 (m, 5H, C**H$_{\mathbf{Ar}}$**), 5.13 (br s, 2H, PhC**H$_2$**O-), 4.31 (m, 2H, -NC**H$_2$**-), 3.96 (m, 1H, -NC**H**-), 2.77 (br s, 2H, -NC**H$_2$**-), 1.80 (br s, 4H, -C**H$_2$**-), 1.27 (s, 9H, -C**H$_3$**).

^{13}C NMR: (126 MHz, CDCl$_3$) δ 155.5, 155.1, 151.2, 140.5, 136.7, 131.1, 128.7, 128.2, 128.1, 124.1, 84.9, 67.5, 62.3, 43.5, 27.9.

HRMS (DART-MS): m/z $[M + H]^+$ calcd for $C_{24}H_{30}N_3O_9S$: 536.1697 found 536.2711.

tert-butyl ((1R,3R)-3-methylcyclohexyl)(((4-nitrophenyl)sulfonyl)oxy)carbamate (S24)



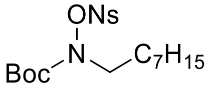
Prepared according to general procedure III using tert-butyl hydroxy((1R,3R)-3-methylcyclohexyl)carbamate **S15** (120 mg, 0.523 mmol), triethylamine (58 mg, 0.576 mmol), and nosyl chloride (128 mg, 0.576 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate afforded **S24** in 54% yield (117 mg, 0.282 mmol).

^{1}H NMR: (500 MHz, CDCl$_3$) δ 8.41 – 8.32 (m, 2H, C**H$_{\mathbf{Ar}}$**), 8.22 – 8.15 (m, 2H, C**H$_{\mathbf{Ar}}$**), 4.06 – 3.96 (m, 1H, -NC**H**-), 2.16 (m, 1H, -C**H$_2$-**), 1.78 (m, 2H, -C**H$_2$-**), 1.67 – 1.48 (m, 4H, -C**H$_2$-**C**H**CH$_3$), 1.40 (m, 2H, -C**H$_2$-**), 1.29 (s, 9H, -C**H$_3$**), 0.97 (d, J = 7.3 Hz, 3H, -C**H$_3$**).

^{13}C NMR: (126 MHz, CDCl$_3$) δ 156.2, 151.1, 140.9, 131.1, 124.0, 84.2, 59.7, 30.6, 28.4, 28.1, 27.9, 20.4, 17.9.

HRMS (DART-MS): m/z $[M + H]^+$ calcd for 415.1533 $C_{18}H_{27}N_2O_7S$: found 415.1554.

tert-butyl (((4-nitrophenyl)sulfonyl)oxy)(octyl)carbamate (S25)



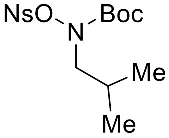
Prepared according to general procedure III using tert-butyl hydroxy(octyl)carbamate **S16** (800 mg, 3.26 mmol), triethylamine (363 mg, 3.59 mmol), and nosyl chloride (795 mg, 3.59 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate afforded **S25** in 69% yield (970 mg, 2.253 mmol).

^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.41 – 8.35 (m, 2H, C**H$_{Ar}$**), 8.19 (m, 2H, C**H$_{Ar}$**), 3.63 (br s, 2H, -NC**H$_2$**-), 1.62 (br s, 2H, -C**H$_2$**-), 1.32 – 1.24 (m, 10H, -C**H$_2$**-), 1.23 (s, 9H, -C**H$_3$**), 0.87 (m, 3H, -C**H$_3$**).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.3, 151.2, 140.1, 131.2, 124.0, 84.0, 53.7, 31.9, 29.3, 29.3, 27.8, 26.6, 25.8, 22.8, 14.2.

HRMS (DART-MS): m/z $[M + H]^+$ calcd for 431.1846 $C_{19}H_{31}N_2O_7S$: found 431.1868.

tert-butyl isobutyl(((4-nitrophenyl)sulfonyl)oxy)carbamate (S26)



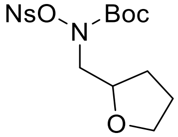
Prepared according to general procedure III using tert-butyl hydroxy(isobutyl)carbamate **S17** (500 mg, 2.64 mmol), triethylamine (294 mg, 2.91 mmol), and nosyl chloride (644 mg, 2.91 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate afforded **S26** in 58% yield (577 mg, 1.54 mmol).

^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.42 – 8.35 (m, 2H, C**H$_{Ar}$**), 8.22 – 8.16 (m, 2H, C**H$_{Ar}$**), 3.53 (m, 2H, -NC**H$_2$**-), 2.18 (m, 1H, -C**H**-), 1.22 (s, 9H, -C**H$_3$**), 0.91 (d, *J* = 6.7 Hz, 6H, -C**H$_3$**).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 155.2, 151.3, 140.1, 131.2, 124.0, 83.9, 60.1, 27.8, 26.2, 20.1.

HRMS (DART-MS): m/z $[M + H]^+$ calcd for $C_{15}H_{23}N_2O_7S$: 375.1220 found 375.1261.

tert-butyl (((4-nitrophenyl)sulfonyl)oxy)((tetrahydrofuran-2-yl)methyl)carbamate (S27)



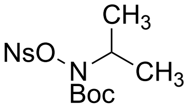
Prepared according to general procedure III using tert-butyl hydroxy((tetrahydrofuran-2-yl)methyl)carbamate **S18** (500 mg, 2.30 mmol), triethylamine (256 mg, 2.53 mmol), and nosyl chloride (561 mg, 2.53 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate afforded **S27** in 67% yield (623 mg, 1.55 mmol).

^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.38 (m, 2H, C**H$_{Ar}$**), 8.20 (m, 2H, C**H$_{Ar}$**), 4.36 (br s, 1H, -OC**H**-), 3.76 (m, 3H, -NC**H$_2$**-, -OC**H$_2$**-), 3.58 (br s, 1H, -OC**H$_2$**-), 2.04 (m, 1H, -C**H$_2$**-), 1.96 – 1.84 (m, 2H, -C**H$_2$**-), 1.56 (m, 1H, -C**H$_2$**-), 1.22 (s, 9H, -C**H$_3$**).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 151.2, 140.0, 131.3, 124.0, 83.9, 67.9, 56.8, 29.3, 27.7, 25.7.

HRMS (DART-MS): m/z $[M + H]^+$ calcd for $C_{16}H_{23}N_2O_8S$: 403.1170 found 403.1214.

tert-butyl isopropyl(((4-nitrophenyl)sulfonyl)oxy)carbamate (S28)



Prepared according to general procedure III using *tert*-butyl hydroxy(isopropyl)carbamate (2.3 g, 13.1 mmol), triethylamine (1.6 g, 15.8 mmol), and nosyl chloride (2.9 g, 13.1 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate afforded **S28** in 85% yield (4.0 g, 11.0 mmol).

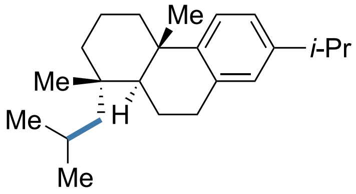
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 – 8.28 (m, 2H, -C**H**$_{Ar}$), 8.14 – 8.10 (m, 2H, -C**H**$_{Ar}$), 4.10 (p, *J* = 6.7 Hz, 1H, -C**H**-), 1.22 (s, 9H, -C(C**H**$_3$)$_3$), 1.15 (d, *J* = 6.7 Hz, 6H, -(C**H**$_3$)$_2$).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 156.1, 151.1, 140.8, 131.1, 124.2, 84.3, 56.9, 27.8, 19.2.

HRMS (DART-MS): *m/z* $[M + H]^+$ calcd for $C_{14}H_{21}N_2O_7S$: 361.1064 found 361.1055.

5. Product Characterization

(1S,4aS,10aS)-1-isobutyl-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (7)



Prepared according to general procedure A using *(+)-leelamine* (29 mg, 0.10 mmol) and *N*-isopropyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (38 mg, 0.10 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate ($R_f = 0.6$) afforded **7** in 85% yield (27 mg, 0.085 mmol).

Scale-up: Prepared according to general procedure A using *(+)-leelamine* (290 mg, 1.0 mmol) and *N*-isopropyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (380 mg, 1.0 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate ($R_f = 0.6$) afforded **7** in 62% yield (197 mg, 0.62 mmol).

^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.1 Hz, 1H, -C**H**$_{Ar}$), 6.94 (d, *J* = 8.2, 1H, -C**H**$_{Ar}$), 6.83 (s, 1H, -C**H**$_{Ar}$), 2.84 – 2.72 (m, 4H, -C**H**$_2$-, -C**H**-), 2.30 – 2.24 (m, 1H, -C**H**-), 1.87 – 1.68 (m, 5H, -C**H**-, -C**H**$_3$), 1.47 – 1.39 (m, 6H, -C**H**$_3$), 1.15 (d, *J* = 6.8 Hz, 14H, -C**H**$_2$-, -C**H**-, -C**H**$_3$), 1.09 (s, 3H, -C**H**$_3$).

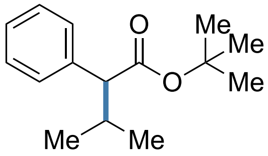
^{13}C NMR: (126 MHz, $CDCl_3$) δ 146.2, 146.0, 134.5, 127.0, 124.2, 124.0, 49.9, 42.8, 37.8, 36.3, 33.5, 32.0, 29.8, 28.2, 27.6, 25.2, 24.0, 24.0, 21.4, 17.8, 14.0.

IR (ATR): 2980, 2947, 2831, 2359, 2340, 1700, 1648, 1617, 1576, 1518, 1448, 1395, 1115, 1022, 953.

$[\alpha]_D$ +33.3 (c 0.6, 20ºC, MeOH)

HRMS (DART-MS): *m/z* $[M + H]^+$ calcd for $C_{23}H_{37}$: 313.2895 found 313.2901.

tert-butyl 3-methyl-2-phenylbutanoate (8)



Prepared according to general procedure A using *t-Bu-DL-phenylglycinate* (21 mg, 0.10 mmol) and *N*-isopropyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (38 mg, 0.10 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate ($R_f = 0.5$) afforded **8** in 91% yield (21 mg, 0.091 mmol).

Scale-up: Prepared according to general procedure A using *t-Bu-phenylglycinate* (210 mg, 1.0 mmol) and *N*-isopropyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (380 mg, 1.0 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate ($R_f = 0.5$) afforded **8** in 71% yield (168 mg, 0.71 mmol).

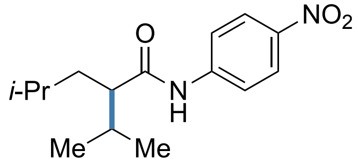
^{1}H NMR: (500 MHz, MeOD) δ 7.30 – 7.16 (m, 5H, -C**H**$_{Ar}$), 3.09 (d, *J* = 6.8 Hz, 1H, -C**H**C(O)-), 1.99 (m, 1H, -C**H**-), 1.31 (s, 9H, -C(C**H**$_3$)$_3$), 0.79 (d *J* = 6.6 Hz, 3H, -(C**H**$_3$)$_2$) 0.81 (d, *J* = 6.6 Hz, 3H, -(C**H**$_3$)$_2$).

^{13}C NMR: (126 MHz, MeOD) δ 169.1, 135.6, 130.6, 130.0, 128.8, 85.1, 55.5, 37.7, 28.0, 23.1, 22.9.

IR (ATR): 2978, 2936, 1723, 1636, 1454, 1368, 1310, 1249, 1153, 1021, 842.

HRMS (DART-MS): *m/z* $[M + H]^+$ calcd for $C_{15}H_{23}O_2$: 235.1693 found 235.1685.

2-isopropyl-4-methyl-N-(4-nitrophenyl)pentanamide (9)



Prepared according to general procedure A using *L-leucine p-nitroanilide* (25 mg, 0.10 mmol) and *N*-isopropyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (38 mg, 0.10 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate afforded ($R_f = 0.3$) **9** in 91% yield (25 mg, 0.091 mmol).

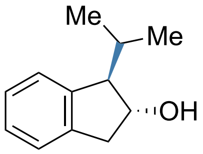
^{1}H NMR: (500 MHz, CDCl$_3$) δ 8.11 – 7.97 (m, 2H, -C**H**$_{Ar}$), 7.80 – 7.66 (m, 2H, -C**H**$_{Ar}$), 1.97 (m, 1H, -C**H**-), 1.71 (m, 1H, -C**H**-), 1.66 – 1.58 (m, 2H, -C**H**$_2$-), 1.02 – 0.99 (m, 1H, -C**H**-), 0.88 (d, *J* = 5.6 Hz, 6H, -(C**H**$_3$)$_2$), 0.76 (d, *J* = 6.6 Hz, 3H, -(C**H**$_3$)$_2$), 0.71 (d, *J* = 6.6 Hz, 3H, -(C**H**$_3$)$_2$).

^{13}C NMR: (126 MHz, CDCl$_3$) δ 168.4, 143.7, 143.6, 124.7, 119.6, 52.2, 40.3, 36.6, 28.1, 24.4, 22.3, 21.8.

IR (ATR): 2958, 2917, 2849, 1685, 1597, 1509, 1410, 1342, 1302, 1253, 1176, 1112, 854, 752.

HRMS (DART-MS): *m/z* $[M + H]^+$ calcd for $C_{15}H_{23}N_2O_3$: 279.1703 found 279.1713.

(1R,2R)-1-isopropyl-2,3-dihydro-1H-inden-2-ol (10)



Prepared according to general procedure A using *(1R,2R)-1-amino-2,3-dihydro-1H-inden-2-ol* (30 mg, 0.20 mmol) and *N*-isopropyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (76 mg, 0.20 mmol). Purification by column chromatography on silica gel using 90:10 hexanes: ethyl acetate (R_f = 0.3) afforded **10** in 88% yield (15 mg, 0.088 mmol, *dr*= >98:2). NOTE: *(1S,2R)-1-amino-2,3-dihydro-1H-inden-2-ol* afforded the same product when used as starting material.

^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H, -C**H**$_{Ar}$), 7.28 – 7.23 (m, 2H, -C**H**$_{Ar}$), 4.76 (m, 1H, -C**H**OH), 3.30 (m, 1H, - ArC**H**$_2$-), 3.27 (m, 1H, ArC**H**$_2$-), 3.00 (m, 1H, ArC**H**-), 1.62 – 1.50 (m, 1H, -C**H**-), 0.95 (d, *J* = 6.6 Hz, 6H, -(C**H**$_3$)$_2$).

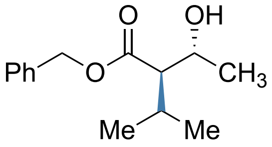
^{13}C NMR: (126 MHz, $CDCl_3$) δ 140.8, 126.7, 126.5, 125.3, 125.0, 73.2, 42.7, 36.8, 28.3, 22.7.

IR (ATR): 3336, 3197, 3070, 3019, 2981, 2949, 2888, 2746, 1607, 1475, 1459, 1440, 1373, 1297, 1211, 1080, 1020, 840, 744.

$[\alpha]_D$ +24.6 (c 0.65, 20ºC, MeOH)

HRMS (DART-MS): *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{17}O$: 177.1274 found 177.1270.

benzyl (2R,3R)-3-hydroxy-2-isopropylbutanoate (11)



Prepared according to general procedure A using *L-threonine benzyl ester* (21 mg, 0.10 mmol) and *N*-isopropyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (38 mg, 0.10 mmol). Purification by column chromatography on silica gel using 70:30 hexanes: ethyl acetate (R_f = 0.4) afforded **11** in 75% yield (18 mg, 0.075 mmol, *dr*= >98:2). Relative stereochemistry was determined by comparison to known analogue.[9]

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(9) Cuetos, A.; Rioz-Martínez, A.; Bisogno, F. R.; Grischek, B.; Lavandera, I.; de Gonzalo, G.; Kroutil, W.; Gotor, V. Access to Enantiopure α-Alkyl-β-Hydroxy Esters through Dynamic Kinetic Resolutions Employing Purified/Overexpressed Alcohol Dehydrogenases. *Adv. Synth. Catal.* **2012**, *354*, 1743–1749.

^{1}H NMR: (500 MHz, CDCl$_3$) δ 7.45 – 7.34 (m, 5H, -C**H**$_{Ar}$), 5.34 (ds 2H, -C**H**$_2$-), 5.09 (m, 1H, -C**H**OH-), 3.49 (m, 1H, -C**H**-), 1.52 (m, 1H, -C**H**-), 1.44 (d, *J* = 6.6 Hz, 3H, -C**H**$_3$), 0.93 (d, *J* = 6.8 Hz, 6H, -(C**H**$_3$)$_2$).

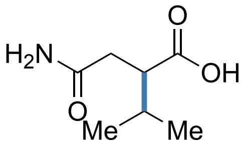
^{13}C NMR: (126 MHz, CDCl$_3$) δ 162.9, 134.9, 129.0, 128.3, 109.1, 81.5, 67.9, 31.4, 28.9, 27.3, 20.3.

IR (ATR): 2972, 2917, 2848, 1636, 1541, 1452, 1419, 1389, 1261, 1144, 1078, 1077, 1055, 1005, 967, 855, 827, 748.

[α]$_D$: insufficient sample for absorption

HRMS (DART-MS): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{21}O_3$: 237.1485 found 237.1393.

4-amino-2-isopropyl-4-oxobutanoic acid (12)



Prepared according to general procedure B using *L-asparagine* (26 mg, 0.20 mmol) and *N*-isopropyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (76 mg, 0.20 mmol). Purification by column chromatography on silica gel using 80:20 dichloromethane: methanol (R_f = 0.1) afforded **12** in 61% yield (19 mg, 0.122 mmol).

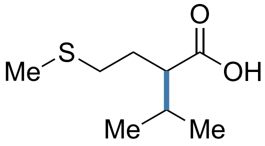
^{1}H NMR: (500 MHz, MeOD) δ 2.30 (d, *J* = 3.1 Hz, 2H, -H$_2$NC(O)C**H**$_2$-), 2.11 (m, 1H, -C**H**-), 1.54 – 1.44 (m, 1H, -C**H**C(O)OH-), 0.91 (d, 3H, *J* = 6.1 Hz, -(C**H**$_3$)$_2$), 0.88 (d, 3H, *J* = 6.1 Hz, -(C**H**$_3$)$_2$).

^{13}C NMR: (126 MHz, MeOD) δ 175.3, 173.9, 52.3, 35.4, 25.5, 23.2, 22.7.

IR (ATR): 3353, 2975, 2917, 2848, 1746, 1647, 1530, 1386, 1350, 1198, 1159, 1123, 1109, 1009, 853, 777, 742.

HRMS (DART-MS): *m*/*z* [M + H]$^+$ calcd for $C_7H_{14}NO_3$: 160.0968 found 160.0975.

2-isopropyl-4-(methylthio)butanoic acid (13)



Prepared according to general procedure B using *L-methionine* (30 mg, 0.20 mmol) and *N*-isopropyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (76 mg, 0.20 mmol). Purification by column chromatography on silica gel using 60:40 hexanes: ethyl acetate ($R_f = 0.2$) afforded **13** in 82% yield (29 mg, 0.164 mmol).

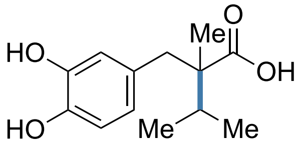
^{1}H NMR: (500 MHz, MeOD) δ 2.66 (m, 2H, -SC**H**$_2$-), 2.30 – 2.21 (m, 2H, -C**H**-), 2.13 (m, 2H, -C**H**$_2$-), 2.10 (s, 3H, -SC**H**$_3$), 0.90 (d, *J* = 6.6 Hz, 3H, -(C**H**$_3$)$_2$), 0.88 (d, *J* = 6.6 Hz, 3H, -(C**H**$_3$)$_2$).

^{13}C NMR: (126 MHz, MeOD) δ 174.9, 53.2, 31.1, 30.2, 25.7, 23.0, 15.0.

IR (ATR): 2980, 2922, 1727, 1657, 1430, 1184, 1139, 1033, 969, 841, 798, 723.

HRMS (DART-MS): *m*/*z* $[M + H]^+$ calcd for $C_8H_{17}O_2S$: 177.0944 found 177.0937.

2-(3,4-dihydroxybenzyl)-2,3-dimethylbutanoic acid (14)



Prepared according to general procedure B using *(S)-methyldopa* (21 mg, 0.10 mmol) and *N*-isopropyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (38 mg, 0.10 mmol). Purification by column chromatography on silica gel using 60:40 hexanes: ethyl acetate ($R_f = 0.2$) afforded **14** in 59% yield (14 mg, 0.059 mmol).

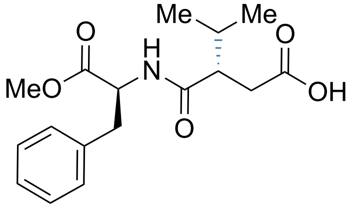
^{1}H NMR: (500 MHz, MeOD) δ 6.73 – 6.70 (m, 2H, -C**H**$_{Ar}$), 6.58 (d, *J* = 8.1Hz, 1H, -C**H**$_{Ar}$), 3.15 (d, *J* = 14.2 Hz, 1H, -C**H**$_2$-), 2.74 (d, *J* = 14.2 Hz, 1H, -C**H**$_2$-), 1.47 (m, 4H, -C**H**$_{3,}$ -C**H**-), 0.88 (d, *J* = 6.6 Hz, 6H, -(C**H**$_3$)$_2$).

^{13}C NMR: (126 MHz, MeOD) δ 175.0, 145.1, 144.6, 125.9, 121.3, 116.9, 115.1, 61.5, 36.6, 28.1, 22.1, 21.7.

IR (ATR): 3375, 2470, 1598, 1518, 1438, 1401, 1370, 1288, 1208, 1117, 969, 872.

HRMS (DART-MS): *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{19}O_4$: 239.1278 found 239.1285.

(*S*)-3-(((*S*)-1-methoxy-1-oxo-3-phenylpropan-2-yl)carbamoyl)-4-methylpentanoic acid (15)



Prepared according to general procedure B using *aspartame* (29 mg, 0.10 mmol) and *N*-isopropyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (38 mg, 0.10 mmol). Purification by column chromatography on silica gel using 60:40 hexanes: ethyl acetate ($R_f = 0.2$) afforded **15** in 68% yield (22 mg, 0.068 mmol, *dr*= 4:1). Major diastereomer assigned by hydrolysis followed by comparison of optical rotation data of product to literature reference (see below). [10]

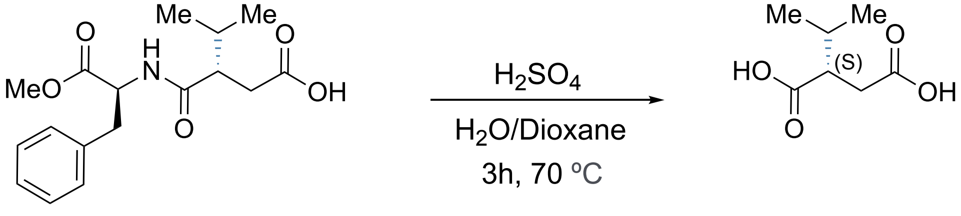
^{1}H NMR: (500 MHz, MeOD, major diastereomer) δ 7.36 – 7.32 (m, 2H, -C**H**$_{Ar}$),), 7.26 (m, 3H, -C**H**$_{Ar}$), 4.13 (dd, *J* = 8.9, 5.0 Hz, 1H, -NC**H**-), 3.72 (s, 3H, -OC**H**$_3$), 3.19 (d, *J* = 5.9 Hz, 1H, -C**H**$_2$COOH), 3.06 (d, *J* = 8.8 Hz, 1H, -C**H**$_2$COOH), 2.75 (d, *J* = 5.0 Hz, 1H, ArC**H**$_2$-), 2.63 (d, *J* = 8.9 Hz, 1H, ArC**H**$_2$-), 2.57 – 2.50 (m, 1H, -C**H**-), 2.14 (m, 1H, -C**H**-), 0.97 (d, *J* = 6.4 Hz, 6H, -(C**H**$_3$)$_2$).

^{13}C NMR: (126 MHz, MeOD) δ 176.3, 173.6, 170.4, 137.5, 130.1, 129.7, 128.1, 55.7, 51.8, 46.3, 38.1, 35.8, 26.2, 14.9.

IR (ATR): 3396, 2958, 2916, 2848, 1736, 1652, 1588, 1465, 1223, 1203, 1118, 970, 765, 700.

HRMS (DART-MS): *m*/*z* $[M + H]^+$ calcd for $C_{17}H_{24}NO_5$: 322.1649 found 322.1653.

Stereochemical Assignment:



A solution of **15** (22 mg, 0.068 mmol, *dr*= 4:1) in 3M H_2SO_4 in 1:1 H_2O/1,4-dioxane (2 mL) was heated at 75 °C. After 3h, the reaction mixture was cooled to room temperature, diluted with water and extracted with dichloromethane (3 x 5mL). The resultant organic phase was dried with

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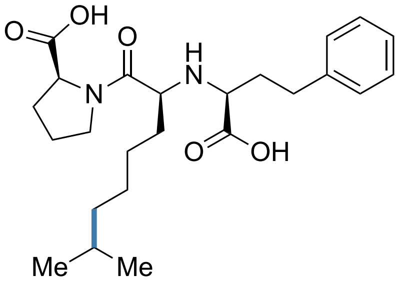
(10) Deyo, D. T.; Aebi, J. D.; Rich, D. H. Preparative-Scale, Facile Synthesis of (2R,4E)-2-Methyl-4-Hexenal: A Key Intermediate of (2S,3R,4R,6E)-3-Hydroxy-4-Methyl-2-Methylamino-6-Octenoic Acid (MeB. *Synthesis* **1988**, *1988*, 608–610.

sodium sulfate and concentrated to yield 2-isopropylsuccinic acid, which matched ^{1}H NMR literature values[11] and was directly subject to optical rotation measurement.

Optical rotation: $[\alpha]_D$ –16.0 (c 0.75, 20ºC, MeOH), major diastereomer assigned as (S)-enantiomer

Literature reference for pure enantiomers:
[(*S*)-2-isopropylsuccinic acid] $[\alpha]_D$ –17.1 (c 1.0, 25ºC, CH_3Cl)[12]
[(*R*)-2-isopropylsuccinic acid] $[\alpha]_D$ +15.0 (c 1.05, 20ºC, EtOH)[13]

((S)-2-(((S)-1-carboxy-3-phenylpropyl)amino)-7-methyloctanoyl)-L-proline (16)



Prepared according to general procedure B using *(S)-lisinopril* (41 mg, 0.10 mmol) and *N*-isopropyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (38 mg, 0.10 mmol). Purification by column chromatography on silica gel using 90:10 dichloromethane: methanol (R_f = 0.5) afforded **16** in 38% yield (16 mg, 0.038 mmol).

^{1}H NMR: (500 MHz, MeOD) δ 7.25 – 7.08 (m, 5H, -C**H**$_{Ar}$), 4.22 (m, 1H, -NC**H**-), 3.61 (m, 2H, -NC**H**$_2$-), 3.38 (t, *J* = 6.1 Hz, 1H, -NC**H**-), 2.95 (q, *J* = 7.3 Hz, 2H, -C**H**$_2$-), 2.31 – 2.07 (m, 4H, -C**H**$_2$-), 1.95 (m, 4H, -C**H**$_2$-, -C**H**-), 1.65 (m, 4H, -C**H**$_2$-), 1.51 – 1.38 (m, 1H, -C**H-**), 1.16 – 1.11 (m, 2H, -C**H**$_2$-), 0.85 (d, *J* = 6.6 Hz, 6H, -(C**H**$_3$)$_2$).

^{13}C NMR: (126 MHz, MeOD) δ 175.4, 172.0, 167.4, 128.1, 127.0, 125.8, 123.3, 121.8, 62.1, 61.1, 59.9, 38.8, 36.6, 32.9, 31.2, 29.5, 28.9, 28.1, 26.4, 24.4, 21.7, 20.7.

IR (ATR): 3276, 2972, 2949, 2831, 1699, 1645, 1614, 1572, 1516, 1439, 1394, 1295, 1120, 1022, 951.

$[\alpha]_D$ –95.7 (c 0.7, 20ºC, MeOH)

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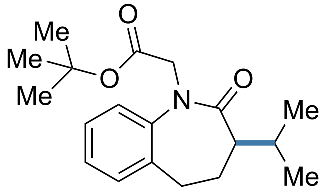
(11) Zhu, R.; Jiang, J.-L.; Li, X.-L.; Deng, J.; Fu, Y. A Comprehensive Study on Metal Triflate-Promoted Hydrogenolysis of Lactones to Carboxylic Acids: From Synthetic and Mechanistic Perspectives. *ACS Catal.* **2017**, *7*, 7520–7528.

(12) Hein, J. E.; Zimmerman, J.; Sibi, M. P.; Hultin, P. G. Stereoselective Conjugate Radical Additions: Application of a Fluorous Oxazolidinone Chiral Auxiliary for Efficient Tin Removal. *Org. Lett.* **2005**, *7*, 2755–2758.

(13) Edwards, J. D.; Ichikawa, N. Preparation of (S)-(—)-2,4-Dimethyl-4-Isopropylcyclopent-2-Enone. *J. Org. Chem.* **1964**, *29*, 503–504.

HRMS (DART-MS): *m/z* $[M + H]^+$ calcd for $C_{24}H_{37}N_2O_5$: 433.2697 found 433.2703.

tert-butyl 2-(3-isopropyl-2-oxo-2,3,4,5-tetrahydro-1H-benzo[b]azepin-1-yl)acetate (17)



Prepared according to general procedure A using *tert-butyl (S)-2-(3-amino-2-oxo-2,3,4,5-tetrahydro-1H-benzo[b]azepin-1-yl)acetate* (29 mg, 0.10 mmol) and *N*-isopropyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (38 mg, 0.10 mmol). Purification by column chromatography on silica gel using 60:40 hexanes: ethyl acetate ($R_f = 0.4$) afforded **17** in 76% yield (24 mg, 0.076 mmol).

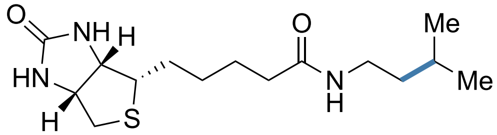
^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.28 – 7.04 (m, 4H, -C**H**$_{Ar}$), 4.54 – 4.29 (m, 2H, -NC**H**$_2$C(O)-), 3.40 – 3.37 (m, 1H, ArC**H**$_2$-), 3.22 – 3.16 (m, 1H, ArC**H**$_2$-), 2.55 (m, 1H, -C**H**$_2$-), 2.43 – 2.33 (m, 1H, -C**H**$_2$-), 2.22 (m, 1H, -C**H**$_2$-), 1.88 (m, 1H, -C**H**$_2$-), 1.40 (s, 9H, -C(C**H**$_3$)$_3$), 0.87 (d, *J* = 6.6 Hz, 3H, -(C**H**$_3$)$_2$), 0.83 (d, *J* = 6.6 Hz, 3H, -(C**H**$_3$)$_2$),

^{13}C NMR: (126 MHz, $CDCl_3$) δ 175.8, 166.3, 141.3, 136.2, 129.4, 127.7, 126.7, 122.4, 82.0, 52.4, 51.8, 39.2, 28.7, 28.1, 24.5, 22.8, 22.6.

IR (ATR): 2979, 2866, 1740, 1664, 1600, 1491, 1458, 1393, 1358, 1222, 1152, 1005, 914, 841, 754, 732, 646.

HRMS (DART-MS): *m/z* $[M + H]^+$ calcd for $C_{19}H_{27}NO_3$: 318.4359 found 318.4363.

N-isopentyl-5-((3aS,4S,6aR)-2-oxohexahydro-1H-thieno[3,4-d]imidazol-4-yl)pentanamide (18)



Prepared according to general procedure B using *aminoethyl biotinamide* (29 mg, 0.10 mmol) and *N*-isopropyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (38 mg, 0.10 mmol). Purification by column chromatography on silica gel using 90:10 dichloromethane: methanol ($R_f = 0.3$) afforded **18** in 75% yield (24 mg, 0.075 mmol).

^{1}H NMR: (500 MHz, MeOD) δ 4.52 – 4.42 (m, 1H, -NHC**H**-), 4.28 (m, 1H, -NHC**H**-), 3.23 (t, *J* = 6.9 Hz, 2H, -NHC**H**$_2$-), 2.94 – 2.88 (m, 1H, -SC**H**$_2$-), 2.81 – 2.77 (m, 1H, -SC**H**$_2$-), 2.48 – 2.43

(m, 1H, -SC**H**-), 2.19 (dd, *J* = 8.6, 6.1 Hz, 2H, -C(O)C**H**$_2$-), 1.74 – 1.57 (m, 7H, -C**H**$_2$-, -C**H**-), 1.47 – 1.36 (m, 2H, -C**H**$_2$-), 0.86 (d, *J* = 6.6 Hz, 6H, -(C**H**$_3$)$_2$).

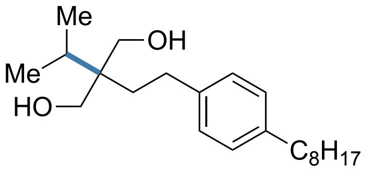
^{13}C NMR: (126 MHz, MeOD) δ 175.0, 164.7, 62.0, 60.2, 55.6, 39.6, 37.5, 36.6, 35.3, 30.1, 28.3, 28.1, 27.7, 25.4, 21.7.

IR (ATR): 2920, 1638, 1557, 1460, 1434, 1386, 1321, 1264, 1157, 1032, 954, 820.

$[\alpha]_D$ insufficient solubility for measurement

HRMS (DART-MS): *m*/*z* $[M + H]^+$ calcd for $C_{15}H_{28}N_3O_2S$: 314.1897 found 314.1890.

2-isopropyl-2-(4-octylphenethyl)propane-1,3-diol (19)



Prepared according to general procedure A using *fingolimod* (31 mg, 0.10 mmol) and *N*-isopropyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (38 mg, 0.10 mmol). Purification by column chromatography on silica gel using 80:20 hexanes: ethyl acetate (R_f = 0.4) afforded **19** in 51% yield (17 mg, 0.051 mmol).

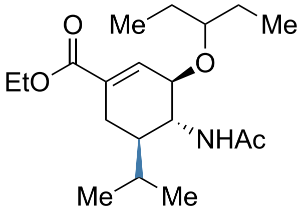
^{1}H NMR: (500 MHz, CDCl$_3$) δ 7.16 – 6.92 (m, 4H, -C**H**$_{Ar}$), 4.21 (s, 2H, -O**H**), 3.83 (m, 4H, -C**H**$_2$OH), 2.98 – 2.86 (m, 1H, -C**H**-), 2.74 (t, *J* = 7.6 Hz, 1H, -C**H**-), 2.56 (m, 3H, -C**H**$_2$-, -C**H**-), 1.70 – 1.40 (m, 4H, -C**H**$_2$-) 1.48 – 1.23 (m, 10H, -C**H**$_2$-, -C**H**-), 1.20 (m, 6H, -(C**H**$_3$)$_2$), 0.90 (t, *J* = 7.0 Hz, 3H, -C**H**$_3$).

^{13}C NMR: (126 MHz, CDCl$_3$) δ 128.7, 128.1, 127.2, 123.7, 68.4, 40.1, 35.6, 31.9, 31.6, 29.7, 29.5, 29.5, 29.4, 29.3, 29.3, 29.2, 22.7, 14.1.

IR (ATR): 3336, 3068, 2956, 2932, 2854, 1605, 1529, 1457, 1348, 1215, 1185, 1124, 1060, 1034, 1008, 854, 742, 688, 643, 557.

HRMS (DART-MS): *m*/*z* $[M + H]^+$ calcd for $C_{22}H_{39}O_2$: 335.2945 found 335.2952.

ethyl (3R,4R,5R)-4-acetamido-5-isopropyl-3-(pentan-3-yloxy)cyclohex-1-ene-1-carboxylate (20)



Prepared according to general procedure B using *(3R,4R,5S)-oseltamivir* (31 mg, 0.10 mmol) and *N*-isopropyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (38 mg, 0.10 mmol). Purification by column chromatography on silica gel using 50:50 hexanes: ethyl acetate ($R_f = 0.3$) afforded **20** in 77% yield (26 mg, 0.077 mmol, *dr* = >98:2).

^{1}H NMR: (500 MHz, MeOD) δ 6.79 (t, *J* = 2.5 Hz, 1H, -C=C**H**-), 4.21 (q, *J* = 7.1 Hz, 2H, -COC**H**$_{2,}$), 4.12 (br s, 1H, -N**H**-), 3.77 (m, 1H, -C=C-C**H**O-), 3.40 (m, 1H, OC**H**-), 3.06 (m, 1H, -NC**H**-),), 2.83 (m, 1H, -C**H**-), 2.53 – 2.42 (m, 1H, -C**H**-), 2.22 (m, 1H, -C=CC**H**$_2$-), 2.16 – 2.07 (m, 1H, -C=CC**H**$_2$-), 2.03 (s, 3H, -C**H**$_3$), 1.86 – 1.75 (m, 1H, -C**H**-), 1.61 – 1.46 (m, 3H, -C**H**$_2$-), 1.29 (t, *J* = 7.1 Hz, 3H, -C**H**$_3$), 1.10 – 0.92 (d, *J* = 6.6 Hz, 6H, -(C**H**$_3$)$_2$), 0.94 – 0.86 (m, 6H, -C**H**$_3$).

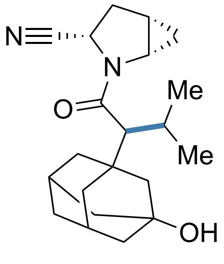
^{13}C NMR: (126 MHz, MeOD) δ 174.4, 167.5, 139.4, 130.0, 83.5, 76.7, 62.1, 58.3, 46.3, 44.0, 38.6, 35.9, 32.8, 27.2, 26.7, 26.5, 23.2, 14.8, 9.9.

IR (ATR): 2980, 2920, 2880, 2850, 1637, 1561, 1445, 1377, 1305, 1188, 1125, 1077, 1033, 1009, 907, 828, 742.

$[\alpha]_D$ –31.1 (c 0.9, 20ºC, MeOH)

HRMS (DART-MS): *m/z* $[M + H]^+$ calcd for $C_{19}H_{34}NO_4$: 340.2482 found 340.2490.

(1S,3S,5S)-2-(2-(3-hydroxyadamantan-1-yl)-3-methylbutanoyl)-2-azabicyclo[3.1.0]hexane-3-carbonitrile (21)



Prepared according to general procedure A using *(S)-L-saxagliptin* (32 mg, 0.10 mmol) and *N*-isopropyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (38 mg, 0.10 mmol). Purification by column chromatography on silica gel using 70:30 hexanes: ethyl acetate ($R_f = 0.4$) afforded **21** in 59% yield (20 mg, 0.059 mmol, *dr* = 1:1).

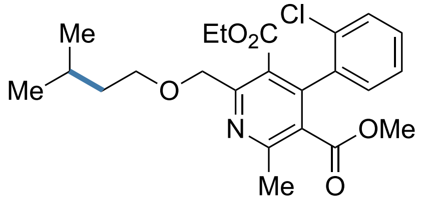
^{1}H NMR: (500 MHz, MeOD) δ 4.11 (t, *J* = 6.4 Hz, 1H, NCC**H**-), 2.25 – 2.21 (m, 1H, -NC**H**-), 2.14 (dt, *J* = 13.6, 3.2 Hz, 2H, -C**H**-), 1.86 – 1.79 (m, 3H, -C**H**$_2$-, -C**H**-), 1.70 – 1.54 (m, 12H, -C**H**$_2$-, -C**H**-), 1.38 – 1.31 (m, 2H, -C**H**$_2$-), 0.98 (d, *J* = 6.4 Hz, 6H, -(C**H**$_3$)$_2$), 0.87 – 0.76 (m, 2H, -C**H**$_2$-).

^{13}C NMR (126 MHz, MeOD) δ 167.5, 160.0, 119.5, 119.5, 69.5, 67.9, 60.1, 59.8, 46.1, 45.6, 45.3, 45.0, 44.7, 44.5, 44.4, 44.2, 44.0, 43.9, 43.9, 40.8, 40.5, 38.8, 37.8, 37.1, 36.9, 34.5, 33.8, 30.4, 30.0, 25.1, 19.7, 17.4, 16.9, 14.8, 14.3, 13.6, 13.5, 12.7, 10.7, 6.7, 6.6.

IR (ATR): 3341, 2906, 2851, 2473, 2066, 1628, 1457, 1335, 1310, 1100, 1027, 976, 814.

HRMS (DART-MS): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{31}N_2O_2$: 343.2380 found 343.2374.

3-ethyl 5-methyl 4-(2-chlorophenyl)-2-((isopentyloxy)methyl)-6-methylpyridine-3,5-dicarboxylate (22)



Prepared according to general procedure B using *amlopidine* (41 mg, 0.10 mmol) and *N*-isopropyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (38 mg, 0.10 mmol). Purification by column chromatography on silica gel using 60:40 hexanes: ethyl acetate (R_f = 0.3) afforded **22** in 84% yield (36 mg, 0.084 mmol).

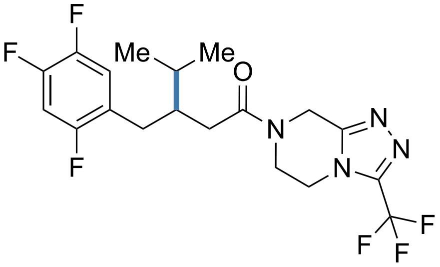
^{1}H NMR: (500 MHz, CDCl$_3$) δ 7.39 – 7.29 (m, 2H, -C**H**$_{Ar}$), 7.13 – 7.06 (m, 2H, -C**H**$_{Ar}$), 4.72 – 4.68 (s, 2H, -OC**H**$_2$Ar-), 3.94 – 3.89 (m, 2H, -OC**H**$_2$-), 3.47 (m, 5H, -C**H**$_3$, -OC**H**$_2$-), 2.57 (s, 3H, -C**H**$_3$), 1.42 – 1.35 (m, 1H, -C**H**-), 1.18 (m, 2H, -C**H**$_2$-), 0.95 – 0.71 (m, 9H, -(C**H**$_3$)$_2$, -C**H**$_3$).

^{13}C NMR: (126 MHz, CDCl$_3$) δ 167.3, 161.1, 155.9, 148.4, 145.2, 134.9, 132.9, 130.1, 129.2, 128.4, 127.4, 126.3, 123.5, 73.1, 69.6, 61.7, 61.4, 52.3, 37.7, 29.7, 23.3, 13.5.

IR (ATR): 2946, 2833, 1726, 1656, 1559, 1436, 1232, 1108, 1019, 854, 757, 637.

HRMS (DART-MS): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{29}ClNO_5$: 434.1729 found 434.1736.

4-methyl-3-(2,4,5-trifluorobenzyl)-1-(3-(trifluoromethyl)-5,6-dihydro-[1,2,4]triazolo[4,3-a]pyrazin-7(8H)-yl)pentan-1-one (23)



Prepared according to general procedure B using *(R)-sitagliptin* (41 mg, 0.10 mmol) and *N*-isopropyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (38 mg, 0.10 mmol). Purification by column chromatography on silica gel using 90:10 dichloromethane: methanol (R_f = 0.5) afforded **23** in 52% yield (23 mg, 0.052 mmol).

^{1}H NMR: (500 MHz, MeOD) δ 7.35 – 7.03 (m, 2H -C**H**$_{Ar}$) 5.08 – 4.89 (m, 2H, -NC**H**$_2$-) 4.30 (m, 1H, -NC**H**$_2$-,), 4.21 (m, 1H, -NC**H**$_2$-), 4.07 (m, 2H, -NC**H**$_2$-), 3.48 (m, 1H, -C**H**$_2$-), 2.88 – 2.72 (m, 2H, -C**H**$_2$-), 2.66 – 2.51 (m, 2H, -C**H**-), 1.54 – 1.43 (m, 1H, -C**H**-), 0.88 (d, *J* = 6.6 Hz, 6H, -(C**H**$_3$)$_2$).

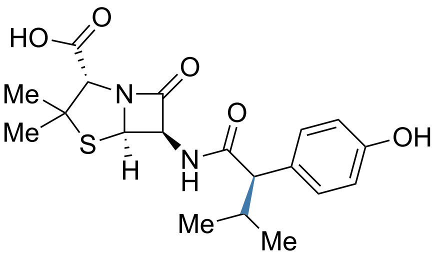
^{13}C NMR: (126 MHz, MeOD) δ 171.2, 157.3, 155.4, 151.3, 145.6, 143.5, 122.2, 119.4, 105.1, 48.4, 43.7, 41.1, 38.8, 37.6, 36.6, 35.2, 28.1, 21.7.

^{19}F NMR (470 MHz, CDCl$_3$) δ -81.8, -91.1, -92.6, -94.2.

IR (ATR): 2980, 2948, 2836, 1626, 1602, 1510, 1447, 1399, 1352, 1278, 1190, 1152, 1123, 1021, 855, 742.

HRMS (DART-MS): *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{21}F_6N_4O$: 435.1614 found 435.1623.

(2*S*,5*R*,6*R*)-6-((*R*)-2-(4-hydroxyphenyl)-3-methylbutanamido)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid (24)



Prepared according to general procedure B using *D-amoxicillin* (37 mg, 0.10 mmol) and *N*-isopropyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (38 mg, 0.10 mmol). Purification by column chromatography on silica gel using 90:20 dichloromethane: methanol (R_f = 0.2) afforded

24 in 72% yield (28 mg, 0.072 mmol, *dr* = 3:2). Diastereoselectivity determined by ^{1}H NMR. Major diastereomer assigned by hydrolysis followed by comparison of optical rotation data of product to analogue [(*R/S*)-3-methyl-2-phenylbutanoic acid] in literature reference.[10]

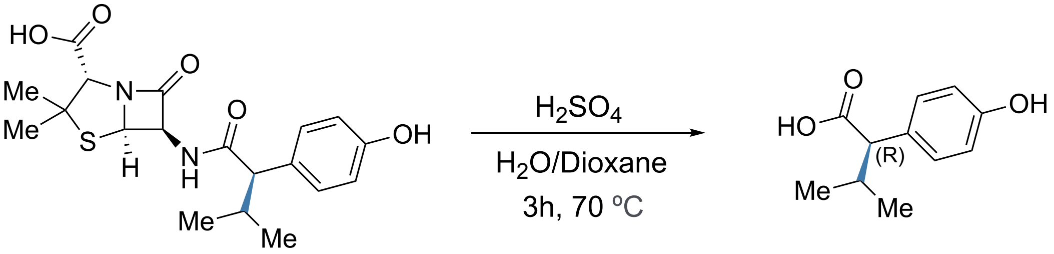
^{1}H NMR: (500 MHz, MeOD, major diastereomer) δ 7.29 – 7.19 (m, 2H, -C**H**$_{Ar}$), 6.79 – 6.71 (m, 2H, -C**H**$_{Ar}$), 5.47 (m, 2H, -C**H**NH-, -SC**H**N-), 4.16 (s, 1H, -C**H**-), 2.09 (m, 1H, -C**H**-), 1.60 (s, 3H, -C**H**$_3$), 1.53 (s, 3H, -C**H**$_3$), 1.20 – 1.17 (m, 1H, -C**H**-), 0.90 (d, *J* = 6.6 Hz, 3H, -(C**H**$_3$)$_2$), 0.88 (d, *J* = 6.6 Hz, 3H, -(C**H**$_3$)$_2$).

^{13}C NMR: (126 MHz, MeOD) δ 176.0, 175.2, 174.9, 158.5, 132.6, 129.6, 116.4, 75.0, 68.2, 65.6, 59.2, 46.3, 38.6, 31.4, 26.5, 21.1, 15.0.

IR (ATR): 3292, 2970, 2931, 2359, 2341, 1761, 1662, 1591, 1514, 1457, 1395, 1251, 1130, 1083, 1018, 967, 837.

HRMS (DART-MS): *m/z* [M + H]$^+$ calcd for $C_{19}H_{25}N_2O_5S$: 393.1479 found 393.1485.

Stereochemical Assignment:



A solution of **24** (28 mg, 0.072 mmol, *dr* = 3:2) in 3M H_2SO_4 in 1:1 H_2O/1,4-dioxane (2 mL) was heated at 75 °C. After 3h, the reaction mixture was cooled to room temperature, diluted with water and extracted with dichloromethane (3 x 5mL). The resultant organic phase was dried with sodium sulfate and concentrated to yield 2-(4-hydroxyphenyl)-3-methylbutanoic acid which matched ^{1}H NMR literature values,[14] and was directly subject to optical rotation measurement.

Optical rotation: $[\alpha]_D$ –10.5 (c 0.95, 20ºC, MeOH), major diastereomer assigned as (*R*)-enantiomer

Literature reference for pure enantiomers of analogue:

[(*S*)-3-methyl-2-phenylbutanoic acid] $[\alpha]_D$ +58.3 (c 1.0, 23ºC, CH_3Cl)[15]
[(*R*)-3-methyl-2-phenylbutanoic acid] $[\alpha]_D$ –56.5 (c 2.0, 20ºC, CH_3Cl)[16]

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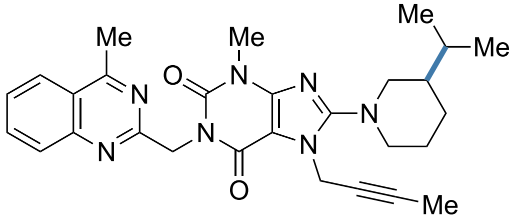
(14) Zhang, Z.; Feng, Y.; Li, J. A new method for the synthesis of α-isopropyl-4-hydroxyphenylacetic acid. *Chinese Science Bulletin* **1989**, *34*, 2022–2024.
(15) Stivala, C. E.; Zakarian, A. Highly Enantioselective Direct Alkylation of Arylacetic Acids with Chiral Lithium Amides as Traceless Auxiliaries. *J. Am. Chem. Soc.* **2011**, *133*, 11936–11939.
(16) Song, S.; Zhu, S.-F.; Li, Y.; Zhou, Q.-L. Iridium-Catalyzed Enantioselective Hydrogenation of α,β-Unsaturated Carboxylic Acids with Tetrasubstituted Olefins. *Org. Lett.* **2013**, *15*, 3722–3725.

7-(but-2-yn-1-yl)-8-(3-isopropylpiperidin-1-yl)-3-methyl-1-((4-methylquinazolin-2-yl)methyl)-3,7-dihydro-1H-purine-2,6-dione (25)



Prepared according to general procedure B using *(R)-linagliptin* (47 mg, 0.10 mmol) and *N*-isopropyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (38 mg, 0.10 mmol). Purification by column chromatography on silica gel using 90:10 dichloromethane: methanol ($R_f = 0.4$) afforded **25** in 72% yield (36 mg, 0.072 mmol).

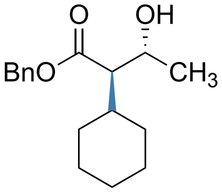
^{1}H NMR: (500 MHz, MeOD) δ 8.22 (m, 1H, -C**H**$_{Ar}$), 7.92 – 7.82 (m, 2H, -C**H**$_{Ar}$), 7.66 (m, 1H, -C**H**$_{Ar}$), 5.47 (s, 2H, -NC**H**$_2$-), 4.96 – 4.87 (m, 2H, -NC**H**$_2$-), 4.87 (s, 3H, , -C**H**$_3$), 3.75 (m, 1H, -NC**H**$_2$-), 3.67 (m, 1H, -NC**H**$_2$-), 3.53 (s, 3H, -C**H**$_3$), 3.13 (m, 1H, -NC**H**$_2$-), 3.03 (m, 1H, -NC**H**$_2$-), 2.93 (s, 3H, -C**H**$_3$), 2.09 (p, *J* = 6.6 Hz, 1H, -C**H**-), 1.89 (m, 1H, -C**H**-), 1.77 (m, 4H, -C**H**$_2$-), 0.89 (dd, *J* = 6.6 Hz, 6H,-(C**H**$_3$)$_2$).

^{13}C NMR: (126 MHz, MeOD) δ 169.4, 160.6, 156.5, 153.9, 151.6, 149.1, 148.2, 133.8, 127.1, 126.9, 125.0, 122.5, 104.0, 80.6, 72.5, 56.5, 49.9, 45.3, 36.3, 35.0, 31.9, 28.5, 27.8, 22.9, 21.4, 20.0, 1.4.

IR (ATR): 3026, 3017, 2932, 2918, 2850, 2358, 2334, 1737, 1618, 1572, 1426, 1406, 1334, 1290, 1134, 1010, 967, 701.

HRMS (DART-MS): *m/z* $[M + H]^+$ calcd for $C_{28}H_{34}N_7O_2$: 500.2768 found 500.2755.

benzyl (3R)-2-cyclohexyl-3-hydroxybutanoate (27)



Prepared according to general procedure A using *L-threonine benzyl ester* (25 mg, 0.121 mmol)) and *N*-cyclohexyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (50 mg, 0.121 mmol). Purification by column chromatography on silica gel using 70:30 hexanes: ethyl acetate ($R_f = 0.5$) afforded **27** in 63% yield (21 mg, 0.076 mmol, *dr* = >98:2). Relative stereochemistry determined by ^{1}H NMR based on reported analogue.[9]

^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.45 – 7.34 (m, 5H, -C**H**$_{Ar}$), 5.34 (s, 2H, -OC**H**$_2$-), 5.06 (m, 1H, -C**H**OH), 1.94 – 1.45 (m, 10H, -C**H**$_2$-, -C**H**-), 1.43 (d, *J* = 6.6 Hz, 3H, -C**H**$_3$), 1.41 – 1.26 (m, 2H, -C**H**$_2$-).

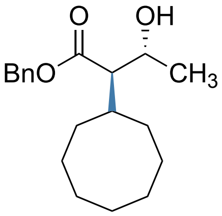
^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6, 134.7, 128.7, 128.6, 80.8, 66.9, 37.9, 36.1, 27.3, 25.2, 22.3, 20.5.

IR (ATR): 2980, 2917, 2949, 1636, 1574, 1541, 1547, 1378, 1346, 1261, 1239, 1151, 1124, 1060, 1033, 1008, 950, 831.

$[\alpha]_D$: insufficient sample for absorption

HRMS (DART-MS): *m/z* $[M + H]^+$ calcd for $C_{17}H_{25}O_3$: 277.1798 found 227.1788.

benzyl (3R)-2-cyclooctyl-3-hydroxybutanoate (28)



Prepared according to general procedure A using *L-threonine benzyl ester* (29 mg, 0.12 mmol) and *N*-cyclooctyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (50 mg, 0.12 mmol). Purification by column chromatography on silica gel using 70:30 hexanes: ethyl acetate (R_f = 0.5) afforded **28** in 57% yield (21 mg, 0.069 mmol, *dr* = >98:2). Relative stereochemistry determined by ^{1}H NMR based on reported analogue. [9]

^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 5H, -C**H**$_{Ar}$), 5.27 (s, 2H, -OC**H**$_2$-), 4.98 (m, 1H, -C**H**OH), 2.30 – 2.24 (m, 1H, -C**H**-), 1.86 – 1.44 (m, 15H, -C**H**$_2$-, -C**H**-), 1.36 (d, *J* = 6.6 Hz, 3H, -C**H**$_3$).

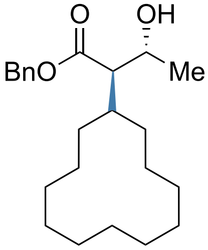
^{13}C NMR: (126 MHz, $CDCl_3$) δ 162.7, 134.9, 128.8, 128.7, 128.7, 80.7, 67.7, 38.1, 36.4, 27.0, 25.0, 22.9, 22.8, 20.6.

IR (ATR): 2972, 2916, 2848, 1652, 1569, 1541, 1472, 1457, 1354, 1261, 1154, 1077, 1055, 1033, 1004, 957, 748.

$[\alpha]_D$: insufficient sample for absorption

HRMS (DART-MS): *m/z* $[M + H]^+$ calcd for $C_{19}H_{29}O_3$: 305.2111 found 305.2119.

benzyl (3R)-2-cyclododecyl-3-hydroxybutanoate (29)



Prepared according to general procedure A using *L-threonine benzyl ester* (19 mg, 0.08 mmol) and *N*-cyclododecyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (38 mg, 0.08 mmol). Purification by column chromatography on silica gel using 70:30 hexanes: ethyl acetate ($R_f = 0.5$) afforded **29** in 51% yield (15 mg, 0.041 mmol, *dr* = >98:2). Relative stereochemistry determined by ^{1}H NMR based on reported analogue. [9]

^{1}H NMR: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.28 (m, 5H, -C**H**$_{Ar}$), 5.36 – 5.17 (s, 2H, -OC**H**$_2$-), 5.04 (m, 1H, -C**H**OH), 2.48 – 2.44 (m, 1H, -C**H**-), 1.72 (d, *J* = 6.4 Hz, 3H, -C**H**$_3$), 1.58 – 1.17 (m, 23H, -C**H**$_2$-).

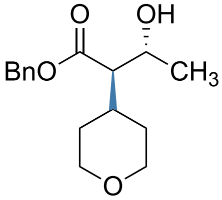
^{13}C NMR: (126 MHz, $CDCl_3$) δ 162.6, 134.7, 128.7, 128.6, 80.6, 67.6, 38.0, 36.3, 27.9, 24.8, 24.4, 22.7, 22.7, 22.5, 20.4, 14.6.

IR (ATR): 2916, 2828, 1637, 1558, 1458, 1331, 1317, 1265, 1209, 1155, 1078, 1023.

$[\alpha]_D$: insufficient sample for absorption

HRMS (DART-MS): *m/z* $[M + H]^+$ calcd for $C_{23}H_{37}O_3$: 361.2737 found 361.2717.

benzyl (3R)-3-hydroxy-2-(tetrahydro-2H-pyran-4-yl)butanoate (30)



Prepared according to general procedure A using *L-threonine benzyl ester* (18 mg, 0.072 mmol) and *N*-tetrahydro-2*H*-pyran-4-yl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (30 mg, 0.072 mmol). Purification by column chromatography on silica gel using 70:30 hexanes: ethyl acetate ($R_f = 0.5$) afforded **30** in 60% yield (12 mg, 0.043 mmol, *dr* = >98:2). Relative stereochemistry determined by ^{1}H NMR based on reported analogue. [9]

^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 5H, -C**H**$_{Ar}$), 5.28 (s, 2H, -OC**H**$_2$-), 5.03 (m, 1H, -C**H**OH-), 3.84 (m, 2H, -OC**H**$_2$-), 3.72 (m, 2H, -OC**H**$_2$-), 2.08 – 1.89 (m, 2H, -C**H**-), 1.67 – 1.51 (m, 2H, -C**H**$_2$-), 1.38 (d, *J* = 6.6 Hz, 3H, -C**H**$_3$), 1.25 – 1.12 (m, 2H, -C**H**$_2$-).

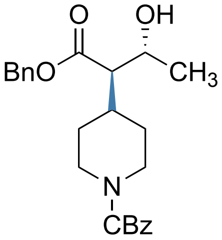
^{13}C NMR: (126 MHz, CDCl$_3$) δ 163.8, 160.9, 134.7, 128.8, 128.7, 81.1, 67.9, 64.9, 38.4, 36.7, 30.0, 20.4.

IR (ATR): 2971, 2917, 2948, 1723, 1684, 1674, 1574, 1472, 1381, 1273, 1239, 1152, 1073, 1008, 967, 906, 800, 742.

[α]$_D$ –40.0 (c 0.4, 20ºC, MeOH)

HRMS (DART-MS): *m/z* [M + H]$^+$ calcd for $C_{16}H_{23}O_4$: 279.1591 found 279.1580.

benzyl 4-((2*R*,3*R*)-1-(benzyloxy)-3-hydroxy-1-oxobutan-2-yl)piperidine-1-carboxylate (31)



Prepared according to general procedure B using *L-threonine benzyl ester* (81 mg, 0.181 mmol) and *N*-((benzyloxy)carbonyl)piperidin-4-yl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (120 mg, 0.181 mmol). Purification by column chromatography on silica gel using 70:30 hexanes: ethyl acetate (R$_f$ = 0.4) afforded **31** in 55% yield (41 mg, 0.10 mmol, *dr* = >98:2). Relative stereochemistry determined by ^{1}H NMR based on reported analogue. [9]

^{1}H NMR: (500 MHz, CDCl$_3$) δ 7.44 – 7.28 (m, 10H, -C**H**$_{Ar}$), 5.34 (s, 2H, -OC**H**$_2$-), 5.14 (s, 2H, - -OC**H**$_2$-), 5.10 (q, *J* = 6.6 Hz, 1H, -C**H**OH), 3.87 (d, *J* = 15.9 Hz, 2H, -NC**H**$_2$-), 3.46 (m, 2H, -NC**H**$_2$-), 2.06 – 1.84 (m, 2H, -C**H**-), 1.64 (m, 3H, -C**H**$_2$-), 1.44 (d, *J* = 6.7 Hz, 3H, -C**H**$_3$), 1.34 – 1.20 (m, 1H, -C**H**$_2$-).

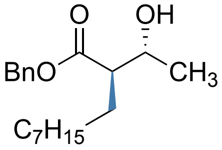
^{13}C NMR: (126 MHz, CDCl$_3$) δ 164.0, 160.8, 155.2, 136.8, 134.6, 128.8, 128.7, 128.5, 128.0, 127.9, 81.3, 67.9, 67.2, 41.1, 37.5, 35.7, 20.4.

IR (ATR): 2980, 2920, 2849, 1698, 1661, 1575, 1471, 1430, 1368, 1344, 1276, 1228, 1142, 1074, 1033, 948, 906, 829, 742, 697.

[α]$_D$ –47.3 (c 1.1, 20ºC, MeOH)

HRMS (DART-MS): *m/z* [M + H]$^+$ calcd for $C_{24}H_{30}NO_5$: 412.2118 found 412.2122.

benzyl (*R*)-2-((*R*)-1-hydroxyethyl)decanoate (32)



Prepared according to general procedure B using *L-threonine benzyl ester* (33 mg, 0.135 mmol) and *N*-octyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (60 mg, 0.135 mmol). Purification by column chromatography on silica gel using 70:30 hexanes: ethyl acetate ($R_f = 0.5$) afforded **32** in 19% yield (8 mg, 0.026 mmol, *dr* = 1:1). Diastereoselectivity determined by ^{1}H NMR.

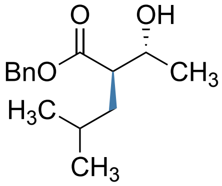
^{1}H NMR (500 MHz, $CDCl_3$, mixture of diastereomers) δ 7.36 – 7.25 (m, 10H, -C**H**$_{Ar}$), 5.29 – 5.22 (m, 4H, -OC**H**$_2$-), 5.12 – 5.08 (m, 1H, -OC**H**$_2$-), 4.95 – 4.91 (m, 1H, -OC**H**$_2$-), 1.83 (m, 1H, -C**H**-), 1.71 – 1.60 (m, 1H, -C**H**-), 1.49 – 1.44 (m, 6H, -C**H**$_3$), 1.43 – 1.11 (m, 28H, -C**H**$_2$-), 0.91 – 0.67 (m, 6H, -C**H**$_3$).

^{13}C NMR (126 MHz, $CDCl_3$, mixture of diastereomers) δ 164.5, 160.8, 134.7, 134.6, 129.6, 129.5, 128.8, 128.8, 128.6, 128.6, 81.8, 81.3, 68.0, 67.9, 29.7, 29.4, 22.7, 22.3, 21.1, 20.9, 20.2, 19.8, 18.4, 18.0, 14.1, 14.1.

IR (ATR): 2972, 2921, 1718, 1456, 1386, 1267, 1056, 1033, 1014, 733, 696.

HRMS (DART-MS): *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{31}O_3$: 291.1955 found 291.1962.

benzyl 2-((R)-1-hydroxyethyl)-4-methylpentanoate (33)



Prepared according to general procedure A using *L-threonine benzyl ester* (19 mg, 0.077 mmol) and *N*-isobutyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (30 mg, 0.077 mmol). Purification by column chromatography on silica gel using 70:30 hexanes: ethyl acetate ($R_f = 0.5$) afforded **33** in 62% yield (12 mg, 0.048 mmol, *dr* = 1:1). Diastereoselectivity determined by ^{1}H NMR.

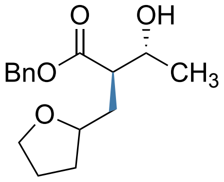
^{1}H NMR: (500 MHz, $CDCl_3$, mixture of diastereomers) δ 7.46 – 7.33 (m, 10H), 5.57 – 5.24 (m, 4H, -OC**H**$_2$-), 5.24 – 5.00 (m, 2H, -C**H**OH), 2.12 – 2.00 (m, 1H, -C**H**-), 1.82 – 1.72 (m, 1H, -C**H**-), 1.48 (d, *J* = 6.6 Hz, 3H, -C**H**$_3$), 1.41 (d, *J* = 6.7 Hz, 3H, -C**H**$_3$), 1.38 – 1.30 (m, 6H, -C**H**$_2$-, -C**H**-), 1.05 – 0.89 (m, 12H, -(C**H**$_3$)$_2$).

^{13}C NMR (126 MHz, $CDCl_3$, mixture of diastereomers) δ 166.0, 165.8, 133.9, 130.3, 129.8, 129.7, 128.6, 128.6, 128.3, 127.5, 72.3, 72.1, 67.6, 67.6, 39.3, 38.4, 30.4, 30.2, 29.8, 27.5, 24.1, 22.7, 14.1, 13.8.

IR (ATR): 2919, 2850, 1723, 1457, 1378, 1266, 1101, 1020, 800.

HRMS (DART-MS): *m/z* $[M + H]^+$ calcd for $C_{15}H_{23}O_3$: 251.1642 found 251.1630.

benzyl (3R)-3-hydroxy-2-((tetrahydrofuran-2-yl)methyl)butanoate (34)



Prepared according to general procedure A using *L-threonine benzyl ester* (18 mg, 0.072 mmol) and *N*-((tetrahydrofuran-2-yl)methyl)-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (30 mg, 0.072 mmol). Purification by column chromatography on silica gel using 70:30 hexanes: ethyl acetate ($R_f = 0.5$) afforded **34** in 60% yield (12 mg, 0.043 mmol, *dr* = 1:1:1). Diastereoselectivity determined by ^{1}H NMR.

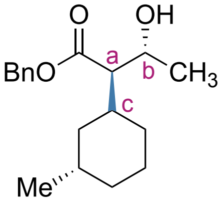
^{1}H NMR: (500 MHz, $CDCl_3$, mixture of diastereomers) δ 7.43 – 7.28 (m, 10H, -C**H**$_{Ar}$), 5.38 – 5.31 (m, 2H, -C**H**OH-), 5.24 – 5.16 (m, 4H, -OC**H**$_2$-), 4.27 (t, *J* = 5.6 Hz, 1H, -OC**H**-), 4.25 – 4.15 (m, 1H, -OC**H**-), 4.08 – 4.01 (m, 2H, -OC**H**$_2$-), 3.78 (m, 1H, -OC**H**$_2$-), 3.53 (m, 1H, -OC**H**$_2$-), 1.67 – 1.50 (m, 2H, -C**H**-), 1.48 (m, 2H, -C**H**-), 1.55 – 1.38 (m, 6H, -C**H**$_3$), 1.34 – 1.19 (m, 10H, -C**H**$_2$-).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 170.6, 129.5, 128.8, 128.7, 128.6, 128.4, 128.4, 78.6, 72.1, 68.3, 67.2, 67.8, 67.4, 67.4, 66.2, 39.0, 38.7, 29.8, 29.0, 24.0, 23.0, 19.9, 17.2, 14.1, 11.0.

IR (ATR): 2971, 2921, 1734, 1719, 1456, 1378, 1268, 1050, 1033, 733, 697.

HRMS (DART-MS): *m/z* $[M + H]^+$ calcd for $C_{16}H_{23}O_4$: 279.1591 found 279.1599.

benzyl (3R)-3-hydroxy-2-(3-methylcyclohexyl)butanoate (35)



Prepared according to general procedure B using *L-threonine benzyl ester* (17 mg, 0.072 mmol) and *N*-3-methylcyclohexyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (50 mg, 0.072 mmol). Purification by column chromatography on silica gel using 70:30 hexanes: ethyl acetate ($R_f = 0.5$) afforded **35** in 38% yield (8 mg, 0.028 mmol, *dr (a:b)* = >98:2, *dr (a:c)* = 5:1).

^{1}H NMR: (500 MHz, $CDCl_3$, major diastereomer) δ 7.44 – 7.33 (m, 5H, -C**H**$_{Ar}$), 5.39 – 5.27

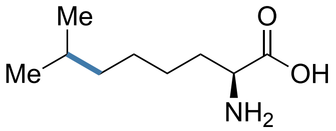
(s, 2H, -OC**H**$_2$-), 5.02 (m, 1H, -C**H**OH), 1.55 (m, 2H, -C**H**-), 1.53 (d, *J* = 6.1 Hz, 3H, -C**H**$_3$), 1.47 (m, 3H, -C**H**$_2$-), 1.48 (d, *J* = 6.3, 3H, -C**H**$_3$), 1.42 (m, 2H, -C**H**$_2$-), 1.36 – 1.11 (m, 4H, -C**H**$_2$-).

^{13}C NMR: (126 MHz, CDCl$_3$) δ 165.6, 134.7, 128.8, 128.7, 81.8, 67.8, 34.5, 30.9, 29.7, 22.6, 21.4, 21.4, 20.3, 18.5, 15.6.

IR (ATR): 2978, 2924, 2871, 2851, 1724, 1456, 1387, 1366, 1327, 1264, 1163, 1080, 975, 862, 735, 697.

HRMS (DART-MS): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{27}O_3$: 291.1955 found 291.1967.

(*S*)-2-amino-7-methyloctanoic acid (37)



Prepared according to general procedure A using *DL-lysine* (29 mg, 0.20 mmol) and *N*-isopropyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (76 mg, 0.20 mmol). Purification by column chromatography on silica gel using 90:10 dichloromethane: methanol (R$_f$ = 0.1) afforded **37** in 68% yield (24 mg, 0.136 mmol).

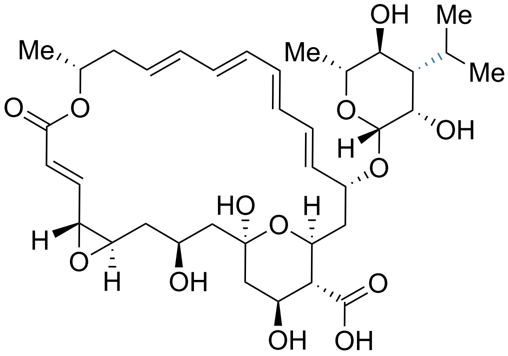
^{1}H NMR: (500 MHz, MeOD) δ 5.02 (s, 1H, -N**H**$_2$), 3.63 (t, *J* = 8.9 Hz, 1H, -H$_2$NC**H**-), 1.78 – 1.73 (m, 2H, -C**H**$_2$-), 1.67 – 1.62 (m, 1H, -C**H**-), 1.00 – 0.95 (m, 6H, -C**H**$_2$-), 0.89 (d, *J* = 6.5 Hz, 6H, -(C**H**$_3$)$_2$).

^{13}C NMR: (126 MHz, MeOD) δ 174.4, 53.4, 40.1, 36.5, 28.0, 24.4, 22.0, 20.8.

IR (ATR): 2970, 2917, 2849, 1745, 1578, 1522, 1472, 1406, 1386, 1349, 1198, 1158, 1109, 1033, 1008, 850, 777, 756, 682, 639.

HRMS (DART-MS): *m*/*z* [M + H]$^+$ calcd for $C_9H_{20}NO_2$: 174.1489 found 174.1491.

(1*R*,3*S*,5*R*,7*R*,8*E*,12*R*,14*E*,16*E*,18*E*,20*E*,22*R*,24*S*,25*R*,26*S*)-22-(((2*R*,3*S*,4*S*,5*S*,6*R*)-3,5-dihydroxy-4-isopropyl-6-methyltetrahydro-2*H*-pyran-2-yl)oxy)-1,3,26-trihydroxy-12-methyl-10-oxo-6,11,28-trioxatricyclo[22.3.1.0^{5,7}]octacosa-8,14,16,18,20-pentaene-25-carboxylic acid (39)



Prepared according to general procedure B using *natamycin* (67 mg, 0.10 mmol) and *N*-isopropyl-*O*-((4-nitrophenyl)sulfonyl)hydroxylamine salt (38 mg, 0.10 mmol). Purification by column chromatography on silica gel using 80:20 dichloromethane: methanol (R_f = 0.1) afforded **39** in 48% yield (33 mg, 0.048 mmol, *dr* = >98:2). See stereochemical assignment below.

^{1}H NMR: (500 MHz, MeOD) δ 6.35 (m, 2H, -C=C**H**-), 6.19 – 6.01 (m, 5H, -C=C**H**-), 6.00 – 5.86 (m, 2H, -C=C**H**-), 5.50 (m, 1H, -C=C**H**-), 4.66 – 4.58 (m, 1H, -OC**H**-), 4.25 (m, 5H, -OC**H**-), 3.30 (m, 2H, -OC**H**-), 3.16 – 3.03 (m, 3H, -OC**H**-), 2.74 (m, 1H, -C**H**-), 2.38 – 2.08 (m, 4H, -C**H**$_2$-), 2.01 – 1.84 (m, 4H, -C**H**$_2$-, -C**H**-), 1.64 – 1.46 (m, 4H, -C**H**$_2$-, -C**H**-), 1.37 – 1.05 (m, 12H, -C**H**$_3$, -(C**H**$_3$)$_2$).

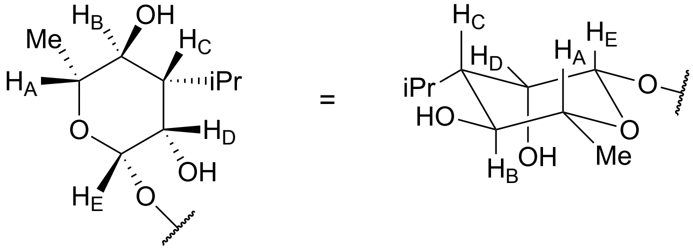
^{13}C NMR: (126 MHz, MeOD) δ 178.8, 165.6, 144.8, 136.0, 135.2, 133.2, 132.2, 131.9, 131.8, 129.0, 128.3, 124.1, 97.5, 97.5, 77.9, 73.2, 70.2, 68.9, 67.6, 67.1, 66.4, 66.1, 60.3, 58.2, 55.7, 54.0, 53.4, 46.7, 43.6, 40.6, 39.6, 38.3, 19.3, 18.6, 16.4, 16.4.

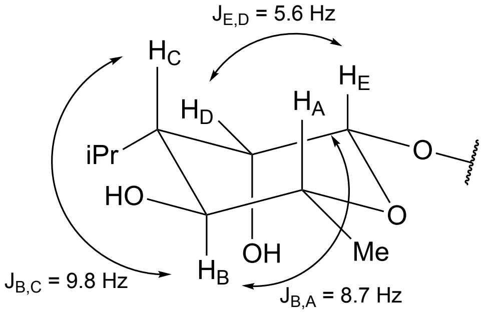
IR (ATR): 3360, 2981, 2920, 2850, 1653, 1603, 1568, 1525, 1457, 1395, 1368, 1349, 1302, 1263, 1221, 1183, 1154, 1123, 1060, 1033, 1008.

$[\alpha]_D$ +120.5 (c 0.17, 20ºC, MeOH)

HRMS (DART-MS): *m/z* $[M + H]^+$ calcd for $C_{36}H_{53}O_{13}$: 693.3481 found 693.3493.

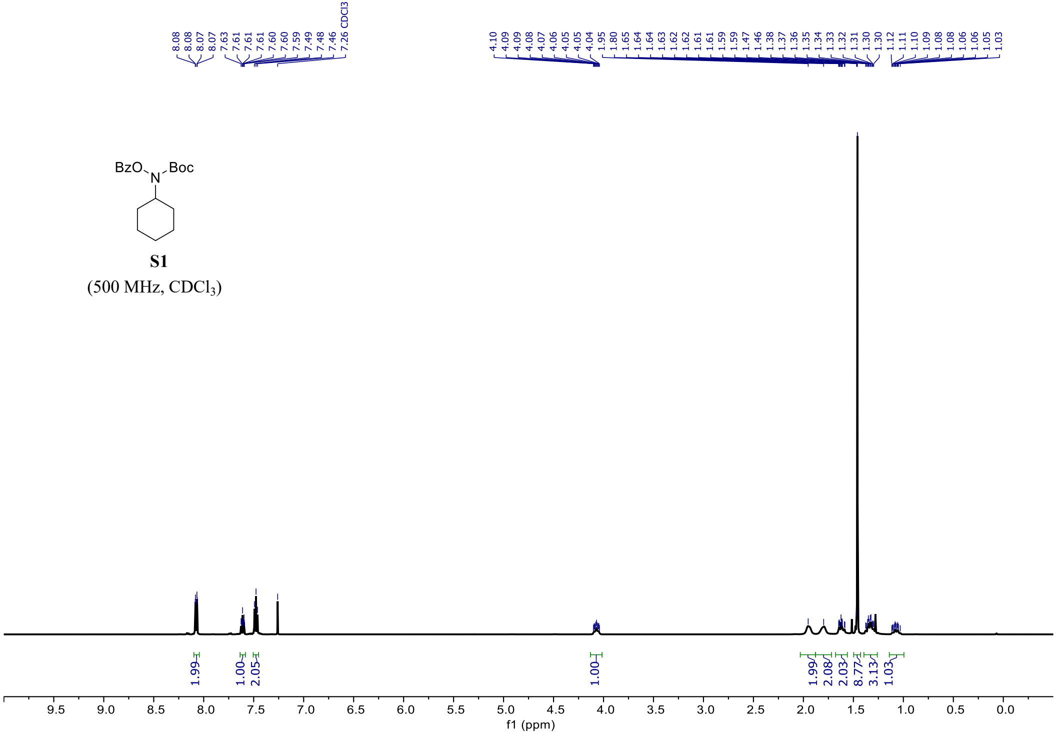
Stereochemical Assignment:



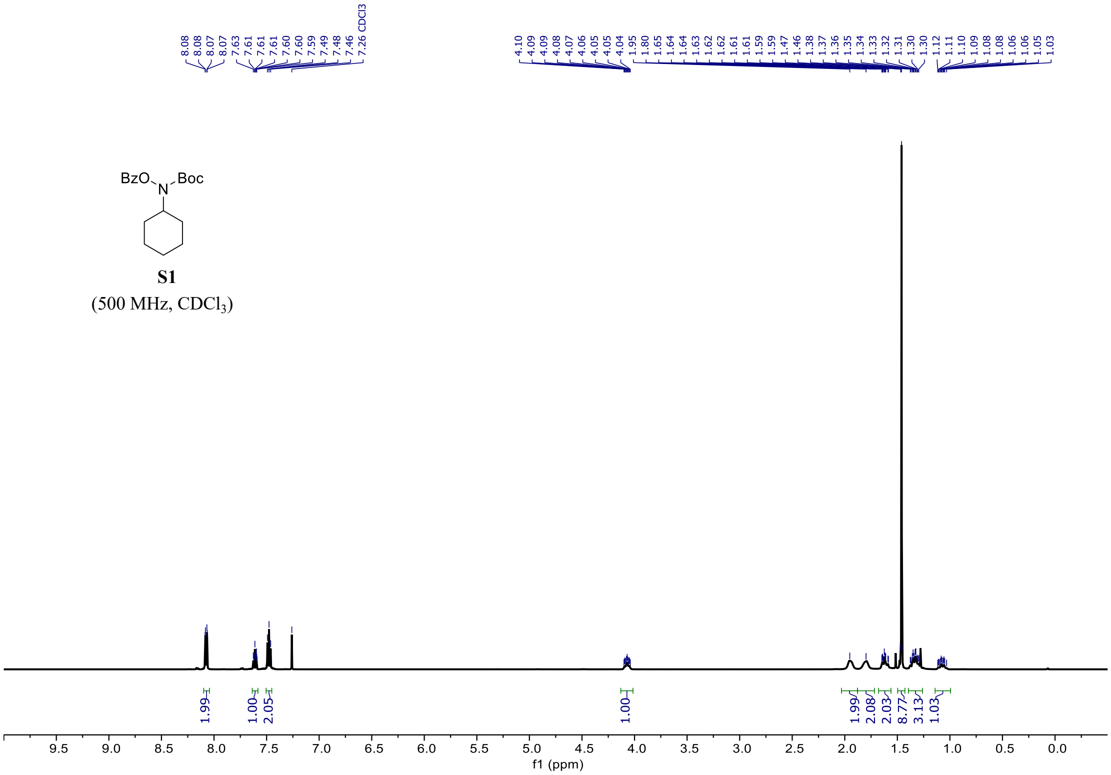


^{1}H NMR: (500 MHz, MeOD) δ 6.35 (m, 2H, -C=C**H**-), 6.19 – 6.01 (m, 6H, -C=C**H**-), 6.00 – 5.86 (m, 2H, -C=C**H**-), 5.50 (ddd, *J* = 14.7, 9.8, $J_{E,D}$ =5.6 Hz, 1H, -OC**H_E**-), 4.66 – 4.58 (m, 1H, -OC**H**-), 4.36 – 4.31 (m, 1H, -OC**H**-), 4.31 – 4.25 (dd, $J_{B,C}$ = 9.8, $J_{B,A}$ = 8.7 Hz, 1H, -OC**H_B**-), 4.25 – 4.20 (m, 1H, -OC**H**-), 4.18 (m, 1H, -OC**H**-), 3.30 (m, 2H, -OC**H**-), 3.16 – 3.03 (m, 3H, -OC**H**-), 2.74 (m, 1H, -C**H**-), 2.38 – 2.08 (m, 4H, -C**H**$_2$-), 2.01 – 1.84 (m, 4H, -C**H**$_2$-, -C**H**-), 1.64 – 1.46 (m, 4H, -C**H**$_2$-, -C**H**-), 1.37 – 1.05 (m, 12H, -C**H**$_3$, -(C**H**$_3$)$_2$).

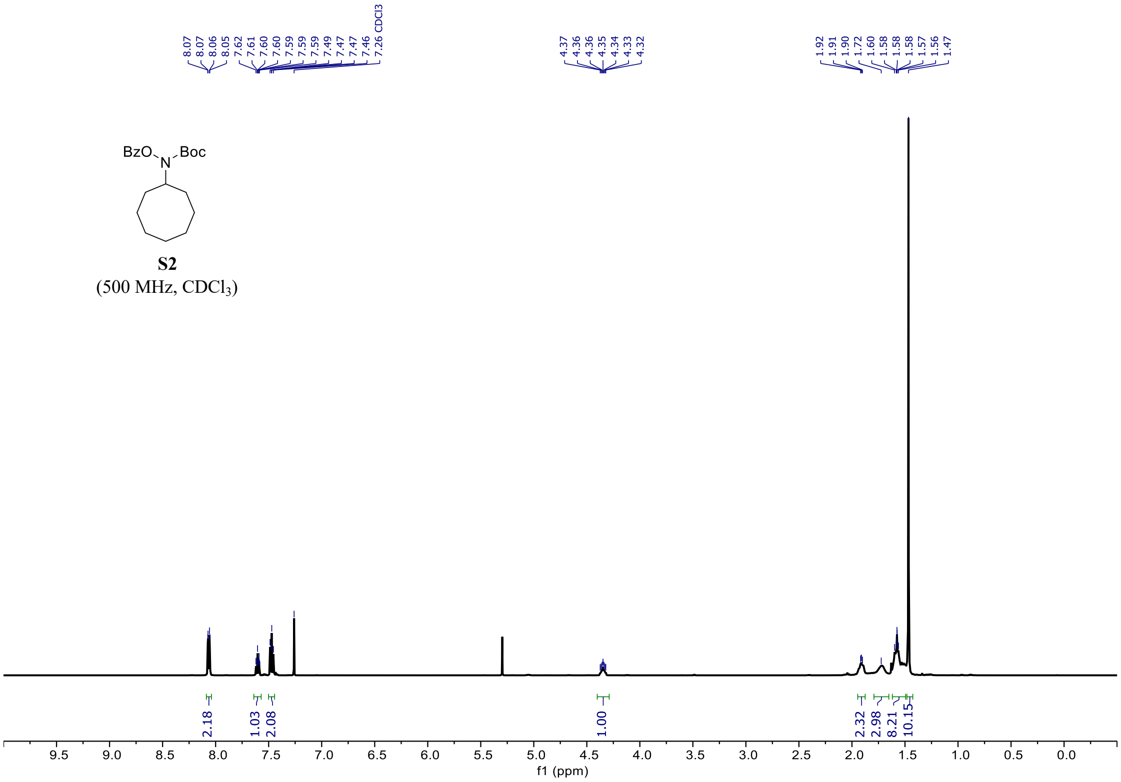
6. NMR Spectra



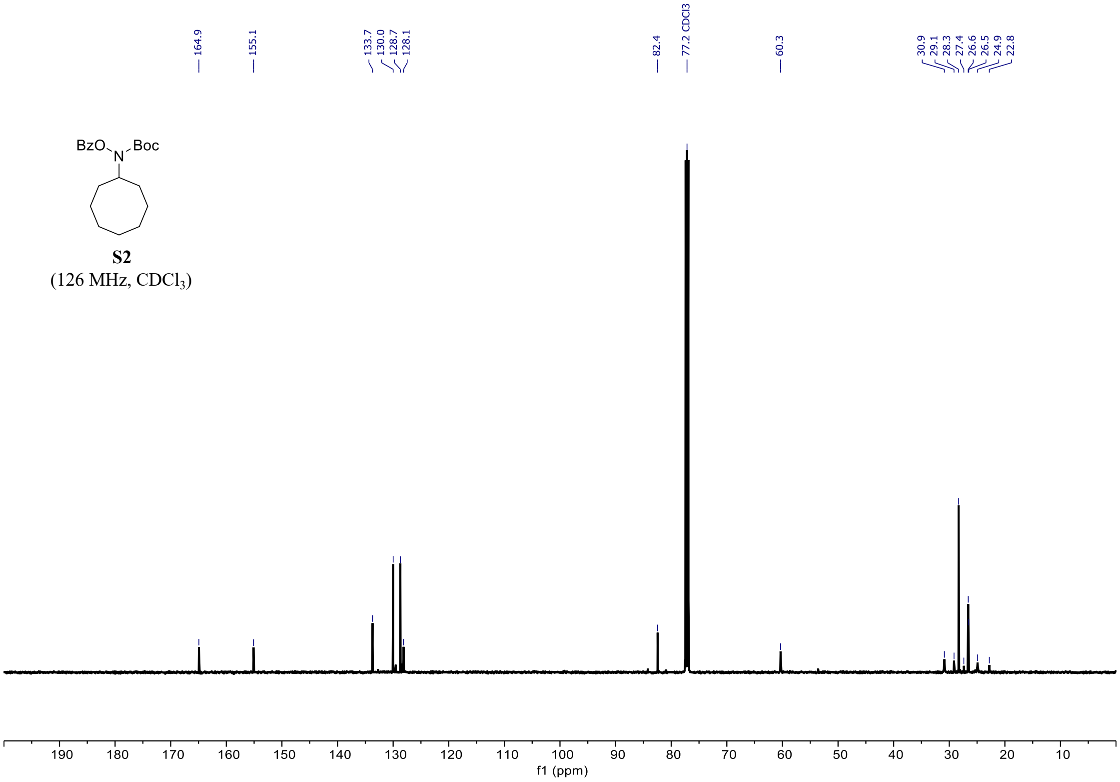
S1
(500 MHz, $CDCl_3$)



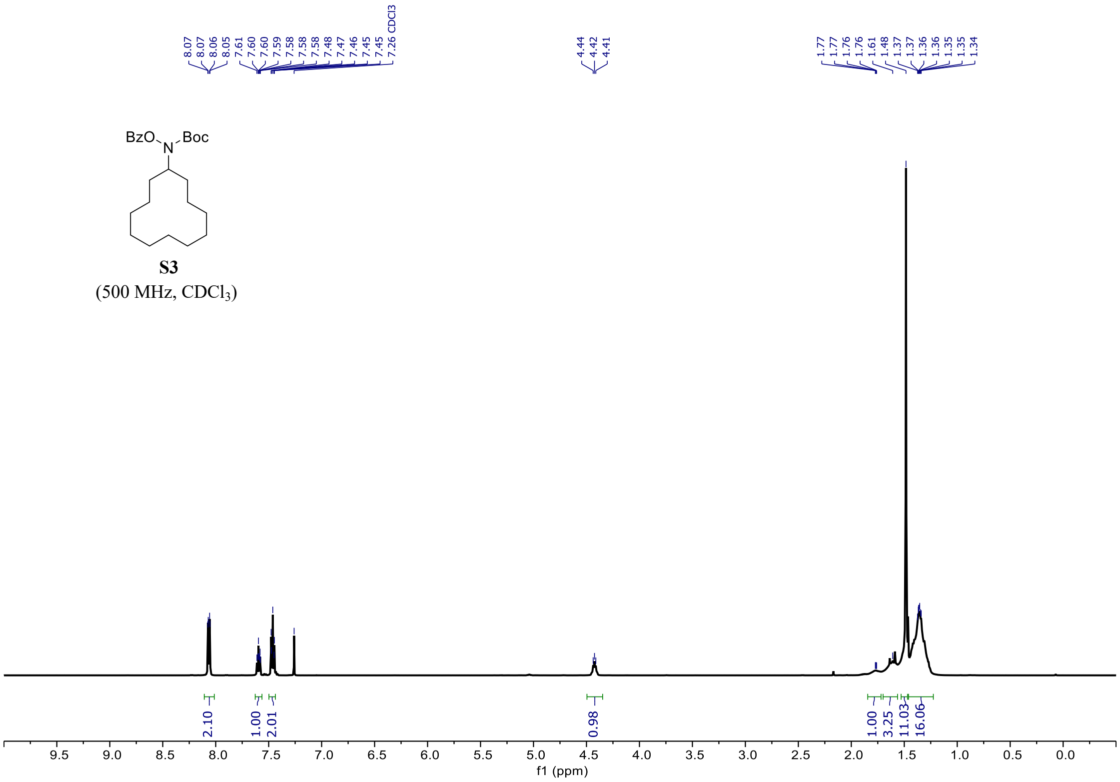
S1
(500 MHz, $CDCl_3$)



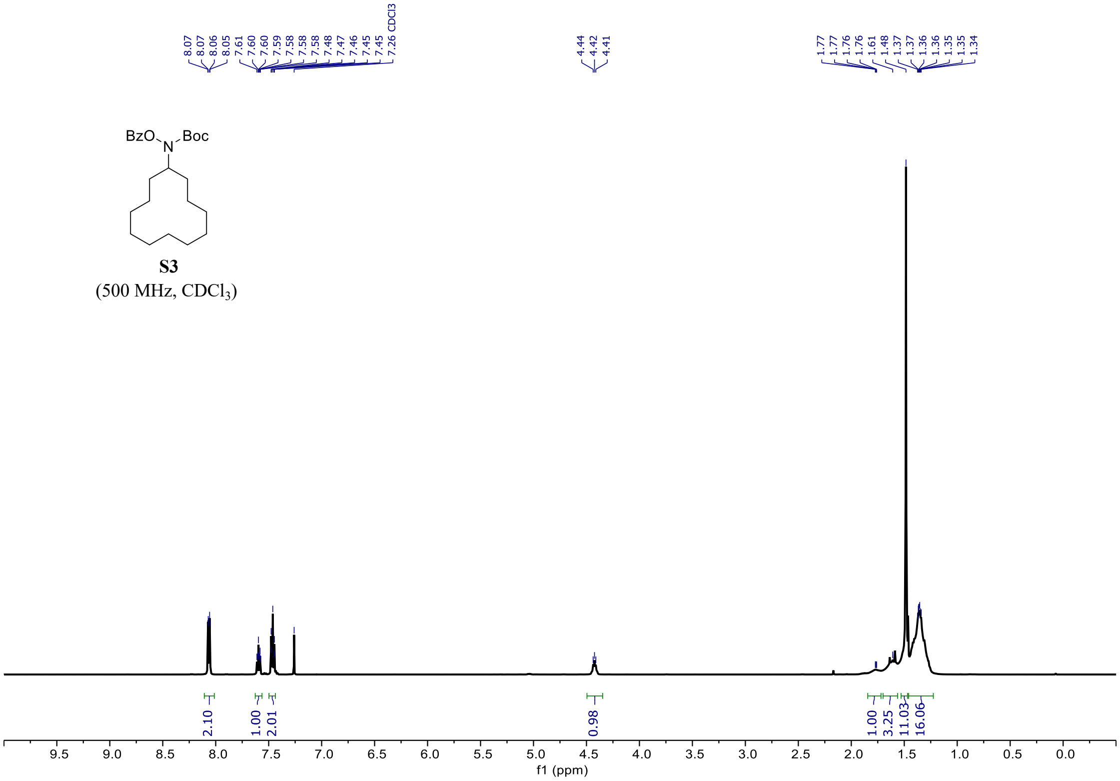
S2
(500 MHz, $CDCl_3$)

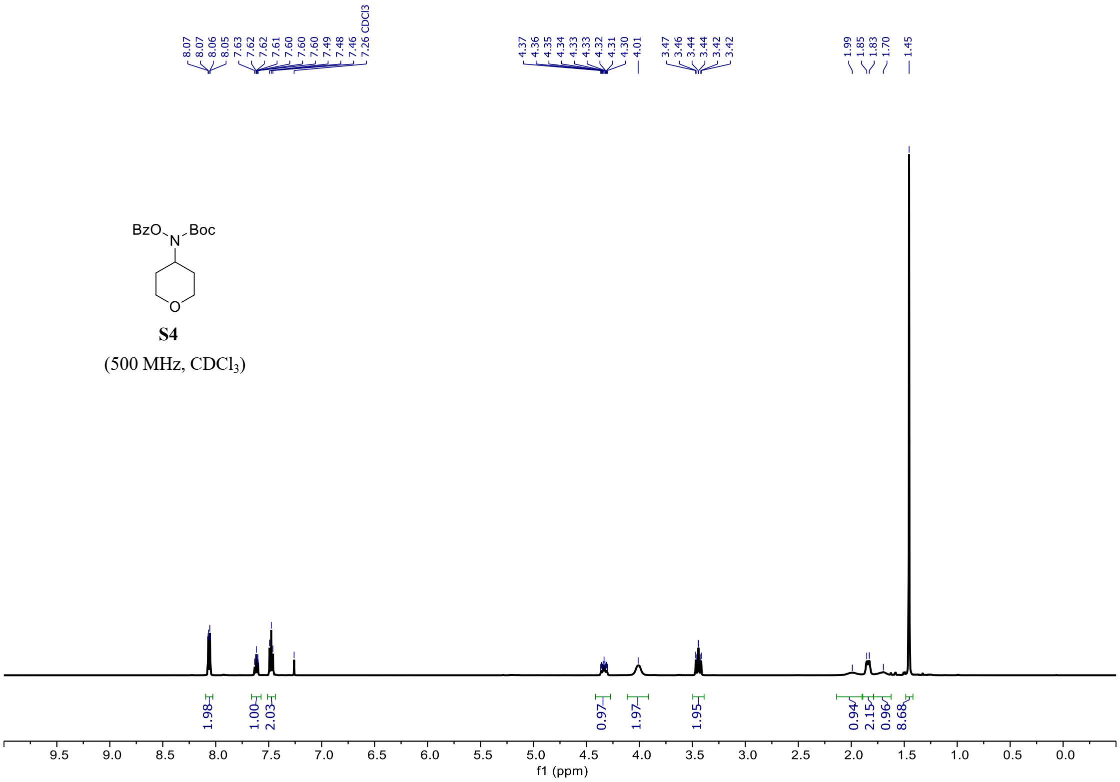


S2
(126 MHz, $CDCl_3$)



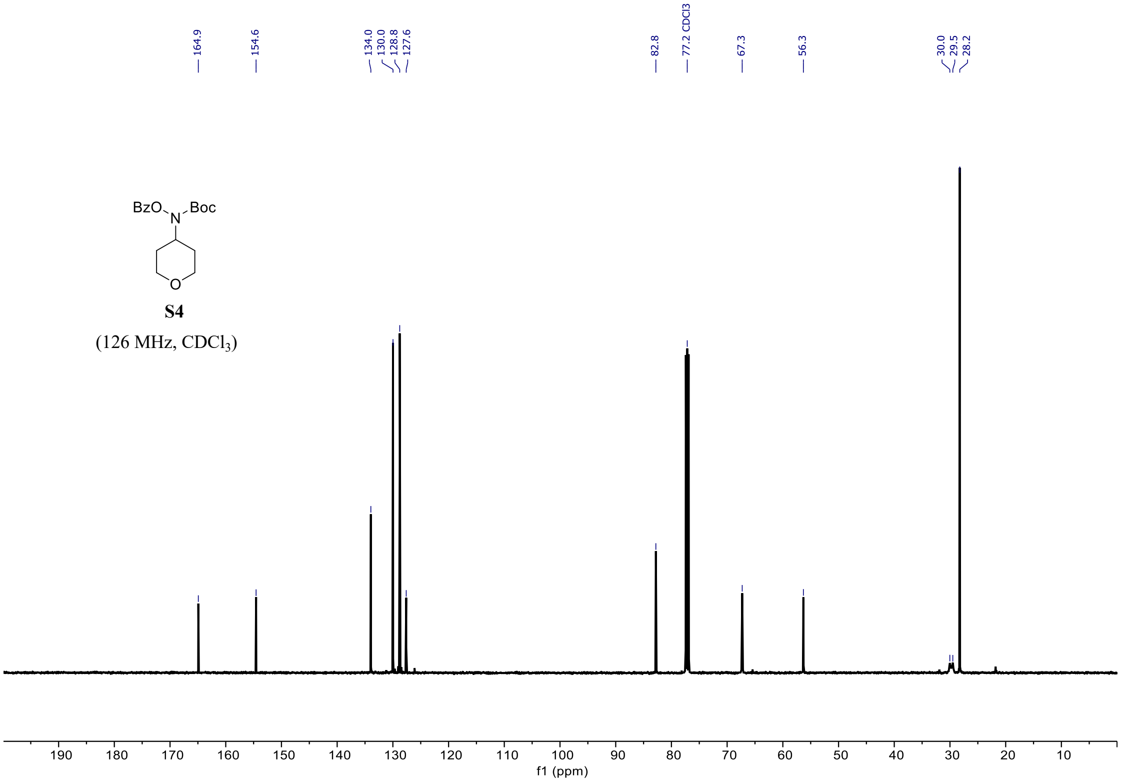
S3
(500 MHz, $CDCl_3$)


S3
(500 MHz, $CDCl_3$)



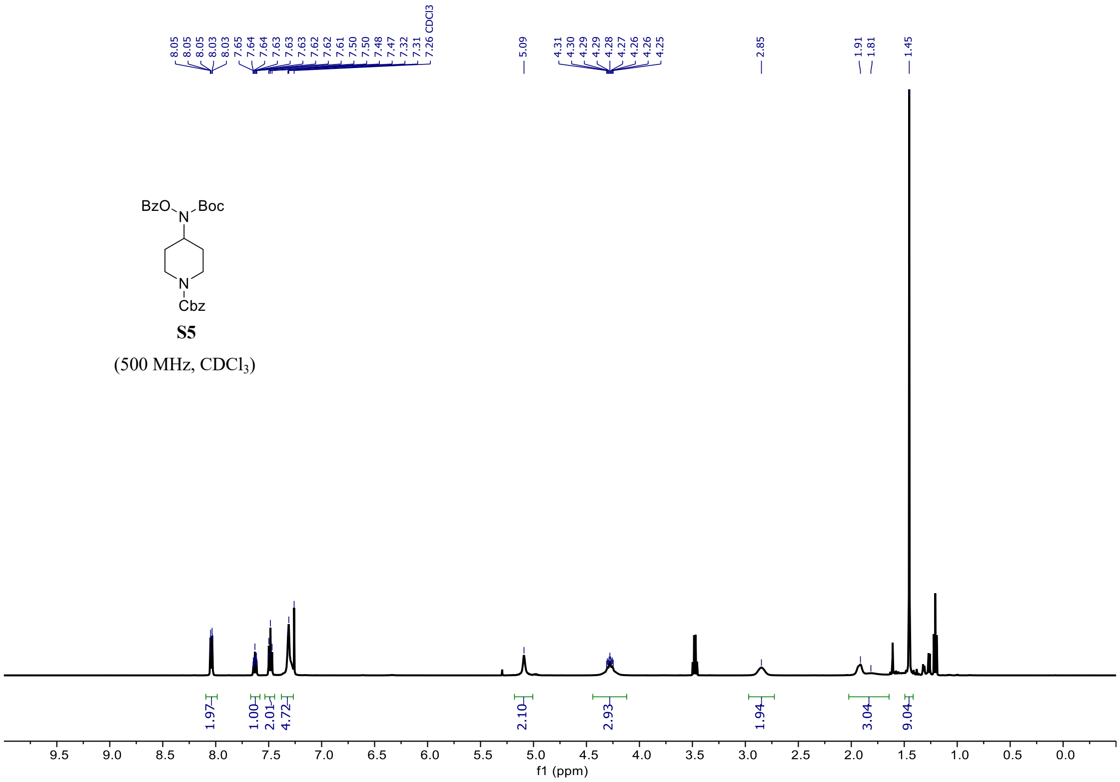
S4

(500 MHz, CDCl$_3$)



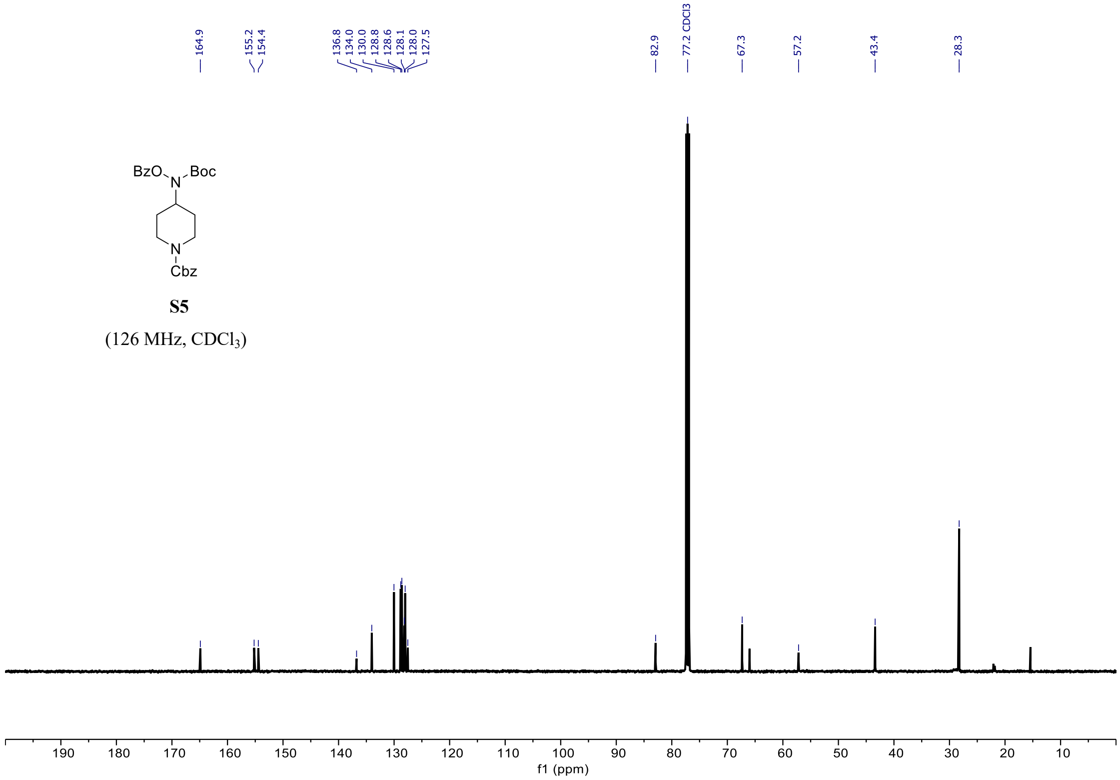
S4

(126 MHz, CDCl$_3$)



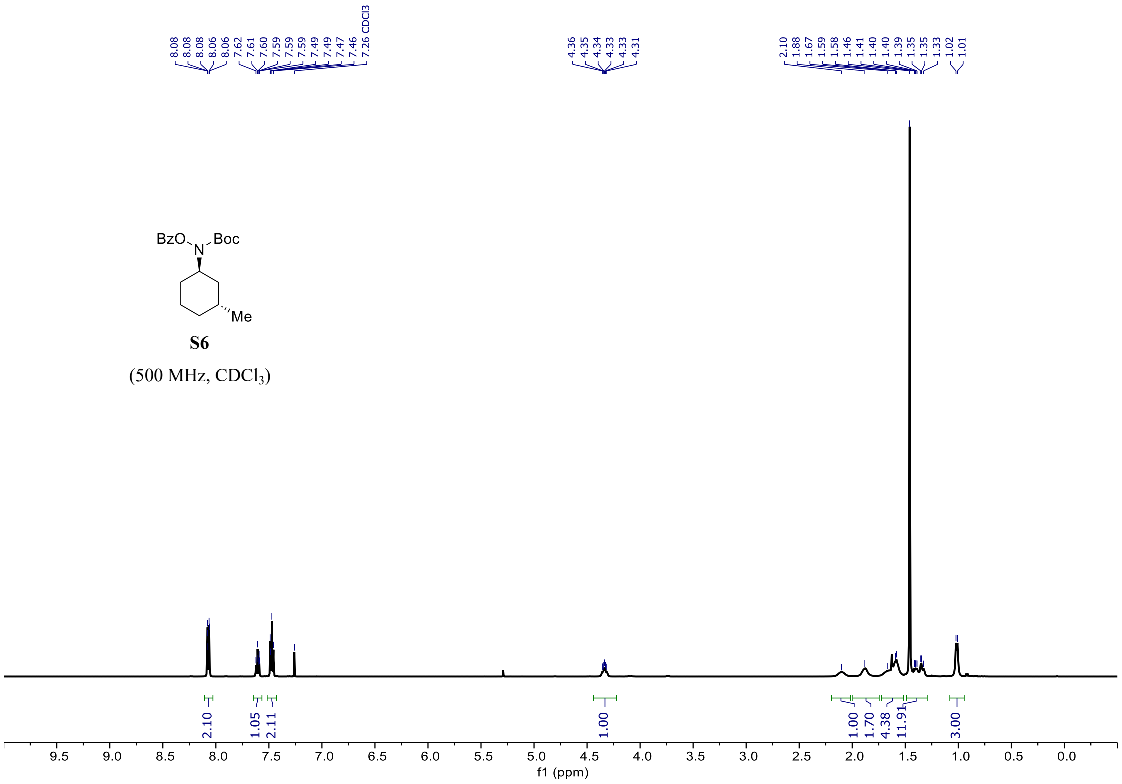
S5

(500 MHz, CDCl$_3$)



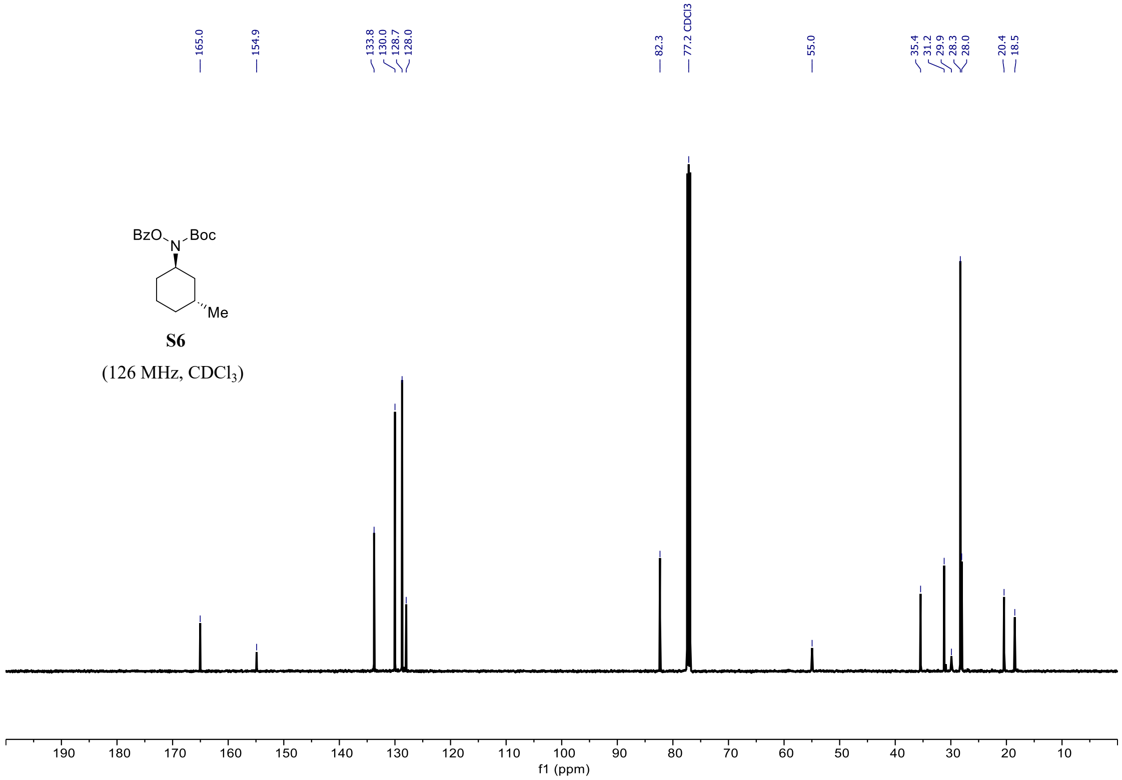
S5

(126 MHz, CDCl$_3$)



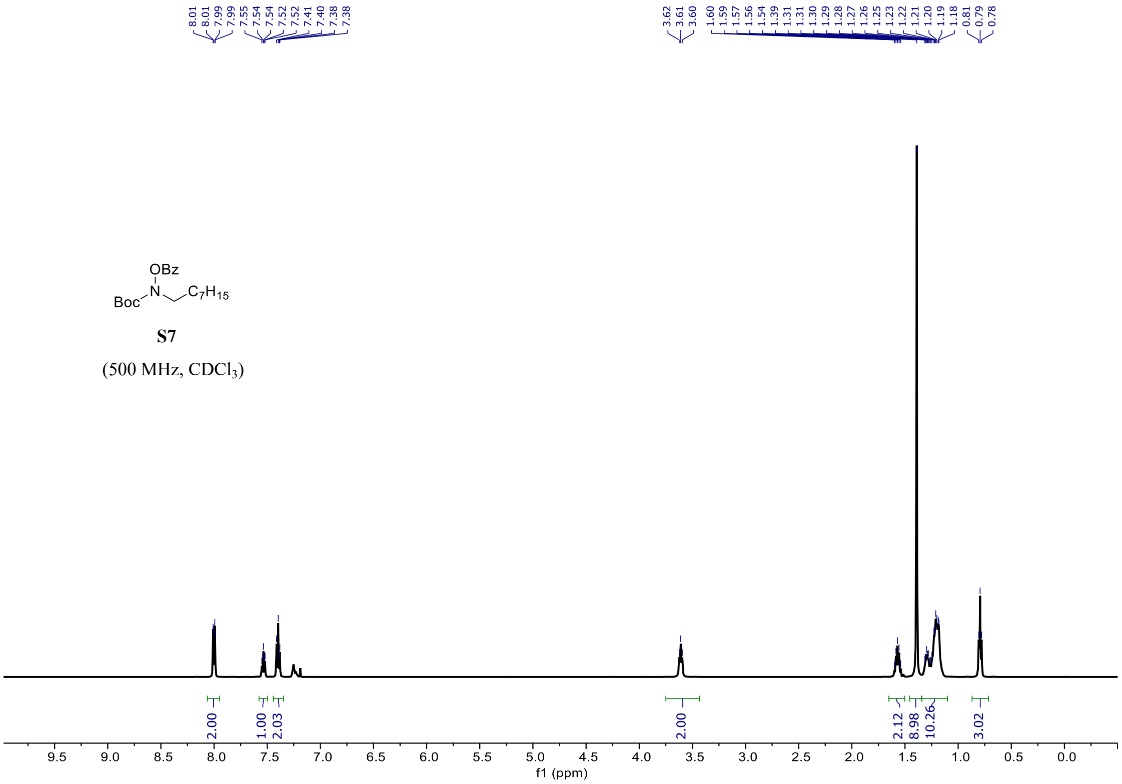
S6

(500 MHz, $CDCl_3$)



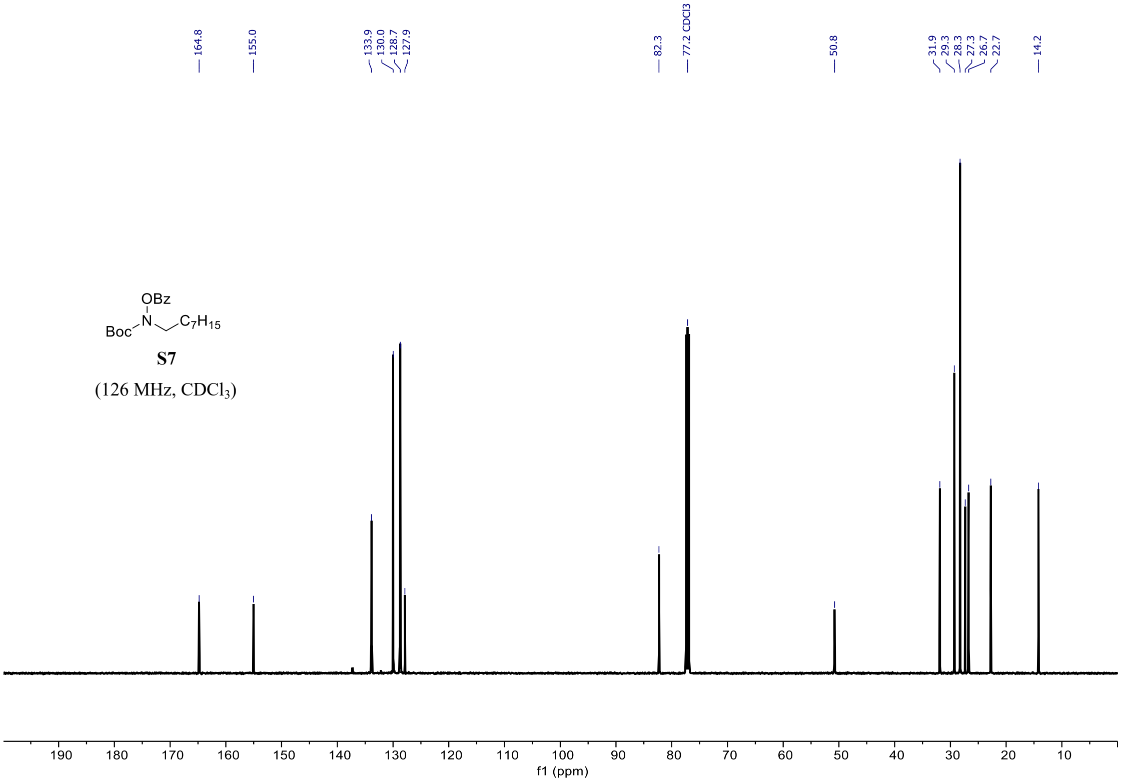
S6

(126 MHz, $CDCl_3$)



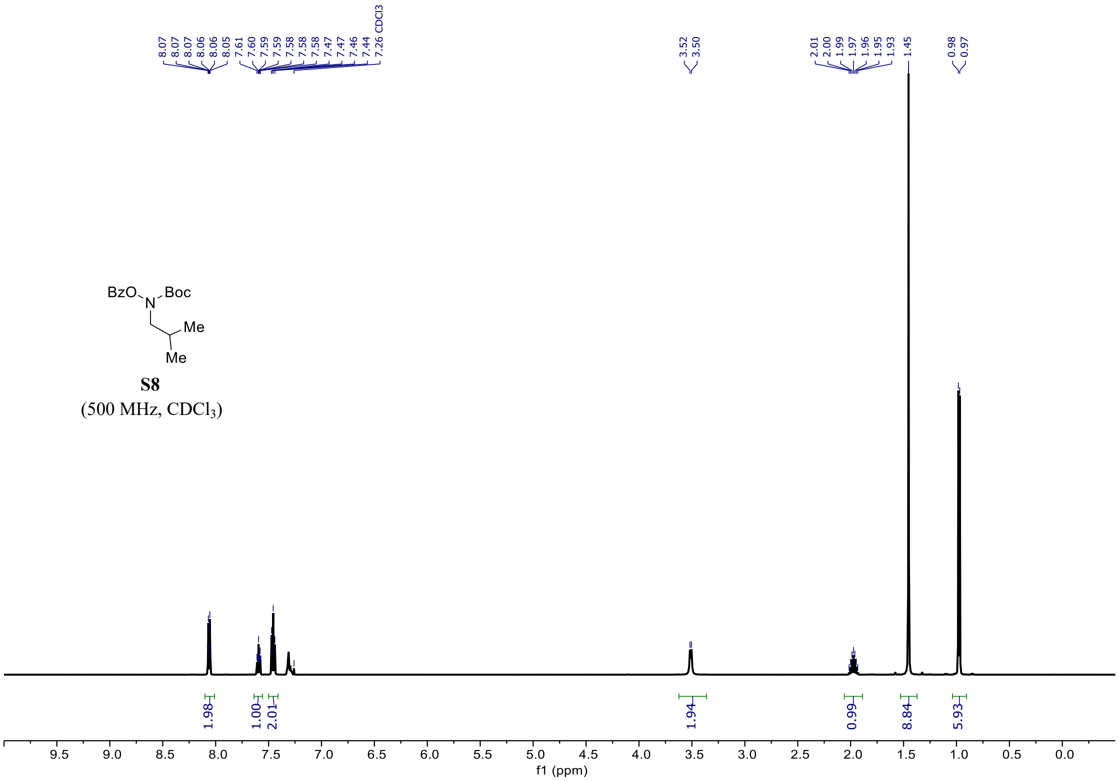
S7

(500 MHz, $CDCl_3$)



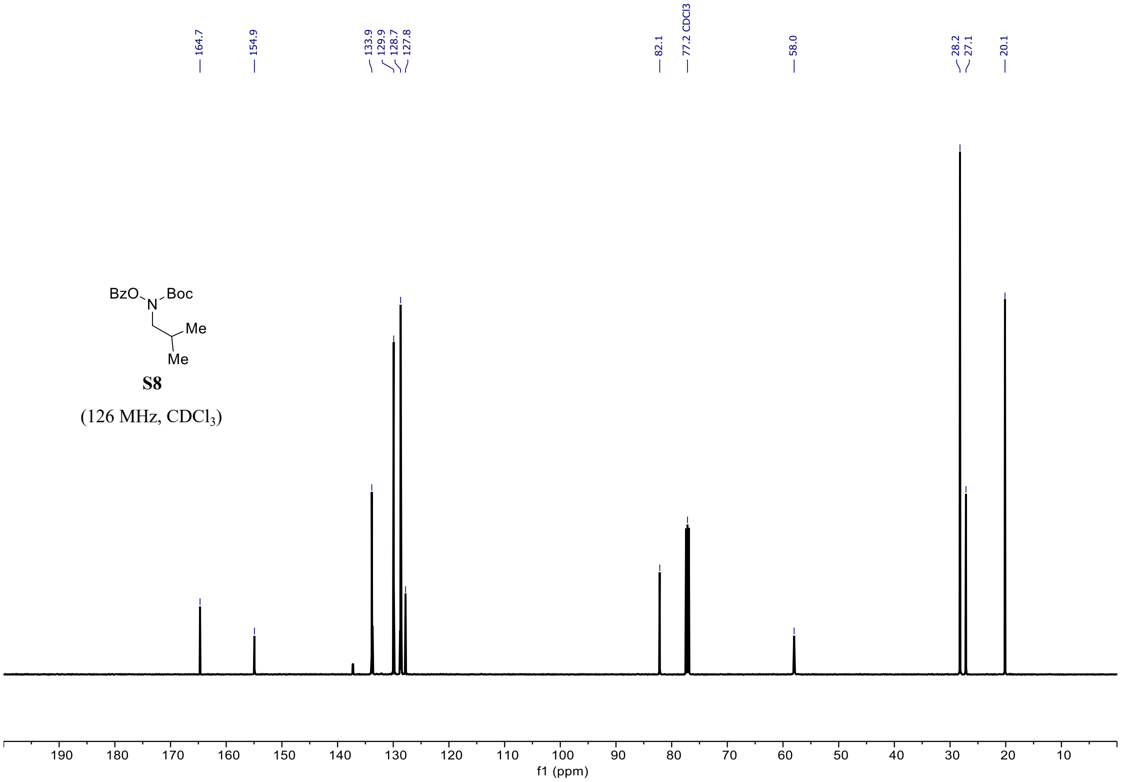
S7

(126 MHz, $CDCl_3$)



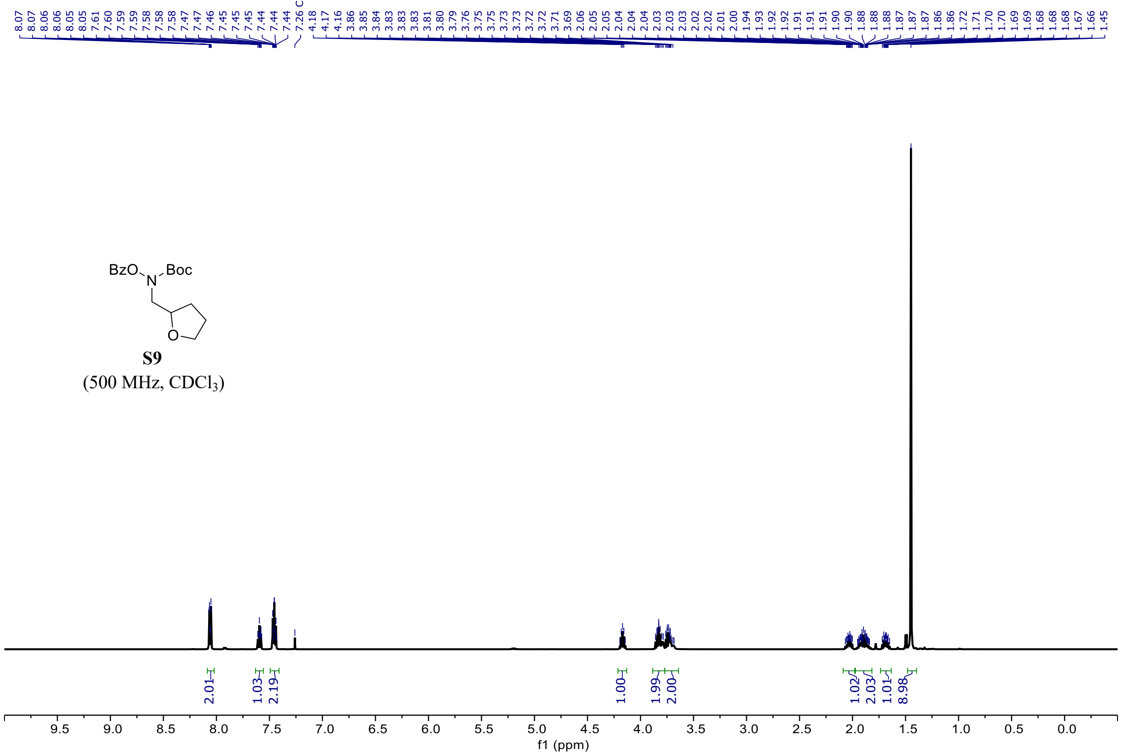
S8

(500 MHz, $CDCl_3$)



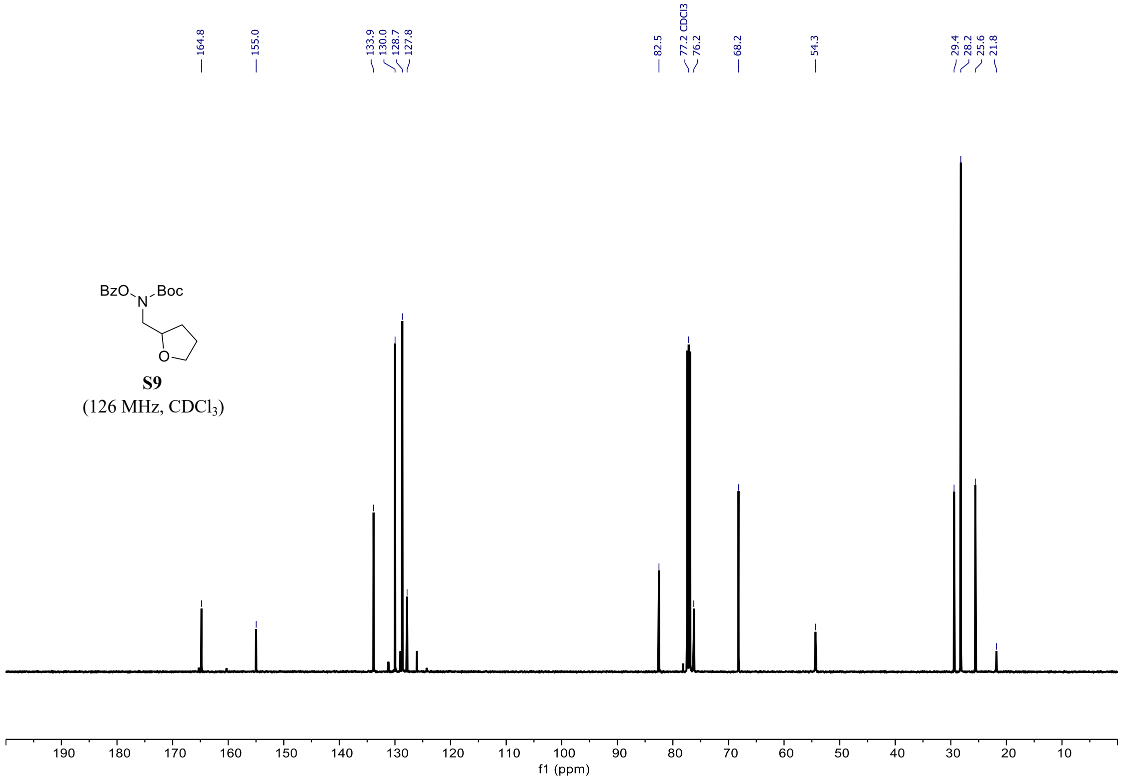
S8

(126 MHz, $CDCl_3$)



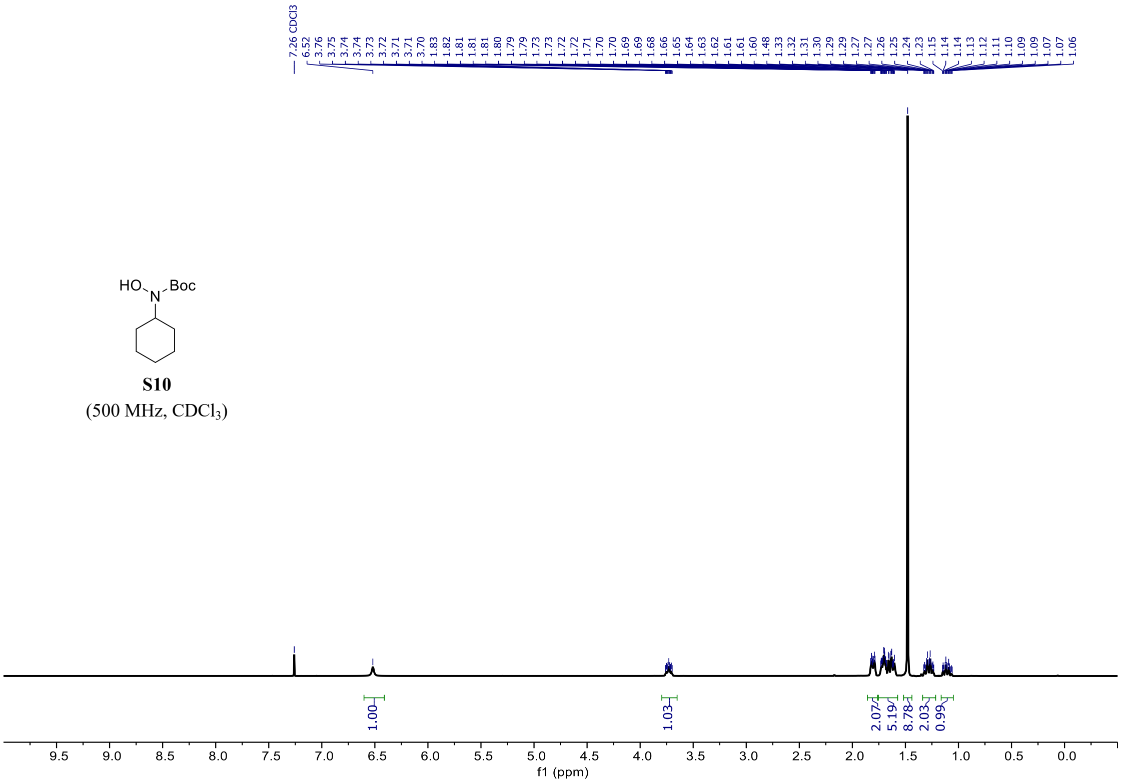
S9

(500 MHz, CDCl$_3$)

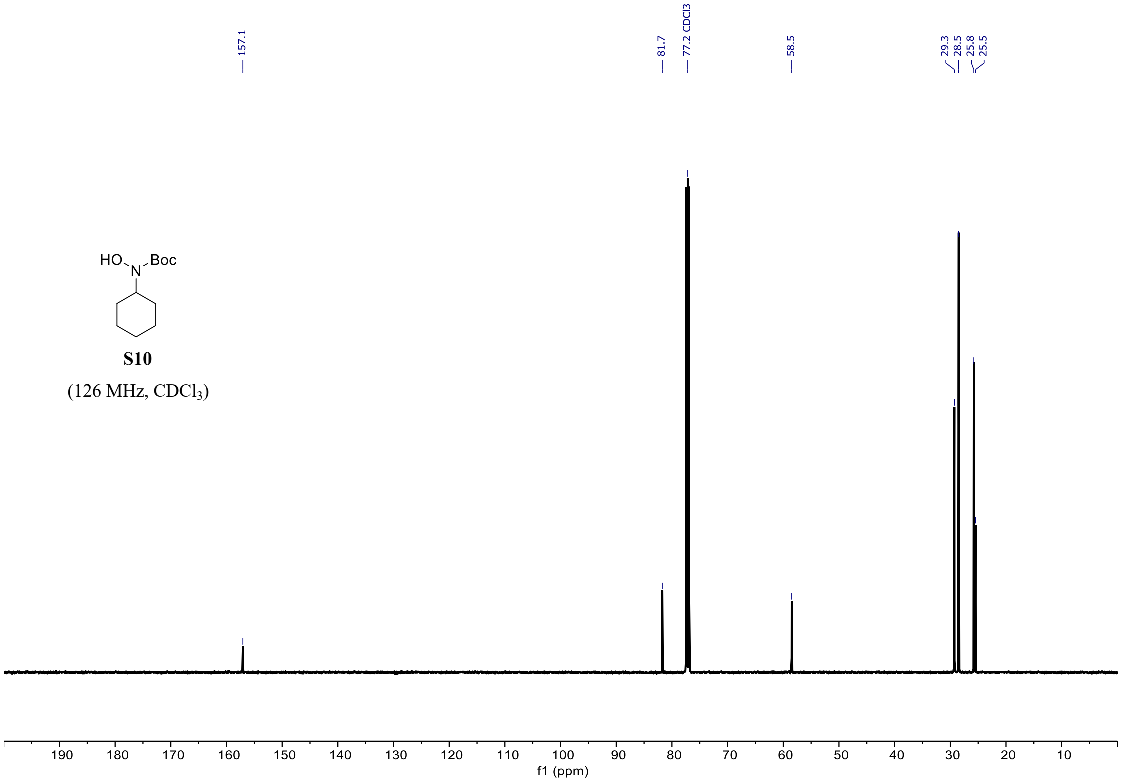


S9

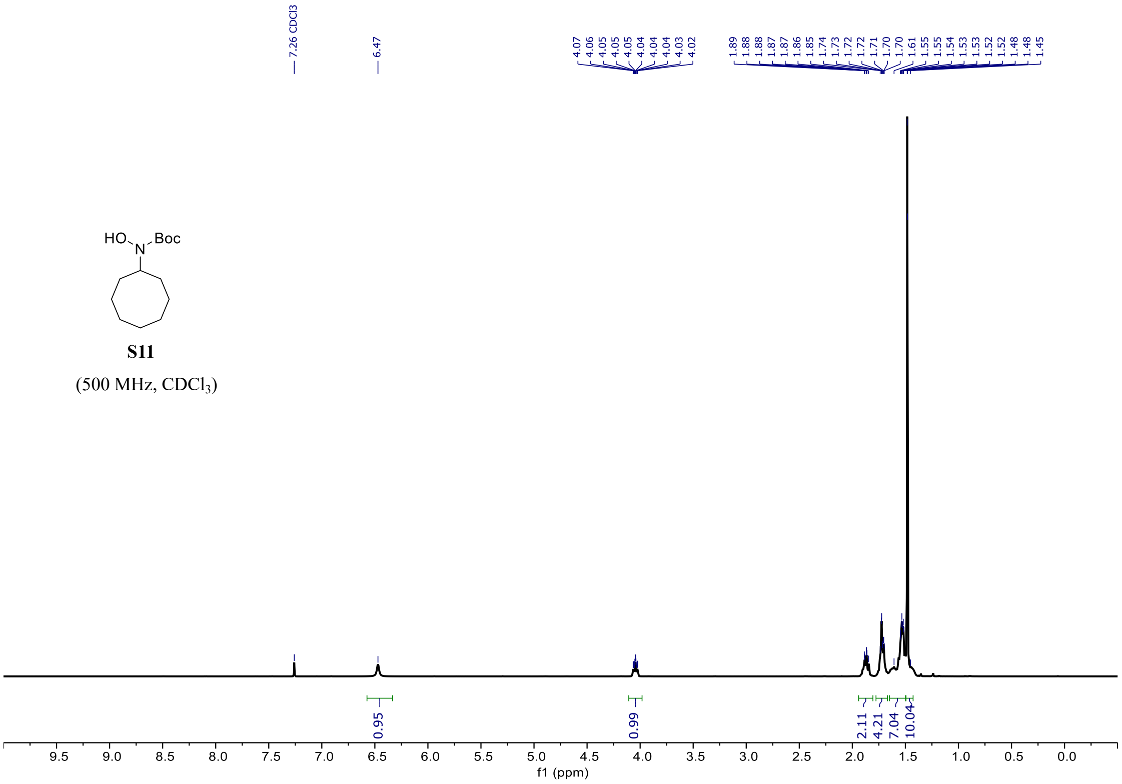
(126 MHz, CDCl$_3$)



S10
(500 MHz, $CDCl_3$)

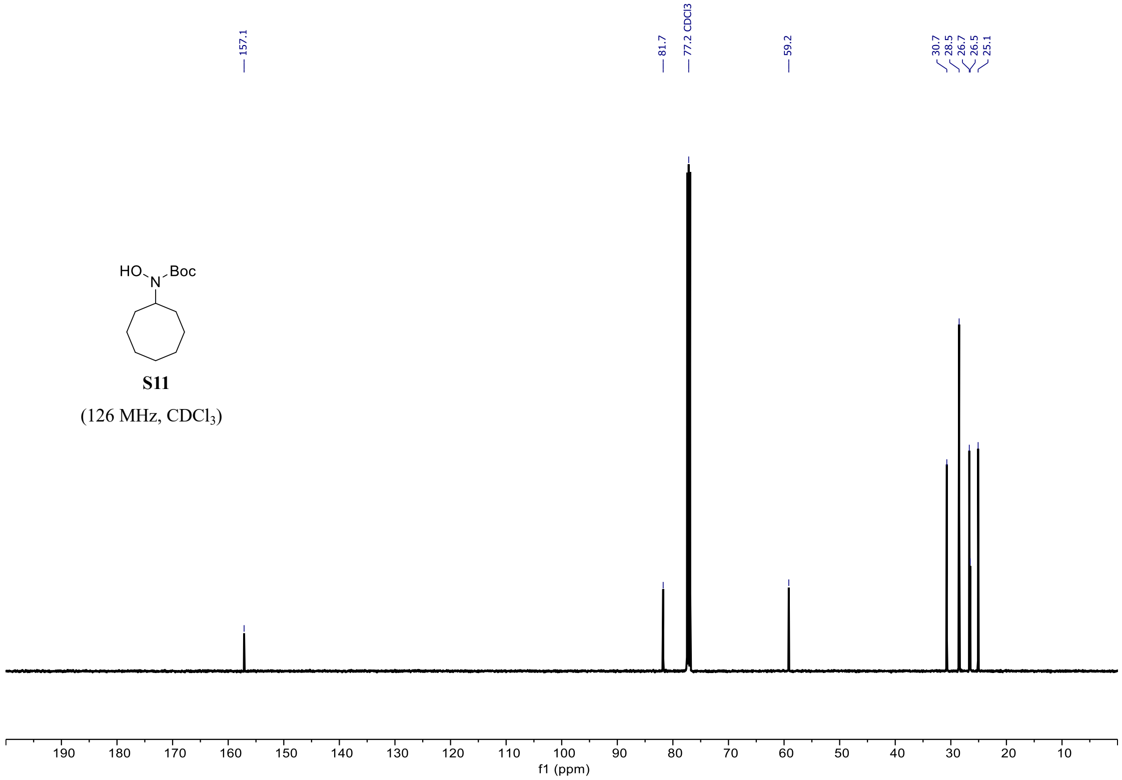


S10
(126 MHz, $CDCl_3$)



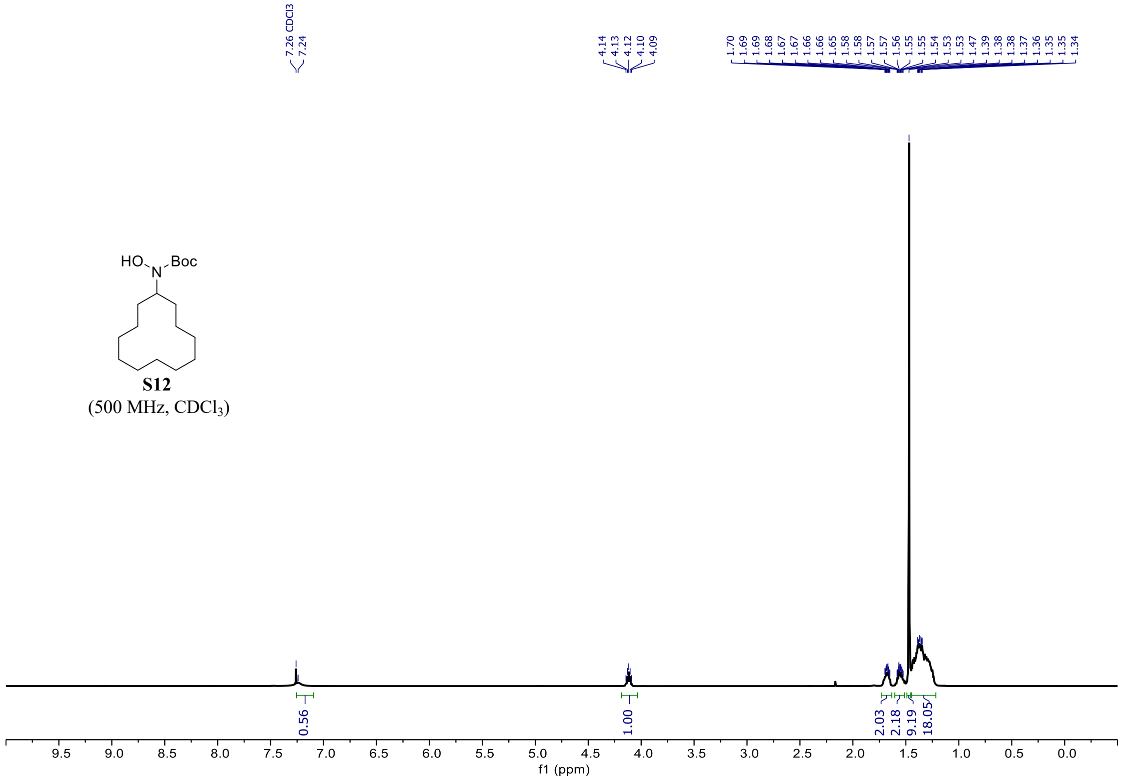
S11

(500 MHz, $CDCl_3$)

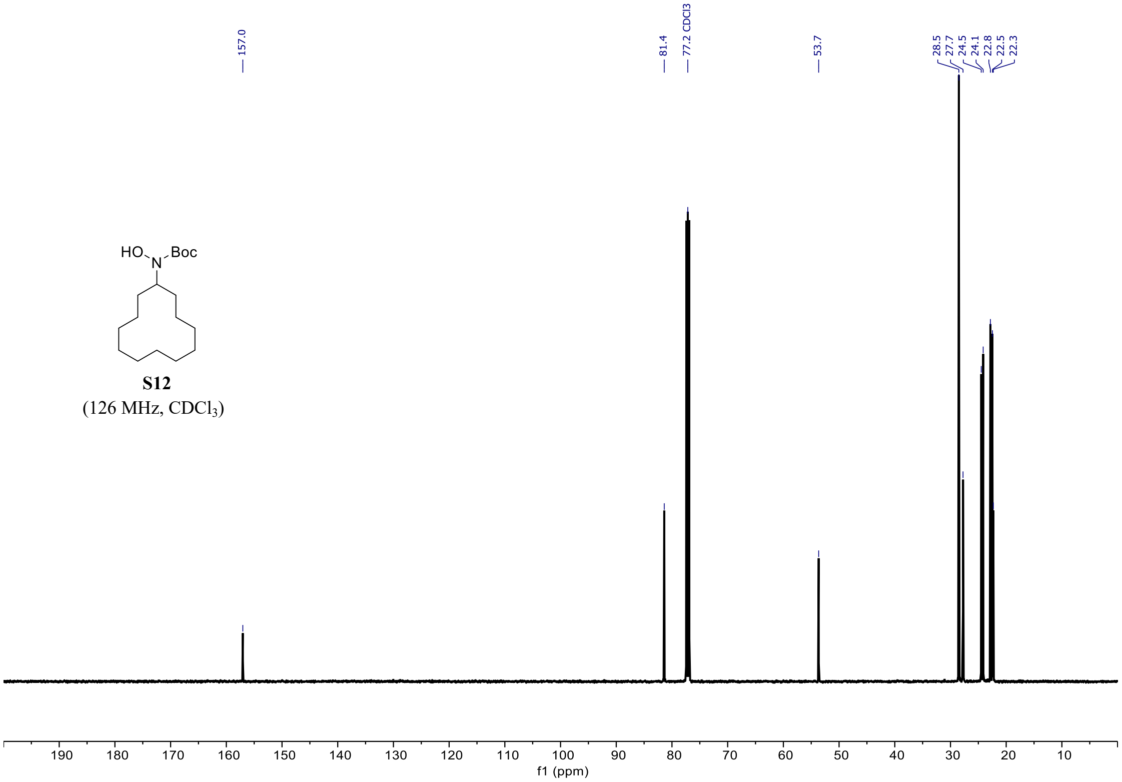


S11

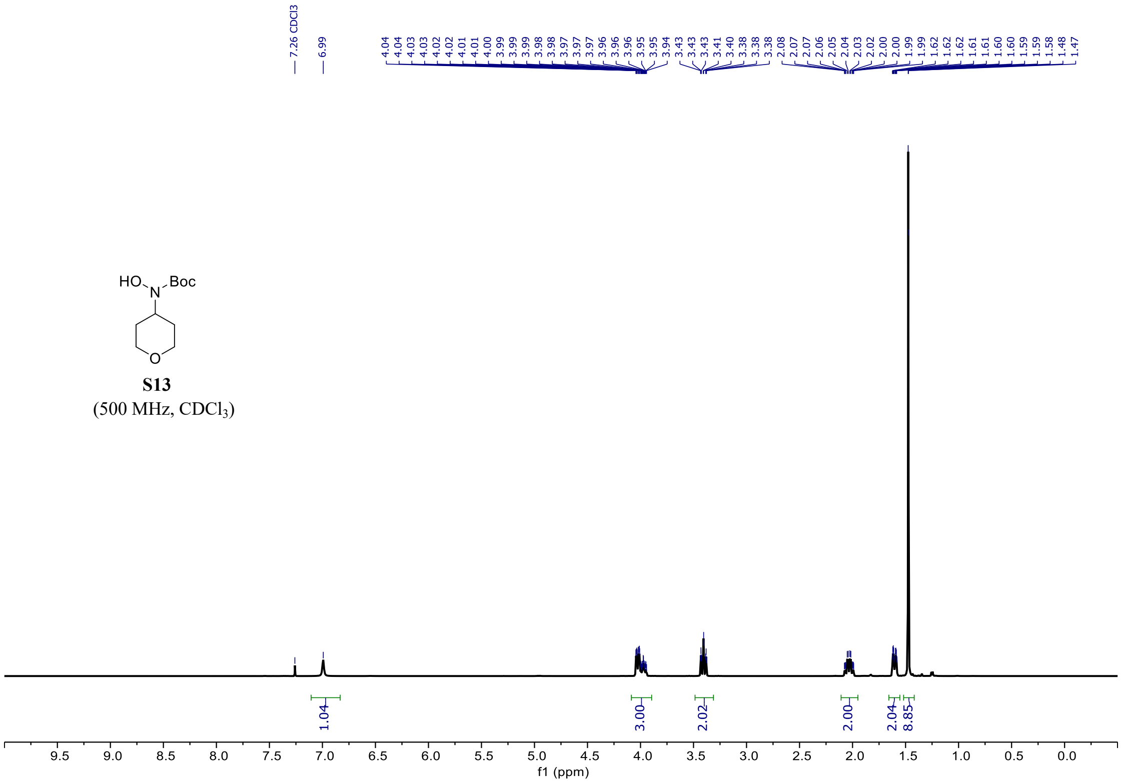
(126 MHz, $CDCl_3$)



S12
(500 MHz, $CDCl_3$)

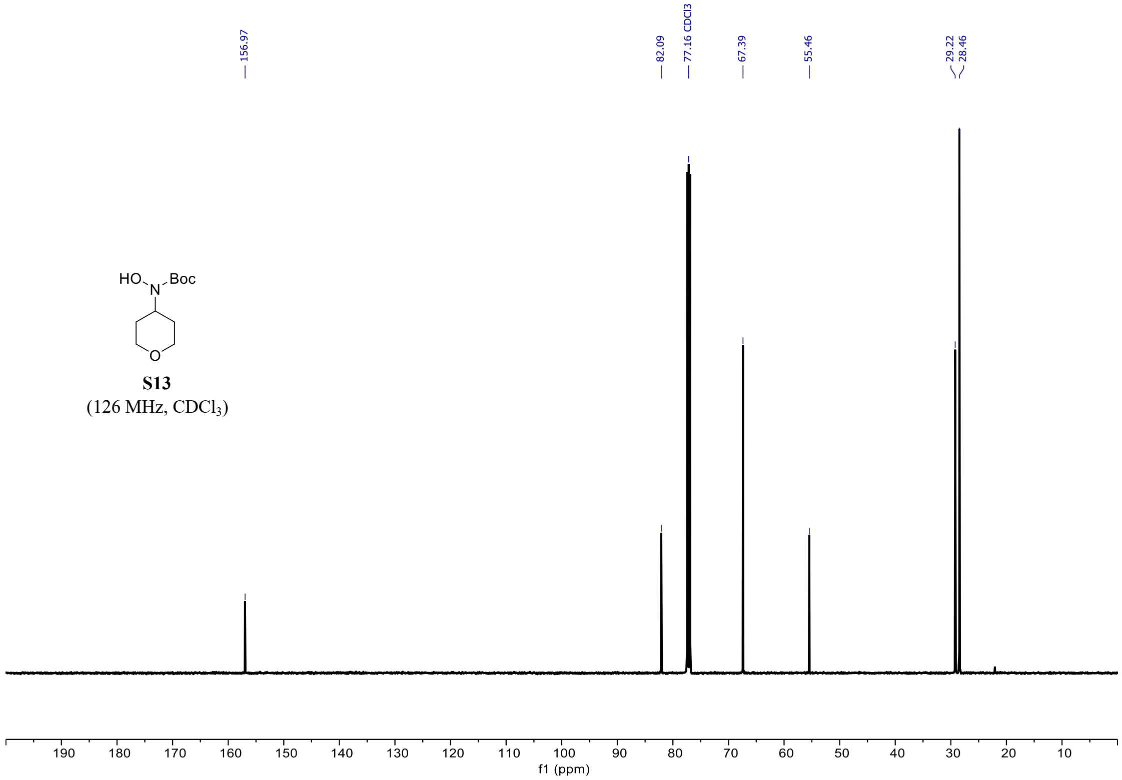


S12
(126 MHz, $CDCl_3$)



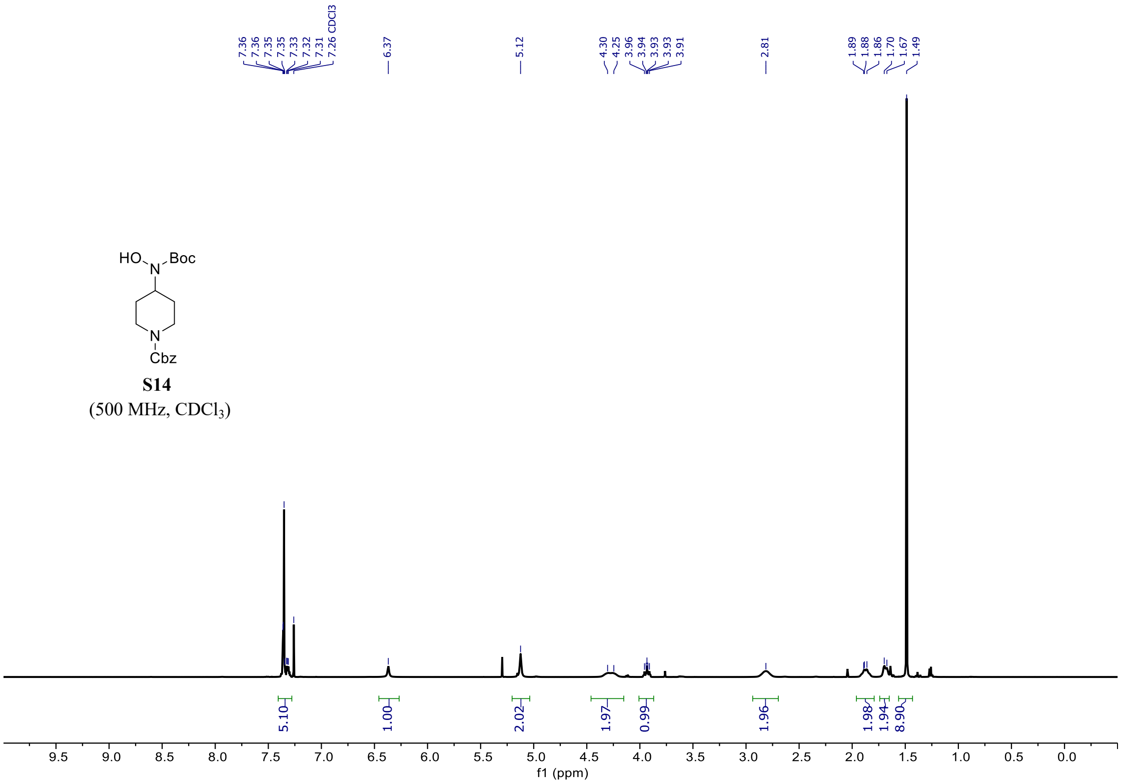
S13

(500 MHz, $CDCl_3$)



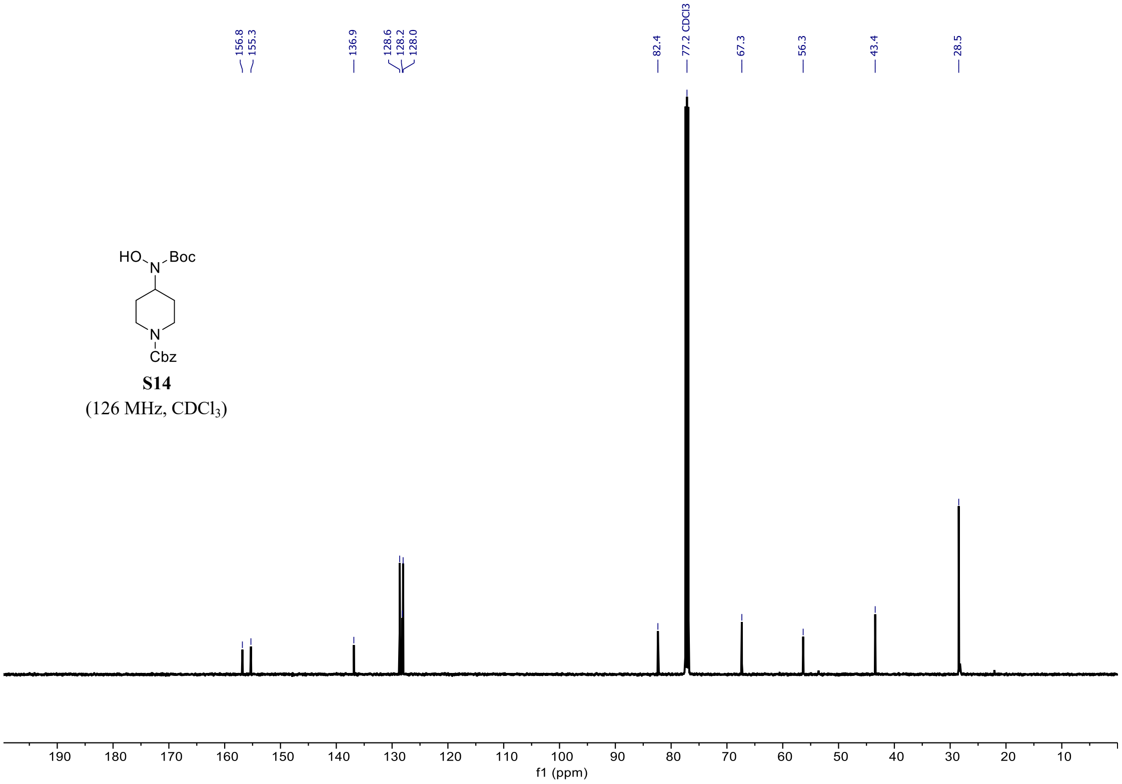
S13

(126 MHz, $CDCl_3$)



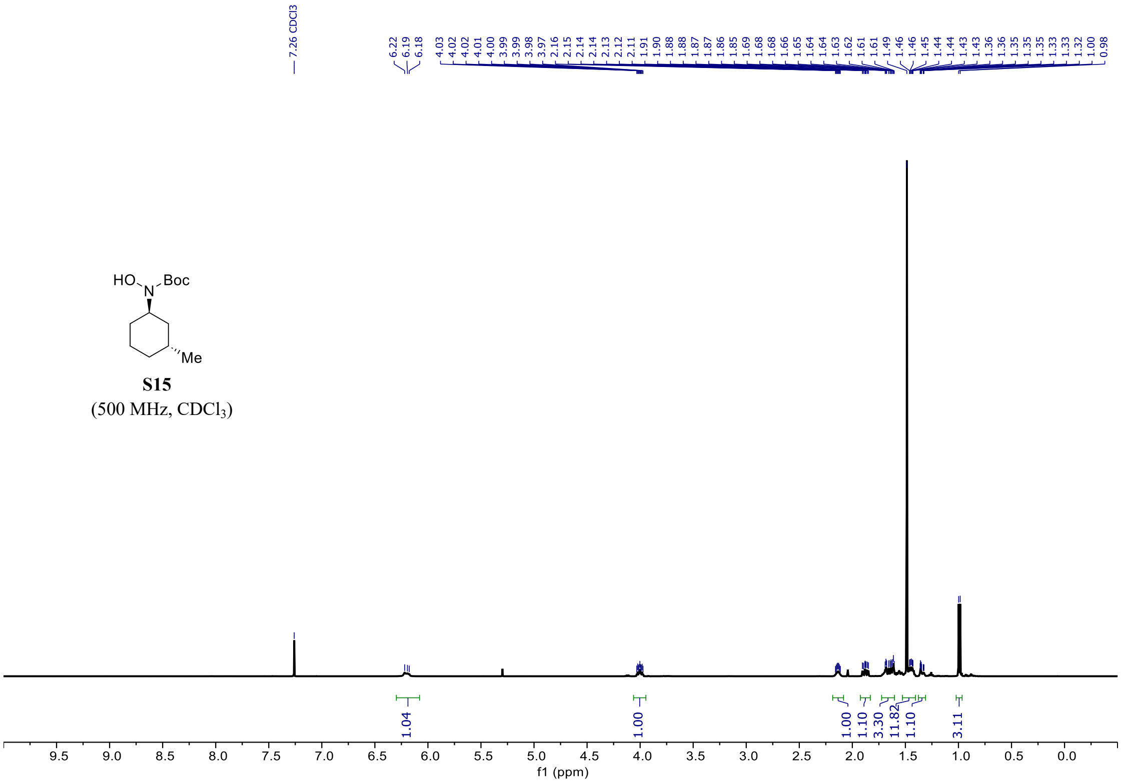
S14

(500 MHz, $CDCl_3$)

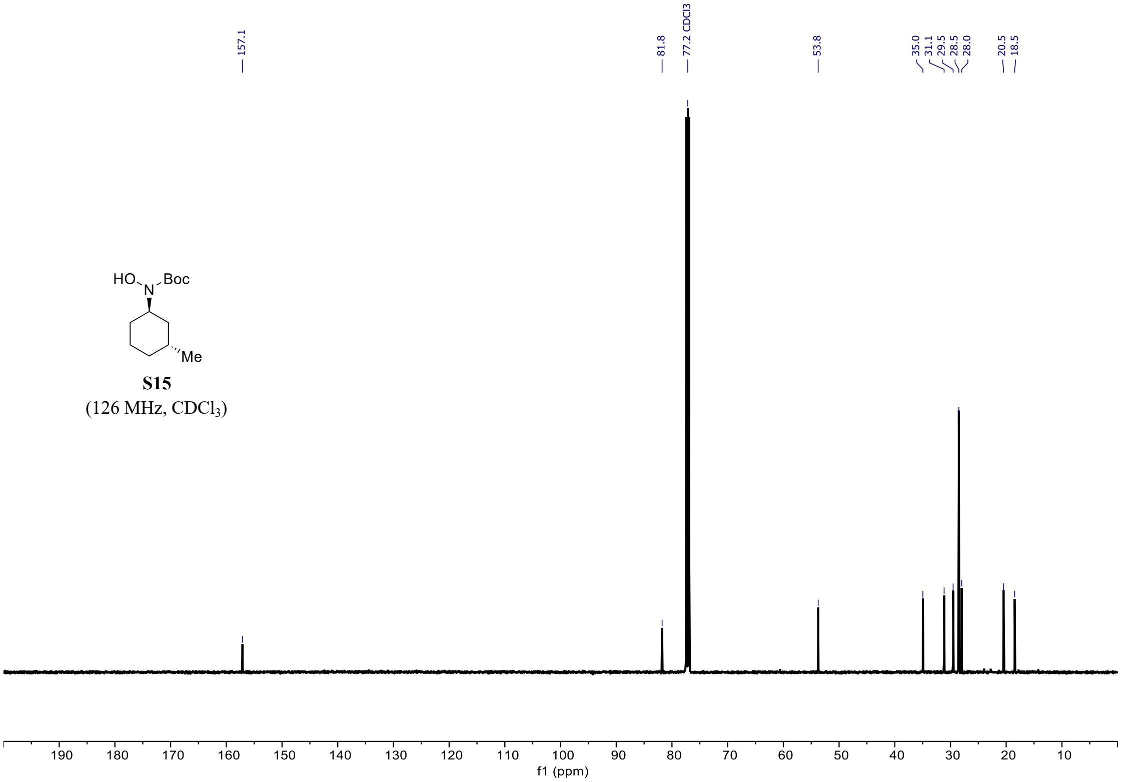


S14

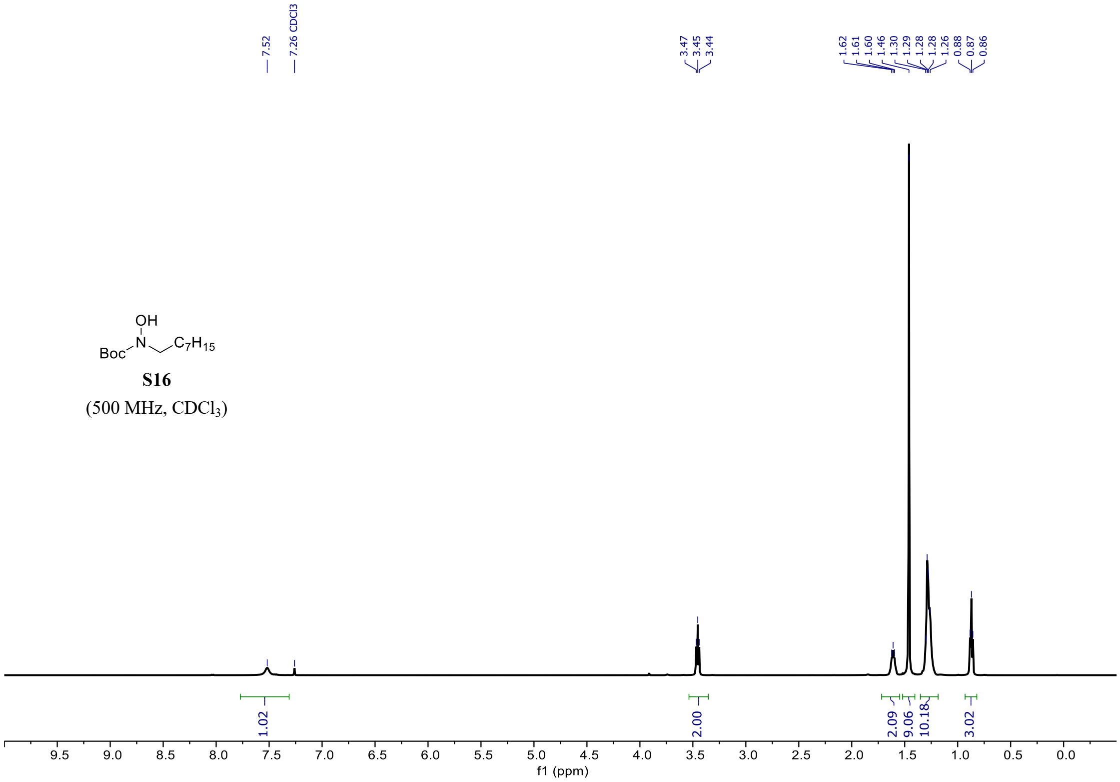
(126 MHz, $CDCl_3$)



S15
(500 MHz, $CDCl_3$)

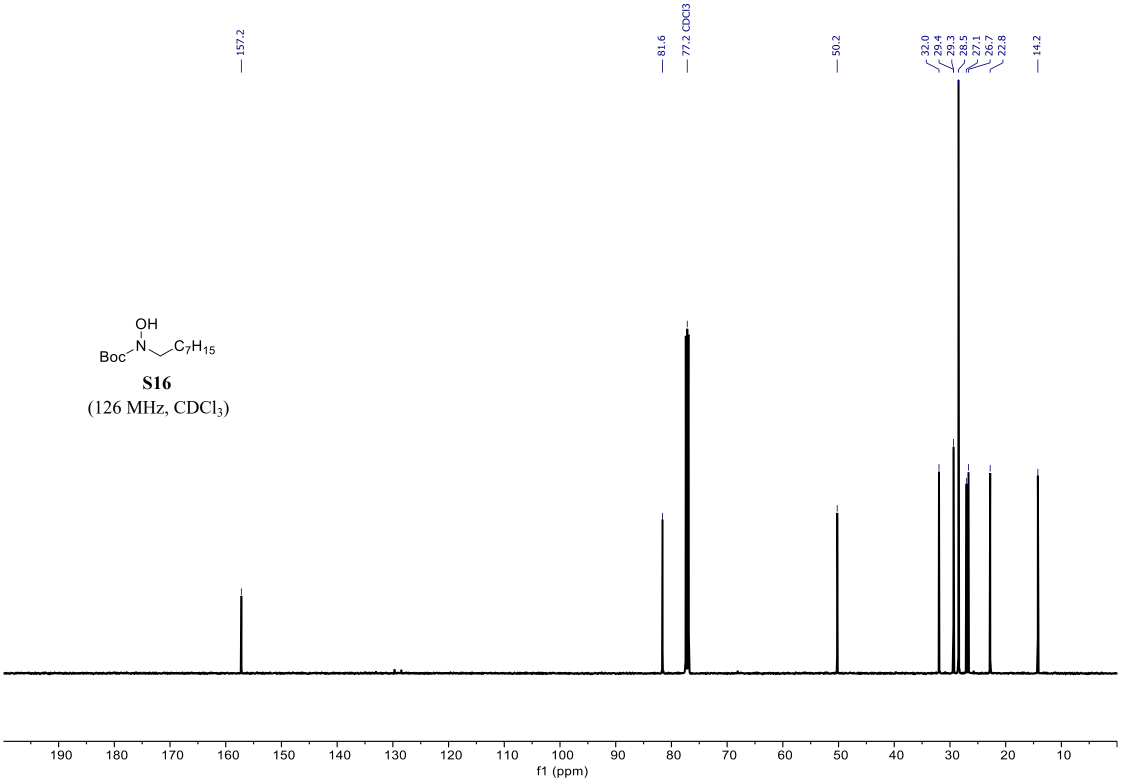


S15
(126 MHz, $CDCl_3$)



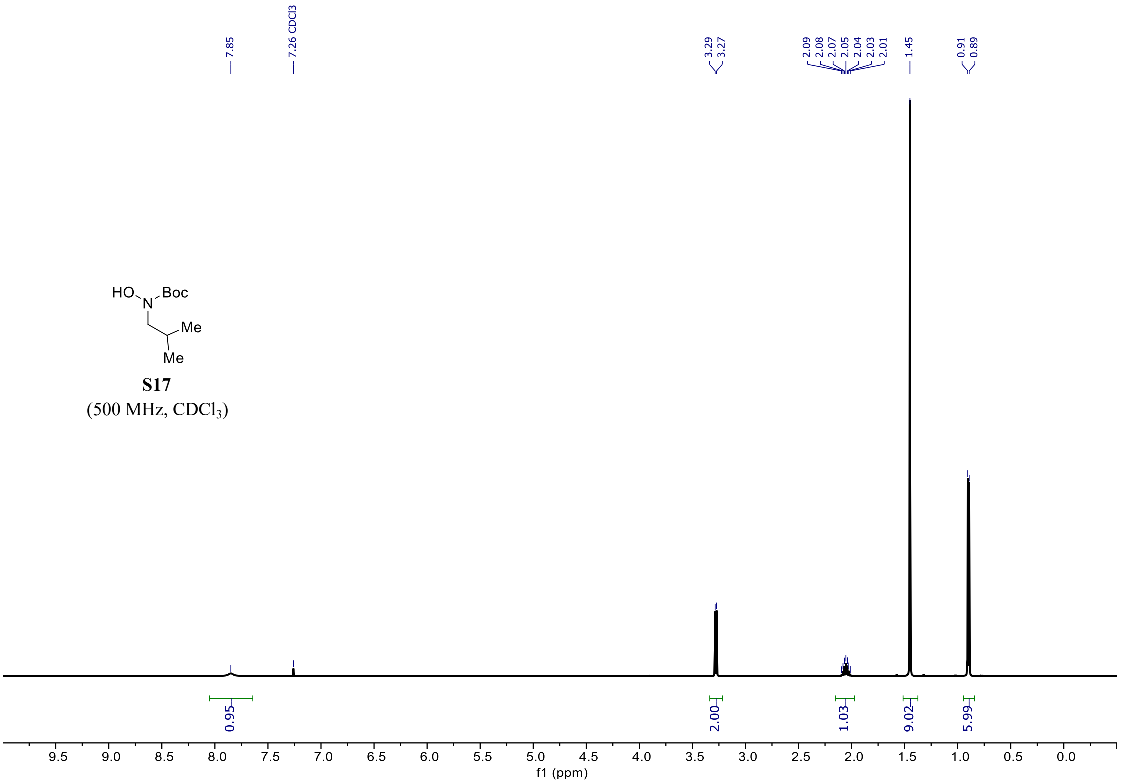
S16

(500 MHz, CDCl$_3$)

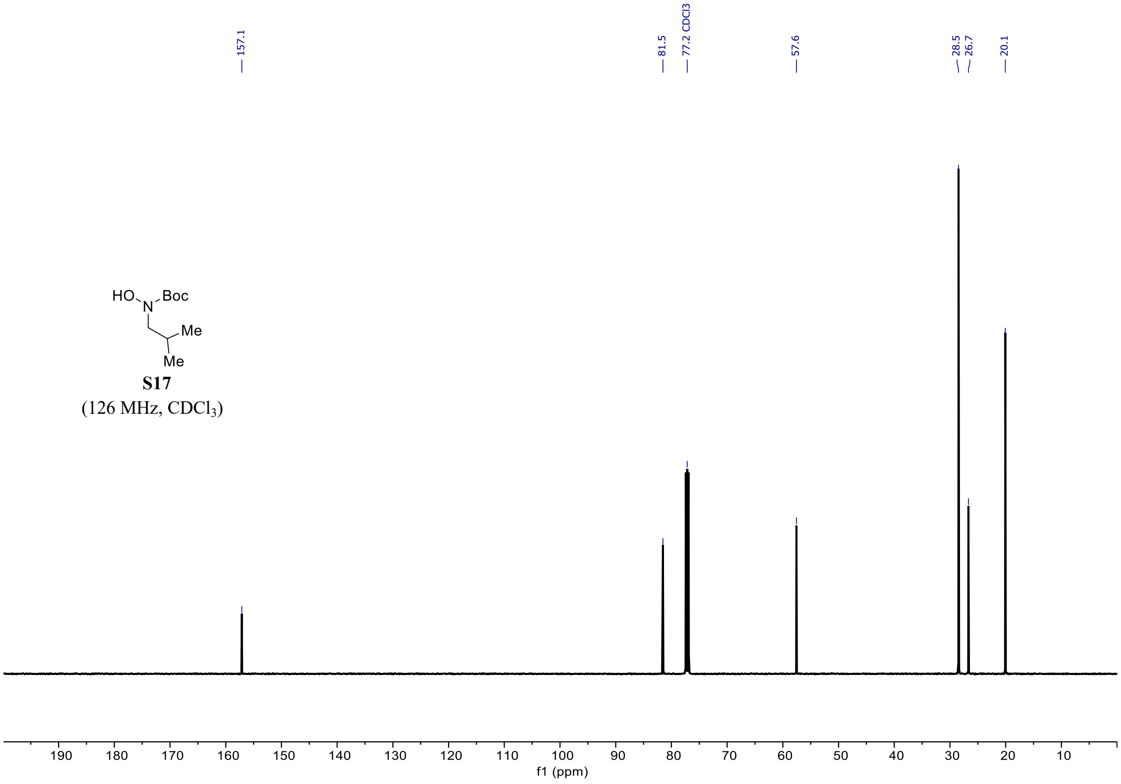


S16

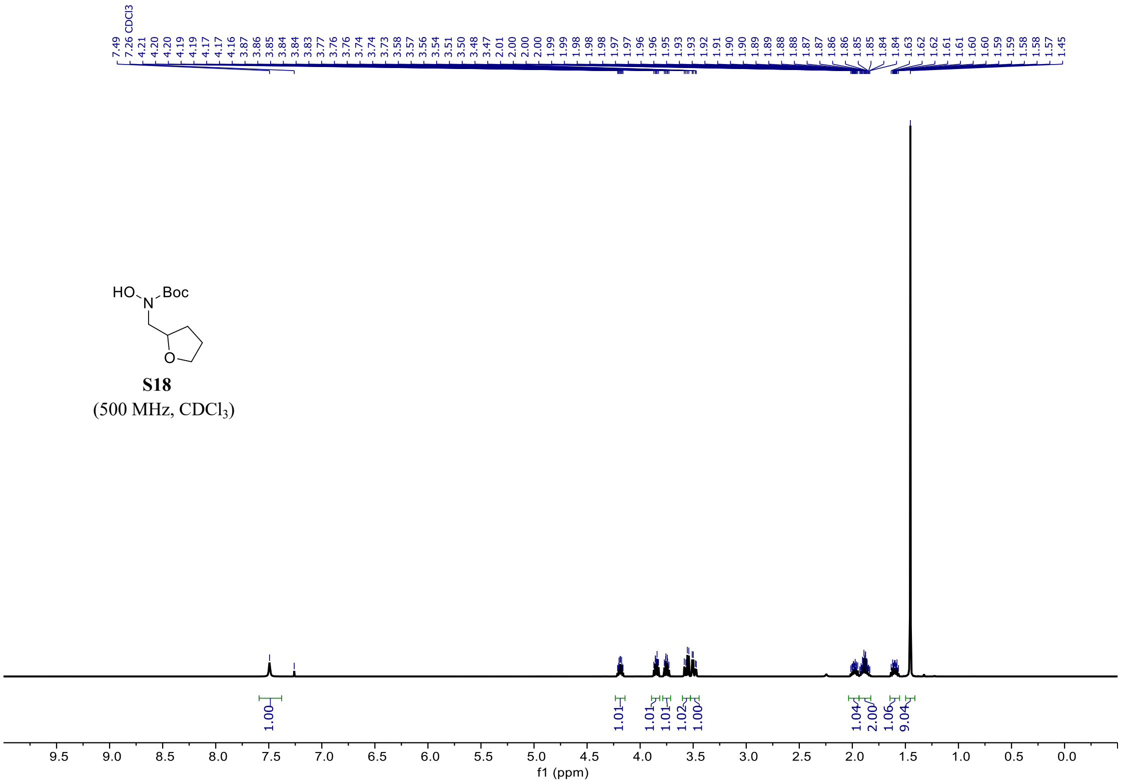
(126 MHz, CDCl$_3$)



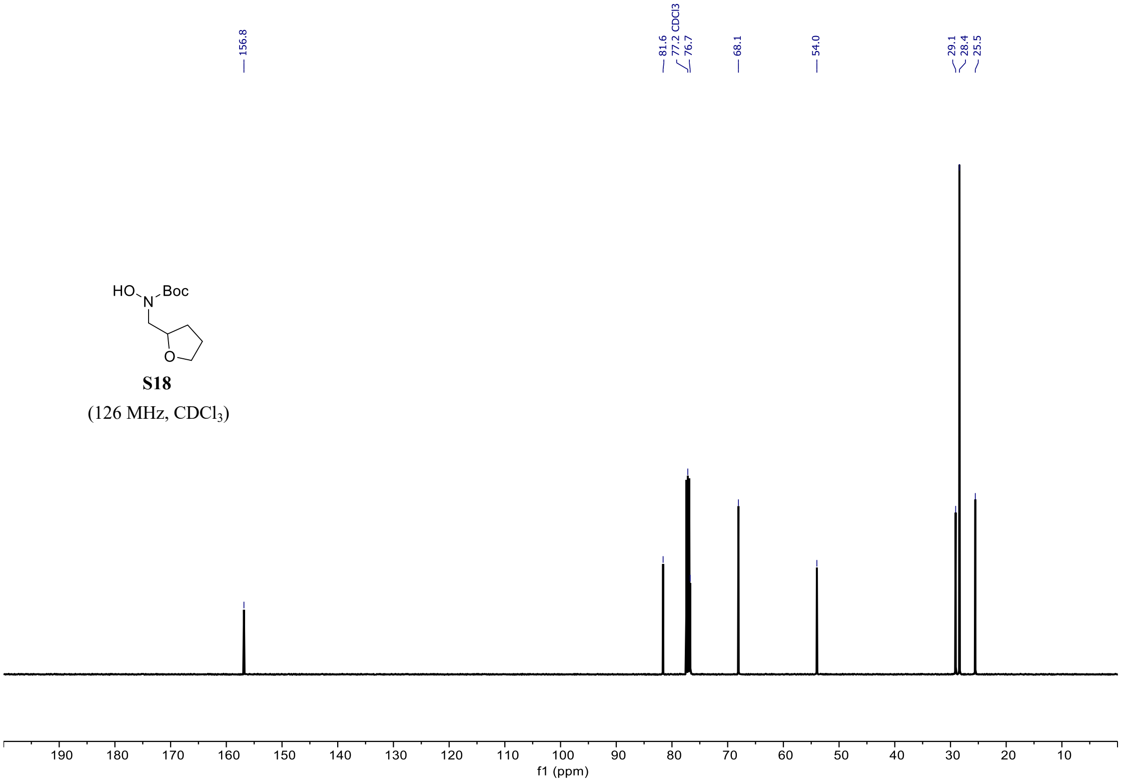
S17
(500 MHz, $CDCl_3$)



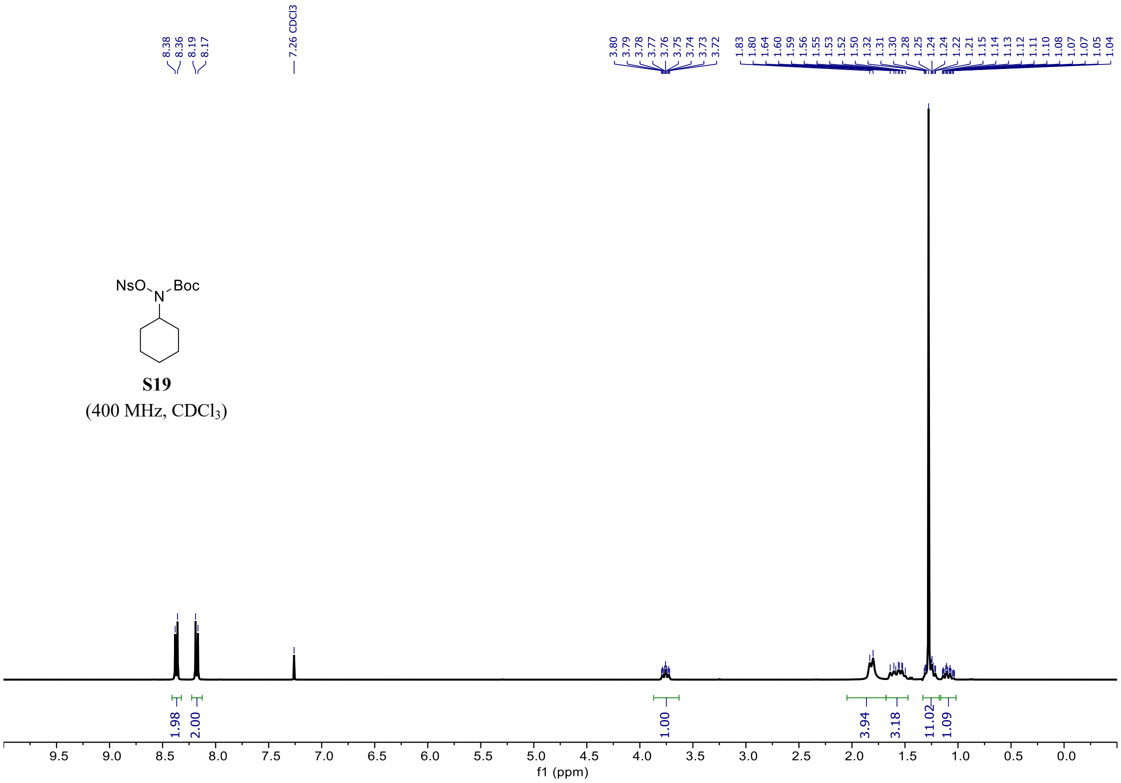
S17
(126 MHz, $CDCl_3$)



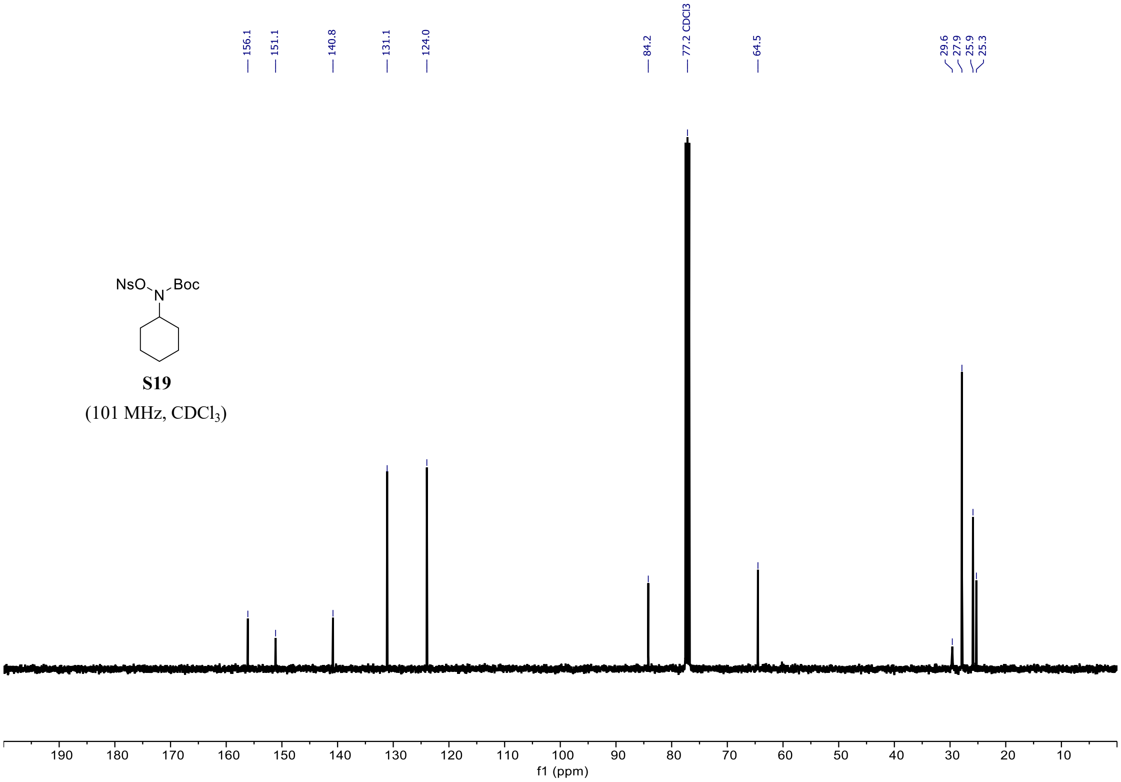
S18
(500 MHz, $CDCl_3$)



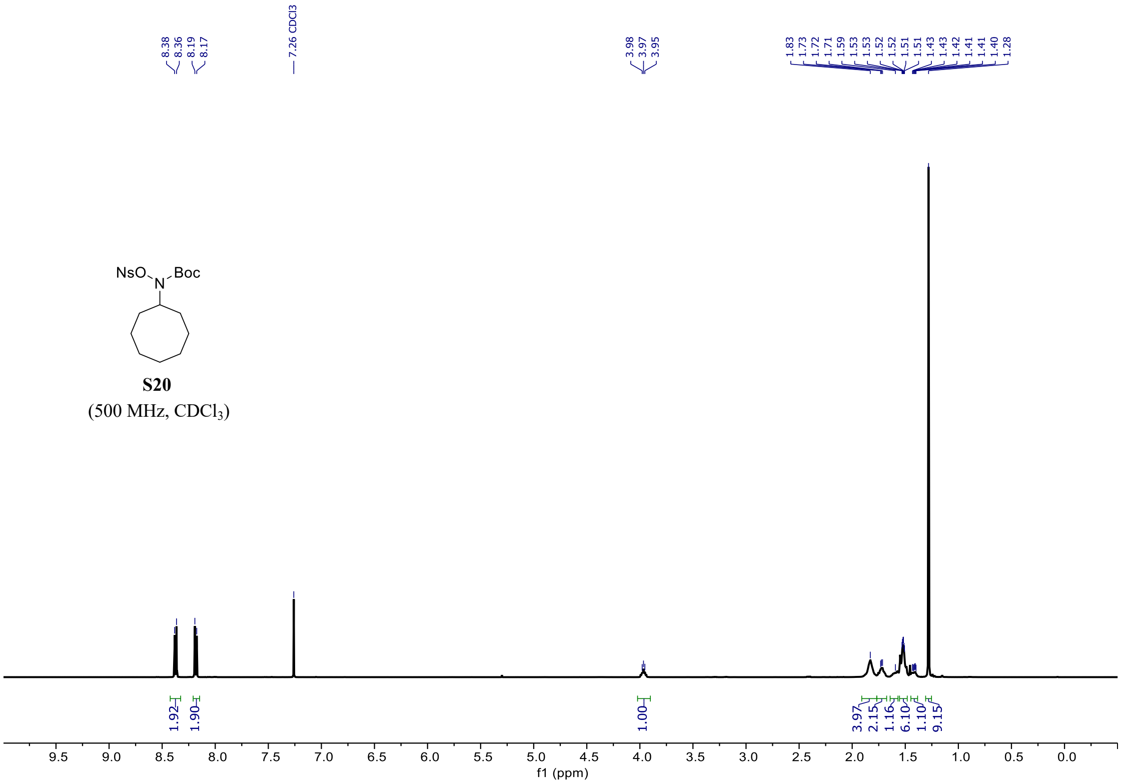
S18
(126 MHz, $CDCl_3$)



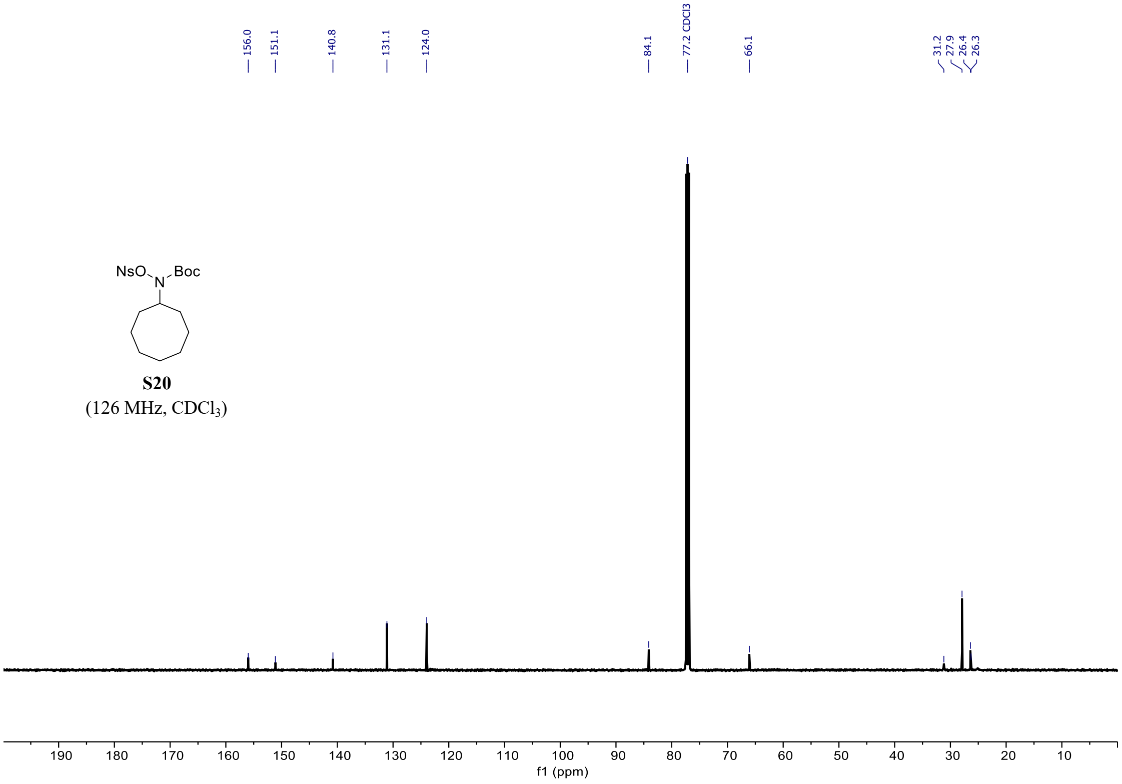
S19
(400 MHz, $CDCl_3$)



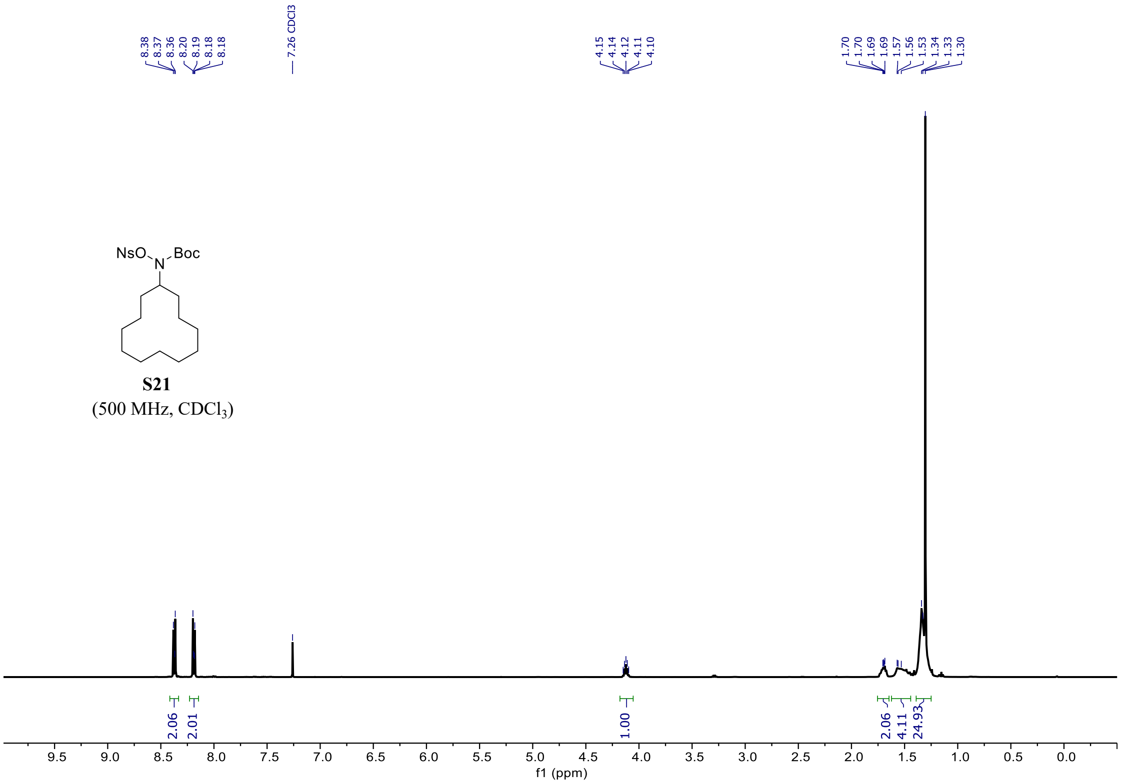
S19
(101 MHz, $CDCl_3$)



S20
(500 MHz, $CDCl_3$)

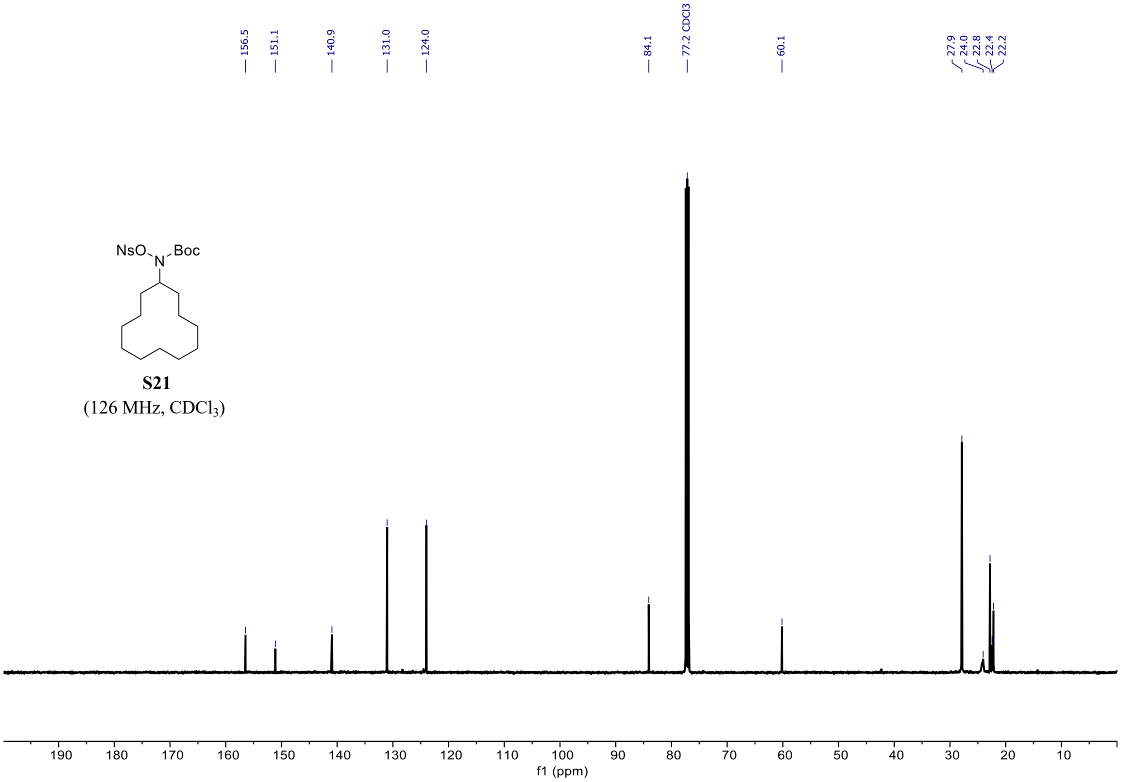


S20
(126 MHz, $CDCl_3$)



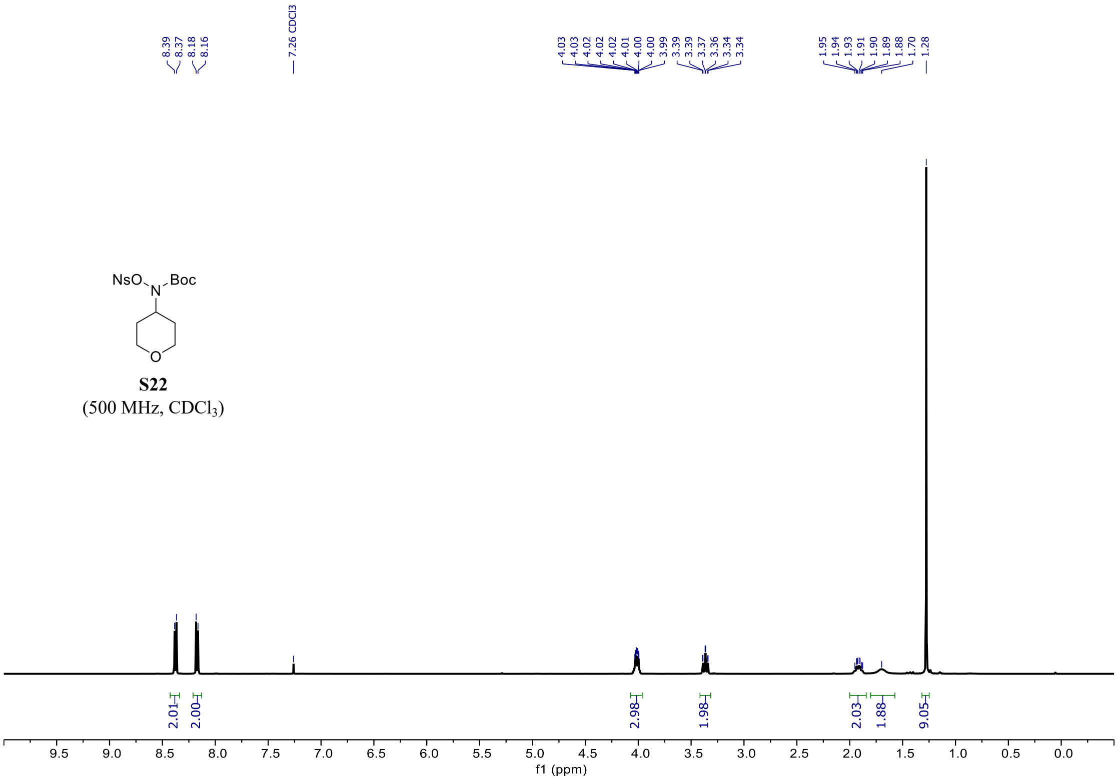
S21

(500 MHz, $CDCl_3$)

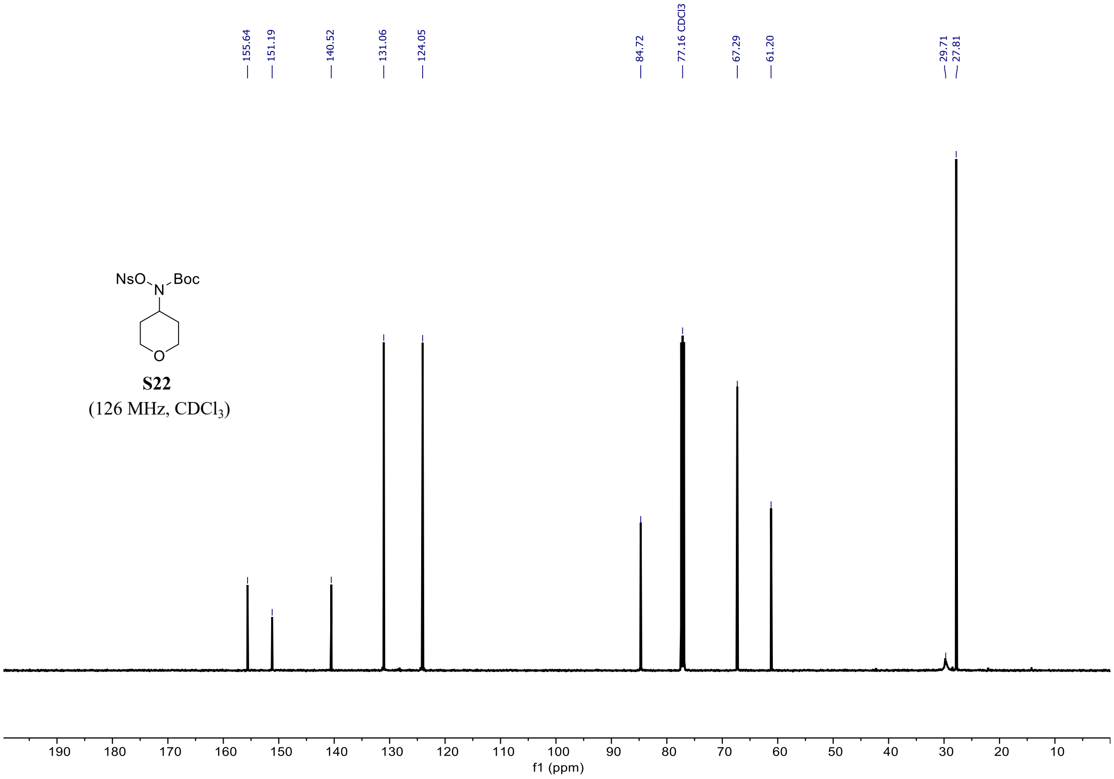


S21

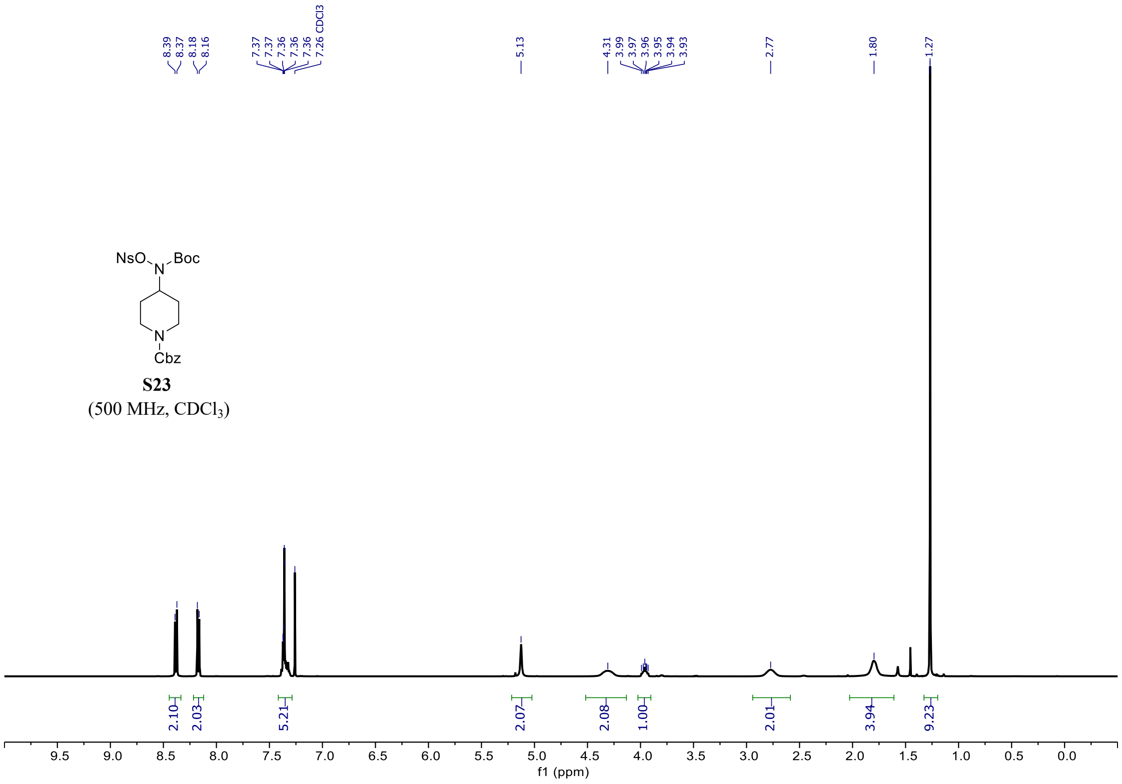
(126 MHz, $CDCl_3$)



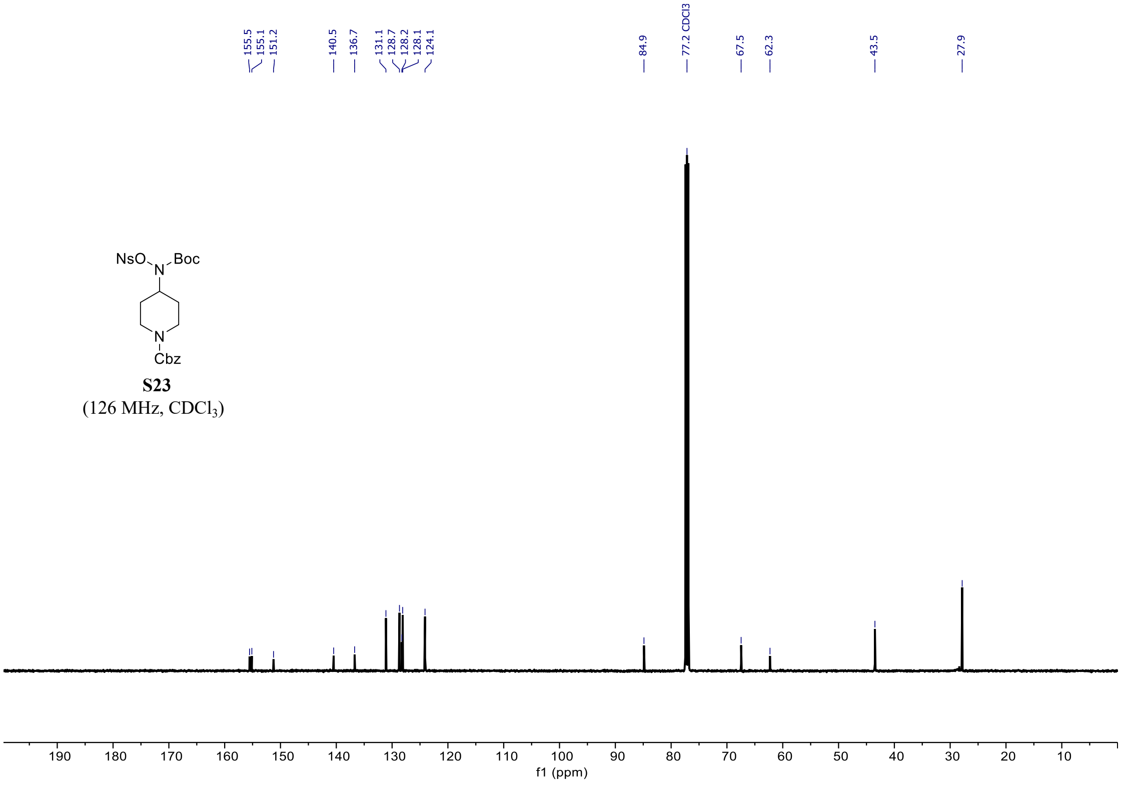
S22
(500 MHz, $CDCl_3$)



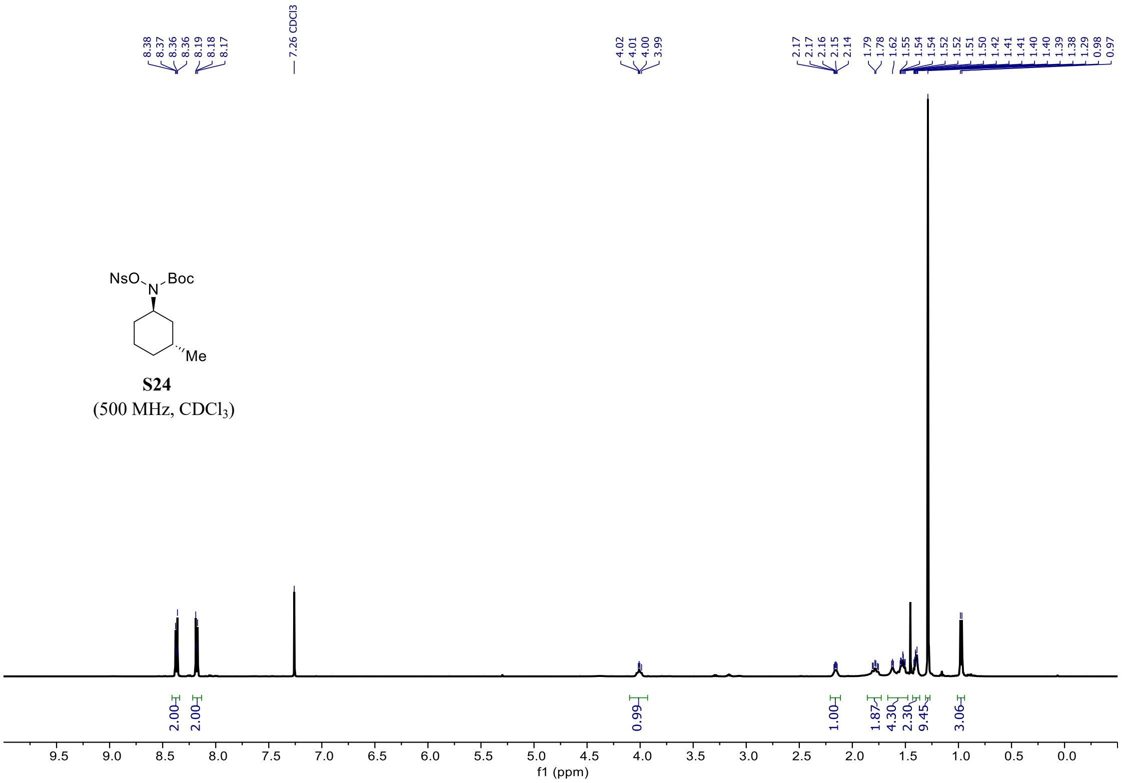
S22
(126 MHz, $CDCl_3$)



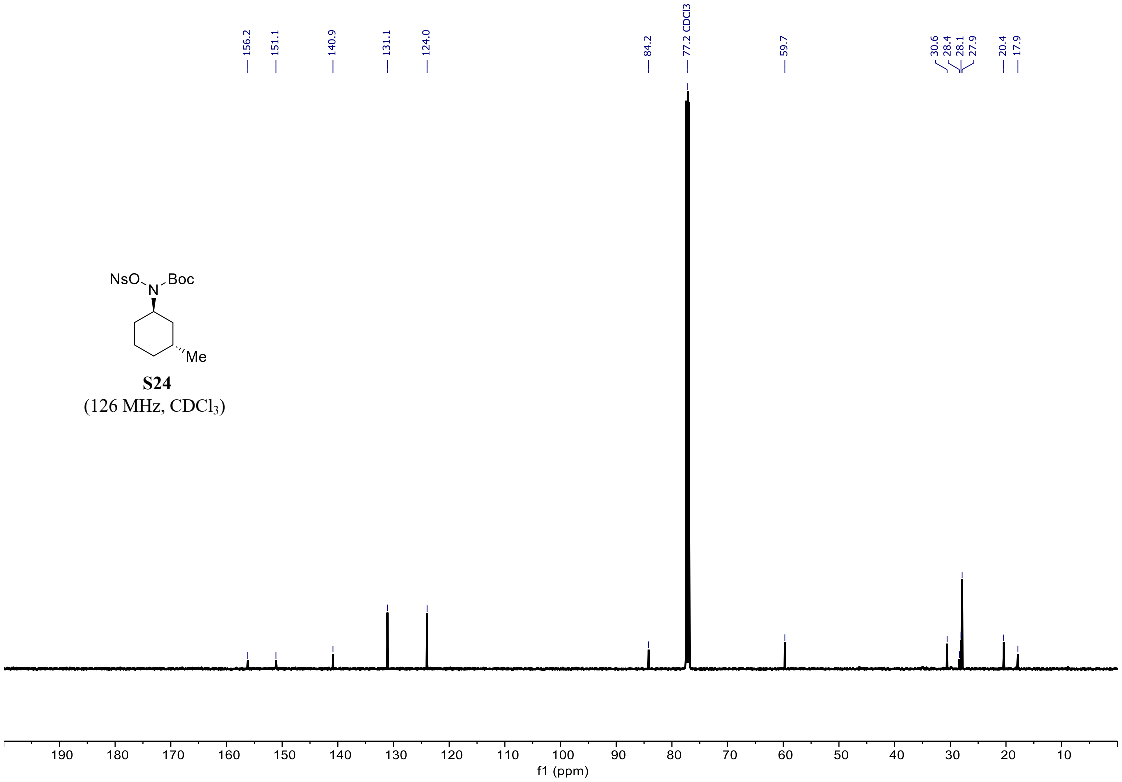
S23
(500 MHz, $CDCl_3$)



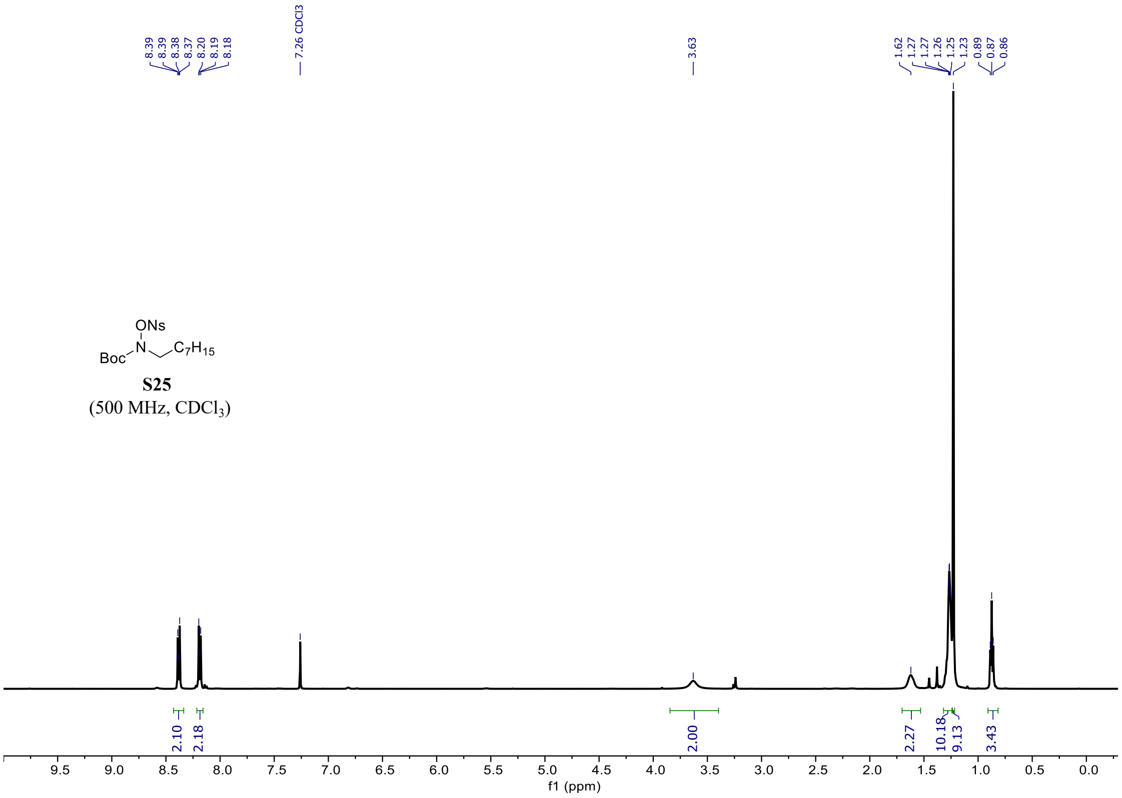
S23
(126 MHz, $CDCl_3$)



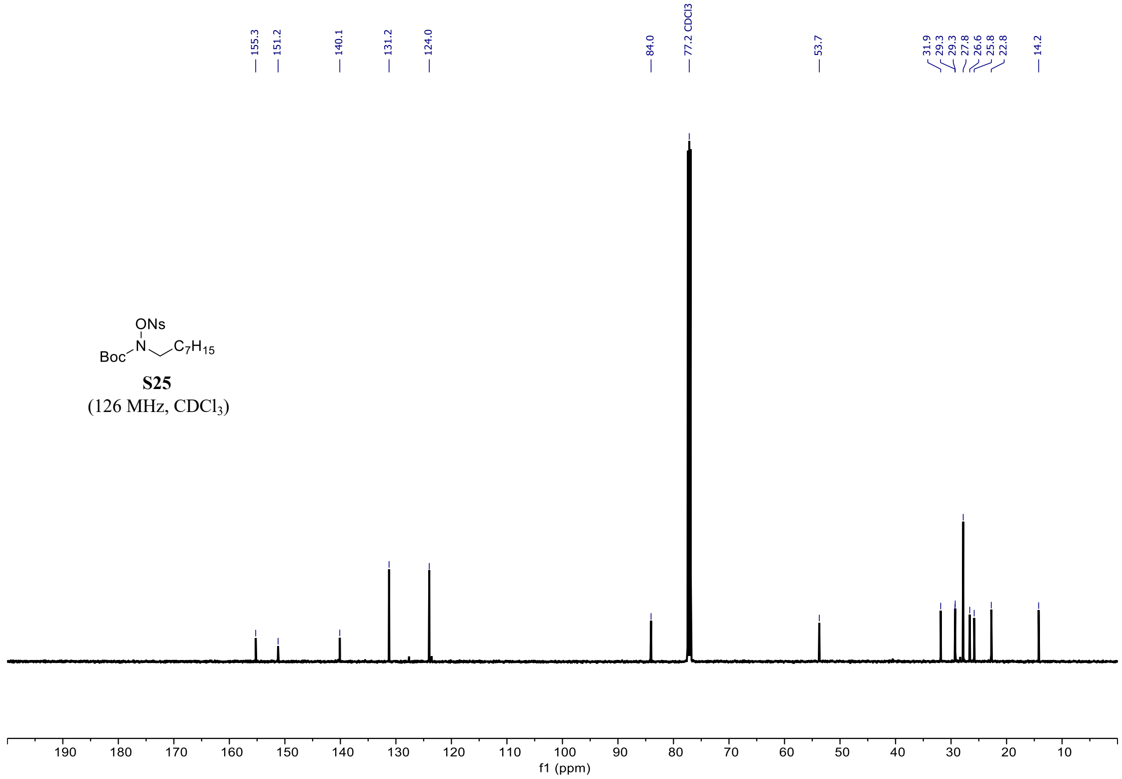
S24
(500 MHz, $CDCl_3$)



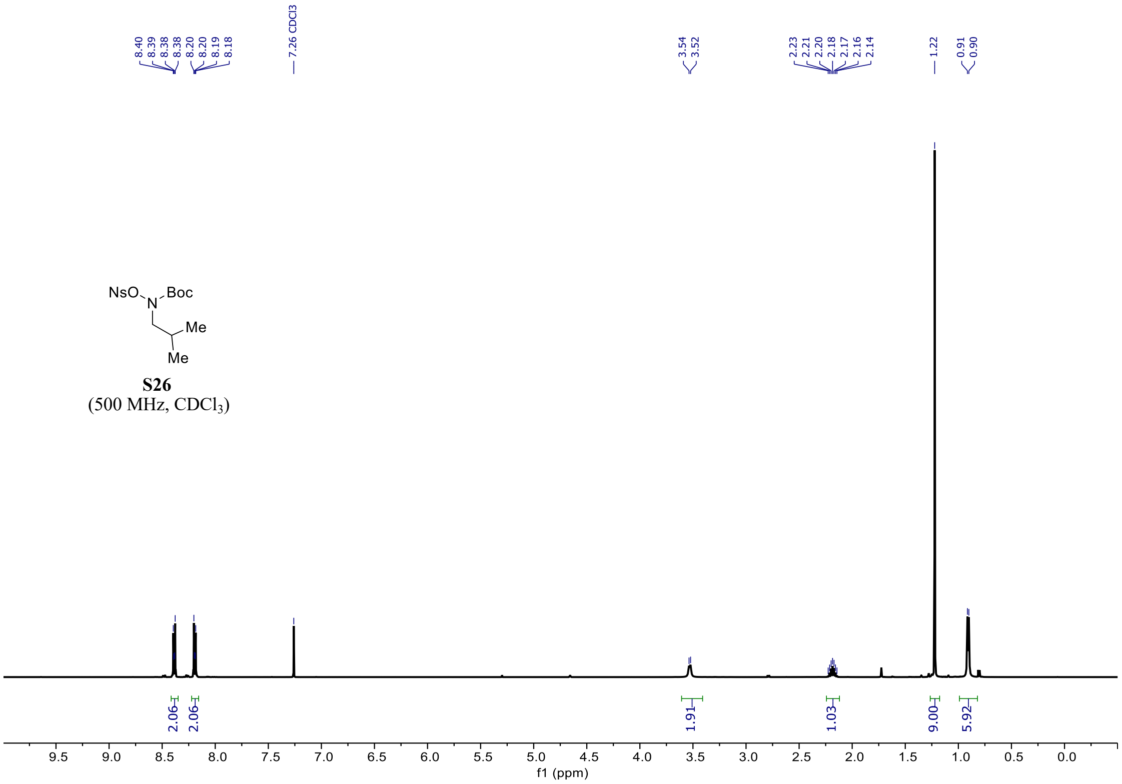
S24
(126 MHz, $CDCl_3$)



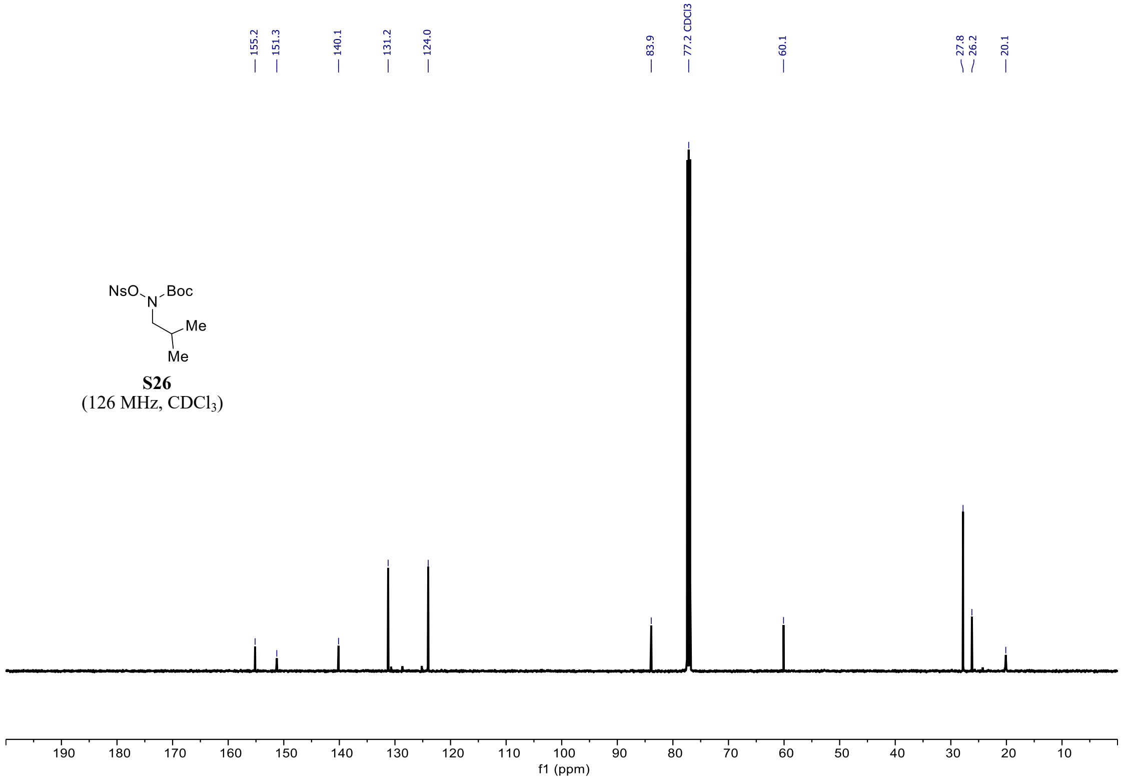
S25
(500 MHz, $CDCl_3$)



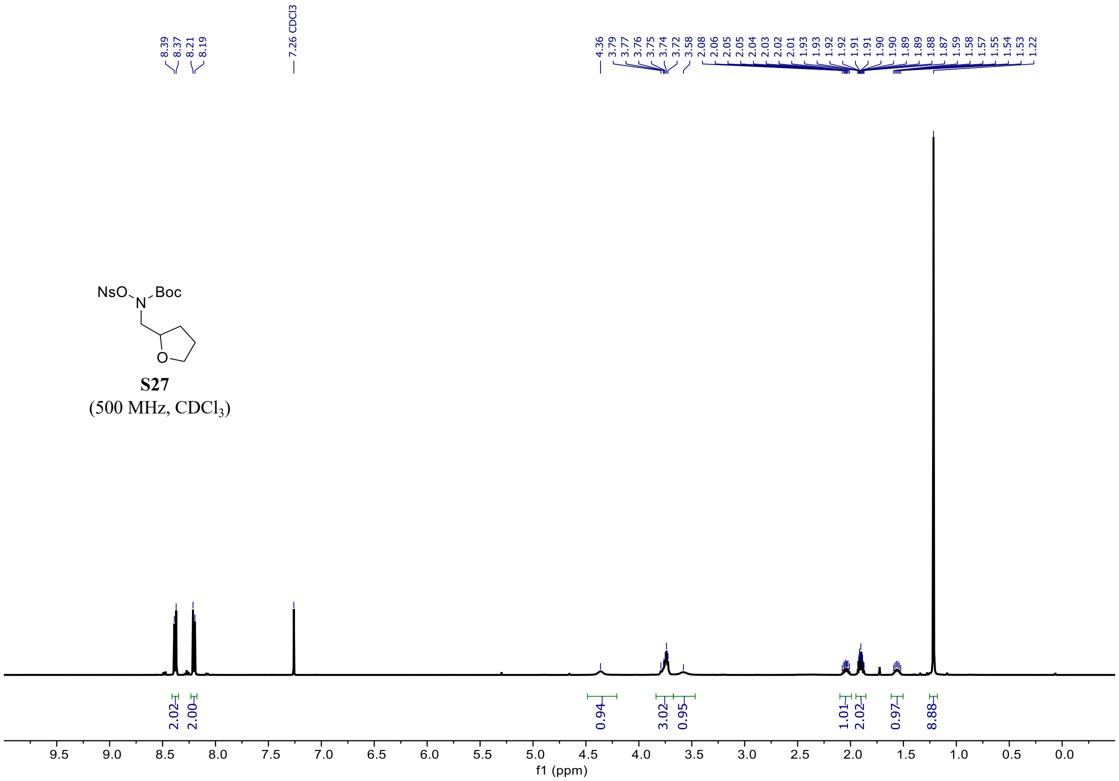
S25
(126 MHz, $CDCl_3$)



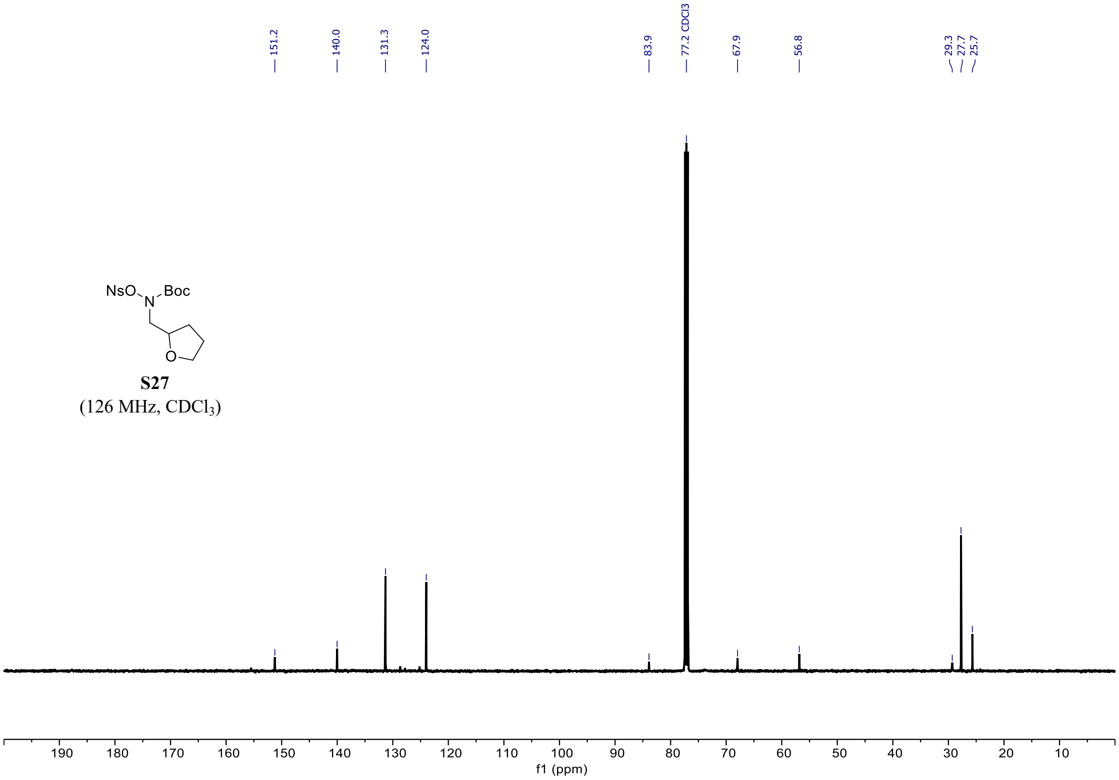
S26
(500 MHz, $CDCl_3$)



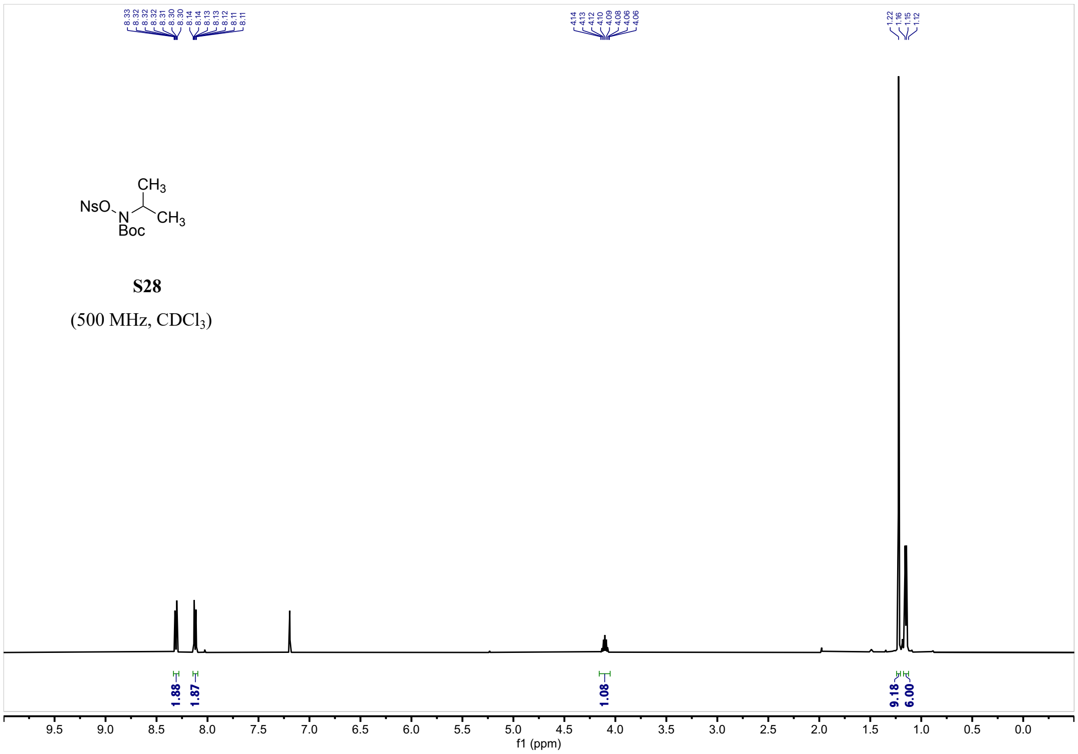
S26
(126 MHz, $CDCl_3$)



S27
(500 MHz, $CDCl_3$)

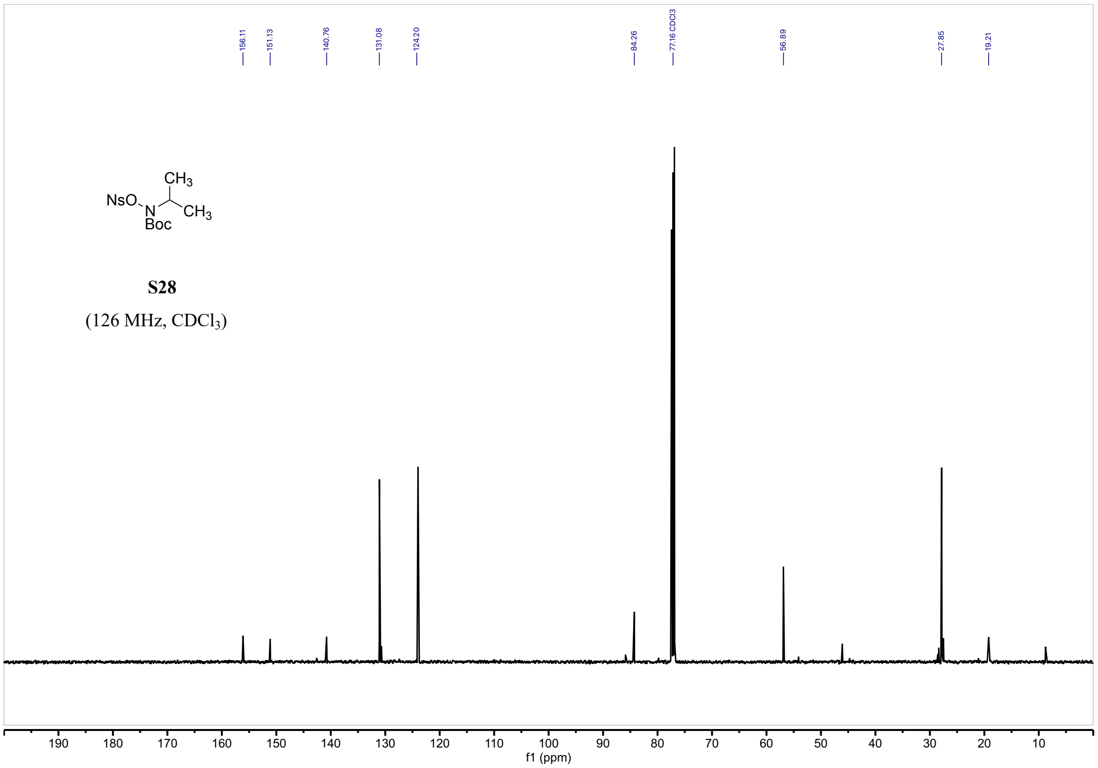


S27
(126 MHz, $CDCl_3$)



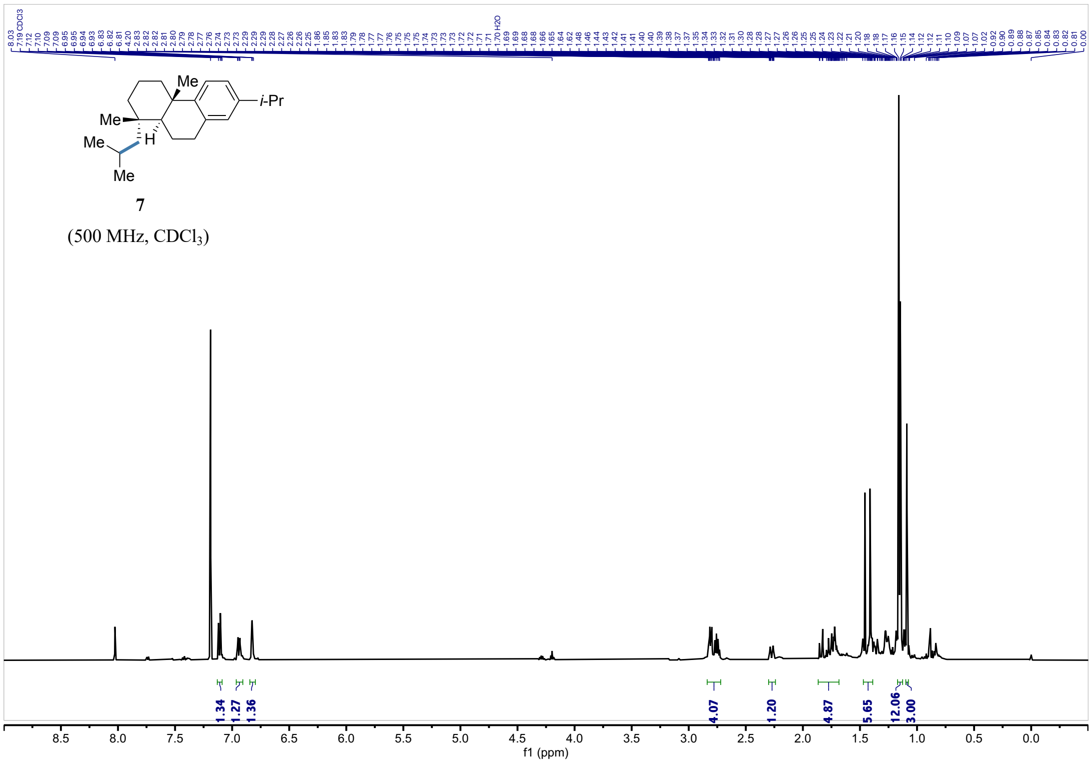
S28

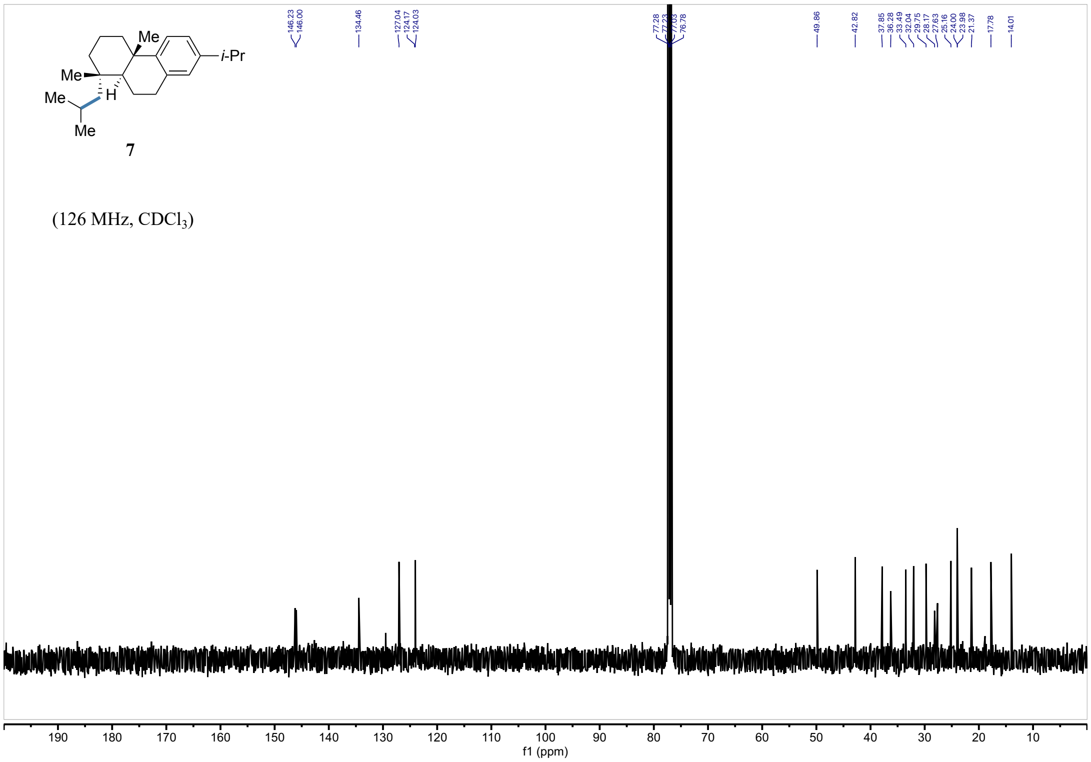
(500 MHz, $CDCl_3$)

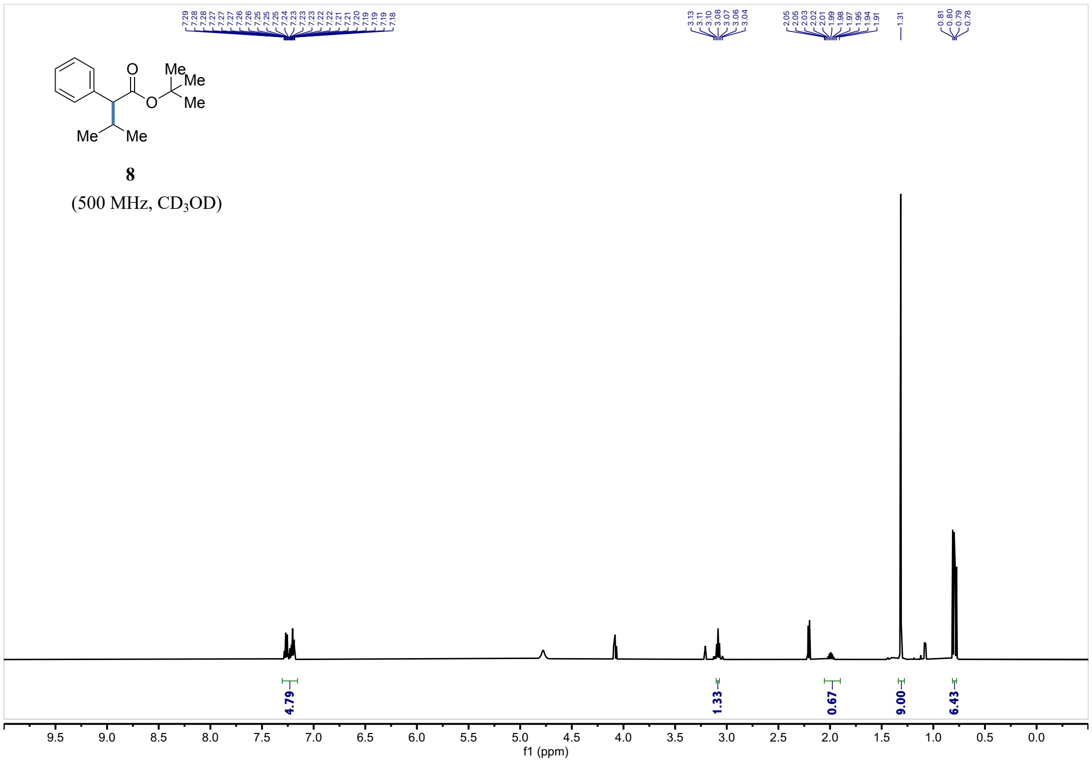


S28

(126 MHz, $CDCl_3$)

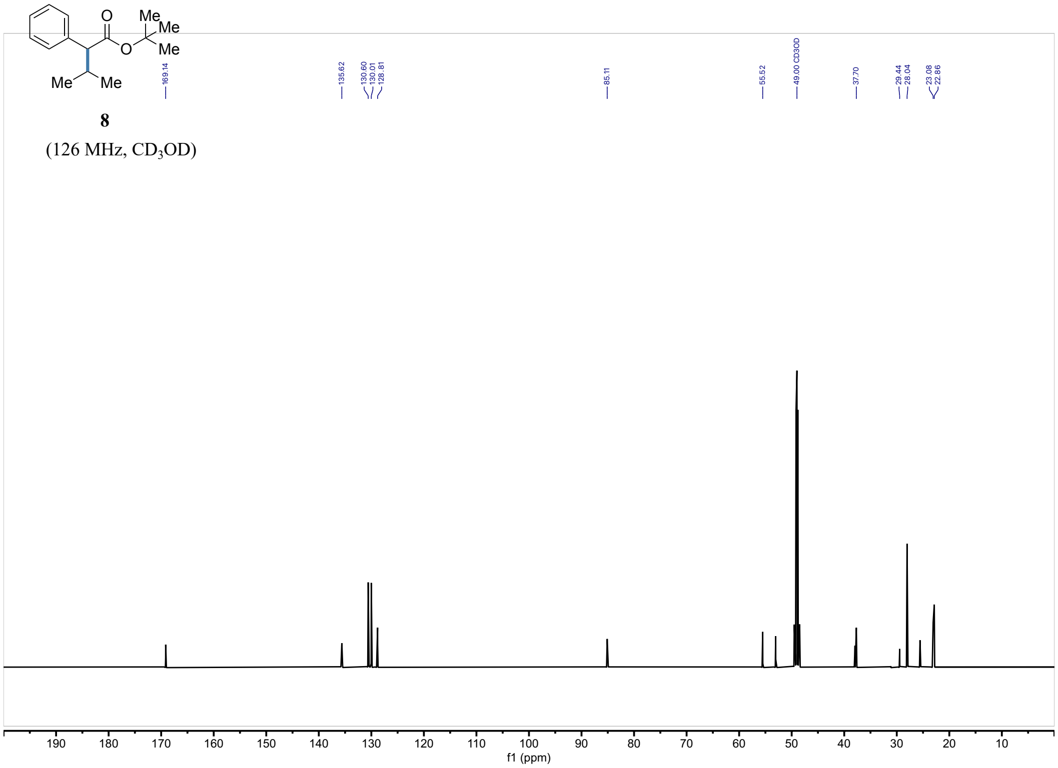

Me
i-Pr
Me
Me
H
Me
7
(500 MHz, CDCl3)
1.34
1.27
1.36
4.07
1.20
4.87
5.65
12.06
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


146.23
146.00
134.46
127.04
124.17
124.03
77.28
77.03
76.78
49.86
42.82
37.85
36.28
33.49
32.04
29.75
28.17
27.63
25.16
24.00
23.98
21.37
17.78
14.01
Me
i-Pr
Me
Me
H
Me
7
(126 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



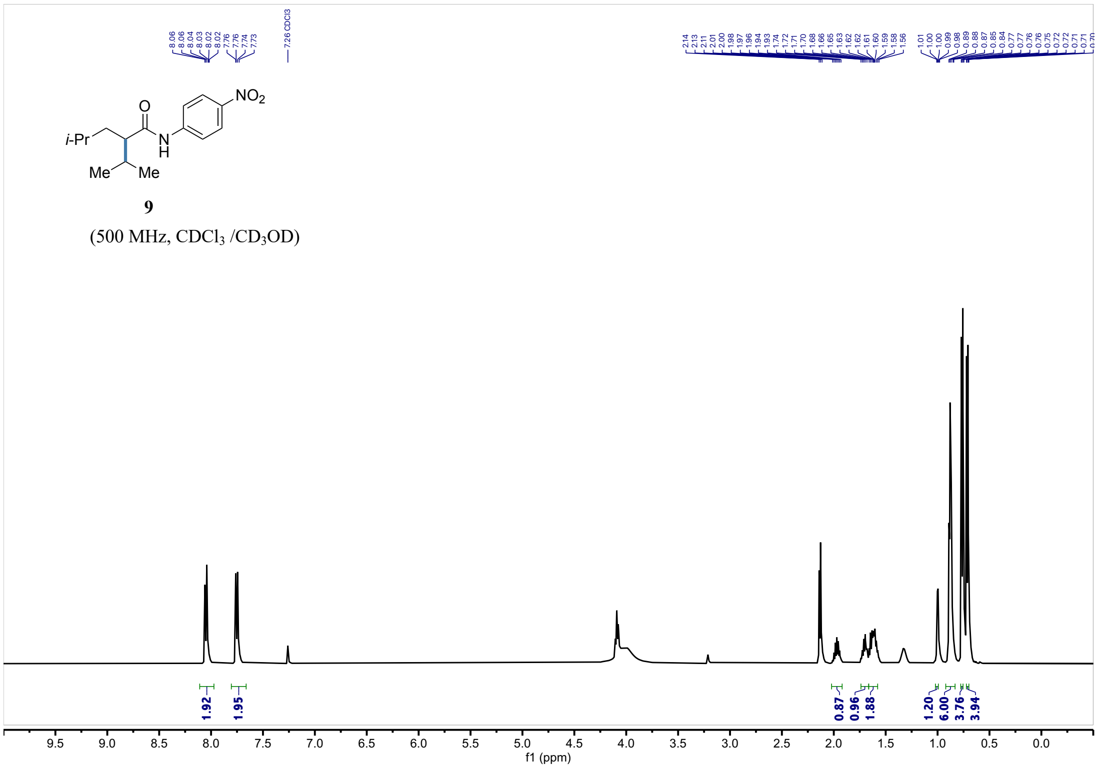
8

(500 MHz, CD$_3$OD)



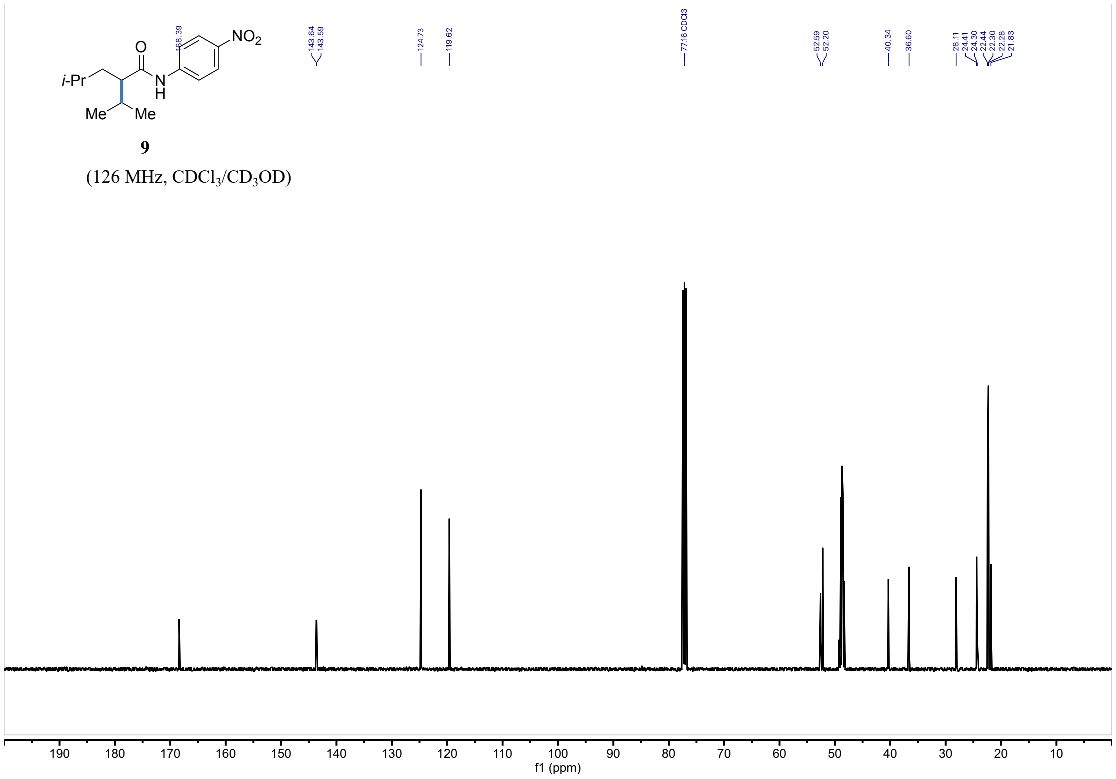
8

(126 MHz, CD$_3$OD)



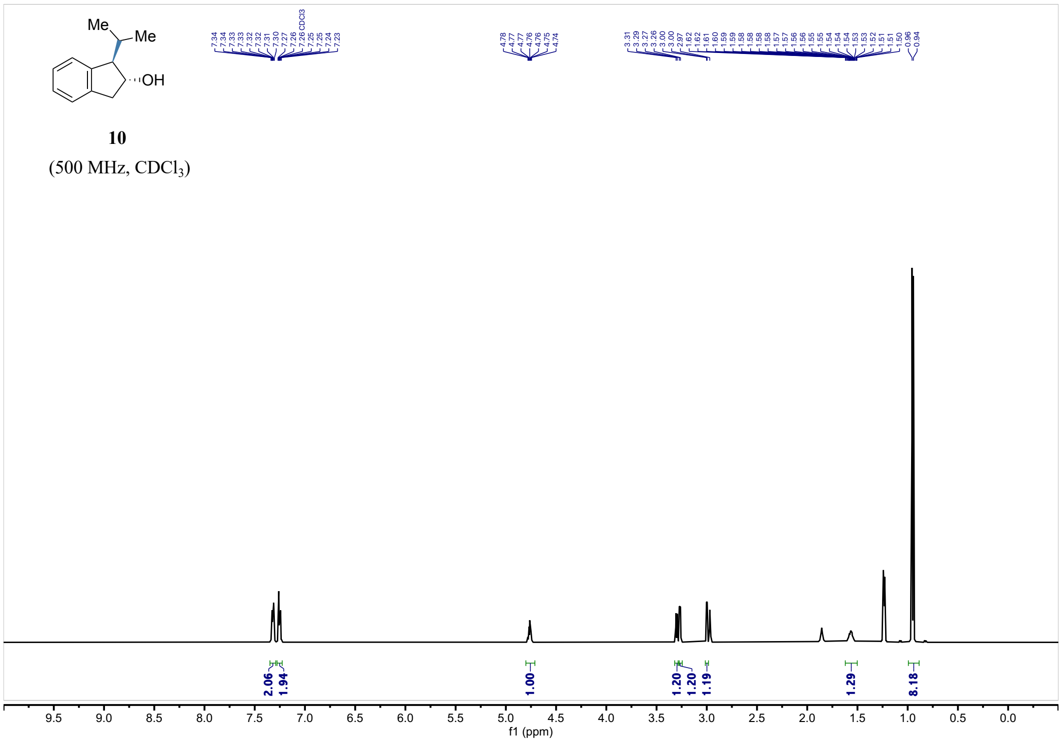
9

(500 MHz, $CDCl_3$ /CD_3OD)



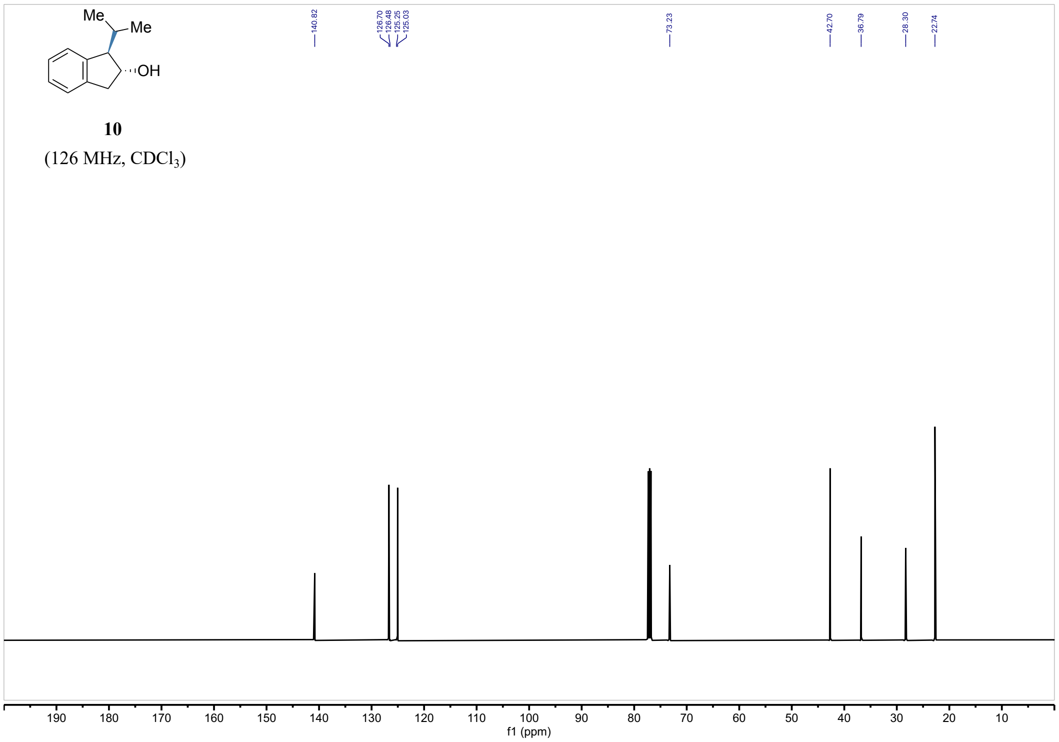
9

(126 MHz, $CDCl_3$/CD_3OD)



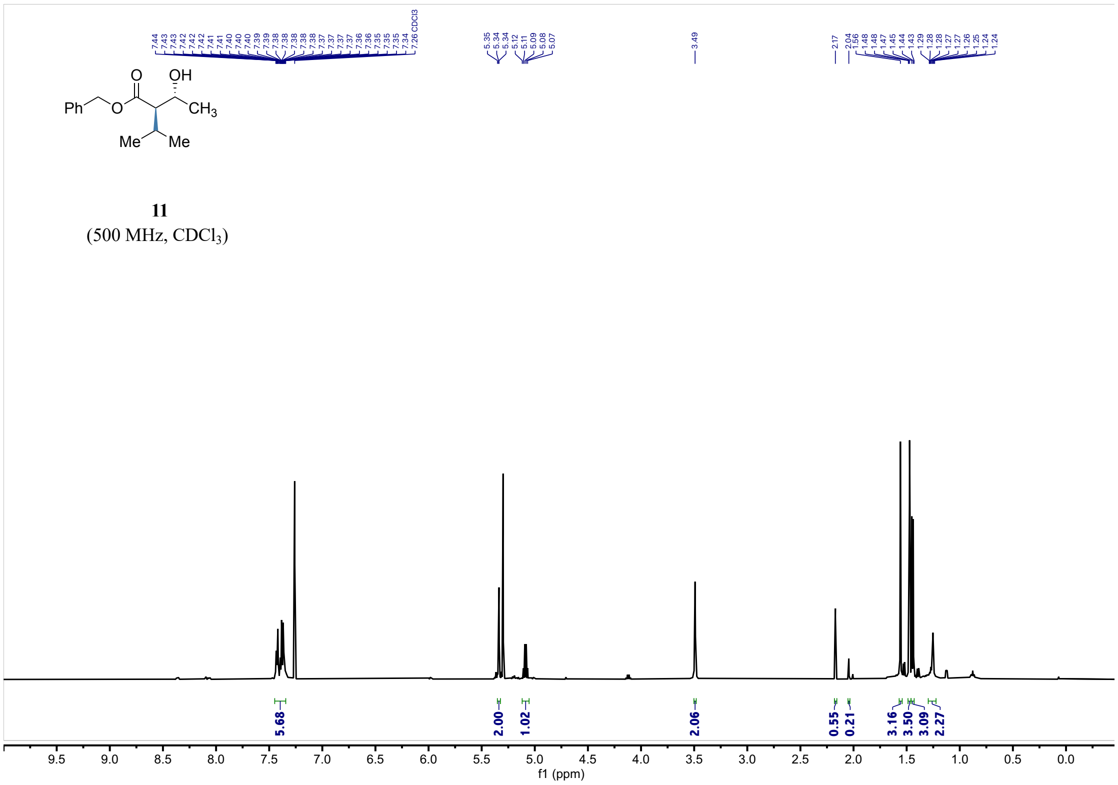
10

(500 MHz, $CDCl_3$)

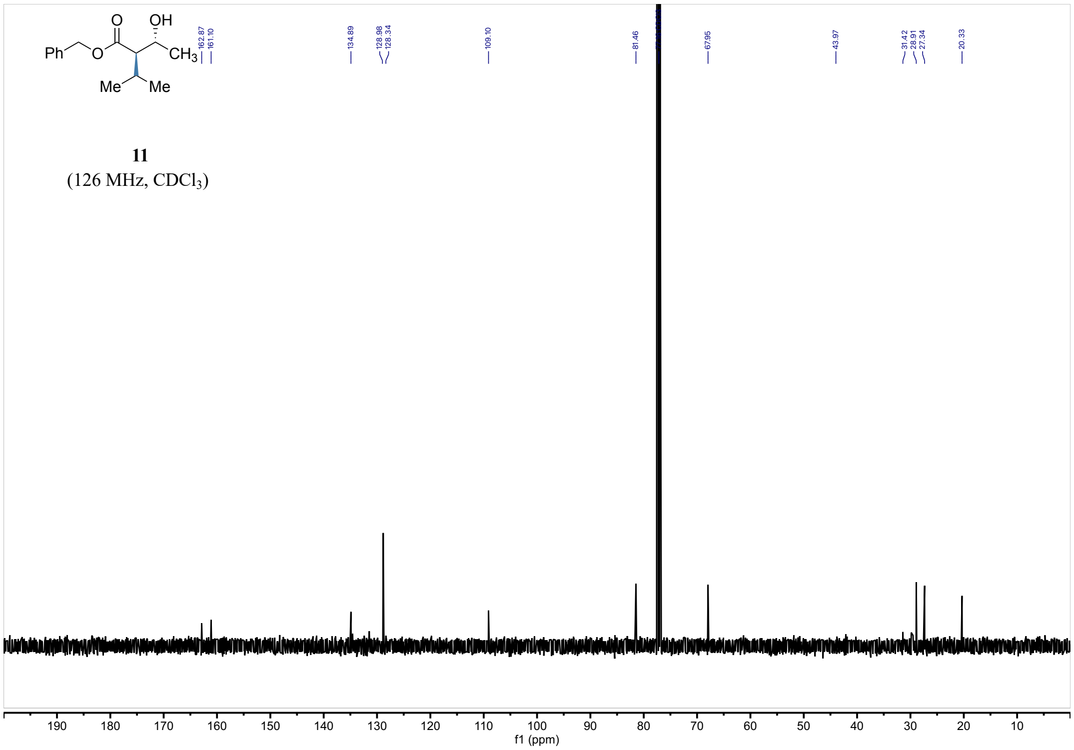


10

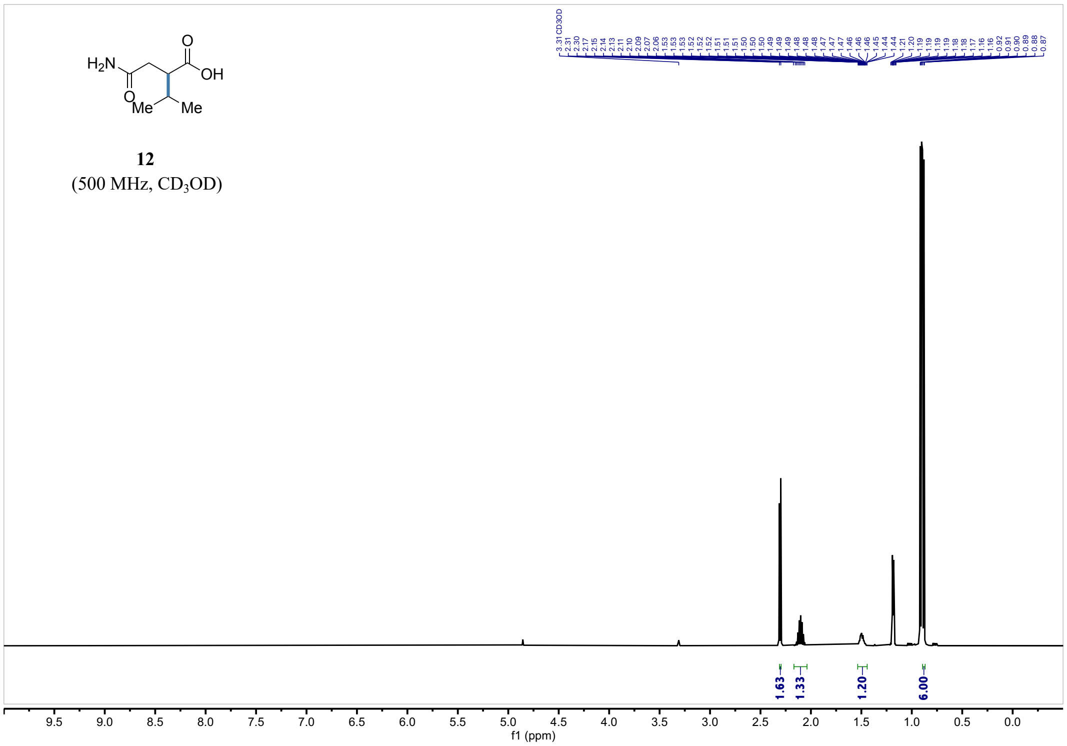
(126 MHz, $CDCl_3$)



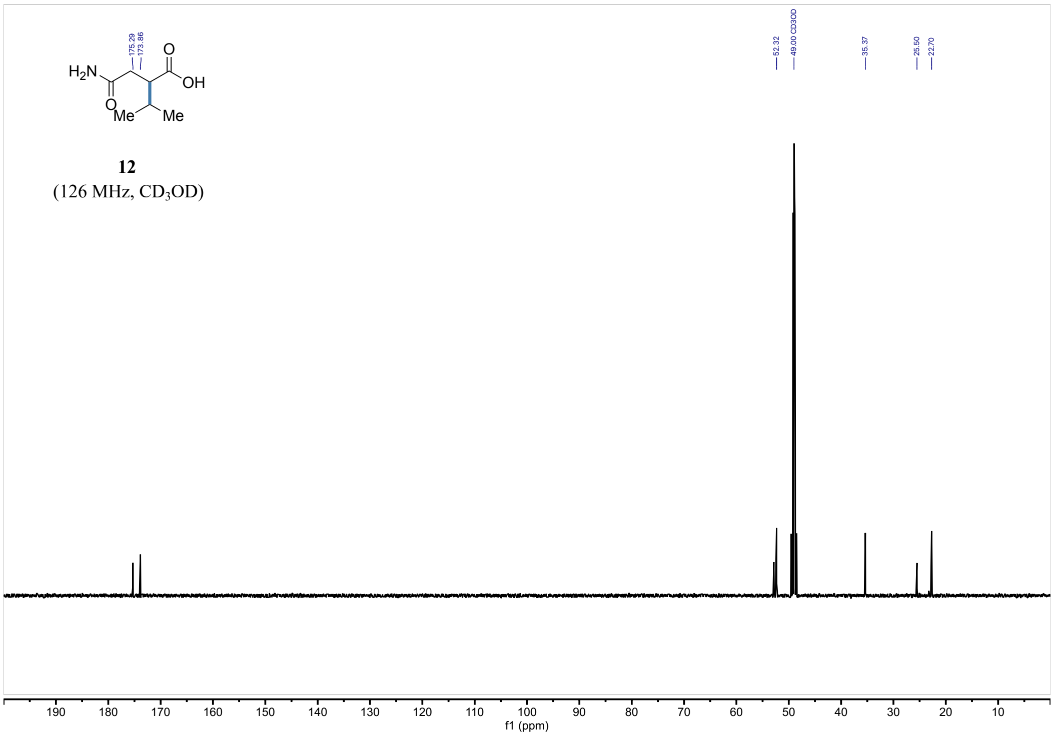
11
(500 MHz, $CDCl_3$)



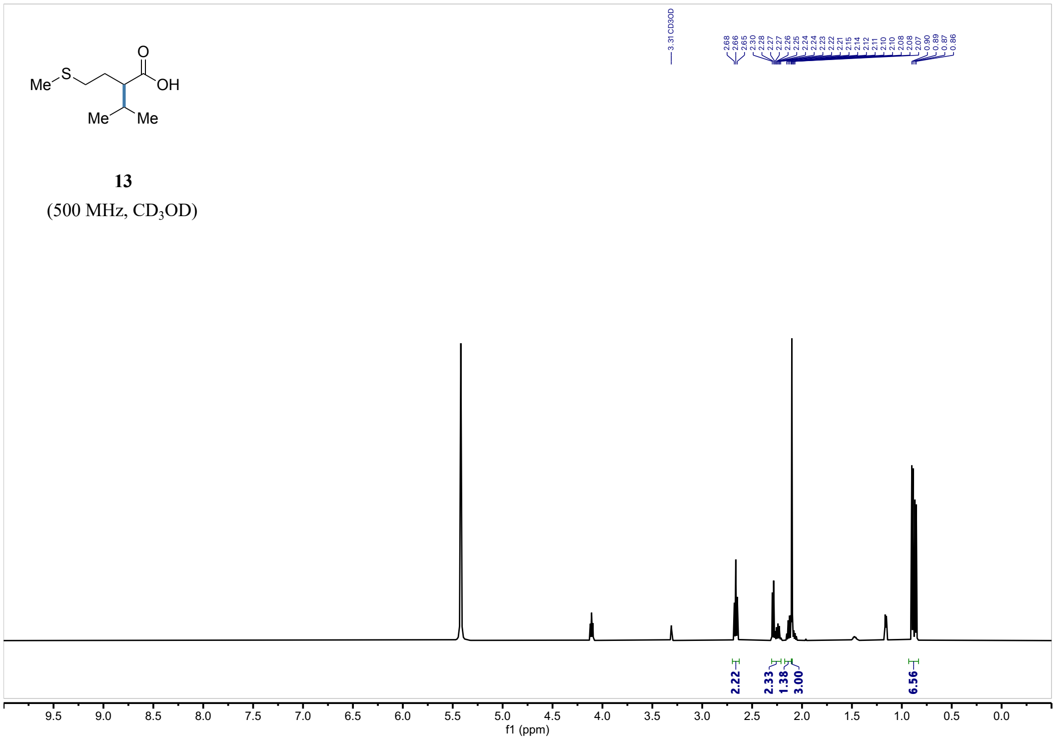
11
(126 MHz, $CDCl_3$)



12
(500 MHz, CD_3OD)

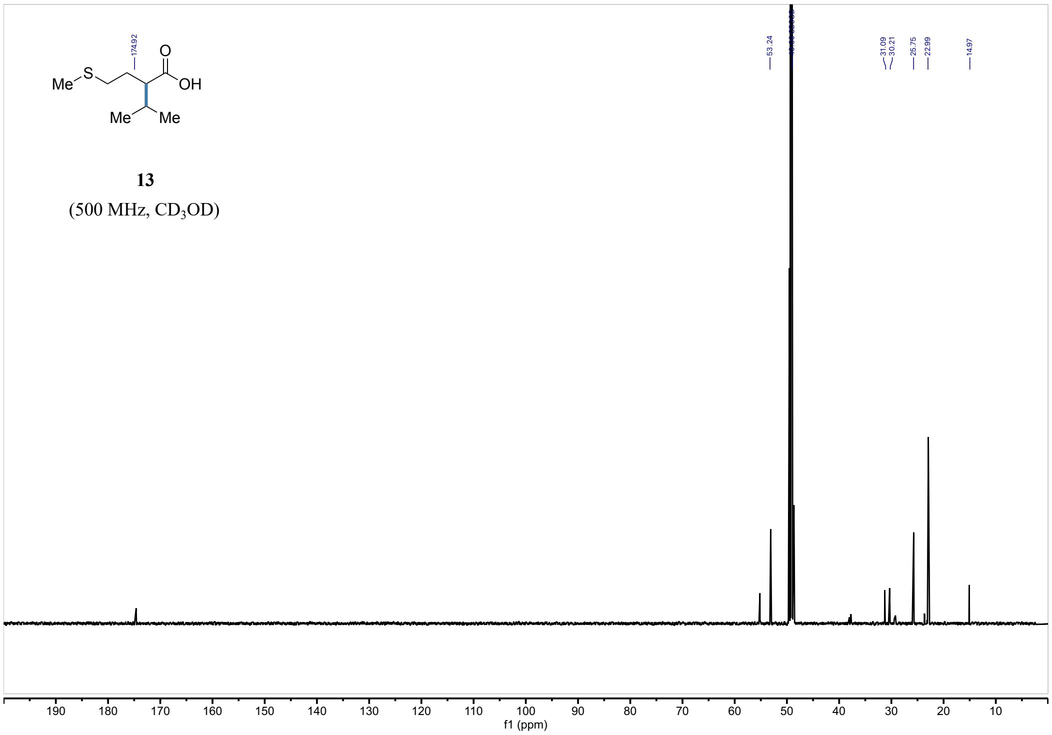


12
(126 MHz, CD_3OD)



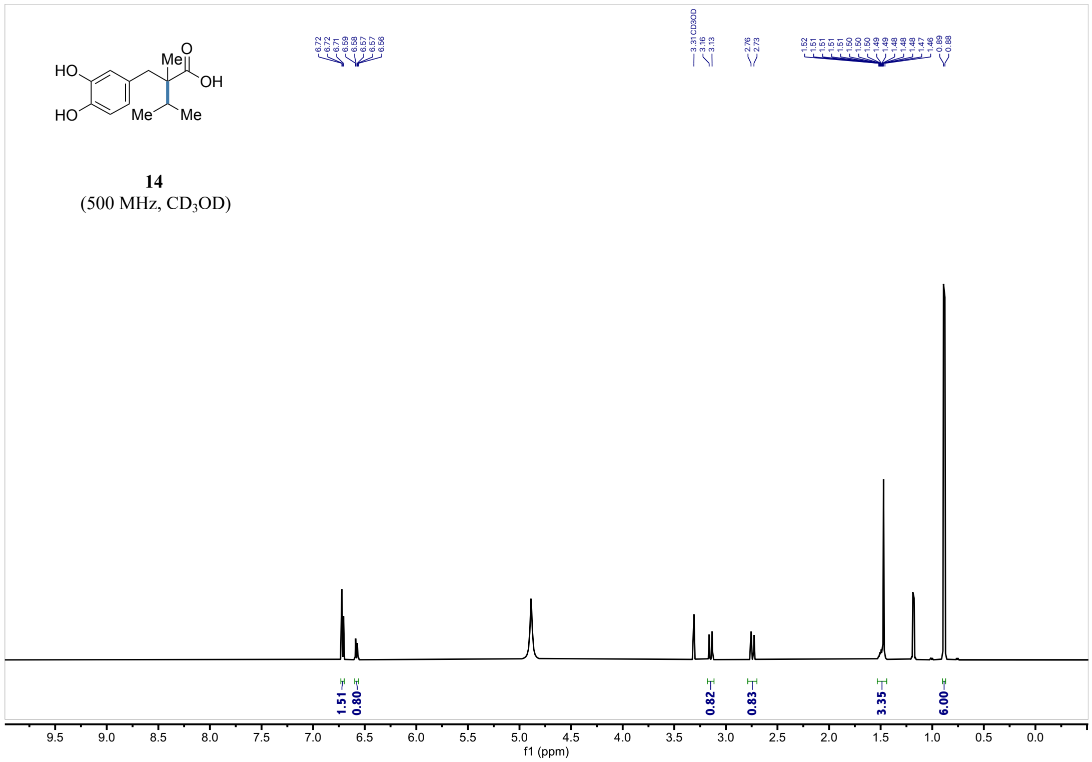
13

(500 MHz, CD_3OD)

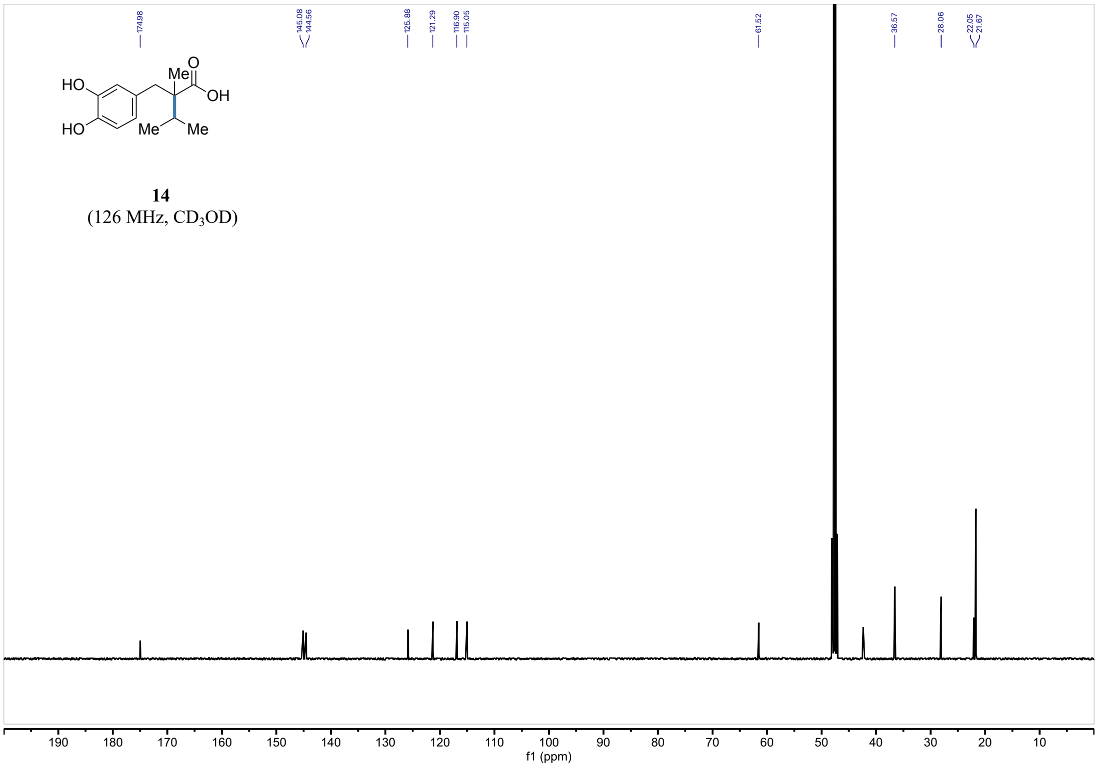


13

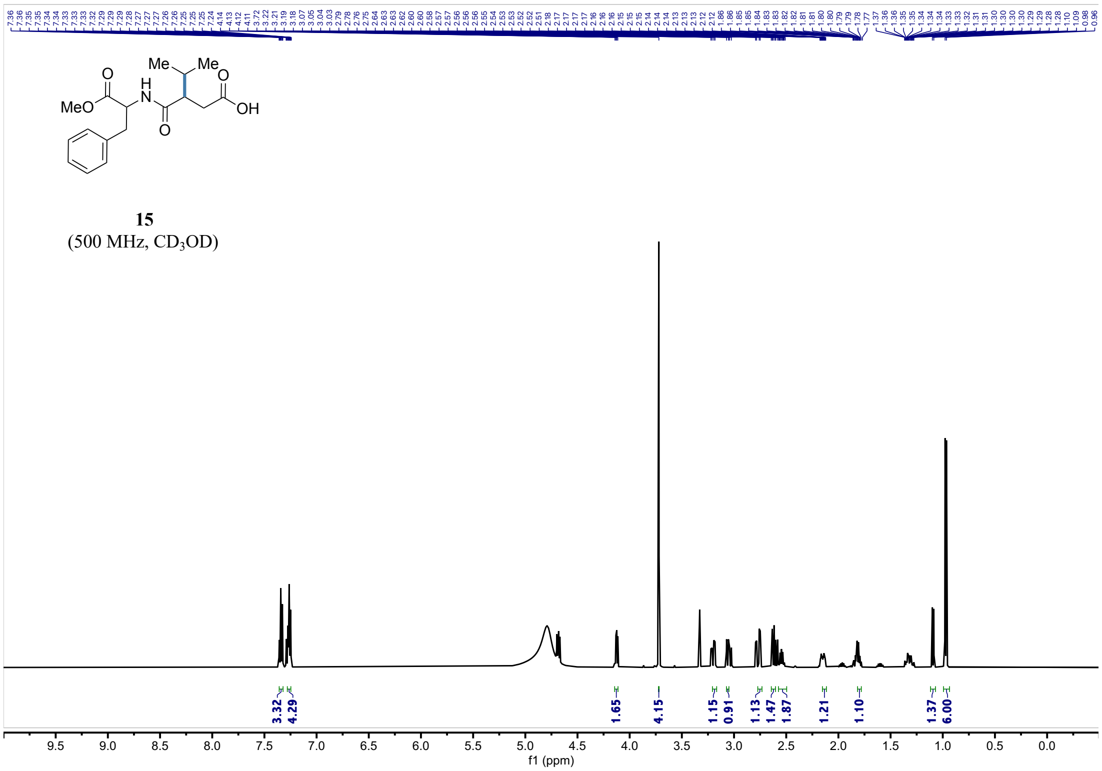
(500 MHz, CD_3OD)



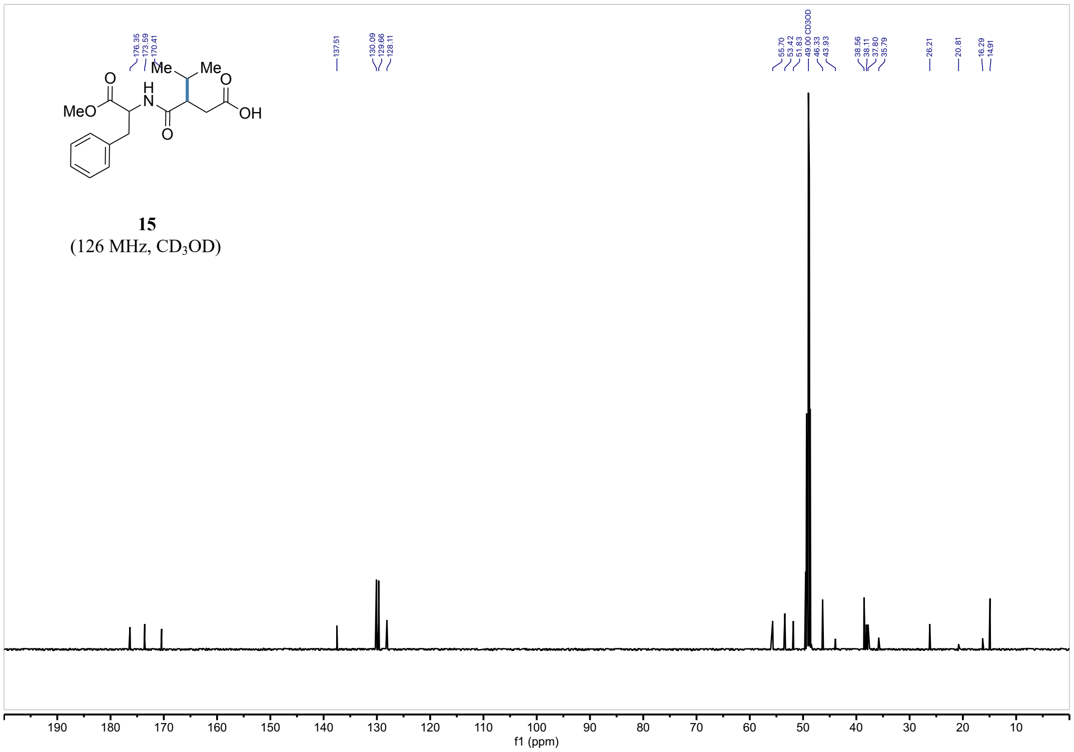
14
(500 MHz, CD_3OD)



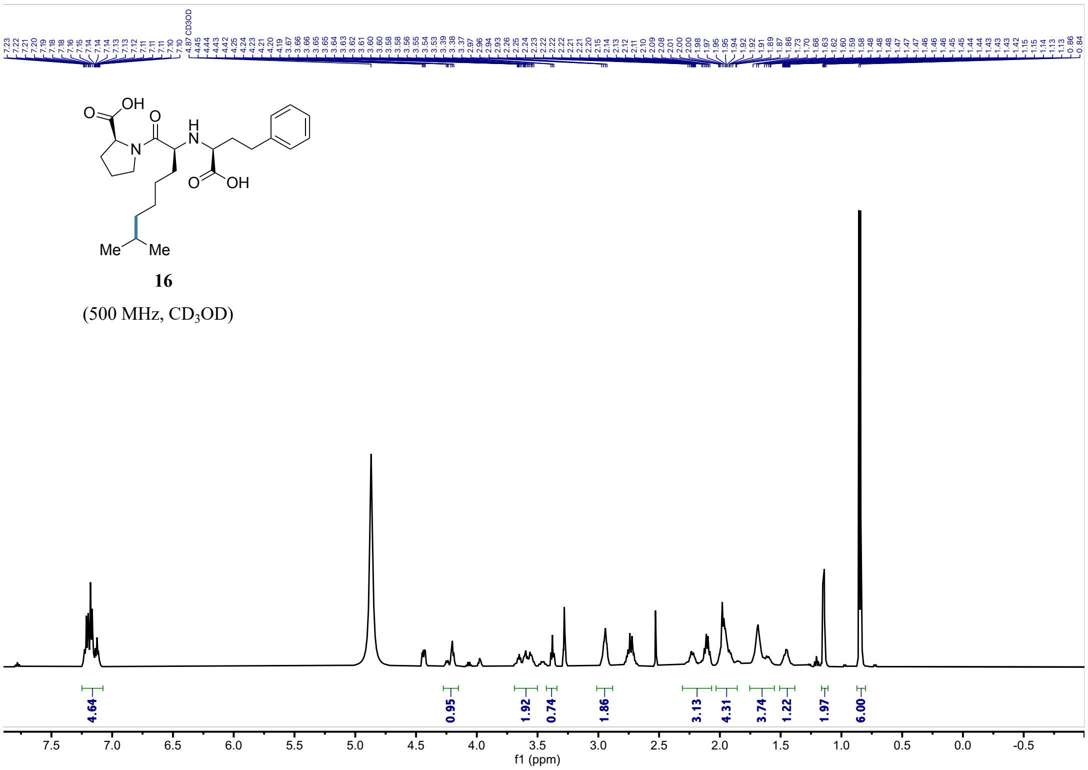
14
(126 MHz, CD_3OD)



15
(500 MHz, CD_3OD)

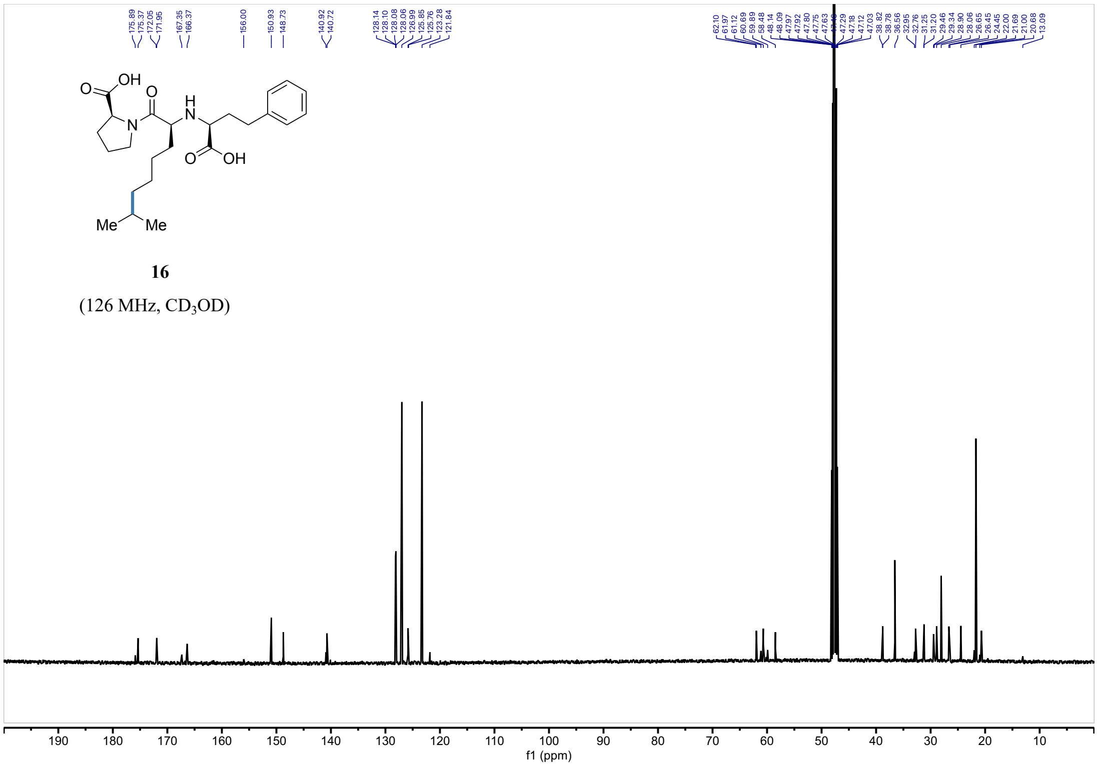


15
(126 MHz, CD_3OD)



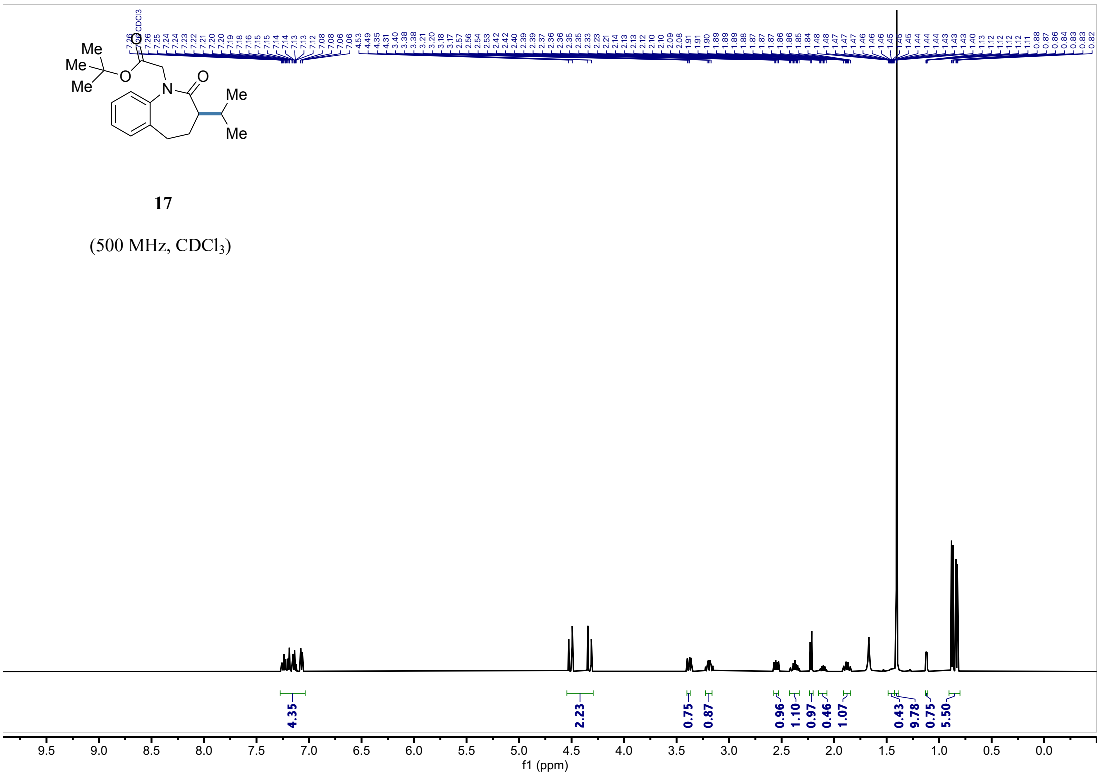
16

(500 MHz, CD$_3$OD)



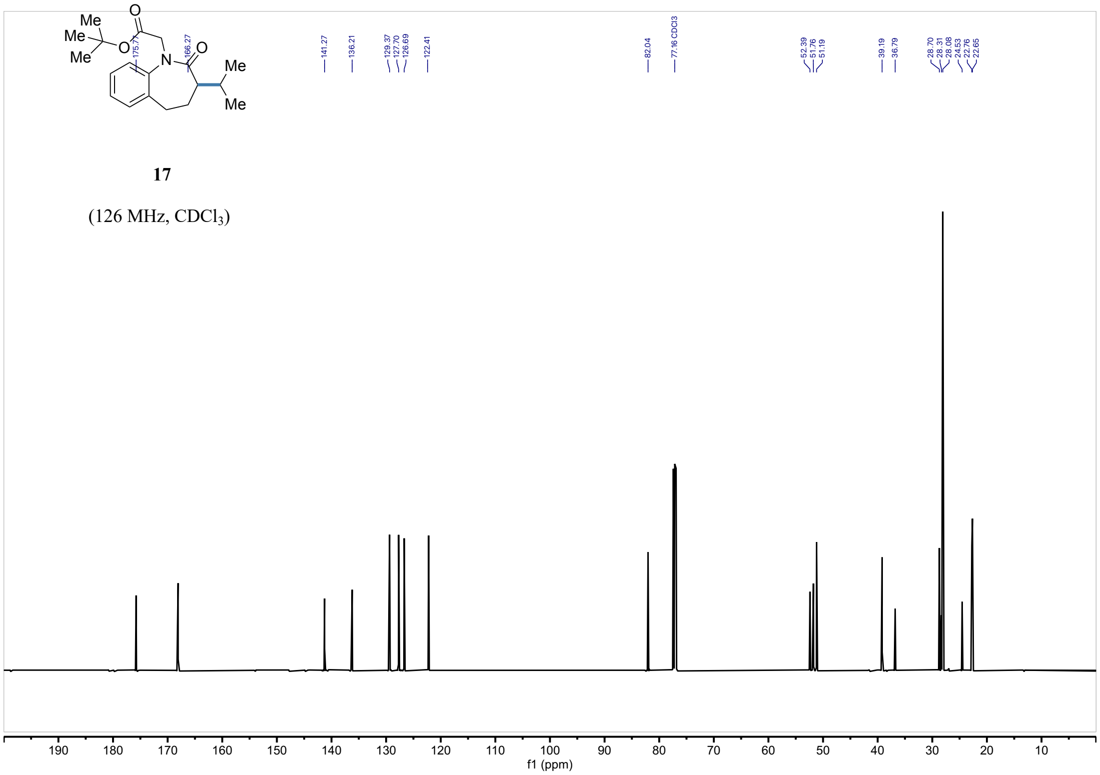
16

(126 MHz, CD$_3$OD)



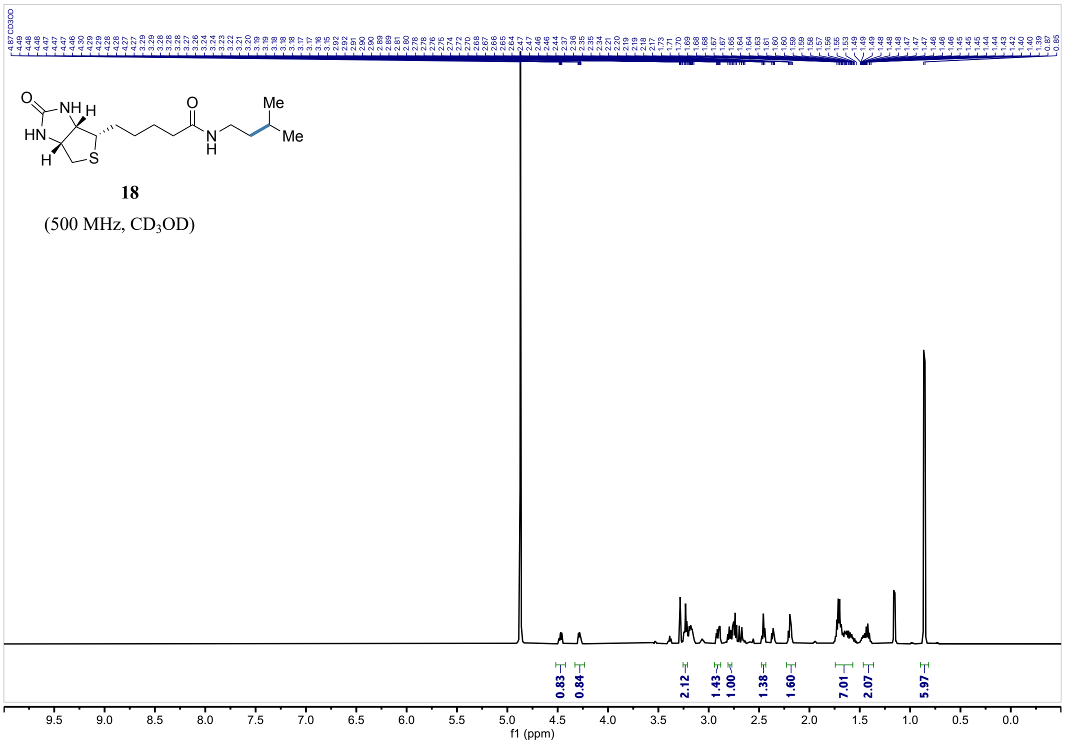
17

(500 MHz, $CDCl_3$)



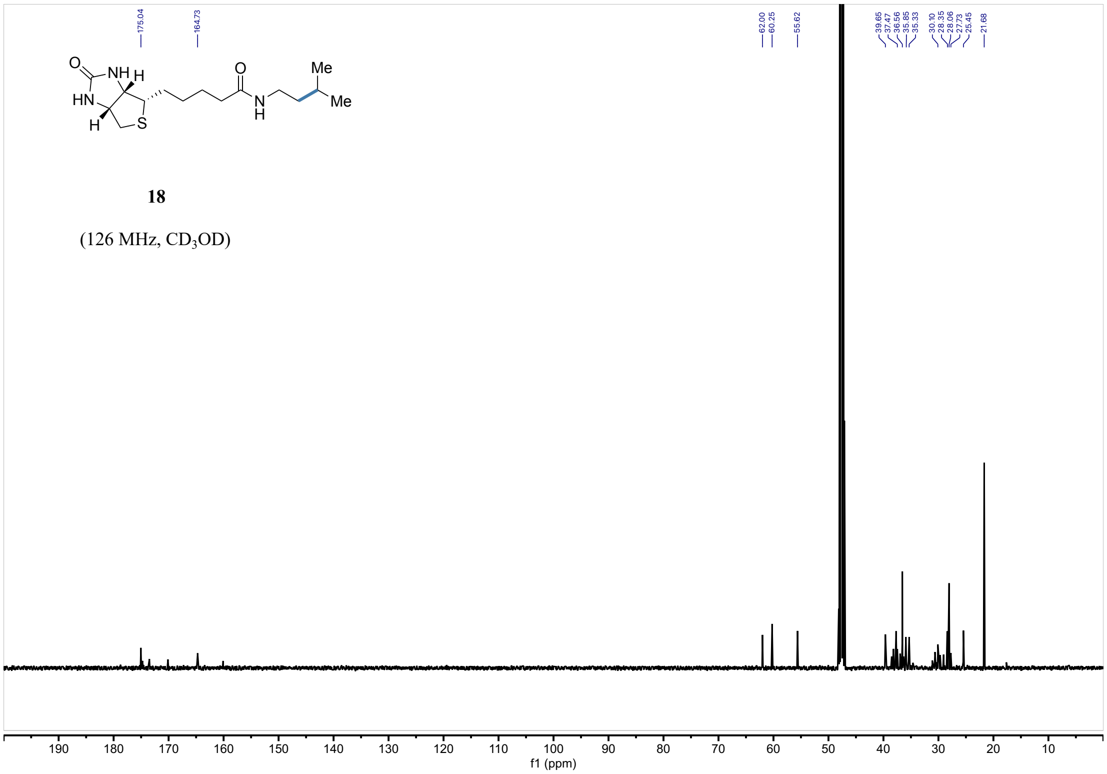
17

(126 MHz, $CDCl_3$)



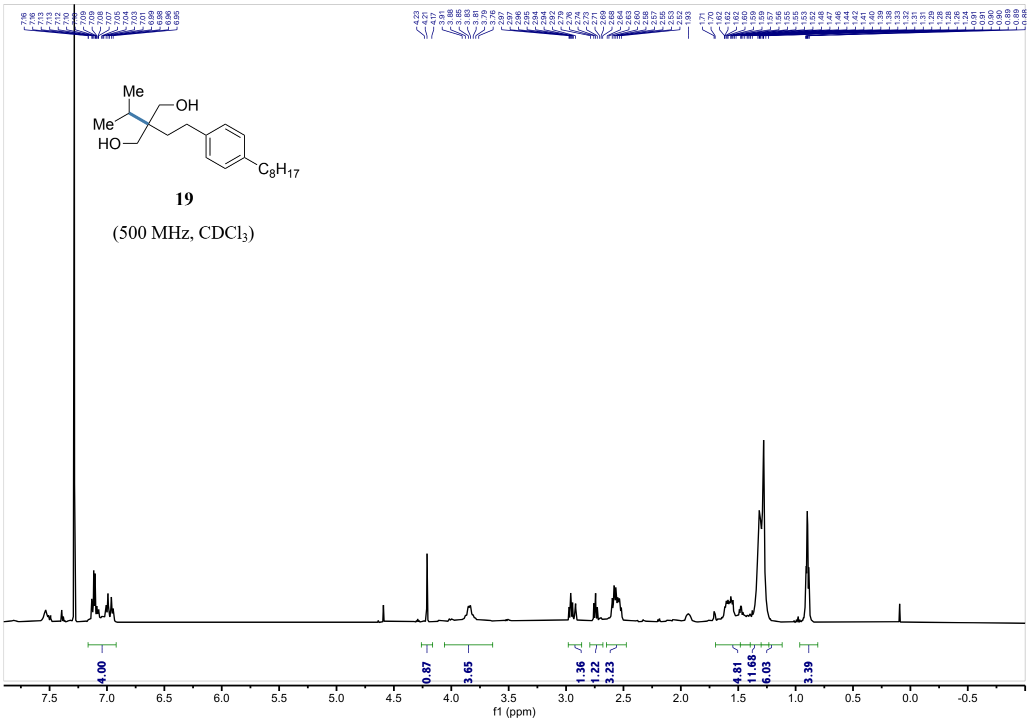
18

(500 MHz, CD_3OD)



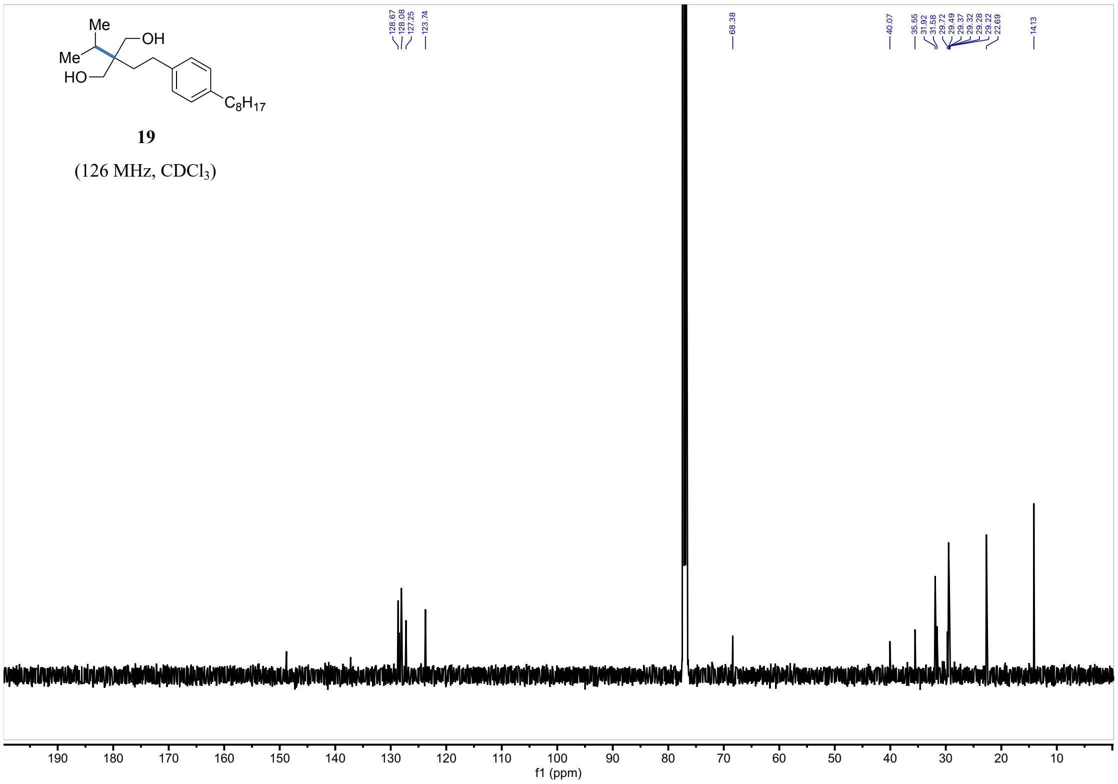
18

(126 MHz, CD_3OD)



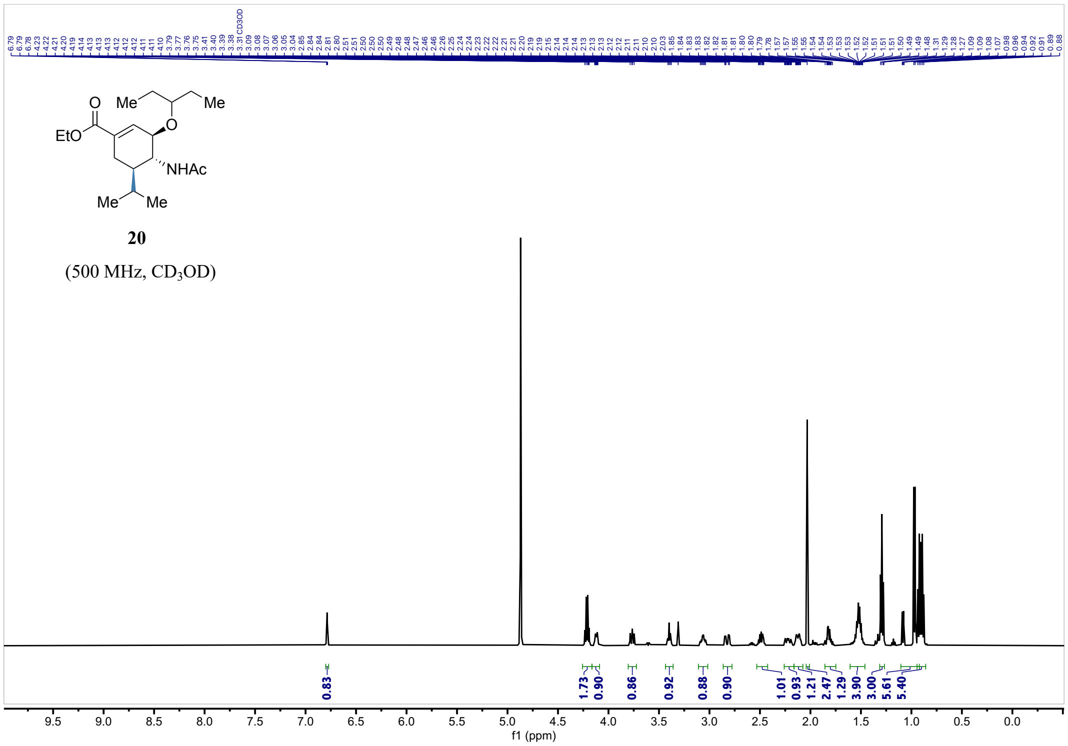
19

(500 MHz, $CDCl_3$)



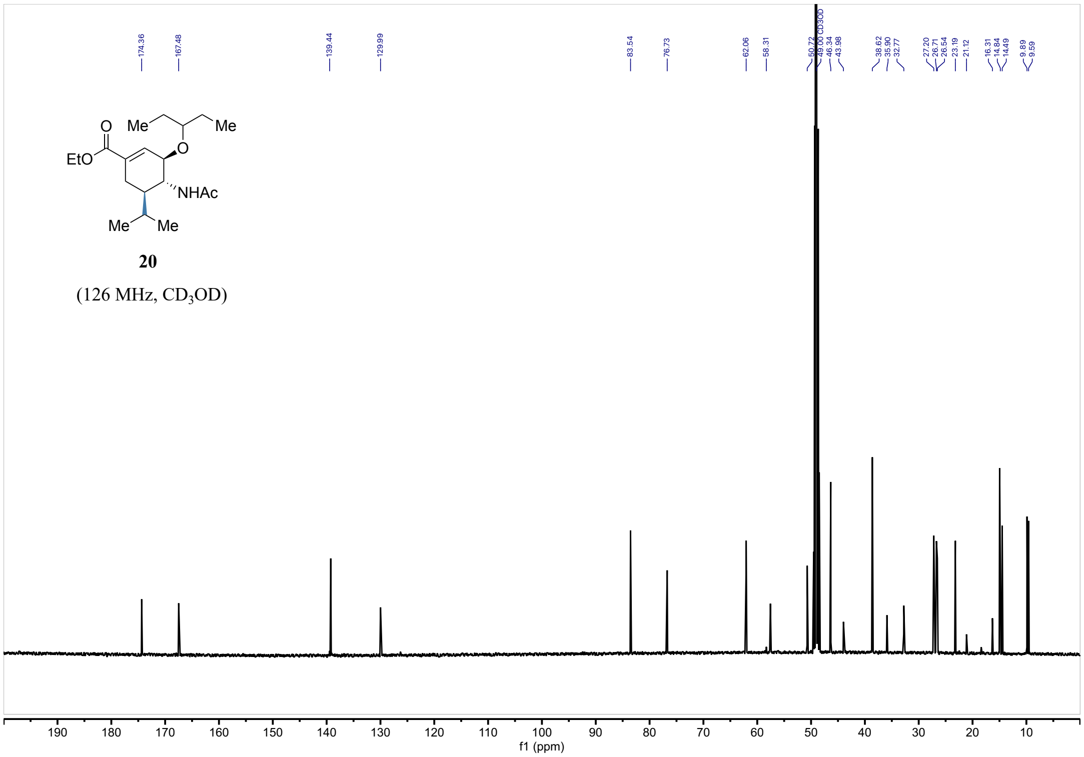
19

(126 MHz, $CDCl_3$)



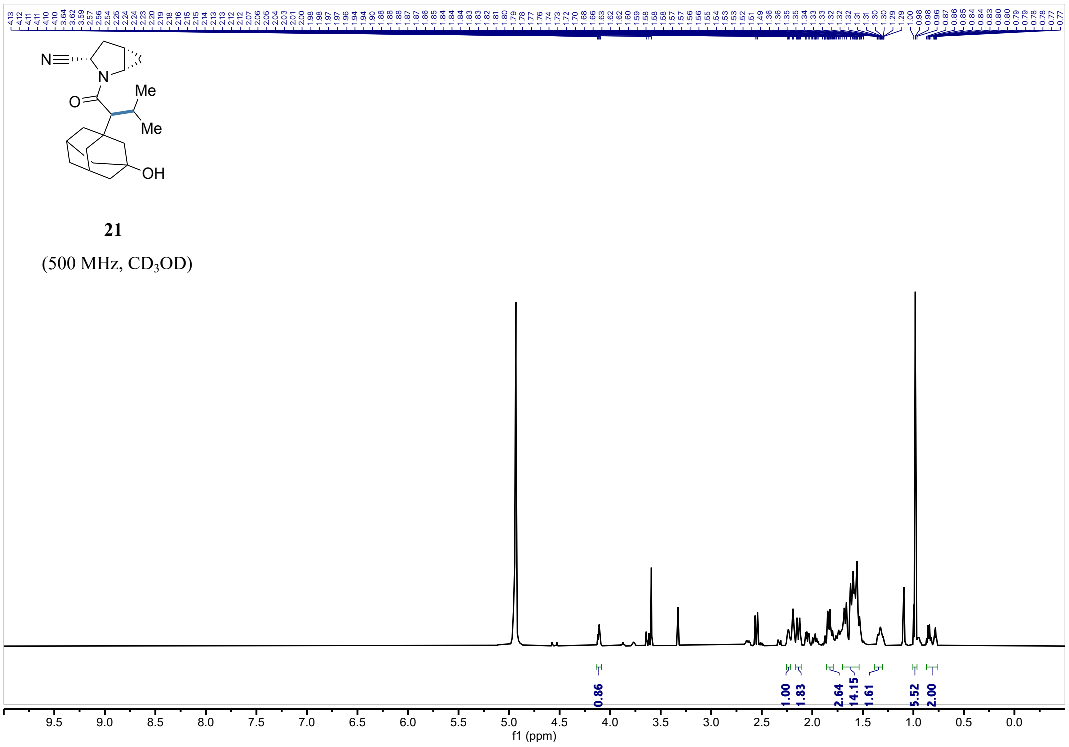
20

(500 MHz, CD_3OD)



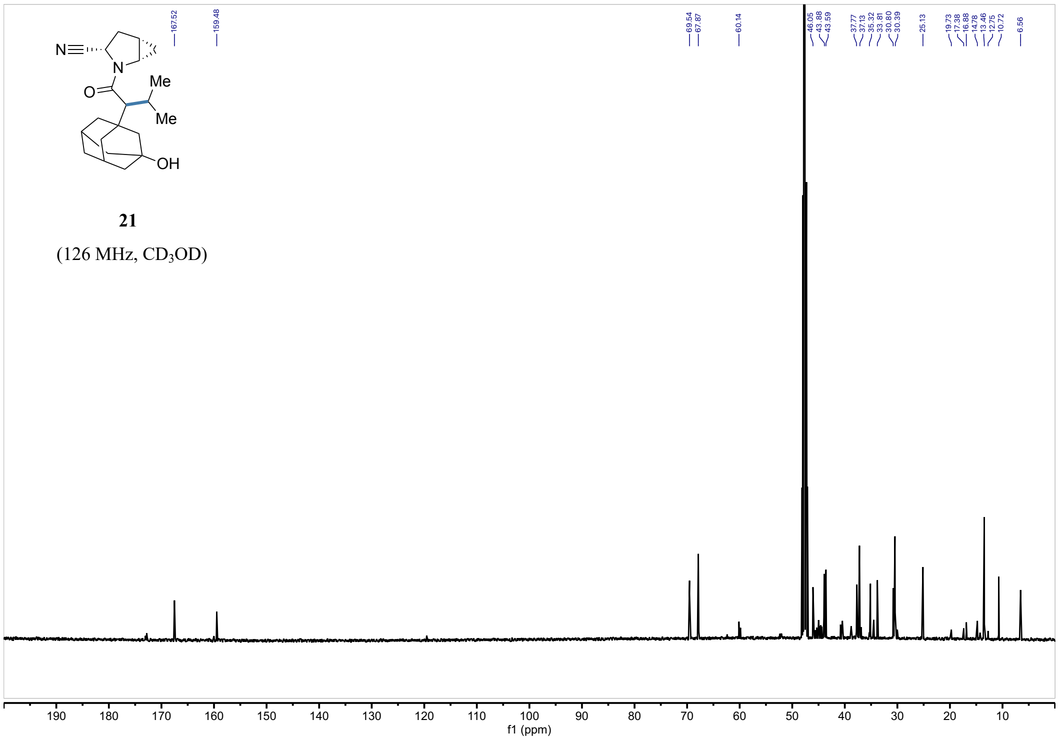
20

(126 MHz, CD_3OD)



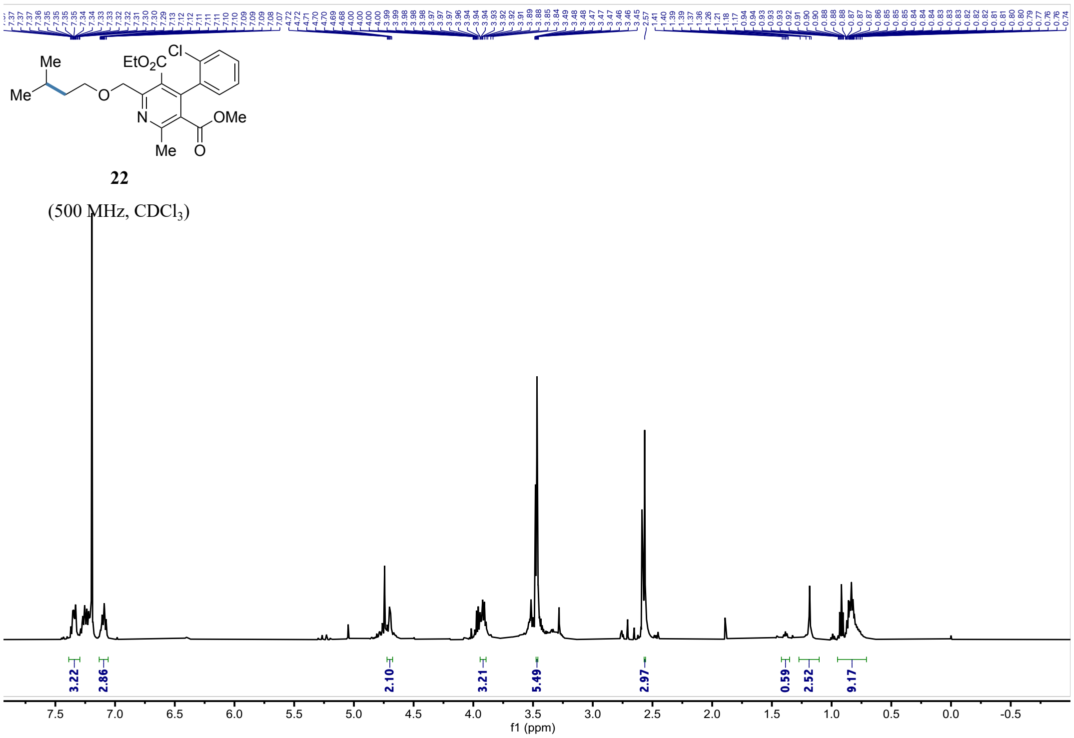
21

(500 MHz, CD_3OD)



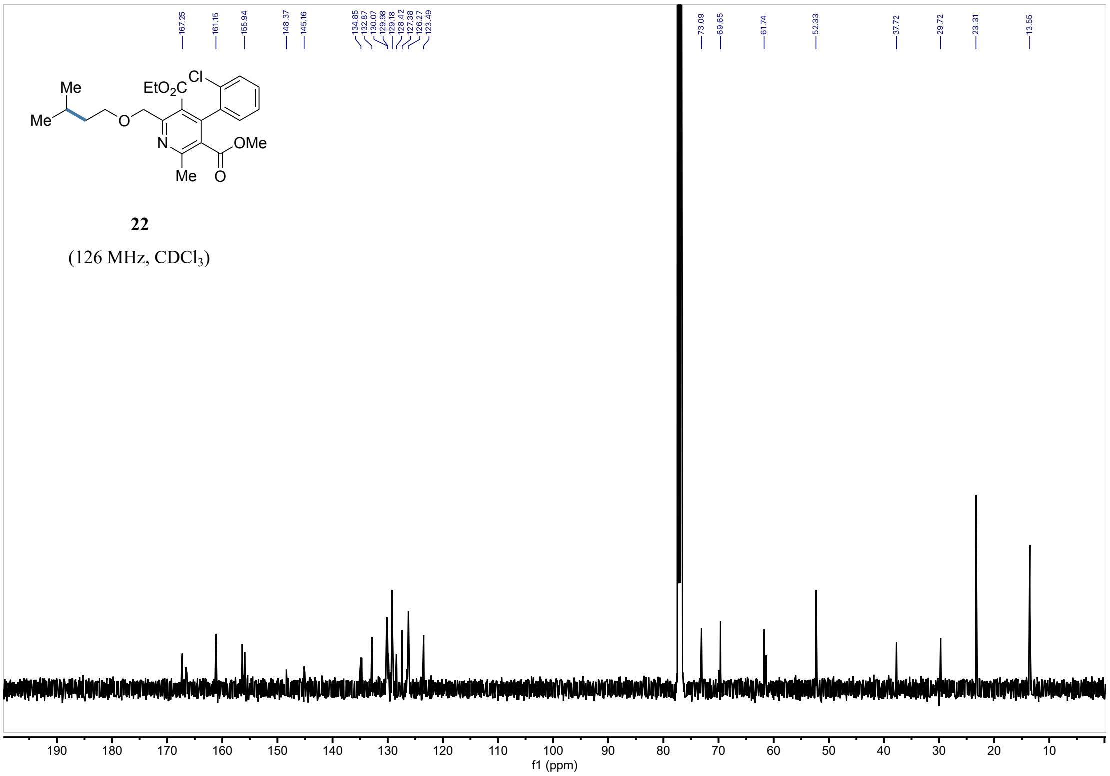
21

(126 MHz, CD_3OD)



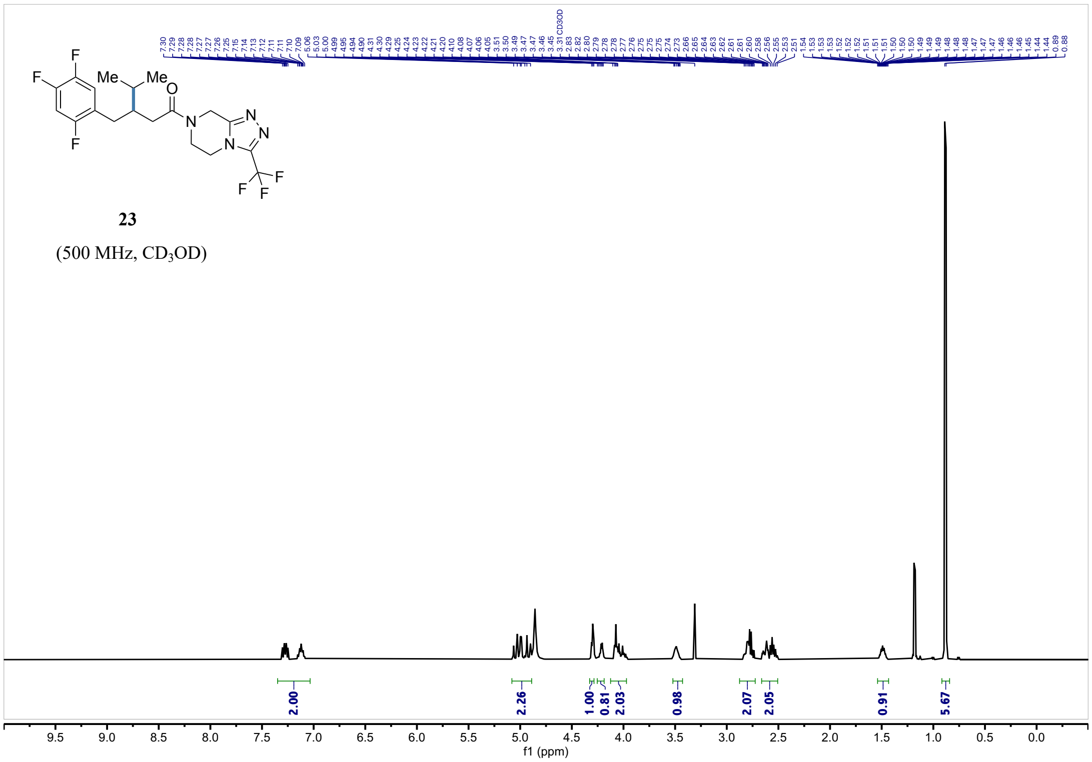
22

(500 MHz, $CDCl_3$)



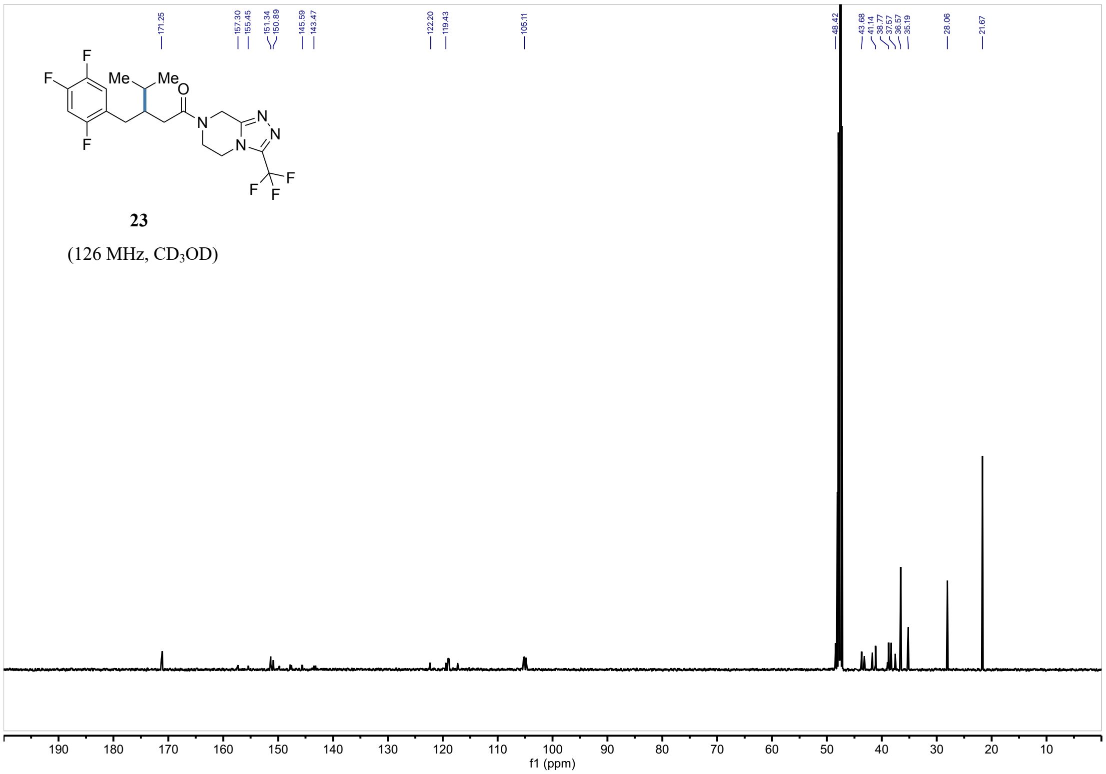
22

(126 MHz, $CDCl_3$)



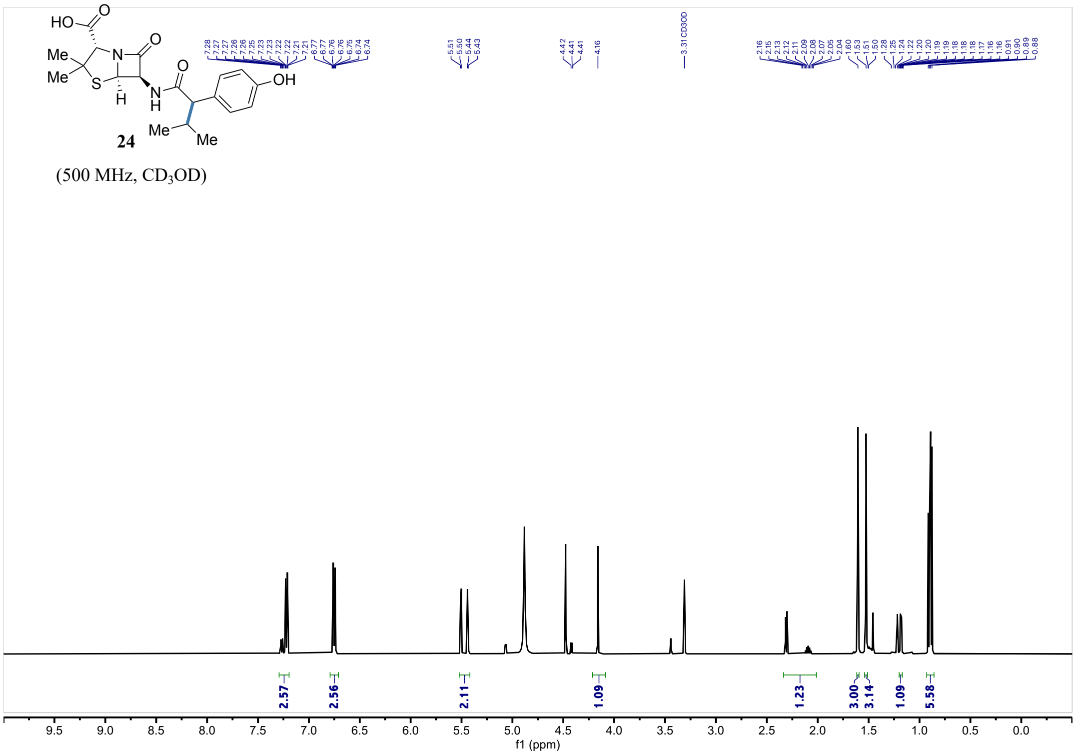
23

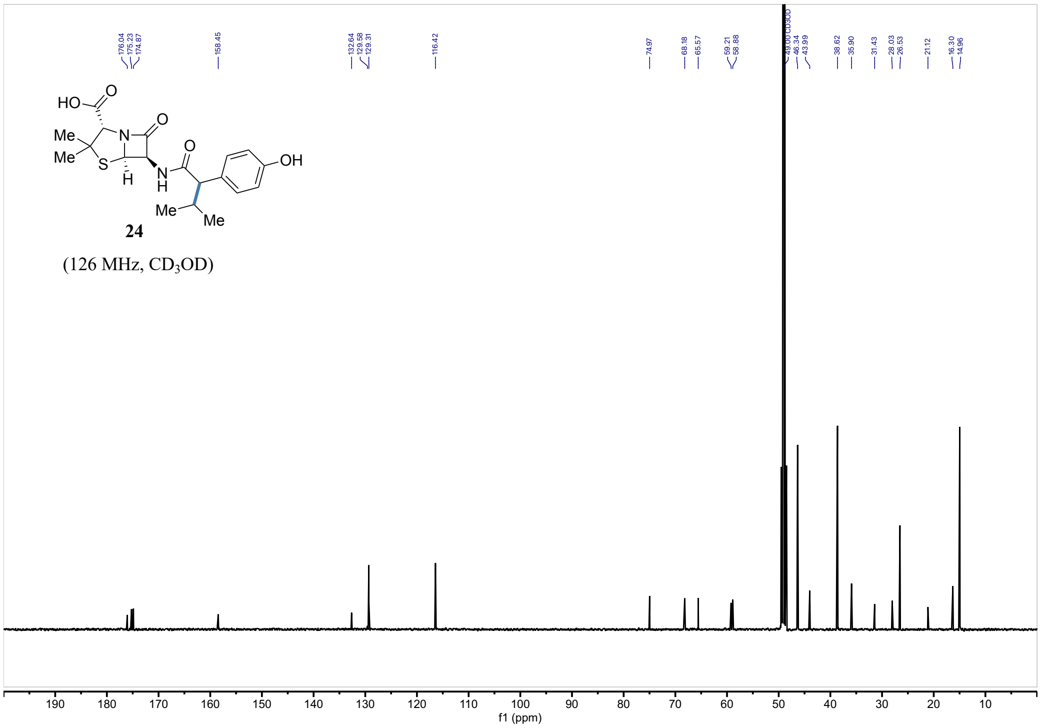
(500 MHz, CD_3OD)

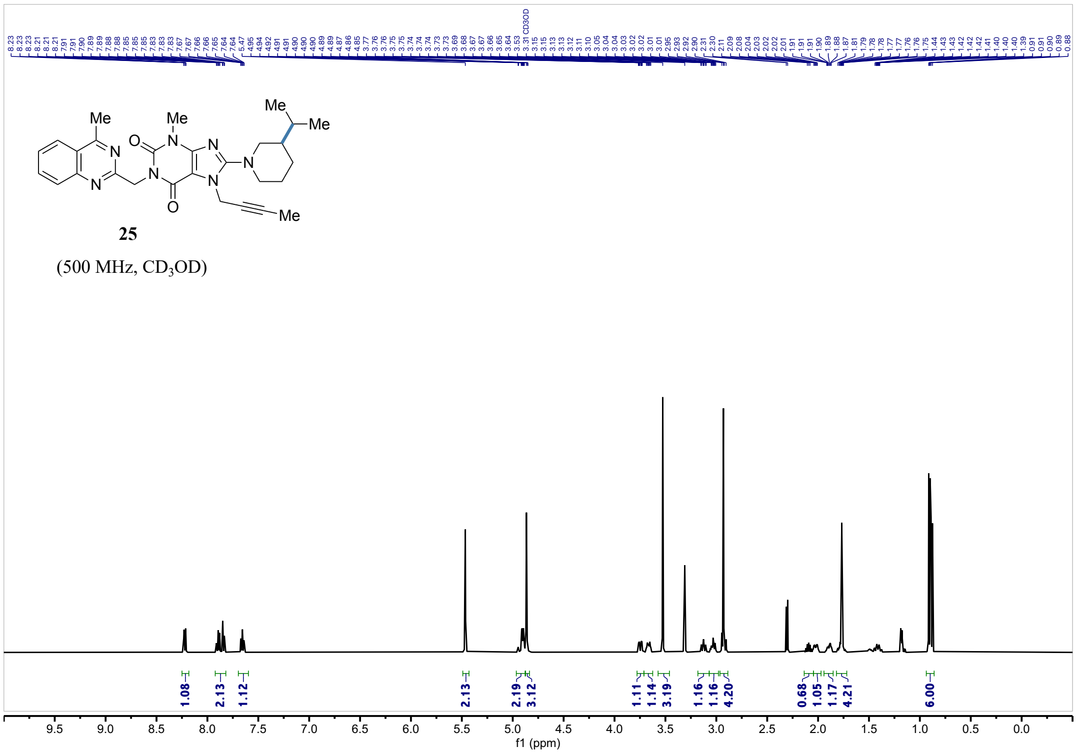


23

(126 MHz, CD_3OD)

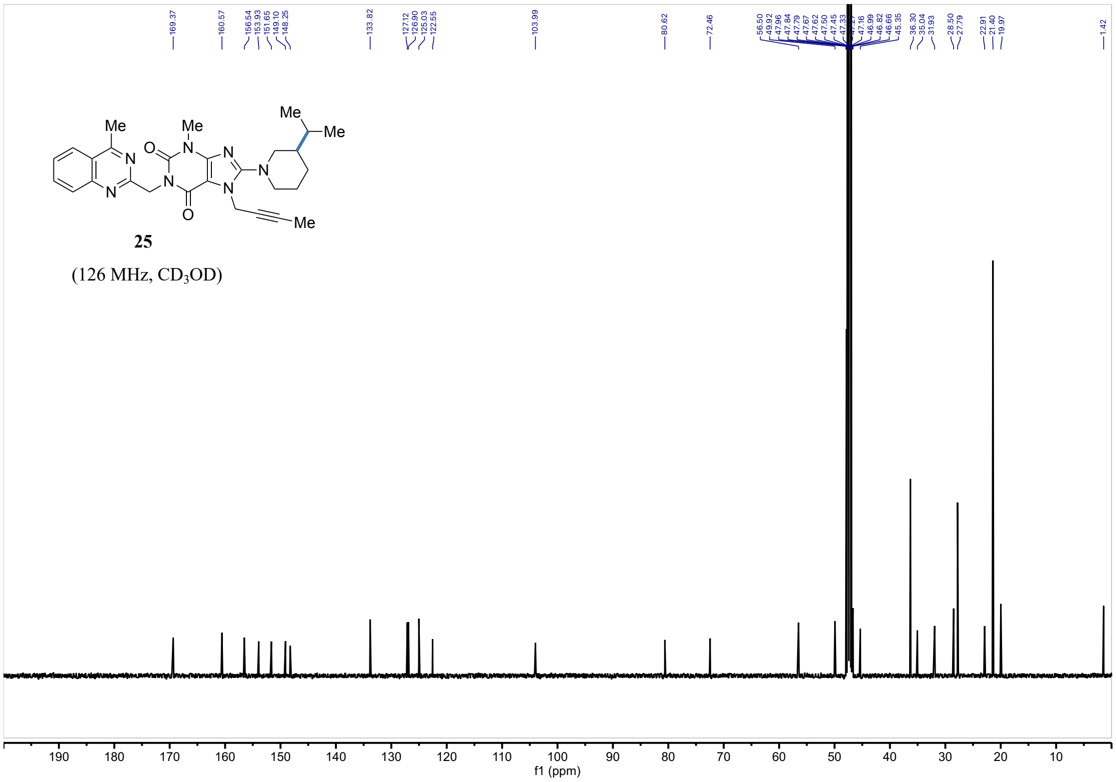

24
(500 MHz, CD₃OD)
7.28 7.27 7.27 7.26 7.26 7.25 7.23 7.23 7.22 7.22 7.21 7.21 6.77 6.77 6.76 6.76 6.75 6.74 6.74
5.51 5.50 5.44 5.43
4.42 4.41 4.41
4.16
3.31 CD3OD
2.16 2.15 2.13 2.12 2.11 2.09 2.08 2.07 2.05 2.04 1.60 1.53 1.51 1.50 1.28 1.25 1.24 1.22 1.20 1.20 1.19 1.19 1.18 1.18 1.18 1.17 1.16 0.91 0.90 0.89 0.88
2.57
2.56
2.11
1.09
1.23
3.00
3.14
1.09
5.58
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


176.04 175.23 174.87
158.45
132.64 129.58 129.31
116.42
74.97
68.18
65.57
59.21 58.88
49.00 CD3OD
46.34 43.99
38.62
35.90
31.43
28.03 26.53
21.12
16.30 14.96
24
(126 MHz, CD₃OD)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



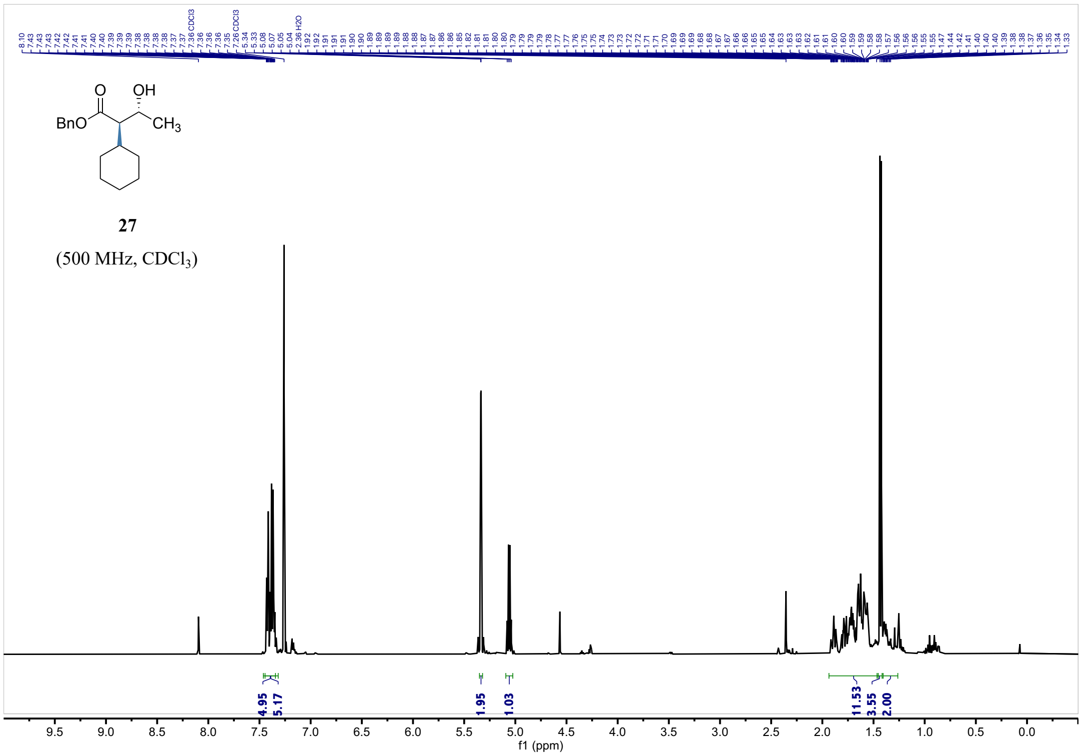
25

(500 MHz, CD_3OD)



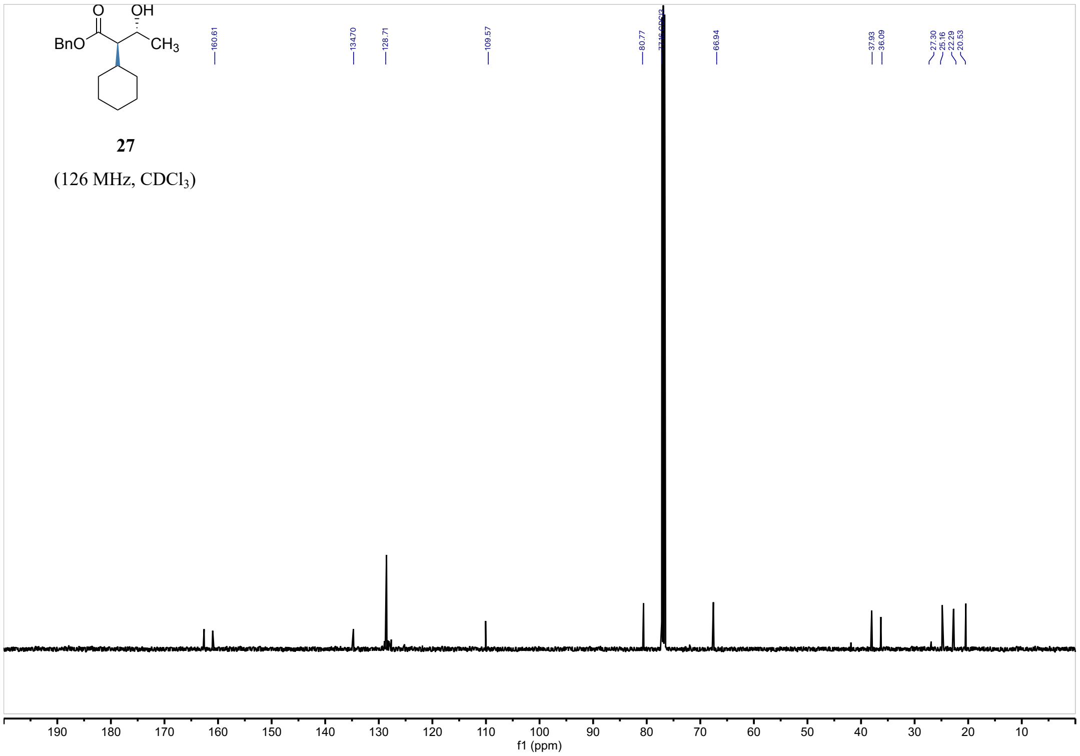
25

(126 MHz, CD_3OD)



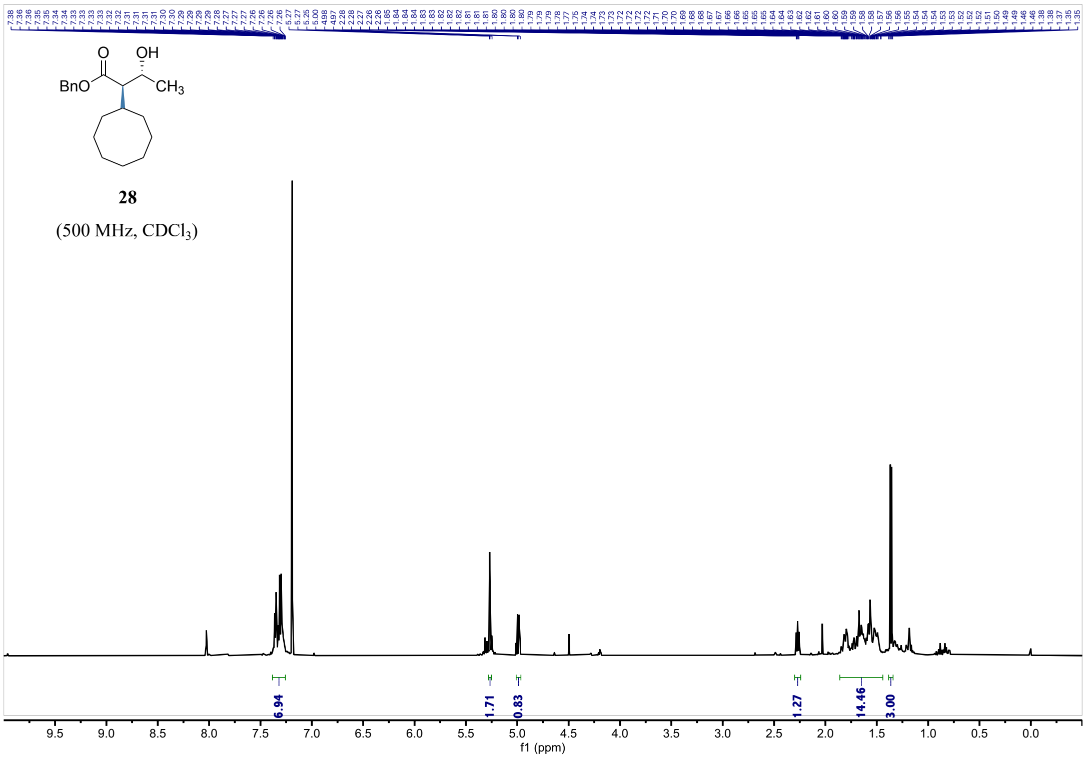
27

(500 MHz, $CDCl_3$)

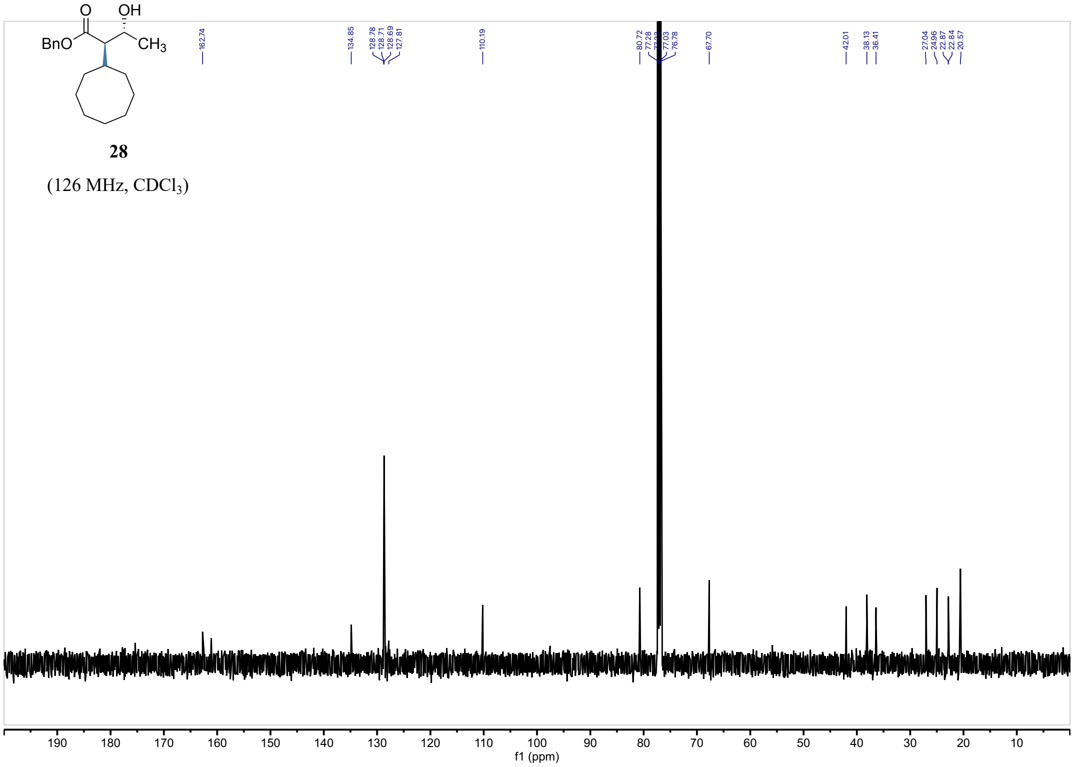


27

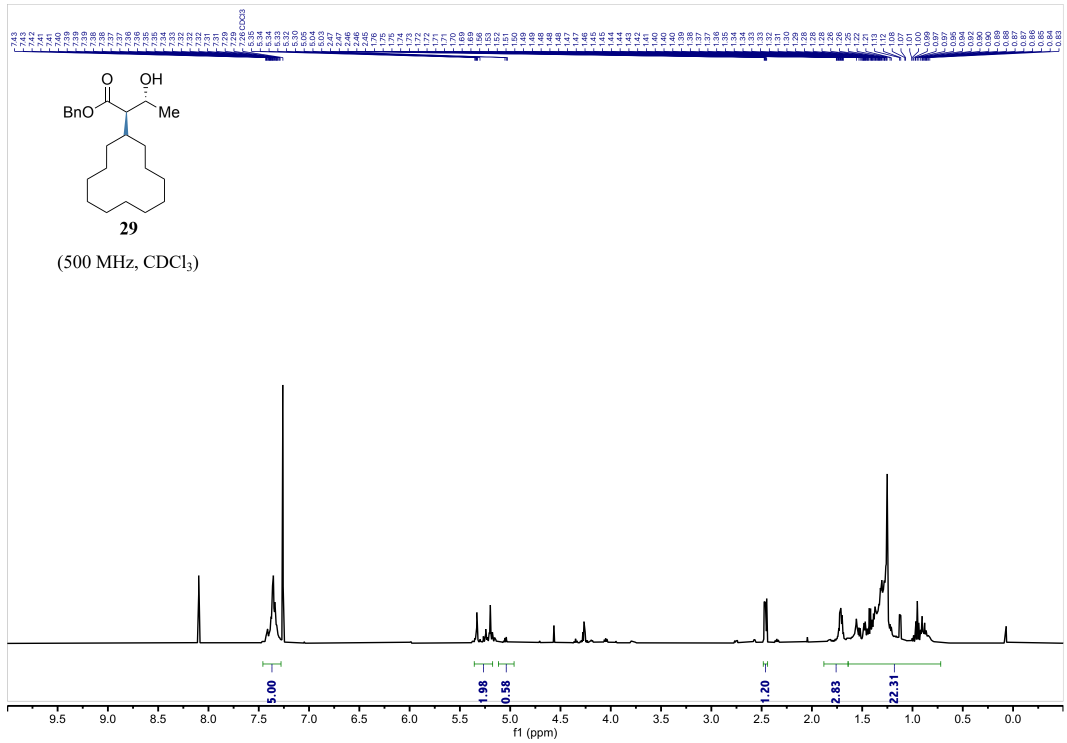
(126 MHz, $CDCl_3$)


28

(500 MHz, $CDCl_3$)

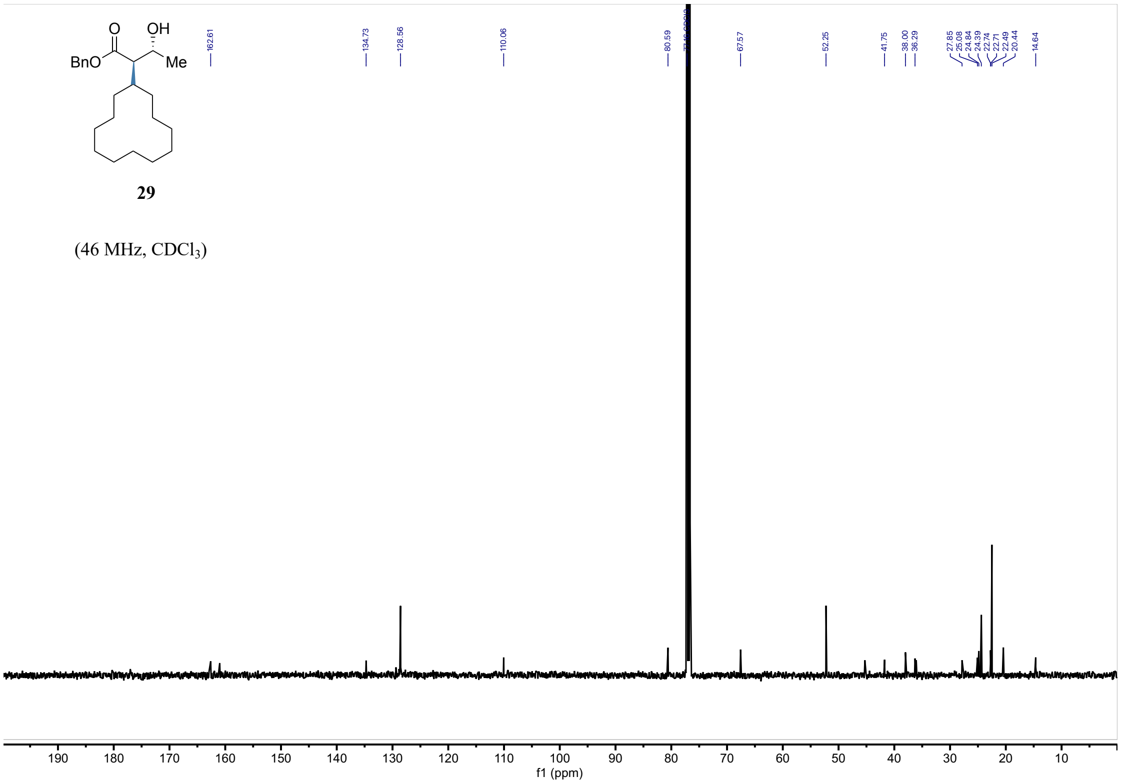

28

(126 MHz, $CDCl_3$)



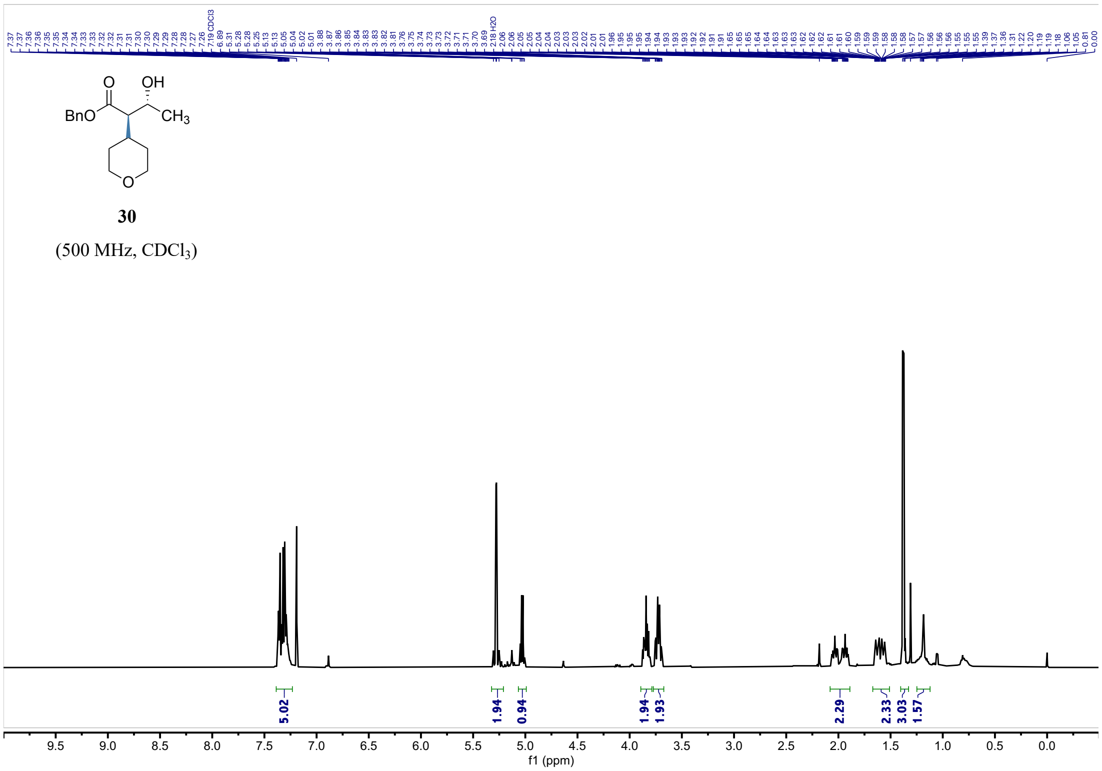
29

(500 MHz, CDCl$_3$)



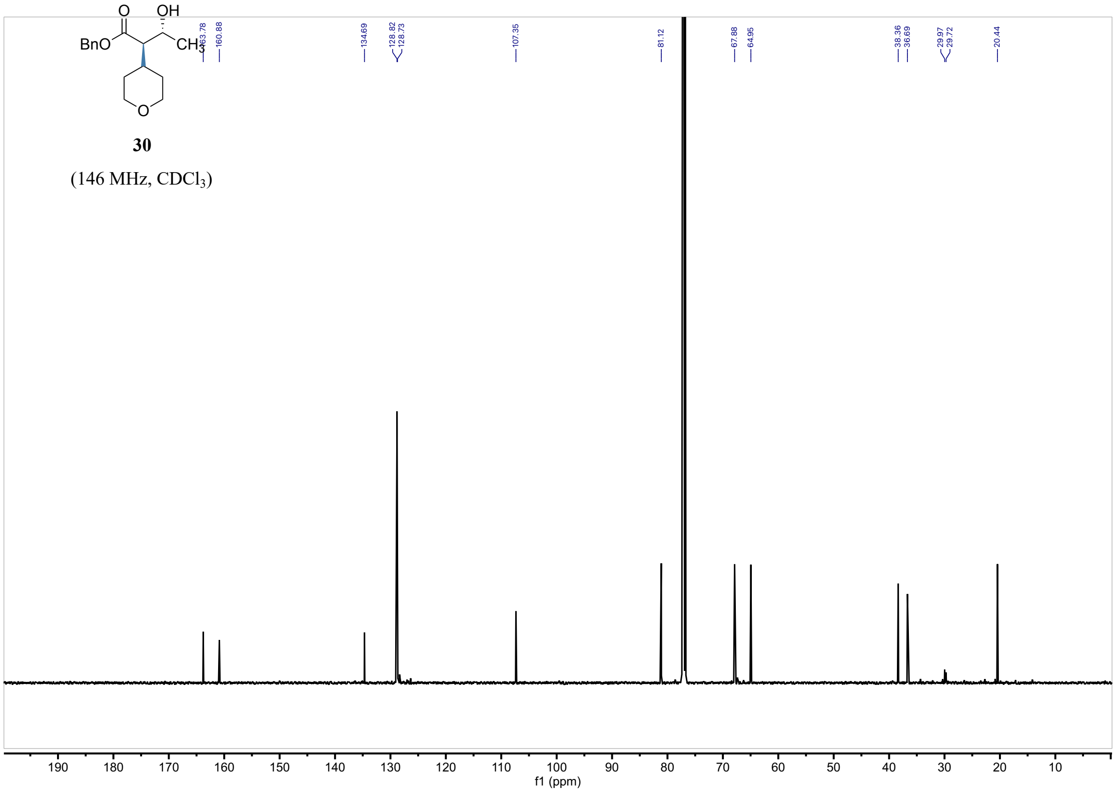
29

(46 MHz, CDCl$_3$)



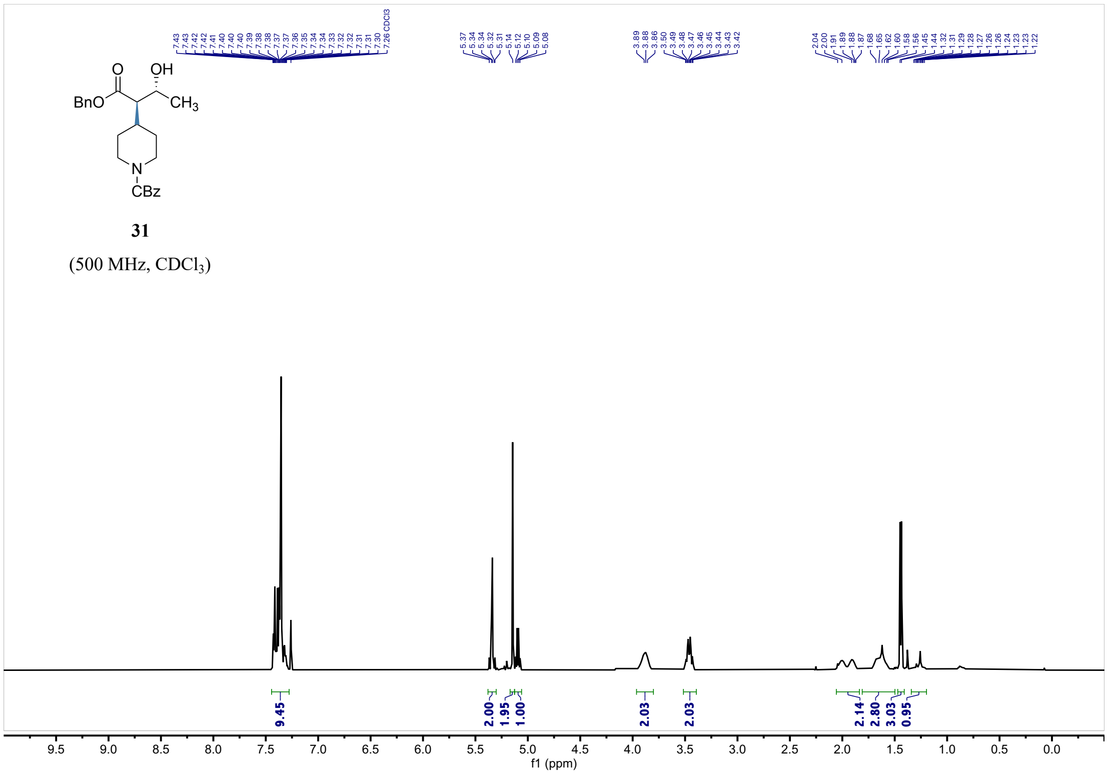
30

(500 MHz, $CDCl_3$)



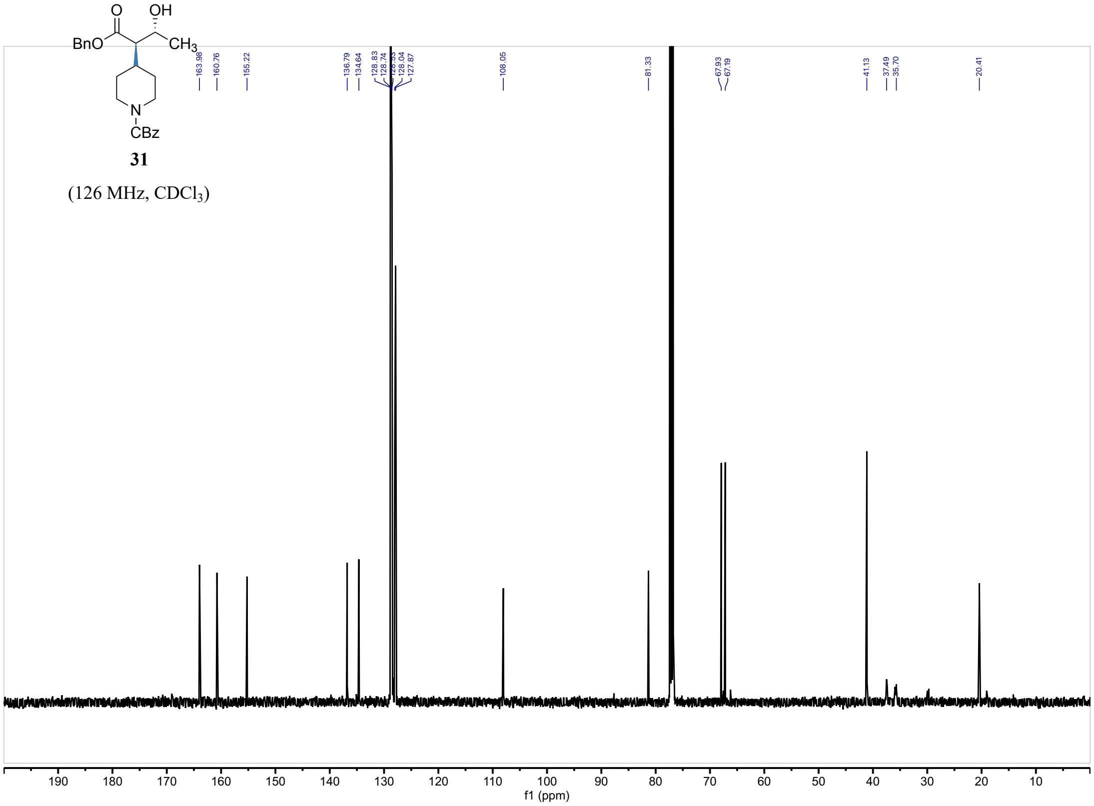
30

(146 MHz, $CDCl_3$)



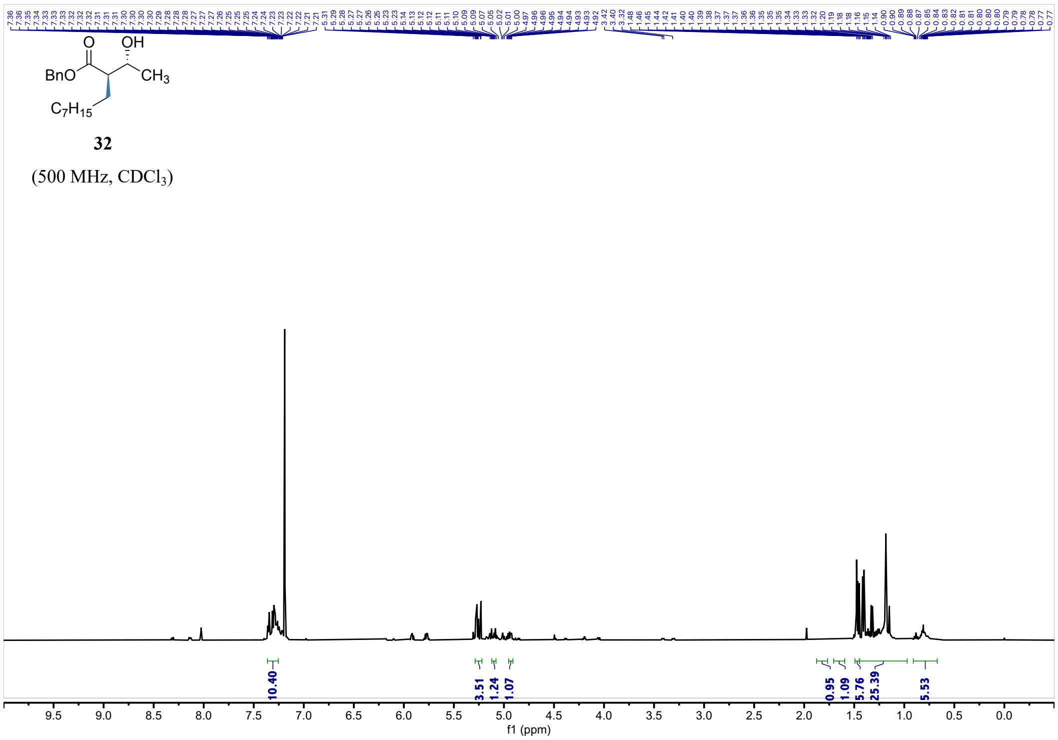
31

(500 MHz, $CDCl_3$)



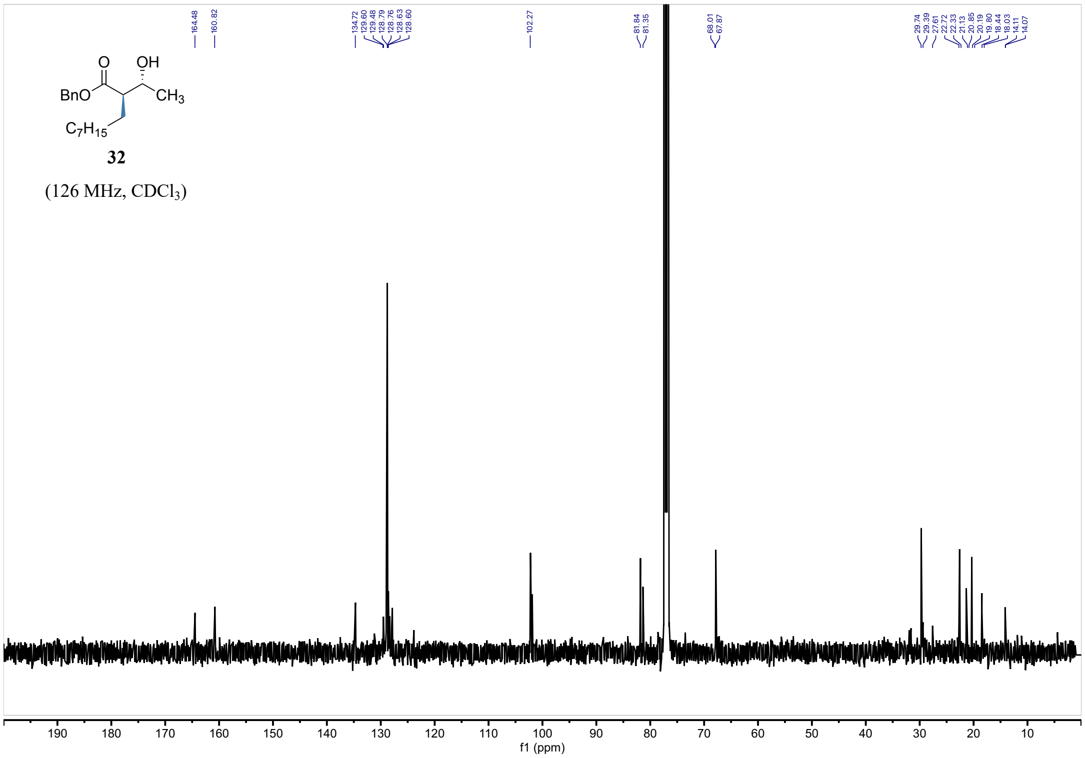
31

(126 MHz, $CDCl_3$)



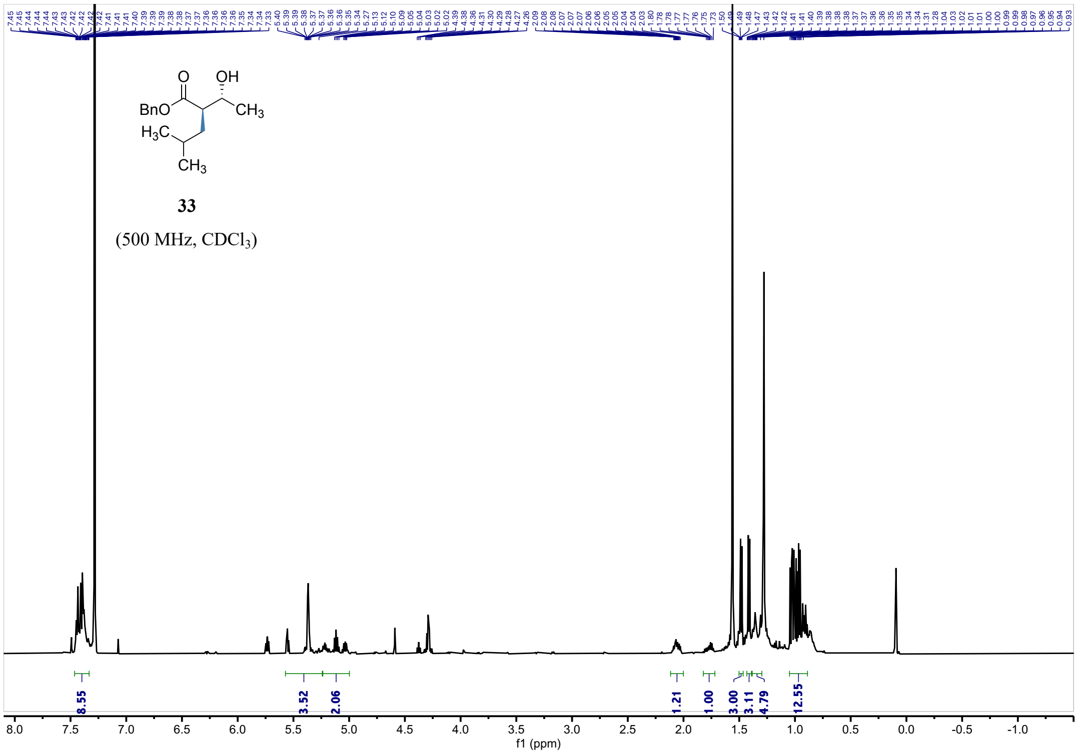
32

(500 MHz, CDCl$_3$)



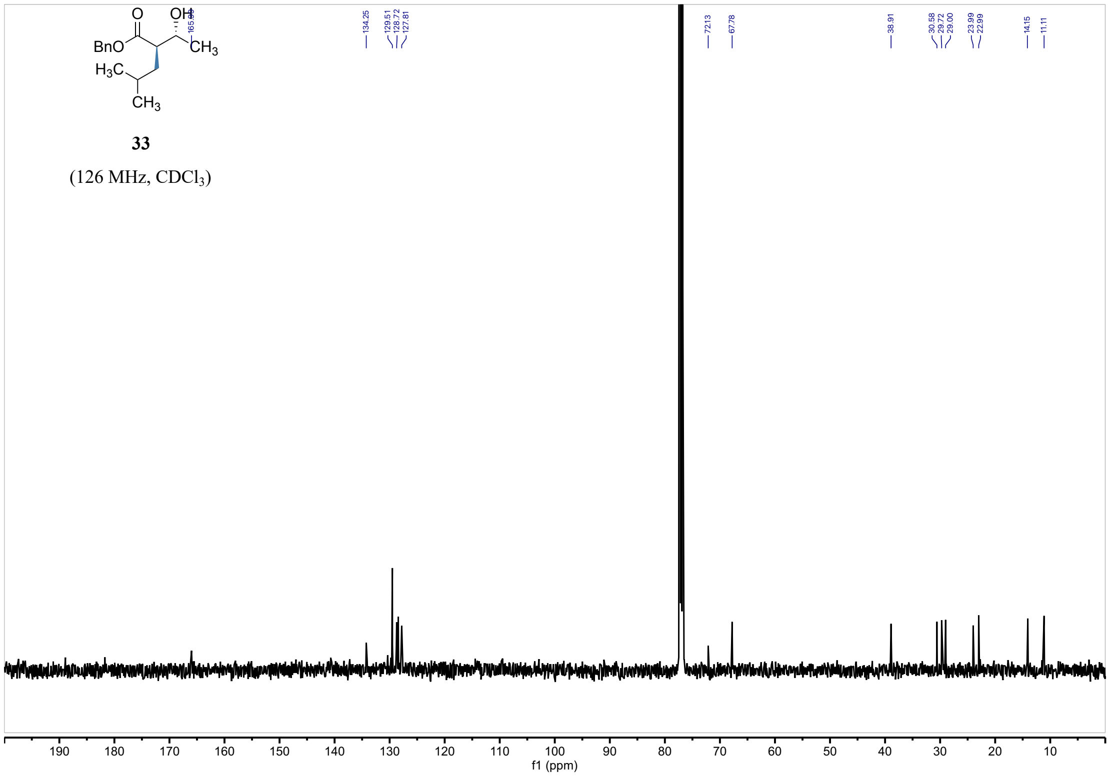
32

(126 MHz, CDCl$_3$)



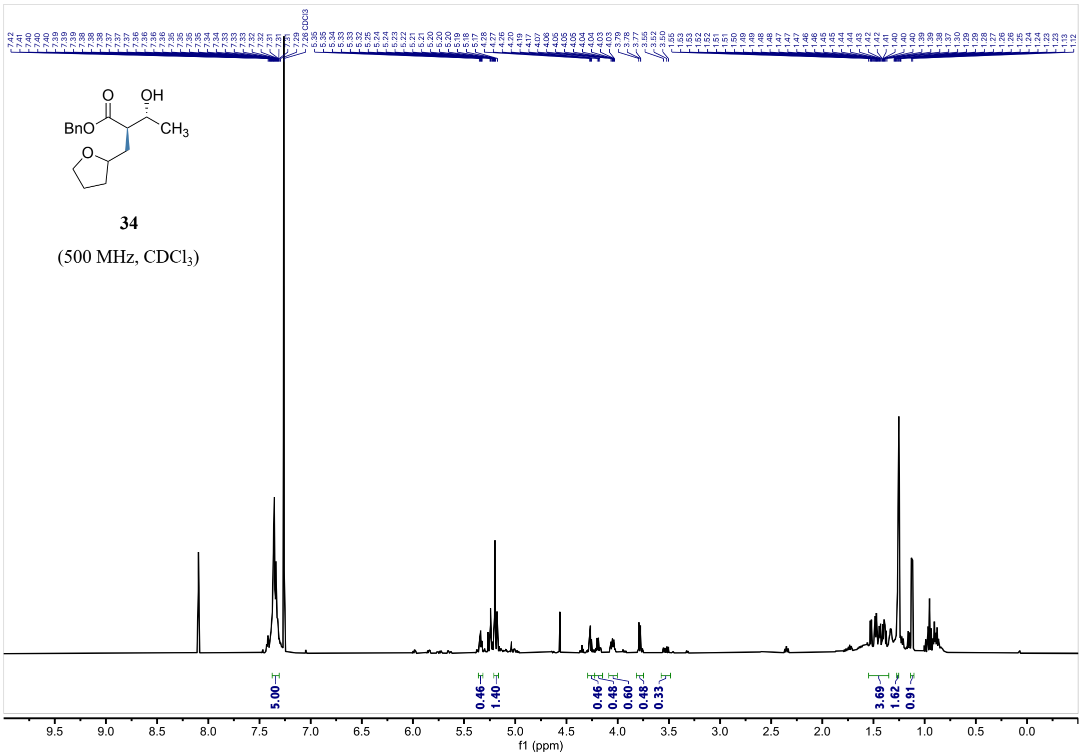
33

(500 MHz, $CDCl_3$)



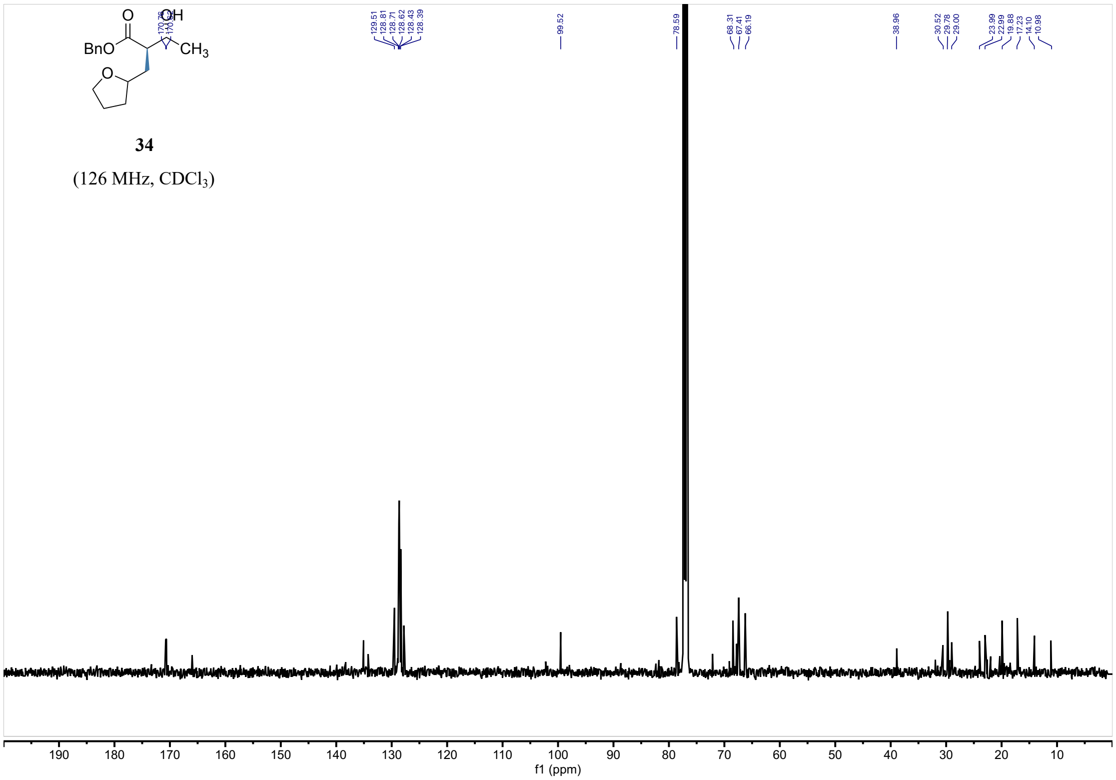
33

(126 MHz, $CDCl_3$)



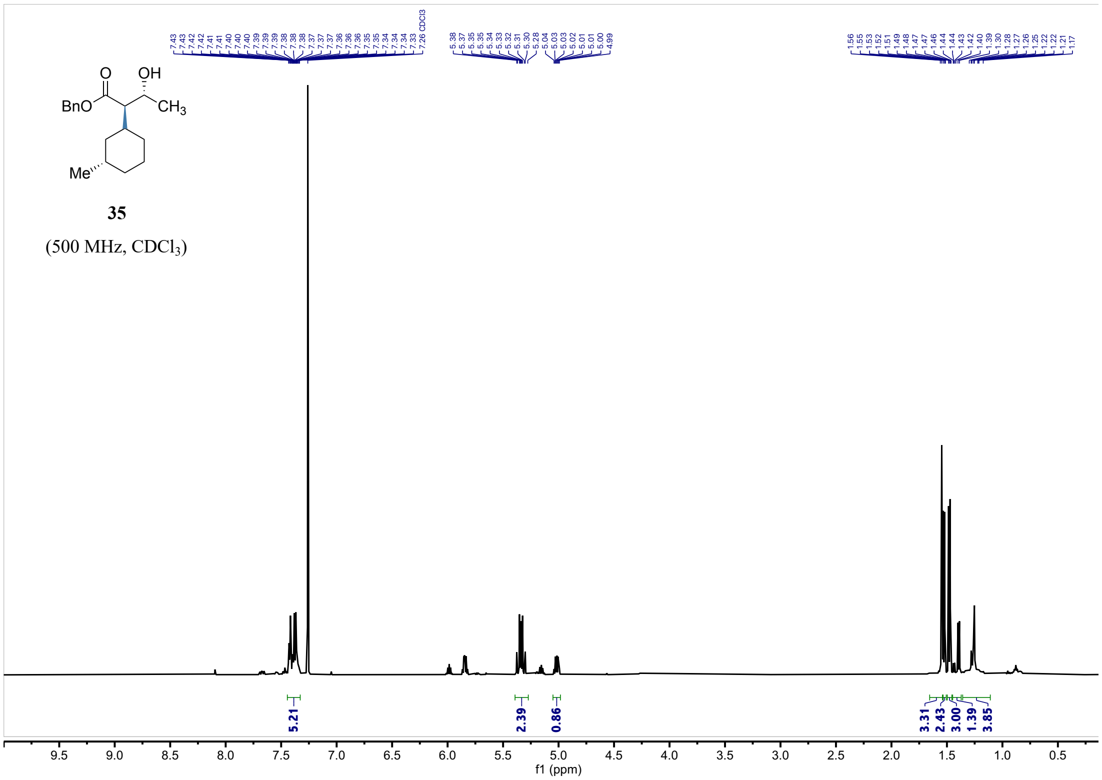
34

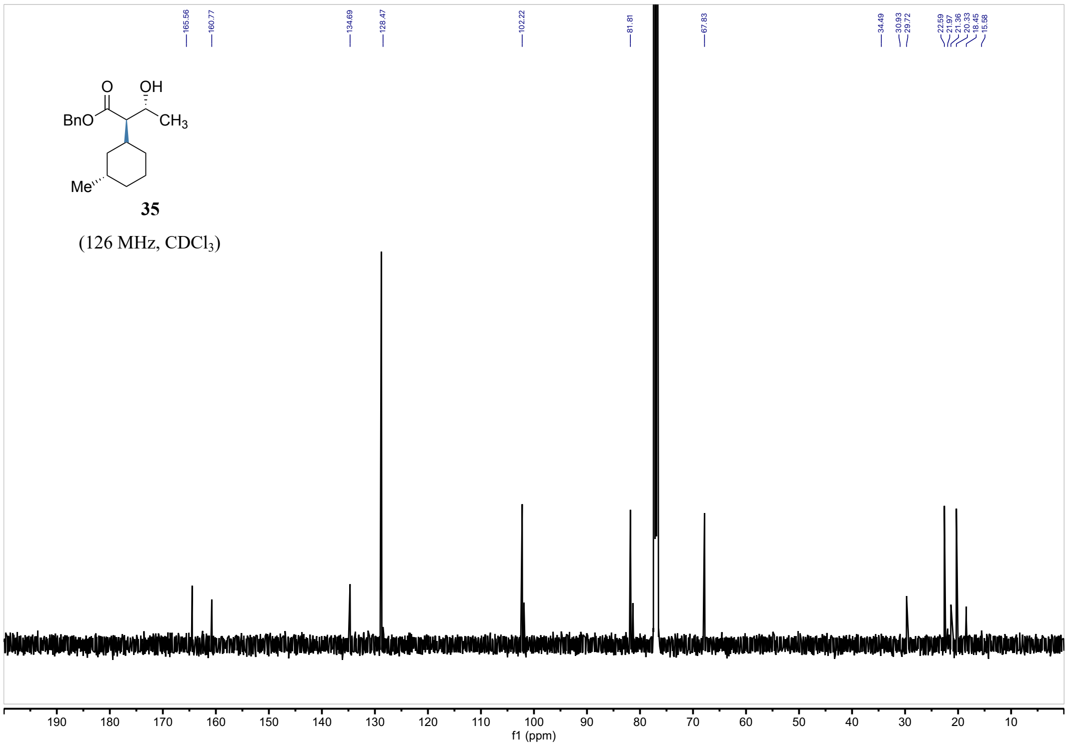
(500 MHz, $CDCl_3$)

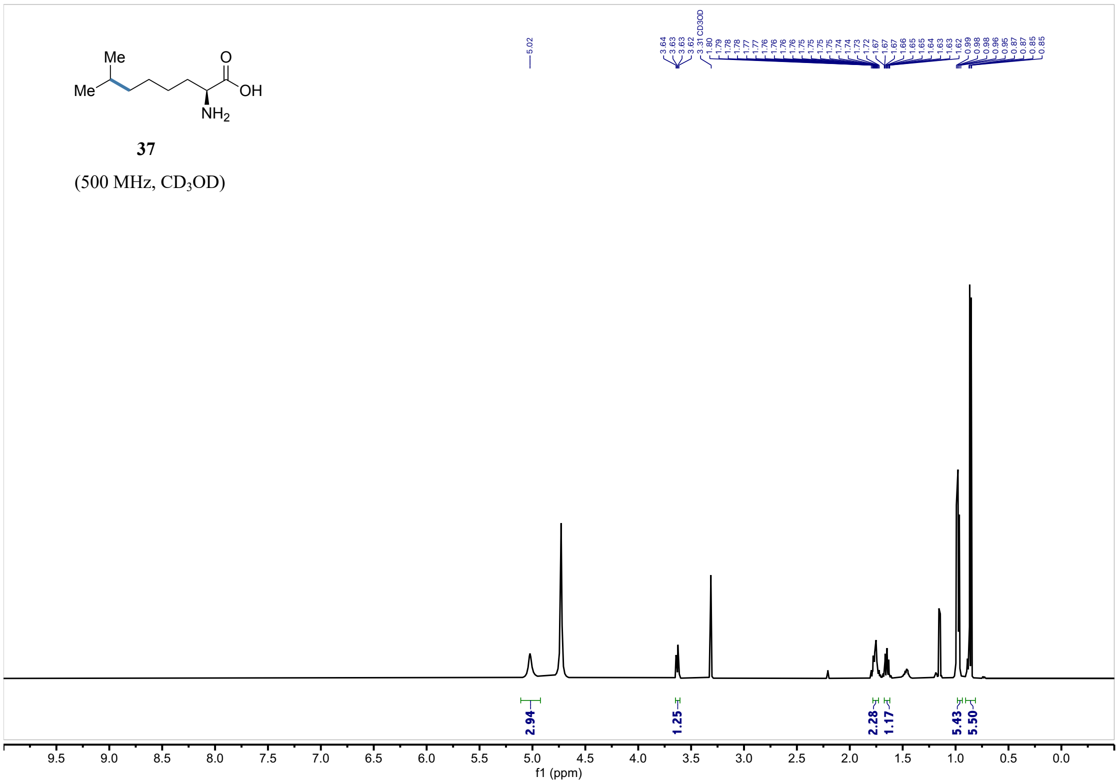


34

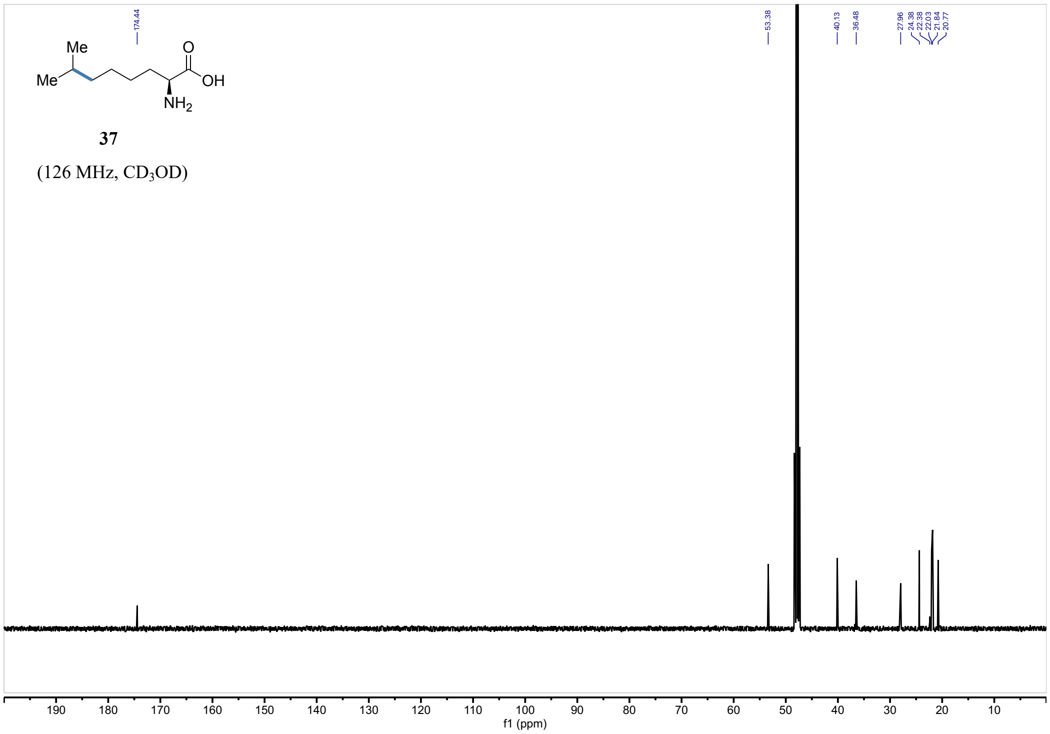
(126 MHz, $CDCl_3$)


7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.40
7.39
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.36
7.35
7.35
7.34
7.34
7.34
7.33
7.26 CDCl3
5.38
5.37
5.35
5.35
5.34
5.33
5.32
5.31
5.30
5.28
5.04
5.03
5.03
5.02
5.01
5.01
5.00
4.99
1.56
1.55
1.53
1.52
1.51
1.49
1.48
1.47
1.47
1.46
1.44
1.44
1.43
1.42
1.40
1.39
1.30
1.28
1.27
1.26
1.25
1.22
1.22
1.21
1.17
O
OH
BnO
CH3
Me
35
(500 MHz, CDCl3)
5.21
2.39
0.86
3.31
2.43
3.00
1.39
3.85
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

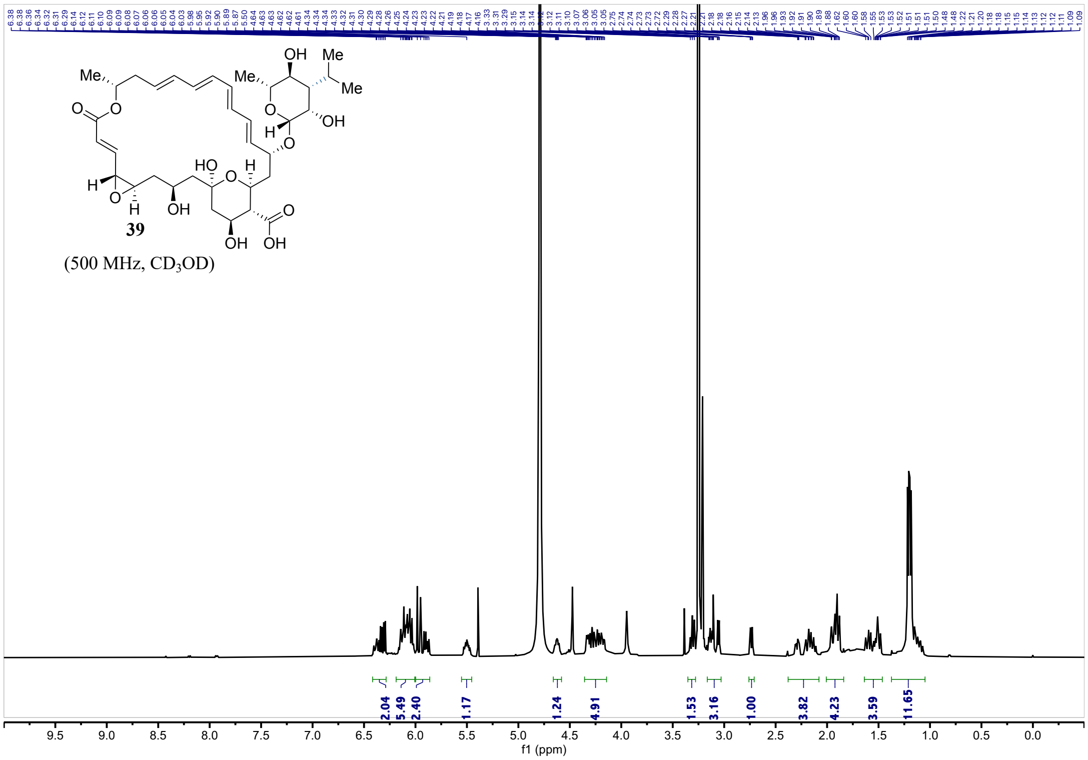

165.56
160.77
134.69
128.47
102.22
81.81
67.83
34.49
30.93
29.72
22.59
21.97
21.36
20.33
18.45
15.58
O
OH
BnO
CH3
Me
35
(126 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


37

(500 MHz, CD_3OD)

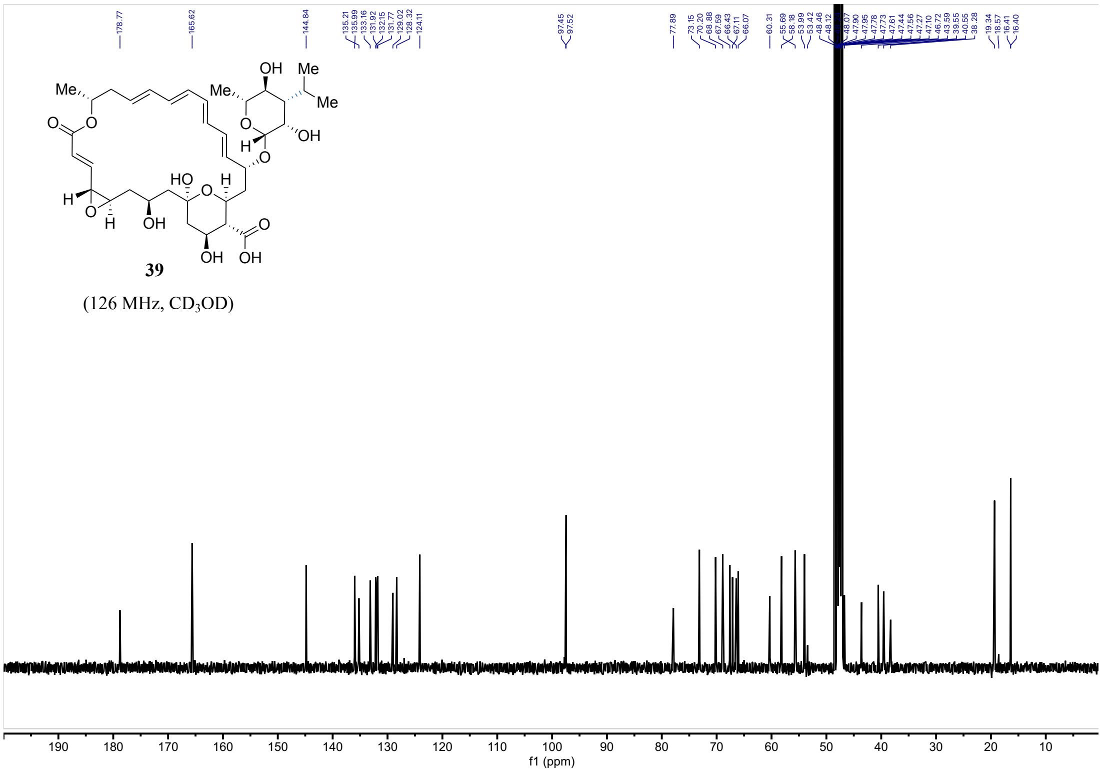

37

(126 MHz, CD_3OD)



39

(500 MHz, CD_3OD)



39

(126 MHz, CD_3OD)