SUPPORTING INFORMATION

Metal-Free, Photoinduced Remote C(sp^3)–H Borylation

Jiachen He, Silas P. Cook *

Department of Chemistry, Indiana University
800 East Kirkwood Avenue, Bloomington, IN 47405 (United States)

Table of Contents

1. General Information

All reactions were carried out under nitrogen atmosphere in glass vials fitted with rubber septa, unless otherwise stated. Analytical grade solvents and commercially available reagents were purchased from commercial sources and used directly without further purification unless otherwise stated. Dry solvents were obtained by distillation from drying reagents according to procedures described in Purification of Laboratory Chemicals (5th Edition) written by Wilfred L.F. Armarego and Christina L.L. Chai (Elsevier, 2003).

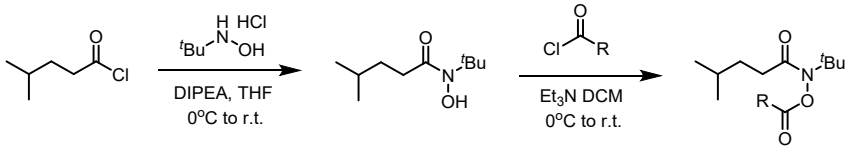
Thin-layer chromatography (TLC) was carried out on Merck 60 F_{254} precoated, glass silica flash plates which were visualized with either ultraviolet light or stained with $KMnO_4$. Automated column chromatography was performed on a Biotage Isolera One using Biotage Snap Ultra cartridges (25g or 50g SiO_2) or a Yamazen Universal Premium column (55g SiO_2).

^{1}H-NMR and ^{13}C-NMR spectra were recorded at room temperature using a Varian I400 (^{1}H-NMR at 400 MHz and ^{13}C-NMR at 100 MHz), Varian VXR400 (^{1}H-NMR at 400 MHz and ^{13}C-NMR at 100 MHz), Varian I500 (^{1}H-NMR at 500 MHz and ^{13}C-NMR at 125 MHz), Varian I600 (^{1}H-NMR at 600 MHz). ^{19}F-NMR spectra were recorded at room temperature using a Varian I400 or VXR400 (^{19}F-NMR at 376 MHz). Chemical shifts are reported in ppm with reference to solvent signals [^{1}H-NMR: $CDCl_3$ (7.26 ppm); ^{13}C-NMR: $CDCl_3$ (77.16 ppm)]. Signal patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; and m, multiplet.

High Resolution Mass (HRMS) analysis was obtained using Electron Impact Ionization (EI, Agilent 7890B Gas Chromatograph (GC) with an Agilent 7250 Quadrupole-Time-of-Flight (Q-TOF)) and reported as m/z (relative intensity) for the molecular ion [M], or using Atmospheric Pressure Chemical Ionization (APCI, Agilent 1200 HPLC-6130 MSD with a quadrapole mass spectrometer) and reporting the molecular ion $[M+H]^+$ or a suitable fragment ion.

All photochemical reactions were performed in 10 mL long-neck vials (unless noted otherwise) under an argon atmosphere at room temperature. The reactions were carried out with irradiation by Kessil lamps PR160L (max 45 W, λ_{max} = 440 nm). Degassing of reactions was achieved by three freeze-pump-thaw cycles.

2. Preparation of Starting Materials

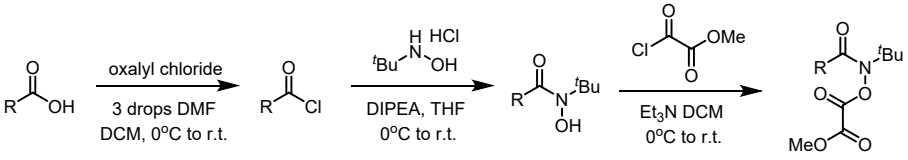


General procedure A:

Starting materials were prepared from corresponding acyl chloride or carboxylic acid on a 2-4 mmol scale. The yields have not been optimized.

Step 1: To a solution of *N*-(*tert*-Butyl)hydroxylamine hydrochloride (1.0 equiv) in anhydrous THF (0.4 M) at 0 ℃ was added DIPEA (2.0 equiv) slowly. The mixture was stirred for 10 minutes at the same temperature. Then, *4*-methylvaleryl chloride (1.0 equiv) in anhydrous THF was added dropwise over 20 minutes and the mixture was allowed to warm to room temperature overnight. The solvent was removed in *vacuo*. The mixture was diluted with saturated $NaHCO_3$ and EtOAc. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with 1.0 M HCl, saturated $NaHCO_3$, and brine. The crude mixture was then concentrated via rotary evaporation. The intermediate was used directly for the next step or simply purified by flash column chromatography on silica gel.

Step 2: To a solution of hydroxylamine intermediate (1.0 equiv) in anhydrous CH_2Cl_2 (0.4 M) at 0 ℃ was added Et_3N (2.0 equiv) dropwise. Then a corresponding acid chloride (1.5 equiv) was added dropwise over 10 minutes. The reaction was stirred vigorously at room temperature for 4 hours. The reaction was quenched by saturated $NaHCO_3$. The layers were separated. The aqueous layer was extracted with DCM. The combined organic layers were subsequently washed with 1.0 M HCl, saturated $NaHCO_3$, and brine. The crude was then concentrated. Purification by column chromatography on silica gel eluting with hexanes/EA gave **6-10**. (*The products were found to decompose slowly on silica gel. The compounds are relatively stable at room temperature (around one month) and should be stored in the freezer for long-term storage.*)



General procedure B:

The starting materials were prepared from corresponding acyl chloride or carboxylic acid on a 2-4 mmol scale. The yields have not been optimized.

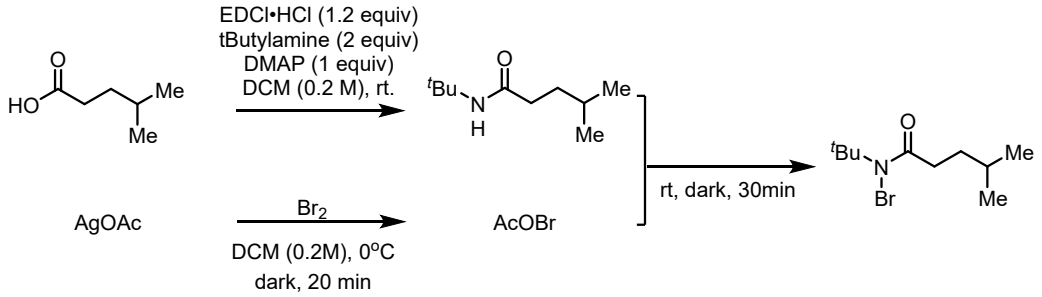
Step 1: To a solution of carboxylic acid (1.0 equiv) and 3-5 drops of anhydrous DMF in anhydrous CH_2Cl_2 (0.5 M) at 0 ℃ was added oxalyl chloride (2.0 equiv) dropwise over 15 minutes. The reaction was stirred vigorously at room temperature for 4 hours. The solvent was removed in *vacuo*. The resulting acyl chloride was redissolved in anhydrous THF (1-2 mL) and used directly for the next step without further purification.

Step 2: To a solution of *N*-(*tert*-Butyl)hydroxylamine hydrochloride (1.0 equiv) in anhydrous THF (0.4 M) at 0 ℃was added DIPEA (2.0 equiv) slowly. The mixture was stirred for 10 minutes at the same temperature. Then, acyl chloride (1.0 equiv) in anhydrous THF was added dropwise over 20 minutes. The reaction mixture was allowed to warm to room temperature overnight. The solvent was removed in *vacuo*. The mixture was diluted with saturated $NaHCO_3$ and EtOAc. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with 1.0 M HCl, saturated $NaHCO_3$, and brine. The crude was then concentrated under reduce pressure. The intermediate was used directly for the next step or simply purified by flash column chromatography on silica gel.

Step 3: To a solution of hydroxylamine intermediate (1.0 equiv) in anhydrous CH_2Cl_2 (0.4 M) at 0 ℃, Et_3N (2.0 equiv) was added dropwise. Then methyl oxalyl chloride (1.5 equiv) was added dropwise over 10 minutes. The reaction was stirred vigorously at room temperature for 4 hours. The mixture was diluted with saturated $NaHCO_3$ and DCM. The layers were separated. The aqueous layer was extracted with DCM. The combined organic layers were washed with 1.0 M HCl, saturated $NaHCO_3$, and brine. The crude was then concentrated under reduce pressure. Purification by column chromatography on silica gel eluting with hexanes/EA gave **1a**-**48a, 53a**. (*The products were found to decompose slowly on silica gel. The compounds are relatively stable at room temperature (around one month) and should be stored in the freezer for long-term storage.*)

The compounds **1**[1]**, 2**[2]**, 3**[3]**, 5**[4], **9**[5]**, 11a**[1], **13a-15a**[1]**, 20a-23a**,[1] **25a-28a**[1], **29a**[5], **31a**[5]**, 54a**[1] were synthesized according to previous literature.

Characterization of Substrates



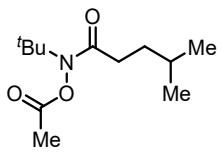
***N-bromo-N-(tert-butyl)-4-methylpentanamide (4)*:** To a flame-dried round bottom flask equipped with a stir bar was subsequently added carboxylic acid (1.0 equiv), DMAP (1.0 equiv), EDCI•HCl (1.2 equiv), and DCM (0.2 M). The solution was stirred at room temperature until all solid dissolved. *tert*-Butylamine (2.0 equiv) was added, and the reaction was stirred at room temperature for overnight. The reaction was quenched with 1.0 M aqueous HCl (30 mL) and extracted with DCM (3 x 50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated by rotary evaporation. The crude amide was used without further purification or purified by flash column chromatography on silica gel.

Follow a procedure described in the literature,[6] to a flame-dried round bottom flask equipped with a stir bar was added AgOAc (3.2 equiv) and CCl_4 or DCM, (0.2 M). The solution was stirred at 0 °C and wrapped with aluminum foil. Br_2 (3.0 equiv) was then added dropwise. After 20 minutes, the reaction mixture was gravity-filtrated into another flame-dried round bottom flask pre-loaded with an amide (1.0 equiv). The round-bottom flask was wrapped with aluminum foil and stirred at room temperature for 30 minutes. The reaction was concentrated by rotary evaporation. The crude was purified by sflash column chromatography on silica gel, providing bromoamide in 65% yield. The product should be stored in aluminum-wrapped containers.

^{1}H NMR (500 MHz, $CDCl_3$): δ2.60 – 2.55 (m, 2H), 1.59 – 1.55 (m, 1H), 1.51 – 1.48 (m, 2H), 1.47 (s, 9H), 0.91 (d, J = 6.6 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 178.1, 64.5, 36.2, 34.9, 29.8, 27.9, 22.6.

HRMS (EI): Calcd. for $C_{10}H_{20}BrNO$ $[M]^+$, 249.0723. Found: 249.0723.

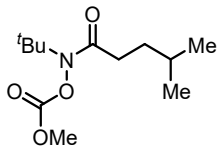


***N-acetoxy-N-(tert-butyl)-4-methylpentanamide (6)*:** Prepared according to **General Procedure A** from commercially available acetyl chloride. Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 20% EtOAc in Hexanes, 14 min). 72 % yield over three steps. Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.22 – 2.18 (m, 1H), 2.17 (s, 3H), 2.05 – 1.98 (m, 1H), 1.55 – 1.49 (m, 1H), 1.47 – 1.41 (m, 2H), 1.39 (s, 9H), 0.85 (d, *J* = 6.5 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 174.9, 169.7, 62.2, 33.0, 32.3, 27.7, 27.4, 22.5, 22.4, 18.3.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{12}H_{23}O_3NNa$ 252.1570; Found: 252.1572.

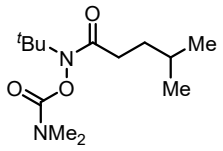


***N-(tert-butyl)-N-((methoxycarbonyl)oxy)-4-methylpentanamide (7)*:** Prepared according to **General Procedure A** from commercially available methyl chloroformate. Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 20% EtOAc in Hexanes, 14 min). 57 % yield over three steps. Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3H), 2.36 – 2.18 (m, 1H), 2.14 – 2.01 (m, 1H), 1.57 – 1.39 (m, 3H), 1.39 (s, 9H), 0.84 (d, J = 6.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 156.2, 63.1, 56.5, 32.8, 32.3, 27.7, 27.3, 22.5, 22.4.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. For $C_{12}H_{23}O_4NNa$ 268.1519; Found: 268.1521.

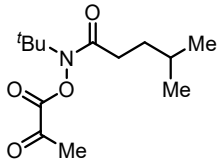


***N-(tert-butyl)-N-((dimethylcarbamoyl)oxy)-4-methylpentanamide (8)*:** Prepared according to **General Procedure A** from commercially available dimethylcarbamyl chloride. Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 20% EtOAc in Hexanes, 14 min). 56 % yield over three steps. Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.01 (s, 6H), 2.26 – 2.19 (m, 1H), 2.15 – 2.07 (m, 1H), 1.57 – 1.50 (m, 1H), 1.49 – 1.45 (m, 2H), 1.41 (s, 9H), 0.86 (d, J = 6.5 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ174.9, 155.5, 62.2, 37.7, 36.1, 33.2, 32.2, 27.8, 27.5, 22.6, 22.5.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{13}H_{26}O_3N_2Na$ 281.1836; Found: 281.1839.

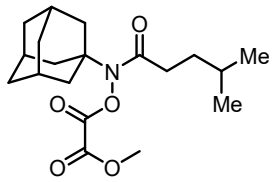


***N-(tert-butyl)-4-methyl-N-((2-oxopropanoyl)oxy)pentanamide (10)*:** Prepared according to **General Procedure A** from pyruvic acid chloride. Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 20% EtOAc in Hexanes, 14 min). 24 % yield over three steps. Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.55 (s, 3H), 2.28 – 2.16 (m, 1H), 2.09 – 1.99 (m, 1H), 1.57 – 1.44 (m, 3H), 1.42 (s, 9H), 0.85 (d, J = 6.3 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.0, 175.8, 160.4, 63.3, 32.8, 32.5, 27.7, 27.5, 27.4, 22.4.

HRMS (ESI) m/z: $[M+CH_3OH+Na]^+$ Calcd. for $C_{14}H_{27}O_5NNa$ 312.1781; Found: 312.1784.

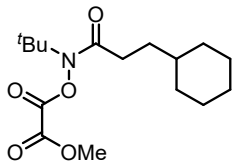


***Methyl 2-((N-((3s,5s,7s)-adamantan-1-yl)-4-methylpentanamido)oxy)-2-oxoacetate (12a)*:** Prepared according to **General Procedure A,** replacing *N*-(*tert*-Butyl)hydroxylamine hydrochloride with 1-(Hydroxylamino)adamantane hydrochloride.[7] *1*-(Hydroxylamino)adamantane hydrochloride was synthesized according to previous literature. [cite]Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 20% EtOAc in Hexanes, 14 min). 42 % yield over three steps. Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.97 (s, 3H), 2.29 – 2.20 (m, 1H), 2.20 – 2.13 (m, 6H), 2.10 – 2.07 (m, 4H), 1.69 – 1.60 (m, 6H), 1.55 – 1.49 (m, 1H), 1.47 – 1.42 (m, 2H), 0.84 (d, *J* = 6.5 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.3, 157.7, 157.1, 65.0, 54.2, 39.3, 36.2, 32.8, 32.7, 29.9, 27.6, 22.4.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{19}H_{29}O_5NNa$ 374.1938; Found: 374.1940.

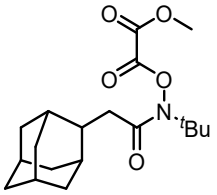


***Methyl 2-((N-(tert-butyl)-3-cyclohexylpropanamido)oxy)-2-oxoacetate (16a)*:** Prepared according to **General Procedure B** from commercially available cyclohexane propionic acid. Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 20% EtOAc in Hexanes, 14 min). 41 % yield over two steps. Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ3.96 (s, 3H), 2.31 – 2.19 (m, 1H), 2.16 – 2.04 (m, 1H), 1.69 – 1.55 (m, 5H), 1.47 – 1.42 (m, 2H), 1.41 (s, 9H), 1.22 – 1.07 (m, 4H), 0.88 – 0.78 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.1, 157.4, 157.0, 63.5, 54.1, 37.2, 33.1, 32.0, 31.3, 27.5, 26.6, 26.3.

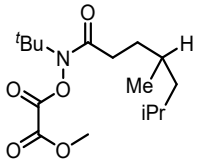
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{16}H_{27}O_5NNa$ 336.1781; Found: 336.1783.



***Methyl 2-((2-((1R,2S,5S)-adamantan-2-yl)-N-(tert-butyl)acetamido)oxy)-2-oxoacetate (17a)*:** Prepared according to **General Procedure B** from commercially available 2-(adamantan-2-yl)acetic acid. Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 20% EtOAc in Hexanes, 14 min). 42 % yield over three steps. Colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.98 (s, 3H), 2.45 – 2.32 (m, 1H), 2.30 – 2.21 (m, 2H), 1.89 – 1.84 (m, 1H), 1.82 – 1.63 (m, 11H), 1.53 (d, J = 12.6 Hz, 2H), 1.43 (d, J = 1.2 Hz, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.5, 157.6, 157.2, 63.6, 54.2, 39.9, 39.1, 38.3, 37.7, 32.3, 31.9, 28.0, 27.6.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{19}H_{29}O_5NNa$ 374.1938; Found: 374.1938.

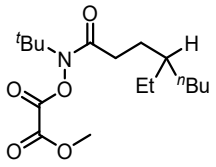


***Methyl 2-((N-(tert-butyl)-4,6-dimethylheptanamido)oxy)-2-oxoacetate (18a)*:** Prepared according to **General Procedure B** from 4,6-dimethylheptanoic acid. 4,6-dimethylheptanoic acid was synthesized according to previous literature.[8] Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 20% EtOAc in Hexanes, 14 min). 43 % yield over three steps. Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.97 (s, 3H), 2.34 – 2.19 (m, 1H), 2.17 – 1.99 (m, 1H), 1.66 – 1.52 (m, 2H), 1.49 – 1.43 (m, 1H), 1.43 (s, 9H), 1.39 – 1.30 (m, 1H), 1.09 – 1.03 (m, 1H), 1.01 – 0.94 (m, 1H), 0.88 – 0.82 (m, 3H), 0.82 – 0.79 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.1, 157.5, 157.1, 63.5, 54.2, 46.6, 32.3, 31.3, 30.0, 27.5, 25.3, 23.4, 22.4, 19.6.

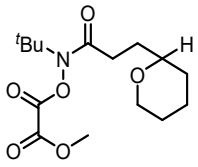
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{16}H_{29}O_5NNa$ 338.1938; Found: 338.1940.



***Methyl 2-((N-(tert-butyl)-4-ethyloctanamido)oxy)-2-oxoacetate (19a)*:** Prepared according to **General Procedure B** from commercially available 4-ethyloctanoic acid. Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 20% EtOAc in Hexanes, 14 min). 43 % yield over three steps. Colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.97 (s, 3H), 2.28 – 2.17 (m, 1H), 2.12 – 2.00 (m, 1H), 1.55 – 1.47 (m, 2H), 1.43 (s, 9H), 1.29 – 1.13 (m, 9H), 0.86 (t, J = 7.0 Hz, 3H), 0.82 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.2, 157.5, 157.1, 63.5, 54.2, 38.44 32.7, 32.1, 28.9, 27.5, 27.4, 25.8, 23.2, 14.2, 10.8.

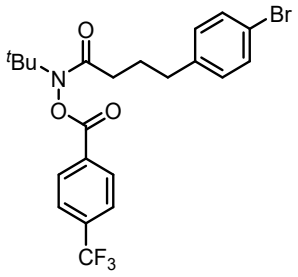
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{31}O_5NNa$ 352.2074; Found: 352.2096.



***Methyl 2-((N-(tert-butyl)-3-(tetrahydro-2H-pyran-2-yl)propanamido)oxy)-2-oxoacetate (24a)*:** Prepared according to **General Procedure B** from 3-(tetrahydropyran-2-yl)propionic acid. 3-(tetrahydropyran-2-yl)propionic acid was synthesized according to previous literature.[9] Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 20% EtOAc in Hexanes, 14 min). 35 % yield over three steps. Colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.96 (s, 3H), 3.92 – 3.85 (m, 1H), 3.41 – 3.30 (m, 1H), 3.25 – 3.15 (m, 1H), 2.50 – 2.34 (m, 1H), 2.28 – 2.13 (m, 1H), 1.81 – 1.71 (m, 2H), 1.69 – 1.59 (m, 1H), 1.58 – 1.52 (m, 1H), 1.51 – 1.44 (m, 3H), 1.43 (s, 9H), 1.27 – 1.17 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.8, 157.3, 156.9, 76.7, 68.5, 63.6, 54.2, 32.1, 30.6, 30.4, 27.5, 26.2, 23.6.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{15}H_{25}O_6NNa$ 338.1574; Found: 338.1577.



***4-(4-bromophenyl)-N-(tert-butyl)-N-((4-(trifluoromethyl)benzoyl)oxy)butanamide (30a)*:** Modifying from **General Procedure B**. To a solution of 4-bromobenzenebutanoic acid (1.0 equiv) and 3-5 drops of anhydrous DMF in anhydrous CH_2Cl_2 (0.5 M) at 0 ℃ was added oxalyl chloride (2.0 equiv) dropwise over 15 minutes. The reaction was stirred vigorously at room temperature for 4 hours. The solvent was removed in *vacuo*. The resulting acyl chloride was redissolved in anhydrous THF (1-2 mL) and used directly for the next step without further purification.

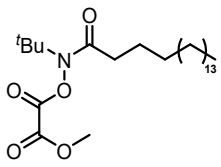
To a solution of *N*-(*tert*-Butyl)hydroxylamine hydrochloride (1.0 equiv) in anhydrous THF (0.4 M) at 0 ℃ was added DIPEA (2.0 equiv) slowly. The mixture was stirred for 10 minutes at the same temperature. Then, acyl chloride (1.0 equiv) in anhydrous THF was added dropwise over 20 minutes. The reaction mixture was allowed to warm to room temperature overnight. The solvent was removed in *vacuo*. The mixture was diluted with saturated $NaHCO_3$ and EtOAc. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with 1.0 M HCl, saturated $NaHCO_3$, and brine. The crude was then concentrated under reduce pressure. The intermediate was used directly for the next step or simply purified by flash column chromatography on silica gel.

To a solution of hydroxylamine intermediate (1.0 equiv) in anhydrous CH_2Cl_2 (0.4 M) at 0 ℃, Et_3N (2.0 equiv) was added dropwise. Then 4-trifluoromethyl-benzoyl chloride (1.5 equiv) was added dropwise over 10 minutes. The reaction was stirred vigorously at room temperature for 4 hours. The mixture was diluted with saturated $NaHCO_3$ and DCM. The layers were separated. The aqueous layer was extracted with DCM. The combined organic layers were washed with 1.0 M HCl, saturated $NaHCO_3$, and brine. The crude was then concentrated under reduce pressure. Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 30% EtOAc in Hexanes, 14 min). 56 % yield over three steps. Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 8.1 Hz, 2H), 7.80 (d, J = 8.3 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.00 – 6.90 (m, 2H), 2.61 – 2.51 (m, 2H), 2.29 – 2.21 (m, 1H), 2.14 – 2.04 (m, 1H), 1.94 – 1.84 (m, 2H), 1.48 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.2, 164.6, 140.7, 136.0 (q, J = 33.0 Hz), 131. 4, 130.5, 130.3, 130.1, 126.2 (q, J = 3.7 Hz), 123.5 (q, J = 273.0 Hz), 119.7, 63.07, 34.5, 33.3, 27.6, 25.6.

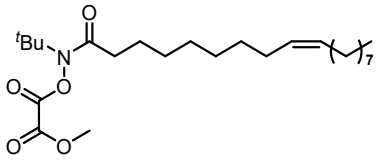
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{23}O_3NBrF_3Na$ 510.0688; Found: 508.0706.



***Methyl 2-((N-(tert-butyl)stearamido)oxy)-2-oxoacetate (32a)*:** Prepared according to **General Procedure B** from commercially available stearic acid. Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 20% EtOAc in Hexanes, 14 min). 52 % yield over three steps. Colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.97 (s, 3H), 2.33 – 2.15 (m, 1H), 2.11 – 2.02 (m, 1H), 1.59 – 1.53 (m, 2H), 1.43 (s, 9H), 1.30 – 1.13 (m, 28H), 0.87 (d, *J* = 7.2Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 157.4, 157.1, 63.5, 54.2, 34.5, 32.1, 29.8, 29.8, 29.8, 29.7, 29.6, 29.6, 29.5, 29.2, 27.5, 24.0, 22.8, 14.3.

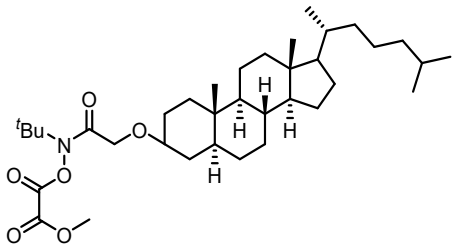
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{47}O_5NNa$ 464.3346; Found: 464.3347.



***Methyl 2-((N-(tert-butyl)oleamido)oxy)-2-oxoacetate (33a)*:** Prepared according to **General Procedure B** from commercially available oleic acid. Purification by flash column chromatography(Biotage, Snap Ultra 25g, 5% to 20% EtOAc in Hexanes, 14 min). 42 % yield over three steps. Colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.39 – 5.24 (m, 2H), 3.98 (s, 3H), 2.35 – 2.21 (m, 1H), 2.14 – 2.04 (m, 1H), 2.04 – 1.94 (m, 4H), 1.59 – 1.53 (m, 2H), 1.43 (s, 9H), 1.34 – 1.20 (m, 20H), 0.87 (t, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 157.4, 157.1, 130.1, 129.9, 63.5, 54.2, 34.5, 32.0, 29.9, 29.8, 29.7, 29.5, 29.3, 29.2, 27.5, 27.4, 27.3, 24.0, 22.8, 14.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{45}O_5NNa$ 462.3190; Found: 462.3191.

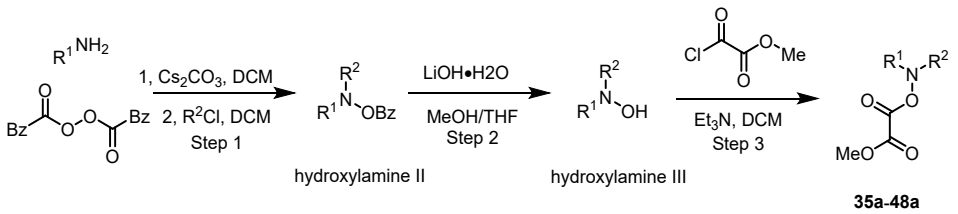


***Methyl 2-((N-(tert-butyl)-2-(((5S,8R,9S,10S,13R,14S)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)acetamido)oxy)-2-oxoacetate (34a)*:** Prepared according to **General Procedure B** from *O*-acetic acid-dihydrocholesterol. O-acetic acid-dihydrocholesterol was synthesized according to previous literature.[10] Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 30% EtOAc in Hexanes, 14 min). 47 % yield over three steps. White solid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.03 (s, 2H), 3.96 (s, 3H), 3.33 – 3.23 (m, 1H), 1.94 (dt, J = 12.7, 3.5 Hz, 1H), 1.86 – 1.74 (m, 2H), 1.71 – 1.47 (m, 6H), 1.44 (s, 9H), 1.37 – 0.91 (m, 21H), 0.88 (d, J = 6.4 Hz, 3H), 0.84 (d, J = 6.7, 1.7 Hz, 6H), 0.76 (s, 3H), 0.62 (s, 3H), 0.60 – 0.54 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.8, 157.0, 156.8, 79.6, 67.8, 63.9, 56.6, 56.5, 54.5, 54.2, 44.8, 42.7, 40.1, 39.6, 37.0, 36.3, 35.9, 35.8, 35.6, 34.2, 32.2, 28.9, 28.4, 28.1, 27.8, 27.11, 24.31, 23.93, 22.9, 22.7, 21.3, 18.8, 12.4, 12.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{36}H_{62}O_6N$ 604.4572; Found: 604.4572.

General procedure C:



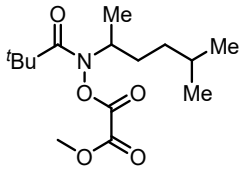
Starting materials were prepared from corresponding acyl chloride or carboxylic acid on a 2-4 mmol scale. The yields have not been optimized.

Following a procedure described in the literature:[10]

Step 1: To a round-bottom flask equipped with a magnetic bar was added BPO (wetted with ca. 25% H_2O) (2.0 equiv), Cs_2CO_3 (3.0 equiv), and DCM (0.1). The heterogeneous mixture was stirred for 2 h at room temperature. After that, a solution of amine (1.0 equiv) in DCM (0.25 M) was then added, and the mixture was vigorously stirred for 14 h. Then, a solution of BzCl (2.0 equiv) in DCM (0.5 M) was added. The reaction was allowed to stir for another 6 h. After the reaction completion as monitored by TLC, water was added. The reaction mixture was stirred for 15 min, extracted with DCM, washed with sat. $NaHCO_3$ solution, brine, and concentrated under reduce pressure. The crude product was purified by silica gel column chromatography using petroleum ether/ EtOAc as eluent, affording hydroxylamine II.

Step 2: To a stirred solution of the hydroxylamine II (1.0 equiv) in MeOH (0.5 M) and THF (1.0 M) was added $LiOH.H_2O$ (3.0 equiv). After the reaction completion as monitored by TLC (0.5-1 h), the reaction mixture was concentrated under reduced pressure. Water was then added. The product was extracted with EtOAc, washed with brine, concentrated under reduced pressure, and purified by silica gel column chromatography using petroleum ether/ EtOAc as eluent to give hydroxylamine III.

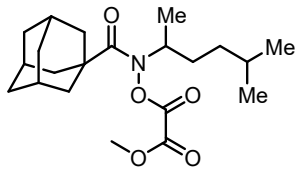
Step 3: To a solution of the hydroxylamine III (1.0 equiv) in anhydrous CH_2Cl_2 (0.35 M) at 0 ˚C was added Et_3N (1.5 equiv) dropwise. 4-Trifluoromethyl-benzoyl chloride (for **1y**, using 4-methylpentanoyl chloride generated from step 1 of General Procedure A) (1.0 equiv) was then added dropwise over 5 minutes. The reaction was vigorously stirred at room temperature for 2 h. The reaction mixture was then concentrated under reduce pressure. The resulting residue was added saturated $NaHCO_3$ and THF and stirred for 30 minutes. The aqueous layer was extracted with EtOAc, successively washed with 1.0 M HCl, saturated $NaHCO_3$, and brine. The crude product was concentrated and purified by column chromatography on silica gel with petroleum ether/ EtOAc as eluent to give **35a**-**48a**.



***Methyl 2-((N-(5-methylhexan-2-yl)pivalamido)oxy)-2-oxoacetate (35a)*:** Prepared according to **General Procedure C** from commercially available 2-amino-5-methylhexane and trimethyl acetyl chloride. Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 20% EtOAc in Hexanes, 14 min). 56 % yield over three steps. Colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.38 (q, *J* = 6.9 Hz, 1H), 3.96 (s, 3H), 1.66 – 1.58 (m, 1H), 1.53 – 1.41 (m, 2H), 1.23 (s, 9H), 1.21 (d, *J* = 6.7 Hz, 3H), 1.20 – 1.14 (m, 1H), 0.86 (d, J = 6.6 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.8, 157.1, 156.3, 58.7, 54.1, 39.8, 35.7, 31.8, 28.1, 27.6, 22.7, 22.6, 17.8.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{15}H_{27}O_5NNa$ 324.1781; Found: 324.1784.

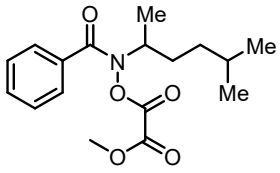


***Mthyl 2-(((3r,5r,7r)-N-(5-methylhexan-2-yl)adamantane-1-carboxamido)oxy)-2-oxoacetate (36a)*:** Prepared according to **General Procedure C** from commercially available 2-amino-5-methylhexane and 1-adamantanecarbonyl chloride. Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 20% EtOAc in Hexanes, 14 min). 42 % yield over three steps. Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.39 (q, *J* = 6.9 Hz, 1H), 3.96 (s, 3H), 2.06 – 2.02 (m, 3H), 1.98 – 1.93 (m, 6H), 1.75 – 1.67 (m, 6H), 1.66 – 1.59 (m, 1H), 1.54 – 1.46 (m, 2H), 1.30 – 1.15 (m, 2H), 1.22 (d, J = 6.6 Hz, 3H), 0.87 (d, J = 6.6, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.2, 157.2, 156.3, 59.1, 54.0, 42.7, 38.5, 36.6, 35.6, 31.9, 28.3, 28.1, 22.7, 22.6, 18.1.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{21}H_{33}O_5NNa$ 402.2251; Found: 402.2249.



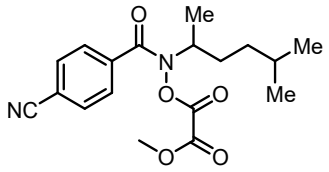
***Methyl 2-((N-(5-methylhexan-2-yl)benzamido)oxy)-2-oxoacetate (37a)*:** Prepared according to **General Procedure C** from commercially available 2-amino-5-methylhexane and benzoyl

chloride. Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 30% EtOAc in Hexanes, 14 min). 57 % yield over three steps. Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.37 (m, 5H), 4.30 – 4.17 (m, 1H), 3.93 (s, 3H), 1.81 – 1.66 (m, 1H), 1.49 – 1.41 (m, 2H), 1.32 – 1.28 (m, 1H), 1.24 (d, J = 6.6 Hz, 3H), 1.17 – 1.08 (m, 1H), 0.84 (dd, J = 6.6, 3.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 156.6, 155.3, 133.5, 131.5, 128.7, 127.9, 58.7, 54.0, 35.3, 31.8, 27.8, 22.5, 22.5, 18.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{23}O_5NNa$ 344.1468; Found: 344.1468.

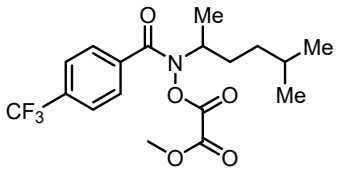


***Methyl 2-((4-cyano-N-(5-methylhexan-2-yl)benzamido)oxy)-2-oxoacetate (38a)*:** Prepared according to **General Procedure C** from commercially available 2-amino-5-methylhexane and 4-cyanobenzoyl chloride. Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 30% EtOAc in Hexanes, 14 min). 46 % yield over three steps. White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 1.8 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 4.29 – 4.22 (m, 1H), 3.93 (s, 3H), 1.74 – 1.65 (m, 1H), 1.52 – 1.42 (m, 2H), 1.34 – 1.22 (m, 1H), 1.25 (d, J = 6.6 Hz, 3H), 1.17 – 1.08 (m, 1H), 0.85 (dd, J = 6.6, 2.7 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 156.2, 155.3, 137.7, 132.5, 128.5, 117.9, 115.1, 58.2, 54.2, 35.4, 31.7, 27.8, 22.5, 22.5, 18.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{22}O_5N_2Na$ 369.1421; Found: 369.1422.

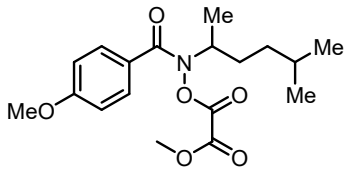


***Methyl 2-((N-(5-methylhexan-2-yl)-4-(trifluoromethyl)benzamido)oxy)-2-oxoacetate (39a)*:** Prepared according to **General Procedure C** from commercially available 2-amino-5-methylhexane and *p*-trifluoromethylbenzoyl chloride. Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 30% EtOAc in Hexanes, 14 min). 68 % yield over three steps. Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ7.75 – 7.56 (m, 4H), 4.27 – 4.17 (m, 1H), 3.90 (s, 3H), 1.77 – 1.66 (m, 1H), 1.49 – 1.39 (m, 2H), 1.33 – 1.26 (m, 1H), 1.24 (d, *J* = 6.7 Hz, 3H), 1.14 – 1.09 (m, 1H), 0.83 (dd, *J* = 6.6, 3.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 156.3, 155.2, 137.0, 133.1 (q, *J* = 32.8 Hz), 128.3, 125.7 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 272.6 Hz), 58.5, 54.1, 35.3, 31.7, 27.8, 22.4, 22.4, 18.2.

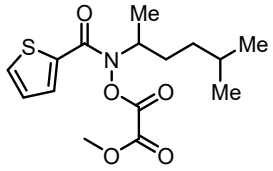
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{22}O_5NF_3Na$ 412.1342; Found: 412.1345.



***Methyl 2-((4-methoxy-N-(5-methylhexan-2-yl)benzamido)oxy)-2-oxoacetate (40a)*:** Prepared according to **General Procedure C** from commercially available 2-amino-5-methylhexane and 4-methoxybenzoyl chloride. Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 30% EtOAc in Hexanes, 14 min). 32 % yield over three steps. White solid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 2H), 6.97 – 6.89 (m, 2H), 4.31 – 4.21 (m, 1H), 3.94 (s, 3H), 3.85 (s, 3H), 1.78 – 1.67 (m, 1H), 1.50 – 1.42 (m, 2H), 1.36 – 1.26 (m, 1H), 1.25 (d, *J* = 6.6 Hz, 3H), 1.20 – 1.11 (m, 1H), 0.85 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 162.4, 156.8, 155.4, 130.3, 125.4, 114.1, 59.2, 55.6, 54.0, 35.4, 31.8, 27.9, 22.6, 22.5, 18.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{25}O_6NNa$ 374.1721; Found: 374.1722.

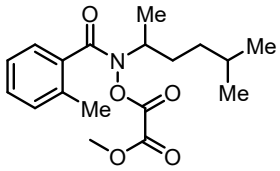


***Methyl 2-((N-(5-methylhexan-2-yl)thiophene-2-carboxamido)oxy)-2-oxoacetate (41a)*:** Prepared according to **General Procedure C** from commercially available 2-amino-5-methylhexane and 2-thiophenecarbonyl chloride. Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 30% EtOAc in Hexanes, 14 min). 25 % yield over three steps. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.55 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.08 (dd, *J* = 5.0, 3.8 Hz, 1H), 4.70 – 4.63 (m, 1H), 3.98 (s, 3H), 1.78 – 1.69 (m, 1H), 1.56 – 1.46 (m, 2H), 1.36 – 1.18 (m, 2H), 1.28 (d, *J* = 6.7 Hz, 3H),0.87 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.7, 156.6, 156.1, 134.4, 132.6, 131.8, 127. 6, 58.4, 54.3, 35.5, 31.8, 28.0, 22.6, 22.6, 18.0.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{15}H_{21}O_5NSNa$ 350.1029; Found: 350.1029.

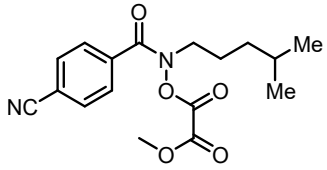


***Methyl 2-((2-methyl-N-(5-methylhexan-2-yl)benzamido)oxy)-2-oxoacetate (42a)*:** Prepared according to **General Procedure C** from commercially available 2-amino-5-methylhexane and 2-methylbenzoyl chloride. Purification by flash column chromatography (Biotage, Snap Ultra 25g, 10% to 20 % EtOAc in Hexanes, 14 min). 45 % yield over three steps. Light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.29 – 7.20 (m, 2H), 4.18 – 3.90 (m, 1H), 3.95 (s, 3H), 2.45 (s, 3H), 1.72 – 1.58 (m, 1H), 1.52 – 1.40 (m, 2H), 1.35 – 1.28 (m, 1H), 1.26 (d, J = 6.7 Hz, 3H), 1.17 – 1.07 (m, 1H), 0.87 (dd, J = 6.6, 4.3 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 156.5, 155.3, 136.0, 133.5, 131.0, 130.2, 127.0, 125.8, 57.9, 54.0, 35.5, 31.8, 27.9, 22.5, 22.5, 19.3, 18.4.

HRMS (APCI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{26}O_5N$ 336.1805; Found: 336.1806.

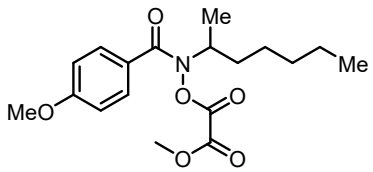


***Methyl 2-((4-cyano-N-(4-methylpentyl)benzamido)oxy)-2-oxoacetate (43a)*:** Prepared according to **General Procedure C** from commercially available 4-methylpentylamine and 4-cyanobenzoyl chloride. Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 30% EtOAc in Hexanes, 14 min). 47 % yield over three steps. White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.64 (m, 4H), 3.91 (s, 3H), 3.76 (t, J = 7.4 Hz, 2H), 1.75 – 1.63 (m, 2H), 1.60 – 1.45 (m, 1H), 1.28 – 1.18 (m, 2H), 0.88 (d, J = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 155.9, 155.4, 137.1, 132.4, 128.7, 117.9, 115.3, 54.4, 51.1, 35.6, 27.8, 25.0, 22.5.

HRMS (APCI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{21}O_5N_2$ 333.1445; Found: 333.1445.

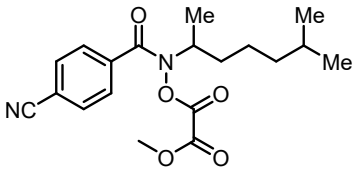


***Methyl 2-((N-(heptan-2-yl)-4-methoxybenzamido)oxy)-2-oxoacetate (44a)*:** Prepared according to **General Procedure C** from commercially available (±)-2-aminoheptane and 4-methoxybenzoyl chloride. Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 30% EtOAc in Hexanes, 14 min). 35 % yield over three steps. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.55 (m, 2H), 6.97 – 6.83 (m, 2H), 4.34 – 4.26 (m, 1H), 3.94 (s, 3H), 3.84 (s, 3H), 1.78 – 1.71 (m, 1H), 1.47 – 1.34 (m, 2H), 1.31 – 1.16 (m, 5H), 1.24 (d, J = 6.7 Hz, 3H), 0.85 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3, 162.4, 156.7, 155.4, 130.2, 125.4, 114.0, 58.9, 55.5, 54.0, 34.0, 31.6, 26.0, 22.5, 18.1, 14.1.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{25}O_6NNa$ 374.1574; Found: 374.1576.

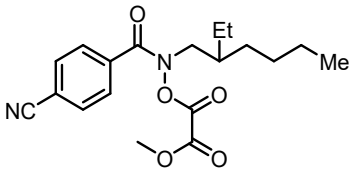


***Methyl 2-((4-cyano-N-(6-methylheptan-2-yl)benzamido)oxy)-2-oxoacetate (45a)*:** Prepared according to General **Procedure C** from commercially available 2-amino-6-methylheptane and 4-cyanobenzoyl chloride. Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 30% EtOAc in Hexanes, 14 min). 45 % yield over three steps. White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 2H), 4.34 – 4.23 (m, 1H), 3.92 (s, 3H), 1.75 – 1.63 (m, 1H), 1.53 – 1.30 (m, 3H), 1.28 – 1.18 (m, 1H), 1.24 (d, J = 6.6 Hz, 3H) 1.13 – 1.07 (m, 2H), 0.83 (d, J = 6.6Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.8, 156.1, 155.3, 137.7, 132.5, 128.5, 117.8, 115.1, 57.9, 54.9, 38.5, 34.0, 27.8, 24.1, 22.6, 22.5, 18.1.

HRMS (APCI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{25}O_5N_2$ 361.1758; Found: 361.1758.

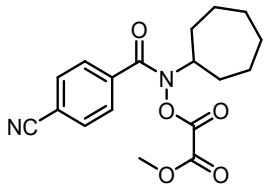


***Methyl 2-((4-cyano-N-(2-ethylhexyl)benzamido)oxy)-2-oxoacetate (46a)*:** Prepared according to **General Procedure C** from commercially available 2-ethylhexylamine and 4-cyanobenzoyl chloride. Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 30% EtOAc in Hexanes, 14 min). 52 % yield over three steps. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.58 (m, 4H), 3.89 (s, 3H), 3.71 (d, *J* = 7.0 Hz, 2H), 1.77 – 1.69 (m, 1H), 1.49 – 1.17 (m, 8H), 0.86 (dt, *J* = 9.1, 7.3 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 155.8, 155.41 137.1, 132.3, 128.7, 117.9, 115.1, 54.3, 53.81, 37.4, 30.4, 28.5, 23.8, 23.0, 14.1, 10.5.

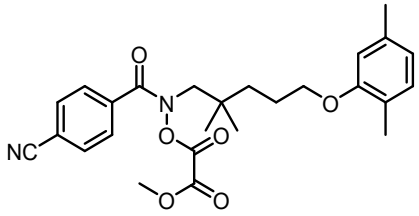
HRMS (APCI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{25}O_5N_2$ 361.1758; Found: 361.1761.



***Methyl 2-((4-cyano-N-cycloheptylbenzamido)oxy)-2-oxoacetate (47a)*:** Prepared according to **General Procedure C** from commercially available cycloheptanamine and 4-cyanobenzoyl chloride. Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 30% EtOAc in Hexanes, 14 min). 35 % yield over three steps. White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.64 (m, 4H), 4.29 – 4.25 (m, 1H), 3.92 (s, 3H), 2.04 – 1.90 (m, 2H), 1.86 – 1.78 (m, 2H), 1.75 – 1.67 (m, 2H), 1.56 – 1.47 (m, 4H), 1.43 – 1.35 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 156.2, 155.4, 137.7, 132.5, 128.4, 117.9, 115.1, 62.9, 54.3, 32.1, 28.0, 24.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{21}N_2O_5$ 345.1442; Found: 345.1443.

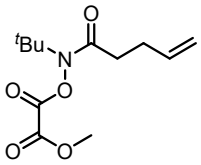


***Methyl 2-((4-cyano-N-(2,2-dimethyl-5-(2,4,5-trimethylphenoxy)pentyl)benzamido)oxy)-2-oxoacetate (48a)*:** Prepared according to **General Procedure C** from 5-(2,5-Dimethylphenoxy)-2,2-dimethyl-1-pentanamine and 4-cyanobenzoyl chloride. 5-(2,5-Dimethylphenoxy)-2,2-dimethyl-1-pentanamine were synthesized according to previous literature.[11] Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 30% EtOAc in Hexanes, 14 min). 58 % yield over three steps. White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 4H), 7.00 (d, J = 7.4 Hz, 1H), 6.66 (d, J = 7.5 Hz, 1H), 6.62 (d, J = 1.5 Hz, 1H), 3.93 (t, J = 6.3 Hz, 2H), 3.83 (s, 3H), 3.75 – 3.67 (m, 2H), 2.30 (s, 3H), 2.16 (s, 3H), 1.84 – 1.75 (m, 2H), 1.58 – 1.45 (m, 2H), 1.06 (s, 6H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 157.0, 155.8, 155.7, 136.9, 136.6, 132.2, 130.4, 128.9, 123.6, 120.9, 118.0, 115.1, 112.1, 68.3, 59.3, 54.4, 36.6, 35.5, 25.6, 24.3, 21.5, 15.9.

HRMS (APCI) m/z: $[M+H]^+$ Calcd. for $C_{26}H_{31}O_6N_2$ 467.2177; Found: 467.2178.



***Methyl 2-((N-(tert-butyl)pent-4-enamido)oxy)-2-oxoacetate (53a)*:** Prepared according to **General Procedure B** from commercially available4-Pentenoic acid. Purification by flash column chromatography (Biotage, Snap Ultra 25g, 5% to 20% EtOAc in Hexanes, 14 min). 57 % yield over three steps. Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86 – 5.72 (m, 1H), 5.11 – 4.89 (m, 2H), 2.46 – 2.12 (m, 4H), 1.44 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ174.9, 157.4, 157.0, 137.0, 115.5, 63.7, 54.2, 33.7, 28.0, 27.5.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{12}H_{19}NO_5Na$ 280.1155; Found: 280.1156.

3. Additional Optimization Studies

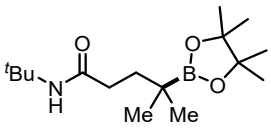
1 **11**

Entry	deviations	yield (%)[b]
1	None	98
2	MeCN	n.d.
3	THF	n.d.
4	DCM	n.d.
5	EtOAc	n.d.
6	3.0 equiv. of $B_2(cat)_2$ at 60 °C (no light)	n.d.
7	0.25 M DMF, 5 h	25
8	0.25 M DMF, 10 h	45
9	0.25 M DMF, 16 h	65
10	0.25 M DMF, 32 h	62

[a] Performed with 0.1 mmol scale (0.1 mmol **1**) in 0.05 M solvent. [b] Yields were determined using ^{1}H NMR analysis with 1,3,5-trimethoxybenzene (Ar–H) as internal standard.

4. C(sp^3)-H bonds Borylation

General procedure D: To a flame-dried reaction tube equipped with a stir bar was charged B_2cat_2 (3.0 equiv.). The tube was capped with a rubber septum. After the tube was evacuated and backfilled with nitrogen 5 times, O-oxalate hydroxamic esters (0.1 mmol, 1.0 equiv.) and DMF (0.05 M or 0.025 M) were added via a syringe. The resultant reaction mixture was stirred under Blue LED (45 W, 440 nm) irradiation for 24 - 48 h. After the reaction was complete as monitored by TLC, a solution of pinacol (2.0 equiv. based on B_2cat_2) in Et_3N (1.0 mL) was added via a syringe. The mixture was stirred for an additional 1 h at room temperature. After that, the reaction mixture was partitioned between EtOAc and water. The organic layer was collected, washed with an aqueous solution of NH_4Cl, dried over $MgSO_4$, and concentrated under reduced pressure. The resulting reaction mixture was purified via flash chromatography on silica gel with an appropriate gradient of eluent to give the desired product.

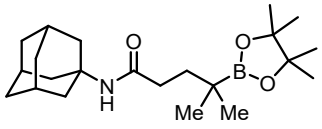


***N-(tert-butyl)-4-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide* (11):** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes , 14 min). 29 mg, 98 % yield. White solid.

^{1}H NMR: (500 MHz, $CDCl_3$) δ 5.30 (s, 1H), 2.17–1.93 (m, 2H), 1.63–1.50 (m, 2H), 1.34 (s, 9H), 1.23 (s, 12H), 0.93 (s, 6H).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 173.3, 83.2, 51.1, 36.9, 35.2, 29.9, 29.0, 24.9, 24.7. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{33}BNO_3$ 298.2548; Found: 298.2549.

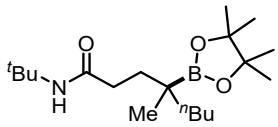


***N-((3s,5s,7s)-adamantan-1-yl)-4-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide* (12):** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes , 14 min). 22 mg, 57 % yield. White solid.

^{1}H NMR: (500 MHz, $CDCl_3$) δ 5.16 (s, 1H), 2.08 – 2.04 (m, 5H), 2.01 – 1.97 (m, 6H), 1.68 – 1.66 (m, 6H), 1.59 – 1.54 (m, 2H), 1.23 (s, 12H), 0.92 (s, 6H).

^{13}C NMR: (126 MHz, $CDCl_3$) δ173.2, 83.2, 51.8, 41.9, 36.9, 36.6, 35.4, 29.6, 24.9, 24.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{39}O_3NB$ 376.3018; Found: 376.3021.

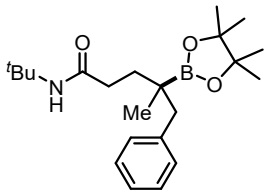


***N-(tert-butyl)-4-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octanamide* (13):** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes, 14 min). 24 mg, 70 % yield. White solid.

^{1}H NMR: (500 MHz, $CDCl_3$) δ 5.29 (s, 1H), 2.11–2.00 (m, 2H), 1.72–1.66 (m, 1H), 1.54–1.45 (m, 1H), 1.34 (s, 9H), 1.30–1.16 (m, 6H), 1.23(s, 12H), 0.89 (s, 3H), 0.87 (t, J = 7.2 Hz, 3H).

^{13}C NMR: (101 MHz, $CDCl_3$) δ 173.5, 83.2, 51.1, 38.8, 34.9, 34.7, 29.0, 28.1, 25.0, 23.7, 21.5, 14.3. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{39}BNO_3$ 340.3018; Found: 340.3018.

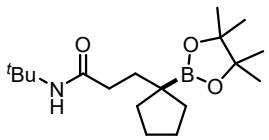


***N-(tert-butyl)-4-methyl-5-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (14)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes , 14 min). 20 mg, 53 % yield. White solid.

^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.25–7.15 (m, 5H), 5.27 (s, 1H), 2.74 (d, J = 13.1 Hz, 1H), 2.55 (d, J = 13.1 Hz, 1H), 2.18–2.08 (m, 2H), 1.80–1.71 (m, 1H), 1.56–1.51 (m, 1H), 1.33 (s, 9H), 1.21 (d, J = 13.2 Hz, 12H), 0.91 (s, 3H).

^{13}C NMR: (126MHz, $CDCl_3$) δ 173.2, 139.8, 130.5, 127.9, 126.0, 83.5, 51.1, 44.7, 35.0, 34.8, 29.0, 25.2, 25.0, 21.5. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{37}BNO_3$ 374.2861; Found: 374.2860.

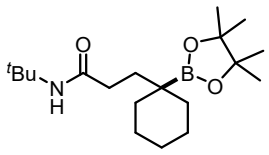


***N-(tert-butyl)-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl)propanamide (15)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes , 14 min). 22 mg, 67 % yield. White solid.

^{1}H NMR: (500 MHz, $CDCl_3$) δ 5.34 (s, 1H), 2.11–2.03 (m, 2H), 1.82–1.73 (m, 2H), 1.68–1.58 (m, 6H), 1.58 – 1.49 (m, 2H), 1.34 (s, 9H), 1.23 (s, 12H).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 173.3, 83.2, 51.1, 36.7, 35.3, 34.6, 29.0, 25.4, 24.9. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{35}BNO_3$ 324.2705; Found: 324.2706.

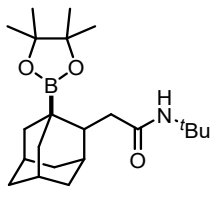


***N-(tert-Butyl)-4-methyl-4-(4-(methylsulfonyl)phenyl)pentanamide (16)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes , 14 min). 17 mg, 52 % yield. White solid.

^{1}H NMR: (600 MHz, $CDCl_3$) δ 5.22 (s, 1H), 2.09–2.02 (m, 2H), 1.86–1.82 (m, 2H), 1.66–1.53 (m, 6H), 1.33 (s, 9H), 1.29–1.27 (m, 1H), 1.25 (s, 12H), 1.18–1.11(m, 1H), 0.96–0.90 (m, 2H).

^{13}C NMR: (151 MHz, $CDCl_3$) δ 173.2, 83.2, 51.1, 36.4, 35.0, 34.4, 29.0, 26.7, 25.2, 25.0. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{37}BNO_3$ 338.2861; Found: 338.2864.



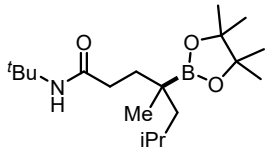
17, 81%

***N-(tert-butyl)-2-((1S,2S,5S)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)adamantan-2-yl)acetamide (17)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes , 14 min). 30 mg, 81 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) 5.55 (s, 1H), 2.29 (dd, *J* = 13.3, 10.7 Hz, 1H), 2.15 (d, *J* = 11.1 Hz, 1H), 2.07 (dd, *J* = 13.3, 2.8 Hz, 1H), 1.94 – 1.70 (m, 11H), 1.63 (d, *J* = 10.6 Hz, 1H), 1.55 (dd, *J* = 12.9, 2.7 Hz, 1H), 1.34 (s, 9H), 1.22 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.1, 83.1, 51.0, 43.2, 41. 6, 40.1, 38.9, 38.1, 32.5, 31.5, 29.9, 29.1, 27.3, 27.2, 25.0, 24.8. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{39}BNO_3$ 376.3018; Found: 376.3020.

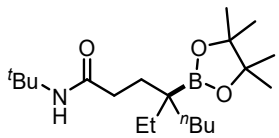


***N-(tert-butyl)-4,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptanamide (18)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes, 14 min). 25 mg, 74 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ5.27 (s, 1H), 2.11 – 2.01 (m, 2H), 1.71 – 1.61 (m, 2H), 1.54 – 1.47 (m, 1H), 1.33 (s, 9H), 1.33 – 1.29 (m, 1H), 1.23 (s, 12H), 1.17 (dd, *J* = 13.6, 6.4 Hz, 1H), 0.90 (s, 3H), 0.89 – 0.86 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.5, 83.3, 51.1, 48.0, 35.4, 34.2, 29.0, 25.7, 25.1, 25.1, 24.5, 24.2, 21.9. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{39}BNO_3$ 340.3018; Found: 340.3019.

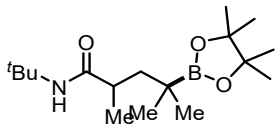


***N-(tert-butyl)-4-ethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octanamide (19)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes, 14 min). 18 mg, 51 % yield. White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.29 (s, 1H), 2.06 – 1.94 (m, 2H), 1.67 – 1.61 (m, 2H), 1.34 (s, 9H), 1.41 – 1.13 (m, 8H), 1.23 (s, 12H), 0.88 (t, *J* = 7.1 Hz, 3H), 0.81 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6, 83.2, 51.1, 34.0, 33.8, 29.9, 29.0, 27.1, 26.9, 25.1, 23.8, 14.3, 9.3. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for : $C_{20}H_{41}BNO_3$ 354.3174; Found: 354.3173.

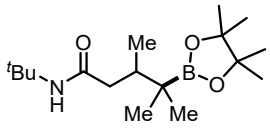


***N-(tert-butyl)-2,4-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (20)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes, 14 min). 16 mg, 51 % yield. White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.57 (s, 1H), 2.07 (q, *J* = 6.4 Hz, 1H), 1.69 (q, *J* = 6.4 Hz, 1H), 1.34 (s, 9H), 1.33 – 1.30 (m, 1H), 1.24 (d, *J* = 2.3 Hz, 12H), 1.09 (d, *J* = 6.8 Hz, 3H), 0.94 (s, 3H), 0.92 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ177.0, 83.3, 50.8, 45.3, 40.4, 29.0, 26.1, 24.9, 24.6, 19.5. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{35}BNO_3$ 312.2705; Found: 312.2707.

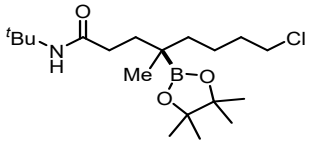


***N-(tert-butyl)-3,4-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (21)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes , 14 min). 14 mg, 46 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.37 (s, 1H), 2.25 (d, *J* = 15.9 Hz, 1H), 1.91 – 1.85 (m, 1H), 1.71 (dd, *J* = 13.3, 11.0 Hz, 1H), 1.34 (s, 9H), 1.23 (s, 12H), 0.90 (s, 3H), 0.88 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.3, 83.2, 51.1, 42.3, 38.4, 29.0, 24.9, 24.8, 21.9, 21.4, 15.4. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{35}BNO_3$ 312.2706; Found: 312.2705.

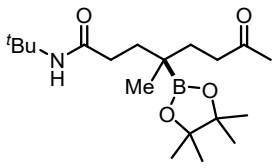


***(S)-N-(tert-butyl)-8-chloro-4-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octanamide (22)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes , 14 min). 21 mg, 56 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.28 (s, 1H), 3.52 (t, *J* = 6.7 Hz, 2H), 2.14 – 1.84 (m, 2H), 1.82 – 1.65 (m, 3H), 1.54 – 1.46 (m, 1H), 1.42 – 1.18 (m, 4H), 1.33 (s, 9H), 1.22 (s, 12H), 0.90 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ173.2, 83.3, 51.1, 45.2, 38.2, 34.7, 34.5, 33.5, 29.0, 25.0, 23.2, 21.4. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{38}BClNO_3$ 374.2628; Found: 374.2628.

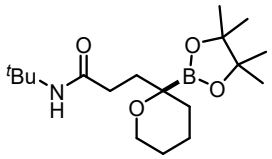


***(S)-N-(tert-butyl)-4-methyl-7-oxo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octanamide (23)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes , 14 min). 19 mg, 54 % yield. White solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.31 (s, 1H), 2.45 – 2.35 (m, 2H), 2.12 (s, 3H), 2.07 – 2.02 (m, 2H), 1.66 – 1.56 (m, 2H), 1.56 – 1.46 (m, 2H), 1.32 (s, 9H), 1.21 (s, 12H), 0.89 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 209.6, 173.0, 83.4, 51.1, 40.1, 34.2, 34.2, 31.9, 30.0, 29.0, 24.9, 24.9, 21.4. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{37}BNO_4$ 354.2810; Found: 354.2811.

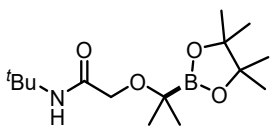


***(S)-N-(tert-butyl)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)tetrahydro-2H-pyran-2-yl)propanamide (24)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes , 14 min). 19 mg, 58 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ5.86 (s, 1H), 3.92 – 3.82 (m, 1H), 3.72 – 3.54 (m, 1H), 2.42 – 2.28 (m, 1H), 2.21 – 2.10 (m, 1H), 1.86 – 1.76 (m, 5H), 1.52 – 1.45 (m, 2H), 1.43 – 1.37 (m, 1H), 1.31 (s, 9H), 1.29 (d, J = 2.2 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 84.3, 65.7, 51.0, 34.8, 33.9, 33.4, 28.9, 26.4, 25.1, 24.9, 22.5. (The carbon attached to boron was not observed due to quadrupolar relaxation).

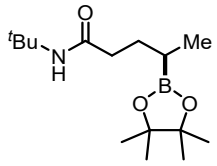
HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{35}BNO_{44}$ 340.2654; Found: 340.2654.



***N-(tert-butyl)-2-((2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)oxy)acetamide (25)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes , 14 min). 23mg, 75 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ δ 6.61 (s, 1H), 3.78 (s, 2H), 1.37 (s, 9H), 1.25 (s, 12H), 1.23 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 84.3, 65. 6, 50.7, 28.9, 24.8, 24.1. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{31}BNO_4$ 300.2341; Found: 300.2342.

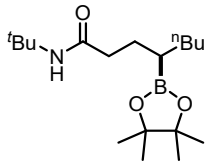


***(R)-N-(tert-butyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (26)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes , 14 min). 21mg, 75 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.46 (s, 1H), 2.19 – 2.05 (m, 2H), 1.72 – 1.59 (m, 2H), 1.34 (s, 9H), 1.24 (s, 12H), 1.05 – 0.99 (m, 1H), 0.97 (d, J = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (126 MHz, $CDCl_3$) δ 173.0, 83.2, 51.1, 37.5, 29.7, 29.0, 25.0, 25.0, 15.7. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{31}BNO_3$ 284.2392; Found: 284.2394.

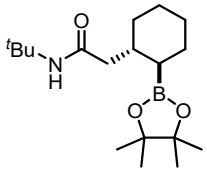


***(R)-N-(tert-butyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octanamide (27)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes , 14 min). 23mg, 71 % yield. White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49 (s, 1H), 2.16 – 2.08 (m, 2H), 1.75 – 1.68 (m, 1H), 1.68 – 1.61 (m, 1H), 1.47 – 1.40 (m, 1H), 1.34 (s, 9H), 1.32 – 1.25 (m, 5H), 1.25 (d, J = 1.4 Hz, 12H), 1.01 – 0.94 (m, 1H), 0.87 (t, J = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 83.2, 51.1, 37.8, 31.5, 31.1, 29.0, 27.8, 25.2, 25.0, 23.1, 14.2. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{35}BNO_3$ 324.2705; Found: 324.2707.

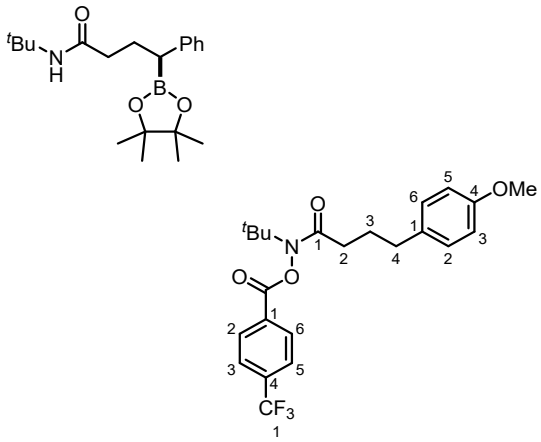


***N*-(tert-butyl)-2-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)acetamide (trans) (28)**: Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes , 14 min). 23mg, 69 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ. 5.66 (s, 1H), 2.22 (dd, *J* = 13.1, 3.5 Hz, 1H), 1.85 – 1.79 (m, 2H), 1.73 – 1.66 (m, 4H), 1.34 (s, 9H), 1.31 – 1.25 (m, 2H), 1.24 (d, *J* = 3.5 Hz, 12H), 1.18 – 1.10 (m, 1H), 1.07 – 0.99 (m, 1H), 0.81 – 0.72 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) 172.0, 83.2, 51.1, 45.6, 36.8, 33.1, 29.0, 28.1, 26.9, 26.3, 25.0, 24.9. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{37}BNO_3$ 326.2861; Found: 326.2863.



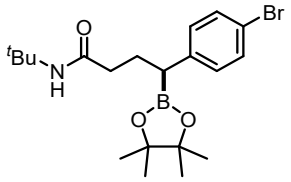
N-(*tert*-butyl)-4-(4-methoxyphenyl)-*N*-((4-(trifluoromethyl)benzoyl)oxy)butanamide

***N*-(tert-butyl)-4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (29):** Modifying from **General Procedure D** by replacing corresponding *O*-oxalate hydroxamic esters with *N*-(tert-butyl)-4-phenyl-*N*-((4-(trifluoromethyl)benzoyl)oxy)butanamide. The resultant reaction mixture was stirred under Blue LED (45 W, 440 nm) irradiation for 48 h. Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes, 14 min). 20mg, 58 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.23 – 7.13 (m, 3H), 5.18 (s, 1H), 2.31 (t, *J* = 7.6 Hz, 1H), 2.19 – 2.15 (m, 1H), 2.07 – 1.94 (m, 3H), 1.34 (s, 9H), 1.21 (d, *J* = 11.2 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.4, 142.5, 128.7, 128.6, 125.6, 83.6, 51.2, 37.1, 29.0, 28.5, 24.8, 24.8. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{33}BNO_3$ 346.2550; Found: 346.2548.

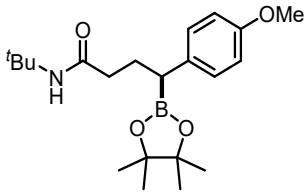


***4-(4-bromophenyl)-N-(tert-butyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (30)*:** Modifying from **General Procedure D** by replacing corresponding *O*-oxalate hydroxamic esters with 4-(4-bromophenyl)-*N*-(tert-butyl)-*N*-((4-(trifluoromethyl)benzoyl)oxy)butanamide The resultant reaction mixture was stirred under Blue LED (45 W, 440 nm) irradiation for 48 h. Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes, 14 min). 21mg, 51 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 5.17 (s, 1H), 2.28 – 2.22 (m, 1H), 2.17 – 2.07 (m, 1H), 2.02 – 1.95 (m, 2H), 1.95 – 1.85 (m, 1H), 1.32 (s, 9H), 1.19 (d, *J* = 8.2 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 141.7, 132.1, 131.6, 130.4, 129.8, 119.3, 83.7, 51.3, 36.9, 29.0, 28.2, 24.8, 24.8. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{32}BBrNO_3$ 424.1653; Found: 424.1656.

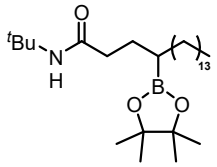


***N-(tert-butyl)-4-(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (31)*:** Modifying from **General Procedure D** by replacing corresponding *O*-oxalate hydroxamic esters with *N*-(tert-butyl)-4-(4-methoxyphenyl)-*N*-((4-(trifluoromethyl)benzoyl)oxy)butanamide. The resultant reaction mixture was stirred under Blue LED (45 W, 440 nm) irradiation for 48 h. Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes, 14 min). 30mg, 78 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 – 7.07 (m, 2H), 6.83 – 6.77 (m, 2H), 5.16 (s, 1H), 3.78 (s, 3H), 2.25 – 2.20 (m, 1H), 2.16 – 2.07 (m, 1H), 2.05 – 1.95 (m, 2H), 1.94 – 1.86 (m, 1H), 1.31 (s, 9H), 1.19 (d, *J* = 10.5 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ. 172.5, 157.7, 134.4, 129.6, 114.0, 83.5, 55.3, 51.1, 37.0, 29.0, 28.7, 24.8, 24.8. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{35}BNO_4$ 376.2654; Found: 376.2653.

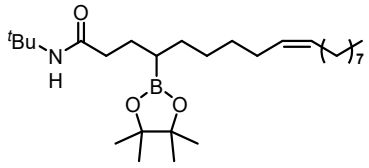


***N-(tert-butyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octadecanamide (32)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes , 14 min). 25mg, 54 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.49 (s, 1H), 2.15 – 2.03 (m, 2H), 1.73 – 1.58 (m, 3H), 1.34 (s, 9H), 1.30 – 1.18 (m, 25H), 1.24 (s,12H), 1.00 – 0.95 (m, 1H), 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 83.2, 51.1, 37.8, 32.1, 31.4, 30.0, 29.9, 29.8, 29.8, 29.8, 29.7, 29.5, 29.3, 29.0, 27.8, 25.0, 22.8, 14.3.

HRMS (APCI) m/z: $[M+H]^+$ Calcd. for $C_{28}H_{57}O_3NB$ 466.4426; Found: 466.4433.

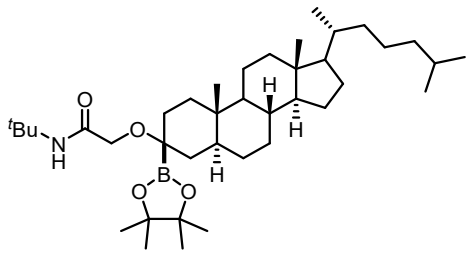


***N-(tert-butyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octadec-9-enamide (33)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes , 14 min). 13mg, 28 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.47 (s, 1H), 5.39 – 5.26 (m, 2H), 2.16 – 2.02 (m, 2H), 2.00 (q, J = 6.2 Hz, 4H), 1.75 – 1.60 (m, 2H), 1.34 (s, 9H), 1.32 – 1.20 (m, 18H), 1.25 (s, 12H), 1.01 – 0.94 (m, 1H), 0.88 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 130.1, 129.9, 83.2, 51.1, 37.7, 32.1, 31.3, 30.2, 29.9, 29.9, 29.7, 29.5, 29.5, 29.0, 27.8, 27.4, 27.3, 25.0, 22.8, 14.3.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{28}H_{54}O_3NBNa$ 486.4089; Found: 486.4093.

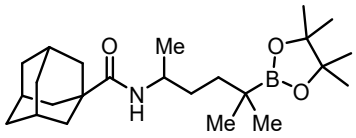


***(S)-4-(4-bromophenyl)-N-(tert-butyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (34)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes , 14 min). 40mg, 64 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.73 (s, 1H), 3.75 (s, 2H), 1.96 (dd, *J* = 12.9, 3.6 Hz, 1H), 1.83 – 1.24 (m, 15H), 1.38 (s, 9H), 1.22 (s, 12H), 1.20 – 0.94 (m, 14H), 0.89 (d, *J* = 6.4 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 6H), 0.80 (s, 3H), 0.70 – 0.66 (m, 1H), 0.64 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 84.1, 65.7, 56.8, 56.4, 55.0, 50.7, 42.8, 40.2, 39.7, 39.7, 36.3, 35.9, 35.86, 35.7, 33.7, 32.9, 32.4, 29.0, 28.5, 28.4, 28.2, 27.0, 24.8, 24.8, 24.3, 24.0, 23.0, 22.7, 20.9, 18.8, 12.25, 11.86. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{39}H_{70}O_4NBNa$ 650.5297; Found: 650.5295.

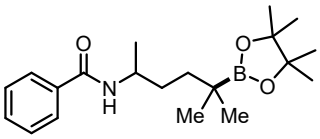


***(3r,5r,7r)-N-(5-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-yl)adamantane-1-carboxamide (36)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 20 % EtOAc in hexanes , 14 min). 23mg, 58 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.39 (d, *J* = 8.1 Hz, 1H), 3.90 – 3.82 (m, 1H), 2.13 – 1.98 (m, 3H), 1.87 – 1.80 (m, 6H), 1.77 – 1.65 (m, 6H), 1.46 – 1.40 (m, 1H), 1.33 – 1.24 (m, 3H), 1.22 (d, *J* = 2.1 Hz, 12H), 1.09 (d, *J* = 6.5 Hz, 3H), 0.91 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.3, 83.1, 45.4, 40.6, 39.5, 36.9, 36.8, 34.2, 28.4, 25.3, 24.9, 24.86, 24.7, 21.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{43}BNO_3$ 404.3331; Found: 404.3330.

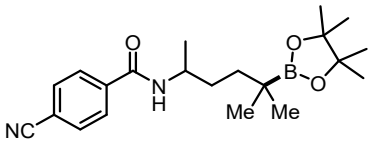


***N-(5-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-yl)benzamide (37)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 15 % Actone in hexanes , 14 min). 25mg, 73 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ. 7.81 – 7.75 (m, 2H), 7.50 – 7.45 (m, 1H), 7.45 – 7.38 (m, 2H), 6.18 – 6.11 (m, 1H), 4.14 – 4.03 (m, 1H), 1.61 – 1.53 (m, 1H), 1.46 – 1.39 (m, 2H), 1.33 – 1.28 (m, 1H), 1.23 (d, *J* = 6.5 Hz, 3H), 1.21 (d, *J* = 3.4 Hz, 12H), 0.93 (d, *J* = 3.9 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ. 167.2, 135.5, 131.3, 128.6, 127.1, 83.2, 46.6, 36.7, 34.3, 25.2, 24.9, 24.8, 24.6, 21.2. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{33}BNO_3$ 346.2548; Found: 346.2550.

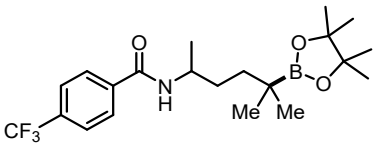


***4-Cyano-N-(5-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-yl)benzamide (38)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 15 % Actone in hexanes , 14 min). 36mg, 98 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 6.35 – 6.24 (m, 1H), 4.27 – 3.67 (m, 1H), 1.61 – 1.53 (m, 1H), 1.44 – 1.34 (m, 2H), 1.32 – 1.25 (m, 1H), 1.22 (d, *J* = 6.5 Hz, 3H), 1.19 (d, *J* = 3.2 Hz, 12H), 0.91 (d, *J* = 3.8 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.4, 139.4, 132.4, 127.8, 118.2, 114.8, 83.2, 47.0, 36.5, 34.1, 25.2, 24.8, 24.8, 24.5, 21.0. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{32}BN_2O_3$ 371.2500; Found: 371.2501.



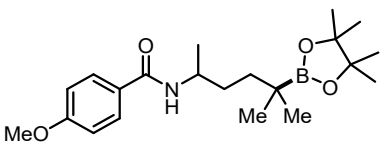
***N-(5-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-yl)-4-(trifluoromethyl)benzamide (39)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 15 % Actone in hexanes , 14 min). 33mg, 80 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ. 7.89 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 6.22 (d, *J* = 7.6 Hz, 1H), 4.12 – 3.96 (m, 1H), 1.63 – 1.54 (m, 1H), 1.45 – 1.37 (m, 2H), 1.33 – 1.27 (m, 1H), 1.24 (d, *J* = 6.5 Hz, 3H), 1.20 (d, *J* = 3.1 Hz, 12H), 0.93 (d, *J* = 4.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 138.8, 133.1 (q, *J* = 32.6 Hz), 127.6, 125.6 (q, *J* = 3.7 Hz), 123.9 (q, *J* = 272.5 Hz), 83.3, 46.9, 36.6, 34.2, 25.2, 24.9, 24.8, 24.6, 21.1. (The carbon attached to boron was not observed due to quadrupolar relaxation).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.95.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{32}BF_3NO_3$ 414.2422; Found: 414.2422.

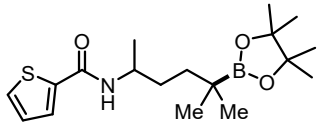


***4-Methoxy-N-(5-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-yl)benzamide (40)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 15 % Actone in hexanes , 14 min). 35mg, 94 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ. 7.75 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.03 (d, *J* = 7.7 Hz, 1H), 4.15 – 3.99 (m, 1H), 3.85 (s, 3H), 1.58 – 1.51 (m, 1H), 1.45 – 1.37 (m, 2H), 1.33 – 1.25 (m, 1H), 1.23 – 1.20 (m, 15H), 0.93 (d, *J* = 4.3 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ166.7, 162.1, 128.8, 127.7, 113.8, 83.2, 55.5, 46.5, 36.7, 34.3, 25.2, 24.9, 24.8, 24.7, 21.3.(The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{35}BNO_4$ 376.2654; Found: 376.2654.

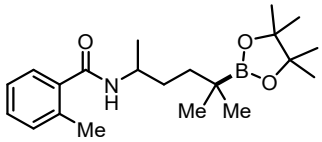


***N-(5-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-yl)thiophene-2-carboxamide (41)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 15 % Actone in hexanes , 14 min). 33mg, 95 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.44 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.05 (dd, *J* = 5.0, 3.7 Hz, 1H), 5.95 (d, *J* = 7.8 Hz, 1H), 4.09 – 3.90 (m, 1H), 1.57 – 1.49 (m, 1H), 1.45 – 1.36 (m, 2H), 1.32 – 1.27 (m, 1H), 1.23 – 1.19 (m, 15H), 0.92 (d, *J* = 3.8 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5, 139.9, 129.6, 127.7, 127.5, 83.2, 46.7, 36.7, 34.1, 25.1, 24.9, 24.8, 24.7, 21.2. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{30}BNO_3S$ 352.2112; Found: 352.2113.

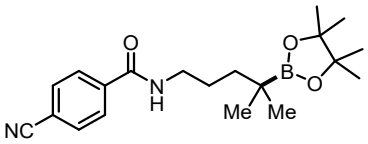


***2-Methyl-N-(5-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-yl)benzamide (42)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 15 % Actone in hexanes , 14 min). 9mg, 25 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 1H), 7.30 – 7.27 (m, 1H), 7.22 – 7.18 (m, 2H), 5.86 (d, *J* = 7.9 Hz, 1H), 4.12 – 4.03 (m, 1H), 2.45 (s, 3H), 1.60 – 1.52 (m, 1H), 1.46 – 1.40 (m, 1H), 1.38 – 1.26 (m, 3H), 1.24 (d, *J* = 6.5 Hz, 3H), 1.14 (d, *J* = 4.7 Hz, 12H), 0.93 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.9, 137.5, 135.9, 130.9, 129.7, 126.8, 125.8, 83.2, 46.5, 36.7, 34.2, 25.3, 24.7, 24.7, 24.5, 21.3, 19.8. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{35}BNO_3$ 360.2705; Found: 360.2705.

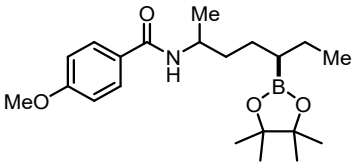


***4-Cyano-N-(4-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)benzamide (43)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 15 % Actone in hexanes , 14 min). 25mg, 70 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 6.41 (s, 1H), 3.55 – 3.29 (m, 2H), 1.63 – 1.57 (m, 2H), 1.40 – 1.32 (m, 2H), 1.20 (s, 12H), 0.95 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 139.1, 132.5, 127.8, 118.2, 115.0, 83.3, 40.7, 37.7, 26.5, 24.9, 24.8. (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{30}BN_2O_3$ 357.2344; Found: 357.2346.

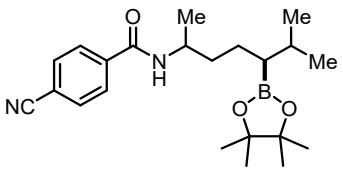


***4-Methoxy-N-((5R)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptan-2-yl)benzamide (44)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 15 % Actone in hexanes , 14 min). 27mg, 72 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.62 (m, 2H), 6.99 – 6.84 (m, 2H), 5.93 (dd, *J* = 16.0, 7.9 Hz, 1H), 4.22 – 4.01 (m, 1H), 3.84 (s, 3H), 1.57 – 1.33 (m, 6H), 1.26 – 1.20 (m, 16H), 0.89 (t, *J* = 7.4 Hz, 3H). (Two diastereomers)

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 166.5, 162.1, 128.8, 128.8, 127.7, 127.7, 113.8, 83.1, 55.5, 46.4, 46.2, 36.7, 36.5, 27.3, 27.1, 25.0, 25.0, 25.0, 24.9, 24.3, 24.3, 21.3, 21.2, 13.7, 13.7. (Two diastereomers) (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{35}BNO_4$ 376.2654; Found: 376.2654.

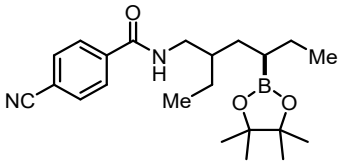


***4-Cyano-N-((5S)-6-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptan-2-yl)benzamide (45)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 15 % Actone in hexanes , 14 min). 30mg, 78 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.82 (m, 2H), 7.77 – 7.68 (m, 2H), 6.24 – 6.15 (m, 1H), 4.20 – 4.04 (m, 1H), 1.77 – 1.67 (m, 1H), 1.61 – 1.37 (m, 4H), 1.29 – 1.15 (m, 16H), 0.93 – 0.87 (m, 6H). (Two diastereomers)

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 165.3, 139.3, 139.2, 132.5, 127.8, 118.2, 115.0, 83.3, 83.2, 47.1, 47.0, 36.8, 36.5, 29.8, 25.4, 25.2, 25.1, 25.0, 24.8, 22.4, 22.3, 21.9, 21.7, 21.3, 20.8. (Two diastereomers) (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{34}BN_2O_3$ 385.2657; Found: 385.2656.

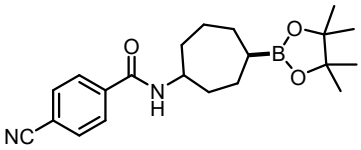


***4-Cyano-N-((4R)-2-ethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)benzamide (46)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 15 % Actone in hexanes , 14 min). 36mg, 93 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.86 (m, 2H), 7.73 – 7.69 (m, 2H), 6.96 – 6.74 (m, 1H), 3.57 – 3.10 (m, 2H), 1.63 – 1.26 (m, 7H), 1.23 – 1.15 (m, 12H), 1.05 – 0.98 (m, 1H), 0.95 – 0.88 (m, 6H). (Two diastereomers)

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 165.6, 139.2, 139.1, 132.4, 132.4, 127.9, 118.2, 118.2, 114.9, 114.9, 83.5, 83.4, 44.1, 43.3, 40.4, 39.2, 34.1, 33.3, 26.0, 25.5, 25.2, 25.2, 25.00, 24.94, 24.9, 24.9, 13.7, 13.5, 11.6, 11.5. (Two diastereomers) (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{34}BN_2O_3$ 385.2657; Found: 385.2656.

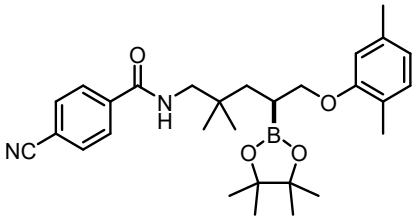


***4-Cyano-N-((4S)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cycloheptyl)benzamide (19)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 15 % Actone in hexanes , 14 min). 13mg, 34 % yield. White solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 2H), 7.78 – 7.66 (m, 2H), 6.14 – 5.90 (m, 1H), 4.28 – 4.05 (m, 1H), 2.17 – 1.39 (m, 11H), 1.24 – 1.21 (m, 12H), 1.23 – 1.09 (m, 1H). (Two diastereomers)

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 139.3, 139.2, 132.6, 127.8, 127.7, 118.2, 115.0, 83.2, 51.88, 50.8, 36.7, 35.7, 34.8, 34.6, 30.1, 29.1, 25.8, 25.4, 25.0, 24.9, 24.9, 24.8, 24.1. (Two diastereomers) (The carbon attached to boron was not observed due to quadrupolar relaxation).

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{30}BN_2O_3$ 369.2344; Found: 369.2344.

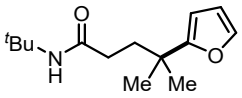


***4-Cyano-N-(2,2-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(2,4,5-trimethylphenoxy)pentyl)benzamide (48)*:** Purification by flash column chromatography (Biotage, Yamazen universal column 16g, 2 % to 15 % Actone in hexanes , 14 min). 24mg, 47 % yield. White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.9 Hz, 2H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.44 – 7.36 (m, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 6.66 (s, 1H), 4.06 – 3.94 (m, 2H), 3.57 (dd, *J* = 13.7, 7.8 Hz, 1H), 3.01 (dd, *J* = 13.7, 5.2 Hz, 1H), 2.31 (s, 3H), 2.16 (s, 3H), 1.88 (dd, *J* = 14.2, 9.4 Hz, 1H), 1.59 – 1.54 (m, 1H), 1.42 (d, *J* = 14.3 Hz, 1H), 1.20 (d, *J* = 22.2 Hz, 12H), 0.98 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 157.0, 139.1, 136.8, 132.4, 130.5, 127.9, 123.8, 121.5, 118.2, 114.9, 113.1, 84.1, 71.9, 47.4, 37.5, 35.7, 26.8, 25.4, 24.9, 24.8, 21.5, 15.9.

HRMS (APCI) m/z: $[M+H]^+$ Calcd. for $C_{29}H_{40}O_4N_2B$ 491.3076; Found: 491.3080.



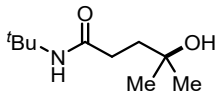
***N-(tert-butyl)-4-(furan-2-yl)-4-methylpentanamide* (49):** Cross coupling of boronic ester **11** with furan was carried out based on Aggarwal's protocol.[11] A 4 mL vial equipped with a stir bar and a septum was flame-dried under vacuum. The vial was allowed to cool (temperature) under vacuum and backfilled with N_2. Furan (29 μL, 0.40 mmol, 2.0 equiv.) was added, followed by addition of THF (1.0 mL) under N_2 atmosphere. After the vial was cooled to –78 °C by a dry ice/acetone bath, *n*-BuLi (2.4 M in hexane, 0.17 mL, 0.40 mmol, 2.0 equiv.) was added dropwise. The cooling bath was removed, and the mixture was allowed to warm to room temperature for 1 h. The mixture was cooled to –78 °C again, and a solution of secondary boronic ester **11** (60 mg, 0.20 mmol, 1.0 equiv) in THF (0.5 mL) was added dropwise. The resulting mixture was stirred at – 78 °C for 1 h. Then, a solution of *N*-bromosuccinimide (71.2 mg, 0.400 mmol, 2.00 equiv) in THF (1.0 mL) was added dropwise. After stirring at –78 °C for 1 h, saturated aqueous solution of $Na_2S_2O_3$ (3.0 mL) was

added. The reaction mixture was allowed to warm to room temperature. The reaction mixture was then diluted with Et_2O (5 mL) and water (5 mL). The crude mixture was extracted with Et_2O (2 x 5.0 mL), washed with brine, dried over anhydrous $MgSO_4$, and concentrated via rotary evaporation. Purification by flash column chromatography on silica gel (5-10% EtOAc in Hexane) gave the desired product **49** as a white solid (37mg, 78% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 1H), 6.33 – 6.23 (m, 1H), 6.03 – 5.94 (m, 1H), 5.14 (s, 1H), 1.97 – 1.81 (m, 4H), 1.30 (s, 9H), 1.25 (s, 6H).

^{13}C NMR: (101 MHz, $CDCl_3$) δ 172.5, 162.2, 141.0, 109.8, 103.8, 51.1, 37.6, 35.6, 33.5, 28.9, 26.9.

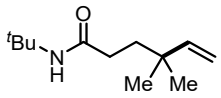
HRMS (EI) m/z: $[M]^+$ Calcd. for $C_{14}H_{23}NO_2$ 237.1734; Found: 237.1729.



N-(tert-butyl)-4-hydroxy-4-methylpentanamide **(50):** To a flame-dried vial was added **11** (60.0 mg, 0.20 mmol, 1 equiv.) and 2.0 mL THF. The vial was cooled to 0 °C (ice bath), followed by the addition of 1.0 mL 2 M NaOH (aq.) and 0.5 mL H_2O_2. After the reaction completion as monitored by TLC (~1 h), 10 mL water was added. The crude product was extracted with EtOAc (3 x 10 mL), washed with brine (10 mL), dried over Na_2SO_4, and concentrated in reduced pressure, affording **50** as a white solid (33.0 mg, , 89% yield).
^{1}H NMR: (400 MHz, $CDCl_3$) δ 5.42 (s, 1H), 2.75 (s, 1H), 2.26 (t, *J* = 7.1 Hz, 2H), 1.79 (t, *J* = 7.2 Hz, 2H), 1.33 (s, 9H), 1.22 (s, 6H).

^{13}C NMR: (101 MHz, $CDCl_3$) δ 173.4, 70.0, 51.4, 38.4, 32.5, 29.6, 28.9.

HRMS (EI) m/z: $[M]^+$ Calcd. for $C_{10}H_{21}NO_2$ 187.1569; Found: 187.1575.



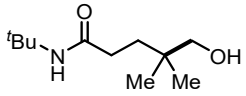
N-(tert-butyl)-4,4-dimethylhex-5-enamide **(51):** To a solution of **11** (60.0 mg, 0.20 mmol, 1 equiv.) in THF (2.0 mL) was added vinylmagnesium bromide (4.0 equiv). The resulting mixture was stirred at room temperature for 1h. The above solution was then cooled to –78 °C, and iodine (4.0 equiv) in methanol (1.0 mL) was added. The reaction mixture was stirred at the –78 °C for 1 h, followed by addition of a solution of NaOMe (8.0 equiv) in methanol (2.0 mL). The reaction was allowed to warm to room temperature and stirred for another 1.5 h. After that, the reaction was diluted with pentane (20 mL) and washed with a saturated aqueous solution of $Na_2S_2O_3$ (3 mL). The crude mixture was extracted with EtOAc (20 mL) was added, washed with brine (10 mL), dried over Na_2SO_4, and concentrated via rotary evaporation. Purification by flash column

chromatography on silica gel (5-30% EtOAc in Hexane) gave the desired product **51** as a white solid (31mg, 79% yield).

^{1}H NMR: (500 MHz, $CDCl_3$) δ 5.77 – 5.69 (m, 1H), 5.21 (s, 1H), 4.96 – 4.85 (m, 2H), 2.05 – 1.91 (m, 2H), 1.63 – 1.56 (m, 2H), 1.32 (s, 9H), 0.98 (s, 6H).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 172.9, 147.7, 111.2, 51.2, 37.9, 36.4, 33.3, 29.0, 26.7.

HRMS (EI) m/z: $[M]^+$ Calcd. for $C_{12}H_{23}NO$ 197.1775; Found: 197.1781.



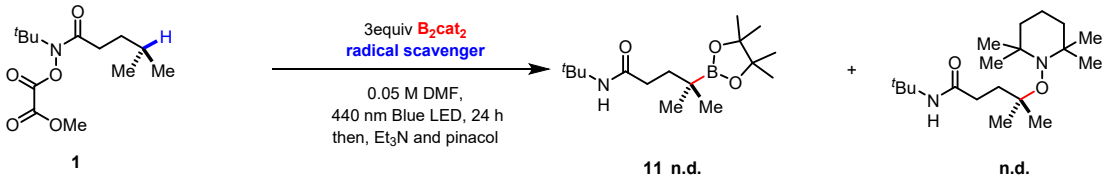
N-(tert-butyl)-5-hydroxy-4,4-dimethylpentanamide **(52):** To an oven-dried 10 mL Schlenk tube containing a stirring bar was charged **11** (30 mg, 0.1 mmol). The tube was tightly sealed with a septum. Then, anhydrous THF (1.0 mL) was added, followed by CH_2Br_2 (21 µL, 0.3 mmol) under N_2 atmosphere. The reaction mixture was cooled down to -78 ºC, and *n*-BuLi (0.15 mL (1.6M), 0. 25 mmol) was added dropwise over 5–6 min. The reaction mixture was stirred at the same temperature for 1 h and at room temperature for another 1 h. Next, the reaction mixture was again cooled to -78 ºC, and *n*-BuLi (0.16 mL (1.6 M), 0.25 mmol) was added dropwise over 5–6 min. The reaction stirred at the same temperature for 1 h, followed by stirring at room temperature for another 1 h. NaOH (3.0 M, 1.0 mL) and methanol (1.0 mL) were subsequently added. After the reaction was cooled to 0 ºC, 30% aqueous H_2O_2 (0.25 mL) was added dropwise. The reaction was stirred at room temperature for 3 h. The crude product was extracted with EtOAc (10 mL), washed with brine (5 mL), dried over Na_2SO_4, and concentrated under reduce pressure. Purification by flash column chromatography on silica gel (5-30% EtOAc in Hexane) gave product **52** as a white solid (9 mg, 47% yield).

^{1}H NMR: (400 MHz, $CDCl_3$) δ 5.34 (s, 1H), 3.22 (s, 1H), 2.12 (t, J = 7.0 Hz, 2H), 1.59 (t, J = 6.8 Hz, 2H), 1.34 (s, 9H), 0.87 (s, 6H).
^{13}C NMR: (101 MHz, $CDCl_3$) δ 173.6, 70.3, 51.5 35.4, 32.7, 32.1, 28.9, 24.6.

HRMS (EI) m/z: $[M]^+$ Calcd. for $C_{11}H_{23}NO_2$ 201.1724; Found: 201.1727.

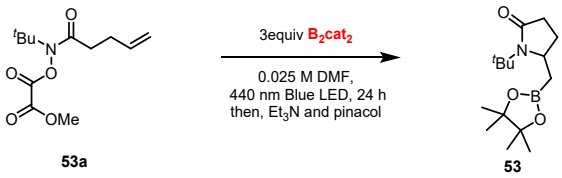
5. Mechanistic Studies

5.1 Radical trapping experiment

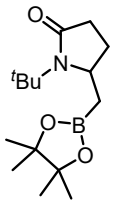


To a flame-dried reaction tube equipped with a stir bar was charged B_2cat_2 (3.0 equiv.) and TEMPO or BHT. The tube was tightly sealed with a rubber septum. After evacuation and backfilled nitrogen for 5 times, **1** (0.2 mmol, 1.0 equiv.) and DMF (0.05 M) were added via syringes. The resulting mixture was stirred under Blue LED (45 W, 440 nm) irradiation for 24 h. After the reaction was complete as monitored by TLC, the irradiation was stopped. Pinacol (2.0 equiv. based on B_2cat_2) in Et_3N (1.0 mL) was added via a syringe, and the mixture was stirred for additional 1 h at room temperature. The reaction mixture was then partitioned between EtOAc and water. The organic layer was collected, washed with an aqueous solution of NH_4Cl, dried over $MgSO_4$, and concentrated under reduced pressure. Product **11** was not observed based on ^1H NMR spectroscopy and GCMS analysis.

5.2 Cyclization experiment



To a flame-dried reaction tube equipped with a stir bar was charged B_2cat_2 (3.0 equiv.). The tube was sealed with a rubber septum. After evacuation and backfilled nitrogen for 5 times, **53a** (0.2 mmol, 1.0 equiv.) and DMF (0.025 M) were added via syringes. The resulting mixture was stirred under Blue LED (45 W, 440 nm) irradiation for 24 h. After the reaction was complete, the light irradiation was stopped. Pinacol (2.0 equiv. based on B_2cat_2) dissolved in Et_3N (1.0 mL) was added via a syringe, and the mixture was stirred for additional 1 h at room temperature. The reaction mixture was partitioned between EtOAc and water. The organic layer was collected, washed with saturated aqueous NH_4Cl, dried over $MgSO_4$, and concentrated under reduced pressure. The resulting reaction mixture was purified by flash chromatography on silica gel to give product **53**.



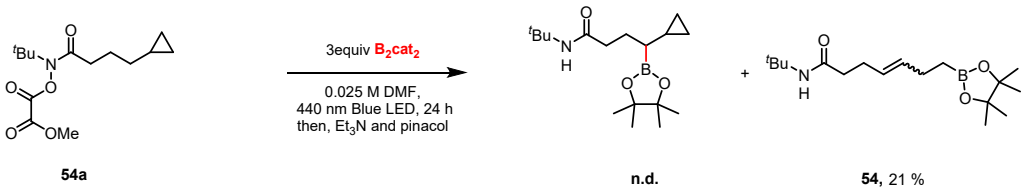
***1-(tert-butyl)-5-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pyrrolidin-2-one* (53):** 21% NMR yield. Purification by flash column chromatography (Biotage, Yamazen universal column 55g, 25 % EtOAc in Hexanes, 14 min). White solid.

^{1}H NMR (500 MHz, $CDCl_3$) 4.14 – 4.03 (m, 1H),2.60 – 2.52 (m, 1H), 2.30 – 2.20 (m, 1H), 2.12 – 2.06 (m, 1H), 1.64 – 1.57 (m, 1H), 1.44 (s, 9H), 1.30 – 1.10 (m, 2H), 1.25 (s, 6H), 1.24 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) 175.6, 83.7, 56.1, 54.4, 31.6, 28.5, 27.1, 25.1, 24.8.

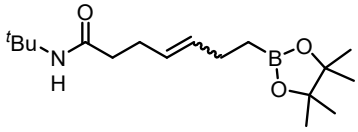
Spectral data is consistent with those reported in literature:
Org. Lett. **2021**, *23, 7688−7692.*

5.3 Radical clock experiment



54a **n.d.** **54**, 21 %

To a flame-dried reaction tube equipped with a stir bar was added B_2cat_2 (3.0 equiv.). The tube was sealed with a rubber septum. After evacuation and backfilled nitrogen for 5 times, **54a** (0.2 mmol, 1.0 equiv.) and DMF (0.025 M) were added via syringes. The resulting reaction mixture was stirred under Blue LED (45 W, 440 nm) irradiation for 24 h. After the reaction was complete, the light irradiation was stopped. Pinacol (2.0 equiv. based on B_2cat_2) dissolved in Et_3N (1.0 mL) was added via a syringe, and the mixture was stirred for additional 1 h at room temperature. After that, the reaction mixture was partitioned between EtOAc and water. The organic layer was collected, washed with saturated aqueous NH_4Cl, dried over $MgSO_4$, and concentrated under reduced pressure. The resulting reaction mixture was purified by flash chromatography on silica gel to give **54** as a mixture of two diastereoisomers.



***N-(tert-butyl)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-4-enamide* (54):** 21% NMR yield. Purification by flash column chromatography (Biotage, Yamazen universal column 55g, 25 % EtOAc in Hexanes, 14 min). White solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.58 – 5.48 (m, 1H), 5.45 – 5.33 (m, 1H), 5.28 (s, 1H), 2.37 – 2.24 (m, 2H), 2.17 – 2.05 (m, 4H), 1.33 (s, 9H), 1.24 (s, 12H), 0.84 (t, *J* = 7.8 Hz, 2H). (Two diastereomers)

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.1, 133.7, 133.4, 127.6, 127.2, 83.2, 83.2, 51.2, 37.8, 37.7, 29.0, 29.0, 28.8, 27.0, 25.0. (Two diastereomers)

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{32}BNO_3Na$ 332.2371; Found: 332.2373.

5.4 UV/VIS Absorption Spectroscopy

The reaction of *O*-oxalate hydroxamic ester **1** and $B_2(cat)_2$ was investigated by UV/Vis spectroscopy to determine whether an EDA complex forms under the reaction conditions (Figure S1). When comparing a DMF solution of $B_2(cat)_2$ (red) to a mixture of **1** and $B_2(cat)_2$ both before (blue) and after (green) light irradiation, no significant signal for an EDA complex exists.[12] The spectra for $B_2(cat)_2$ alone, however, does have an absorption tail that extends to 450 nm. This suggests that $B_2(cat)_2$ can potentially be excited by 440 nm light.

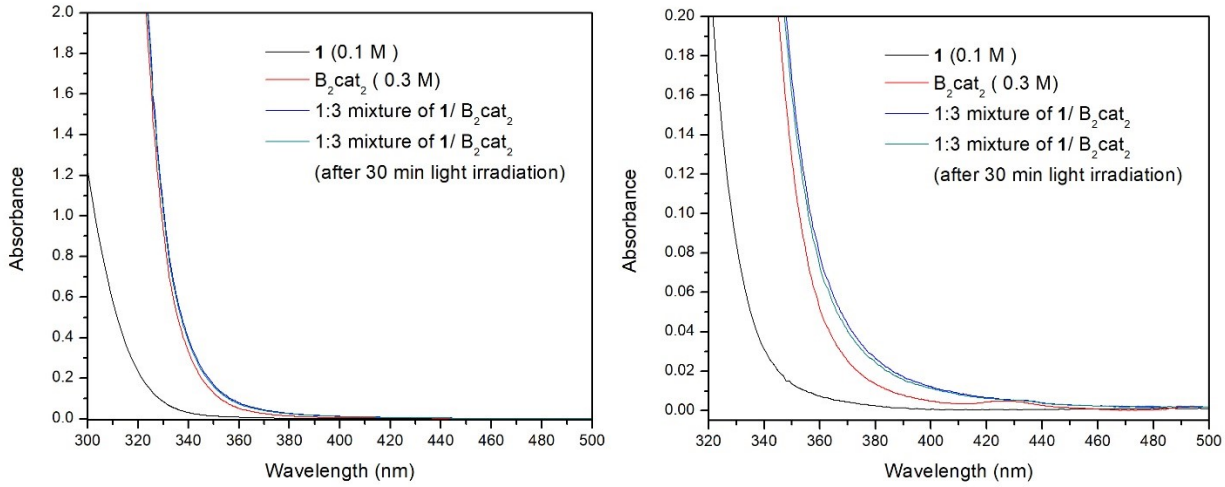


Figure S1. UV/Vis absorption spectra of DMF solutions of B_2cat_2 (0.3 M), **1** (0.10 M), and a mixture of B_2cat_2 (0.3 M) and **1** (0.10 M) before and after light irradiation, respectively. Left box: full region; Right box: expanded region.

The concentration of B_2cat_2 under standard reaction conditions was set as 0.3 M. We carried out UV-Vis studies for a set of mixtures of B_2cat_2 with oxalate **1** at different concentrations of **1** (0.008, 0.016, 0.033, 0.066 and 0.1 M) in DMF. UV-Vis spectra showed weak absorption at λmax ~430 nm, suggesting the formation of a DMF·$B_2(cat)_2$ adduct which corresponds to literature.[13] It was observed that the absorption intensity at ~430 nm decreases when **1** was added.

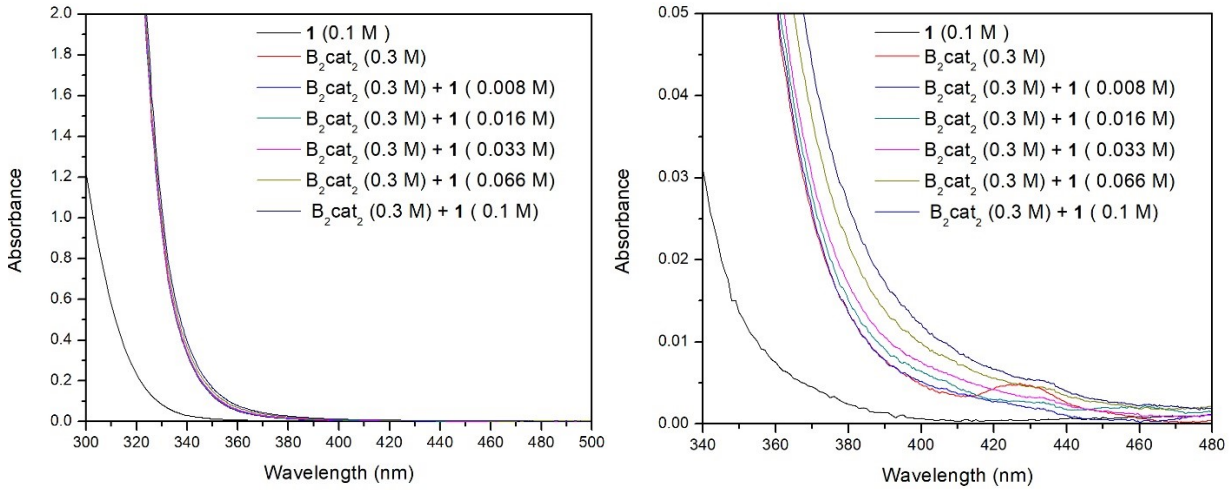


Figure S2. UV/vis absorption spectra of **1** (0.1 M) and B_2cat_2 (0.3 M) and mixtures of **1**(0.008, 0.016, 0.033, 0.066 and 0.1 M) and B_2cat_2 (0.3 M) in DMF. Left box: full region; Right box: expanded region.

The UV/vis absorption spectra of *O*-benzoyl hydroxamic ester **9** in DMF (0.10 M), B_2cat_2 (0.3 M), and a mixture of **9** (0.10 M) and B_2cat_2 (0.3 M) are shown in Figure S3. The bathochromic shift is indicative of EDA complex formation.[12]

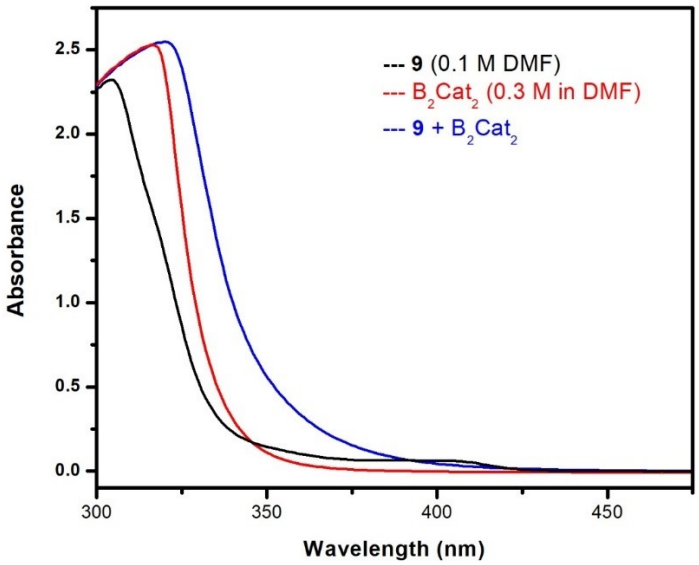


Figure S3. UV/vis absorption spectra of **9**, B_2cat_2, and a 1:3 mixture of **9** and B_2cat_2 in DMF.

6. References

[1] Liu, Z.; Cook, S. P. *Org. Lett.* **2022***, 24,* 3313−3318.

[2] Pinter, E. N.; Bingham, J. E., AbuSalim, D. I., Cook, S. P. *Chem. Sci.* **2020**, *11*, 1102–1106.

[3] Zeng, X.; Yan, W.; Paeth, M.; Zacate, S. B.; Hong, P. -H.; Wang, Y.; Yang, D.; Yang, K.; Yan, T.; Song, C.; Cao, Z.; Cheng, M. -J.; Liu, W. *J. Am. Chem. Soc.* **2019**, *141*, 19941–19949.

[4] Morcillo, S. P.; Dauncey, E. D.; Kim, J. H.; Douglas, J. J.; Sheikh, N. S.; Leonori, D. *Angew. Chem. Int. Ed.* **2018**, *57*, 12945-12949.

[5] Chen, H.; Guo, L.; Yu, S. *Org. Lett.* **2018**, *20*, 6255–6259.

[6] Valerie A. S.; Ryan, K. Q.; Andrew, T. B.; Erik. J. A. *J. Am. Chem. Soc*. **2014**, *136*, 14389-14392.

[7] Tokuyama, H. *Org. Synth.* **2003**, *80*, 207-2018.

[8] Dian, F. C.; John, C. K.; Tomislav, R. *J. Am. Chem. Soc.* **2017**, *139*, 14897–14900.

[9] Marinus, A. B.; Sean, A. R.; Christina, M. W. *J. Am. Chem. Soc.* **2012**, *134*, 9721–9726.

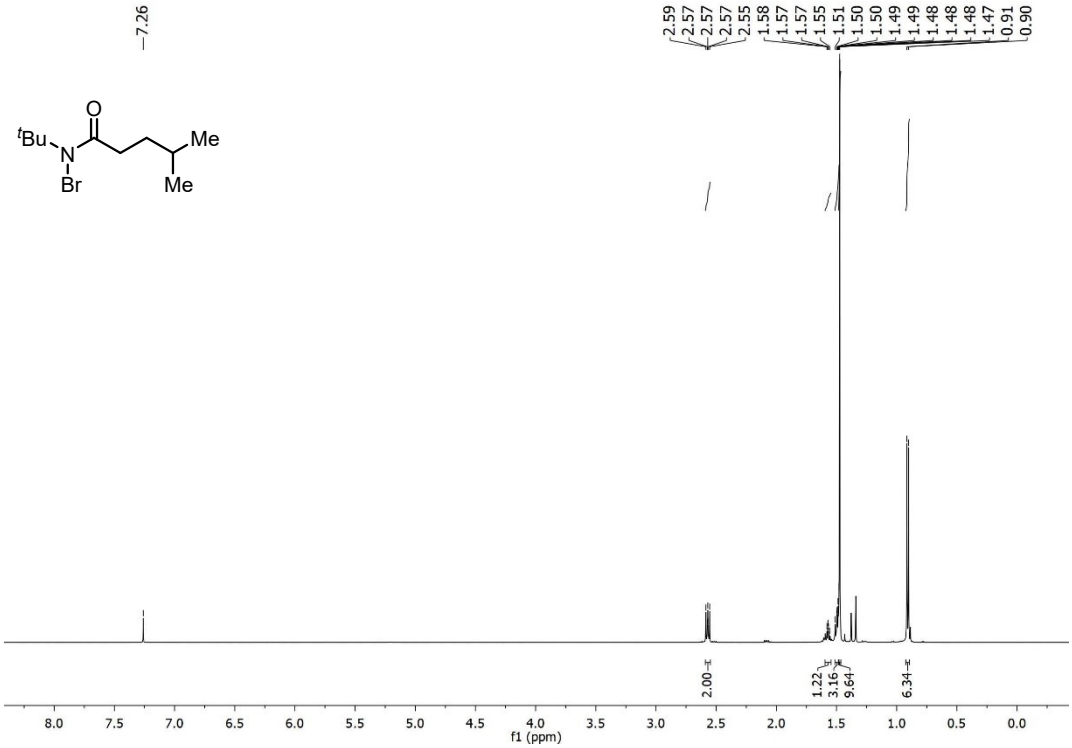
[10] Hui, C.; Wen, J. F.; Xiang, A. Y.; Shou, Y. Y. *Nat. Commun*. **2019**, *10*, 4743.

[11] Yu, Q. M.; Jia, X. K.; Yan, N. M.; Xue, N. C. *Green Chem.* **2021**, *23*, 3595-3599.

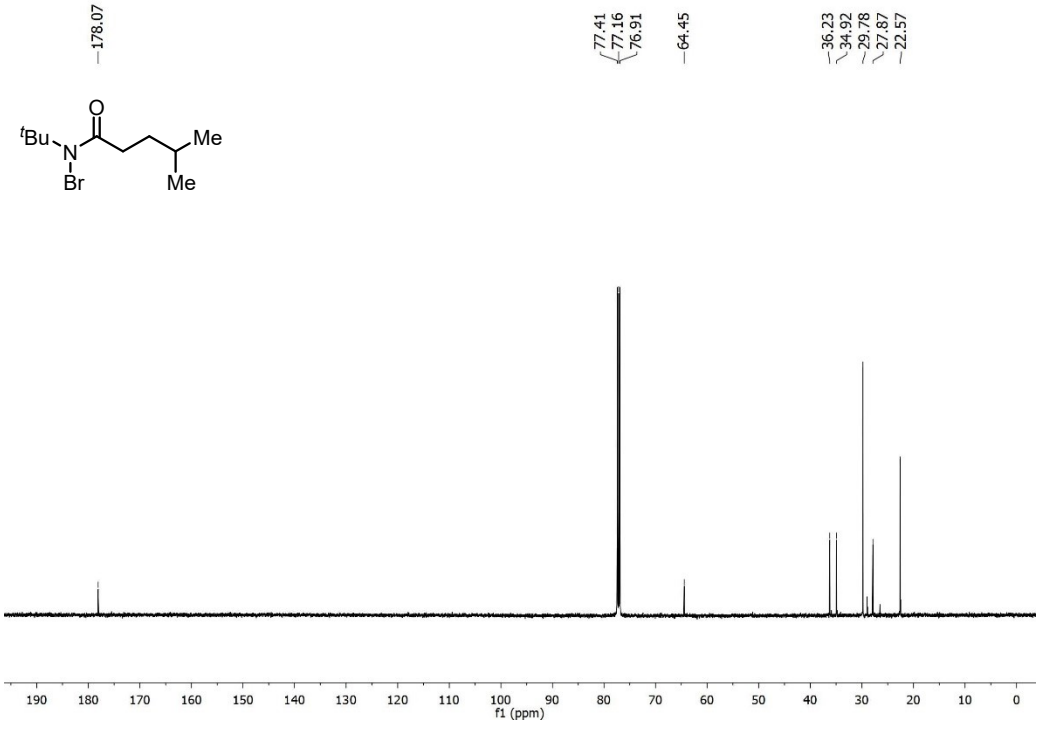
[12] C. Shu, R. Madhavachary, A. Noble, V. K. Aggarwal, *Org. Lett.* **2020**, *22*, 7213–7218.

[13] Ma, G. B.; Chen, C. Z.; Talukdar, S.; Zhao, X. L.; Lei, C. H.; Gong, H. G. *Chem. Commun.* **2020**, *56*, 10219-10222.

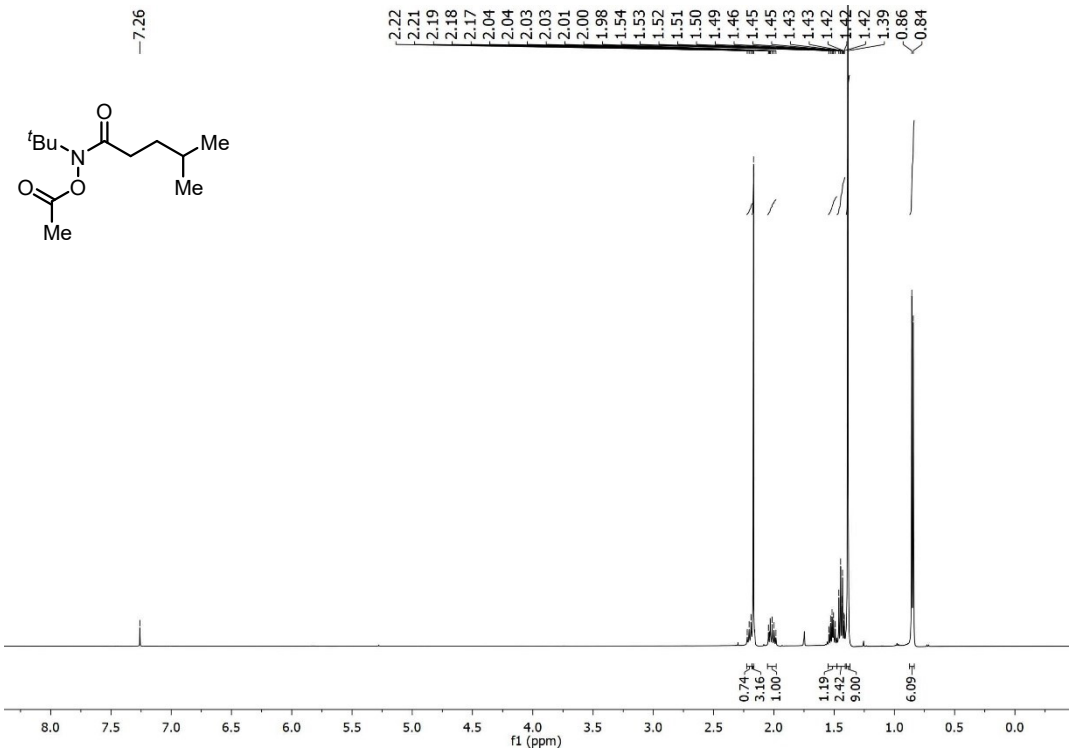
7. NMR Spectrum



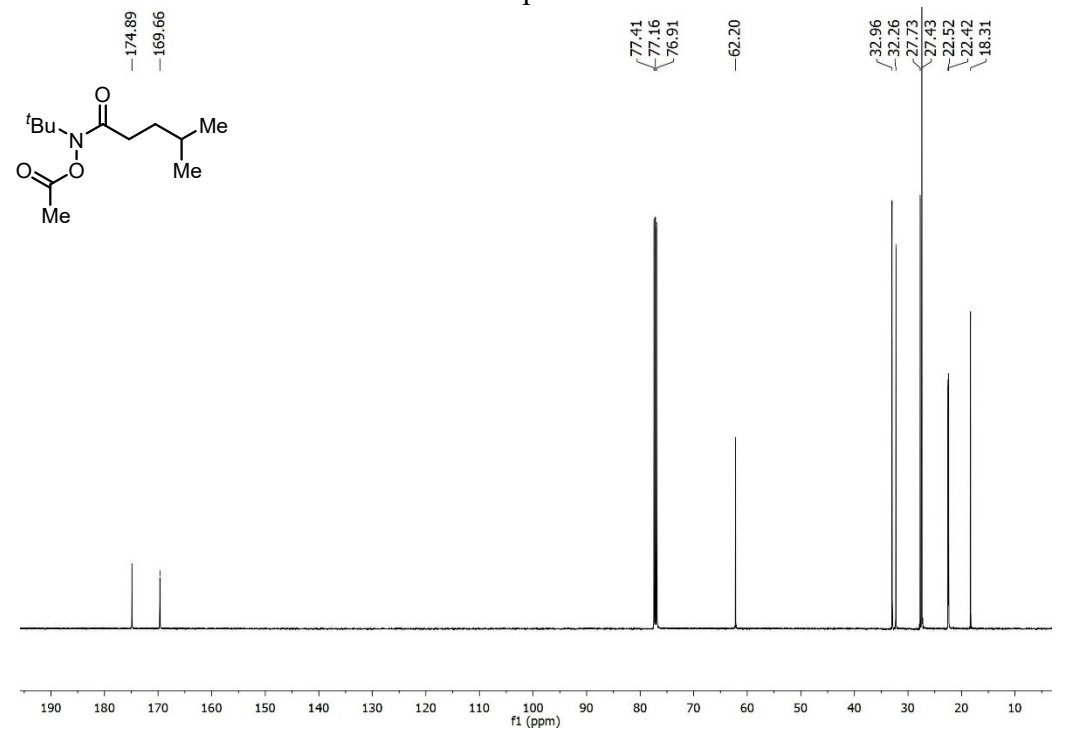
^{1}H NMR spectrum of **4**



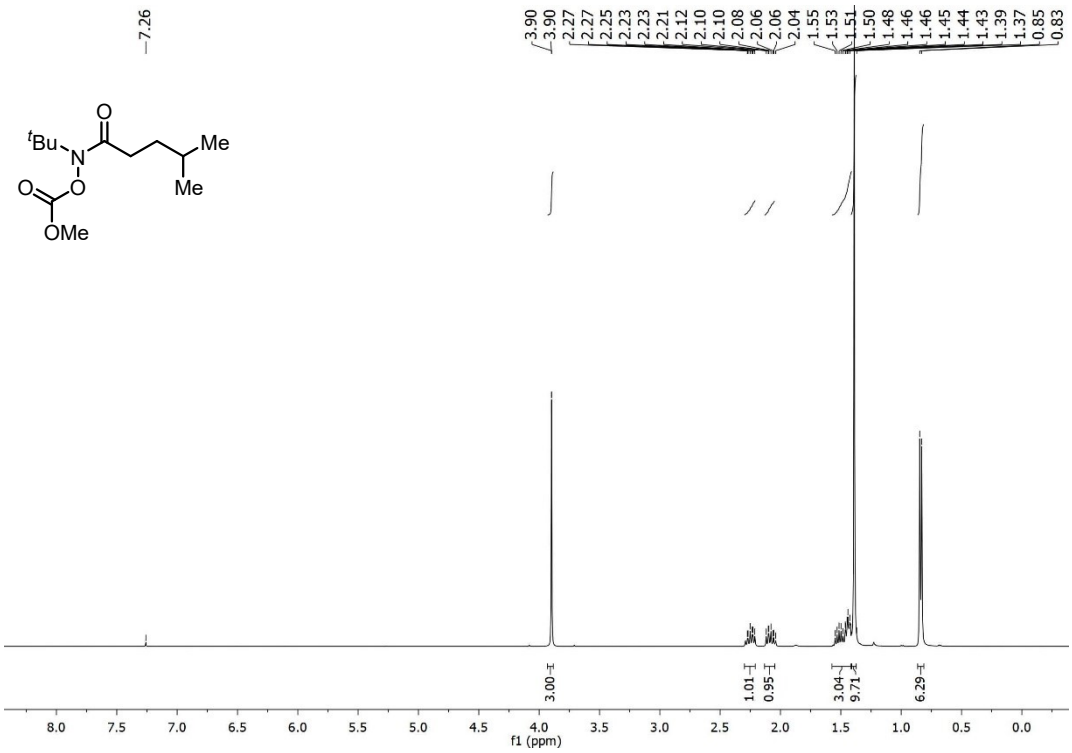
^{13}C NMR spectrum of **4**



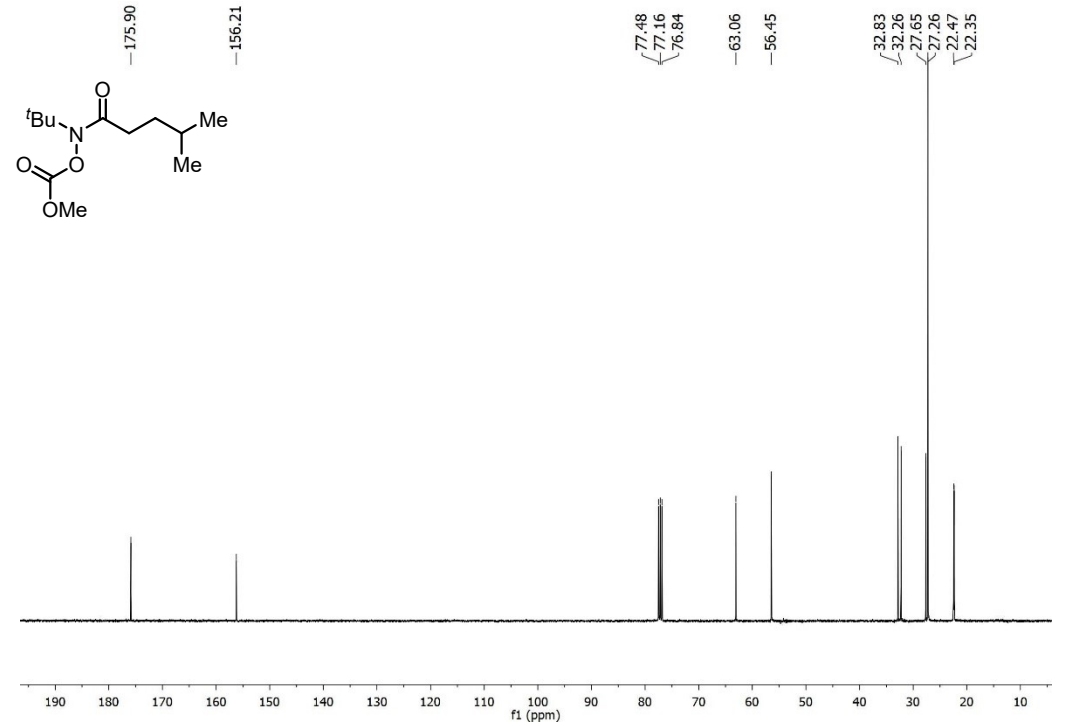
^{1}H NMR spectrum of **6**



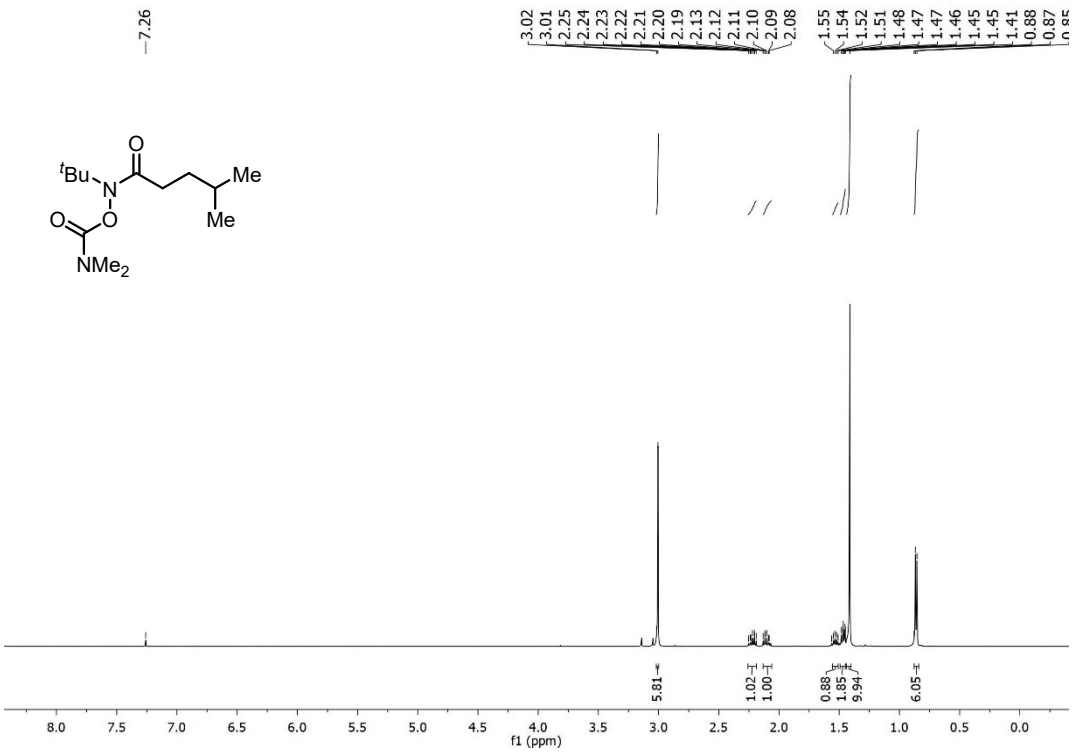
^{13}C NMR spectrum of **6**



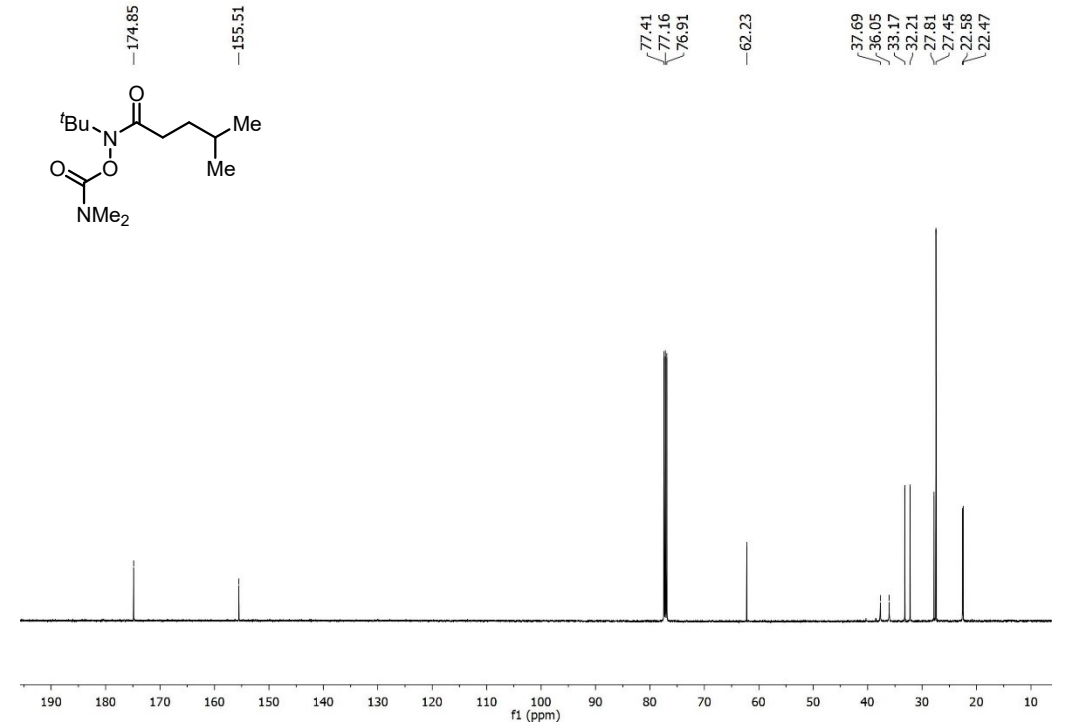
^{1}H NMR spectrum of **7**



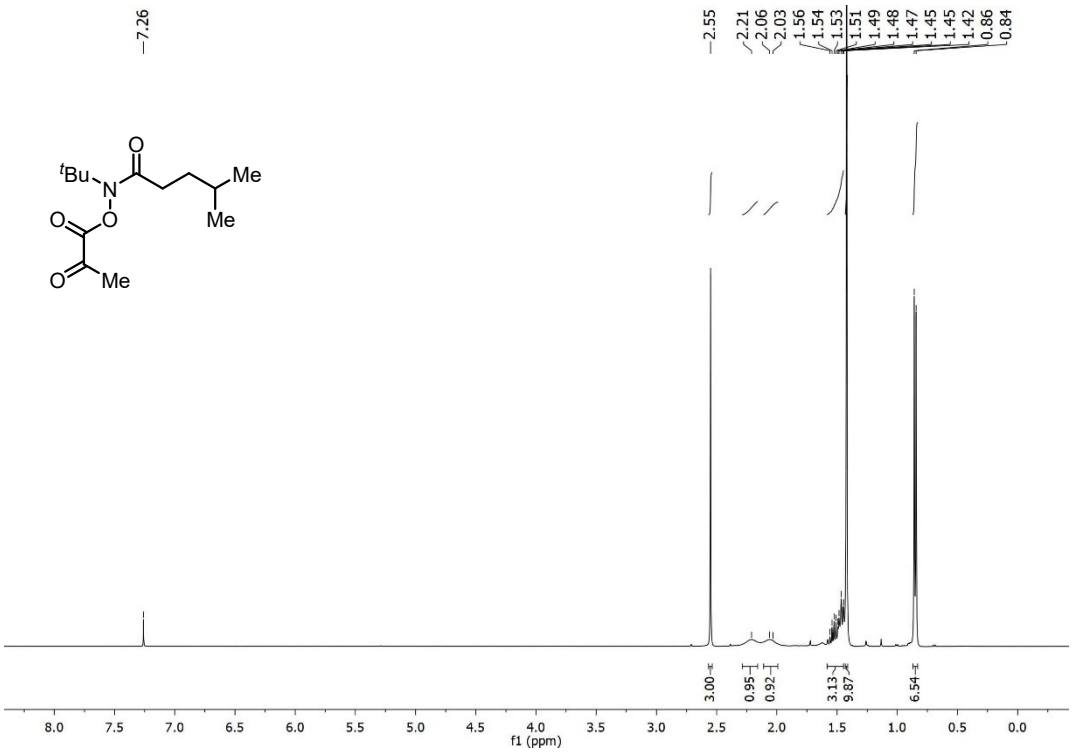
^{13}C NMR spectrum of **7**



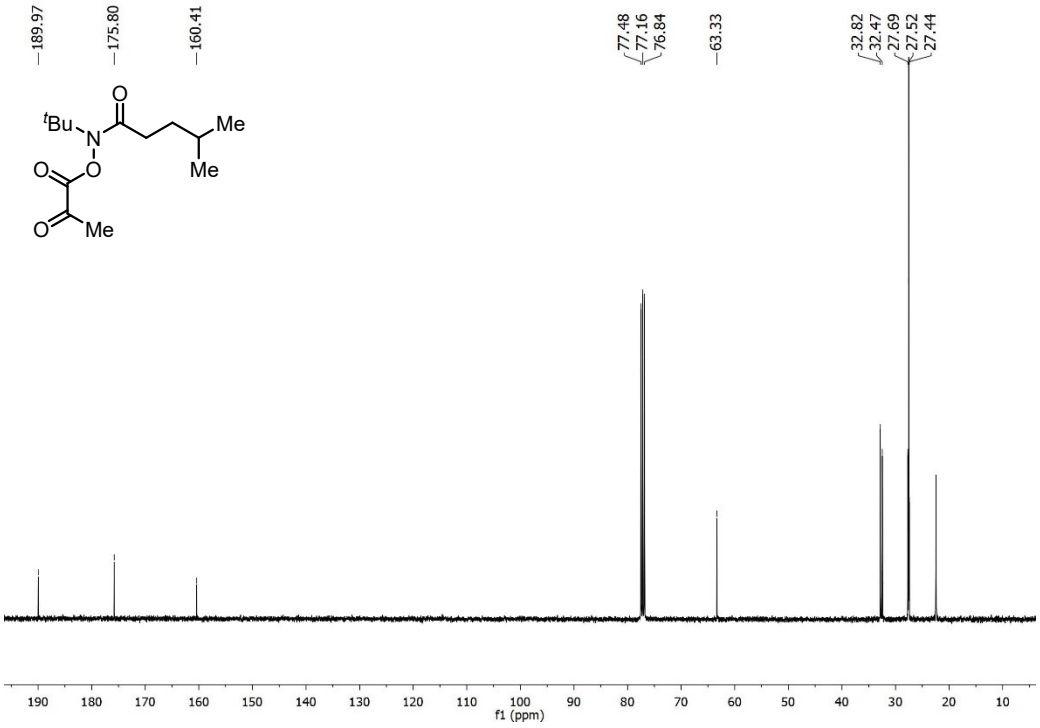
^{1}H NMR spectrum of **8**



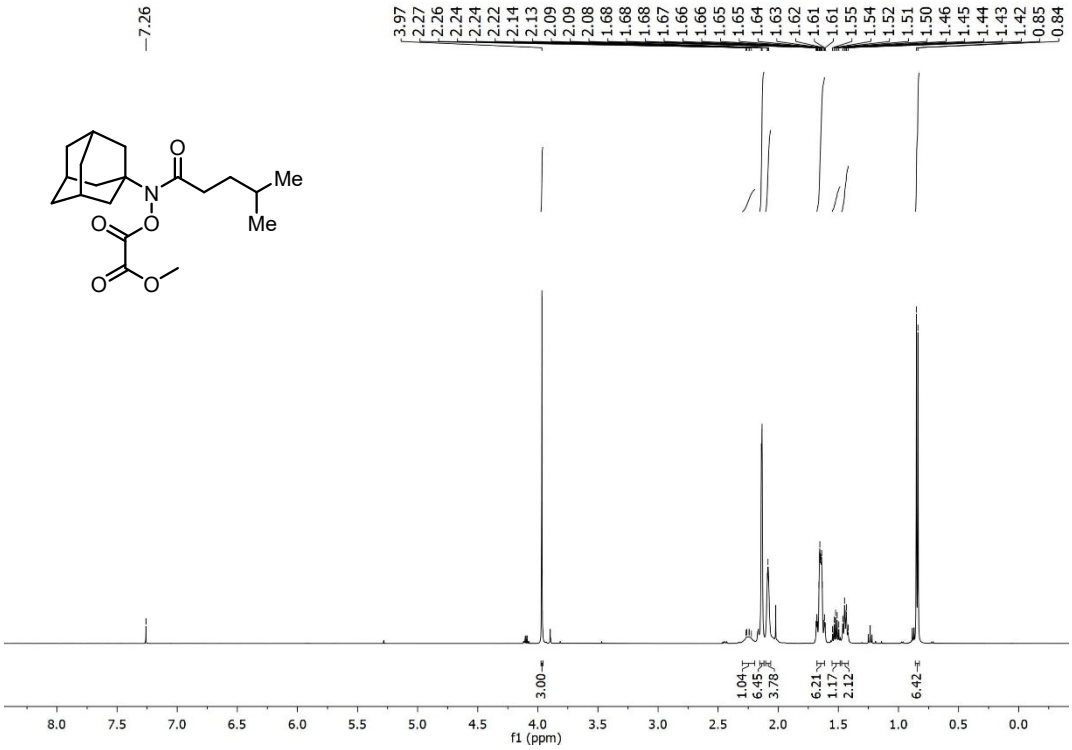
^{13}C NMR spectrum of **8**



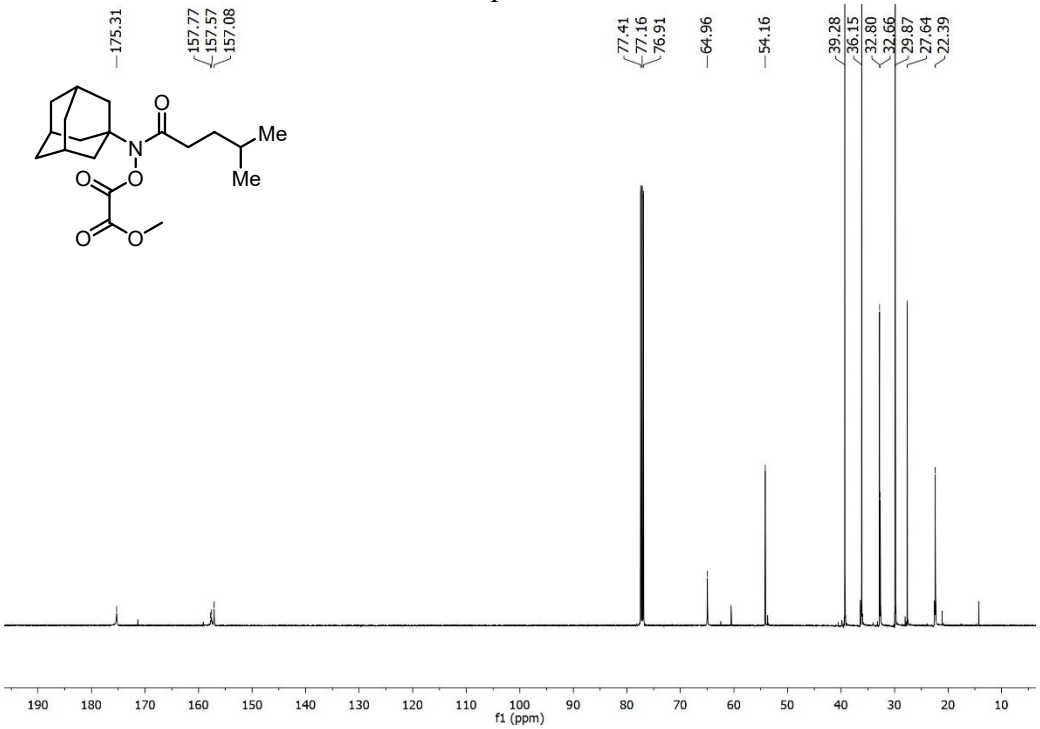
^{1}H NMR spectrum of **10**



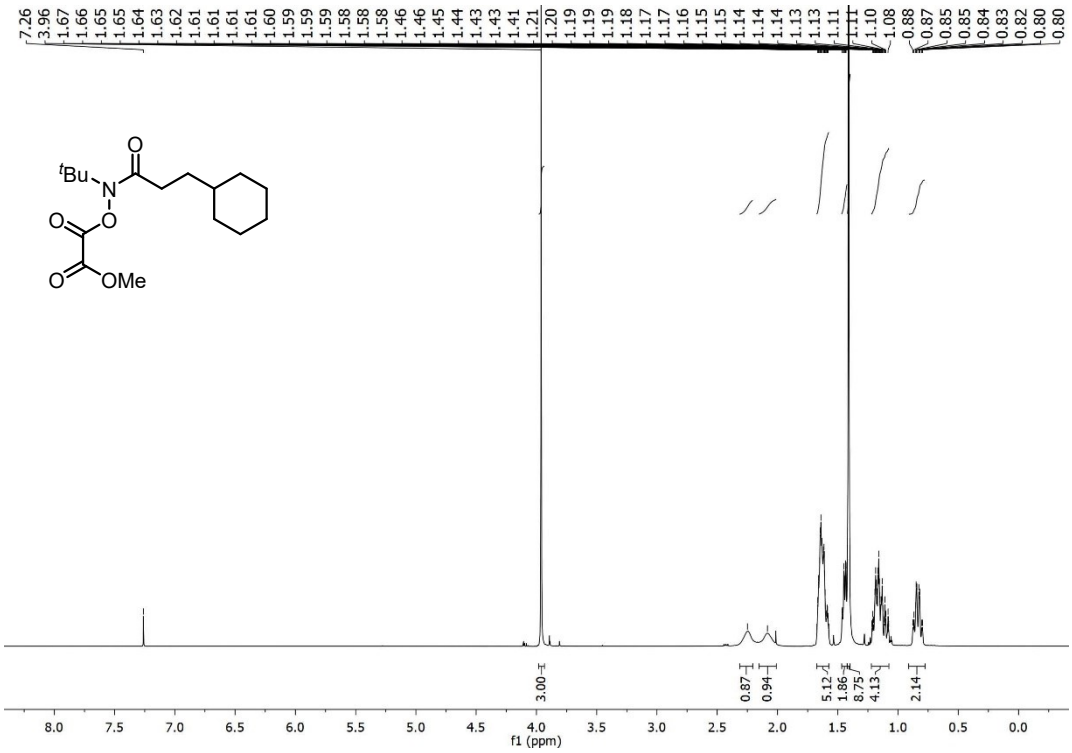
^{13}C NMR spectrum of **10**



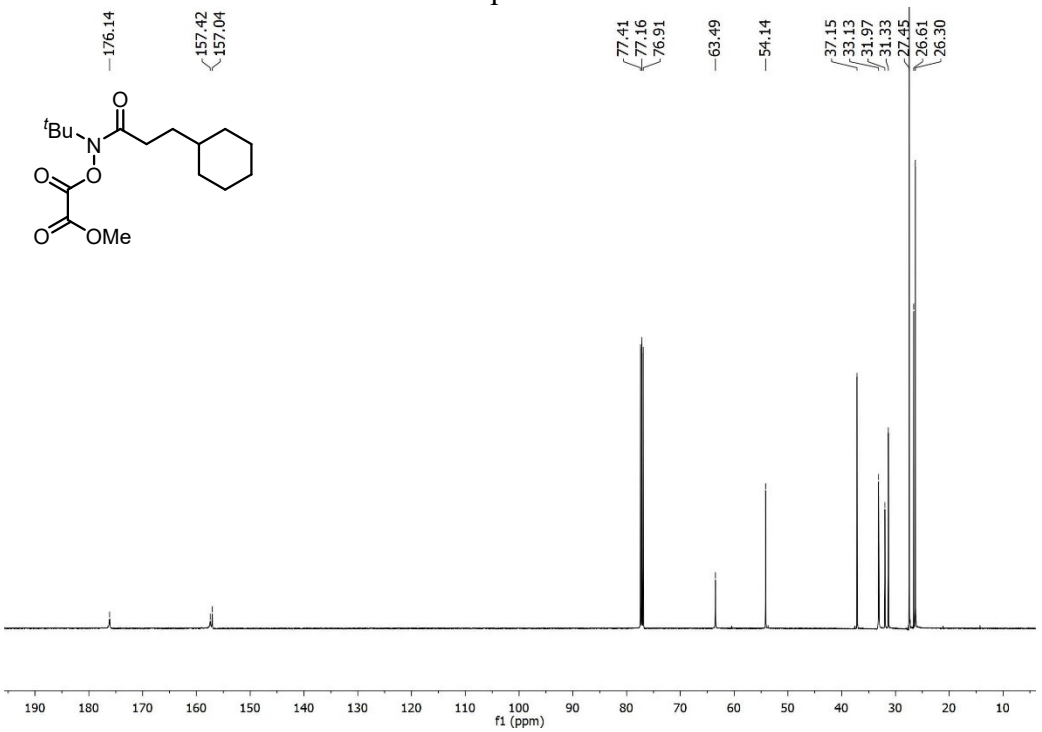
^{1}H NMR spectrum of **12a**



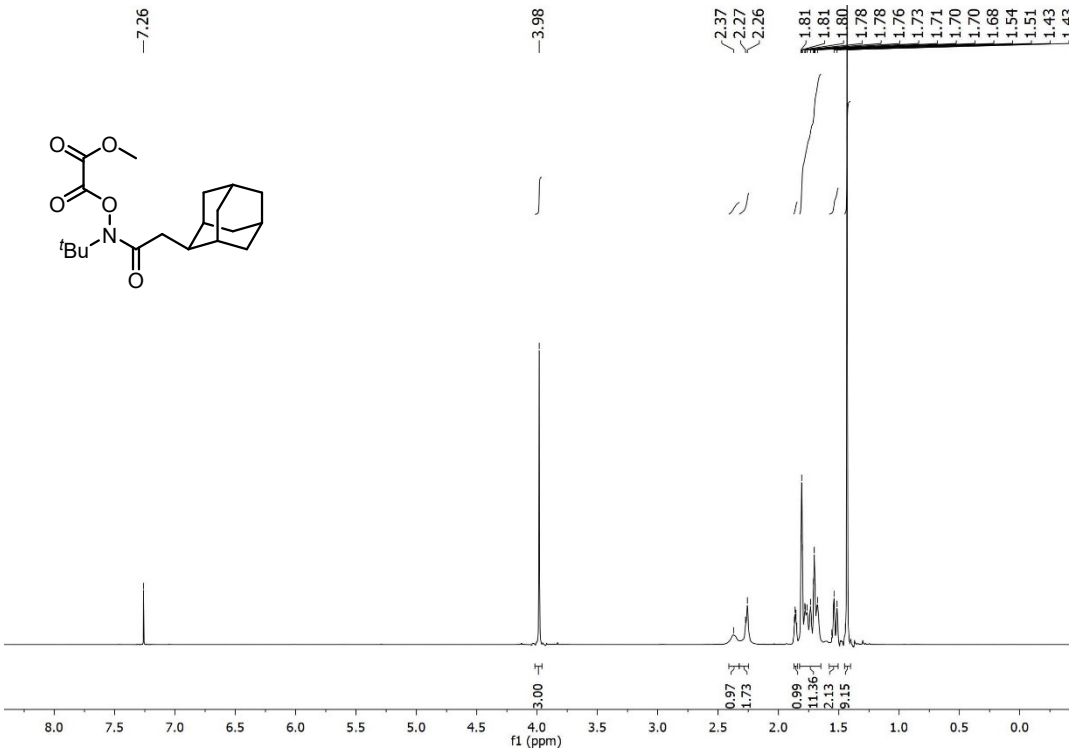
^{13}C NMR spectrum of **12a**



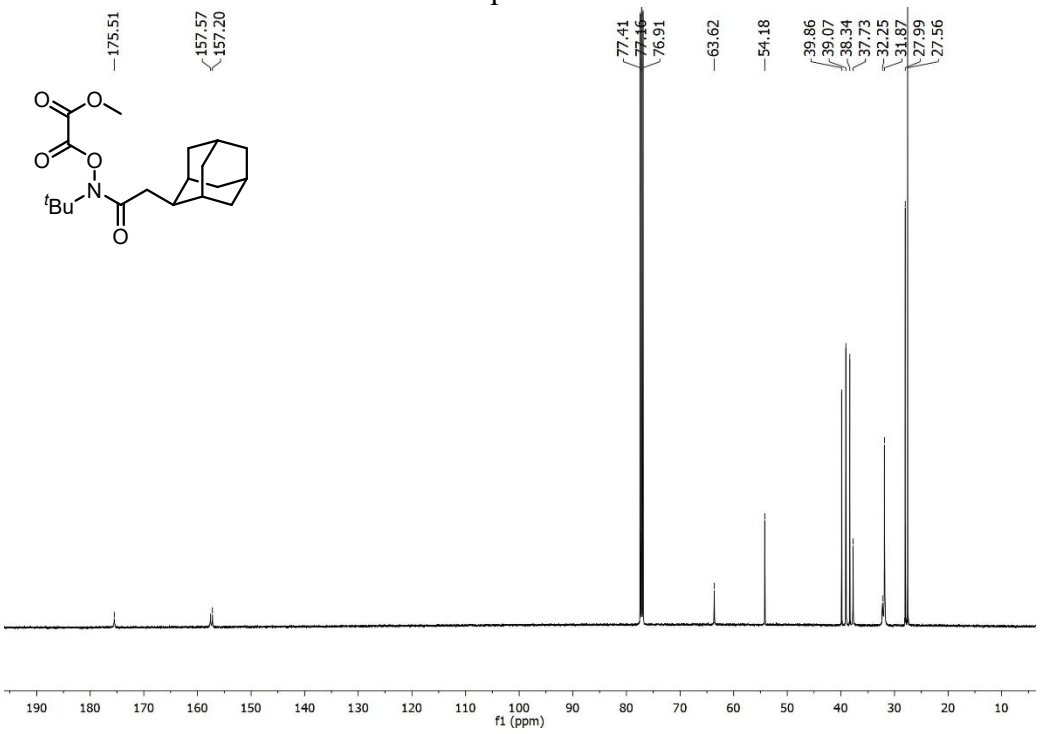
^{1}H NMR spectrum of **16a**



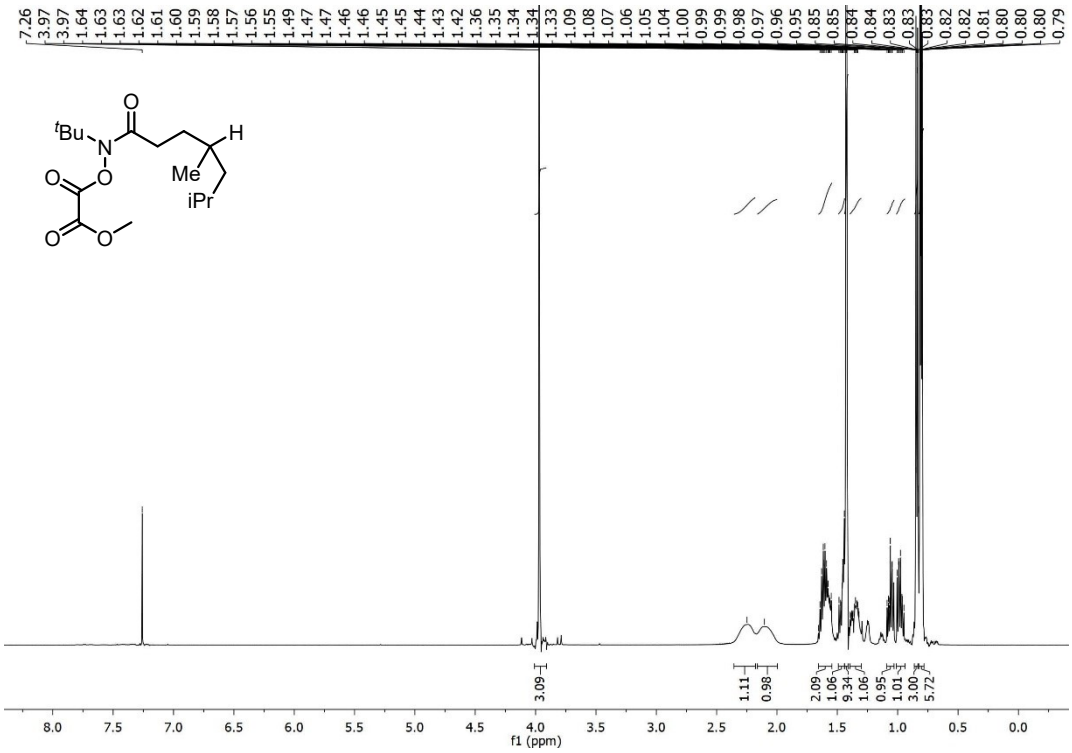
^{13}C NMR spectrum of **16a**



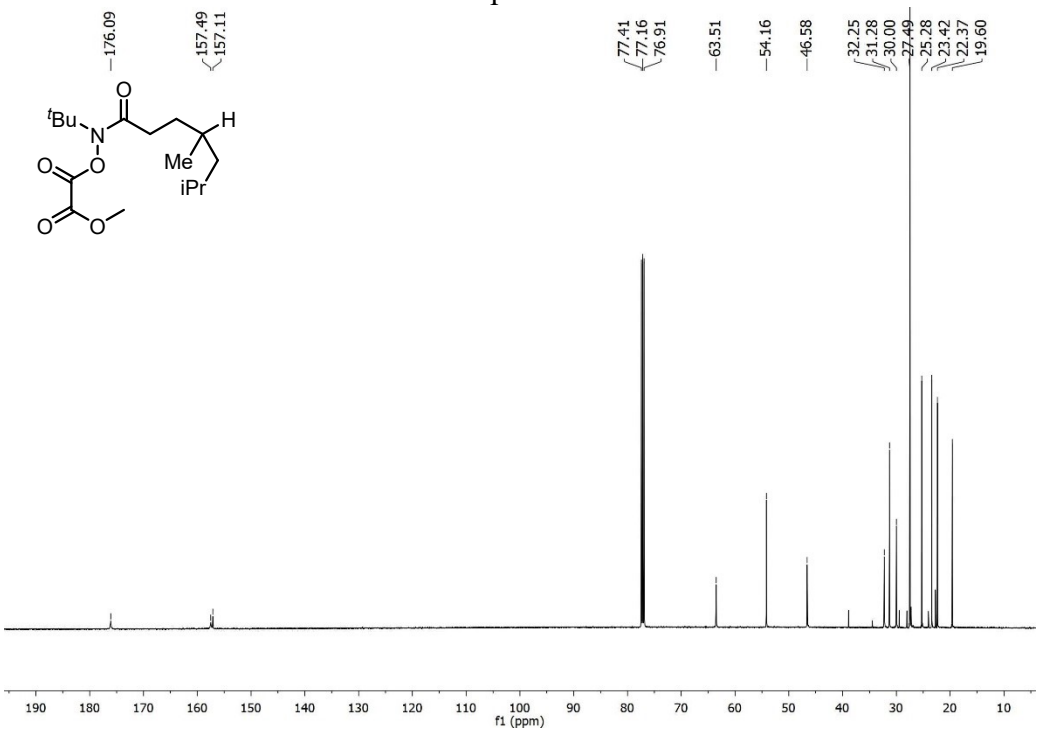
^{1}H NMR spectrum of **17a**



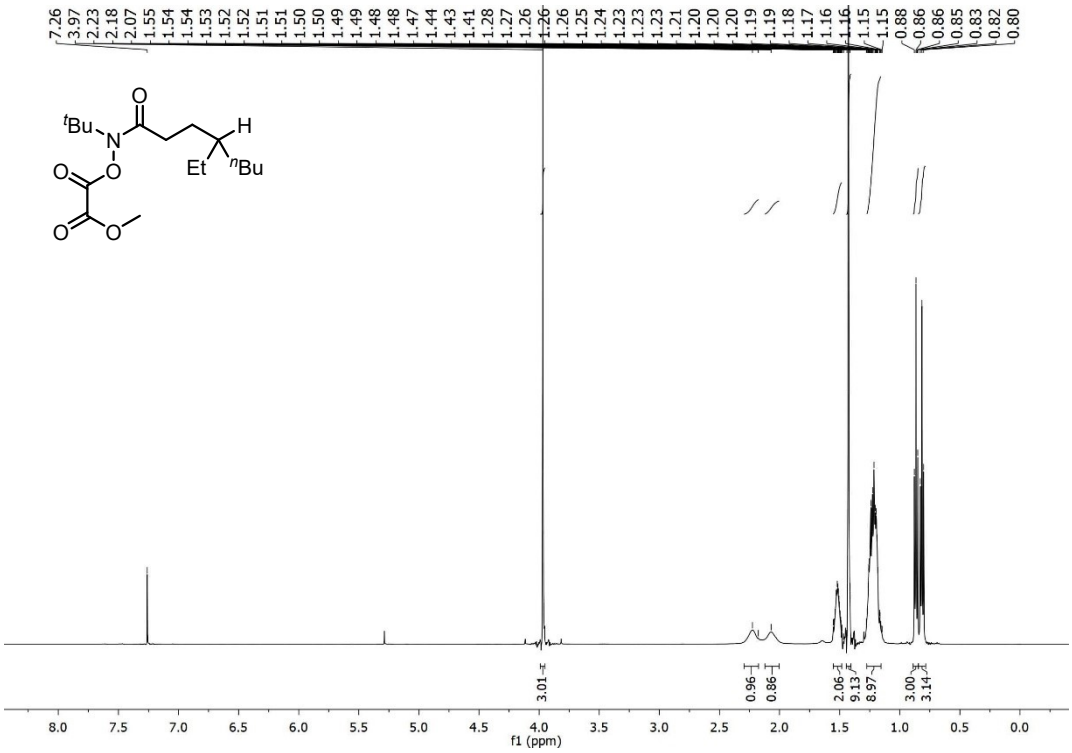
^{13}C NMR spectrum of **17a**



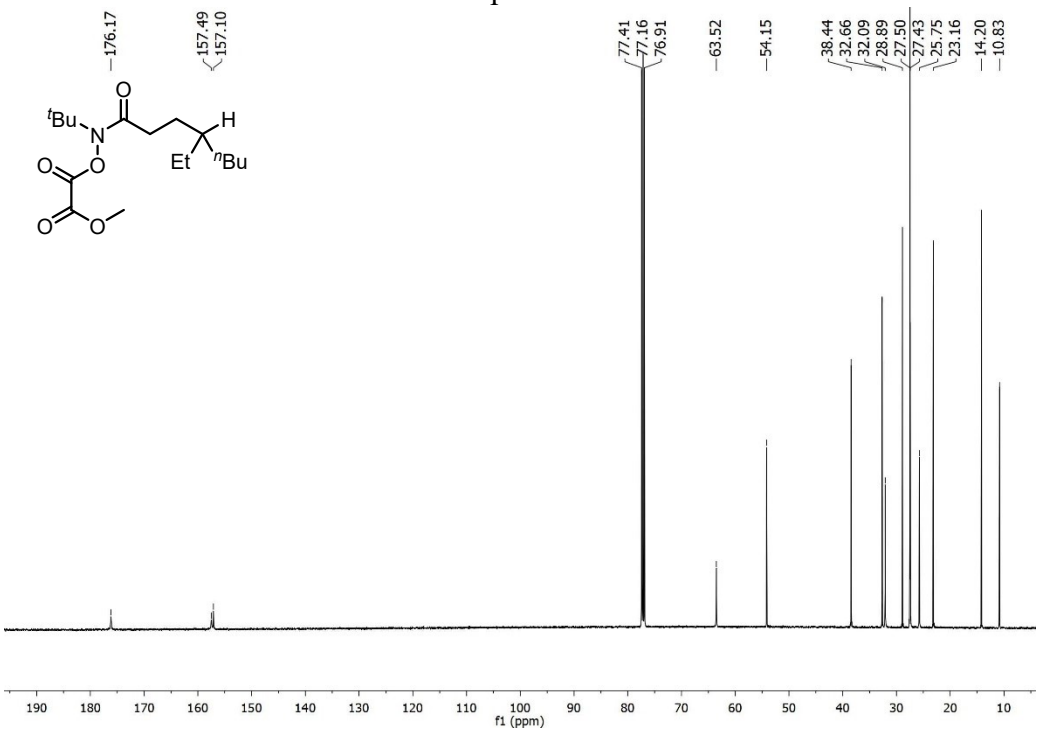
^{1}H NMR spectrum of **18a**



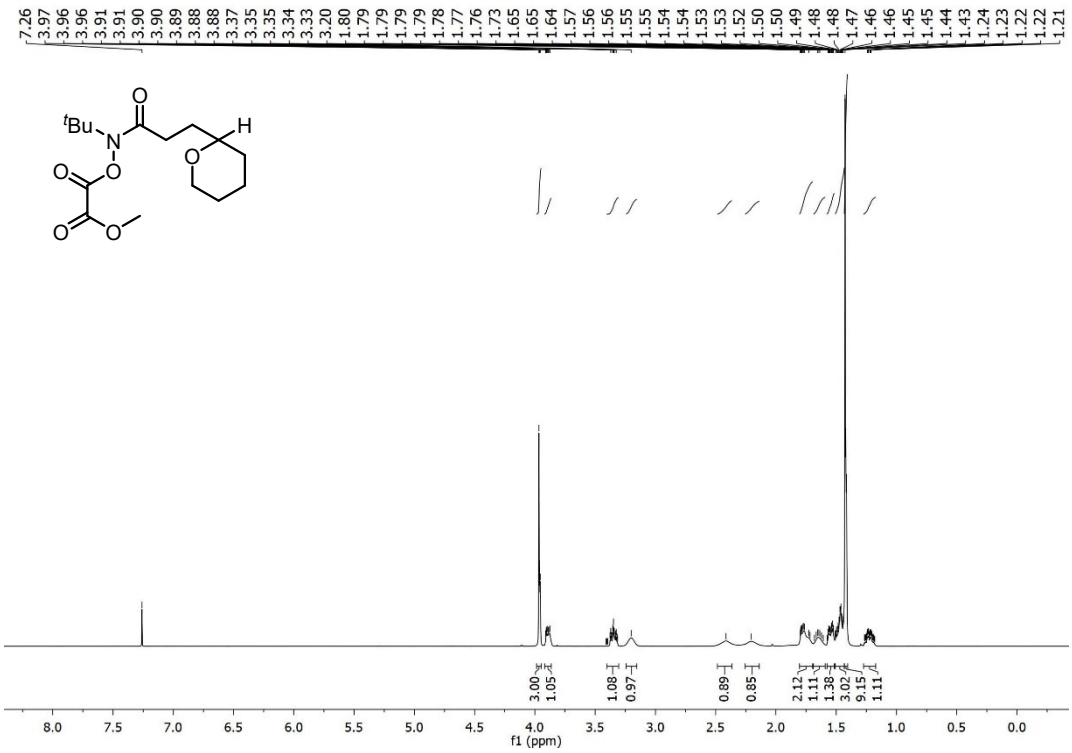
^{13}C NMR spectrum of **18a**



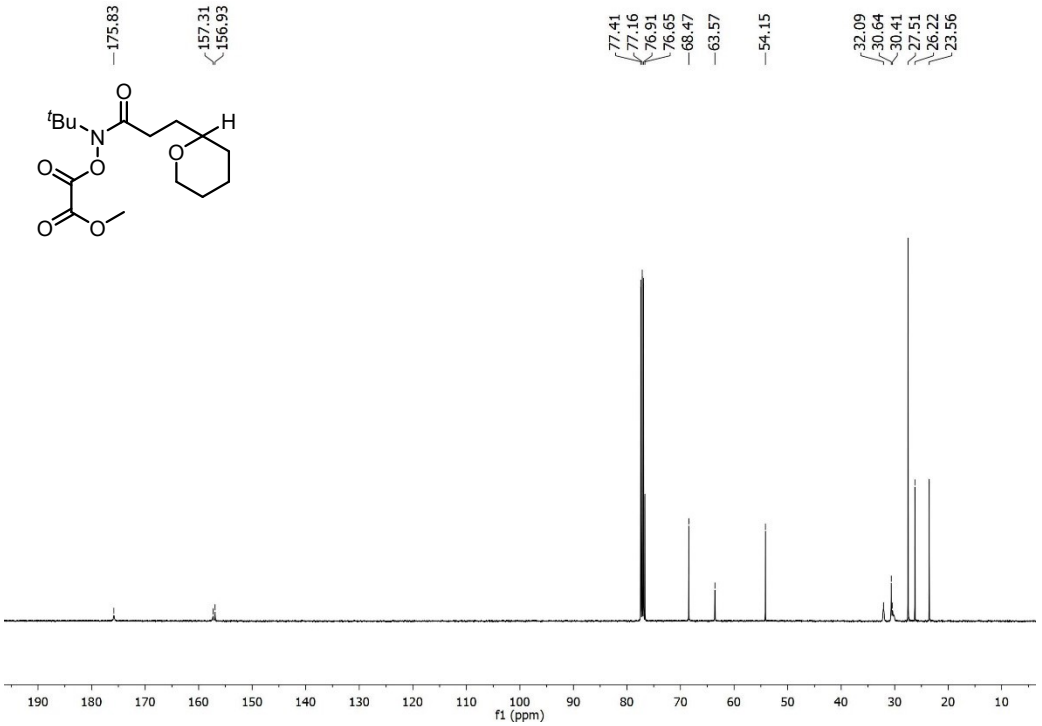
^{1}H NMR spectrum of **19a**



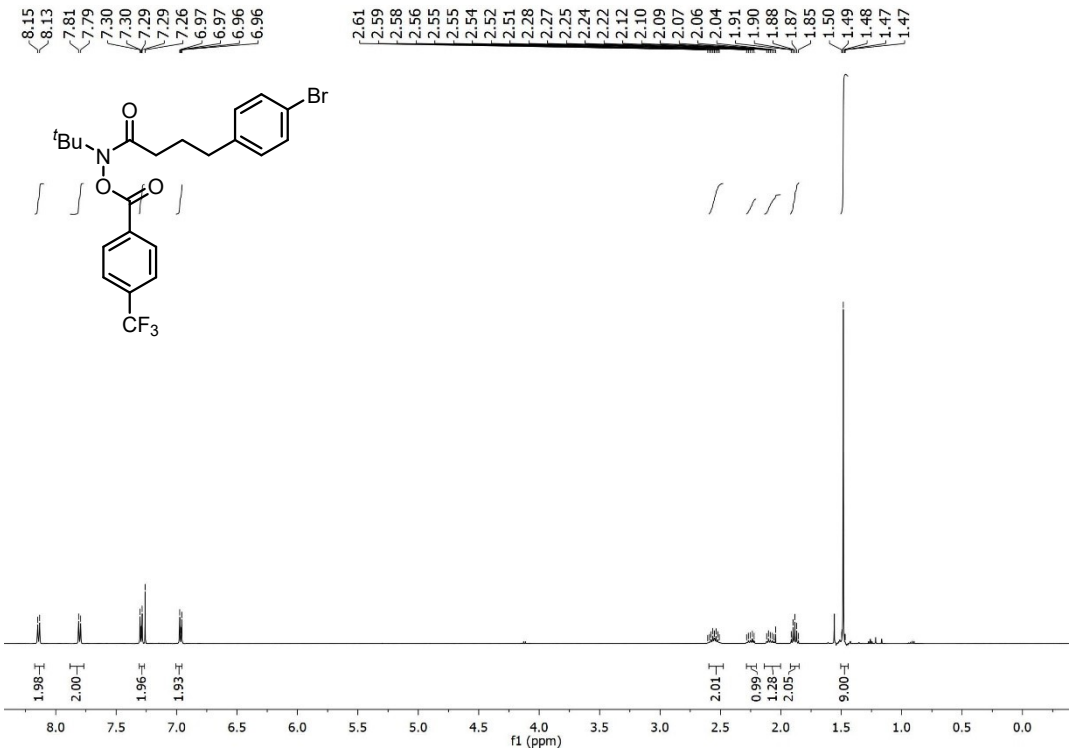
^{13}C NMR spectrum of **19a**



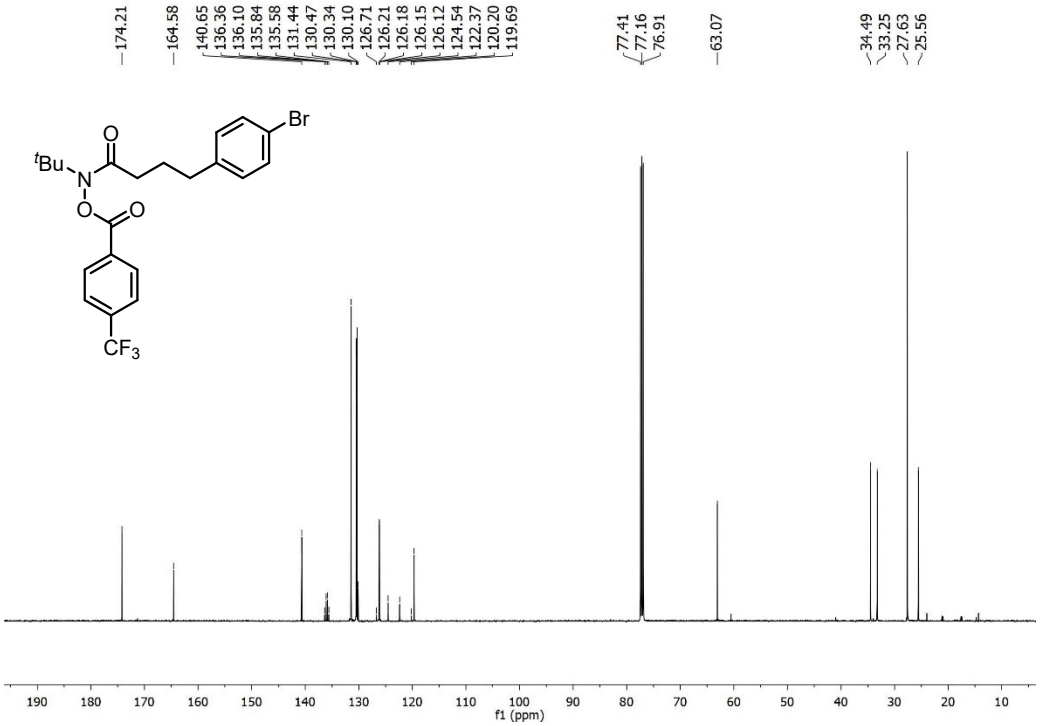
^{1}H NMR spectrum of **24a**



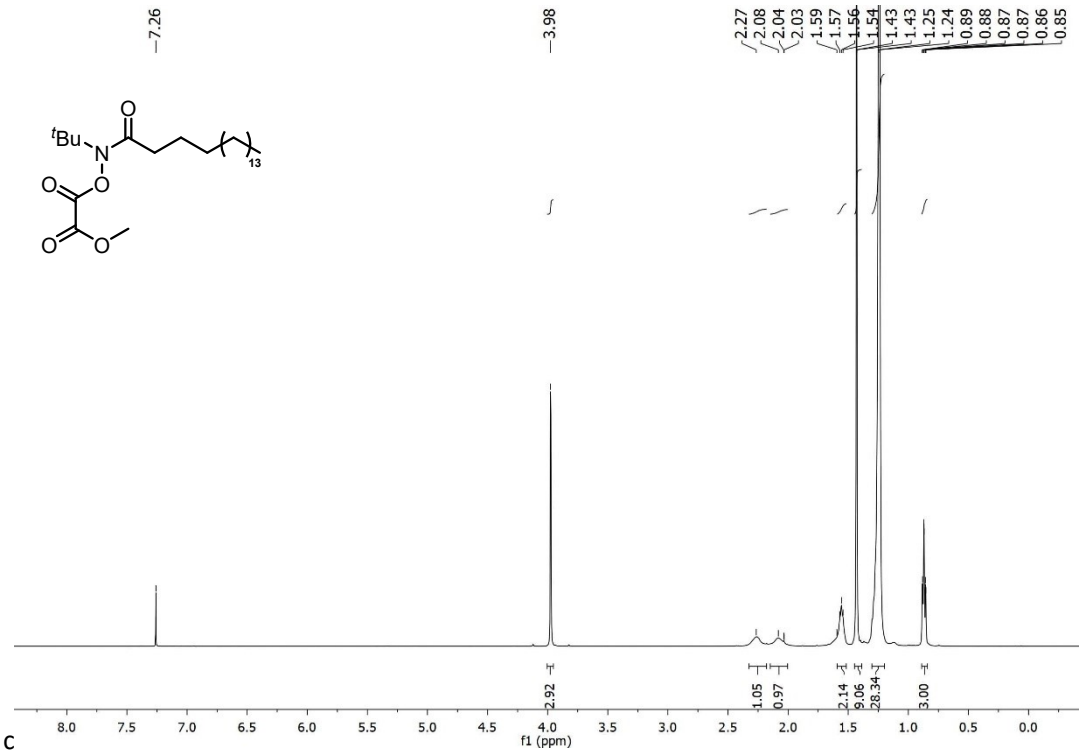
^{13}C NMR spectrum of **24a**



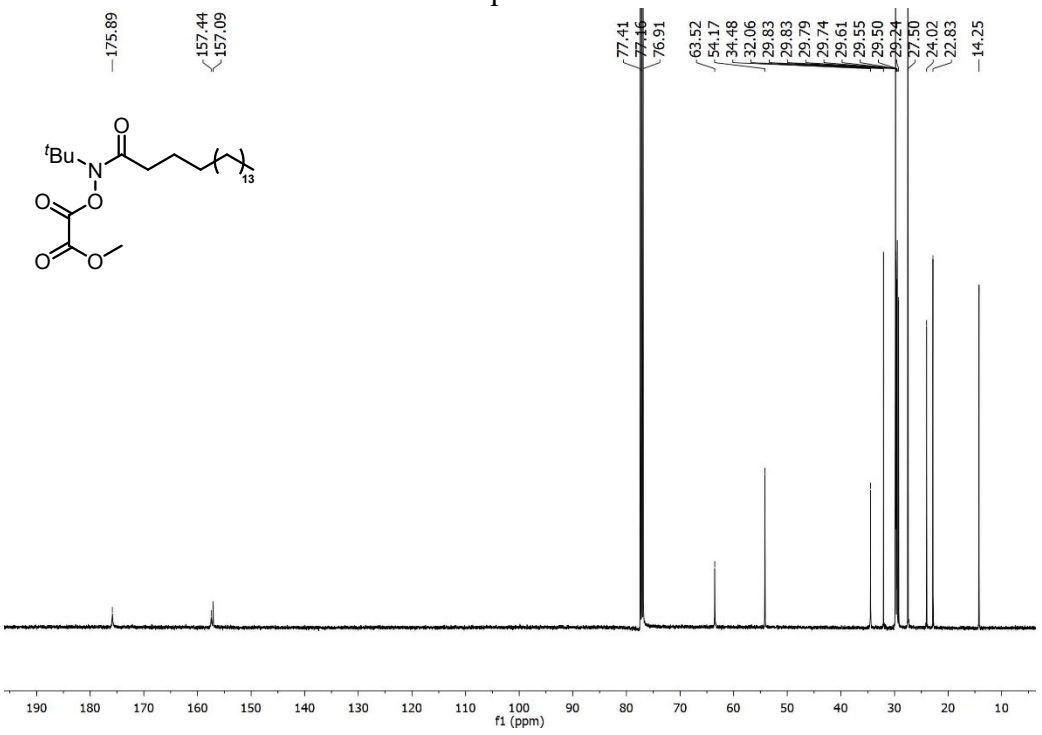
^{1}H NMR spectrum of **30a**



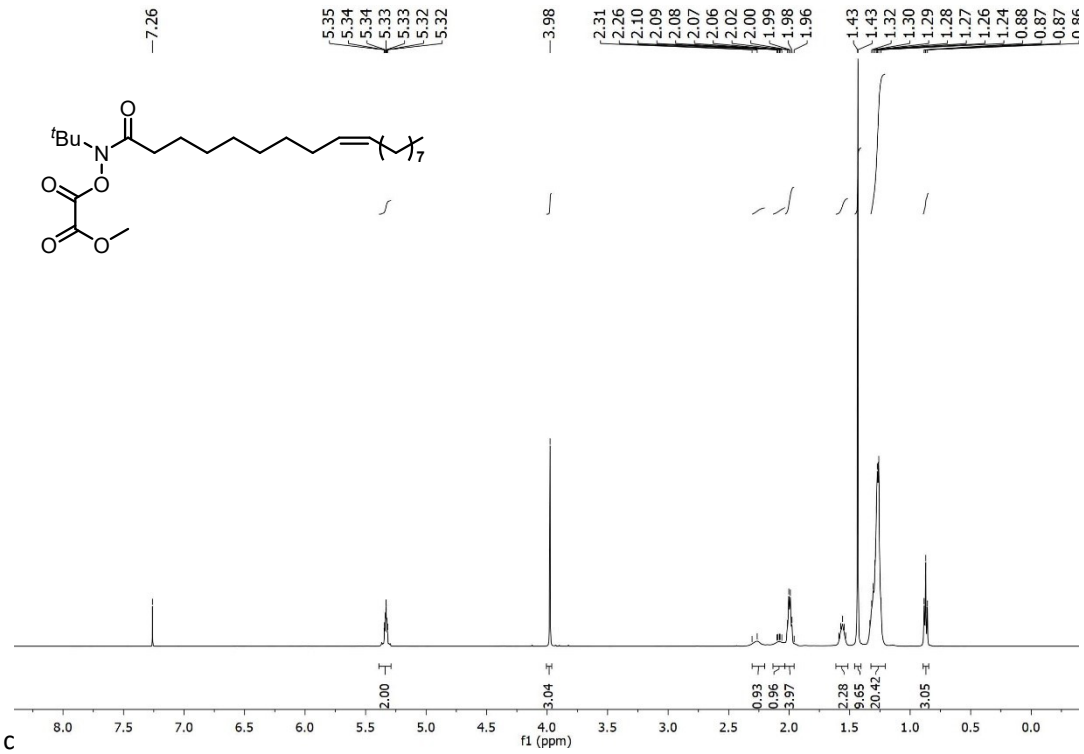
^{13}C NMR spectrum of **30a**



^{1}H NMR spectrum of **32a**

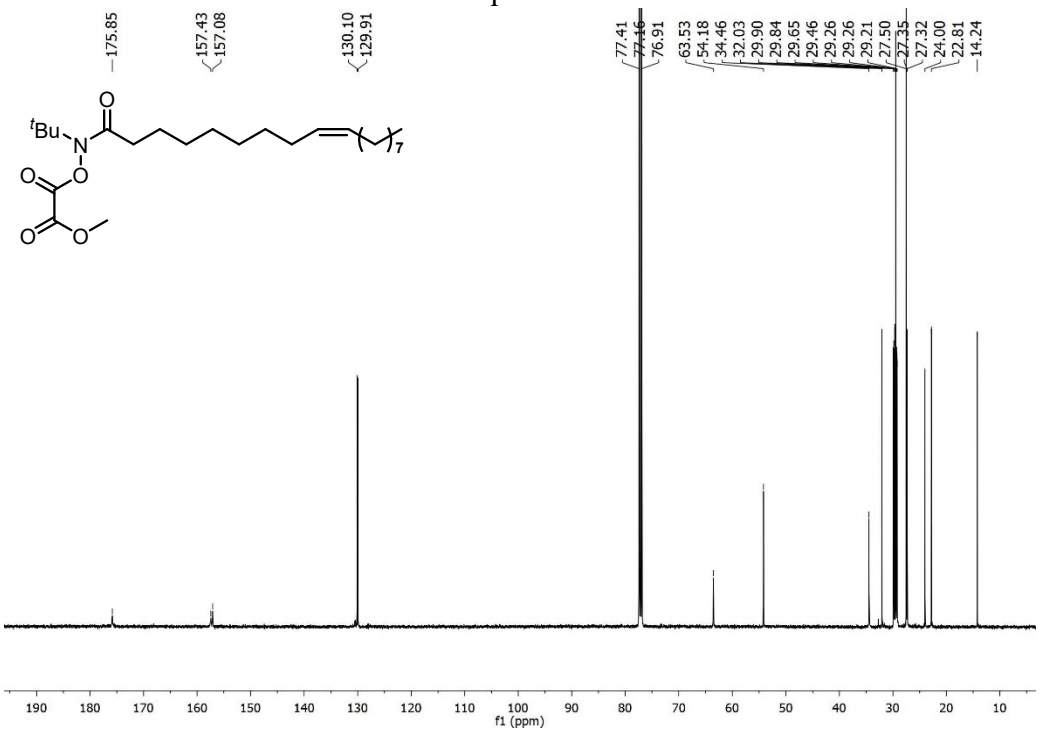


^{13}C NMR spectrum of **32a**

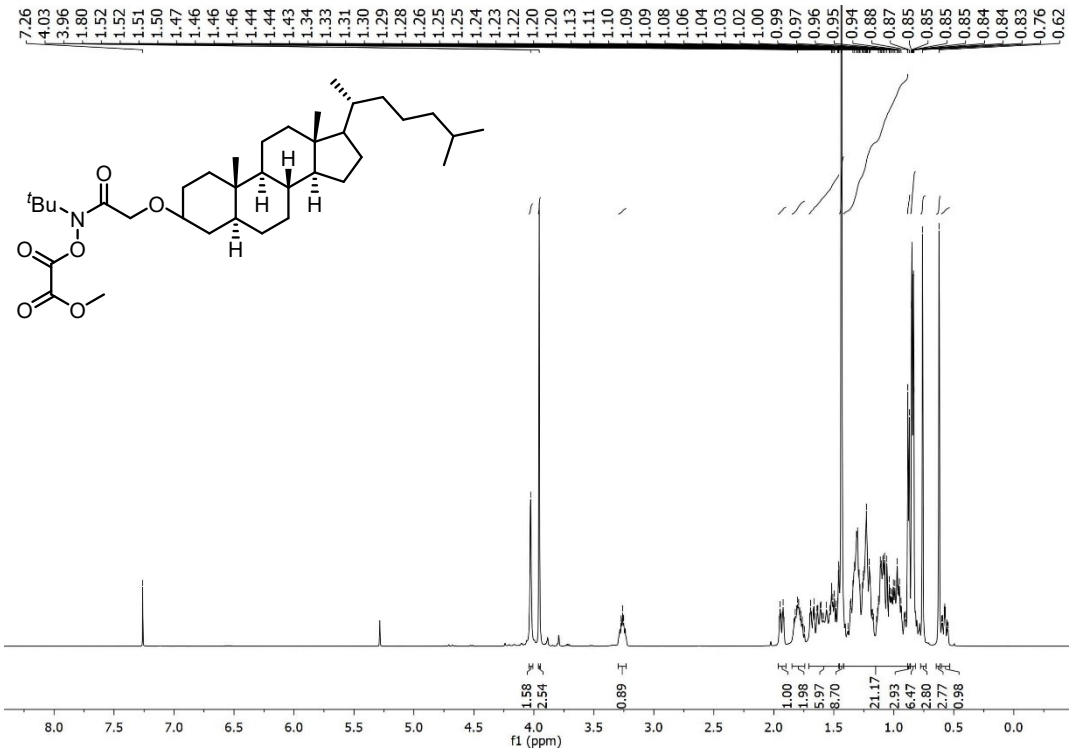


C

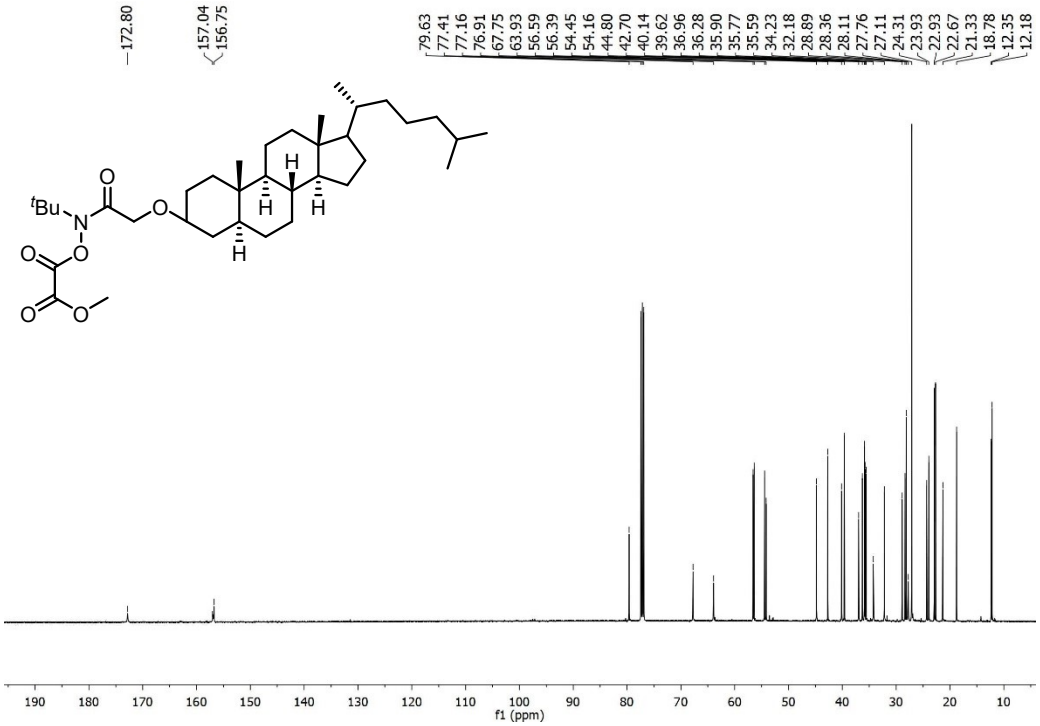
^{1}H NMR spectrum of **33a**



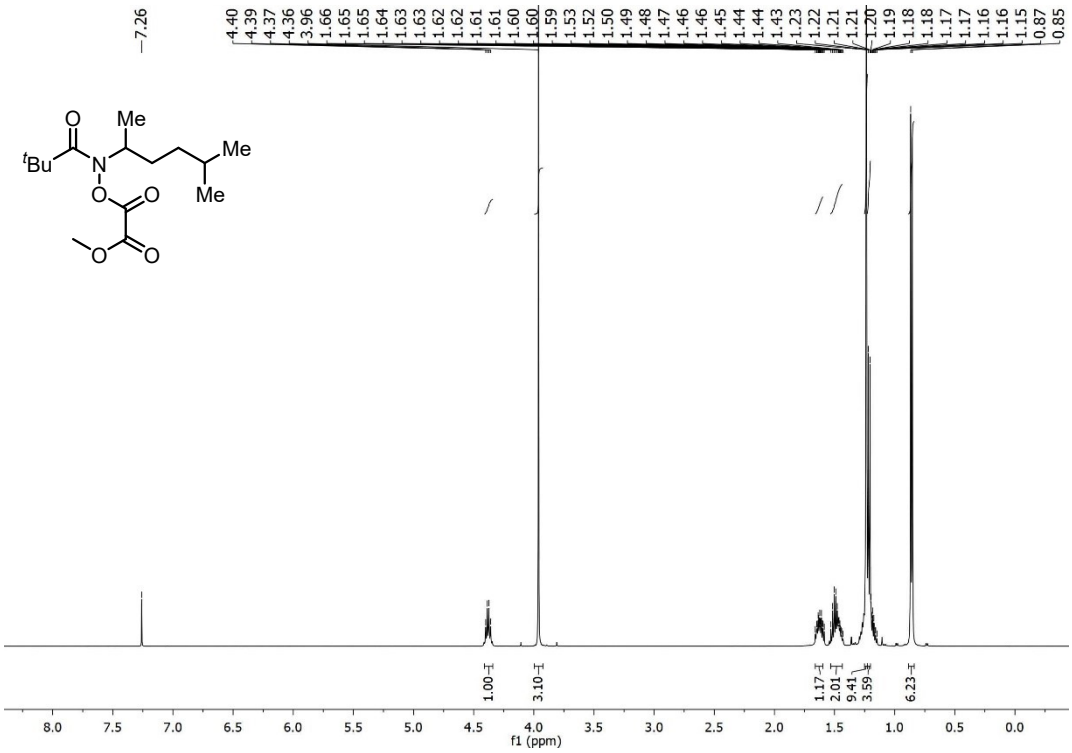
^{13}C NMR spectrum of **33a**



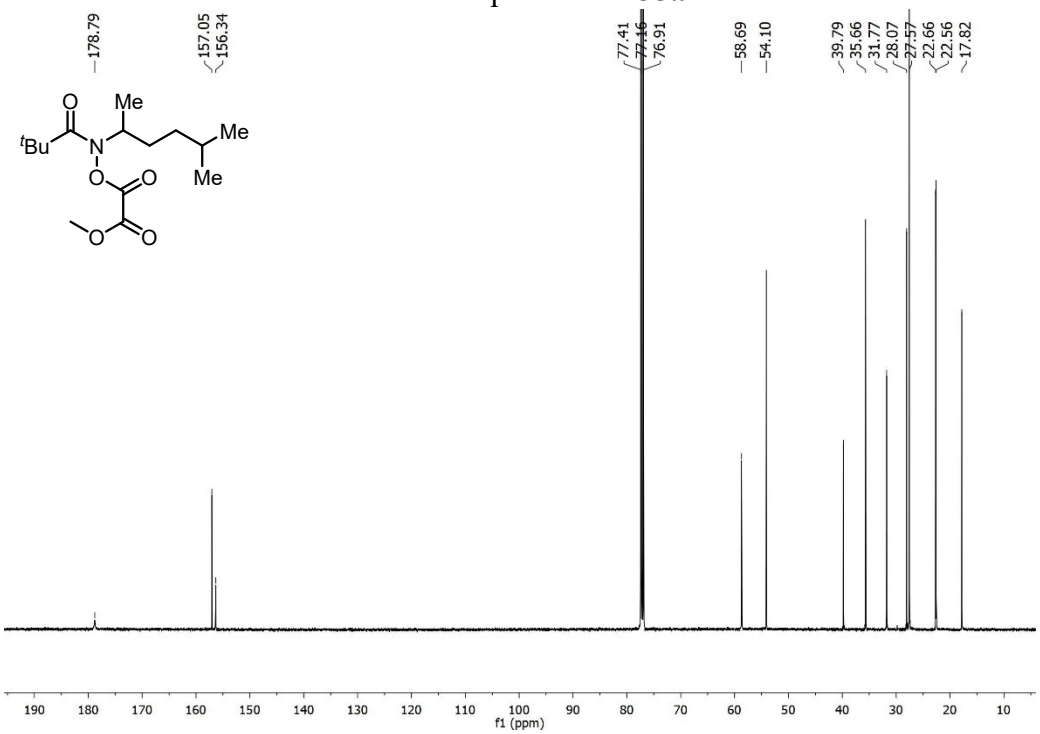
^{1}H NMR spectrum of **34a**



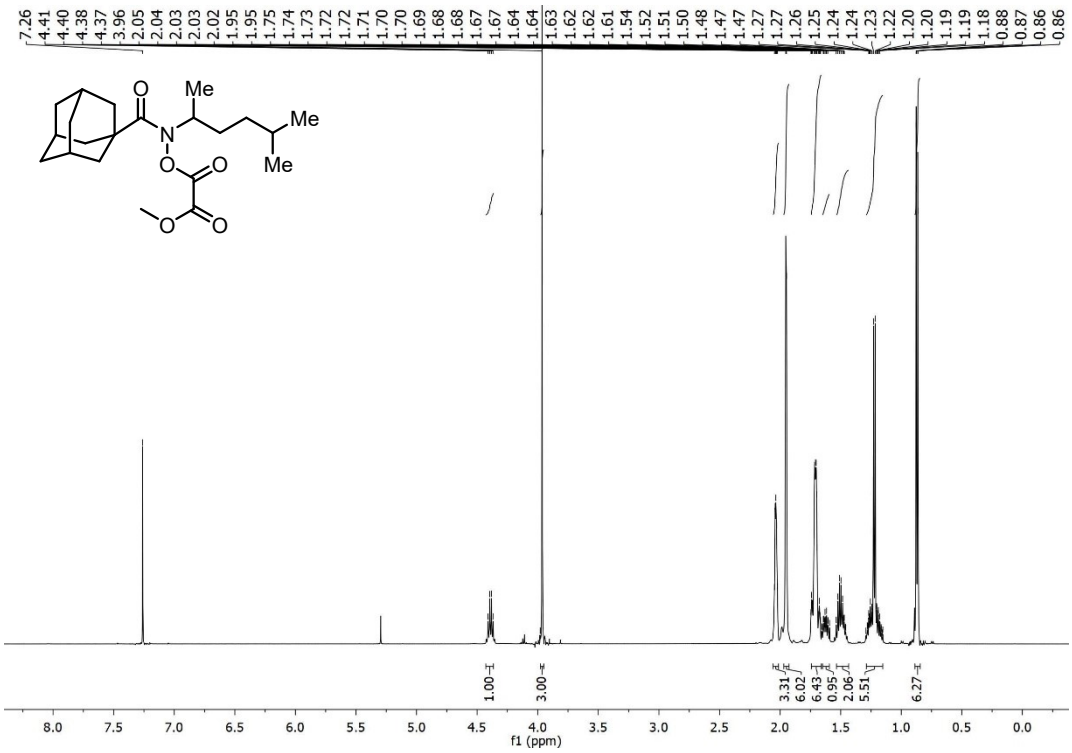
^{13}C NMR spectrum of **34a**



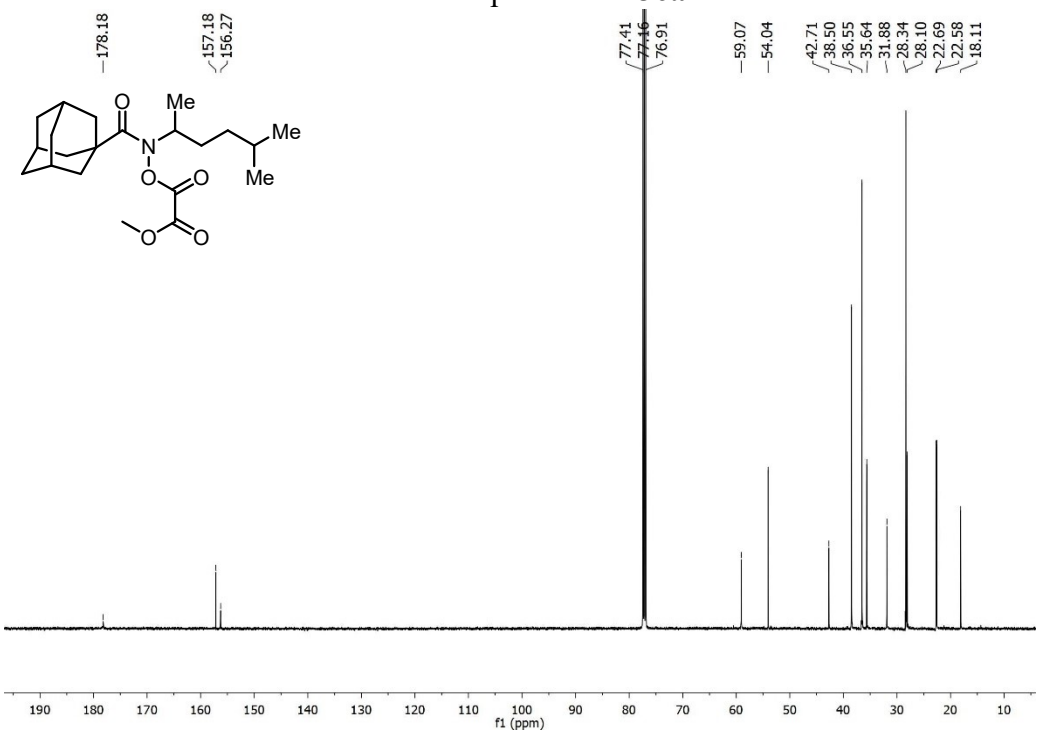
^{1}H NMR spectrum of **35a**



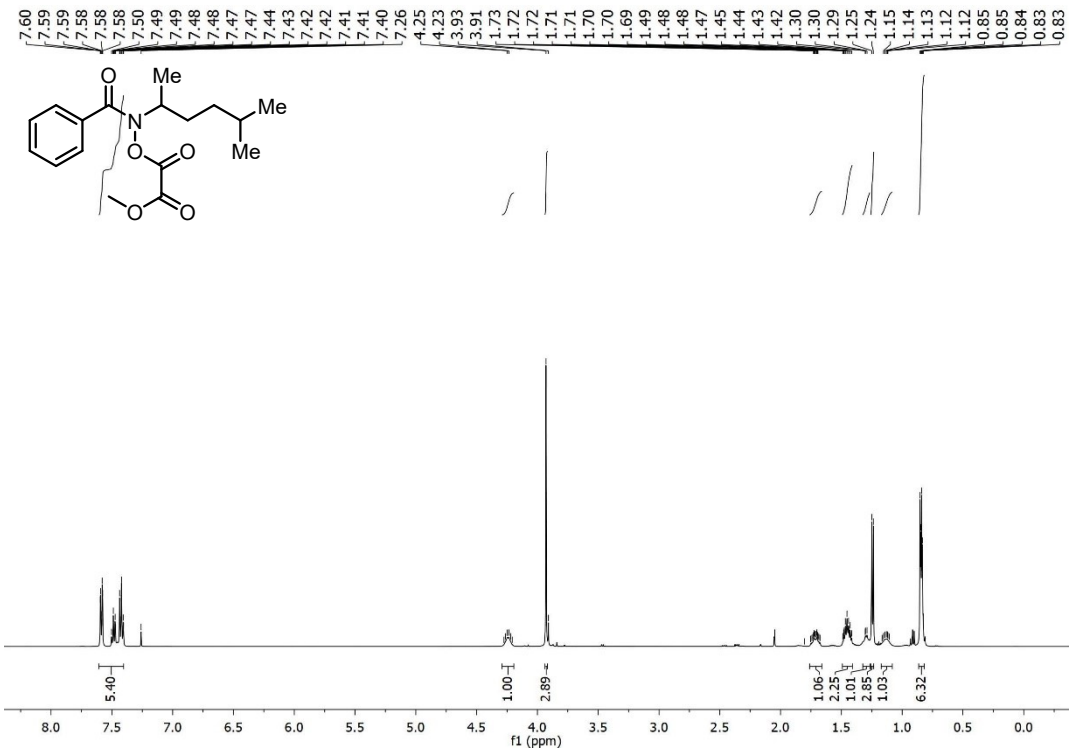
^{13}C NMR spectrum of **35a**



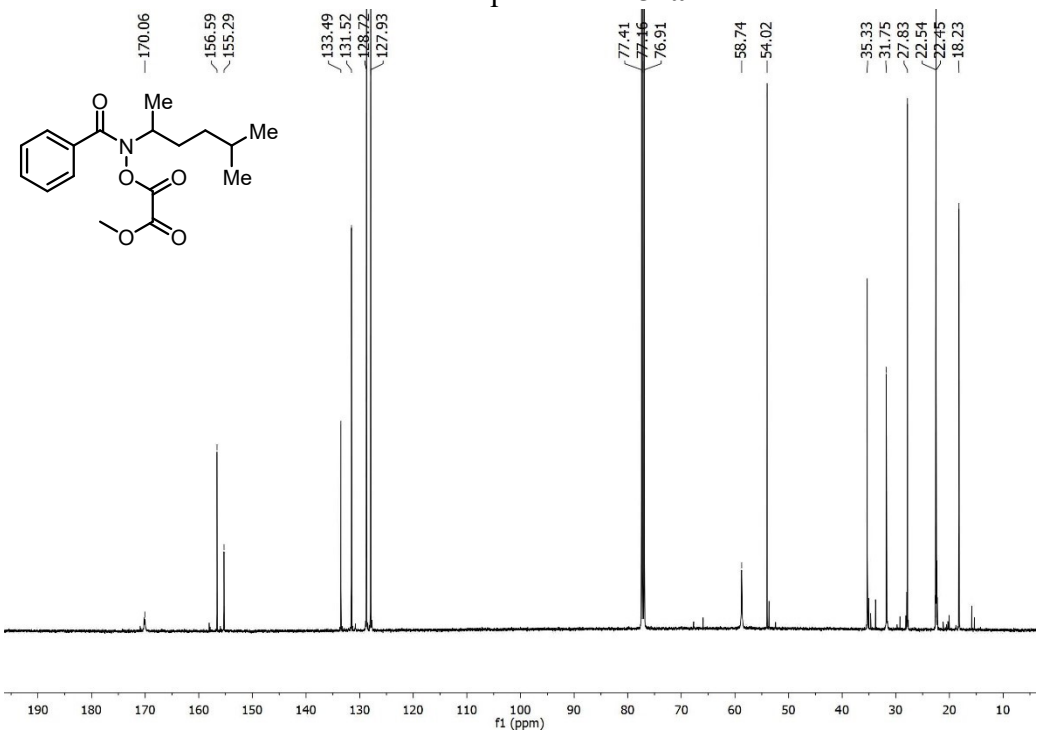
^{1}H NMR spectrum of **36a**



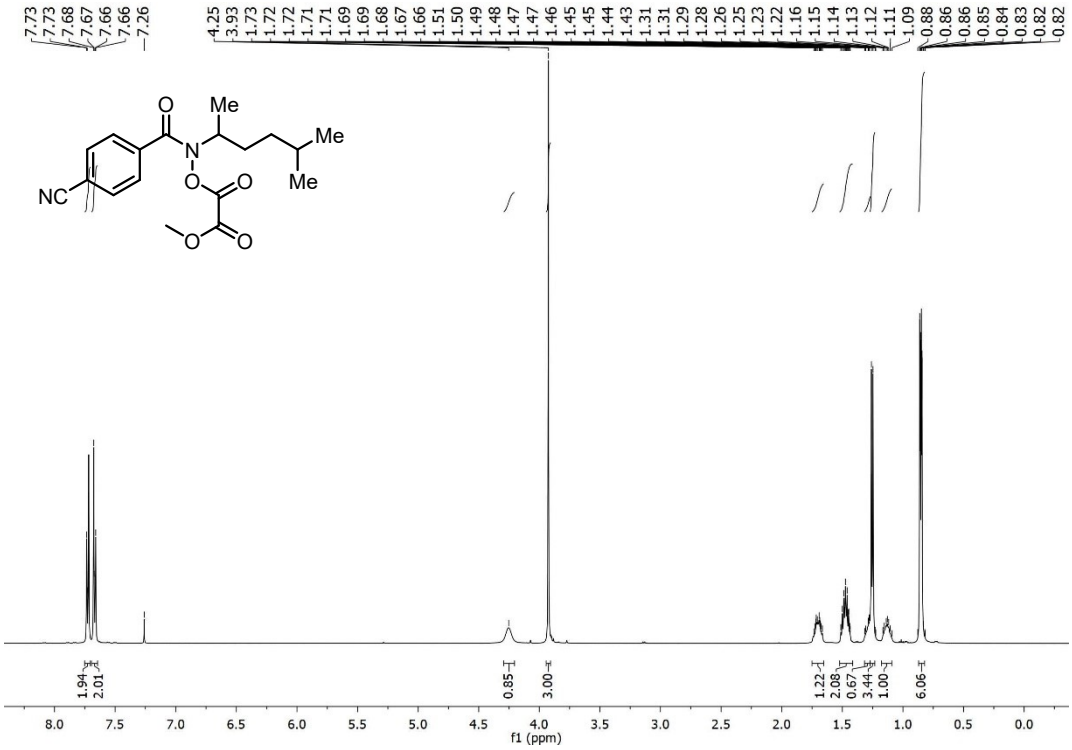
^{13}C NMR spectrum of **36a**



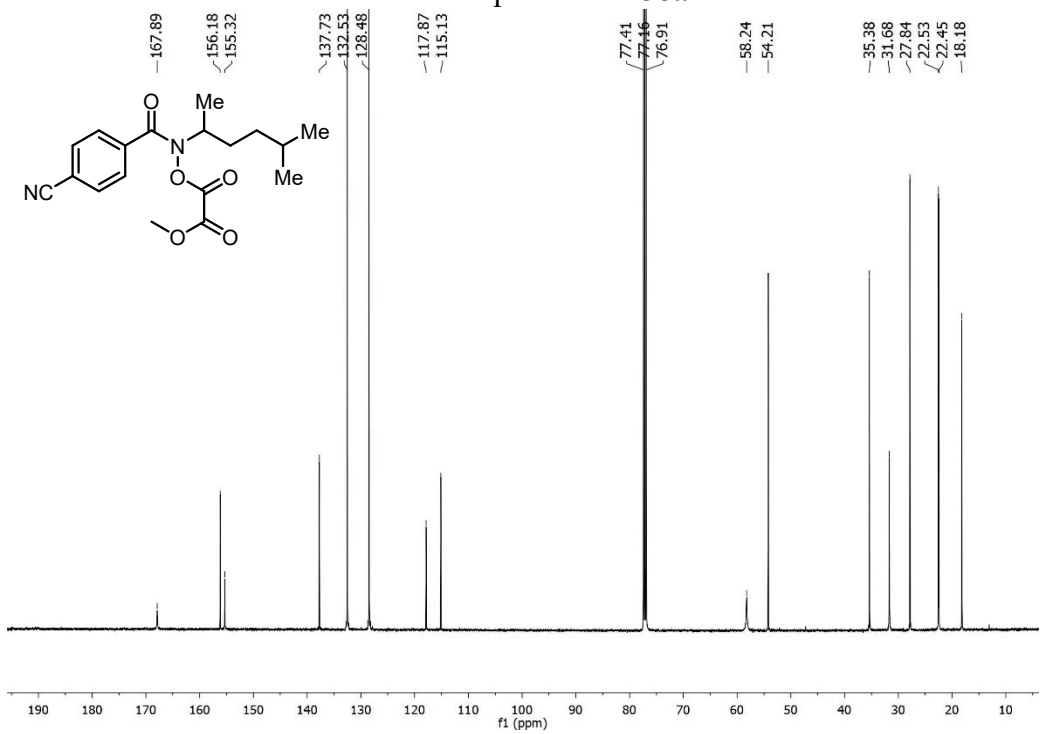
^{1}H NMR spectrum of **37a**



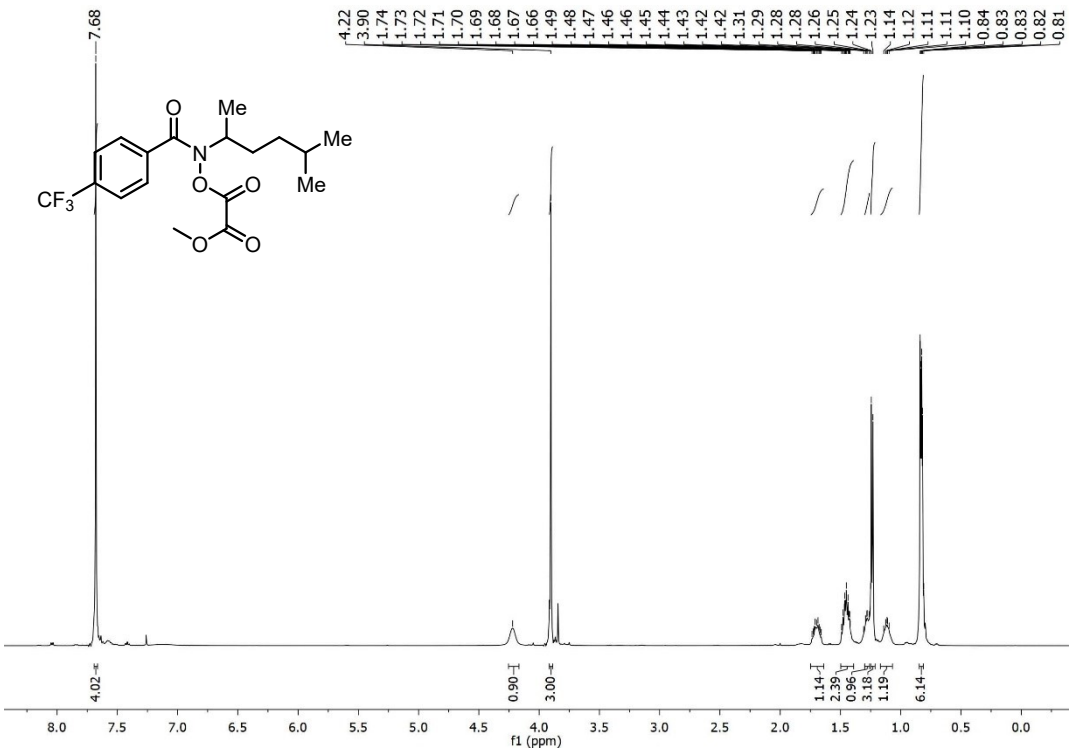
^{13}C NMR spectrum of **37a**



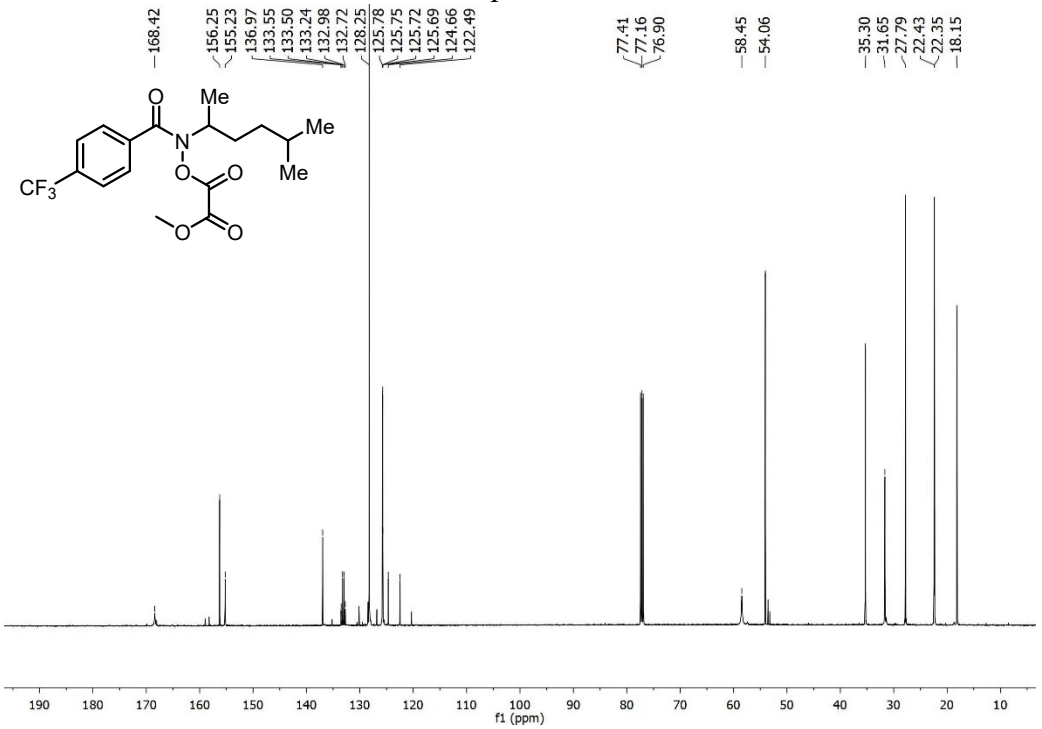
^{1}H NMR spectrum of **38a**



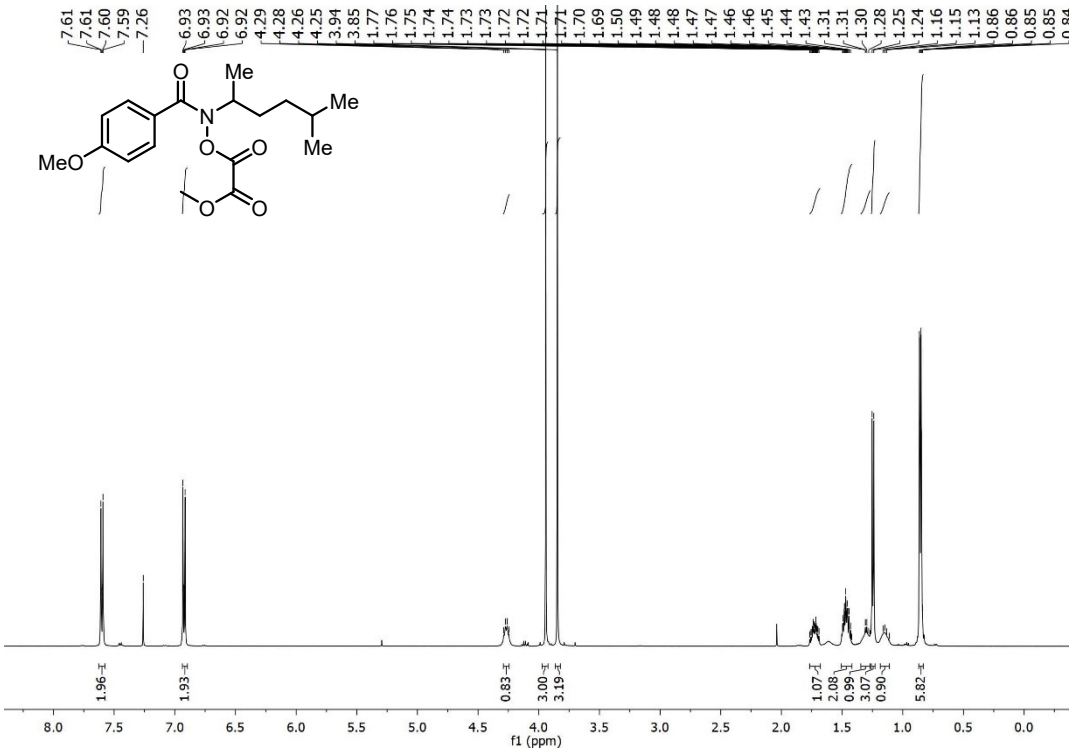
^{13}C NMR spectrum of **38a**



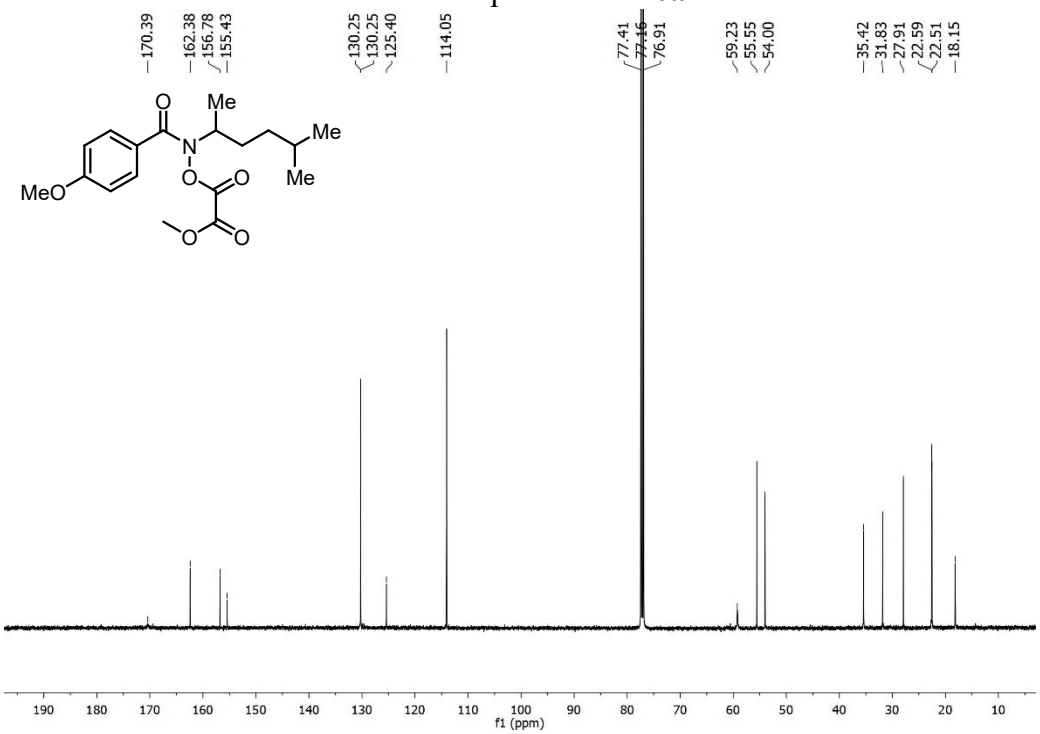
^{1}H NMR spectrum of **39a**



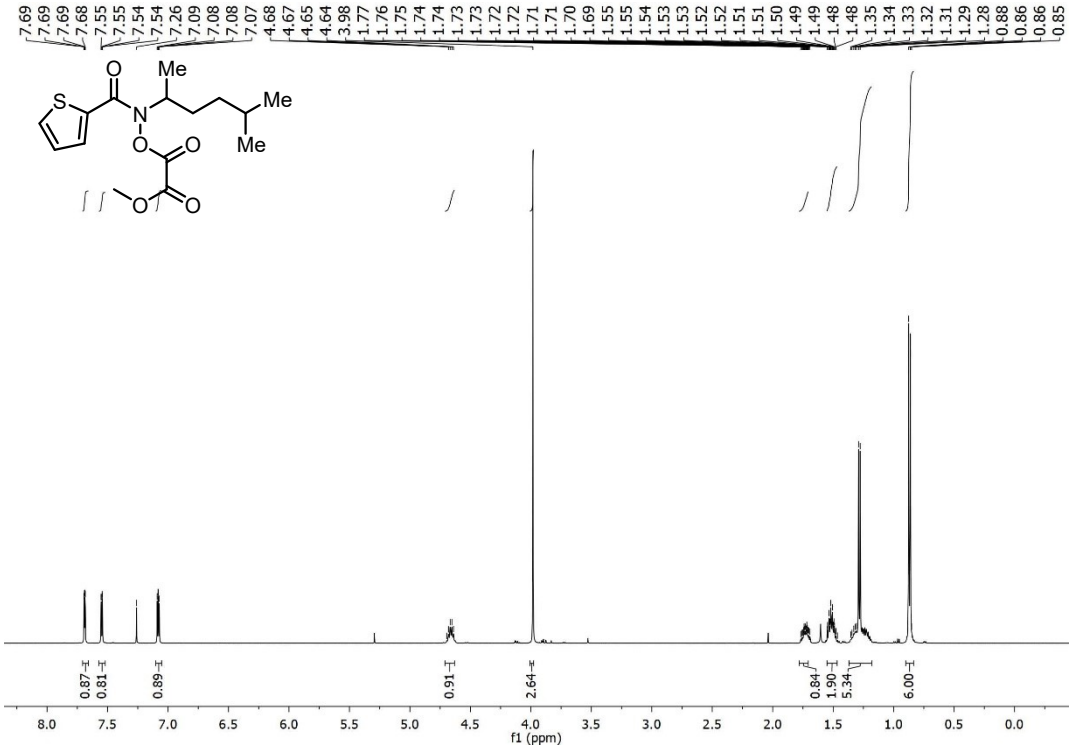
^{13}C NMR spectrum of **39a**



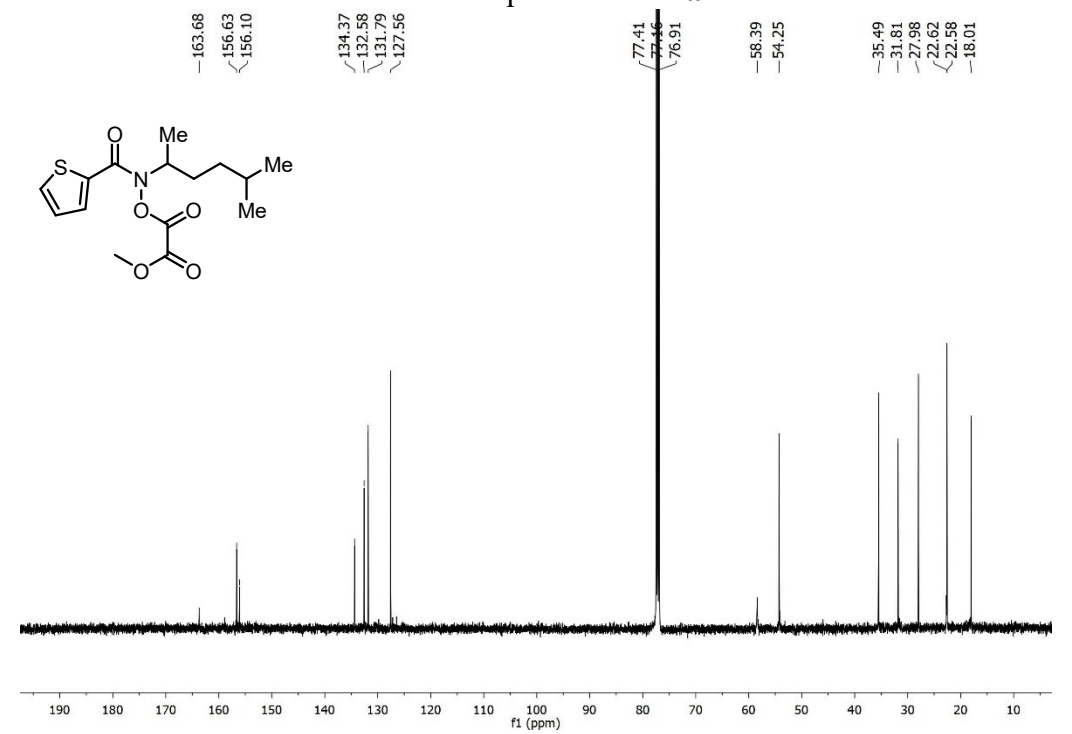
^{1}H NMR spectrum of **40a**



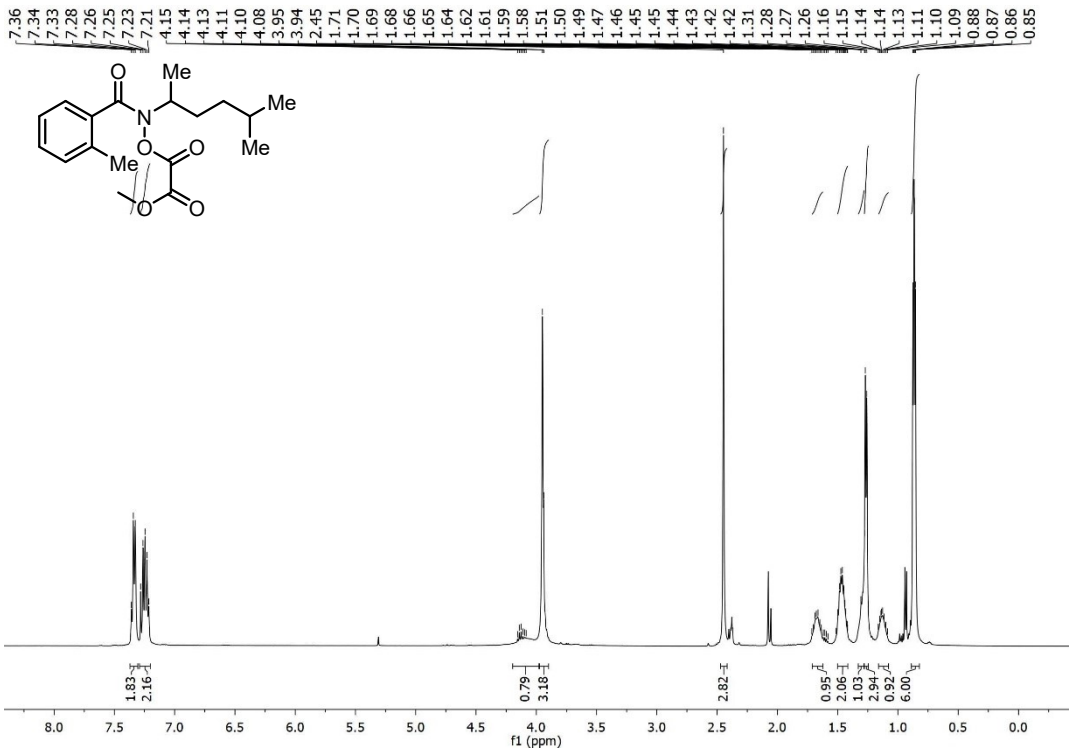
^{13}C NMR spectrum of **40a**



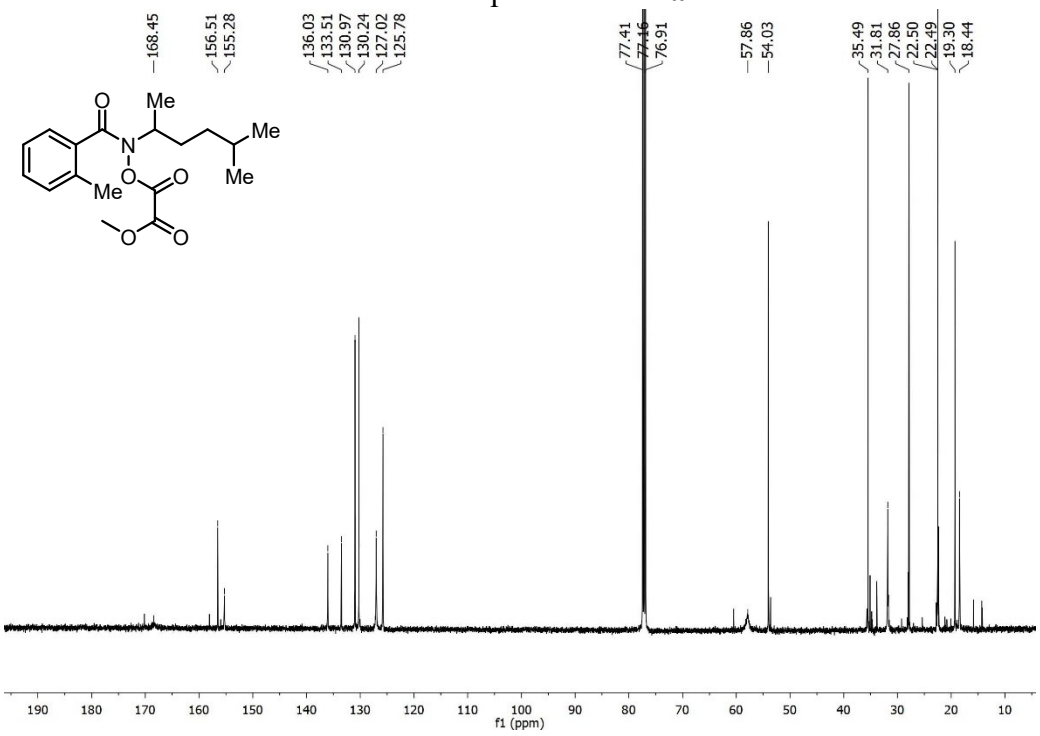
^{1}H NMR spectrum of **41a**



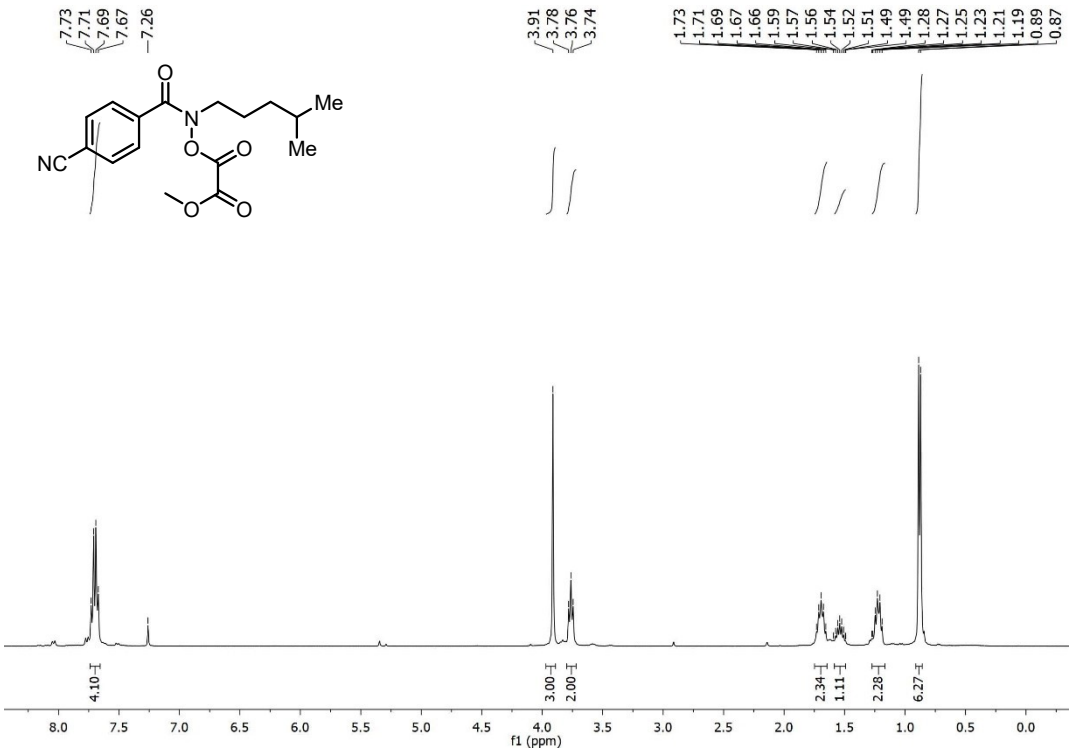
^{13}C NMR spectrum of **41a**



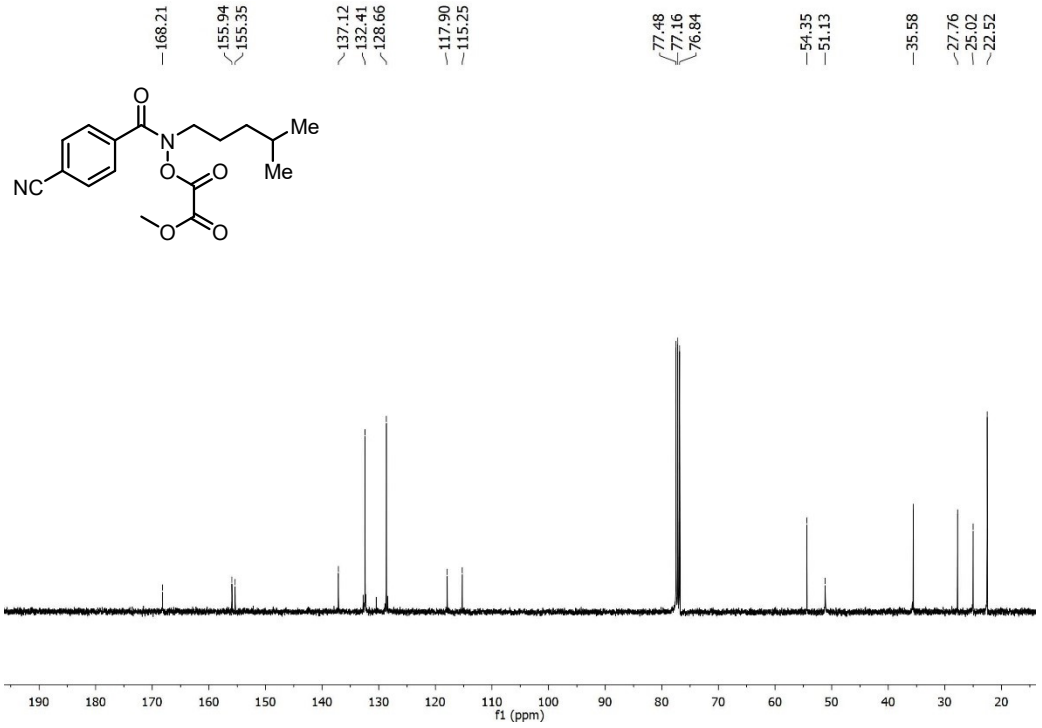
^{1}H NMR spectrum of **42a**



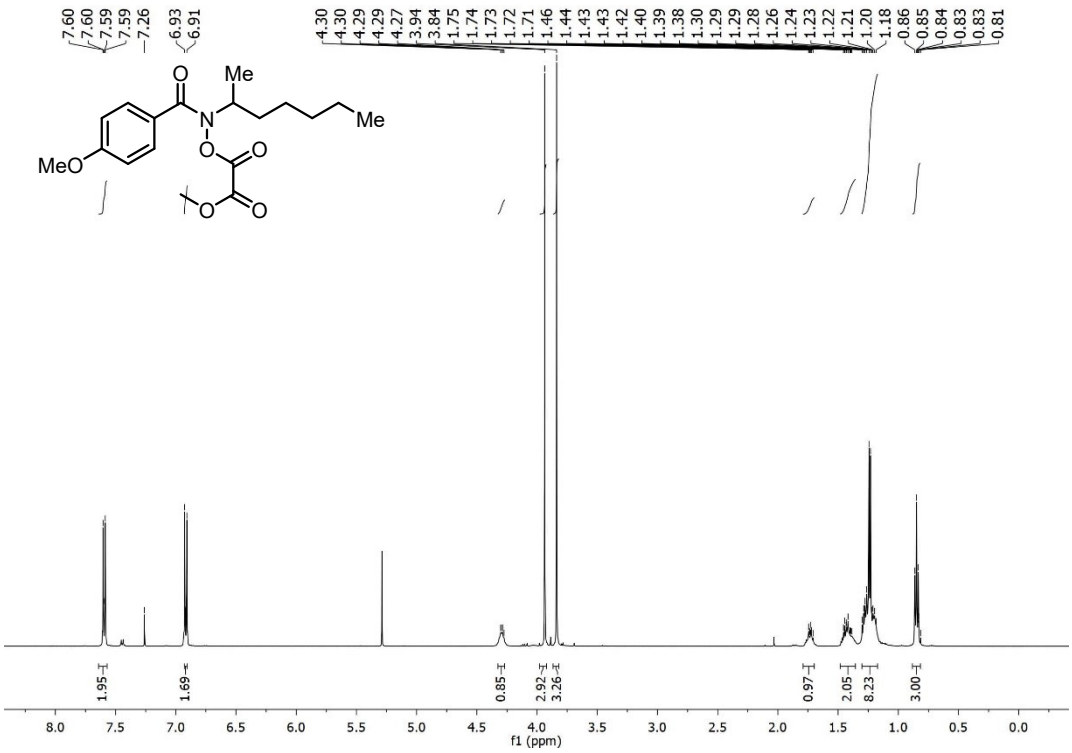
^{13}C NMR spectrum of **42a**



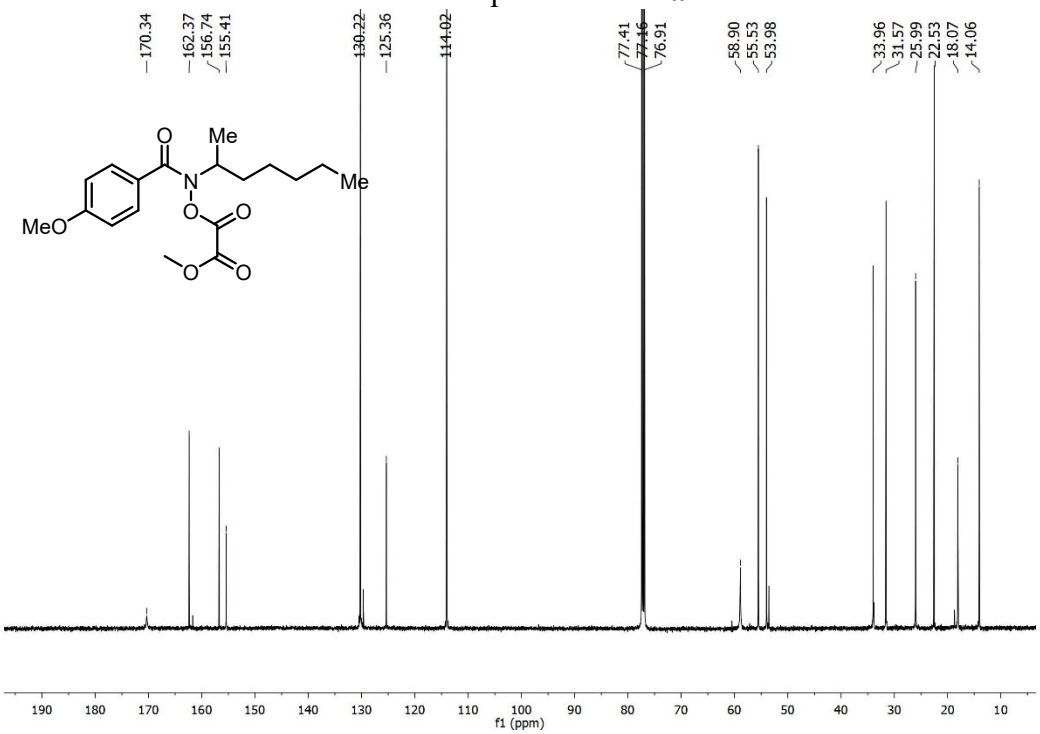
^{1}H NMR spectrum of **43a**



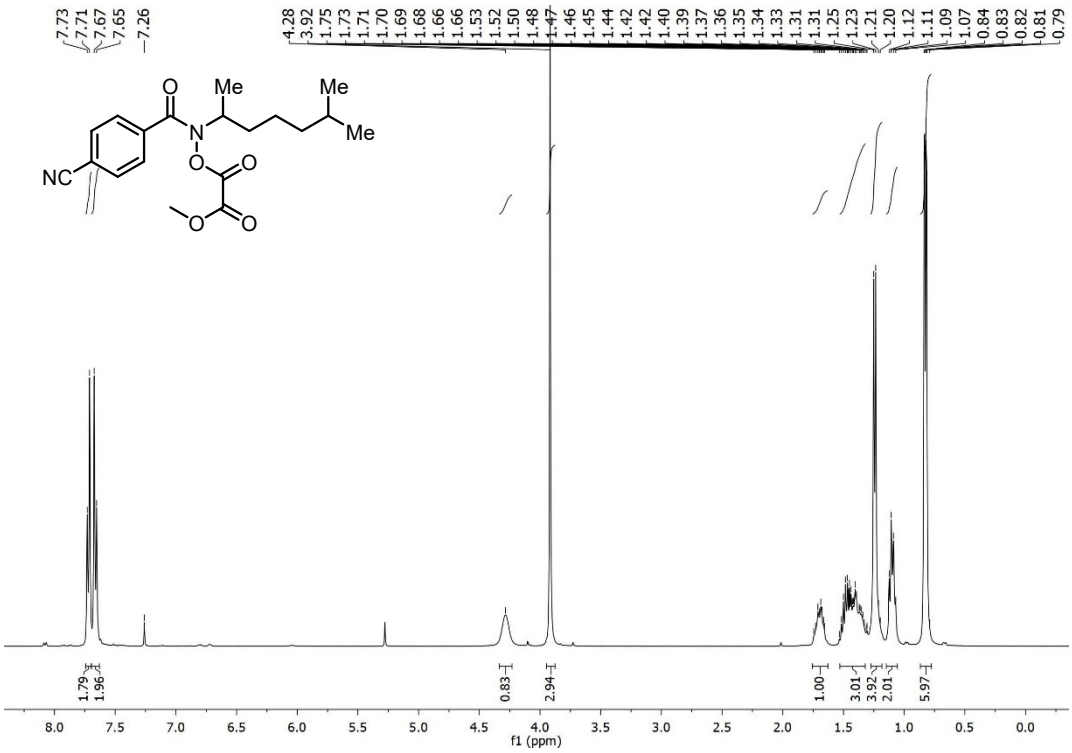
^{13}C NMR spectrum of **43a**



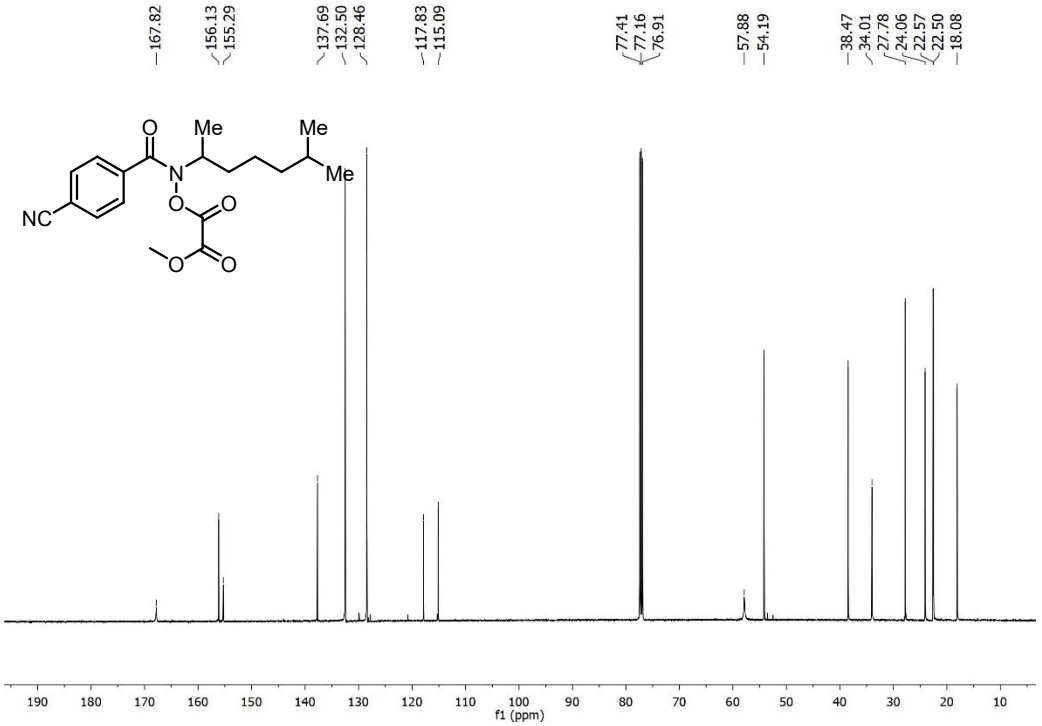
^{1}H NMR spectrum of **44a**



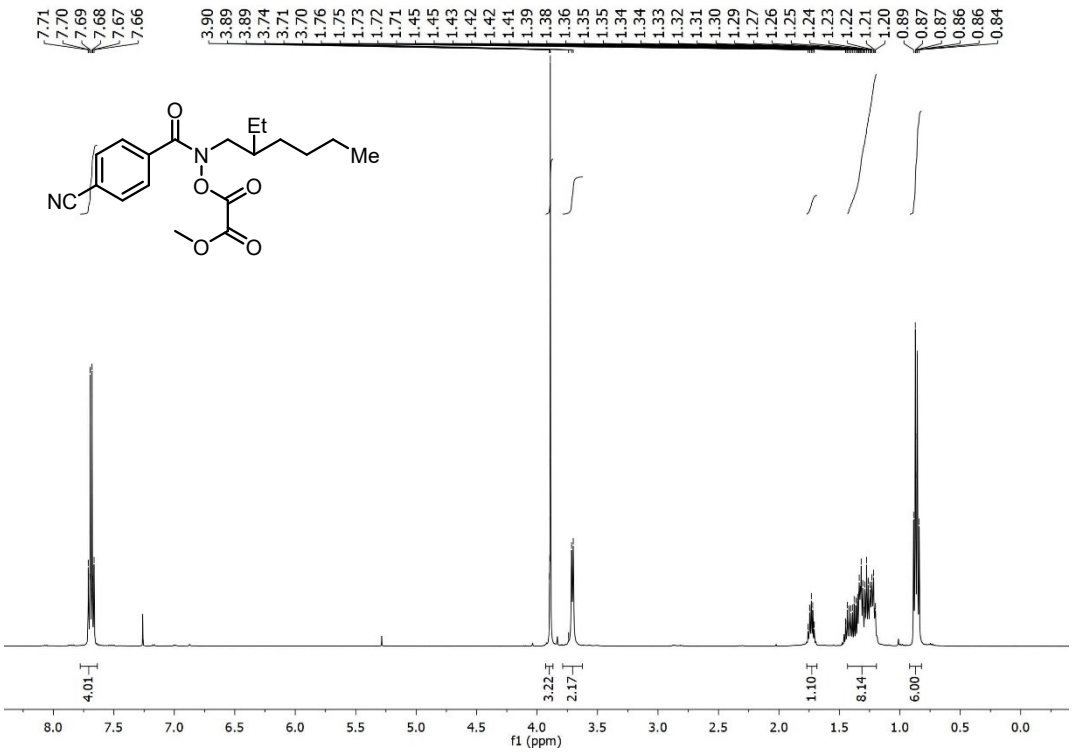
^{13}C NMR spectrum of **44a**



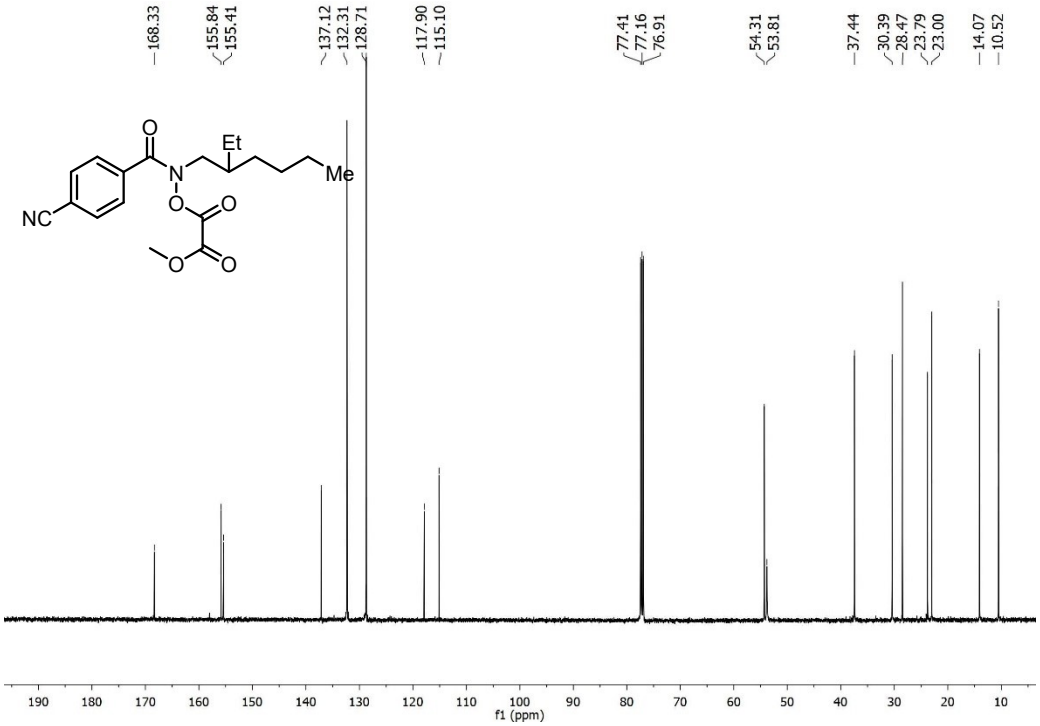
^{1}H NMR spectrum of **45a**



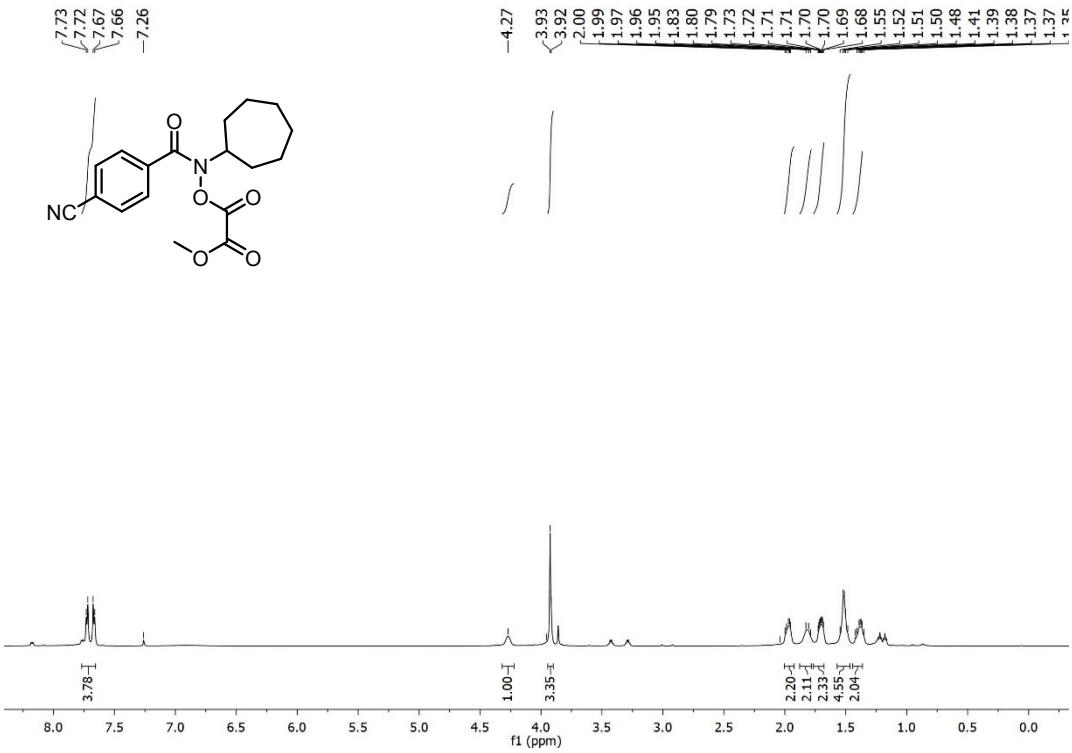
^{13}C NMR spectrum of **45a**



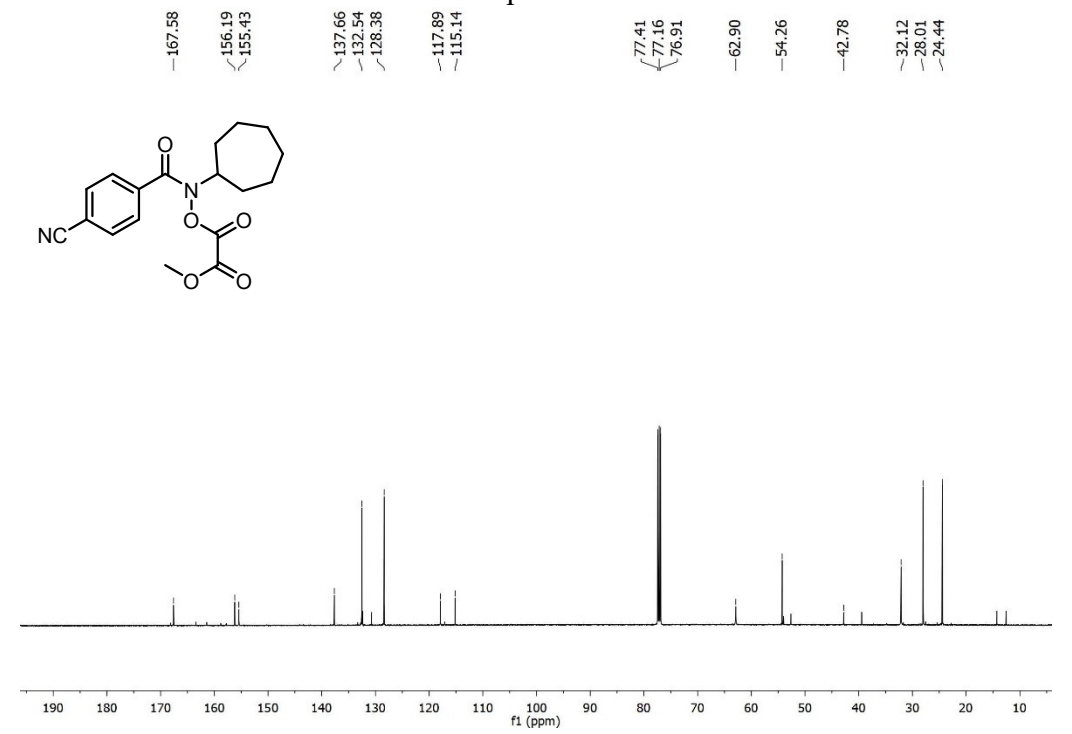
^{1}H NMR spectrum of **46a**



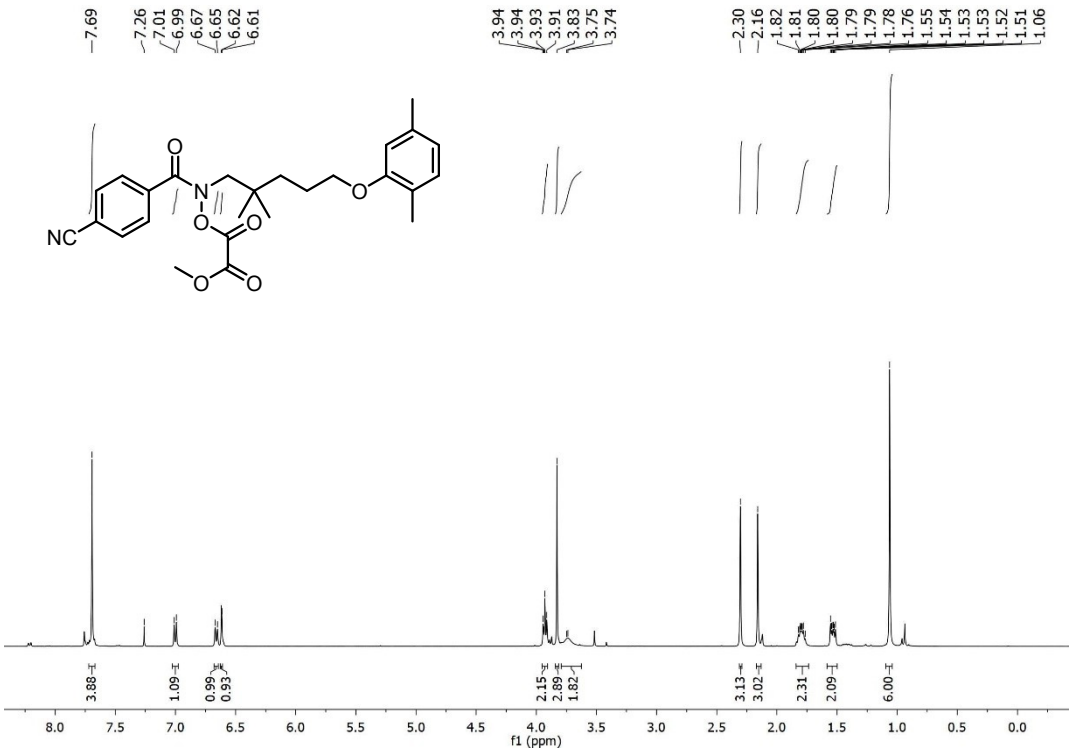
^{13}C NMR spectrum of **46a**



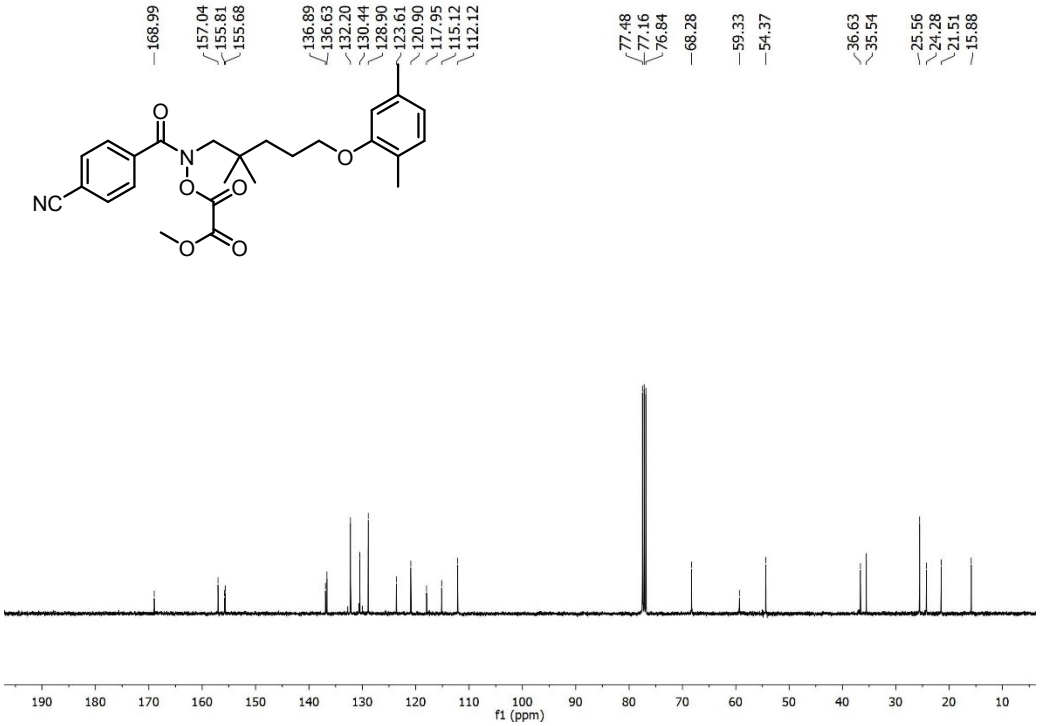
^{1}H NMR spectrum of **47a**



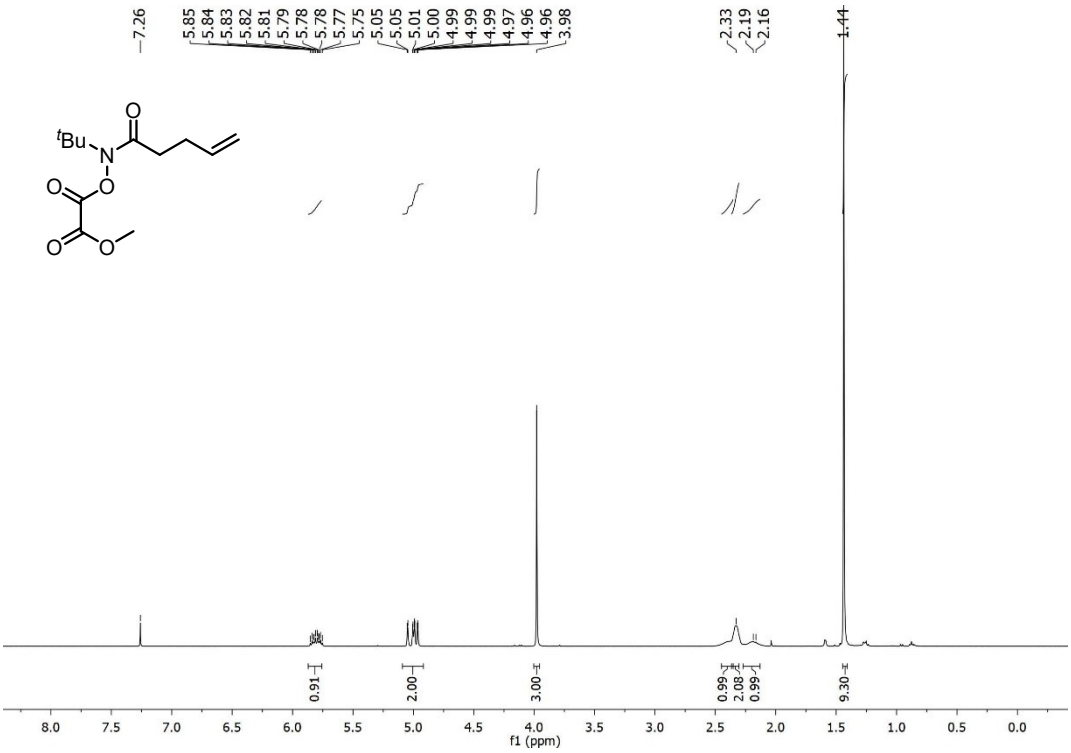
^{13}C NMR spectrum of **47a**



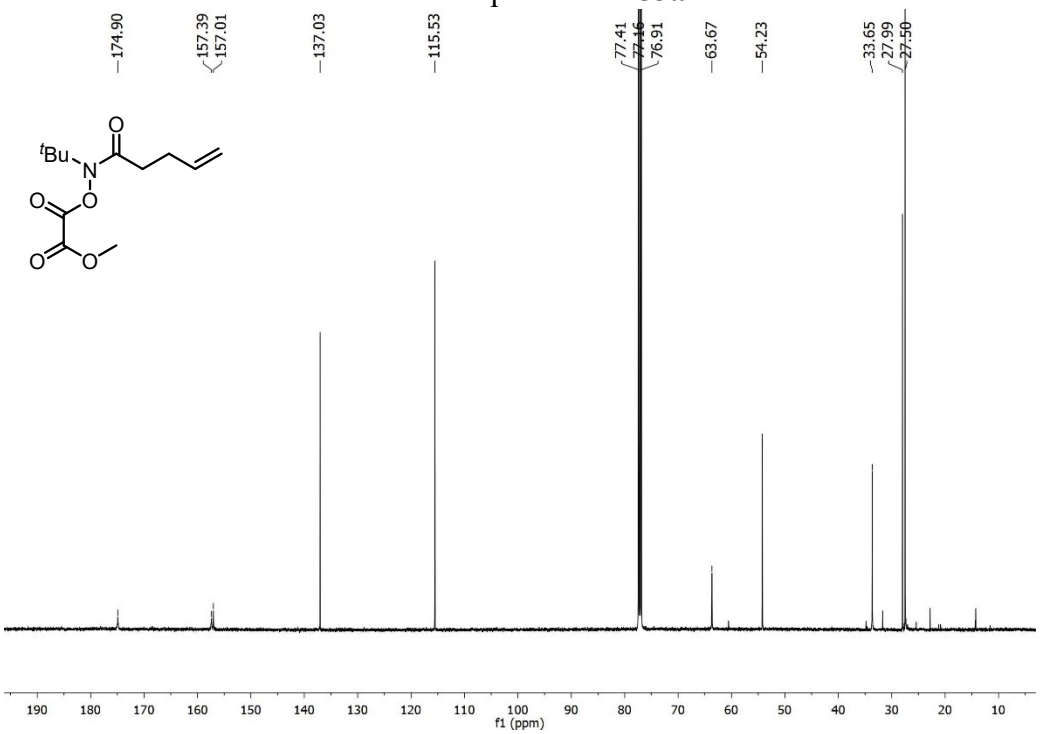
^{1}H NMR spectrum of **48a**



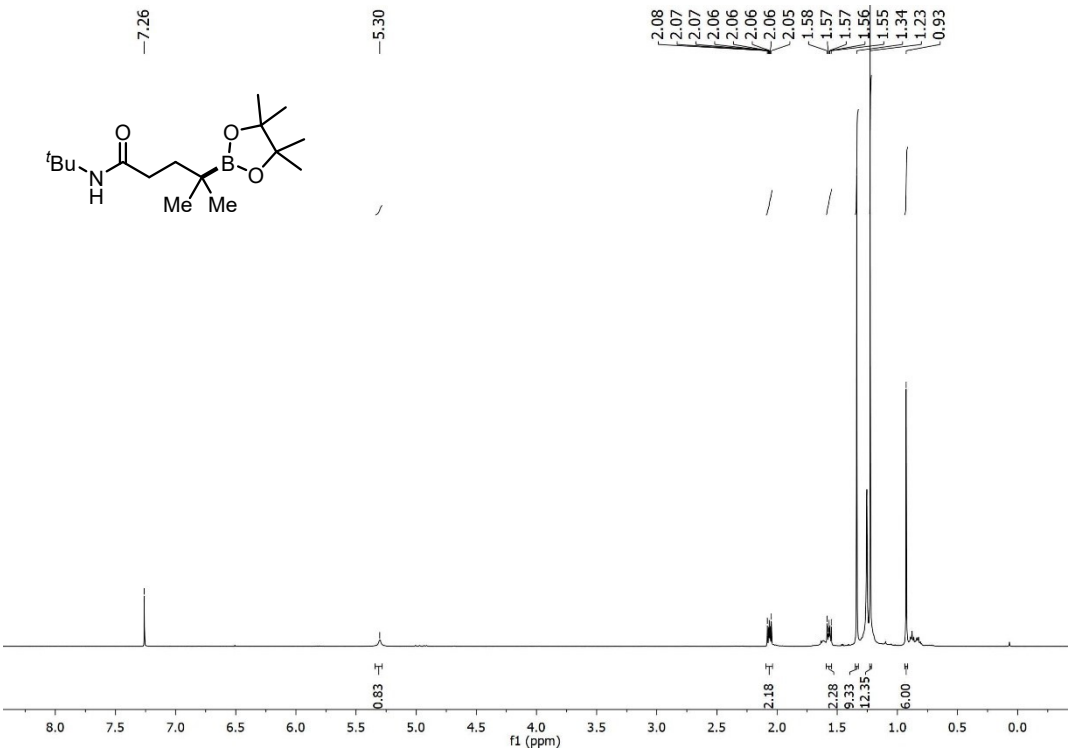
^{13}C NMR spectrum of **48a**



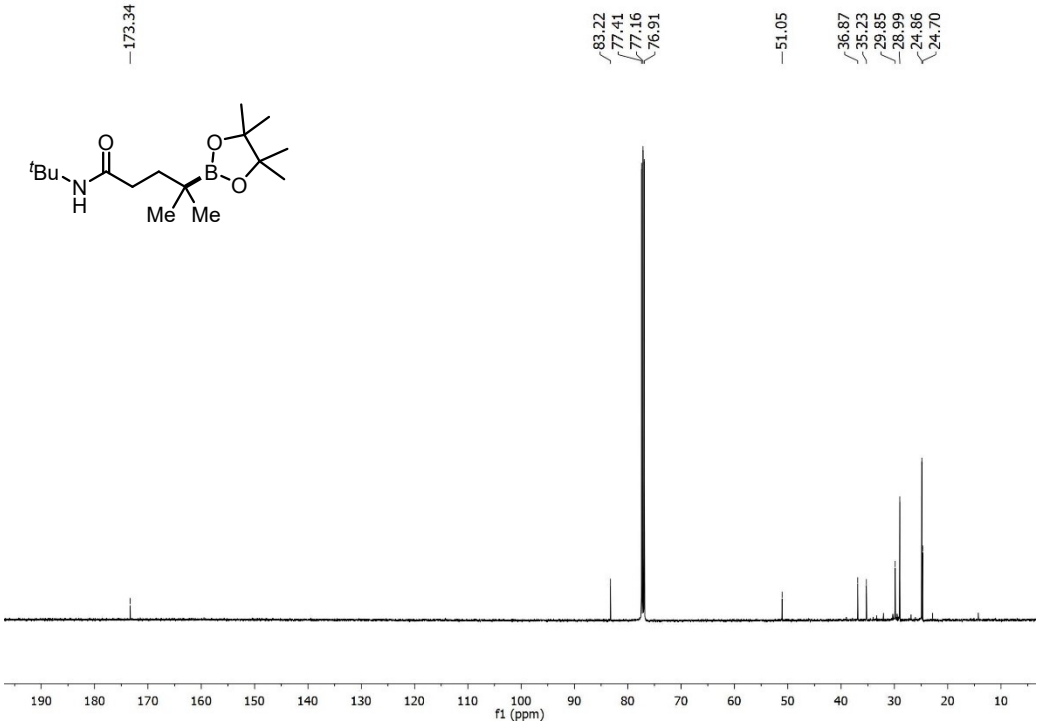
^{1}H NMR spectrum of **53a**



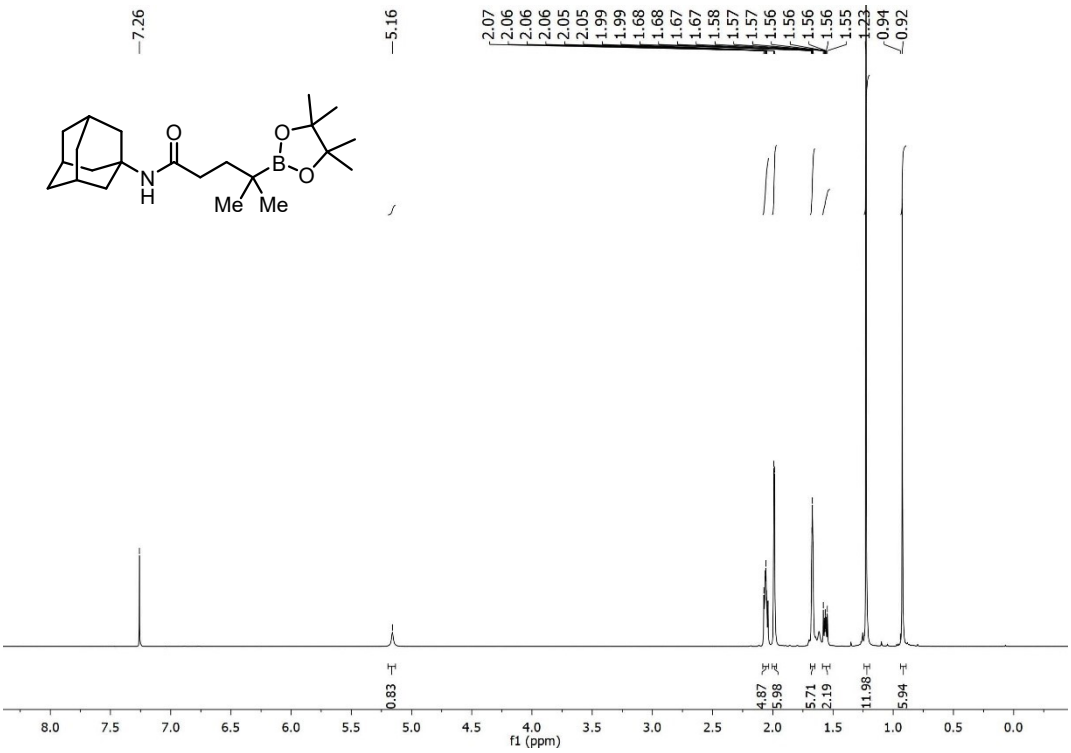
^{13}C NMR spectrum of **53a**



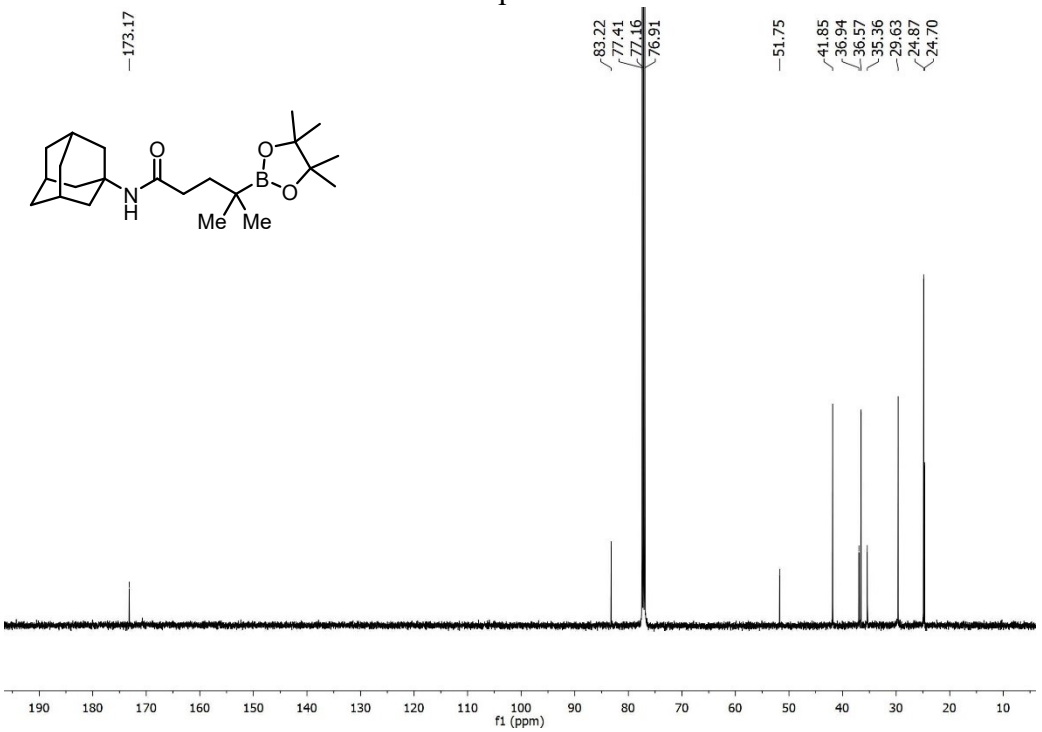
^{1}H NMR spectrum of **11**



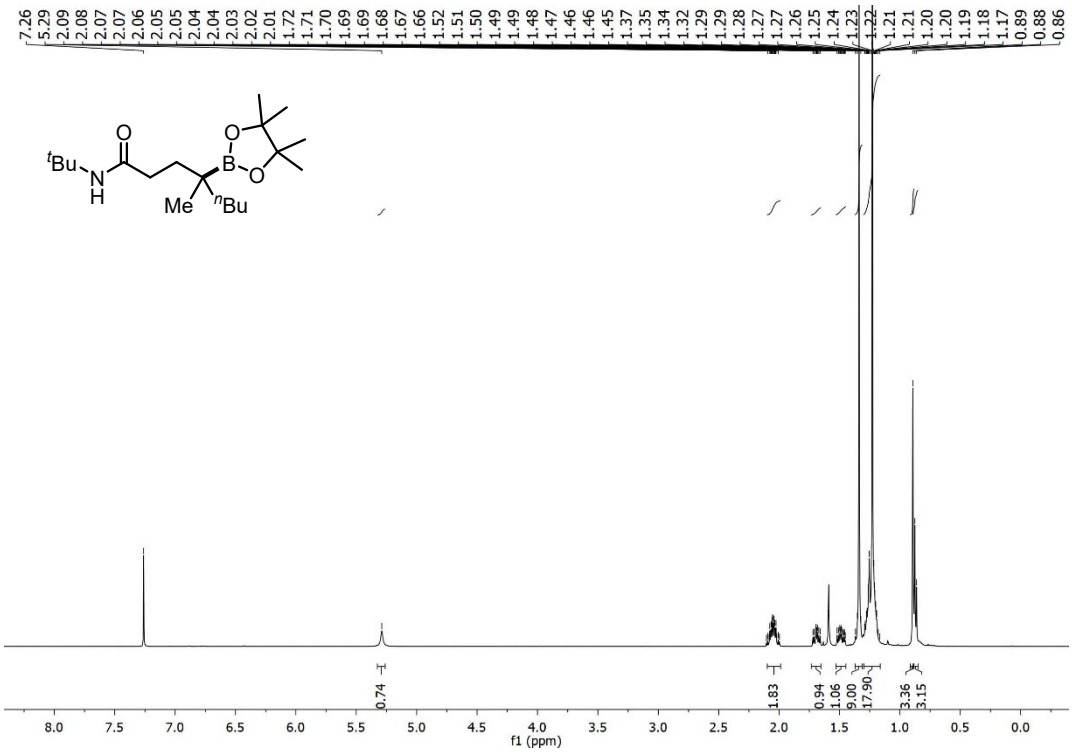
^{13}C NMR spectrum of **11**



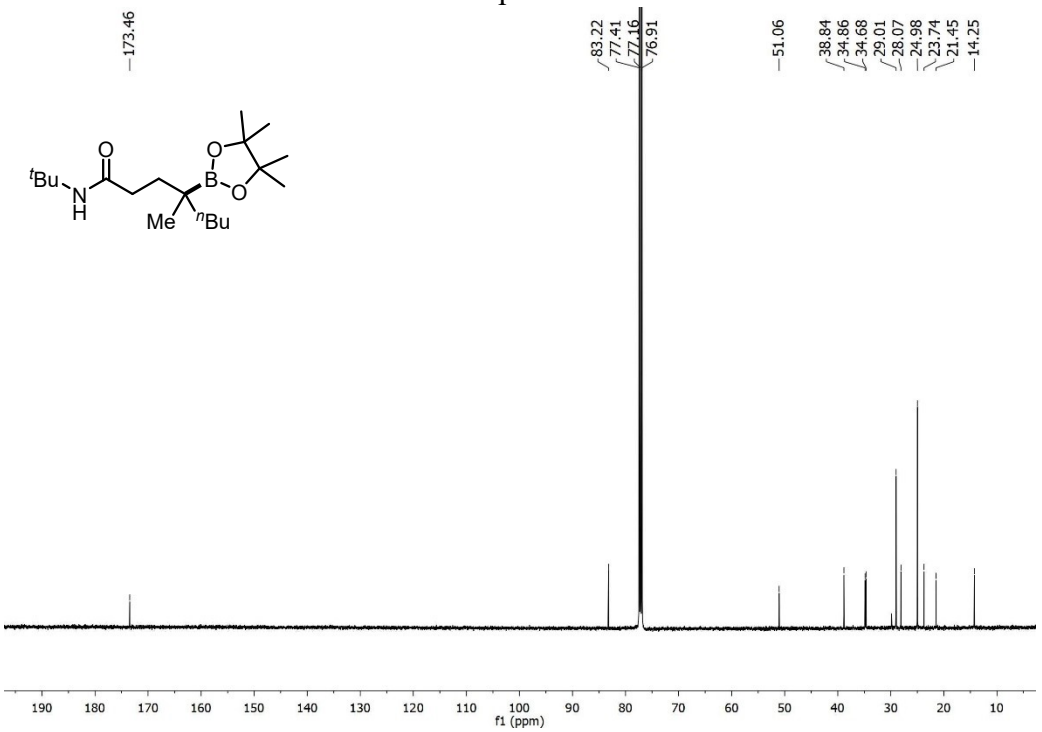
^{1}H NMR spectrum of **12**



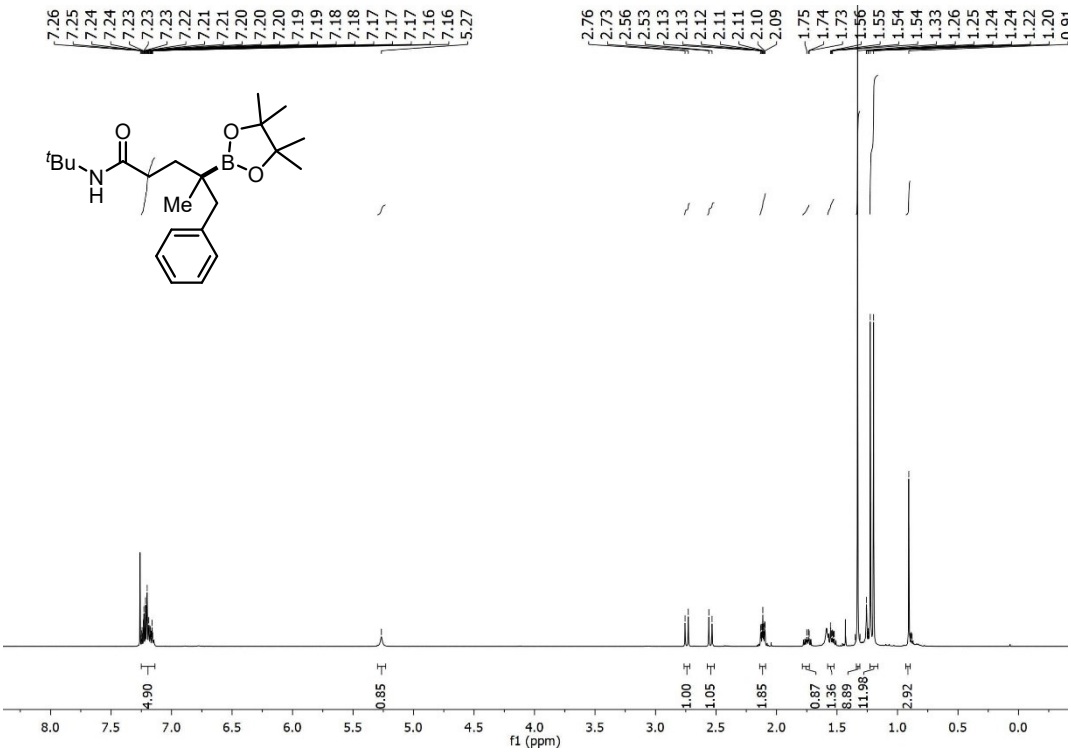
^{13}C NMR spectrum of **12**



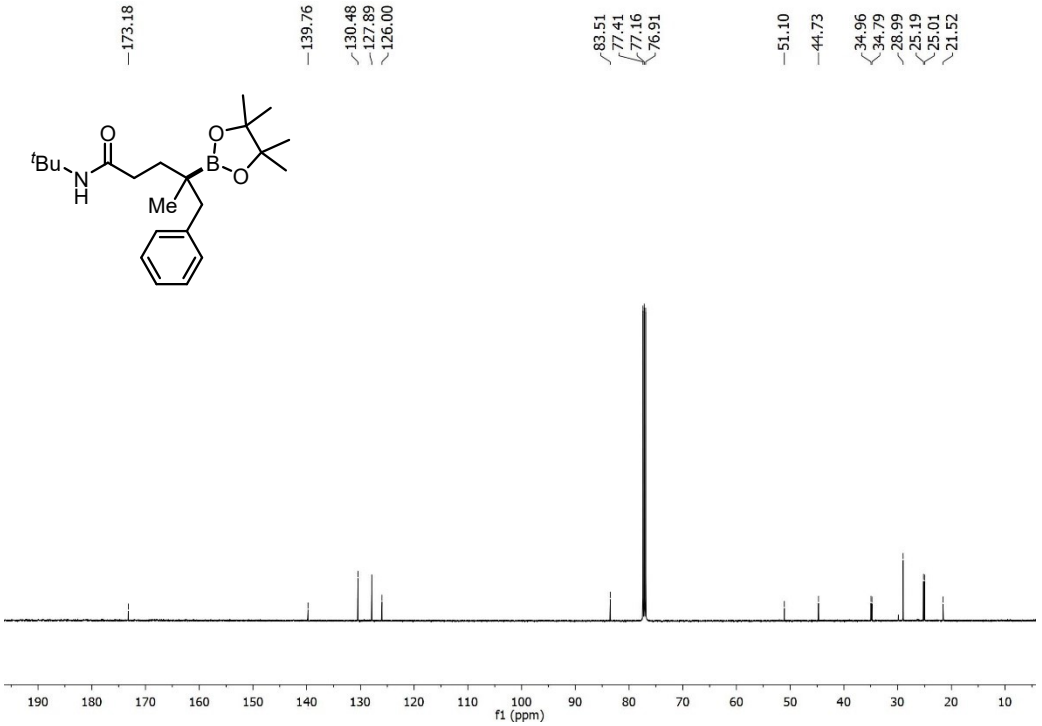
^{1}H NMR spectrum of **13**



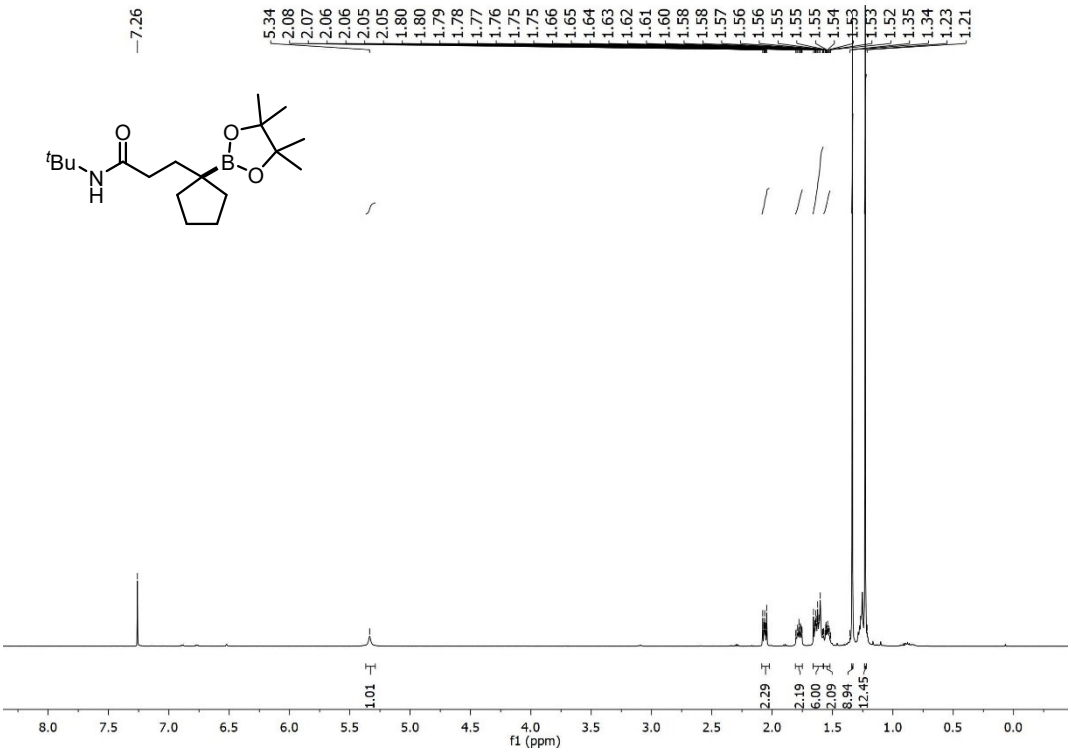
^{13}C NMR spectrum of **13**



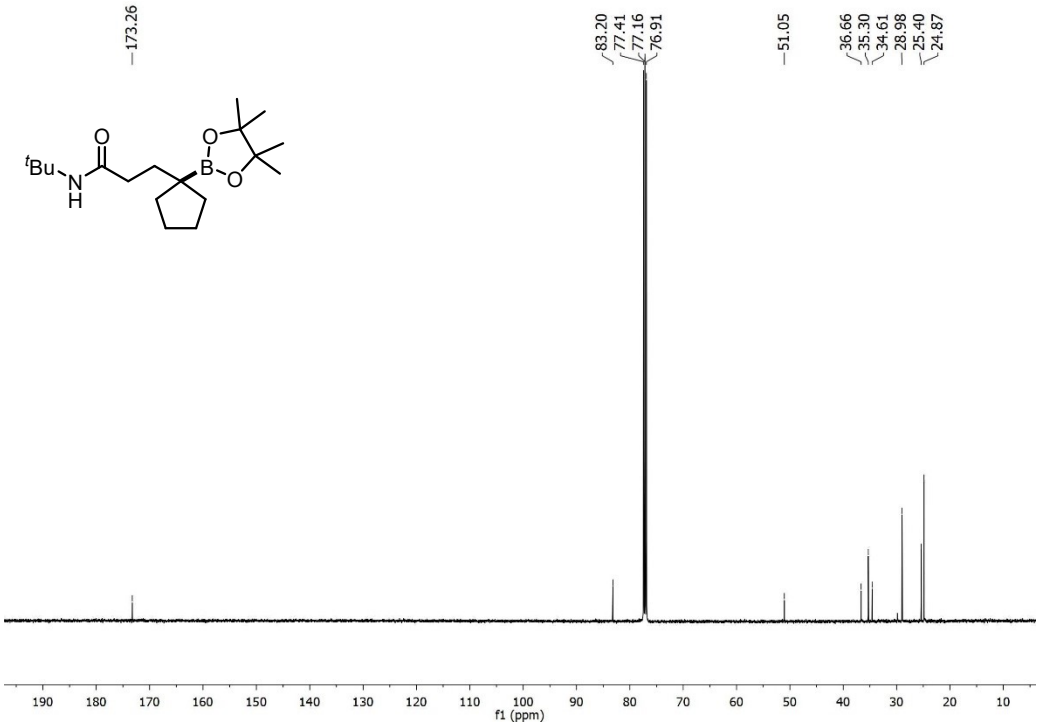
^{1}H NMR spectrum of **14**



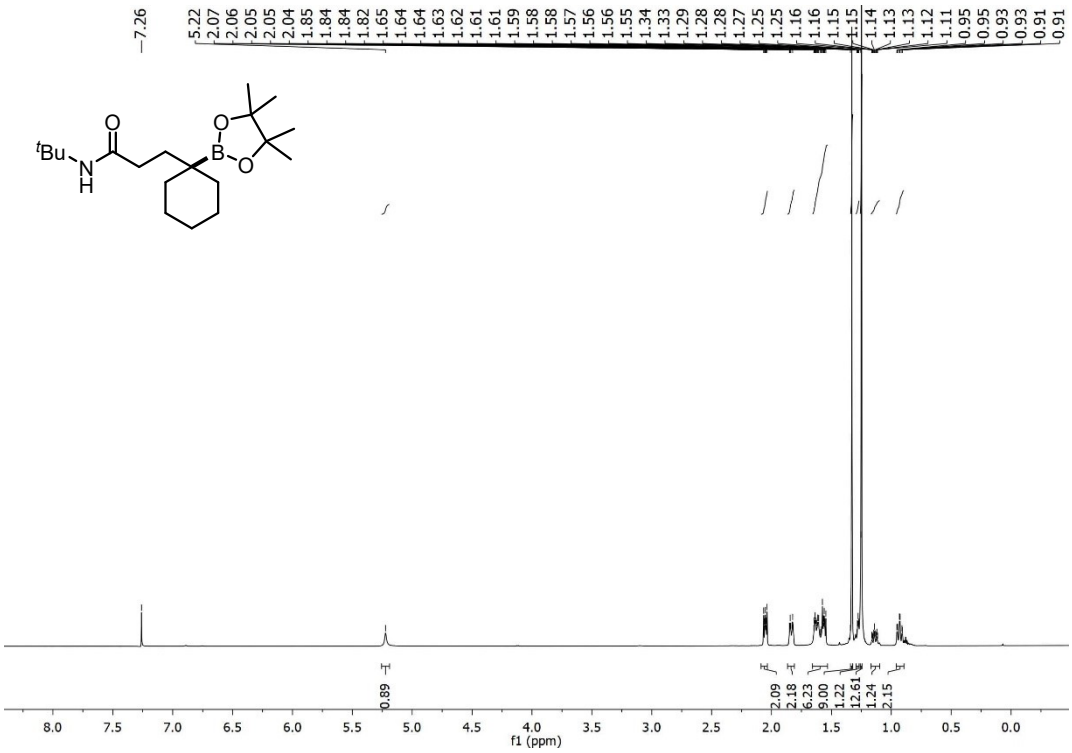
^{13}C NMR spectrum of **14**



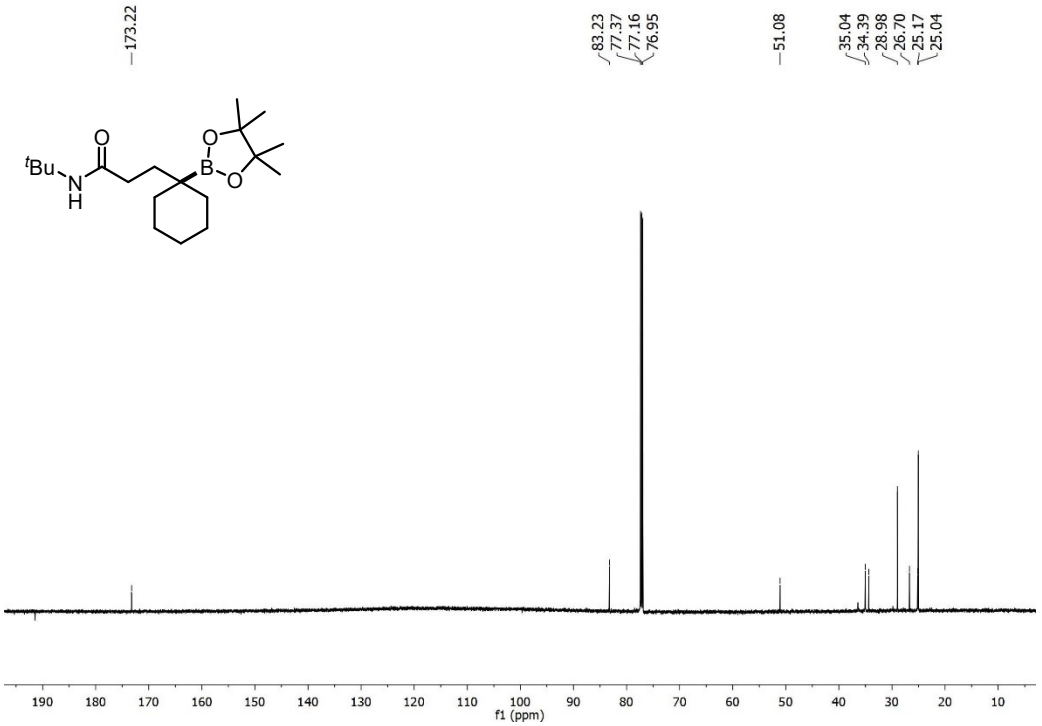
^{1}H NMR spectrum of **15**



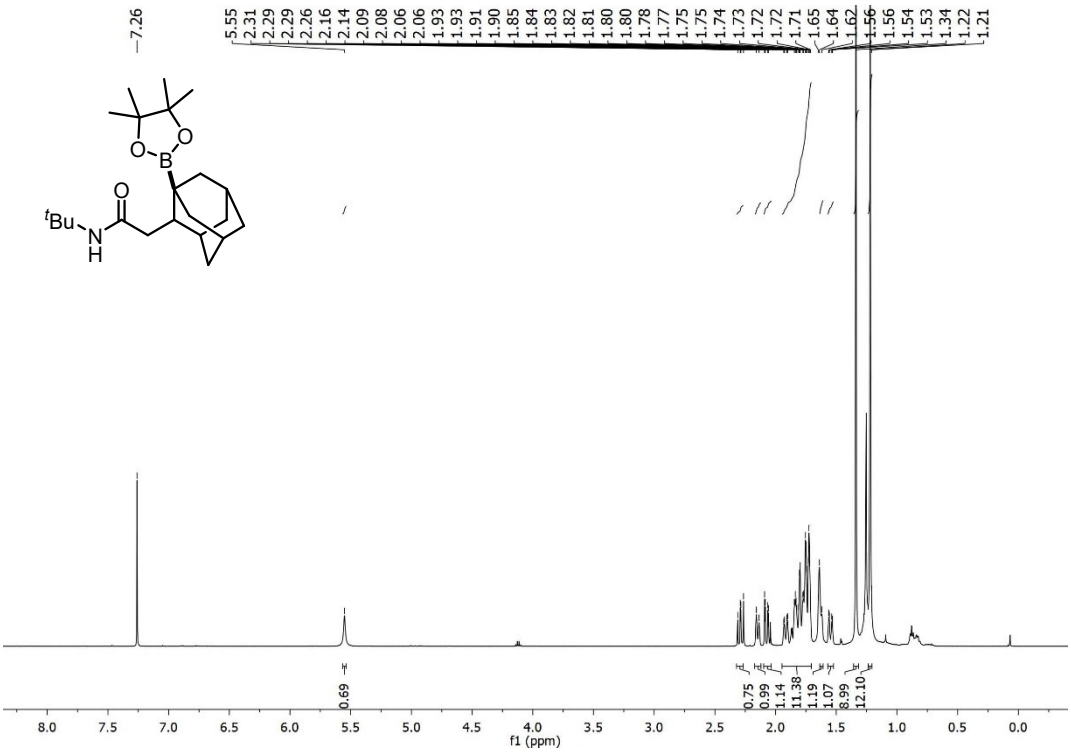
^{13}C NMR spectrum of **15**



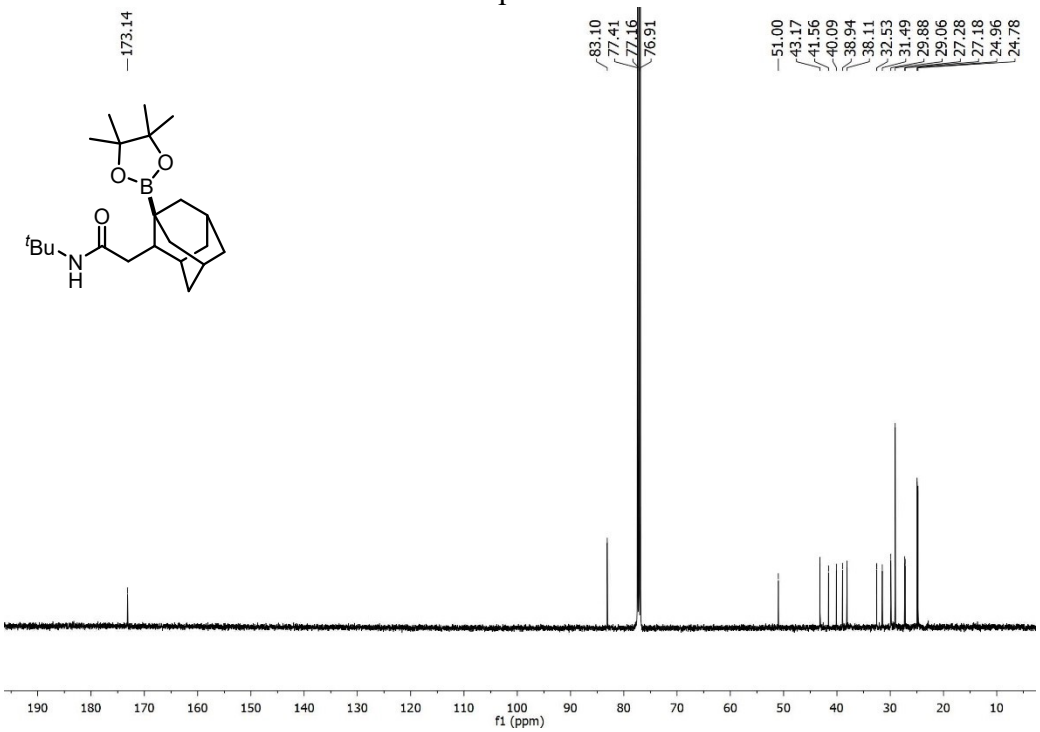
^{1}H NMR spectrum of **16**



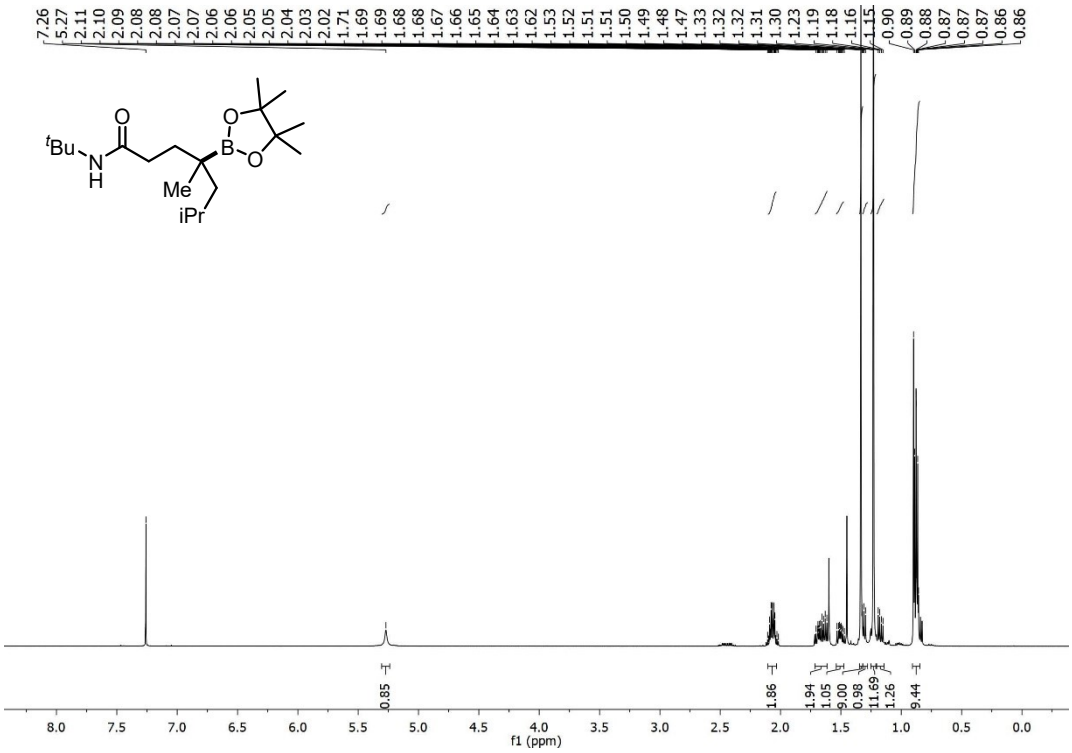
^{13}C NMR spectrum of **16**



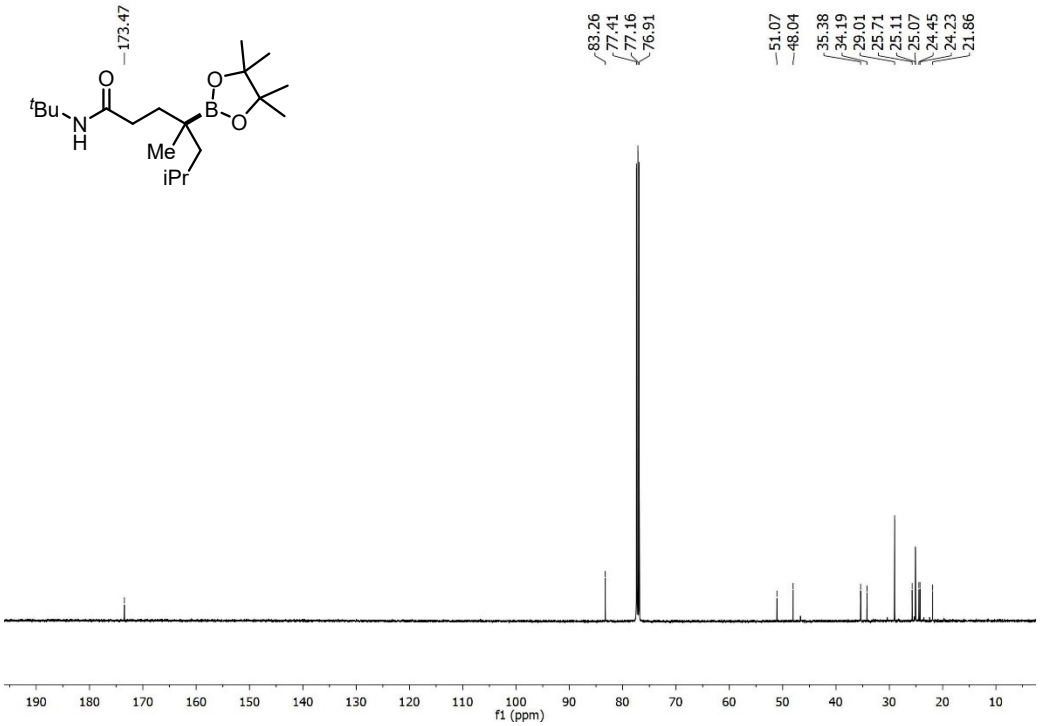
^{1}H NMR spectrum of **17**



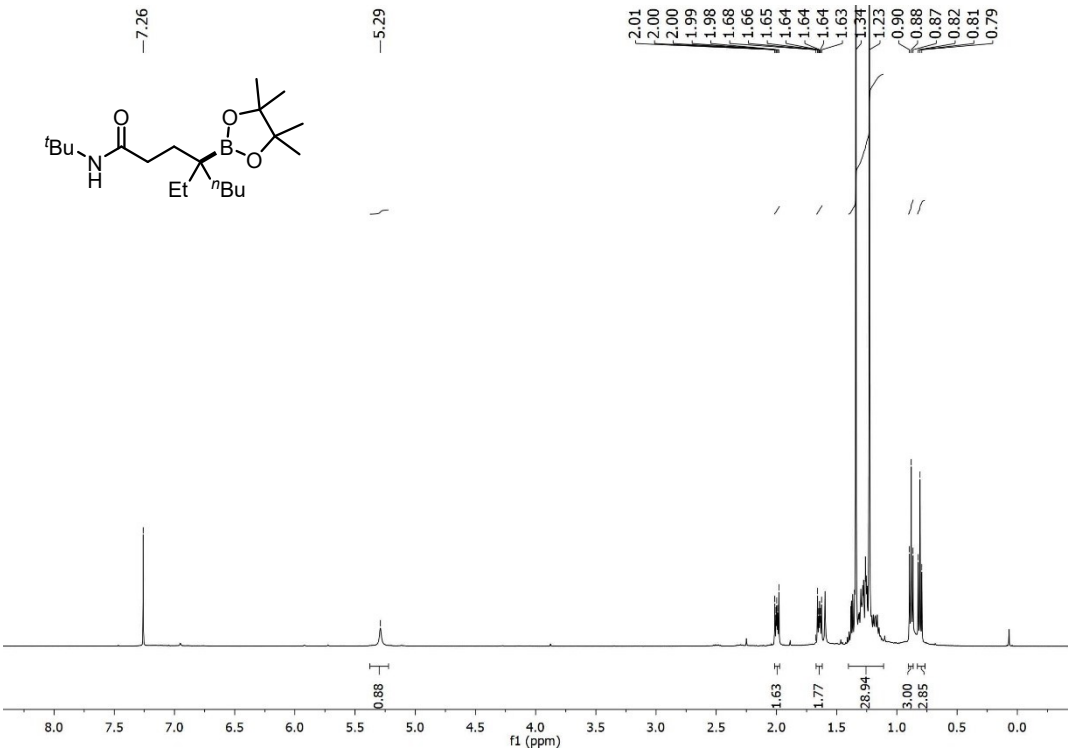
^{13}C NMR spectrum of **17**



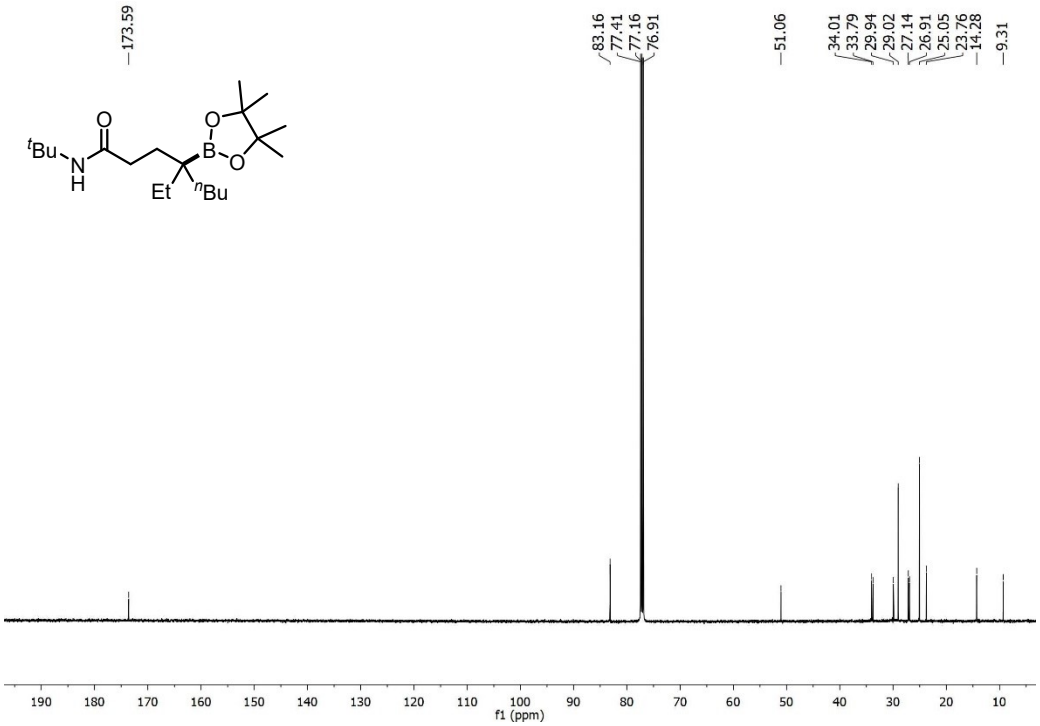
^{1}H NMR spectrum of **18**



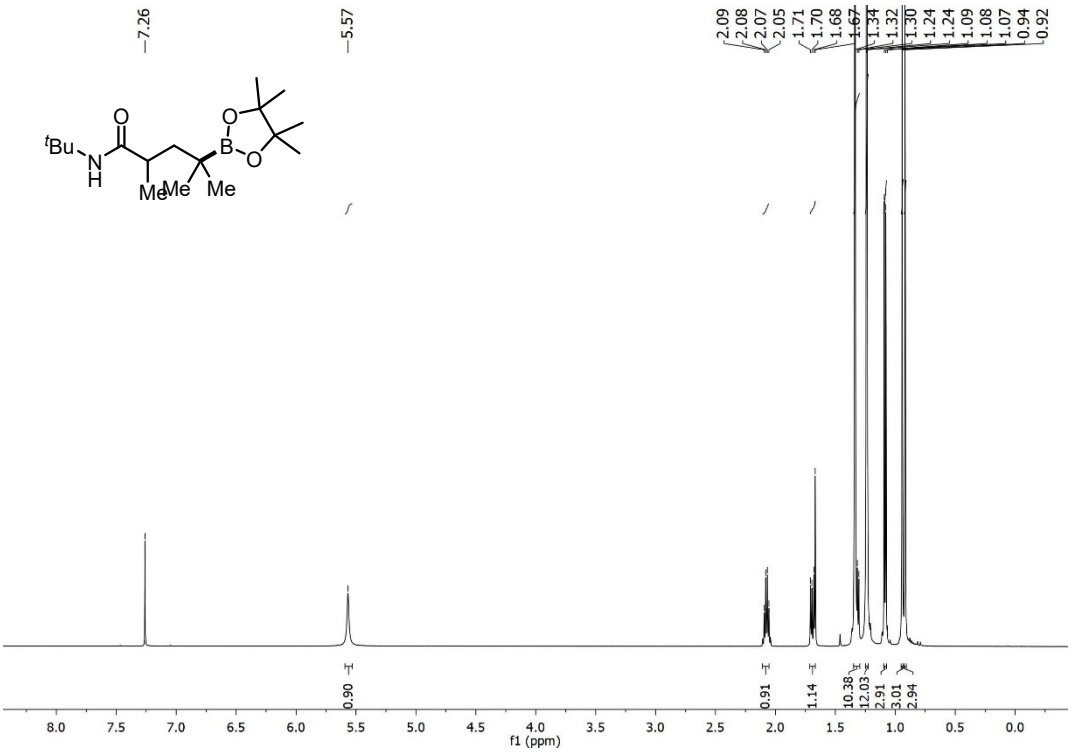
^{13}C NMR spectrum of **18**



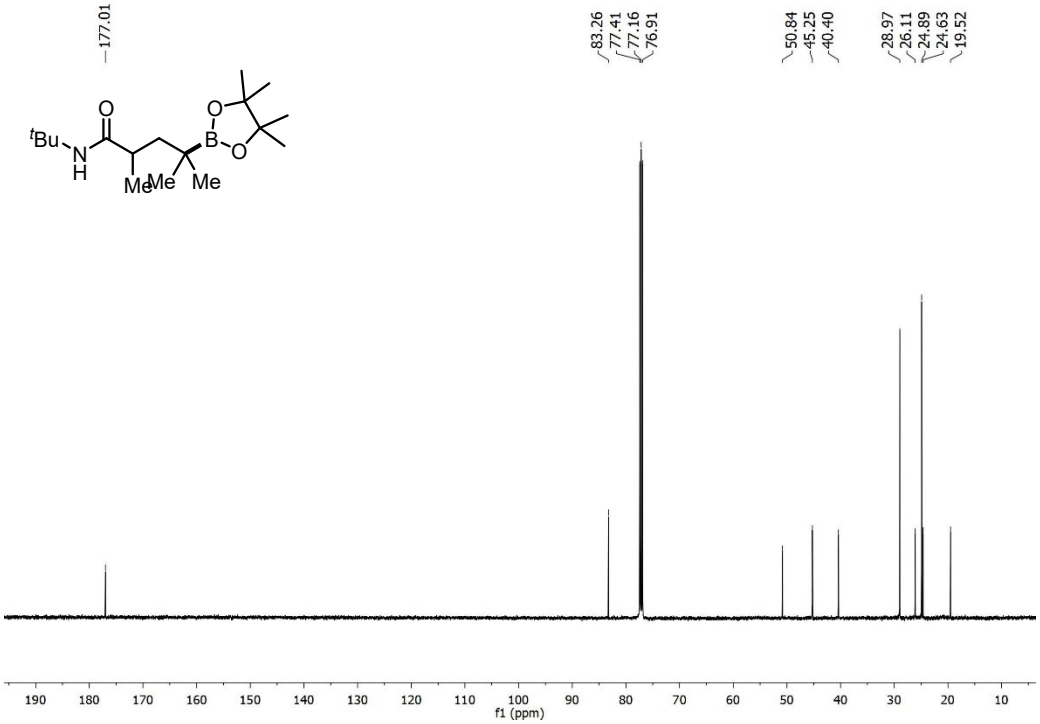
^{1}H NMR spectrum of **19**



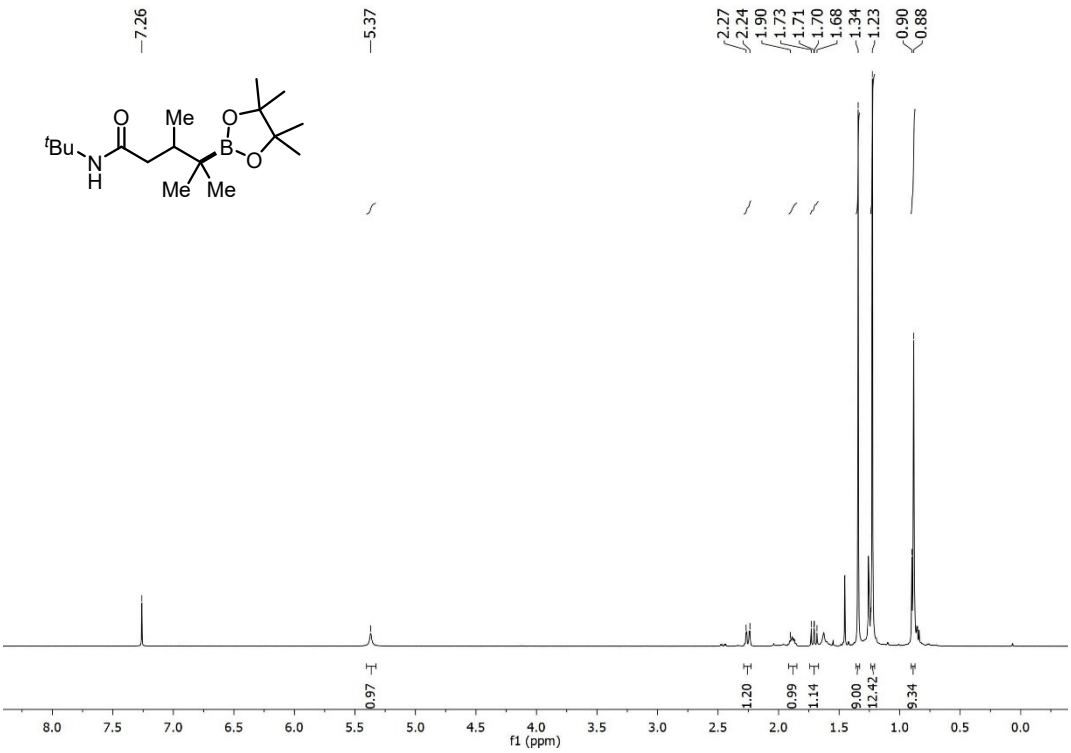
^{13}C NMR spectrum of **19**



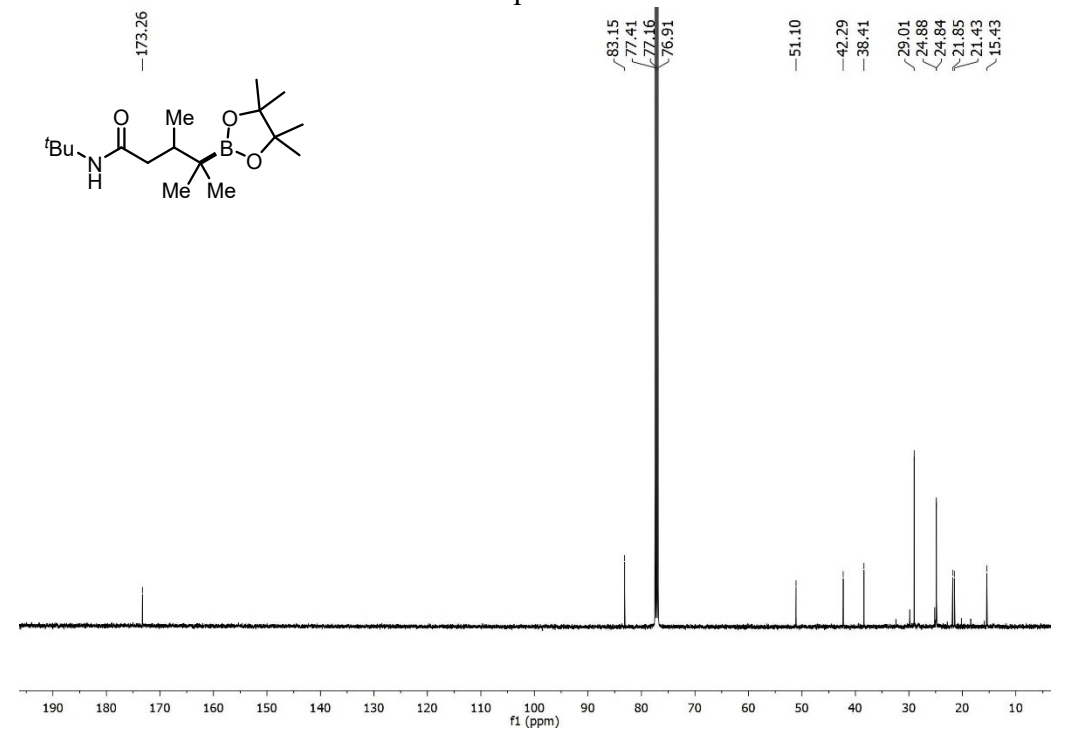
^{1}H NMR spectrum of **20**



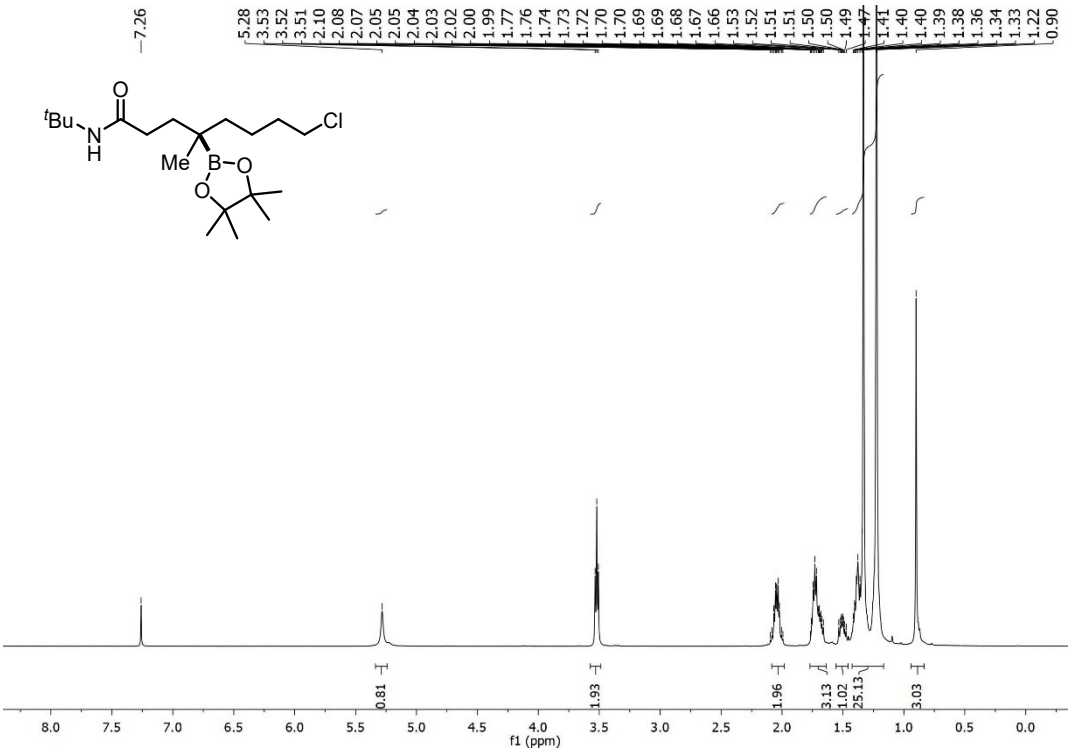
^{13}C NMR spectrum of **20**



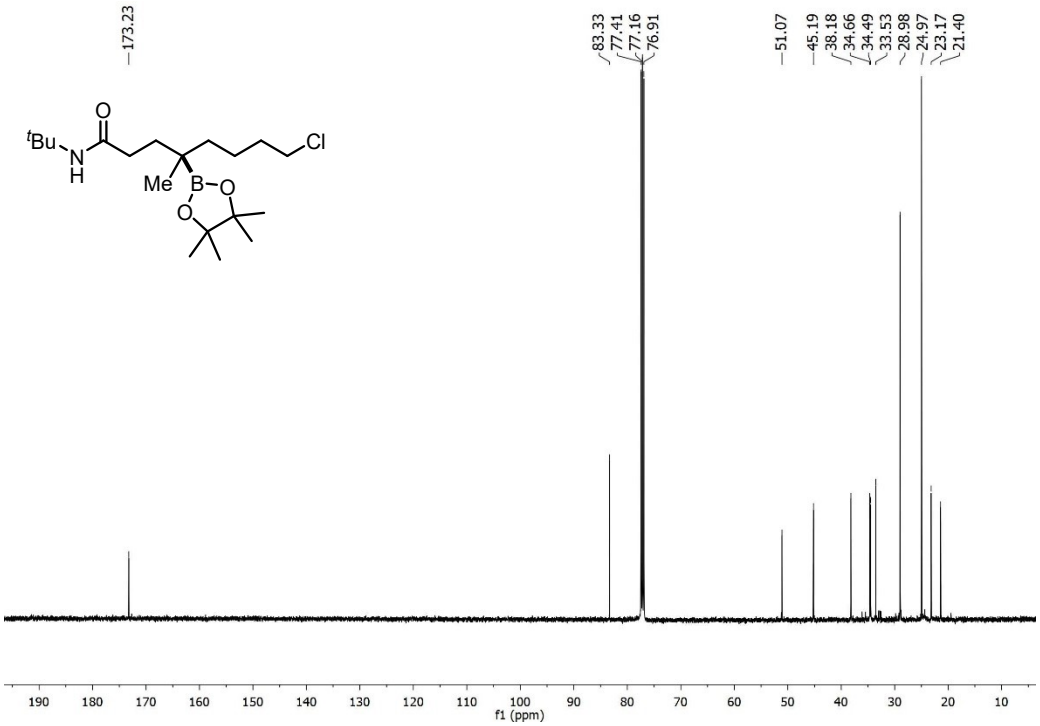
^{1}H NMR spectrum of **21**



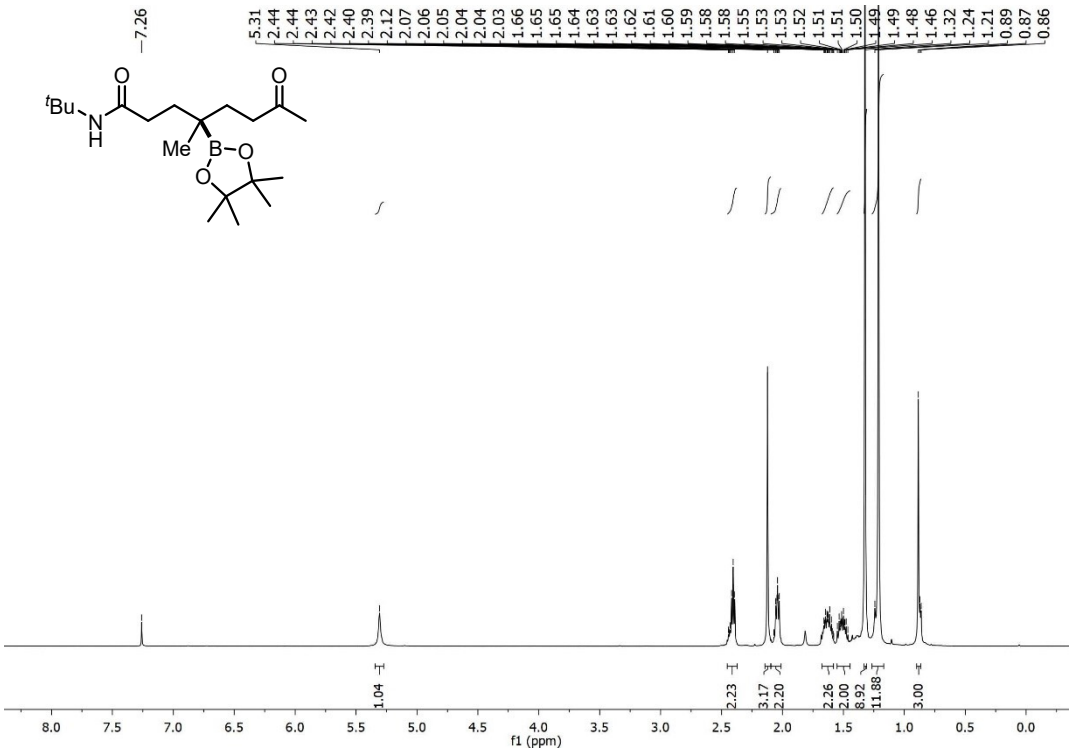
^{13}C NMR spectrum of **21**



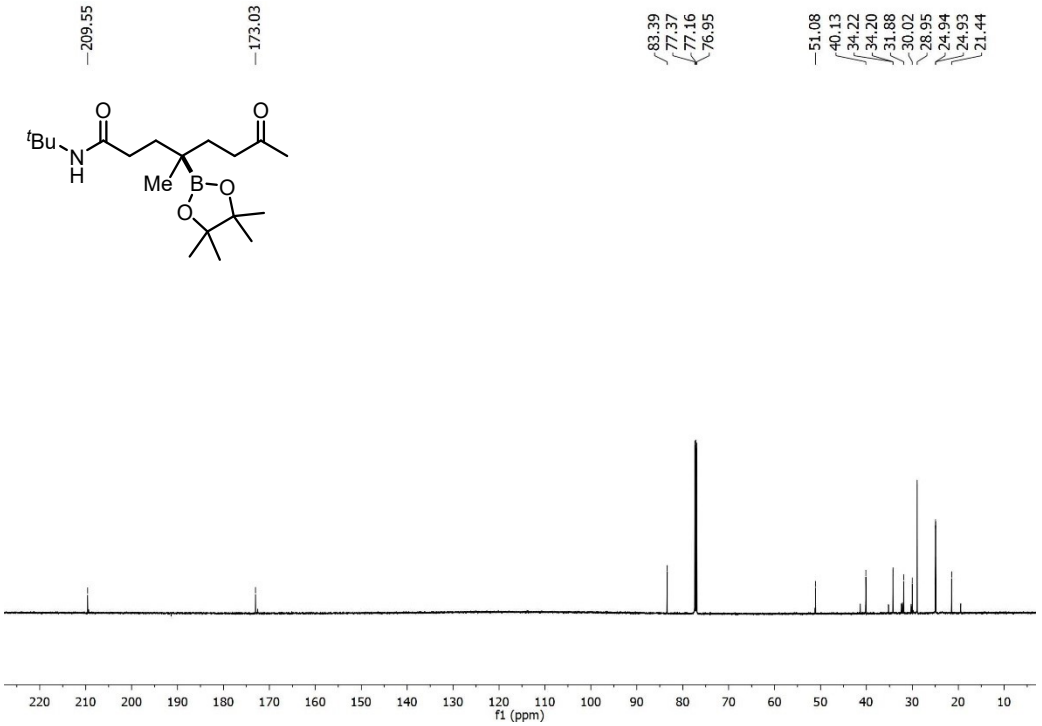
^{1}H NMR spectrum of **22**



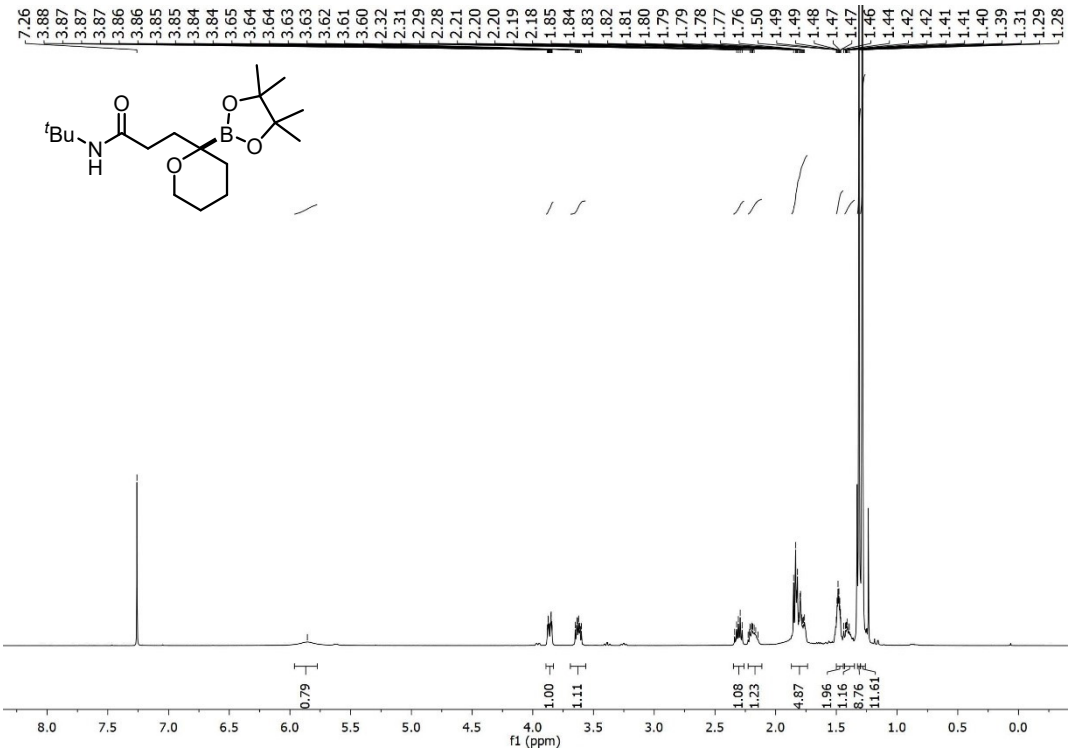
^{13}C NMR spectrum of **22**



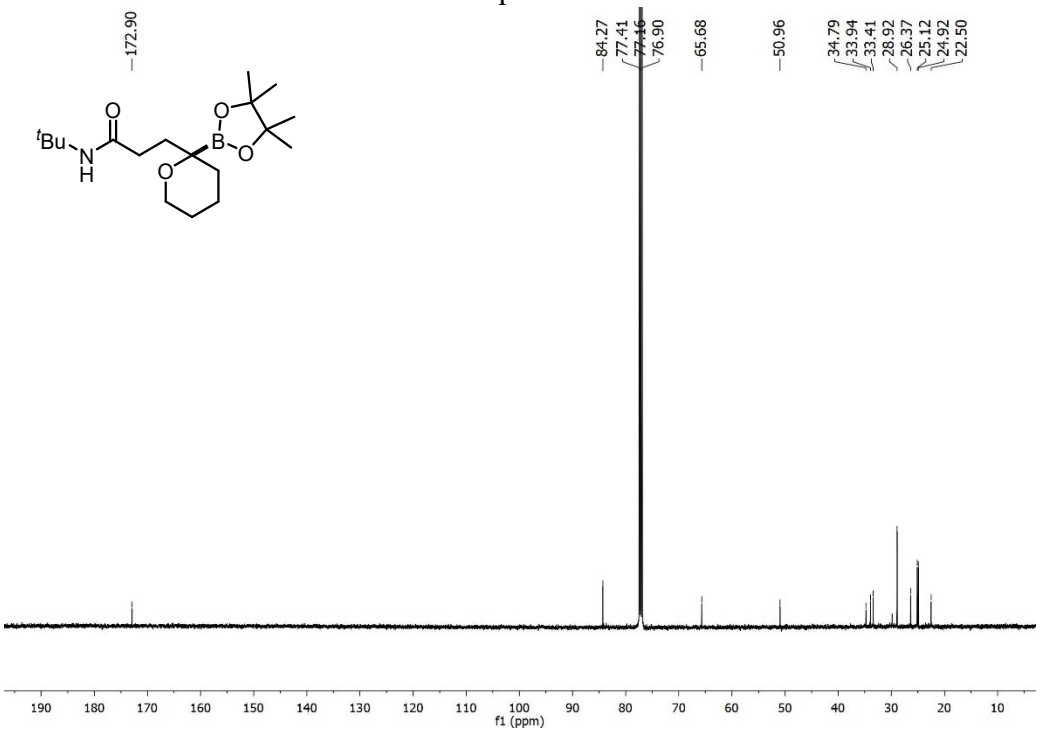
^{1}H NMR spectrum of **23**



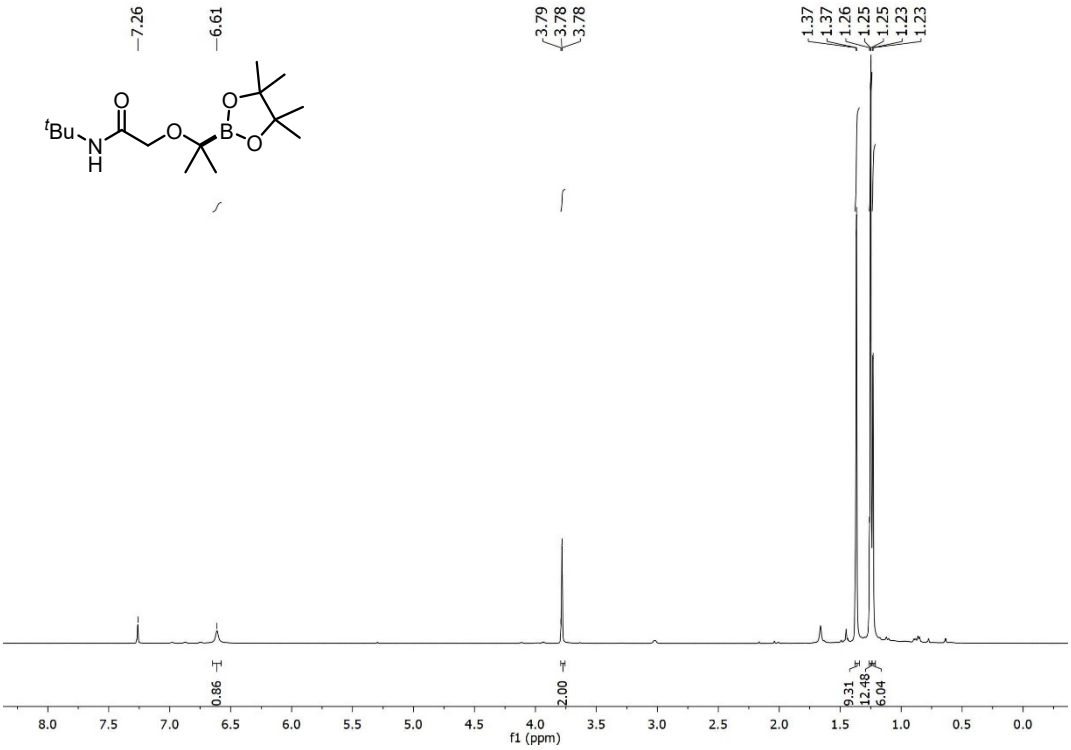
^{13}C NMR spectrum of **23**



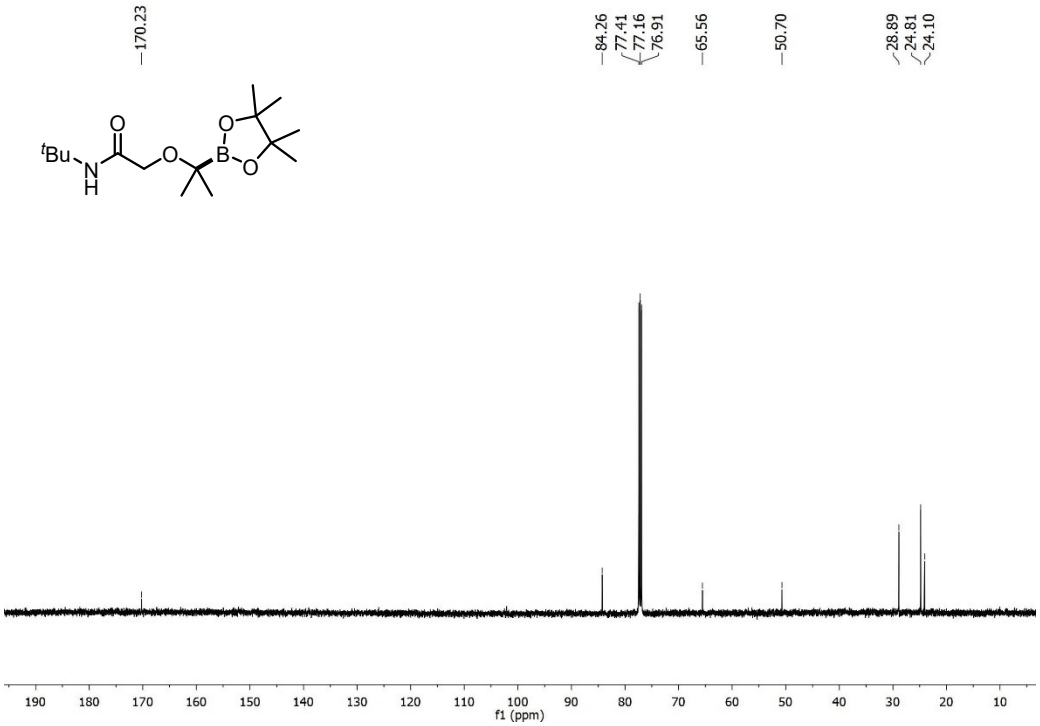
^{1}H NMR spectrum of **24**



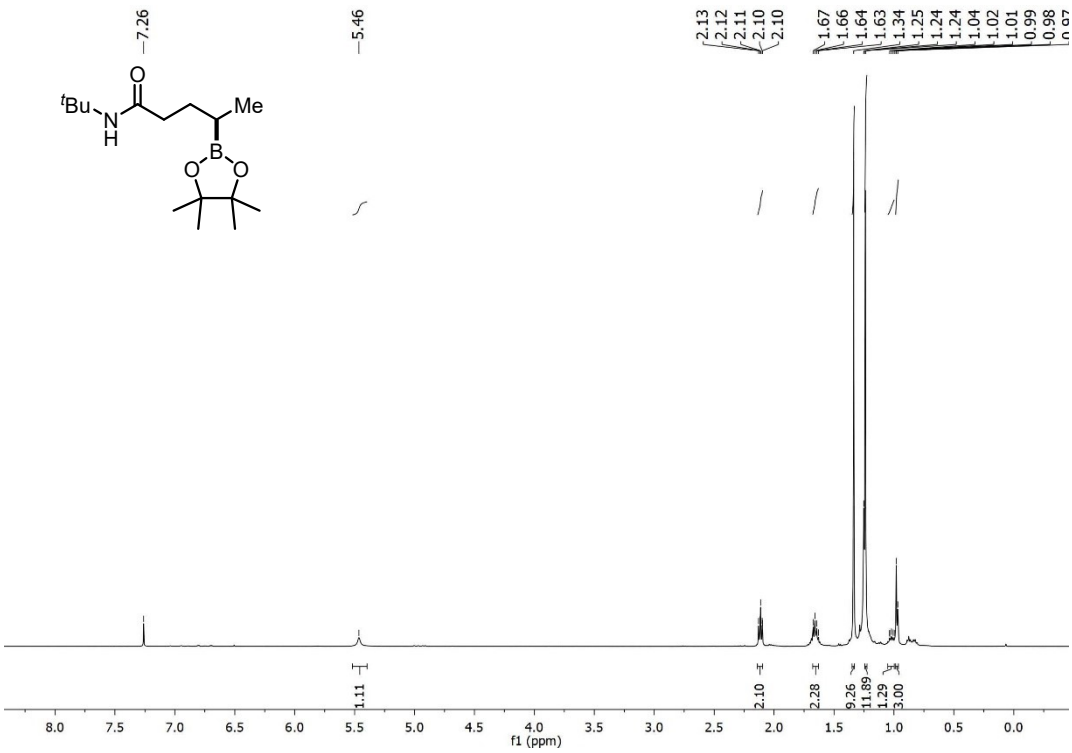
^{13}C NMR spectrum of **24**



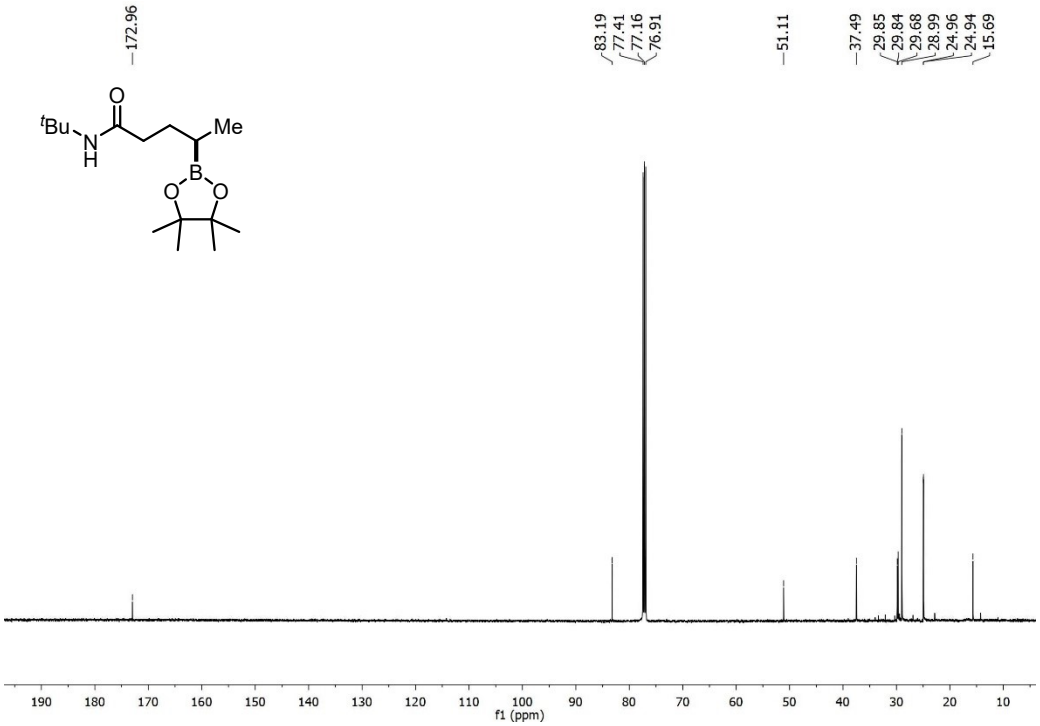
^{1}H NMR spectrum of **25**



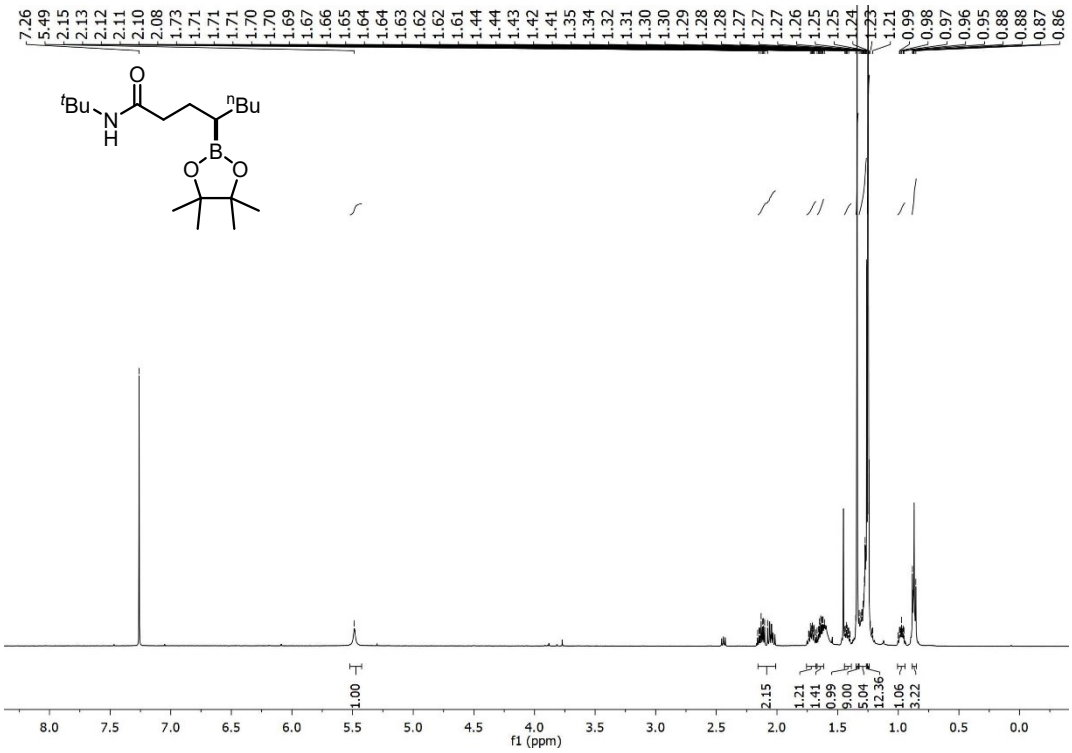
^{13}C NMR spectrum of **25**



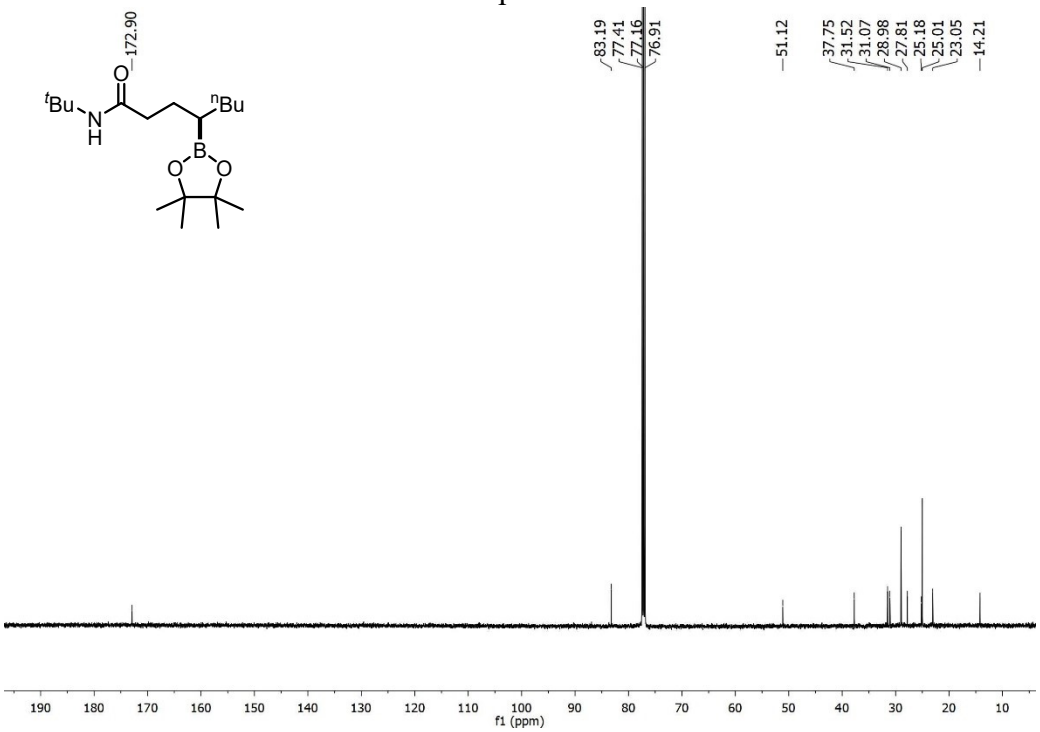
^{1}H NMR spectrum of **26**



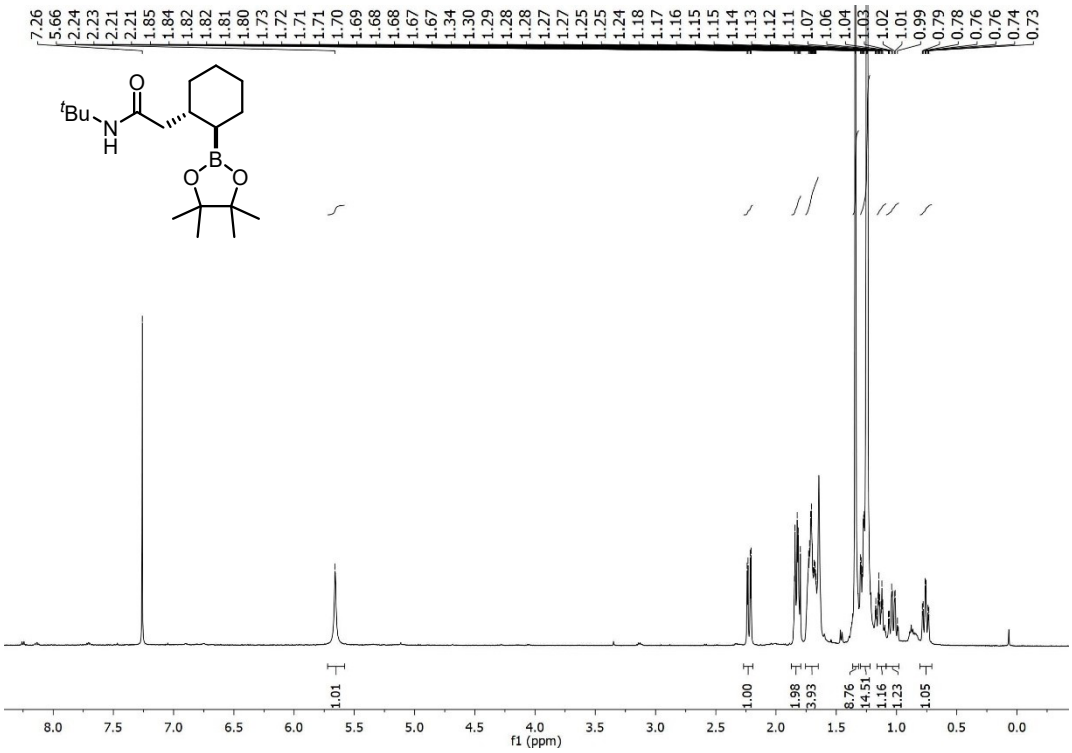
^{13}C NMR spectrum of **26**



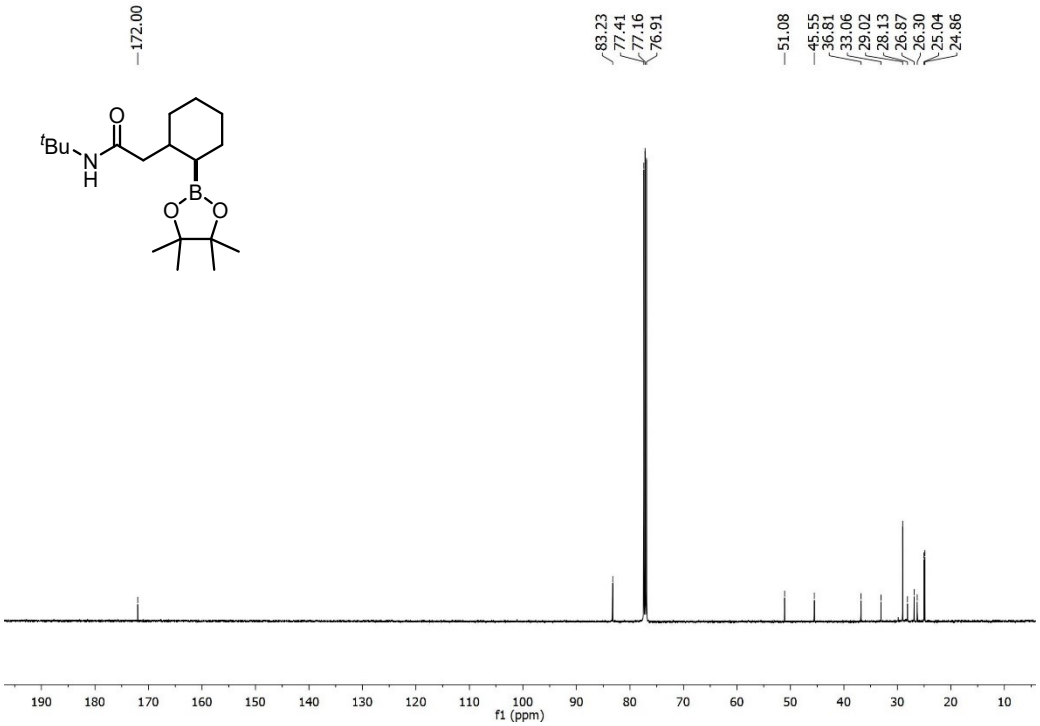
^{1}H NMR spectrum of **27**



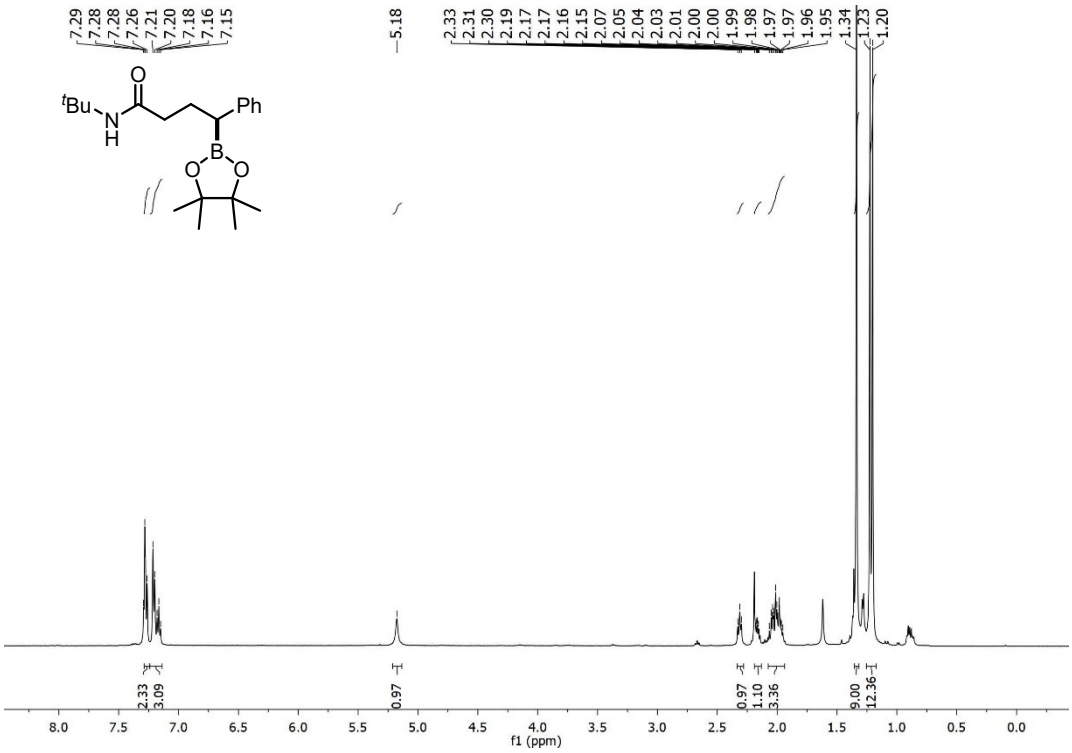
^{13}C NMR spectrum of **27**



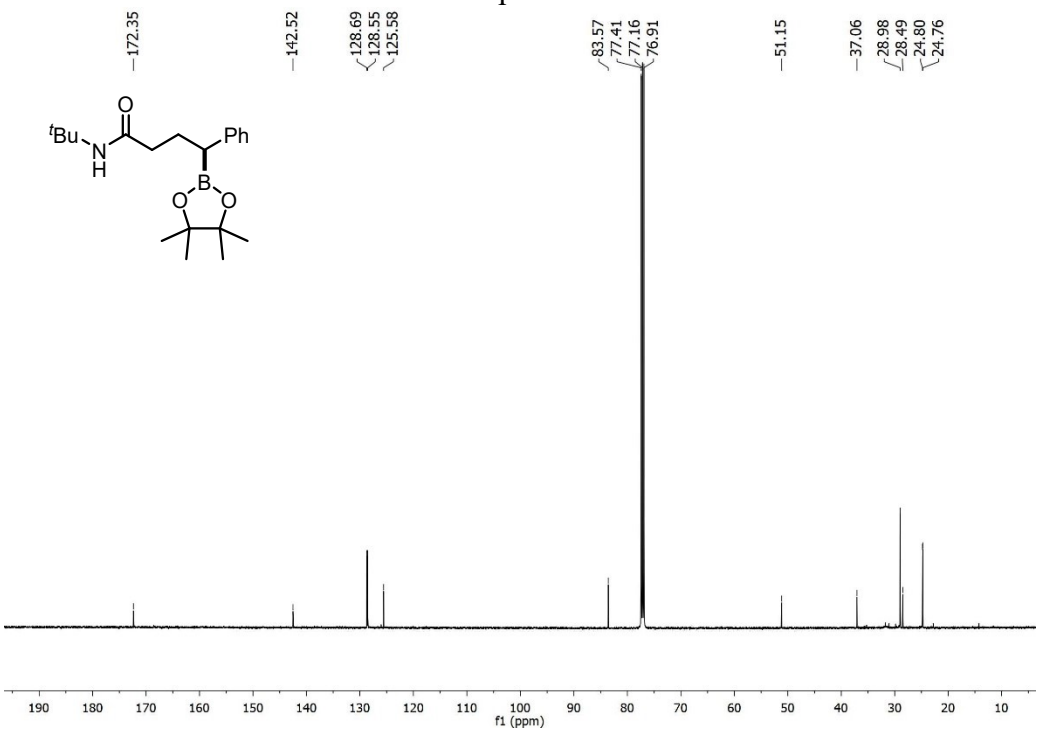
^{1}H NMR spectrum of **28**



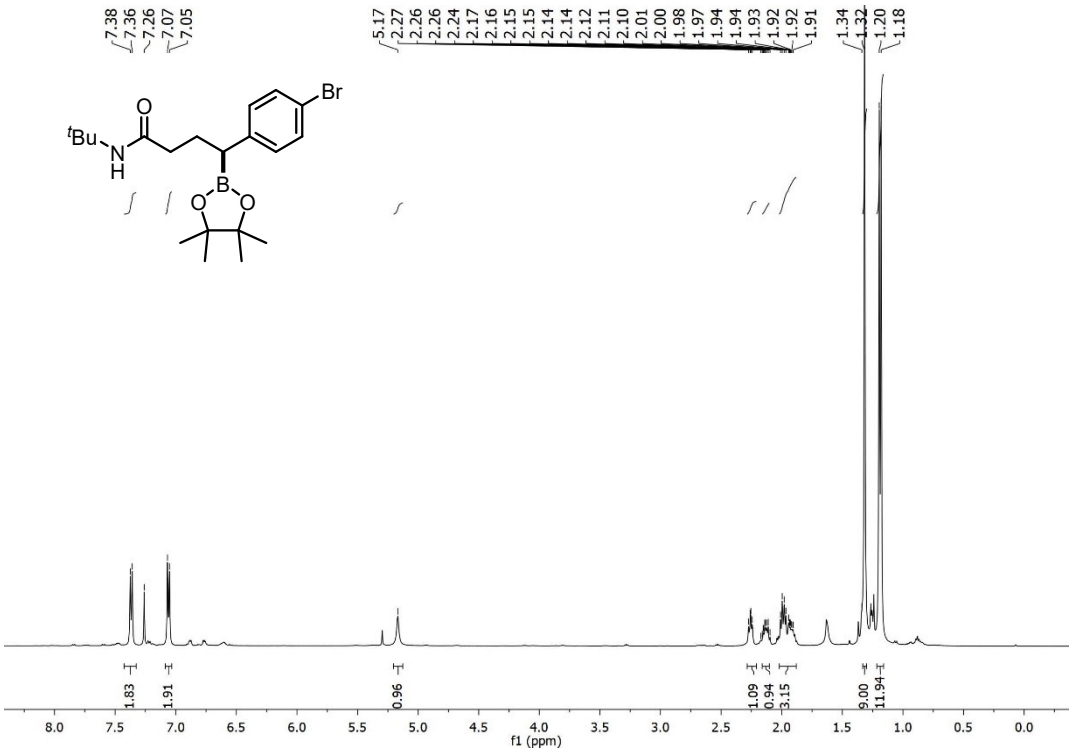
^{13}C NMR spectrum of **28**



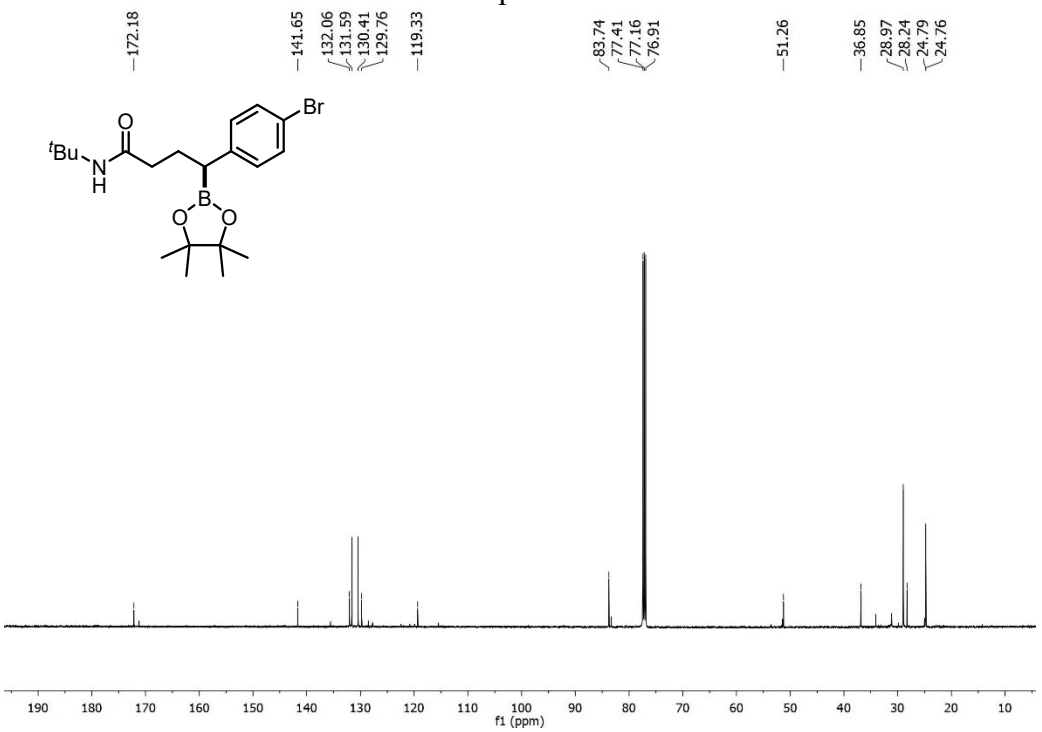
^{1}H NMR spectrum of **29**



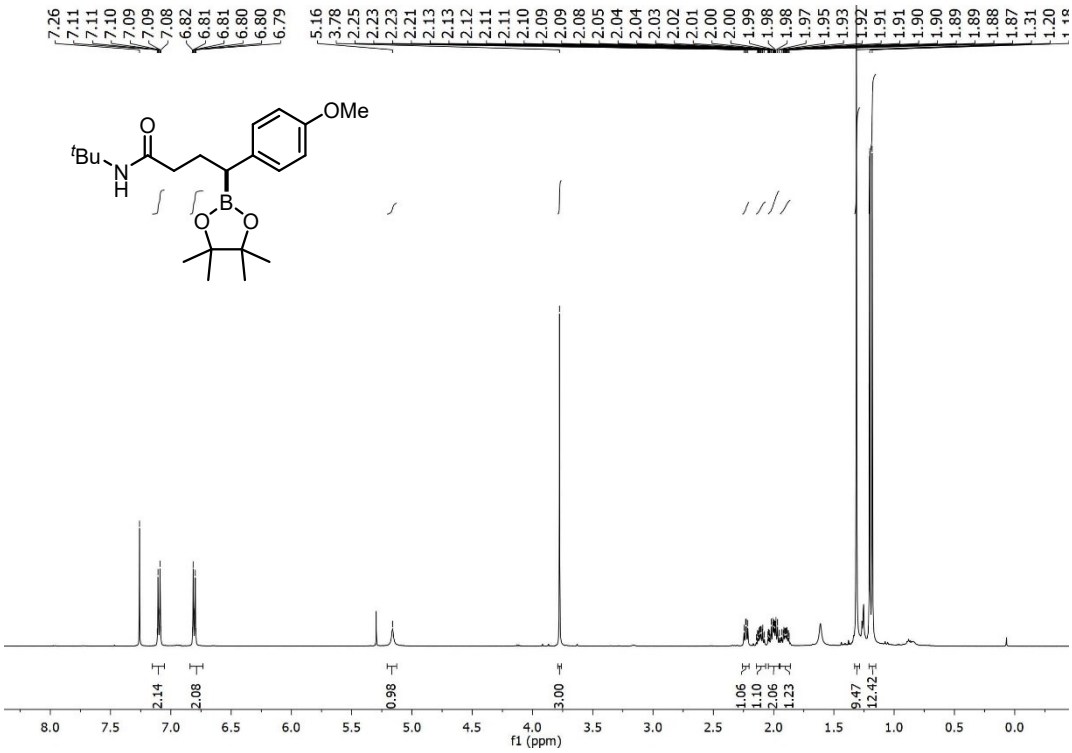
^{13}C NMR spectrum of **29**



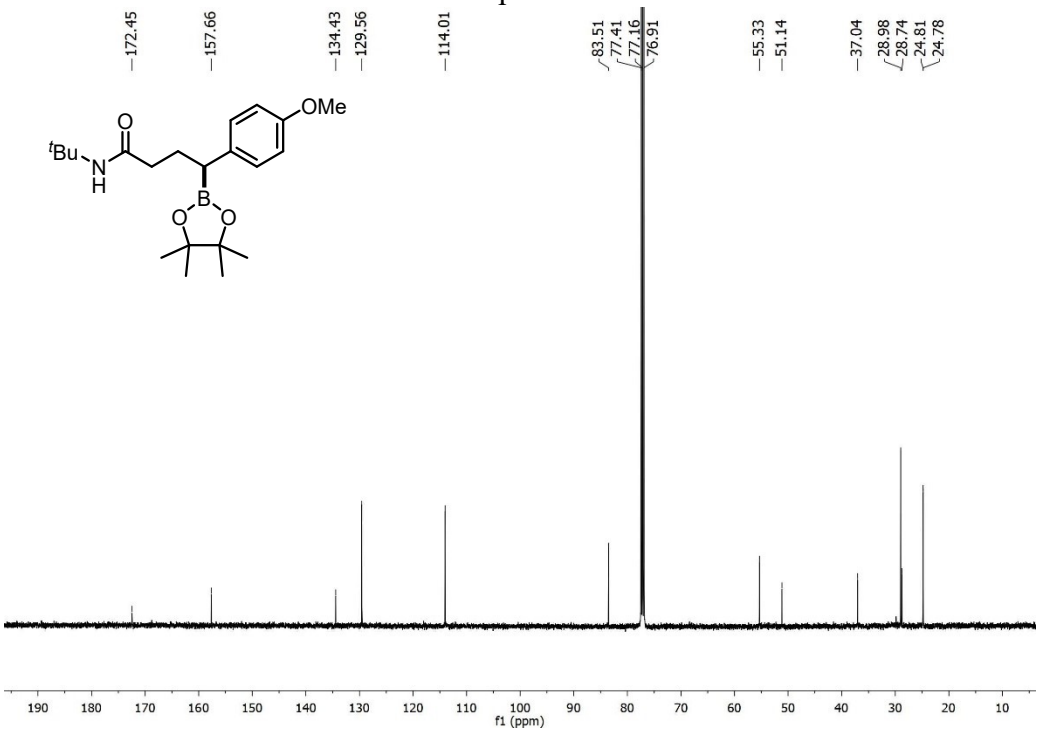
^{1}H NMR spectrum of **30**



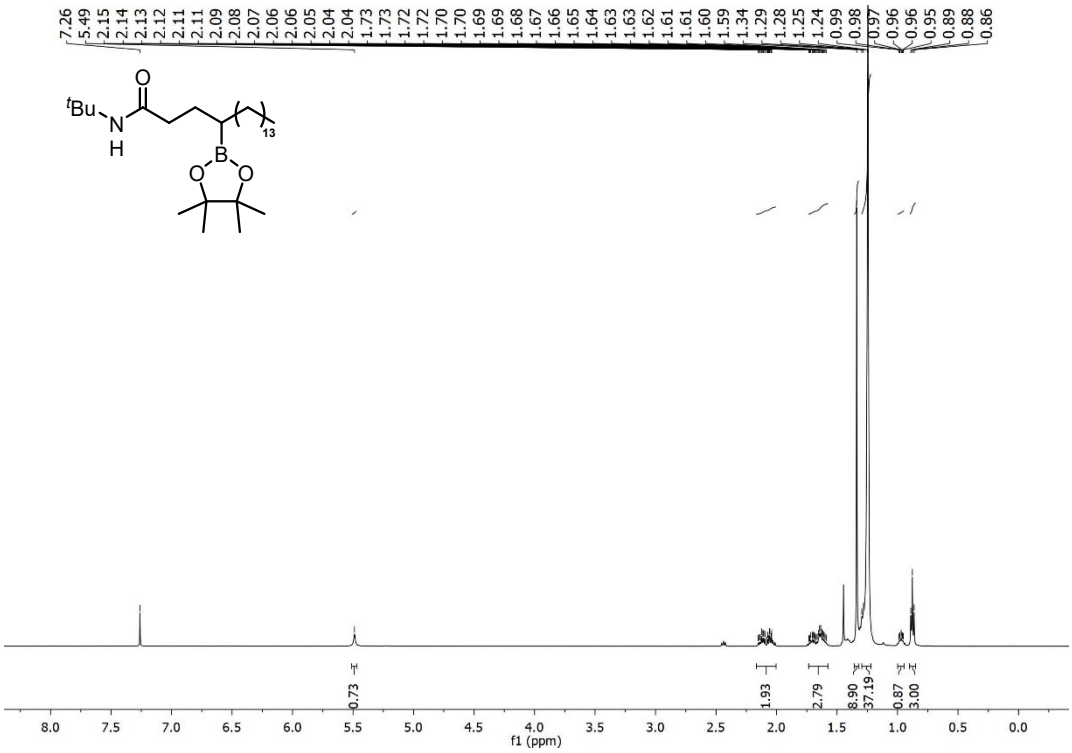
^{13}C NMR spectrum of **30**



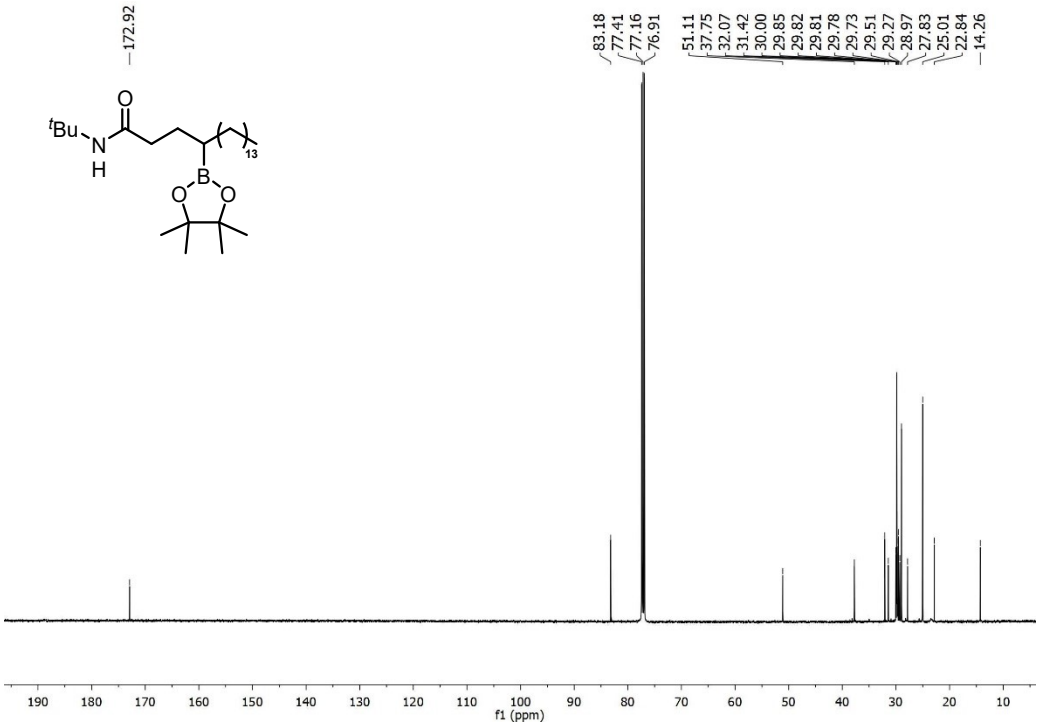
^{1}H NMR spectrum of **31**



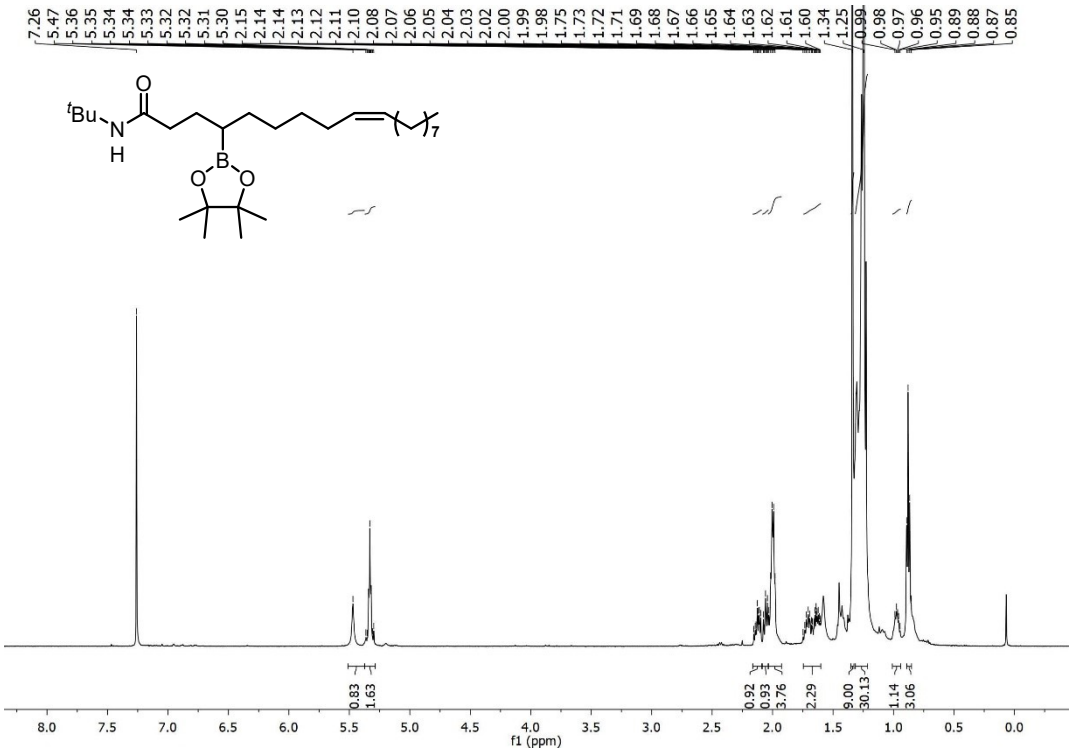
^{13}C NMR spectrum of **31**



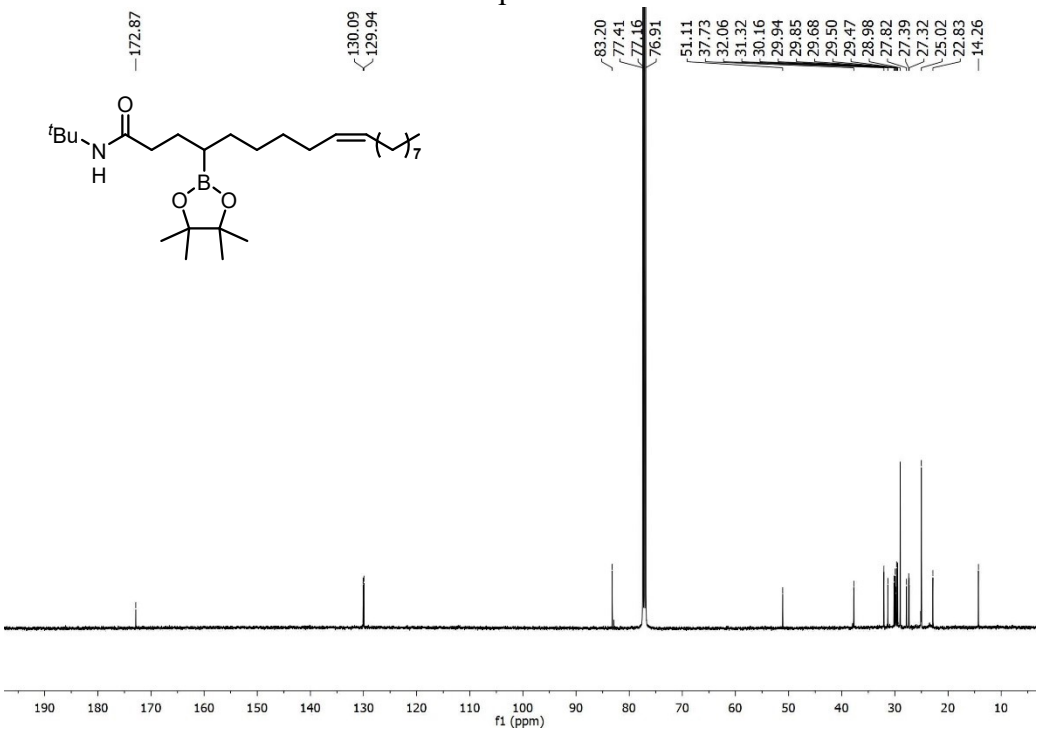
^{1}H NMR spectrum of **32**



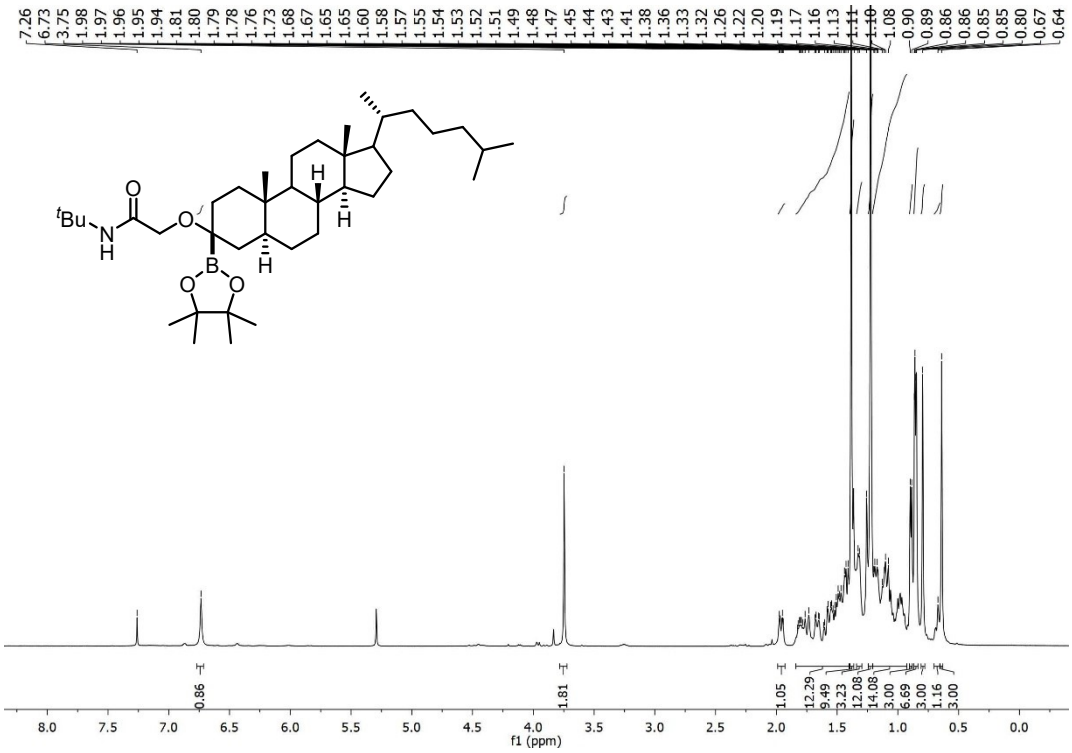
^{13}C NMR spectrum of **32**



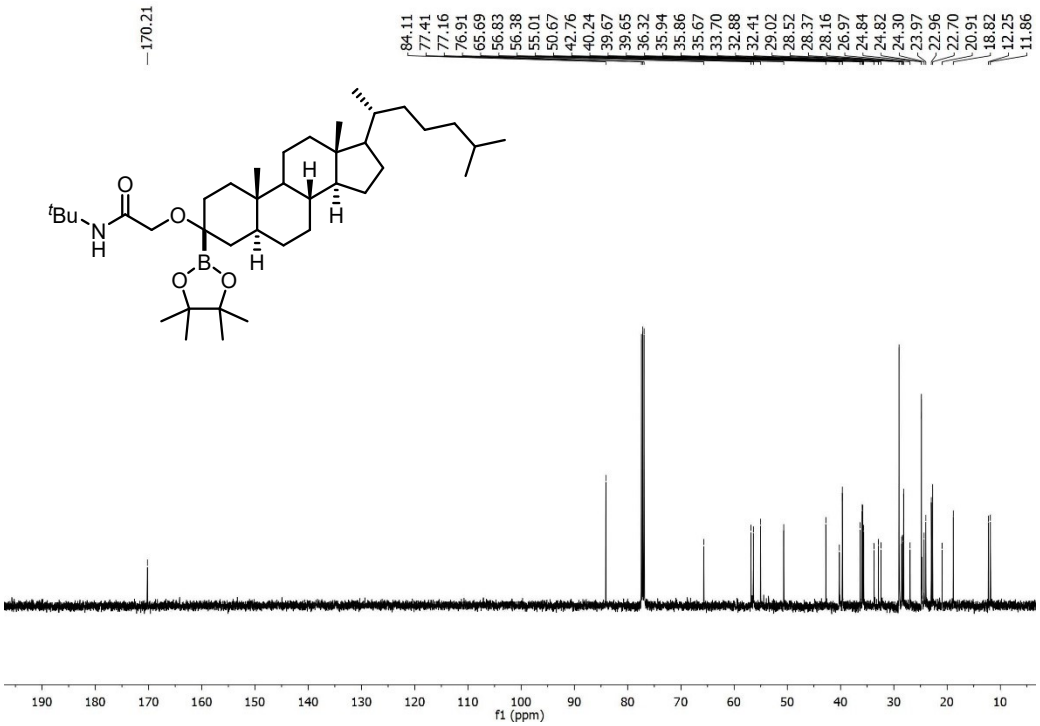
^{1}H NMR spectrum of **33**



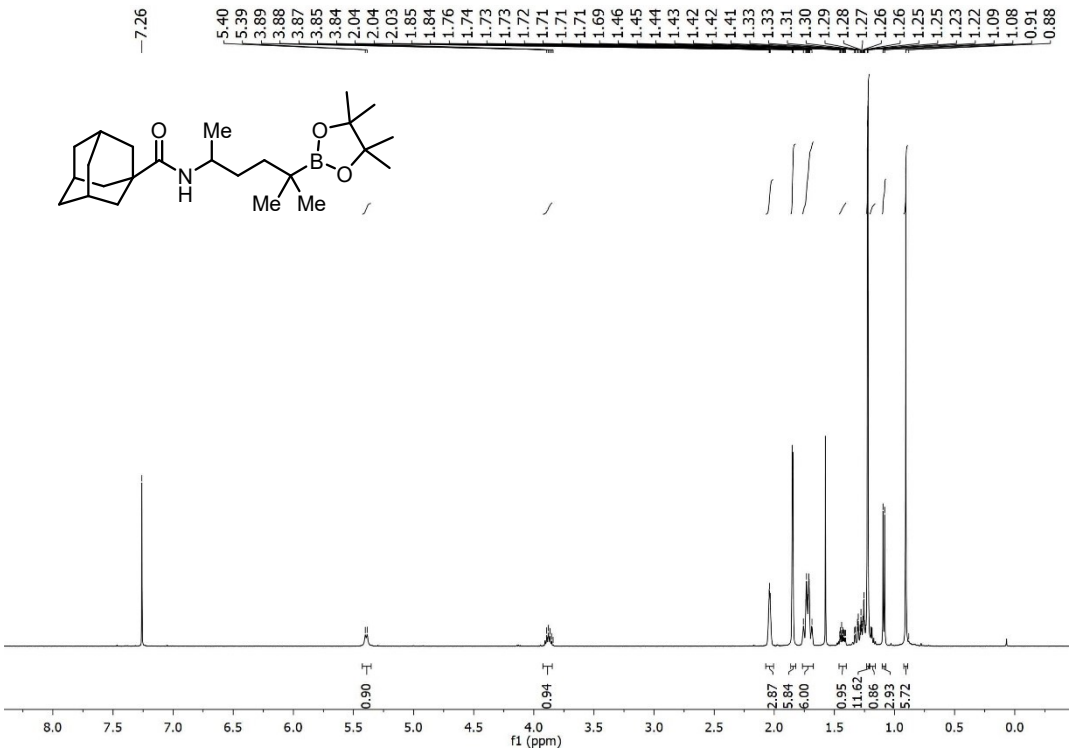
^{13}C NMR spectrum of **33**



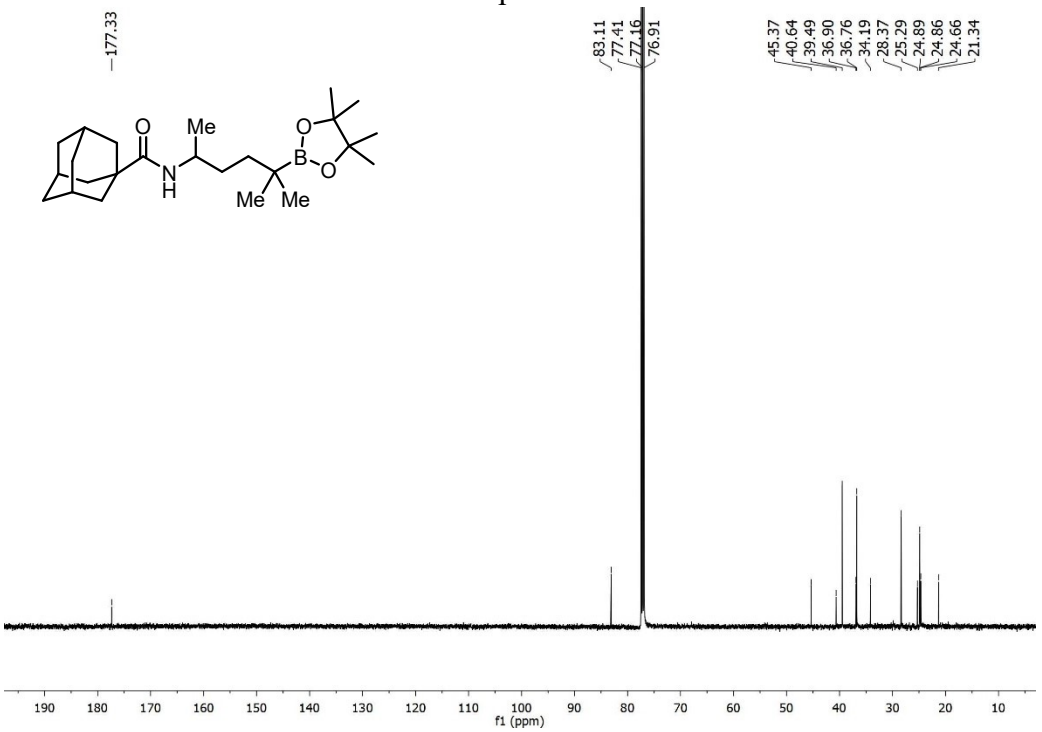
^{1}H NMR spectrum of **34**



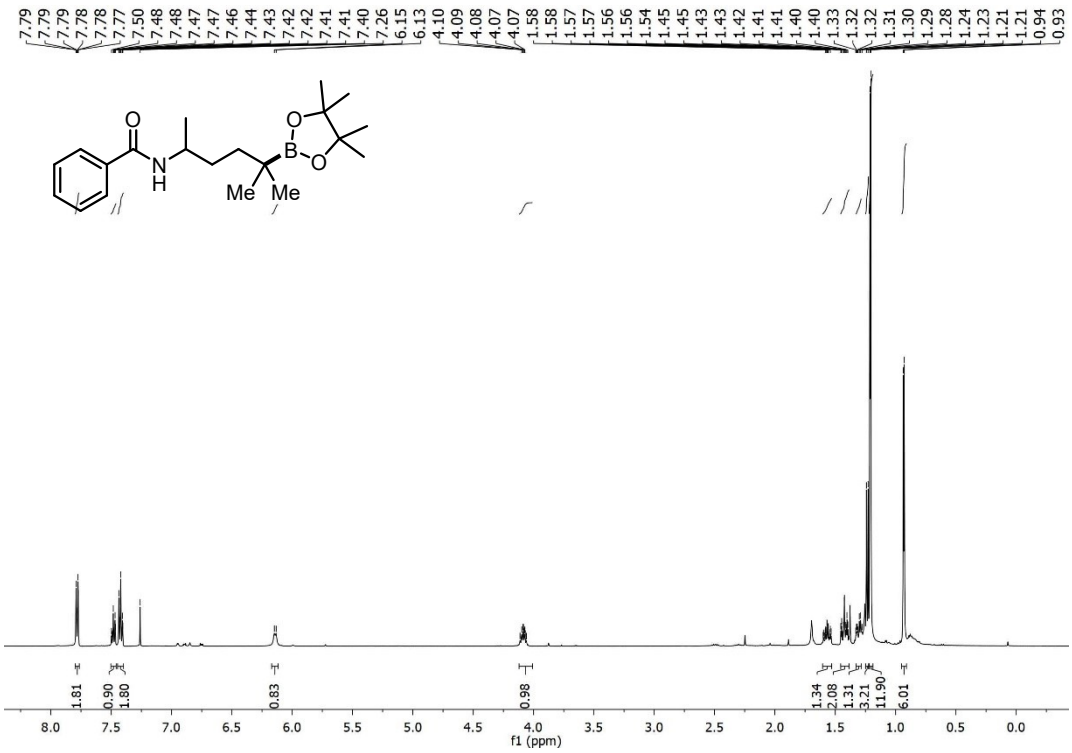
^{13}C NMR spectrum of **34**



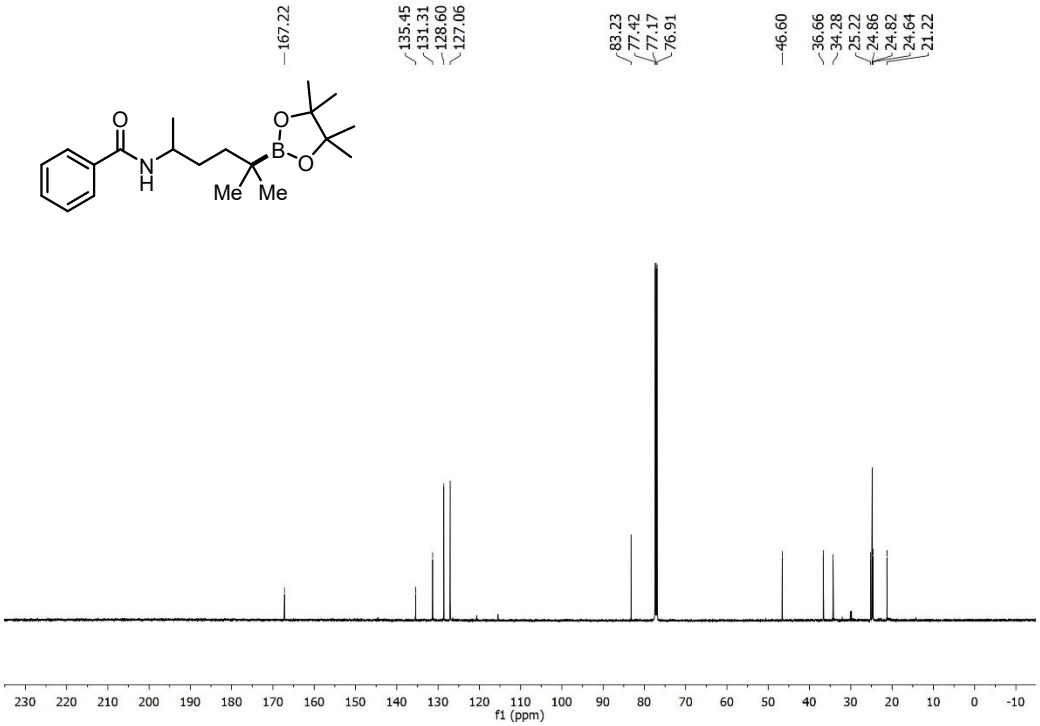
^{1}H NMR spectrum of **36**



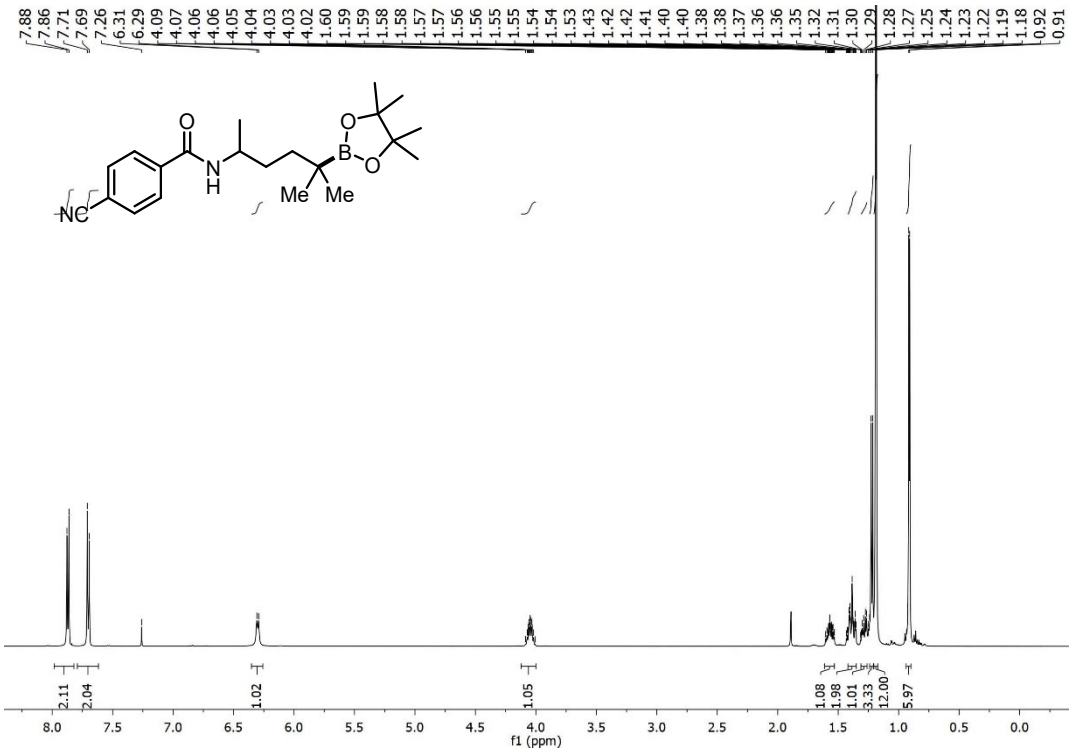
^{13}C NMR spectrum of **36**



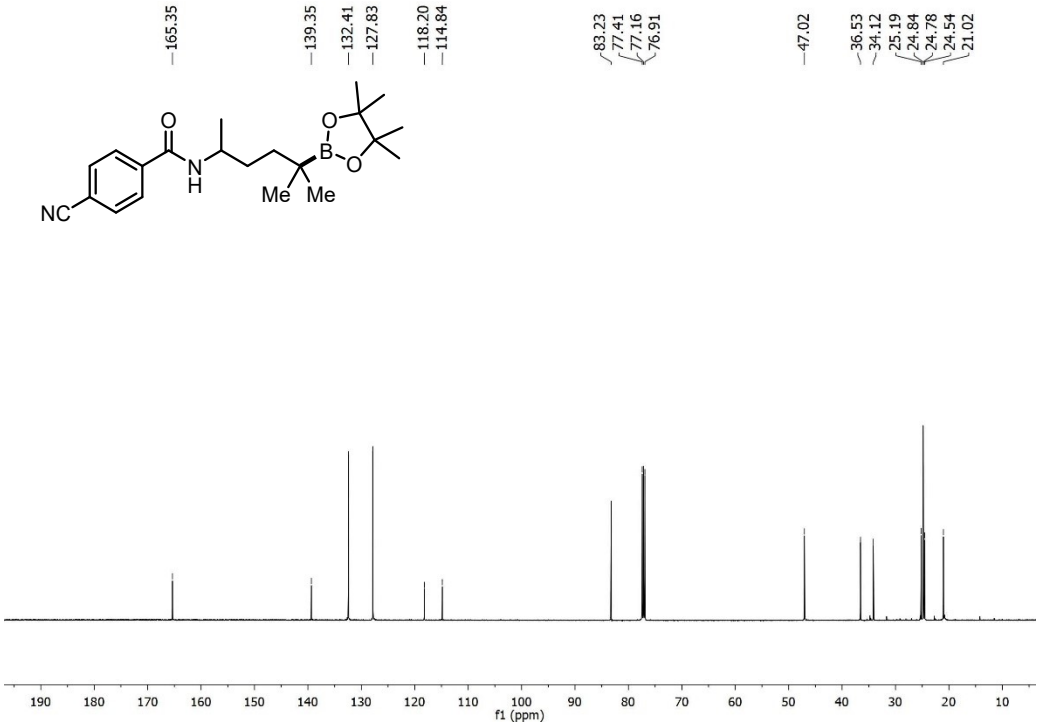
^{1}H NMR spectrum of **37**



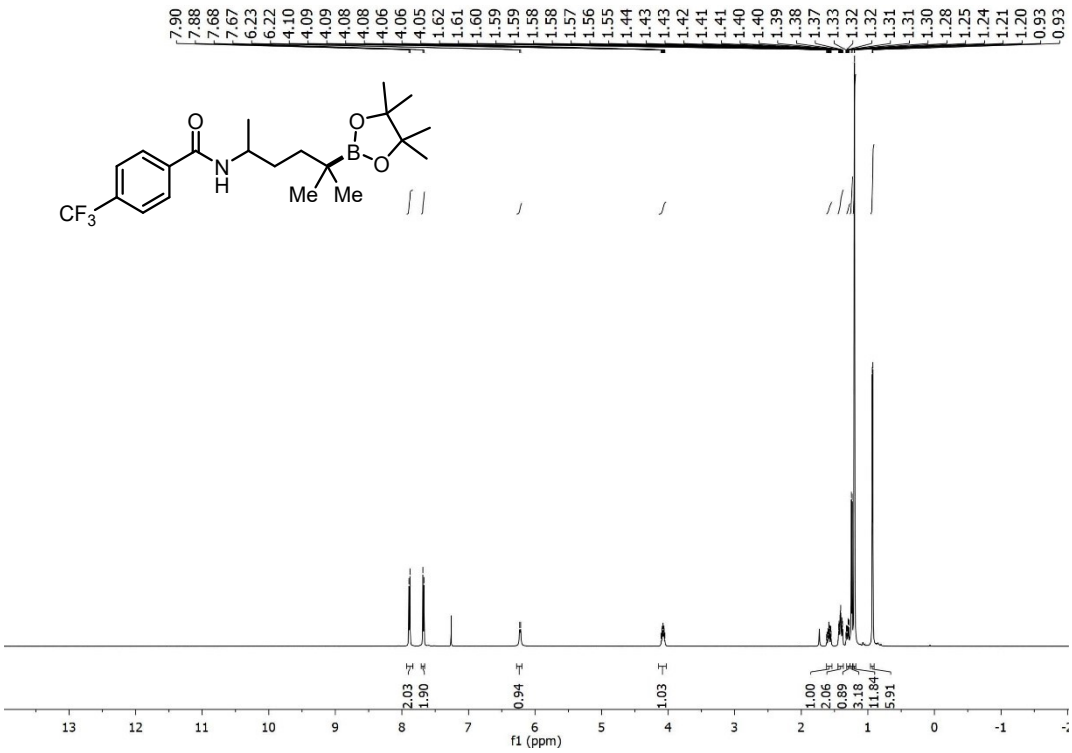
^{13}C NMR spectrum of **37**



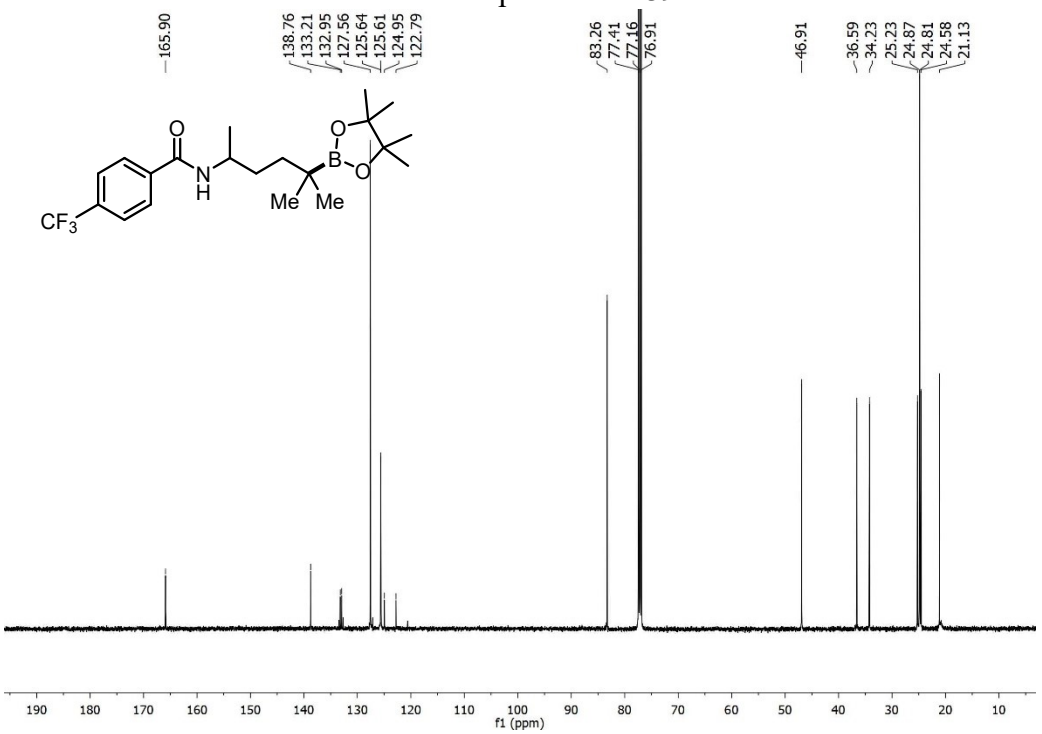
^{1}H NMR spectrum of **38**



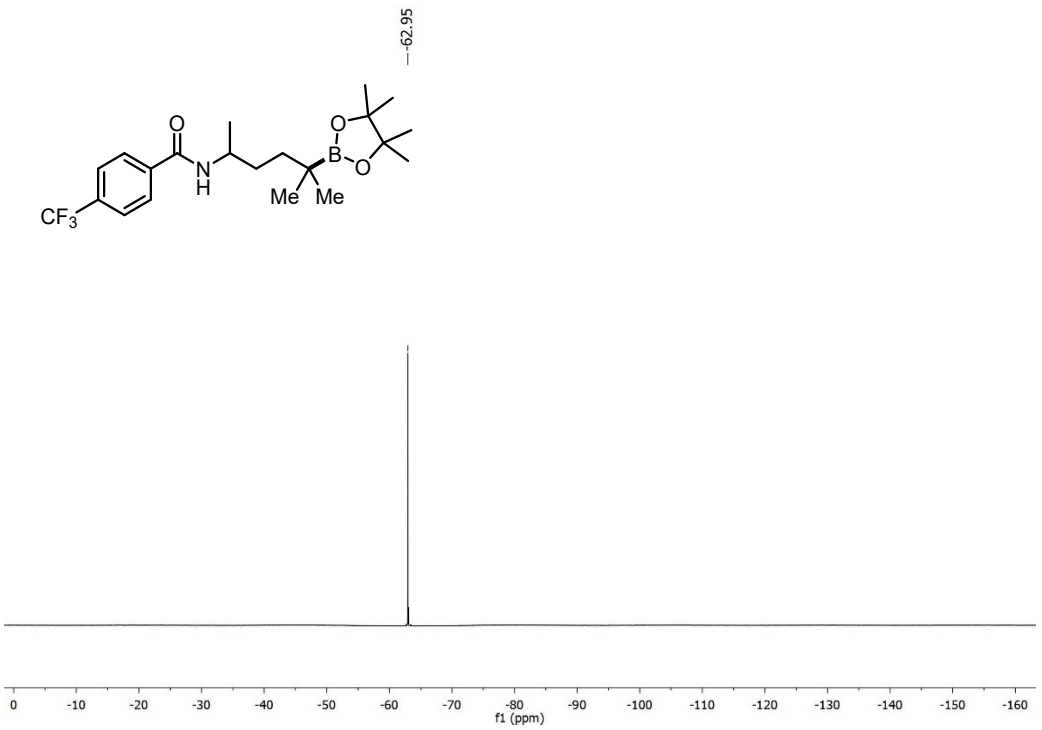
^{13}C NMR spectrum of **38**



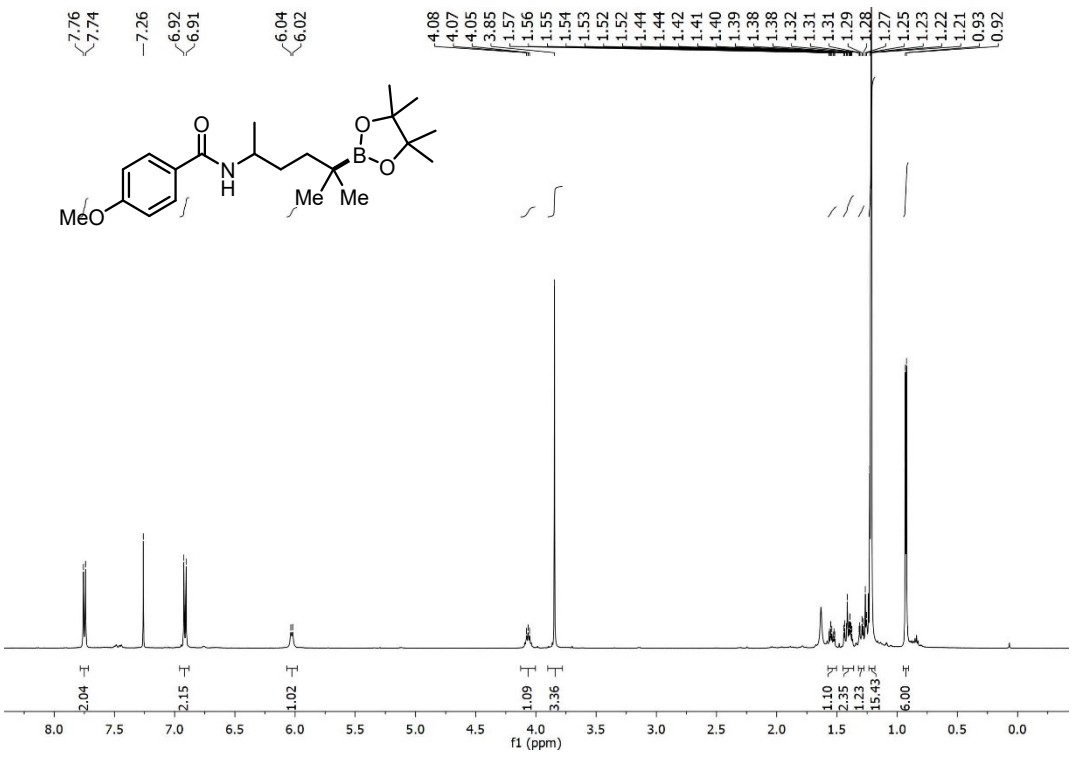
^{1}H NMR spectrum of **39**



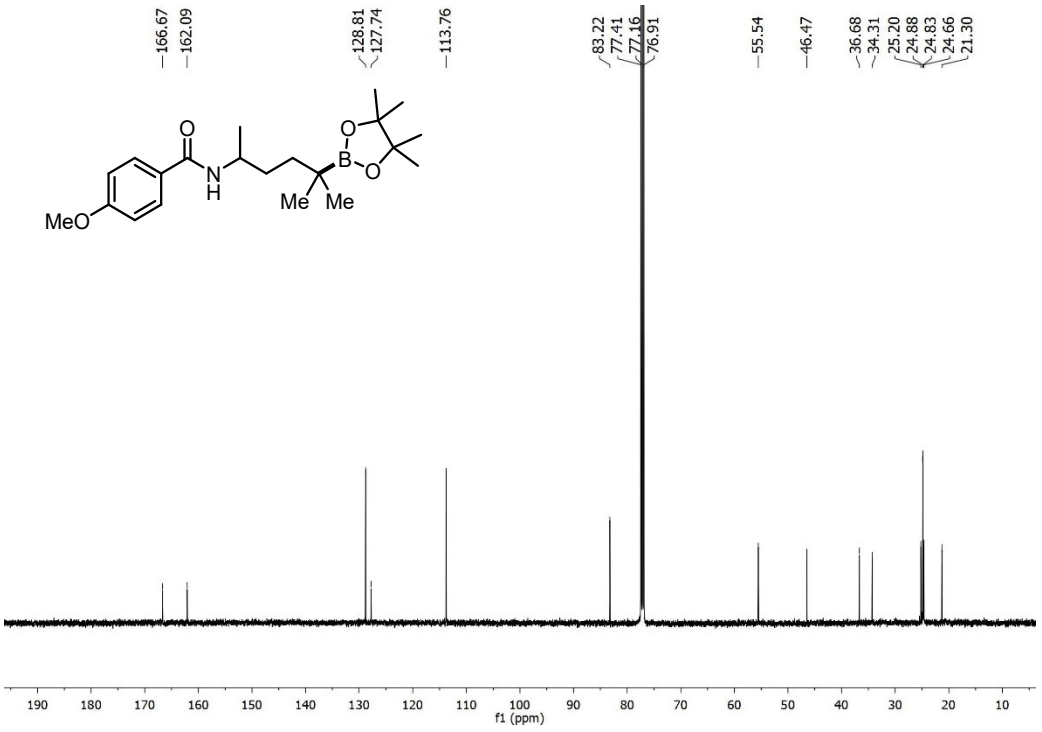
^{13}C NMR spectrum of **39**



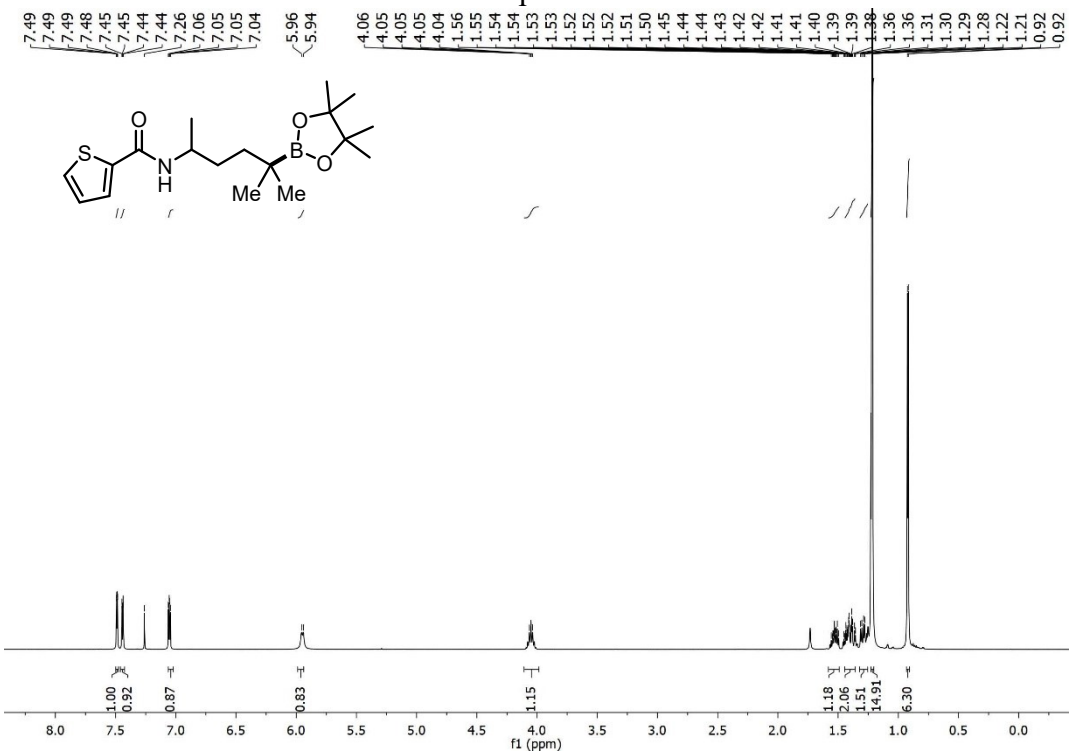
^{19}F NMR spectrum of **39**



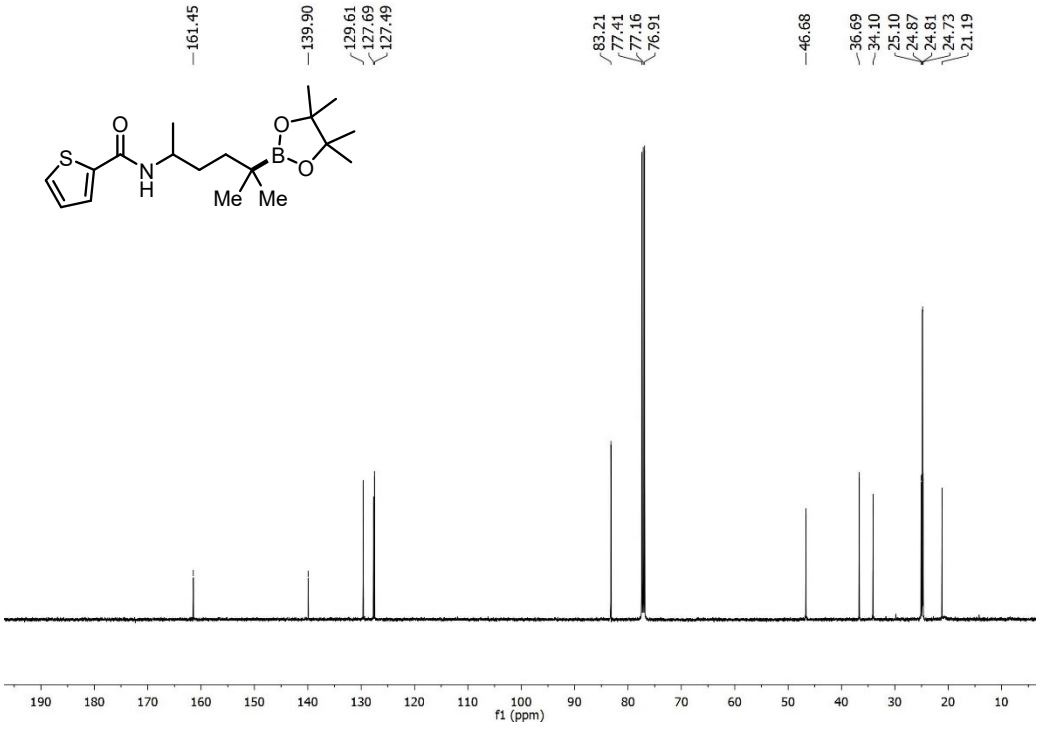
^{1}H NMR spectrum of **40**



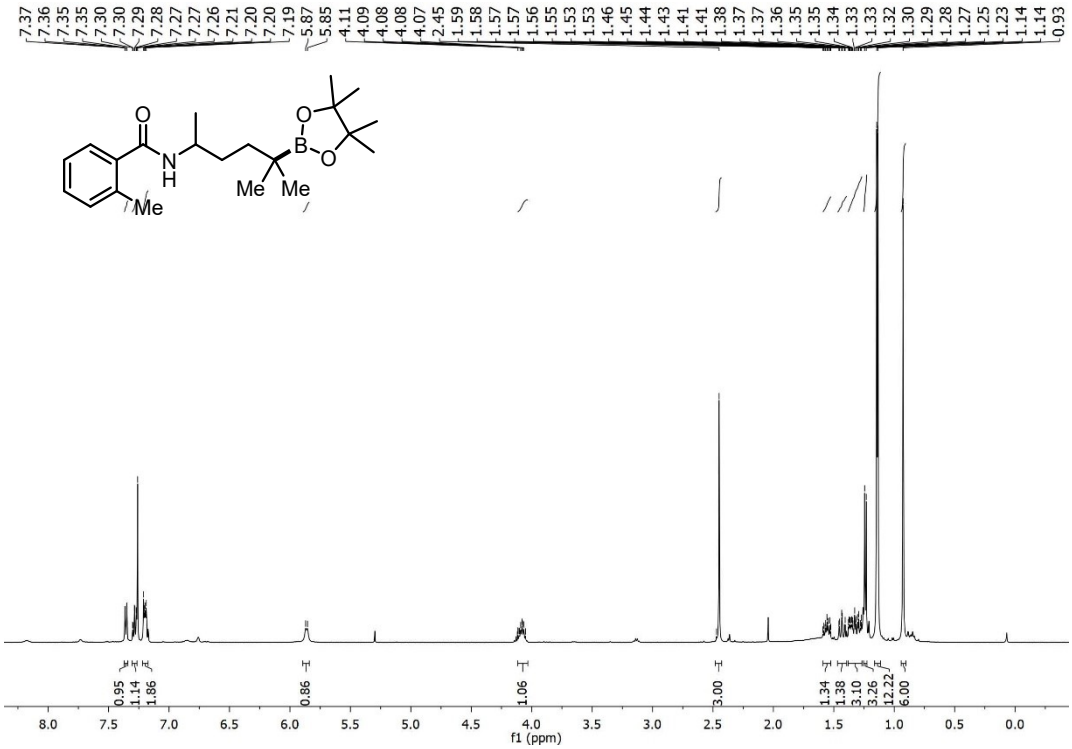
^{13}C NMR spectrum of **40**



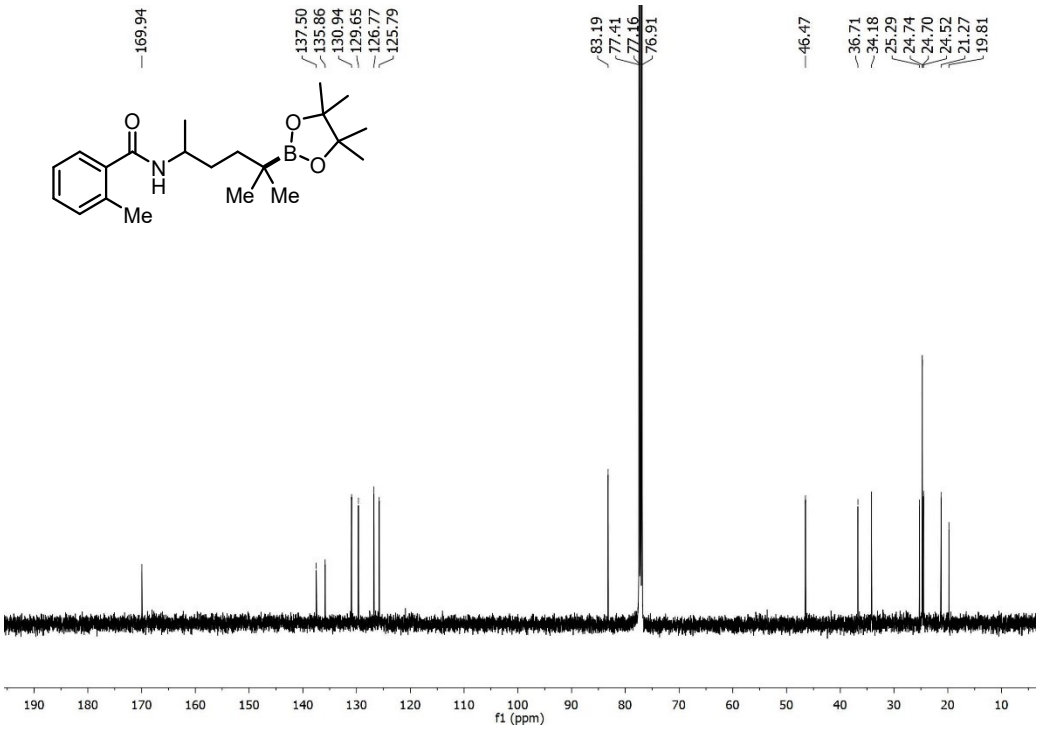
^{1}H NMR spectrum of **41**



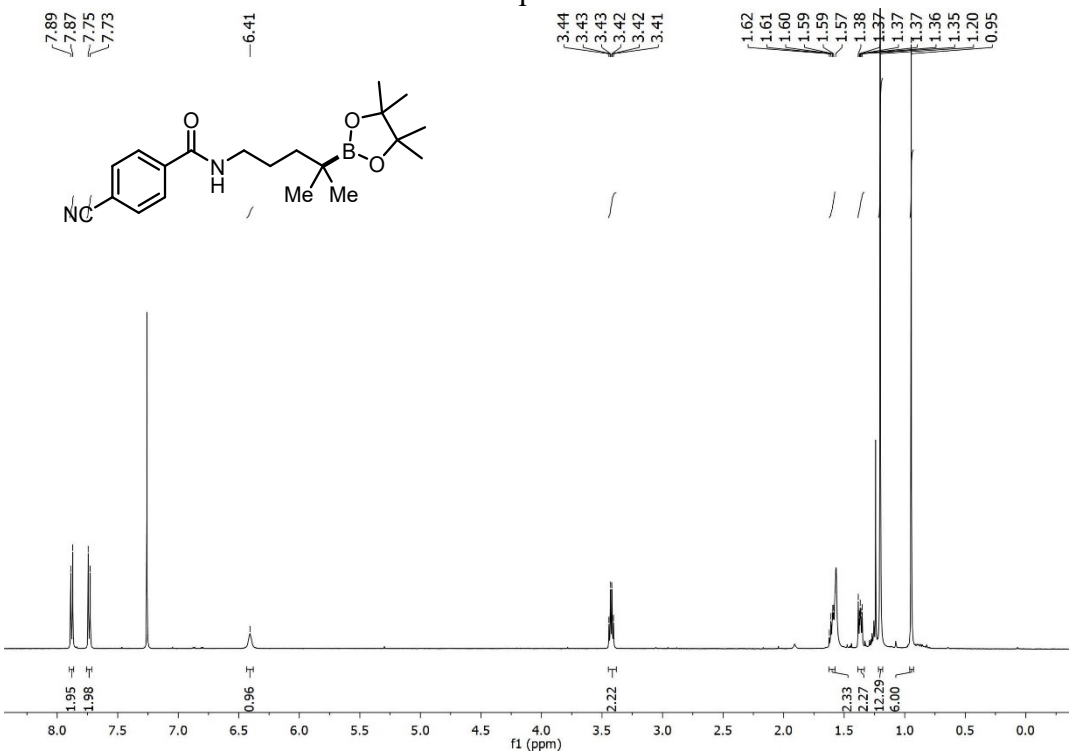
^{13}C NMR spectrum of **41**



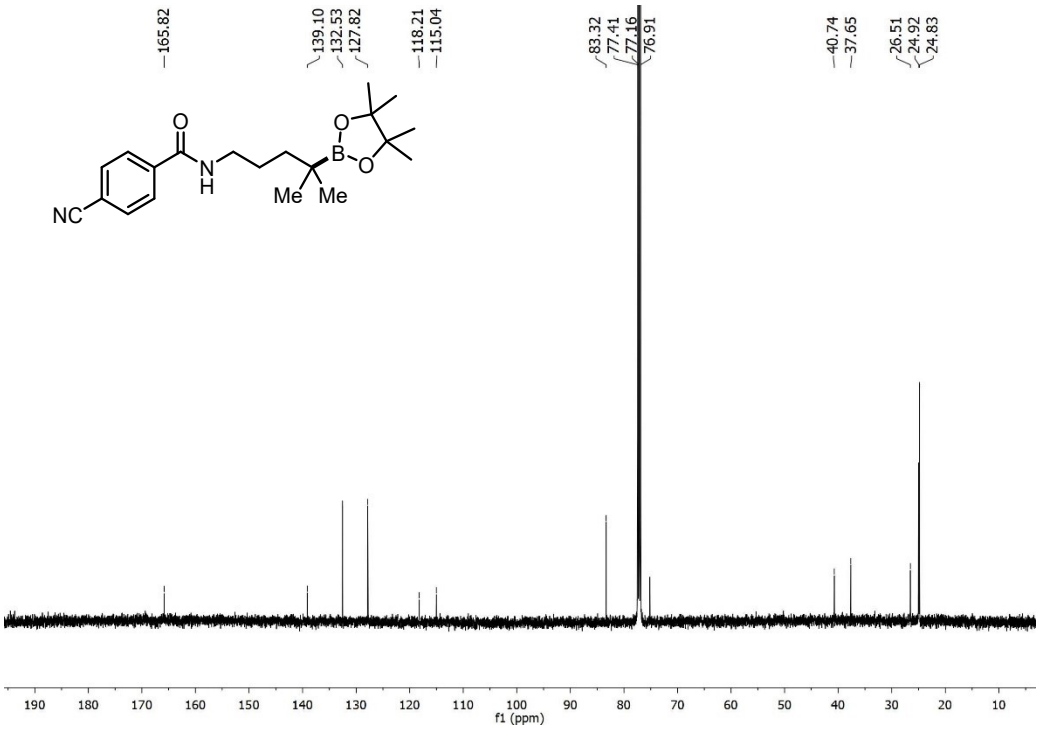
^{1}H NMR spectrum of **42**



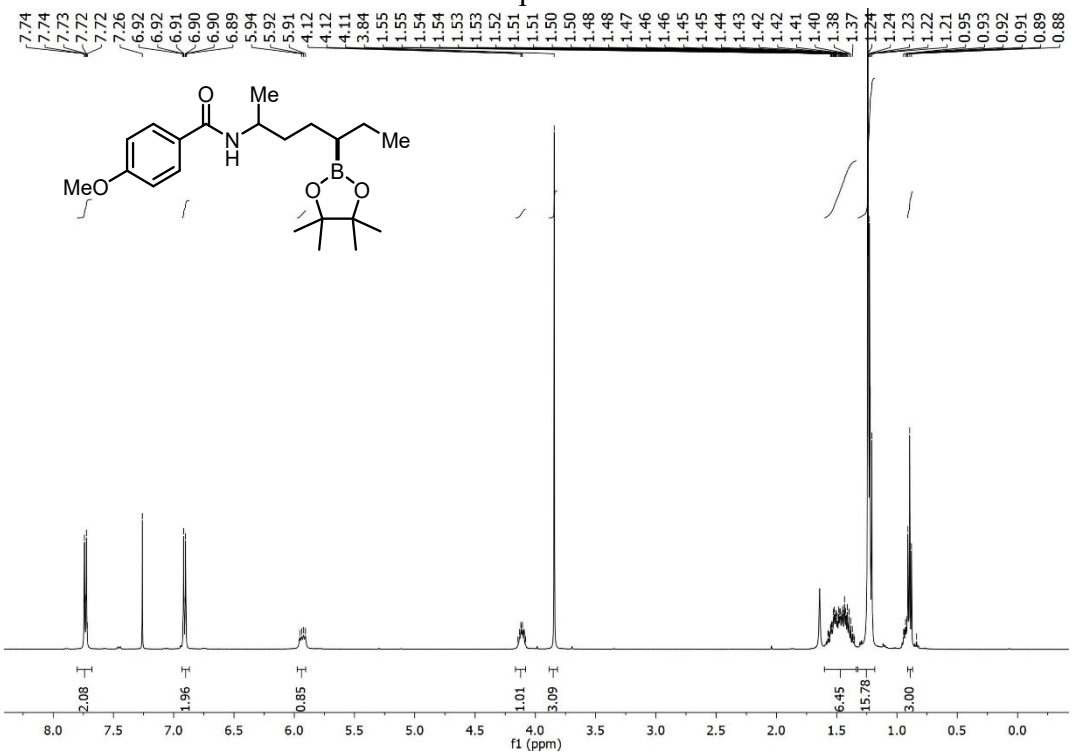
^{13}C NMR spectrum of **42**



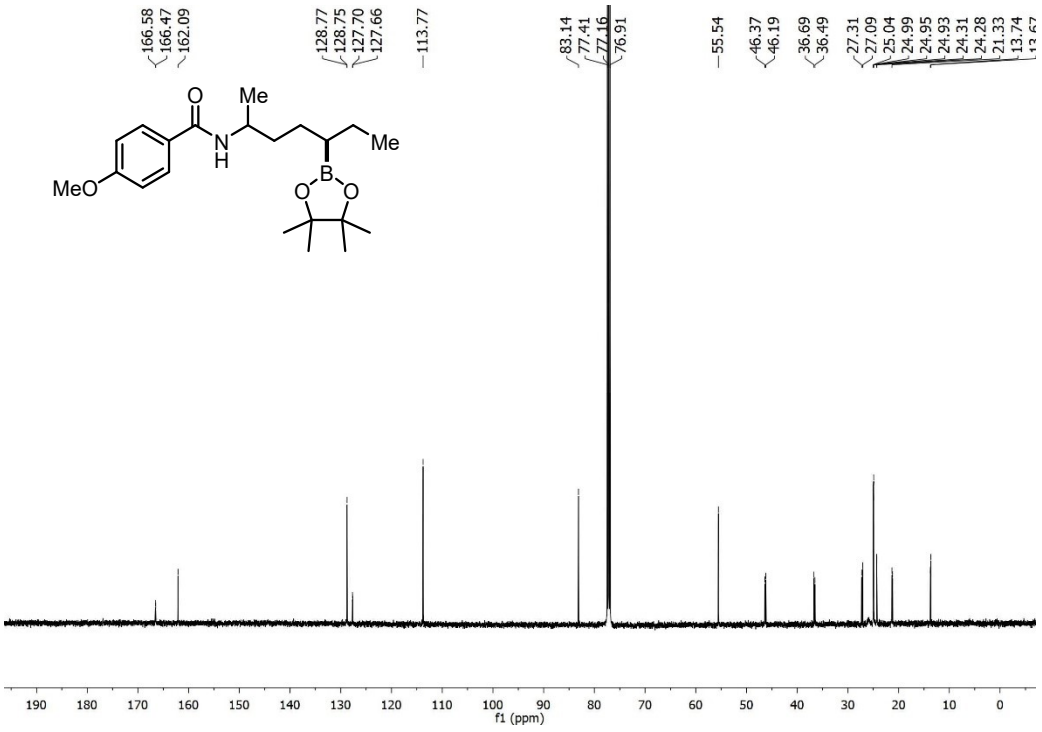
^{1}H NMR spectrum of **43**



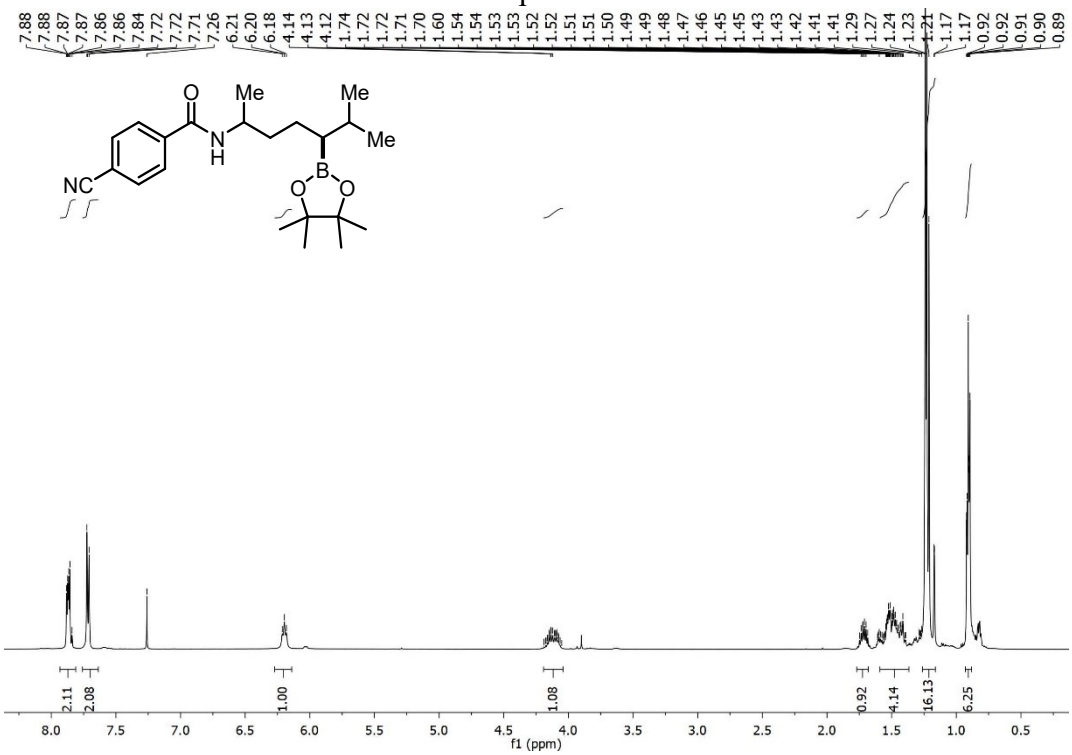
^{13}C NMR spectrum of **43**



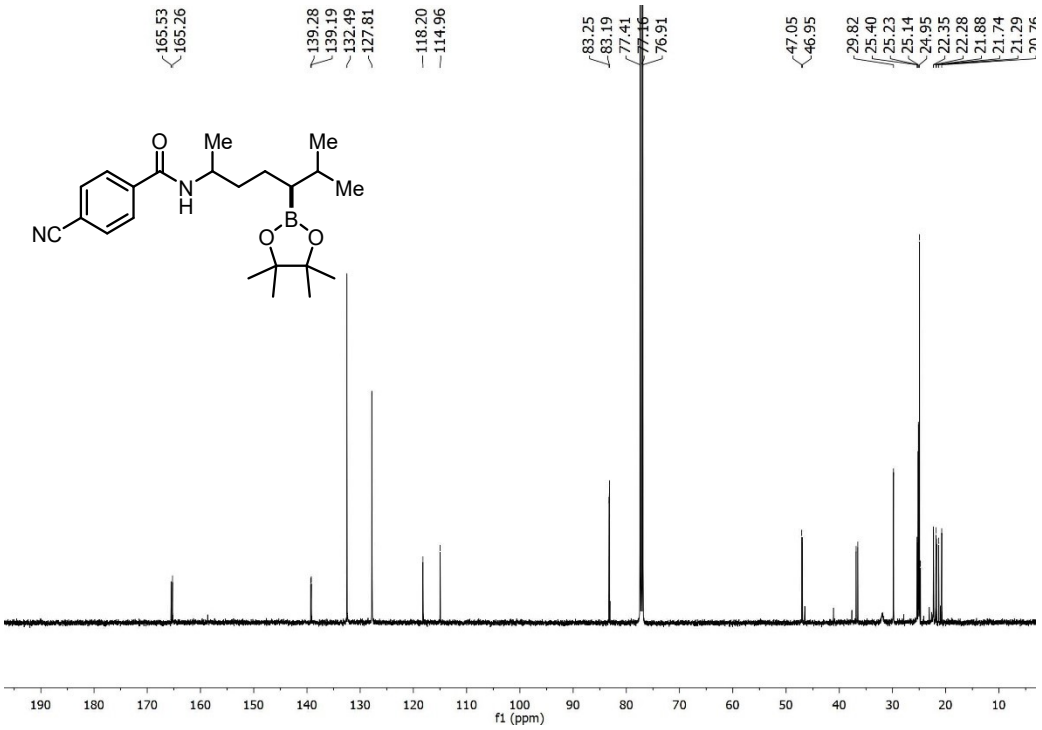
^{1}H NMR spectrum of **44**



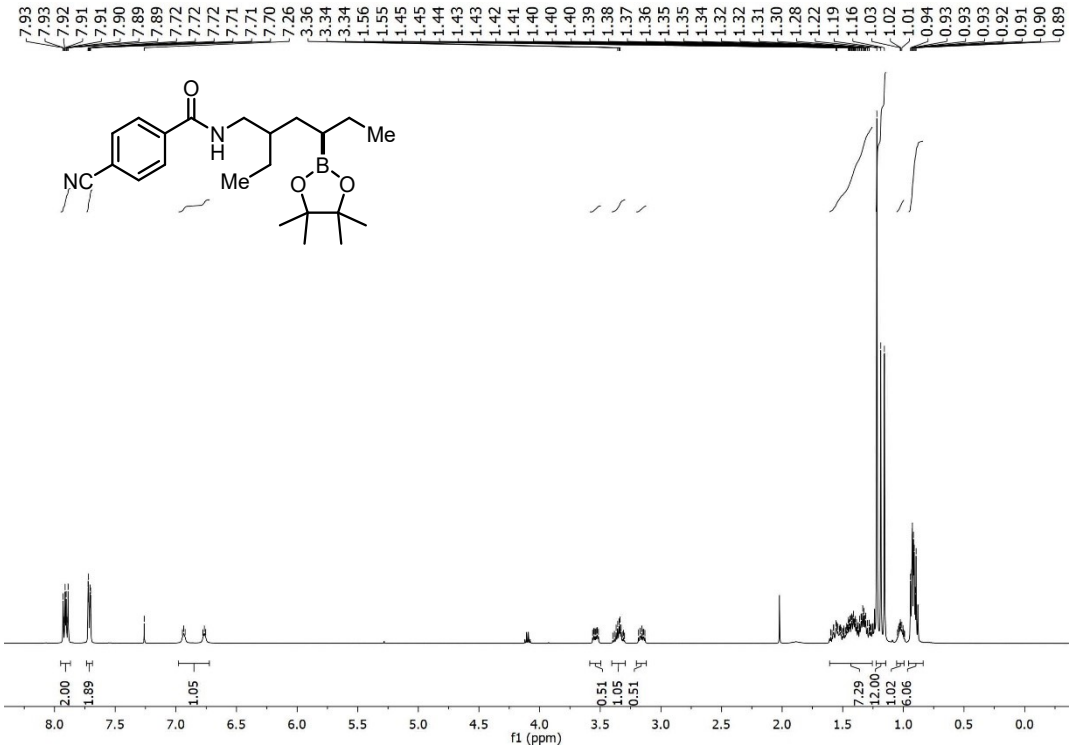
^{13}C NMR spectrum of **44**



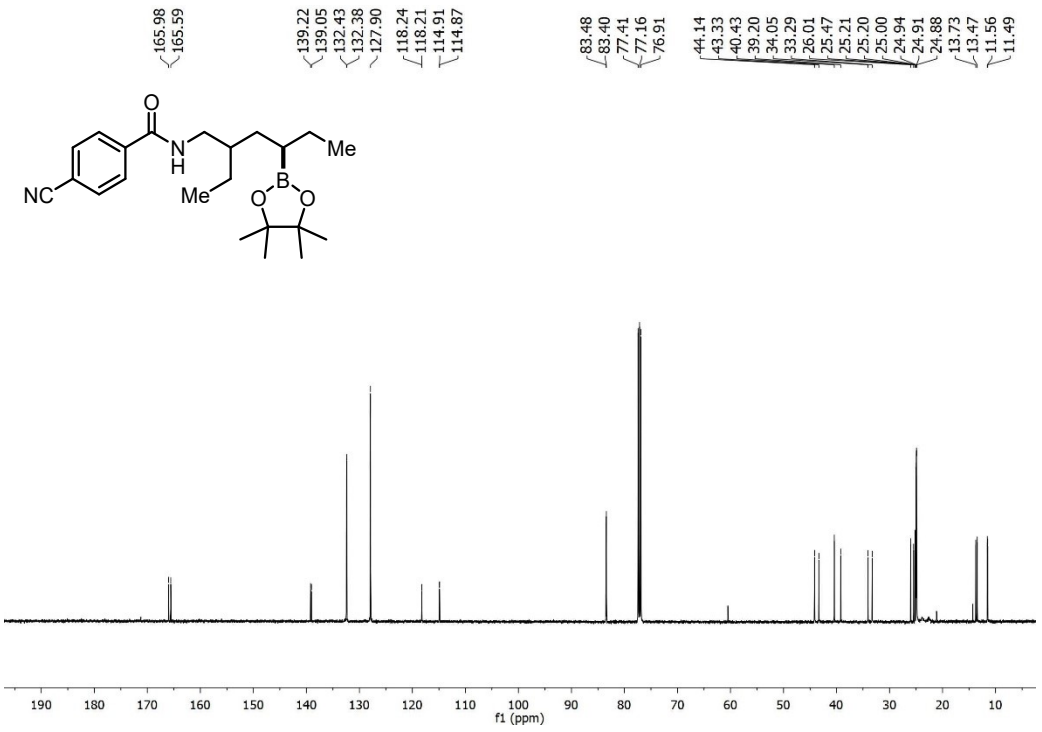
^{1}H NMR spectrum of **45**



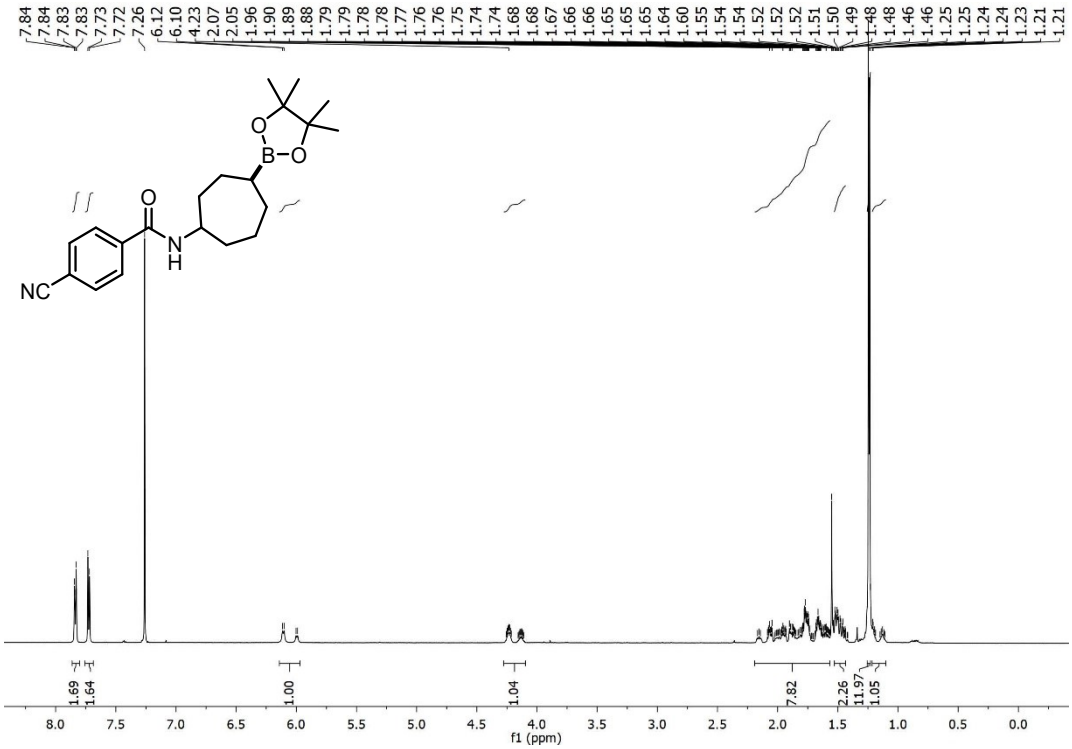
^{13}C NMR spectrum of **45**



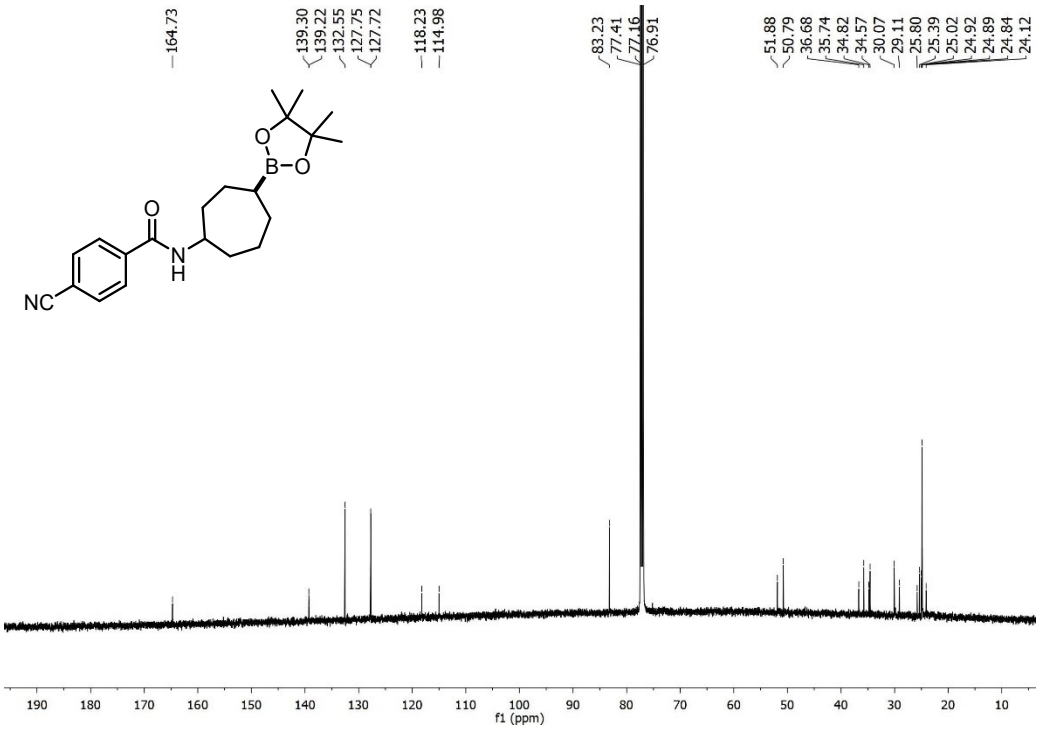
^{1}H NMR spectrum of **46**



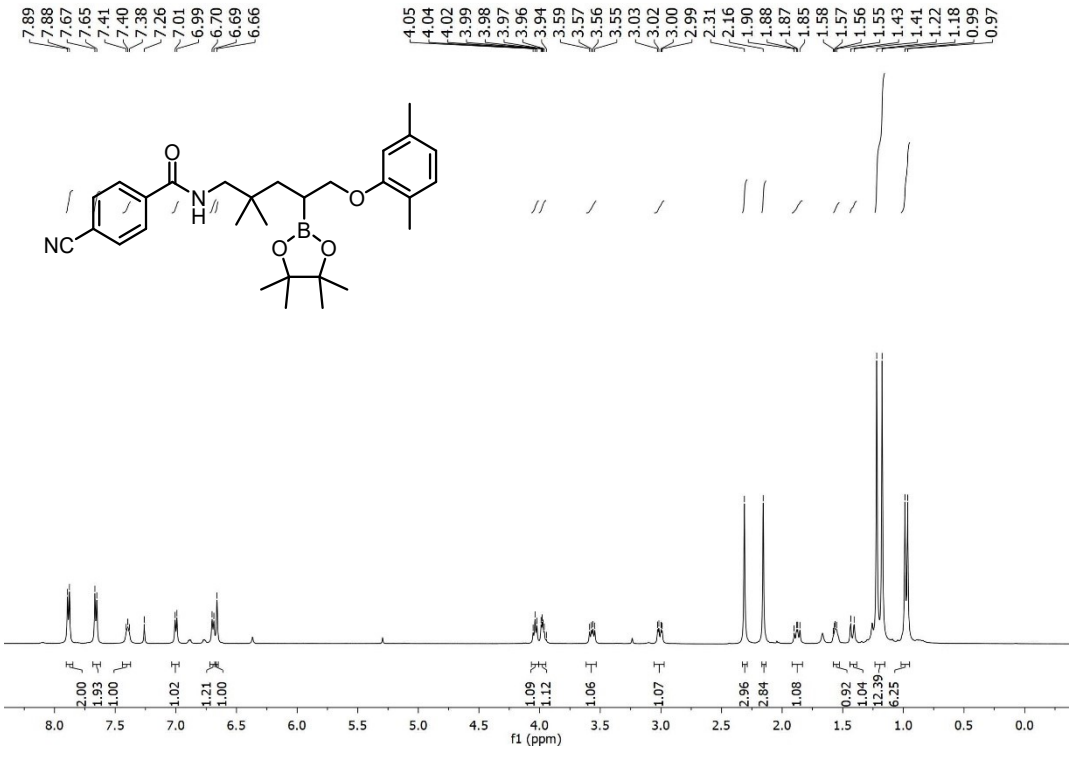
^{13}C NMR spectrum of **46**



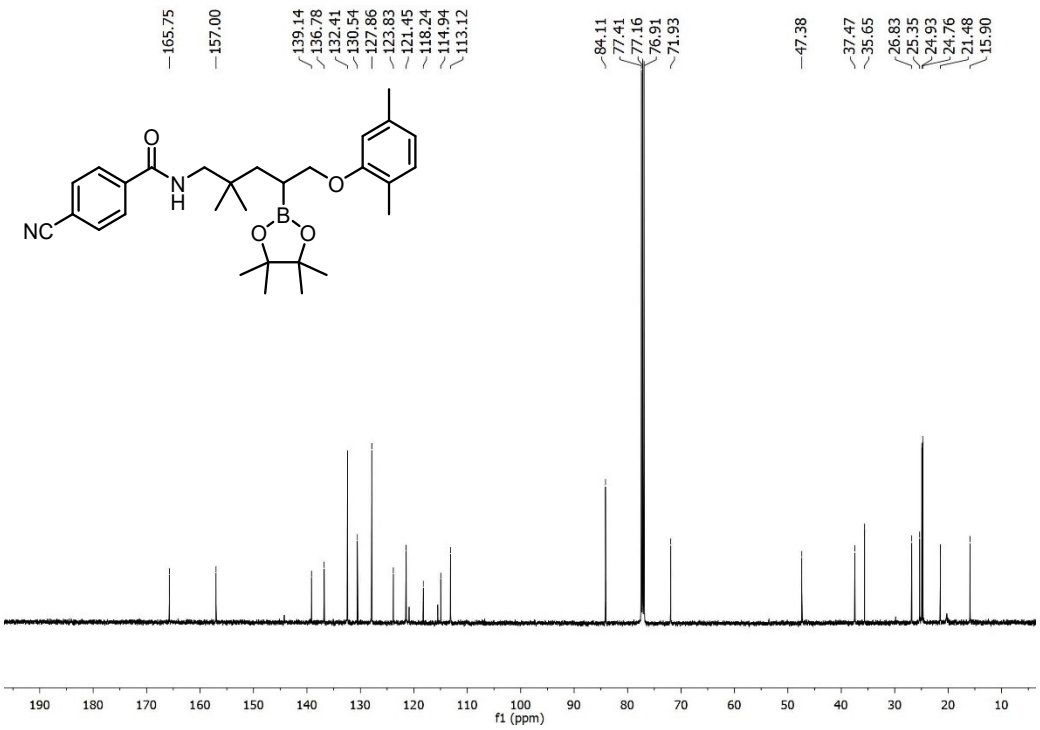
^{1}H NMR spectrum of **47**



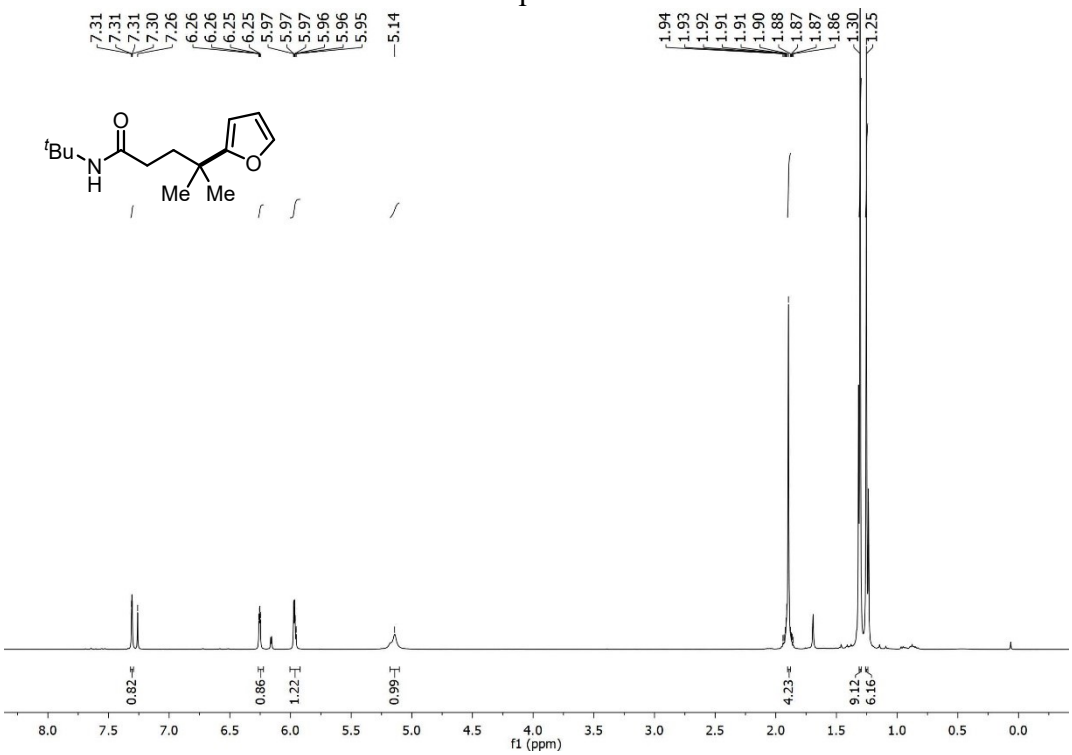
^{13}C NMR spectrum of **47**



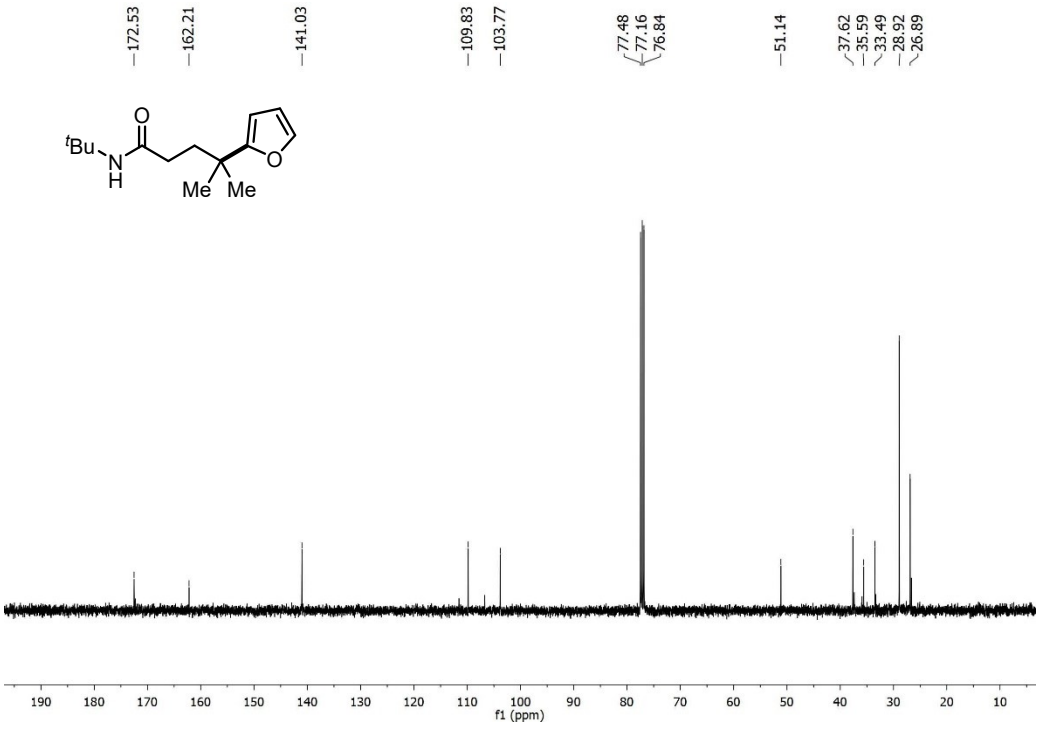
^{1}H NMR spectrum of **48**



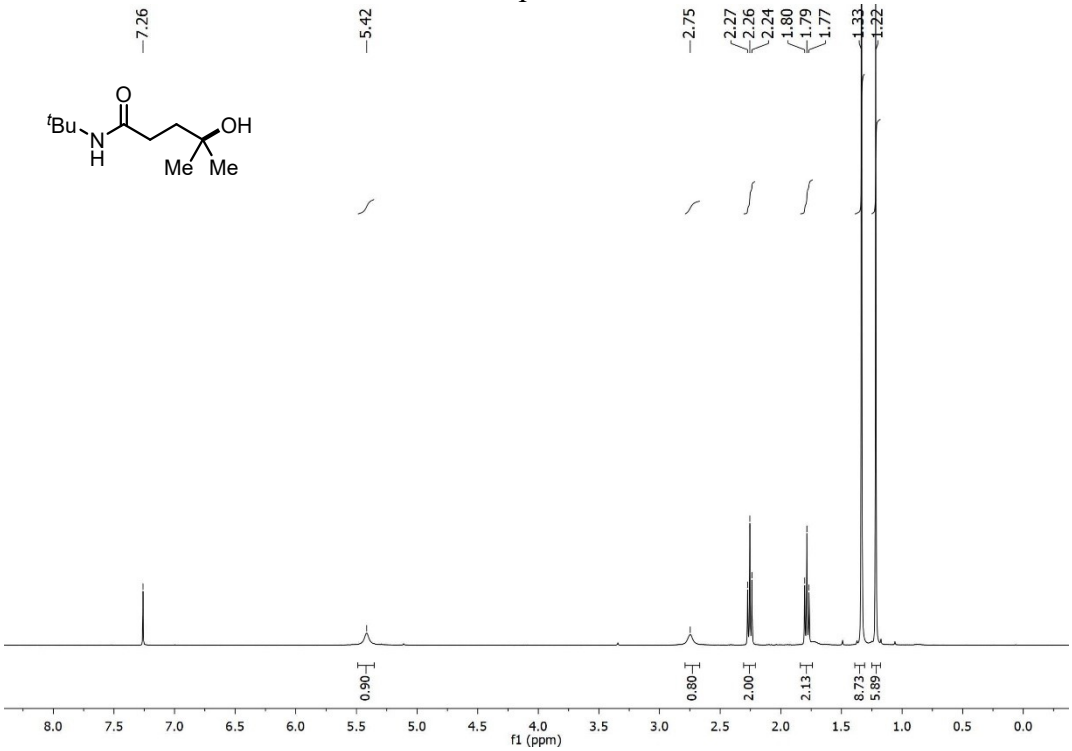
^{13}C NMR spectrum of **48**



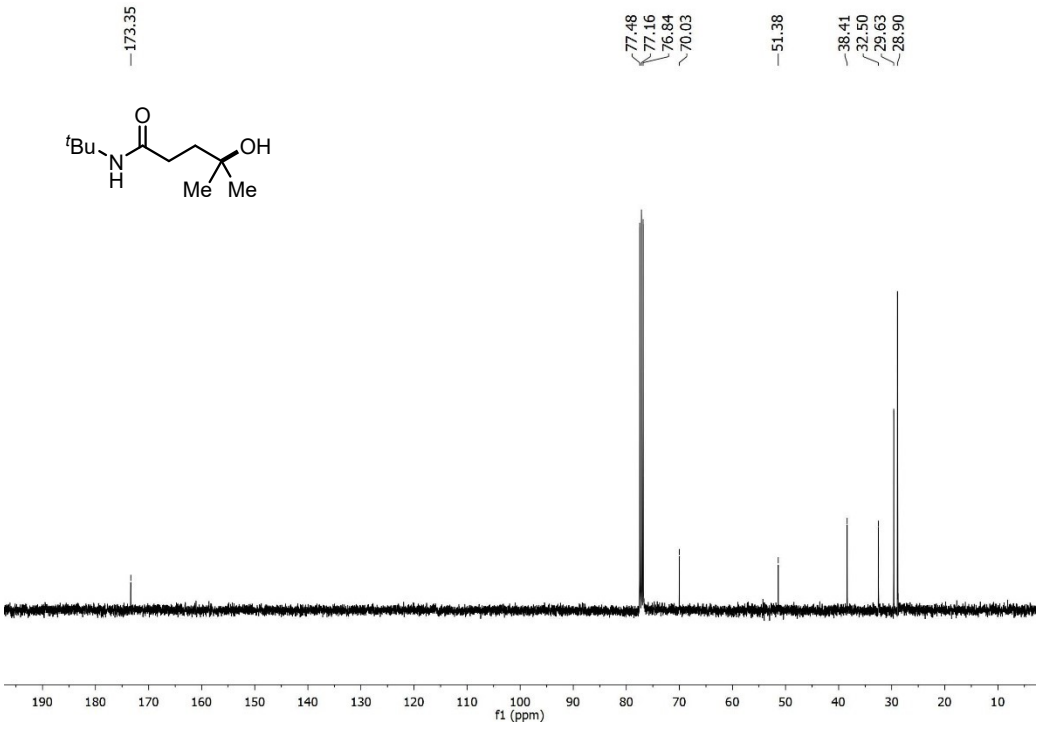
^{1}H NMR spectrum of **49**



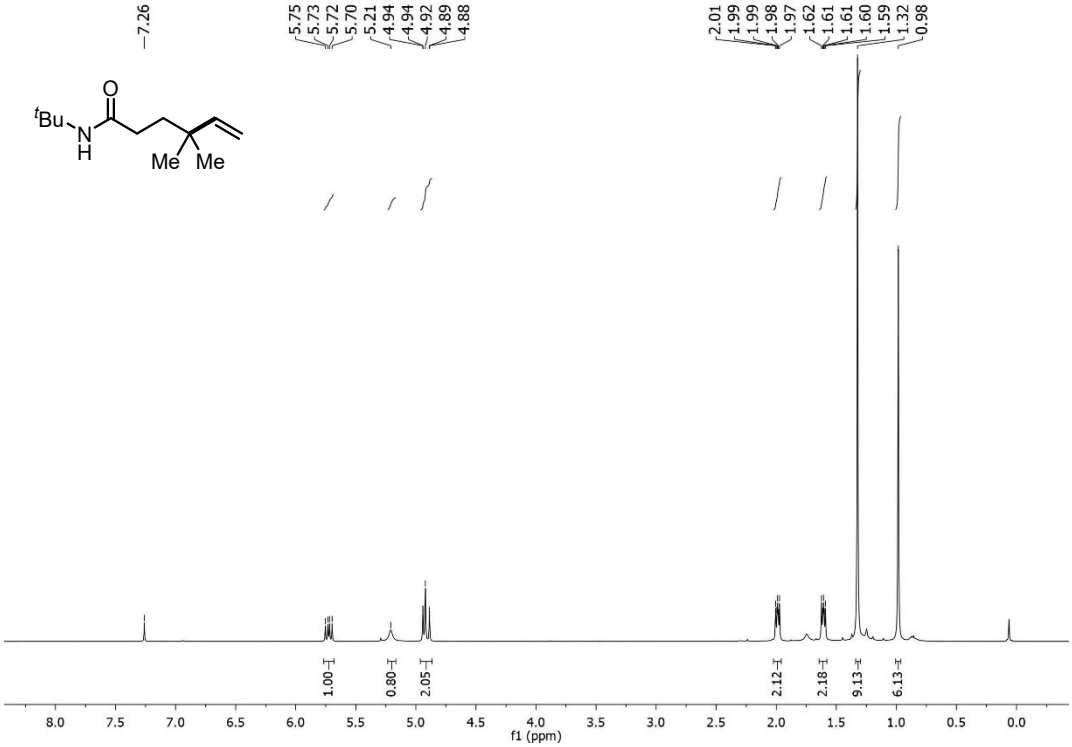
^{13}C NMR spectrum of **49**



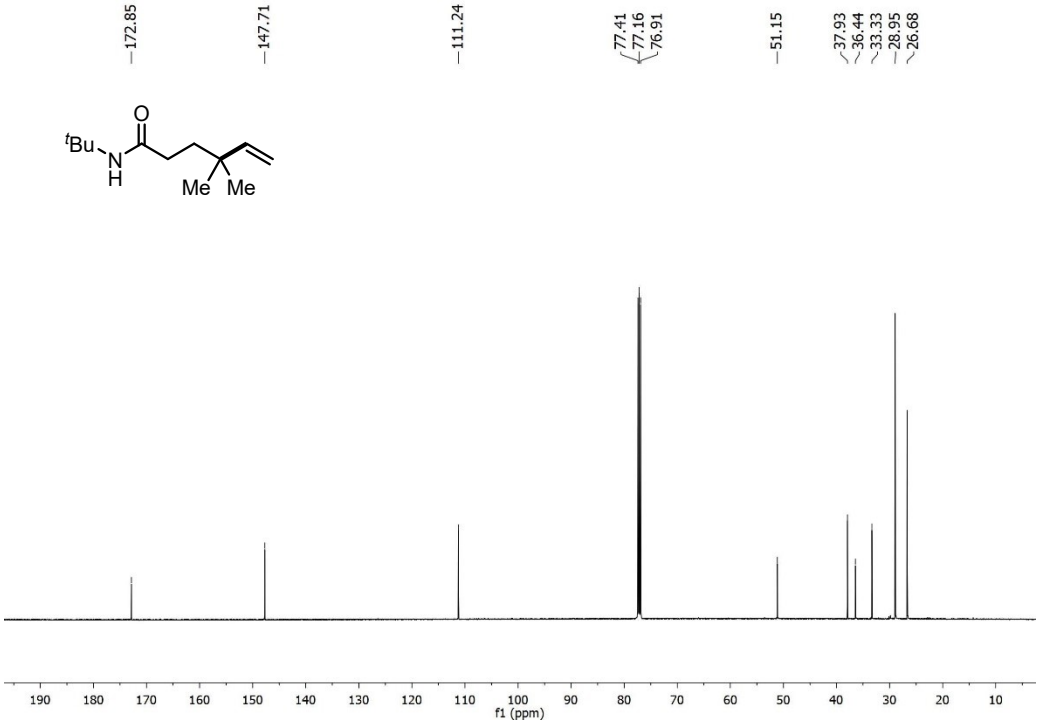
^{1}H NMR spectrum of **50**



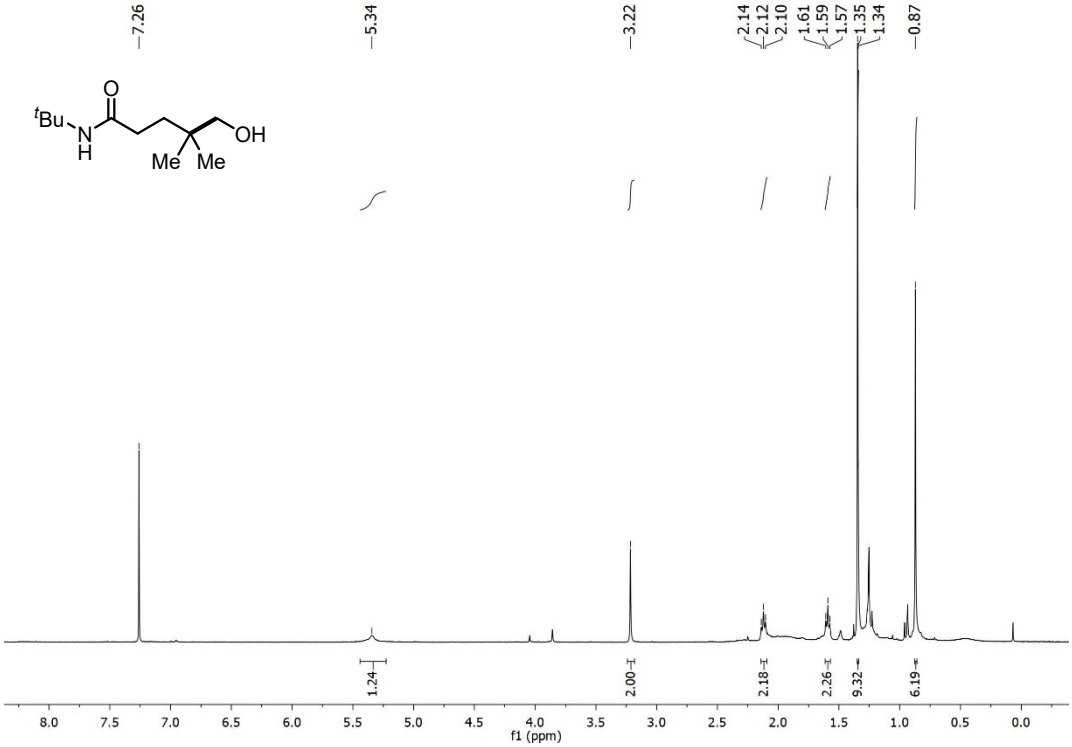
^{13}C NMR spectrum of **50**



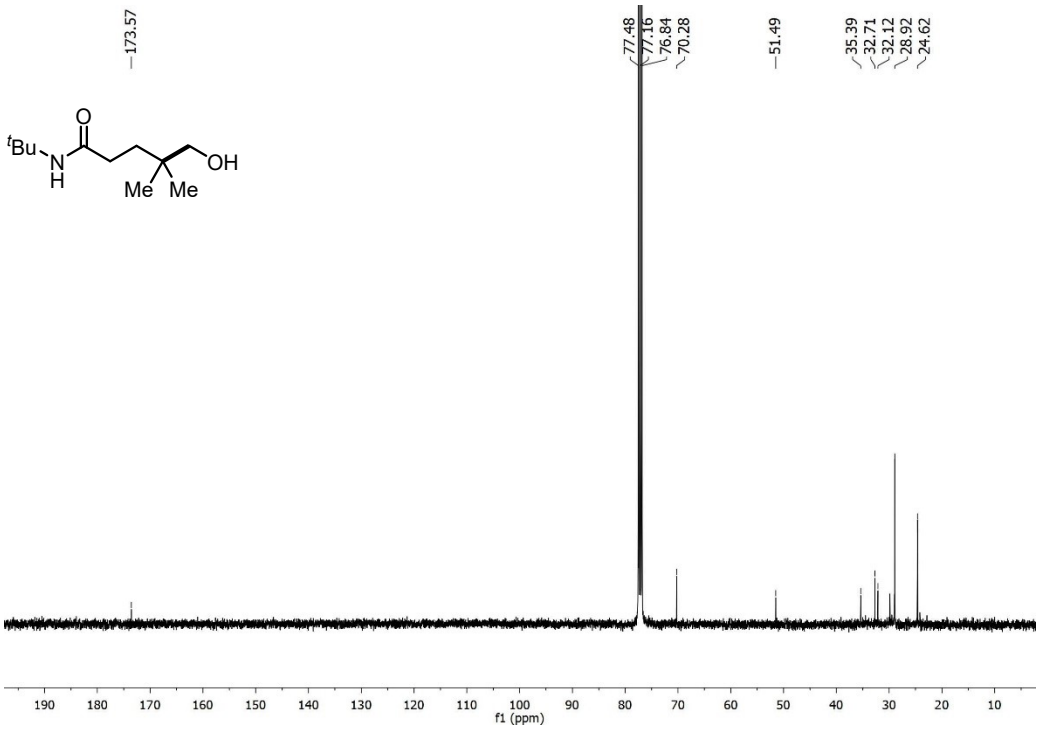
^{1}H NMR spectrum of **51**



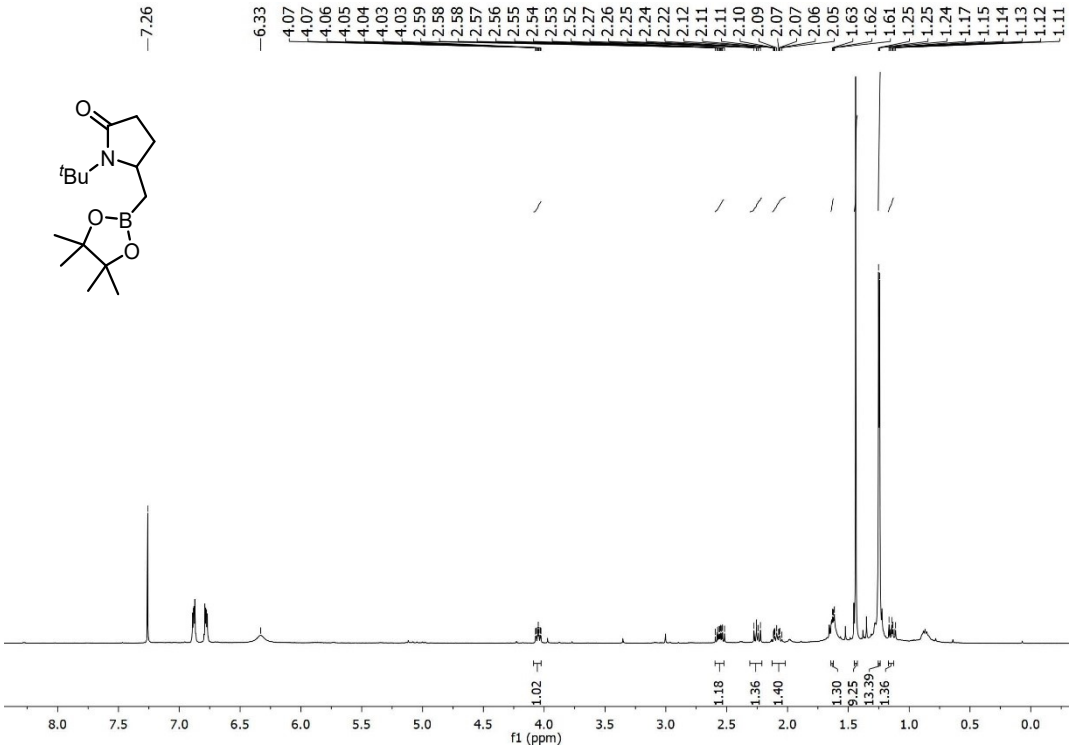
^{13}C NMR spectrum of **51**



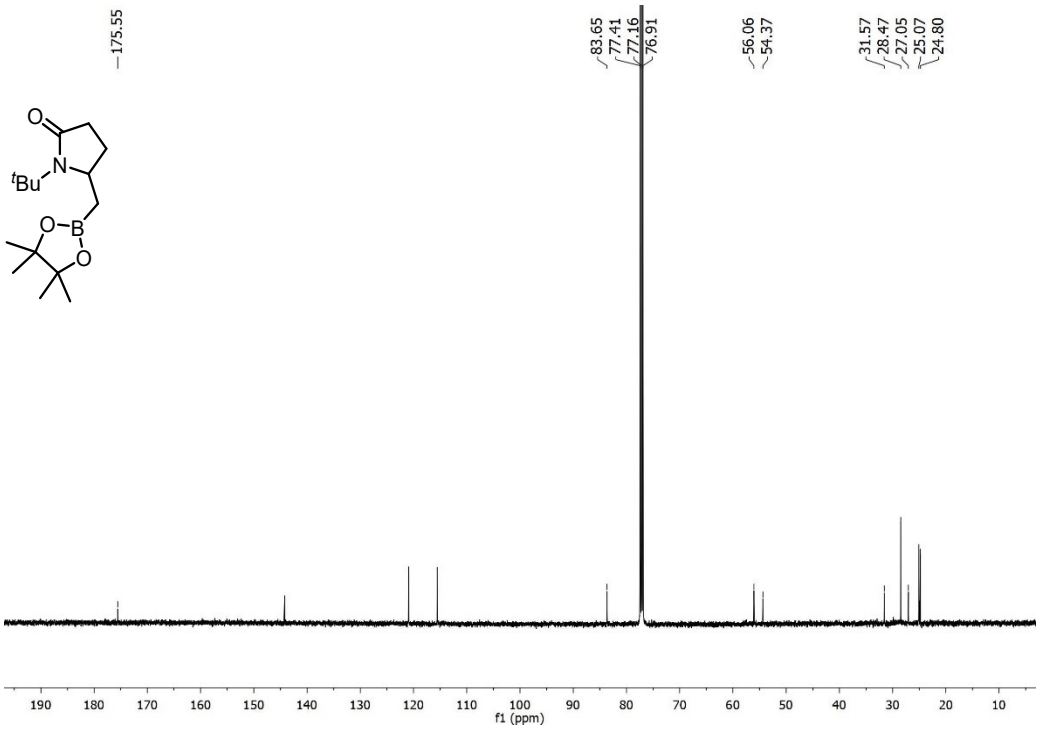
^{1}H NMR spectrum of **52**



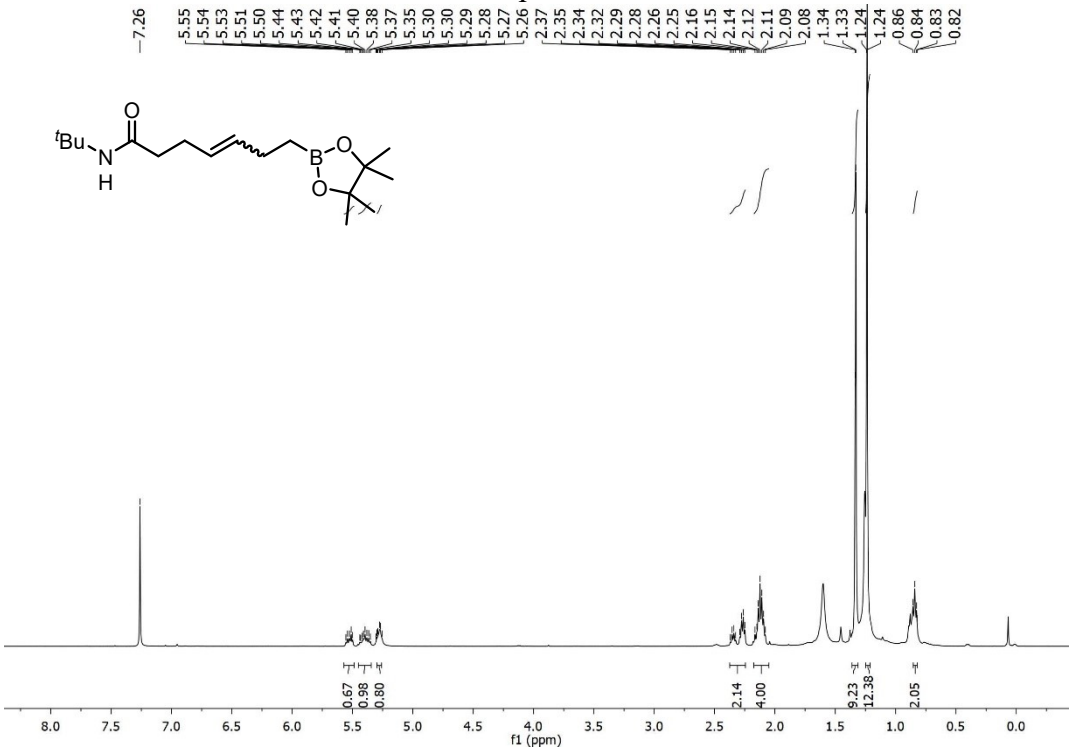
^{13}C NMR spectrum of **52**



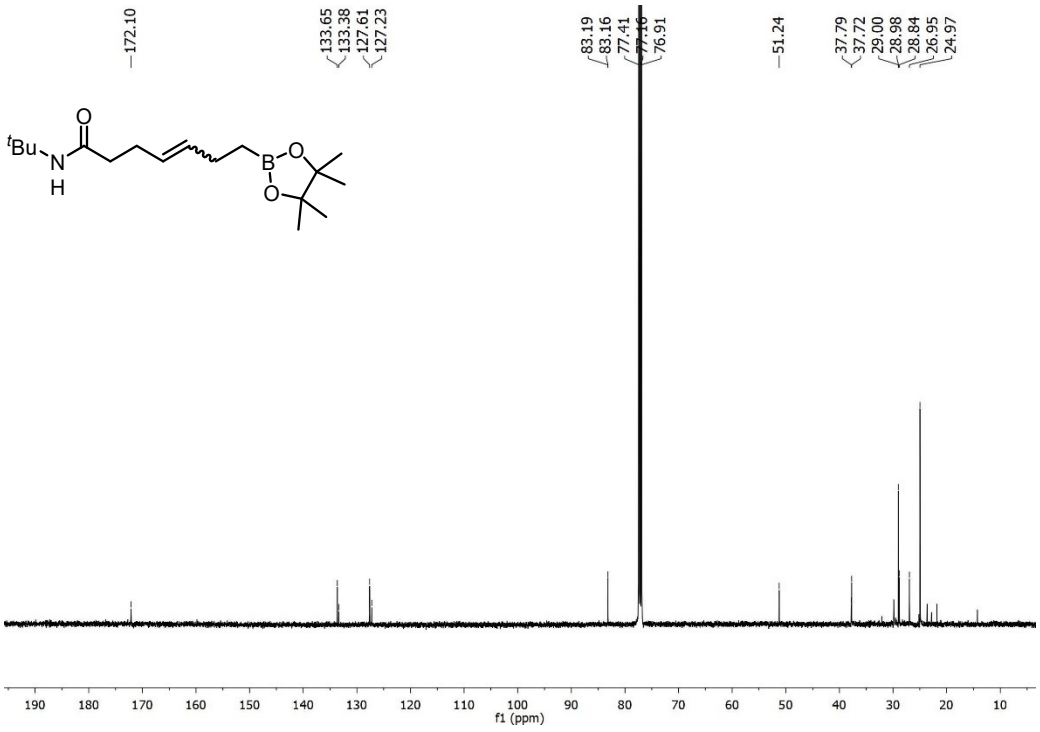
^{1}H NMR spectrum of **53**



^{13}C NMR spectrum of **53**



^{1}H NMR spectrum of **54**



^{13}C NMR spectrum of **54**