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Synthesis of Fluorinated Amphoteric Organoborons via Iodofluorination of Alkynyl and Alkenyl MIDA Boronates

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Supporting Information

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I. General Information

Unless otherwise noted, all commercially available materials were used without further purification.

NMR–spectra were recorded on Bruker AvanceIII–400M and AscendTM 500M in solvents as indicate. Chemical shifts (δ) are given in ppm relative to tetramethylsilane (δ = 0). The residual solvent signals were used as references. The following abbreviations were used to describe peak splitting patterns: s (singlet), d (doublet), t (triplet), q (quartet), septet (sept), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), triplet of doublets (td). Coupling constants (*J*) were reported in hertz unit (Hz).

High–resolution mass spectra (HRMS) were recorded on a Bruker VPEXII spectrometer with EI and ESI mode unless otherwise stated.

IR spectra were recorded on a Perkin Elmer-100 spectrometer and are reported in terms of frequency of absorption (cm^{-1}).

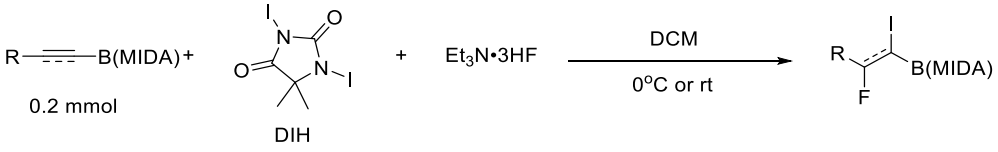
Analytical thin layer chromatography was performed on Polygram SIL G/UV254 plates. Visualization was accomplished by UV light (254 nm), or $KMnO_4$ staining solutions followed by heating, also by Gas chromatograph-Mass spectrometer analysis (GC-MS) on Agilent Technologies 5977A MSD. Flash column chromatography was performed using silica gel (200–300 mesh).

No attempts were made to optimize yields for substrate synthesis or products derivatizations.

All the starting materials[1–4] were prepared according to literature procedures.

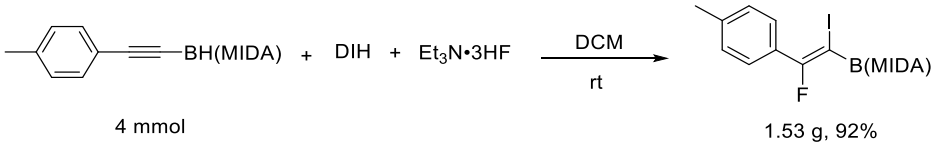
II. Synthesis and Characterization of Compounds

i. General Procedure for Iodofluorination Reaction (general procedure A)

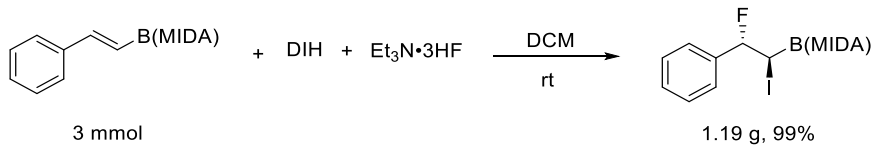


To a 15-mL screw cap vial equipped with a stirring bar, were added alkynyl (alkenyl) MIDA boronates (0.2 mmol, 1.0 equiv), 1,3-diiodo-5,5-dimethylhydantoin/DIH (0.2 mmol, 1.0 equiv), CH_2Cl_2 (0.1-1.0 mL) and $Et_3N{\cdot}3HF$ (280 μL, 9.0 equiv). The solution was stirred at room temperature or 0 ℃ for 5-60 min (for alkynyl MIDA boronates) or 1-5 min (for alkenyl MIDA boronates). The resulting mixture was quenched with 0.2 M $Na_2S_2O_3$ solution and then extracted with EtOAc. The organic phase was washed with 0.2 M HCl and saturated NaCl. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. After removing the EtOAc under vacuum, the crude product was obtained. If necessary, recrystallization (acetone/diethyl ether) was conducted to get pure product.

ii. Gram-scale reactions



To a 100-mL round-bottom flask equipped with a stirring bar, were added 4-methylphenyl ethynyl MIDA boronates (4 mmol, 1.0 equiv), DIH (1.0 equiv), CH_2Cl_2 (20 mL) and $Et_3N{\cdot}3HF$ (9.0 equiv). The solution was stirred at room temperature for 15 min. The resulting mixture was quenched with 0.2 M $Na_2S_2O_3$ solution and then extracted with EtOAc. The organic phase was washed with 0.2 M HCl and saturated NaCl. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. After removing the EtOAc under vacuum, the product was obtained as light yellow solid (1.53 g, 92%).



To a 100-mL round-bottom flask equipped with a stirring bar, were added phenylvinyl MIDA boronates (3 mmol, 1.0 equiv), DIH (1.0 equiv), CH_2Cl_2 (15 mL) and $Et_3N{\cdot}3HF$ (9.0 equiv). The solution was stirred at room temperature for 5 min. The resulting mixture was quenched with 0.2 M $Na_2S_2O_3$ solution and then extracted with EtOAc. The organic phase was washed with 0.2 M HCl and saturated NaCl. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. After removing the EtOAc under vacuum, the product was obtained as white to light yellow solid (1.19 g, 99%).

iii. Preparation of Starting Materials

a) Preparation of alkynyl MIDA boronates

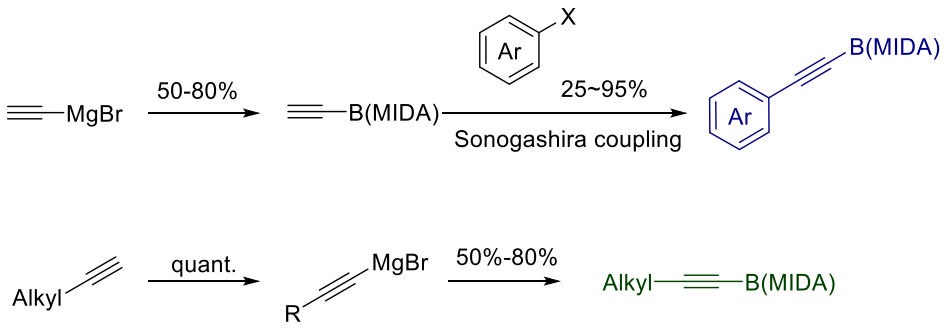
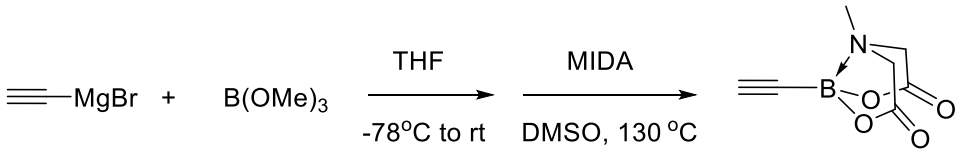
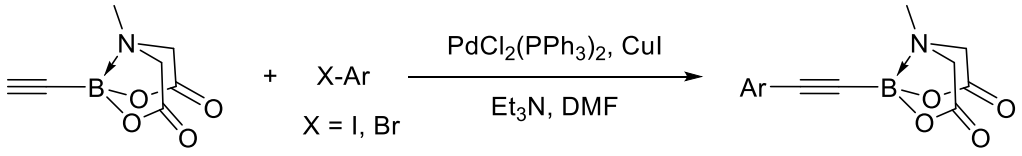


Figure S1 General procedure for the preparation of alkynyl MIDA boronates



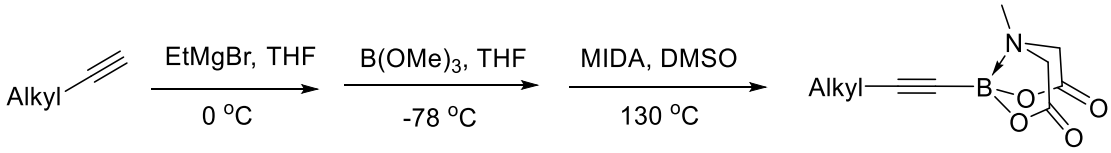
Preparation of 1-Ethynylboronate ester. According to the synthetic procedure in the literature,[1] to an oven-dried 100-mL round-bottomed flask equipped with a magnetic stir bar, were added THF (15 mL) and trimethylborate (2.45 mL, 22 mmol, 1.1 equiv) via a syringe. The resulting solution was cooled to -78 °C. The addition funnel was charged with the first portion of ethynyl magnesium bromide solution (20 mL, 20 mmol, 1 M in THF) which was then added dropwise over 30 min. The reaction mixture was stirred at -78 ºC for 1 h and warmed up to ambient temperature over 3 h to result in a thick white slurry. A 100 mL of 3-neck round-bottomed flask equipped with a stirring bar, a thermometer, and a distillation train was charged with *N*-methyliminodiacetic acid/MIDA (44 mmol, 2.2 equiv) and DMSO (20 mL). The solution was heated to 130 °C. 20 mL of hexanes was added dropwise to the MIDA solution, resulting in a homogeneous light-orange solution. The previously prepared suspension was added over the course of 30 min via a syringe. After the addition was completed the reaction vessel was washed with THF (2*10 mL) and the washes were transferred to the reaction vessel containing the MIDA solution. The volatiles (THF and MeOH) were allowed to distill off (~15 min). The reaction vessel was allowed to cool to ambient temperature. The reaction mixture was then transferred to a 1 L separatory funnel. To this was added 150 mL water, 150 mL of brine, 210 mL of ethyl acetate, and 140 mL of acetone. The organic layer was separated, and the aqueous layer was extracted twice with 300 mL of a 3:2 ethyl acetate: acetone solution. The combined organic fractions were then washed with 100 mL of brine (five times) and dried over Na_2SO_4. The organic fractions were then concentrated to form a light brown solid. The solid was dissolved in 10 mL of

dichloromethane and then was precipitated by 500 mL of diethyl ether, then stirred for 30 min. The resulting solid was collected via filtration and washed with diethyl ether (2*50 mL). The resulting solid was ethynyl MIDA boronate (around 60% yield).



Preparation of arylethynyl MIDA boronates 1a-1o. According to the synthetic procedure in the literature, [2] a 25-mL round-bottom flask equipped with a magnetic stir bar was charged with an aryl iodide (2 mmol, 1.0 equiv), ethynyl MIDA boronate (380 mg, 2 mmol, 1.0 equiv), CuI (38.1 mg, 10 mol %), $PdCl_2(PPh_3)_2$ (70.2 mg, 5 mol %), and placed under nitrogen atmosphere. Then, anhydrous DMF (10 mL) and Et_3N (0.84 mL) were introduced via a syringe, and the reaction mixture was allowed to stir at room temperature until ethynyl B(MIDA) boronate was consumed completely, after which the mixture was poured into a separatory funnel containing water. Extraction with ethyl acetate (3*25 mL) was carried out, and the combined organic extracts were washed with brine (3*20 mL), dried over Na_2SO_4 and concentrated *in vacuo* to give a crude residue. The crude product was subsequently subjected to flash column chromatography on silica gel to afford the desired compound.

Preparation of alkylethynyl MIDA boronates.



According to the synthetic procedure in the literature, [1] to a THF (10 mL) solution of alkyl acetylene (20 mmoL, 1.0 equiv) in a 50 mL of Schlenk tube equipped with a magnetic stir bar under an argon atmosphere, ethyl magnesium bromide solution (20 mL, 20 mmol, 1.0 M in THF) was added dropwise over 30 min at 0 ºC. The reaction mixture was stirred at 0 ºC for 1 h. Then the reaction mixture was added dropwise to a solution of trimethylborate (2.45 mL, 22 mmol, 1.1 equiv) in THF (10 mL) at -78 ºC over 30 min. The reaction mixture was stirred at -78 ºC for 1 h and warmed up to ambient temperature over 3 h to result in a white slurry. A 100 mL of 3-neck round-bottomed flask equipped with a stirring bar, a thermometer, and a distillation train was charged with *N*-methyliminodiacetic acid (MIDA, 44 mmol, 2.2 equiv) and DMSO (20 mL). The solution was heated to 130 °C. 20 mL of hexanes was added dropwise to the MIDA solution, resulting in a homogeneous light orange solution. The previously prepared suspension was added over a course of 30 min via a syringe. After the addition

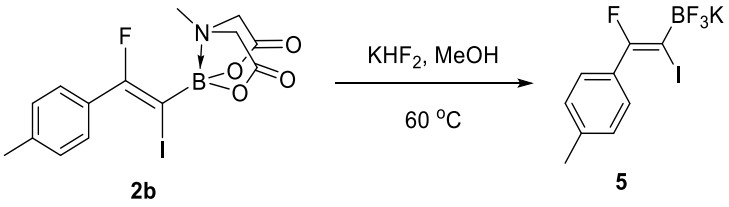
was completed, the reaction vessel was washed with THF (2*10 mL) and the washes were transferred to the reaction vessel containing the MIDA solution. The volatiles (THF and MeOH) were allowed to distill off (~15 min). The reaction vessel was allowed to cool to ambient temperature. The reaction mixture was then transferred to a 1 L separatory funnel. To this was added 150 mL of de-ionized water, 150 mL of brine, 210 mL of ethyl acetate, and 140 mL of acetone. The organic layer was separated, and the aqueous layer was extracted twice with 300 mL of a 3:2 ethyl acetate: acetone solution. The combined organic fractions were then washed with 100 mL of brine (at least five times) and dried over Na_2SO_4. The organic fractions were then concentrated to form a light brown solid. The solid was dissolved in 10 mL of dichloromethane and then was precipitated by 500 mL of diethyl ether. The resulting solid was collected via filtration and washed with diethyl ether (2*50 mL). The resulting white solid was product (around 50% yield).

b) Preparation of alkenyl MIDA boronates

All the alkenyl MIDA boronates were prepared according to literature procedures.[3]

iv. Derivatizations of Products

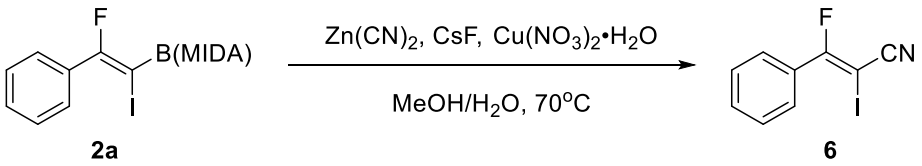
Conversion of MIDA Boronate to Trifluoroborate



2b **5**

According to the synthetic procedure in the literature,[4] to a stirred solution of **2b** (0.2 mmol) in methanol (40 mL/mmol) was added aq KHF_2 solution (3 equiv, 4.5 M solution) and the mixture was stirred at 70 °C for 0.5 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.

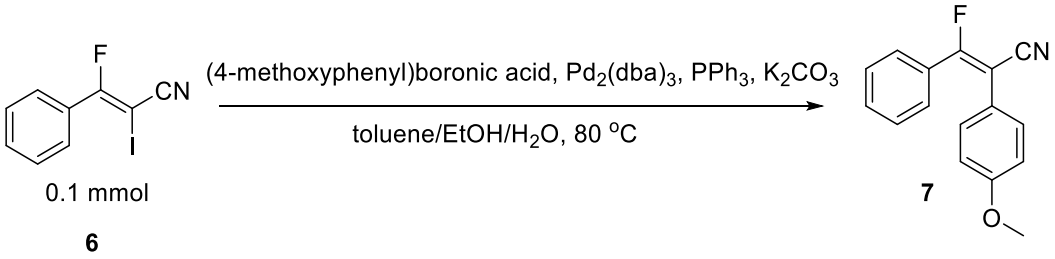
Synthesis of compound 6



2a **6**

According to the synthetic prodecure in the literature,[5] to a mixture of **2a** (0.3 mmol, 1.0 equiv), $Zn(CN)_2$ (0.9 mmol, 3.0 equiv), $Cu(NO_3)_2 \cdot 3H_2O$ (0.6 mmol, 2.0 equiv) and CsF (0.3 mmol, 1.0 equiv) was added MeOH/H_2O (5:1, 3.6 mL). The mixture was stirred at 70 °C overnight. After cooled to the room temperature, the solution was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel with a mixture of petroleum ether and EtOAc as eluent to afford the product as colorless oil.

Synthesis of compound 7

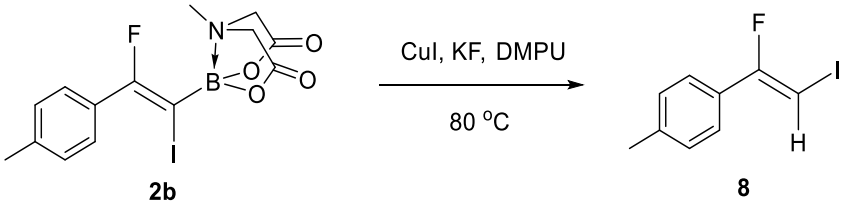


0.1 mmol

6 **7**

The product 7 was synthesized according to the procedure in the literature.[6]

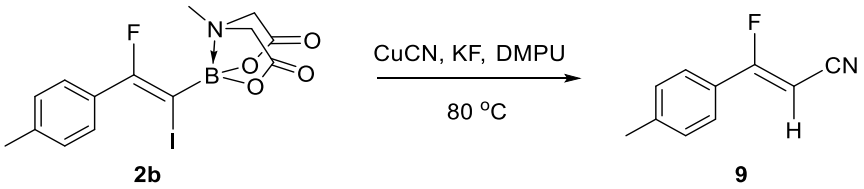
Synthesis of compound 8



2b **8**

To a 15 mL Schlenk tube equipped with a stirring bar, were added **2b** (0.1 mmol, 42 mg, 1.0 equiv), CuI (0.17 mmol, 32.5 mg, 1.7 equiv) and KF (0.15 mmol, 9 mg, 1.5 equiv) in glovebox. The reaction vessel was taken out, and 0.375 mL dry DMPU were added under N_2 protection. The reaction mixture was stirred at 80 °C until **2b** was consumed (about 24 h). The resulting mixture was quenched with saturated NH_4Cl and extracted with EtOAc. 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 petroleum ether as eluent.

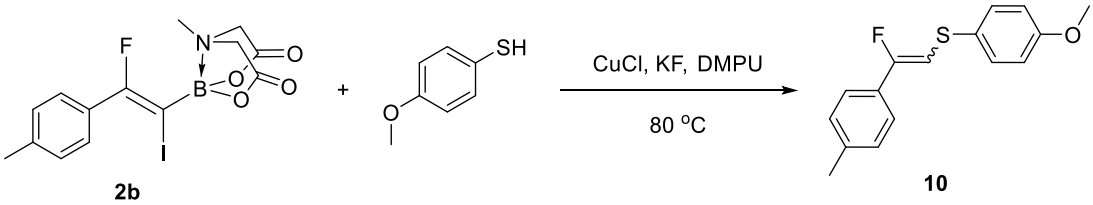
Synthesis of compound 9



2b **9**

To a 15 mL Schlenk tube equipped with a stirring bar, were added **2b** (0.1 mmol, 42 mg, 1.0 equiv), CuCN (0.17 mmol, 15.2 mg, 1.7 equiv) and KF (0.15 mmol, 9 mg, 1.5 equiv) in glovebox. The reaction vessel was taken out, and 0.375 mL dry DMPU were added under N_2 protection. The reaction mixture was stirred at 80 °C until **2b** was consumed (about 12 h). The resulting mixture was quenched with saturated NH_4Cl and extracted with EtOAc. 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 (petroleum ether: EtOAc = 10:1).

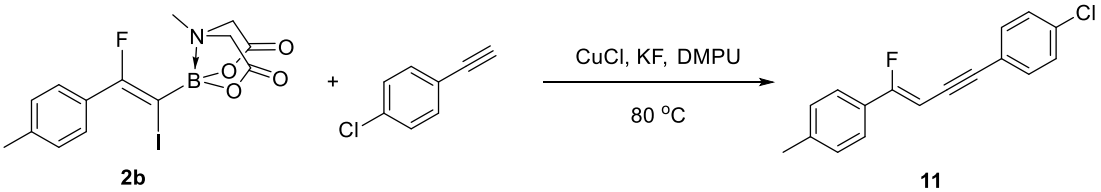
Synthesis of compound 10



2b **10**

To a 15 mL Schlenk tube equipped with a stirring bar were added **2b** (0.2 mmol, 84 mg, 1.0 equiv), CuCl (0.34 mmol, 33.6 mg, 1.7 equiv) and KF (0.85 mmol, 50 mg, 4.3 equiv) in glovebox. The reaction vessel was taken out, and 4-methoxybenzenethiol(0.3 mmol, 42 mg, 1.5 equiv) in 0.8 mL dry DMPU were added via syringe under N_2 protection. The reaction mixture was stirred at 80 °C until **2b** was consumed (about 18 h). The resulting mixture was quenched with saturated NH_4Cl and extracted with EtOAc. 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 (petroleum ether).

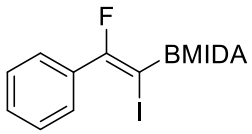
Synthesis of compound 11



2b **11**

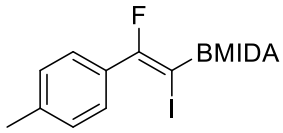
To a 15 mL Schlenk tube equipped with a stirring bar were added **2b** (0.15 mmol, 63 mg, 1.0 equiv), CuCl (0.225 mmol, 25.5 mg, 1.7 equiv) and KF (0.66 mmol, 37.5 mg, 4.3 equiv) in glovebox. The reaction vessel was taken out, and ethynylbenzene (0.225 mmol, 23 mg, 1.5 equiv) in 0.6 mL dry DMPU were added via syringe under N_2 protection. The reaction mixture was stirred at 80 °C until **2b** was consumed (about 24 h). The resulting mixture was quenched with saturated NH_4Cl and extracted with EtOAc. 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 (petroleum ether).

v. Characterization of compounds



2a

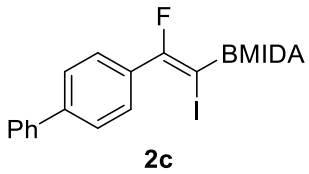
Following general procedure A (the reaction was stirred at room temperature for 30 min), **2a** was obtained in 87% yield (70 mg) as a white to light yellow solid after removing the solvent. R*f* (dichloromethane/EtOAc 1:1): 0.35. ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.70 – 7.68 (m, 2H), 7.48 – 7.46 (m, 3H), 4.41 (d, *J* = 17.1 Hz, 2H), 4.22 (d, *J* = 17.1 Hz, 2H), 3.24(s, 3H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 168.4 , 163.8 (d, *J* = 258.8 Hz), 135.4 (d, *J* = 31.7 Hz), 131.0 (d, *J* = 2.6 Hz), 130.3 (d, *J* = 3.6 Hz), 129.0 , 63.88, 63.86, 47.7. ^{19}F NMR (376 MHz, Acetone- d_6) δ -59.60. ^{11}B NMR (128 MHz, Acetone-d_6) δ 9.88. **HRMS (EI) m/z** calcd for $C_{13}H_{12}BFINO_4Na$ $[M+Na]^+$: 425.9783, found: 425.9780. **ATR-FTIR (cm^{-1}):** 2960, 2921, 2850, 1761, 1635, 1617, 1444, 1335, 1282, 1225, 1124, 1036, 1012, 1047, 768, 692, 603, 540.



2b

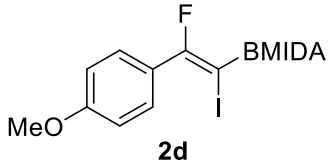
Following general procedure A (the reaction was stirred at room temperature for 20 min), **2b** was obtained in 82% yield (68 mg) as a light yellow solid after removing the solvent. R*f* (dichloromethane/EtOAc 1:1): 0.35. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.59 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 4.40 (d, *J* = 17.1 Hz, 2H), 4.21 (d, *J* = 17.1 Hz, 2H), 3.22 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.4 , 163.9 (d, *J* = 258.2 Hz), 141.2 , 132.5 (d, *J* = 31.6 Hz), 130.2 (d, *J* = 3.7 Hz), 129.5 , 63.90, 63.87, 47.7 , 21.4. ^{19}F NMR (376 MHz, Acetone-d_6) δ -59.74. ^{11}B NMR (128 MHz, Acetone-d_6) δ 9.84.

HRMS (EI) m/z calcd for $C_{14}H_{14}BFINO_4Na$ $[M+Na]^+$: 439.9939, found: 439.9941. **ATR-FTIR (cm^{-1}):** 2960, 2921, 2850, 1761, 1635, 1617, 1444, 1335, 1282, 1225, 1124, 1036, 1012, 1047, 768, 692, 603, 540. **ATR-FTIR (cm^{-1}):** 3012, 2973, 2921, 2852, 1782, 1763, 1618, 1335, 1280, 1112, 1078, 1052, 894, 820, 697, 504, 432, 404.



2c

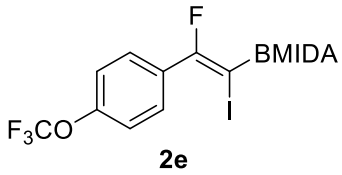
Following general procedure A (the reaction was stirred at room temperature for 20 min), **2c** was obtained in 77% yield (74 mg) as a light yellow solid after removing the solvent. R*f* (dichloromethane/EtOAc 1:1): 0.38. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.91 – 7.66 (m, 6H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 4.42 (d, *J* = 17.2 Hz, 2H), 4.23 (d, *J* = 17.1 Hz, 2H), 3.26 (s, 3H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 168.4, δ 163.5 (d, *J* = 257.8 Hz), 143.5, 140.7, 134.2 (d, *J* = 31.9 Hz), 130.9 (d, *J* = 3.6 Hz), 129.9, 128.8, 127.9, 127.4, 63.9, 47.8. ^{19}F NMR (376 MHz, Acetone-d_6) δ -60.43. ^{11}B NMR (128 MHz, Acetone-d_6) δ 9.64. **HRMS (EI) m/z** calcd for $C_{19}H_{16}BFINO_4Na$ $[M+Na]^+$: 502.0097, found: 502.0099. **ATR-FTIR (cm^{-1}):** 3010, 2922, 1765, 1619, 1450, 1338, 1295, 1060, 962, 834, 770, 699.



2d

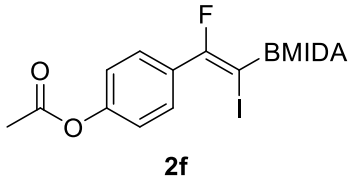
Following general procedure A (the reaction was stirred at 0 °C for 20 min), **2d** was obtained in 87% yield (75 mg) as a light yellow solid after removing the solvent. R*f* (dichloromethane/EtOAc 1:1): 0.35. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.67 (d, *J* = 8.9 Hz, 2H), 7.01 (d, *J* = 8.6 Hz, 2H), 4.39 (d, *J* = 17.0 Hz, 2H), 4.20 (d, *J* = 17.1 Hz, 2H), 3.86 (s, 3H), 3.21 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.4, 163.5 (d, *J* = 257.3 Hz), 162.5, 132.0 (d, *J* = 3.9 Hz), 127.4 (d, *J* = 32.7 Hz), 114.1 , 63.89, 63.87, 55.7 , 47.7. ^{19}F NMR (376 MHz, Acetone-d_6) δ -59.82. ^{11}B NMR (128 MHz, Acetone-d_6) δ 9.93. **HRMS (EI) m/z** calcd for $C_{14}H_{14}BFINO_5Na$ $[M+Na]^+$: 455.9889, found: 455.9888. **ATR-**

FTIR (cm^{-1}): 3013, 2921, 2849, 1775, 1757, 1632, 1508, 1454, 1285, 1252, 1128, 1040, 1024, 952, 828, 790.



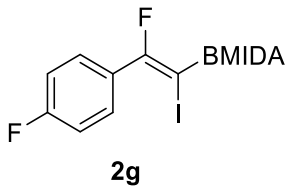
2e

Following general procedure A (the reaction was stirred at room temperature for 60 min), **2e** was obtained in 92% yield (90 mg) as a light yellow solid after removing the solvent. R*f* (dichloromethane/EtOAc 1:1): 0.34. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.86 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 4.42 (d, *J* = 17.0 Hz, 2H), 4.22 (d, *J* = 17.1 Hz, 2H), 3.24 (s, 3H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 162.3 (d, *J* = 258.3 Hz), 134.4 (d, *J* = 32.6 Hz), 121.3 (q, *J* = 256.3 Hz). ^{19}F NMR (376 MHz, Acetone-d_6) δ -57.69 – -58.70 (m), -59.60 – -61.34 (m). ^{11}B NMR (128 MHz, Acetone-d_6) δ 9.89. **HRMS (EI) m/z** calcd for $C_{14}H_{11}BF_4INO_5Na$ [M+Na]$^+$: 509.9606, found: 509.9604.



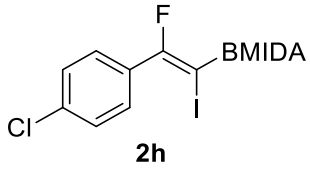
2f

Following general procedure A (the reaction was stirred at room temperature for 45 min), **2f** was obtained in 89% yield (82 mg) as a light yellow solid after removing the solvent. R*f* (dichloromethane/EtOAc 1:1): 0.31. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.76 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 4.40 (d, *J* = 17.0 Hz, 2H), 4.21 (d, *J* = 17.1 Hz, 2H), 3.23 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 169.4 , 168.4 , 163.0 (d, *J* = 258.1 Hz), 153.0 (d, *J* = 2.6 Hz), 132.7 (d, *J* = 32.2 Hz), 131.7 (d, *J* = 3.6 Hz), 122.4 , 47.7 , 21.0. ^{19}F NMR (376 MHz, Acetone-d_6) δ -59.90. ^{11}B NMR (128 MHz, Acetone-d_6) δ 9.94. **HRMS (EI) m/z** calcd for $C_{15}H_{14}BFINO_6Na$ [M+Na]$^+$: 483.9838, found: 483.9836. **ATR-FTIR (cm^{-1}):** 3012, 2920, 2849, 1771, 1758, 1633, 1502, 1450, 1335, 1285, 1127, 1043, 1022, 951, 871, 829, 635, 570.



2g

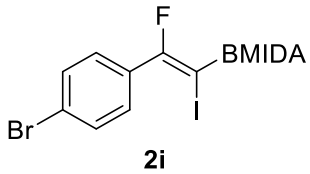
Following general procedure A (the reaction was stirred at room temperature for 30 min), **2g** was obtained in 91% yield (76 mg) as a light yellow solid after removing the solvent. R*f* (dichloromethane/EtOAc 1:1): 0.32. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.77 (ddd, *J* = 8.9, 5.4, 1.0 Hz, 2H), 7.25 (td, *J* = 8.9, 0.8 Hz, 2H), 4.42 (dd, *J* = 17.0, 1.1 Hz, 2H), 4.21 (d, *J* = 17.1 Hz, 2H), 3.23 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 168.5, 162.9 (d, *J* = 248.8 Hz), δ 161.1 (d, *J* = 258.7 Hz), 132.0 (d, *J* = 8.8 Hz), 130.6 (d, *J* = 32.7 Hz), 115.3 (d, *J* = 21.9 Hz), 62.7, 47.0. ^{19}F NMR (376 MHz, Acetone-d_6) δ -59.59, -111.06 (td, *J* = 9.7, 9.2, 4.6 Hz). ^{11}B NMR (128 MHz, Acetone-d_6) δ 9.82. **HRMS (EI) m/z** calcd for $C_{13}H_{11}BF_2INO_4Na$ $[M+Na]^+$: 443.9689, found: 443.9690. **ATR-FTIR (cm^{-1}):** 3012, 2960, 2921, 2850, 1760, 1631, 1503, 1334, 1282, 1225, 1124, 1047, 955, 839, 804, 700, 566, 514.



2h

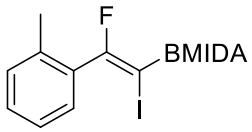
Following general procedure A (the reaction was stirred at room temperature for 45 min), **2h** was obtained in 78% yield (68 mg) as a light yellow solid after removing the solvent. R*f* (dichloromethane/EtOAc 1:1): 0.33. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 4.41 (d, *J* = 17.1 Hz, 2H), 4.21 (d, *J* = 17.1 Hz, 2H), 3.23 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.4, 162.5 (d, *J* = 258.2 Hz), 136.3 (d, *J* = 2.3 Hz), 134.1 (d, *J* = 32.7 Hz), 132.1 (d, *J* = 3.4 Hz), 129.2, 63.9, 47.7. ^{19}F NMR (376 MHz, Acetone-d_6) δ -60.56. ^{11}B NMR (128 MHz, Acetone-d_6) δ 9.77. **HRMS (EI) m/z** calcd for $C_{13}H_{11}BClFINO_4Na$ $[M+Na]^+$: 459.9393, found: 459.9390. **ATR-FTIR (cm^{-1}):** 3009, 2959, 2921, 2850, 1760, 1632, 1484, 1456, 1335, 1280, 1126, 1046, 1015, 954, 829, 751, 537, 457.

Following general procedure A (the reaction was stirred at room temperature for 50 min), **2i** was obtained in 84% yield (81 mg) as a light yellow solid after removing the solvent. R*f*



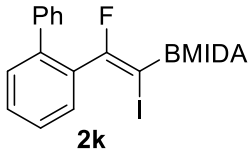
2i

(dichloromethane/EtOAc 1:1): 0.33. ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.69 – 7.65 (m, 4H), 4.41 (dd, J = 17.1, 1.1 Hz, 2H), 4.22 (d, J = 17.1 Hz, 2H), 3.23 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.4, 162.6 (d, J = 258.4 Hz), 134.5 (d, J = 32.4 Hz), 132.3 (d, J = 3.5 Hz), 132.2, 124.7 (d, J = 3.2 Hz), 63.9, 47.7. ^{19}F NMR (376 MHz, Acetone-d_6) δ -60.78. ^{11}B NMR (128 MHz, Acetone-d_6) δ 9.75. **HRMS (EI) m/z** calcd for $C_{13}H_{11}BBrFINO_4Na$ $[M+Na]^+$: 503.8888, found: 503.8888. **ATR-FTIR (cm^{-1}):** 2961, 2921, 2850, 1760, 1645, 1632, 1484, 1334, 1280, 1045, 1015, 954, 828, 751, 700, 539.



2j

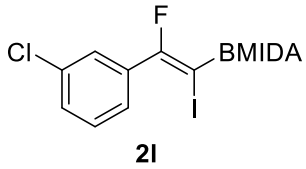
Following general procedure A (the reaction was stirred at room temperature for 20 min), **2j** was obtained in 96% yield (80 mg) as a light yellow solid after removing the solvent. R*f* (dichloromethane/EtOAc 1:1): 0.35. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.40 – 7.26 (m, 4H), 4.42 (d, J = 17.0 Hz, 2H), 4.22 (d, J = 17.0 Hz, 2H), 3.29 (s, 3H), 2.37 (d, J = 2.2 Hz, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.4, 165.0 (d, J = 264.2 Hz), 137.1, 136.0 (d, J = 29.0 Hz), 130.1 (dd, J = 8.3, 5.7 Hz), 126.7, 63.8, 47.8 , 19.5. ^{19}F NMR (376 MHz, Acetone-d_6) δ -56.82. ^{11}B NMR (128 MHz, Acetone-d_6) δ 9.72. **HRMS (EI) m/z** calcd for $C_{14}H_{14}BFINO_4Na$ $[M+Na]^+$: 439.9939, found: 439.9940. **ATR-FTIR (cm^{-1}):** 3019, 3009, 2962, 2921, 2850, 1760, 1737, 1648, 1449, 1289, 1121, 1057, 992, 869, 838, 793, 767, 608.



2k

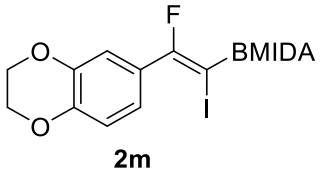
Following general procedure A (the reaction was stirred at room temperature for 60 min), **2k** was obtained in 58% yield (56 mg) as a light yellow solid after recrystallization. R*f* (dichloromethane/EtOAc 1:1): 0.37. ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.59 – 7.50 (m, 3H), 7.50 – 7.42 (m, 5H), 7.42 – 7.37 (m, 1H), 4.26 (d, J = 17.0 Hz, 2H), 3.93 (d, J = 17.0 Hz, 2H), 2.61 (s, 3H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 167.3, 164.1 (d, J = 265.1 Hz), 141.8, 140.6, 134.5 (d, J = 28.4 Hz), 130.5, 130.2 (d, J = 2.5 Hz), 129.9, 128.8 (d, J = 1.4 Hz), 128.3, 127.7, 127.6 (d, J = 2.0 Hz), 62.6,

46.2. ^{19}F NMR (471 MHz, Acetone-d_6) δ -51.09. ^{11}B NMR (128 MHz, Acetone-d_6) δ 9.47. **HRMS (EI) m/z** calcd for $C_{19}H_{16}BFINO_4Na$ $[M+Na]^+$: 502.0097, found: 502.0104.



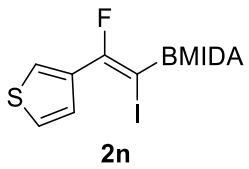
2l

Following general procedure A (the reaction was stirred at room temperature for 30 min), **2l** was obtained in 91% yield (80 mg) as a light yellow solid after removing the solvent. R*f* (dichloromethane/EtOAc 1:1): 0.32. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.74 – 7.72 (m, 1H), 7.70 – 7.63 (m, 1H), 7.55 – 7.44 (m, 2H), 4.40 (d, *J* = 17.0 Hz, 2H), 4.21 (d, *J* = 17.1 Hz, 2H), 3.25 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.4, 162.1 (d, *J* = 259.1 Hz), 137.3 (d, *J* = 32.3 Hz), 134.3, 131.0, 131.0 (d, *J* = 1.9 Hz), 130.2 (d, *J* = 3.1 Hz), 129.0 (d, *J* = 3.1 Hz), 63.9, 63.8, 47.8. ^{19}F NMR (376 MHz, Acetone-d_6) δ -60.46. ^{11}B NMR (128 MHz, Acetone-d_6) δ 9.72. **HRMS (EI) m/z** calcd for $C_{13}H_{11}BClFINO_4Na$ $[M+Na]^+$: 459.9393, found: 459.9392. **ATR-FTIR (cm^{-1}):** 3111, 3071, 3008, 2960, 2922, 2850, 1745, 1590, 1469, 1338, 1299, 1113, 1078, 1055, 1008, 951, 877, 851, 791, 682, 606, 447.



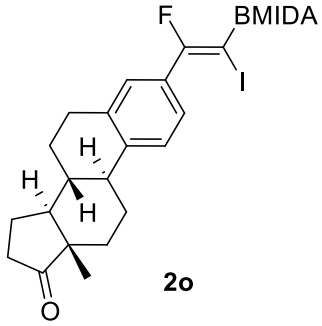
2m

Following general procedure A (the reaction was stirred at room temperature for 15 min), **2m** was obtained in 86% yield (79 mg) as a white solid after removing the solvent. R*f* (dichloromethane/EtOAc 1:1): 0.35. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.20 – 7.18 (m, 2H), 6.89 (d, *J* = 9.2 Hz, 1H), 4.38 (d, *J* = 17.0 Hz, 2H), 4.34 – 4.29 (m, 4H), 4.19 (d, *J* = 17.1 Hz, 2H), 3.20 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.4, 163.3 (d, *J* = 257.5 Hz), 146.2, 143.9, 128.2 (d, *J* = 32.4 Hz), 123.8 (d, *J* = 4.3 Hz), 119.3 (d, *J* = 3.7 Hz), 117.5 , 65.4 , 65.1 , 63.91, 63.88, 47.7. ^{19}F NMR (376 MHz, Acetone-d6) δ -59.65. ^{11}B NMR (128 MHz, Acetone-d_6) δ 9.82. **HRMS (EI) m/z** calcd for $C_{15}H_{14}BFINO_6Na$ $[M+Na]^+$: 483.9838, found: 483.9837. **ATR-FTIR (cm^{-1}):** 2921, 1760, 1632, 1504, 1278, 1240, 1120, 1046, 871, 815, 711.



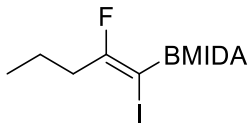
2n

Following general procedure A (the reaction was stirred at room temperature for 6 min), **2n** was obtained in 61% yield (50 mg) as a light yellow solid after recrystallization. R*f* (dichloromethane/EtOAc 1:1): 0.40. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.20 (d, *J* = 2.4 Hz, 1H), 7.64 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.63 (ddd, *J* = 5.0, 3.0, 1.3 Hz, 1H), 4.39 (d, *J* = 17.0 Hz, 2H), 4.20 (d, *J* = 17.1 Hz, 2H), 3.18 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.6, 158.7 (d, *J* = 251.4 Hz), 134.0 (d, *J* = 35.4 Hz), 129.8 (d, *J* = 6.5 Hz), 127.8 (d, *J* = 4.4 Hz), 128.2 , 62.8 , 47.1. ^{19}F NMR (376 MHz, Acetone-d_6) δ -62.58. ^{11}B NMR (128 MHz, Acetone-d_6) δ 9.96. **HRMS (EI) m/z** calcd for $C_{11}H_{10}BFINO_4SNa$ [M+Na]$^+$: 431.9347, found: 431.9350. **ATR-FTIR (cm^{-1}):** 3115, 3012, 2933, 1761, 1615, 1338, 1287, 1123, 1052, 1023, 955, 872, 791, 681.



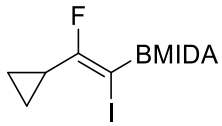
2o

Following general procedure A (the reaction was stirred at room temperature for 15 min), **2o** was obtained in 65% yield (75 mg) as a light yellow solid after recrystallization. R*f* (dichloromethane/EtOAc 1:1): 0.38. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.41 (d, *J* = 8.2 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.35 (s, 1H), 4.37 (d, *J* = 17.3 Hz, 2H), 4.12 (d, *J* = 17.3 Hz, 2H), 2.93 (s, 3H), 2.88 (dd, *J* = 8.6, 3.9 Hz, 2H), 2.48 – 2.38 (m, 2H), 2.31 (d, *J* = 9.4 Hz, 1H), 2.08 (dt, *J* = 18.5, 8.7 Hz, 1H), 1.97 (dd, *J* = 8.6, 4.5 Hz, 2H), 1.81 – 1.76 (m, 1H), 1.57 (dd, *J* = 16.4, 7.1 Hz, 2H), 1.49 – 1.37 (m, 3H), 0.84 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 220.6, 169.1, 162.7 (d, *J* = 257.7 Hz), 142.5, 136.8, 131.7 (d, *J* = 31.8 Hz), 129.8, 127.1, 125.6, 63.2, 50.1, 47.8, 47.4, 44.3, 37.8, 35.8, 31.7, 29.2, 26.2, 25.5, 21.6, 13.9. ^{19}F NMR (376 MHz, DMSO-d_6) δ -59.17. ^{11}B NMR (128 MHz, Acetone-d_6) δ 9.74. **HRMS (EI) m/z** calcd for $C_{25}H_{28}BFINO_5Na$ [M+Na]$^+$: 602.0986, found: 602.0936. **ATR-FTIR (cm^{-1}):** 2964, 2931, 2865, 1776, 1761, 1730, 1627, 1451, 1284, 1123, 1043, 1025, 1011, 873, 801, 703, 541.



2p

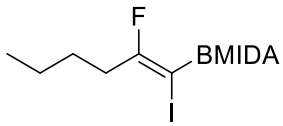
Following general procedure A (the reaction was stirred at room temperature for 20 min), **2p** was obtained in 88% yield (65 mg) as a white solid after removing the solvent. R*f* (dichloromethane/EtOAc 1:1): 0.43. ^{1}H NMR (400 MHz, Acetone-d_6) δ 4.32 (d, *J* = 17.0 Hz, 2H), 4.10 (d, *J* = 17.1 Hz, 2H), 3.09 (s, 3H), 2.74 (dt, *J* = 23.6, 7.5 Hz, 2H), 1.61 (h, *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.3 (d, *J* = 264.0 Hz), 168.3, 63.6 , 47.5 , 37.7 (d, *J* = 29.9 Hz), 20.1 , 13.7. ^{19}F NMR (376 MHz, Acetone-d_6) δ -71.21 (t, *J* = 23.5 Hz). ^{11}B NMR (128 MHz, Acetone-d_6) δ 9.62. **HRMS (EI) m/z** calcd for $C_{10}H_{14}BFINO_4Na$ $[M+Na]^+$: 391.9939, found: 391.9937. **ATR-FTIR (cm^{-1}):** 3010, 2963, 2921, 2851, 1760, 1749, 1642, 1456, 1337, 1282, 1252, 1042, 1016, 870, 829, 751,700.



2q

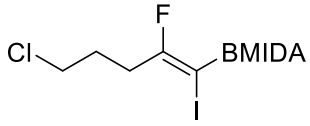
Following general procedure A (the reaction was stirred at room temperature for 10 min), **2q** was obtained in 86% yield (63 mg) as a white solid after removing the solvent. R*f* (dichloromethane/EtOAc 1:1): 0.39. ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 4.00 (d, *J* = 17.0 Hz, 2H), 3.85 (d, *J* = 17.4 Hz, 2H), 2.85 (s, 3H), 2.48 – 2.38 (m, 1H), 0.86 – 0.84 (m, 4H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.4, 166.5 (d, *J* = 258.2 Hz), 63.6 , 47.5 , 16.4 (d, *J* = 29.2 Hz), 6.7 (d, *J* = 3.4 Hz). ^{19}F NMR (376 MHz, Acetone-d_6) δ -91.26 (d, *J* = 27.7 Hz). ^{11}B NMR (128 MHz, Acetone-d_6) δ 9.57. **HRMS (EI) m/z** calcd for $C_{10}H_{12}BFINO_4Na$ $[M+Na]^+$: 389.9782, found: 389.9780. **ATR-FTIR (cm^{-1}):** 3006, 2959, 2932, 2871, 1759, 1745, 1637, 1450, 1337, 1285, 1252, 1110, 1032, 967, 897, 866, 700, 599.

Following general procedure A (the reaction was stirred at room temperature for 20 min), **2r** was obtained in 96% yield (74 mg) as a white solid after removing the solvent. R*f*



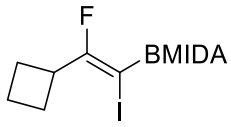
2r

(dichloromethane/EtOAc 1:1): 0.40. ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 4.02 (d, *J* = 17.1 Hz, 2H), 3.88 (d, *J* = 17.2 Hz, 2H), 2.86 (s, 3H), 2.75 (dt, *J* = 24.0, 7.5 Hz, 2H), 1.56 (p, *J* = 7.3 Hz, 2H), 1.39 (h, *J* = 7.2 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.5 (d, *J* = 264.5 Hz), 168.4, 168.3, 63.6, 47.5, 35.6 (d, *J* = 30.0 Hz), 28.8, 22.7 , 14.1. ^{19}F NMR (376 MHz, Acetone-d_6) δ -71.38 (t, *J* = 23.2 Hz). ^{11}B NMR (128 MHz, Acetone-d_6) δ 9.61. **HRMS (EI) m/z** calcd for $C_{11}H_{16}BFINO_4Na$ $[M+Na]^+$: 406.0095, found: 406.0093. **ATR-FTIR (cm^{-1}):** 3006, 2960, 2938, 2871, 1736, 1641, 1450, 1337, 1286, 1252, 1111, 1034, 966, 897, 866, 758, 599, 402.



2s

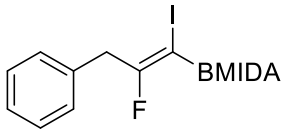
Following general procedure A (the reaction was stirred at room temperature for 15 min), **2s** was obtained in 91% yield (73 mg) as a white solid after removing the solvent. R*f* (dichloromethane/EtOAc 1:1): 0.38. ^{1}H NMR (500 MHz, Acetone-d_6) δ 4.31 (d, *J* = 16.9 Hz, 2H), 4.10 (d, *J* = 17.0 Hz, 2H), 3.67 (t, *J* = 6.5 Hz, 2H), 3.08 (s, 3H), 2.93 (dt, 2H), 2.07 – 2.03 (m, 2H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 168.3, 167.1 (d, *J* = 263.7 Hz), 63.62, 63.61, 47.6, 44.8, 33.6 (d, *J* = 30.2 Hz), 29.8. ^{19}F NMR (376 MHz, Acetone-d_6) δ -71.69 (t, *J* = 22.5 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 14.63. **HRMS (EI) m/z** calcd for $C_{10}H_{13}BClFINO_4Na$ $[M+Na]^+$: 425.9549, found: 425.9551. **ATR-FTIR (cm^{-1}):** 3009, 2969, 2920, 2850, 1763, 1640, 1338, 1300, 1291, 1040, 955, 875, 829, 754, 700, 638, 536, 401.



2t

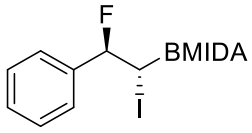
Following general procedure A (the reaction was stirred at room temperature for 15 min), **2t** was obtained in 94% yield (72 mg) as a white solid after removing the solvent. R*f* (dichloromethane/EtOAc 1:1): 0.41. ^{1}H NMR (400 MHz, Acetone-d_6) δ 4.32 (d, *J* = 17.2 Hz, 2H), 4.12 (d, *J* = 17.0 Hz, 2H), 4.03 (dt, *J* = 26.9, 8.8 Hz, 1H), 3.06 (s, 3H), 2.22 – 2.15 (m, 4H), 2.02 – 1.92 (m, 1H), 1.84 – 1.71 (m, 1H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.4, 168.2 (d, *J* = 263.3

Hz), 63.6 , 47.5 , 40.4 (d, *J* = 33.4 Hz), 26.0 , 18.3. ^{19}F NMR (376 MHz, Acetone-d_6) δ -81.13 (d, *J* = 26.9 Hz). ^{11}B NMR (128 MHz, Acetone-d_6) δ 9.55. **HRMS (EI) m/z** calcd for $C_{11}H_{14}BFINO_4Na$ $[M+Na]^+$: 403.9939, found: 403.9938. **ATR-FTIR (cm^{-1}):** 2988, 2939, 2859, 1758, 1631, 1455, 1333, 1278, 1114, 1027, 956, 906, 873, 804, 408.



2u

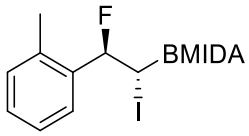
Following general procedure A (the reaction was stirred at room temperature for 20 min), **2u** was obtained in 90% yield (75 mg) as a white solid after removing the solvent. R*f* (dichloromethane/EtOAc 1:1): 0.41. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.38 – 7.32 (m, 4H), 7.30 – 7.25 (m, 1H), 4.32 (d, *J* = 17.2 Hz, 2H), 4.15 (d, *J* = 24.7 Hz, 2H), 4.10 (d, *J* = 17.2 Hz, 2H), 3.04 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 167.5, 165.7 (d, *J* = 263.4 Hz), 135.8 (d, *J* = 1.9 Hz), 128.7 , 128.5 , 127.0 , 62.9 , 46.7 , 41.0 (d, *J* = 30.8 Hz). ^{19}F NMR (376 MHz, Acetone-d_6) δ -70.18 (t, *J* = 24.2 Hz). ^{11}B NMR (128 MHz, Acetone-d_6) δ 9.65. **HRMS (EI) m/z** calcd for $C_{14}H_{14}BFINO_4Na$ $[M+Na]^+$: 439.9939, found: 439.9940. **ATR-FTIR (cm^{-1}):** 2965, 2901, 1772, 1759, 1638, 1334, 1287, 1221, 1126, 1106, 1039, 870, 776, 701, 520.



4a

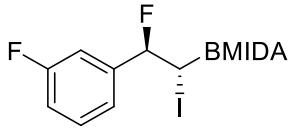
Following general procedure A (the reaction was stirred at room temperature for 3 min), **4a** was obtained in 71% yield (58 mg) as a white solid after removing the solvent. R*f* (dichloromethane/EtOAc 1:1): 0.40. ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.52 (d, *J* = 7.0 Hz, 2H), 7.46 – 7.32 (m, 3H), 5.59 (dd, *J* = 46.1, 8.6 Hz, 1H), 4.42 (d, *J* = 17.2 Hz, 1H), 4.31 (d, *J* = 17.1 Hz, 1H), 4.23 (d, *J* = 17.2 Hz, 1H), 4.13 (dd, *J* = 8.92, 7.55 Hz, 2H), 3.38 (s, 3H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 168.1, 168.0, 139.4 (d, *J* = 20.7 Hz), 129.7 (d, *J* = 2.2 Hz), 128.8, 128.3 (d, *J* = 5.9 Hz), 96.7 (d, *J* = 170.3 Hz), 65.2, 63.6, 63.5, 47.2 (d, *J* = 4.5 Hz). ^{19}F NMR (376 MHz, Acetone-d_6) δ -146.04 (d, *J* = 45.9 Hz). ^{11}B NMR (128 MHz, Acetone-d_6) δ 11.02. **HRMS (EI) m/z** calcd for $C_{13}H_{14}BFINO_4Na$ $[M+Na]^+$: 427.9939, found: 427.9943. **ATR-FTIR (cm^{-1}):**

3014, 2994, 2921, 1759, 1449, 1340, 1294, 1205, 1124, 1048, 1035, 949, 904, 861, 762, 692, 579. 452.



4b

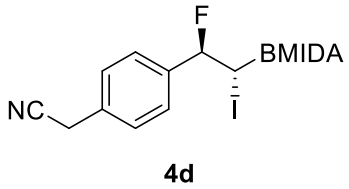
Following general procedure A (the reaction was stirred at room temperature for 2 min), **4b** was obtained in 93% yield (78 mg) as a white solid after removing the solvent. R*f* (dichloromethane/EtOAc 1:1): 0.41. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.57 – 7.48 (m, 1H), 7.32 – 7.19 (m, 3H), 5.80 (dd, *J* = 46.6, 11.1 Hz, 1H), 4.52 (d, *J* = 17.5 Hz, 1H), 4.29 – 4.23 (m, 1H), 4.20 (d, *J* = 17.6 Hz, 1H), 4.15 (dd, *J* = 11.1, 4.4 Hz, 1H), 3.94 (dd, *J* = 17.3, 1.2 Hz, 1H), 3.13 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.3, 136.4 (d, *J* = 4.3 Hz), 136.3 (d, *J* = 19.3 Hz), 130.3, 129.1 (d, *J* = 3.1 Hz), 126.4 (d, *J* = 4.1 Hz), 126.2 (d, *J* = 1.9 Hz), 92.4 (d, *J* = 166.2 Hz), 64.3, 62.5, 62.4, 46.9 (d, *J* = 6.4 Hz), 19.1. ^{19}F NMR (376 MHz, DMSO-d_6) δ -139.63 (d, *J* = 46.5 Hz). ^{11}B NMR (128 MHz, DMSO-d_6) δ 11.09. **HRMS (EI) m/z** calcd for $C_{14}H_{16}BFINO_4Na$ $[M+Na]^+$: 442.0096, found: 442.0093. **ATR-FTIR (cm^{-1}):** 3022, 2995, 2973, 2921, 1756, 1339, 1287, 1048, 1029, 1006, 905, 859, 759, 720, 585, 455.



4c

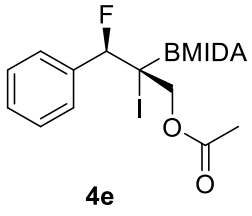
Following general procedure A (the reaction was stirred at room temperature for 2 min), **4c** was obtained in 92% yield (78 mg) as a white solid after removing the solvent. R*f* (dichloromethane/EtOAc 1:1): 0.38. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.44 (dd, *J* = 13.9, 7.9 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 10.0 Hz, 1H), 7.18 – 7.10 (m, 1H), 5.60 (dd, *J* = 45.9, 7.8 Hz, 1H), 4.41 (d, *J* = 17.1 Hz, 1H), 4.34 (dd, *J* = 17.1, 2.5 Hz, 1H), 4.21 (d, *J* = 17.1 Hz, 1H), 4.15 (m, 2H), 3.39 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.0, 167.9, 163.2 (d, *J* = 243.6 Hz), 142.3 (dd, *J* = 21.2, 7.3 Hz), 130.6 (d, *J* = 8.3 Hz), 124.4 (dd, *J* = 6.4, 2.8 Hz), 116.3 (dd, *J* = 21.2, 2.0 Hz), 114.9 (dd, *J* = 22.7, 6.5 Hz), 95.4 (d, *J* = 174.8 Hz), 65.1, 63.63, 63.59, 47.2 (d, *J* = 3.8 Hz). ^{19}F NMR (376 MHz, Acetone-d_6) δ -114.84 (td, *J* = 9.5, 5.9 Hz), -149.79 (d, *J* = 45.9 Hz). ^{11}B NMR (128 MHz, Acetone-d_6) δ 10.79. **HRMS (EI) m/z** calcd for

$C_{13}H_{13}BF_2INO_4Na$ $[M+Na]^+$: 445.9845, found: 445.9851. **ATR-FTIR (cm^{-1}):** 2998, 2944, 1760, 1595, 1450, 1340, 1340, 1283, 1292, 1206, 1050, 1033, 1007, 864, 787, 698, 669, 553, 459, 405.



4d

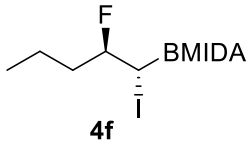
Following general procedure A (the reaction was stirred at room temperature for 1 min), **4d** was obtained in 75% yield (67 mg) as a white solid after removing the solvent. R*f* (dichloromethane/EtOAc 1:1): 0.30. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.49 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 5.54 (dd, *J* = 46.0, 8.2 Hz, 1H), 4.41 (d, *J* = 17.4 Hz, 1H), 4.29 (dd, *J* = 17.2, 2.4 Hz, 1H), 4.18 – 4.05 (m, 4H), 4.00 (d, *J* = 17.7 Hz, 1H), 3.11 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.25, 168.20, 137.8 (d, *J* = 20.9 Hz), 131.9, 127.9 (d, *J* = 5.8 Hz), 127.7, 119.2, 94.8 (d, *J* = 171.0 Hz), 63.9, 62.54, 62.50, 46.7, 22.2. ^{19}F NMR (376 MHz, DMSO-d_6) δ -146.06 (d, *J* = 44.9 Hz). ^{11}B NMR (128 MHz, DMSO-d_6) δ 11.02. **HRMS (EI) m/z** calcd for $C_{15}H_{15}BFIN_2O_4Na$ $[M+Na]^+$: 467.0049, found: 467.0053. **ATR-FTIR (cm^{-1}):** 3003, 2961, 1773, 1747, 1343, 1309, 1079, 1038, 866, 692, 574, 555, 451.



4e

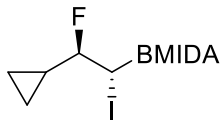
Following general procedure A (the reaction was stirred at room temperature for 7 min), **4e** was obtained in 96% yield (91 mg) as a white solid after removing the solvent. R*f* (dichloromethane/EtOAc 1:1): 0.30. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.69 – 7.55 (m, 2H), 7.43 – 7.33 (m, 3H), 5.89 (d, *J* = 43.7 Hz, 1H), 4.61 (d, *J* = 12.3 Hz, 1H), 4.48 (d, *J* = 12.3 Hz, 1H), 4.36 (d, *J* = 17.1 Hz, 1H), 4.31 (dd, *J* = 17.0, 1.3 Hz, 1H), 4.22 (d, *J* = 16.9 Hz, 1H), 4.21 (d, *J* = 17.1 Hz, 1H), 3.29 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 170.2, 167.8, 167.7, 137.1 (d, *J* = 22.2 Hz), 129.7, 129.5 (d, *J* = 7.3 Hz), 128.4, 97.1 (d, *J* = 177.6 Hz), 67.8, 65.1, 64.4, 64.3, 47.7 (d, *J* = 5.6 Hz), 20.8. ^{19}F NMR (376 MHz, Acetone-d_6) δ -160.20. ^{11}B NMR (128 MHz, Acetone-d_6) δ 11.03. **HRMS (EI) m/z** calcd for $C_{16}H_{18}BFINO_6Na$ $[M+Na]^+$: 500.0151,

found: 500.0148. **ATR-FTIR (cm^{-1}):** 3006, 2960, 2922, 1765, 1732, 1738, 1453, 1340, 1283, 1225, 1036, 964, 860, 761, 701, 588, 450.



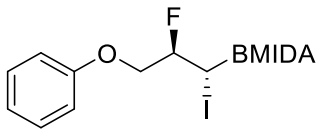
4f

Following general procedure A (the reaction was stirred at room temperature for 1 min), **4f** was obtained in 91% yield (67 mg) as a white solid after removing the solvent. R*f* (dichloromethane/EtOAc 1:1): 0.36. ^{1}H NMR (400 MHz, Acetone-d_6) δ 4.35 (dd, *J* = 17.1, 4.6 Hz, 2H), 4.29 – 4.09 (m, 3H), 3.92 (dd, *J* = 11.1, 4.1 Hz, 1H), 3.33 (s, 3H), 1.91 – 1.62 (m, 2H), 1.61 – 1.40 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.0, 167.9, 94.4 (d, *J* = 175.8 Hz), 64.6, 63.7, 46.6, 38.1 (d, *J* = 20.7 Hz), 19.2 (d, *J* = 2.5 Hz), 14.2. ^{19}F NMR (376 MHz, Acetone-d_6) δ -165.85 (t, *J* = 42.5 Hz). ^{11}B NMR (128 MHz, Acetone-d_6) δ 10.39. **HRMS (EI) m/z** calcd for $C_{10}H_{16}BFINO_4Na$ [M+Na]$^+$: 394.0095, found: 394.0081. **ATR-FTIR (cm^{-1}):** 2996, 2959, 2933, 2911, 2876, 1759, 1449, 1339, 1295, 1099, 1029, 1007, 946, 856.



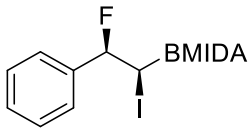
4g

Following general procedure A (the reaction was stirred at room temperature for 1 min), **4g** was obtained in 62% yield (46 mg) as a white solid after recrystallization. R*f* (dichloromethane/EtOAc 1:1): 0.35. ^{1}H NMR (500 MHz, Acetone-d_6) δ 4.35 (d, *J* = 17.2 Hz, 2H), 4.33 (d, *J* = 16.9 Hz, 1H), 4.21 (d, *J* = 16.8 Hz, 1H), 4.14 (d, *J* = 17.2 Hz, 1H), 3.94 (dd, *J* = 10.3, 3.3 Hz, 1H), 3.53 (ddd, *J* = 47.2, 8.3, 3.8 Hz, 1H), 3.33 (s, 3H), 1.35 – 1.21 (m, 1H), 0.66 – 0.56 (m, 2H), 0.57 – 0.44 (m, 2H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 168.1, 168.0, 98.4 (d, *J* = 176.6 Hz), 64.5, 63.7, 46.5, 16.7 (d, *J* = 25.5 Hz), 4.9 (d, *J* = 9.7 Hz), 3.5 (d, *J* = 3.2 Hz). ^{19}F NMR (376 MHz, Acetone-d_6) δ -153.74 (d, *J* = 47.2 Hz). ^{11}B NMR (128 MHz, Acetone-d_6) δ 10.36. **HRMS (EI) m/z** calcd for $C_{10}H_{14}BFINO_4Na$ [M+Na]$^+$: 391.9939, found: 391.9943. **ATR-FTIR (cm^{-1}):** 3010, 2920, 1771, 1756, 1331, 1277, 1234, 1070, 1015, 1003, 955, 852, 721, 658, 542, 483.



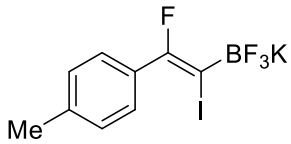
4h

Following general procedure A (the reaction was stirred at room temperature for 2 min), **4h** was obtained in 93% yield (81 mg) as a white solid after removing the solvent. R*f* (dichloromethane/EtOAc 1:1): 0.39. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.31 (dd, *J* = 8.8, 7.3 Hz, 2H), 6.97 (t, *J* = 8.5 Hz, 3H), 4.91 – 4.64 (m, 1H), 4.41 (ddd, *J* = 15.1, 10.3, 3.4 Hz, 4H), 4.26 (d, *J* = 17.1 Hz, 1H), 4.17 (d, *J* = 17.2 Hz, 1H), 4.02 (dd, *J* = 10.3, 5.6 Hz, 1H), 3.37 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 167.8, 159.6, 130.4, 122.0, 115.5, 93.5 (d, *J* = 179.9 Hz), 72.0 (d, *J* = 20.9 Hz), 64.9, 63.90, 63.88, 46.9. ^{19}F NMR (376 MHz, Acetone-d_6) δ -159.44 – -181.89 (m). ^{11}B NMR (128 MHz, Acetone-d_6) δ 10.57. **HRMS (EI) m/z** calcd for $C_{14}H_{16}BFINO_5Na$ $[M+Na]^+$: 458.0045, found: 458.0045. **ATR-FTIR (cm^{-1}):** 3023, 2949, 1761, 1485, 1281, 1241, 1047, 1034, 1024, 948, 819, 506.



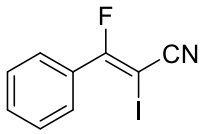
4i

Following general procedure A (the reaction was stirred at room temperature for 2 min), **4i** was obtained in 95% yield (77 mg) as a light yellow solid after removing the solvent. R*f* (dichloromethane/EtOAc 1:1): 0.40. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.43 – 7.36 (m, 2H), 7.32 (m, 3H), 5.47 (d, *J* = 45.9 Hz, 1H), 4.44 (d, *J* = 17.3 Hz, 1H), 4.30 (d, *J* = 17.1 Hz, 1H), 4.13 (d, *J* = 17.4 Hz, 1H), 4.03 (d, *J* = 17.1 Hz, 1H), 3.91 (dd, *J* = 43.6, 1.7 Hz, 1H), 3.09 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 168.4, 168.2, 141.3 (d, *J* = 20.9 Hz), 127.9, 127.6, 124.7 (d, *J* = 8.6 Hz), 92.0 (d, *J* = 177.6 Hz), 63.1, 62.8, 46.1. ^{19}F NMR (376 MHz, Acetone-d_6) δ -181.02 – -181.60 (m). ^{11}B NMR (128 MHz, Acetone-d_6) δ 10.66. **HRMS (EI) m/z** calcd for $C_{13}H_{14}BFINO_4Na$ $[M+Na]^+$: 427.9939, found: 427.9940.



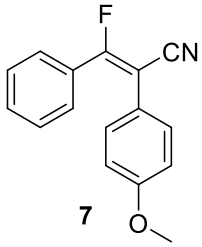
5

The product **5** was obtained in 99% yield (73 mg) as a white solid after recrystallization. R*f* (dichloromethane/EtOAc 1:1): 0.08 ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 157.32 (d, *J* = 244.1 Hz), 139.06, 134.64 (d, *J* = 35.0 Hz), 130.24 (d, *J* = 3.2 Hz), 128.98, 21.27. ^{19}F NMR (376 MHz, Acetone-d_6) δ -61.54 – -94.73 (m), -138.90 (q, *J* = 43.9 Hz). ^{11}B NMR (128 MHz, Acetone-d_6) δ 1.36 (q, *J* = 42.3 Hz). **HRMS (EI) m/z** calcd for $C_9H_7BF_4I$ $[M-K]^-$: 328.9629, found: 328.9625.



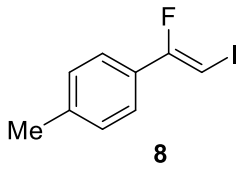
6

The product **6** was obtained in 65% NMR yield (45% isolated yield, 37 mg) as a light yellow oil. R*f* (petroleum ether): 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.61 (d, *J* = 281.3 Hz), 132.79, 129.31 (d, *J* = 5.7 Hz), 128.91 (d, *J* = 25.3 Hz), 128.68, 115.20 (d, *J* = 4.1 Hz), 34.88 (d, *J* = 30.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -55.27.



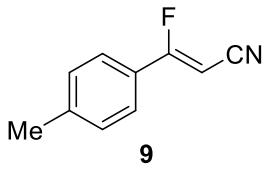
7

The product **7** was obtained in 70% yield (18 mg) as a colorless oil. R*f* (petroleum ether/EtOAc 20:1): 0.22. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.3 Hz, 1H), 7.27 (d, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.7 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 3.73 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4 (d, *J* = 270.3 Hz), 160.4, 131.7, 130.8 (d, *J* = 2.9 Hz), 129.2 (d, *J* = 25.6 Hz), 128.7, 128.7, 122.0 (d, *J* = 3.8 Hz), 115.9 (d, *J* = 3.2 Hz), 114.8, 96.3 (d, *J* = 21.2 Hz), 55.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.15. **HRMS (EI) m/z** calcd for $C_{16}H_{12}FNONa$ $[M+Na]^+$: 276.0795, found: 276.0790.



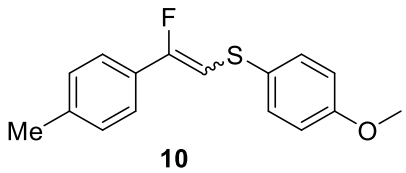
8

The product **8**[7] was obtained in 50% yield (13 mg) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.99 (d, *J* = 34.6 Hz, 1H), 2.36 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -89.79 (d, *J* = 34.6 Hz).



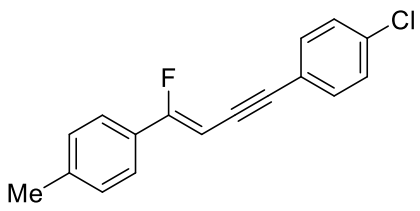
9

The product **9**[8] was obtained in 45% yield (8mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.35 (d, *J* = 32.8 Hz, 1H), 2.42 (s, 3H).



10

The product **10** was obtained in 65% yield (36 mg, E:Z = 1:1) as a colorless oil. R*f* (petroleum ether): 0.30. For *E*-isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.12 (d, *J* = 20.1 Hz, 1H), 3.80 (s, 3H), 2.39 (s, 3H). For *Z*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.0 Hz, 2H), 7.37 (d, *J* = 7.0 Hz, 2H), 7.16 (d, *J* = 7.7 Hz, 2H), 6.89 (d, *J* = 7.0 Hz, 2H), 6.06 (dd, *J* = 34.7, 1.6 Hz, 1H), 3.81 (s, 3H), 2.36 (s, 3H). For *E*-isomer: ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 156.8 (d, *J* = 247.2 Hz), 139.7, 131.6, 129.0, 128.3 (d, *J* = 28.5 Hz), 127.1 (d, *J* = 6.6 Hz), 126.5, 115.0, 104.3 (d, *J* = 38.3 Hz), 55.6, 21.6. For *Z*-isomer: ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5, 156.2 (d, *J* = 247.3 Hz), 139.0, 132.7, 129.4, 128.9 (d, *J* = 27.6 Hz), 125.7, 123.7 (d, *J* = 6.6 Hz), 115.0, 102.4 (d, *J* = 19.6 Hz), 55.6, 21.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -99.22 (d, *J* = 20.1 Hz), -110.92 (d, *J* = 34.7 Hz). **HRMS (EI) m/z** calcd for $C_{16}H_{15}FOSK$ $[M+K]^+$: 313.0459, found: 313.0479.



11

The product **11**[7] was obtained in 46% yield (18 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.9 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 5.73 (d, *J* = 33.2 Hz, 1H), 2.39 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.14 (d, *J* = 33.2 Hz).

vi. X-ray Crystal Structure Data

Crystal structure data for 2a:

Experimental

Single crystals of $C_{13}H_{12}NO_4IBF$ **2a** were colorless crystal. A suitable crystal was selected on a **XtaLAB Synergy R, DW system, HyPix** diffractometer. The crystal was kept at 99.99(10) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of 2a

Crystal Data for $C_{13}H_{12}NO_4IBF$ (*M* =402.95 g/mol): monoclinic, space group I2/a (no. 15), *a* = 27.8895(3) Å, *b* = 6.86390(10) Å, *c* = 34.3921(3) Å, *β* = 105.2960(10)°, *V* = 6350.48(13) Å^3, *Z* = 16, *T* = 99.99(10) K, μ(CuKα) = 16.076 mm^{-1}, *Dcalc* = 1.686 g/cm^3, 31719 reflections measured (5.328° ≤ 2Θ ≤ 154.028°), 6495 unique (R_{int} = 0.0332, R_{sigma} = 0.0232) which were used in all calculations. The final R_1 was 0.0310 (I > 2σ(I)) and wR_2 was 0.0844 (all data).

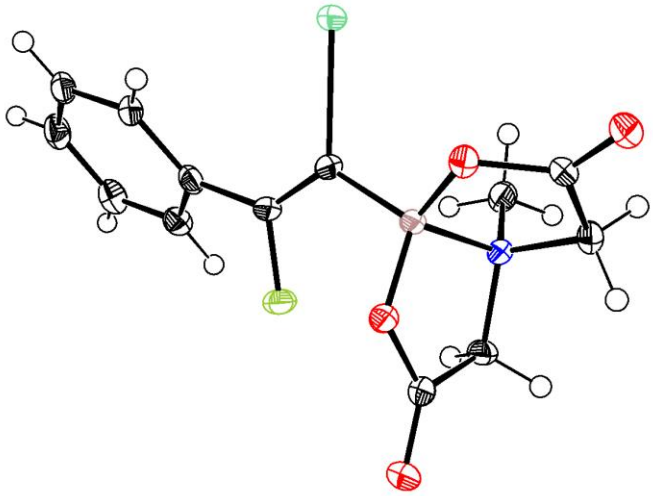


Fig. S2. Absolute configuration of **2a** (CCDC 1942792).

Table 1 Crystal data and structure refinement for 2a.	
Identification code	fanwx_190220_2
Empirical formula	$C_{13}H_{12}NO_4IBF$
Formula weight	402.95
Temperature/K	99.99(10)
Crystal system	monoclinic
Space group	I2/a
a/Å	27.8895(3)
b/Å	6.86390(10)
c/Å	34.3921(3)
α/°	90
β/°	105.2960(10)
γ/°	90
Volume/Å^3	6350.48(13)
Z	16
ρ_{calc}g/cm^3	1.686
μ/mm^{-1}	16.076
F(000)	3136.0
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.328 to 154.028
Index ranges	-35 ≤ h ≤ 34, -8 ≤ k ≤ 6, -43 ≤ l ≤ 43
Reflections collected	31719

Independent reflections	6495 [R_{int} = 0.0332, R_{sigma} = 0.0232]
Data/restraints/parameters	6495/0/381
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0310, wR_2 = 0.0820
Final R indexes [all data]	R_1 = 0.0324, wR_2 = 0.0844
Largest diff. peak/hole / e $Å^{-3}$	0.85/-1.26

Crystal structure data for 4b:

Experimental

Single crystals of $C_{14}H_{16}INO_4BF$ **4b** were colorless crystal. A suitable crystal was selected on a **XtaLAB Synergy R, DW system, HyPix** diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of 4b

Crystal Data for $C_{14}H_{16}INO_4BF$ (*M* =418.99 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 12.7883(2) Å, *b* = 11.1705(2) Å, *c* = 10.9261(2) Å, *β* = 102.020(2)°, *V* = 1526.59(5) $Å^3$, *Z* = 4, *T* = 100.00(10) K, μ(CuKα) = 16.743 mm^{-1}, *Dcalc* = 1.823 g/cm^3, 29253 reflections measured (7.068° ≤ 2Θ ≤ 154.102°), 3120 unique (R_{int} = 0.0461, R_{sigma} = 0.0205) which were used in all calculations. The final R_1 was 0.0309 (I > 2σ(I)) and wR_2 was 0.0870 (all data).

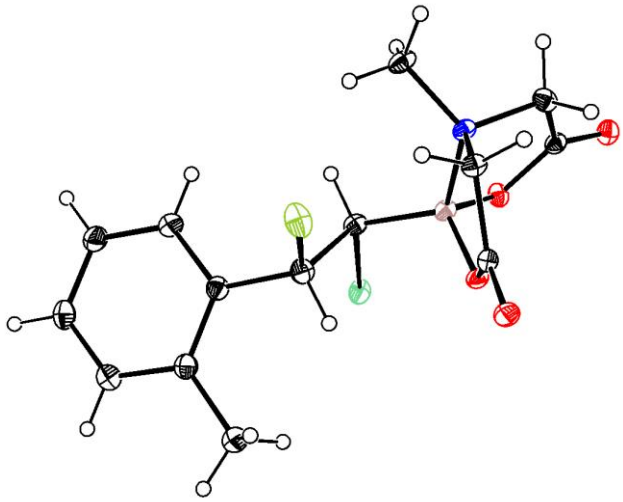


Fig. S3. Absolute configuration of **4b** (CCDC 1953148).

Table 1 Crystal data and structure refinement for 4b.	
Identification code	fanwx_190911_2
Empirical formula	$C_{14}H_{16}INO_4BF$
Formula weight	418.99
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.7883(2)
b/Å	11.1705(2)
c/Å	10.9261(2)
α/°	90
β/°	102.020(2)
γ/°	90
Volume/Å^3	1526.59(5)
Z	4
ρ_{calc}g/cm^3	1.823
μ/mm^{-1}	16.743
F(000)	824.0
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.068 to 154.102
Index ranges	-16 ≤ h ≤ 15, -13 ≤ k ≤ 12, -13 ≤ l ≤ 13

Reflections collected	29253
Independent reflections	3120 [R_{int} = 0.0461, R_{sigma} = 0.0205]
Data/restraints/parameters	3120/0/202
Goodness-of-fit on F^2	1.137
Final R indexes [I>=2σ (I)]	R_1 = 0.0309, wR_2 = 0.0862
Final R indexes [all data]	R_1 = 0.0322, wR_2 = 0.0870
Largest diff. peak/hole / e $Å^{-3}$	1.17/-1.02

Crystal structure data for 4j:

Experimental

Single crystals of $C_{13}H_{14}NO_4IBF$ **4j** were colorless crystal. A suitable crystal was selected on a **XtaLAB Synergy R, DW system, HyPix** diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of 4j

Crystal Data for $C_{13}H_{14}NO_4IBF$ (*M* =404.96 g/mol): orthorhombic, space group Pbca (no. 61), *a* = 12.6367(3) Å, *b* = 14.4997(3) Å, *c* = 15.6349(4) Å, *V* = 2864.76(12) $Å^3$, *Z* = 8, *T* = 100.00(10) K, μ(CuKα) = 17.818 mm^{-1}, *Dcalc* = 1.878 g/cm^3, 9854 reflections measured (10.876° ≤ 2Θ ≤ 152.32°), 2867 unique (R_{int} = 0.0739, R_{sigma} = 0.0577) which were used in all calculations. The final R_1 was 0.0631 (I > 2σ(I)) and wR_2 was 0.1931 (all data).

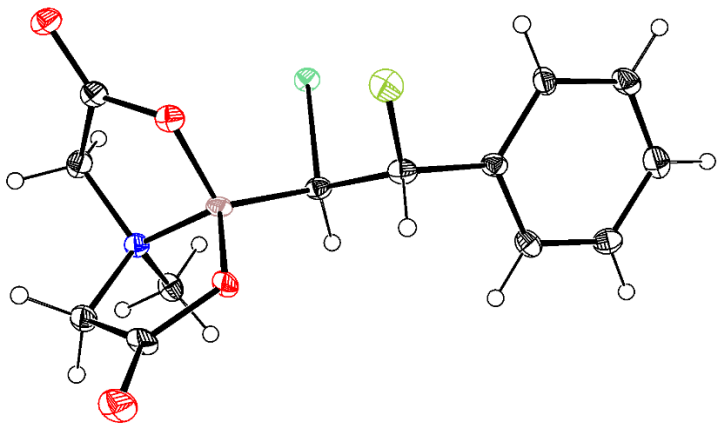


Fig. S4. Absolute configuration of **4j** (CCDC 1956650).

Table 1 Crystal data and structure refinement for fanwx_190923.	
Identification code	fanwx_190923
Empirical formula	$C_{13}H_{14}NO_4IBF$
Formula weight	404.96
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	12.6367(3)
b/Å	14.4997(3)
c/Å	15.6349(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2864.76(12)
Z	8
ρ_{calc}g/cm^3	1.878
μ/mm^{-1}	17.818
F(000)	1584.0
Crystal size/mm^3	0.2 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.876 to 152.32
Index ranges	-10 ≤ h ≤ 15, -17 ≤ k ≤ 17, -19 ≤ l ≤ 7
Reflections collected	9854
Independent reflections	2867 [R_{int} = 0.0739, R_{sigma} = 0.0577]
Data/restraints/parameters	2867/0/191
Goodness-of-fit on F^2	1.117
Final R indexes [I>=2σ (I)]	R_1 = 0.0631, wR_2 = 0.1825
Final R indexes [all data]	R_1 = 0.0688, wR_2 = 0.1931
Largest diff. peak/hole / e Å^{-3}	1.84/-3.04

III. References

1. S. J. Lee, T. M. Anderson and M. D. Burke, *Angew. Chem. Int. Ed.* 2010, **49**, 8860-8863.

2. J. M. Chan, G. W. Amarante and F. D. Toste, *Tetrahedron*, 2011, **67**, 4306-4312.

3. W. X. Lv, Y. F. Zeng, Q. Li, Y. Chen, D. H. Tan, L. Yang and H. Wang, Angew. Chem. Int. Ed., 2016, **55**, 10069-10073

4. Q. I. Churches, J. F. Hooper, C. A. Hutton, *J. Org. Chem*. 2015, **80**, 5428-5435.

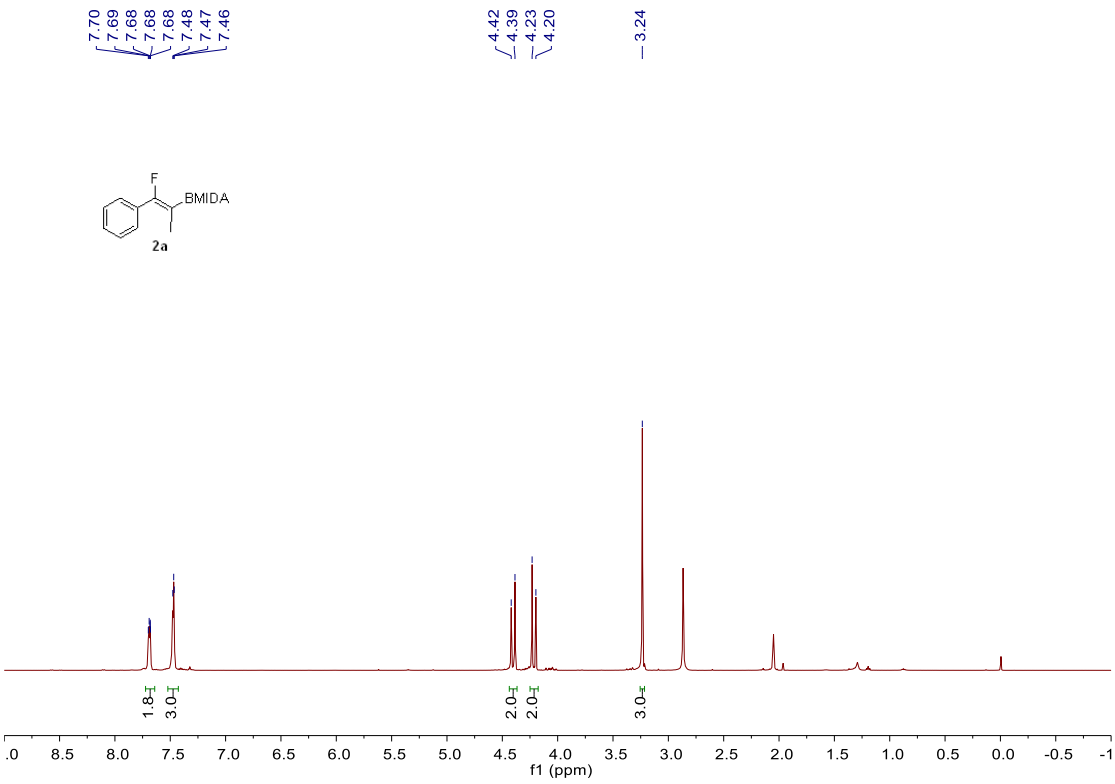
5. Y. F. Zeng, W. W. Ji, W. X. Lv, Y. Chen, D. H. Tan, Q. Li and H. Wang, *Angew. Chem. Int. Ed.*, 2017, **56**, 14707-14711

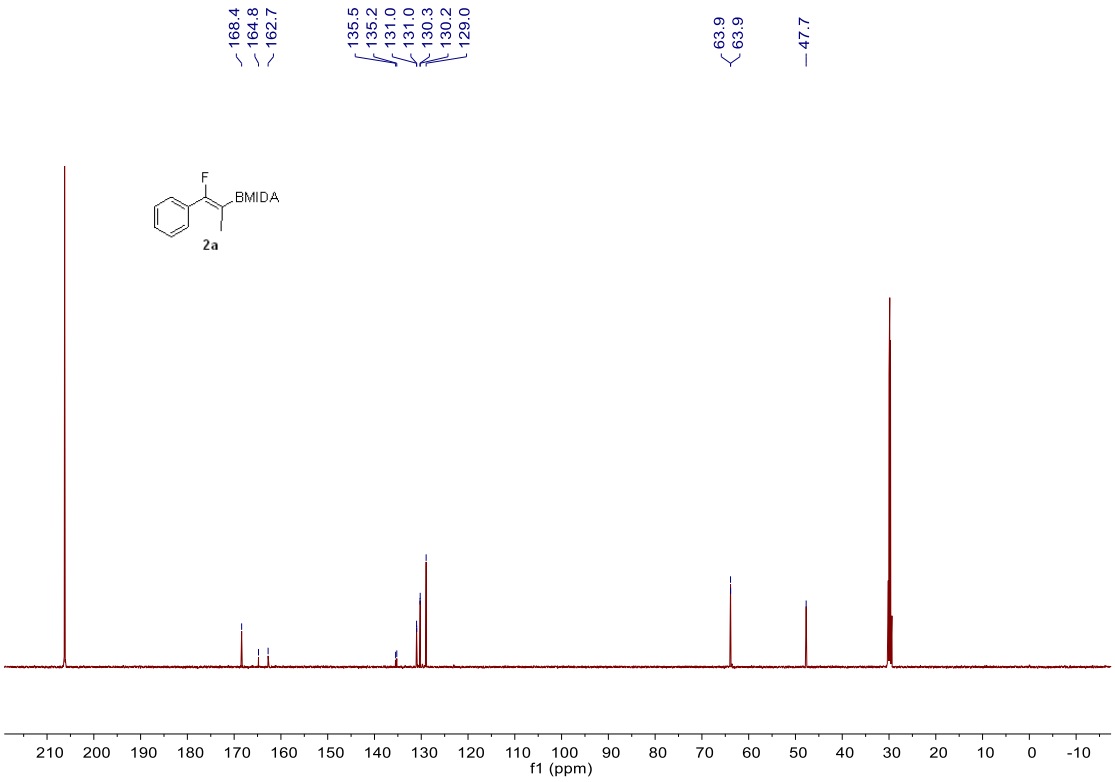
6. L. Pfeifer and V. Gouverneur, *Org. Lett.*, 2018, **20**, 1576-1579;

7. Y. Li, X. Liu, D. Ma, B. Liu and H. Jiang, *Adv. Synth. Catal.*, 2012, **354**, 2683-2688;

8. T. J. O'Connor, F. D. Toste, *ACS Cat.*, 2018, **8**, 5947-5951;

IV. NMR Spectra

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131.0
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130.2
129.0
63.9
63.9
47.7
F
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2a
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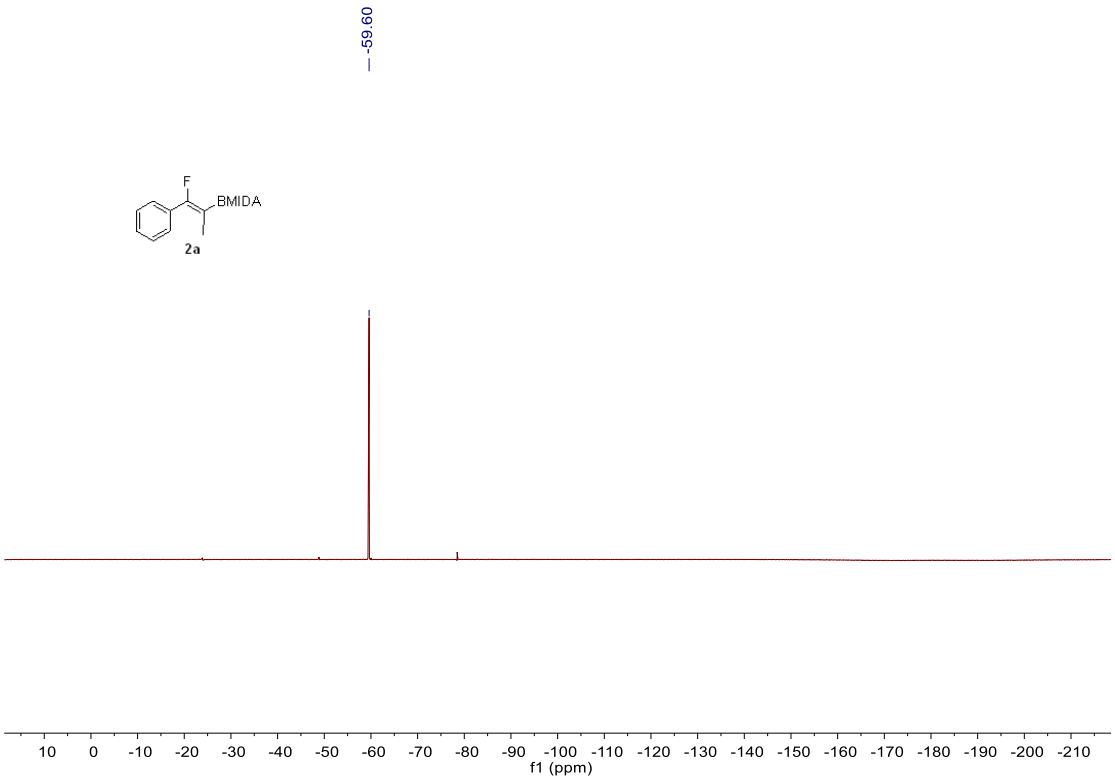
f1 (ppm)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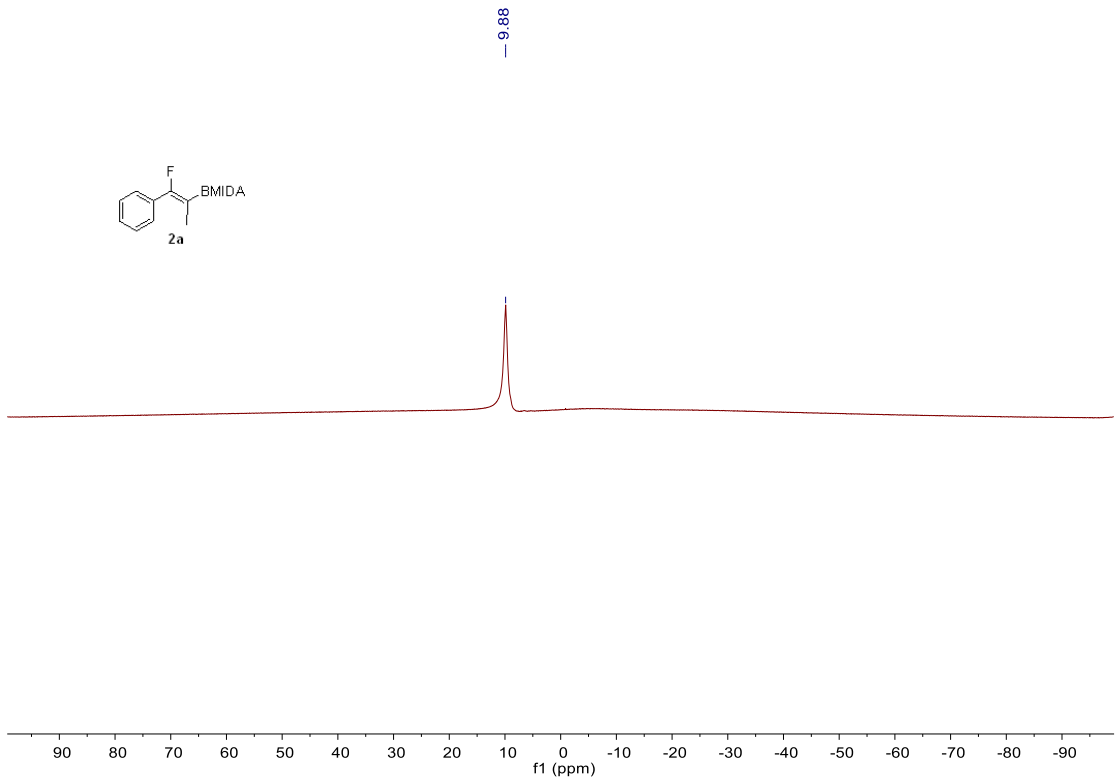
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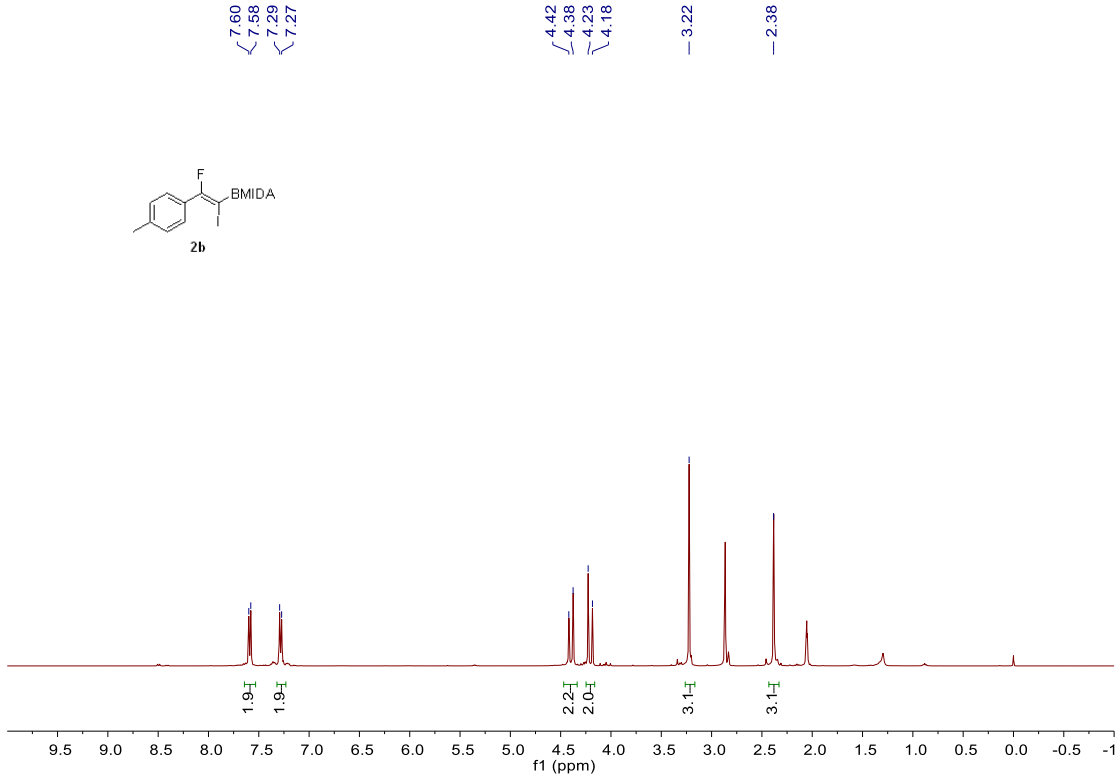
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1.9
2.2
2.0
3.1
3.1
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
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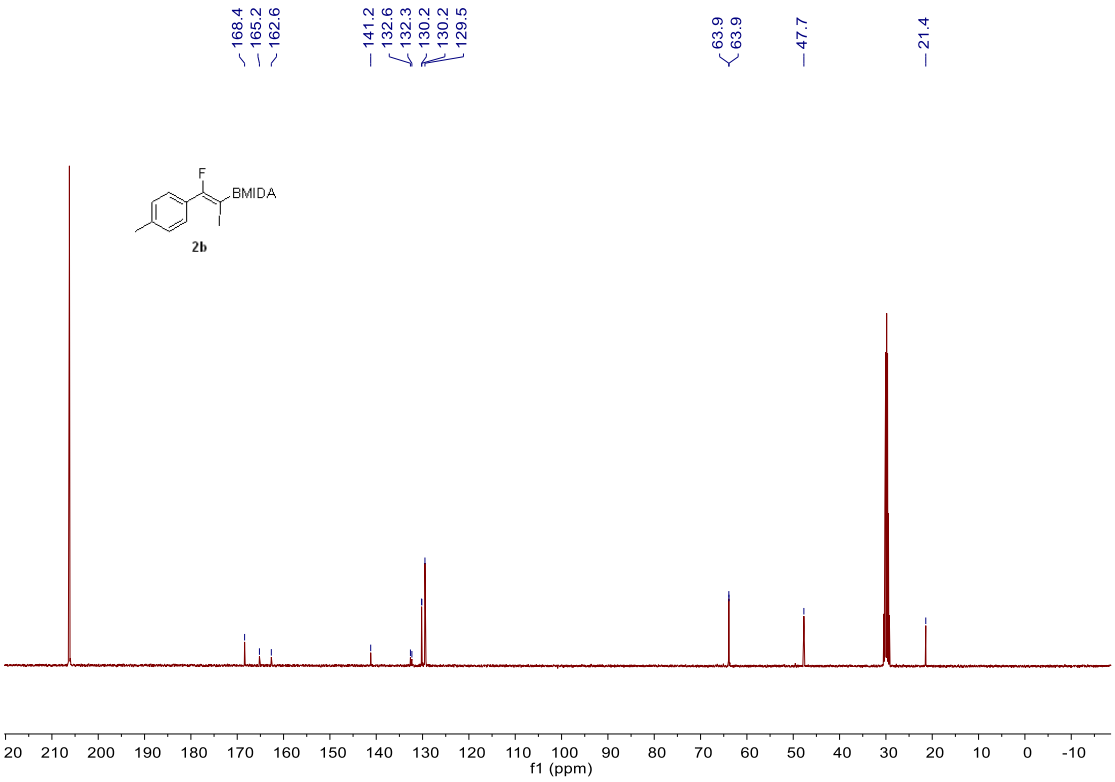
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63.9
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21.4
F
BMIDA
2b
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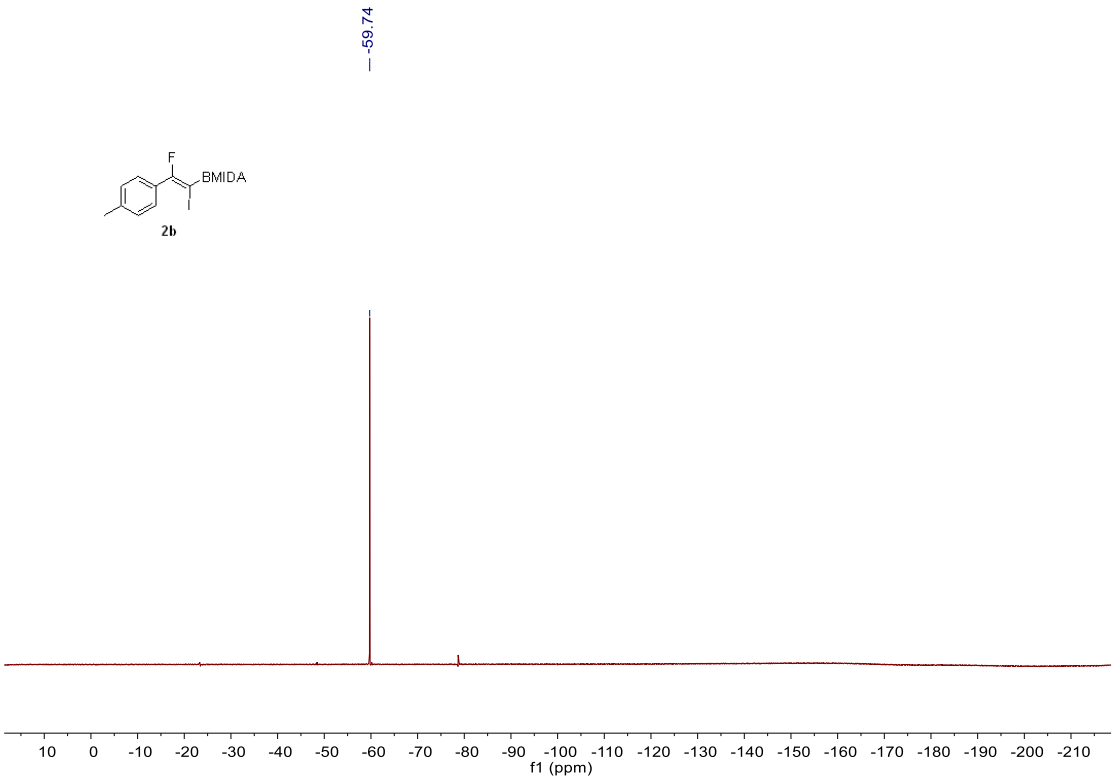
f1 (ppm)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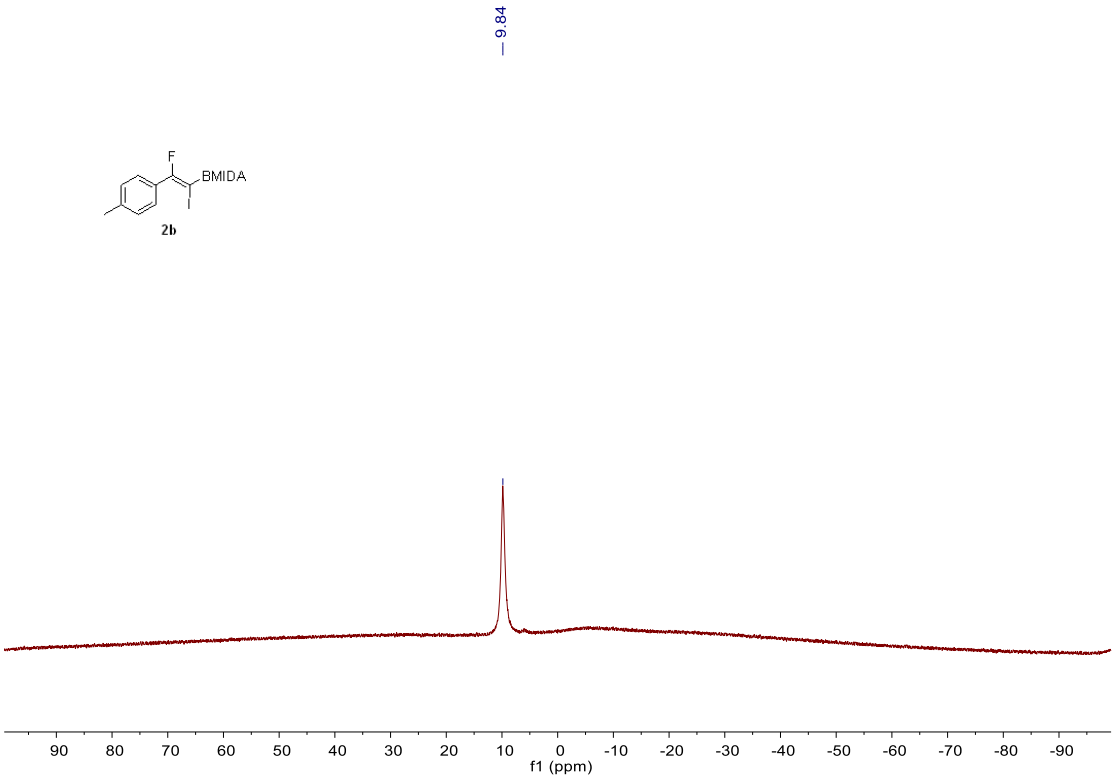
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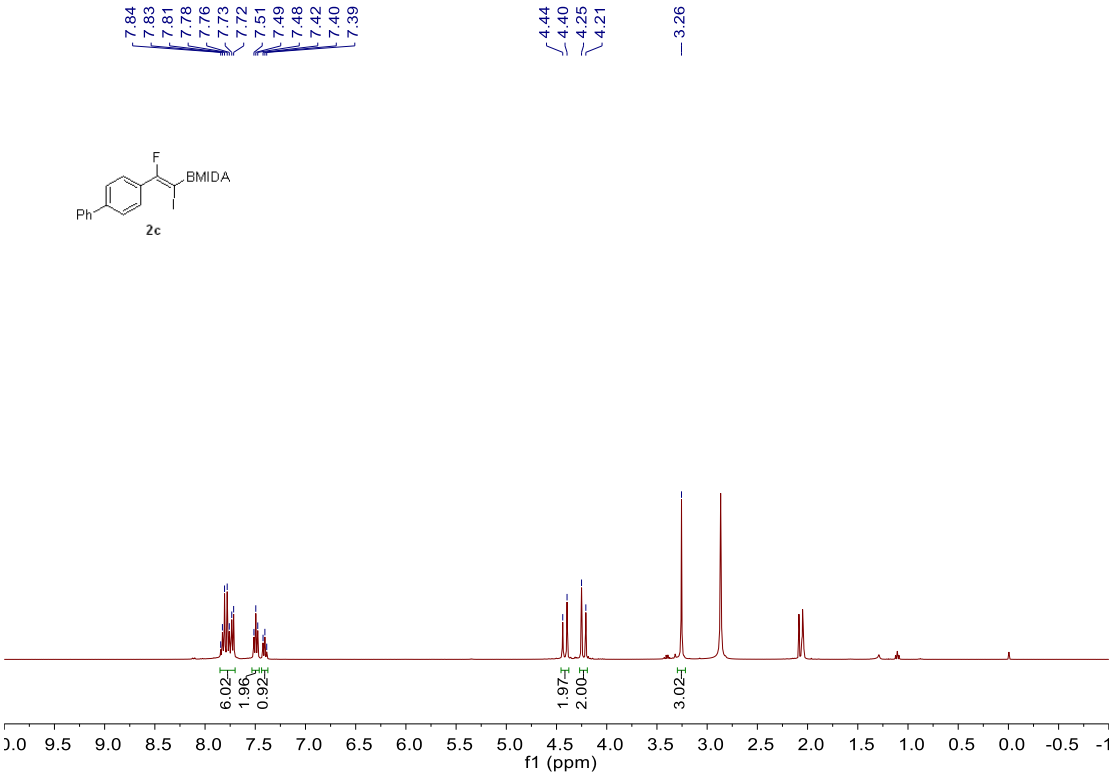
f1 (ppm)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4.40
4.25
4.21
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BMIDA
Ph
I
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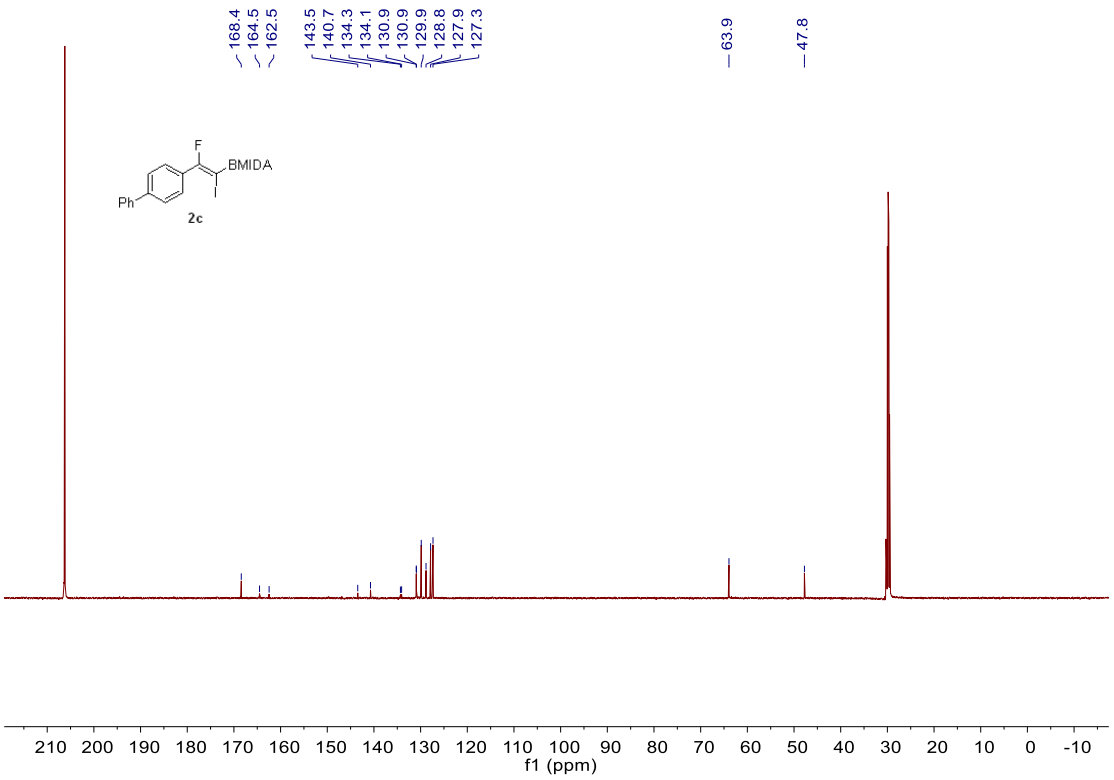
3.02
f1 (ppm)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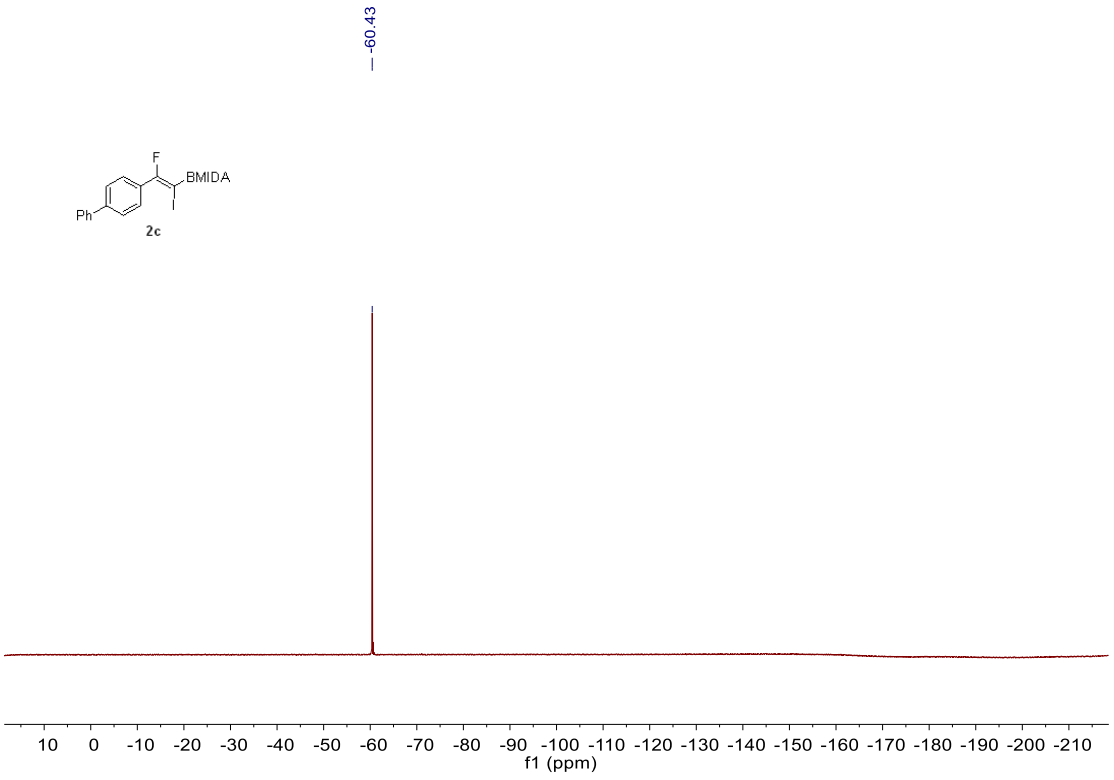
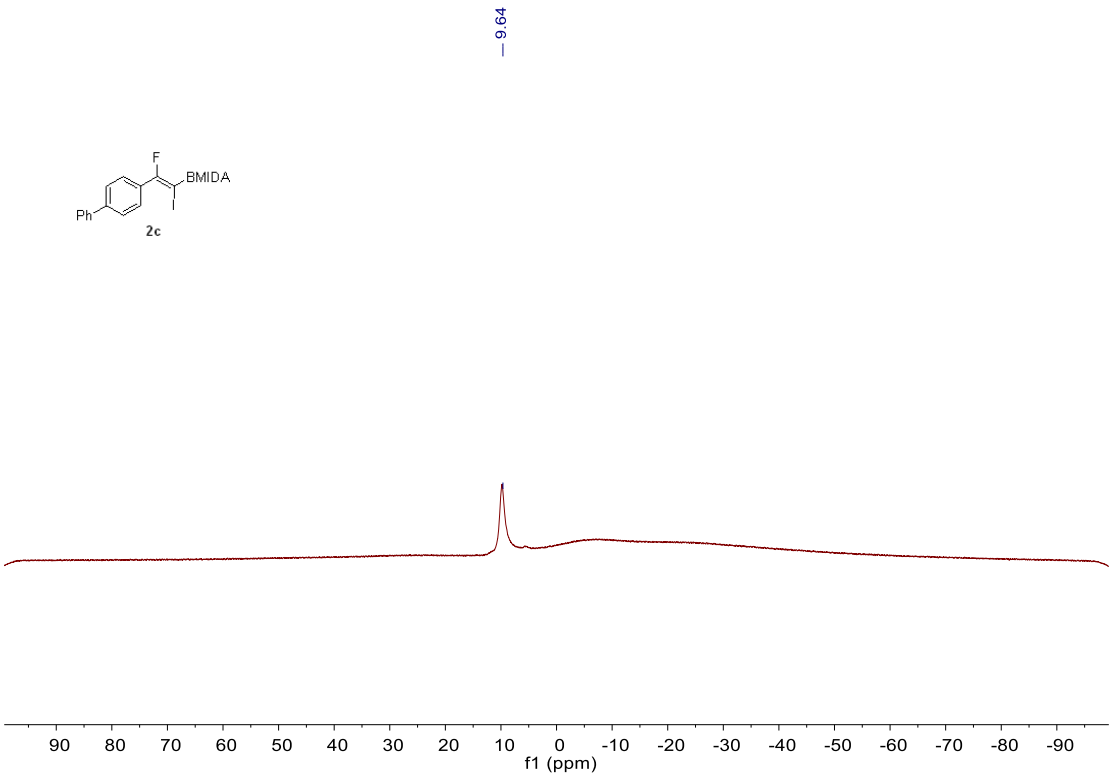
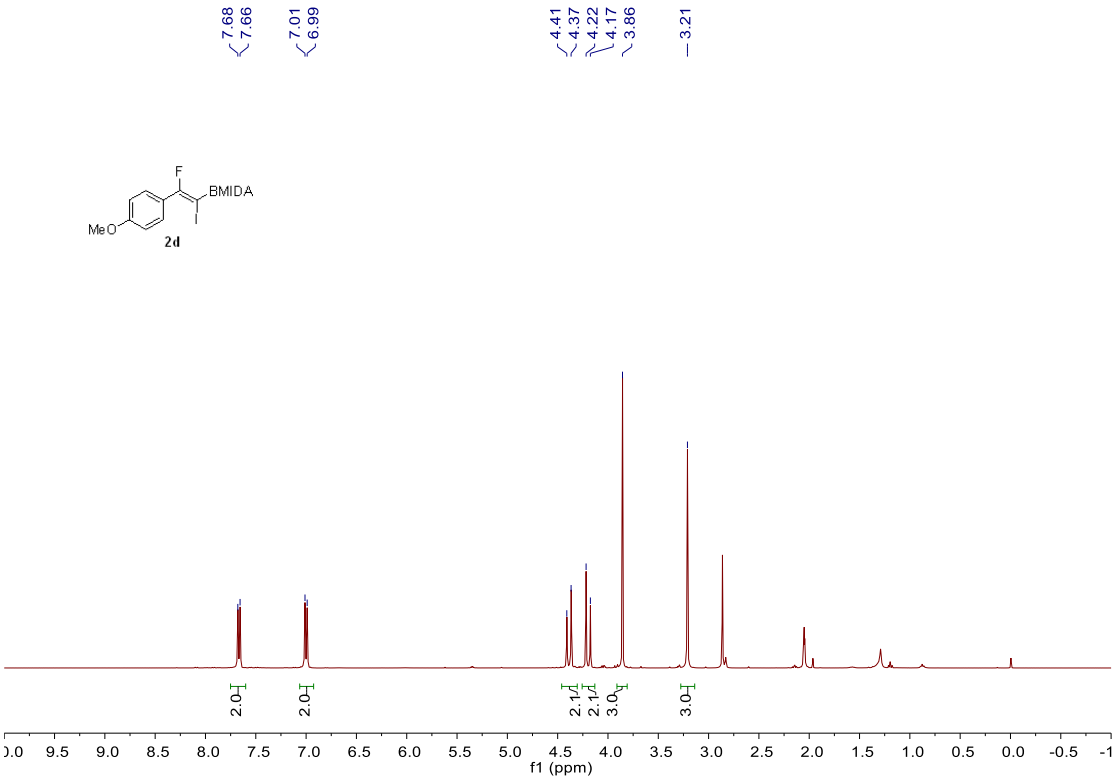
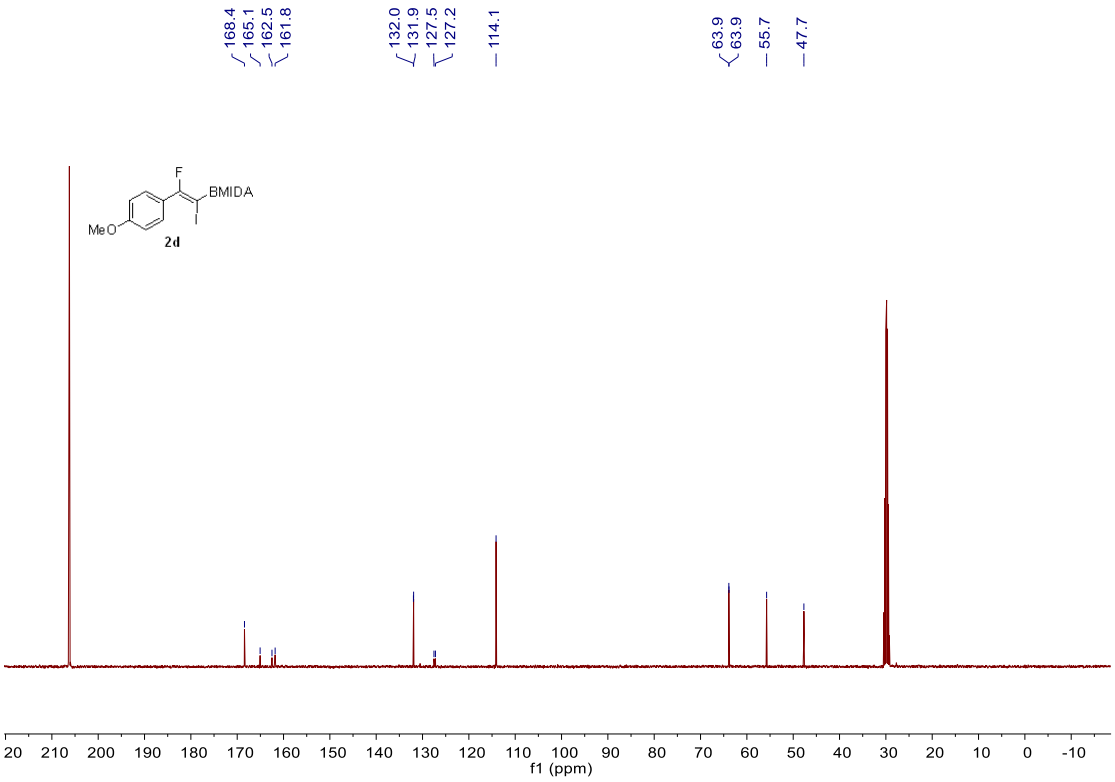
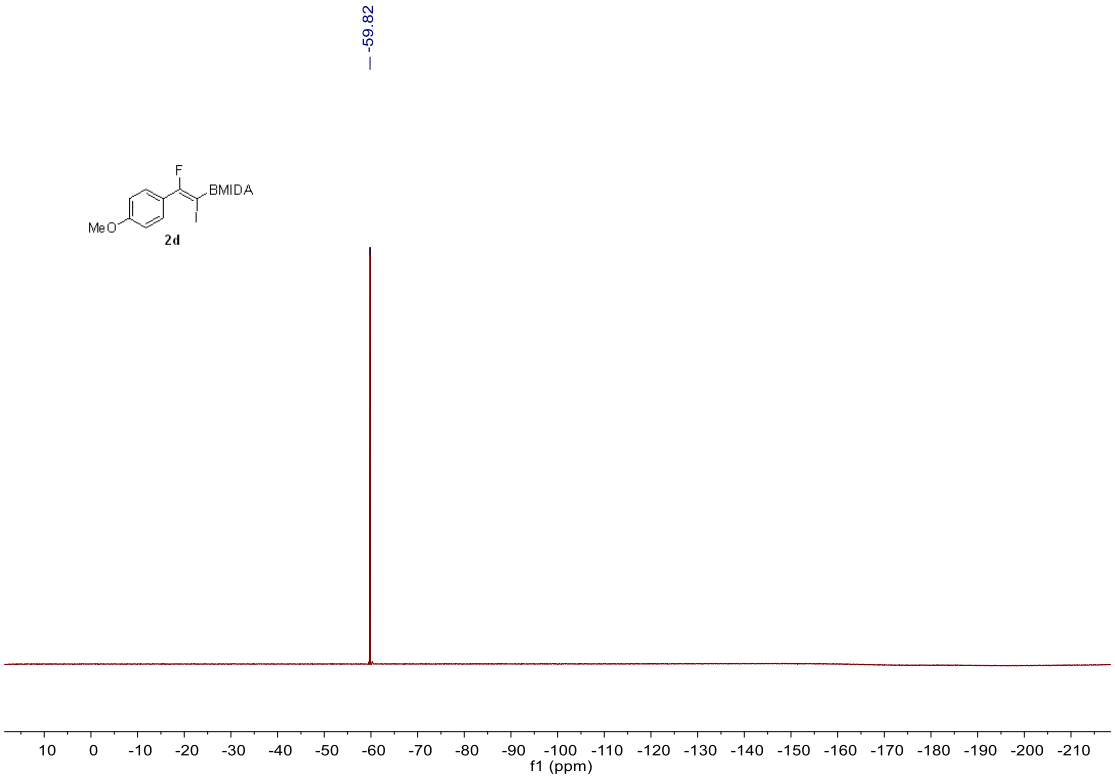
128.8
127.9
127.3
63.9
47.8
F
BMIDA
Ph
2c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

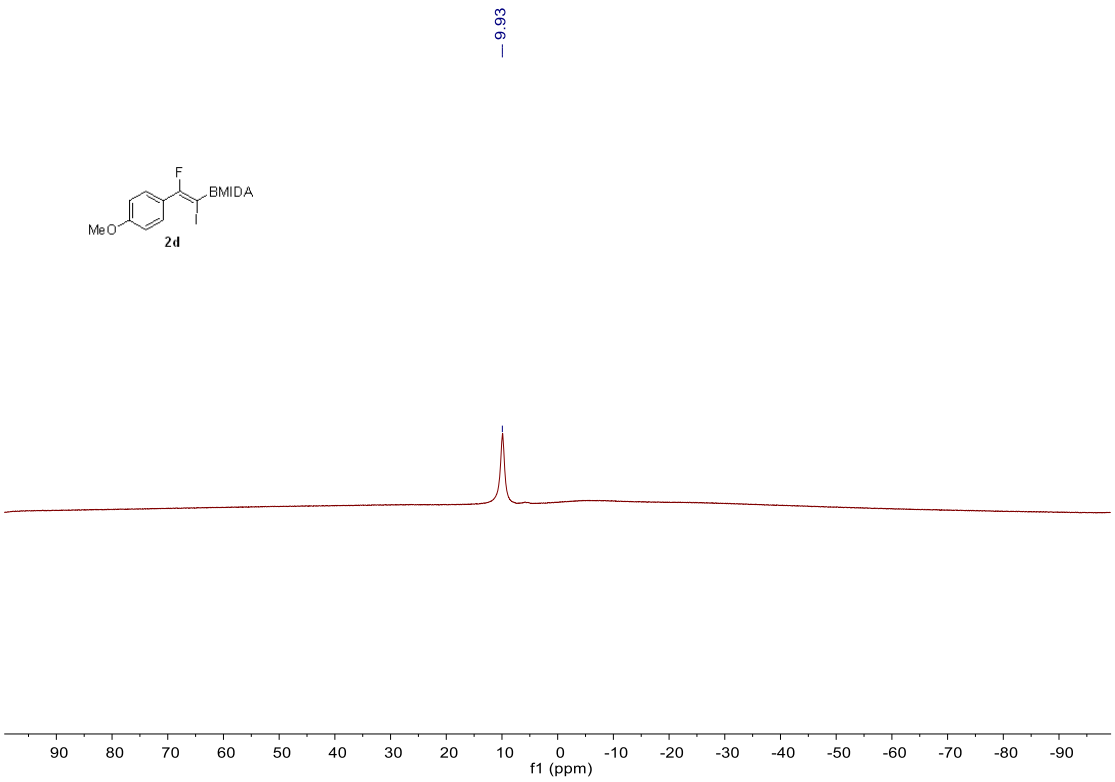

-60.43
F
BMIDA
Ph
2c
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

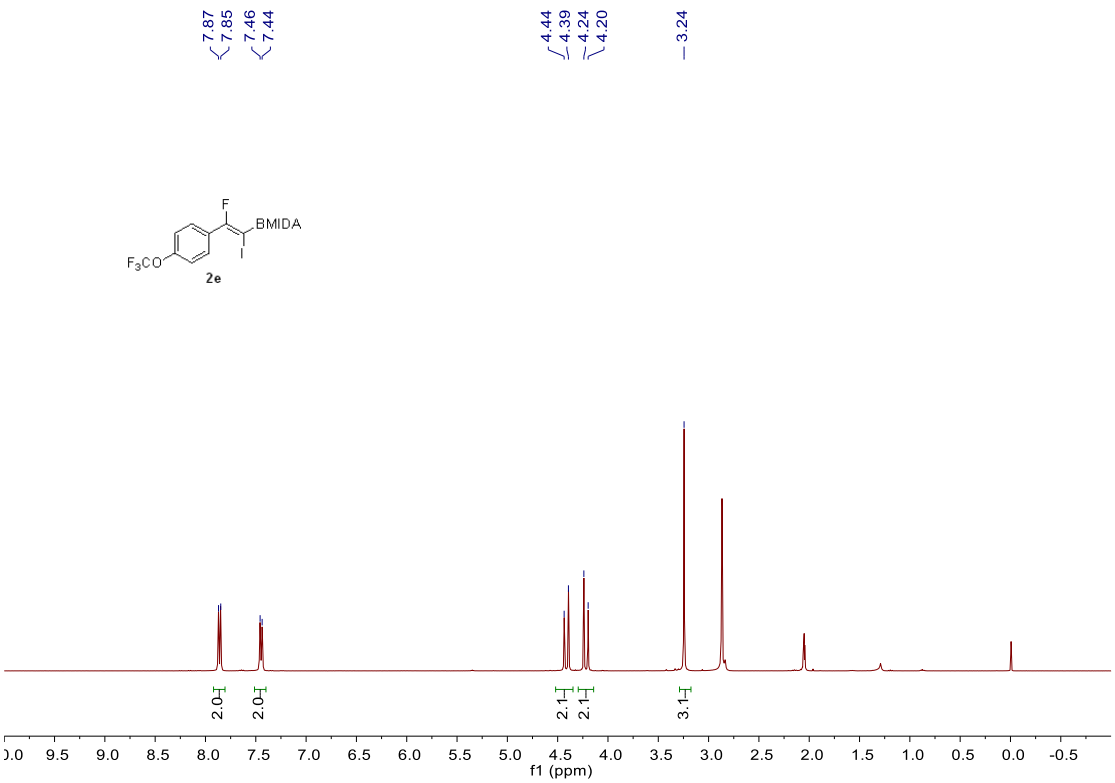

9.64
F
BMIDA
Ph
2c
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

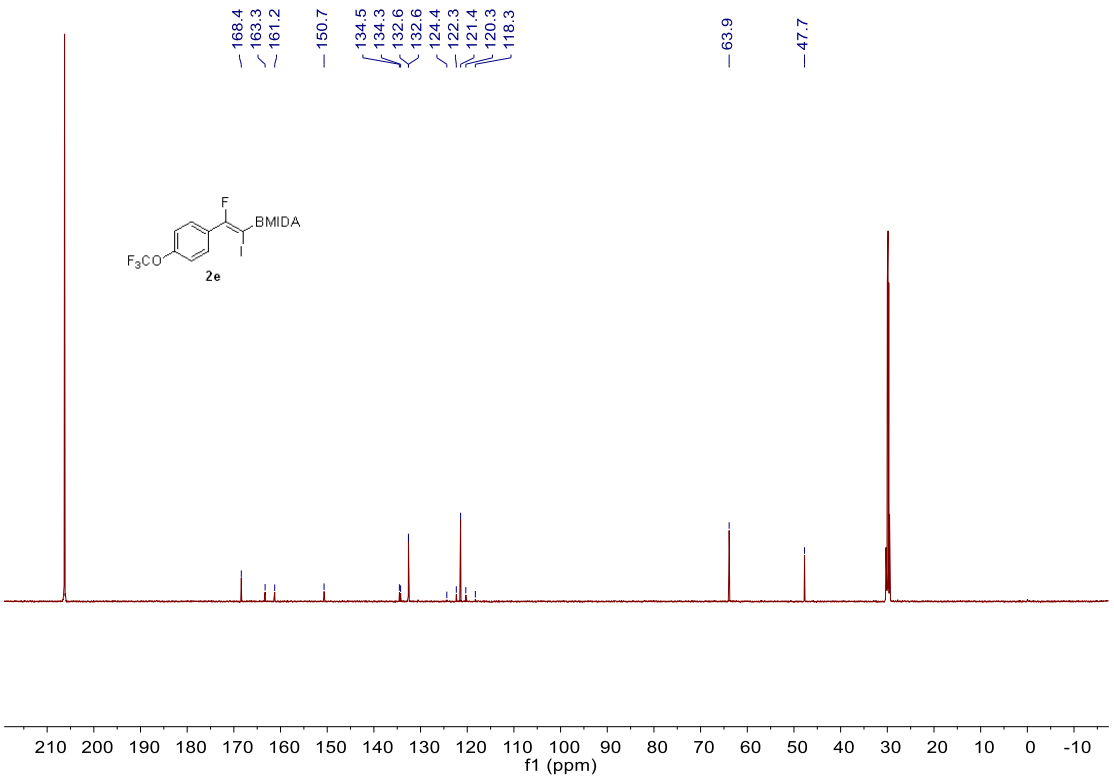

7.68
7.66
7.01
6.99
4.41
4.37
4.22
4.17
3.86
3.21
F
BMIDA
MeO
2d
2.0
2.0
2.1
2.1
3.0
3.0
f1 (ppm)

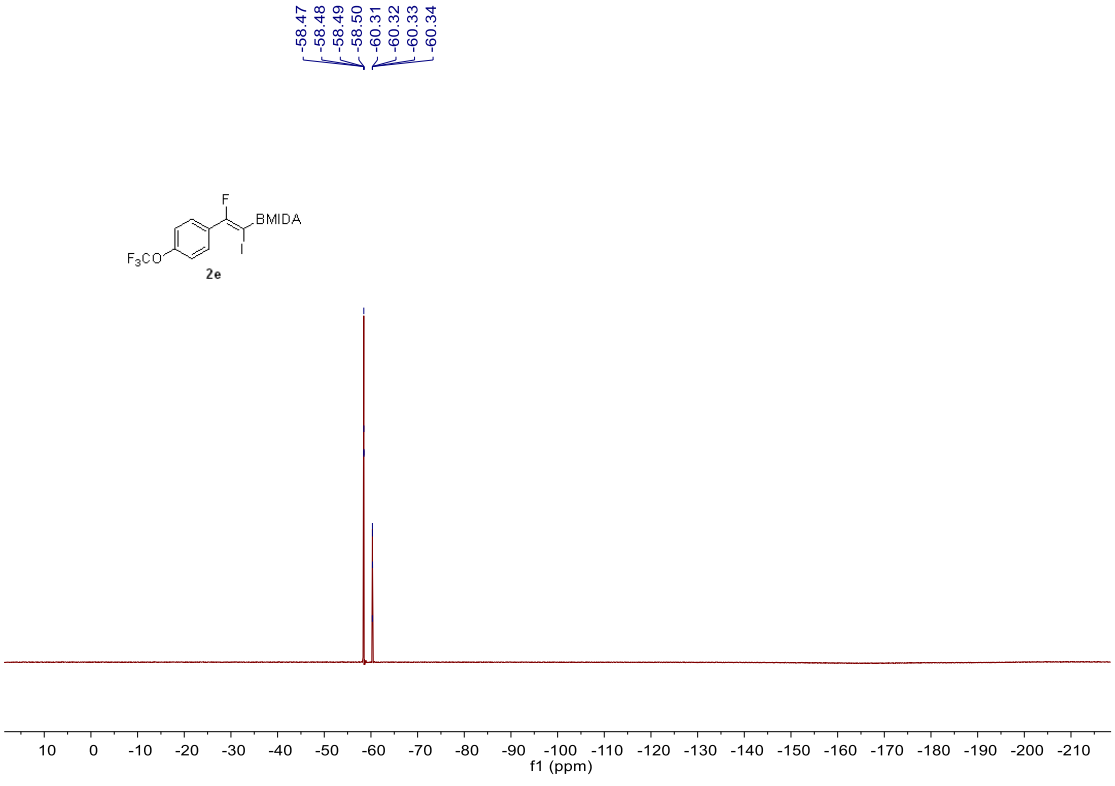

168.4
165.1
162.5
161.8
132.0
131.9
127.5
127.2
114.1
63.9
63.9
55.7
47.7
F
BMIDA
MeO
I
2d
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

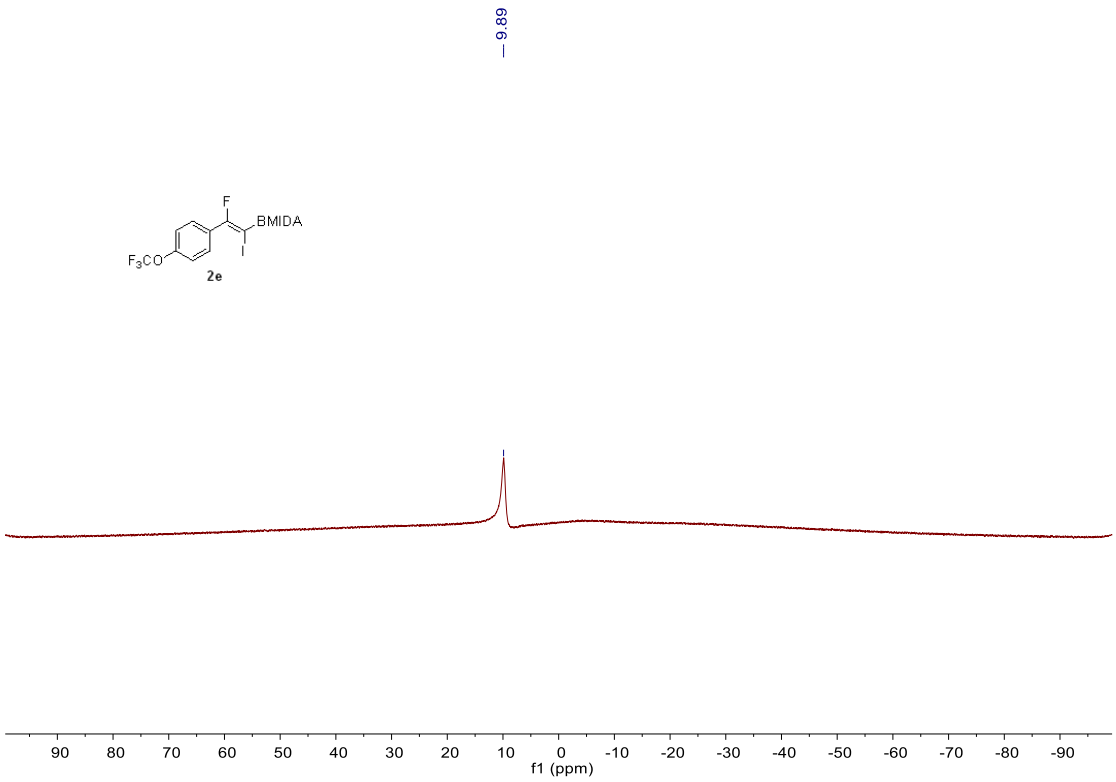

-59.82
F
BMIDA
MeO
I
2d
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

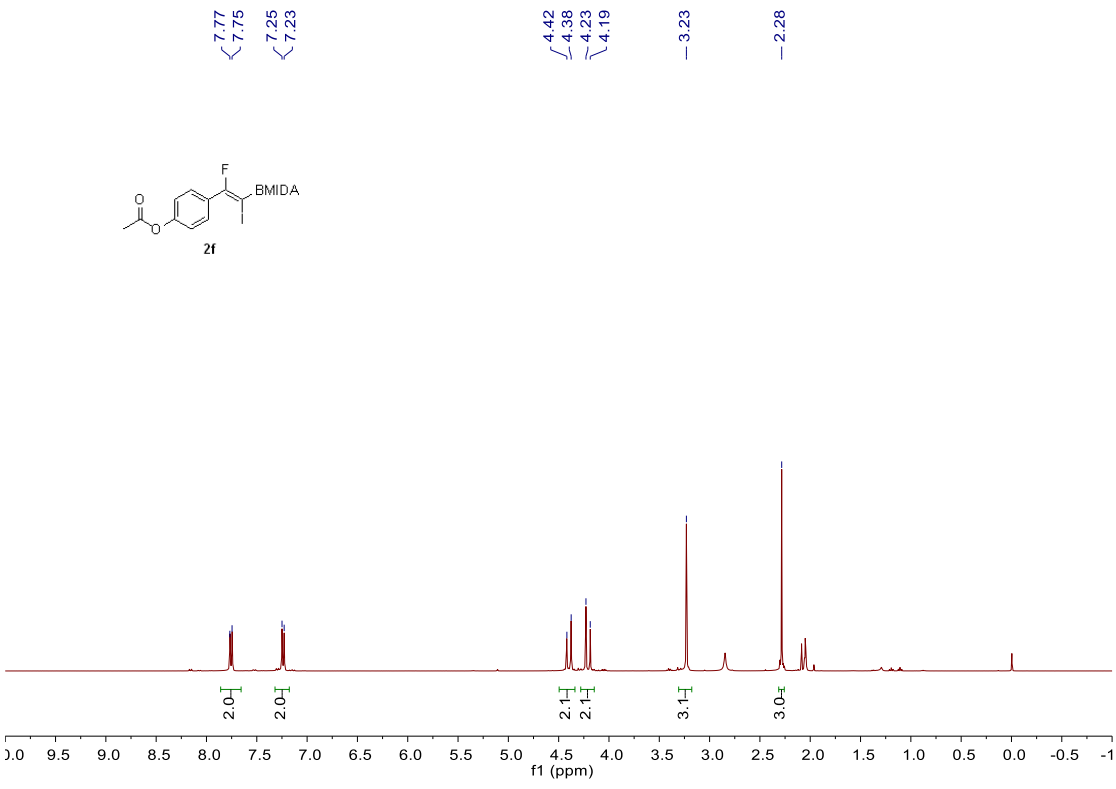

-9.93
F
BMIDA
I
MeO
2d
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

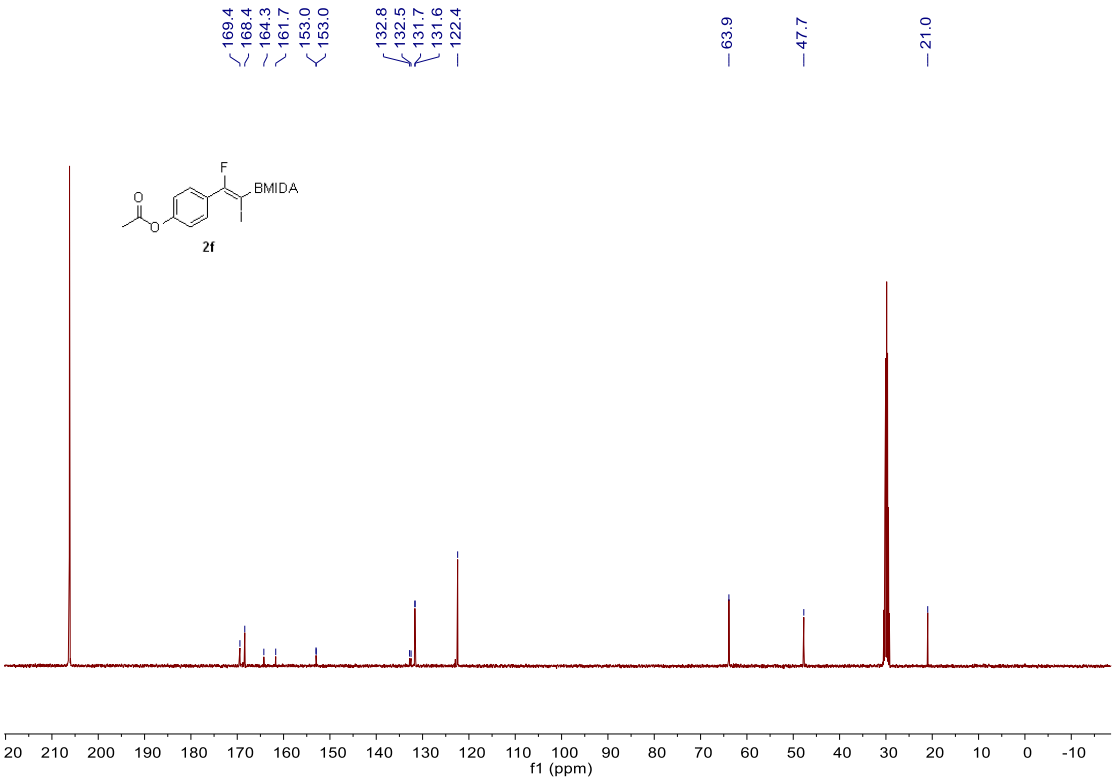

7.87
7.85
7.46
7.44
4.44
4.39
4.24
4.20
3.24
F
BMIDA
I
F3CO
2e
2.0
2.0
2.1
2.1
3.1
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

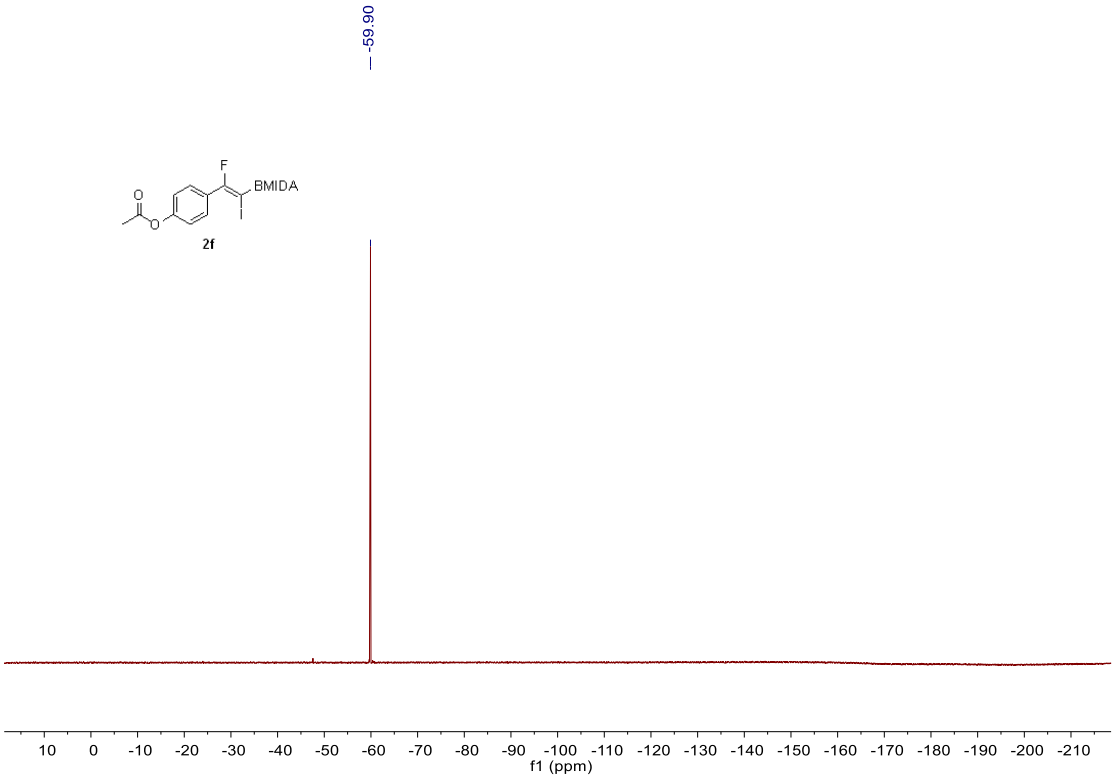

168.4
163.3
161.2
150.7
134.5
134.3
132.6
132.6
124.4
122.3
121.4
120.3
118.3
63.9
47.7
F
BMIDA
I
F3CO
2e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

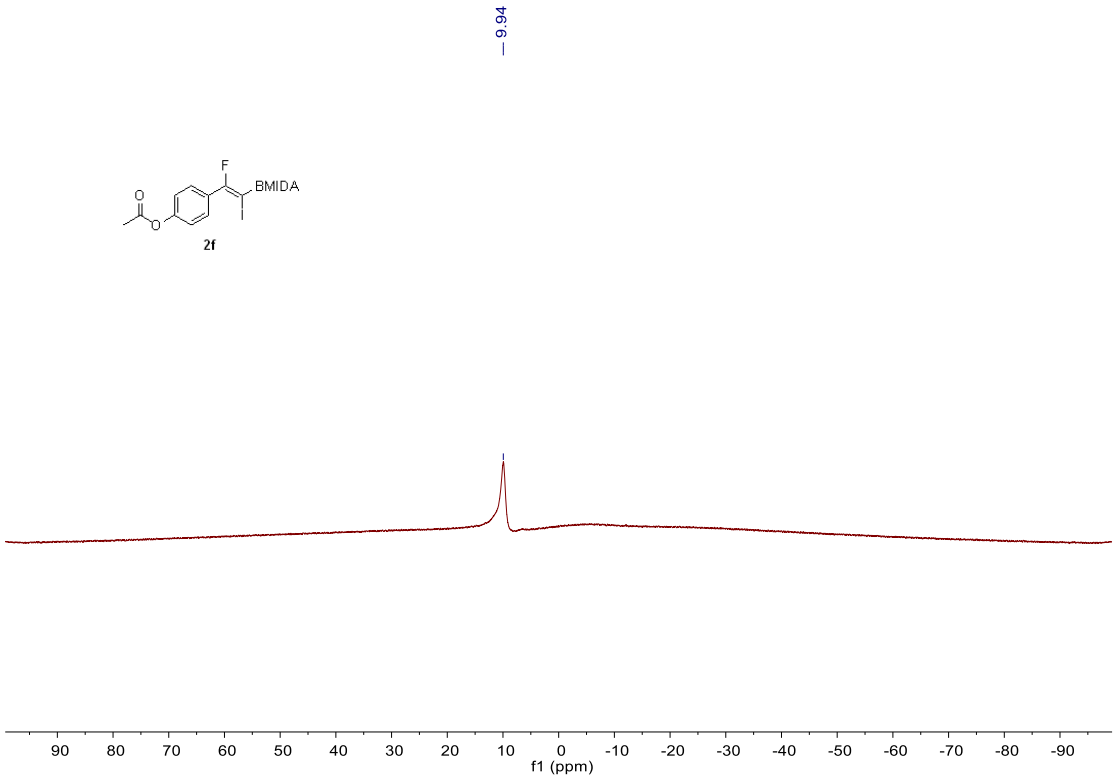

-58.47
-58.48
-58.49
-58.50
-60.31
-60.32
-60.33
-60.34
F
BMIDA
I
F3CO
2e
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

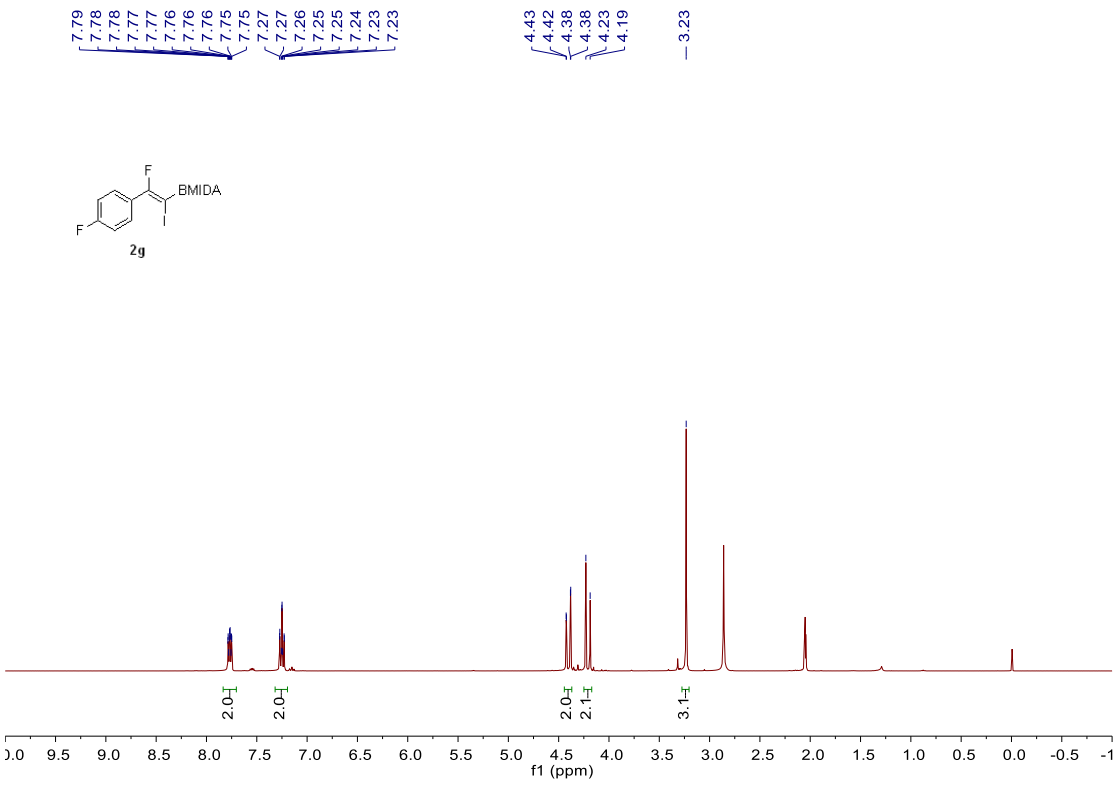

-9.89
F
BMIDA
I
F3CO
2e
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

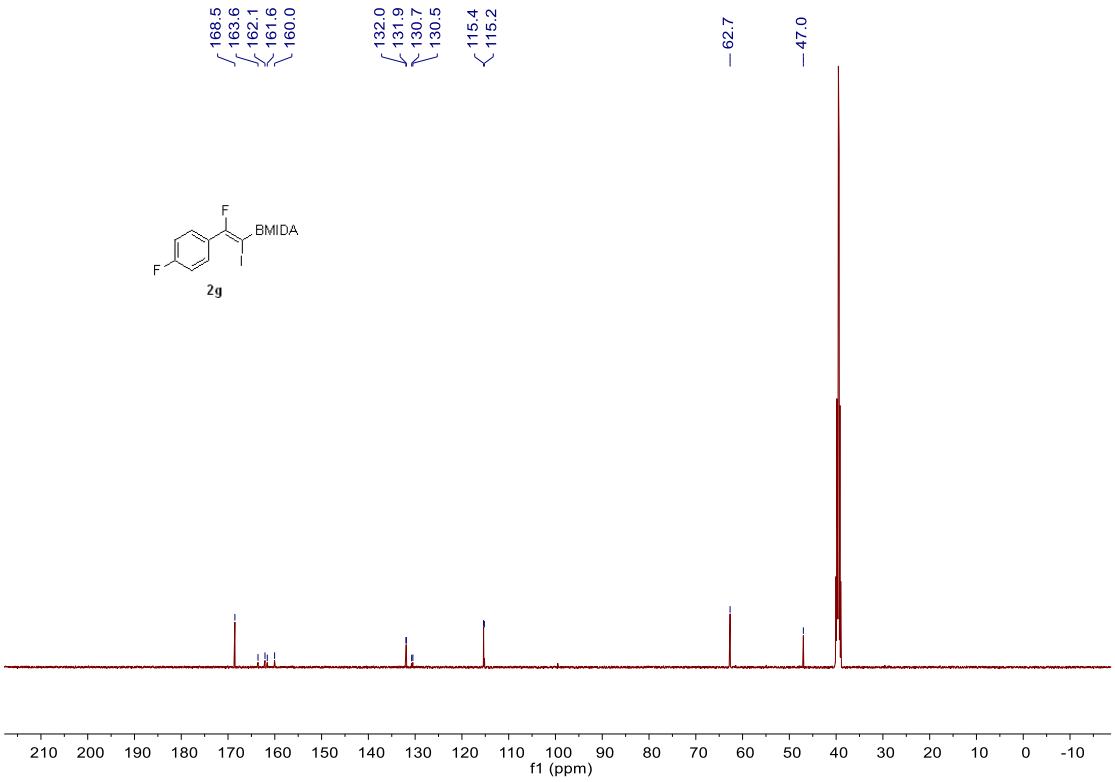

7.77
7.75
7.25
7.23
4.42
4.38
4.23
4.19
3.23
2.28
F
BMIDA
I
O
O
2f
2.0
2.0
2.1
2.1
3.1
3.0
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

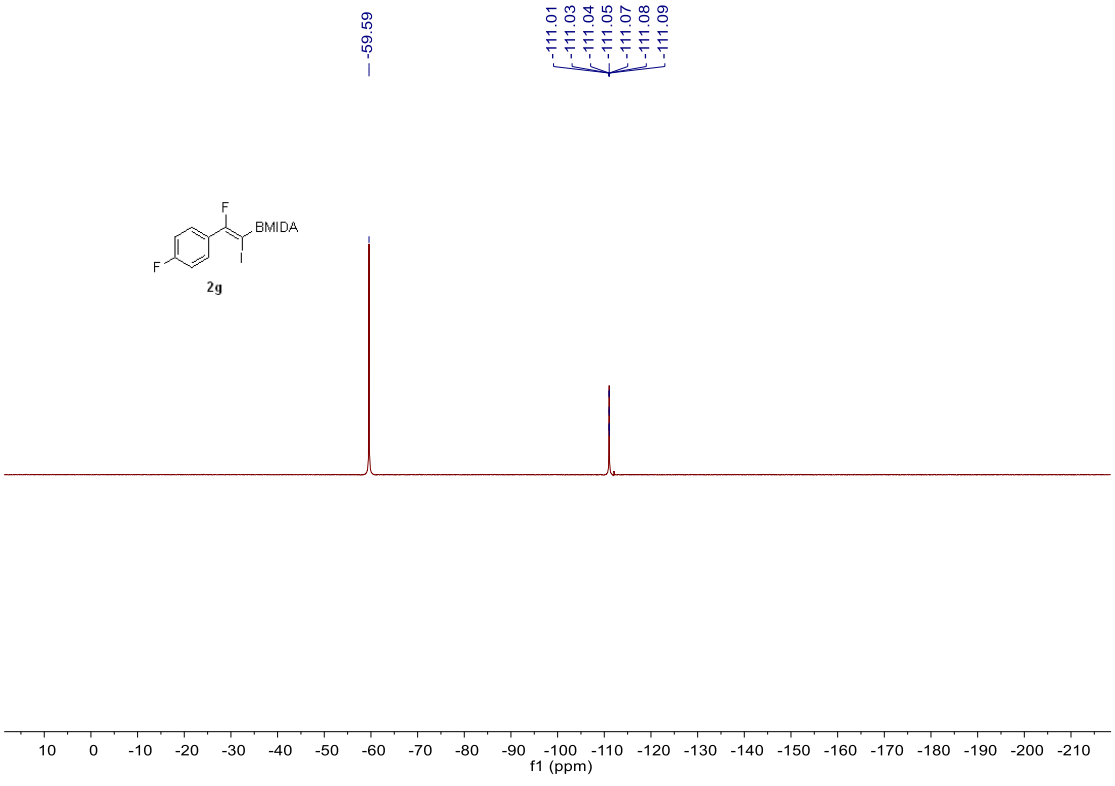

169.4
168.4
164.3
161.7
153.0
153.0
132.8
132.5
131.7
131.6
122.4
63.9
47.7
21.0
F
BMIDA
O
O
2f
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

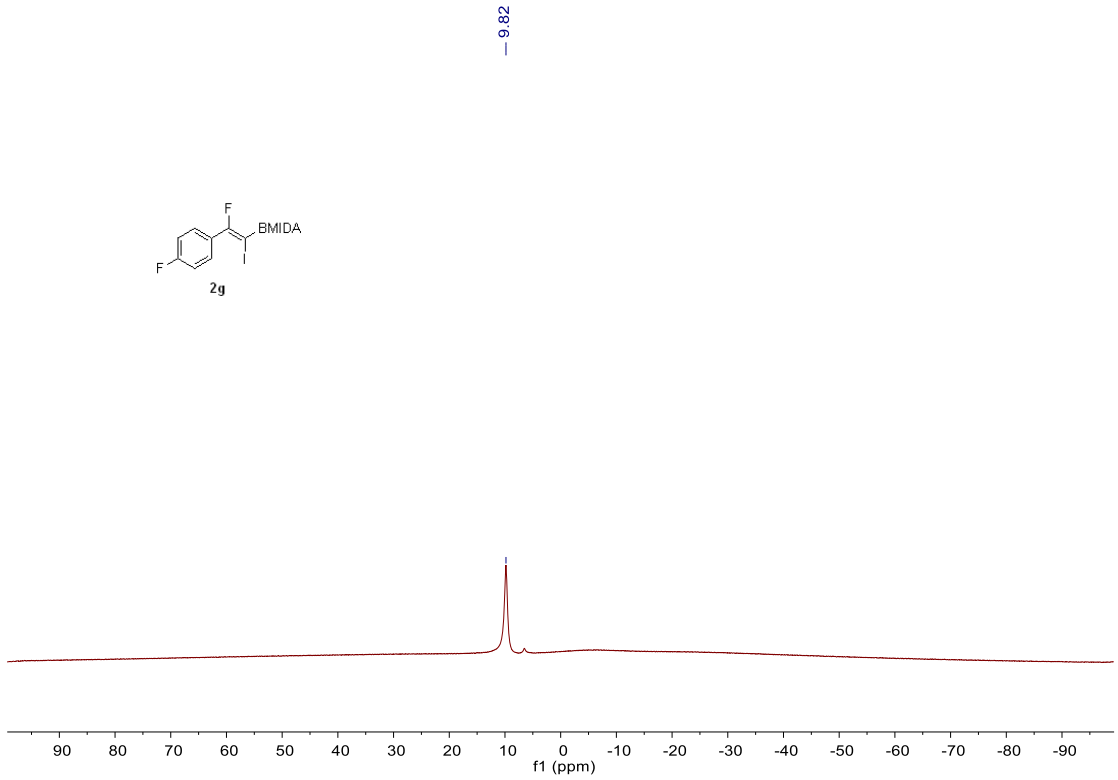

-59.90
F
BMIDA
O
O
2f
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

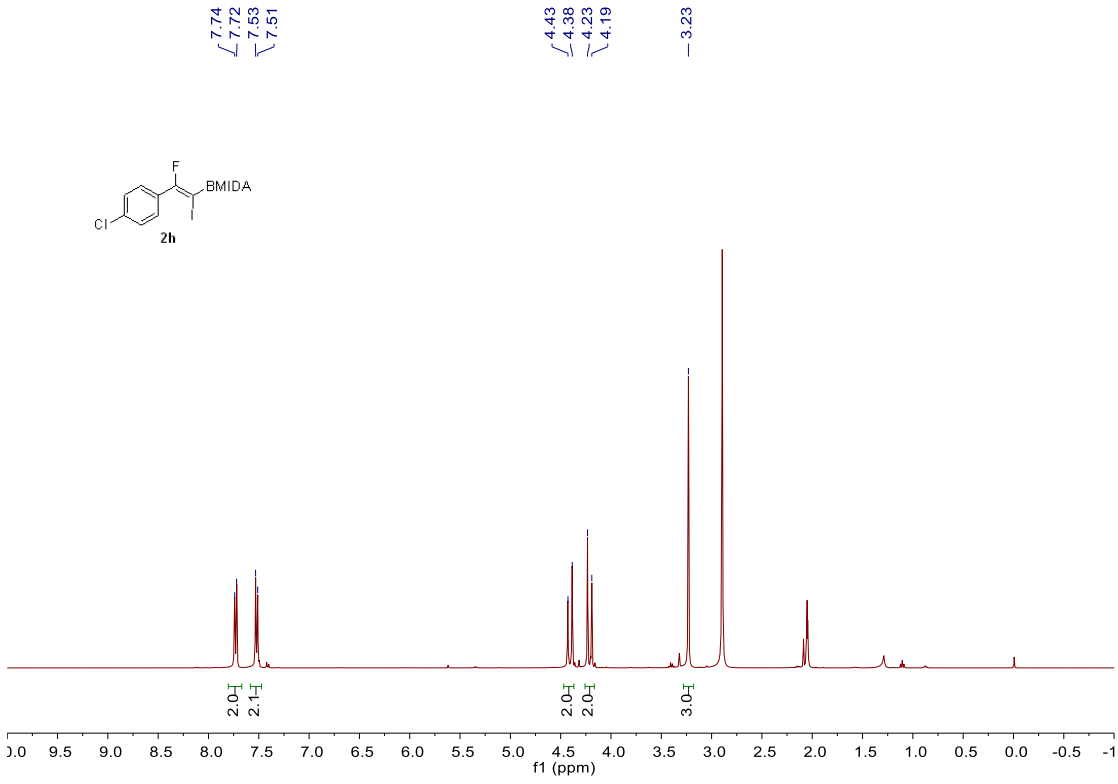

9.94
F
BMIDA
O
O
2f
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

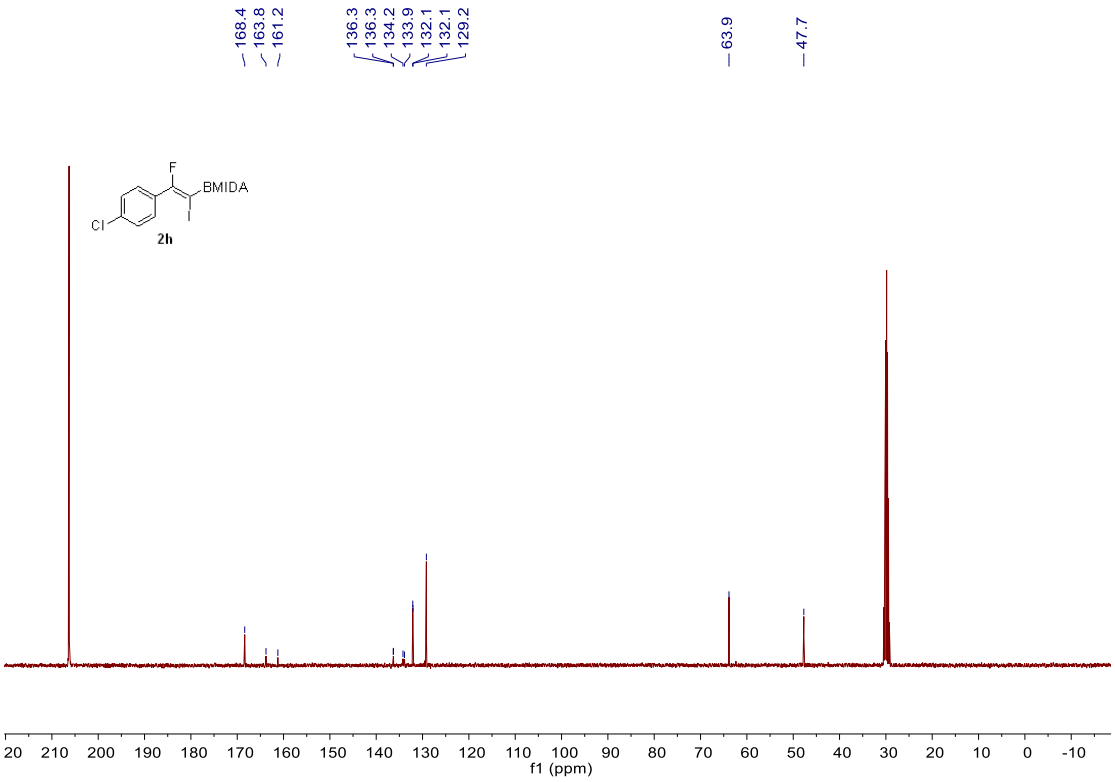

7.79 7.78 7.78 7.77 7.77 7.76 7.76 7.76 7.75 7.75
7.27 7.27 7.26 7.25 7.25 7.24 7.23 7.23
4.43 4.42 4.38 4.38 4.23 4.19
3.23
F
BMIDA
F
2g
2.0 2.0 2.0 2.1 3.1
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

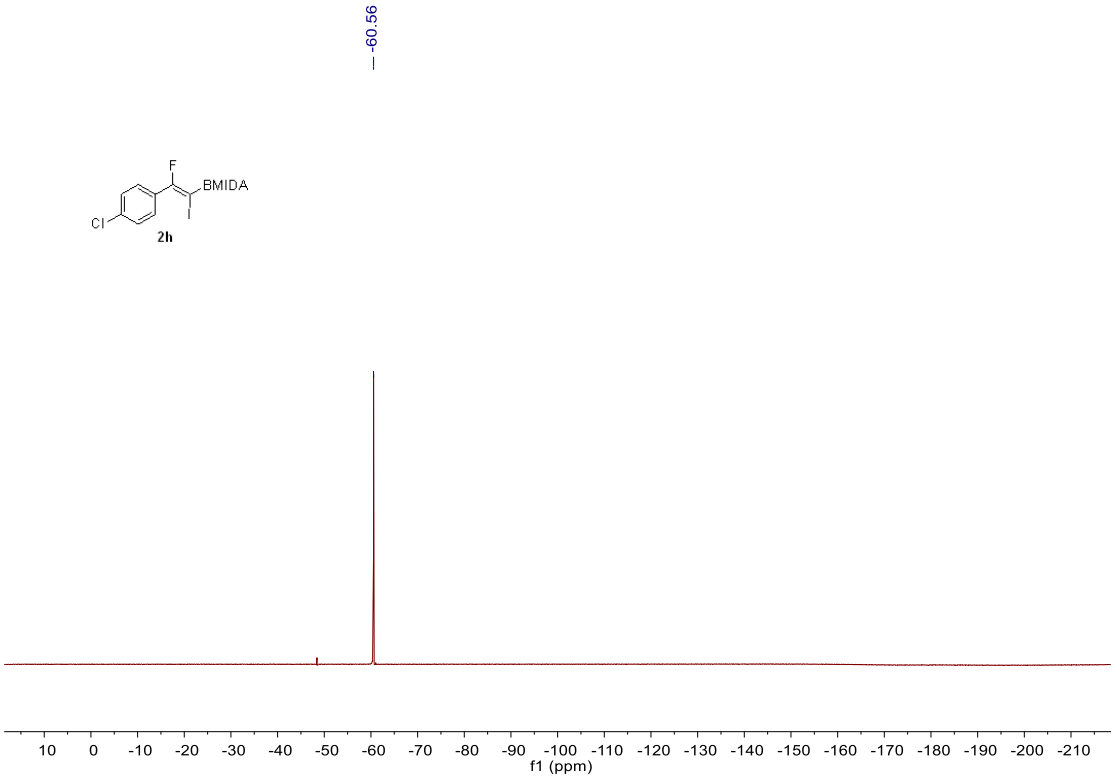

168.5
163.6
162.1
161.6
160.0
132.0
131.9
130.7
130.5
115.4
115.2
62.7
47.0
F
BMIDA
F
I
2g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

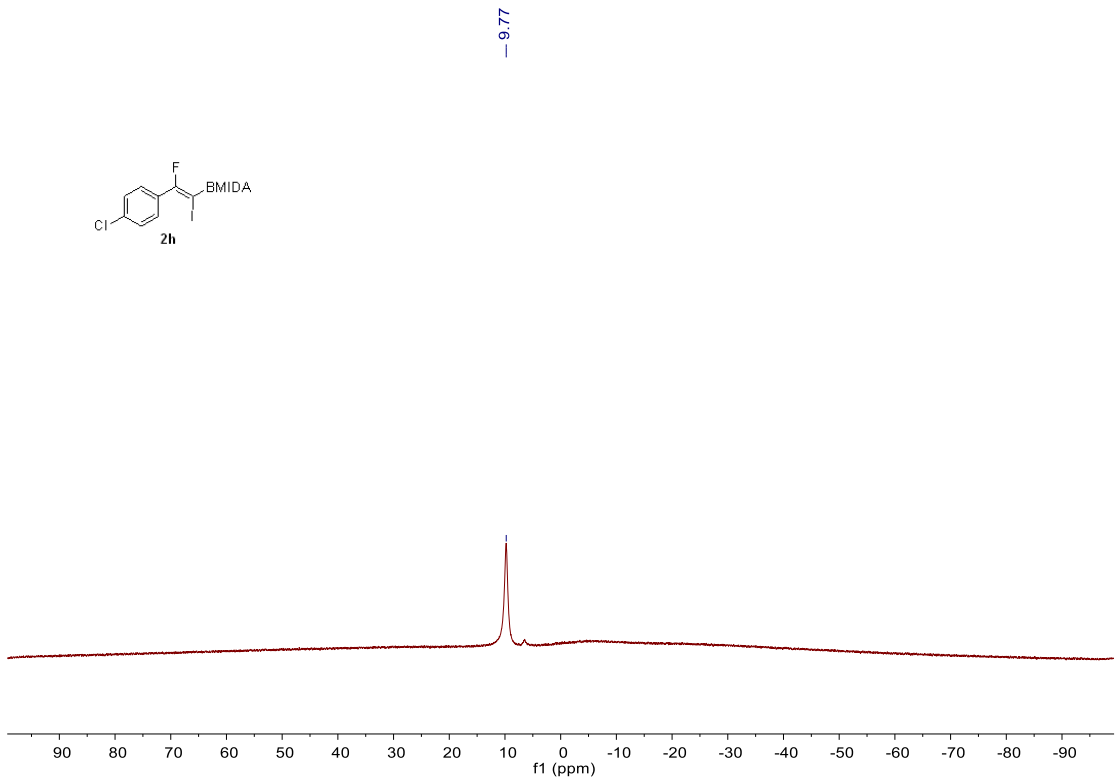

-59.59
-111.01
-111.03
-111.04
-111.05
-111.07
-111.08
-111.09
F
BMIDA
F
I
2g
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

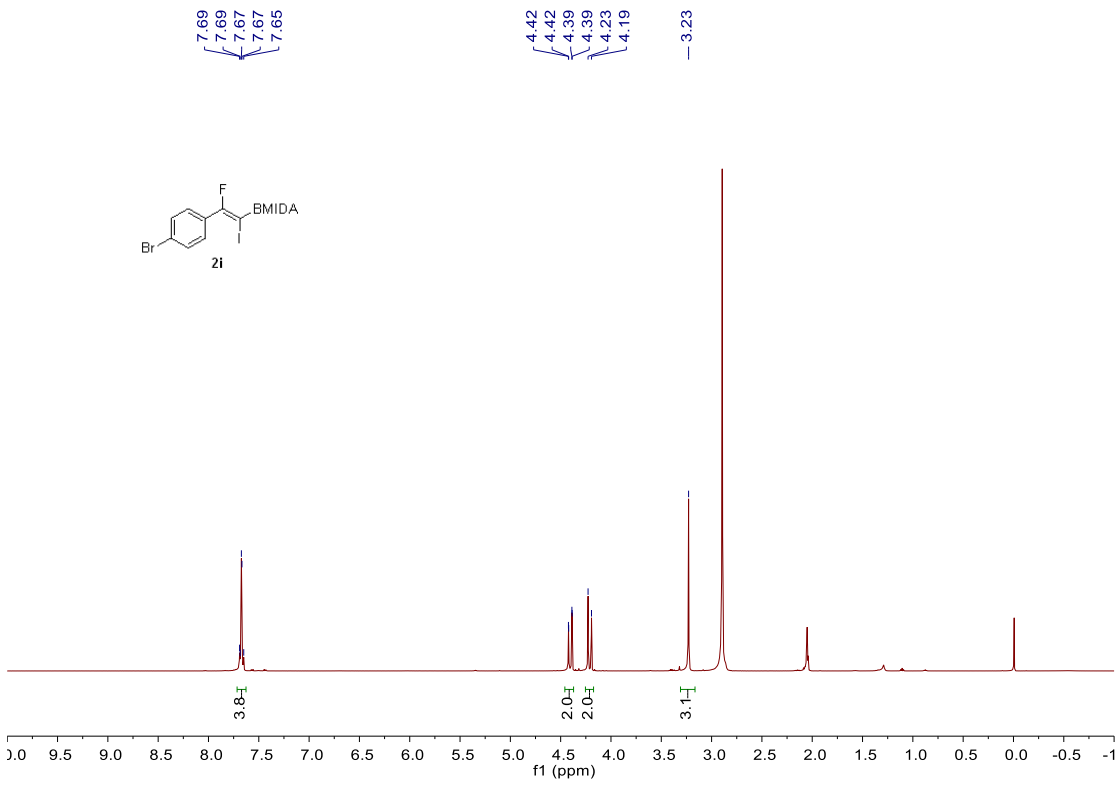

-9.82
F
BMIDA
F
2g
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

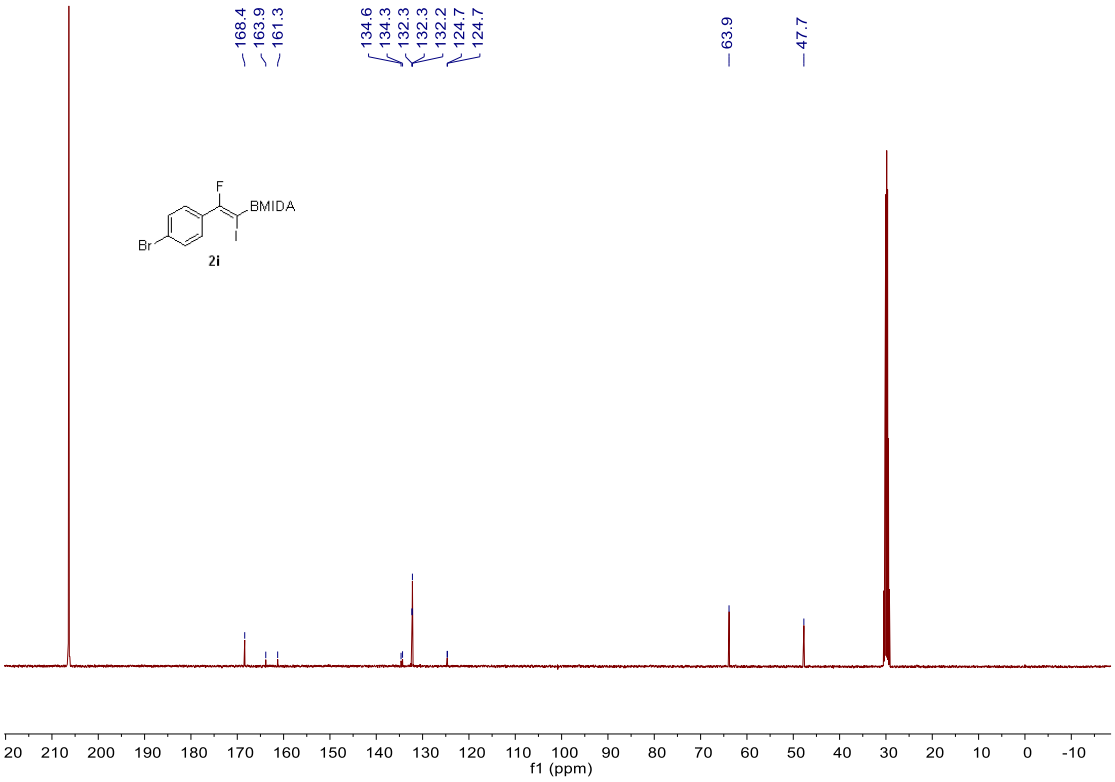

7.74
7.72
7.53
7.51
4.43
4.38
4.23
4.19
3.23
F
BMIDA
Cl
2h
2.0
2.1
2.0
2.0
3.0
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

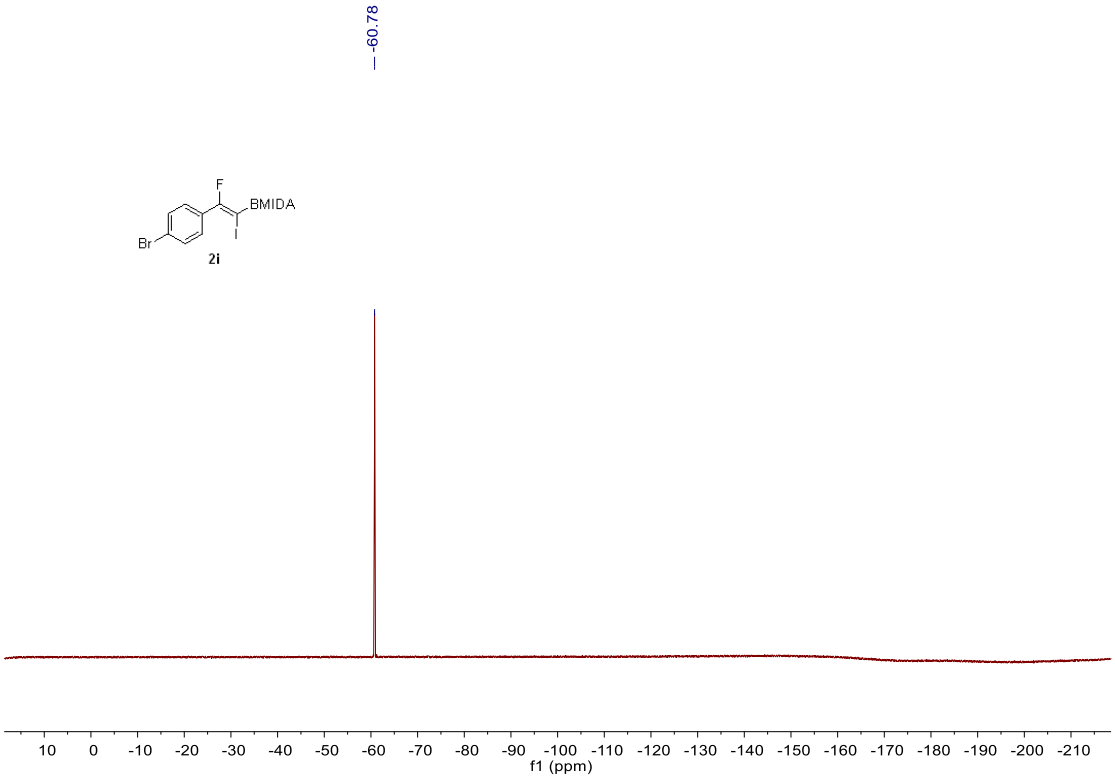

168.4
163.8
161.2
136.3
136.3
134.2
133.9
132.1
132.1
129.2
63.9
47.7
F
BMIDA
Cl
2h
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

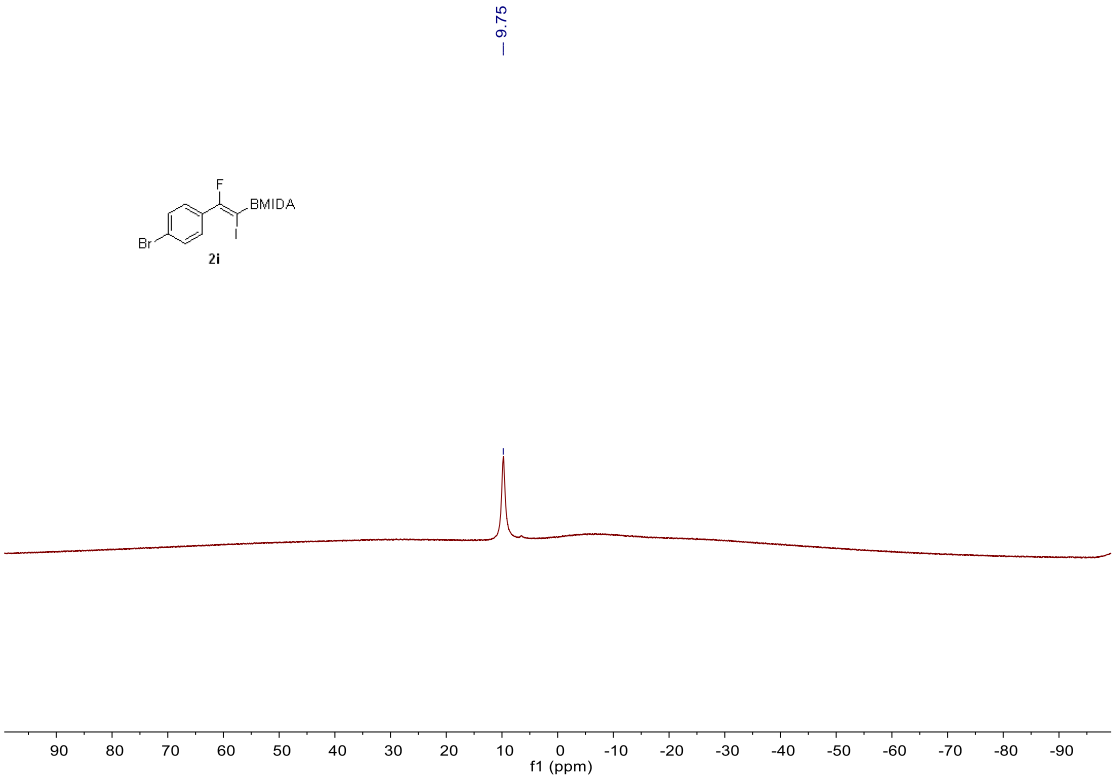

-60.56
F
BMIDA
Cl
2h
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

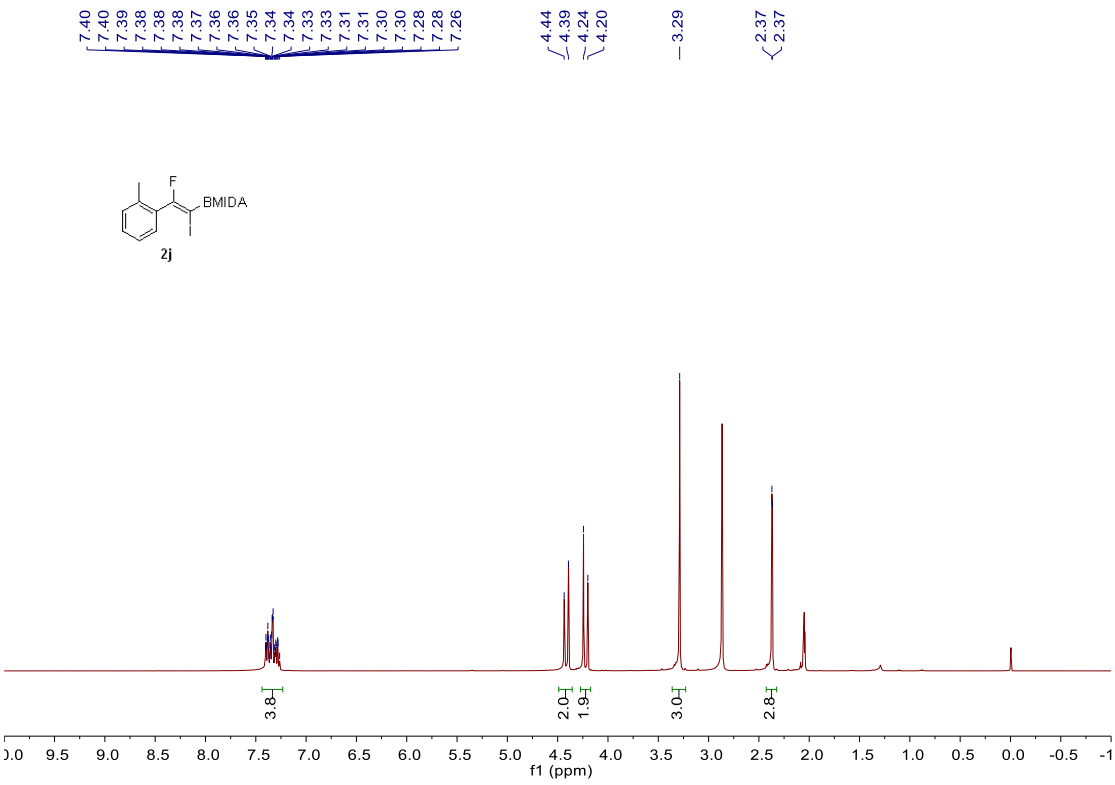

-9.77
F
BMIDA
Cl
2h
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

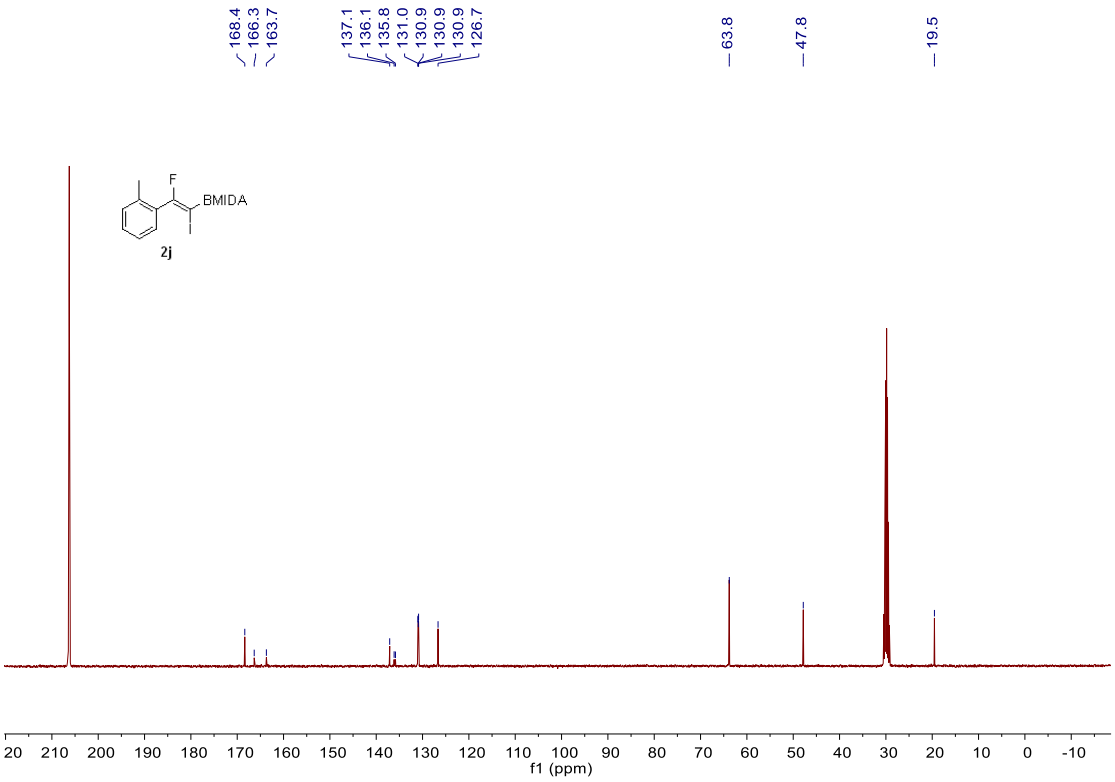

7.69
7.69
7.67
7.67
7.65
4.42
4.42
4.39
4.39
4.23
4.19
-3.23
F
BMIDA
Br
2i
3.8
2.0
2.0
3.1
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

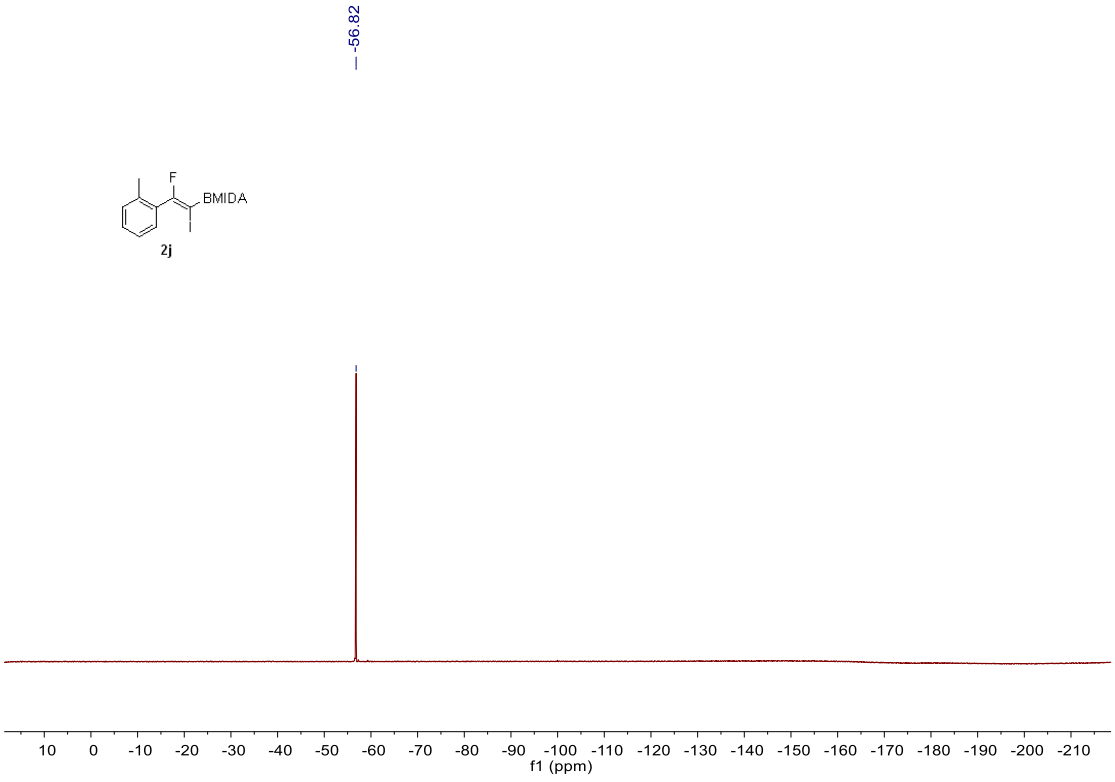

168.4
163.9
161.3
134.6
134.3
132.3
132.3
132.2
124.7
124.7
63.9
47.7
F
BMIDA
Br
I
2i
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

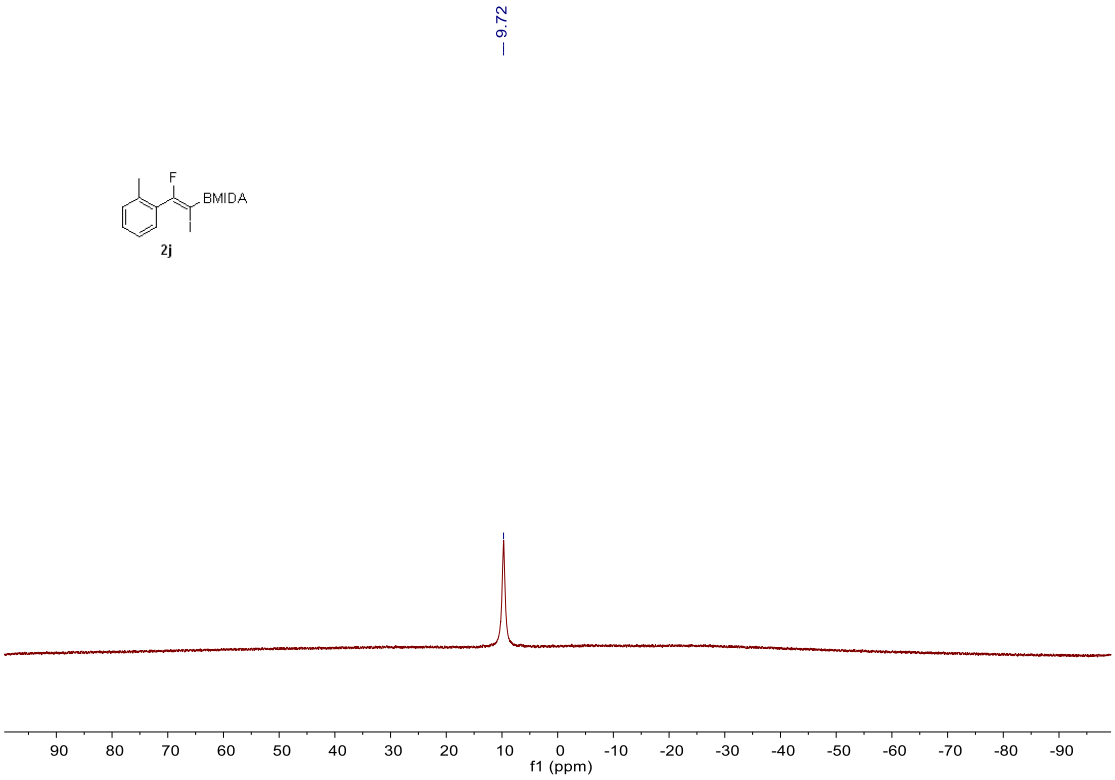

-60.78
F
BMIDA
Br
I
2i
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

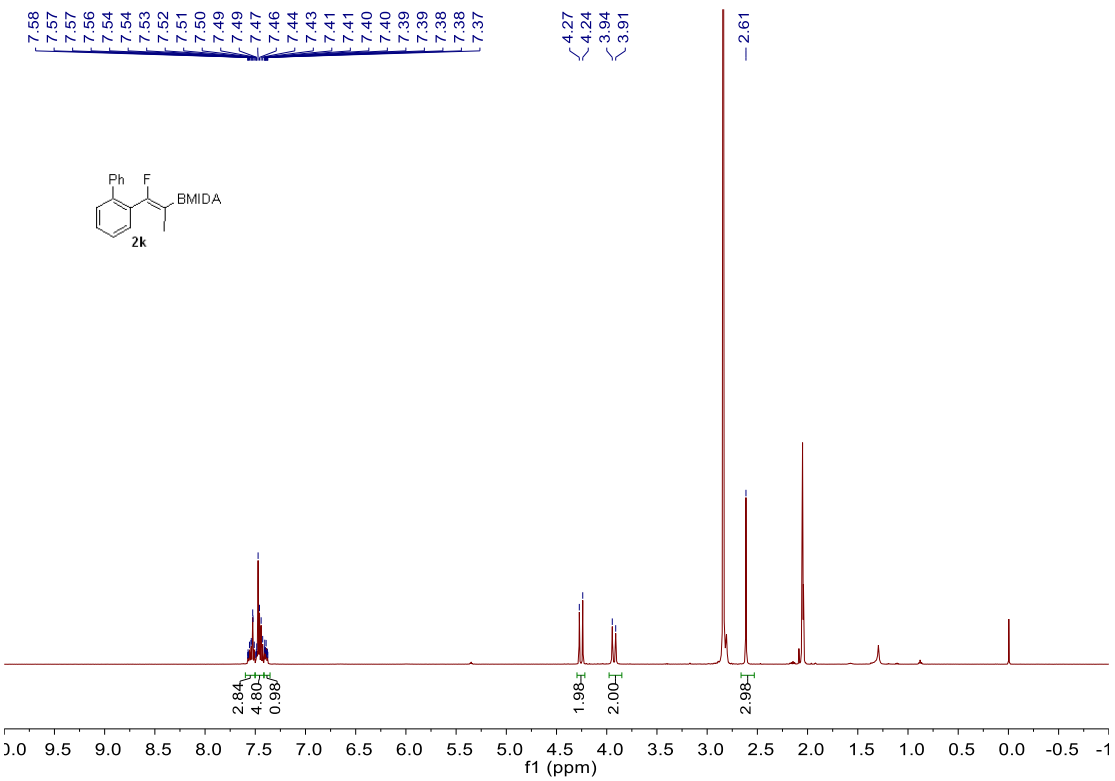

9.75
F
BMIDA
Br
2i
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

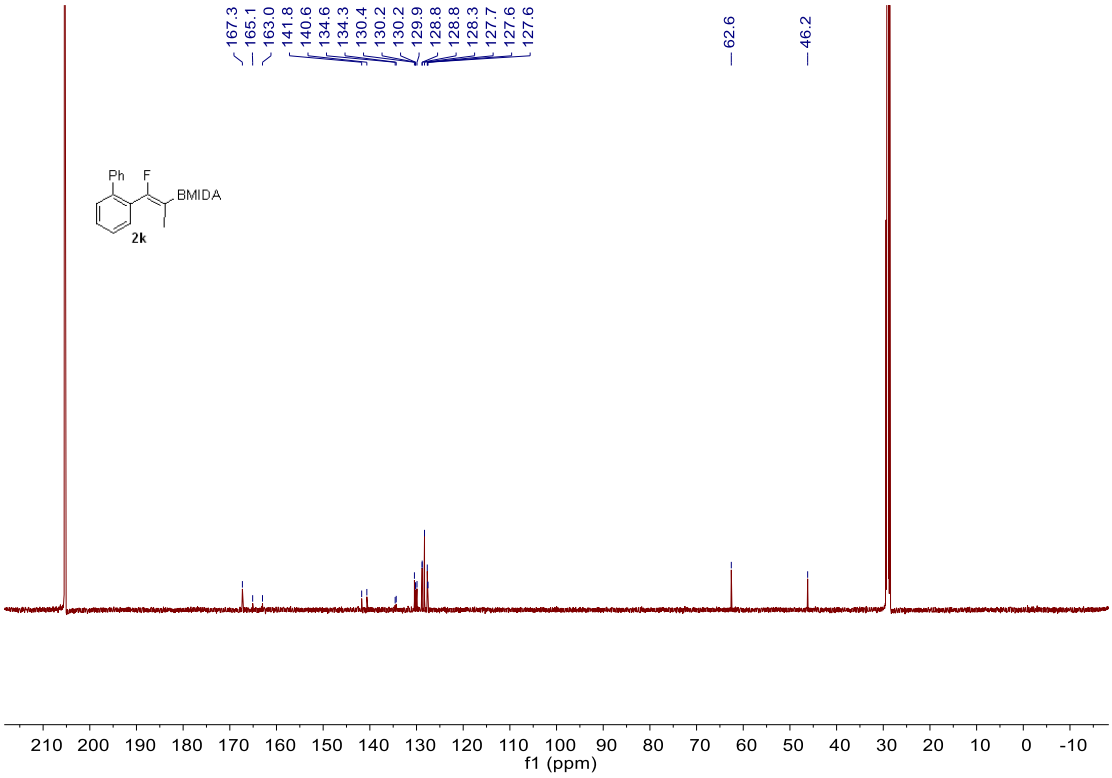

7.40 7.40 7.39 7.38 7.38 7.38 7.37 7.36 7.36 7.35 7.34 7.34 7.33 7.33 7.31 7.31 7.30 7.30 7.28 7.28 7.26
4.44 4.39 4.24 4.20
3.29
2.37 2.37
F
BMIDA
2j
3.8 2.0 1.9 3.0 2.8
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

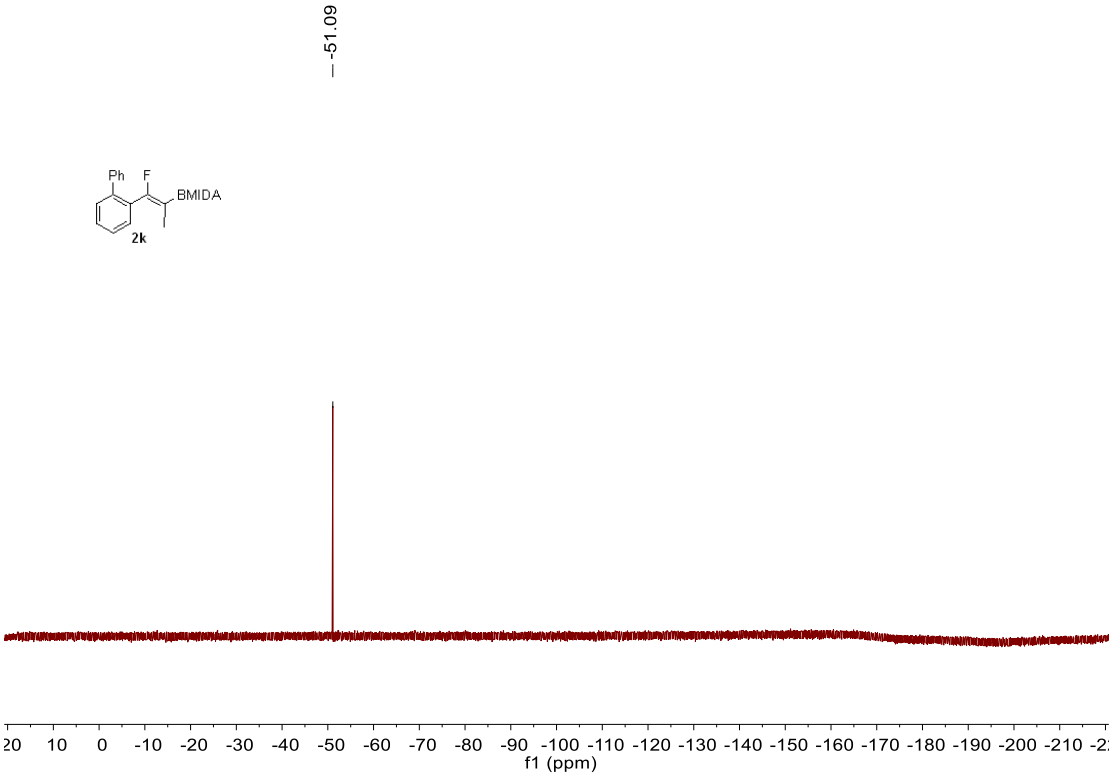

168.4
166.3
163.7
137.1
136.1
135.8
131.0
130.9
130.9
130.9
126.7
63.8
47.8
19.5
F
BMIDA
2j
f1 (ppm)

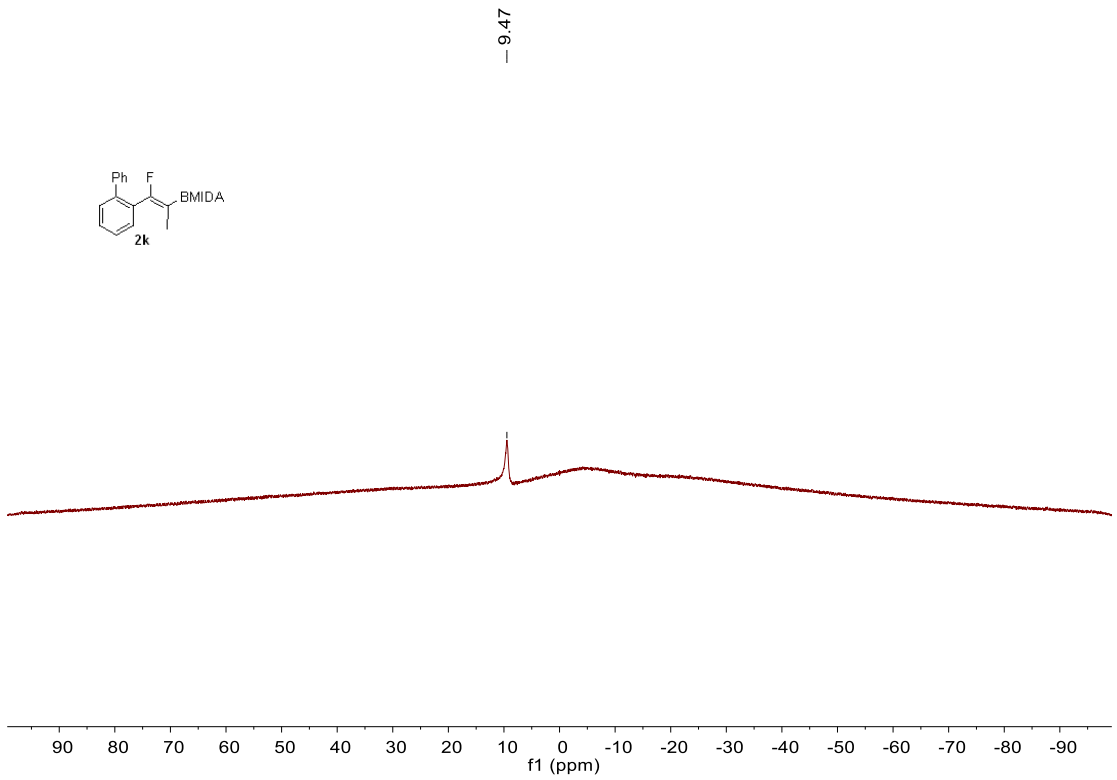

-56.82
F
BMIDA
2j
f1 (ppm)

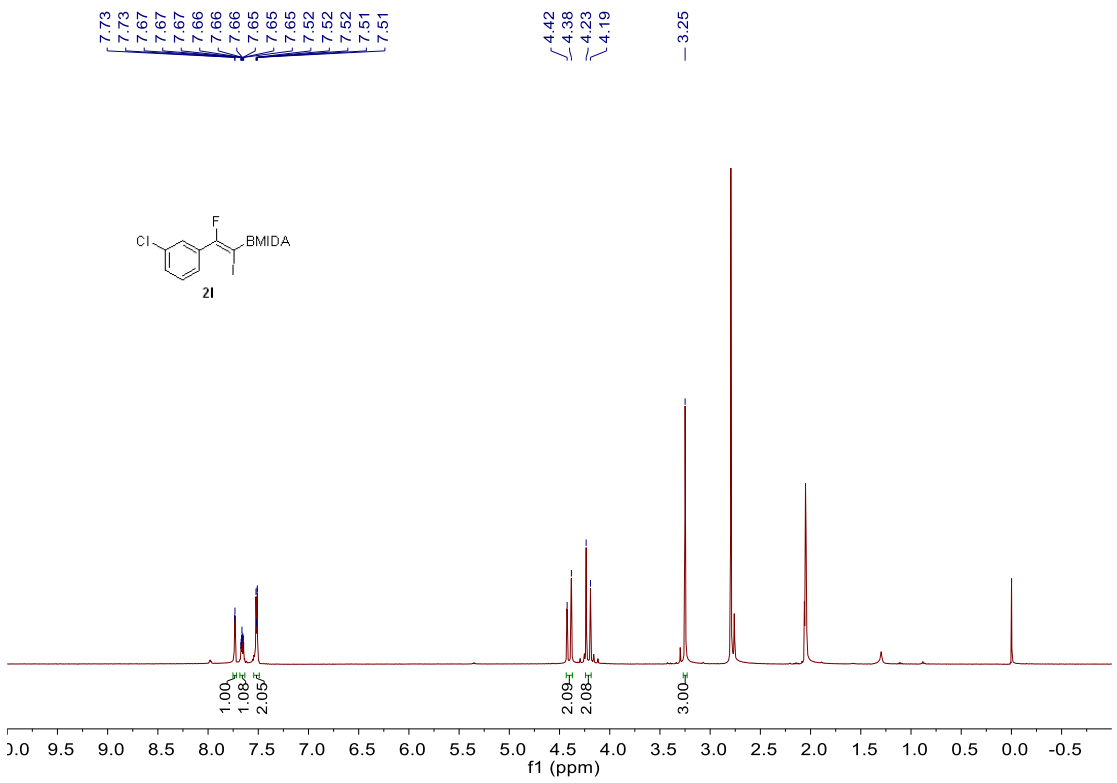

-9.72
F
BMIDA
2j
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

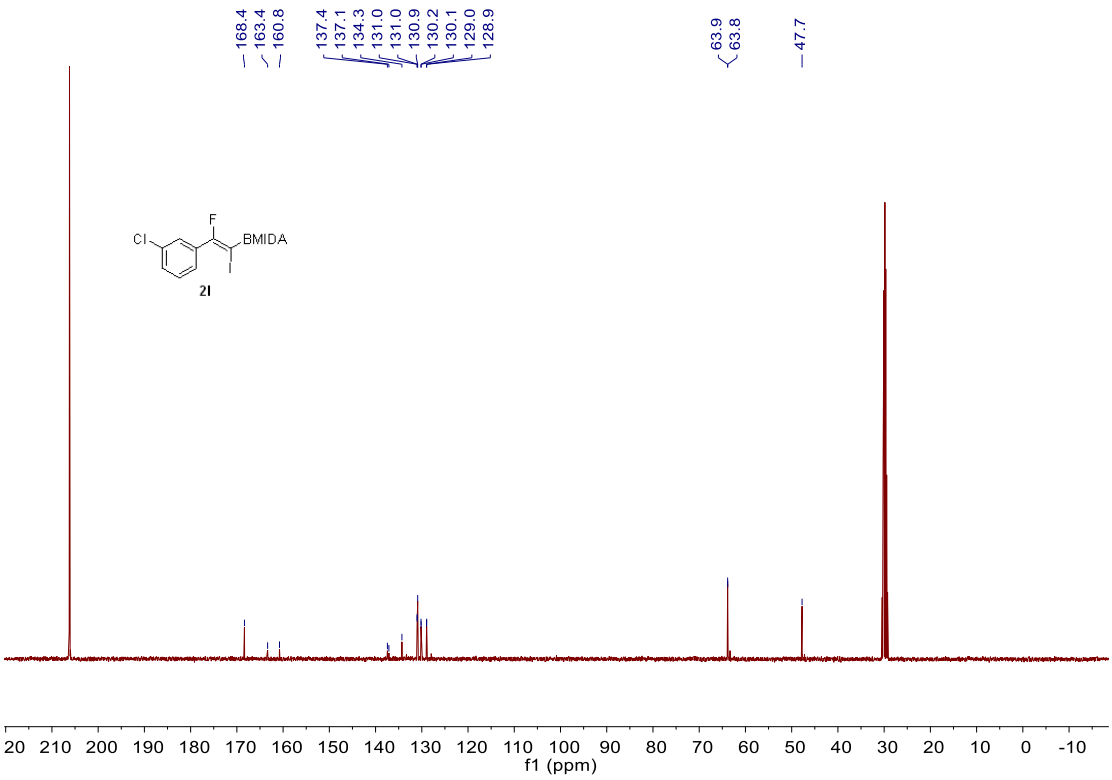

7.58 7.57 7.57 7.56 7.54 7.54 7.53 7.52 7.51 7.50 7.49 7.49 7.47 7.46 7.44 7.43 7.41 7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.37
4.27 4.24 3.94 3.91
2.61
Ph F
BMIDA
2k
2.84 4.80 0.98
1.98 2.00 2.98
f1 (ppm)

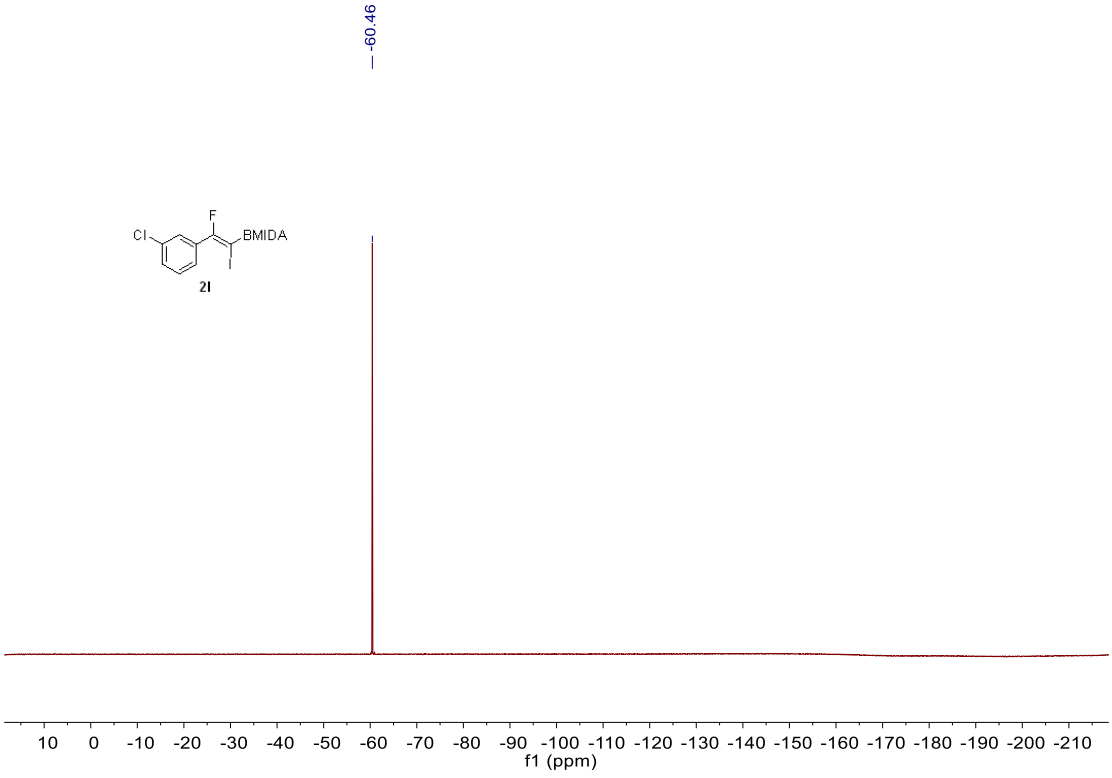

167.3
165.1
163.0
141.8
140.6
134.6
134.3
130.4
130.2
130.2
129.9
128.8
128.8
128.3
127.7
127.6
127.6
62.6
46.2
Ph
F
BMIDA
2k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

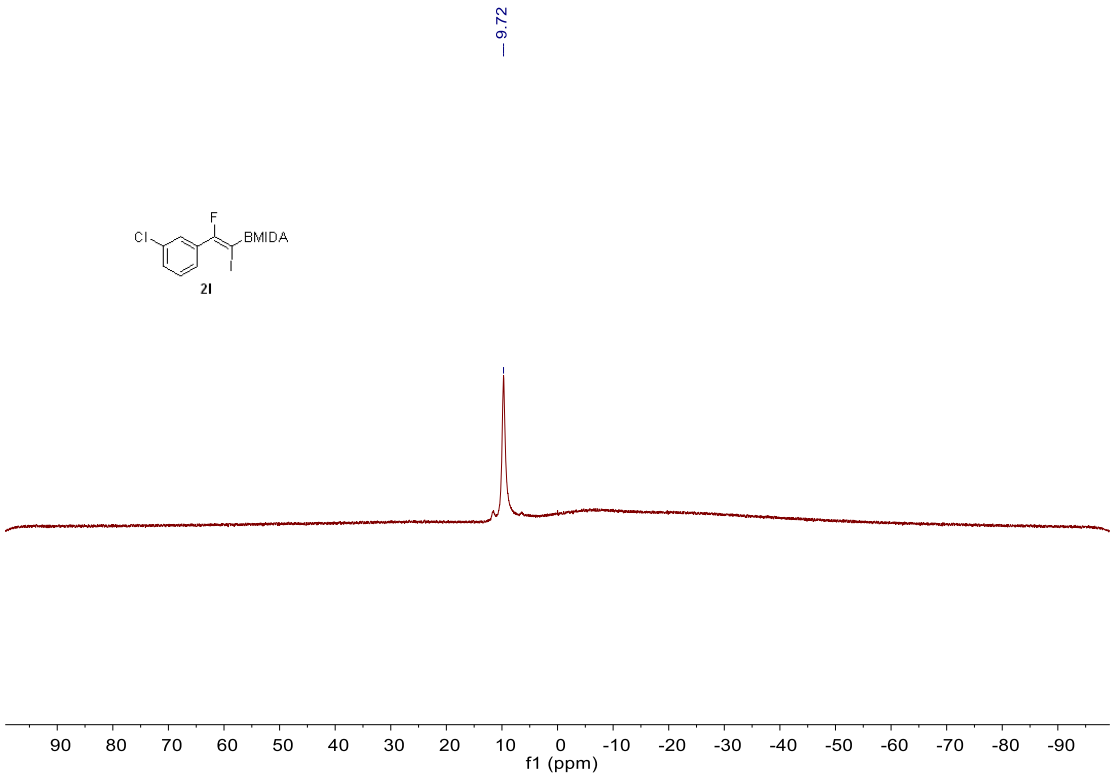

-51.09
Ph
F
BMIDA
2k
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

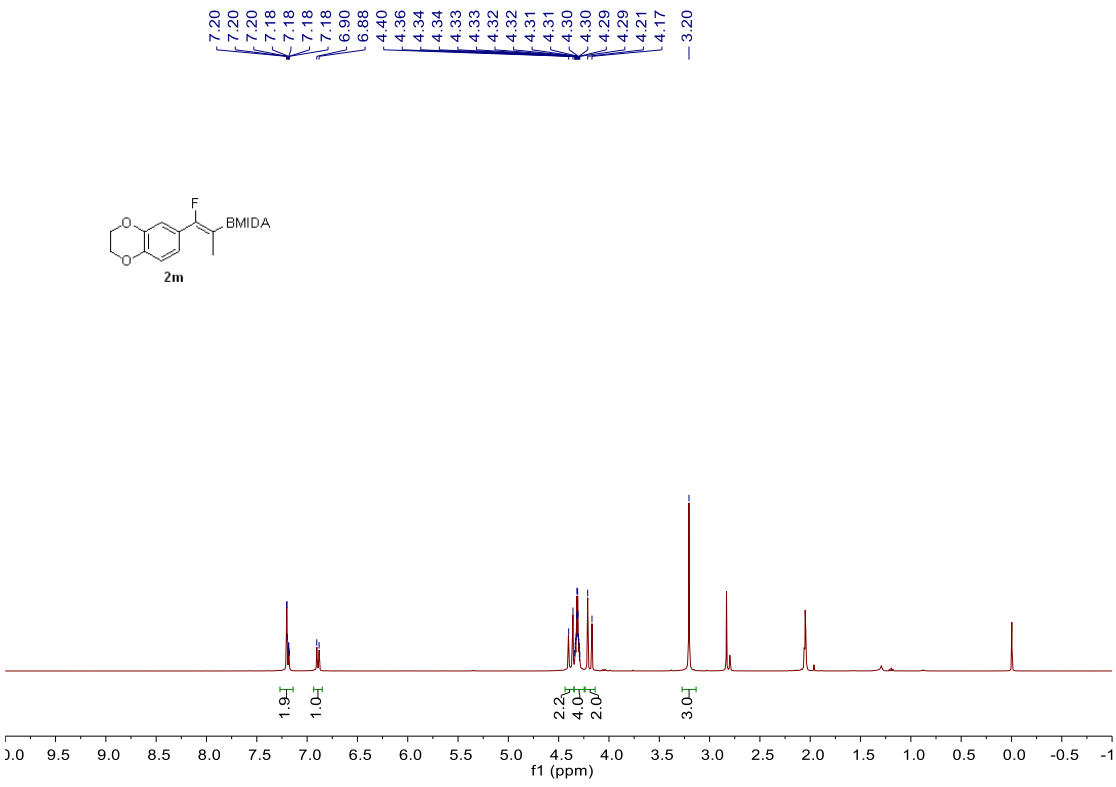

9.47
Ph
F
BMIDA
2k
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

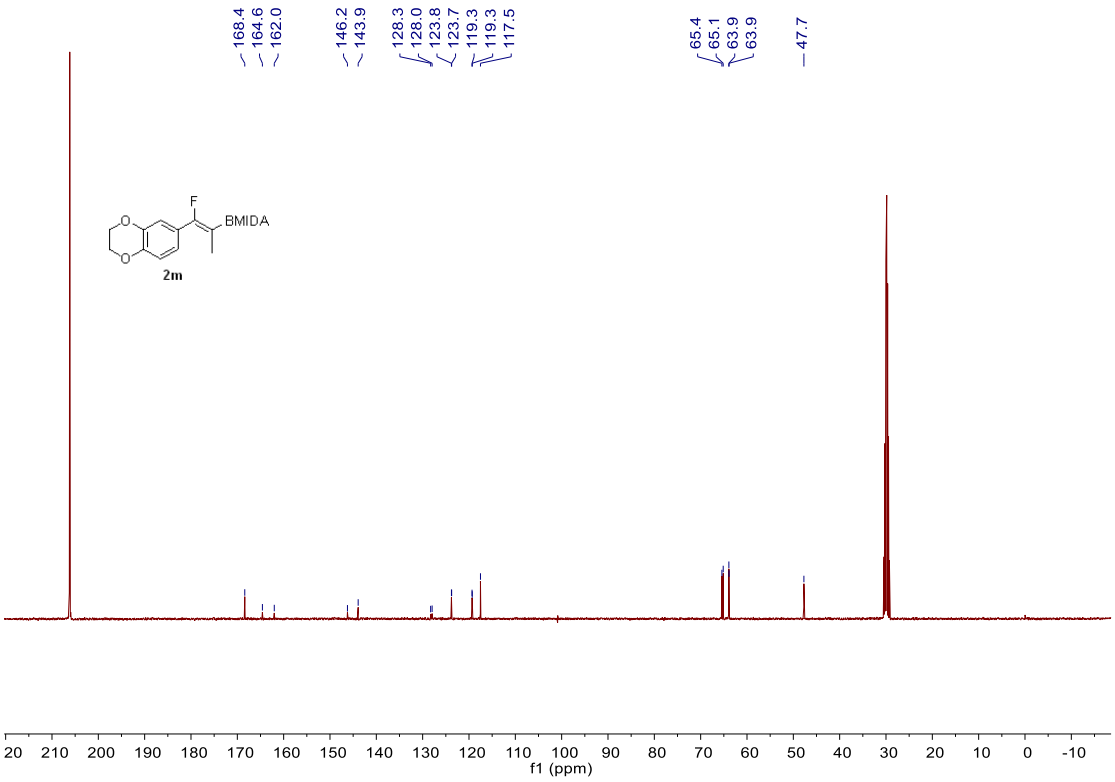

7.73
7.73
7.67
7.67
7.67
7.66
7.66
7.66
7.65
7.65
7.65
7.52
7.52
7.52
7.51
7.51
4.42
4.38
4.23
4.19
3.25
F
Cl
BMIDA
2l
1.00
1.08
2.05
2.09
2.08
3.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

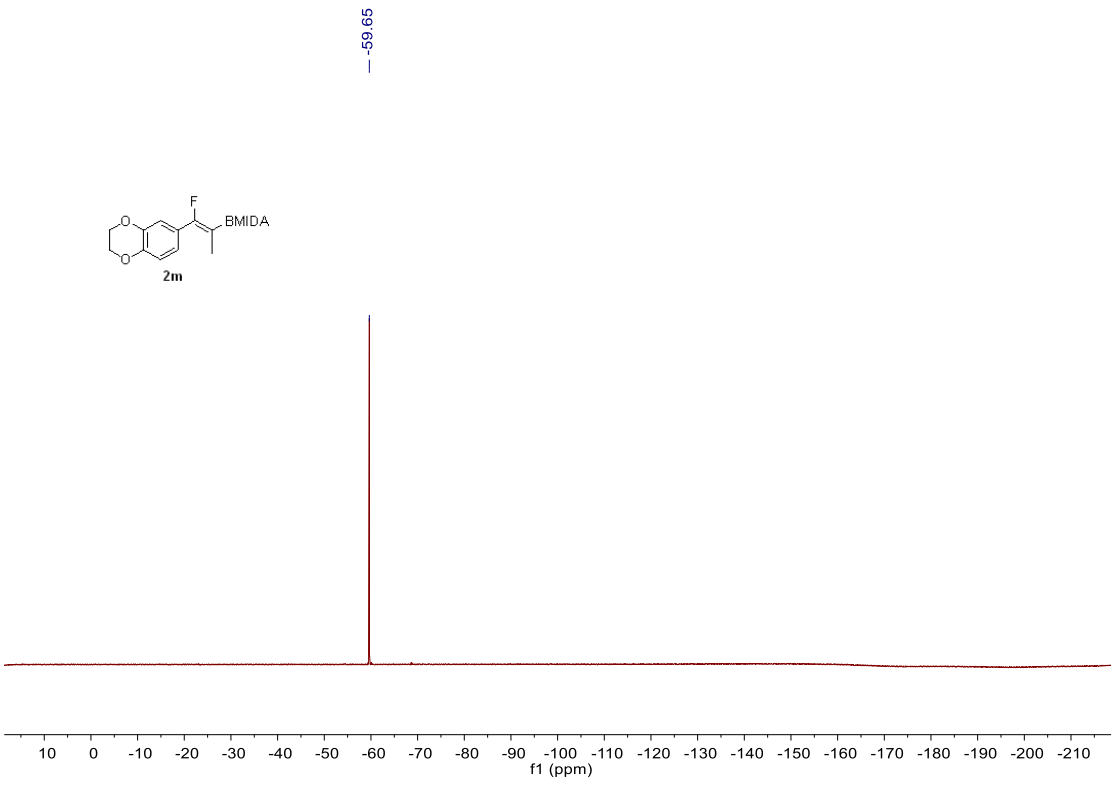

168.4
163.4
160.8
137.4
137.1
134.3
131.0
131.0
130.9
130.2
130.1
129.0
128.9
63.9
63.8
47.7
F
Cl
BMIDA
2l
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

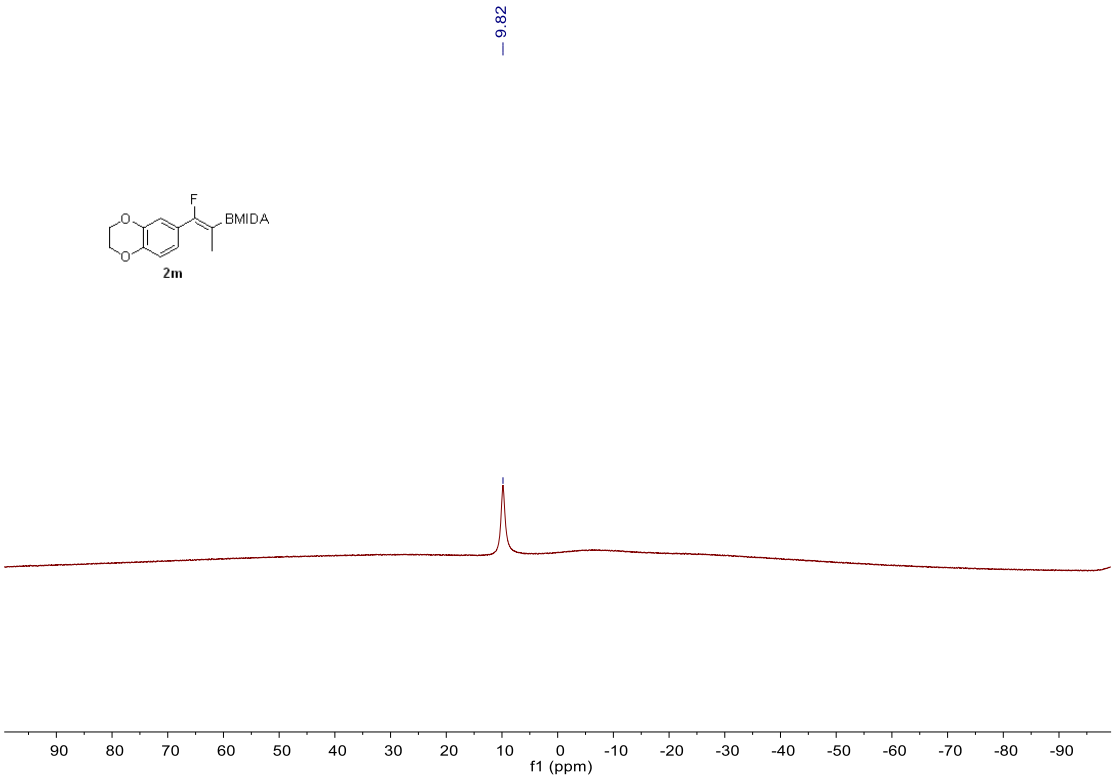

-60.46
F
Cl
BMIDA
2l
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

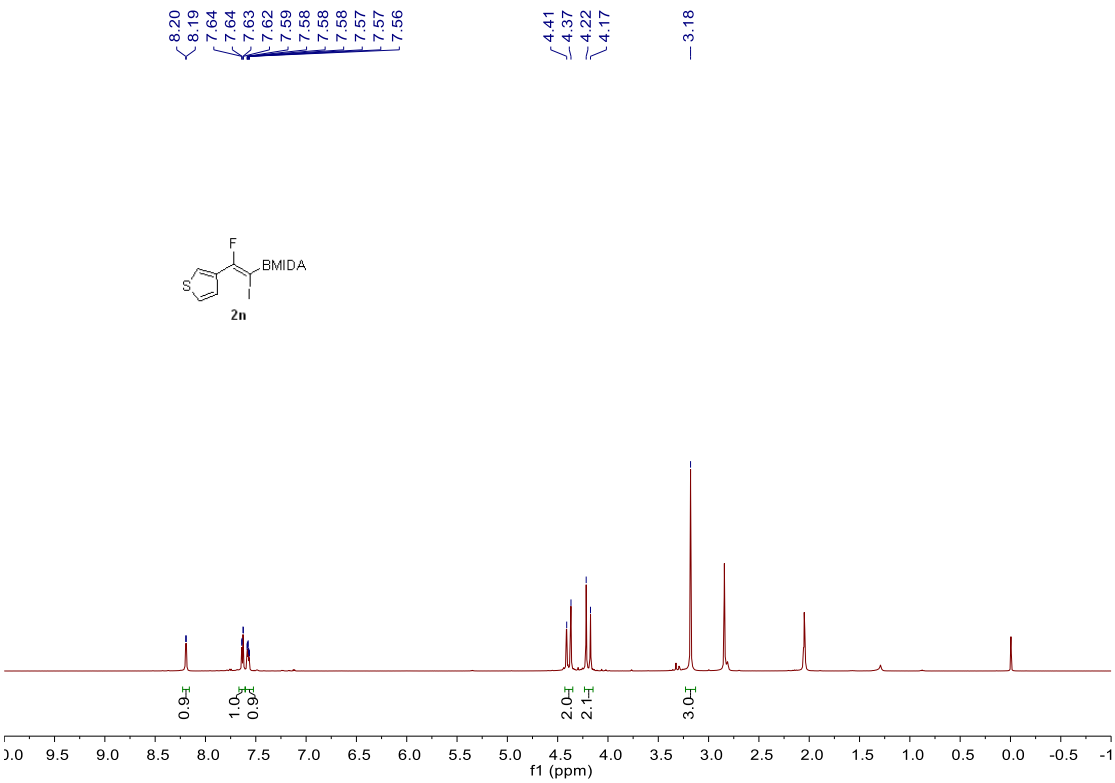

9.72
F
Cl
BMIDA
I
2l
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

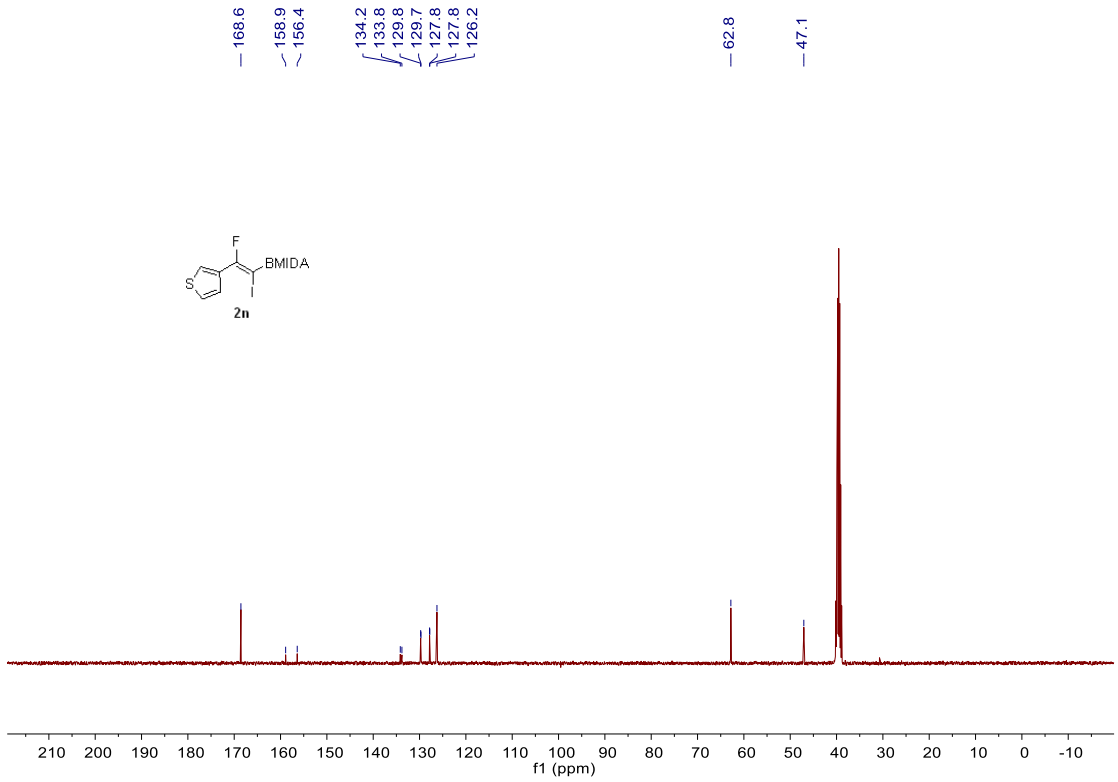

7.20 7.20 7.20 7.18 7.18 7.18 7.18 6.90 6.88 4.40 4.36 4.34 4.34 4.33 4.33 4.32 4.32 4.31 4.31 4.30 4.30 4.29 4.29 4.21 4.17 3.20
F
BMIDA
O
O
2m
1.9 1.0 2.2 4.0 2.0 3.0
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

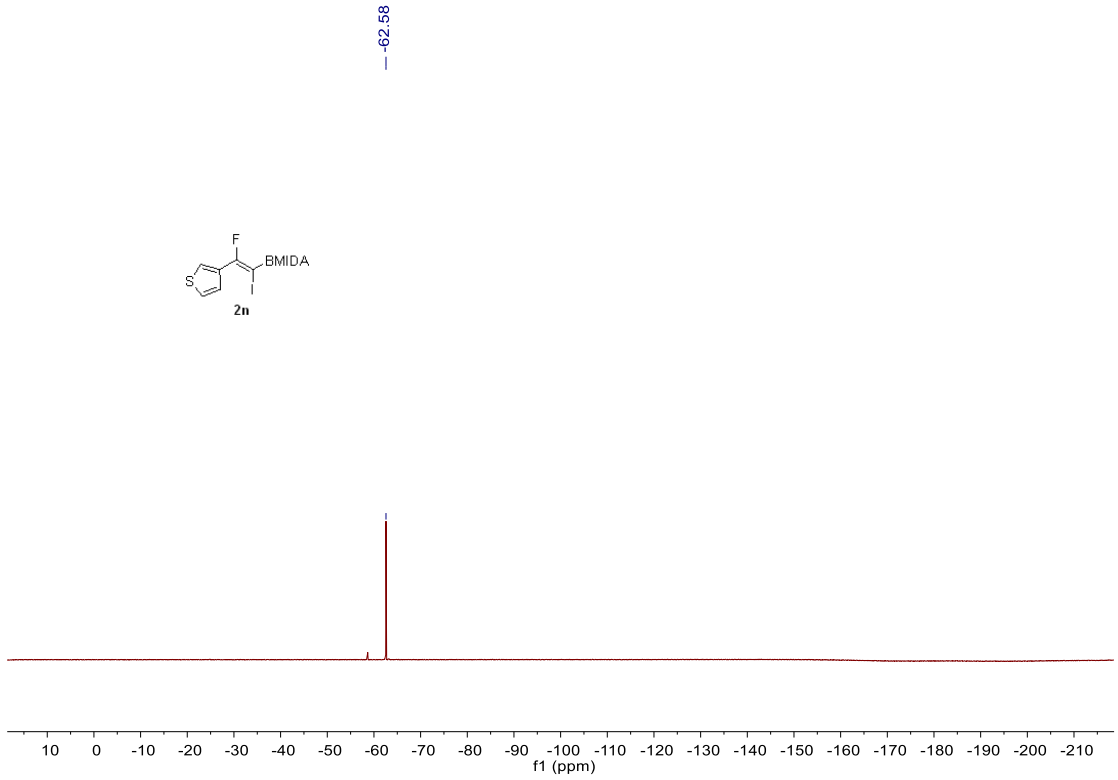

168.4
164.6
162.0
146.2
143.9
128.3
128.0
123.8
123.7
119.3
119.3
117.5
65.4
65.1
63.9
63.9
47.7
F
BMIDA
2m
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

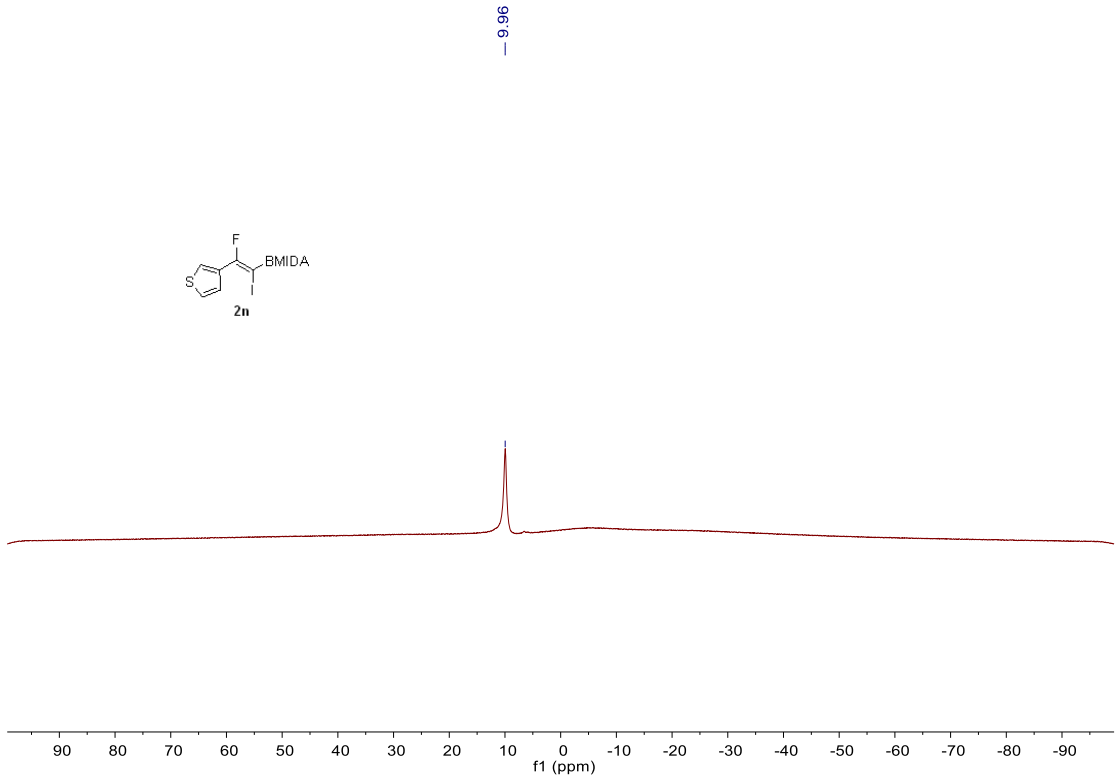

-59.65
F
BMIDA
2m
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

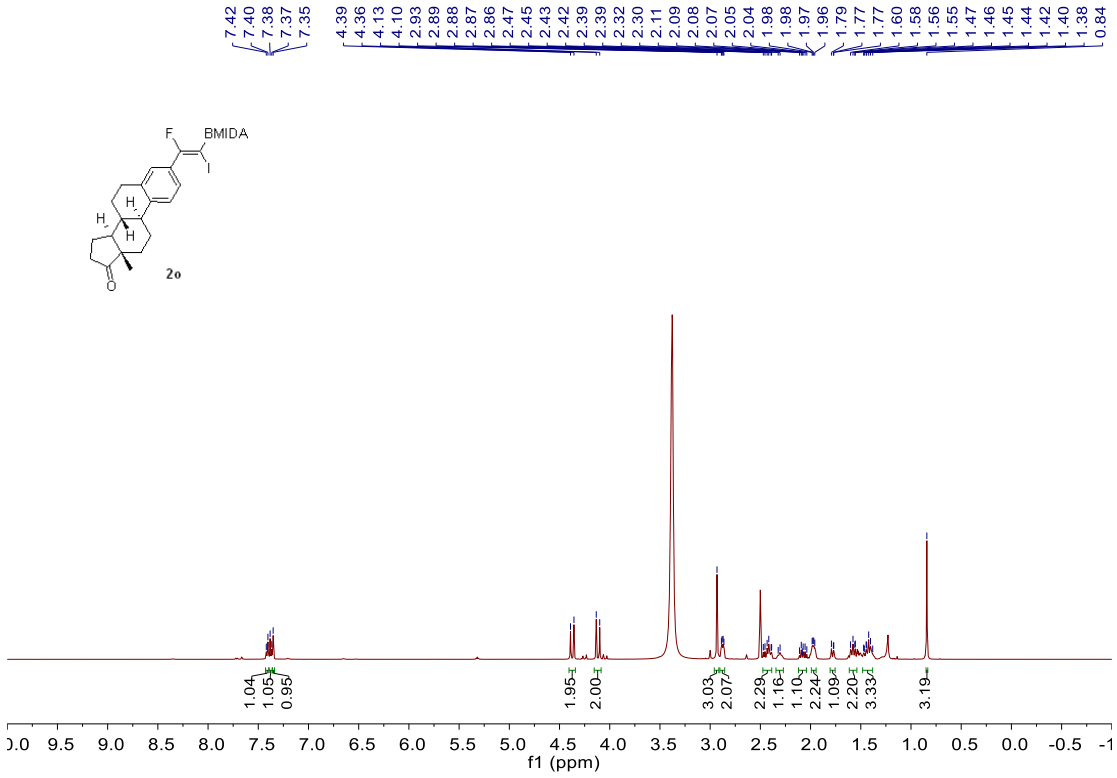

9.82
F
BMIDA
2m
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

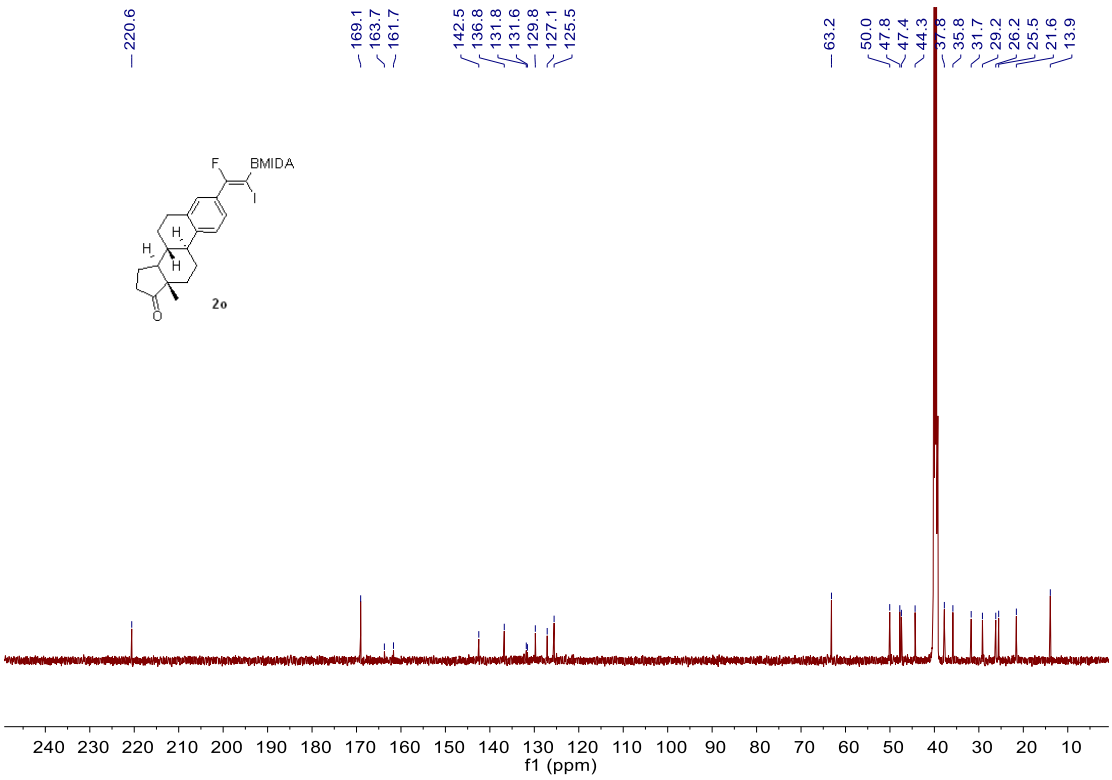

8.20
8.19
7.64
7.64
7.63
7.62
7.59
7.58
7.58
7.58
7.57
7.57
7.56
4.41
4.37
4.22
4.17
3.18
F
BMIDA
S
2n
0.9
1.0
0.9
2.0
2.1
3.0
f1 (ppm)

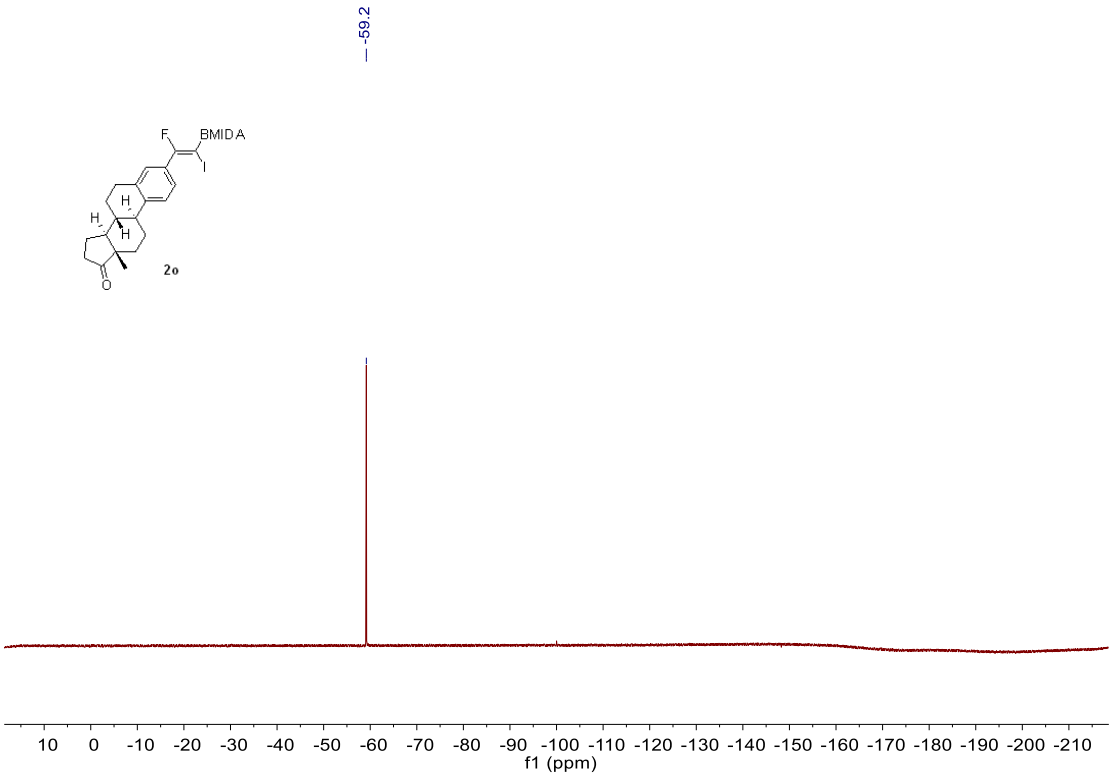

168.6
158.9
156.4
134.2
133.8
129.8
129.7
127.8
127.8
126.2
62.8
47.1
F
BMIDA
S
I
2n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

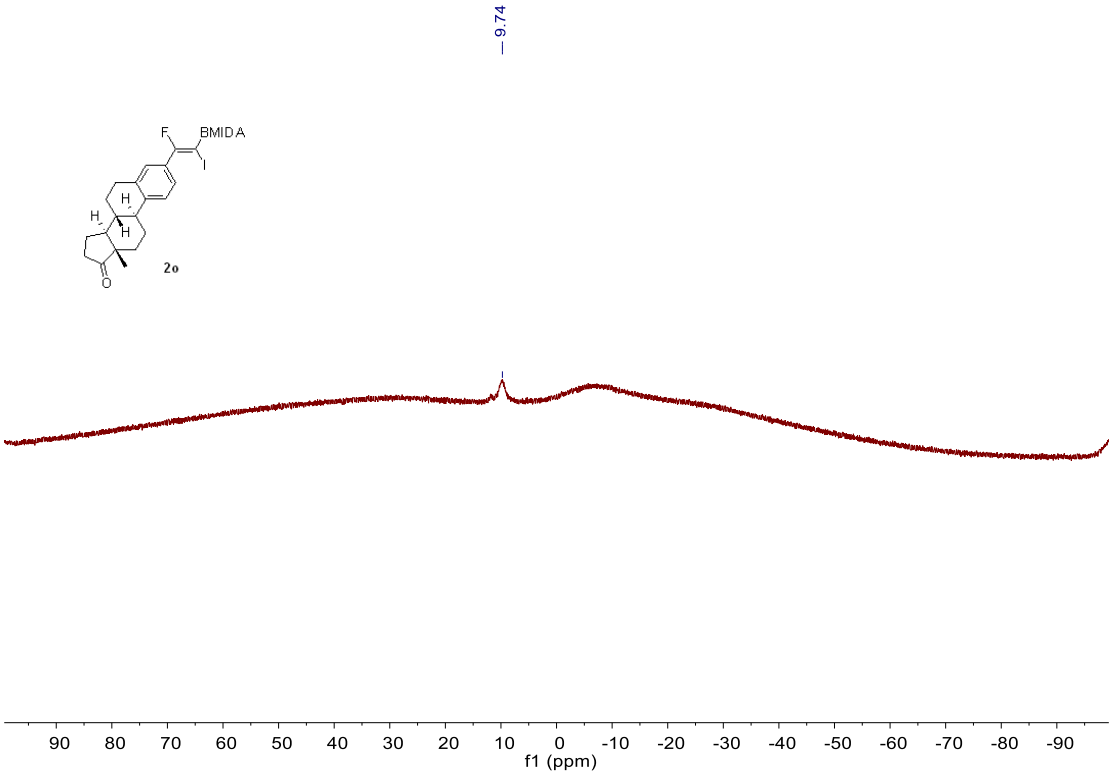

-62.58
F
BMIDA
S
I
2n
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

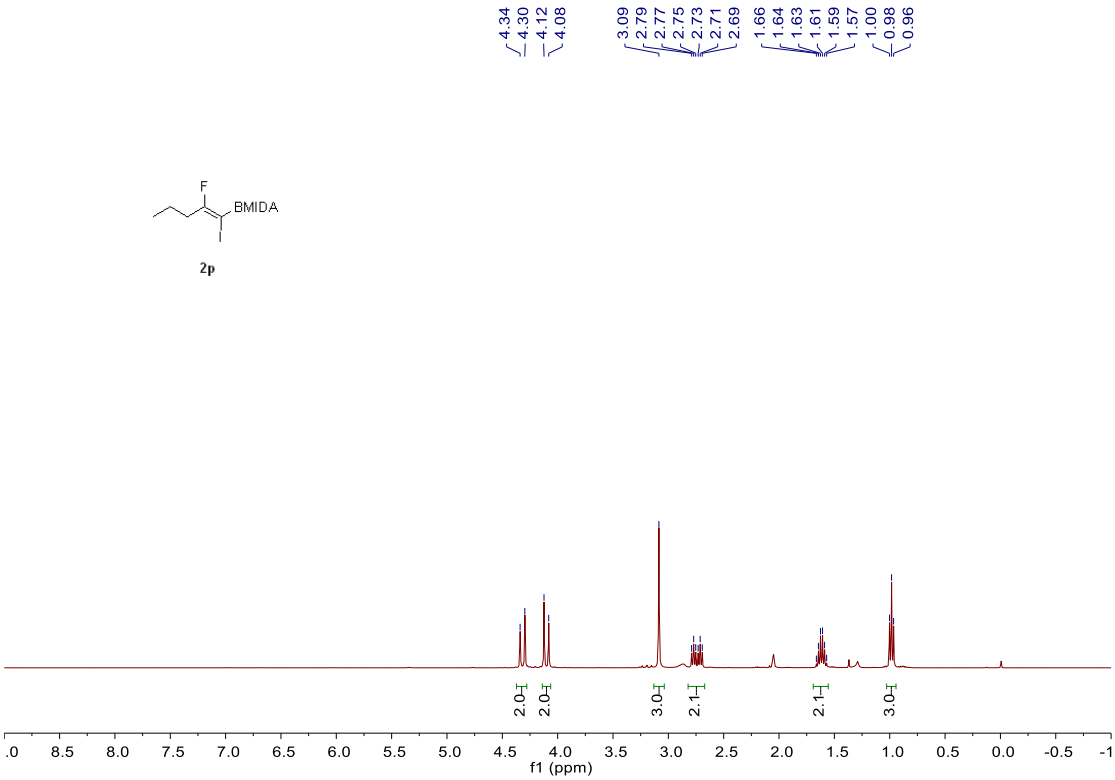

9.96
F
BMIDA
S
I
2n
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

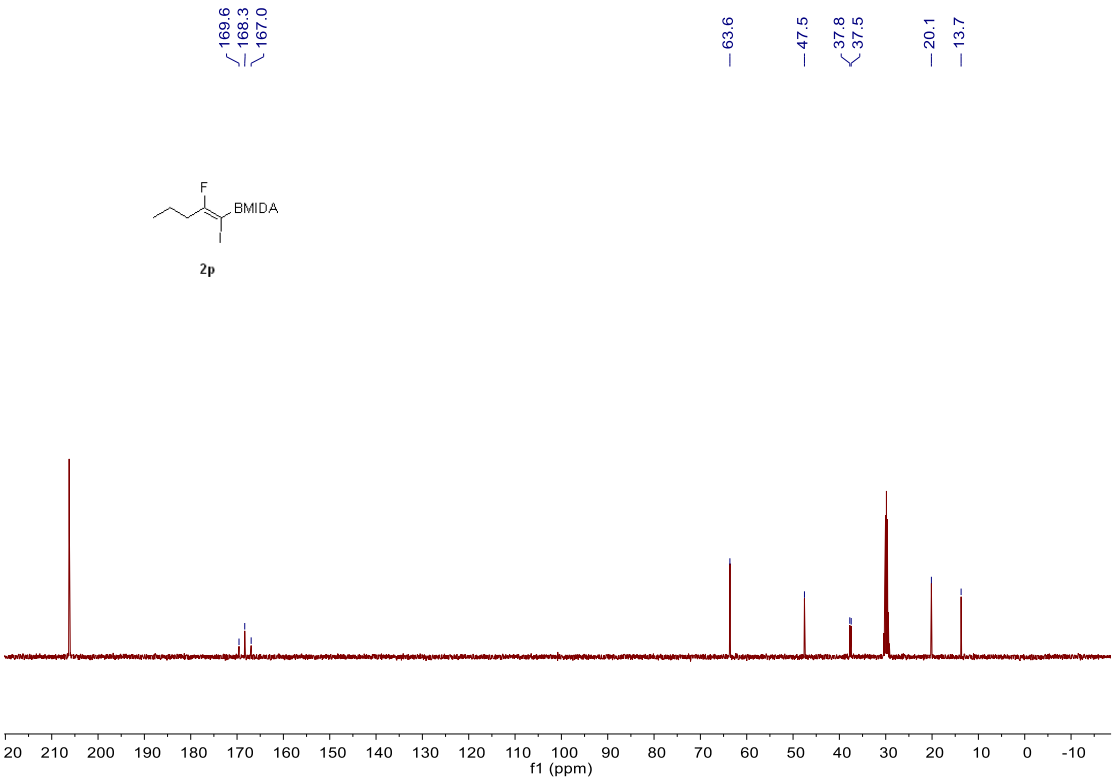

7.42 7.40 7.38 7.37 7.35
4.39 4.36 4.13 4.10 2.93 2.89 2.88 2.87 2.86 2.47 2.45 2.43 2.42 2.39 2.39 2.32 2.30 2.11 2.09 2.08 2.07 2.05 2.04 1.98 1.98 1.97 1.96 1.79 1.77 1.77 1.60 1.58 1.56 1.55 1.47 1.46 1.45 1.44 1.42 1.40 1.38 0.84
F
BMIDA
I
H
H
H
O
2o
1.04 1.05 0.95 1.95 2.00 3.03 2.07 2.29 1.16 1.10 2.24 1.09 2.20 3.33 3.19
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

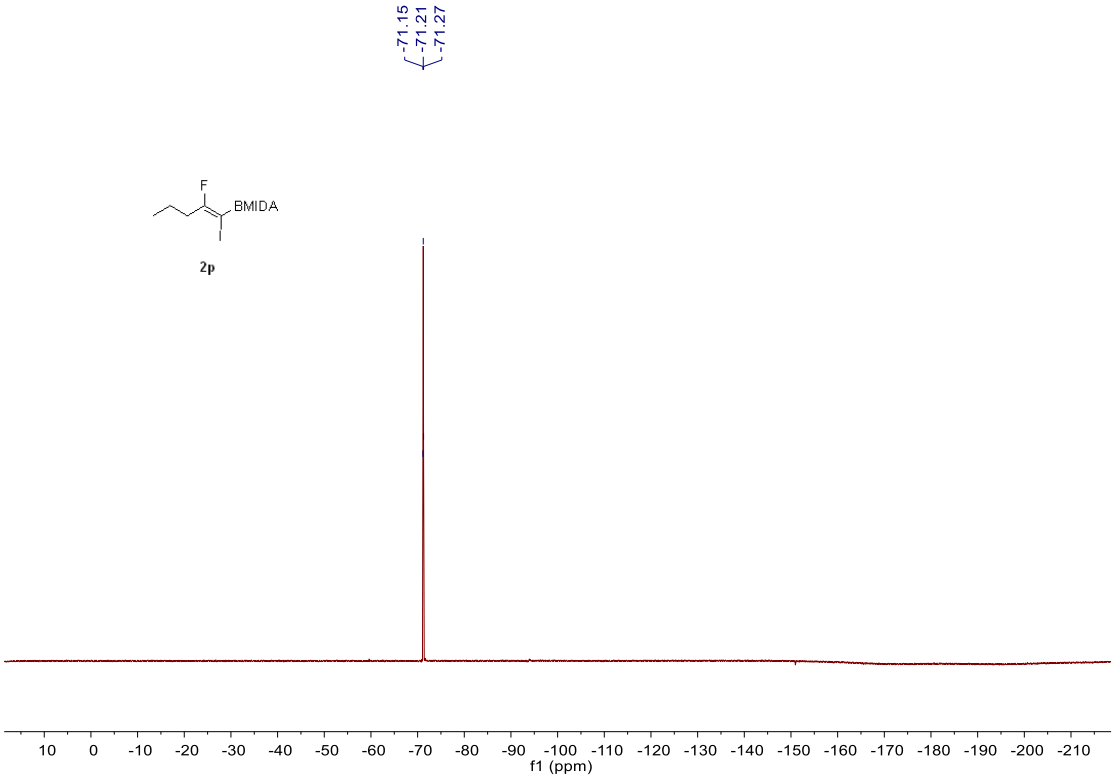

220.6
169.1
163.7
161.7
142.5
136.8
131.8
131.6
129.8
127.1
125.5
63.2
50.0
47.8
47.4
44.3
37.8
35.8
31.7
29.2
26.2
25.5
21.6
13.9
F
BMIDA
I
H
H
H
O
2o
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

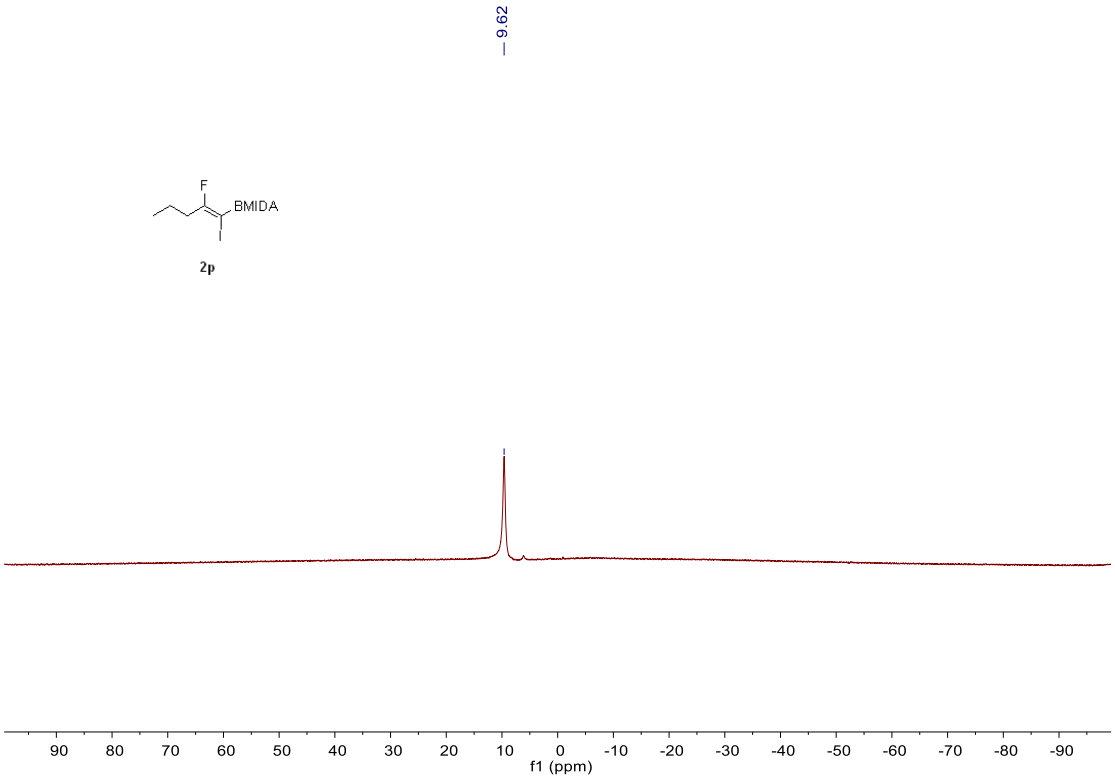

-59.2
F
BMIDA
I
H
H
H
O
2o
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

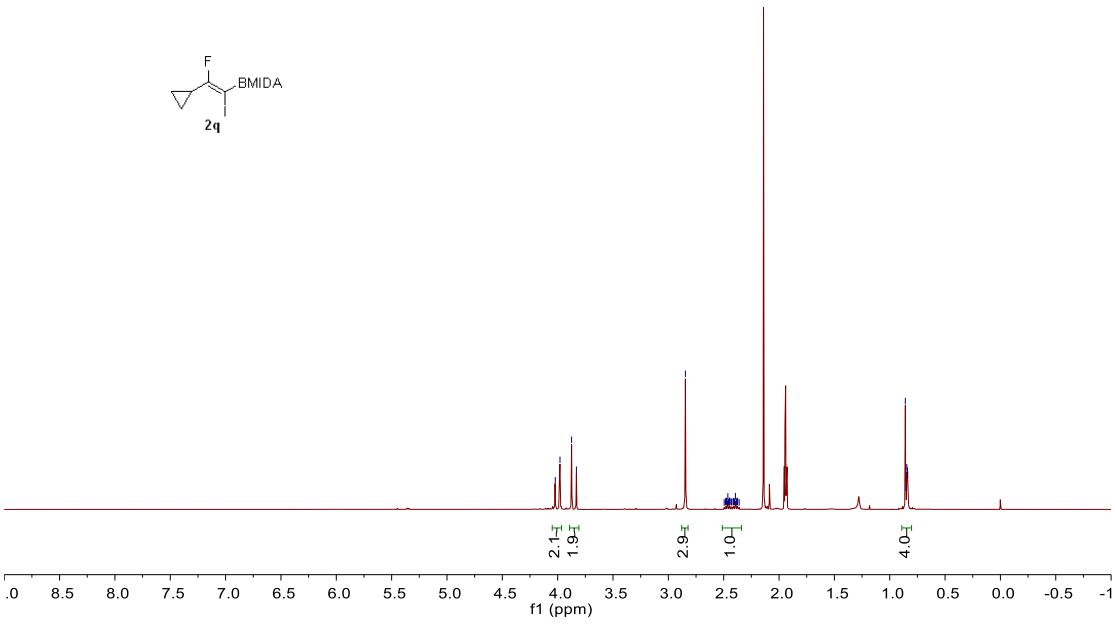

9.74
F
BMIDA
I
H
H
H
O
2o
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

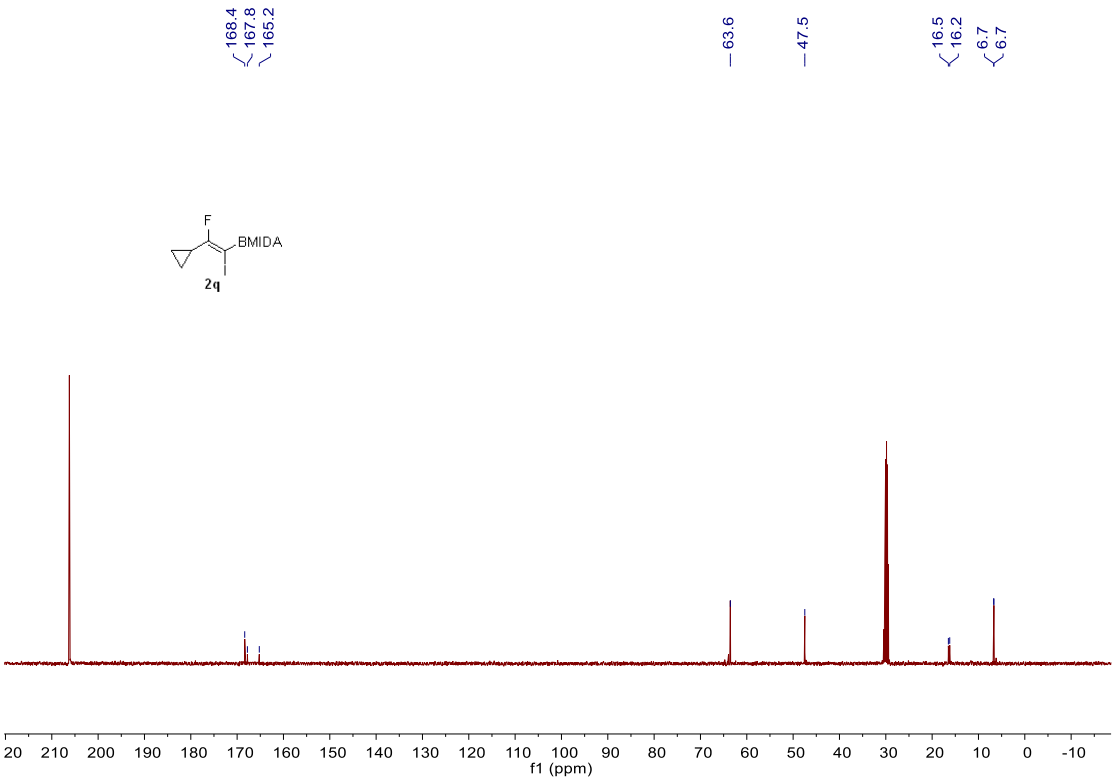

4.34
4.30
4.12
4.08
3.09
2.79
2.77
2.75
2.73
2.71
2.69
1.66
1.64
1.63
1.61
1.59
1.57
1.00
0.98
0.96
F
BMIDA
I
2p
2.0
2.0
3.0
2.1
2.1
3.0
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

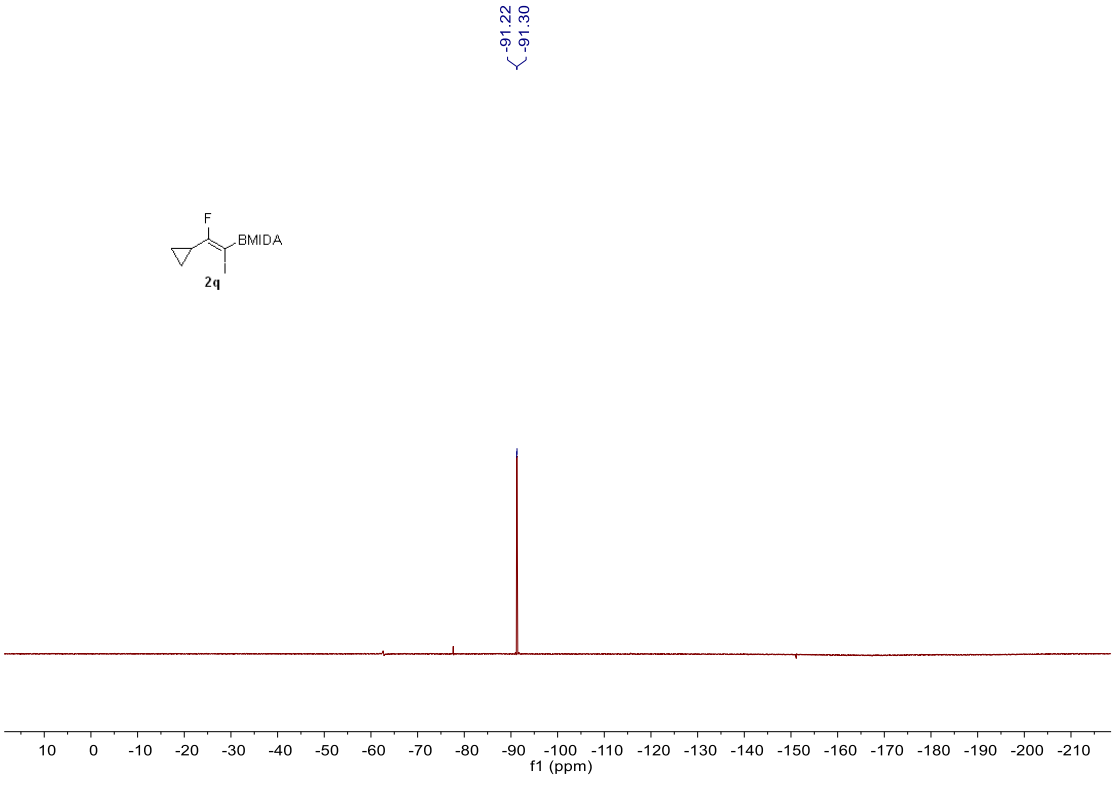

169.6
168.3
167.0
63.6
47.5
37.8
37.5
20.1
13.7
F
BMIDA
2p
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

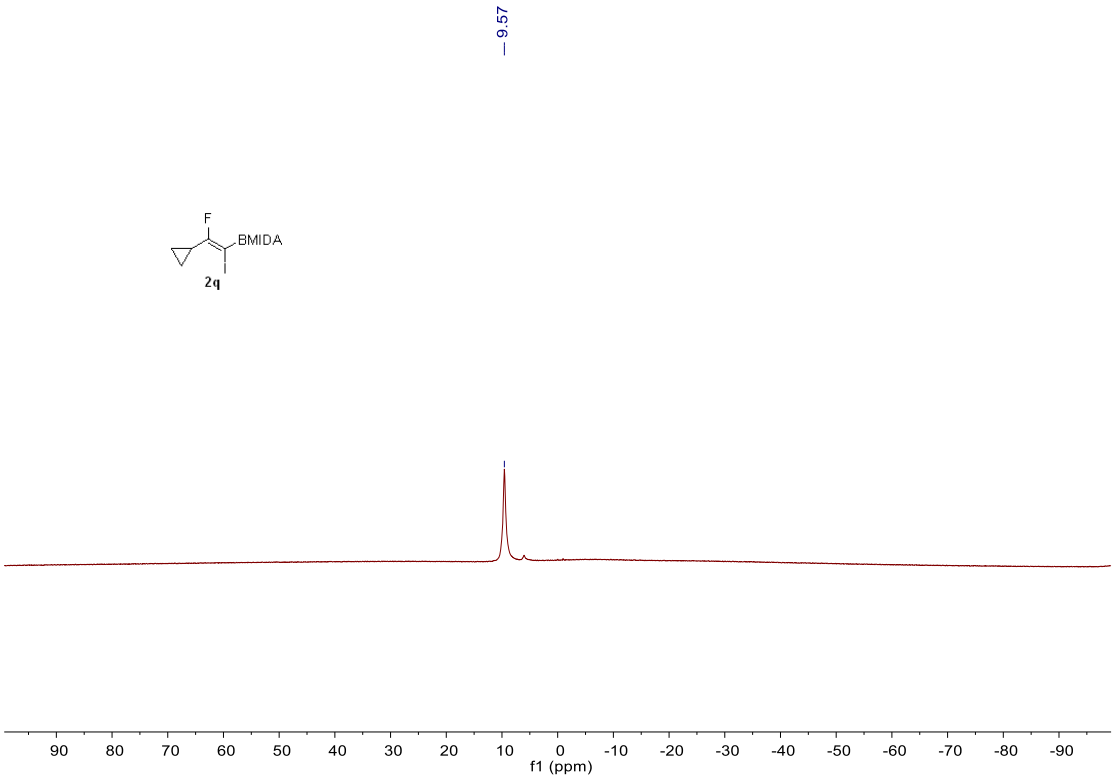

-71.15
-71.21
-71.27
F
BMIDA
2p
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

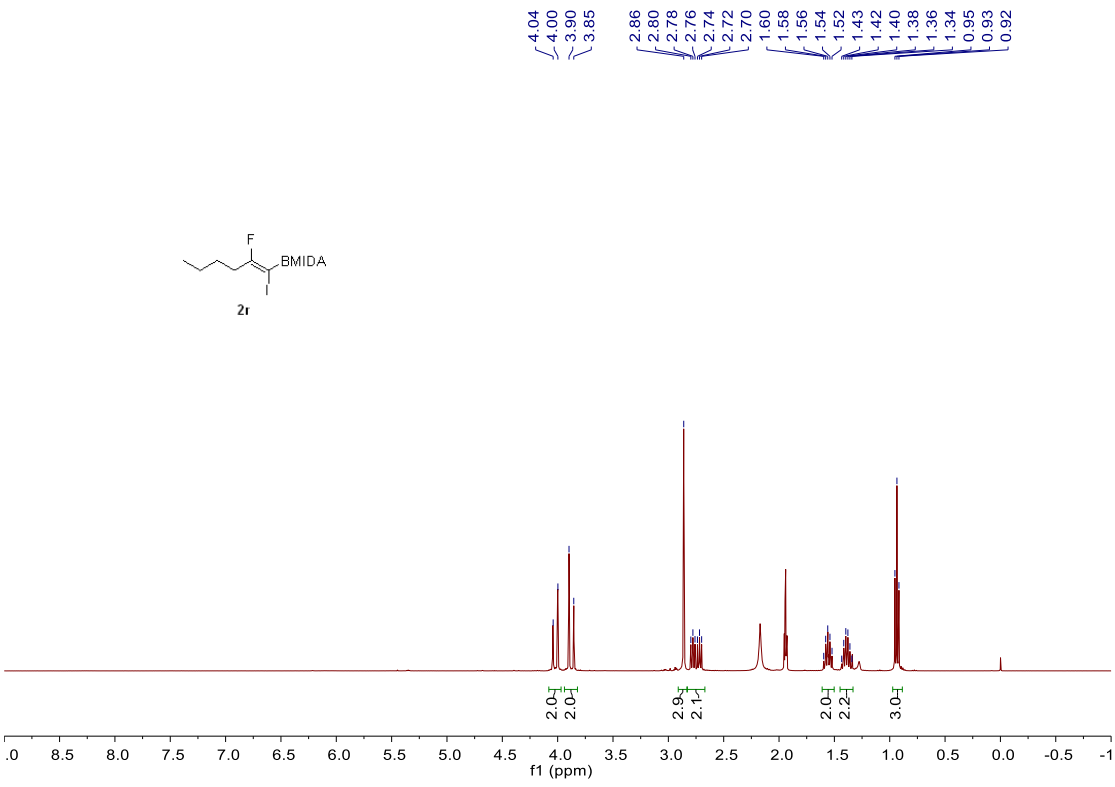

9.62
F
BMIDA
2p
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)
4.02
3.98
3.87
3.83
2.85
2.48
2.48
2.48
2.46
2.45
2.45
2.45
2.41
2.41
2.41
2.41
2.39
2.39
2.38
2.38
2.38
2.37
0.86
0.85
0.85
0.84

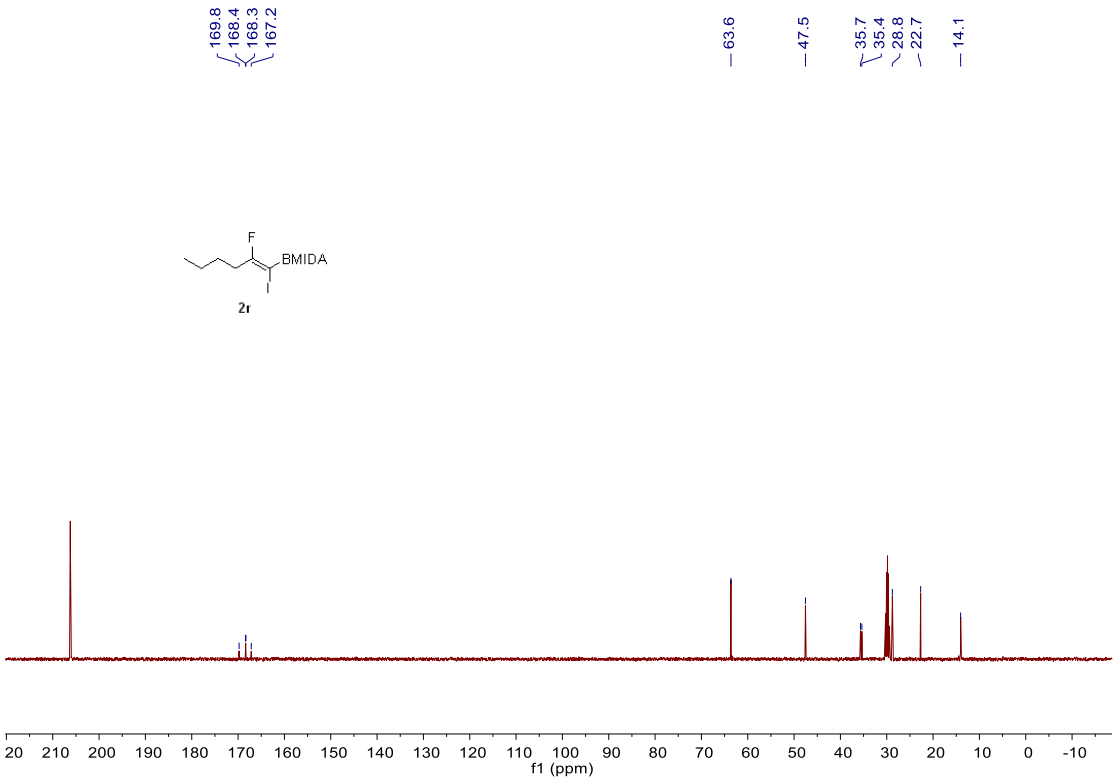

F
BMIDA
2q
2.1
1.9
2.9
1.0
4.0
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

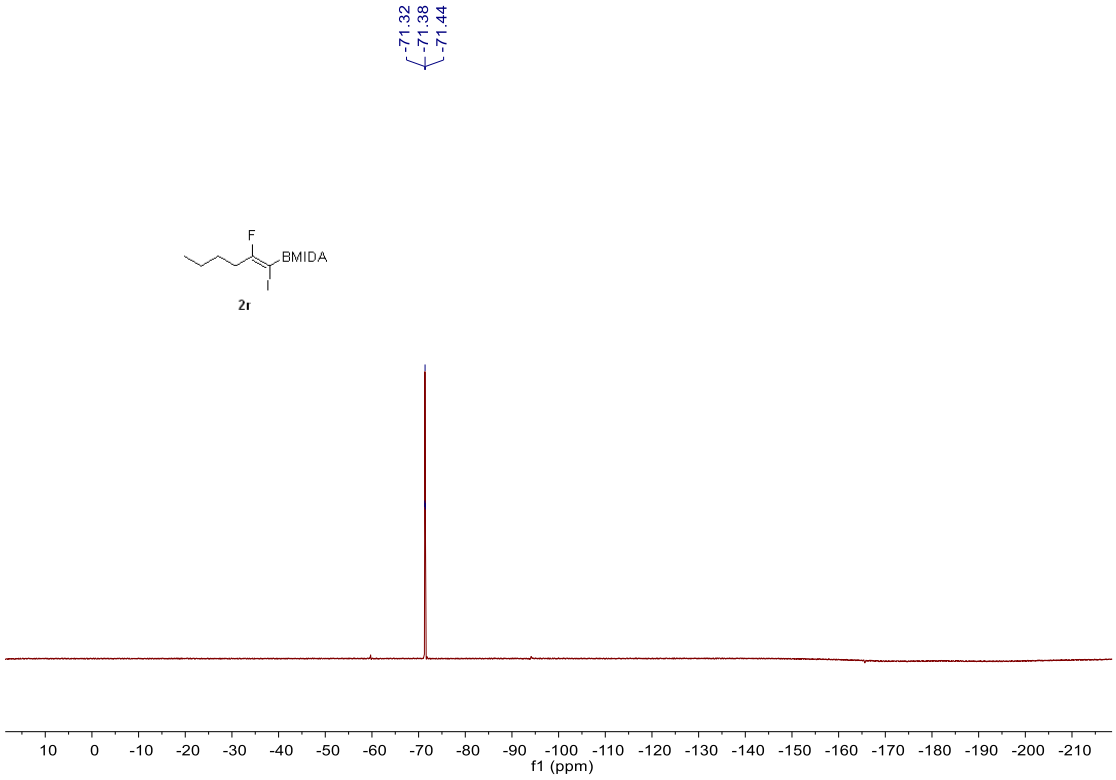

168.4
167.8
165.2
63.6
47.5
16.5
16.2
6.7
6.7
F
BMIDA
2q
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

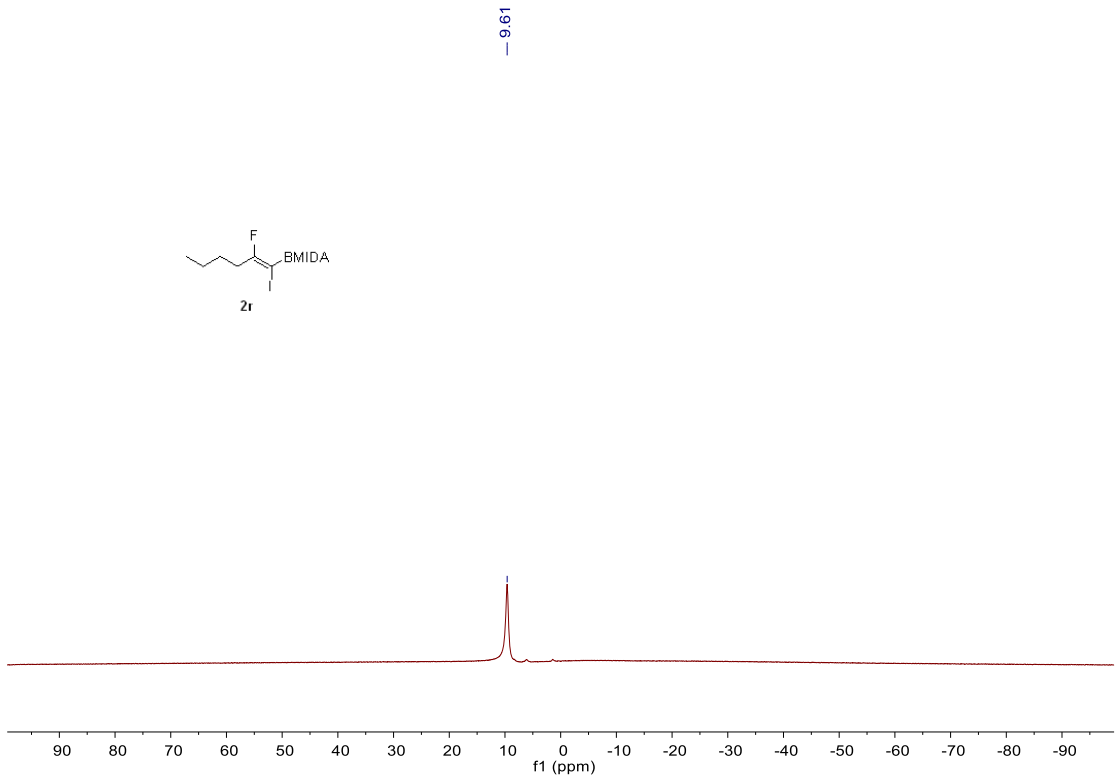

-91.22
-91.30
F
BMIDA
2q
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

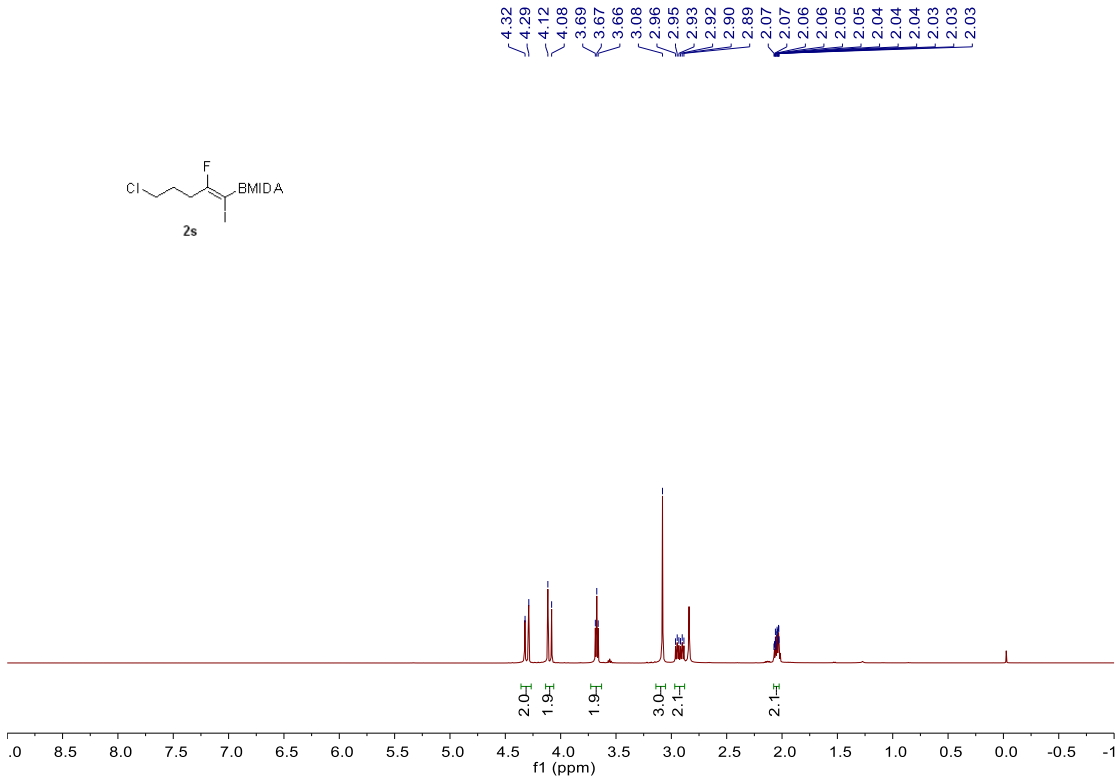

— 9.57
F
BMIDA
2q
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

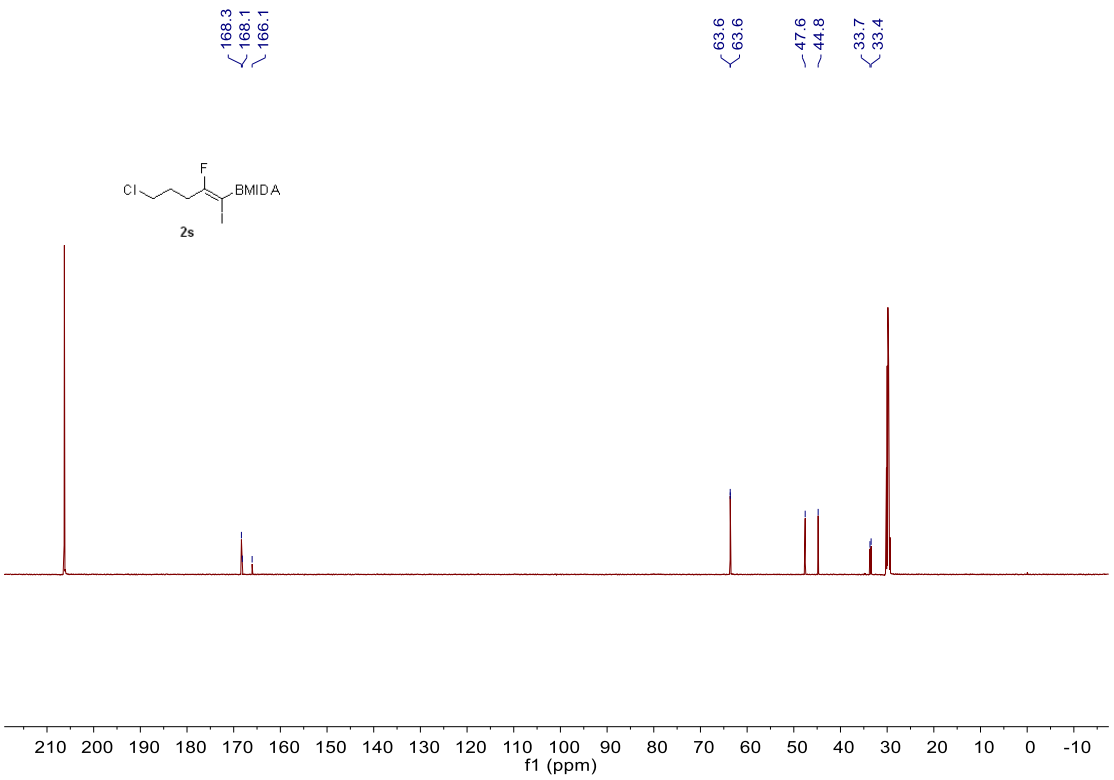

4.04
4.00
3.90
3.85
2.86
2.80
2.78
2.76
2.74
2.72
2.70
1.60
1.58
1.56
1.54
1.52
1.43
1.42
1.40
1.38
1.36
1.34
0.95
0.93
0.92
F
BMIDA
2r
2.0
2.0
2.9
2.1
2.0
2.2
3.0
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

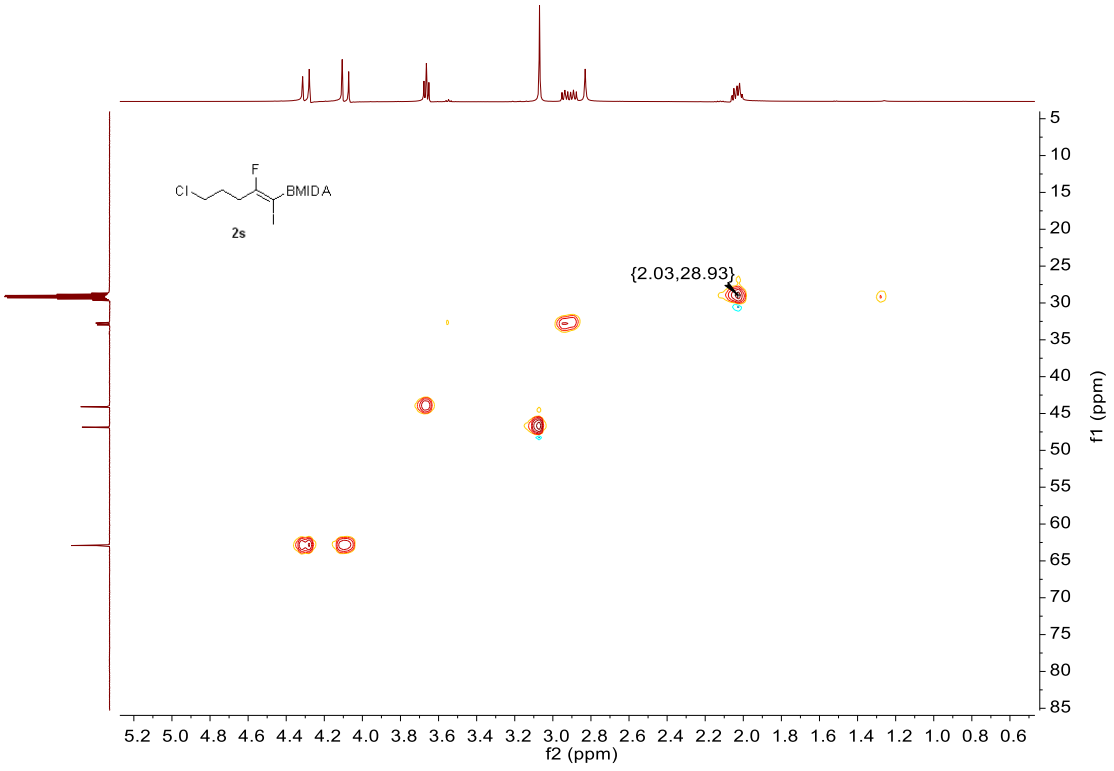

169.8
168.4
168.3
167.2
63.6
47.5
35.7
35.4
28.8
22.7
14.1
F
BMIDA
I
2r
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

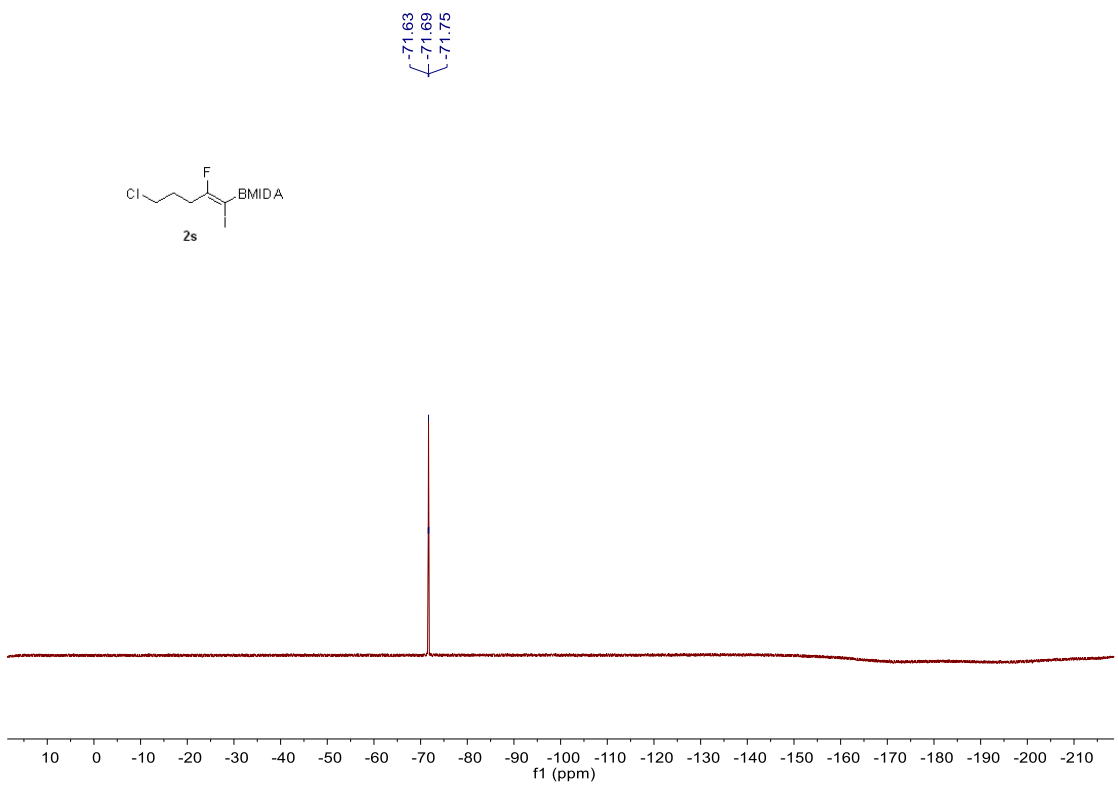

-71.32
-71.38
-71.44
F
BMIDA
I
2r
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

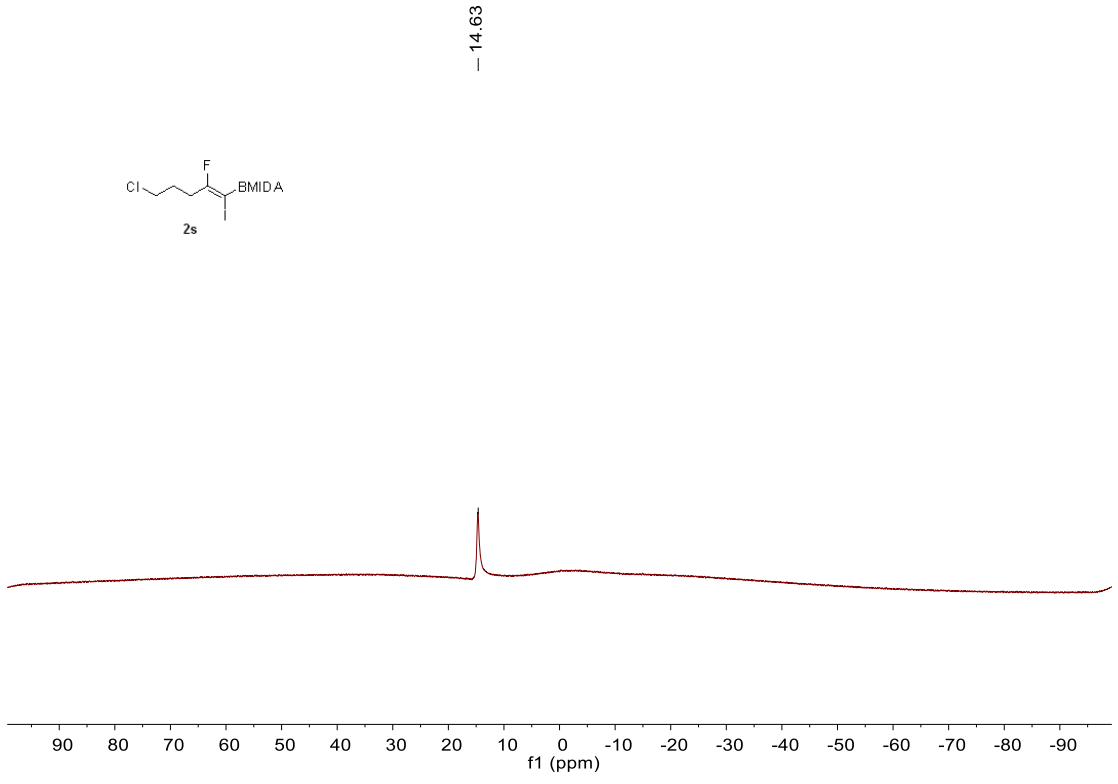

9.61
F
BMIDA
I
2r
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

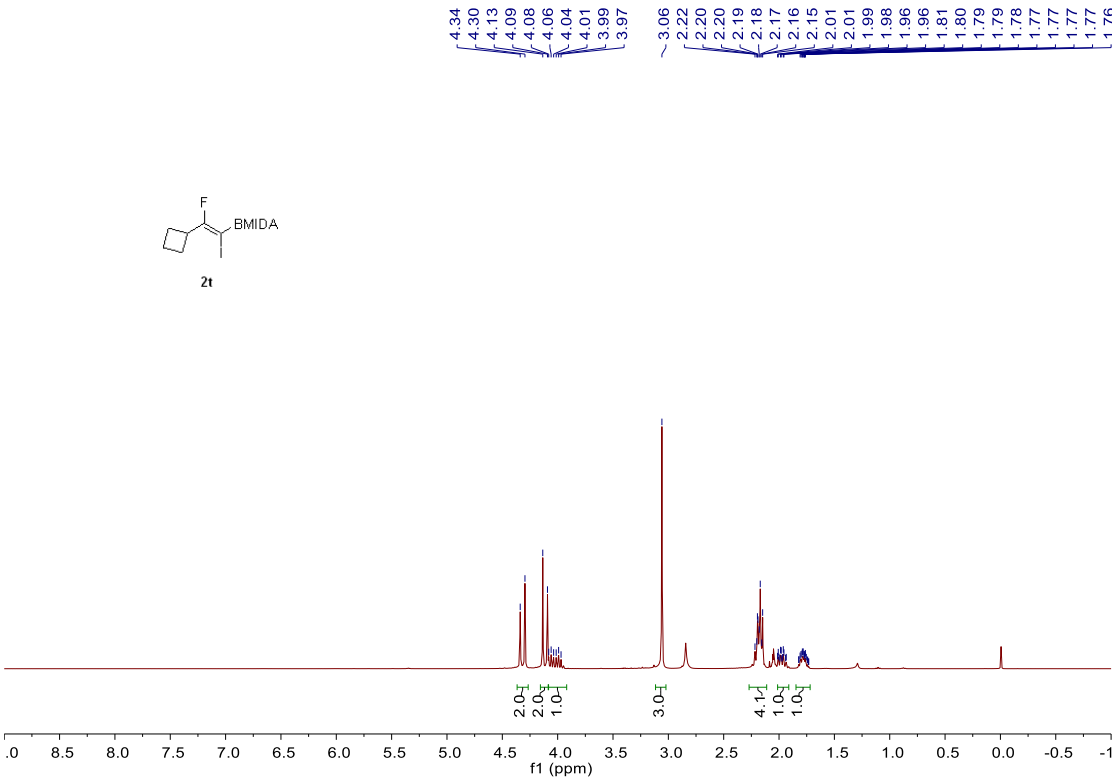

4.32
4.29
4.12
4.08
3.69
3.67
3.66
3.08
2.96
2.95
2.93
2.92
2.90
2.89
2.07
2.07
2.06
2.06
2.05
2.05
2.04
2.04
2.04
2.03
2.03
2.03
F
Cl
BMIDA
I
2s
2.0
1.9
1.9
3.0
2.1
2.1
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

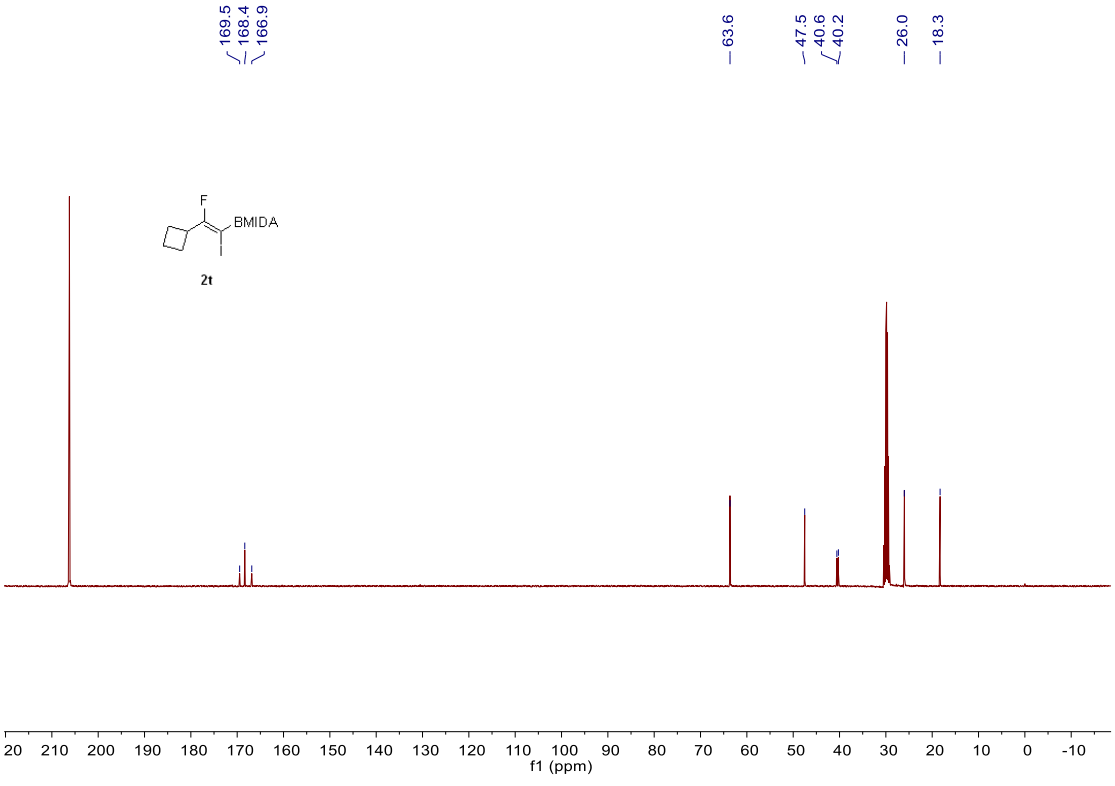

168.3
168.1
166.1
63.6
63.6
47.6
44.8
33.7
33.4
F
Cl
BMIDA
2s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

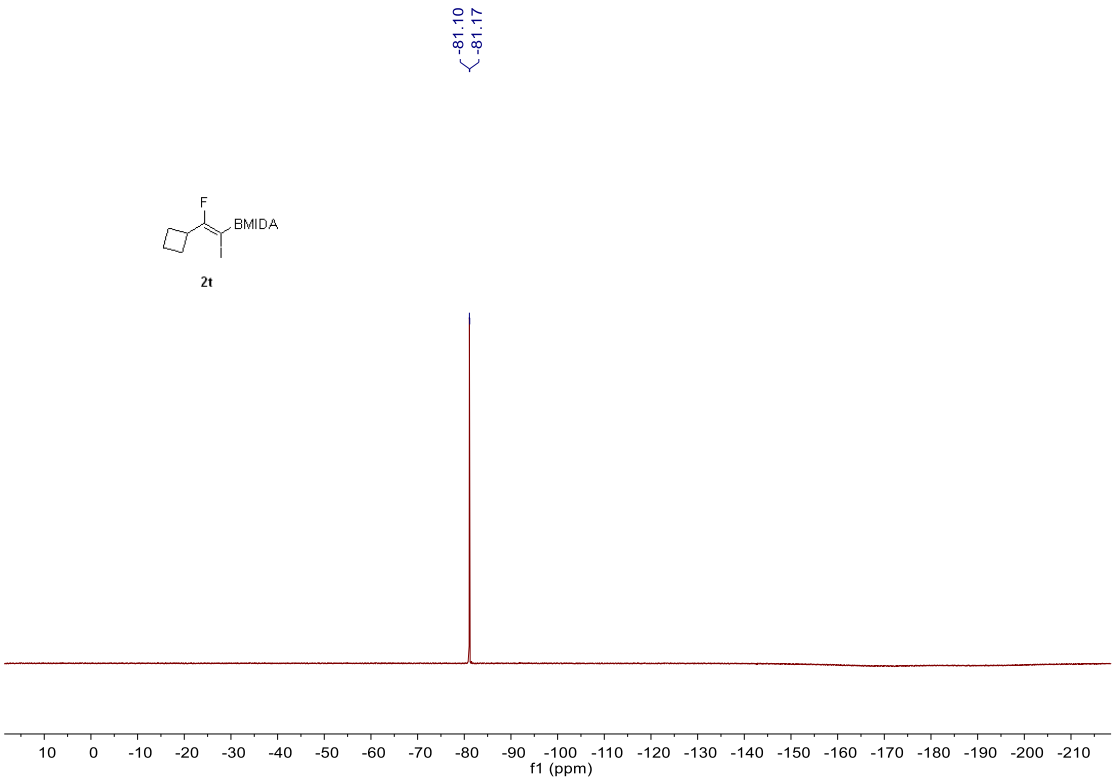

F
Cl
BMIDA
2s
{2.03,28.93}
5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85
f1 (ppm)
5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
f2 (ppm)

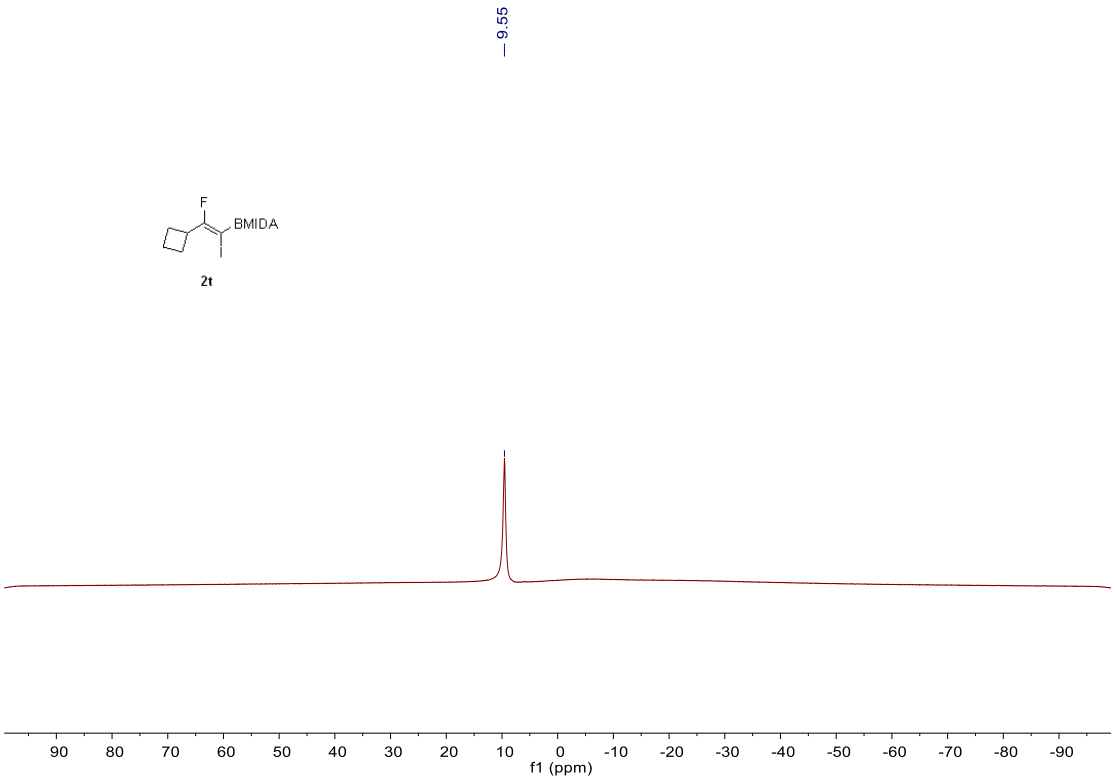

-71.63
-71.69
-71.75
F
Cl
BMIDA
2s
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

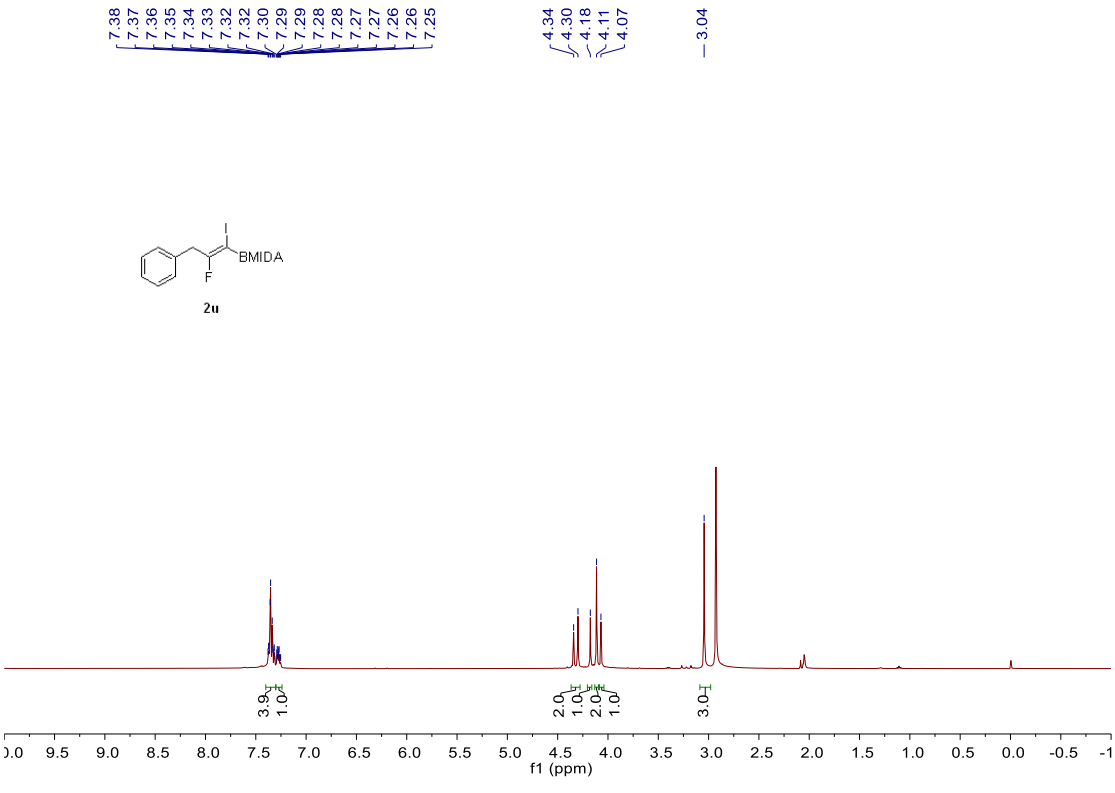

14.63
F
Cl
BMIDA
2s
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

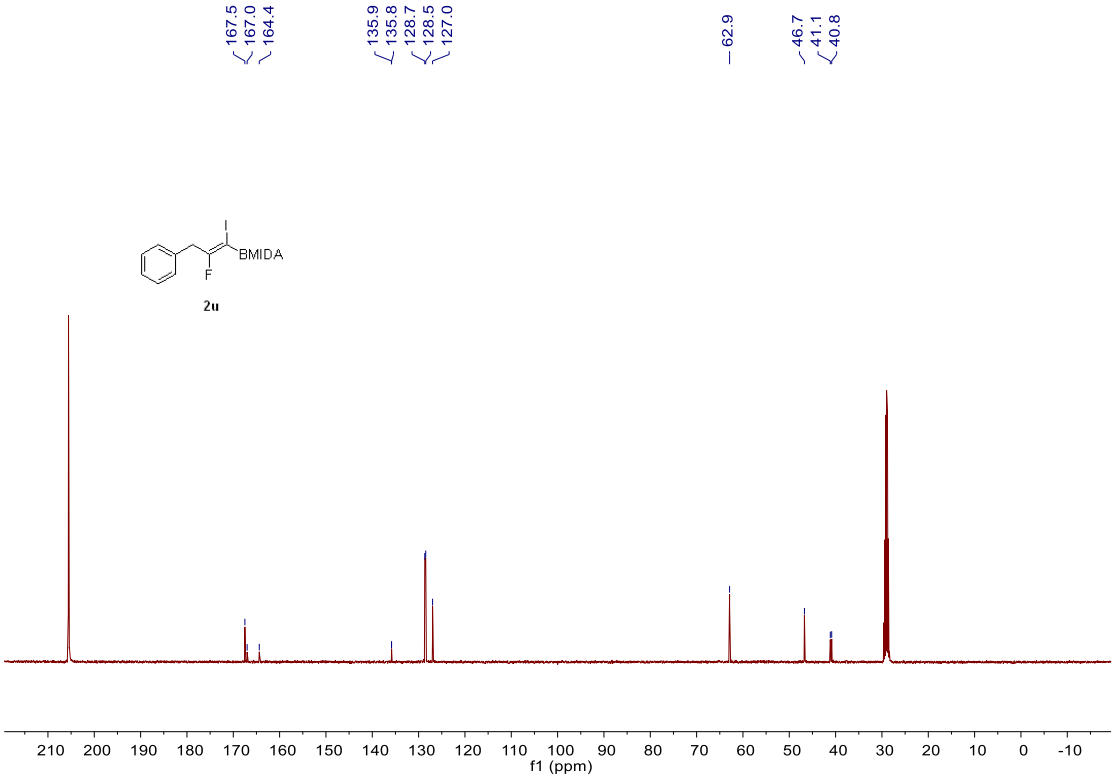

4.34
4.30
4.13
4.09
4.08
4.06
4.04
4.01
3.99
3.97
3.06
2.22
2.20
2.20
2.19
2.18
2.17
2.16
2.15
2.01
2.01
1.99
1.98
1.96
1.96
1.81
1.80
1.79
1.79
1.78
1.77
1.77
1.77
1.77
1.76
F
BMIDA
2t
2.0
2.0
1.0
3.0
4.1
1.0
1.0
f1 (ppm)

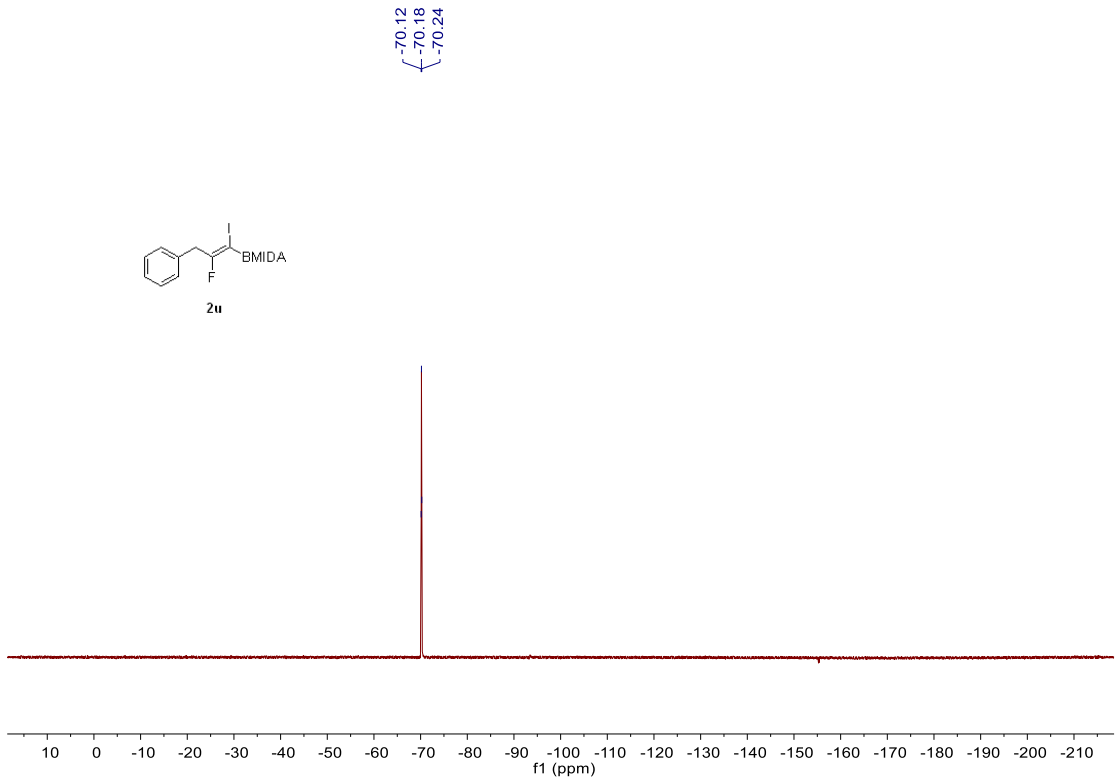

169.5
168.4
166.9
63.6
47.5
40.6
40.2
26.0
18.3
F
BMIDA
2t
f1 (ppm)

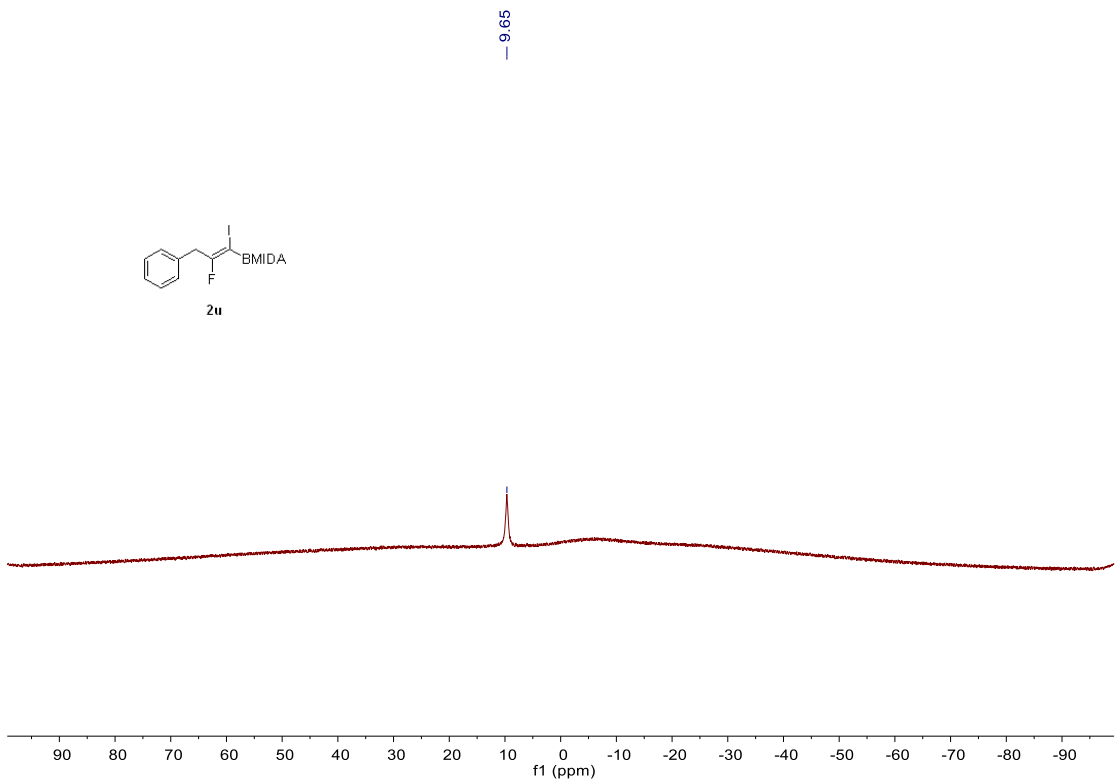

-81.10
-81.17
F
BMIDA
2t
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

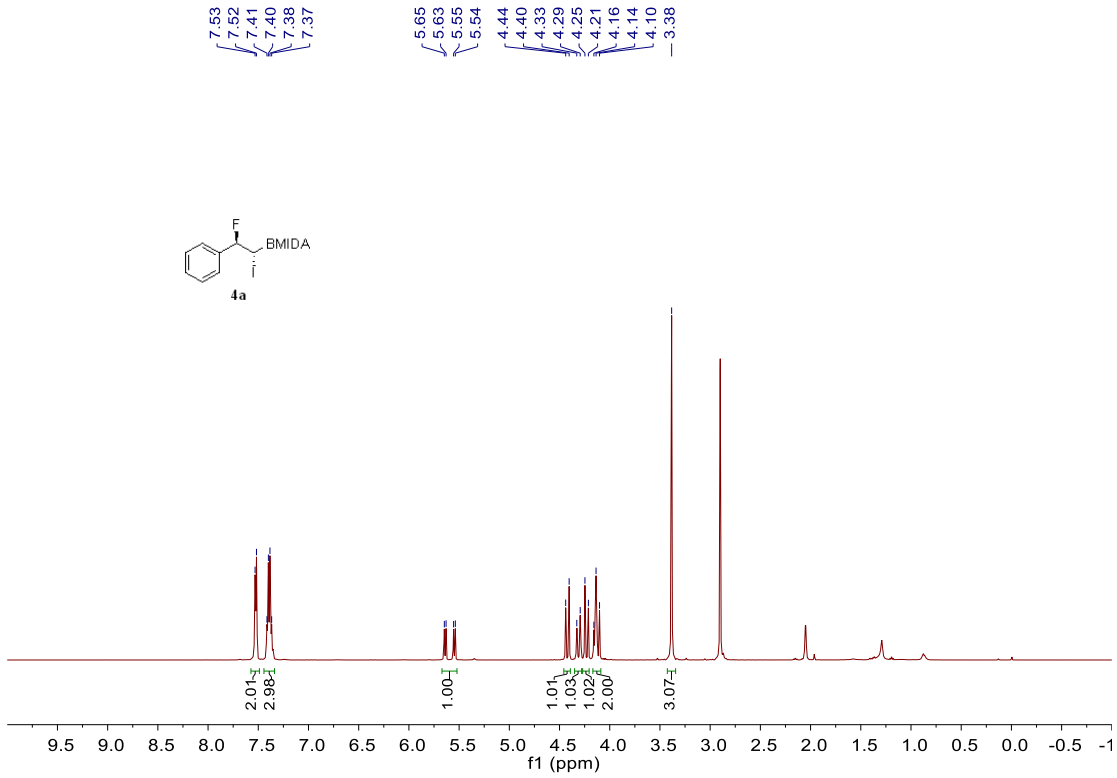

9.55
F
BMIDA
2t
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

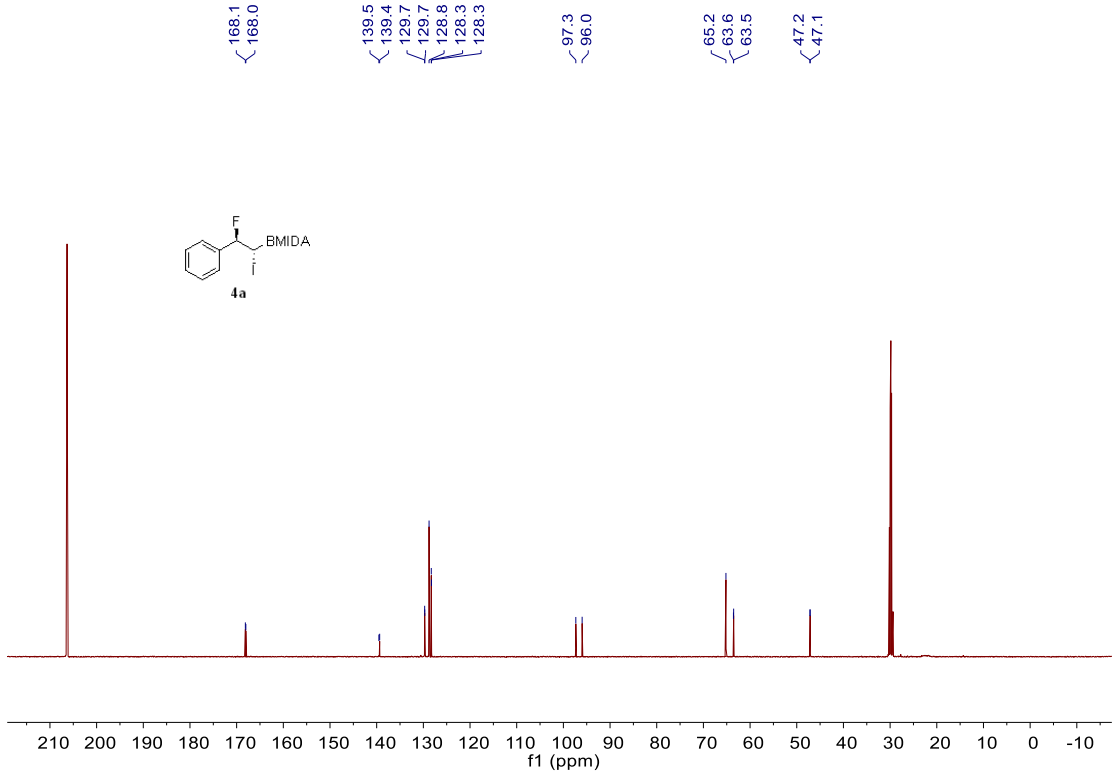

7.38
7.37
7.36
7.35
7.34
7.33
7.32
7.32
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.26
7.25
4.34
4.30
4.18
4.11
4.07
3.04
I
BMIDA
F
2u
3.9
1.0
2.0
1.0
2.0
1.0
3.0
f1 (ppm)

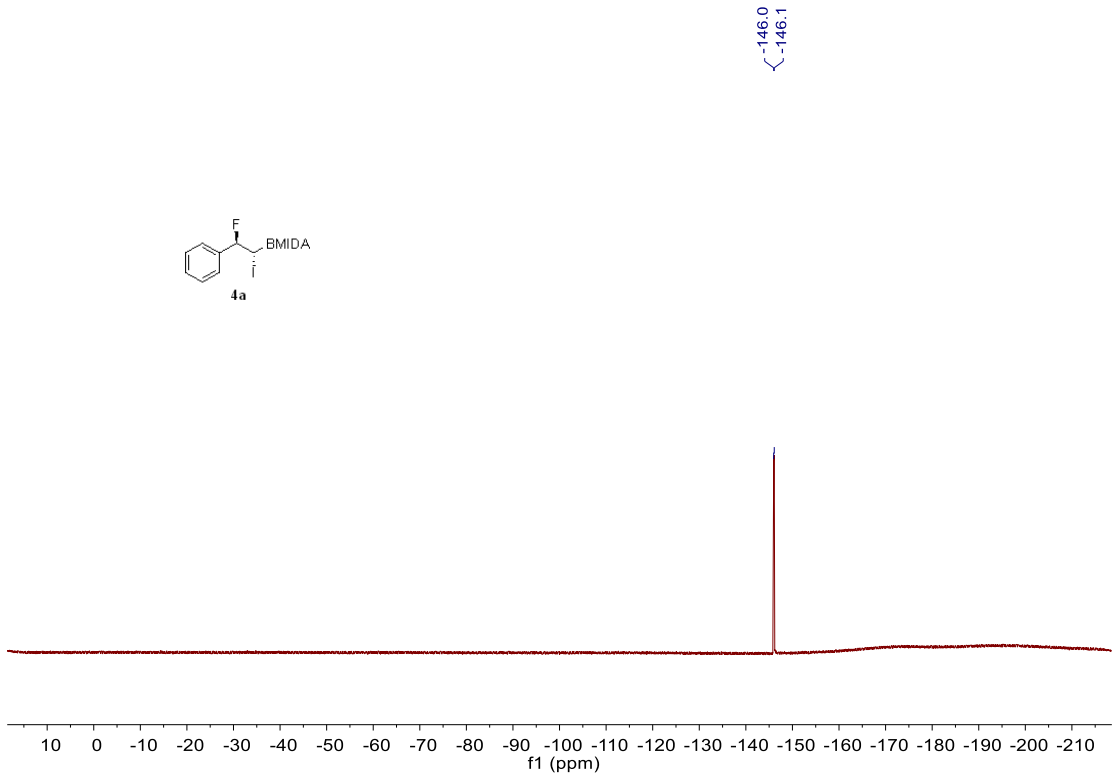

167.5
167.0
164.4
135.9
135.8
128.7
128.5
127.0
62.9
46.7
41.1
40.8
I
BMIDA
F
2u
f1 (ppm)

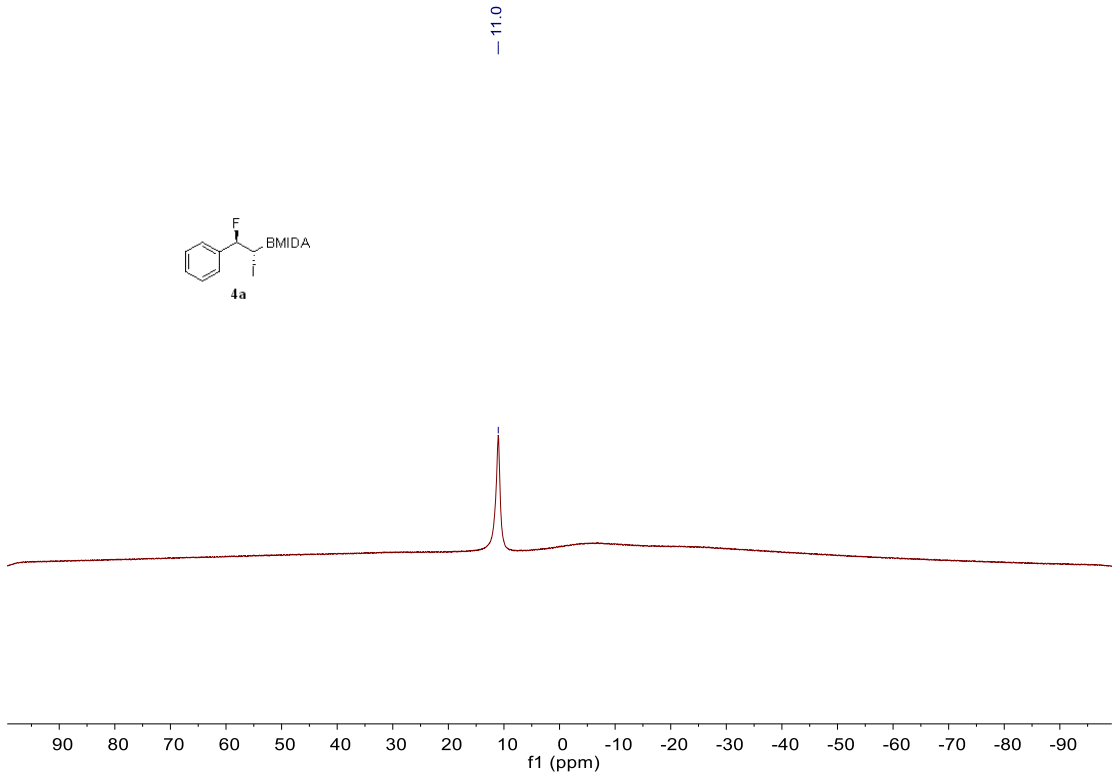

-70.12
-70.18
-70.24
I
BMIDA
F
2u
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

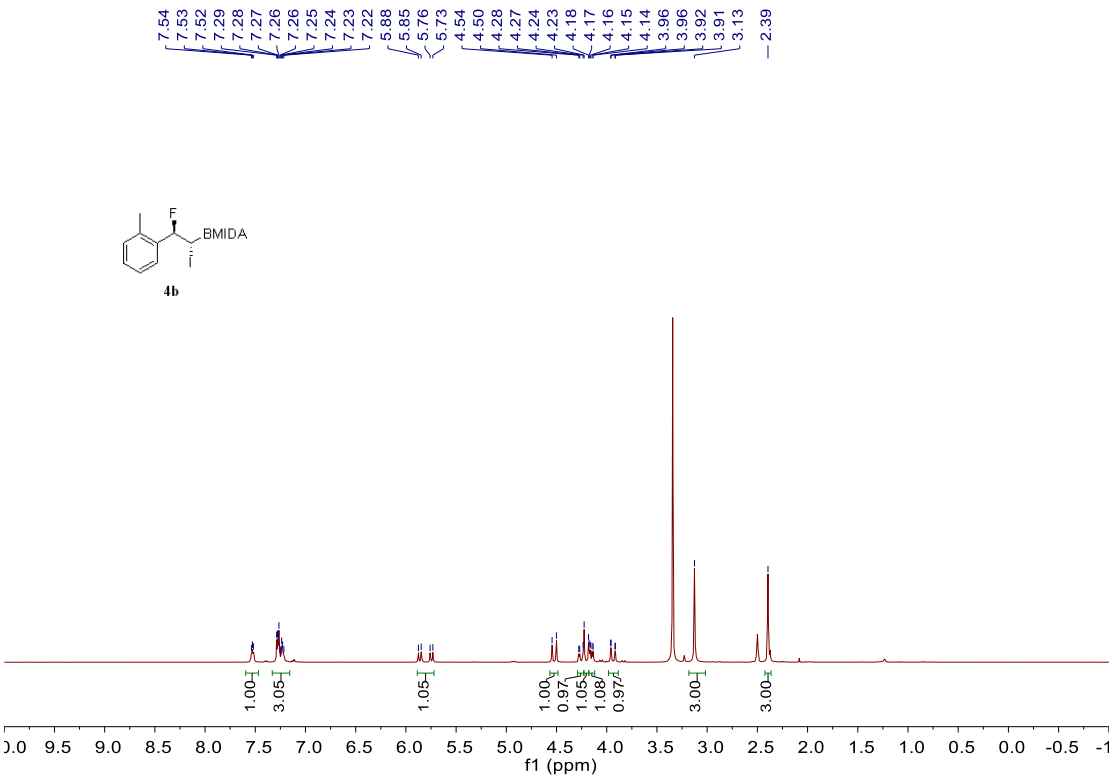

9.65
I
BMIDA
F
2u
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

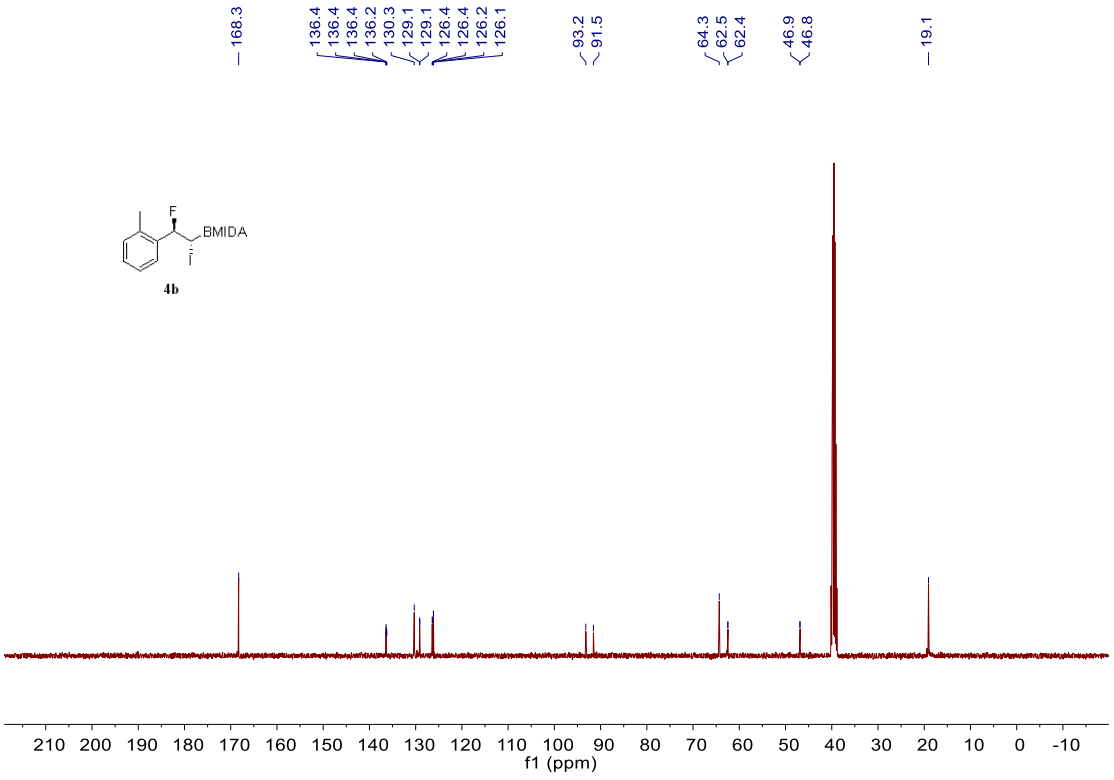

7.53
7.52
7.41
7.40
7.38
7.37
5.65
5.63
5.55
5.54
4.44
4.40
4.33
4.29
4.25
4.21
4.16
4.14
4.10
3.38
F
BMIDA
4a
2.01
2.98
1.00
1.01
1.03
1.02
2.00
3.07
f1 (ppm)

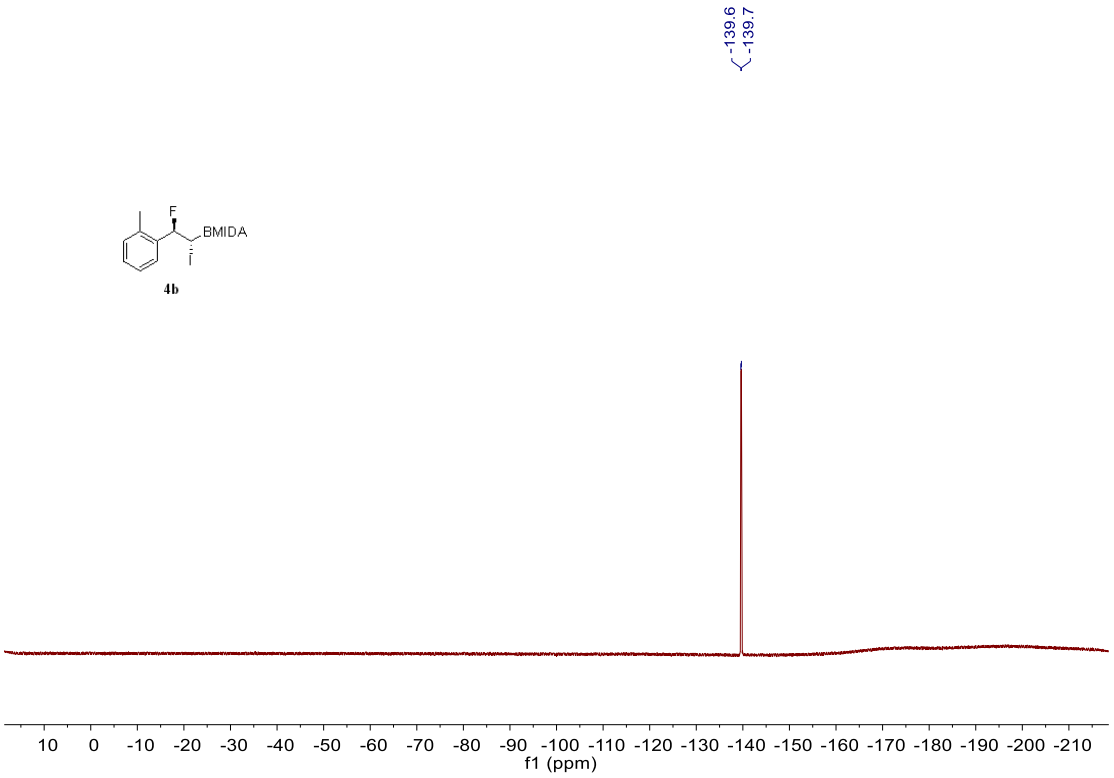

168.1
168.0
139.5
139.4
129.7
129.7
128.8
128.3
128.3
97.3
96.0
65.2
63.6
63.5
47.2
47.1
F
BMIDA
4a
f1 (ppm)


-146.0
-146.1
F
BMIDA
4a
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

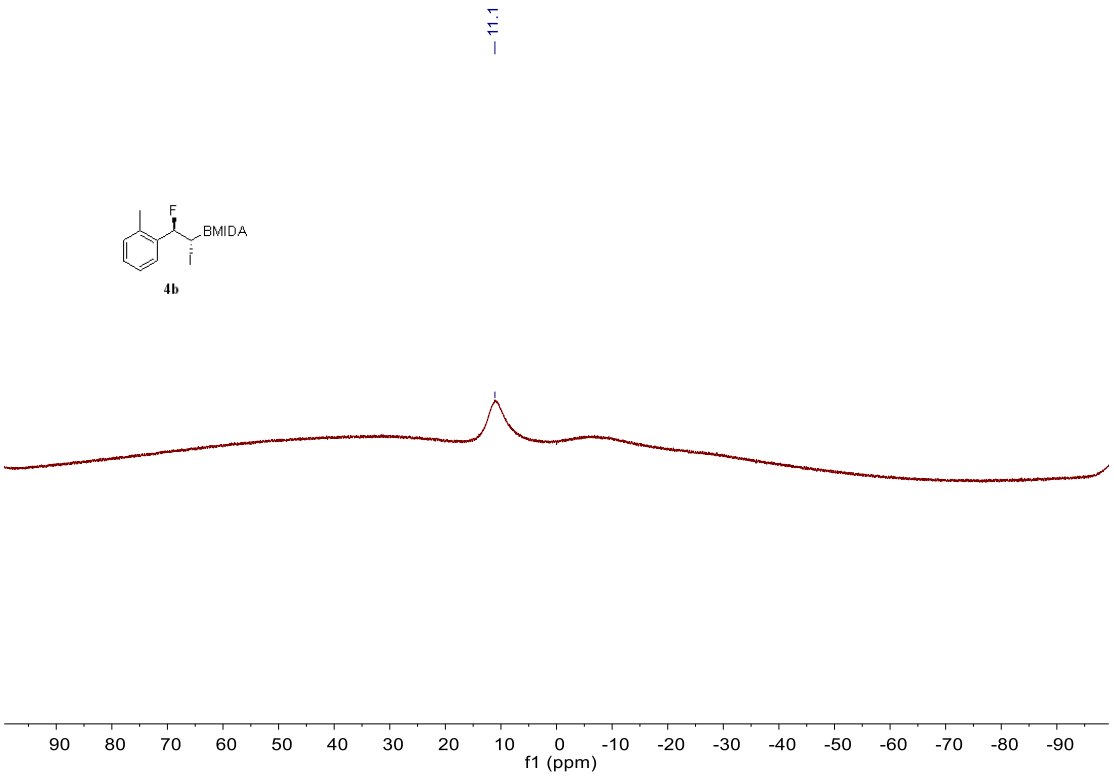

11.0
F
BMIDA
4a
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


7.54
7.53
7.52
7.29
7.28
7.27
7.26
7.26
7.25
7.24
7.23
7.22
5.88
5.85
5.76
5.73
4.54
4.50
4.28
4.27
4.24
4.23
4.18
4.17
4.16
4.15
4.14
3.96
3.96
3.92
3.91
3.13
2.39
F
BMIDA
4b
1.00
3.05
1.05
1.00
0.97
1.05
1.08
0.97
3.00
3.00
f1 (ppm)

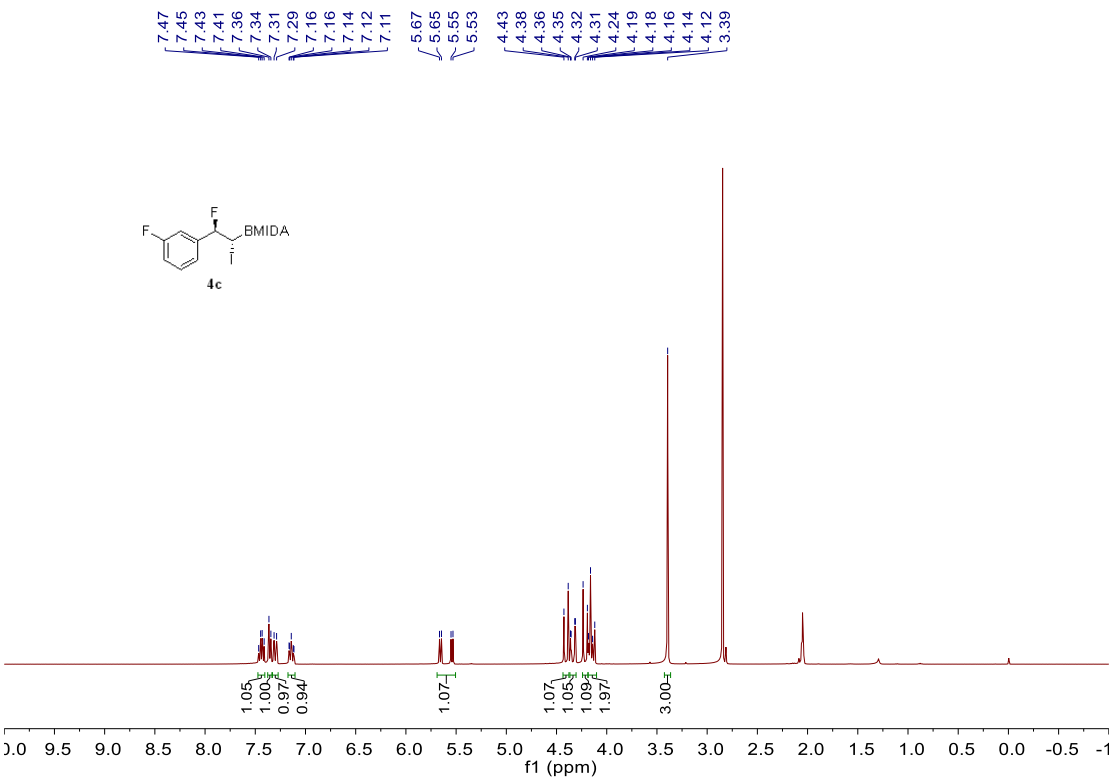

168.3
136.4
136.4
136.4
136.2
130.3
129.1
129.1
126.4
126.4
126.2
126.1
93.2
91.5
64.3
62.5
62.4
46.9
46.8
19.1
F
BMIDA
4b
f1 (ppm)


-139.6
-139.7
F
BMIDA
I
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

4b


11.1
F
BMIDA
I
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

4b


7.47
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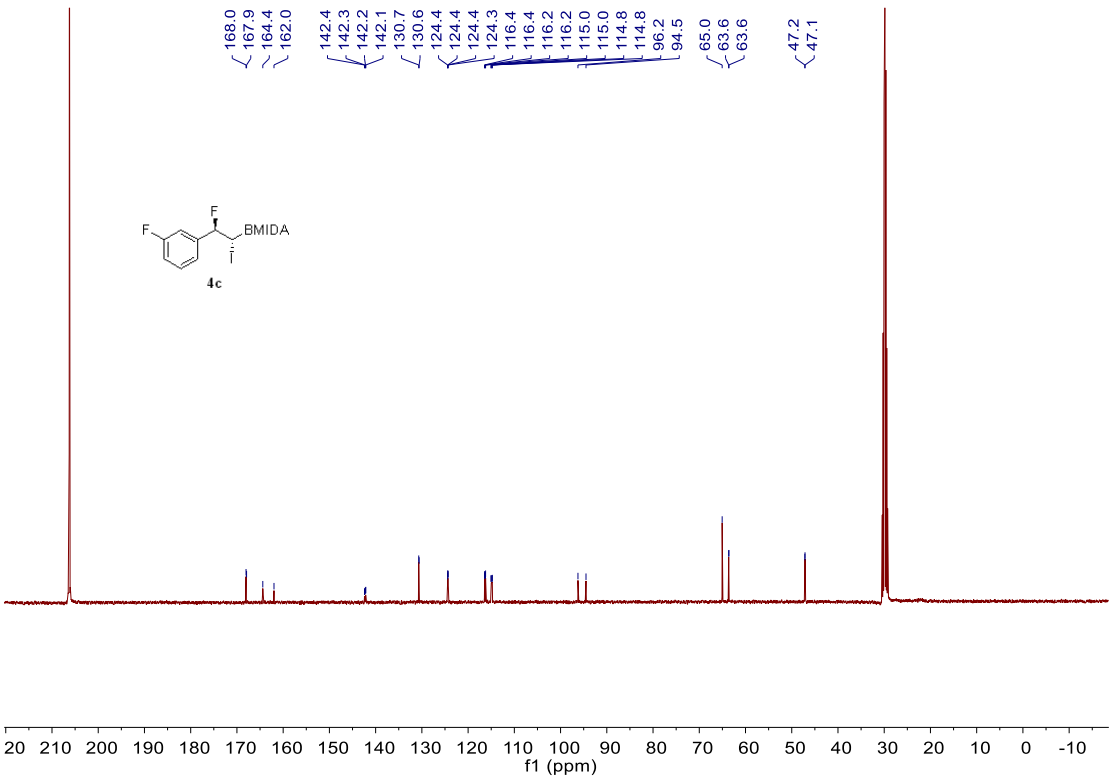
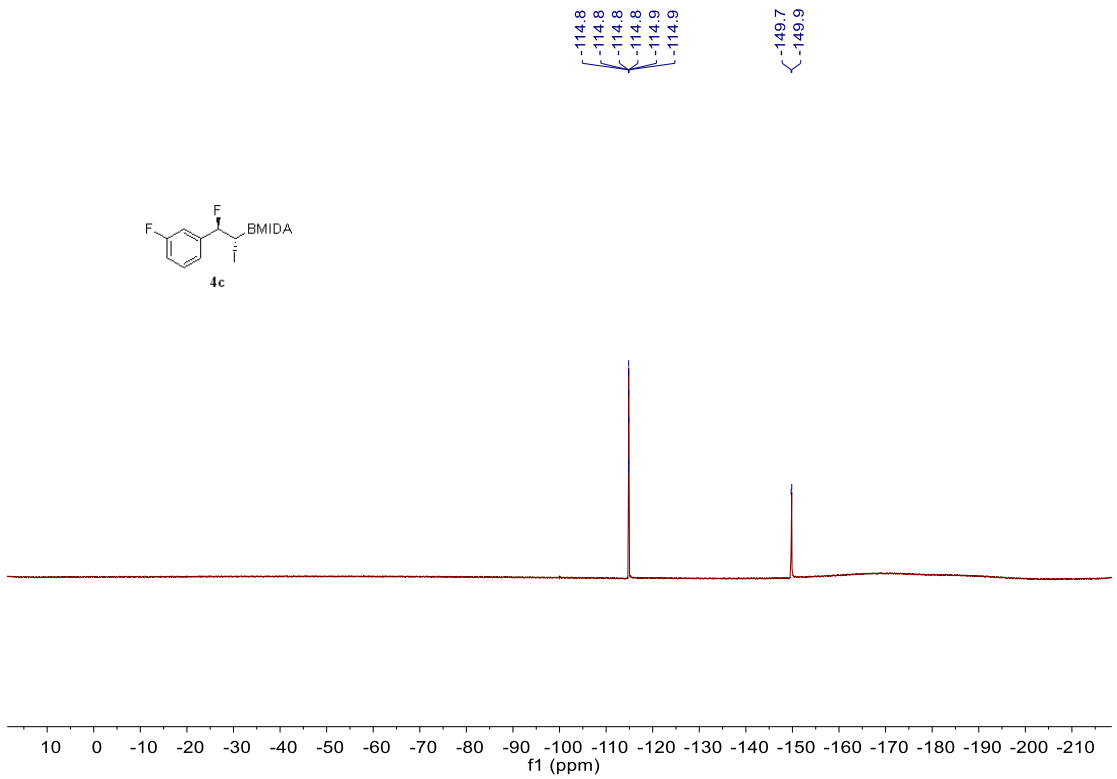
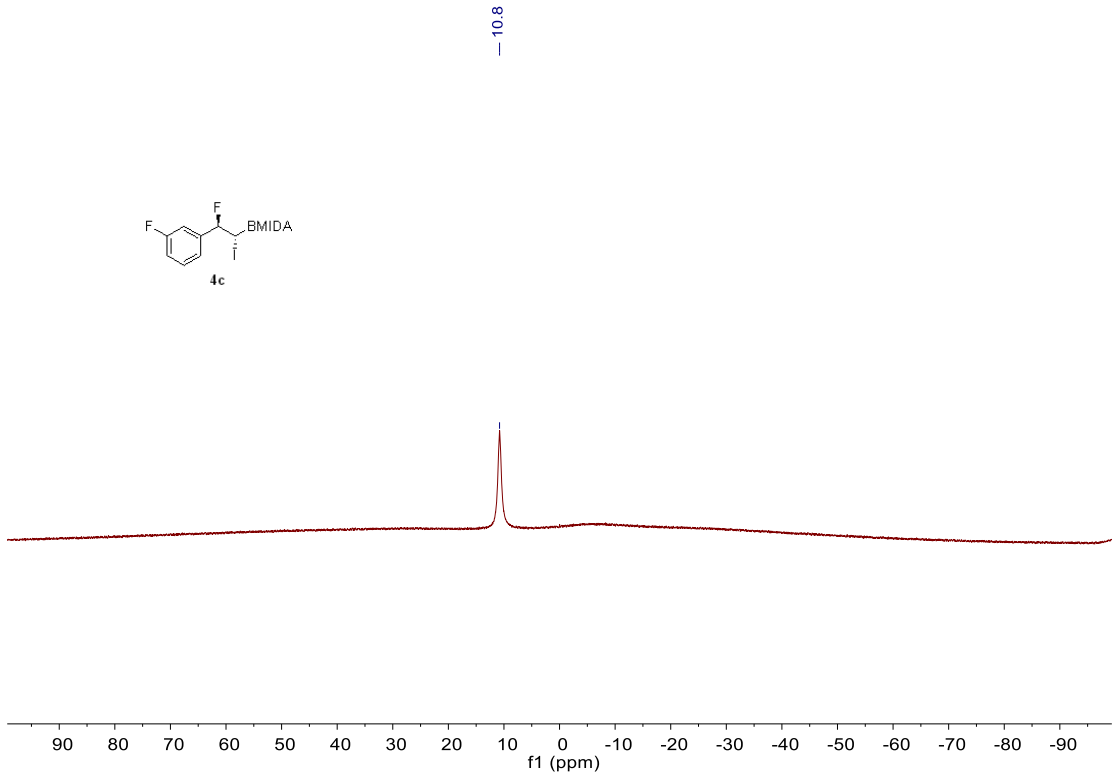
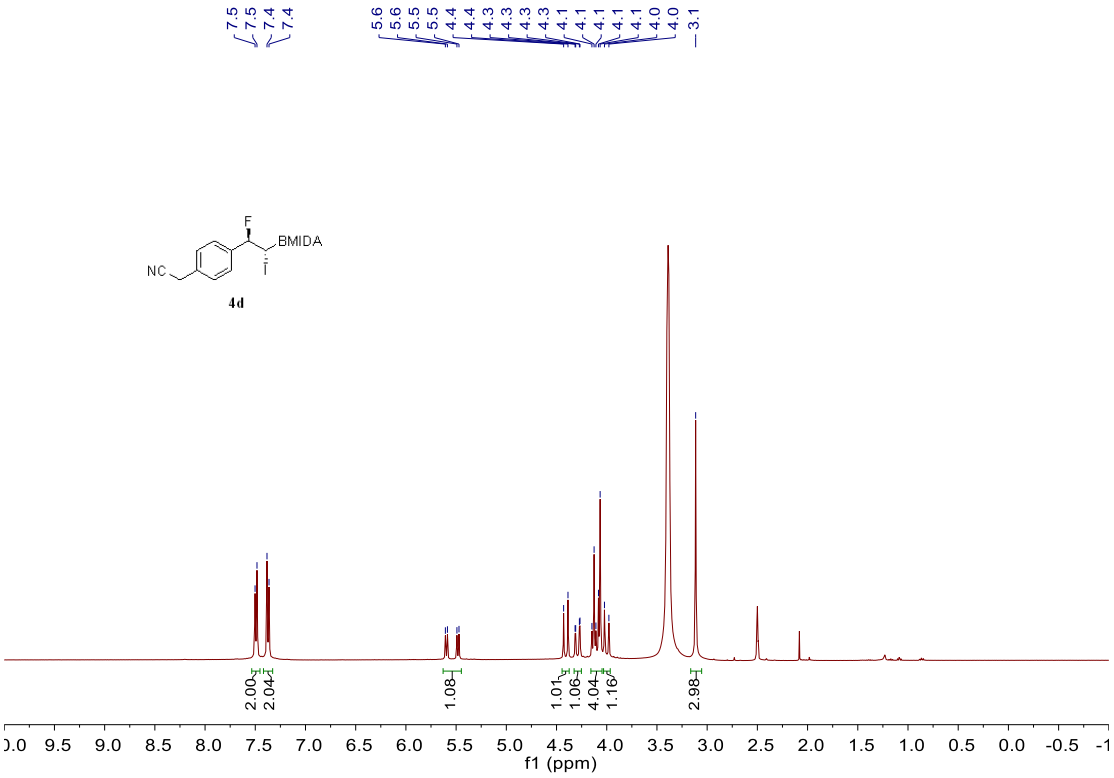
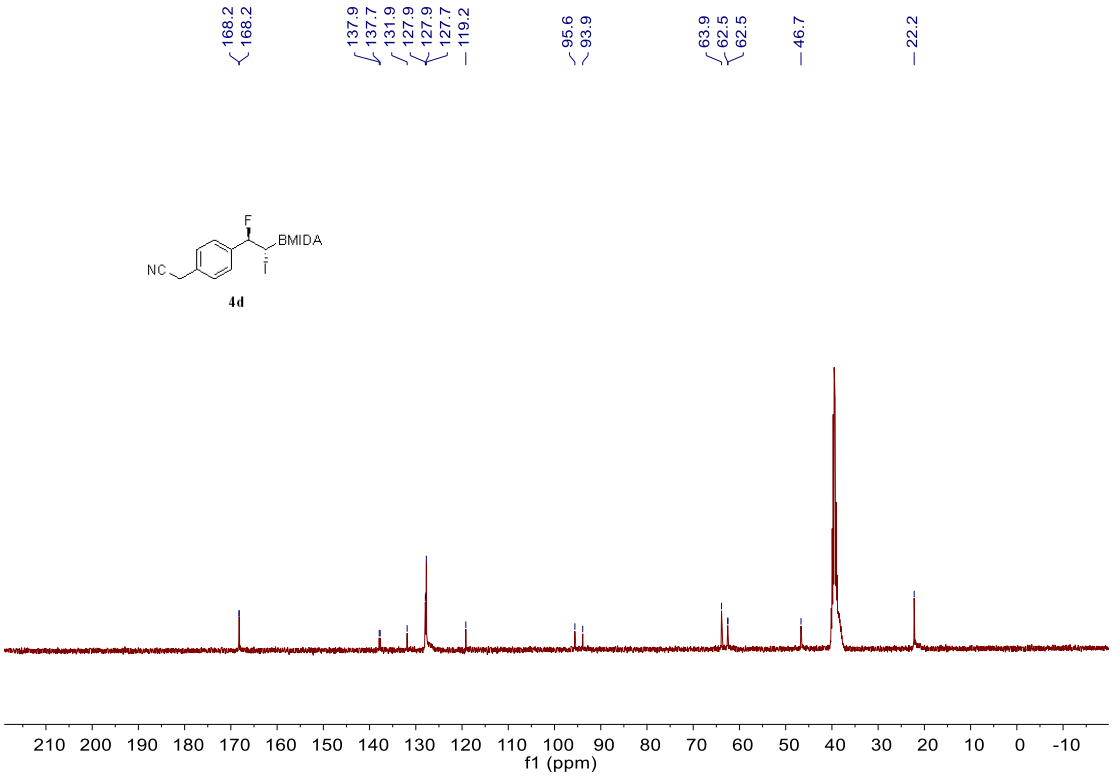
7.43
7.41
7.36
7.34
7.31
7.29
7.16
7.16
7.14
7.12
7.11
5.67
5.65
5.55
5.53
4.43
4.38
4.36
4.35
4.32
4.31
4.24
4.19
4.18
4.16
4.14
4.12
3.39
F
F
BMIDA
4c
1.05
1.00
0.97
0.94
1.07
1.07
1.05
1.09
1.97
3.00
f1 (ppm)

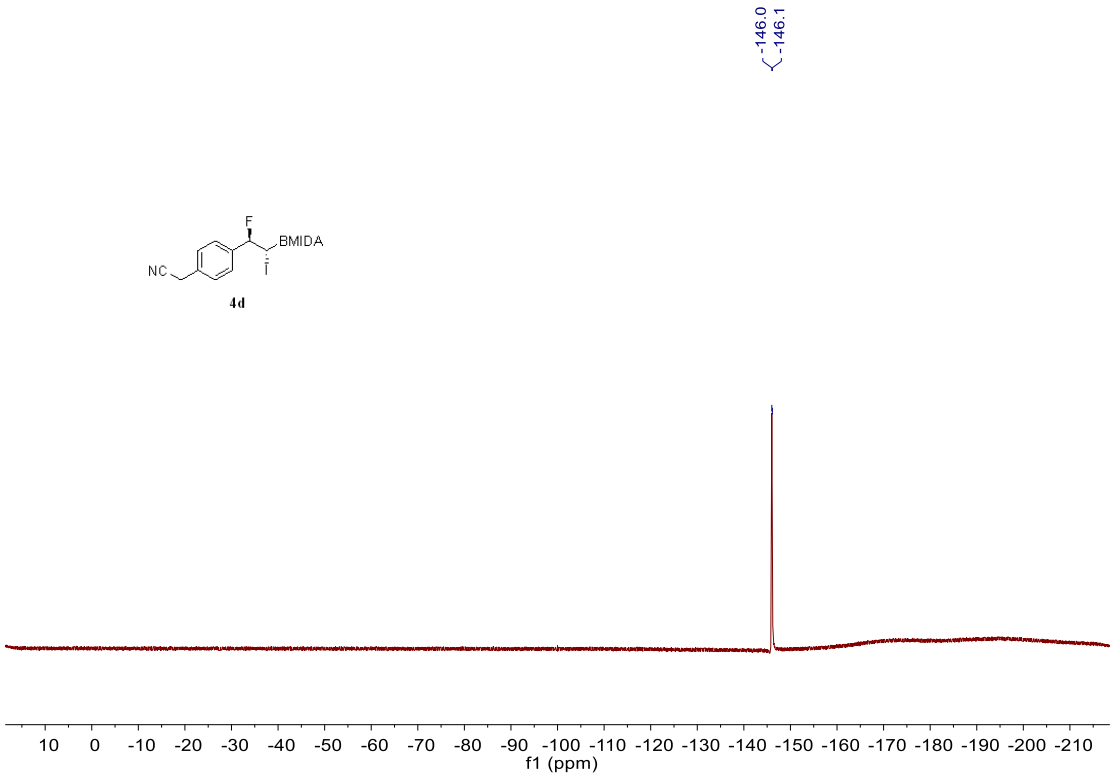

168.0
167.9
164.4
162.0
142.4
142.3
142.2
142.1
130.7
130.6
124.4
124.4
124.4
124.3
116.4
116.4
116.2
116.2
115.0
115.0
114.8
114.8
96.2
94.5
65.0
63.6
63.6
47.2
47.1
F
F
BMIDA
4c
f1 (ppm)

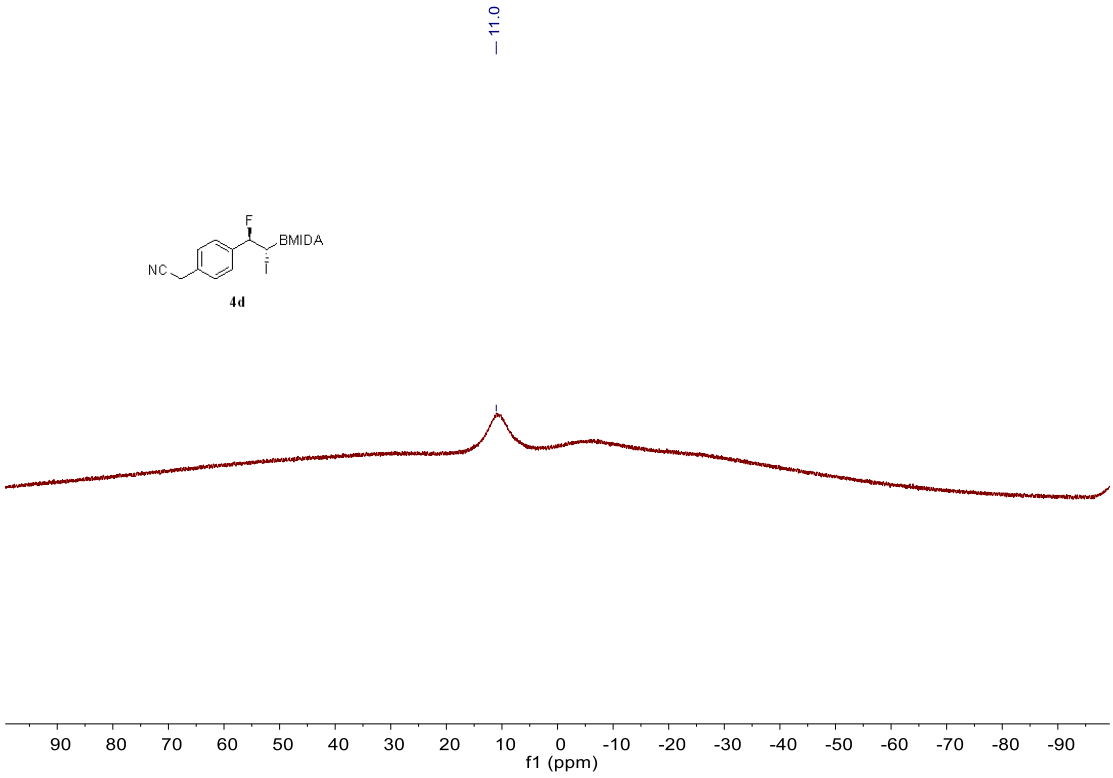

-114.8
-114.8
-114.8
-114.8
-114.9
-114.9
-149.7
-149.9
F
F
BMIDA
4c
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

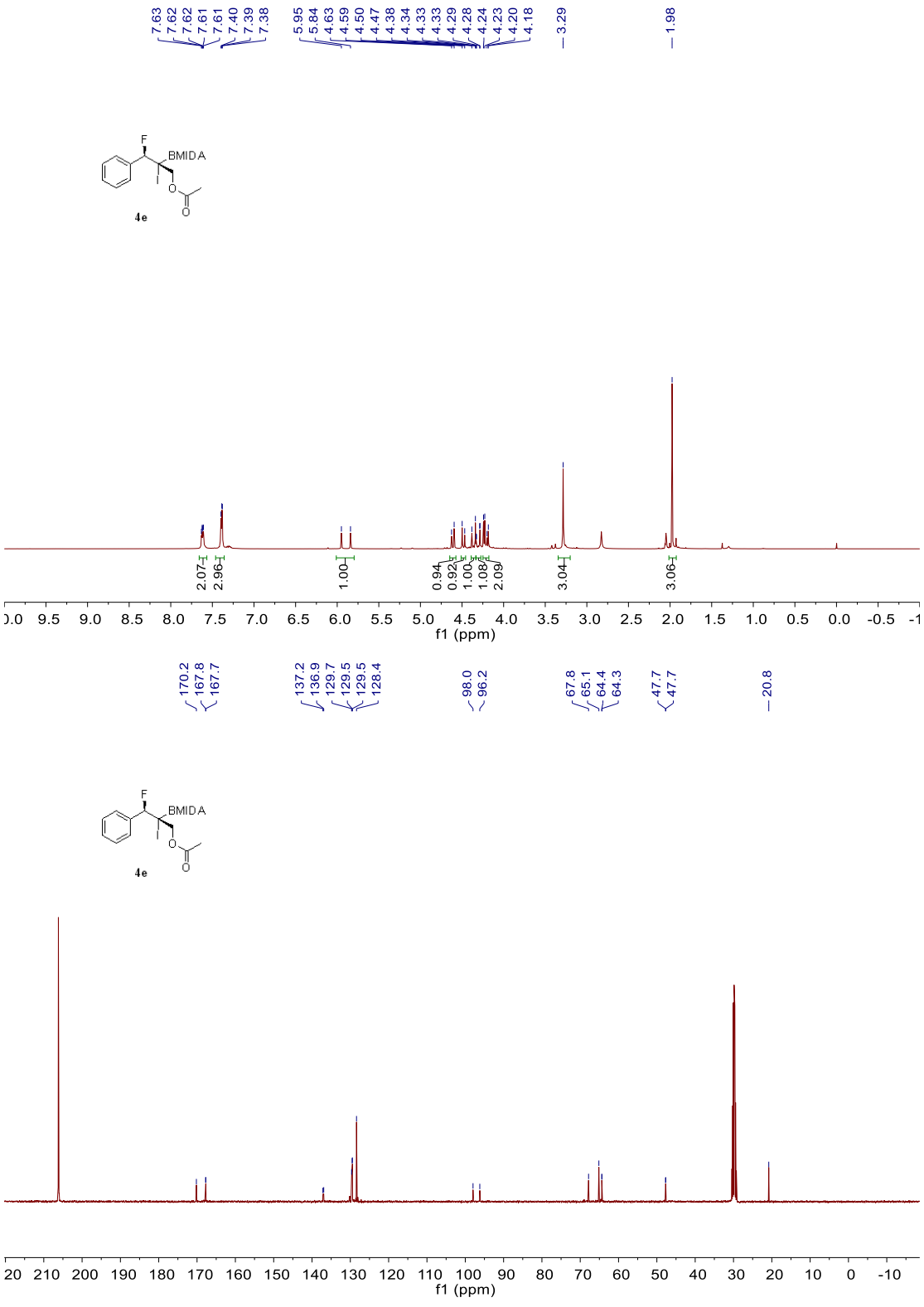

10.8
F
F
BMIDA
4c
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

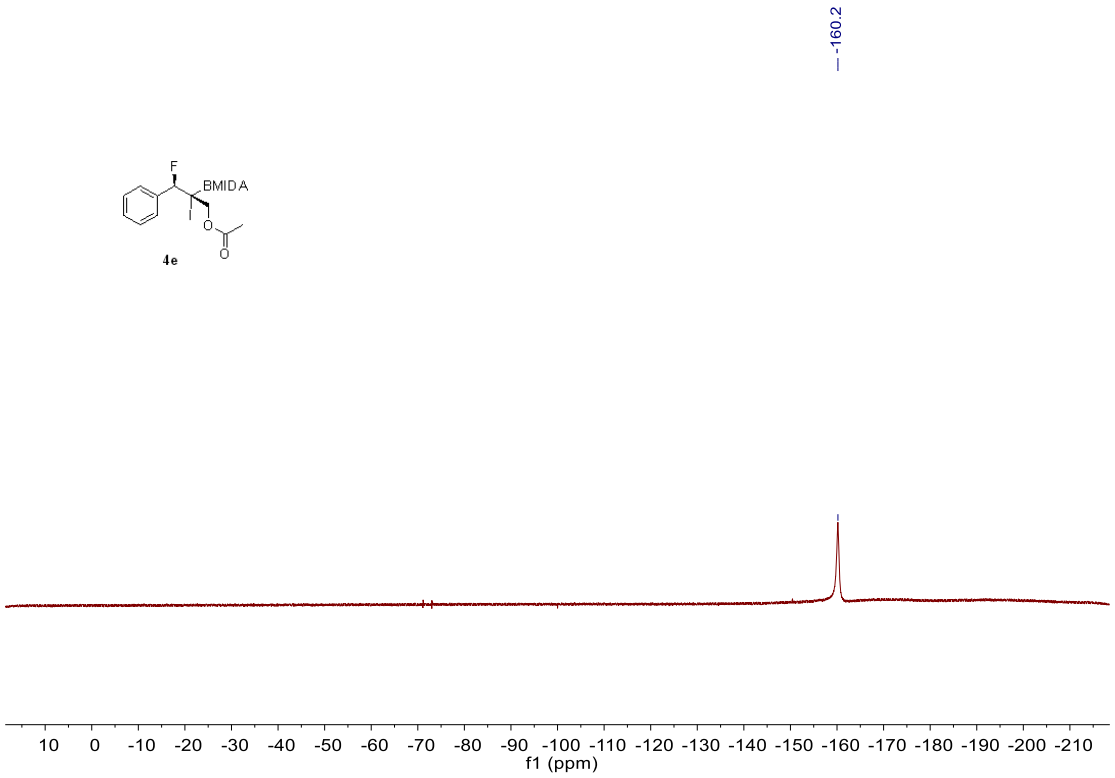

7.5
7.5
7.4
7.4
5.6
5.6
5.5
5.5
4.4
4.4
4.3
4.3
4.3
4.3
4.1
4.1
4.1
4.1
4.1
4.0
4.0
3.1
F
BMIDA
NC
I
4d
2.00
2.04
1.08
1.01
1.06
4.04
1.16
2.98
f1 (ppm)

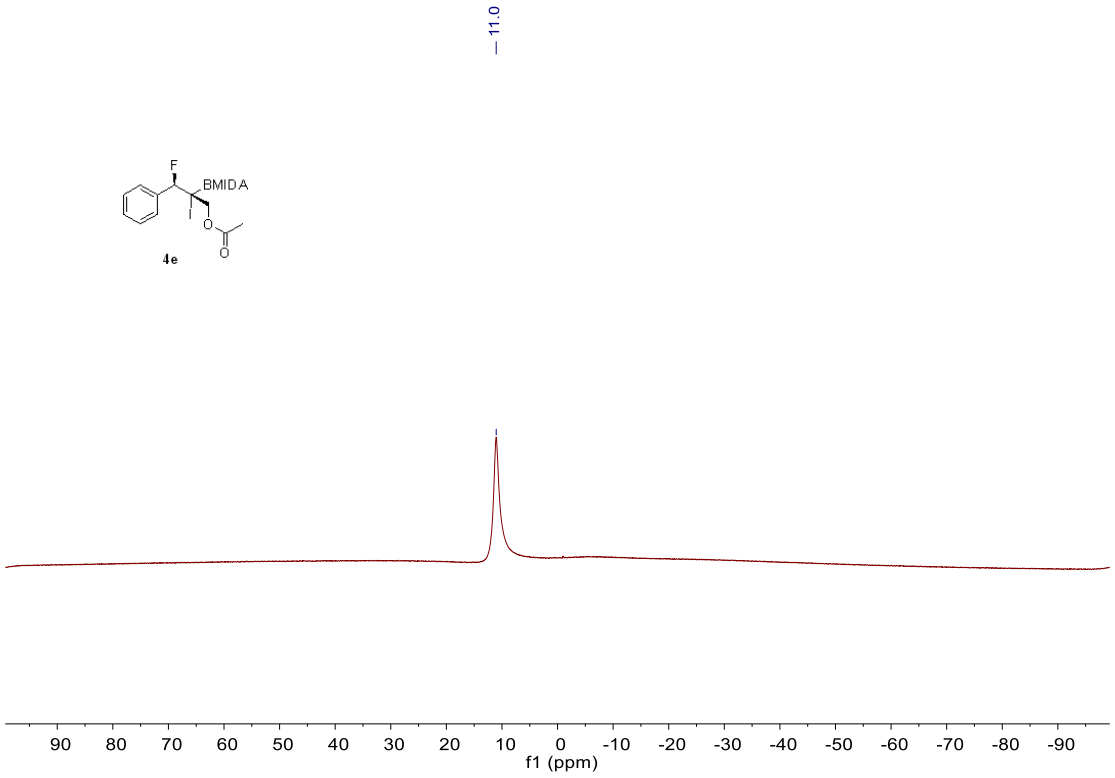

168.2
168.2
137.9
137.7
131.9
127.9
127.9
127.7
119.2
95.6
93.9
63.9
62.5
62.5
46.7
22.2
F
BMIDA
NC
I
4d
f1 (ppm)

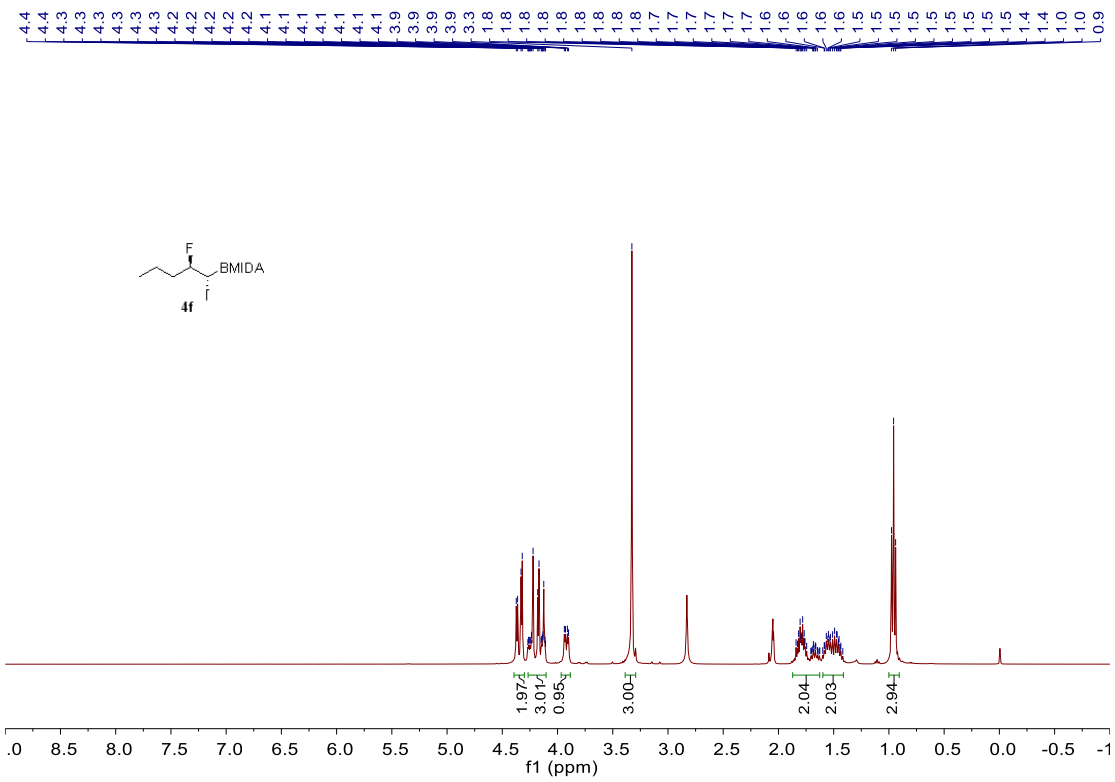

-146.0
-146.1
F
BMIDA
NC
4d
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

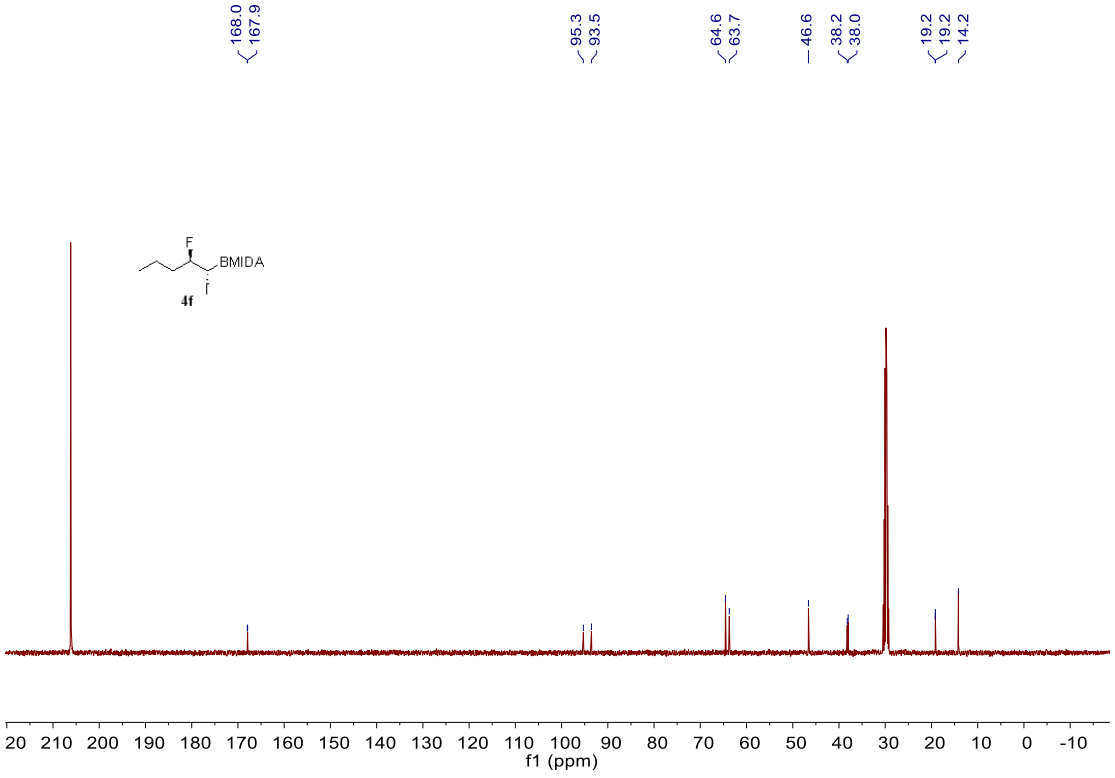

11.0
F
BMIDA
NC
4d
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

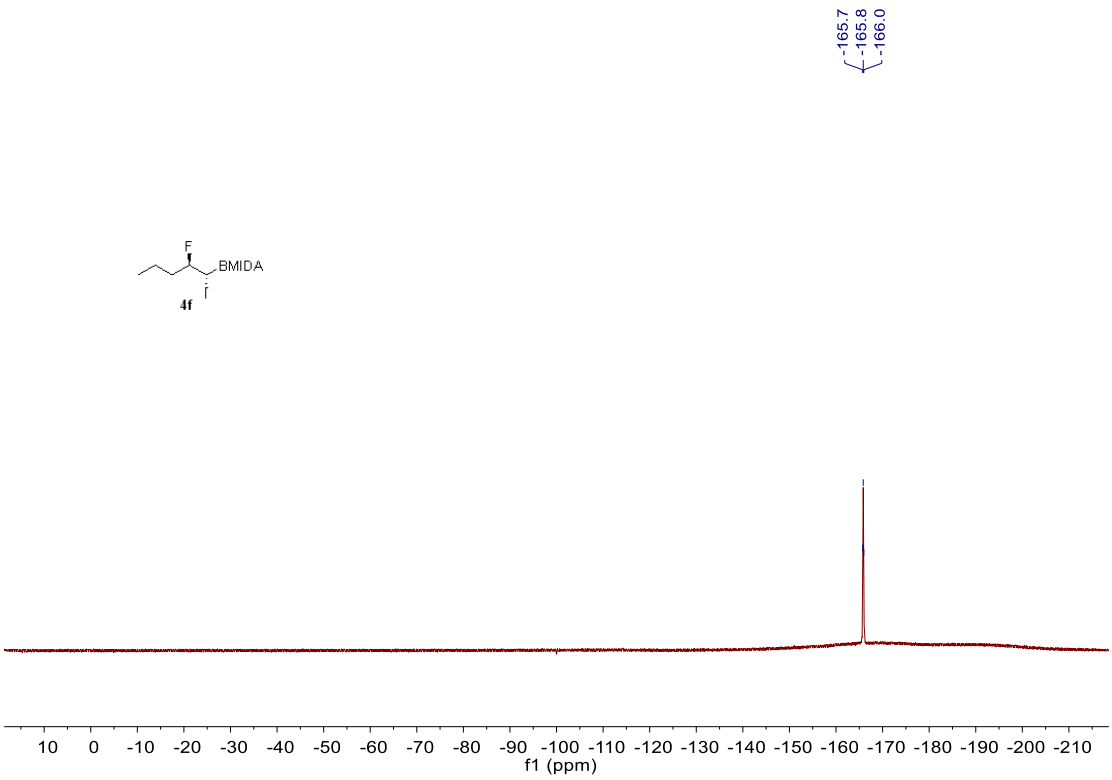

7.63
7.62
7.62
7.61
7.61
7.40
7.39
7.38
5.95
5.84
4.63
4.59
4.50
4.47
4.38
4.34
4.33
4.29
4.28
4.24
4.23
4.20
4.18
3.29
1.98
F
BMIDA
O
O
4e
2.07
2.96
1.00
0.94
0.92
1.05
1.08
2.09
3.04
3.06
f1 (ppm)
170.2
167.8
167.7
137.2
136.9
129.7
129.5
129.5
128.4
98.0
96.2
67.8
65.1
64.4
64.3
47.7
47.7
20.8
F
BMIDA
O
O
4e
f1 (ppm)

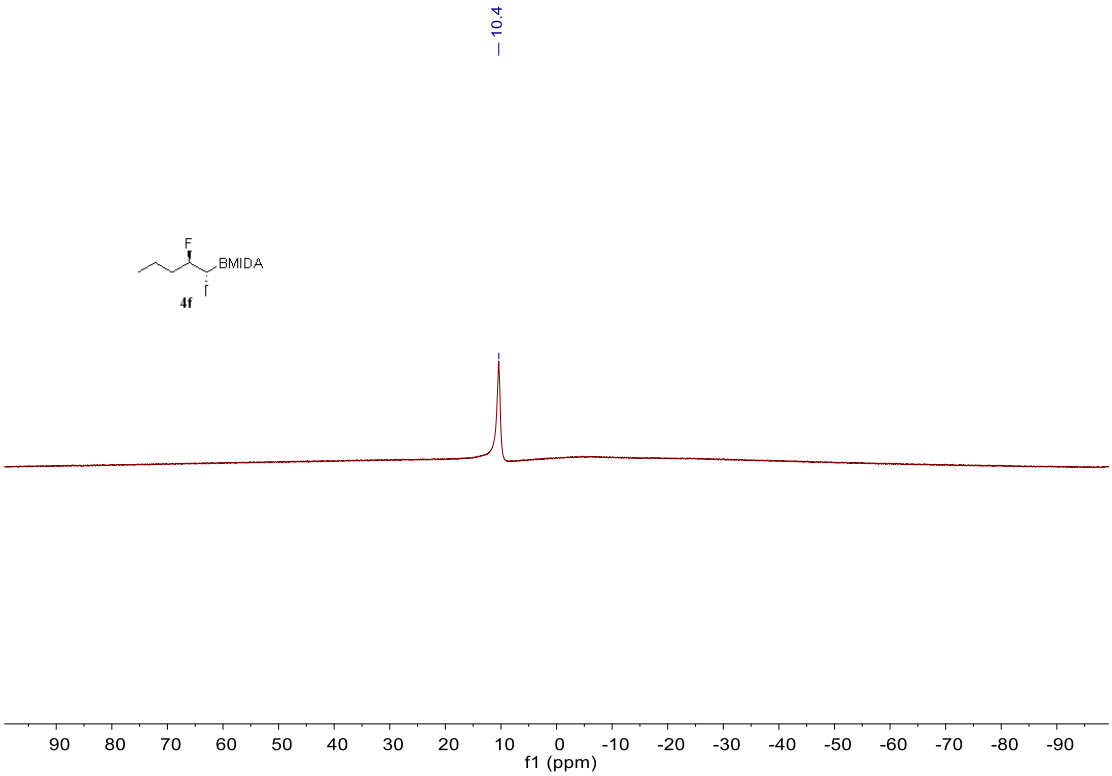

-160.2
F
BMIDA
O
O
4e
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

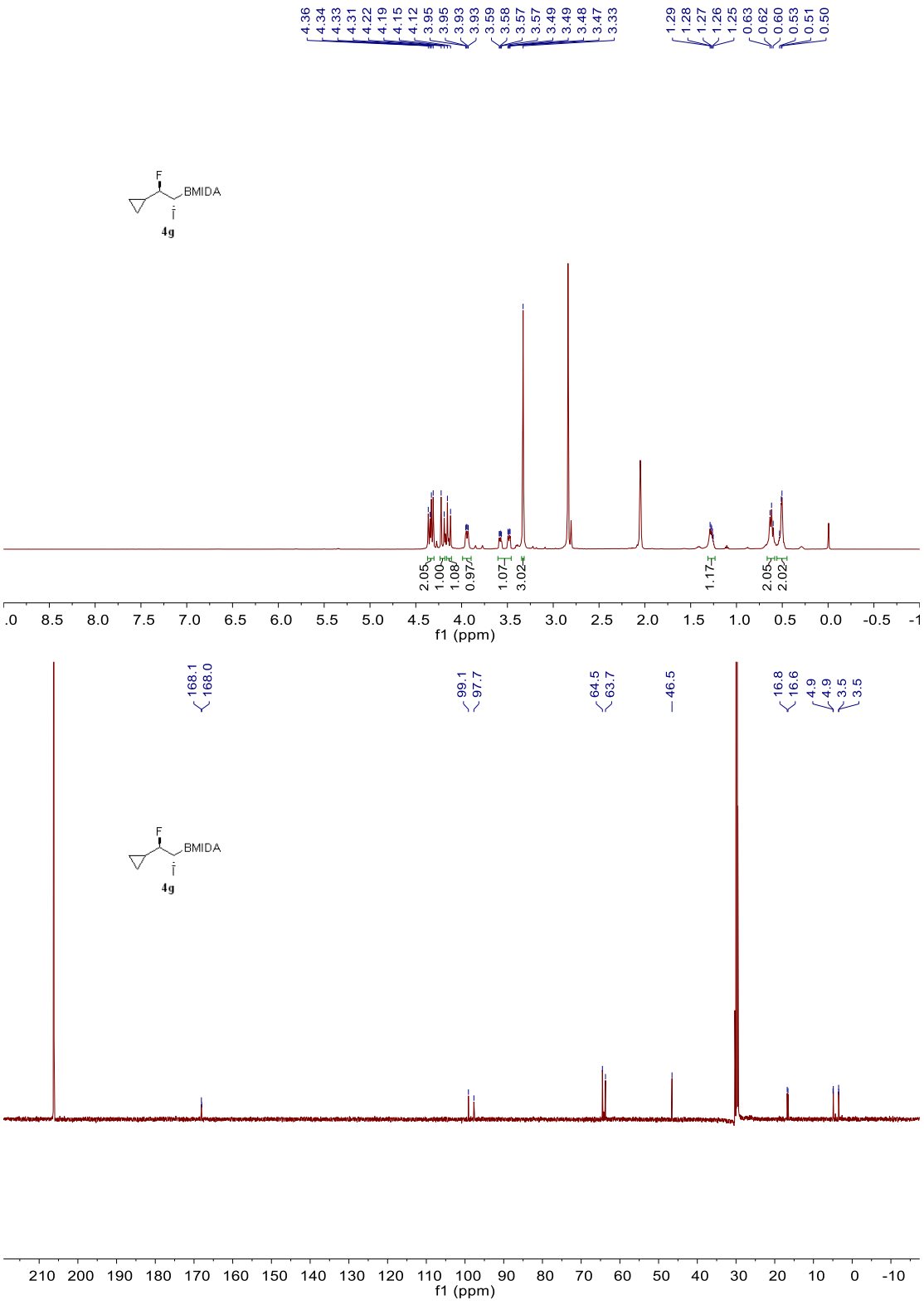

11.0
F
BMIDA
O
O
4e
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

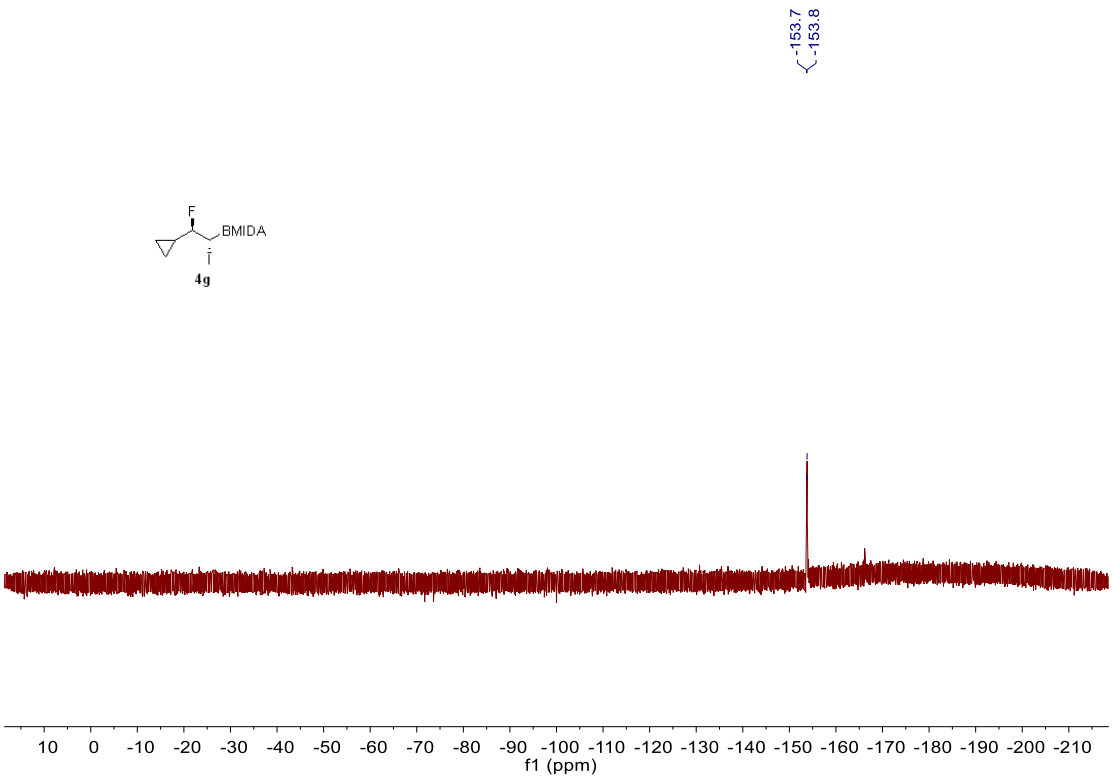

4.4 4.4 4.3 4.3 4.3 4.3 4.3 4.3 4.2 4.2 4.2 4.2 4.2 4.1 4.1 4.1 4.1 4.1 4.1 4.1 3.9 3.9 3.9 3.9 3.3 1.8 1.8 1.8 1.8 1.8 1.8 1.8 1.8 1.8 1.7 1.7 1.7 1.7 1.7 1.6 1.6 1.6 1.6 1.6 1.5 1.5 1.5 1.5 1.5 1.5 1.5 1.5 1.5 1.5 1.4 1.4 1.0 1.0 0.9
F
BMIDA
I
4f
1.97
3.01
0.95
3.00
2.04
2.03
2.94
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

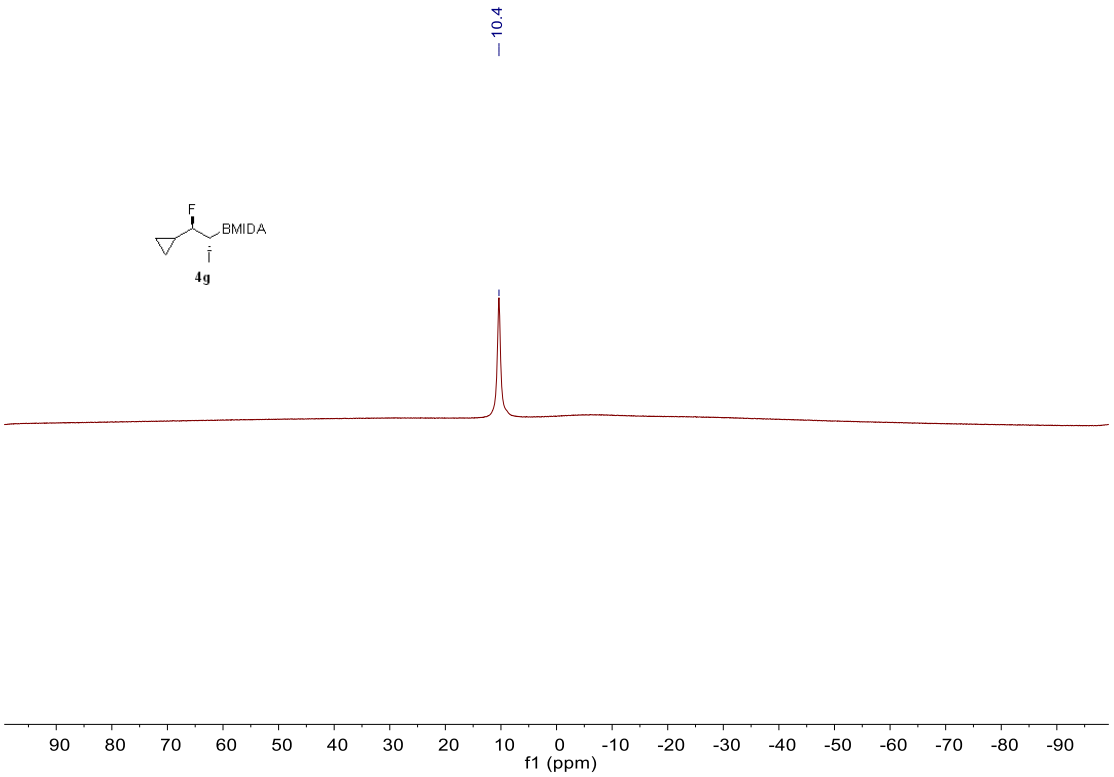

168.0
167.9
95.3
93.5
64.6
63.7
46.6
38.2
38.0
19.2
19.2
14.2
F
BMIDA
I
4f
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-165.7
-165.8
-166.0
F
BMIDA
I
4f
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

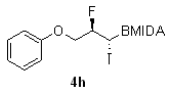

10.4
F
BMIDA
I
4f
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


4.36
4.34
4.33
4.31
4.22
4.19
4.15
4.12
3.95
3.95
3.93
3.93
3.59
3.58
3.57
3.57
3.49
3.49
3.48
3.47
3.33
1.29
1.28
1.27
1.26
1.25
0.63
0.62
0.60
0.53
0.51
0.50
F
BMIDA
4g
2.05
1.00
1.08
0.97
1.07
3.02
1.17
2.05
2.02
f1 (ppm)
168.1
168.0
99.1
97.7
64.5
63.7
46.5
16.8
16.6
4.9
4.9
3.5
3.5
F
BMIDA
4g
f1 (ppm)

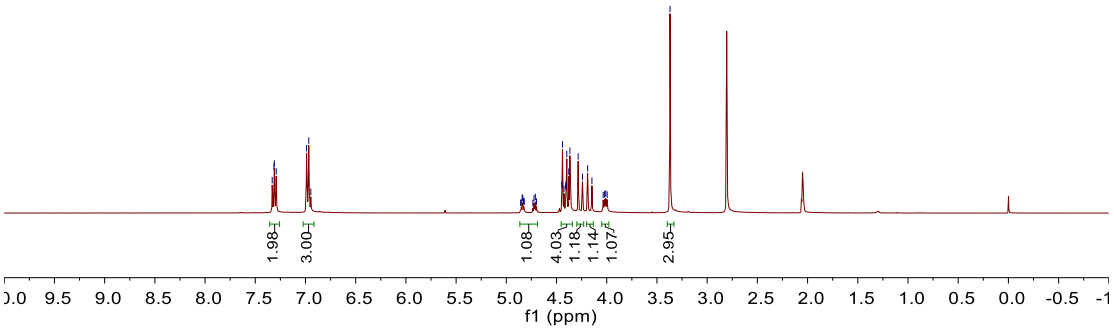

-153.7
-153.8
F
BMIDA
I
4g
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

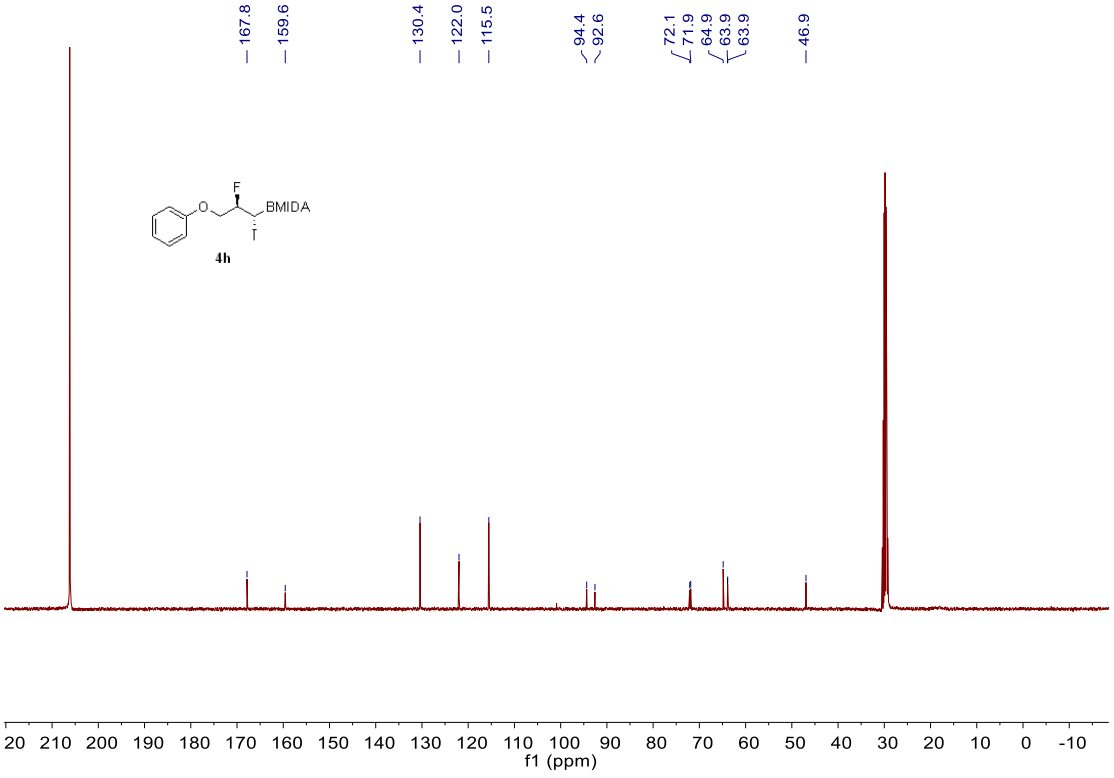

10.4
F
BMIDA
I
4g
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


7.33
7.31
7.31
7.29
6.99
6.97
6.95
4.86
4.85
4.84
4.84
4.83
4.82
4.74
4.72
4.71
4.70
4.45
4.44
4.43
4.41
4.40
4.40
4.38
4.37
4.28
4.24
4.19
4.15
4.04
4.02
4.01
4.00
3.37

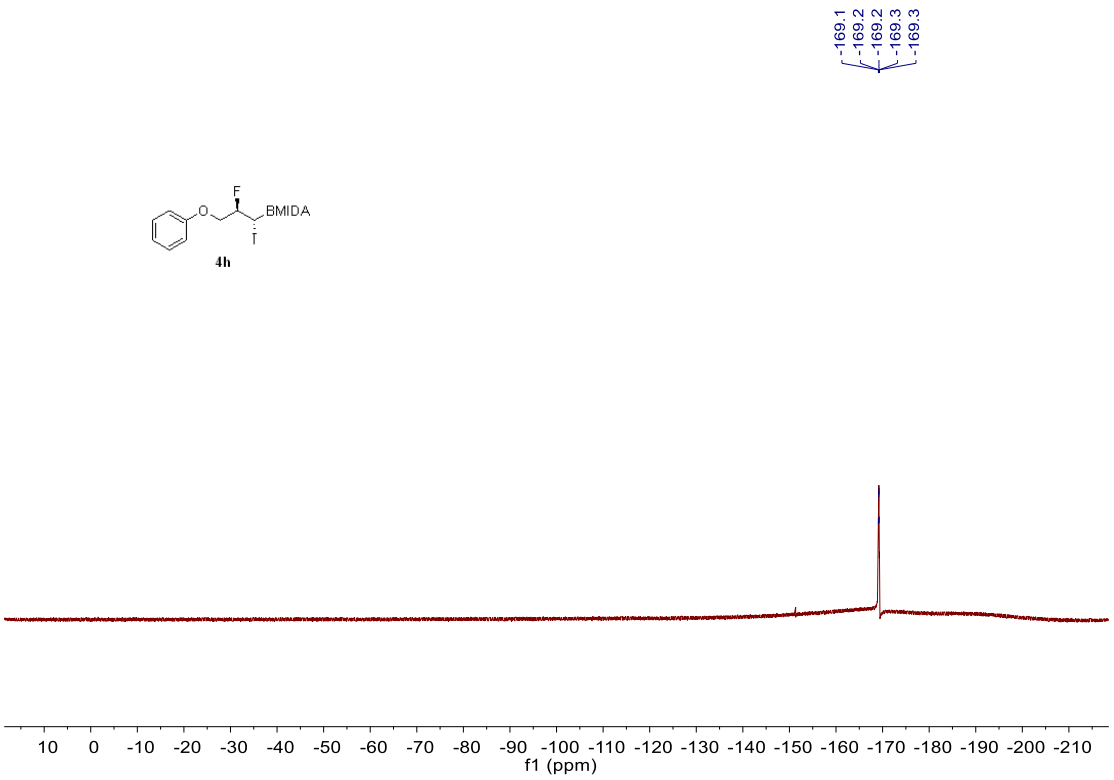

F
O
BMIDA
I

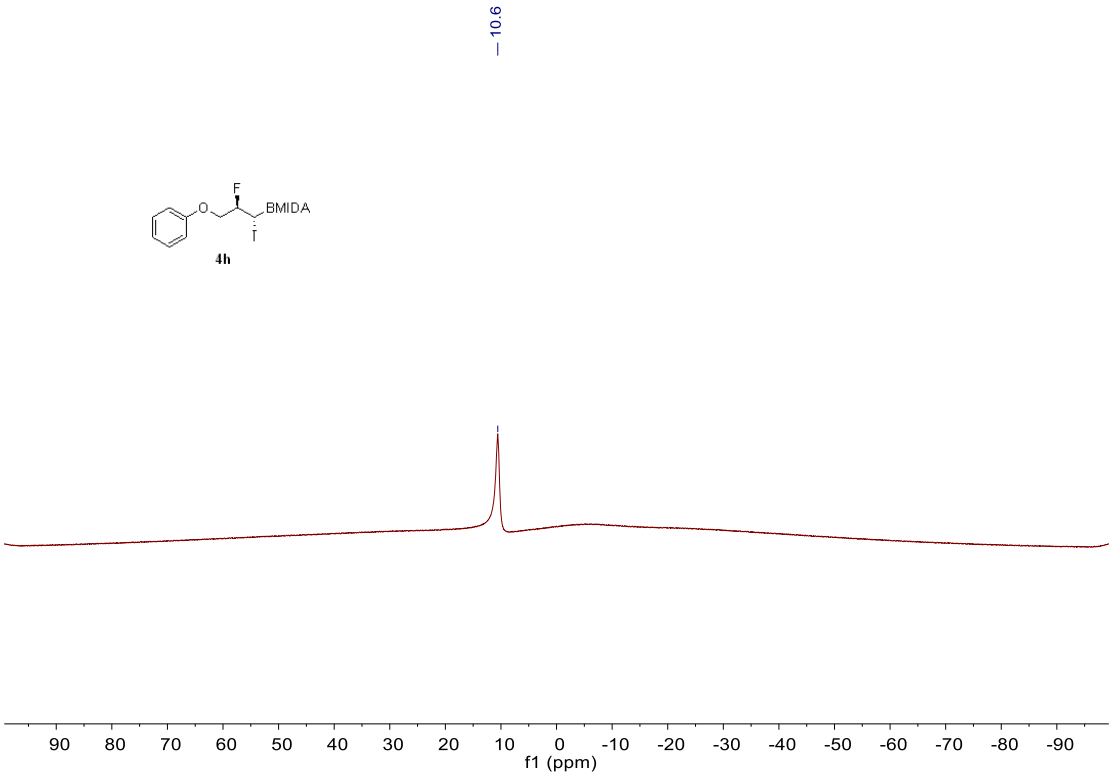
4h

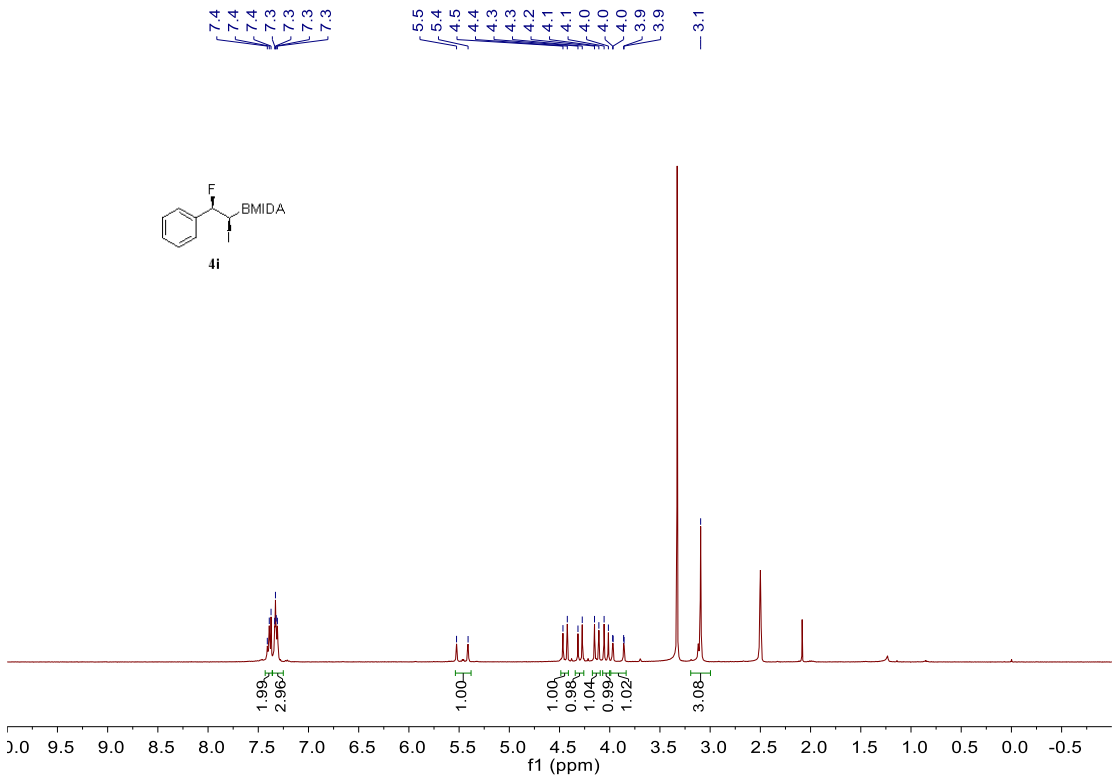

1.98
3.00
1.08
4.03
1.18
1.14
1.07
2.95
f1 (ppm)

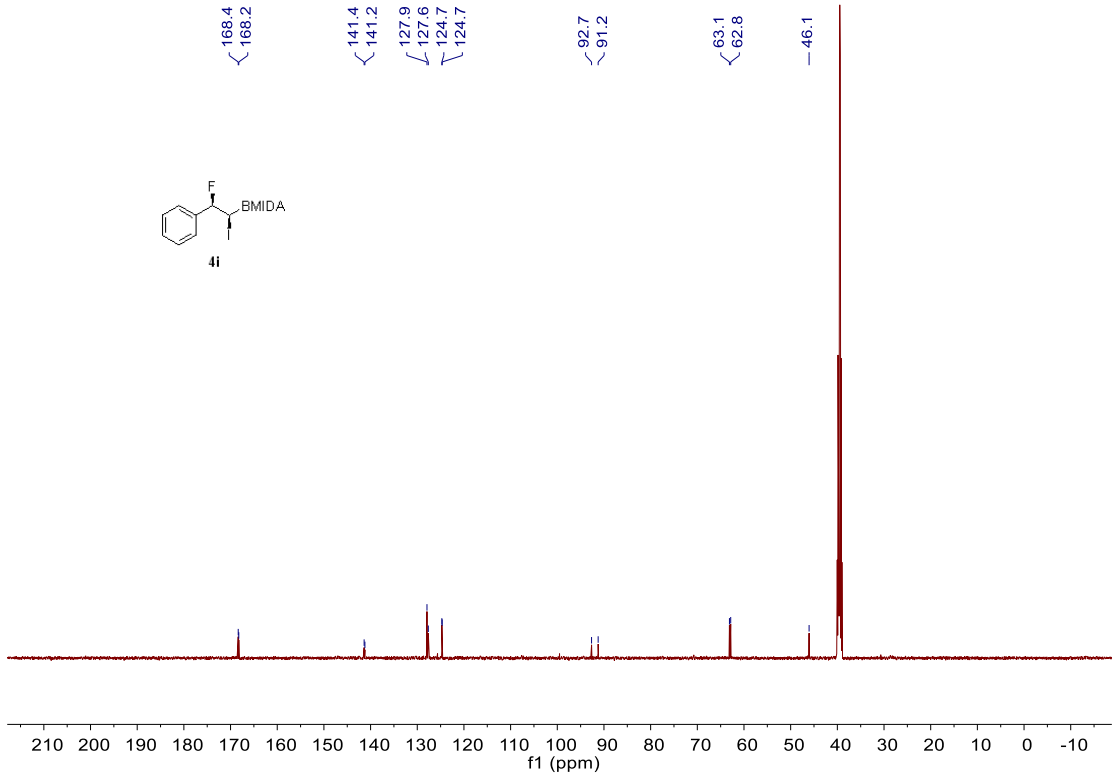

167.8
159.6
130.4
122.0
115.5
94.4
92.6
72.1
71.9
64.9
63.9
63.9
46.9
F
O
BMIDA
I
f1 (ppm)

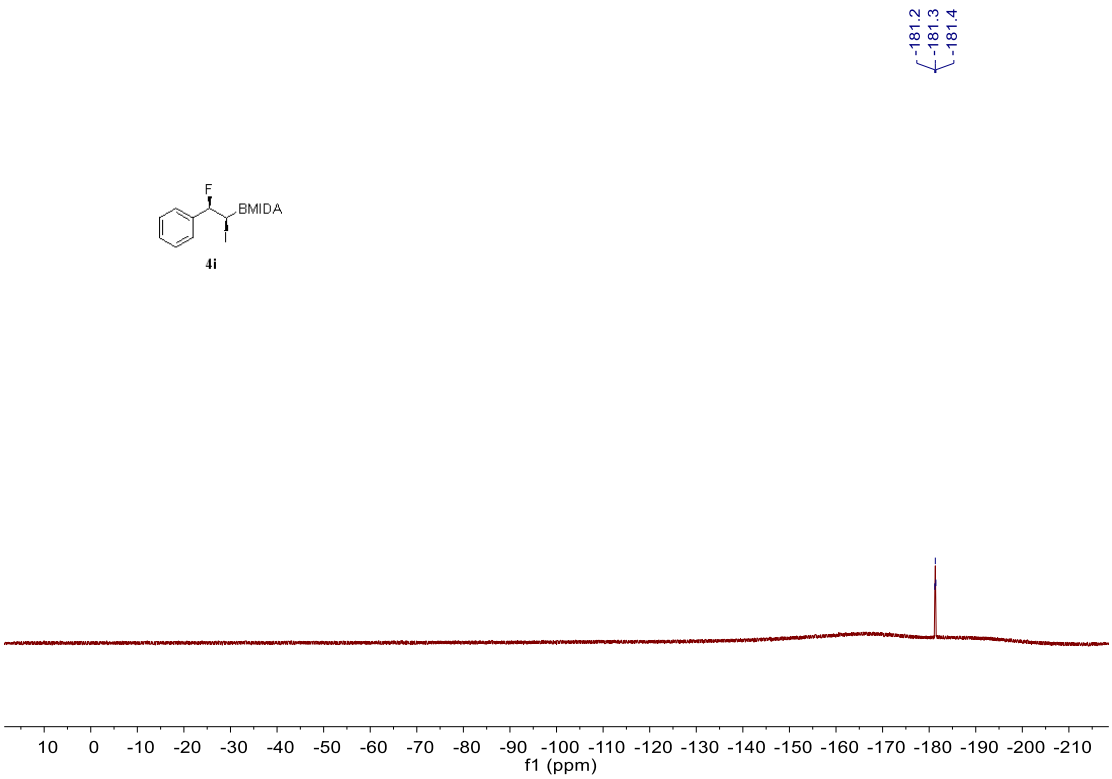
4h

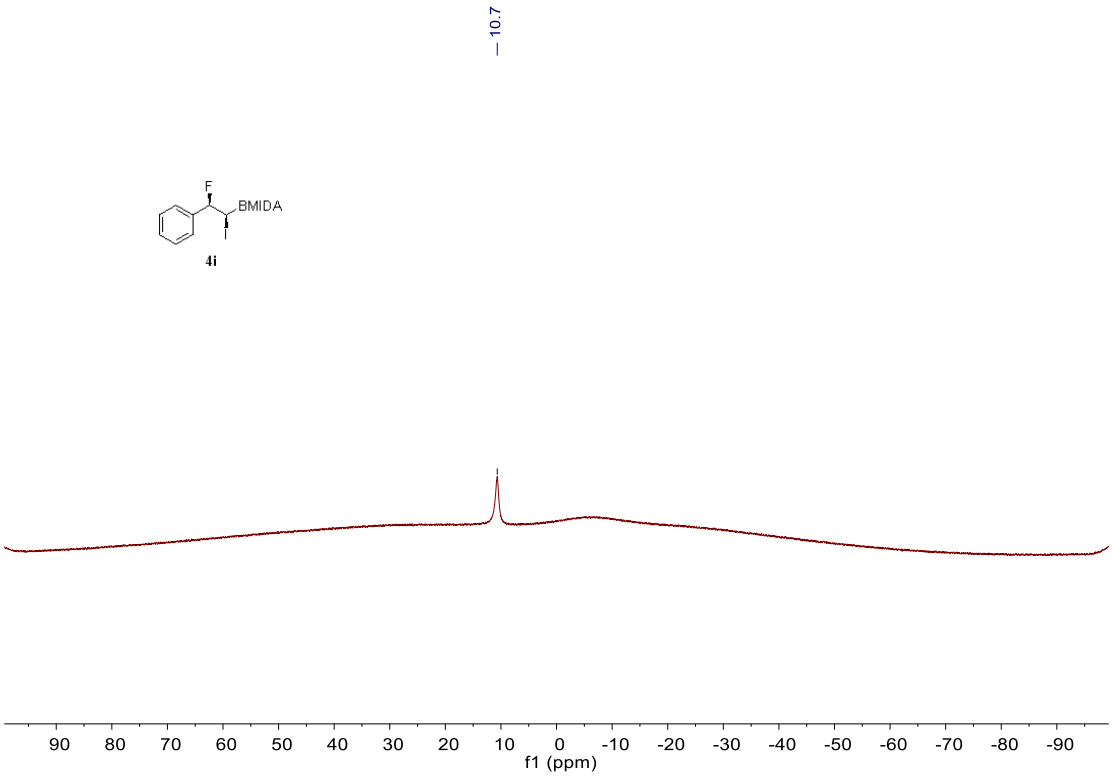

-169.1
-169.2
-169.2
-169.3
-169.3
F
O
BMIDA
T
4h
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

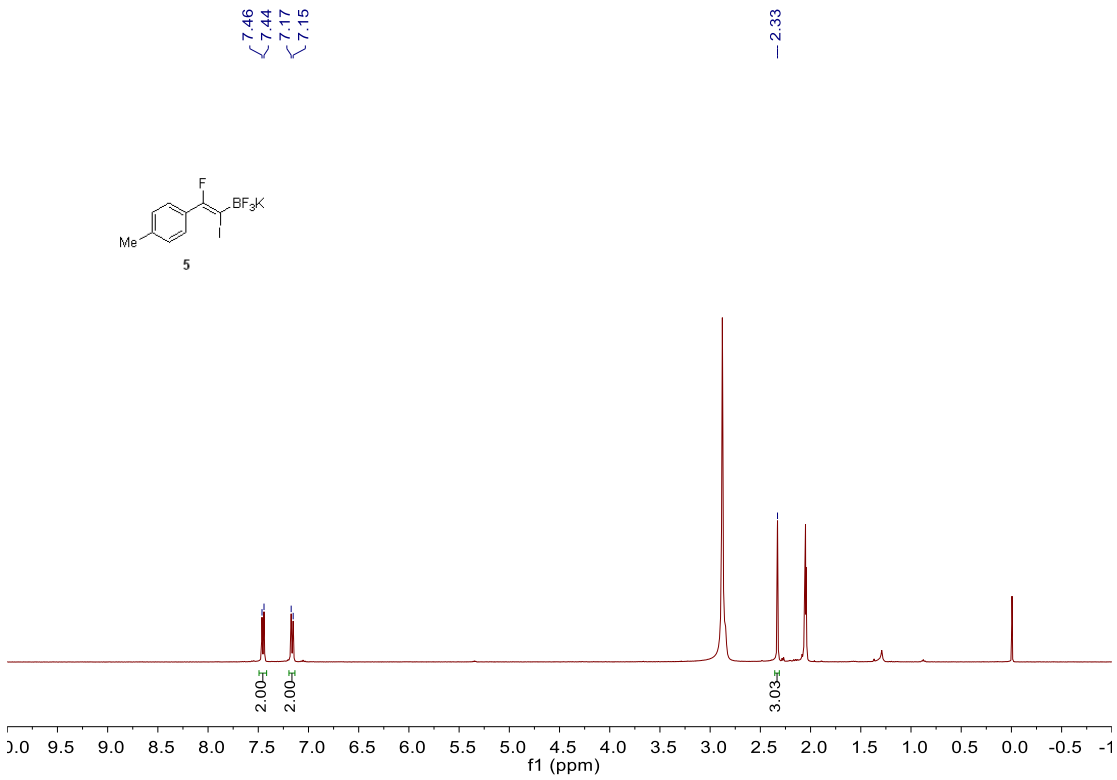

10.6
F
O
BMIDA
T
4h
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

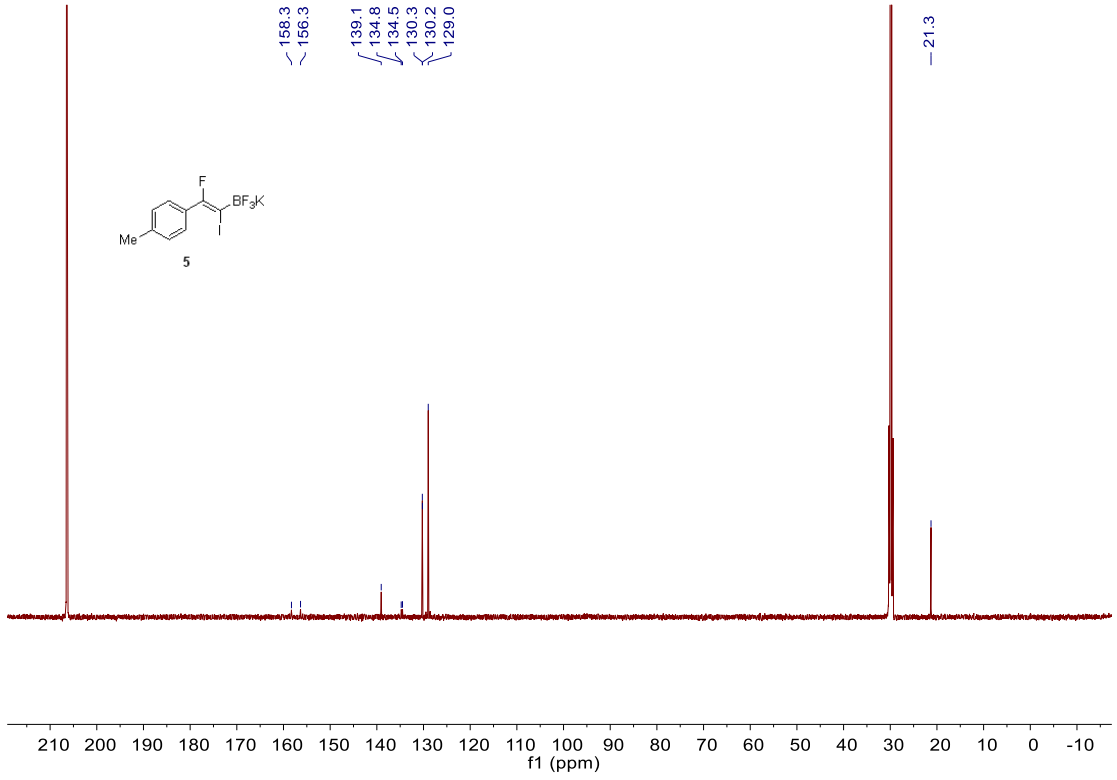

7.4
7.4
7.4
7.3
7.3
7.3
7.3
5.5
5.4
4.5
4.4
4.3
4.3
4.2
4.1
4.1
4.0
4.0
4.0
3.9
3.9
3.1
F
BMIDA
4i
1.99
2.96
1.00
1.00
0.98
1.04
0.99
1.02
3.08
f1 (ppm)

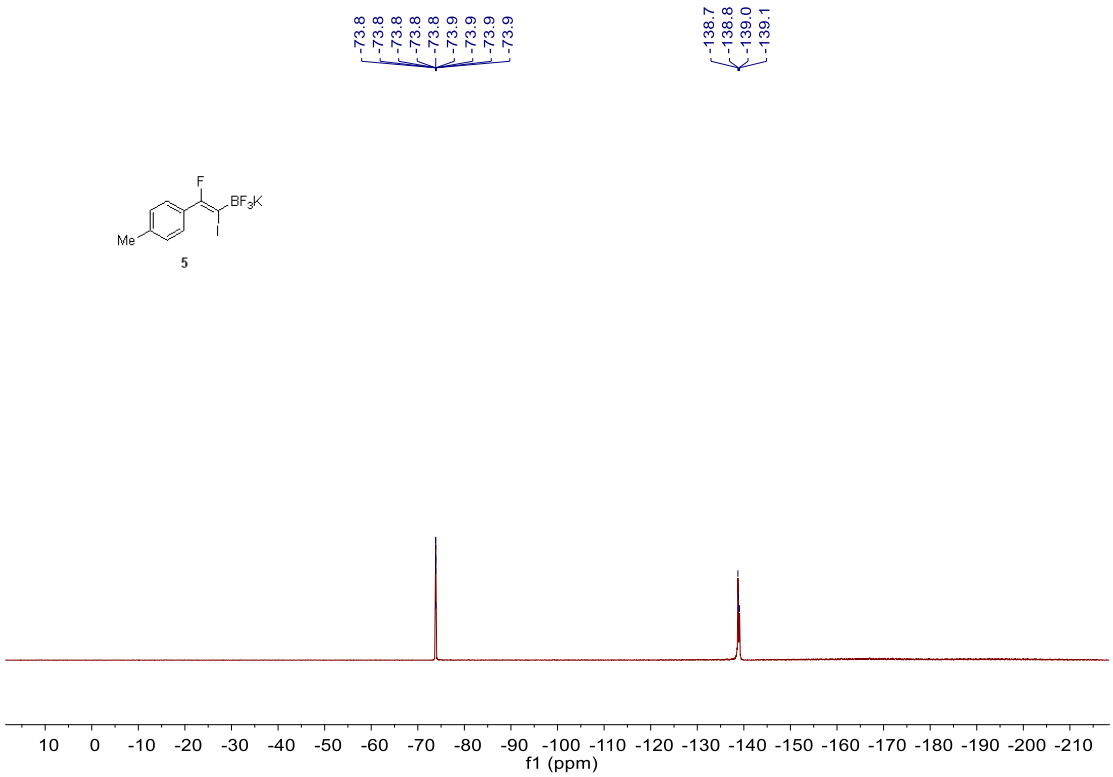

168.4
168.2
141.4
141.2
127.9
127.6
124.7
124.7
92.7
91.2
63.1
62.8
46.1
F
BMIDA
4i
f1 (ppm)

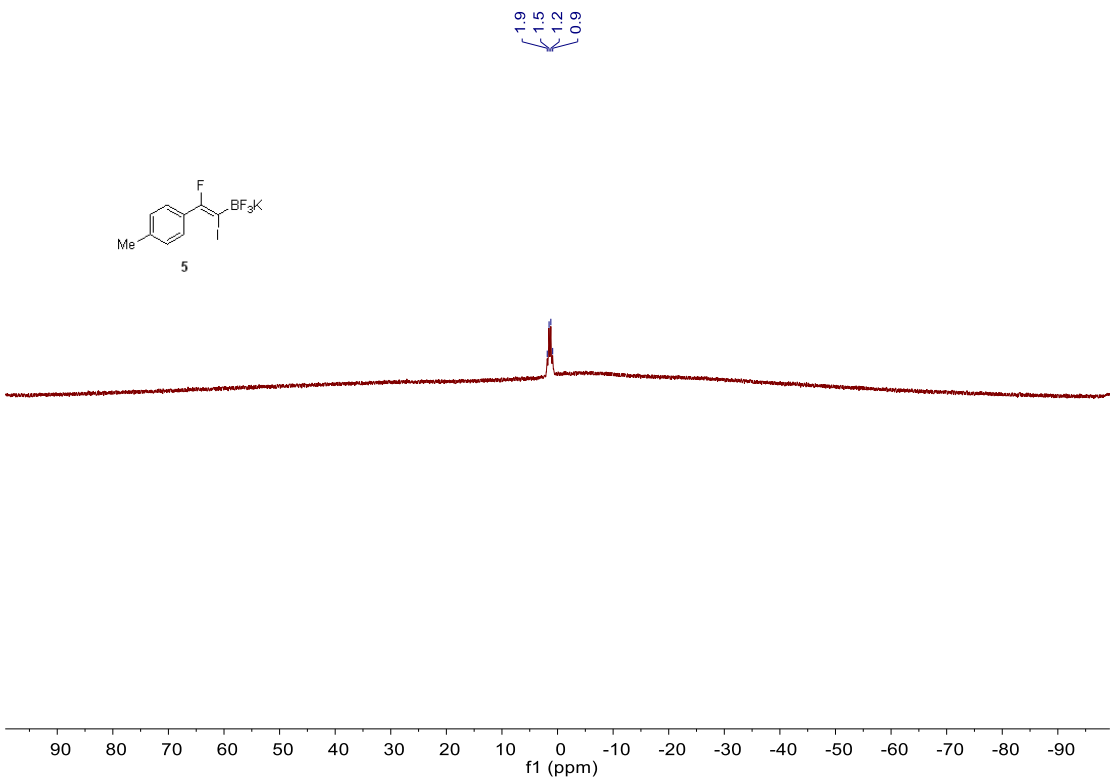

-181.2
-181.3
-181.4
F
BMIDA
4i
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

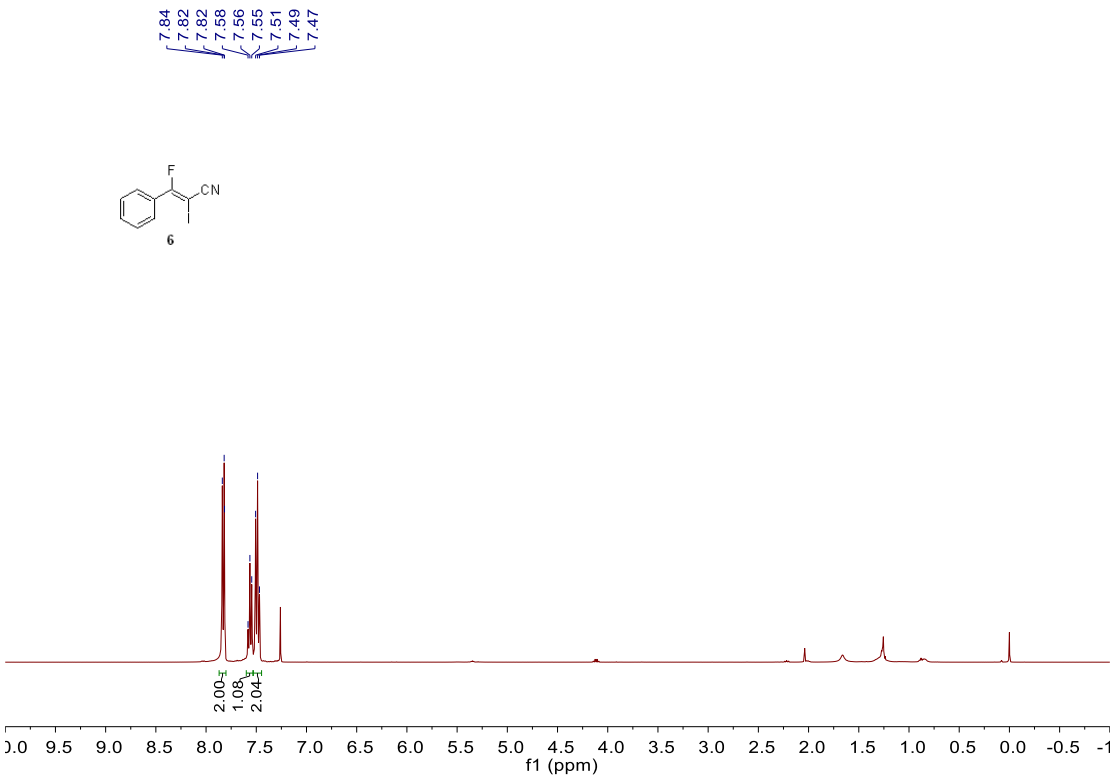

10.7
F
BMIDA
4i
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

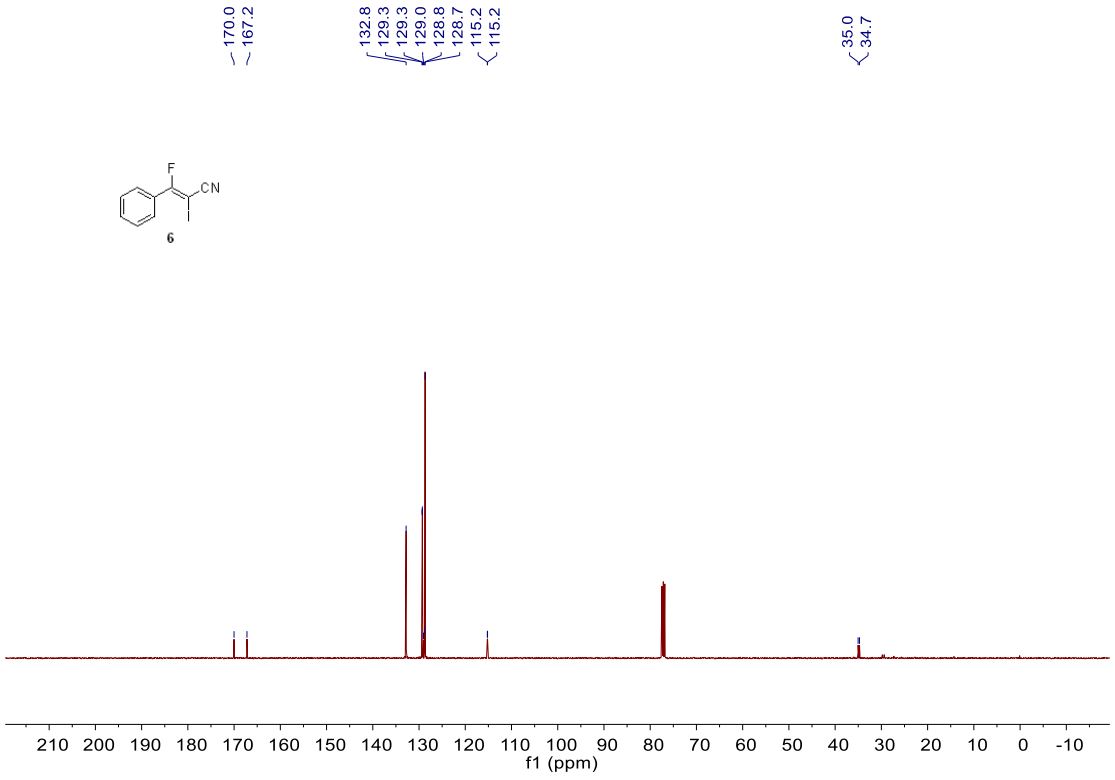

7.46
7.44
7.17
7.15
2.33
F
BF3K
Me
I
5
2.00
2.00
3.03
f1 (ppm)

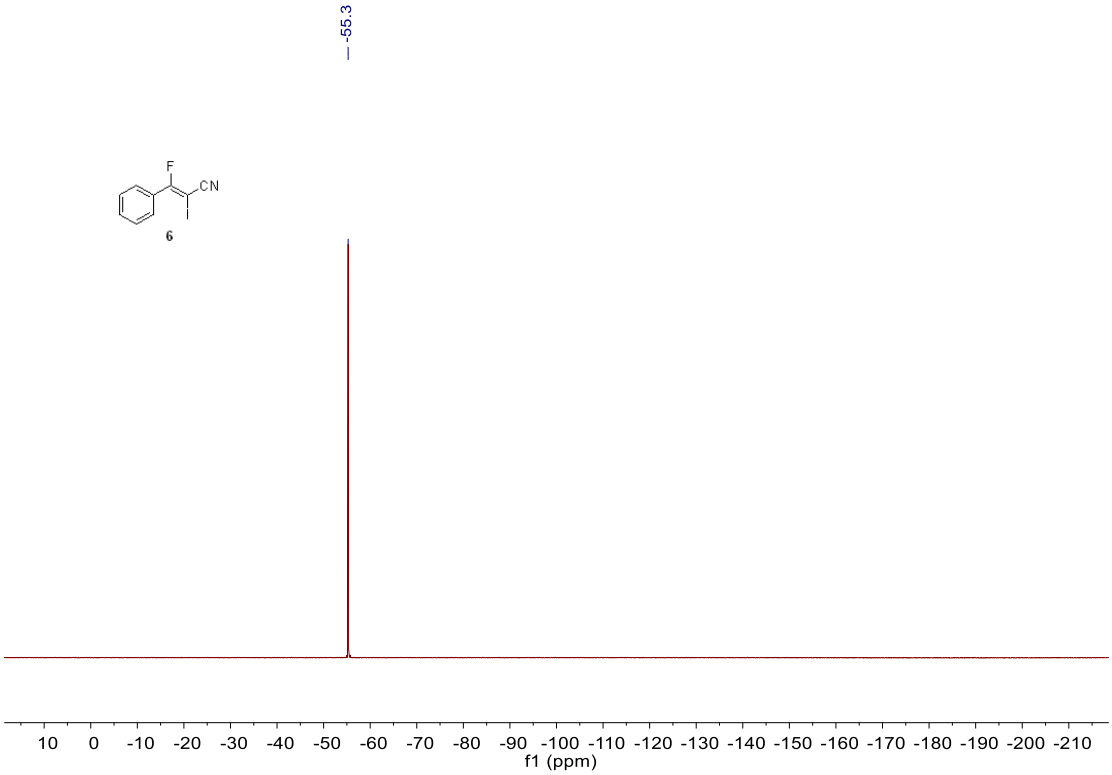

158.3
156.3
139.1
134.8
134.5
130.3
130.2
129.0
21.3
F
BF3K
Me
I
5
f1 (ppm)

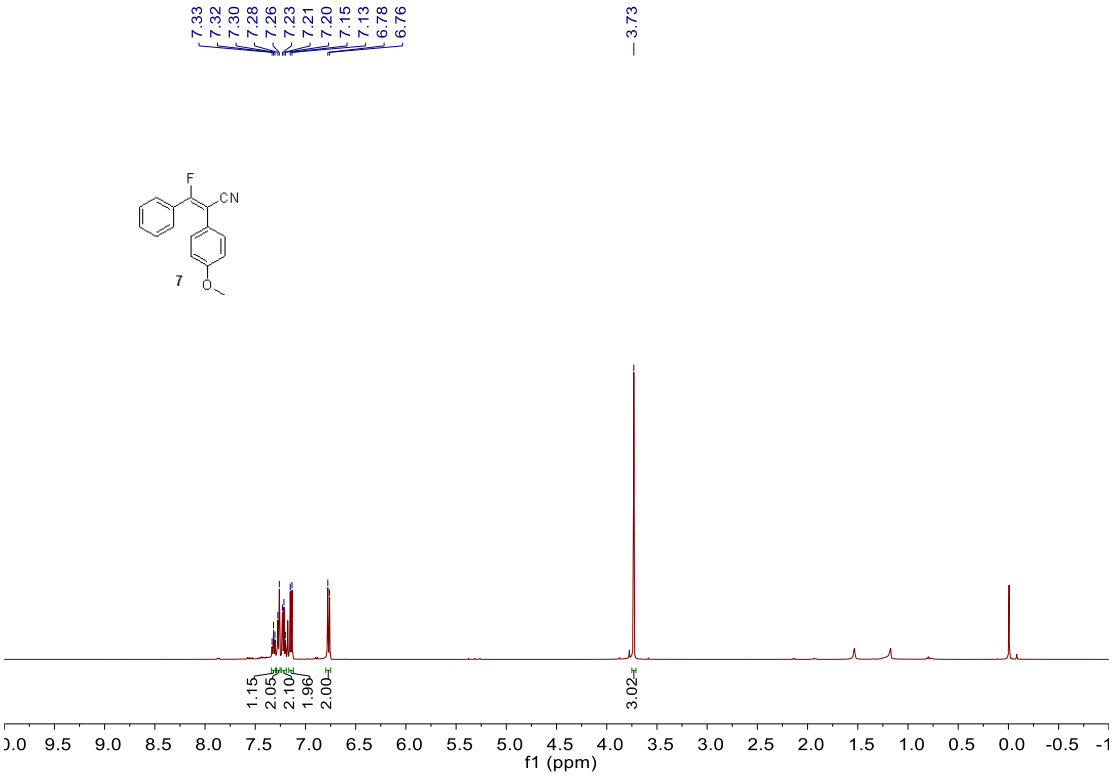

-73.8
-73.8
-73.8
-73.8
-73.8
-73.9
-73.9
-73.9
-73.9
-138.7
-138.8
-139.0
-139.1
F
BF3K
Me
I
5
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

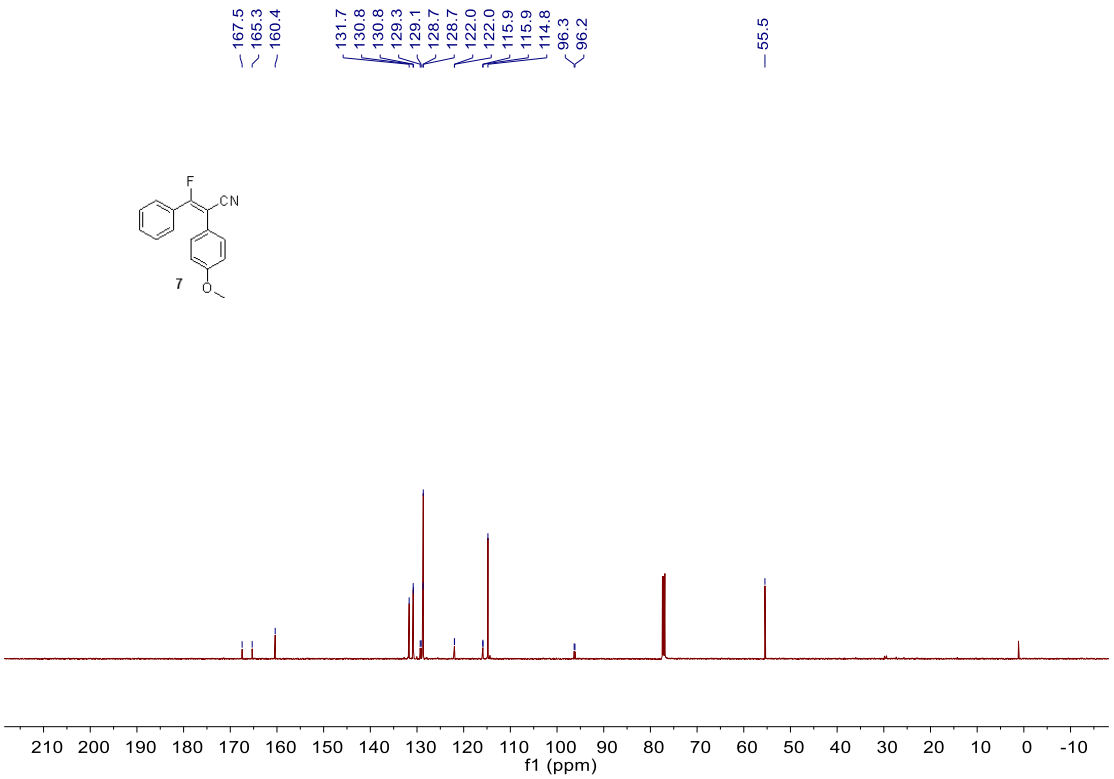

1.9
1.5
1.2
0.9
F
BF3K
Me
I
5
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

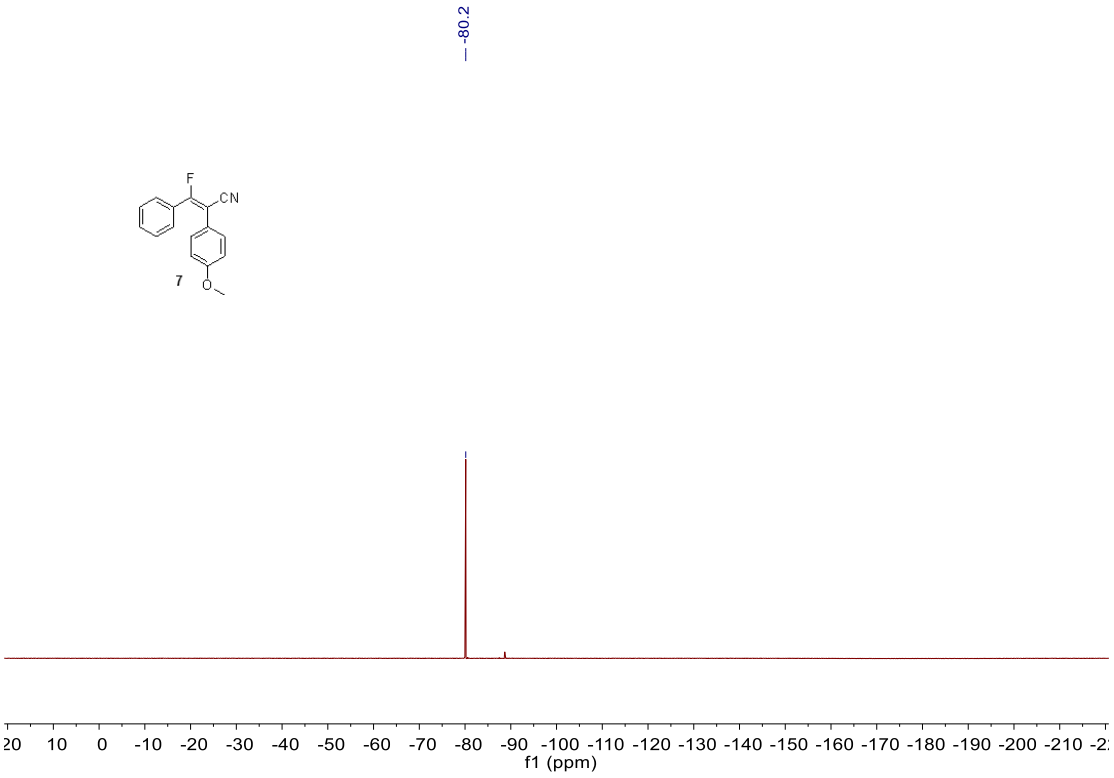

7.84
7.82
7.82
7.58
7.56
7.55
7.51
7.49
7.47
F
CN
6
2.00
1.08
2.04
f1 (ppm)

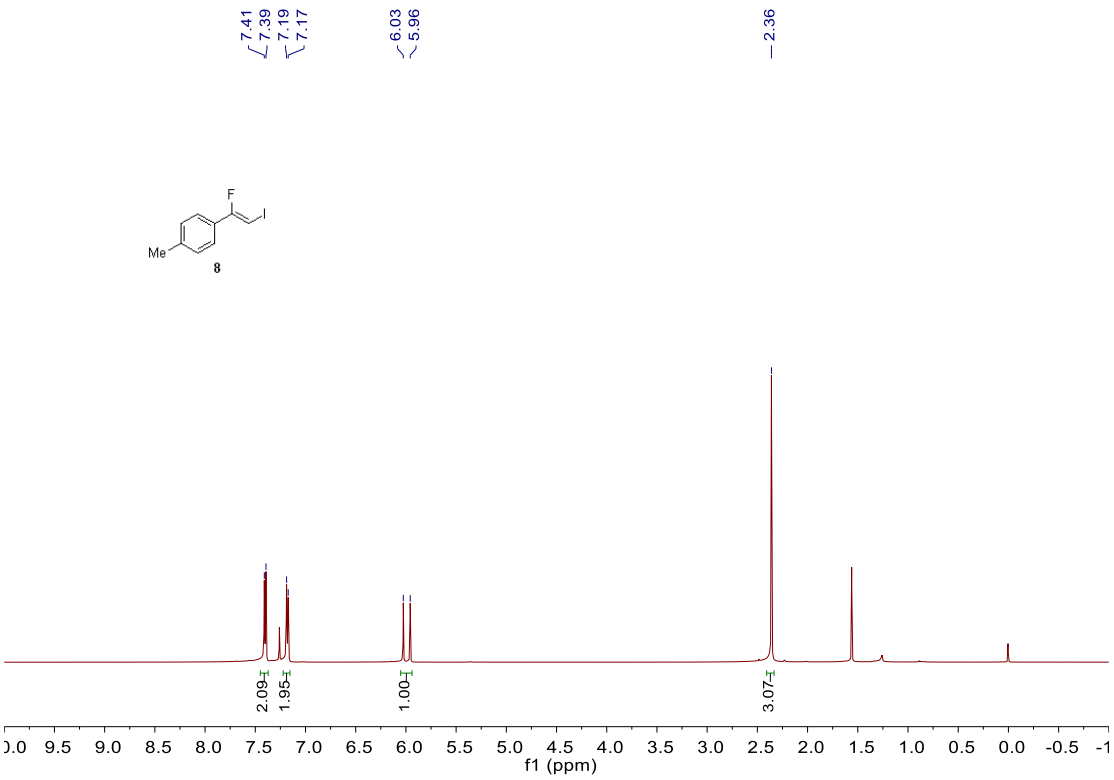

170.0
167.2
132.8
129.3
129.3
129.0
128.8
128.7
115.2
115.2
35.0
34.7
F
CN
6
f1 (ppm)

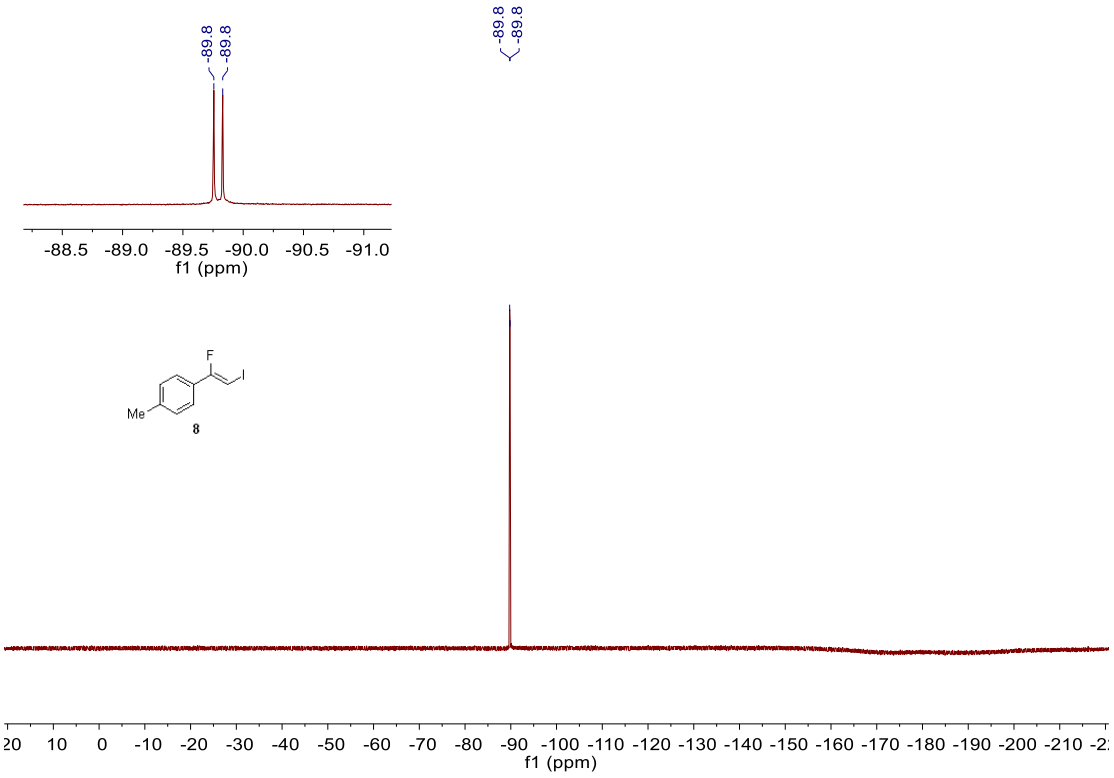

-55.3
F
CN
6
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

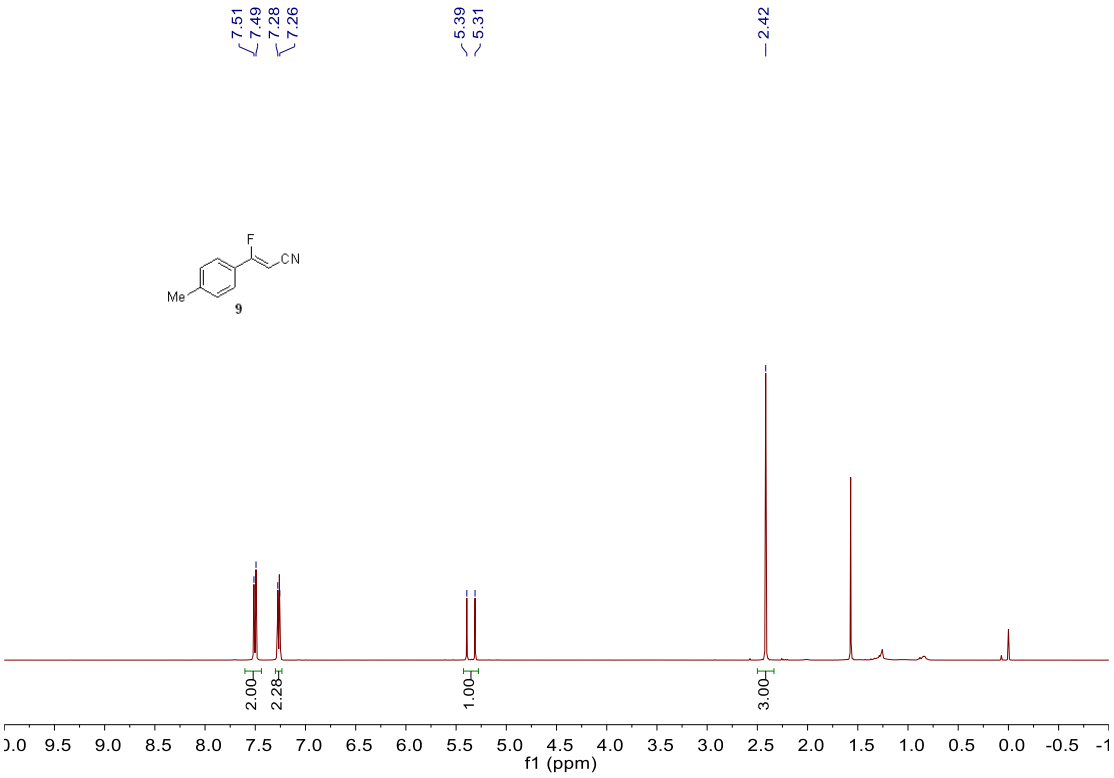

7.33
7.32
7.30
7.28
7.26
7.23
7.21
7.20
7.15
7.13
6.78
6.76
3.73
F
CN
7
O
1.15
2.05
2.10
1.96
2.00
3.02
f1 (ppm)

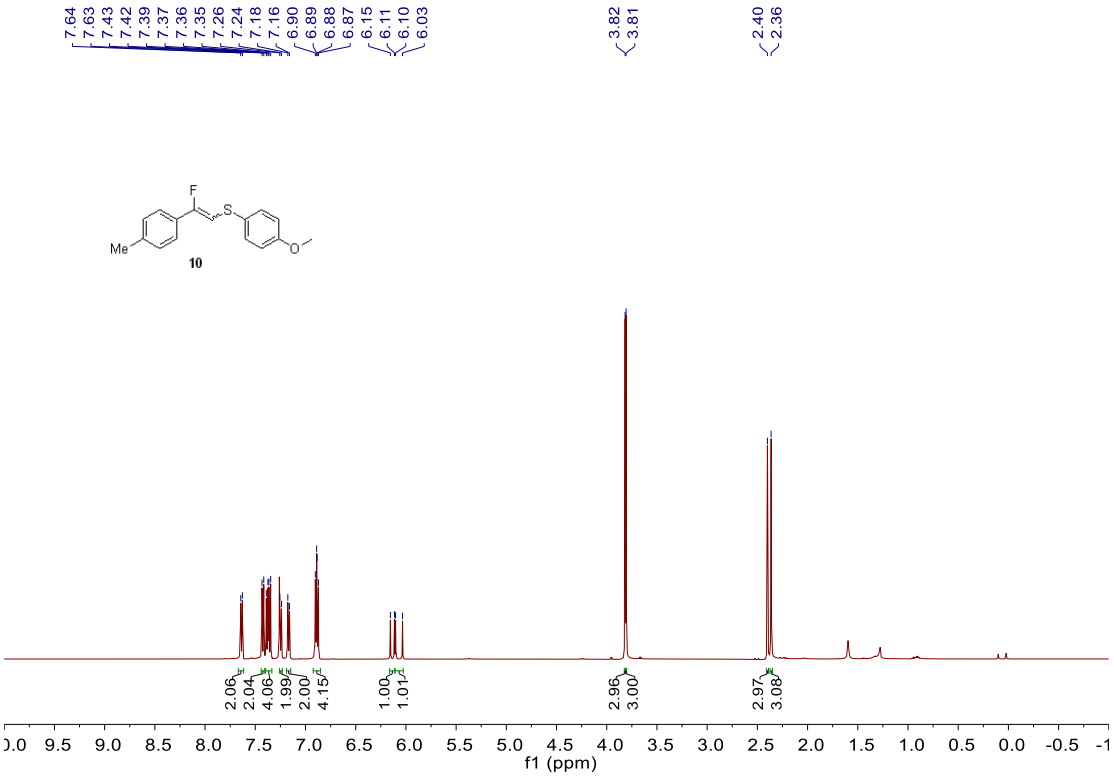

167.5
165.3
160.4
131.7
130.8
130.8
129.3
129.1
128.7
128.7
122.0
122.0
115.9
115.9
114.8
96.3
96.2
55.5
F
CN
7
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

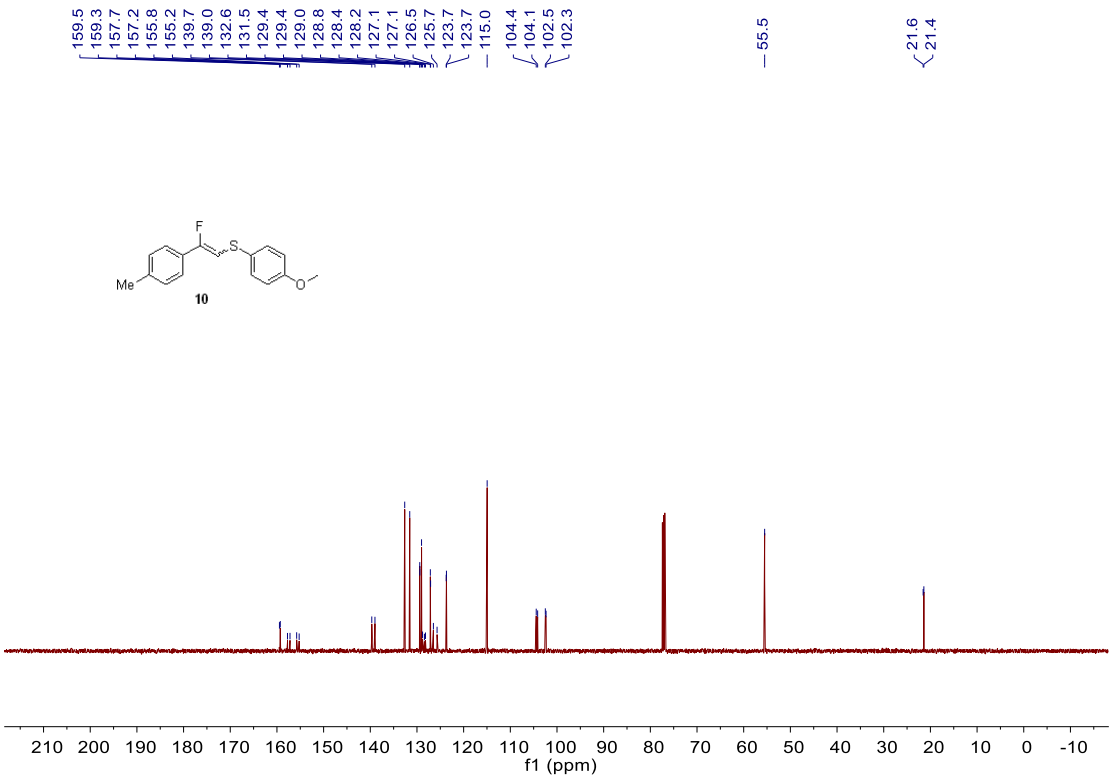

-80.2
F
CN
7
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

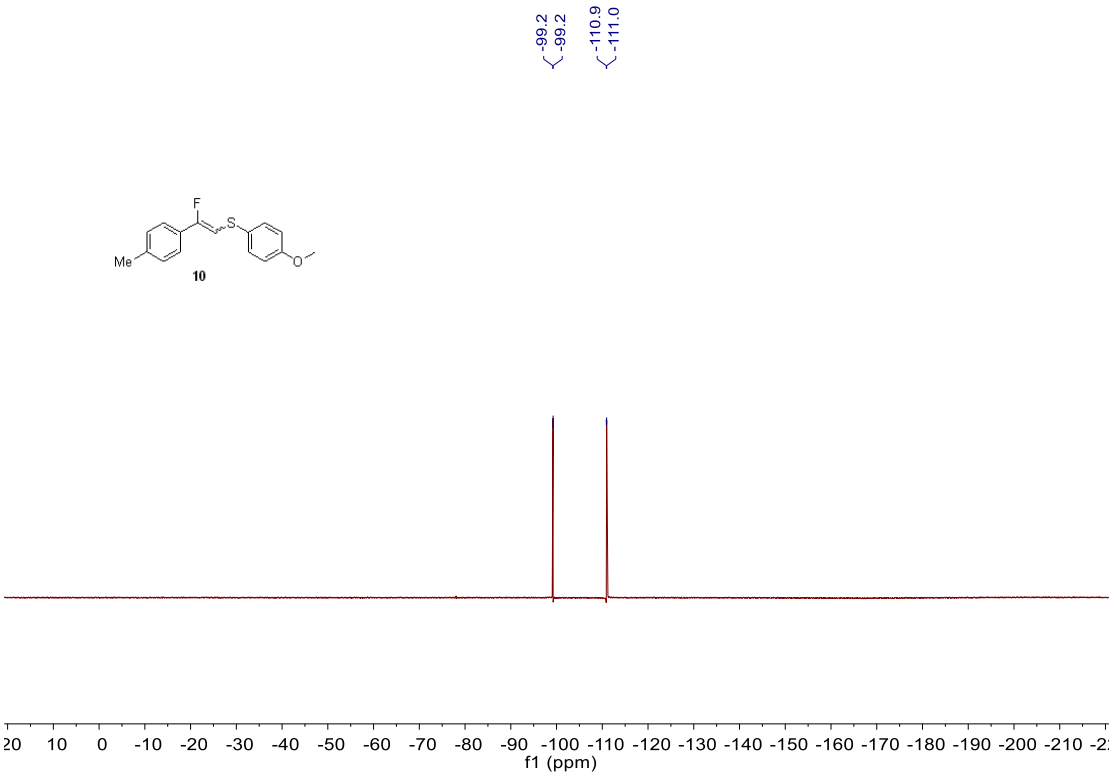

7.41
7.39
7.19
7.17
6.03
5.96
2.36
F
I
Me
8
2.09
1.95
1.00
3.07
f1 (ppm)

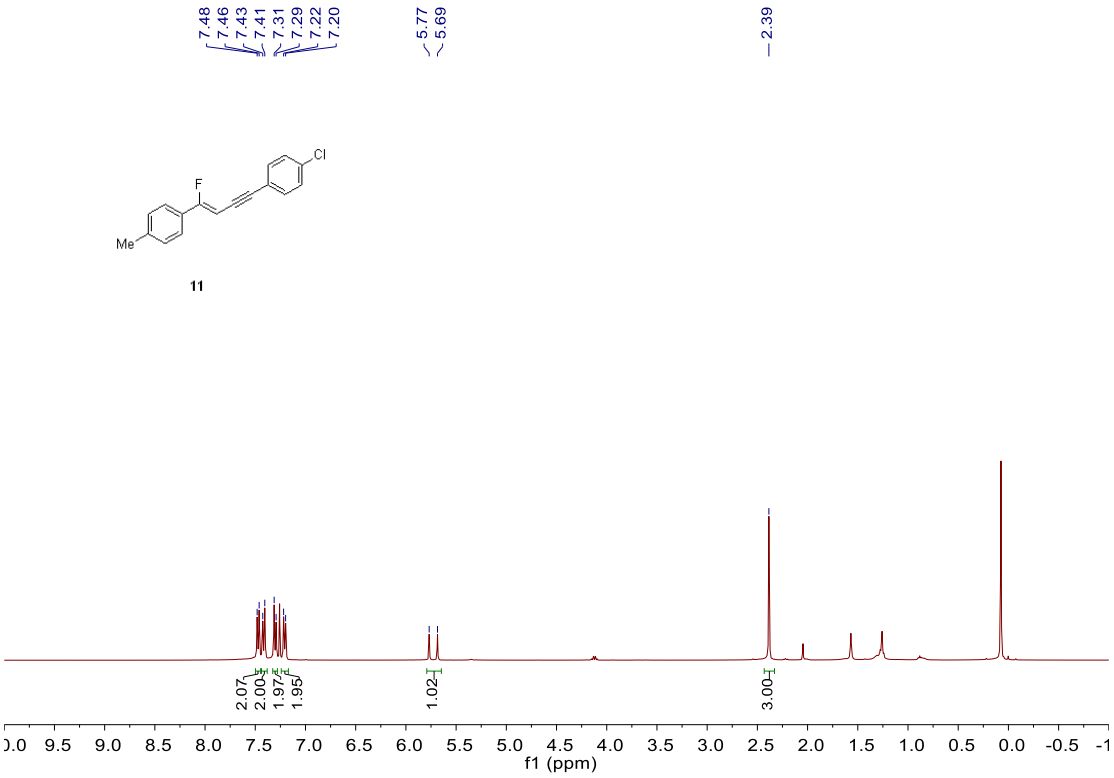

-89.8
-89.8
-89.8
-89.8
-88.5 -89.0 -89.5 -90.0 -90.5 -91.0
f1 (ppm)
F
I
Me
8
f1 (ppm)

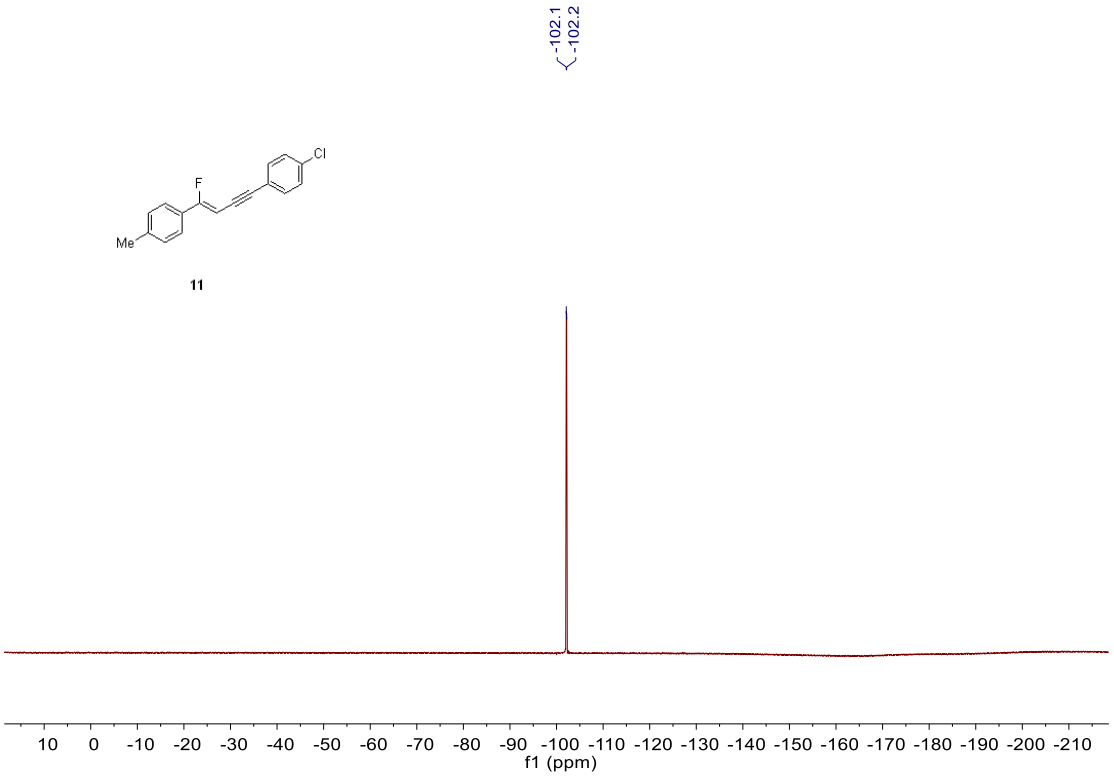

7.51
7.49
7.28
7.26
5.39
5.31
2.42
F
CN
Me
9
2.00
2.28
1.00
3.00
f1 (ppm)


7.64
7.63
7.43
7.42
7.39
7.37
7.36
7.35
7.26
7.24
7.18
7.16
6.90
6.89
6.88
6.87
6.15
6.11
6.10
6.03
3.82
3.81
2.40
2.36
F
S
Me
O
10
2.06
2.04
4.06
1.99
2.00
4.15
1.00
1.01
2.96
3.00
2.97
3.08
f1 (ppm)


159.5
159.3
157.7
157.2
155.8
155.2
139.7
139.0
132.6
131.5
129.4
129.4
129.0
128.8
128.4
128.2
127.1
127.1
126.5
125.7
123.7
123.7
115.0
104.4
104.1
102.5
102.3
55.5
21.6
21.4
F
S
Me
O
10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-99.2
-99.2
-110.9
-111.0
F
S
Me
O
10
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)


7.48
7.46
7.43
7.41
7.31
7.29
7.22
7.20
5.77
5.69
2.39
Cl
F
Me
11
2.07
2.00
1.97
1.95
1.02
3.00
f1 (ppm)


-102.1
-102.2
Cl
F
Me
11
f1 (ppm)