Supporting Information

B(MIDA)-Directed Site-Selective Intermolecular Halofluoroalkylation of Alkenes: Synthesis of Diversely Functionalized Building Blocks

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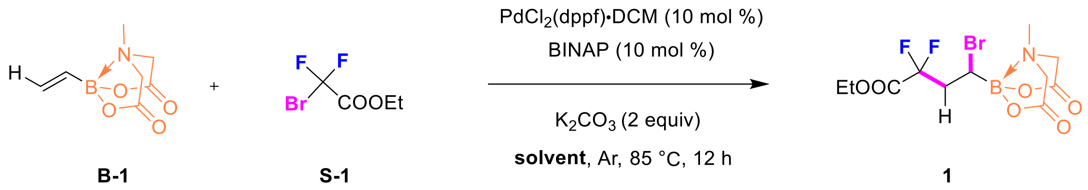
1. General Information

Analytical thin layer chromatography (TLC) was HSGF 254 (0.15-0.2 mm thickness). Preparative thin layer chromatography (PTLC) was HSGF 254 (0.4-0.5 mm thickness). All products were characterized by their NMR and MS spectra. ^{1}H, ^{19}F, ^{31}P, ^{11}B and ^{13}C NMR spectra were recorded on a 400 MHz, 500 MHz, 600 MHz or 800 MHz instrument. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), doublet of doublets (dd), doublet of triplets (dt), triplet of doublets (td), doublet of doublet of doublets (ddd), doublet of doublet of triplets (ddt) and broad (br). NMR yield was determined by ^{19}F NMR using fluorobenzene as an internal standard before working up the reaction. High-resolution mass spectra (HRMS) were measured on Micromass Ultra Q-TOF spectrometer. Other reagents (chemicals) were purchased from Alfa Aesar, TCI, J&K Chemicals, Energy Chemical, Hangzi Biological Technology Co., Ltd., Shanghai, Bide Pharmatech Co., Ltd. and Adamas and used without further purification. Flash chromatography was performed on silica gel (300-400 mesh) using petroleum ether (PE)/ethyl acetate (EA) or dichloromethane (DCM)/methanol (MeOH).

2. Optimization of reaction conditions

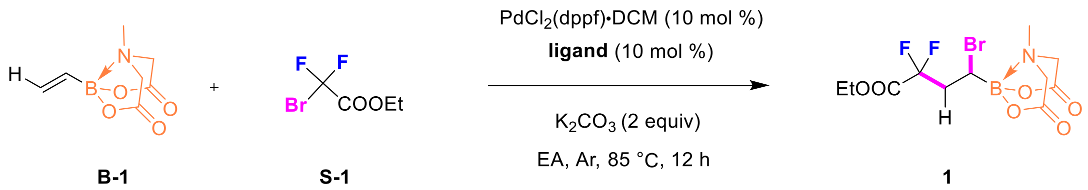
Table S1. Screening of solvents[a]



entry	solvent	yield[b] (%)
1	**EtOAc**	**90 (89)**
2	Dioxane	61
3	DMF	43
4	DCE	44
5	MeOH	trace
6	MeCN	54
7	toluene	trace

[a]Reaction conditions: **B-1** (0.27 mmol, 1.0 equiv), **S-1** (2.0 equiv), PdCl$_2$(dppf)•DCM (10 mol %), BINAP (10 mol %), K_2CO_3 (2.0 equiv), solvent (2 mL), 85 °C, Ar, 12 h, if otherwise noted. [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard, and the number in parentheses is isolated yield.

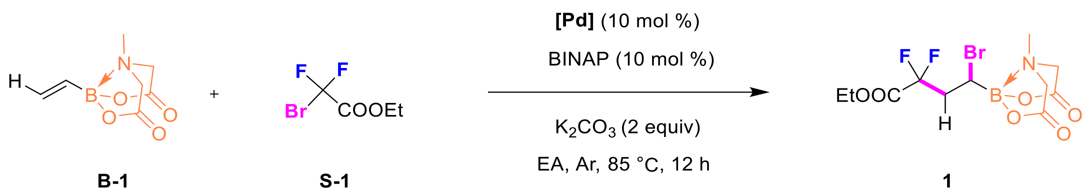
Table S2. Screening of ligands[a]



entry	ligand	yield[b] (%)
1	XPhos	40
2	Davephos	51
3	dppe	15
4	**BINAP**	**90 (89)**
5	Xantphos	62
6	CTC-Q-Phos	44
7	T-BINAP	72

[a]Reaction conditions: **B-1** (0.27 mmol, 1.0 equiv), **S-1** (2.0 equiv), PdCl$_2$(dppf)•DCM (10 mol %), ligand (10 mol %), K_2CO_3 (2.0 equiv), EtOAc (2 mL), 85 °C, Ar, 12 h, if otherwise noted. [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard, and the number in parentheses is isolated yield.

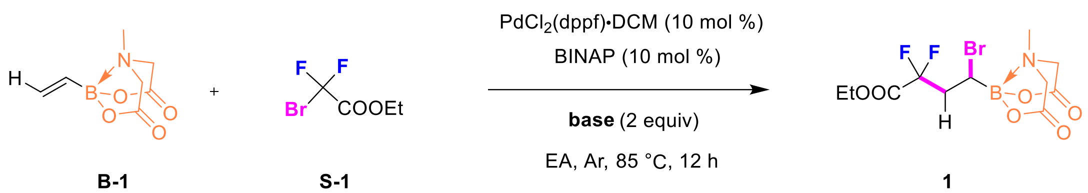
Table S3. Screening of palladium catalysts[a]



entry	[Pd]	yield[b] (%)
1	$PdCl_2(MeCN)_2$	59
2	$Pd(PPh_3)_4$	85
3	**$PdCl_2$(dppf)·DCM**	**90 (89)**
4	$Pd(OAc)_2$	82
5	Sphos Pd G2	76

[a]Reaction conditions: **B-1** (0.27 mmol, 1.0 equiv), **S-1** (2.0 equiv), [Pd] (10 mol %), BINAP (10 mol %), K_2CO_3 (2.0 equiv), EtOAc (2 mL), 85 °C, Ar, 12 h, if otherwise noted. [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard, and the number in parentheses is isolated yield.

Table S4. Screening of bases[a]



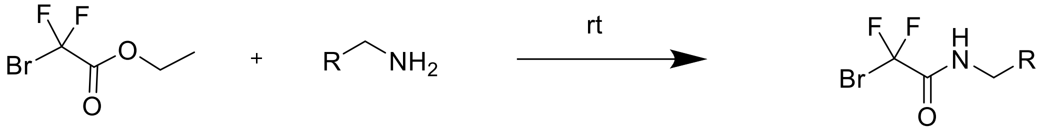
entry	base	yield[b] (%)
1	KOAc	38
2	**K_2CO_3**	**90 (89)**
3	^{t}BuOK	23
4	NaOAc	17
5	^{t}BuONa	trace
6	Na_2CO_3	51
7	$NaHCO_3$	22
8	Cs_2CO_3	77
9	Li_2CO_3	trace

[a]Reaction conditions: **B-1** (0.27 mmol, 1.0 equiv), **S-1** (2.0 equiv), $PdCl_2$(dppf)·DCM (10 mol %), BINAP (10 mol %), base (2.0 equiv), EtOAc (2 mL), 85 °C, Ar, 12 h, if otherwise noted. [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard, and the number in parentheses is isolated yield.

3. General procedure and characterization of starting materials

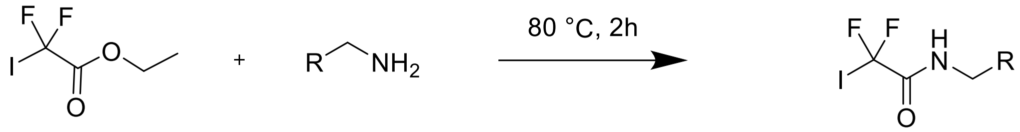
Starting materials of **1**, **2**, **15-23**, **36** and **37** are commercially available. Others were prepared according to the following procedure. Especially, starting materials of **3-6**,[1] **25**,[2] **26** and **29**,[3] **39**,[4] **41**,[5] **44**,[6] **46** and **48**[7], **56** and **59**[8] are known compounds and spectroscopic data of them were consistent with the reported values.

General procedure A:[1]



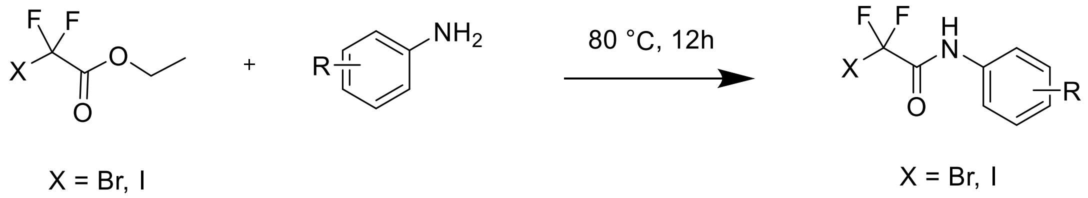
A mixture of bromodifluoroacetate (1 equiv.) and amine (1 equiv.) was stirred vigorously at room temperature for 2 hours. After the reaction was judged to be complete by TLC analysis, the reaction mixture was purified directly by column chromatography on silica gel with an appropriate solvent as eluent to afford the corresponding amide.

General procedure B:



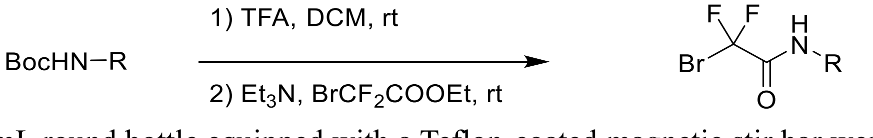
A mixture of iododifluoroacetate (1 equiv.) and amine (1 equiv.) was stirred vigorously at 80 °C for 2 hours. After the reaction was judged to be complete by TLC analysis, the reaction mixture was purified directly by column chromatography on silica gel with an appropriate solvent as eluent to afford the corresponding amide.

General procedure C:



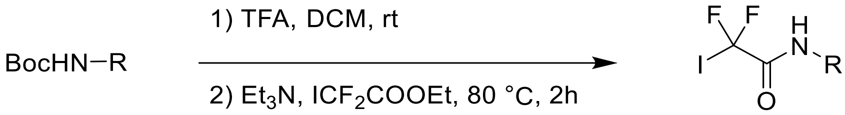
A mixture of iododifluoroacetate or bromodifluoroacetate (1 equiv.) and aniline (1 equiv.) was stirred vigorously at 80 °C for 12 hours. After the reaction was judged to be complete by TLC analysis, the reaction mixture was purified directly by column chromatography on silica gel with an appropriate solvent as eluent to afford the corresponding amide.

General procedure D:[9]



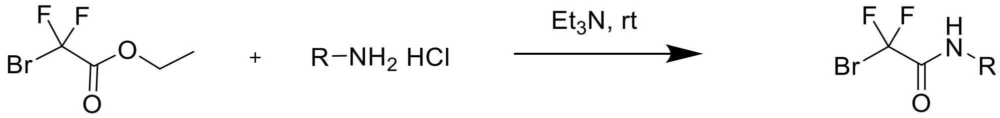
To a 100 mL round bottle equipped with a Teflon-coated magnetic stir bar were added Boc and OMe-protected amino acids (1 equiv.) and DCM (20 mL). Subsequently, TFA (8 equiv.) was added dropwise. After the reaction was stirred at room temperature overnight, the solvent was removed. Then, Et_3N (10 equiv.) and $BrCF_2CO_2Et$ (2 equiv.) were added to the crude oil product. The resulting mixture was stirred at room temperature vigorously for 2 hours. After the reaction was judged to be complete by TLC analysis, the reaction mixture was diluted with EtOAc, washed with brine for three times and the collected organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The concentrated crude product was purified by flash chromatography on silica gel with an appropriate solvent as eluent to afford the pure product.

General procedure E:



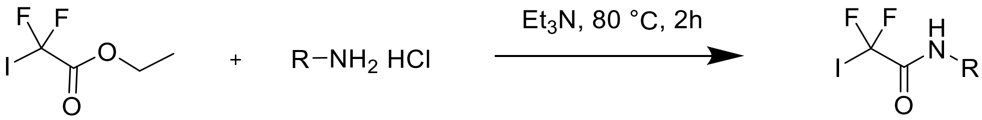
To a 100 mL round bottle equipped with a Teflon-coated magnetic stir bar were added Boc and OMe-protected amino acids (1 equiv.) and DCM (20 mL). Subsequently, TFA (8 equiv.) was added dropwise. After the reaction was stirred at room temperature overnight, the solvent was removed. Then, Et_3N (10 equiv.) and ICF_2CO_2Et (2 equiv.) were added to the crude oil product. The resulting mixture was stirred at 80 °C vigorously for 2 hours. After the reaction was judged to be complete by TLC analysis, the reaction mixture was diluted with EtOAc, washed with brine for three times and the collected organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The concentrated crude product was purified by flash chromatography on silica gel with an appropriate solvent as eluent to afford the pure product.

General procedure F:



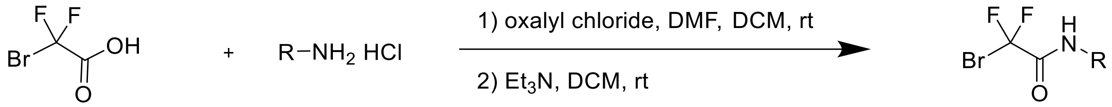
A mixture of bromodifluoroacetate (1 equiv.), Et_3N (20 equiv.) and amine (1 equiv.) was stirred vigorously in a 50 mL round bottom flask at room temperature for 2 hours. After the reaction was judged to be complete by TLC analysis, the mixture was diluted with EtOAc, washed with brine for three times and the collected organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The concentrated crude product was purified by flash chromatography on silica gel with an appropriate solvent as eluent to afford the pure product.

General procedure G:



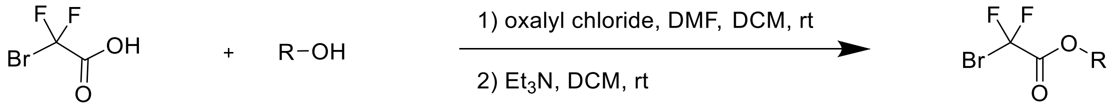
A mixture of iododifluoroacetate (1 equiv.), Et_3N (20 equiv.) and amine (1 equiv.) was stirred vigorously in a 50 mL round bottom flask at 80 °C for 2 hours. After the reaction was judged to be complete by TLC analysis, the mixture was diluted with EtOAc, washed with brine for three times and the collected organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The concentrated crude product was purified by flash chromatography on silica gel with an appropriate solvent as eluent to afford the pure product.

General procedure H:[7]



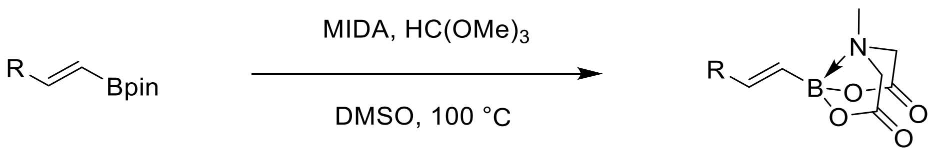
To a stirred solution of 2-bromo-2,2-difluoroacetic acid (875 mg, 5.0 mmol, 1.0 equiv.) and oxalyl chloride (0.46 mL, 1.1 equiv.) in 10 mL of anhydrous CH_2Cl_2, was added 2 drops of anhydrous DMF at room temperature. The mixture was allowed to stir for 2 hours at rt before it was cooled to 0 °C and a solution of the corresponding amine hydrochloride (1.1 equiv.) and Et_3N (6.91 mL, 10.0 equiv.) in 10 mL anhydrous CH_2Cl_2 was added dropwise. The resulting reaction mixture was stirred at room temperature until completion as monitored by TLC. The reaction was diluted with H_2O and extracted with CH_2Cl_2. The combined organic layer was washed with a saturated aqueous solution of $NaHCO_3$ and dried over Na_2SO_4 then the solvent was removed. The crude was purified with silica gel chromatography with an appropriate solvent as eluent to afford the pure product. ***Note:*** **Starting material of 39 was synthesized through this protocol and the spectroscopic data was consistent with the reported value.**[4]

General procedure I:[7]



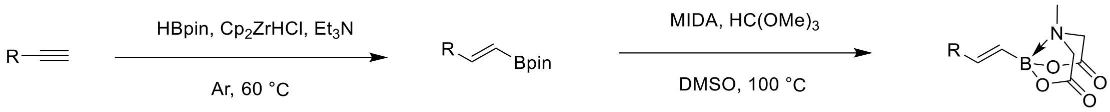
To a stirred solution of 2-bromo-2,2-difluoroacetic acid (875 mg, 5.0 mmol, 1.0 equiv.) and oxalyl chloride (0.46 mL, 1.1 equiv.) in 10 mL of anhydrous CH_2Cl_2, was added 2 drops of anhydrous DMF at room temperature. The mixture was allowed to stir for 2 hours at rt before it was cooled to 0 °C and a solution of the corresponding alcohol (1.1 equiv.) and Et_3N (0.76 mL, 1.1 equiv.) in 10 mL anhydrous CH_2Cl_2 was added dropwise. The resulting reaction mixture was stirred at room temperature until completion as monitored by TLC. The reaction was diluted with H_2O and extracted with CH_2Cl_2. The combined organic layer was washed with a saturated aqueous solution of $NaHCO_3$ and dried over Na_2SO_4 then the solvent was removed. The crude was purified with silica gel chromatography with an appropriate solvent as eluent to afford the pure product.

General procedure J:[10]



The anhydrous DMSO (5 mL) was added to dissolve the olefin Bpin (1.0 equiv.) which was then added via syringe to a suspension of *N*-methyliminodiacetic acid (MIDA, 1.5 equiv.) and $CH(OMe)_3$ (3.0 equiv.) in anhydrous DMSO (5 mL). The resulting mixture was stirred at 100 ºC until the starting material was totally consumed by TLC monitoring. After cooling to room temperature, the reaction mixture was diluted with EtOAc (20 mL) and water (10 mL). The organic phase was separated and the aqueous layer was extracted with ethyl acetate (20 mL) for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with an appropriate solvent as eluent to afford the pure product.

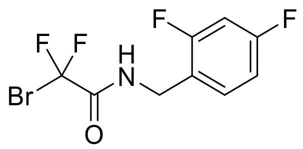
General procedure K:[10]



Alkyne (1.0 equiv.) was added to a dry, cooled Schlenk tube. The tube was pumped under high vacuum and then backfilled with argon, and this cycle repeated three times. Then pinacolborane (HBpin, 1.2 equiv.) was added, followed by Et_3N (0.1 equiv.) and Schwartz's reagent (0.1 equiv.). The resulting beige slurry was heated to 60 °C and stirred vigorously for 24 hours while protected from light. After the reaction was completed, the crude reaction mixture was purified through a short column of silica gel and concentrated in vacuo to a heavy oil. The anhydrous DMSO (5 mL) was added to dissolve the olefin Bpin oil (1.0 equiv.) which was then added via syringe to a suspension of *N*-methyliminodiacetic acid (MIDA, 1.5 equiv.) and $CH(OMe)_3$ (3.0 equiv.) in anhydrous DMSO (5 mL). The resulting mixture was stirred at 100 ºC until the starting material was totally consumed by TLC monitoring. After cooling to room temperature, the reaction mixture was diluted with EtOAc (20 mL) and water (10 mL). The organic phase was seperated and the aqueous layer was extracted with ethyl acetate (20 mL) for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with an appropriate solvent as eluent to afford the pure product.

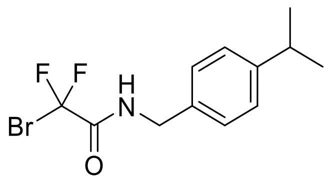
Characterization of starting materials

2-bromo-*N*-(2,4-difluorobenzyl)-2,2-difluoroacetamide (S-7)



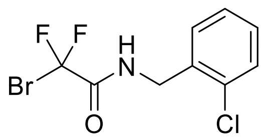
Following the general procedure A, the **S-7** was obtained in 62% yield as a white solid. **^{1}H NMR** (800 MHz, $CDCl_3$) δ 7.35 (td, *J* = 8.5, 6.4 Hz, 1H), 6.89 (ddd, *J* = 8.5, 2.2, 1.1 Hz, 1H), 6.85 (ddd, *J* = 10.5, 8.6, 2.3 Hz, 1H), 6.58 (s, 1H), 4.54 (d, *J* = 6.1 Hz, 2H). **^{13}C NMR** (201 MHz, $CDCl_3$) δ 163.1 (dd, *J* = 250.2, 12.1 Hz), 161.3 (dd, *J* = 249.8, 12.0 Hz), 160.1 (t, *J* = 27.7 Hz), 131.5 (dd, *J* = 9.5, 5.7 Hz), 119.3 (dd, *J* = 14.7, 3.7 Hz), 112.0 (dd, *J* = 21.4, 3.0 Hz), 111.7 (t, *J* = 315.9 Hz), 104.4 (t, *J* = 25.2 Hz), 37.9 (d, *J* = 2.6 Hz). **^{19}F NMR** (753 MHz, $CDCl_3$) δ -60.7 (s, 2F), -109.0 (m, 1F), -114.3 (q, *J* = 8.6 Hz, 1F). **HRMS (ESI)** calcd. for $C_9H_7BrF_4NO$ $[M+H]^+$: 299.9642, found: 299.9639.

2-bromo-2,2-difluoro-*N*-(4-isopropylbenzyl)acetamide (S-8)



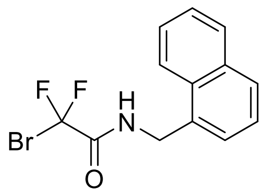
Following the general procedure A, the **S-8** was obtained in 62% yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 4H), 6.43 (s, 1H), 4.50 (d, J = 5.7 Hz, 2H), 2.92 (hept, J = 6.9 Hz, 1H), 1.25 (d, J = 6.9 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.9 (t, J = 27.5 Hz), 149.4, 133.4, 128.2 (2C), 127.3 (2C), 111.9 (t, J = 316.1 Hz), 44.1, 34.0, 24.1 (2C). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -60.5 (s, 2F). **HRMS (ESI)** calcd. for $C_{12}H_{15}BrF_2NO$ $[M+H]^+$: 306.0300, found: 306.0297.

2-bromo-*N*-(2-chlorobenzyl)-2,2-difluoroacetamide (S-9)



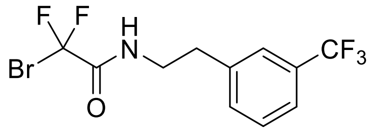
Following the general procedure A, the **S-9** was obtained in 52% yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 2H), 7.32 – 7.26 (m, 2H), 6.65 (s, 1H), 4.63 (d, J = 6.0 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.0 (t, J = 27.7 Hz), 134.0, 133.7, 130.6, 130.0 (2C), 127.6, 111.8 (t, J = 316.0 Hz), 42.3. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -60.5 (s, 2F). **HRMS (ESI)** calcd. for $C_9H_8BrClF_2NO$ $[M+H]^+$: 297.9440, found: 297.9440.

2-bromo-2,2-difluoro-*N*-(naphthalen-1-ylmethyl)acetamide (S-10)



Following the general procedure A, the **S-10** was obtained in 56% yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (t, J = 8.4 Hz, 2H), 7.88 (dt, J = 7.6, 3.8 Hz, 1H), 7.60 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.50 – 7.44 (m, 2H), 6.43 (s, 1H), 4.99 (d, J = 5.4 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8 (t, J = 27.6 Hz), 134.1, 131.4 (2C), 129.6, 129.2, 127.4, 127.3, 126.5, 125.5, 123.1, 111.8 (t, J = 316.2 Hz), 42.5. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -60.6 (s, 2F). **HRMS** calcd. for $C_{13}H_{14}BrF_2N_2O$ $[M+NH_4]^+$: 331.0252, found: 331.0257.

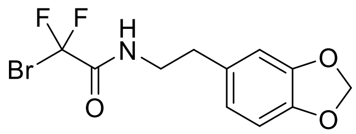
2-bromo-2,2-difluoro-*N*-(3-(trifluoromethyl)phenethyl)acetamide (S-11)



Following the general procedure A, the **S-11** was obtained in 84% yield as a white solid.

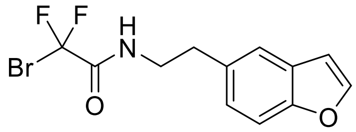
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.52 (m, 1H), 7.48 – 7.44 (m, 2H), 7.42 – 7.39 (m, 1H), 6.24 (s, 1H), 3.64 (q, J = 6.8 Hz, 2H), 2.97 (t, J = 7.0 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.2 (t, J = 27.7 Hz), 138.8, 132.3, 131.4 (q, J = 32.2 Hz), 129.5, 125.7 (q, J = 3.6 Hz), 124.12 (q, J = 272.4 Hz), 124.06 (dd, J = 7.4, 3.6 Hz), 111.7 (t, J = 315.9 Hz), 41.2, 35.0. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -60.7 (s, 2F), -62.7 (s, 3F). **HRMS (ESI)** calcd. for $C_{11}H_{10}BrF_5NO$ $[M+H]^+$: 345.9860, found: 345.9865.

***N*-(2-(benzo[*d*][1,3]dioxol-5-yl)ethyl)-2-bromo-2,2-difluoroacetamide (S-12)**



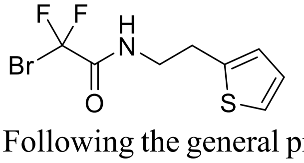
Following the general procedure A, the **S-12** was obtained in 63% yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.76 (d, J = 7.9 Hz, 1H), 6.68 (d, J = 1.6 Hz, 1H), 6.64 (dd, J = 7.9, 1.7 Hz, 1H), 6.23 (s, 1H), 5.95 (s, 2H), 3.57 (q, J = 6.7 Hz, 2H), 2.80 (t, J = 6.9 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.0 (t, J = 27.4 Hz), 148.2, 146.7, 131.4, 121.9, 111.9 (t, J = 316.1 Hz), 109.1, 108.7, 101.2, 41.5, 34.9. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -60.5 (s, 2F). **HRMS (ESI)** calcd. for $C_{11}H_{11}BrF_2NO_3$ $[M+H]^+$: 321.9885, found: 321.9884.

***N*-(2-(benzofuran-5-yl)ethyl)-2-bromo-2,2-difluoroacetamide (S-13)**



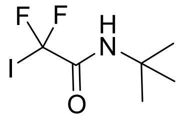
Following the general procedure A, the **S-13** was obtained in 63% yield as a white solid. **^{1}H NMR** (800 MHz, $CDCl_3$) δ 7.58 (d, J = 7.7 Hz, 1H), 7.50 (d, J = 7.2 Hz, 2H), 7.34 (t, J = 7.7 Hz, 1H), 7.28 (t, J = 7.5 Hz, 1H), 6.34 (s, 1H), 3.70 (q, J = 6.6 Hz, 2H), 3.00 (t, J = 6.8 Hz, 2H). **^{13}C NMR** (201 MHz, $CDCl_3$) δ 160.2 (t, J = 27.6 Hz), 155.6, 142.2, 127.5, 124.9, 122.9, 119.4, 116.4, 111.9, 111.8 (t, J = 316.2 Hz), 39.7, 23.4. **^{19}F NMR** (753 MHz, $CDCl_3$) δ -60.6 (s, 2F). **HRMS (ESI)** calcd. for $C_{12}H_{11}BrF_2NO_2$ $[M+H]^+$: 317.9936, found: 317.9938.

2-bromo-2,2-difluoro-*N*-(2-(thiophen-2-yl)ethyl)acetamide (S-14)



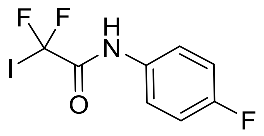
Following the general procedure A, the **S-14** was obtained in 88% yield as a white solid. **^{1}H NMR** (800 MHz, $CDCl_3$) δ 7.20 (d, J = 5.1 Hz, 1H), 6.97 (dd, J = 4.9, 3.5 Hz, 1H), 6.87 (d, J = 3.2 Hz, 1H), 6.35 (s, 1H), 3.64 (q, J = 6.4 Hz, 2H), 3.12 (t, J = 6.6 Hz, 2H). **^{13}C NMR** (201 MHz, $CDCl_3$) δ 160.1 (t, J = 27.4 Hz), 139.9, 127.4, 126.0, 124.7, 111.8 (t, J = 316.0 Hz), 41.5, 29.3. **^{19}F NMR** (753 MHz, $CDCl_3$) δ -60.6 (s, 2F). **HRMS (ESI)** calcd. for $C_8H_9BrF_2NOS$ $[M+H]^+$: 283.9551, found: 283.9549.

N-(*tert*-butyl)-2,2-difluoro-2-iodoacetamide (S-24)



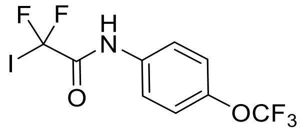
Following the general procedure B, the **S-24** was obtained in 25% yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.90 (s, 1H), 1.41 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.3 (t, J = 23.7 Hz), 92.3 (t, J = 325.5 Hz), 52.6, 28.2 (3C). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -56.2 (s, 2F). **HRMS (ESI)** calcd. for $C_6H_{11}F_2INO$ $[M+H]^+$: 277.9848, found: 277.9847.

2,2-difluoro-N-(4-fluorophenyl)-2-iodoacetamide (S-27)



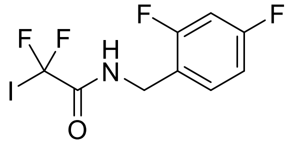
Following the general procedure C, the **S-27** was obtained in 28% yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.57 – 7.52 (m, 2H), 7.13 – 7.05 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.5 (d, J = 246.4 Hz), 159.0 (t, J = 24.8 Hz), 131.3 (d, J = 2.7 Hz), 122.5 (d, J = 8.2 Hz, 2C), 116.3 (d, J = 22.9 Hz, 2C), 90.6 (t, J = 324.3 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -56.9 (s, 2F), -115.1 (m, 1F). **HRMS (ESI)** calcd. for $C_8H_6F_3INO$ $[M+H]^+$: 315.9441, found: 315.9443.

2,2-difluoro-2-iodo-N-(4-(trifluoromethoxy)phenyl)acetamide (S-28)



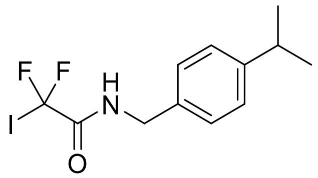
Following the general procedure C, the **S-28** was obtained in 24% yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.65 – 7.59 (m, 2H), 7.26 (d, J = 8.5 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.0 (t, J = 25.0 Hz), 146.8, 134.0, 122.2 (2C), 121.9 (2C), 120.5 (q, J = 257.5 Hz), 90.3 (t, J = 324.5 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -57.1 (s, 2F), -58.1 (s, 3F). **HRMS (ESI)** calcd. for $C_9H_6F_5INO_2$ $[M+H]^+$: 381.9358, found: 381.9358.

N-(2,4-difluorobenzyl)-2,2-difluoro-2-iodoacetamide (S-30)



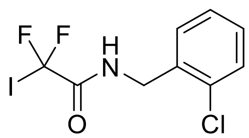
Following the general procedure B, the **S-30** was obtained in 90% yield as a white solid. **^{1}H NMR** (800 MHz, $CDCl_3$) δ 7.35 (td, J = 8.5, 6.3 Hz, 1H), 6.91 – 6.88 (m, 1H), 6.87 – 6.84 (m, 1H), 6.50 (s, 1H), 4.54 (d, J = 6.1 Hz, 2H). **^{13}C NMR** (201 MHz, $CDCl_3$) δ 163.1 (dd, J = 250.1, 12.1 Hz), 161.4 (t, J = 25.0 Hz), 161.3 (dd, J = 249.9, 12.2 Hz), 131.5 (dd, J = 9.6, 5.3 Hz), 119.4 (dd, J = 14.9, 3.8 Hz), 112.0 (dd, J = 21.3, 3.5 Hz), 104.4 (t, J = 25.3 Hz), 90.9 (t, J = 323.4 Hz), 37.8. **^{19}F NMR** (753 MHz, $CDCl_3$) δ -57.0 (s, 2F), -109.1 (s, 1F), -114.3 (d, J = 14.8 Hz, 1F). **HRMS (ESI)** calcd. for $C_9H_7F_4INO$ $[M+H]^+$: 347.9503, found: 347.9505.

2,2-difluoro-2-iodo-*N*-(4-isopropylbenzyl)acetamide (S-31)



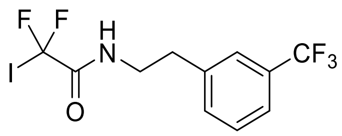
Following the general procedure B, the **S-31** was obtained in 69% yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 4H), 6.39 (s, 1H), 4.49 (d, J = 5.7 Hz, 2H), 2.92 (hept, J = 6.9 Hz, 1H), 1.25 (d, J = 6.9 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.3 (t, J = 24.8 Hz), 149.3, 133.6, 128.2 (2C), 127.2 (2C), 91.2 (t, J = 323.7 Hz), 44.0, 34.0, 24.1 (2C). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -56.6 (s, 2F). **HRMS (ESI)** calcd. for $C_{12}H_{15}F_2INO$ $[M+H]^+$: 354.0161, found: 354.0163.

***N*-(2-chlorobenzyl)-2,2-difluoro-2-iodoacetamide (S-32)**



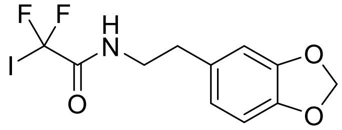
Following the general procedure B, the **S-32** was obtained in 68% yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.32 – 7.26 (m, 2H), 6.58 (s, 1H), 4.62 (d, J = 6.0 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.7 (t, J = 25.1 Hz), 133.4, 133.2, 130.0, 129.4, 129.3, 127.0, 90.4 (t, J = 323.6 Hz), 41.6. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -56.8 (s, 2F). **HRMS (ESI)** calcd. for $C_9H_8ClF_2INO$ $[M+H]^+$: 345.9302, found: 345.9305.

2,2-difluoro-2-iodo-*N*-(3-(trifluoromethyl)phenethyl)acetamide (S-33)



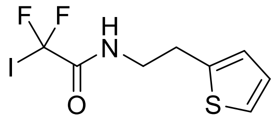
Following the general procedure B, the **S-33** was obtained in 78% yield as a yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 (d, J = 7.6 Hz, 1H), 7.47 (dd, J = 8.8, 5.3 Hz, 2H), 7.41 (d, J = 7.7 Hz, 1H), 6.21 (s, 1H), 3.63 (q, J = 6.8 Hz, 2H), 2.97 (t, J = 7.0 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.6 (t, J = 24.7 Hz), 138.8, 132.3, 131.4 (q, J = 32.1 Hz), 129.5, 125.7 (dd, J = 7.2, 3.6 Hz), 124.1 (q, J = 272.5 Hz), 124.0 (dd, J = 7.4, 3.7 Hz), 90.9 (t, J = 323.4 Hz), 41.1, 34.9. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -56.9 (s, 2F), -62.6 (s, 3F). **HRMS (ESI)** calcd. for $C_{11}H_{10}F_5INO$ $[M+H]^+$: 393.9722, found: 393.9722.

N-(2-(benzo[d][1,3]dioxol-5-yl)ethyl)-2,2-difluoro-2-iodoacetamide (S-34)



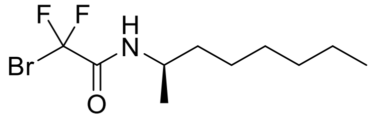
Following the general procedure B, the **S-34** was obtained in 66% yield as a white solid. **^{1}H NMR** (800 MHz, $CDCl_3$) δ 6.76 (d, J = 7.8 Hz, 1H), 6.69 (s, 1H), 6.65 (d, J = 7.8 Hz, 1H), 6.18 (s, 1H), 5.95 (s, 2H), 3.56 (q, J = 6.6 Hz, 2H), 2.80 (t, J = 6.9 Hz, 2H). **^{13}C NMR** (201 MHz, $CDCl_3$) δ 161.4 (t, J = 24.6 Hz), 148.2, 146.7, 131.5, 121.9, 109.2, 108.7, 101.2, 91.2 (t, J = 323.6 Hz), 41.4, 34.8. **^{19}F NMR** (753 MHz, $CDCl_3$) δ -56.7 (s, 2F). **HRMS (ESI)** calcd. for $C_{11}H_{11}F_2INO_3$ $[M+H]^+$: 369.9746, found: 369.9749.

2,2-difluoro-2-iodo-N-(2-(thiophen-2-yl)ethyl)acetamide (S-35)



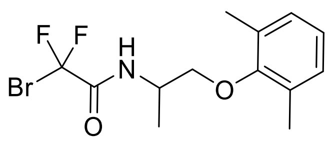
Following the general procedure B, the **S-35** was obtained in 85% yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20 (dd, J = 5.1, 1.1 Hz, 1H), 6.97 (dd, J = 5.1, 3.4 Hz, 1H), 6.88 (dd, J = 3.4, 0.8 Hz, 1H), 6.29 (s, 1H), 3.63 (q, J = 6.4 Hz, 2H), 3.11 (t, J = 6.6 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.5 (t, J = 24.9 Hz), 140.0, 127.4, 126.0, 124.6, 91.1 (t, J = 323.6 Hz), 41.4, 29.3. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -56.8 (s, 2F). **HRMS (ESI)** calcd. for $C_8H_9F_2INOS$ $[M+H]^+$: 331.9412, found: 331.9412.

(R)-2-bromo-2,2-difluoro-N-(octan-2-yl)acetamide (S-38)



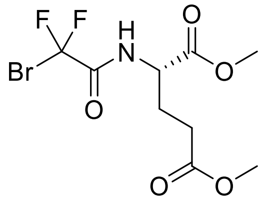
Following the general procedure A, the **S-38** was obtained in 55% yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.92 (s, 1H), 4.07 – 3.93 (m, 1H), 1.55 – 1.48 (m, 2H), 1.38 – 1.24 (m, 8H), 1.21 (d, J = 6.6 Hz, 3H), 0.88 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.4 (t, J = 26.9 Hz), 112.1 (t, J = 316.5 Hz), 46.9, 36.6, 31.8, 29.1, 25.9, 22.7, 20.5, 14.2. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -60.5 (s, 2F). **HRMS (ESI)** calcd. for $C_{10}H_{19}BrF_2NO$ $[M+H]^+$: 286.0613, found: 286.0621.

2-bromo-N-(1-(2,6-dimethylphenoxy)propan-2-yl)-2,2-difluoroacetamide (S-40)



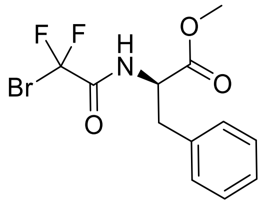
Following the general procedure F, the **S-40** was obtained in 30% yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.02 (d, J = 7.5 Hz, 2H), 6.95 (dd, J = 8.2, 6.6 Hz, 1H), 6.76 (d, J = 4.6 Hz, 1H), 4.41 – 4.32 (m, 1H), 3.87 (dd, J = 9.4, 3.6 Hz, 1H), 3.78 (dd, J = 9.4, 3.0 Hz, 1H), 2.26 (s, 6H), 1.51 (d, J = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.5 (t, J = 27.4 Hz), 154.5, 130.8 (2C), 129.3 (2C), 124.6, 112.0 (t, J = 316.1 Hz), 72.9, 46.7, 17.4, 16.3 (2C). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -60.5 (m, 2F). **HRMS (ESI)** calcd. for $C_{13}H_{17}BrF_2NO_2$ $[M+H]^+$: 336.0405, found: 336.0405.

dimethyl (2-bromo-2,2-difluoroacetyl)-*L*-glutamate (S-42)



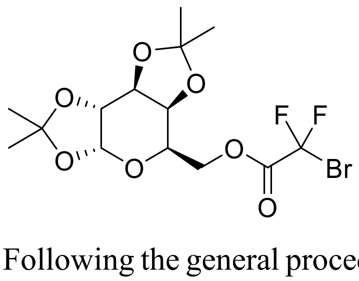
Following the general procedure D, the **S-42** was obtained in 74% yield as a yellow oil. **^{1}H NMR** (800 MHz, $CDCl_3$) δ 7.34 (d, J = 6.4 Hz, 1H), 4.59 (td, J = 7.8, 5.0 Hz, 1H), 3.78 (s, 3H), 3.68 (s, 3H), 2.48 – 2.38 (m, 2H), 2.32 – 2.23 (m, 1H), 2.11 (td, J = 14.7, 6.9 Hz, 1H). **^{13}C NMR** (201 MHz, $CDCl_3$) δ 173.4, 170.9, 160.0 (t, J = 28.1 Hz), 111.4 (t, J = 315.9 Hz), 53.1, 52.5, 52.2, 29.9, 26.6. **^{19}F NMR** (753 MHz, $CDCl_3$) δ -61.0 (m, 2F). **HRMS (ESI)** calcd. for $C_9H_{13}BrF_2NO_5$ $[M+H]^+$: 331.9940, found: 331.9945.

methyl (2-bromo-2,2-difluoroacetyl)-*D*-phenylalaninate (S-43)



Following the general procedure F, the **S-43** was obtained in 45% yield as a white solid. **^{1}H NMR** (800 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 2H), 7.29 – 7.26 (m, 1H), 7.11 – 7.05 (m, 2H), 6.71 (d, J = 5.4 Hz, 1H), 4.87 (dt, J = 7.5, 5.6 Hz, 1H), 3.79 (s, 3H), 3.25 (dd, J = 14.1, 5.7 Hz, 1H), 3.18 (dd, J = 14.1, 5.5 Hz, 1H). **^{13}C NMR** (201 MHz, $CDCl_3$) δ 170.6, 159.4 (t, J = 28.2 Hz), 134.7, 129.4 (2C), 129.0 (2C), 127.7, 111.4 (t, J = 315.9 Hz), 53.8, 53.0, 37.4. **^{19}F NMR** (753 MHz, $CDCl_3$) δ -60.8 (m, 2F). **HRMS (ESI)** calcd. for $C_{12}H_{11}BrF_2NO_3$ $[M-H]^-$: 333.9896, found: 333.9894.

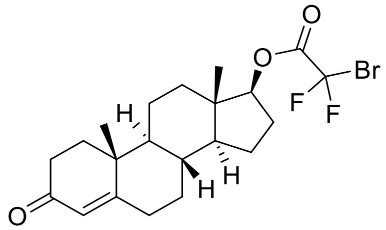
((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl 2-bromo-2,2-difluoroacetate (S-45)



Following the general procedure I, the **S-45** was obtained in 51% yield as a yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.53 (d, J = 4.9 Hz, 1H), 4.64 (dd, J = 7.9, 2.6 Hz, 1H), 4.52 (dd, J = 11.4, 4.7 Hz, 1H), 4.47 (dd, J = 11.4, 7.6 Hz, 1H), 4.34 (dd, J = 5.0, 2.6 Hz, 1H), 4.25 (dd, J = 7.9, 1.9 Hz, 1H), 4.12 – 4.07 (m, 1H), 1.51 (s, 3H), 1.46 (s, 3H), 1.34 (s, 3H), 1.33 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.6 (t, J = 31.6 Hz), 110.1, 109.1, 108.7 (t, J = 314.1 Hz), 96.3, 70.9, 70.8, 70.5, 66.8, 65.7, 26.1, 26.1, 25.1, 24.6.

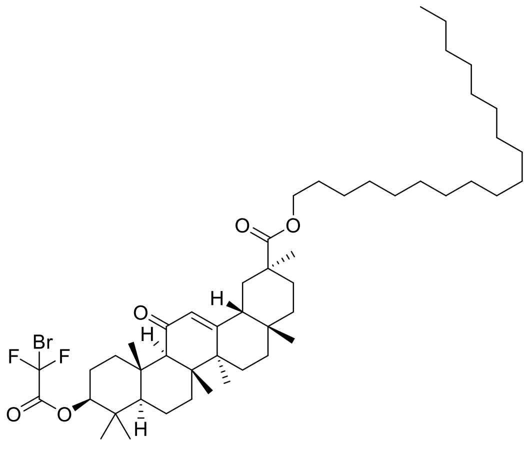
^{19}**F NMR** (471 MHz, $CDCl_3$) δ -60.9 (m, 2F). Compound is decomposed in **HRMS**.

(8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl 2-bromo-2,2-difluoroacetate (S-47)



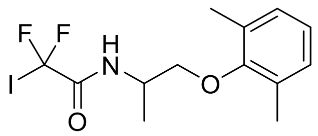
Following the general procedure I, the **S-47** was obtained in 45% yield as a colorless oil. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 5.81 (s, 1H), 4.81 – 4.76 (m, 1H), 2.51 – 2.37 (m, 3H), 2.36 – 2.20 (m, 2H), 2.06 – 2.00 (m, 1H), 1.91 – 1.80 (m, 2H), 1.77 – 1.64 (m, 3H), 1.60 (ddd, *J* = 13.9, 7.2, 3.7 Hz, 2H), 1.49 – 1.37 (m, 2H), 1.24 (td, *J* = 12.8, 4.6 Hz, 1H), 1.20 (s, 3H), 1.16 – 1.00 (m, 2H), 1.00 – 0.93 (m, 1H), 0.90 (s, 3H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 201.5, 173.4, 159.7 (t, *J* = 31.0 Hz), 123.8, 109.0 (t, *J* = 314.6 Hz), 86.6, 53.6, 50.1, 43.3, 38.9, 36.5, 35.5, 35.4, 33.7, 32.9, 31.4, 26.9, 23.5, 20.5, 17.5, 11.9. ^{19}**F NMR** (471 MHz, $CDCl_3$) δ -60.7 (m, 2F). **HRMS (ESI)** calcd. for $C_{21}H_{28}BrF_2O_3$ $[M+H]^+$: 445.1184, found: 445.1189.

Octadecyl (2*S*,4a*S*,6a*S*,6b*R*,8a*R*,10*S*,12a*S*,12b*R*,14b*R*)-10-(2-bromo-2,2-difluoroacetoxy)-2,4a,6a,6b,9,9,12a-heptamethyl-13-oxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydropicene-2-carboxylate (S-49)



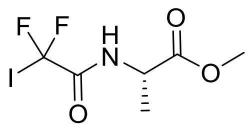
Following the general procedure I, the **S-49** was obtained in 31% yield as a white solid. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 5.66 (s, 1H), 4.69 (dd, *J* = 12.0, 4.7 Hz, 1H), 4.12 – 4.04 (m, 2H), 2.90 (dt, *J* = 13.6, 3.5 Hz, 1H), 2.36 (s, 1H), 2.13 (dd, *J* = 13.3, 3.4 Hz, 1H), 2.07 – 1.96 (m, 2H), 1.95 – 1.89 (m, 1H), 1.89 – 1.79 (m, 2H), 1.75 – 1.68 (m, 1H), 1.68 – 1.57 (m, 5H), 1.52 – 1.45 (m, 1H), 1.45 – 1.40 (m, 1H), 1.40 – 1.34 (m, 5H), 1.34 – 1.30 (m, 4H), 1.29 – 1.19 (m, 28H), 1.18 (s, 3H), 1.14 (d, *J* = 5.8 Hz, 6H), 1.11 – 1.04 (m, 1H), 1.04 – 0.99 (m, 1H), 0.95 (d, *J* = 1.7 Hz, 6H), 0.87 (t, *J* = 7.0 Hz, 3H), 0.83 (d, *J* = 11.6 Hz, 1H), 0.80 (s, 3H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 199.9, 176.6, 169.6, 159.5 (t, J = 30.8 Hz), 128.6, 109.1 (t, J = 314.7 Hz), 86.2, 64.7, 61.7, 55.1, 48.5, 45.5, 44.1, 43.4, 41.2, 38.7, 38.6, 37.9, 37.0, 32.8, 32.1, 32.0, 31.3, 29.8 (8C), 29.7 (2C), 29.5, 29.3, 28.9, 28.7, 28.6, 28.1, 26.6, 26.5, 26.1, 23.5, 23.2, 22.8, 18.8, 17.5, 16.6, 16.5, 14.3. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -60.6 (m, 2F). **HRMS (ESI)** calcd. for $C_{50}H_{82}BrF_2O_5$ $[M+H]^+$: 879.5308, found: 879.5310.

***N*-(1-(2,6-dimethylphenoxy)propan-2-yl)-2,2-difluoro-2-iodoacetamide (S-50)**



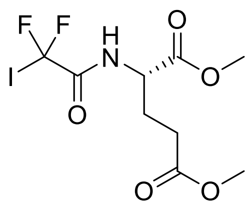
Following the general procedure G, the **S-50** was obtained in 67% yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.02 (d, J = 7.6 Hz, 2H), 6.95 (dd, J = 8.2, 6.7 Hz, 1H), 6.70 (d, J = 5.5 Hz, 1H), 4.36 (dqd, J = 10.3, 6.9, 3.4 Hz, 1H), 3.86 (dd, J = 9.4, 3.7 Hz, 1H), 3.77 (dd, J = 9.4, 3.0 Hz, 1H), 2.27 (s, 6H), 1.49 (d, J = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.9 (t, J = 24.7 Hz), 154.6, 130.8 (2C), 129.3 (2C), 124.6, 91.4 (t, J = 323.7 Hz), 73.0, 46.6, 17.3, 16.4 (2C). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -56.6 (m, 2F). **HRMS (ESI)** calcd. for $C_{13}H_{17}F_2INO_2$ $[M+H]^+$: 384.0267, found: 384.0271.

methyl (2,2-difluoro-2-iodoacetyl)-*L*-alaninate (S-51)



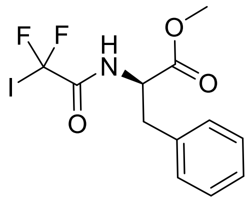
Following the general procedure E, the **S-51** was obtained in 27% yield as a yellow oil. **^{1}H NMR** (800 MHz, $CDCl_3$) δ 6.91 (s, 1H), 4.57 (p, J = 7.2 Hz, 1H), 3.78 (s, 3H), 1.47 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (201 MHz, $CDCl_3$) δ 172.2, 160.8 (t, J = 25.3 Hz), 90.7 (t, J = 323.4 Hz), 53.0, 48.8, 17.8. **^{19}F NMR** (753 MHz, $CDCl_3$) δ -57.2 (s, 2F). **HRMS (ESI)** calcd. for $C_6H_9F_2INO_3$ $[M+H]^+$: 307.9590, found: 307.9589.

dimethyl (2,2-difluoro-2-iodoacetyl)-*L*-glutamate (S-52)



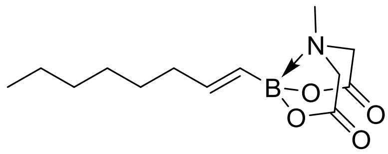
Following the general procedure E, the **S-52** was obtained in 29% yield as a yellow oil. **^{1}H NMR** (800 MHz, $CDCl_3$) δ 7.21 (d, J = 6.0 Hz, 1H), 4.60 (td, J = 7.8, 5.2 Hz, 1H), 3.79 (d, J = 1.0 Hz, 3H), 3.69 (s, 3H), 2.50 – 2.38 (m, 2H), 2.32 – 2.25 (m, 1H), 2.16 – 2.08 (m, 1H). **^{13}C NMR** (201 MHz, $CDCl_3$) δ 173.4, 171.0, 161.3 (t, J = 25.3 Hz), 90.4 (t, J = 323.5 Hz), 53.1, 52.4, 52.3, 29.9, 26.7. **^{19}F NMR** (753 MHz, $CDCl_3$) δ -57.3 (m, 2F). **HRMS (ESI)** calcd. for $C_9H_{13}F_2INO_5$ $[M+H]^+$: 379.9801, found: 379.9804.

methyl (2,2-difluoro-2-iodoacetyl)-*D*-phenylalaninate (S-53)



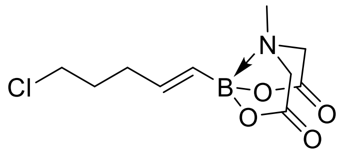
Following the general procedure G, the **S-53** was obtained in 29% yield as a yellow solid. **^{1}H NMR** (800 MHz, $CDCl_3$) δ 7.33 – 7.30 (m, 2H), 7.29 – 7.26 (m, 1H), 7.12 – 7.10 (m, 2H), 6.65 (d, J = 5.8 Hz, 1H), 4.86 (dt, J = 7.6, 5.7 Hz, 1H), 3.79 (s, 3H), 3.24 (dd, J = 14.1, 5.6 Hz, 1H), 3.17 (dd, J = 14.1, 5.6 Hz, 1H). **^{13}C NMR** (201 MHz, $CDCl_3$) δ 170.7, 160.7 (t, J = 25.5 Hz), 134.8, 129.4 (2C), 129.0 (2C), 127.7, 90.5 (t, J = 323.4 Hz), 53.6, 52.9, 37.5. **^{19}F NMR** (753 MHz, $CDCl_3$) δ -57.0 (m, 2F). **HRMS (ESI)** calcd. for $C_{12}H_{13}F_2INO_3$ $[M+H]^+$: 383.9903, found: 383.9903.

(*E*)-6-methyl-2-(oct-1-en-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (B-2)



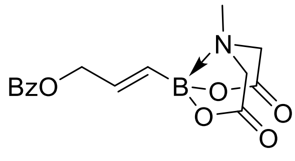
Following the general procedure J, the **B-2** was obtained in 59% yield as a white solid. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 5.94 (dt, J = 17.6, 6.4 Hz, 1H), 5.37 (d, J = 17.6 Hz, 1H), 4.17 (d, J = 17.1 Hz, 2H), 3.95 (d, J = 17.0 Hz, 2H), 2.73 (s, 3H), 2.07 (td, J = 7.6, 1.1 Hz, 2H), 1.40 – 1.32 (m, 2H), 1.31 – 1.21 (m, 6H), 0.86 (t, J = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 169.2 (2C), 144.2, 61.2 (2C), 46.7, 34.8, 31.2, 28.3 (2C), 22.1, 13.9. **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.16. **HRMS (ESI)** calcd. for $C_{13}H_{23}[^{11}B]NO_4$ $[M+H]^+$: 268.1715, found: 268.1718.

(*E*)-2-(5-chloropent-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (B-3)



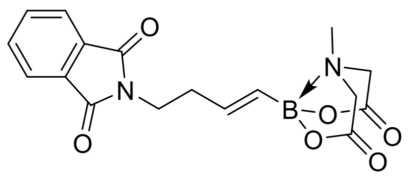
Following the general procedure J, the **B-3** was obtained in 59% yield as a light yellow solid. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 5.93 (dt, J = 17.7, 6.4 Hz, 1H), 5.43 (d, J = 17.7 Hz, 1H), 4.18 (d, J = 17.1 Hz, 2H), 3.97 (d, J = 17.0 Hz, 2H), 3.63 (t, J = 6.6 Hz, 2H), 2.74 (s, 3H), 2.20 (dt, J = 7.5, 3.8 Hz, 2H), 1.86 – 1.78 (m, 2H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 169.2 (2C), 142.4, 61.2 (2C), 46.7, 44.9, 31.9, 31.1. **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.16. **HRMS (ESI)** calcd. for $C_{10}H_{16}[^{11}B]ClNO_4$ $[M+H]^+$: 260.0855, found: 260.0856.

(*E*)-3-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)allyl benzoate (B-5)



Following the general procedure K, the **B-5** was obtained in 62% yield as a yellow solid over two steps. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 8.03 – 7.99 (m, 2H), 7.70 – 7.65 (m, 1H), 7.54 (dd, *J* = 10.8, 4.7 Hz, 2H), 6.13 (dt, *J* = 17.9, 4.8 Hz, 1H), 5.78 (dt, *J* = 17.8, 1.5 Hz, 1H), 4.85 (dd, *J* = 4.8, 1.5 Hz, 2H), 4.23 (d, *J* = 17.1 Hz, 2H), 4.02 (d, *J* = 17.0 Hz, 2H), 2.77 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 169.1 (2C), 165.4, 137.3, 133.4, 129.7, 129.2 (2C), 128.8 (2C), 66.1, 61.5 (2C), 46.8. **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.17. **HRMS (ESI)** calcd. for $C_{15}H_{16}[^{11}B]NNaO_6$ $[M+Na]^+$: 340.0963, found: 340.0962.

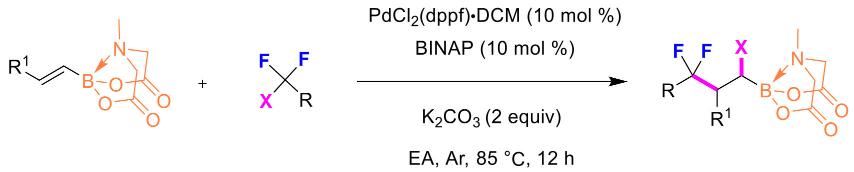
(*E*)-2-(4-(1,3-dioxoisoindolin-2-yl)but-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (B-6)



Following the general procedure K, the **B-6** was obtained in 30% yield as a yellow solid over two steps. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 7.88 – 7.81 (m, 4H), 5.91 (dt, *J* = 17.6, 6.7 Hz, 1H), 5.41 (d, *J* = 17.6 Hz, 1H), 4.15 (d, *J* = 17.0 Hz, 2H), 3.87 (d, *J* = 17.0 Hz, 2H), 3.67 (t, *J* = 6.9 Hz, 2H), 2.55 (s, 3H), 2.41 (q, *J* = 6.6 Hz, 2H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 169.1 (2C), 167.9 (2C), 140.4, 134.4 (2C), 131.5 (2C), 128.9 (α-C of boron), 123.0 (2C), 61.1 (2C), 46.2, 36.9, 34.0. **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.45. **HRMS (ESI)** calcd. for $C_{17}H_{18}[^{11}B]N_2O_6$ $[M+H]^+$: 357.1252, found: 357.1248.

4. General procedure and characterization of products

General procedure

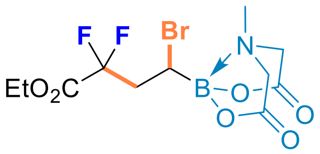


To an oven-dried 25 mL of Schlenk tube were added vinyl B(MIDA) derivatives (0.27 mmol, 1.0 equiv.), difluoro halides (2.0 equiv.), $PdCl_2$(dppf)•DCM (10 mol %), BINAP (10 mol %), K_2CO_3 (2.0 equiv.) sequentially, ethyl acetate (EtOAc, 2.0 mL) was then added to dissolve the complex above. The mixture was then evacuated and backfilled with Ar for 3 times. The Schlenk tube was screw capped and stirred at 85 °C for 12 h. After the solution was cooled to room temperature, the crude reaction mixture was diluted with EA (5 mL) and washed with saturated aqueous NaCl (3 x 5 mL). The aqueous layer was extracted with EA (3 x 5 mL) and the combined organic layer was dried over anhydrous Na_2SO_4. Then, the solvent was removed under vacuo, and the residue was purified by a silica gel column chromatography with an appropriate solvent as eluent to give the desired product.

Caution：Pressure tube must be used for the reaction.

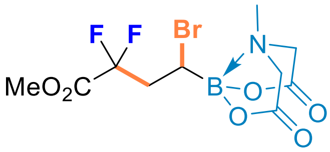
Characterization of products

Ethyl 4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoate (1)



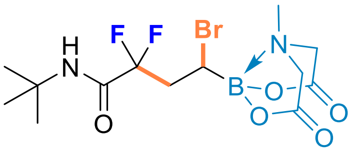
Following the general procedure, compound **1** was obtained in 89% yield (94 mg) as a yellow solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 4.47 (d, *J* = 17.4 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.28 (d, *J* = 17.1 Hz, 1H), 4.11 (d, *J* = 17.4 Hz, 1H), 4.08 (d, *J* = 17.1 Hz, 1H), 3.66 (d, *J* = 10.4 Hz, 1H), 3.10 (s, 3H), 2.78 (dd, *J* = 31.2, 14.9 Hz, 1H), 2.70 – 2.55 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.2, 168.1, 163.2 (t, *J* = 32.4 Hz), 115.8 (t, *J* = 248.5 Hz), 63.4, 63.2, 63.1, 45.8, 38.1 (t, *J* = 23.8 Hz), 13.6. **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -101.6 (dt, *J* = 257.0, 14.0 Hz, 1F), -106.6 (dt, *J* = 256.8, 17.6 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.14. **HRMS (ESI)** calcd. for $C_{11}H_{19}BBrF_2N_2O_6$ $[M+NH_4]^+$: 402.0518, found: 402.0516.

Methyl 4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoate (2)



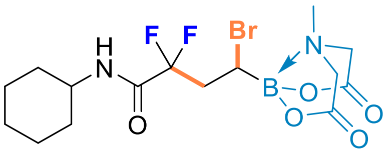
Following the general procedure, compound **2** was obtained in 82% yield (83 mg) as a yellow solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 4.47 (d, *J* = 17.4 Hz, 1H), 4.28 (d, *J* = 17.1 Hz, 1H), 4.11 (d, *J* = 17.3 Hz, 1H), 4.08 (d, *J* = 17.0 Hz, 1H), 3.86 (s, 3H), 3.66 (d, *J* = 11.0 Hz, 1H), 3.10 (s, 3H), 2.80 (dd, *J* = 30.9, 15.3 Hz, 1H), 2.72 – 2.55 (m, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.2, 168.1, 163.7 (t, *J* = 32.5 Hz), 115.8 (dd, *J* = 252.8, 247.8 Hz), 63.4, 63.2, 53.7, 45.8, 38.2 (t, *J* = 23.7 Hz), 33.3 (α-C of boron). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -101.5 (dt, *J* = 257.3, 13.7 Hz, 1F), -106.7 (dt, *J* = 257.2, 18.0 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.05. **HRMS (ESI)** calcd. for $C_{10}H_{14}[^{11}B]BrF_2NO_6$ $[M+H]^+$: 372.0060, found: 372.0055.

4-bromo-*N*-(*tert*-butyl)-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (3)



Following the general procedure, compound **3** was obtained in 67% yield (75 mg) as a white solid after column chromatography. **^{1}H NMR** (600 MHz, DMSO-*d6*) δ 7.96 (s, 1H), 4.47 (d, *J* = 17.4 Hz, 1H), 4.27 (d, *J* = 17.1 Hz, 1H), 4.10 (d, *J* = 17.5 Hz, 1H), 4.07 (d, *J* = 17.2 Hz, 1H), 3.62 (d, *J* = 11.0 Hz, 1H), 3.09 (s, 3H), 2.72 – 2.63 (m, 1H), 2.62 – 2.53 (m, 1H), 1.31 (s, 9H). **^{13}C NMR** (151 MHz, DMSO-*d6*) δ 168.3, 168.2, 162.6 (t, *J* = 27.9 Hz), 117.1 (t, *J* = 253.7 Hz), 63.4, 63.2, 51.2, 45.6, 37.6 (t, *J* = 24.0 Hz), 33.6 (α-C of boron), 28.1 (3C). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -101.9 (dt, *J* = 247.4, 15.3 Hz, 1F), -105.1 (m, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 9.78. **HRMS (ESI)** calcd. for $C_{13}H_{21}BBrF_2N_2O_5$ $[M+H]^+$: 412.0726, found: 412.0722.

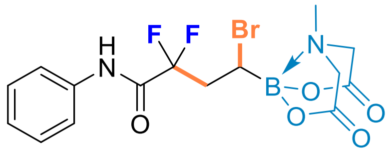
4-bromo-*N*-cyclohexyl-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (4)



Following the general procedure, compound **4** was obtained in 70% yield (84 mg) as a light red solid after column chromatography. **^{1}H NMR** (600 MHz, DMSO-*d6*) δ 8.55 (d, *J* = 7.9 Hz, 1H), 4.46 (d, *J* = 17.4 Hz, 1H), 4.27 (d, *J* = 17.0 Hz, 1H), 4.10 (d, *J* = 17.7 Hz, 1H), 4.07 (d, *J* = 17.2 Hz, 1H), 3.61 (d, *J* = 11.3 Hz, 1H), 3.58 (d, *J* = 8.0 Hz, 1H), 3.09 (s, 3H), 2.70 (dd, *J* = 32.4, 16.2 Hz, 1H), 2.62 – 2.52 (m, 1H), 1.75 – 1.66 (m, 4H), 1.57 (d, *J* = 12.7 Hz, 1H), 1.36 – 1.22 (m, 4H), 1.12 – 1.04 (m, 1H). **^{13}C NMR** (151 MHz, DMSO-*d6*) δ 168.3, 168.2, 162.2 (t, *J* = 28.3 Hz), 117.4 (t, *J* = 252.6 Hz), 63.4, 63.2, 48.4, 45.6, 37.7 (t, *J* = 23.9 Hz), 33.6 (α-C of boron), 31.8, 31.6, 25.0, 24.8

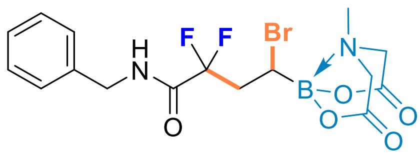
(2C). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -102.3 (dt, *J* = 248.9, 15.3 Hz, 1F), -105.6 (m, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.55. **HRMS (ESI)** calcd. for $C_{15}H_{23}[^{11}B]BrF_2N_2O_5$ $[M+H]^+$: 439.0846, found: 439.0852.

4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-*N*-phenylbutanamide (5)



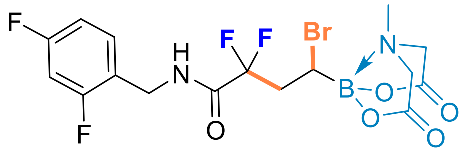
Following the general procedure, compound **5** was obtained in 73% yield (86 mg) as a red solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 10.56 (s, 1H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 3H), 7.16 (t, *J* = 7.3 Hz, 1H), 4.47 (d, *J* = 17.4 Hz, 1H), 4.29 (d, *J* = 17.1 Hz, 1H), 4.12 (d, *J* = 17.3 Hz, 1H), 4.06 (d, *J* = 17.3 Hz, 1H), 3.72 (d, *J* = 11.1 Hz, 1H), 3.12 (s, 3H), 2.85 (dd, *J* = 31.2, 16.2 Hz, 1H), 2.79 – 2.68 (m, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.2, 168.1, 161.7 (t, *J* = 29.2 Hz), 137.3, 128.7 (2C), 124.8, 120.9 (2C), 117.2 (t, *J* = 253.5 Hz), 63.4, 63.2, 45.7, 37.8 (t, *J* = 23.9 Hz), 33.5 (α-C of boron). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -101.2 (dt, *J* = 250.8, 13.9 Hz, 1F), -105.6 (dt, *J* = 250.6, 17.7 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 9.52. **HRMS (ESI)** calcd. for $C_{15}H_{17}[^{11}B]BrF_2N_2O_5$ $[M+H]^+$: 433.0376, found: 433.0377.

***N*-benzyl-4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (6)**



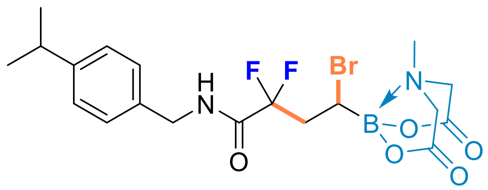
Following the general procedure, compound **6** was obtained in 65% yield (79 mg) as a yellow solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 9.33 (t, *J* = 5.9 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.27 (d, *J* = 7.1 Hz, 2H), 7.24 (dd, *J* = 11.4, 4.1 Hz, 1H), 4.45 (d, *J* = 17.4 Hz, 1H), 4.34 – 4.32 (m, 2H), 4.25 (d, *J* = 17.1 Hz, 1H), 4.09 (d, *J* = 16.2 Hz, 1H), 4.05 (d, *J* = 16.2 Hz, 1H), 3.60 (d, *J* = 10.9 Hz, 1H), 3.06 (s, 3H), 2.75 (dd, *J* = 34.1, 15.7 Hz, 1H), 2.65 – 2.51 (m, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.2, 168.1, 163.3 (t, *J* = 28.6 Hz), 138.3, 128.3 (2C), 127.3 (2C), 127.0, 117.5 (t, *J* = 252.7 Hz), 63.4, 63.2, 45.6, 42.4, 37.6 (t, *J* = 23.7 Hz), 33.3 (α-C of boron). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -102.7 (dt, *J* = 250.7, 15.9 Hz, 1F), -105.1 (ddd, *J* = 250.7, 18.2, 14.4 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.07. **HRMS (ESI)** calcd. for $C_{16}H_{19}BBrF_2N_2O_5$ $[M+H]^+$: 446.0569, found: 446.0576.

4-bromo-*N*-(2,4-difluorobenzyl)-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (7)



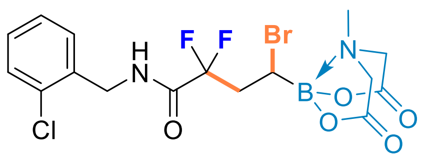
Following the general procedure, compound **7** was obtained in 63% yield (83 mg) as a white solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 9.36 (t, *J* = 5.7 Hz, 1H), 7.39 (dd, *J* = 15.4, 8.6 Hz, 1H), 7.21 (td, *J* = 10.3, 2.5 Hz, 1H), 7.07 (td, *J* = 8.5, 1.9 Hz, 1H), 4.47 (d, *J* = 17.4 Hz, 1H), 4.35 (d, *J* = 5.7 Hz, 2H), 4.27 (d, *J* = 17.1 Hz, 1H), 4.11 (d, *J* = 17.5 Hz, 1H), 4.07 (d, *J* = 17.1 Hz, 1H), 3.60 (d, *J* = 11.0 Hz, 1H), 3.08 (s, 3H), 2.74 (dd, *J* = 33.7, 15.6 Hz, 1H), 2.65 – 2.52 (m, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.2, 168.1, 163.4 (t, *J* = 28.8 Hz), 161.5 (dd, *J* = 245.5, 12.1 Hz), 160.0 (dd, *J* = 247.8, 12.4 Hz), 131.1 (dd, *J* = 9.8, 5.8 Hz), 121.2 (dd, *J* = 15.0, 3.5 Hz), 117.4 (t, *J* = 252.6 Hz), 111.3 (dd, *J* = 21.2, 3.5 Hz), 103.7 (t, *J* = 25.8 Hz), 63.4, 63.2, 45.6, 37.6 (t, *J* = 23.9 Hz), 35.9 (d, *J* = 3.5 Hz), 33.4 (α-C of boron). **^{19}F NMR** (753 MHz, DMSO-*d6*) δ -102.4 (dt, *J* = 27.7, 13.6 Hz, 1F), -105.4 (dt, *J* = 251.4, 16.3 Hz, 1F), -111.6 (m, 1F), -114.0 (dd, *J* = 17.3, 8.5 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.37. **HRMS (ESI)** calcd. for $C_{16}H_{17}[^{11}B]BrF_4N_2O_5$ $[M+H]^+$: 483.0345, found: 483.0354.

4-bromo-2,2-difluoro-*N*-(4-isopropylbenzyl)-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (8)



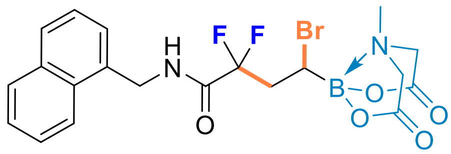
Following the general procedure, compound **8** was obtained in 60% yield (80 mg) as a yellow solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 9.31 (t, *J* = 5.9 Hz, 1H), 7.21 – 7.17 (m, 4H), 4.47 (d, *J* = 17.4 Hz, 1H), 4.32 – 4.25 (m, 3H), 4.09 (t, *J* = 16.4 Hz, 2H), 3.62 (d, *J* = 10.6 Hz, 1H), 3.09 (s, 3H), 2.85 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.77 (dd, *J* = 33.9, 15.0 Hz, 1H), 2.66 – 2.52 (m, 1H), 1.18 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.3, 168.2, 163.3 (t, *J* = 28.5 Hz), 147.2, 135.8, 127.4 (2C), 126.2 (2C), 117.5 (t, *J* = 252.9 Hz), 63.4, 63.2, 45.6, 42.2, 37.7 (t, *J* = 23.7 Hz), 33.5 (α-C of boron), 33.1, 23.9 (2C). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -102.9 (dt, *J* = 250.5, 15.9 Hz, 1F), -105.0 (ddd, *J* = 250.5, 18.2, 14.2 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.54. **HRMS (ESI)** calcd. for $C_{19}H_{25}[^{11}B]BrF_2N_2O_5$ $[M+H]^+$: 489.1002, found: 489.1010.

4-bromo-*N*-(2-chlorobenzyl)-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (9)



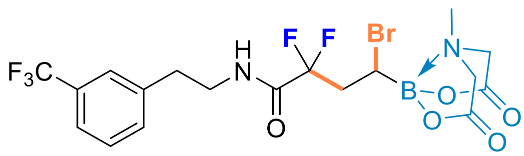
Following the general procedure, compound **9** was obtained in 72% yield (94 mg) as a brown solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 9.37 (t, *J* = 5.7 Hz, 1H), 7.45 (d, *J* = 7.4 Hz, 1H), 7.36 – 7.28 (m, 3H), 4.47 (d, *J* = 17.4 Hz, 1H), 4.43 (dd, *J* = 5.6, 3.4 Hz, 2H), 4.28 (d, *J* = 17.1 Hz, 1H), 4.11 (d, *J* = 17.4 Hz, 1H), 4.08 (d, *J* = 17.0 Hz, 1H), 3.65 (d, *J* = 10.6 Hz, 1H), 3.10 (s, 3H), 2.79 (dd, *J* = 34.2, 15.5 Hz, 1H), 2.70 – 2.55 (m, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.2, 168.1, 163.5 (t, *J* = 28.8 Hz), 135.0, 132.0, 129.2, 128.8, 128.7, 127.1, 117.4 (t, *J* = 252.6 Hz), 63.4, 63.2, 45.6, 40.2, 37.6 (t, *J* = 23.6 Hz), 33.5 (α-C of boron). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -102.7 (dt, *J* = 251.3, 15.8 Hz, 1F), -104.8 (m, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.20. **HRMS (ESI)** calcd. for $C_{16}H_{18}[^{11}B]BrClF_2N_2O_5$ $[M+H]^+$: 481.0143, found: 481.0148.

4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-*N*-(naphthalen-1-ylmethyl)butanamide (10)



Following the general procedure, compound **10** was obtained in 52% yield (70 mg) as a white solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 9.42 (t, *J* = 5.7 Hz, 1H), 8.13 (d, *J* = 8.1 Hz, 1H), 7.97 – 7.93 (m, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.56 (pd, *J* = 6.8, 1.3 Hz, 2H), 7.51 – 7.44 (m, 2H), 4.89 – 4.76 (m, 2H), 4.47 (d, *J* = 17.4 Hz, 1H), 4.28 (d, *J* = 17.1 Hz, 1H), 4.13 – 4.04 (m, 2H), 3.62 (d, *J* = 10.4 Hz, 1H), 3.07 (s, 3H), 2.79 (dd, *J* = 34.0, 15.4 Hz, 1H), 2.70 – 2.55 (m, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.3, 168.1, 163.3 (t, *J* = 28.8 Hz), 133.4, 133.3, 130.8, 128.5, 127.8, 126.3, 125.8, 125.6, 125.3, 123.4, 117.5 (t, *J* = 253.1 Hz), 63.4, 63.2, 45.6, 40.5, 37.7 (t, *J* = 23.7 Hz), 33.5 (α-C of boron). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -102.4 (dt, *J* = 251.1, 15.7 Hz, 1F), -104.8 (m, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.36. **HRMS (ESI)** calcd. for $C_{20}H_{21}[^{11}B]BrF_2N_2O_5$ $[M+H]^+$: 497.0689, found: 497.0689.

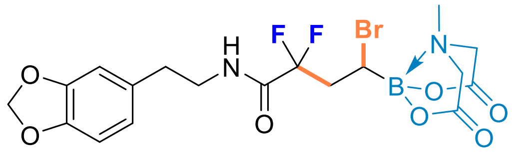
4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-*N*-(3-(trifluoromethyl)phenethyl)butanamide (11)



Following the general procedure, compound **11** was obtained in 59% yield (85 mg) as a white solid after column chromatography. **^{1}H NMR** (600 MHz, DMSO-*d6*) δ 8.89 (t, *J* = 5.5 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.53 – 7.51 (m, 2H), 4.47 (d, *J* = 17.4 Hz, 1H), 4.28 (d, *J* = 17.1 Hz, 1H), 4.11 (d, *J* = 17.4 Hz, 1H), 4.06 (d, *J* = 17.1 Hz, 1H), 3.59 (t, *J* = 12.2 Hz, 1H), 3.41 (dd, *J* = 13.2, 6.9 Hz, 2H), 3.09 (s, 3H), 2.90 (t, *J* = 7.1 Hz, 2H), 2.65 (ddd, *J* = 19.0, 16.9, 8.5 Hz, 1H), 2.55 – 2.41 (m, 1H). **^{13}C NMR** (151 MHz, DMSO-*d6*) δ 168.3, 168.2, 163.3 (t, *J* = 28.5 Hz), 140.5, 132.9, 129.3, 129.1 (q, *J* = 31.4 Hz), 125.3 (d, *J* = 3.7 Hz), 124.3 (q, *J* = 272.1 Hz), 123.0 (d, *J* = 3.7 Hz), 117.3 (t,

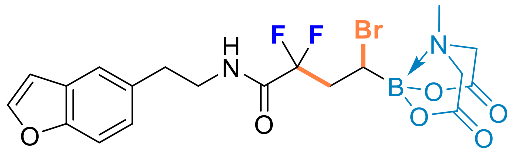
J = 254.3 Hz), 63.4, 63.2, 45.7, 40.0, 37.6 (t, J = 23.6 Hz), 33.9, 33.4 (α-C of boron). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -61.0 (s, 3F), -103.3 (dt, J = 250.0, 15.8 Hz, 1F), -105.8 (m, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.59. **HRMS (ESI)** calcd. for $C_{18}H_{18}[^{11}B]BrF_5N_2O_5$ $[M-H]^-$: 527.0418, found: 527.0424.

_N_-(2-(benzo[_d_][1,3]dioxol-5-yl)ethyl)-4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (12)



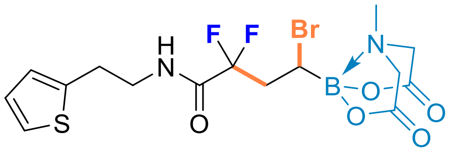
Following the general procedure, compound **12** was obtained in 50% yield (69 mg) as a yellow solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 8.80 (t, J = 5.5 Hz, 1H), 6.79 (dd, J = 12.0, 4.6 Hz, 2H), 6.65 (dd, J = 7.9, 1.4 Hz, 1H), 5.96 (s, 2H), 4.46 (d, J = 17.4 Hz, 1H), 4.27 (d, J = 17.1 Hz, 1H), 4.09 (t, J = 17.3 Hz, 2H), 3.60 (d, J = 10.6 Hz, 1H), 3.36 – 3.29 (m, 2H), 3.09 (d, J = 6.6 Hz, 3H), 2.79 – 2.63 (m, 3H), 2.59 – 2.43 (m, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.3, 168.1, 163.2 (t, J = 28.4 Hz), 147.2, 145.6, 132.7, 121.5, 117.4 (t, J = 254.9 Hz), 109.0, 108.1, 100.7, 63.4, 63.2, 45.7, 40.6, 37.6 (t, J = 23.6 Hz), 34.0, 33.3 (α-C of boron). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -103.5 (dt, J = 249.5, 15.7 Hz, 1F), -105.5 (ddd, J = 249.5, 19.3, 14.0 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.41. **HRMS (ESI)** calcd. for $C_{18}H_{21}[^{11}B]BrF_2N_2O_7$ $[M+H]^+$: 505.0588, found: 505.0599.

_N_-(2-(benzofuran-5-yl)ethyl)-4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (13)



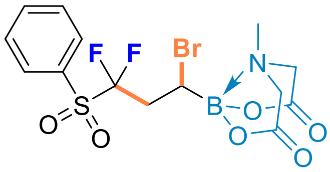
Following the general procedure, compound **13** was obtained in 34% yield (47 mg) as a yellow solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 8.97 (t, J = 5.6 Hz, 1H), 7.81 (s, 1H), 7.67 (d, J = 7.3 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.29 (dtd, J = 21.8, 7.3, 1.1 Hz, 2H), 4.46 (d, J = 17.4 Hz, 1H), 4.27 (d, J = 17.1 Hz, 1H), 4.08 (t, J = 17.6 Hz, 2H), 3.61 (d, J = 10.3 Hz, 1H), 3.47 (dd, J = 13.3, 7.1 Hz, 2H), 3.08 (s, 3H), 2.88 (t, J = 7.3 Hz, 2H), 2.73 (dd, J = 34.5, 14.9 Hz, 1H), 2.65 – 2.53 (m, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.3, 168.2, 163.3 (t, J = 28.6 Hz), 154.6, 142.3, 127.8, 124.3, 122.5, 119.7, 117.4 (t, J = 253.3 Hz), 117.2, 111.3, 63.4, 63.2, 45.6, 38.6, 37.6 (t, J = 23.9 Hz), 22.7. **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -103.0 (dt, J = 250.0, 15.5 Hz, 1F), -105.6 (m, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.47. **HRMS (ESI)** calcd. for $C_{19}H_{21}[^{11}B]BrF_2N_2O_6$ $[M+H]^+$: 501.0639, found: 501.0637.

4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-_N_-(2-(thiophen-2-yl)ethyl)butanamide (14)



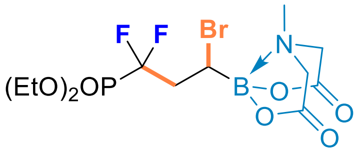
Following the general procedure, compound **14** was obtained in 45% yield (57 mg) as a yellow solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 8.92 (t, *J* = 5.5 Hz, 1H), 7.34 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.95 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.90 – 6.87 (m, 1H), 4.46 (d, *J* = 17.4 Hz, 1H), 4.27 (d, *J* = 17.1 Hz, 1H), 4.08 (dd, *J* = 21.5, 12.1 Hz, 2H), 3.62 (d, *J* = 10.3 Hz, 1H), 3.38 (dd, *J* = 13.2, 7.1 Hz, 2H), 3.09 (s, 3H), 3.01 (t, *J* = 7.2 Hz, 2H), 2.80 – 2.66 (m, 1H), 2.65 – 2.51 (m, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.3, 168.2, 163.3 (t, *J* = 28.4 Hz), 141.0, 127.0, 125.3, 124.2, 117.4 (t, *J* = 254.1 Hz), 63.4, 63.2, 45.7, 40.6, 37.6 (t, *J* = 23.5 Hz), 28.5. **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -103.4 (dt, *J* = 249.6, 15.6 Hz, 1F), -105.7 (m, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.31. **HRMS (ESI)** calcd. for $C_{15}H_{19}[^{11}B]BrF_2N_2O_5S$ $[M+H]^+$: 467.0254, found: 467.0258.

2-(1-bromo-3,3-difluoro-3-(phenylsulfonyl)propyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (15)



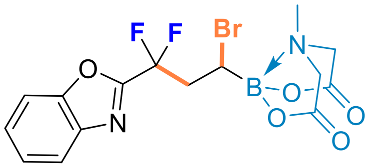
Following the general procedure, compound **15** was obtained in 62% yield (76 mg) as a white solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.96 (t, *J* = 7.5 Hz, 1H), 7.80 (t, *J* = 7.9 Hz, 2H), 4.51 (d, *J* = 17.4 Hz, 1H), 4.29 (d, *J* = 17.1 Hz, 1H), 4.11 (d, *J* = 17.4 Hz, 1H), 4.09 (d, *J* = 17.1 Hz, 1H), 3.82 (d, *J* = 10.2 Hz, 1H), 3.12 (s, 3H), 3.08 (dt, *J* = 16.7, 12.2 Hz, 1H), 2.64 (tdd, *J* = 17.1, 11.4, 6.2 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.2, 168.1, 136.5, 130.9, 130.5 (2C), 130.2 (2C), 123.7 (t, *J* = 288.1 Hz), 63.5, 63.2, 45.9, 32.9 (t, *J* = 19.2 Hz), 31.3 (α-C of boron). **^{19}F NMR** (376 MHz, DMSO-*d6*) δ -101.9 (dd, *J* = 227.6, 30.7 Hz, 1F), -106.8 (dd, *J* = 228.3, 25.8 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.02. **HRMS (ESI)** calcd. for $C_{14}H_{15}BBrClF_2NO_6S$ $[M+Cl]^-$: 486.9595, found: 486.9598.

Diethyl (3-bromo-1,1-difluoro-3-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)propyl)phosphonate (16)



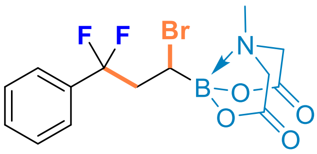
Following the general procedure, compound **16** was obtained in 30% yield (37 mg) as a yellow solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 4.49 (d, *J* = 17.4 Hz, 1H), 4.27 (d, *J* = 17.0 Hz, 1H), 4.22 (dd, *J* = 14.8, 7.5 Hz, 4H), 4.10 (d, *J* = 17.4 Hz, 1H), 4.08 (d, *J* = 17.1 Hz, 1H), 3.78 (d, *J* = 10.5 Hz, 1H), 3.12 (s, 3H), 2.81 (ddd, J = 38.7, 24.4, 8.7 Hz, 1H), 2.48 – 2.39 (m, 1H), 1.30 (t, J = 7.0 Hz, 6H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.2, 168.1, 120.1 (td, J = 262.7, 214.4 Hz), 64.4 (2C), 63.5, 63.2, 45.7, 37.0 (dd, J = 35.3, 19.5 Hz), 31.8 (α-C of boron), 16.2 (2C). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -110.8 (ddd, J = 132.9, 102.4, 27.3 Hz, 1F), -114.5 (dddd, J = 292.9, 106.4, 29.4, 9.5 Hz, 1F). **^{31}P NMR** (202 MHz, DMSO-*d6*) δ 6.5 (t, J = 103.7 Hz, 1P). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.30. **HRMS (ESI)** calcd. for $C_{12}H_{20}[^{11}B]BrF_2NNaO_7P$ $[M+Na]^+$: 472.0114, found: 472.0114.

2-(3-(benzo[*d*]oxazol-2-yl)-1-bromo-3,3-difluoropropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (17)



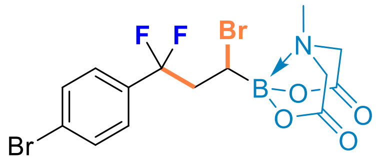
Following the general procedure, compound **17** was obtained in 78% yield (92 mg) as a brown solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 7.90 (dd, J = 13.6, 8.0 Hz, 2H), 7.59 – 7.55 (m, 1H), 7.52 – 7.48 (m, 1H), 4.49 (d, J = 17.4 Hz, 1H), 4.29 (dd, J = 16.8, 6.7 Hz, 1H), 4.13 (d, J = 17.4 Hz, 1H), 4.08 (d, J = 17.1 Hz, 1H), 3.83 (d, J = 10.9 Hz, 1H), 3.22 (td, J = 17.3, 12.6 Hz, 1H), 3.12 (s, 3H), 2.98 (qd, J = 16.4, 11.8 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.2, 168.1, 156.9 (t, J = 33.3 Hz), 150.0, 139.5, 127.2, 125.6, 121.0, 116.6 (t, J = 243.3 Hz), 111.8, 63.4, 63.2, 45.8, 39.5 (t, J = 24.0 Hz), 33.1 (α-C of boron). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -92.9 (d, J = 270.1 Hz, 1F), -100.9 (dt, J = 270.2, 17.7 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 9.98. **HRMS (ESI)** calcd. for $C_{15}H_{15}[^{11}B]BrF_2N_2O_5$ $[M+H]^+$: 431.0220, found: 431.0226.

2-(1-bromo-3,3-difluoro-3-phenylpropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (18)



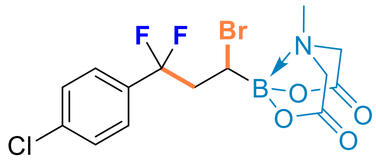
Following the general procedure, compound **18** was obtained in 81% yield (86 mg) as a yellow solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 7.56 (dd, J = 6.9, 2.7 Hz, 2H), 7.51 (dd, J = 5.0, 1.7 Hz, 3H), 4.44 (d, J = 17.4 Hz, 1H), 4.27 (d, J = 17.1 Hz, 1H), 4.08 (t, J = 16.9 Hz, 2H), 3.54 (d, J = 10.0 Hz, 1H), 3.07 (s, 3H), 2.94 – 2.80 (m, 1H), 2.72 (tt, J = 16.6, 11.1 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.3, 168.2, 136.2 (t, J = 26.0 Hz), 130.2, 128.6 (2C), 124.9 (t, J = 5.9 Hz, 2C), 122.8 (t, J = 243.6 Hz), 63.4, 63.3, 45.6, 42.0 (t, J = 27.5 Hz), 34.3 (α-C of boron). **^{19}F NMR** (376 MHz, DMSO-*d6*) δ -92.3 (m, 2F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 9.97. **HRMS (ESI)** calcd. for $C_{14}H_{14}[^{11}B]BrF_2NO_4$ $[M-H]^-$: 388.0173, found: 388.0175.

2-(1-bromo-3-(4-bromophenyl)-3,3-difluoropropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (19)



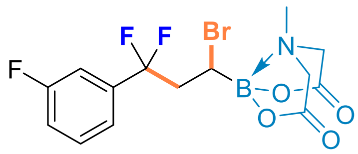
Following the general procedure, compound **19** was obtained in 78% yield (103 mg) as a brown solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 7.71 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 4.44 (t, *J* = 17.4 Hz, 1H), 4.26 (d, *J* = 17.1 Hz, 1H), 4.08 (d, *J* = 17.0 Hz, 1H), 4.05 (d, *J* = 16.9 Hz, 1H), 3.50 (d, *J* = 10.1 Hz, 1H), 3.06 (s, 3H), 2.93 – 2.78 (m, 1H), 2.72 (td, *J* = 27.2, 15.9 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.3, 168.2, 135.4 (t, *J* = 26.6 Hz), 131.7 (2C), 127.4 (t, *J* = 5.8 Hz, 2C), 123.8, 122.5 (t, *J* = 243.9 Hz), 63.4, 63.3, 45.7, 41.7 (t, *J* = 27.4 Hz), 34.3 (α-C of boron). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -91.9 (m, 2F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 9.97. **HRMS (ESI)** calcd. for $C_{14}H_{13}[^{11}B]Br_2F_2NO_4$ $[M-H]^-$: 465.9278, found: 465.9273.

2-(1-bromo-3-(4-chlorophenyl)-3,3-difluoropropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (20)



Following the general procedure, compound **20** was obtained in 76% yield (88 mg) as a brown solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 7.58 (q, *J* = 8.8 Hz, 4H), 4.44 (d, *J* = 17.4 Hz, 1H), 4.27 (d, *J* = 17.1 Hz, 1H), 4.07 (t, *J* = 17.3 Hz, 2H), 3.52 (d, *J* = 10.1 Hz, 1H), 3.07 (s, 3H), 2.94 – 2.80 (m, 1H), 2.73 (td, *J* = 27.4, 16.0 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.3, 168.1, 135.0 (t, *J* = 26.7 Hz), 135.0, 128.7 (2C), 127.1 (t, *J* = 5.8 Hz, 2C), 122.5 (t, *J* = 243.9 Hz), 63.4, 63.3, 45.7, 41.8 (t, *J* = 27.5 Hz), 34.2 (α-C of boron). **^{19}F NMR** (376 MHz, DMSO-*d6*) δ -91.7 (m, 2F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 9.92. **HRMS (ESI)** calcd. for $C_{14}H_{13}[^{11}B]BrClF_2NO_4$ $[M-H]^-$: 421.9783, found: 421.9785.

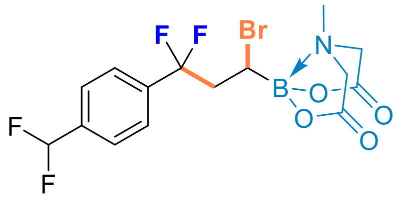
2-(1-bromo-3,3-difluoro-3-(3-fluorophenyl)propyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (21)



Following the general procedure, compound **21** was obtained in 74% yield (83 mg) as a yellow solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 7.59 – 7.53 (m, 1H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.36 (td, *J* = 8.6, 1.6 Hz, 1H), 4.44 (d, *J* = 17.4 Hz, 1H), 4.31 – 4.22 (m, 1H), 4.09 (d, *J* = 17.6 Hz, 1H), 4.05 (d, *J* = 17.1 Hz, 1H), 3.54 (d, *J* = 9.8 Hz, 1H), 3.07 (s, 3H), 2.87 (dd, *J* = 32.5, 16.2 Hz, 1H), 2.74 (ddd, *J* = 20.7, 16.4, 13.9 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.3, 168.2, 162.0 (d, *J* = 244.7 Hz), 138.6 (td, *J* = 26.7, 7.3 Hz), 131.0 (d, *J* = 8.2 Hz), 122.1 (t, *J* = 243.6 Hz), 121.3

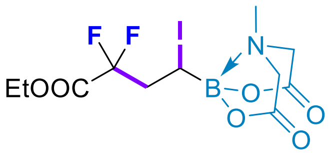
(d, J = 2.2 Hz), 117.2 (d, J = 20.9 Hz), 112.5 (dt, J = 23.7, 6.0 Hz), 63.4, 63.3, 45.7, 41.7 (t, J = 27.2 Hz), 34.2 (α-C of boron). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -91.5 (dt, J = 243.7, 15.5 Hz, 1F), -92.3 (m, 1F), -112.0 (dd, J = 15.4, 9.3 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.07. **HRMS (ESI)** calcd. for $C_{14}H_{13}[^{11}B]BrF_3NO_4$ $[M-H]^-$: 406.0079, found: 406.0070.

2-(1-bromo-3-(4-(difluoromethyl)phenyl)-3,3-difluoropropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (22)



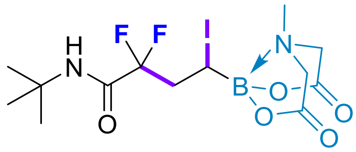
Following the general procedure, compound **22** was obtained in 80% yield (96 mg) as a brown solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 7.72 (s, 4H), 7.11 (t, J = 55.7 Hz, 1H), 4.44 (d, J = 17.4 Hz, 1H), 4.27 (d, J = 17.0 Hz, 1H), 4.07 (t, J = 17.1 Hz, 2H), 3.55 (d, J = 10.8 Hz, 1H), 3.08 (s, 3H), 2.88 (q, J = 16.4 Hz, 1H), 2.82 – 2.68 (m, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.3, 168.2, 138.7 (t, J = 26.1 Hz), 135.8 (t, J = 22.3 Hz), 126.1 (t, J = 5.9 Hz, 2C), 125.7 (t, J = 5.7 Hz, 2C), 122.5 (t, J = 243.9 Hz), 114.4 (t, J = 236.5 Hz), 63.4, 63.3, 45.7, 41.8 (t, J = 27.2 Hz), 34.1 (α-C of boron). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -92.4 (t, J = 14.8 Hz, 2F), -110.5 (s, 1F), -110.6 (s, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.39. **HRMS (ESI)** calcd. for $C_{15}H_{14}[^{11}B]BrF_4NO_4$ $[M-H]^-$: 438.0141, found: 438.0153.

Ethyl 2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoate (23)



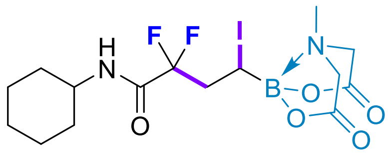
Following the general procedure, compound **23** was obtained in 83% yield (98 mg) as a brown solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 4.41 (d, J = 17.4 Hz, 1H), 4.31 (dt, J = 10.5, 5.3 Hz, 3H), 4.14 (d, J = 17.4 Hz, 1H), 4.11 (d, J = 17.1 Hz, 1H), 3.41 (d, J = 10.4 Hz, 1H), 3.09 (s, 3H), 2.89 (q, J = 15.9 Hz, 1H), 2.62 (qd, J = 16.3, 11.5 Hz, 1H), 1.30 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.0, 167.9, 163.1 (t, J = 32.4 Hz), 116.0 (t, J = 250.8 Hz), 63.7, 63.4, 63.1, 45.7, 38.9 (t, J = 23.5 Hz), 13.6, 6.8 (α-C of boron). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -102.3 (m, 1F), -106.1 (dt, J = 255.6, 17.2 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.13. **HRMS (ESI)** calcd. for $C_{11}H_{19}BF_2IN_2O_6$ $[M+NH_4]^+$: 450.0380, found: 450.0376.

***N*-(*tert*-butyl)-2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (24)**



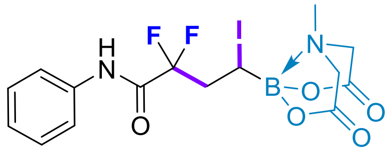
Following the general procedure, compound **24** was obtained in 74% yield (93 mg) as a colorless oil after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 8.00 (s, 1H), 4.41 (d, *J* = 17.4 Hz, 1H), 4.31 (d, *J* = 17.2 Hz, 1H), 4.14 (d, *J* = 17.2 Hz, 1H), 4.09 (d, *J* = 17.0 Hz, 1H), 3.39 (dd, *J* = 11.1, 1.4 Hz, 1H), 3.08 (s, 3H), 2.84 – 2.72 (m, 1H), 2.57 (ddd, *J* = 16.6, 14.8, 8.2 Hz, 1H), 1.31 (s, 9H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.1, 168.0, 162.6 (t, *J* = 28.1 Hz), 117.2 (t, *J* = 254.2 Hz), 63.7, 63.5, 51.3, 45.6, 38.3 (t, *J* = 23.6 Hz), 28.1 (3C), 7.4 (α-C of boron). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -102.9 (m, 1F), -104.4 (ddd, *J* = 246.9, 19.0, 13.5 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.53. **HRMS (ESI)** calcd. for $C_{13}H_{21}[^{11}B]F_2IN_2O_5$ $[M+H]^+$: 461.0551, found: 461.0557.

N-cyclohexyl-2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (25)



Following the general procedure, compound **25** was obtained in 82% yield (109 mg) as a light brown solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 8.53 (d, *J* = 7.9 Hz, 1H), 4.40 (d, *J* = 17.4 Hz, 1H), 4.30 (d, *J* = 17.1 Hz, 1H), 4.14 (d, *J* = 16.8 Hz, 1H), 4.09 (d, *J* = 16.6 Hz, 1H), 3.62 – 3.53 (m, 1H), 3.39 (d, *J* = 10.6 Hz, 1H), 3.09 (s, 3H), 2.79 (dd, *J* = 33.3, 16.3 Hz, 1H), 2.62 – 2.51 (m, 1H), 1.79 – 1.67 (m, 4H), 1.58 (d, *J* = 12.8 Hz, 1H), 1.35 – 1.25 (m, 4H), 1.08 (dd, *J* = 22.7, 10.6 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.0 (2C), 162.1 (t, *J* = 28.4 Hz), 117.5 (t, *J* = 253.2 Hz), 63.7, 63.5, 48.4, 45.6, 38.4 (t, *J* = 23.8 Hz), 31.8, 31.6, 25.0, 24.8 (2C), 7.4 (α-C of boron). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -103.1 (dt, *J* = 248.0, 15.8 Hz, 1F), -105.2 (m, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.34. **HRMS (ESI)** calcd. for $C_{15}H_{23}BF_2IN_2O_5$ $[M+H]^+$: 486.0744, found: 486.0743.

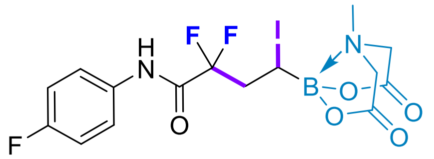
2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-N-phenylbutanamide (26)



Following the general procedure, compound **26** was obtained in 76% yield (99 mg) as a purple solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 10.58 (s, 1H), 7.70 (d, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 4.41 (d, *J* = 17.4 Hz, 1H), 4.32 (d, *J* = 17.1 Hz, 1H), 4.13 (t, *J* = 17.7 Hz, 2H), 3.49 (d, *J* = 10.3 Hz, 1H), 3.11 (s, 3H), 3.00 – 2.86 (m, 1H), 2.81 – 2.62 (m, 1H). **^{13}C NMR** (126

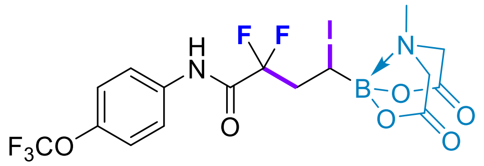
MHz, DMSO-*d6*) δ 168.1 (2C), 161.7 (t, *J* = 29.2 Hz), 137.3, 128.7 (2C), 124.8, 121.0 (2C), 117.5 (t, *J* = 254.2 Hz), 63.7, 63.5, 45.6, 38.5 (t, *J* = 23.6 Hz). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -101.8 (dt, *J* = 250.0, 13.5 Hz, 1F), -105.5 (dt, *J* = 30.9, 14.8 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.71. **HRMS (ESI)** calcd. for $C_{15}H_{17}[^{11}B]F_2IN_2O_5$ $[M+H]^+$: 481.0238, found: 481.0237.

2,2-difluoro-*N*-(4-fluorophenyl)-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (27)



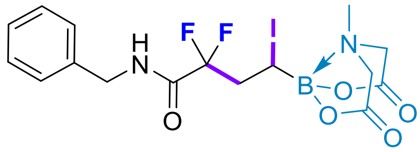
Following the general procedure, compound **27** was obtained in 53% yield (54 mg) as a brown solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 10.68 (s, 1H), 7.75 – 7.70 (m, 2H), 7.24 – 7.18 (m, 2H), 4.41 (d, *J* = 17.4 Hz, 1H), 4.32 (d, *J* = 17.2 Hz, 1H), 4.16 (d, *J* = 17.4 Hz, 1H), 4.12 (d, *J* = 17.2 Hz, 1H), 3.52 – 3.42 (m, 1H), 3.11 (s, 3H), 3.01 – 2.86 (m, 1H), 2.80 – 2.62 (m, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.1 (2C), 161.7 (t, *J* = 29.2 Hz), 159.0 (d, *J* = 241.5 Hz), 133.6 (d, *J* = 2.4 Hz), 123.0 (d, *J* = 8.0 Hz, 2C), 117.5 (t, *J* = 253.6 Hz), 115.4 (d, *J* = 22.4 Hz, 2C), 63.7, 63.5, 45.7, 38.5 (t, *J* = 23.6 Hz), 7.2 (α-C of boron). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -101.8 (dt, *J* = 249.8, 13.5 Hz, 1F), -105.8 (dd, *J* = 140.2, 124.8 Hz, 1F), -117.4 (m, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.72. **HRMS (ESI)** calcd. for $C_{15}H_{16}[^{11}B]F_3IN_2O_5$ $[M+H]^+$: 499.0144, found: 499.0144.

2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-*N*-(4-(trifluoromethoxy)phenyl)butanamide (28)



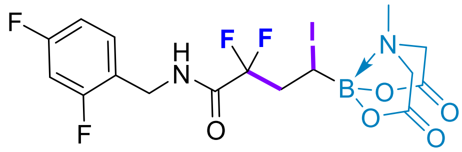
Following the general procedure, compound **28** was obtained in 72% yield (110 mg) as a purple solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 10.79 (s, 1H), 7.83 (d, *J* = 9.0 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 4.42 (d, *J* = 17.4 Hz, 1H), 4.33 (d, *J* = 17.1 Hz, 1H), 4.14 (t, *J* = 17.4 Hz, 2H), 3.49 (d, *J* = 11.0 Hz, 1H), 3.12 (s, 3H), 2.95 (dd, *J* = 31.0, 16.6 Hz, 1H), 2.83 – 2.65 (m, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.1, 168.0, 161.9 (t, *J* = 29.4 Hz), 144.7, 136.5, 122.5 (2C), 121.5 (2C), 120.7 (q, *J* = 255.8 Hz), 117.4 (t, *J* = 254.0 Hz), 63.7, 63.5, 45.7, 38.5 (t, *J* = 23.7 Hz), 7.2 (α-C of boron). **^{19}F NMR** (753 MHz, DMSO-*d6*) δ -57.1 (s, 3F), -101.7 (d, *J* = 250.6 Hz, 1F), -105.7 (d, *J* = 250.7 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.74. **HRMS (ESI)** calcd. for $C_{16}H_{16}[^{11}B]F_5IN_2O_6$ $[M+H]^+$: 565.0061, found: 565.0062.

***N*-benzyl-2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (29)**



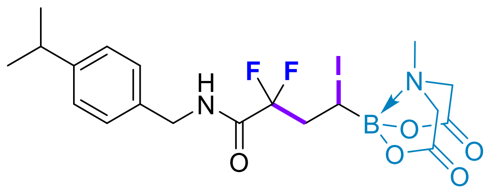
Following the general procedure, compound **29** was obtained in 80% yield (108 mg) as a colorless oil after column chromatography. **^{1}H NMR** (600 MHz, DMSO-*d6*) δ 9.37 (t, *J* = 6.0 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.29 (s, 1H), 7.26 (dd, *J* = 14.0, 6.7 Hz, 2H), 4.41 (d, *J* = 17.4 Hz, 1H), 4.34 (t, *J* = 5.9 Hz, 2H), 4.30 (d, *J* = 17.1 Hz, 1H), 4.13 (d, *J* = 17.7 Hz, 1H), 4.10 (d, *J* = 17.3 Hz, 1H), 3.41 – 3.36 (m, 1H), 3.06 (s, 3H), 2.93 – 2.79 (m, 1H), 2.64 – 2.52 (m, 1H). **^{13}C NMR** (151 MHz, DMSO-*d6*) δ 168.1 (2C), 163.4 (t, *J* = 28.7 Hz), 138.3, 128.4 (2C), 127.4 (2C), 127.1, 117.7 (t, *J* = 253.1 Hz), 63.7, 63.5, 45.6, 42.4, 38.4 (t, *J* = 23.2 Hz), 7.2 (α-C of boron). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -103.8 (dt, *J* = 249.4, 16.4 Hz, 1F), -104.8 (ddd, *J* = 249.4, 18.0, 13.7 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.87. **HRMS (ESI)** calcd. for $C_{16}H_{19}[^{11}B]F_2IN_2O_5$ $[M+H]^+$: 495.0394, found: 495.0406.

_N_-(2,4-difluorobenzyl)-2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (30)



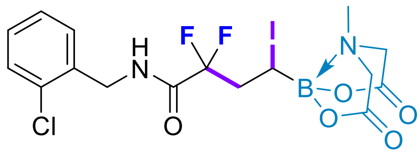
Following the general procedure, compound **30** was obtained in 76% yield (110 mg) as a white solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 9.35 (t, *J* = 5.7 Hz, 1H), 7.39 (dd, *J* = 15.4, 8.6 Hz, 1H), 7.22 (td, *J* = 10.3, 2.5 Hz, 1H), 7.07 (td, *J* = 8.5, 2.1 Hz, 1H), 4.41 (d, *J* = 17.4 Hz, 1H), 4.35 (d, *J* = 5.7 Hz, 2H), 4.30 (d, *J* = 17.2 Hz, 1H), 4.12 (dd, *J* = 17.1, 15.4 Hz, 2H), 3.38 (d, *J* = 10.6 Hz, 1H), 3.07 (s, 3H), 2.84 (dd, *J* = 34.4, 15.1 Hz, 1H), 2.66 – 2.53 (m, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.1, 168.0, 163.4 (t, *J* = 28.9 Hz), 161.5 (dd, *J* = 245.6, 12.2 Hz), 160.1 (dd, *J* = 247.9, 12.4 Hz), 131.1 (dd, *J* = 9.9, 5.8 Hz), 121.2 (dd, *J* = 15.0, 3.5 Hz), 117.5 (t, *J* = 252.4 Hz), 111.4 (dd, *J* = 21.2, 3.5 Hz), 103.7 (t, *J* = 25.8 Hz), 63.7, 63.5, 45.6, 38.4 (t, *J* = 23.5 Hz), 35.9 (d, *J* = 3.6 Hz). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -103.5 (dt, *J* = 249.8, 16.1 Hz, 1F), -105.2 (m, 1F), -111.6 (m, 1F), -114.0 (dd, *J* = 17.3, 8.7 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.76. **HRMS (ESI)** calcd. for $C_{16}H_{17}[^{11}B]F_4IN_2O_5$ $[M+H]^+$: 531.0206, found: 531.0209.

2,2-difluoro-4-iodo-_N_-(4-isopropylbenzyl)-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (31)



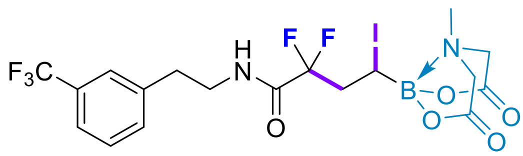
Following the general procedure, compound **31** was obtained in 67% yield (98 mg) as a white solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 9.30 (t, *J* = 5.9 Hz, 1H), 7.20 (s, 4H), 4.41 (d, *J* = 17.4 Hz, 1H), 4.31 (dd, *J* = 11.4, 5.9 Hz, 3H), 4.12 (t, *J* = 16.7 Hz, 2H), 3.39 (d, *J* = 10.2 Hz, 1H), 3.07 (s, 3H), 2.92 – 2.79 (m, 2H), 2.58 (ddd, *J* = 24.3, 17.4, 12.4 Hz, 1H), 1.18 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.0 (2C), 163.2 (t, *J* = 28.7 Hz), 147.2, 135.7, 127.4 (2C), 126.2 (2C), 117.6 (t, *J* = 253.2 Hz), 63.7, 63.5, 45.6, 42.2, 38.4 (t, *J* = 23.4 Hz), 33.1, 23.9 (2C), 7.2 (α-C of boron). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -103.9 (dt, *J* = 249.2, 16.4 Hz, 1F), -104.9 (ddd, *J* = 249.3, 18.4, 13.4 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.82. **HRMS (ESI)** calcd. for $C_{19}H_{25}[^{11}B]F_2IN_2O_5$ $[M+H]^+$: 537.0864, found: 537.0863.

***N*-(2-chlorobenzyl)-2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (32)**



Following the general procedure, compound **32** was obtained in 62% yield (89 mg) as a white solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 9.38 (t, *J* = 5.7 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.26 (m, 3H), 4.43 (d, *J* = 3.7 Hz, 2H), 4.41 (d, *J* = 8.8 Hz, 1H), 4.31 (d, *J* = 17.2 Hz, 1H), 4.14 (d, *J* = 17.3 Hz, 1H), 4.11 (d, *J* = 17.1 Hz, 1H), 3.42 (d, *J* = 10.3 Hz, 1H), 3.08 (s, 3H), 2.89 (dd, *J* = 34.3, 16.8 Hz, 1H), 2.61 (ddd, *J* = 24.6, 17.1, 12.9 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.1, 168.0, 163.6 (t, *J* = 29.0 Hz), 135.1, 132.0, 129.2, 128.9, 128.7, 127.2, 117.6 (t, *J* = 253.0 Hz), 63.7, 63.5, 45.6, 40.3, 38.4 (t, *J* = 23.3 Hz). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -103.6 (dt, *J* = 249.9, 16.2 Hz, 1F), -104.6 (m, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.62. **HRMS (ESI)** calcd. for $C_{16}H_{18}[^{11}B]ClF_2IN_2O_5$ $[M+H]^+$: 529.0005, found: 529.0007.

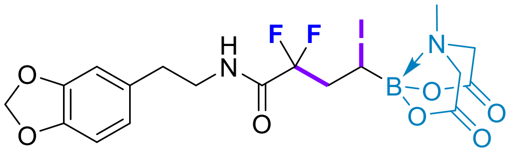
2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-*N*-(3-(trifluoromethyl)phenethyl)butanamide (33)



Following the general procedure, compound **33** was obtained in 70% yield (110 mg) as a white solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 8.89 (t, *J* = 5.5 Hz, 1H), 7.55 (d, *J* = 5.2 Hz, 2H), 7.52 (d, *J* = 2.9 Hz, 2H), 4.42 (d, *J* = 17.4 Hz, 1H), 4.33 (d, *J* = 17.1 Hz, 1H), 4.15 (d, *J* = 17.4 Hz, 1H), 4.11 (d, *J* = 17.1 Hz, 1H), 3.45 – 3.41 (m, 2H), 3.39 (d, *J* = 11.9 Hz, 1H), 3.09 (s, 3H), 2.92 (t, *J* = 7.1 Hz, 2H), 2.89 – 2.72 (m, 1H), 2.60 – 2.36 (m, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.1, 168.0, 163.3 (t, *J* = 28.6 Hz), 140.5, 132.9, 129.3, 129.1 (q, *J* = 31.3 Hz), 125.3 (d, *J* = 3.6 Hz), 124.3 (q, *J* = 272.3 Hz), 123.0 (d, *J* = 3.6 Hz), 117.5 (t, *J* = 253.1 Hz), 63.7, 63.5, 45.6, 40.0, 38.4 (t, *J* = 23.4 Hz), 33.9, 7.1 (α-C of boron). **^{19}F NMR** (753 MHz, DMSO-*d6*) δ -61.1 (s, 3F), -104.2 (d, *J* = 249.2 Hz, 1F), -105.6 (d, *J* = 249.2 Hz, 1F).

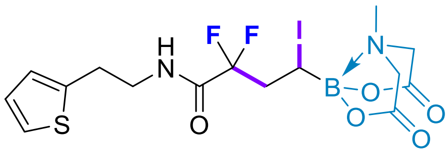
^{11}**B NMR** (160 MHz, DMSO-*d6*) δ 10.75. **HRMS (ESI)** calcd. for $C_{18}H_{20}[^{11}B]F_5IN_2O_5$ $[M+H]^+$: 577.0425, found: 577.0432.

***N*-(2-(benzo[*d*][1,3]dioxol-5-yl)ethyl)-2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (34)**



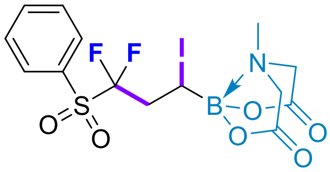
Following the general procedure, compound **34** was obtained in 52% yield (78 mg) as a light purple solid after column chromatography. ^{1}**H NMR** (500 MHz, DMSO-*d6*) δ 8.81 (t, *J* = 5.5 Hz, 1H), 6.83 – 6.76 (m, 2H), 6.65 (d, *J* = 7.9 Hz, 1H), 5.96 (s, 2H), 4.40 (d, *J* = 17.4 Hz, 1H), 4.31 (d, *J* = 17.1 Hz, 1H), 4.12 (t, *J* = 17.7 Hz, 2H), 3.40 – 3.29 (m, 3H), 3.08 (s, 3H), 2.80 (dd, *J* = 35.3, 15.8 Hz, 1H), 2.71 (t, *J* = 7.3 Hz, 2H), 2.59 – 2.43 (m, 1H). ^{13}**C NMR** (126 MHz, DMSO-*d6*) δ 168.1, 168.0, 163.1 (t, *J* = 28.4 Hz), 147.2, 145.6, 132.8, 121.5, 117.5 (t, *J* = 253.2 Hz), 109.0, 108.1, 100.7, 63.7, 63.5, 45.6, 40.6, 38.4 (t, *J* = 23.5 Hz), 34.1, 7.2 (α-C of boron). ^{19}**F NMR** (471 MHz, DMSO-*d6*) δ -104.3 (dt, *J* = 248.2, 16.2 Hz, 1F), -105.3 (m, 1F). ^{11}**B NMR** (160 MHz, DMSO-*d6*) δ 10.94. **HRMS (ESI)** calcd. for $C_{18}H_{21}[^{11}B]F_2IN_2O_7$ $[M+H]^+$: 553.0449, found: 553.0447.

2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-*N*-(2-(thiophen-2-yl)ethyl)butanamide (35)



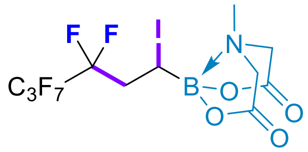
Following the general procedure, compound **35** was obtained in 64% yield (89 mg) as a colorless oil after column chromatography. ^{1}**H NMR** (500 MHz, DMSO-*d6*) δ 8.92 (t, *J* = 5.5 Hz, 1H), 7.34 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.95 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.91 – 6.88 (m, 1H), 4.40 (d, *J* = 17.4 Hz, 1H), 4.31 (d, *J* = 17.2 Hz, 1H), 4.13 (d, *J* = 17.3 Hz, 1H), 4.10 (d, *J* = 17.1 Hz, 1H), 3.42 – 3.36 (m, 3H), 3.08 (s, 3H), 3.02 (t, *J* = 7.3 Hz, 2H), 2.81 (dd, *J* = 35.1, 15.2 Hz, 1H), 2.65 – 2.51 (m, 1H). ^{13}**C NMR** (126 MHz, DMSO-*d6*) δ 168.1, 168.0, 163.3 (t, *J* = 28.6 Hz), 141.0, 127.0, 125.3, 124.2, 117.5 (t, *J* = 253.6 Hz), 63.7, 63.5, 45.6, 40.6, 38.4 (t, *J* = 23.3 Hz), 28.5. ^{19}**F NMR** (471 MHz, DMSO-*d6*) δ -104.3 (dt, *J* = 248.3, 16.0 Hz, 1F), -105.5 (m, 1F). ^{11}**B NMR** (160 MHz, DMSO-*d6*) δ 10.51. **HRMS (ESI)** calcd. for $C_{15}H_{19}[^{11}B]F_2IN_2O_5S$ $[M+H]^+$: 515.0115, found: 515.0113.

2-(3,3-difluoro-1-iodo-3-(phenylsulfonyl)propyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (36)



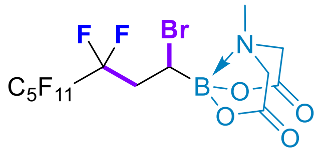
Following the general procedure, compound **36** was obtained in 57% yield (78 mg) as a white solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 8.01 (d, *J* = 7.8 Hz, 2H), 7.96 (t, *J* = 7.5 Hz, 1H), 7.80 (t, *J* = 7.8 Hz, 2H), 4.46 (d, *J* = 17.4 Hz, 1H), 4.31 (d, *J* = 17.1 Hz, 1H), 4.12 (dd, *J* = 17.3, 2.4 Hz, 2H), 3.55 (d, *J* = 10.5 Hz, 1H), 3.29 – 3.20 (m, 1H), 3.11 (s, 3H), 2.67 (dddd, *J* = 28.4, 17.0, 11.3, 6.0 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.0, 167.9, 136.4, 131.0, 130.5 (2C), 130.1 (2C), 123.7 (t, *J* = 288.5 Hz), 63.6 (2C), 45.7, 33.6 (t, *J* = 19.0 Hz), 4.3 (α-C of boron). **^{19}F NMR** (376 MHz, DMSO-*d6*) δ -102.5 (dd, *J* = 227.2, 27.6 Hz, 1F), -106.8 (dd, *J* = 224.5, 27.4 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.53. **HRMS (ESI)** calcd. for $C_{14}H_{15}[^{11}B]F_2INNaO_6S$ $[M+Na]^+$: 523.9618, found: 523.9616.

6-methyl-2-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)-1,3,6,2-dioxazaborocane-4,8-dione (37)



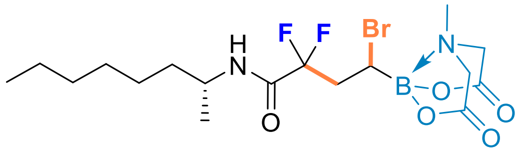
Following the general procedure, compound **37** was obtained in 81% yield (117 mg) as a brown solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 4.45 (d, *J* = 17.4 Hz, 1H), 4.31 (d, *J* = 17.1 Hz, 1H), 4.13 (d, *J* = 17.3 Hz, 2H), 3.58 (dd, *J* = 10.8, 1.3 Hz, 1H), 3.12 (s, 3H), 3.11 – 2.99 (m, 1H), 2.77 – 2.59 (m, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.0, 167.9, 121.3 – 115.2 (m, 2C), 114.3 – 109.3 (m), 109.1 – 105.1 (m), 63.6 (2C), 45.7, 35.0 (t, *J* = 20.6 Hz), 3.4 (α-C of boron). **^{19}F NMR** (376 MHz, DMSO-*d6*) δ -80.9 (s, 3F), -113.7 (d, *J* = 277.1 Hz, 1F), -115.6 (d, *J* = 258.7 Hz, 1F), -124.7 (s, 2F), -126.1 (s, 2F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.19. **HRMS (ESI)** calcd. for $C_{11}H_{10}[^{11}B]F_9INNaO_4$ $[M+Na]^+$: 551.9496, found: 551.9494.

2-(1-bromo-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (37-2)



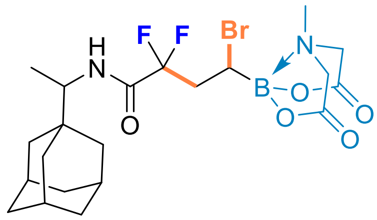
Following the general procedure, compound **37-2** was obtained in 72% yield (114 mg) as a brown solid after column chromatography. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 4.50 (d, *J* = 17.4 Hz, 1H), 4.30 (d, *J* = 17.1 Hz, 1H), 4.11 (dd, *J* = 17.2, 6.1 Hz, 2H), 3.83 (d, *J* = 10.1 Hz, 1H), 3.14 (s, 3H), 2.97 – 2.79 (m, 1H), 2.73 – 2.58 (m, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.2, 168.1, 121.0 – 104.5 (m, 6C), 63.5, 63.2, 45.9, 34.2 (t, *J* = 20.8 Hz), 30.5 (α-C of boron). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -80.4 (t, *J* = 8.9 Hz, 3F), -112.0 (dd, *J* = 237.1, 140.3 Hz, 1F), -114.8 (dd, *J* = 267.9, 21.7 Hz, 1F), -121.7 (s, 2F), -122.8 (s, 2F), -123.4 (s, 2F), -125.9 (d, *J* = 9.4 Hz, 2F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.06. **HRMS (ESI)** calcd. for $C_{14}H_{11}[^{11}B]BrF_{13}NO_6$ $[M+HCOO]^-$: 625.9661, found: 625.9666.

4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-*N*-((*R*)-octan-2-yl)butanamide (38)



Following the general procedure, compound **38** was obtained in 75% yield (96 mg) as a brown solid after column chromatography, dr = 1:1 (determined by NMR). **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 8.51 (s, 1H), 8.50 (s, 1H*), 4.47 (d, *J* = 17.4 Hz, 2H), 4.27 (d, *J* = 17.1 Hz, 2H), 4.10 (d, *J* = 17.2 Hz, 2H), 4.07 (d, *J* = 17.0 Hz, 2H), 3.86 – 3.76 (m, 2H), 3.64 – 3.61 (m, 1H), 3.60 (d, *J* = 11.4 Hz, 1H*), 3.10 (s, 6H), 2.71 (dd, *J* = 33.1, 16.4 Hz, 2H), 2.63 – 2.53 (m, 2H), 1.54 – 1.44 (m, 2H), 1.43 – 1.34 (m, 2H), 1.23 (s, 16H), 1.08 (d, *J* = 6.6 Hz, 6H), 0.85 (t, *J* = 6.8 Hz, 6H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.3 (2C), 168.2, 168.1*, 162.5 (t, *J* = 28.1 Hz), 162.4* (t, *J* = 28.1 Hz), 117.5 (t, *J* = 252.9 Hz), 117.4* (t, *J* = 250.8 Hz), 63.4 (2C), 63.2 (2C), 45.6 (2C), 45.0, 44.9*, 37.7 (t, *J* = 24.0 Hz, 2C), 35.3 (2C), 31.2 (2C), 28.5 (2C), 25.6 (2C), 22.0 (2C), 20.2, 20.1*, 13.9 (2C). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -102.5 (m, 2F), -105.2 (m, 2F*). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.39. **HRMS (ESI)** calcd. for $C_{17}H_{29}[^{11}B]BrF_2N_2O_5$ $[M+H]^+$: 469.1315, found: 469.1322.

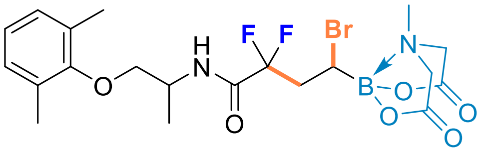
***N*-(1-((3*r*,5*r*,7*r*)-adamantan-1-yl)ethyl)-4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (39)**



Following the general procedure, compound **39** was obtained in 70% yield (99 mg) as a brown solid after column chromatography, dr = 1:1 (determined by NMR). **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 8.25 (d, *J* = 9.4 Hz, 1H), 8.21 (d, *J* = 9.3 Hz, 1H*), 4.47 (dd, *J* = 17.4, 2.7 Hz, 2H), 4.26 (dd, *J* = 17.1, 1.9 Hz, 2H), 4.13 – 4.05 (m, 4H), 3.64 (d, *J* = 11.0 Hz, 1H), 3.61 (d, *J* = 7.0 Hz, 1H*), 3.58 (d, *J* = 10.2 Hz, 2H), 3.09 (s, 3H), 3.08 (s, 3H*), 2.80 – 2.66 (m, 2H), 2.65 – 2.54 (m, 2H), 1.92 (s, 6H), 1.64 (d, *J* = 11.8 Hz, 6H), 1.57 (d, *J* = 11.5 Hz, 6H), 1.50 (d, *J* = 12.3 Hz, 6H), 1.45 (d, *J* = 12.5 Hz, 6H), 1.03 (d, *J* = 2.4 Hz, 3H), 1.01 (d, *J* = 2.4 Hz, 3H*). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.3 (2C), 168.2, 168.1*, 162.8 (t, *J* = 28.5 Hz), 162.7* (t, *J* = 28.1 Hz), 117.8 (t, *J* = 253.2 Hz), 117.4* (t, *J* = 253.2 Hz), 63.5, 63.4*, 63.2 (2C), 53.0 (2C), 45.6, 45.5*, 38.0 (6C), 37.6 (t, *J* = 24.0 Hz, 2C), 36.6 (6C), 36.0, 35.9*, 27.7 (6C), 13.5, 13.3*. **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -102.1 (m, 3F), -104.1 (ddd, *J* = 33.1, 17.5, 15.1 Hz, 1F*). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.45. **HRMS (ESI)** calcd. for $C_{21}H_{31}[^{11}B]BrF_2N_2O_5$ $[M+H]^+$: 519.1472, found: 519.1467.

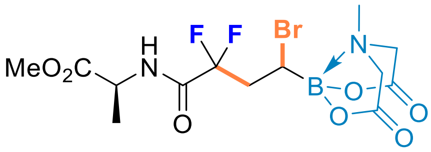
4-bromo-*N*-(1-(2,6-dimethylphenoxy)propan-2-yl)-2,2-difluoro-4-(6-methyl-4,8-

dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (40)



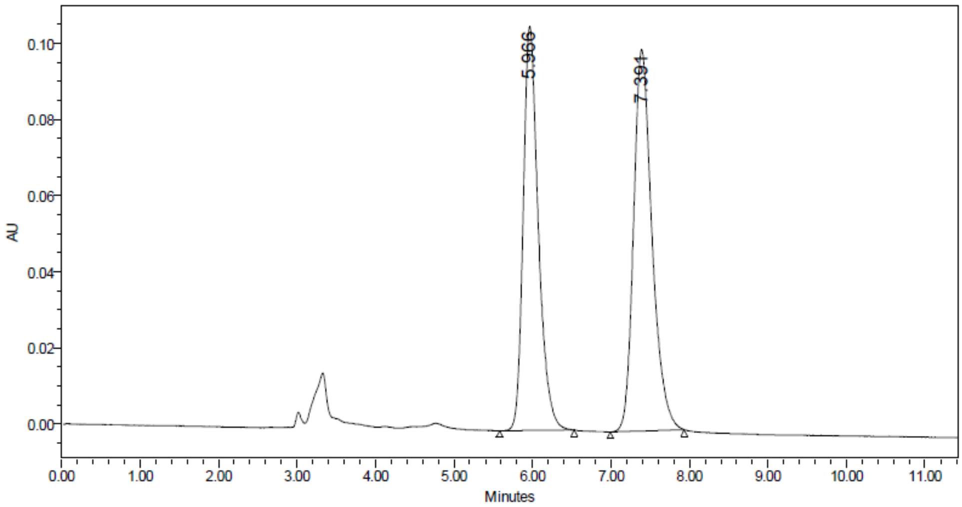
Following the general procedure, compound **40** was obtained in 54% yield (76 mg) as a purple oil after column chromatography, dr = 1:1 (determined by NMR). **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 8.78 (s, 1H), 8.77 (s, 1H*), 7.00 (d, *J* = 7.0 Hz, 4H), 6.90 (t, *J* = 7.2 Hz, 2H), 4.47 (d, *J* = 17.5 Hz, 2H), 4.27 (d, *J* = 17.0 Hz, 4H), 4.08 (t, *J* = 14.7 Hz, 4H), 3.73 (dd, *J* = 14.0, 7.4 Hz, 4H), 3.66 (d, *J* = 11.3 Hz, 2H), 3.10 (s, 3H), 3.08 (s, 3H*), 2.82 – 2.69 (m, 2H), 2.67 – 2.56 (m, 2H), 2.20 (s, 12H), 1.27 (t, *J* = 6.8 Hz, 6H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.3 (2C), 168.2 (2C), 162.9 (t, *J* = 28.3 Hz, 2C), 155.0 (2C), 130.3 (4C), 128.8 (4C), 123.8 (2C), 117.4 (t, *J* = 255.1 Hz), 117.3* (t, *J* = 253.3 Hz), 73.5, 73.4*, 63.4 (2C), 63.2 (2C), 45.7, 45.6*, 45.5 (2C), 37.7 (t, *J* = 23.3 Hz, 2C), 33.4 (α-C of boron, 2C), 16.7, 16.5*, 15.9 (4C). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -103.2 (m, 2F), -105.9 (m, 2F*). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.31. **HRMS (ESI)** calcd. for $C_{20}H_{27}[^{11}B]BrF_2N_2O_6$ $[M+H]^+$: 519.1108, found: 519.1109.

Methyl (4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoyl)-*L*-alaninate (41)



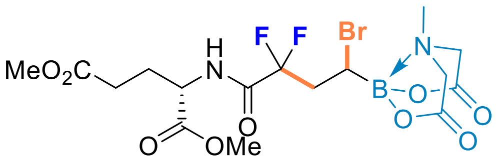
Following the general procedure, compound **41** was obtained in 66% yield (80 mg) as a red solid after column chromatography, dr = 1.16:1 (determined by chiral HPLC analysis). **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 9.18 (s, 1H), 9.17 (s, 1H*), 4.47 (d, *J* = 17.4 Hz, 2H), 4.42 – 4.32 (m, 2H), 4.27 (dd, *J* = 17.1, 1.8 Hz, 2H), 4.09 (t, *J* = 16.3 Hz, 4H), 3.66 (d, *J* = 4.1 Hz, 1H), 3.64 (s, 6H), 3.63 – 3.62 (m, 1H*), 3.10 (s, 6H), 2.74 (qd, *J* = 16.9, 8.0 Hz, 2H), 2.59 (ddd, *J* = 27.6, 9.6, 6.8 Hz, 2H), 1.36 (s, 3H), 1.35 (s, 3H*). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 172.0 (2C), 168.3 (2C), 168.2 (2C), 163.3 (t, *J* = 29.0 Hz, 2C), 117.3 (t, *J* = 253.2 Hz), 117.2* (t, *J* = 252.8 Hz), 63.4 (2C), 63.2 (2C), 52.1 (2C), 47.9 (2C), 45.7 (2C), 37.8 (t, *J* = 23.3 Hz, 2C), 33.3 (α-C of boron, 2C), 16.3, 16.2*. **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -104.3 (m, 3F), -105.3 (m, 1F*). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.51. **HRMS (ESI)** calcd. for $C_{13}H_{19}[^{11}B]BrF_2N_2O_7$ $[M+H]^+$: 443.0431, found: 443.0432.

Conditions: ChiralPak IB column; hexane/EtOH = 50:50; flow rate = 1.0 mL/min; λ= 214 nm; tR1 = 6.0 min; tR2 = 7.4 min.



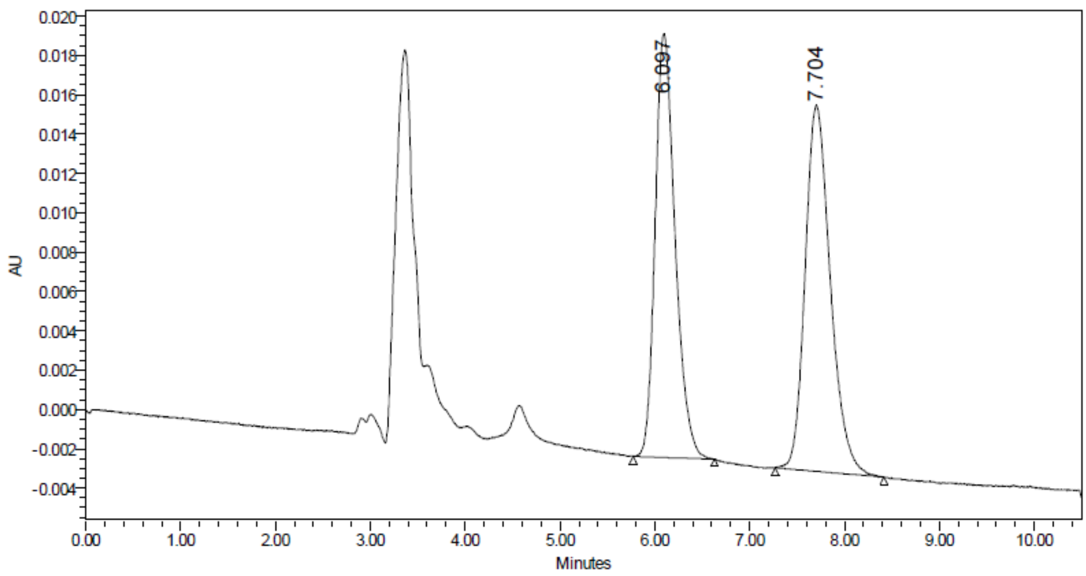
	RT	Area	% Area	Height
1	5.966	1420110	46.32	106218
2	7.391	1645894	53.68	100258

Dimethyl (4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoyl)-*L*-glutamate (42)



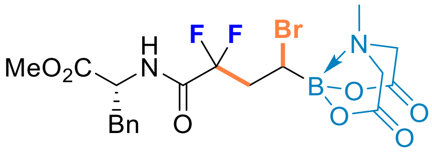
Following the general procedure, compound **42** was obtained in 71% yield (100 mg) as a yellow solid after column chromatography, dr = 1.1:1 (determined by chiral HPLC analysis). **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 9.18 (dd, *J* = 7.1, 3.3 Hz, 2H), 4.48 (d, *J* = 17.4 Hz, 2H), 4.35 (tt, *J* = 9.8, 4.8 Hz, 2H), 4.27 (d, *J* = 17.1 Hz, 2H), 4.10 (d, *J* = 17.3 Hz, 2H), 4.08 (d, *J* = 17.1 Hz, 2H), 3.65 (s, 6H), 3.63 (d, *J* = 5.0 Hz, 1H), 3.60 (s, 1H*), 3.58 (s, 6H), 3.10 (s, 6H), 2.81 – 2.67 (m, 2H), 2.65 – 2.53 (m, 2H), 2.41 (t, *J* = 7.2 Hz, 4H), 2.15 – 2.06 (m, 2H), 2.03 – 1.91 (m, 2H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 172.6 (2C), 171.1 (2C), 168.3 (2C), 168.2 (2C), 163.8 (t, *J* = 30.2 Hz), 163.7* (t, *J* = 29.1 Hz), 117.3 (t, *J* = 253.2 Hz, 2C), 63.4 (2C), 63.2 (2C), 52.2 (2C), 51.5 (2C), 51.4 (2C), 45.6 (2C), 37.7 (t, *J* = 23.1 Hz, 2C), 33.3 (α-C of boron, 2C), 29.7 (2C), 25.1 (2C). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -103.7 (m, 3F), -105.3 (m, 1F*). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.44. **HRMS (ESI)** calcd. for $C_{16}H_{21}[^{11}B]BrF_2N_2O_9$ $[M-H]^-$: 513.0497, found: 513.0505.

Conditions: ChiralPak IB column; hexane/EtOH = 40:60; flow rate = 1.0 mL/min; λ= 214 nm; tR1 = 6.1 min; tR2 = 7.7 min.



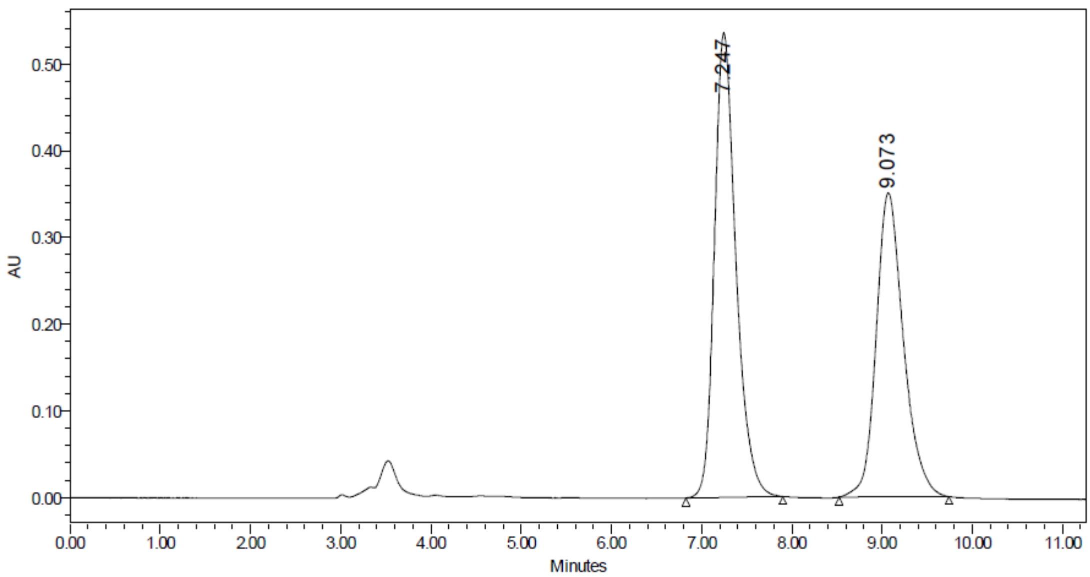
	RT	Area	% Area	Height
1	6.097	315277	47.90	21545
2	7.704	342964	52.10	18609

Methyl (4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoyl)-*D*-phenylalaninate (43)



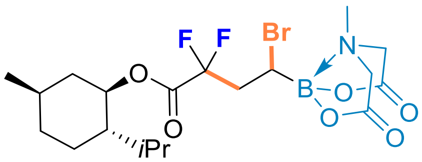
Following the general procedure, compound **43** was obtained in 71% yield (101 mg) as a yellow solid after column chromatography, dr = 1.2:1 (determined by chiral HPLC analysis). **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 9.21 (d, *J* = 3.5 Hz, 1H), 9.19 (d, *J* = 3.5 Hz, 1H*), 7.30 – 7.26 (m, 4H), 7.24 (d, *J* = 6.9 Hz, 4H), 7.22 – 7.17 (m, 2H), 4.61 – 4.53 (m, 2H), 4.47 (d, *J* = 17.4 Hz, 2H), 4.26 (d, *J* = 17.1 Hz, 2H), 4.09 (dd, *J* = 25.2, 9.7 Hz, 4H), 3.644 (s, 3H), 3.640 (s, 3H*), 3.58 (d, *J* = 10.2 Hz, 1H), 3.51 (t, *J* = 9.5 Hz, 1H*), 3.16 (ddd, *J* = 13.6, 4.9, 1.6 Hz, 2H), 3.08 (s, 3H), 3.06 (s, 3H*), 3.05 – 3.00 (m, 2H*), 2.69 – 2.53 (m, 2H), 2.48 – 2.33 (m, 2H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 171.0 (2C), 168.3 (2C), 168.1 (2C), 163.5 (t, *J* = 29.1 Hz, 2C), 137.2 (2C), 129.1 (4C), 128.3 (2C), 128.2 (2C), 126.6 (2C), 117.2 (t, *J* = 253.4 Hz, 2C), 63.4 (2C), 63.2 (2C), 53.7 (2C), 52.2 (2C), 45.6 (2C), 37.5 (t, *J* = 23.1 Hz, 2C), 35.7 (2C), 33.0 (α-C of boron, 2C). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -104.5 (ddd, *J* = 249.4, 21.3, 10.9 Hz, 1F), -105.3 (t, *J* = 16.5 Hz, 2F*), -105.7 (ddd, *J* = 249.4, 19.4, 14.5 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.39. **HRMS (ESI)** calcd. for $C_{19}H_{21}[^{11}B]BrF_2N_2O_7$ $[M-H]^-$: 517.0599, found: 517.0608.
Conditions: ChiralPak IB column; hexane/EtOH = 50:50; flow rate = 1.0 mL/min; λ=

214 nm; tR1 = 7.2 min; tR2 = 9.1 min.



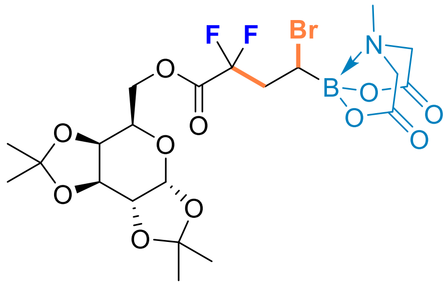
	RT	Area	% Area	Height
1	7.247	8902972	54.68	535024
2	9.073	7379435	45.32	350319

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoate (44)



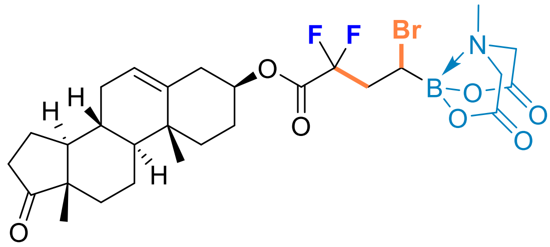
Following the general procedure, compound **44** was obtained in 74% yield (100 mg) as a light brown solid after column chromatography, dr = 1:1 (determined by NMR). ^{1}**H NMR** (500 MHz, DMSO-*d6*) δ 4.81 – 4.76 (m, 1H), 4.74 (dd, *J* = 11.0, 4.3 Hz, 1H*), 4.48 (d, *J* = 17.4 Hz, 2H), 4.27 (d, *J* = 17.1 Hz, 2H), 4.13 – 4.05 (m, 4H), 3.68 – 3.61 (m, 2H), 3.10 (s, 6H), 2.76 (dt, *J* = 17.1, 11.1 Hz, 2H), 2.71 – 2.58 (m, 2H), 2.01 (dd, *J* = 8.6, 5.4 Hz, 2H), 1.85 (ddtd, *J* = 20.8, 13.7, 6.8, 2.5 Hz, 2H), 1.65 (d, *J* = 10.5 Hz, 4H), 1.55 – 1.45 (m, 4H), 1.14 – 1.02 (m, 4H), 0.89 (d, *J* = 2.1 Hz, 6H), 0.88 (d, *J* = 2.5 Hz, 6H*), 0.86 (d, *J* = 7.7 Hz, 2H), 0.74 (s, 3H), 0.72 (s, 3H*). ^{13}**C NMR** (126 MHz, DMSO-*d6*) δ 168.2 (2C), 168.1 (2C), 162.9 (t, *J* = 32.2 Hz), 162.8* (t, *J* = 32.4 Hz), 115.9 (t, *J* = 250.9 Hz, 2C), 77.2 (2C), 63.4 (2C), 63.2 (2C), 46.2 (2C), 45.7 (2C), 39.7, 39.5*, 37.8 (t, *J* = 23.7 Hz, 2C), 33.4 (2C), 30.7 (2C), 25.7 (2C), 22.9, 22.8*, 21.7 (2C), 20.4 (2C), 16.2, 16.1*. ^{19}**F NMR** (471 MHz, DMSO-*d6*) δ -100.6 (ddt, *J* = 257.7, 28.8, 14.0 Hz, 2F), -106.3 (ddt, *J* = 62.2, 33.4, 16.5 Hz, 2F*). ^{11}**B NMR** (160 MHz, DMSO-*d6*) δ 10.32. **HRMS (ESI)** calcd. for $C_{19}H_{29}[^{11}B]BrF_2NNaO_6$ $[M+Na]^+$: 518.1132, found: 518.1145.

((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl 4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoate (45)



Following the general procedure, compound **45** was obtained in 78% yield (128 mg) as a brown solid after column chromatography, dr = 1:1 (determined by NMR). **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 5.47 (d, *J* = 3.1 Hz, 1H), 5.46 (d, *J* = 3.0 Hz, 1H*), 4.64 (d, *J* = 2.4 Hz, 1H), 4.63 (d, *J* = 2.4 Hz, 1H*), 4.47 (dd, *J* = 17.4, 0.9 Hz, 2H), 4.43 – 4.37 (m, 4H), 4.33 – 4.24 (m, 6H), 4.09 (dd, *J* = 17.2, 10.8 Hz, 4H), 4.02 (dd, *J* = 3.5, 1.6 Hz, 1H), 4.00 (dd, *J* = 3.5, 1.7 Hz, 1H*), 3.68 (d, *J* = 1.7 Hz, 1H), 3.66 (d, *J* = 3.0 Hz, 1H*), 3.10 (s, 6H), 2.85 – 2.72 (m, 2H), 2.69 – 2.54 (m, 2H), 1.43 (s, 3H), 1.42 (s, 3H*), 1.37 (s, 6H), 1.295 (s, 3H), 1.291 (s, 3H*), 1.27 (s, 6H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.2 (2C), 168.1 (2C), 163.2 (t, *J* = 32.8 Hz), 163.1* (t, *J* = 32.6 Hz), 115.7 (t, *J* = 250.7 Hz, 2C), 108.8 (2C), 108.2, 108.1*, 95.5 (2C), 70.2, 70.1*, 70.0 (2C), 69.7 (2C), 65.7, 65.6*, 65.4, 65.2*, 63.4 (2C), 63.2 (2C), 45.7 (2C), 38.1 (t, *J* = 24.1 Hz, 2C), 33.0 (α-C of boron, 2C), 25.9 (2C), 25.7 (2C), 24.8 (2C), 24.3 (2C). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -102.6 (m, 2F), -106.0 (ddt, *J* = 256.7, 113.4, 17.2 Hz, 2F*). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.12. **HRMS (ESI)** calcd. for $C_{21}H_{29}[^{11}B]BrF_2NNaO_{11}$ $[M+Na]^+$: 622.0877, found: 622.0890.

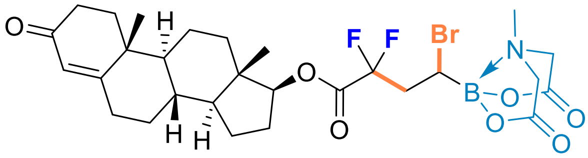
(3*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-10,13-dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoate (46)



Following the general procedure, compound **46** was obtained in 84% yield (144 mg) as a yellow solid after column chromatography, dr = 1:1 (determined by NMR). **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 5.44 (s, 1H), 5.43 (s, 1H*), 4.67 (ddd, *J* = 16.1, 10.2, 4.2 Hz, 2H), 4.47 (d, *J* = 17.4 Hz, 2H), 4.28 (d, *J* = 17.1 Hz, 2H), 4.09 (t, *J* = 17.5 Hz, 4H), 3.65 (d, *J* = 11.1 Hz, 2H), 3.10 (s, 6H), 2.78 (q, *J* = 15.1 Hz, 2H), 2.70 – 2.57 (m, 2H), 2.44 – 2.36 (m, 6H), 2.11 – 2.04 (m, 2H), 2.04 – 1.97 (m, 2H), 1.87 (ddd, *J* = 18.2, 12.1, 7.7 Hz, 6H), 1.69 (ddd, *J* = 23.0, 10.8, 3.5 Hz, 6H), 1.60 (dd, *J* = 12.5, 8.4 Hz, 4H), 1.54 – 1.47 (m, 2H), 1.42 (ddd, *J* = 17.3, 13.5, 4.9 Hz, 2H), 1.32 – 1.25 (m, 2H), 1.19 (td, *J* =

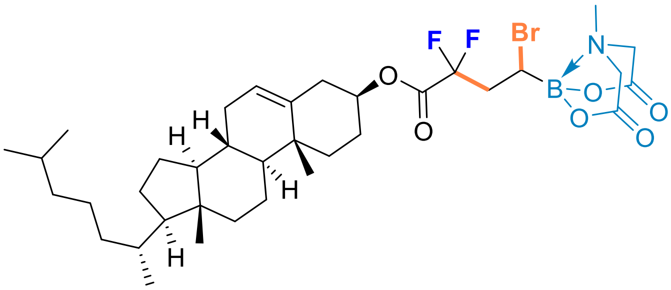
13.0, 4.0 Hz, 2H), 1.16 – 1.08 (m, 2H), 1.03 (s, 6H), 1.01 – 0.96 (m, 2H), 0.81 (s, 6H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 219.6 (2C), 168.2 (2C), 168.1 (2C), 162.6 (t, J = 32.3 Hz, 2C), 139.0 (2C), 122.4 (2C), 115.8 (t, J = 250.0 Hz, 2C), 76.8 (2C), 63.4 (2C), 63.2 (2C), 50.8 (2C), 49.5 (2C), 46.8 (4C), 45.8 (2C), 38.1 (t, J = 23.0 Hz, 2C), 37.0 (2C), 36.2 (2C), 35.3 (2C), 33.3 (α-C of boron, 2C), 31.1 (2C), 30.9 (2C), 30.2 (2C), 26.9, 26.8*, 21.4 (2C), 19.9 (2C), 18.9 (2C), 13.2 (2C). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -101.3 (dt, J = 257.4, 13.3 Hz, 2F), -106.4 (ddt, J = 257.0, 50.0, 17.2 Hz, 2F*). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.31. **HRMS (ESI)** calcd. for $C_{28}H_{37}[^{11}B]BrClF_2NO_7$ $[M+Cl]^-$: 662.1509, found: 662.1504.

(8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl 4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoate (47)



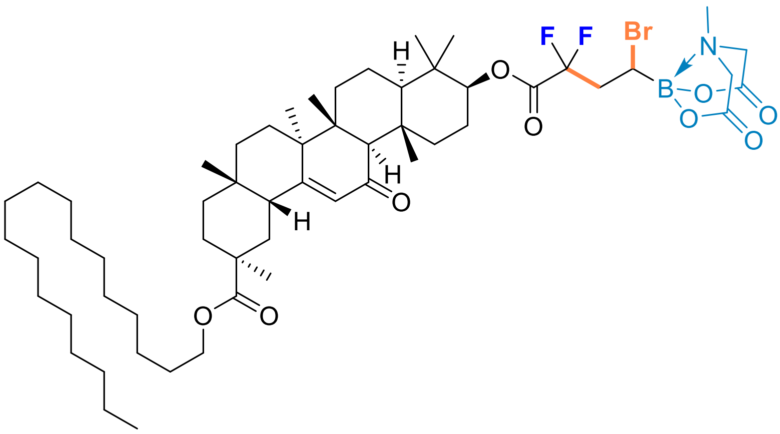
Following the general procedure, compound **47** was obtained in 83% yield (142 mg) as a yellow solid after column chromatography, dr = 1:1 (determined by NMR). **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 5.63 (s, 2H), 4.70 (dd, J = 18.0, 9.2 Hz, 2H), 4.47 (d, J = 17.4 Hz, 2H), 4.28 (d, J = 17.1 Hz, 2H), 4.09 (t, J = 16.5 Hz, 4H), 3.67 – 3.59 (m, 2H), 3.10 (s, 6H), 2.77 (q, J = 15.3 Hz, 2H), 2.70 – 2.58 (m, 2H), 2.45 – 2.34 (m, 4H), 2.25 (d, J = 14.1 Hz, 2H), 2.15 (d, J = 16.2 Hz, 4H), 1.96 (d, J = 12.9 Hz, 2H), 1.84 – 1.68 (m, 4H), 1.59 (dd, J = 22.3, 9.1 Hz, 8H), 1.53 (d, J = 11.6 Hz, 2H), 1.43 – 1.30 (m, 4H), 1.26 – 1.18 (m, 2H), 1.15 (s, 6H), 1.10 (d, J = 11.4 Hz, 2H), 1.01 – 0.88 (m, 4H), 0.85 (s, 3H), 0.84 (s, 3H*). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 198.0 (2C), 170.7 (2C), 168.2 (2C), 168.1 (2C), 163.1 (t, J = 32.3 Hz, 2C), 123.2 (2C), 115.8 (t, J = 250.0 Hz, 2C), 84.9 (2C), 63.4 (2C), 63.2 (2C), 52.9 (2C), 49.2 (2C), 45.7 (2C), 42.5, 42.4*, 38.2 (2C), 38.1 (t, J = 23.9 Hz, 2C), 36.0 (2C), 35.1 (2C), 34.6 (2C), 33.6 (2C), 31.8 (2C), 31.1 (2C), 26.7 (2C), 23.0 (2C), 20.0 (2C), 16.9 (2C), 11.8, 11.7*. **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -100.4 (m, 2F), -106.4 (ddt, J = 147.0, 34.2, 16.9 Hz, 2F*). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.16. **HRMS (ESI)** calcd. for $C_{28}H_{37}[^{11}B]BrClF_2NO_7$ $[M+H]^+$: 628.1887, found: 628.1890.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoate (48)



Following the general procedure, compound **48** was obtained in 86% yield (170 mg) as a yellow solid after column chromatography, dr = 1:1 (determined by NMR). **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 5.37 (s, 2H), 4.64 (s, 2H), 4.46 (d, J = 17.5 Hz, 2H), 4.27 (d, J = 17.1 Hz, 2H), 4.07 (dd, J = 25.1, 17.2 Hz, 4H), 3.63 (d, J = 11.4 Hz, 2H), 3.09 (s, 6H), 2.88 – 2.70 (m, 2H), 2.70 – 2.55 (m, 2H), 2.37 (s, 4H), 2.06 – 1.74 (m, 12H), 1.56 – 1.44 (m, 9H), 1.42 – 1.29 (m, 9H), 1.08 (s, 16H), 0.98 (s, 12H), 0.88 (d, J = 2.6 Hz, 6H), 0.83 (d, J = 5.8 Hz, 12H), 0.64 (s, 6H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.2 (2C), 168.1 (2C), 162.5 (t, J = 32.2 Hz, 2C), 138.8 (2C), 122.7 (2C), 115.7 (t, J = 250.7 Hz, 2C), 76.7 (2C), 63.3 (2C), 63.1 (2C), 56.1 (2C), 55.6 (2C), 49.4 (2C), 45.7 (2C), 41.8 (2C), 39.2 (2C), 39.0 (2C), 38.1 (t, J = 22.8 Hz, 2C), 37.0 (2C), 36.3 (2C), 36.0 (2C), 35.7 (2C), 35.3 (2C), 31.3 (2C), 27.8 (2C), 27.4 (4C), 26.8 (2C), 23.8 (2C), 23.3 (2C), 22.6 (2C), 22.3 (2C), 20.5 (2C), 18.9 (2C), 18.5 (2C), 11.6 (2C). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -101.2 (d, J = 256.6 Hz, 2F), -106.7 (dd, J = 253.0, 31.5 Hz, 2F*). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.17. **HRMS (ESI)** calcd. for $C_{36}H_{55}[^{11}B]BrClF_2NO_6$ $[M+Cl]^-$: 760.2968, found: 760.2946.

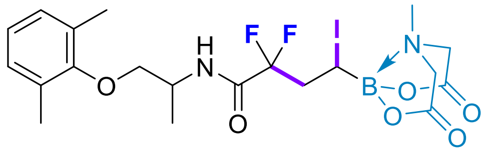
Octadecyl (2*S*,4a*S*,6a*S*,6b*R*,8a*R*,10*S*,12a*S*,12b*R*,14b*R*)-10-((4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoyl)oxy)-2,4a,6a,6b,9,9,12a-heptamethyl-13-oxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydropicene-2-carboxylate (49)



Following the general procedure, compound **49** was obtained in 85% yield (247 mg) as a brown solid after column chromatography, dr = 1:1 (determined by NMR). **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 5.43 (s, 2H), 4.58 (s, 2H), 4.46 (d, J = 17.4 Hz, 2H), 4.27 (d,

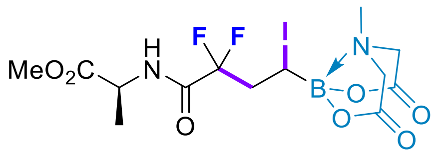
J = 16.9 Hz, 2H), 4.07 (dd, J = 29.0, 17.3 Hz, 4H), 3.98 (s, 4H), 3.63 (t, J = 10.6 Hz, 2H), 3.09 (s, 6H), 2.83 – 2.69 (m, 2H), 2.68 – 2.57 (m, 2H), 2.12 – 1.92 (m, 4H), 1.68 (dd, J = 95.4, 52.2 Hz, 20H), 1.39 – 0.96 (m, 98H), 0.96 – 0.76 (m, 26H), 0.72 (s, 6H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 198.1 (2C), 175.2 (2C), 168.6 (2C), 168.1 (2C), 168.0 (2C), 162.9 (t, J = 31.9 Hz, 2C), 127.5 (2C), 115.8 (t, J = 251.7 Hz, 2C), 83.6 (2C), 63.5 (2C), 63.3 (2C), 63.1 (2C), 60.7 (2C), 53.5 (2C), 47.7 (2C), 45.6 (2C), 44.7 (2C), 43.4 (2C), 42.8 (2C), 37.9 (t, J = 21.1 Hz, 2C), 37.8, 37.7*, 36.4 (2C), 31.5 (2C), 31.3 (2C), 29.3 (36C), 29.2 (2C), 29.0 (2C), 28.8 (2C), 28.3 (2C), 28.2 (2C), 27.6 (2C), 27.4 (2C), 25.6 (2C), 23.0 (2C), 22.2 (2C), 18.2 (2C), 16.3 (2C), 16.0 (2C), 13.7 (2C). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -100.8 (t, J = 281.2 Hz, 2F), -106.3 (m, 2F*). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 9.53. **HRMS (ESI)** calcd. for $C_{57}H_{90}[^{11}B]BrF_2NO_9$ [M-H]$^-$: 1060.5866, found: 1060.5864.

N-(1-(2,6-dimethylphenoxy)propan-2-yl)-2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (50)



Following the general procedure, compound **50** was obtained in 67% yield (104 mg) as a purple oil after column chromatography, dr = 1:1 (determined by NMR). **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 8.78 (dd, J = 8.0, 4.3 Hz, 2H), 7.00 (d, J = 7.5 Hz, 4H), 6.93 – 6.84 (m, 2H), 4.41 (d, J = 17.4 Hz, 2H), 4.30 (d, J = 17.1 Hz, 2H), 4.27 – 4.19 (m, 2H), 4.13 (dd, J = 13.3, 4.1 Hz, 2H), 4.11 – 4.07 (m, 2H), 3.72 (qd, J = 9.1, 3.8 Hz, 4H), 3.43 (d, J = 11.2 Hz, 2H), 3.09 (s, 3H), 3.07 (s, 3H*), 2.96 – 2.77 (m, 2H), 2.66 – 2.53 (m, 2H), 2.21 (s, 12H), 1.29 (d, J = 2.6 Hz, 3H), 1.27 (d, J = 2.7 Hz, 3H*). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.1 (2C), 168.0 (2C), 162.9 (t, J = 28.5 Hz, 2C), 155.0 (2C), 130.3 (4C), 128.8 (4C), 123.8 (2C), 117.5 (t, J = 253.9 Hz), 117.4* (t, J = 253.6 Hz), 73.5, 73.4*, 63.7, 63.6*, 63.5 (2C), 45.6 (2C), 45.5 (2C), 38.5 (t, J = 23.4 Hz), 38.4* (t, J = 23.5 Hz), 16.7, 16.6*, 15.9 (4C), 7.1 (α-C of boron, 2C). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -104.2 (m, 2F), -105.6 (m, 2F*). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.79. **HRMS (ESI)** calcd. for $C_{20}H_{27}[^{11}B]F_2IN_2O_6$ [M+H]$^+$: 567.0969, found: 567.0967.

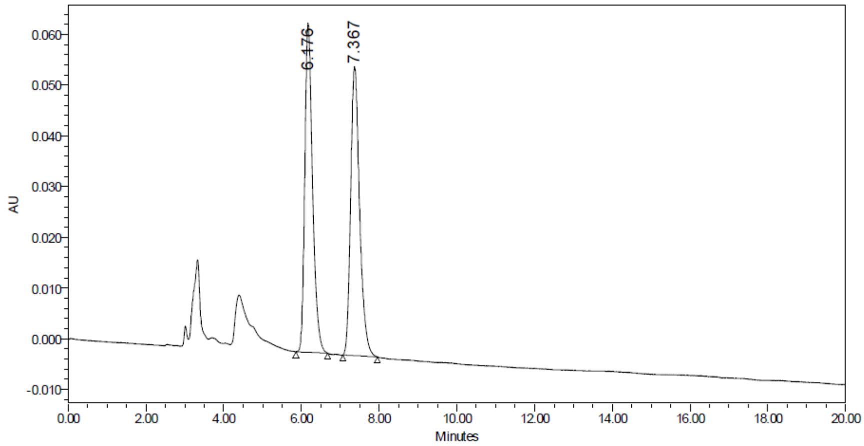
Methyl (2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoyl)-*L*-alaninate (51)



Following the general procedure, compound **51** was obtained in 75% yield (100 mg) as a brown solid after column chromatography, dr = 1:1 (determined by chiral HPLC analysis). **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 9.20 (s, 1H), 9.18 (s, 1H*), 4.43 (d, J = 17.4 Hz, 2H), 4.40 – 4.35 (m, 2H), 4.32 (dd, J = 17.1, 4.2 Hz, 2H), 4.17 – 4.09 (m, 4H), 3.65 (s, 6H), 3.42 (d, J = 10.9 Hz, 2H), 3.10 (s, 6H), 2.96 – 2.77 (m, 2H), 2.67 – 2.53

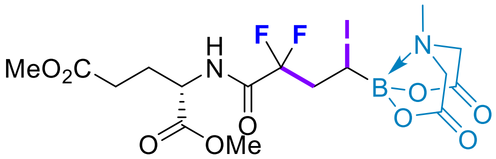
(m, 2H), 1.38 (d, J = 2.9 Hz, 3H), 1.37 (d, J = 2.9 Hz, 3H*). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 172.1, 172.0*, 168.1 (2C), 168.0 (2C), 163.3 (t, J = 29.2 Hz, 2C), 117.4 (t, J = 253.1 Hz), 117.3* (t, J = 253.1 Hz), 63.7 (2C), 63.5 (2C), 52.1 (2C), 47.9 (2C), 45.6 (2C), 38.5 (t, J = 23.1 Hz, 2C), 16.3, 16.2*, 7.0 (α-C of boron, 2C). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -104.3 (ddd, J = 248.8, 21.0, 11.2 Hz, 1F), -105.0 (t, J = 16.2 Hz, 2F*), -105.6 (ddd, J = 248.8, 18.9, 14.8 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.51. **HRMS (ESI)** calcd. for $C_{13}H_{19}[^{11}B]F_2IN_2O_7$ $[M+H]^+$: 491.0293, found: 491.0294.

Conditions: ChiralPak IB column; hexane/EtOH = 50:50; flow rate = 1.0 mL/min; λ= 214 nm; tR1 = 6.2 min; tR2 = 7.4 min.



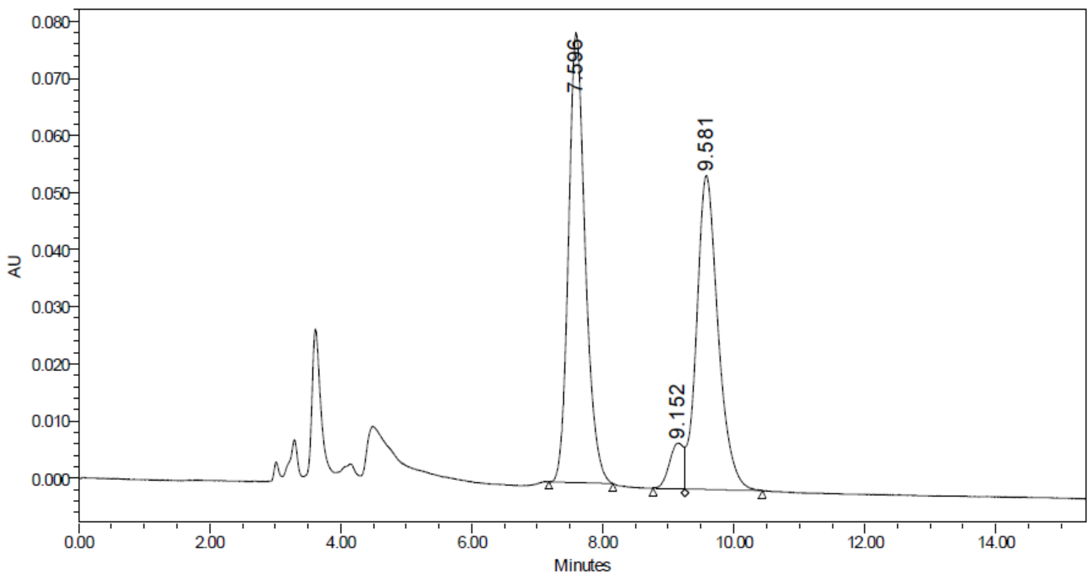
	RT	Area	% Area	Height
1	6.176	899760	49.29	64809
2	7.367	925704	50.71	56963

Dimethyl (2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoyl)-*L*-glutamate (52)



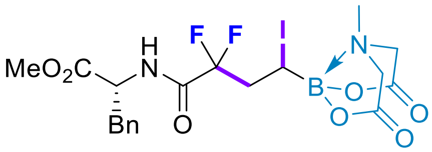
Following the general procedure, compound **52** was obtained in 76% yield (117 mg) as a brown solid after column chromatography, dr = 1:1 (determined by chiral HPLC analysis). **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 9.19 (s, 1H), 9.17 (s, 1H*), 4.42 (d, J = 17.4 Hz, 2H), 4.37 – 4.27 (m, 4H), 4.12 (dd, J = 17.2, 9.3 Hz, 4H), 3.65 (s, 6H), 3.59 (s, 6H), 3.39 (t, J = 12.2 Hz, 2H), 3.09 (s, 6H), 2.97 – 2.76 (m, 2H), 2.66 – 2.52 (m, 2H), 2.41 (t, J = 7.3 Hz, 4H), 2.10 (td, J = 13.0, 7.0 Hz, 2H), 2.04 – 1.92 (m, 2H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 172.6 (2C), 171.1 (2C), 168.1 (2C), 168.0 (2C), 163.8 (t, J = 29.4 Hz), 163.7* (t, J = 29.3 Hz), 117.4 (t, J = 253.7 Hz, 2C), 63.7 (2C), 63.5 (2C), 52.2 (2C), 51.6, 51.5*, 51.4 (2C), 45.6 (2C), 38.4 (t, J = 23.3 Hz, 2C), 29.8 (2C), 25.2 (2C), 7.1 (α-C of boron, 2C). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -103.5 (ddd, J = 249.5, 20.3, 10.8 Hz, 1F), -104.7 (t, J = 16.2 Hz, 2F*), -105.1 (m, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.69. **HRMS (ESI)** calcd. for $C_{16}H_{23}[^{11}B]F_2IN_2O_9$ $[M+H]^+$:

563.0504, found: 563.0510.
Conditions: ChiralPak IB column; hexane/EtOH = 50:50; flow rate = 1.0 mL/min; λ= 214 nm; tR1 = 7.6 min; tR2 = 9.6 min.



	RT	Area	% Area	Height
1	7.596	1397095	50.45	78701
2	9.152	119663	4.32	8030
3	9.581	1252260	45.22	54962

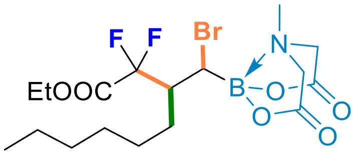
Methyl (2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoyl)-*D*-phenylalaninate (53)



Following the general procedure, compound **53** was obtained in 69% yield (107 mg) as a red solid after column chromatography, dr = 1:1 (determined by NMR). **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 9.20 (t, *J* = 7.1 Hz, 2H), 7.31 – 7.26 (m, 4H), 7.24 (d, *J* = 7.0 Hz, 4H), 7.19 (td, *J* = 7.0, 2.7 Hz, 2H), 4.61 – 4.52 (m, 2H), 4.41 (dd, *J* = 17.4, 2.4 Hz, 2H), 4.30 (dd, *J* = 17.1, 3.9 Hz, 2H), 4.16 – 4.06 (m, 4H), 3.65 (s, 3H), 3.64 (s, 3H*), 3.36 (d, *J* = 4.7 Hz, 1H), 3.25 (d, *J* = 10.5 Hz, 1H*), 3.19 – 3.12 (m, 2H), 3.10 – 3.03 (m, 5H), 3.01 (s, 3H*), 2.80 – 2.62 (m, 2H), 2.39 (ddd, *J* = 18.6, 16.1, 9.3 Hz, 2H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 171.5, 171.4*, 168.6, 168.53*, 168.5 (2C), 164.0 (t, *J* = 29.1 Hz), 163.9* (t, *J* = 29.1 Hz), 137.7, 137.6*, 129.6 (4C), 128.8 (2C), 128.7 (2C), 127.1, 127.0*, 117.7 (t, *J* = 253.0 Hz, 2C), 64.2, 64.1*, 64.0, 63.9*, 54.2 (2C), 52.7, 52.6*, 46.0 (2C), 38.8 (t, *J* = 22.9 Hz, 2C), 36.2 (2C), 7.2 (α-C of boron, 2C). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -104.1 (ddd, *J* = 248.2, 21.9, 8.7 Hz, 1F), -105.3 (ddd, *J* =

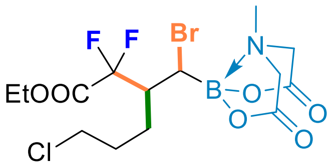
248.2, 20.5, 11.2 Hz, 1F*), -106.1 (m, 1F*), -106.7 (ddd, J = 248.1, 20.9, 14.0 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.72. **HRMS (ESI)** calcd. for $C_{19}H_{23}[^{11}B]F_2IN_2O_7$ $[M+H]^+$: 567.0606, found: 567.0607.

Ethyl (3*S*)-3-(bromo(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-2,2-difluorononanoate (54)



Following the general procedure, compound **54** was obtained in 25% yield (32 mg) as a brown oil after column chromatography and preparative HPLC (TFA), dr = 4:1 (determined by NMR). **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 4.43 (d, J = 10.8 Hz, 1H), 4.36 (dd, J = 17.5, 7.6 Hz, 1H), 4.28 – 4.20 (m, 3H), 4.11 (dd, J = 17.4, 7.4 Hz, 1H), 3.97 (dd, J = 25.2, 17.4 Hz, 1H), 3.03 (d, J = 6.3 Hz, 3H), 3.00 – 2.81 (m, 1H), 1.36 – 1.20 (m, 13H), 0.87 (dd, J = 9.2, 4.4 Hz, 3H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.6, 168.5*, 168.2*, 167.7, 164.2 (t, J = 33.1 Hz), 164.1* (t, J = 32.7 Hz), 119.0 (dd, J = 258.3, 247.6 Hz), 63.1, 63.0, 62.9*, 62.8*, 62.5, 62.3*, 55.9 (TFA-N-CH_3), 52.9* (TFA-N-CH_3), 47.2*, 46.7*, 39.5 (t, J = 20.9 Hz), 37.0, 35.7*, 31.10, 31.07*, 28.6, 28.1*, 27.8, 27.7*, 22.0, 13.9, 13.61, 13.59*. **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -96.1 (dd, J = 272.9, 19.2 Hz, 1F), -96.8 (dd, J = 270.7, 20.4 Hz, 1F*), -101.6 (dd, J = 270.6, 15.9 Hz, 1F*), -102.0 (dd, J = 272.9, 18.9 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.22. **HRMS (ESI)** calcd. for $C_{17}H_{28}[^{11}B]BrF_2NO_6$ $[M+H]^+$: 470.1156, found: 470.1157.

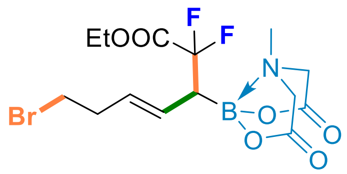
Ethyl (3*S*)-3-(bromo(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-6-chloro-2,2-difluorohexanoate (55)



Following the general procedure, compound **55** was obtained in 30% yield (37 mg) as a yellow oil after column chromatography and preparative HPLC (TFA), dr = 2.5:2:1 (determined by NMR). **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 4.50 – 4.40 (m, 1H), 4.39 – 4.34 (m, 1H), 4.34 – 4.20 (m, 3H), 4.14 – 4.06 (m, 1H), 4.05 – 3.92 (m, 1H), 3.74 – 3.58 (m, 2H), 3.10 – 3.02 (m, 3H), 3.02 – 2.82 (m, 1H), 2.22 – 1.87 (m, 2H), 1.86 – 1.70 (m, 2H), 1.31 – 1.25 (m, 3H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.6, 168.5, 168.3*, 168.1*, 168.0*, 167.7*, 164.0 (t, J = 32.7 Hz), 163.3 (t, J = 32.6 Hz)*, 118.2 (ddd, J = 417.4, 251.4, 243.3 Hz), 63.4, 63.2, 63.1*, 63.0*, 62.9*, 62.7*, 62.3, 61.5*, 54.6 (TFA-N-CH_3), 51.7* (TFA-N-CH_3), 47.2*, 46.6*, 45.7*, 45.1, 44.6*, 44.5*, 43.5 (t, J = 20.8 Hz), 34.8, 33.5*, 32.0*, 31.5, 30.8*, 23.6*, 13.73, 13.67*, 13.6*. **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -96.8 (dd, J = 272.9, 21.5 Hz, 1F), -97.1 (dd, J = 271.3, 21.1 Hz, 1F*), -101.2 (dd, J = 271.3, 15.1 Hz, 1F*), -101.7 (dd, J = 272.9, 16.5 Hz, 1F), -105.1 (dd, J = 253.4, 10.7 Hz, 1F*), -108.4 (dd, J = 253.4, 18.7 Hz, 1F*). **^{11}B NMR**

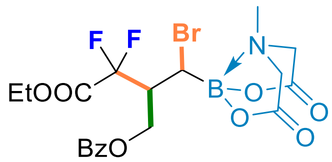
(160 MHz, DMSO-*d6*) δ 10.24. **HRMS (ESI)** calcd. for $C_{14}H_{21}[^{11}B]BrClF_2NO_6$ $[M+H]^+$: 462.0296, found: 462.0299.

Ethyl (*S*,*E*)-7-bromo-2,2-difluoro-3-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hept-4-enoate (56a)



Following the general procedure, compound **56a** was obtained in 35% yield (40 mg) as a yellow oil after column chromatography and preparative HPLC (TFA). **56b** was detected by ^{19}F NMR. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 5.66 – 5.60 (m, 1H), 5.43 (dd, *J* = 15.5, 10.4 Hz, 1H), 4.27 (d, *J* = 7.8 Hz, 1H), 4.26 – 4.16 (m, 3H), 4.05 (d, *J* = 17.0 Hz, 1H), 3.84 (d, *J* = 17.2 Hz, 1H), 3.57 – 3.48 (m, 2H), 2.93 (s, 3H), 2.77 (ddd, *J* = 27.6, 13.2, 10.4 Hz, 1H), 2.64 – 2.52 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.6, 167.9, 163.9 (t, *J* = 33.2 Hz), 133.7, 125.0, 117.6 (dd, *J* = 253.8, 248.5 Hz), 62.4, 61.9, 61.5, 46.0, 36.8 (α-C of boron), 35.5, 34.0, 13.7. **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -97.0 (dd, *J* = 254.3, 13.2 Hz, 1F), -102.1 (dd, *J* = 249.9, 4.8 Hz, 1F of **56b**), -105.7 (dd, *J* = 254.3, 27.7 Hz, 1F), -114.0 (dd, *J* = 249.9, 23.3 Hz, 1F of **56b**). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.03. **HRMS (ESI)** calcd. for $C_{14}H_{20}[^{11}B]BrF_2NO_6$ $[M+H]^+$: 426.0530, found: 426.0533.

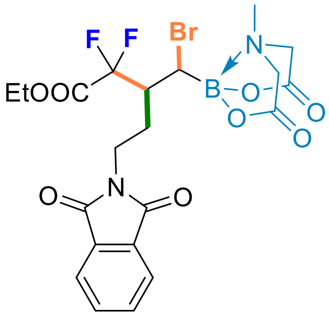
(2*S*)-2-(bromo(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-4-ethoxy-3,3-difluoro-4-oxobutyl benzoate (57)



Following the general procedure, compound **57** was obtained in 25% yield (35 mg) as a yellow oil after column chromatography and preparative HPLC, dr = 5:1 (determined by NMR). **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 8.03 – 7.88 (m, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.55 (q, *J* = 7.7 Hz, 2H), 4.68 – 4.63 (m, 1H), 4.60 – 4.41 (m, 2H), 4.31 – 4.25 (m, 1H), 4.25 – 3.95 (m, 5H), 3.42 – 3.34 (m, 1H), 3.15 (s, 3H), 3.11 (s, 3H*), 3.07 (d, *J* = 4.6 Hz, 1H*), 1.27 (t, *J* = 7.1 Hz, 3H*), 1.10 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.7*, 168.3, 168.0, 167.6*, 165.1, 163.2 (t, *J* = 32.1 Hz), 133.8, 133.6*, 129.3* (2C), 129.2 (2C), 128.9, 128.83* (2C), 128.78 (2C), 115.4 (dd, *J* = 261.5, 250.3 Hz), 63.4 (2C), 63.2* (2C), 63.0, 61.6, 46.7*, 46.0, 42.6 (t, *J* = 21.0 Hz), 35.1 (α-C of boron), 13.6*, 13.4. **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -97.3 (dd, *J* = 271.3, 20.7 Hz, 1F*), -101.3 (dd, *J* = 271.5, 18.2 Hz, 1F*), -105.0 (d, *J* = 260.1 Hz, 1F), -114.7 (dd, *J* = 260.0, 22.8 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.11. **HRMS (ESI)** calcd. for $C_{19}H_{22}BBrF_2NO_8$ $[M+H]^+$: 519.0621, found: 519.0625.

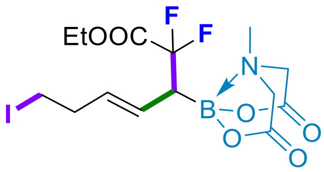
Ethyl (3*S*)-3-(bromo(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-5-

(1,3-dioxoisoindolin-2-yl)-2,2-difluoropentanoate (58)



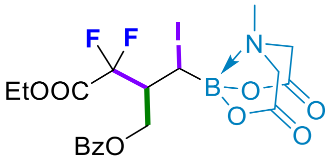
Following the general procedure, compound **58** was obtained in 23% yield (35 mg) as a brown oil after column chromatography and preparative HPLC, dr = 3.3:1 (determined by NMR). **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 7.86 – 7.79 (m, 4H), 4.47 – 4.30 (m, 3H), 4.29 – 4.23 (m, 2H*), 4.23 – 4.14 (m, 2H), 4.13 – 4.08 (m, 2H*), 4.00 (dt, *J* = 21.0, 10.7 Hz, 2H), 3.75 (s, 1H), 3.70 (ddd, *J* = 9.3, 8.5, 4.7 Hz, 2H), 3.65 (dd, *J* = 7.9, 5.9 Hz, 2H*), 3.13 (s, 3H*), 3.04 (s, 3H), 3.01 (d, *J* = 3.8 Hz, 1H*), 2.10 – 2.04 (m, 2H*), 2.05 – 1.93 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.0 Hz, 3H*). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 169.1*, 168.0*, 167.9, 167.8, 167.7 (2C), 163.1 (t, *J* = 32.7 Hz), 134.6* (2C), 134.2 (2C), 131.6 (2C), 131.4* (2C), 123.2* (2C), 123.0 (2C), 117.1 (t, *J* = 254.8 Hz), 64.0*, 63.4, 63.1, 62.8, 62.6*, 61.1*, 45.9*, 45.7, 42.3 (t, *J* = 21.5 Hz), 36.2, 25.5, 13.6, 13.4*. **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -100.7 (dd, *J* = 260.9, 6.0 Hz, 1F*), -105.2 (dd, *J* = 253.0, 15.7 Hz, 1F), -106.1 (dd, *J* = 253.0, 12.5 Hz, 1F), -110.2 (dd, *J* = 260.8, 21.3 Hz, 1F*). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.50. **HRMS (ESI)** calcd. for $C_{21}H_{23}[^{11}B]BrF_2N_2O_8$ $[M+H]^+$: 559.0693, found: 559.0697.

Ethyl (*S*,*E*)-2,2-difluoro-7-iodo-3-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hept-4-enoate (59a)



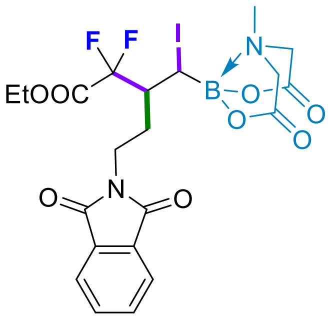
Following the general procedure, compound **59a** was obtained in 31% yield (40 mg) as a brown oil after column chromatography and preparative HPLC (TFA). **59b** was detected by ^{19}F NMR. **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 5.65 – 5.56 (m, 1H), 5.41 (dd, *J* = 15.5, 10.3 Hz, 1H), 4.27 (d, *J* = 11.9 Hz, 1H), 4.25 – 4.17 (m, 3H), 4.05 (d, *J* = 17.0 Hz, 1H), 3.86 (d, *J* = 17.2 Hz, 1H), 3.29 – 3.20 (m, 2H), 2.94 (s, 3H), 2.76 (ddd, *J* = 27.7, 13.0, 10.6 Hz, 1H), 2.65 – 2.52 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.6, 167.9, 163.9 (t, *J* = 33.3 Hz), 135.4, 124.5, 117.6 (dd, *J* = 253.7, 248.4 Hz), 62.5, 61.9, 61.5, 46.1, 36.7 (α-C of boron), 36.2, 13.7, 7.4. **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -96.9 (dd, *J* = 254.5, 13.0 Hz, 1F), -102.3 (dd, *J* = 248.0, 5.3 Hz, 1F of **59b**), -105.8 (dd, *J* = 254.5, 27.9 Hz, 1F), -115.1 (dd, *J* = 248.0, 23.4 Hz, 1F of **59b**). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 9.92. **HRMS (ESI)** calcd. for $C_{14}H_{20}[^{11}B]F_2INO_6$ $[M+H]^+$: 474.0391, found: 474.0392.

(2*S*)-4-ethoxy-3,3-difluoro-2-(iodo(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-4-oxobutyl benzoate (60)



Following the general procedure, compound **60** was obtained in 32% yield (49 mg) as a purple solid after column chromatography and preparative HPLC, dr = 6.7:1 (determined by NMR). **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 7.92 (dd, *J* = 17.2, 7.7 Hz, 2H), 7.69 (t, *J* = 7.2 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 4.56 – 4.38 (m, 3H), 4.30 (d, *J* = 17.2 Hz, 1H), 4.17 – 3.91 (m, 4H), 3.78 – 3.63 (m, 1H), 3.16 (s, 3H), 3.14 – 3.04 (m, 1H), 3.01 (s, 3H*), 1.11 (dt, *J* = 14.0, 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.4* (2C), 168.0 (2C), 165.1, 164.4*, 163.3 (t, *J* = 32.4 Hz), 133.8, 133.6*, 129.4* (2C), 129.2 (2C), 128.82, 128.78 (2C), 119.4 (t, *J* = 257.6 Hz), 64.5, 63.53, 63.49, 63.3, 45.8, 41.5 (t, *J* = 21.5 Hz), 13.4. **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -96.9 (dd, *J* = 275.7, 11.4 Hz, 1F), -104.0 (dd, *J* = 274.5, 20.4 Hz, 1F), -105.3 (d, *J* = 258.4 Hz, 1F*), -115.6 (dd, *J* = 258.3, 22.4 Hz, 1F*). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.44. **HRMS (ESI)** calcd. for $C_{19}H_{22}BF_2INO_8$ $[M+H]^+$: 567.0482, found: 567.0482.

Ethyl (3*S*)-5-(1,3-dioxoisoindolin-2-yl)-2,2-difluoro-3-(iodo(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)pentanoate (61)

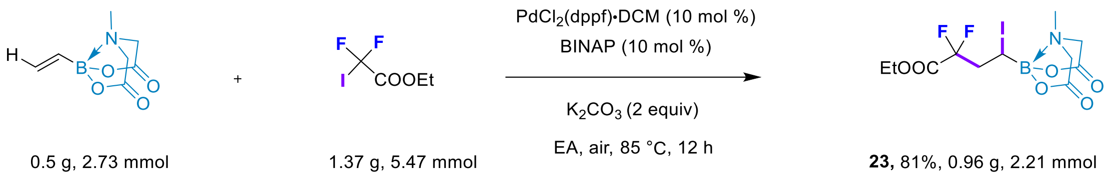


Following the general procedure, compound **61** was obtained in 22% yield (36 mg) as a purple solid after column chromatography and preparative HPLC, dr = 2.5:1 (determined by NMR). **^{1}H NMR** (500 MHz, DMSO-*d6*) δ 7.86 – 7.79 (m, 4H), 4.44 – 4.30 (m, 3H), 4.26 (d, *J* = 17.2 Hz, 2H*), 4.22 – 4.17 (m, 2H), 4.14 – 4.08 (m, 2H*), 4.01 (dd, *J* = 17.0, 15.7 Hz, 2H), 3.75 – 3.66 (m, 2H), 3.63 (dd, *J* = 13.7, 6.9 Hz, 2H*), 3.52 (s, 1H), 3.15 (s, 3H*), 3.04 (s, 3H), 2.98 (s, 1H*), 1.91 (dd, *J* = 12.8, 7.2 Hz, 2H), 1.86 (dd, *J* = 9.6, 4.3 Hz, 2H*), 1.31 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H*). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 169.1*, 168.3*, 168.0, 167.9, 167.7 (2C), 167.6* (2C), 163.1 (t, *J* = 32.2 Hz), 134.6* (2C), 134.2 (2C), 131.7 (2C), 131.4* (2C), 123.2* (2C), 123.0 (2C), 117.2 (t, *J* = 255.1 Hz), 64.0*, 63.4, 63.2, 63.1, 62.8*, 61.1*, 45.8*, 45.5, 41.3 (t, *J* = 21.4 Hz), 36.0, 28.8, 13.6, 13.4*. **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -100.4 (dd, *J* = 260.3, 3.8 Hz, 1F*), -104.9 (dd, *J* = 252.5, 15.6 Hz, 1F), -106.6 (dd, *J* = 252.5, 13.1 Hz, 1F), -112.3 (dd, *J* = 260.1, 22.6 Hz, 1F*). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ

10.23. **HRMS (ESI)** calcd. for $C_{21}H_{23}[^{11}B]F_2IN_2O_8$ $[M+H]^+$: 607.0555, found: 607.0558.

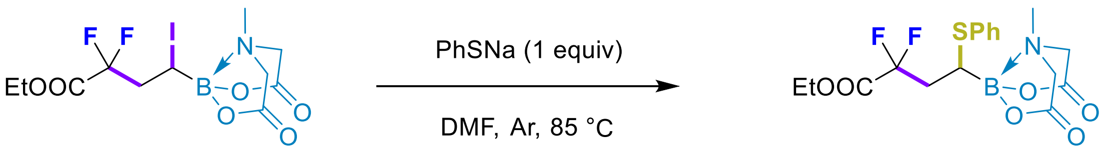
5. Gram-scale preparation and transformations

Gram-scale preparation



To an oven-dried 25 mL of Schlenk tube were added vinyl B(MIDA) (0.5 g, 2.73 mmol, 1.0 equiv.), ICF_2COOEt (1.37 g, 5.47 mmol, 2.0 equiv.), $PdCl_2(dppf)\cdot DCM$ (221.51 mg, 0.273 mmol, 10 mol %), BINAP (170.16 mg, 0.273 mmol, 10 mol %), K_2CO_3 (755.34 mg, 5.47 mmol, 2.0 equiv.) sequentially, ethyl acetate (EtOAc, 10.0 mL) was then added to dissolve the complex above. The Schlenk tube was screw capped and stirred at 85 °C for 12 h. After the solution was cooled to room temperature, the crude reaction mixture was diluted with EA (30 mL) and washed with saturated aqueous NaCl (3 x 30 mL). The aqueous layer was extracted with EA (3 x 30 mL) and the combined organic layer was dried over anhydrous Na_2SO_4. Then, the solvent was removed under vacuo, and the residue was purified by a silica gel column chromatography with an appropriate solvent as eluent to give the desired product **23** (0.96 g, 81% yield).

Synthesis of 62:

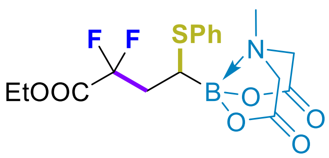


23

62, 70%

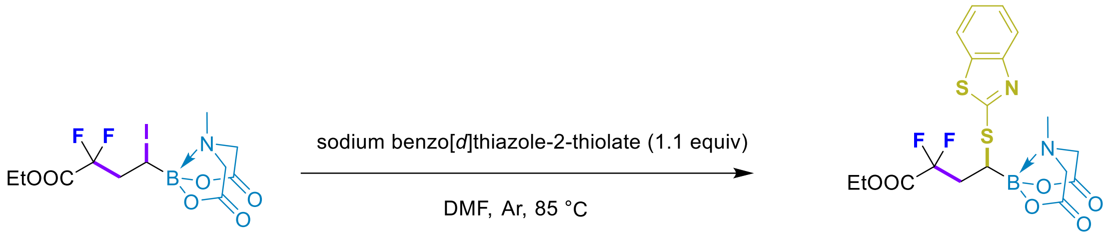
To the 25 mL Schlenk tube with **23** (65.52 mg, 0.15 mmol, 1.0 equiv.) was added PhSNa (20 mg, 0.15 mmol, 1.0 equiv.). The reaction mixture was dissolved in anhydrous DMF (2.5 mL) and was then evacuated and backfilled with Ar for 3 times. The mixture was vigorously stirred at 85 °C for 12 h. After the reaction was complete, the reaction mixture was quenched with water (5 mL) and extracted with EtOAc (10 mL). The combined organic layer was concentrated in vacuo and the residue was purified by flash chromatography on silica gel with a mixture of Petroleum ether and EtOAc as eluent to afford the pure product **62** in 70% yield (44 mg) as a white solid.

Ethyl 2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-4-(phenylthio)butanoate (62)



^{1}**H NMR** (500 MHz, Acetone-*d6*) δ 7.47 – 7.43 (m, 2H), 7.33 (dd, J = 10.6, 4.9 Hz, 2H), 7.23 – 7.19 (m, 1H), 4.39 (d, J = 17.2 Hz, 1H), 4.32 (d, J = 16.8 Hz, 1H), 4.25 – 4.19 (m, 4H), 3.30 (s, 3H), 3.03 (dd, J = 8.1, 4.6 Hz, 1H), 2.80 – 2.72 (m, 1H), 2.51 (ddd, J = 32.1, 15.7, 8.3 Hz, 1H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}**C NMR** (126 MHz, Acetone-*d6*) δ 168.2, 168.1, 164.6 (t, J = 32.5 Hz), 137.0, 129.9 (2C), 129.8 (2C), 127.0, 117.0 (t, J = 249.9 Hz), 64.5, 64.2, 63.5, 46.7, 38.6 (t, J = 23.9 Hz), 28.0 (α-C of boron), 14.0. ^{19}**F NMR** (471 MHz, Acetone-*d6*) δ -103.9 (q, J = 16.1 Hz, 2F). ^{11}**B NMR** (160 MHz, DMSO-*d6*) δ 11.48. **HRMS (ESI)** calcd. for $C_{17}H_{21}[^{11}B]F_2NO_6S$ $[M+H]^+$: 416.1145, found: 416.1151.

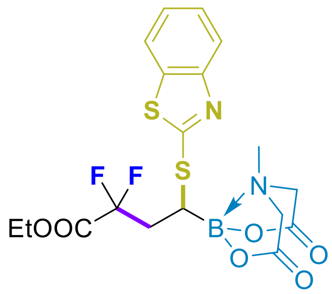
Synthesis of 63:



23 **63**, 60%

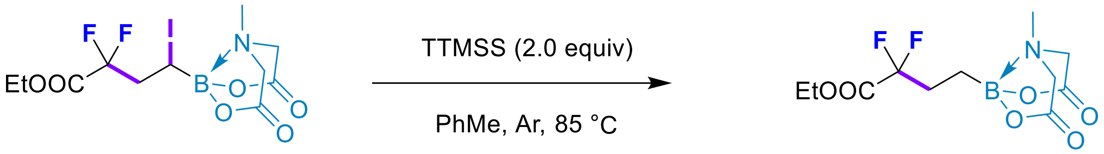
To the 25 mL Schlenk tube with **23** (50 mg, 0.12 mmol, 1.0 equiv.) was added sodium benzo[*d*]thiazole-2-thiolate (24 mg, 0.13 mmol, 1.1 equiv.). The reaction mixture was dissolved in anhydrous DMF (2.5 mL) and was then evacuated and backfilled with Ar for 3 times. The mixture was vigorously stirred at 85 °C for 12 h. After the reaction was complete, the reaction mixture was quenched with water (5 mL) and extracted with EtOAc (10 mL). The combined organic layer was concentrated in vacuo and the residue was purified by flash chromatography on silica gel with a mixture of Petroleum ether and EtOAc as eluent to afford the pure product **63** in 60% yield (31 mg) as a yellow solid.

Ethyl 4-(benzo[*d*]thiazol-2-ylthio)-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoate (63)



^{1}**H NMR** (600 MHz, Acetone-*d6*) δ 7.94 (d, J = 7.9 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.4 Hz, 1H), 4.47 (d, J = 17.4 Hz, 1H), 4.37 (d, J = 16.9 Hz, 1H), 4.29 (dd, J = 17.2, 5.4 Hz, 2H), 4.26 – 4.20 (m, 2H), 4.11 (dd, J = 10.3, 2.6 Hz, 1H), 3.37 (s, 3H), 2.95 – 2.86 (m, 1H), 2.64 – 2.52 (m, 1H), 1.20 (t, J = 7.1 Hz, 3H). ^{13}**C NMR** (151 MHz, Acetone-*d6*) δ 168.2, 168.0, 167.0, 164.3 (t, J = 32.5 Hz), 153.8, 136.4, 127.0, 125.4, 122.3, 122.2, 117.1 (t, J = 250.3 Hz), 64.5, 64.2, 63.5, 47.0, 37.8 (t, J = 23.6 Hz), 14.0. **^{19}F NMR** (376 MHz, Acetone-*d6*) δ -102.7 (dt, J = 266.3, 15.7 Hz, 1F), -104.0 (ddd, J = 266.4, 18.3, 14.5 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 11.18. **HRMS (ESI)** calcd. for $C_{18}H_{20}[^{11}B]F_2N_2O_6S_2$ $[M+H]^+$: 473.0818, found: 473.0812.

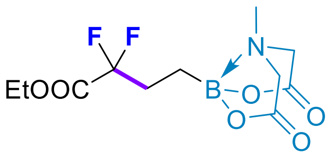
Synthesis of 64:[11]



23 **64**, 65%

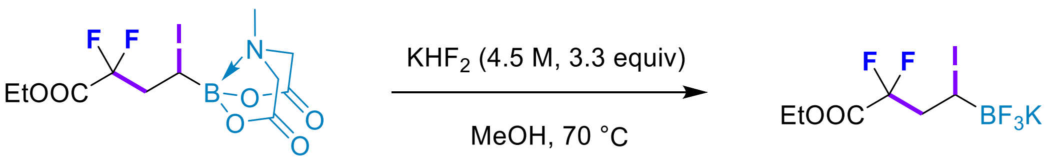
To the 25 mL Schlenk tube with **23** (50 mg, 0.12 mmol, 1.0 equiv.) was added TTMSS (57.43 mg, 0.23 mmol, 2.0 equiv.). The reaction mixture was dissolved in PhMe (2.0 mL) and was then evacuated and backfilled with Ar for 3 times. The mixture was vigorously stirred at 85 °C for 12 h. After the reaction was complete, the solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel with a mixture of Petroleum ether and EtOAc as eluent to afford the pure product **64** in 65% yield (23 mg) as a white solid.

Ethyl 2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoate (64)



^{1}H NMR (600 MHz, DMSO-*d6*) δ 4.30 (q, J = 7.1 Hz, 2H), 4.22 (d, J = 17.0 Hz, 2H), 4.04 (d, J = 17.0 Hz, 2H), 2.87 (s, 3H), 2.10 – 1.92 (m, 2H), 1.27 (t, J = 7.1 Hz, 3H), 0.64 – 0.58 (m, 2H). **^{13}C NMR** (151 MHz, DMSO-*d6*) δ 168.8 (2C), 163.7 (t, J = 33.0 Hz), 117.3 (t, J = 248.5 Hz), 62.8, 61.9 (2C), 45.6, 29.4 (t, J = 23.6 Hz), 13.8, 6.8 (α-C of boron). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -105.9 (t, J = 17.2 Hz, 2F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 12.46. **HRMS (ESI)** calcd. for $C_{11}H_{17}[^{11}B]F_2NO_6$ $[M+H]^+$: 308.1112, found: 308.1113.

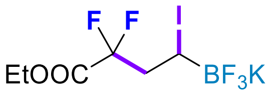
Synthesis of 65:



23 **65**, 75%

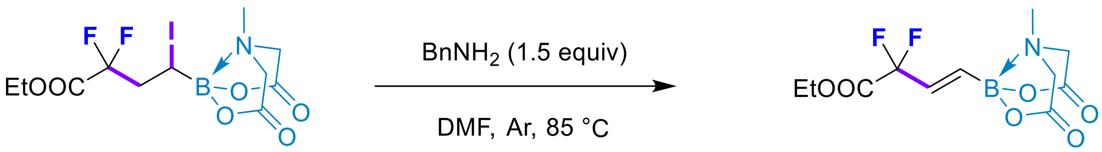
To a stirred solution of the **23** (163 mg, 0.38 mmol, 1.0 equiv.) in methanol (4.5 mL) was added aq KHF_2 solution (276 µL, 1.24 mmol, 3.3 equiv, 4.5 M solution) and the mixture was stirred at 70 °C for 12 h. The solvent was removed under reduced pressure and the crude residue was thoroughly dried under high vacuum. The solid was extracted with hot acetone and filtered and the solvent evaporated. The crude product was recrystallized (acetone/hexanes) to yield the corresponding potassium trifluoroborate derivative **65** as a brown solid (108 mg, 75%).

Ethyl 2,2-difluoro-4-iodo-4-(trifluoro-λ4-boraneyl)butanoate, potassium salt (65)



^{1}H NMR (500 MHz, Acetone-*d6*) δ 4.26 (q, *J* = 7.1 Hz, 2H), 2.90 (d, *J* = 4.5 Hz, 1H), 2.73 – 2.60 (m, 1H), 2.58 – 2.41 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, Acetone-*d6*) δ 164.8 (t, *J* = 32.9 Hz), 117.8 (t, *J* = 249.0 Hz), 63.2, 41.1 (t, *J* = 23.4 Hz), 14.0. **^{19}F NMR** (471 MHz, Acetone-*d6*) δ -101.9 (dddd, *J* = 148.8, 28.4, 15.7, 12.3 Hz, 1F), -107.3 (m, 1F), -149.7 (s, 3F). **^{11}B NMR** (160 MHz, Acetone-*d6*) δ 3.33 (t, *J* = 40.3 Hz). **HRMS (ESI)** calcd. for $C_6H_8[^{11}B]F_5IO_2$ $[M-K]^-$: 344.9588, found: 344.9585.

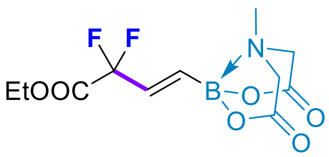
Synthesis of 66:



23 **66,** 78%

To the 25 mL Schlenk tube with **23** (80.81 mg, 0.19 mmol, 1.0 equiv.) was added $BnNH_2$ (30 mg, 0.28 mmol, 1.5 equiv.). The reaction mixture was dissolved in anhydrous DMF (2.5 mL) and was then evacuated and backfilled with Ar for 3 times. The mixture was vigorously stirred at 85 °C for 12 h. After the reaction was complete, the reaction mixture was quenched with water (5 mL) and extracted with EtOAc (10 mL). The combined organic layer was concentrated in vacuo and the residue was purified by flash chromatography on silica gel with a mixture of Petroleum ether and EtOAc as eluent to afford the pure product **66** in 78% yield (44 mg) as a yellow solid.

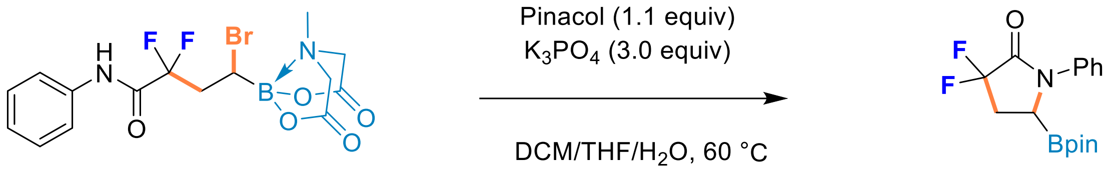
Ethyl (*E*)-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)but-3-enoate (66)



^{1}H NMR (500 MHz, Acetone-*d6*) δ 6.39 (dt, *J* = 18.0, 2.3 Hz, 1H), 6.25 (dt, *J* = 18.0, 10.6 Hz, 1H), 4.35 – 4.29 (m, 4H), 4.15 (d, *J* = 17.0 Hz, 2H), 3.07 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Acetone-*d6*) δ 168.8 (2C), 164.3 (t, *J* = 34.2 Hz), 136.6 (α-C of boron), 134.0 (t, *J* = 25.5 Hz), 113.5 (t, *J* = 246.9 Hz), 63.7, 62.8 (2C), 47.7, 14.2. **^{19}F NMR** (471 MHz, Acetone-*d6*) δ -104.9 (d, *J* = 10.0 Hz, 2F). **^{11}B NMR** (160 MHz, Acetone-*d6*) δ 10.42. **HRMS (ESI)** calcd. for $C_{11}H_{13}[^{11}B]F_2NO_6$ $[M-H]^-$:

304.0809, found: 304.0810.

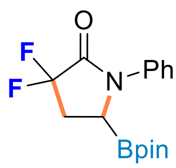
Synthesis of 67:[12]



5 **67,** 81%

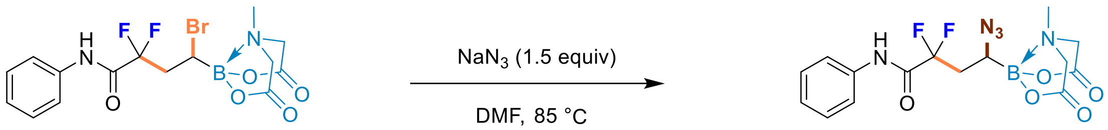
To the 25 mL Schlenk tube with **5** (177.7 mg, 0.41 mmol, 1.0 equiv.) were added pinacol (53.35 mg, 0.45 mmol, 1.1 equiv.) and K_3PO_4 (261.33 mg, 1.23 mmol, 3.0 equiv.). The reaction mixture was dissolved in THF (1.0 M), DCM (0.1 M) and H_2O (0.2 M) and then the mixture was vigorously stirred at 60 °C for 12 h. After the reaction was complete, the reaction mixture was quenched with water (10 mL) and extracted with DCM (20 mL). The combined organic layer was concentrated in vacuo and the residue was purified by flash chromatography on silica gel with a mixture of Petroleum ether and EtOAc as eluent to afford the pure product **67** in 81% yield (107 mg) as a yellow solid.

3,3-difluoro-1-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrolidin-2-one (67)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H), 7.39 (dd, J = 10.8, 5.2 Hz, 2H), 7.22 (t, J = 7.4 Hz, 1H), 3.90 (t, J = 7.5 Hz, 1H), 2.74 (tdd, J = 14.7, 10.4, 7.9 Hz, 1H), 2.57 – 2.43 (m, 1H), 1.14 (s, 6H), 1.04 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.6 (t, J = 31.5 Hz), 138.4, 129.1 (2C), 126.4, 121.7 (2C), 117.9 (t, J = 250.3 Hz), 85.1 (2C), 40.6 (α-C of boron), 31.9 (t, J = 22.7 Hz), 24.7 (2C), 24.3 (2C). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -105.4 (ddd, J = 266.2, 15.6, 10.6 Hz, 1F), -106.0 (ddd, J = 266.2, 18.1, 15.1 Hz, 1F). **^{11}B NMR** (160 MHz, $CDCl_3$) δ 32.11. **HRMS (ESI)** calcd. for $C_{16}H_{21}[^{11}B]F_2NO_3$ $[M+H]^+$: 324.1577, found: 324.1584.

Synthesis of 68:

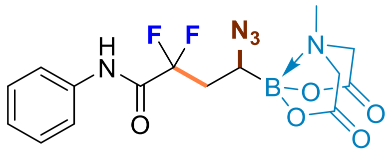


5 **68,** 45%

To the 25 mL round bottom flask with **5** (253 mg, 0.58 mmol, 1.0 equiv.) was added

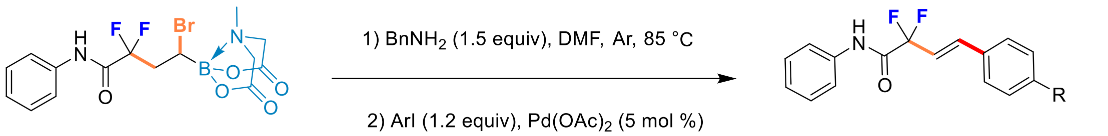
NaN$_3$ (56.98 mg, 0.88 mmol, 1.5 equiv.). The reaction mixture was dissolved in anhydrous DMF (4.0 mL) and was vigorously stirred at 85 °C for 12 h. After the reaction was complete, the reaction mixture was quenched with water (10 mL) and extracted with EtOAc (30 mL). The combined organic layer was concentrated in vacuo and the residue was purified by flash chromatography on silica gel with a mixture of Petroleum ether and EtOAc as eluent to afford the pure product **68** in 45% yield (104 mg) as a yellow oil.

4-azido-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-*N*-phenylbutanamide (68)



^{1}H NMR (500 MHz, DMSO-*d6*) δ 10.61 (s, 1H), 7.72 – 7.67 (m, 2H), 7.40 – 7.33 (m, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 4.39 (d, *J* = 17.3 Hz, 1H), 4.29 (d, *J* = 17.1 Hz, 1H), 4.16 (d, *J* = 17.1 Hz, 1H), 4.11 (d, *J* = 17.2 Hz, 1H), 3.29 – 3.25 (m, 1H), 3.04 (s, 3H), 2.52 – 2.45 (m, 1H), 2.43 (dd, *J* = 15.4, 4.4 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.5, 168.2, 161.9 (t, *J* = 29.2 Hz), 137.3, 128.7 (2C), 124.9, 121.0 (2C), 117.5 (t, *J* = 252.9 Hz), 62.9, 62.6, 46.1, 45.3 (α-C of boron), 34.0 (t, *J* = 23.5 Hz). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -103.2 (dt, *J* = 32.1, 16.3 Hz, 1F), -105.1 (dt, *J* = 250.0, 18.5 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 10.55. **HRMS (ESI)** calcd. for $C_{15}H_{16}[^{11}B]F_2N_5NaO_5$ $[M+Na]^+$: 418.1105, found: 418.1104.

Synthesis of 69 and 70:[13]



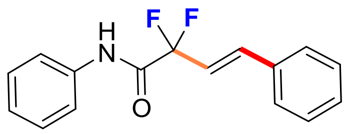
5

69, R=H, 22% over two steps
70, R=COMe, 20% over two steps

To the 25 mL Schlenk tube with **5** (250 mg, 0.58 mmol, 1.0 equiv.) was added BnNH$_2$ (92.8 mg, 0.87 mmol, 1.5 equiv.). The reaction mixture was dissolved in anhydrous DMF (3.5 mL) and was then evacuated and backfilled with Ar for 3 times. The mixture was vigorously stirred at 85 °C for 12 h. After the reaction was complete, the reaction mixture was quenched with water (5 mL) and extracted with EtOAc (10 mL). The combined organic layer was concentrated in vacuo and the residue was purified by flash chromatography on silica gel with a mixture of Petroleum ether and EtOAc as eluent to afford the eliminated product. Immediately, to the 25 mL Schlenk tube were added Pd(OAc)$_2$ (5 mol %), SPhos (10 mol %), eliminated MIDA boronate (1.0 equiv.) and aryl iodide (1.2 equiv.). THF (5 mL) and 3.0 M aqueous K$_3$PO$_4$ (7.5 equiv of base) were introduced to dissolve the mixture above. Then the Schlenk tube was evacuated and backfilled with Ar for 3 times and the reaction mixture was vigorously stirred at 60 °C for 12 h. After the reaction was complete, the reaction mixture was quenched with water

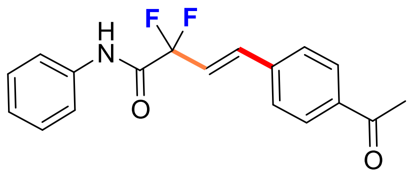
(5 mL) and extracted with EtOAc (15 mL). The combined organic layer was concentrated in vacuo and the residue was purified by flash chromatography on silica gel with a mixture of Petroleum ether and EtOAc as eluent to afford the pure product **69** in 22% yield (35 mg) and **70** in 20% yield (36 mg) as a yellow solid respectively over two steps.

(*E*)-2,2-difluoro-*N*,4-diphenylbut-3-enamide (69)



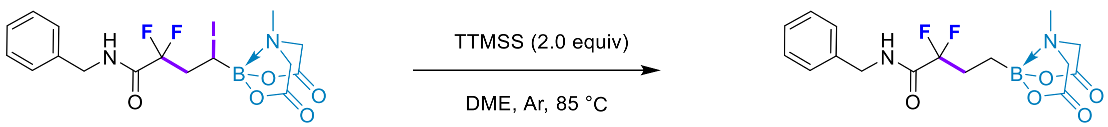
^{1}H NMR (500 MHz, DMSO-*d6*) δ 10.63 (s, 1H), 7.71 (d, *J* = 7.7 Hz, 2H), 7.67 – 7.63 (m, 2H), 7.46 – 7.35 (m, 5H), 7.15 (dd, *J* = 16.7, 9.3 Hz, 2H), 6.78 – 6.68 (m, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 161.6 (t, *J* = 31.3 Hz), 137.3, 136.1 (t, *J* = 9.5 Hz), 133.9, 129.6, 128.9 (2C), 128.8 (2C), 127.6 (2C), 124.9, 120.8 (2C), 119.7 (t, *J* = 25.2 Hz), 114.4 (t, *J* = 249.0 Hz). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -100.3 (d, *J* = 10.8 Hz, 2F). **HRMS (ESI)** calcd. for $C_{16}H_{12}F_2NO$ $[M-H]^-$: 272.0892, found: 272.0897.

(*E*)-4-(4-acetylphenyl)-2,2-difluoro-*N*-phenylbut-3-enamide (70)



^{1}H NMR (500 MHz, DMSO-*d6*) δ 10.67 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.72 – 7.69 (m, 2H), 7.38 (dd, *J* = 10.8, 5.1 Hz, 2H), 7.24 (d, *J* = 16.3 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.90 (dt, *J* = 16.3, 11.4 Hz, 1H), 2.59 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 197.4, 161.4 (t, *J* = 31.1 Hz), 138.3, 137.2 (2C), 135.1 (t, *J* = 9.5 Hz), 128.8 (2C), 128.7 (2C), 127.9 (2C), 124.9, 122.3 (t, *J* = 25.2 Hz), 120.9 (2C), 114.2 (t, *J* = 249.5 Hz), 26.8. **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -100.7 (d, *J* = 11.2 Hz, 2F). **HRMS (ESI)** calcd. for $C_{18}H_{14}F_2NO_2$ $[M-H]^-$: 314.0998, found: 314.1004.

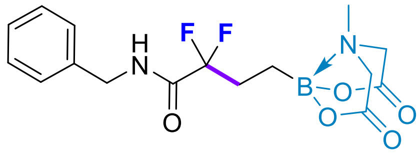
Synthesis of 71:[11]



29 **71**, 85%

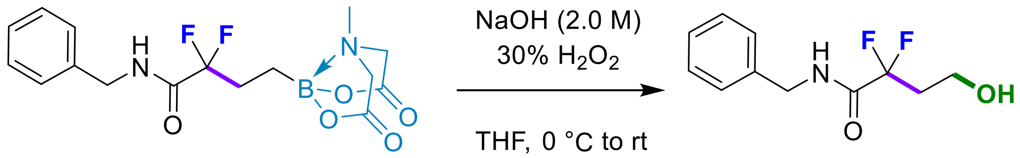
To the 25 mL Schlenk tube with **29** (229 mg, 0.46 mmol, 1.0 equiv.) was added TTMSS (230.52 mg, 0.93 mmol, 2.0 equiv.). The reaction mixture was dissolved in DME (4.0 mL) and was then evacuated and backfilled with Ar for 3 times. The mixture was vigorously stirred at 85 °C for 12 h. After the reaction was complete, the solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel with a mixture of Petroleum ether and EtOAc as eluent to afford the pure product **71** in 85% yield (145 mg) as a yellow solid.

***N*-benzyl-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (71)**



^{1}H NMR (500 MHz, DMSO-*d6*) δ 9.24 (t, *J* = 6.0 Hz, 1H), 7.32 (dd, *J* = 9.7, 5.2 Hz, 2H), 7.28 – 7.23 (m, 3H), 4.34 (d, *J* = 6.1 Hz, 2H), 4.21 (d, *J* = 17.1 Hz, 2H), 4.03 (d, *J* = 17.0 Hz, 2H), 2.84 (s, 3H), 2.06 – 1.92 (m, 2H), 0.64 – 0.56 (m, 2H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.8 (2C), 163.9 (t, *J* = 29.5 Hz), 138.6, 128.4 (2C), 127.2 (2C), 127.0, 119.0 (t, *J* = 250.5 Hz), 61.9 (2C), 45.6, 42.1, 29.3 (t, *J* = 24.2 Hz), 7.1 (α-C of boron). **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -105.9 (t, *J* = 17.1 Hz, 2F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 12.84. **HRMS (ESI)** calcd. for $C_{16}H_{20}[^{11}B]F_2N_2O_5$ $[M+H]^+$: 369.1428, found: 369.1429.

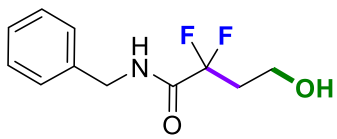
Synthesis of 72:[14]



71 **72,** 88%

To a stirred solution of **71** (143.5 mg, 0.39 mmol, 1.0 equiv.) in THF (4 mL) at 0 °C was successively added 1.46 mL of NaOH (2.0 M, 7.5 equiv.) and 0.97 mL of 30% H_2O_2 dropwise. The reaction was stirred 10 minutes at 0 °C, followed by 1 hour at room temperature. Upon the completion of the reaction as determined by TLC, the mixture was cooled to 0 °C and saturated aqueous sodium thiosulfate solution (5.84 mL) was added dropwise. The aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography on silica gel to provide **72** as a colorless oil (78 mg, 88%).

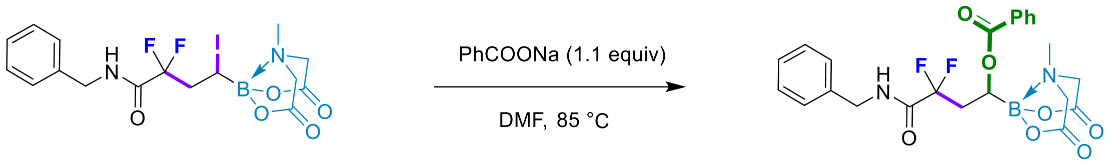
***N*-benzyl-2,2-difluoro-4-hydroxybutanamide (72)**



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.31 – 7.25 (m, 3H), 6.99 (s, 1H), 4.47 (d, *J* = 5.8 Hz, 2H), 3.81 (t, *J* = 5.8 Hz, 2H), 2.81 (s, 1H), 2.35 (tt, *J* = 16.3, 5.8 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.8 (t, *J* = 29.0 Hz), 136.7, 129.0 (2C), 128.1, 127.9 (2C), 117.6 (t, *J* = 252.6 Hz), 56.3 (t, *J* = 6.2 Hz), 43.7, 37.4 (t, *J* = 22.6 Hz). **^{19}F**

NMR (471 MHz, $CDCl_3$) δ -103.6 (t, *J* = 16.3 Hz, 2F). **HRMS (ESI)** calcd. for $C_{11}H_{14}F_2NO_2$ $[M+H]^+$: 230.0987, found: 230.0991.

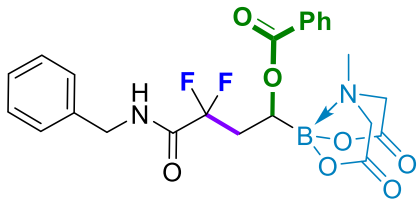
Synthesis of 73:



29 **73**, 42%

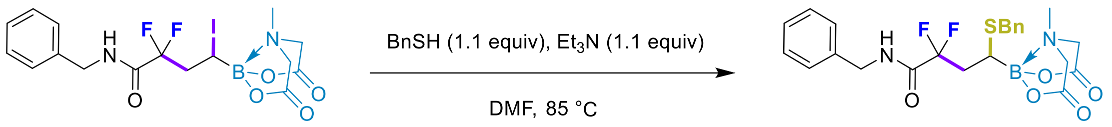
To the 25 mL round bottom flask with **29** (147 mg, 0.3 mmol, 1.0 equiv.) was added PhCOONa (47.17 mg, 0.33 mmol, 1.1 equiv.). The reaction mixture was dissolved in anhydrous DMF (2.5 mL) and was vigorously stirred at 85 °C for 12 h. After the reaction was complete, the reaction mixture was quenched with water (5 mL) and extracted with EtOAc (10 mL). The combined organic layer was concentrated in vacuo and the residue was purified by flash chromatography on silica gel with a mixture of Petroleum ether and EtOAc as eluent to afford the pure product **73** in 42% yield (61 mg) as a light yellow oil.

4-(benzylamino)-3,3-difluoro-1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-4-oxobutyl benzoate (73)



^{1}**H NMR** (500 MHz, DMSO-*d6*) δ 9.20 (t, *J* = 6.0 Hz, 1H), 7.92 – 7.88 (m, 2H), 7.67 – 7.62 (m, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.21 (tt, *J* = 14.9, 7.6 Hz, 3H), 5.34 (dd, *J* = 11.0, 1.4 Hz, 1H), 4.39 (d, *J* = 17.3 Hz, 1H), 4.27 (d, *J* = 17.2 Hz, 1H), 4.21 (dd, *J* = 15.0, 6.2 Hz, 1H), 4.14 – 4.10 (m, 1H), 4.08 (d, *J* = 17.2 Hz, 1H), 3.97 (d, *J* = 17.2 Hz, 1H), 2.98 (s, 3H), 2.65 – 2.54 (m, 1H), 2.48 – 2.34 (m, 1H). ^{13}**C NMR** (126 MHz, DMSO-*d6*) δ 168.6, 168.3, 165.3, 163.5 (t, *J* = 28.8 Hz), 138.3, 133.1, 130.1, 129.2 (2C), 128.6 (2C), 128.3 (2C), 127.2 (2C), 126.9, 117.7 (t, *J* = 252.2 Hz), 62.7, 62.4, 59.6 (α-C of boron), 46.1, 42.1, 34.8 (t, *J* = 23.5 Hz). ^{19}**F NMR** (471 MHz, DMSO-*d6*) δ -103.8 (m, 1F), -105.3 (ddd, *J* = 255.3, 21.2, 13.5 Hz, 1F). ^{11}**B NMR** (160 MHz, DMSO-*d6*) δ 10.34. **HRMS (ESI)** calcd. for $C_{23}H_{24}[^{11}B]F_2N_2O_7$ $[M+H]^+$: 489.1639, found: 489.1644.

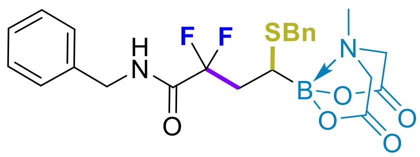
Synthesis of 74:



29 **74**, 77%

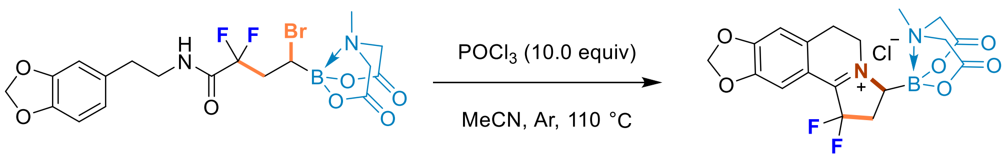
To the 25 mL round bottom flask with **29** (140 mg, 0.28 mmol, 1.0 equiv.) were added BnSH (38.72 mg, 0.31 mmol, 1.1 equiv.) and Et_3N (31.54 mg, 0.31 mmol, 1.1 equiv.). The reaction mixture was dissolved in anhydrous DMF (2.5 mL) and was vigorously stirred at 85 °C for 12 h. After the reaction was complete, the reaction mixture was quenched with water (5 mL) and extracted with EtOAc (10 mL). The combined organic layer was concentrated in vacuo and the residue was purified by flash chromatography on silica gel with a mixture of Petroleum ether and EtOAc as eluent to afford the pure product **74** in 77% yield (107 mg) as a light yellow oil.

_N_-benzyl-4-(benzylthio)-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (74)



^{1}H NMR (500 MHz, DMSO-*d6*) δ 9.35 (t, *J* = 6.0 Hz, 1H), 7.30 (ddd, *J* = 8.6, 4.8, 4.3 Hz, 5H), 7.28 – 7.20 (m, 5H), 4.41 – 4.31 (m, 3H), 4.19 (d, *J* = 16.9 Hz, 1H), 4.00 (d, *J* = 17.3 Hz, 1H), 3.92 (d, *J* = 16.9 Hz, 1H), 3.82 (d, *J* = 12.0 Hz, 1H), 3.72 (d, *J* = 12.0 Hz, 1H), 2.71 (s, 3H), 2.69 – 2.55 (m, 1H), 2.47 – 2.30 (m, 1H), 2.24 (dd, *J* = 8.9, 3.2 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.5, 168.2, 163.9 (t, *J* = 28.9 Hz), 138.5, 138.1, 129.1 (2C), 128.4 (4C), 127.3 (2C), 127.0, 126.9, 118.1 (t, *J* = 251.9 Hz), 63.2, 63.1, 45.2, 42.3, 37.1 (t, *J* = 23.2 Hz), 36.0. **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -103.2 (t, *J* = 17.8 Hz, 2F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 11.80. **HRMS (ESI)** calcd. for $C_{23}H_{26}[^{11}B]F_2N_2O_5S$ $[M+H]^+$: 491.1618, found: 491.1623.

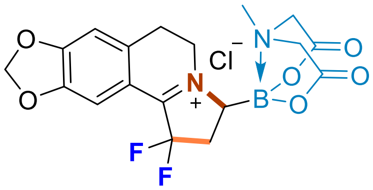
Synthesis of 75:[15,16]



12 **75**, 53%

To the 50 mL round bottom flask with **12** (349 mg, 0.69 mmol, 1.0 equiv.) was added $POCl_3$ (1.06 g, 6.91 mmol, 10.0 equiv.). The reaction mixture was dissolved in anhydrous MeCN (5.0 mL) and was then evacuated and backfilled with Ar for 3 times. The reaction mixture was vigorously stirred at 110 °C for 12 h. After the reaction was complete, the solvent was removed under vacuum. The crude product was directly purified by preparative HPLC with a mixture of MeCN and water (0.1% HCl) as eluent to afford the pure product **75** in 53% yield (149 mg) as a green solid.

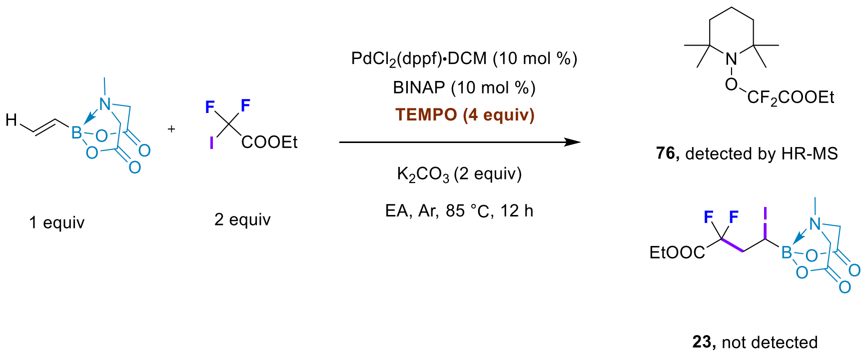
(*S*)-1,1-difluoro-3-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2,3,5,6-tetrahydro-1*H*-[1,3]dioxolo[4,5-*g*]pyrrolo[2,1-*a*]isoquinolin-4-ium (75)



^{1}H NMR (500 MHz, DMSO-*d6*) δ 7.35 (s, 1H), 7.29 (s, 1H), 6.29 (s, 2H), 4.68 (s, 1H), 4.45 (d, *J* = 17.0 Hz, 2H), 4.34 (d, *J* = 16.8 Hz, 2H), 4.18 (d, *J* = 29.8 Hz, 3H), 3.40 – 3.28 (m, 1H), 3.16 (d, *J* = 18.5 Hz, 1H), 3.11 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-*d6*) δ 168.3, 168.0, 160.9 (t, *J* = 32.3 Hz), 155.9, 147.6, 138.0, 126.6 (t, *J* = 250.1 Hz), 112.6, 109.9, 106.7, 103.6, 63.3, 63.0, 59.3 (α-C of boron), 47.5, 46.5, 33.6 (t, *J* = 22.5 Hz), 25.5. **^{19}F NMR** (471 MHz, DMSO-*d6*) δ -84.3 (dt, *J* = 273.5, 20.6 Hz, 1F), -88.0 (dd, *J* = 272.6, 17.4 Hz, 1F). **^{11}B NMR** (160 MHz, DMSO-*d6*) δ 19.99, 9.76. **HRMS (ESI)** calcd. for $C_{18}H_{18}[^{11}B]F_2N_2O_6$ $[M-Cl]^+$: 407.1220, found: 407.1219.

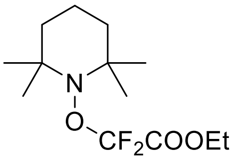
6. Mechanistic studies

Radical inhibition experiment

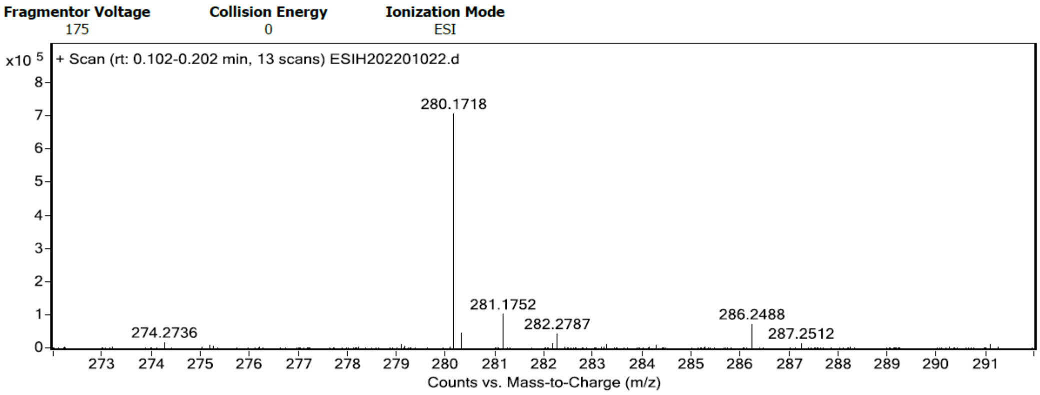


To an oven-dried 25 mL of Schlenk tube were added vinyl B(MIDA) (50 mg, 0.27 mmol, 1.0 equiv.), ICF_2COOEt (136.63 mg, 0.55 mmol, 2.0 equiv.), $PdCl_2$(dppf)•DCM (22.15 mg, 0.027 mmol, 10 mol %), BINAP (17.02 mg, 0.027 mmol, 10 mol %), K_2CO_3 (75.53 mg, 0.55 mmol, 2.0 equiv.), TEMPO (170.79 mg, 1.09 mmol, 4.0 equiv.) sequentially, ethyl acetate (EtOAc, 2.0 mL) was then added to dissolve the complex above. The mixture was then evacuated and backfilled with Ar for 3 times. The Schlenk tube was screw capped and stirred at 85 °C for 12 h. After the solution was cooled to room temperature, the crude reaction mixture was diluted with EA (5 mL) and washed with saturated aqueous NaCl (3 x 5 mL). The aqueous layer was extracted with EA (3 x 5 mL) and the combined organic layer was dried over anhydrous Na_2SO_4. Then, the solvent was removed under vacuo, and the residue was purified by a silica gel column chromatography with an appropriate solvent as eluent to give the mixture of TEMPO-CF_2COOEt adduct (**76**) and TEMPO.

Ethyl 2,2-difluoro-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acetate (76)



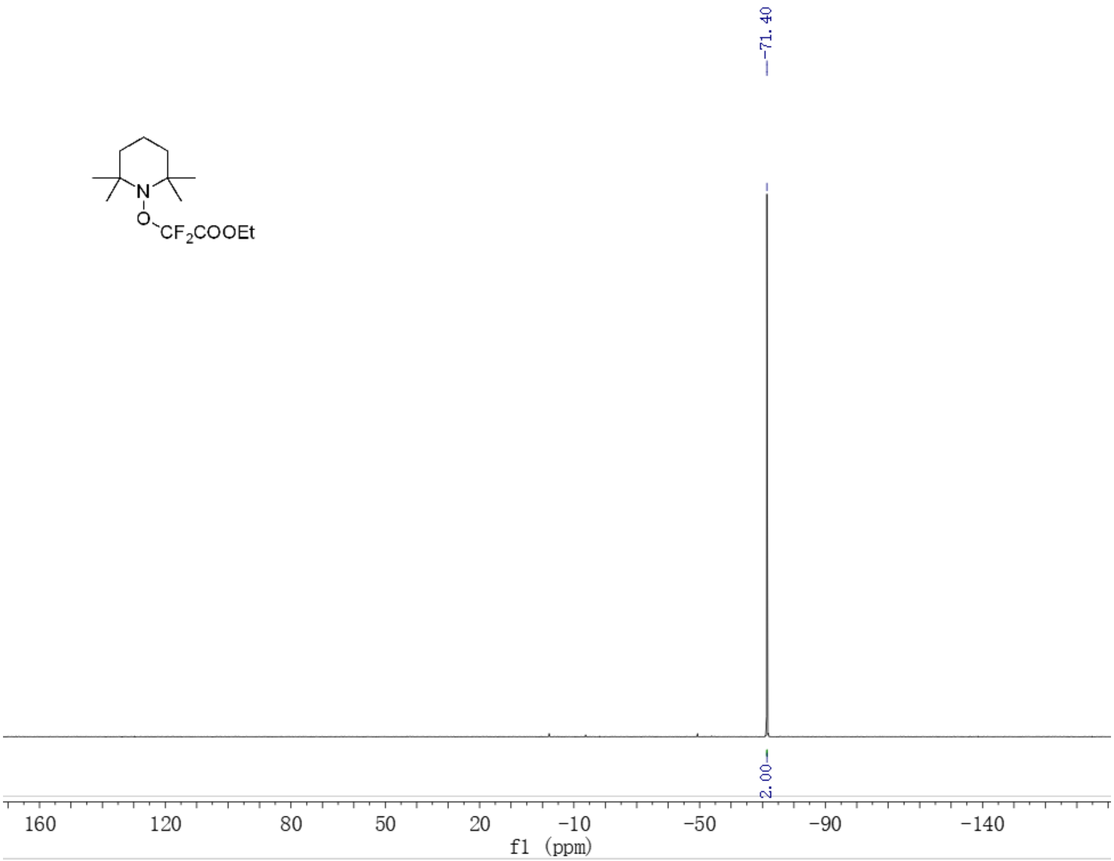
Known compound.[17]



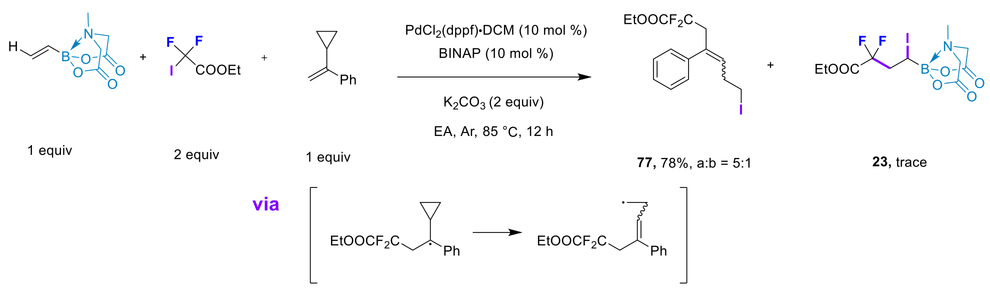
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
280.1718	280.1719	0.08	0.29	C13 H24 F2 N O3	(M+H)+

^{19}F NMR (471 MHz, $CDCl_3$) δ -71.4 (s, 2F). **HRMS (ESI)** calcd. for $C_{13}H_{24}F_2NO_3$ $[M+H]^+$: 280.1719, found: 280.1718.

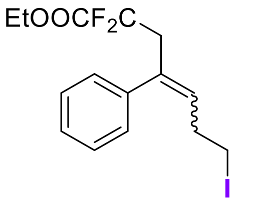


Radical clock experiment



To an oven-dried 25 mL of Schlenk tube were added vinyl B(MIDA) (50 mg, 0.27 mmol, 1.0 equiv.), ICF_2COOEt (136.63 mg, 0.55 mmol, 2.0 equiv.), $PdCl_2(dppf)\cdot DCM$ (22.15 mg, 0.027 mmol, 10 mol %), BINAP (17.02 mg, 0.027 mmol, 10 mol %), K_2CO_3 (75.53 mg, 0.55 mmol, 2.0 equiv.), 1-phenylvinylcyclopropane (39.41 mg, 0.27 mmol, 1.0 equiv.) sequentially, ethyl acetate (EtOAc, 2.0 mL) was then added to dissolve the complex above. The mixture was then evacuated and backfilled with Ar for 3 times. The Schlenk tube was screw capped and stirred at 85 °C for 12 h. After the solution was cooled to room temperature, the crude reaction mixture was diluted with EA (5 mL) and washed with saturated aqueous NaCl (3 x 5 mL). The aqueous layer was extracted with EA (3 x 5 mL) and the combined organic layer was dried over anhydrous Na_2SO_4. Then, the solvent was removed under vacuo, and the residue was purified by a silica gel column chromatography with an appropriate solvent as eluent to give the pure product (**77**) in 78% yield (84 mg) with an isomerism ratio of 5:1 as a colorless oil.

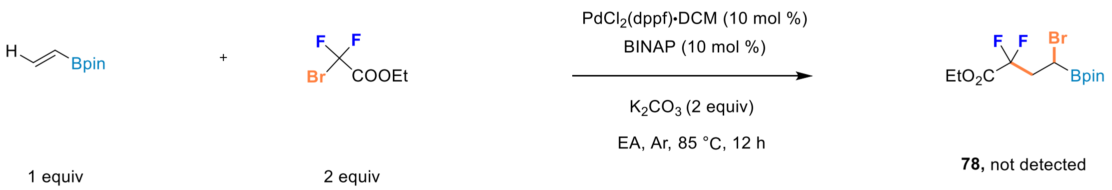
Ethyl 2,2-difluoro-7-iodo-4-phenylhept-4-enoate (77)



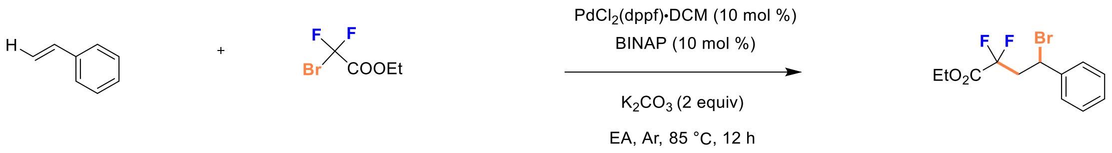
Known compound.[18]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 5H), 7.29 – 7.26 (m, 5H*), 5.93 (t, J = 7.3 Hz, 1H*), 5.85 (t, J = 7.3 Hz, 1H), 4.03 (q, J = 7.2 Hz, 2H*), 3.89 (q, J = 7.2 Hz, 2H), 3.34 (t, J = 15.7 Hz, 2H), 3.24 (t, J = 7.0 Hz, 2H), 3.17 (t, J = 15.3 Hz, 2H*), 3.08 (t, J = 7.0 Hz, 2H*), 2.86 (q, J = 7.1 Hz, 2H), 2.74 (q, J = 6.9 Hz, 2H*), 1.21 (t, J = 7.2 Hz, 3H*), 1.15 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.8 (t, J = 32.5 Hz), 141.8, 134.5, 132.4 (t, J = 4.0 Hz), 128.6* (2C), 128.5 (2C), 127.7, 127.6*, 127.0 (2C), 115.0 (t, J = 252.5 Hz), 62.93, 62.86*, 35.9 (t, J = 24.6 Hz), 33.1, 32.9*, 14.0, 13.8*, 4.8, 4.4*. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -103.2 (t, J = 15.7 Hz, 2F), -103.4 (t, J = 15.5 Hz, 2F*). **HRMS (ESI)** calcd. for $C_{15}H_{18}F_2IO_2$ $[M+H]^+$: 395.0314, found: 395.0310.

Comparative experiment



To an oven-dried 25 mL of Schlenk tube were added vinyl Bpin (50 mg, 0.32 mmol, 1.0 equiv.), $BrCF_2COOEt$ (131.79 mg, 0.65 mmol, 2.0 equiv.), $PdCl_2$(dppf)•DCM (26.32 mg, 0.032 mmol, 10 mol %), BINAP (20.22 mg, 0.032 mmol, 10 mol %), K_2CO_3 (89.73 mg, 0.65 mmol, 2.0 equiv.) sequentially, ethyl acetate (EtOAc, 2.0 mL) was then added to dissolve the complex above. The mixture was then evacuated and backfilled with Ar for 3 times. The Schlenk tube was screw capped and stirred at 85 °C for 12 h. No target product **78** was detected by LC-MS.



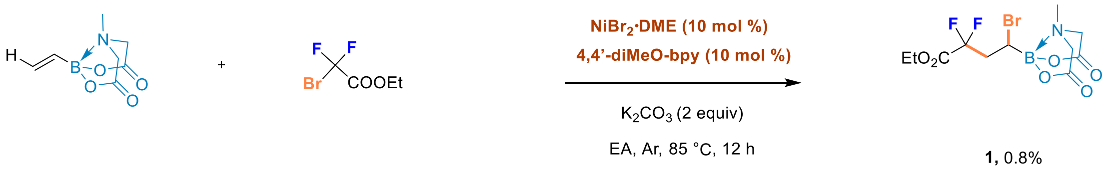
1 equiv 2 equiv **79,** not detected

To an oven-dried 25 mL of Schlenk tube were added styrene (50 mg, 0.48 mmol, 1.0 equiv.), $BrCF_2COOEt$ (194.89 mg, 0.96 mmol, 2.0 equiv.), $PdCl_2$(dppf)•DCM (38.91 mg, 0.048 mmol, 10 mol %), BINAP (29.89 mg, 0.048 mmol, 10 mol %), K_2CO_3 (132.7 mg, 0.96 mmol, 2.0 equiv.) sequentially, ethyl acetate (EtOAc, 2.0 mL) was then added to dissolve the complex above. The mixture was then evacuated and backfilled with Ar for 3 times. The Schlenk tube was screw capped and stirred at 85 °C for 12 h. No target product **79** was detected by LC-MS.

Control experiment

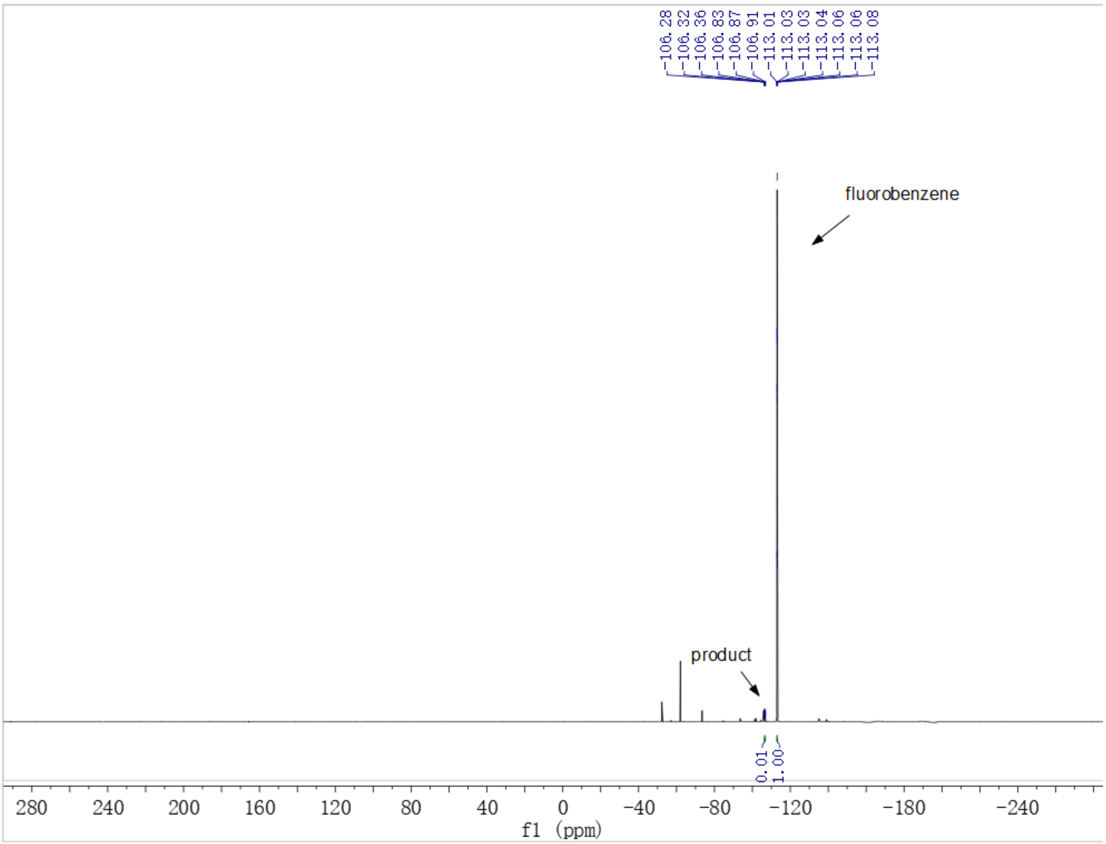
1 equiv 2 equiv **1,** N.R.

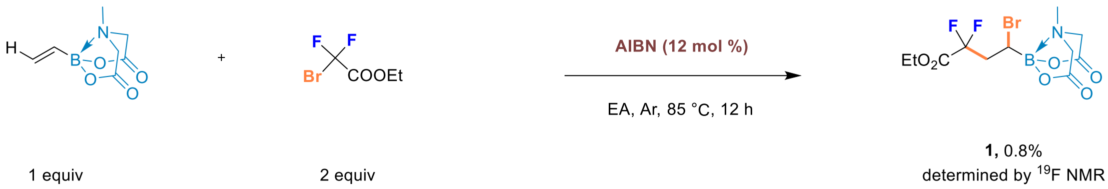
To an oven-dried 25 mL of Schlenk tube were added vinyl B(MIDA) (50 mg, 0.27 mmol, 1.0 equiv.), $BrCF_2COOEt$ (110.94 mg, 0.55 mmol, 2.0 equiv.), BINAP (17.02 mg, 0.027 mmol, 10 mol %), K_2CO_3 (75.53 mg, 0.55 mmol, 2.0 equiv.) sequentially, ethyl acetate (EtOAc, 2.0 mL) was then added to dissolve the complex above. The mixture was then evacuated and backfilled with Ar for 3 times. The Schlenk tube was screw capped and stirred at 85 °C for 12 h. No target product was detected by LC-MS.



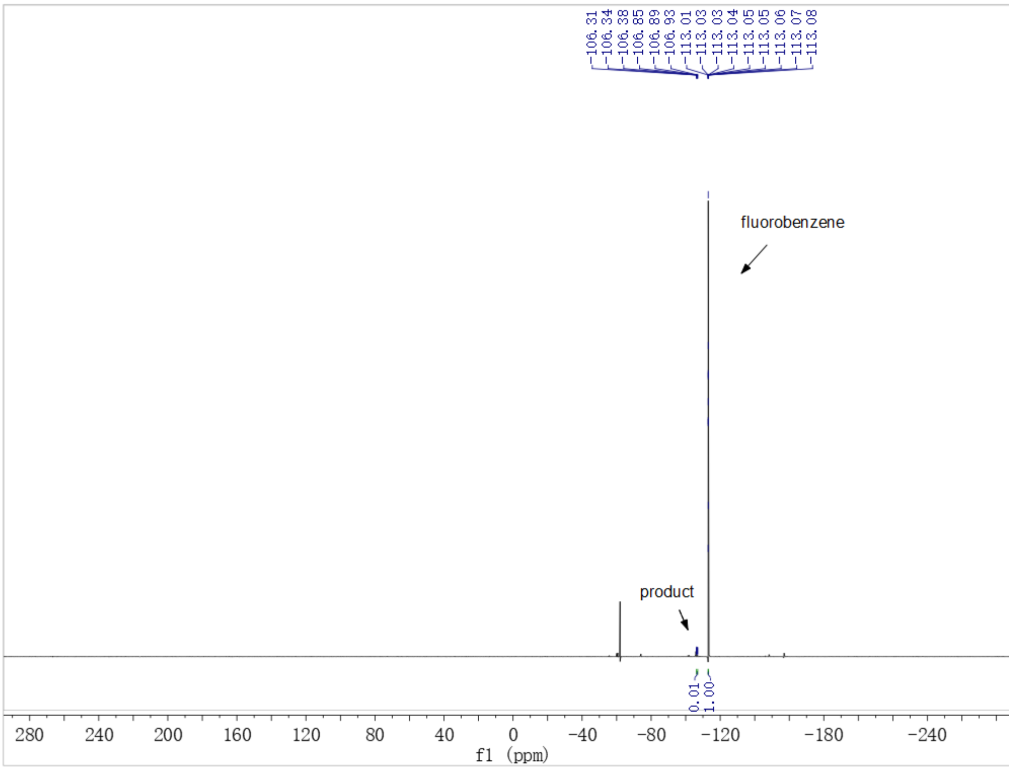
1 equiv 2 equiv **1,** 0.8%
determined by ^{19}F NMR

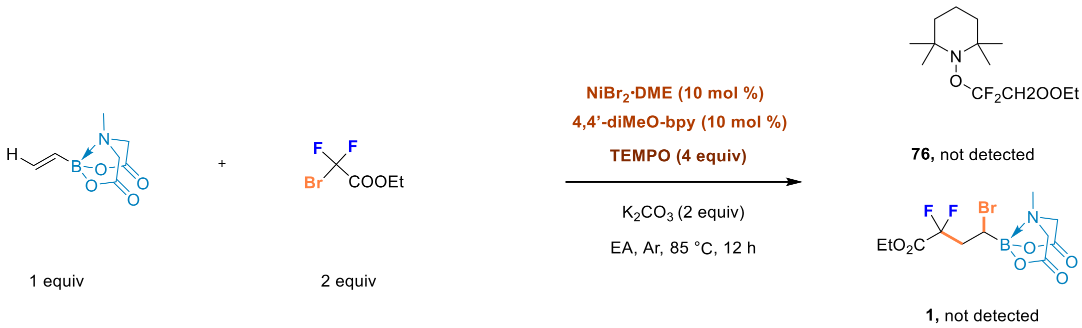
To an oven-dried 25 mL of Schlenk tube were added vinyl B(MIDA) (50 mg, 0.27 mmol, 1.0 equiv.), $BrCF_2COOEt$ (110.94 mg, 0.55 mmol, 2.0 equiv.), $NiBr_2$•DME (8.43 mg, 0.027 mmol, 10 mol %), 4,4'-diMeO-bpy (5.91 mg, 0.027 mmol, 10 mol %), K_2CO_3 (75.53 mg, 0.55 mmol, 2.0 equiv.) sequentially, ethyl acetate (EtOAc, 2.0 mL) was then added to dissolve the complex above. The mixture was then evacuated and backfilled with Ar for 3 times. The Schlenk tube was screw capped and stirred at 85 °C for 12 h. After the solution was cooled to room temperature, fluorobenzene (20 µL, 0.2131 mmol) was added. The yield was determined by ^{19}F NMR.



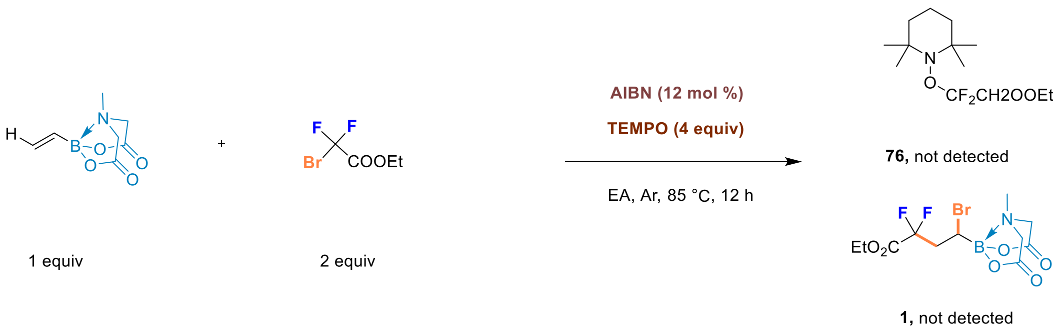


To an oven-dried 25 mL of Schlenk tube were added vinyl B(MIDA) (50 mg, 0.27 mmol, 1.0 equiv.), $BrCF_2COOEt$ (110.94 mg, 0.55 mmol, 2.0 equiv.), AIBN (5.38 mg, 0.033 mmol, 12 mol %) sequentially, ethyl acetate (EtOAc, 2.0 mL) was then added to dissolve the complex above. The mixture was then evacuated and backfilled with Ar for 3 times. The Schlenk tube was screw capped and stirred at 85 °C for 12 h. After the solution was cooled to room temperature, fluorobenzene (20 µL, 0.2131 mmol) was added. The yield was determined by ^{19}F NMR.

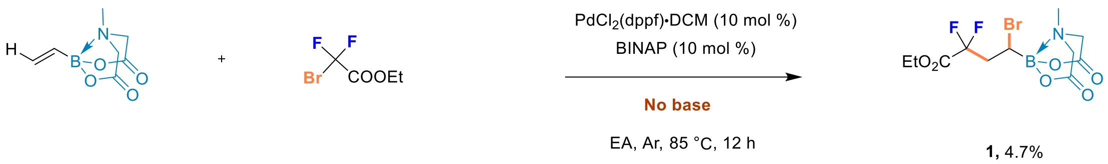




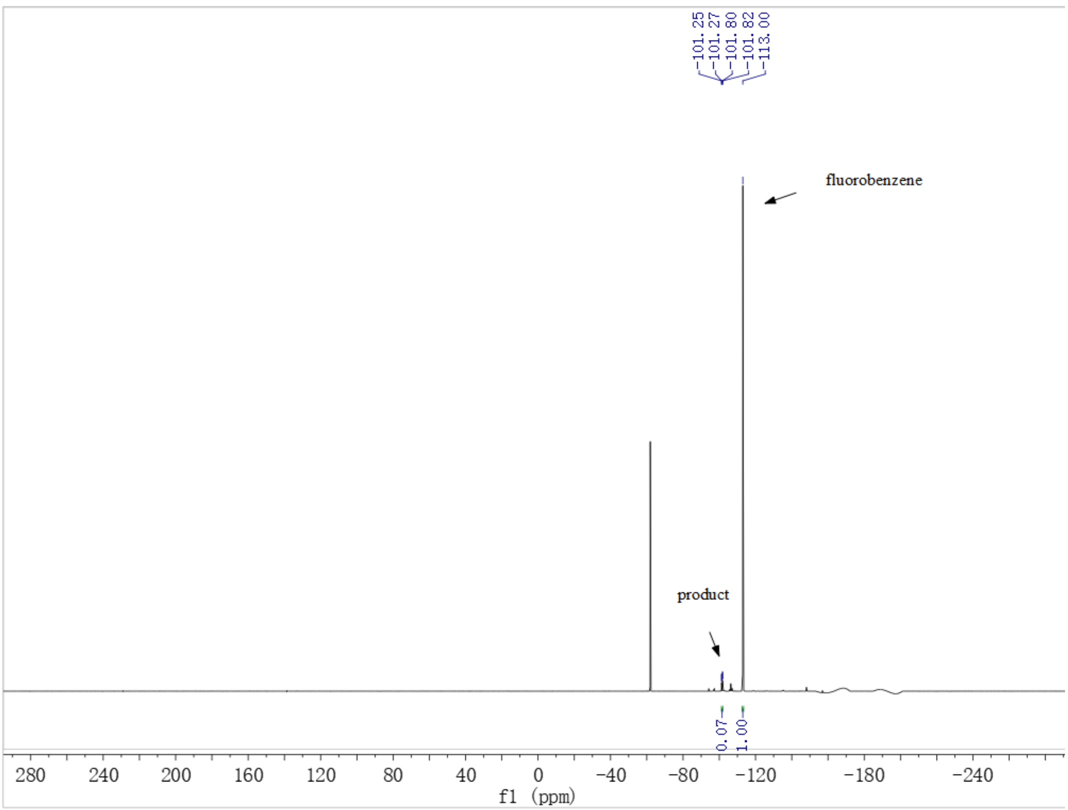
To an oven-dried 25 mL of Schlenk tube were added vinyl B(MIDA) (50 mg, 0.27 mmol, 1.0 equiv.), $BrCF_2COOEt$ (110.94 mg, 0.55 mmol, 2.0 equiv.), $NiBr_2$•DME (8.43 mg, 0.027 mmol, 10 mol %), 4,4'-diMeO-bpy (5.91 mg, 0.027 mmol, 10 mol %), K_2CO_3 (75.53 mg, 0.55 mmol, 2.0 equiv.), TEMPO (170.79 mg, 1.09 mmol, 4.0 equiv.) sequentially, ethyl acetate (EtOAc, 2.0 mL) was then added to dissolve the complex above. The mixture was then evacuated and backfilled with Ar for 3 times. The Schlenk tube was screw capped and stirred at 85 °C for 12 h. No target product **76** and **1** were detected by LC-MS.



To an oven-dried 25 mL of Schlenk tube were added vinyl B(MIDA) (50 mg, 0.27 mmol, 1.0 equiv.), $BrCF_2COOEt$ (110.94 mg, 0.55 mmol, 2.0 equiv.), AIBN (5.38 mg, 0.033 mmol, 12 mol %), TEMPO (170.79 mg, 1.09 mmol, 4.0 equiv.) sequentially, ethyl acetate (EtOAc, 2.0 mL) was then added to dissolve the complex above. The mixture was then evacuated and backfilled with Ar for 3 times. The Schlenk tube was screw capped and stirred at 85 °C for 12 h. No target product **76** and **1** were detected by LC-MS.

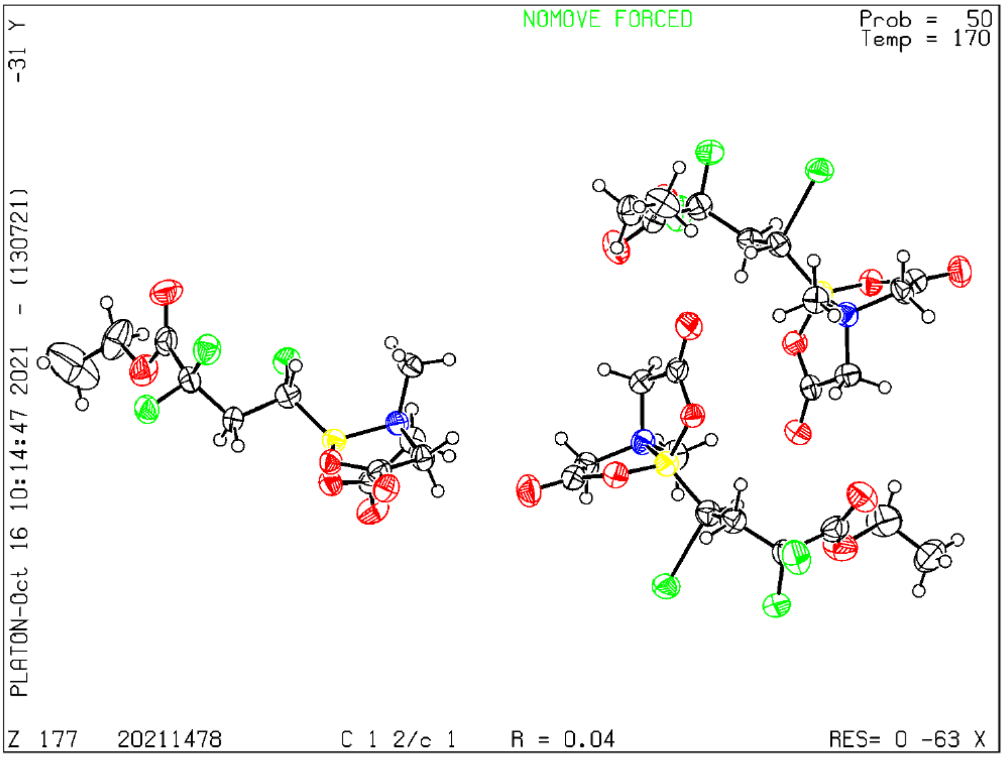


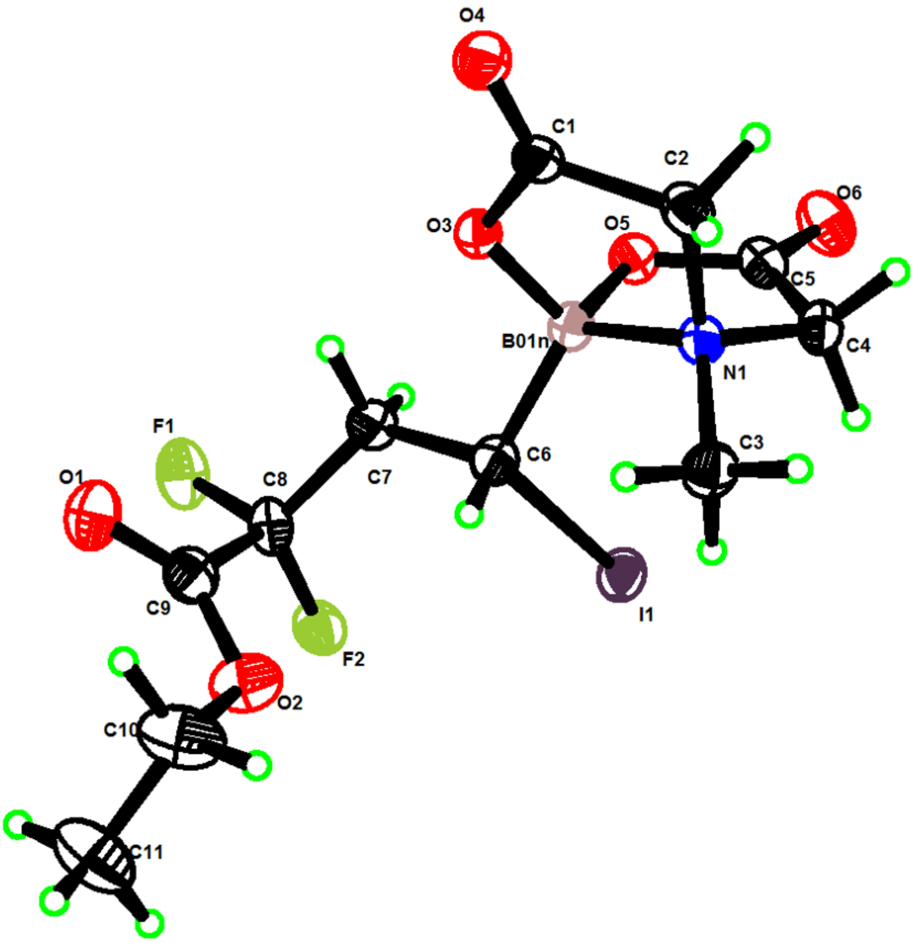
To an oven-dried 25 mL of Schlenk tube were added vinyl B(MIDA) (50 mg, 0.27 mmol, 1.0 equiv.), $BrCF_2COOEt$ (110.94 mg, 0.55 mmol, 2.0 equiv.), $PdCl_2(dppf)\cdot DCM$ (22.15 mg, 0.027 mmol, 10 mol %), BINAP (17.02 mg, 0.027 mmol, 10 mol %) sequentially, ethyl acetate (EtOAc, 2.0 mL) was then added to dissolve the complex above. The mixture was then evacuated and backfilled with Ar for 3 times. The Schlenk tube was screw capped and stirred at 85 °C for 12 h. After the solution was cooled to room temperature, fluorobenzene (20 μL, 0.2131 mmol) was added. The yield was determined by ^{19}F NMR.



7. X-ray crystallographic data

The single crystal structure of 23 (CCDC 2236620)





Bond precision:	C-C = 0.0104 A	Wavelength=0.71073	
Cell:	a=51.208(5)	b=7.1184(7)	c=31.560(4)
	alpha=90	beta=126.597(7)	gamma=90
Temperature:	170 K		

	Calculated	Reported
Volume	9236.2(19)	9236.0(18)
Space group	C 2/c	C 1 2/c 1
Hall group	-C 2yc	-C 2yc
Moiety formula	C11 H15 B F2 I N O6	C11 H15 B F2 I N O6
Sum formula	C11 H15 B F2 I N O6	C11 H15 B F2 I N O6
Mr	432.95	432.95
Dx,g cm-3	1.868	1.868
Z	24	24
Mu (mm-1)	2.128	2.128
F000	5088.0	5088.0
F000’	5079.72	
h,k,lmax	60,8,37	60,8,37
Nref	8235	7974
Tmin,Tmax	0.743,0.938	0.015,0.033
Tmin’	0.342	
Correction method= # Reported T Limits: AbsCorr = MULTI-SCAN	Tmin=0.015	Tmax=0.033
Data completeness= 0.968	Theta(max)= 25.084	
R(reflections)= 0.0421(5860)	wR2(reflections)= 0.0963(7974)	
S = 1.025	Npar= 601	

8. DFT calculations

Computational Studies

Density functional theory (DFT) calculations were performed with Gaussian16[19]. The B3LYP functional[20] with Grimme's D3BJ dispersion correction and a mixed basis set 6-31G(d)-SDD(Pd)[21] were employed for geometry optimizations. All geometry optimizations were completed by using the continuum method PCM[22] in the solution of ethyl acetate. Frequency calculations were performed to obtain thermodynamic energy corrections and to characterize the stationary points on the potential energy surface at the same level of theory as the optimizations. Intrinsic reaction coordinate (IRC) calculations were conducted to verify that transition states (TS) connected to the corresponding reactants and products. Based on the optimized geometries, single-point calculations were performed with the M06 functional[23] including Grimme D3 dispersion correction with zero-damping and the basis set 6-311++G(d,p)[21c,24] for main elements and SDD for Pd. The energies showed in this work represent M06-D3/6-311++G(d,p)-calculated single-point energies with B3LYP-D3(BJ)/6-31G(d)-calculated thermodynamic corrections, briefly denoted as ΔG for the sake of clarity. The molecular structures in the Supporting Information were drawn using CYLview[25]. The type of interaction between Br and B was analyzed by IGM[26] using Multiwfn[27] and visualized by VMD[28].

Table S5. Energy values for the reported species and imaginary frequencies for the Pathway1 and Pathway2

Zero-point energy, energy corrections, enthalpy corrections and free energy corrections of the structures calculated at B3LYP-D3(BJ)/6-31G(d) SDD, single point energies at the M06-D3/6-311++G(d,p) SDD//B3LYP-D3(BJ)/6-31G(d) SDD level of theory and imaginary frequencies of the transition states.

structures	ZPE (Hartree)	corr. to E (Hartree)	corr. to H (Hartree)	corr. to G (Hartree)	SP (Hartree)	IF
S-1	0.093162	0.103061	0.104005	0.055415	-3079.49308622	—
C1	0.625032	0.663816	0.664761	0.552542	-2505.73565155	—
C2	0.626732	0.667741	0.668686	0.548971	-5079.81731114	—
INT1	0.090831	0.099434	0.100378	0.056098	-505.417555359	—
B-1	0.180320	0.192022	0.192967	0.142626	-653.181674979	—
P1-TS1	0.273020	0.293654	0.294599	0.222732	-1158.61022798	-328.72
P1-INT2	0.275524	0.295858	0.296802	0.225138	-1158.65873729	—
P1-INT3	0.907480	0.968833	0.969777	0.810029	-6238.50050757	—
K^+	0.000000	0.001416	0.002360	-0.015176	-599.836728198	—
P1-INT4	0.908480	0.972020	0.972964	0.807378	-6838.35896245	—
P1-TS2	0.905314	0.968572	0.969516	0.805708	-6838.32869441	-322.79
1	0.279369	0.301201	0.302145	0.226138	-3732.73238517	—
P2-TS1	0.271846	0.292838	0.293782	0.219498	-1158.60126385	-357.89
P2-INT2	0.273111	0.294118	0.295062	0.221025	-1158.64373521	—
P2-INT3	0.907515	0.968705	0.969649	0.810344	-6238.50292927	—
P2-INT4	0.908481	0.971834	0.972779	0.808478	-6838.35489822	—
P2-TS2	0.905866	0.969889	0.970833	0.801750	-6838.31490383	-339.76
C3	0.279663	0.301211	0.302156	0.227888	-3732.73300239	—

Table S6. Energy values for the reported species and imaginary frequencies for the Pathway3 and Pathway4

Zero-point energy, energy corrections, enthalpy corrections and free energy corrections of the structures calculated at B3LYP-D3(BJ)/6-31G(d) SDD, single point energies at the M06-D3/6-311++G(d,p) SDD//B3LYP-D3(BJ)/6-31G(d) SDD level of theory and imaginary frequencies of the transition states.

structures	ZPE (Hartree)	corr. to E (Hartree)	corr. to H (Hartree)	corr. to G (Hartree)	SP (Hartree)	IF
S-1	0.093162	0.103061	0.104005	0.055415	-3079.49308622	—
C1	0.625032	0.663816	0.664761	0.552542	-2505.73565155	—
C2	0.626732	0.667741	0.668686	0.548971	-5079.81731114	—
INT1	0.090831	0.099434	0.100378	0.056098	-505.417555359	—
B-4	0.243359	0.258098	0.259042	0.200710	-769.830050544	—
P3-TS1	0.335512	0.359282	0.360226	0.281345	-1275.24690321	-282.24
P3-INT2	0.336920	0.360763	0.361707	0.281227	-1275.29508330	—
P3-TS2a	0.335120	0.358832	0.359776	0.279576	-1275.27484331	-635.10
P3-INT2a	0.335408	0.359678	0.360622	0.280838	-1275.29350148	—
P3-INT3	0.969017	1.033914	1.034858	0.864900	-6355.14052127	—
P3-INT4	0.970683	1.037477	1.038421	0.865088	-6954.99962672	—
P3-TS2	0.968336	1.035313	1.036257	0.862165	-6954.97176618	-317.38
K^+	0.000000	0.001416	0.002360	-0.015176	-599.836728198	—
56a	0.341558	0.366773	0.367717	0.284542	-3849.38359596	—
P4-TS1	0.335035	0.359075	0.360019	0.278439	-1275.24975462	-398.31
P4-INT2	0.337442	0.360319	0.361263	0.283241	-1275.29093225	—
P4-INT3	0.970400	1.034472	1.035416	0.872395	-6355.12552484	—
P4-INT4	0.971746	1.037891	1.038835	0.870676	-6954.98527661	—
P4-TS2	0.968680	1.035585	1.036529	0.864171	-6954.95741039	-275.11
56b	0.341937	0.366740	0.367684	0.285437	-3849.37262202	—

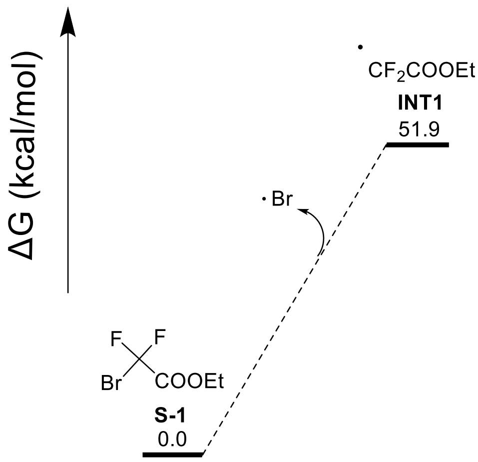


Figure S1. Calculations for the generation of radical **INT1.**

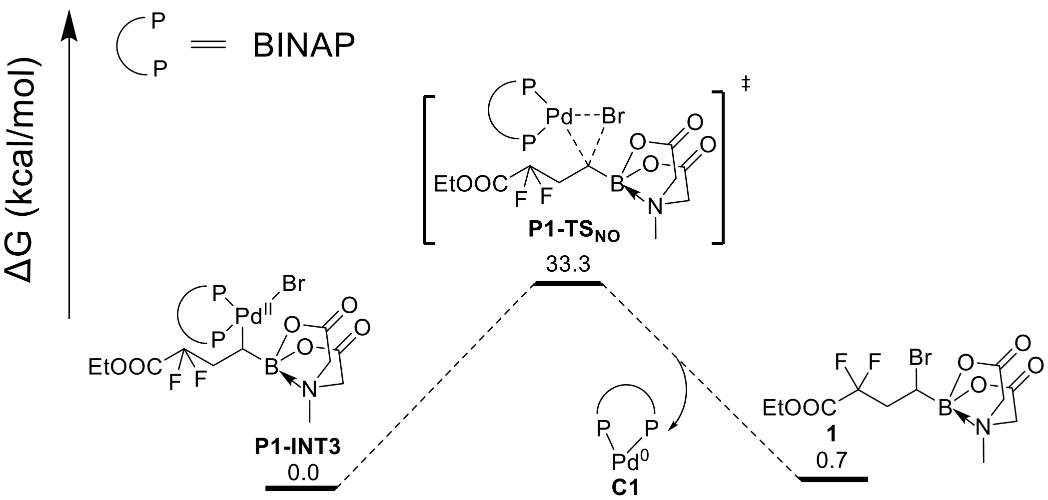


Figure S2. Calculations for the direct reductive elimination without $\mathbf{K^+}$.

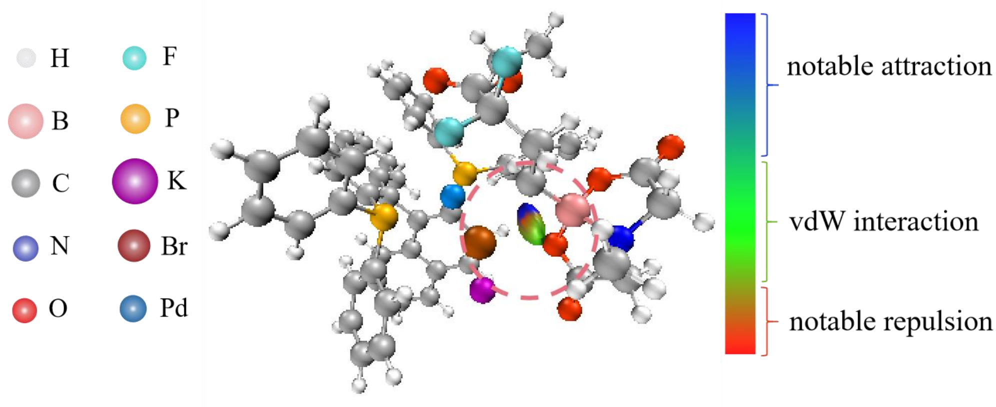


Figure S3. The type of interaction between Br and B of **P1-TS2** analyzed by IGM using Multiwfn.

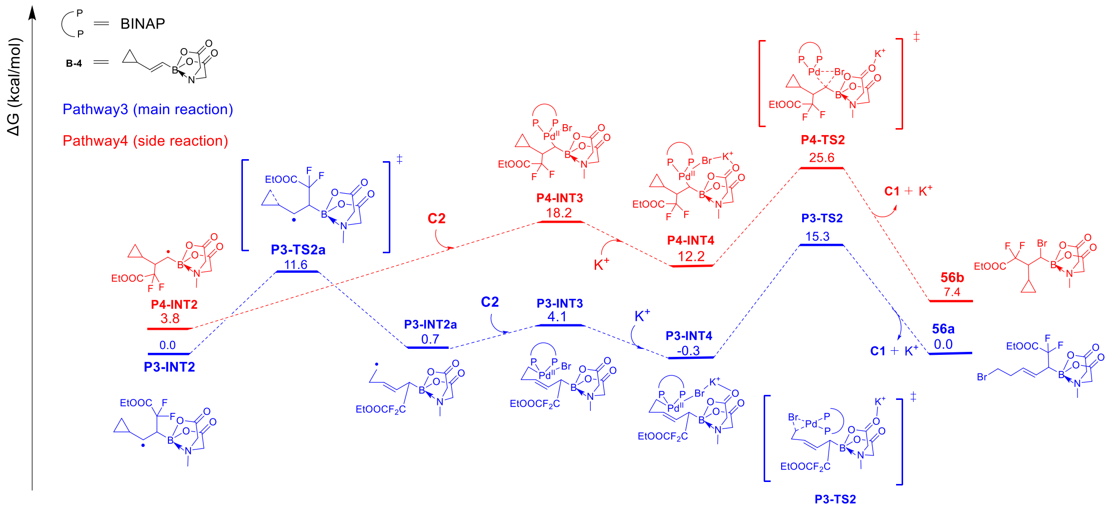
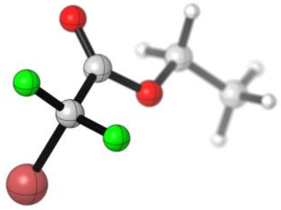


Figure S4. Free-energy profile for the formation of **56a** and **56b**, calculated at the M06-D3/6-311++G(d,p) SDD//B3LYP-D3(BJ)/6-31G(d) SDD level of theory. The SDD basis set was used for Pd. Free energies are given in kcal/mol.

DFT calculations were also carried out for the reaction between **S-1** and a substrate containing a cyclopropyl group, **B-4**, to explain the selectivity different from that in Pathway1 and Pathway2 in the model reaction (**Figure S4**). The intermediates **P3-INT2** and **P4-INT2** could be formed via similar process to that depicted in **Figure 1**. For brief, the free radical intermediate **P3-INT2** in the main reaction was selected as the zero-point of the potential energy surface (0.0 kcal/mol). However, **P3-INT2** was unstable and quickly underwent a cyclopropyl ring opening and electronic rearrangement via **P3-TS2a** to form **P3-INT2a** with a free energy barrier of 11.6 kcal/mol. The following reaction also exhibited similarity to that described in **Figure 1**. **C2** and **K$^+$** bound to the free radical intermediates **P3-INT2a** and **P4-INT2** successively to form **P3-INT4** and **P4-INT4**, wherein the free energy barrier of the latter (14.4 kcal/mol) was 11.0 kcal/mol higher than the former (3.4 kcal/mol). The transfer of Br to the α-C of the boron atom via the corresponding transient states **P3-TS2** and **P4-TS2**, with a free energy barrier of 15.6 kcal/mol and 13.4 kcal/mol respectively. Finally, the final products **56a** and **56b** were generated with the dissociation of **K$^+$** and **C1**. It was observed that each intermediate and transition state of the side reaction exhibited higher energy compared to the corresponding structure of the main reaction, which indicated that Pathway3 was thermodynamic stable thus more favorable, however, pathway4 should be also feasible because of the reasonable free energy barriers, which might result in the possibility of the formation of **56b**. Experimentally, the product of Pathway4 (**56b**) was indeed obtained.

Cartesian coordinates of the calculated structures

S-1



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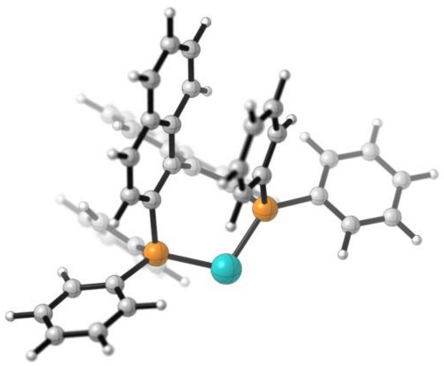
F	-1.49640800	1.74883500	0.08226400
C	0.64598900	0.83140200	-0.30798800
O	0.83808200	1.59956100	-1.21938300
O	1.50751600	-0.01428100	0.23546200
C	2.84314700	-0.03872200	-0.35500500
C	3.64257100	-1.08389800	0.39120900
Br	-1.59894400	-0.94855900	-0.25984100
H	2.73573700	-0.27272300	-1.41736300
H	3.27114000	0.96265600	-0.26149200
H	4.65285500	-1.13247500	-0.02727000
H	3.71959900	-0.83276400	1.45327700
H	3.18015200	-2.07077400	0.29524700

C1



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C	-0.19197800	-0.14727700	1.33395000
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C	-4.70262900	-1.05491700	-0.66404000
C	-3.17510700	1.73088800	0.30231400
C	-2.16934100	2.12966900	-1.85913300

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H	-1.59540600	1.76166800	-2.70569300
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C	-0.11037200	-1.77405100	3.20245500
C	1.41804100	0.13625400	3.22264200
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C	-5.65875200	-3.18451200	-1.31276400
H	-4.26865500	-4.62580300	-2.11962800
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C	4.04252700	-0.33046100	-2.91810800

C	3.23070800	-1.41186400	1.01271500
C	1.48151600	-2.76600300	0.04477300
H	1.23233700	4.56410500	-0.90470300
H	-0.06311200	5.75920400	0.80973400
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H	1.90425600	-1.82037900	5.96353000
C	5.64319300	1.38570300	-1.41371300
H	3.96902100	1.53907000	-0.07677300
C	5.34018900	-0.03800300	-3.34279600
H	3.41043300	-0.98904700	-3.50928700
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H	3.82471300	-0.50501900	1.03036000
C	1.71800400	-3.75729400	0.99569000
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H	-1.46371300	5.73026900	2.85533000
C	6.14263600	0.82198800	-2.59122800
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H	5.71926300	-0.47356300	-4.26301400
C	2.71016100	-3.57560500	1.96062300
H	4.23556800	-2.25292300	2.71698200
H	1.12124200	-4.66494200	0.98901100
H	7.14957800	1.05815300	-2.92324400
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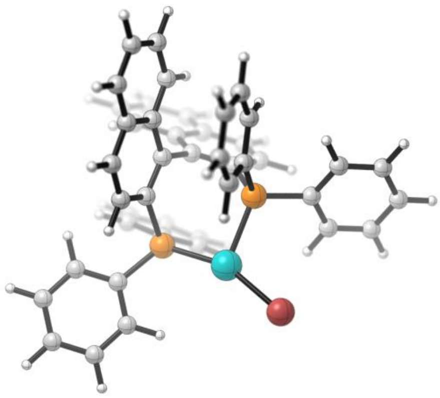
C2



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C	1.53112400	-1.77127600	-1.20938700
C	-1.25640800	-1.26968000	0.69381000
C	0.17935000	-1.61873500	2.63068600
C	3.38206200	-0.42208300	2.31600100

C	3.59330900	-2.51004700	1.10971500
C	1.21634400	-3.13828400	-1.18930500
C	1.86122900	-1.15612400	-2.42457600
C	-1.46060800	-0.97550300	-0.76008700
C	-2.40022900	-1.52955300	1.51395100
C	-0.90935100	-1.85569400	3.43223000
H	1.17396900	-1.65751000	3.05787100
C	4.45464500	-0.78119700	3.13034100
H	2.89687500	0.54010100	2.44975300
C	4.67617900	-2.86063000	1.91772000
H	3.27233500	-3.18246200	0.32238400
C	1.23767200	-3.87894200	-2.36881600
H	0.92637100	-3.61377400	-0.25760300
C	1.87530100	-1.89960200	-3.60469500
H	2.09173600	-0.09494800	-2.43834300
C	-1.32009300	0.30990900	-1.27795900
C	-1.76673700	-2.06765500	-1.63984600
C	-2.22365900	-1.80703200	2.90646700
C	-3.72467400	-1.48531500	0.99801600
H	-0.77246900	-2.08129500	4.48645500
C	5.10457300	-2.00199000	2.93175100
H	4.79249300	-0.10167400	3.90713500
H	5.18491400	-3.80596400	1.75251300
C	1.56273800	-3.25978400	-3.57793400
H	0.97480200	-4.93170700	-2.34808300
H	2.12081200	-1.41366100	-4.54438600
P	-0.74263500	1.72116800	-0.25422200
C	-1.38843900	0.51674100	-2.68554000
C	-1.83821500	-1.83808500	-3.05017400
C	-1.97617100	-3.39093000	-1.16394300
C	-3.36330100	-2.01873200	3.72507900
H	-3.87233200	-1.26806700	-0.05334500
C	-4.81084400	-1.70078700	1.81555300
H	5.94775000	-2.27770900	3.55833400
H	1.56374600	-3.83621300	-4.49833000
C	-1.42412900	3.21019800	-1.07980800
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C	-1.62942400	-0.52543100	-3.54331600
H	-1.23449900	1.51289300	-3.08417300
C	-2.10290400	-2.92505400	-3.92264800
H	-1.91811000	-3.58470900	-0.09988700
C	-2.24606500	-4.42377800	-2.03383100
H	-3.21291700	-2.22139800	4.78208900
C	-4.63201500	-1.96757900	3.19395600

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C	-0.90410900	1.67672300	2.52411700
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H	-2.14435500	-2.73407200	-4.99164100
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H	-2.40545900	-5.42603000	-1.64691900
H	-5.49791200	-2.13015100	3.82891100
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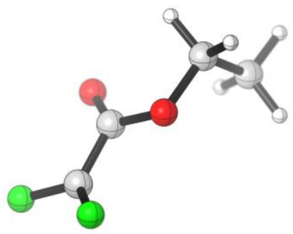
C	-1.12375600	5.55325300	-1.64368500
H	0.36446100	4.33998300	-0.66296200
C	-3.69212200	1.63557700	2.63618900
H	-3.63737500	1.65489200	0.49142400
C	-1.55098100	1.64837200	3.75950200
H	0.18085300	1.68136600	2.47007700
H	-2.51145000	-5.01825400	-4.10396100
C	-2.40212700	5.58684700	-2.20204100
H	-4.18524200	4.45409600	-2.64446500
H	-0.50264300	6.44402900	-1.64467200
C	-2.94506100	1.62354000	3.81662900
H	-4.77644800	1.60483400	2.67689100
H	-0.96558600	1.63624400	4.67416000
H	-2.78140700	6.50579300	-2.63927700
H	-3.45006600	1.59159400	4.77751300
Pd	1.55357200	1.56209100	-0.12405300
Br	3.95225000	2.25762100	-0.38073300

INT1



C	1.49077000	-0.11925500	0.18676200
F	1.85010200	-1.38332500	0.08185000
F	2.50647600	0.71777200	0.18562000
C	0.16462200	0.35223800	-0.16398100
O	-0.10550100	1.54074500	-0.25383600
O	-0.68764300	-0.67839400	-0.30417200
C	-2.07549700	-0.32705200	-0.55786500

C	-2.79873200	0.01245000	0.73417700
H	-2.48830600	-1.21876700	-1.03195700
H	-2.10088600	0.50479800	-1.26495600
H	-3.85643000	0.20228900	0.52177500
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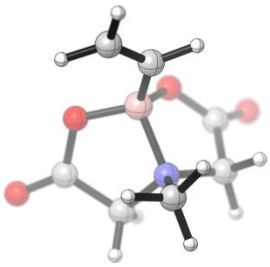
H	-2.73211900	-0.81684400	1.44512600

B-1



C	-0.42151300	2.15973100	-0.19527600
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B	-0.16208200	0.62366200	-0.43638500
O	1.07619100	0.32942200	-1.20264400
O	-1.31254700	-0.10843400	-0.96808700
C	-1.47278800	-1.32257300	-0.44369900
C	-0.42237700	-1.58092800	0.63581800
O	-2.31780300	-2.11866900	-0.77880000
C	2.09112000	-0.12137700	-0.47093000
C	1.66402000	-0.28386700	0.98960000
O	3.20376600	-0.35176100	-0.88614400
N	0.17800400	-0.25072900	0.96425700
C	-0.42283800	0.31302300	2.20292100
H	0.43216500	2.79601200	0.05371300
H	-1.77494000	3.80750600	-0.13923800
H	-2.50625800	2.16427800	-0.55861300
H	0.34353600	-2.24522100	0.22825300
H	-0.85570200	-2.05248800	1.51851400
H	2.03048200	0.57022900	1.56524100
H	2.05161800	-1.20058300	1.43610000
H	-1.50473800	0.36596300	2.07452800
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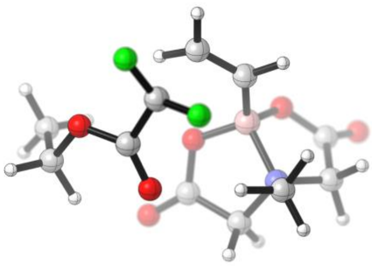
H	-0.17676000	-0.32563900	3.05448700

P1-TS1



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C	2.22648200	-1.65441200	0.00647500
B	-1.31672200	-0.16853300	-0.68493300
O	-2.58143200	0.09167500	-1.41309900
O	-0.49398800	1.04240700	-0.63970600
C	-0.63374600	1.76471000	0.46827700
C	-1.57356300	1.07856000	1.45363800
O	-0.10467300	2.83336300	0.67054700
C	-3.69345100	-0.05021000	-0.70017700
C	-3.36249000	-0.49545400	0.72131600
O	-4.81672200	0.11099800	-1.12030700
N	-1.89766000	-0.27704500	0.89884300
F	1.70337100	-2.58409100	0.80294900
F	3.28717700	-2.11925600	-0.65230000
C	-1.27858400	-1.35467300	1.72801100
C	2.29222200	-0.29119700	0.56298500
O	1.57385400	0.07035500	1.48420100
O	3.12318900	0.47145900	-0.14894800
C	2.72147900	2.62171400	-1.17478500
C	3.12355400	1.91014100	0.10186700
H	-1.01167100	-2.41849800	-1.14744100
H	1.19022100	-0.42867600	-1.93821100
H	1.18229500	-2.25229700	-2.19041300
H	-1.09707000	0.99159600	2.43004400
H	-2.48116600	1.67574200	1.55974300
H	-3.57630100	-1.56360100	0.80946300
H	-3.95235300	0.03639100	1.46861000
H	-0.21023300	-1.16450000	1.80630200
H	-1.44911100	-2.31429200	1.24116800
H	-1.74200000	-1.35240200	2.71774800
H	2.78236600	3.70418700	-1.01891500
H	3.38655000	2.35183400	-2.00117900
H	1.69119700	2.37252500	-1.43916900
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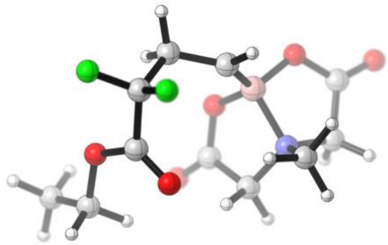
H	4.14473600	2.15183900	0.40633500

P1-INT2



C	-0.50445500	-1.62560100	-0.56226500
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C	1.99309500	-1.76109300	-0.21040600
B	-1.45459300	-0.37963500	-0.58896300
O	-2.77480600	-0.66117900	-1.17148700
O	-0.83640300	0.82893700	-1.18139000
C	-0.52770500	1.78339800	-0.30848100
C	-0.98657700	1.40637900	1.09744200
O	0.07369500	2.80043600	-0.57626000
C	-3.80130200	-0.12257800	-0.51644700
C	-3.31539500	0.62567900	0.72230800
O	-4.95906000	-0.19817100	-0.85548200
N	-1.88779200	0.23305300	0.92980200
F	1.77818400	-2.76158800	0.69483100
F	3.16171500	-2.04839900	-0.86355700
C	-1.75154300	-0.75326700	2.03934600
C	2.16419700	-0.44683300	0.57162000
O	1.66364900	-0.25996300	1.66353200
O	2.84418400	0.43743100	-0.14187100
C	3.51229200	2.66944900	-0.67980600
C	3.05603200	1.76106300	0.43992700
H	-0.82454300	-2.54766400	-0.07917700
H	1.02373200	-0.83664000	-1.86631500
H	0.93948200	-2.60815900	-1.82215700
H	-0.11200700	1.10461000	1.67701200
H	-1.48047800	2.23659500	1.60345900
H	-3.92269600	0.38985700	1.59699900
H	-3.38720300	1.69914300	0.53186400
H	-0.71104800	-1.07137500	2.09480400
H	-2.38977300	-1.61218600	1.82626700
H	-2.05879600	-0.28878700	2.97906700
H	3.72007400	3.66497500	-0.27443400
H	4.42372700	2.28910600	-1.15071100
H	2.72612600	2.76160300	-1.43399200
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H	3.80256800	1.65339300	1.23157100

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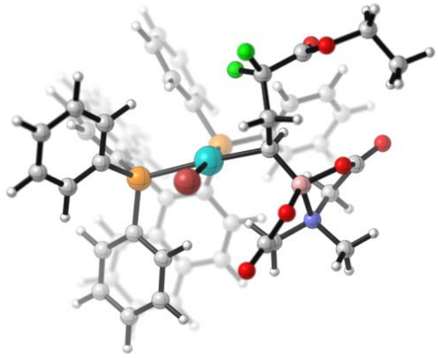

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C	-3.45375000	0.62563700	2.44165700
C	-1.14090300	-1.44220500	3.78192500
C	-2.83333300	-2.96006900	2.95509500
C	-3.86168200	-2.39870300	-0.27555600
C	-1.63801900	-3.08181100	-0.94066300
C	-2.67861500	0.67842200	-1.28102500
C	-3.89859400	2.29232800	0.22290400
C	-4.17241300	1.78434300	2.60236400
H	-3.28323200	-0.01333600	3.29775600
C	-1.29450900	-1.96335300	5.06409500
H	-0.40308900	-0.66741000	3.59831600
C	-2.97543600	-3.49226700	4.23892400
H	-3.42916500	-3.35479000	2.13942300
C	-4.40846300	-3.25504900	-1.22976000
H	-4.51553100	-1.78677800	0.33731500
C	-2.18699600	-3.93404100	-1.89740300
H	-0.56575700	-3.04523900	-0.80335900
C	-1.33576000	0.75617500	-1.62579900
C	-3.62789500	0.13184900	-2.21134900
C	-4.38892000	2.66335900	1.51419000
C	-4.10491600	3.18605800	-0.86338700
H	-4.56628400	2.04967100	3.57976900
C	-2.21217300	-2.99279600	5.29467000
H	-0.68697600	-1.57974300	5.87849000
H	-3.68327300	-4.29803400	4.41074200
C	-3.57251400	-4.01633100	-2.04923500
H	-5.48598300	-3.30909700	-1.34794900
H	-1.52586000	-4.53299400	-2.51670000

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C	-3.16697200	-0.41638200	-3.44875400
C	-5.02121100	0.08781000	-1.93508300
C	-5.05625600	3.90536600	1.67455100
H	-3.73063100	2.91743500	-1.84479200
C	-4.74880700	4.38816800	-0.67557600
H	-2.32452100	-3.40778500	6.29206900
H	-4.00115900	-4.67288500	-2.80085900
C	1.08642000	2.35654600	-1.45444800
C	-0.61440700	2.51607800	0.73064700
C	-1.78083100	-0.36808600	-3.74437400
H	0.14997000	0.25286200	-3.13433900
C	-4.09768400	-0.99698500	-4.34754900
H	-5.38839700	0.49389500	-1.00079500
C	-5.90464300	-0.46654200	-2.83455700
H	-5.41900400	4.17719200	2.66213500
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H	-4.88746500	5.06379300	-1.51446300
C	0.78339500	2.82740900	-2.74080200
C	2.27147800	2.78117000	-0.83177000
C	-1.07126700	3.76170400	0.27333000
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H	-1.42561500	-0.79002800	-4.68048700
H	-3.72809300	-1.41876600	-5.27823900
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H	-6.96568800	-0.48657000	-2.60426200
H	-5.73346200	5.70678300	0.73909100
C	1.68412400	3.65660900	-3.41236100
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C	3.17368200	3.59589800	-1.51163700
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C	-1.46282900	4.73916300	1.18312800
H	-1.12643900	3.96349200	-0.79119800
C	-0.91034400	3.26020500	3.01531200
H	-0.14924000	1.32095100	2.45608900
H	-6.14794200	-1.46409600	-4.74572600
C	2.88772100	4.02612500	-2.80916100
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H	4.09931400	3.87744500	-1.02194400
C	-1.38368900	4.48945400	2.55608100
H	-1.83649700	5.69184800	0.82136200
H	-0.84162000	3.06248700	4.08084600
H	3.59433300	4.65349800	-3.34403000

H	-1.68828700	5.25390500	3.26479400
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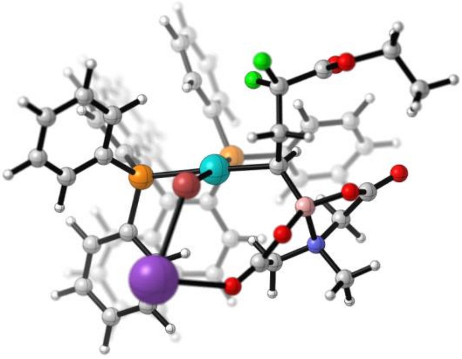
B	3.40567400	-1.47433200	-1.17258600
O	4.73316900	-0.83552200	-1.46026400
O	3.24968300	-2.92916800	-1.00312200
C	2.11521600	-3.29885600	-1.62592400
C	1.56836700	-2.12664300	-2.48888100
O	1.61456700	-4.39669900	-1.57684300
C	4.49513900	0.19199100	-2.29319700
C	3.09316400	0.05212300	-2.95819600
O	5.26324000	1.09978800	-2.51387100
N	2.82795200	-1.38235500	-2.71775400
C	3.62962100	-2.15535200	-3.72947500
H	2.84546000	0.48068400	-0.30856900
H	1.09370500	-2.47740300	-3.40572400
H	0.87215800	-1.53273600	-1.89369300
H	3.12151400	0.31494200	-4.01622400
H	2.37346200	0.68313200	-2.44379800
H	3.65809700	-3.21065900	-3.46655900
H	4.64928600	-1.77764600	-3.76779700
H	3.14929100	-2.02919200	-4.70242100
C	3.55050600	-0.78915000	1.25598800
C	3.65869300	0.41445900	2.17759500
F	2.47920100	1.11714000	2.25980400
F	3.94303400	-0.00473300	3.45627900
C	4.76026900	1.40704600	1.75484100
O	4.54260400	2.48016500	1.23400900
O	5.95759000	0.88552200	2.01050400
C	7.52776300	1.13312200	0.16354700
C	7.12445000	1.62251400	1.54265300
H	3.15074000	-1.61048900	1.85148200
H	4.58493600	-1.06226200	1.00690700
H	8.44094700	1.65066600	-0.15152100
H	7.72994600	0.05745500	0.18127700
H	6.74606100	1.32560800	-0.57629200
H	6.88621500	2.68729200	1.54830200
H	7.88981200	1.41518200	2.29226300

K^+

K	0.00000000	0.00000000	0.00000000

P1-INT4



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C	-2.74583800	-2.90507800	2.88083500
C	-3.90024200	-2.26159700	-0.21102100
C	-1.71582800	-2.68353100	-1.15759400
C	-2.72707200	0.88593000	-1.22909000
C	-3.88640400	2.49168800	0.33387800
C	-4.09458300	1.94789300	2.71395500
H	-3.20374900	0.12913700	3.35502600
C	-1.19891500	-1.93130300	4.99477600
H	-0.40384100	-0.53418300	3.56845000
C	-2.83069500	-3.49812700	4.14341200
H	-3.34751500	-3.29186400	2.06592900
C	-4.47638700	-3.07289400	-1.18798200
H	-4.53263300	-1.75707500	0.51247700
C	-2.29219700	-3.49273700	-2.13701400
H	-0.64494800	-2.52846900	-1.14338700
C	-1.39609700	0.95681000	-1.62327900
C	-3.71417100	0.35301300	-2.12748200
C	-4.33411400	2.84562800	1.64580700
C	-4.12221400	3.40114300	-0.73293400
H	-4.45778400	2.20167500	3.70604600
C	-2.06295200	-3.01094000	5.20181000
H	-0.59031500	-1.55354800	5.81087900
H	-3.50197300	-4.33809300	4.29797800
C	-3.67588200	-3.68744400	-2.15402800
H	-5.55341700	-3.20328500	-1.21078400
H	-1.65989400	-3.95465100	-2.89013600
P	-0.02313800	1.44281900	-0.49720500

C	-1.01304600	0.42630800	-2.89085000
C	-3.30646500	-0.17355100	-3.39304900
C	-5.09375500	0.29818000	-1.79033400
C	-4.98662200	4.08983000	1.84527500
H	-3.78206400	3.14457600	-1.72989800
C	-4.75266100	4.60369600	-0.50710700
H	-2.13317000	-3.47100700	6.18296200
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C	1.07835600	2.50726400	-1.50565400
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C	-1.93309500	-0.12812100	-3.74158200
H	0.02471400	0.46518000	-3.19600700
C	-4.27507700	-0.73604800	-4.26272700
H	-5.42097900	0.68526300	-0.83350100
C	-6.01444200	-0.24171300	-2.66095900
H	-5.31638700	4.34962700	2.84740300
C	-5.18806300	4.95468100	0.79378900
H	-4.91522000	5.29170700	-1.33135400
C	0.79567000	2.95652300	-2.80450100
C	2.26046200	2.93361400	-0.87677700
C	-1.03772800	3.94362300	0.25578800
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H	-1.61700500	-0.53379800	-4.69870800
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C	-5.60473100	-0.76816500	-3.90755300
H	-7.06407300	-0.26987600	-2.38442100
H	-5.68134300	5.90807600	0.95717200
C	1.71636700	3.75822400	-3.48285400
H	-0.13582300	2.69419700	-3.29045700
C	3.18248600	3.71988900	-1.56337700
H	2.47120700	2.65694400	0.14831700
C	-1.41221100	4.92529100	1.16803800
H	-1.09919100	4.14567500	-0.80841200
C	-0.86378700	3.44012900	2.99664800
H	-0.12741800	1.49362000	2.43591500
H	-6.34038100	-1.19776500	-4.58068400
C	2.91907000	4.12223800	-2.87484000
H	1.48888000	4.09716500	-4.48910000
H	4.10418200	4.00284400	-1.06726700
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H	-0.79090600	3.24202100	4.06169800
H	3.64064800	4.72737900	-3.41499200
H	-1.61926500	5.44163600	3.25084600

Pd	0.63141700	-0.56247300	0.44024100
Br	1.06109700	-2.84513200	1.51224500
C	2.70035300	-0.37708200	-0.07608800
B	3.41613600	-1.27957400	-1.22327300
O	4.77623300	-0.70122300	-1.42838400
O	3.16664300	-2.74196900	-1.09823400
C	2.04860800	-3.02019300	-1.76502100
C	1.61979400	-1.82116400	-2.65243000
O	1.44304500	-4.07428000	-1.71595900
C	4.62228100	0.36257900	-2.24300100
C	3.25708000	0.29363000	-2.98824000
O	5.43343800	1.24487700	-2.38954300
N	2.92191500	-1.13499900	-2.79147100
C	3.74509400	-1.92236700	-3.77671600
H	2.83421700	0.66804200	-0.35939800
H	1.18261200	-2.13977900	-3.59947600
H	0.91746300	-1.20161300	-2.09278200
H	3.35835400	0.56893000	-4.03805000
H	2.52908900	0.94304800	-2.50836300
H	3.70011400	-2.98495700	-3.54685200
H	4.78357200	-1.60104500	-3.73787600
H	3.33604000	-1.74005800	-4.77250500
K	0.10321000	-5.52818100	0.10855900
C	3.53344800	-0.59957300	1.20930800
C	3.59961000	0.58636200	2.16028800
F	2.40987300	1.27369000	2.21952800
F	3.84493600	0.13803800	3.43573900
C	4.70136200	1.59887300	1.78936800
O	4.48442300	2.65596800	1.23676400
O	5.89323300	1.11093500	2.12008600
C	7.59092700	1.33979500	0.38787000
C	7.06882600	1.87113700	1.71016300
H	3.15465500	-1.44235900	1.78749300
H	4.57679600	-0.83853600	0.96422300
H	8.50295400	1.88247500	0.11495000
H	7.83540700	0.27584900	0.46968500
H	6.85756100	1.46809700	-0.41312300
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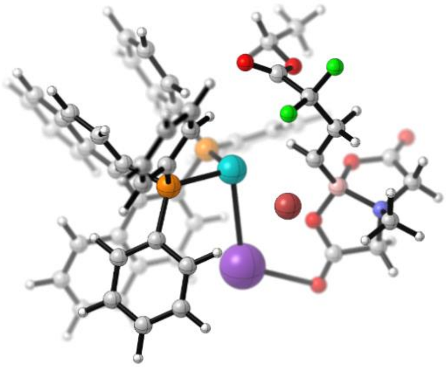
H	7.78102000	1.72274200	2.52335800

P1-TS2



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C	3.28656900	0.65750400	2.90152900
B	3.98839800	-0.41425500	-0.95375500
O	4.50899000	0.86929900	-1.46138900
O	3.07533100	-1.04589200	-1.91621900
C	3.66344500	-1.93682000	-2.70868200
C	5.16411000	-1.94289400	-2.47556600
O	3.05848000	-2.63739500	-3.49370800
C	5.83973800	0.96393400	-1.52931400
C	6.47644900	-0.35405700	-1.09471100
O	6.44311200	1.95498300	-1.86024900
N	5.36446000	-1.35277500	-1.10586900
F	2.57956100	-0.34930300	3.48369800
F	4.19357400	1.09527700	3.84150400
C	5.58818700	-2.44813300	-0.11307100
C	2.31614200	1.83762300	2.67623300
O	1.27942500	1.95599400	3.28921400
O	2.82060200	2.70373400	1.80206600
C	2.99241400	4.92617600	0.91239500
C	2.06807600	3.94254500	1.59441300
H	2.54471000	0.62217200	0.28792700
H	4.65212700	-0.70793200	2.06836100
H	4.78338400	0.94657000	1.44763500
H	5.59187600	-2.94272900	-2.54397600
H	5.63440600	-1.30515700	-3.22854300
H	7.29829200	-0.65506600	-1.74498100
H	6.85833300	-0.25541700	-0.07576900
H	4.73559200	-3.12399400	-0.13107400
H	6.50698400	-2.97828700	-0.37156400
H	5.68027800	-2.01830900	0.88161200
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H	3.86875500	5.13485800	1.53345100

H	3.32571100	4.54817600	-0.05759900
H	1.19412400	3.69762500	0.98784200
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K	0.59275100	-2.58412900	-2.00634100
P	-1.54476800	-1.30158600	1.25839100
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C	-1.45632300	-1.68024500	3.05034600
C	-2.06849400	-2.90994500	0.55235800
C	-3.35830900	0.41949900	-0.10752800
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C	-1.09397100	-3.92111100	0.44231600
C	-2.76007900	0.00750100	-1.42022900
C	-4.35651000	1.44779200	-0.13335500
C	-4.62832300	1.20414800	2.28843900
H	-3.40709400	-0.25209500	3.23504200
C	-0.47899100	-1.15414600	5.20840700
H	0.01513000	-0.13469500	3.38067500
C	-2.09632300	-2.94308800	5.01949300
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C	-3.67412400	-4.39120400	-0.50847300
H	-4.13164200	-2.41575400	0.20685300
C	-1.40824100	-5.14844500	-0.14260800
H	-0.09274200	-3.74560000	0.82816700
C	-1.50913700	0.45140900	-1.84810500
C	-3.55018200	-0.83615200	-2.27990500
C	-4.98493600	1.85759500	1.08477900
C	-4.72417600	2.11426700	-1.33532200
H	-5.11495600	1.50106700	3.21362300
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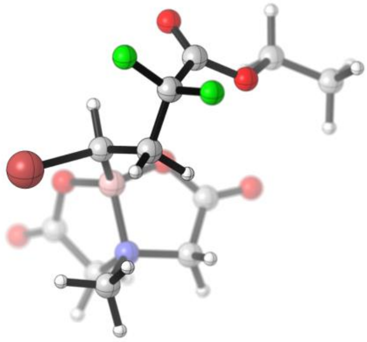
H	-2.68223700	-3.73531800	5.47674900
C	-2.69835700	-5.38075700	-0.63430200
H	-4.68062200	-4.56414400	-0.87734000
H	-0.64961200	-5.92347000	-0.21142100
P	-0.33749300	1.39589900	-0.77869700
C	-0.99521400	-0.00928700	-3.09998300
C	-3.00795700	-1.29612800	-3.52329400
C	-4.87497700	-1.23438100	-1.94708500
C	-5.93832400	2.90866400	1.06091800
H	-4.25119100	1.82351700	-2.26584400
C	-5.65370600	3.12929700	-1.32814400

H	-1.14435800	-2.36372700	6.86588000
H	-2.94147700	-6.33252000	-1.09737100
C	0.58555700	2.41457700	-2.00805300
C	-1.31206500	2.67304300	0.11521200
C	-1.71316600	-0.85705000	-3.90776100
H	-0.01549600	0.32683600	-3.42316300
C	-3.77271100	-2.16194500	-4.34826500
H	-5.32009900	-0.87088000	-1.02911900
C	-5.59902500	-2.06654900	-2.77174400
H	-6.40110800	3.21076800	1.99660600
C	-6.26815300	3.53441100	-0.11931200
H	-5.91457300	3.62823900	-2.25689900
C	0.00691700	2.96619100	-3.16474100
C	1.94316600	2.65137700	-1.75986200
C	-1.98342900	3.71584800	-0.54031000
C	-1.34795900	2.61173600	1.51408100
H	-1.30003900	-1.19100400	-4.85670300
H	-3.33977300	-2.50294700	-5.28517200
C	-5.04190800	-2.54756200	-3.97977200
H	-6.60808300	-2.35472200	-2.49270300
H	-6.99768900	4.33876300	-0.12740700
C	0.77115300	3.73579900	-4.04026900
H	-1.03628700	2.77594000	-3.39543500
C	2.71418500	3.41282400	-2.64064600
H	2.41289900	2.23367700	-0.87912700
C	-2.69143700	4.66610600	0.19197800
H	-1.96559100	3.78510400	-1.62144100
C	-2.05396100	3.56535700	2.24643400
H	-0.81938500	1.81564400	2.02383000
H	-5.62172000	-3.20657400	-4.61875700
C	2.12738500	3.96004100	-3.78132200
H	0.30992700	4.15519500	-4.92980400
H	3.77275000	3.54987700	-2.44180800
C	-2.73045000	4.59167200	1.58643400
H	-3.22461800	5.45676000	-0.32697500
H	-2.07767600	3.49992400	3.33010900
H	2.72231400	4.55042900	-4.47188600
H	-3.28794100	5.33098500	2.15404500
Pd	0.52523000	-0.34886600	0.50048400

1



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C	-1.92965200	-1.72800200	0.36210300
B	1.00592400	0.55029800	-0.34478700
O	-0.11147600	1.48565100	-0.60942800
O	2.03936800	0.62701300	-1.36397200
C	3.05228800	1.43728000	-1.05661300
C	2.83434100	2.06062500	0.31898600
O	3.99905500	1.66831000	-1.76804500
C	-0.33545600	2.38514600	0.34756500
C	0.64899600	2.19215800	1.49871900
O	-1.21233400	3.21630100	0.32693300
N	1.71912100	1.29260900	0.97220300
F	-1.68620200	-2.91616300	-0.26008500
F	-2.79888100	-1.96974300	1.39341700
C	2.26221600	0.39148800	2.03310200
C	-2.59670000	-0.78022100	-0.65517600
O	-2.54453500	-0.95133200	-1.85220100
O	-3.14623500	0.25185000	-0.02359600
C	-4.42256500	2.27471500	0.04873000
C	-3.71434900	1.30102700	-0.86655600
H	-0.01596400	-1.17399500	-1.15635400
H	-0.27953500	-1.84580900	1.68406200
H	-0.90502500	-0.21945500	1.41838500
H	3.73913500	2.02659500	0.92595400
H	2.54311300	3.10523900	0.18768800
H	1.05222900	3.13746100	1.86276100
H	0.13629700	1.69626900	2.32654100
H	3.00895400	-0.26623600	1.59280500
H	2.70549900	0.99999600	2.82364000
H	1.45248200	-0.21197700	2.44000800
H	-4.86623000	3.07594600	-0.55133400
H	-5.22199800	1.77802500	0.60741800
H	-3.71425000	2.72294900	0.74983700

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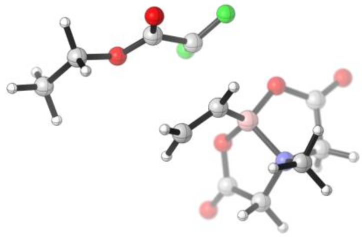
P2-TS1



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C	0.84009000	1.09514700	1.29118000
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B	-1.11713000	-0.01691300	0.03461500
O	-1.53413400	-1.30929000	-0.50300800
O	-1.05381500	1.03117300	-1.00573800
C	-1.77081800	2.12173500	-0.73847600
C	-2.54654400	1.93985300	0.56770800
O	-1.79204600	3.12344500	-1.41467600
C	-2.85671100	-1.47215400	-0.55450000
C	-3.56531100	-0.27148200	0.07163800
O	-3.42090000	-2.42556100	-1.03523800
N	-2.51667700	0.47768200	0.83172300
F	1.03153500	-2.55448200	-0.15163900
F	1.21783600	-0.92203700	-1.61385300
C	-2.56870100	0.14253000	2.28068600
C	2.78608500	-1.00049500	0.20970900
O	3.25272200	-1.60210700	1.15935600
O	3.30337300	0.09216100	-0.36163200
C	4.83455600	1.92135100	-0.44694300
C	4.51230700	0.61573500	0.24864400
H	0.23265100	-0.87045600	1.70855200
H	1.56739900	1.14081300	2.09808700
H	-2.01417400	2.45453400	1.37154700
H	-3.56271600	2.33111400	0.50756700
H	-4.38656300	-0.57757800	0.72019400
H	-3.96795800	0.35578300	-0.72727600
H	-1.72700700	0.62009600	2.78041200
H	-2.49111500	-0.94010100	2.39381300
H	-3.51187200	0.49292500	2.70544700
H	5.74434000	2.35156600	-0.01589100
H	4.99958200	1.76358400	-1.51709400
H	4.01780100	2.63892800	-0.32200000

H	4.32751800	0.74982000	1.31816500
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H	0.75585800	1.98428200	0.67178600

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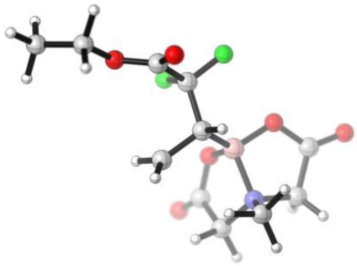

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B	-1.21780200	-0.09932200	-0.12695600
O	-1.72376500	-1.36782000	-0.63907300
O	-1.34849300	0.98845000	-1.11486300
C	-1.99344100	2.06642700	-0.67028800
C	-2.51740300	1.82486700	0.74633300
O	-2.13260500	3.09720400	-1.28538400
C	-3.03064100	-1.54285800	-0.43553500
C	-3.60134700	-0.37848400	0.37143600
O	-3.67769200	-2.47925800	-0.83787900
N	-2.42287100	0.35178700	0.94410200
F	0.95693500	-1.95504100	-0.90959700
F	1.36709400	0.11203000	-1.53990700
C	-2.21044300	-0.03545500	2.36641300
C	2.68473400	-0.84534100	0.20677200
O	2.91299200	-1.69889900	1.03696100
O	3.53415800	0.09041200	-0.20642800
C	5.62988500	1.24083600	-0.15459600
C	4.84815900	0.07913000	0.42039200
H	0.23522700	-0.94766900	1.34758200
H	0.90183400	1.25837100	2.16162500
H	-1.85402700	2.32123300	1.45842800
H	-3.53360100	2.19663200	0.88445300
H	-4.27619800	-0.71973800	1.15661000
H	-4.15579300	0.27867700	-0.30250300
H	-1.31167100	0.45502700	2.73638100
H	-2.08898600	-1.11803800	2.42402700
H	-3.07312600	0.27149700	2.96168300
H	6.62833000	1.26606400	0.29376300
H	5.73982600	1.13902000	-1.23846900

H	5.13040800	2.19086600	0.05860200
H	4.71012200	0.16326900	1.50192600
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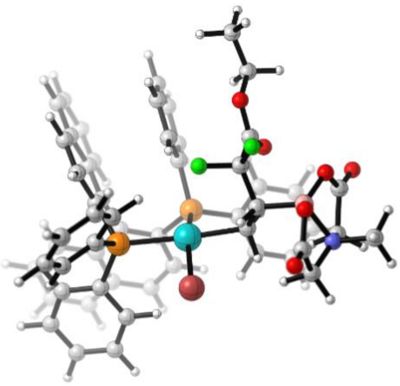
H	0.90617400	1.94688700	0.43370200

P2-INT3



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F	-4.14035400	0.46016900	-2.43567600
C	-2.97335300	2.01647400	-1.10799400
O	-2.80204400	2.42767700	0.01840600
O	-3.00948800	2.77997300	-2.19838900
C	-2.81489700	4.87665100	-3.32957000
C	-2.85945600	4.20915500	-1.97189100
H	-3.29408000	-1.43624600	-0.88747500
H	-2.58801500	-1.19606800	1.48908000
H	-2.71362700	5.95919600	-3.20021300
H	-1.95980800	4.51727000	-3.91049000
H	-3.73018000	4.67913400	-3.89583100
H	-3.70773300	4.54523700	-1.36901500
H	-1.94156100	4.37133500	-1.40357900
H	-2.40724500	0.55053400	1.24401400
P	1.63239400	-1.57163900	-0.83173700
C	2.60038900	-0.11060500	-1.41512400
C	1.38473500	-2.56867500	-2.34752500
C	2.76948500	-2.51711900	0.23319300
C	3.16700400	0.77812200	-0.50260400
C	2.61864400	0.20072300	-2.80157200
C	0.29573200	-2.23557800	-3.16991800
C	2.21273800	-3.63805600	-2.70730000
C	4.11654300	-2.71784900	-0.09975200
C	2.27412500	-3.02101000	1.44404900

C	3.19655000	0.47502900	0.96339100
C	3.77776200	1.98879100	-0.96528700
C	3.18087000	1.36681500	-3.25993500
H	2.17846200	-0.49196400	-3.50812200
C	0.05883800	-2.94380400	-4.34615400
H	-0.37239000	-1.43102000	-2.88157100
C	1.96423400	-4.35510700	-3.87987000
H	3.04304700	-3.92340200	-2.07156500
C	4.95571400	-3.41640700	0.76581400
H	4.51524700	-2.30076900	-1.01937000
C	3.11895700	-3.71212000	2.31189000
H	1.23136500	-2.86028000	1.69848200
C	2.06674400	0.58465600	1.77539000
C	4.44728000	0.05731100	1.53086300
C	3.77135400	2.29087800	-2.36388200
C	4.38324300	2.92157200	-0.07862900
H	3.18230500	1.59055400	-4.32345400
C	0.89280700	-4.00694300	-4.70329100
H	-0.78657000	-2.67669300	-4.97339100
H	2.60932000	-5.18740500	-4.14644500
C	4.45965000	-3.90880300	1.97476300
H	6.00163200	-3.55199000	0.50952000
H	2.73207200	-4.08955700	3.25399600
P	0.39292300	0.95976800	1.07081400
C	2.16893900	0.27075500	3.15859800
C	4.51501300	-0.29196600	2.91593200
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C	4.35508200	3.50199200	-2.81927400
H	4.38780300	2.71174600	0.98422600
C	4.95151700	4.08279500	-0.55081700
H	0.70133600	-4.56681800	-5.61412000
H	5.11961200	-4.43848300	2.65546100
C	-0.60736400	1.52418900	2.50307600
C	0.65211700	2.41725900	0.00754200
C	3.34827800	-0.16638700	3.70714600
H	1.30454000	0.38173300	3.79846400
C	5.74324000	-0.74175600	3.46716200
H	5.60442500	0.20349700	-0.29694000
C	6.81631800	-0.47452900	1.32010200
H	4.33553900	3.71915500	-3.88393100
C	4.93615000	4.38084800	-1.93404100
H	5.40774300	4.78128600	0.14454400
C	-1.07809300	2.83463600	2.63309000
C	-1.04174500	0.55187800	3.42296100

C	1.26967400	3.57692800	0.49801900
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H	3.39916500	-0.41032500	4.76491200
H	5.77204600	-1.01005900	4.51978400
C	6.87385000	-0.83038800	2.68827800
H	7.71007400	-0.54791800	0.70749200
H	5.38303700	5.30343200	-2.29262100
C	-1.94489500	3.17295200	3.67525700
H	-0.80396500	3.58737700	1.90544100
C	-1.89317400	0.89378000	4.47004700
H	-0.74179000	-0.48385500	3.29076300
C	1.48839300	4.66332600	-0.34699900
H	1.59917400	3.62304600	1.53144600
C	0.51479000	3.43261200	-2.18599300
H	-0.18903200	1.45267500	-1.72221100
H	7.81021600	-1.17258200	3.11894200
C	-2.34968000	2.20964600	4.59767300
H	-2.31331800	4.19125500	3.75347500
H	-2.21487100	0.13106400	5.17325600
C	1.11656300	4.59119900	-1.69111700
H	1.97523800	5.55410100	0.03693500
H	0.23781100	3.36381700	-3.23339700
H	-3.02862100	2.47551000	5.40232700
H	1.30737800	5.43081100	-2.35242000
Pd	-0.46282500	-0.93869500	0.13723500
Br	-1.36705400	-3.31222500	-0.13014000
B	-5.04223700	-0.35531900	-0.03944000
O	-5.45971900	1.03709900	0.19352600
O	-5.75746800	-1.29906500	-0.92877300
C	-5.63582900	-2.52161300	-0.37053500
C	-5.17849700	-2.40185200	1.11611700
O	-5.86997000	-3.56268200	-0.93350100
C	-5.25552000	1.32550000	1.49922900
C	-5.01336800	0.02561900	2.32000600
O	-5.29284700	2.43406000	1.97040800
N	-5.55856200	-0.98955300	1.38311300
C	-7.05684800	-0.94988900	1.53978900
H	-5.70050600	-3.11473300	1.75529900
H	-4.09938900	-2.55207600	1.18889500
H	-5.55349700	0.05284400	3.26689800
H	-3.95285900	-0.11749000	2.50636500
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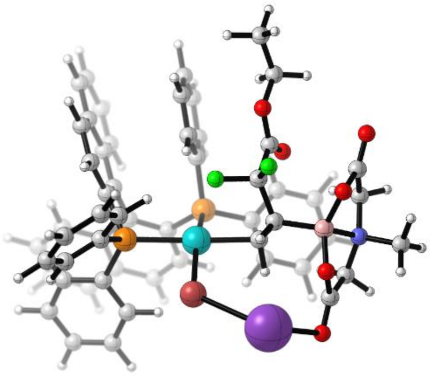
P2-INT4



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F	1.76908800	0.32570300	2.12891700
F	3.89071000	0.57792700	2.55309500
C	2.82736500	2.14620200	1.13044100
O	2.66648500	2.50862300	-0.01885600
O	2.86469400	2.94277100	2.18525900
C	2.72568000	5.08587900	3.24035700
C	2.78371300	4.37381600	1.90707500
H	3.32407300	-1.27358800	1.00684600
H	2.43521400	-1.37034300	-1.24015300
H	2.67815900	6.16657800	3.07191400
H	1.83647800	4.78542100	3.80356700
H	3.61294400	4.86747800	3.84199200
H	3.66983500	4.64052500	1.32496000
H	1.89289500	4.55230700	1.30209300
H	2.27091900	0.39361400	-1.29940700
P	-1.81659600	-1.38446900	1.00296100
C	-2.78752300	0.14223600	1.36679000
C	-1.64061000	-2.20038000	2.63300500
C	-2.90782200	-2.44625300	0.00416300
C	-3.31724000	0.91115900	0.33205700
C	-2.84329500	0.62676100	2.70155000
C	-0.60973000	-1.75527600	3.47719200
C	-2.46698800	-3.24756300	3.05613200
C	-4.26627400	-2.61766300	0.30648300
C	-2.36438700	-3.07777600	-1.12330300
C	-3.31579000	0.42507100	-1.08369000
C	-3.92126700	2.17877800	0.61719500
C	-3.40107900	1.84819100	2.98961700
H	-2.43754100	0.02463800	3.50477700

C	-0.43085300	-2.32841600	4.73429300
H	0.06058800	-0.97064000	3.14358800
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H	-3.25261600	-3.61889100	2.40841100
C	-5.06902400	-3.41414900	-0.50740200
H	-4.70126500	-2.10468300	1.15861200
C	-3.17297300	-3.86692100	-1.94055000
H	-1.31364800	-2.93570600	-1.35648300
C	-2.16797600	0.42508100	-1.87735200
C	-4.55839300	-0.04777500	-1.62412300
C	-3.94837200	2.65815200	1.96500600
C	-4.48366700	2.99811300	-0.40008200
H	-3.43178600	2.20515400	4.01557700
C	-1.26408100	-3.36933000	5.15411100
H	0.36677800	-1.97178600	5.37954100
H	-2.92065900	-4.64513300	4.62743400
C	-4.52503000	-4.03441000	-1.63419400
H	-6.12357400	-3.52782800	-0.27786400
H	-2.74987600	-4.34303400	-2.82023200
P	-0.51087800	0.85983500	-1.17622500
C	-2.24575800	-0.04249000	-3.21800500
C	-4.60098500	-0.55821600	-2.95928900
C	-5.76204700	-0.05485500	-0.86557800
C	-4.52112100	3.92667800	2.24344400
H	-4.46330100	2.65314800	-1.42682400
C	-5.04087200	4.21991400	-0.09827500
H	-1.11962000	-3.82236600	6.13056900
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C	-0.76449200	2.43344500	-0.29458700
C	-3.41872300	-0.53021300	-3.73662900
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C	-6.93337300	-0.54272500	-1.39878100
H	-4.52837200	4.27855900	3.27150300
C	-5.05859500	4.69343000	1.23505400
H	-5.46333700	4.83023300	-0.89098100
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C	-1.34003900	3.53700600	-0.94112700
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H	-5.83121900	-1.45558400	-4.49214600

C	-6.96613300	-1.05832000	-2.71598800
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C	2.03460100	2.71671900	-3.85591200
H	0.84986600	3.33232500	-2.17426900
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H	0.59489600	-0.82397500	-3.25690000
C	-1.55377400	4.72300900	-0.24143600
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H	-0.40825500	3.76228100	2.81658800
H	3.13065600	1.82824500	-5.48578000
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Pd	0.31719200	-0.89153400	0.03254600
Br	1.20029300	-3.20245100	0.74935400
B	4.90767900	-0.30106800	-0.09498000
O	5.70809300	0.68918000	0.64108300
O	5.25504200	-1.74588900	-0.31771100
C	4.89732500	-2.07209800	-1.57753100
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C	5.62882600	1.86731500	-0.02925100
C	5.11898000	1.63721500	-1.47916600
O	5.91690200	2.93634300	0.44669100
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H	5.66554300	2.24876100	-2.19777500
H	4.05027000	1.84411800	-1.53706100
H	7.43178000	0.60591800	-1.06671500
H	7.12138400	0.39862100	-2.81139300
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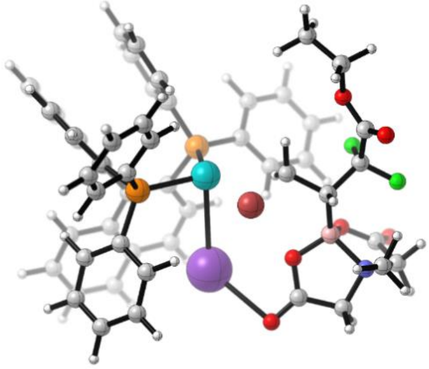
K	4.24835500	-4.27392800	0.65288200

P2-TS2



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H	-4.51308400	0.27284700	1.43412000
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H	-2.94228700	-5.53294700	3.40500100
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H	-5.17526700	-4.67267100	2.61456400
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P	1.94056000	0.78343200	1.61452800
C	3.45301300	-0.06258500	0.98163900
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C	3.68958400	-0.23653200	-0.38513400
C	4.30005800	-0.70928900	1.92583700
C	1.29330300	-0.56014300	3.96863700
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C	2.89444500	0.42347200	-1.47941500
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H	4.30493000	2.50313300	0.85214900
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H	0.23793200	3.01339200	2.15090400
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H	5.95748700	-2.01265100	2.26751200
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C	6.11582800	-2.09551300	-2.57914600
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H	5.28976800	1.61377400	-0.92025400
C	5.27009400	3.22319000	-2.31754200
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H	6.31998400	-2.24143600	-3.63579700
C	-0.49159600	-3.42701500	-2.58139000
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C	-2.58505700	-3.14884500	-3.77072700
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C	3.70558400	-4.78557800	-0.12491300
H	4.16597100	-4.76795800	-2.23213300
H	3.06341100	-4.55131900	1.92121800
H	-3.38654200	-3.56560000	-4.37335800
H	4.41582300	-5.57465300	0.10353500
Pd	-0.06356300	-0.14748300	0.76305500
Br	-1.97244700	0.86090900	2.21180200
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O	-4.39697700	0.56490000	-2.03802100
O	-3.17624200	2.01902000	-0.57619500
C	-3.54052600	3.28648600	-0.71567200
C	-5.04533000	3.41165100	-0.86370700
O	-2.75351600	4.21220100	-0.74666400
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O	-5.85705600	0.42682700	-3.74545800
N	-5.62574700	2.05473900	-0.57666400
C	-6.34101900	2.06564800	0.73719500
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H	-5.27201300	3.71738400	-1.88727100
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H	-5.64476500	2.38555300	1.51385100
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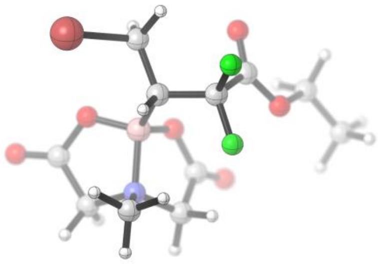
C3



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O	1.54312400	2.23559700	-1.19768700
O	2.95511800	0.96159100	0.03672800
C	5.17727300	0.27418600	-0.51311400
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H	-1.10401900	1.50621000	-1.54589500
H	5.95688600	0.28896200	-1.28167100
H	5.57403500	0.74783200	0.39032200
H	4.92541600	-0.76642700	-0.29289300
H	3.52599500	0.53559000	-1.90464900
H	4.16230500	2.06127900	-1.24818400
H	-1.06043700	2.77031800	-0.29369400
Br	-3.24581300	1.57643400	-0.25169600
B	-0.41382700	-0.71525500	-0.15251300
O	0.82167100	-0.91652800	-0.94119900
O	-1.59400300	-1.08088600	-0.92491500
C	-1.99088700	-2.34220500	-0.76221700
C	-1.09032900	-3.05360500	0.24253300
O	-2.91627400	-2.85949800	-1.33882900
C	1.69246900	-1.78461200	-0.42095000
C	1.17737500	-2.30728200	0.91683100
O	2.75017200	-2.08446900	-0.92147800
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H	1.36577300	-3.37211100	1.05285000
H	1.67005400	-1.74870400	1.71384700
H	-1.86264900	-1.45987600	2.22257600
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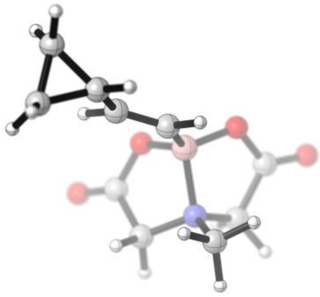
B-4



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C	4.53120100	0.07424100	0.59326800
B	-0.46197100	-0.37575300	-0.37331600
O	-1.40982600	-1.32977300	-0.96478600
O	-0.39795300	0.88581700	-1.15304900
C	-0.61971000	1.98679200	-0.44003100
C	-0.99458600	1.62306900	0.99825000
O	-0.52216100	3.11855200	-0.85636300
C	-2.66868500	-1.16403800	-0.56222400
C	-2.75318000	-0.05748500	0.48979400
O	-3.61929000	-1.78776400	-0.97319800
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C	-1.07380600	-0.53483200	2.22128800
H	0.96670500	-1.98330600	0.45057800
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H	5.35186700	-1.35165800	-0.91638900
H	4.42437500	0.05000300	-1.63238500
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H	5.20405200	-0.26540600	1.37533500
H	-0.11555400	1.74768300	1.63582600
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H	-0.01345400	-0.43707600	2.45123900
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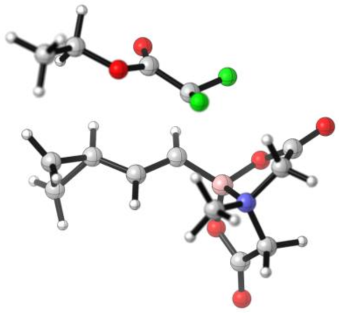
P3-TS1



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O	-2.23307200	-0.85537600	-1.24485700
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O	-4.20791300	2.69192500	-0.18854800
C	-2.62327800	-1.86656800	-0.47166800
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O	-3.06653500	-2.91767200	-0.87091700
N	-2.24162400	-0.03541900	1.02049400
C	-1.41551700	0.43868100	2.16565500
C	1.92898300	1.98425200	-0.78138800
C	2.20426600	3.48914100	-0.81239400
C	2.93878800	2.62982600	0.16236300
C	0.90693200	-1.48543400	-0.06083900
F	0.74947500	-1.68908000	1.26685900
F	0.20927900	-2.40386800	-0.74358600
C	2.30190400	-1.31034500	-0.52318100
O	2.62616200	-1.43591600	-1.69049500
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H	0.25813200	2.08422600	0.59038500
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H	-4.35350400	-0.00968400	0.70533400
H	-1.50818100	-1.98990200	1.36355500
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H	-1.88907100	0.13321200	3.10163600
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H	1.41941600	4.14169300	-0.44107300

H	2.66704500	2.68648000	1.21269900
H	3.98880700	2.42330500	-0.01976800
H	6.22628400	0.08195400	1.12226500
H	4.71499200	0.74504200	1.77798700
H	5.16864600	-0.93930400	2.11786000
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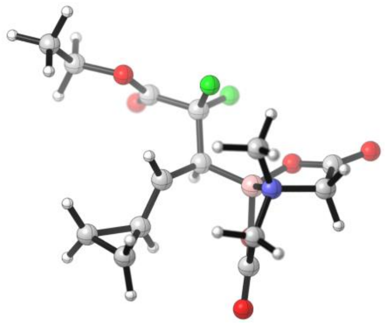
P3-INT2



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C	-2.43869800	1.38032600	1.03341900
O	-3.10849200	2.74736100	-0.85702900
C	-2.99678100	-1.99828400	-0.10040800
C	-3.31321800	-0.93894700	0.95189900
O	-3.63454200	-3.00948100	-0.26932100
N	-2.09396600	-0.06881200	1.05287900
C	-1.29673100	-0.44365300	2.25502900
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C	1.63602000	3.50322600	-0.37193300
C	1.08240500	-1.33968400	-0.33592100
F	1.00650600	-1.68764600	0.99455500
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C	2.55122700	-1.05078300	-0.70871800
O	2.91944800	-1.02407800	-1.86249100
O	3.30446100	-0.79313400	0.35878500
C	5.31580000	-0.04332900	1.41137000
C	4.67724200	-0.39403200	0.08454800
H	0.28609000	-0.02041900	-1.73686300
H	1.26366600	1.01206600	0.95072400
H	-1.59806300	1.94949000	1.43412100

H	-3.33296600	1.59750500	1.61926600
H	-3.56446000	-1.38246500	1.91525600
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H	-1.05714800	-1.50403000	2.20511500
H	-1.88428600	-0.23007500	3.15065500
H	0.07456400	2.44761000	-1.54580500
H	-0.39473900	4.38664700	-0.06281400
H	0.27329500	3.48201300	1.38082400
H	2.49527000	3.23231000	0.23556800
H	1.86334000	4.14553900	-1.21778200
H	6.35445000	0.26129500	1.24761900
H	4.78487700	0.78414300	1.89245100
H	5.31029600	-0.90342500	2.08785400
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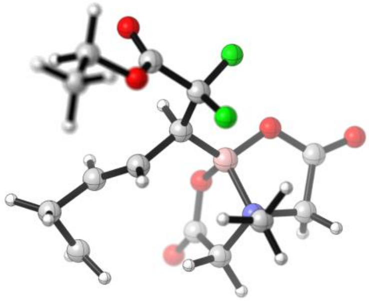
P3-TS2a



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C	-2.47390200	1.30812700	1.05352800
O	-3.16707900	2.68148200	-0.82362800
C	-2.94607400	-2.05957500	-0.13971700
C	-3.29496900	-1.02845500	0.92995900
O	-3.56285800	-3.07923200	-0.33568200
N	-2.09718500	-0.13228400	1.05742000
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C	-0.05061200	3.87942800	0.10929800
C	1.38529600	3.60578900	-0.12955700
C	1.12105200	-1.31683400	-0.30350800
F	1.06670900	-1.63796700	1.03524900

F	0.74861100	-2.43935200	-0.98893200
C	2.58054400	-1.01317600	-0.70036200
O	2.93040800	-0.99070900	-1.86011000
O	3.34804400	-0.74135200	0.35291600
C	5.37432600	0.01946500	1.36822000
C	4.71221300	-0.33219700	0.05324600
H	0.29981700	-0.03462800	-1.71797100
H	1.17156900	1.05740200	1.00275100
H	-1.64849900	1.88572500	1.47073900
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H	-3.54135600	-1.49675700	1.88278100
H	-4.15887400	-0.45117800	0.59192400
H	-0.40008900	0.09401300	2.29478100
H	-1.03800900	-1.55910300	2.19949800
H	-1.91037900	-0.32264700	3.15470600
H	0.47860200	2.36681300	-1.70606300
H	-0.66536600	4.37563200	-0.63055800
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H	4.84623900	0.84081000	1.86259000
H	5.38945300	-0.84295100	2.04162800
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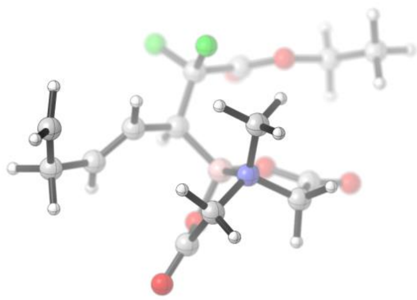
P3-INT2a



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O	1.24969300	1.40259000	-1.34214900
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O	3.15289000	2.56960100	-1.01017700
C	-1.64473000	2.03947300	-0.39241400
C	-0.64591400	2.59942400	0.61614800

O	-2.74624400	2.48949300	-0.60126300
N	0.33823400	1.49509100	0.87219000
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C	-0.03230700	0.77115500	2.12162600
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C	3.08879900	-1.05786000	-0.67619900
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C	4.53397900	-1.73449000	1.30632000
F	-0.12417100	-3.18199600	-0.50762400
F	-0.45082800	-1.96672700	1.28648400
C	-1.89111100	-1.65028900	-0.58515800
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C	-4.60658900	0.06514300	1.10330100
C	-3.96811700	-0.64471000	-0.07050900
H	0.61090600	-1.11369000	-1.69141300
H	2.37211600	1.24201300	1.39122200
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H	5.31784700	-1.41591500	1.98486000
H	3.94249200	-2.60006300	1.58880600
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H	-4.65503000	-0.58805100	1.98010400
H	-4.04579300	0.96858700	1.35991900
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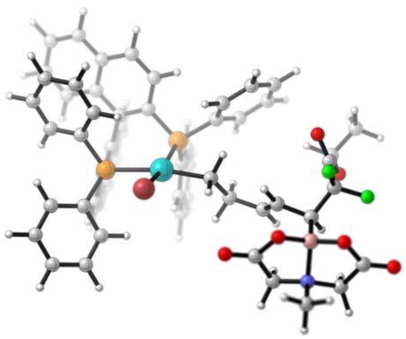
P3-INT3



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C	-3.75281200	1.28645300	2.56758700
C	-3.27733900	1.58399500	-2.74345600
C	-5.21739100	2.00318100	-1.35407800
C	-3.63052800	4.42757600	0.32235400
C	-1.70000600	3.74094500	1.60556500
C	-3.96102100	-1.11209500	-0.39300200
C	-4.61051600	-1.33681700	2.03080400
C	-4.25610800	0.52018600	3.58966500
C	-4.09368600	1.56996800	-3.87396700
C	-6.02888000	1.99645600	-2.48661200
C	-3.56015100	5.69504600	0.90586500
C	-1.64012100	5.00011500	2.19752500
C	-2.75129500	-1.52392100	-0.95351200
C	-5.17669900	-1.23052800	-1.14756900
C	-4.69052400	-0.80728500	3.35727800
C	-5.06939600	-2.66446300	1.80777200
C	-5.46894200	1.77435800	-3.74658100
C	-2.57149300	5.98196800	1.84729200
P	-1.12289900	-1.24783100	-0.10807300
C	-2.73704200	-2.03703800	-2.28021600
C	-5.13206700	-1.72149300	-2.48972800
C	-6.44066800	-0.85187900	-0.61534400
C	-5.20198300	-1.61890500	4.40344600
C	-5.57077800	-3.42430700	2.84022500
C	-1.35443800	-1.79282100	1.61734600
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C	-5.63425100	-2.90134500	4.15372400
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C	-0.96594100	-0.93312100	2.65320200
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C	1.19708100	-4.59904000	-0.89697000

C	-1.68269400	-2.56205200	4.28886600
C	1.68571000	-4.32295400	-2.17355400
Pd	-0.49078500	0.92584800	-0.41810700
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H	-3.43646500	2.30146800	2.77151200
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H	-0.95552700	2.98987700	1.85329100
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H	-8.44821800	-1.50498500	-3.28377700
H	-2.52880200	-4.38013500	3.49488900
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H	1.73038900	-2.89014200	-3.78585300
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H	1.71925300	-0.27543600	-1.32050200
C	3.53325900	-0.39861800	0.90509300
H	1.57432600	-1.20792300	1.00379800
H	1.72793900	0.39229500	1.68250600
C	4.41196100	-0.06833900	-0.04610900
H	3.90884600	-0.81520000	1.84384400

C	5.90910800	-0.21755700	0.07966000
H	4.05509400	0.34008600	-0.98719300
C	6.36937500	-1.25179300	-0.94911900
H	6.12171100	-0.69252600	1.04389400
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F	7.63382700	-1.71098300	-0.66045700
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O	5.50554000	-3.14322500	0.15091600
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C	4.94065700	-5.48539500	-0.35778600
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H	5.93480800	-5.80869400	-0.03335300
H	2.03598700	1.33763100	-0.66404600
B	6.72839000	1.21486100	-0.12282000
O	8.11753400	0.97806900	-0.54072100
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C	5.07188400	2.71519700	0.28899500
C	5.67168200	2.33056900	1.67831400
O	4.08038000	3.38147200	0.13250400
C	8.82796000	0.66175900	0.56250500
C	8.03712400	1.04821400	1.85266000
O	9.93328700	0.18206600	0.55763500
N	7.06297300	2.00847700	1.28316800
C	7.78819400	3.31095100	1.07071500
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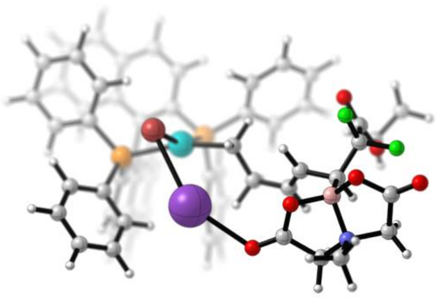

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C	-5.34119700	-1.73660900	-2.40239300
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C	-1.30971800	-1.14255100	4.04676400
C	1.03909800	-3.67285700	-2.54295300
C	0.93356400	-4.88551400	-0.45854900

C	-1.93746800	-2.32207500	4.45234700
C	1.38895000	-4.78442800	-1.77282000
Pd	-0.60924700	0.66461500	-0.59818900
Br	0.00543700	2.73196100	-1.98581100
H	-3.47721500	2.45066700	2.66389500
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H	-7.12633800	2.88784900	-2.07027700
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C	1.90851400	-0.28571900	0.75260400
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C	4.29552600	-0.15252300	-0.08768700
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H	3.95769800	0.28085400	-1.02526000
C	6.18971100	-1.33641700	-1.08056700
H	5.96484200	-0.93304400	0.94864300
F	6.12980500	-0.73743200	-2.30205300
F	7.48454500	-1.77577700	-0.89615500
C	5.26724100	-2.57356400	-1.11988200
O	4.48607400	-2.80166600	-2.01405600
O	5.42839000	-3.28615400	-0.00316700
C	4.49507900	-4.38449600	0.20656700
C	4.89806700	-5.62209300	-0.57455000
H	4.53423900	-4.55519600	1.28369700
H	3.49813400	-4.03899800	-0.07176600
H	4.22006200	-6.44546400	-0.32403900
H	4.83737100	-5.43838900	-1.65001200
H	5.91806300	-5.92785600	-0.32177100
H	1.91437600	0.91748200	-1.06575900
B	6.62781600	1.06831800	0.01184400
O	7.78808600	1.05754800	-0.87013100
O	5.65450200	2.19215900	0.09222200
C	5.25525000	2.26977900	1.36770400
C	6.22188600	1.49264400	2.30834900
O	4.27988100	2.88515500	1.74817600
C	8.81412600	0.47661200	-0.19892100
C	8.45769100	0.33411200	1.31391200
O	9.86151500	0.15560500	-0.69381000
N	7.40844700	1.38059100	1.42440400
C	8.11058200	2.71502300	1.44552100
H	6.42040100	2.04600400	3.22661700
H	5.80664500	0.51518700	2.55475900
H	9.32083900	0.52611900	1.95076500
H	8.05898600	-0.65922200	1.51930300
H	7.39358600	3.51913500	1.29227100
H	8.85706200	2.75929700	0.65530200
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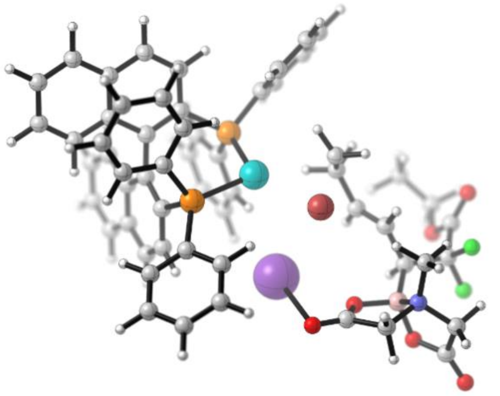
K	2.05567900	3.47664300	0.31319900

P3-TS2



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C	3.49405400	-2.09942800	-1.38201200
C	1.65780700	-3.52828800	0.30943900
C	3.74721800	-0.01685300	1.27688300
C	2.25756700	-1.44960600	2.56101200
C	3.42551300	-1.46881400	-2.63239300
C	4.59919300	-2.90733900	-1.08318200
C	2.40966300	-4.32726500	1.18717600
C	0.47696400	-4.05162000	-0.24265600
C	4.33110700	0.50967000	0.00001800
C	4.16327300	0.61008100	2.50227200
C	2.59919200	-0.82132400	3.73135600
C	4.45519800	-1.62360700	-3.55966700
C	5.62714400	-3.06295000	-2.01095900
C	1.98960100	-5.61949800	1.50041800
C	0.05745000	-5.34696200	0.07125200
C	3.62573600	1.38939100	-0.82594000
C	5.67620700	0.14472400	-0.33066700
C	3.56986000	0.21214600	3.74177600
C	5.14966100	1.63383000	2.53496900
C	5.56010100	-2.41749600	-3.24767800
C	0.81341100	-6.13222800	0.94326100
P	1.82569500	1.70458200	-0.54909700
C	4.25558700	1.91563900	-1.98600300
C	6.27845100	0.65945400	-1.52192100
C	6.43985800	-0.73897600	0.48083600
C	3.96535000	0.84761900	4.94653900
C	5.52853900	2.21997500	3.72232100
C	1.75007800	2.40875300	1.13835600
C	1.38974200	3.11013700	-1.64649300
C	5.53673200	1.55767700	-2.32710100
C	7.59929400	0.26697000	-1.86241600
C	7.72251800	-1.09418400	0.13034600

C	4.92934400	1.83049800	4.94208300
C	2.65287800	3.38430900	1.58453400
C	0.76983600	1.93532700	2.01926800
C	1.23281700	2.83776700	-3.01970500
C	1.04483600	4.38395500	-1.17184600
C	8.31016300	-0.59106500	-1.05476300
C	2.57433500	3.87044600	2.88822300
C	0.69133900	2.41765300	3.32482700
C	0.77999700	3.82208200	-3.89665600
C	0.57129400	5.36222000	-2.04872400
C	1.59828100	3.38491300	3.76167400
C	0.44209500	5.08860800	-3.41152700
Pd	0.57371800	-0.19932200	-0.96560800
Br	-1.76529600	-1.20233800	-1.75770400
H	1.54244500	-2.26494100	2.58594500
H	2.56932800	-0.83772000	-2.85659100
H	4.66962300	-3.40170300	-0.12060400
H	3.31418300	-3.93459400	1.64073300
H	-0.11562700	-3.43565000	-0.91444200
H	2.14214500	-1.12485000	4.67008500
H	4.39966400	-1.11638200	-4.51850600
H	6.48994200	-3.67280500	-1.76125500
H	2.58036000	-6.22829200	2.17889000
H	-0.86173200	-5.73431000	-0.35796900
H	5.60724600	1.95539000	1.60770200
H	6.36908400	-2.53081000	-3.96326500
H	0.48903700	-7.13880100	1.19042900
H	3.71552800	2.61297000	-2.61460500
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H	3.49770000	0.53450000	5.87641500
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H	5.99872100	1.96773600	-3.22135800
H	8.03921100	0.66169700	-2.77442800
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H	5.23132700	2.30648300	5.87026100
H	3.43073900	3.74423800	0.91817700
H	0.08585900	1.16966700	1.66793000
H	1.46751300	1.84492400	-3.39793500
H	1.14220100	4.61430100	-0.11706300
H	9.32107300	-0.88381200	-1.32265500
H	3.29037000	4.61059500	3.23092600
H	-0.06266000	2.02979900	4.00432100
H	0.67788600	3.59593000	-4.95404700
H	0.30788700	6.34326300	-1.66363100

H	1.55171200	3.75384900	4.78175200
H	0.07548600	5.85280600	-4.09020700
C	-1.66124100	1.14178400	-2.06116000
C	-1.99689400	1.94894300	-0.83995600
H	-0.72960300	1.40173200	-2.54783400
C	-3.18482000	1.52836300	-0.01446300
H	-2.19159100	2.96798000	-1.22971300
H	-1.11922400	2.04362200	-0.19948700
C	-4.22990600	0.82091700	-0.45153600
H	-3.17382400	1.86889000	1.02095700
C	-5.40121900	0.42723500	0.41248100
H	-4.26232500	0.50988200	-1.49086100
C	-6.65357500	1.18066700	-0.02549100
H	-5.20630300	0.79804700	1.42782100
F	-7.09955700	0.73474400	-1.25126000
F	-7.68556000	0.97371200	0.85130800
C	-6.42203900	2.70025000	-0.16420200
O	-6.47812700	3.29075700	-1.21762300
O	-6.13328000	3.22048900	1.02770300
C	-5.82973100	4.64675400	1.06130600
C	-4.37924000	4.90273300	0.69091800
H	-6.51636000	5.15884700	0.38491700
H	-6.04633000	4.93664300	2.08999700
H	-4.16901700	5.97461000	0.77020200
H	-3.70308900	4.36838800	1.36537400
H	-4.17863200	4.58712700	-0.33651500
H	-2.46912300	1.02119800	-2.77331700
K	-1.57941200	-1.42369800	1.65491000
B	-5.57421800	-1.16772800	0.63818100
O	-6.63235300	-1.50576900	1.59950600
O	-4.28109000	-1.74893400	1.05693000
C	-4.10756600	-3.00118100	0.63475700
C	-5.29103800	-3.44714100	-0.20514300
O	-3.12879300	-3.66694400	0.90128500
C	-7.71789700	-2.06139100	1.04872200
C	-7.47944000	-2.29591500	-0.44309400
O	-8.73350700	-2.32919000	1.64122600
N	-5.99941300	-2.18381900	-0.60842600
C	-5.58947400	-1.80862600	-1.99564600
H	-4.98074500	-4.02452200	-1.07592900
H	-5.94595200	-4.06738500	0.41181600
H	-7.86057400	-3.25861700	-0.78537100
H	-7.95452300	-1.49426100	-1.01163000
H	-4.50191500	-1.72615000	-2.02974900

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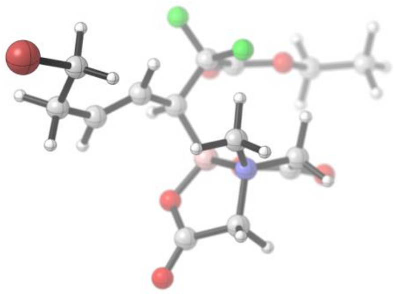
56a



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O	-0.35257000	1.98983600	-1.36685900
C	-0.21457400	3.17275800	-0.76836700
C	-0.78894900	3.11659100	0.64344200
O	0.27487300	4.15431400	-1.27280300
C	-3.20973200	1.24309200	0.34274600
C	-2.29085000	1.36675600	1.55295300
O	-4.41577300	1.31747900	0.37339700
N	-0.94577300	1.66075400	0.98011400
C	1.11954300	-0.55335700	-0.54467200
C	0.16650800	1.22243600	1.87240600
C	-1.09098800	-1.64642300	-0.21187200
C	2.06393300	-0.02668200	-1.32768600
C	3.54936100	-0.03886600	-1.07078700
C	3.94523800	-0.72981800	0.22247200
Br	5.91290200	-0.67871900	0.46796700
F	-0.43694900	-2.82278200	-0.48876800
F	-1.08798400	-1.54113100	1.17065500
C	-2.53357800	-1.83224900	-0.72049800
O	-2.76187500	-2.06266300	-1.88652100
O	-3.43093500	-1.71894400	0.25323100
C	-5.66339000	-1.72543700	1.10871200
C	-4.82962600	-1.83763300	-0.14847900
H	-0.51720900	-0.58593500	-1.91560300
H	-0.14685100	3.62092600	1.36531400
H	-1.76500100	3.60817600	0.64447900
H	-2.25624700	0.39787500	2.05532200
H	-2.61552000	2.13299800	2.25720400
H	1.39912500	-1.06148100	0.37503500
H	1.11412400	1.42196300	1.37260400

H	0.06685600	0.15692100	2.05873700
H	0.11136900	1.77791200	2.81118300
H	1.76607500	0.47662800	-2.24636100
H	4.05927700	-0.52613900	-1.91227300
H	3.92218900	0.99397400	-1.05869400
H	3.53780800	-0.23878200	1.10554800
H	3.68367000	-1.78708300	0.23308200
H	-6.72311100	-1.81938400	0.85017200
H	-5.40991300	-2.51770500	1.82004900
H	-5.50798500	-0.75244900	1.58218600
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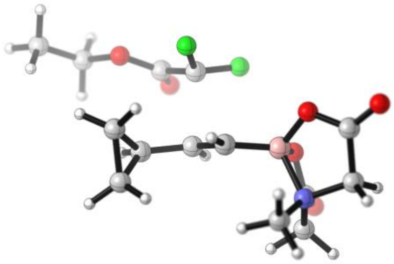
P4-TS1



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B	1.79481500	-0.05451200	-0.22153700
O	2.29354700	-0.52512700	-1.51890500
O	1.74743900	-1.14165500	0.78210800
C	2.40735900	-0.88532400	1.90916900
C	3.12718600	0.46106800	1.80954100
O	2.42447700	-1.59932500	2.88487300
C	3.62158400	-0.50772800	-1.62830800
C	4.25393600	0.09796600	-0.37464300
O	4.24722300	-0.91940100	-2.57675000
N	3.14630900	0.78102800	0.35925000
C	3.14012500	2.24126000	0.08053600
C	-1.74286400	1.60477000	0.61476500
C	-1.50108900	3.10371000	0.53863600
C	-2.21960500	2.40352900	-0.57663600
C	-1.59710500	-0.98211600	-0.66192400
F	-1.73248200	-0.50576400	-1.90098100
F	-0.70101500	-1.96721400	-0.62265800
C	-2.83065900	-1.22711600	0.11330100
O	-2.83859100	-1.87718100	1.14469100
O	-3.86819500	-0.54408000	-0.39188200
C	-6.06953900	0.36944800	-0.26961100

C	-5.07855900	-0.55388800	0.40741600
H	0.43947400	1.59311700	-1.07735900
H	-0.51013600	-0.05132200	1.33195700
H	2.53546900	1.21793200	2.33113100
H	4.12763300	0.43223100	2.24318300
H	5.05847800	0.79154400	-0.62137300
H	4.66610200	-0.70919600	0.23590700
H	2.25747100	2.68237500	0.54290900
H	3.09597100	2.39399100	-0.99918400
H	4.04810000	2.69733200	0.48165800
H	-2.51434800	1.29250900	1.31296000
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H	-1.69518800	2.25056900	-1.51518700
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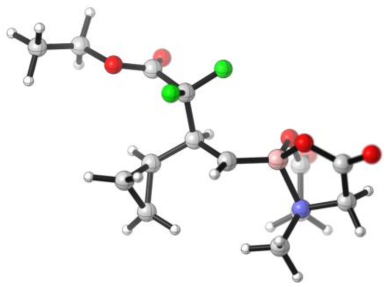
P4-INT2



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C	0.75596600	0.38563600	-0.23158600
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O	-2.38662100	-0.95255200	1.38157300
O	-1.78908900	-1.03366700	-0.98732600
C	-2.41362500	-0.50353700	-2.03723300
C	-3.09640500	0.80743900	-1.64245700
O	-2.42609100	-0.97361300	-3.15088300
C	-3.71650700	-0.91500900	1.46450900
C	-4.29492900	-0.01768600	0.37029300
O	-4.37994700	-1.51175600	2.27916200
N	-3.14901000	0.78259300	-0.15828400
C	-3.11586600	2.13521900	0.45618000
C	1.61252300	1.64004900	-0.40878100
C	1.03812800	3.02913400	-0.29207700

C	1.99354000	2.51675100	0.75596300
C	1.60545400	-0.72909900	0.41741800
F	1.86503000	-0.43577000	1.72682000
F	0.90481100	-1.90774400	0.40333300
C	2.91715200	-0.97153800	-0.34789100
O	2.92693900	-1.48374800	-1.44658100
O	3.97447600	-0.49665900	0.30400400
C	6.28465500	0.09208300	0.47365100
C	5.24894000	-0.59202500	-0.39273700
H	-0.41681500	1.12423900	1.48413400
H	0.51314100	-0.00855400	-1.22522800
H	-2.46772700	1.64361100	-1.96059700
H	-4.08366400	0.91490800	-2.09367200
H	-5.09080900	0.62366200	0.75074700
H	-4.70579600	-0.64985800	-0.42081200
H	-2.21850900	2.65265900	0.11954700
H	-3.08431800	2.02836900	1.54176000
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H	-0.00716300	3.12434700	-0.01289300
H	1.59201700	2.26632600	1.73296300
H	3.00408300	2.91350400	0.78084900
H	7.26189400	0.04313100	-0.01735800
H	6.02754100	1.14440600	0.62943900
H	6.36264800	-0.39699800	1.44933400
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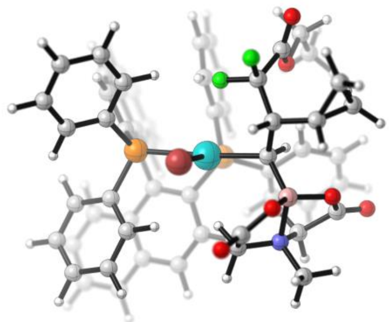
H	5.14019100	-0.11334200	-1.36990000

P4-INT3



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C	3.17606300	0.89280600	-0.14727000
C	3.06635300	0.84269100	-2.57274100

C	0.60288800	-1.06435400	-3.87962900
C	2.35844600	-2.67813100	-3.48283800
C	3.81796200	-2.58340900	-0.45737400
C	1.71636700	-3.32640500	0.48047400
C	2.87684800	0.26942800	1.17509800
C	3.91941600	2.10985800	-0.21179100
C	3.78759400	2.00857900	-2.65519100
H	2.73894100	0.35712900	-3.48262900
C	0.58643700	-1.41042900	-5.22892000
H	-0.09699000	-0.32704700	-3.50717600
C	2.33244400	-3.03184900	-4.83384200
H	3.04398100	-3.18241100	-2.81164400
C	4.48625200	-3.57967500	0.25096900
H	4.38099400	-1.89439500	-1.07863400
C	2.38759800	-4.31870700	1.19418600
H	0.63911100	-3.24253700	0.54038100
C	1.58860000	0.26286900	1.69009900
C	3.92542000	-0.43747800	1.85777400
C	4.20909200	2.68870300	-1.48740500
C	4.33044500	2.80463600	0.95843600
H	4.02633500	2.43364000	-3.62639900
C	1.45180400	-2.39686300	-5.71001000
H	-0.11361800	-0.92201800	-5.90051600
H	3.00106200	-3.80667500	-5.19783600
C	3.77341000	-4.44361700	1.08489800
H	5.56521400	-3.66457400	0.17045500
H	1.82634600	-4.99203900	1.83562900
P	0.13984300	1.05221000	0.87114300
C	1.28999700	-0.54435400	2.82819800
C	3.60947400	-1.22317200	3.00980500
C	5.27387400	-0.41043300	1.41138000
C	4.88843700	3.93311200	-1.54758400
H	4.10799800	2.37687000	1.92963600
C	4.98306400	4.01327900	0.86842200
H	1.43230500	-2.67417000	-6.75996700
H	4.29770100	-5.21055100	1.64740200
C	-0.66318300	1.96849700	2.25060800
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C	2.26452500	-1.27118200	3.45886400
H	0.27456700	-0.58813700	3.20311400
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H	5.52922600	0.17011300	0.53361800
C	6.25453400	-1.11192900	2.07764000
H	5.09773600	4.36473500	-2.52259400

C	5.26468500	4.58589400	-0.39573100
H	5.28142400	4.53535400	1.77276200
C	-0.04220600	2.18540100	3.49054300
C	-1.90788200	2.56687800	2.00015500
C	1.21258300	3.63076500	0.48394800
C	0.37849900	2.52926000	-1.50308500
H	2.01696300	-1.88996300	4.31683700
H	4.37791500	-2.54652100	4.53418400
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H	7.27996400	-1.07289600	1.72228500
H	5.77773900	5.54135900	-0.45171500
C	-0.67188100	2.95771000	4.46769100
H	0.93311000	1.76213600	3.69735700
C	-2.53524000	3.33088200	2.98137100
H	-2.37932000	2.44620700	1.03333200
C	1.51417500	4.76168200	-0.26939200
H	1.41320200	3.62645800	1.54965000
C	0.67342800	3.66771900	-2.25444700
H	-0.07585000	1.66823000	-1.97522200
H	6.71749300	-2.44663800	3.72382300
C	-1.92236400	3.52489400	4.21984700
H	-0.17909900	3.11682400	5.42233100
H	-3.50919000	3.76540800	2.78080200
C	1.24346600	4.78308400	-1.64051800
H	1.96478100	5.62351000	0.21236200
H	0.45738800	3.67804900	-3.31868100
H	-2.41564400	4.11555800	4.98564200
H	1.47482600	5.66806700	-2.22575800
Pd	-0.74102700	-0.70573500	-0.32852300
Br	-1.34051800	-2.85157600	-1.54386800
C	-2.79393000	-0.41031500	0.26811000
C	-3.69038300	-0.43316800	-1.00878700
B	-3.50666800	-1.40362200	1.36701100
O	-4.53940800	-0.61165500	2.11174500
O	-3.79258300	-2.75389900	0.85364500
C	-2.76855300	-3.57681100	1.16719100
C	-1.75698000	-2.83885800	2.09575000
O	-2.70712400	-4.74285700	0.86515000
C	-3.92596200	0.03257500	3.11263100
C	-2.50389600	-0.56143200	3.34240900
O	-4.41609700	0.92507400	3.76486400
N	-2.69402600	-1.89441500	2.74071400
C	-3.52227900	-2.69711200	3.71006000
C	-5.17933500	-0.25100900	-0.66493900

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C	-3.28471700	0.44552000	-2.20474900
F	-1.91817200	0.38597800	-2.45886500
F	-3.86851000	-0.09158100	-3.31822300
C	-3.57262100	1.96733700	-2.28311500
O	-4.23094300	2.44917600	-3.17738700
O	-2.93536100	2.67455200	-1.34409600
C	-2.37128600	4.84163000	-0.38881800
C	-2.96824000	4.12145700	-1.57519500
H	-2.83157600	0.60097700	0.67215400
H	-3.59940500	-1.43523400	-1.43631200
H	-1.27483200	-3.52178600	2.79607800
H	-1.02044200	-2.29389600	1.50154900
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H	-3.89192000	-3.60436300	3.23723500
H	-4.37175900	-2.11553500	4.06042900
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H	-5.20412200	1.95075400	-0.29002800
H	-5.96287400	0.87304000	-2.46013500
H	-7.21024400	-0.08849300	-1.55283100
H	-2.32453300	5.91014100	-0.62563000
H	-2.98786700	4.72144700	0.50497500
H	-1.35916100	4.49482600	-0.17393500
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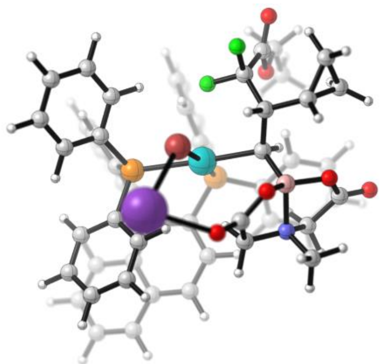
P4-INT4



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C	-3.21334000	1.01809800	0.19726300
C	-3.14853800	0.74644300	2.61107400
C	-0.67171900	-1.19617100	3.78590600
C	-2.30444600	-2.87518700	3.18362200
C	-3.74585700	-2.53011400	0.16300200
C	-1.59724800	-3.06110300	-0.80780000
C	-2.88259800	0.52969300	-1.17359100
C	-3.98571500	2.20807000	0.35767700
C	-3.89512600	1.88584100	2.78454400
H	-2.82816100	0.18570000	3.47917500
C	-0.64217200	-1.68836400	5.08841000
H	-0.02372700	-0.37248200	3.50971400
C	-2.26340100	-3.37605600	4.48742900
H	-2.95191000	-3.34410100	2.45138600
C	-4.34844200	-3.48522500	-0.65513500
H	-4.35479600	-1.93702300	0.83742200
C	-2.20012900	-4.01439500	-1.62873100
H	-0.52756400	-2.90404600	-0.85066000
C	-1.59700100	0.62752500	-1.68839800
C	-3.90742500	-0.14018000	-1.92573000
C	-4.30957500	2.66163400	1.67524700
C	-4.39346200	2.99724500	-0.75223700
H	-4.16047000	2.21503400	3.78536600
C	-1.43699500	-2.78260400	5.44232800
H	0.01209600	-1.22754100	5.82244700
H	-2.88300200	-4.22732000	4.75490800
C	-3.57953000	-4.22503100	-1.55627300
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C	-3.57161200	-0.78012400	-3.15957600
C	-5.25090500	-0.22011000	-1.47019600
C	-5.01682300	3.88125200	1.83604600
H	-4.14856700	2.66420500	-1.75453100
C	-5.07277700	4.17960900	-0.56424300
H	-1.40854600	-3.17122800	6.45600500
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C	-2.23451500	-0.70685700	-3.62693200
H	-0.27733600	0.04337500	-3.31758500
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H	-5.36823600	4.77555300	-1.42256100
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C	1.93342300	2.91233700	-1.67989600
C	-1.28928300	3.82789700	-0.12351600
C	-0.42888600	2.55418000	1.74783400
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H	-4.29935900	-1.96460300	-4.81320500
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C	-0.75099700	3.60541700	2.60723000
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C	2.07038000	4.01561700	-3.82635200
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C	-1.34888600	4.76145400	2.10499200
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H	-0.53340200	3.51694900	3.66736100
H	2.61728600	4.63081500	-4.53393100
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C	2.23186300	-3.14300800	-1.65816500
C	1.43931600	-2.14296900	-2.54040600
O	1.87268500	-4.28458200	-1.44214100
C	4.09539600	0.43150500	-3.05005600
C	2.62783000	0.09945800	-3.44865700
O	4.74017500	1.34996800	-3.49535400
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C	3.29951300	-2.11907800	-4.04970600
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C	6.23580900	0.51977400	1.42244900
C	3.30181600	0.45025200	2.17133200
F	1.94226900	0.35940300	2.45396400
F	3.91592200	-0.18593700	3.21346500
C	3.58382600	1.96060400	2.39080400
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O	2.90239700	2.75257800	1.55718100
C	2.27102900	5.00517500	0.86689300
C	2.92310600	4.16857300	1.94298400
H	2.80997500	0.83221600	-0.70225400
H	3.62353700	-1.35129300	1.23643800
H	0.88980000	-2.64493800	-3.33754000
H	0.76623000	-1.55464600	-1.91040700
H	2.45692700	0.23535900	-4.51716800
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H	3.48184600	-3.12957000	-3.68991200
H	4.25501000	-1.65510100	-4.28154900
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H	5.54327200	-0.89832200	-0.07242900
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H	5.97815600	0.92237400	2.39394500
H	7.21335300	0.04606600	1.39005900
H	2.21309600	6.03757400	1.22828400
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H	2.38386100	4.24118100	2.89097600
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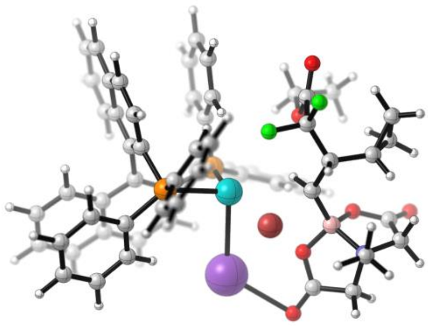
K	0.73271500	-5.67044600	0.54491700

P4-TS2



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C	-0.66522000	-1.33456500	3.60235700
C	-1.56844900	-3.48811500	2.99227800
C	-4.25806100	-2.94073500	1.26646300
C	-3.07160200	-3.11903400	-0.82635100
C	-3.28901400	0.34418900	-1.07132700
C	-4.14712800	2.00824300	0.59801000
C	-3.82607600	1.67130700	3.00355500
H	-2.79759600	-0.09514800	3.58338900
C	-0.15149800	-1.87837600	4.77644100
H	-0.48258600	-0.29053800	3.37877500
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H	-2.11712200	-4.12612800	2.30865300
C	-5.24855500	-3.78817500	0.77516300
H	-4.34252600	-2.53514500	2.27018100
C	-4.06764700	-3.95837900	-1.32690700
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C	-4.67925600	2.79908400	-0.45729200
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C	-0.33690300	-3.23407700	5.06335800
H	0.40417900	-1.24469700	5.46184900
H	-1.18373500	-5.09221600	4.37199200
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H	-6.10107600	-4.04052100	1.39908400
H	-4.00383400	-4.32783900	-2.34590700
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C	-2.10135900	0.12771000	-3.18853200
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C	0.35082700	1.91300400	-2.47187700
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C	-1.56442800	3.77588800	-0.52629300
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H	0.09638400	3.96872700	-5.18185000
H	3.60079500	2.11131200	-3.49512400
C	-1.52431800	4.77038800	1.67876500
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H	2.55345800	3.59600700	-5.21356100
H	-1.73686100	5.60912300	2.33490400
Pd	0.25779200	-0.63791200	0.11753700
Br	1.93644800	-2.46208100	0.95227500
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F	1.59050400	0.41286000	2.52944000
F	3.29721700	0.94557200	3.78489800
C	2.71997500	2.39442500	2.03324500
O	2.81503300	3.32150000	2.80344600

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C	3.45466500	4.44531000	-0.31235300
C	2.17430000	3.81351900	0.19402100
H	2.46045800	0.30063600	0.02011800
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H	5.92974500	-0.39432800	1.61549100
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H	5.13035100	2.27539300	2.93709000
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H	3.91111800	3.82784100	-1.09207800
H	3.21986400	5.42279200	-0.74715800
H	4.17358200	4.59567400	0.49820400
H	1.46634700	3.63268100	-0.61024300
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K	0.34878500	-2.50015000	-2.44438800
B	3.95635900	-0.95071900	-0.96133700
O	4.61605200	0.17240800	-1.65071200
O	3.00952900	-1.59493800	-1.89378000
C	3.48487300	-2.66885600	-2.50617100
C	4.92844700	-2.91951400	-2.12550300
O	2.83465400	-3.35051200	-3.27447000
C	5.93613700	0.05507900	-1.80947500
C	6.43121400	-1.22194300	-1.13824200
O	6.63624800	0.86036400	-2.37357900
N	5.21126000	-2.06160900	-0.92144500
C	5.32831700	-2.92738600	0.29294500
H	5.10891600	-3.97222500	-1.90835500
H	5.56663900	-2.62569900	-2.96229500
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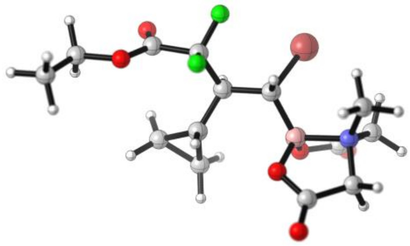
H	6.86896300	-0.96621300	-0.17299200
H	6.19699100	-3.57907500	0.18137100
H	5.44653200	-2.30106800	1.17314400
H	4.41513400	-3.50919100	0.39615200

56b



C	0.44915500	-0.40985600	-0.44005500
C	-0.91777000	-0.21353400	0.25952500

B	1.65861100	0.55096600	0.02190500
O	2.06430800	0.38392600	1.42371900
O	1.39714400	1.94168600	-0.34789500
C	2.47548600	2.60483100	-0.76912700
C	3.68203700	1.67457300	-0.80080300
O	2.49653200	3.77509500	-1.06494500
C	3.20375900	-0.29107800	1.59744900
C	3.88413700	-0.55711500	0.25394000
O	3.63755300	-0.64597800	2.66670600
N	3.13702700	0.27912500	-0.72965900
C	3.07715800	-0.31772400	-2.09588700
C	-1.20737300	1.22345500	0.66819200
C	-2.18057500	1.50184500	1.79594600
C	-0.70830400	1.75086400	1.98544500
C	-2.04962800	-0.69538700	-0.65660100
F	-2.07739800	0.07948000	-1.78827400
F	-1.84611000	-1.98350000	-1.07878300
C	-3.42014500	-0.67630400	0.04398800
O	-3.67647600	-1.44942700	0.94186300
O	-4.22047700	0.26964300	-0.43136400
C	-6.21651000	1.58426100	-0.40263100
C	-5.51180400	0.40309300	0.22878800
Br	1.03001100	-2.31168600	-0.11233000
H	0.31293400	-0.36299000	-1.52162500
H	-0.94522600	-0.83728700	1.15740300
H	4.28801100	1.81886000	-1.69540200
H	4.30084000	1.87683700	0.07653300
H	3.76109100	-1.60926500	-0.00168700
H	4.94638100	-0.31002300	0.27590200
H	2.49065000	0.34091500	-2.73880800
H	2.60039500	-1.29387500	-2.03155900
H	4.08880400	-0.41527100	-2.49462500
H	-1.21982300	1.92866200	-0.15611300
H	-2.84657200	2.35199500	1.68284900
H	-2.61945500	0.65516300	2.31572200
H	-0.15402700	1.06893000	2.62202500
H	-0.34764000	2.77428000	2.00665700
H	-7.19581100	1.71862500	0.06774900
H	-5.63704200	2.50221000	-0.26425400
H	-6.36660600	1.42291100	-1.47441400
H	-6.06162300	-0.53248600	0.09544900
H	-5.33272600	0.54717800	1.29764400

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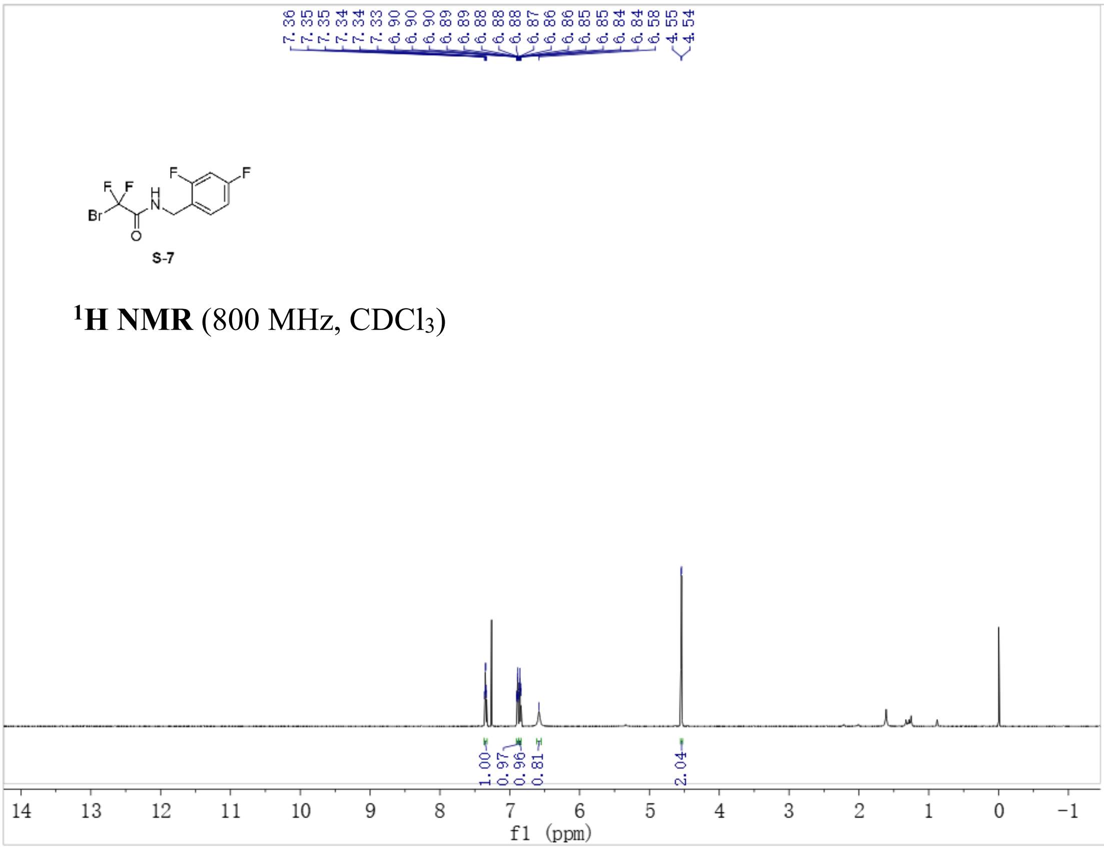
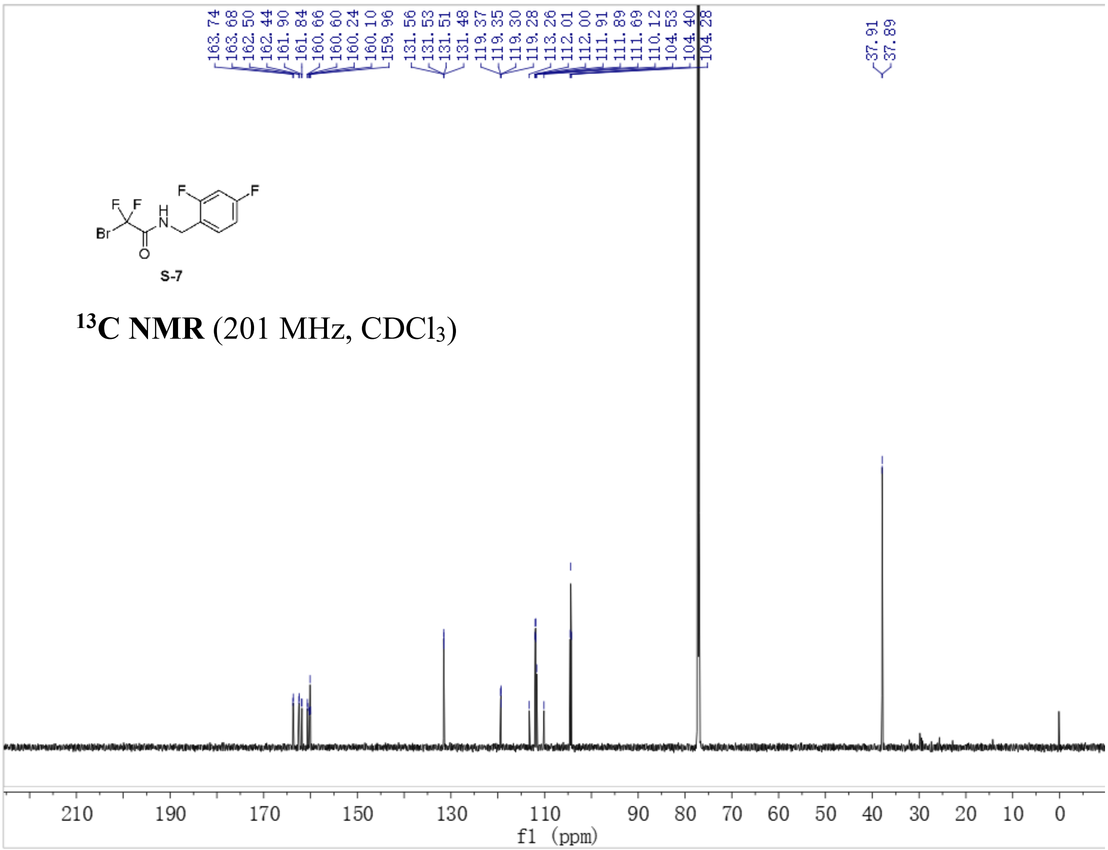
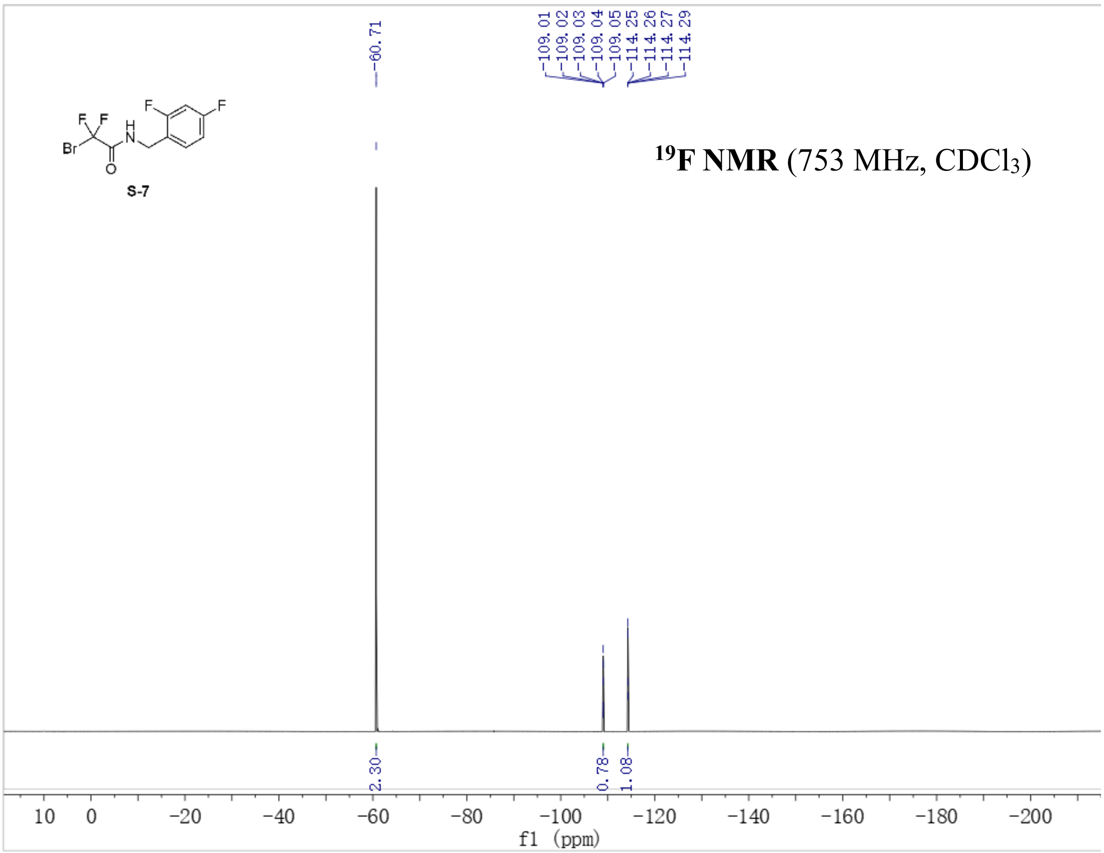
10. NMR spectrum of starting materials and products

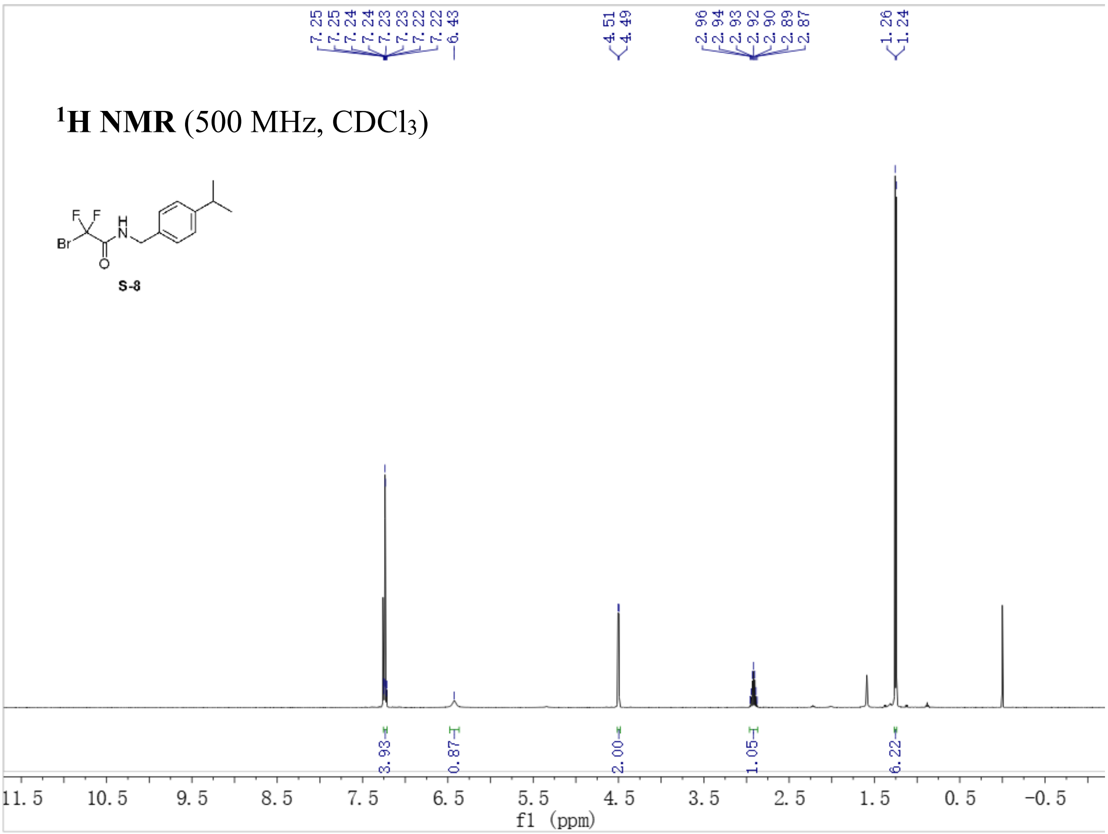
2-bromo-*N*-(2,4-difluorobenzyl)-2,2-difluoroacetamide (S-7)

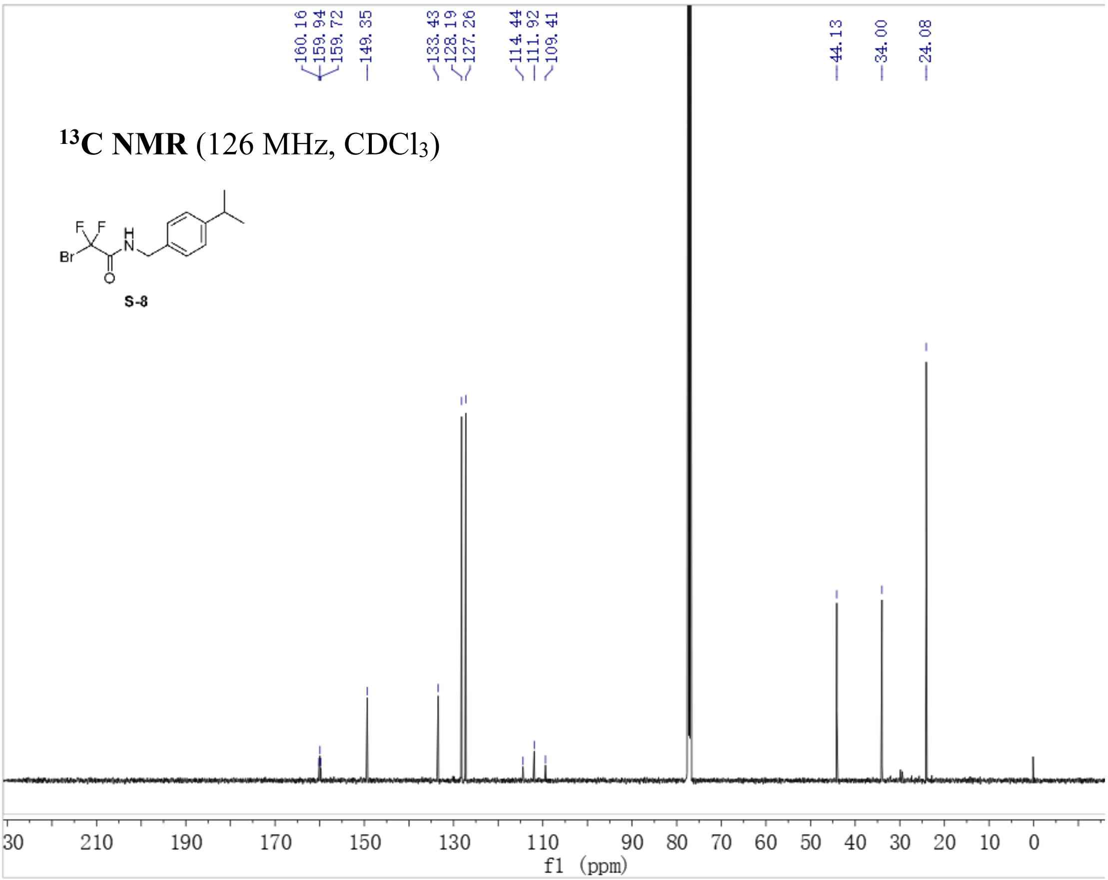


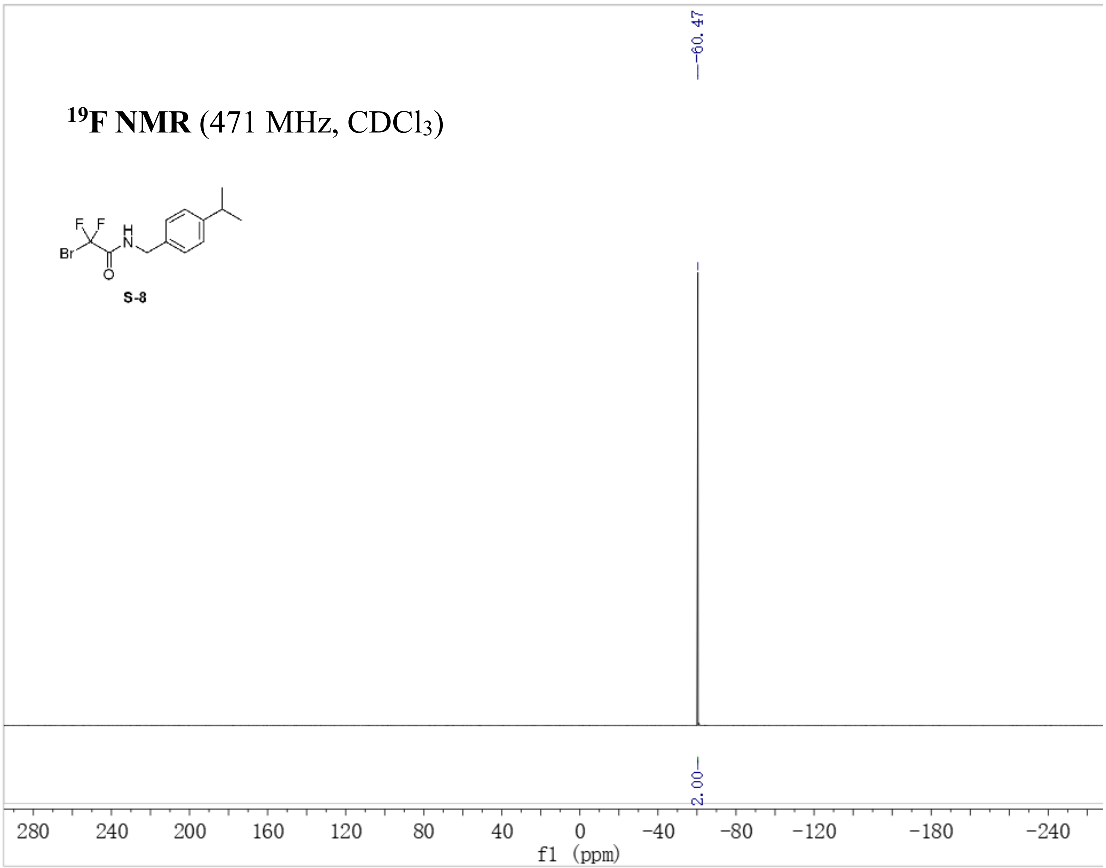




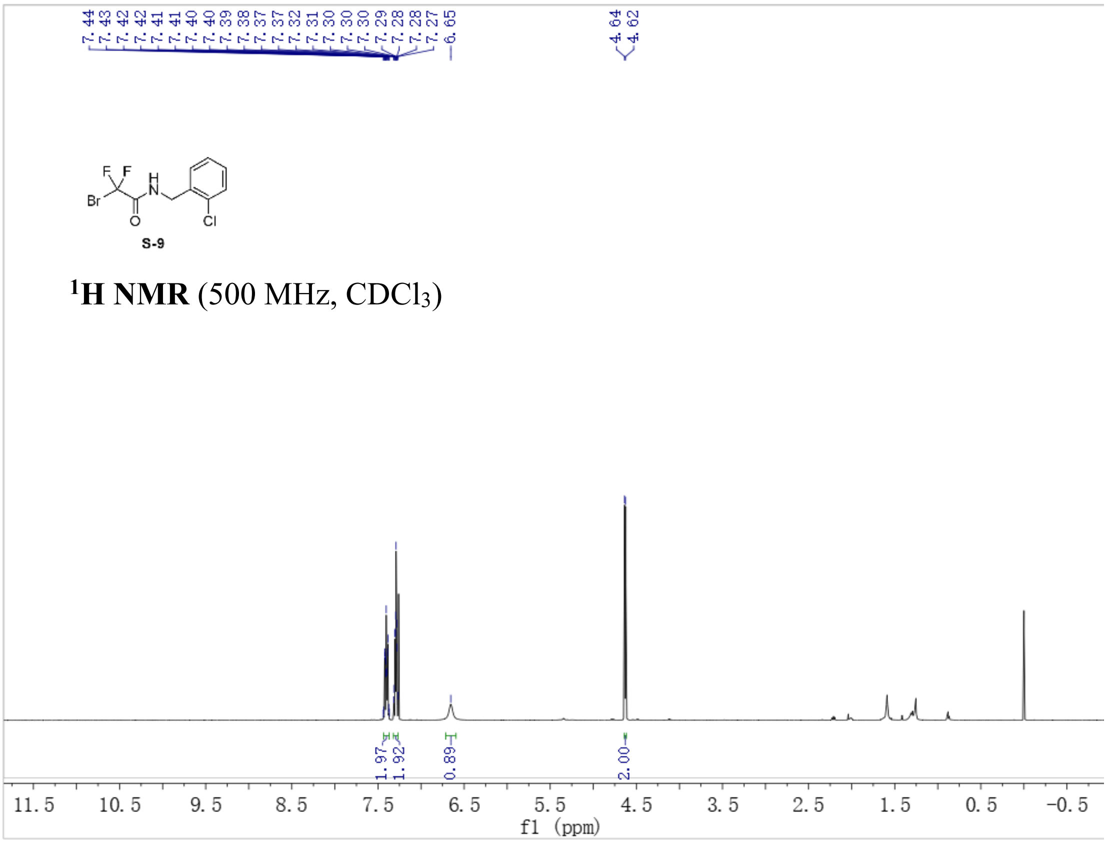
2-bromo-2,2-difluoro-*N*-(4-isopropylbenzyl)acetamide (S-8)

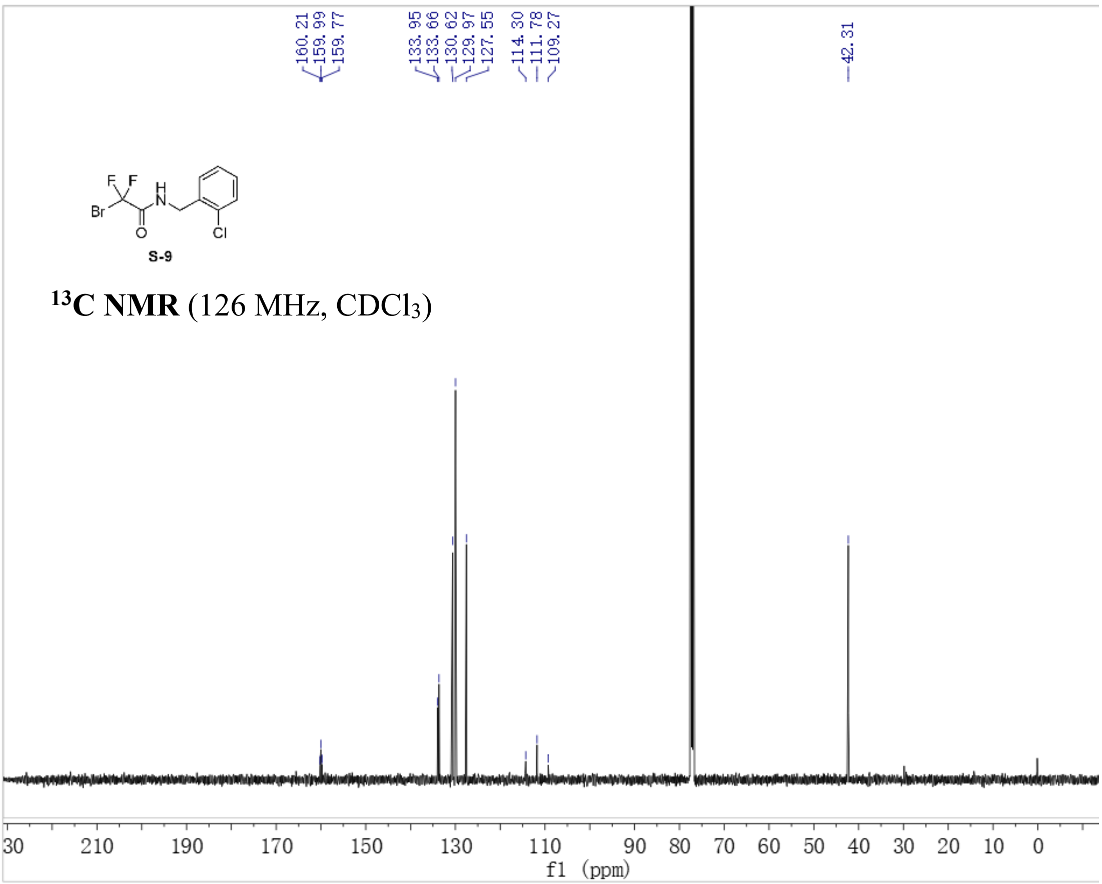


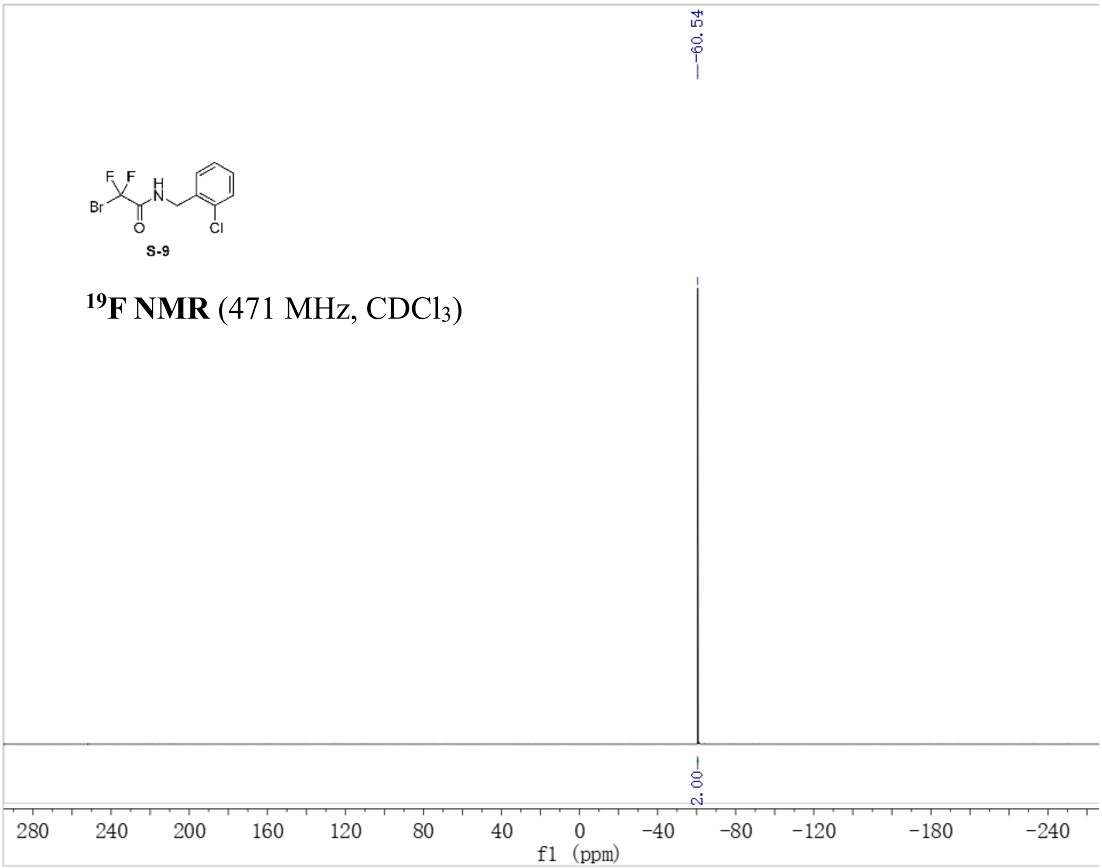

160.16
159.94
159.72
149.35
133.43
128.19
127.26
114.44
111.92
109.41
44.13
34.00
24.08
13C NMR (126 MHz, CDCl3)
F F
H
N
Br
O
S-8
30
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-60.47
19F NMR (471 MHz, CDCl3)
F F
H
N
Br
O
S-8
2.00
280
240
200
160
120
80
40
0
-40
-80
-120
-180
-240
f1 (ppm)

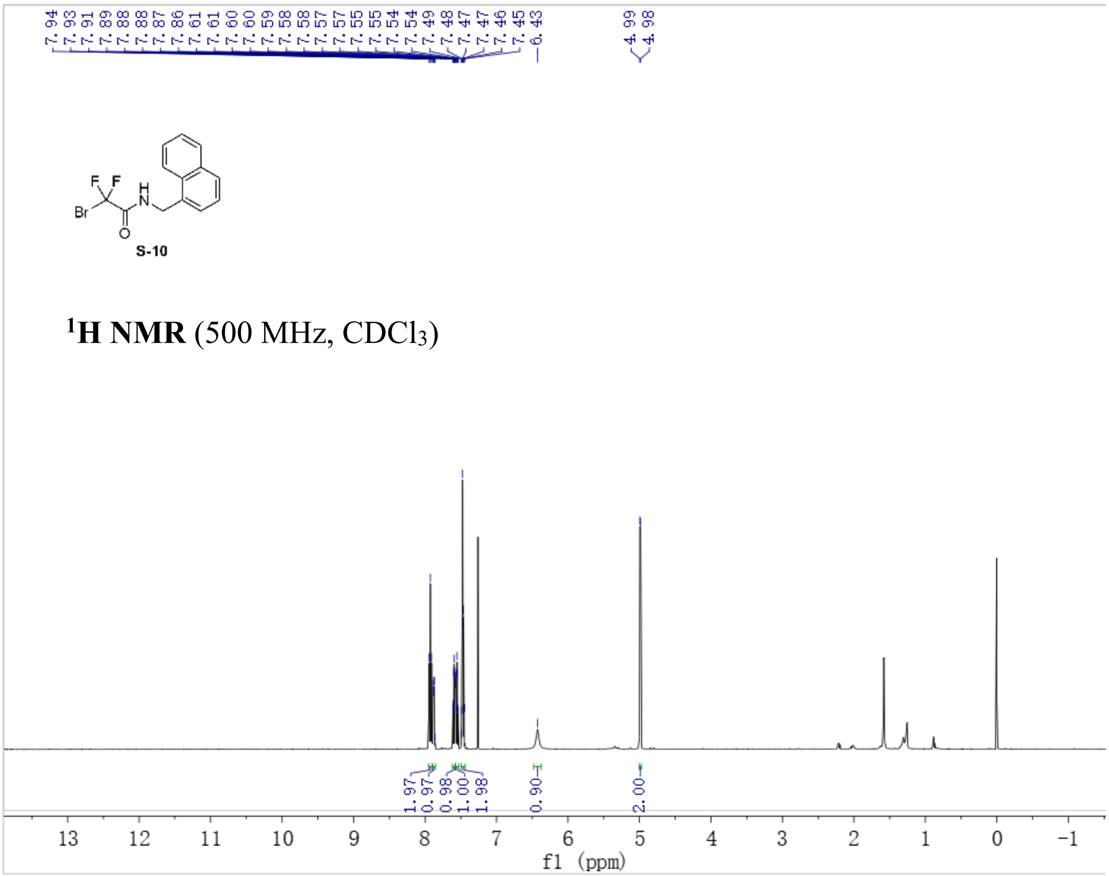
2-bromo-*N*-(2-chlorobenzyl)-2,2-difluoroacetamide (S-9)

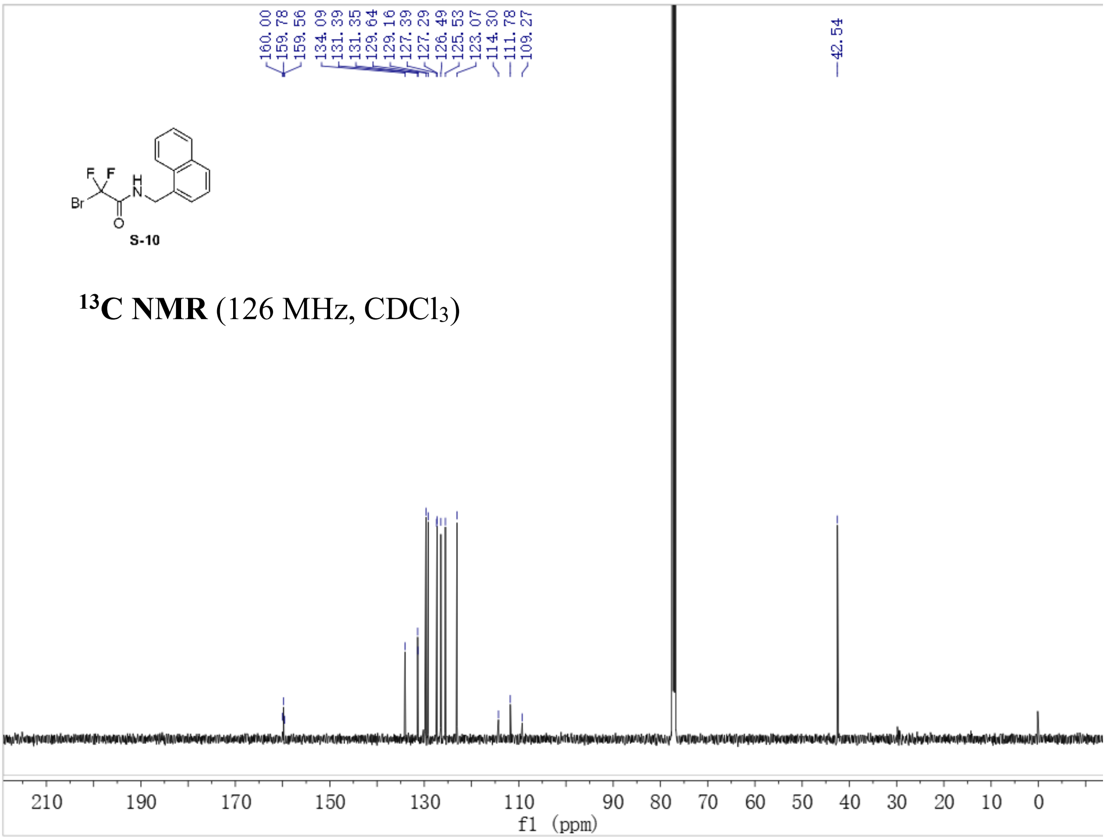


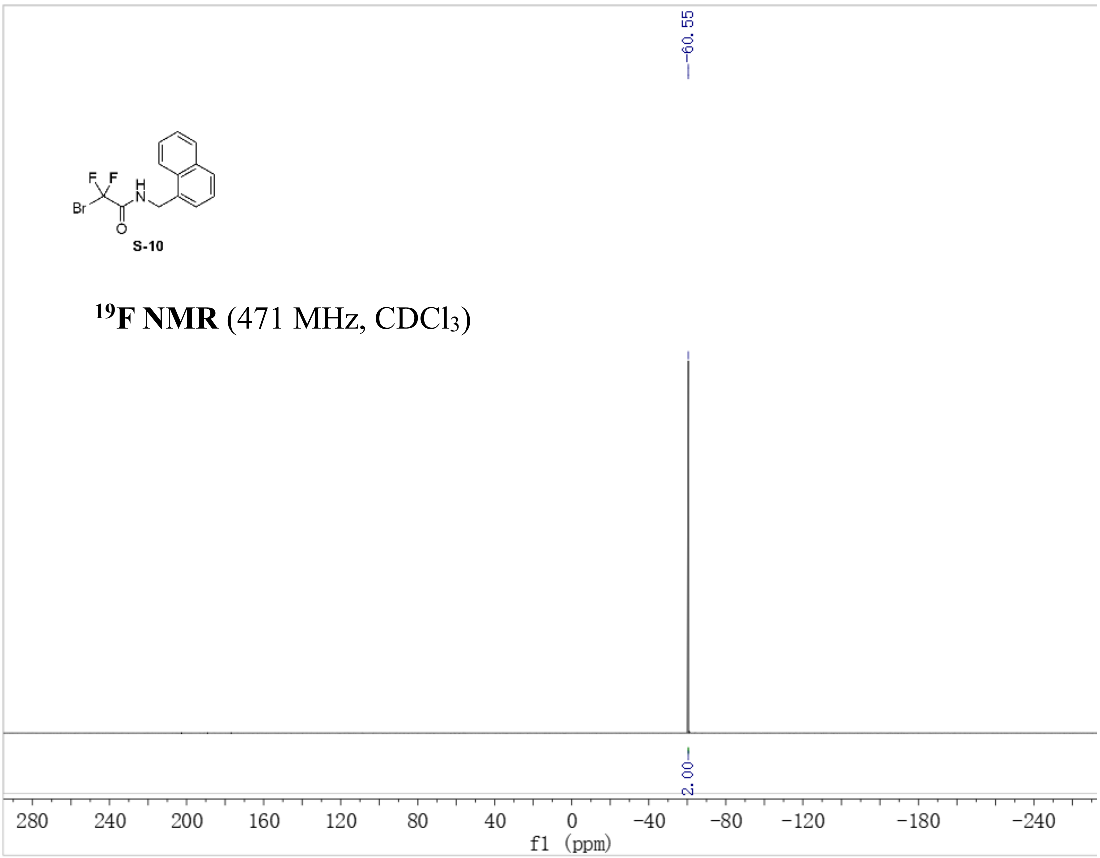




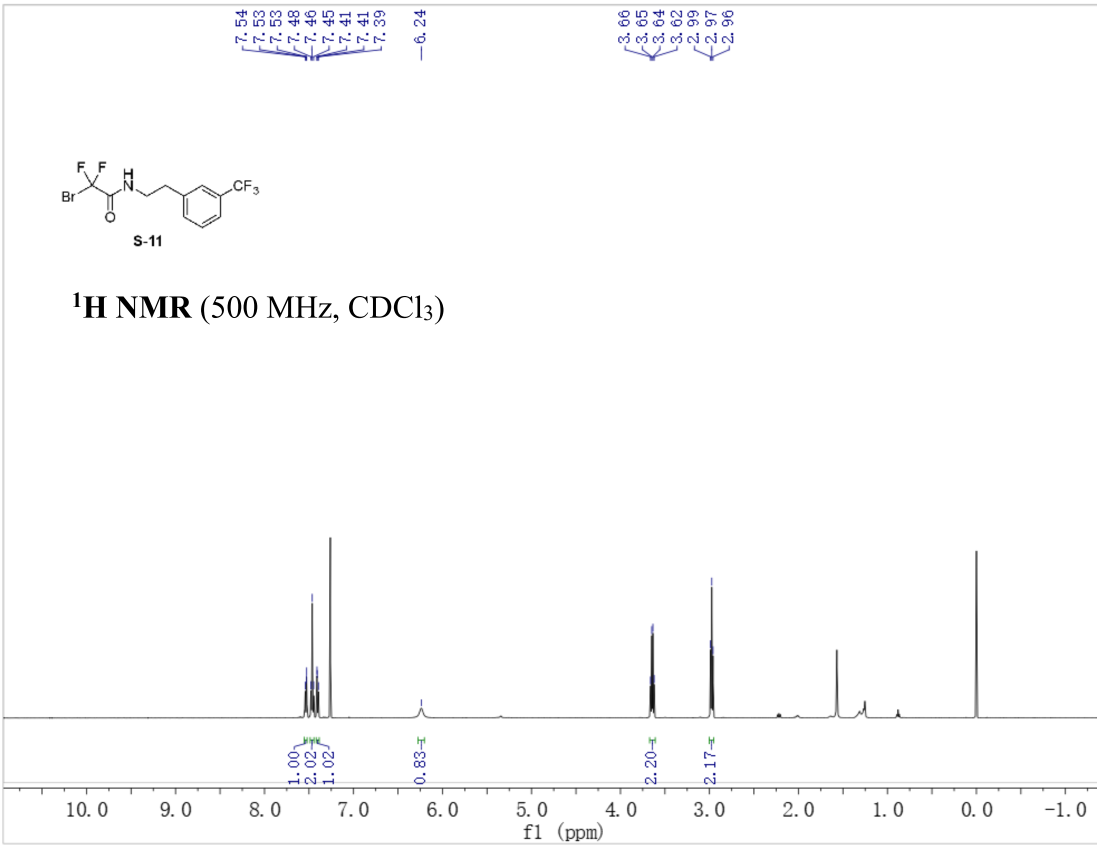
2-bromo-2,2-difluoro-*N*-(naphthalen-1-ylmethyl)acetamide (S-10)

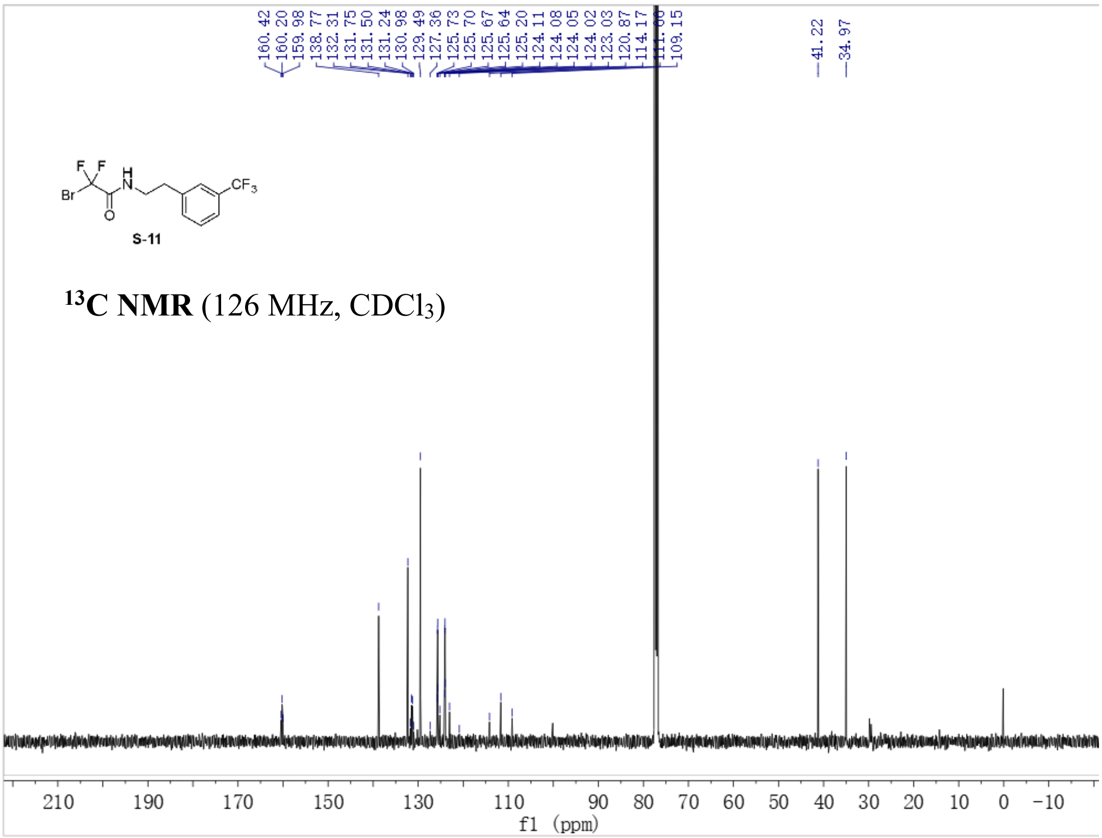

S-10
¹H NMR (500 MHz, CDCl₃)
f1 (ppm)


S-10
¹³C NMR (126 MHz, CDCl₃)
f1 (ppm)

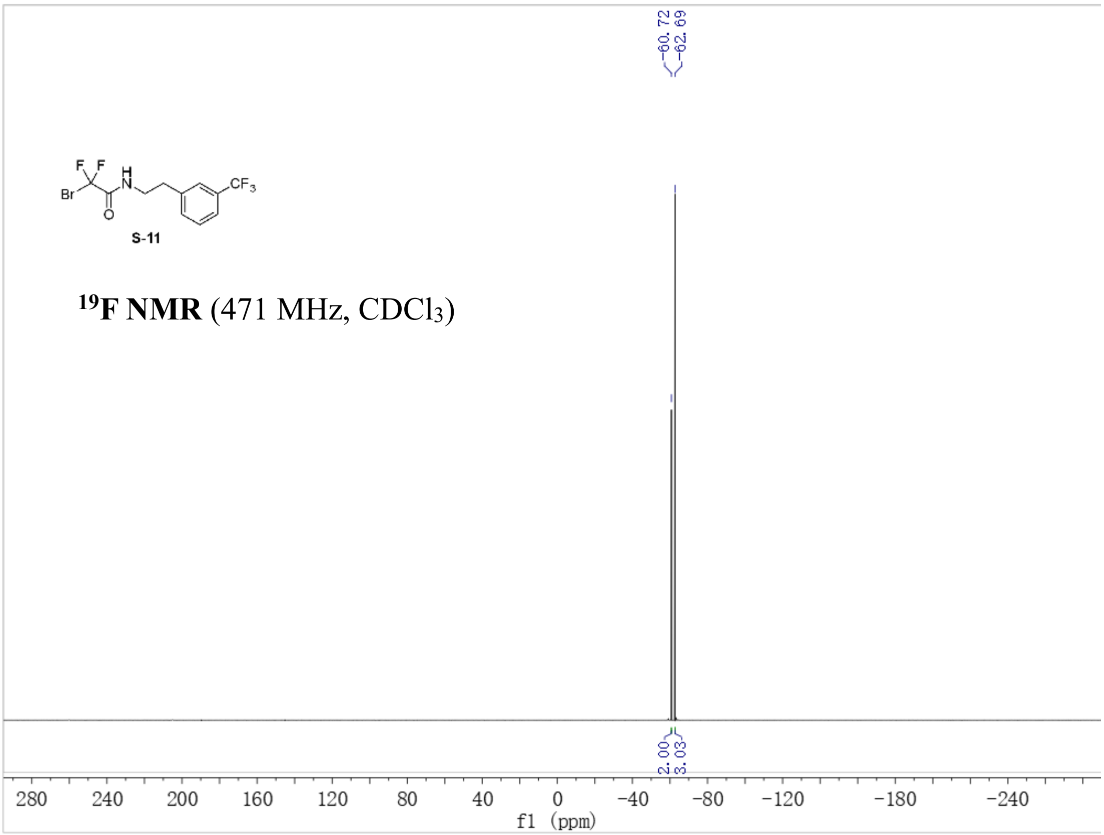


2-bromo-2,2-difluoro-*N*-(3-(trifluoromethyl)phenethyl)acetamide (S-11)



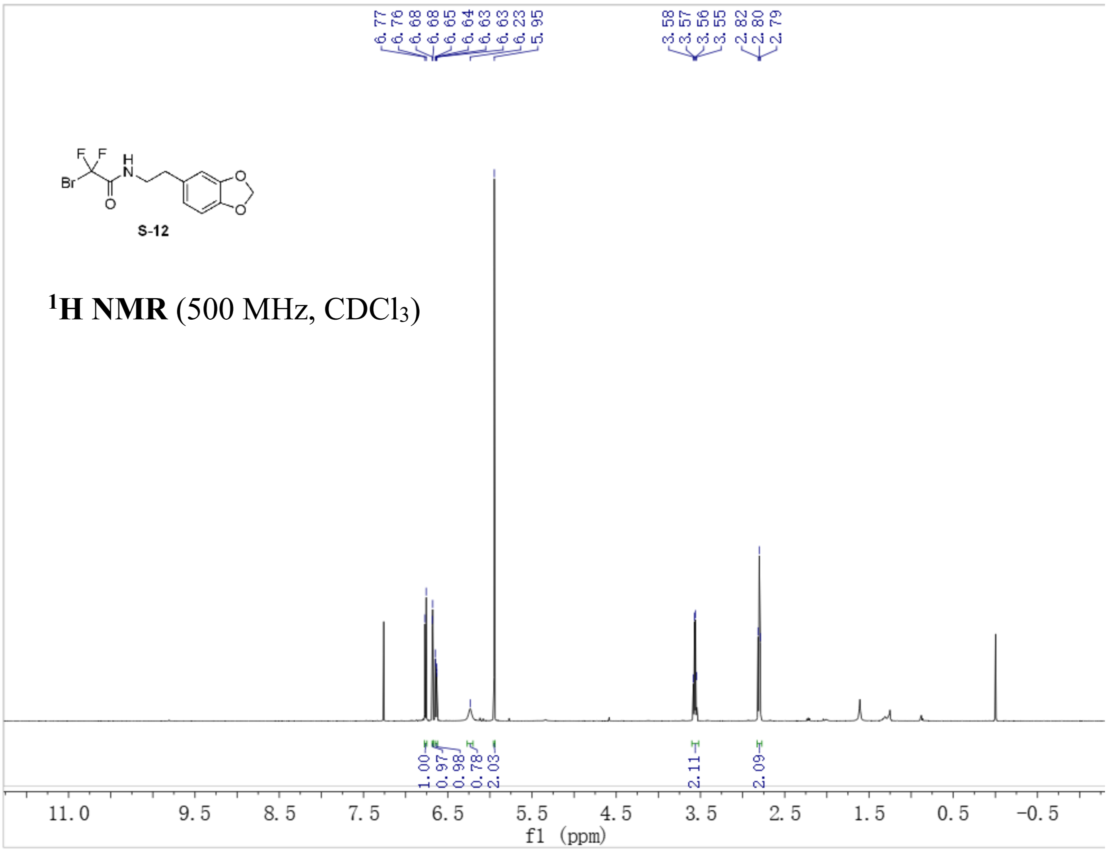


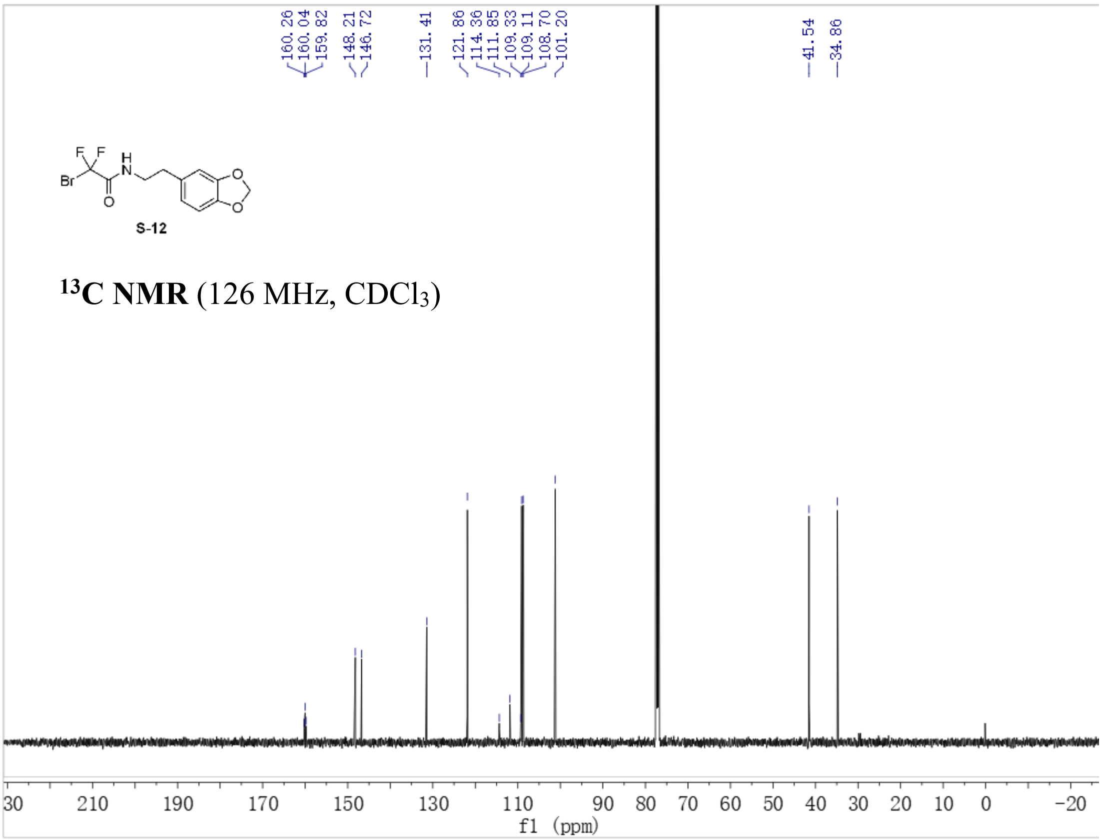
160.42
160.20
159.98
138.77
132.31
131.75
131.50
131.24
130.98
129.49
127.36
125.73
125.70
125.67
125.64
125.20
124.11
124.08
124.05
124.02
123.03
120.87
114.17
109.15
41.22
34.97
F F
H
N
Br
O
CF3
S-11
13C NMR (126 MHz, CDCl3)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

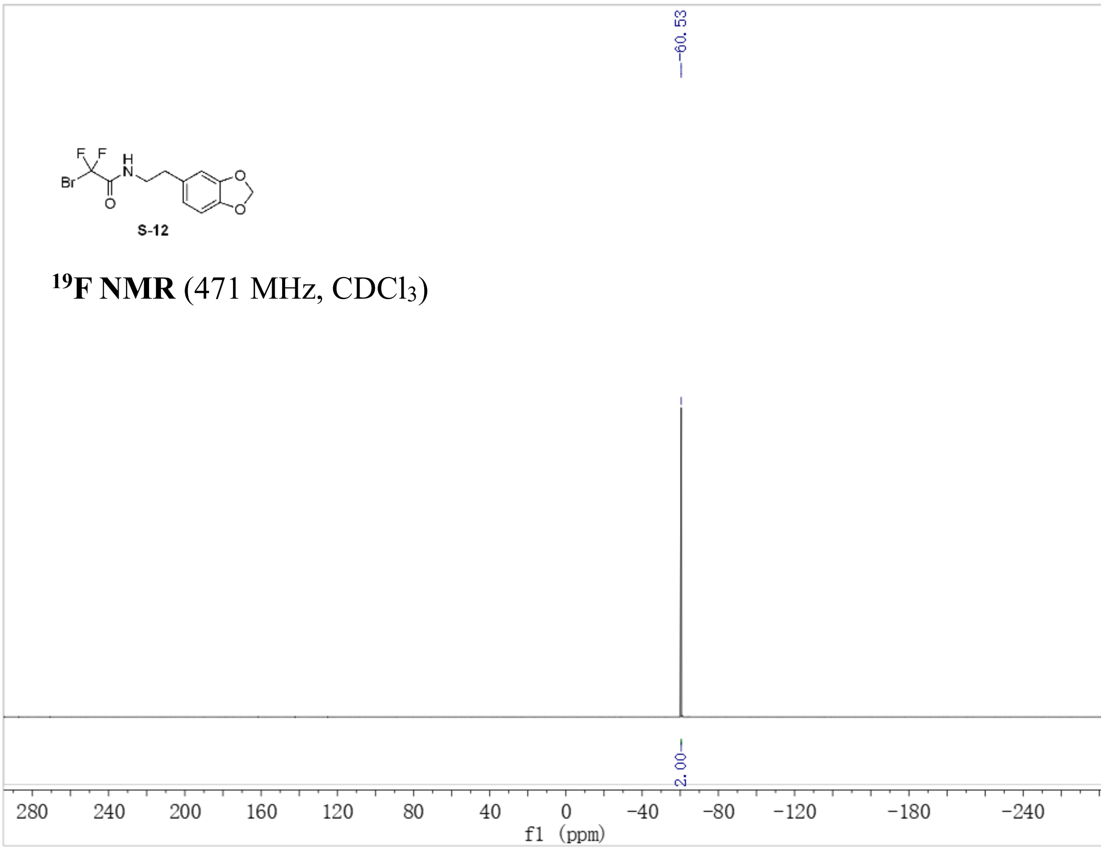


-60.72
-62.69
F F
H
N
Br
O
CF3
S-11
19F NMR (471 MHz, CDCl3)
2.00
3.03
280 240 200 160 120 80 40 0 -40 -80 -120 -180 -240
f1 (ppm)

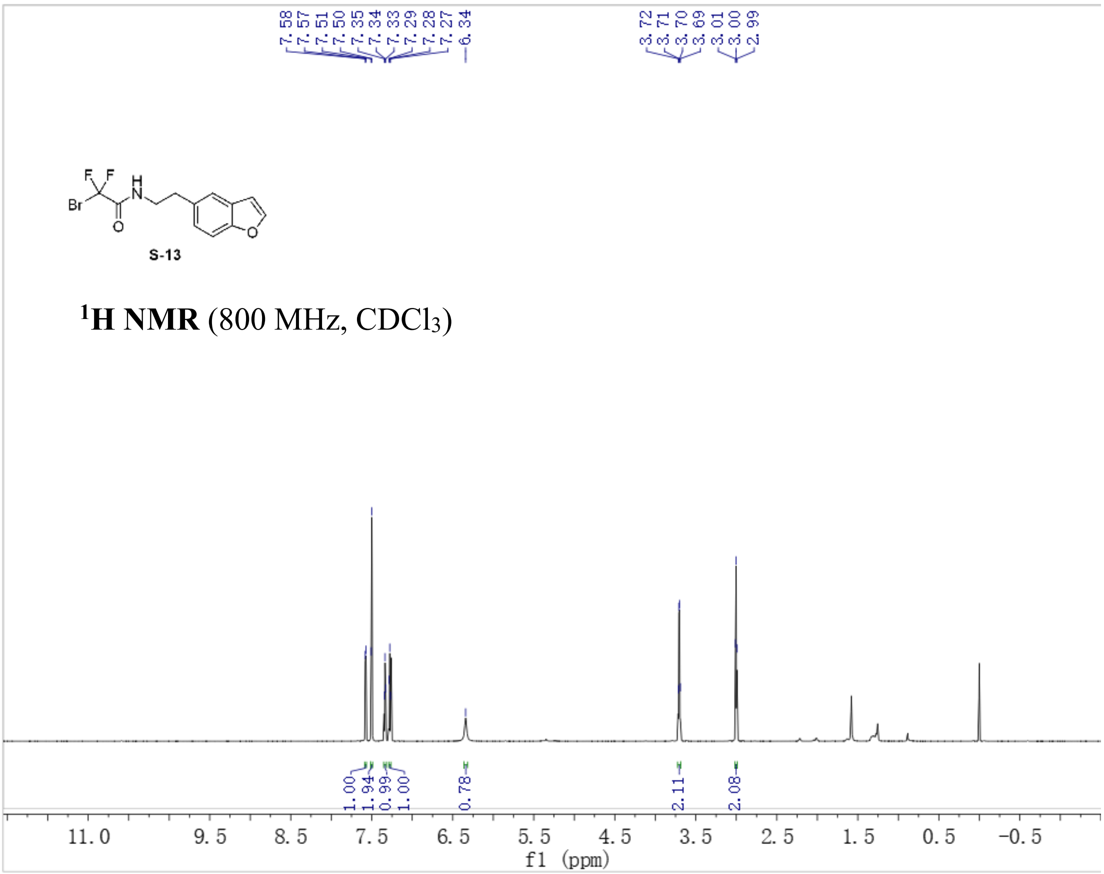
***N*-(2-(benzo[*d*][1,3]dioxol-5-yl)ethyl)-2-bromo-2,2-difluoroacetamide (S-12)**

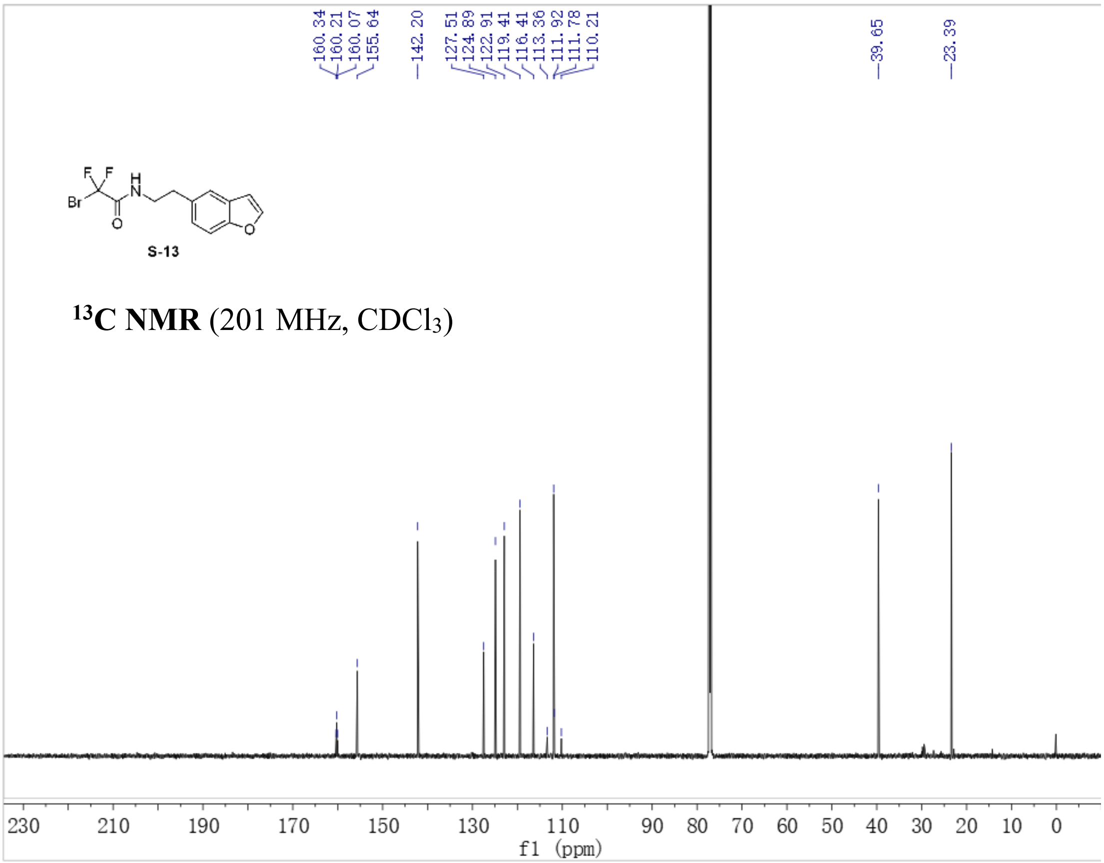




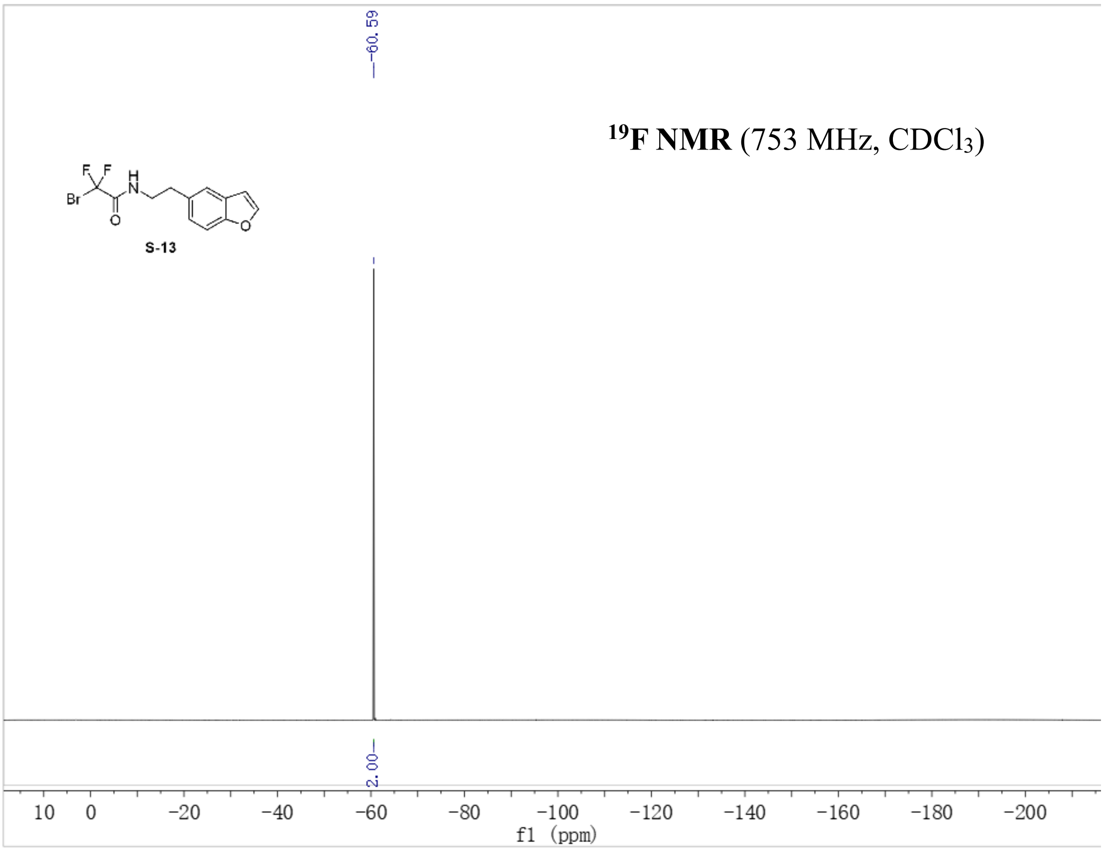


N-(2-(benzofuran-5-yl)ethyl)-2-bromo-2,2-difluoroacetamide (S-13)



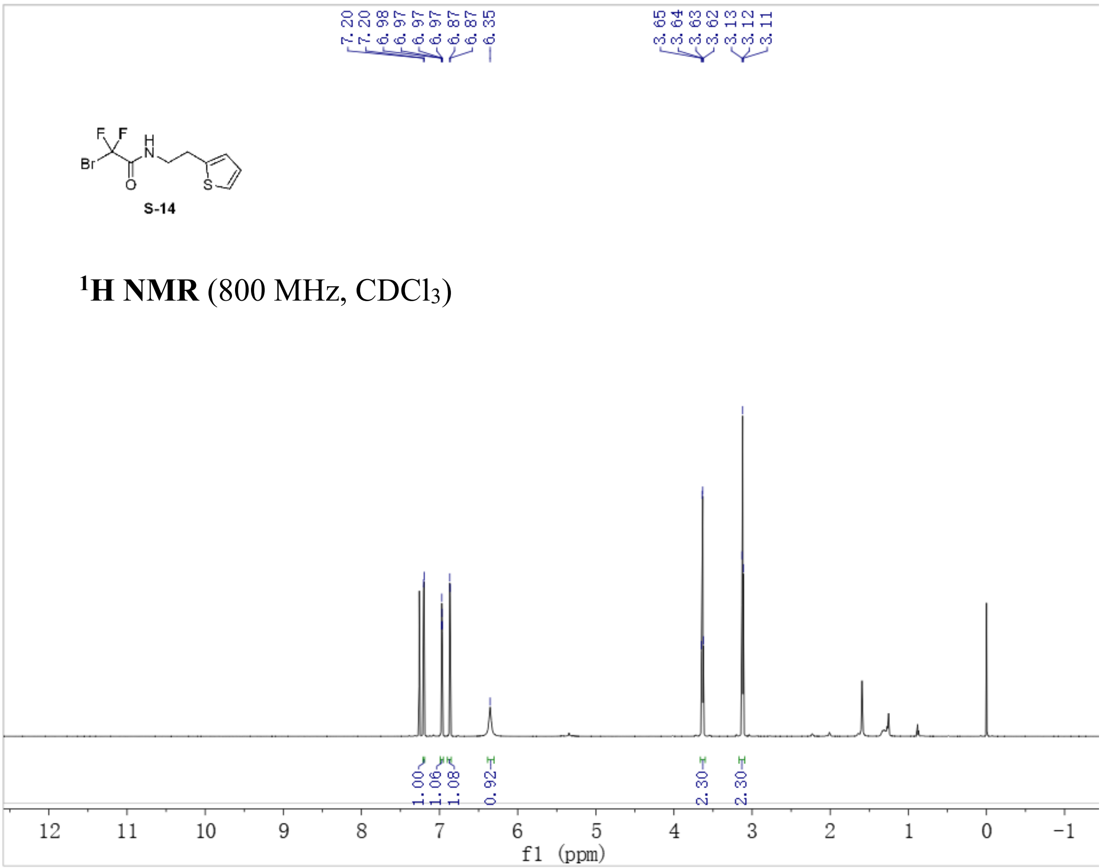


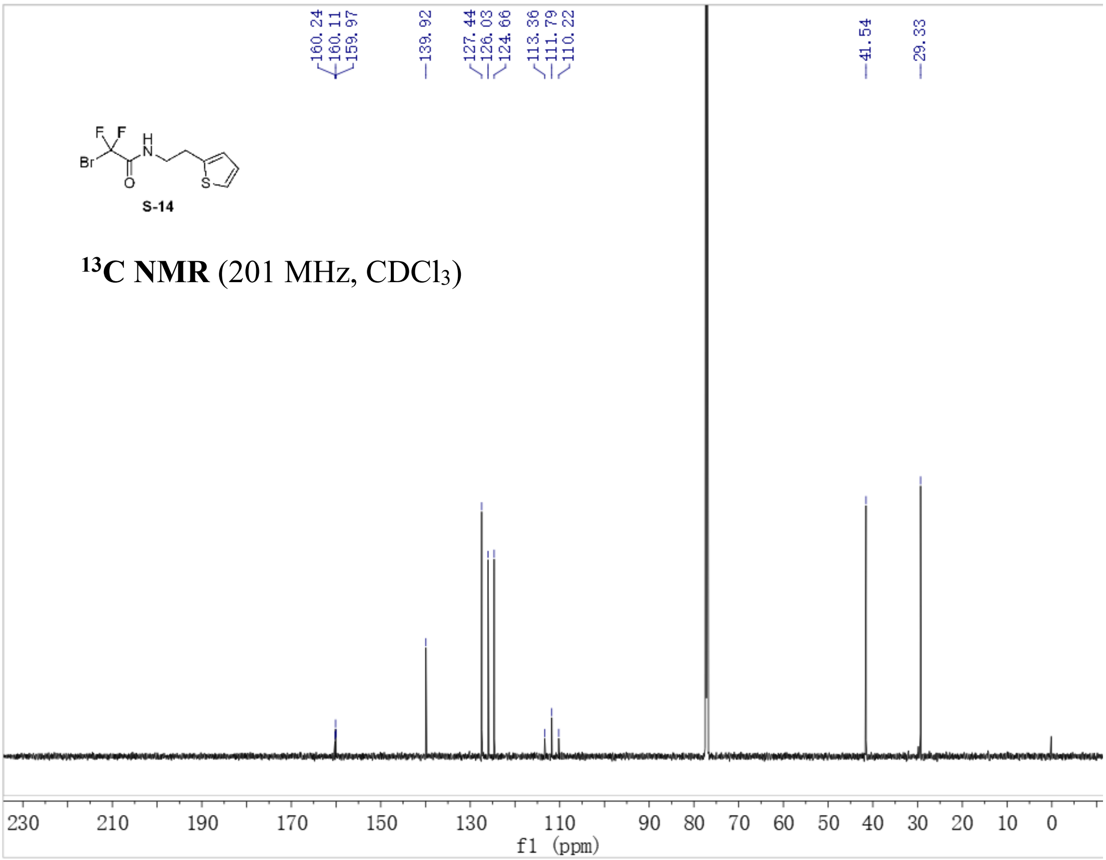
^{13}C NMR (201 MHz, $CDCl_3$)

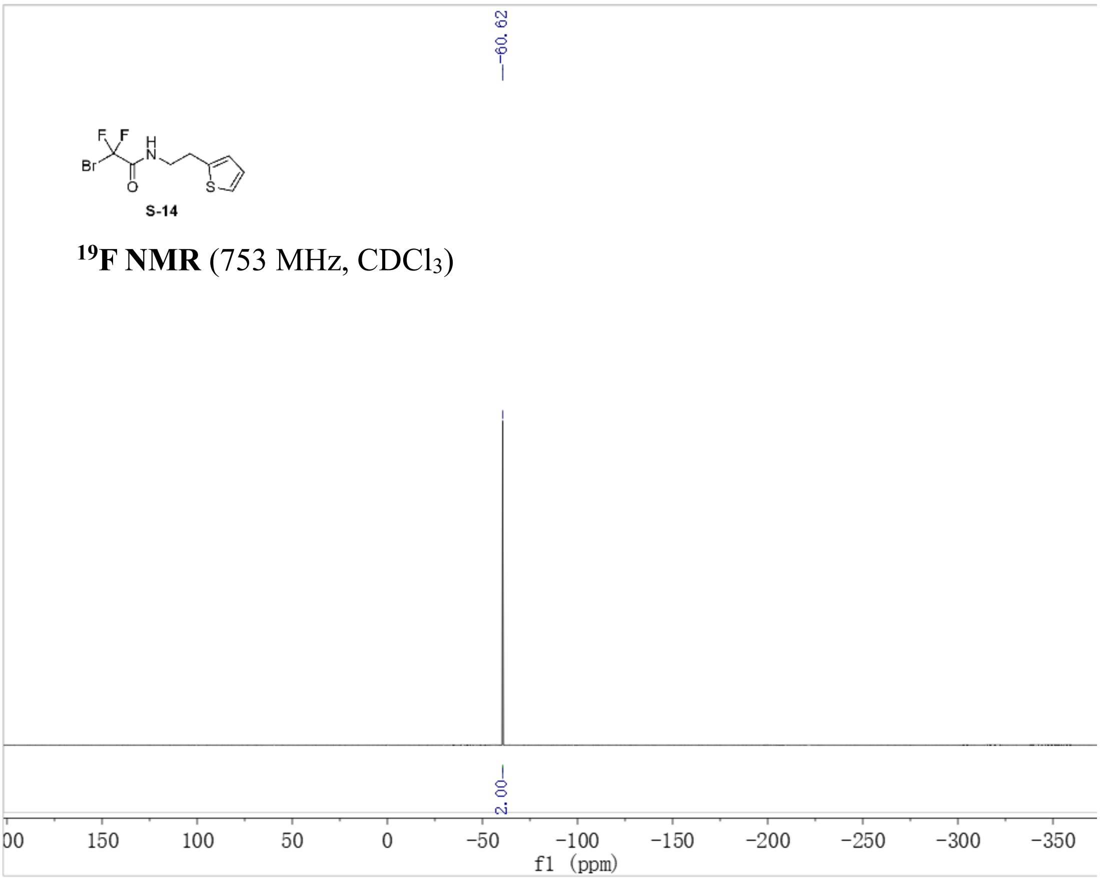


^{19}F NMR (753 MHz, $CDCl_3$)

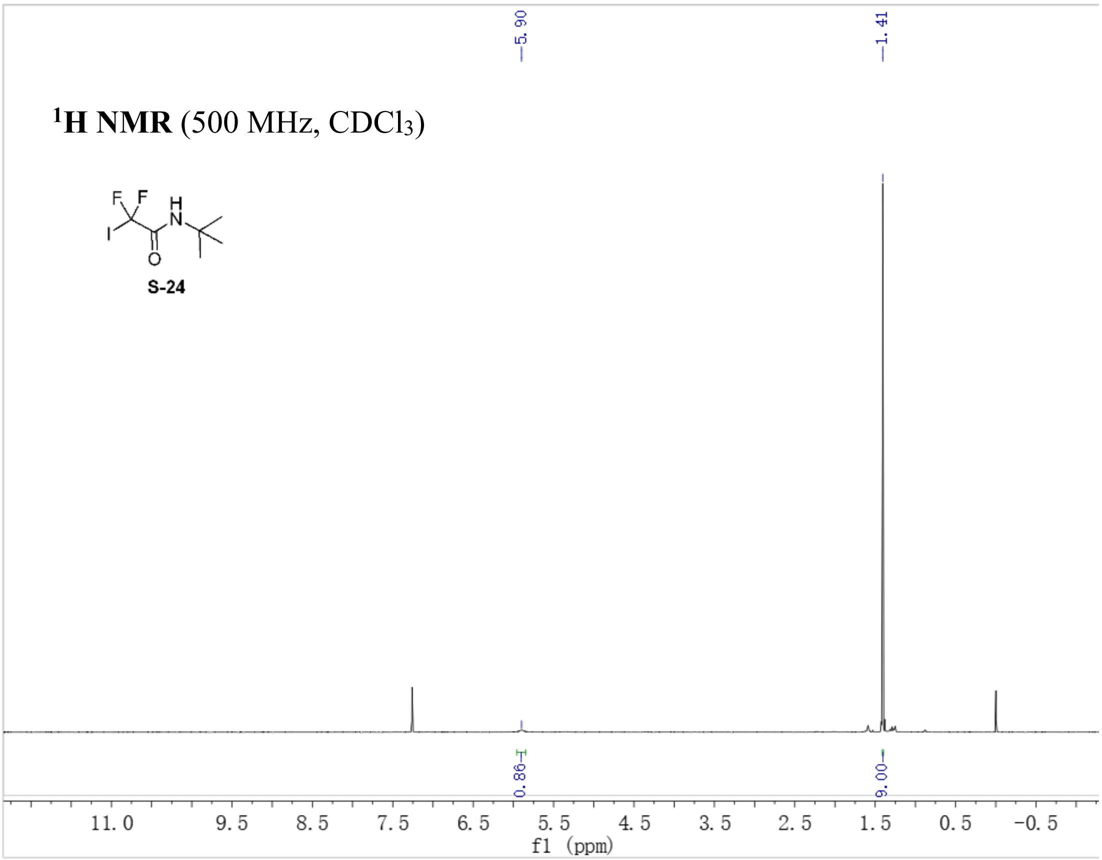
2-bromo-2,2-difluoro-*N*-(2-(thiophen-2-yl)ethyl)acetamide (S-14)

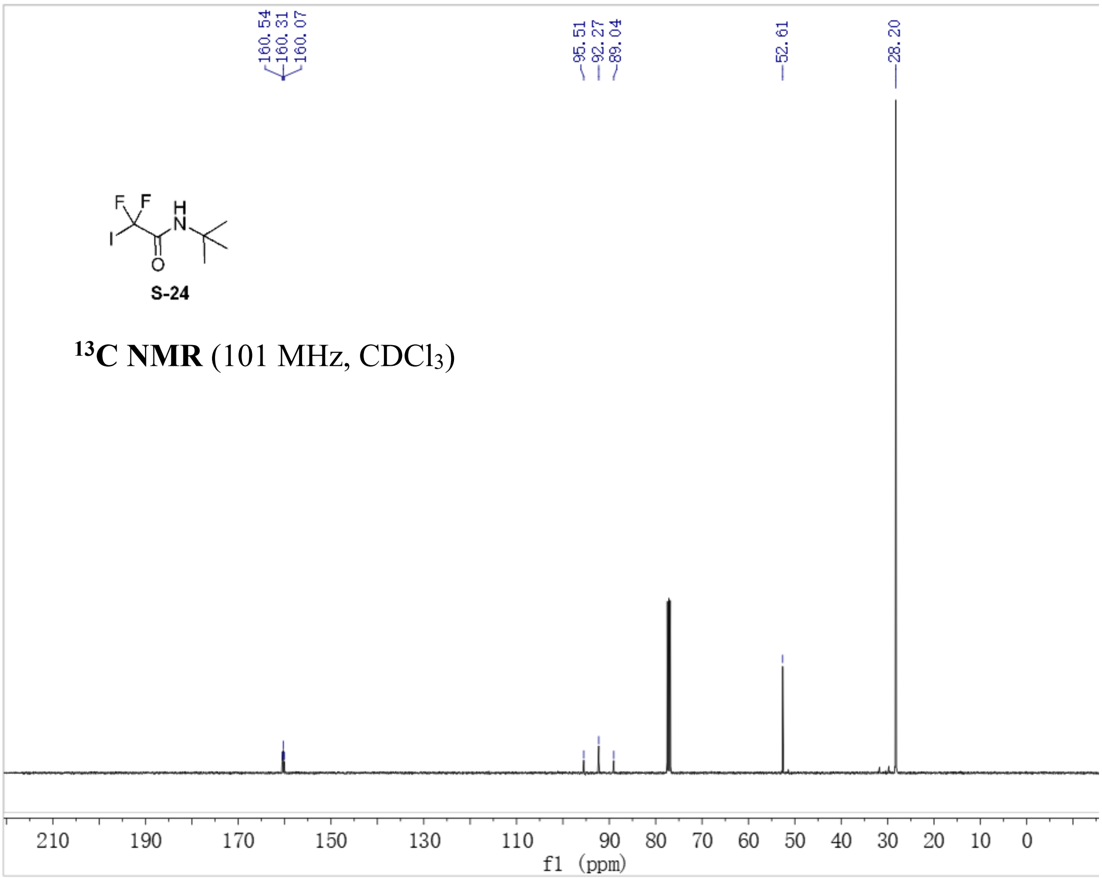


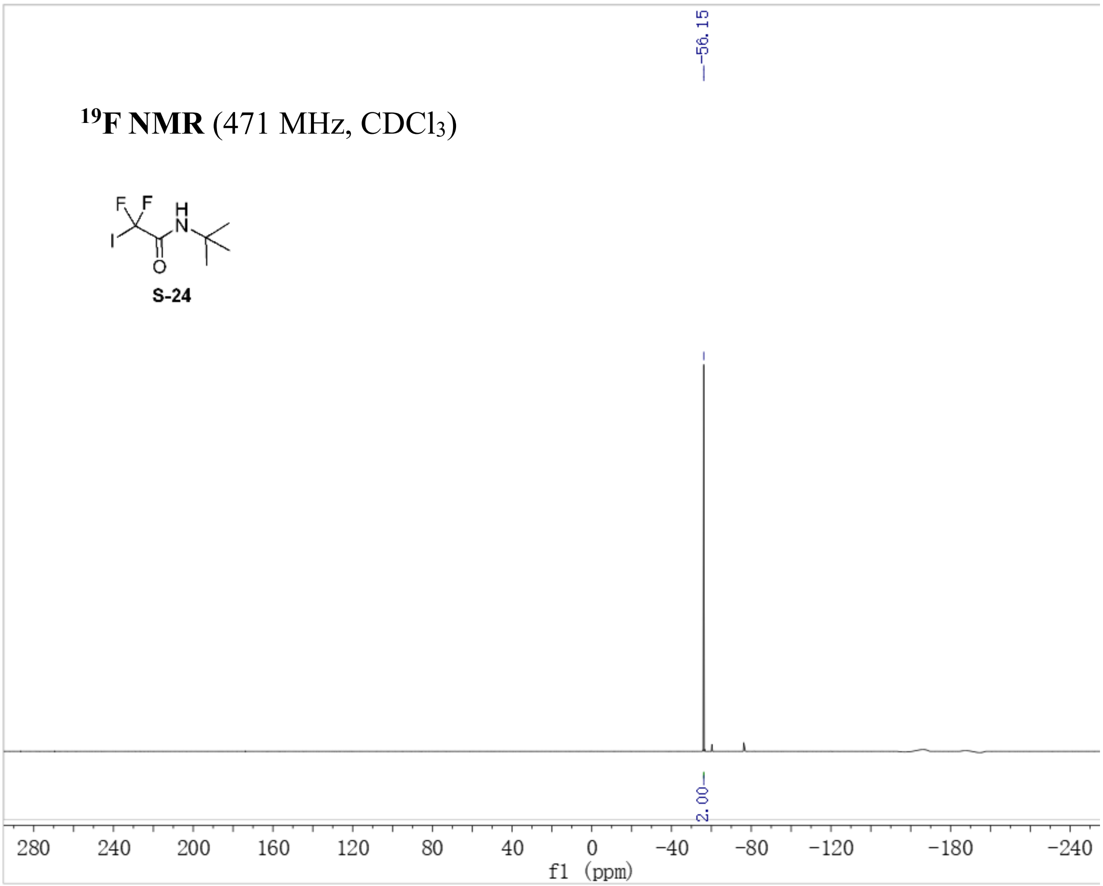




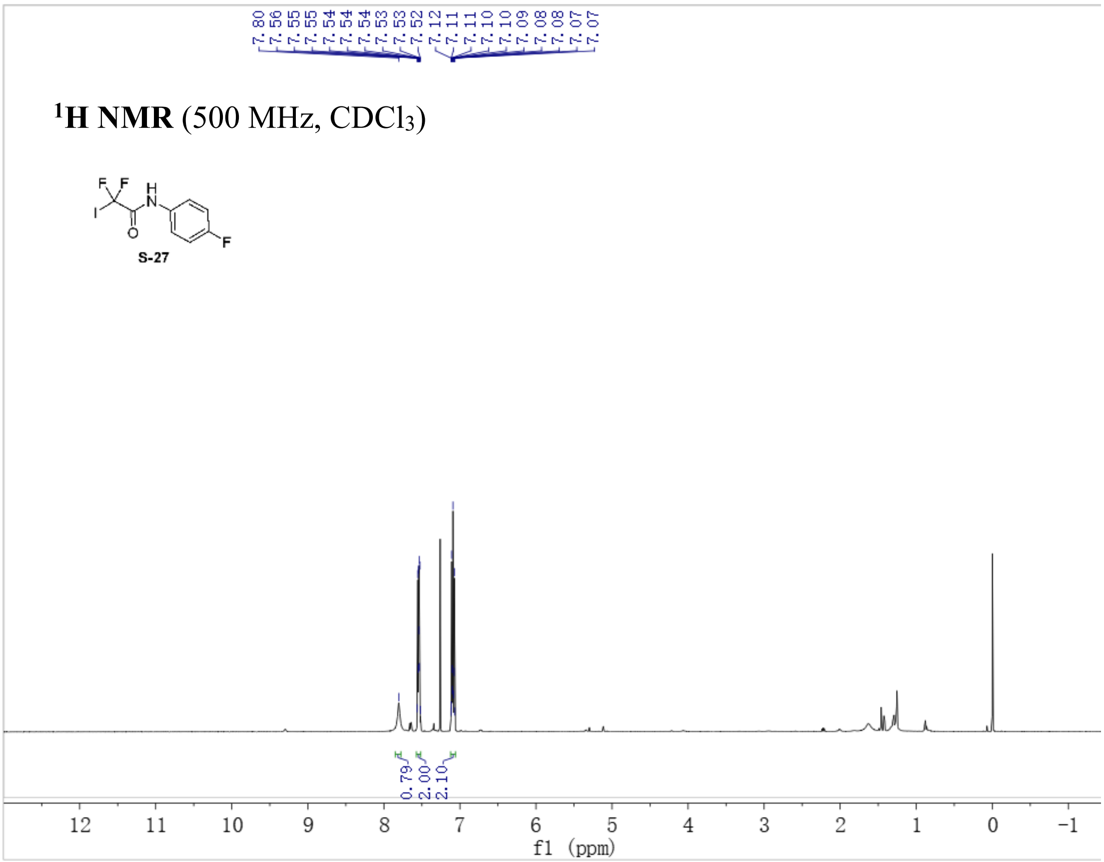
***N*-(*tert*-butyl)-2,2-difluoro-2-iodoacetamide (S-24)**

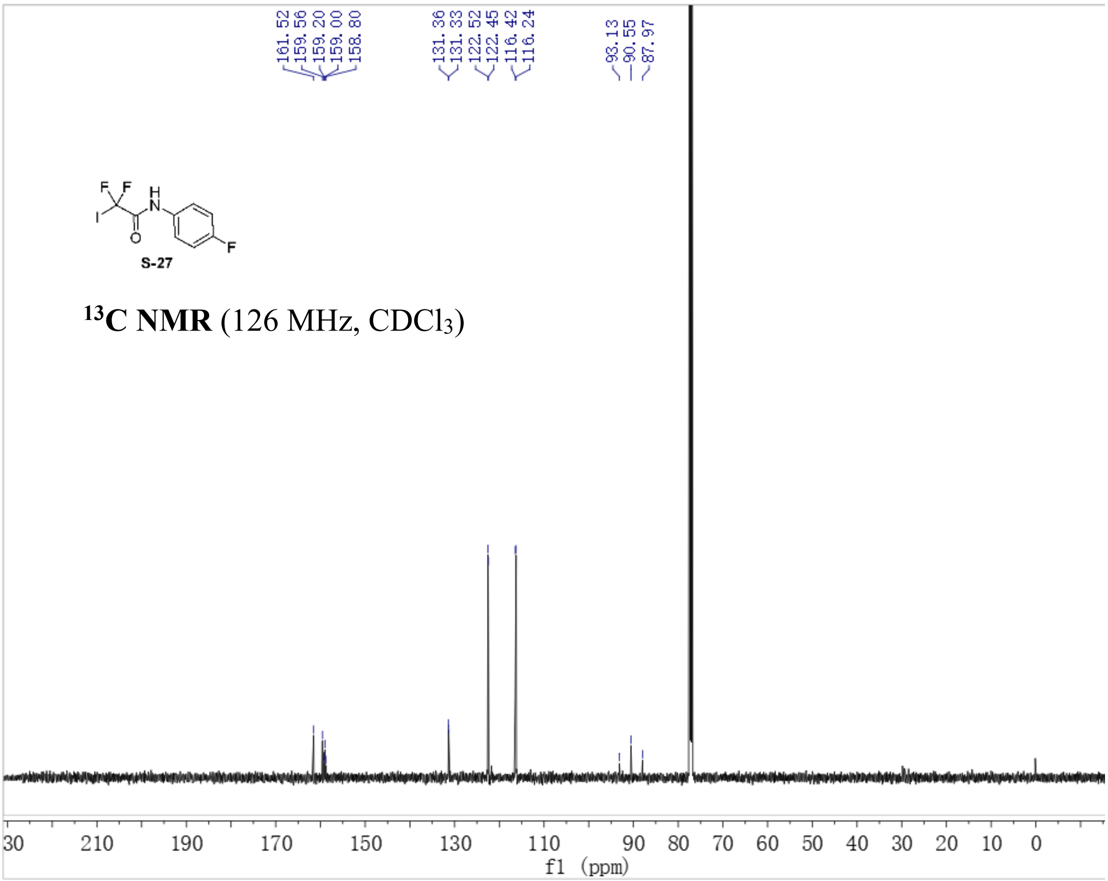



160.54
160.31
160.07
95.51
92.27
89.04
52.61
28.20
S-24
13C NMR (101 MHz, CDCl3)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

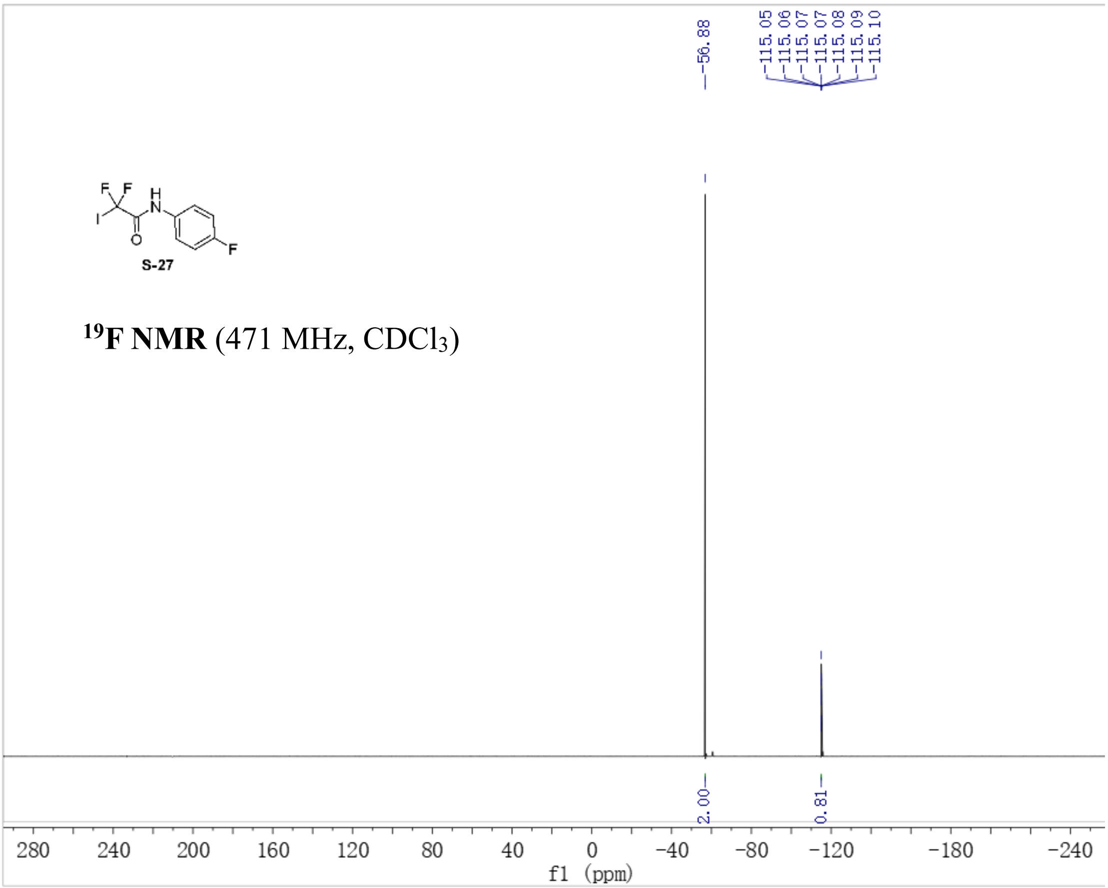

-56.15
19F NMR (471 MHz, CDCl3)
S-24
2.00
280 240 200 160 120 80 40 0 -40 -80 -120 -180 -240
f1 (ppm)

2,2-difluoro-*N*-(4-fluorophenyl)-2-iodoacetamide (S-27)



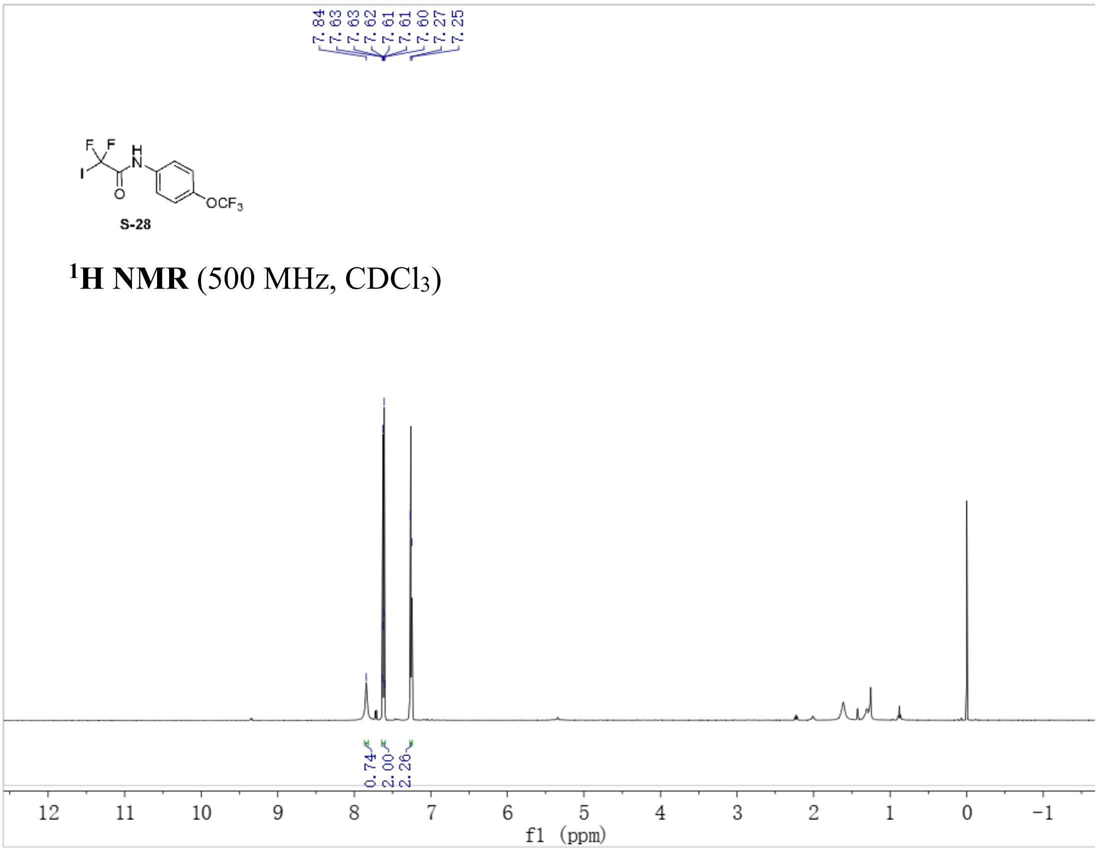


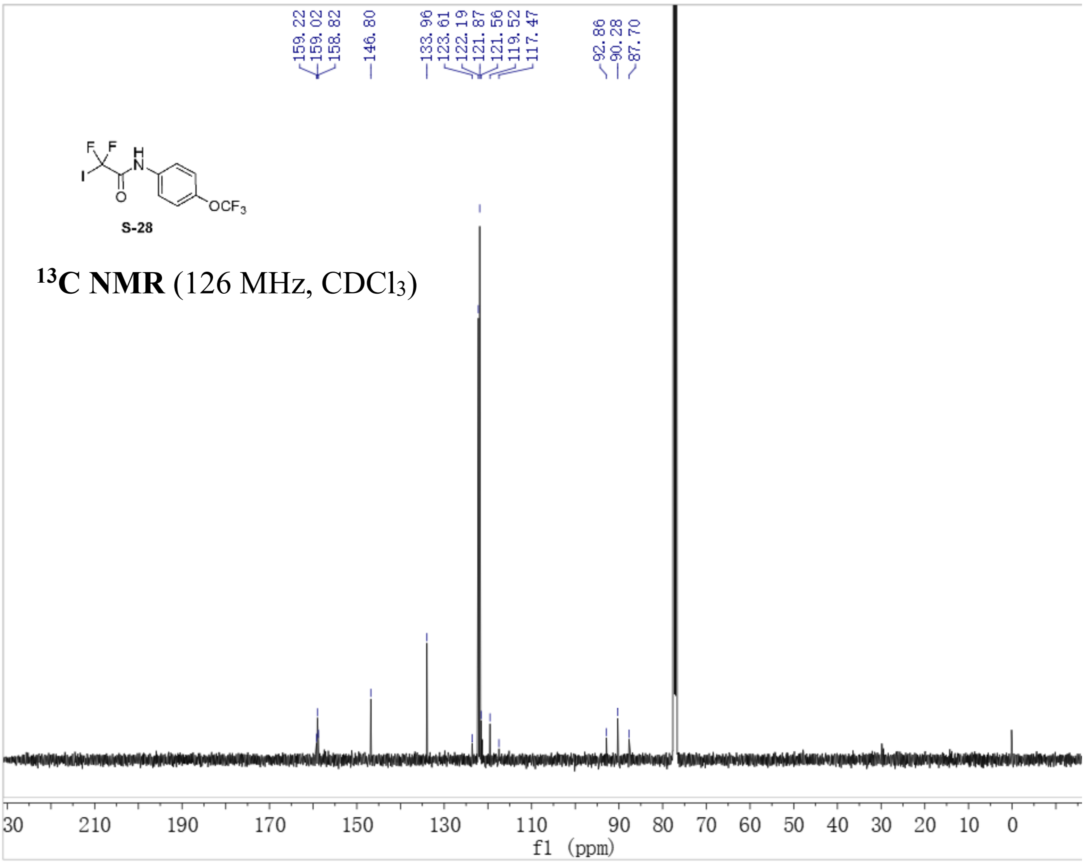
^{13}**C NMR** (126 MHz, $CDCl_3$)

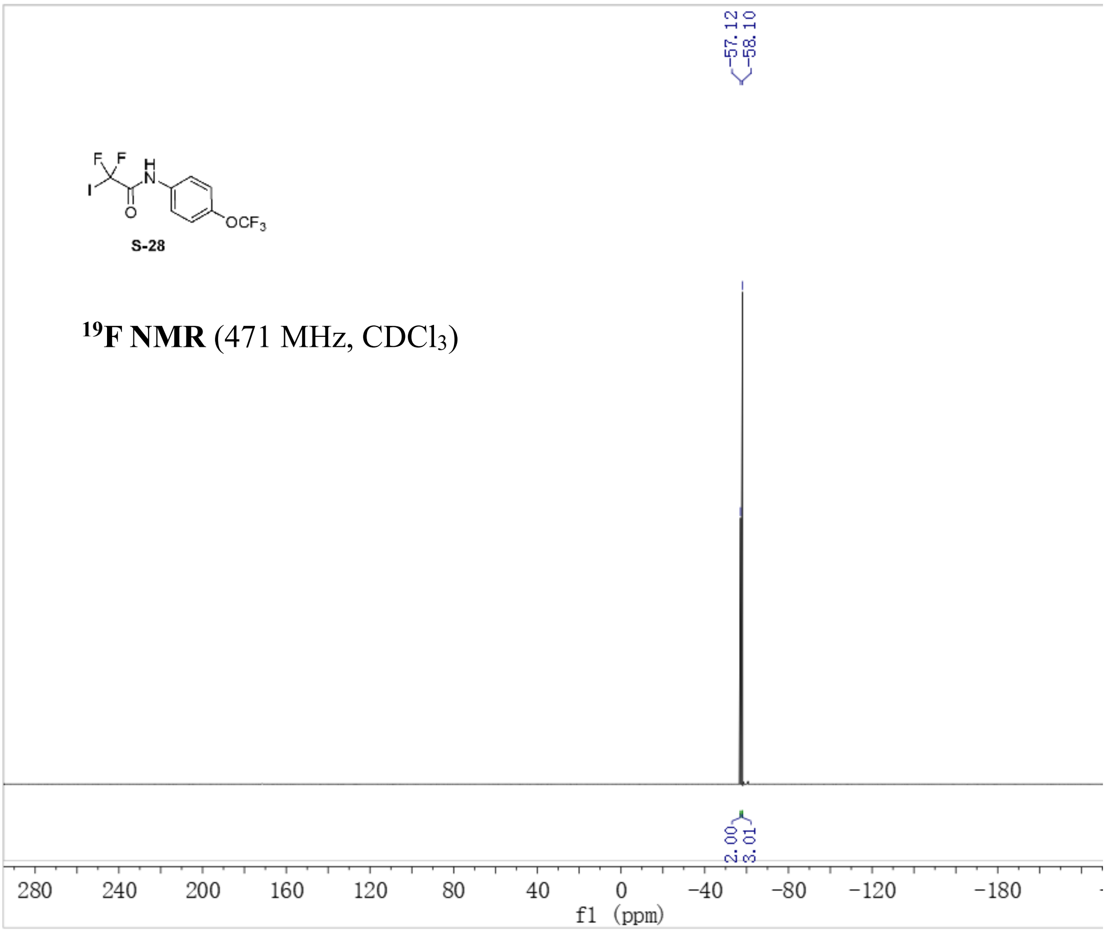


^{19}**F NMR** (471 MHz, $CDCl_3$)

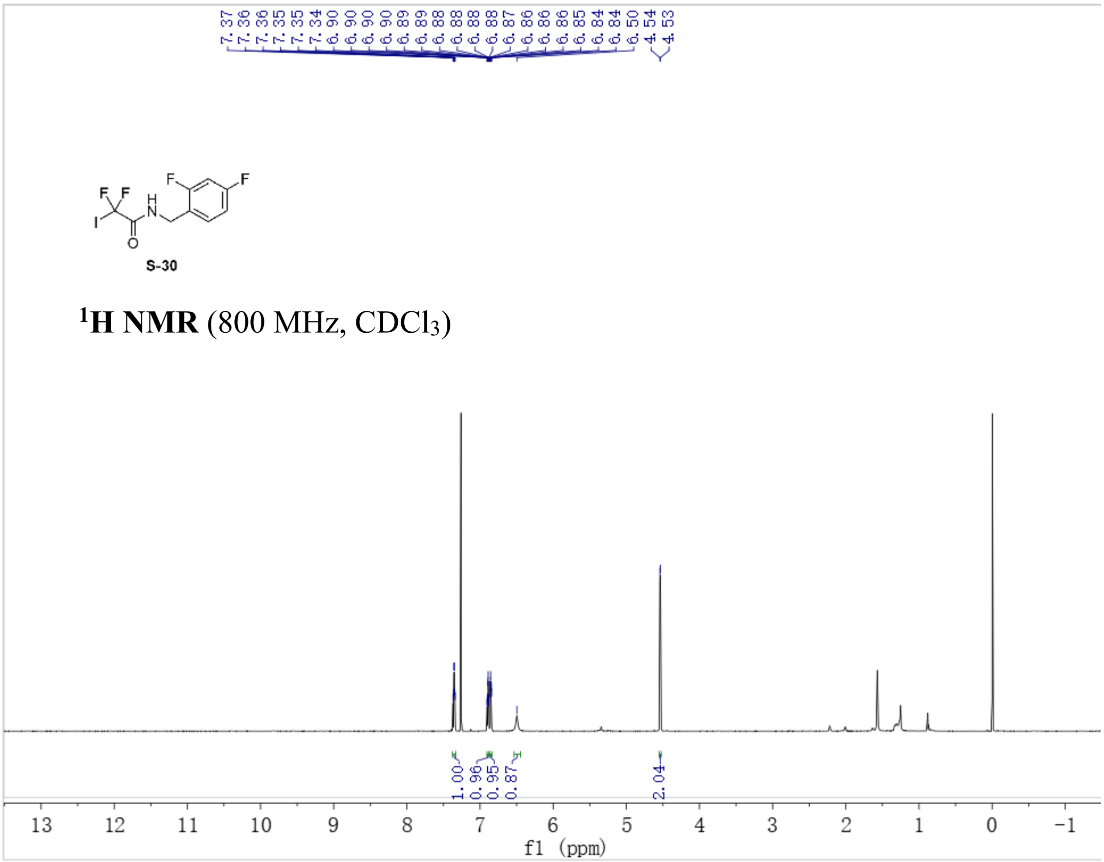
2,2-difluoro-2-iodo-*N*-(4-(trifluoromethoxy)phenyl)acetamide (S-28)

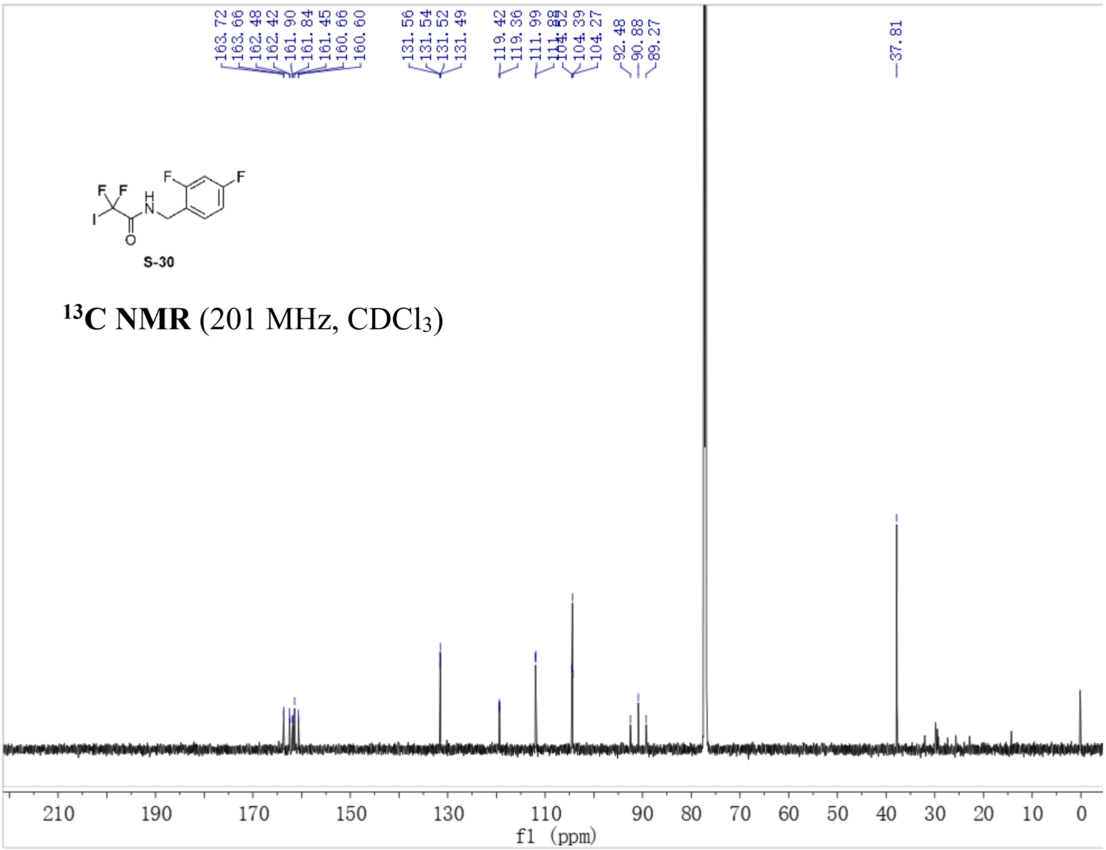


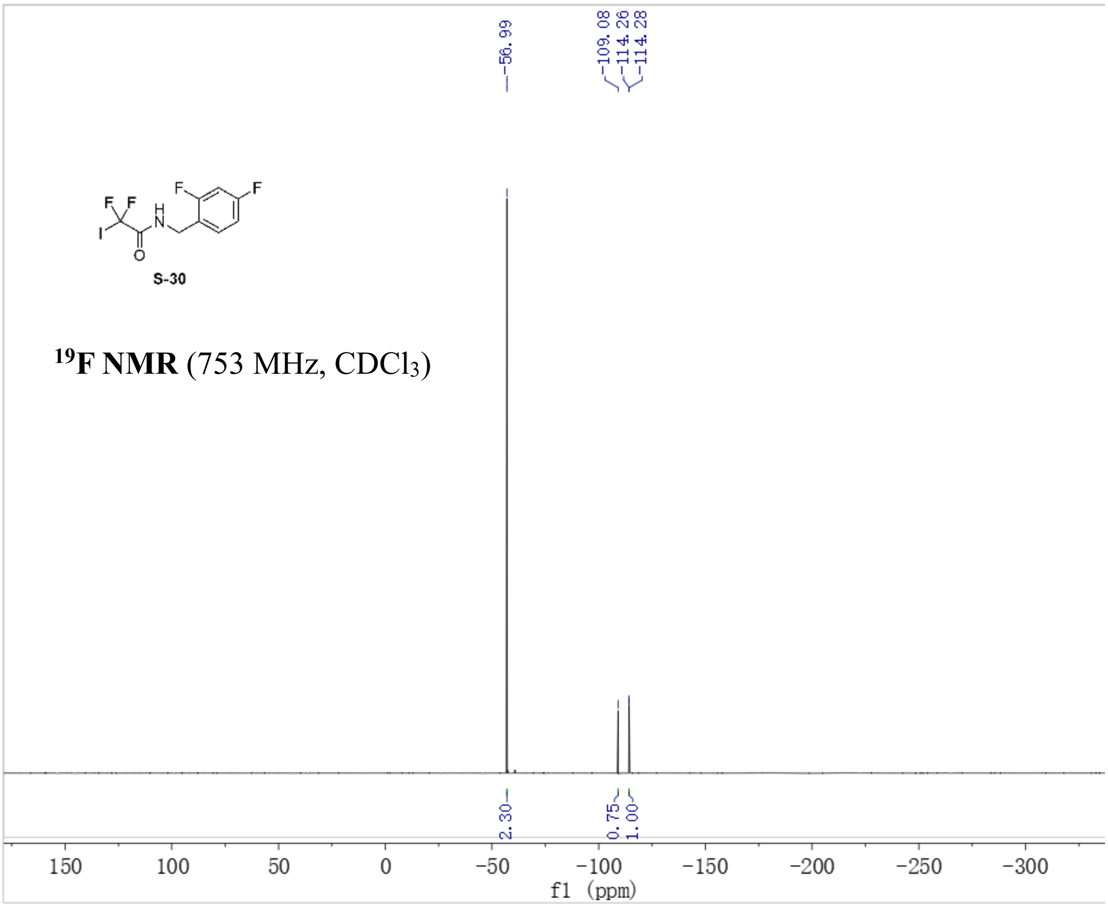




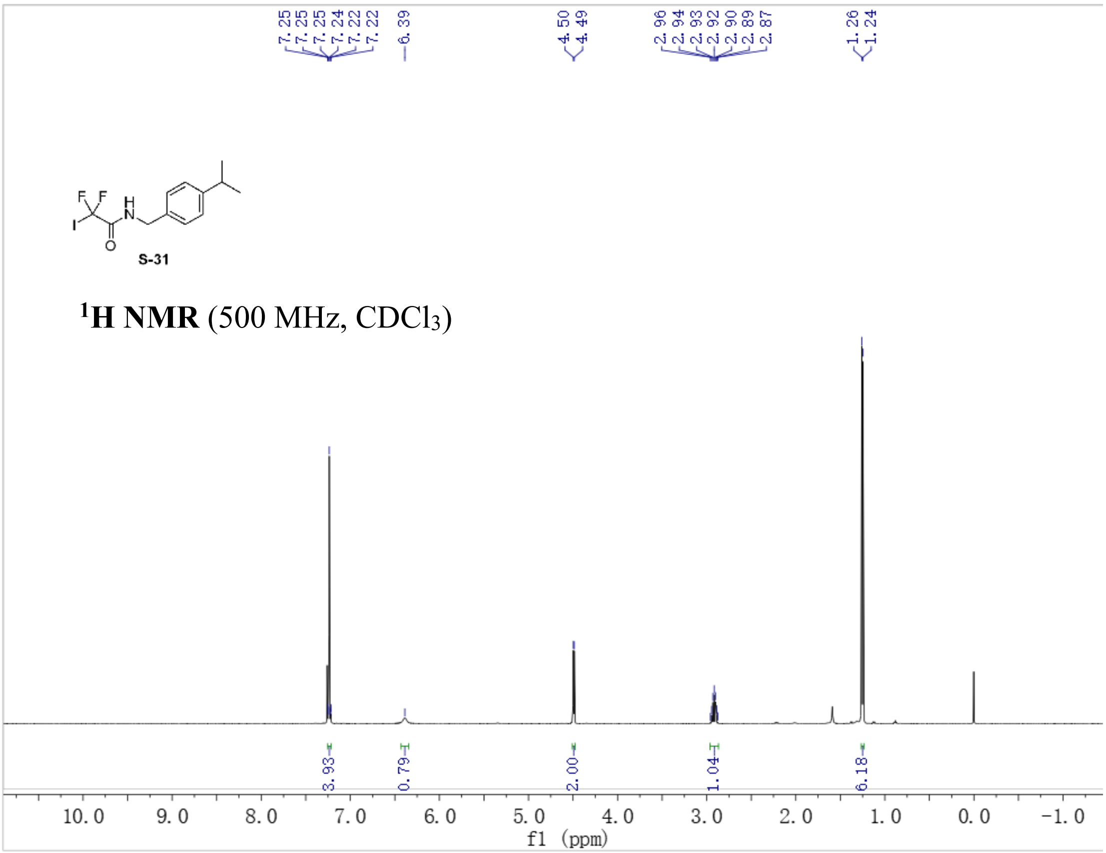
***N*-(2,4-difluorobenzyl)-2,2-difluoro-2-iodoacetamide (S-30)**


7.37 7.36 7.36 7.35 7.35 7.34 6.90 6.90 6.90 6.90 6.89 6.89 6.88 6.88 6.88 6.88 6.87 6.86 6.86 6.86 6.85 6.84 6.84 6.50 4.54 4.53
S-30
1H NMR (800 MHz, CDCl3)
1.00 0.96 0.95 0.87 2.04
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

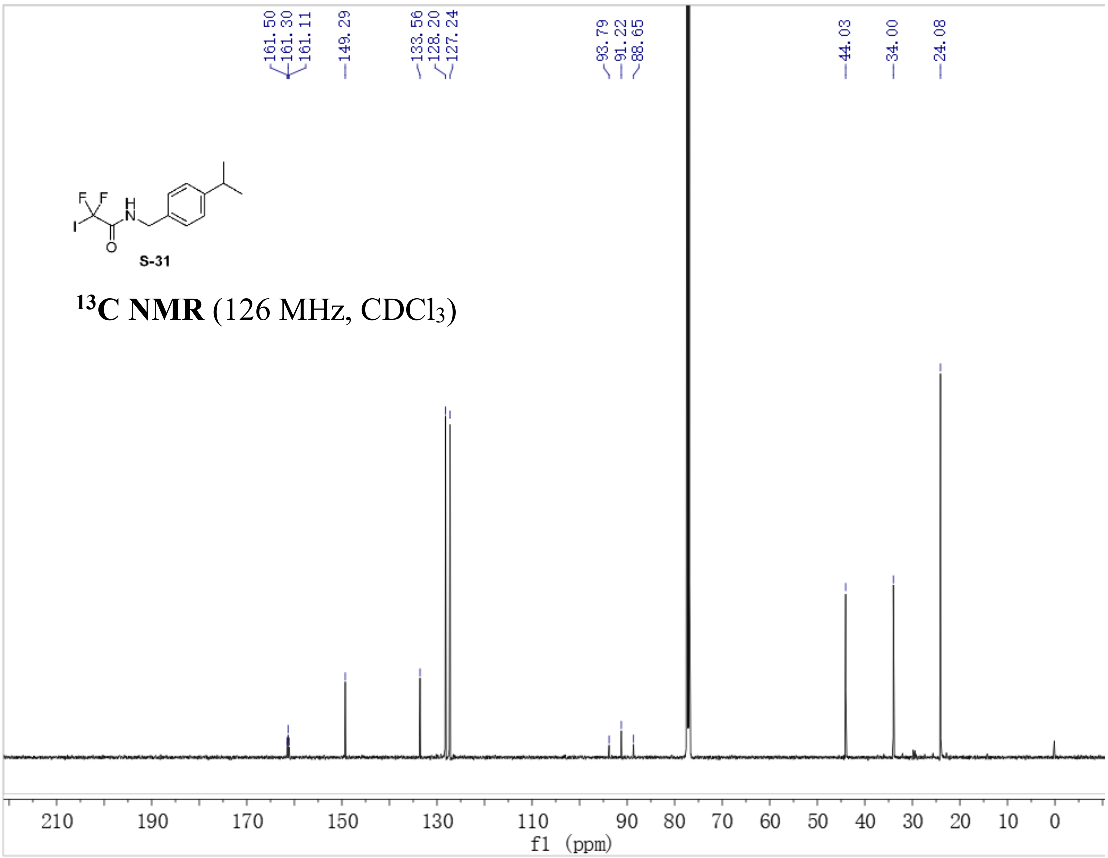

163.72 163.66 162.48 162.42 161.90 161.84 161.45 160.66 160.60
131.56 131.54 131.52 131.49
119.42 119.36 111.99 104.39 104.27 92.48 90.88 89.27
37.81
S-30
13C NMR (201 MHz, CDCl3)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



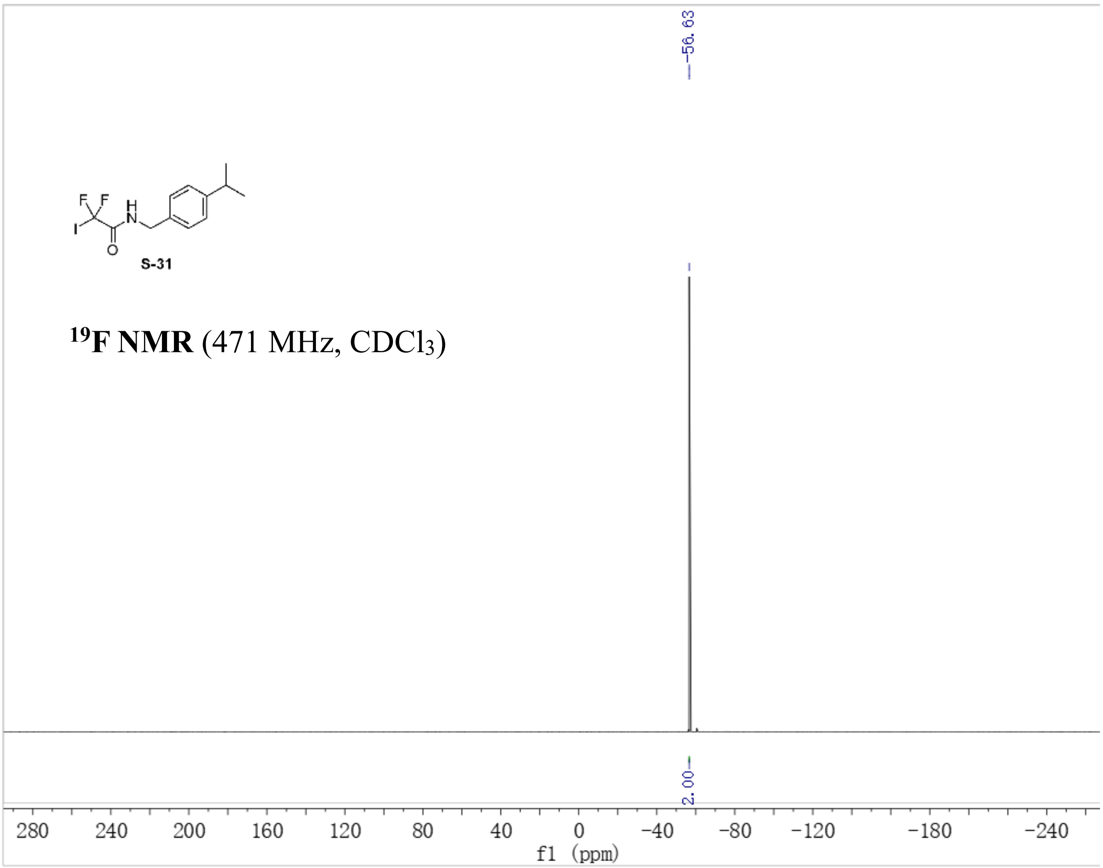
2,2-difluoro-2-iodo-*N*-(4-isopropylbenzyl)acetamide (S-31)



S-31
¹H NMR (500 MHz, CDCl3)
7.25 7.25 7.25 7.24 7.22 7.22 7.22
6.39
4.50 4.49
2.96 2.94 2.93 2.92 2.90 2.89 2.87
1.26 1.24
3.93 0.79 2.00 1.04 6.18
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

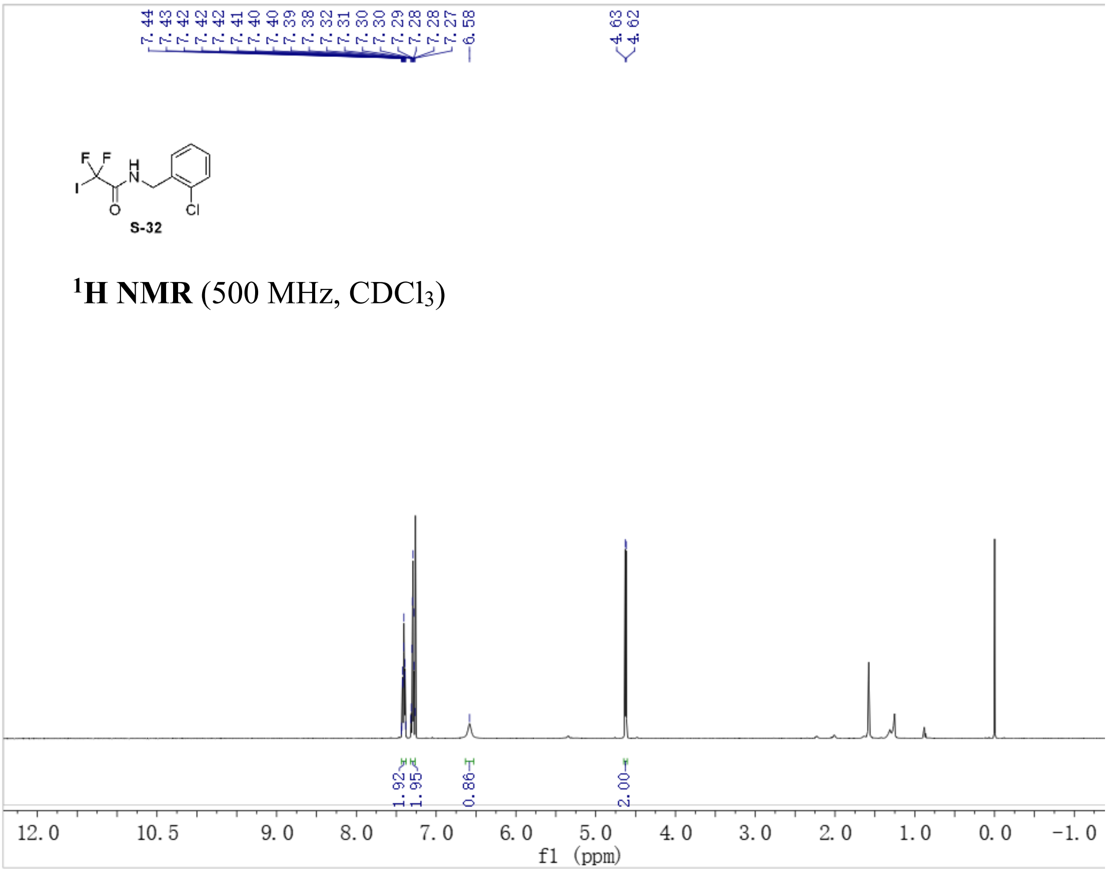


S-31
¹³C NMR (126 MHz, CDCl3)
161.50 161.30 161.11
149.29
133.56 128.20 127.24
93.79 91.22 88.65
44.03
34.00
24.08
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

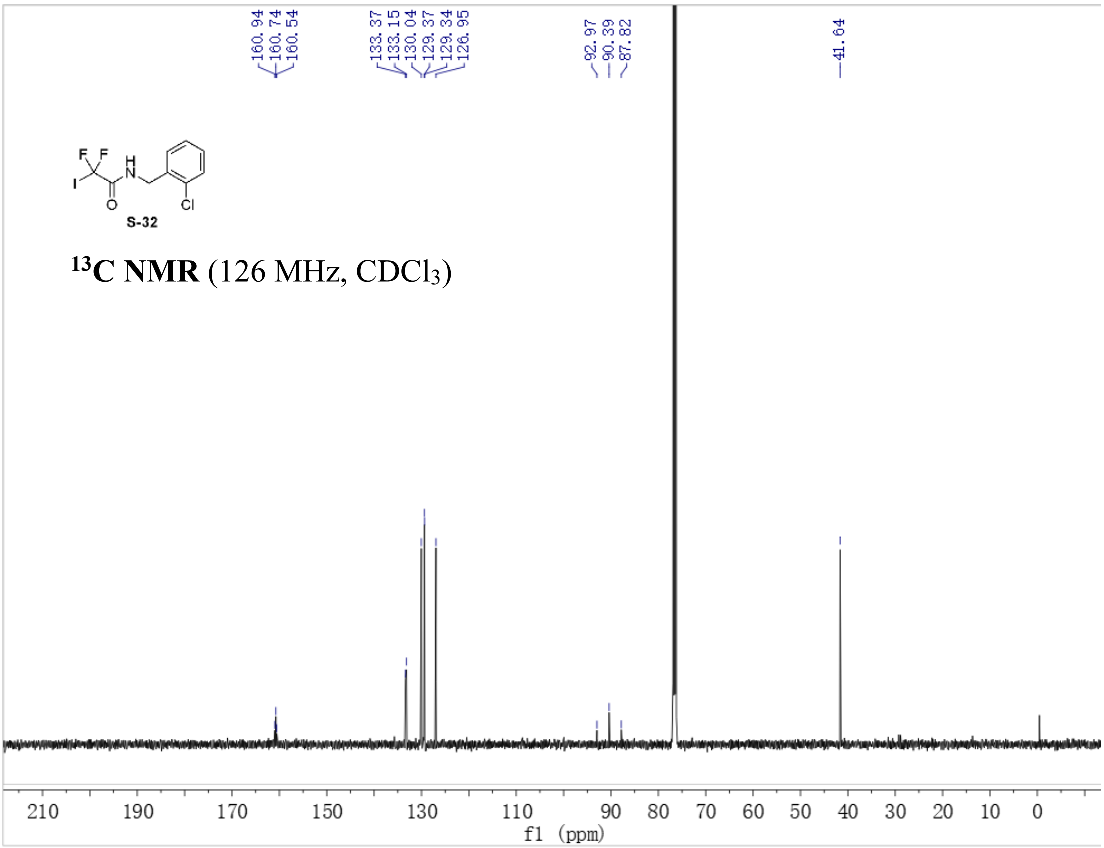


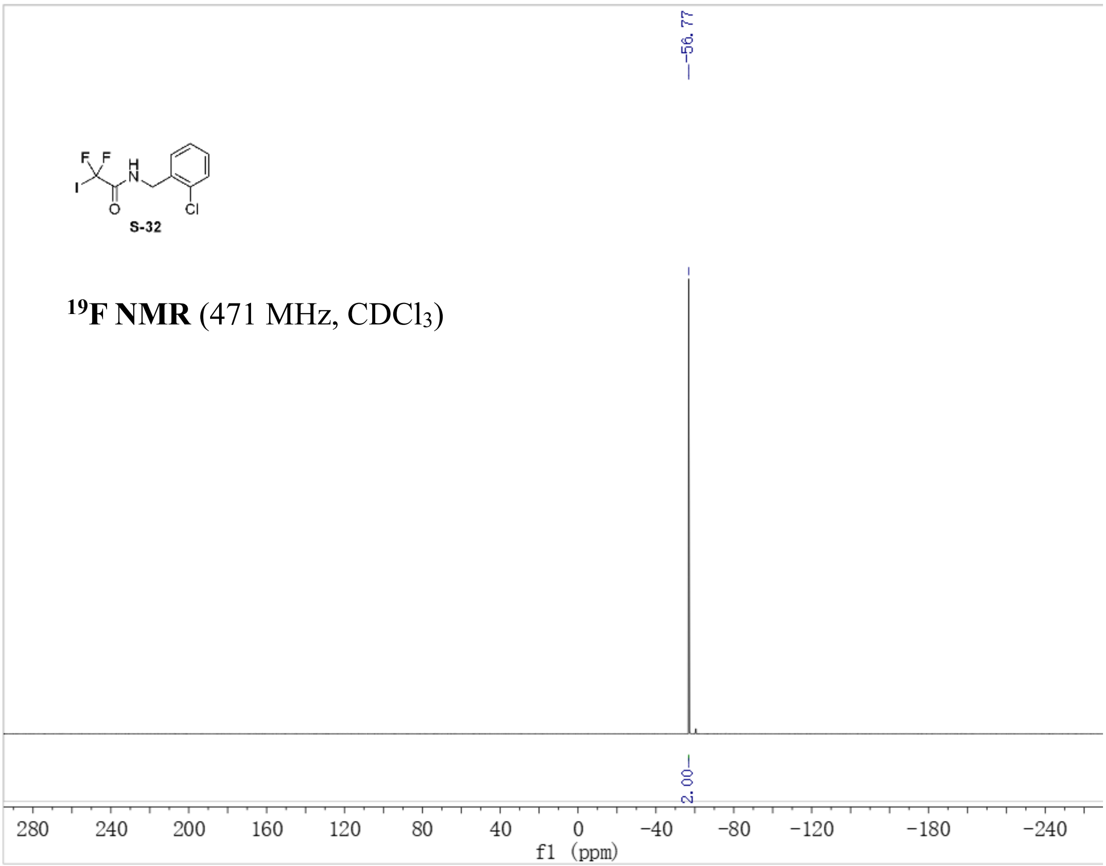
^{19}F NMR (471 MHz, $CDCl_3$)

N-(2-chlorobenzyl)-2,2-difluoro-2-iodoacetamide (S-32)

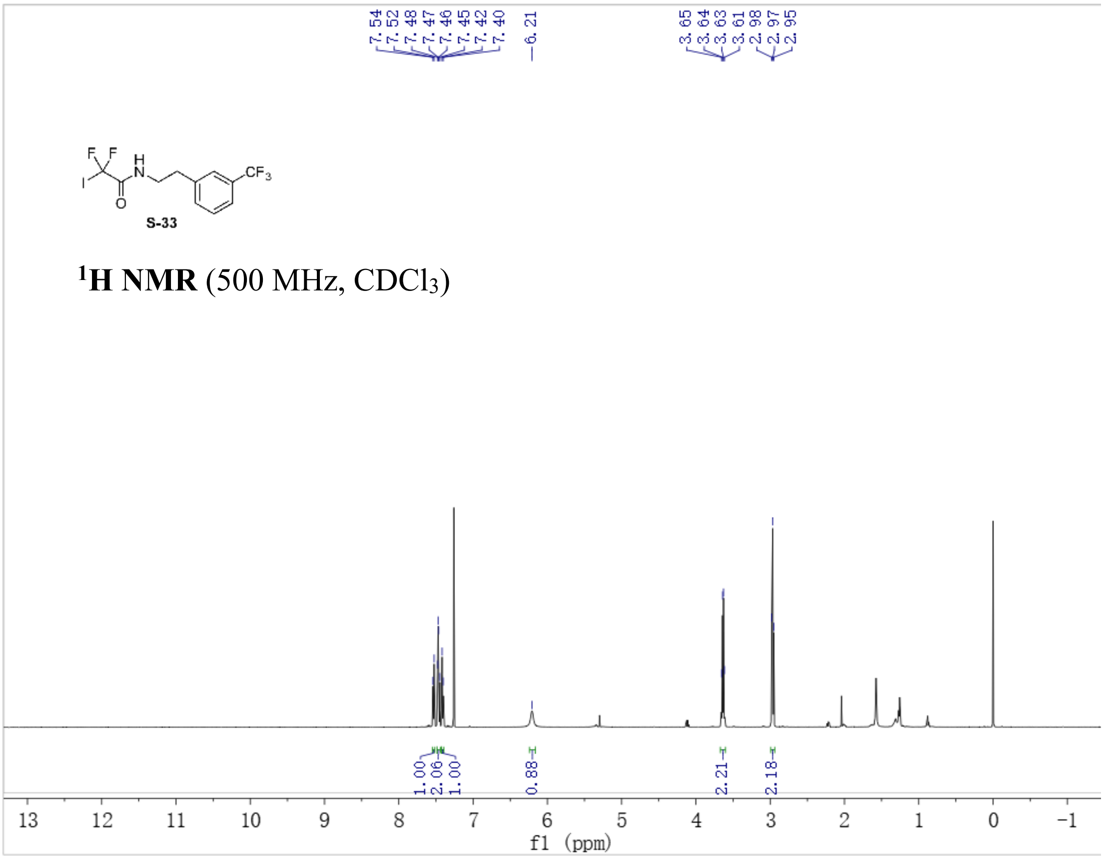


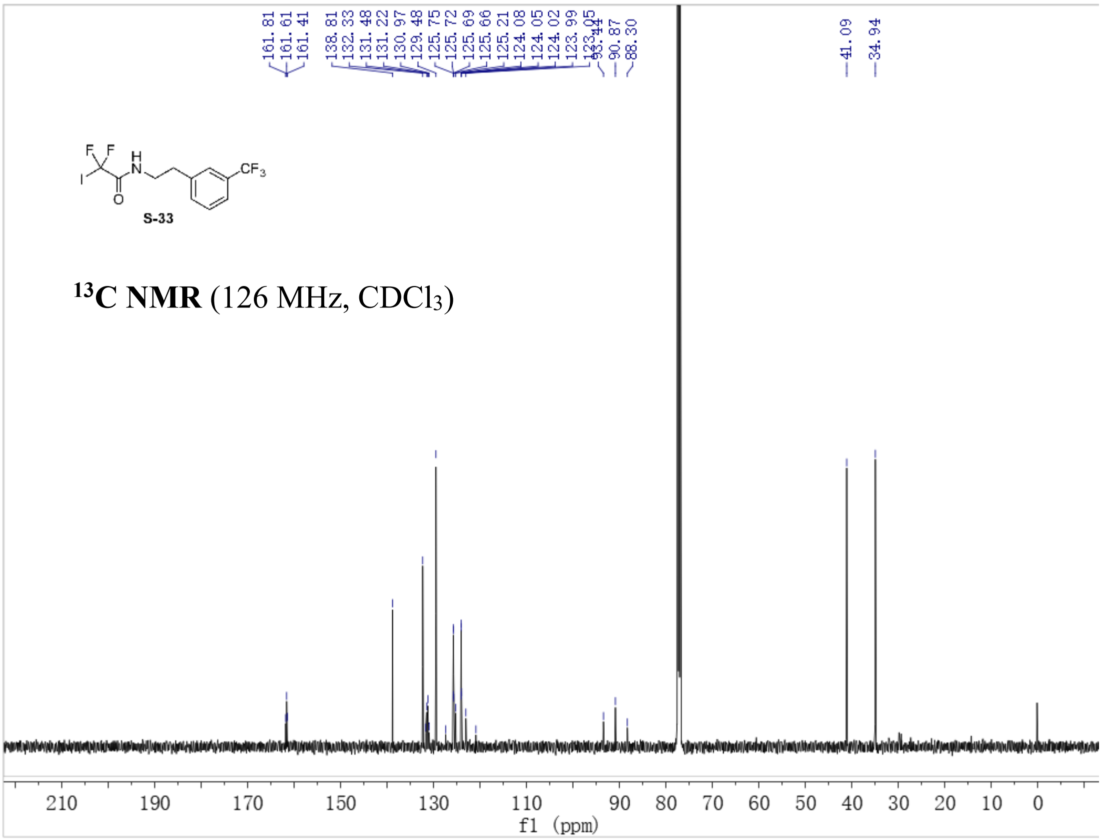
^{1}H NMR (500 MHz, $CDCl_3$)

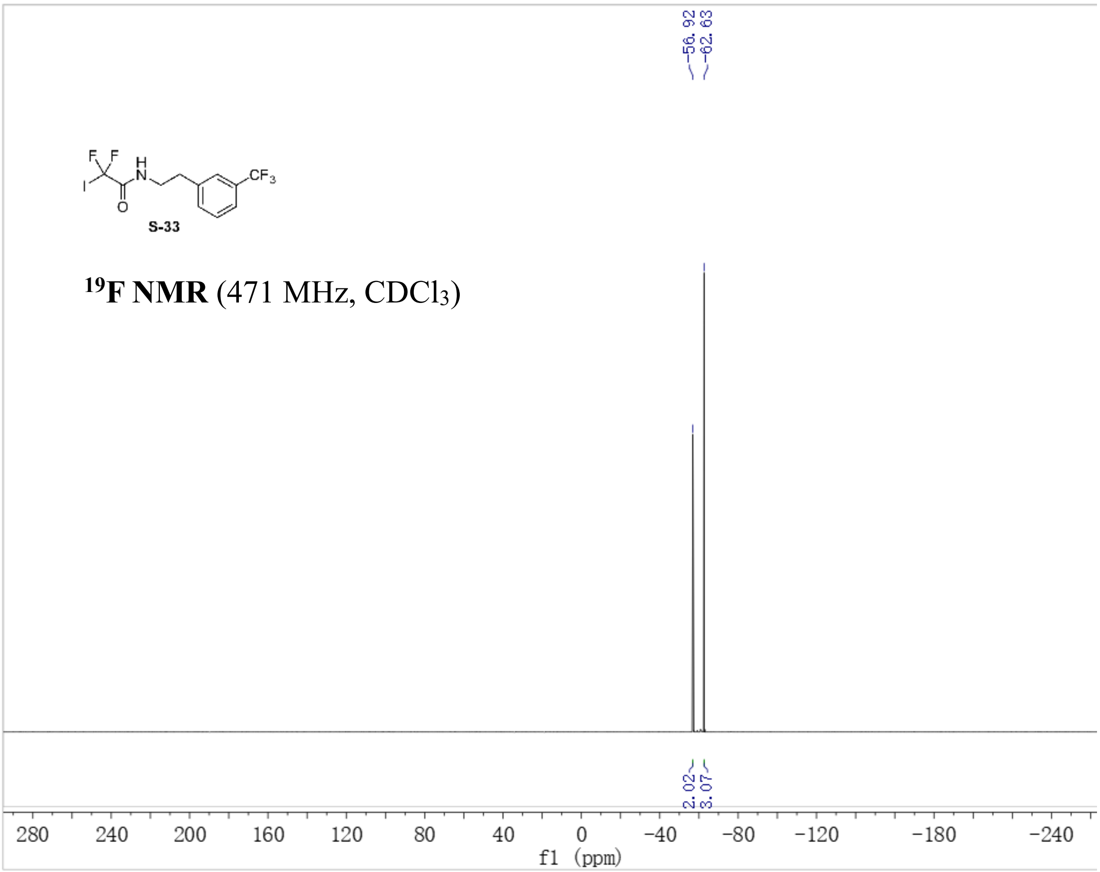

160.94
160.74
160.54
133.37
133.15
130.04
129.37
129.34
126.95
92.97
90.39
87.82
41.64
S-32
13C NMR (126 MHz, CDCl3)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-56.77
S-32
19F NMR (471 MHz, CDCl3)
2.00
280
240
200
160
120
80
40
0
-40
-80
-120
-180
-240
f1 (ppm)

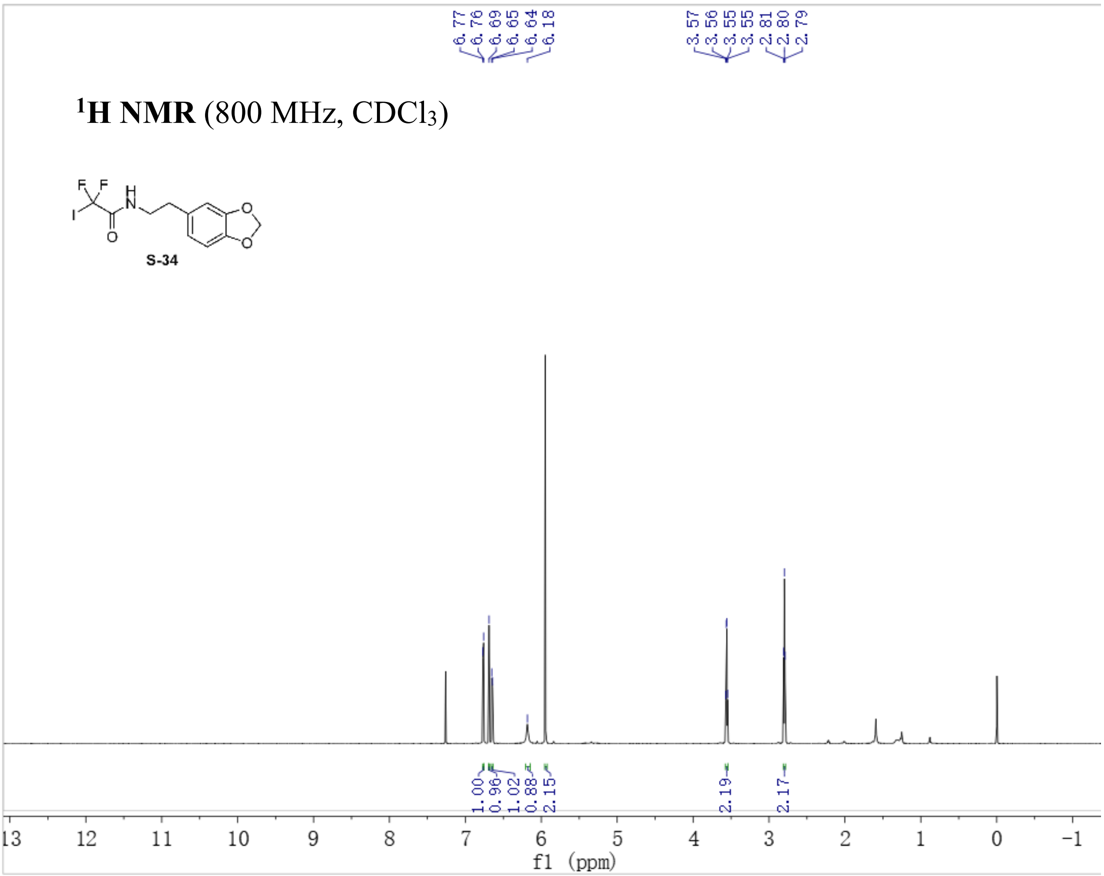
2,2-difluoro-2-iodo-*N*-(3-(trifluoromethyl)phenethyl)acetamide (S-33)



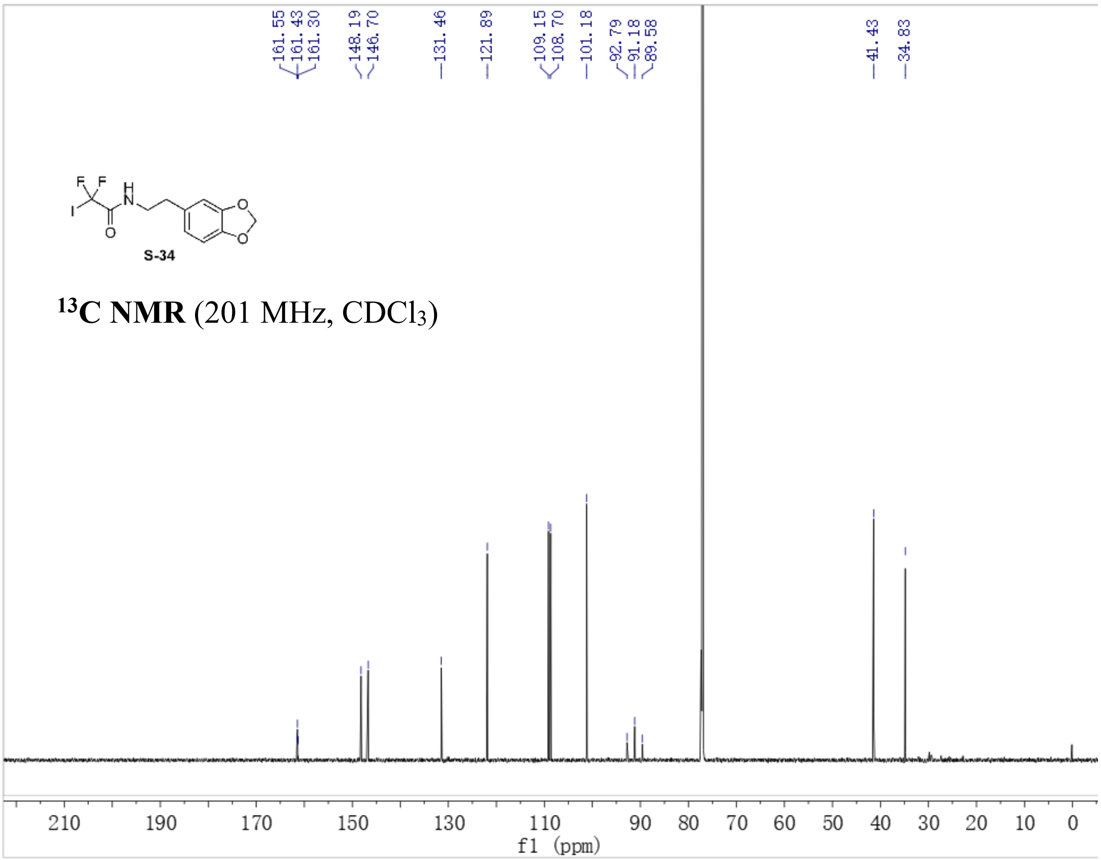




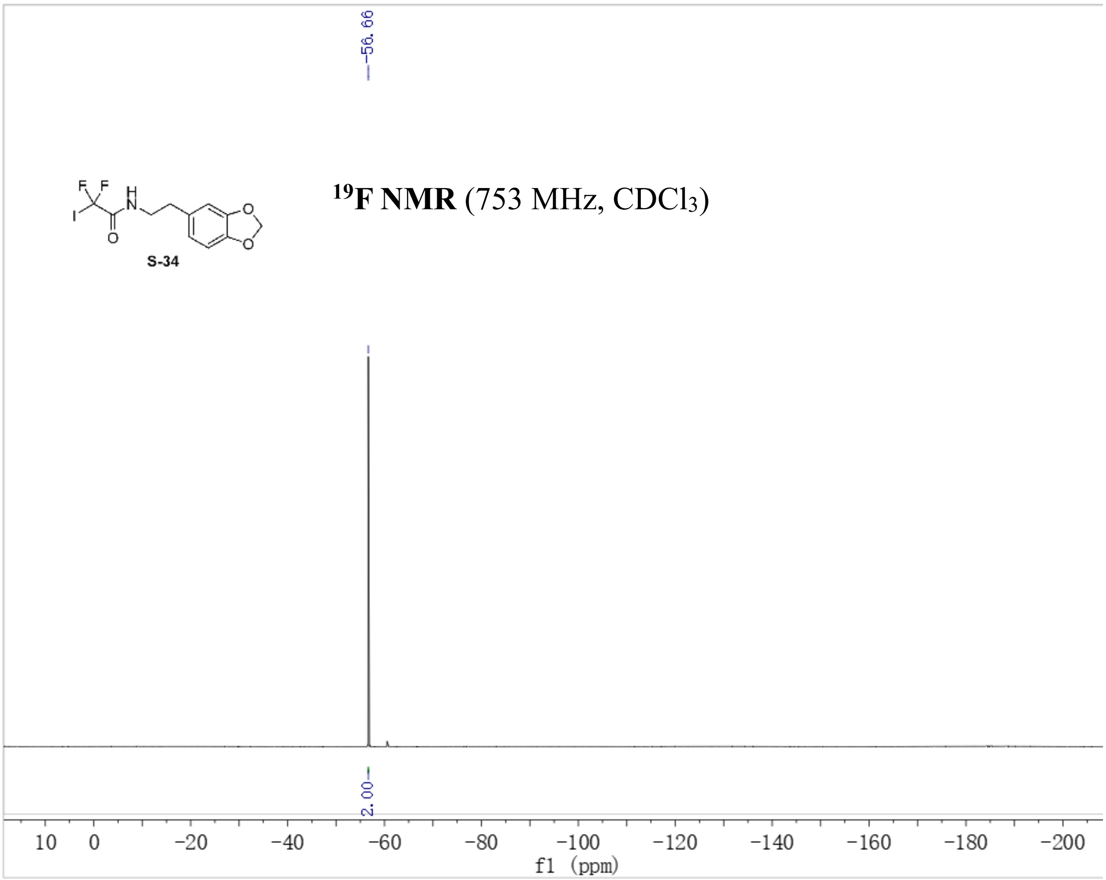
N-(2-(benzo[d][1,3]dioxol-5-yl)ethyl)-2,2-difluoro-2-iodoacetamide (S-34)



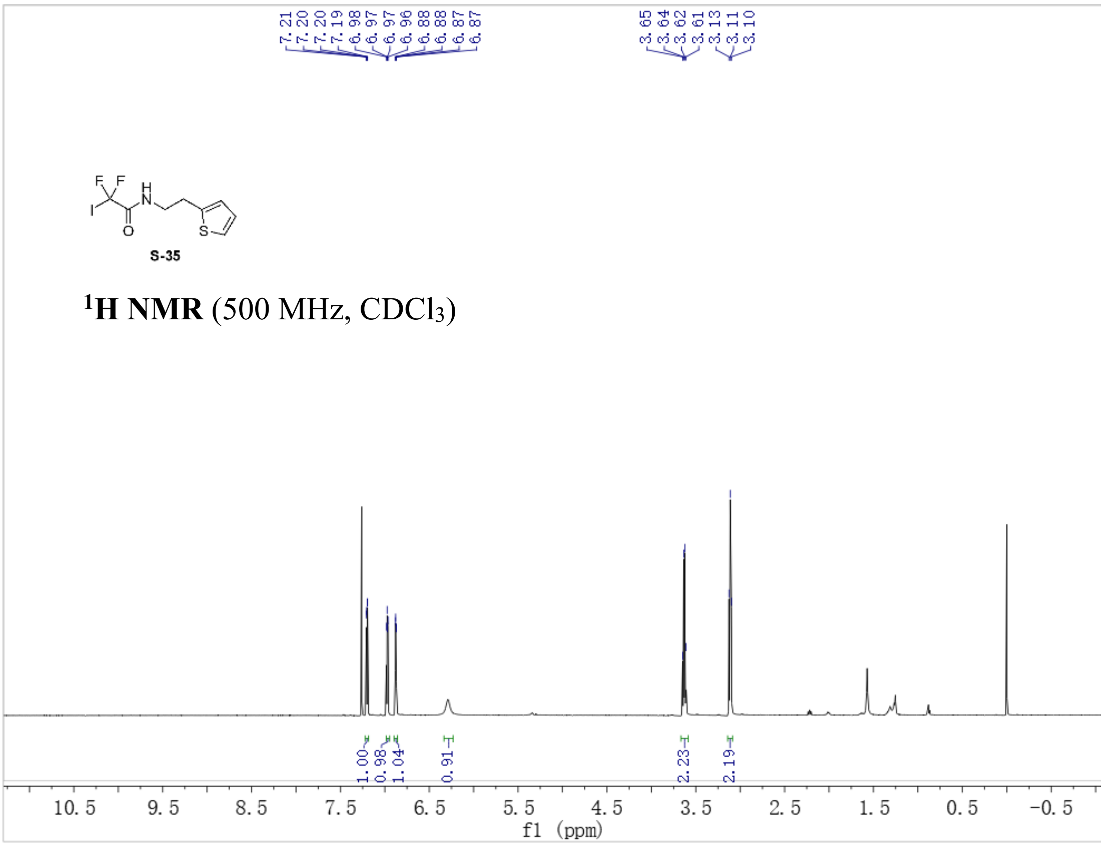
6.77
6.76
6.69
6.65
6.64
6.18
3.57
3.56
3.55
3.55
2.81
2.80
2.79
1H NMR (800 MHz, CDCl3)
S-34
1.00
0.96
1.02
0.88
2.15
2.19
2.17
13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)

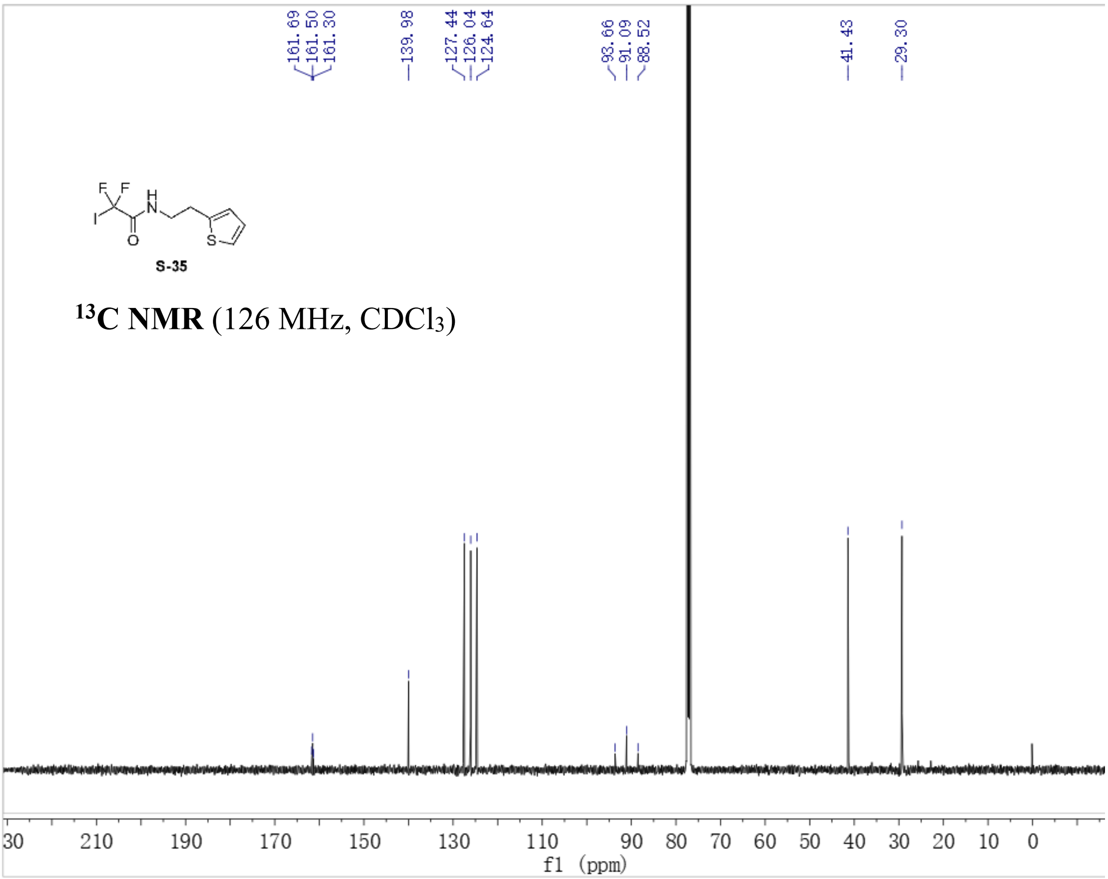


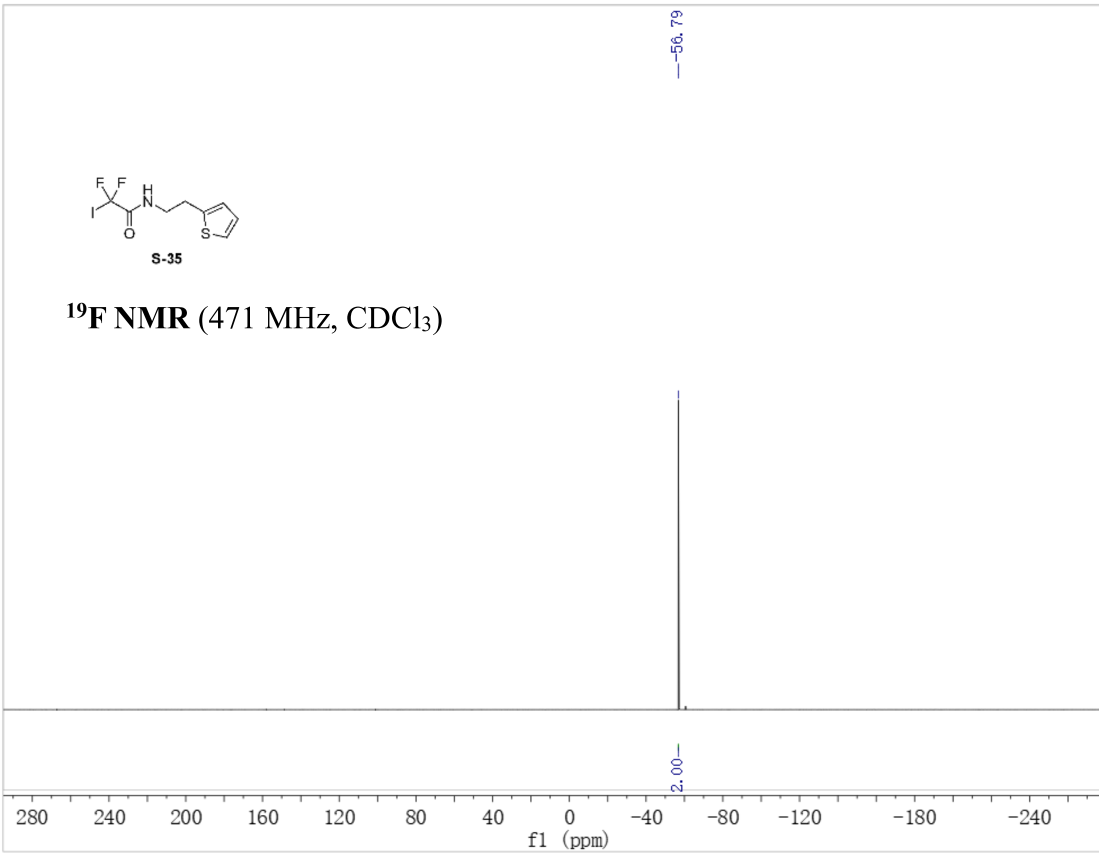
161.55
161.43
161.30
148.19
146.70
131.46
121.89
109.15
108.70
101.18
92.79
91.18
89.58
41.43
34.83
S-34
13C NMR (201 MHz, CDCl3)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



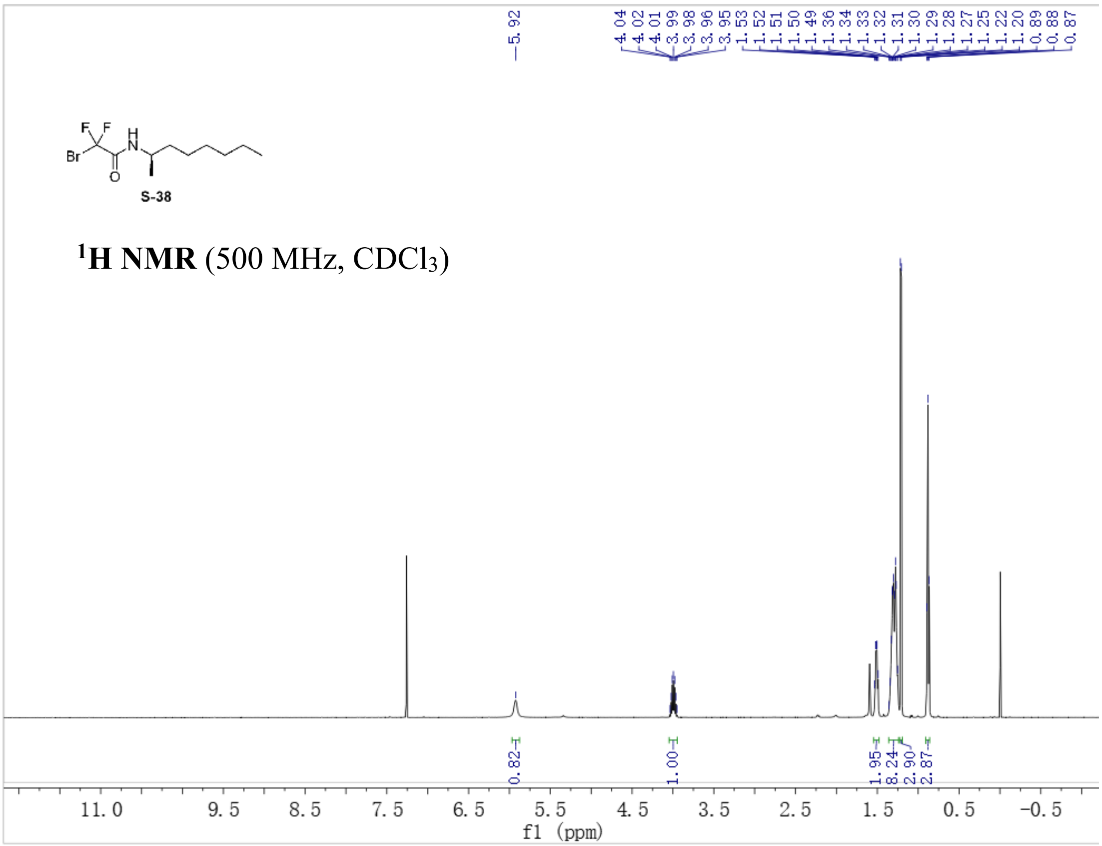
2,2-difluoro-2-iodo-*N*-(2-(thiophen-2-yl)ethyl)acetamide (S-35)

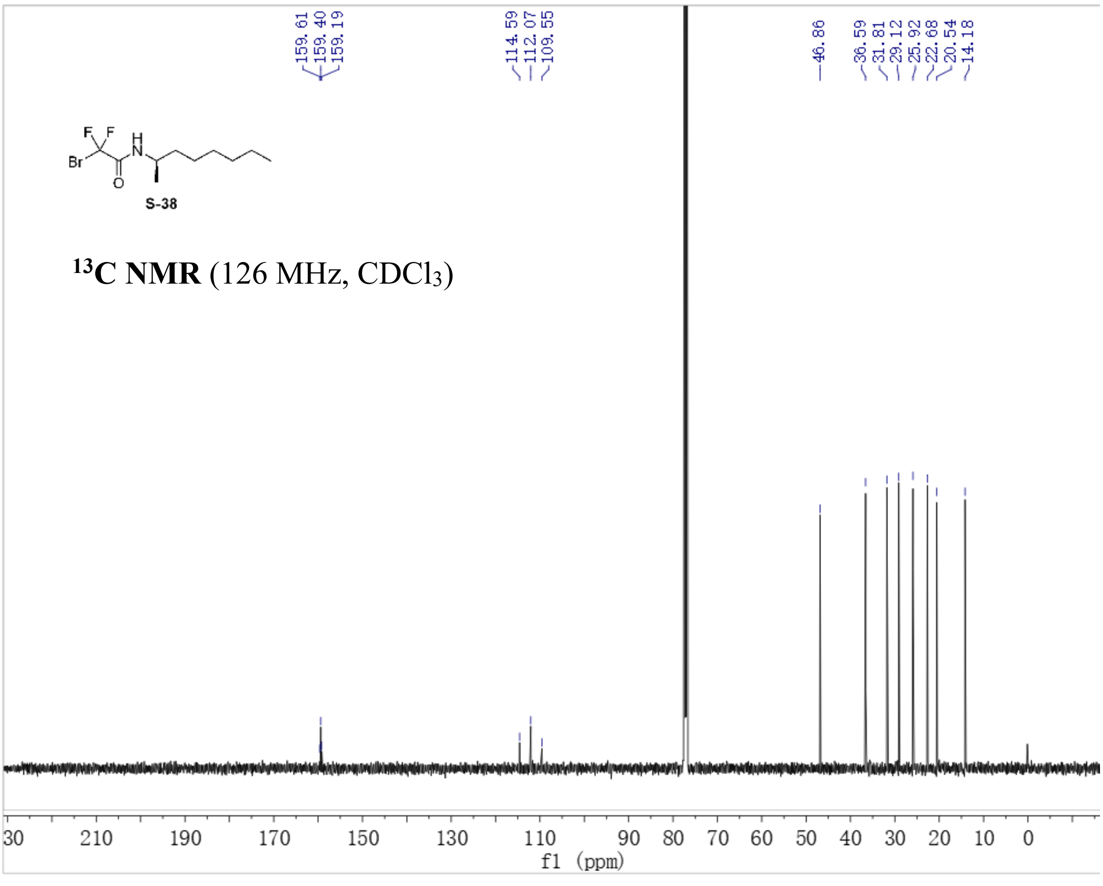


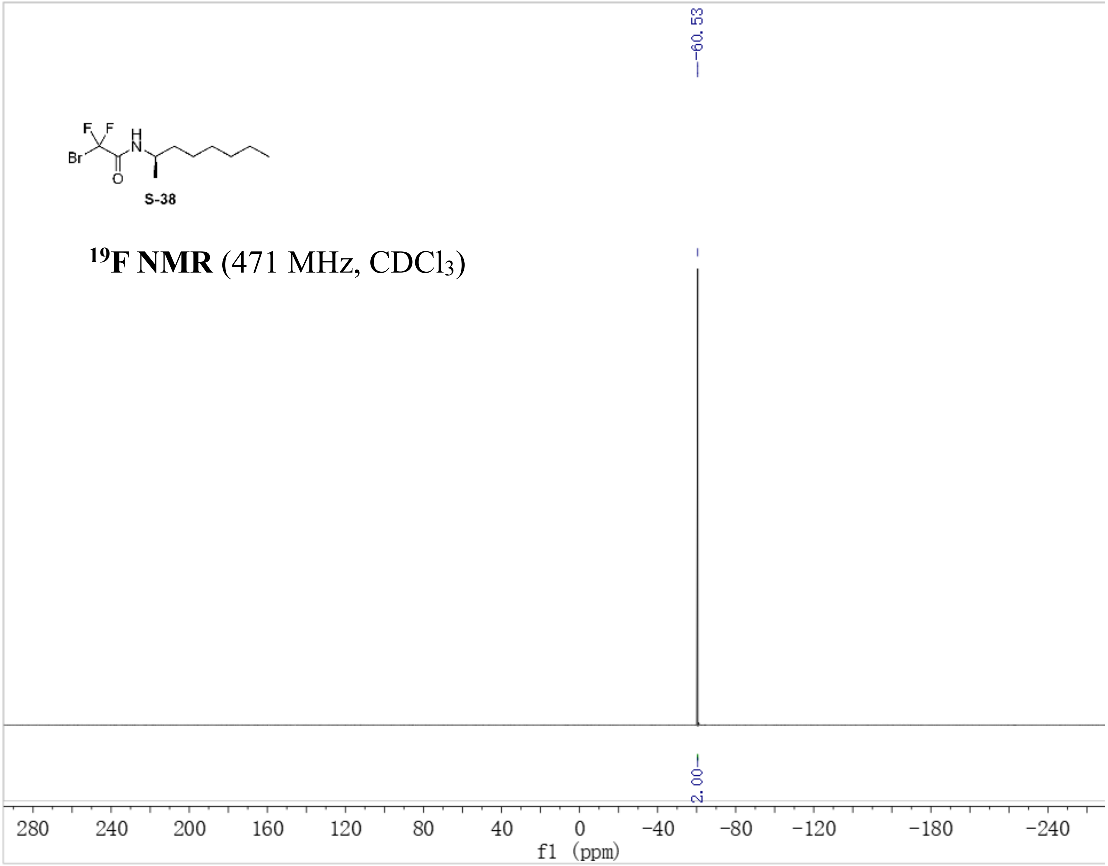

161.69
161.50
161.30
139.98
127.44
126.04
124.64
93.66
91.09
88.52
41.43
29.30
S-35
13C NMR (126 MHz, CDCl3)
f1 (ppm)


-56.79
S-35
19F NMR (471 MHz, CDCl3)
2.00
f1 (ppm)

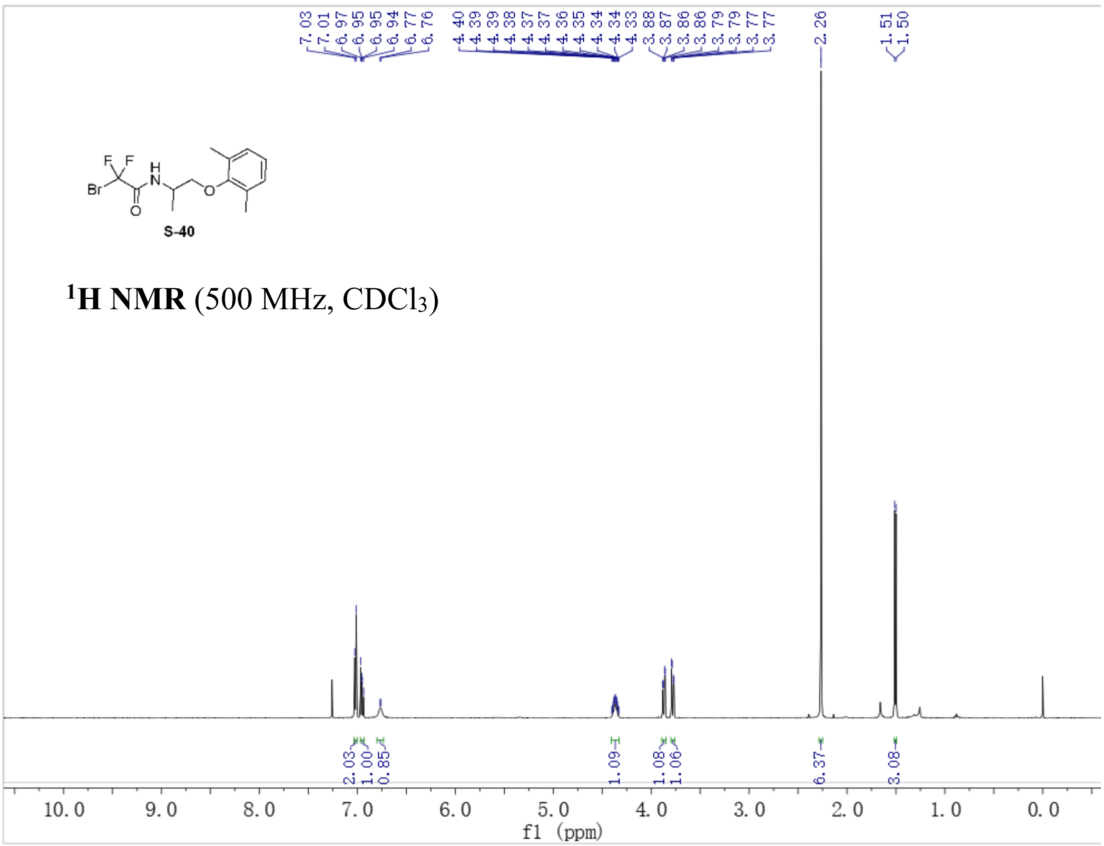
(*R*)-2-bromo-2,2-difluoro-*N*-(octan-2-yl)acetamide (S-38)

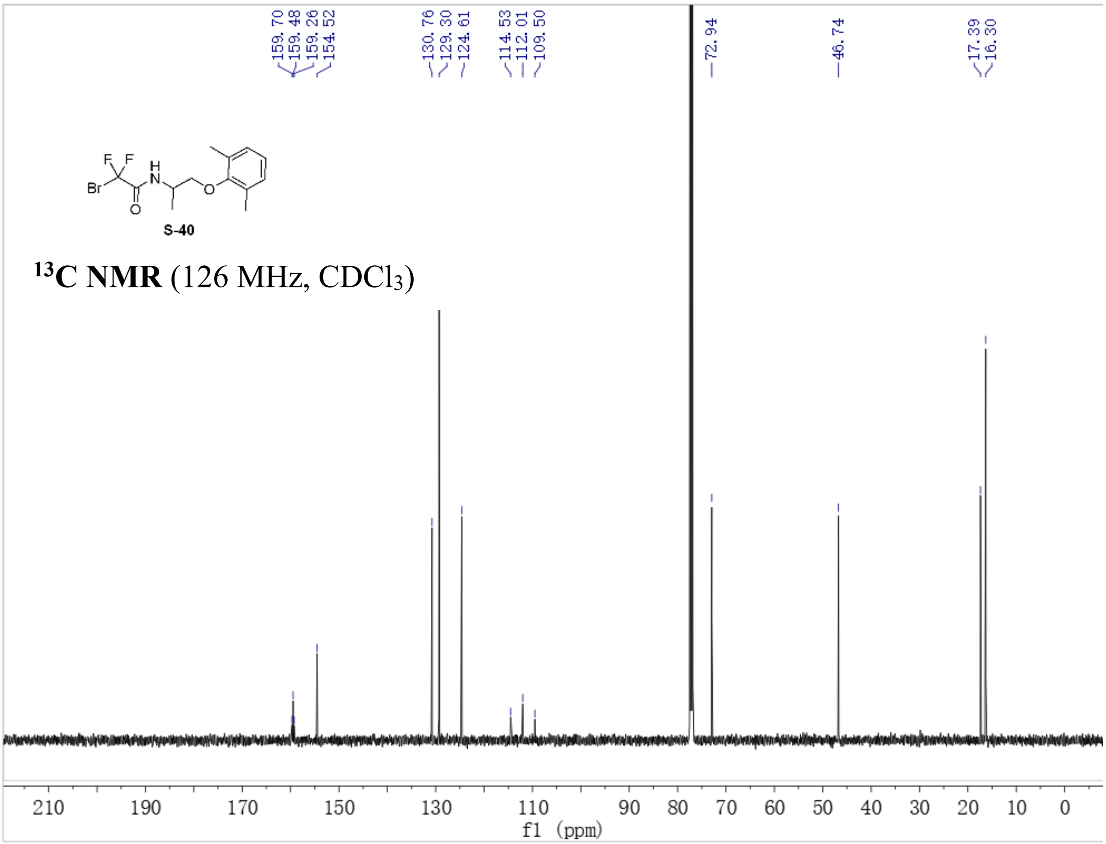


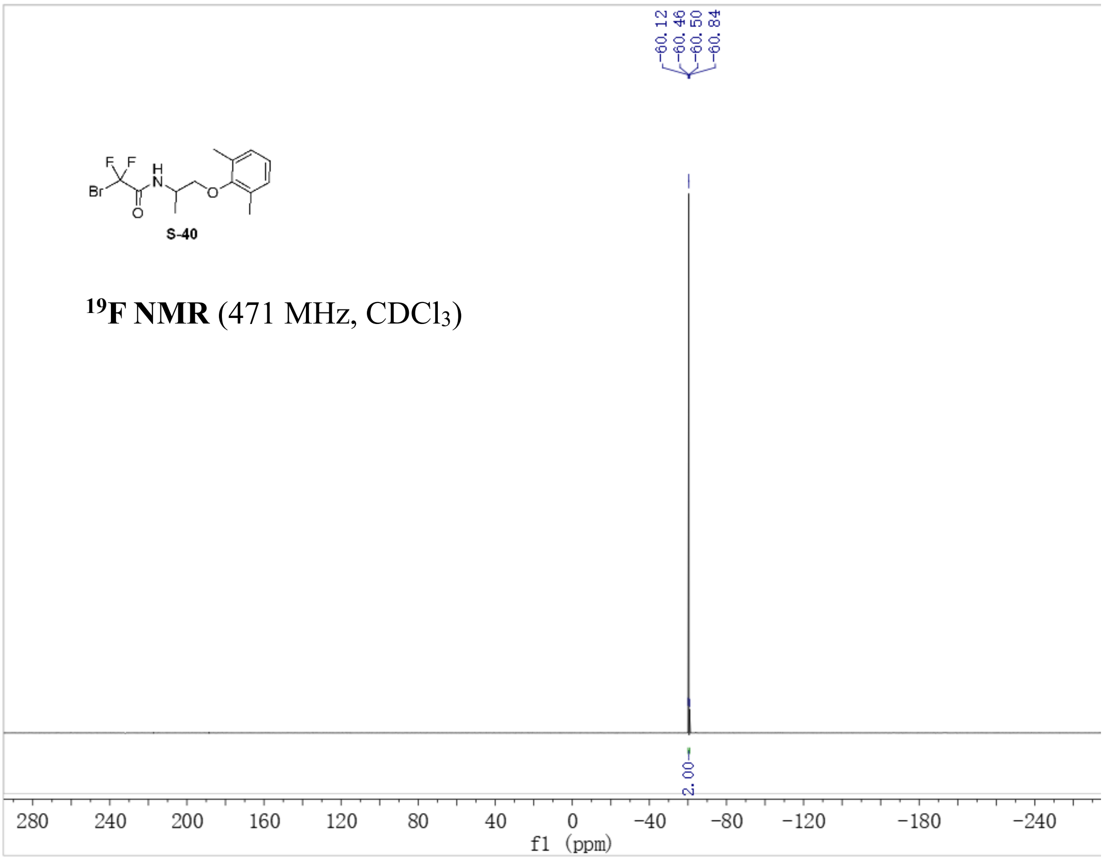




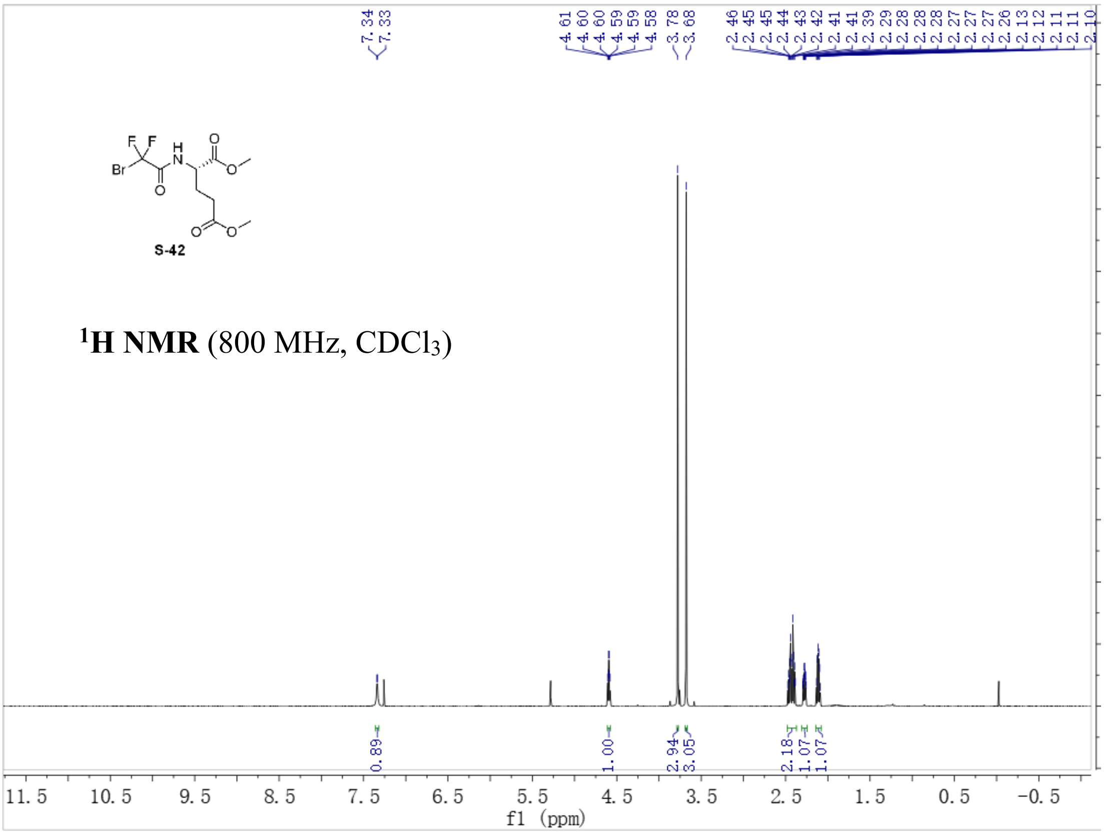
2-bromo-*N*-(1-(2,6-dimethylphenoxy)propan-2-yl)-2,2-difluoroacetamide (S-40)

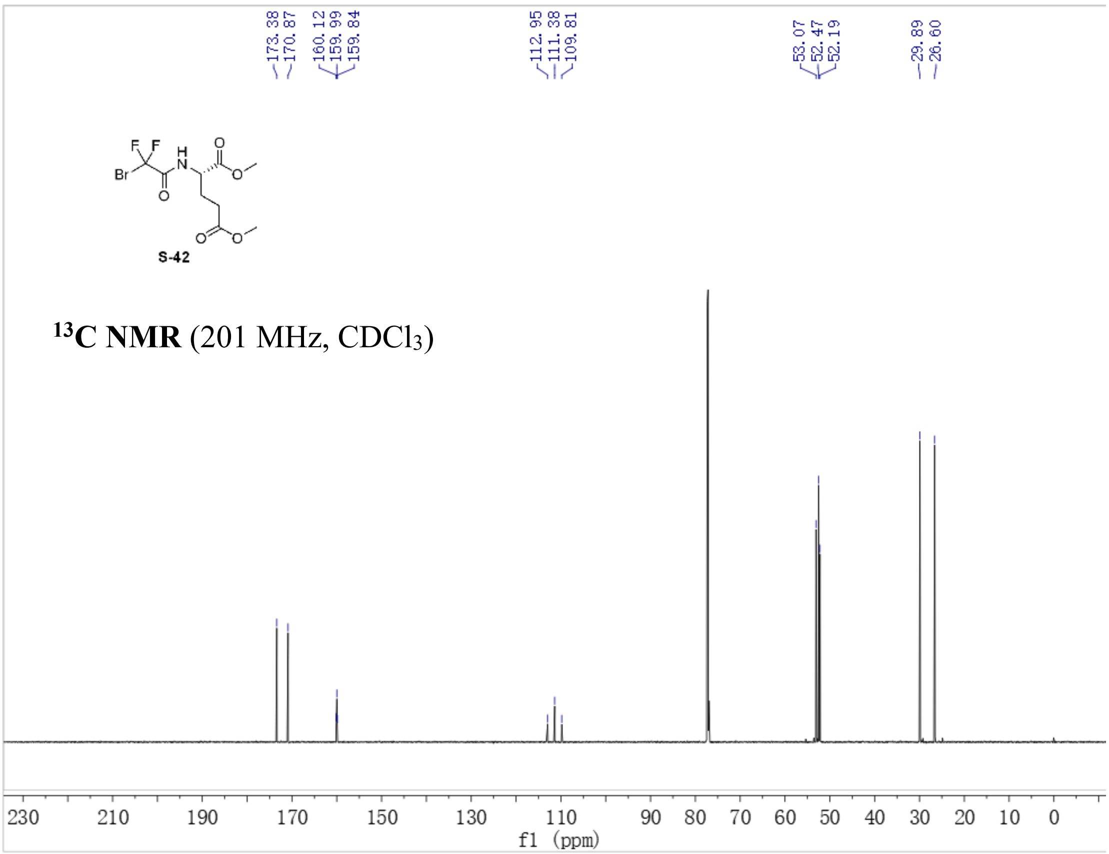


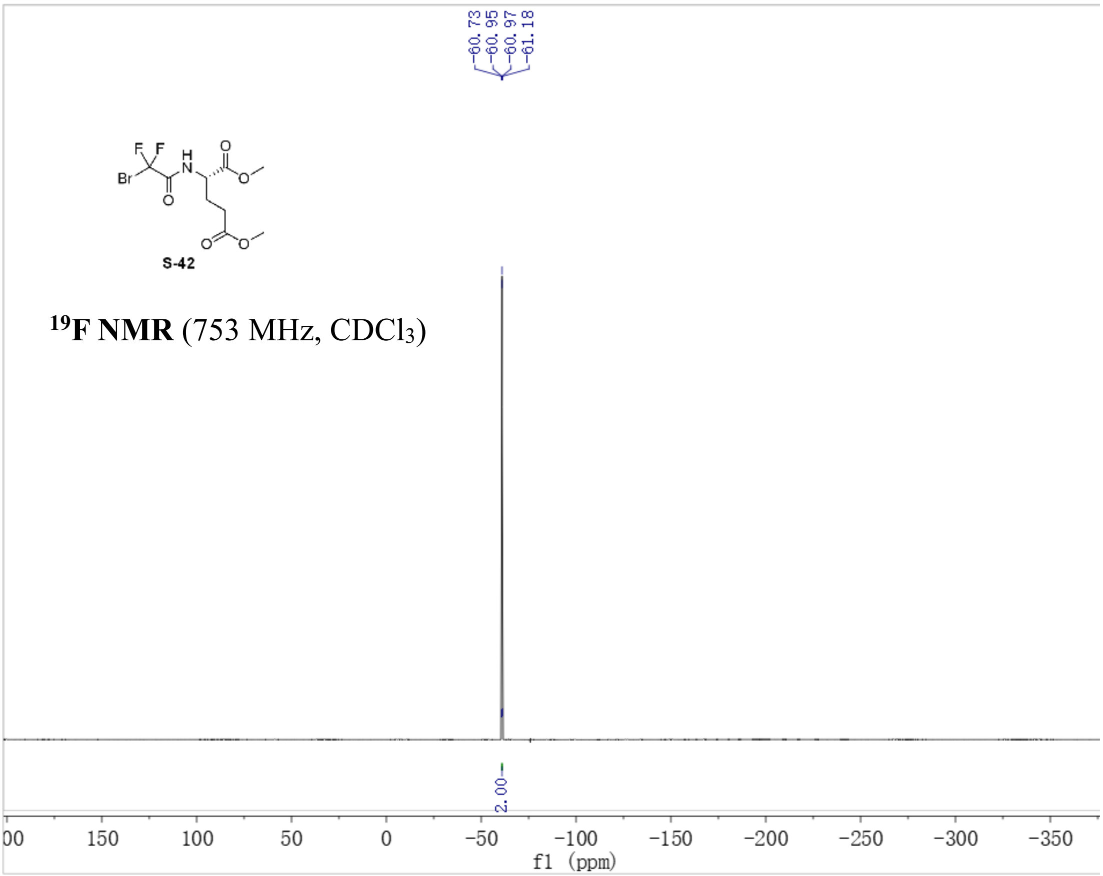

159.70
159.48
159.26
154.52
130.76
129.30
124.61
114.53
112.01
109.50
72.94
46.74
17.39
16.30
S-40
13C NMR (126 MHz, CDCl3)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-60.12
-60.46
-60.50
-60.84
S-40
19F NMR (471 MHz, CDCl3)
2.00
280 240 200 160 120 80 40 0 -40 -80 -120 -180 -240
f1 (ppm)

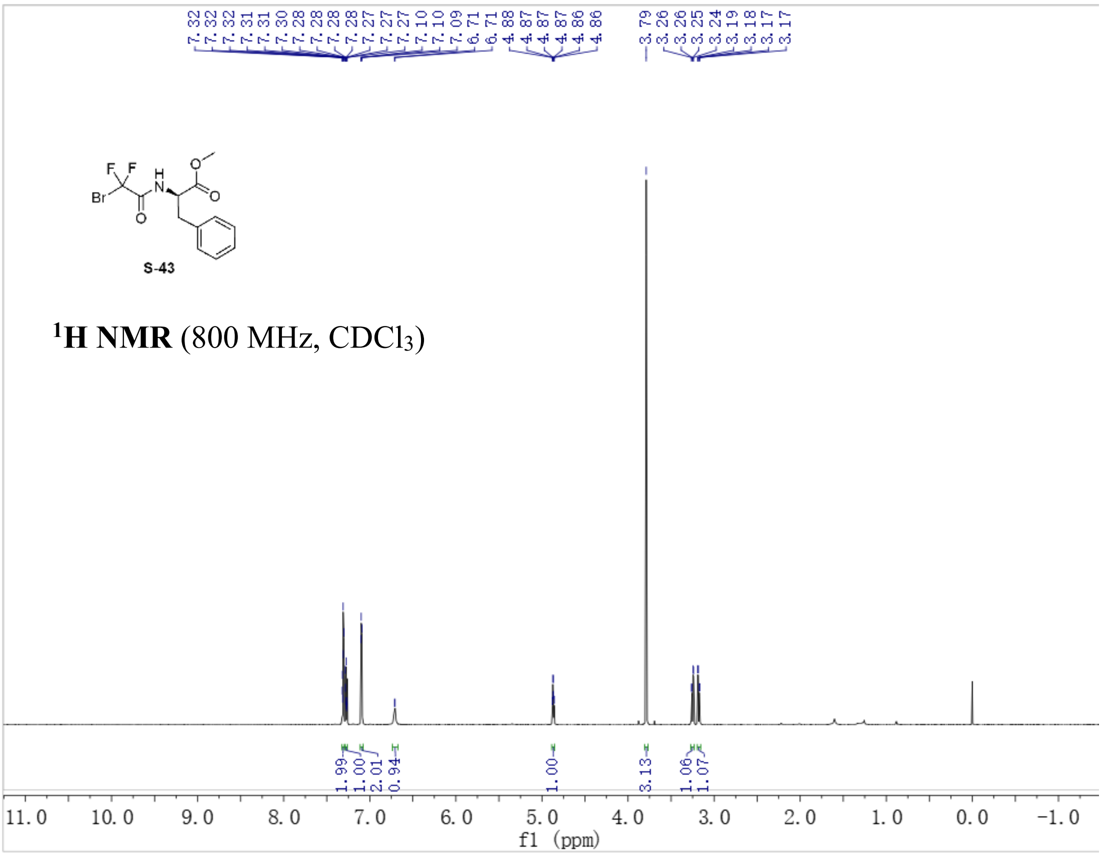
dimethyl (2-bromo-2,2-difluoroacetyl)-*L*-glutamate (S-42)

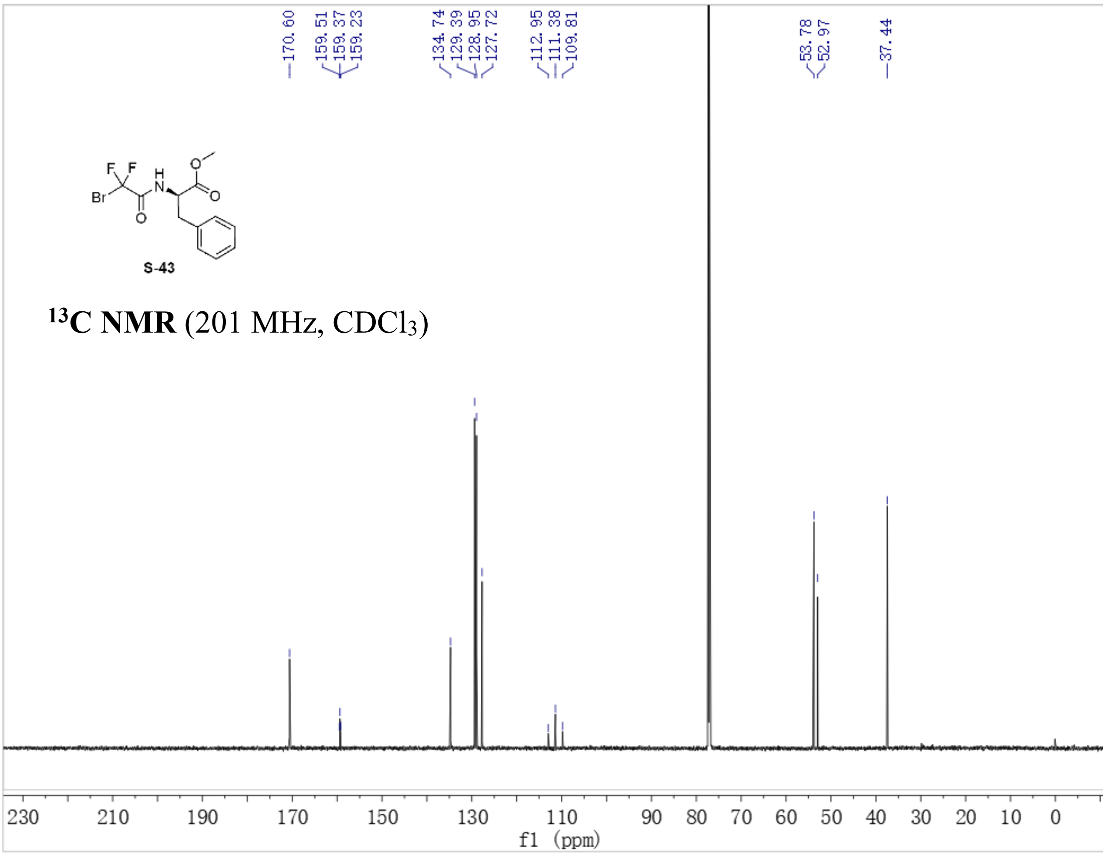




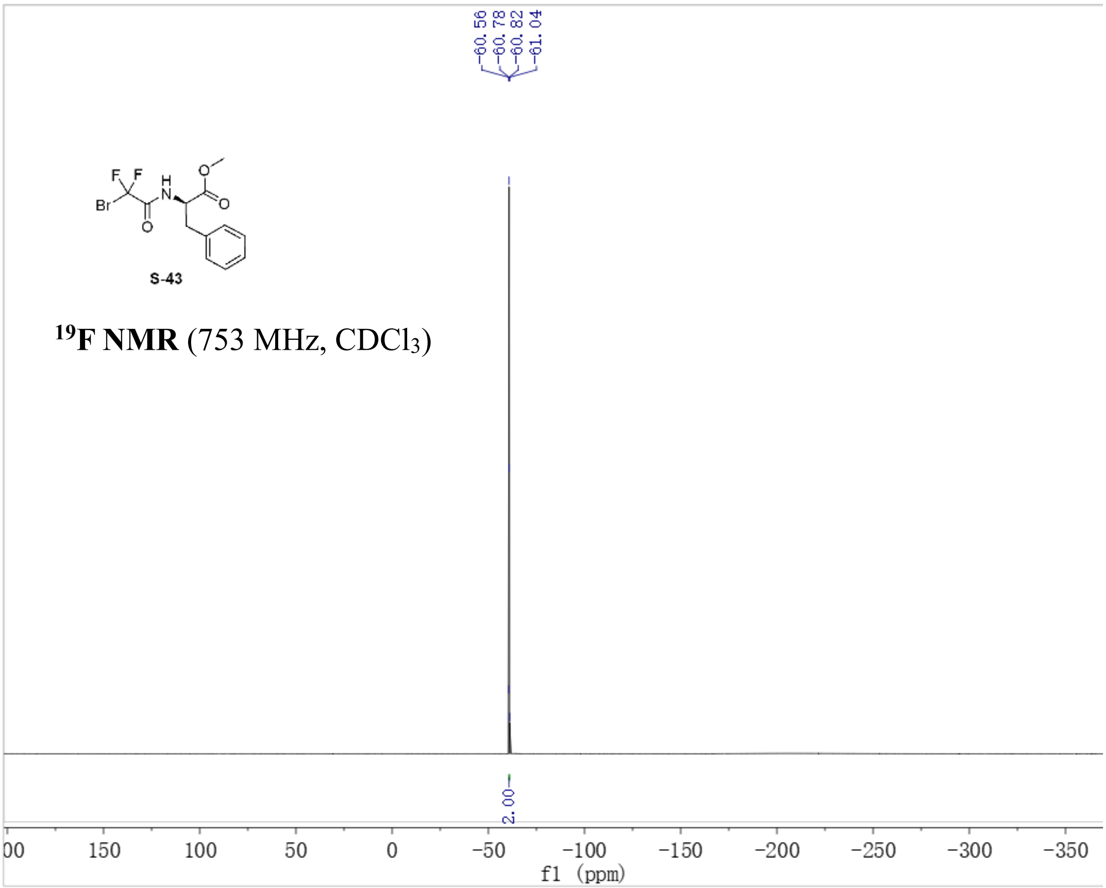


methyl (2-bromo-2,2-difluoroacetyl)-*D*-phenylalaninate (S-43)



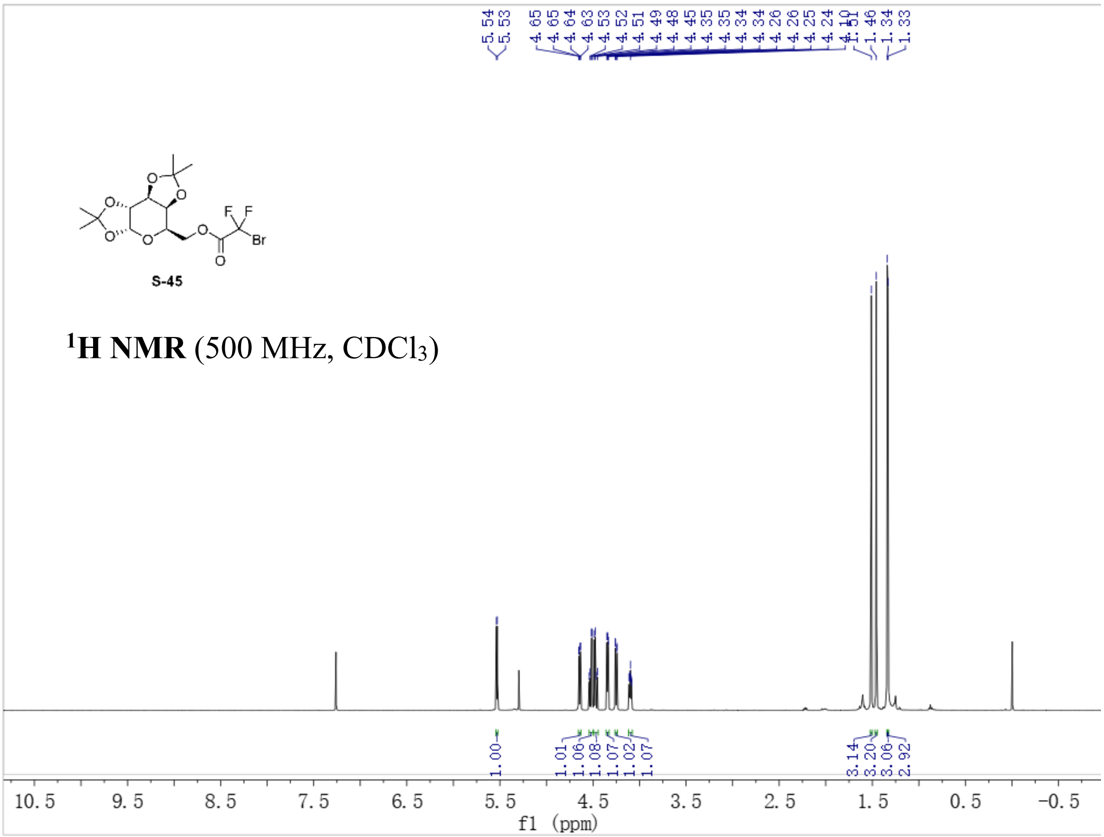


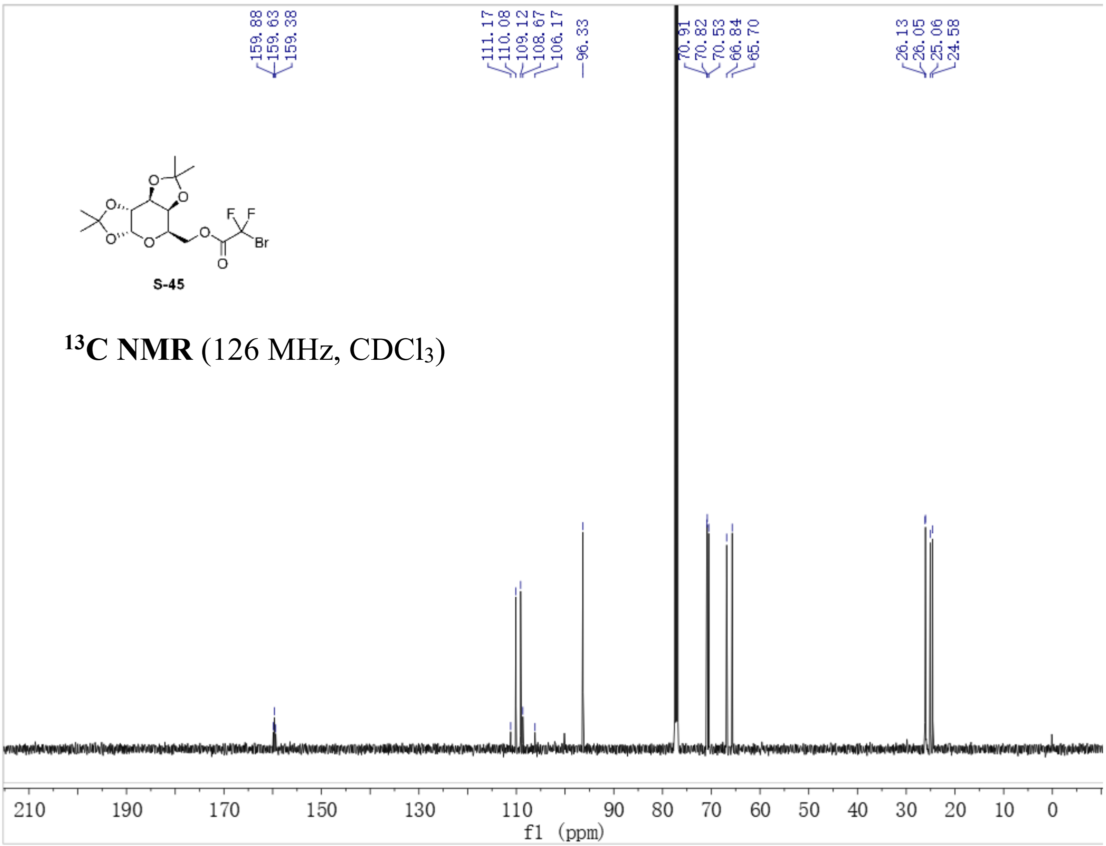
170.60
159.51
159.37
159.23
134.74
129.39
128.95
127.72
112.95
111.38
109.81
53.78
52.97
37.44
Br
F F
H
N
O
O
O
S-43
13C NMR (201 MHz, CDCl3)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

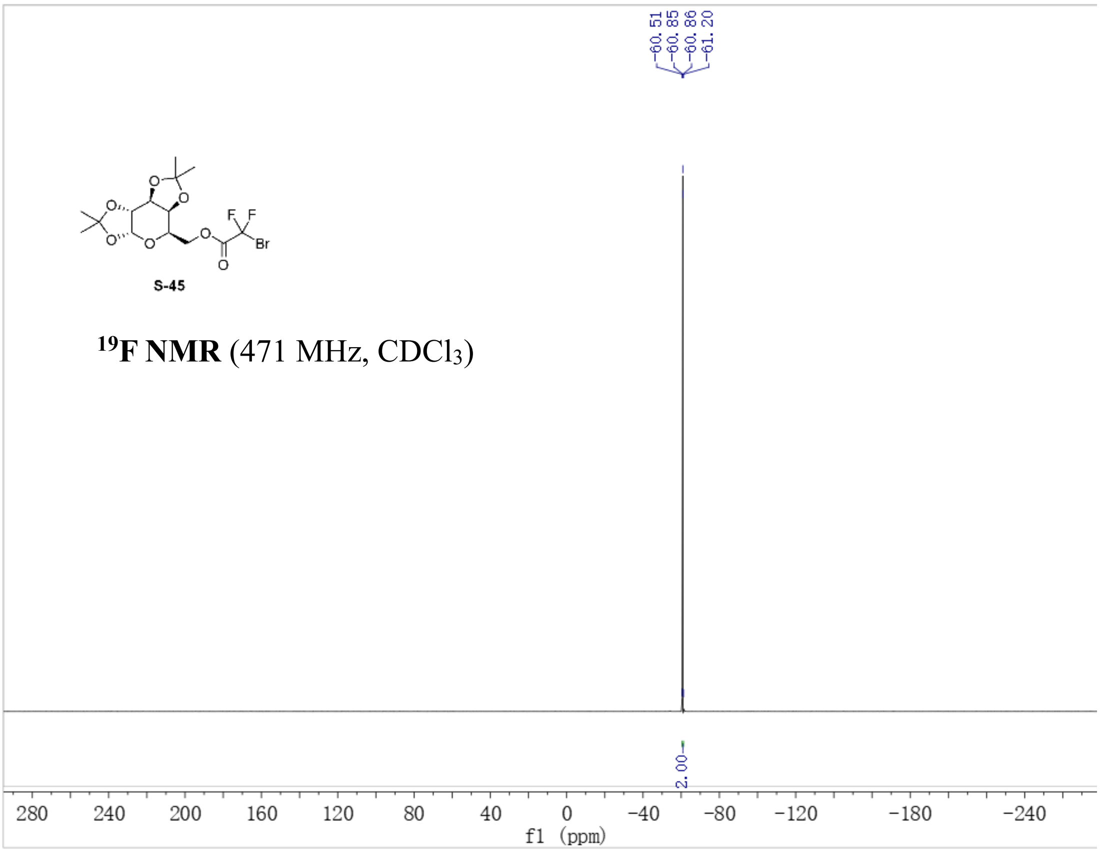


-60.56
-60.78
-60.82
-61.04
Br
F F
H
N
O
O
O
S-43
19F NMR (753 MHz, CDCl3)
2.00
00 150 100 50 0 −50 −100 −150 −200 −250 −300 −350
f1 (ppm)

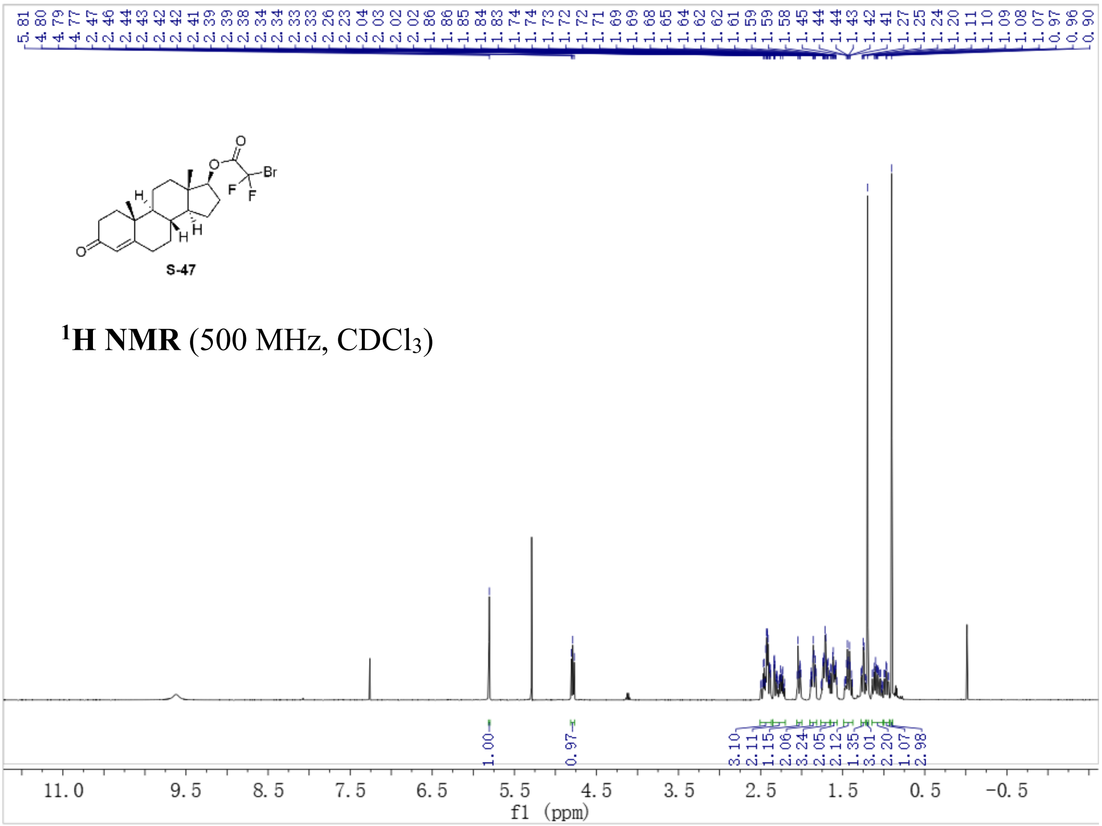
((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl 2-bromo-2,2-difluoroacetate (S-45)

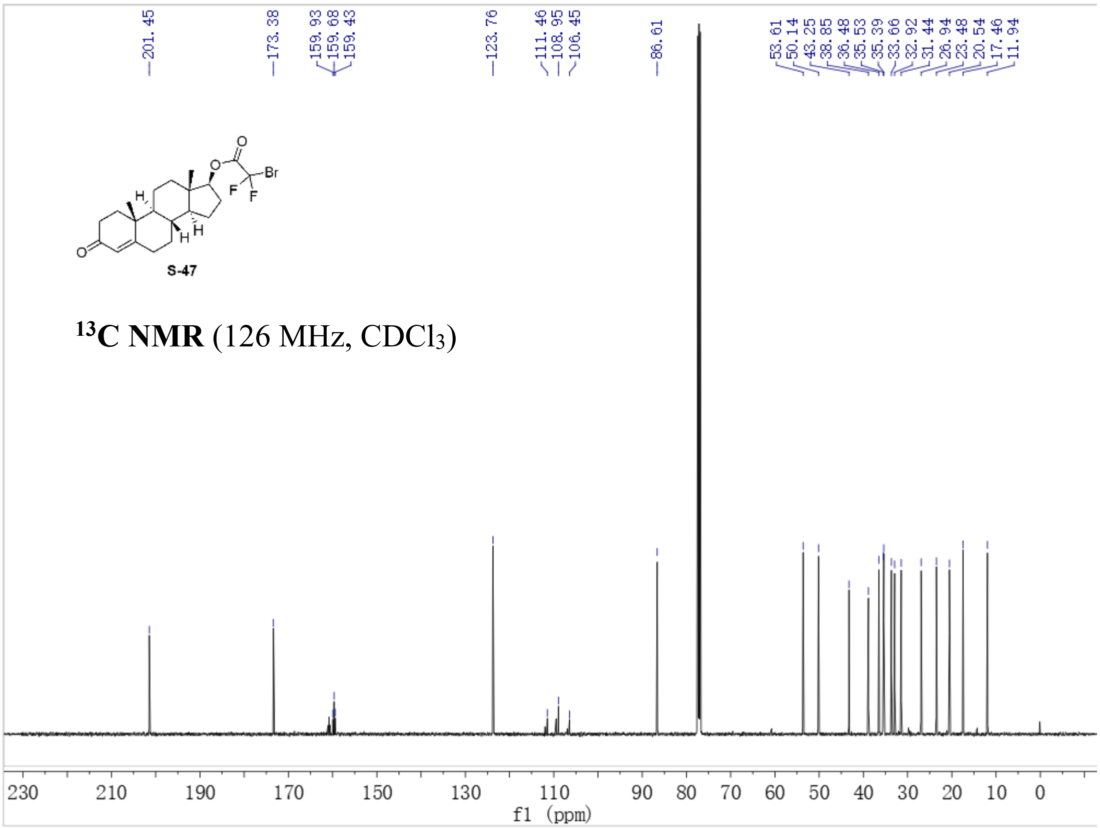


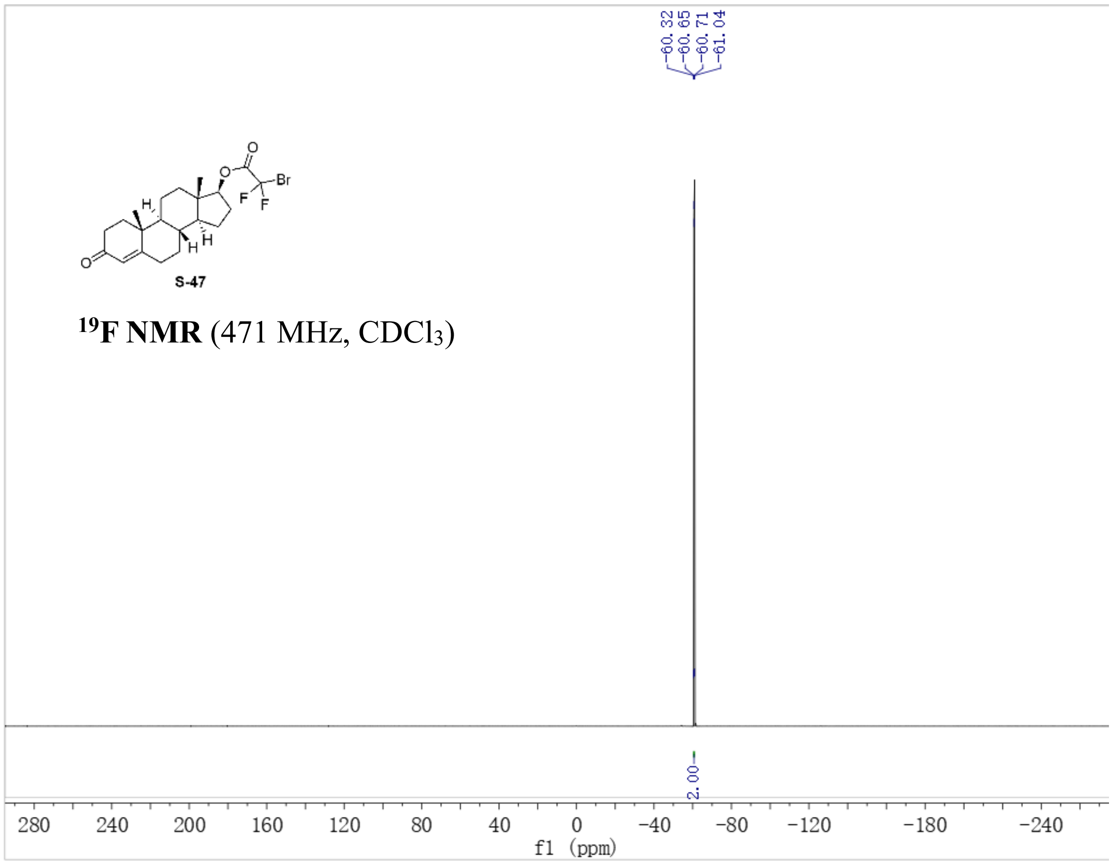




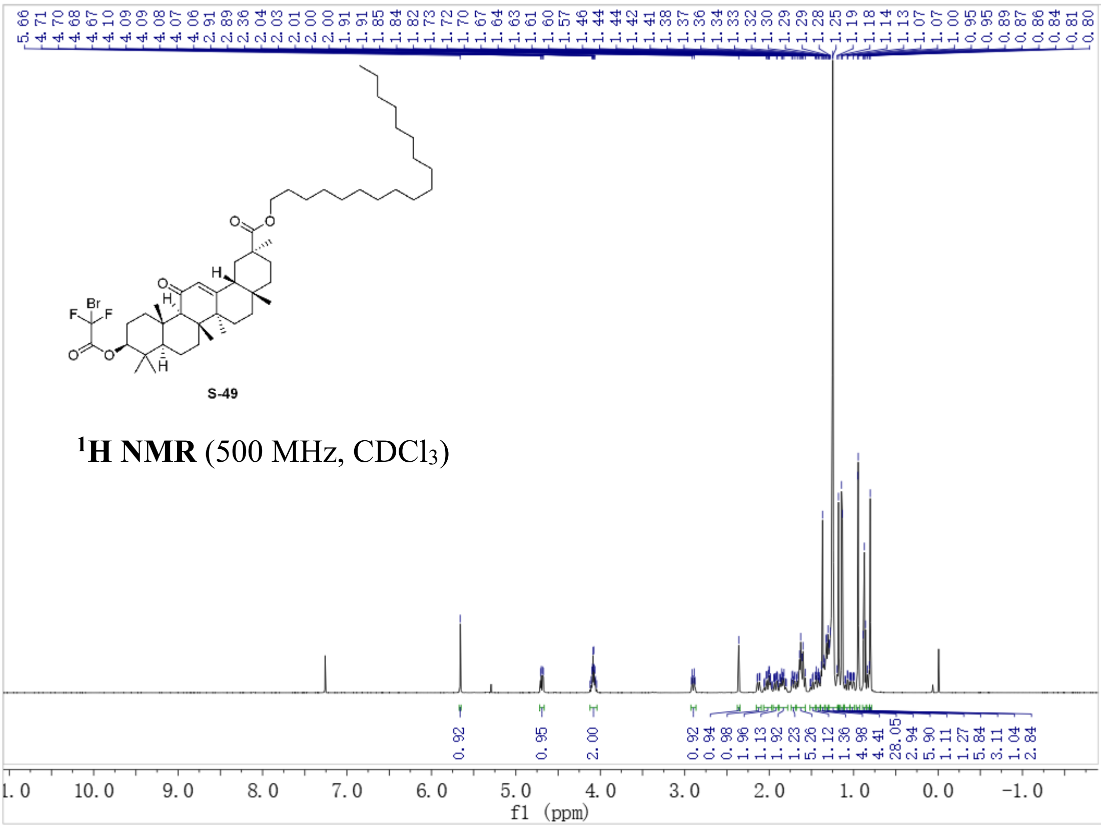
(8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl 2-bromo-2,2-difluoroacetate (S-47)

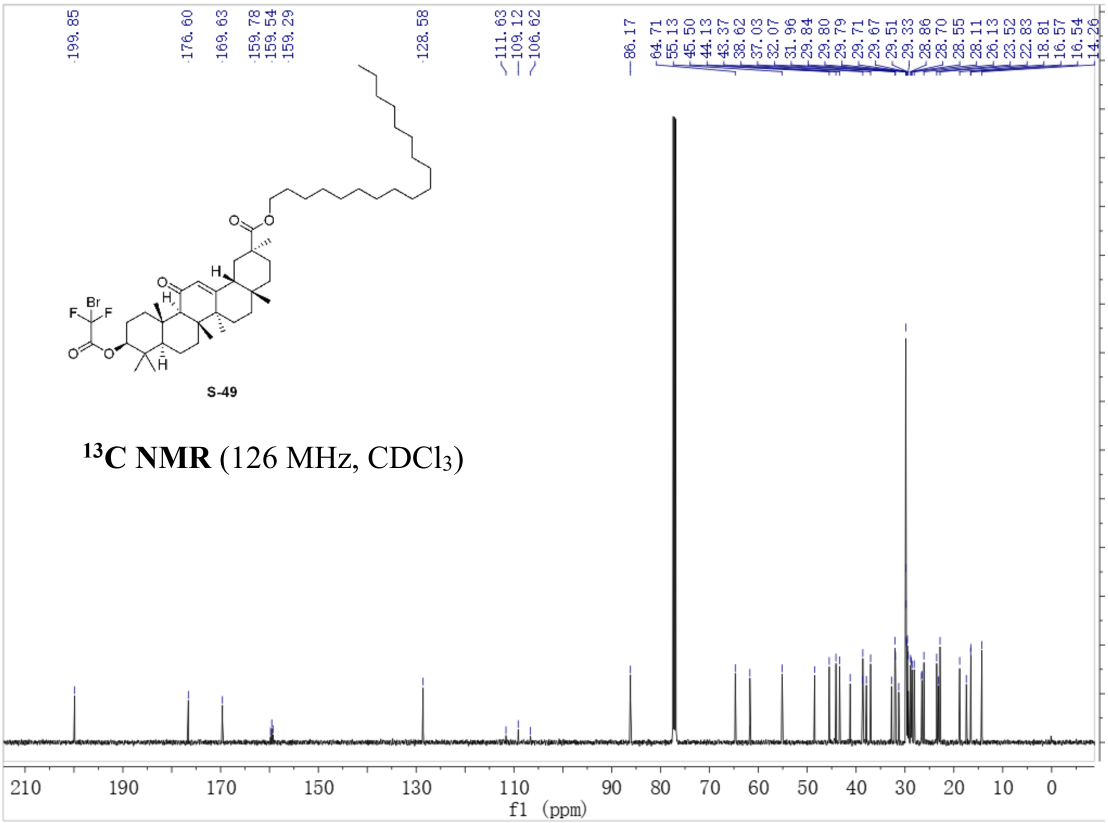



201.45
173.38
159.93
159.68
159.43
123.76
111.46
108.95
106.45
86.61
53.61
50.14
43.25
38.85
36.48
35.53
35.39
33.66
32.92
31.44
26.94
23.48
20.54
17.46
11.94
O
Br
F
F
H
H
H
O
S-47
13C NMR (126 MHz, CDCl3)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

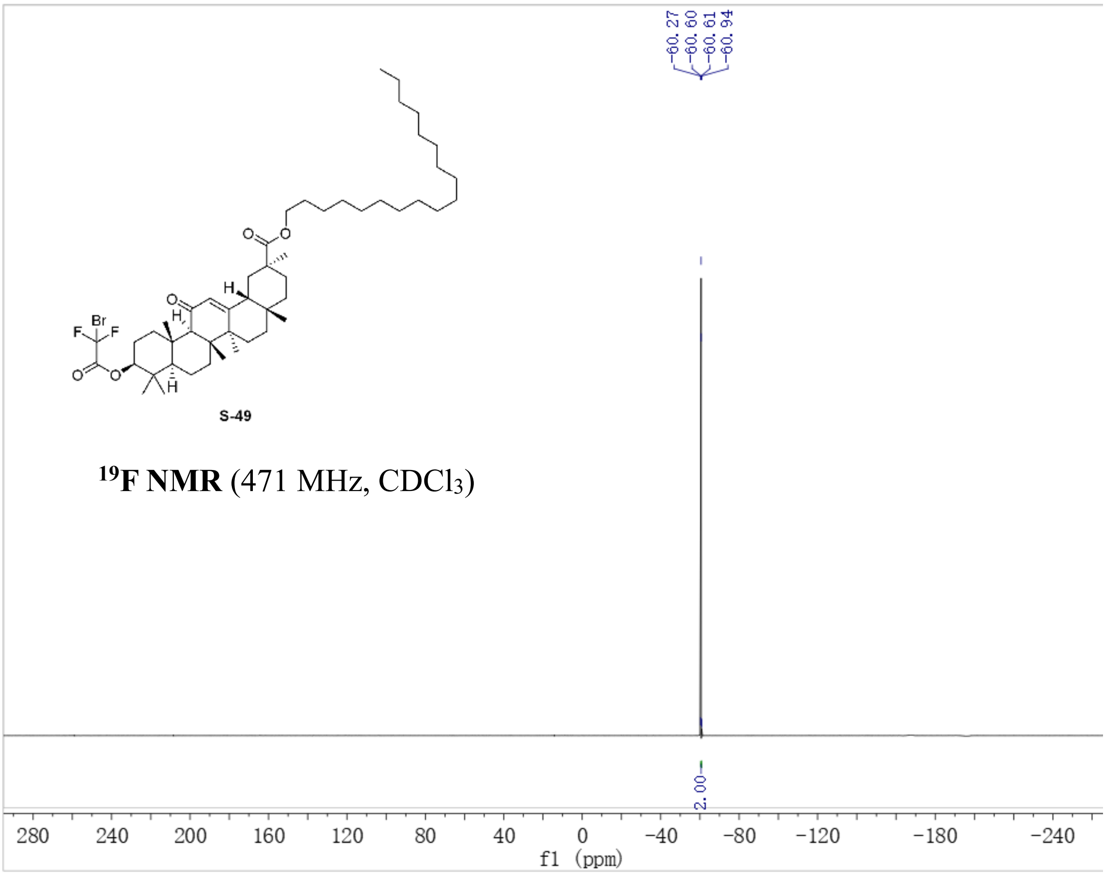

-60.32
-60.65
-60.71
-61.04
O
Br
F
F
H
H
H
O
S-47
19F NMR (471 MHz, CDCl3)
2.00
280 240 200 160 120 80 40 0 −40 −80 −120 −180 −240
f1 (ppm)

Octadecyl (2*S*,4a*S*,6a*S*,6b*R*,8a*R*,10*S*,12a*S*,12b*R*,14b*R*)-10-(2-bromo-2,2-difluoroacetoxy)-2,4a,6a,6b,9,9,12a-heptamethyl-13-oxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydropicene-2-carboxylate (S-49)



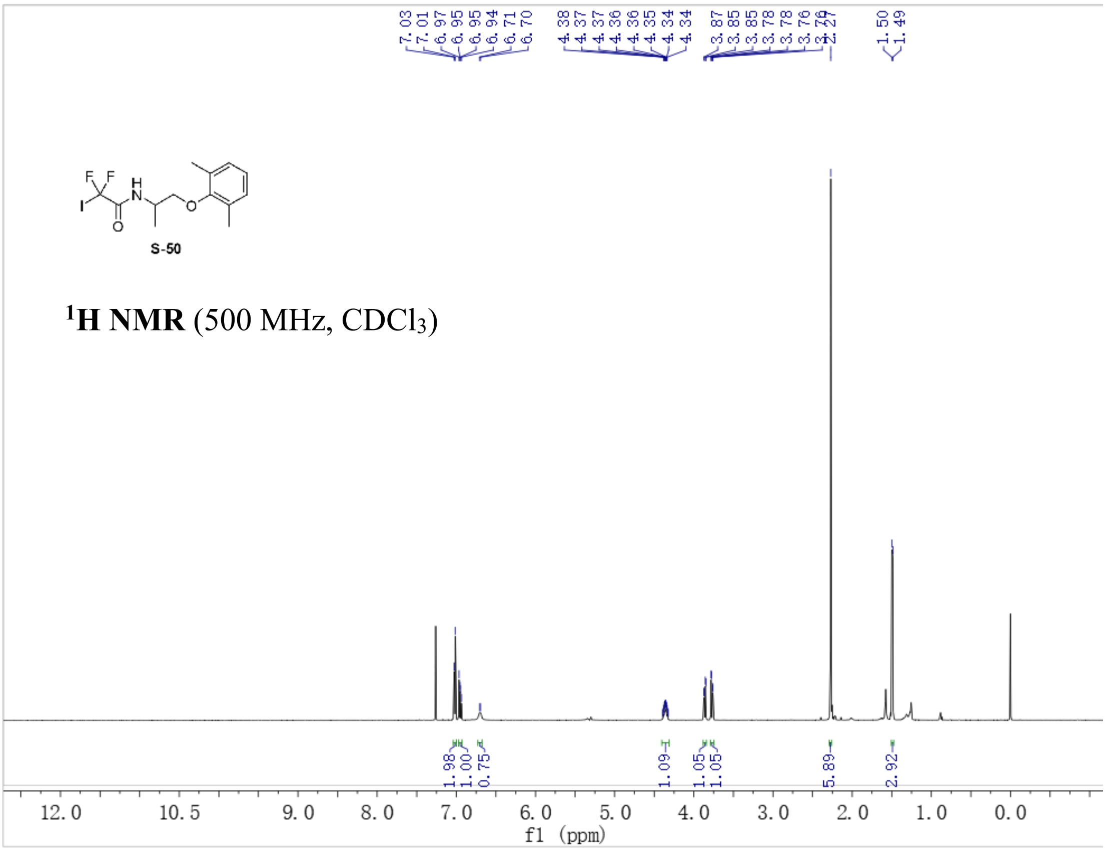


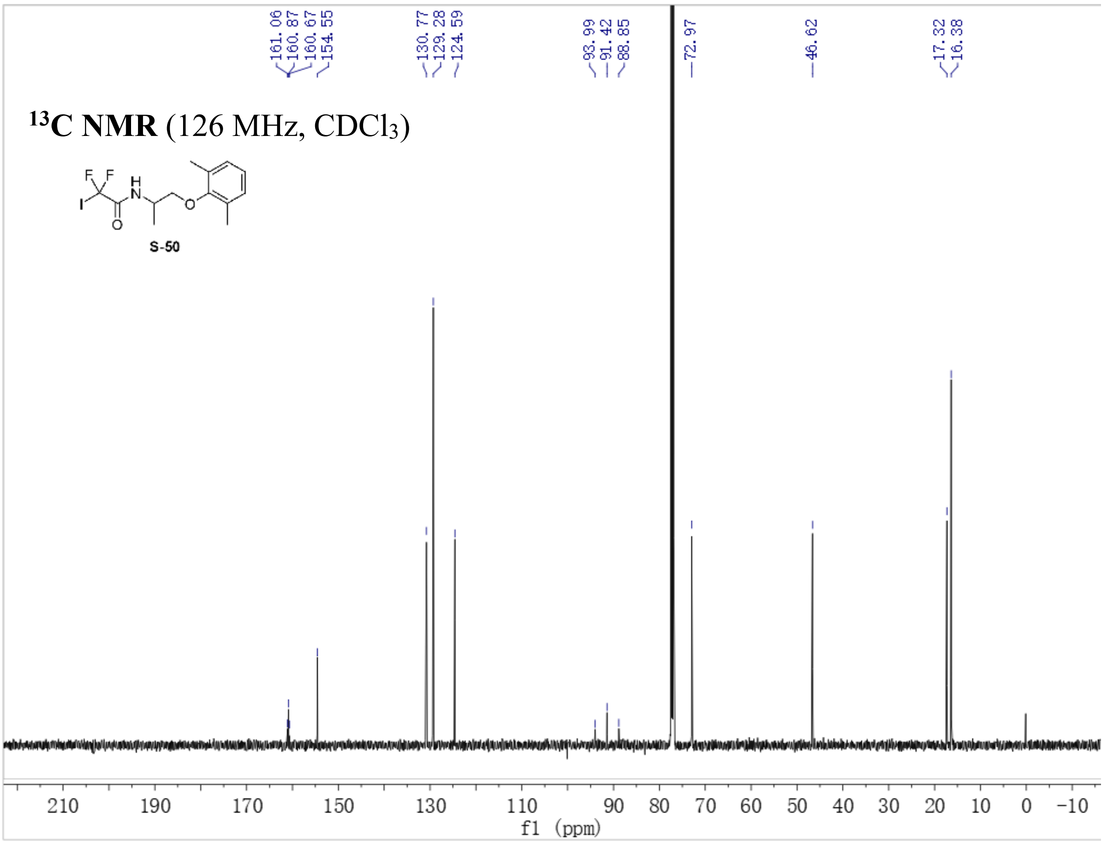
S-49
13C NMR (126 MHz, CDCl3)
199.85
176.60
169.63
159.78
159.54
159.29
128.58
111.63
109.12
106.62
86.17
64.71
55.13
45.50
44.13
43.37
38.62
37.03
32.07
31.96
29.84
29.80
29.79
29.71
29.67
29.51
29.33
28.86
28.70
28.55
28.11
26.13
23.52
22.83
18.81
16.57
16.54
14.26
f1 (ppm)

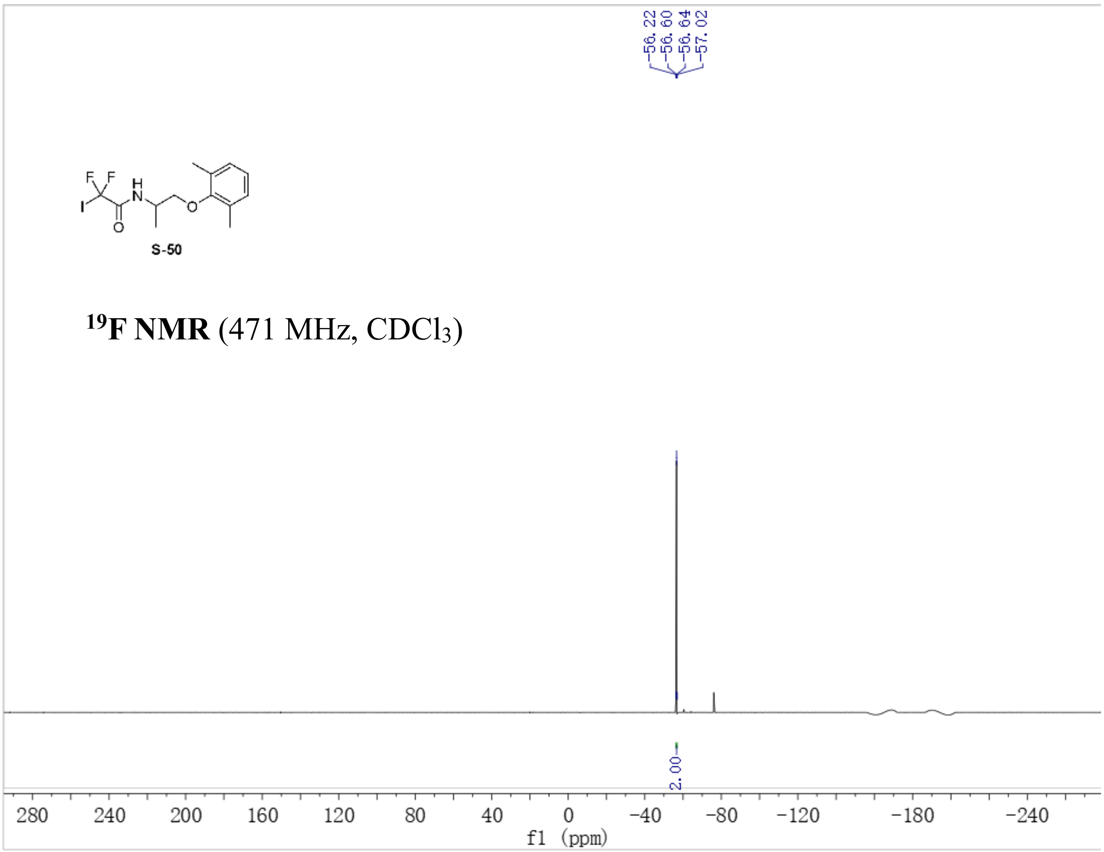


S-49
19F NMR (471 MHz, CDCl3)
-60.27
-60.60
-60.61
-60.94
2.00
f1 (ppm)

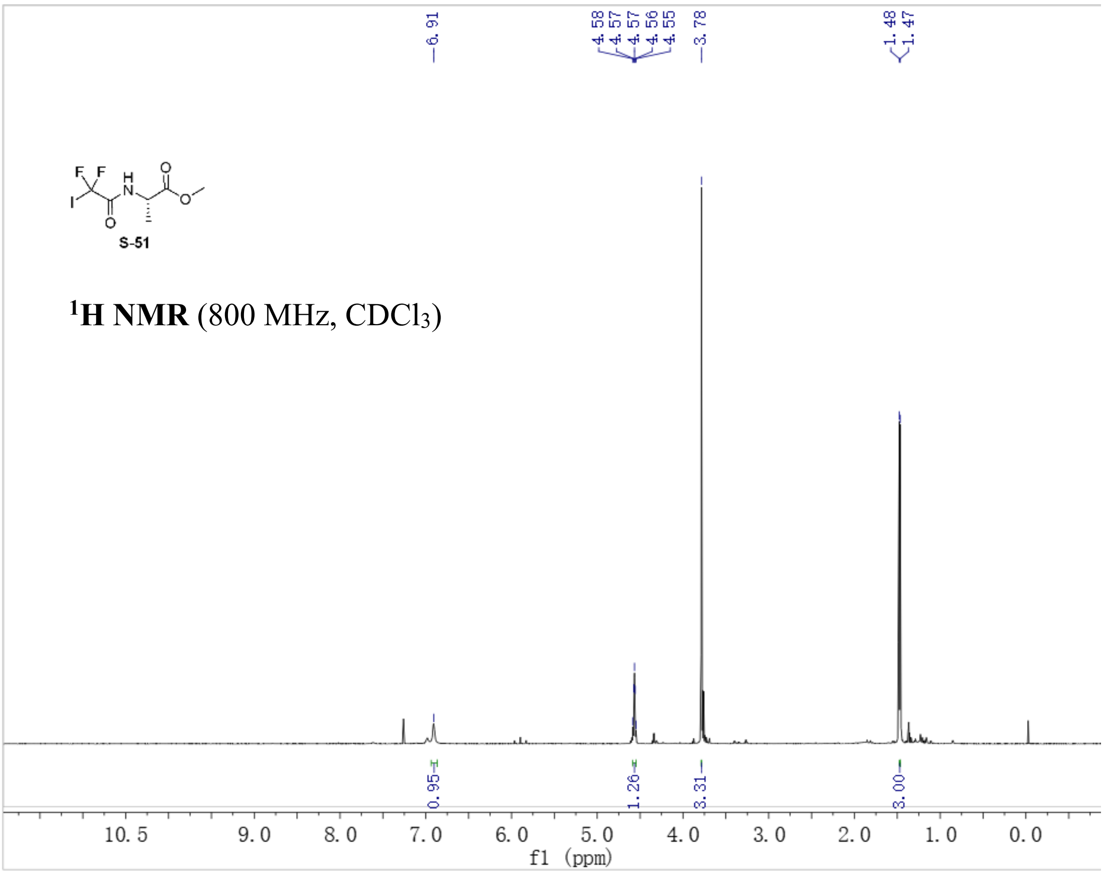
N-(1-(2,6-dimethylphenoxy)propan-2-yl)-2,2-difluoro-2-iodoacetamide (S-50)

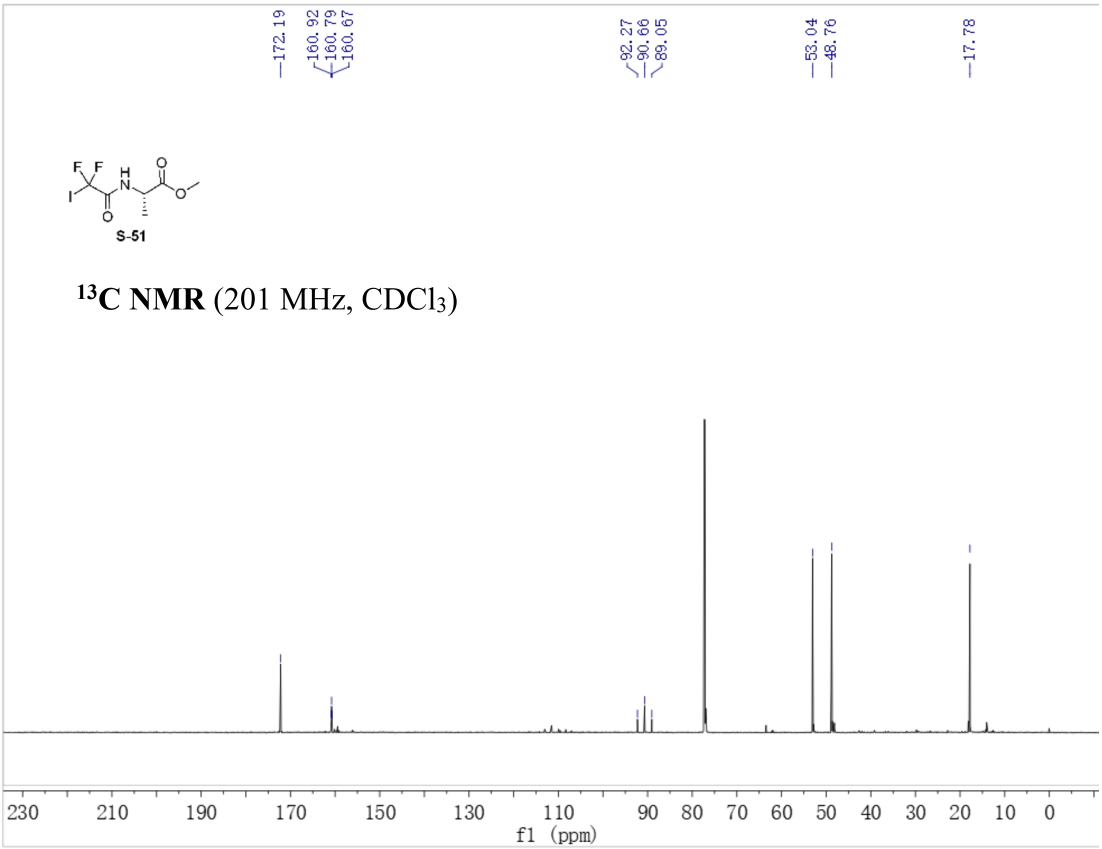


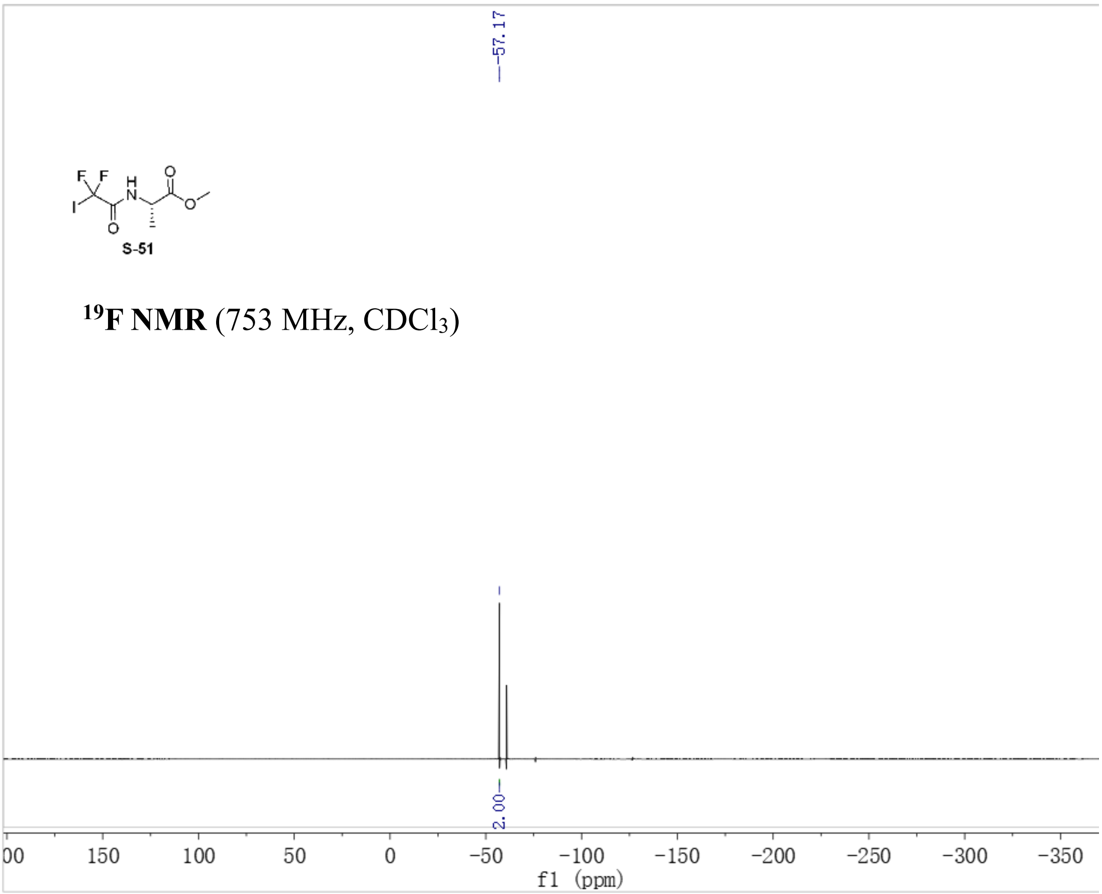




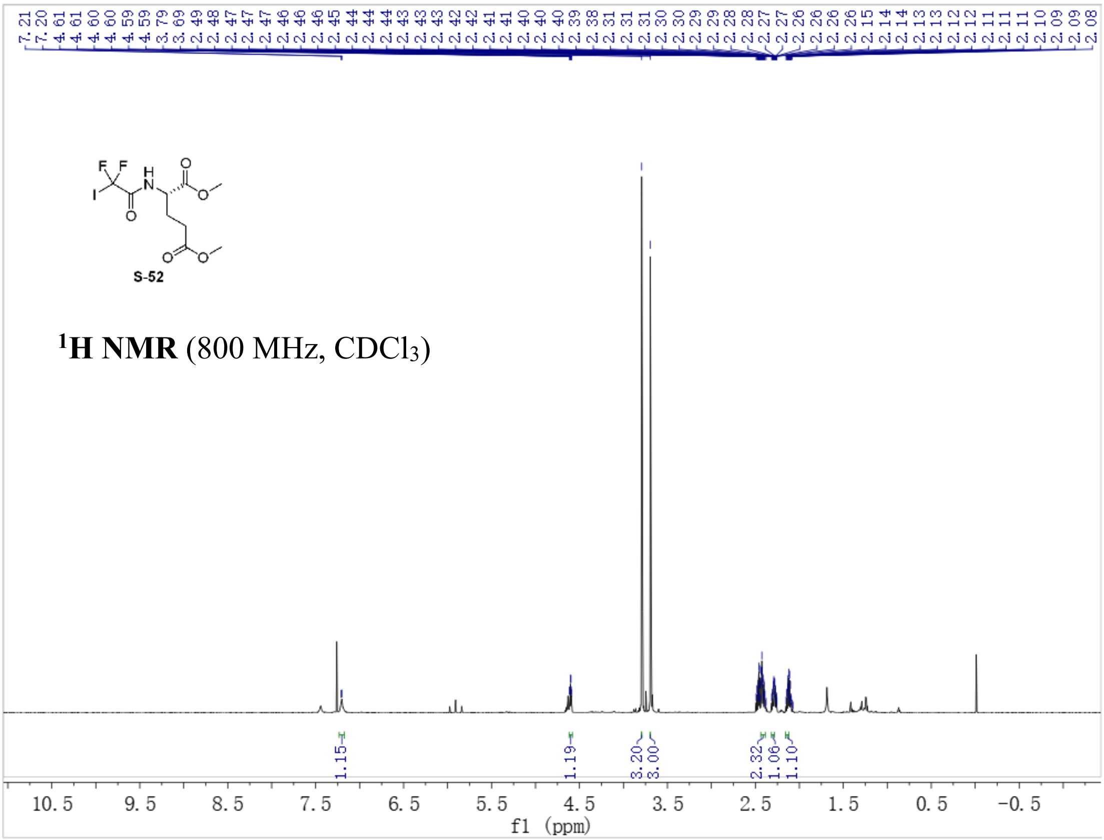
methyl (2,2-difluoro-2-iodoacetyl)-*L*-alaninate (S-51)

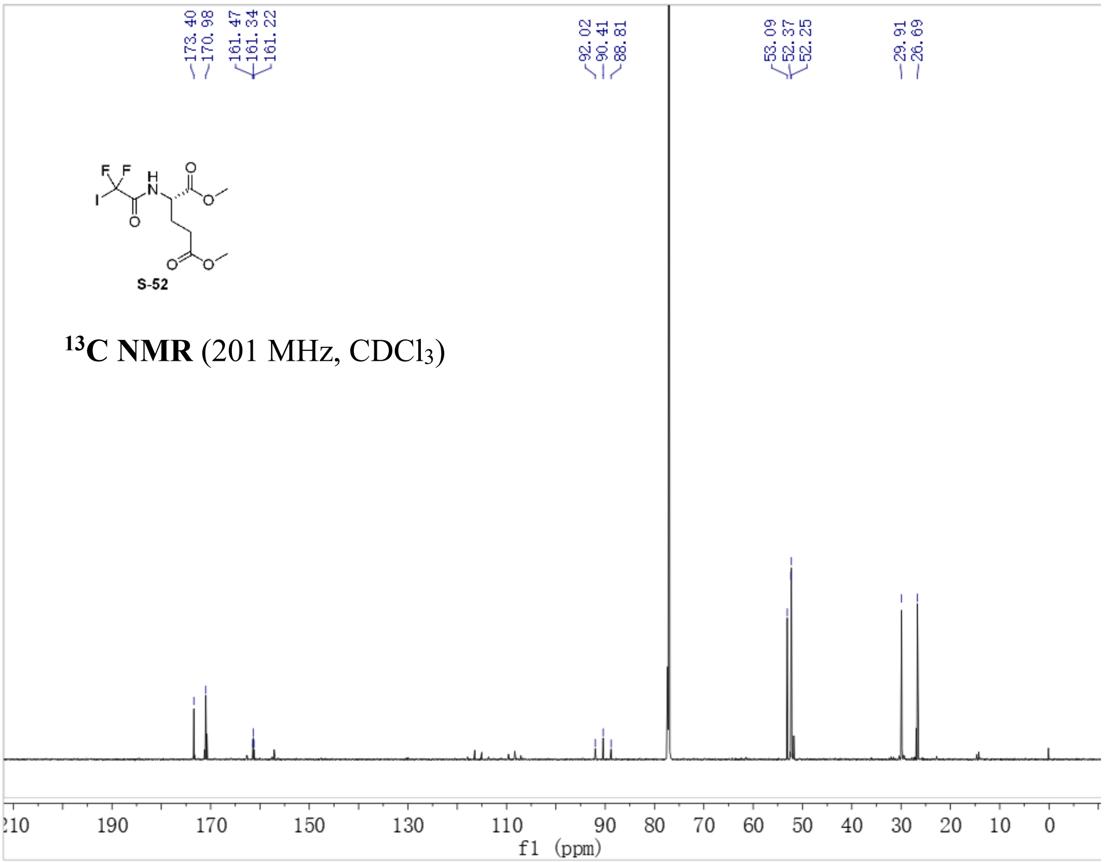


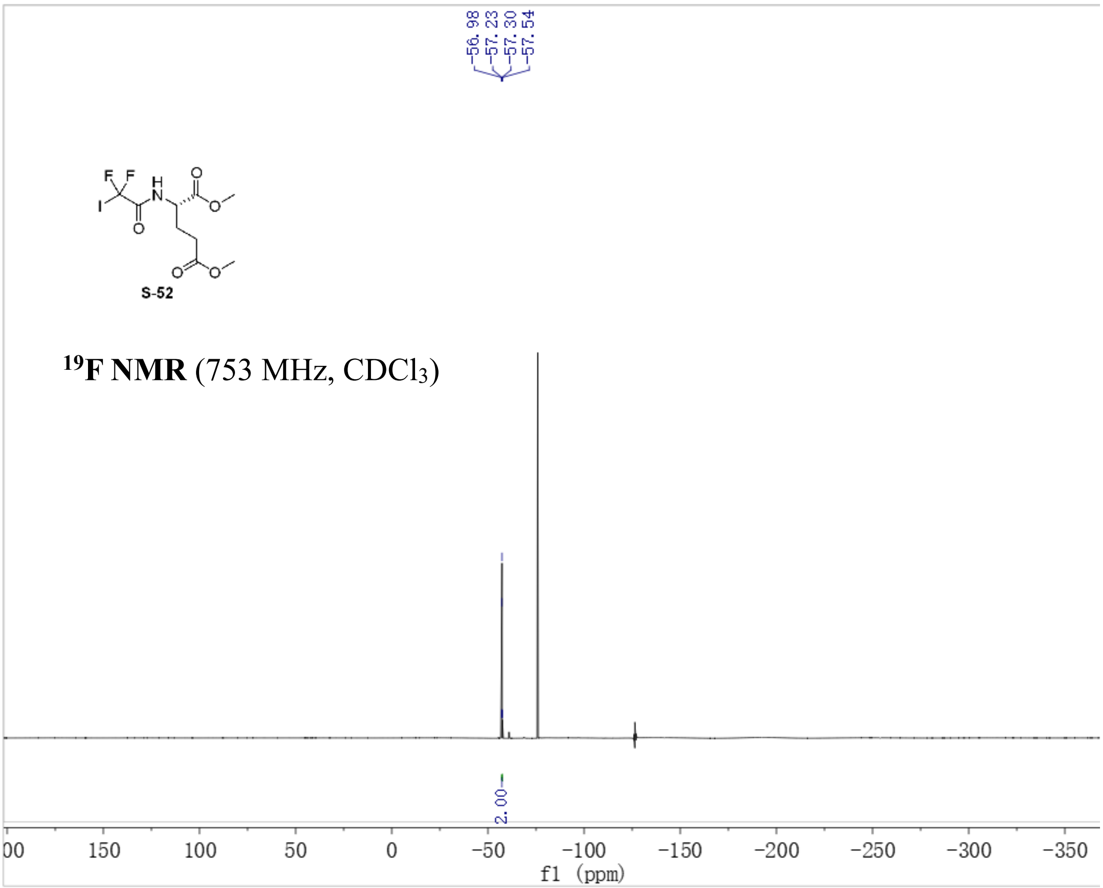

172.19
160.92
160.79
160.67
92.27
90.66
89.05
53.04
48.76
17.78
S-51
13C NMR (201 MHz, CDCl3)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-57.17
S-51
19F NMR (753 MHz, CDCl3)
2.00
00 150 100 50 0 -50 -100 -150 -200 -250 -300 -350
f1 (ppm)

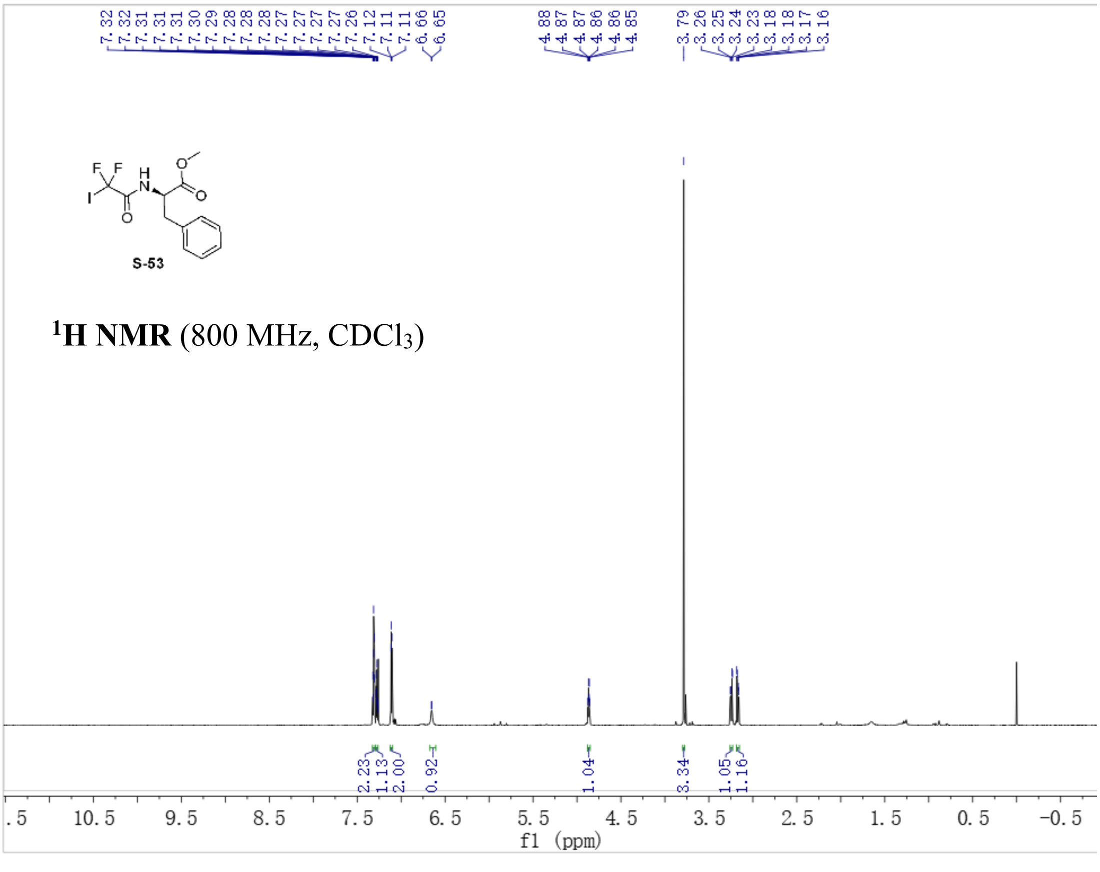
dimethyl (2,2-difluoro-2-iodoacetyl)-*L*-glutamate (S-52)

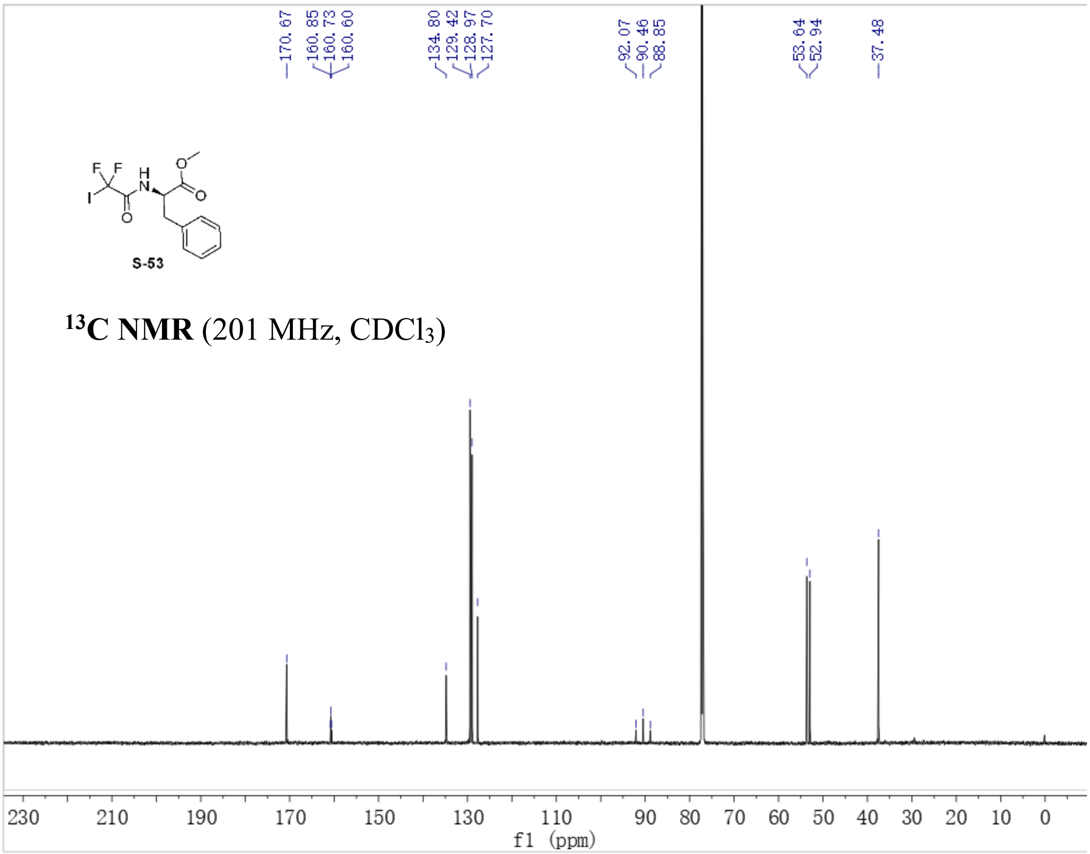


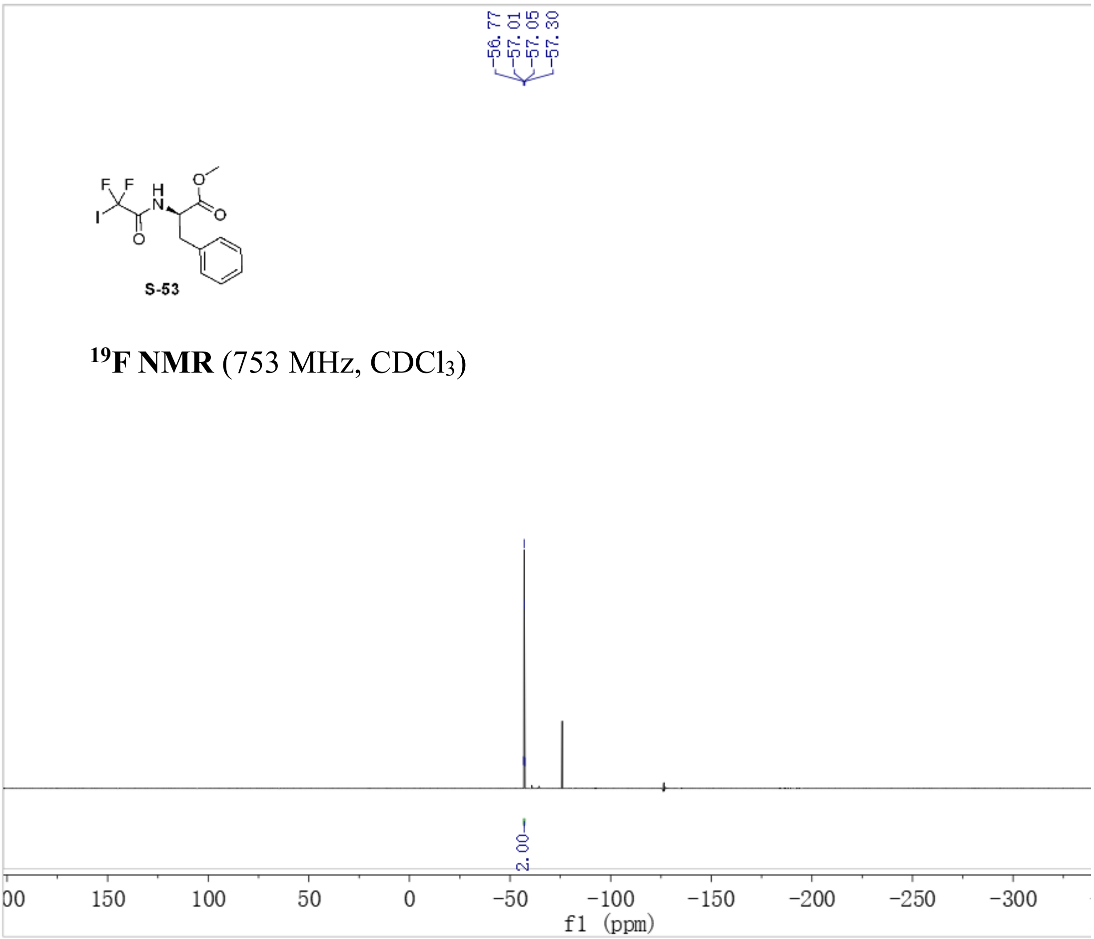




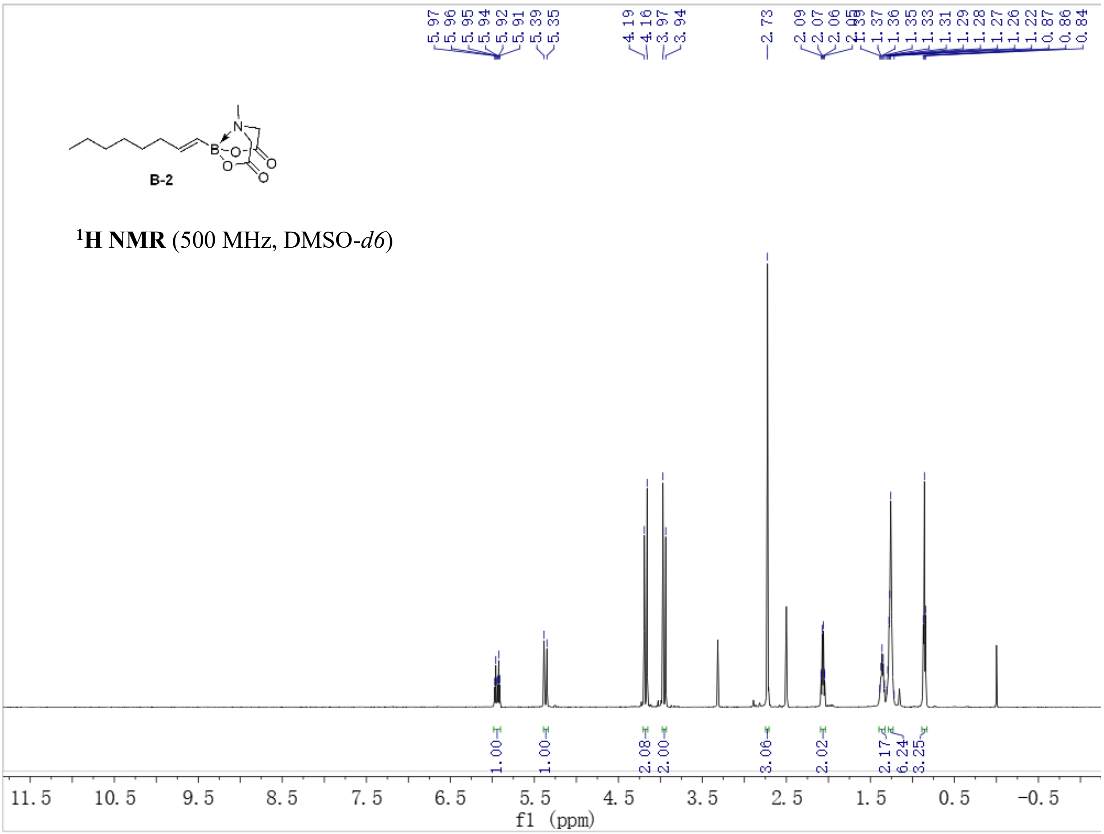
methyl (2,2-difluoro-2-iodoacetyl)-*D*-phenylalaninate (S-53)



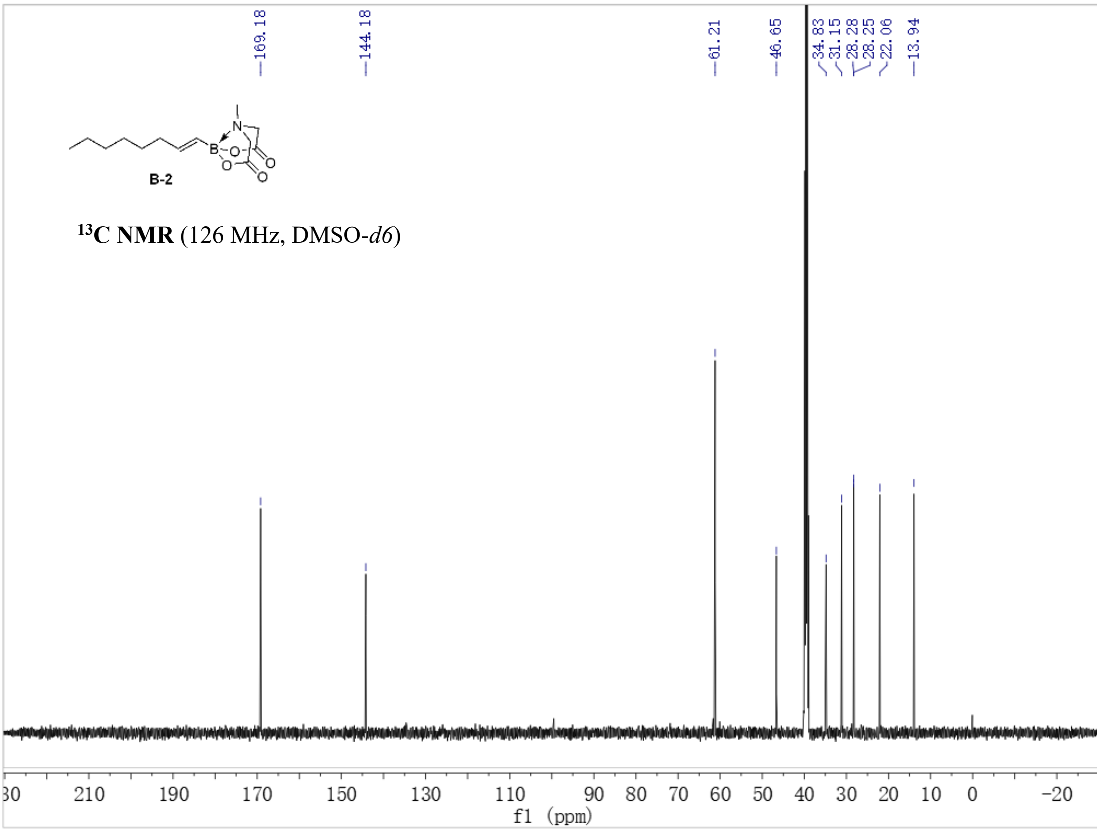

170.67
160.85
160.73
160.60
134.80
129.42
128.97
127.70
92.07
90.46
88.85
53.64
52.94
37.48
S-53
13C NMR (201 MHz, CDCl3)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-56.77
-57.01
-57.05
-57.30
S-53
19F NMR (753 MHz, CDCl3)
2.00
00 150 100 50 0 -50 -100 -150 -200 -250 -300
f1 (ppm)

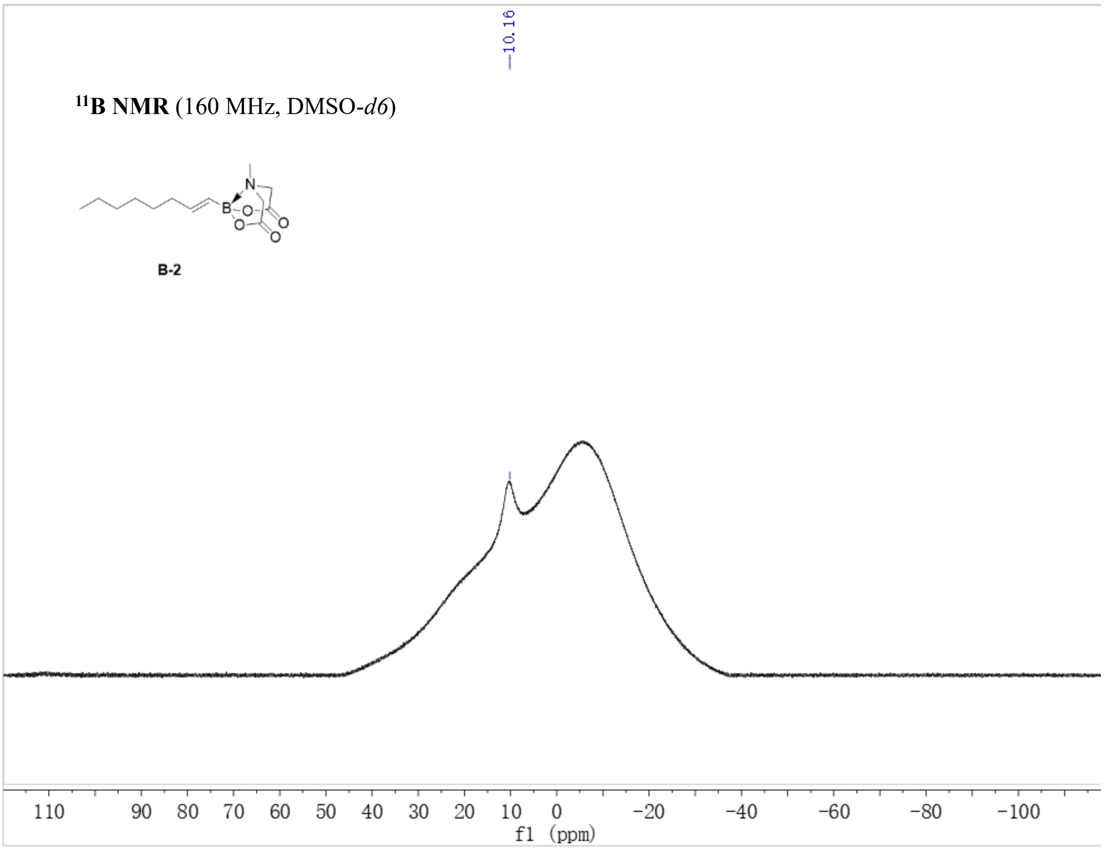
((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-
(*E*)-6-methyl-2-(oct-1-en-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (B-2)



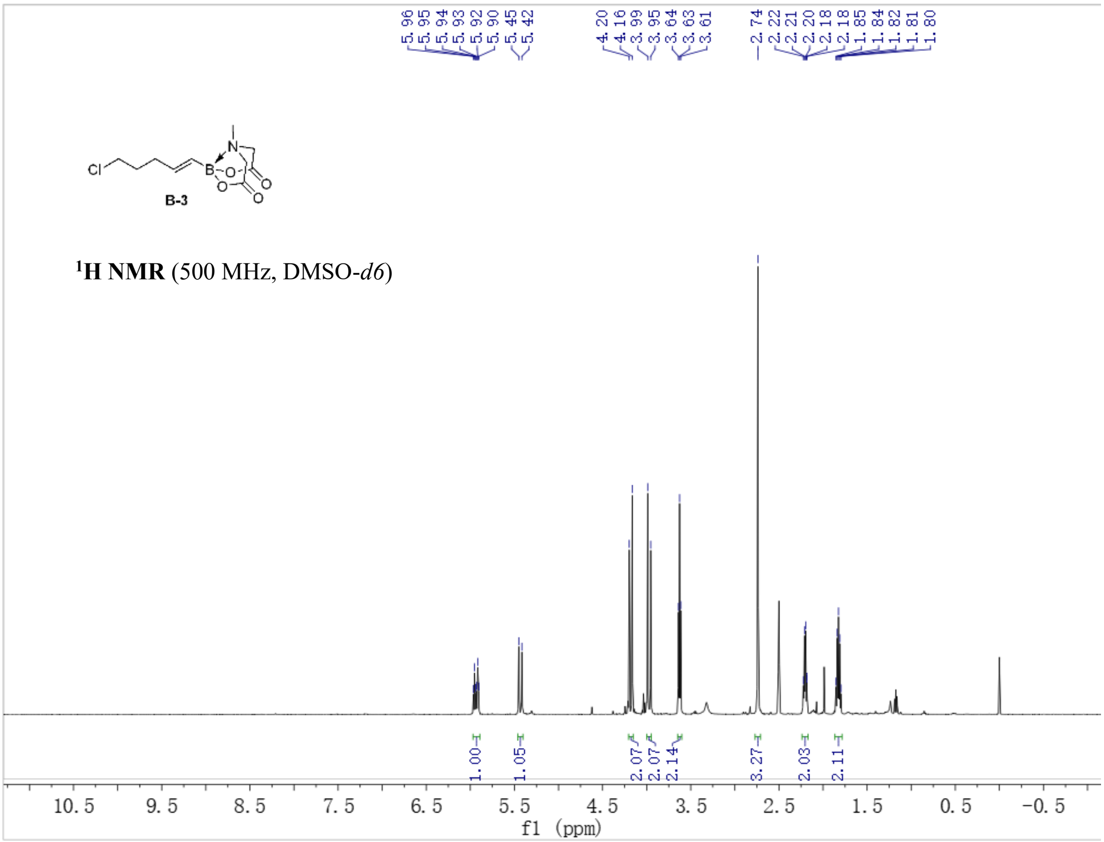
[1]H NMR (500 MHz, DMSO-*d6*)

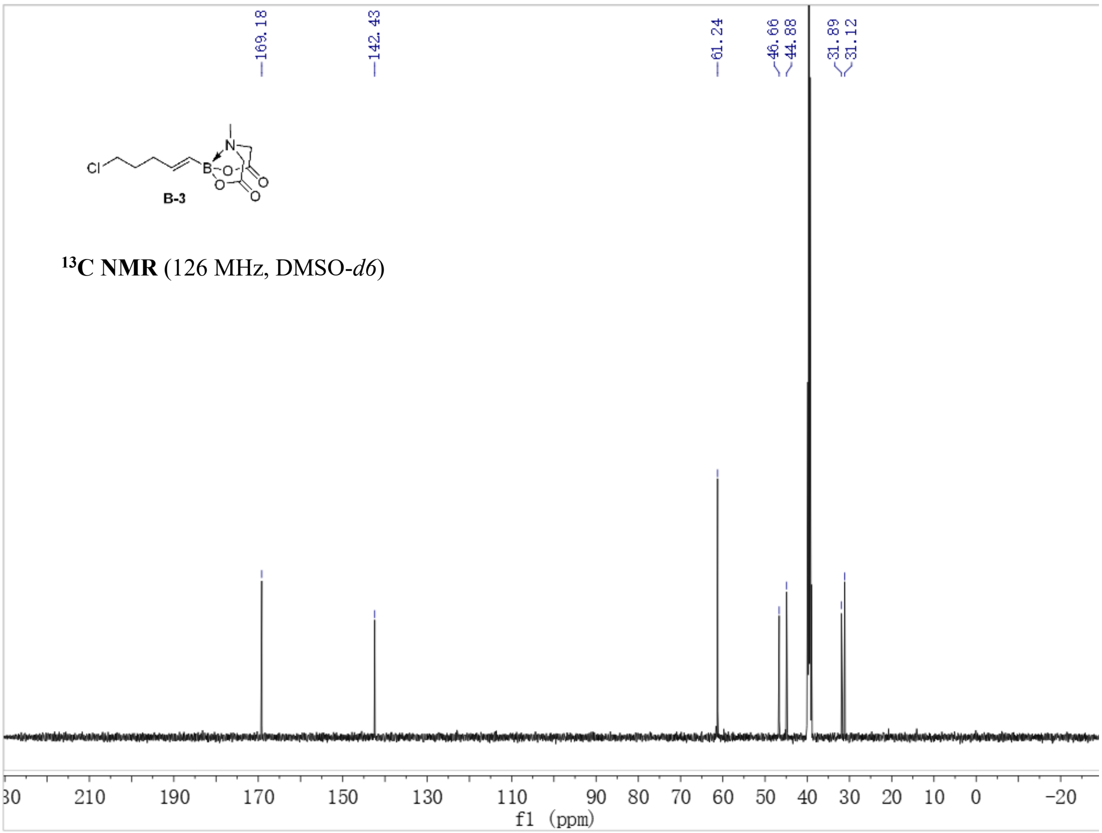


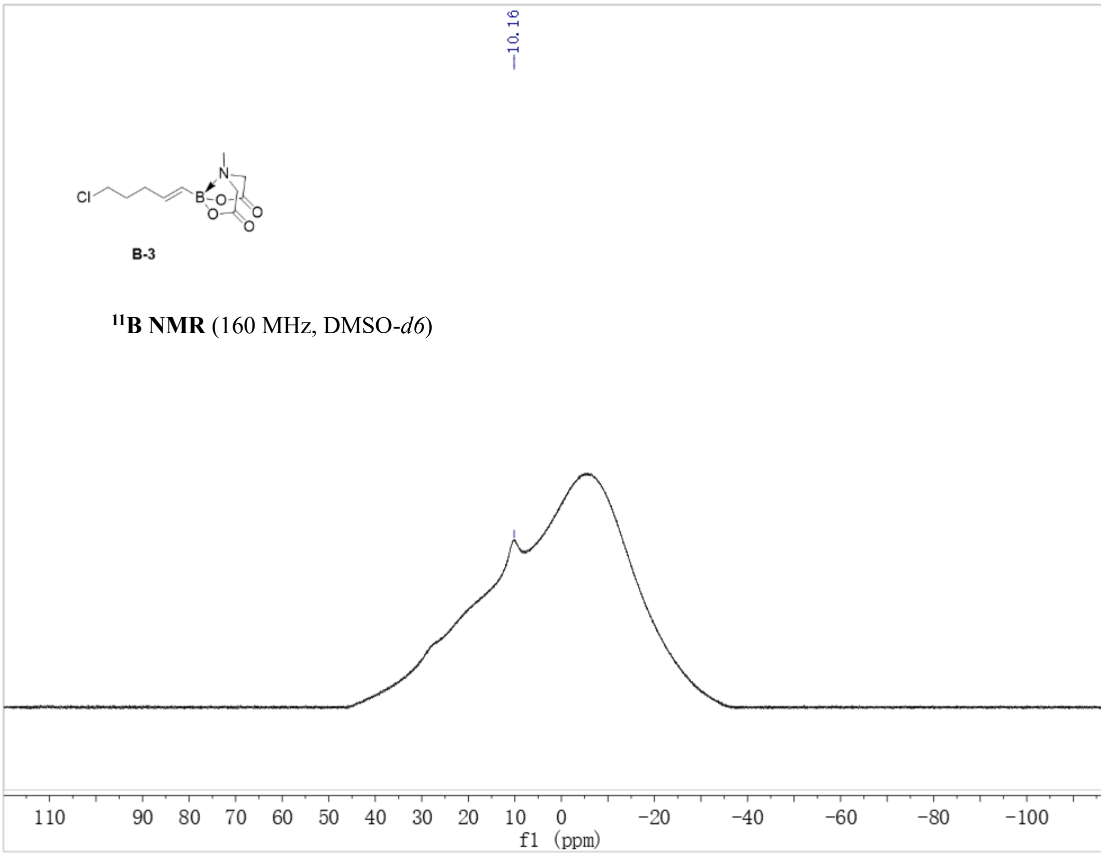
[13]C NMR (126 MHz, DMSO-*d6*)



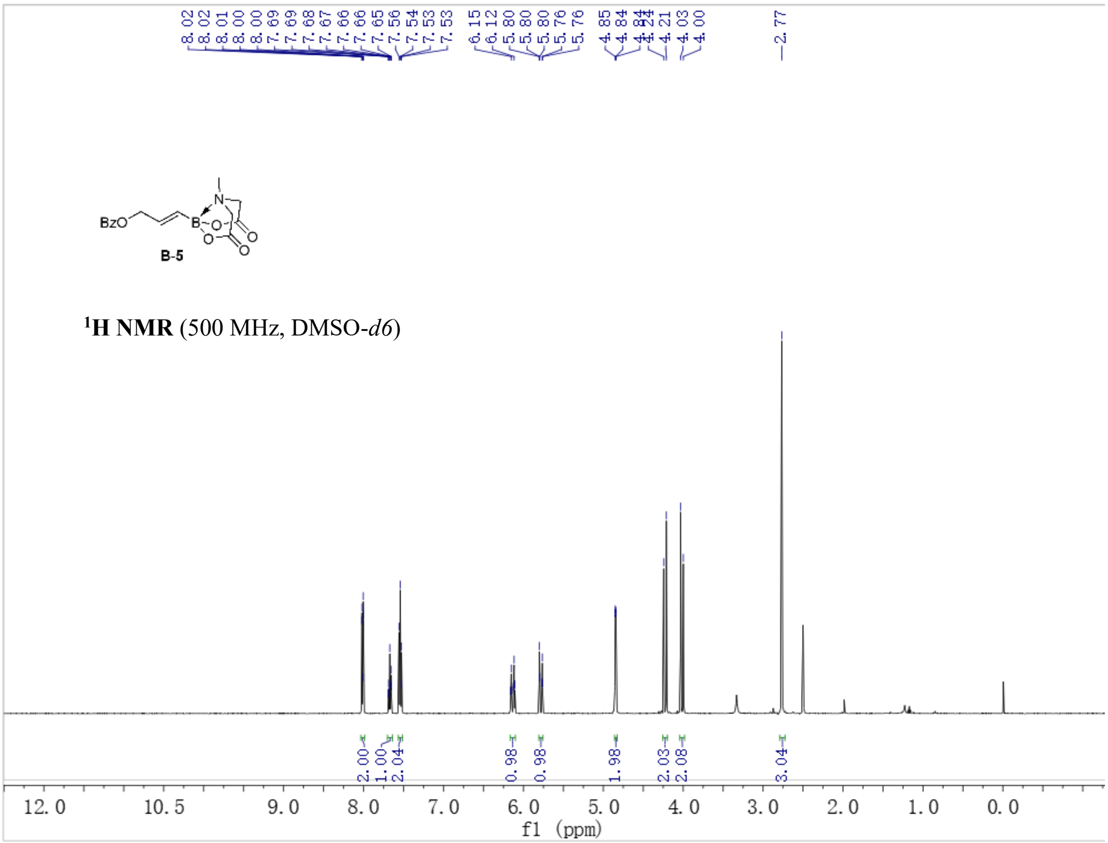
(*E*)-2-(5-chloropent-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (B-3)

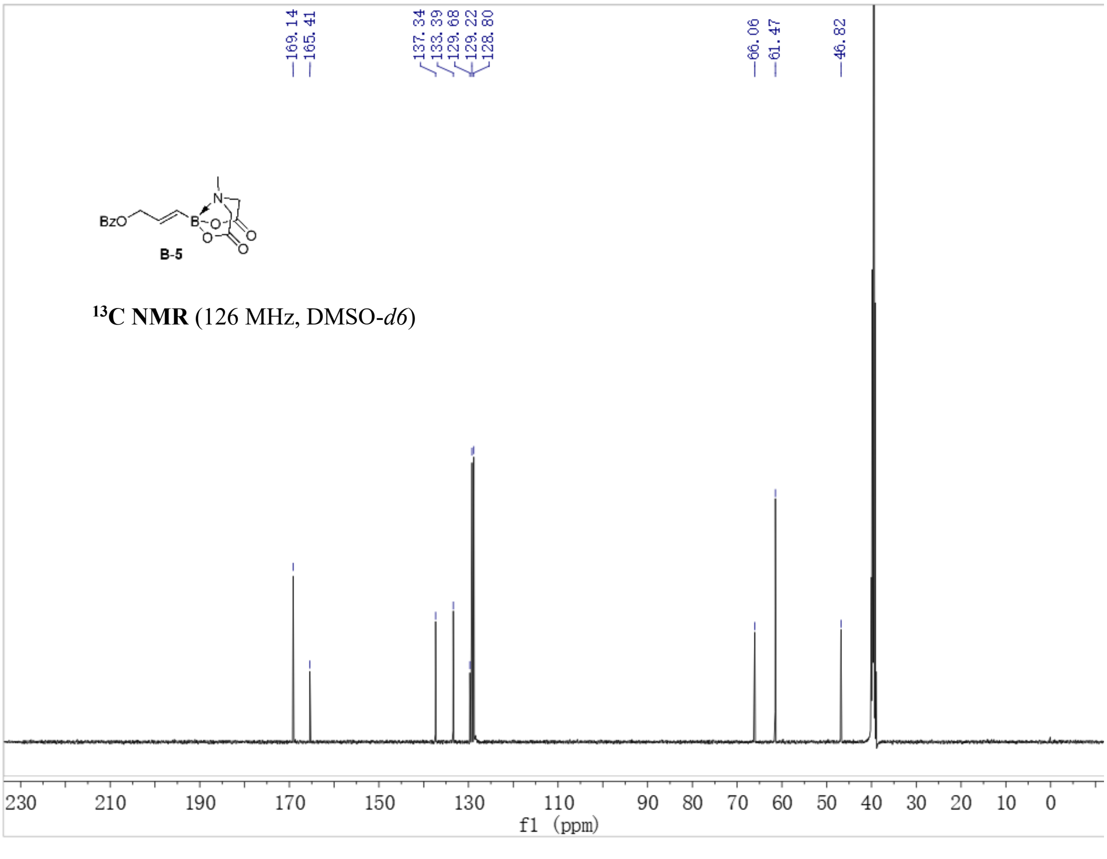


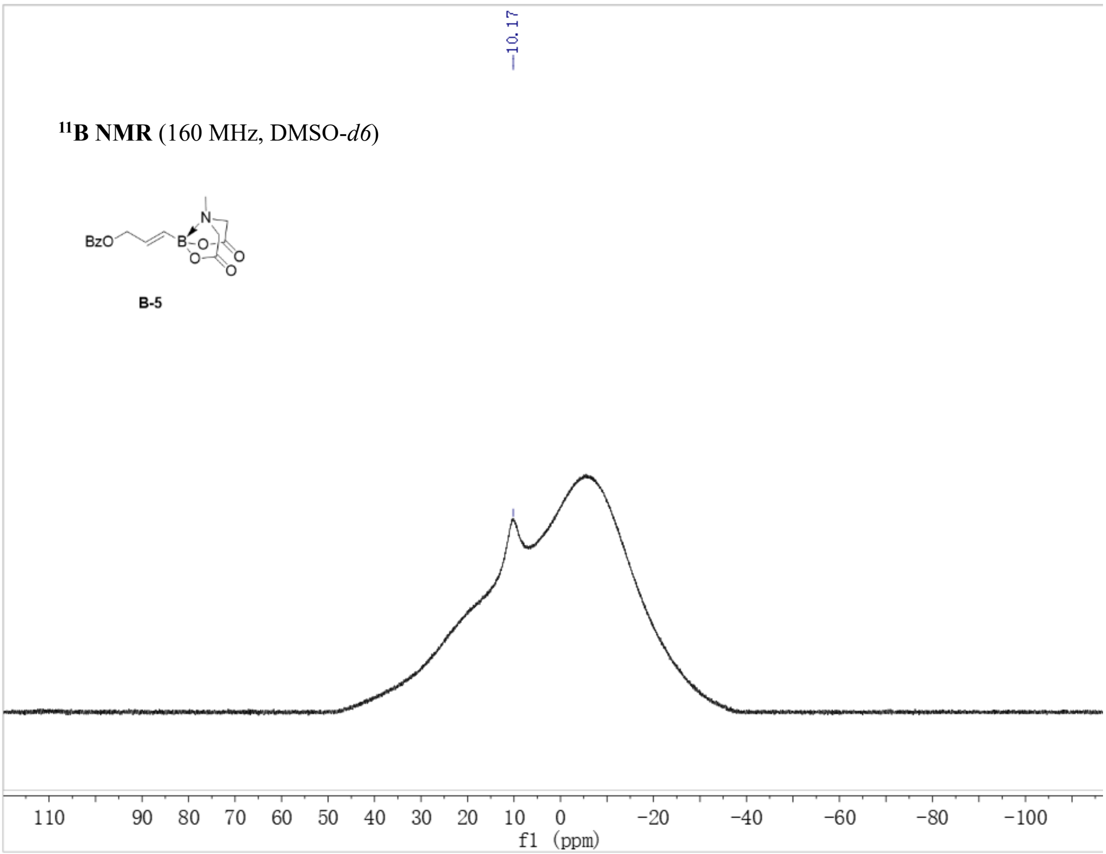

169.18
142.43
61.24
46.66
44.88
31.89
31.12
Cl
N
B
O
B-3
13C NMR (126 MHz, DMSO-d6)
f1 (ppm)


10.16
Cl
N
B
O
B-3
11B NMR (160 MHz, DMSO-d6)
f1 (ppm)

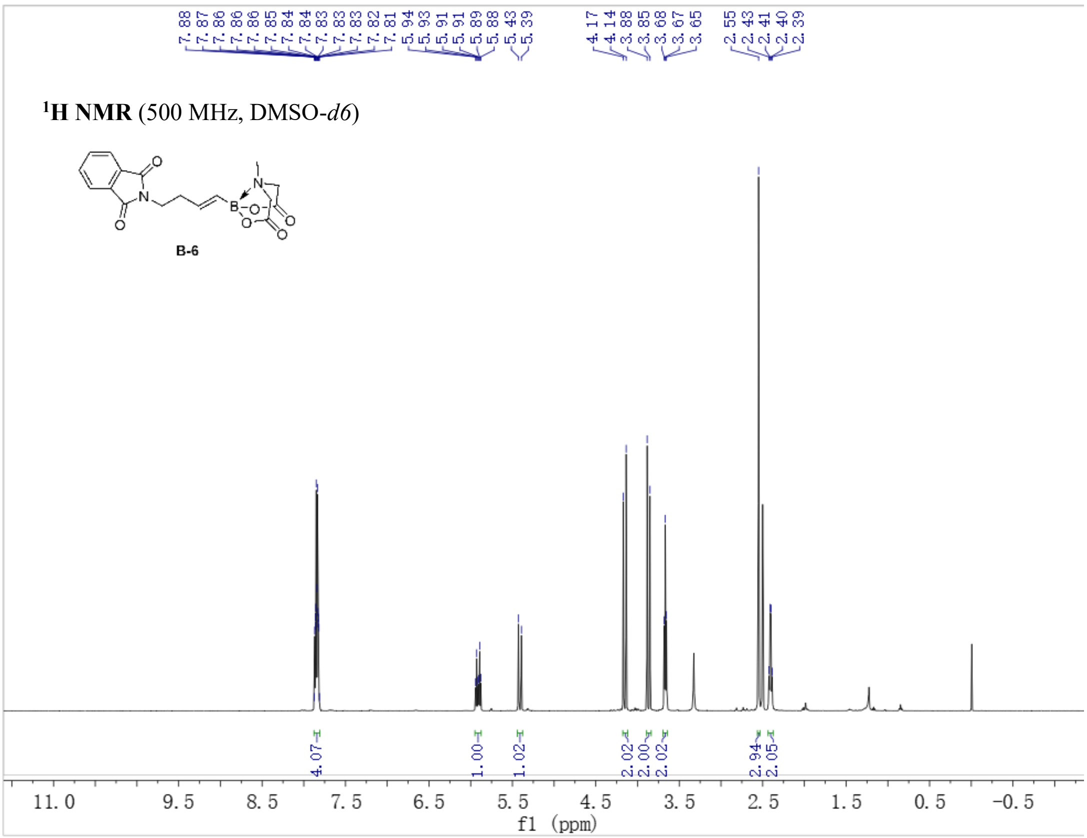
(*E*)-3-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)allyl benzoate (B-5)

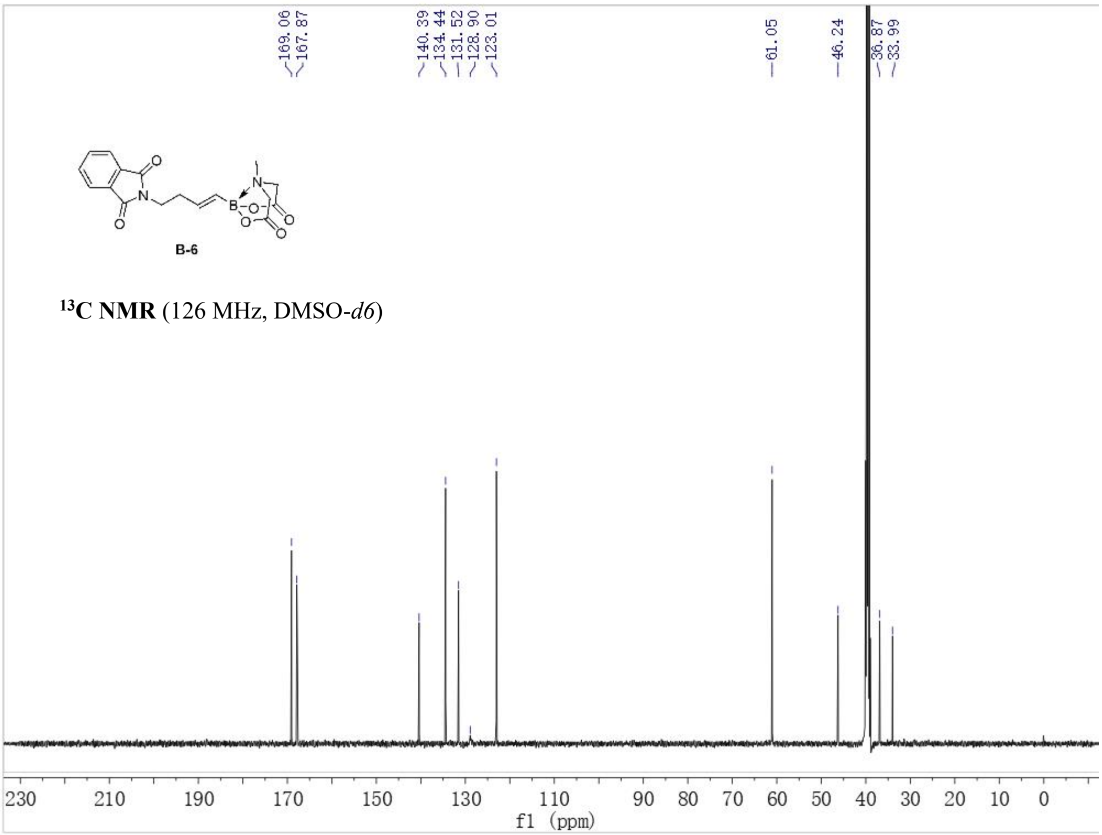


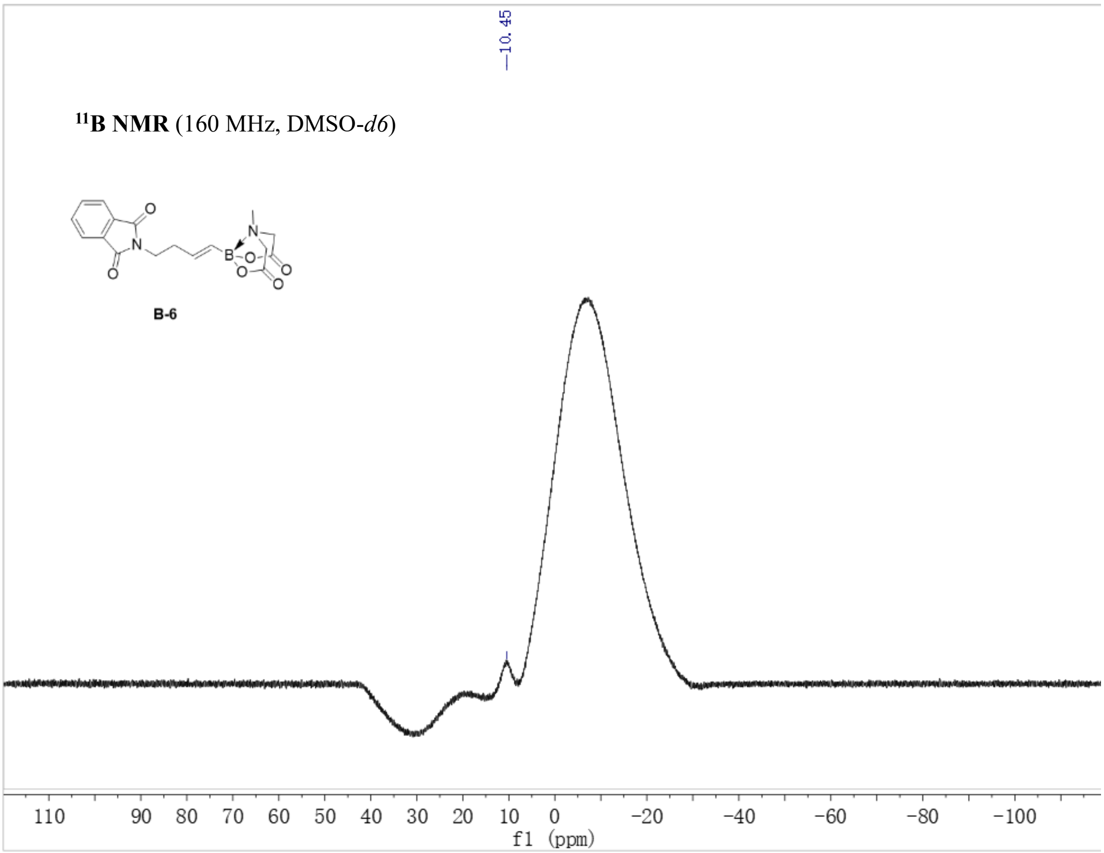




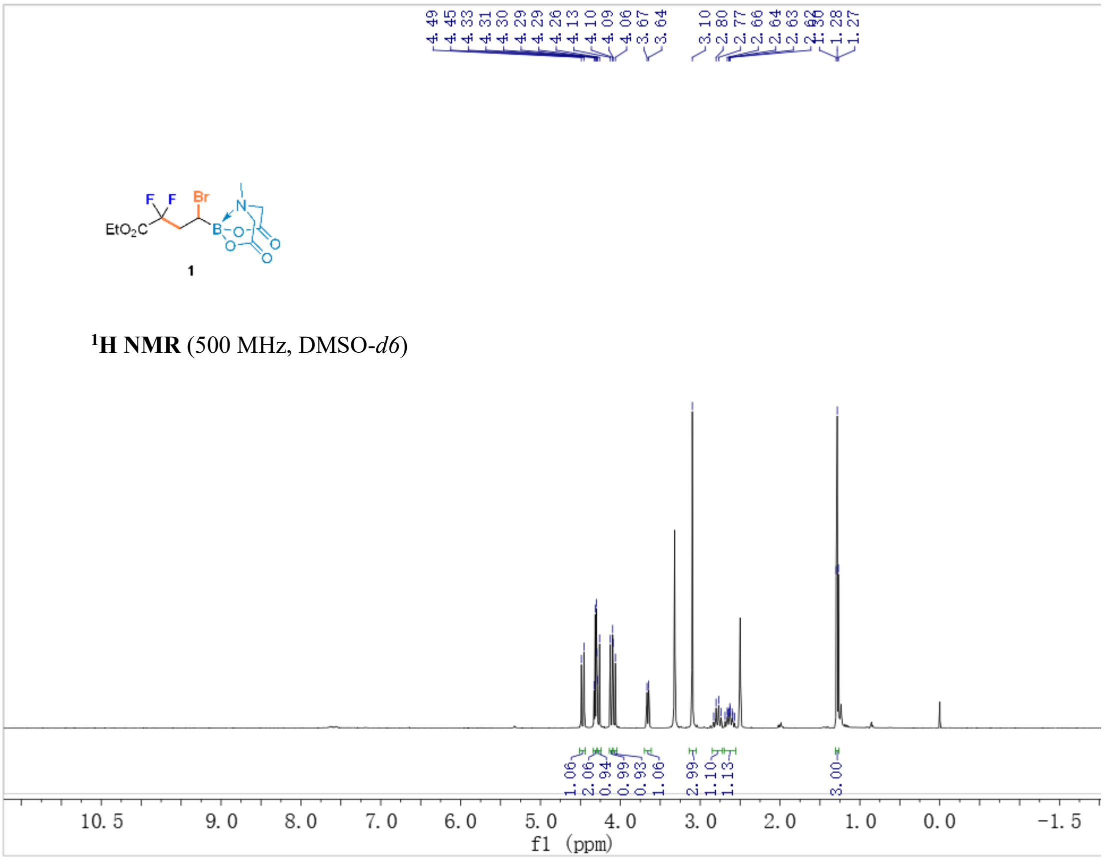
(*E*)-2-(4-(1,3-dioxoisoindolin-2-yl)but-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (B-6)

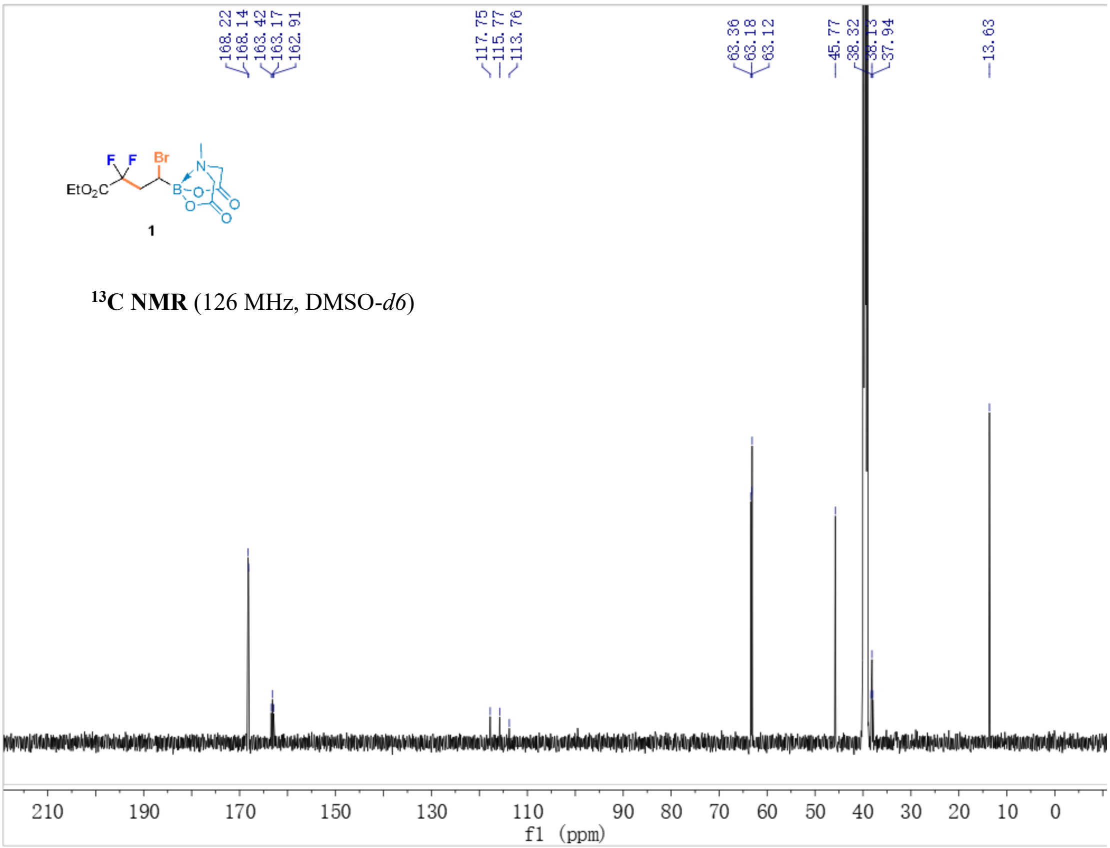


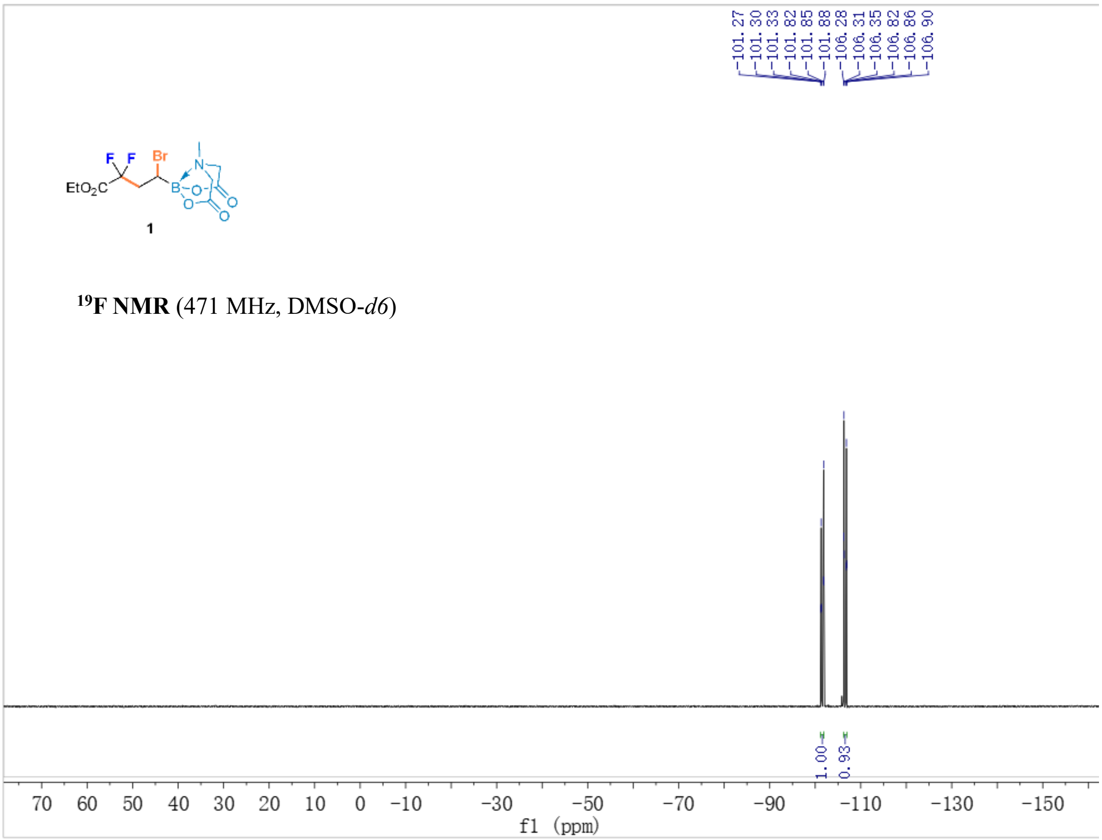

169.06
167.87
140.39
134.44
131.52
128.90
123.01
61.05
46.24
36.87
33.99
B-6
13C NMR (126 MHz, DMSO-d6)
f1 (ppm)

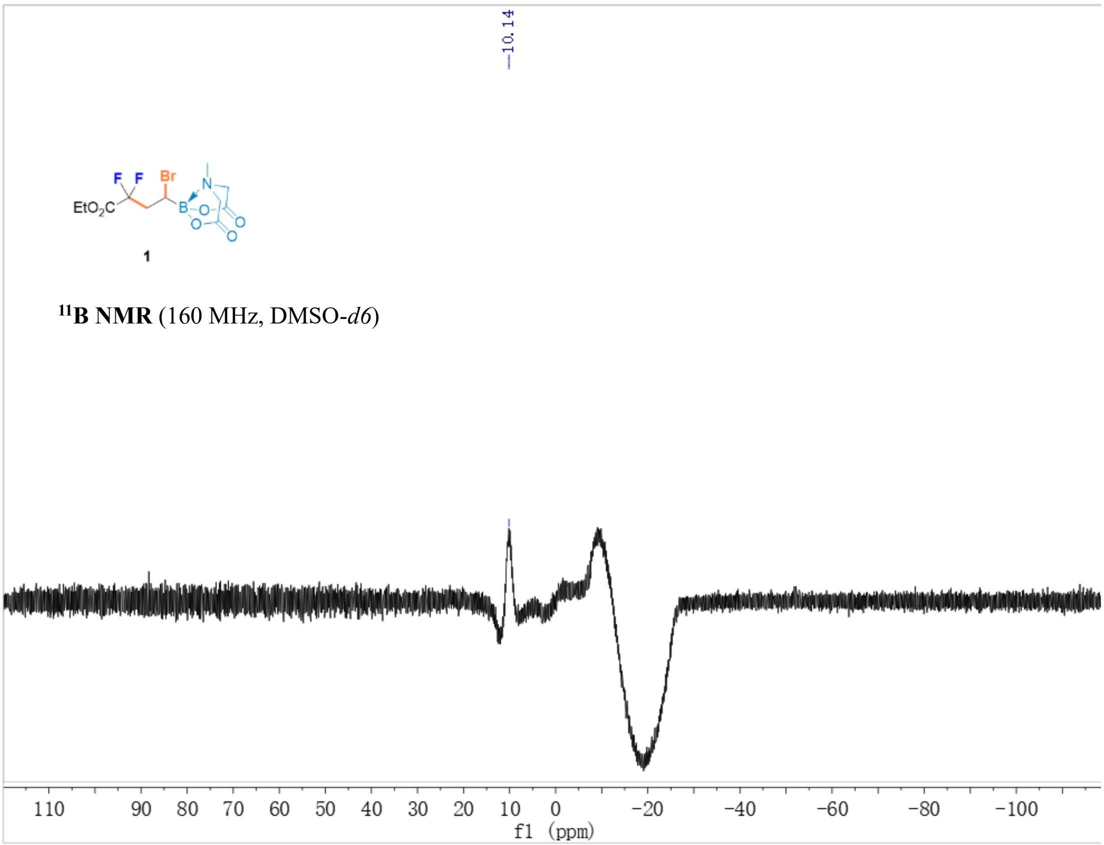

10.45
11B NMR (160 MHz, DMSO-d6)
B-6
f1 (ppm)

Ethyl 4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoate (1)

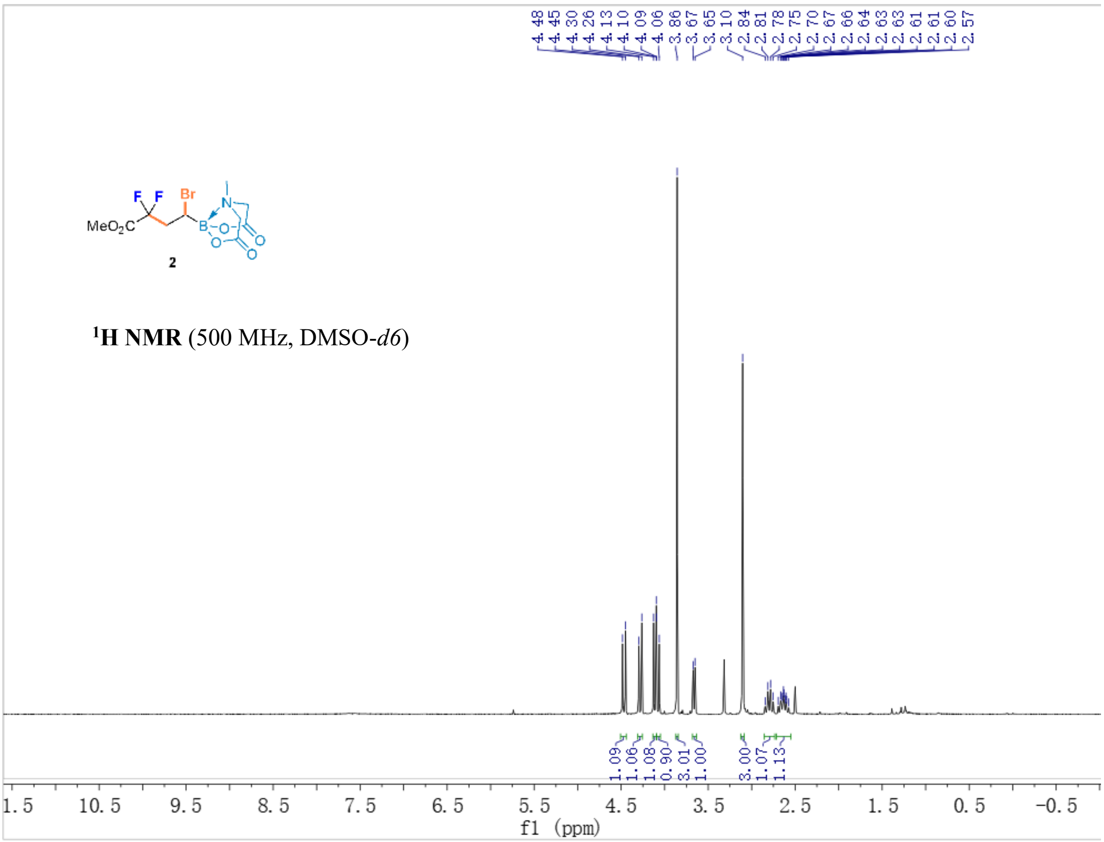


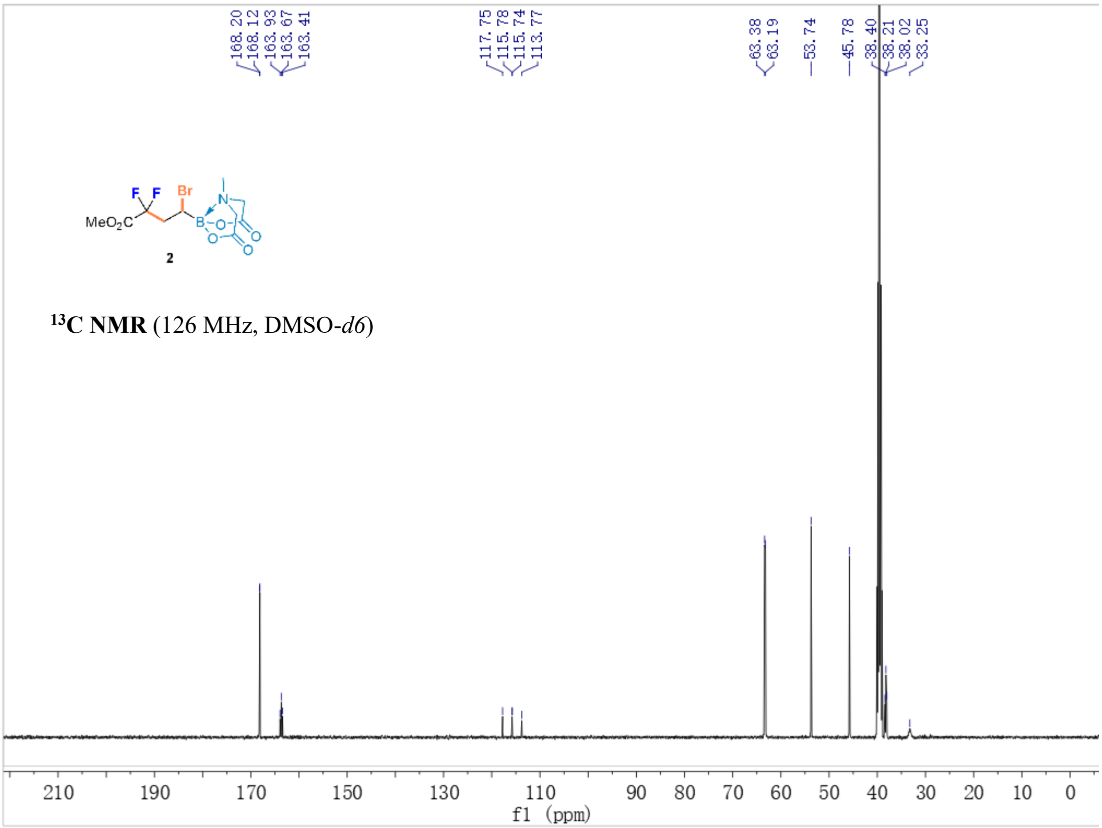

168.22
168.14
163.42
163.17
162.91
117.75
115.77
113.76
63.36
63.18
63.12
45.77
38.32
38.13
37.94
13.63
1
13C NMR (126 MHz, DMSO-d6)
f1 (ppm)

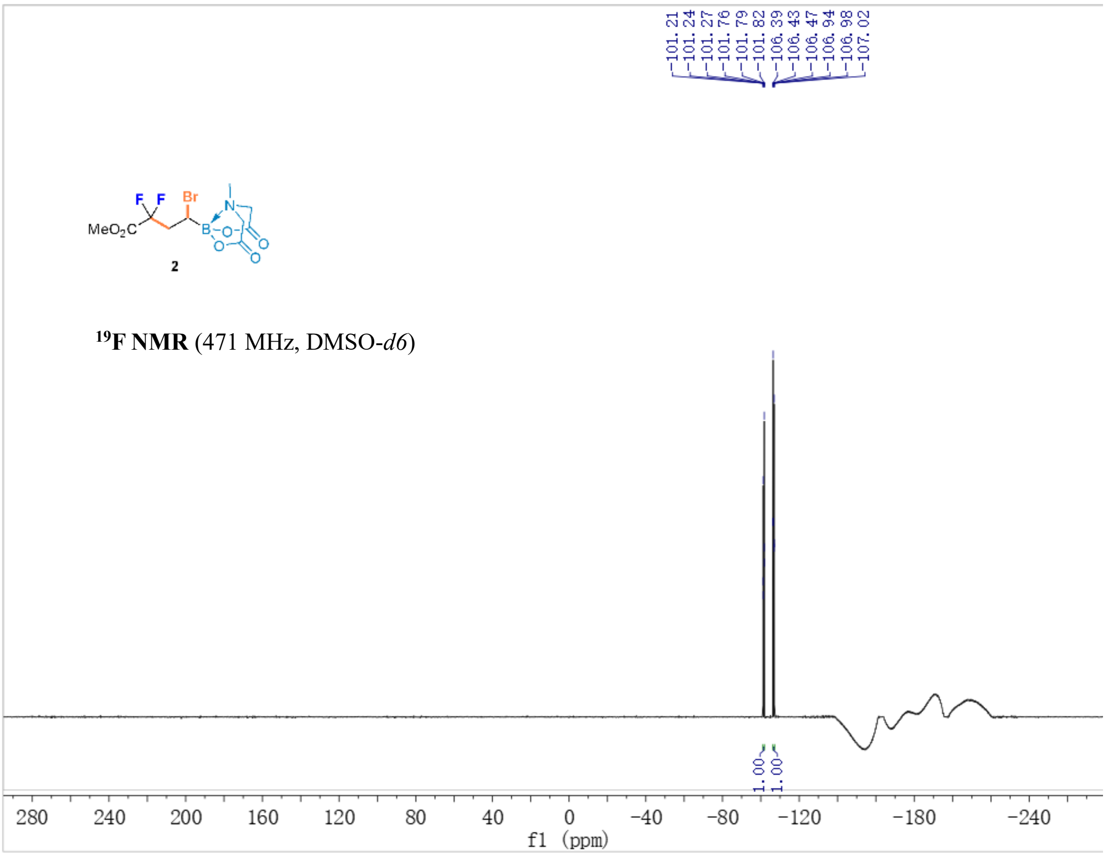

-101.27
-101.30
-101.33
-101.82
-101.85
-101.88
-106.28
-106.31
-106.35
-106.82
-106.86
-106.90
1
19F NMR (471 MHz, DMSO-d6)
1.00
0.93
f1 (ppm)

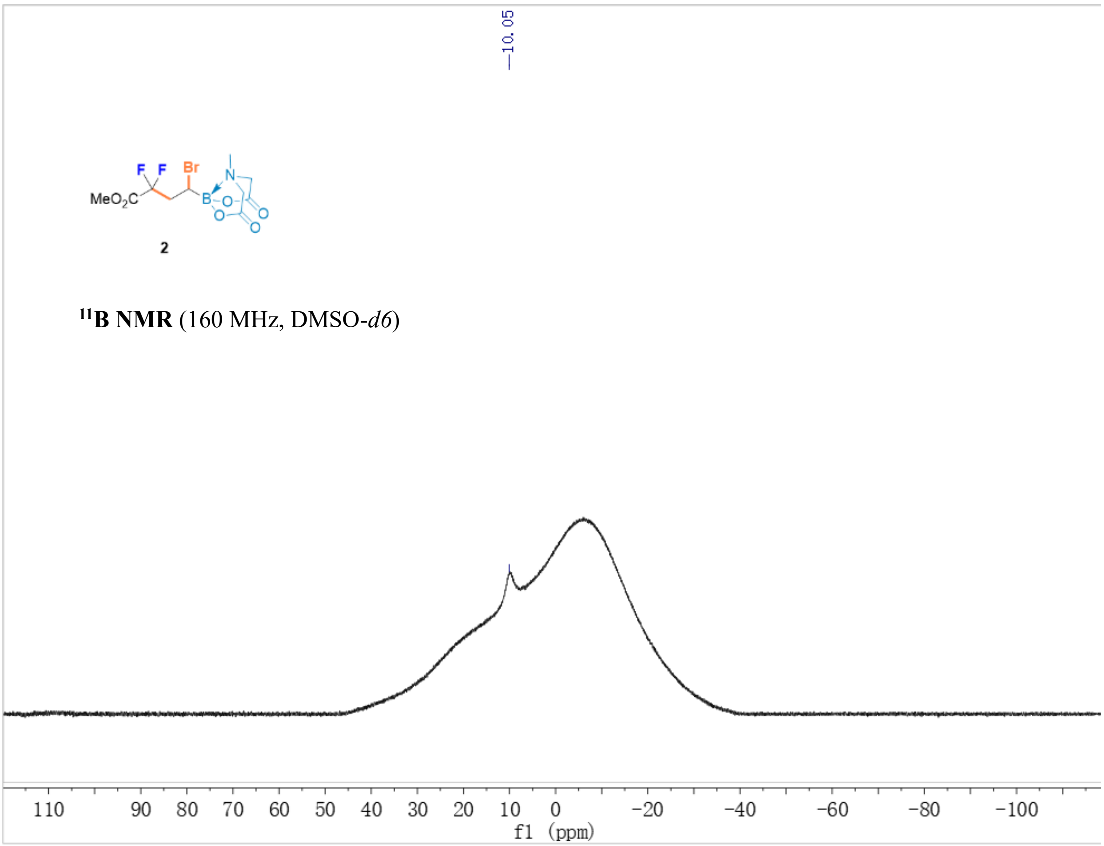


Methyl 4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoate (2)

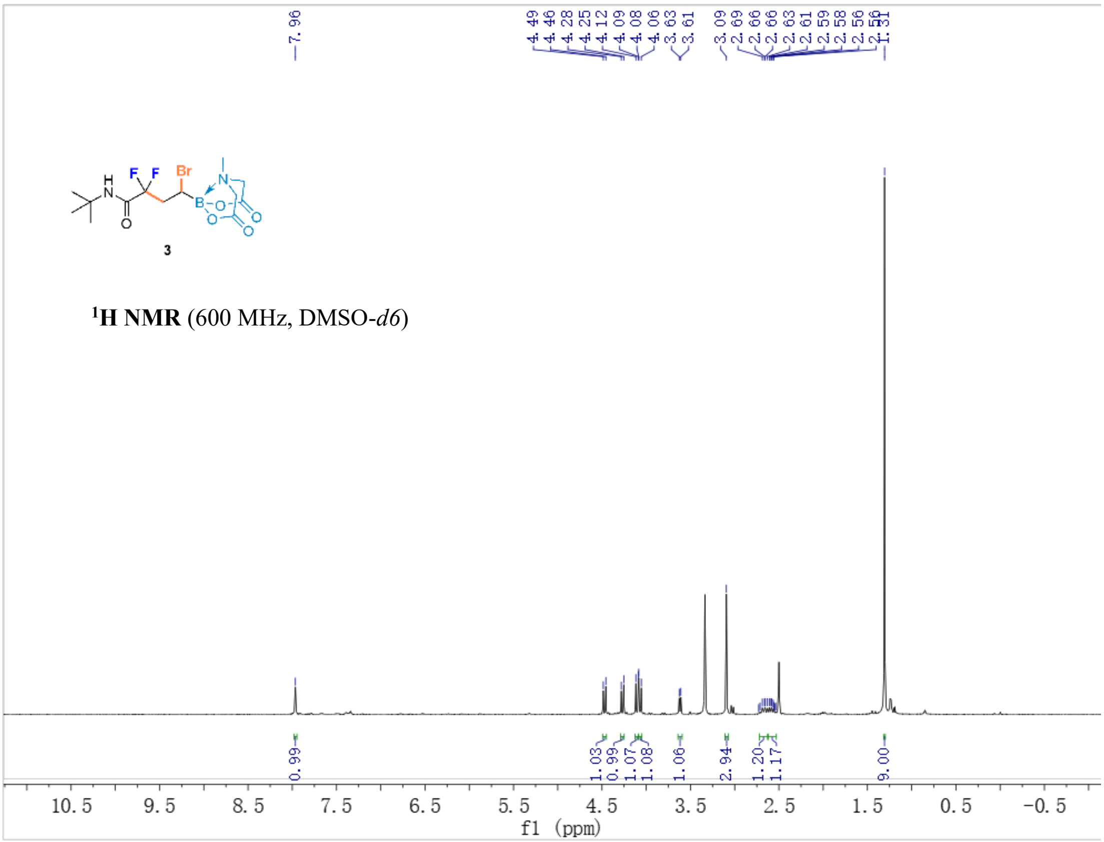


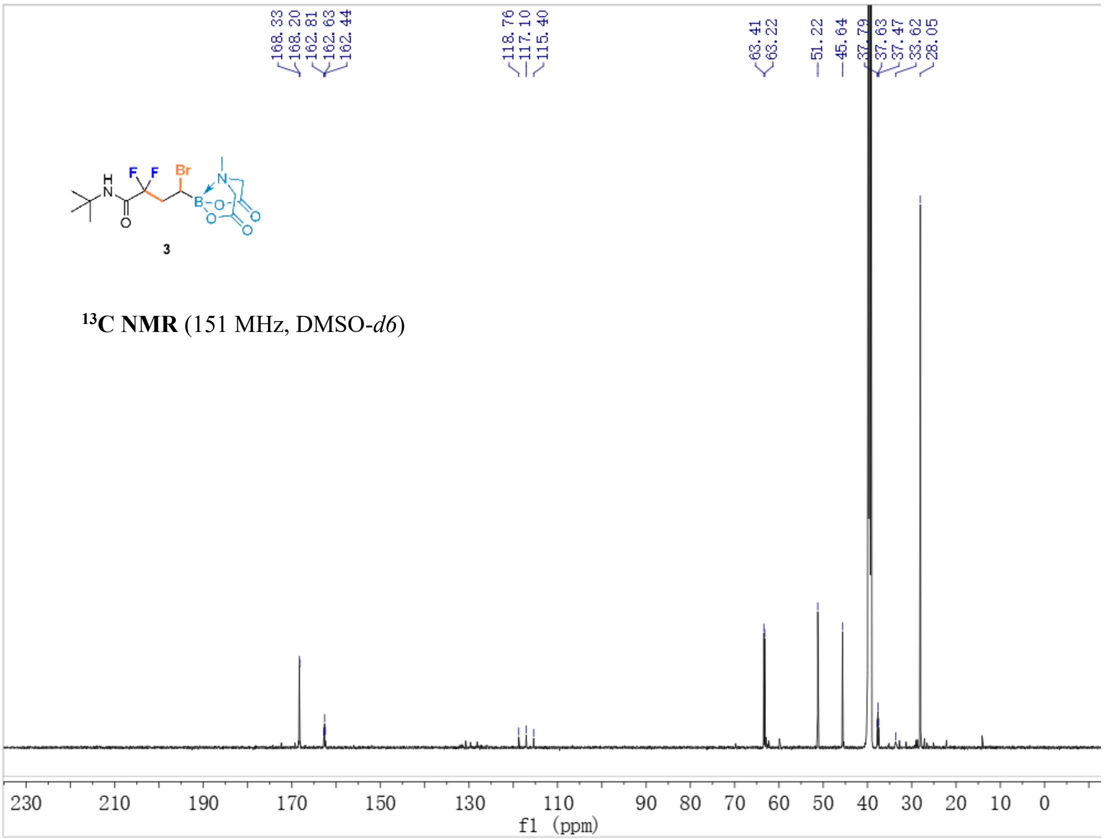

168.20
168.12
163.93
163.67
163.41
117.75
115.78
115.74
113.77
63.38
63.19
53.74
45.78
38.40
38.21
38.02
33.25
MeO$_2$C
F F
Br
N
B
O
O
O
O
2
^{13}C NMR (126 MHz, DMSO-$d6$)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

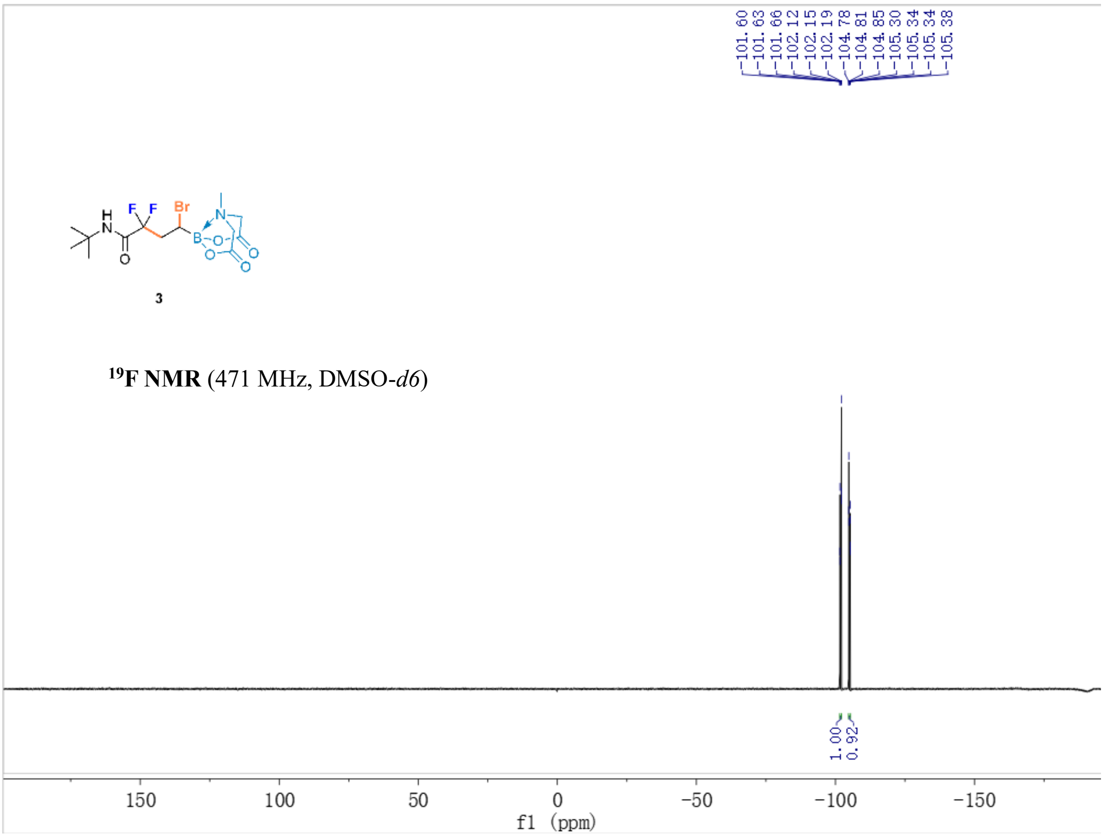

-101.21
-101.24
-101.27
-101.76
-101.79
-101.82
-106.39
-106.43
-106.47
-106.94
-106.98
-107.02
MeO$_2$C
F F
Br
N
B
O
O
O
O
2
^{19}F NMR (471 MHz, DMSO-$d6$)
1.00
1.00
280 240 200 160 120 80 40 0 −40 −80 −120 −180 −240
f1 (ppm)

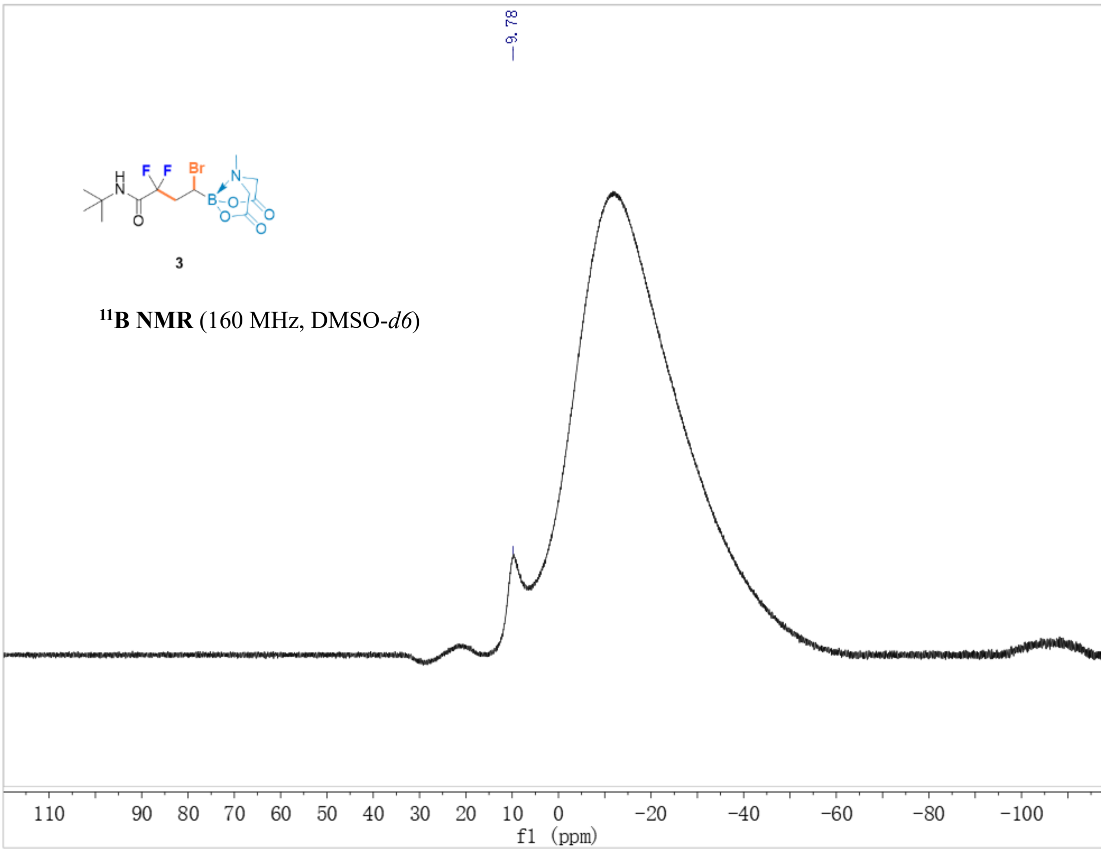


4-bromo-*N*-(*tert*-butyl)-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (3)

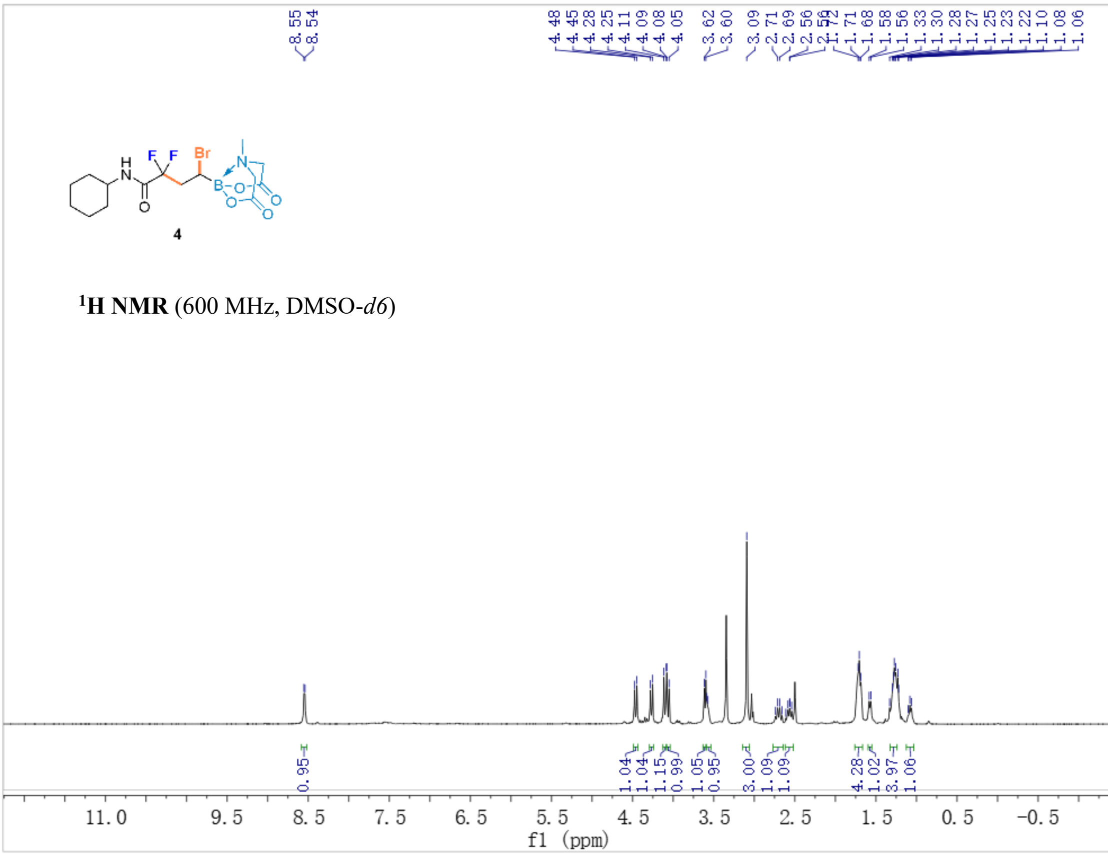


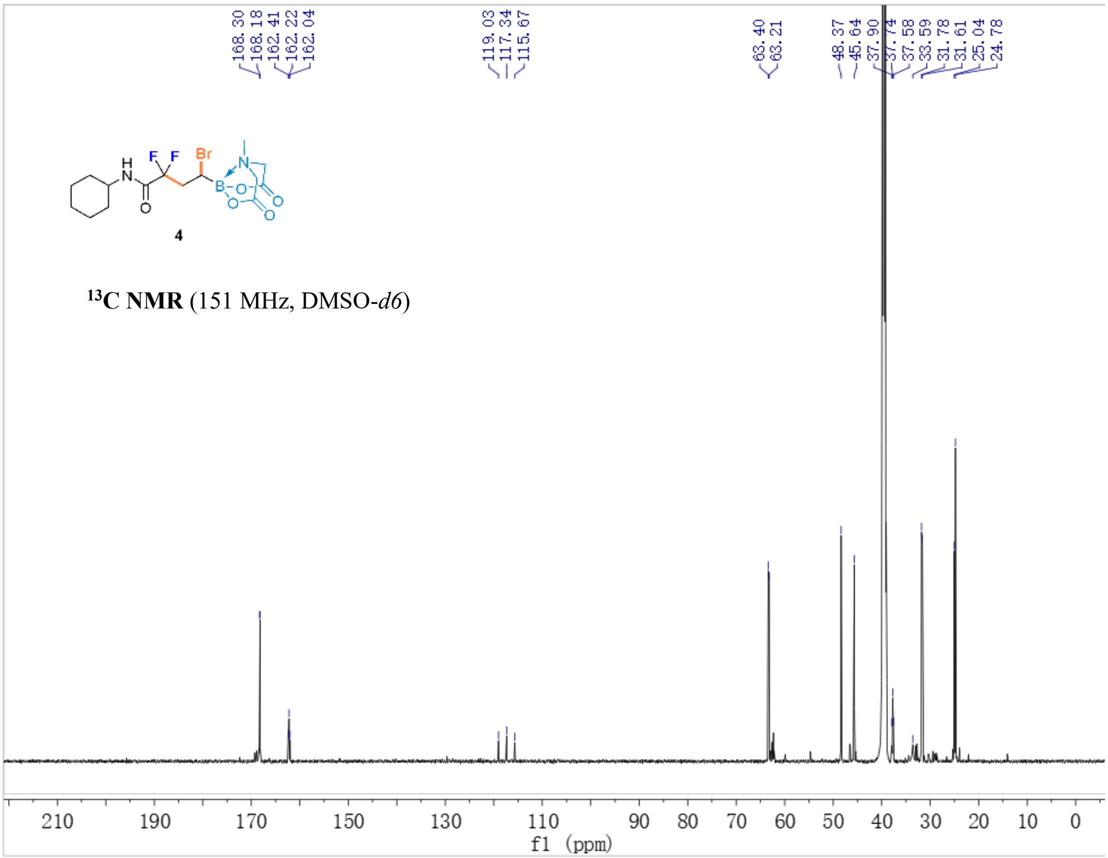

168.33
168.20
162.81
162.63
162.44
118.76
117.10
115.40
63.41
63.22
51.22
45.64
37.79
37.63
37.47
33.62
28.05
3
13C NMR (151 MHz, DMSO-d6)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-101.60
-101.63
-101.66
-102.12
-102.15
-102.19
-104.78
-104.81
-104.85
-105.30
-105.34
-105.34
-105.38
3
19F NMR (471 MHz, DMSO-d6)
1.00
0.92
150 100 50 0 -50 -100 -150
f1 (ppm)

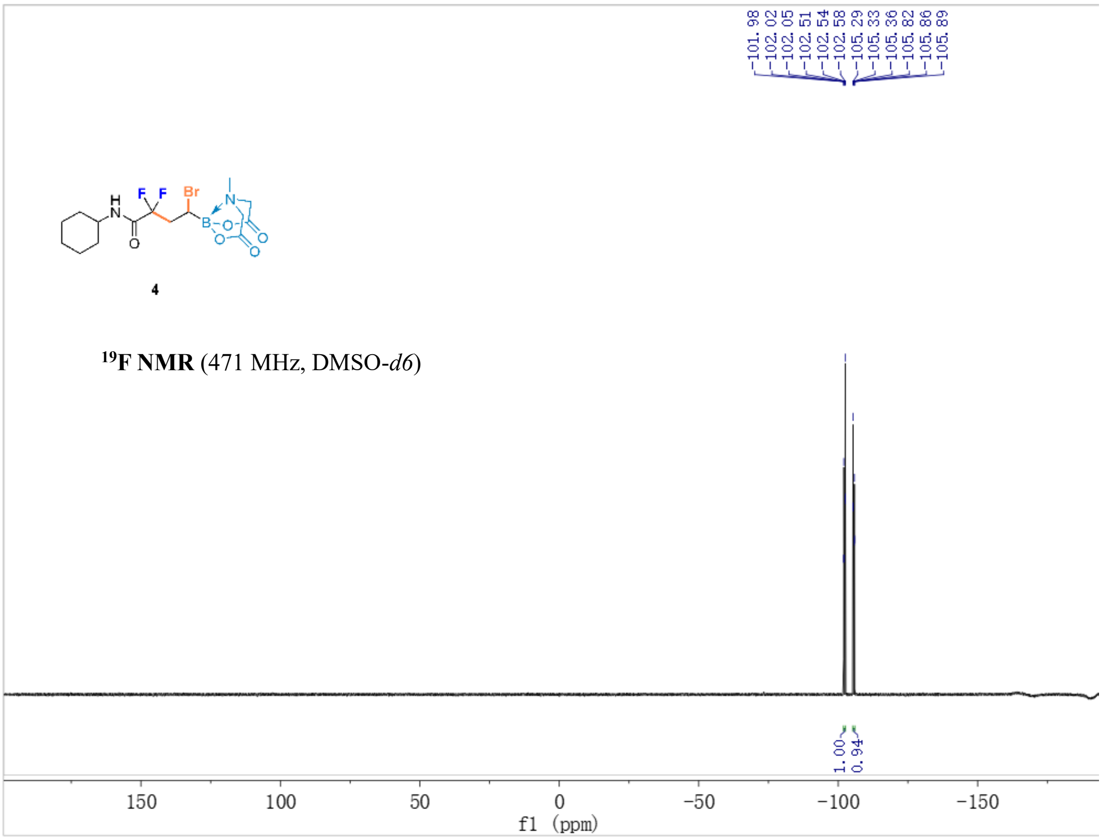


4-bromo-*N*-cyclohexyl-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (4)

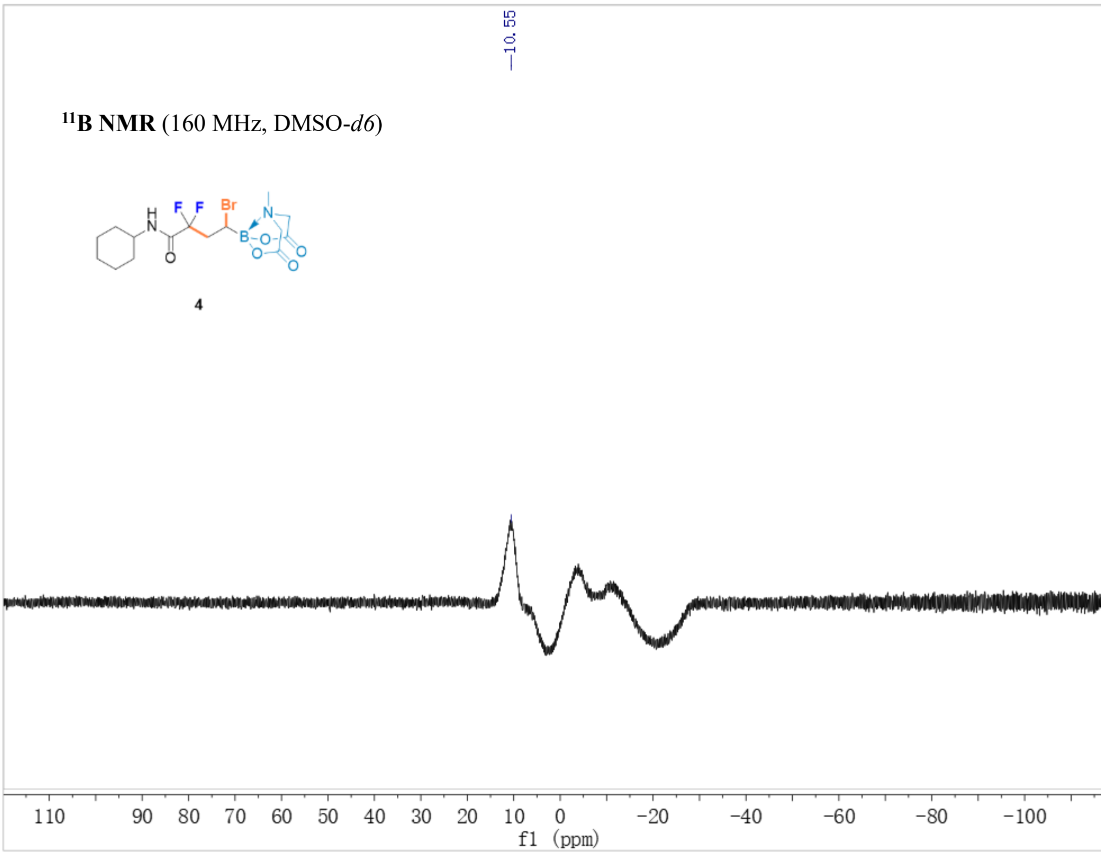




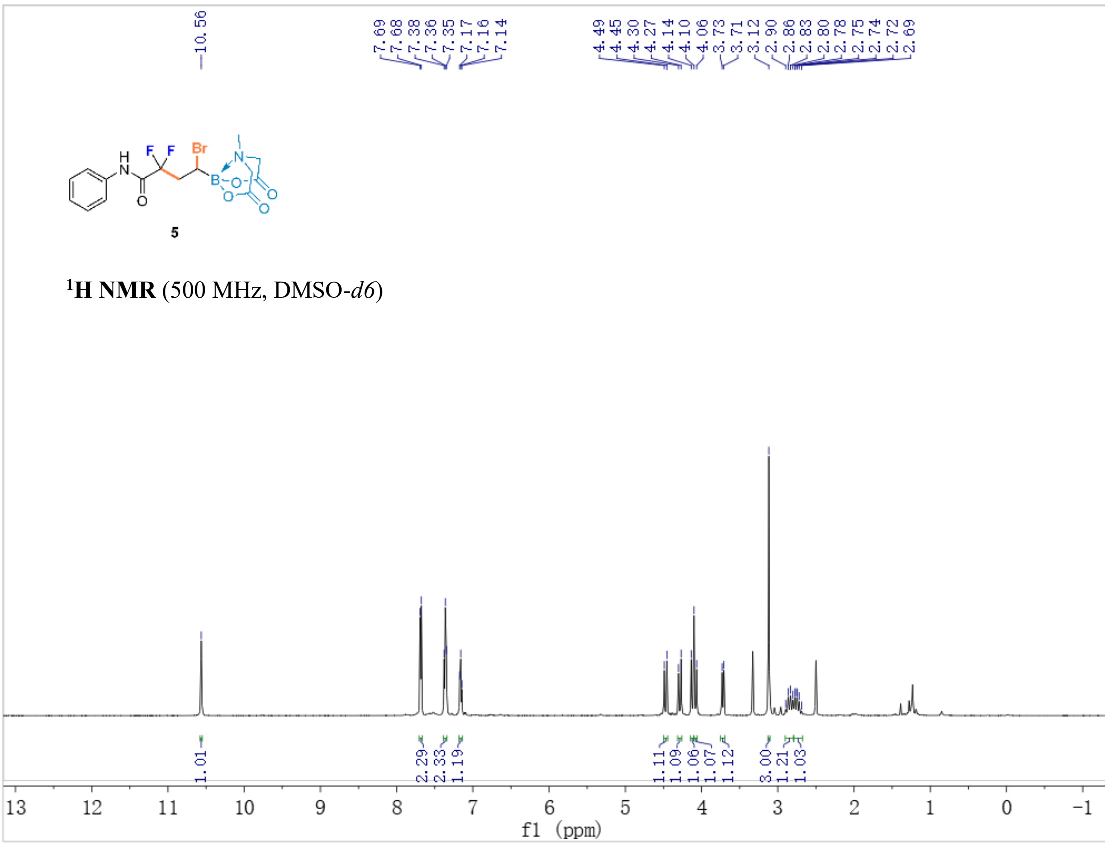
[13]C NMR (151 MHz, DMSO-*d6*)

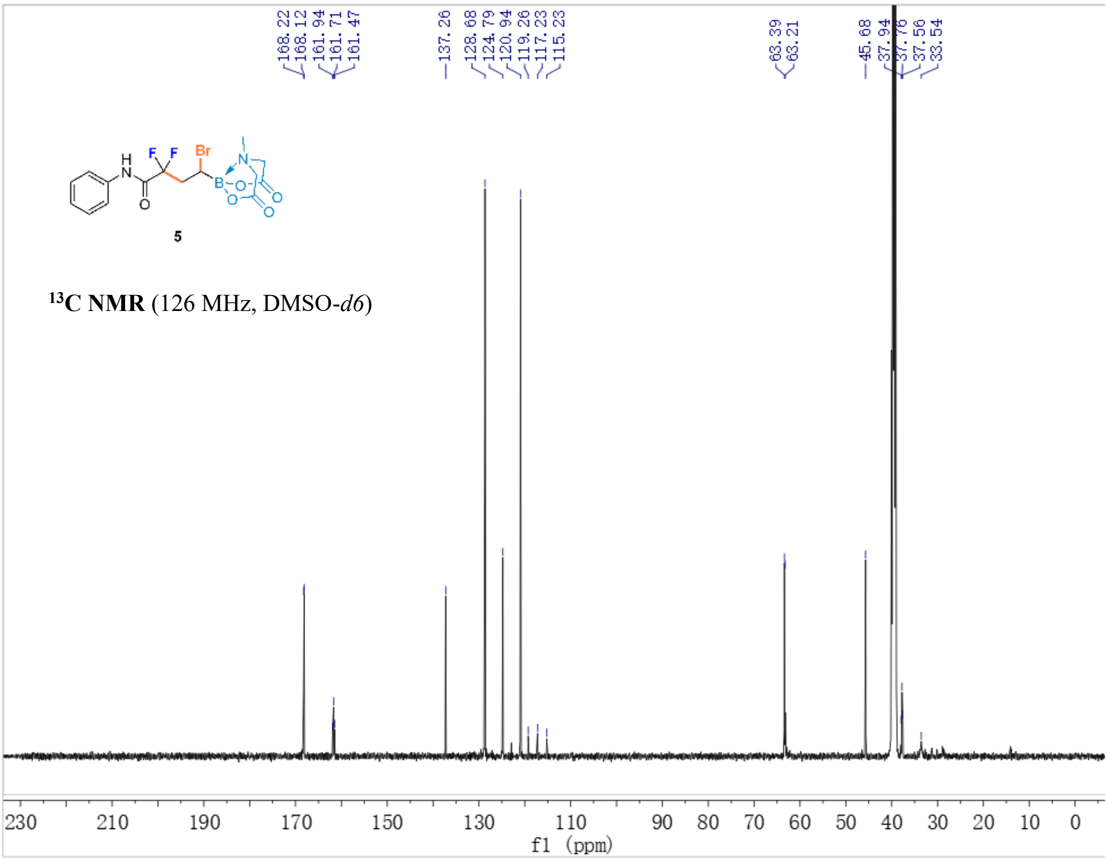


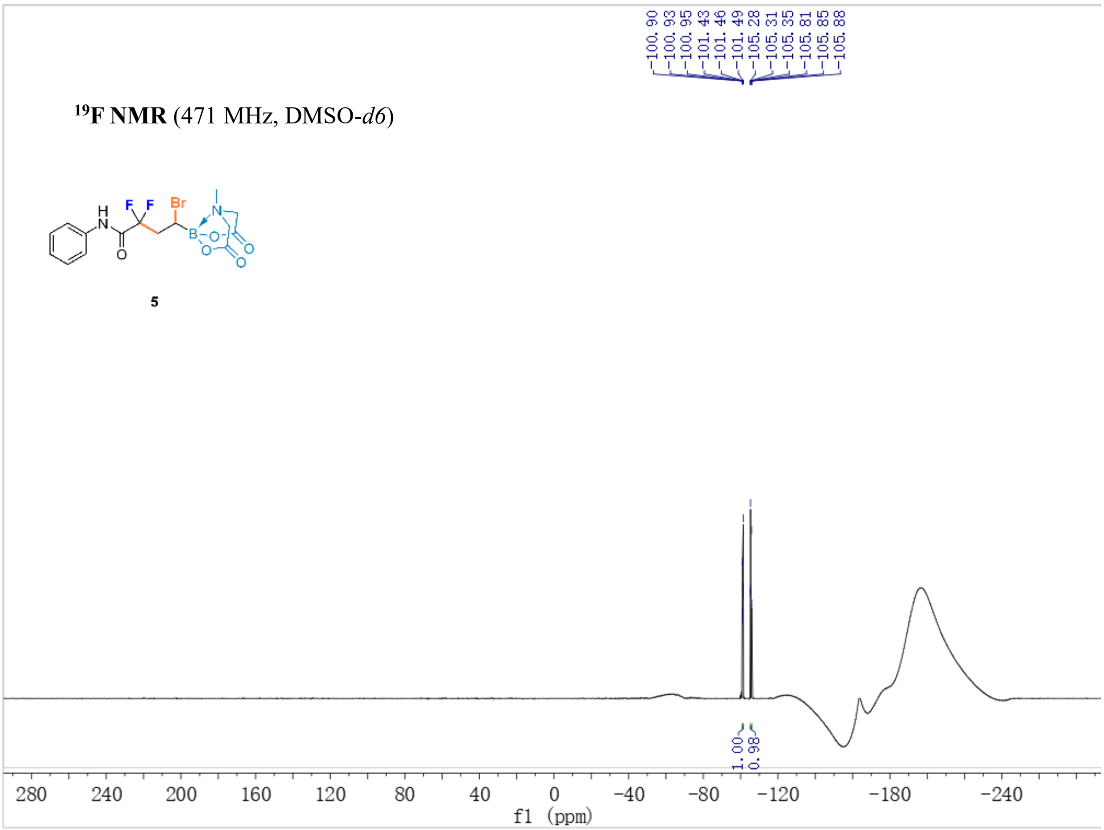
[19]F NMR (471 MHz, DMSO-*d6*)

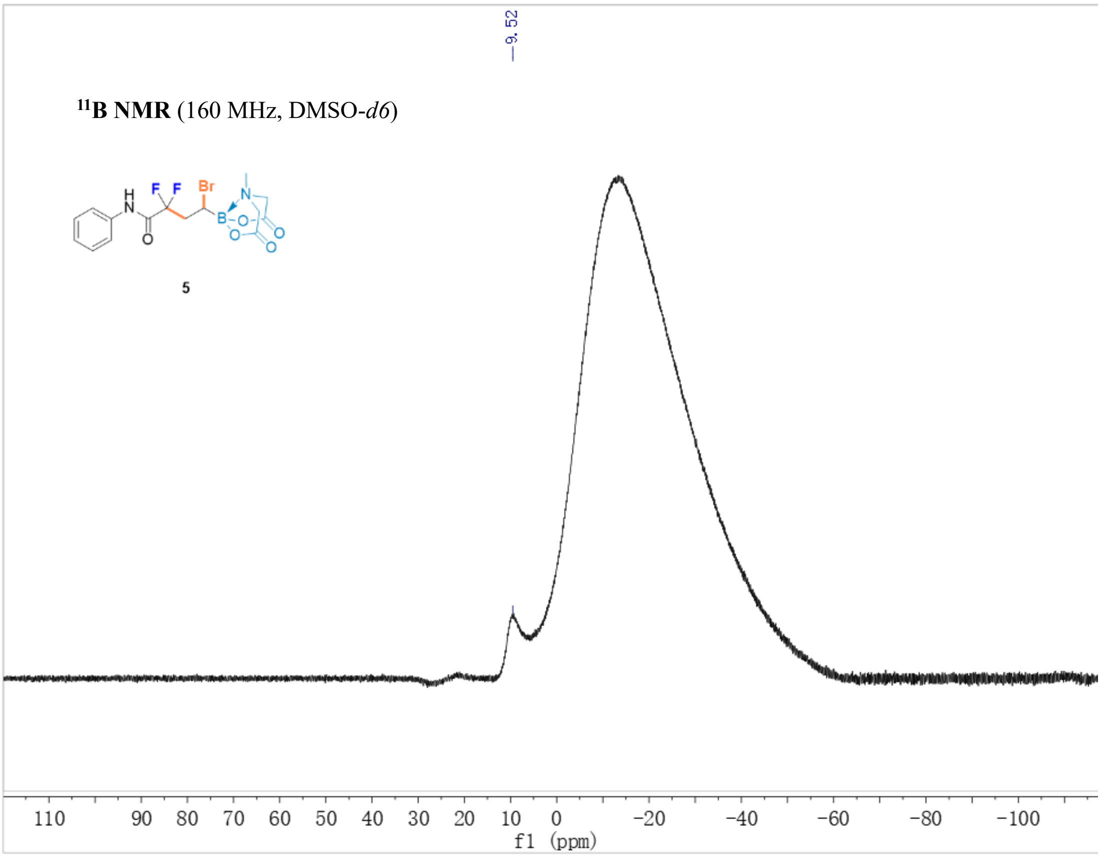


4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-*N*-phenylbutanamide (5)

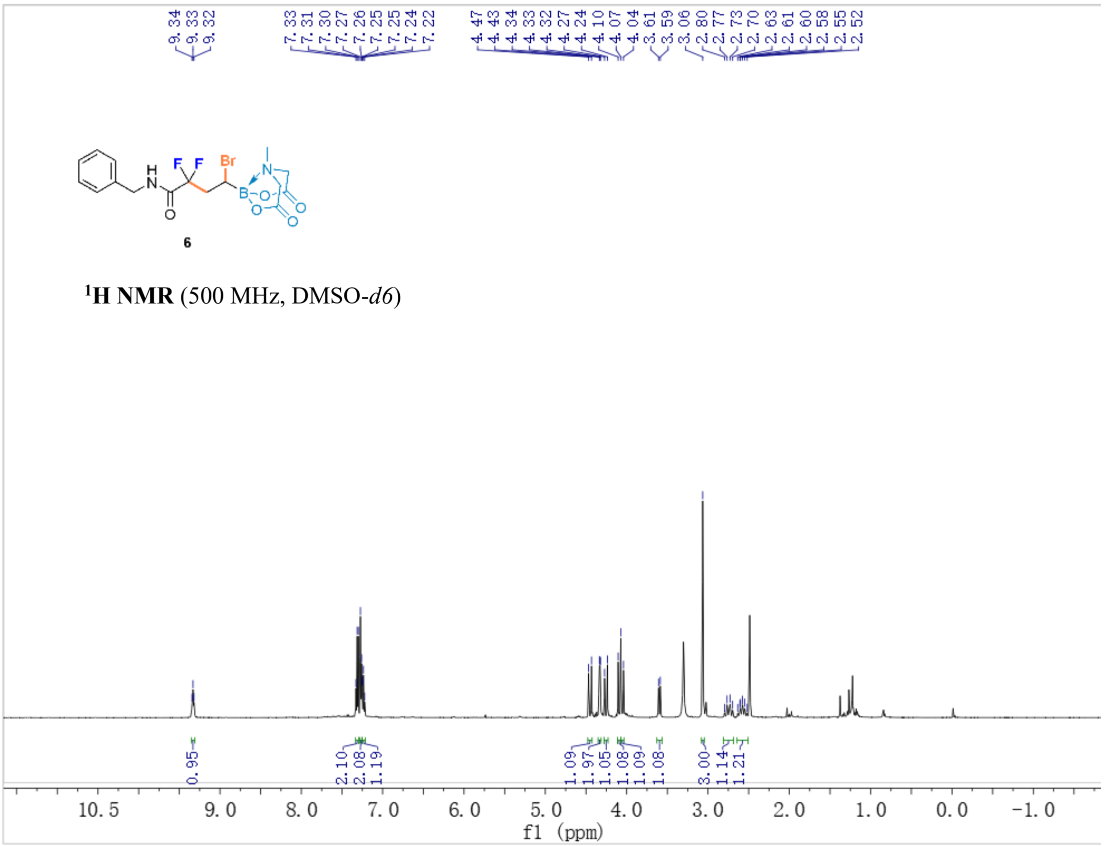


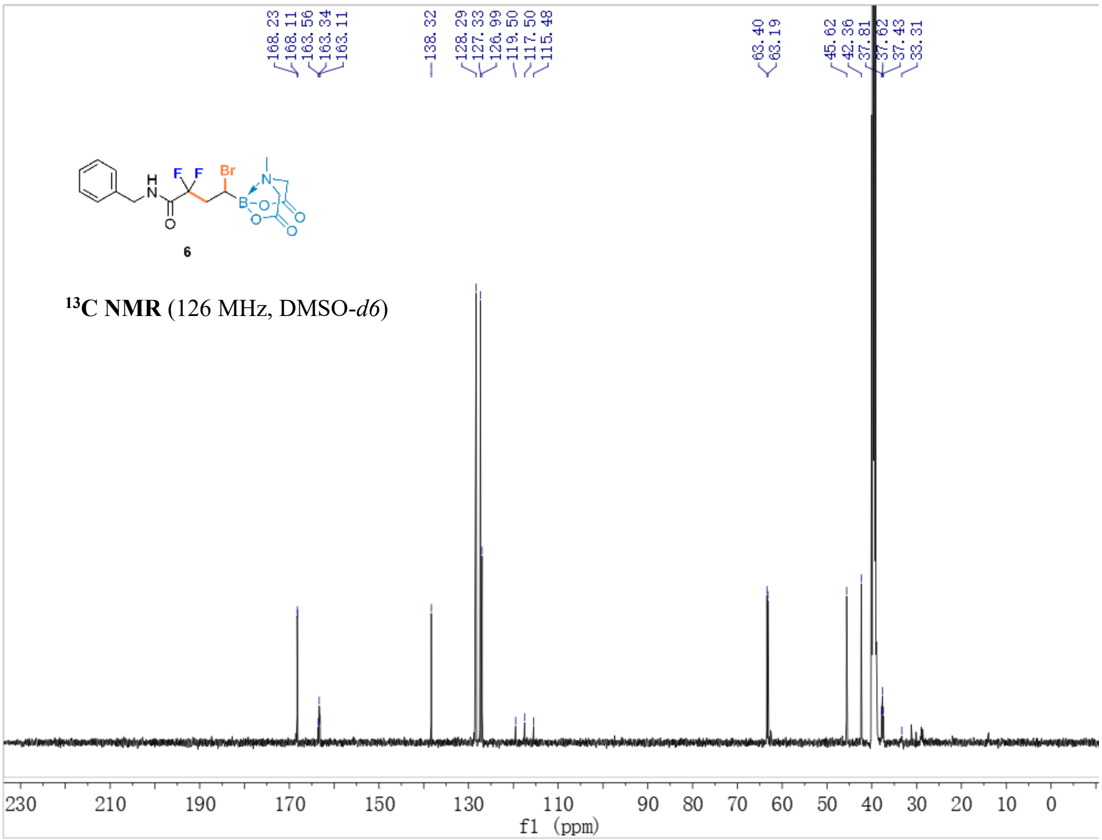

168.22
168.12
161.94
161.71
161.47
137.26
128.68
124.79
120.94
119.26
117.23
115.23
63.39
63.21
45.68
37.94
37.76
37.56
33.54
5
^{13}C NMR (126 MHz, DMSO-d6)
f1 (ppm)

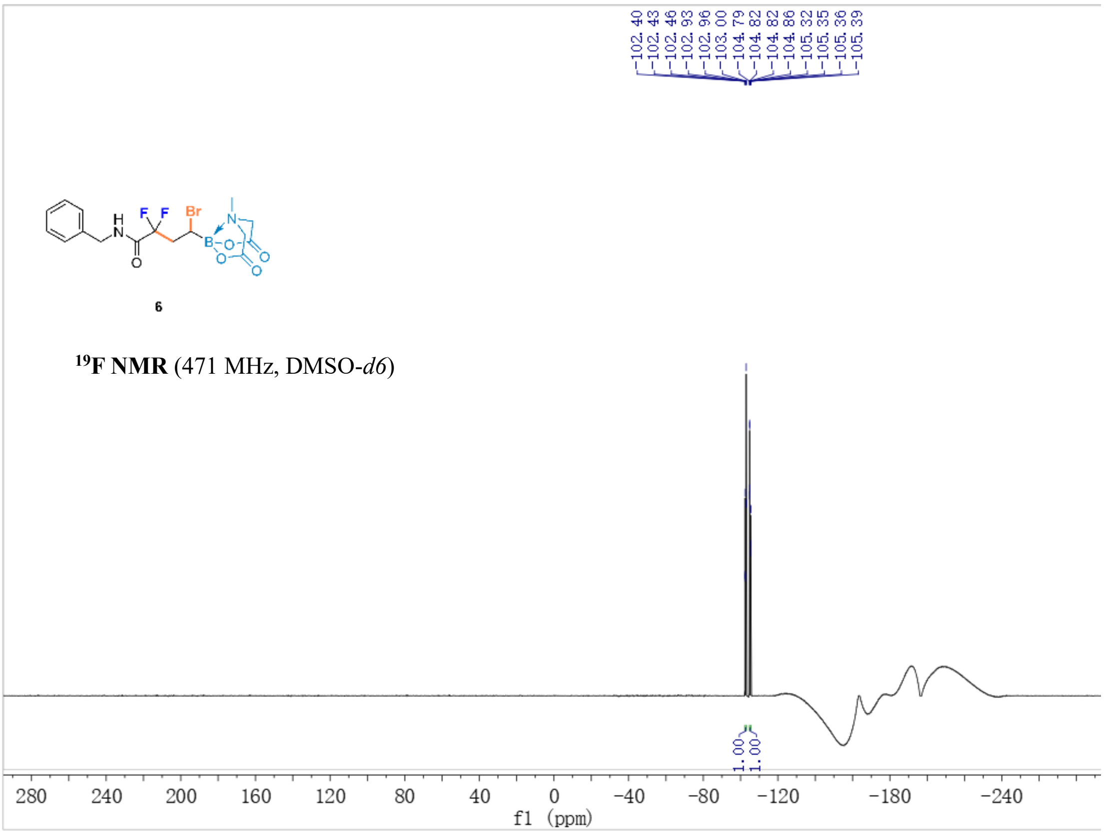

-100.90
-100.93
-100.95
-101.43
-101.46
-101.49
-105.28
-105.31
-105.35
-105.81
-105.85
-105.88
^{19}F NMR (471 MHz, DMSO-d6)
5
1.00
0.98
f1 (ppm)

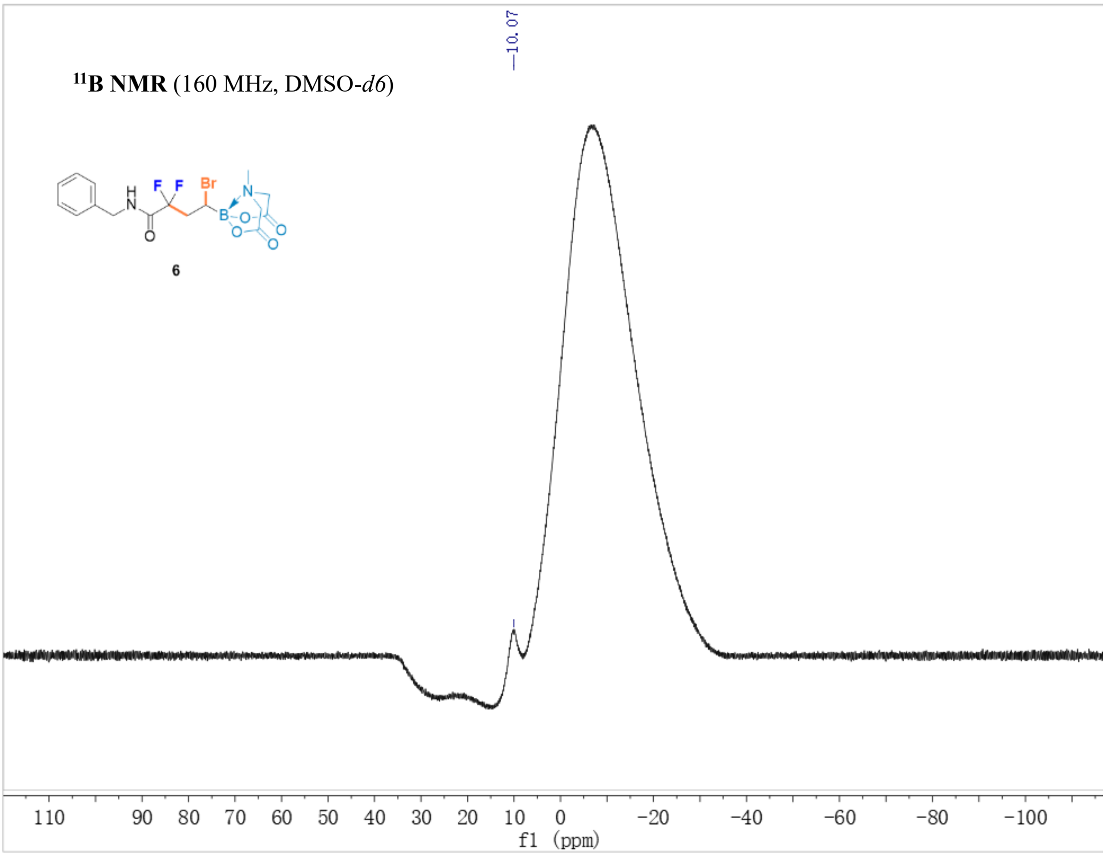


N-benzyl-4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (6)

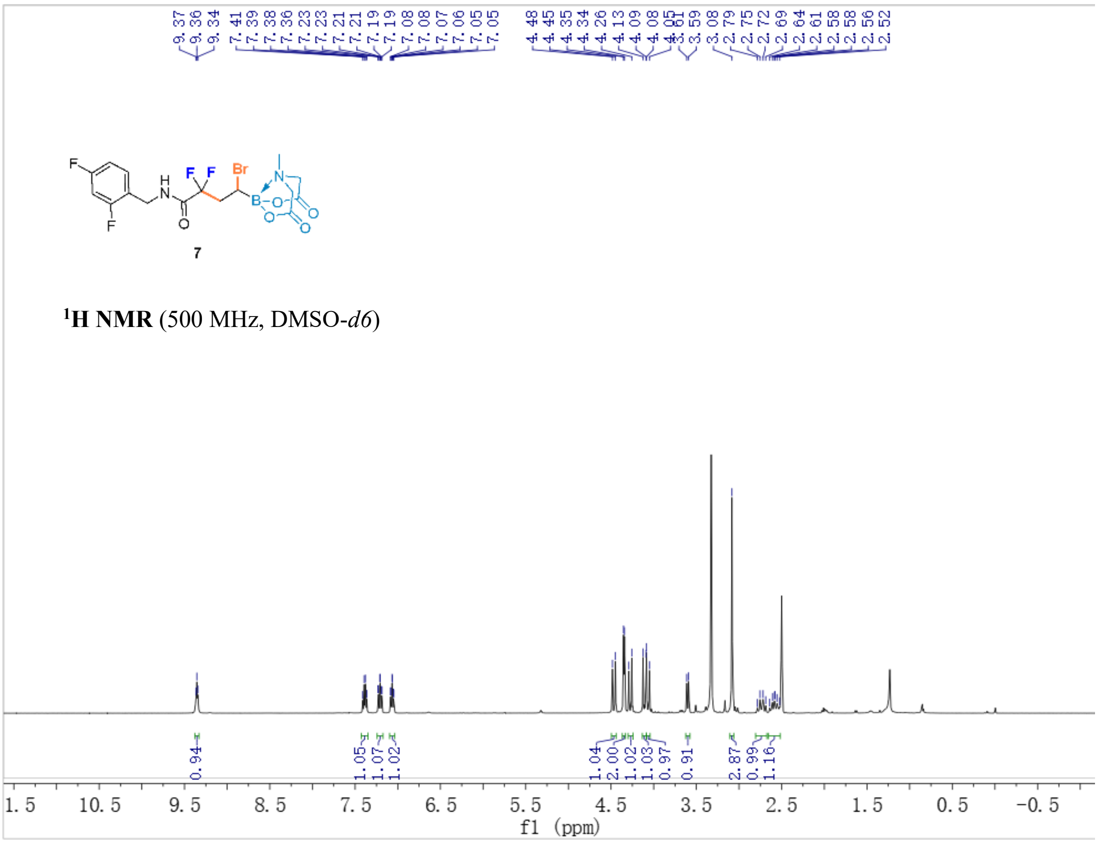


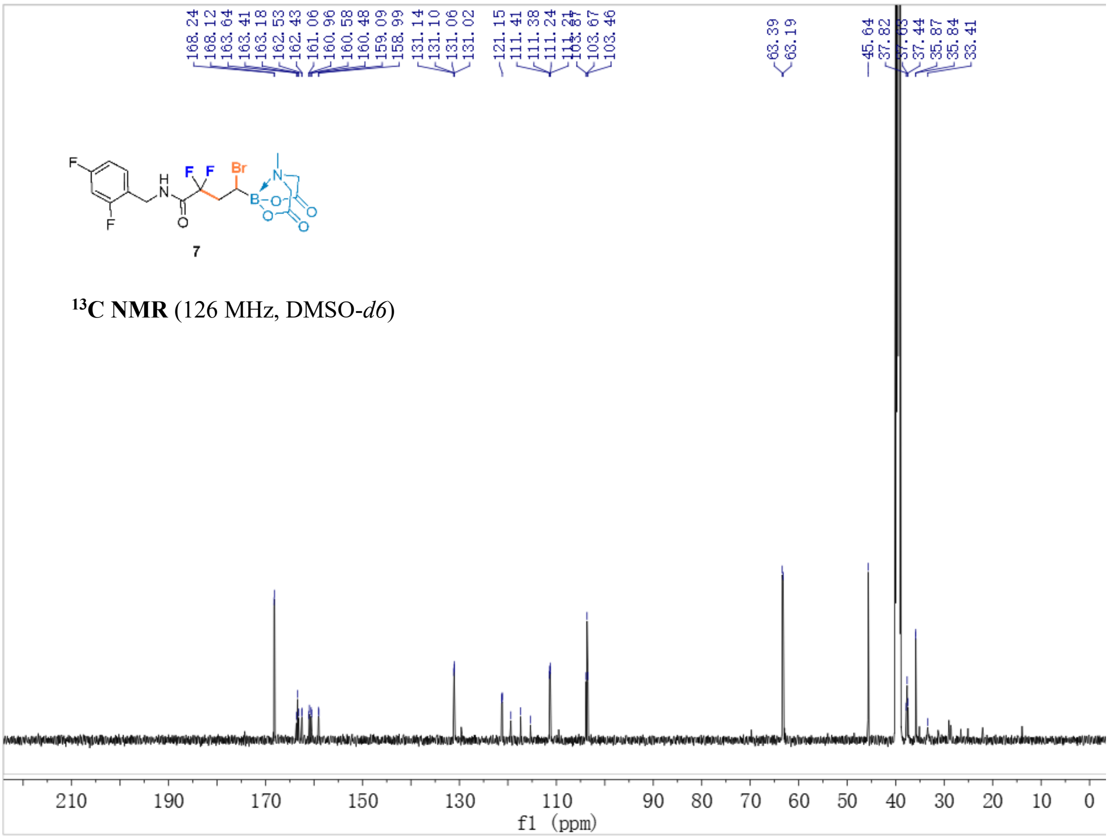

168.23
168.11
163.56
163.34
163.11
138.32
128.29
127.33
126.99
119.50
117.50
115.48
63.40
63.19
45.62
42.36
37.81
37.62
37.43
33.31
6
13C NMR (126 MHz, DMSO-d6)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-102.40
-102.43
-102.46
-102.93
-102.96
-103.00
-104.79
-104.82
-104.82
-104.86
-105.32
-105.35
-105.36
-105.39
6
19F NMR (471 MHz, DMSO-d6)
1.00
1.00
280
240
200
160
120
80
40
0
-40
-80
-120
-180
-240
f1 (ppm)

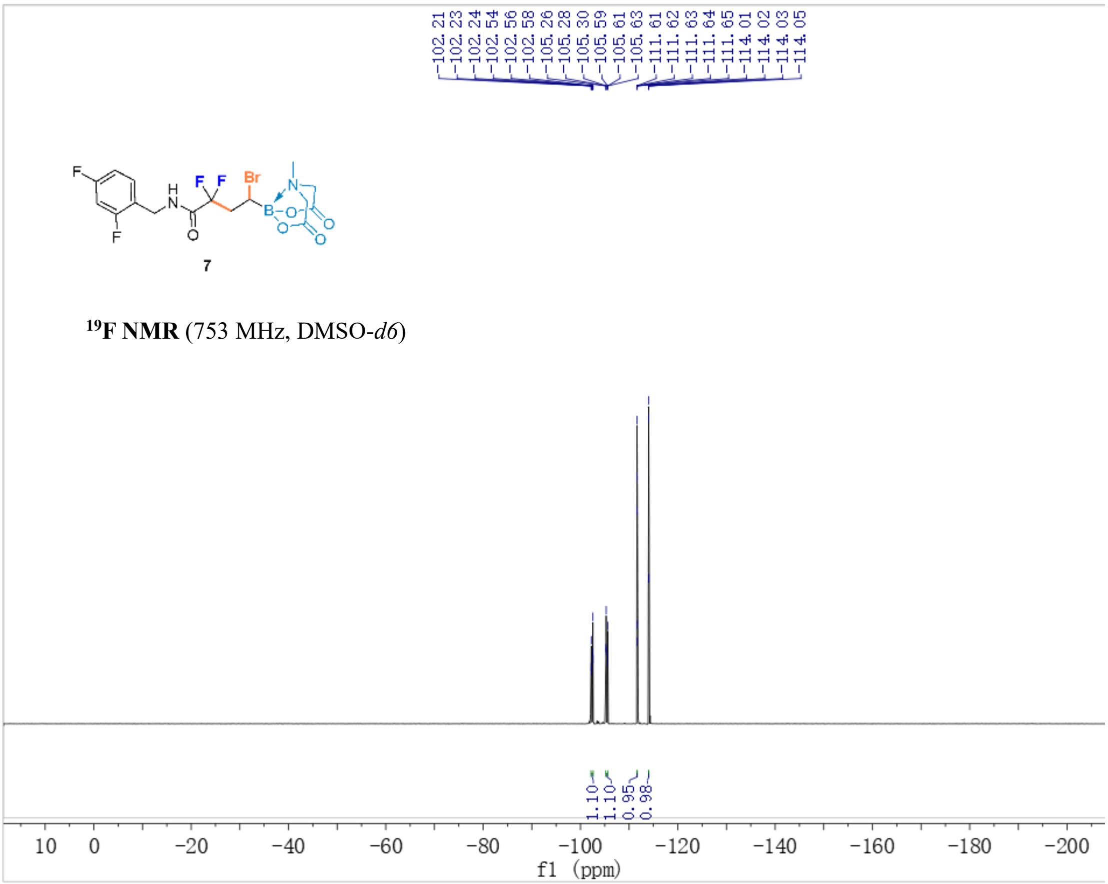


4-bromo-*N*-(2,4-difluorobenzyl)-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (7)

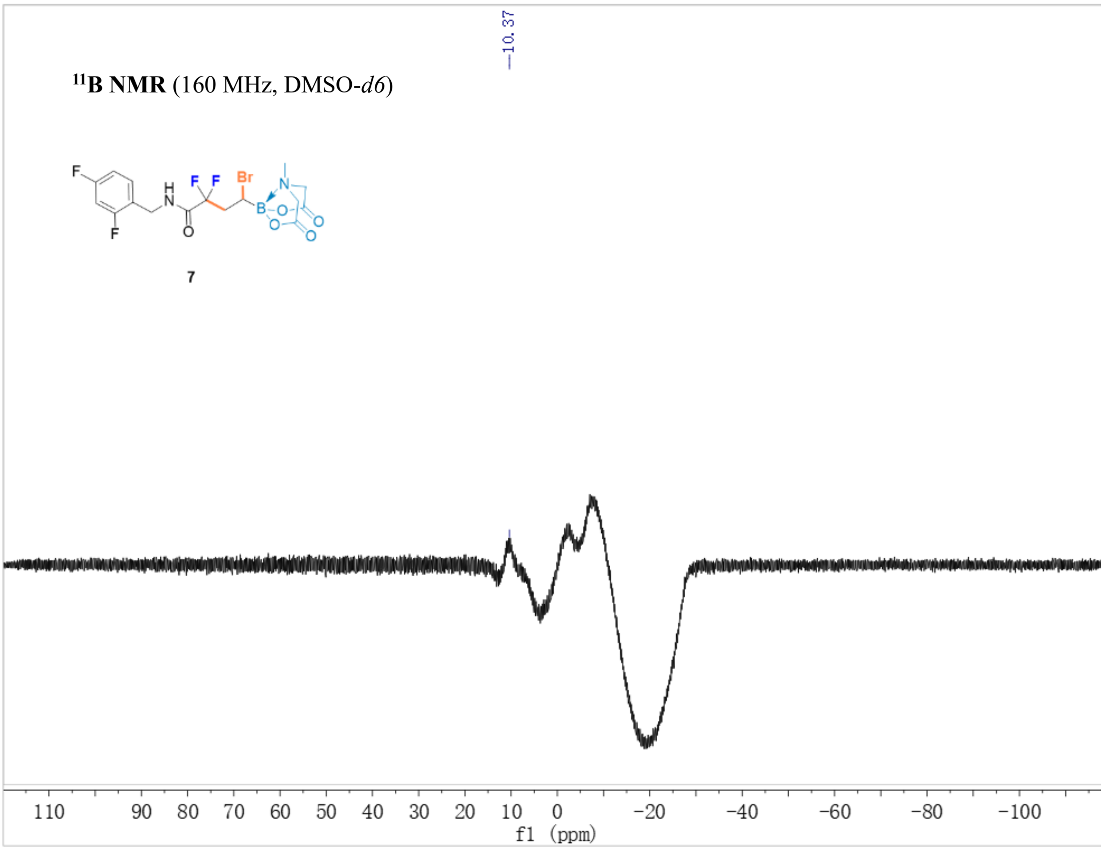




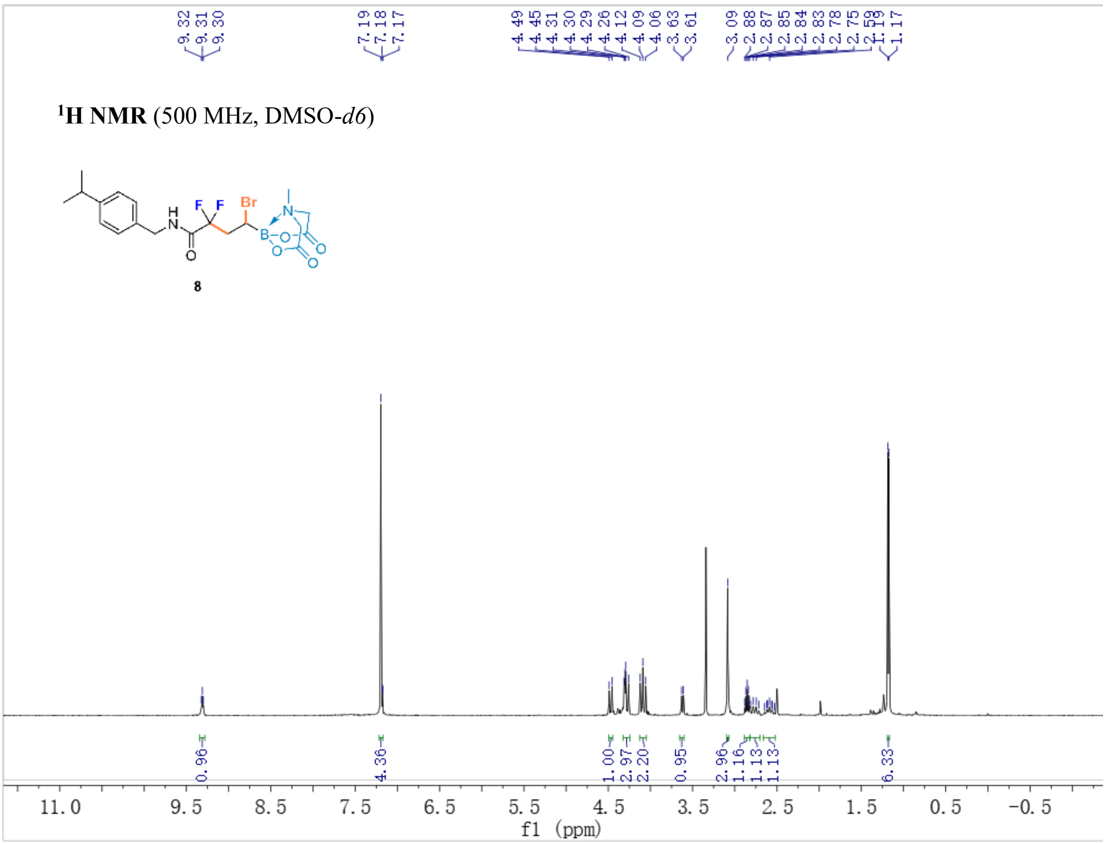
^{13}C NMR (126 MHz, DMSO-*d6*)

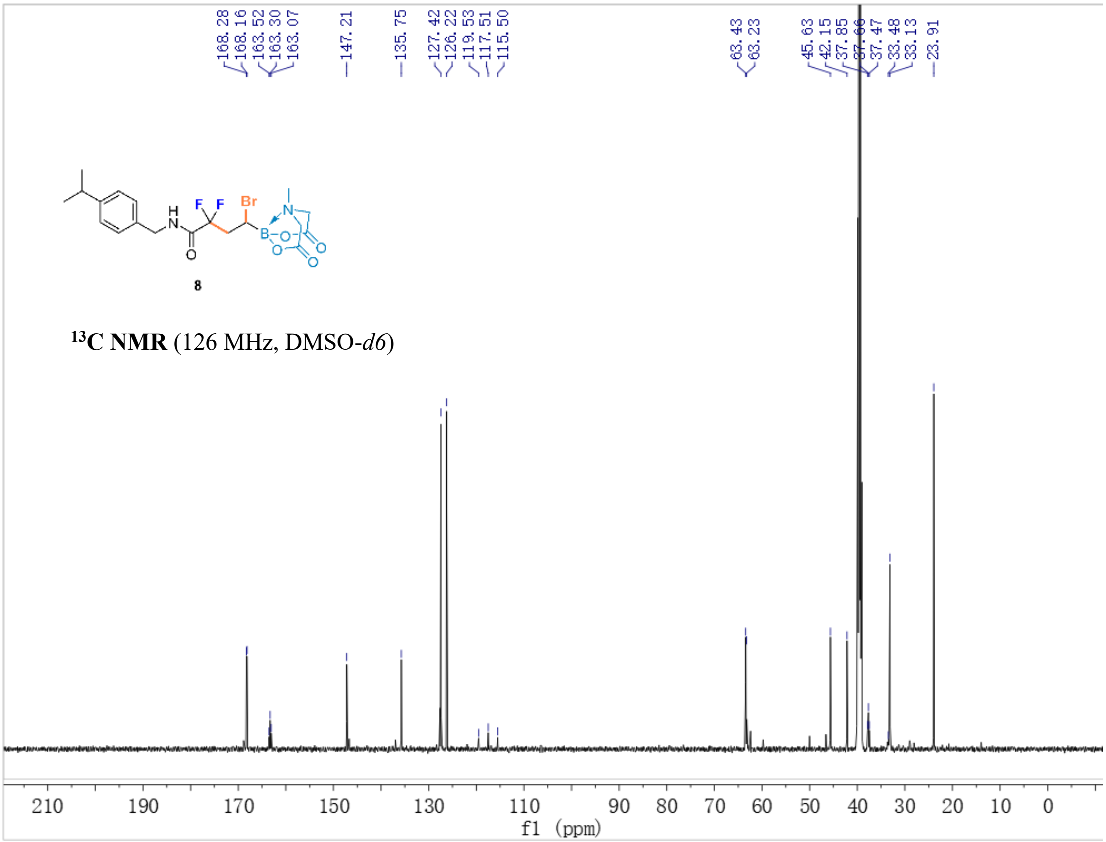


^{19}F NMR (753 MHz, DMSO-*d6*)



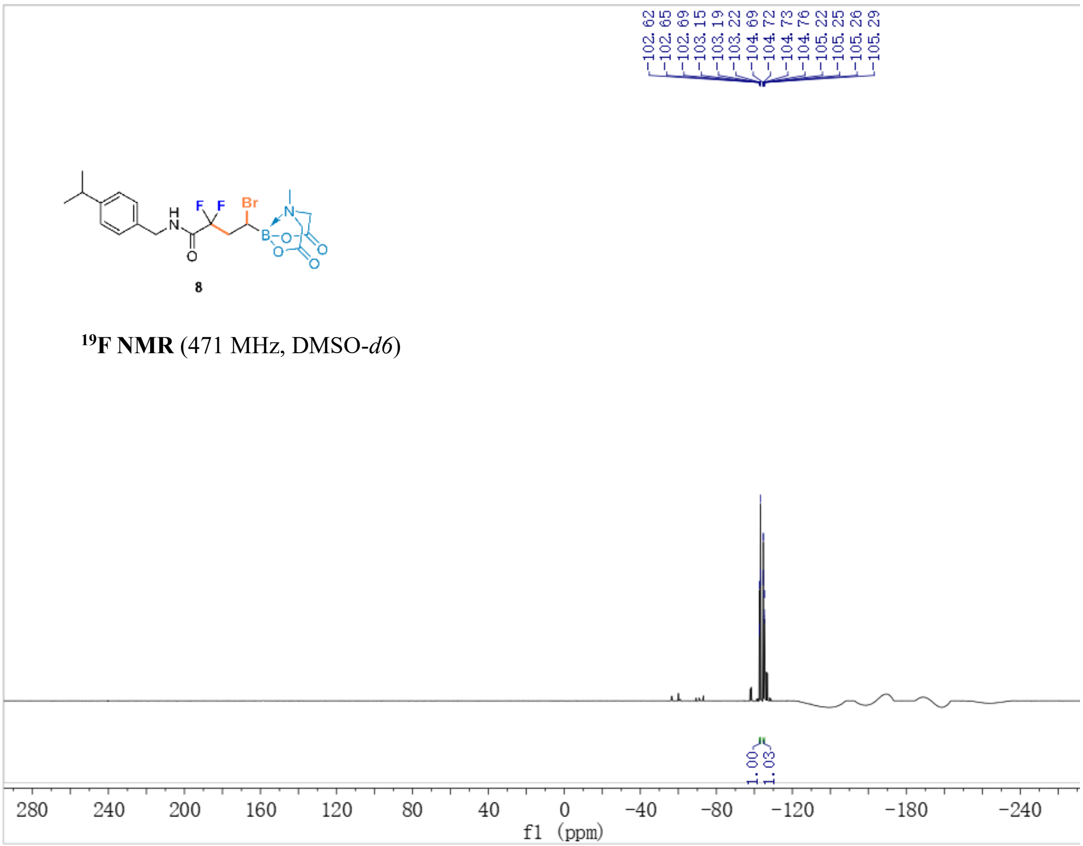
4-bromo-2,2-difluoro-*N*-(4-isopropylbenzyl)-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (8)





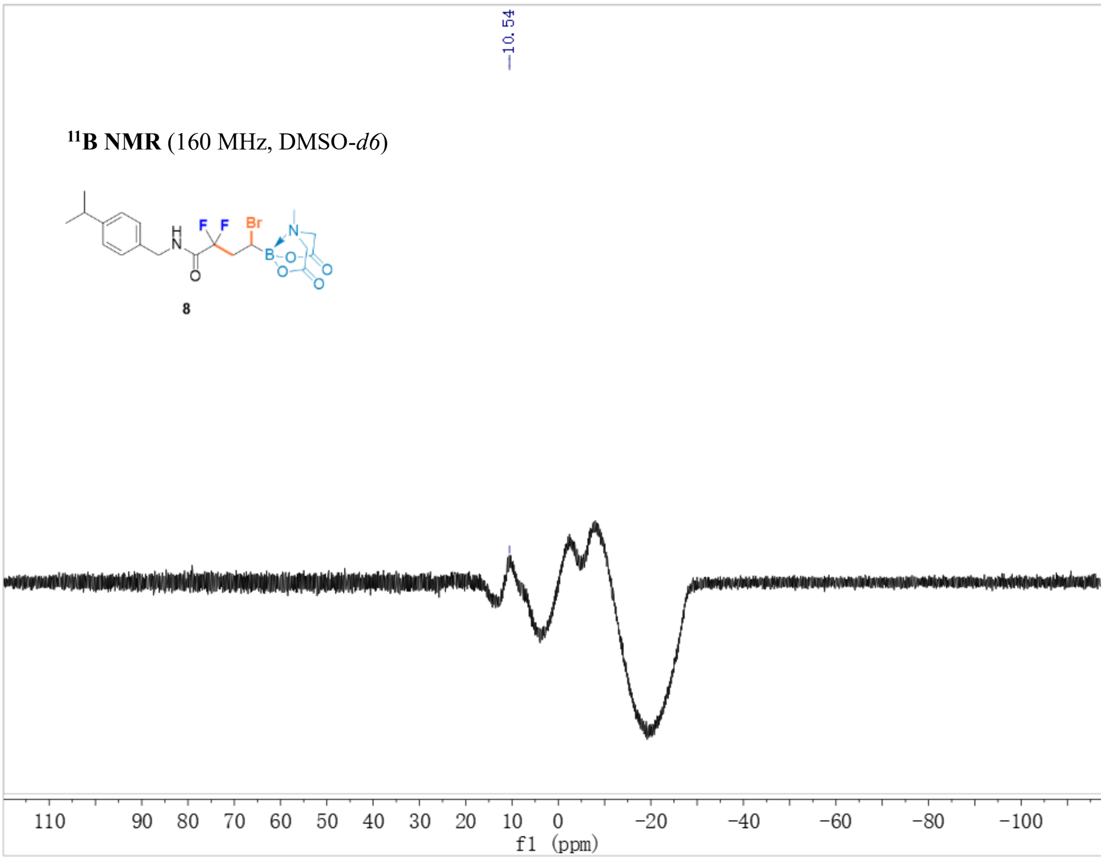
8

^{13}C NMR (126 MHz, DMSO-*d6*)

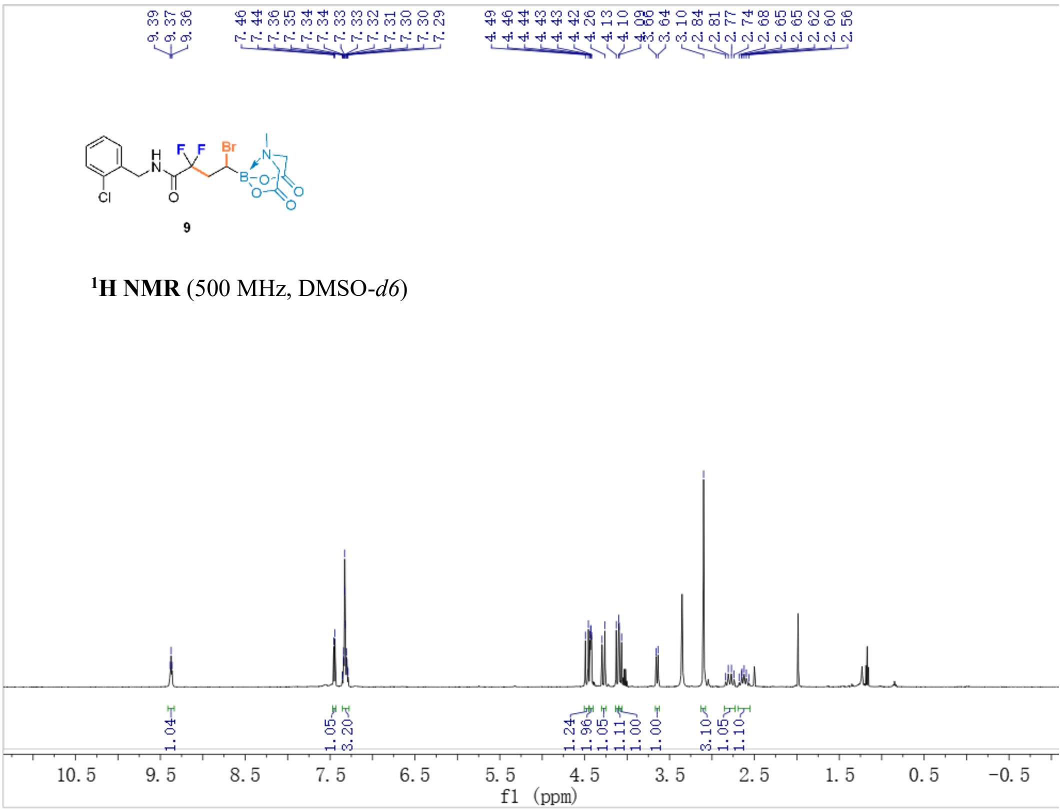


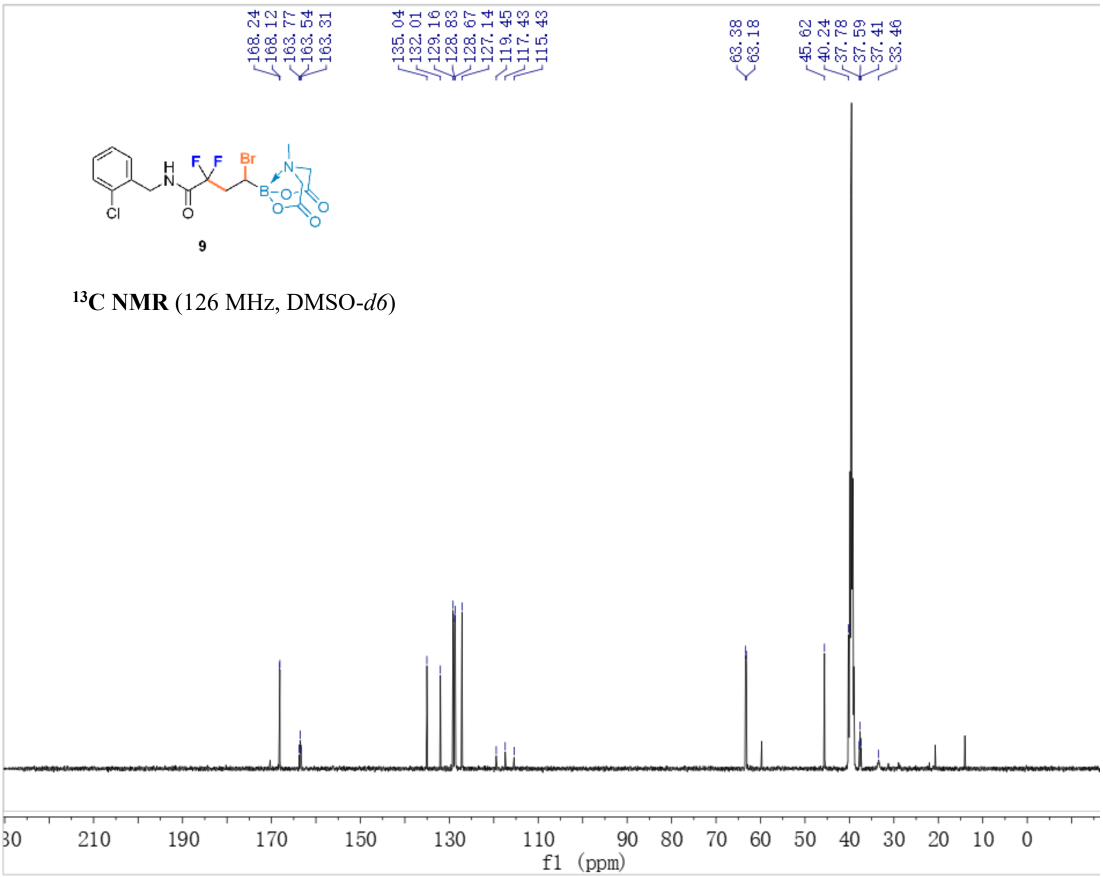
8

^{19}F NMR (471 MHz, DMSO-*d6*)



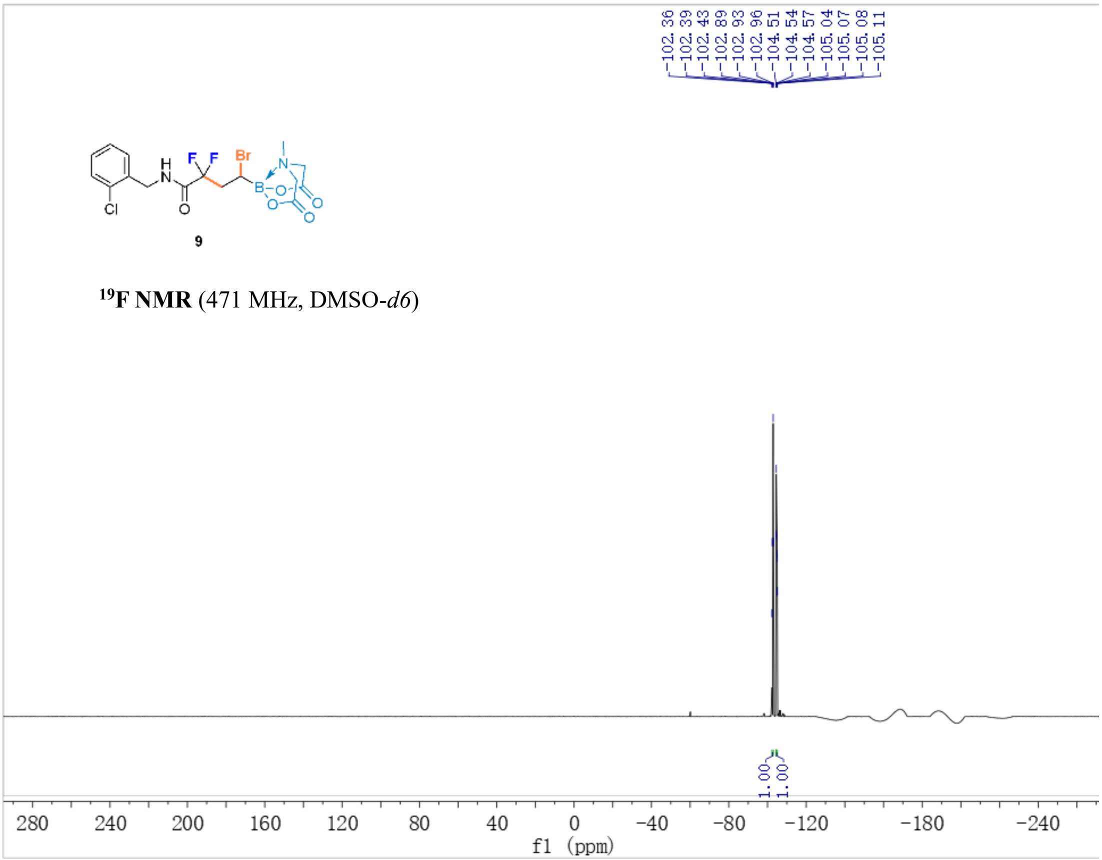
4-bromo-*N*-(2-chlorobenzyl)-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (9)





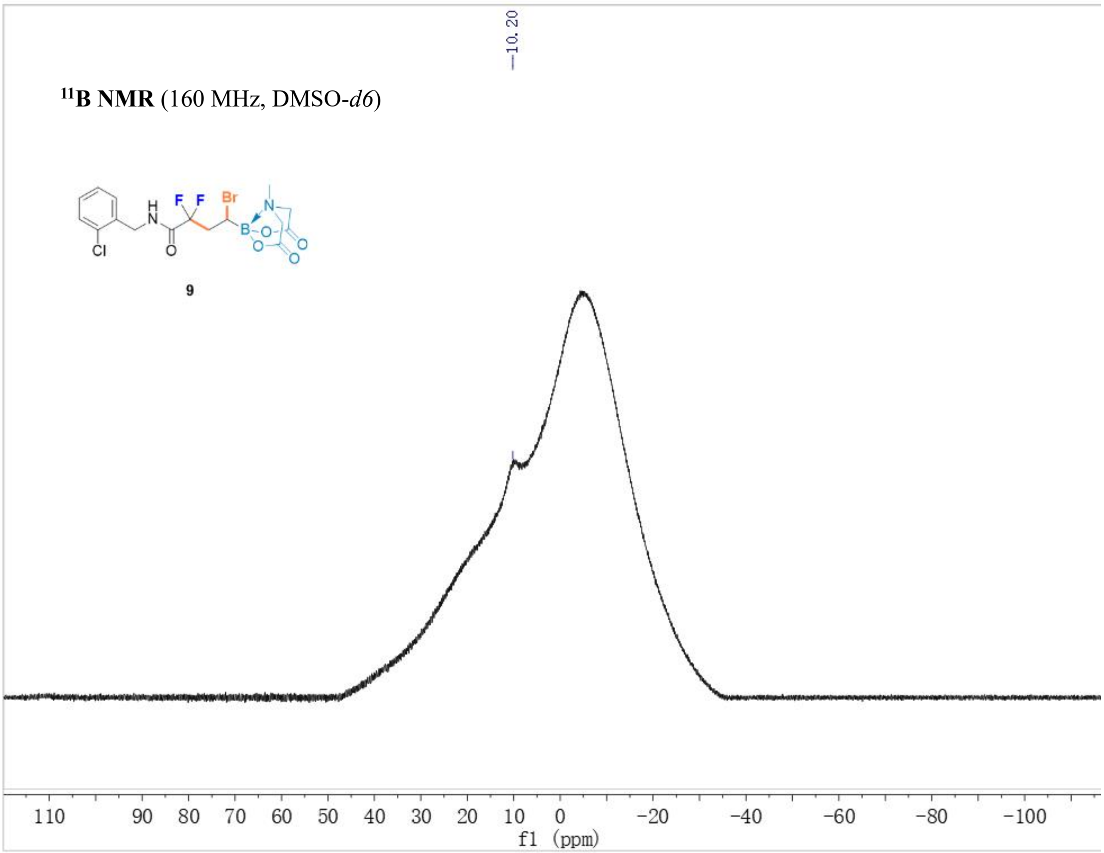
9

^{13}C NMR (126 MHz, DMSO-*d6*)

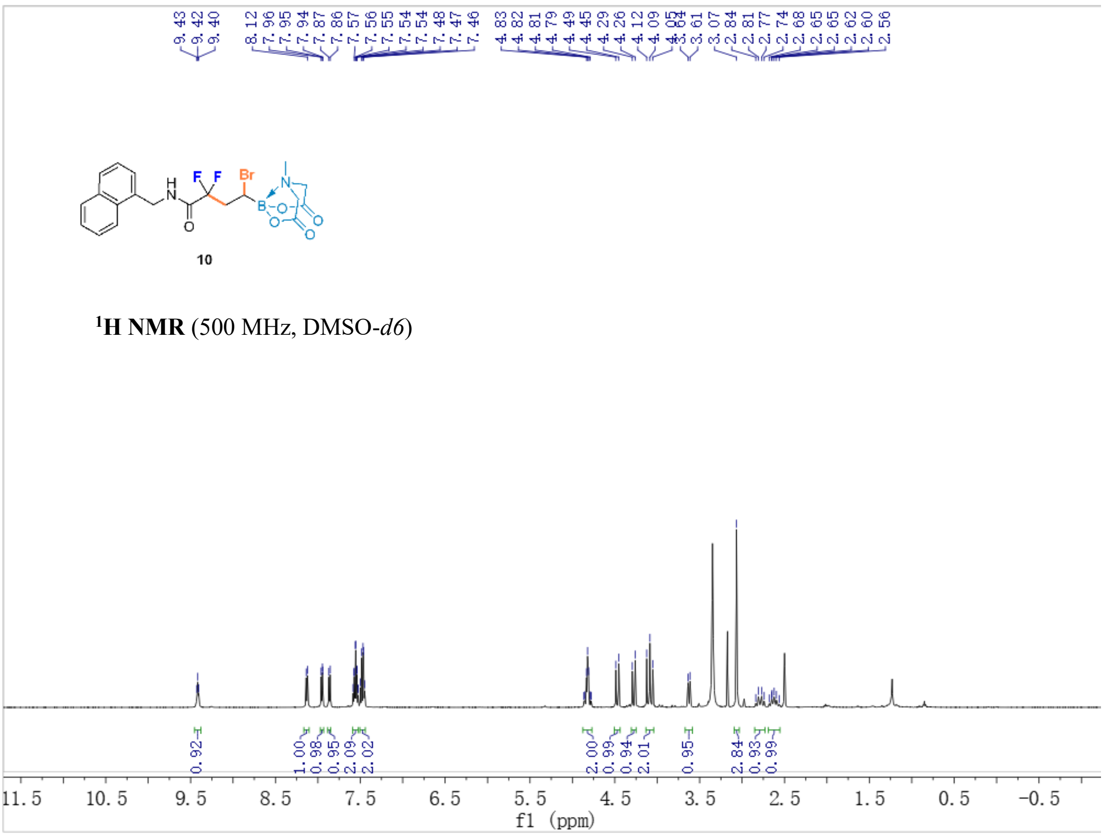


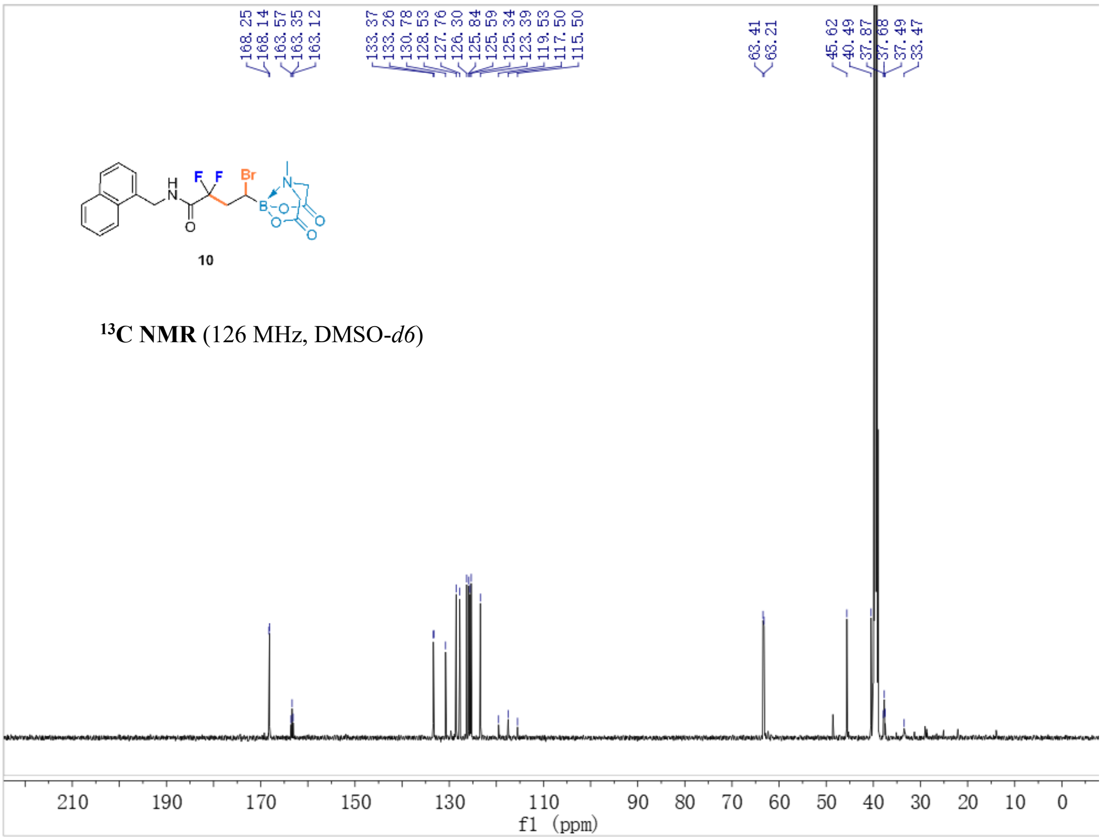
9

^{19}F NMR (471 MHz, DMSO-*d6*)

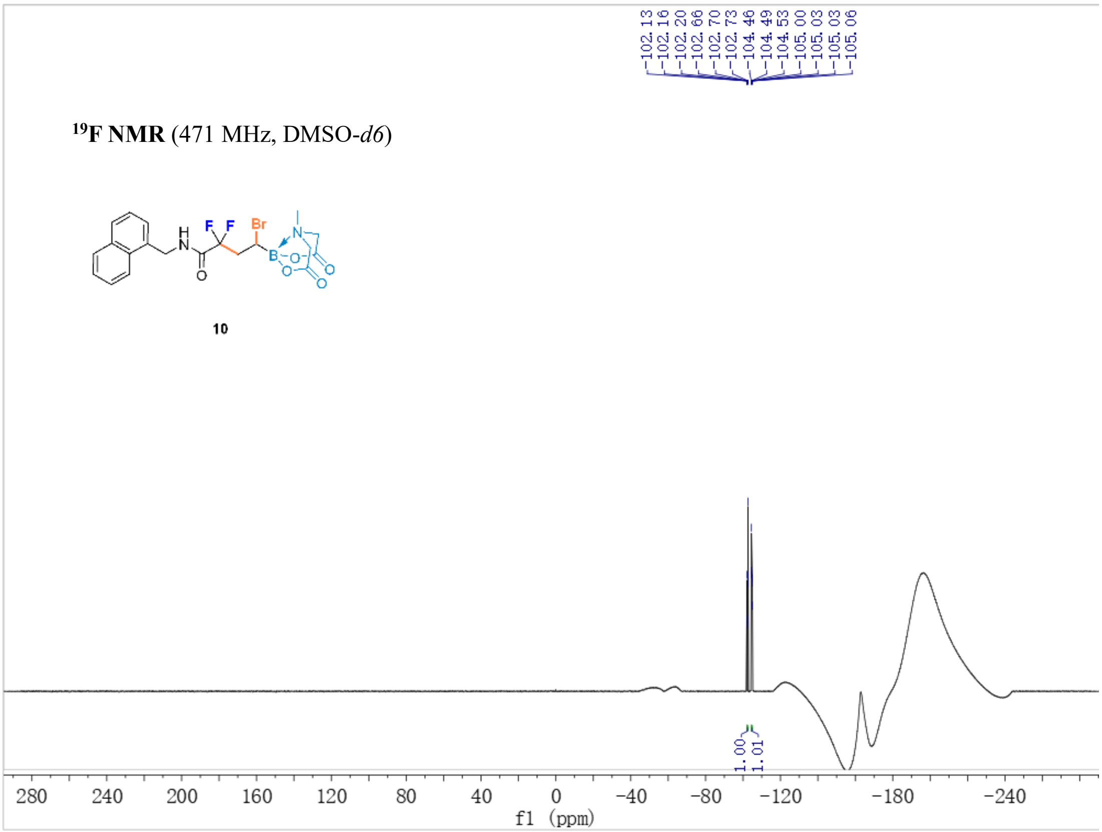


4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-*N*-(naphthalen-1-ylmethyl)butanamide (10)

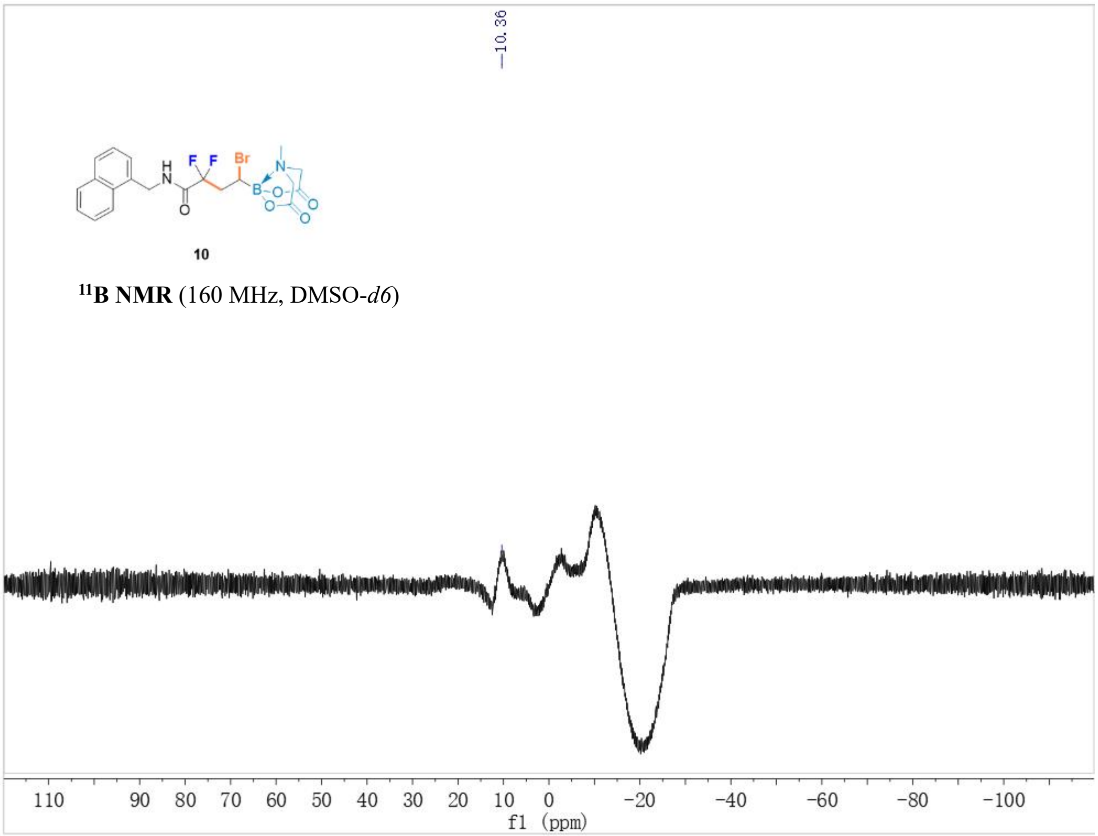




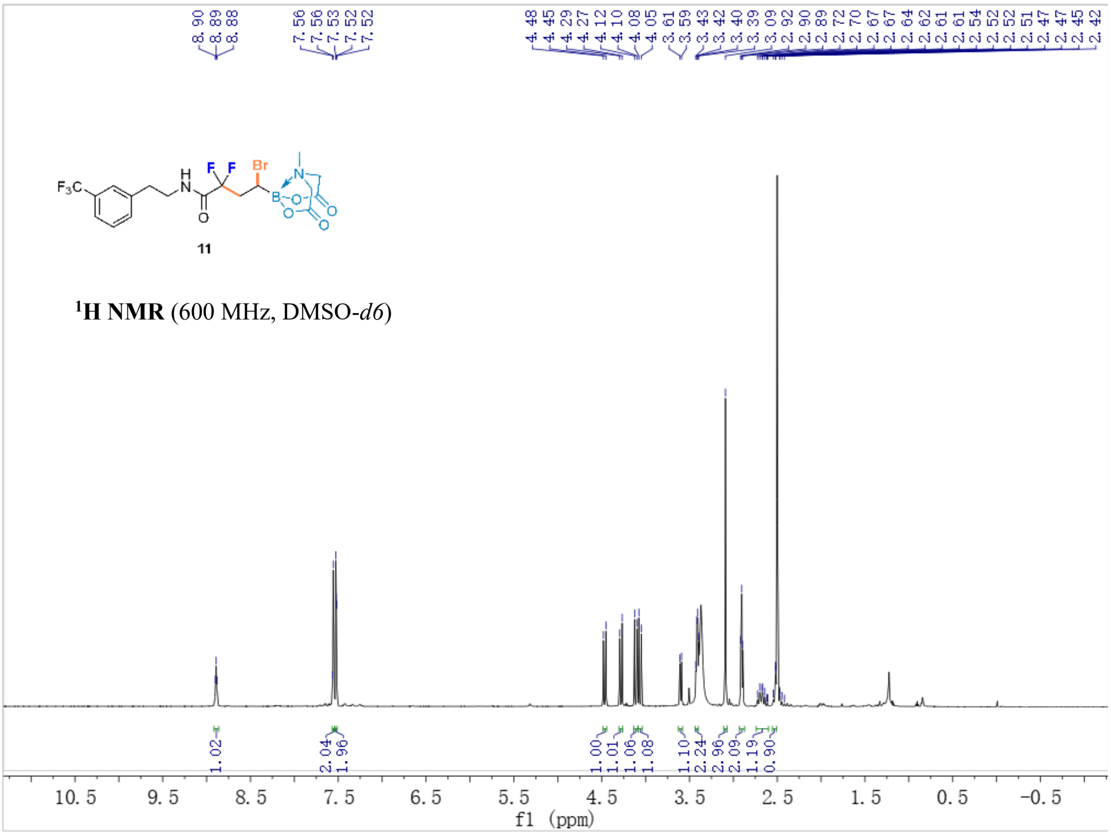
^{13}C NMR (126 MHz, DMSO-*d6*)

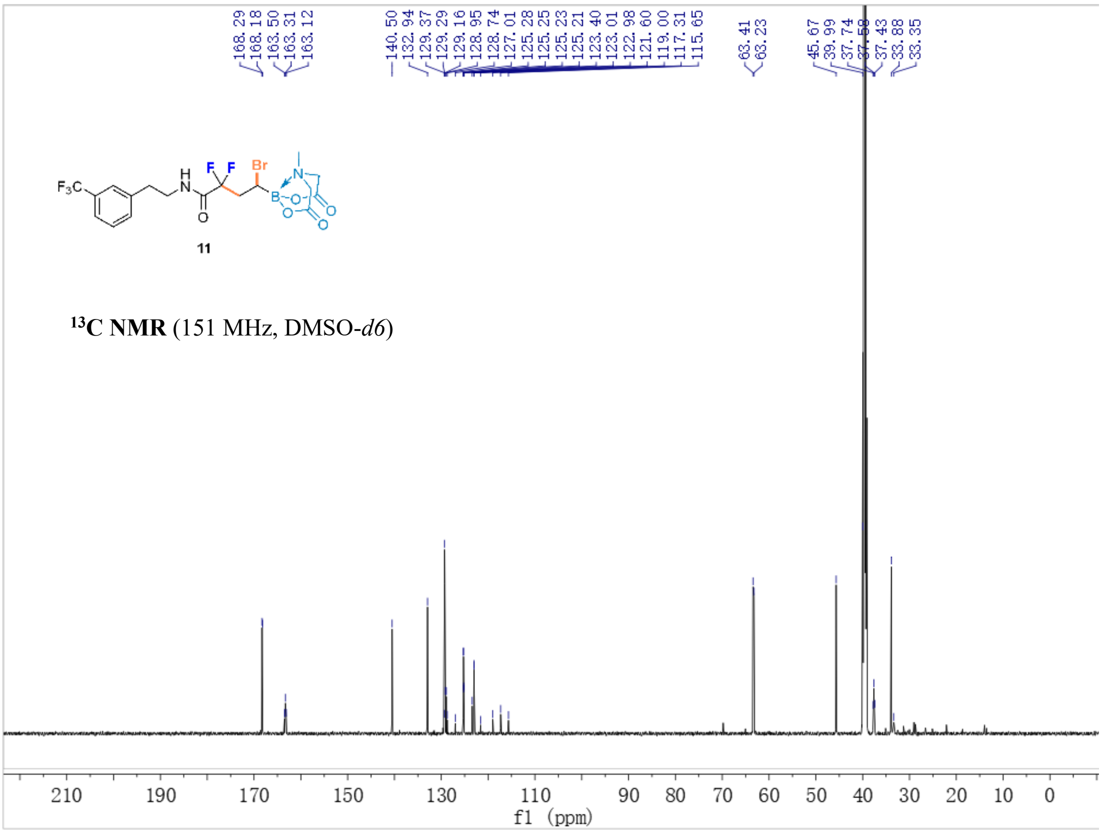


^{19}F NMR (471 MHz, DMSO-*d6*)



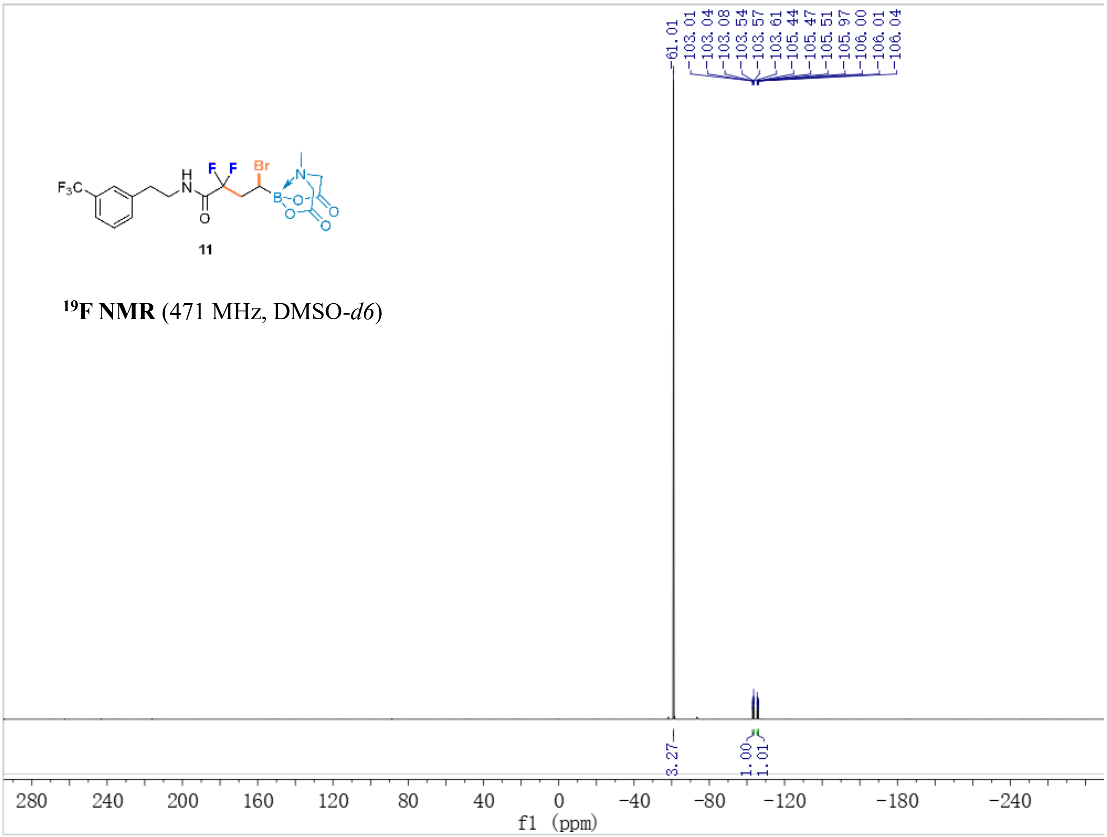
4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-*N*-(3-(trifluoromethyl)phenethyl)butanamide (11)





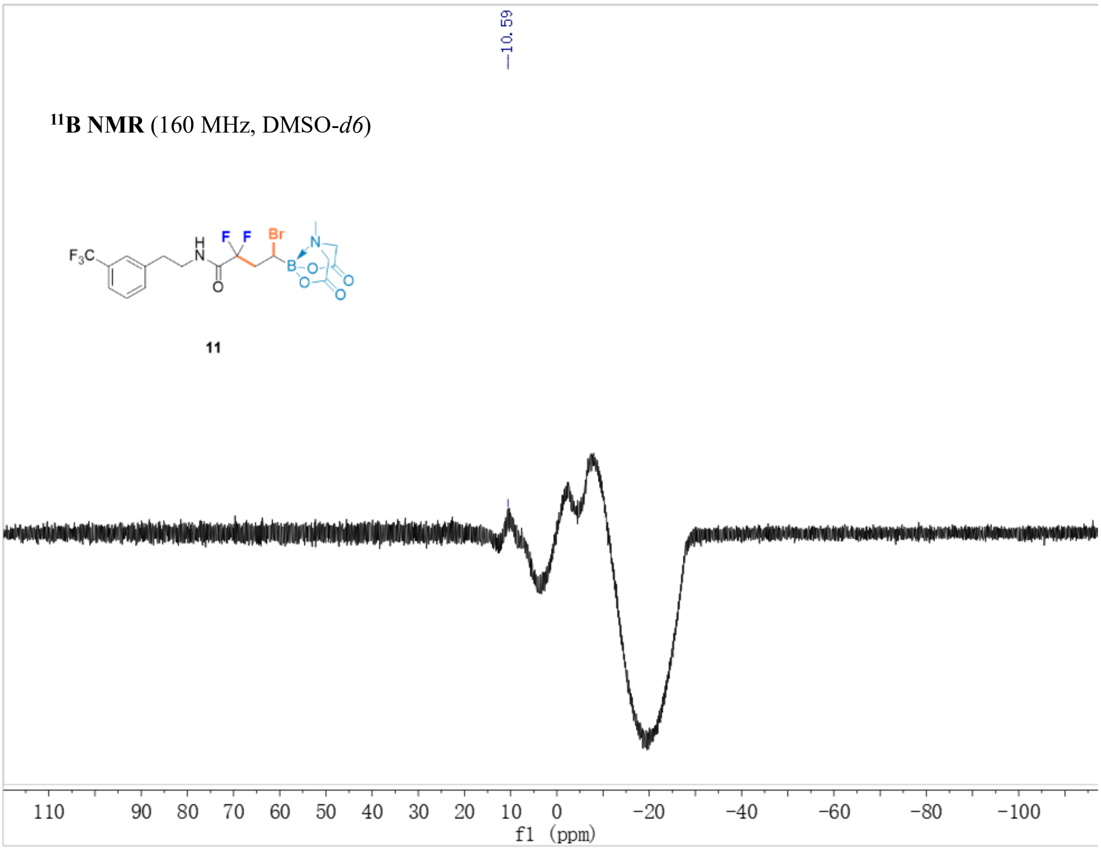
11

^{13}C NMR (151 MHz, DMSO-*d6*)

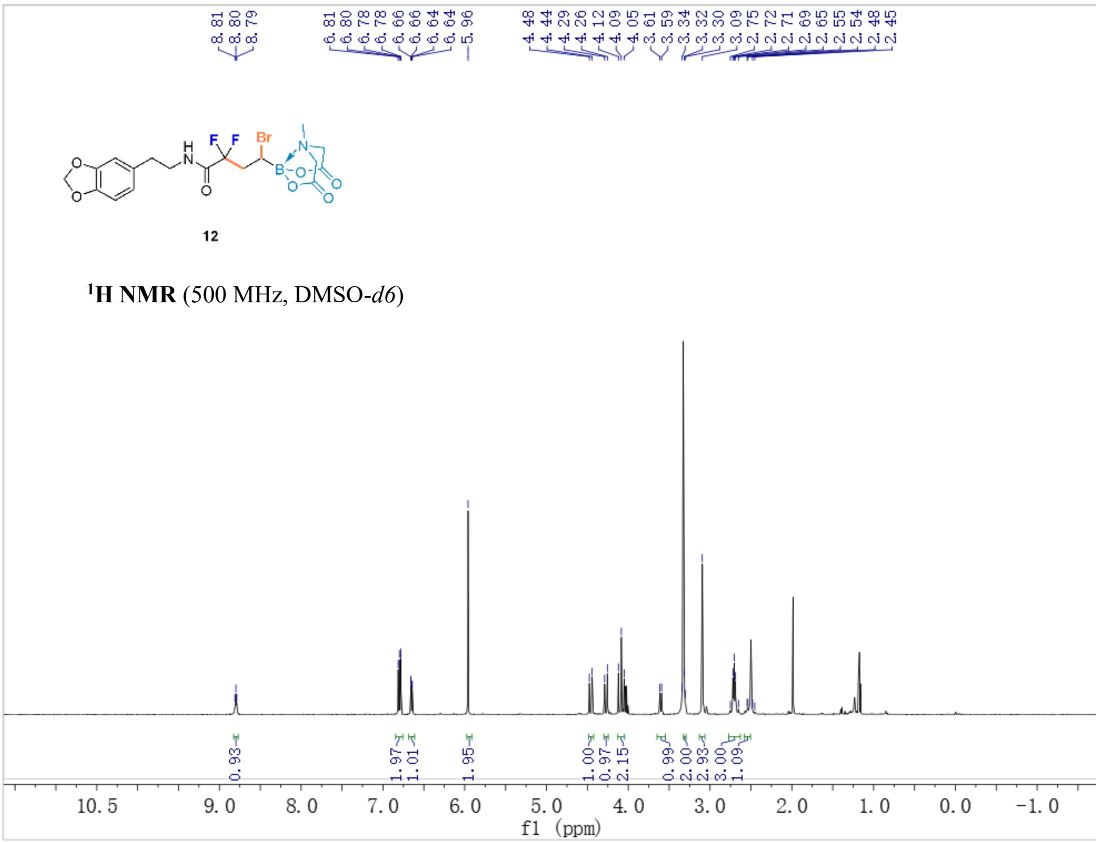


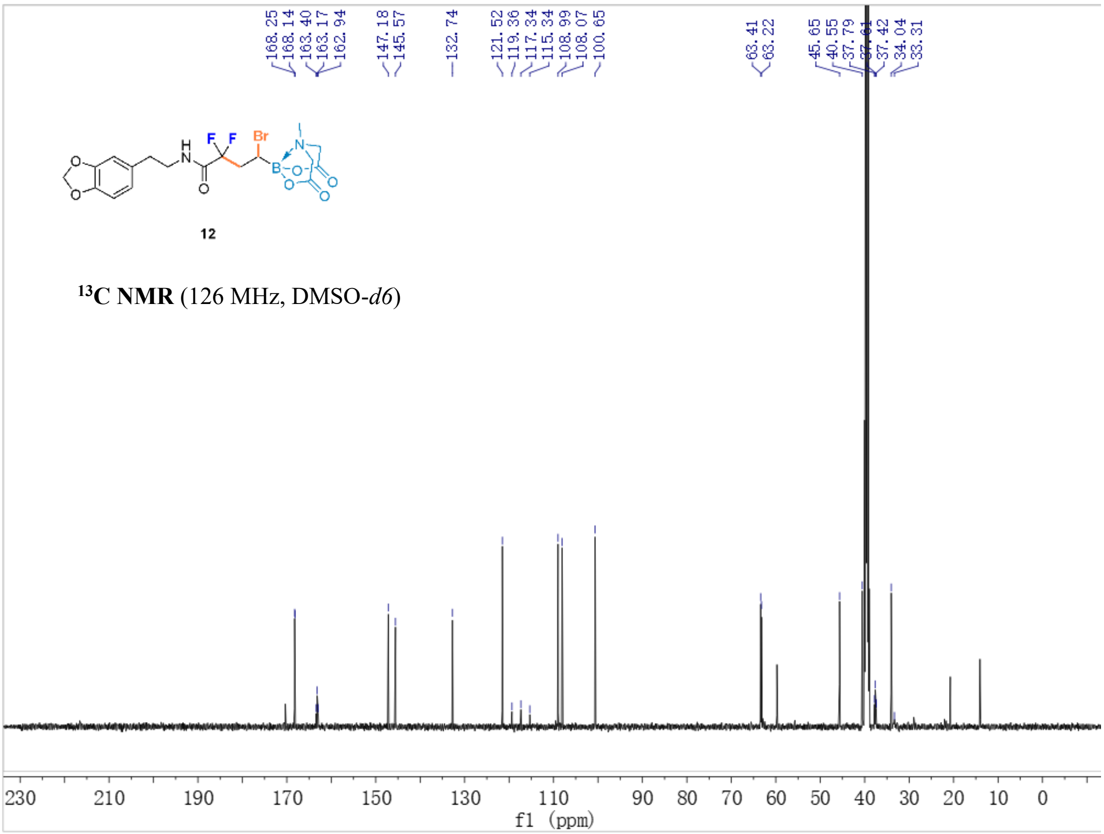
11

^{19}F NMR (471 MHz, DMSO-*d6*)

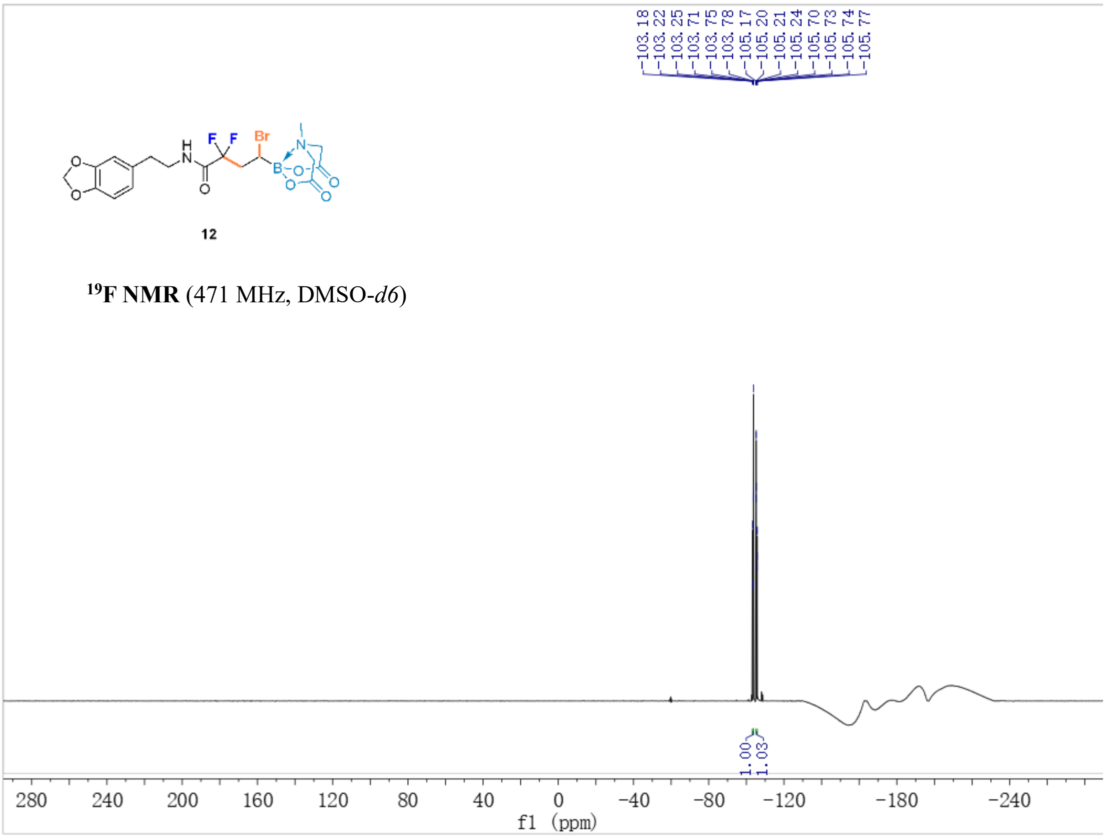


N-(2-(benzo[d][1,3]dioxol-5-yl)ethyl)-4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (12)

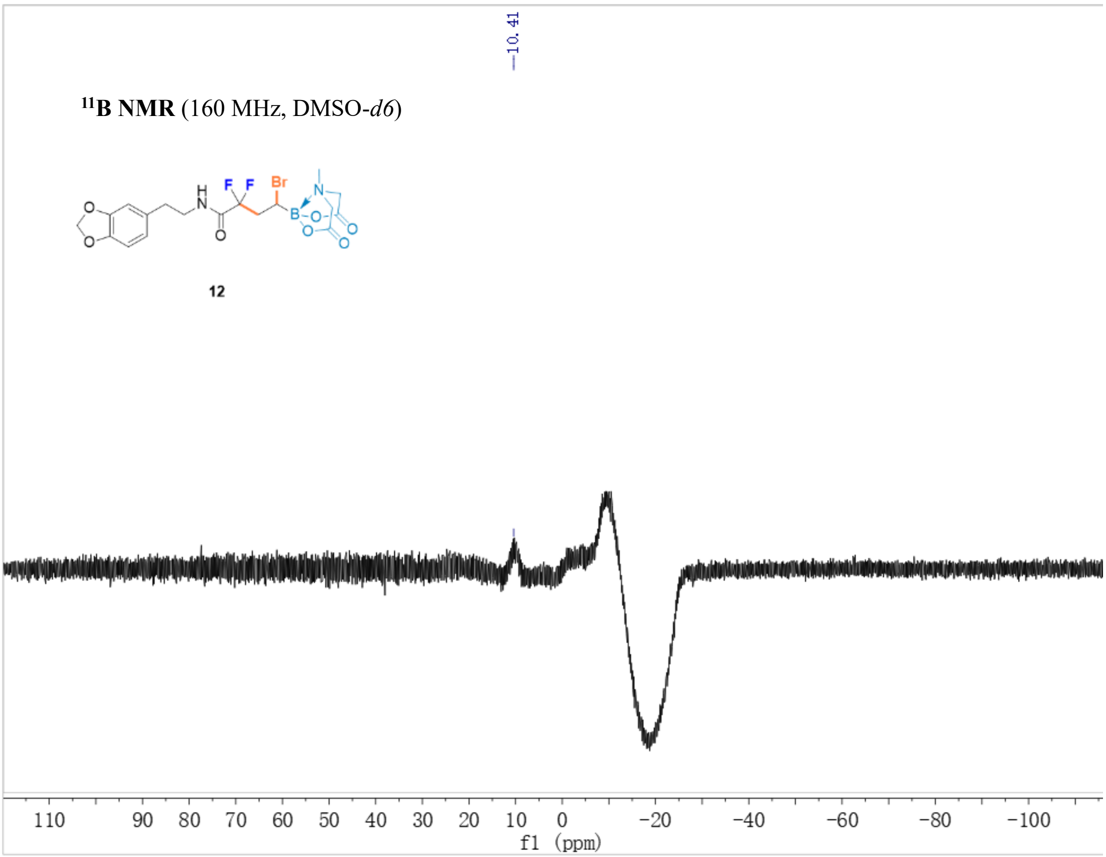




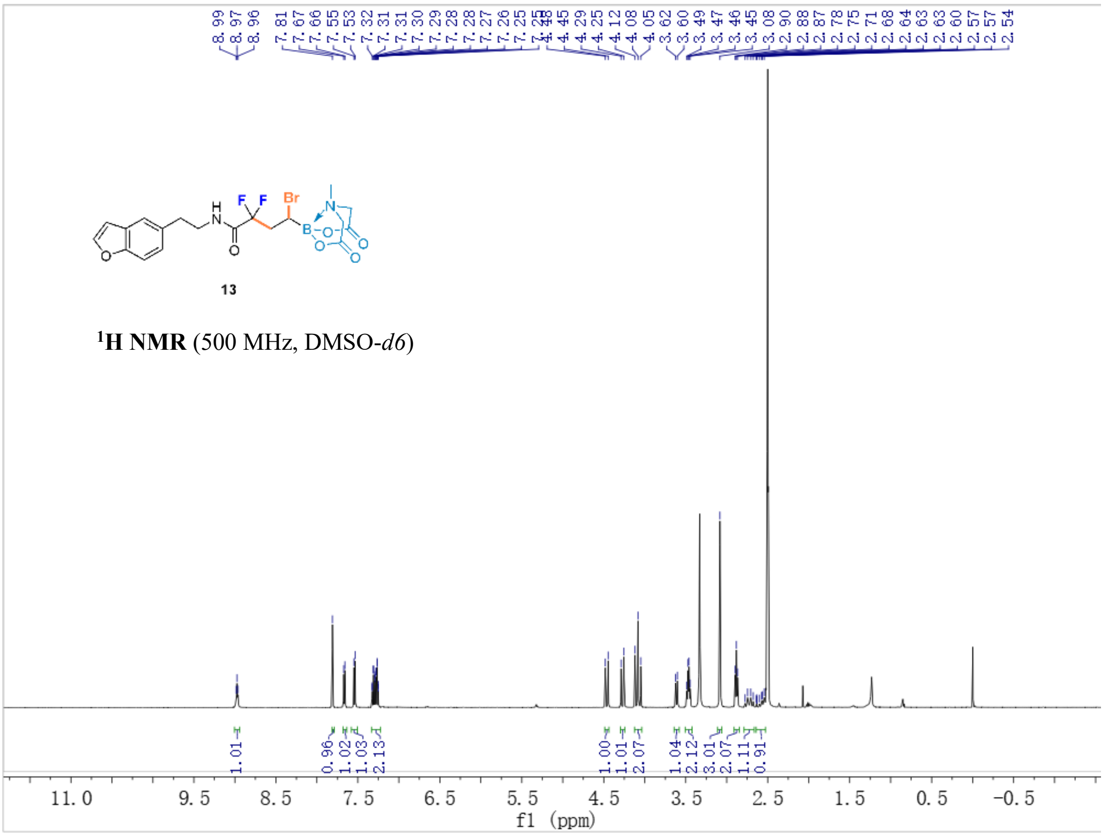
12
^{13}C NMR (126 MHz, DMSO-d6)
168.25 168.14 163.40 163.17 162.94 147.18 145.57 132.74 121.52 119.36 117.34 115.34 108.99 108.07 100.65 63.41 63.22 45.65 40.55 37.79 37.61 37.42 34.04 33.31
f1 (ppm)

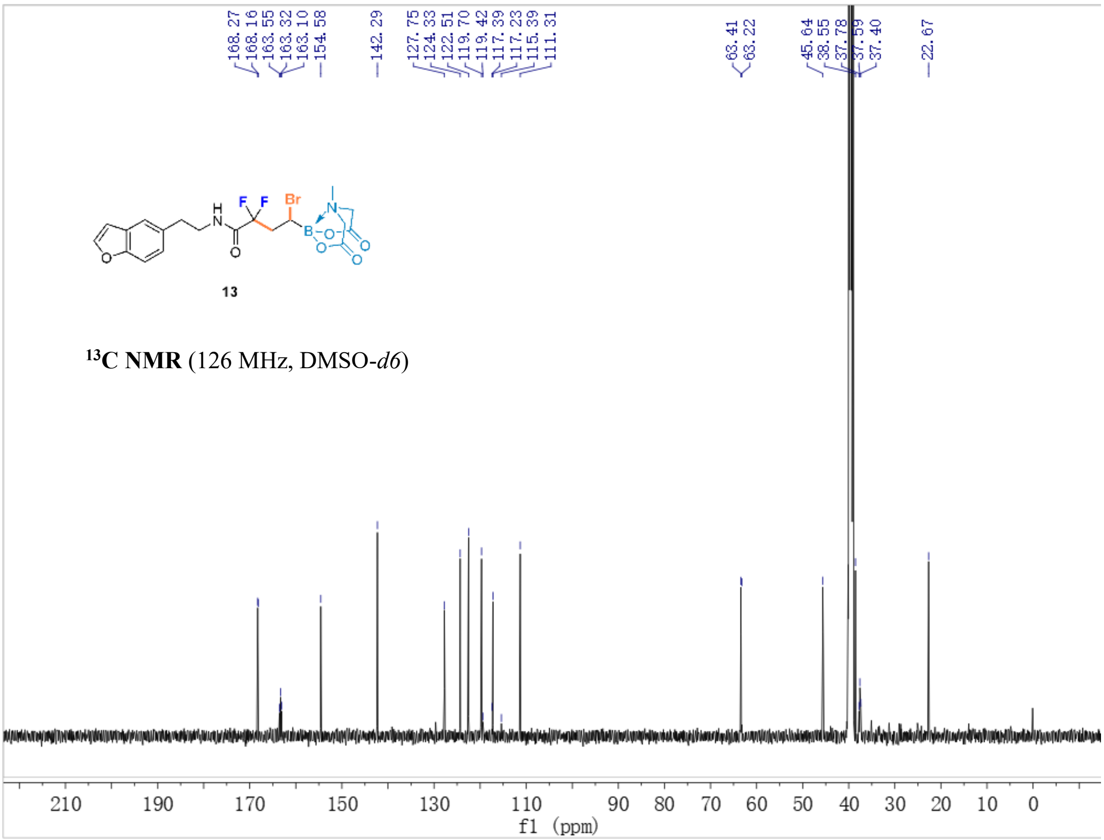


12
^{19}F NMR (471 MHz, DMSO-d6)
-103.18 -103.22 -103.25 -103.71 -103.75 -103.78 -105.17 -105.20 -105.21 -105.24 -105.70 -105.73 -105.74 -105.77
1.00 1.03
f1 (ppm)



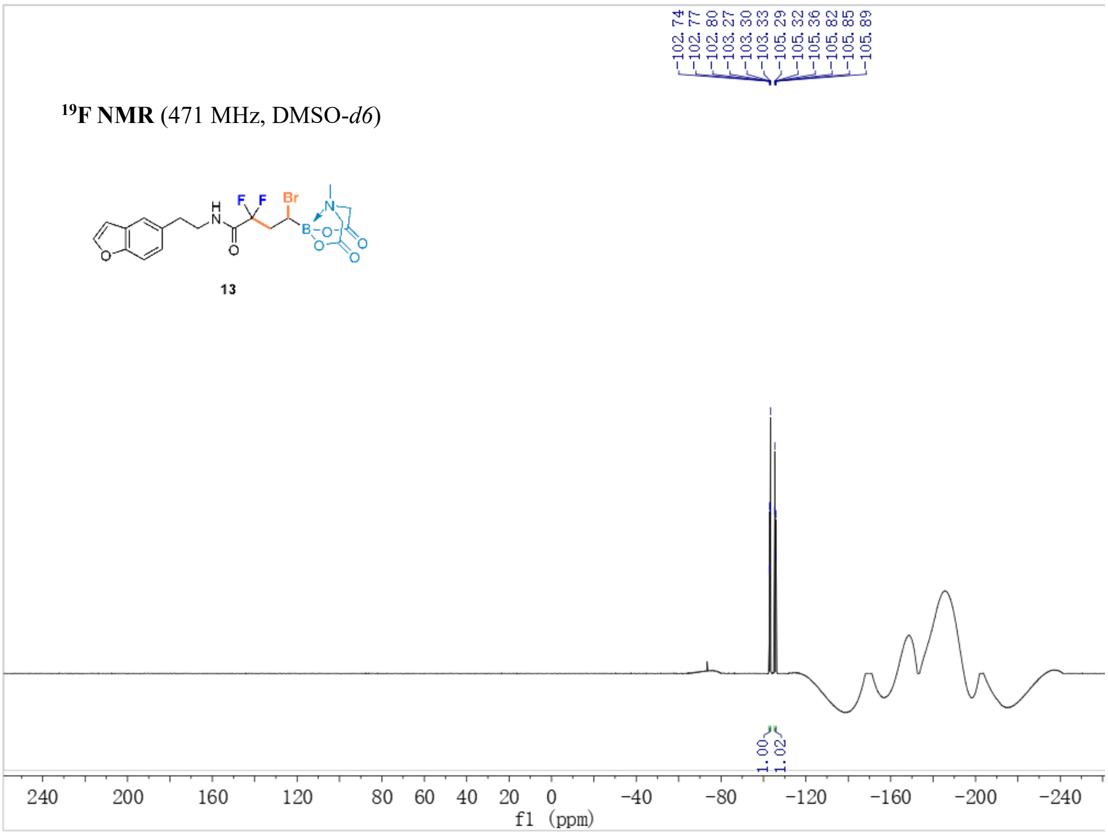
N-(2-(benzofuran-5-yl)ethyl)-4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (13)





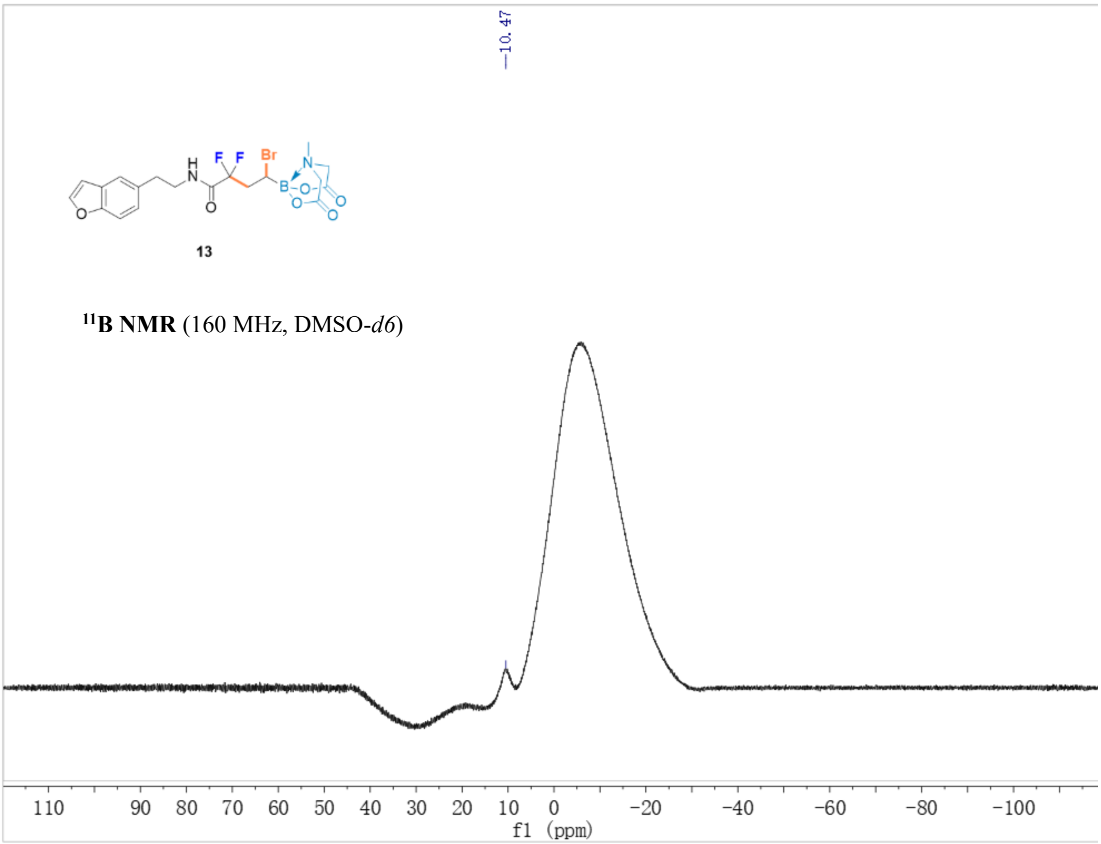
13

[13]C NMR (126 MHz, DMSO-*d6*)

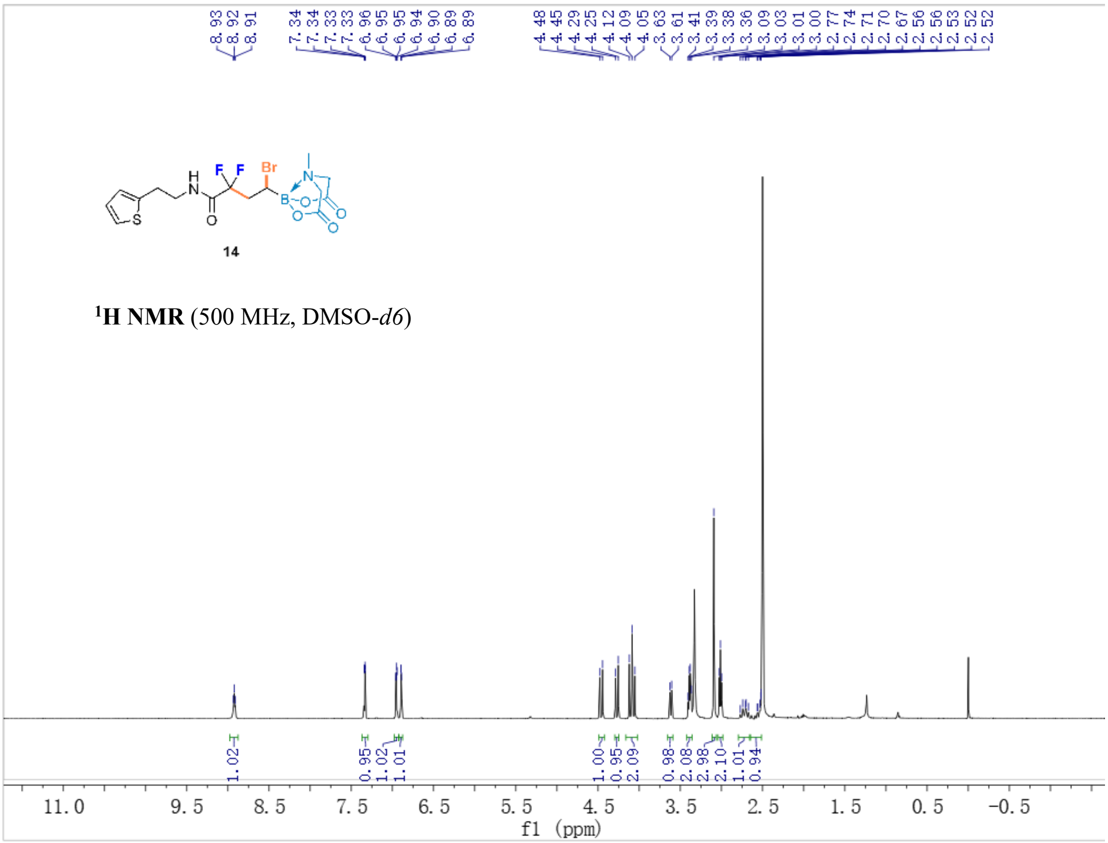


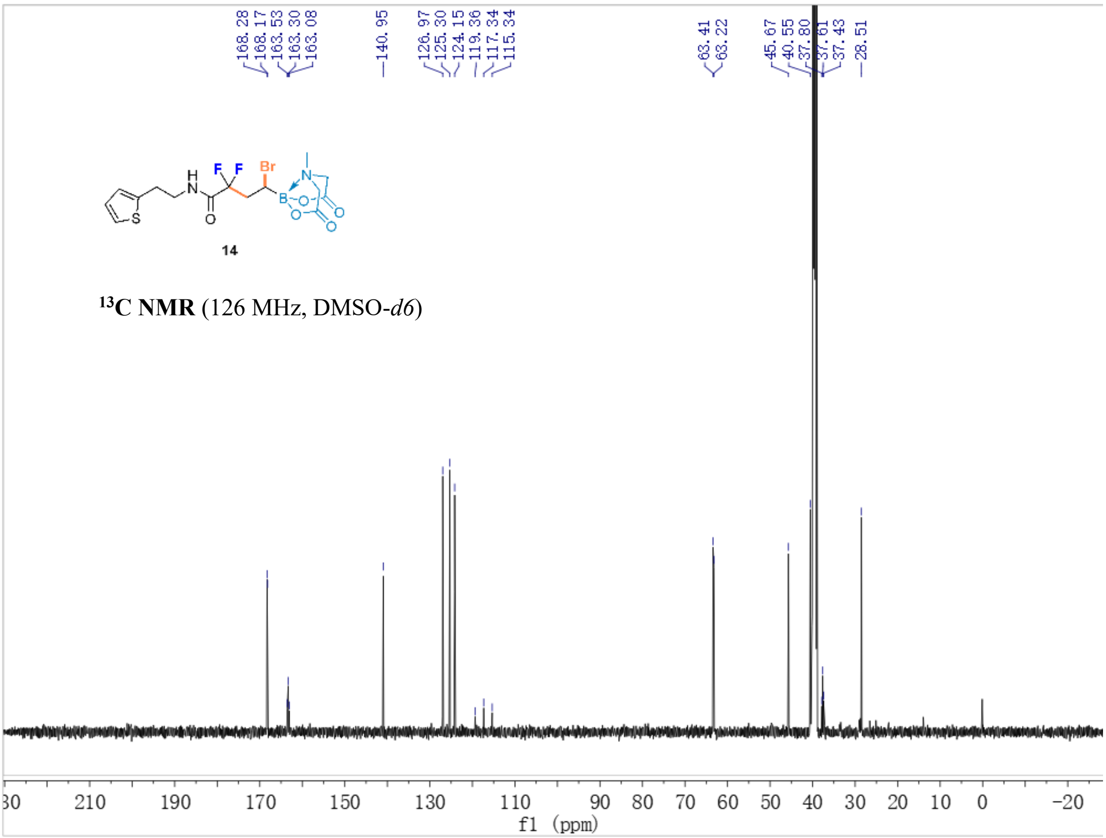
[19]F NMR (471 MHz, DMSO-*d6*)

13

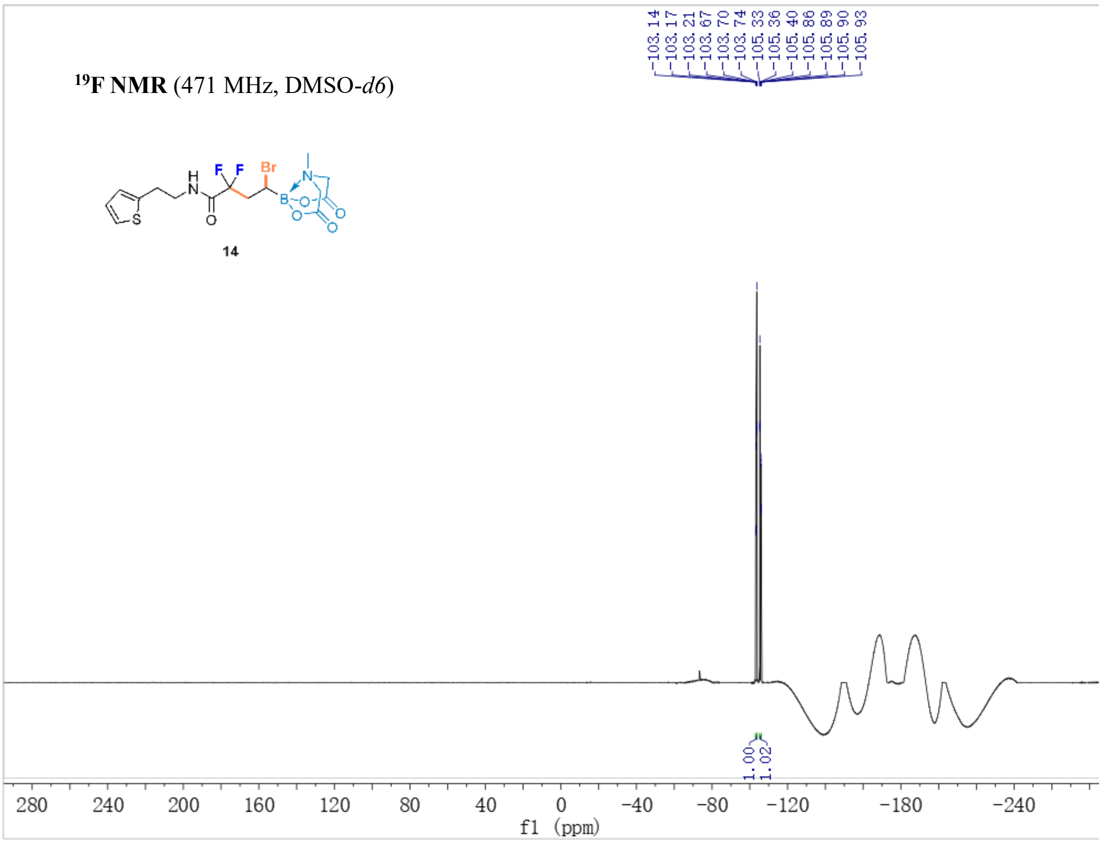


4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-*N*-(2-(thiophen-2-yl)ethyl)butanamide (14)

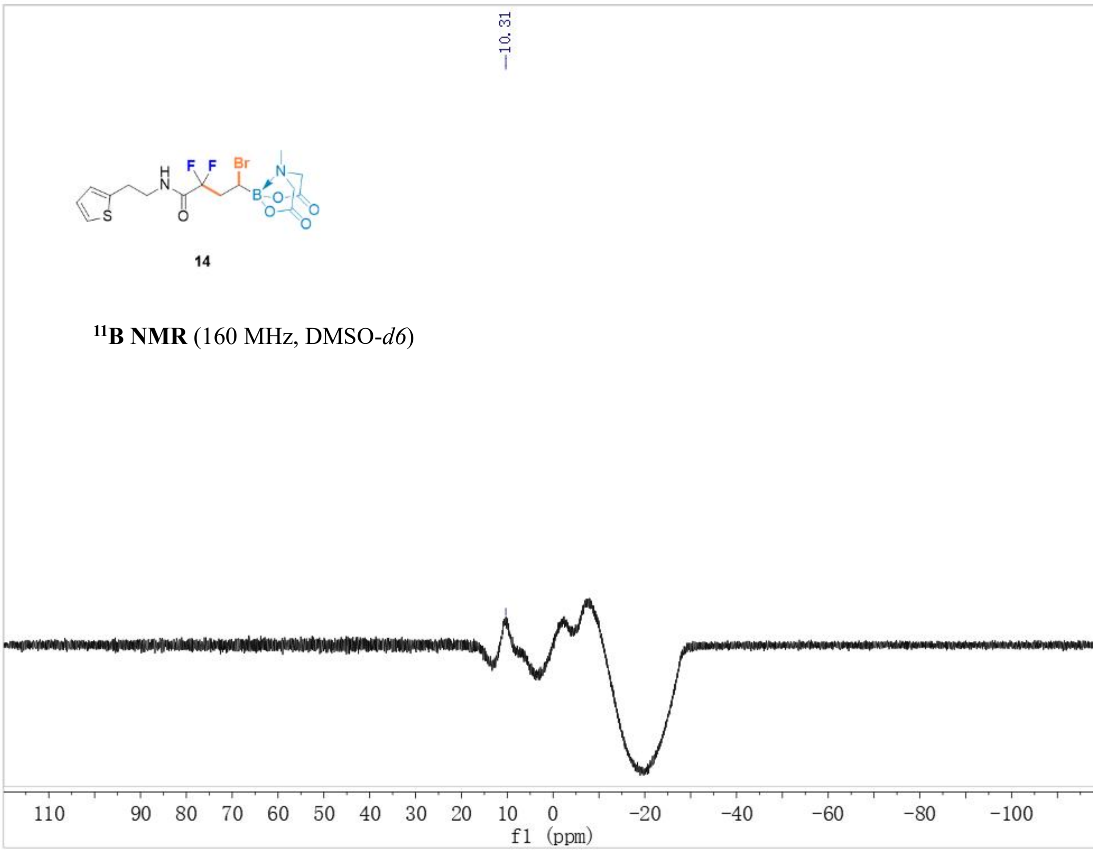




168.28
168.17
163.53
163.30
163.08
140.95
126.97
125.30
124.15
119.36
117.34
115.34
63.41
63.22
45.67
40.55
37.80
37.61
37.43
28.51
14
13C NMR (126 MHz, DMSO-d6)
f1 (ppm)



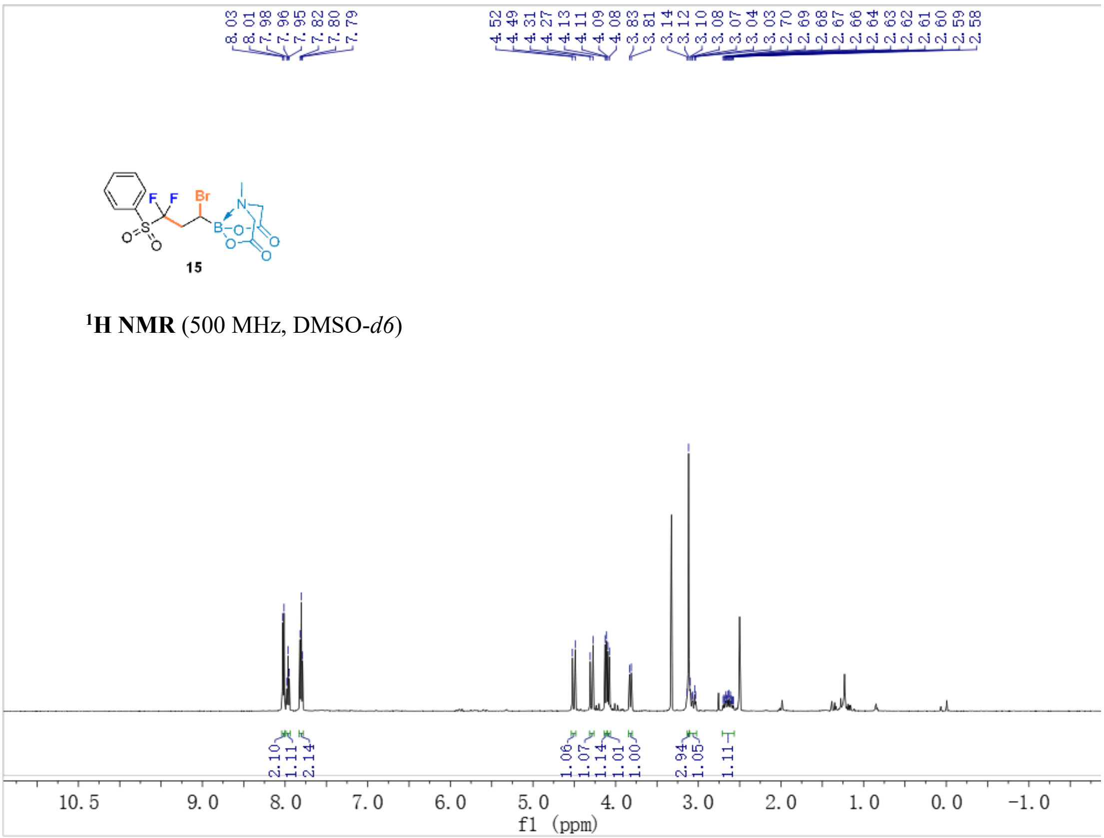
-103.14
-103.17
-103.21
-103.67
-103.70
-103.74
-105.33
-105.36
-105.40
-105.86
-105.89
-105.90
-105.93
19F NMR (471 MHz, DMSO-d6)
14
1.00
1.02
f1 (ppm)



14

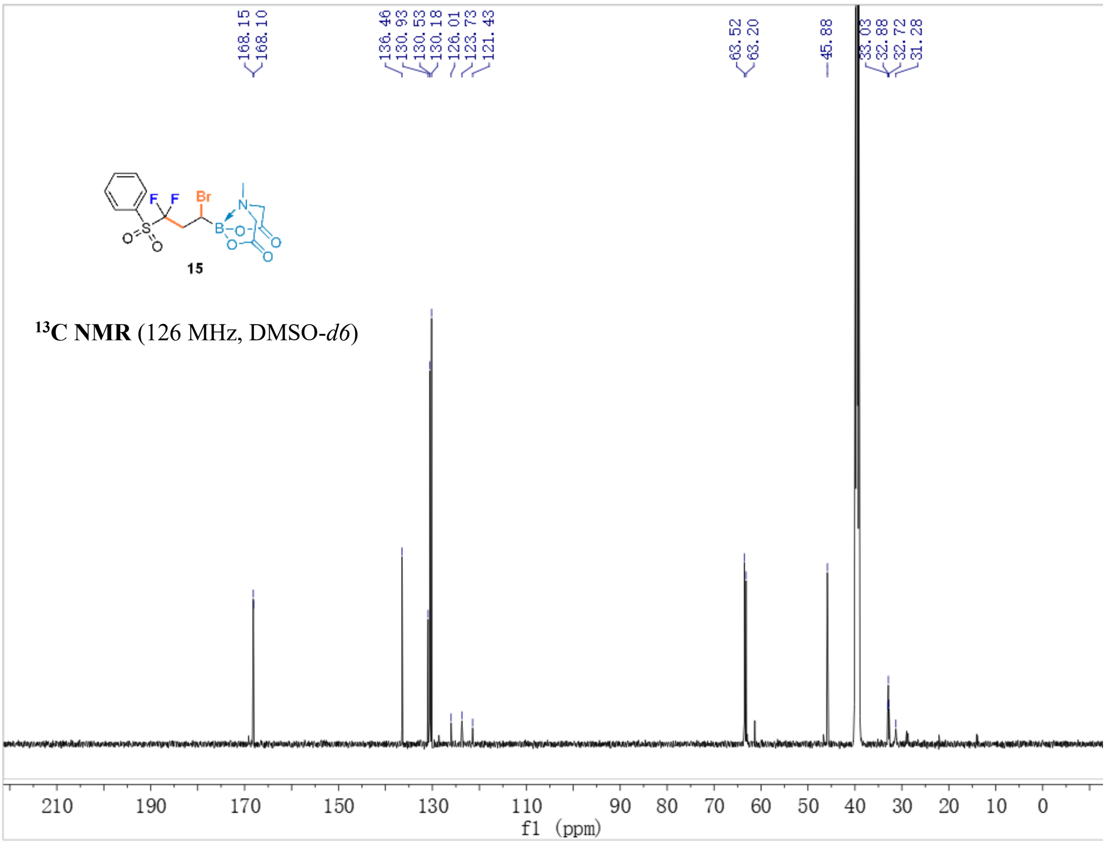
^{11}B NMR (160 MHz, DMSO-*d6*)

2-(1-bromo-3,3-difluoro-3-(phenylsulfonyl)propyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (15)

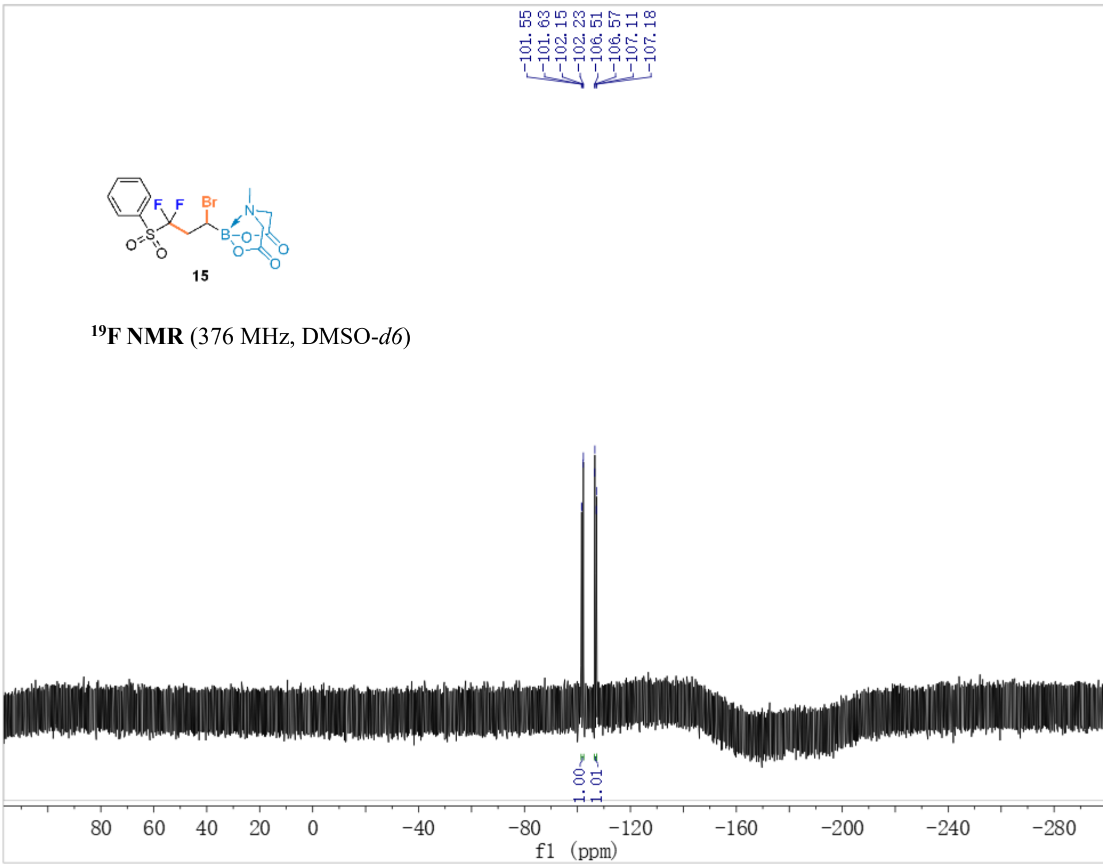


15

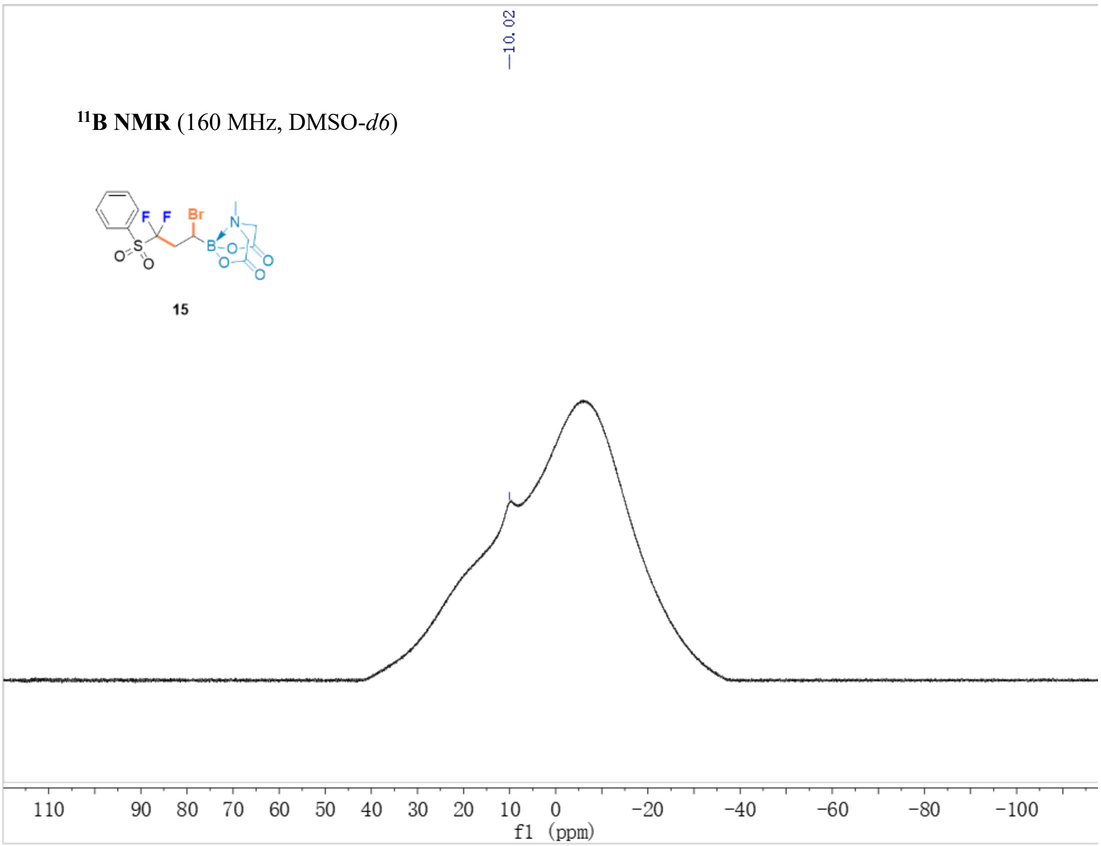
^{1}H NMR (500 MHz, DMSO-*d6*)



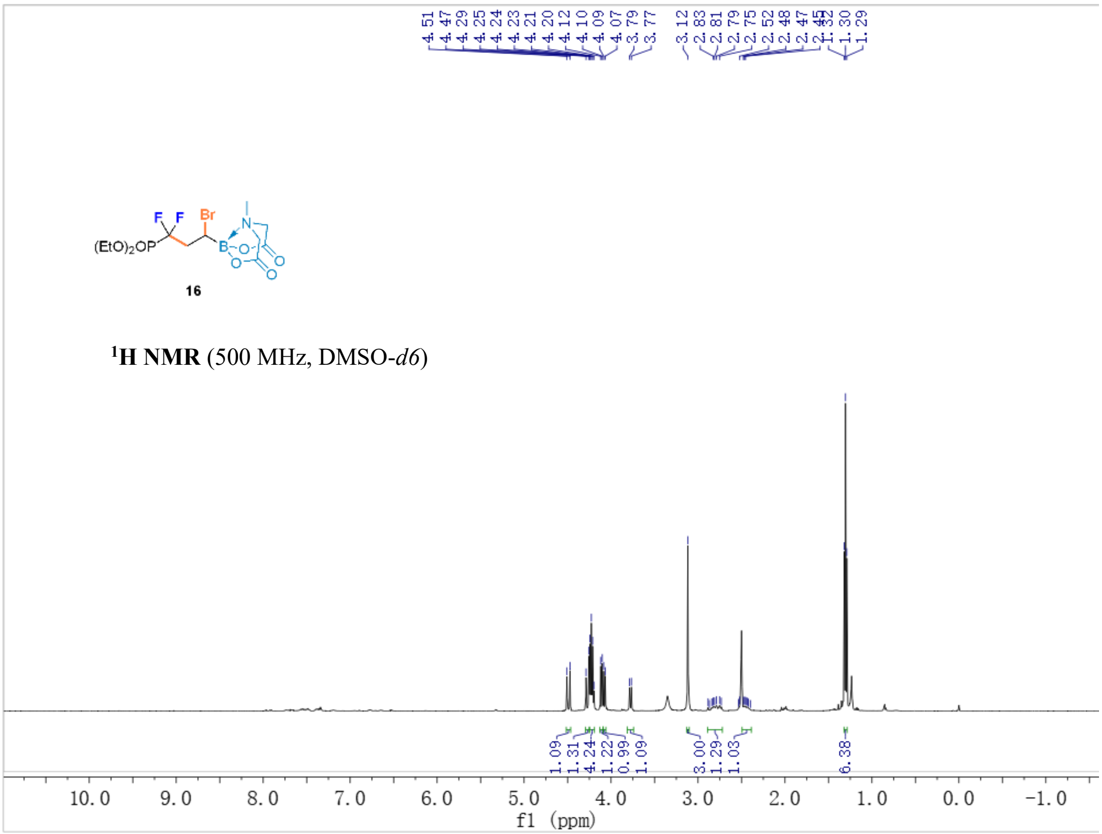
^{13}C NMR (126 MHz, DMSO-*d6*)

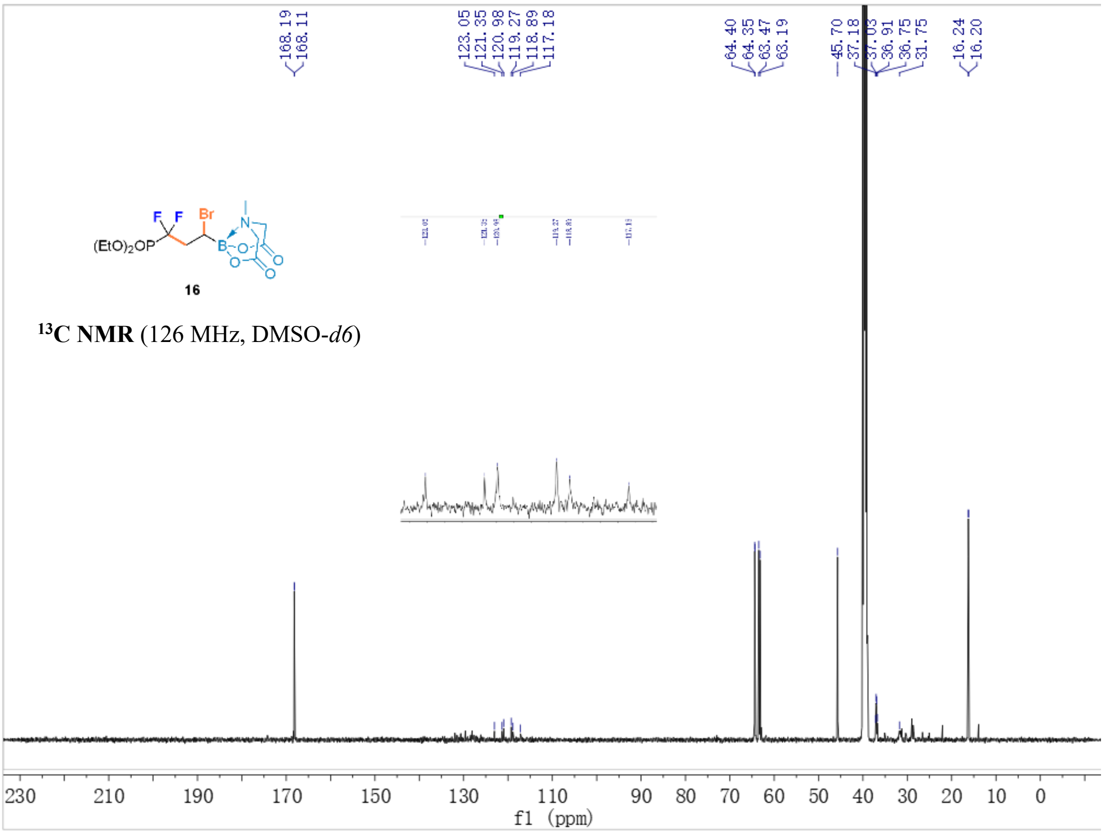


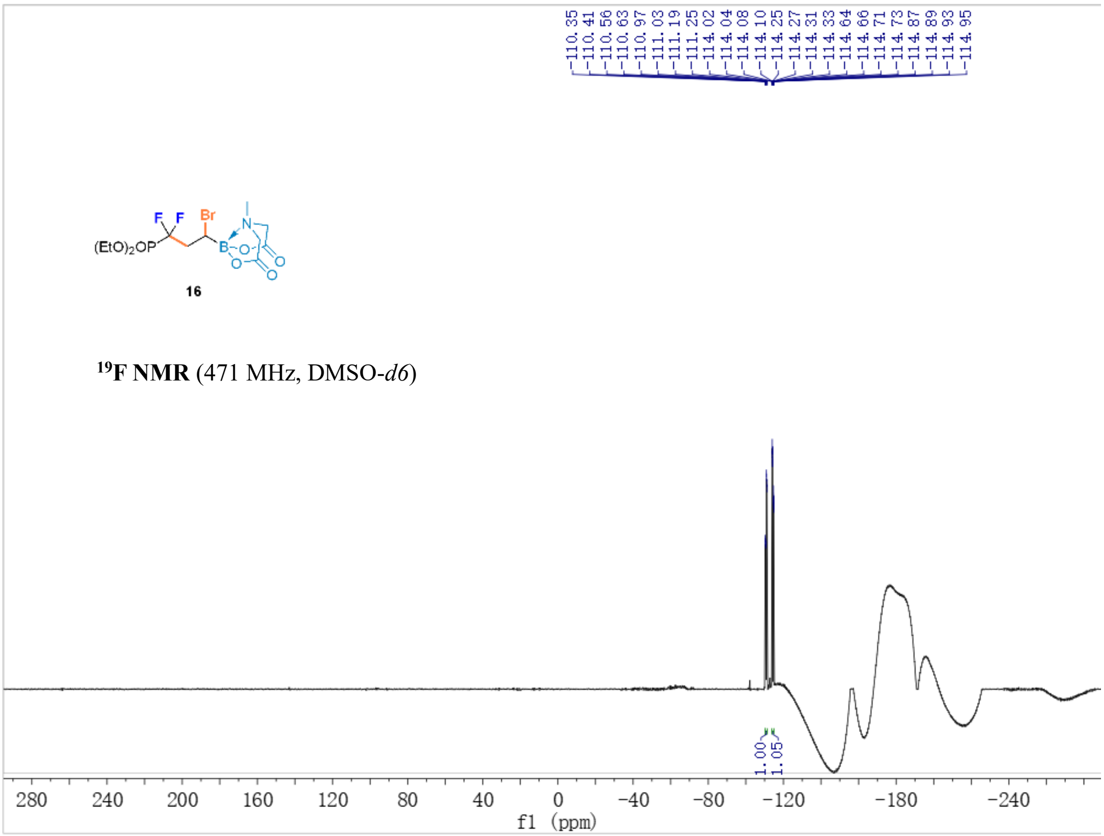
^{19}F NMR (376 MHz, DMSO-*d6*)

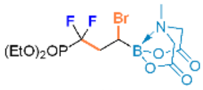


Diethyl (3-bromo-1,1-difluoro-3-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)propyl)phosphonate (16)



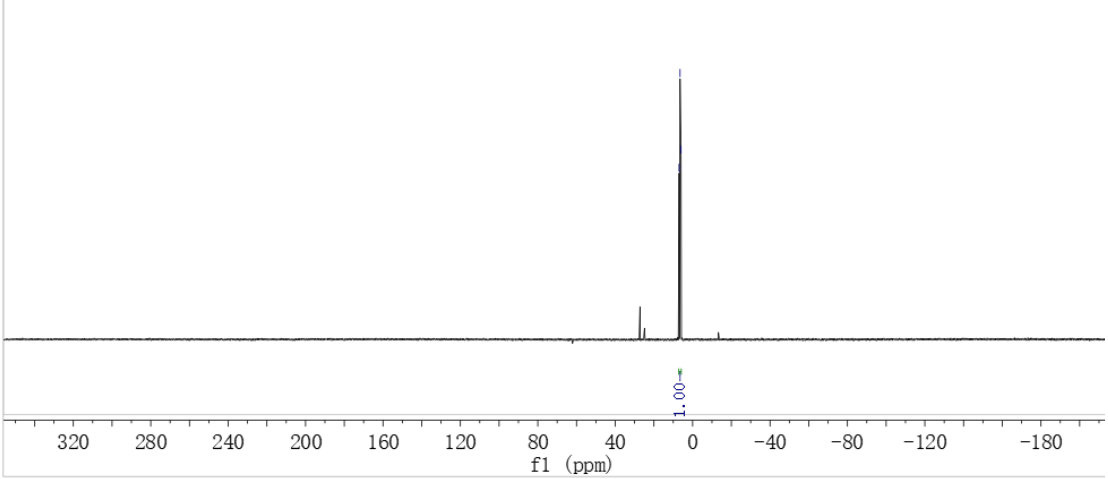

168.19
168.11
123.05
121.35
120.98
119.27
118.89
117.18
64.40
64.35
63.47
63.19
45.70
37.18
37.03
36.91
36.75
31.75
16.24
16.20
F F Br
(EtO)2OP
B
N
O
O
O
O
16
13C NMR (126 MHz, DMSO-d6)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

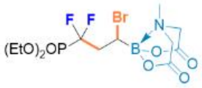

-110.35
-110.41
-110.56
-110.63
-110.97
-111.03
-111.19
-111.25
-114.02
-114.04
-114.08
-114.10
-114.25
-114.27
-114.31
-114.33
-114.64
-114.66
-114.71
-114.73
-114.87
-114.89
-114.93
-114.95
F F Br
(EtO)2OP
B
N
O
O
O
O
16
19F NMR (471 MHz, DMSO-d6)
1.00
1.05
280 240 200 160 120 80 40 0 -40 -80 -120 -180 -240
f1 (ppm)



16

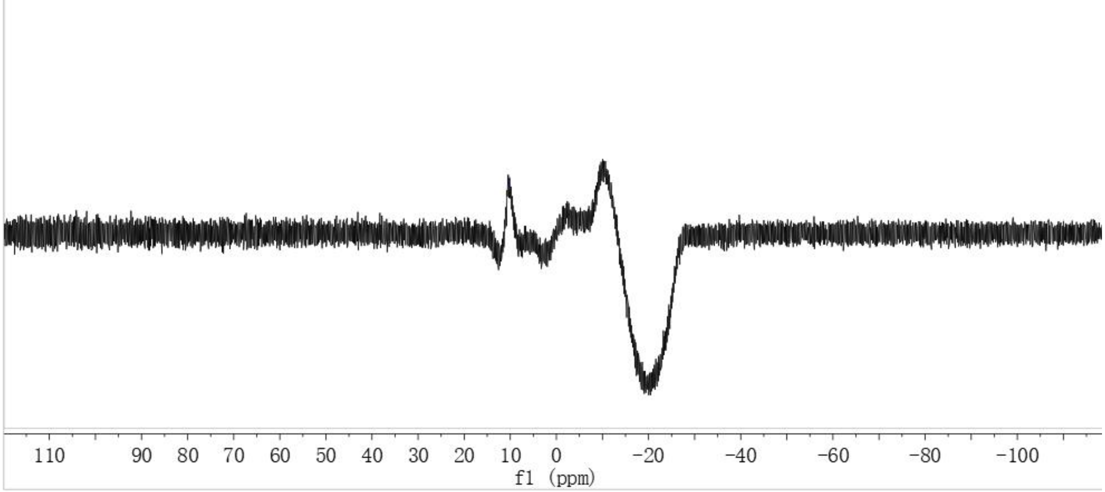
^{31}**P NMR** (202 MHz, DMSO-*d6*)



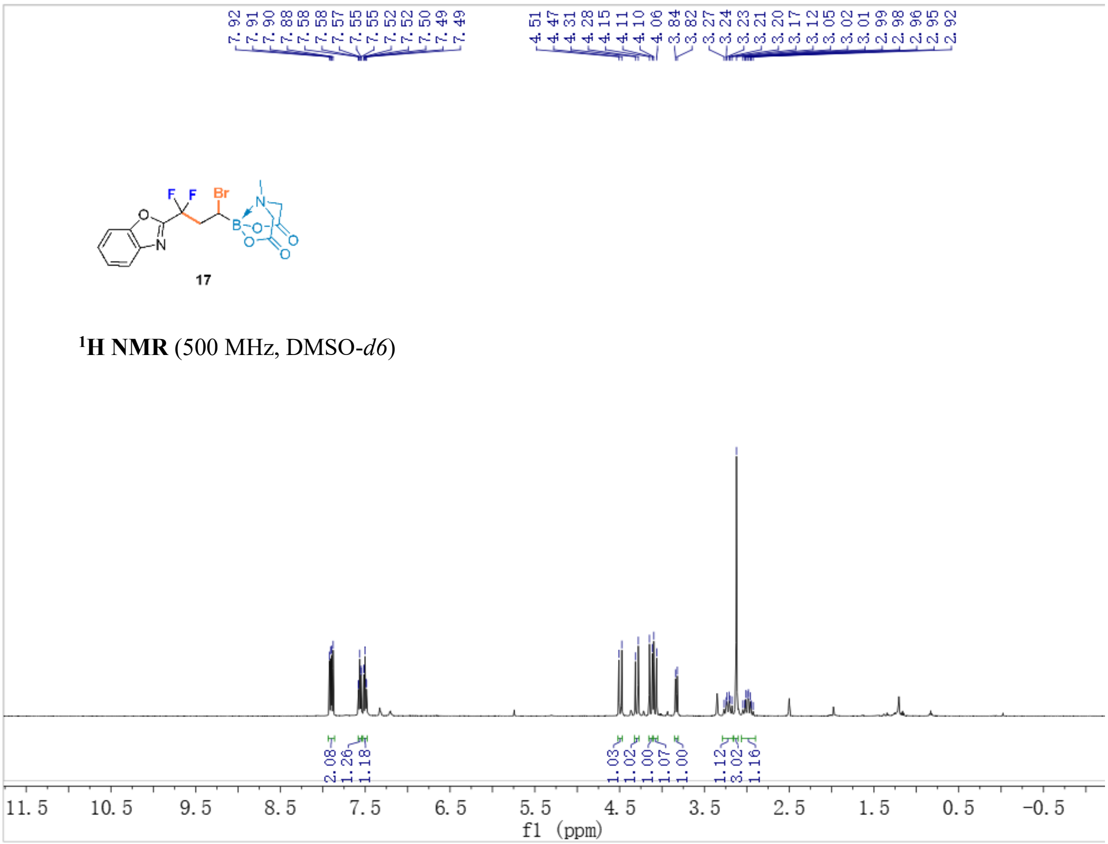


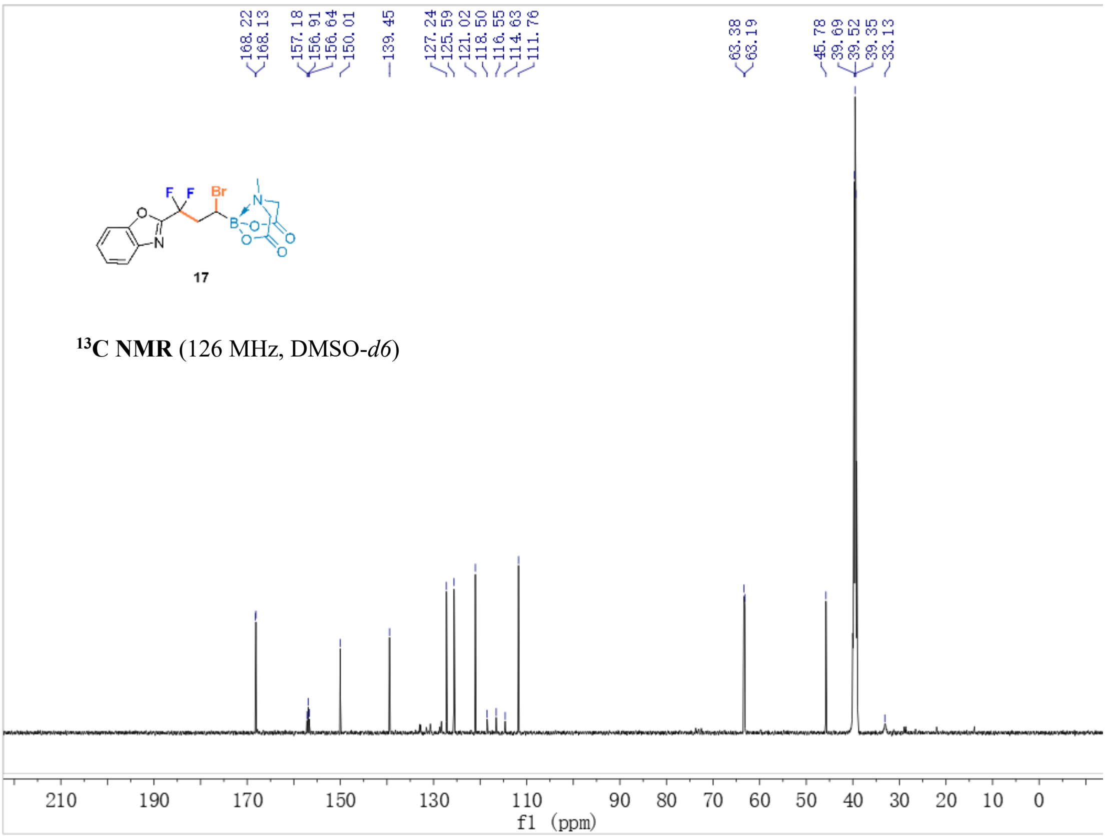
16

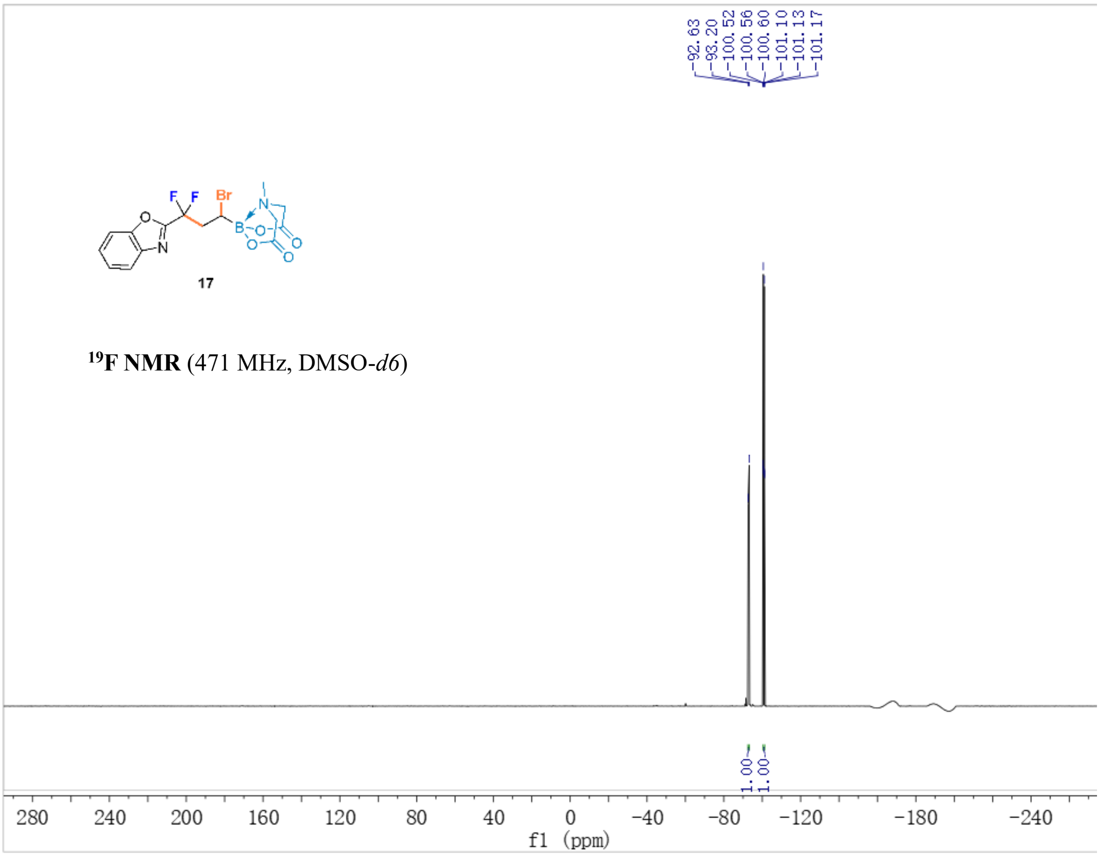
^{11}**B NMR** (160 MHz, DMSO-*d6*)



2-(3-(benzo[*d*]oxazol-2-yl)-1-bromo-3,3-difluoropropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (17)

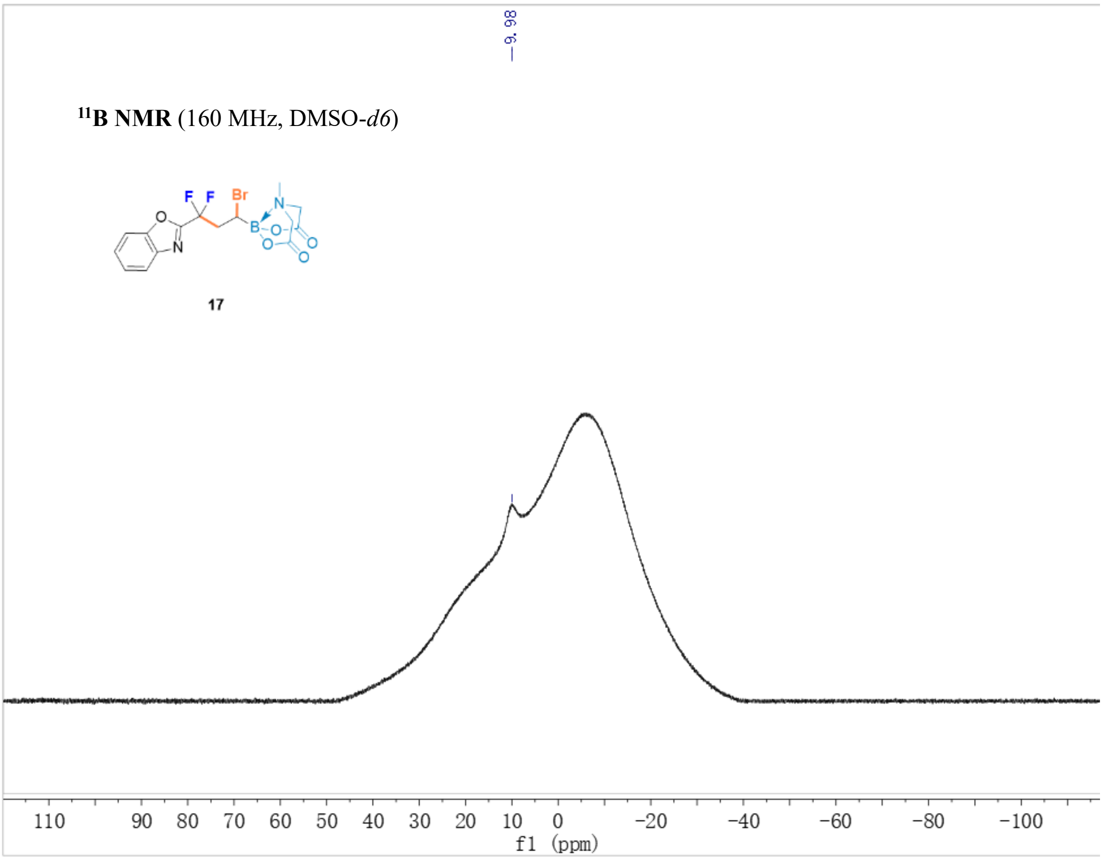




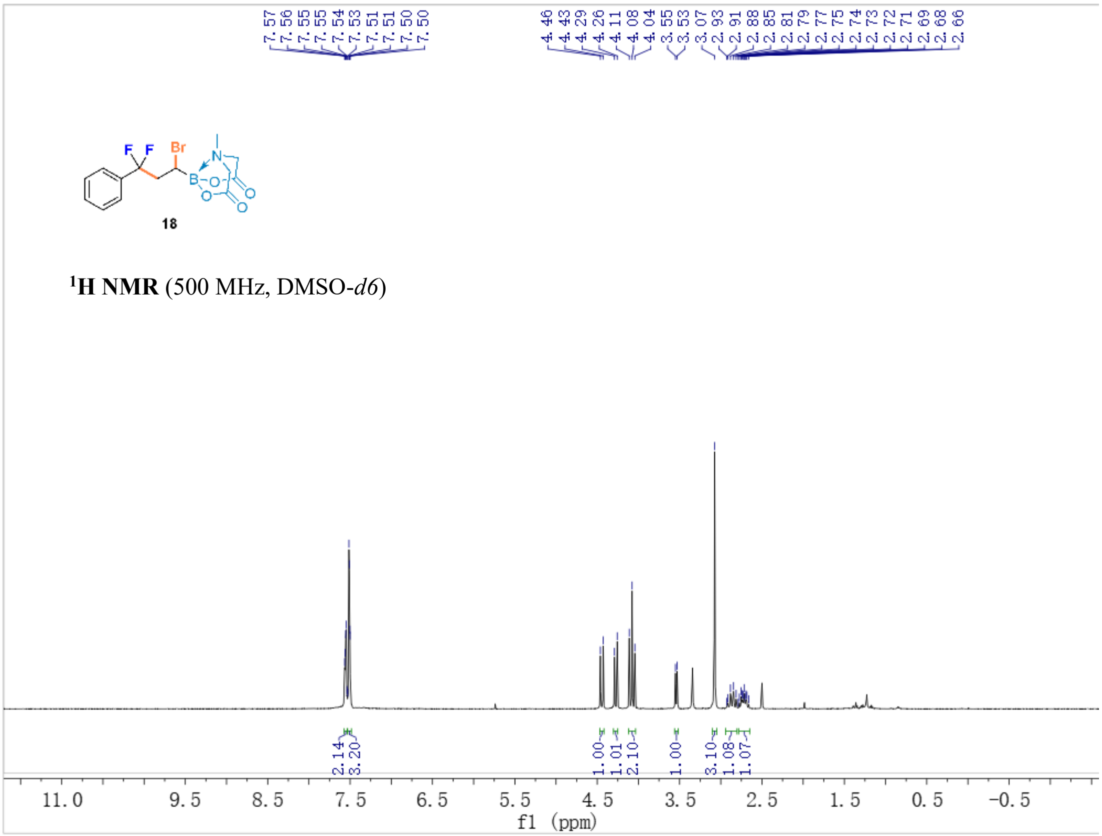


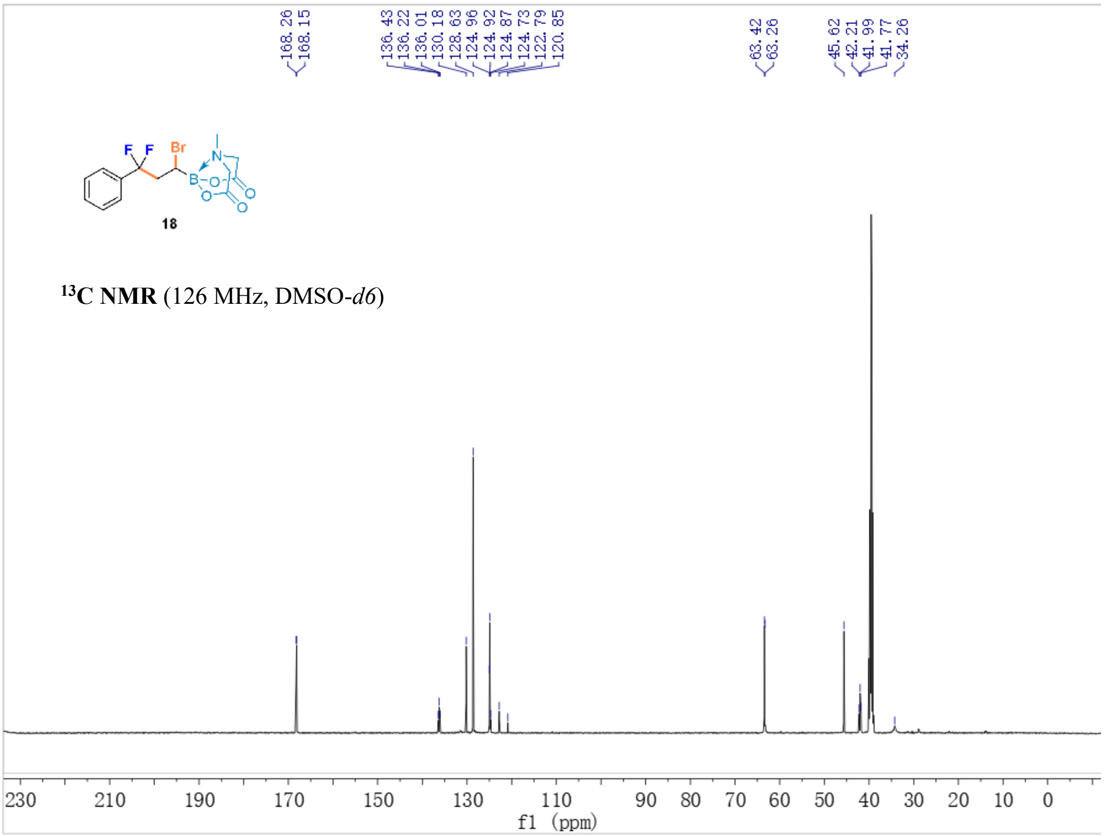
^{19}F NMR (471 MHz, DMSO-*d6*)

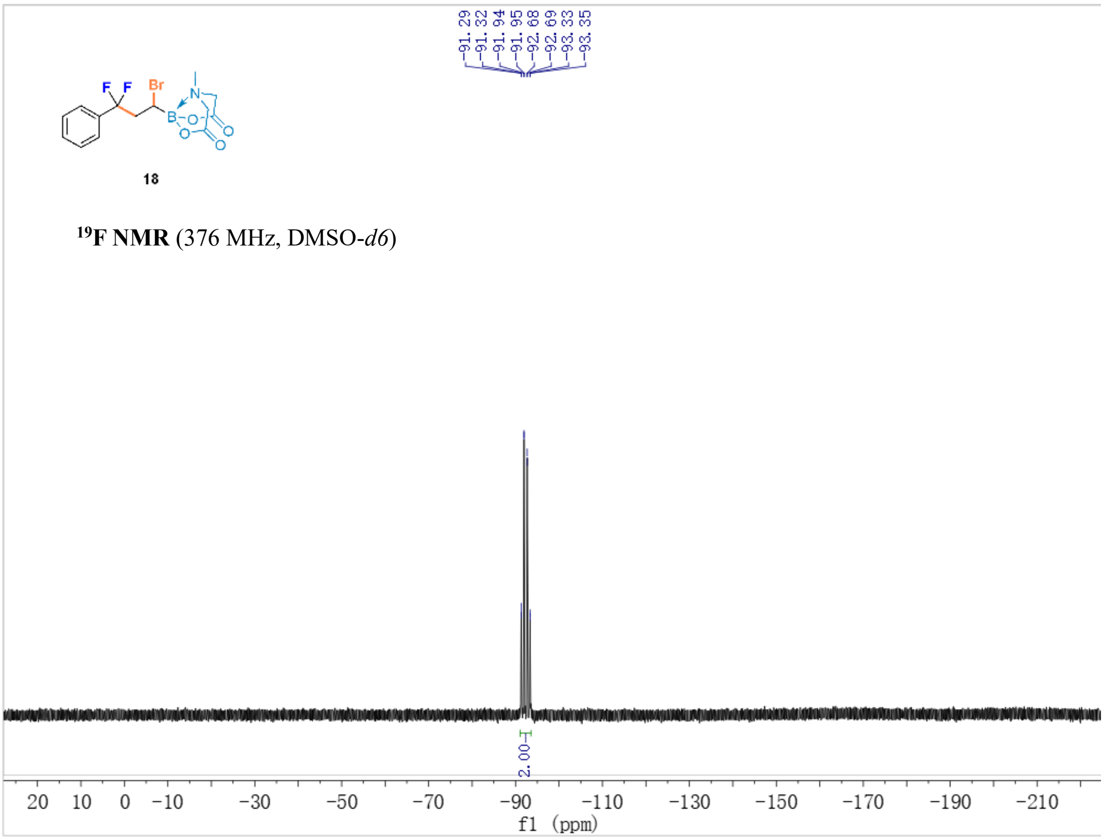
^{11}B NMR (160 MHz, DMSO-*d6*)

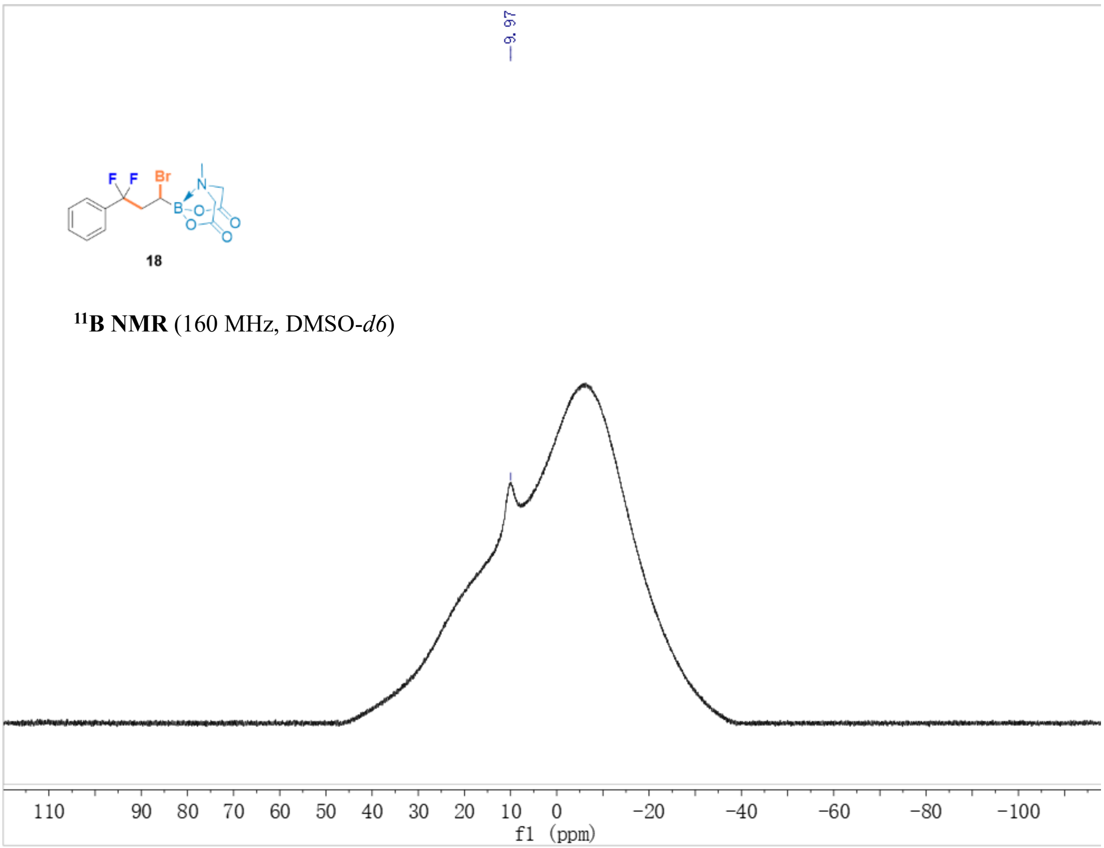


2-(1-bromo-3,3-difluoro-3-phenylpropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (18)

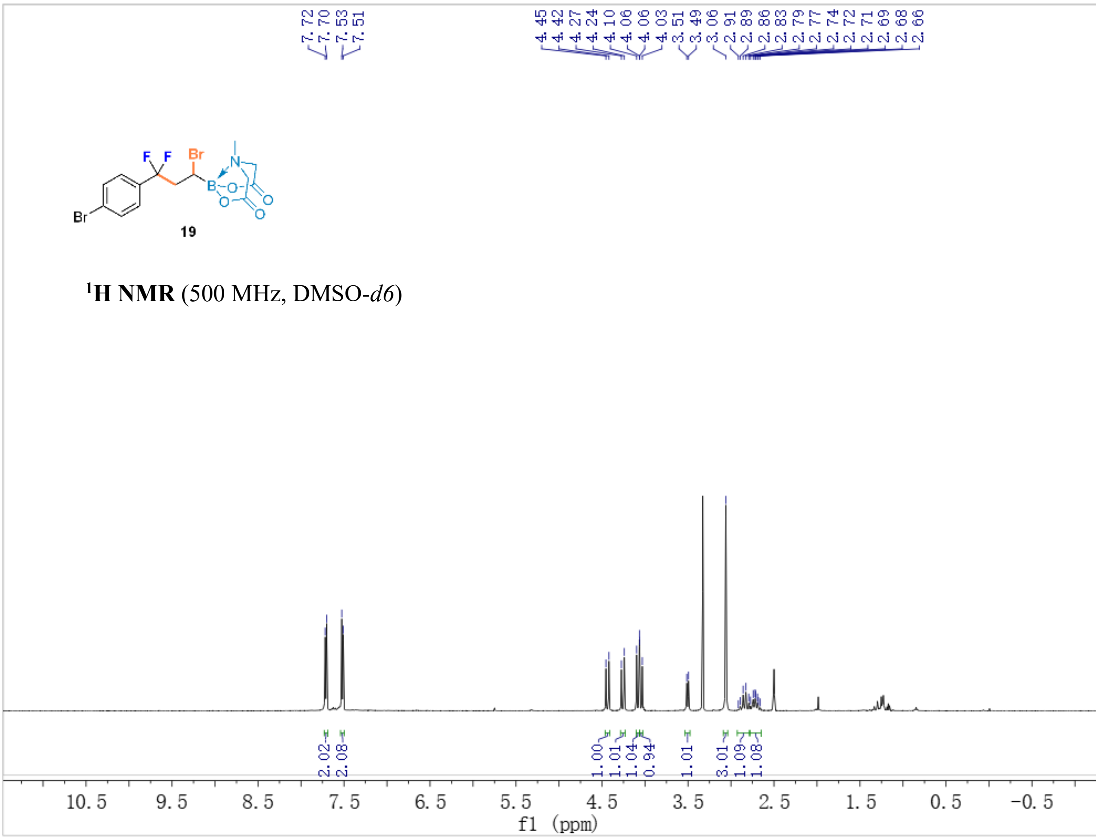


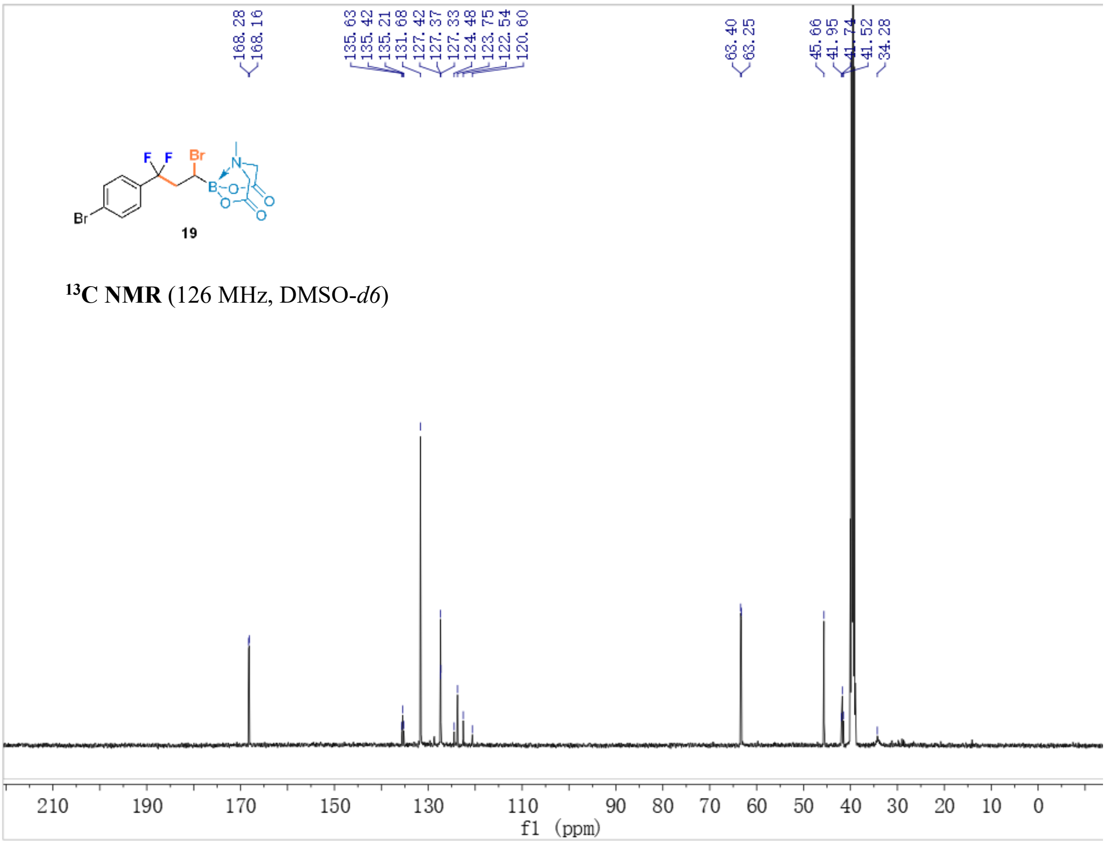


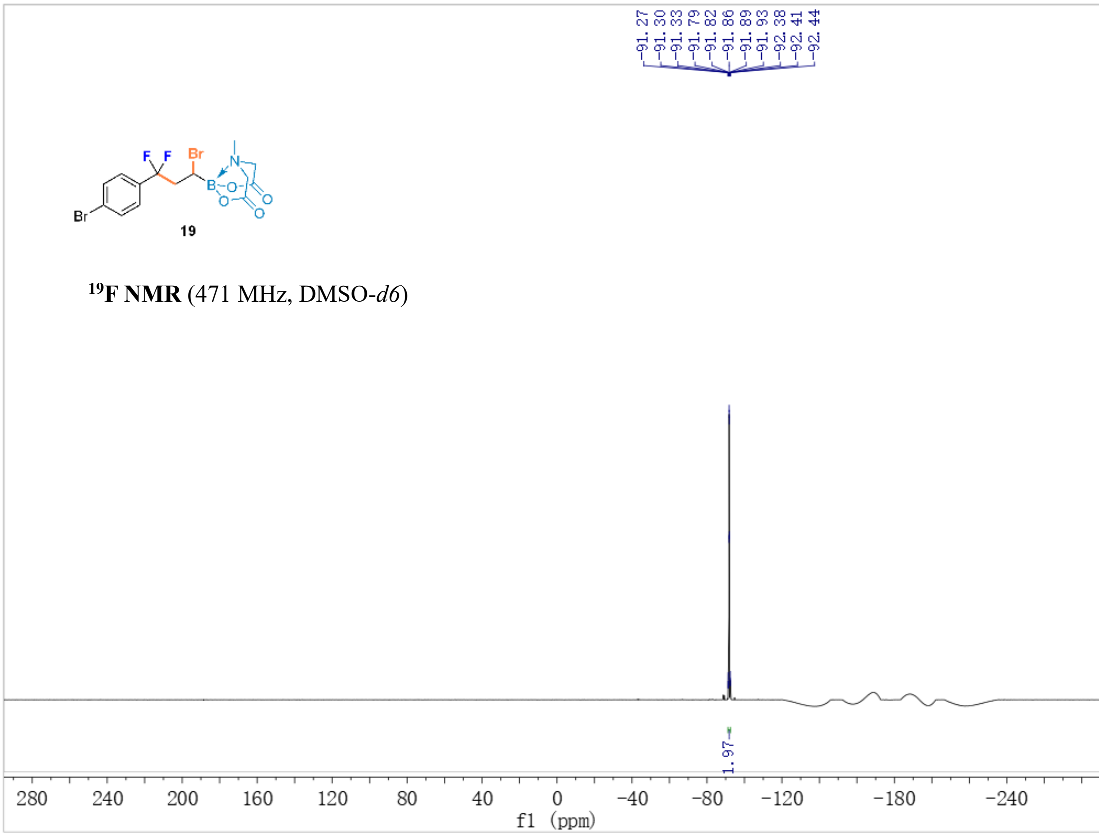

-91.29
-91.32
-91.94
-91.95
-92.68
-92.69
-93.33
-93.35
F F Br
N
B O
O O
O
18
19F NMR (376 MHz, DMSO-d6)
2.00
20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

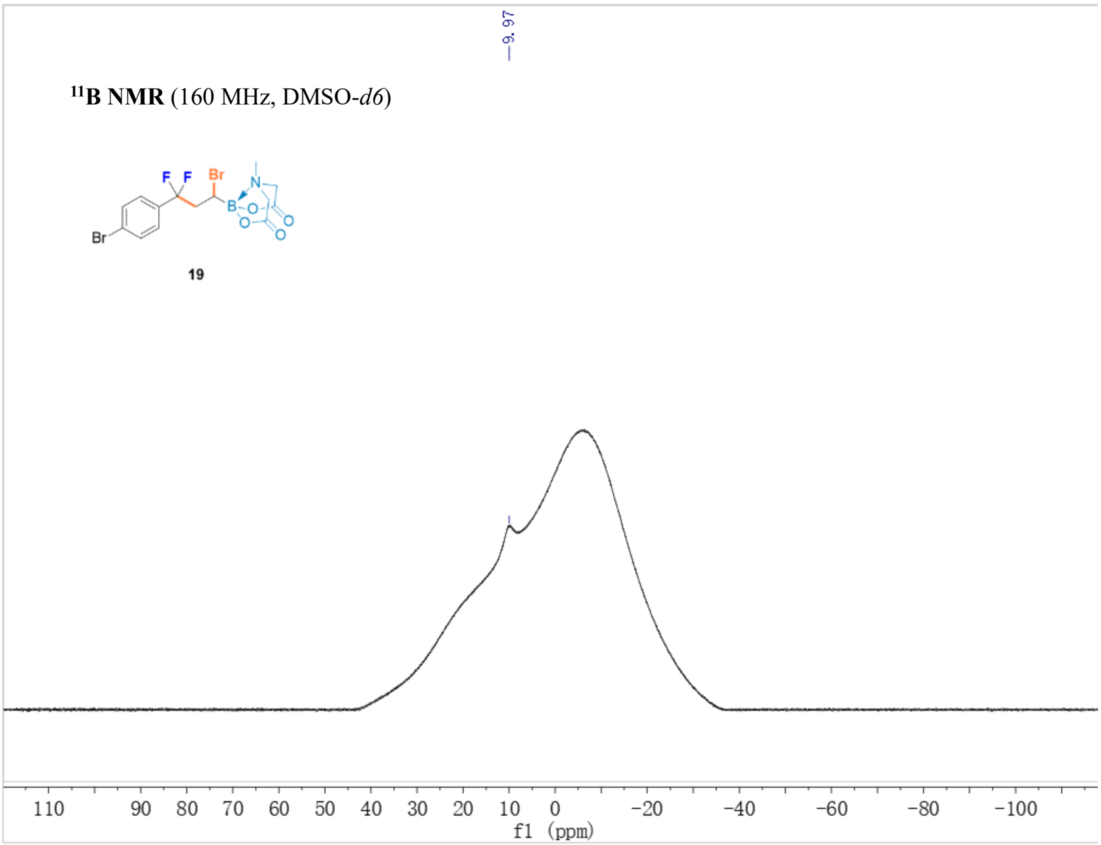

9.97
F F Br
N
B O
O O
O
18
11B NMR (160 MHz, DMSO-d6)
110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100
f1 (ppm)

2-(1-bromo-3-(4-bromophenyl)-3,3-difluoropropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (19)

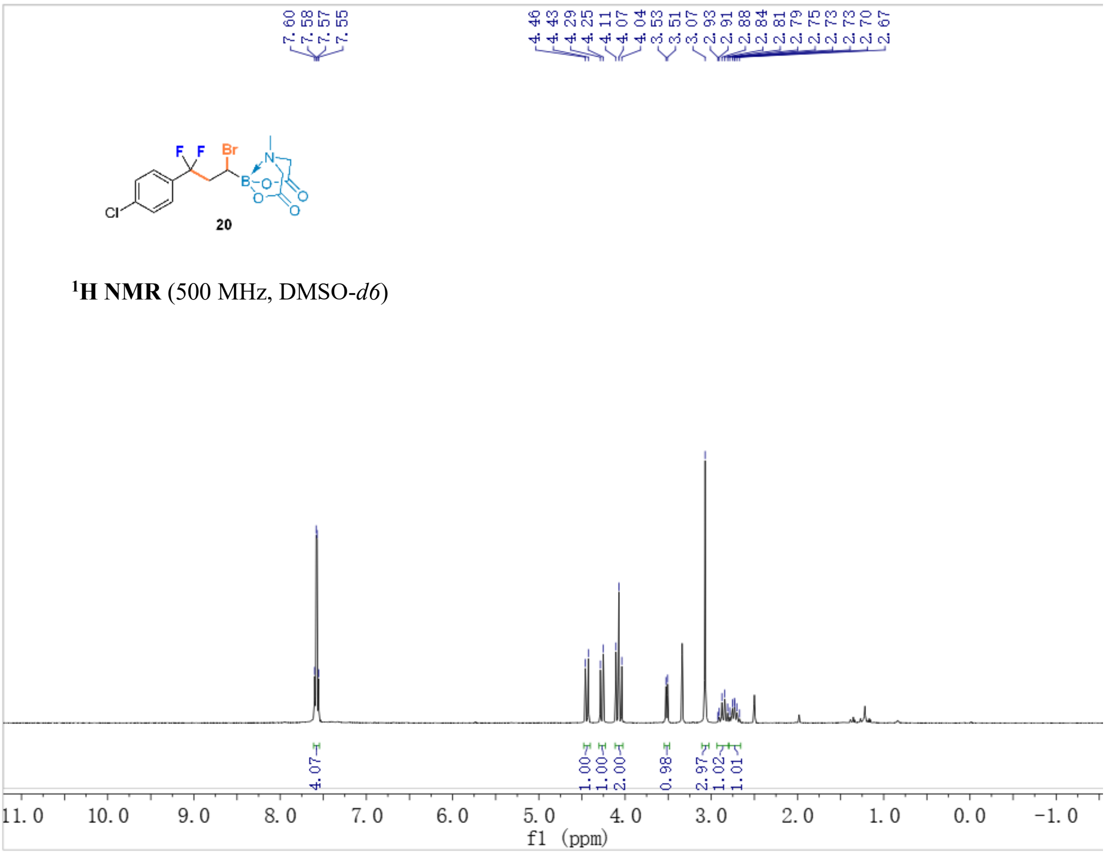


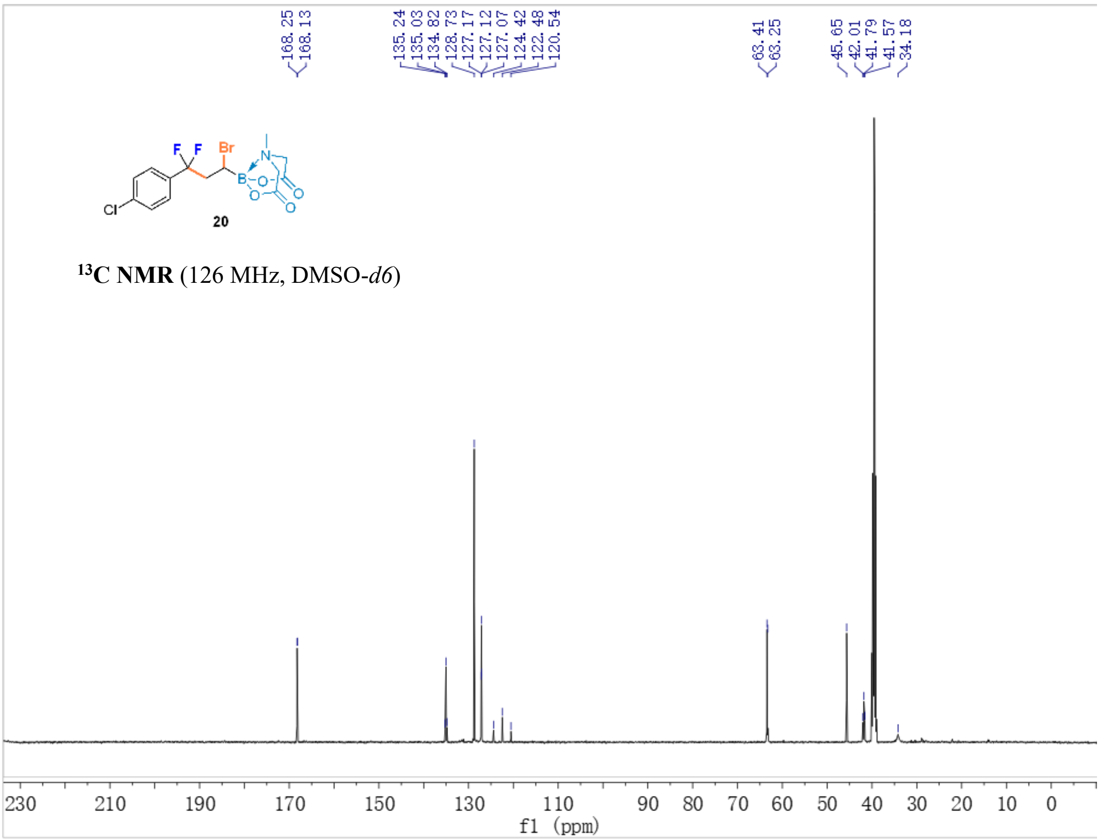


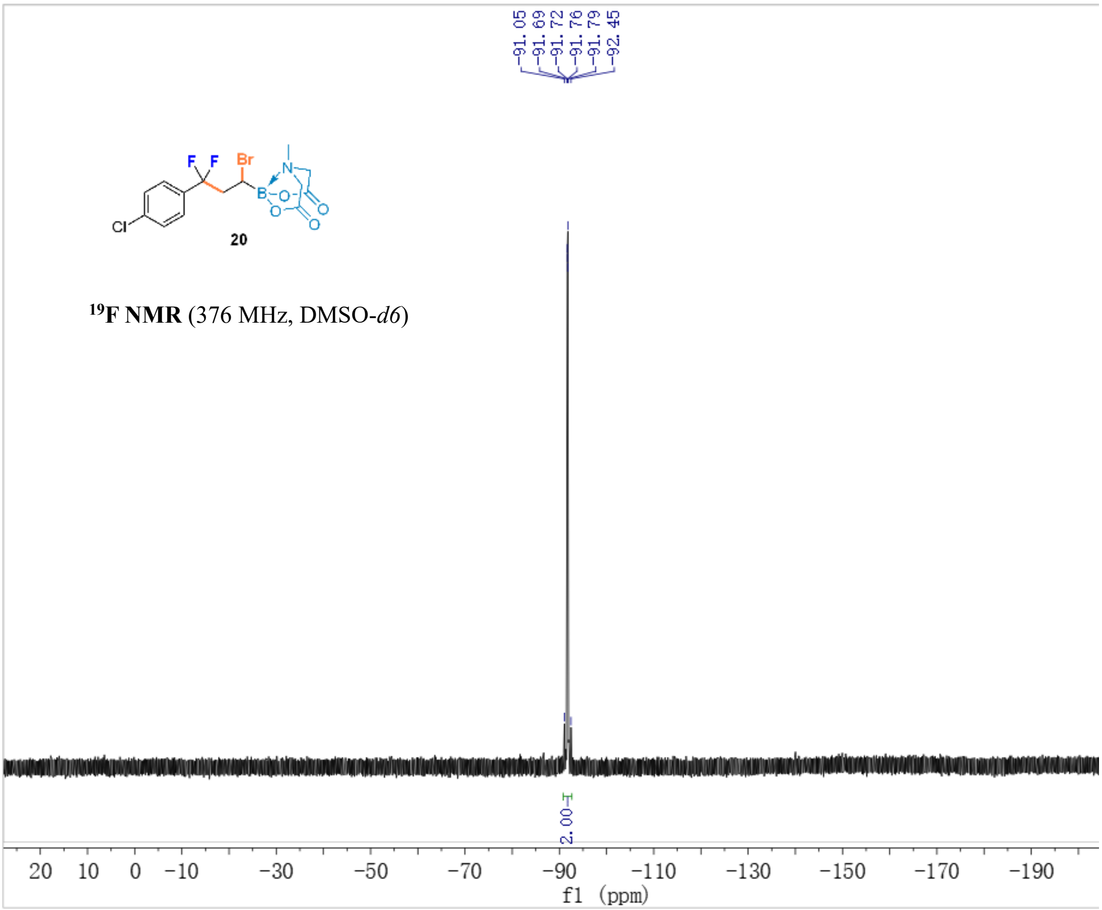

-91.27
-91.30
-91.33
-91.79
-91.82
-91.86
-91.89
-91.93
-92.38
-92.41
-92.44
19
^{19}F NMR (471 MHz, DMSO-*d6*)
1.97
280 240 200 160 120 80 40 0 -40 -80 -120 -180 -240
f1 (ppm)

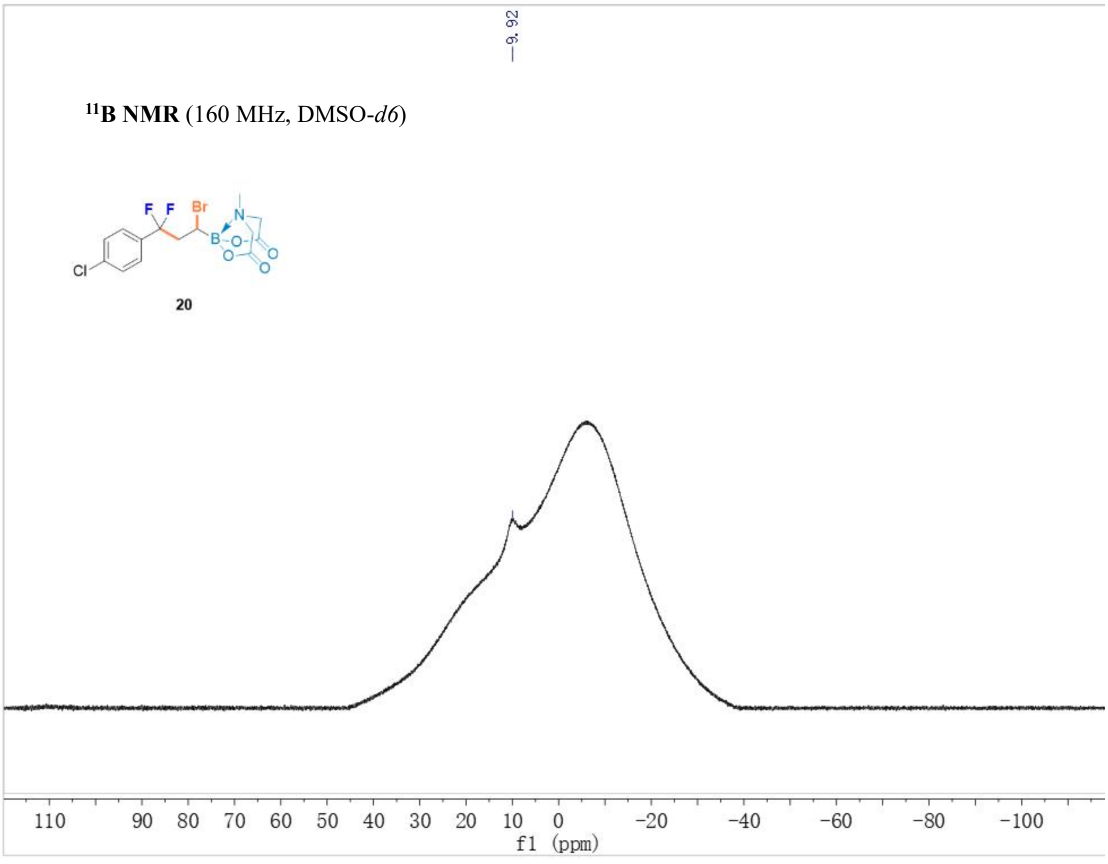

9.97
^{11}B NMR (160 MHz, DMSO-*d6*)
19
110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100
f1 (ppm)

2-(1-bromo-3-(4-chlorophenyl)-3,3-difluoropropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (20)

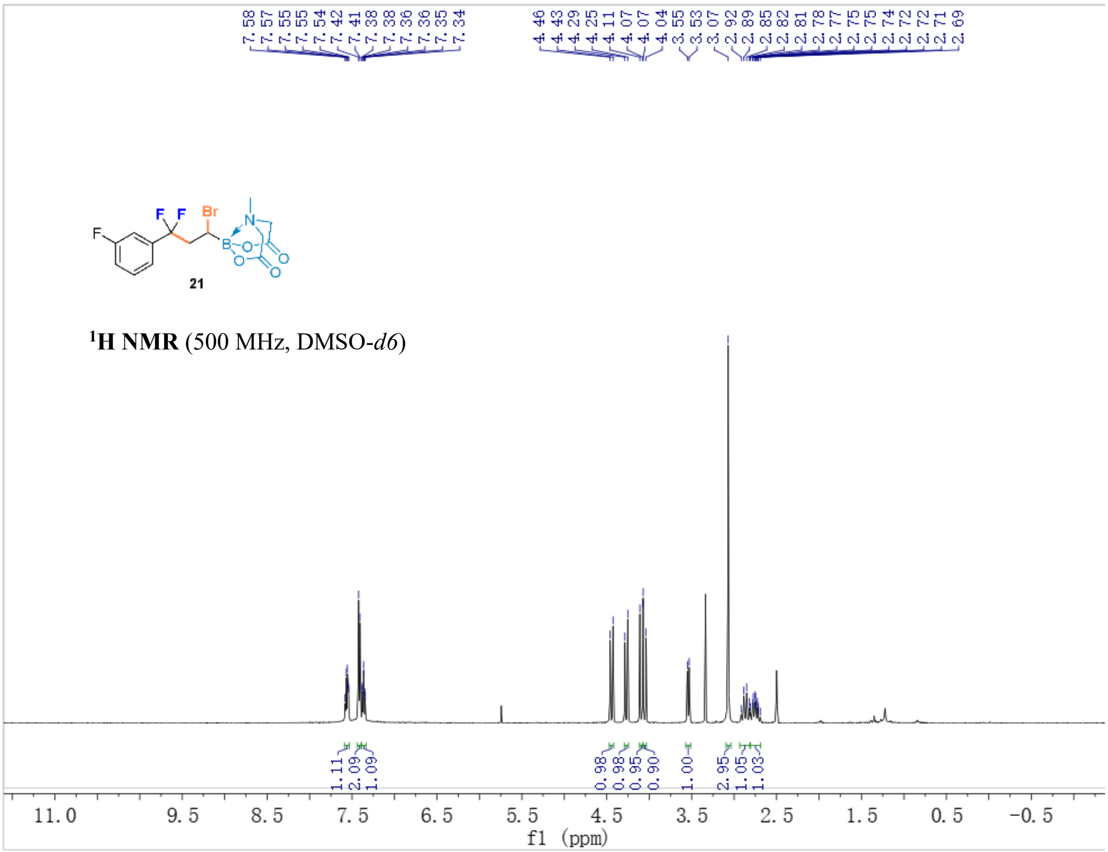


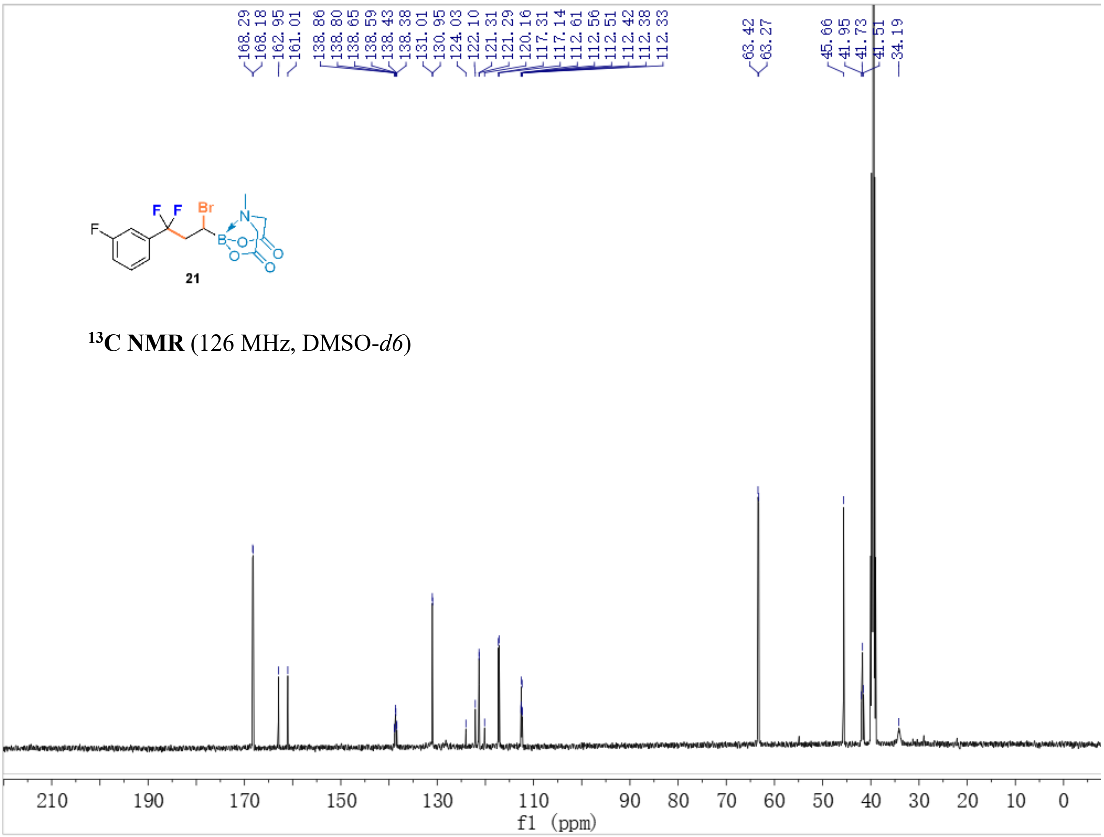


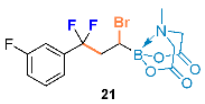

-91.05
-91.69
-91.72
-91.76
-91.79
-92.45
F F Br
N
B O O
O O
Cl
20
19F NMR (376 MHz, DMSO-d6)
2.00
20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190
f1 (ppm)


-9.92
11B NMR (160 MHz, DMSO-d6)
F F Br
N
B O O
O O
Cl
20
110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100
f1 (ppm)

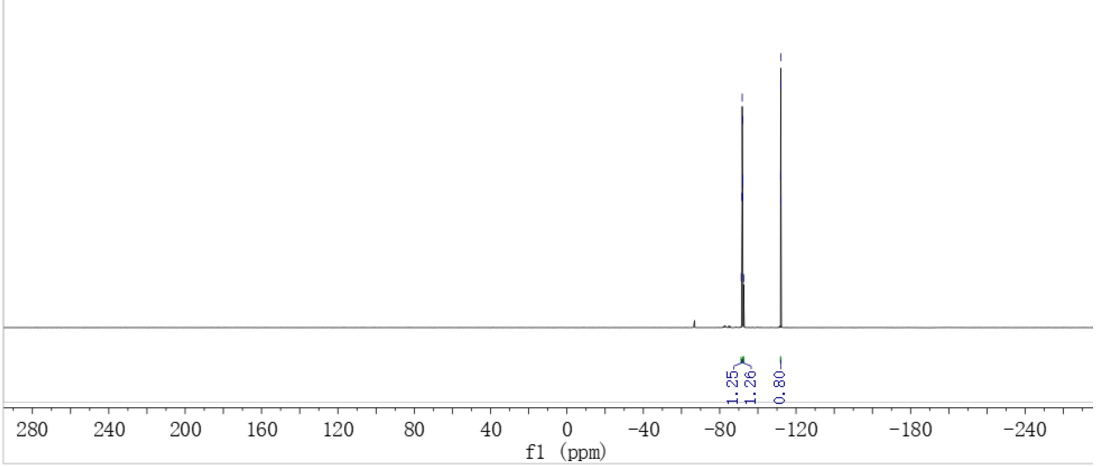
2-(1-bromo-3,3-difluoro-3-(3-fluorophenyl)propyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (21)



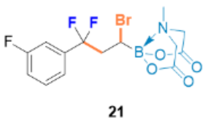


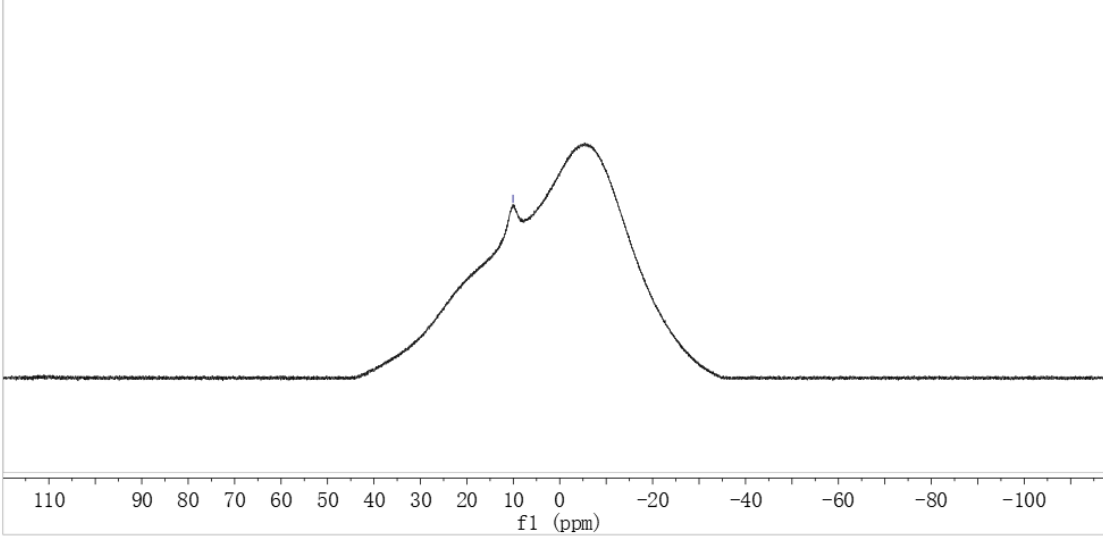


^{19}F NMR (471 MHz, DMSO-*d6*)

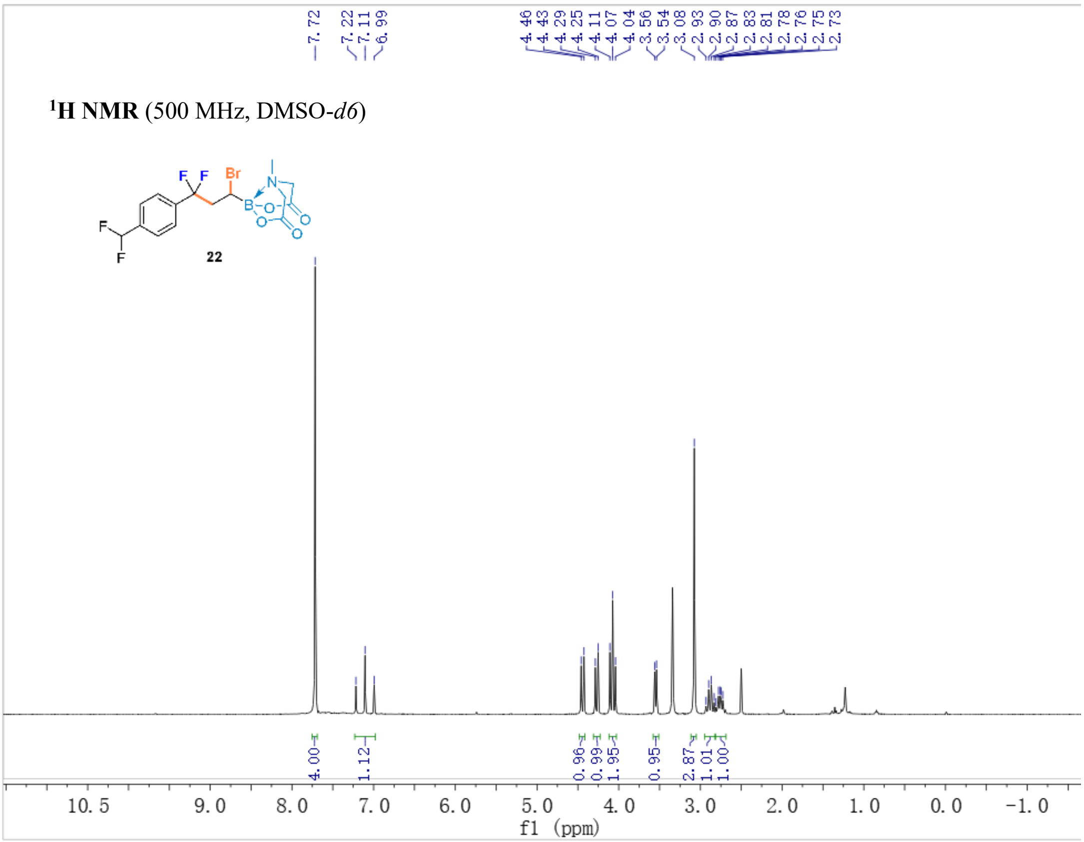


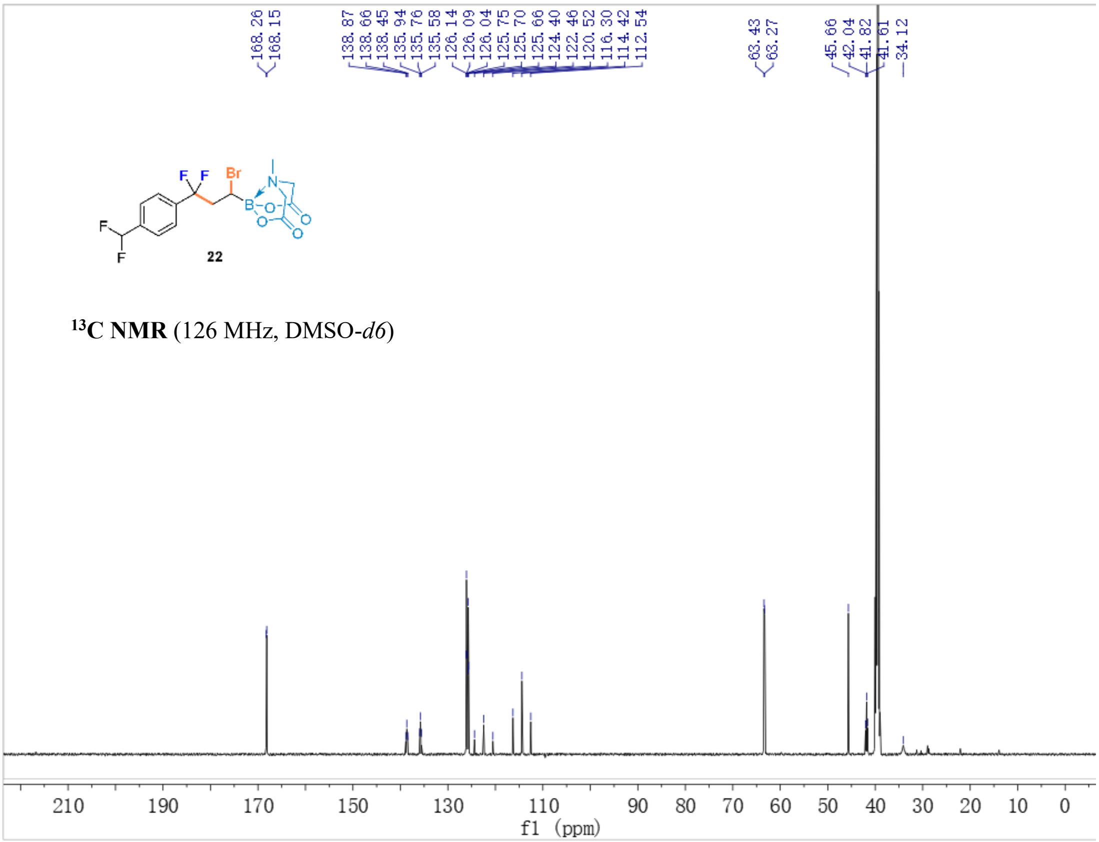
^{11}B NMR (160 MHz, DMSO-*d6*)

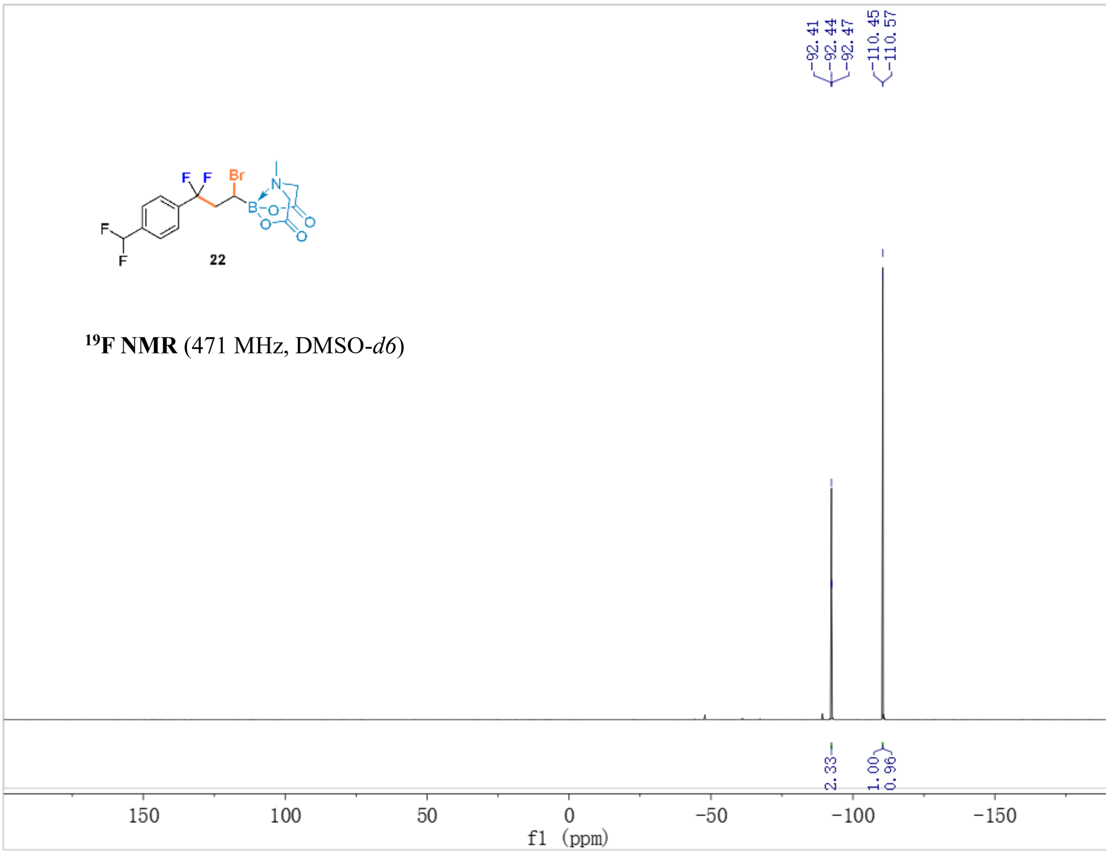


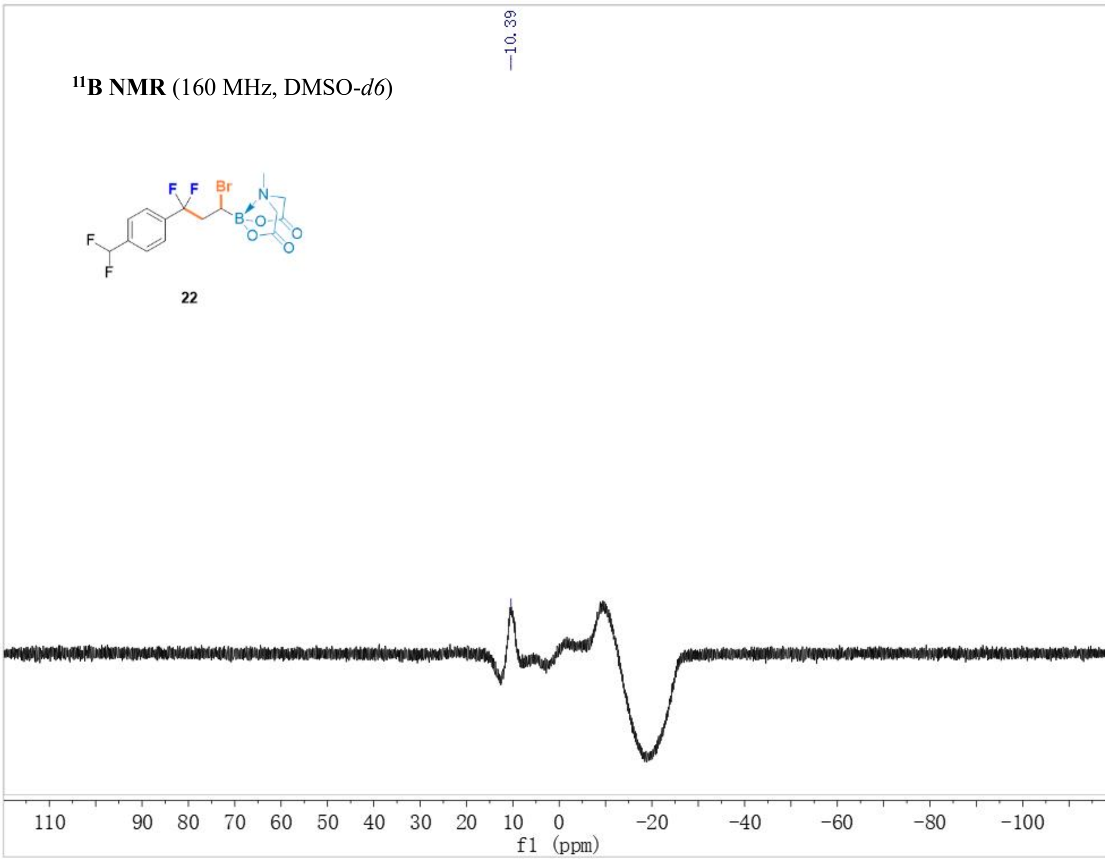


2-(1-bromo-3-(4-(difluoromethyl)phenyl)-3,3-difluoropropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (22)

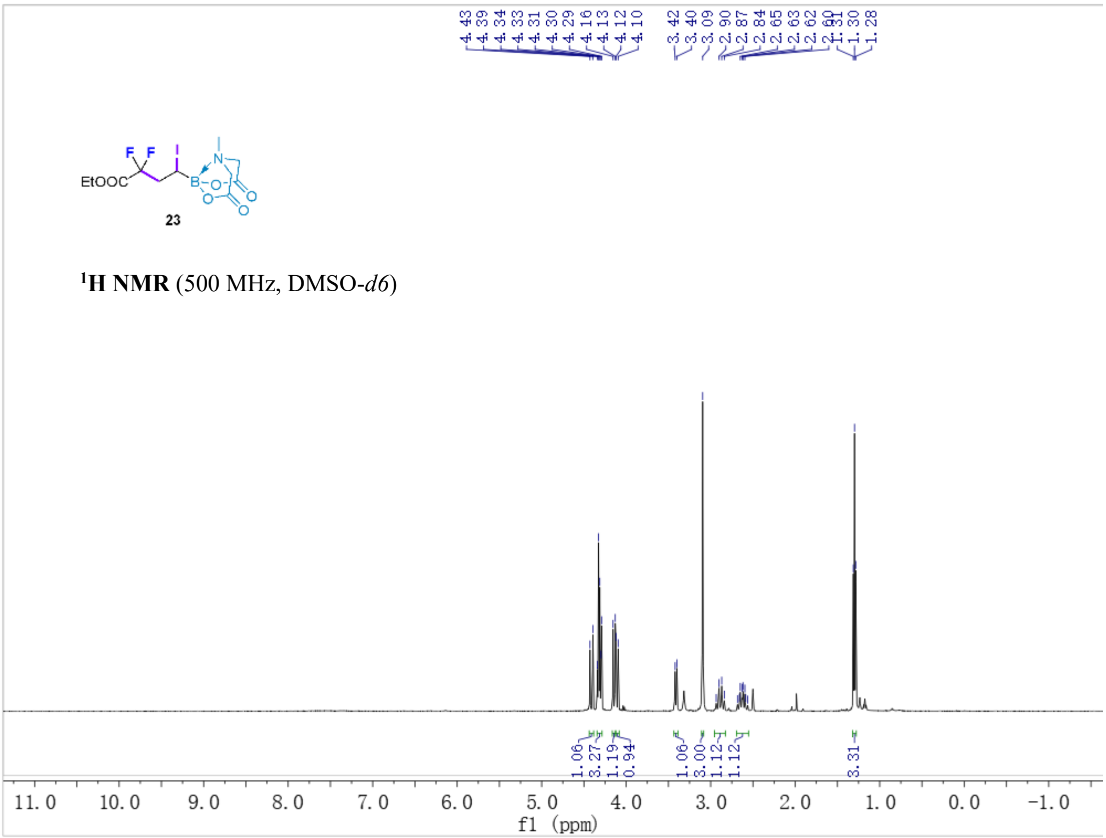


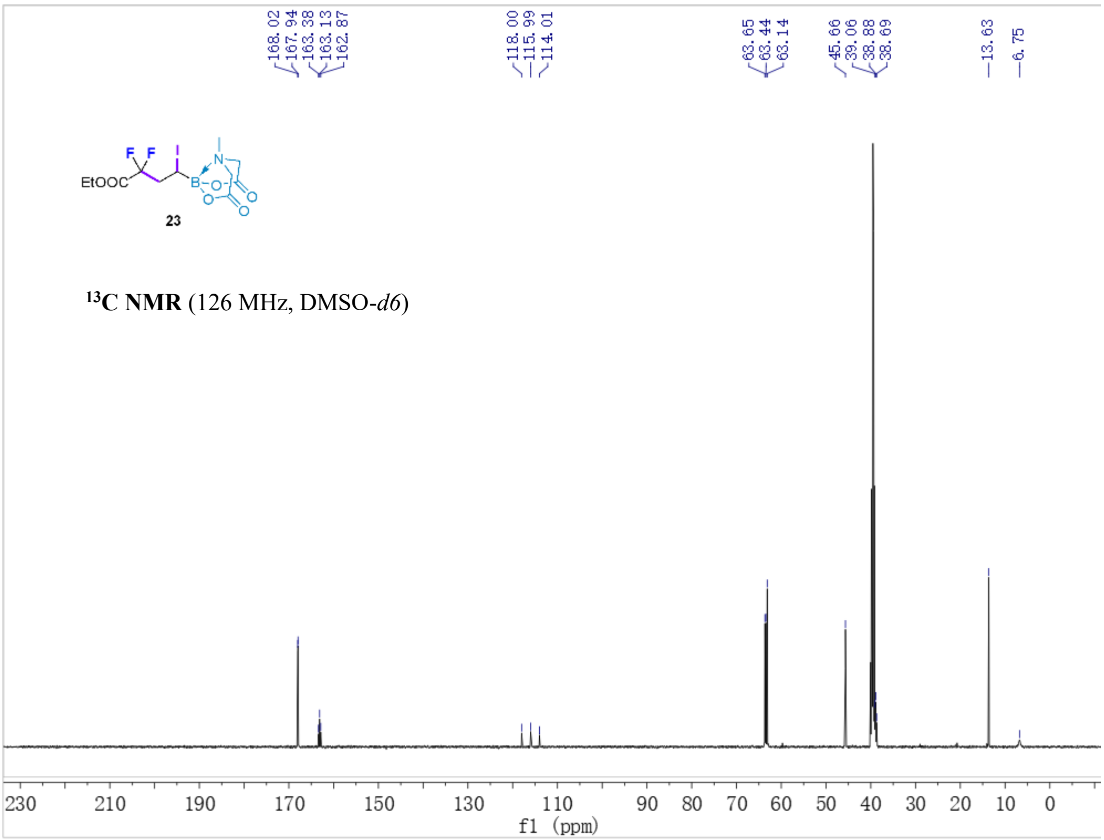


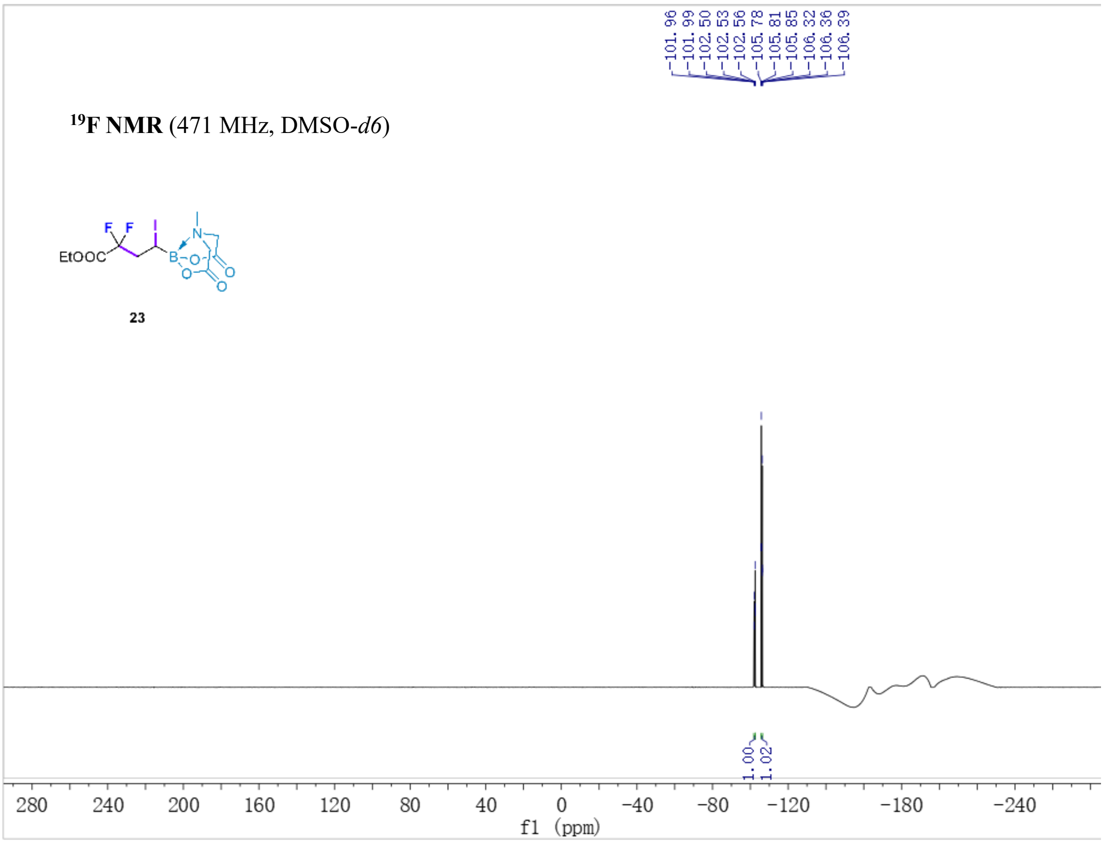

-92.41
-92.44
-92.47
-110.45
-110.57
F
F
Br
N
B
O
O
O
O
F
F
22
19F NMR (471 MHz, DMSO-d6)
2.33
1.00
0.96
150
100
50
0
-50
-100
-150
f1 (ppm)

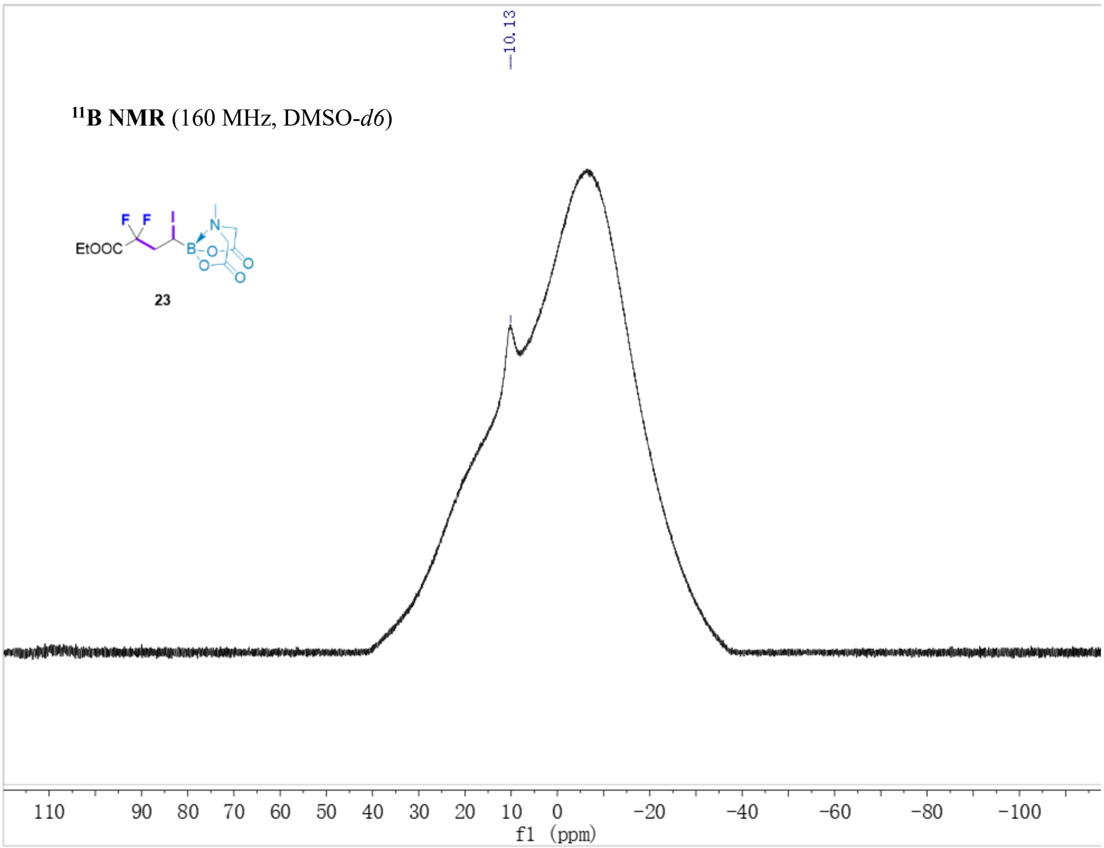

-10.39
11B NMR (160 MHz, DMSO-d6)
F
F
Br
N
B
O
O
O
O
F
F
22
110
90
80
70
60
50
40
30
20
10
0
-20
-40
-60
-80
-100
f1 (ppm)

Ethyl 2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoate (23)

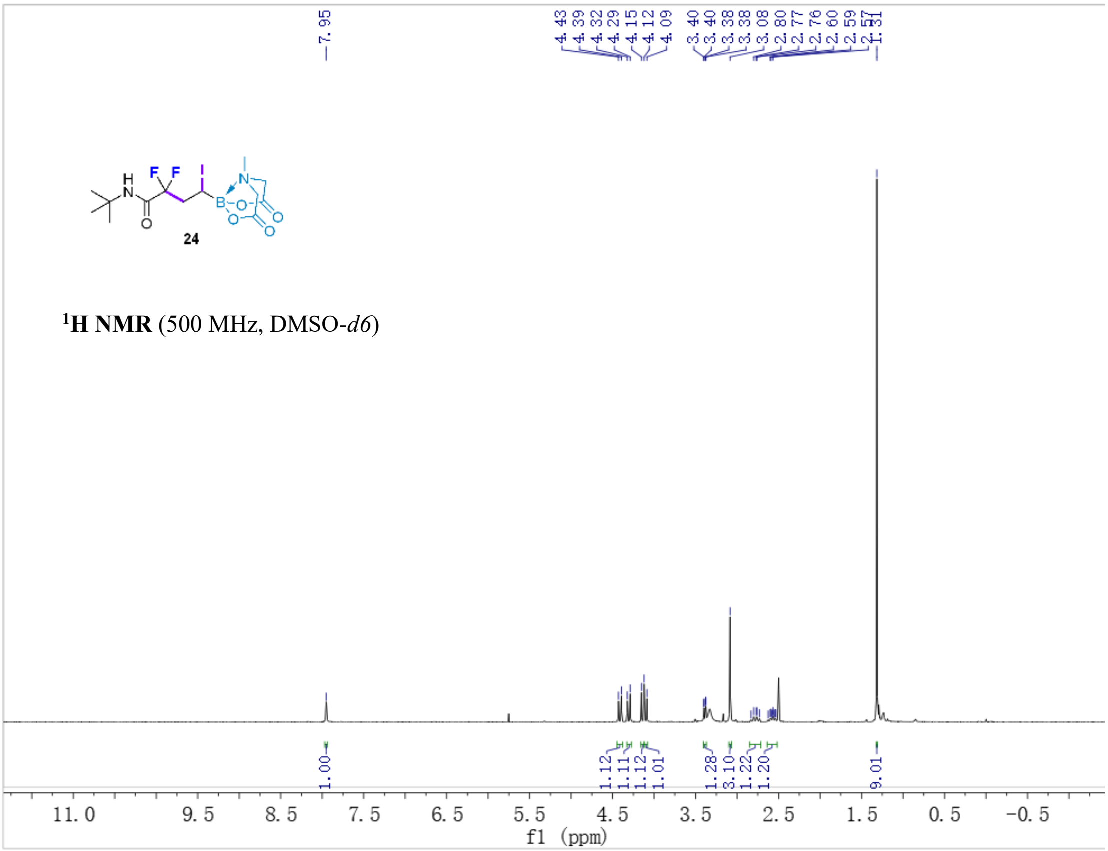


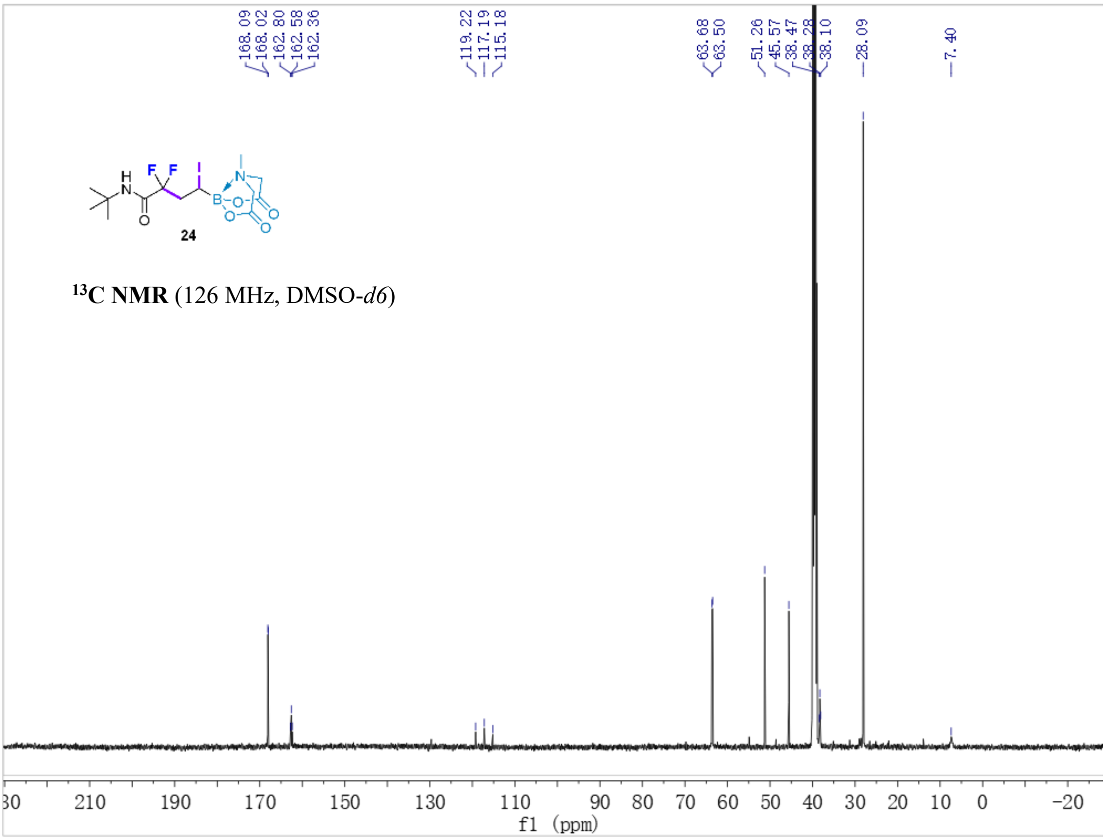


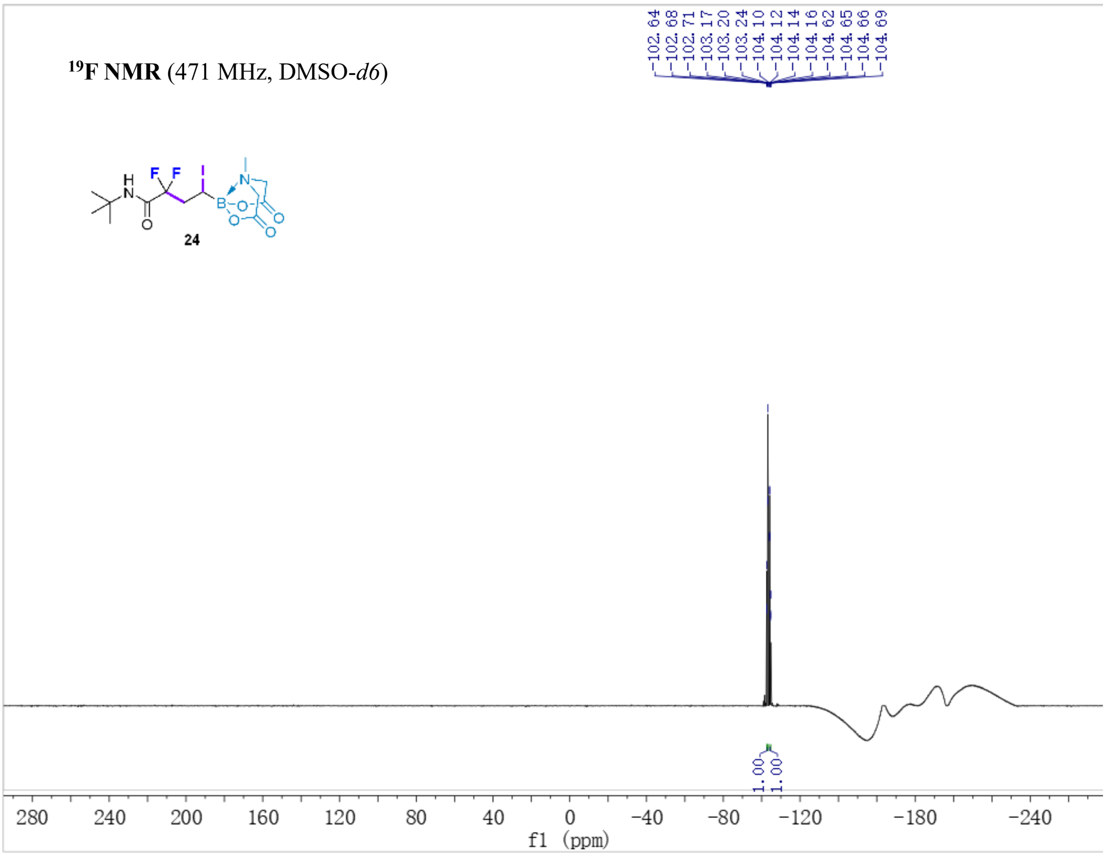

-101.96
-101.99
-102.50
-102.53
-102.56
-105.78
-105.81
-105.85
-106.32
-106.36
-106.39
19F NMR (471 MHz, DMSO-d6)
EtOOC
F F
I
N
B
O
O
O
O
23
1.00
1.02
280 240 200 160 120 80 40 0 -40 -80 -120 -180 -240
f1 (ppm)


-10.13
11B NMR (160 MHz, DMSO-d6)
EtOOC
F F
I
N
B
O
O
O
O
23
110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100
f1 (ppm)

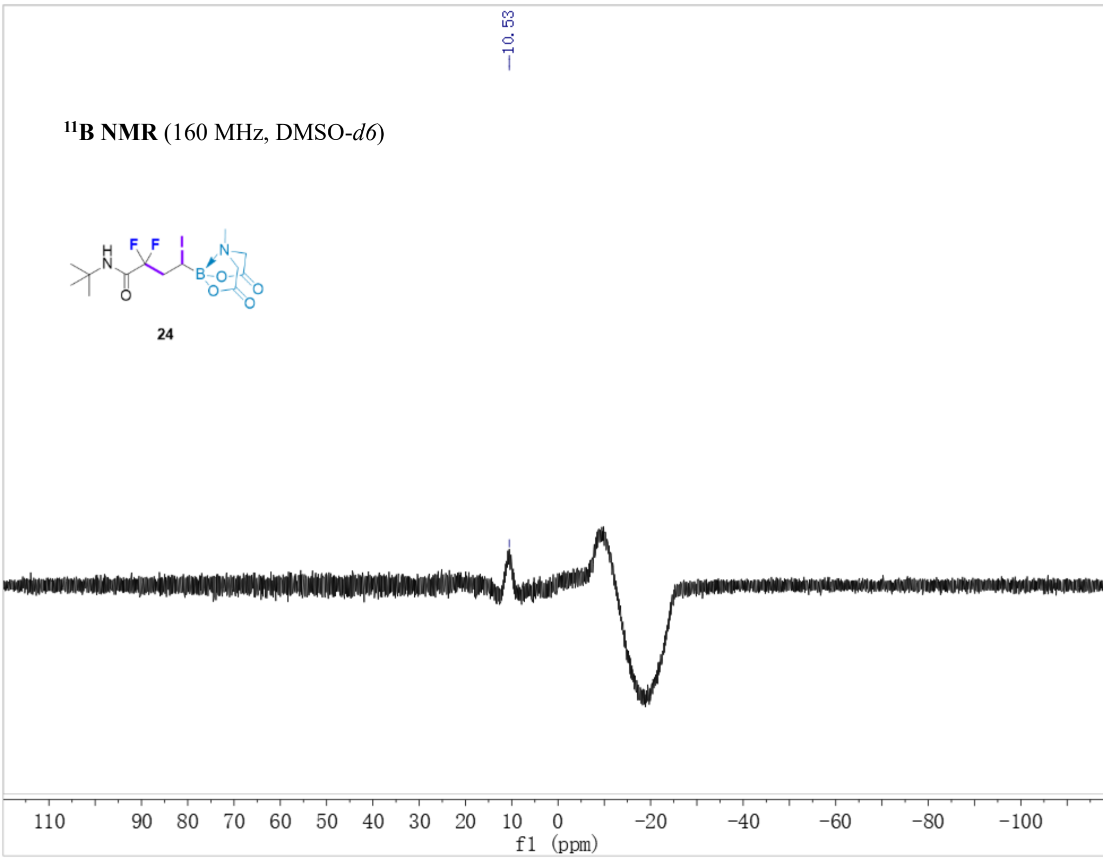
***N*-(*tert*-butyl)-2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (24)**





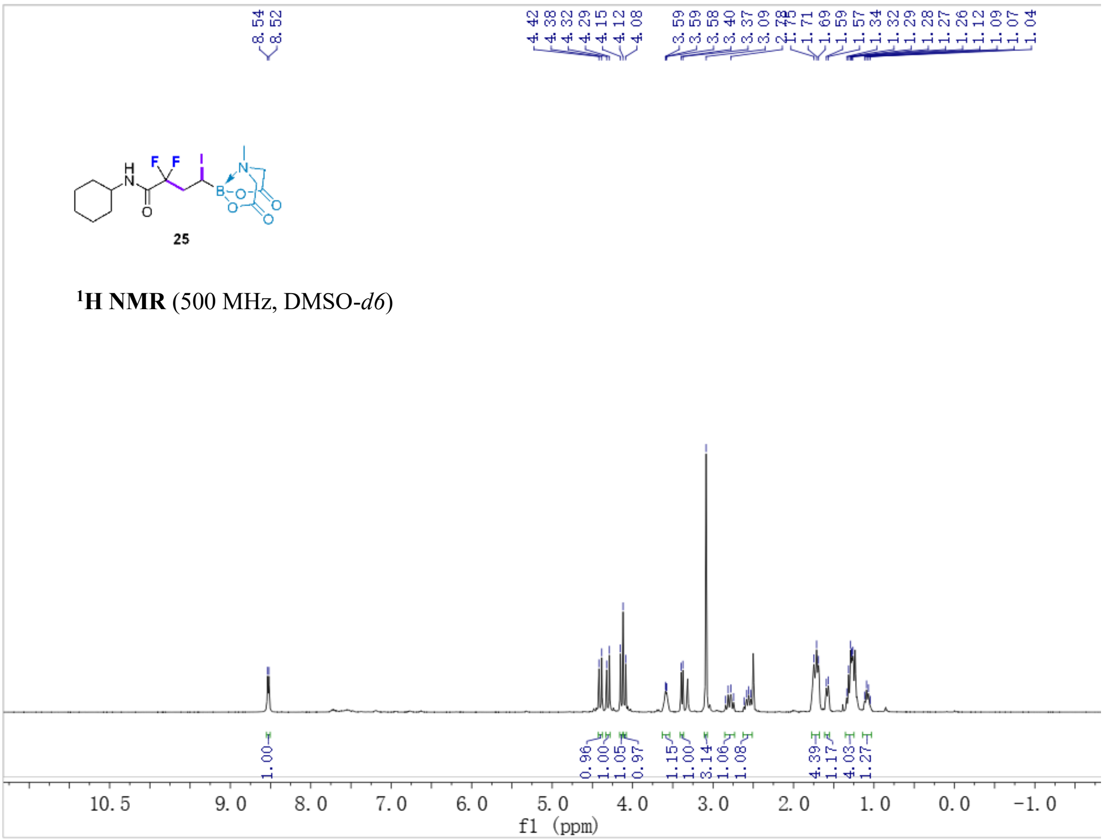


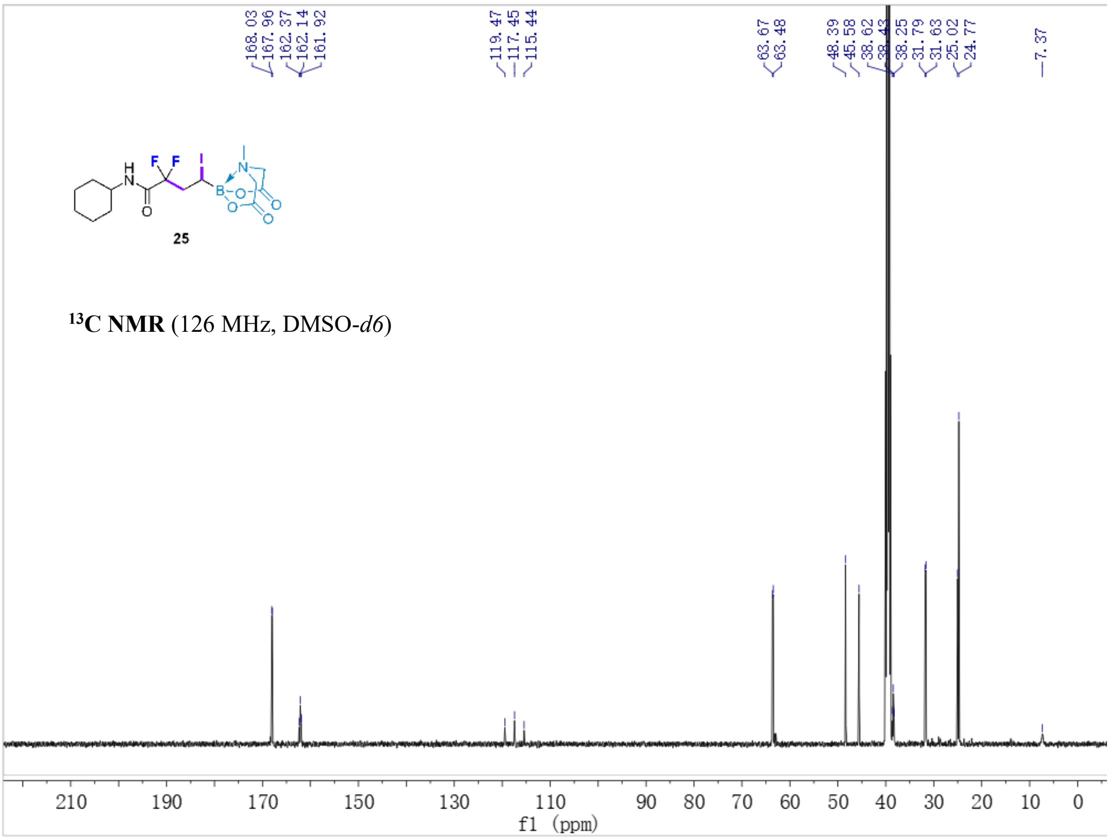
19F NMR (471 MHz, DMSO-d6)
24
-102.64
-102.68
-102.71
-103.17
-103.20
-103.24
-104.10
-104.12
-104.14
-104.16
-104.62
-104.65
-104.66
-104.69
1.00
1.00
280 240 200 160 120 80 40 0 -40 -80 -120 -180 -240
f1 (ppm)

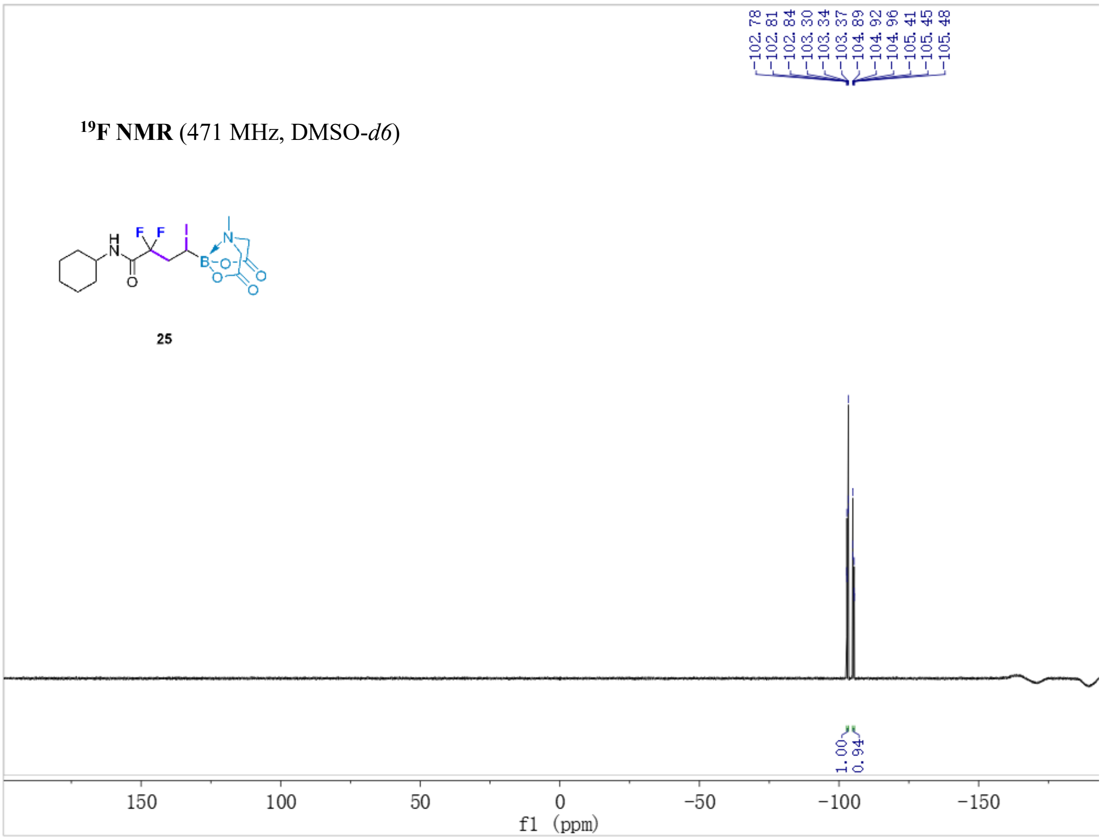


10.53
11B NMR (160 MHz, DMSO-d6)
24
110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100
f1 (ppm)

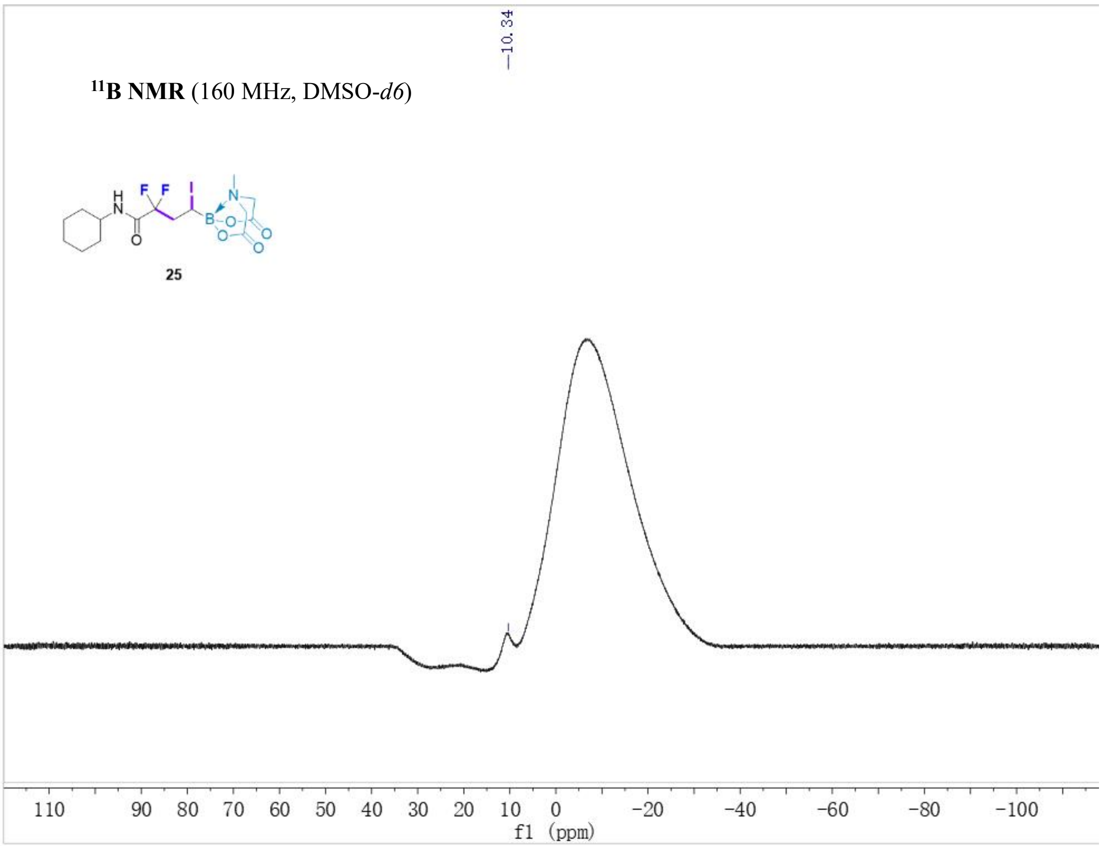
***N*-cyclohexyl-2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (25)**





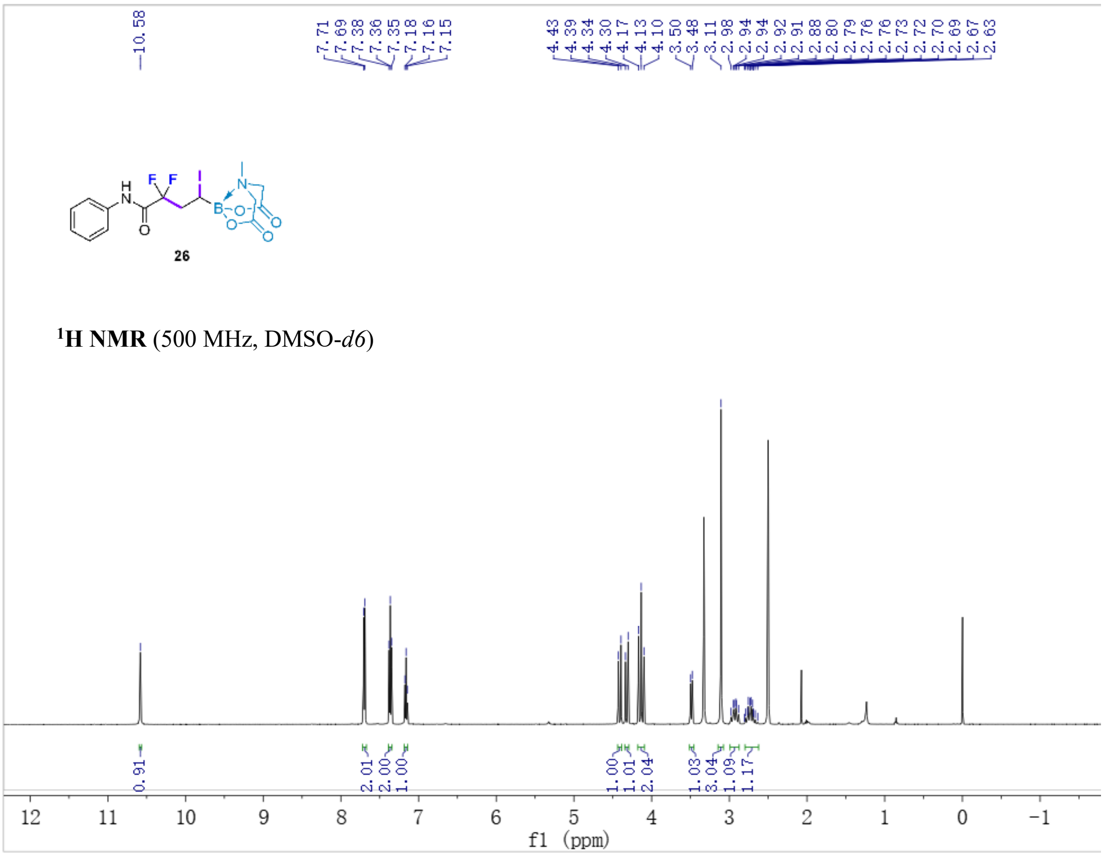


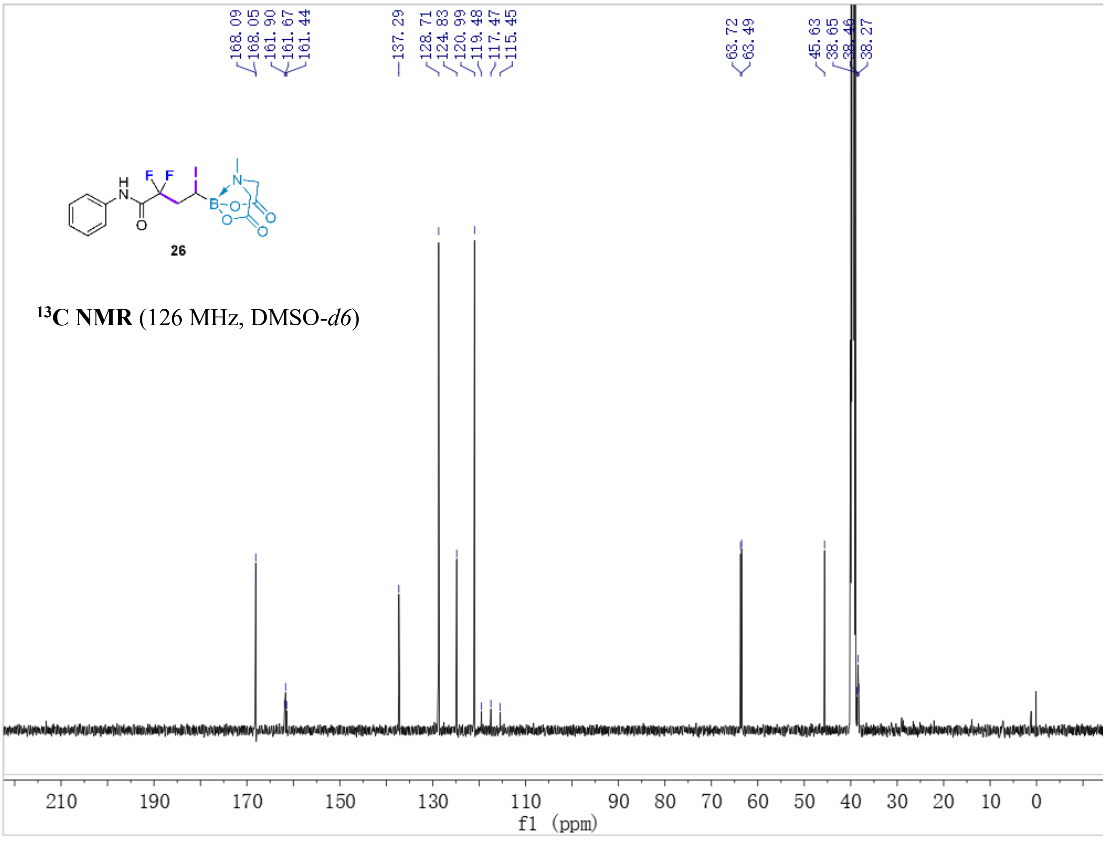
-102.78
-102.81
-102.84
-103.30
-103.34
-103.37
-104.89
-104.92
-104.96
-105.41
-105.45
-105.48
^{19}F NMR (471 MHz, DMSO-*d6*)
25
1.00
0.94
150
100
50
0
-50
-100
-150
f1 (ppm)



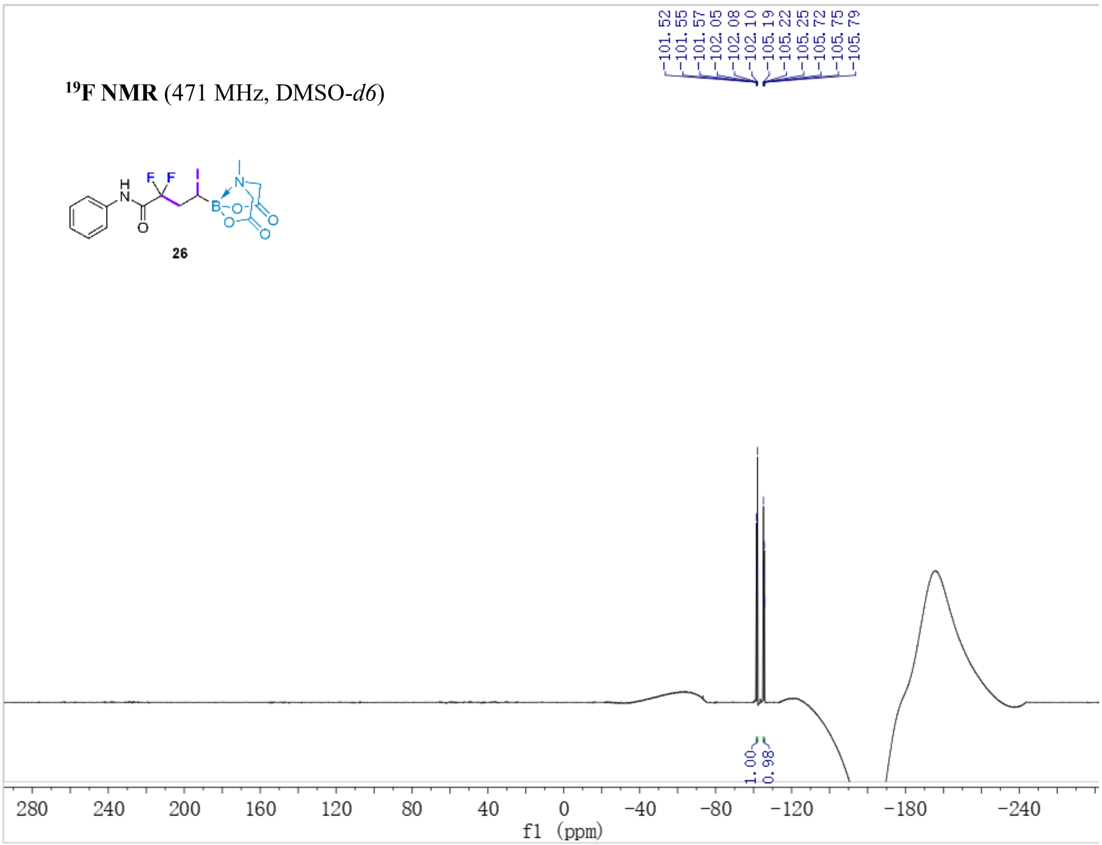
-10.34
^{11}B NMR (160 MHz, DMSO-*d6*)
25
110
90
80
70
60
50
40
30
20
10
0
-20
-40
-60
-80
-100
f1 (ppm)

2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-*N*-phenylbutanamide (26)

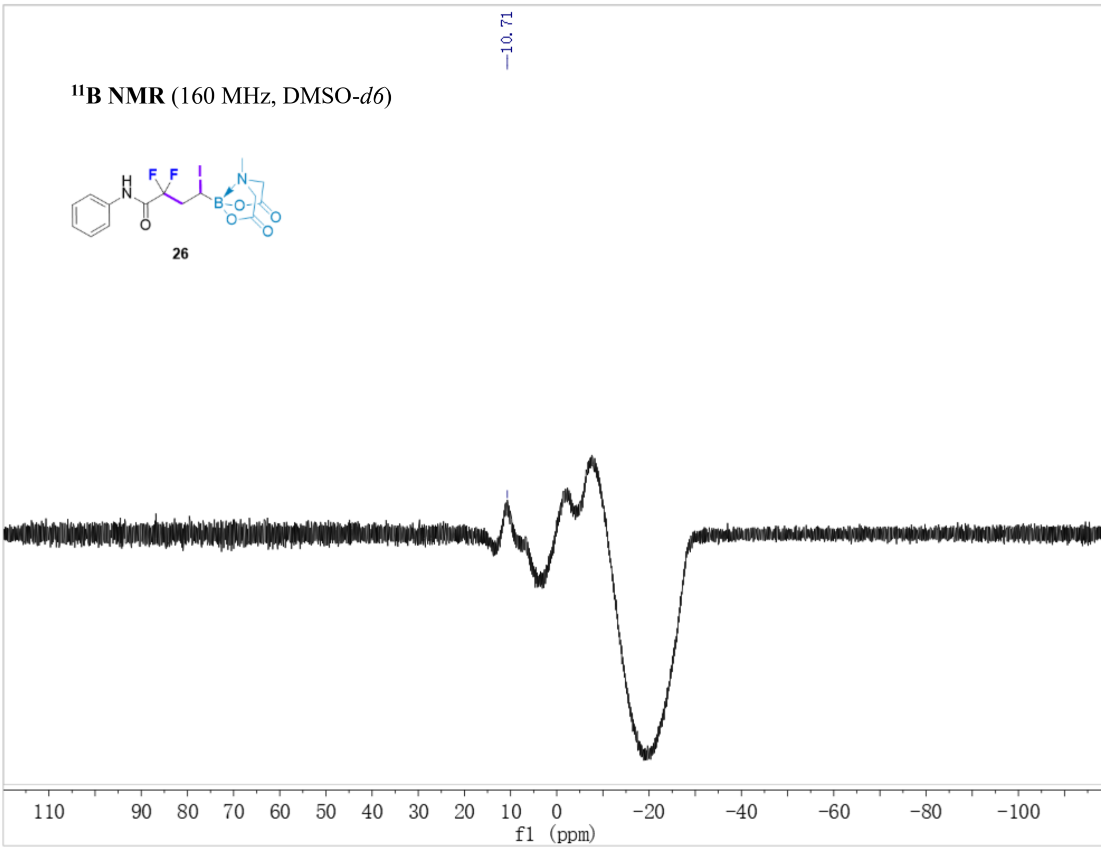




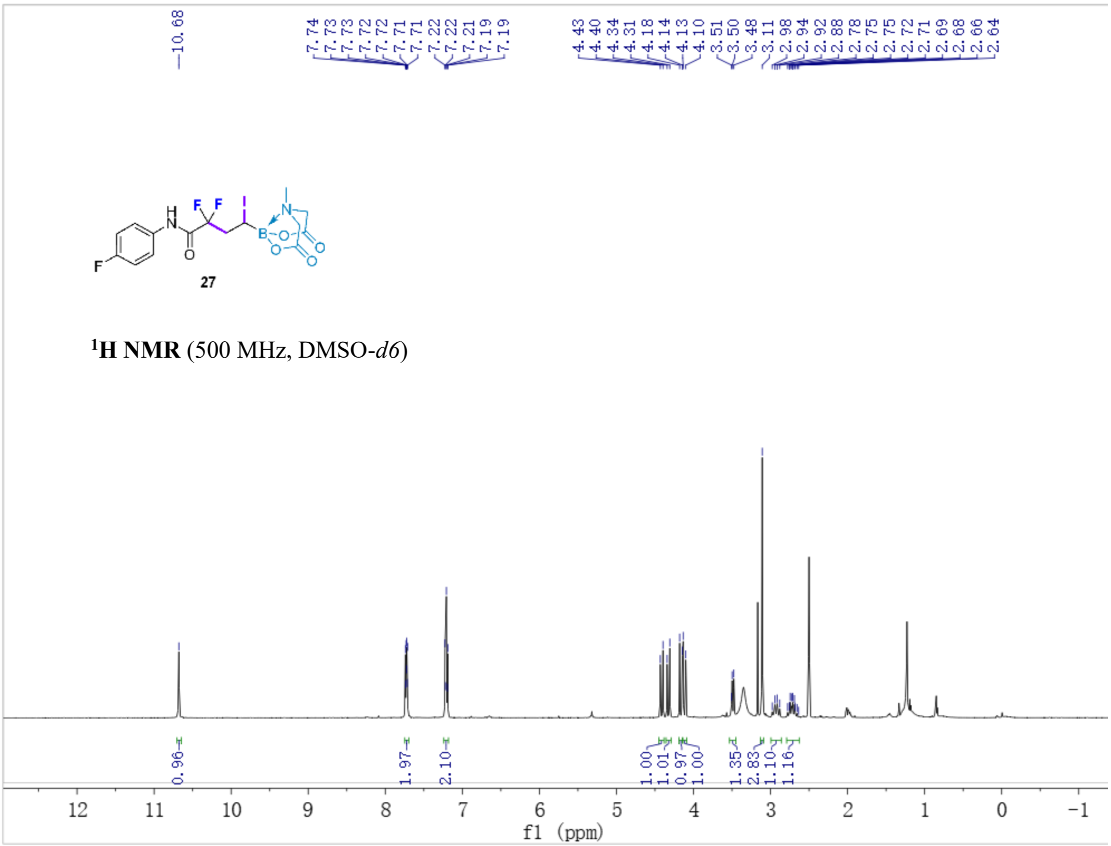
^{19}F NMR (471 MHz, DMSO-*d6*)

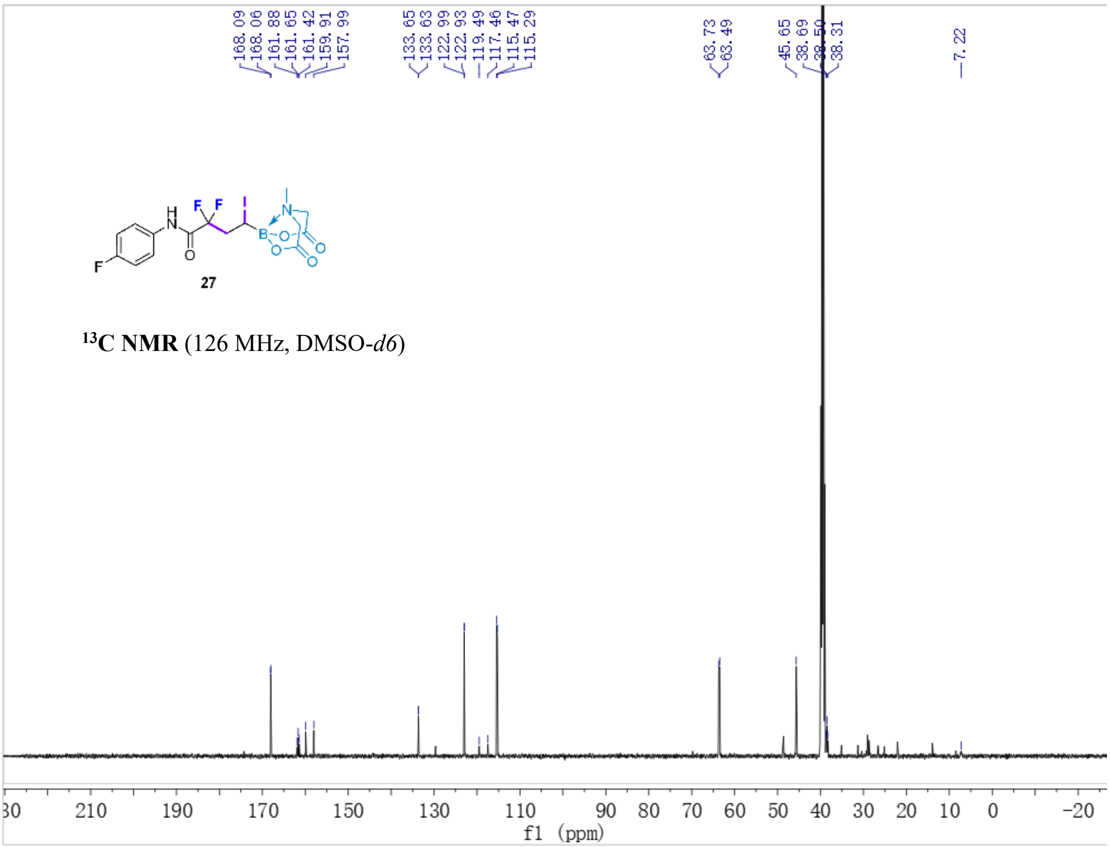


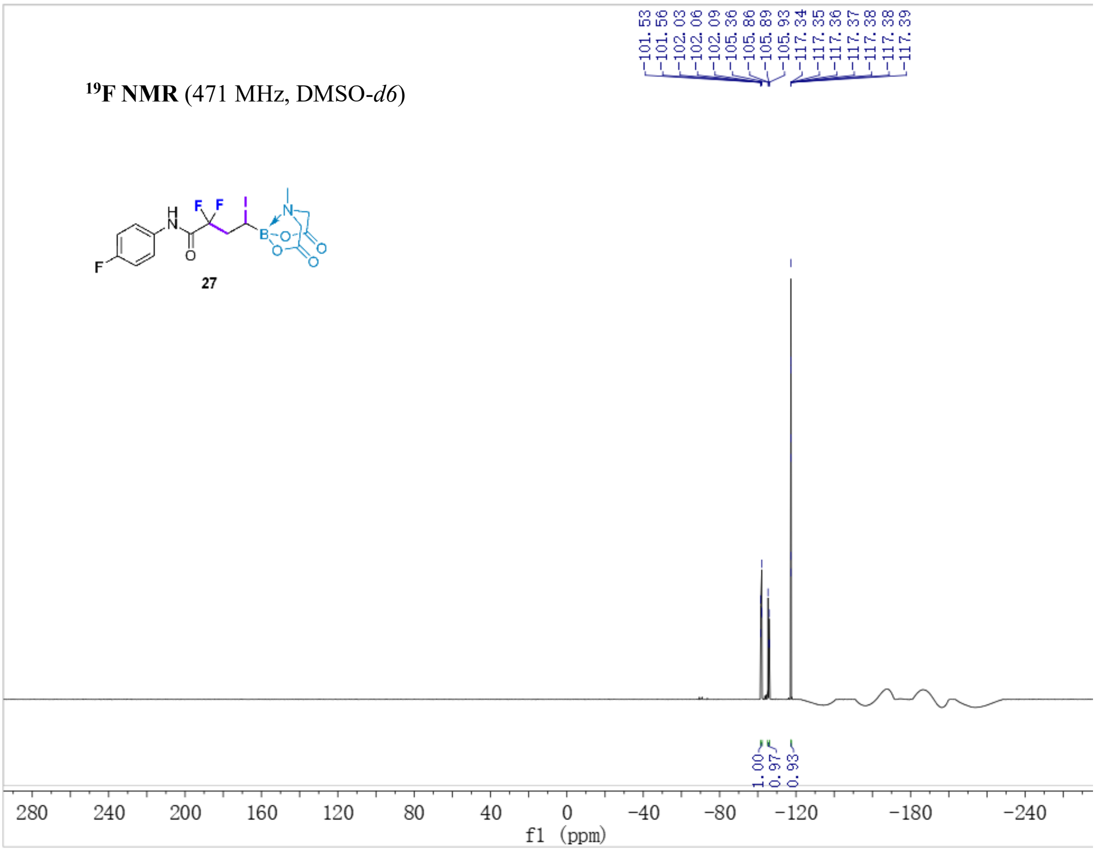
^{11}B NMR (160 MHz, DMSO-*d6*)



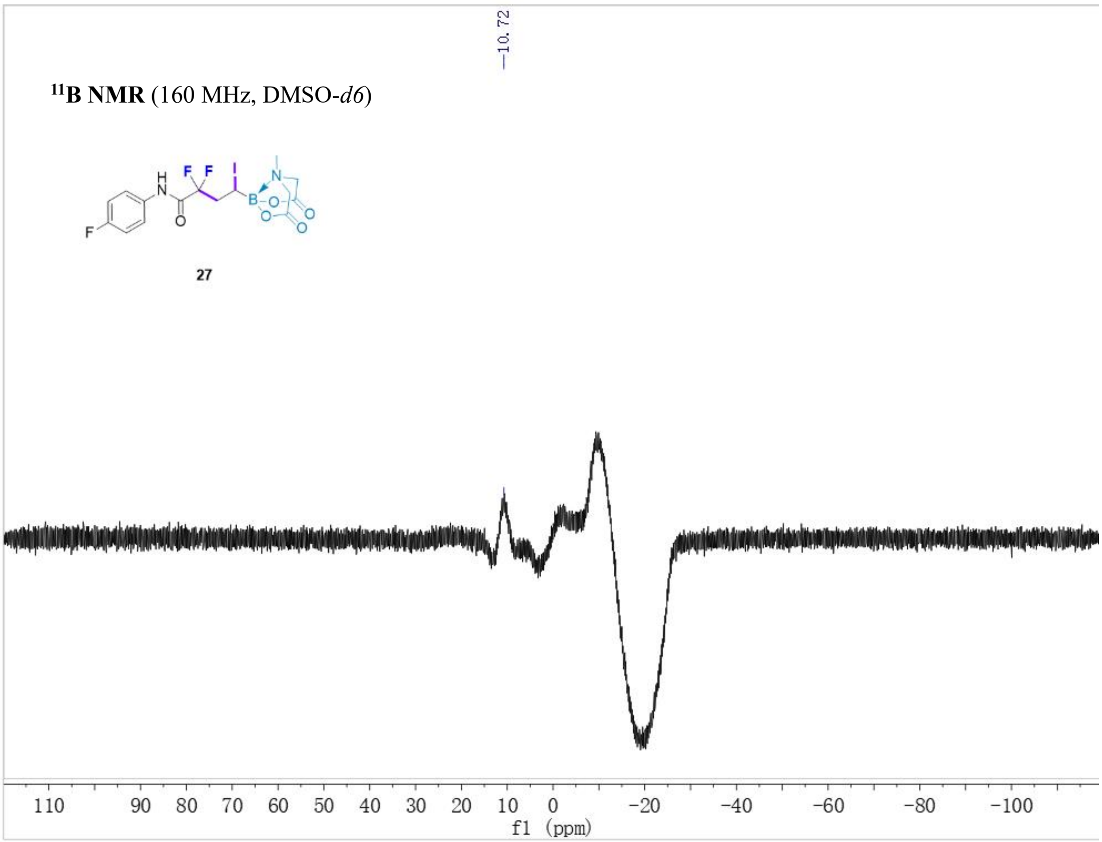
2,2-difluoro-*N*-(4-fluorophenyl)-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (27)





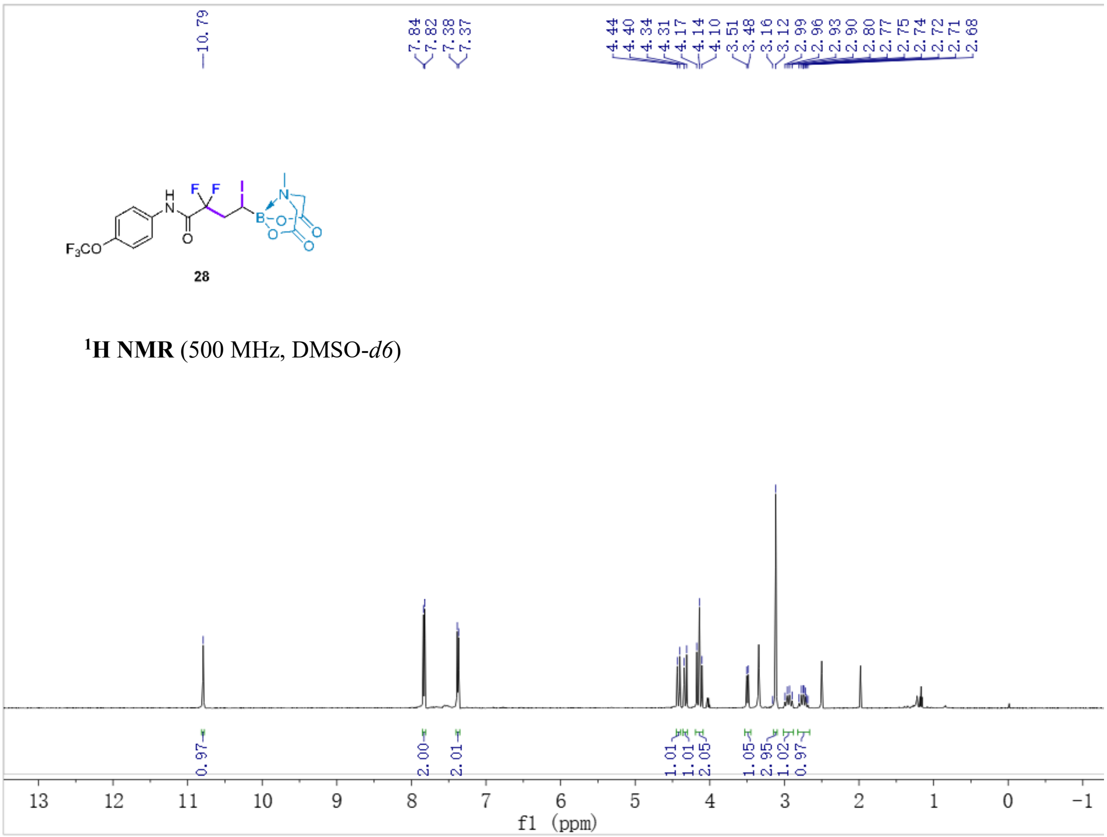


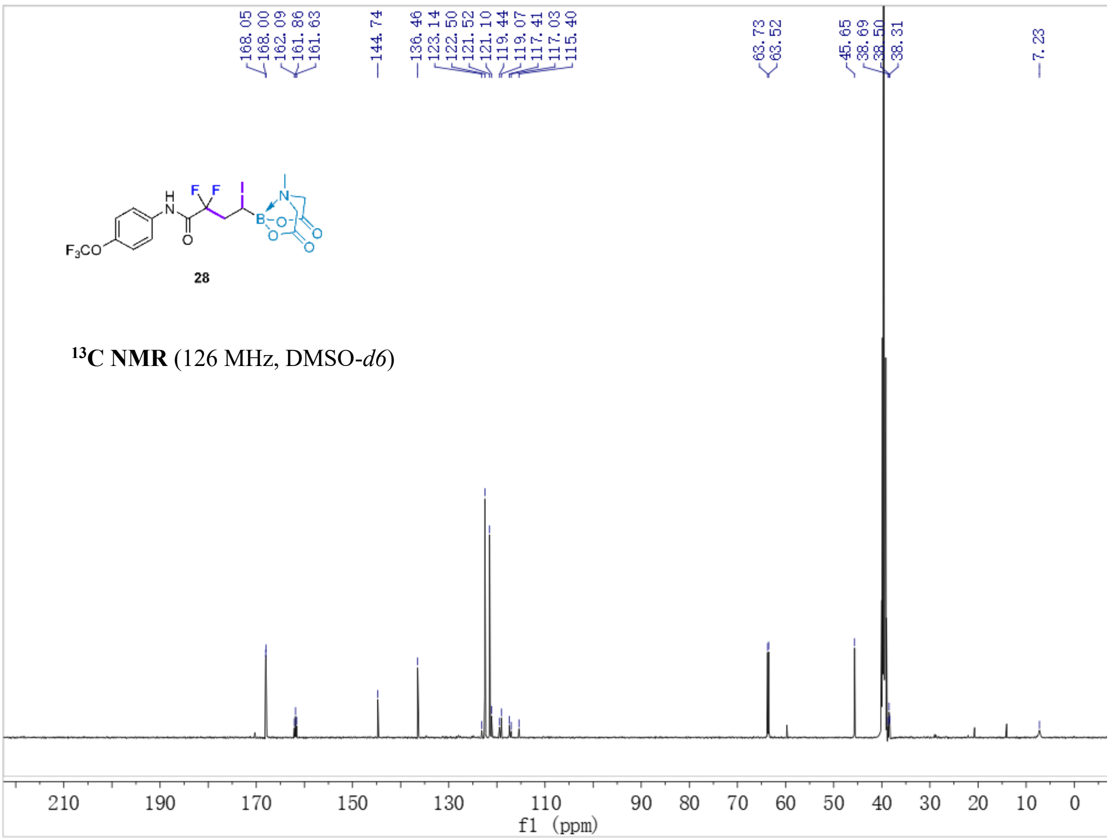
19F NMR (471 MHz, DMSO-d6)
27
-101.53
-101.56
-102.03
-102.06
-102.09
-105.36
-105.86
-105.89
-105.93
-117.34
-117.35
-117.36
-117.37
-117.38
-117.38
-117.39
1.00
0.97
0.93
280 240 200 160 120 80 40 0 −40 −80 −120 −180 −240
f1 (ppm)

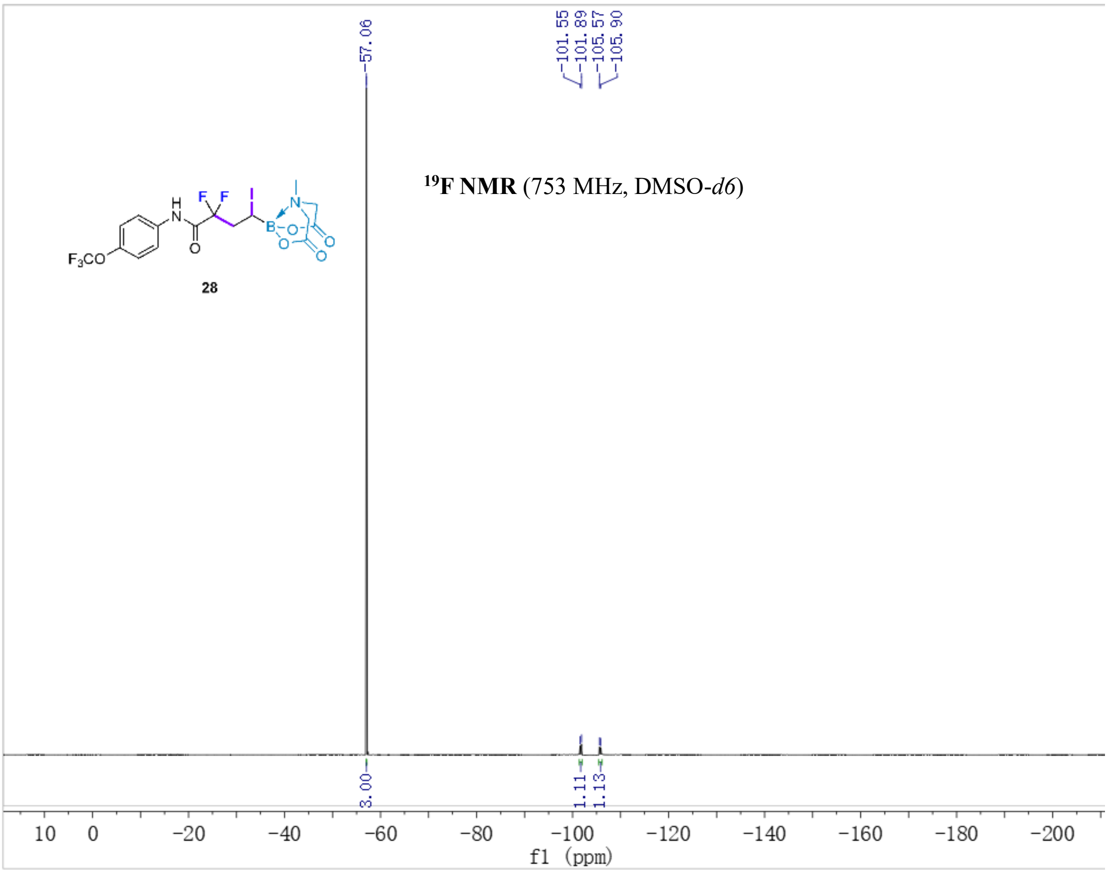


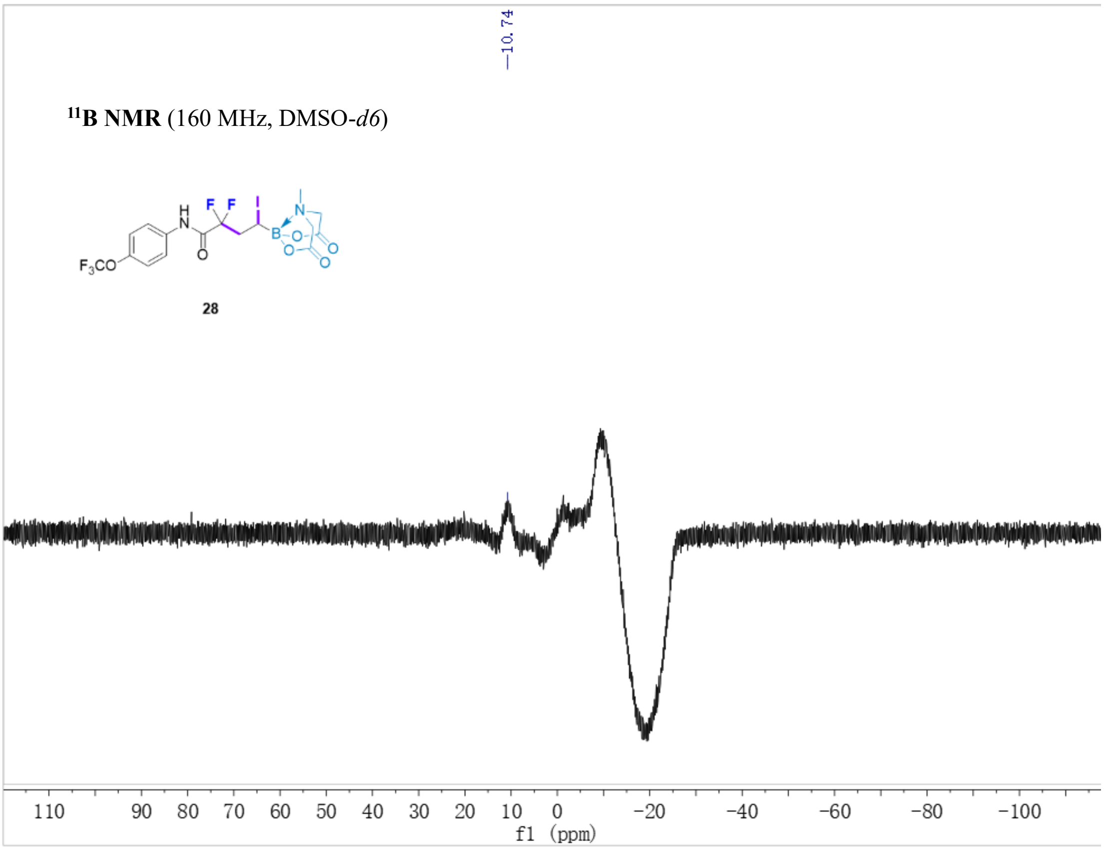
11B NMR (160 MHz, DMSO-d6)
27
-10.72
110 90 80 70 60 50 40 30 20 10 0 −20 −40 −60 −80 −100
f1 (ppm)

2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-*N*-(4-(trifluoromethoxy)phenyl)butanamide (28)

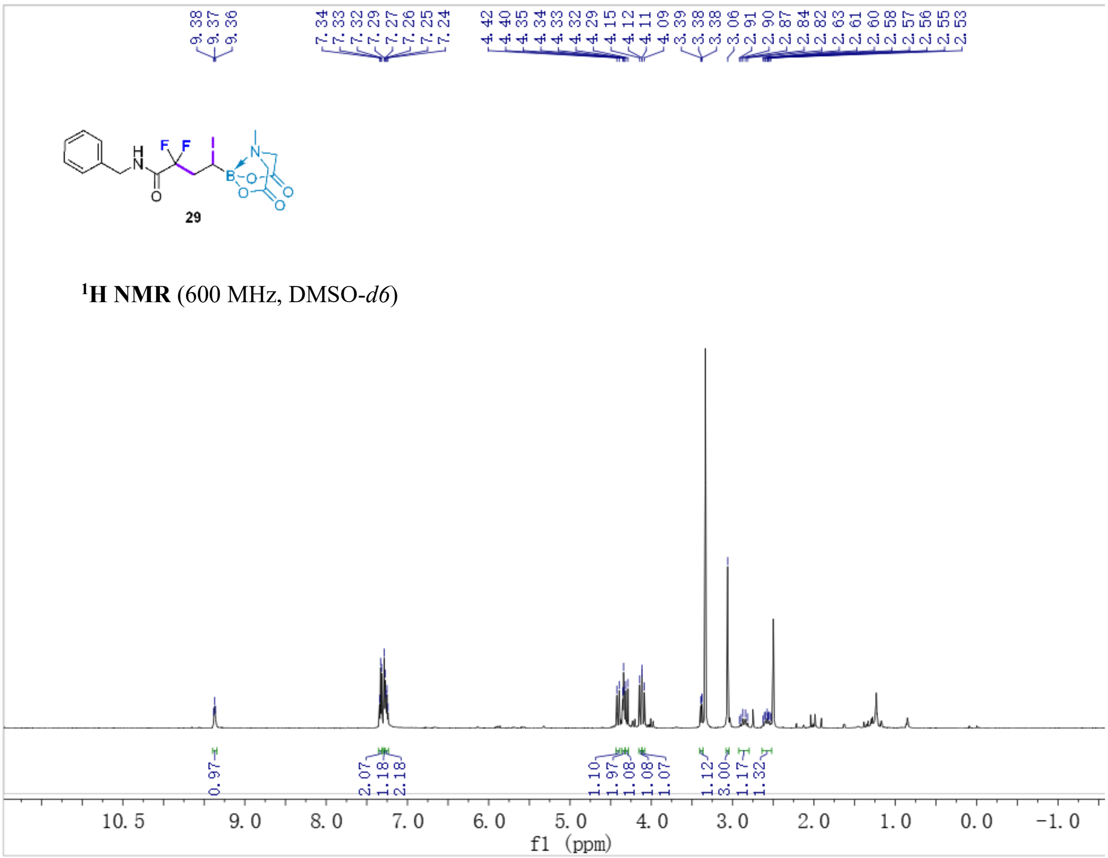


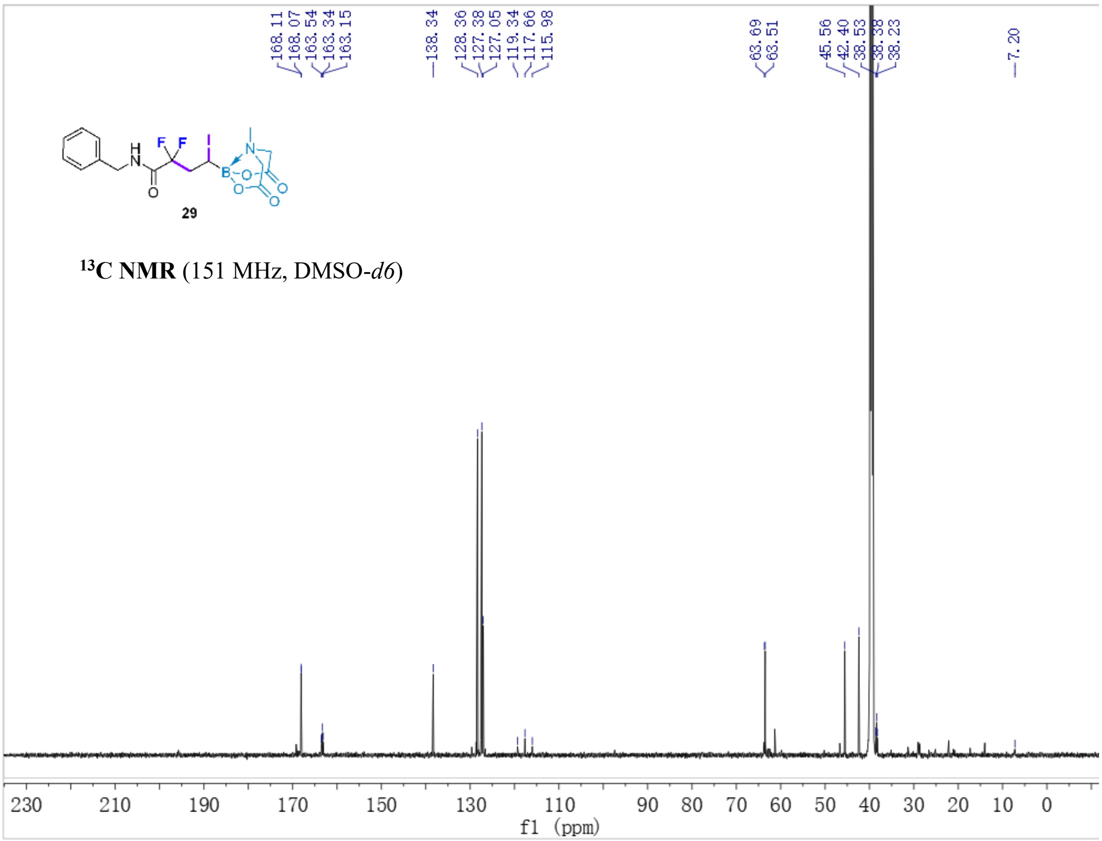


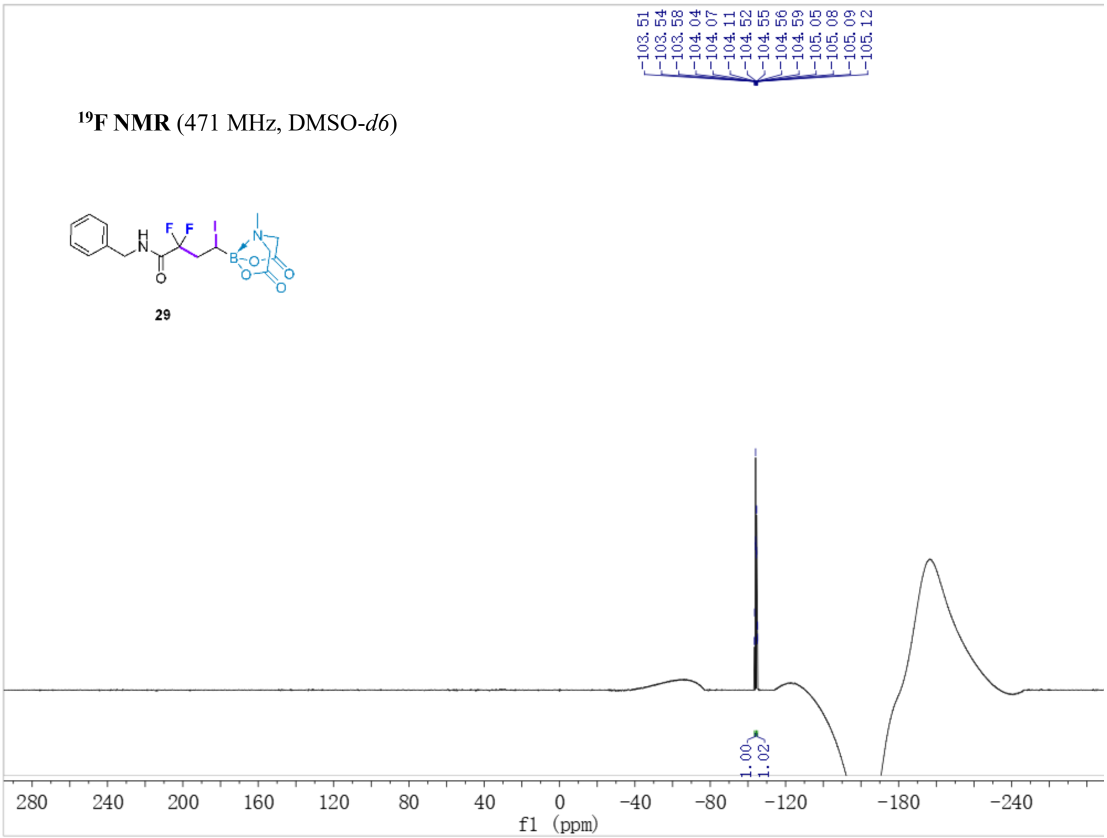

^{19}F NMR (753 MHz, DMSO-$d6$)
-57.06
-101.55
-101.89
-105.57
-105.90
3.00
1.11
1.13
28
f1 (ppm)

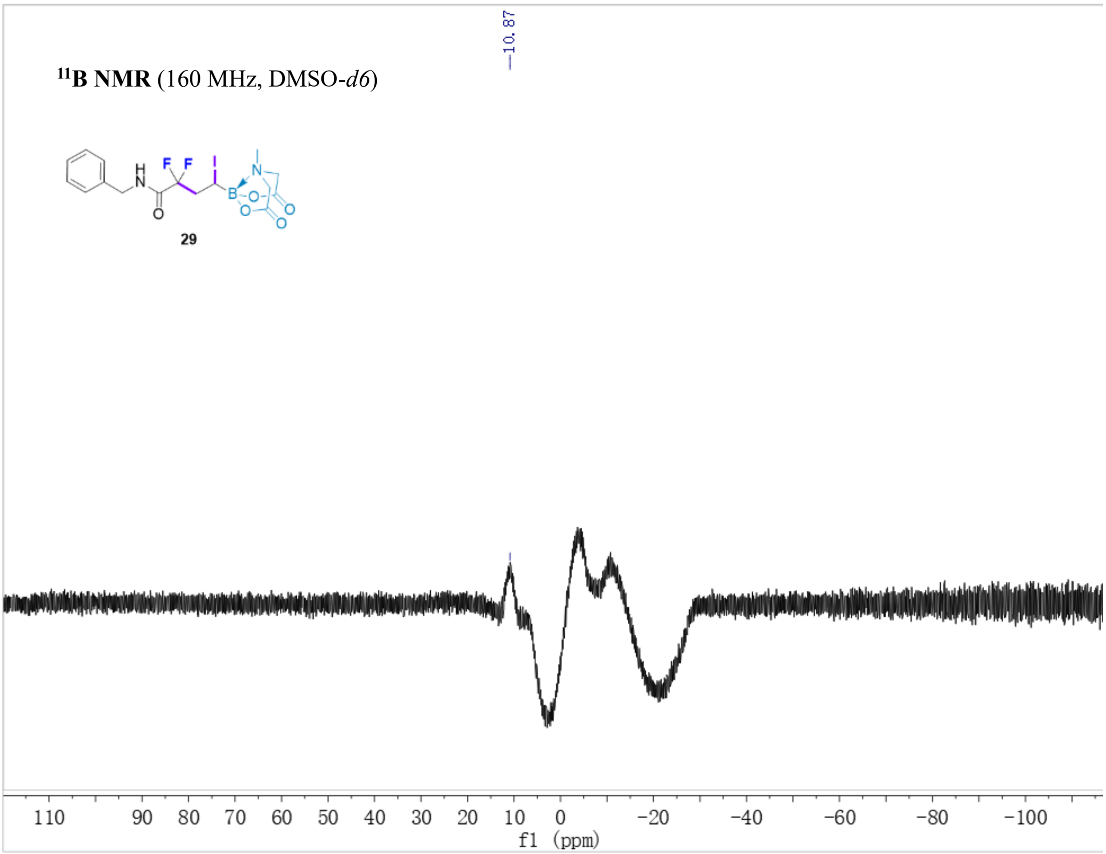

^{11}B NMR (160 MHz, DMSO-$d6$)
-10.74
28
f1 (ppm)

***N*-benzyl-2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (29)**

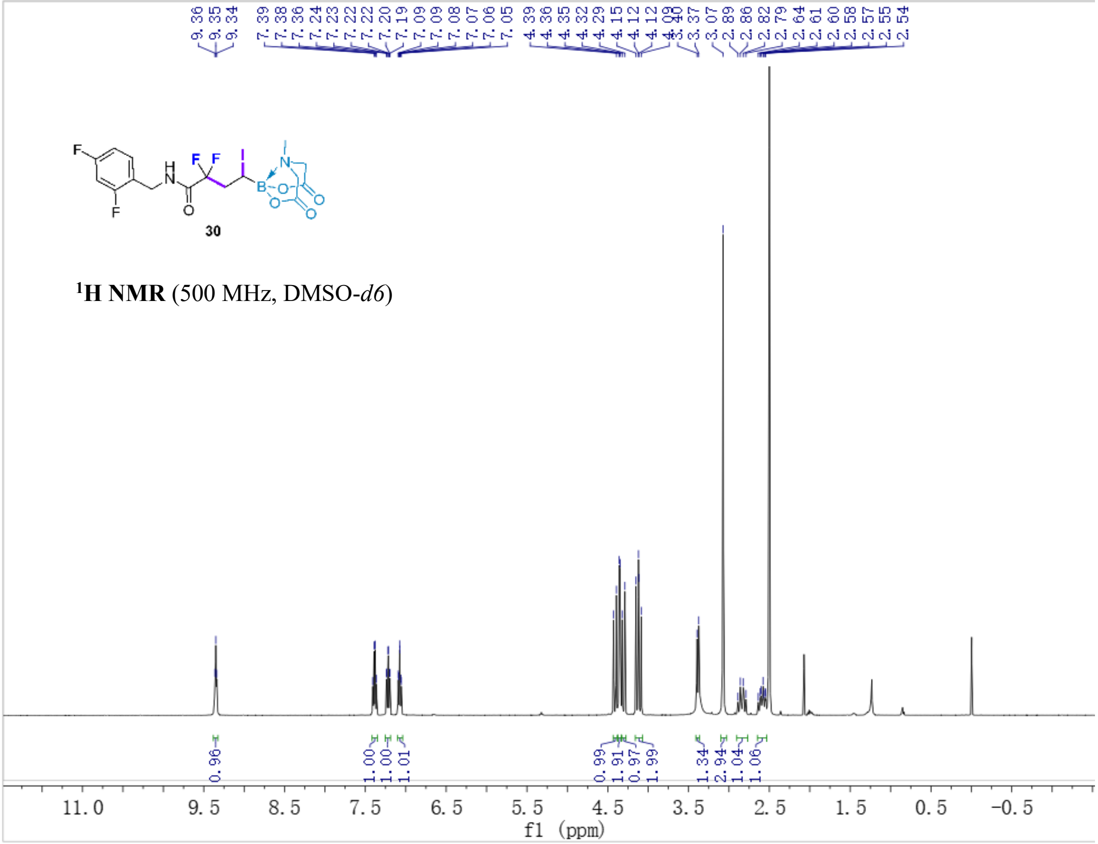


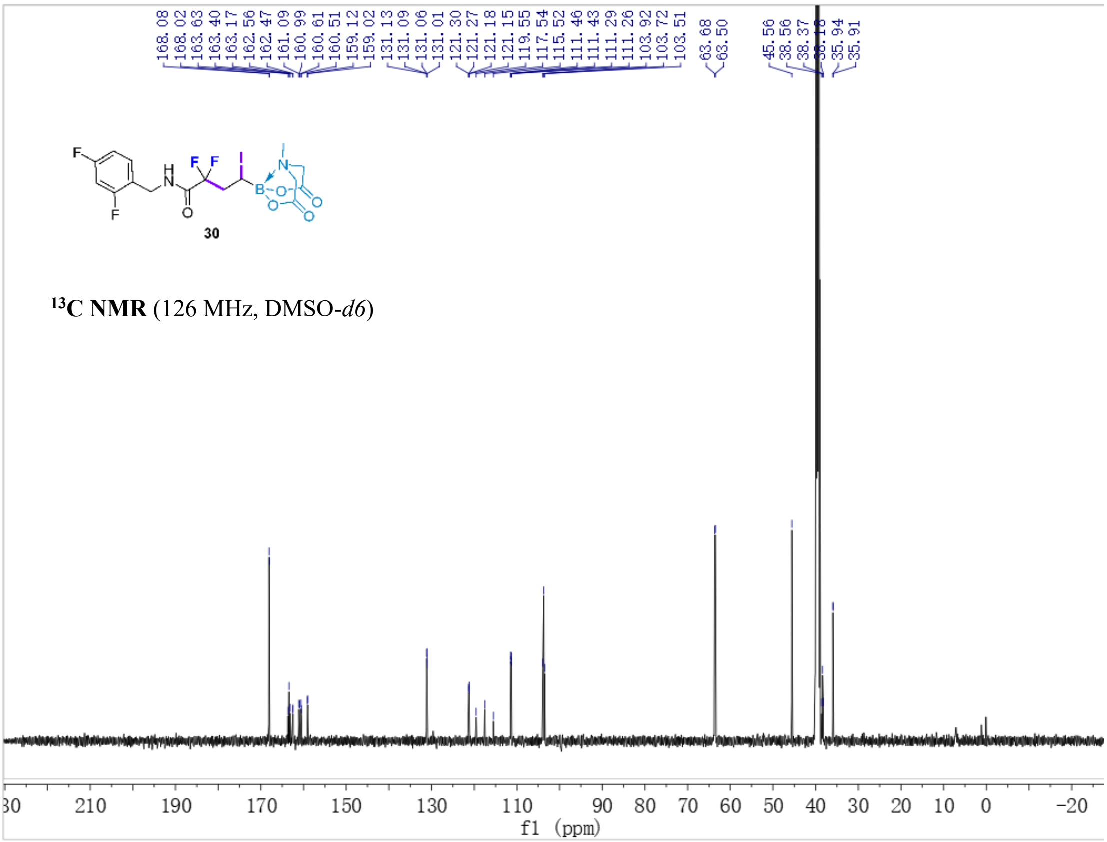



−103.51
−103.54
−103.58
−104.04
−104.07
−104.11
−104.52
−104.55
−104.56
−104.59
−105.05
−105.08
−105.09
−105.12
19F NMR (471 MHz, DMSO-d6)
29
1.00
1.02
280 240 200 160 120 80 40 0 −40 −80 −120 −180 −240
f1 (ppm)

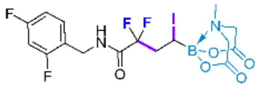

10.87
11B NMR (160 MHz, DMSO-d6)
29
110 90 80 70 60 50 40 30 20 10 0 −20 −40 −60 −80 −100
f1 (ppm)

***N*-(2,4-difluorobenzyl)-2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (30)**

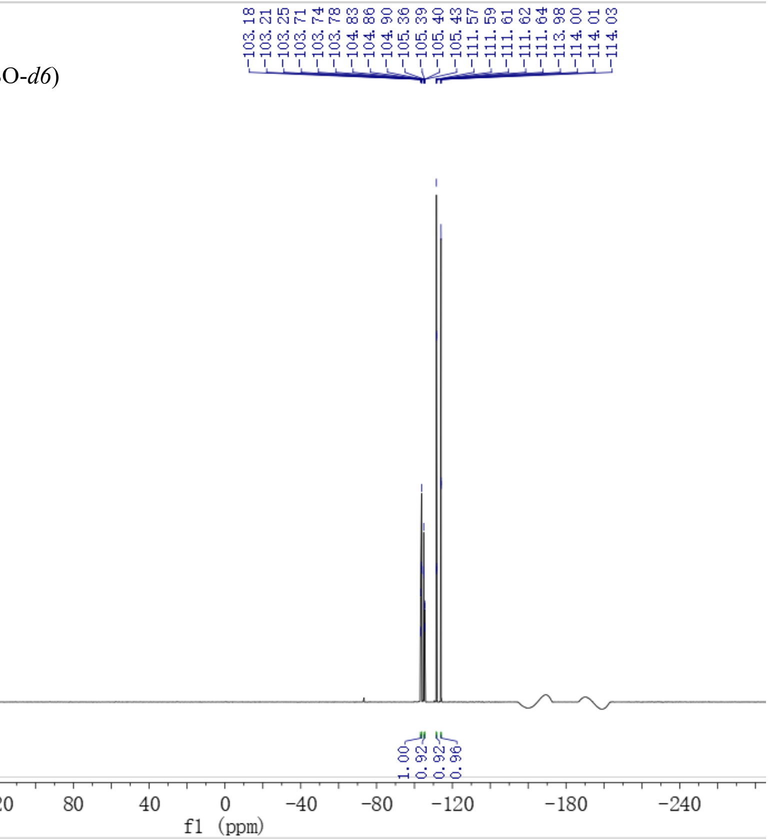




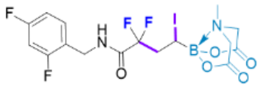
^{19}**F NMR** (471 MHz, DMSO-*d6*)



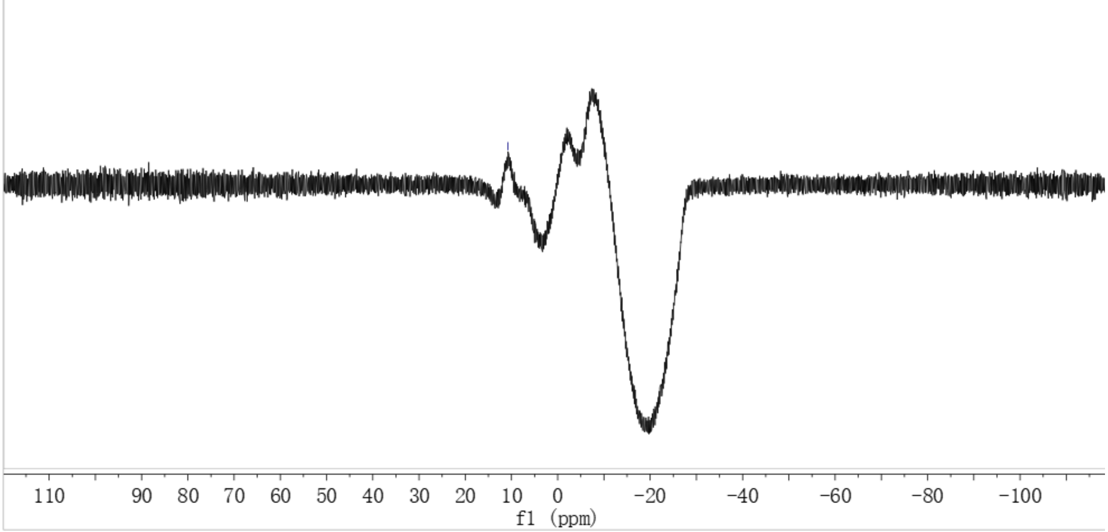
30



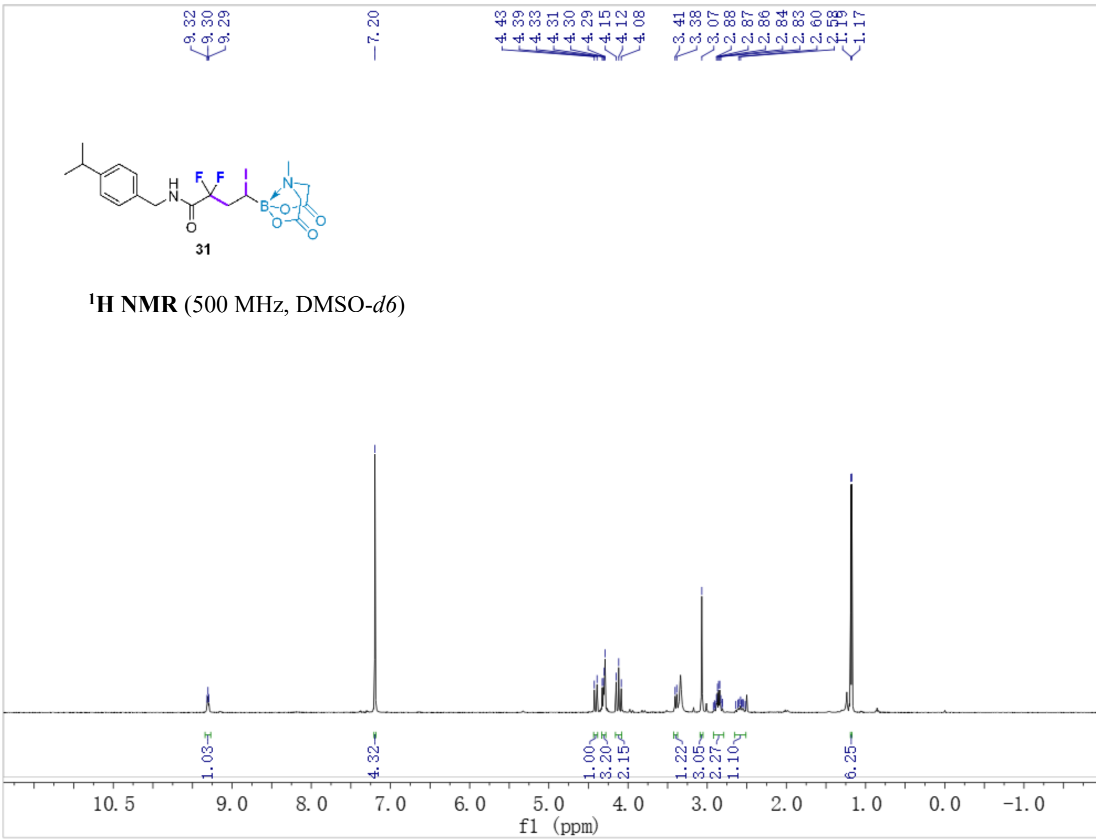
^{11}**B NMR** (160 MHz, DMSO-*d6*)

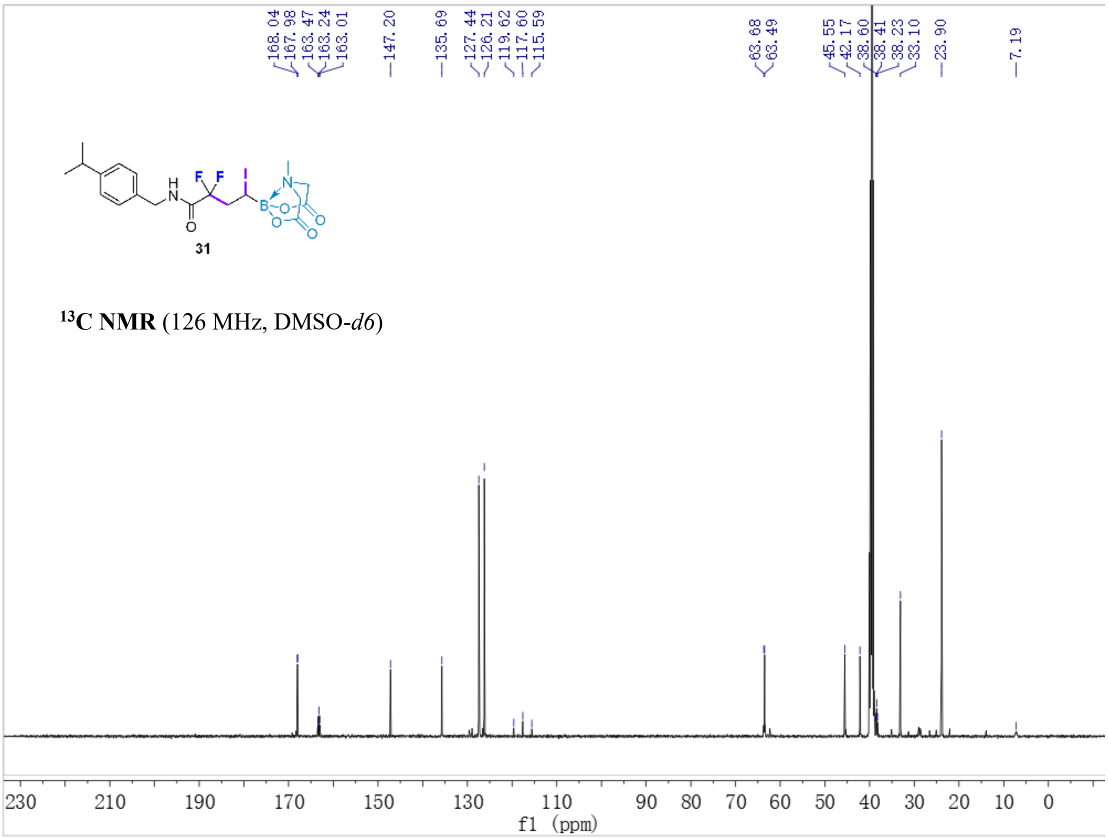


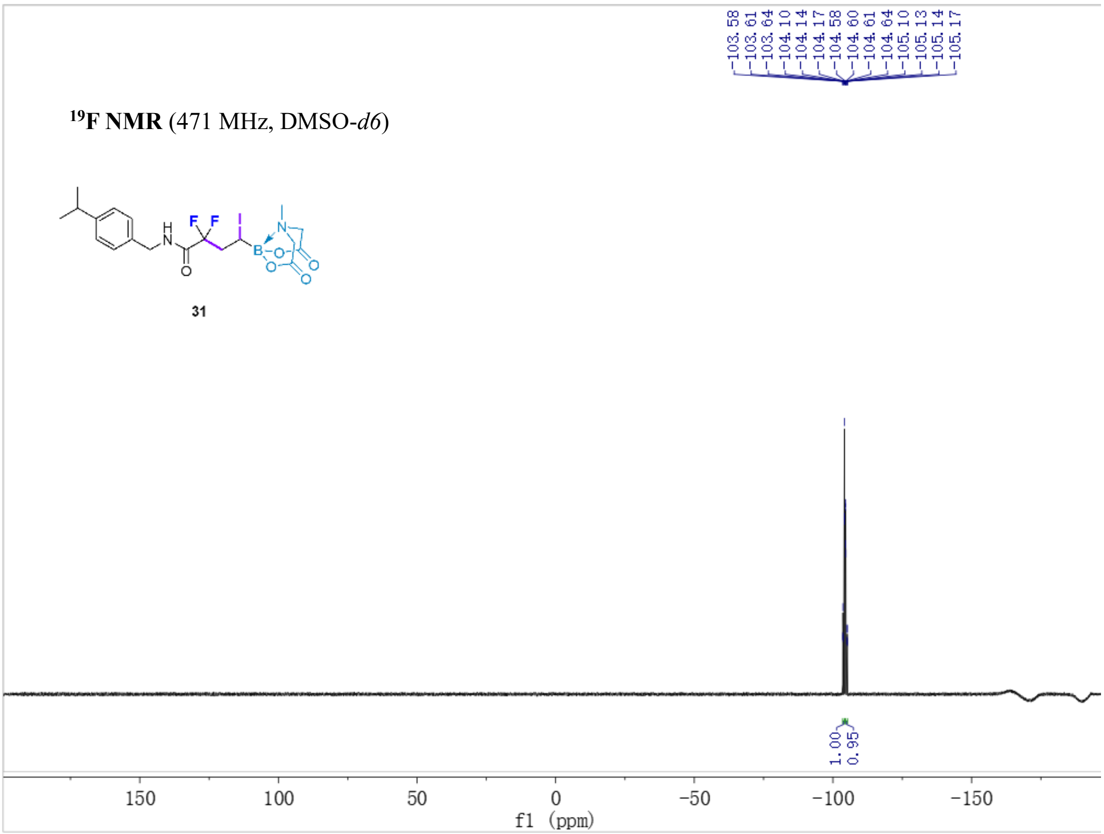
30



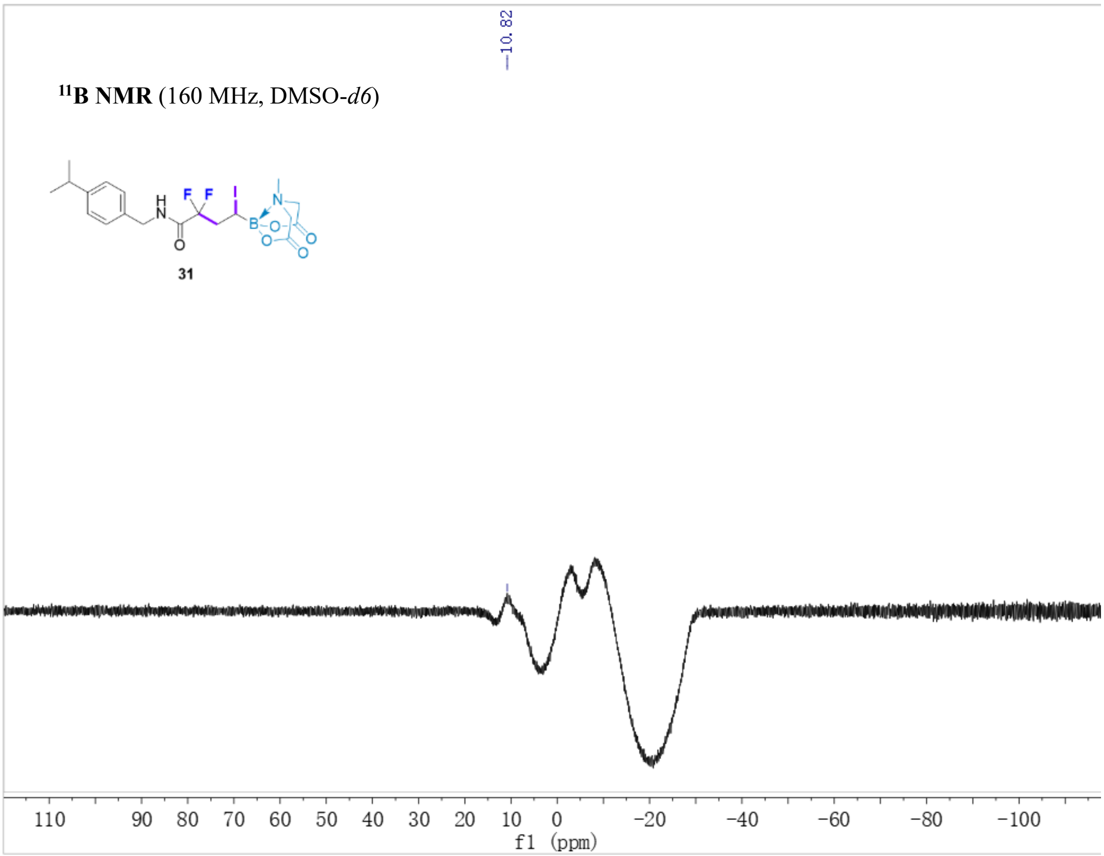
2,2-difluoro-4-iodo-*N*-(4-isopropylbenzyl)-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (31)





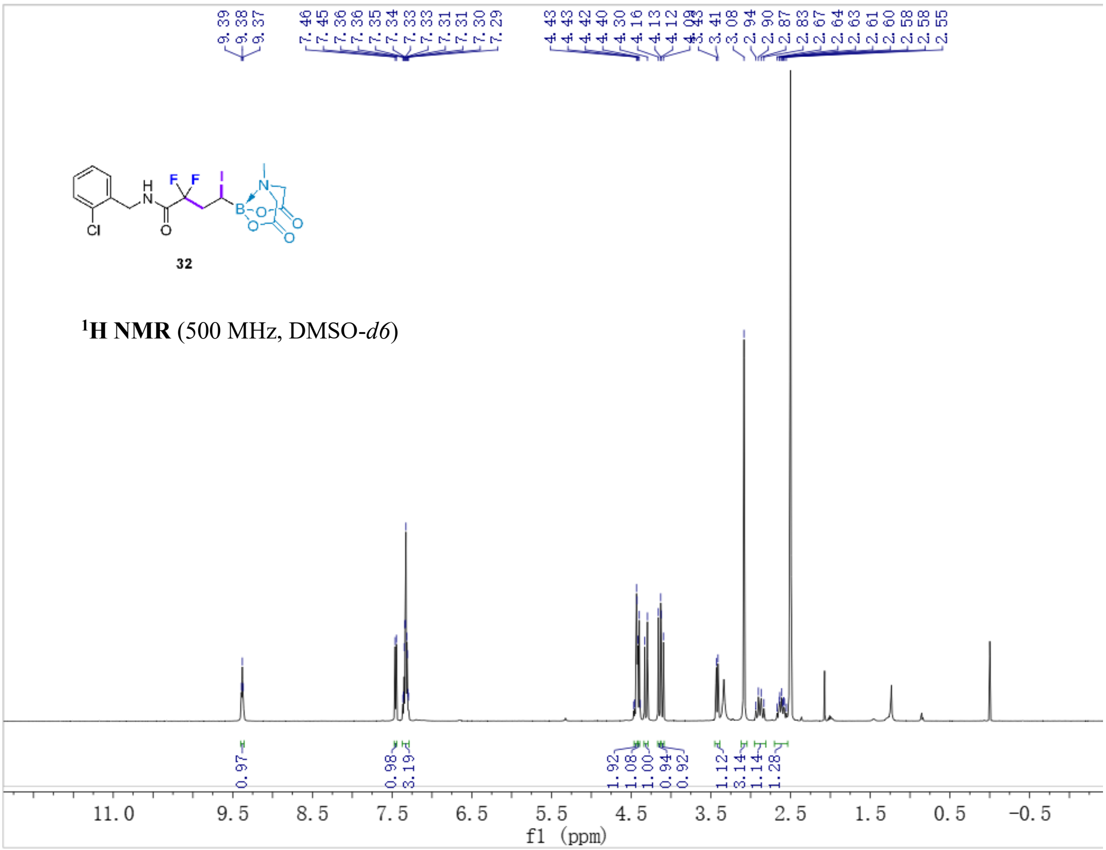


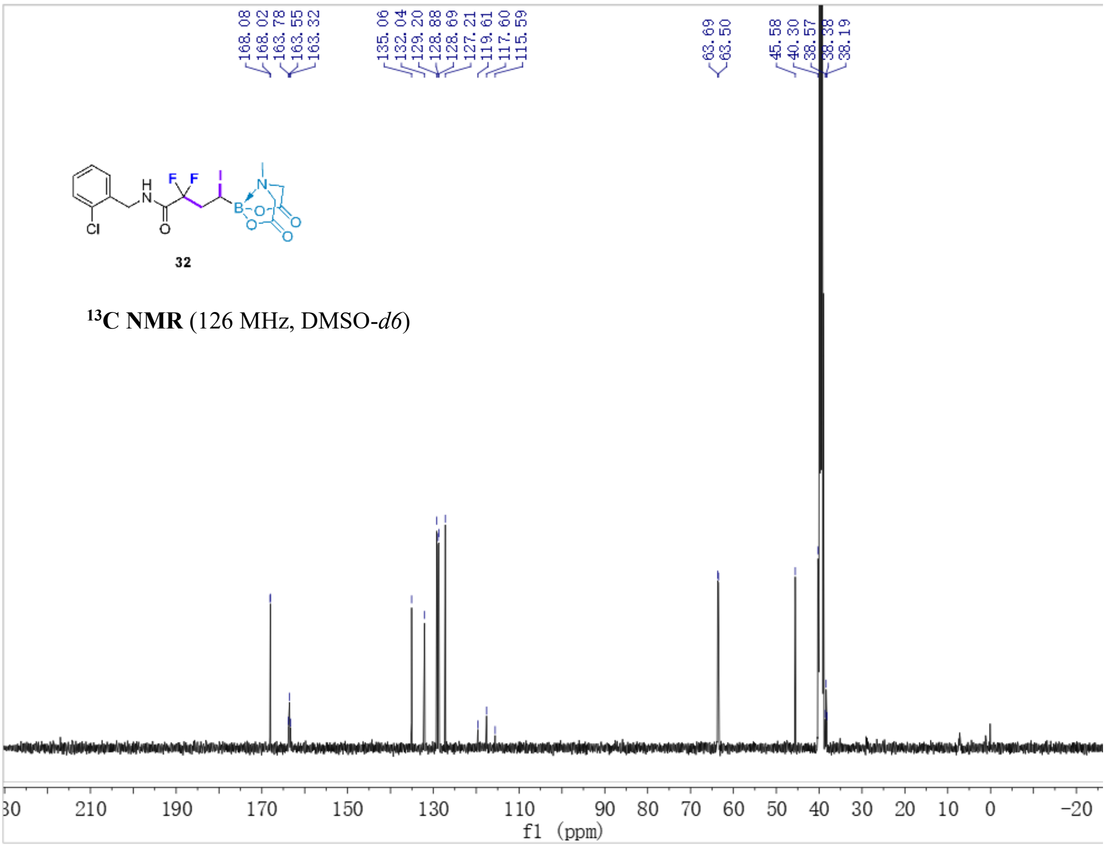
19F NMR (471 MHz, DMSO-d6)
31
-103.58
-103.61
-103.64
-104.10
-104.14
-104.17
-104.58
-104.60
-104.61
-104.64
-105.10
-105.13
-105.14
-105.17
1.00
0.95
150
100
50
0
-50
-100
-150
f1 (ppm)

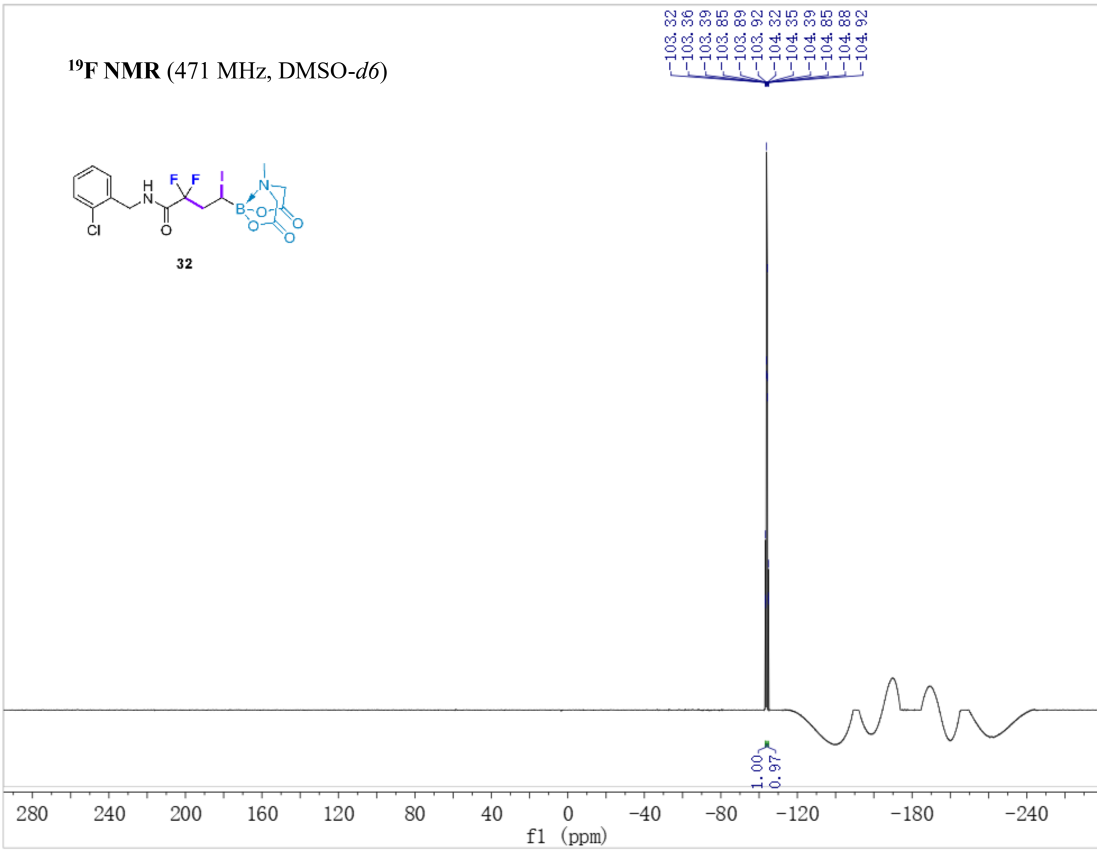


11B NMR (160 MHz, DMSO-d6)
31
-10.82
110
90
80
70
60
50
40
30
20
10
0
-20
-40
-60
-80
-100
f1 (ppm)

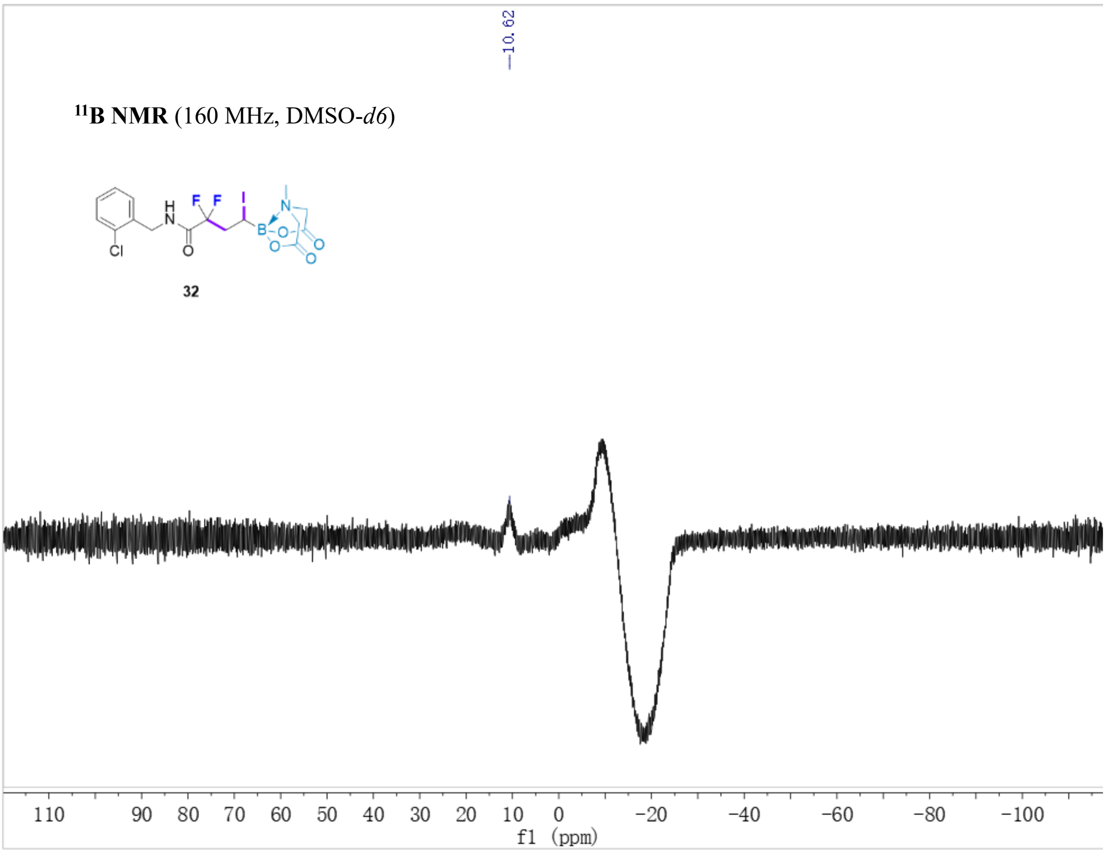
N-(2-chlorobenzyl)-2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (32)





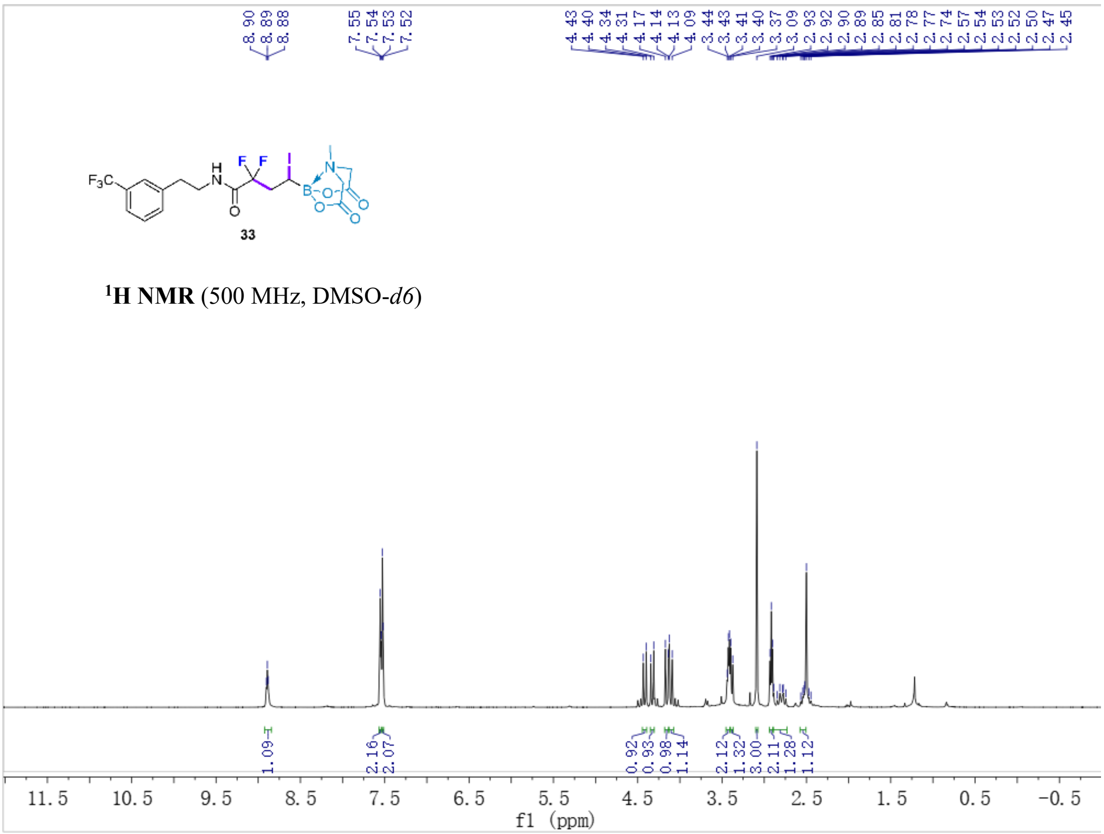


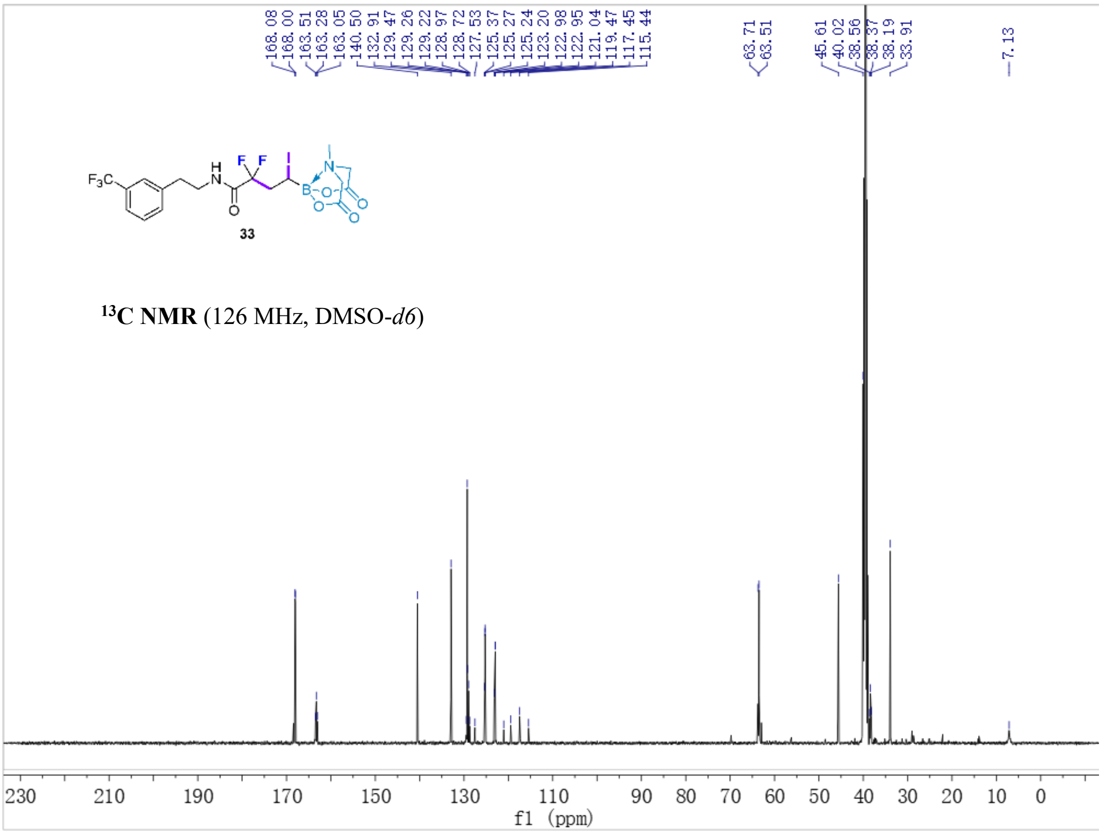
19F NMR (471 MHz, DMSO-d6)
-103.32
-103.36
-103.39
-103.85
-103.89
-103.92
-104.32
-104.35
-104.39
-104.85
-104.88
-104.92
H
N
O
Cl
F F
I
B
N
O
O
O
O
32
1.00
0.97
280 240 200 160 120 80 40 0 -40 -80 -120 -180 -240
f1 (ppm)

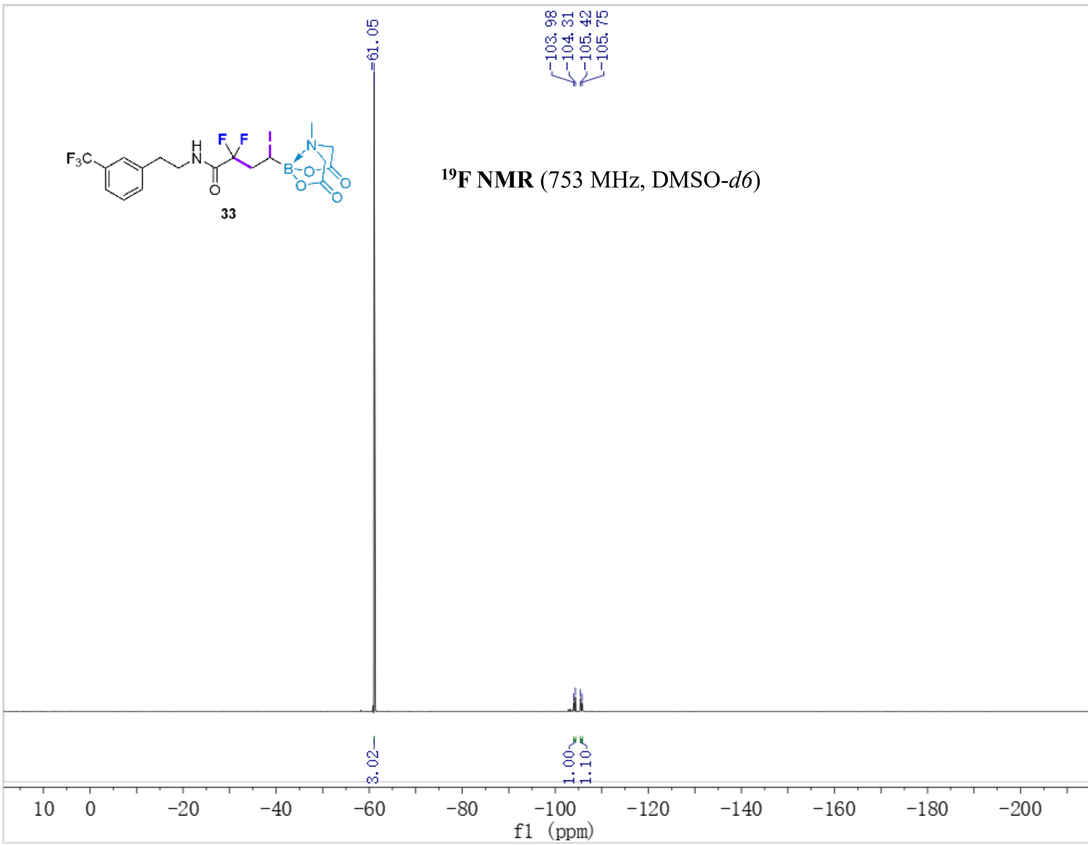


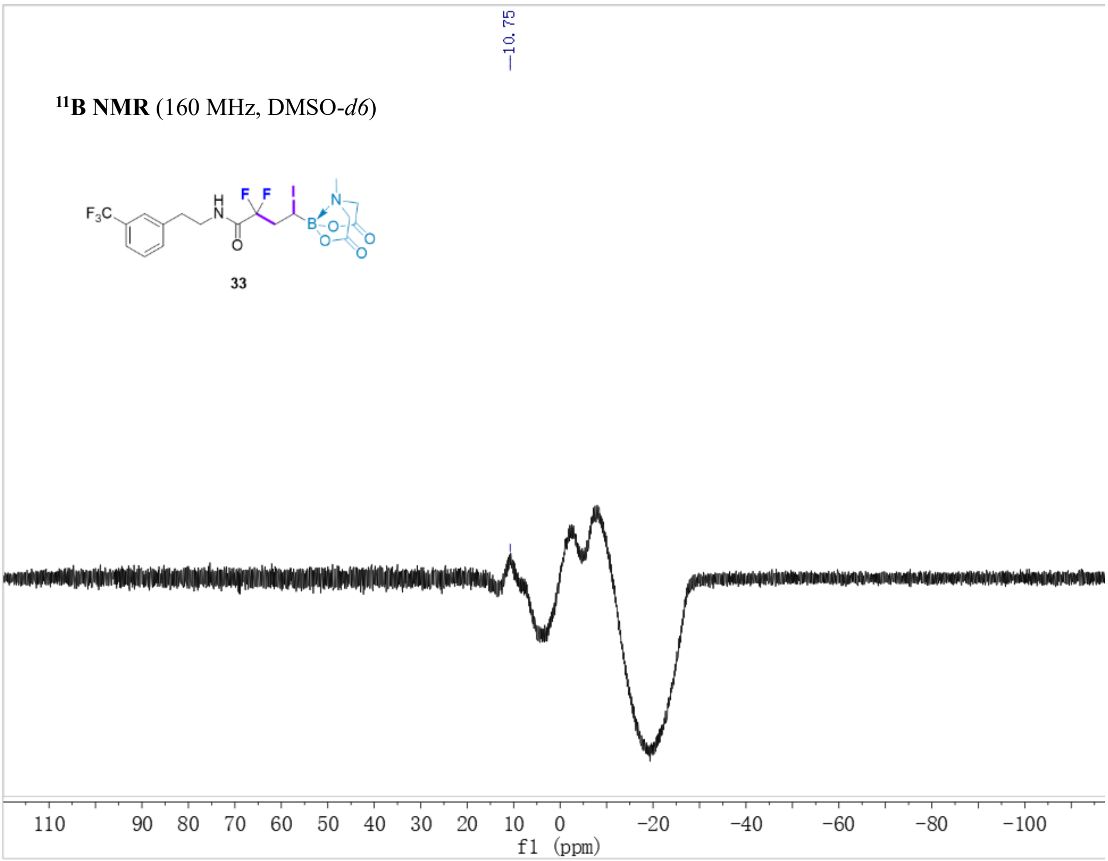
-10.62
11B NMR (160 MHz, DMSO-d6)
H
N
O
Cl
F F
I
B
N
O
O
O
O
32
110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100
f1 (ppm)

2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-*N*-(3-(trifluoromethyl)phenethyl)butanamide (33)

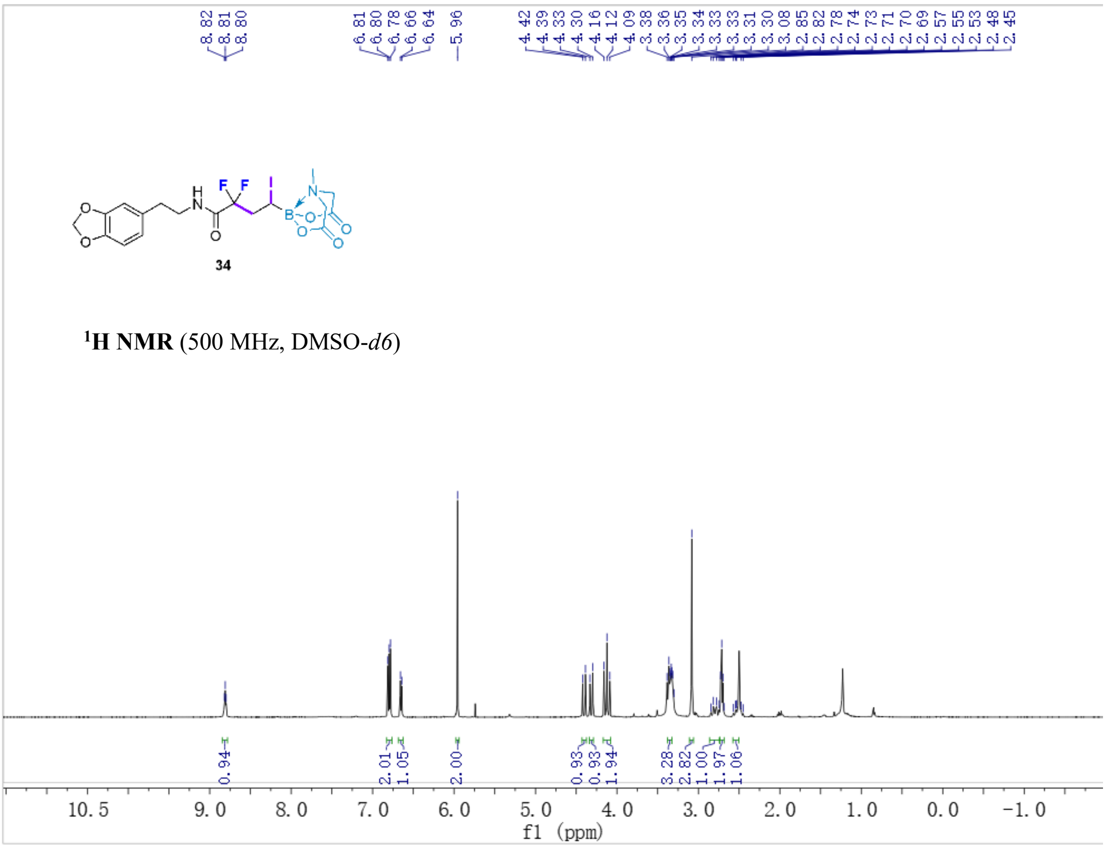




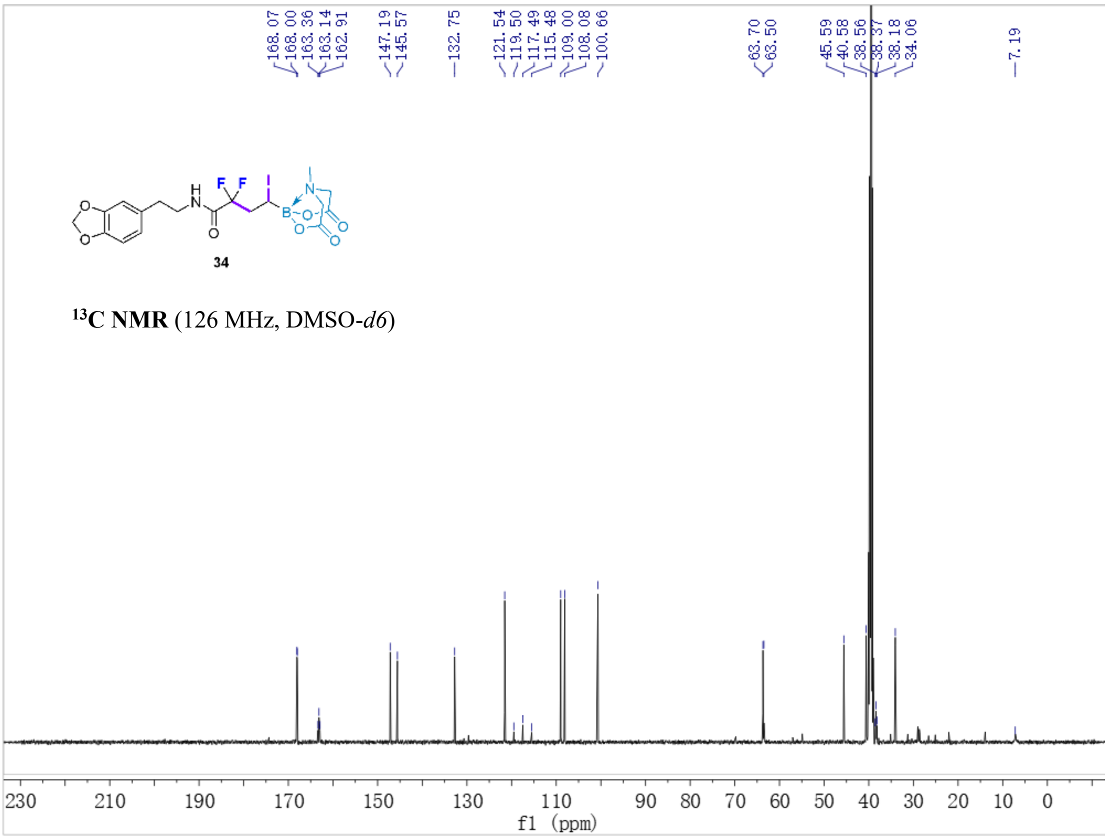

-61.05
-103.98
-104.31
-105.42
-105.75
^{19}F NMR (753 MHz, DMSO-*d6*)
33
3.02
1.00
1.10
10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)


-10.75
^{11}B NMR (160 MHz, DMSO-*d6*)
33
110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100
f1 (ppm)

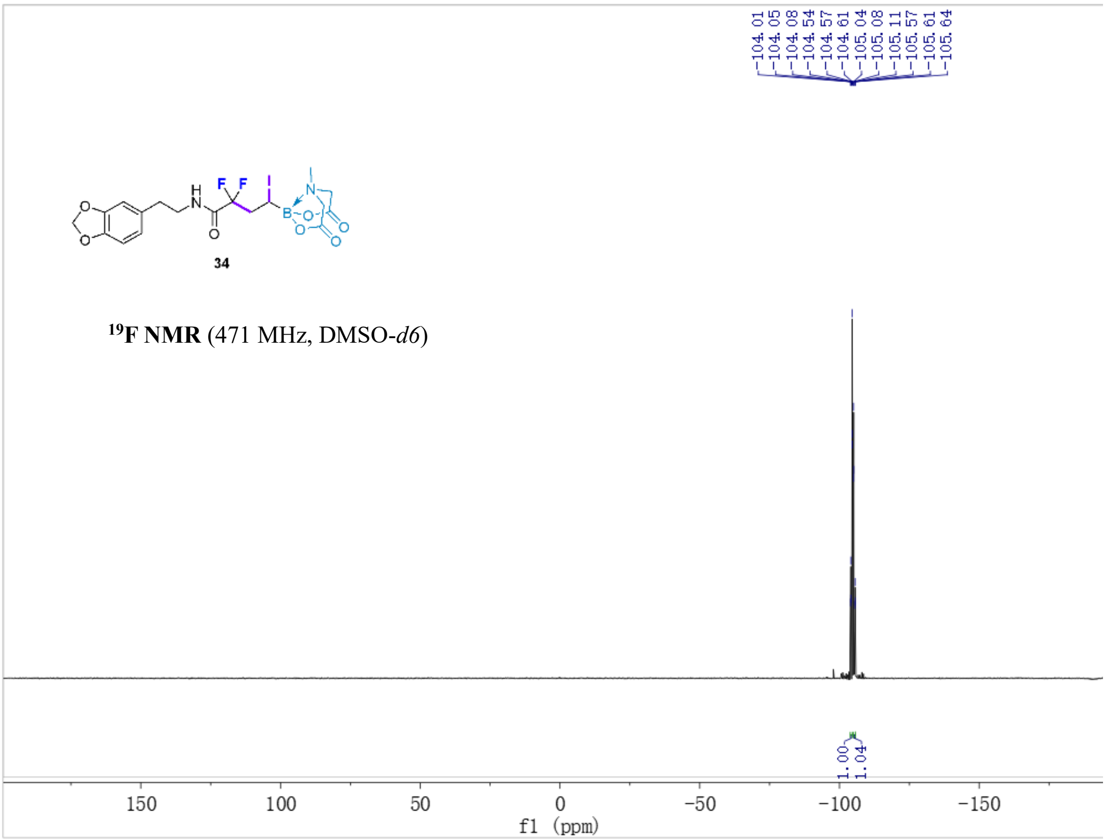
***N*-(2-(benzo[*d*][1,3]dioxol-5-yl)ethyl)-2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (34)**



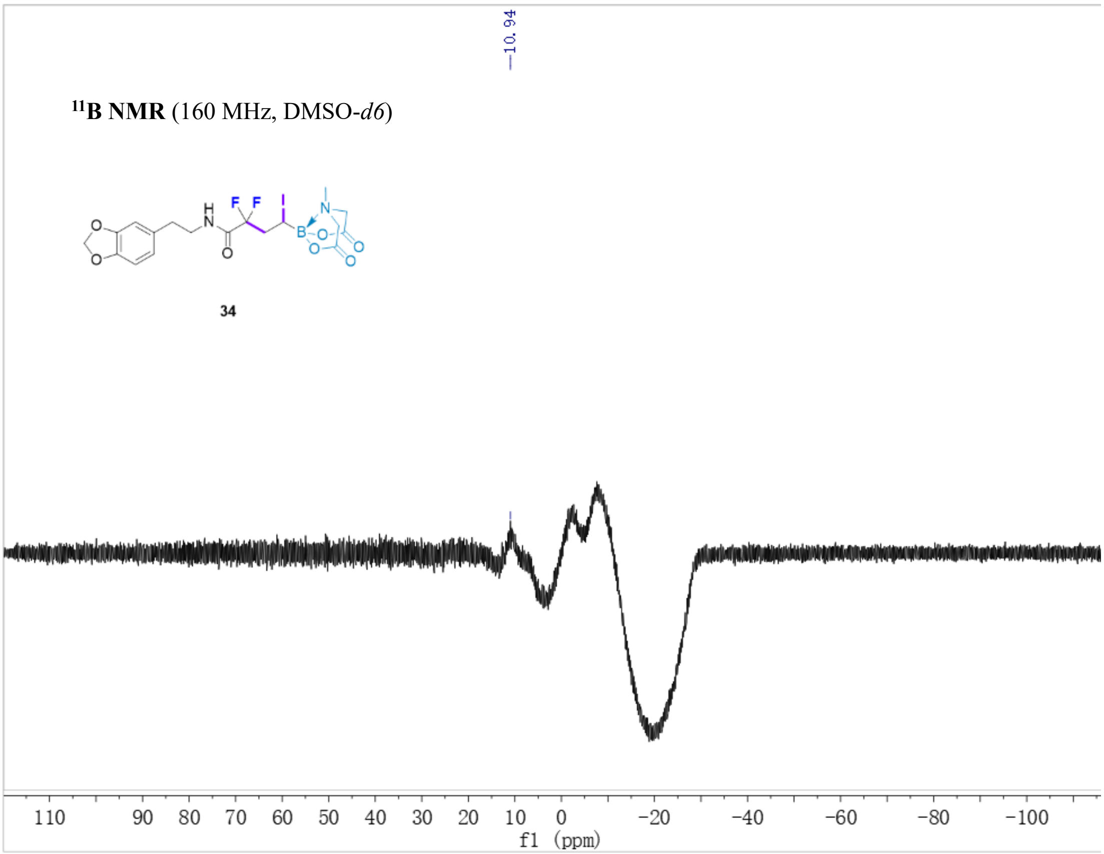
[1]**H NMR** (500 MHz, DMSO-*d6*)



[13]**C NMR** (126 MHz, DMSO-*d6*)

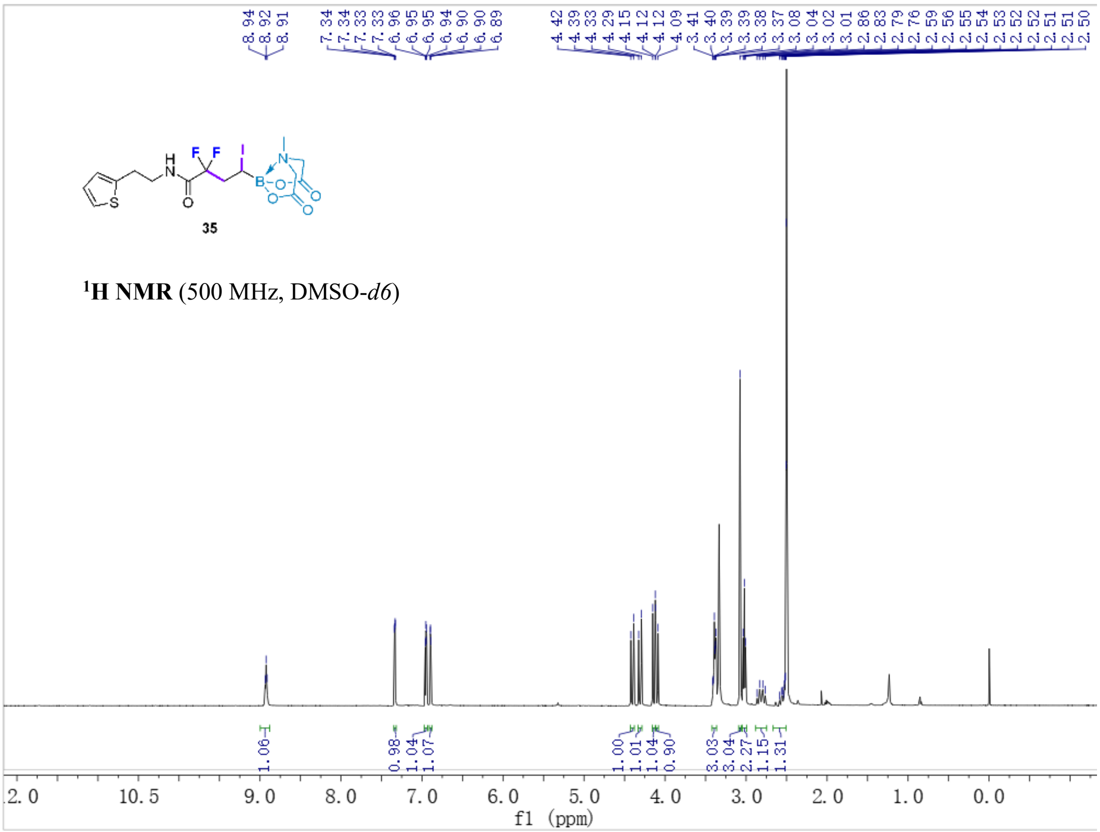


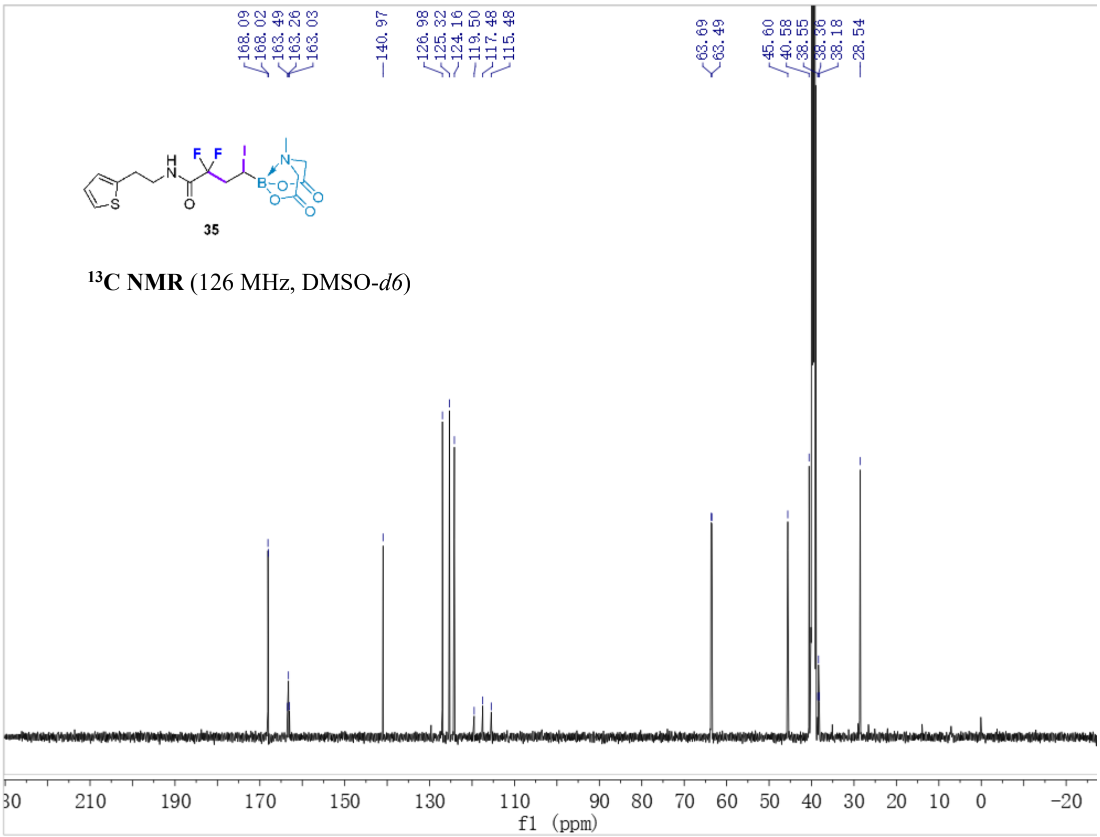
^{19}**F NMR** (471 MHz, DMSO-*d6*)

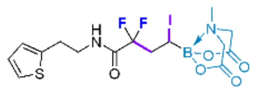


^{11}**B NMR** (160 MHz, DMSO-*d6*)

2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-*N*-(2-(thiophen-2-yl)ethyl)butanamide (35)

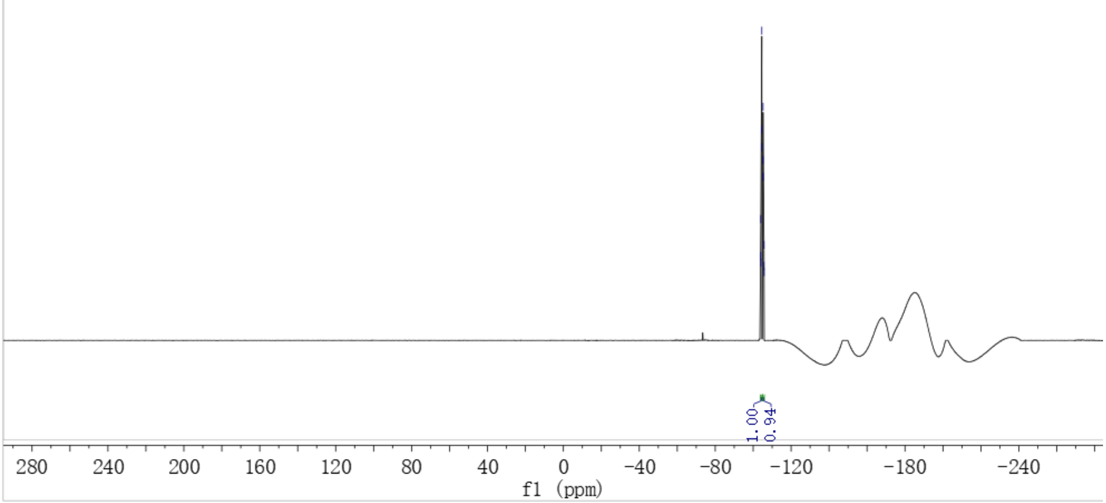




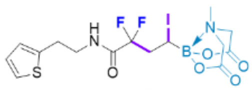


35

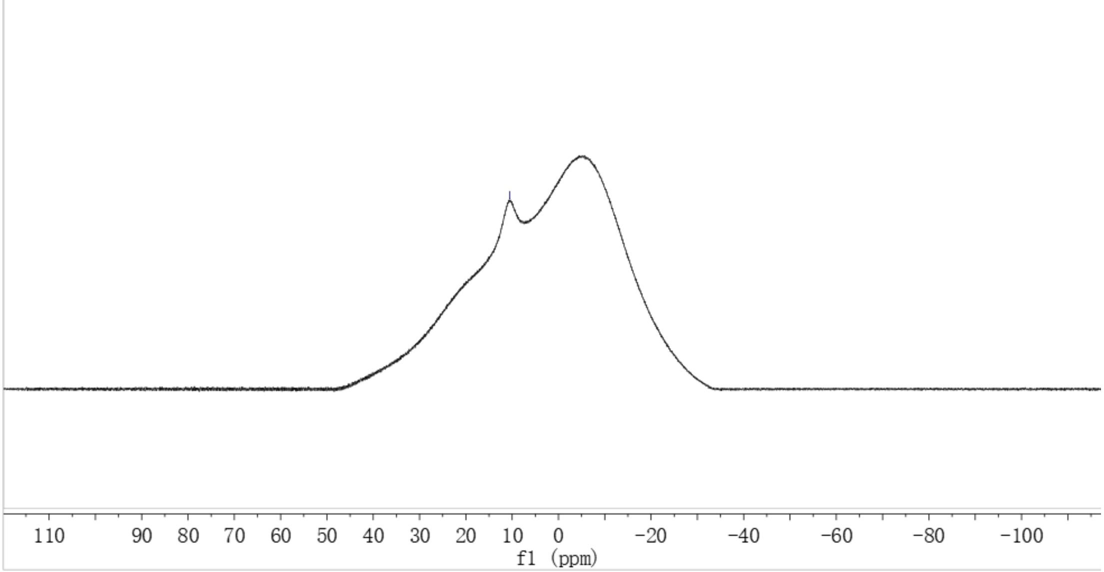
^{19}F NMR (471 MHz, DMSO-*d6*)



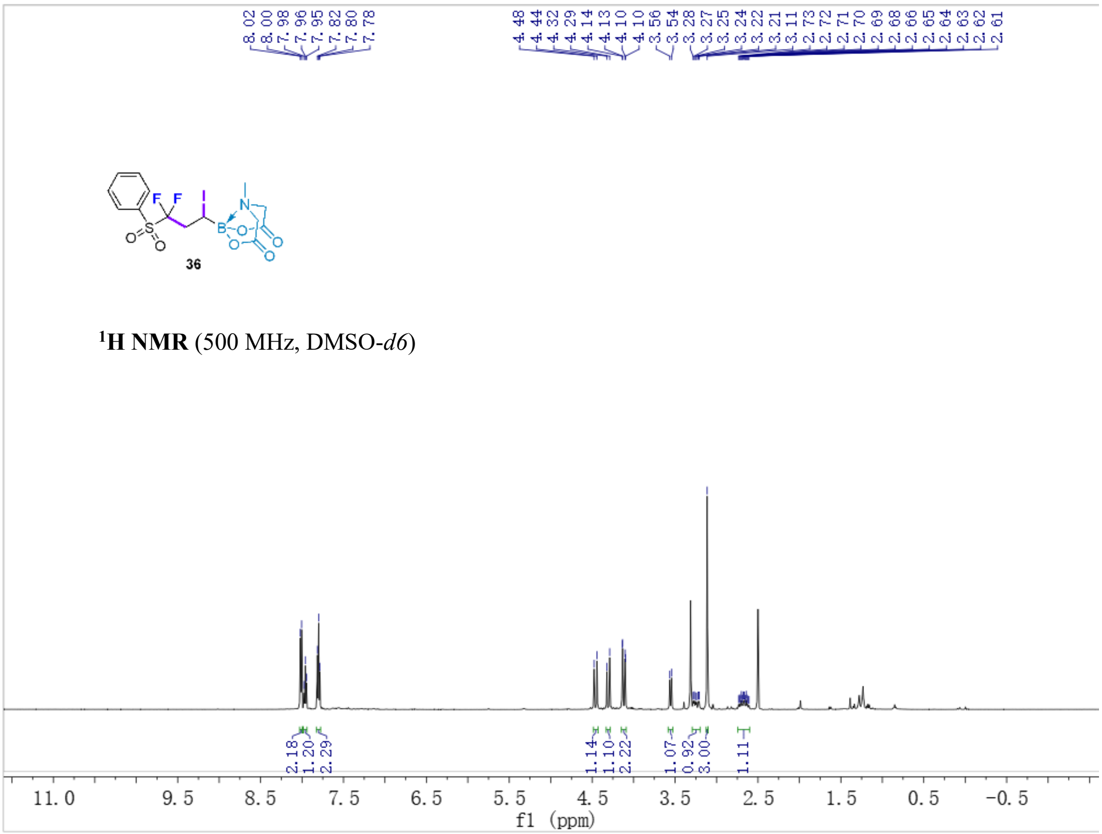
^{11}B NMR (160 MHz, DMSO-*d6*)

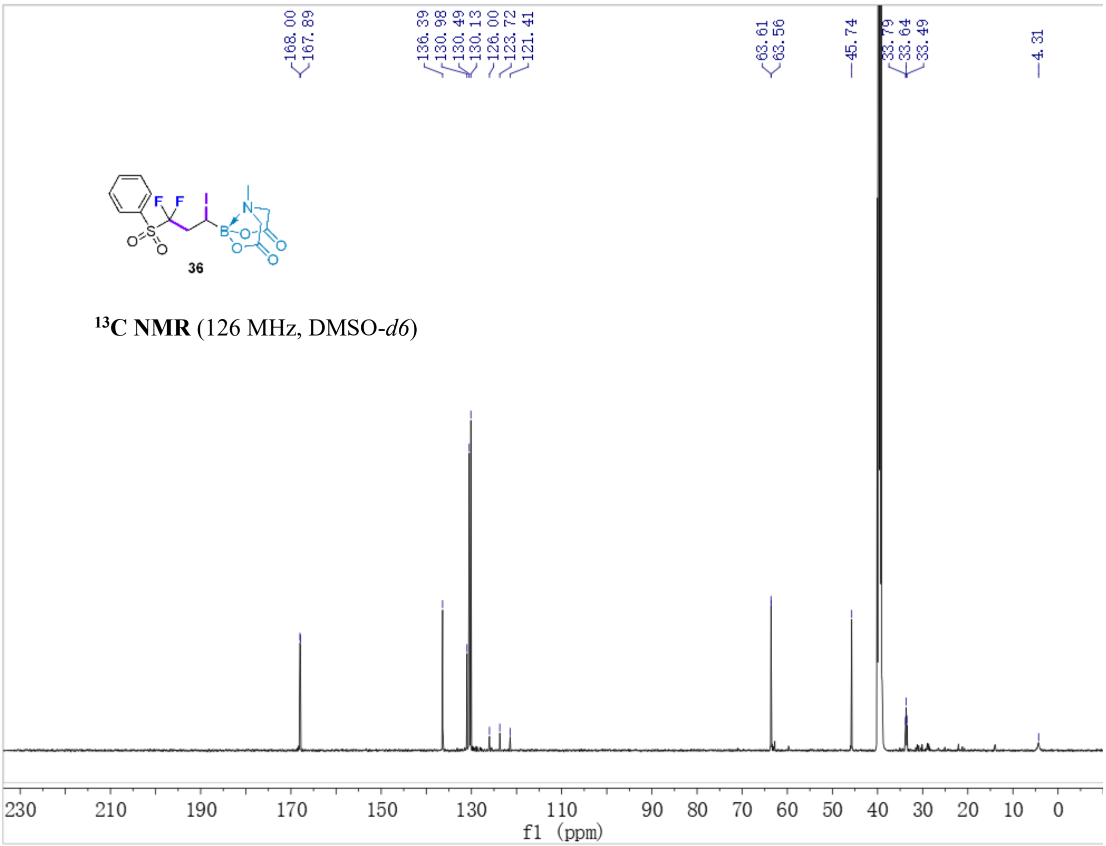


35

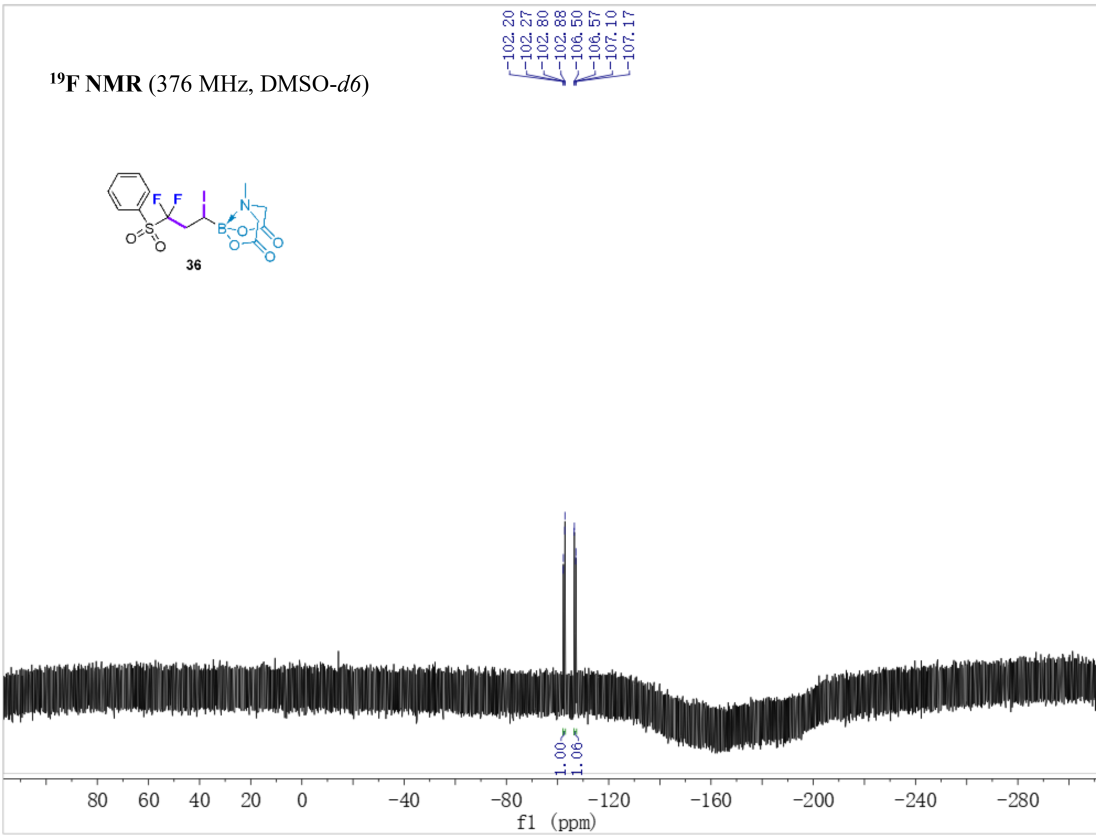


2-(3,3-difluoro-1-iodo-3-(phenylsulfonyl)propyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (36)

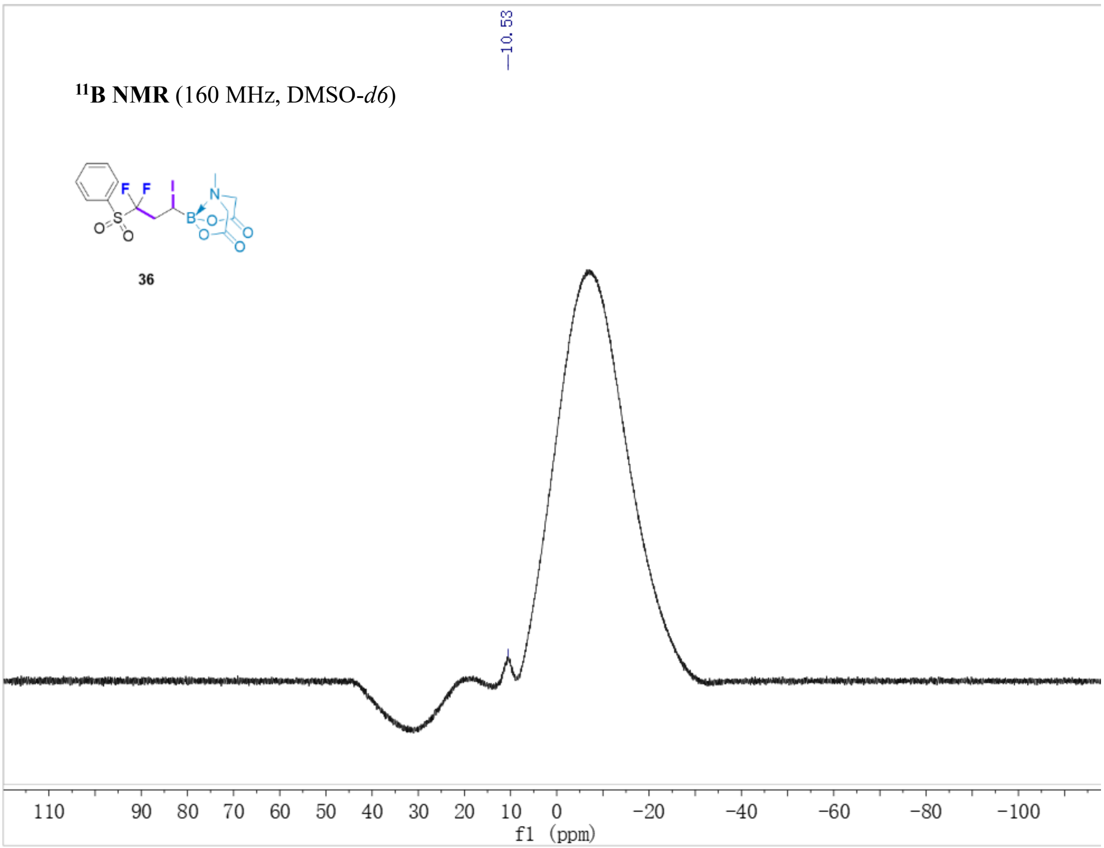




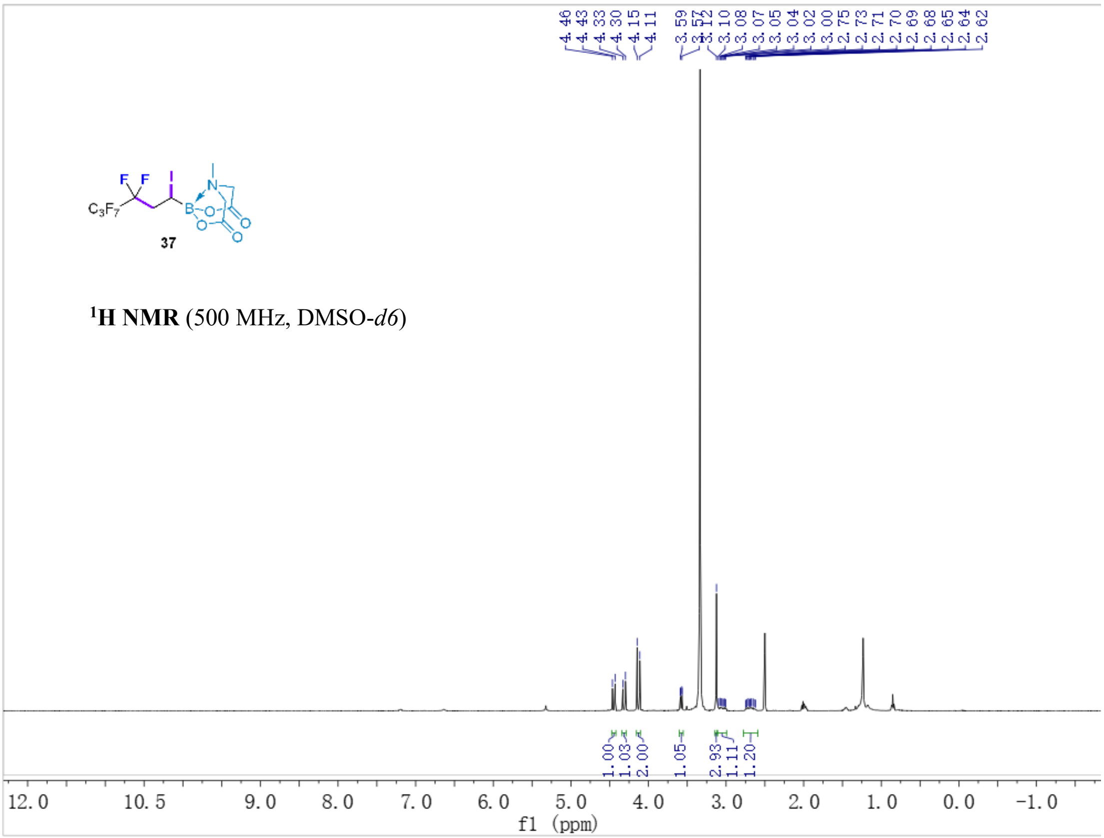
[19]F NMR (376 MHz, DMSO-*d6*)

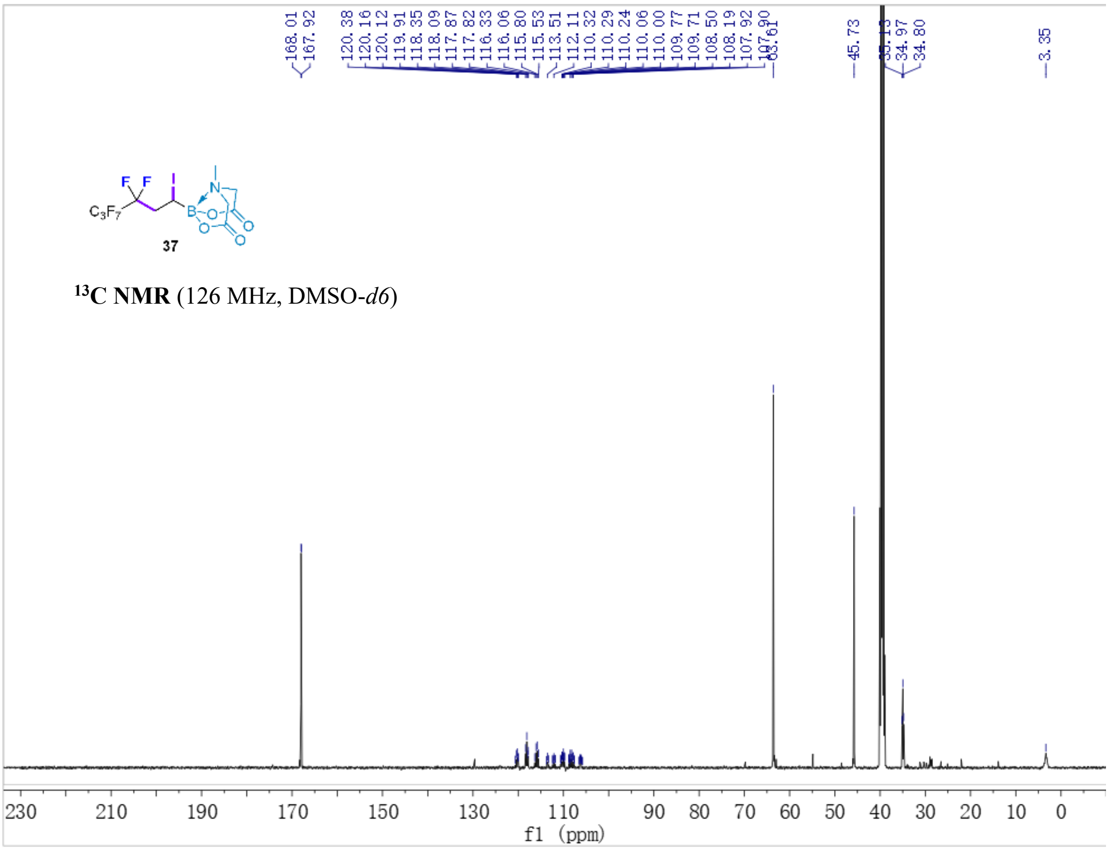


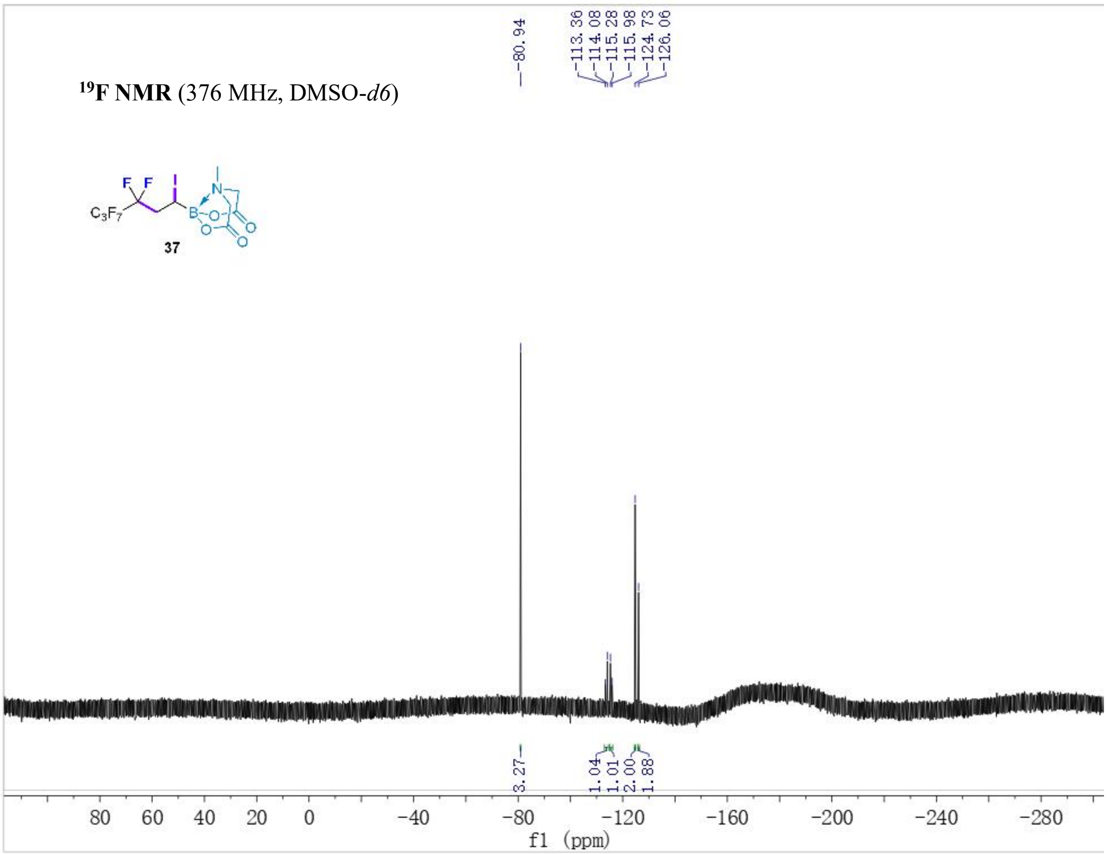
[11]B NMR (160 MHz, DMSO-*d6*)



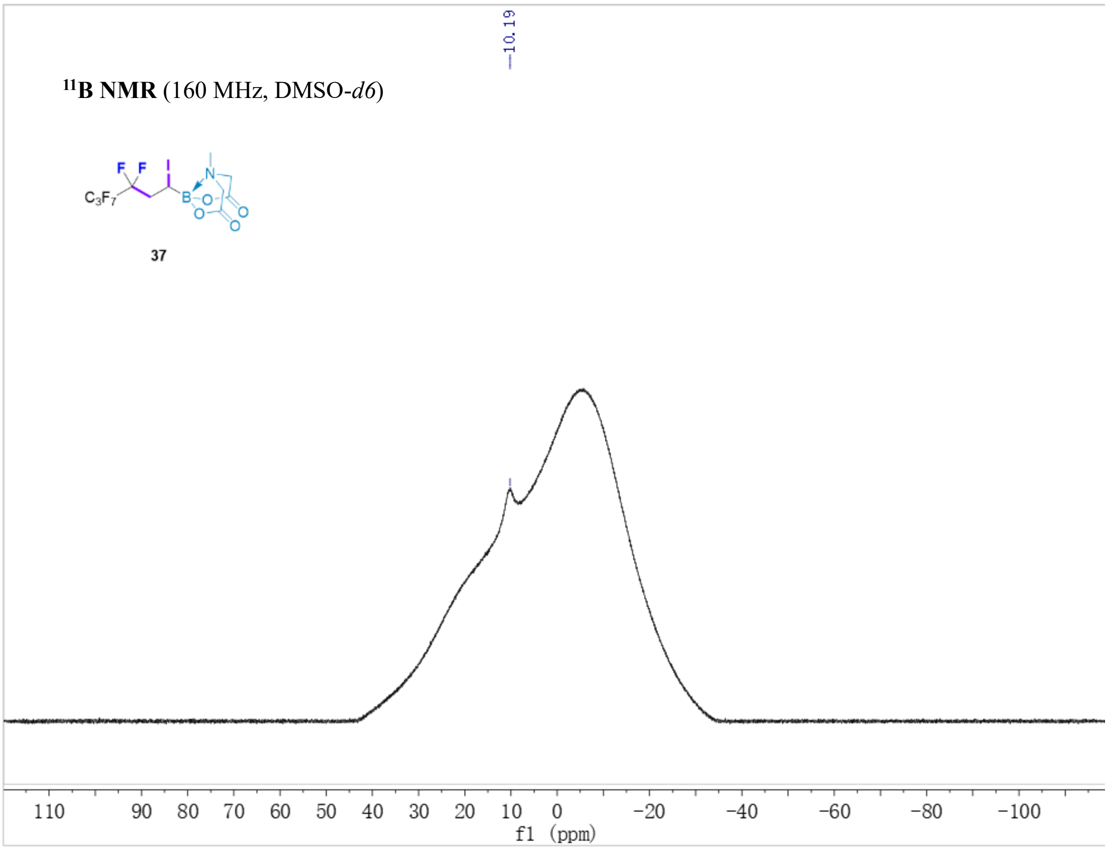
6-methyl-2-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)-1,3,6,2-dioxazaborocane-4,8-dione (37)





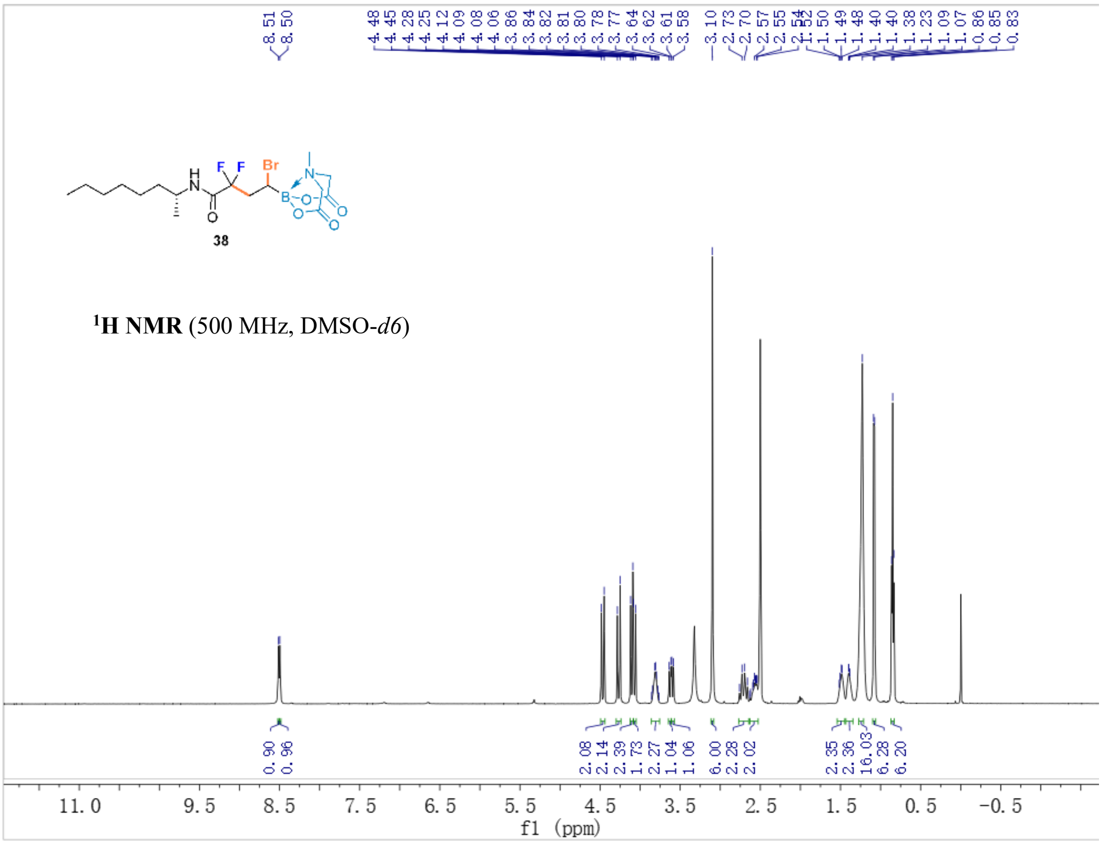


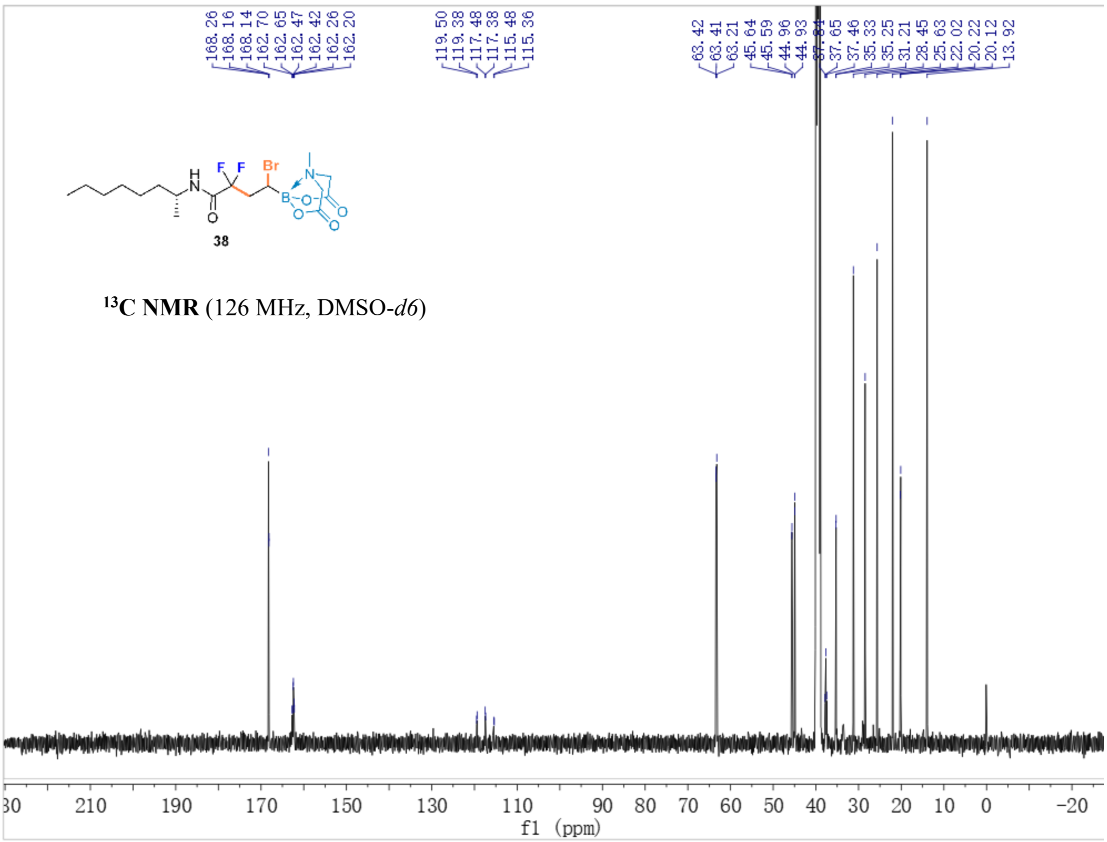
-80.94
-113.36
-114.08
-115.28
-115.98
-124.73
-126.06
19F NMR (376 MHz, DMSO-d6)
C3F7
F F
I
N
B
O
O
O
O
37
3.27
1.04
1.01
2.00
1.88
80 60 40 20 0 -40 -80 -120 -160 -200 -240 -280
f1 (ppm)

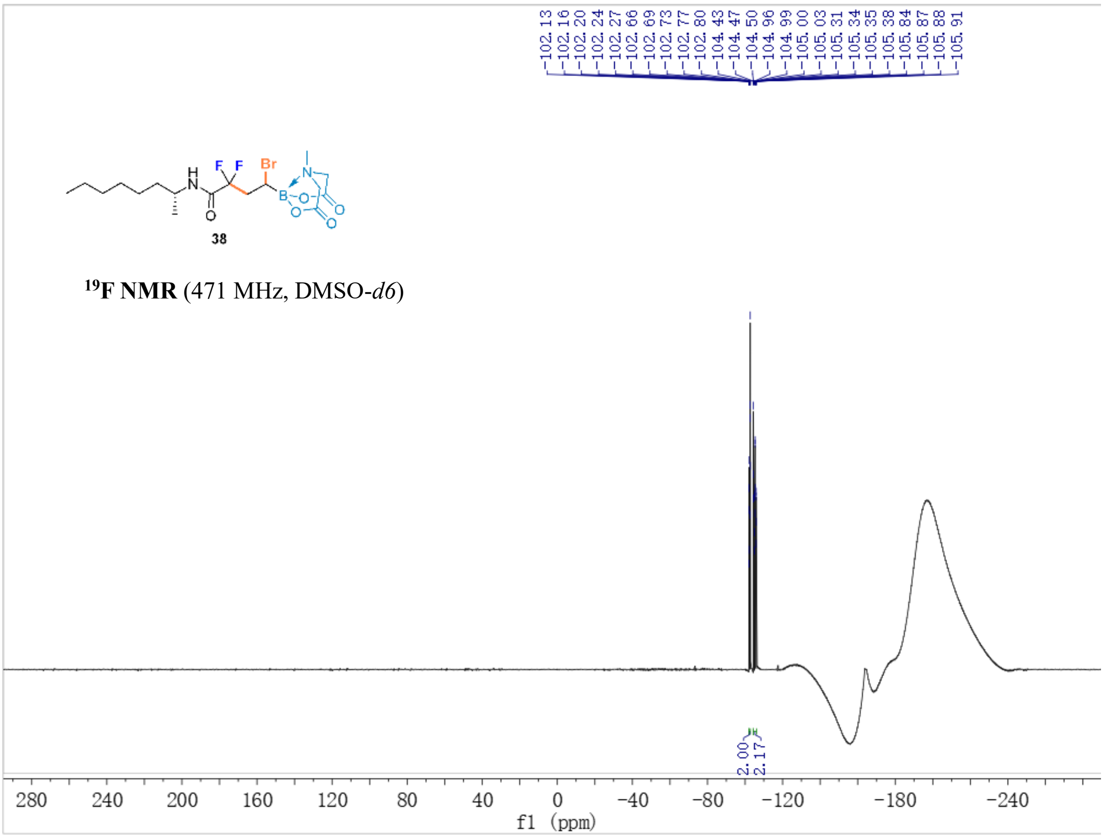


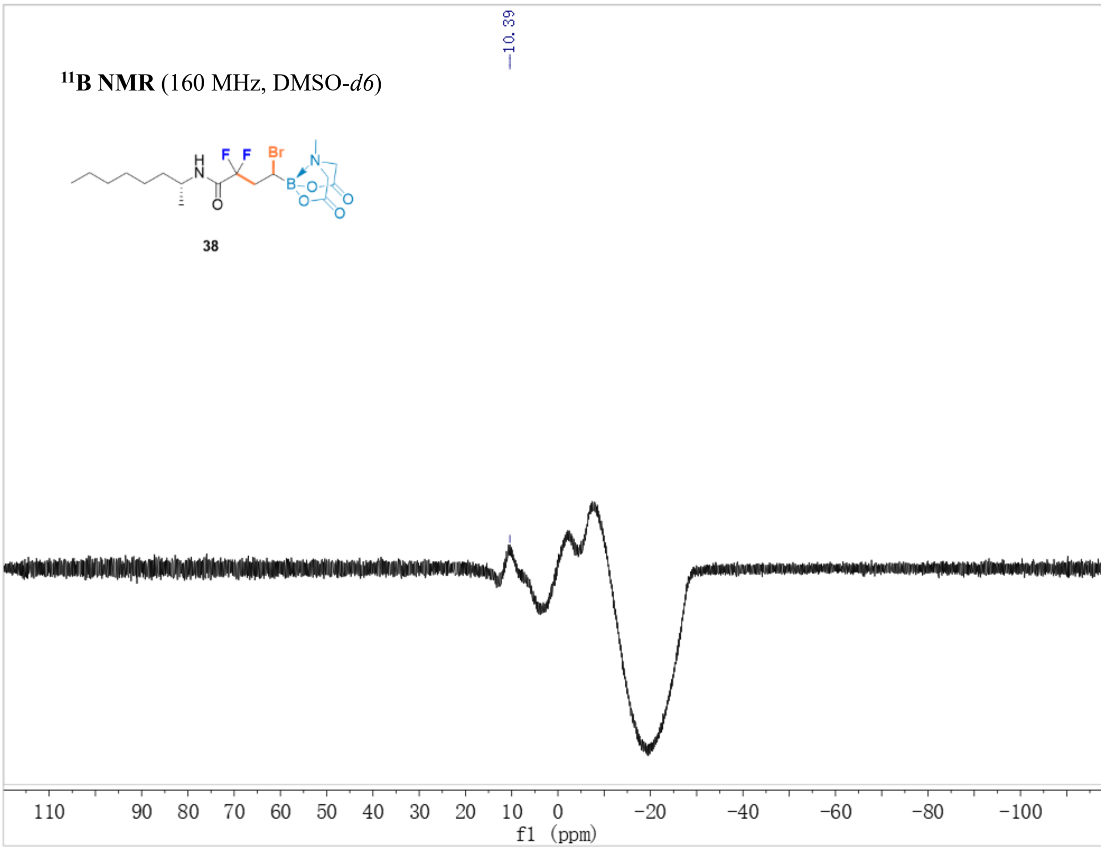
-10.19
11B NMR (160 MHz, DMSO-d6)
C3F7
F F
I
N
B
O
O
O
O
37
110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100
f1 (ppm)

4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-*N*-((*R*)-octan-2-yl)butanamide (38)

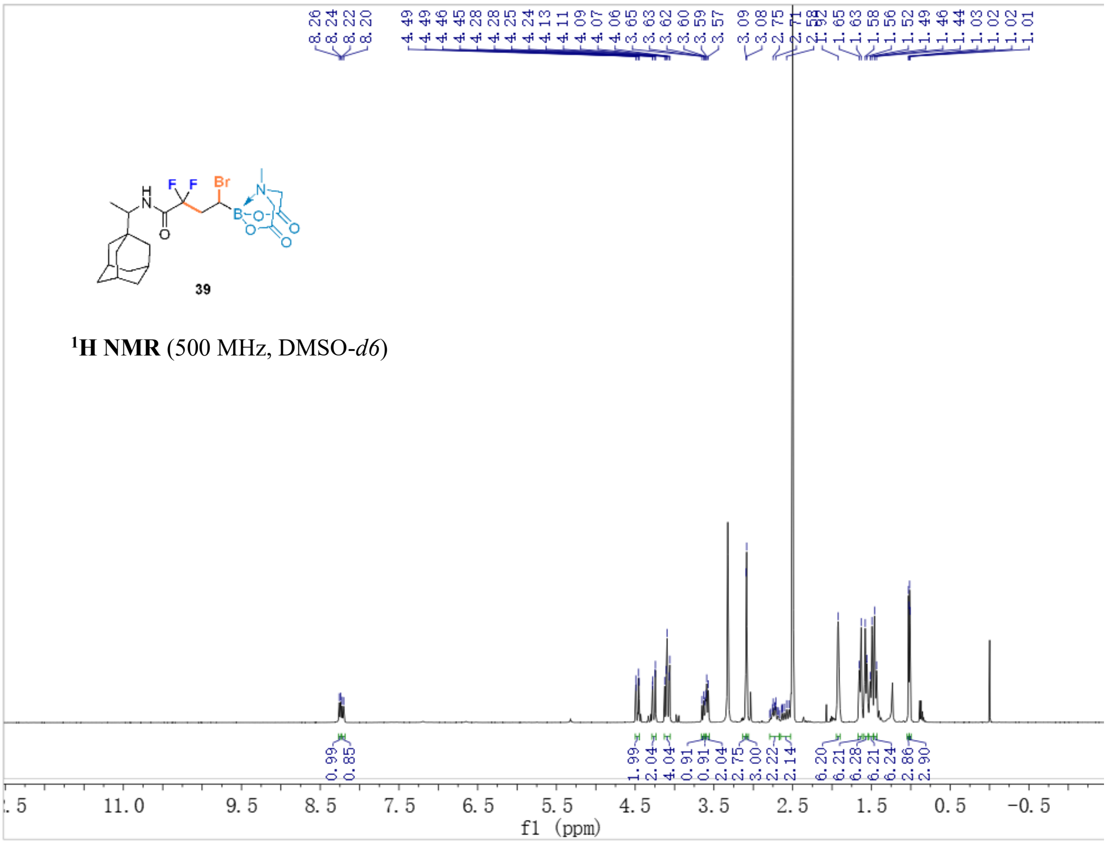


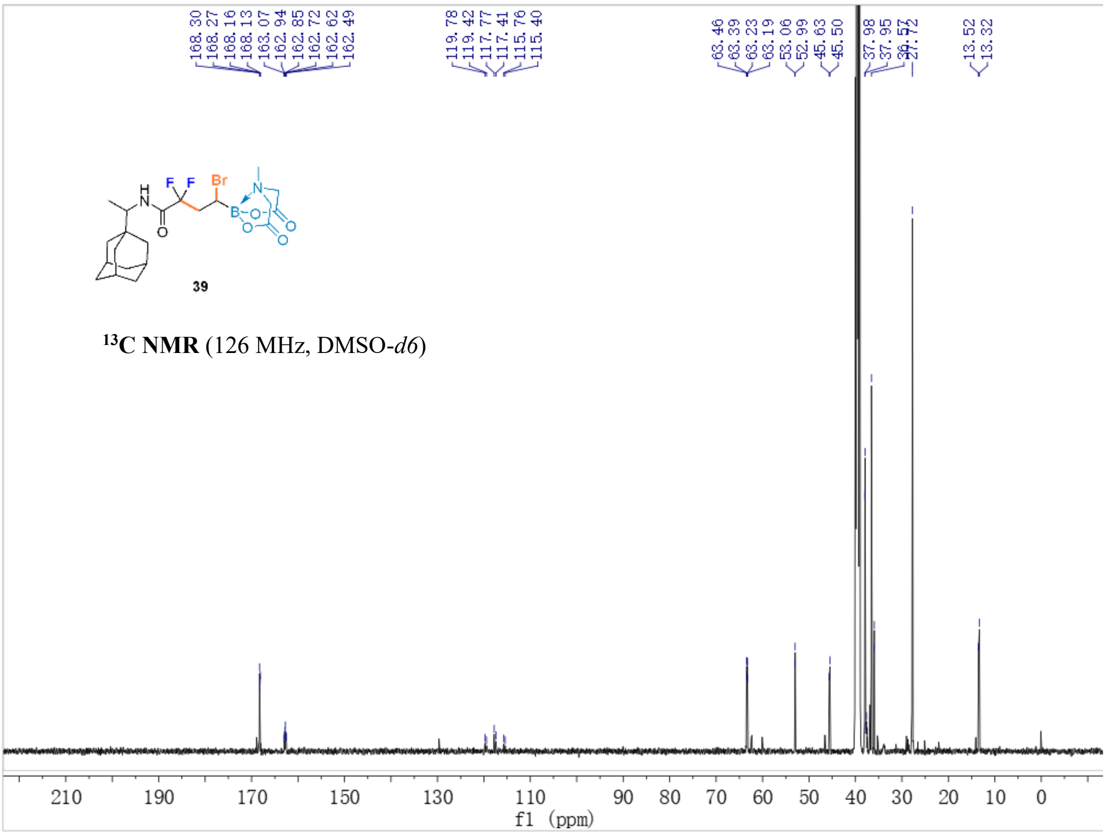


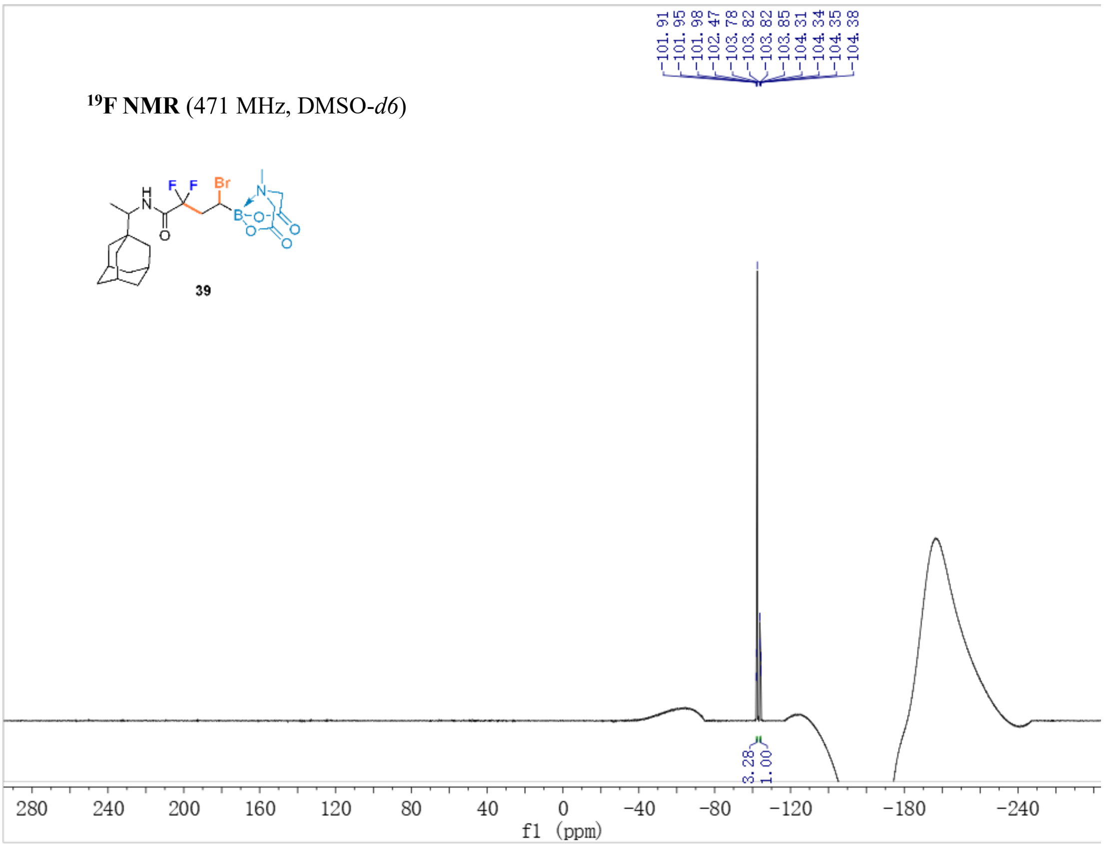

38
^{19}F NMR (471 MHz, DMSO-d6)
-102.13
-102.16
-102.20
-102.24
-102.27
-102.66
-102.69
-102.73
-102.77
-102.80
-104.43
-104.47
-104.50
-104.96
-104.99
-105.00
-105.03
-105.31
-105.34
-105.35
-105.38
-105.84
-105.87
-105.88
-105.91
2.00
2.17
280 240 200 160 120 80 40 0 −40 −80 −120 −180 −240
f1 (ppm)


^{11}B NMR (160 MHz, DMSO-d6)
38
10.39
110 90 80 70 60 50 40 30 20 10 0 −20 −40 −60 −80 −100
f1 (ppm)

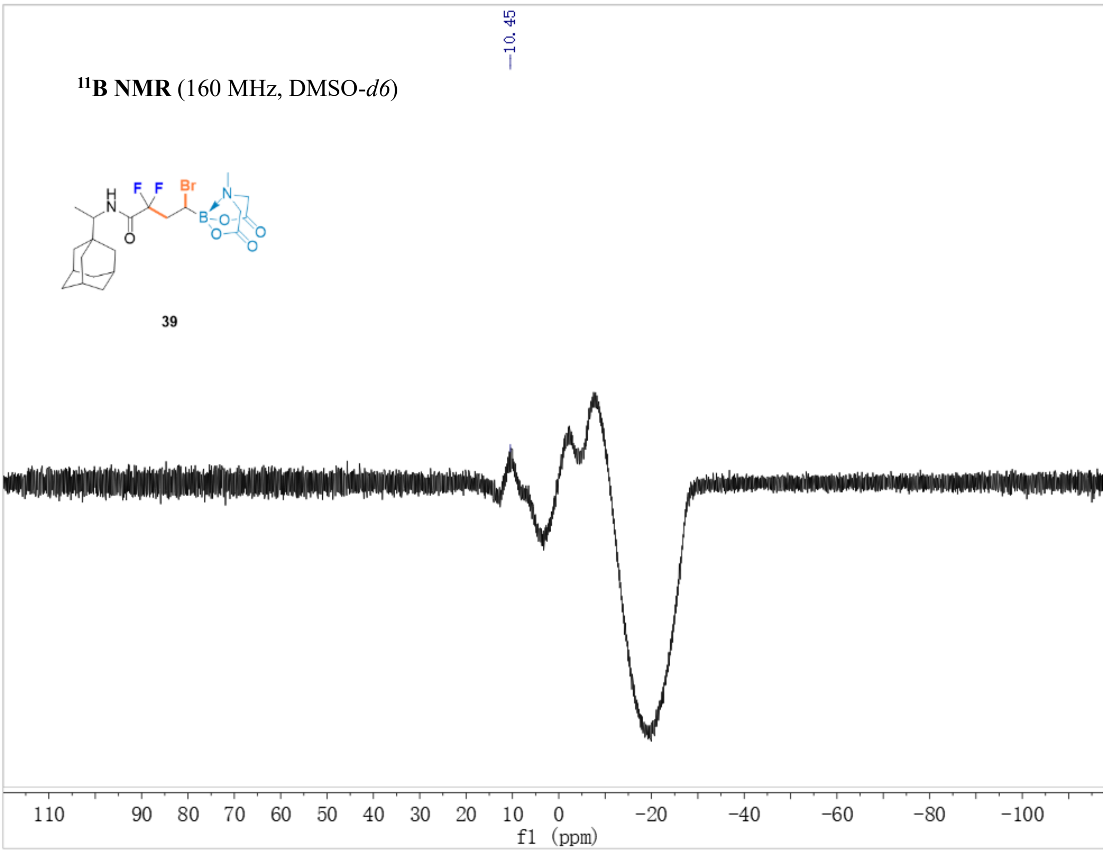
***N*-(1-((3*r*,5*r*,7*r*)-adamantan-1-yl)ethyl)-4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (39)**





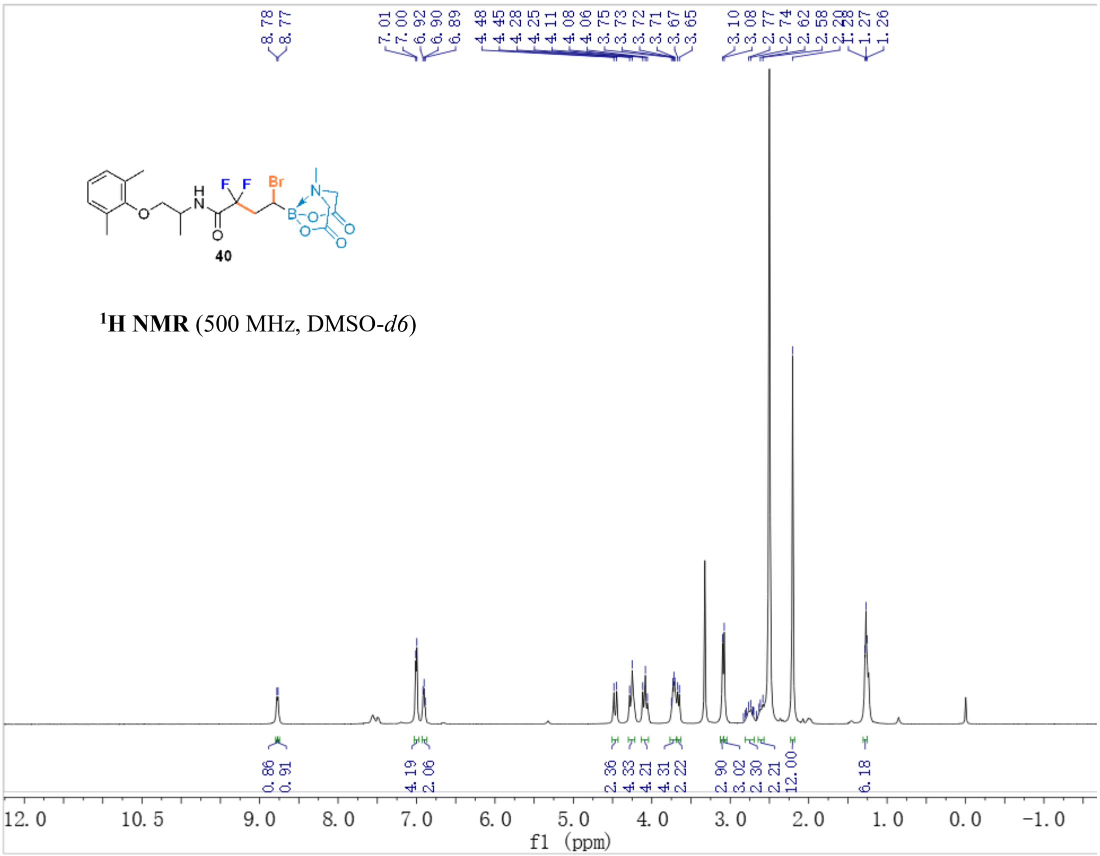


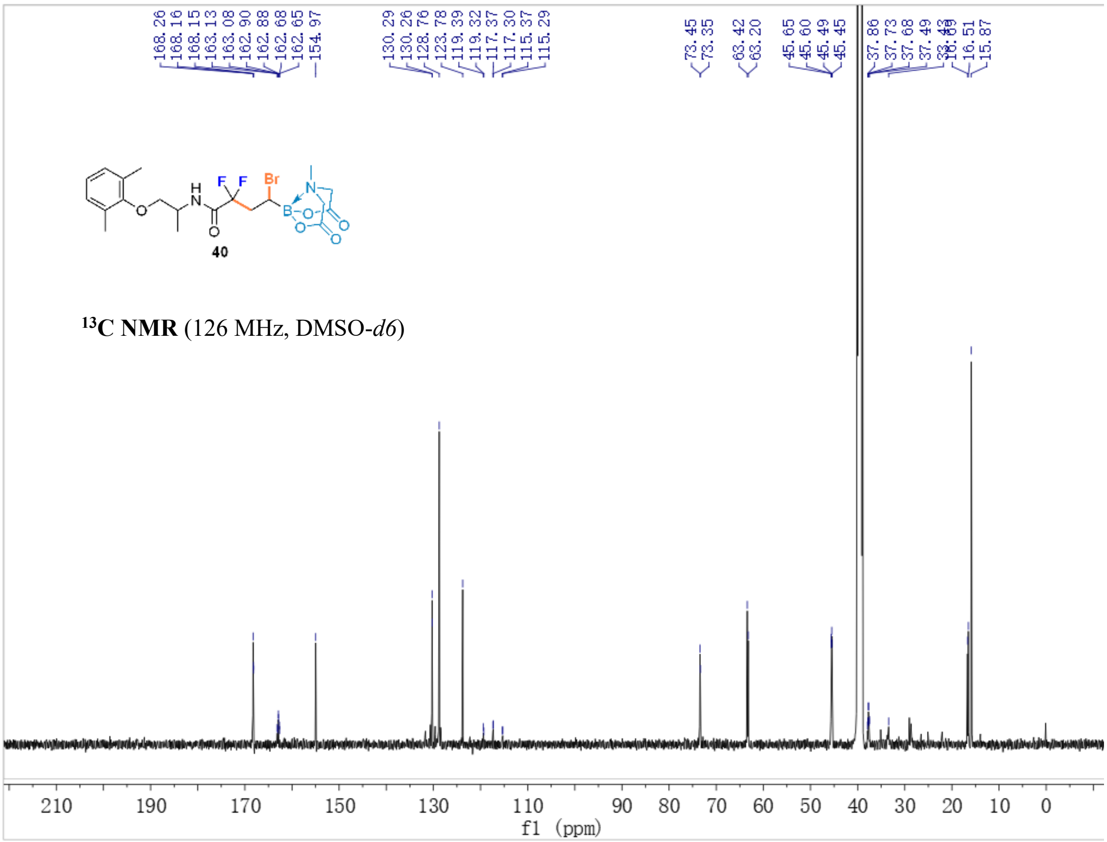
-101.91
-101.95
-101.98
-102.47
-103.78
-103.82
-103.82
-103.85
-104.31
-104.34
-104.35
-104.38
^{19}F NMR (471 MHz, DMSO-$d6$)
39
3.28
1.00
280 240 200 160 120 80 40 0 -40 -80 -120 -180 -240
f1 (ppm)



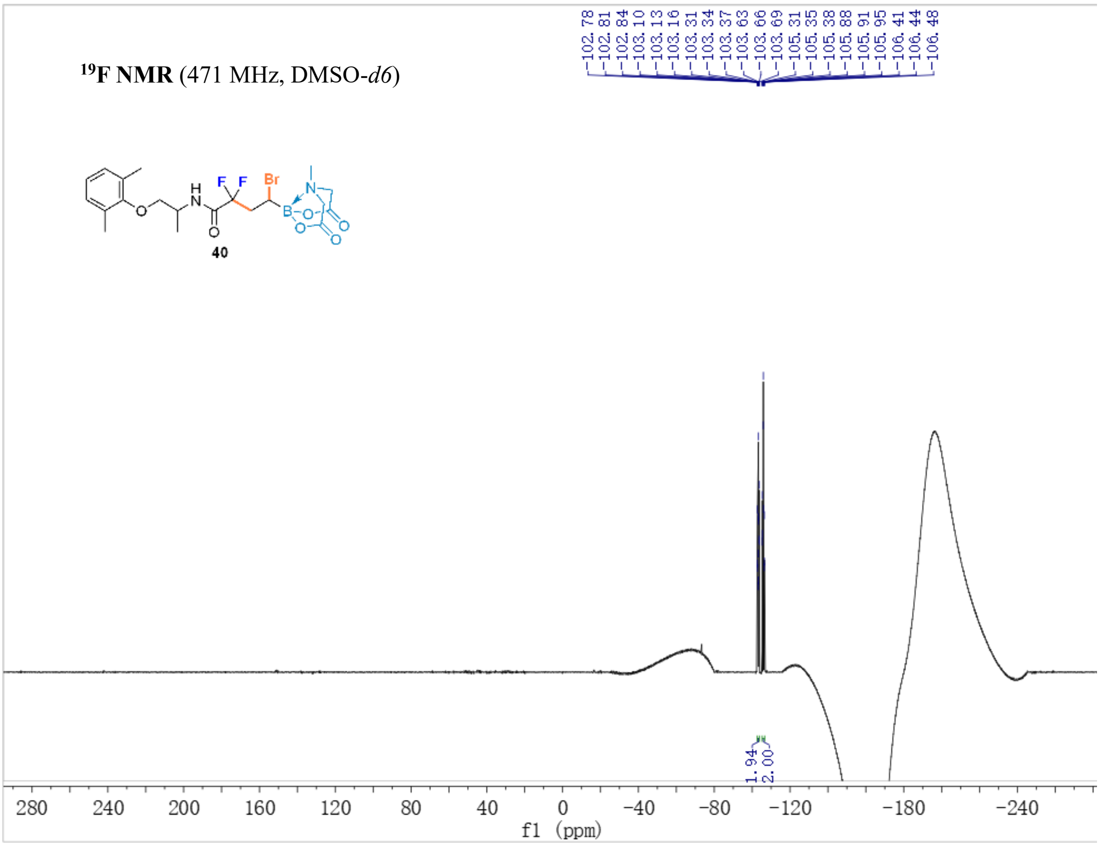
-10.45
^{11}B NMR (160 MHz, DMSO-$d6$)
39
110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100
f1 (ppm)

4-bromo-*N*-(1-(2,6-dimethylphenoxy)propan-2-yl)-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (40)

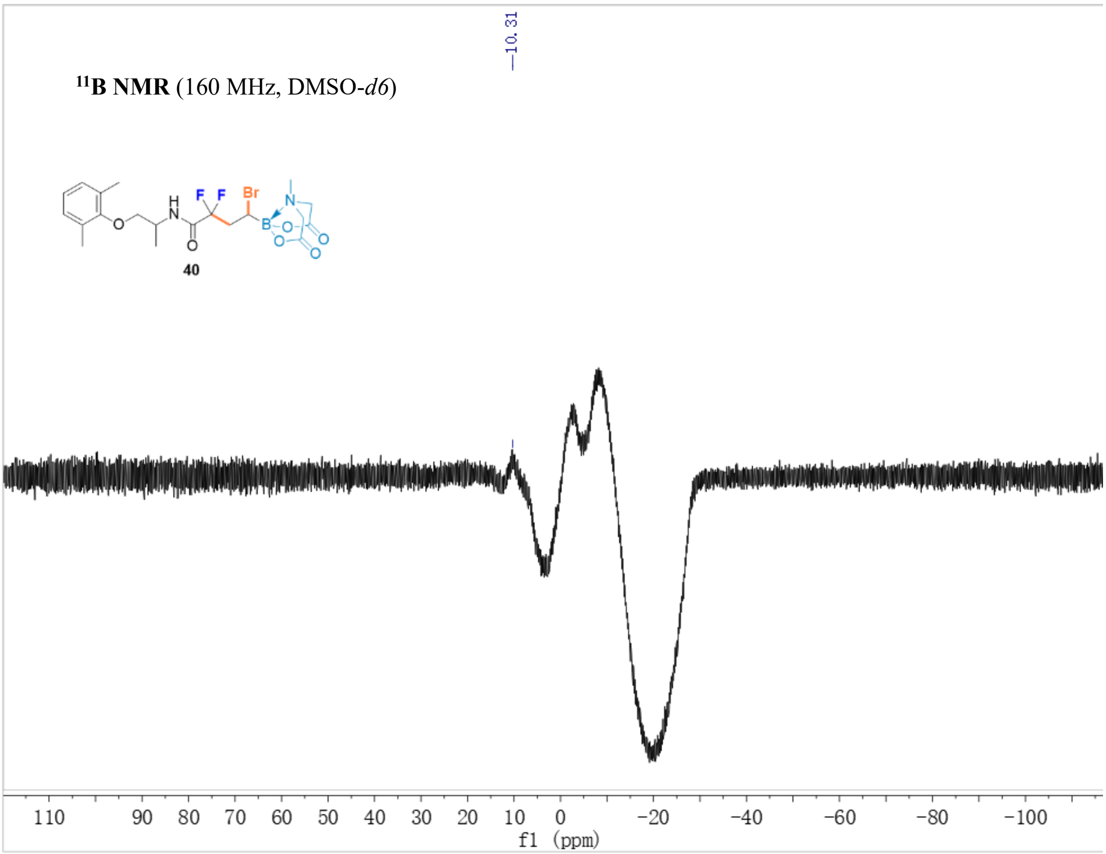




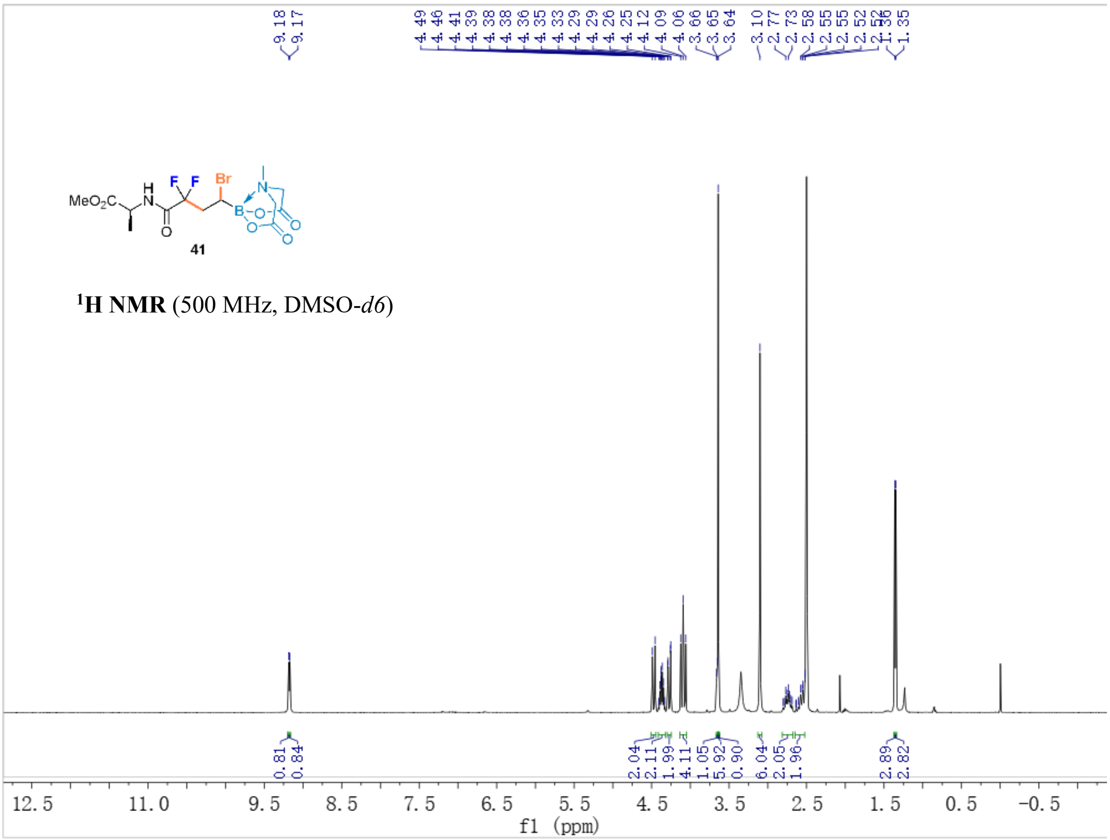
^{19}F NMR (471 MHz, DMSO-*d6*)

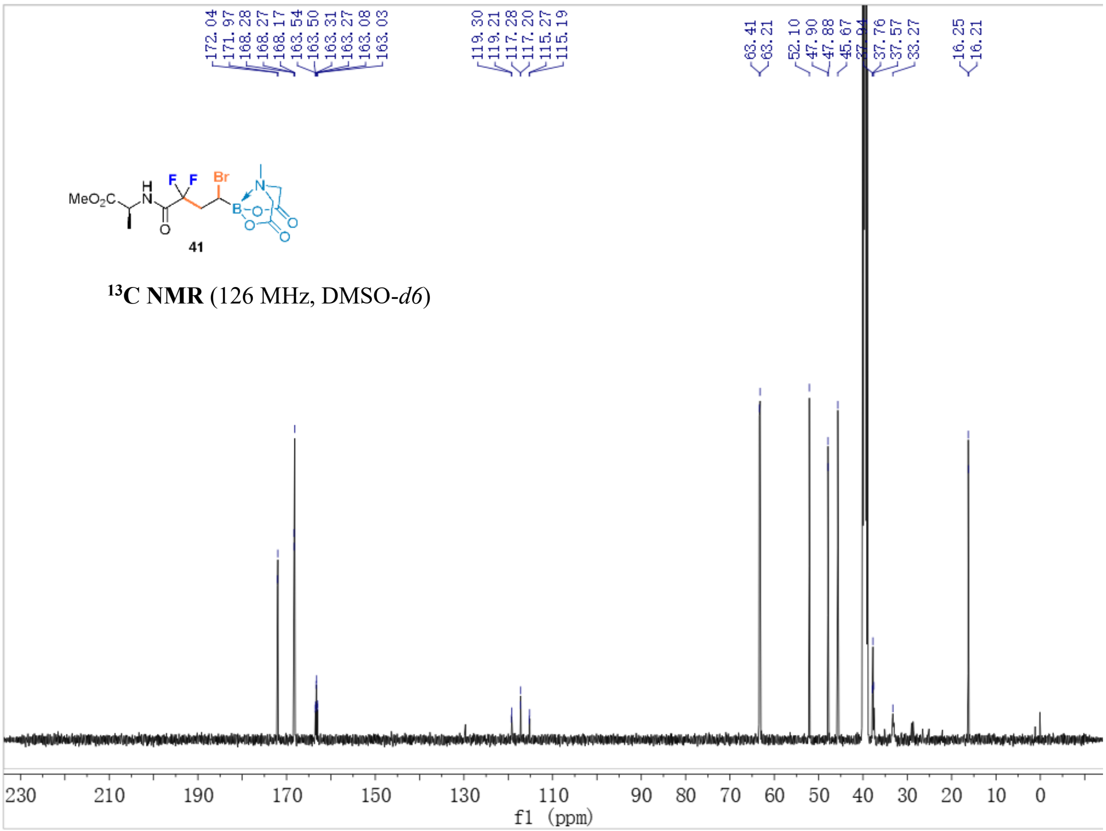


^{11}B NMR (160 MHz, DMSO-*d6*)



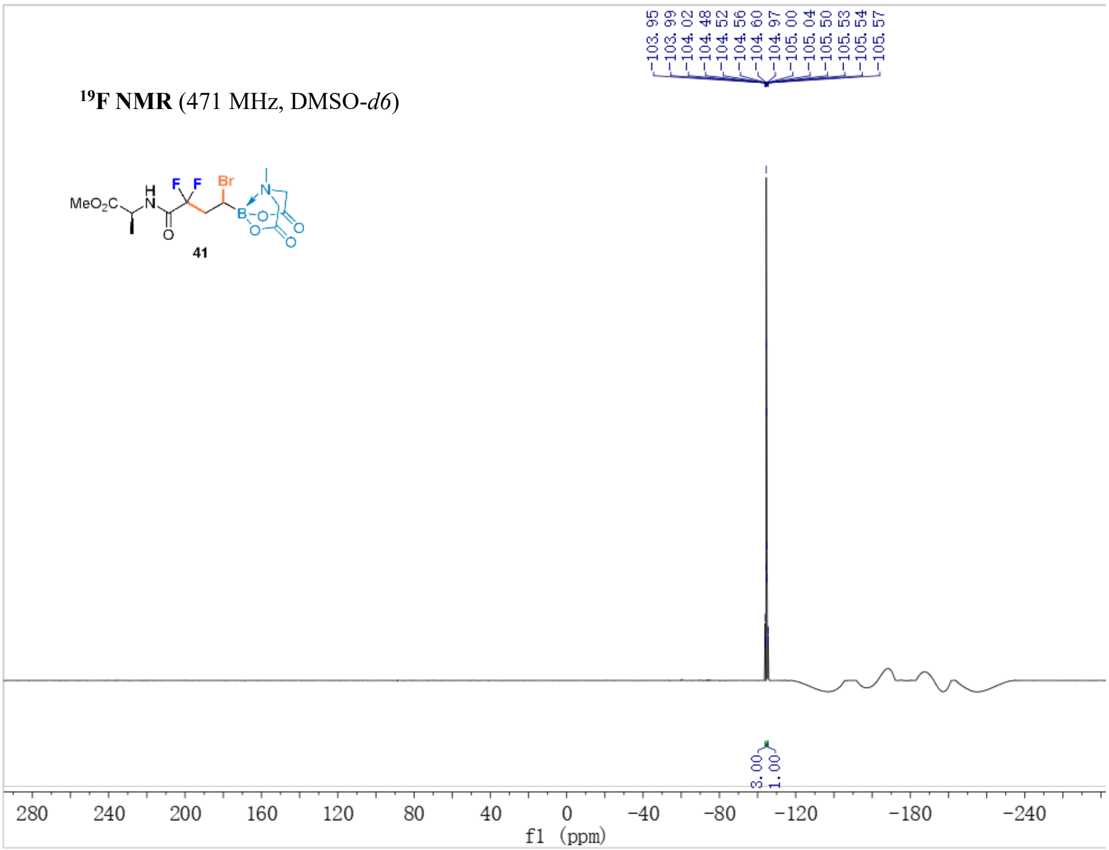
Methyl (4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoyl)-*L*-alaninate (41)





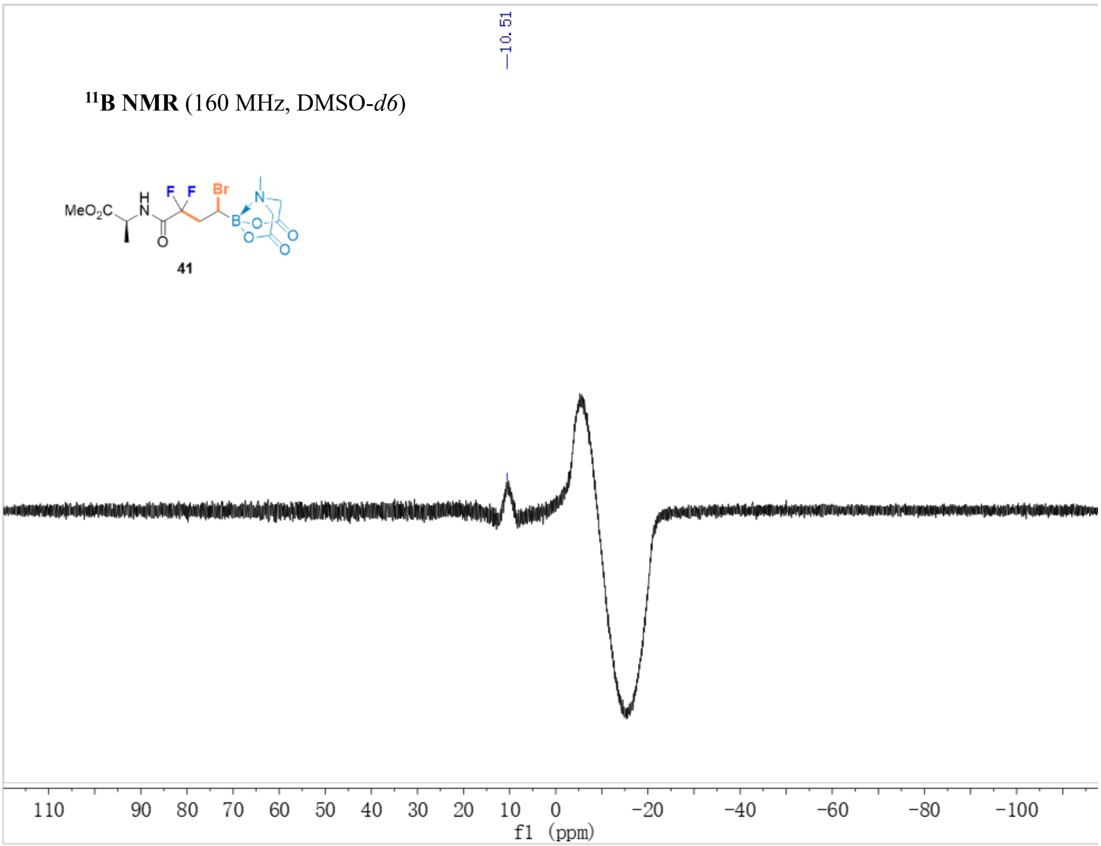
^{19}F NMR (471 MHz, DMSO-*d6*)

41

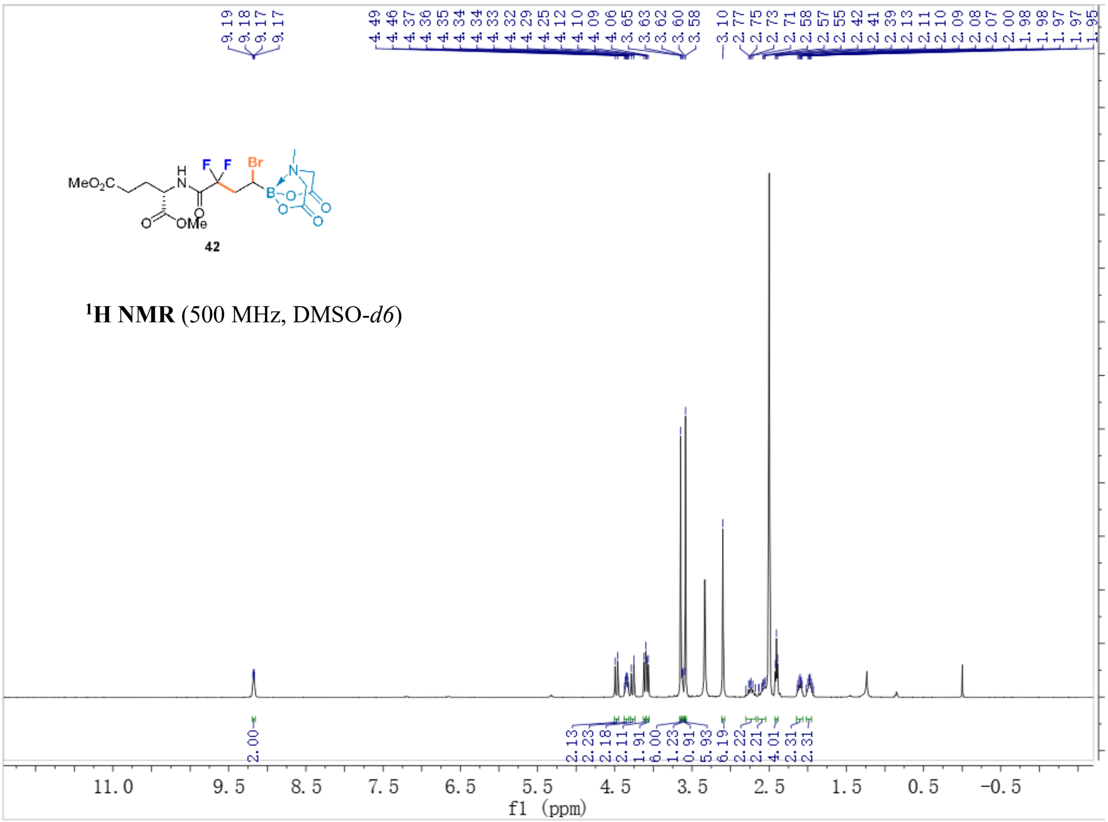


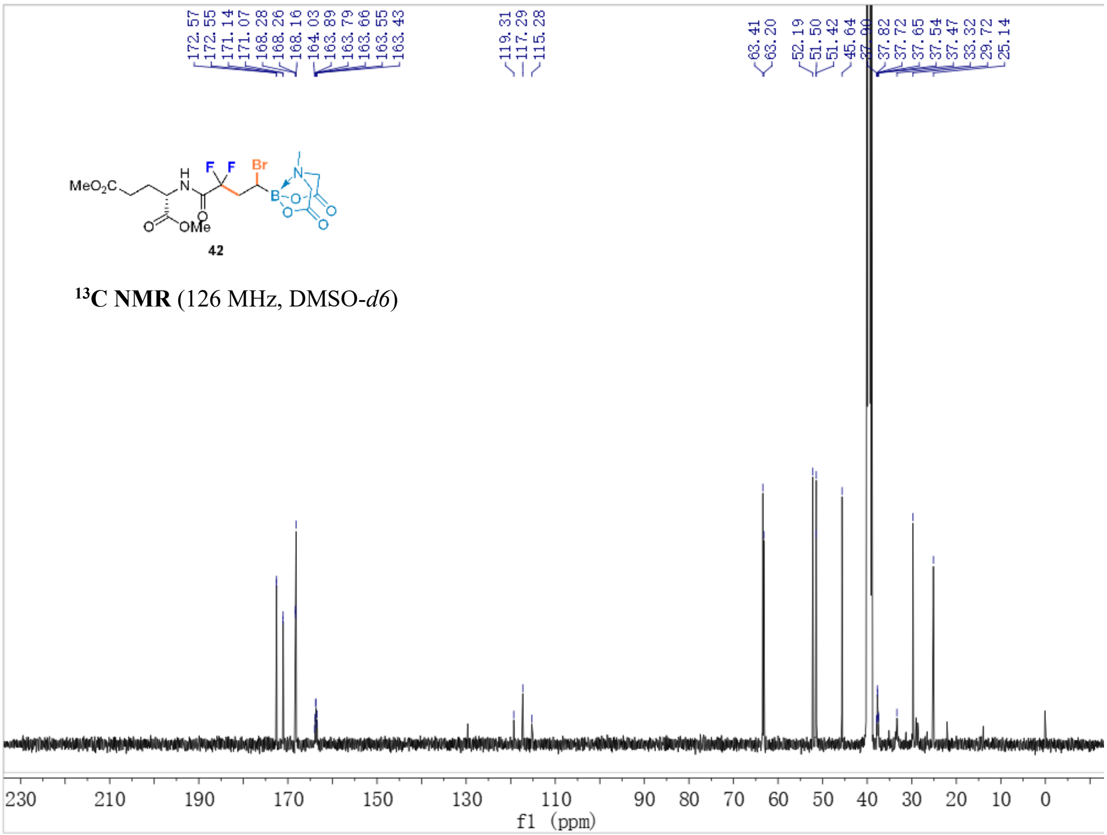
^{11}B NMR (160 MHz, DMSO-*d6*)

41

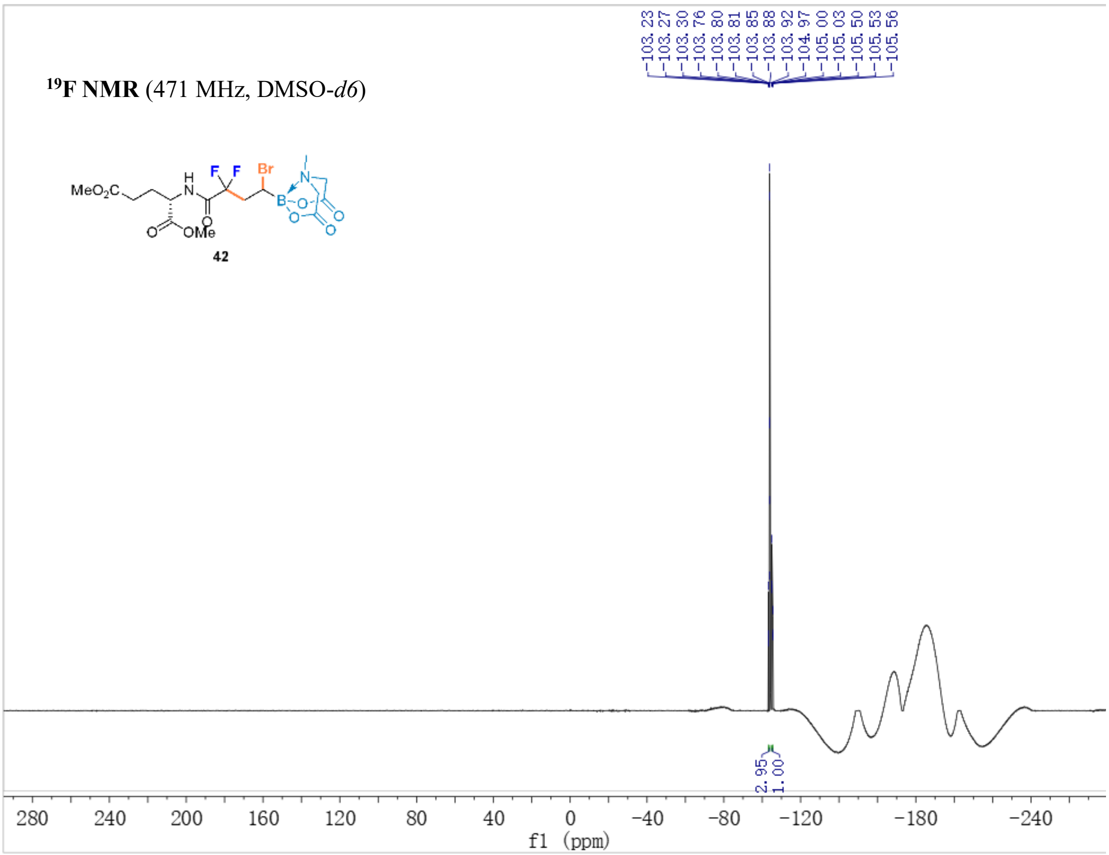


Dimethyl (4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoyl)-*L*-glutamate (42)

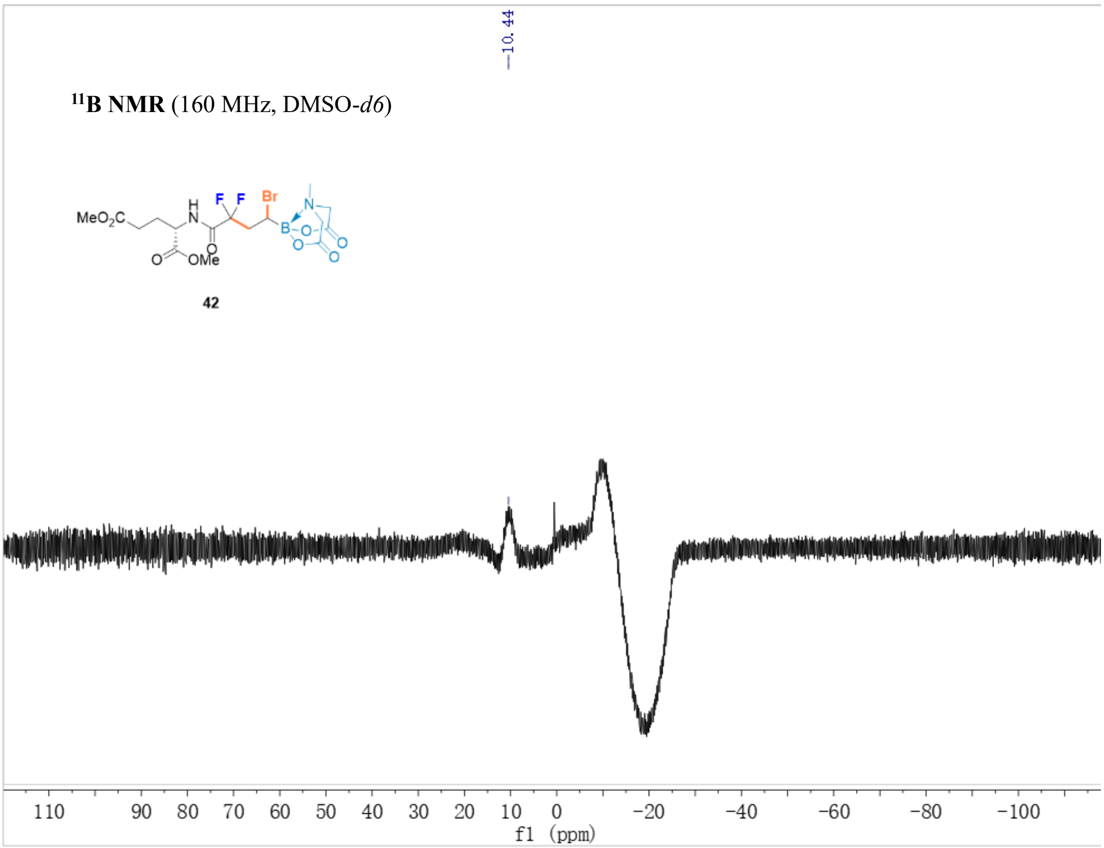




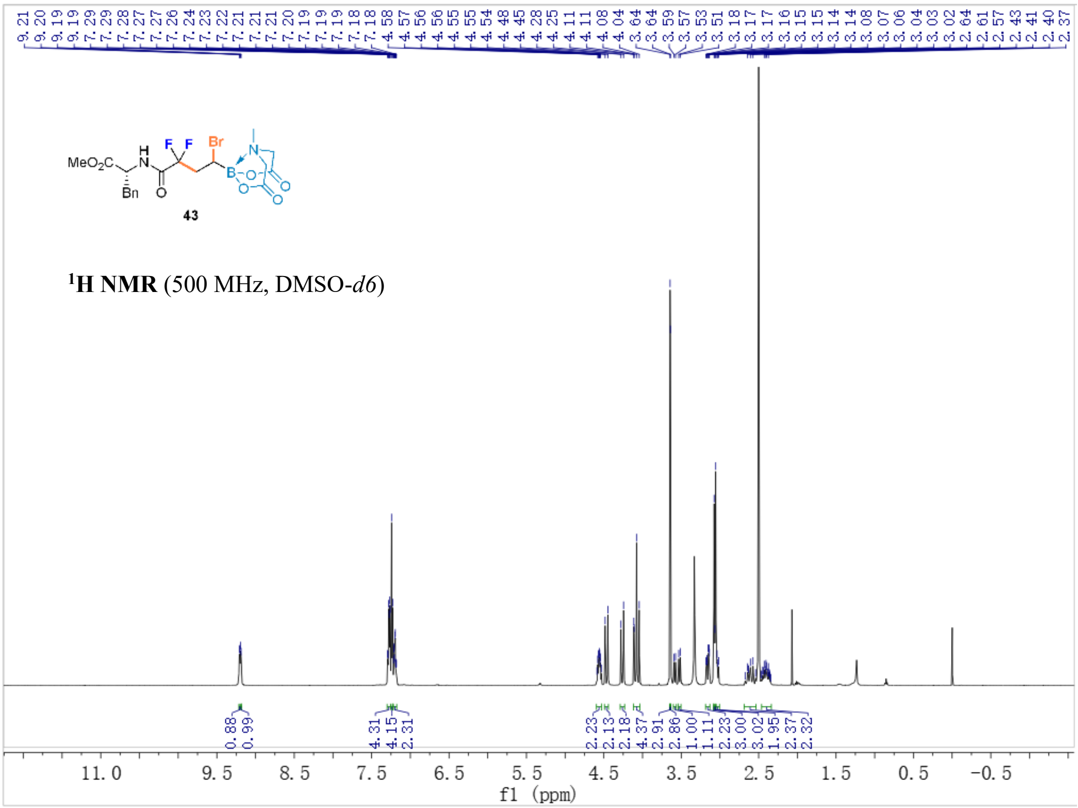
¹⁹F NMR (471 MHz, DMSO-*d6*)

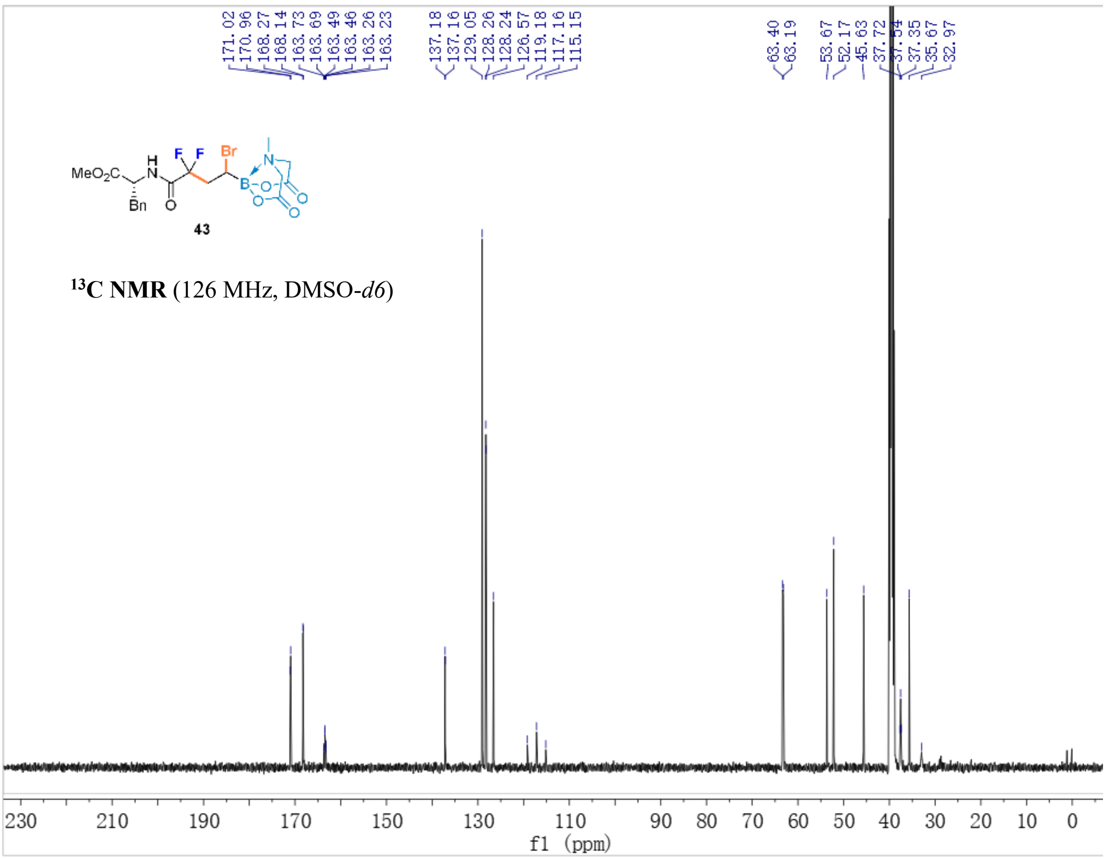


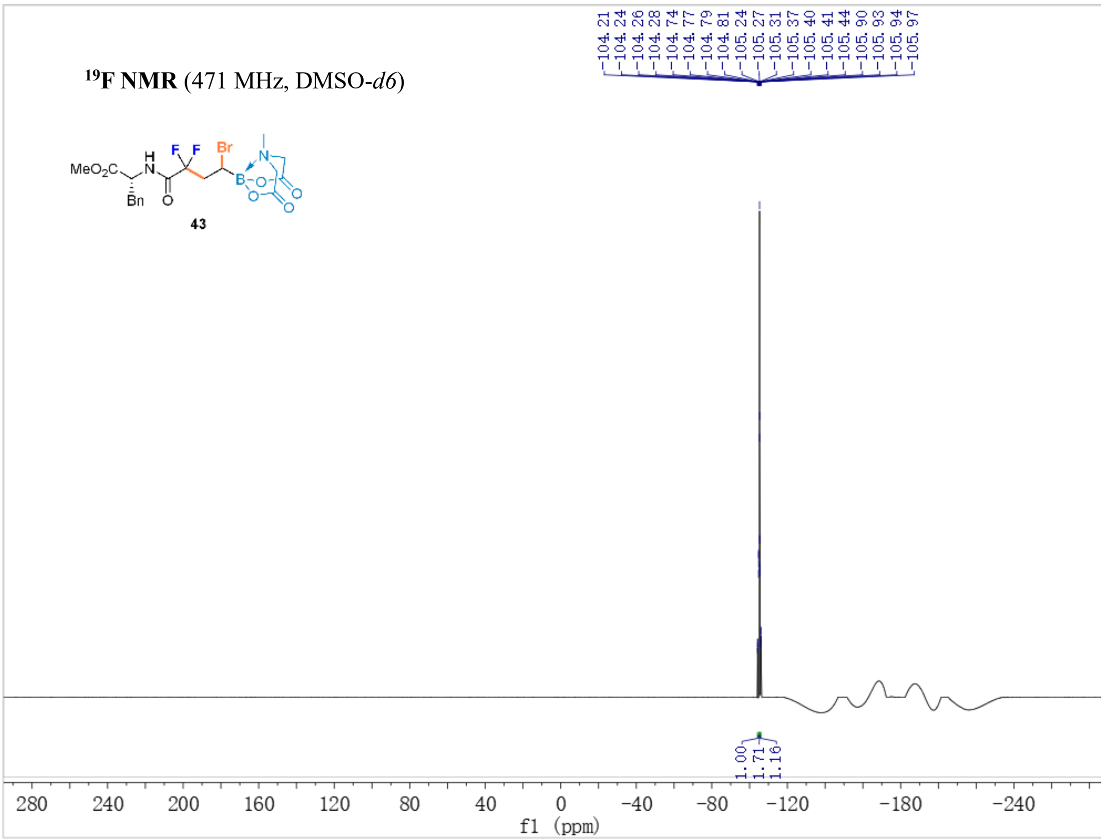
¹¹B NMR (160 MHz, DMSO-*d6*)

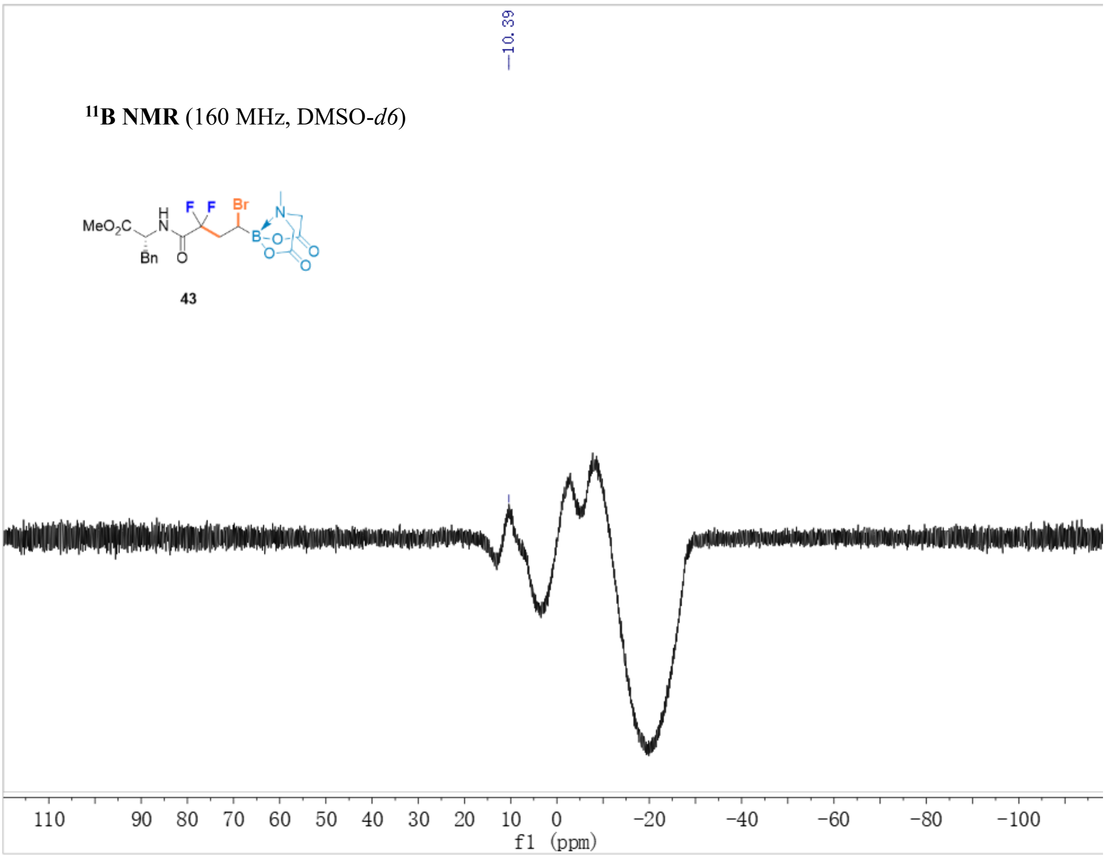


Methyl (4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoyl)-*D*-phenylalaninate (43)

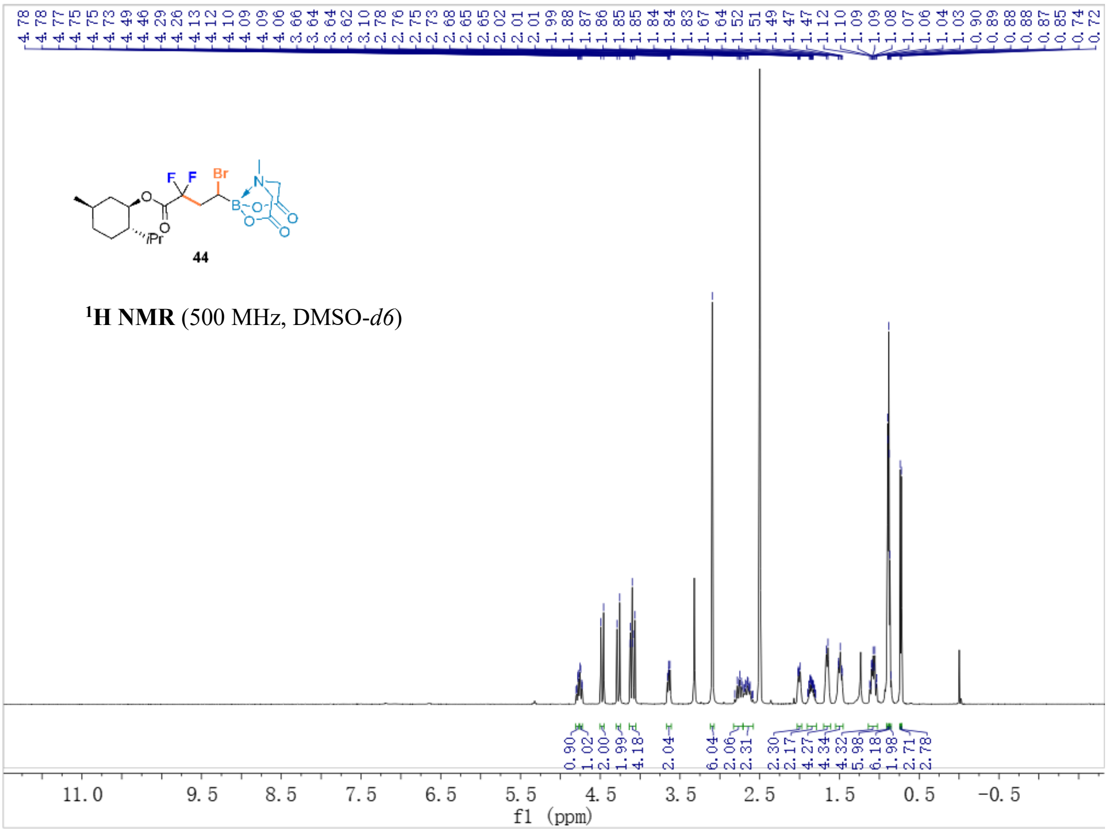


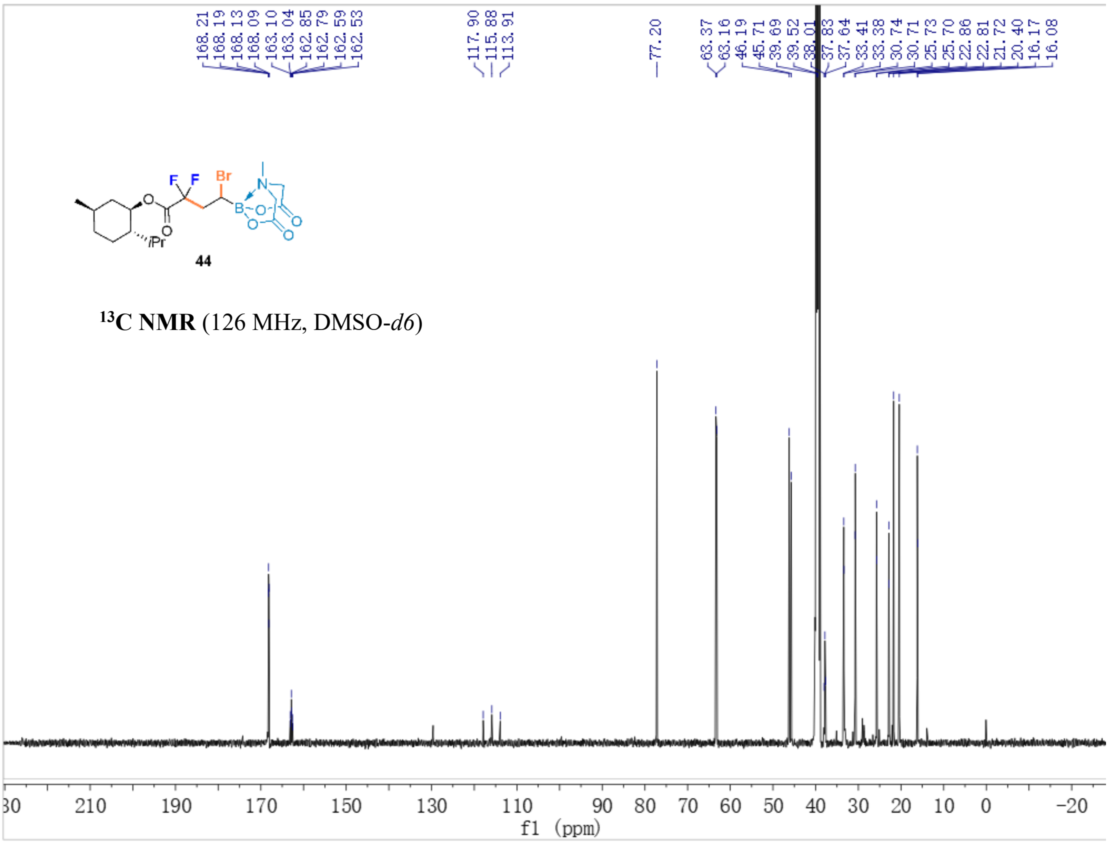


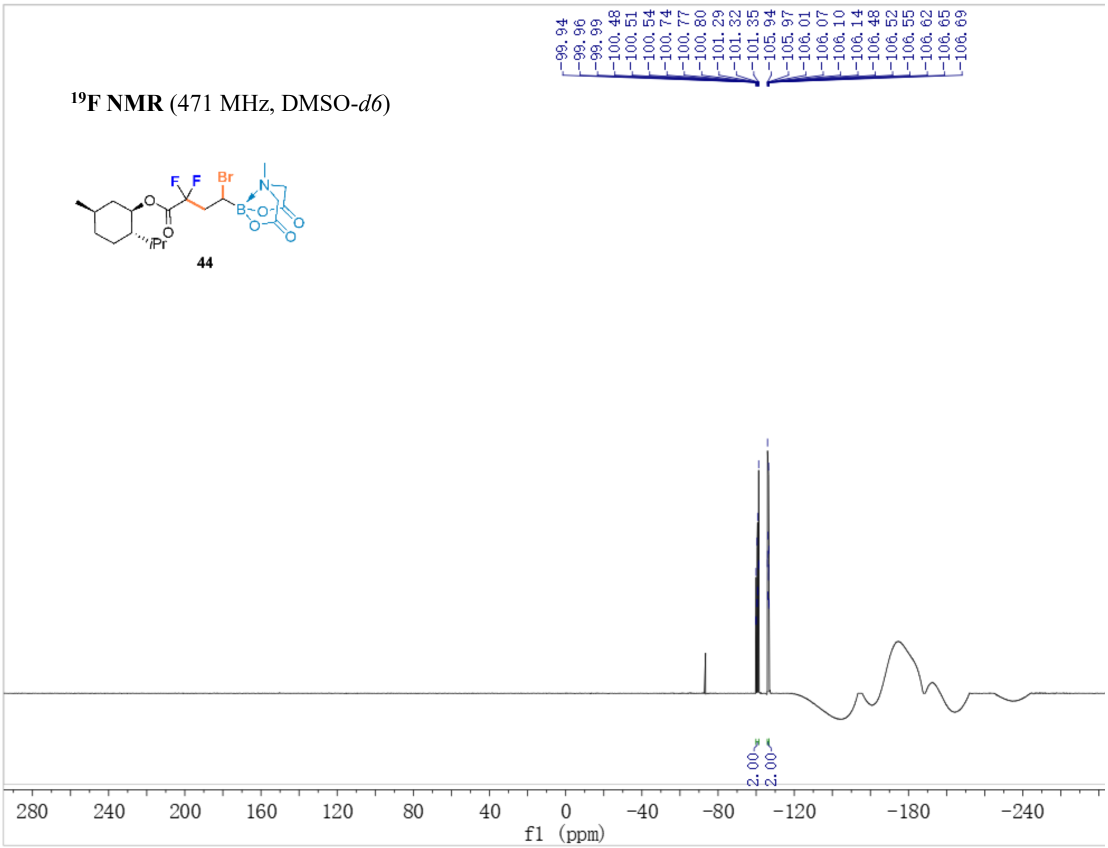

19F NMR (471 MHz, DMSO-d6)
43
-104.21
-104.24
-104.26
-104.28
-104.74
-104.77
-104.79
-104.81
-105.24
-105.27
-105.31
-105.37
-105.40
-105.41
-105.44
-105.90
-105.93
-105.94
-105.97
1.00
1.71
1.16
280 240 200 160 120 80 40 0 -40 -80 -120 -180 -240
f1 (ppm)


10.39
11B NMR (160 MHz, DMSO-d6)
43
110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100
f1 (ppm)

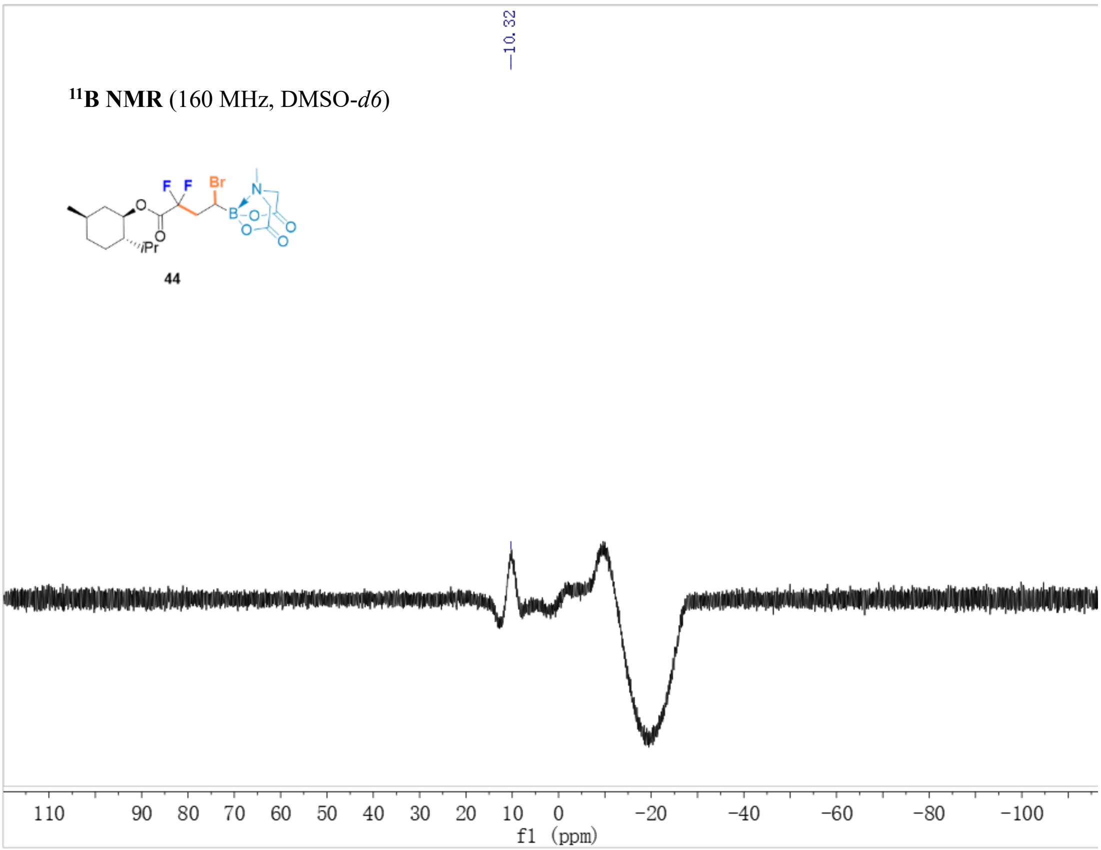
(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoate (44)





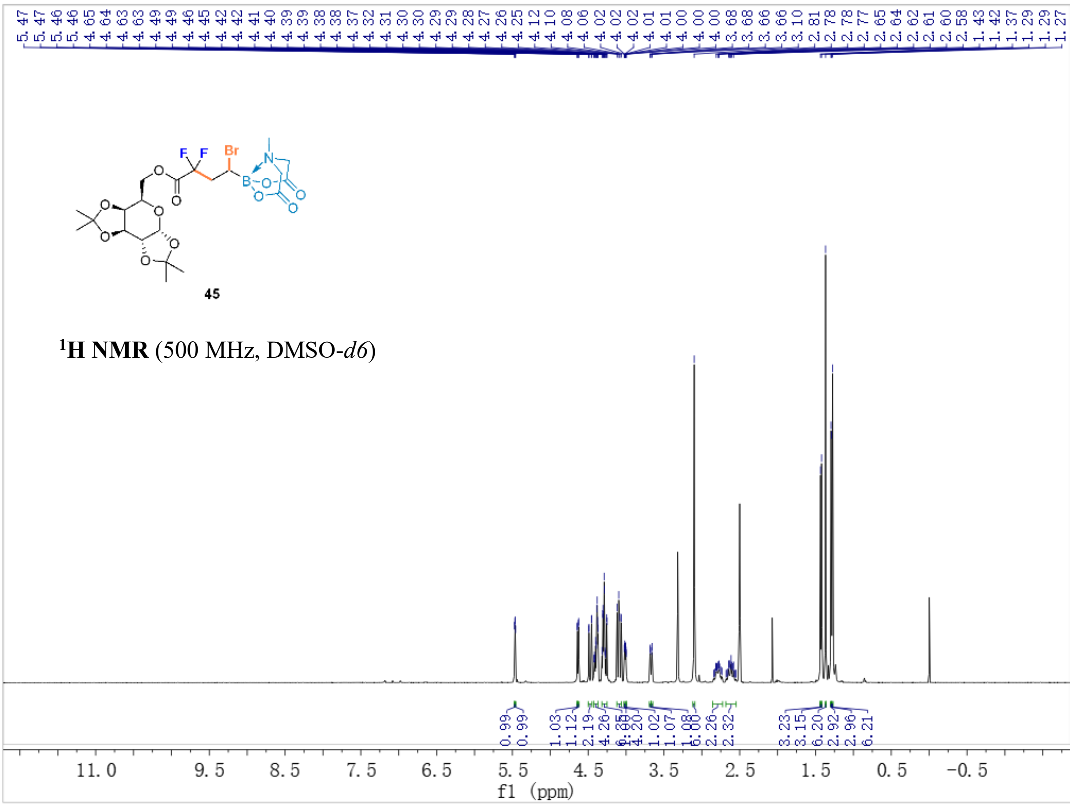


99.94
99.96
99.99
100.48
100.51
100.54
100.74
100.77
100.80
101.29
101.32
101.35
105.94
105.97
106.01
106.07
106.10
106.14
106.48
106.52
106.55
106.62
106.65
106.69
^{19}F NMR (471 MHz, DMSO-d6)
F F Br N B O O O O O iPr
44
2.00
2.00
280 240 200 160 120 80 40 0 −40 −80 −120 −180 −240
f1 (ppm)

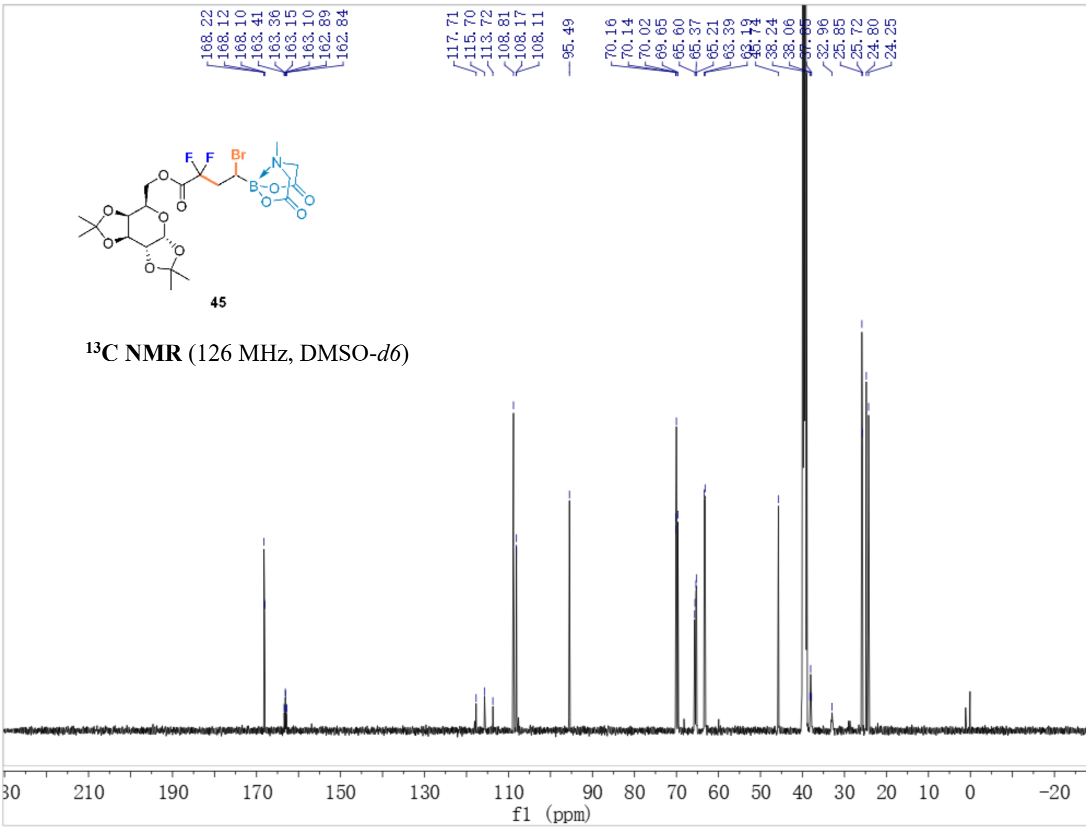


10.32
^{11}B NMR (160 MHz, DMSO-d6)
F F Br N B O O O O O iPr
44
110 90 80 70 60 50 40 30 20 10 0 −20 −40 −60 −80 −100
f1 (ppm)

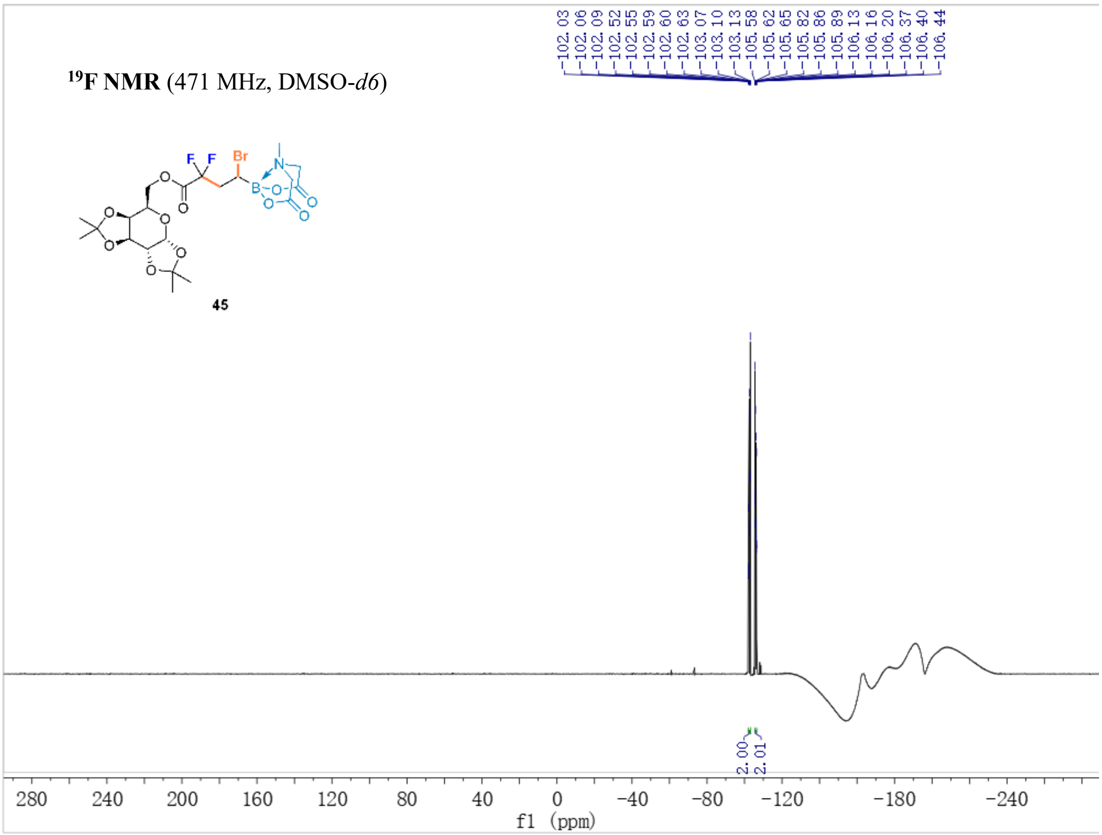
((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl 4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoate (45)

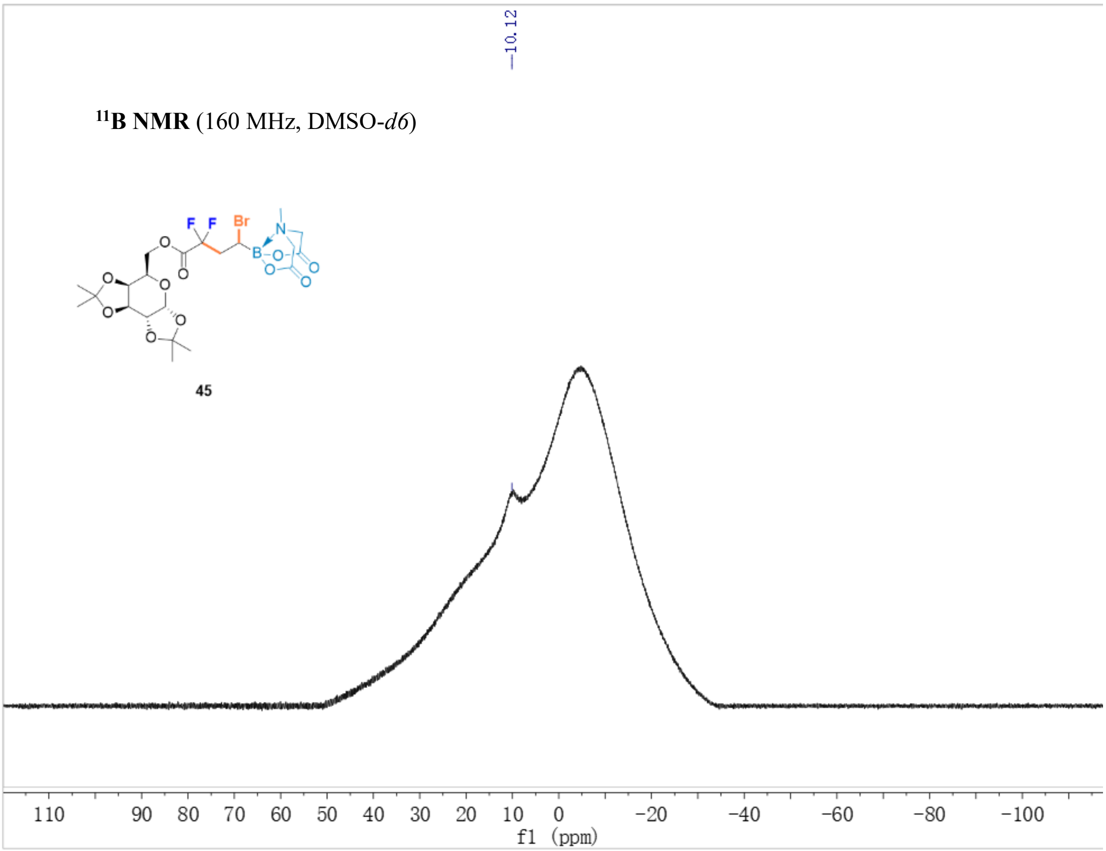


^{1}**H NMR** (500 MHz, DMSO-*d6*)



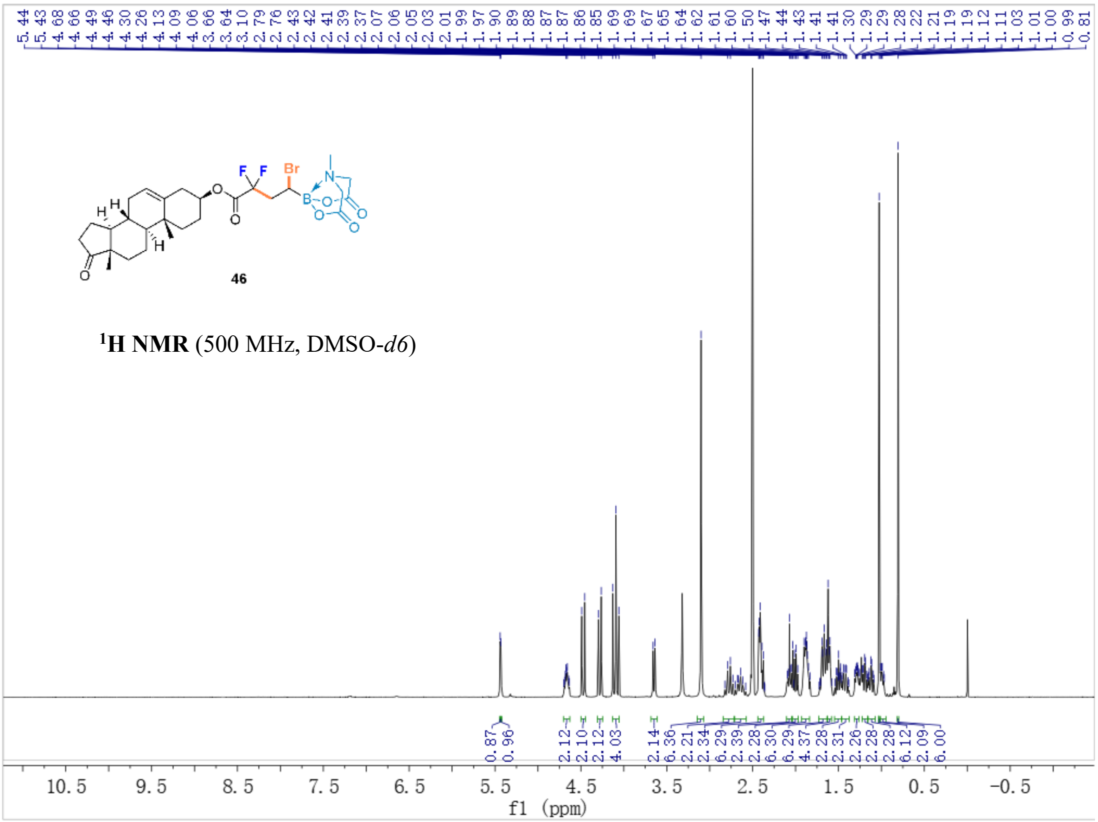
^{13}**C NMR** (126 MHz, DMSO-*d6*)

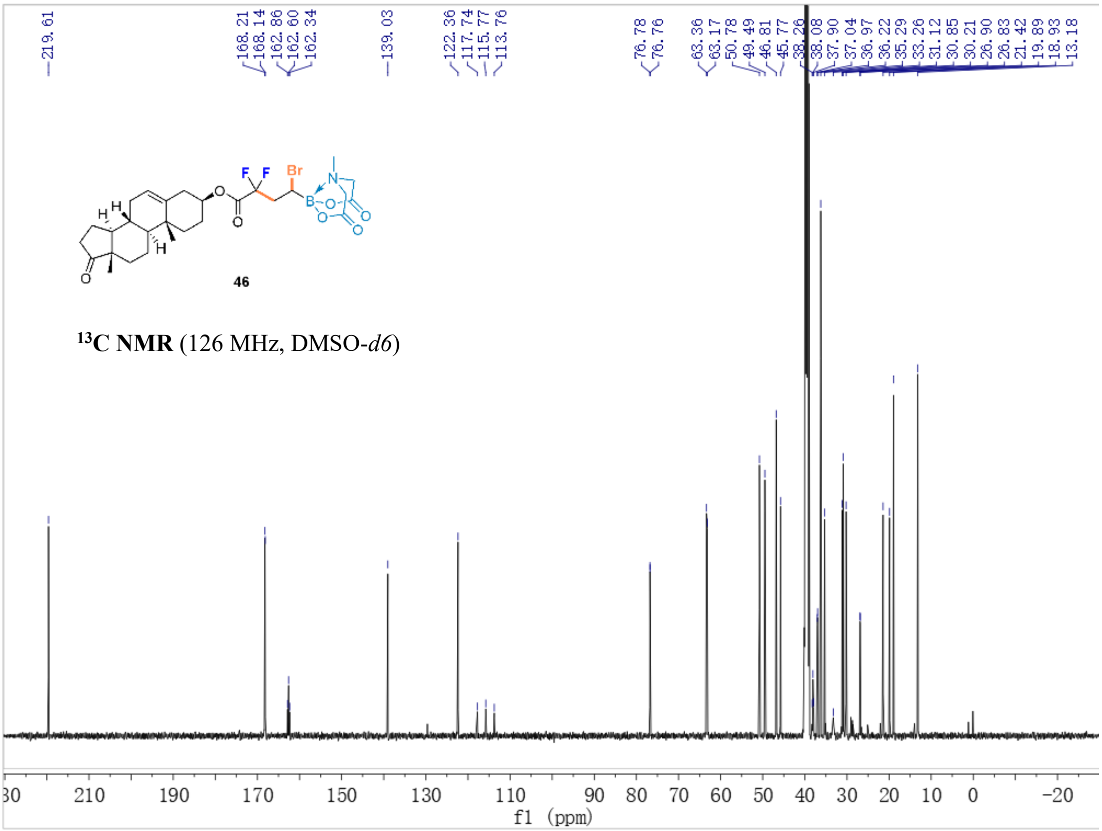


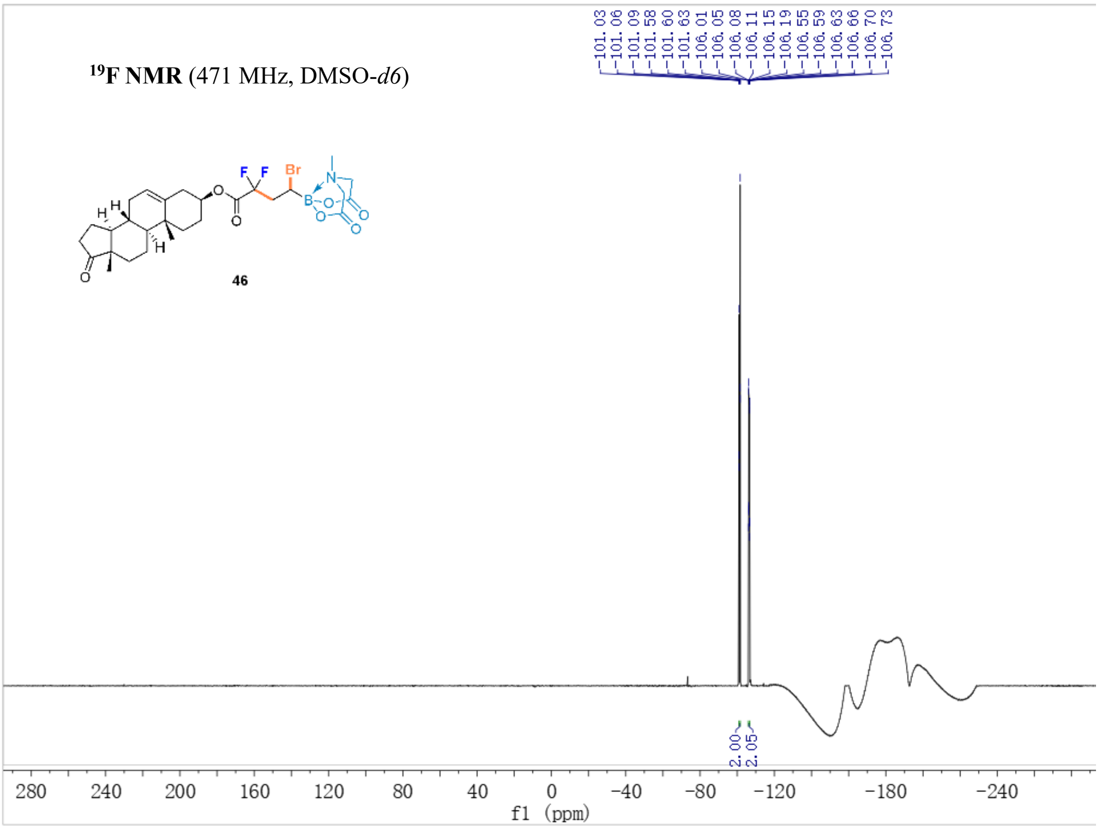


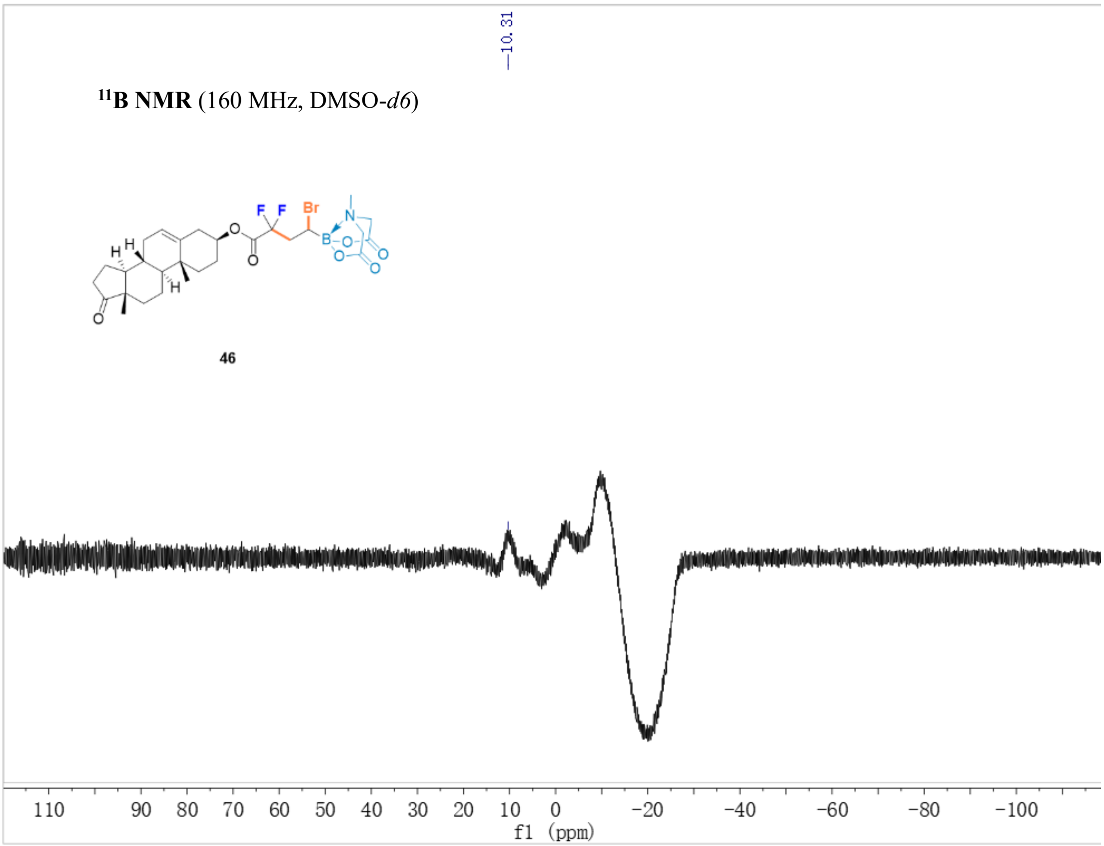
(3*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-10,13-dimethyl-17-oxo-

2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoate (46)



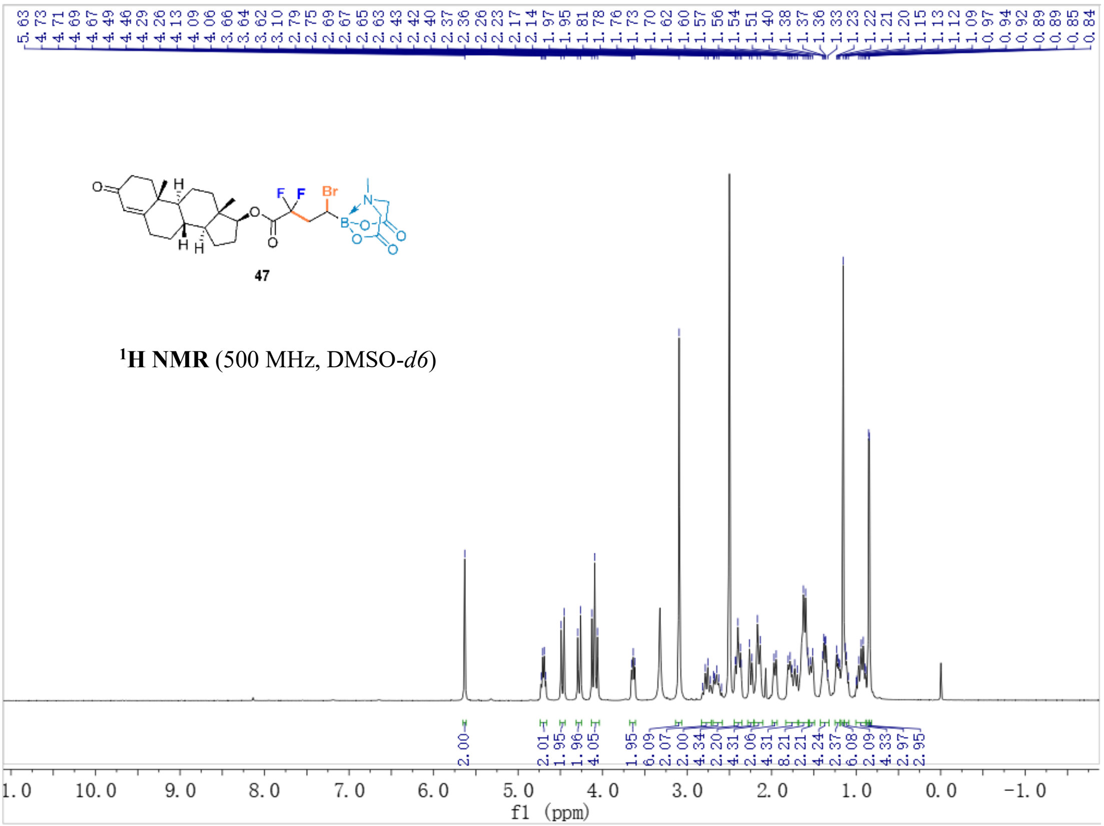


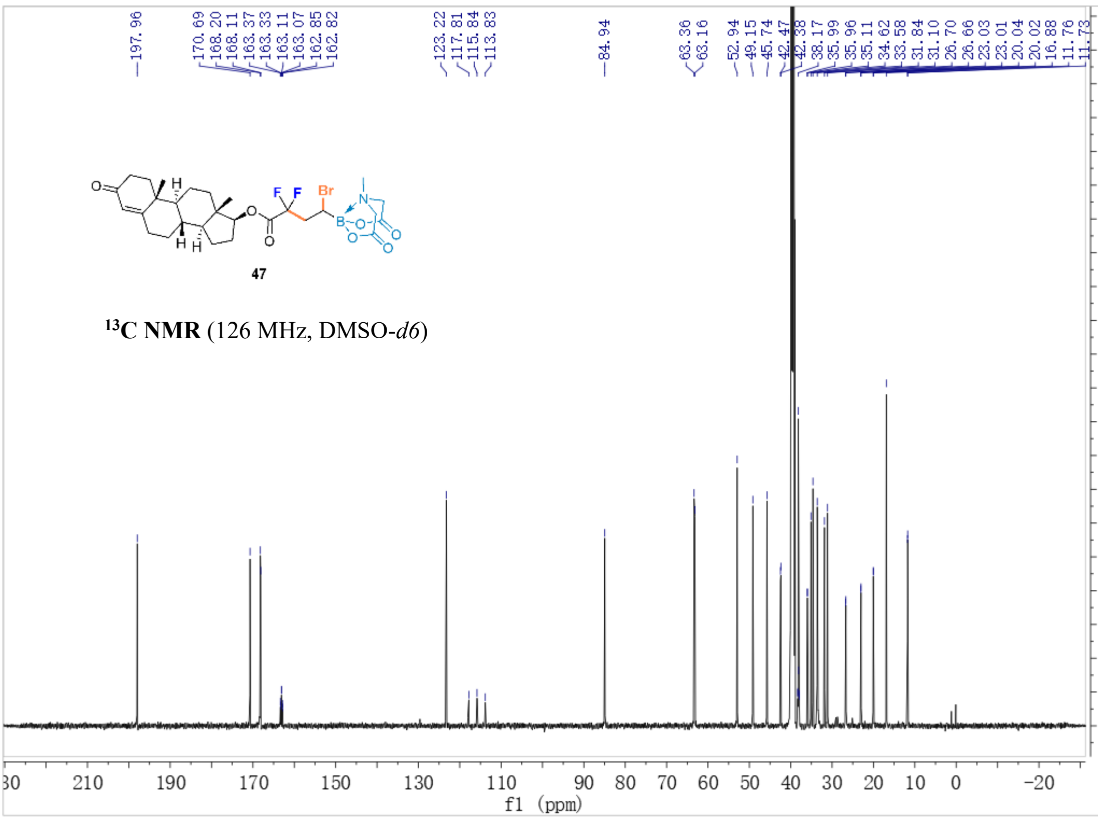


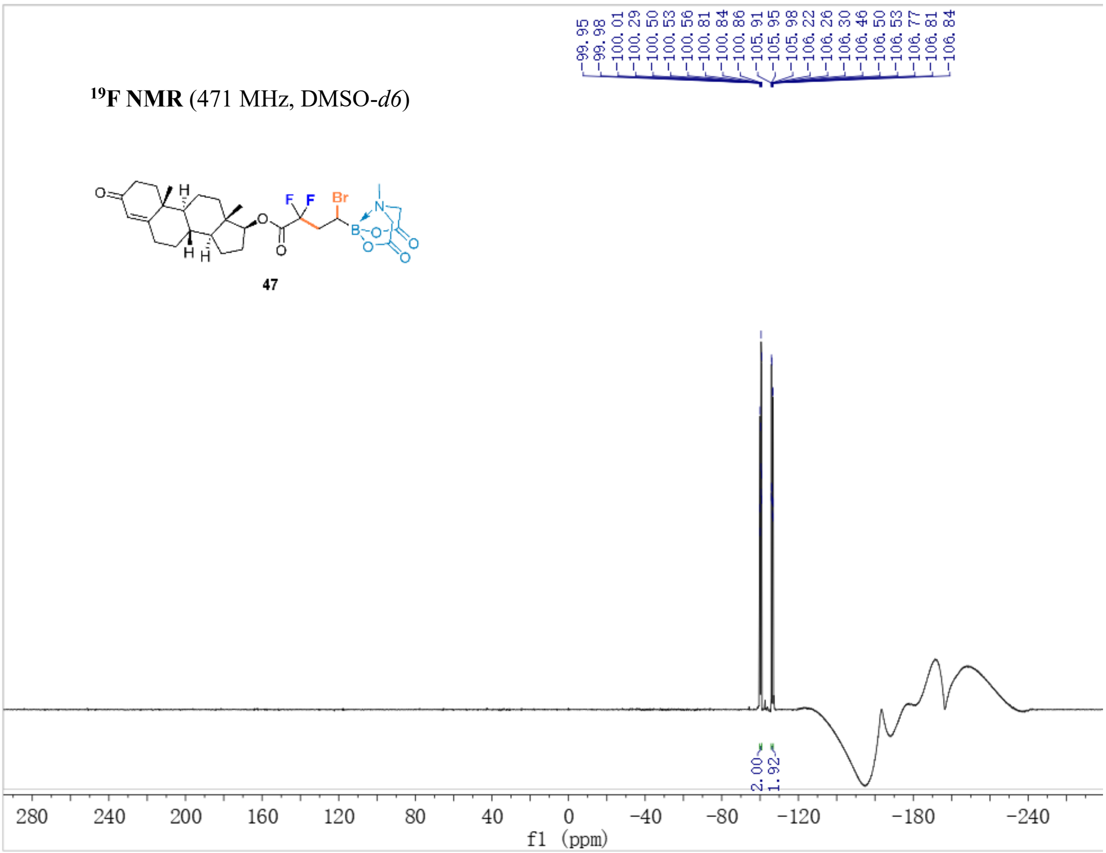


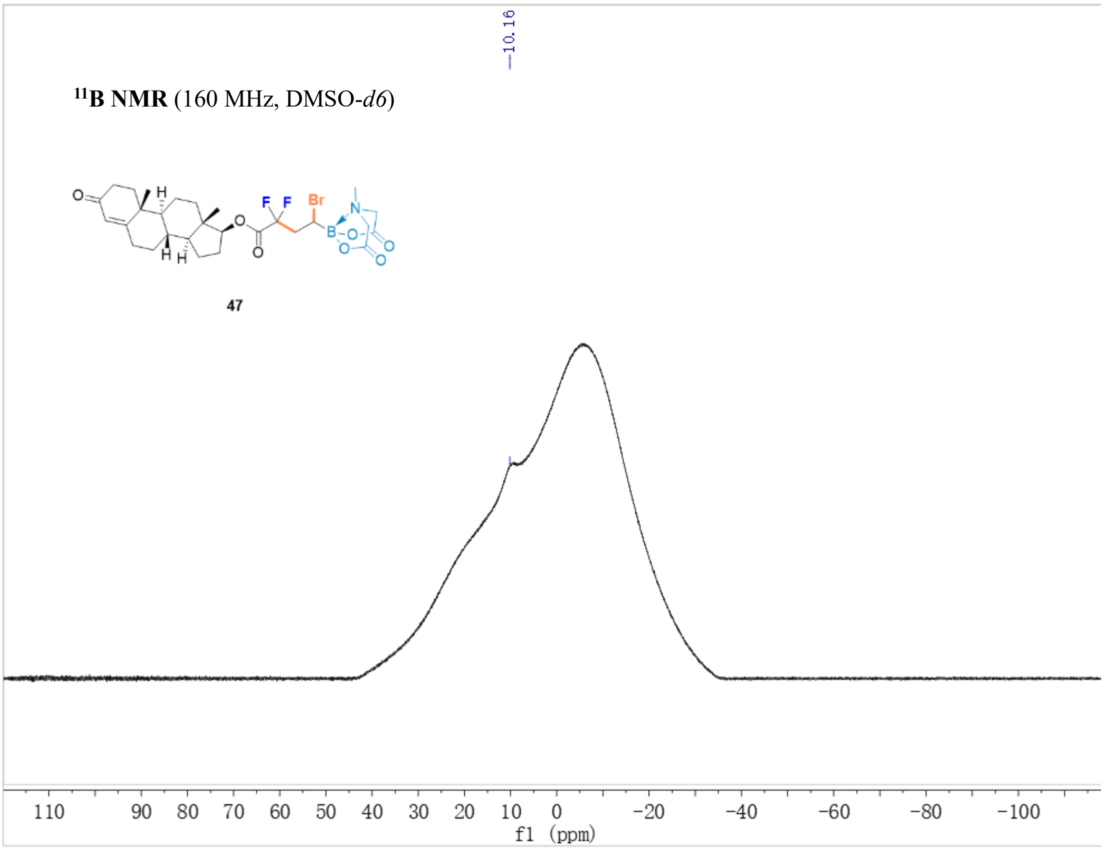
(8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-dimethyl-3-oxo-

2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl 4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoate (47)



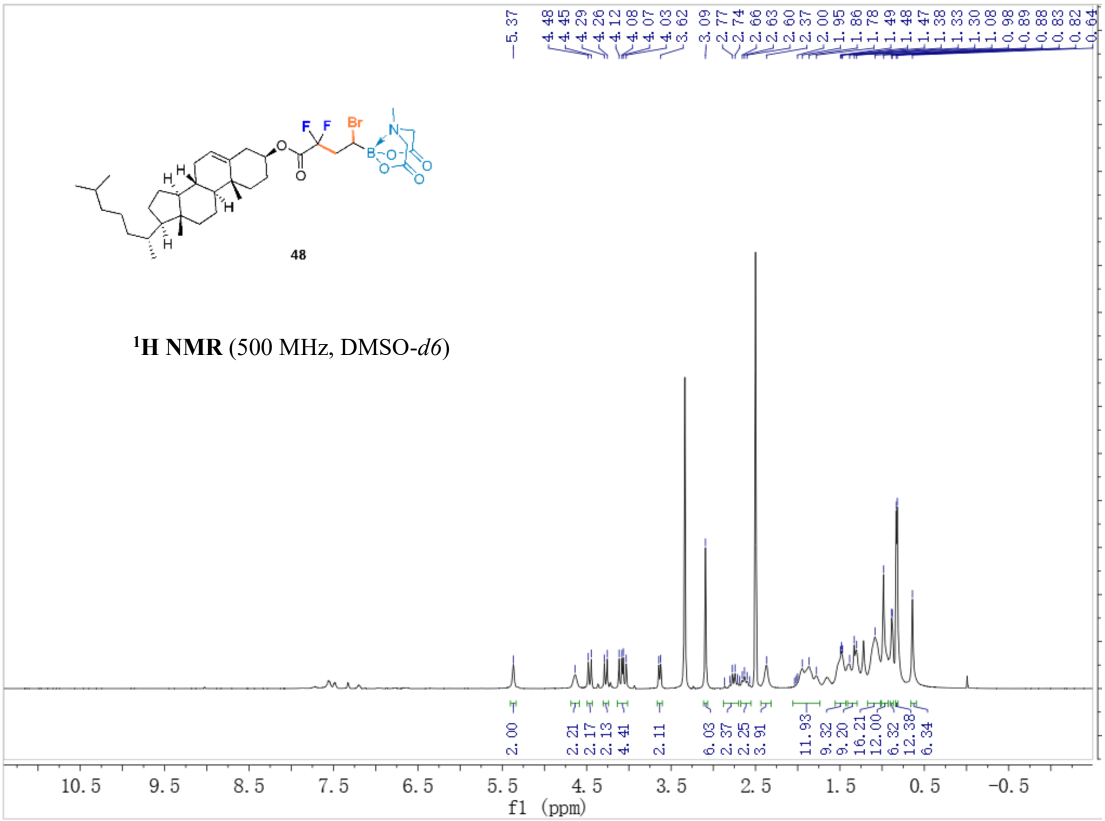


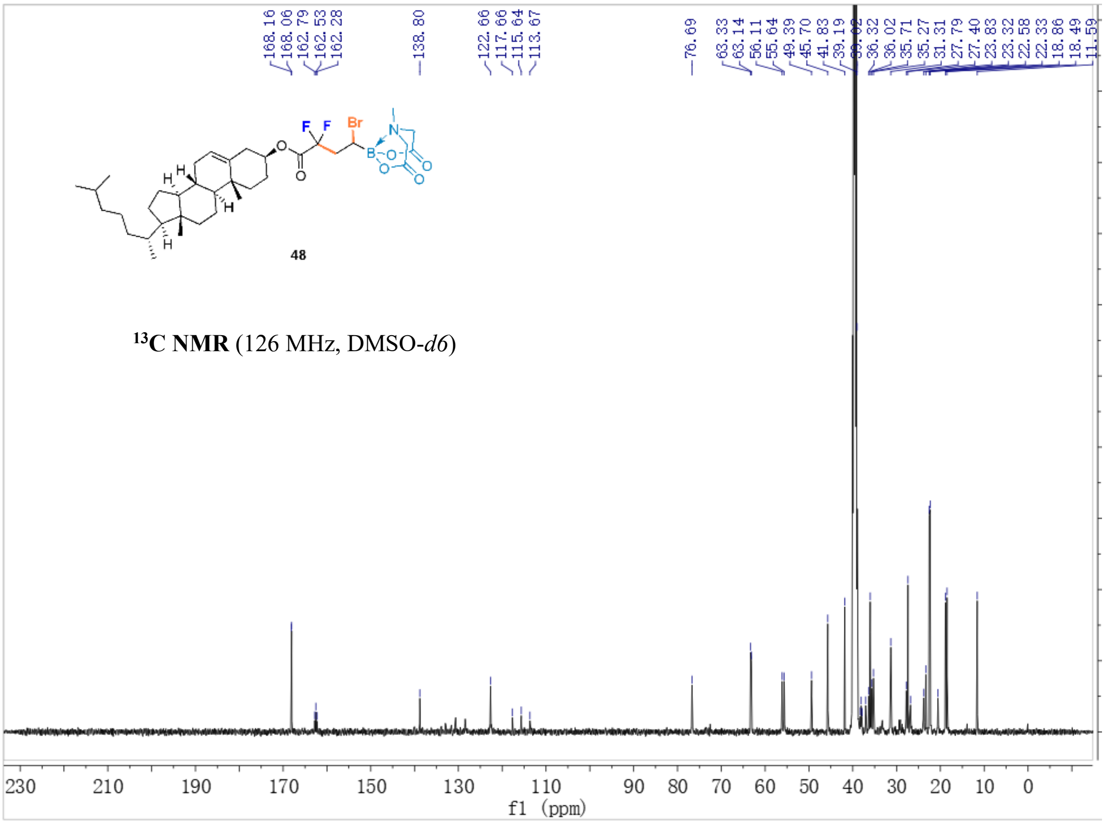


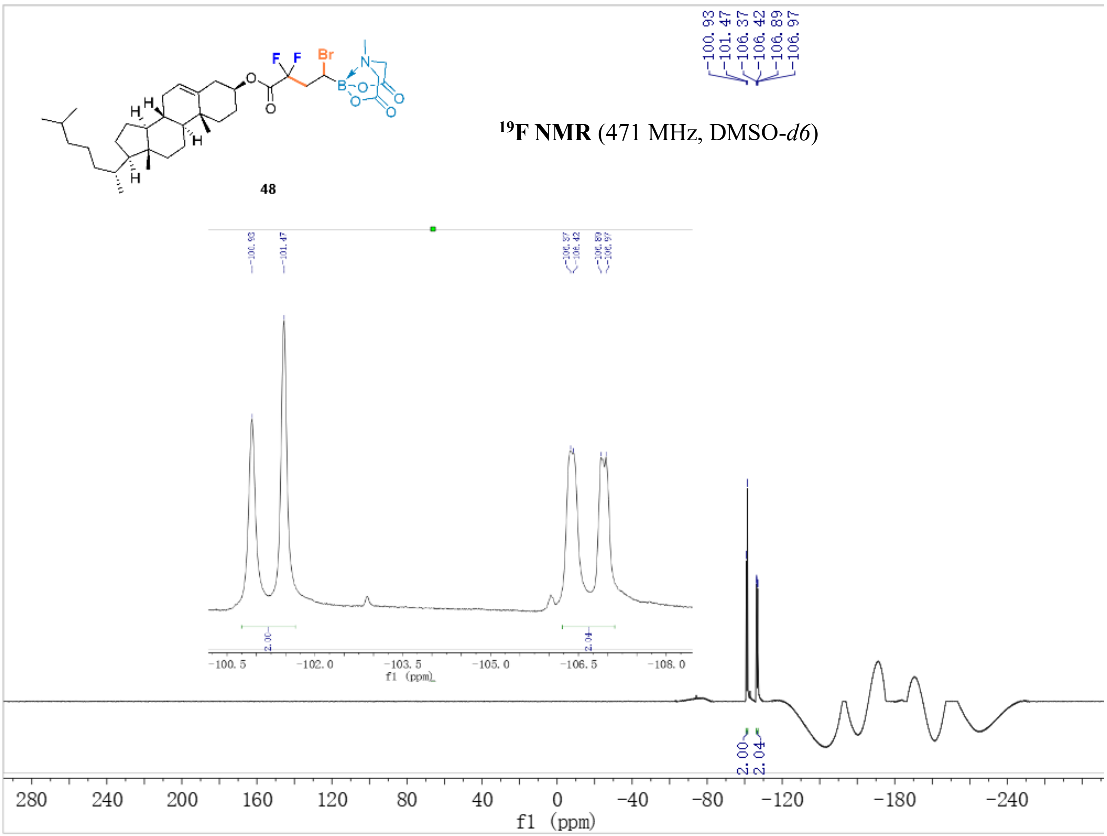


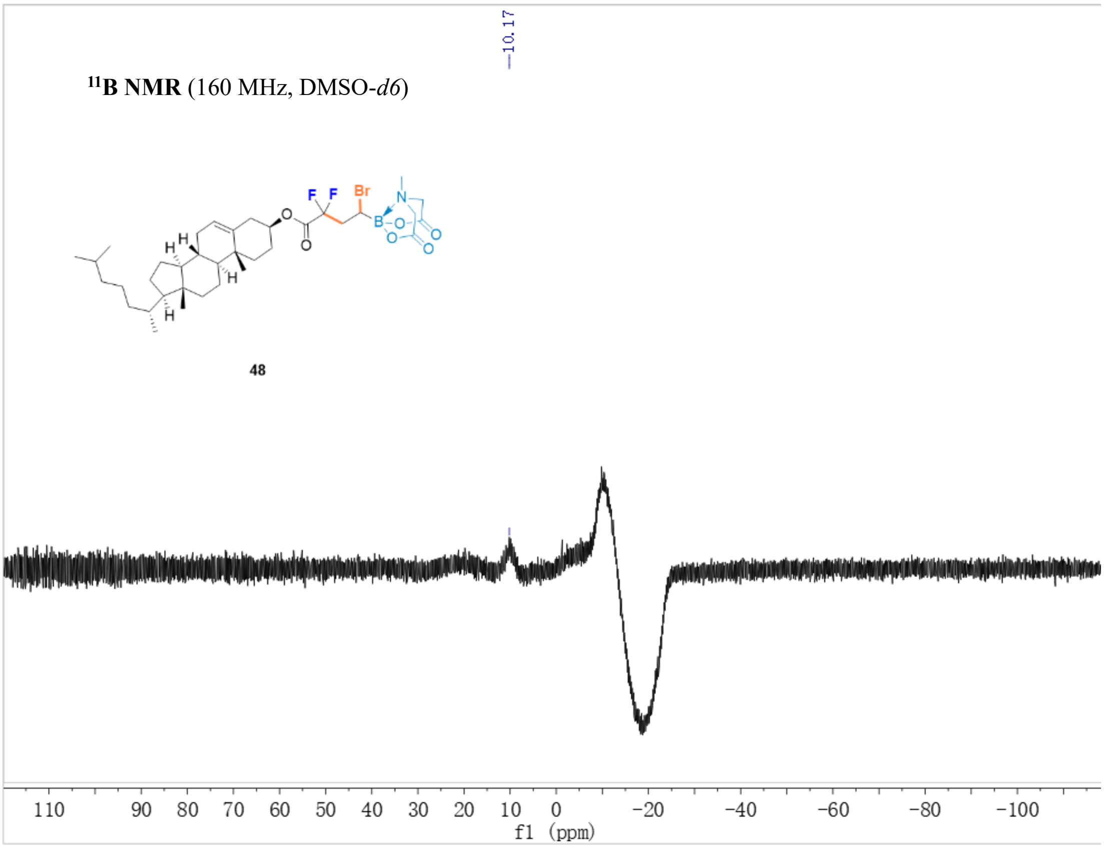
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-

2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoate (48)



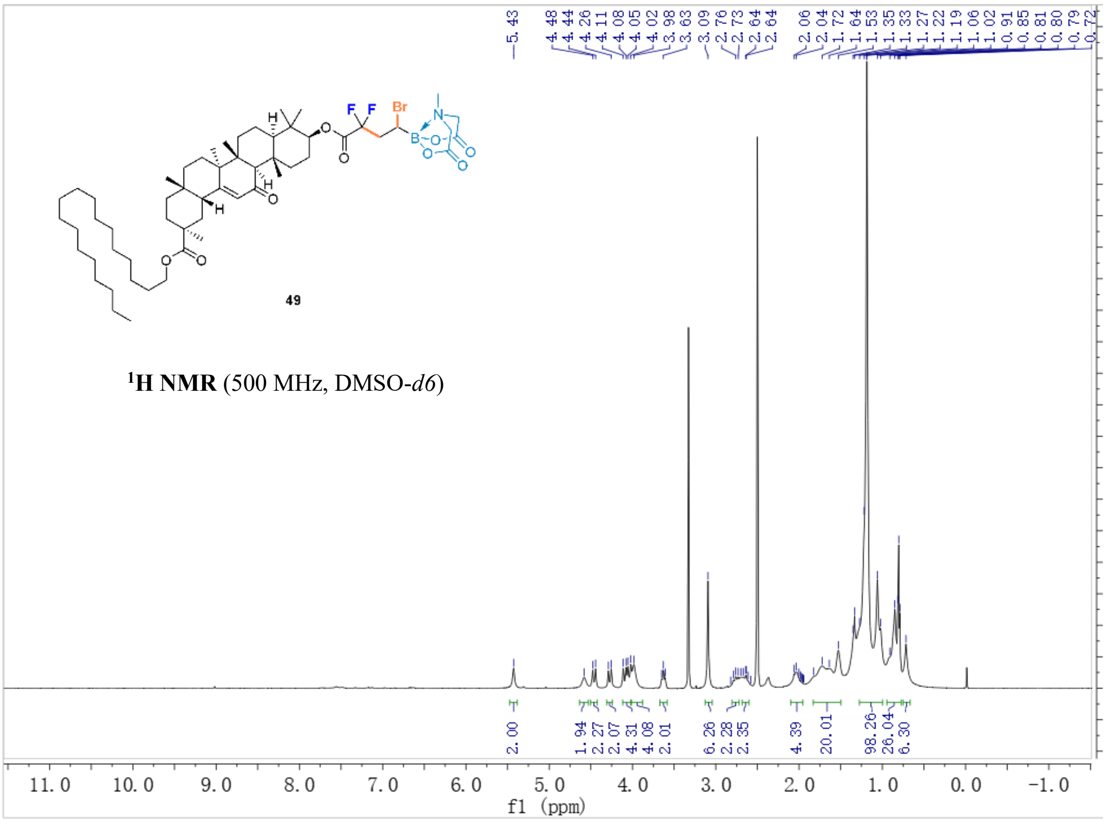


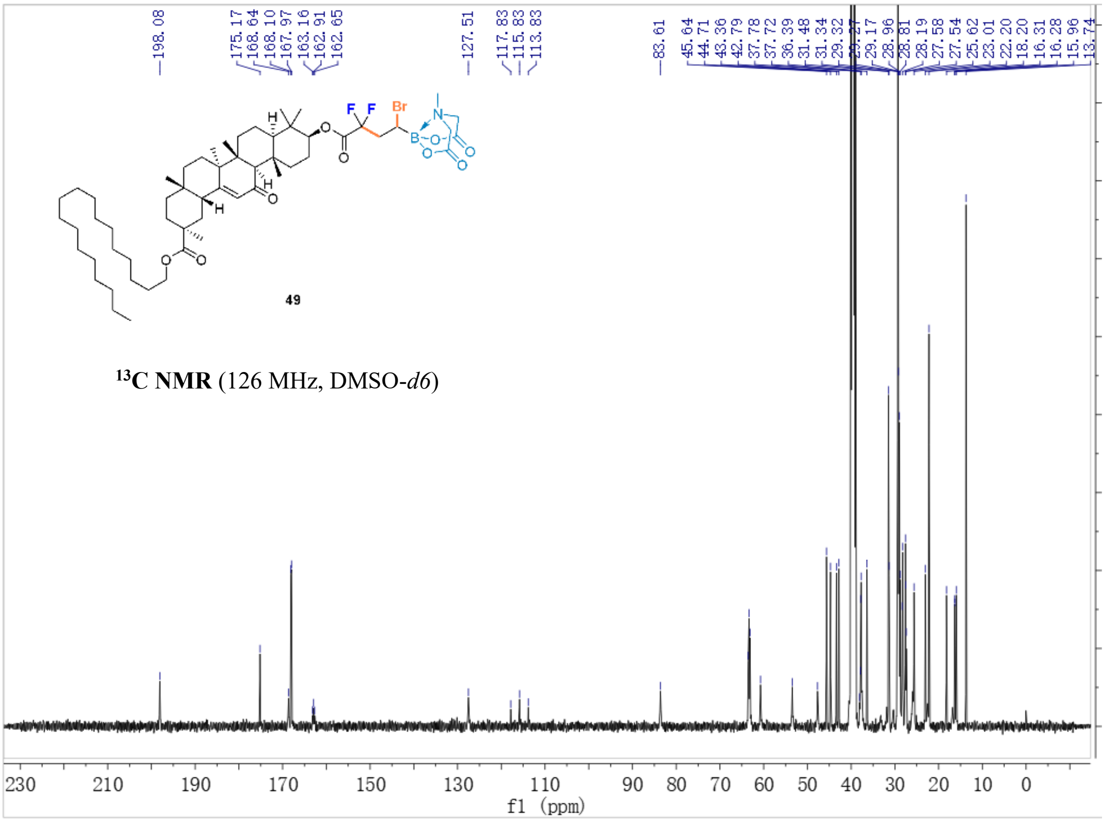


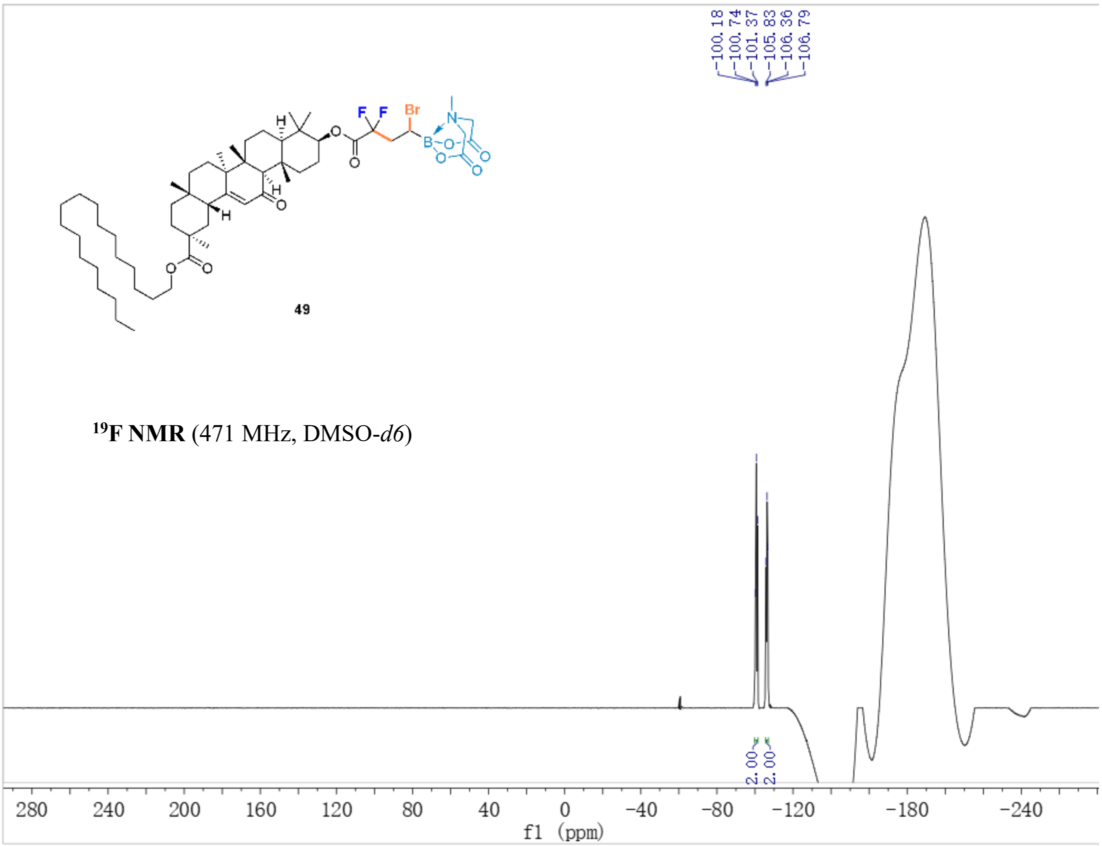


Octadecyl (2*S*,4a*S*,6a*S*,6b*R*,8a*R*,10*S*,12a*S*,12b*R*,14b*R*)-10-((4-bromo-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoyl)oxy)-

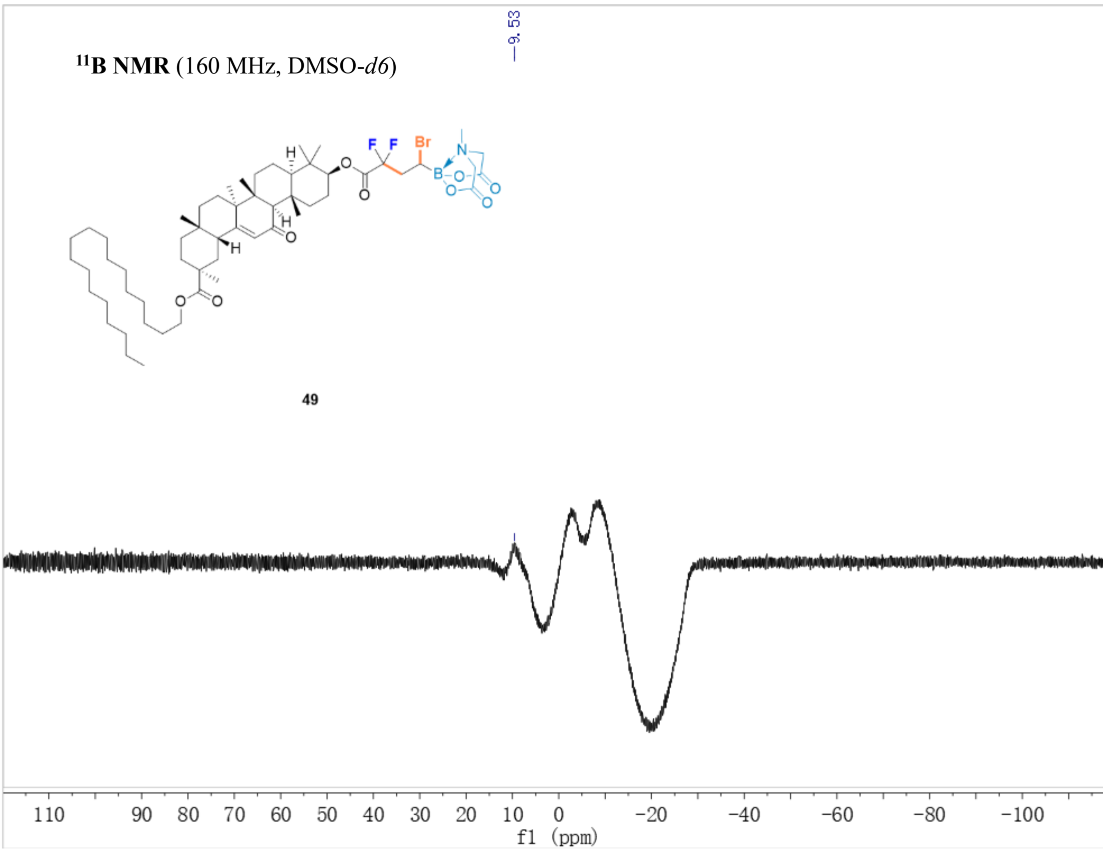
2,4a,6a,6b,9,9,12a-heptamethyl-13-oxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydropicene-2-carboxylate (49)





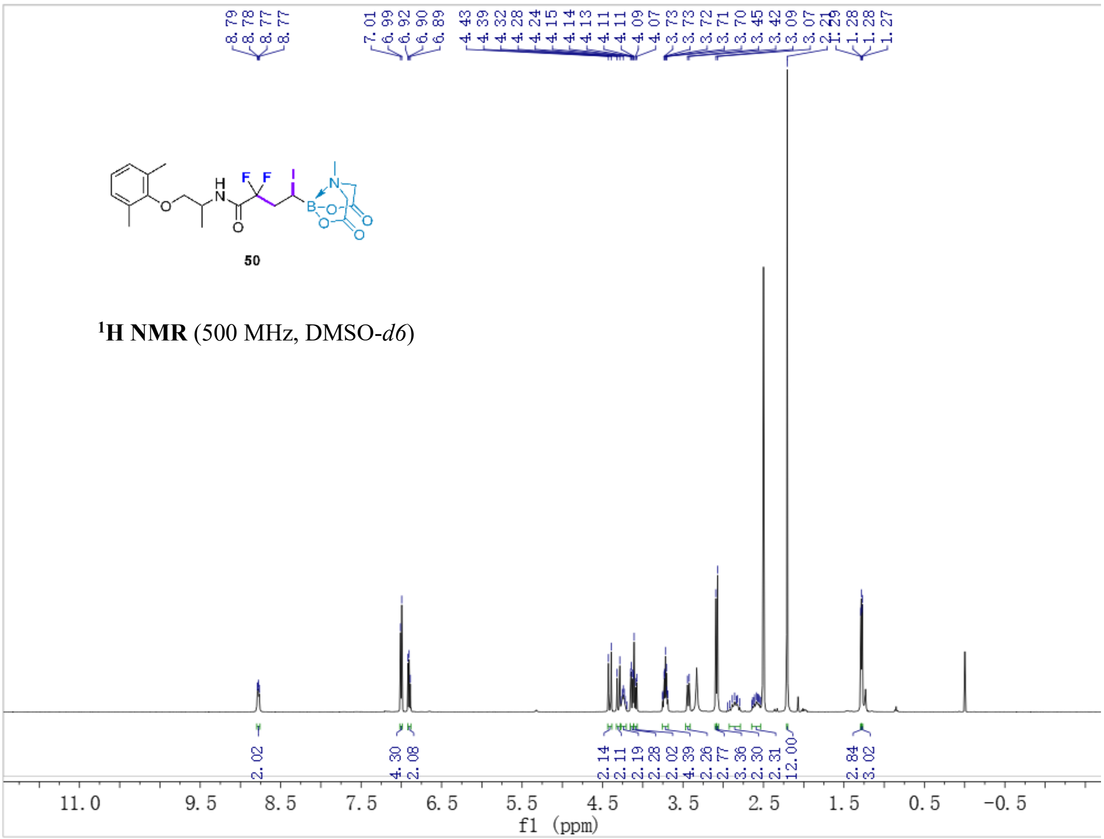


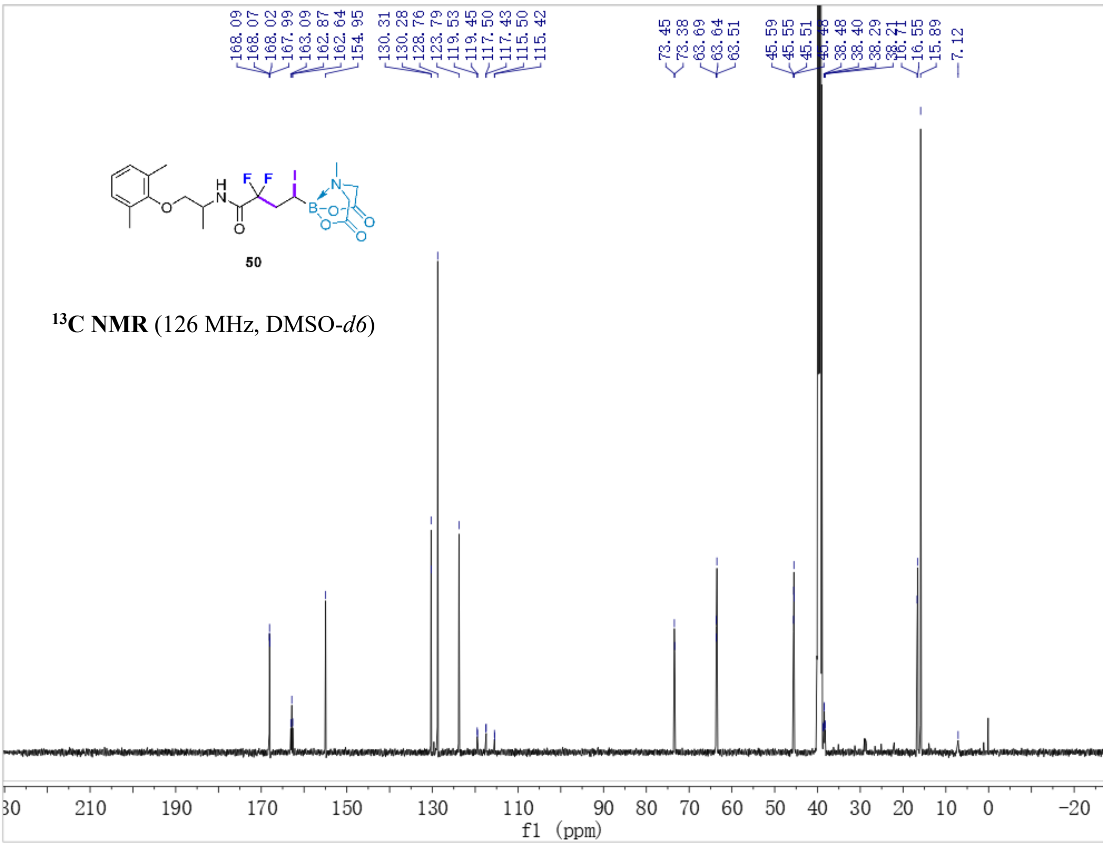
49
^{19}F NMR (471 MHz, DMSO-d6)
-100.18
-100.74
-101.37
-105.83
-106.36
-106.79
2.00
2.00
280 240 200 160 120 80 40 0 -40 -80 -120 -180 -240
f1 (ppm)



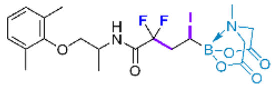
^{11}B NMR (160 MHz, DMSO-d6)
—9.53
49
110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100
f1 (ppm)

N-(1-(2,6-dimethylphenoxy)propan-2-yl)-2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (50)

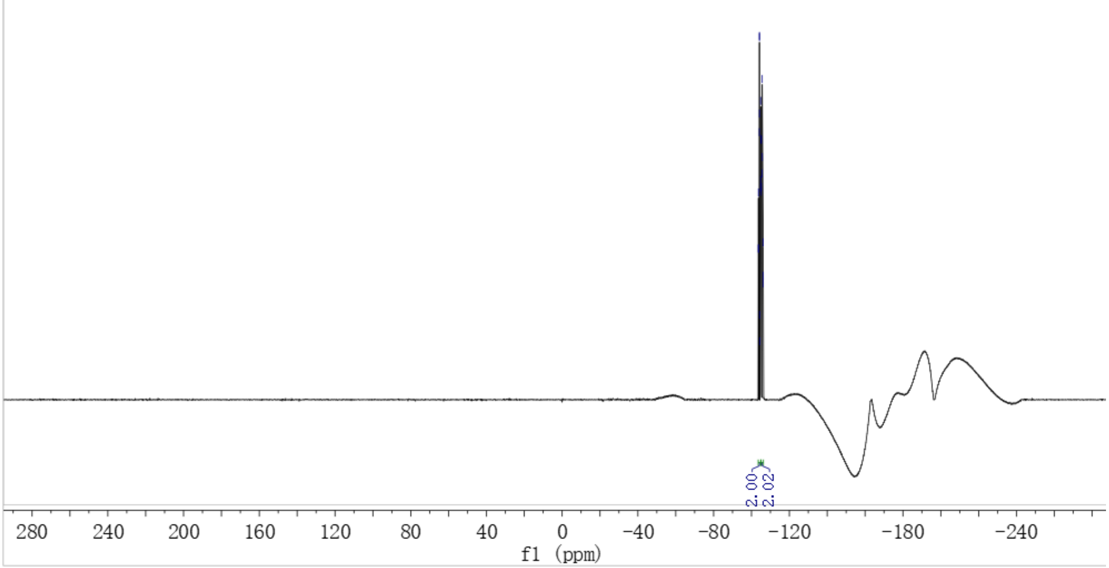




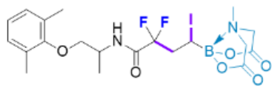
^{19}F NMR (471 MHz, DMSO-*d6*)



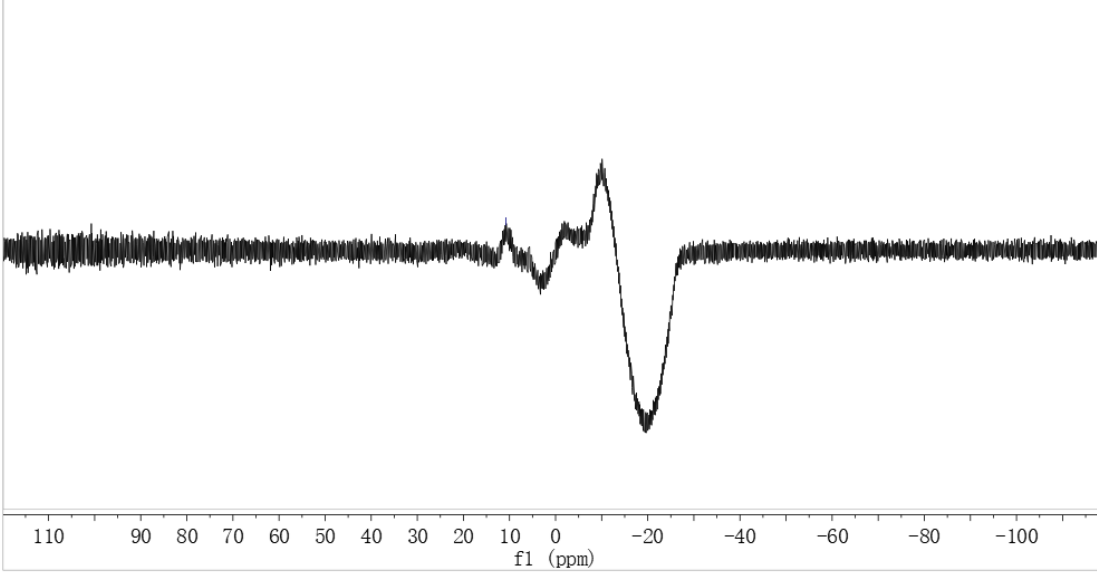
50



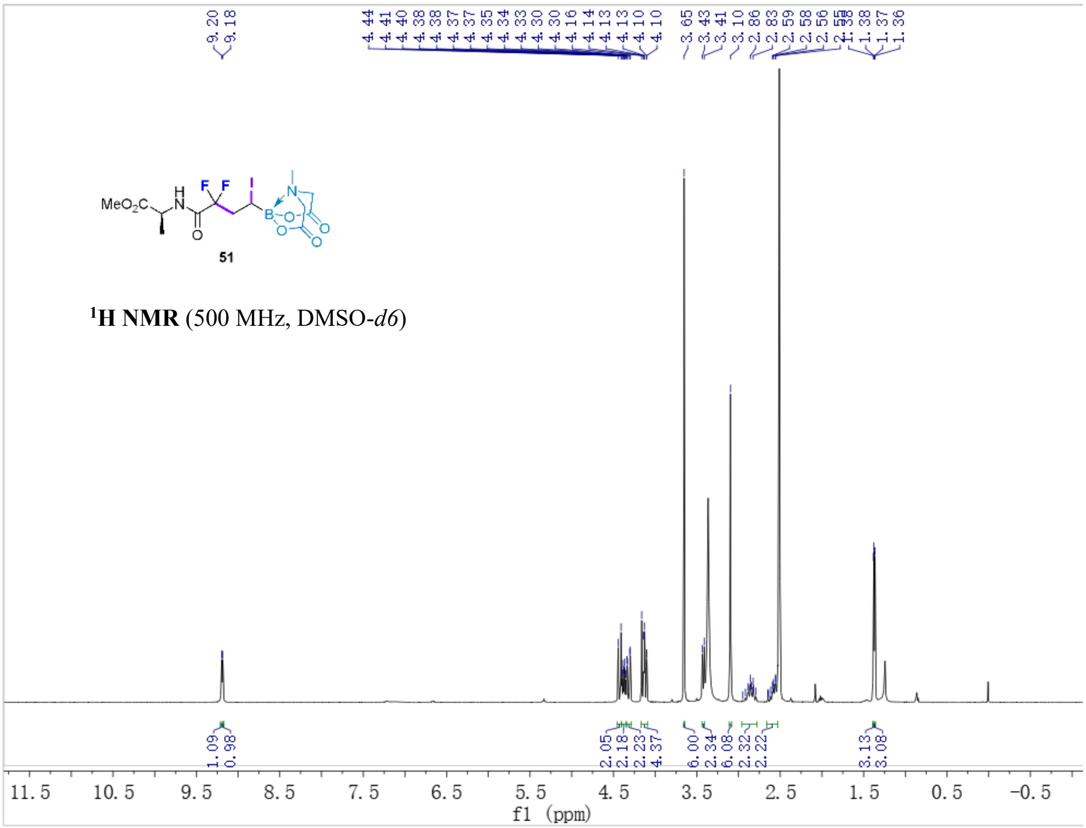
^{11}B NMR (160 MHz, DMSO-*d6*)

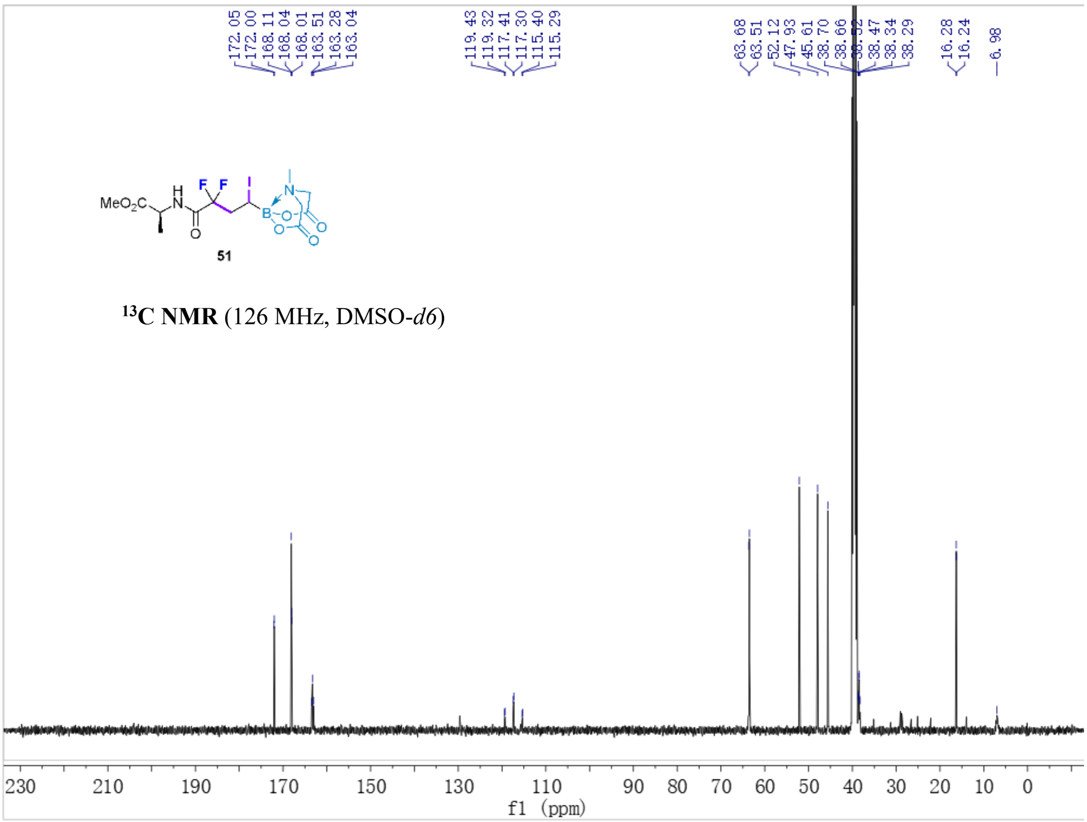


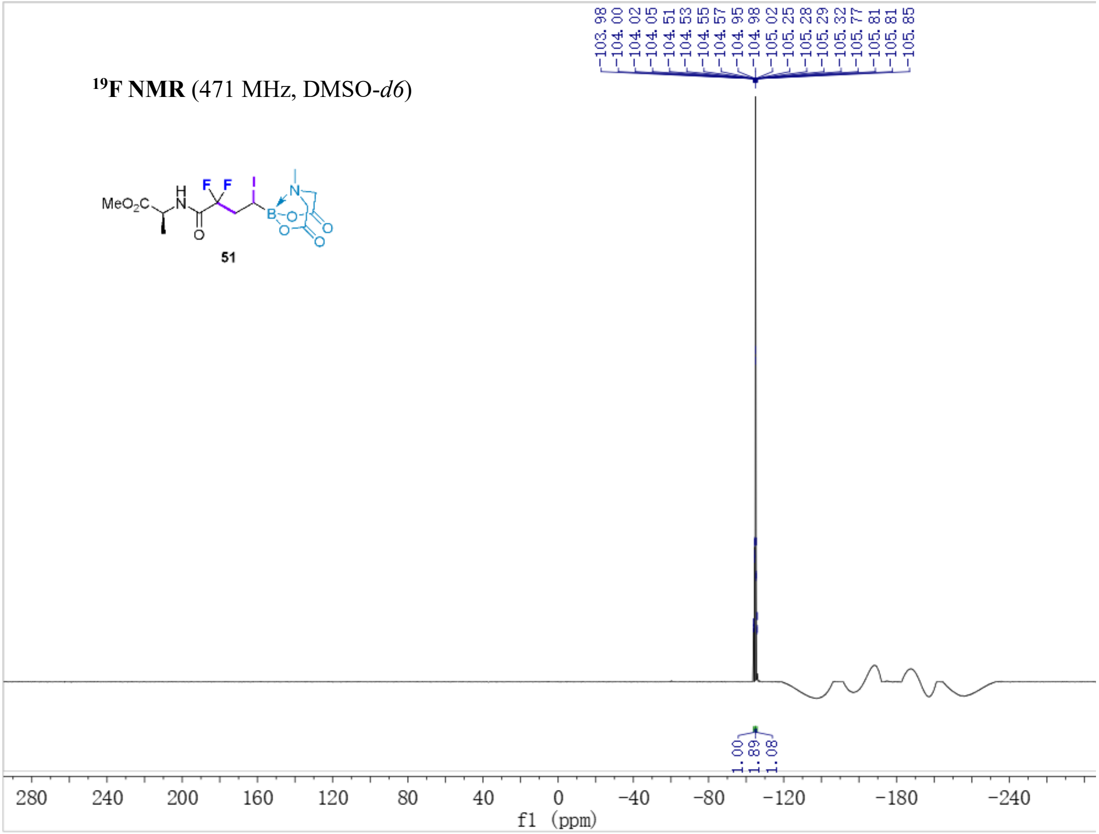
50



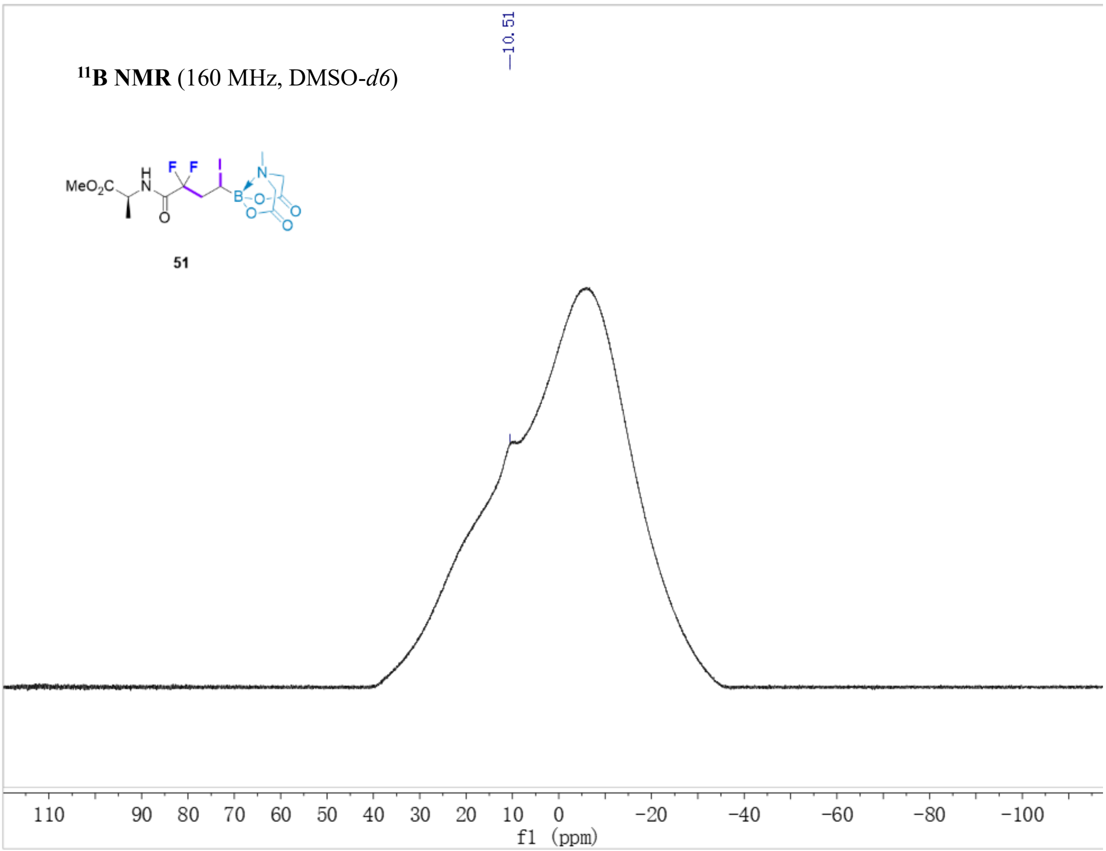
Methyl (2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoyl)-*L*-alaninate (51)





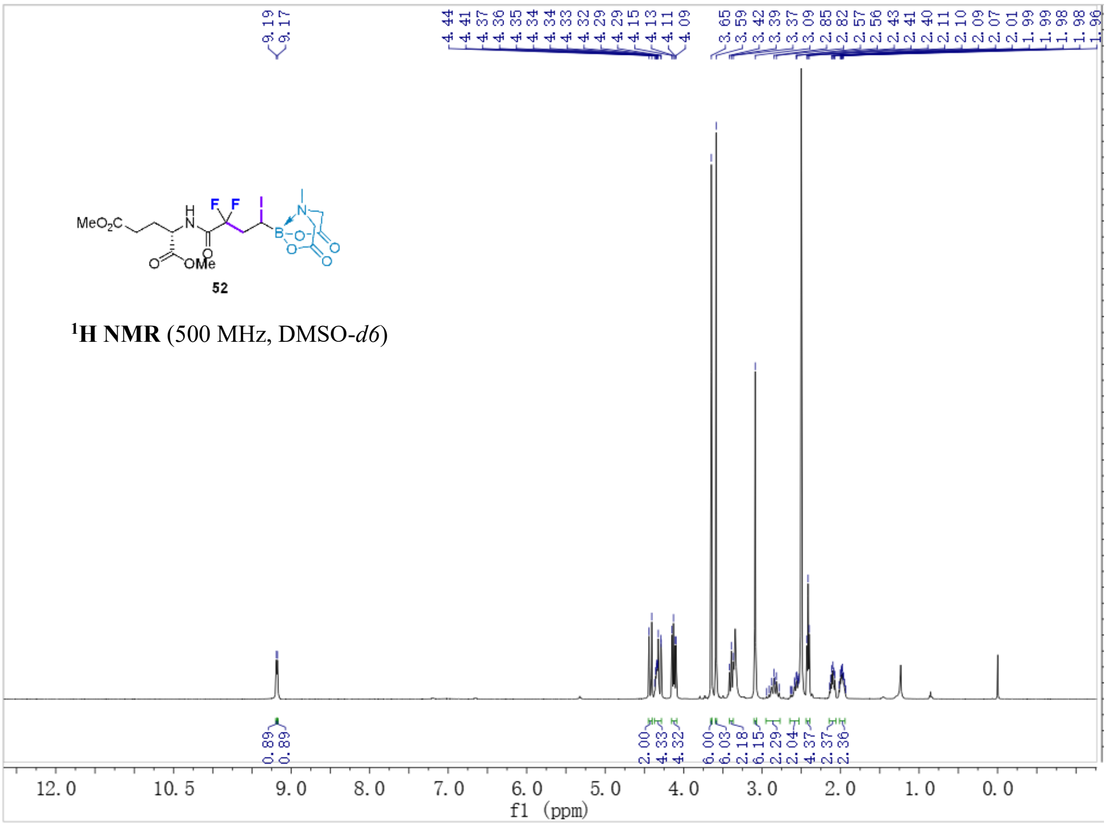


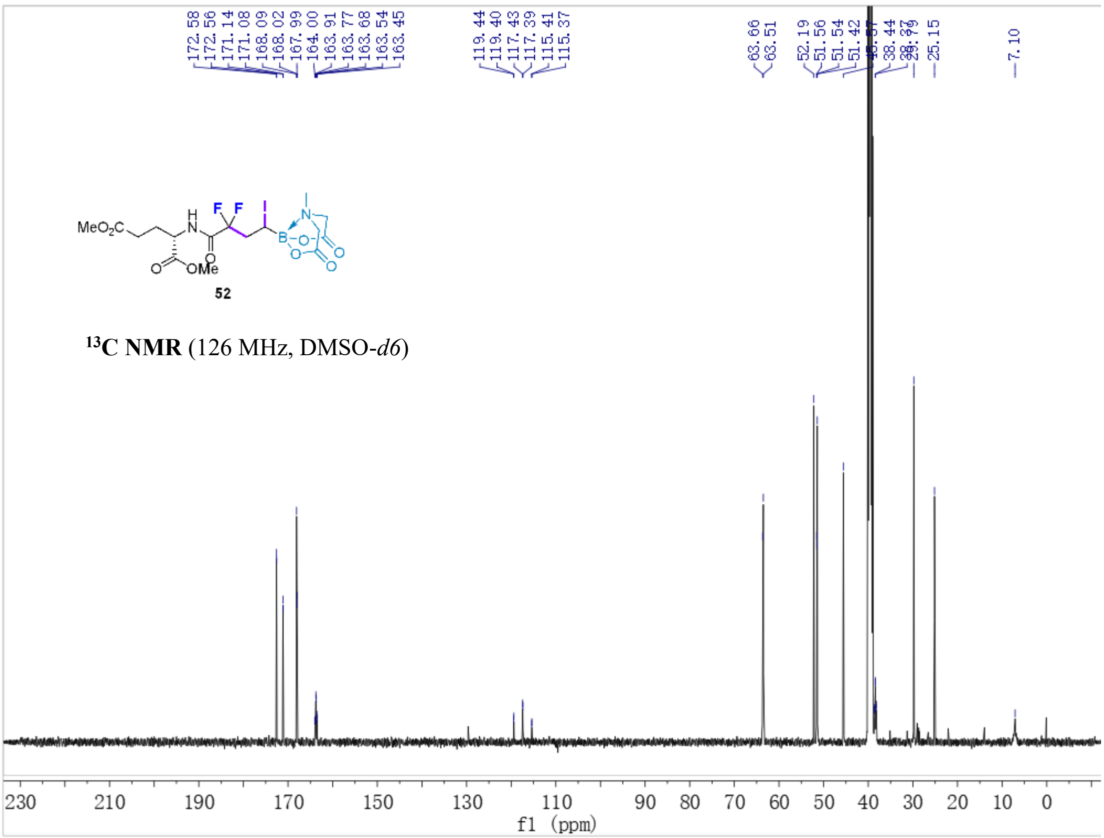
19F NMR (471 MHz, DMSO-d6)
-103.98
-104.00
-104.02
-104.05
-104.51
-104.53
-104.55
-104.57
-104.95
-104.98
-105.02
-105.25
-105.28
-105.29
-105.32
-105.77
-105.81
-105.81
-105.85
51
1.00
1.89
1.08
f1 (ppm)

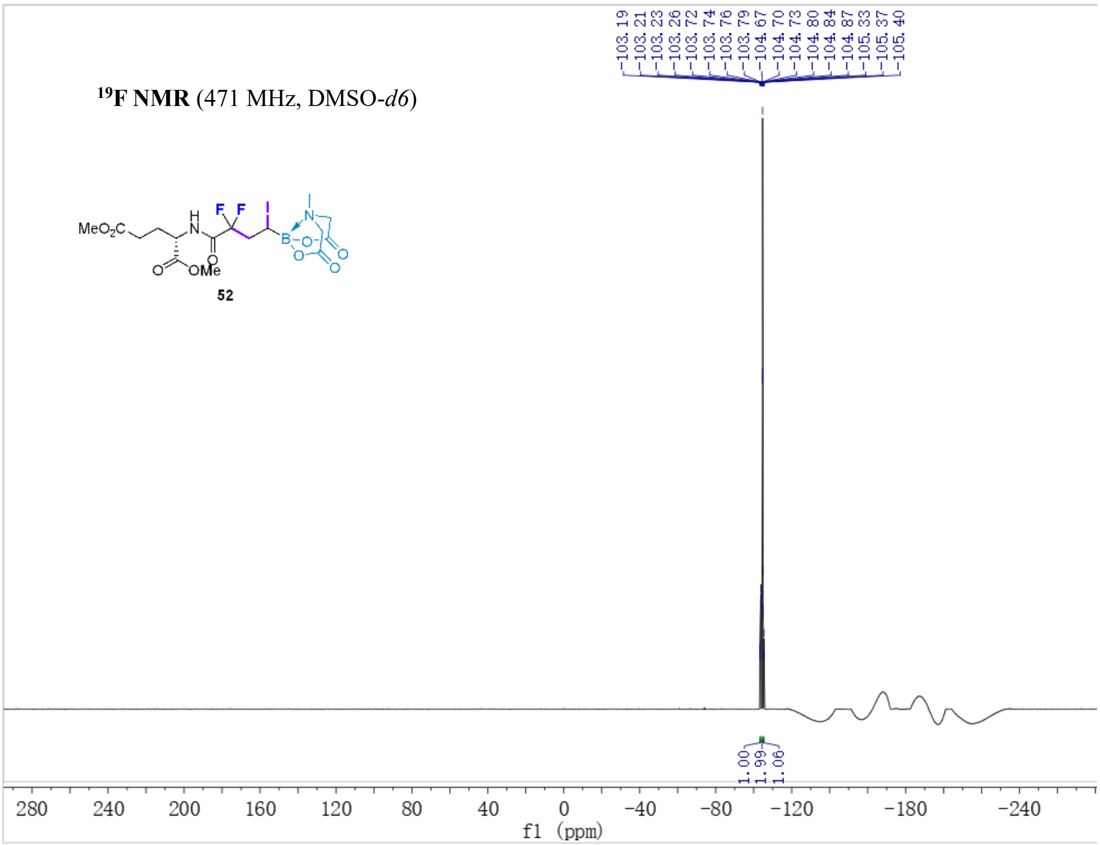


11B NMR (160 MHz, DMSO-d6)
10.51
51
f1 (ppm)

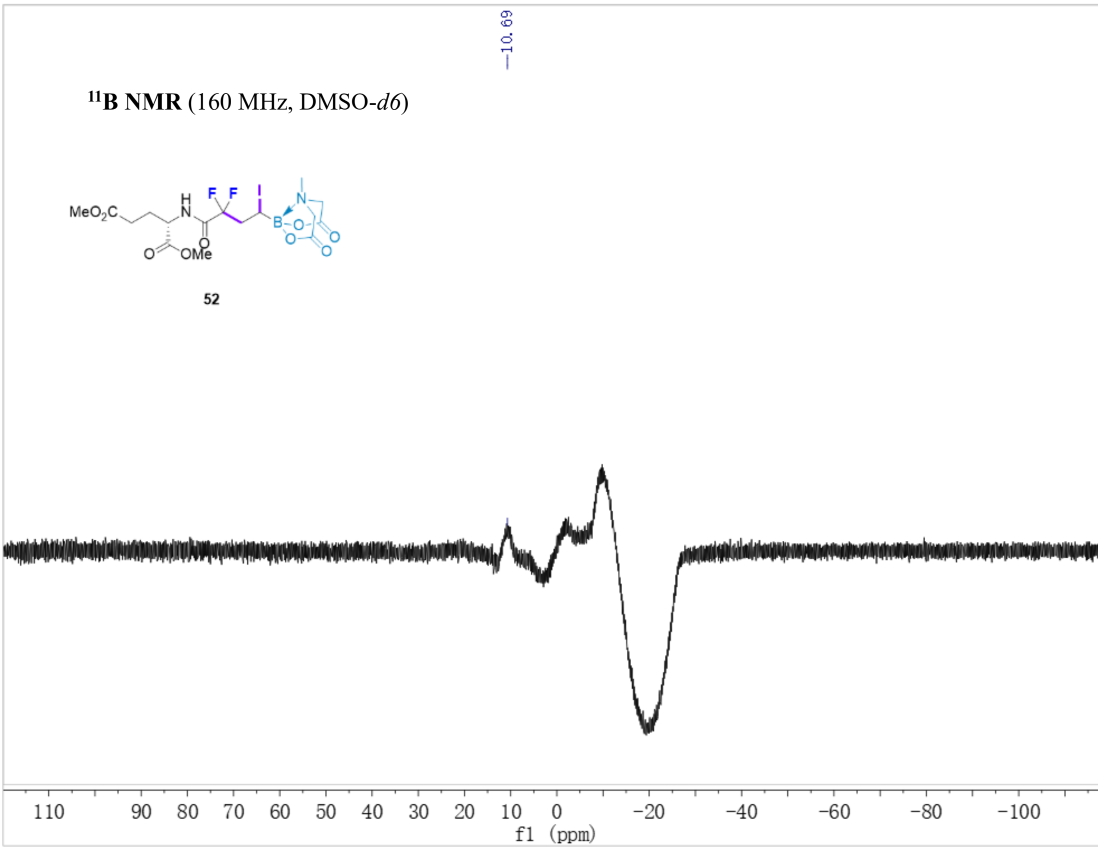
Dimethyl (2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoyl)-*L*-glutamate (52)





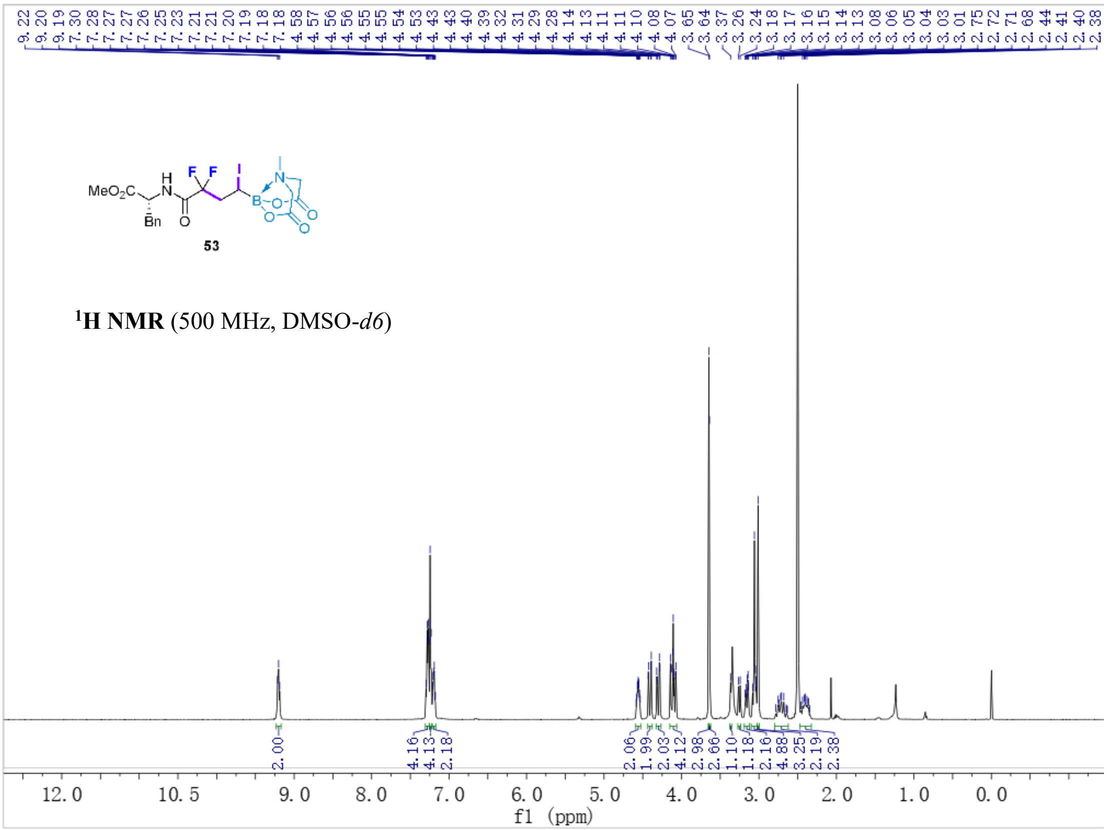


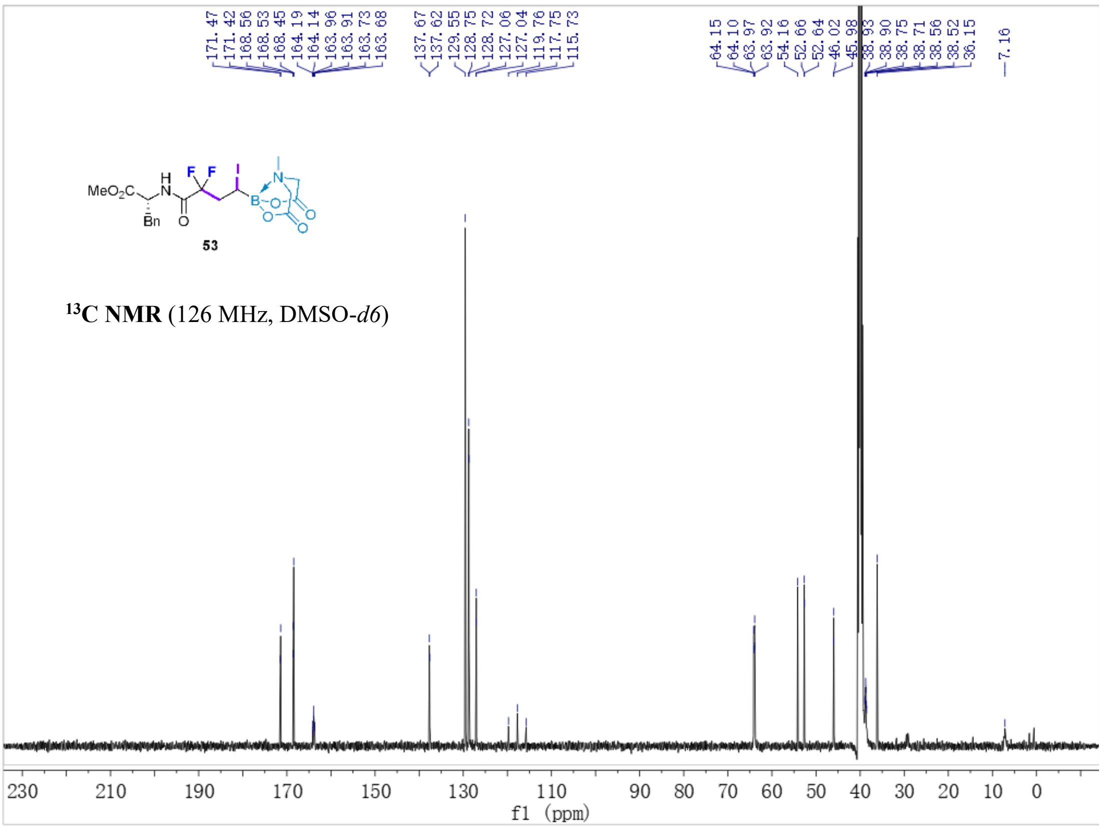
^{19}F NMR (471 MHz, DMSO-d6)
-103.19
-103.21
-103.23
-103.26
-103.72
-103.74
-103.76
-103.79
-104.67
-104.70
-104.73
-104.80
-104.84
-104.87
-105.33
-105.37
-105.40
MeO2C
F F
I
N
H
B
O
OMe
52
1.00
1.99
1.06
280 240 200 160 120 80 40 0 -40 -80 -120 -180 -240
f1 (ppm)



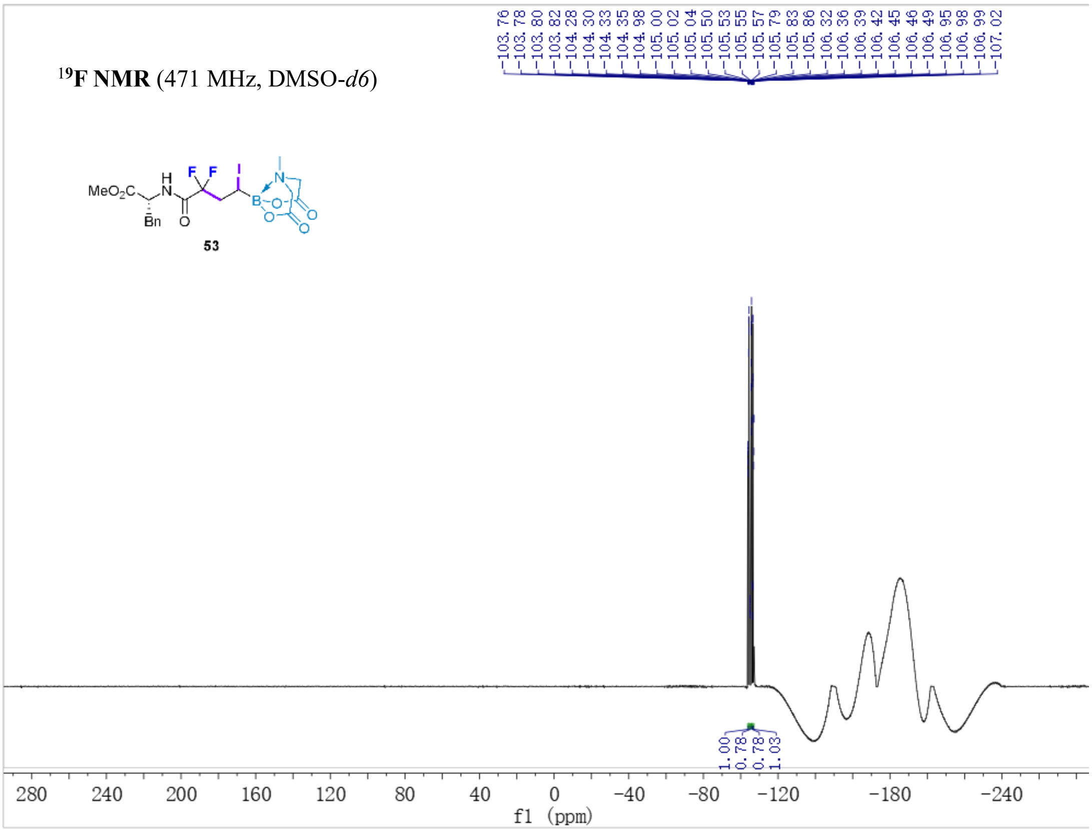
-10.69
^{11}B NMR (160 MHz, DMSO-d6)
MeO2C
F F
I
N
H
B
O
OMe
52
110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100
f1 (ppm)

Methyl (2,2-difluoro-4-iodo-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoyl)-*D*-phenylalaninate (53)

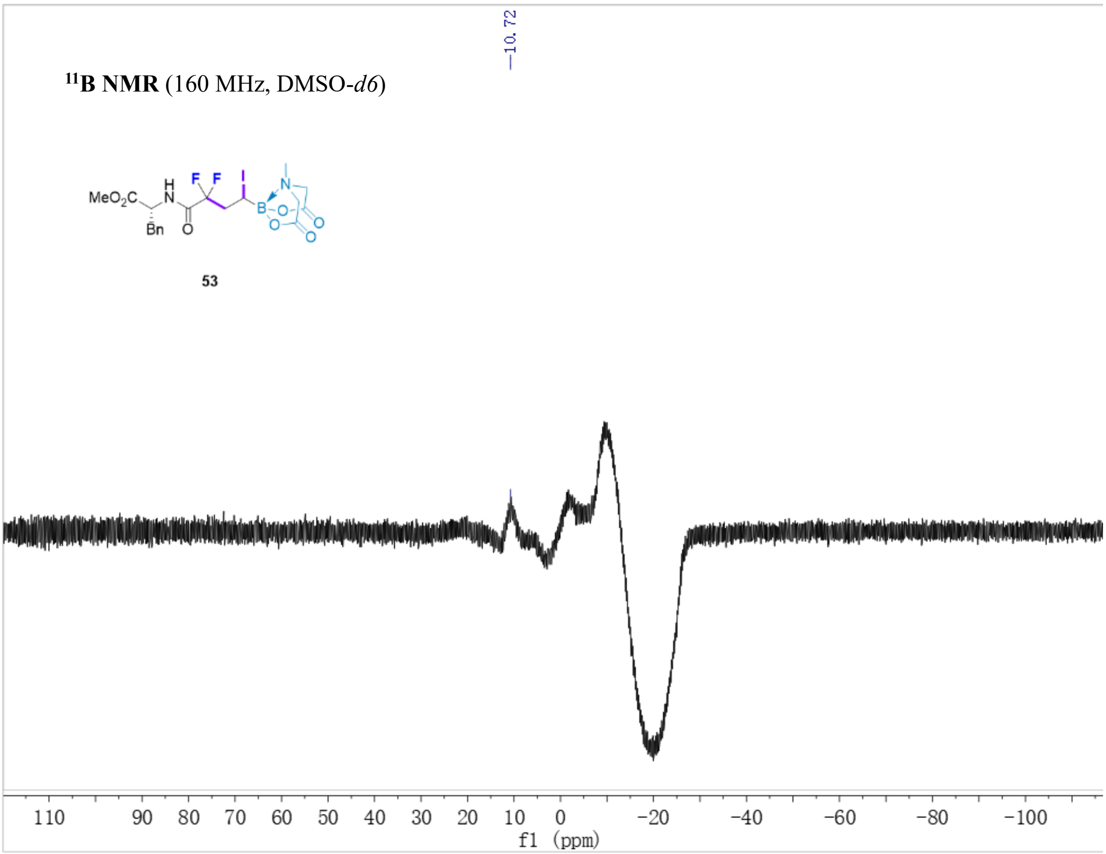




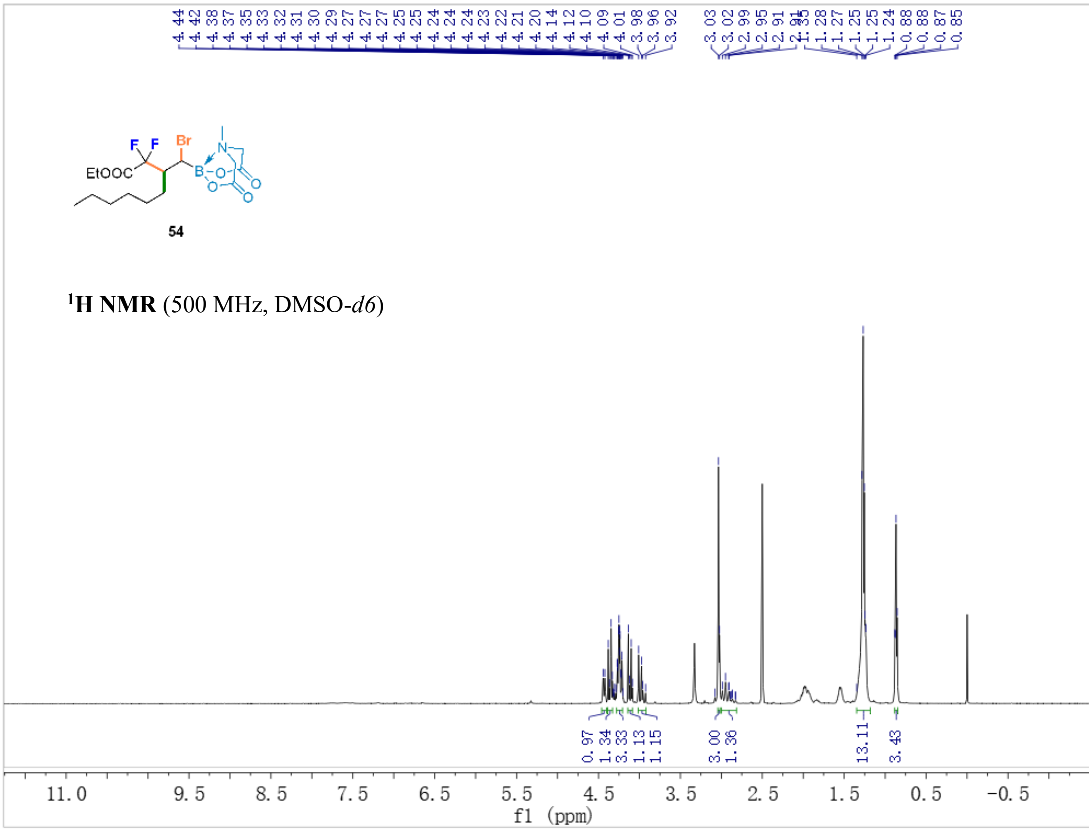
^{19}F NMR (471 MHz, DMSO-*d6*)

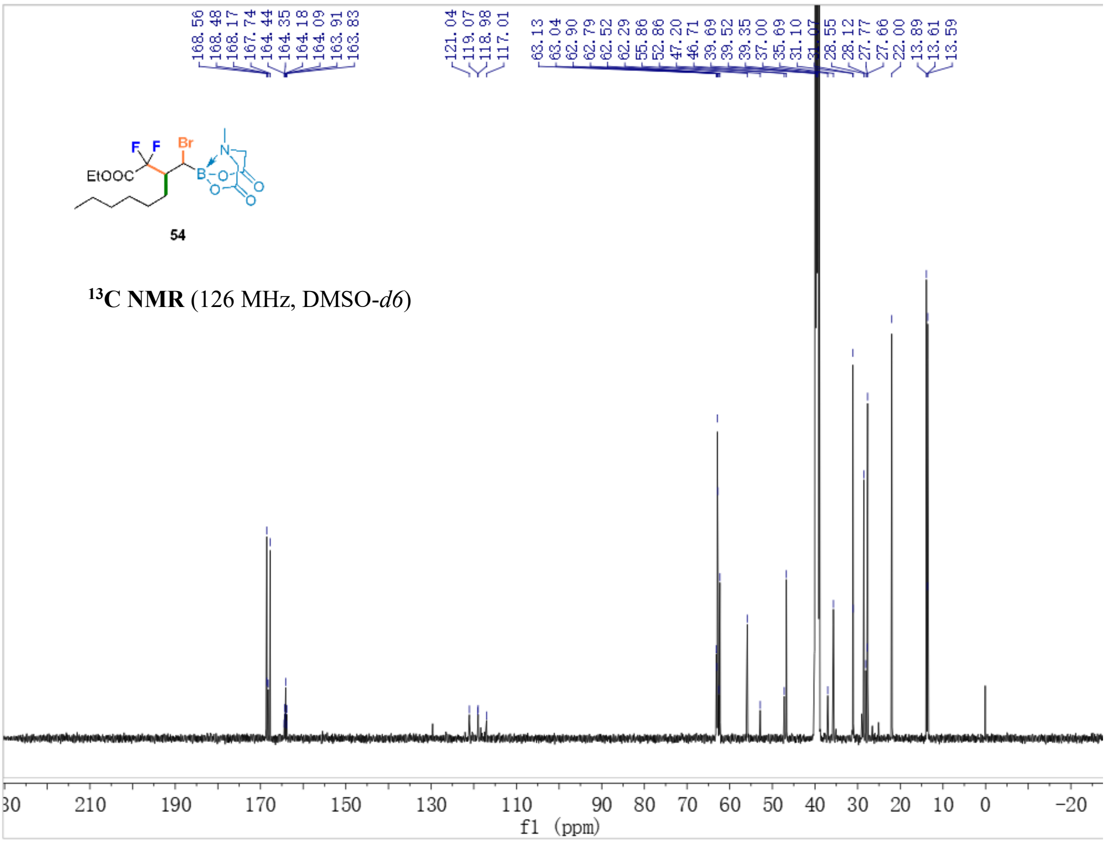


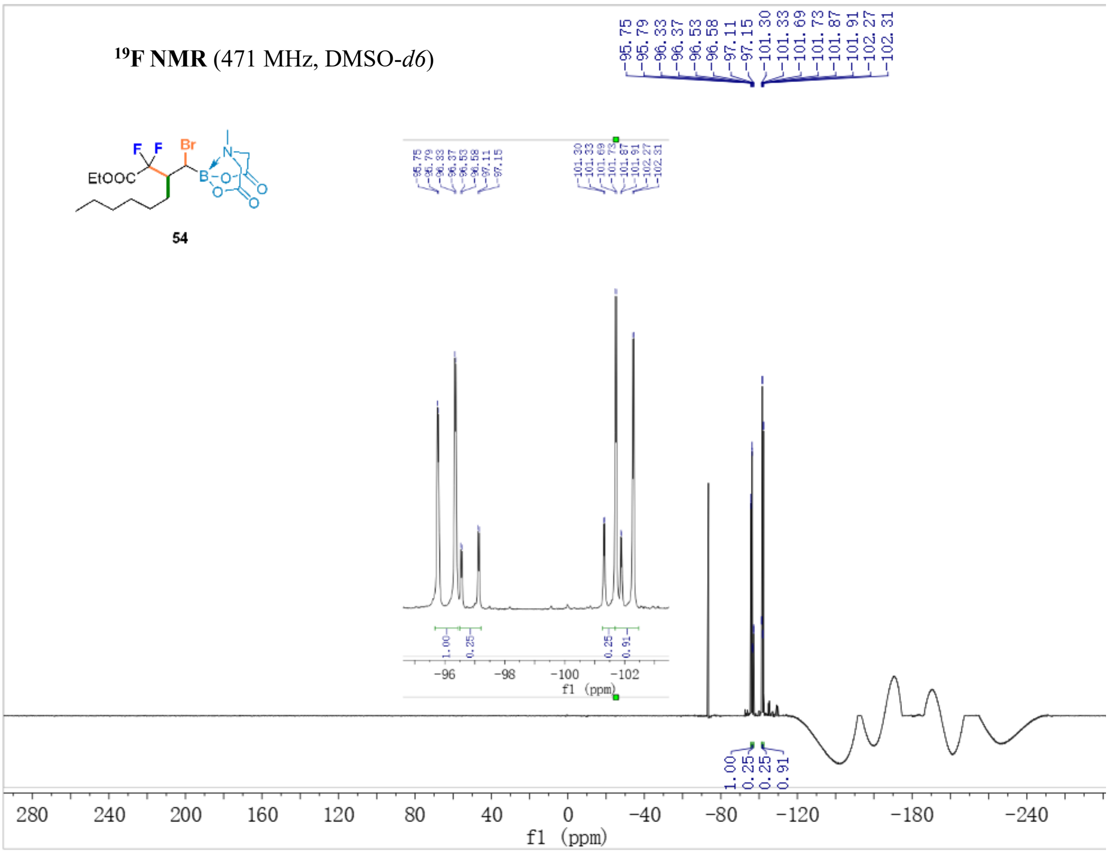
^{11}B NMR (160 MHz, DMSO-*d6*)



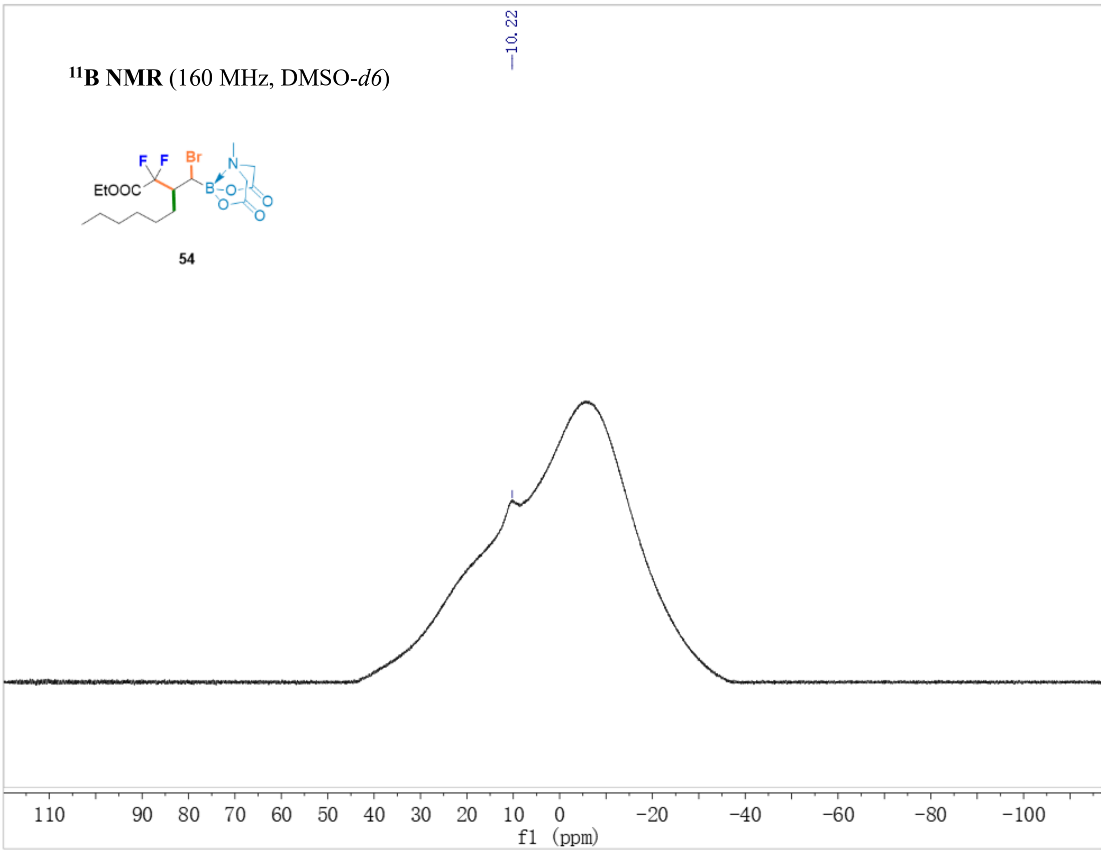
Ethyl (3*S*)-3-(bromo(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-2,2-difluorononanoate (54)





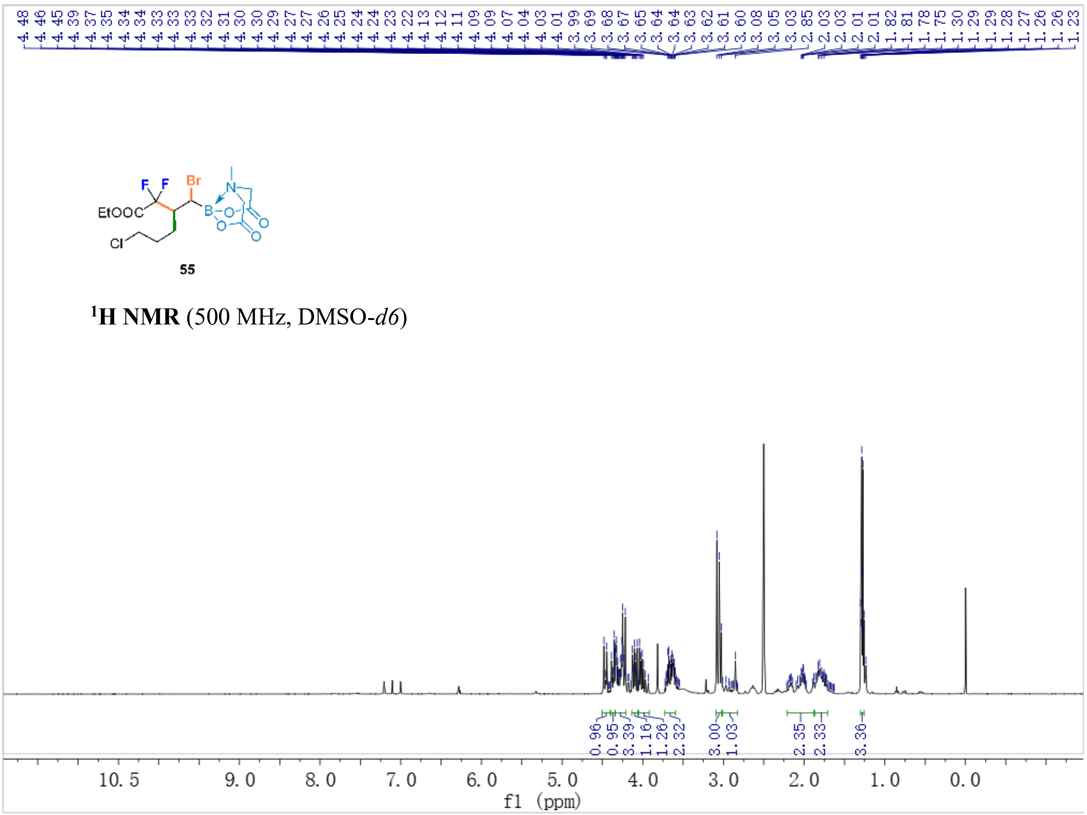


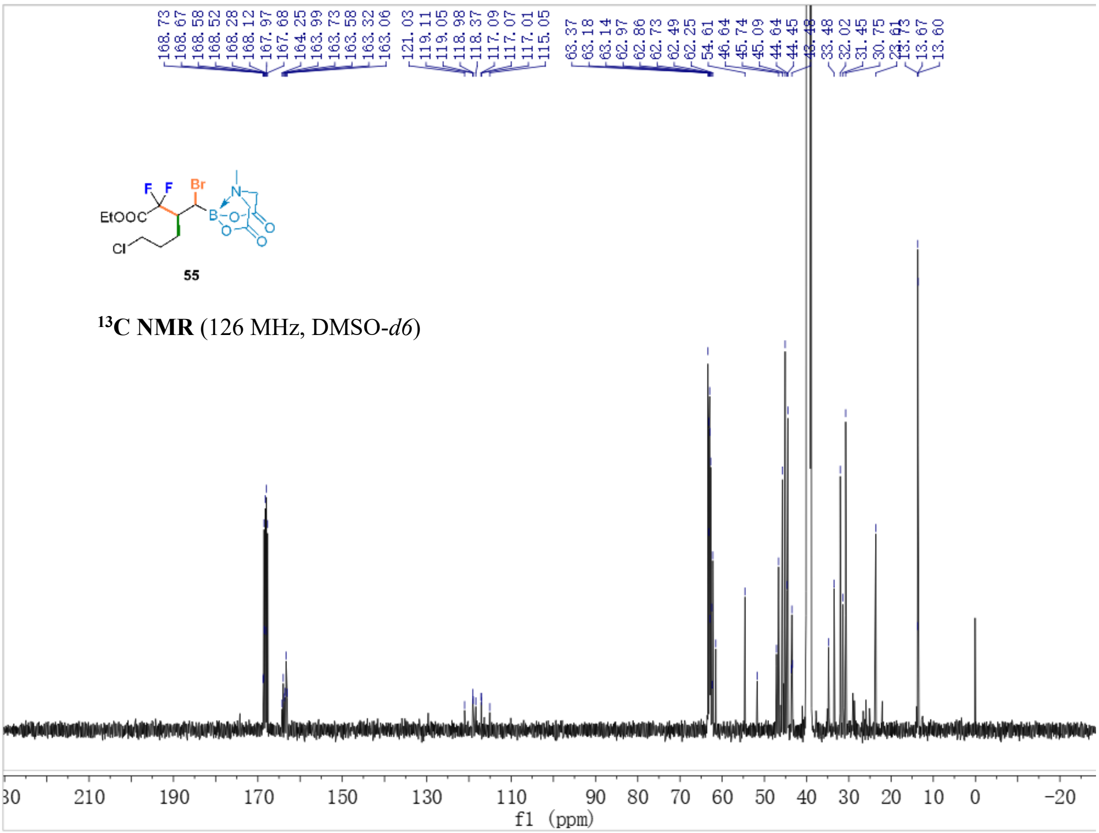
^{19}F NMR (471 MHz, DMSO-*d6*)
EtOOC
F F
Br
N
B
O
O
O
O
54
95.75
95.79
96.33
96.37
96.53
96.58
97.11
97.15
101.30
101.33
101.69
101.73
101.87
101.91
102.27
102.31
1.00
0.25
0.25
0.91
f1 (ppm)

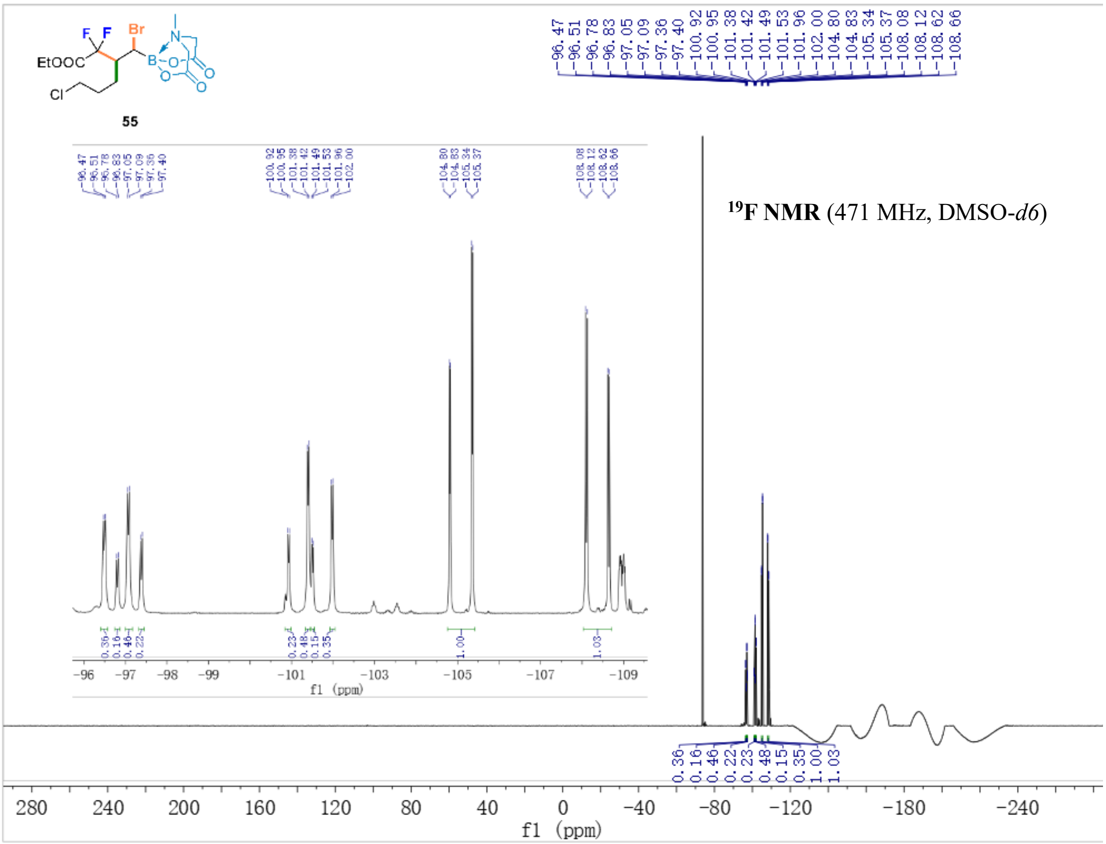


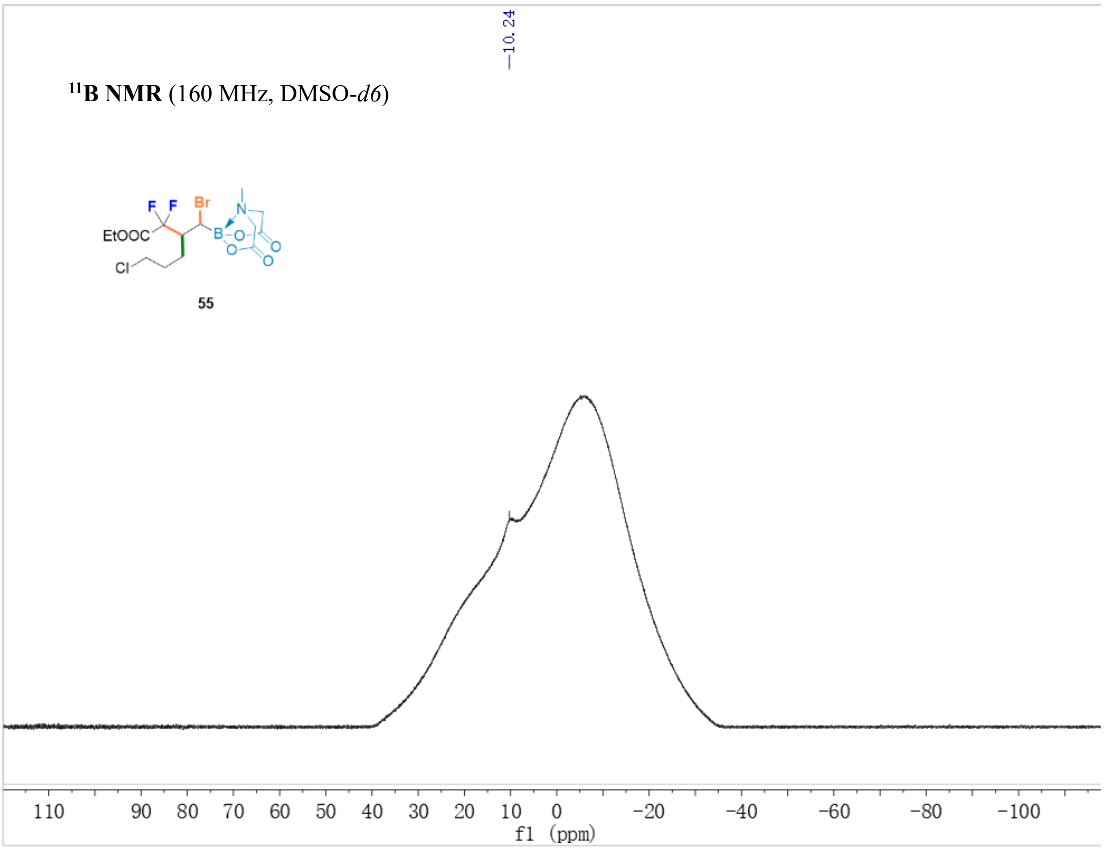
^{11}B NMR (160 MHz, DMSO-*d6*)
EtOOC
F F
Br
N
B
O
O
O
O
54
10.22
f1 (ppm)

Ethyl (3*S*)-3-(bromo(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-6-chloro-2,2-difluorohexanoate (55)

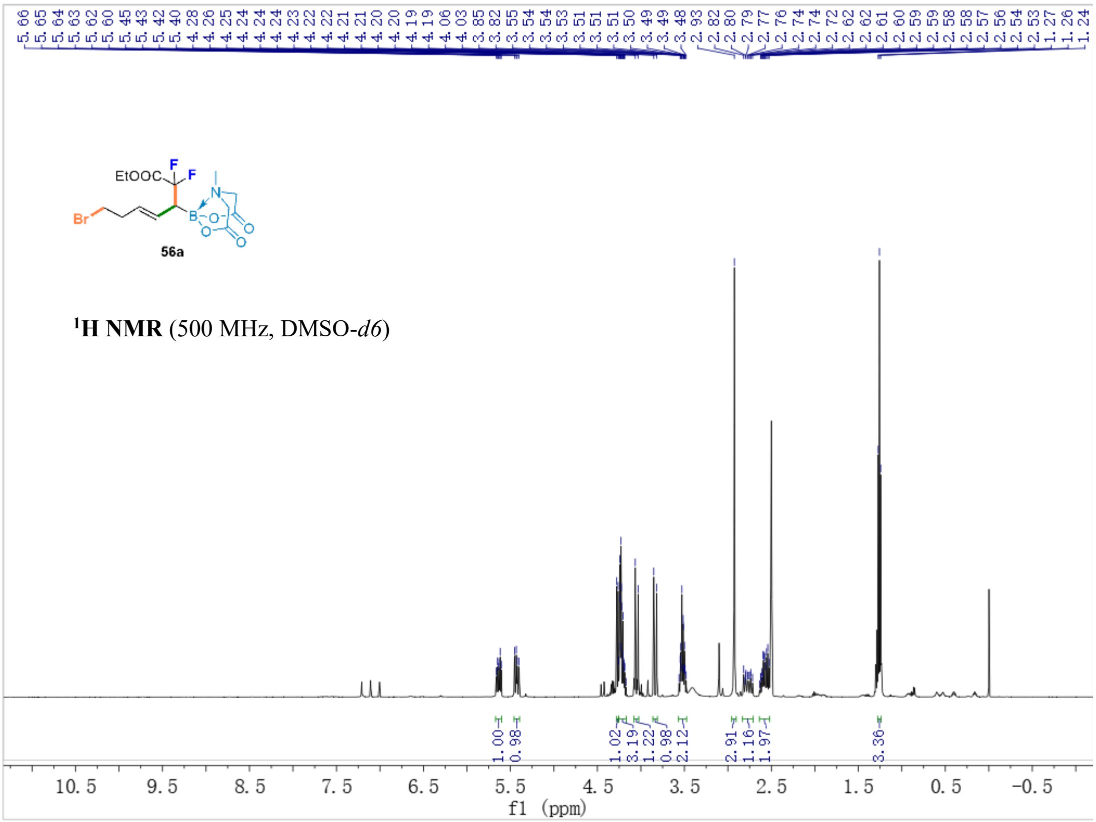


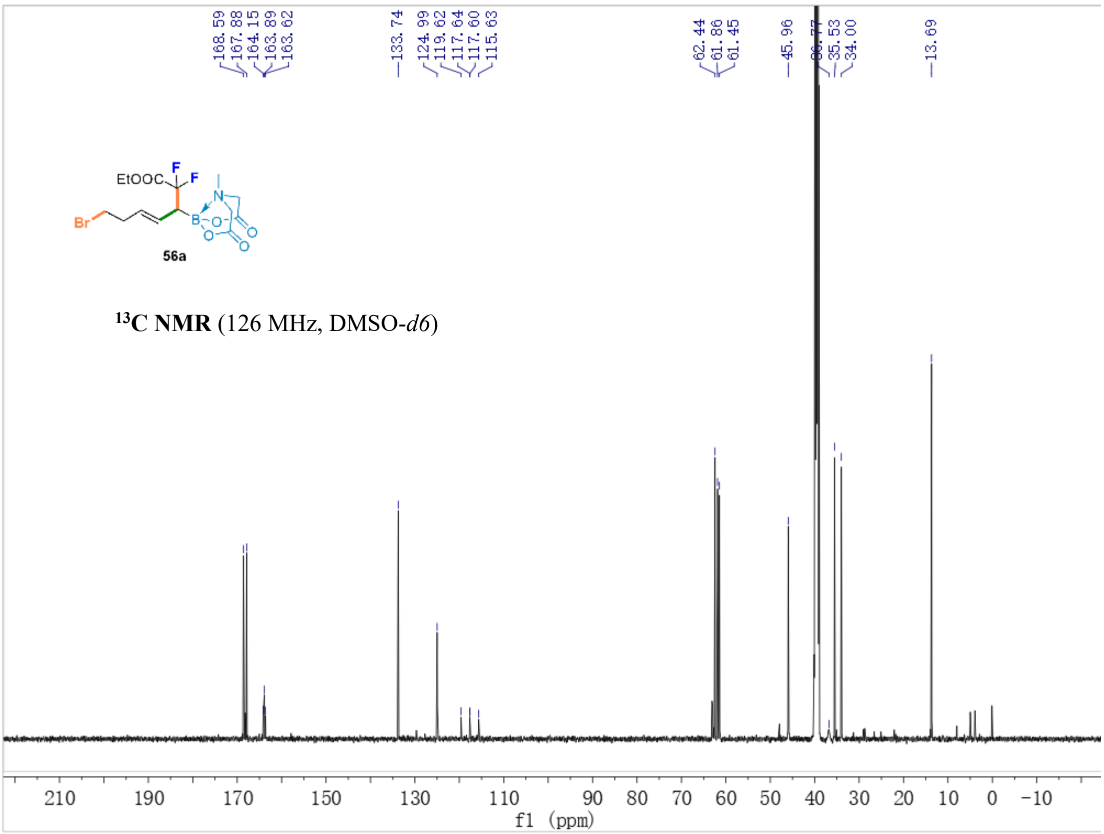


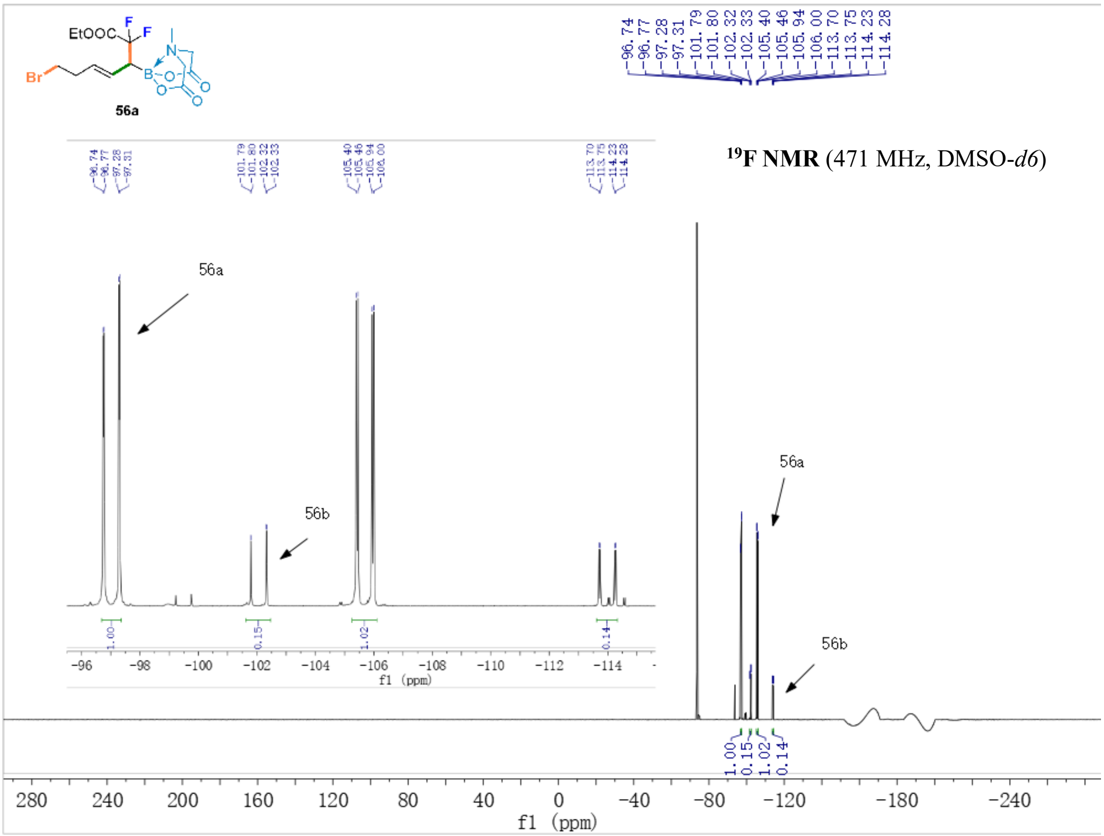

19F NMR (471 MHz, DMSO-d6)
55
f1 (ppm)


11B NMR (160 MHz, DMSO-d6)
−10.24
55
f1 (ppm)

Ethyl (*S*,*E*)-7-bromo-2,2-difluoro-3-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hept-4-enoate (56a)

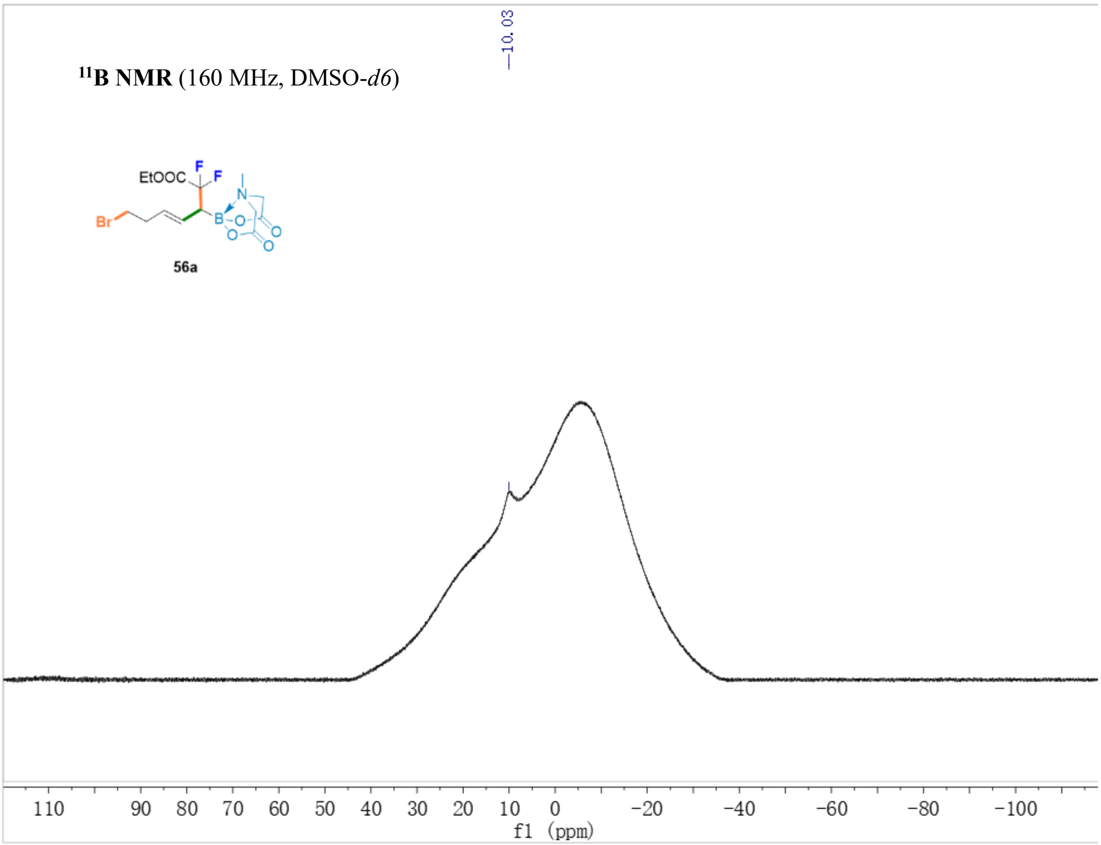




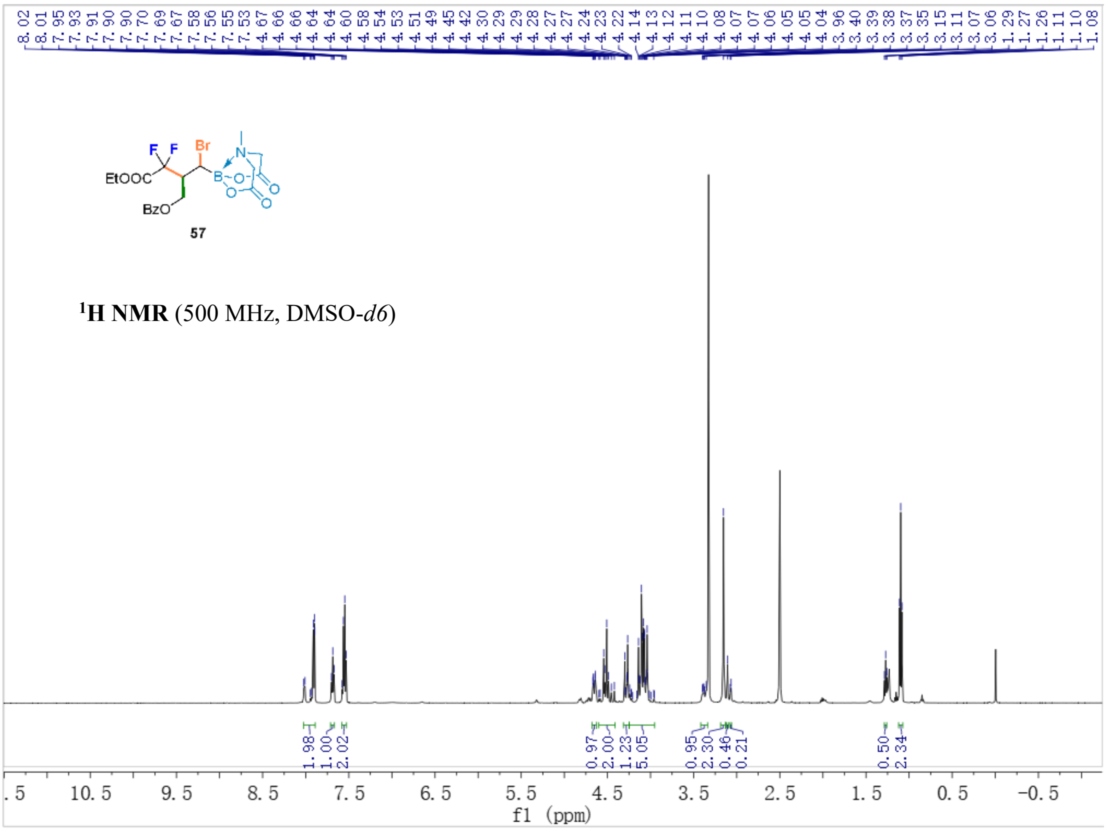


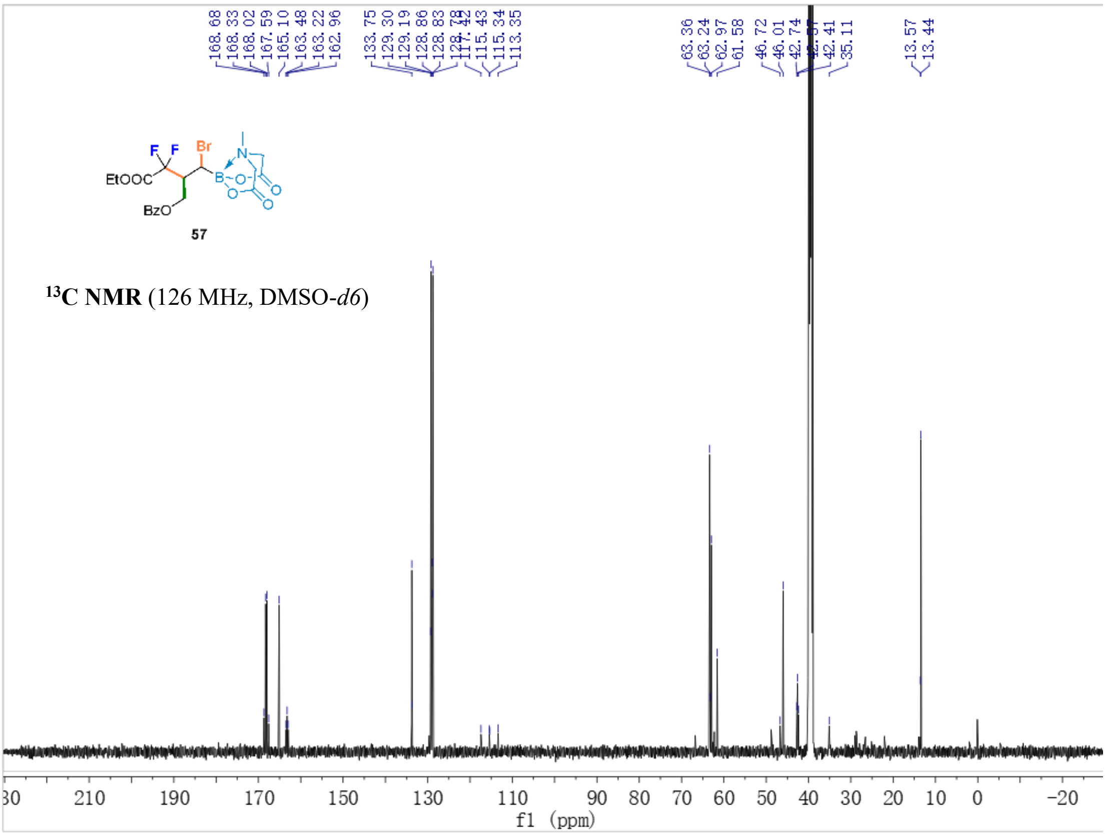
^{19}**F NMR** (471 MHz, DMSO-*d6*)

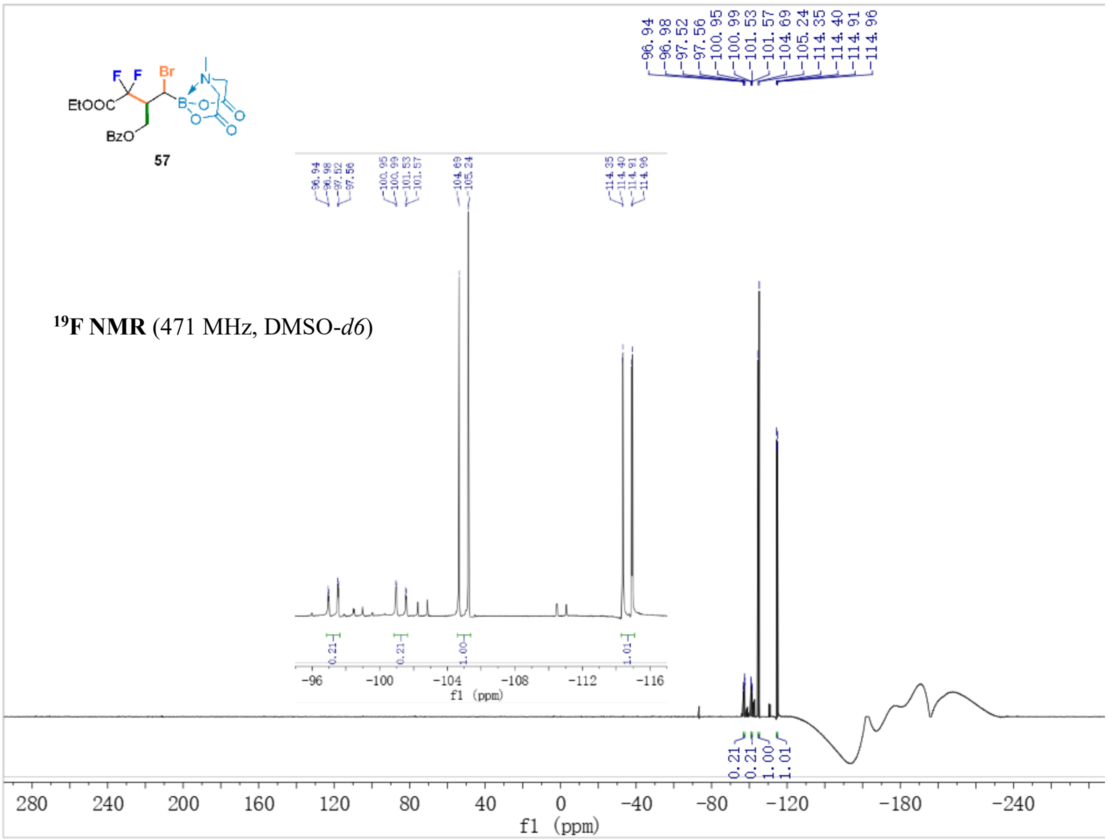
^{11}**B NMR** (160 MHz, DMSO-*d6*)



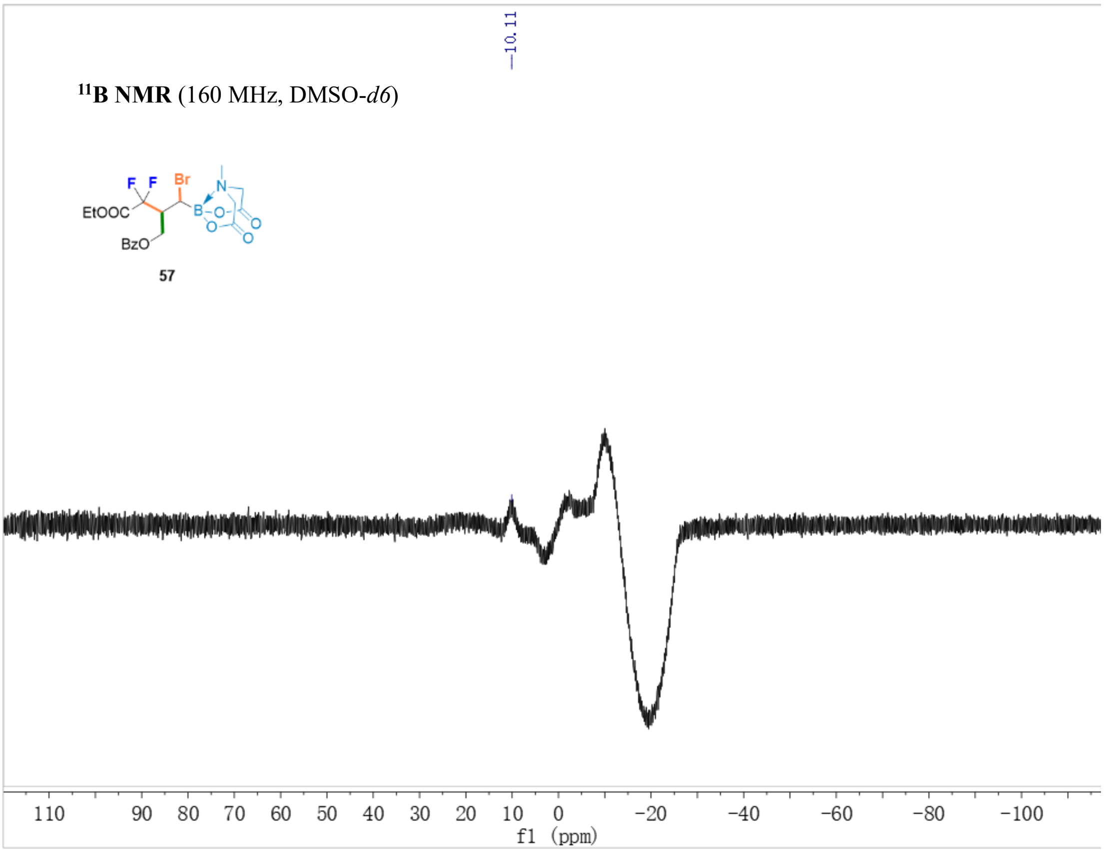
(2*S*)-2-(bromo(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-4-ethoxy-3,3-difluoro-4-oxobutyl benzoate (57)





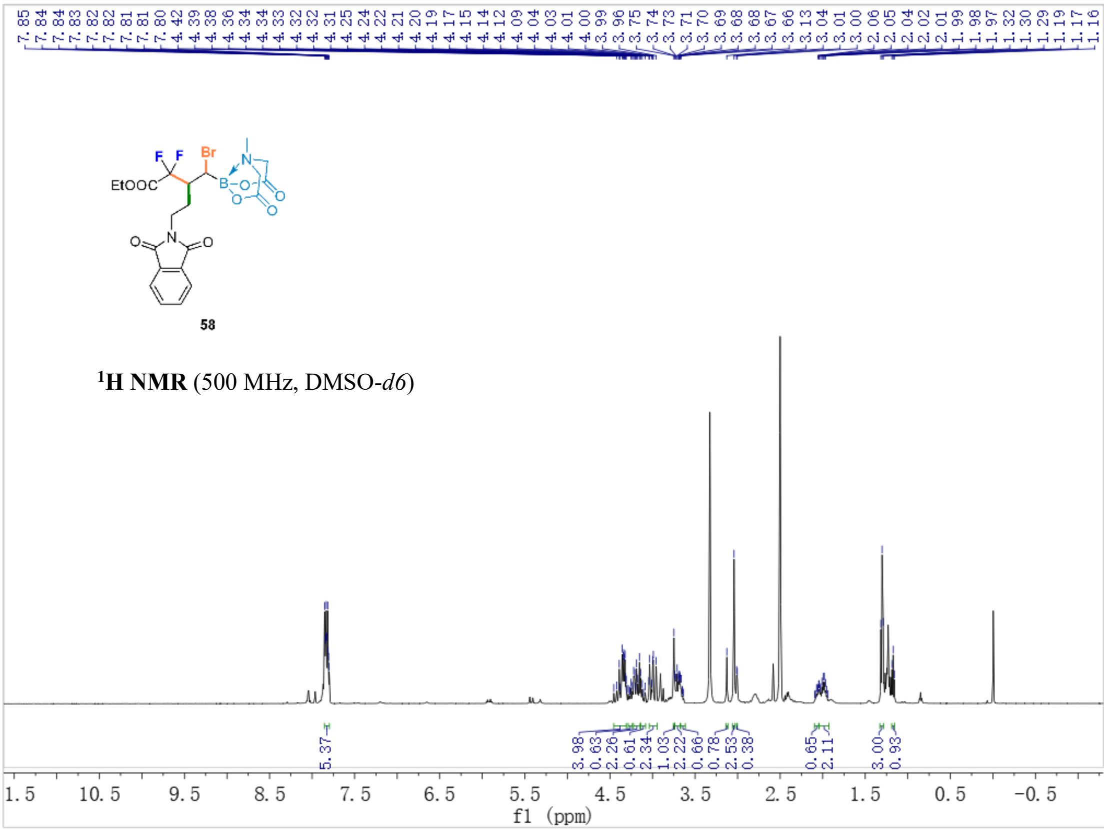


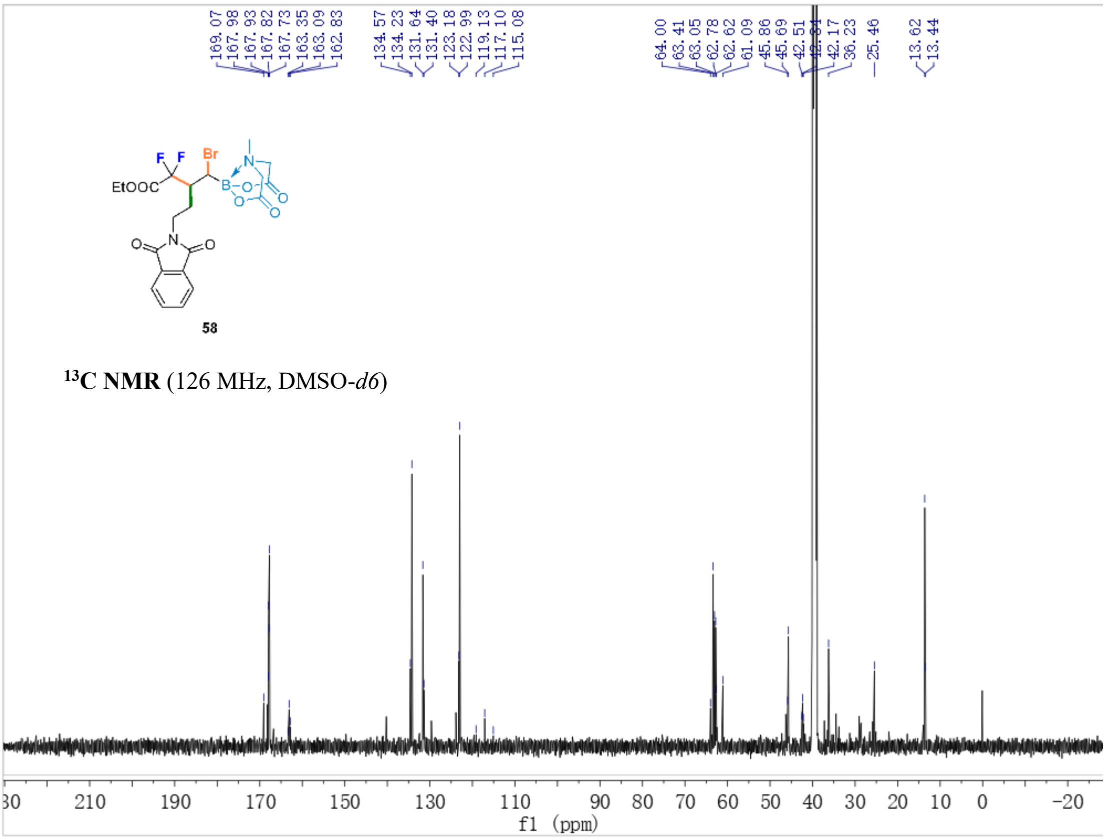
EtOOC
BzO
Br
57
^{19}F NMR (471 MHz, DMSO-d6)
-96.94
-96.98
-97.52
-97.56
-100.95
-100.99
-101.53
-101.57
-104.69
-105.24
-114.35
-114.40
-114.91
-114.96
0.21
0.21
1.00
1.01
f1 (ppm)



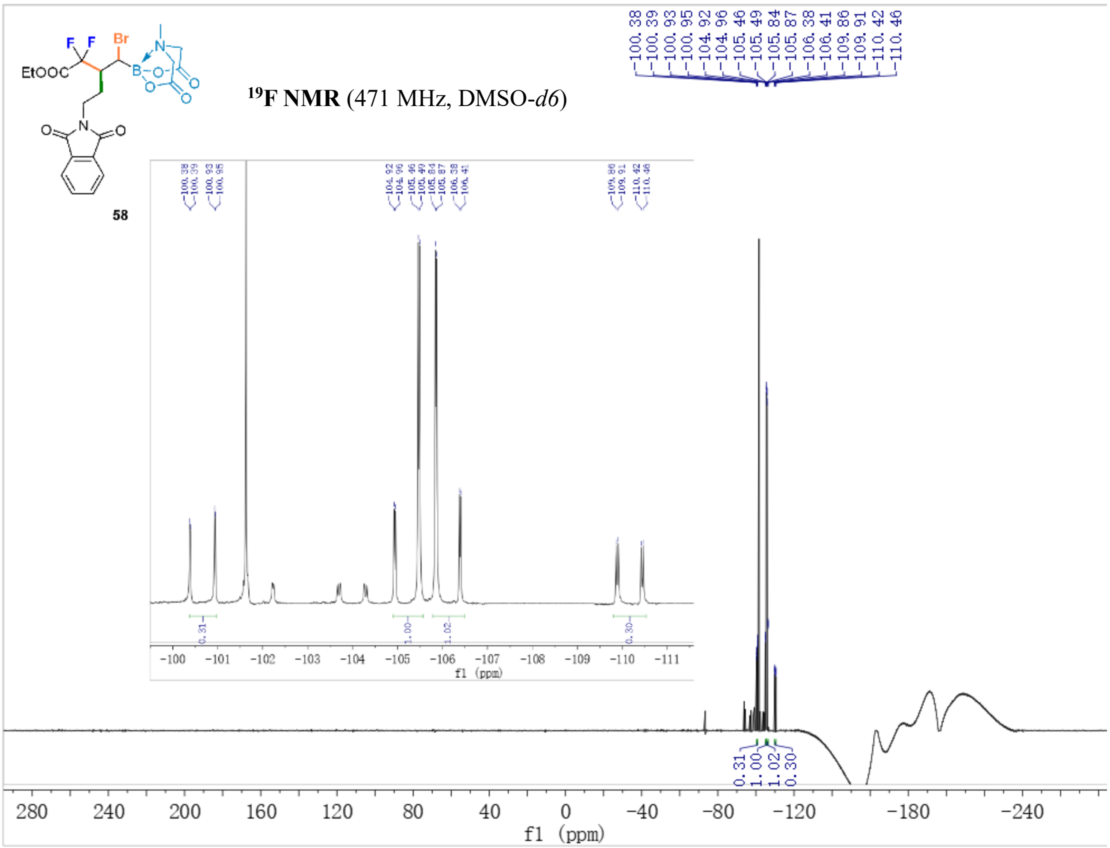
-10.11
^{11}B NMR (160 MHz, DMSO-d6)
EtOOC
BzO
Br
57
f1 (ppm)

Ethyl (3*S*)-3-(bromo(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-5-(1,3-dioxoisoindolin-2-yl)-2,2-difluoropentanoate (58)

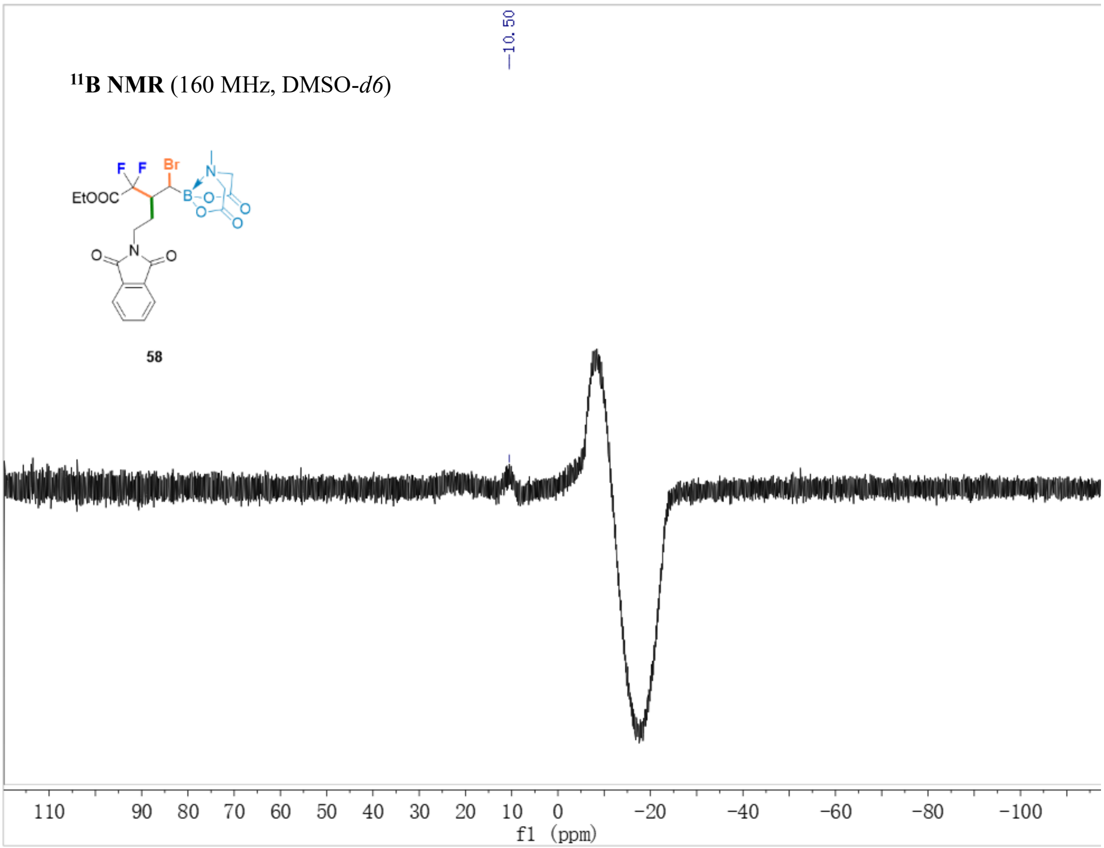




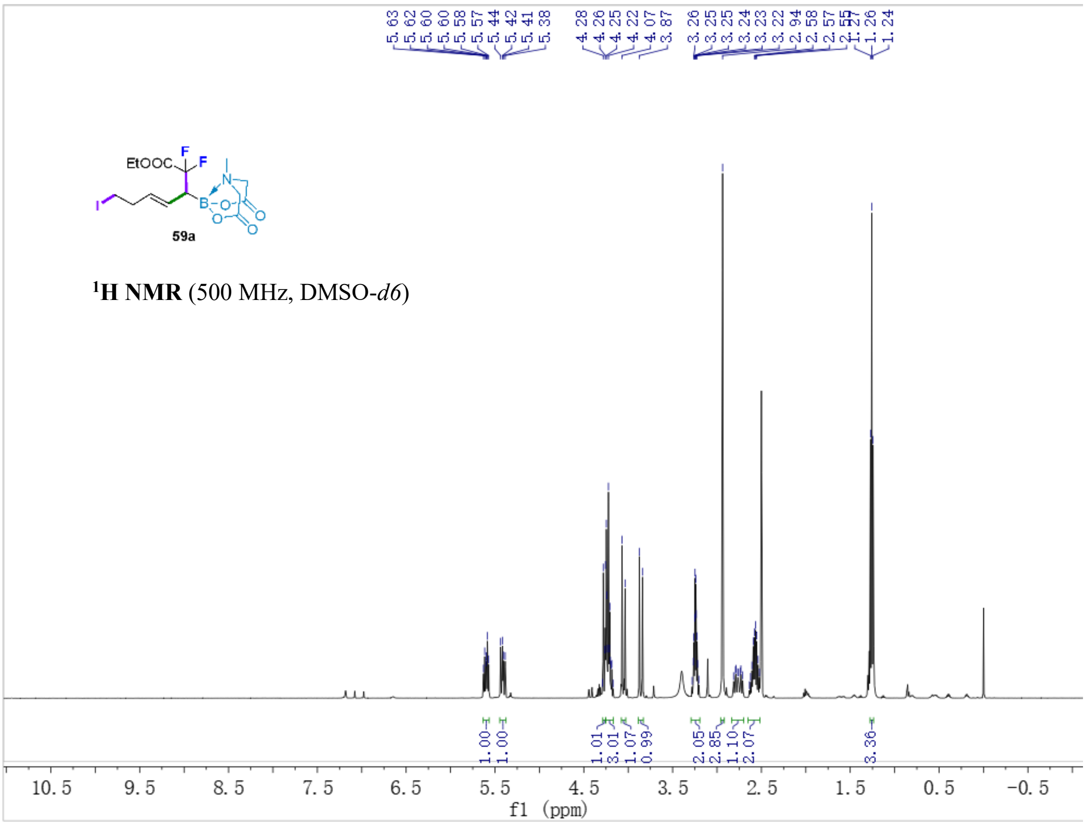
^{19}F NMR (471 MHz, DMSO-*d6*)



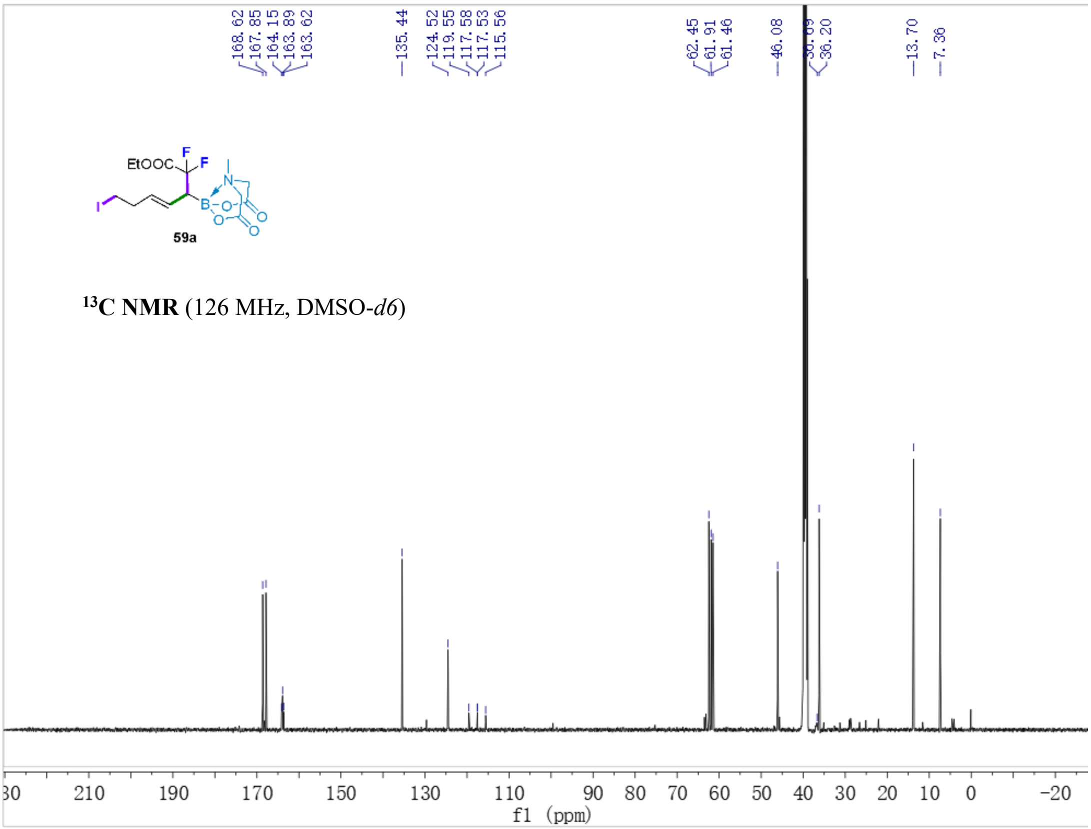
^{11}B NMR (160 MHz, DMSO-*d6*)



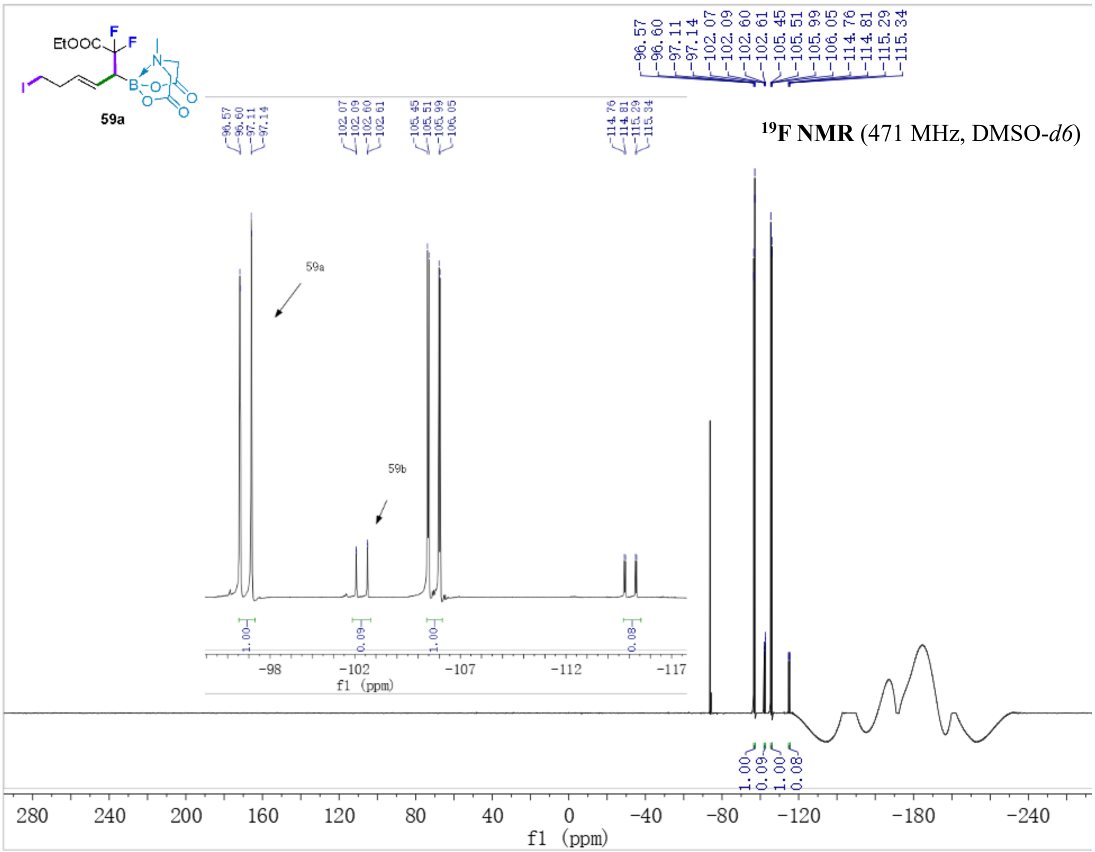
Ethyl (*S*,*E*)-2,2-difluoro-7-iodo-3-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hept-4-enoate (59a)



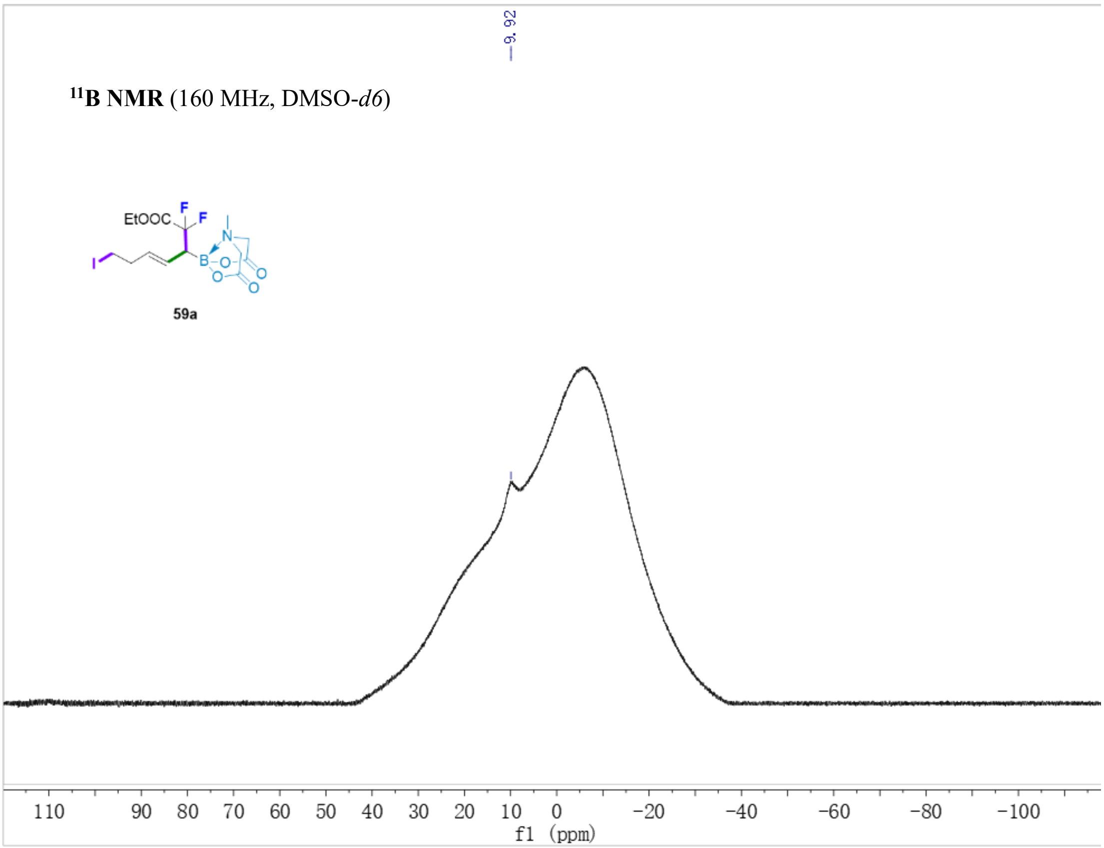
^{1}**H NMR** (500 MHz, DMSO-*d6*)



^{13}**C NMR** (126 MHz, DMSO-*d6*)

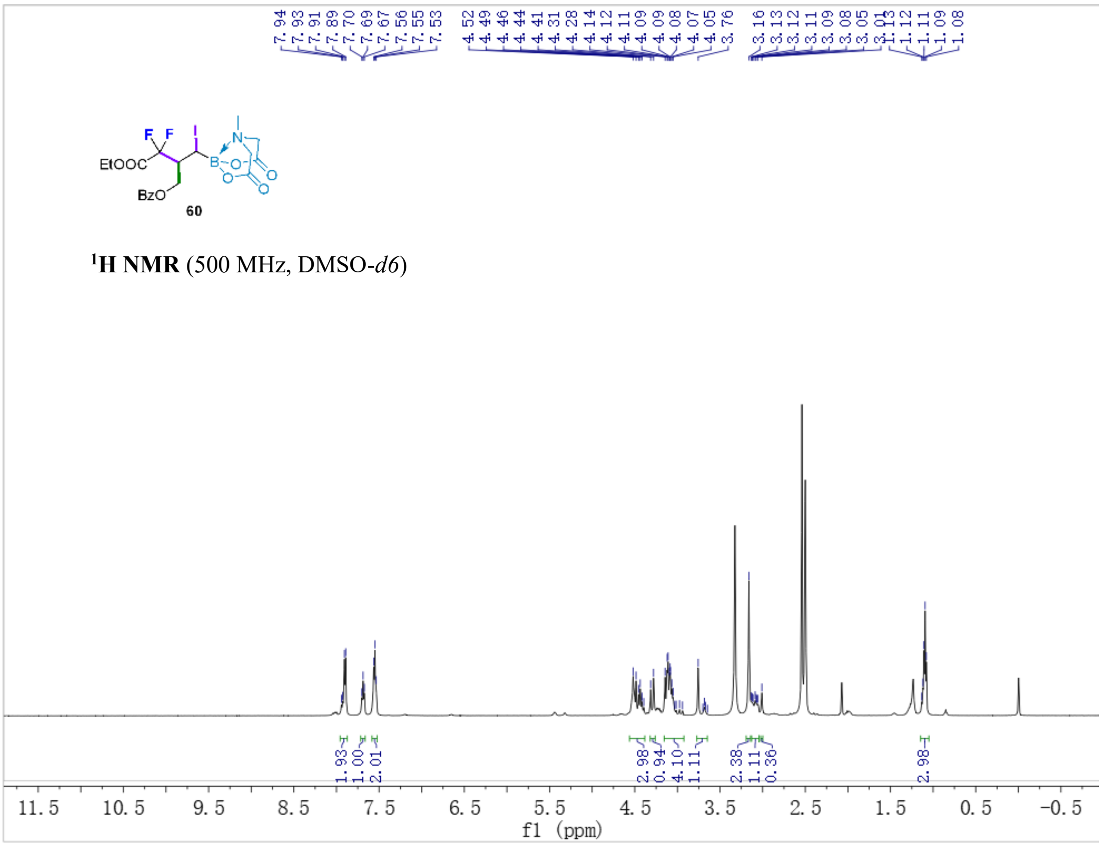


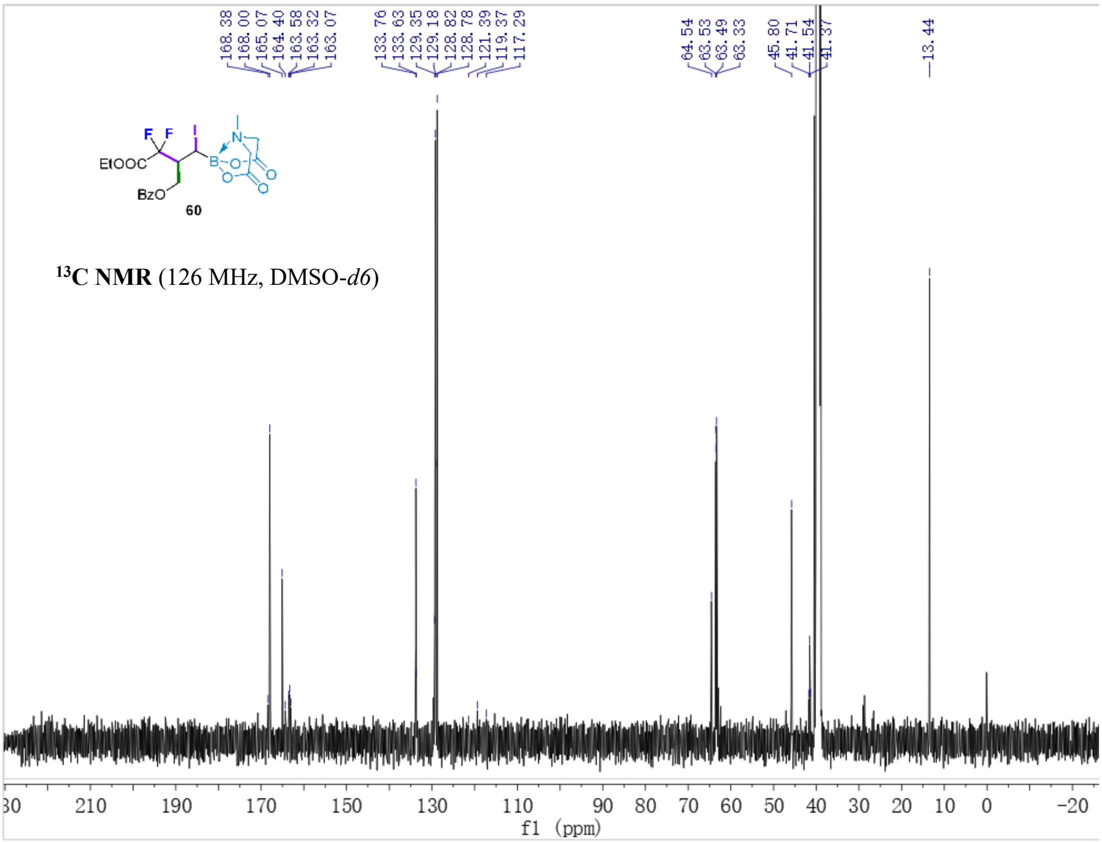
^{19}F NMR (471 MHz, DMSO-$d6$)
59a
59b
f1 (ppm)

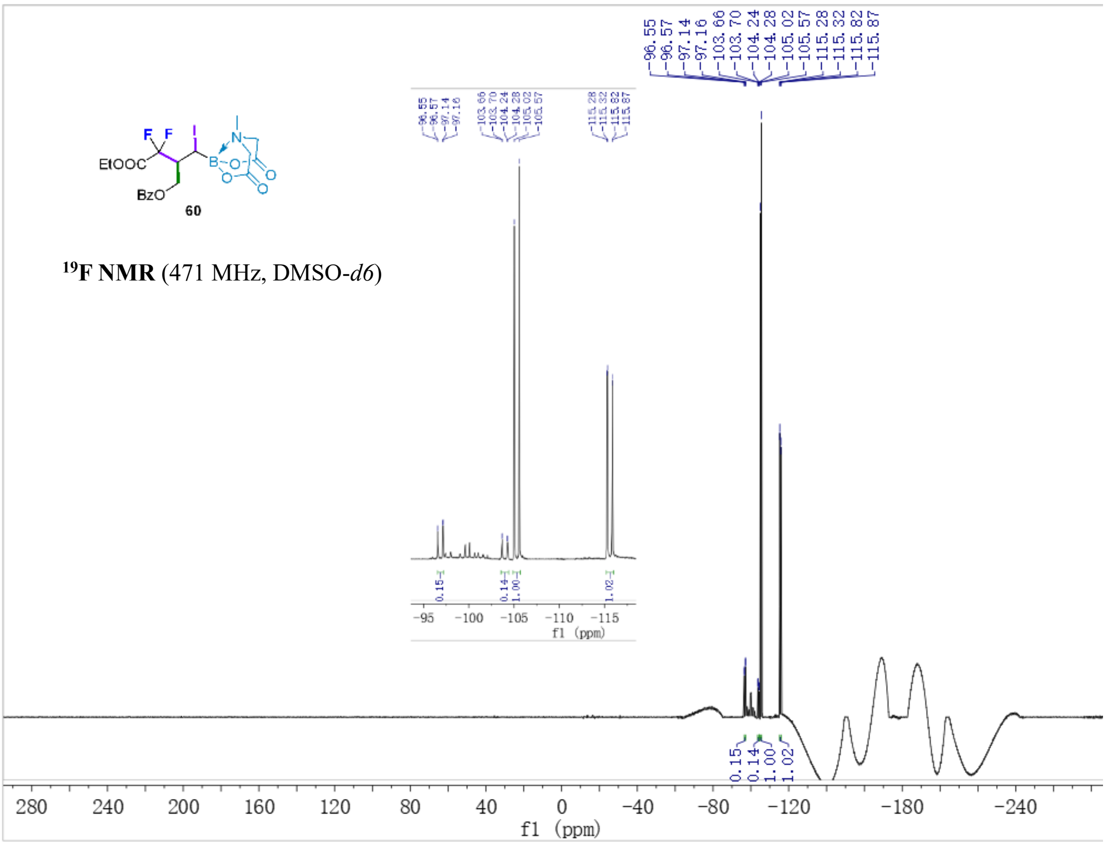


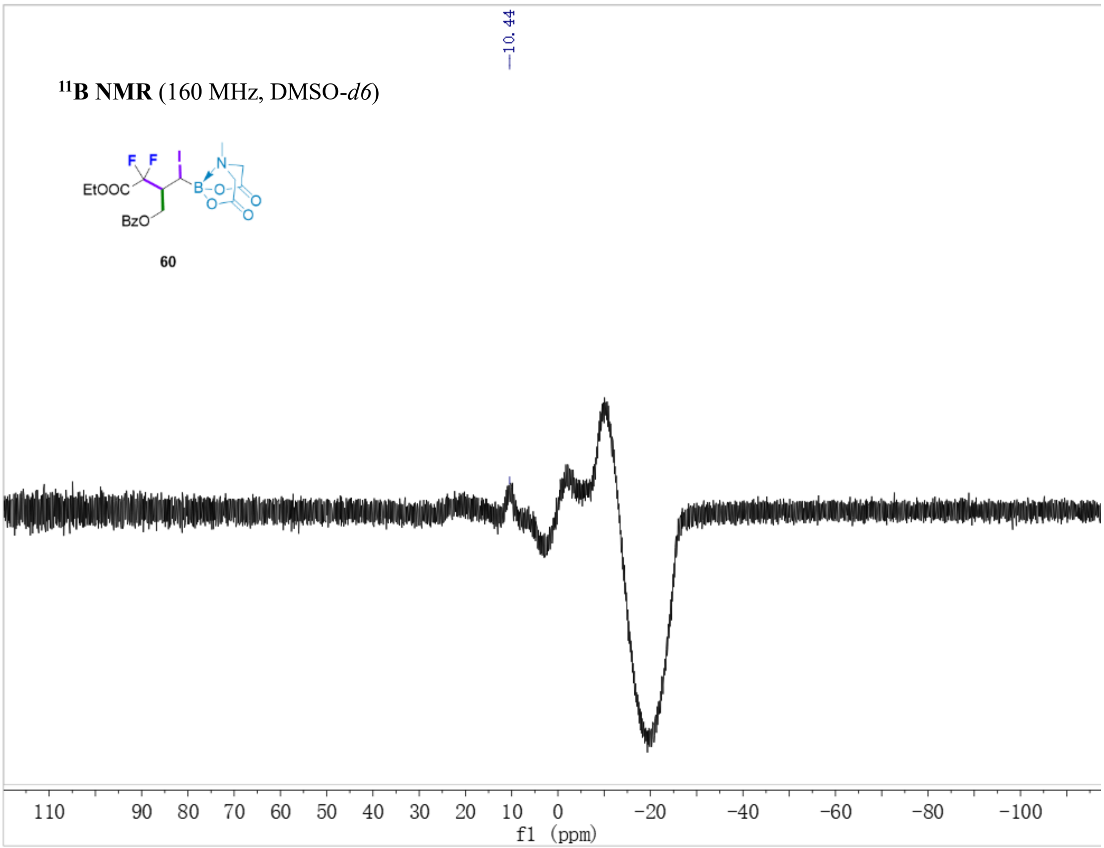
^{11}B NMR (160 MHz, DMSO-$d6$)
59a
f1 (ppm)

(2*S*)-4-ethoxy-3,3-difluoro-2-(iodo(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-4-oxobutyl benzoate (60)

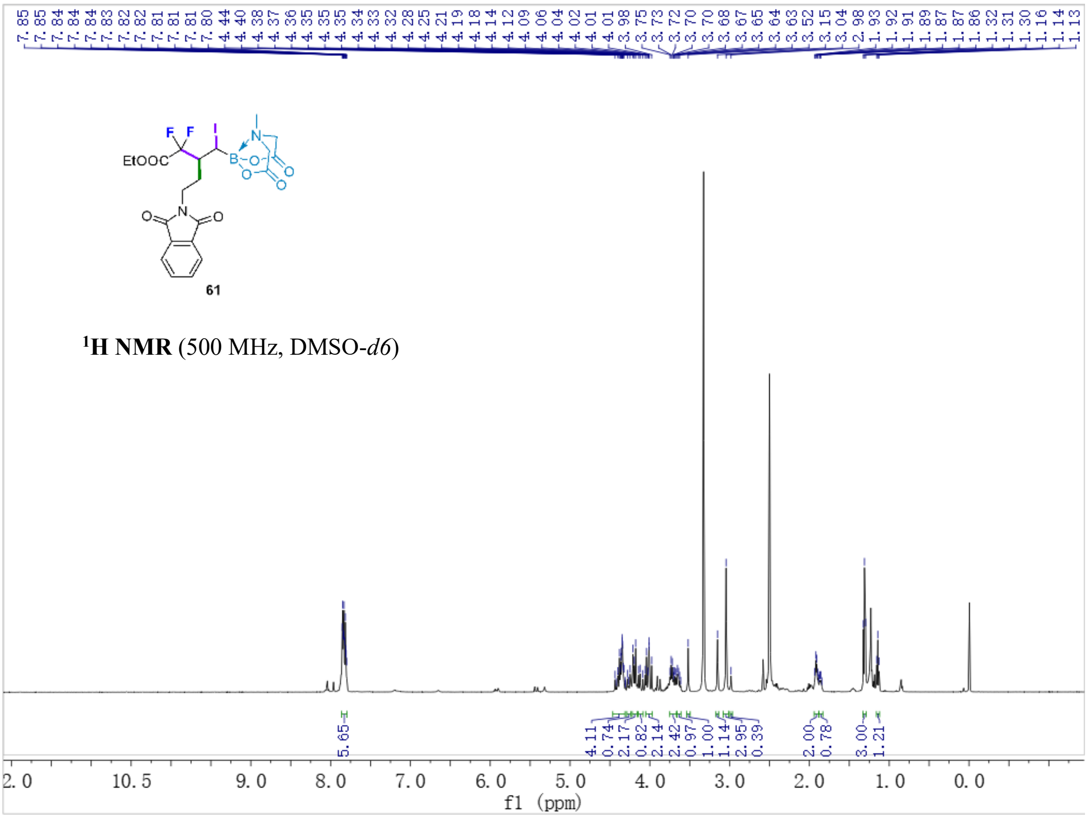


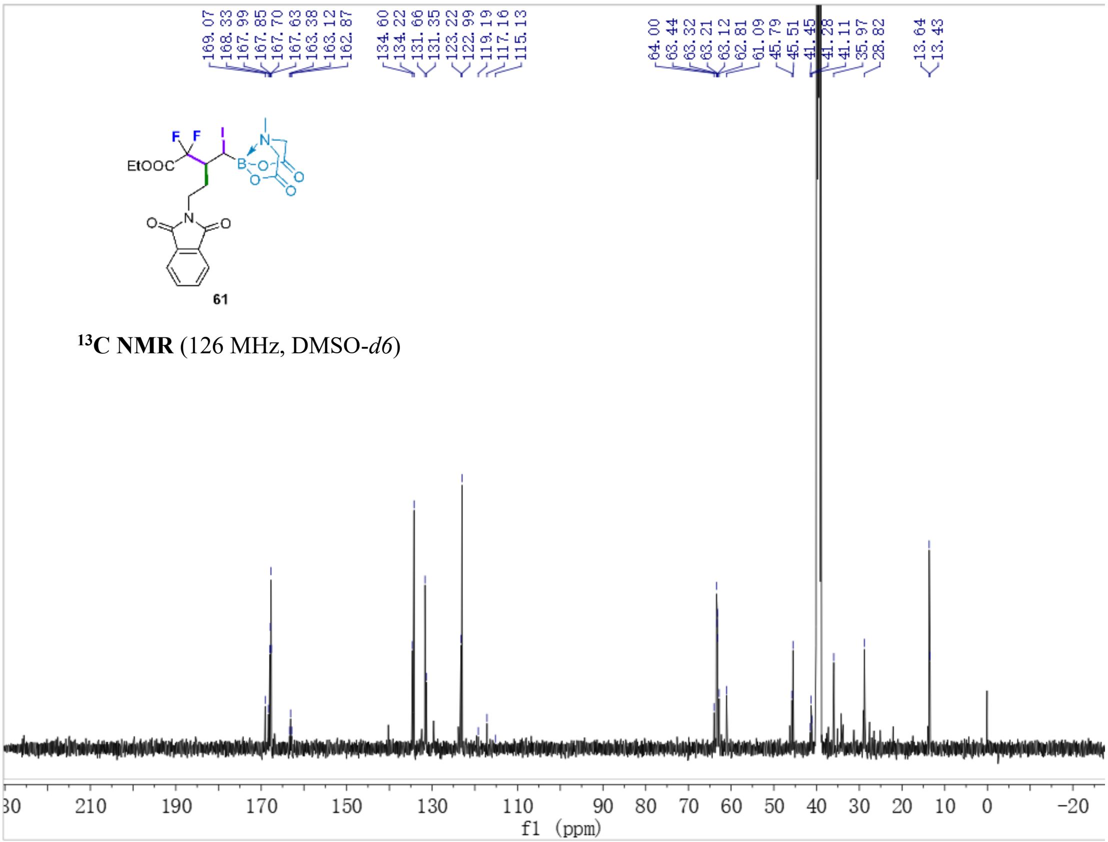


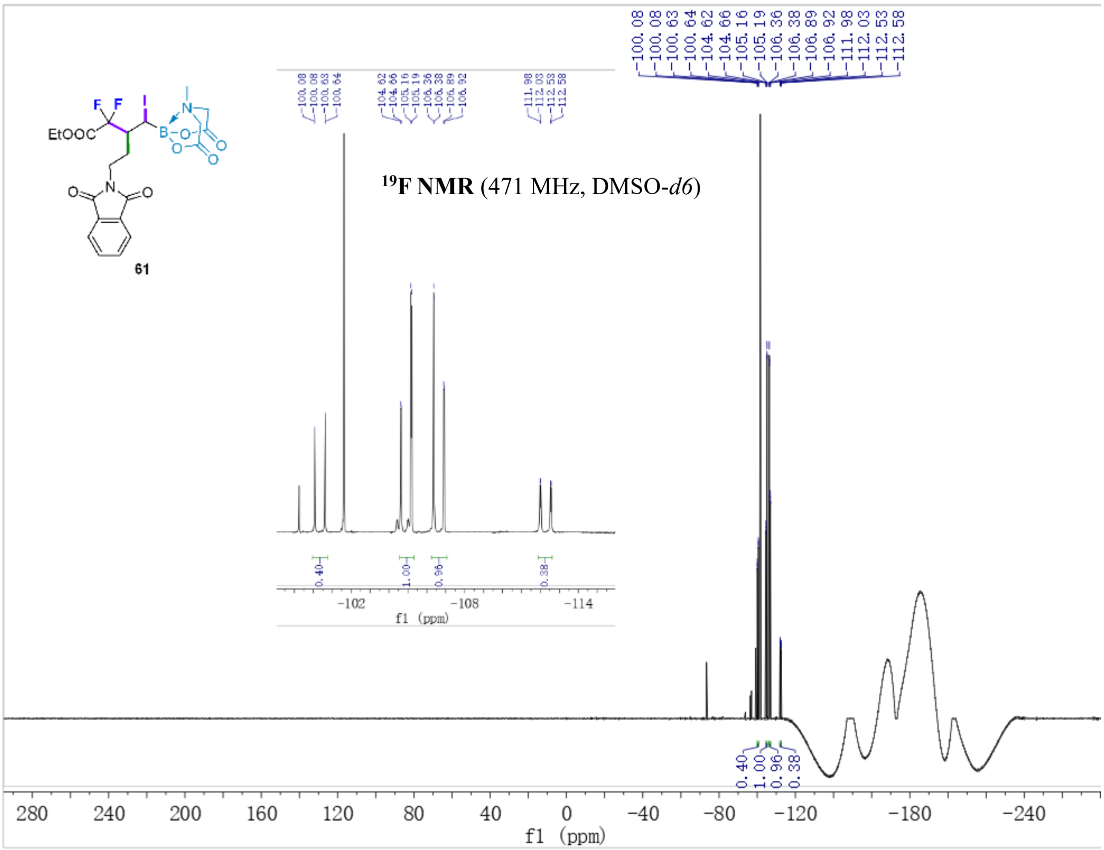

EtOOC
BzO
60
19F NMR (471 MHz, DMSO-d6)
-96.55
-96.57
-97.14
-97.16
-103.66
-103.70
-104.24
-104.28
-105.02
-105.57
-115.28
-115.32
-115.82
-115.87
0.15
0.14
1.00
1.02
f1 (ppm)


-10.44
11B NMR (160 MHz, DMSO-d6)
EtOOC
BzO
60
f1 (ppm)

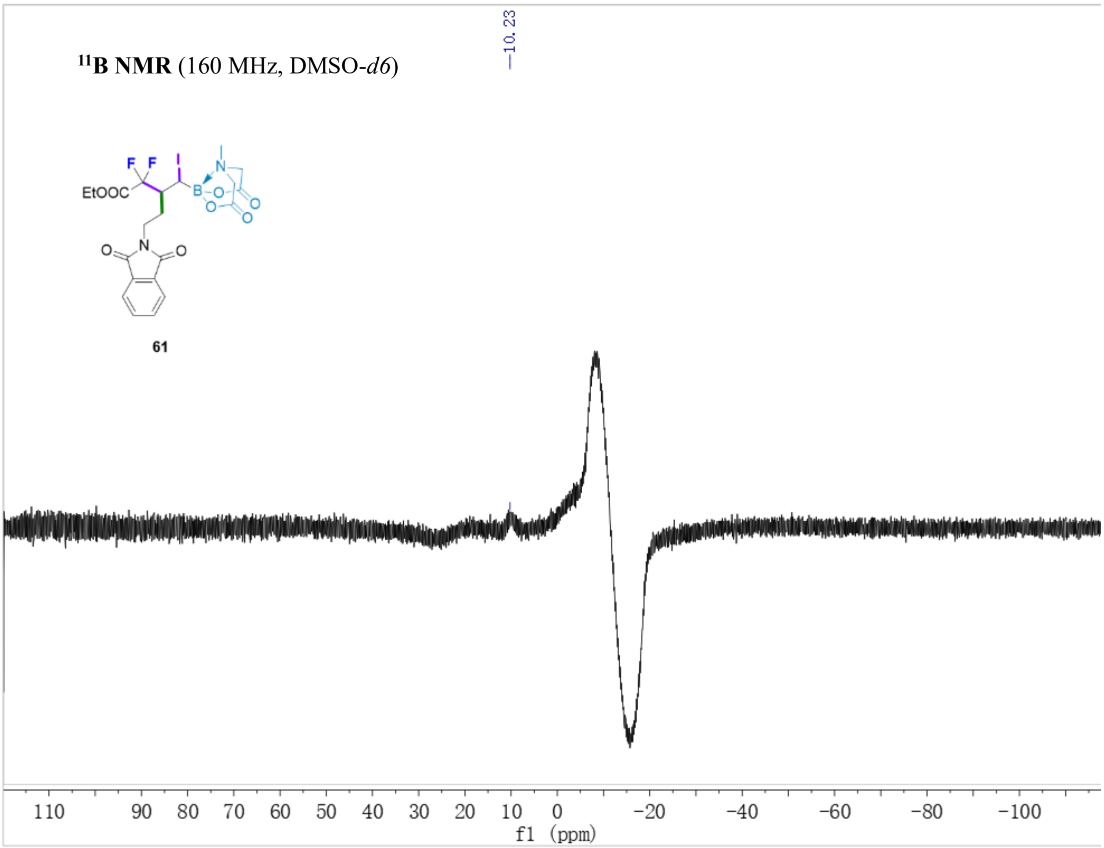
Ethyl (3*S*)-5-(1,3-dioxoisoindolin-2-yl)-2,2-difluoro-3-(iodo(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)pentanoate (61)





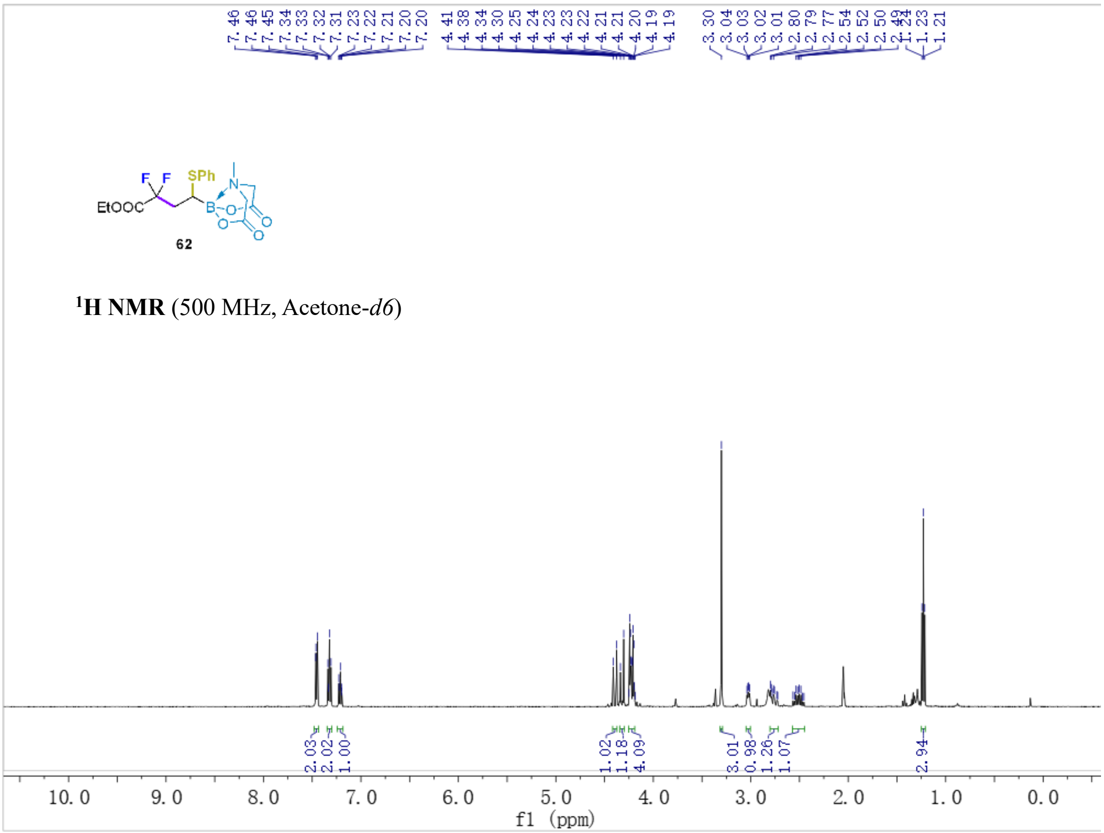


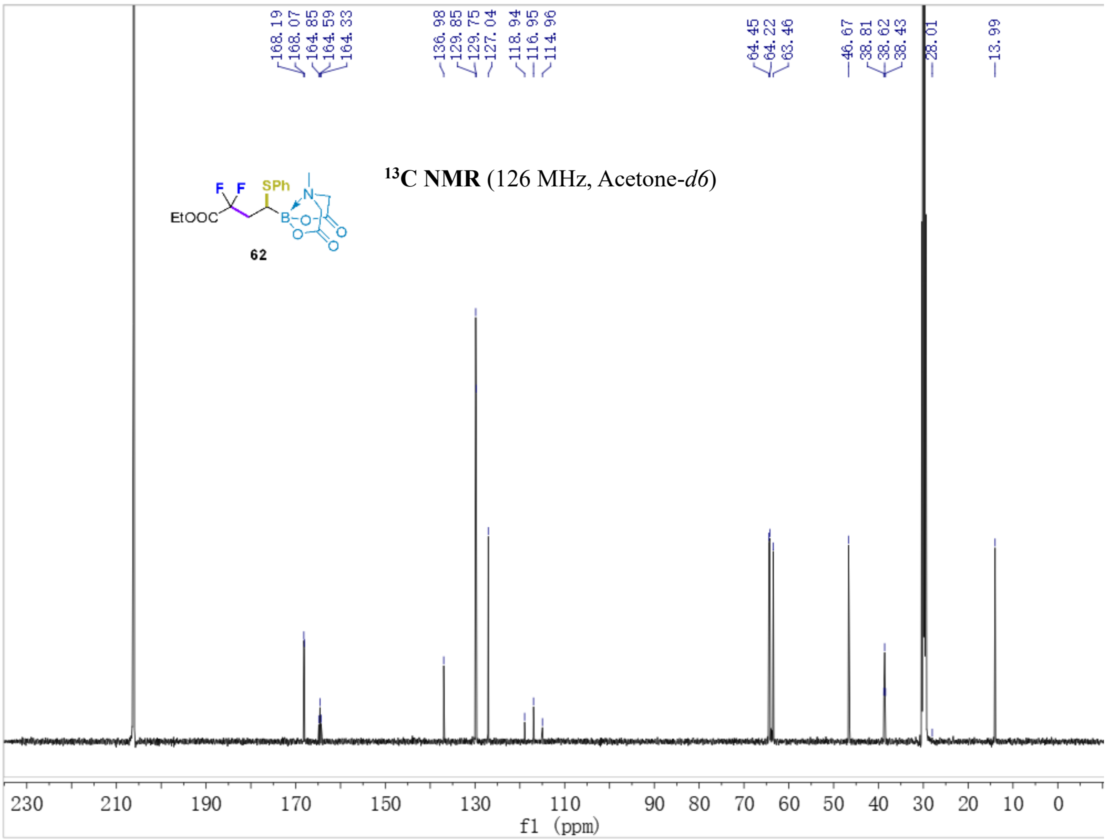
^{19}F NMR (471 MHz, DMSO-$d6$)
61
f1 (ppm)

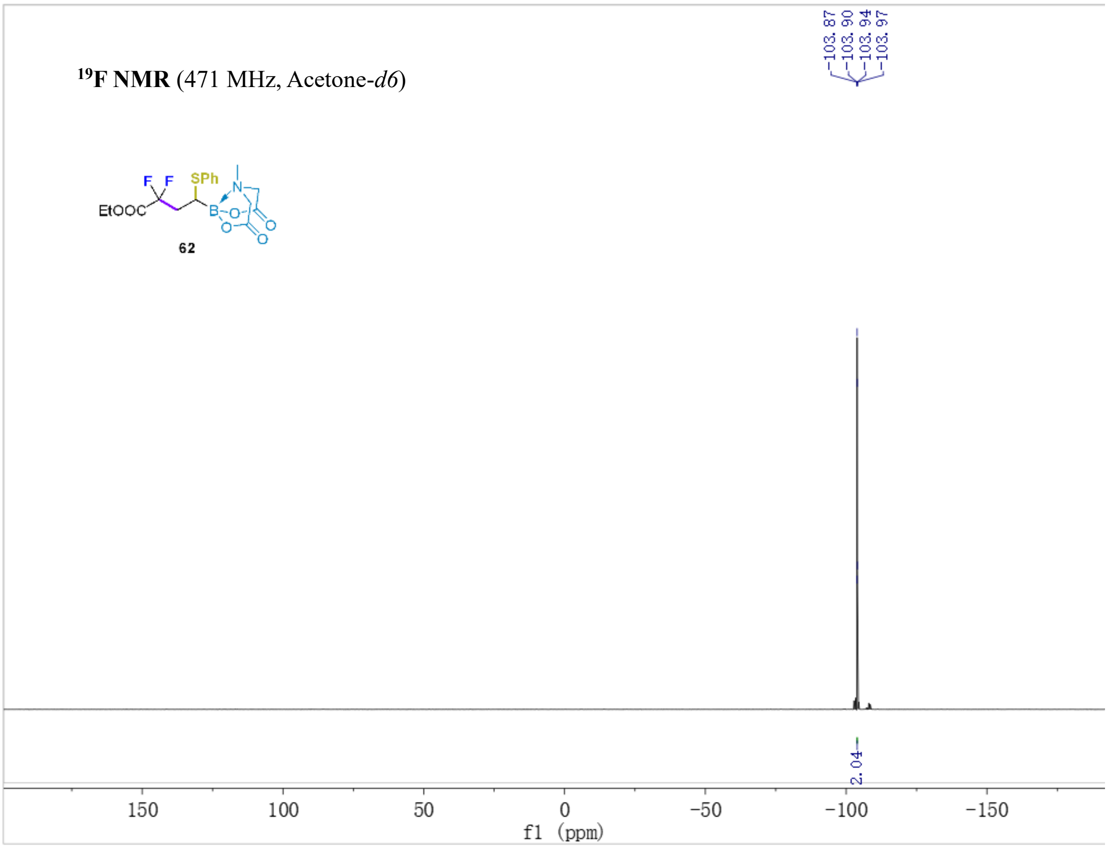


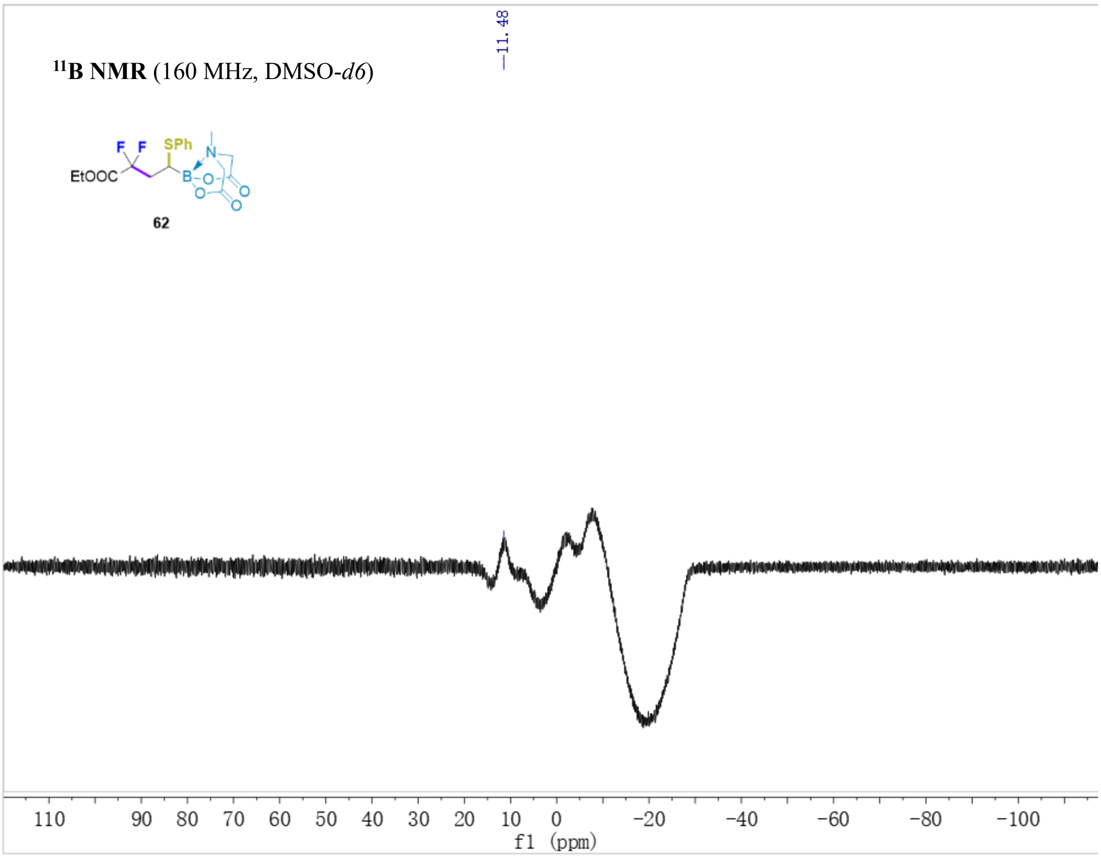
^{11}B NMR (160 MHz, DMSO-$d6$)
61
f1 (ppm)

Ethyl 2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-4-(phenylthio)butanoate (62)

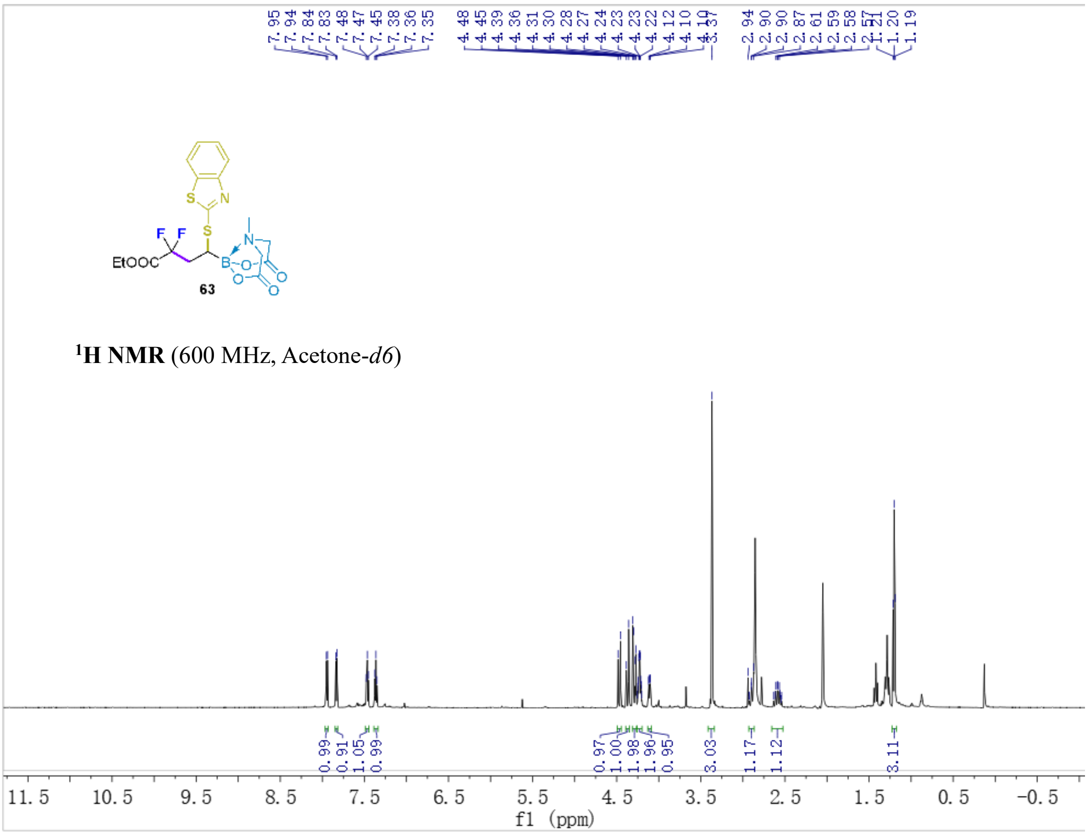


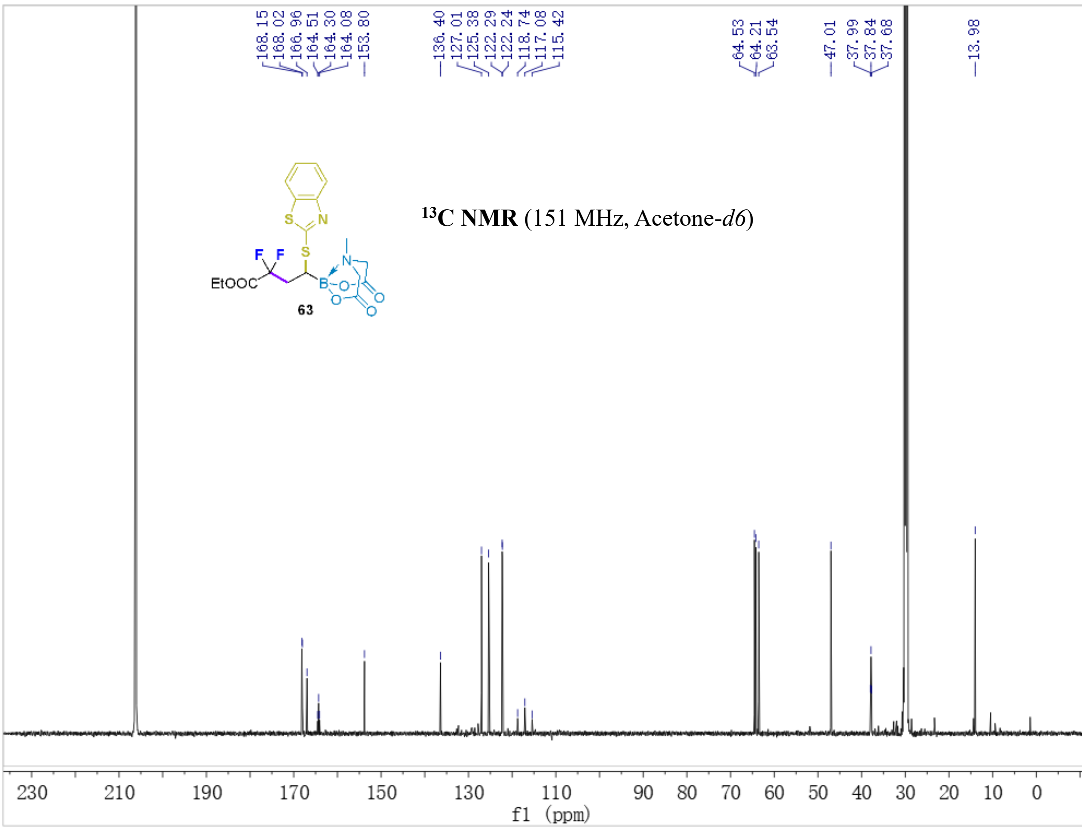


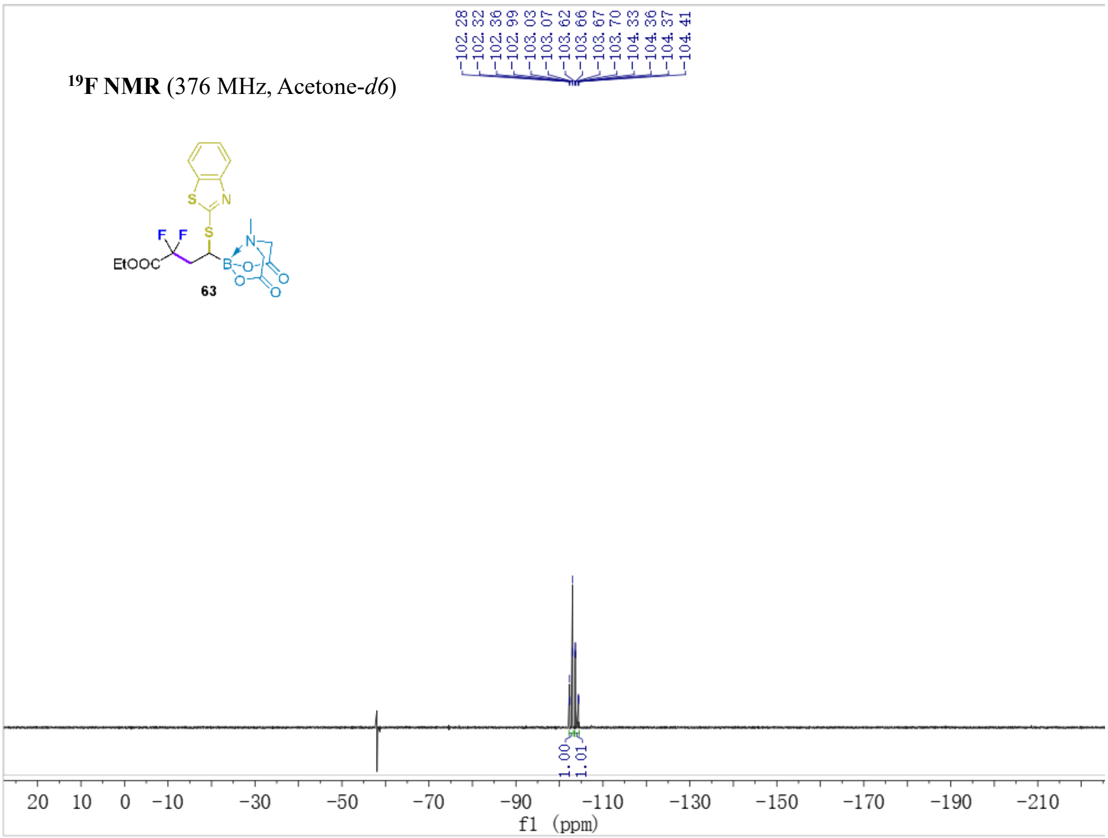

19F NMR (471 MHz, Acetone-d6)
-103.87
-103.90
-103.94
-103.97
F F SPh
EtOOC
N
B O O O O
62
2.04
150 100 50 0 -50 -100 -150
f1 (ppm)


11B NMR (160 MHz, DMSO-d6)
-11.48
F F SPh
EtOOC
N
B O O O O
62
110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100
f1 (ppm)

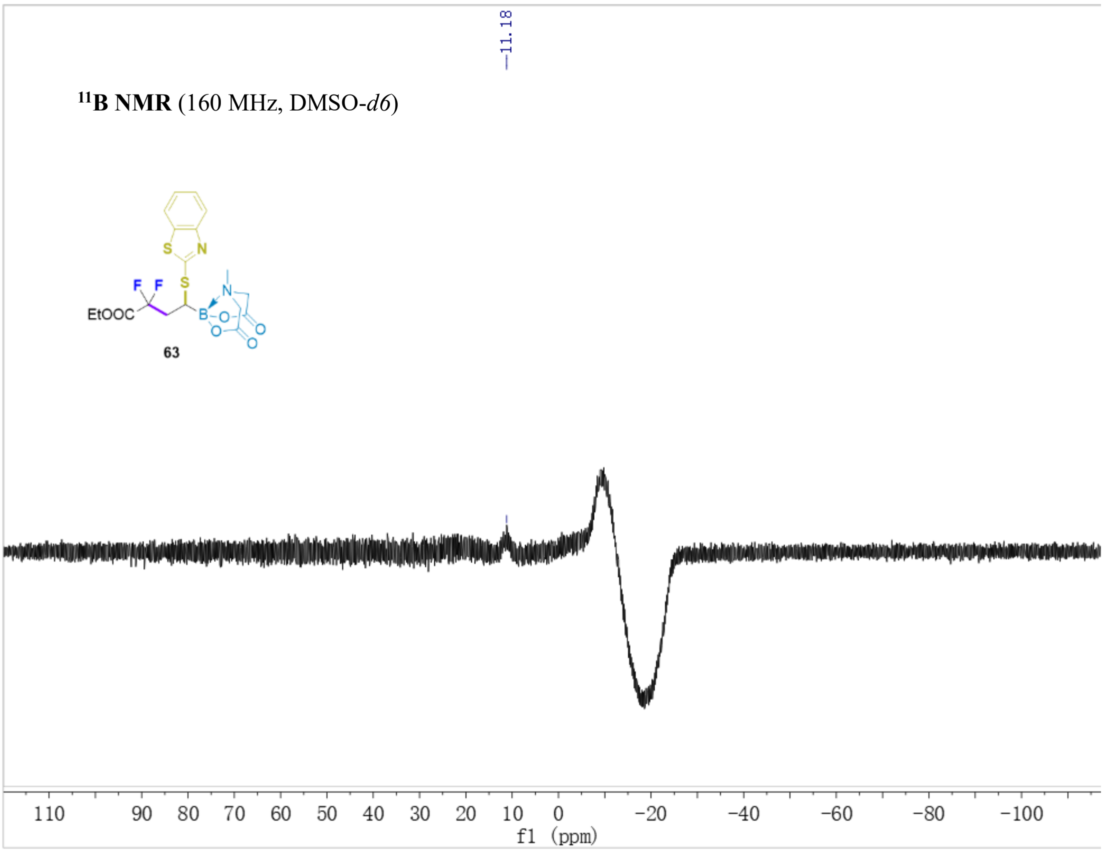
Ethyl 4-(benzo[*d*]thiazol-2-ylthio)-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoate (63)





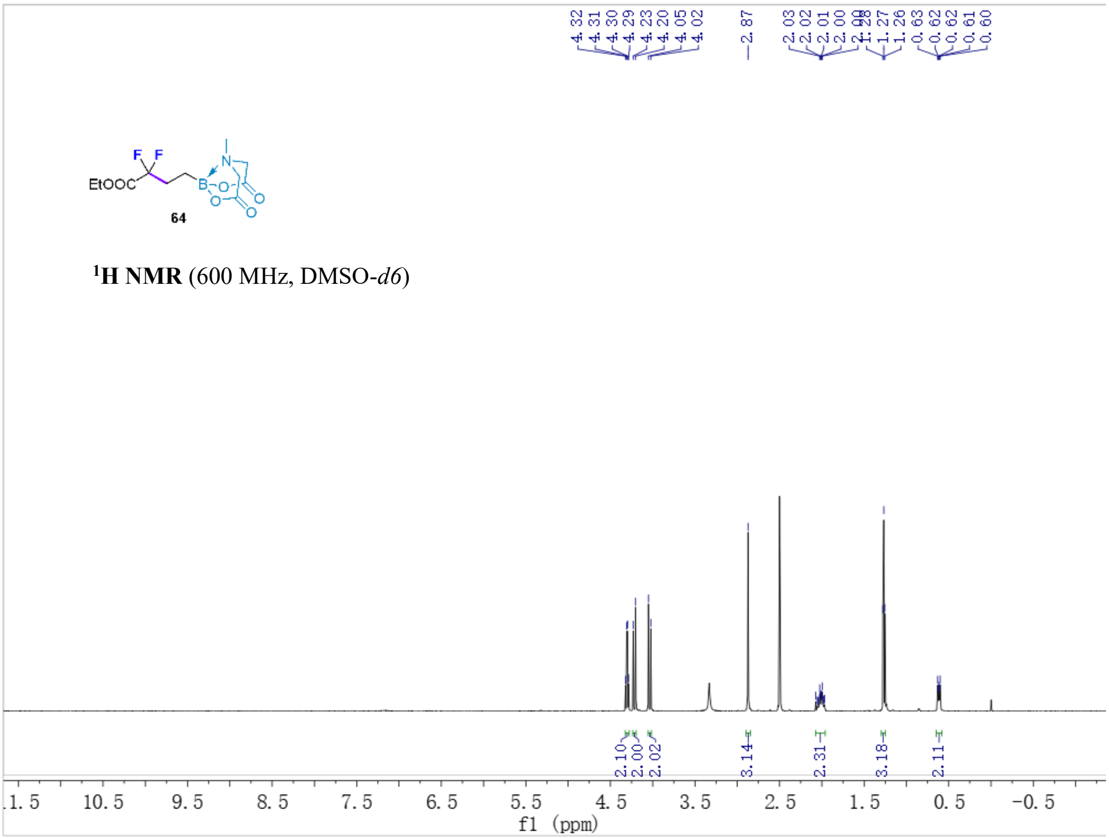


-102.28
-102.32
-102.36
-102.99
-103.03
-103.07
-103.62
-103.66
-103.67
-103.70
-104.33
-104.36
-104.37
-104.41
^{19}F NMR (376 MHz, Acetone-*d6*)
EtOOC
F F
S
S N
N
B
O
O
O
O
63
1.00
1.01
20 10 0 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210
f1 (ppm)

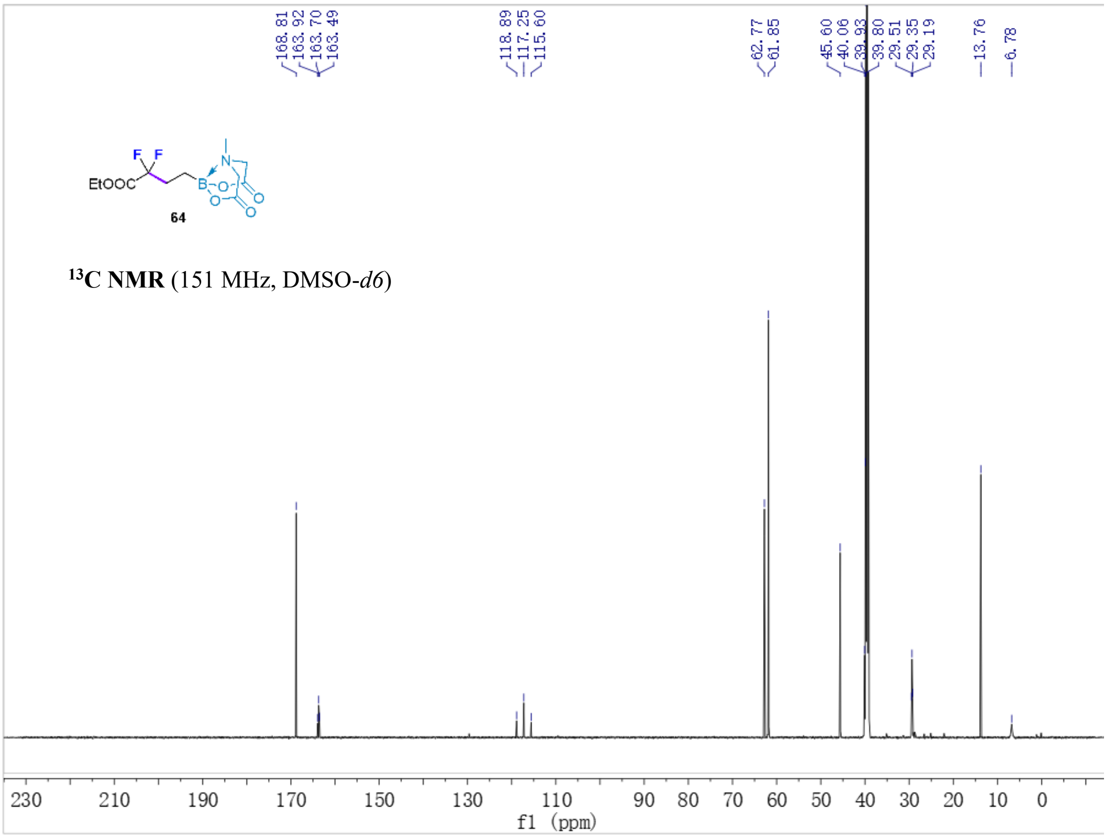


-11.18
^{11}B NMR (160 MHz, DMSO-*d6*)
EtOOC
F F
S
S N
N
B
O
O
O
O
63
110 90 80 70 60 50 40 30 20 10 0 −20 −40 −60 −80 −100
f1 (ppm)

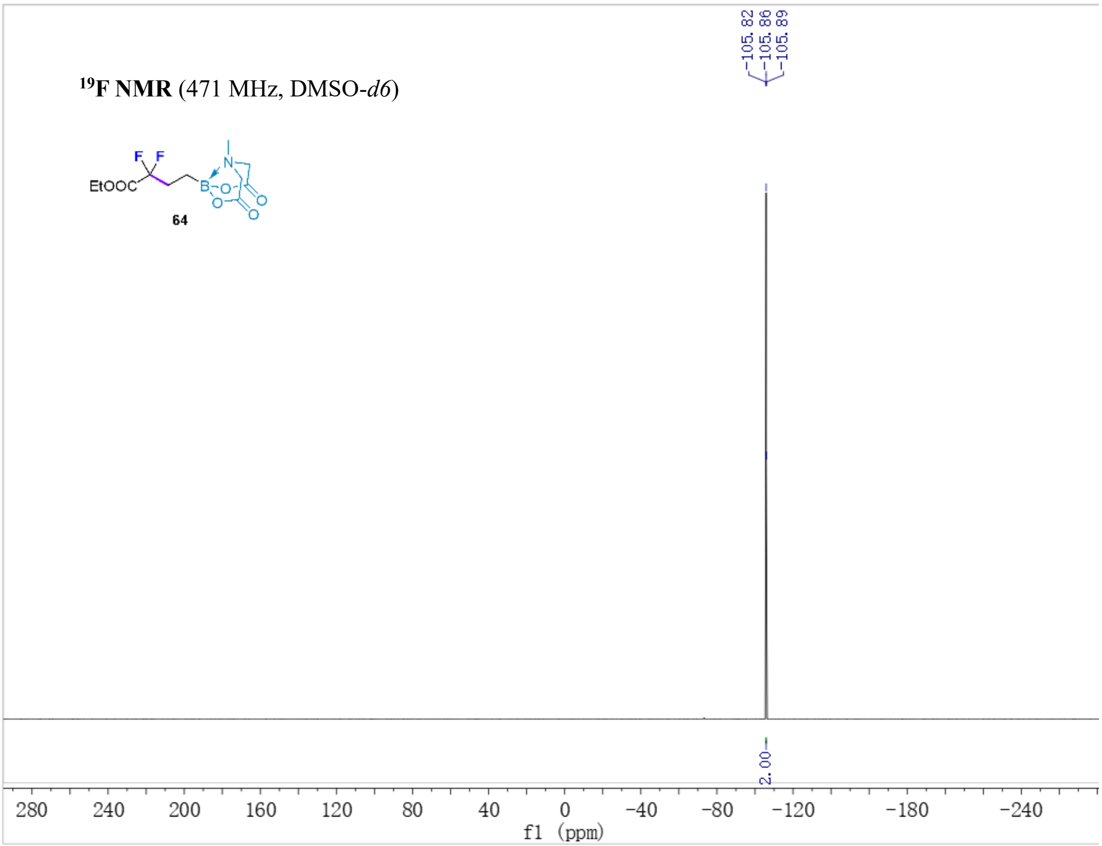
Ethyl 2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanoate (64)



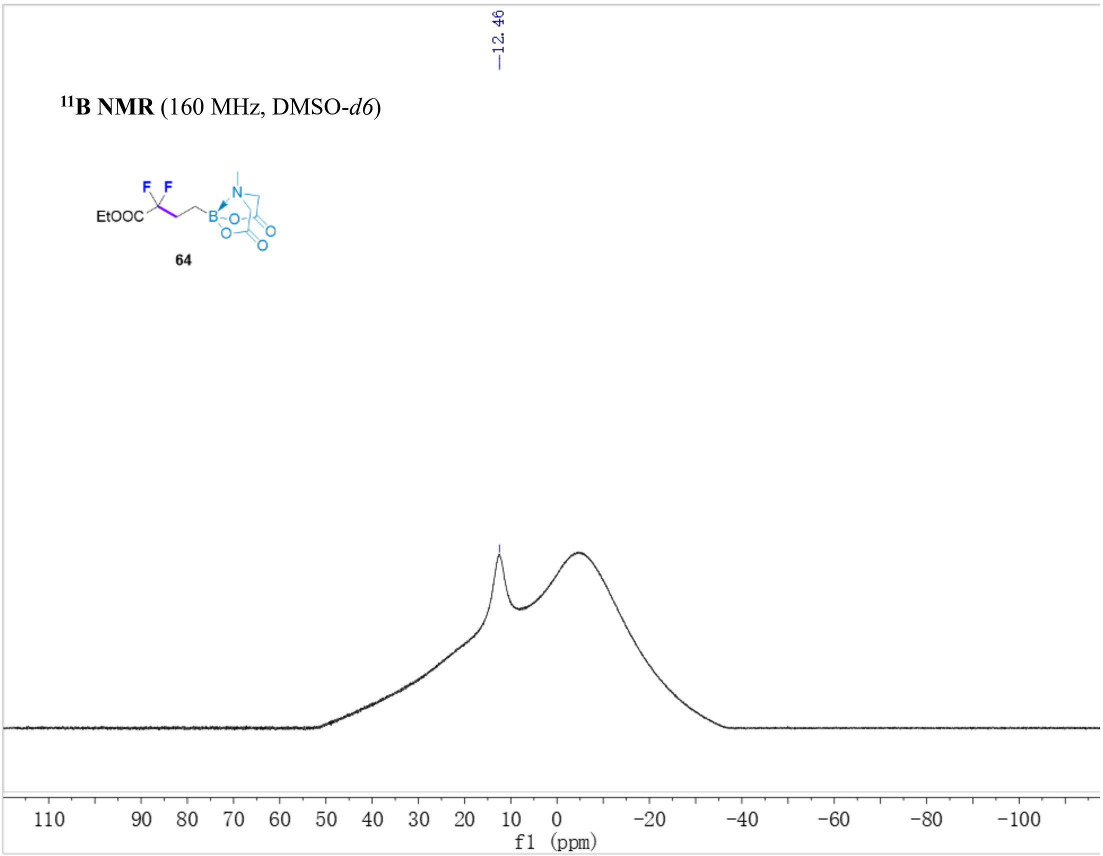
^{1}H NMR (600 MHz, DMSO-*d6*)



^{13}C NMR (151 MHz, DMSO-*d6*)

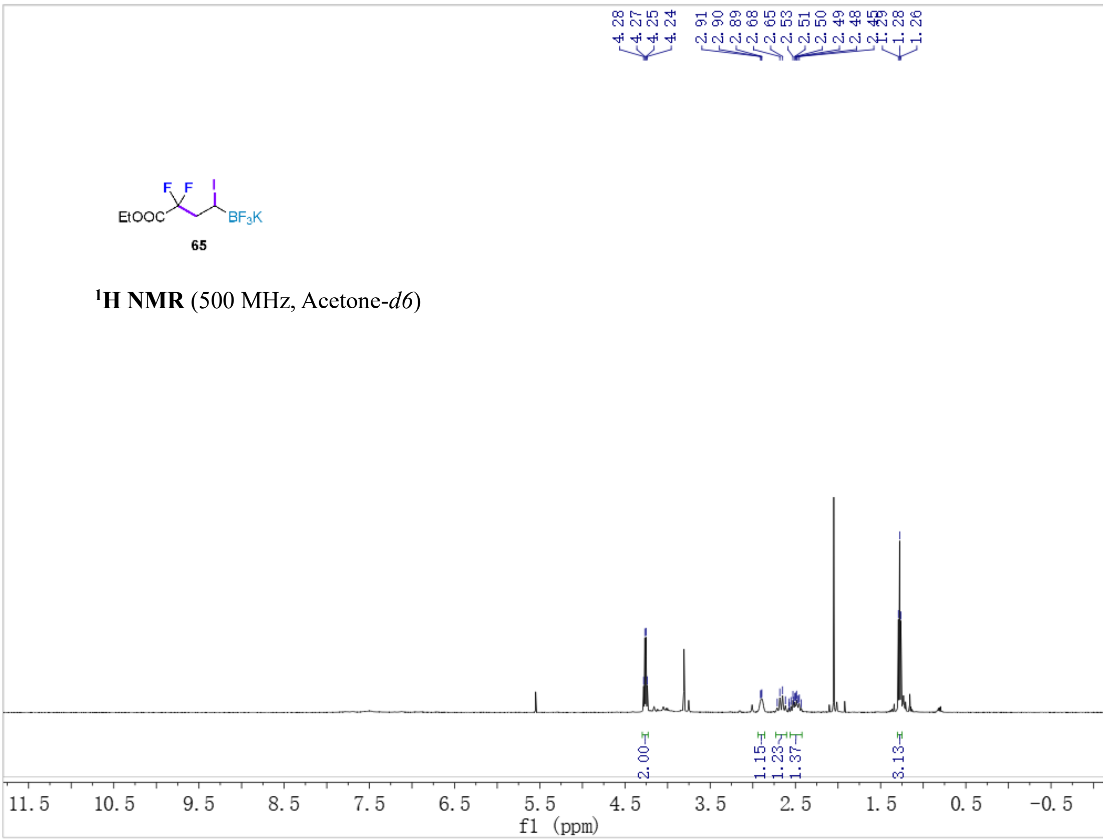


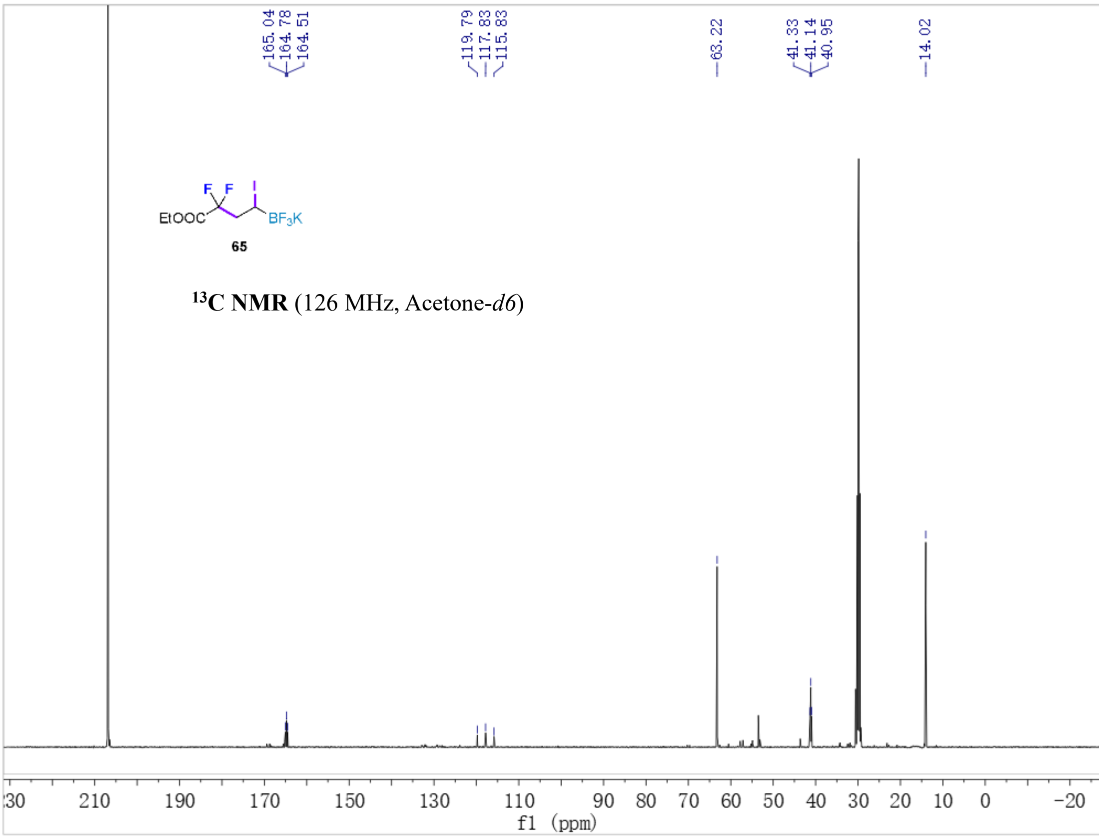
−105.82
−105.86
−105.89
¹⁹F NMR (471 MHz, DMSO-*d6*)
EtOOC
F F
N
B
O
O
O
O
64
2.00
280 240 200 160 120 80 40 0 −40 −80 −120 −180 −240
f1 (ppm)

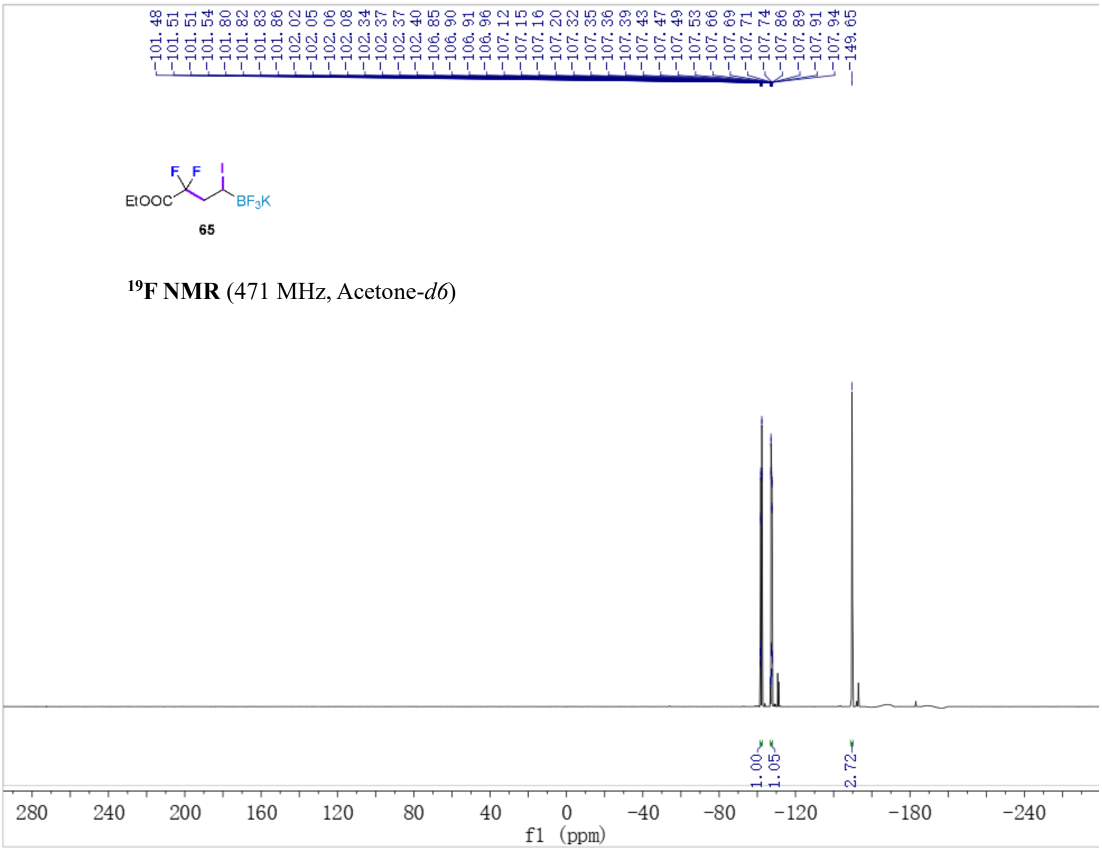


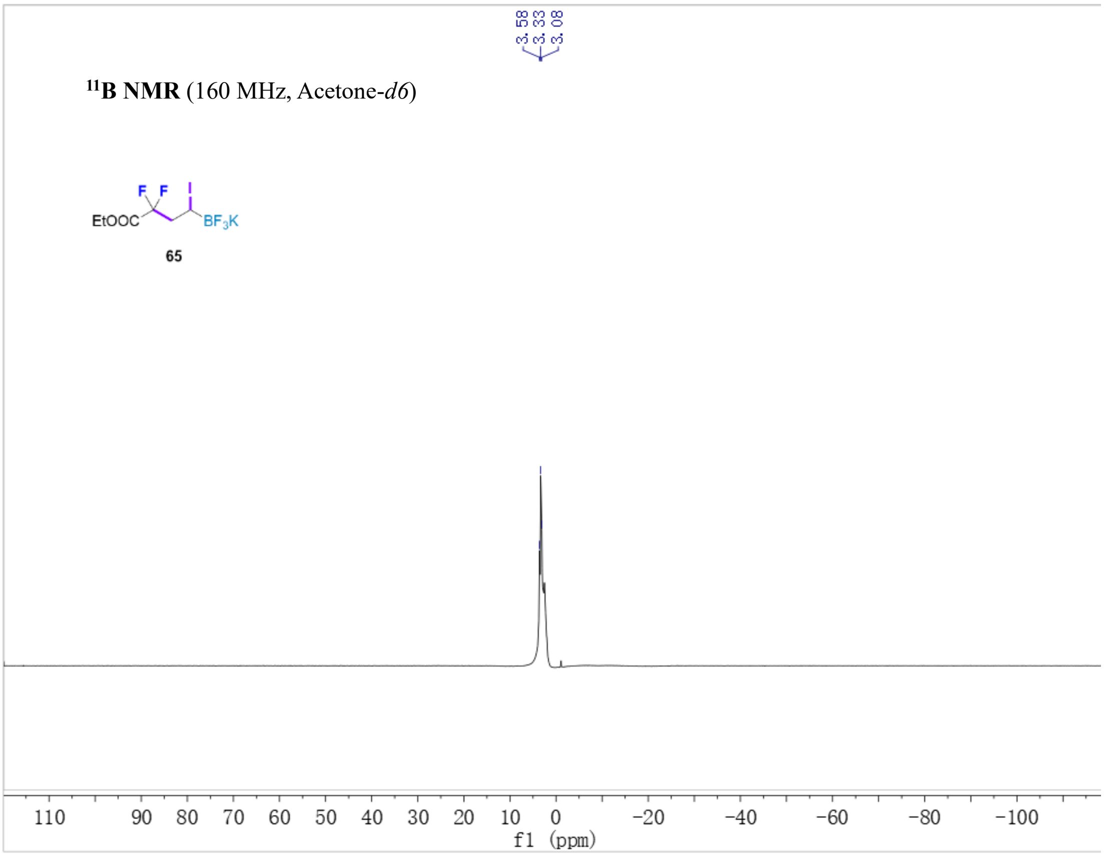
−12.46
¹¹B NMR (160 MHz, DMSO-*d6*)
EtOOC
F F
N
B
O
O
O
O
64
110 90 80 70 60 50 40 30 20 10 0 −20 −40 −60 −80 −100
f1 (ppm)

Ethyl 2,2-difluoro-4-iodo-4-(trifluoro-λ4-boraneyl)butanoate, potassium salt (65)

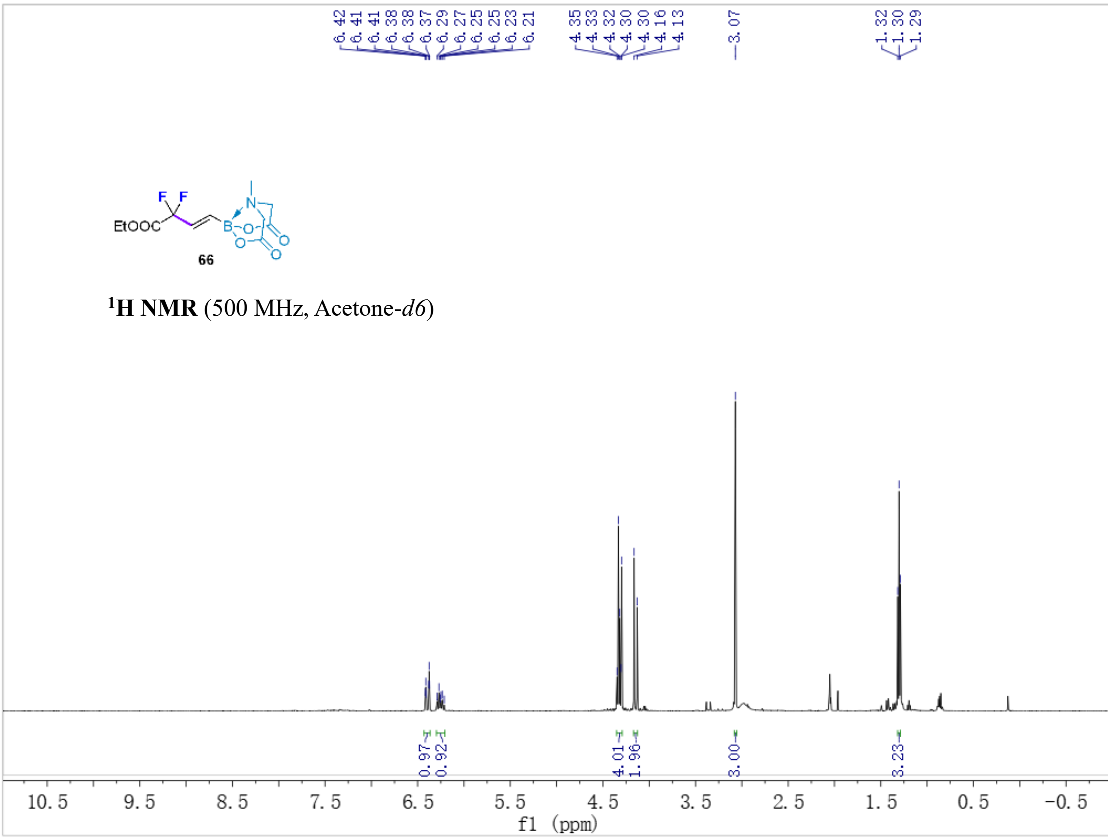


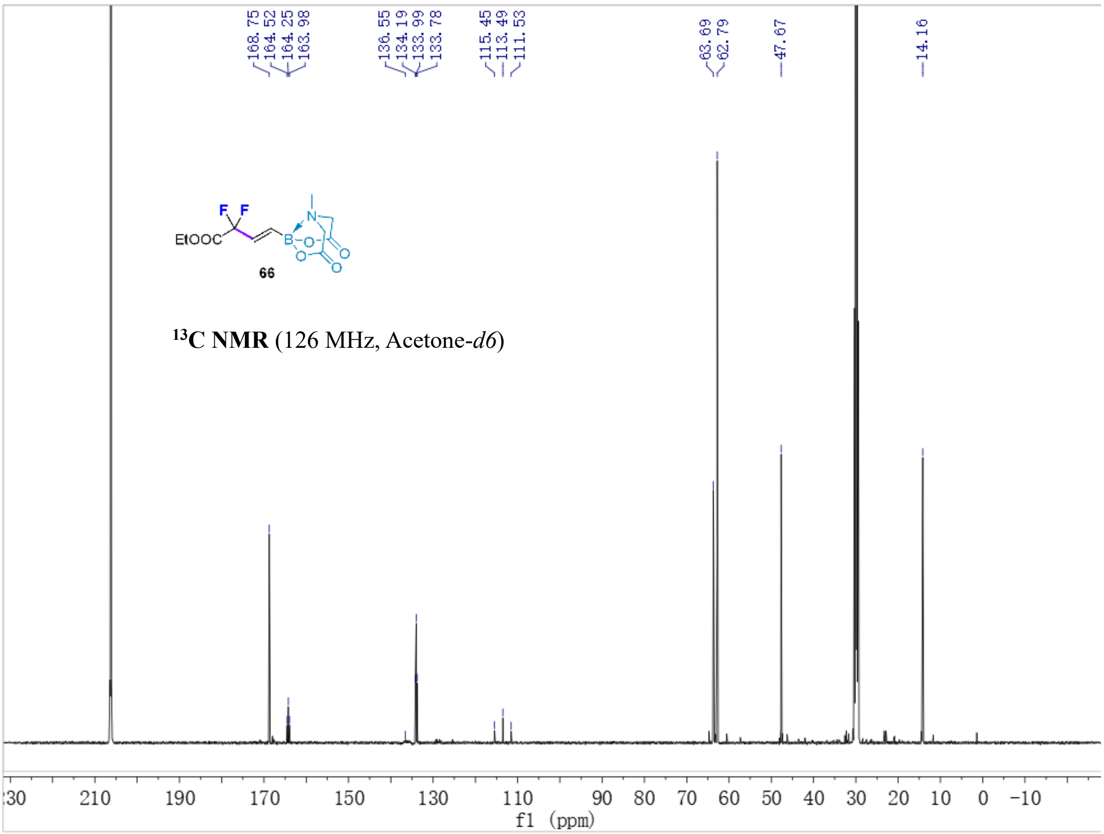



-101.48
-101.51
-101.51
-101.54
-101.80
-101.82
-101.83
-101.86
-102.02
-102.05
-102.06
-102.08
-102.34
-102.37
-102.37
-102.40
-106.85
-106.90
-106.91
-106.96
-107.12
-107.15
-107.16
-107.20
-107.32
-107.35
-107.36
-107.39
-107.43
-107.47
-107.49
-107.53
-107.66
-107.69
-107.71
-107.74
-107.86
-107.89
-107.91
-107.94
-149.65
F F
I
EtOOC
BF3K
65
19F NMR (471 MHz, Acetone-d6)
1.00
1.05
2.72
280 240 200 160 120 80 40 0 -40 -80 -120 -180 -240
f1 (ppm)

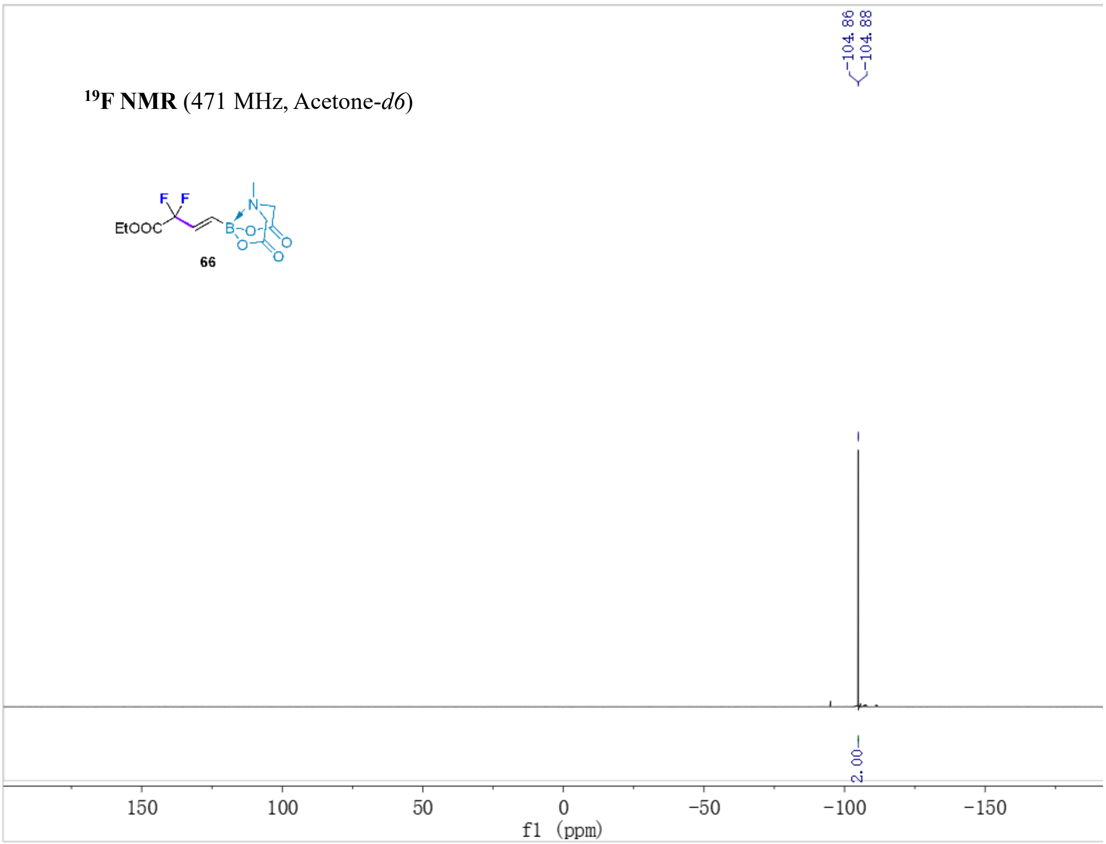

3.58
3.33
3.08
11B NMR (160 MHz, Acetone-d6)
F F
I
EtOOC
BF3K
65
110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100
f1 (ppm)

Ethyl (*E*)-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)but-3-enoate (66)

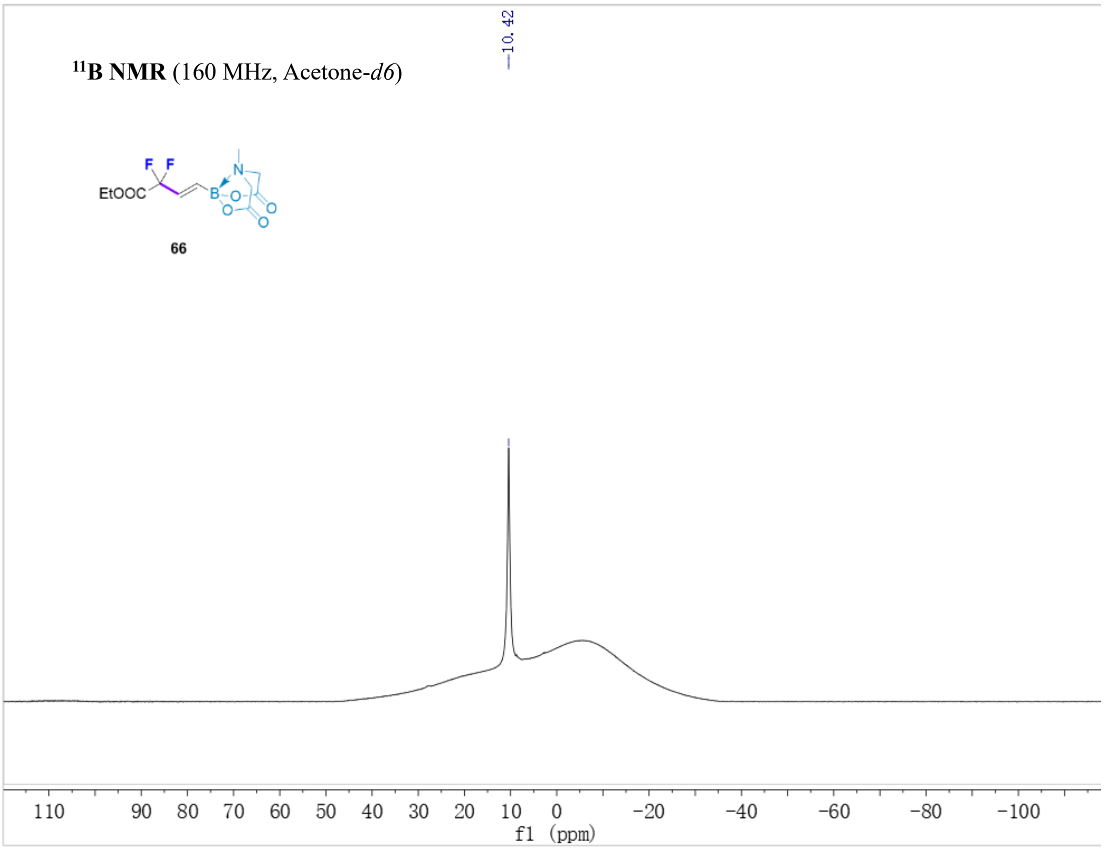




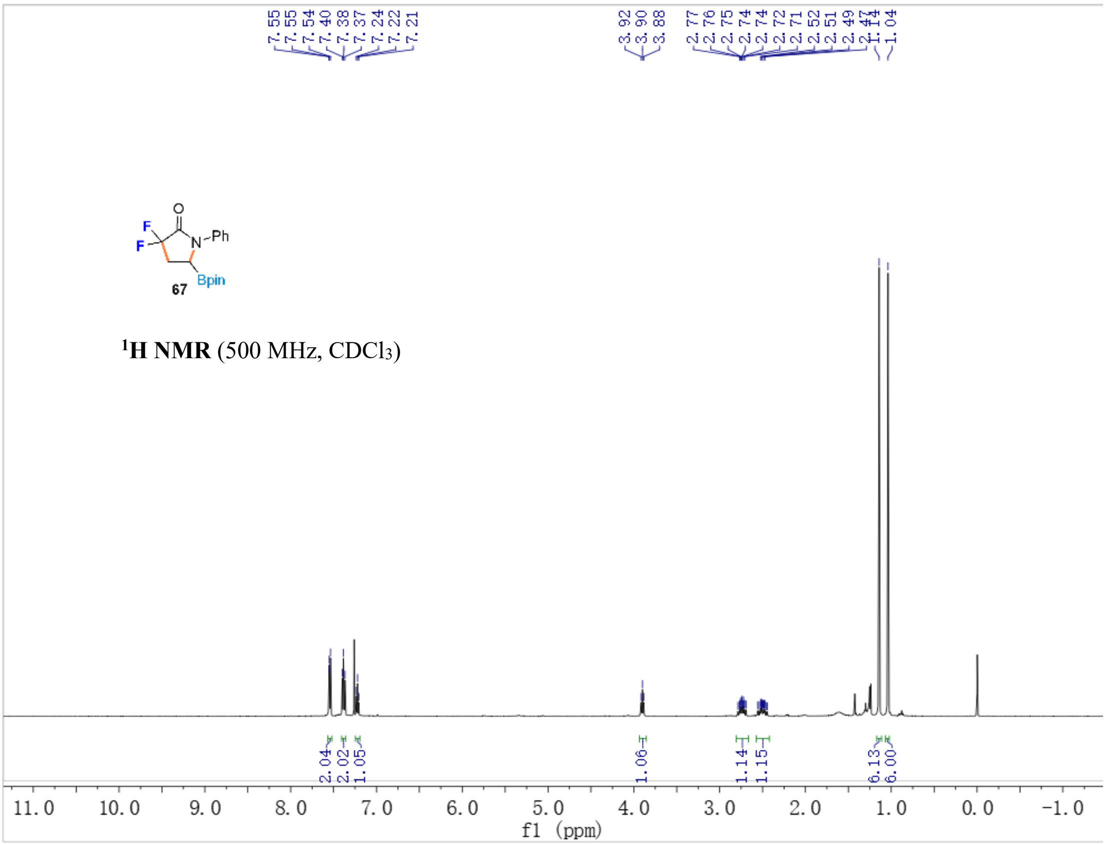
^{19}**F NMR** (471 MHz, Acetone-*d6*)

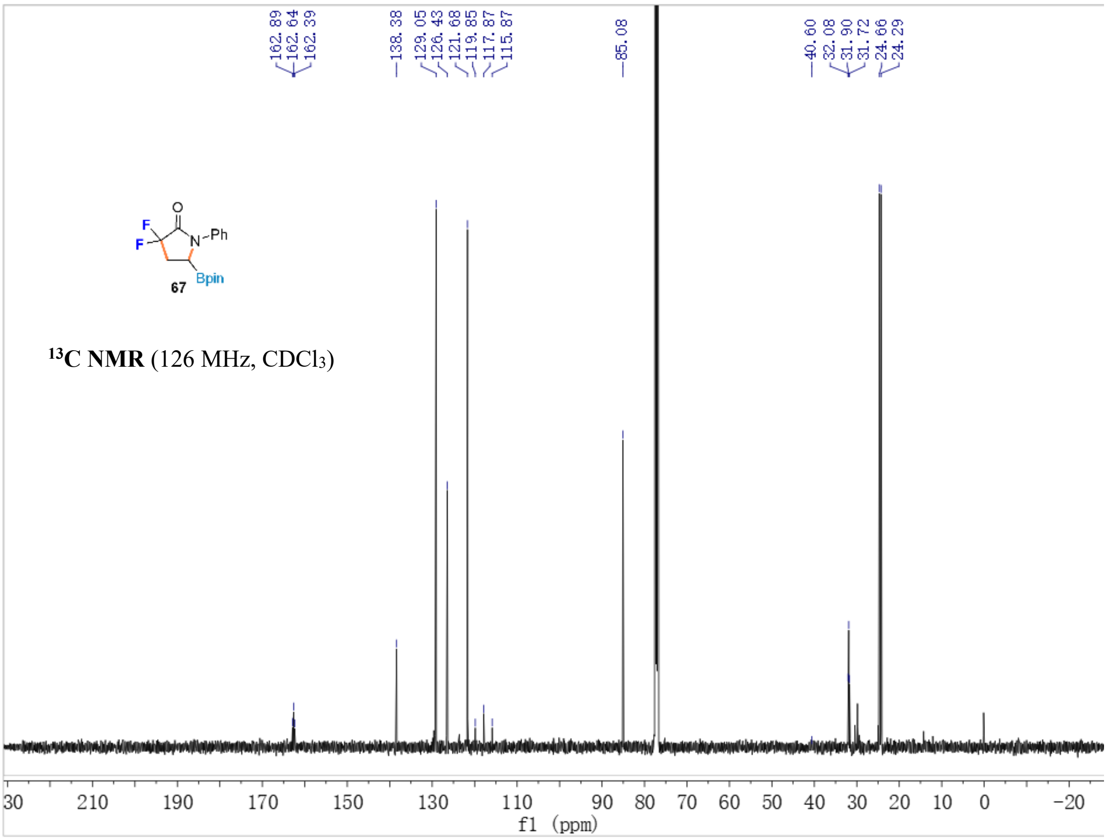


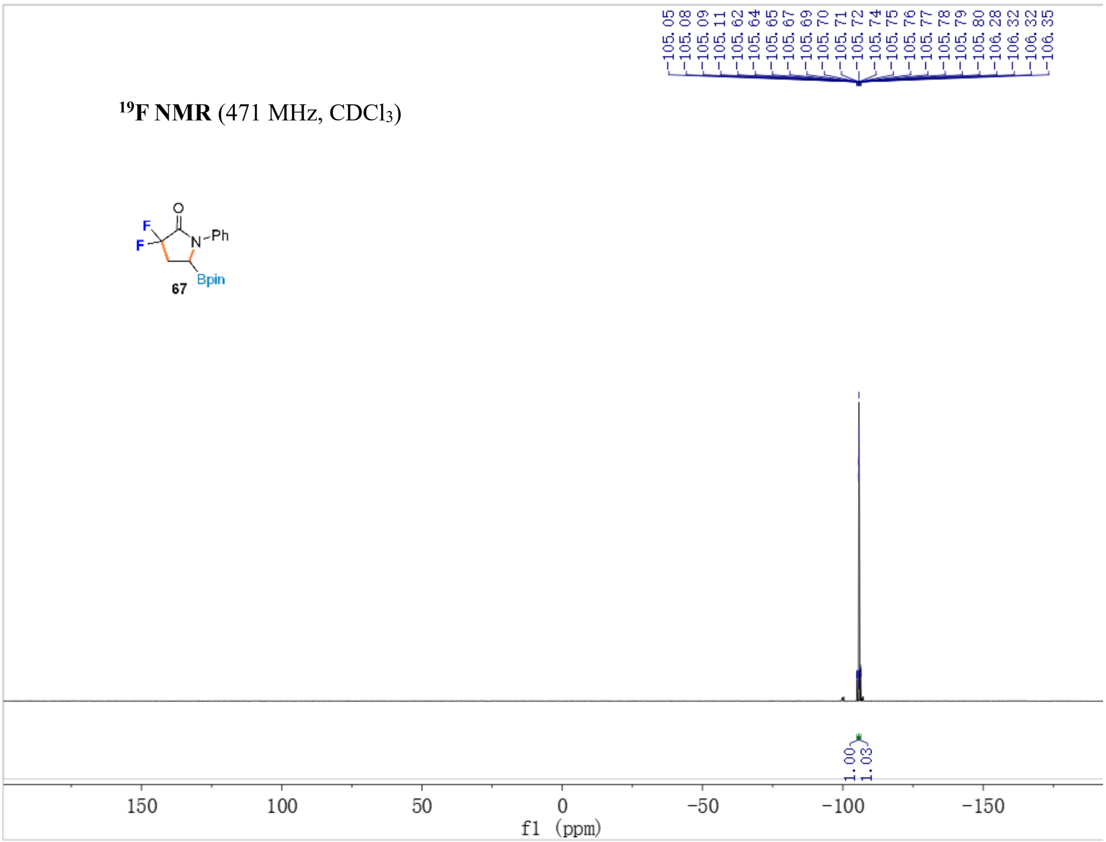
^{11}**B NMR** (160 MHz, Acetone-*d6*)

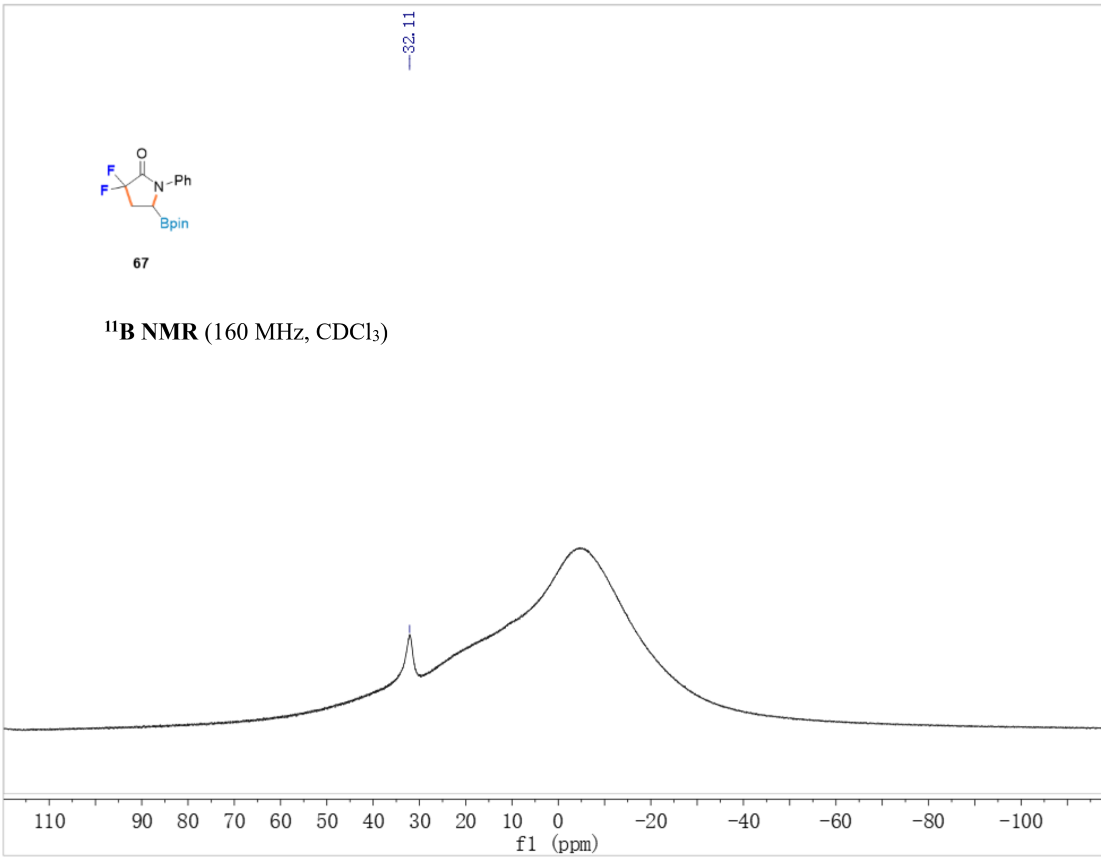


3,3-difluoro-1-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrolidin-2-one (67)

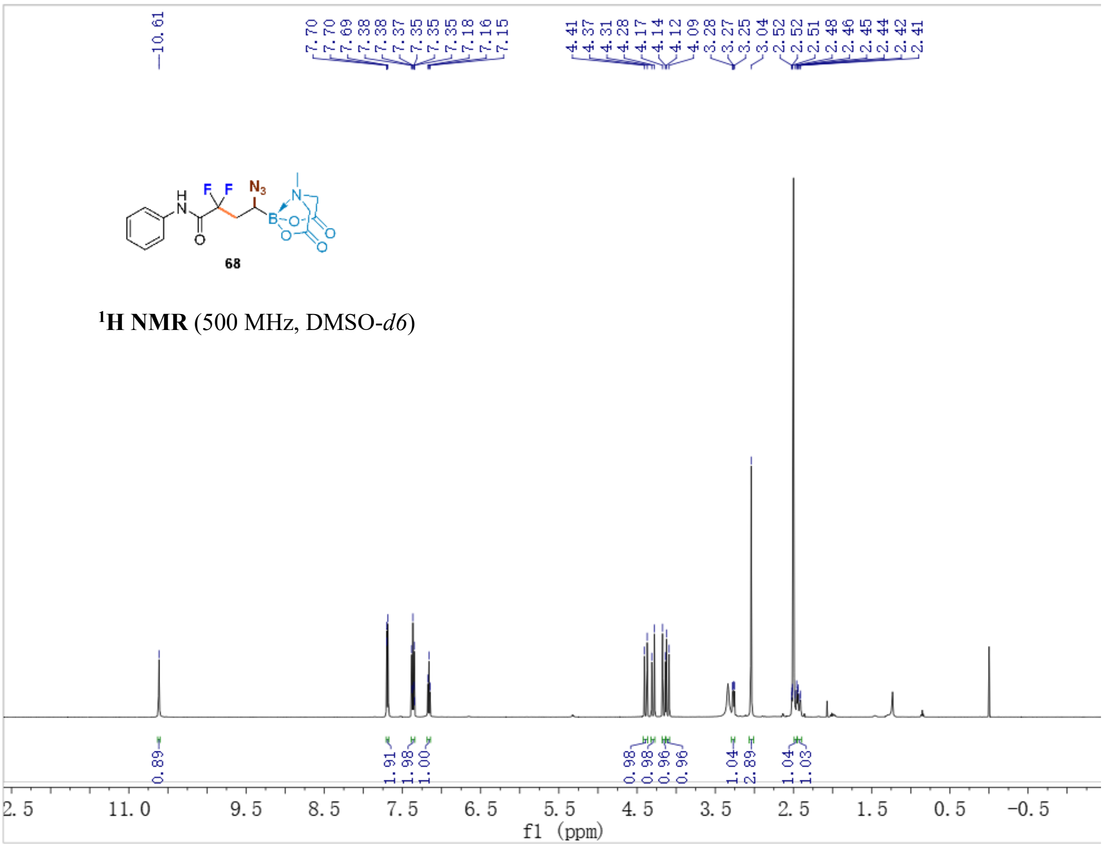


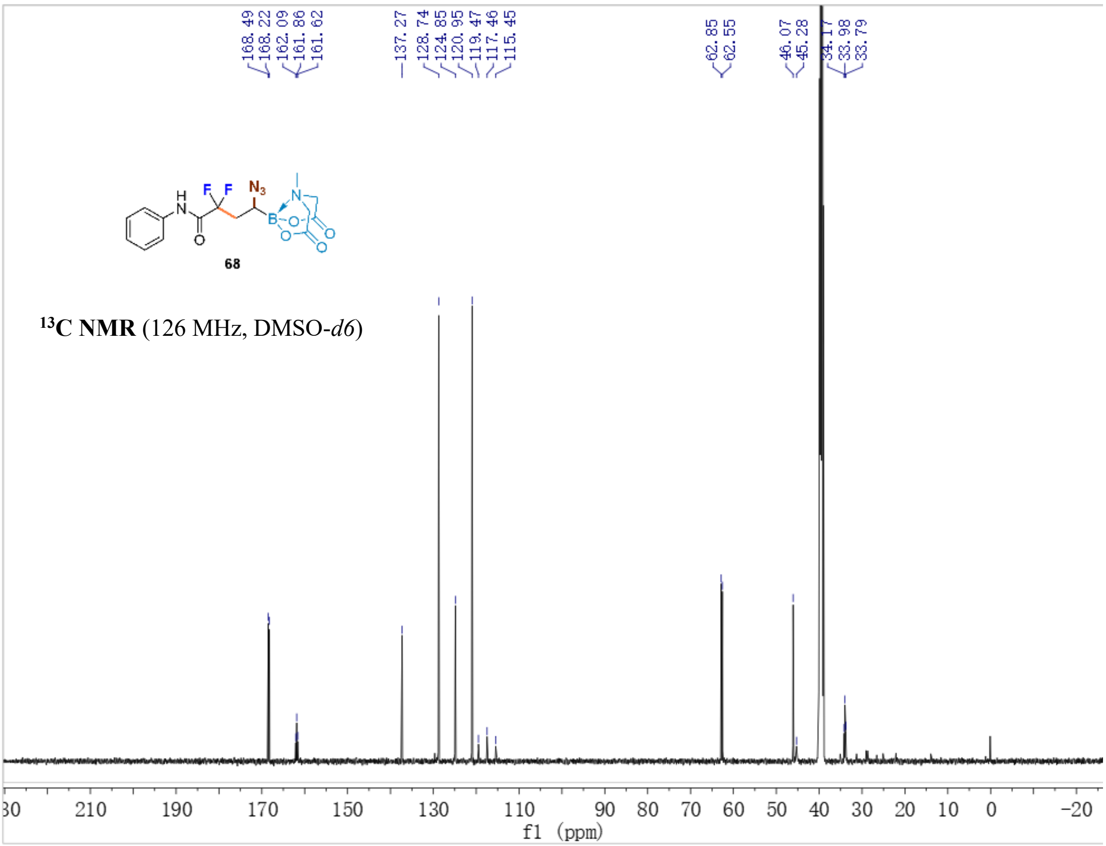


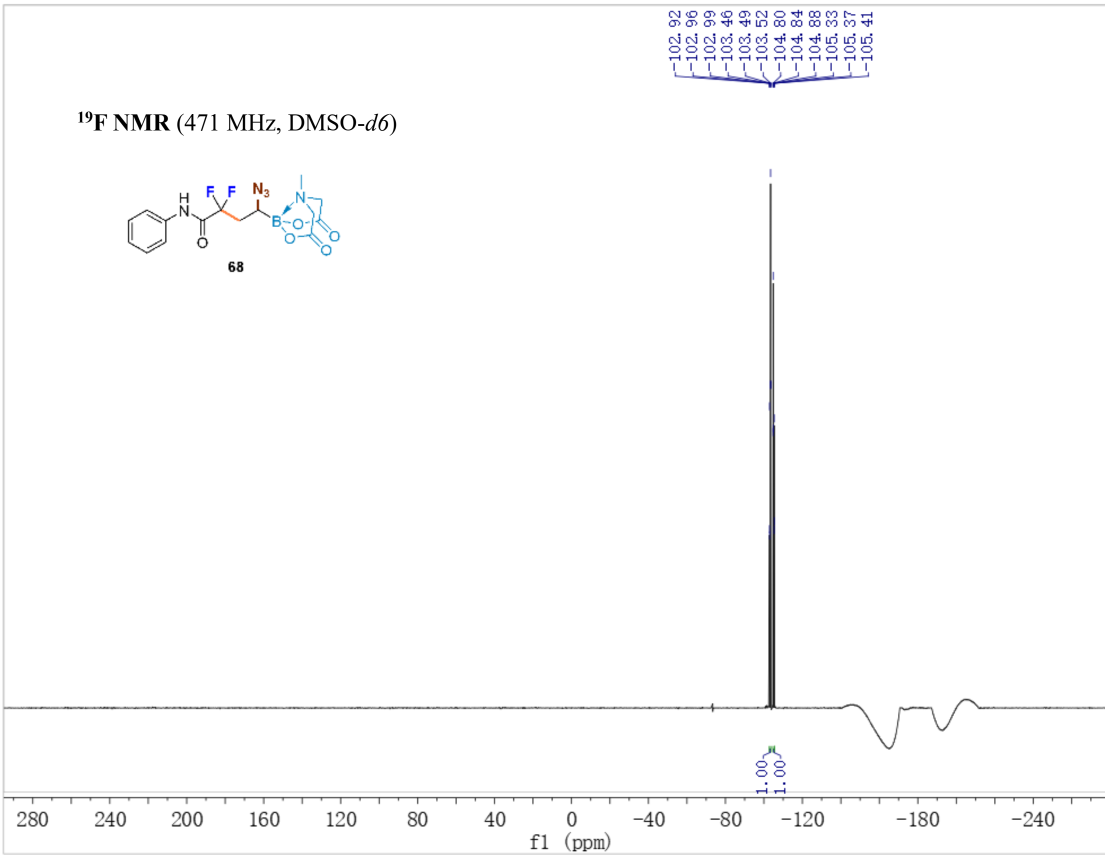

19F NMR (471 MHz, CDCl3)
-105.05
-105.08
-105.09
-105.11
-105.62
-105.64
-105.65
-105.67
-105.69
-105.70
-105.71
-105.72
-105.74
-105.75
-105.76
-105.77
-105.78
-105.79
-105.80
-106.28
-106.32
-106.35
F
F
O
N
Ph
Bpin
67
1.00
1.03
150
100
50
0
-50
-100
-150
f1 (ppm)

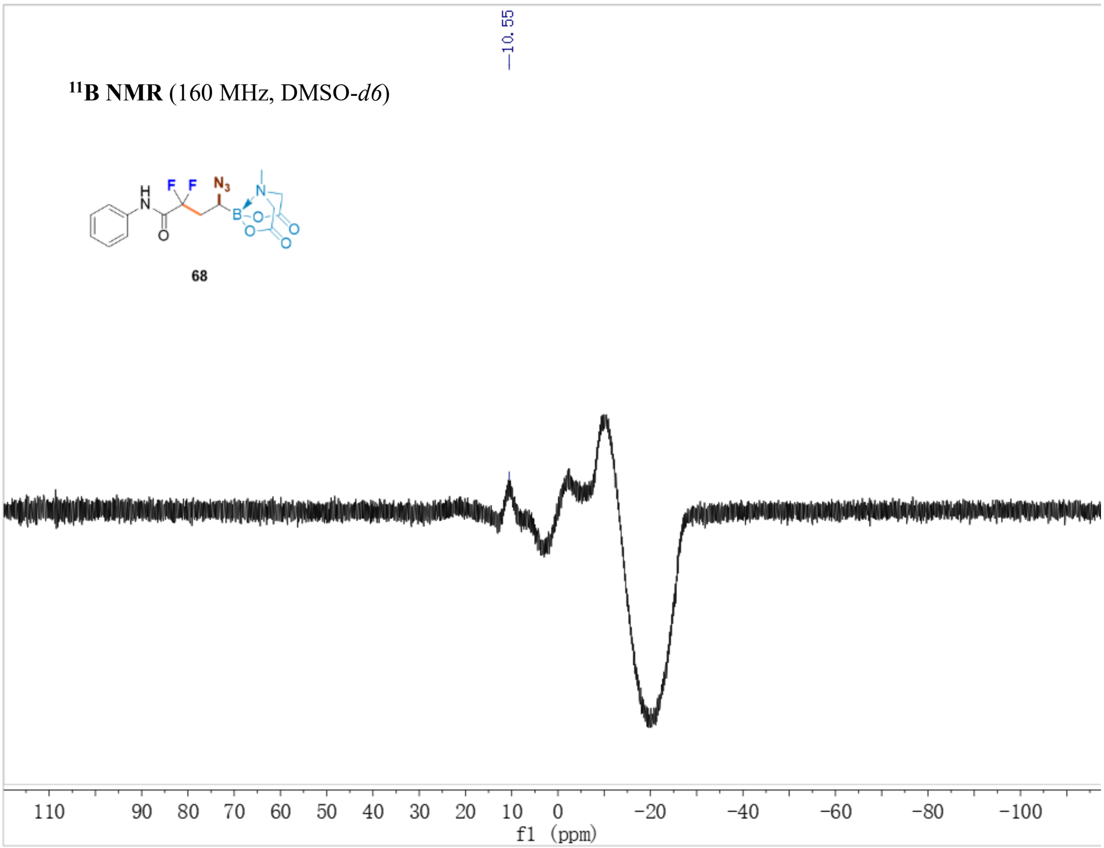

32.11
F
F
O
N
Ph
Bpin
67
11B NMR (160 MHz, CDCl3)
110
90
80
70
60
50
40
30
20
10
0
-20
-40
-60
-80
-100
f1 (ppm)

4-azido-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-*N*-phenylbutanamide (68)

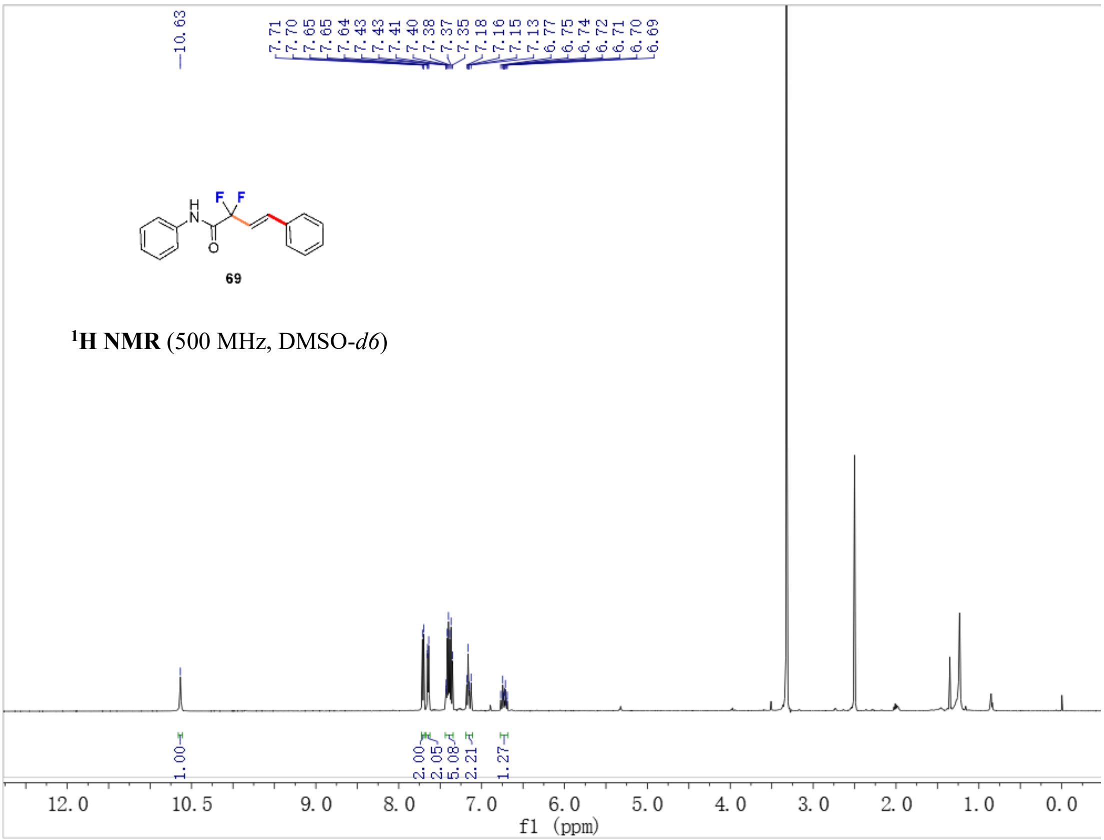


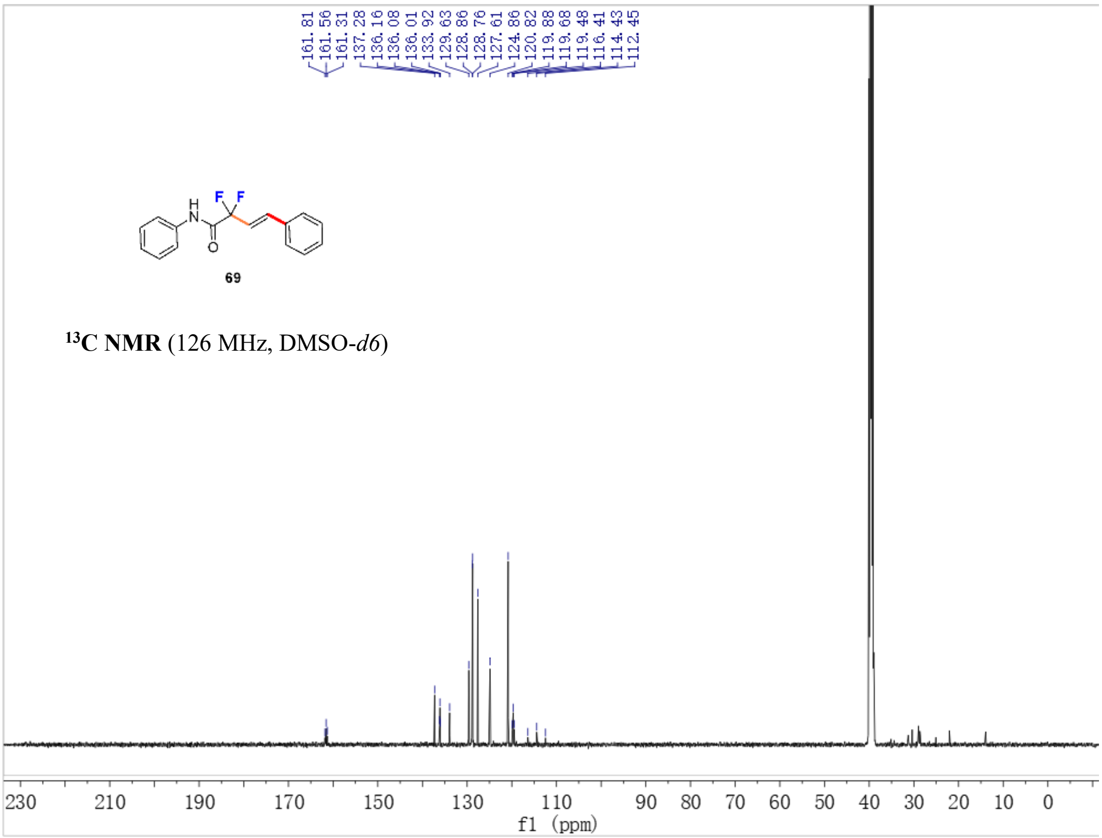


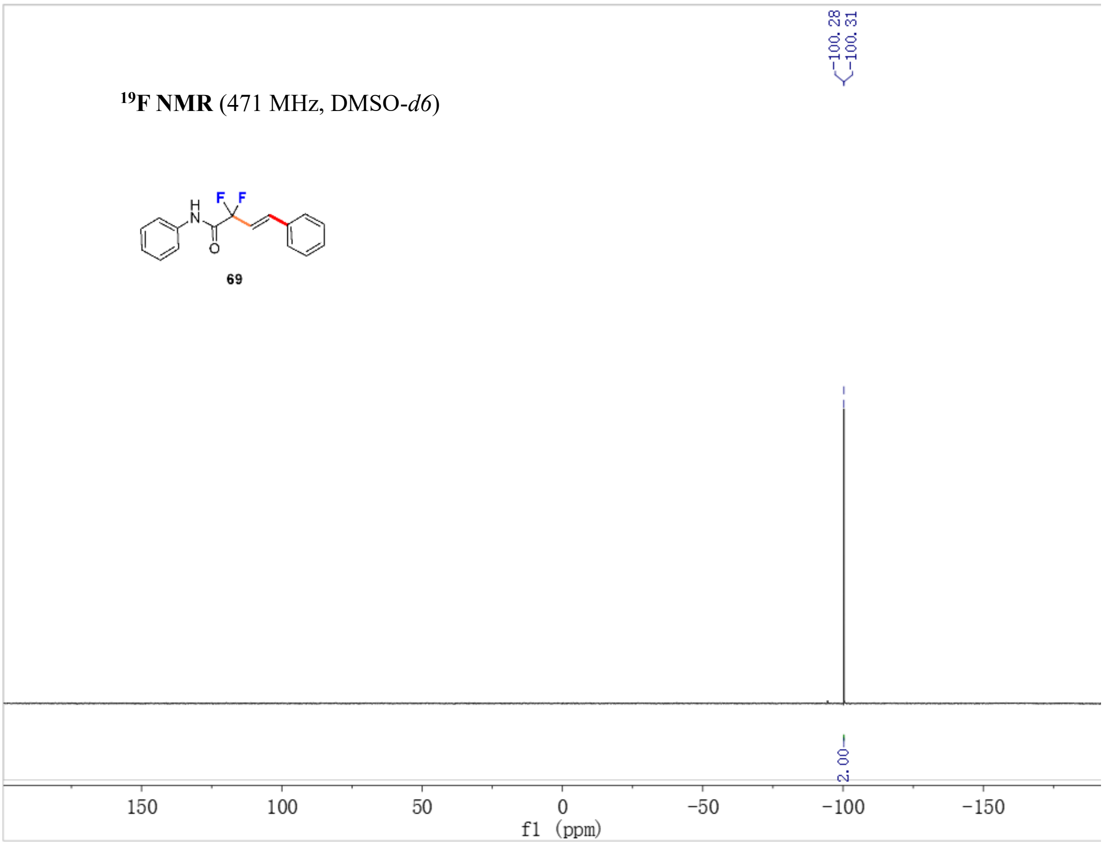




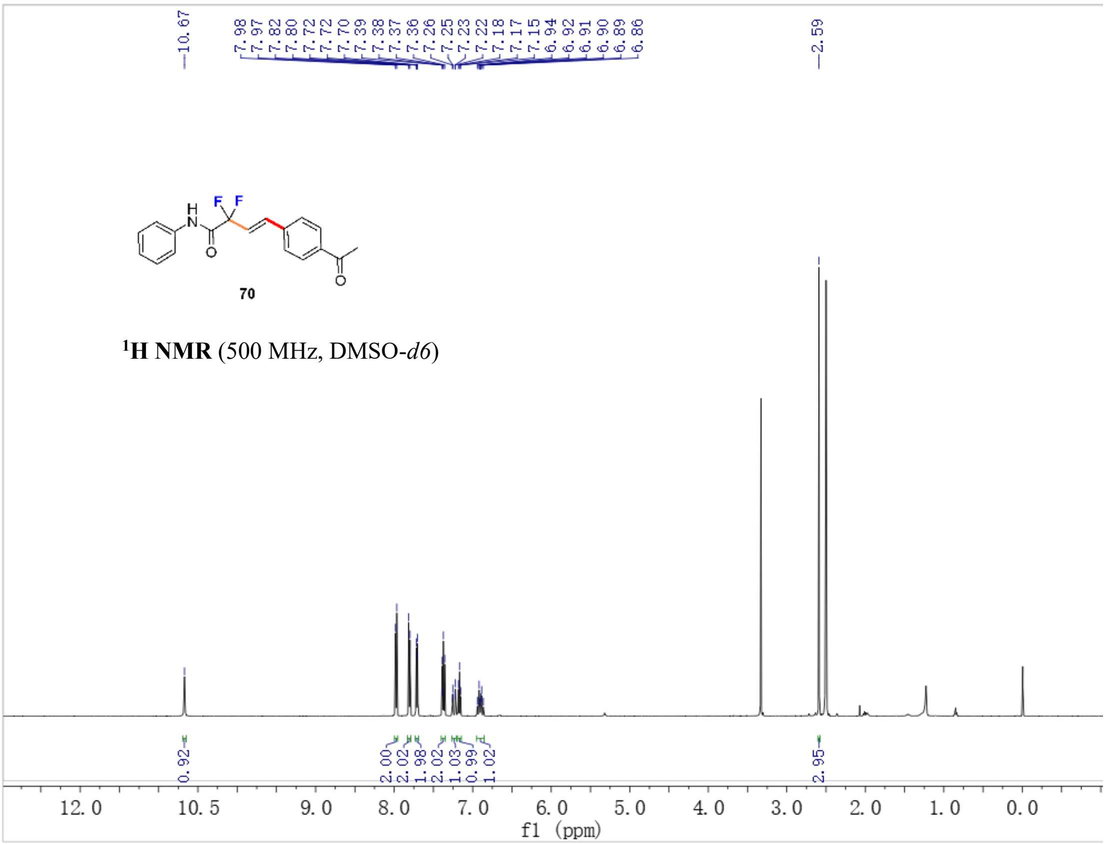
(*E*)-2,2-difluoro-*N*,4-diphenylbut-3-enamide (69)

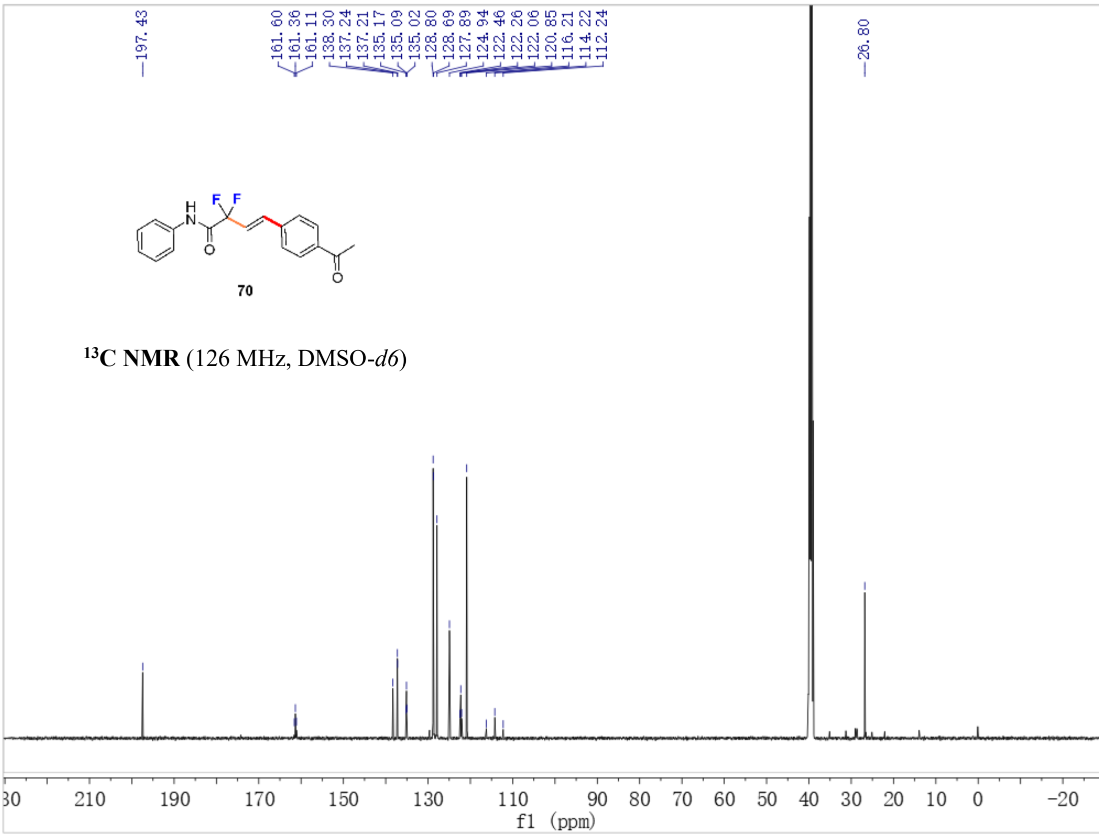

10.63
7.71 7.70 7.65 7.65 7.64 7.43 7.43 7.41 7.40 7.38 7.37 7.35 7.18 7.16 7.15 7.13 6.77 6.75 6.74 6.72 6.71 6.70 6.69
69
^{1}H NMR (500 MHz, DMSO-d6)
1.00 2.00 2.05 5.08 2.21 1.27
12.0 10.5 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

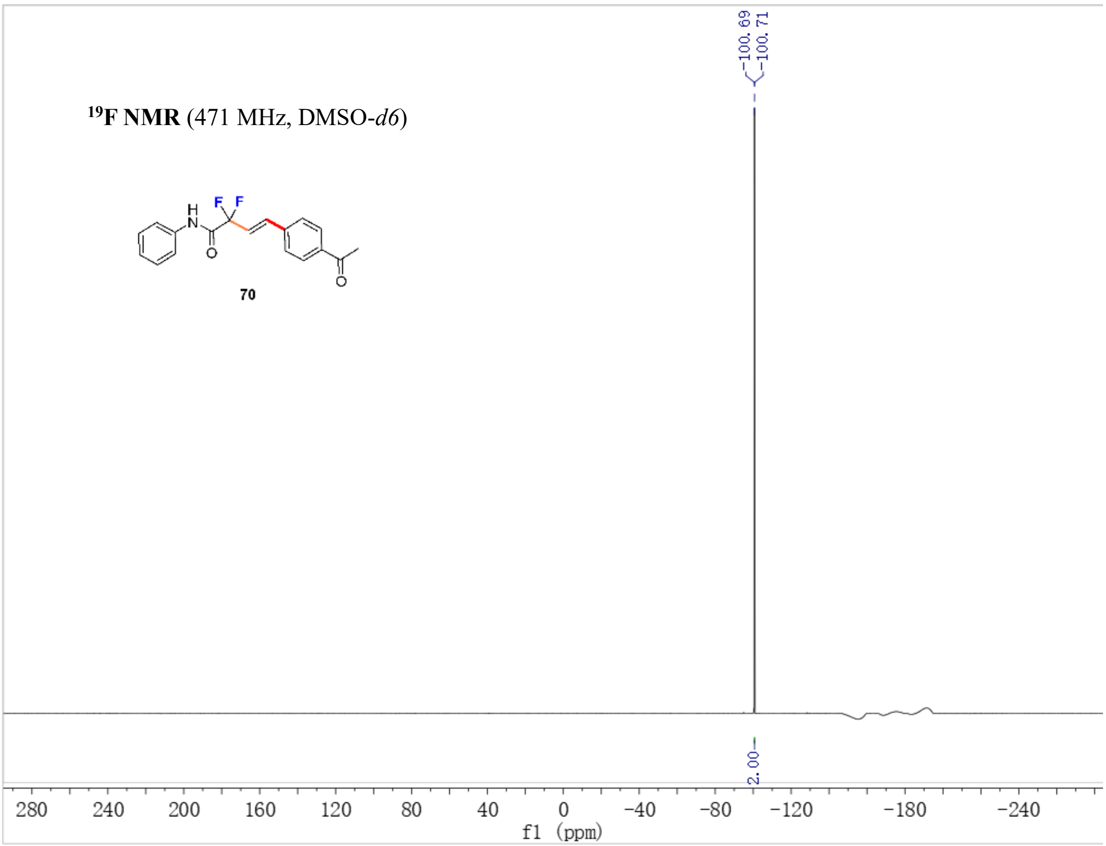

161.81 161.56 161.31 137.28 136.16 136.08 136.01 133.92 129.63 128.86 128.76 127.61 124.86 120.82 119.88 119.68 119.48 116.41 114.43 112.45
69
^{13}C NMR (126 MHz, DMSO-d6)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



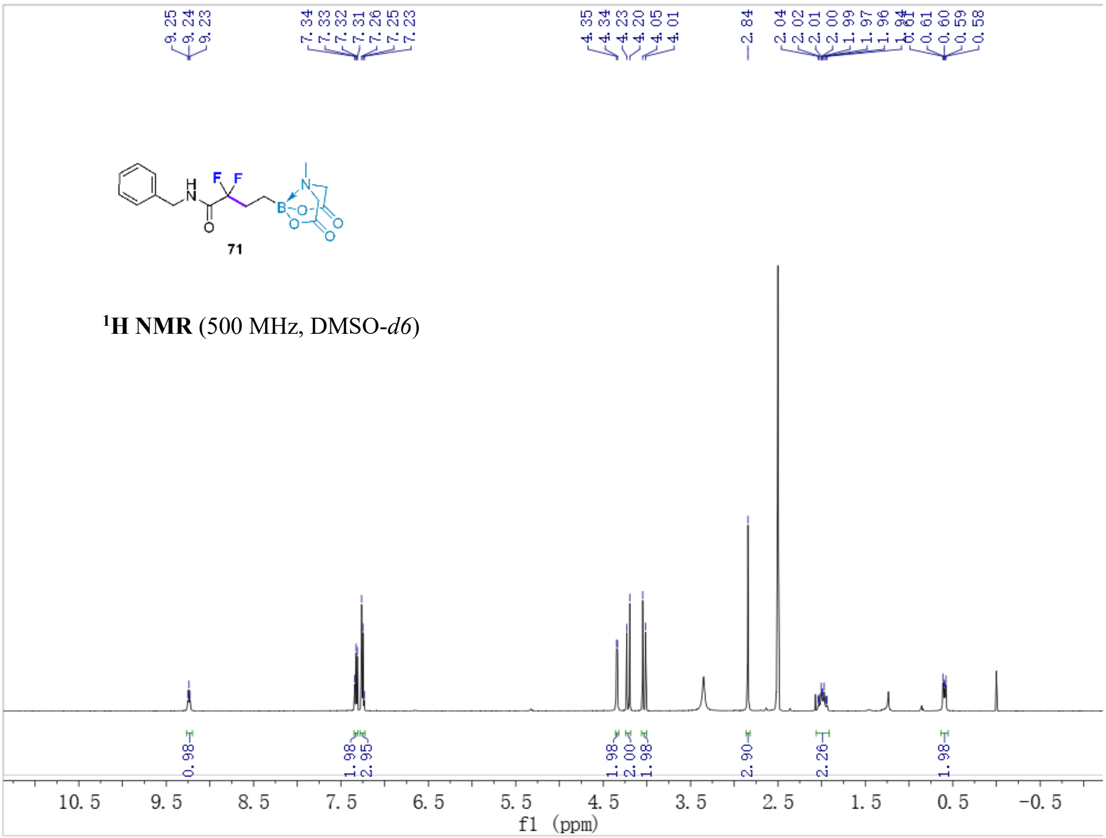
(*E*)-4-(4-acetylphenyl)-2,2-difluoro-*N*-phenylbut-3-enamide (70)

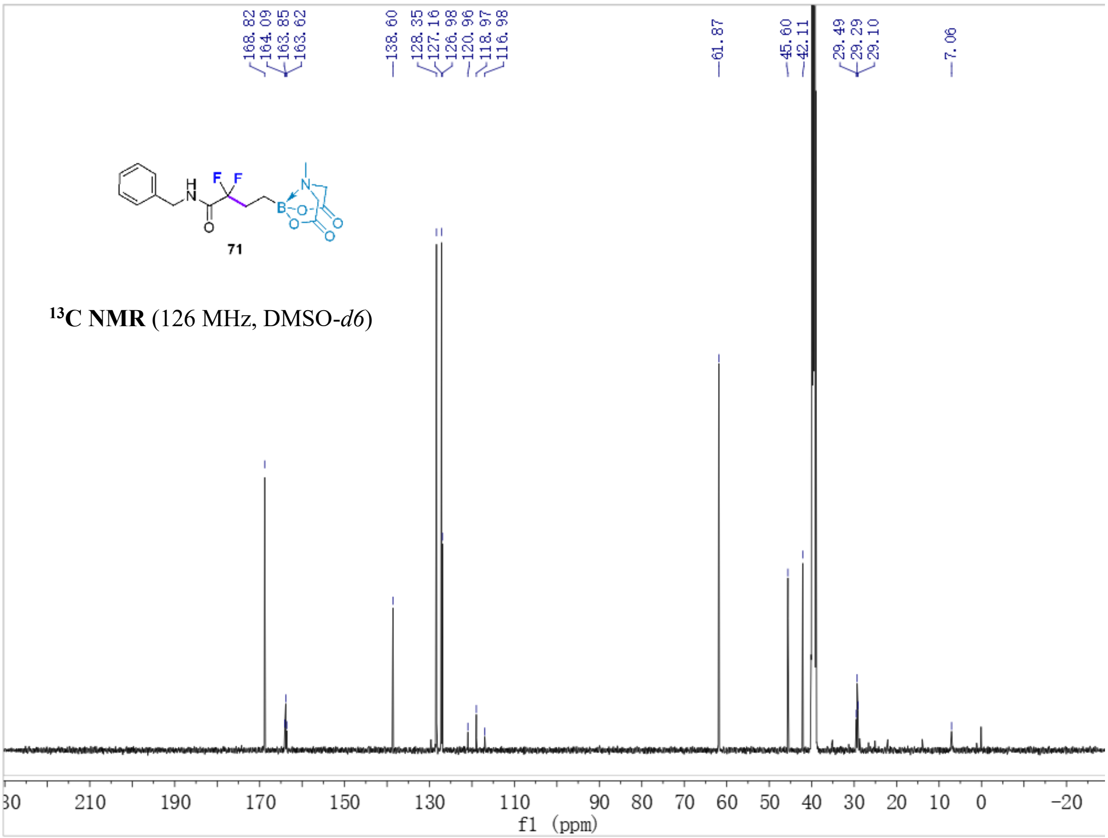



197.43
161.60
161.36
161.11
138.30
137.24
137.21
135.17
135.09
135.02
128.80
128.69
127.89
124.94
122.46
122.26
122.06
120.85
116.21
114.22
112.24
26.80
70
13C NMR (126 MHz, DMSO-d6)
f1 (ppm)

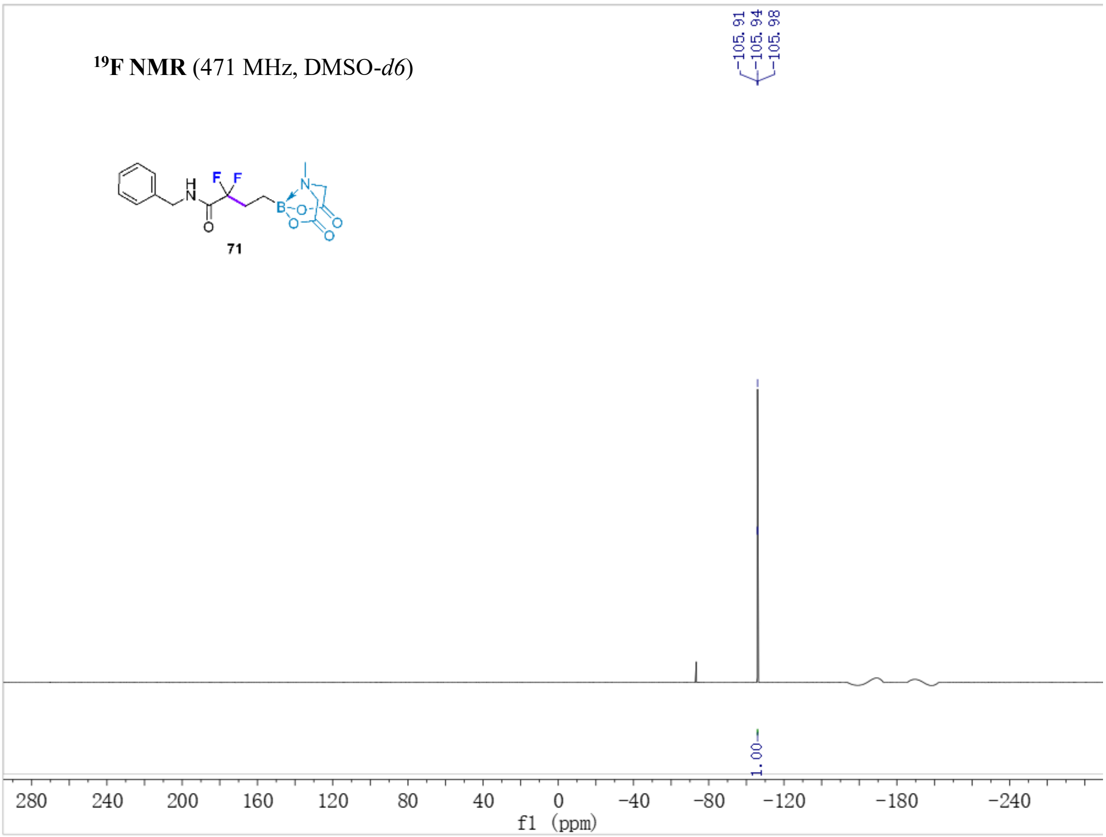

-100.69
-100.71
19F NMR (471 MHz, DMSO-d6)
70
2.00
f1 (ppm)

N-benzyl-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (71)

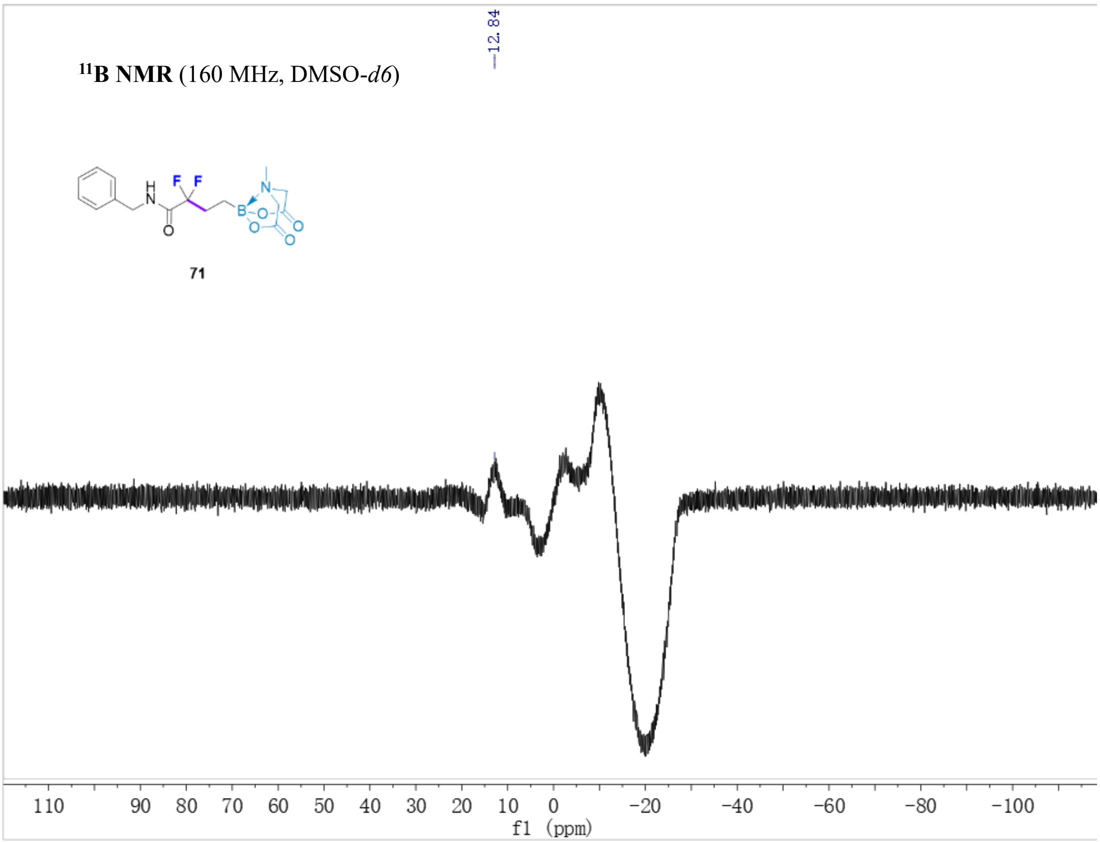




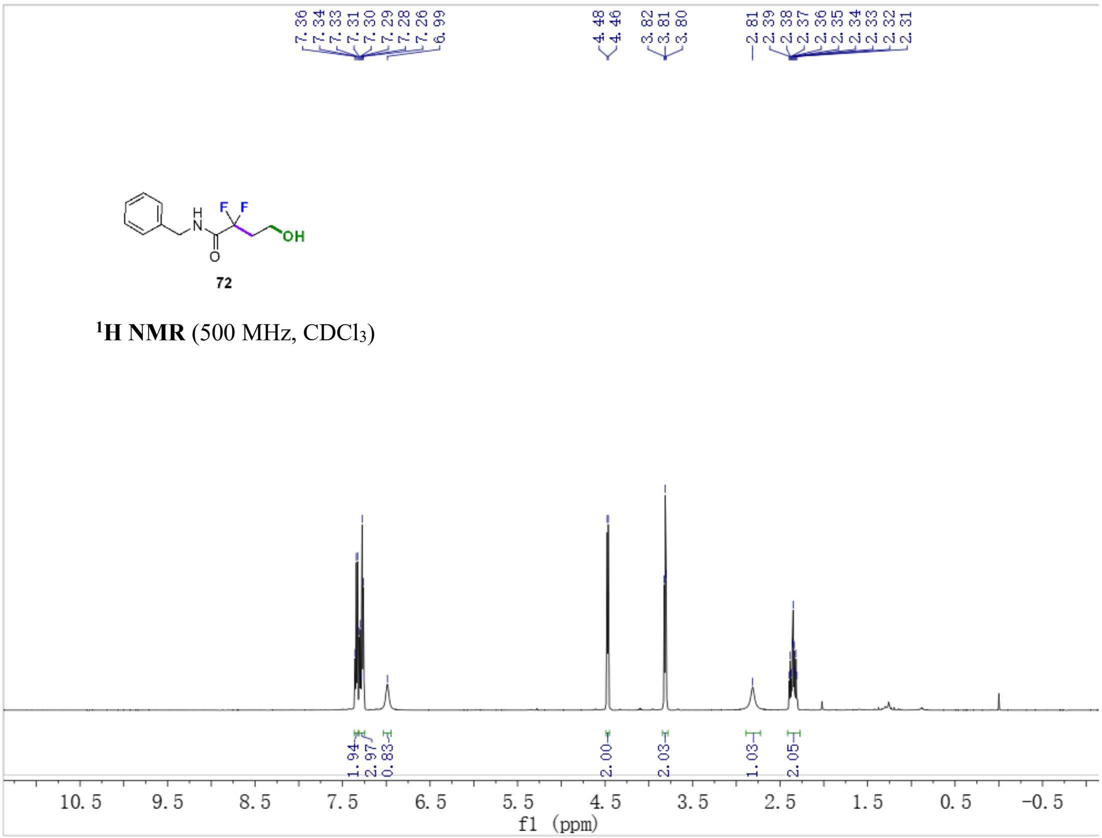
^{19}F NMR (471 MHz, DMSO-*d6*)

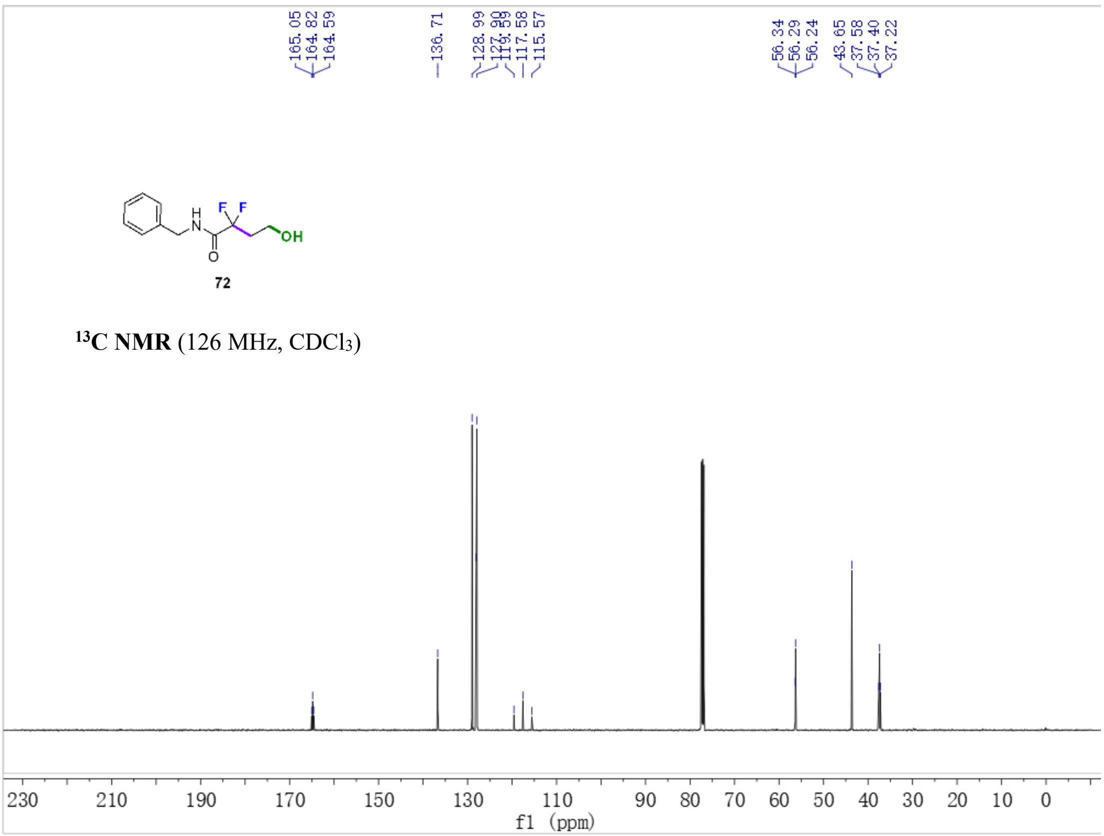


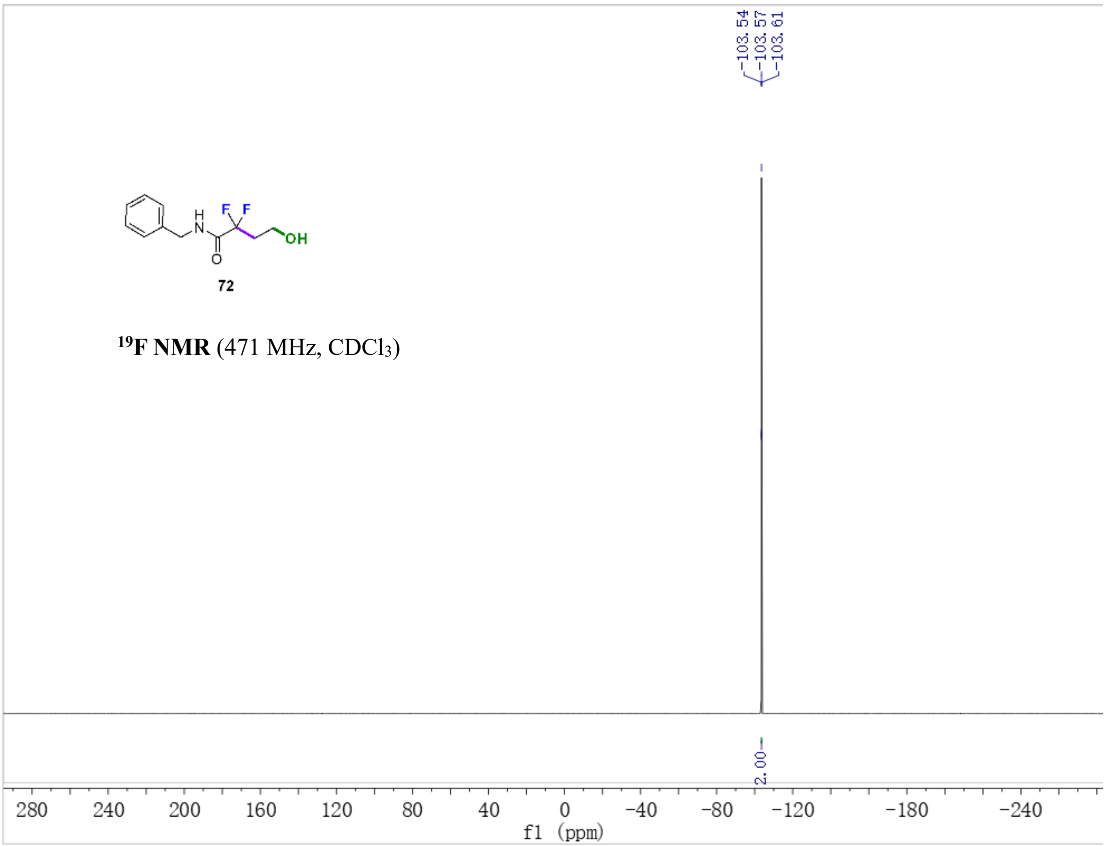
^{11}B NMR (160 MHz, DMSO-*d6*)



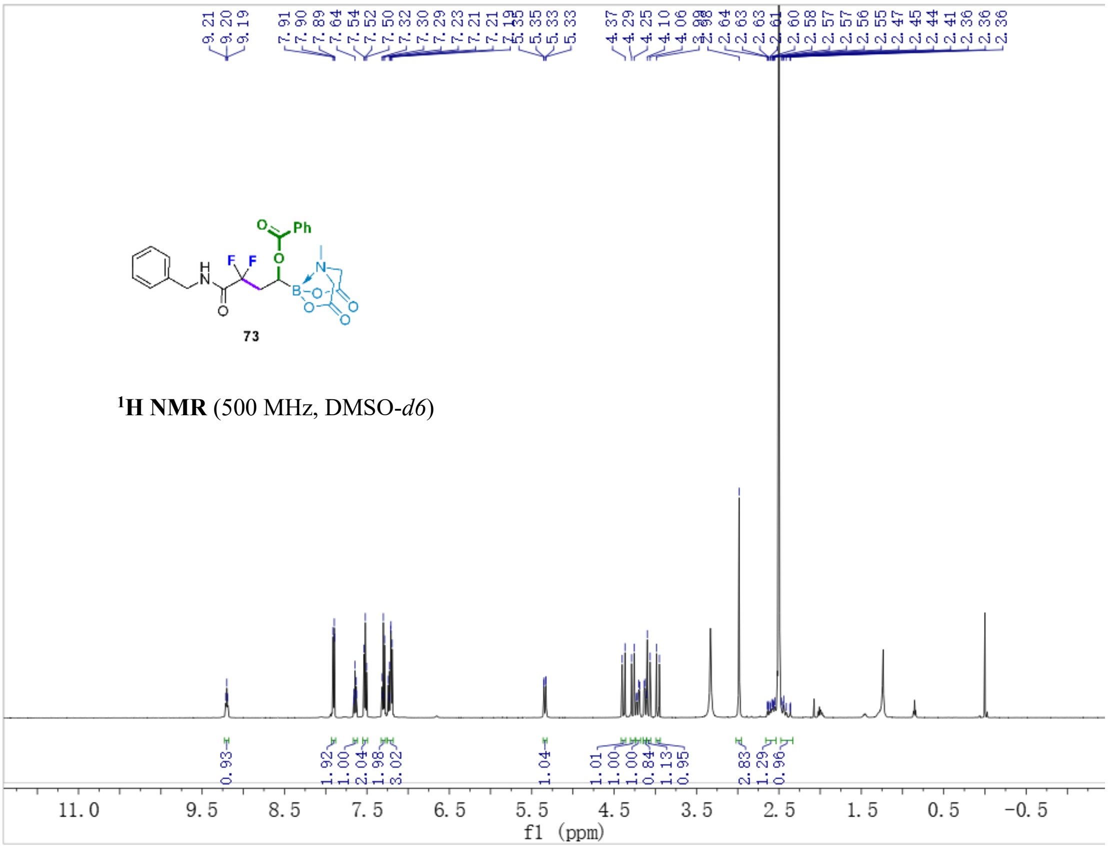
N-benzyl-2,2-difluoro-4-hydroxybutanamide (72)

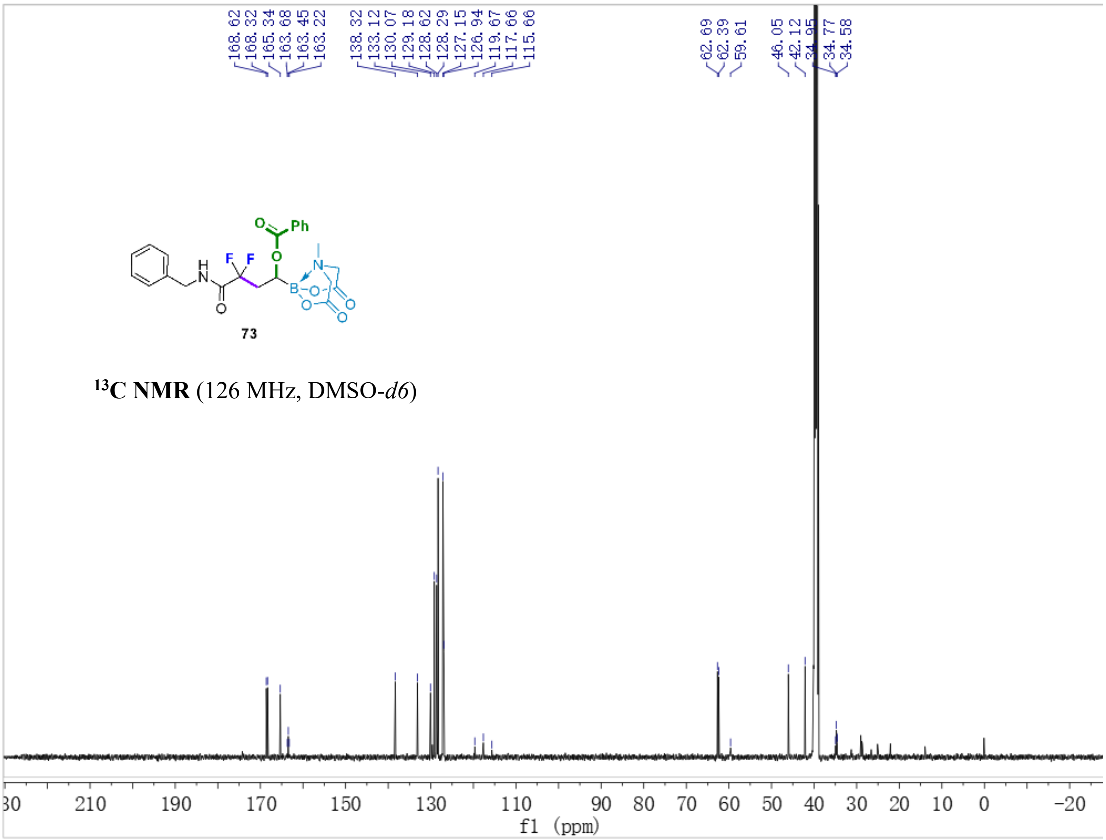




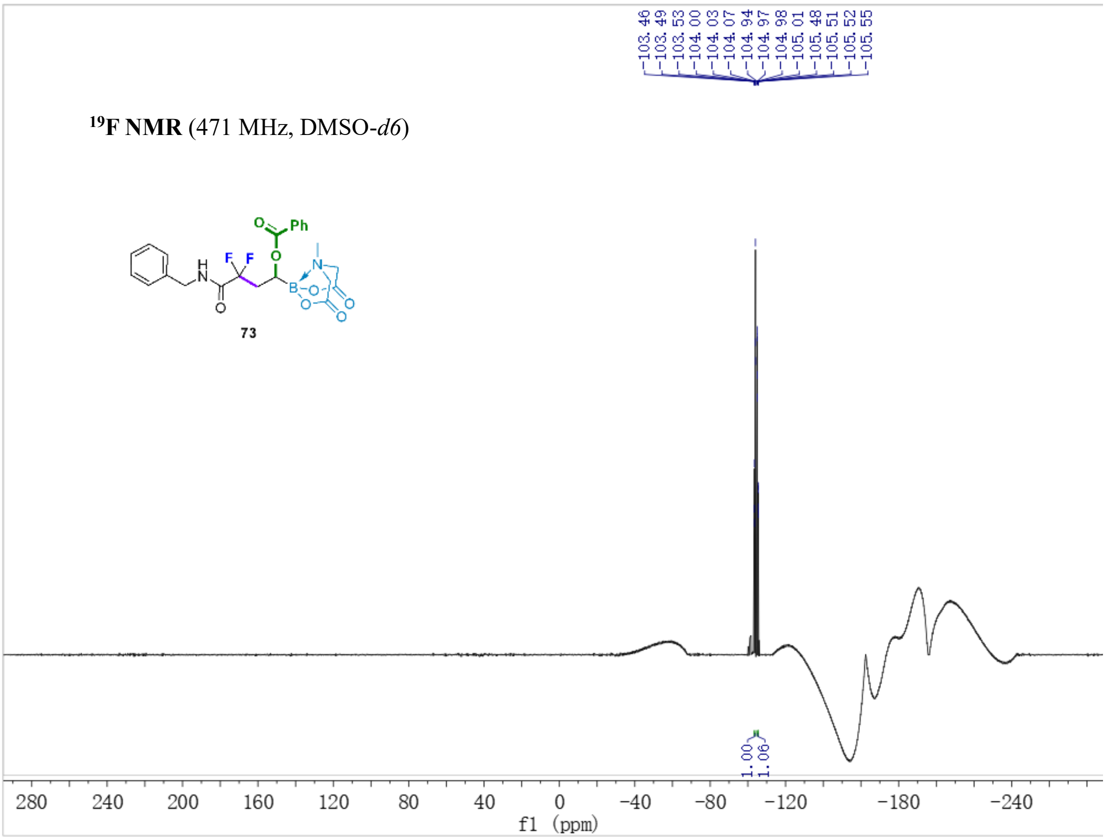


4-(benzylamino)-3,3-difluoro-1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-4-oxobutyl benzoate (73)

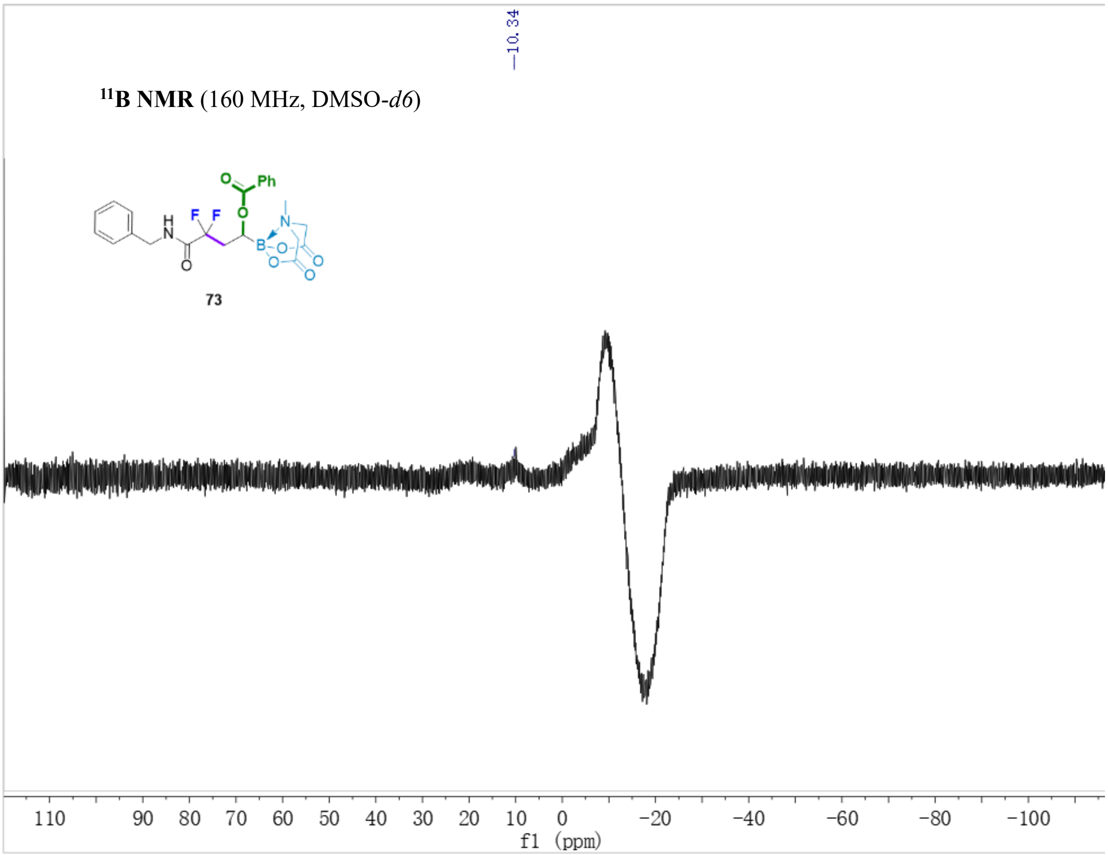




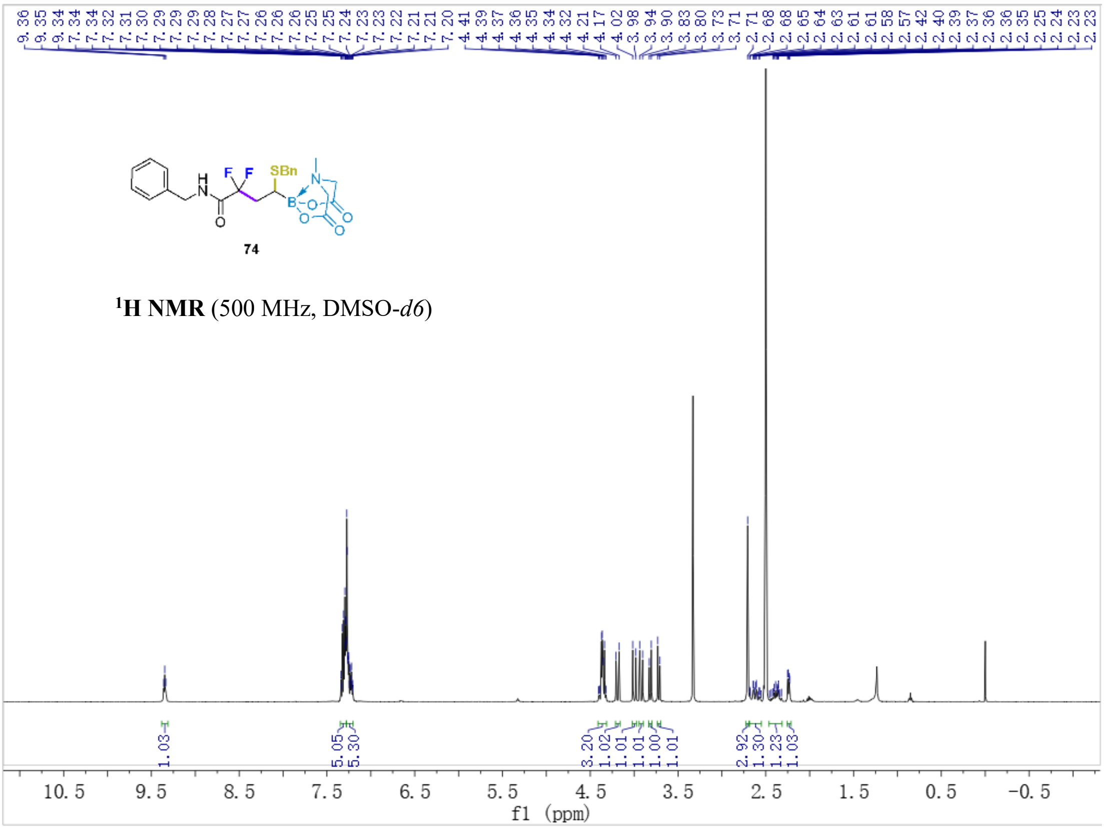
^{13}C NMR (126 MHz, DMSO-*d6*)

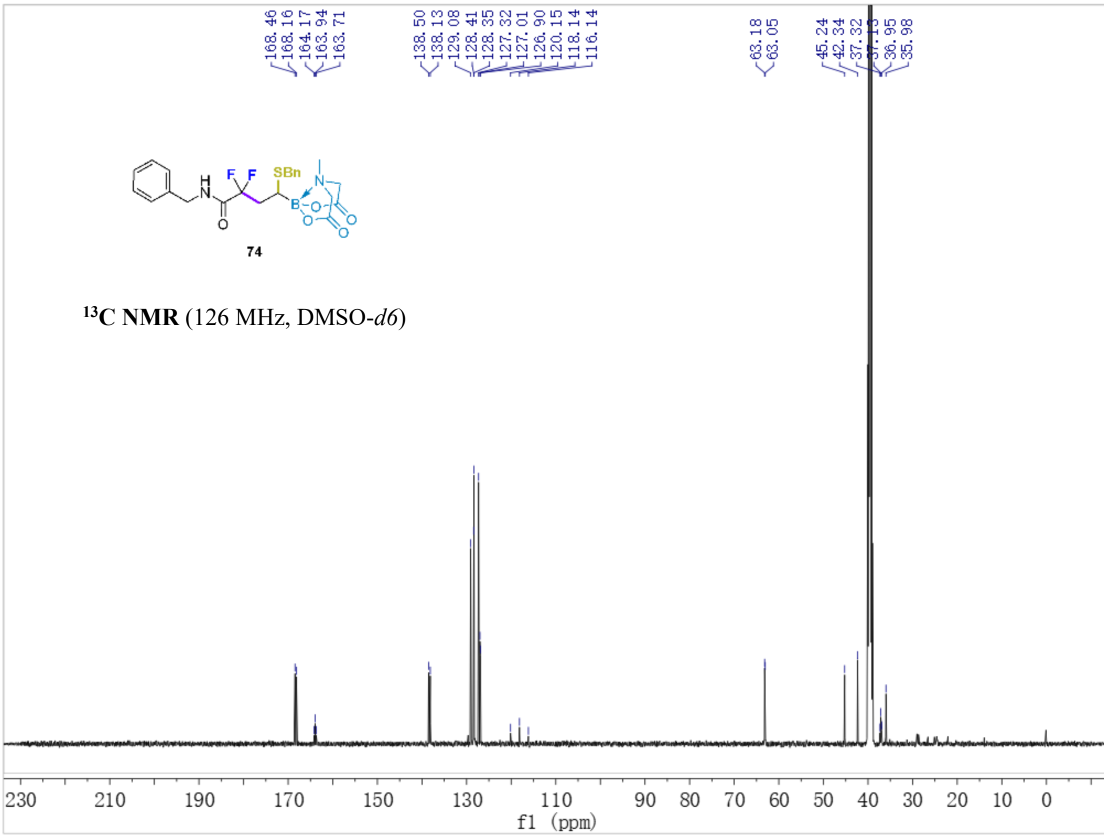


^{19}F NMR (471 MHz, DMSO-*d6*)

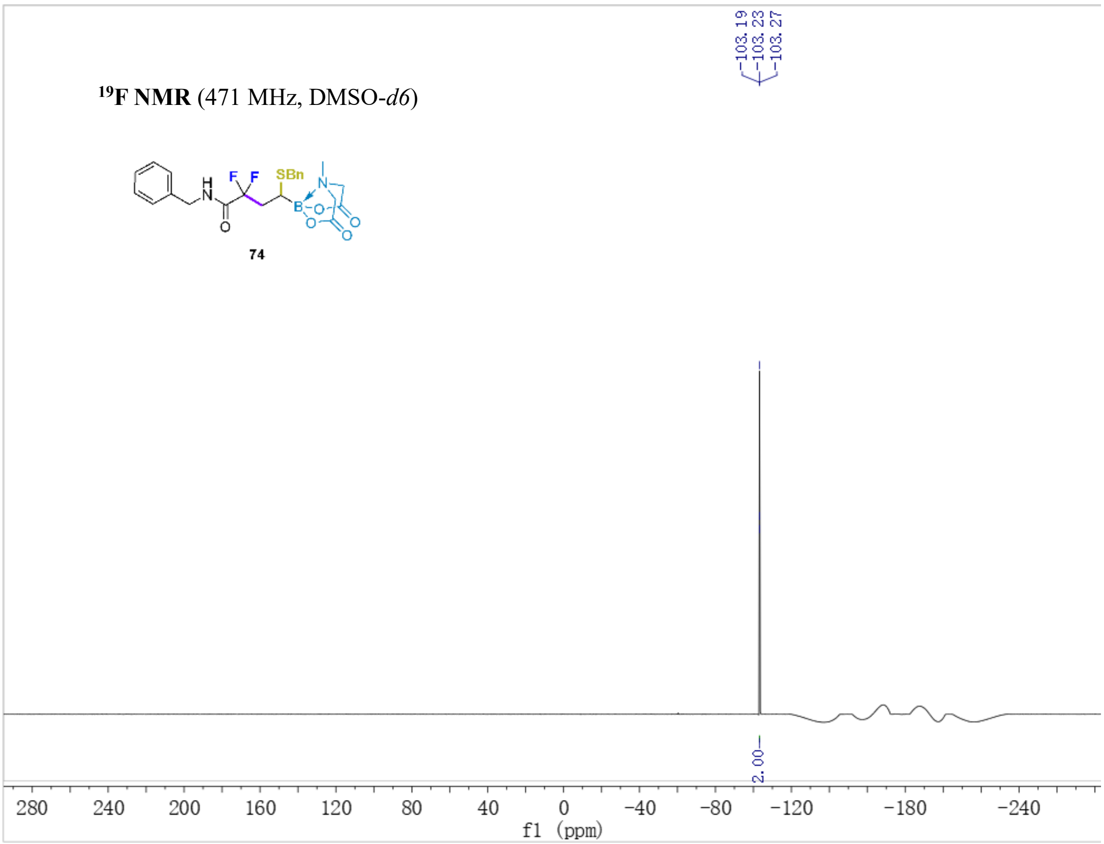


N-benzyl-4-(benzylthio)-2,2-difluoro-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butanamide (74)

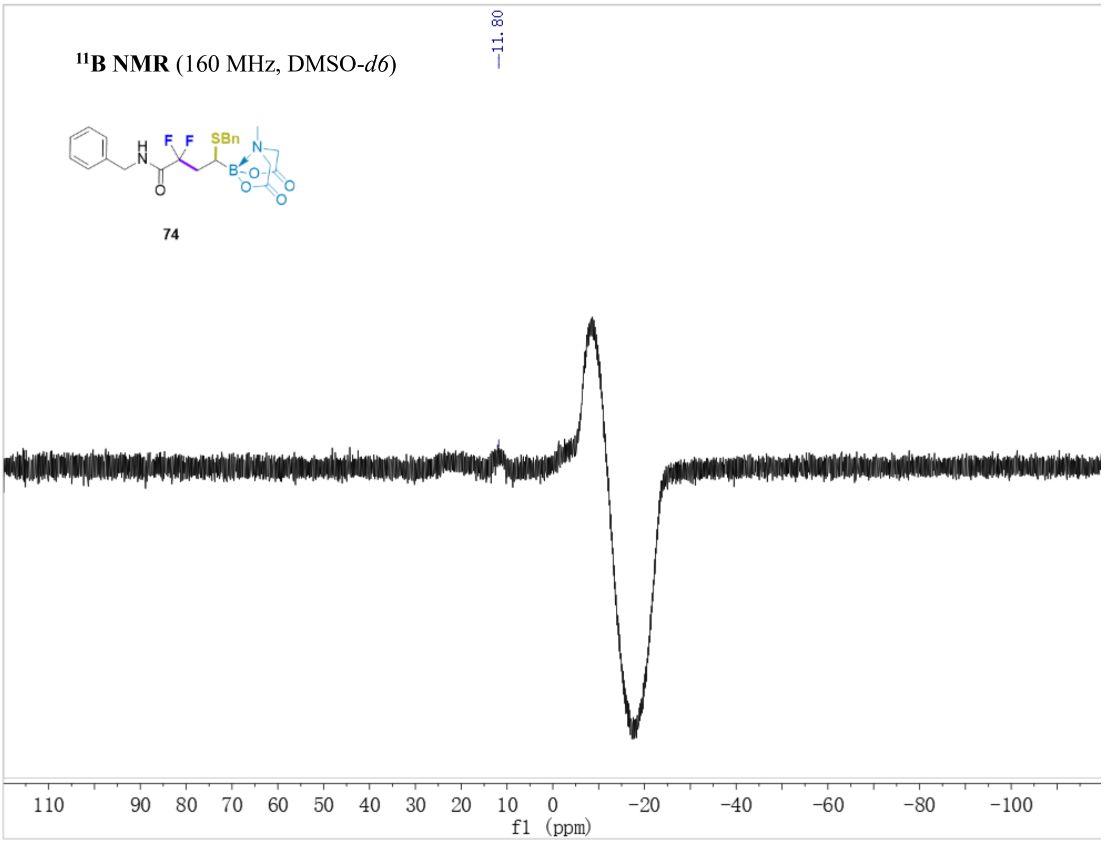




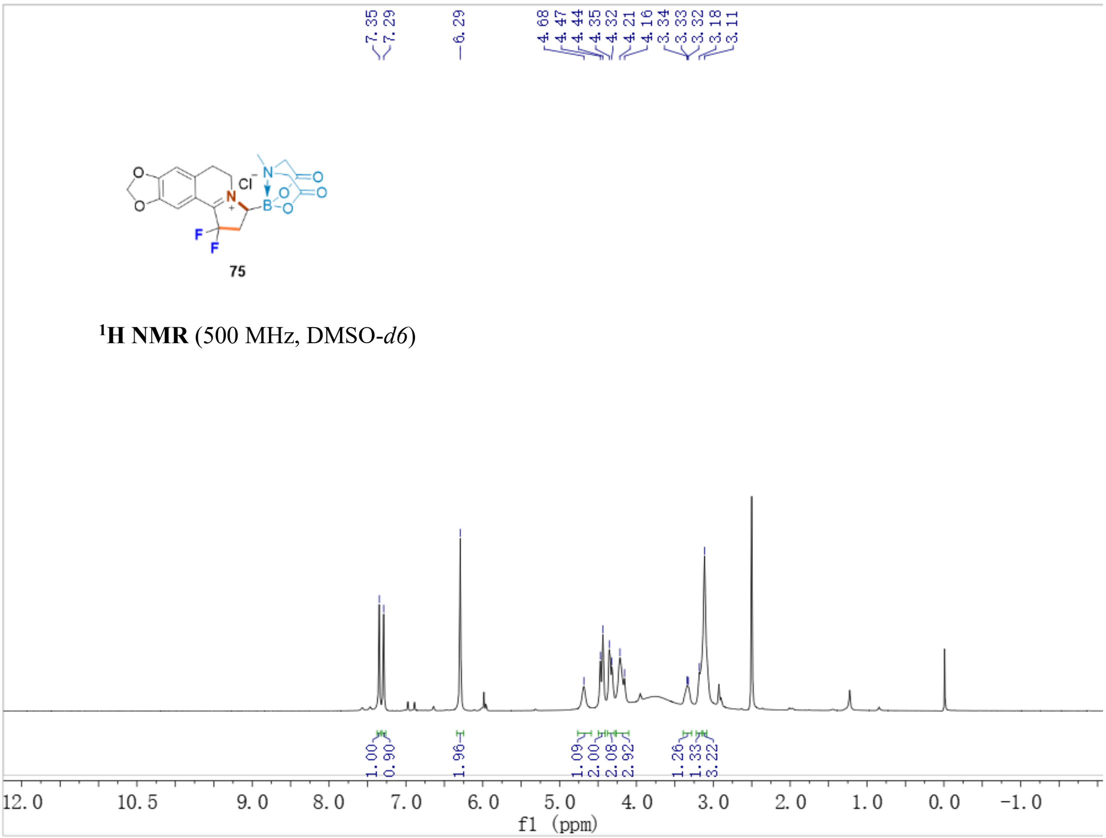
168.46
168.16
164.17
163.94
163.71
138.50
138.13
129.08
128.41
128.35
127.32
127.01
126.90
120.15
118.14
116.14
63.18
63.05
45.24
42.34
37.32
37.13
36.95
35.98
74
13C NMR (126 MHz, DMSO-d6)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

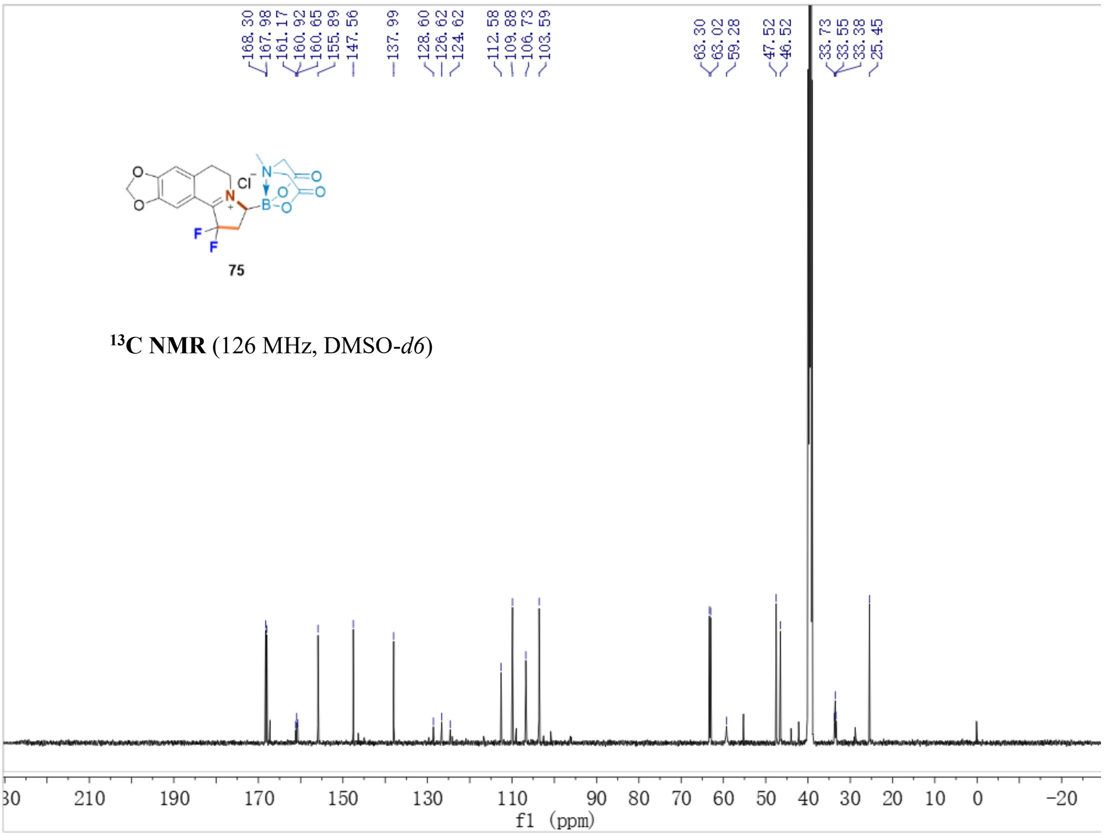


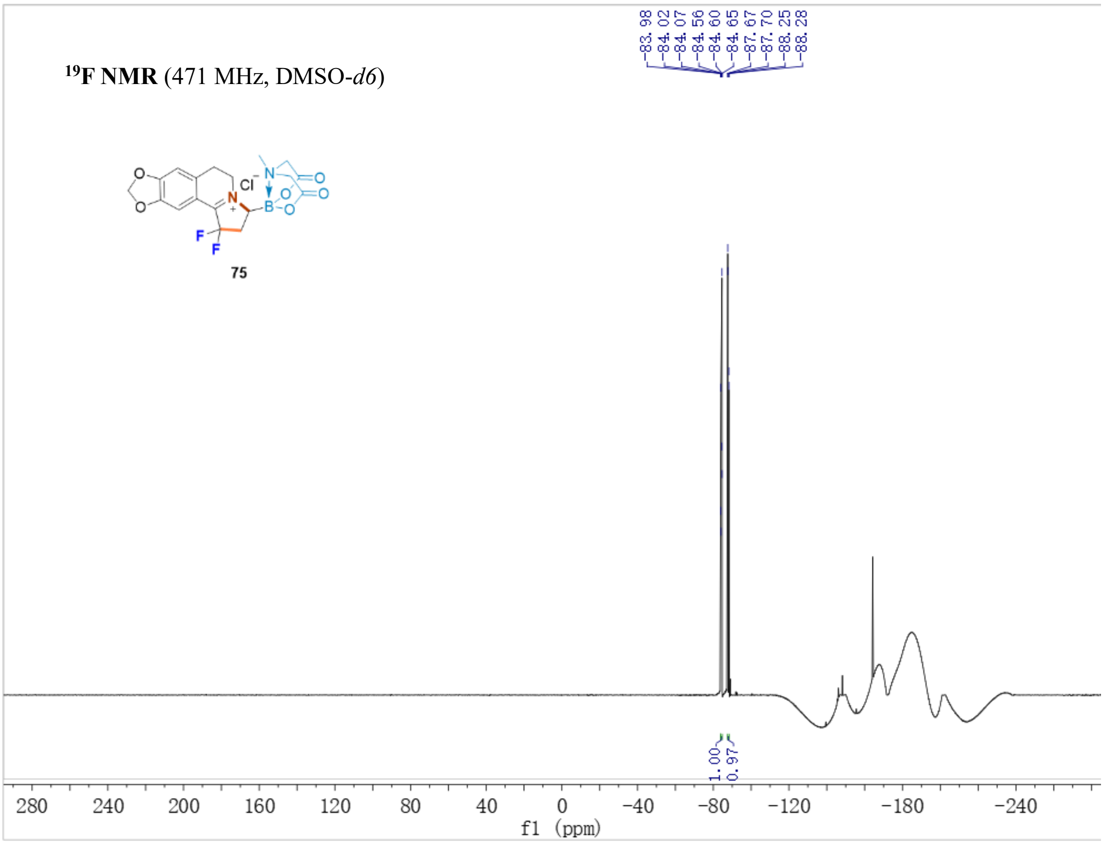
-103.19
-103.23
-103.27
19F NMR (471 MHz, DMSO-d6)
74
2.00
280
240
200
160
120
80
40
0
-40
-80
-120
-180
-240
f1 (ppm)

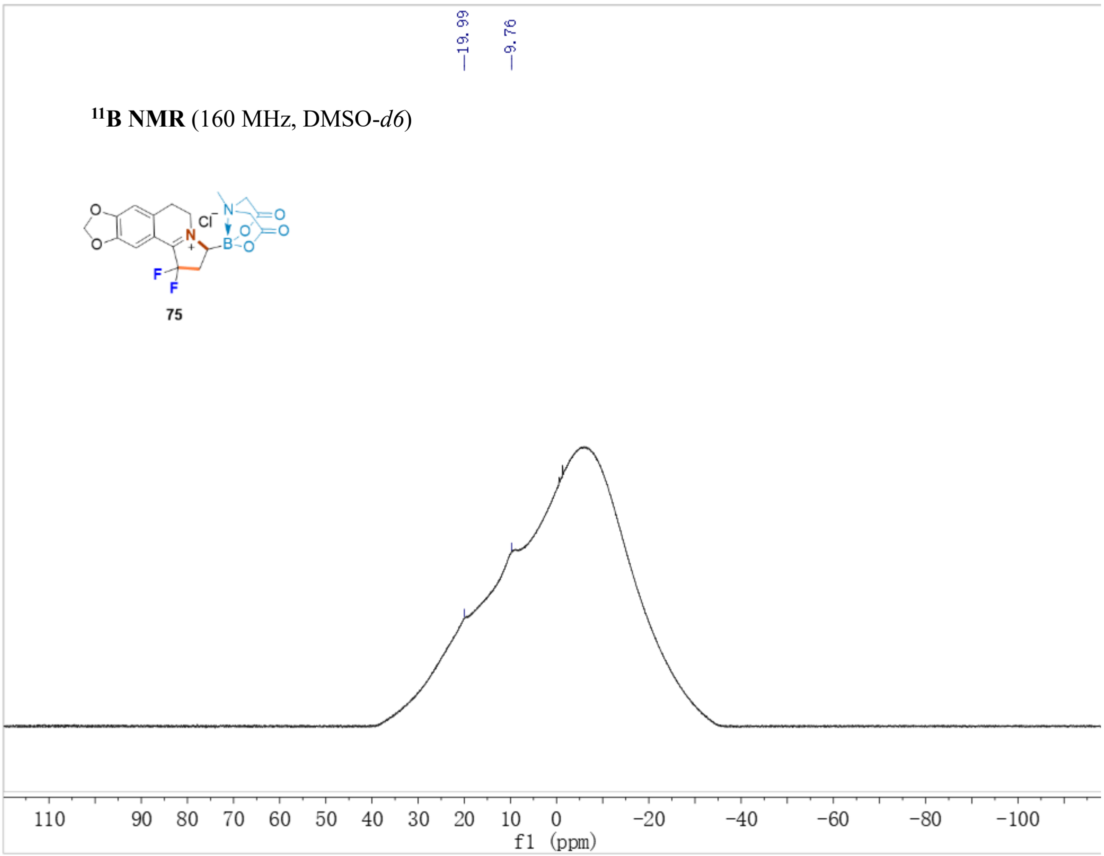


(*S*)-1,1-difluoro-3-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2,3,5,6-tetrahydro-1*H*-[1,3]dioxolo[4,5-*g*]pyrrolo[2,1-*a*]isoquinolin-4-ium (75)

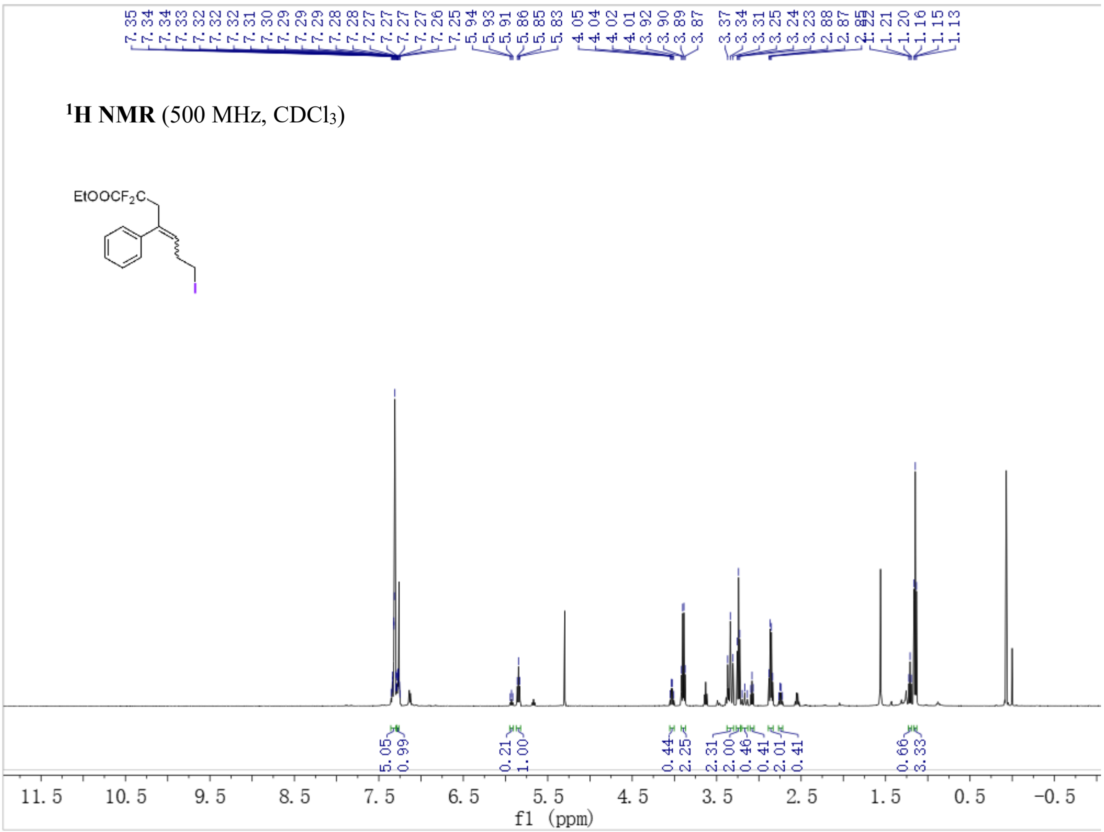


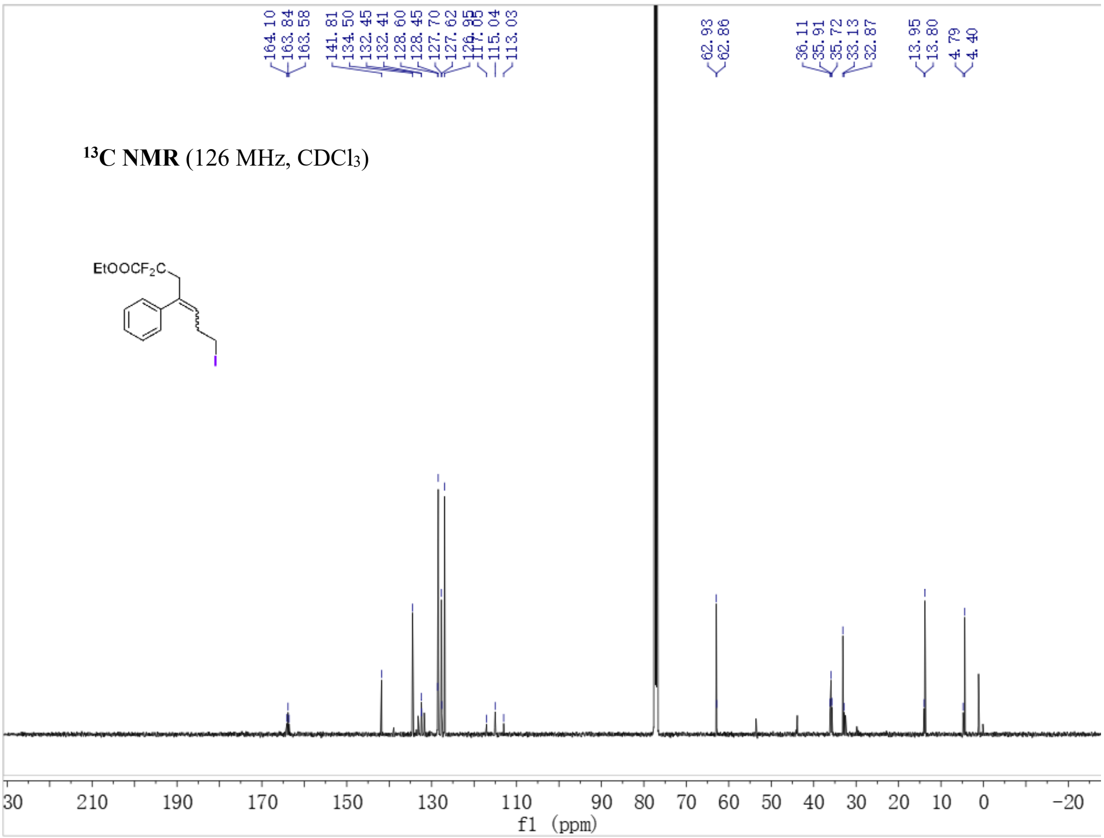

168.30
167.98
161.17
160.92
160.65
155.89
147.56
137.99
128.60
126.62
124.62
112.58
109.88
106.73
103.59
63.30
63.02
59.28
47.52
46.52
33.73
33.55
33.38
25.45
75
^{13}C NMR (126 MHz, DMSO-*d6*)
f1 (ppm)

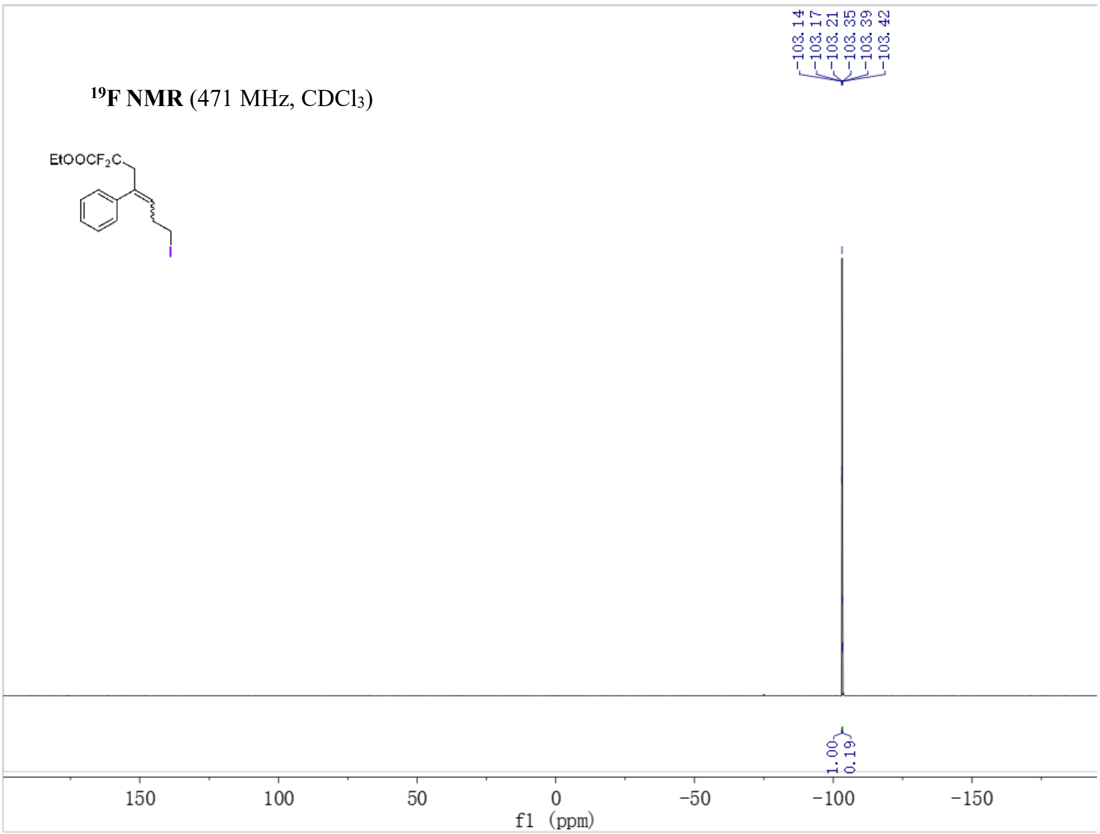

-83.98
-84.02
-84.07
-84.56
-84.60
-84.65
-87.67
-87.70
-88.25
-88.28
^{19}F NMR (471 MHz, DMSO-*d6*)
75
1.00
0.97
f1 (ppm)



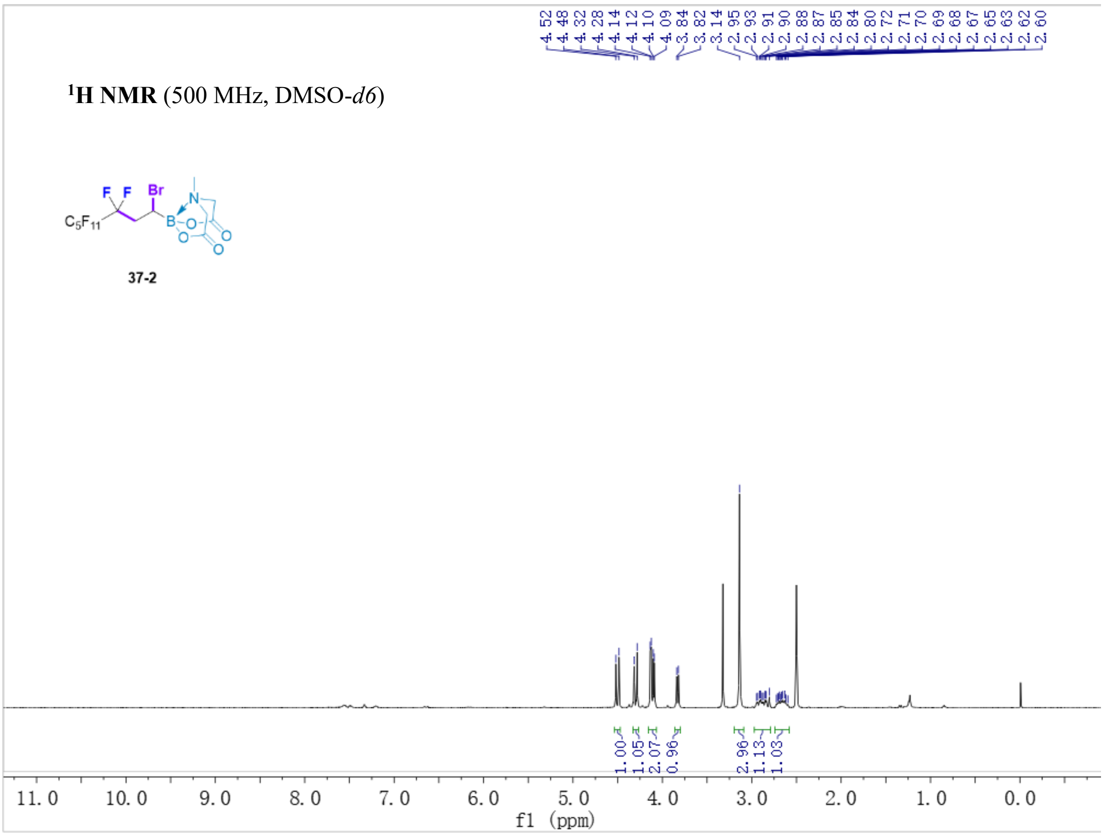
Ethyl 2,2-difluoro-7-iodo-4-phenylhept-4-enoate (77)

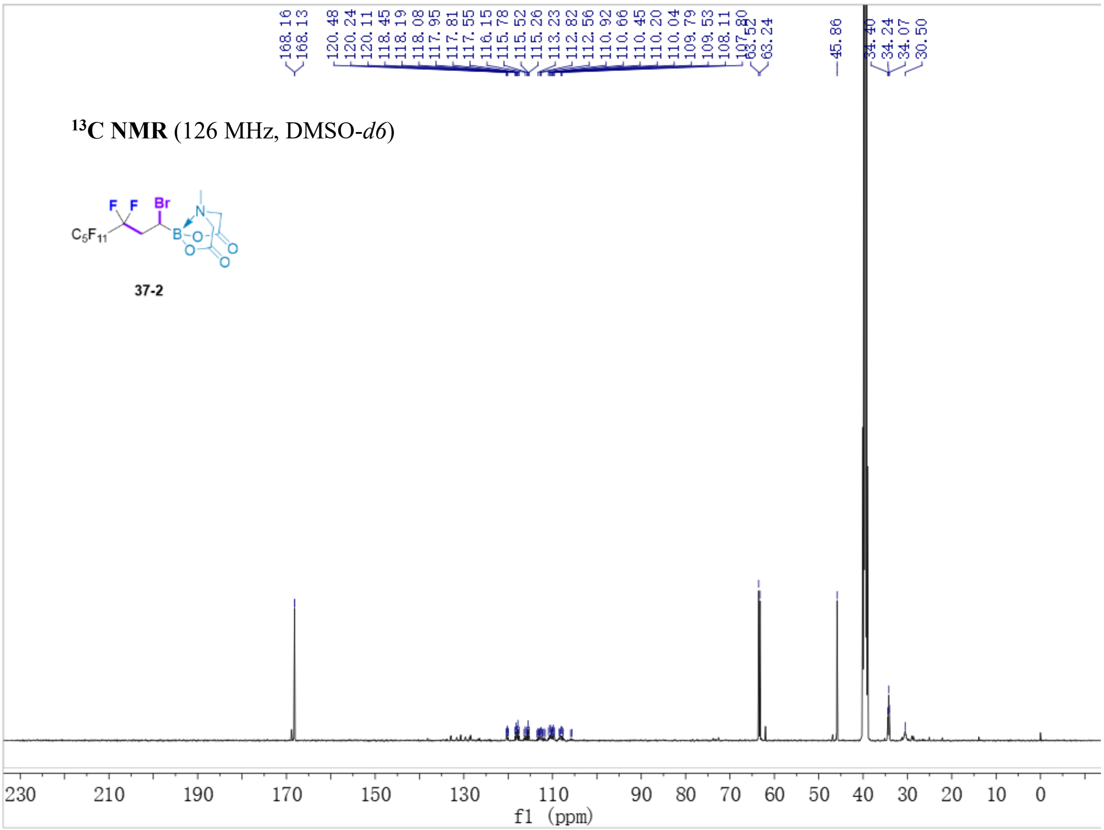


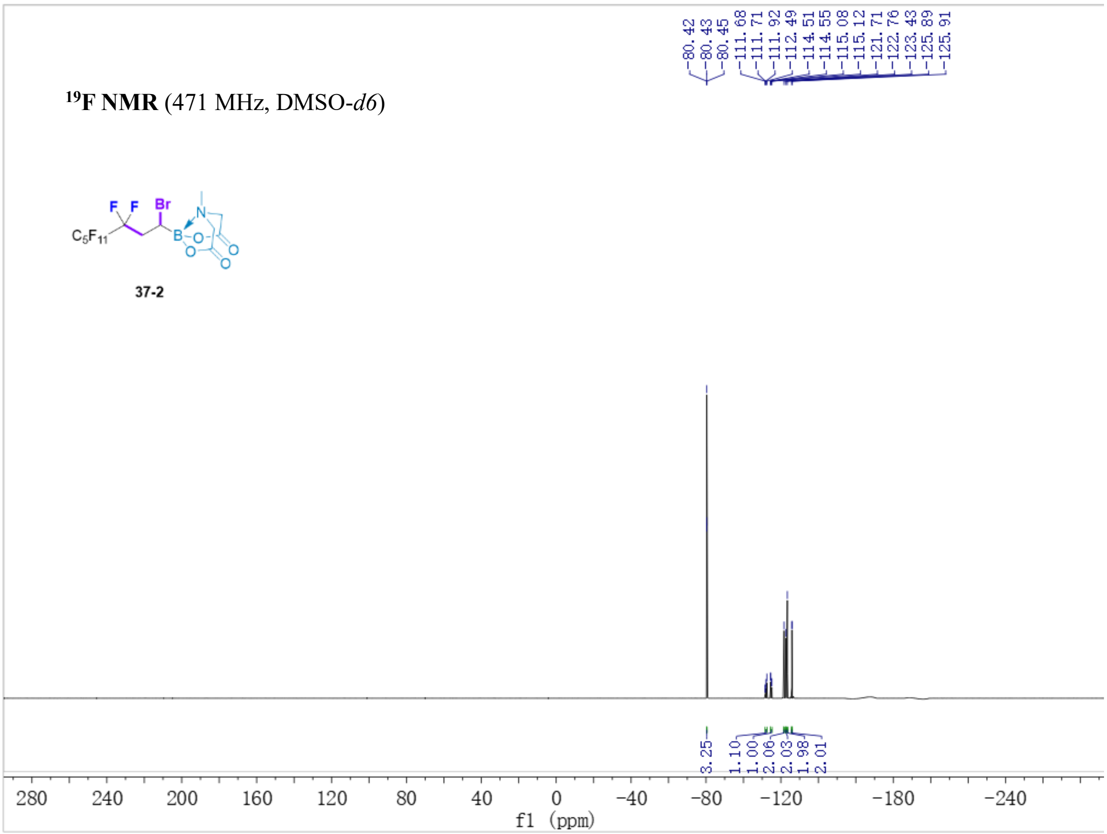

164.10
163.84
163.58
141.81
134.50
132.45
132.41
128.60
128.45
127.70
127.62
115.04
113.03
62.93
62.86
36.11
35.91
35.72
33.13
32.87
13.95
13.80
4.79
4.40
^{13}C NMR (126 MHz, CDCl$_3$)
EtOOCF$_2$C
I
f1 (ppm)

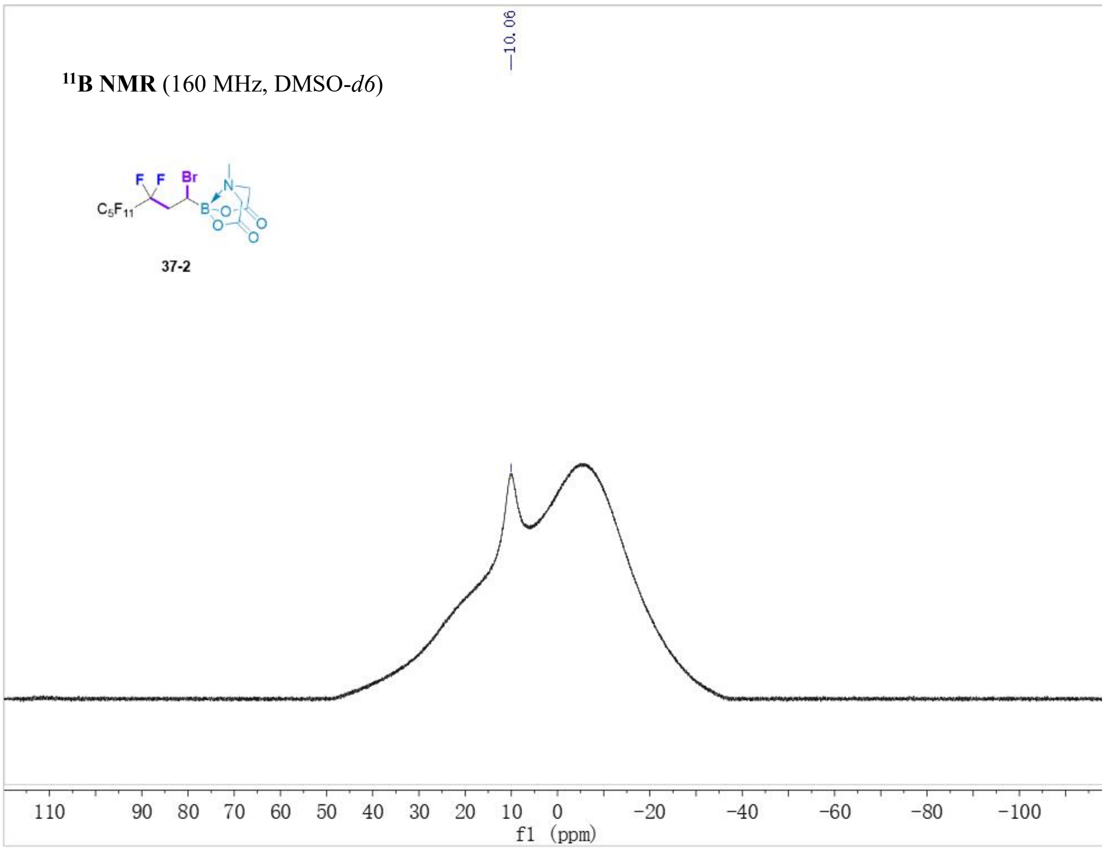

-103.14
-103.17
-103.21
-103.35
-103.39
-103.42
^{19}F NMR (471 MHz, CDCl$_3$)
EtOOCF$_2$C
I
1.00
0.19
f1 (ppm)

2-(1-bromo-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (37-2)






^{19}F NMR (471 MHz, DMSO-*d6*)
C_5F_{11}
F
F
Br
B
O
O
O
O
N
37-2
-80.42
-80.43
-80.45
-111.68
-111.71
-111.92
-112.49
-114.51
-114.55
-115.08
-115.12
-121.71
-122.76
-123.43
-125.89
-125.91
3.25
1.10
1.00
2.06
2.03
1.98
2.01
280
240
200
160
120
80
40
0
-40
-80
-120
-180
-240
f1 (ppm)


^{11}B NMR (160 MHz, DMSO-*d6*)
C_5F_{11}
F
F
Br
B
O
O
O
O
N
37-2
-10.06
110
90
80
70
60
50
40
30
20
10
0
-20
-40
-60
-80
-100
f1 (ppm)