Supporting Information

Selective C−F Bond Carboxylation of *gem*-Difluoroalkenes with CO_2 by Photoredox/Palladium Dual Catalysis

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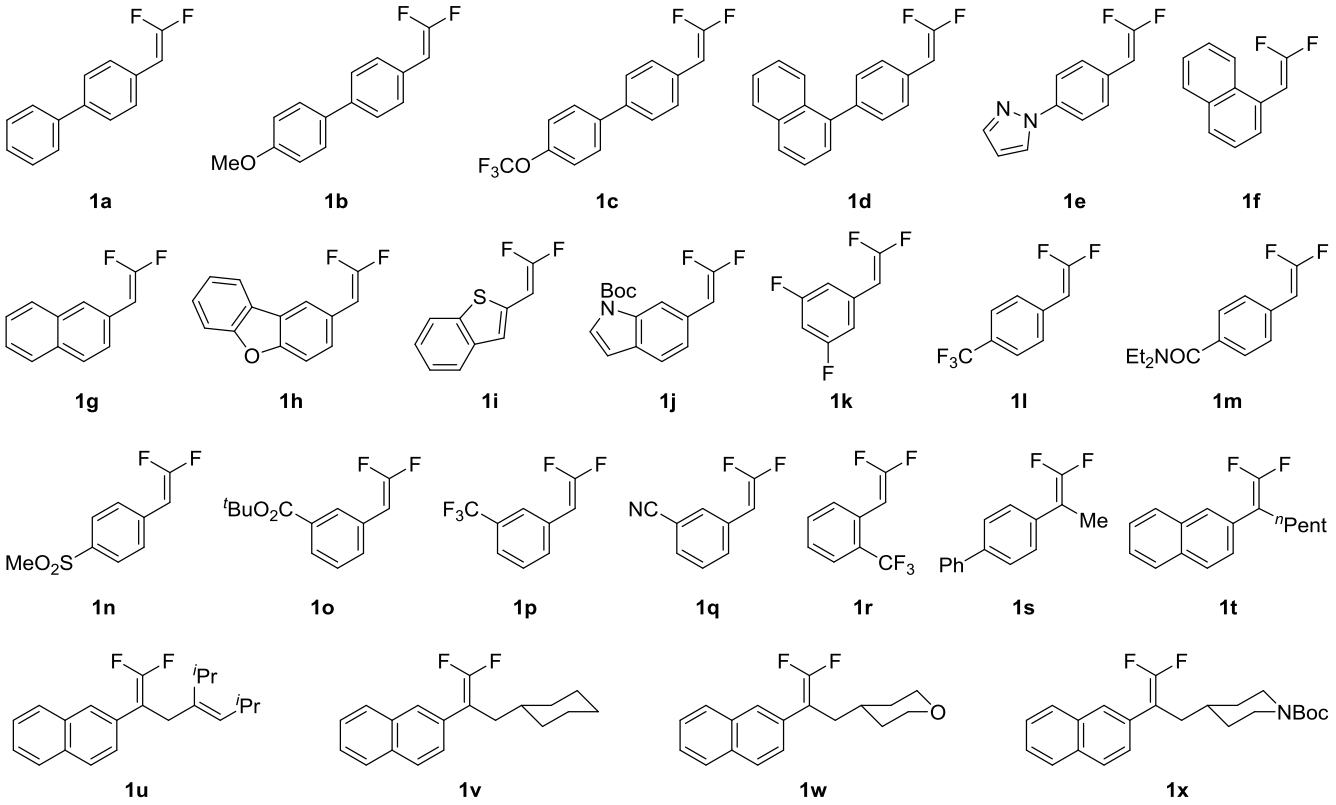
1. General information

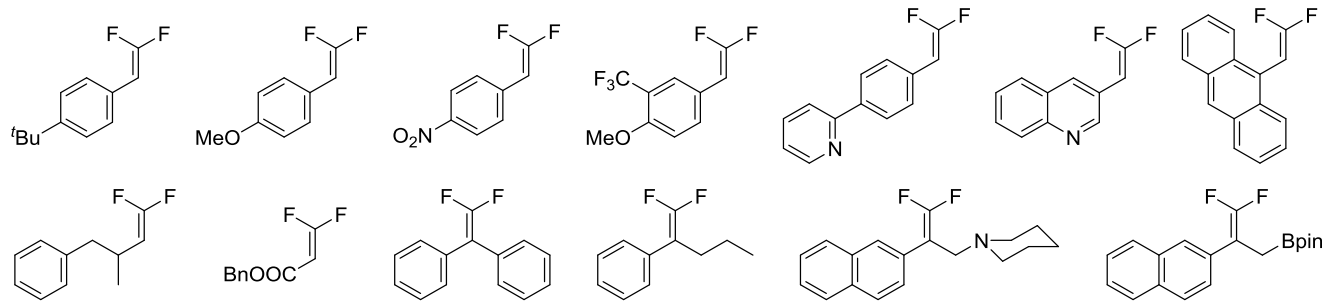
All operations were performed under a nitrogen atmosphere unless otherwise specified. ^{1}H, ^{13}C and ^{19}F-NMR spectra were recorded on a Bruker 400 (400 MHz for ^{1}H, 100 MHz for ^{13}C and 376 MHz for ^{19}F) or a JEOL ECX-400 (400 MHz for ^{1}H, 100 MHz for ^{13}C and 376 MHz for ^{19}F) spectrometer using residue solvent as internal reference. Silica gel (200~300 mesh) was used for flash column chromatography. High resolution mass analyses (ESI+) were performed on a Waters mass spectrometer.

Reagents: Unless otherwise noted, commercial reagents were used as received. Dehydrated DMA was purchased from Energy®. THF, toluene, acetonitrile and dichloromethane were purified by Vigor® solvent purification system. Iridium photocatalysts[1-3] and *gem*-difluoroalkenes **1a**, **1e**,[4] **1f**, **1g**,[5] **1h**,[4] **1i**,[6] **1l**,[7] **1m**,[5] **1p**,[8] **1q**,[9] **1r**,[10] **1s**,[4] and compounds **4**[11] were prepared according to literature procedures.

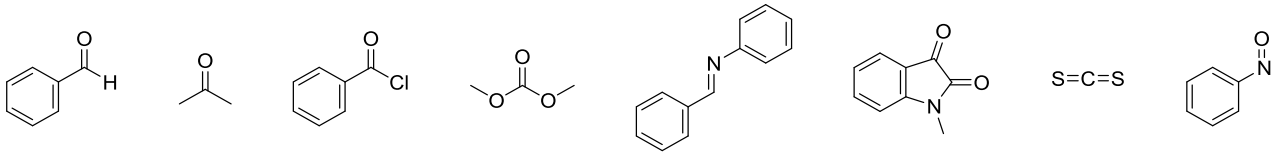
1.1 Structure of *gem*-difluoroalkenes 1a-x



1.2 Unsuccessful *gem*-difluoroalkenes

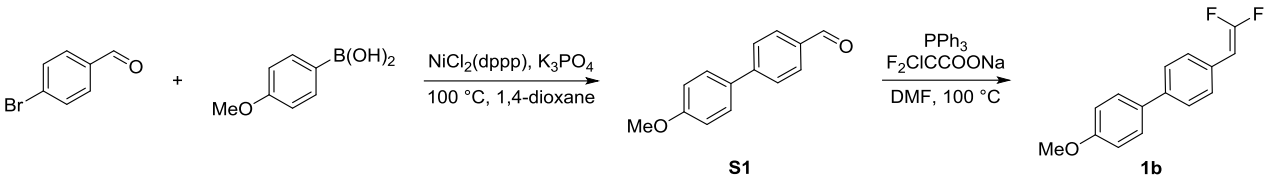


1.3 Unsuccessful carbonyl-like electrophiles



2. Procedure for the preparation of *gem*-difluoroalkenes

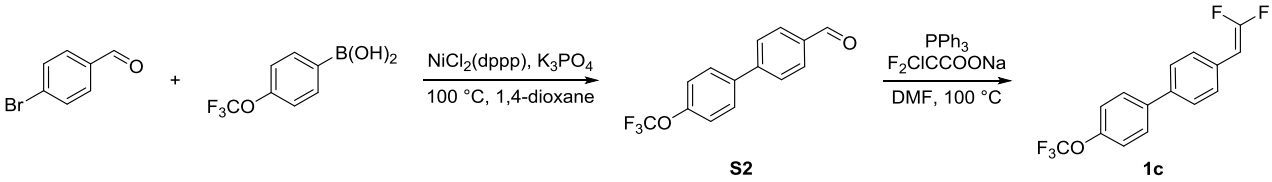
Preparation of *gem*-difluoroalkene **1b**



Step 1: Following the reported procedure, to an oven-dried 100 mL two-neck RBF equiped with condenser and stir bar was added 4-bromobenzaldehyde (1.8 g, 10 mmol, 1.0 equiv), 4-methoxylphenylboronic acid (2.3 g, 15 mmol, 1.5 equiv), $NiCl_2$(dppp) (54 mg, 0.5 mmol), and K_3PO_4 (6.4 g, 30 mmol, 3.0 equiv). The RBF was evacuated and filled with nitrogen (three cycles). To these solids 1,4-dioxane (50 mL) was added and the resulting mixture was stirred at 100 ℃ for 12 h. The reaction mixture was cooled to room temperature, diluted with ethyl acetate and filtered. The filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20 : 1) to afford compound **S1** (1.9 g, 9.0 mmol) in 90% yield as white solid. The ^{1}H NMR data is in accordance with the literature.[12]

Step 2 : A solution of **S1** (1.3 g, 6.1 mmol, 1.0 equiv) and PPh_3 (3.2 g, 12 mmol, 2.0 equiv) in DMF (12 mL) was heated to 100 ℃. To the reaction mixture at 100 ℃ was added $F_2ClCCOONa$ (1.9 g, 12 mmol, 2.0 equiv) slowly. After the reaction was completed according to the TLC (about 30 min), the reaction mixture was cooled to room temperature, quenched with water and extracted with ethyl acetate. The combined organic layers were washed with H_2O_2 (30 wt% in water, 10 mL), brine and dried over Na_2SO_4. After the solvent was removed under reduced pressure, the residual mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20 : 1) to afford compound **1b** (1.1 g, 4.7 mmol) in 78% yield as white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.54 (d, *J* = 8.6 Hz, 4H), 7.39 (d, *J* = 8.3 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 5.31 (dd, *J* = 26.4, 3.8 Hz, 1H), 3.86 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -82.08 (dd, *J* = 31.3, 26.1 Hz), -84.07 (dd, *J* = 31.4, 4.0 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 159.2, 156.2 (dd, *J* = 298.3, 268.0 Hz), 139.4 (t, *J* = 2.2 Hz), 132.9, 128.7 (t, *J* = 6.4 Hz), 127.9, 127.9 (t, *J* = 5.2 Hz), 126.8, 114.2, 81.9 (dd, *J* = 29.1, 13.6 Hz), 55.3. **HRMS (ESI, m/z):** calcd. for $C_{15}H_{13}F_2O$ $[M+H]^+$: 247.0934, found: 247.0929.

Preparation of *gem*-difluoroalkene **1c**

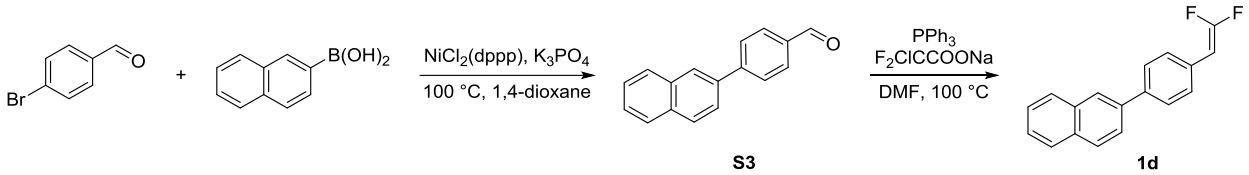


Step 1: To an oven-dried 100 mL two-neck RBF equiped with condenser and stir bar was added 4-bromobenzaldehyde (0.93 g, 5.0 mmol, 1.0 equiv), 4-trifluoromethoxylphenylboronic acid (1.5 g, 7.5 mmol, 1.5 equiv), $NiCl_2$(dppp) (27 mg, 0.25 mmol), and K_3PO_4 (3.2 g, 15 mmol, 3.0 equiv). The RBF was evacuated and filled with nitrogen (three cycles). To these solids 1,4-dioxane (25 mL) was added and the resulting mixture was stirred at 100 ℃ for 12 h. The reaction mixture was cooled to room temperature, diluted with ethyl acetate and filtered. The filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10 : 1) to afford compound **S2** (1.0 g, 3.8 mmol) in 76% yield as white solid. The ^{1}H NMR data is in accordance with the literature.[13]

Step 2 : A solution of **S1** (1.0 g, 3.8 mmol, 1.0 equiv) and PPh_3 (2.0 g, 7.6 mmol, 2.0 equiv) in DMF (8 mL) was heated to 100 ℃. To the reaction mixture at 100 ℃ was added $F_2ClCCOONa$ (1.2 g, 7.6 mmol, 2.0 equiv) slowly. After the reaction

was completed according to the TLC (about 30 min), the reaction mixture was cooled to room temperature, quenched with water and extracted with ethyl acetate. The combined organic layers were washed with H_2O_2 (30 wt% in water, 5 mL), brine and dried over Na_2SO_4. After the solvent was removed under reduced pressure, the residual mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20 : 1) to afford compound **1b** (0.8 g, 2.7 mmol) in 70% yield as white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.60 (d, *J* = 8.7 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 5.33 (dd, *J* = 26.2, 3.7 Hz, 1H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -57.82 (s, 3F), -81.52(dd, *J* = 29.8, 26.1 Hz, 1F), -83.39 (dd, *J* = 29.5, 3.5 Hz, 1F). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 156.4 (dd, *J* = 298.7, 288.9 Hz), 148.7 (d, *J* = 2.0 Hz), 139.2, 138.3 (dd, *J* = 2.1, 2.1 Hz), 129.8 (dd, *J* = 6.5, 6.5 Hz), 128.2, 128.1 (dd, *J* = 6.4, 3.6 Hz), 127.3, 121.3, 120.5 (q, *J* = 257.1 Hz), 81.8 (dd, *J* = 29.3, 13.6 Hz). **HRMS (ESI, m/z):** calcd. for $C_{15}H_{10}F_5O$ $[M+H]^+$: 301.0652, found: 301.0645.

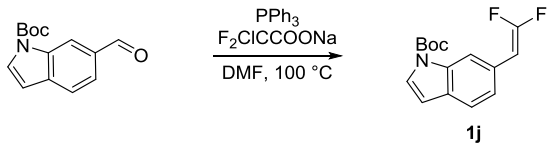
Preparation of compound **1d**



Step 1: To an oven-dried 100 mL two-neck RBF equiped with condenser and stir bar was added 4-bromobenzaldehyde (1.8 g, 10 mmol, 1.0 equiv), 4-methoxylphenylboronic acid (2.3 g, 15 mmol, 1.5 equiv), $NiCl_2$(dppp) (54 mg, 0.5 mmol), and K_3PO_4 (6.4 g, 30 mmol, 3.0 equiv). The RBF was evacuated and filled with nitrogen (three cycles). To these solids 1,4-dioxane (50 mL) was added and the resulting mixture was stirred at 100 ℃ for 12 h. The reaction mixture was cooled to room temperature, diluted with ethyl acetate and filtered. The filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10 : 1) to afford compound **S3** (2.0 g, 8.7 mmol) in 87% yield as white solid. The ^{1}H NMR data is in accordance with the literature.[14]

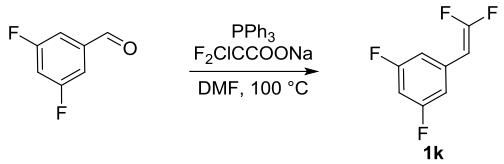
Step 2 : A solution of **S1** (0.9 g, 4.0 mmol, 1.0 equiv) and PPh_3 (2.1 g, 8.0 mmol, 2.0 equiv) in DMF (8 mL) was heated to 100 ℃. To the reaction mixture at 100 ℃ was added $F_2ClCCOONa$ (1.2 g, 8.0 mmol, 2.0 equiv) slowly. After the reaction was completed according to the TLC (about 30 min), the reaction mixture was cooled to room temperature, quenched with water and extracted with ethyl acetate. The combined organic layers were washed with H_2O_2 (30 wt% in water, 5 mL), brine and dried over Na_2SO_4. After the solvent was removed under reduced pressure, the residual mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10 : 1) to afford compound **1b** (0.6 g, 2.3 mmol) in 56% yield as white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.88 (d, *J* = 1.7 Hz, 1H), 7.78-7.67 (m, 3H), 7.57 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.39-7.30 (m, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 5.16 (dd, *J* = 26.4, 3.7 Hz, 1H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -81.66 (dd, *J* = 30.3, 26.3 Hz), -83.62 (dd, *J* = 30.3, 3.7 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 156.3 (dd, *J* = 298.6, 288.6 Hz), 139.6 (t, *J* = 2.2 Hz), 137.7, 133.6, 132.6, 129.4 (dd, *J* = 6.4, 6.4 Hz), 128.5, 128.2, 128.0 (dd, *J* = 6.3, 3.7 Hz), 127.6, 127.5, 126.3, 126.0, 125.5, 125.2, 81.9 (dd, *J* = 29.2, 13.5 Hz). **HRMS (ESI, m/z):** calcd. for $C_{18}H_{13}F_2$ $[M+H]^+$: 267.0985, found: 267.0993.

Preparation of compound **1j**



A solution of *tert*-butyl 6-formyl-1*H*-indole-1-carboxylate (1.2 g, 5.0 mmol, 1.0 equiv) and PPh_3 (2.6 g, 10 mmol, 2.0 equiv) in DMF (20 mL) was heated to 100 ℃. To the reaction mixture at 100 ℃ was added $F_2ClCCOONa$ (1.5 g, 10 mmol, 2.0 equiv) slowly. After the reaction finished according to the TLC (about 30 min), the reaction mixture was cooled to room temperature, quenched with water (100 mL) and extracted with ethyl acetate (20 mL × 3). The combined organic layers were washed with H_2O_2 (30 wt% in water, 20 mL), brine and dried over Na_2SO_4. After solvent was removed under reduced pressure, the residual mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20 : 1) to afford **1j** (838 mg, 3.0 mmol) in 60% yield as white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.19 (s, 1H), 7.60 (d, *J* = 3.7 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.20 (d, *J* = 8.3 Hz, 1H), 6.54 (d, *J* = 3.6 Hz, 1H), 5.40 (dd, *J* = 26.2, 4.0 Hz, 1H), 1.69 (s, 9H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -82.96 (dd, *J* = 33.7, 26.2 Hz, 1F), -85.07 (dd, *J* = 34.0, 4.2 Hz, 1F). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 156.0 (dd, *J* = 297.5, 287.0 Hz), 149.7, 135.4, 129.6, 126.5, 126.3 (dd, *J* = 12.8, 6.5 Hz), 122.5 (dd, *J* = 6.1, 3.4 Hz), 121.0, 114.3 (dd, *J* = 7.4, 3.8 Hz), 107.1, 83.9, 82.9 (dd, *J* = 29.4, 13.5 Hz), 28.1. **HRMS (ESI, m/z):** calcd. for $C_{15}H_{16}F_2NO_2$ $[M+H]^+$: 280.1149, found: 280.1158.

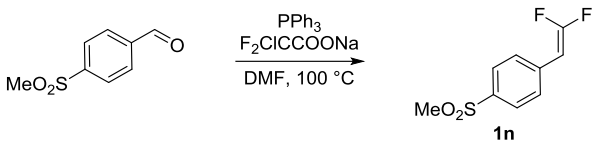
Preparation of compound **1k**



1k

A solution of 3,5-difluorobenzaldehyde (2.8 g, 20 mmol, 1.0 equiv) and PPh_3 (6.3 g, 24 mmol, 1.2 equiv) in DMF (40 mL) was heated to 100 ℃. To the reaction mixture at 100 ℃ was added $F_2ClCCOONa$ (4.6 g, 30 mmol, 1.5 equiv) slowly. After the reaction finished according to the TLC (about 30 min), the reaction mixture was cooled to room temperature, quenched with water (200 mL) and extracted with Et_2O (40 mL × 3). The combined organic layers were washed with H_2O_2 (30 wt% in water, 20 mL), brine and dried over Na_2SO_4. After solvent was removed under reduced pressure, the residual mixture was purified by column chromatography on silica gel (petroleum ether) to afford **1k** (0.95 g, 5.4 mmol) in 27% yield as colorless liquid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.04 – 6.77 (m, 2H), 6.69 (tt, *J* = 8.9, 2.3 Hz, 1H), 5.24 (dd, *J* = 25.1, 3.3 Hz, 1H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -78.73 (dd, *J* = 24.7, 24.7 Hz), -81.26 – -81.38 (m), -109.73 – -109.85 (m). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 163.1 (dd, *J* = 247.6, 13.3 Hz), 156.8 (dd, *J* = 300.1, 290.7 Hz), 134.3 – 133.0 (m), 110.8 – 110.0 (m), 102.5 (ddd, *J* = 27.4, 25.4, 1.9 Hz), 81.5 (dddd, *J* = 31.0, 12.9, 3.0, 3.0 Hz). **HRMS (ESI, m/z):** calcd. for $C_9H_9F_2O_2S$ $[M+H]^+$: 219.0291, found: 219.0285.

Preparation of compound **1n**

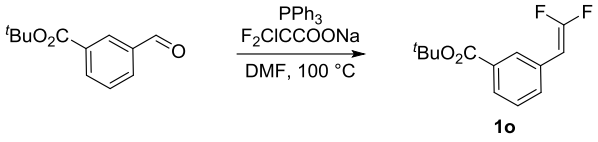


1n

A solution of 4-(methylsulfonyl)benzaldehyde (1.5 g, 10 mmol, 1.0 equiv) and PPh_3 (2.6 g, 10 mmol, 2.0 equiv) in DMF (20 mL) was heated to 100 ℃. To the reaction mixture at 100 ℃ was added $F_2ClCCOONa$ (1.5 g, 10 mmol, 2.0 equiv) slowly. After the reaction finished according to the TLC (about 30 min), the reaction mixture was cooled to room temperature, quenched with water (100 mL) and extracted with ethyl acetate (20 mL × 3). The combined organic layers were washed with H_2O_2 (30 wt% in water, 5 mL), brine and dried over Na_2SO_4. After solvent was removed under reduced pressure, the residual mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20 : 1) to afford **1n** (1.0 g, 4.4 mmol) in 44% yield as white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.88 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 5.37 (dd, *J* = 25.6, 3.4 Hz, 1H), 3.04 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -77.89 (dd, *J* = 25.4, 20.5 Hz), -79.45 (dd, *J* =

20.5, 3.4 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 157.0 (dd, *J* = 301.2, 292.1 Hz), 138.6 (t, *J* = 2.3 Hz), 136.2 (dd, *J* = 7.7, 6.3 Hz), 128.2 (dd, *J* = 6.9, 3.6 Hz), 127.7, 81.6 (dd, *J* = 30.4, 12.8 Hz), 44.4. **HRMS (ESI, m/z):** calcd. for $C_9H_9F_2O_2S$ $[M+H]^+$: 219.0291, found: 219.0285.

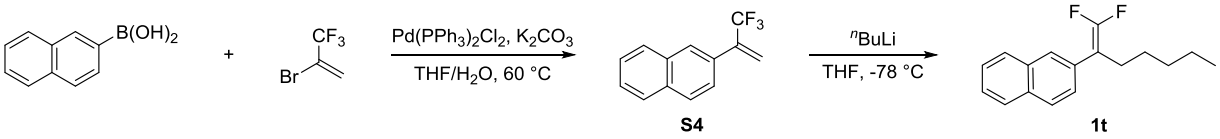
Preparation of compound **1o**



1o

A solution of *tert*-butyl 3-formylbenzoate (0.93 g, 4.5 mmol, 1.0 equiv) and PPh_3 (1.4 g, 5.4 mmol, 1.2 equiv) in DMF (10 mL) was heated to 100 ℃. To the reaction mixture at 100 ℃ was added $F_2ClCCOONa$ (1.0 g, 6.75 mmol, 1.5 equiv) slowly. After the reaction finished according to the TLC (about 30 min), the reaction mixture was cooled to room temperature, quenched with water (50 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with H_2O_2 (30 wt% in water, 10 mL), brine and dried over Na_2SO_4. After solvent was removed under reduced pressure, the residual mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20 : 1) to afford **1o** (0.55 g, 2.3 mmol) in 50% yield as white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.93 (dd, *J* = 1.8, 1.8 Hz, 1H), 7.86 (ddd, *J* = 7.7, 1.5, 1.5 Hz, 1H), 7.56 – 7.46 (m, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 5.32 (dd, *J* = 26.0, 3.6 Hz, 1H), 1.60 (s, 9H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -81.27 (dd, *J* = 29.2, 25.9 Hz), -83.15 (dd, *J* = 29.0, 3.7 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 165.4, 156.4 (dd, *J* = 298.8, 289.0 Hz), 132.4, 131.2 (dd, *J* = 6.9, 3.3 Hz), 130.5 (dd, *J* = 7.3, 5.9 Hz), 128.6 (dd, *J* = 5.8, 3.8 Hz), 128.6, 127.9 (dd, *J* = 1.9, 1.9 Hz), 81.7 (dd, *J* = 29.6, 13.4 Hz), 81.2, 28.1. **HRMS (ESI, m/z):** calcd. for $C_9H_9F_2O_2S$ $[M+H]^+$: 219.0291, found: 219.0285.

Preparation of compound **1t**[15]



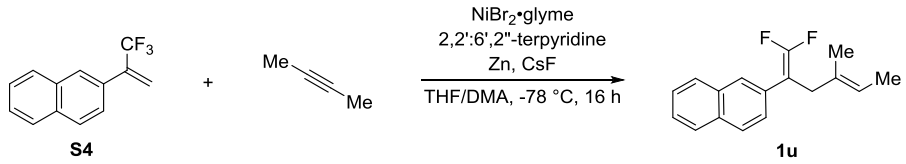
S4 **1t**

Step1: $Pd(PPh_3)_2Cl_2$ (70 mg, 0.1 mmol), K_2CO_3 (5.52 g, 40 mmol) and naphthalen-2-ylboronic acid (1.72 g, 10 mmol) were added to a Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and filled with nitrogen (three cycles). To these solids, THF (30 mL), H_2O (20 mL) and 2-bromo-3,3,3-trifluoroprop-1-ene (3.50 g, 20 mmol) were added under nitrogen atmosphere. The reaction mixture was stirred at relux for 24 h. Next, the reaction mixture was quenched by adding saturated aqueous NH_4Cl (20 mL) and extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by column chromatograph on silica gel (petroleum ether/ethyl acetate = 50 : 1) to afford **S4** (2.0 g, 9.0 mmol) in 90% yield as white solid. The ^{1}H NMR data is in accordance with the literature.[16]

Step 2: A solution of **S4** (222 mg, 1.0 mmol) in THF (10 mL) was cooled to -78 ℃. To the mixture at -78 ℃ was added ^{n}BuLi (0.75 mL, 1.2 mmol, 1.6 mol/L THF solution) slowly. After stirring at -78 ℃ for 1 h, the reaction mixture was quenched with by adding water (5 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4. After solvent was removed under reduced pressure, the residual mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50 : 1) to afford **1t** (0.17 g, 0.65 mmol) in 65% yield as colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.87 – 7.83 (m, 3H), 7.81 (s, 1H), 7.55 – 7.46 (m, 3H), 2.57 – 2.50 (m, 2H), 1.50 – 1.40 (m, 2H), 1.39 – 1.27 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -91.44 (dt, *J* = 44.0, 2.8 Hz, 1F), -91.59 (d, *J* = 44.0 Hz, 1F). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 153.8 (dd, *J* = 290.2,

286.7 Hz), 133.3, 132.4, 131.3 (dd, *J* = 4.3, 2.7 Hz), 127.9, 127.9, 127.6, 127.2 (t, *J* = 3.4 Hz), 126.2, 126.2 (d, *J* = 6.4 Hz), 126.0, 92.6 (dd, *J* = 21.7, 12.7 Hz), 31.2, 27.6, 27.4 (t, *J* = 2.5 Hz), 22.3, 14.0. **HRMS (ESI, m/z):** calcd. for $C_{17}H_{19}F_2$ $[M+H]^+$: 261.1448, found: 261.1455.

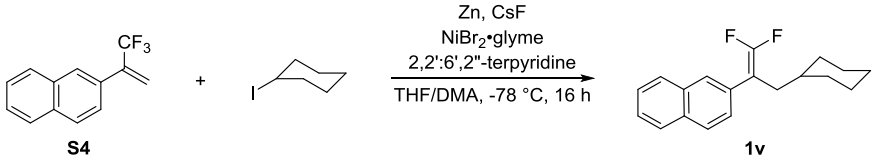
Preparation of compound **1u**[17]



S4 **1u**

$Ni(cod)_2$ (14 mg, 0.05 mmol), PCy_3 (28 mg, 0.1 mmol) and toluene (5 mL) were added to a Schlenk tube equipped with a stir bar in glovebox. To the solution **S4** (222 mg, 1.0 mmol), Et_3SiH (232 mg, 2.0 mmol) and 2-butyne (60 mg, 1.1 mmol) were added at room temperature. After stirring at 50 ℃ for 3 h, the reaction mixture was filtered through a short pad of silica gel and washed with EtOAc. The filtrate was concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography on silica gel (hexane) to afford **1u** (232 mg, 0.9 mmol) in 90% yield as colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.16 – 7.64 (m, 4H), 7.66 – 7.31 (m, 3H), 5.39 – 5.28 (m, 1H), 3.20 (s, 2H), 1.66 (s, 3H), 1.57 (dq, *J* = 6.7, 1.3 Hz, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -90.03 (dt, *J* = 40.3, 3.0 Hz), -90.50 (d, *J* = 40.3 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 154.4 (dd, *J* = 291.9, 287.6 Hz), 133.2, 132.3, 131.8 (t, *J* = 2.5 Hz), 131.4 (t, *J* = 3.9 Hz), 127.9, 127.7, 127.5, 127.2 (t, *J* = 3.6 Hz), 126.1 (dd, *J* = 4.0, 2.9 Hz), 126.1, 126.0, 120.7, 90.7 (dd, *J* = 21.4, 12.1 Hz), 37.6 (d, *J* = 1.7 Hz), 15.5, 13.4. **HRMS (ESI, m/z):** calcd. for $C_{17}H_{17}F_2$ $[M+H]^+$: 259.1298, found: 259.1303.

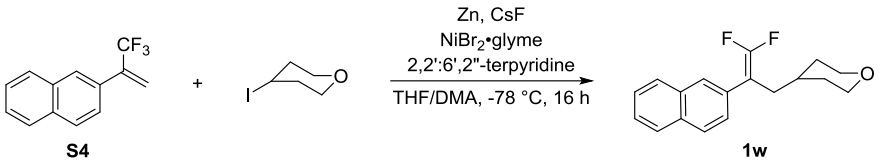
Preparation of compound **1v**[18]



S4 **1v**

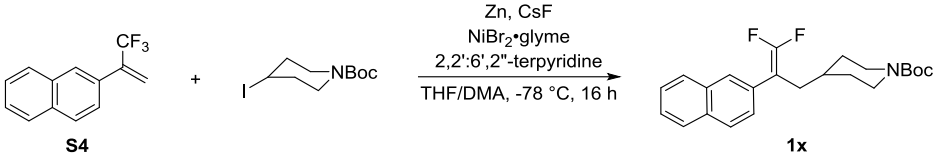
$NiBr_2$·glyme (62 mg, 0.2 mmol), 2,2':6',2"-terpyridine (47 mg, 0.2 mmol), **S4** (444 mg, 2.0 mmol), Zn powder (260 mg, 4.0 mmol) and CsF (304 mg, 2.0 mmol) were added to a Schlenk tube equipped with a stir bar in glovebox. To these solids, THF (16 mL) and DMA (4 mL) was added under nitrogen atmosphere. The resulting mixture was stirred at room temperature for 1 min before alkyliodide (4.0 mmol) was added. The reaction mixture was further stirred at 40 ℃ for 16 h. Next, the reaction mixture was quenched by adding H_2O (20 mL) and extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with H_2O (20 mL), brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by column chromatograph on silica gel (petroleum ether/ethyl acetate = 50 : 1) to afford **1v** (155 mg, 0.5 mmol) in 27% yield as white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.89 – 7.84 (m, 3H), 7.81 (s, 1H), 7.56 – 7.47 (m, 3H), 2.43 (dt, *J* = 7.3, 2.5 Hz, 2H), 1.81–1.61 (m, 5H), 1.39–1.28 (m, 1H), 1.22 – 1.09 (m, 3H), 1.04 – 0.94 (m, 2H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -90.82 (dt, *J* = 43.5, 3.0 Hz, 1F), -91.52 (d, *J* = 42.8 Hz, 1F). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 154.2 (dd, *J* = 290.6, 286.2 Hz), 133.3, 132.4, 131.5 (dd, *J* = 4.6, 3.2 Hz), 127.9, 127.9, 127.6, 127.3 (t, *J* = 3.3 Hz), 126.2 (t, *J* = 3.0 Hz), 126.2, 126.0, 91.2 (dd, *J* = 22.2, 12.4 Hz), 35.7 (t, *J* = 2.4 Hz), 35.3, 32.9, 26.4, 26.0. **HRMS (ESI, m/z):** calcd. for $C_{19}H_{21}F_2$ $[M+H]^+$: 287.1611, found: 287.1611.

Preparation of compound **1w**[18]



Following the procedure for **1v**, compound **1w** (231 mg, 0.8 mmol) was obtained in 40% yield as white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.92 – 7.81 (m, 3H), 7.79 (s, 1H), 7.57 – 7.48 (m, 2H), 7.46 (ddd, *J* = 8.6, 1.8, 1.8 Hz, 1H), 4.00 – 3.87 (m, 2H), 3.25 (td, *J* = 11.8, 2.0 Hz, 2H), 2.48 (dt, *J* = 7.0, 2.4 Hz, 2H), 1.76 – 1.46 (m, 3H), 1.45 – 1.26 (m, 2H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -90.29 (dt, *J* = 41.9, 3.0 Hz), -90.87 (d, *J* = 41.3 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 154.2 (dd, *J* = 291.1, 286.9 Hz), 133.2, 132.4, 131.0 (dd, *J* = 4.3, 3.1 Hz), 128.1, 127.8, 127.6, 127.2 (dd, *J* = 3.3, 3.3 Hz), 126.3, 126.1, 126.0 (dd, *J* = 3.1, 3.1 Hz), 90.5 (dd, *J* = 22.1, 13.1 Hz), 67.7, 34.7 (d, *J* = 1.5 Hz), 33.2 (t, *J* = 2.6 Hz), 32.6. **HRMS (ESI, m/z):** calcd. for $C_{18}H_{19}F_2O$ $[M+H]^+$: 289.1404, found: 289.1400.

Preparation of compound **1x**[18]



Following the procedure for **1v**, compound **1x** (325 mg, 0.8 mmol) was obtained in 42% yield as white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.90 – 7.80 (m, 3H), 7.77 (d, *J* = 1.7 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.44 (ddd, *J* = 8.6, 1.7, 1.7 Hz, 1H), 4.40 – 3.75 (m, 2H), 2.55 (t, *J* = 12.7 Hz, 2H), 2.49 – 2.40 (m, 2H), 1.73 – 1.60 (m, 2H), 1.54 – 1.39 (m, 10H), 1.25 – 1.05 (m, 2H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -90.85 (d, *J* = 42.0 Hz), -90.22 (dt, *J* = 42.8, 3.5 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 154.7, 154.2 (dd, *J* = 291.1, 287.1 Hz), 133.2, 132.4, 131.0 (dd, *J* = 4.3, 3.2 Hz), 128.1, 127.8, 127.5, 127.2 (dd, *J* = 3.3, 3.3 Hz), 126.3, 126.1, 125.9 (t, *J* = 3.1 Hz), 90.6 (dd, *J* = 22.0, 13.1 Hz), 79.2, 34.4 (d, *J* = 0.8 Hz), 34.2 (dd, *J* = 2.5, 2.5 Hz), 31.7, 28.4, 28.3. **HRMS (ESI, m/z):** calcd. for $C_{23}H_{28}F_2NO_2$ $[M+H]^+$: 388.2088, found: 388.2085.

3. Optimization of reaction conditions

Photocatalyst, Pd salt, ligand, Cs_2CO_3 and **1a** (43 mg, 0.2 mmol) were added to a Schlenk tube equipped with a stir bar in glovebox. To these solids, DMA (0.1 M) and ^{i}Pr$_2$NEt was added under nitrogen atmosphere. The Schlenk tube was evacuated and filled with CO_2 (three cycles). Then the Schlenk tube was placed in front of the light source within approximatly 1 cm distance (Figure S1) and stirred at ambient temperature (25~30 ℃) for 24~48 h. Next, the reaction mixture was acidified by adding 1N HCl (10 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with water (10 mL) and brine (10 mL) successively, and dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. To the residue were added 1,1,1-trifluoromethylbenzene (21.0 μL, 0.200 mmol) and $CDCl_3$ (ca. 1 mL), and then ^{19}F NMR analysis was conducted using a portion of this solution. The yields were determined by comparison of an integrated value of the peak that corresponds to a vinylic fluoride of **2a** (both *Z* and *E* configuration) (δ ppm) with that corresponds to three fluorides of 1,1,1-trifluoromethylbenzene (δ ppm). The ratio of *Z* and *E*-**2a** was determined by the integration of corresponding peaks on ^{19}F NMR.

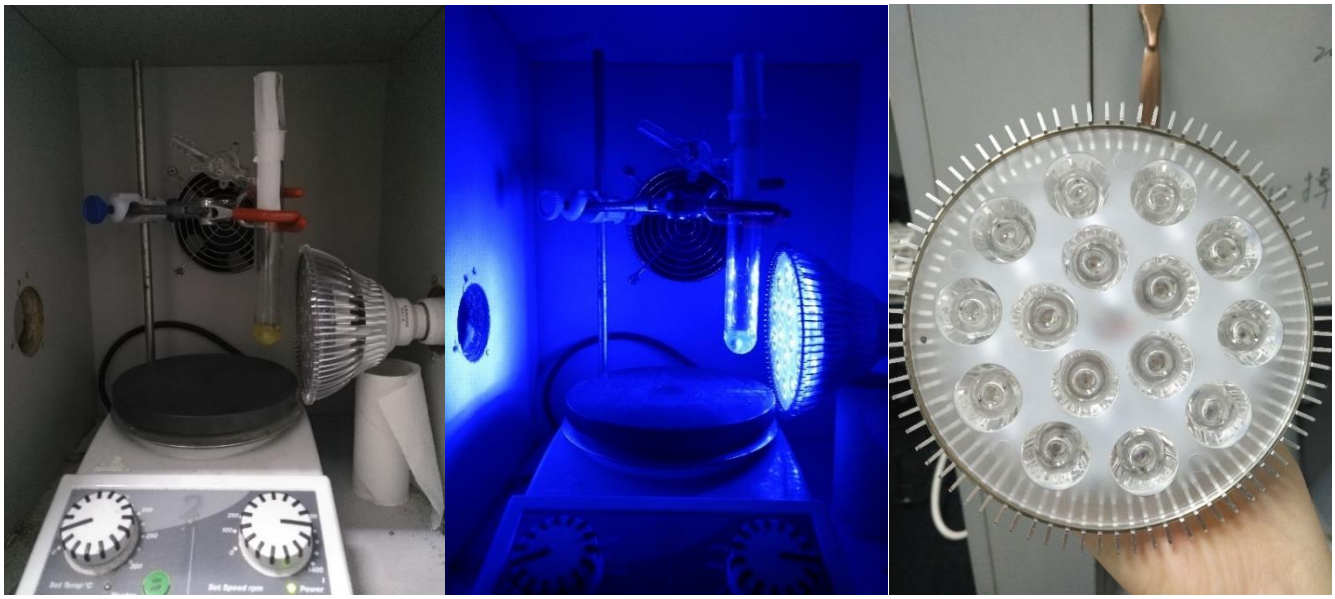
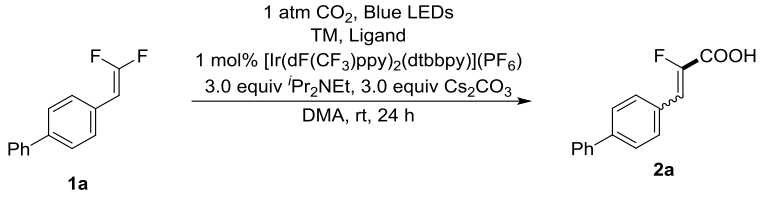


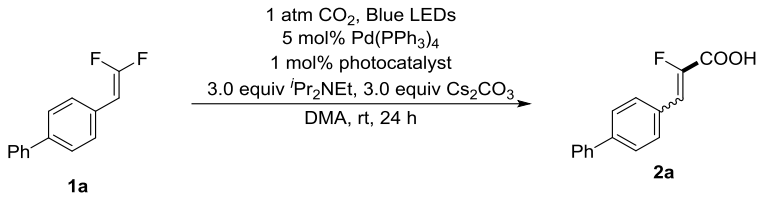
Figure S1. Experimental installation

Table S1. Screening of transition-metal catalyst.



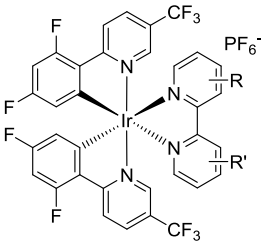
Entry	TM	Ligand	Yield/%	*Z*/*E*
1	**5 mol% $Pd(PPh_3)_4$**	**-**	**71**	**90:10**
2	5 mol% $CoCl_2$	10 mol% neocuproine	0	-
3	5 mol% $NiBr_2$	10 mol% bipyridyl	0	-
4	5 mol% $NiCl_2(PPh_3)_2$	10 mol% PPh_3	0	-

Table S2. Screening of photocatalyst.

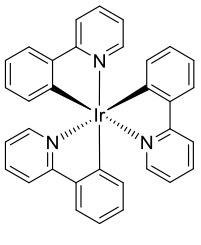


Entry	Photo catalyst	Yield/%	*Z*/*E*
1	**$[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$ PC 1**	**71**	**90:10**
2	$[Ir(dF(CF_3)ppy)_2(bpy)](PF_6)$ PC 2	48	88:12
3	$[Ir(dF(CF_3)ppy)_2(5,5'\text{-}dCF_3bpy)](PF_6)$ PC 3	11	82:18
4	$[Ir(dF(CF_3)ppy)_2(4,4'\text{-}dCF_3bpy)](PF_6)$ PC 4	65	86:14
5	*fac*-$Ir(ppy)_3$ PC 5	0	-
6	tris(2,2′-bipyrazine)ruthenium(II) bis(hexafluorophosphate) PC 6	0	-
7	tris(2,2'-bipyridyl)ruthenium(II) bis(hexafluorophosphate) PC 7	21	95:5

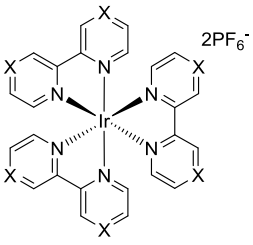
8	9-mesityl-10-methylacridinium perchlorate PC 8	0	-
9	4-CzIPN PC 9	trace	-



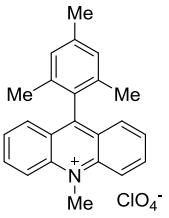
R, R' = 4-^{t}Bu, 4'-^{t}Bu, PC 1
R, R' = H, H, PC 2
R, R' = 5-CF_3, 5'-CF_3, PC 3
R, R' = 4-CF_3, 4'-CF_3, PC 4



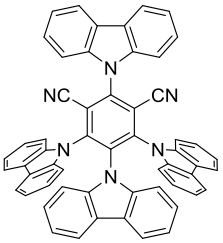
PC 5



X = N PC 6
X = CH PC 7

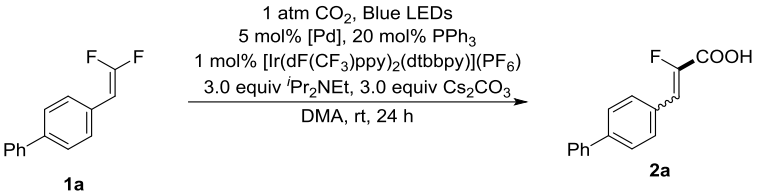


PC 8



PC 9

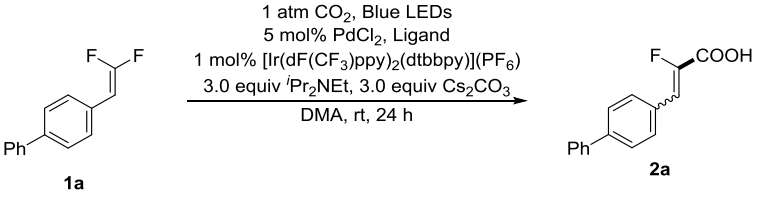
Table S3. Screening of Pd salt.



1a **2a**

Entry	[Pd]	Yield/%	*Z*/*E*
1	$Pd(OAc)_2$	62	90:10
2	$Pd_2(dba)_3$	30	93:7
3	$[(allyl)PdCl]_2$	44	91:9
4	$PdBr_2$	85	90:10
5	$Pd(PPh_3)_4$	71	90:10
6	**$PdCl_2$**	**87**	**92:8**
7	$Pd(acac)_2$	79	92:8
8	$Pd(cod)Cl_2$	57	95:5
9	$Pd(CH_3CN)_2Cl_2$	49	90:10
10	$Pd(4\text{-}CNPh)_2Cl_2$	76	89:11
11	$Pd(OPiv)_2$	45	91:9
12	Na_2PdCl_4	52	88:12
13	$Pd(OH)_2/C$	22	91:9
14	$Pd(TFA)_2$	74	92:8

Table S4. Screening of ligand.



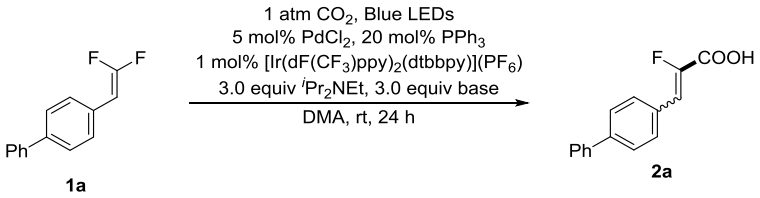
1a **2a**

Entry	Ligand	Yield/%[a]	*Z*/*E*

1	**20 mol% PPh_3**	**87**	**92:8**
2	20 mol% PCy_3	58	93:7
3	10 mol% dppe	50	94:6
4	10 mol% Xantphos	52	86:14
5	20 mol% Xphos	63	92:8
6	20 mol% Sphos	48	94:6
7	20 mol% P(*p*-OMePh)$_3$	65	89:11
8	20 mol% P(*p*-CF_3Ph)$_3$	45	93:7
9	20 mol% TFP	45	93:7
10	20 mol% P(*o*-tolyl)$_3$	74	93:7
11	20 mol% SIPr ·HCl	30	93:7
12	20 mol% P(*t*-Bu)$_3$ ·HBF_4	53	90:10
13	none	45	91:9
14	none	28	89:11[a]

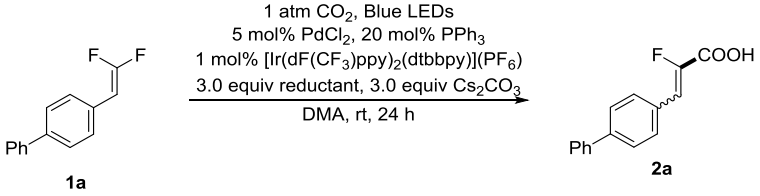
[a] 5 mol% of 10% Pd/C (10.6 mg) was used instead of $PdCl_2$.

Table S5. Screening of base.



Entry	Base	Yield/%	*Z*/*E*
1	**Cs_2CO_3**	**87**	**92:8**
2	K_2CO_3	66	97:3
3	$NaCO_3$	47	94:6
4	KOAc	52	96:4
5	NaOAc	39	92:8
6	CsOAc	53	87:13
7	KO^{t}Bu	31	94:6
8	KOH	53	92:8
9	K_3PO_4	69	96:4

Table S6. Screening of reductant.

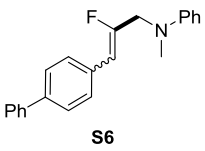


Entry	Reductant	Yield/%	*Z*/*E*

1	**^{i}Pr$_2$NEt**	**87**	**92:8**
2	NEt_3	74	92:8
3	*i*-Pr_2NH	36	78:22
4	HCOONa	6	67:33
5	Cy_2NMe	41	88:12
6[a]	Me_2NPh	11	73:27

[a] In the case of Me_2NPh was used as reductant, an inseparable mixture of *Z* and *E*-**S6** (25 mg, 0.08 mmol) was isolated in 40% yield as by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1).

***N*-(3-([1,1'-biphenyl]-4-yl)-2-fluoroallyl)-*N*-methylaniline S6**

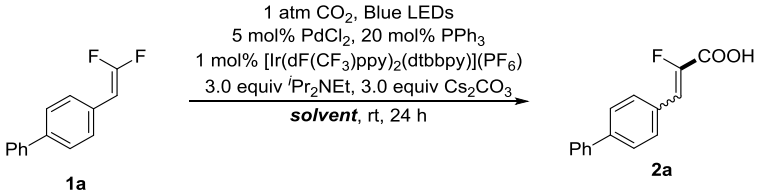


S6

***Z*-S6 ^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.62 – 7.54 (m, 5 H), 7.47 – 7.14 (m, 6H), 6.82 – 6.60 (m, 3H), 5.66 (d, *J* = 39.8 Hz, 1H), 4.12 (d, *J* = 7.7 Hz, 2H), 3.05 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -108.37 (dt, *J* = 39.7, 7.8 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 156.8 (d, *J* = 270.9 Hz), 149.0, 140.7, 139.8 (d, *J* = 2.0 Hz), 132.1(d, *J* = 2.5 Hz), 129.3, 129.0, 128.8, 127.3, 127.1, 127.0, 117.4, 112.7, 106.2 (d, *J* = 6.0 Hz), 54.2 (d, *J* = 33.9 Hz), 38.4. **HRMS (ESI, m/z):** calcd. for $C_{22}H_{17}BrF$ $[M+H]^+$: 379.0498, found: 379.0493.

***E*-S6 ^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.62 – 7.54 (m, 5 H), 7.47 – 7.14 (m, 6H), 6.82 – 6.60 (m, 3H), 6.47 (d, *J* = 20.8 Hz, 1H), 4.28 (d, *J* = 18.7 Hz, 2H), 2.98 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -104.64 (q, *J* = 19.0 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 158.7 (d, *J* = 258.6 Hz), 149.0, 140.4, 140.1, 132.2(d, *J* = 13.0 Hz), 129.3, 129.0, 128.8, 127.5, 127.2, 127.0, 117.3, 113.0, 111.2 (d, *J* = 26.4 Hz), 49.9 (d, *J* = 26.5 Hz), 38.7. **HRMS (ESI, m/z):** calcd. for $C_{22}H_{17}BrF$ $[M+H]^+$: 318.1658, found: 318.1653.

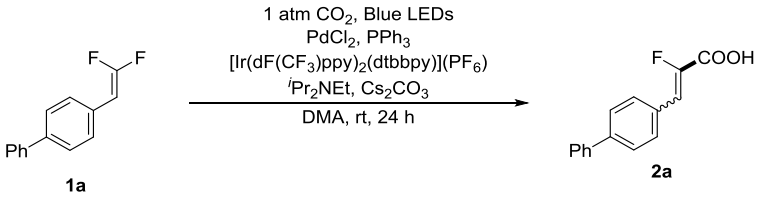
Table S7. Screening of solvent.



1a **2a**

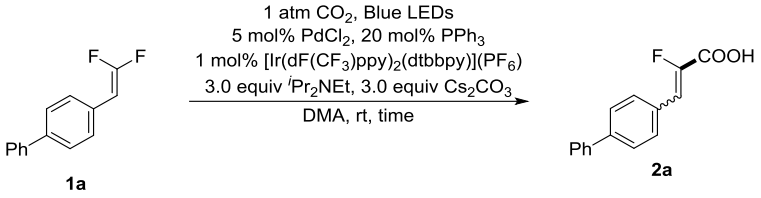
Entry	Solvent	Conversion/%[a]	*Z*/*E*
1	**DMA**	**87**	**92:8**
2	DMF	88	92:8
3	THF	6	83:17
4	CH_3CN	17	88:12
5	Dioxane	0	-
6	DMSO	35	86:14

Table S8. Screening of equivalents of catalysts, base and reductant.



Entry	PC/mol%	$PdCl_2$/mol%	PPh_3/mol%	Cs_2CO_3/equiv	$^iPr_2NEt$/equiv	Yield/%[a]	*Z*/*E*
1	1	5	20	2	3	41	93:7
2	**1**	**5**	**20**	**3**	**3**	**87**	**92:8**
3	1	5	20	4	3	73	93:7
4	1	5	20	5	3	65	92:8
5	1	5	20	3	2	67	90:10
6	1	5	20	3	4	67	90:10
7	1	5	20	3	5	43	91:9
8	0.1	5	20	3	3	73	92:8
9	0.2	5	20	3	3	76	91:9
10	0.5	5	20	3	3	69	91:9
11	1	2.5	10	3	3	42	93:7
12	1	7.5	30	3	3	68	91:9
13	1	5	10	3	3	45	93:7

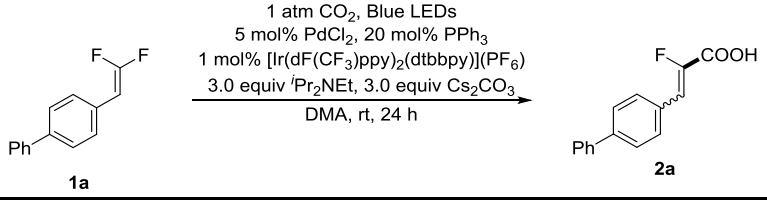
Table S9. Optimization of reaction time.



Entry	Time/h	Yield/%	*Z*/*E*
1	12	67	96:4
2	24	87	92:8
3	36	92	92:8
4	**48**	**100(97)[a]**	**92:8**

[a] The isolated yield of corresponding methyl ester is indicated in the parentheses.

Table S10. Control experiments.

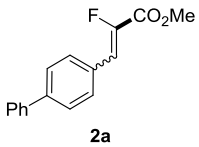


Entry	Variation from the standard conditions	Yield/%	*Z*/*E*
1	Without PC 1	0	-
2	Without $PdCl_2$/PPh_3	0	-
3	Without photo irradiation	0	-
4	Without Cs_2CO_3	41	63:37

4. General procedure for C−F bond carboxylation reaction and spectral data of products

To an oven-dried Schlenk tube equipped with a magnetic stir bar was added [Ir(dF(CF_3)ppy)$_2$(dtbbpy)](PF_6) (2.0 mg, 0.002 mmol, 1.0 mol%), $PdCl_2$ (1.8 mg, 0.01 mmol, 5.0 mol%), PPh_3 (10.4 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (196 mg, 0.6 mmol, 3.0 equiv) in glovebox. To these solids, compound **1** (0.2 mmol, 1.0 equiv), DMA (2.0 mL), $^iPr_2NEt$ (78 mg, 0.6 mmol, 3.0 equiv) was added under nitrogen atmophere. The Schlenk tube was evacuated and filled with CO_2 (3 cycles). Then the Schlenk tube was placed in front of the blue LEDs with 1 cm distance and stirred at ambient temperature for 48 to 96 h. The reaction mixture was quenched with 1N HCl (10 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with water (10 mL), brine (10 mL) and dried over Na_2SO_4. After solvent was removed under reduced pressure, the crude residue was dissolved in Et_2O (2.0 mL) and MeOH (0.5 mL) and cooled to 0 ℃. The Et_2O solution of $TMSCHN_2$ (0.2 mL, 2 mol/L, 0.4 mmol, 2.0 equiv) was added at 0 ℃. The mixture was stirred at 0 ℃ for 30 min. The volatile was removed under reduced pressure and the crude residue was purified by column chromatography or preparative TLC on silica gel (petroleum ether/ethyl acetate = 20:1 ~ 50 : 1) to afford the desired product.

methyl 3-([1,1'-biphenyl]-4-yl)-2-fluoroacrylate 2a



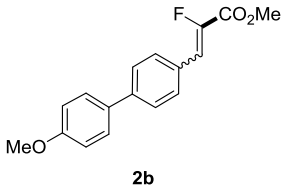
2a

Following general procedure, the reaction mixture was stirred for 48 h and **2a** was obtained as white solid (49.7 mg, 0.13 mmol, 97%, *Z*/*E* = 92:8).

Z-isomer was further isolated and the NMR data was collected. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.73 (d, *J* = 8.4 Hz, 2H), 7.66 – 7.63 (m, 2H), 7.61 (s, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 6.98 (d, *J* = 35.3 Hz, 1H), 3.91 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -125.51 (d, *J* = 35.4 Hz, 1F). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 161.9 (d, *J* = 34.4 Hz), 146.8 (d, *J* = 267.4 Hz), 142.4 (d, *J* = 2.9 Hz), 140.1, 130.8 (d, *J* = 8.2 Hz), 130.0 (d, *J* = 4.5 Hz), 128.9, 127.9, 127.4, 127.0, 117.4 (d, *J* = 4.7 Hz), 52.7. **HRMS (ESI, m/z):** calcd. for $C_{16}H_{14}FO_2$ $[M+H]^+$: 257.0978, found: 257.0969.

E-isomer was further isolated, **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.66–7.56 (m, 6H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 6.96 (d, *J* = 22.9 Hz, 1H), 3.84 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -117.32 (d, *J* = 22.9 Hz, 1F). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 161.0 (d, *J* = 35.5 Hz), 146.5 (d, *J* = 255.9 Hz), 141.7, 140.3, 130.3 (d, *J* = 2.9 Hz), 129.6 (d, *J* = 9.4 Hz), 128.8, 127.6, 127.0, 126.8, 121.8 (d, *J* = 26.5 Hz), 52.4. **HRMS (ESI, m/z):** calcd. for $C_{16}H_{14}FO_2$ $[M+H]^+$: 257.0978, found: 257.0986.

methyl 2-fluoro-3-(4'-methoxy-[1,1'-biphenyl]-4-yl)acrylate 2b

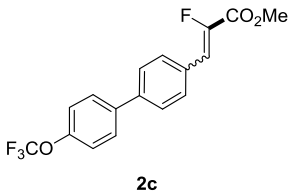


2b

Following general procedure, the reaction mixture was stirred for 48 h and **2b** was obtained as white solid (35.5 mg, 0.13 mmol, 62%, *Z*/*E* = 91:9).

Z-isomer was further isolated and the NMR data was collected. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.70 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.7 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 35.4 Hz, 1H), 3.91 (s, 3H), 3.86 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -125.94 (d, *J* = 35.4 Hz, 1F). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 161.9 (d, *J* = 34.2 Hz), 159.6, 146.6 (d, *J* = 267.0 Hz), 142.0 (d, *J* = 3.0 Hz), 132.5, 130.8 (d, *J* = 8.2 Hz), 129.3 (d, *J* =4.4 Hz), 128.1, 126.9, 117.6 (d, *J* = 4.6 Hz), 114.3, 55.3, 52.6. **HRMS (ESI, m/z):** calcd. for $C_{17}H_{16}FO_3$ $[M+H]^+$: 287.1083, found: 287.1076.

methyl 2-fluoro-3-(4'-(trifluoromethoxy)-[1,1'-biphenyl]-4-yl)acrylate 2c

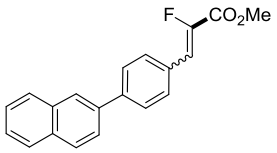


2c

Following general procedure, the reaction mixture was stirred for 48 h and **2c** was obtained as white solid (61.2 mg, 0.18 mmol, 90%, *Z*/*E* = 88:12).

Z-isomer was further isolated and the NMR data was collected. **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 7.73 (d, *J* = 8.4 Hz, 2H), 7.66–7.57 (m, 4H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 35.1 Hz, 1H), 3.92 (s, 3H). **^{19}F NMR (376 MHz, CDCl$_3$):** δ = -57.79 (s, 3F), -125.01 (d, *J* = 35.1 Hz, 1F). **^{13}C NMR (100 MHz, CDCl$_3$):** δ = 161.8 (d, *J* = 34.3 Hz), 149.0, 147.0 (d, *J* = 268.3 Hz), 140.9 (d, *J* =2.4 Hz), 138.8, 130.9 (d, *J* = 8.0 Hz), 130.4 (d, *J* = 4.4 Hz), 128.8, 127.4, 121.4, 120.4 (q, *J* = 256.7 Hz), 117.2 (d, *J* = 4.4 Hz), 52.7. **HRMS (ESI, m/z):** calcd. for $C_{17}H_{13}F_4O_3$ $[M+H]^+$: 341.0801, found: 341.0794.

methyl 2-fluoro-3-(4-(naphthalen-1-yl)phenyl)acrylate 2d

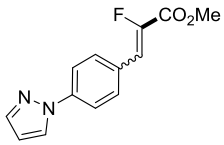


2d

Following general procedure, the reaction mixture was stirred for 48 h and **2d** was obtained as white solid (52.0 mg, 0.17 mmol, 85%, *Z*/*E* = 99:1).

Z-isomer was further isolated and the NMR data was collected. **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 8.08 (s, 1H), 7.98 – 7.85 (m, 3H), 7.82 – 7.73 (m, 5H), 7.56 – 7.47 (m, 2H), 7.00 (d, *J* = 35.3 Hz, 1H), 3.92 (s, 3H). **^{19}F NMR (376 MHz, CDCl$_3$):** δ = -125.33 (d, *J* = 35.3 Hz, 1F). **^{13}C NMR (100 MHz, CDCl$_3$):** δ = 161.9 (d, *J* = 34.4 Hz), 146.8 (d, *J* = 267.6 Hz), 142.3 (d, *J* = 2.9 Hz), 137.4, 133.6, 132.8, 130.9 (d, *J* = 8.2 Hz), 130.0 (d, *J* = 4.6 Hz), 128.6, 128.3, 127.7, 127.6, 126.4, 126.3, 126.0, 125.1, 117.4 (d, *J* = 4.6 Hz), 52.7. **HRMS (ESI, m/z):** calcd. for $C_{20}H_{16}FO_2$ $[M+H]^+$: 307.1134, found: 307.1129.

methyl 3-(4-(1*H*-pyrazol-1-yl)phenyl)-2-fluoroacrylate 2e



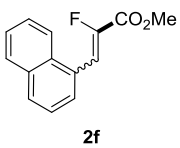
2e

Following general procedure, the reaction mixture was stirred for 48 h and an inseparable mixture of *Z*-**2e** and *E*-**2e** was obtained as white solid was obtained as white solid (17.2 mg, 0.07 mmol, 35%, *Z*/*E* = 56:44).

Z-**2e**, **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 7.97 (d, *J* = 2.5 Hz, 1H), 7.80 – 7.73 (m, 3H), 7.70 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 35.0 Hz, 1H), 6.51 – 6.47 (m, 1H), 3.82 (s, 3H). **^{19}F NMR (376 MHz, CDCl$_3$):** δ = -125.44 (d, *J* = 34.8 Hz). **^{13}C NMR (100 MHz, CDCl$_3$):** δ = 161.7 (d, *J* = 34.4 Hz), 146.8 (d, *J* = 265.8 Hz), 141.4, 140.2, 131.1 (d, *J* = 2.9 Hz), 129.0 (d, *J* = 4.4 Hz), 126.6, 118.4, 116.8, 108.2, 52.7.

E-**2e**, **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 7.95 (d, *J* = 2.5 Hz, 1H), 7.80 – 7.73 (m, 3H), 7.61 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 22.6 Hz, 1H), 6.51 – 6.47 (m, 1H), 3.90 (s, 3H). **^{19}F NMR (376 MHz, CDCl$_3$):** δ = -116.79 (d, *J* = 22.8 Hz). **^{13}C NMR (100 MHz, CDCl$_3$):** δ = 160.9 (d, *J* = 35.7 Hz), 146.6 (d, *J* = 254.7 Hz), 141.6, 140.6 (d, *J* = 3.5 Hz), 131.5 (d, *J* = 8.5 Hz), 128.7 (d, *J* = 9.7 Hz), 126.6, 121.2 (d, *J* = 26.8 Hz), 118.9, 108.0, 52.4. **HRMS (ESI, m/z):** calcd. for $C_{13}H_{12}FN_2O_2$ $[M+H]^+$: 247.0883, found: 247.0874.

methyl 3-([1,1'-biphenyl]-4-yl)-2-fluoroacrylate 2f



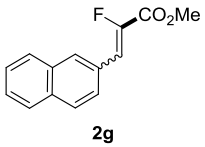
2f

Following general procedure, the reaction mixture was stirred for 48 h and an inseparable mixture of *Z*-**2f** and *E*-**2f** was obtained as white solid (44.2 mg, 0.19 mmol, 96%, *Z*/*E* = 63:37).

Z-isomer, **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 8.10 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 7.3 Hz, 1H), 7.93 – 7.83 (m, 2H), 7.72 (d, *J* = 33.2 Hz, 1H), 7.63 – 7.44 (m, 3H), 3.97 (s, 3H). **^{19}F NMR (376 MHz, CDCl$_3$):** δ = -126.21 (d, *J* = 33.2 Hz). **^{13}C NMR (100 MHz, CDCl$_3$):** δ = 161.8 (d, *J* = 34.8 Hz), 147.5 (d, *J* = 268.2 Hz), 133.5, 131.4, 130.1 (d, *J* = 1.8 Hz), 129.0, 128.8, 128.6, 126.9, 126.1, 125.4, 123.4, 114.1 (d, *J* = 5.3 Hz), 52.7.

E-isomer, **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 7.93 – 7.83 (m, 3H), 7.63 – 7.44 (m, 4H), 7.39 (d, *J* = 19.7 Hz, 1H), 3.64 (s, 3H). **^{19}F NMR (376 MHz, CDCl$_3$):** δ = -116.39 (d, *J* = 19.7 Hz). **^{13}C NMR (100 MHz, CDCl$_3$):** δ = 160.7 (d, *J* = 36.3 Hz), 147.9 (d, *J* = 255.5 Hz), 133.2, 131.3 (d, *J* = 2.6 Hz), 128.7, 128.4, 128.3, 126.9 (d, *J* = 5.7 Hz), 126.5, 126.0, 125.0, 124.3, 119.4 (d, *J* = 23.9 Hz), 52.2. **HRMS (ESI, m/z):** calcd. for $C_{14}H_{12}FO_2$ $[M+H]^+$: 231.0821, found: 231.0821.

methyl 2-fluoro-3-(naphthalen-2-yl)acrylate 2g

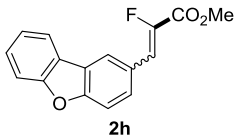


2g

Following general procedure, the reaction mixture was stirred for 48 h and **2g** was obtained as white solid (37.7 mg, 0.16 mmol, 82%, *Z*/*E* = 92:8).

Z-isomer was further isolated and the NMR data was collected. **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 8.10 (s, 1H), 7.91 – 7.81 (m, 3H), 7.78 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.57 – 7.46 (m, 2H), 7.10 (d, *J* = 35.3 Hz, 1H), 3.93 (s, 3H). **^{19}F NMR (376 MHz, CDCl$_3$):** δ = -125.6 (d, *J* = 35.3 Hz, 1F). **^{13}C NMR (100 MHz, CDCl$_3$):** δ = 161.9 (d, *J* = 34.6 Hz), 146.9 (d, *J* = 267.9 Hz), 133.6 (d, *J* = 2.2 Hz), 133.1, 130.8 (d, *J* = 8.0 Hz), 128.6 (d, *J* = 4.5 Hz), 128.6 (d, *J* = 1.0 Hz), 128.5, 127.6, 127.3, 126.7 (d, *J* = 8.3 Hz), 126.6, 117.9 (d, *J* = 4.6 Hz), 52.7. **HRMS (ESI, m/z):** calcd. for $C_{14}H_{12}FO_2$ $[M+H]^+$: 231.0821, found: 231.0813.

methyl 3-(dibenzo[*b*,*d*]furan-3-yl)-2-fluoroacrylate 2h



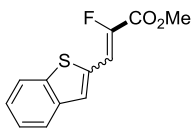
2h

Following general procedure, the reaction mixture was stirred for 96 h and **2h** was obtained as white solid (26.5 mg, 0.10 mmol, 49%, *Z*/*E* = 54:46).

Z-isomer was further isolated and the NMR data was collected. **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 8.28 (d, *J* = 1.8 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.49 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.38 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.09 (d, *J* = 35.1 Hz, 1H), 3.93 (s, 3H). **^{19}F NMR (376 MHz, CDCl$_3$):** δ = -127.48 (d, *J* = 35.3 Hz). **^{13}C NMR (100 MHz, CDCl$_3$):** δ = 162.0 (d, *J* = 34.2 Hz), 156.7, 156.6, 146.2 (d, *J* = 265.3 Hz), 129.7 (d, *J* = 7.6 Hz), 127.8, 125.9 (d, *J* = 4.4 Hz), 124.9, 123.6, 123.1, 122.8, 122.7, 120.9, 117.9 (d, *J* = 4.5 Hz), 112.0 (d, *J* = 25.3 Hz), 52.7. **HRMS (ESI, m/z):** calcd. for $C_{16}H_{11}FO_3$ $[M+H]^+$: 271.0770, found: 271.0772.

E-isomer was further isolated and the NMR data was collected. **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 8.18 (s, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.65 – 7.53 (m, 3H), 7.48 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.36 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.08 (d, *J* = 23.0 Hz, 1H), 3.83 (s, 3H). **^{19}F NMR (376 MHz, CDCl$_3$):** δ = -118.12 (d, *J* = 23.0 Hz). **^{13}C NMR (100 MHz, CDCl$_3$):** δ = 161.1 (d, *J* = 35.7 Hz), 156.6, 156.3, 146.3 (d, *J* = 254.5 Hz), 129.3 (d, *J* = 2.8 Hz), 127.5, 125.3 (d, *J* = 9.4 Hz), 124.3, 123.8, 123.0, 122.5, 122.3, 122.2, 120.8, 111.6 (d, *J* = 41.4 Hz), 52.3. **HRMS (ESI, m/z):** calcd. for $C_{16}H_{11}FO_3$ $[M+H]^+$: 271.0770, found: 271.0774.

methyl 3-(benzo[*b*]thiophen-2-yl)-2-fluoroacrylate 2i



2i

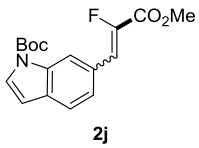
Following general procedure, the reaction mixture was stirred for 48 h and **2i** was obtained as white solid (30.7 mg, 0.13 mmol, 65%, *Z*/*E* = 75:25).

Z-isomer was further isolated and the NMR data was collected. **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 7.89 – 7.74 (m, 2H), 7.56 (s, 1H), 7.42 – 7.35 (m, 2H), 7.28 (d, *J* = 33.6 Hz, 1H), 3.92 (s, 3H). **^{19}F NMR (376 MHz, CDCl$_3$):** δ = -122.67 (d, *J* = 33.5 Hz). **^{13}C NMR (100 MHz, CDCl$_3$):** δ = 161.3 (d, *J* = 33.2 Hz), 146.3 (d, *J* = 268.6 Hz), 141.8 (d, *J* = 7.8 Hz), 138.7, 133.4 (d, *J* = 6.2 Hz), 128.3 (d, *J* = 5.4 Hz), 125.9, 124.8, 124.3 (d, *J* = 2.0 Hz), 122.3, 112.7 (d, *J* = 8.2 Hz), 52.8. **HRMS (ESI, m/z):** calcd. for $C_{12}H_{10}FO_2S$ $[M+H]^+$: 237.0386, found: 237.0385.

E-isomer was further isolated and the NMR data was collected. **^{1}H NMR (400 MHz, CDCl$_3$):** 7.85– 7.75 (m, 2H), 7.62-7.61 (dd, *J* = 1.8, 0.9 Hz 1H), 7.40 – 7.34 (m, 2H), 7.19-7.13 (dd, *J* = 23.3, 0.9 Hz, 1H), 3.96 (s, 3H). **^{19}F NMR (376 MHz,**

$CDCl_3$): δ = -120.26 (d, *J* = 23.3 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 161.2 (d, *J* = 34.5 Hz), 145.3 (d, *J* = 256.5 Hz), 142.4 (d, *J* = 2.8 Hz), 138.5, 133.2 (d, *J* = 9.0 Hz), 131.3 (d, *J* = 6.9 Hz), 126.0 (d, *J* = 1.4 Hz), 124.7, 124.1 (d, *J* = 0.9 Hz), 122.2, 117.8 (d, *J* = 32.8 Hz), 52.6. **HRMS (ESI, m/z):** calcd. for $C_{18}H_{17}FO_2$ $[M+H]^+$: 237.0386, found: 237.0387.

methyl 3-([1,1'-biphenyl]-4-yl)-2-fluoroacrylate 2j



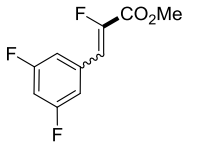
2j

Following general procedure, the reaction mixture was stirred for 48 h and **2j** was obtained as white solid (26.2 mg, 0.08 mmol, 41%, *Z*/*E* = 58:42).

Z-isomer was further isolated and the NMR data was collected. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.52 (s, 1H), 7.70 (d, *J* = 3.5 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.07 (d, *J* = 35.4 Hz, 1H), 6.58 (d, *J* = 3.6 Hz, 1H), 3.90 (s, 3H), 1.70 (s, 9H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -126.98 (d, *J* = 35.5 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 162.1 (d, *J* = 34.4 Hz), 149.6 , 146.1 (d, *J* = 265.5 Hz), 135.1 , 131.9, 128.0, 127.0 (d, *J* = 4.7 Hz), 125.1 (d, *J* = 7.5 Hz), 121.1, 119.0 (d, *J* = 4.2 Hz), 117.4 (d, *J* = 10.0 Hz), 107.2, 84.4, 52.6, 28.2. **HRMS (ESI, m/z):** calcd. for $C_{17}H_{18}FO_2Na$ $[M+H]^+$: 320.1298, found: 320.1287.

E-isomer was further isolated and the NMR data was collected. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.36 (s, 1H), 7.63 (d, *J* = 3.7 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.37 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.06 (d, *J* = 23.2 Hz, 1H), 6.56 (d, *J* = 3.7 Hz, 1H), 3.82 (s, 3H), 1.67 (s, 9H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -118.48 (d, *J* = 23.2 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 161.1 (d, *J* = 36.2 Hz), 149.6, 146.2 (d, *J* = 251.2 Hz), 134.9, 131.1, 127.3, 126.6 (d, *J* = 9.2 Hz), 124.6 (d, *J* = 2.6 Hz), 123.1 (d, *J* = 26.4 Hz), 120.4, 116.8 (d, *J* = 3.1 Hz), 107.2, 84.0, 52.3, 28.2. **HRMS (ESI, m/z):** calcd. for $C_{17}H_{18}FO_2Na$ $[M+Na]^+$: 342.1118, found: 342.1108.

methyl 3-([1,1'-biphenyl]-4-yl)-2-fluoroacrylate 2k

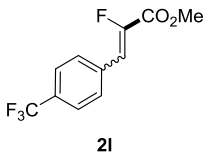


2k

Following general procedure, the reaction mixture was stirred for 48 h and an inseparable mixture of *Z*-**2k and** *E*-**2k** was obtained as white solid (15.1 mg, 0.07 mmol, 35%, *Z*/*E* = 82:18).

Z-isomer, **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.19 – 7.14 (m, 2H), 6.85 (d, *J* = 33.3 Hz, 1H), 6.85 (tt, *J* = 8.8, 2.4 Hz, 1H), 3.91 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -109.01 (t, *J* = 7.9 Hz), -121.51 (d, *J* = 33.3 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 163.0 (dd, *J* = 248.0, 12.9 Hz), 161.2 (d, *J* = 34.4 Hz), 148.0 (d, *J* = 272.4 Hz), 133.7 (td, *J* = 10.3, 4.0 Hz), 115.5 (q, *J* = 3.4 Hz), 112.9 (dd, *J* = 26.6, 8.4 Hz), 105.2 (td, *J* = 25.4, 2.3 Hz), 52.9. **HRMS (ESI, m/z):** calcd. for $C_{10}H_8F_3O_2$ $[M+H]^+$: 217.0476, found: 217.0470.

methyl 2-fluoro-3-(4-(trifluoromethyl)phenyl)acrylate 2l

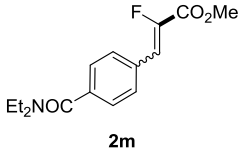


2l

Following general procedure, the reaction mixture was stirred for 48 h and **2l** was obtained as white solid (36.2 mg, 0.15 mmol, 73%, *Z*/*E* = 84:16).

Z-isomer was further isolated and the NMR data was collected. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.75 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 6.96 (d, *J* = 34.3 Hz, 1H), 3.92 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -62.95, -122.38 (d, *J* = 34.2 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 161.4 (d, *J* = 34.5 Hz), 148.0 (d, *J* = 271.6 Hz), 134.4, 131.2 (dd, *J* = 32.8, 2.8 Hz), 130.4 (d, *J* = 8.4 Hz), 125.7 (q, *J* = 3.1 Hz), 123.7 (q, *J* = 272.4 Hz), 116.1 (d, *J* = 4.1 Hz), 52.9. **HRMS (ESI, m/z):** calcd. for $C_{11}H_9F_4O_2$ $[M+H]^+$: 249.0539, found: 249.0538.

methyl 3-(4-(diethylcarbamoyl)phenyl)-2-fluoroacrylate 2m



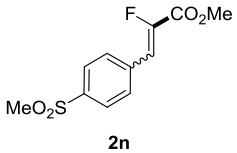
2m

Following general procedure, the reaction mixture was stirred for 48 h and an inseparable mixture of *Z*-**2m** and *E*-**2m** was obtained as white solid (44.6 mg, 0.16 mmol, 80%, *Z*/*E* = 73:27).

Z-isomer, **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 7.66 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 6.92 (d, *J* = 34.9 Hz, 1H), 3.89 (s, 3H), 3.39 (d, *J* = 114.0 Hz, 4H), 1.17 (d, *J* = 52.3 Hz, 6H). **^{19}F NMR (376 MHz, CDCl$_3$):** δ = -124.23 (d, *J* = 34.9 Hz). **^{13}C NMR (100 MHz, CDCl$_3$):** δ = 170.4, 161.6 (d, *J* = 34.4 Hz), 147.2 (d, *J* = 269.1 Hz), 138.3, 131.7 (d, *J* = 4.4 Hz), 130.3 (d, *J* = 8.2 Hz), 126.8, 116.89 (d, *J* = 4.5 Hz), 52.7, 43.2, 39.3.

E-isomer, **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 7.51 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 6.91 (d, *J* = 22.4 Hz, 1H), 3.79 (s, 3H), 3.39 (d, *J* = 114.0 Hz, 4H), 1.17 (d, *J* = 52.3 Hz, 6H). **^{19}F NMR (376 MHz, CDCl$_3$):** δ = -116.04 (d, *J* = 22.4 Hz). **^{13}C NMR (100 MHz, CDCl$_3$):** δ = 170.6, 160.8 (d, *J* = 35.9 Hz), 142.8 (d, *J* = 255.4 Hz), 137.5, 131.6 (d, *J* = 9.5 Hz), 129.8 (d, *J* = 2.9 Hz), 126.1, 121.1 (d, *J* = 26.5 Hz), 52.3, 14.2, 12.8. **HRMS (ESI, m/z):** calcd. for $C_{15}H_{18}FNO_3$ $[M+H]^+$: 280.1349, found: 280.1343.

methyl 2-fluoro-3-(4-(methylsulfonyl)phenyl)acrylate 2n

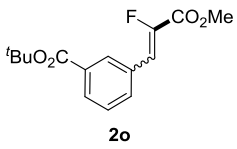


2n

Following general procedure, the reaction mixture was stirred for 48 h and an inseparable mixture of *Z*-**2n** and *E*-**2n** was obtained as white solid (27.9 mg, 0.11 mmol, 54%, *Z*/*E* = 90:10).

Z-isomer was further isolated and the NMR data was collected. **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 7.97 (d, *J* = 8.5 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 33.9 Hz, 1H), 3.92 (s, 3H), 3.07 (s, 3H). **^{19}F NMR (376 MHz, CDCl$_3$):** δ = -120.53 (d, *J* = 33.9 Hz). **^{13}C NMR (100 MHz, CDCl$_3$):** δ = 161.1 (d, *J* = 34.5 Hz), 148.5 (d, *J* = 273.6 Hz), 140.9 (d, *J* = 3.0 Hz), 136.2 (d, *J* = 4.2 Hz), 130.8 (d, *J* = 8.3 Hz), 127.8, 115.5 (d, *J* = 4.3 Hz), 53.0, 44.4. **HRMS (ESI, m/z):** calcd. for $C_{11}H_{12}FO_4S$ $[M+H]^+$: 259.0440, found: 259.0433.

***tert*-butyl 3-(2-fluoro-3-methoxy-3-oxoprop-1-en-1-yl)benzoate 2o**

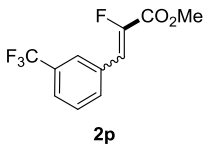


2o

Following general procedure, the reaction mixture was stirred for 48 h and an inseparable mixture of *Z*-**2o** and *E*-**2o** was obtained as white solid (30.8 mg, 0.11 mmol, 55%, *Z*/*E* = 73:27). *Z*-isomer, **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 8.20 (s, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 6.96 (d, *J* = 34.8 Hz, 1H), 3.9 (s, 3H), 1.60 (s, 9H). **^{19}F NMR (376 MHz, CDCl$_3$):** δ = -124.28 (d, *J* = 34.8 Hz). **^{13}C NMR (100 MHz, CDCl$_3$):** δ = 165.0, 161.6 (d, *J* = 34.3 Hz), 147.2 (d, *J* = 268.9 Hz), 133.7 (d, *J* = 9.0 Hz), 132.6, 131.2 (d, *J* = 7.3 Hz), 130.6 (d, *J* = 7.1 Hz), 130.5, 128.8, 116.9 (d, *J* = 4.4 Hz), 81.4, 52.8, 28.1. **HRMS (ESI, m/z):** calcd. for $C_{15}H_{18}FO_4$ $[M+H]^+$: 281.1189, found: 281.1180.

E-isomer, **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 8.04 (s, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 21.8 Hz, 1H),3.78 (s, 3H), 1.59 (s, 9H). **^{19}F NMR (376 MHz, CDCl$_3$):** δ = -116.52 (d, *J* = 21.8 Hz). **^{13}C NMR (100 MHz, CDCl$_3$):** δ = 165.2, 160.7 (d, *J* = 36.1 Hz), 147.1 (d, *J* = 214.0 Hz), 133.4 (d, *J* = 2.3 Hz), 131.9, 131.1 (d, *J* = 4.1 Hz), 130.9 (d, *J* = 9.7 Hz), 129.6, 128.0, 121.0 (d, *J* = 26.1 Hz), 81.3, 52.4, 28.1. **HRMS (ESI, m/z):** calcd. for $C_{15}H_{18}FO_4$ $[M+H]^+$: 281.1189, found: 281.1180.

methyl 2-fluoro-3-(3-(trifluoromethyl)phenyl)acrylate 2p

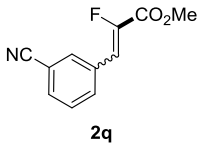


2p

Following general procedure, the reaction mixture was stirred for 48 h and **2p** was obtained as white solid (20.8 mg, 0.08 mmol, 42%, *Z*/*E* = 90:10).

Z-isomer was further isolated and the NMR data was collected. **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 7.87 (s, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.9 Hz, 1H), 6.96 (d, *J* = 34.2 Hz, 1H), 3.92 (s, 3H). **^{19}F NMR (376 MHz, CDCl$_3$):** δ = -62.93, -123.05 (d, *J* = 34.3 Hz). **^{13}C NMR (100 MHz, CDCl$_3$):** δ = 161.4 (d, *J* = 34.5 Hz), 147.7 (d, *J* = 270.4 Hz), 133.2 (d, *J* = 8.3 Hz), 131.7 (d, *J* = 4.0 Hz), 131.3 (d, *J* = 32.6 Hz), 129.4, 126.81 (m), 126.2, 123.7 (q, *J* = 272.5 Hz), 116.1, 52.9. **HRMS (ESI, m/z):** calcd. for $C_{11}H_{10}FO_2$ $[M+H]^+$: 249.0539, found: 249.0541.

methyl 3-(3-cyanophenyl)-2-fluoroacrylate 2q

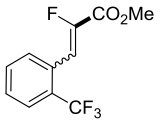


2q

Following general procedure, the reaction mixture was stirred for 48 h and the mixture of *Z*-**2q** and *E*-**2q** was obtained as white solid (31.6 mg, 0.15 mmol, 77%, *Z*/*E* = 86:14).

Z-isomer was further isolated and the NMR data was collected. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.91 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 33.8 Hz, 1H), 3.91 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -121.88 (d, *J* = 33.6 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 161.1 (d, *J* = 34.3 Hz), 148.1 (d, *J* = 271.9 Hz), 134.1 (d, *J* = 8.1 Hz), 133.3 (d, *J* = 8.5 Hz), 132.7 (d, *J* = 2.5 Hz), 132.2 (d, *J* = 4.2 Hz), 129.7, 118.1, 115.2 (d, *J* = 4.3 Hz), 113.3, 52.9. **HRMS (ESI, m/z):** calcd. for $C_{11}H_9FNO_2$ $[M+H]^+$: 206.0617, found: 206.0612.

methyl 2-fluoro-3-(2-(trifluoromethyl)phenyl)acrylate 2r

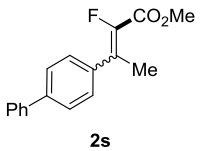


2r

Following general procedure, the reaction mixture was stirred for 48 h and the mixture of *Z*-**2r** and *E*-**2r** was obtained as white solid (19.8 mg, 0.08 mmol, 40%, *Z*/*E* = 93:7).

Z-**2r** was further isolated and the NMR data was collected. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.93 (d, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.60 (dd, *J* = 7.9, 7.6 Hz, 1H), 7.47 (dd, *J* = 7.9, 7.6 Hz, 1H), 7.27 (dq, *J* = 32.2, 1.8 Hz, 1H), 3.92 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -59.55, -124.11 (d, *J* = 32.0 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 161.2 (d, *J* = 35.3 Hz), 147.7 (d, *J* = 269.8 Hz), 132.0, 131.5, 131.4, 129.1 (d, *J* = 1.7 Hz), 128.8 (m), 126.1 (q, *J* = 5.6 Hz), 123.8 (q, *J* = 273.9 Hz), 112.8 (d, *J* = 2.1 Hz), 52.9. **HRMS (ESI, m/z):** calcd. for $C_{11}H_9F_4O_2$ $[M+H]^+$: 249.0539, found: 249.0532.

methyl 3-([1,1'-biphenyl]-4-yl)-2-fluorobut-2-enoate 2s



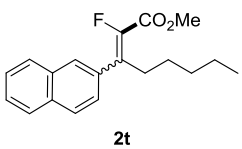
2s

Following general procedure, the reaction mixture was stirred for 96 h and the mixture of *Z*-**2s** and *E*-**2s** was obtained as white solid (43.7 mg, 0.16 mmol, 81%, *Z*/*E* = 75:25).[19]

Z-isomer was further isolated and the NMR data was collected. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.67 – 7.58 (m, 4H), 7.53 – 7.41 (m, 4H), 7.40 – 7.33 (m, 1H), 3.89 (s, 3H), 2.50 (d, *J* = 3.6 Hz, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -126.09 (q, *J* = 3.6 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 162.2 (d, *J* = 34.2 Hz), 143.4 (d, *J* = 254.9 Hz), 141.3, 140.4, 136.4, 130.6 (d, *J* = 10.7 Hz), 128.8, 128.5, 127.6, 127.1, 126.9, 52.2, 18.1. **HRMS (ESI, m/z):** calcd. for $C_{17}H_{16}FO_2$ $[M+H]^+$: 271.1134, found: 271.1126.

E-isomer was further isolated and the NMR data was collected. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.63 – 7.59 (m, 4H), 7.46 – 7.43 (m, 2H), 7.37 – 7.34 (m, 1H), 7.28 – 7.26 (m, 2H), 3.66 (s, 3H), 2.20 (d, *J* = 4.6 Hz, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -123.82 (q, *J* = 4.5 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 160.0 (d, *J* = 35.5 Hz), 144.0 (d, *J* = 253.6 Hz), 140.7, 140.5, 137.1 (d, *J* = 5.5 Hz), 131.6 (d, *J* = 17.3 Hz), 128.8, 127.9 (d, *J* = 3.2 Hz), 127.4, 127.1, 126.6, 52.0, 19.3 (d, *J* = 6.8 Hz). **HRMS (ESI, m/z):** calcd. for $C_{17}H_{16}FO_2$ $[M+H]^+$: 271.1134, found: 271.1144.

methyl 2-fluoro-3-(naphthalen-2-yl)oct-2-enoate 2t



2t

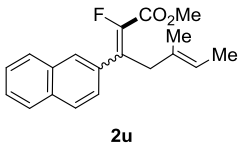
Following general procedure, the reaction mixture was stirred for 96 h and the mixture of *Z*-**2t** and *E*-**2t** was obtained as colorless oil (45.0 mg, 0.15 mmol, 75%, *Z*/*E* = 63:37).[20]

Z-**2t** was further isolated and the NMR data was collected. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.87 – 7.84 (m, 3H), 7.61 (s, 1H), 7.53 – 7.49 (m, 2H), 7.45 – 7.42 (m, 1H), 3.90 (s, 3H), 3.02 – 2.98 (m, 2H), 1.45 – 1.21 (m, 6H), 0.83 (t, *J* = 7.0 Hz, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -125.92. **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 162.1 (d, *J* = 34.7 Hz), 143.3 (d, *J* = 256.6 Hz), 136.5 (d, *J* = 9.5 Hz), 133.7 (d, *J* = 1.4 Hz), 132.9, 128.2, 127.8,

127.6, 127.5, 127.4, 126.5, 126.3, 125.9 (d, *J* = 2.9 Hz), 52.2, 31.6, 31.4, 28.1 (d, *J* = 3.1 Hz), 22.4, 14.0. **HRMS (ESI, m/z):** calcd. for $C_{19}H_{21}FO_2$ $[M+Na]^+$: 323.1423, found: 323.1417.

E-**2t** was further isolated and the NMR data was collected. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.89 – 7.88 (m, 3H), 7.62 (s, 1H), 7.53 – 7.44 (m, 2H), 7.31 – 7.24 (m, 1H), 3.58 (s, 3H), 2.68 – 2.58 (m, 2H), 1.45 – 1.18 (m, 6H), 0.84 (t, *J* = 7.0 Hz, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -125.66 (t, *J* = 3.8 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 161.1 (d, *J* = 35.8 Hz), 144.1 (d, *J* = 254.0 Hz), 136.3 (d, *J* = 16.3 Hz), 134.5, 134.5, 133.0, 132.7, 128.0, 127.7, 127.5, 126.4 (d, *J* = 2.8 Hz), 126.3 (d, *J* = 2.5 Hz), 126.2 (d, *J* = 3.0 Hz), 52.0, 32.8 (d, *J* = 4.9 Hz), 31.4, 26.5, 22.3, 14.0. **HRMS (ESI, m/z):** calcd. for $C_{19}H_{21}FO_2$ $[M+Na]^+$: 323.1423, found: 323.1419.

methyl (5*E*)-2-fluoro-5-methyl-3-(naphthalen-2-yl)hepta-2,5-dienoate 2u



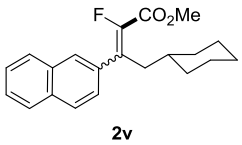
2u

Following general procedure, the reaction mixture was stirred for 96 h and the mixture of *Z*-**2u** and *E*-**2u** was obtained as colorless oil (42.3 mg, 0.14 mmol, 72%, *Z*/*E* = 67:33).[20]

Z-**2u** was further isolated and the NMR data was collected. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.88 – 7.73 (m, 4H), 7.54 – 7.40 (m, 3H), 5.24 – 5.15 (m, 1H), 3.90 (s, 3H), 3.73 (m, 2H), 1.61 – 1.57 (m, 3H), 1.54 – 1.44 (m, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -123.73. **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 162.0 (d, *J* = 34.6 Hz), 144.3 (d, *J* = 256.8 Hz), 133.7 (d, *J* = 1.7 Hz), 133.4, 132.9 (d, *J* = 4.5 Hz), 131.8, 131.8, 128.3, 127.7 (d, *J* = 3.7 Hz), 127.6, 127.6, 126.5, 126.2, 126.1 (d, *J* = 3.7 Hz), 121.0, 52.2, 40.4, 16.0, 13.5. **HRMS (ESI, m/z):** calcd. for $C_{19}H_{20}FO_2$ $[M+H]^+$: 299.1447, found: 299.1444.

E-**2u** was further isolated and the NMR data was collected. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.87 – 7.75 (m, 3H), 7.57 (s, 1H), 7.50 – 7.44 (m, 2H), 7.22 (dd, *J* = 8.4, 1.7 Hz, 1H), 5.16 – 5.06 (m, 1H), 3.58 (s, 3H), 3.29 (d, *J* = 3.3 Hz, 2H), 1.60 (s, 3H), 1.48 (dq, *J* = 6.7, 1.2 Hz, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -124.09 (t, *J* = 3.9 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 161.1 (d, *J* = 36.3 Hz), 144.6 (d, *J* = 254.9 Hz), 134.5, 134.4, 133.8 (d, *J* = 15.9 Hz), 132.9, 132.7, 130.1 (d, *J* = 2.2 Hz), 128.0, 127.7, 127.2, 126.6 (d, *J* = 3.3 Hz), 126.4 (d, *J* = 2.9 Hz), 126.0 (d, *J* = 3.8 Hz), 122.6, 52.0, 42.7 (d, *J* = 4.5 Hz), 15.8, 13.5. **HRMS (ESI, m/z):** calcd. for $C_{19}H_{20}FO_2$ $[M+H]^+$: 299.1447, found: 299.1445.

methyl 4-cyclohexyl-2-fluoro-3-(naphthalen-2-yl)but-2-enoate 2v



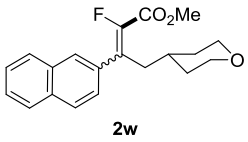
2v

Following general procedure, the reaction mixture was stirred for 96 h and the mixture of *Z*-**2v** and *E*-**2v** was obtained as white solid (51.5 mg, 0.16 mmol, 79%, *Z*/*E* = 60:40).[20]

Z-**2v** was further isolated and NMR data was collected. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.89 – 7.80 (m, 3H), 7.62 (s, 1H), 7.54 – 7.46 (m, 2H), 7.27 (dd, *J* = 8.4, 1.8 Hz, 1H), 3.58 (s, 3H), 2.54 (dd, *J* = 7.2, 4.0 Hz, 2H), 1.76 – 1.54 (m, 5H), 1.38 – 0.92 (m, 6H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -124.5. **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 162.2 (d, *J* = 34.8 Hz), 143.8 (d, *J* = 255.2 Hz), 135.1 (d, *J* = 9.4 Hz), 133.9, 133.8, 133.0 (d, *J* = 2.1 Hz), 128.3, 127.8, 127.6, 127.4 (d, *J* = 3.2 Hz), 126.5, 126.3, 126.0 (d, *J* = 3.4 Hz), 52.1, 38.2, 36.6 (d, *J* = 2.8 Hz), 32.9, 26.2, 26.1. **HRMS (ESI, m/z):** calcd. for $C_{21}H_{23}FO_2$ $[M+H]^+$: 327.1760, found: 327.1765.

E-**2v** was further isolated and NMR data was collected. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.90 – 7.82 (m, 3H), 7.80 (s, 1H), 7.55 – 7.48 (m, 2H), 7.43 (dt, *J* = 8.5, 1.8 Hz, 1H), 3.89 (s, 3H), 2.99 (dd, *J* = 7.2, 1.9 Hz, 2H), 1.68 – 1.53 (m, 5H), 1.29 – 0.97 (m, 6H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = - 124.26 (t, *J* = 4.0 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 161.1 (d, *J* = 36.3 Hz), 144.7 (d, *J* = 253.9 Hz), 135.0, 134.8, 134.7 (d, *J* = 5.5 Hz), 133.0, 132.7, 128.0, 127.7, 127.5, 126.5 (d, *J* = 3.2 Hz), 126.4 (d, *J* = 2.7 Hz), 126.2, 52.0, 40.5 (d, *J* = 3.8 Hz), 35.3 (d, *J* = 2.3 Hz), 33.0, 26.2, 26.0. **HRMS (ESI, m/z):** calcd. for $C_{21}H_{23}FO_2$ $[M+H]^+$: 327.1760, found: 327.1765.

methyl 2-fluoro-3-(naphthalen-2-yl)-4-(tetrahydro-2*H*-pyran-4-yl)but-2-enoate 2w



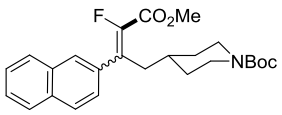
2w

Following general procedure, the reaction mixture was stirred for 96 h and the mixture of *Z*-**2w** and *E*-**2w** was obtained as white solid (55.1 mg, 0.17 mmol, 87%, *Z/E* = 74:26).[20]

Z-**2w** was further isolated and the NMR data was collected. **^{1}H NMR (400 MHz, $CDCl_3$):** 7.91 – 7.77 (m, 3H), 7.63 (s, 1H), 7.51 (dt, *J* = 6.2, 3.4 Hz, 2H), 7.27 (dd, *J* = 8.4, 1.8 Hz, 1H), 3.91 (dd, *J* = 11.8, 3.2 Hz, 2H), 3.59 (s, 3H), 3.24 (td, *J* = 11.6, 2.0 Hz, 2H), 2.62 (dd, *J* = 6.8, 3.9 Hz, 2H), 1.62 – 1.47 (m, 3H), 1.46 – 1.32 (m, 2H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -123.64. **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 161.0 (d, *J* = 36.0 Hz), 145.0 (d, *J* = 255.3 Hz), 134.3, 134.3, 133.7, 133.5, 133.0, 132.8, 128.0, 127.8 (d, *J* = 2.5 Hz), 126.6 (d, *J* = 3.2 Hz), 126.3 (d, *J* = 1.7 Hz), 126.2 (d, *J* = 2.9 Hz), 67.7, 52.0, 39.9 (d, *J* = 4.1 Hz), 32.8 (d, *J* = 2.5 Hz), 32.8. **HRMS (ESI, m/z):** calcd. for $C_{20}H_{21}FO_3$ $[M+H]^+$: 329.1553, found: 329.1563.

E-**2w** was further isolated and NMR data was collected. **^{1}H NMR (400 MHz, $CDCl_3$):** 7.91 – 7.82 (m, 3H), 7.80 (s, 1H), 7.58 – 7.49 (m, 2H), 7.43 (ddd, *J* = 8.6, 1.8, 1.8 Hz, 1H), 3.90 (s, 3H), 3.86 (dd, *J* = 11.3, 3.7 Hz, 2H), 3.20 (t, *J* = 11.0 Hz, 2H), 3.05 (d, *J* = 5.3 Hz, 2H), 1.58 – 1.44 (m, 3H), 1.44 – 1.28 (m, 2H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -123.15 (t, *J* = 4.0 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 162.1 (d, *J* = 34.6 Hz), 144.1(d, *J* = 256.8 Hz), 134.0, 133.9, 133.5(d, *J* = 2.1 Hz), 133.0(d, *J* = 5.9 Hz), 128.3, 128.0, 127.7, 127.5(d, *J* = 3.1 Hz), 126.7, 126.4, 125.8 (d, *J* = 3.5 Hz), 67.8, 52.2, 37.6, 34.2 (d, *J* = 3.2 Hz), 32.6. **HRMS (ESI, m/z):** calcd. for $C_{20}H_{21}FO_3$ $[M+H]^+$: 329.1553, found: 329.1558.

***tert*-butyl 4-(3-fluoro-4-methoxy-2-(naphthalen-2-yl)-4-oxobut-2-en-1-yl)piperidine-1-carboxylate 2x**



2x

Following general procedure, the reaction mixture was stirred for 96 h and an inseparable mixture of *Z*-**2x** and *E*-**2x** was obtained as white solid (70.0 mg, 0.16 mmol, 82%, *Z/E* = 60:40).[20]

Z-**2x** **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.90 – 7.82 (m, 3H), 7.63 (s, 1H), 7.55 – 7.47 (m, 2H), 7.28 (d, *J* = 1.7 Hz, 1H), 3.59 (s, 3H), 3.05 (d, *J* = 6.7 Hz, 2H), 2.51 (br, 4H) 1.70 – 1.55 (m, 1H), 1.40 (s, 9H), 1.35 – 1.05 (m, 4H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -123.8. **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 160.9 (d, *J* = 36.0 Hz), 154.7, 144.9 (d, *J* = 255.4 Hz), 134.2, 134.2, 133.7, 133.6, 132.9, 132.8, 128.0, 127.7, 127.4 (d, *J* = 3.3 Hz), 126.7, 126.6 (d, *J* = 3.3 Hz), 126.1 (d, *J* = 2.8 Hz), 79.2, 52.0, 39.4 (d, *J* = 4.1 Hz), 33.7 (d, *J* = 2.4 Hz), 31.7, 28.4. **HRMS (ESI, m/z):** calcd. for $C_{25}H_{30}FNO_4$ $[M+Na]^+$: 450.2057, found: 450.2056.

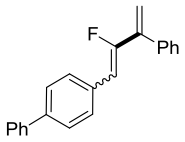
E-**2x** **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.90 – 7.82 (m, 3H), 7.81 (s, 1H), 7.55 – 7.48 (m, 2H), 7.43 (dt, *J* = 8.6, 1.8 Hz, 1H), 4.02 (br, 4H), 3.89 (s, 3H), 2.60 (dd, *J* = 7.2, 3.9 Hz, 2H), 1.70 – 1.55 (m, 1H), 1.39 (s, 9H), 1.35 – 1.05 (m, 4H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -123.11 (t, *J* = 4.0 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 162.0 (d, *J* = 34.5 Hz), 154.6, 144.0 (d, *J* = 257.2 Hz), 134.1, 134.0, 133.7, 133.5*J*, 133.0, 132.9*J*, 128.2,*J* 128.0, 127.6 (d, *J* = 8.9 Hz), 126.4, 126.3 (d, *J* = 1.9 Hz), 125.8 (d, *J* = 3.3 Hz), 79.1, 52.2, 37.2, 35.1 (d, *J* = 3.1 Hz), 31.8, 28.4. **HRMS (ESI, m/z):** calcd. for $C_{25}H_{30}FNO_4$ $[M+Na]^+$: 450.2057, found: 450.2055.

General procedure for the deflruoinative alkenylation of *gem*-difluoroalkene with ketone

To an oven-dried Schlenk tube equipped with a magnetic stir bar was added $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$ (2.0 mg, 0.002 mmol, 1.0 mol%), $PdCl_2$ (1.8 mg, 0.01 mmol, 5.0 mol%), PPh_3 (10.4 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (196 mg, 0.6 mmol, 3.0 equiv) in glovebox. To these solids, compound **1** (0.2 mmol, 1.0 equiv), ketone (0.4 mmol, 2.0 equiv), DMA (2.0 mL), ^{i}Pr_2NEt (78 mg, 0.6 mmol, 3.0 equiv) was added under nitrogen atmophere. Then the Schlenk tube was placed in front of the blue LEDs with 1 cm distance and stirred at ambient temperature for 48 to 96 h. The reaction mixture was quenched with 1N HCl (10 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with water

(10 mL), brine (10 mL) and dried over Na_2SO_4. After solvent was removed under reduced pressure, the crude residue was dissolved in Et_2O (2.0 mL) and MeOH (0.5 mL) and cooled to 0 ℃. The Et_2O solution of $TMSCHN_2$ (0.2 mL, 2 mol/L, 0.4 mmol, 2.0 equiv) was added at 0 ℃. The mixture was stirred at 0 ℃ for 30 min. The volatile was removed under reduced pressure and the crude residue was purified by column chromatography (petroleum ether/ethyl acetate = 50 : 1) to afford the desired product.

4-(2-fluoro-3-phenylbuta-1,3-dien-1-yl)-1,1'-biphenyl 3a



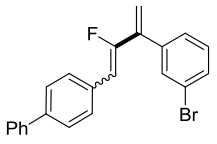
3a

Following general procedure, the reaction mixture was stirred for 48 h and an inseparable mixture of *Z*-**3a** and *E*-**3a** was obtained as white solid (48 mg, 0.12 mmol, 60%, *Z*/*E* = 67:33).

Z-**3a** **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.70 – 7.68 (m, 2H), 7.65 – 7.59 (m, 4H), 7.57 – 7.33 (m, 8H), 5.46 (d, *J* = 28.7 Hz, 1H), 5.20 (dd, *J* = 3.4, 1.0 Hz, 1H), 4.96 (dd, *J* = 3.3, 2.4 Hz, 1H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -82.19 (dd, *J* = 28.7, 2.2 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 156.8 (d, *J* = 1.7 Hz), 154.3 (d, *J* = 288.7 Hz), 140.6, 139.3 (d, *J* = 2.3 Hz), 133.4, 132.5, 131.4 (d, *J* = 6.5 Hz), 129.3, 128.8, 128.5, 128.1 (d, *J* = 7.2 Hz), 127.2 (d, *J* = 3.7 Hz), 127.2, 126.9, 125.3, 92.3, 91.1 (d, *J* = 19.3 Hz).

E-**3a** **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.75 – 7.73 (m, 2H), 7.65 – 7.59 (m, 4H), 7.57 – 7.33 (m, 8H), 5.78 (d, *J* = 5.9 Hz, 1H), 5.19 (d, *J* = 3.6 Hz, 1H), 4.93 (dd, *J* = 3.6, 2.4 Hz, 1H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -82.70 (dd, *J* = 6.1, 2.4 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 154.8 (d, *J* = 2.7 Hz), 153.5 (d, *J* = 282.6 Hz), 140.6, 139.4 (d, *J* = 1.9 Hz), 133.2, 132.9, 131.1 (d, *J* = 8.3 Hz), 129.4, 128.7, 128.5, 127.8 (d, *J* = 3.6 Hz), 127.2, 127.1 (d, *J* = 6.7 Hz), 126.9, 125.3, 92.7 (d, *J* = 37.7 Hz), 91.2. **HRMS (ESI, m/z):** calcd. for calcd. for $C_{22}H_{18}F$ $[M+H]^+$: 301.1393, found: 301.1394.

4-(3-(3-bromophenyl)-2-fluorobuta-1,3-dien-1-yl)-1,1'-biphenyl 3b



3b

Following general procedure, the reaction mixture was stirred for 48 h and an inseparable mixture of *Z*-**3b** and *E*-**3b** was obtained as white solid (34.8 mg, 0.09 mmol, 46%, *Z*/*E* = 66:34).

Z-**3b** **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.80 (dd, *J* = 1.9, 1.9 Hz, 1H), 7.66 – 7.37 (m, 9H), 7.37 – 7.31 (m, 1H), 7.30 – 7.22 (m, 2H), 5.45 (d, *J* = 28.6 Hz, 1H), 5.22 – 5.11 (m, 1H), 4.99 – 4.88 (m, 1H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -82.66 (dd, *J* = 28.6, 2.2 Hz). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 155.4 (d, *J* = 2.1 Hz), 153.8 (d, *J* = 289.7 Hz), 140.6, 139.6 (d, *J* = 2.3 Hz), 135.5, 132.2, 131.1 (d, *J* = 6.5 Hz), 130.0, 128.8, 128.4, 128.2 (d, *J* = 7.2 Hz), 127.3, 127.2, 126.9, 123.9, 122.7, 93.0, 91.7 (d, *J* = 19.1 Hz).

E-**3b** **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.84 (dd, *J* = 2.0, 2.0 Hz, 1H), 7.66 – 7.37 (m, 9H), 7.37 – 7.31 (m, 1H), 7.30 – 7.22 (m, 2H), 5.77 (d, *J* = 5.9 Hz, 1H), 5.22 – 5.11 (m, 1H), 4.99 – 4.88 (m, 1H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -83.34 (dd, *J* = 6.0, 2.1 Hz) **^{13}C NMR (100 MHz, $CDCl_3$):** 154.6, 153.5 (d, *J* = 2.9 Hz), 151.8, 140.5, 139.6 (d, *J* = 2.0 Hz), 135.3, 132.3, 130.8 (d, *J* = 8.2 Hz), 130.0, 128.8, 128.5, 127.9 (d, *J* = 3.6 Hz), 127.3, 127.3, 126.9, 124.0, 122.7, 93.04 (d, *J* = 37.0 Hz). **HRMS (ESI, m/z):** calcd. for $C_{22}H_{17}BrF$ $[M+H]^+$: 379.0498, found: 379.0493.

A mechanistic rationale for the fluoro-diene **3** formation was delineated in Figure S2. Similar as the mechanism for the defluorinative carboxylation, an alcohol intermediate **G** is generated and undergoes dehydration immediately to afford the product **3**.

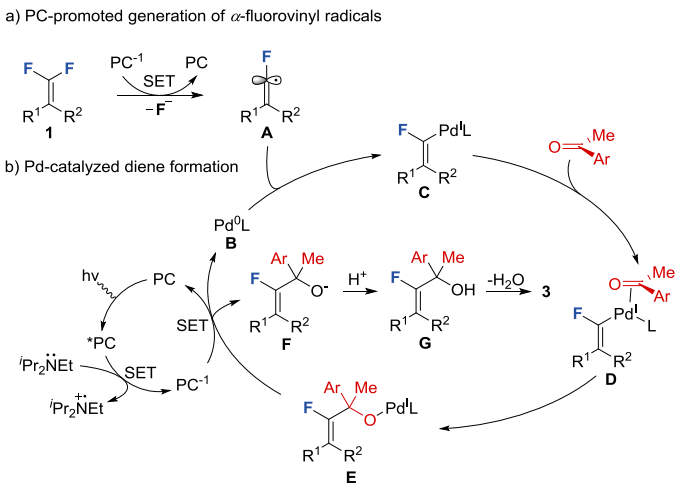
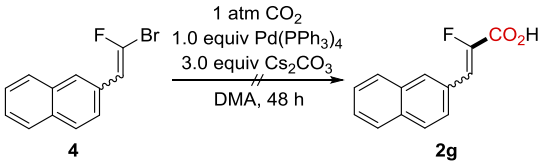


Figure S2. Proposed mechanism for the formation of compound **3**

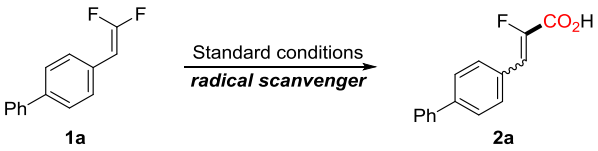
5. Mechanistic Study

5.1 Attempt with 2-(2-bromo-2-fluorovinyl)naphthalene 4



To an oven-dried Schlenk tube equipped with a magnetic stir bar was added $Pd(PPh_3)_4$ (231 mg, 0.2 mmol, 1.0 equiv) and Cs_2CO_3 (196 mg, 0.6 mmol, 3.0 equiv) in glovebox. To these solids, compound **4** (50 mg, 0.2 mmol, 1.0 equiv) and DMA (2.0 mL) were added under nitrogen atmophere. The Schlenk tube was evacuated and filled with CO_2 (3 cycles). Then the reaction mixture was stirred at ambient temperature for 48 h. The reaction mixture was quenched with 1N HCl (10 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with water (10 mL), brine (10 mL) and dried over Na_2SO_4. After solvent was removed under reduced pressure, the ^{19}F NMR analysis of the crude residue indicated no **2a** was formed.

5.2 Radical scavengers and radical trapping studies

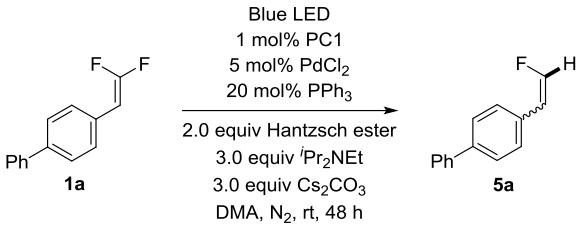


Entry	Radical scavenger	Conversion/%[a]	Yield/%[a]	
			Z-**2a**	*E*-**2a**
1	1.0 equiv of TEMPO	85	39	4
2	2.0 equiv of TEMPO	80	13	2
3	1.0 equiv of BHT	100	64	7
4	2.0 equiv of BHT	98	32	6

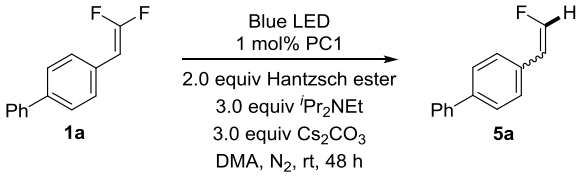
[a] NMR Yield.

To an oven-dried Schlenk tube equipped with a magnetic stir bar was added [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF$_6$) (2.0 mg, 0.002 mmol, 1.0 mol%), PdCl$_2$ (1.8 mg, 0.01 mmol, 5.0 mol%), PPh$_3$ (10.4 mg, 0.04 mmol, 20 mol%) and Cs$_2$CO$_3$ (196 mg, 0.6 mmol, 3.0 equiv) in glovebox. To these solids, compound **1a** (0.2 mmol, 1.0 equiv), radical scavenger, DMA (2.0 mL), ^{i}Pr$_2$NEt (0.6 mmol, 3.0 equiv) were added under nitrogen atmophere. The reaction mixture was evacuated and filled with CO_2 (3 cycles). Then the Schlenk tube was placed in front of blue LEDs with 1 cm distance and stirred at ambient temperature for 48 h. The reaction mixture was quenched with 1N HCl (10 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with water (10 mL), brine (10 mL) and dried over Na$_2$SO$_4$. After solvent was removed under reduced pressure, the crude residue analyzed by ^{19}F NMR.

5.3 Reaction in the presence of Hantzsch ester

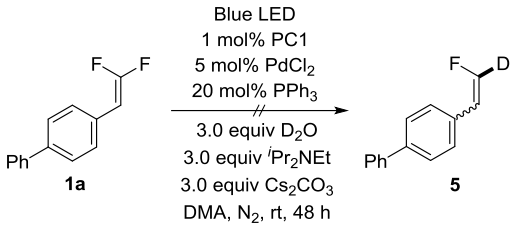


To an oven-dried Schlenk tube equipped with a magnetic stir bar was added [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF$_6$) (2.0 mg, 0.002 mmol, 1.0 mol%), PdCl$_2$ (1.8 mg, 0.01 mmol, 5.0 mol%), PPh$_3$ (10.4 mg, 0.04 mmol, 20 mol%) and Cs$_2$CO$_3$ (196 mg, 0.6 mmol, 3.0 equiv) in glovebox. To these solids, compound **1a** (0.2 mmol, 1.0 equiv), Hantzsch ester (51 mg, 0.4 mmol, 2.0 equiv), DMA (2.0 mL), ^{i}Pr$_2$NEt (0.6 mmol, 3.0 equiv) were added under nitrogen atmophere. Then the Schlenk tube was placed in front of blue LEDs with 1 cm distance and stirred at ambient temperature for 48 h. The reaction mixture was quenched with 1N HCl (10 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with water (10 mL), brine (10 mL) and dried over Na$_2$SO$_4$. After solvent was removed under reduced pressure, 19F NMR analysis of the crude residue indicated 5a was formed in 17% yield with 18:82 *Z*/*E* ratio. Then the crude product was purified by column chromatography on silica gel (hexane only) to afford **5a** (7.1 mg, 0.036 mmol) in 18% yield as a white solid. The NMR data is in accordance with the literature.[21]



To an oven-dried Schlenk tube equipped with a magnetic stir bar was added [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF$_6$) (2.0 mg, 0.002 mmol, 1.0 mol%), and Cs$_2$CO$_3$ (196 mg, 0.6 mmol, 3.0 equiv) in glovebox. To these solids, compound **1a** (0.2 mmol, 1.0 equiv), Hantzsch ester (51 mg, 0.4 mmol, 2.0 equiv), DMA (2.0 mL), ^{i}Pr$_2$NEt (0.6 mmol, 3.0 equiv) were added under nitrogen atmophere. Then the Schlenk tube was placed in front of blue LEDs with 1 cm distance and stirred at ambient temperature for 48 h. The reaction mixture was quenched with 1N HCl (10 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with water (10 mL), brine (10 mL) and dried over Na$_2$SO$_4$. After solvent was removed under reduced pressure, 19F NMR analysis of the crude residue indicated **5a** was formed in 16% yield with 25:75 *Z*/*E* ratio.

5.3 Reaction in the presence of D_2O



To an oven-dried Schlenk tube equipped with a magnetic stir bar was added [Ir(dF(CF_3)ppy)$_2$(dtbbpy)](PF_6) (2.0 mg, 0.002 mmol, 1.0 mol%), $PdCl_2$ (1.8 mg, 0.01 mmol, 5.0 mol%), PPh_3 (10.4 mg, 0.04 mmol, 20 mol%) and Cs_2CO_3 (196 mg, 0.6 mmol, 3.0 equiv) in glovebox. To these solids, compound **1a** (0.2 mmol, 1.0 equiv), D_2O (32 mg, 0.6 mmol, 3.0 equiv), DMA (2.0 mL), ^{i}Pr$_2$NEt (0.6 mmol, 3.0 equiv) were added under nitrogen atmophere. Then the Schlenk tube was placed in front of blue LEDs with 1 cm distance and stirred at ambient temperature for 48 h. The reaction mixture was quenched with 1N HCl (10 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with water (10 mL), brine (10 mL) and dried over Na_2SO_4. After solvent was removed under reduced pressure, the crude residue analyzed by ^{19}F NMR with trifluoromethylbenzene as internal standard and the result indicated that no compound **5** formed while the 58% of **1a** remained.

5.4 Cyclic voltammetry experiments

Cyclic voltammograms were recored on a CH Instruments 600E potentiostat using a glassy carbon working electrode, a saturated calomel (SCE) reference electrode, and a Pt mesh counter electrode. The pH was not adjusted and voltammograms were taken at room temperature in a 100 mM DMA solution of tetrabutylammonium hexafluorophosphate containing 10 mM of **1a**. The scan rate was 100 mV/s. The reduction potentials of **1a** was measured as -0.80 and -1.53 V which are attributed to the single electron reduction of *gem*-difluoroalkene and the the C−F bond cleavage respectively according to the literature (Figure S2).[22] [Ir(dF(CF_3)ppy)$_2$](dtbbpy)$^+$ ($E_{1/2}$[Ir^{II}/Ir^{III}] = -1.37 V vs SCE),[23] reduction of **1a** by the reduced form of PC I is thermodynamically feasible.

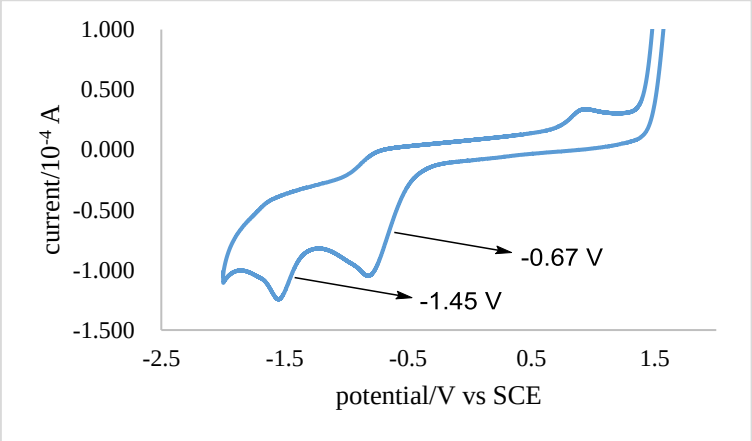


Figure S3. Cyclic voltammogram of **1a**

5.5 Proposed Mechanism

A plausible mechanism including the following steps was proposed: 1) fluorovinyl radical formation through single electron reduction by reduced PC; 2) combination to Pd-catalyst to generate Pd(I) complex **C**; 3) coordination of CO2 to intermediate

C; 4) subsequent carboxylation to produce palladium carboxylate E; 5) final reduction of **E** by PC^{-1} to afford desired product and regenerate Pd(0) catalyst (left). The other reaction pathway involved Pd(I)/Pd(II) was aslo possible for this reaction (right). In this manifold, the fluorovinyl radical was captured by Pd(I) species **B'** to generate fluoroalkenyl-Pd **C'**, to which CO_2 was bounded to form intermediate **D'**. Then single electron reduction and migratory insertion occurred to yield desired product **2** and regenerate catalytically active Pd(I).

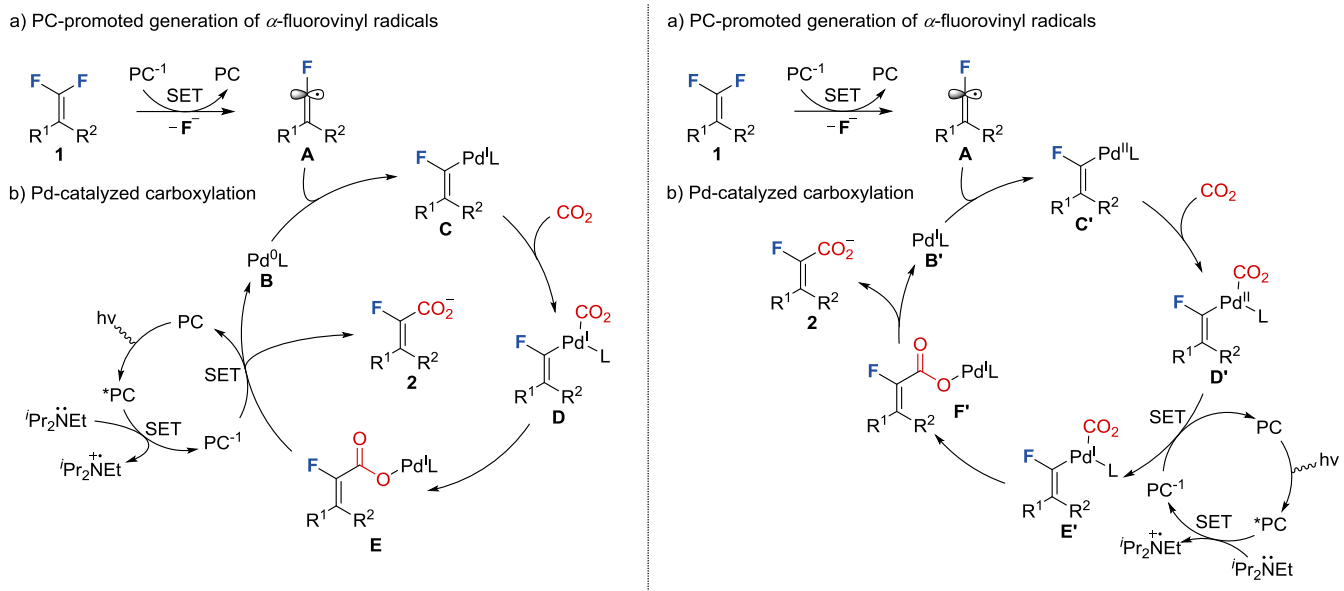


Figure S4. Proposed mechanism

6. References

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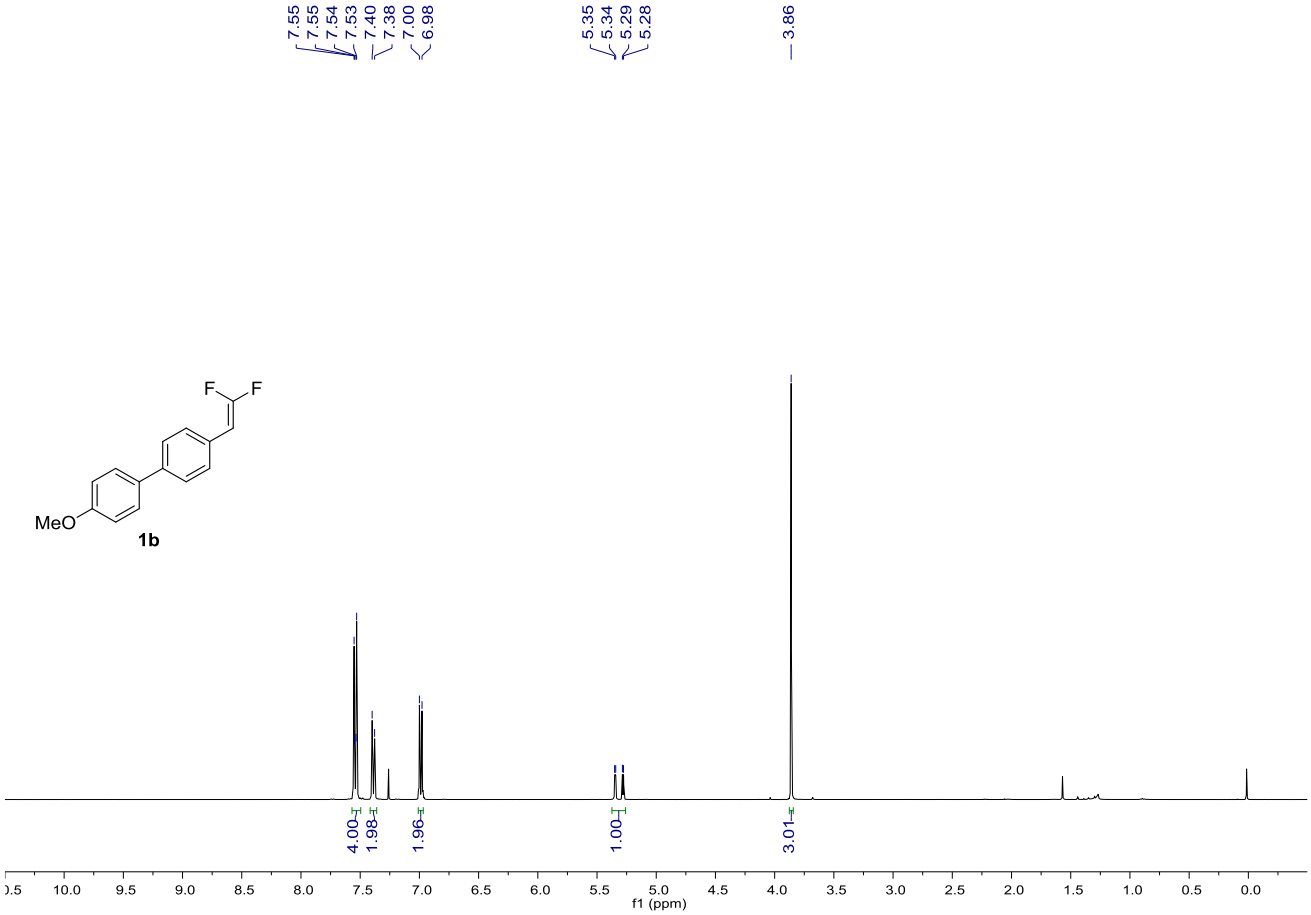
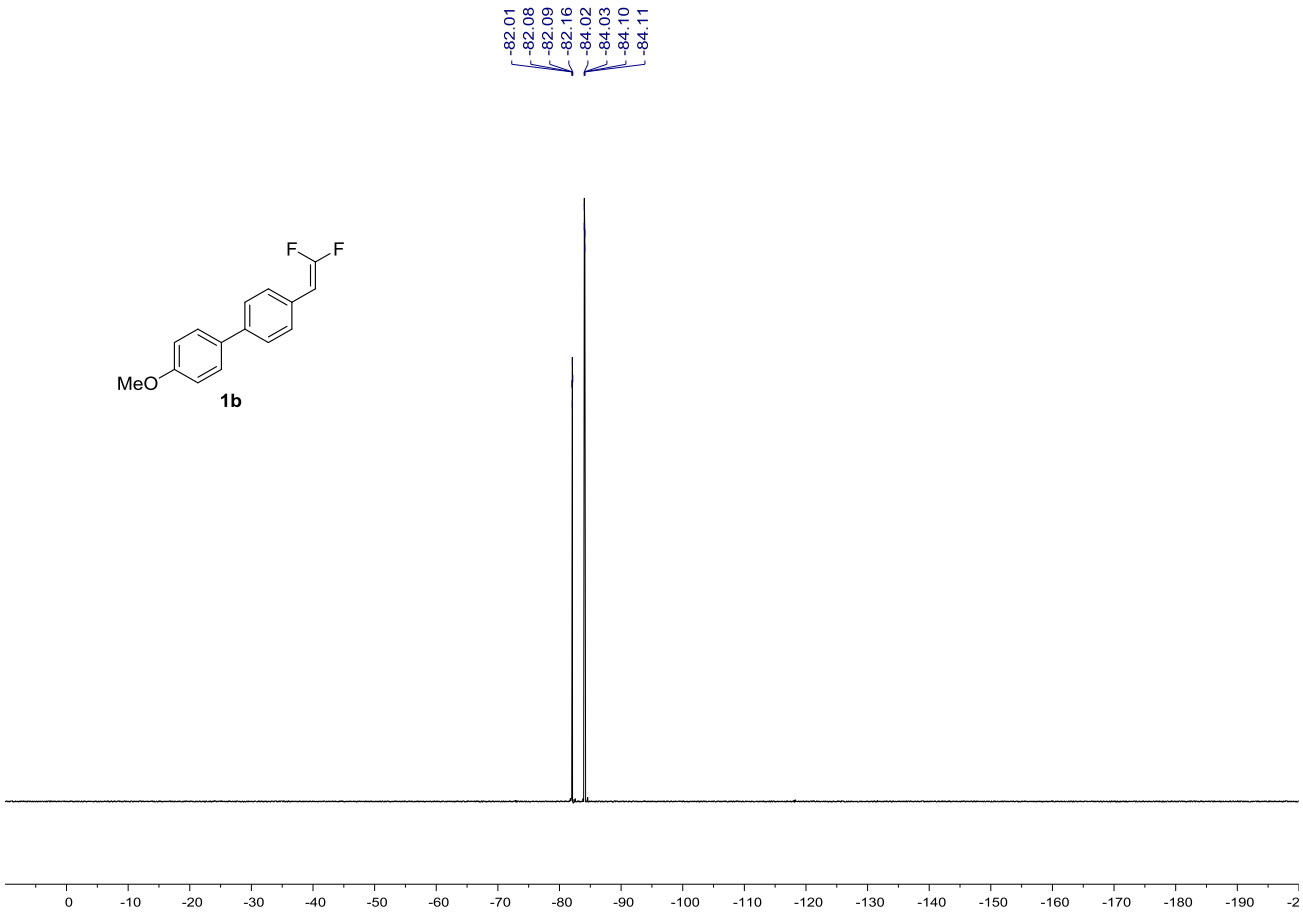
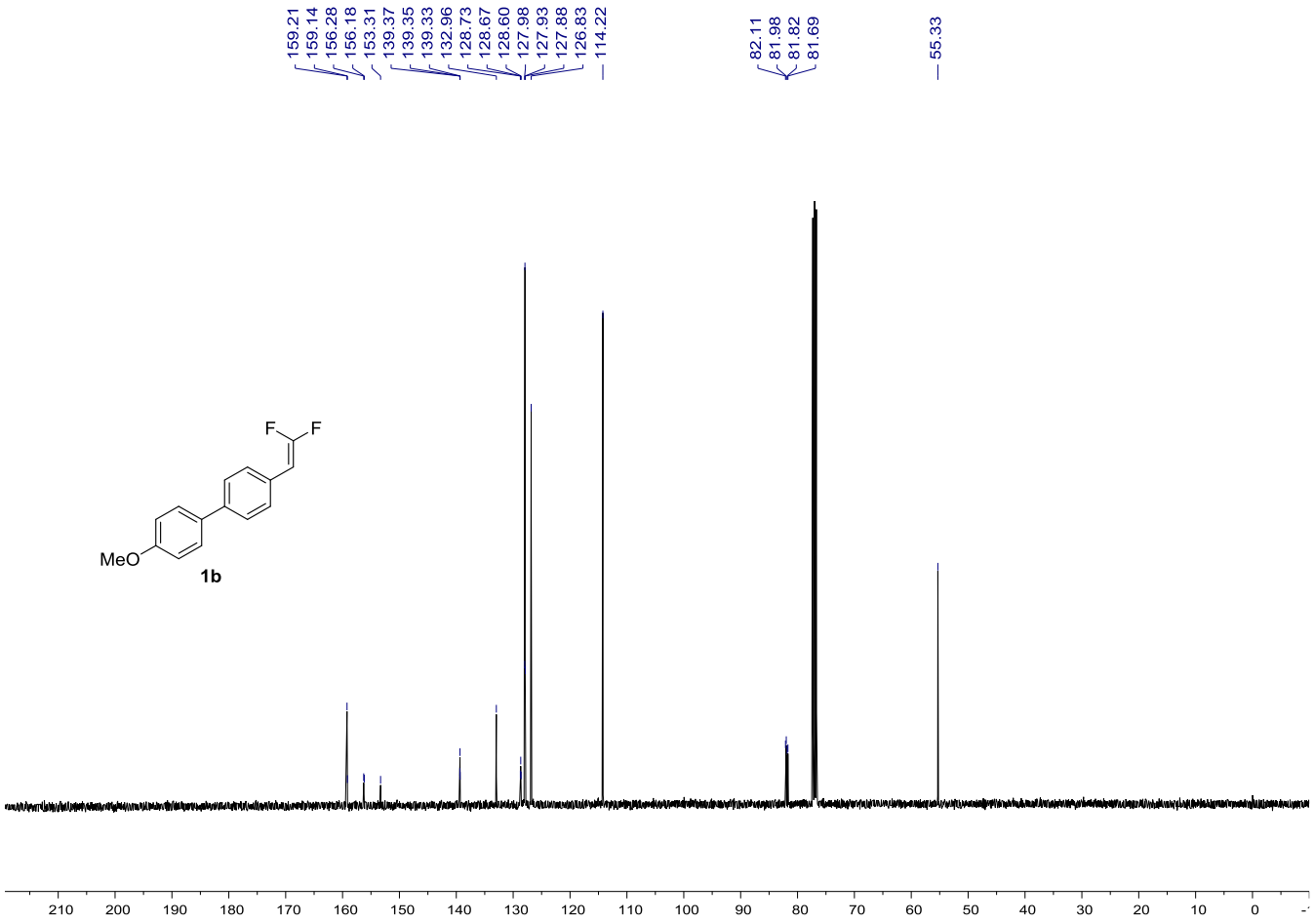
7. NMR spectra



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127.93
127.88
126.83
114.22
82.11
81.98
81.82
81.69
55.33
F
F
MeO
1b
210
200
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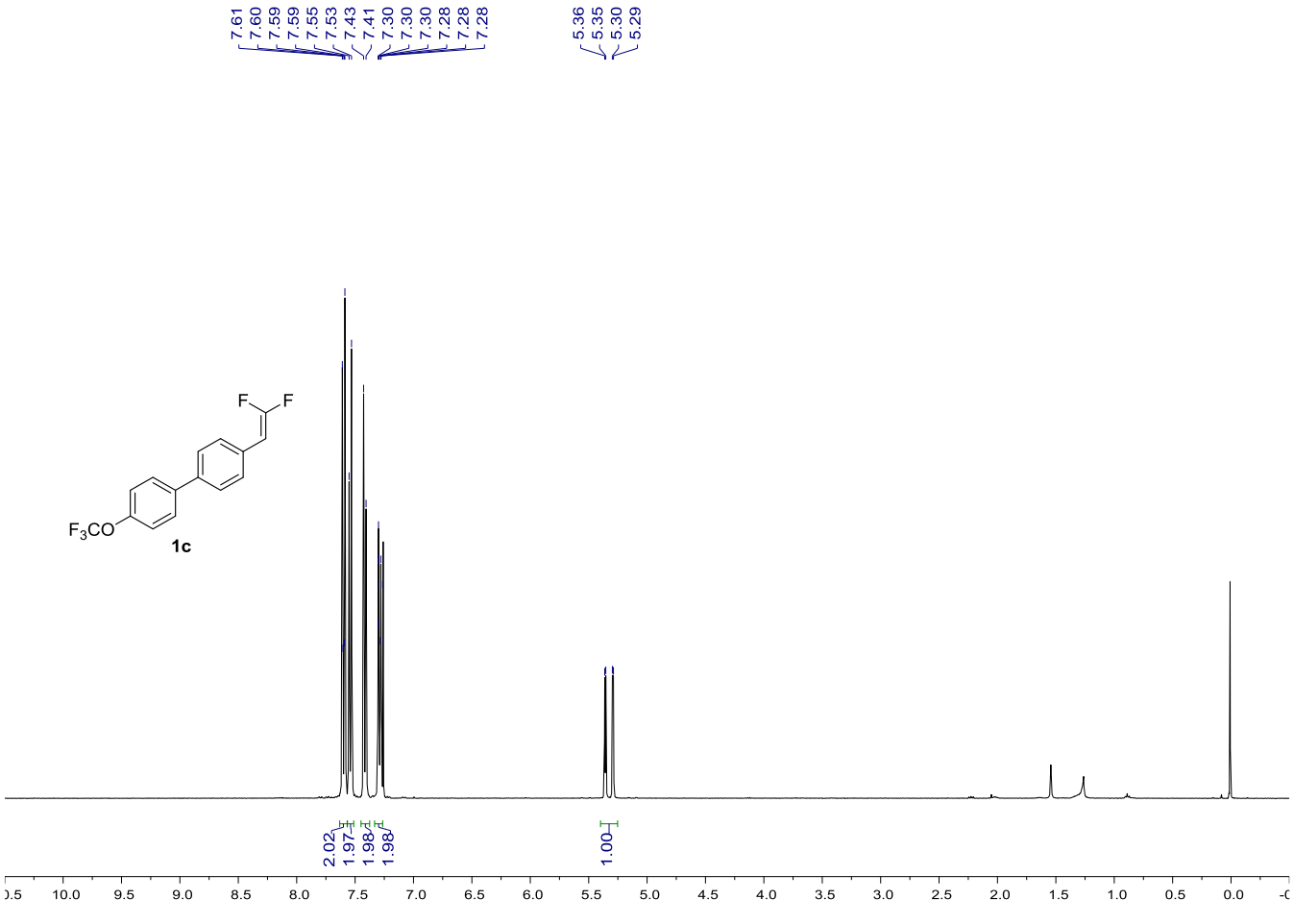
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7.28
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1.98
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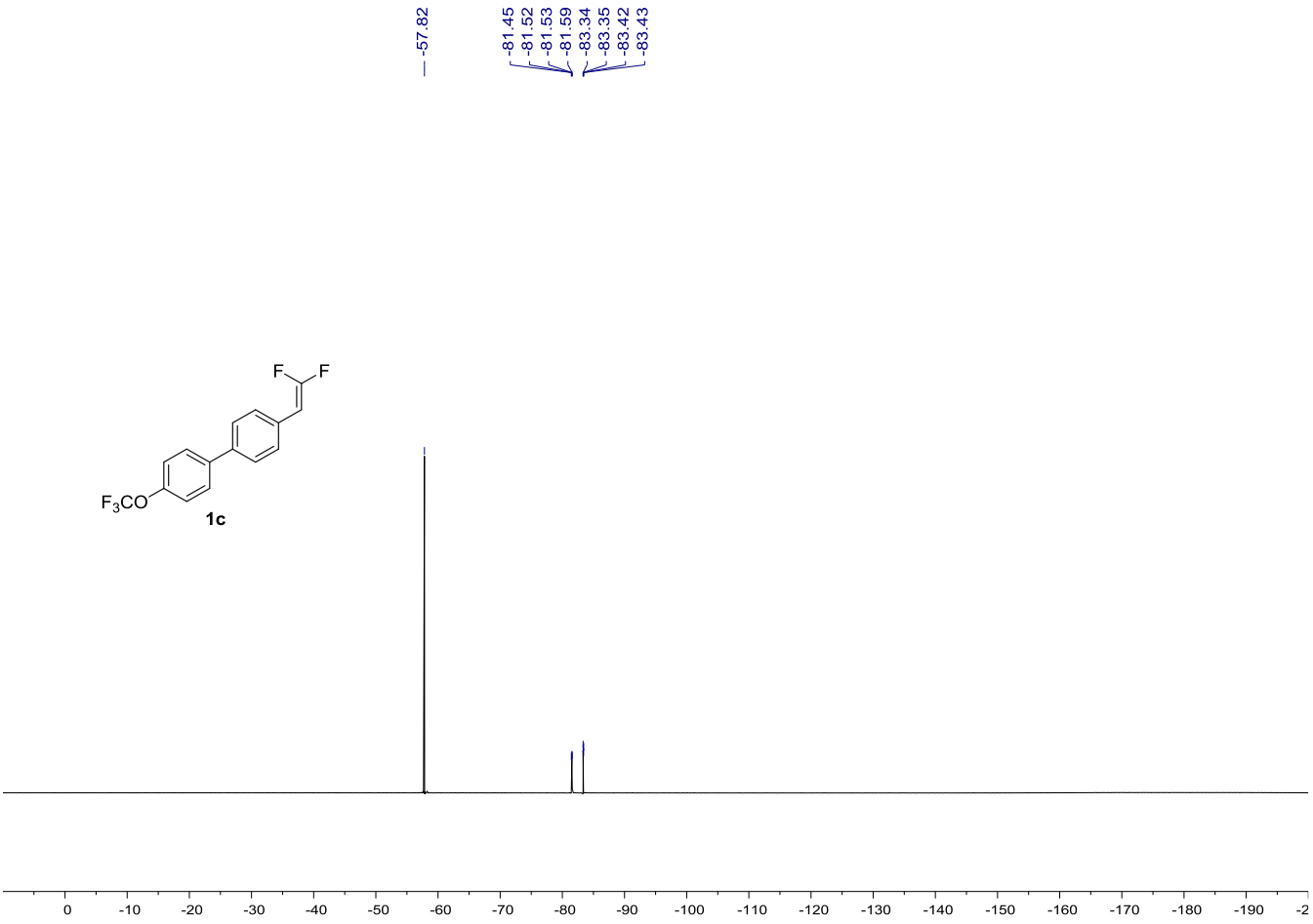
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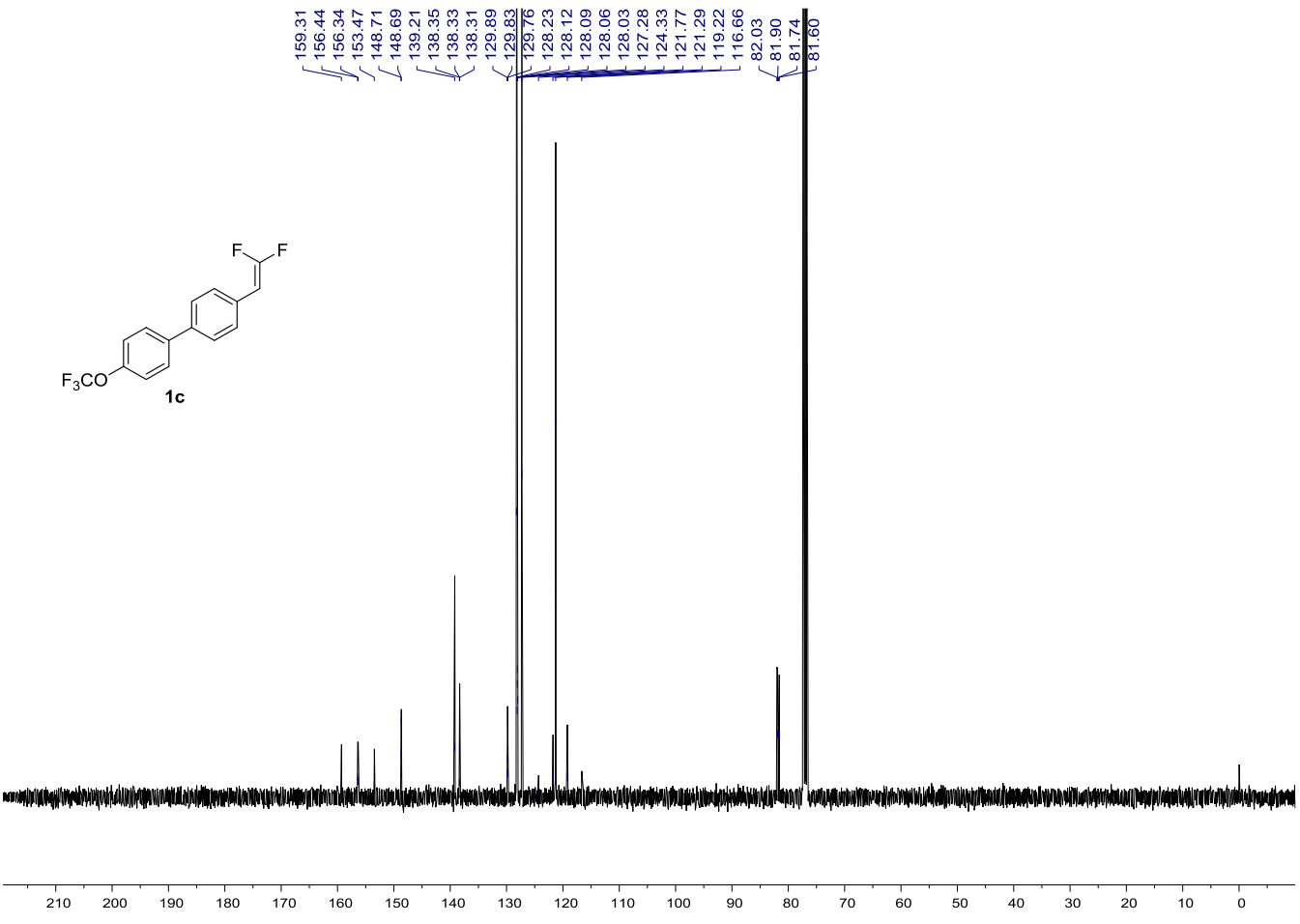
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81.74
81.60
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F
F3CO
1c
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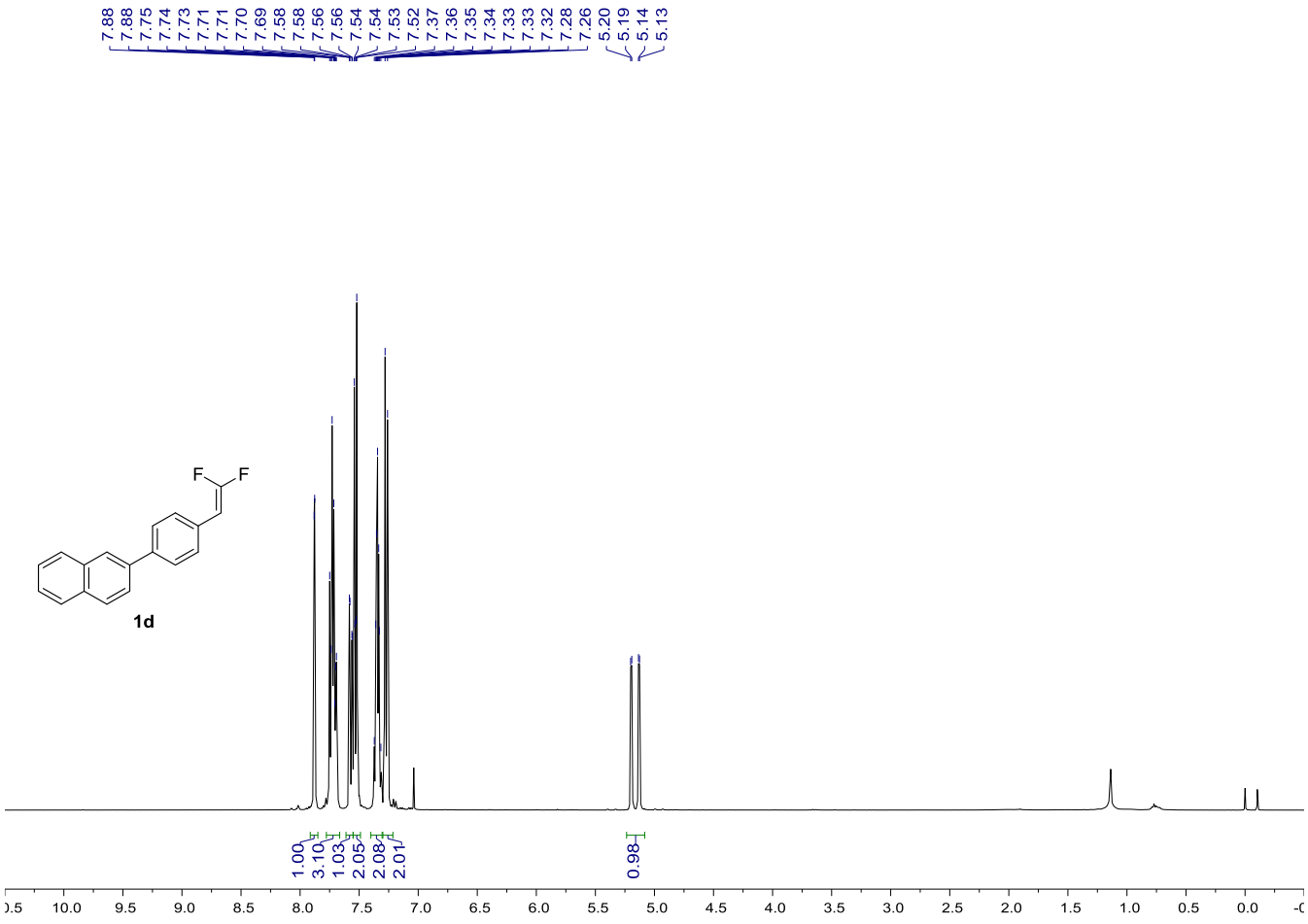
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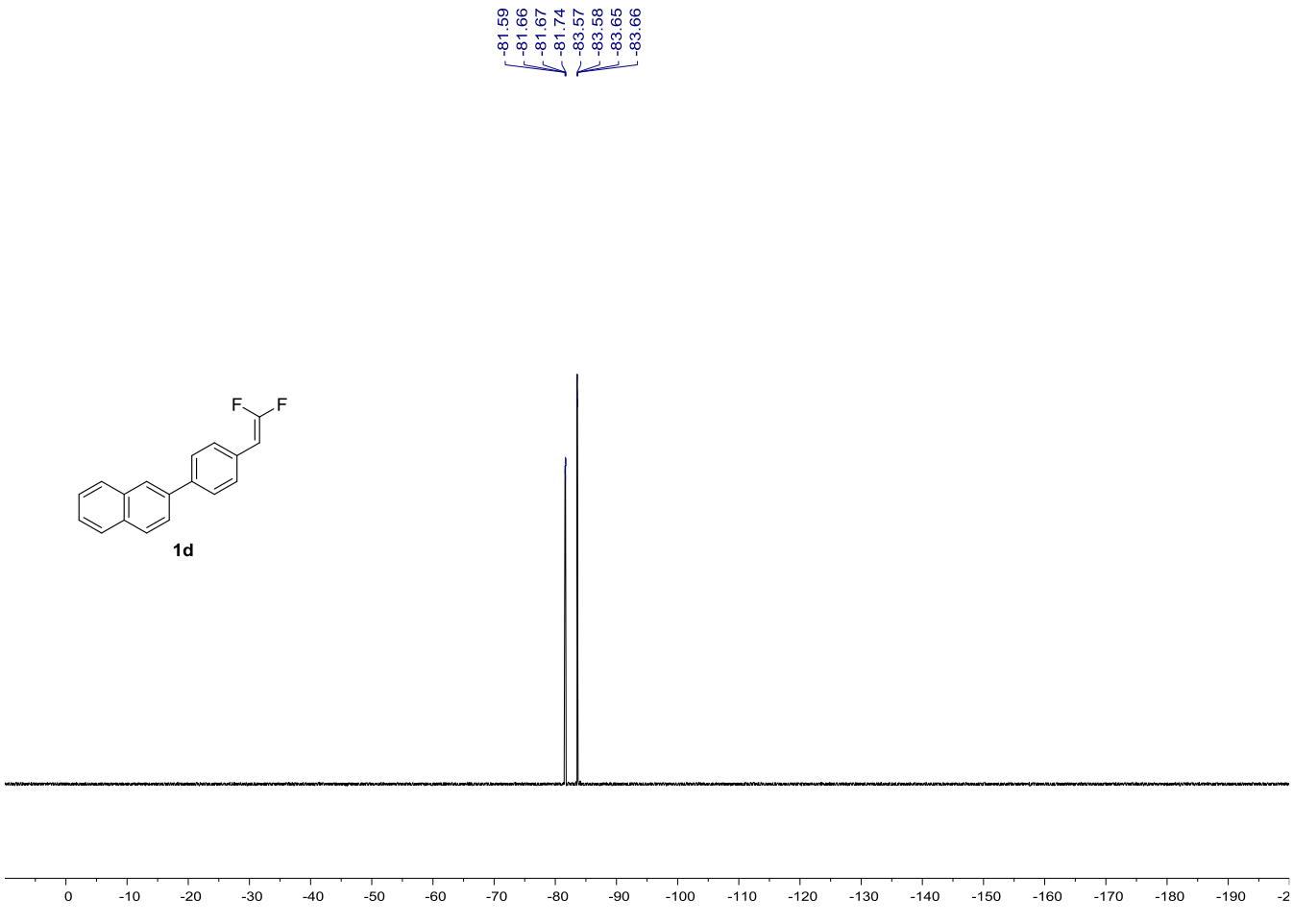
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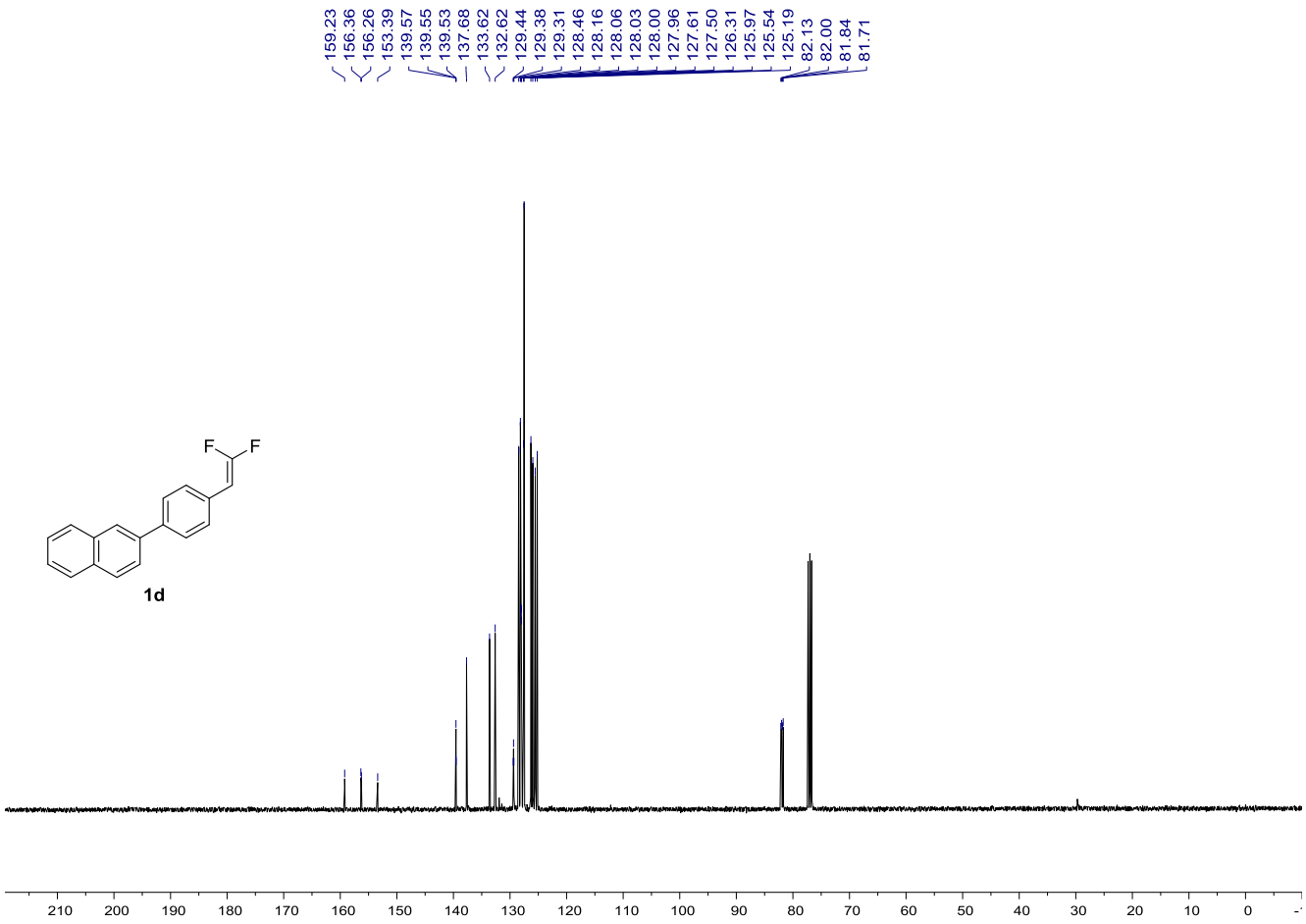
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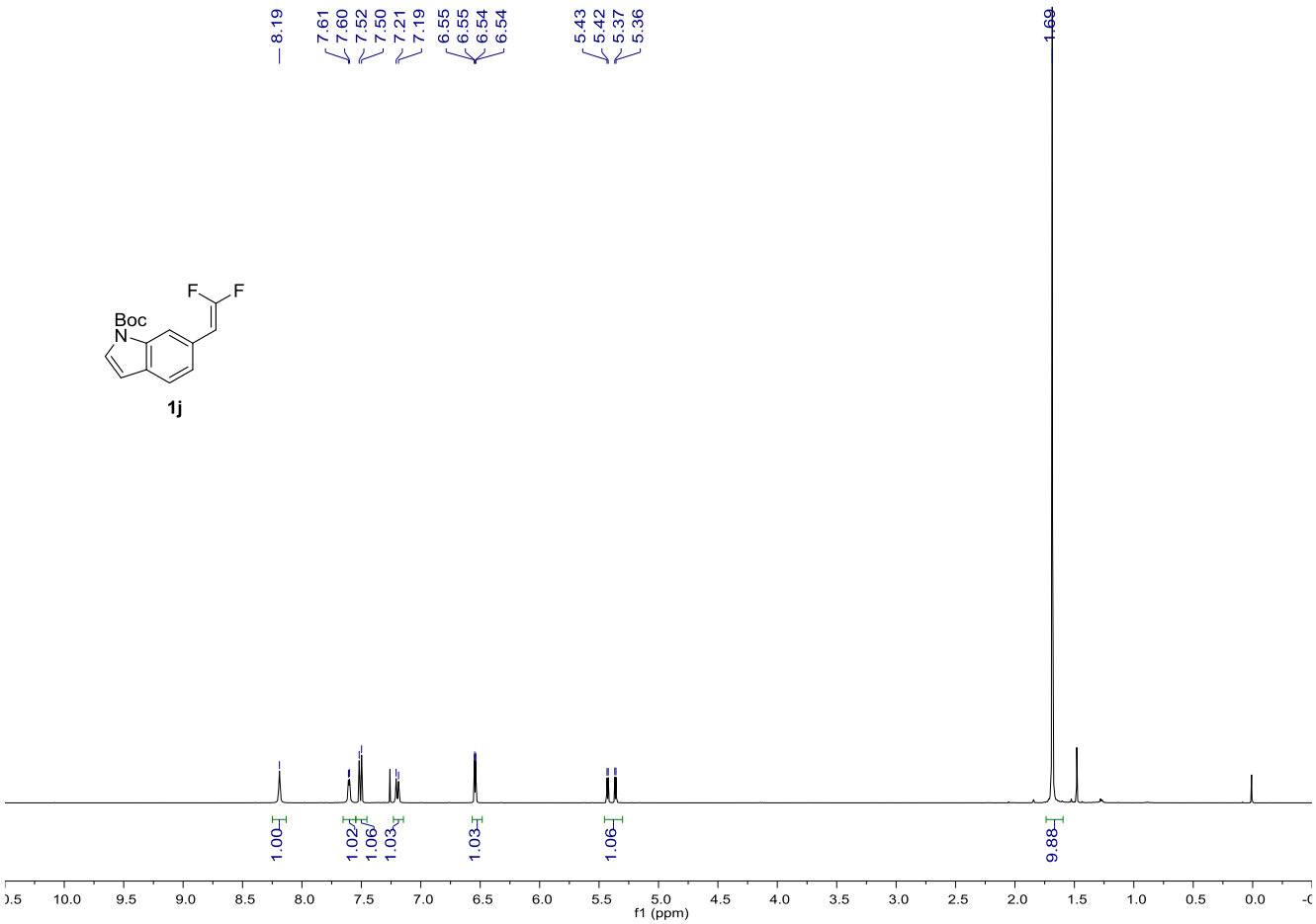
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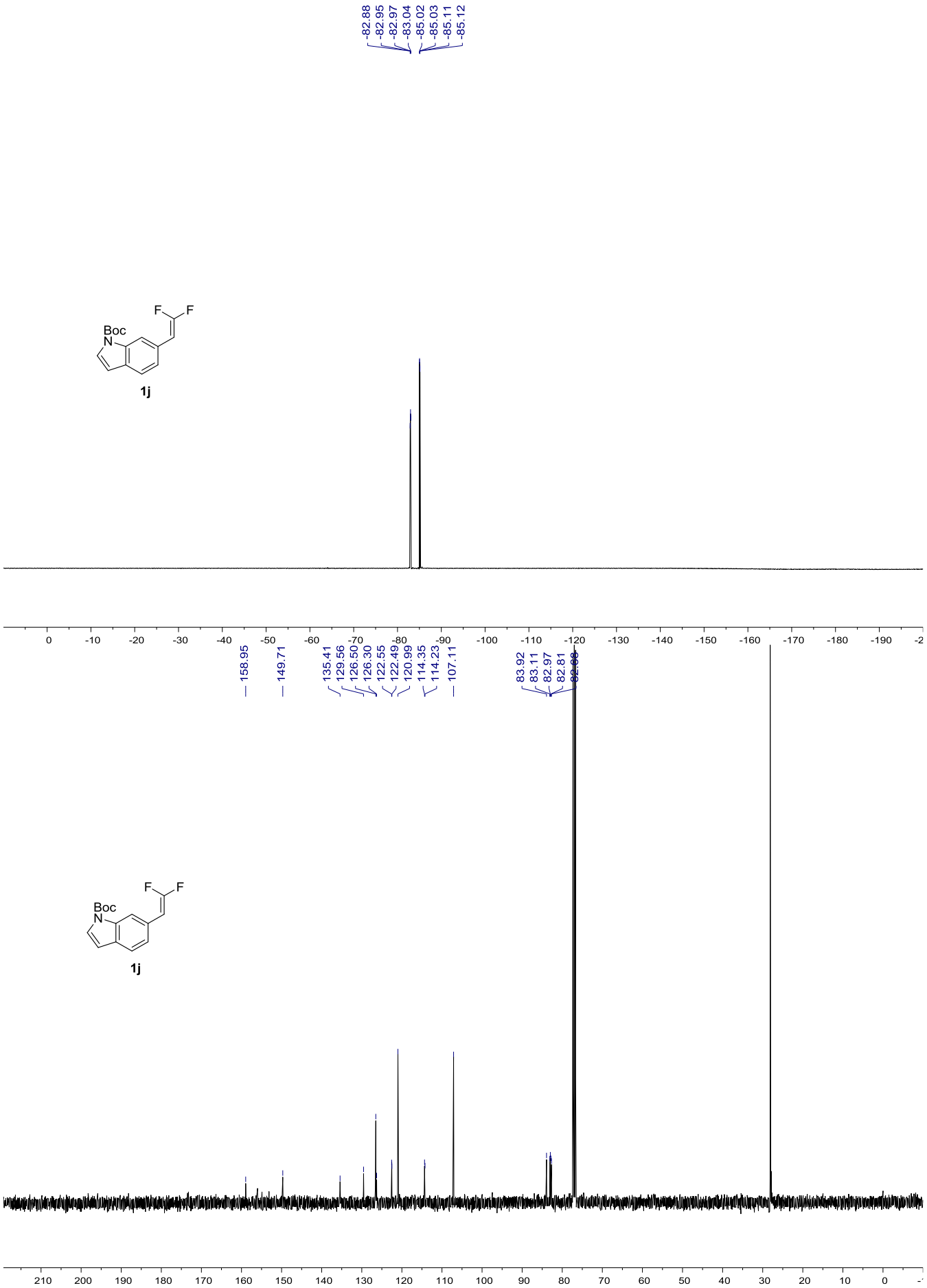
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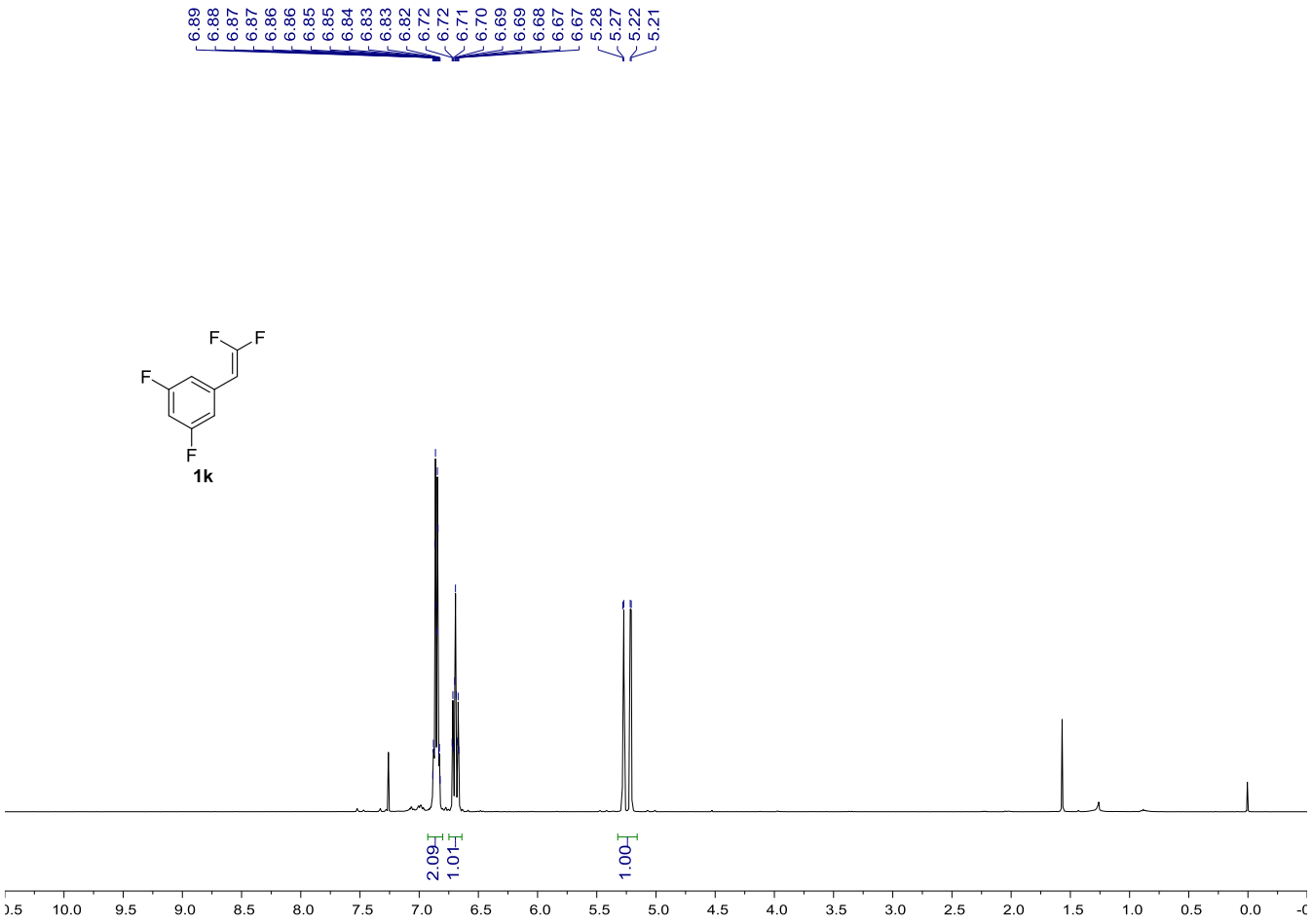
1j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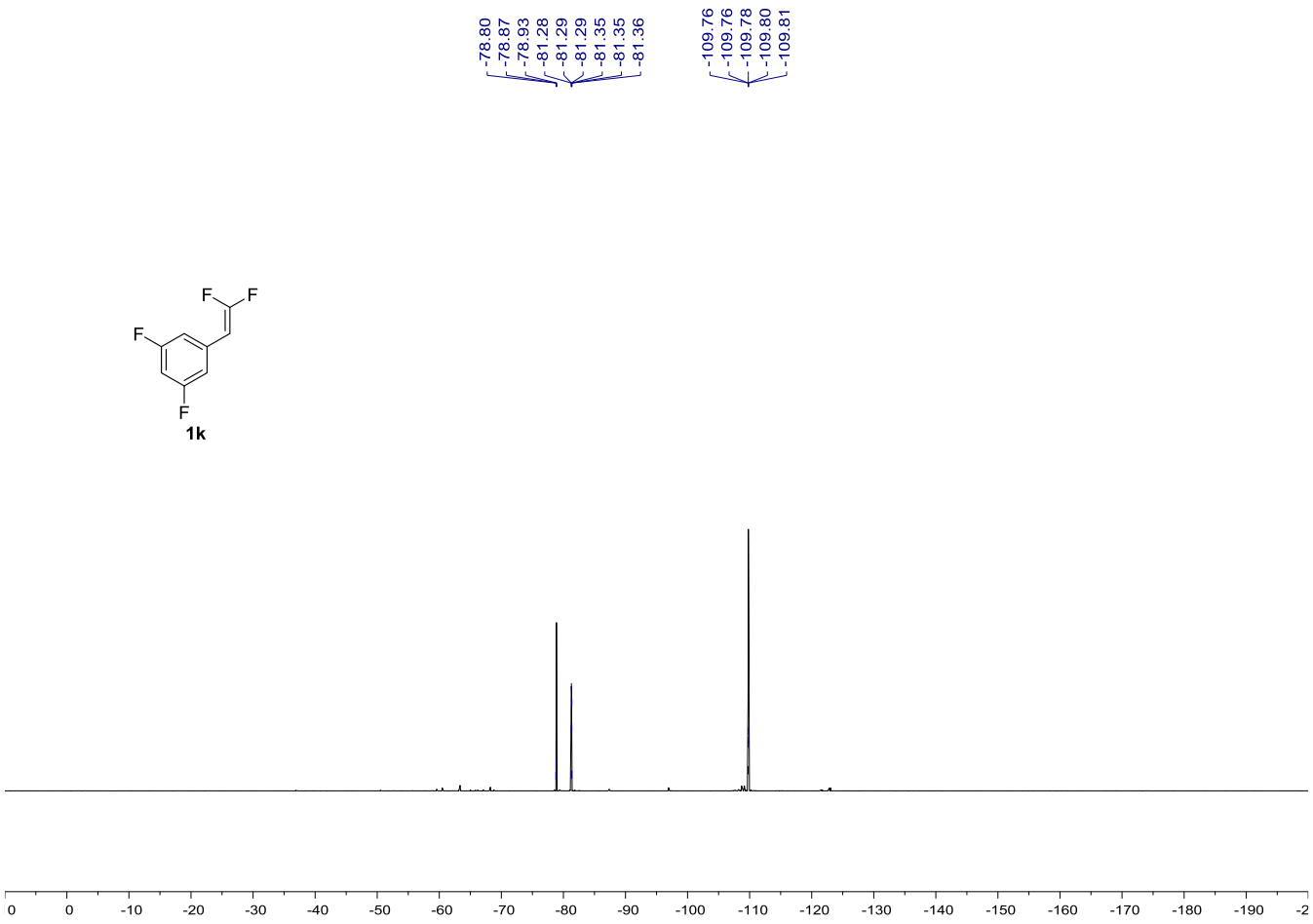
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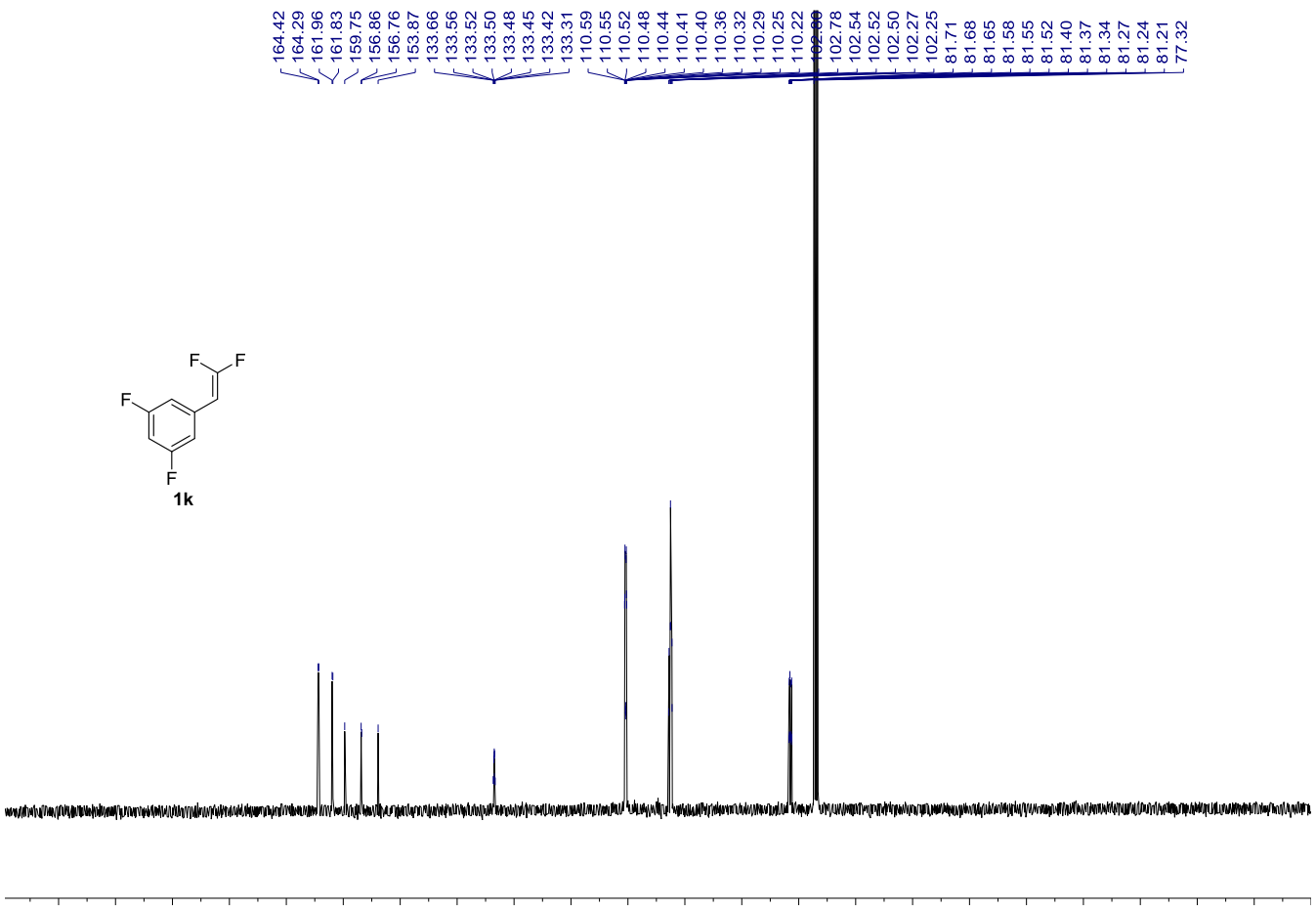
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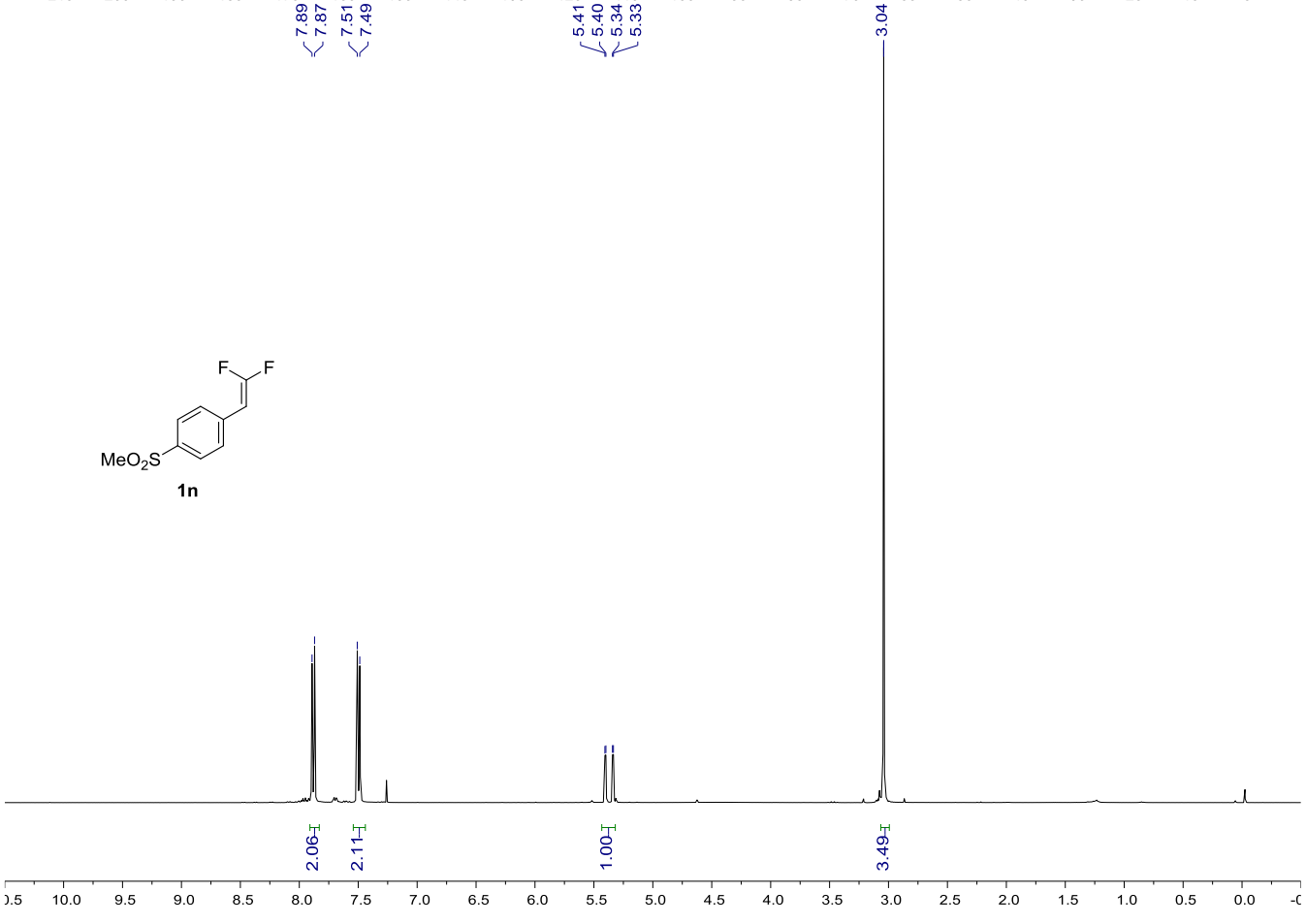
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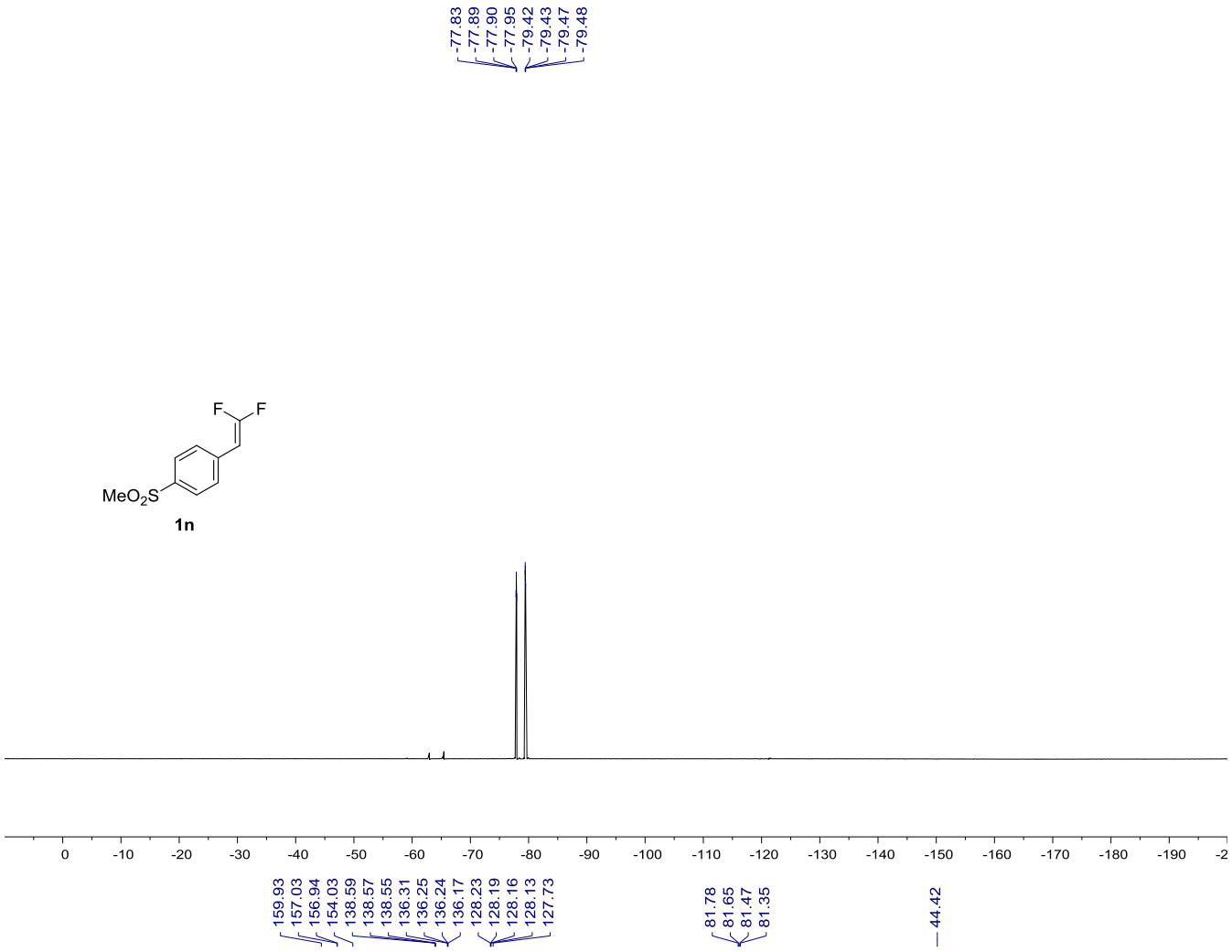
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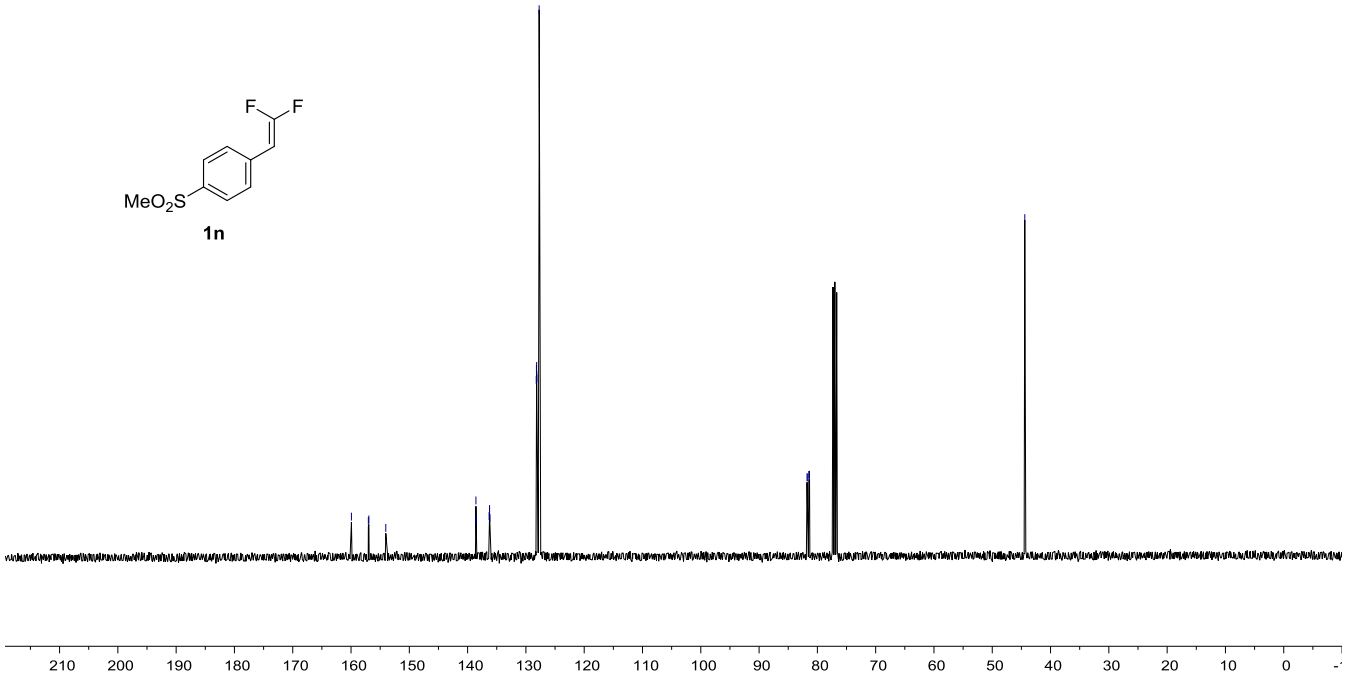
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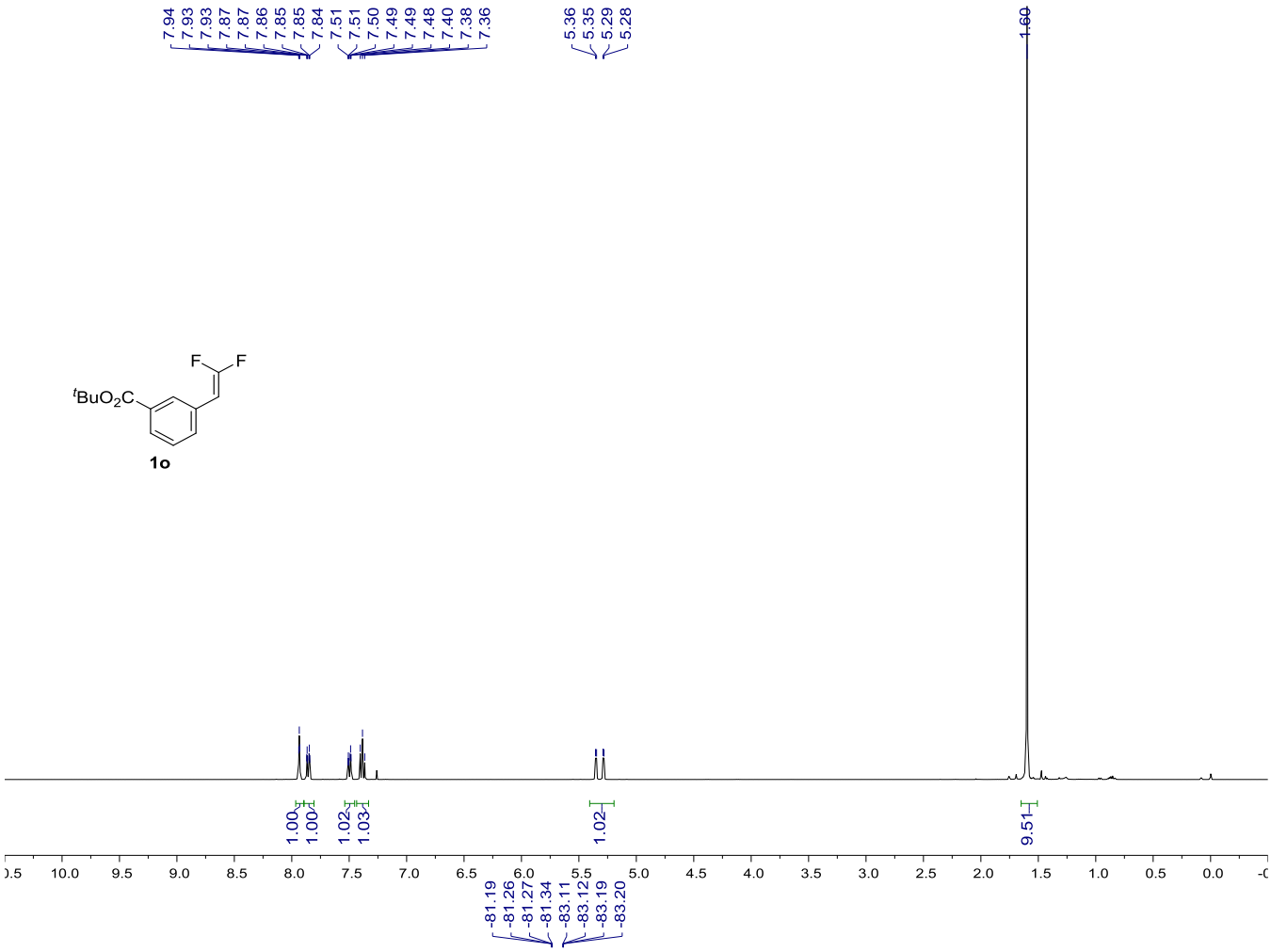
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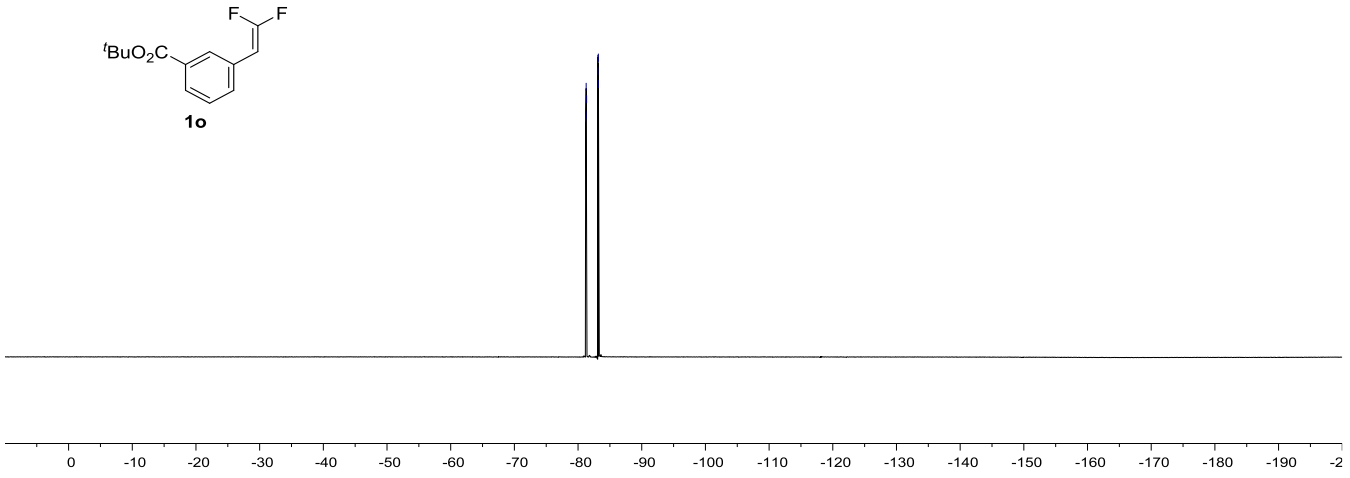
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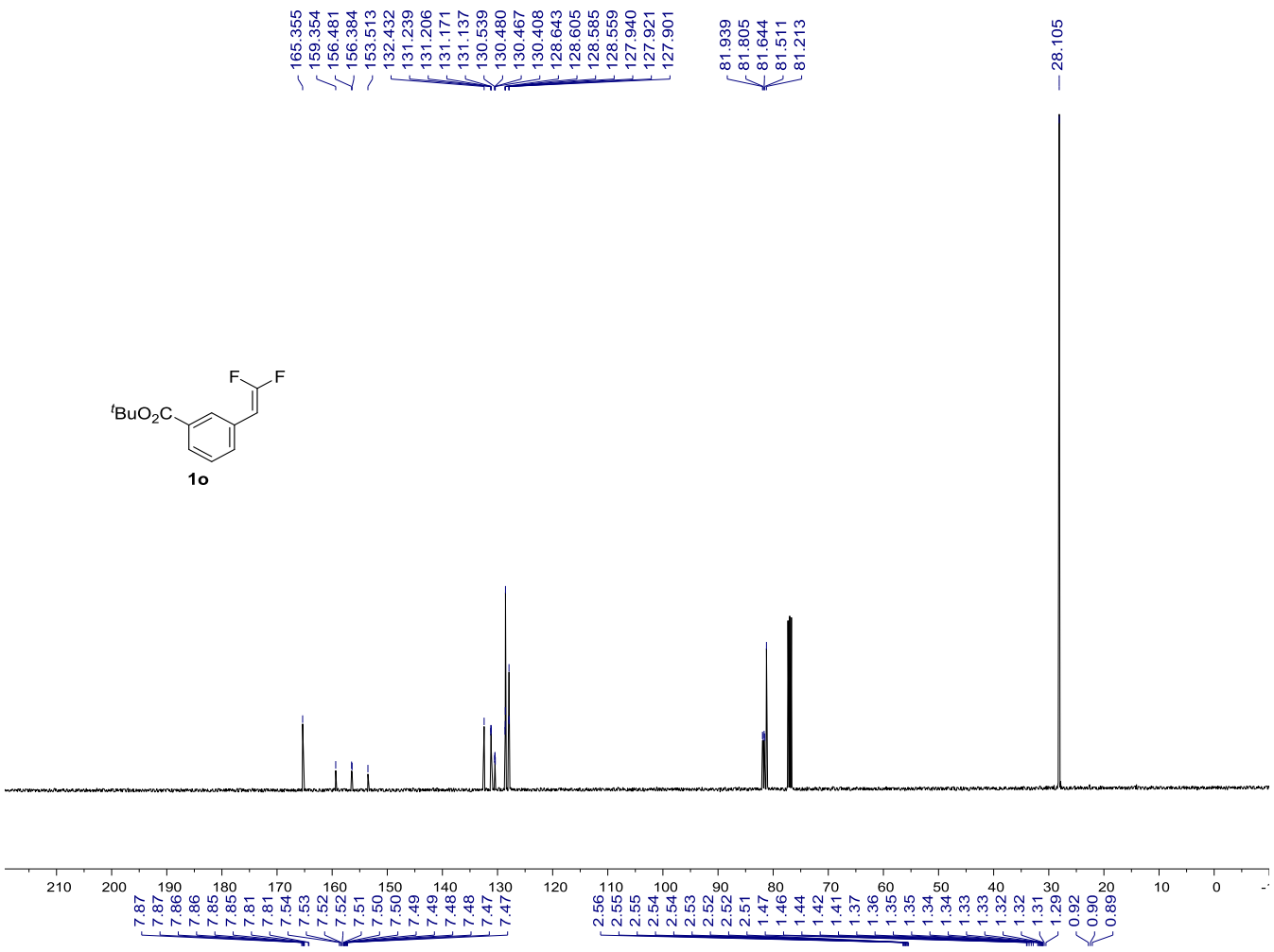
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F
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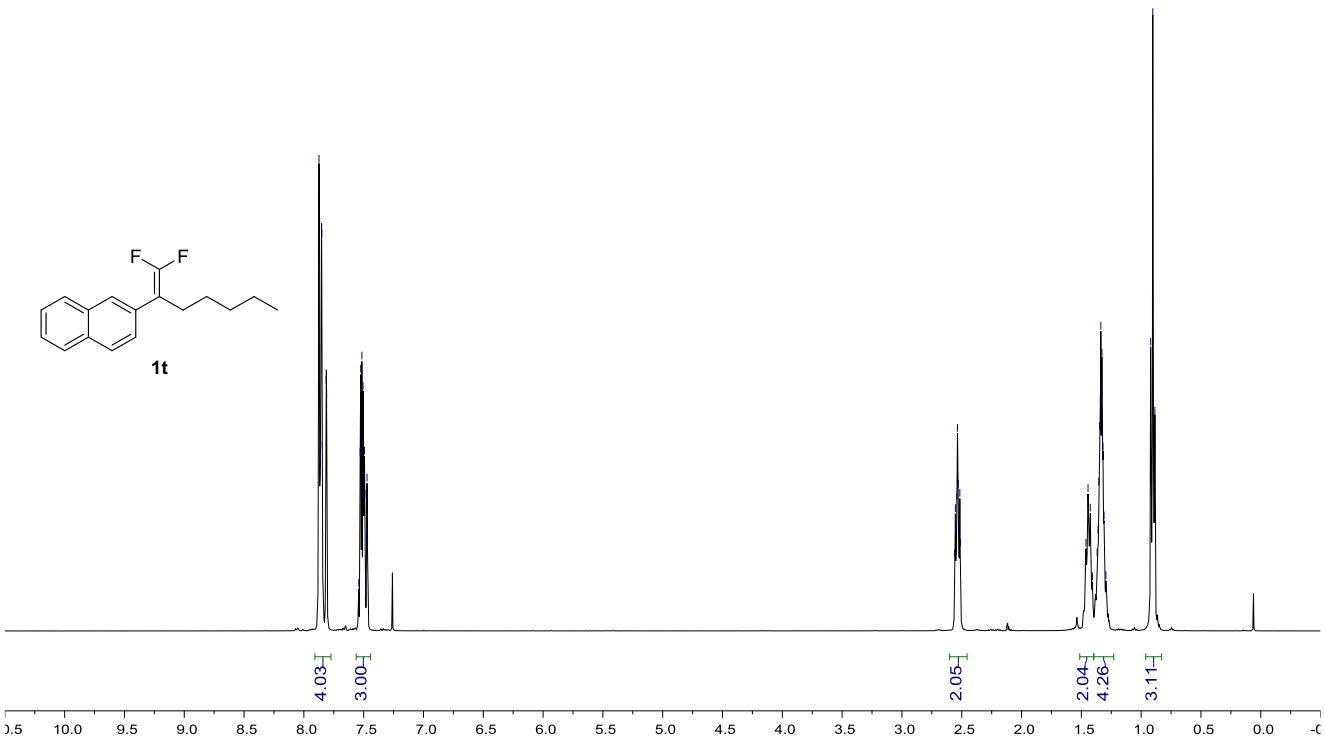
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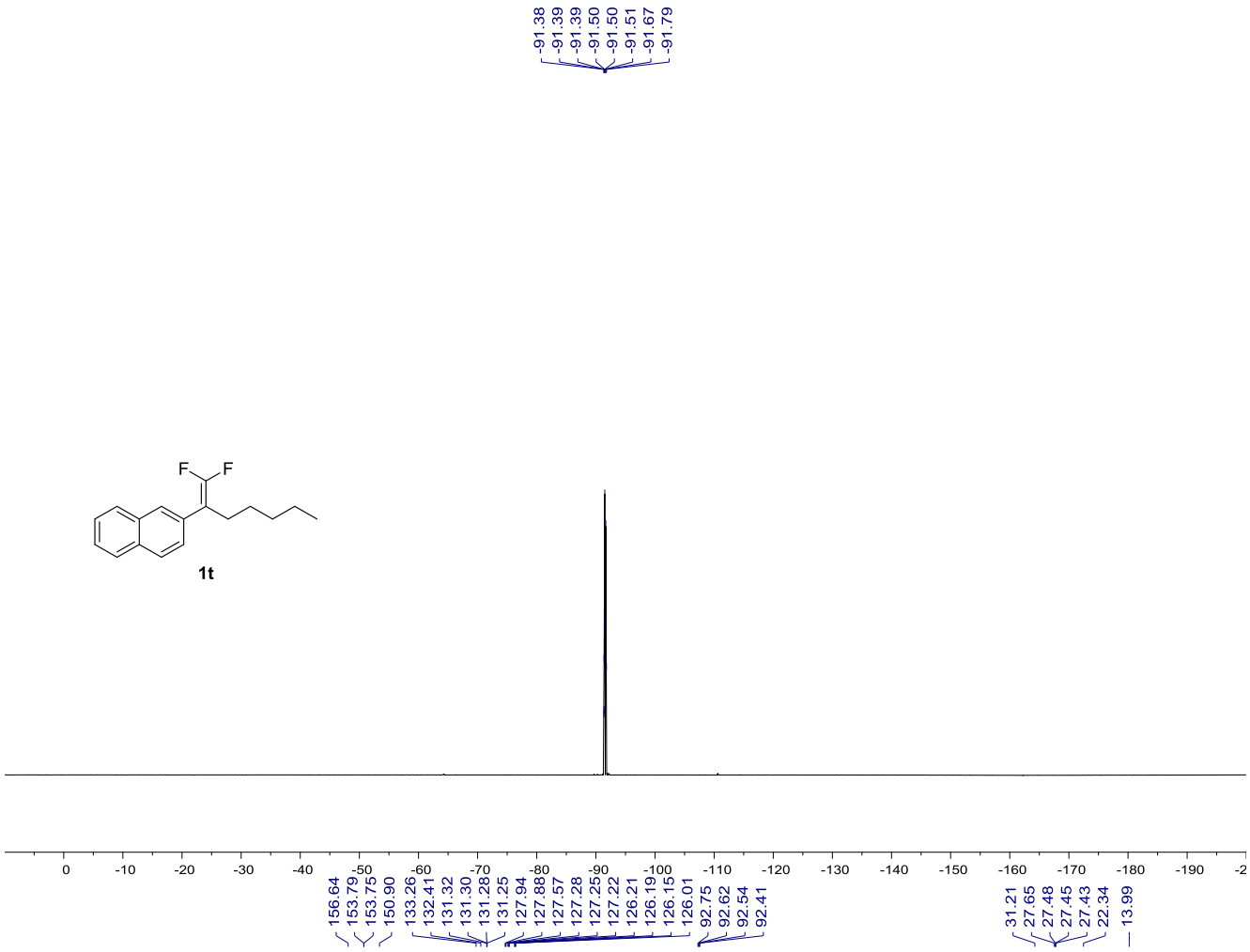
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F
F
1t
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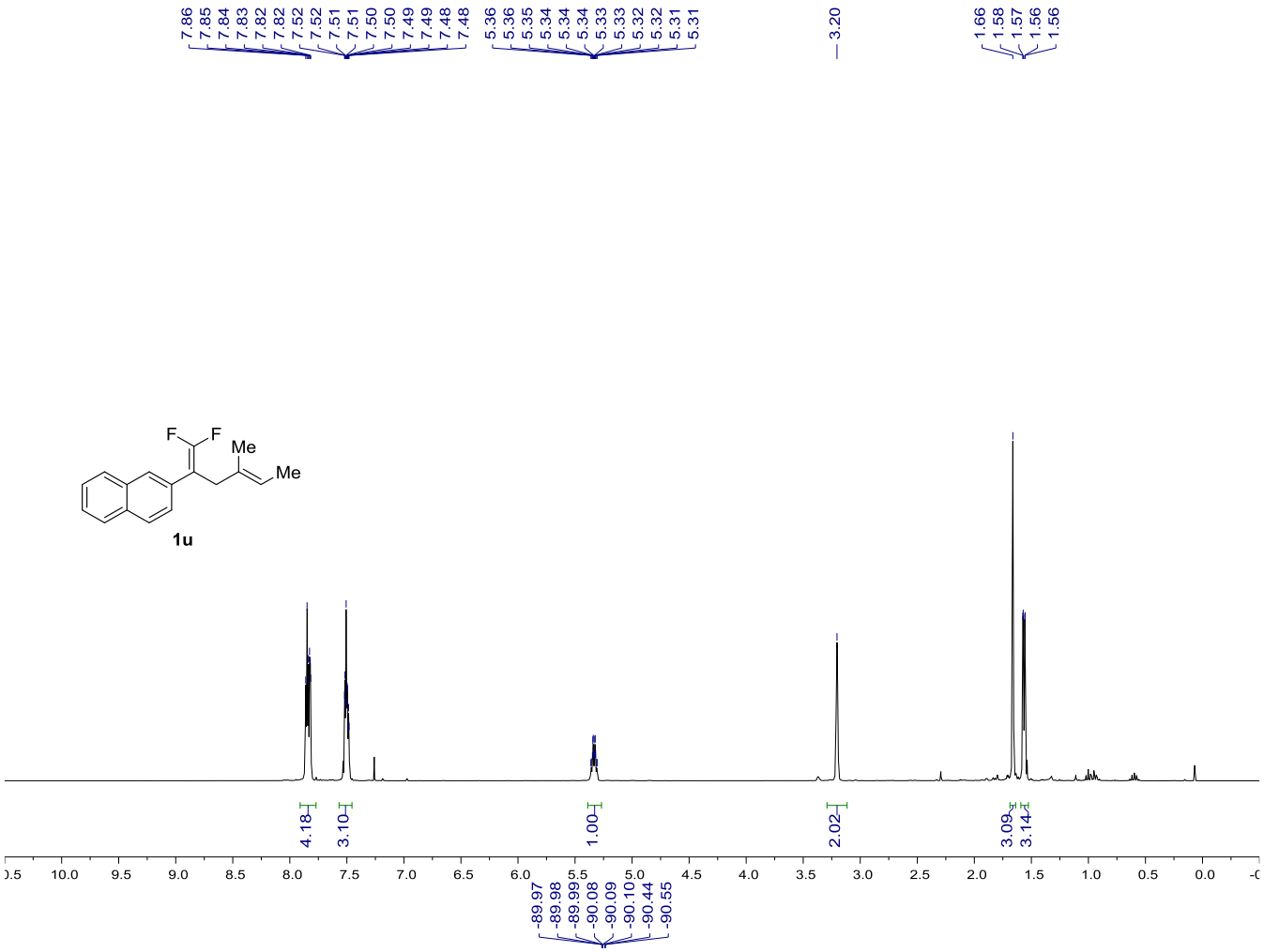
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F
F
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Me
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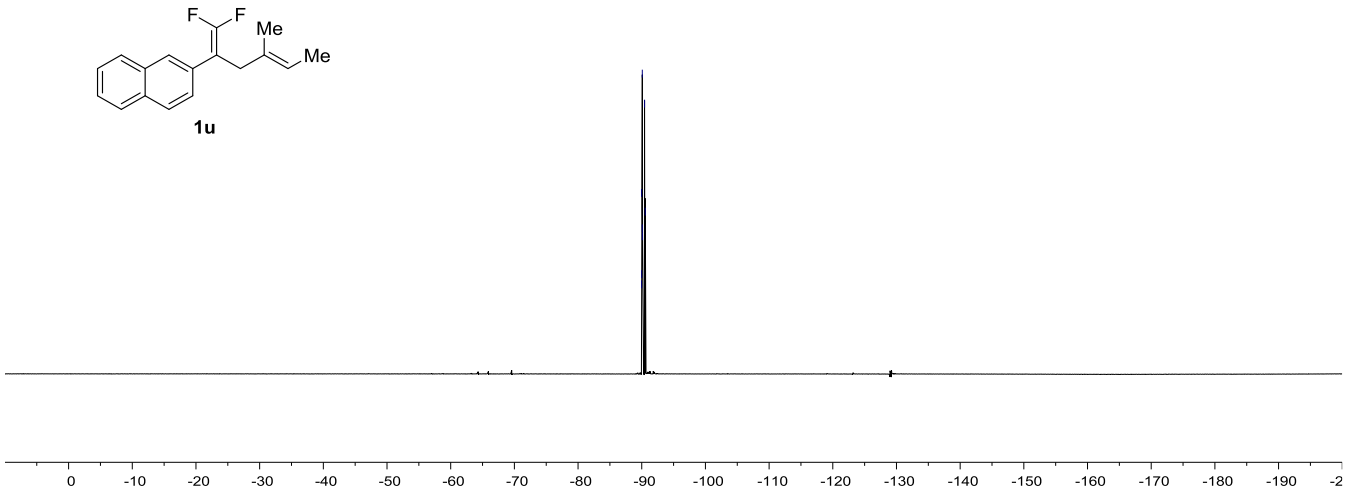
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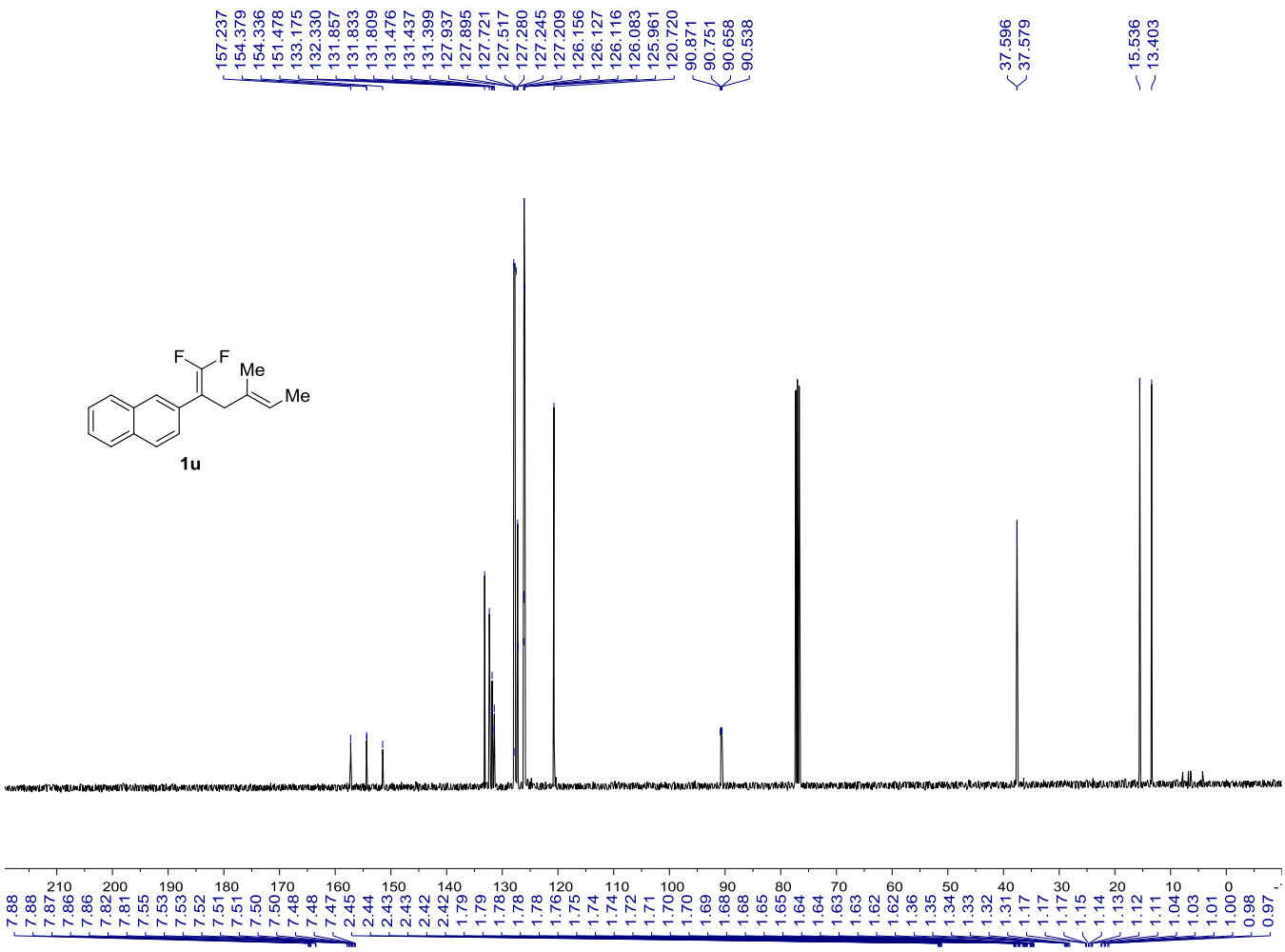
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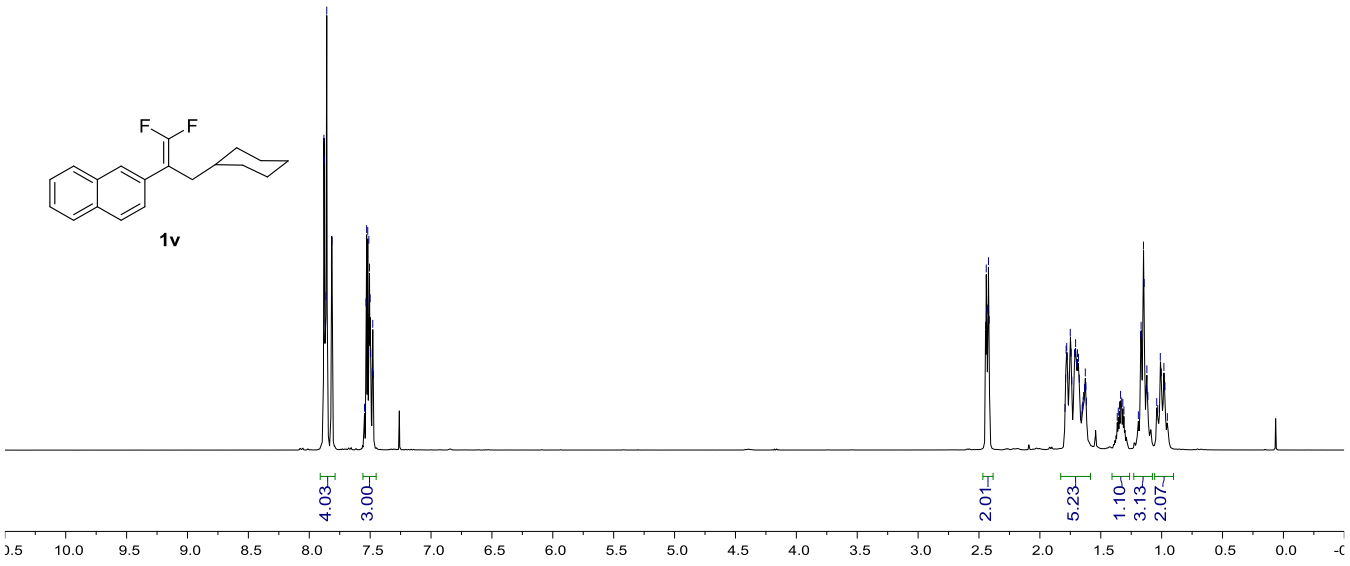
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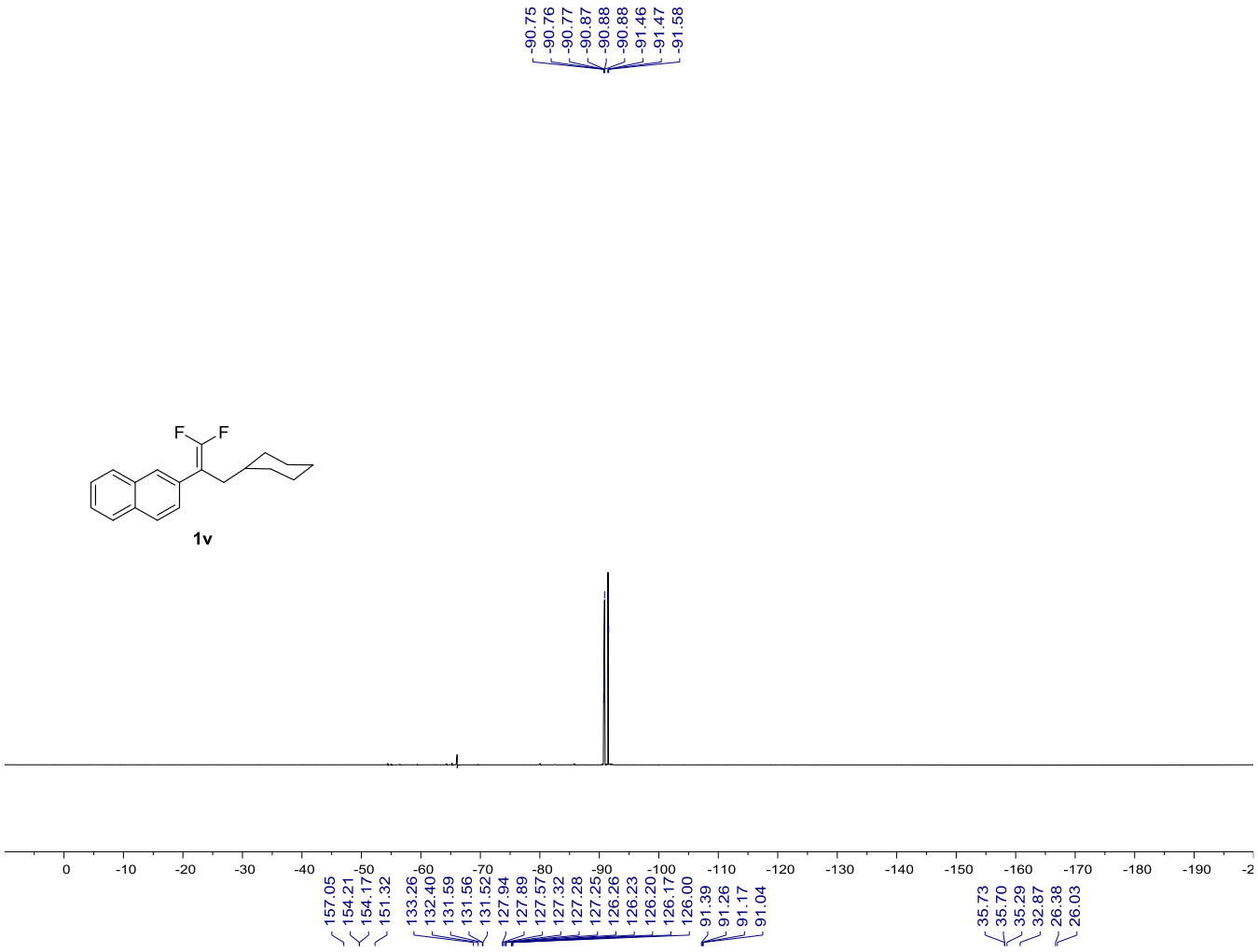
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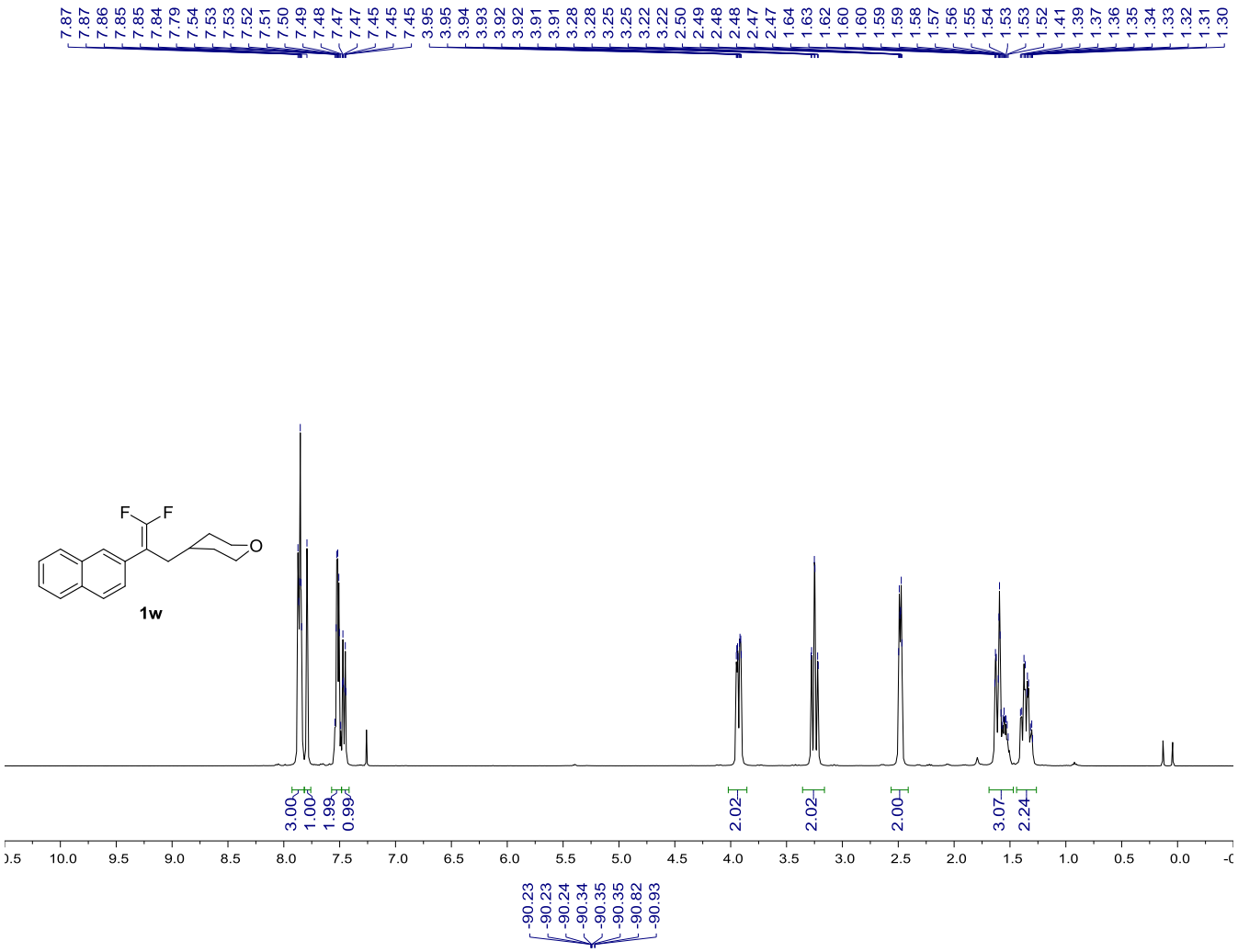
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O
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O
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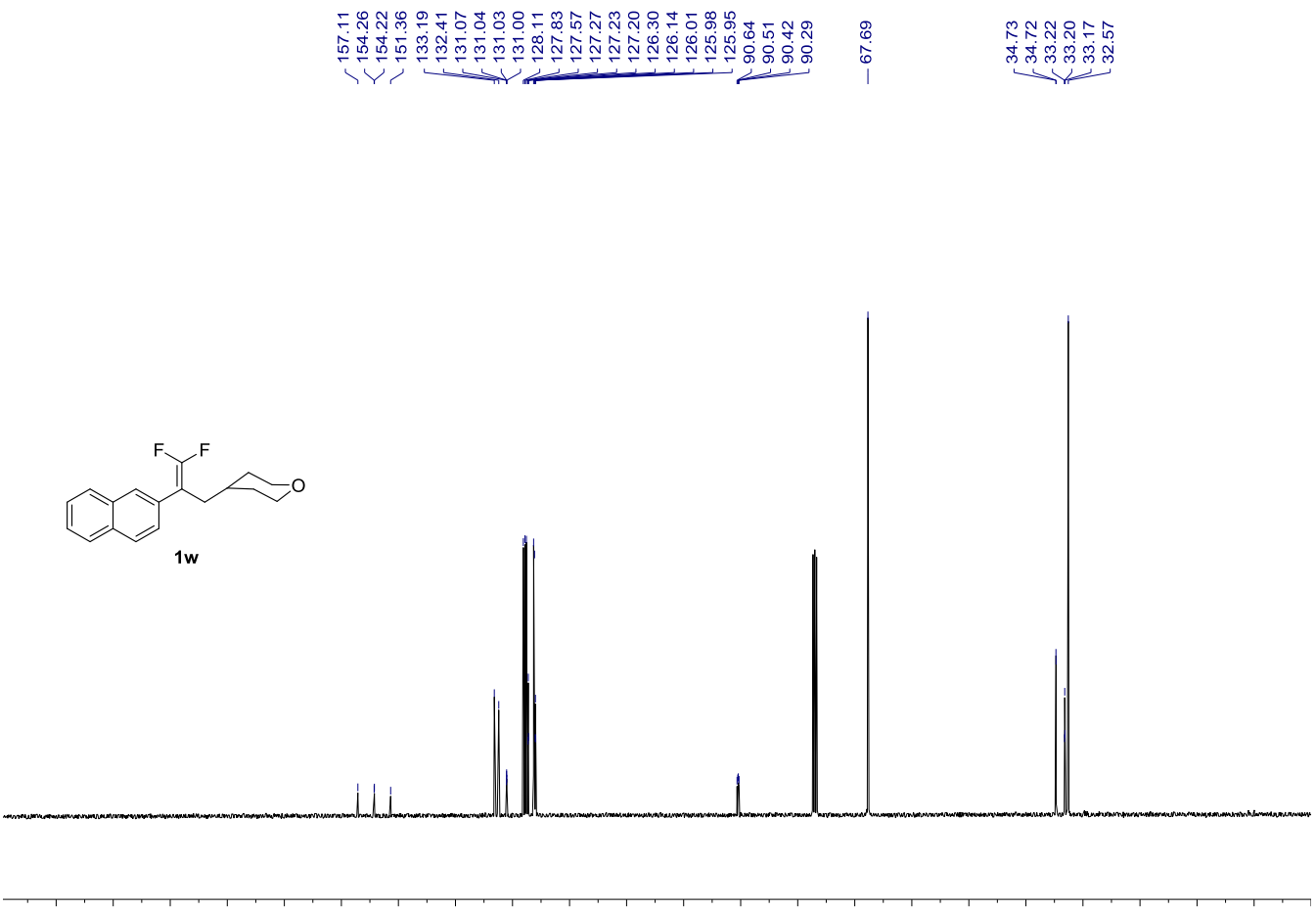
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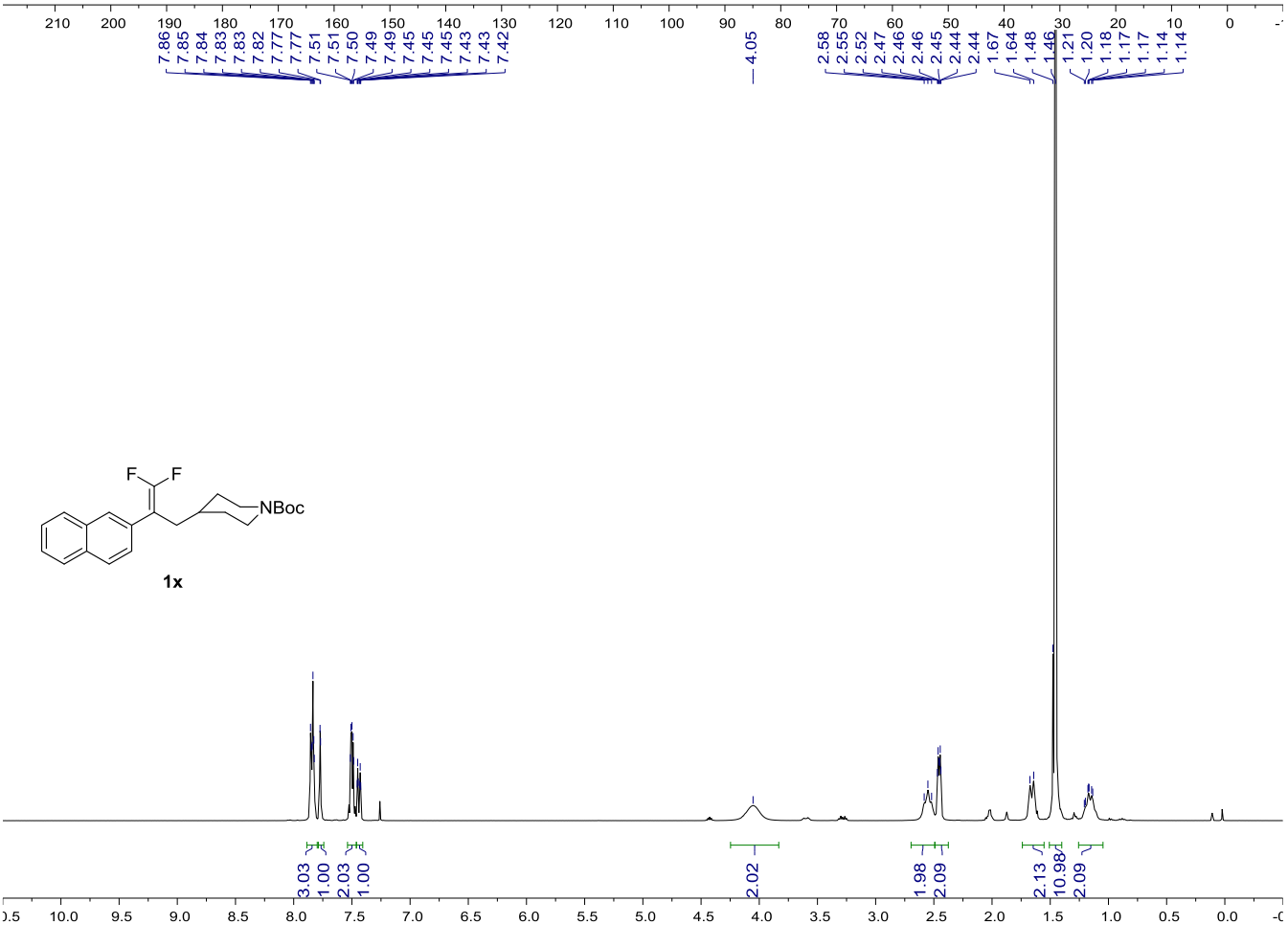
O
1w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2.44
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1.46
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1.17
1.17
1.14
1.14
F
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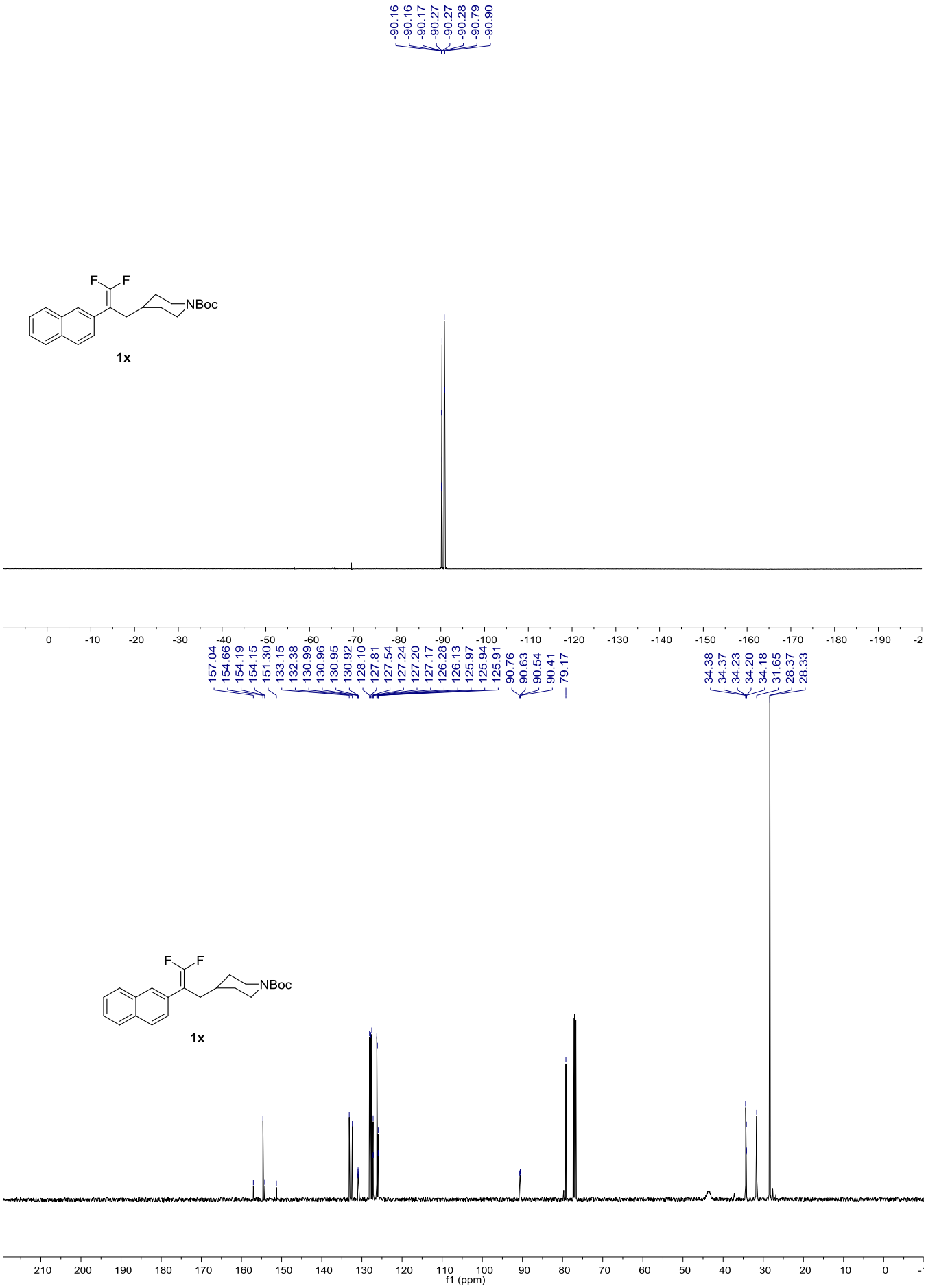
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-150
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28.37
28.33
F
F
NBoc
1x
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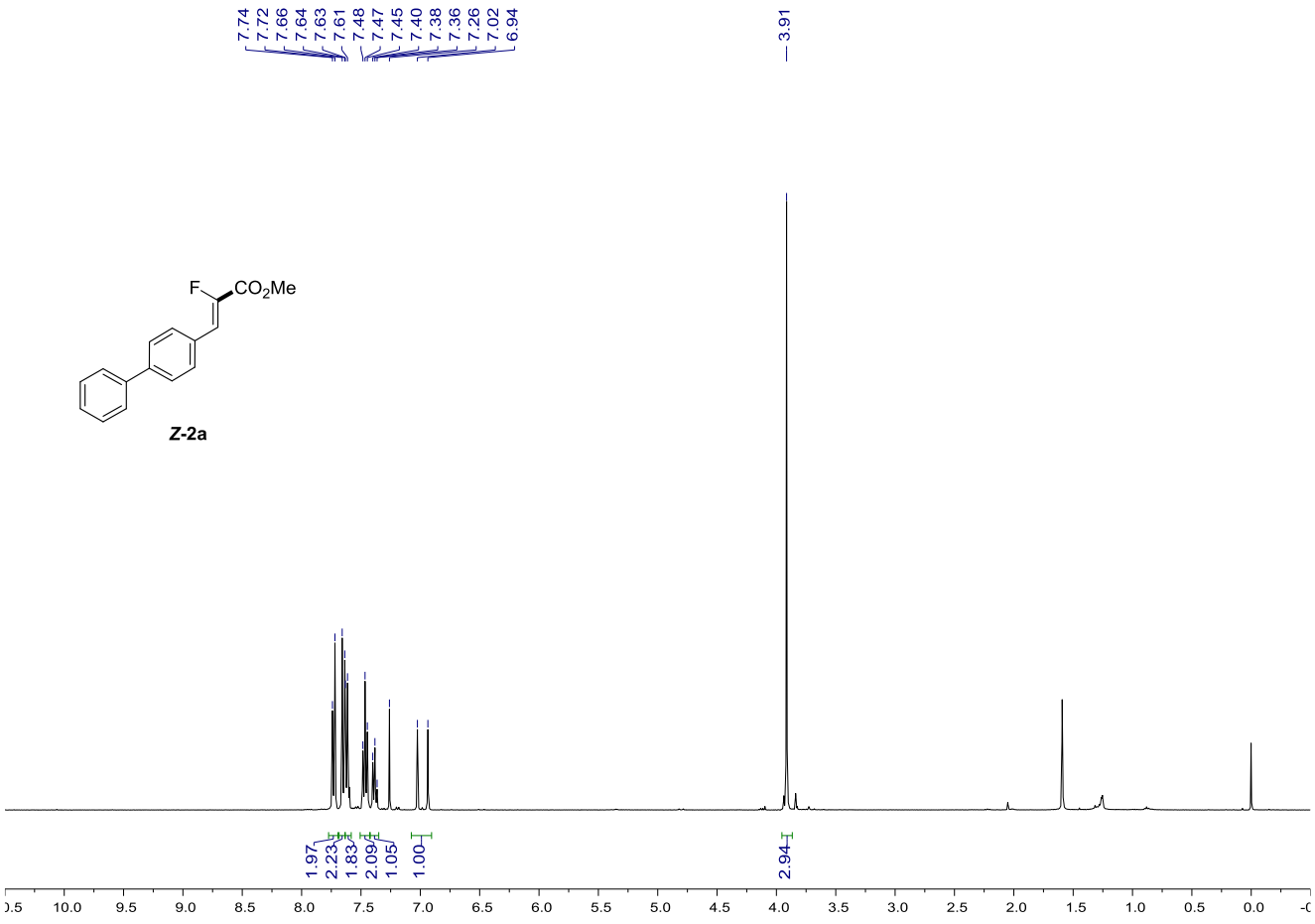
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7.26
7.02
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Z-2a
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2.09
1.05
1.00
2.94


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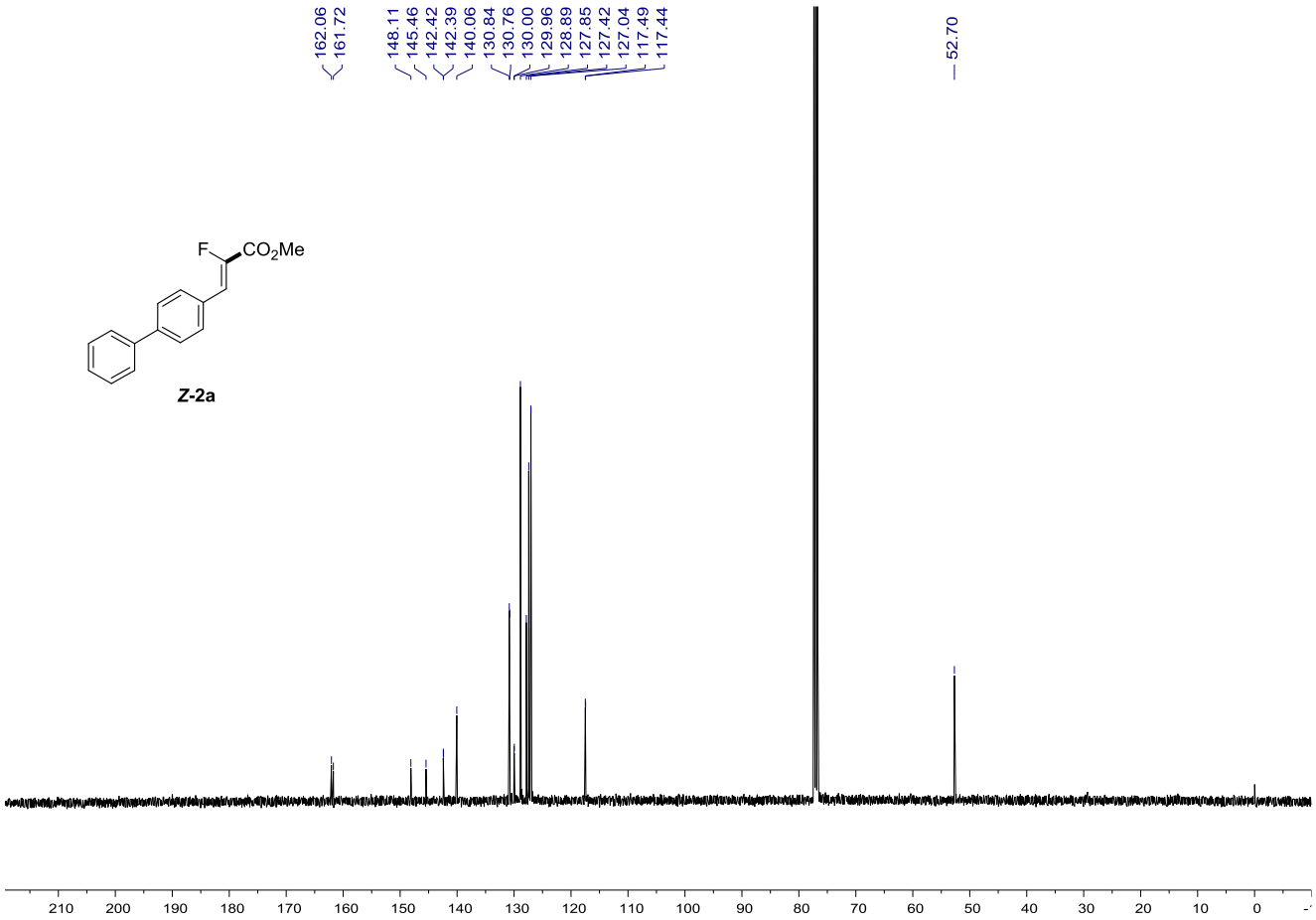
Z-2a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127.42
127.04
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CO2Me
Z-2a
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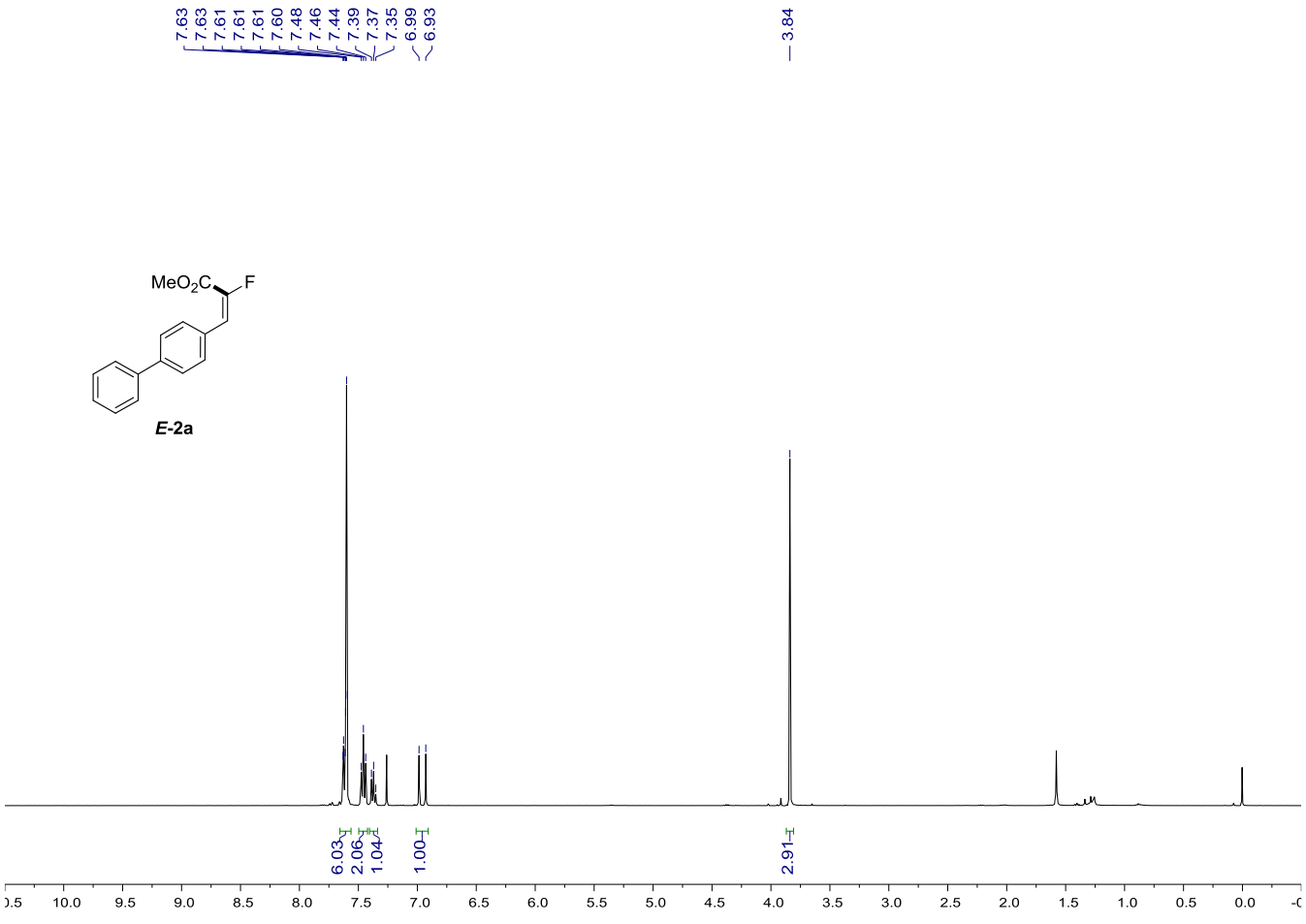
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MeO2C
F
E-2a
6.03
2.06
1.04
1.00
2.91
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8.0
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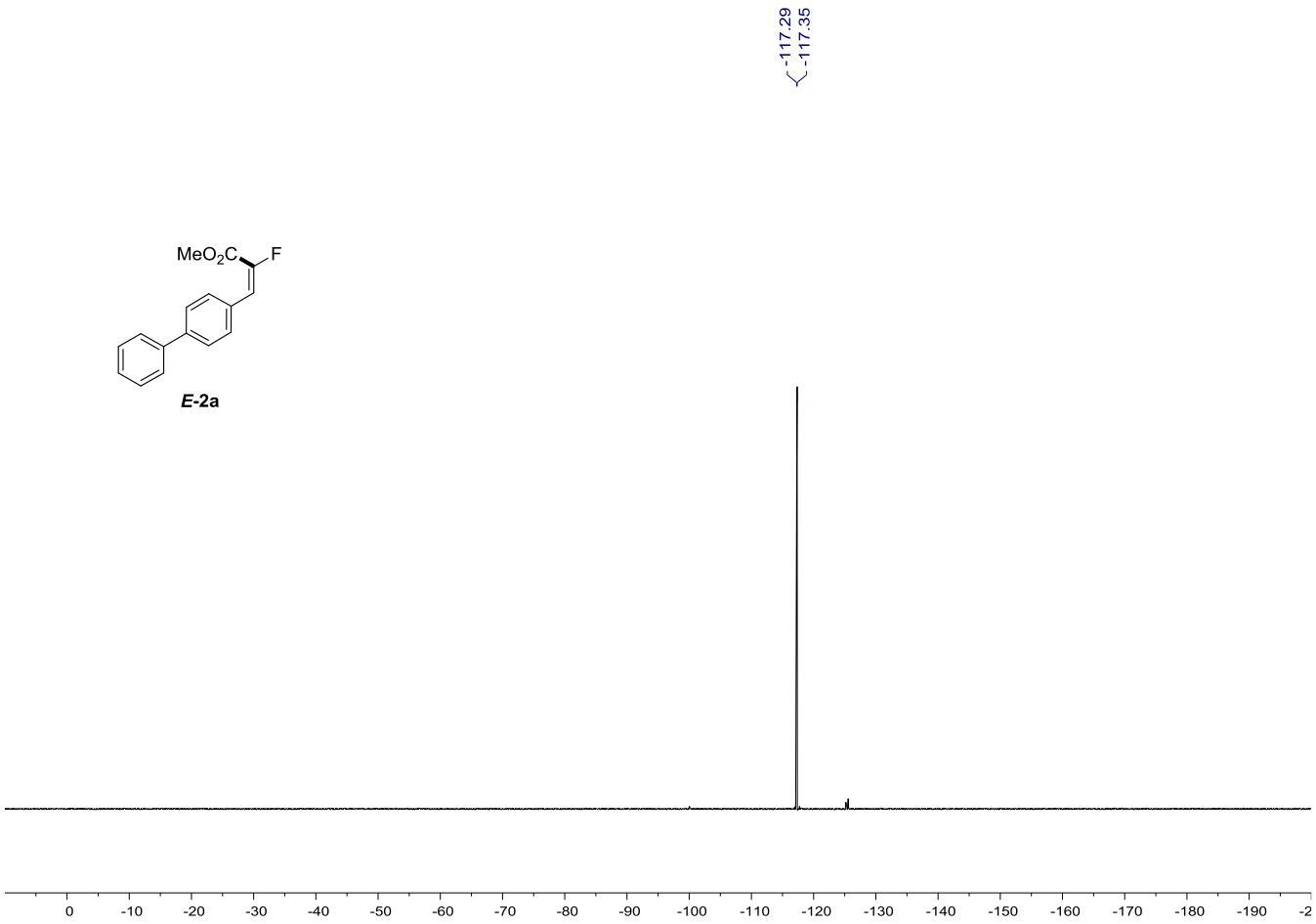
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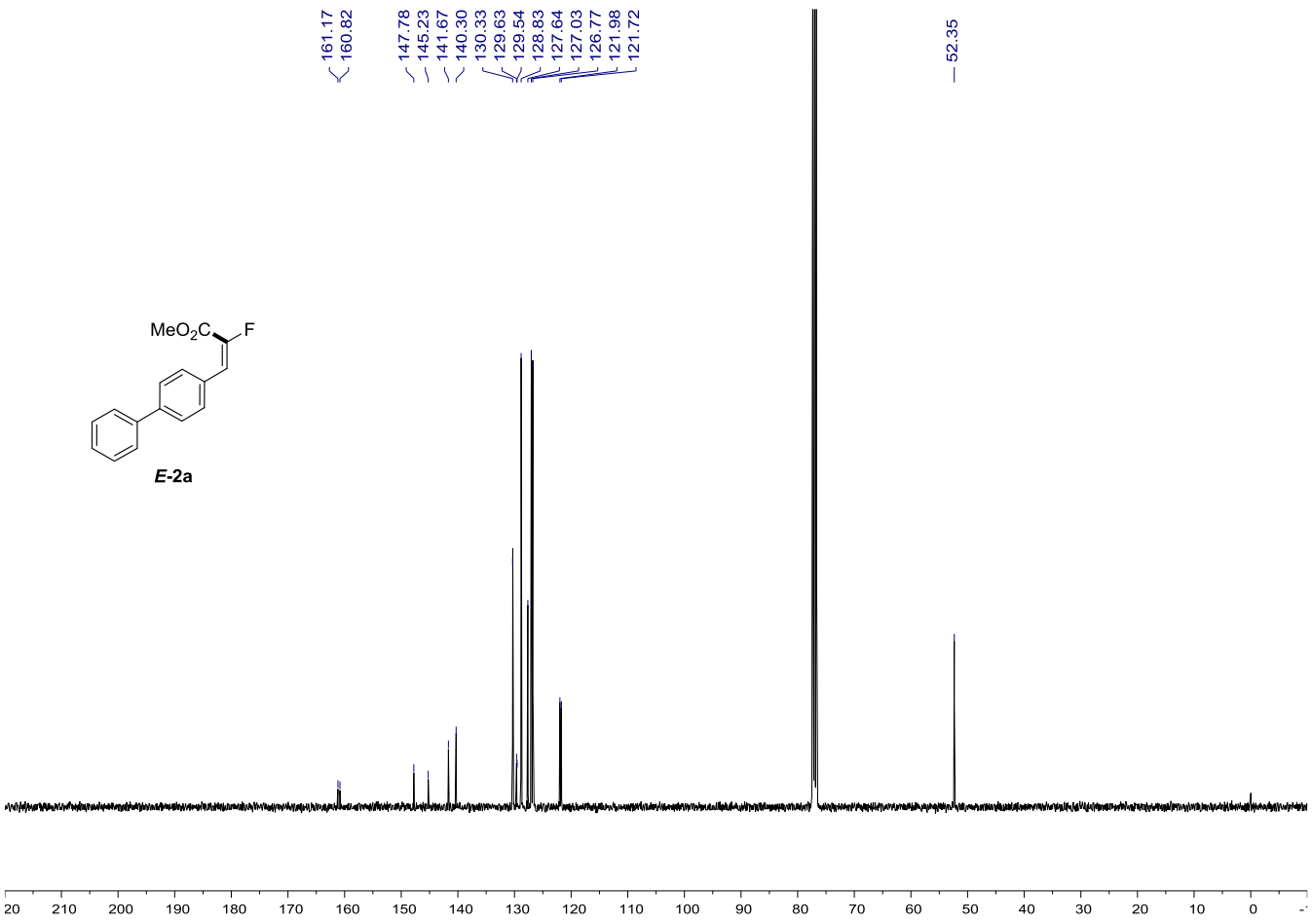
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127.03
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52.35
MeO2C
F
E-2a
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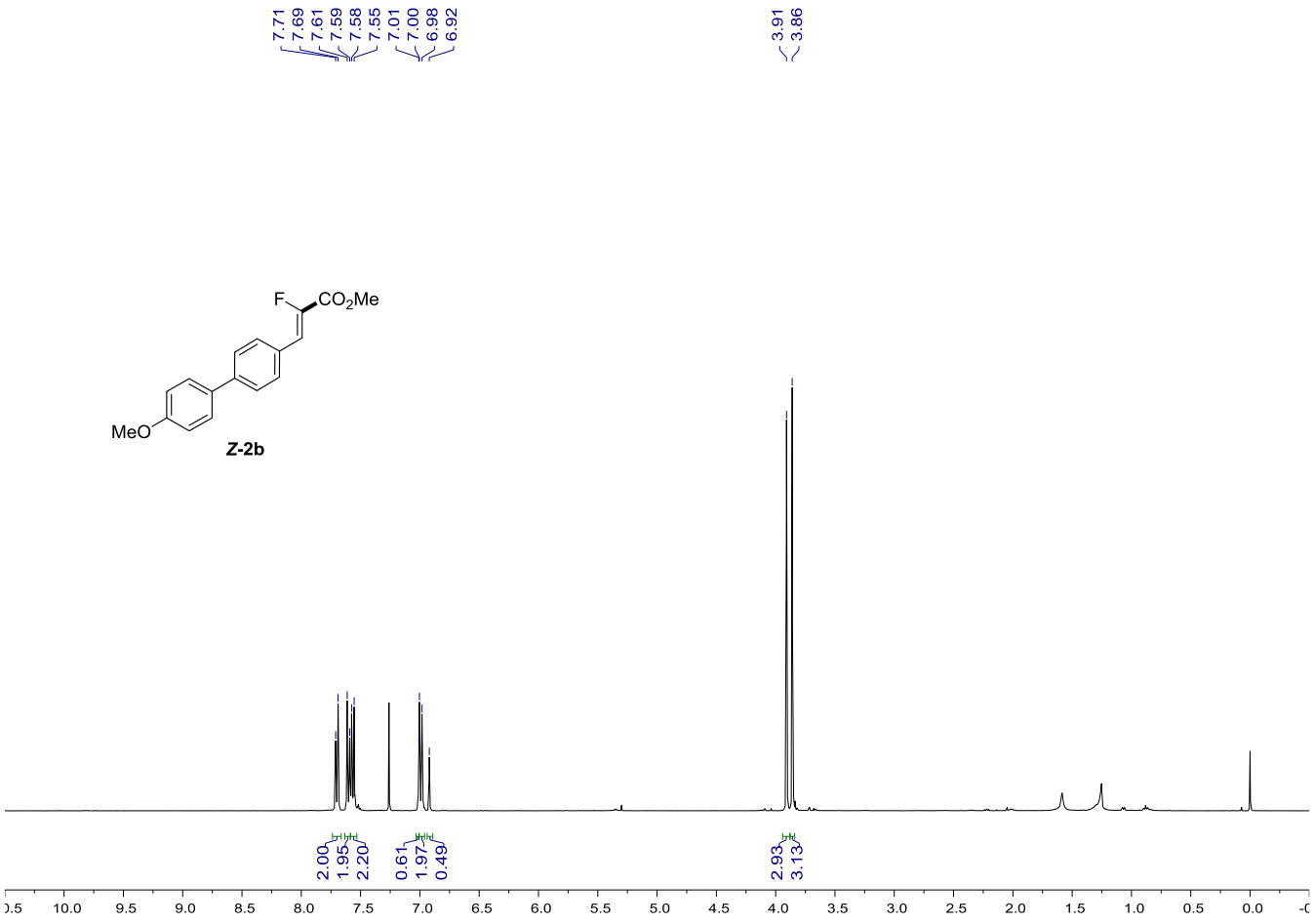
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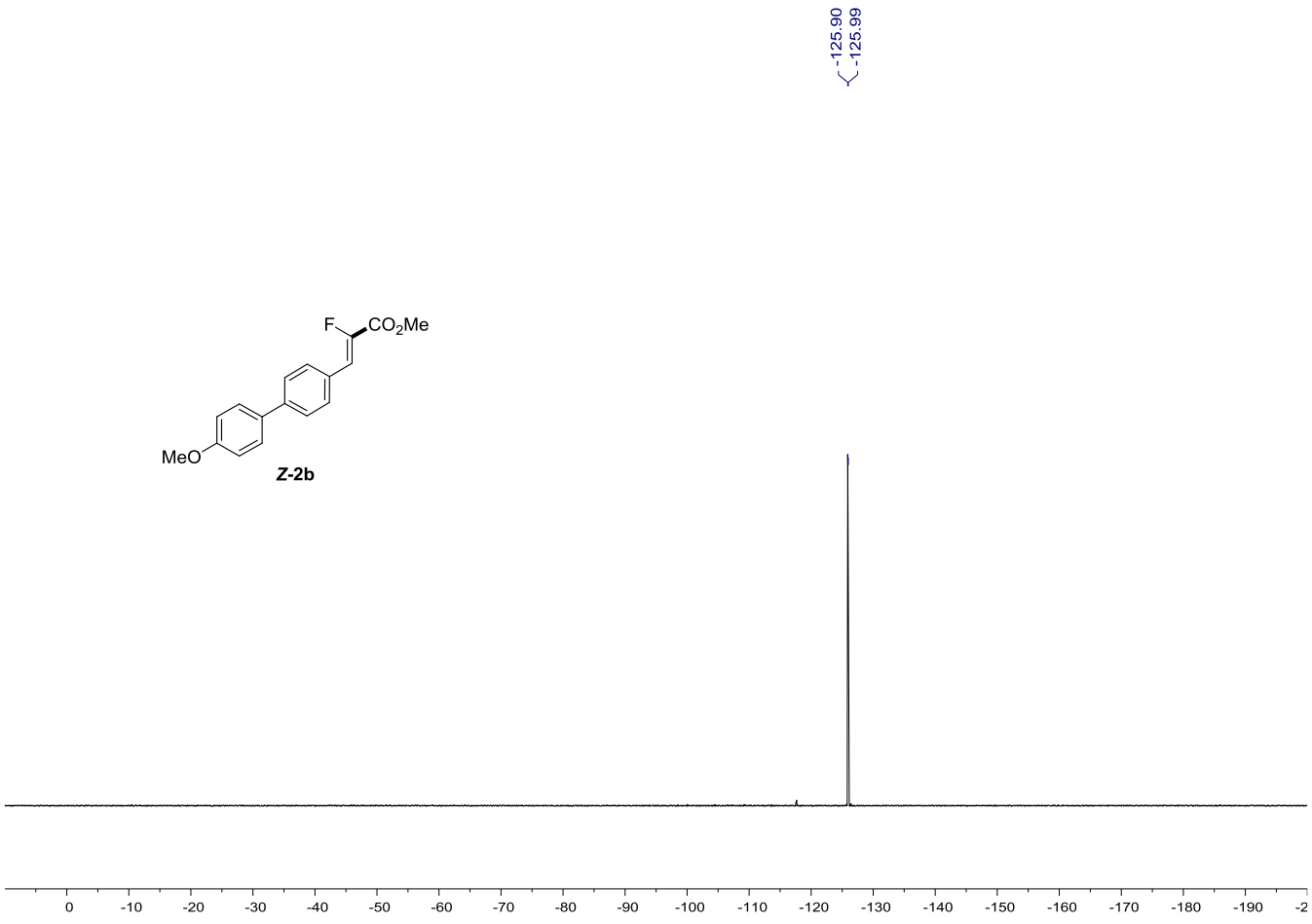
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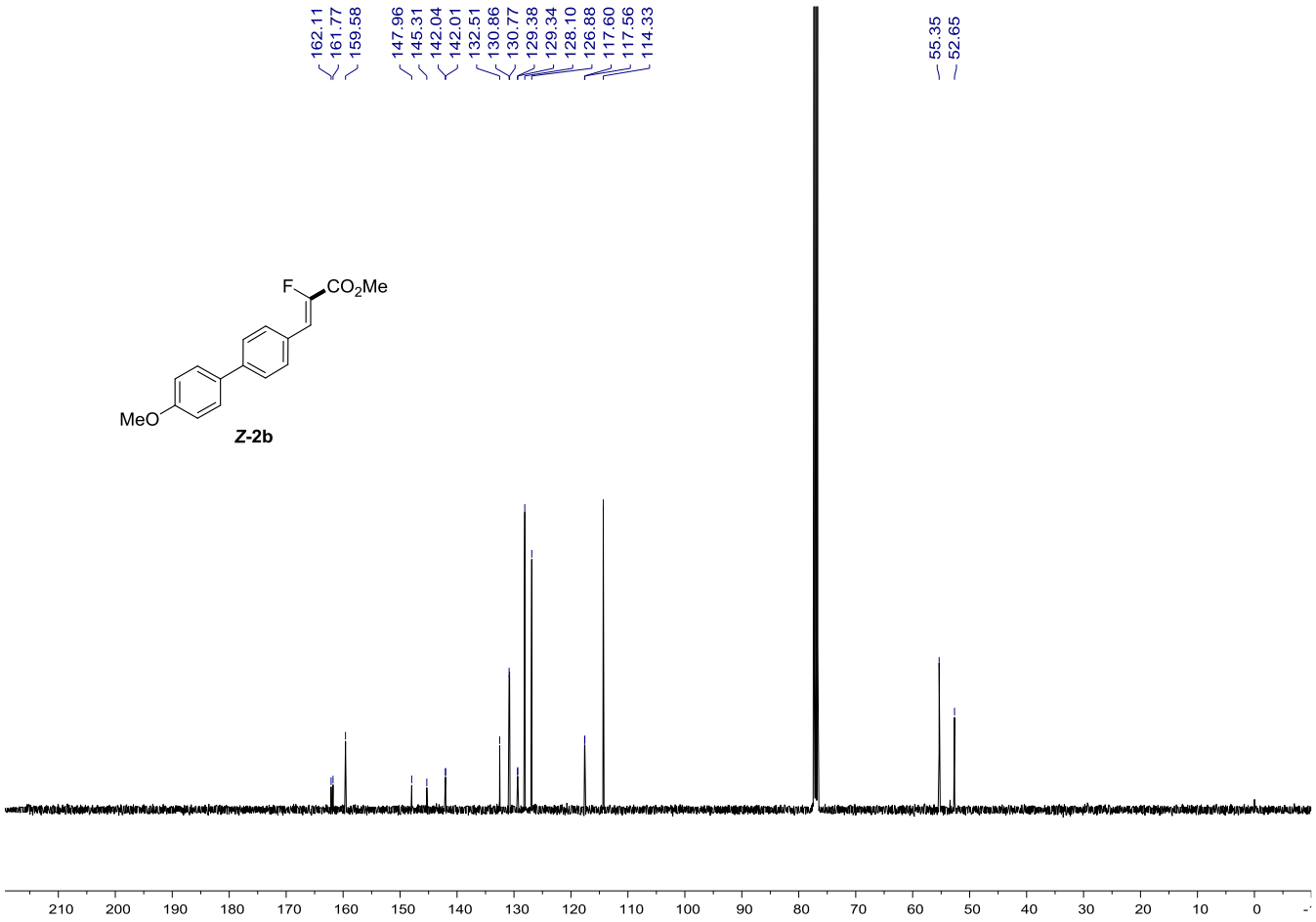
Z-2b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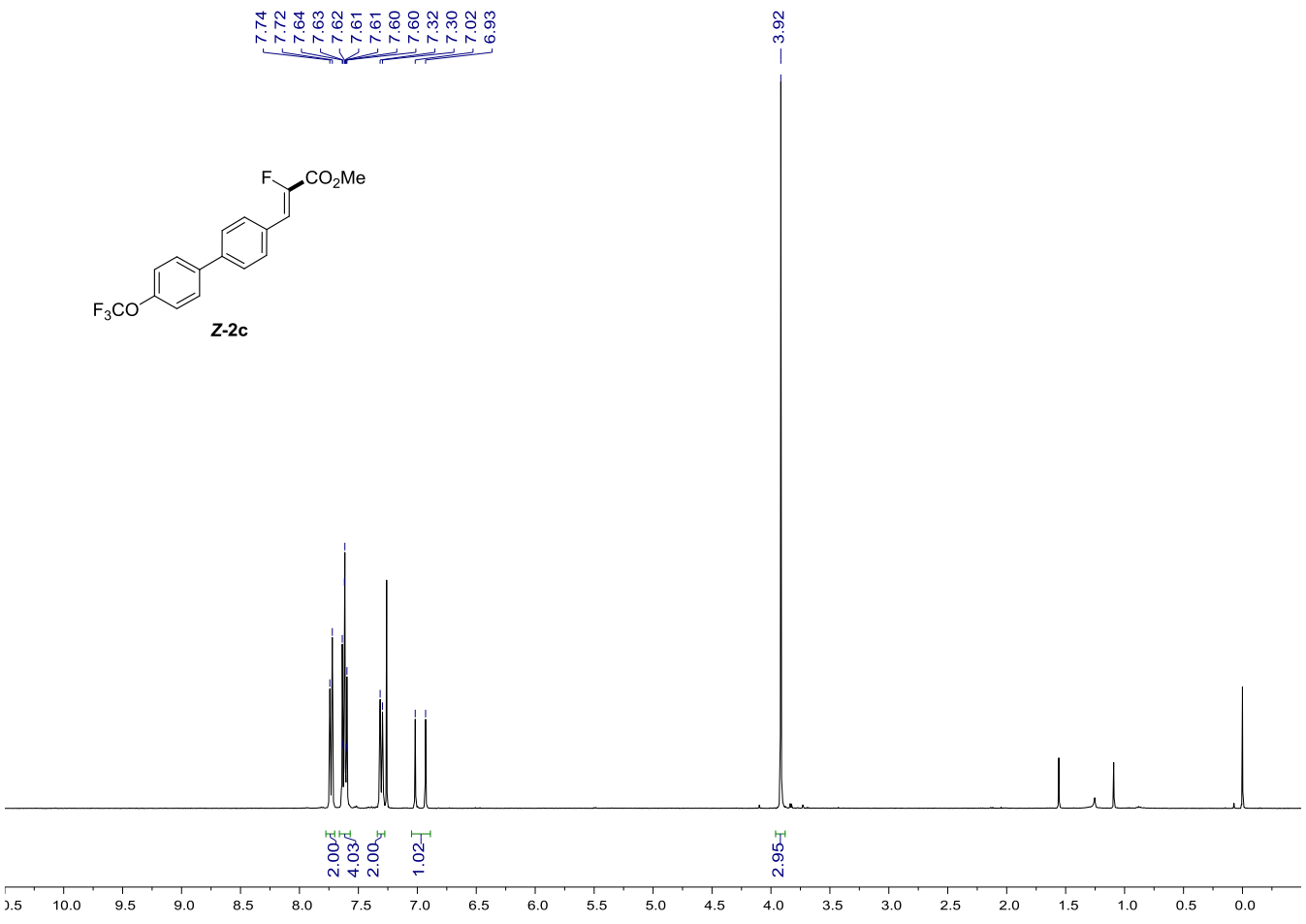
CO2Me
MeO
Z-2b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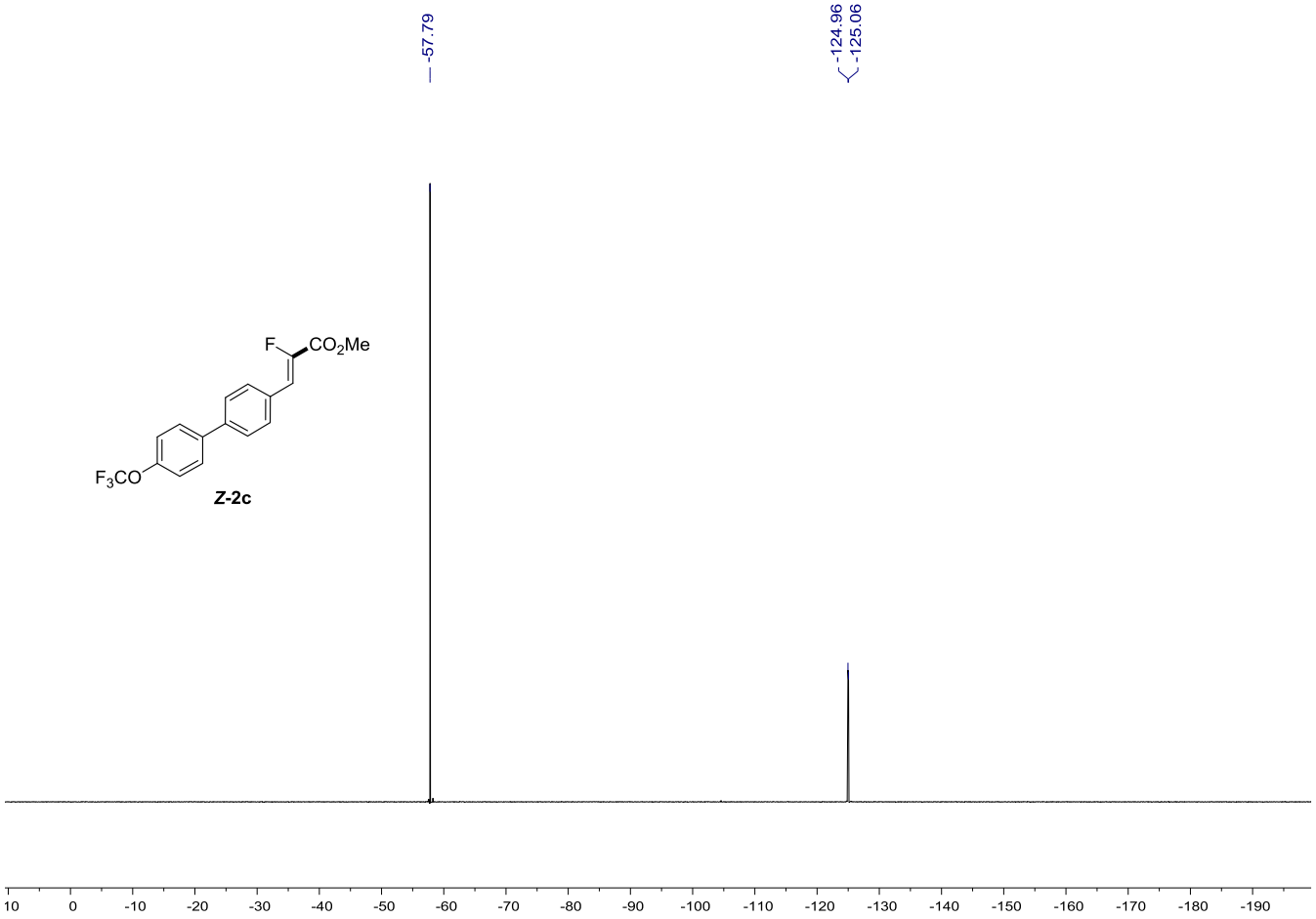
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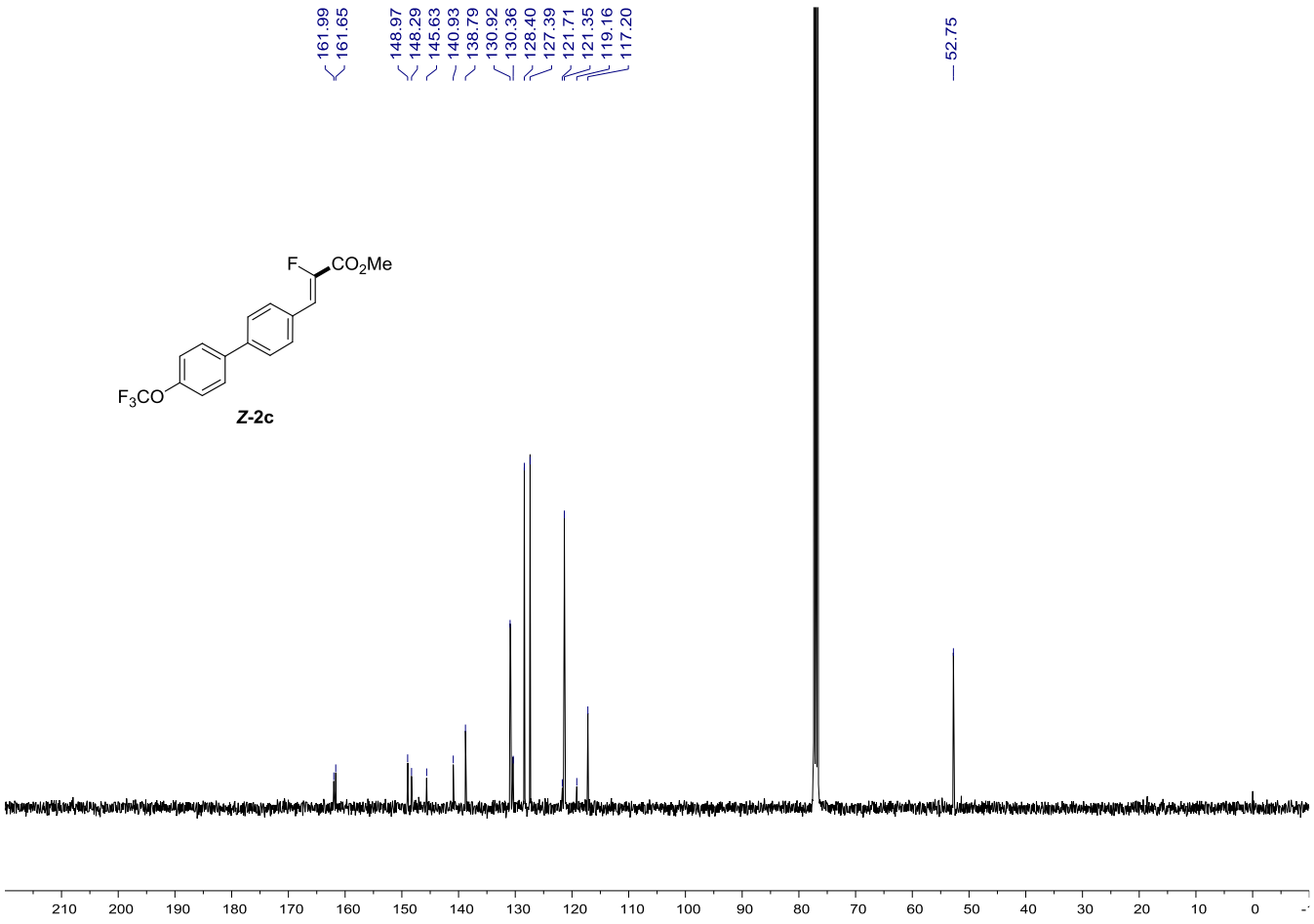
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F3CO
Z-2c
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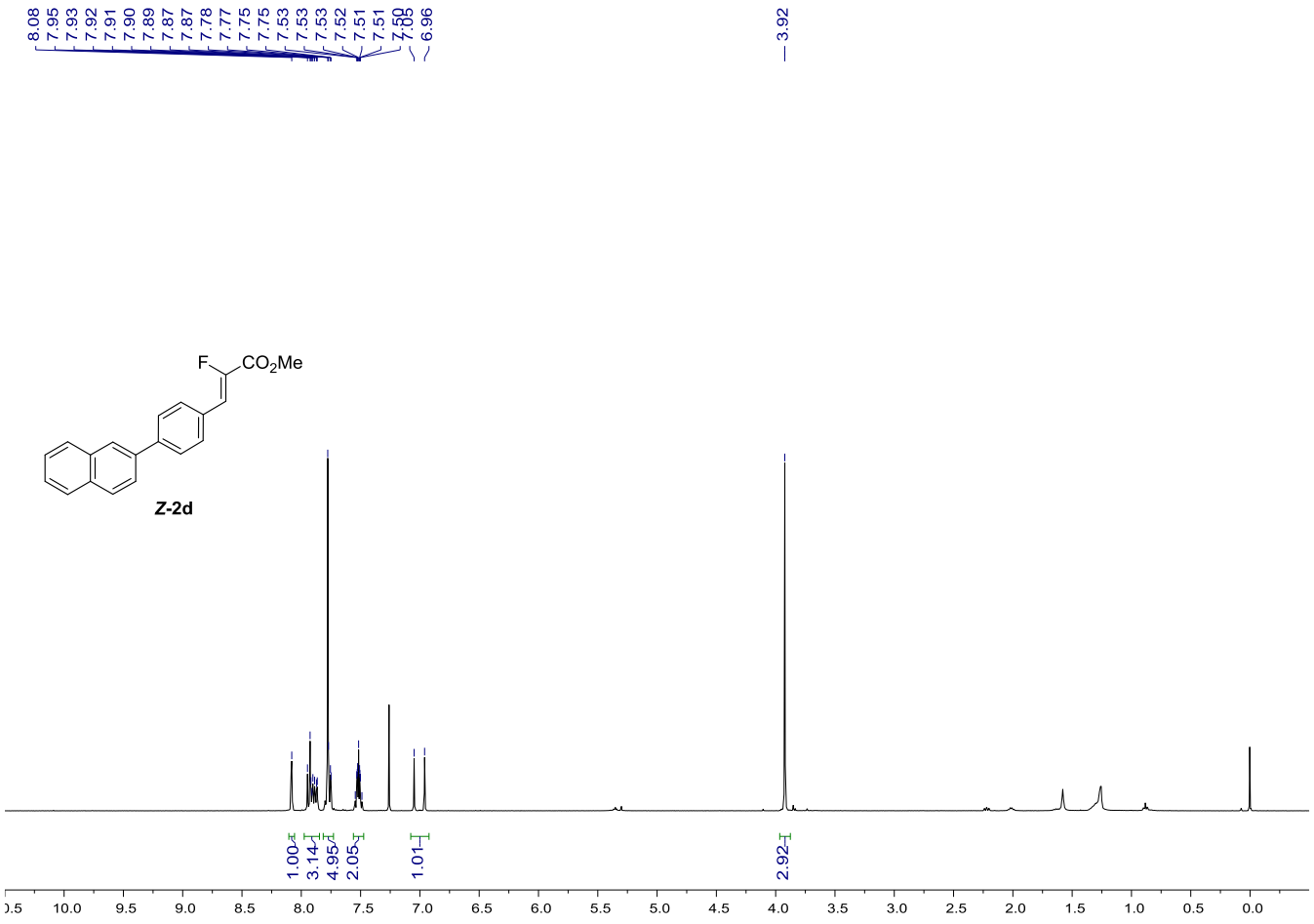
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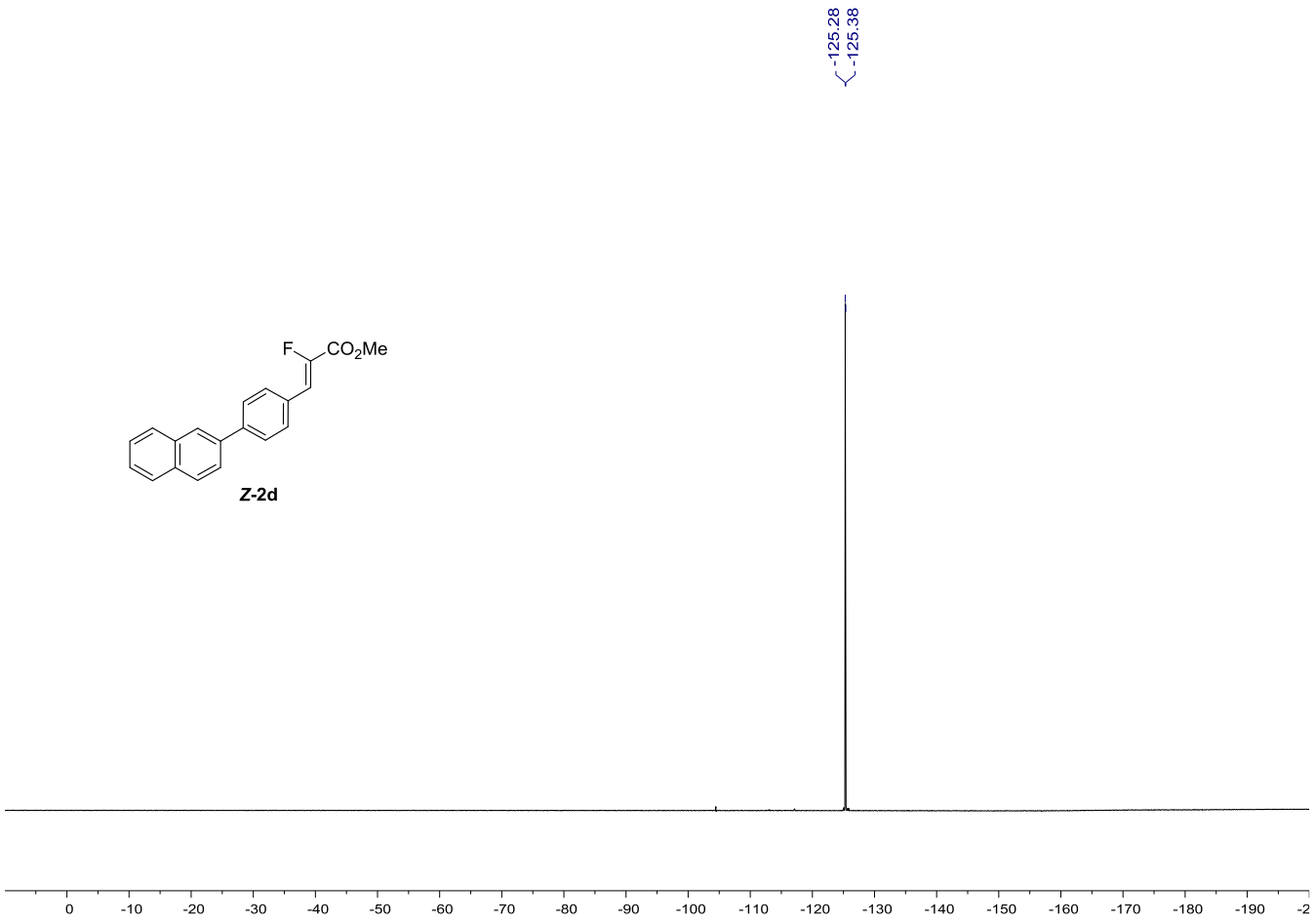
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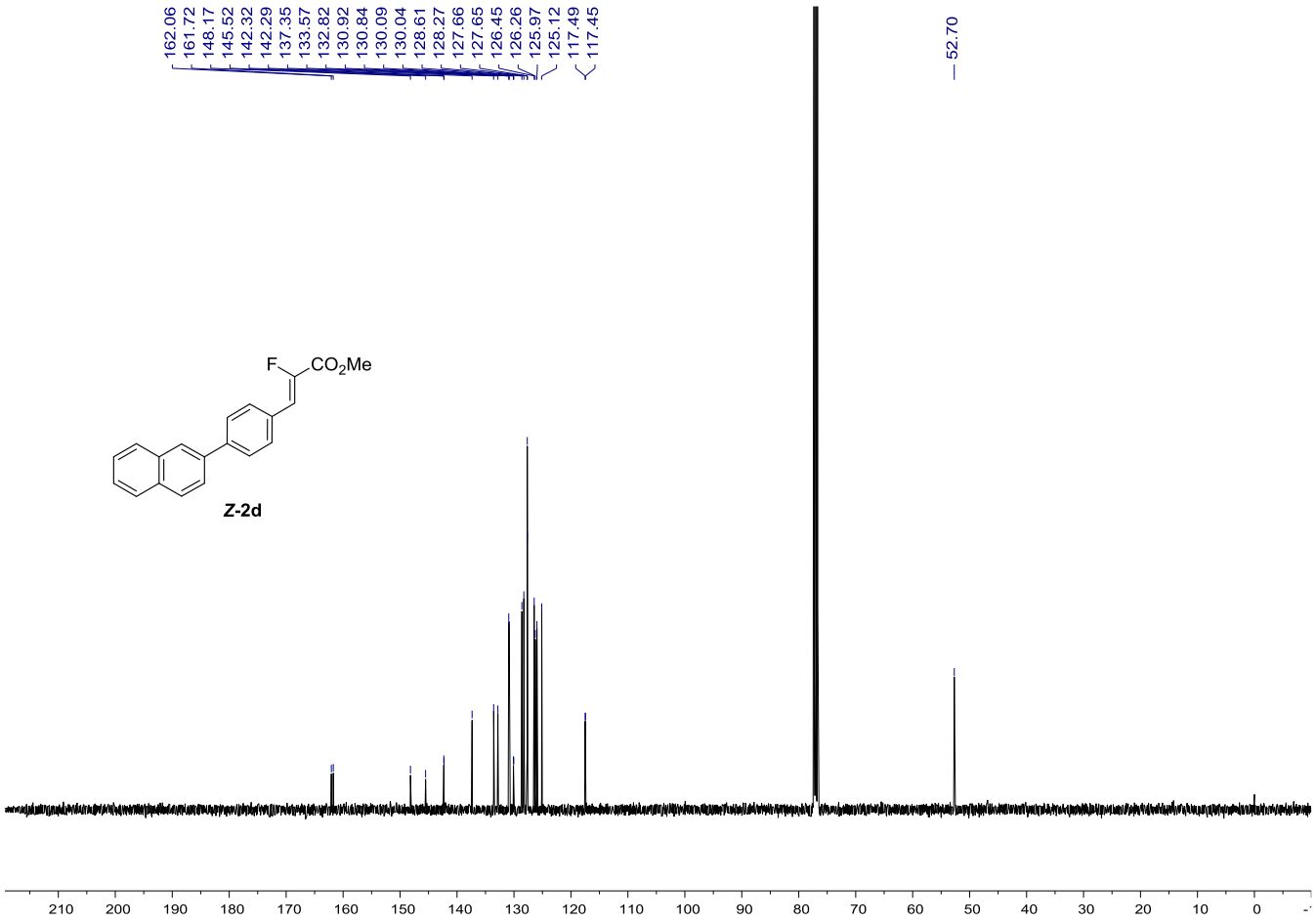
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Z-2d
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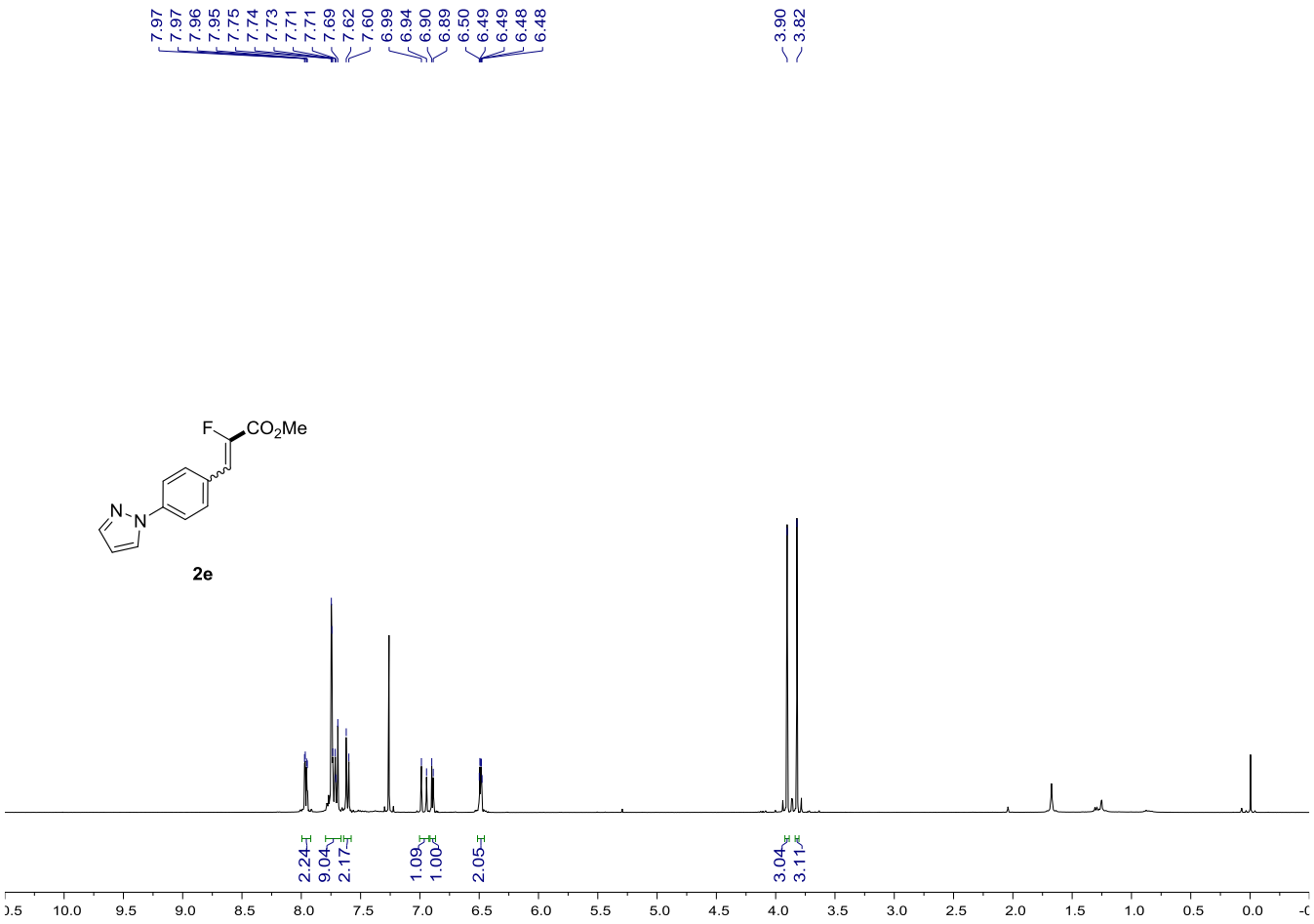
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6.48
6.48
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N
2e
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2.17
1.09
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3.04
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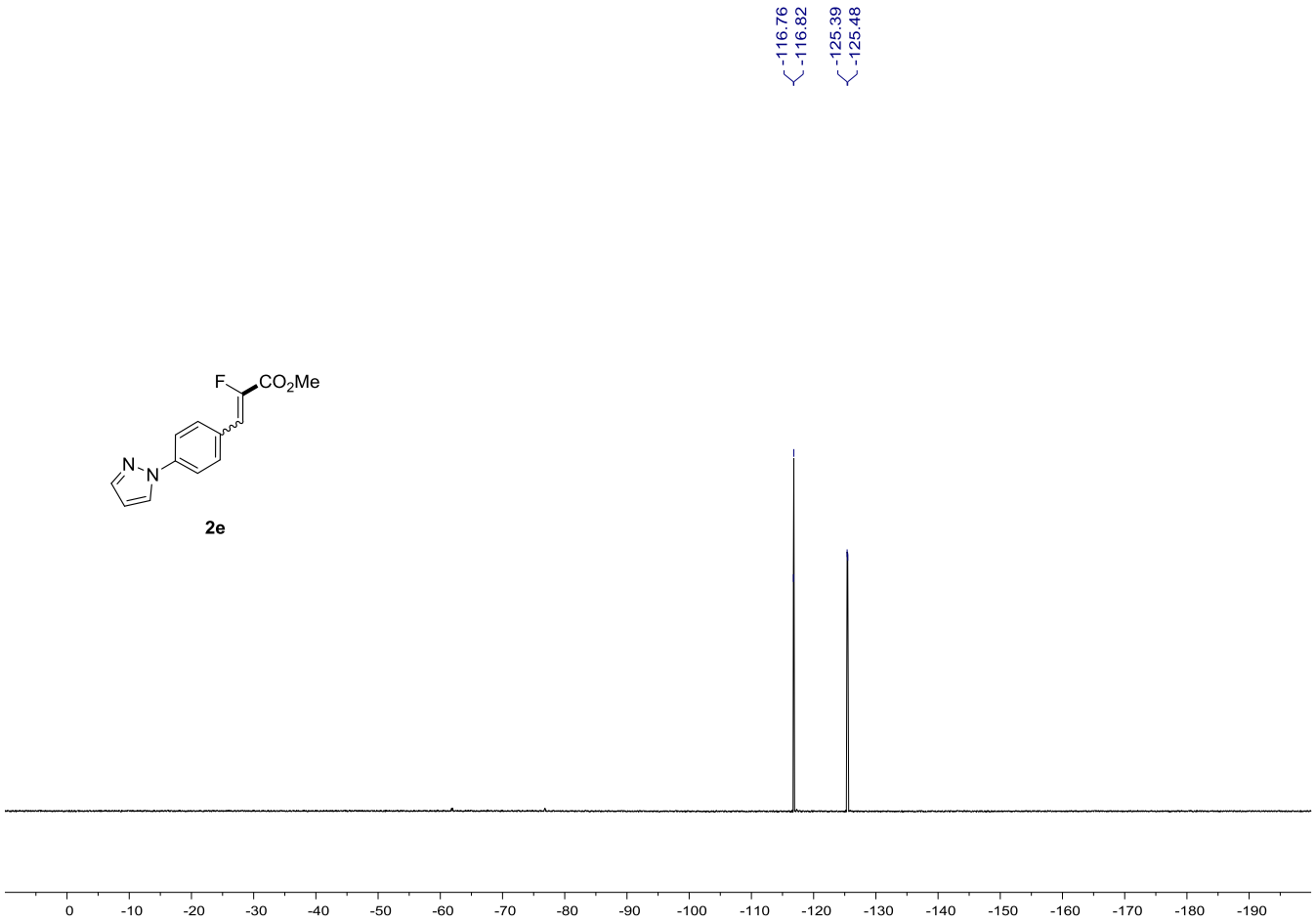
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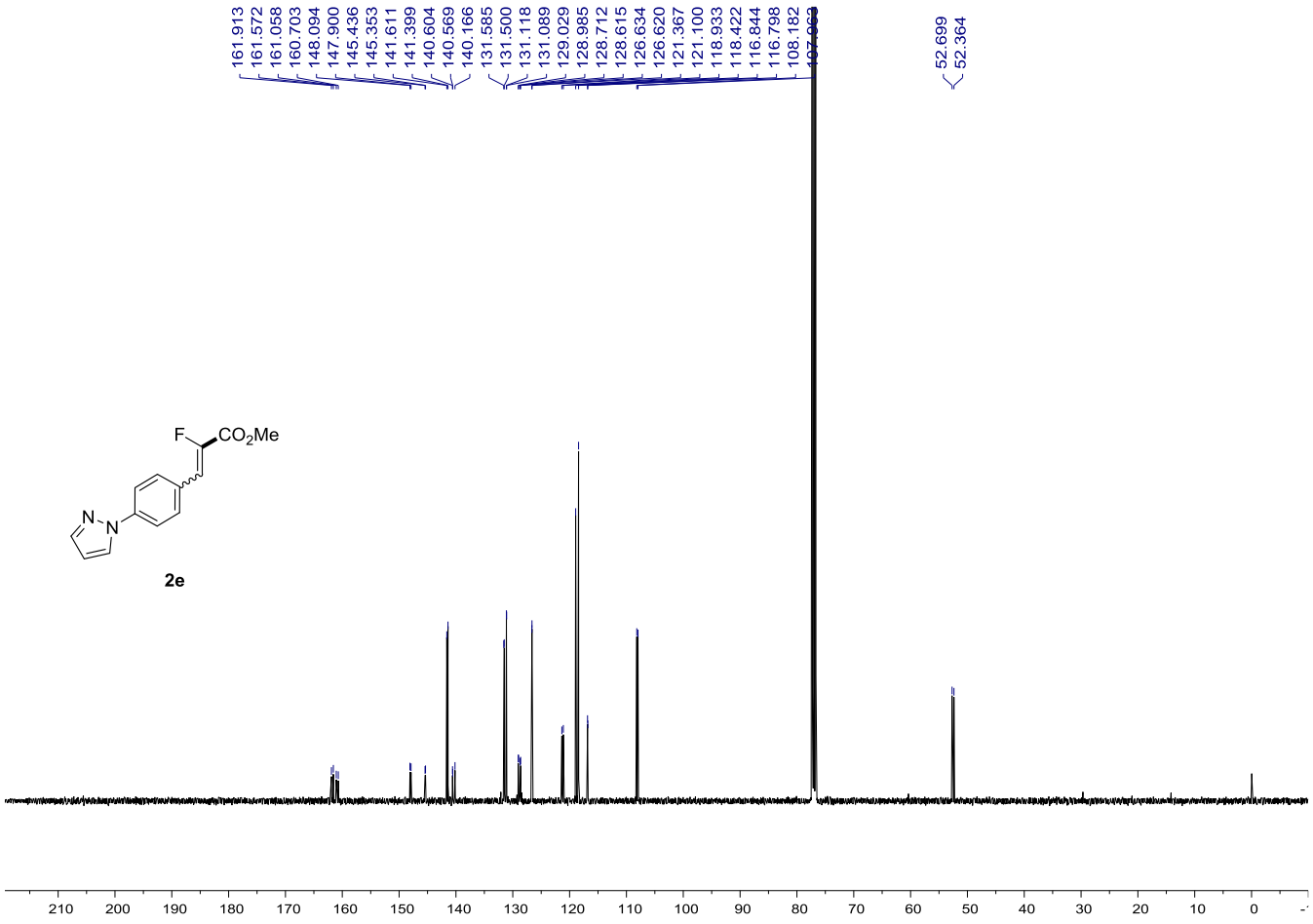
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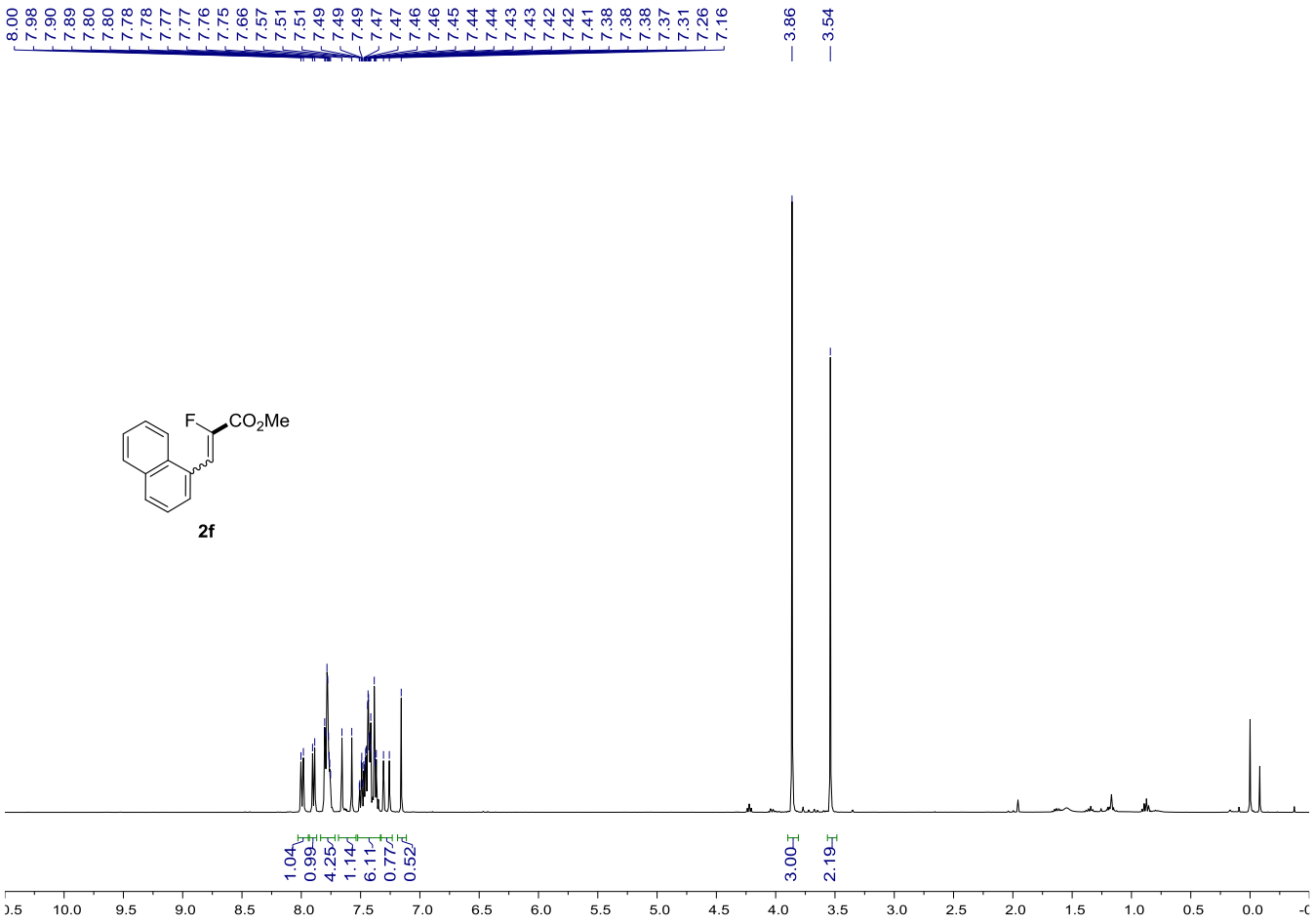
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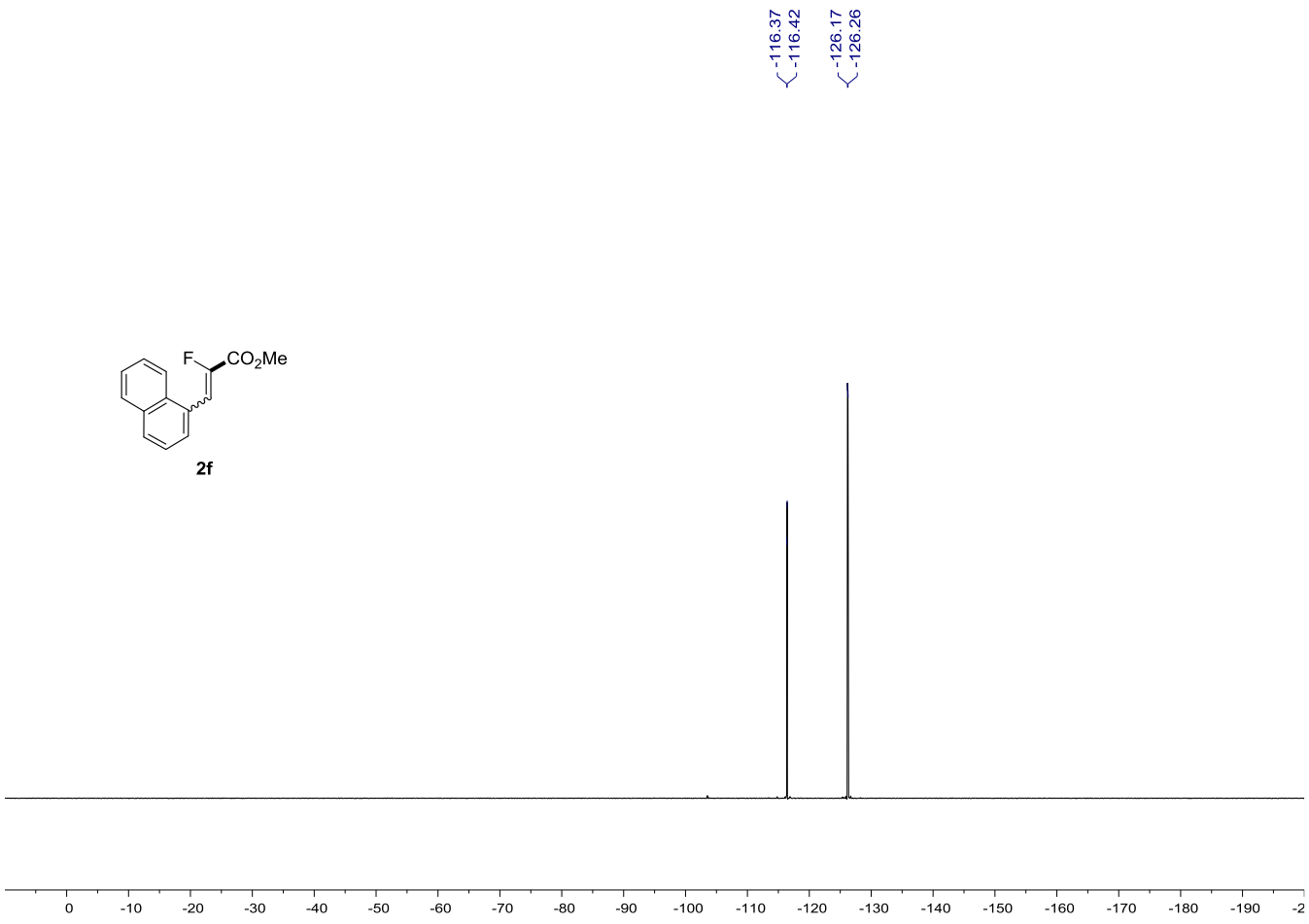
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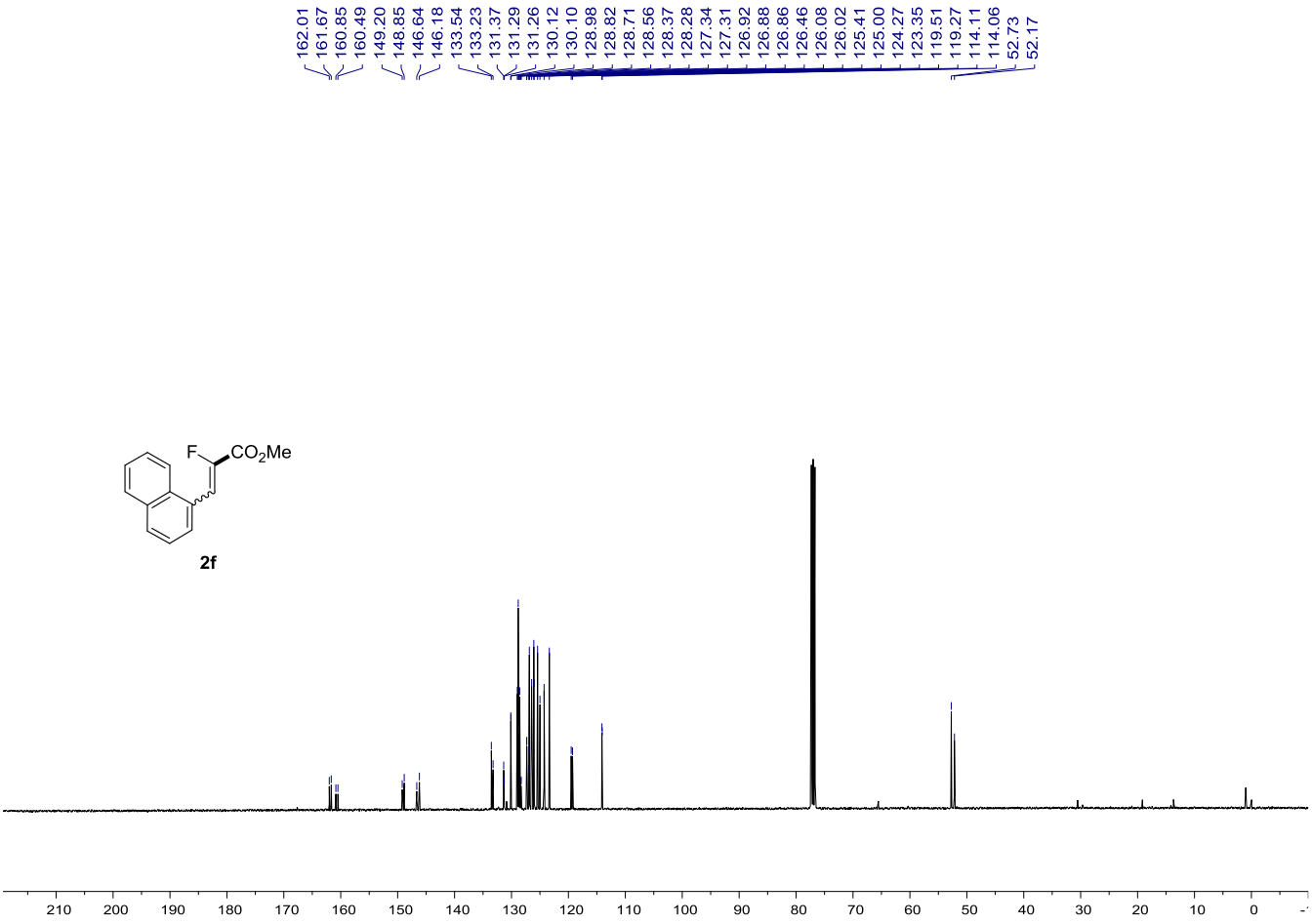
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126.08
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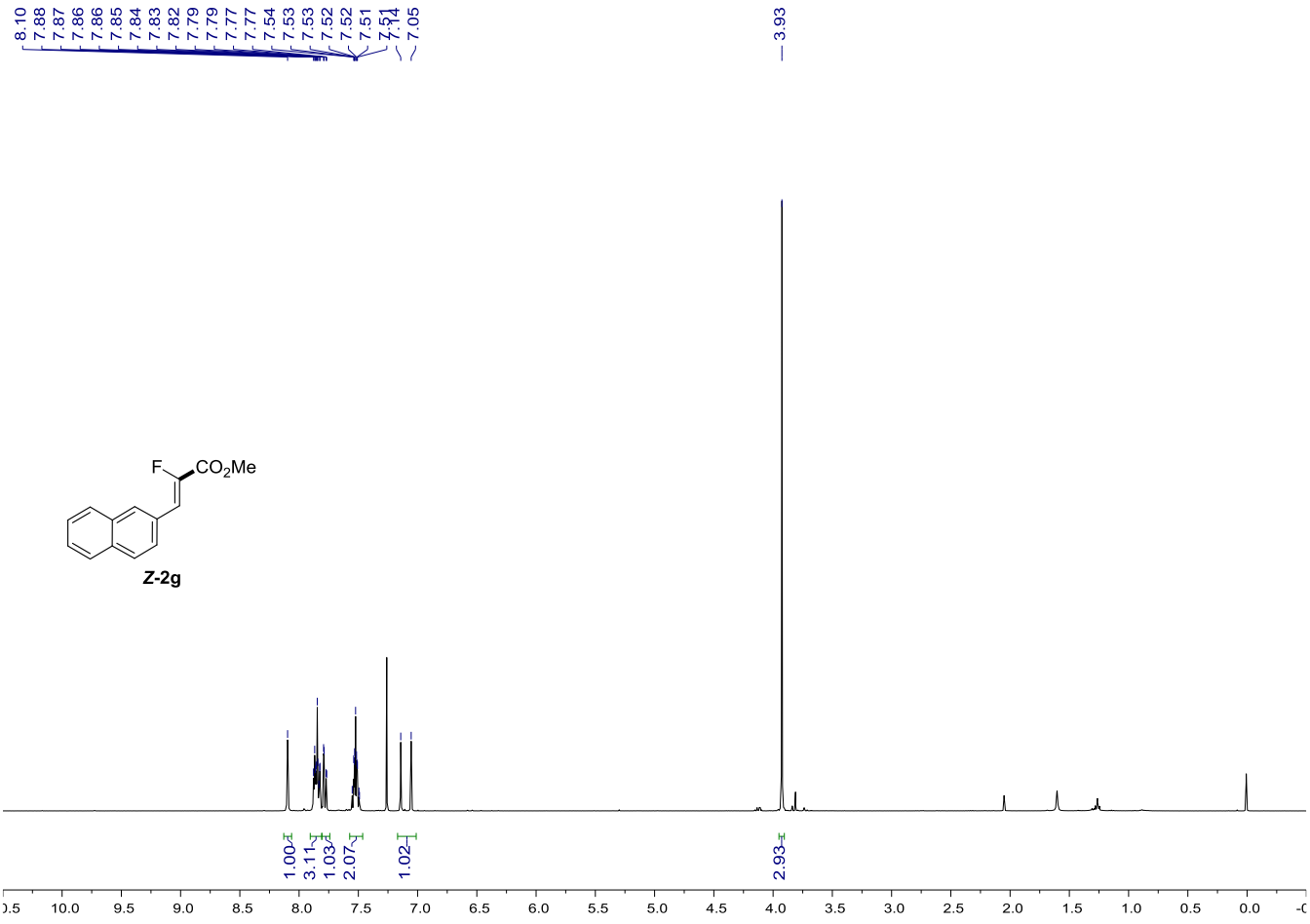
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7.52
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7.51
7.14
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Z-2g
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3.11
1.03
2.07
1.02
2.93
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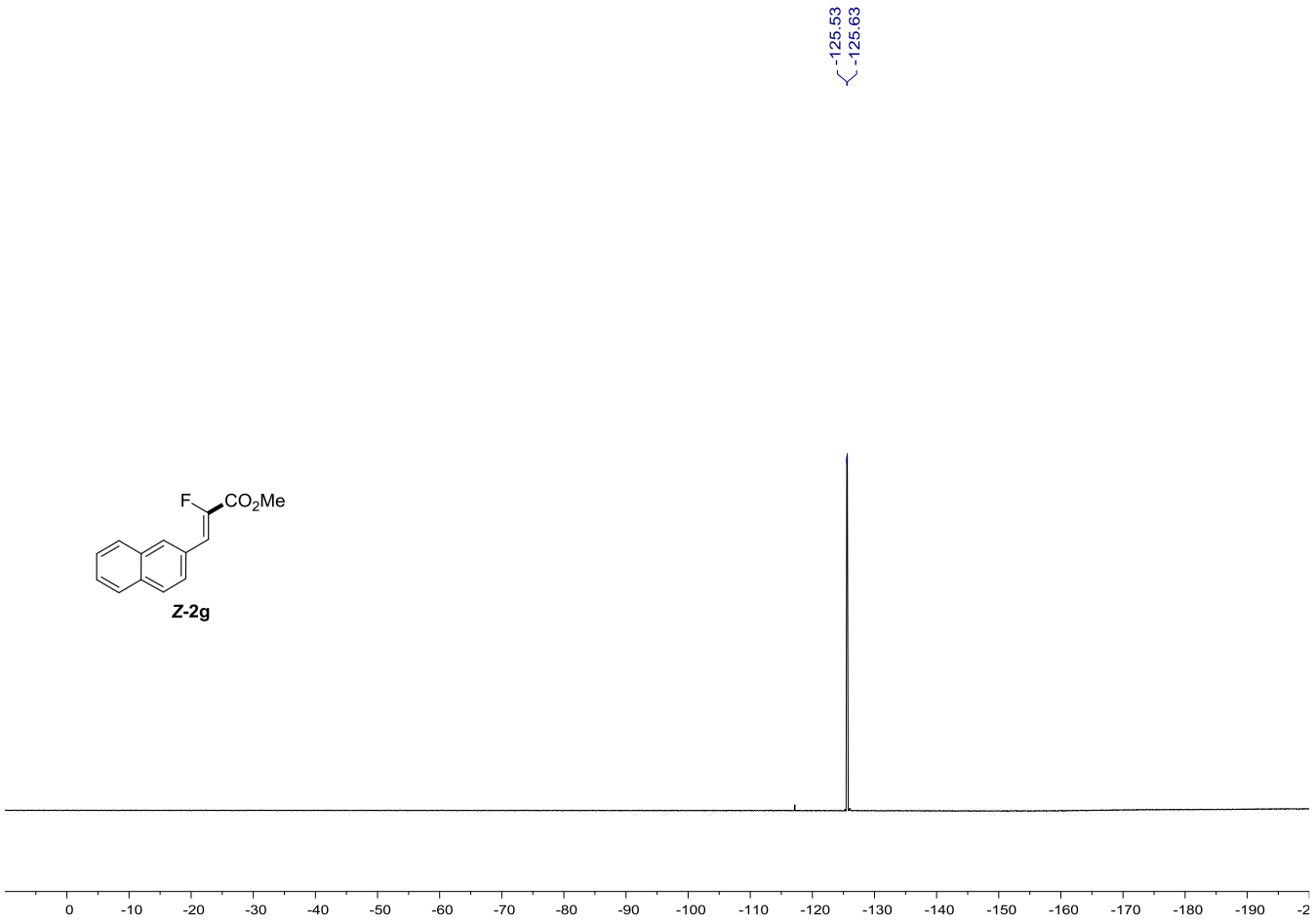
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Z-2g
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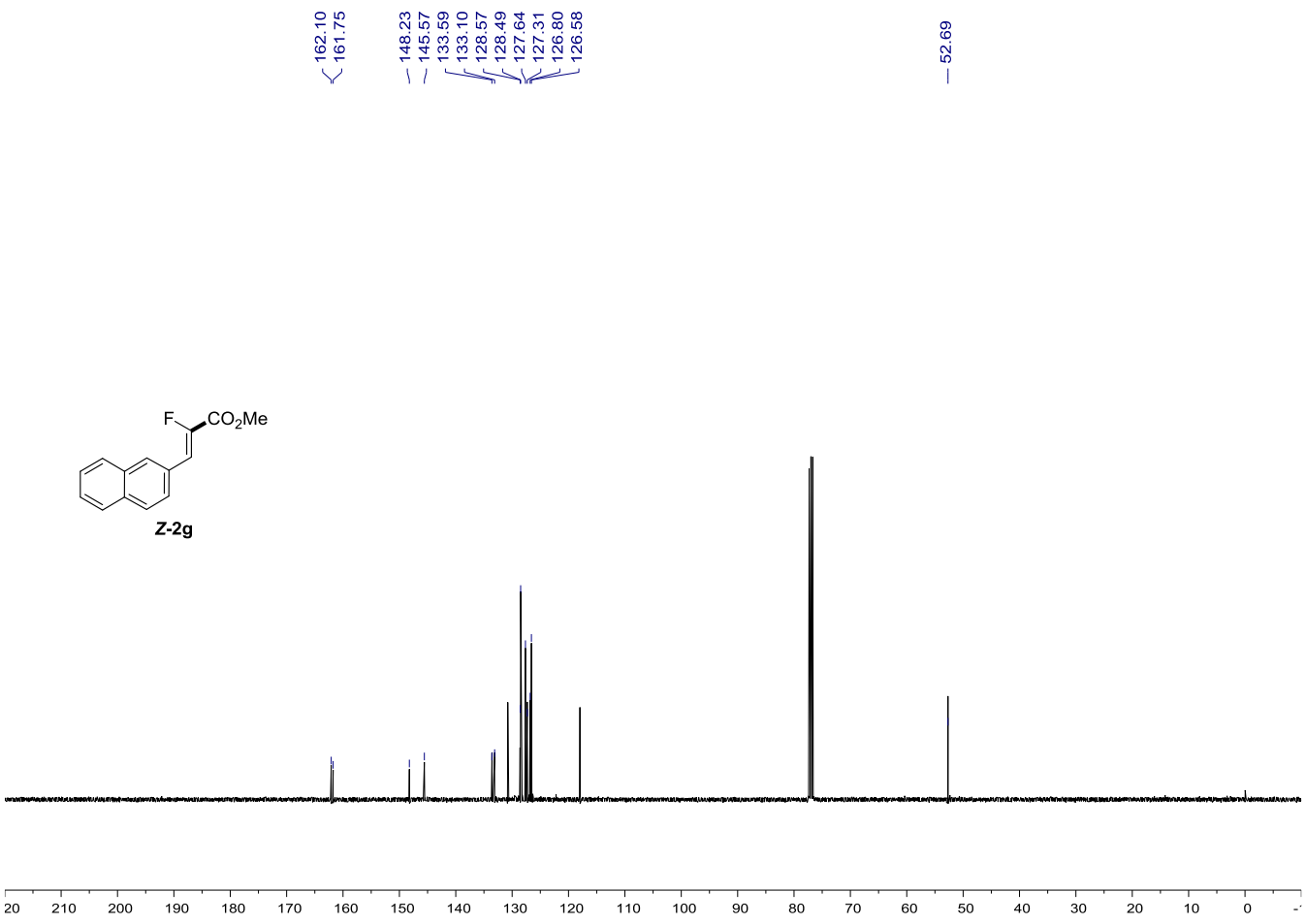
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Z-2g
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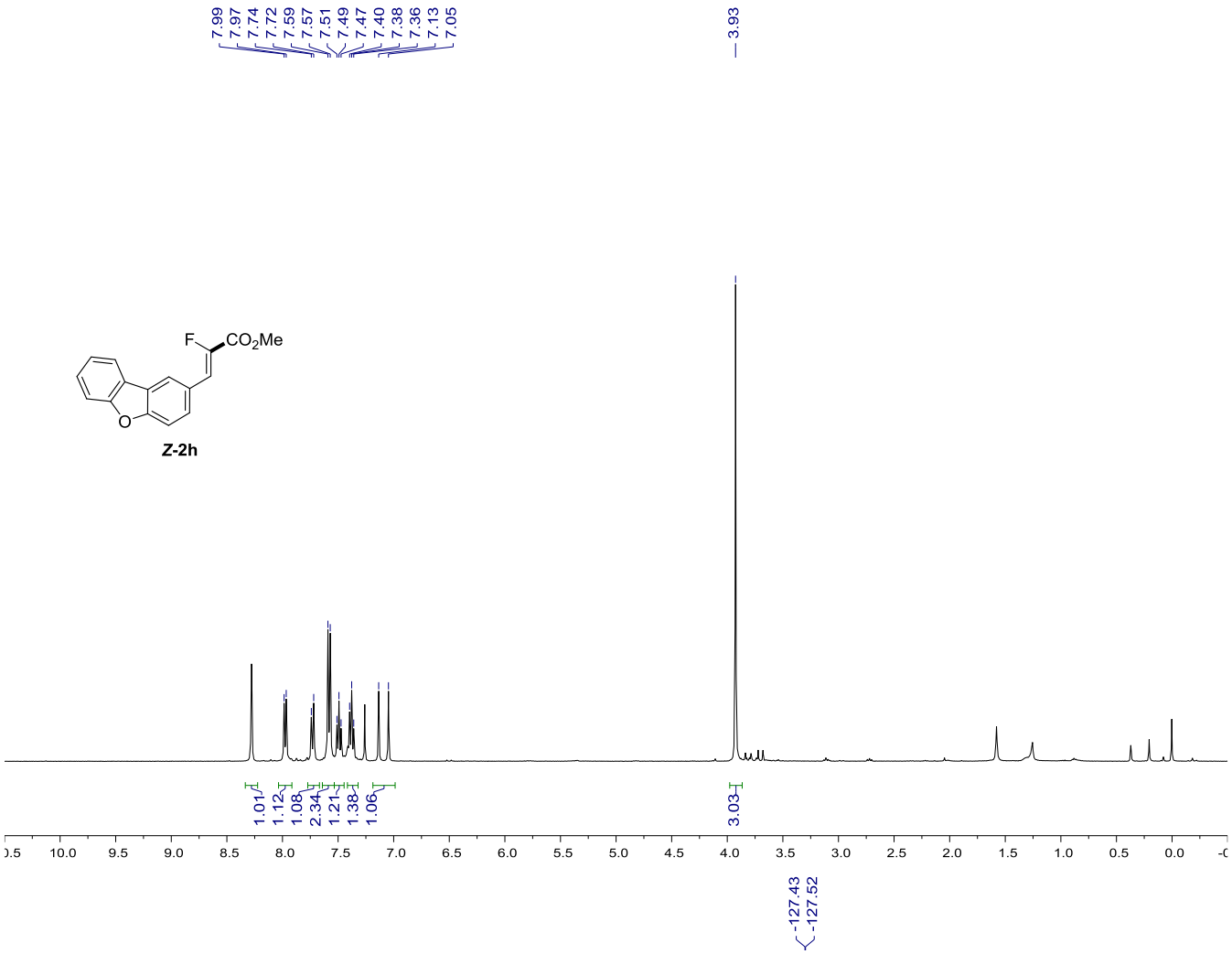
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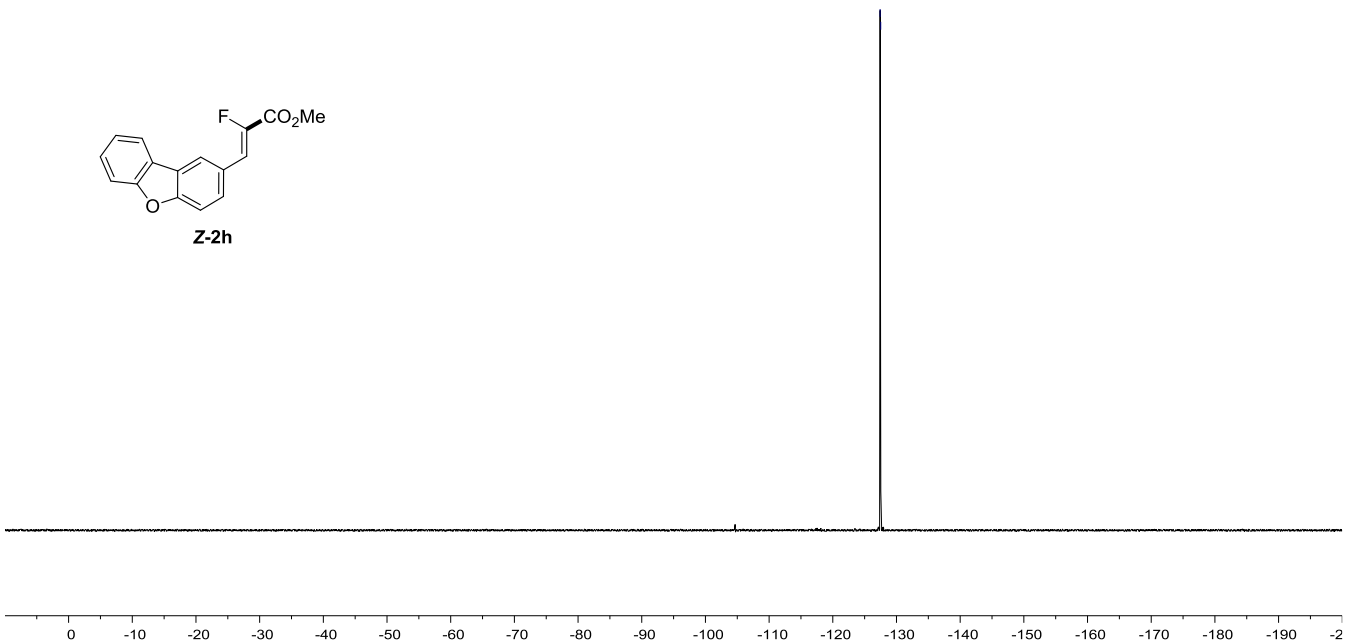
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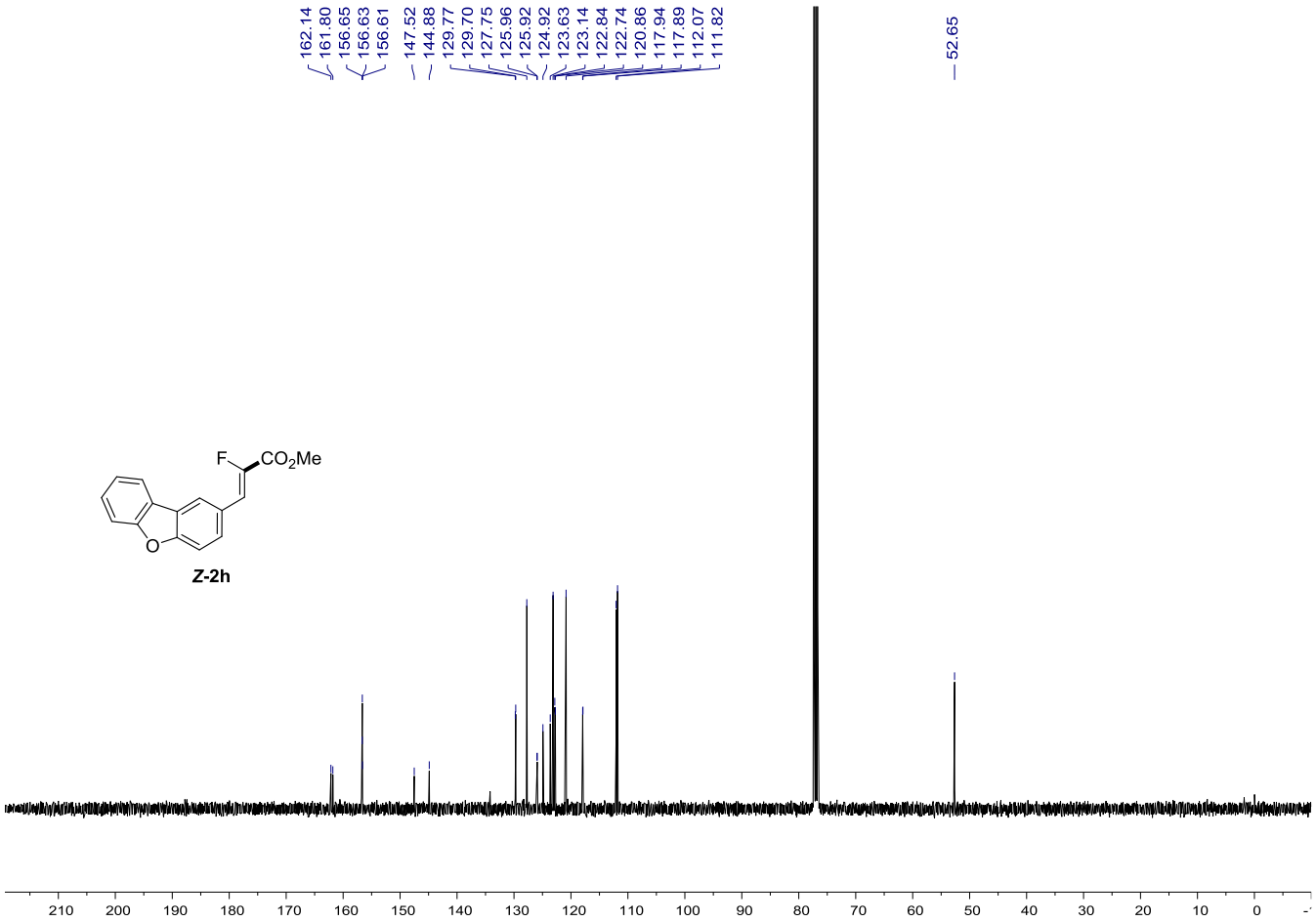
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O
Z-2h
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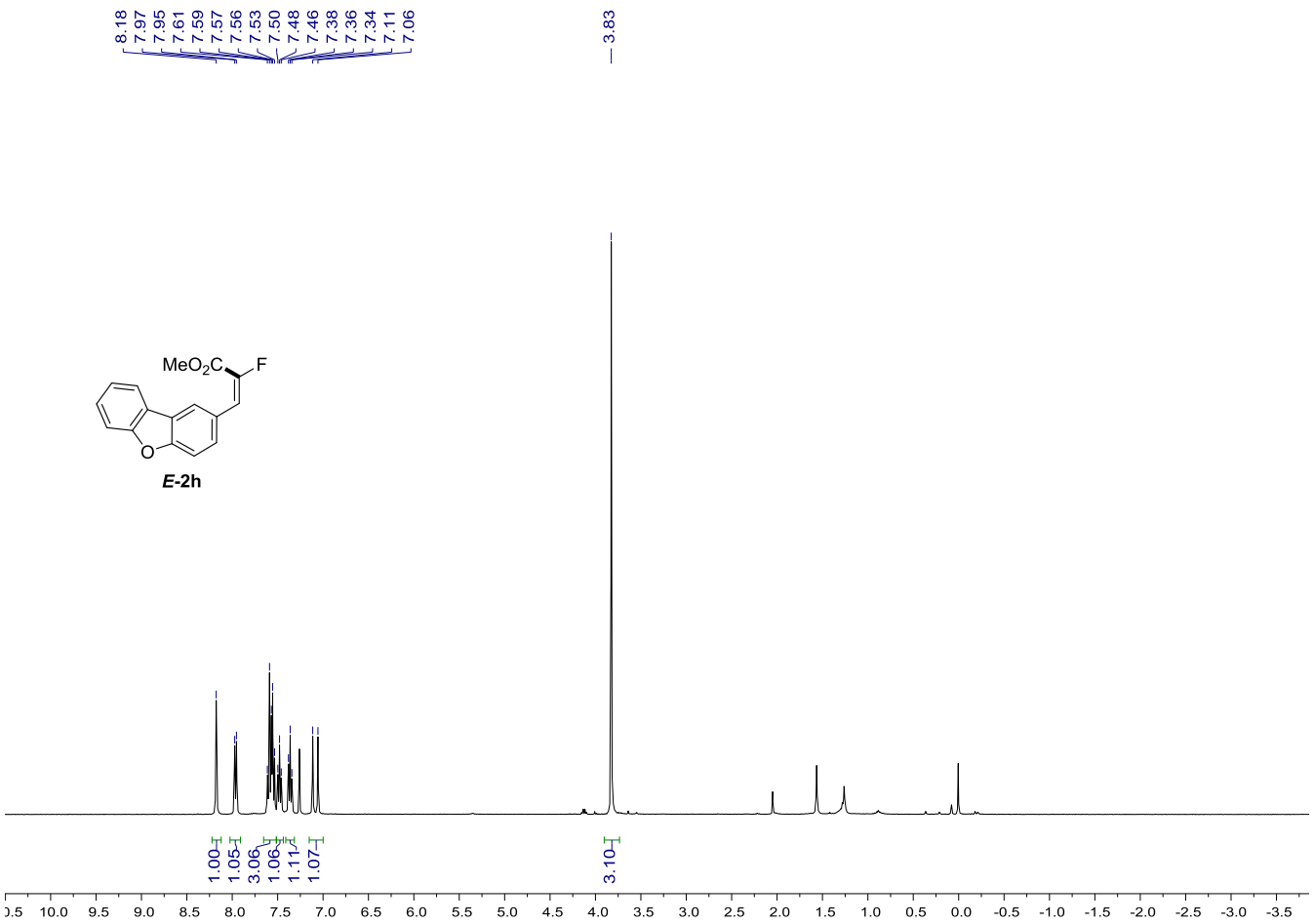
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7.06
3.83
MeO2C
F
O
E-2h
1.00
1.05
3.06
1.06
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1.07
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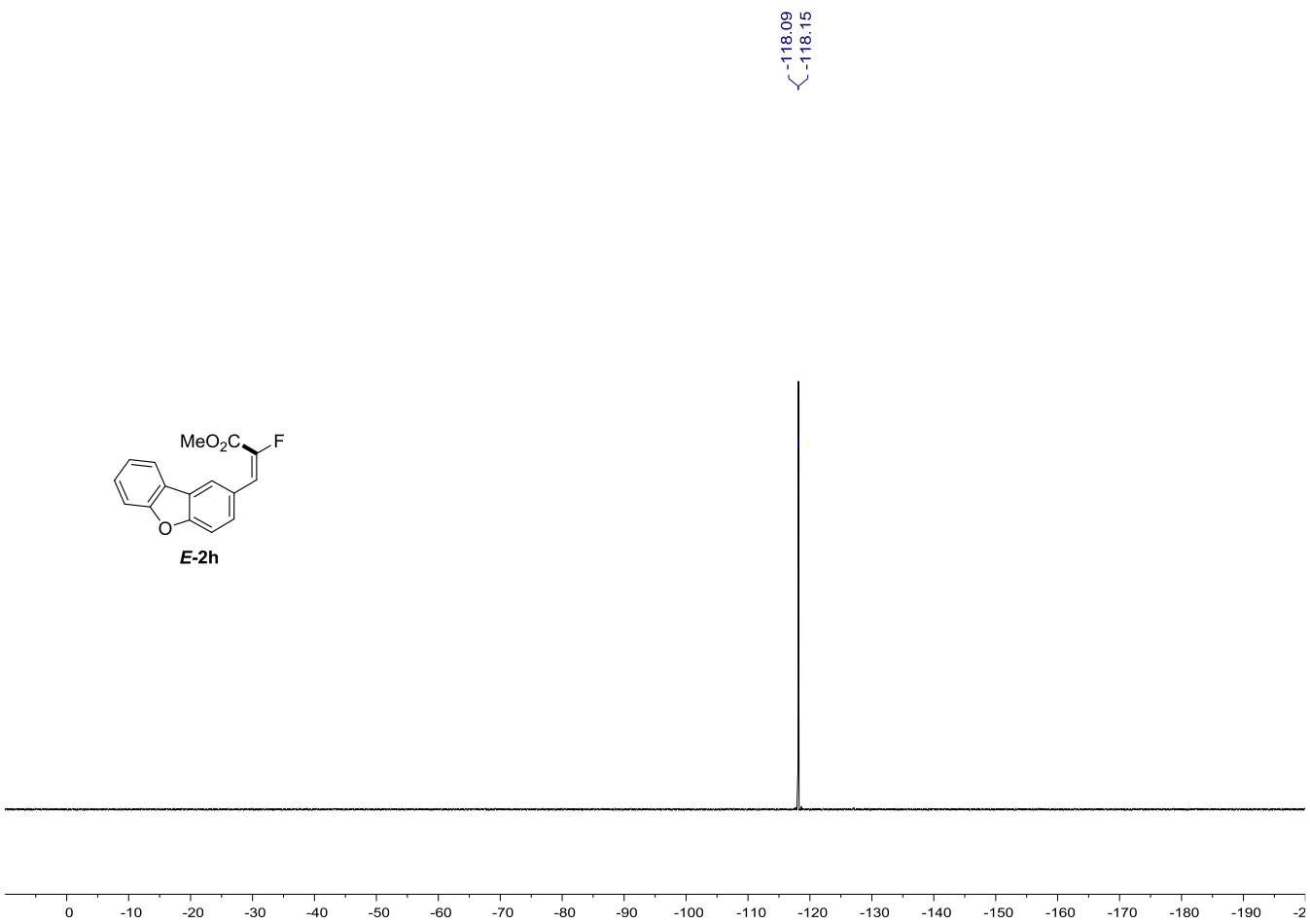
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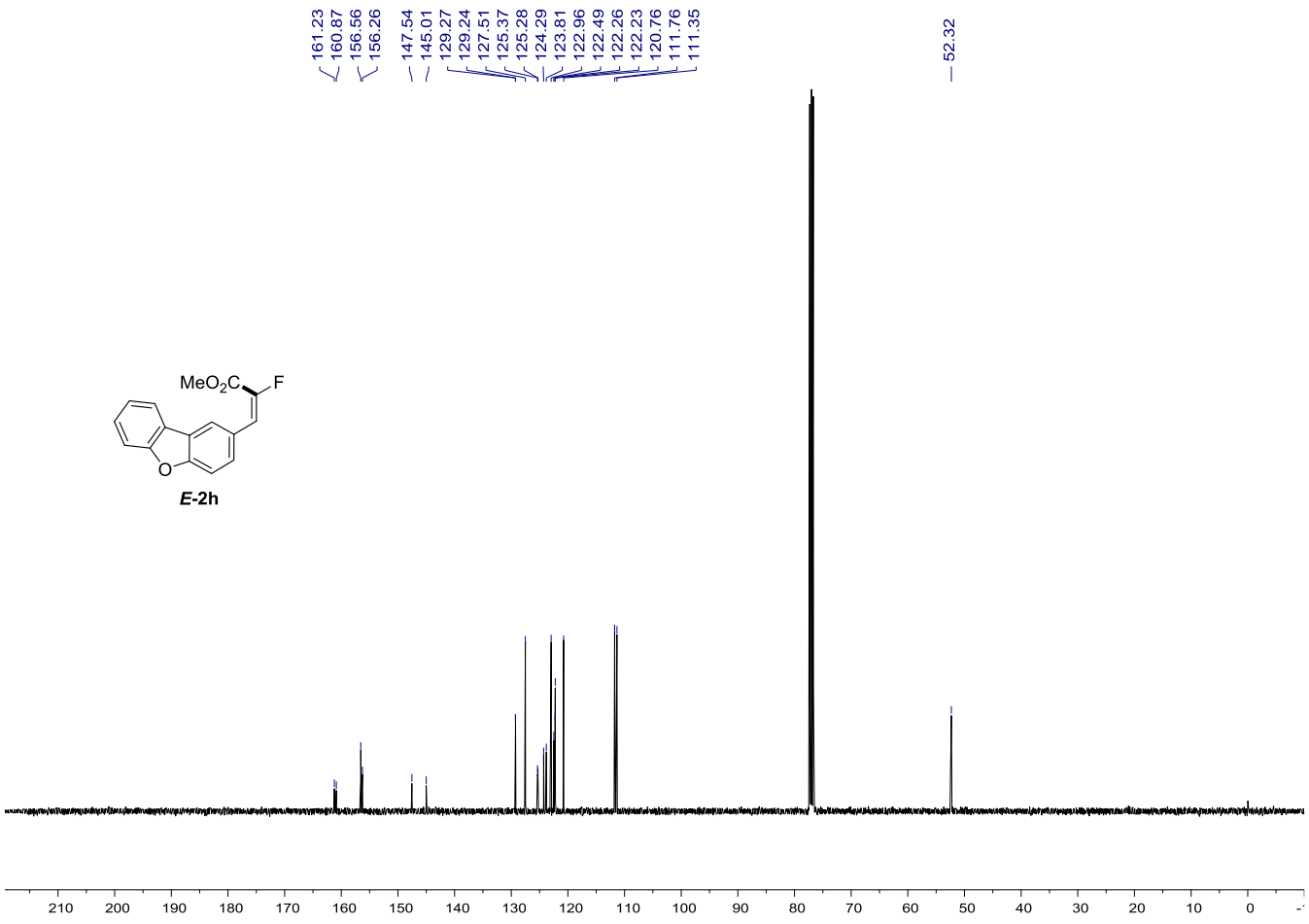
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O
E-2h
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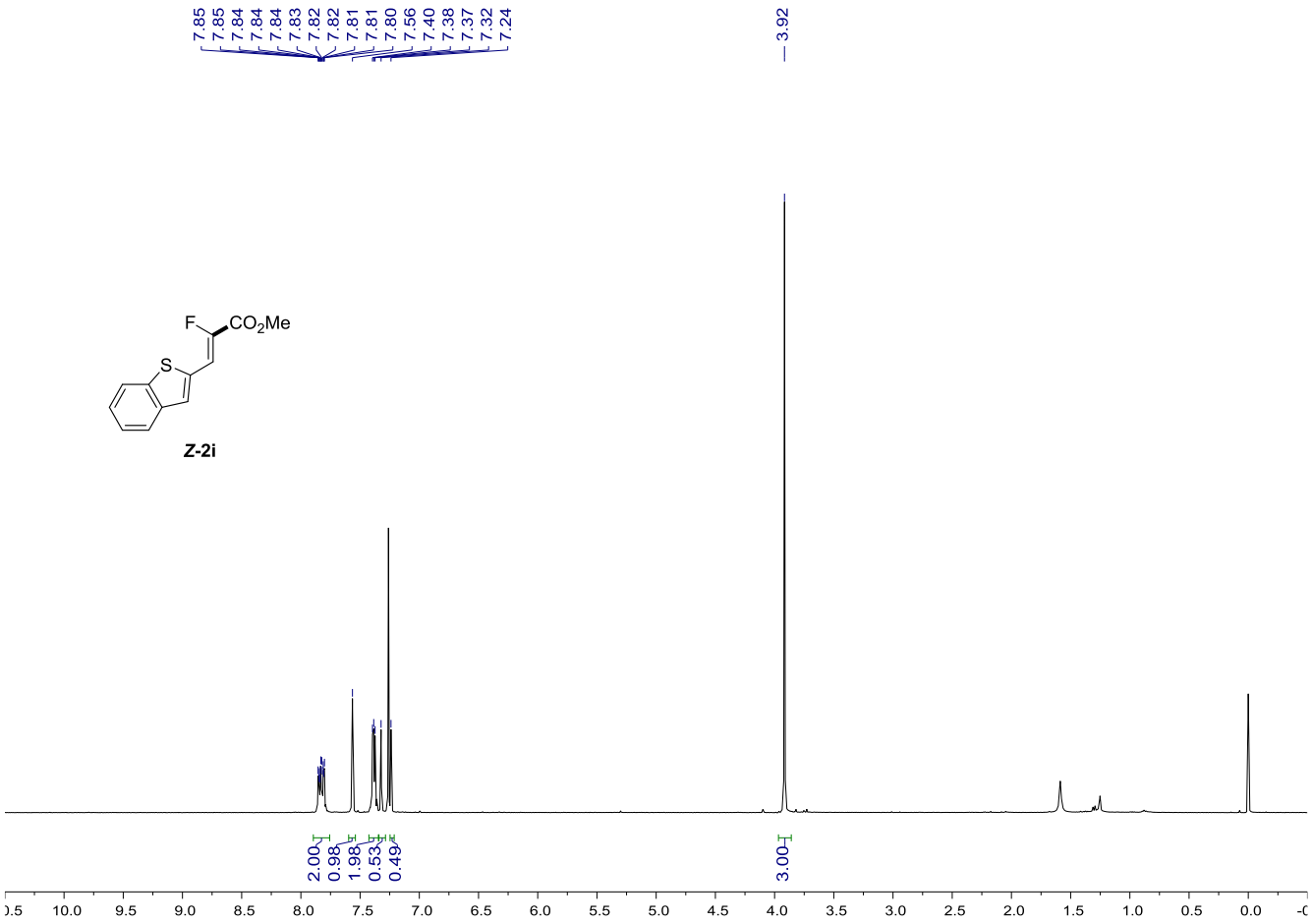
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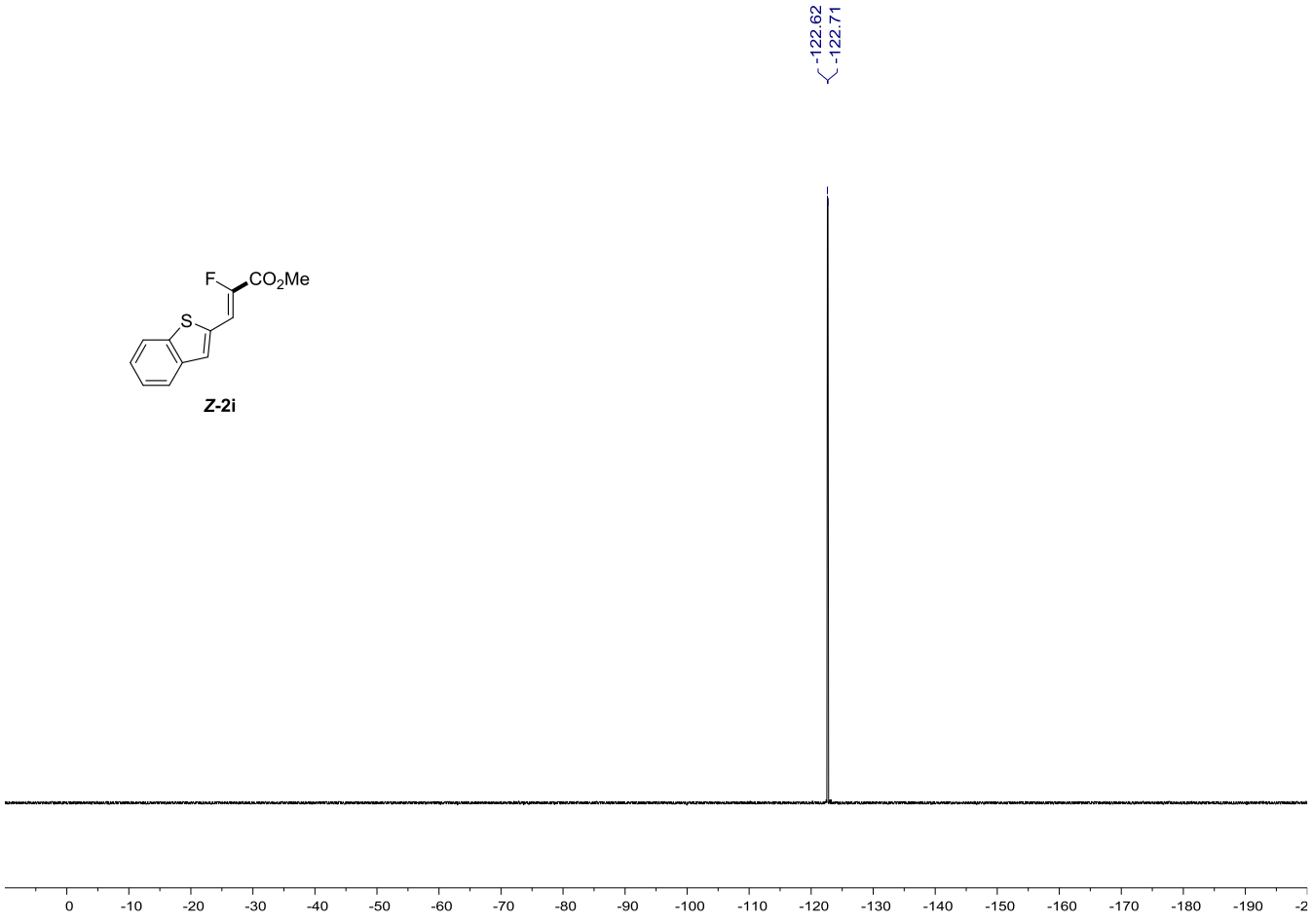
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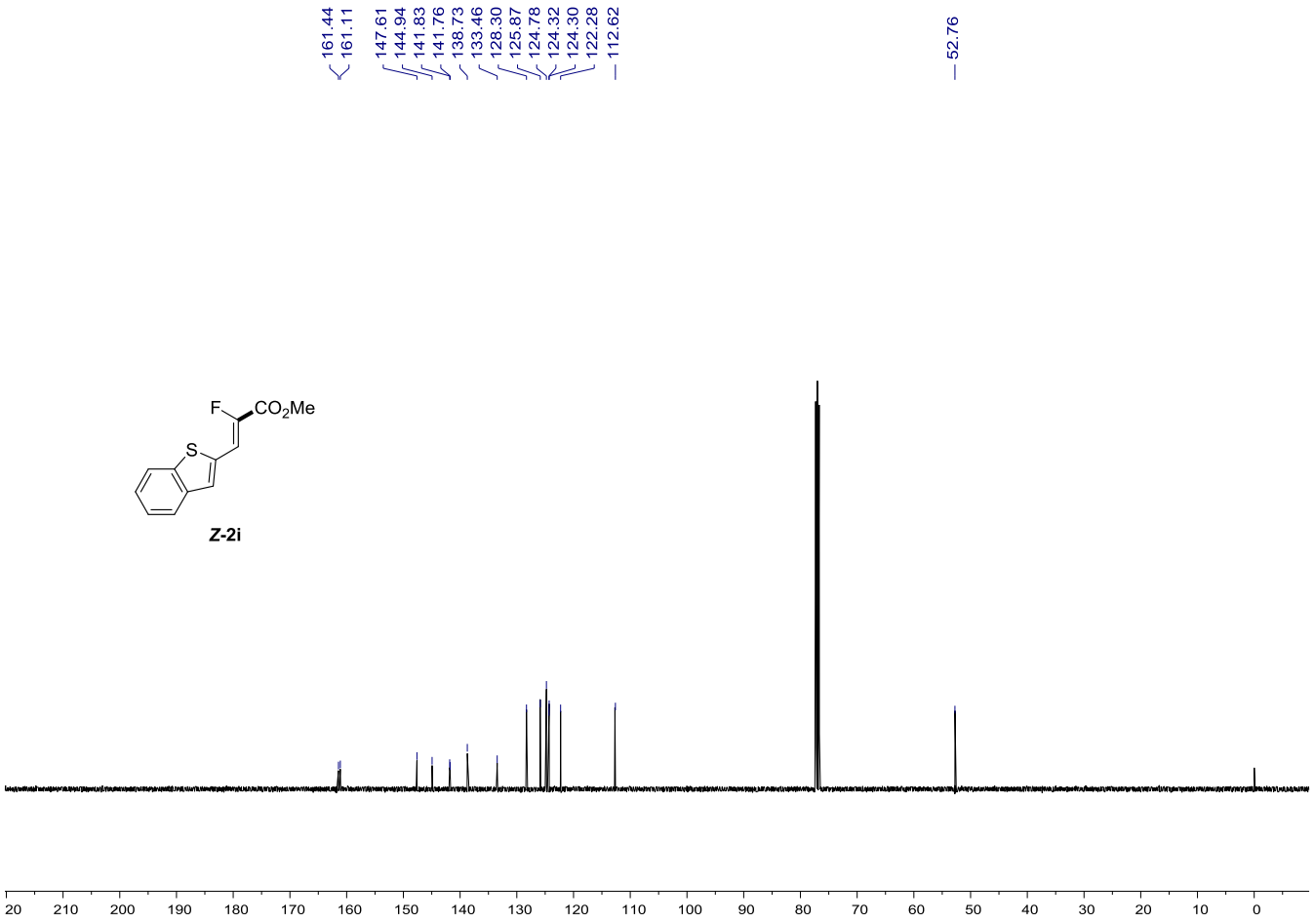
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S
Z-2i
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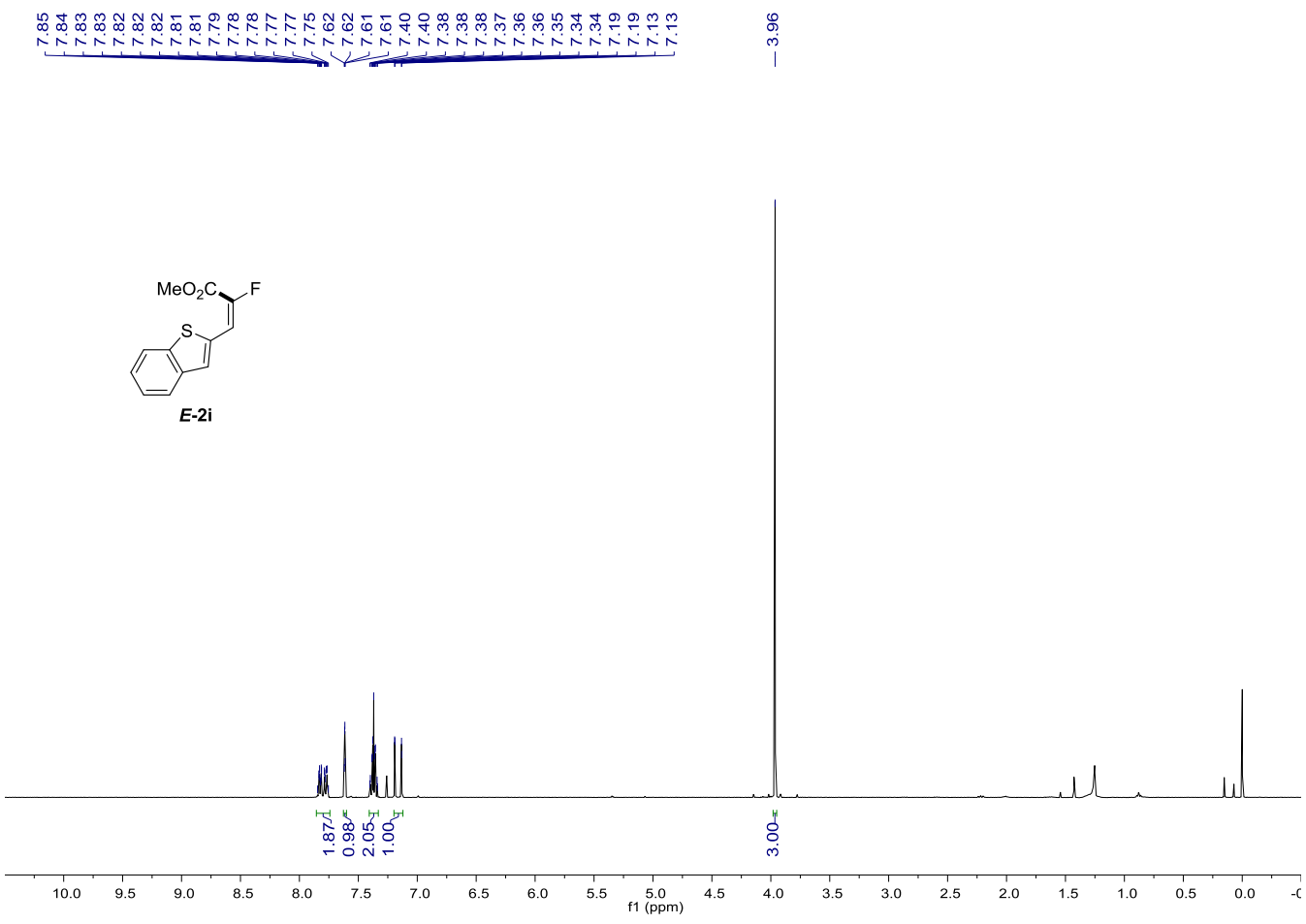
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MeO2C
F
S
E-2i
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2.05
1.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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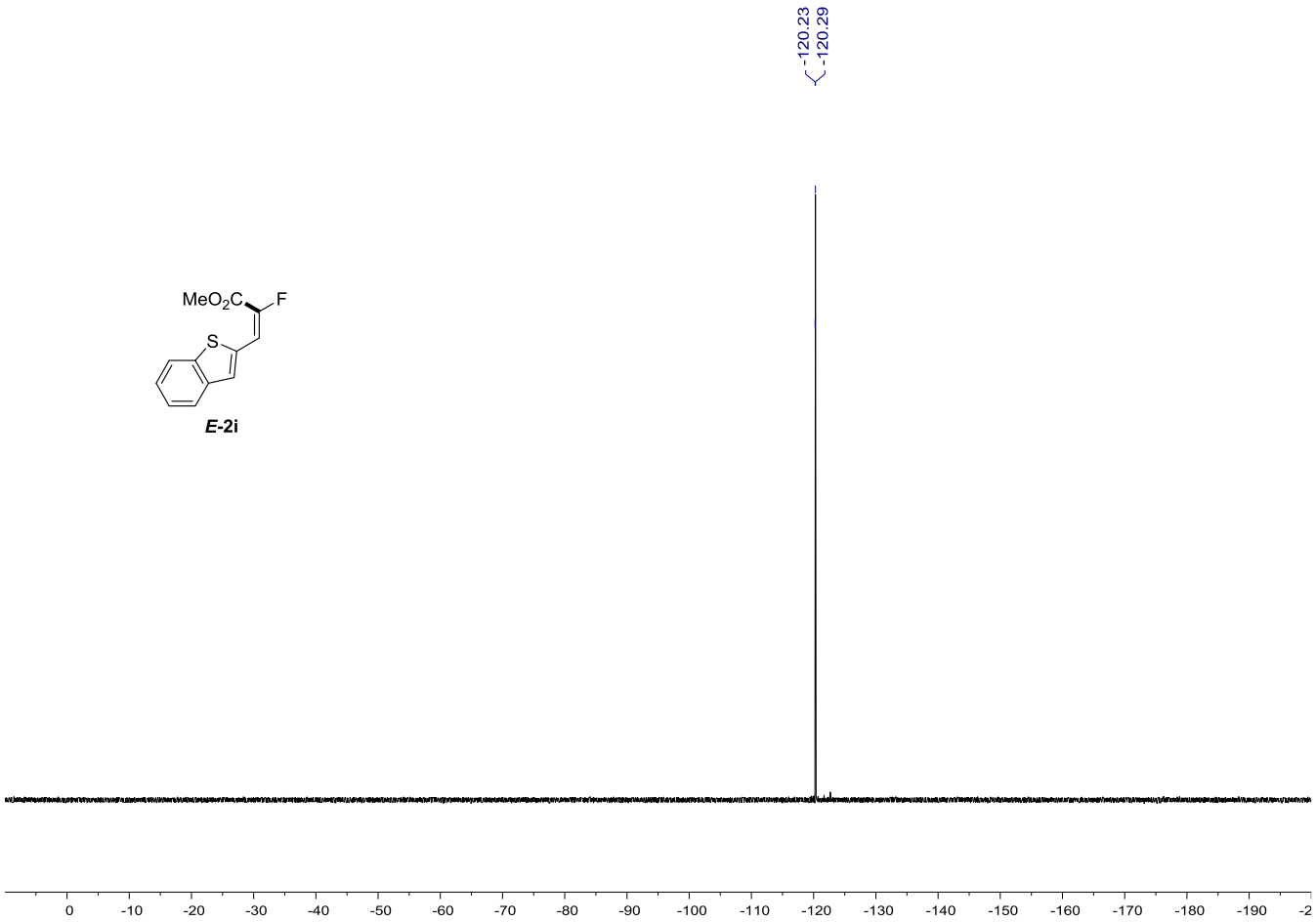
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F
S
E-2i
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-20
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-40
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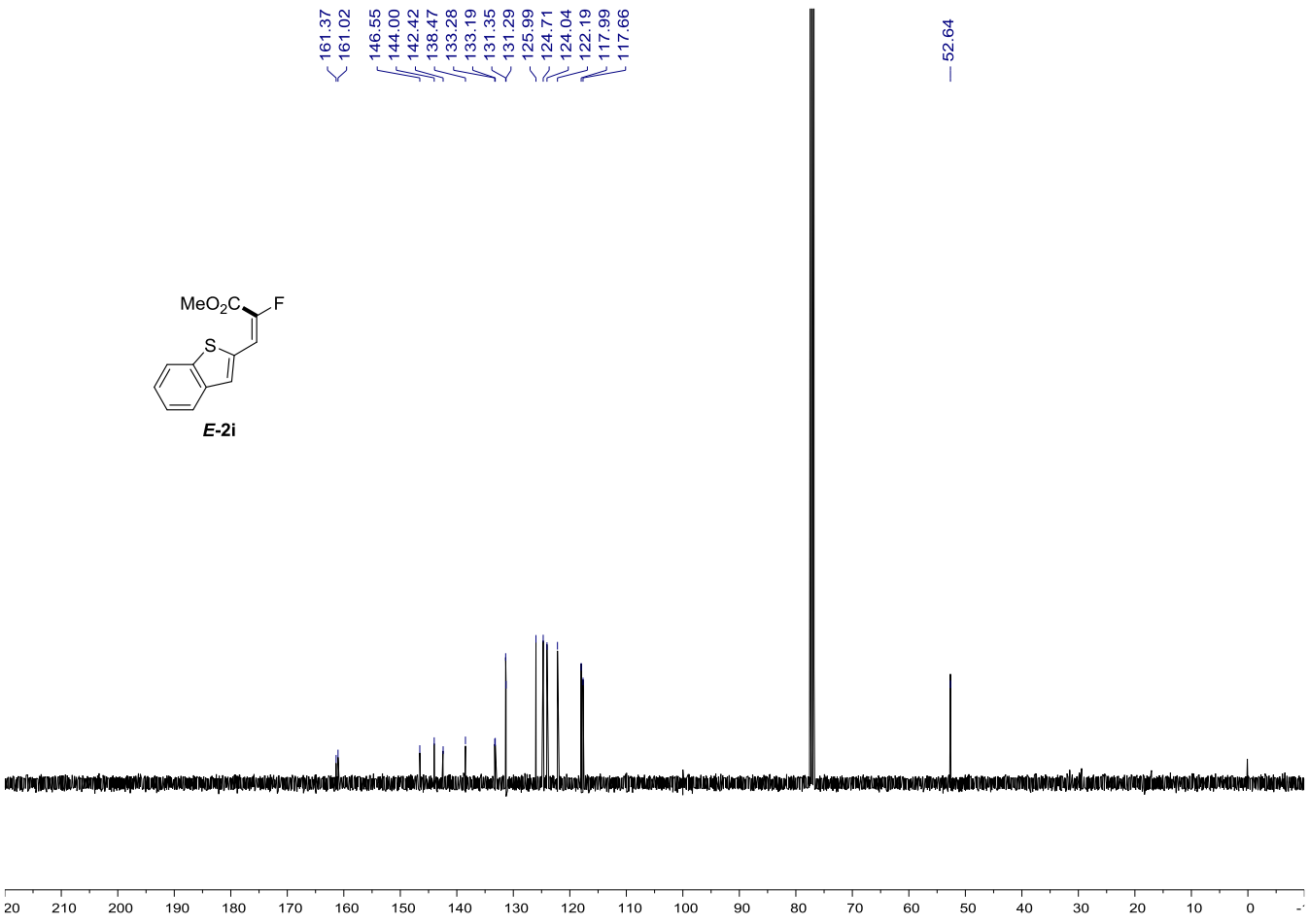
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117.66
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MeO2C
F
S
E-2i
20
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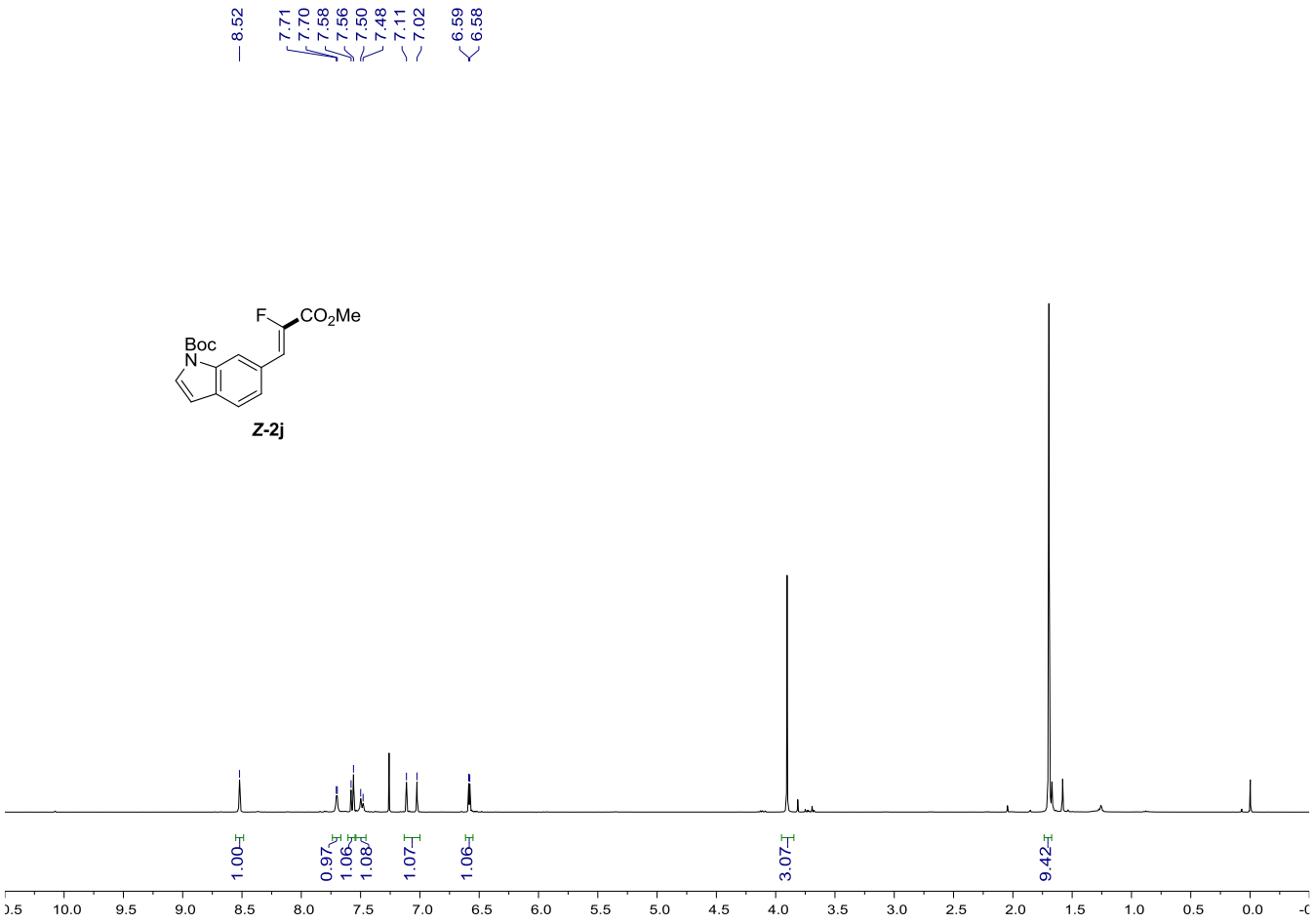
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N
Z-2j
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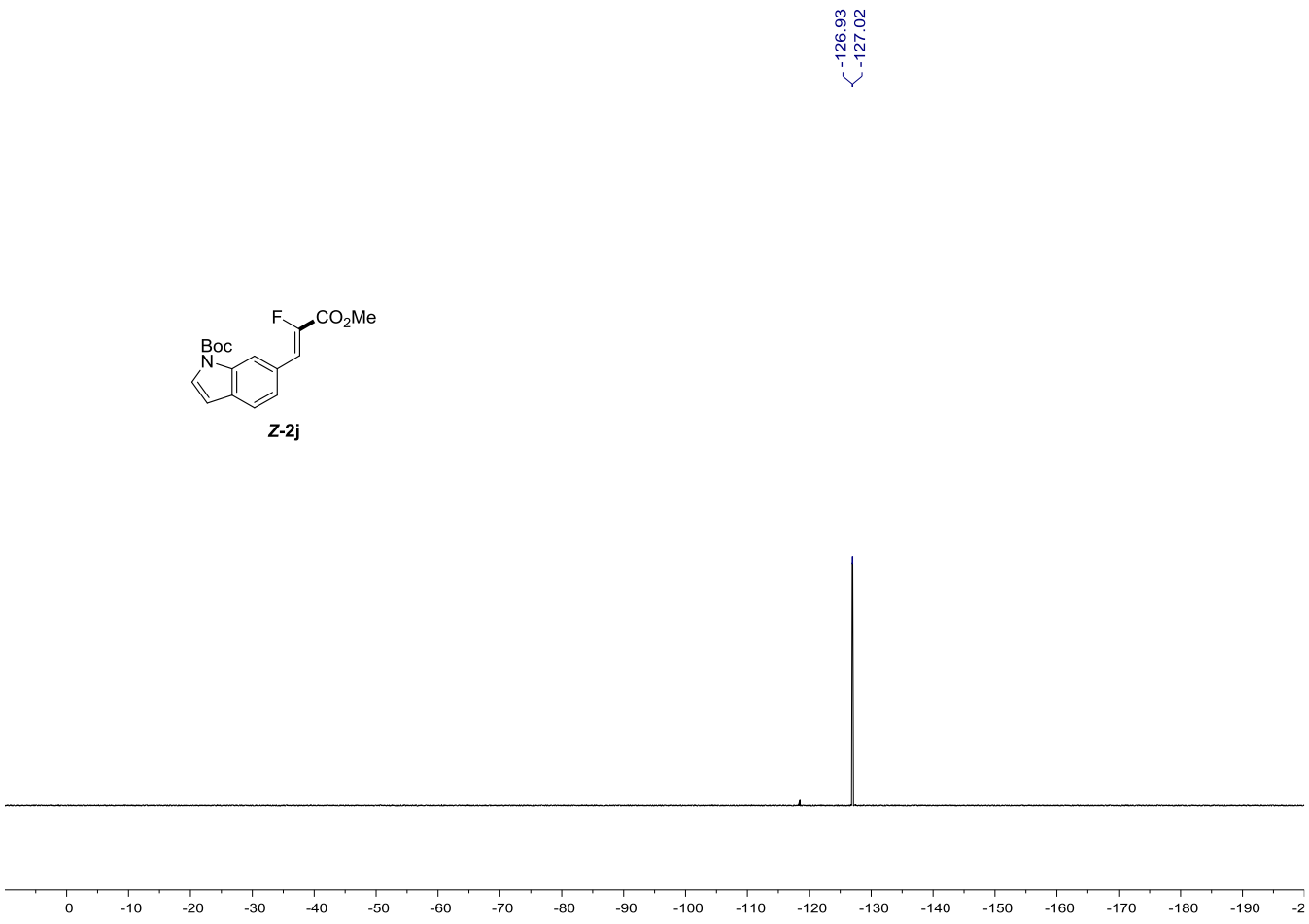
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Boc
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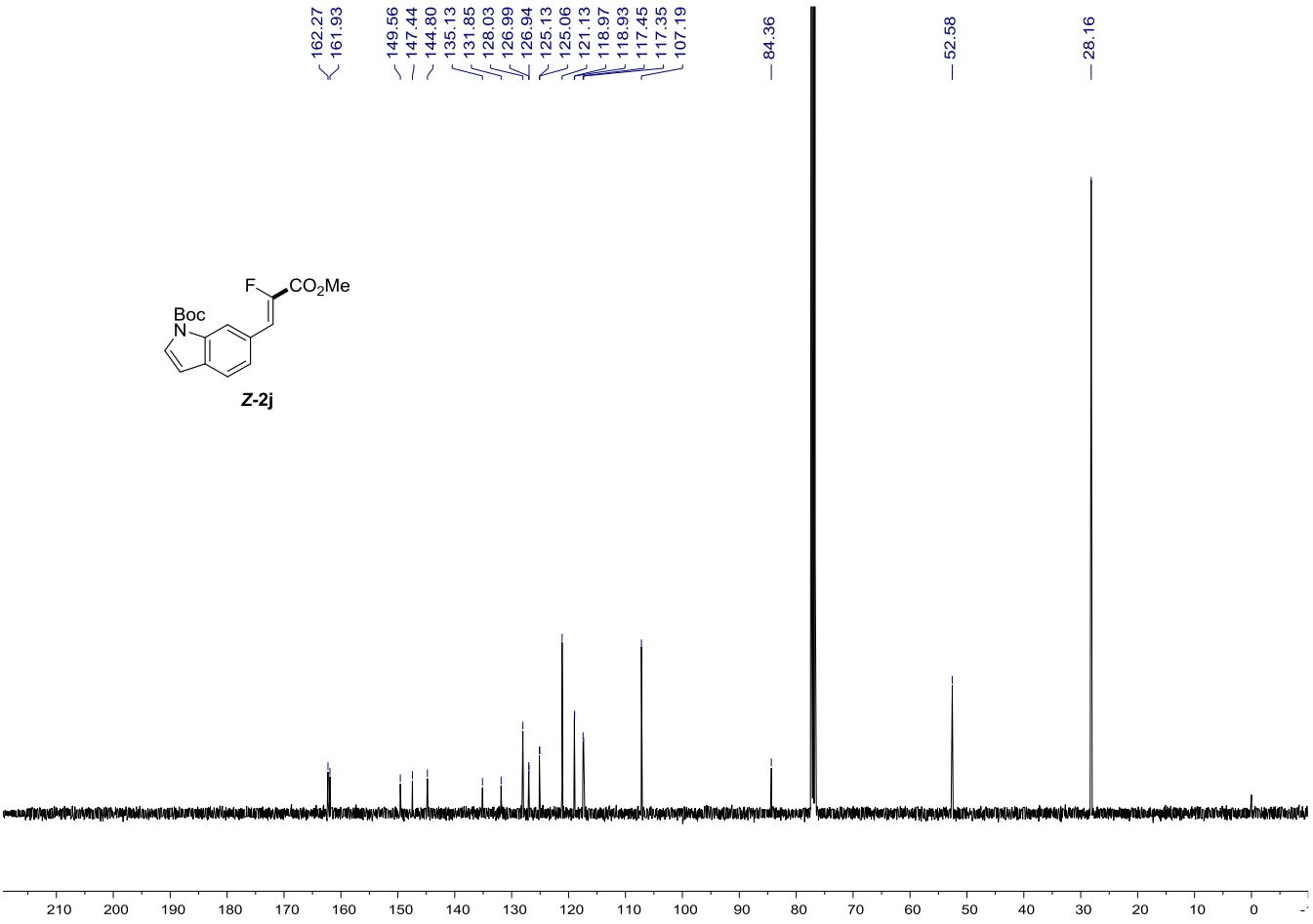
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Boc
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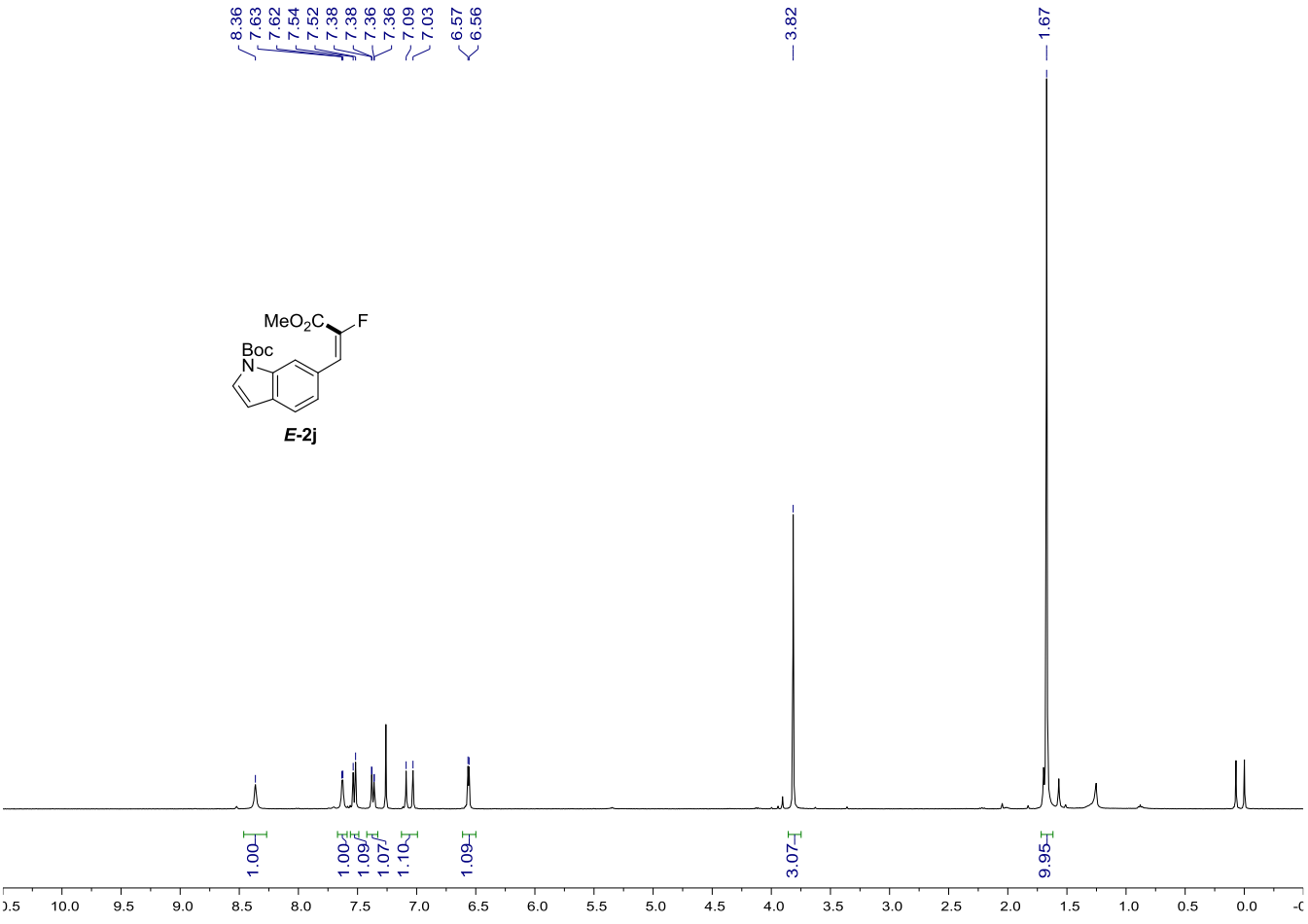
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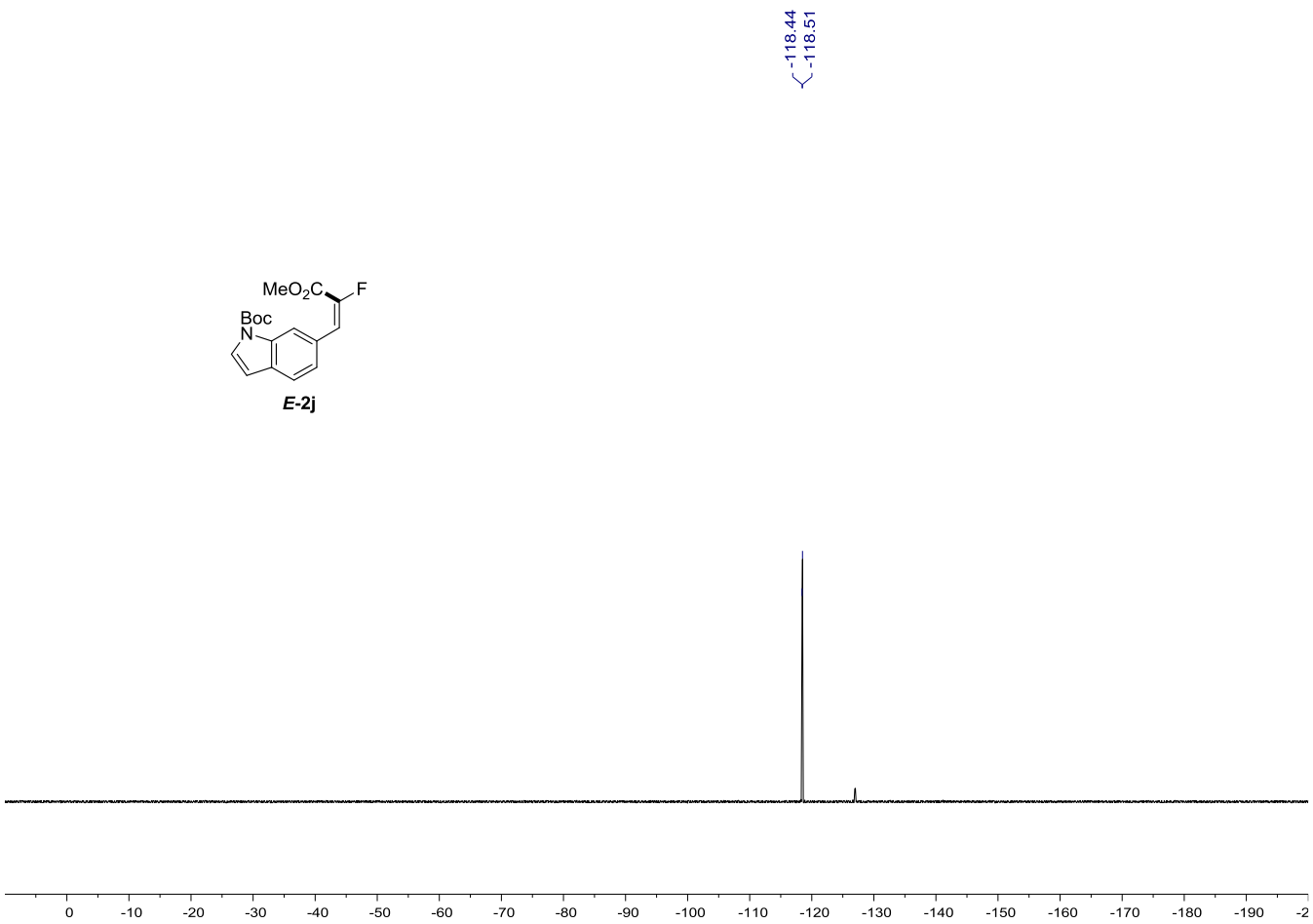
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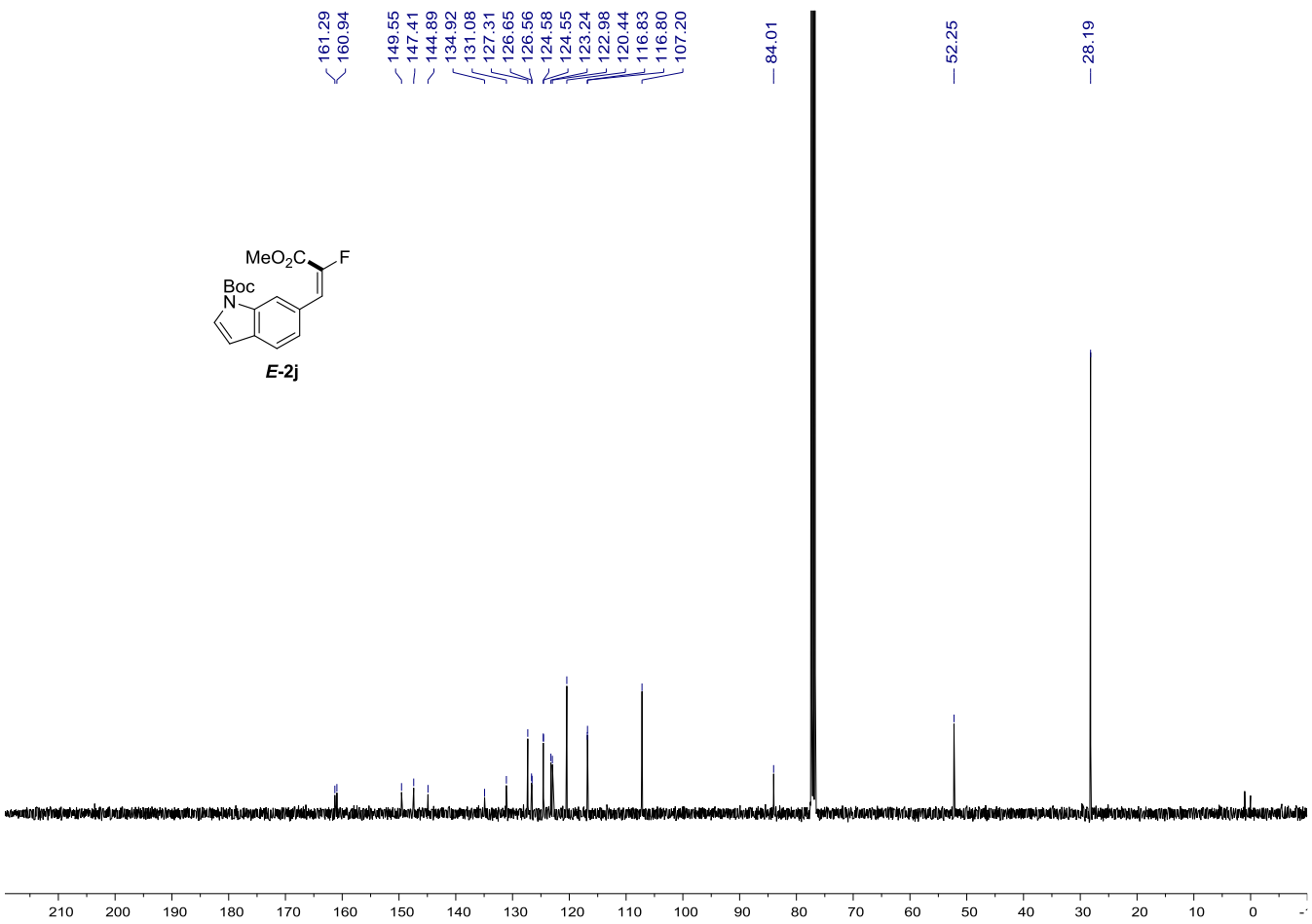
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Boc
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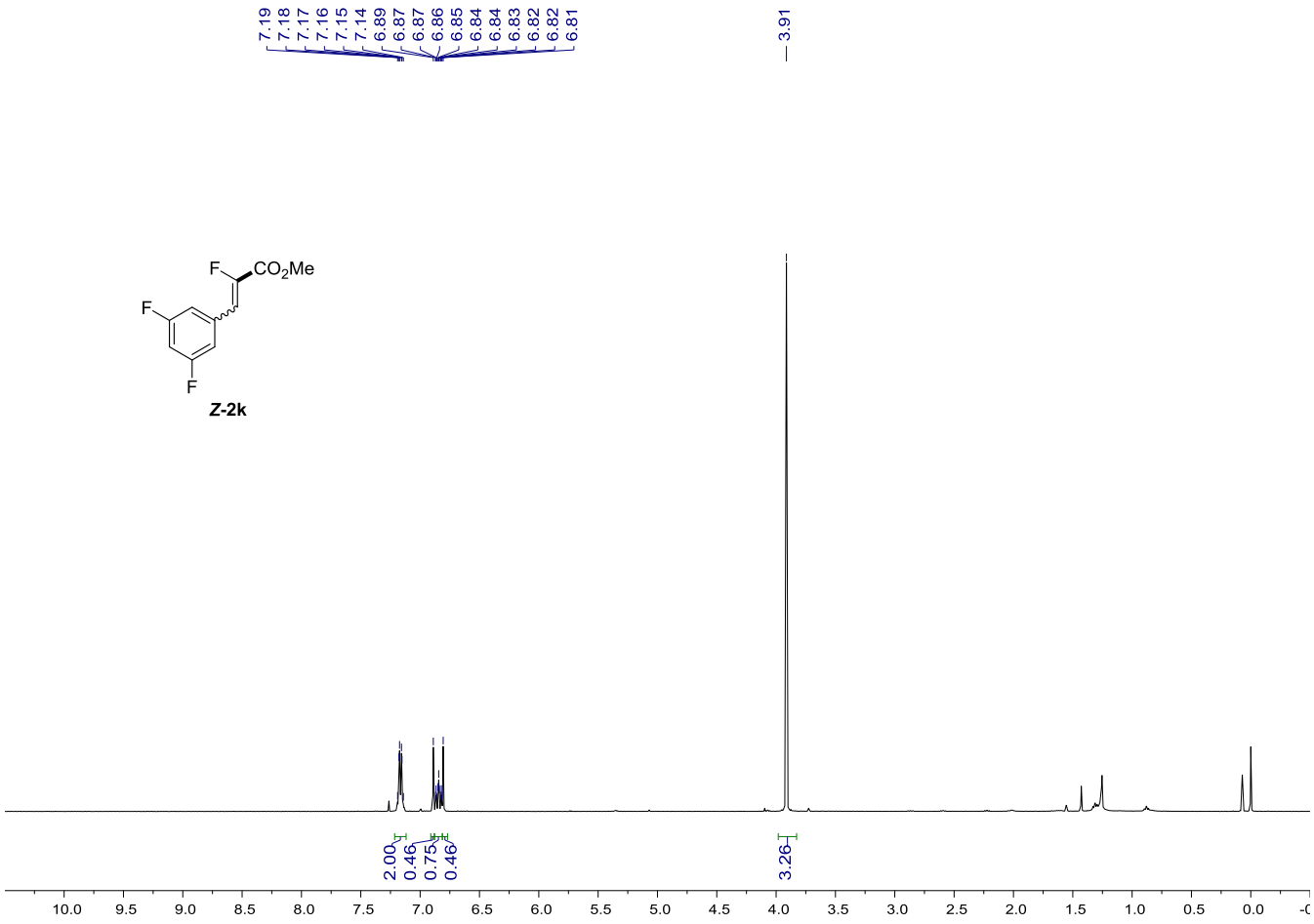
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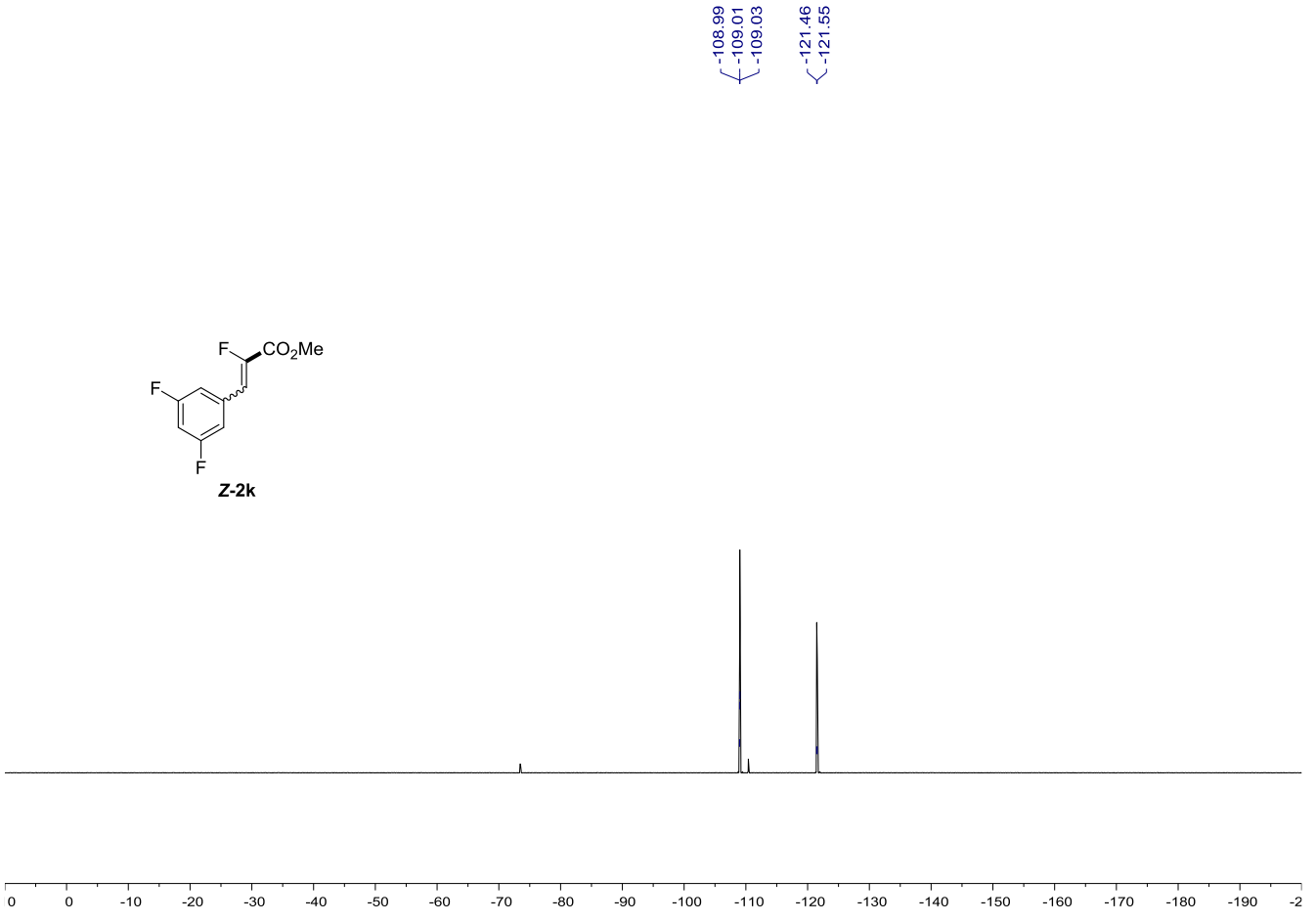
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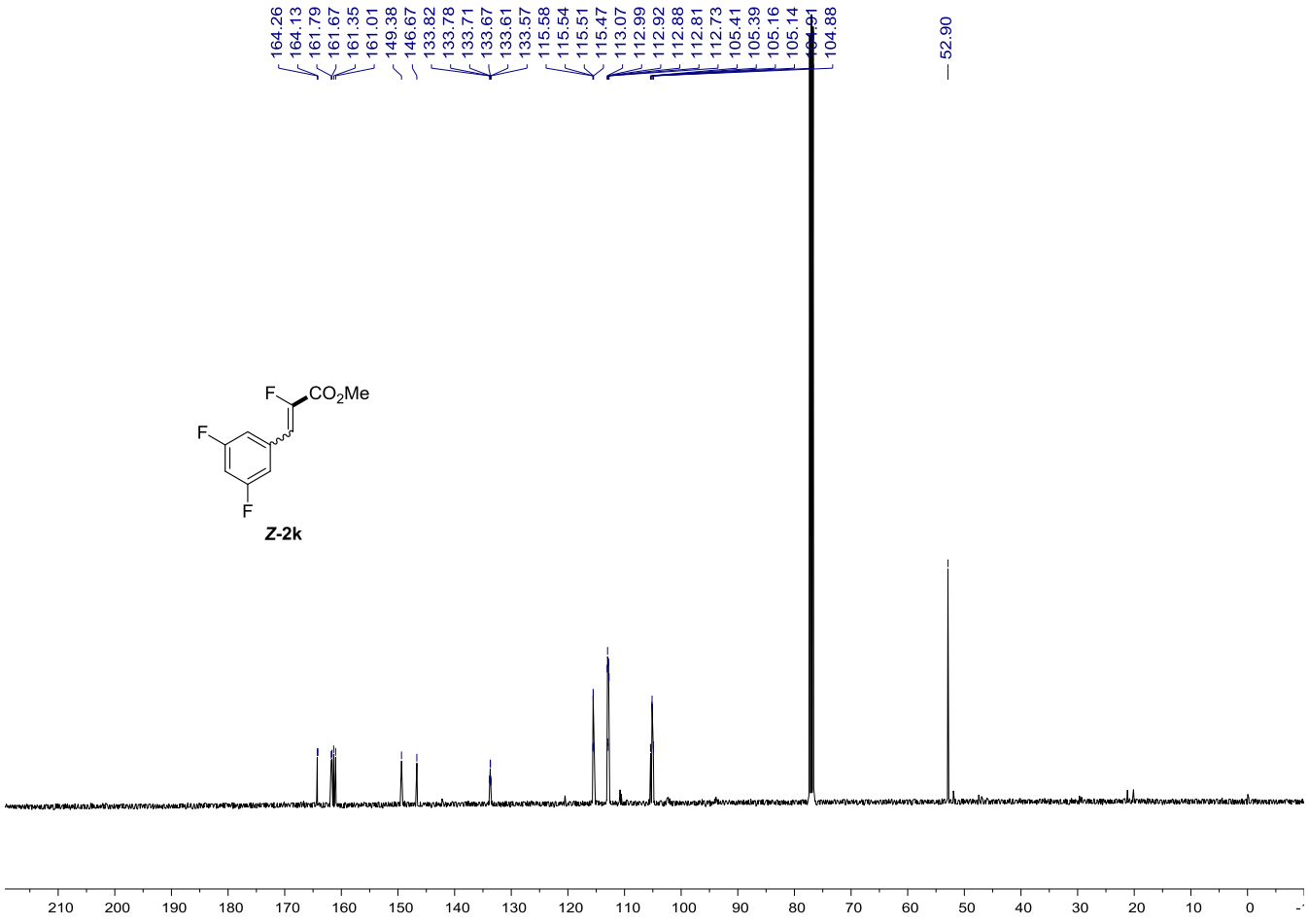
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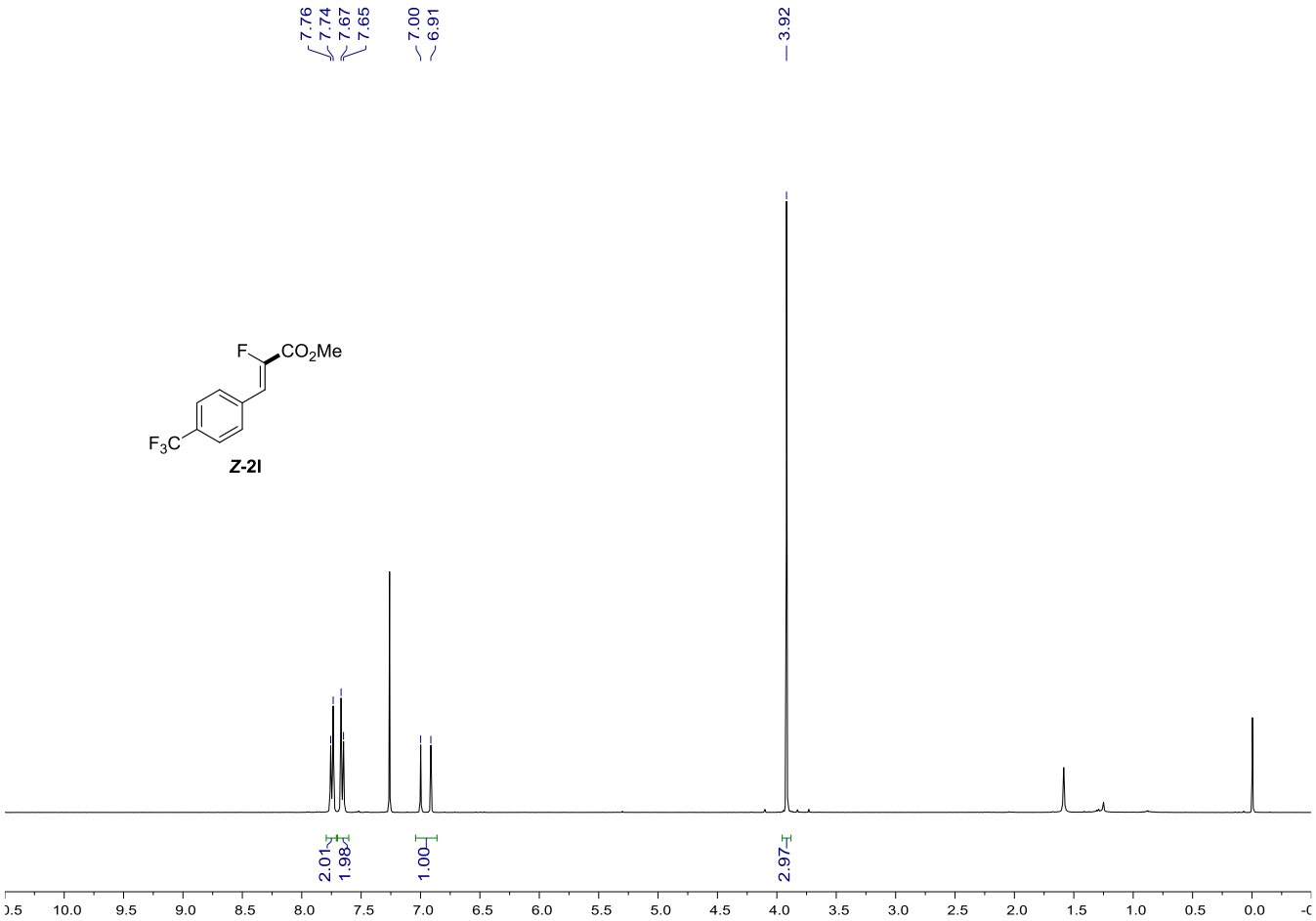
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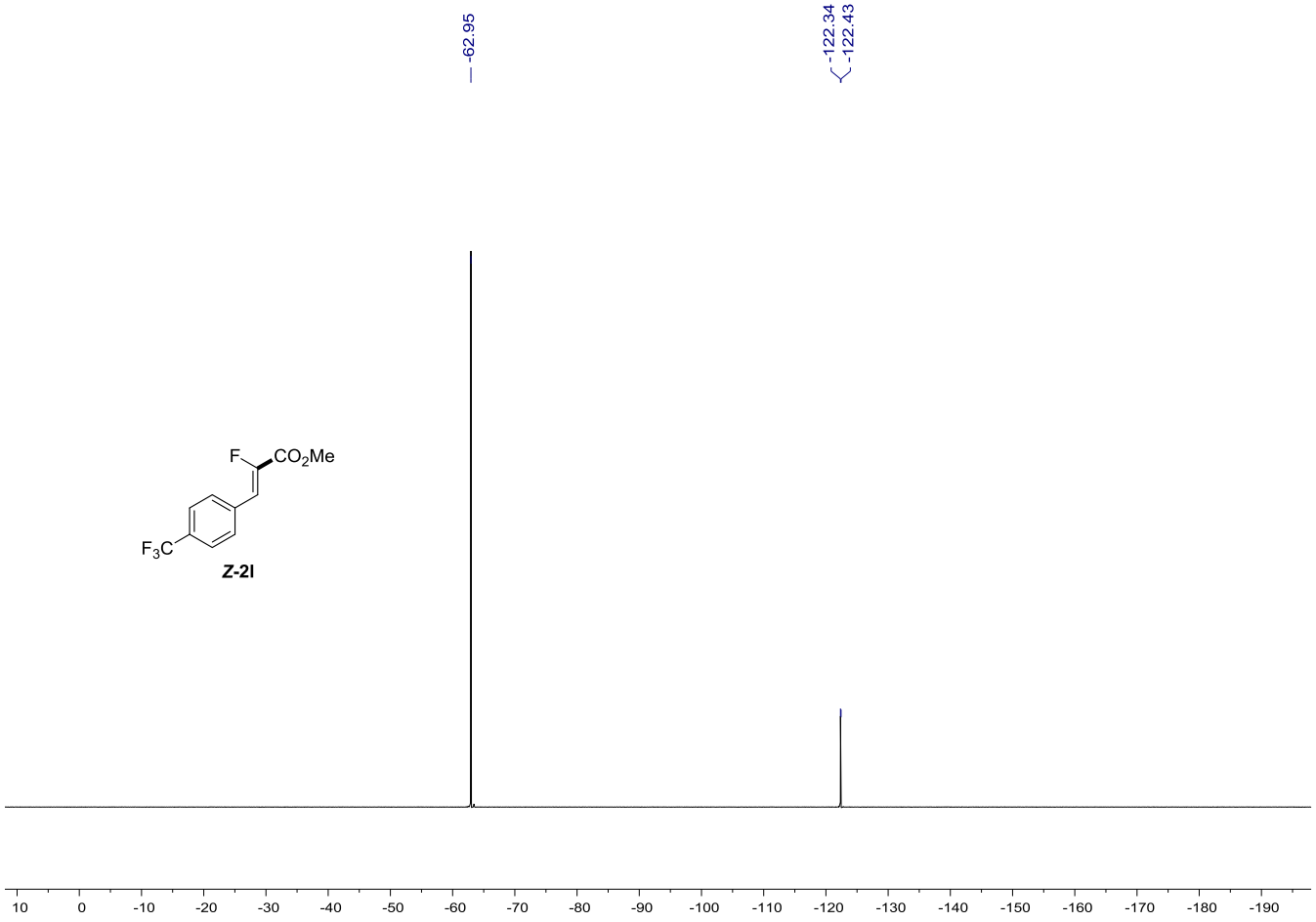
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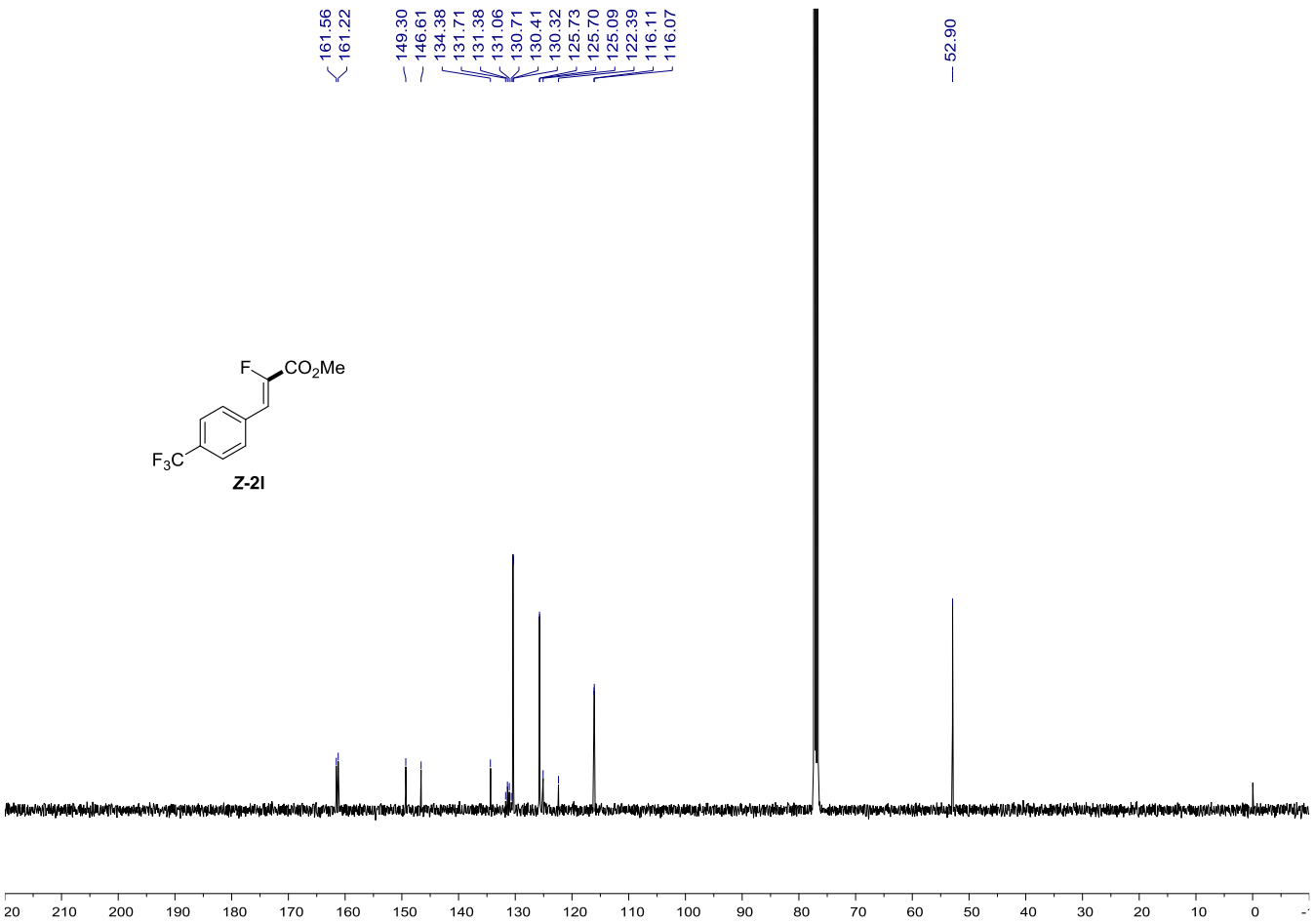
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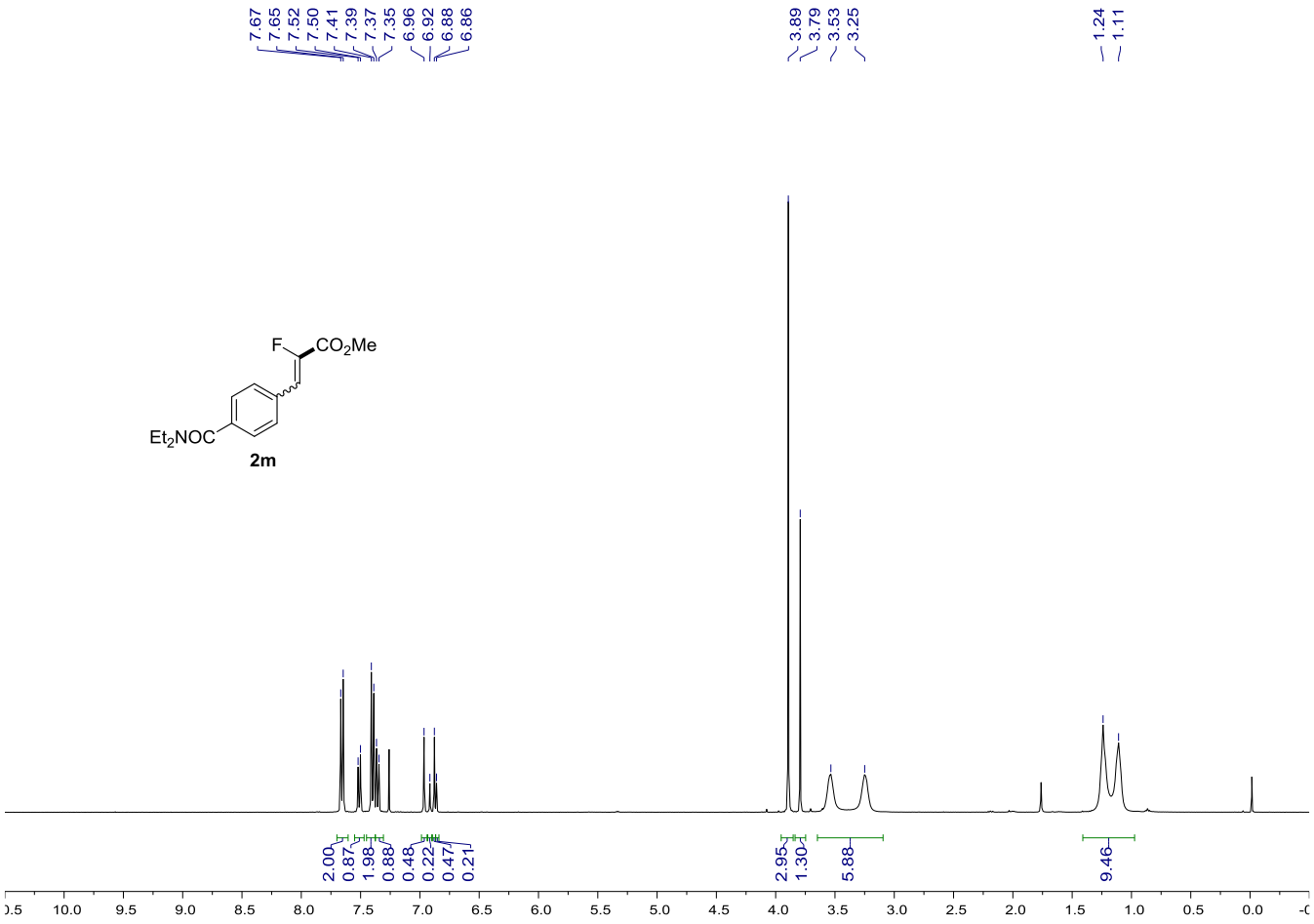
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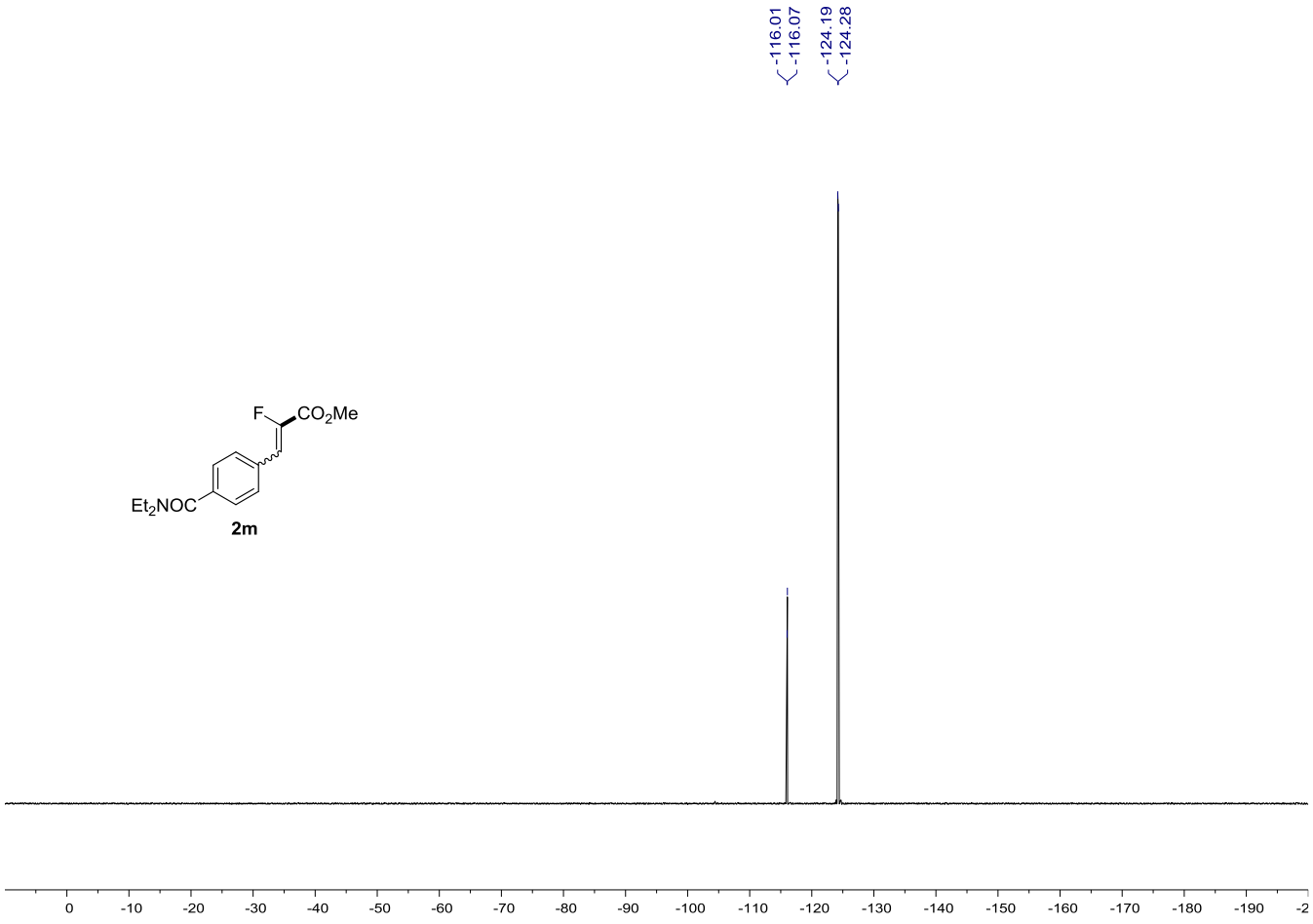
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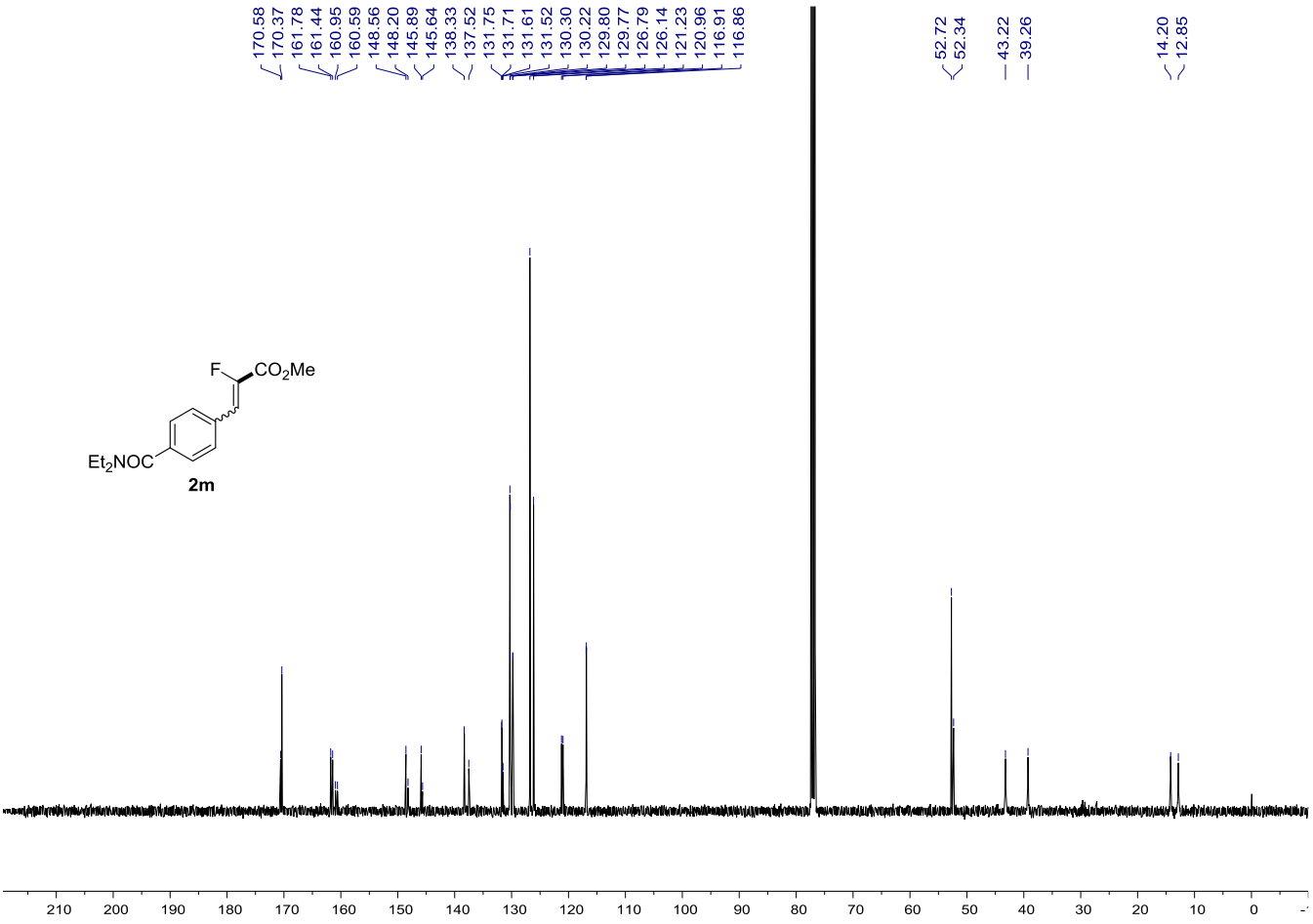
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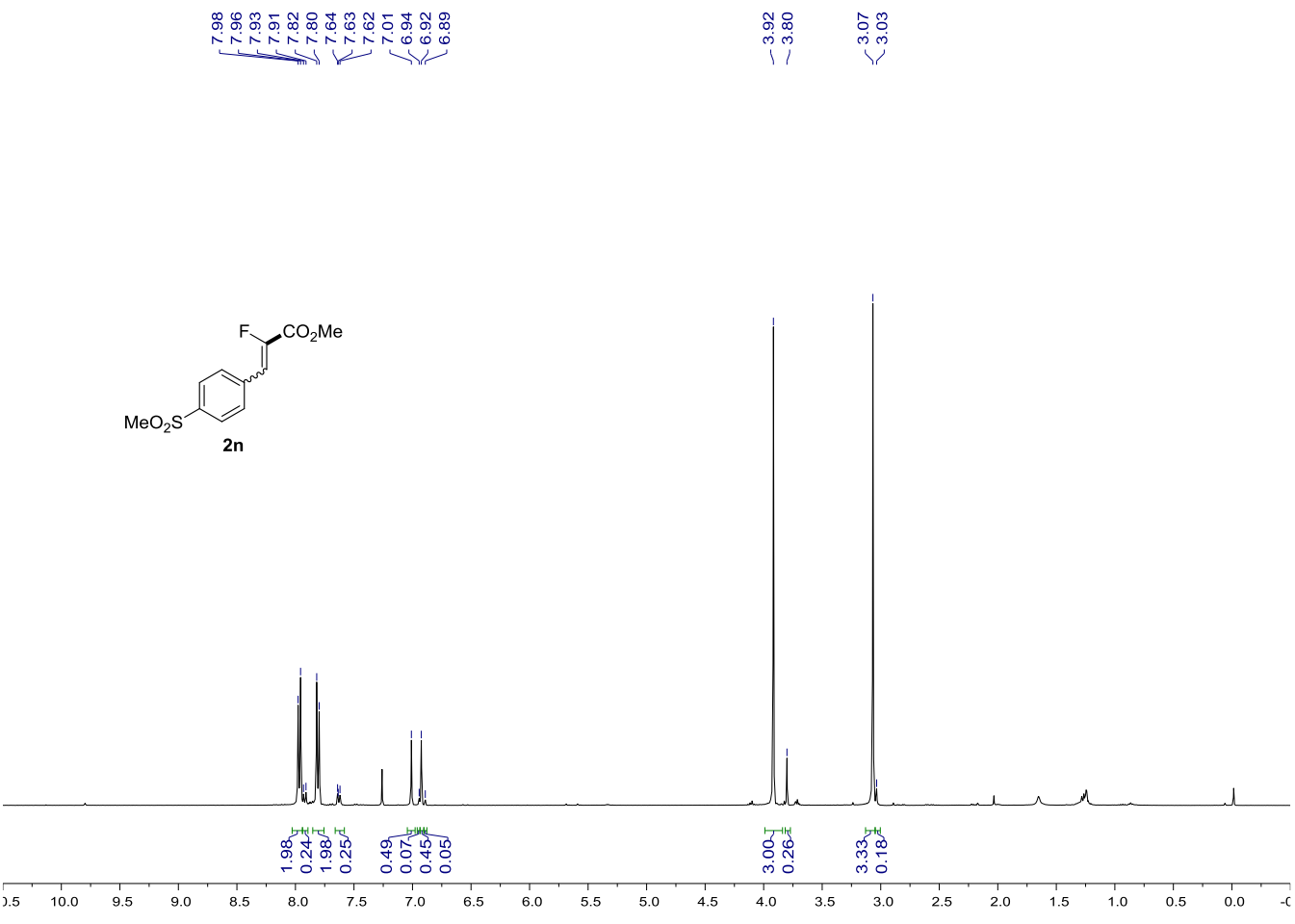
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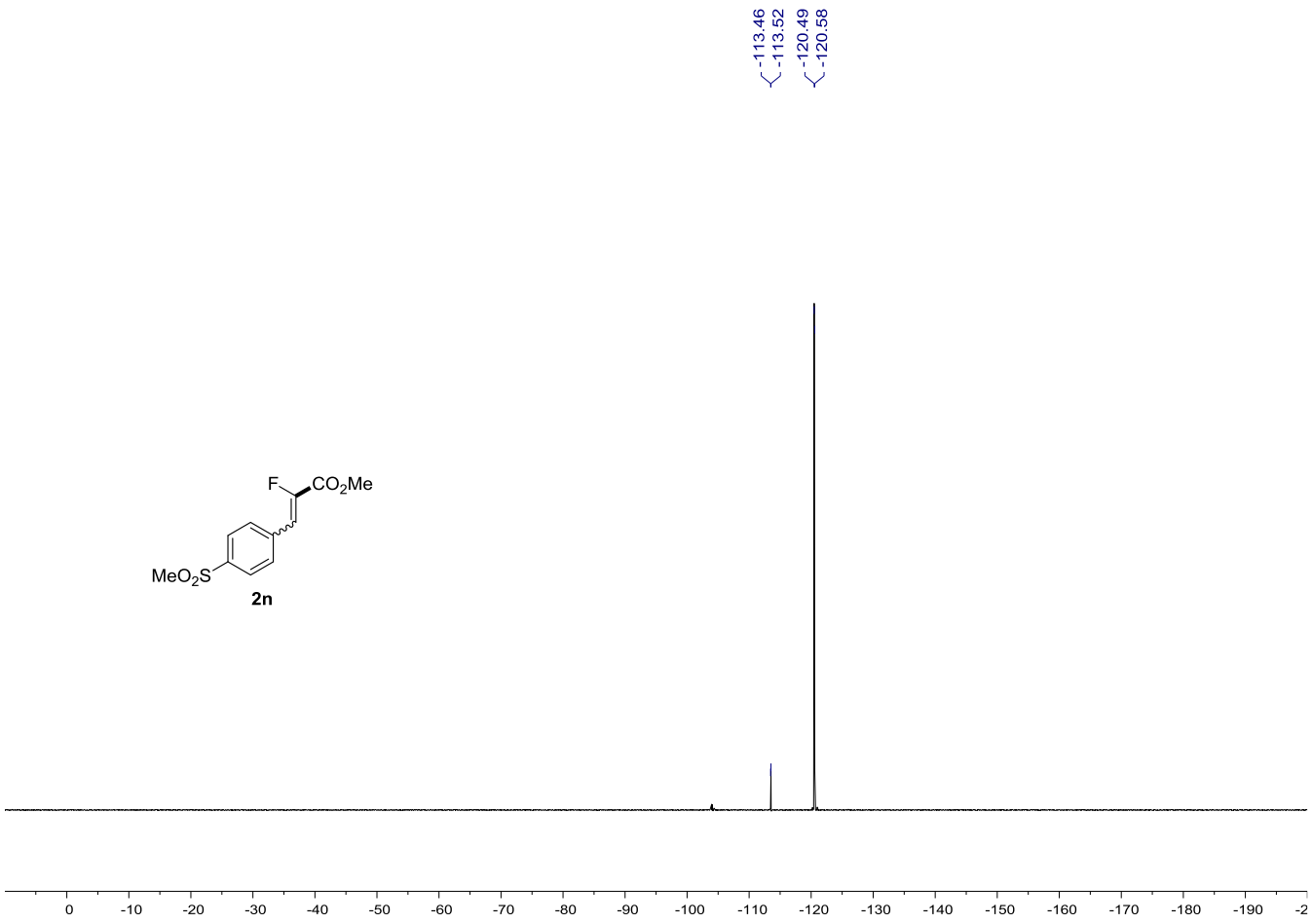
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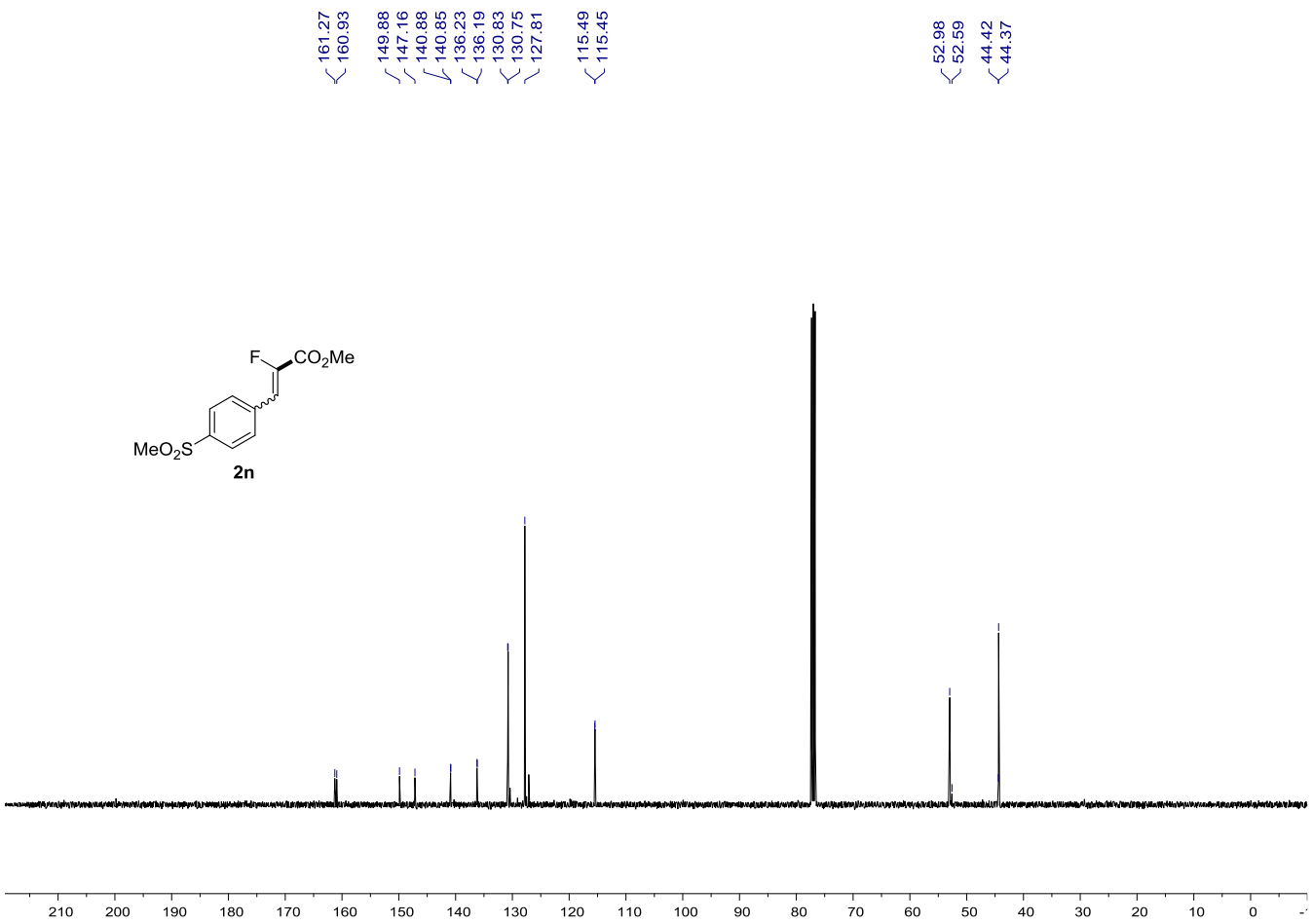
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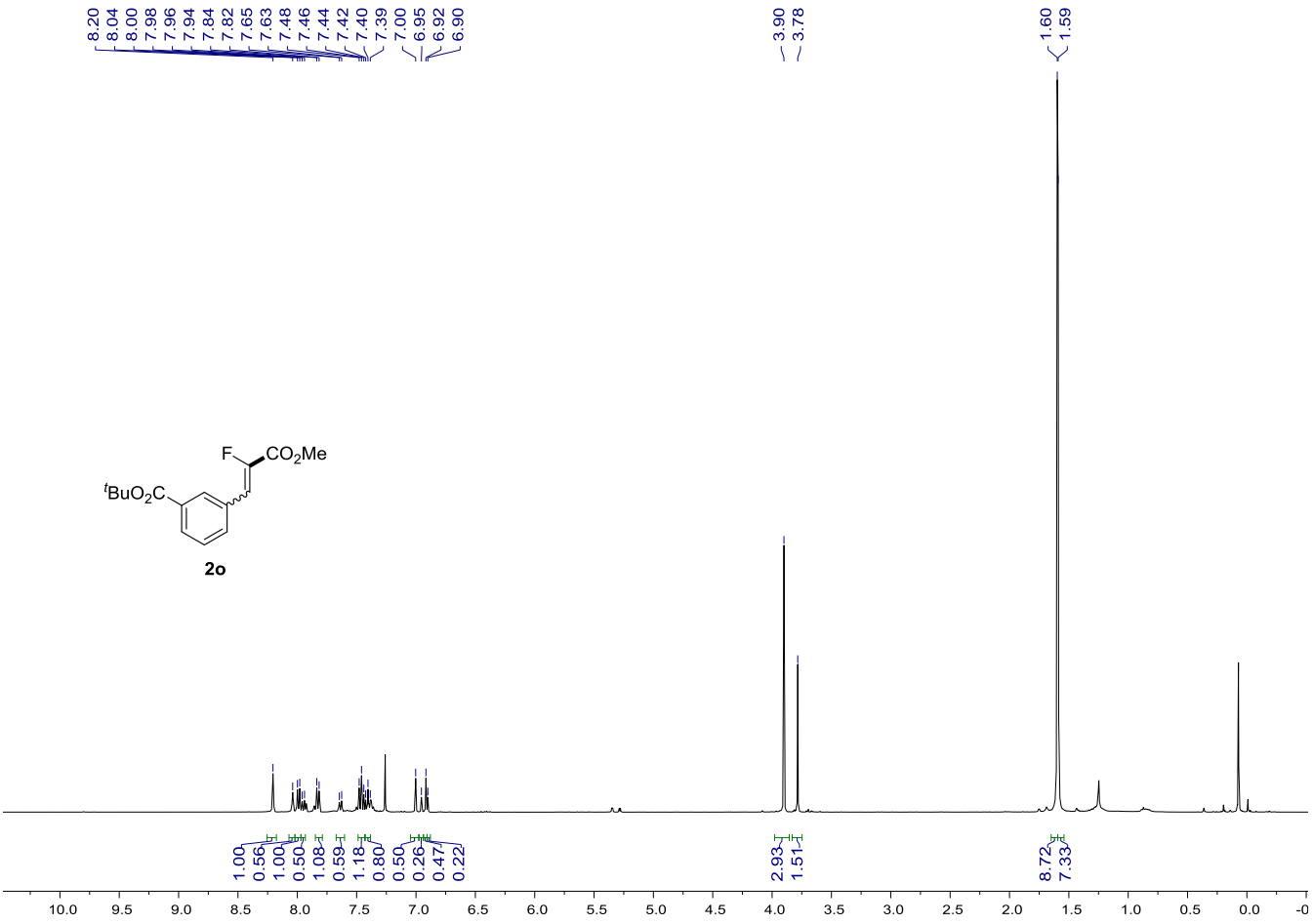
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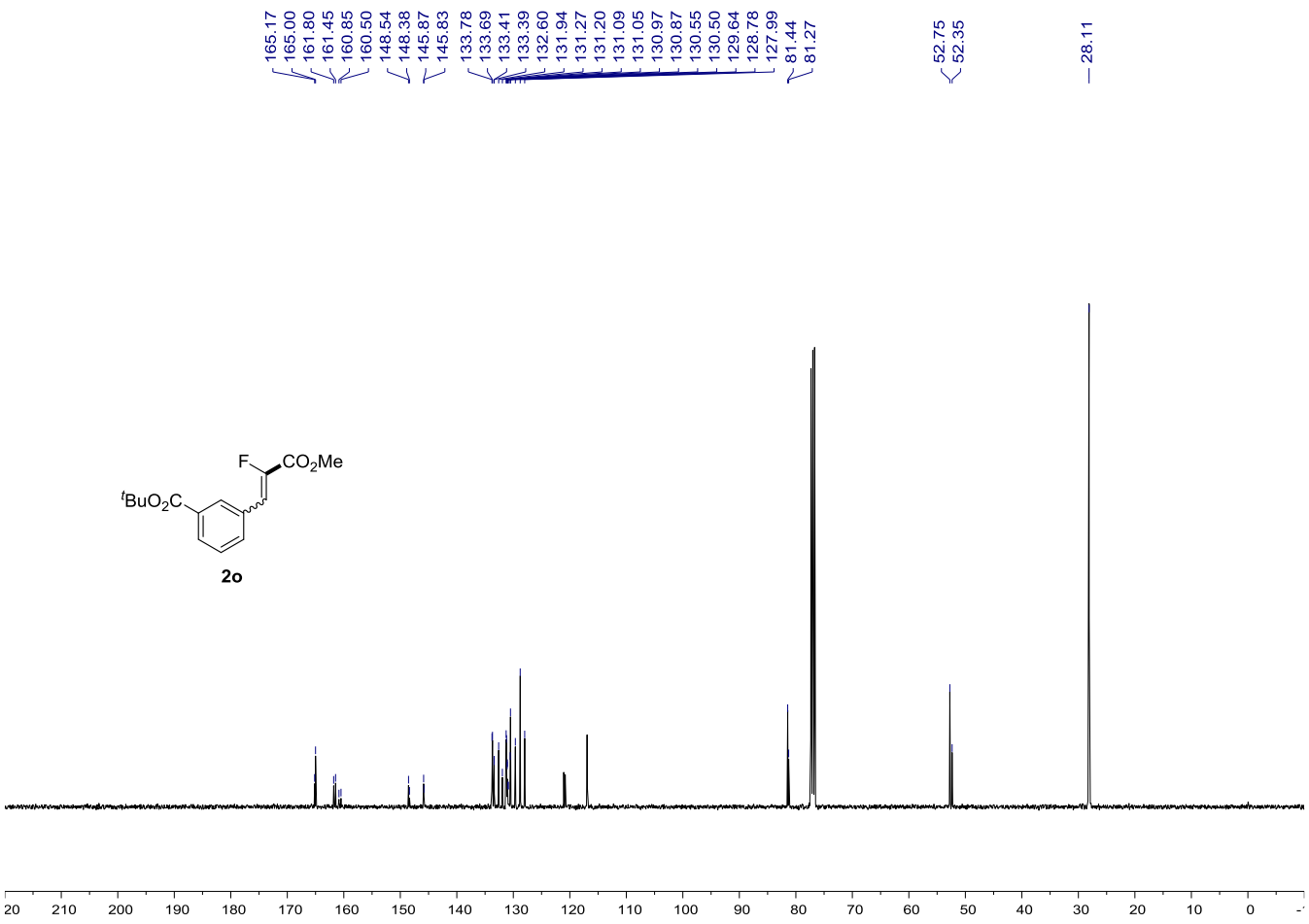
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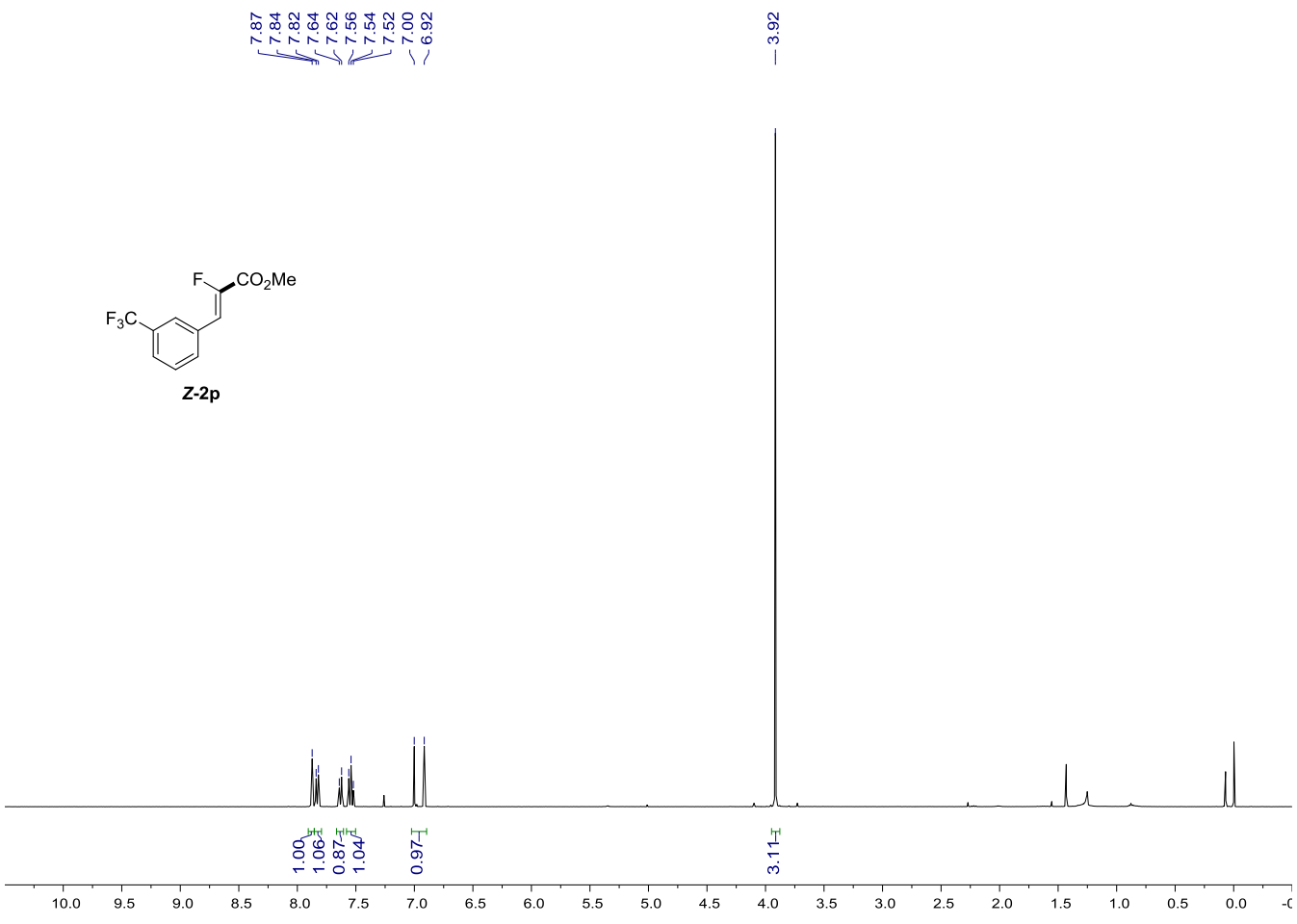
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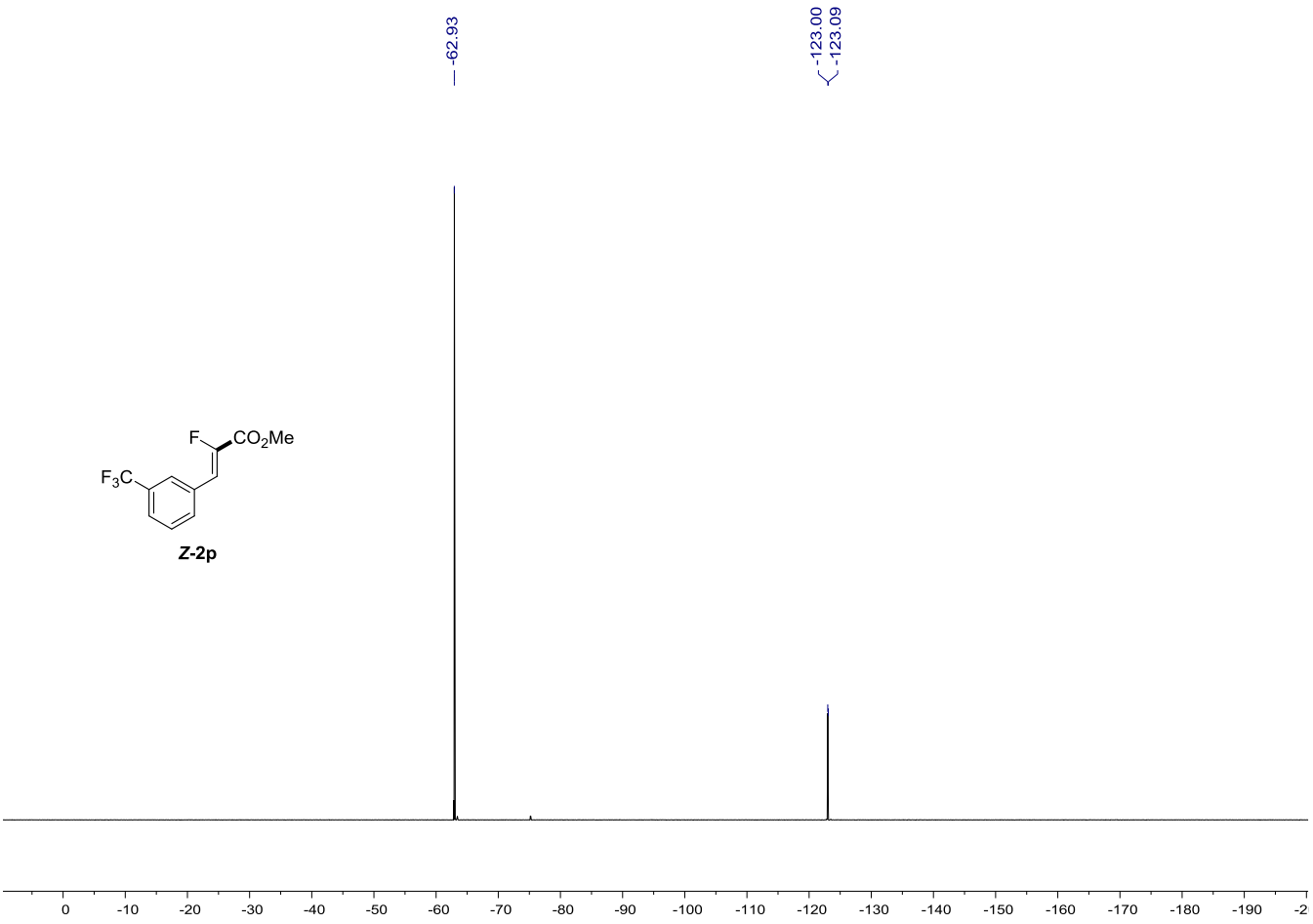
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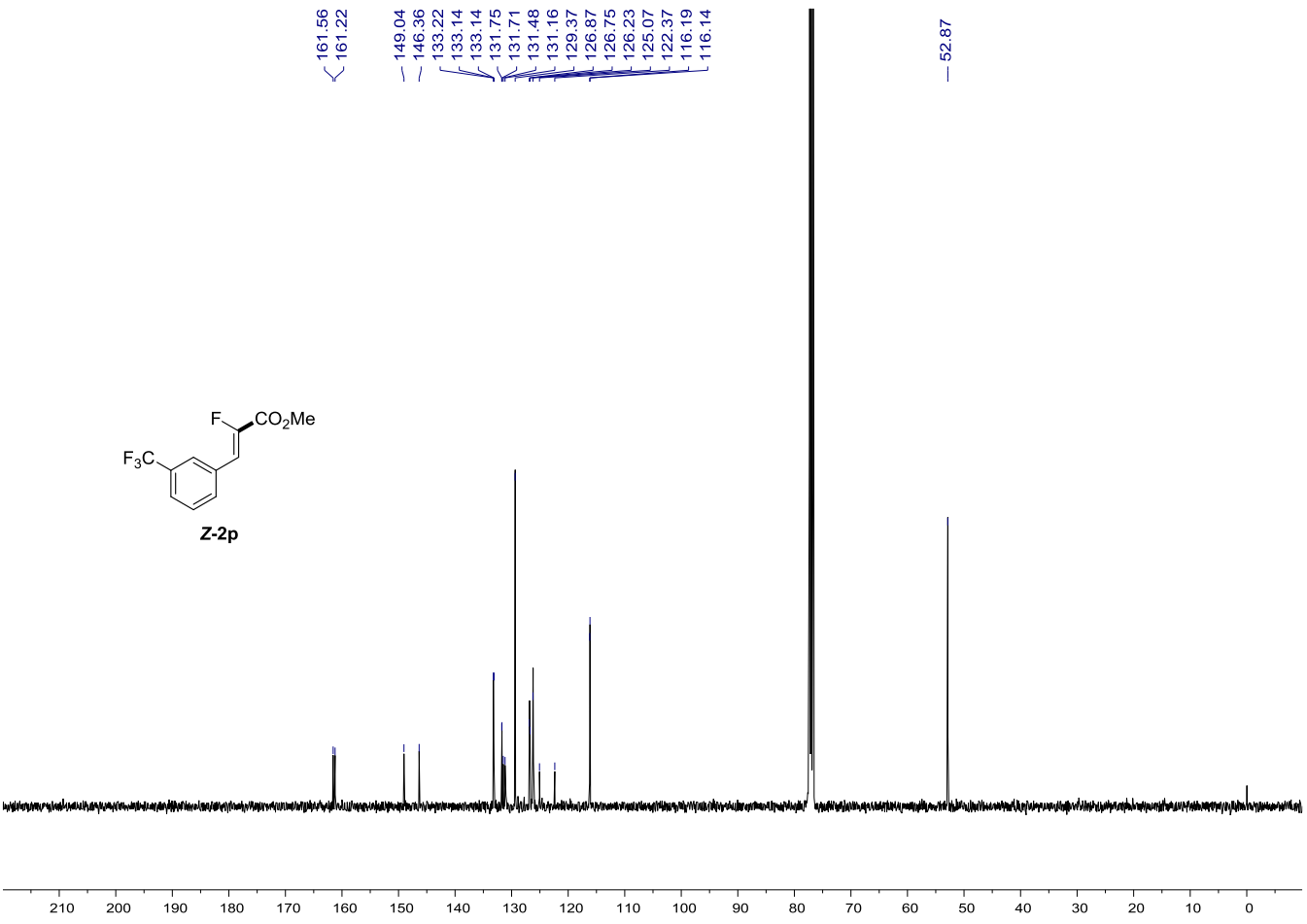
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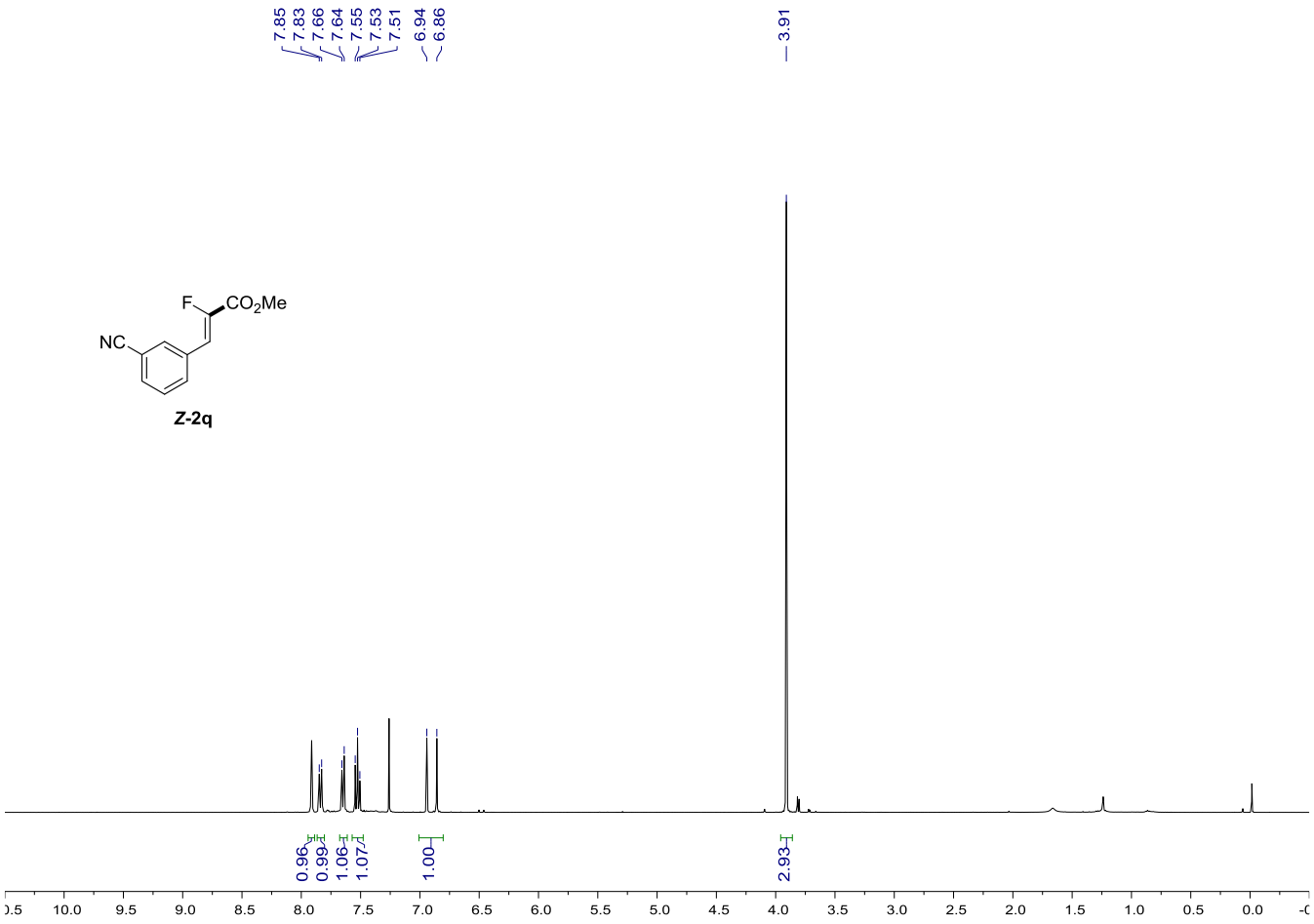
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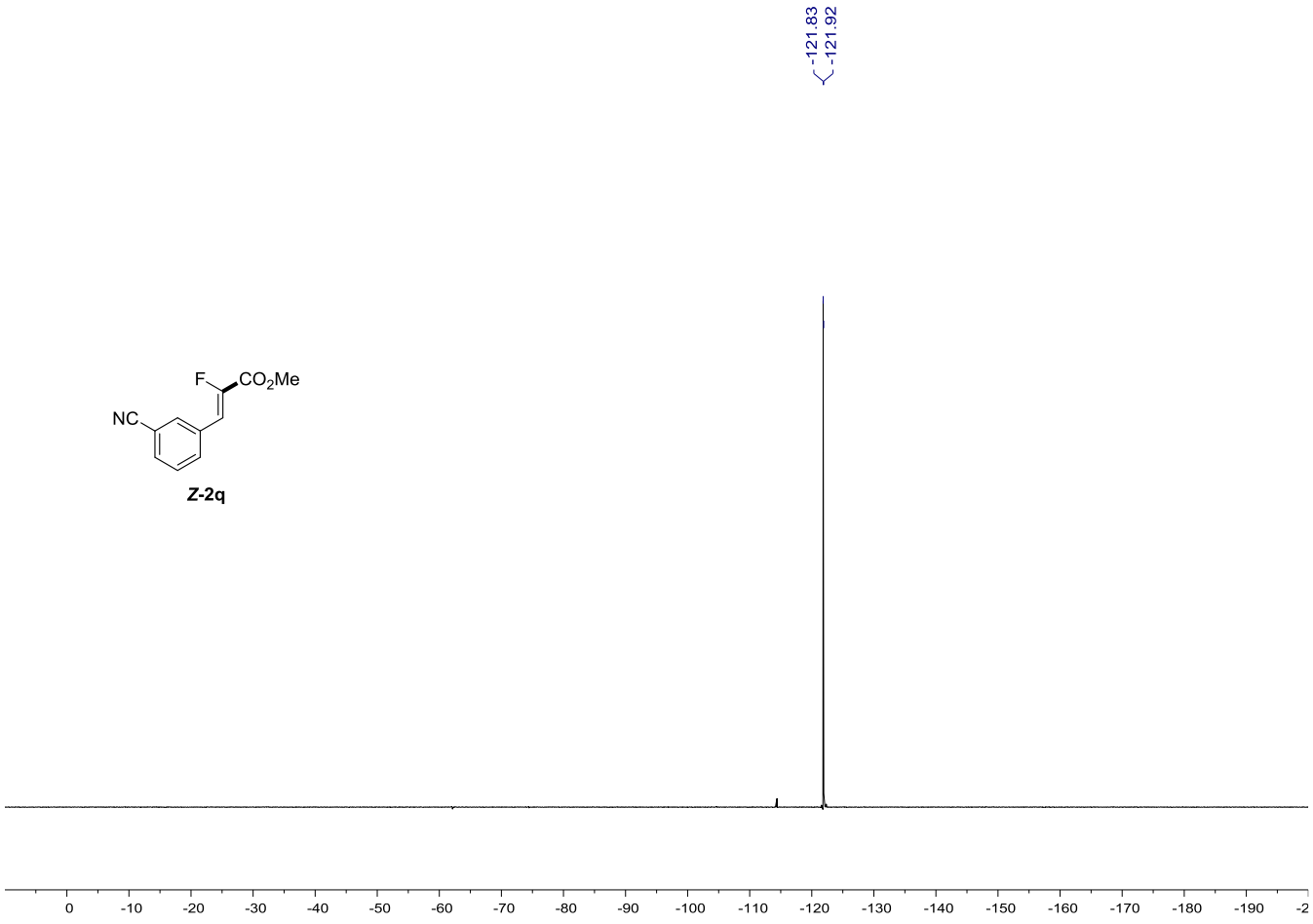
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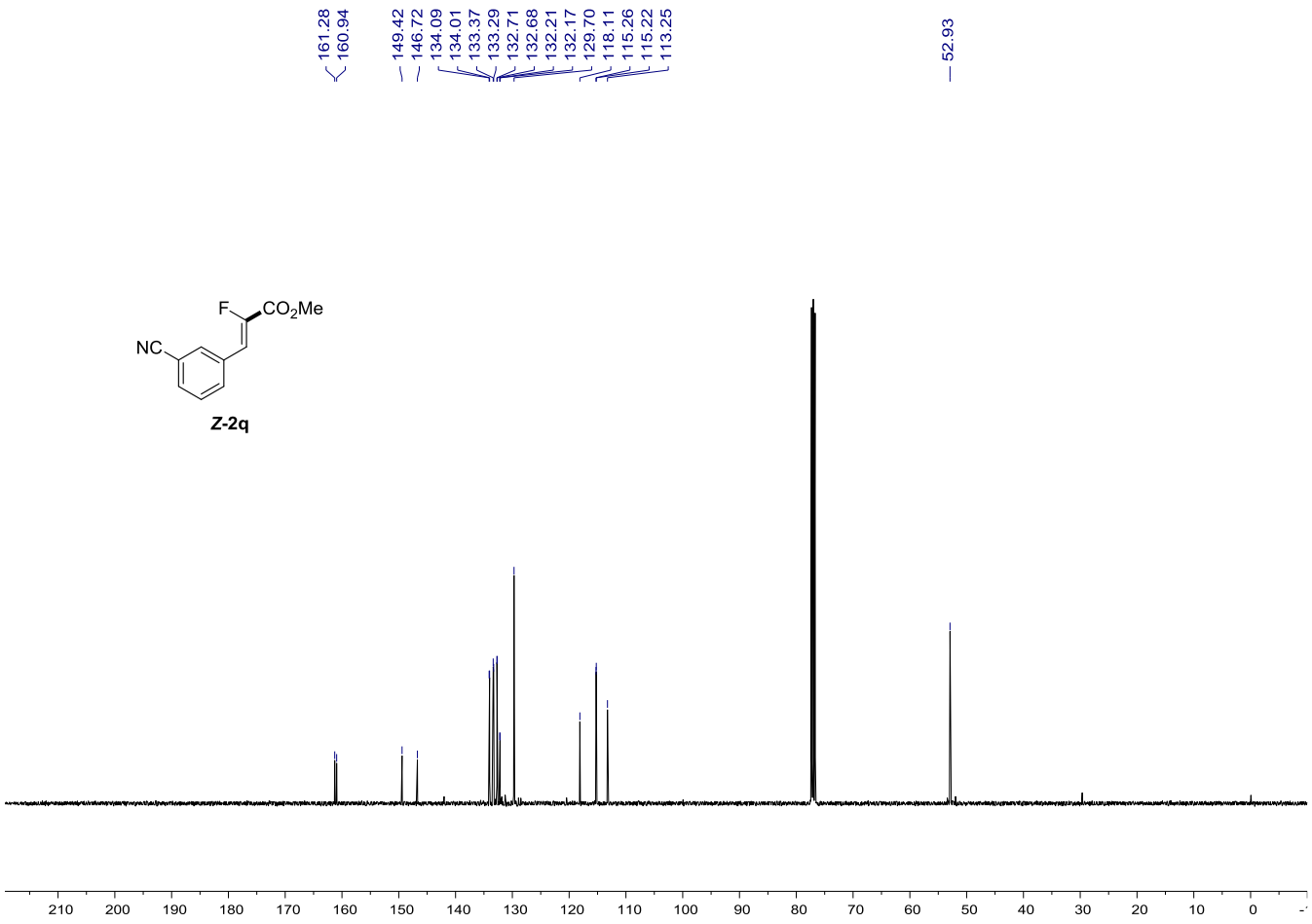
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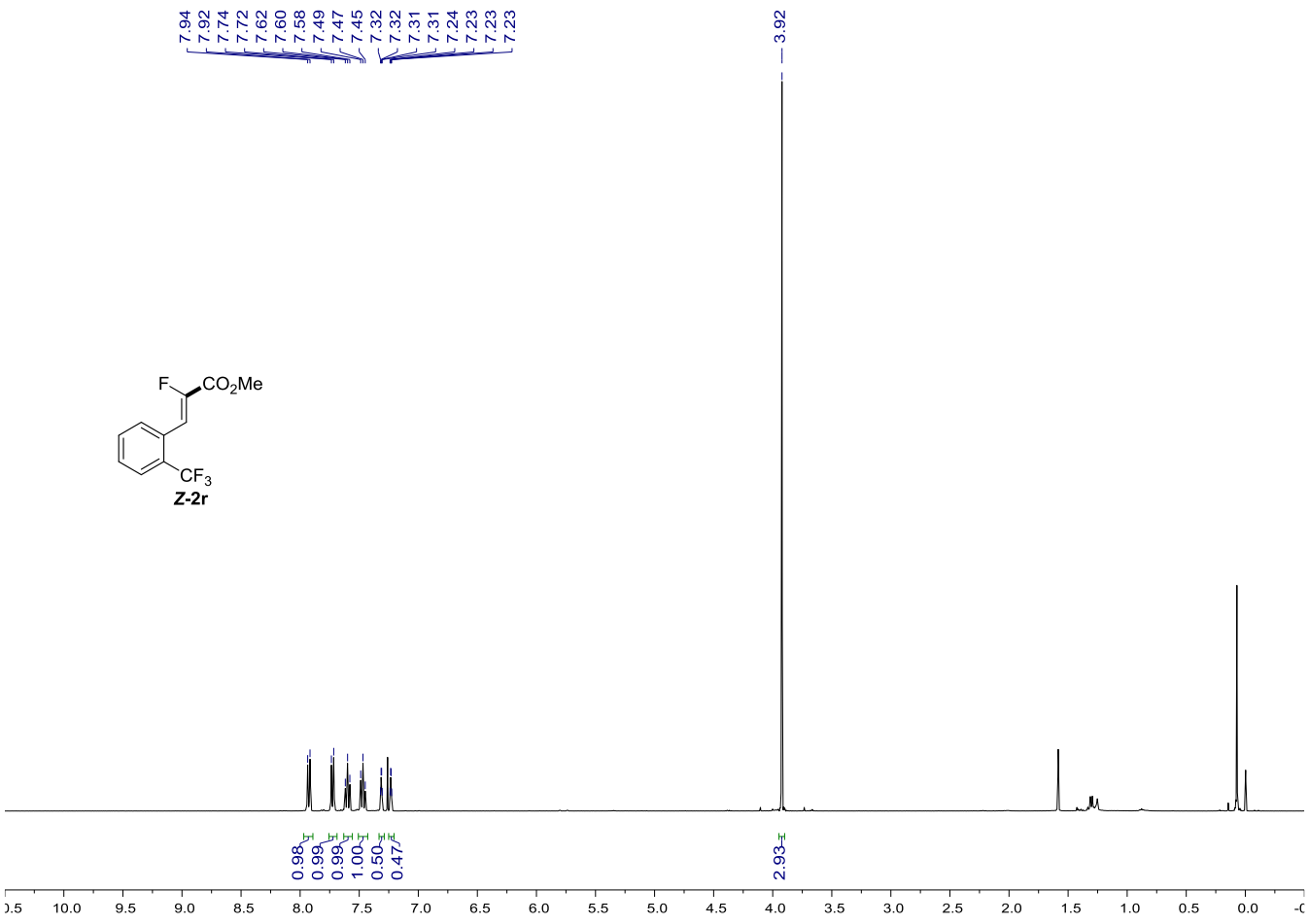
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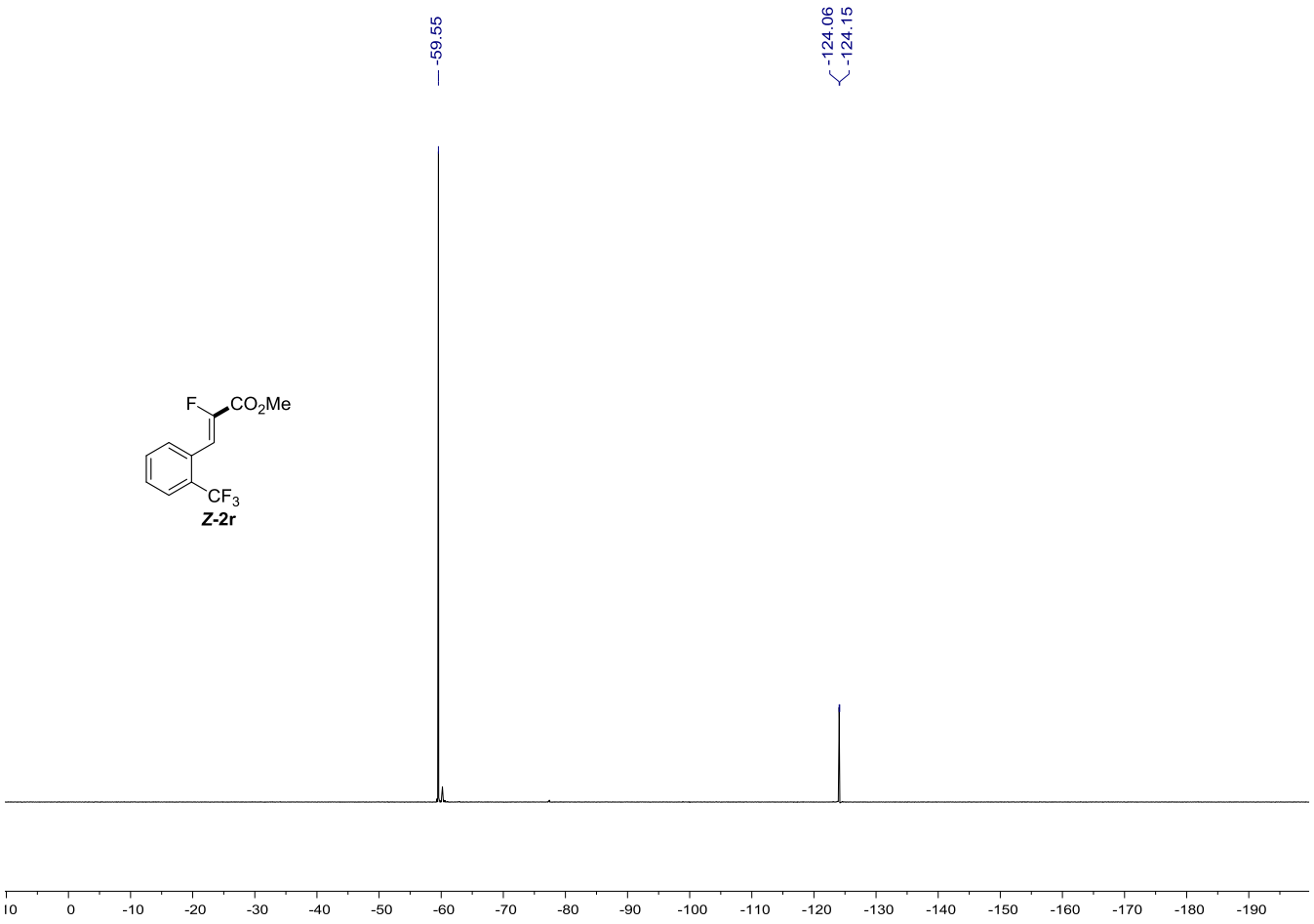
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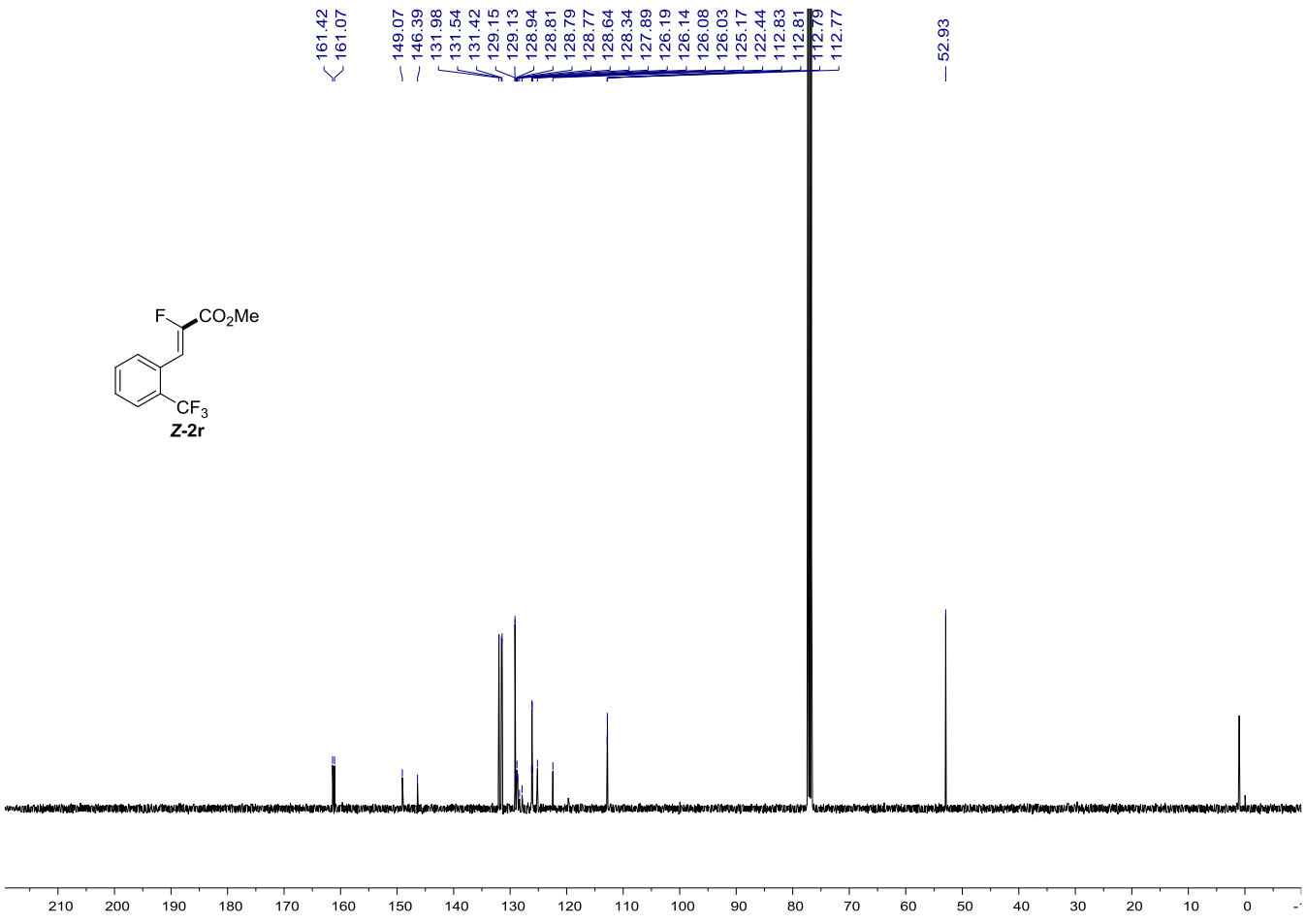
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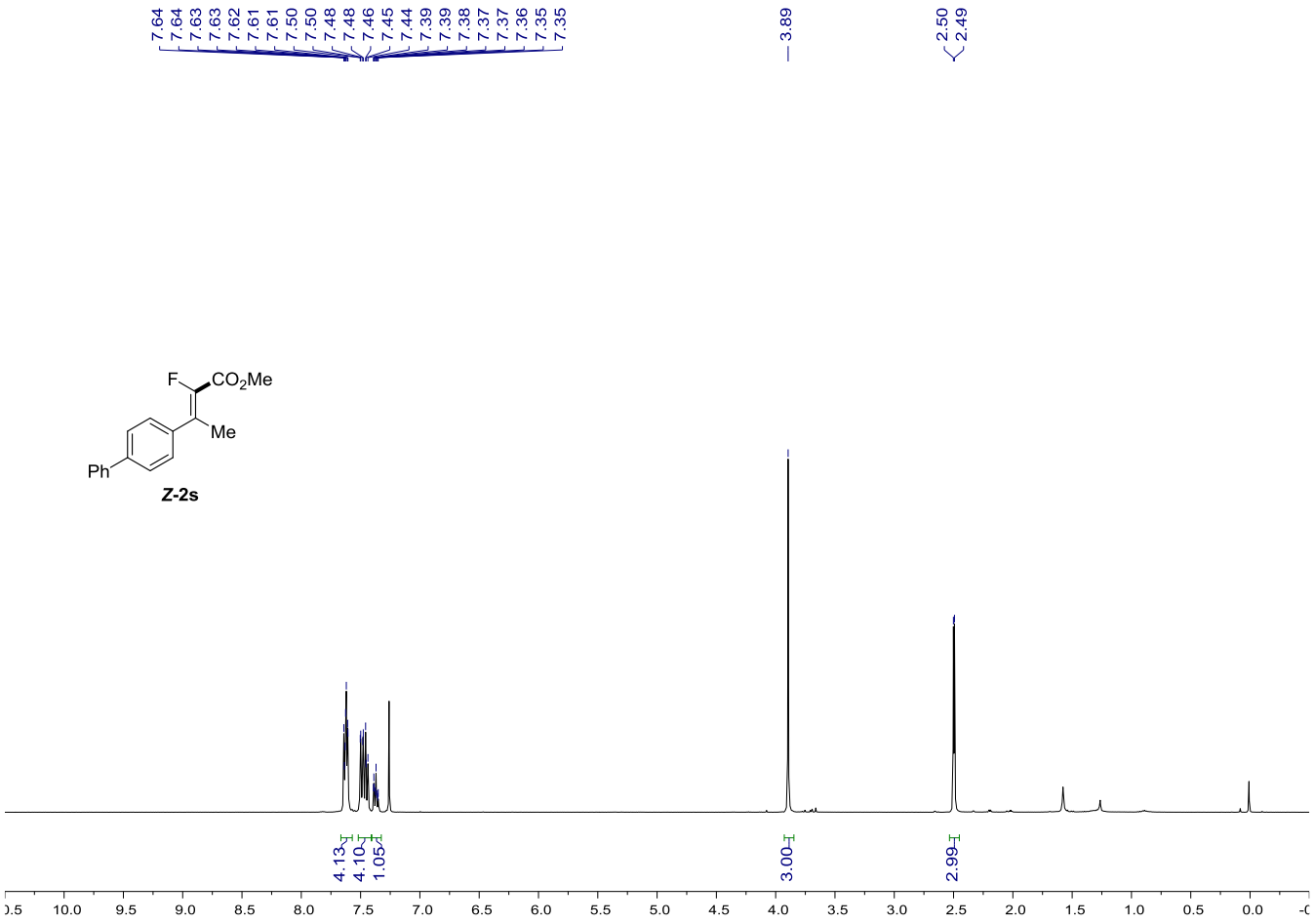
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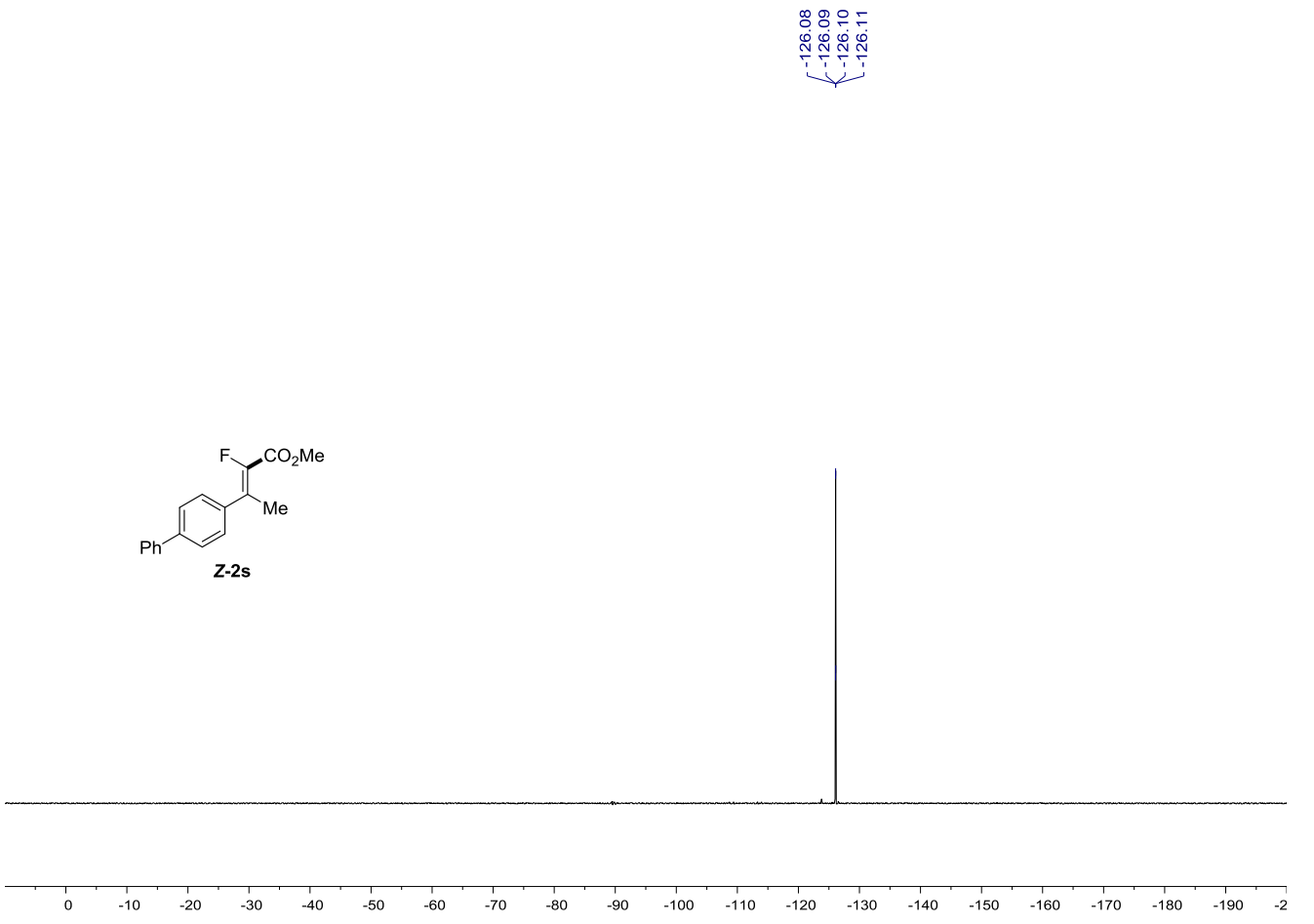
3.00
2.99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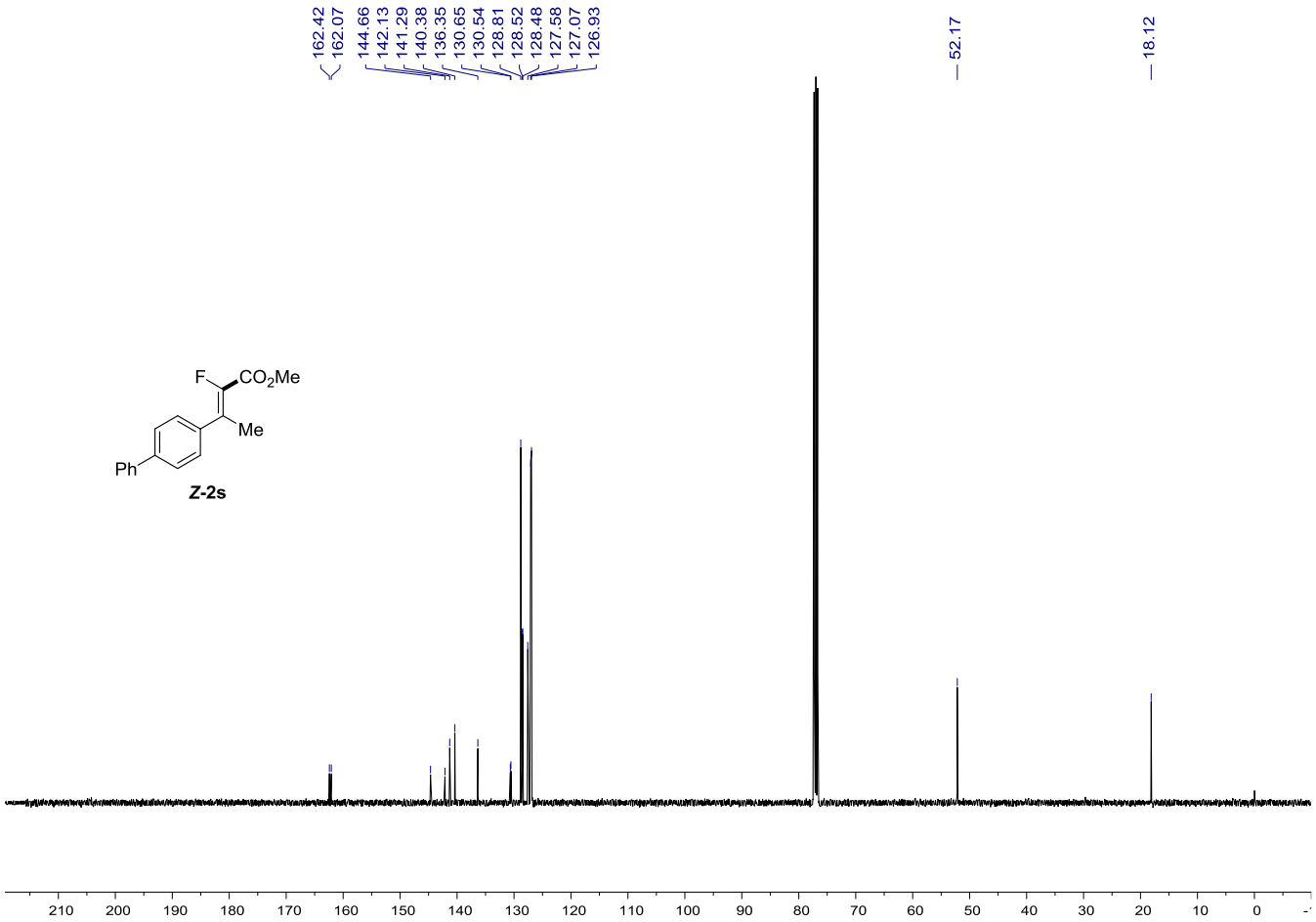
-126.11
F
CO2Me
Me
Ph
Z-2s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127.58
127.07
126.93
52.17
18.12
F
CO2Me
Me
Ph
Z-2s
210
200
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150
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110
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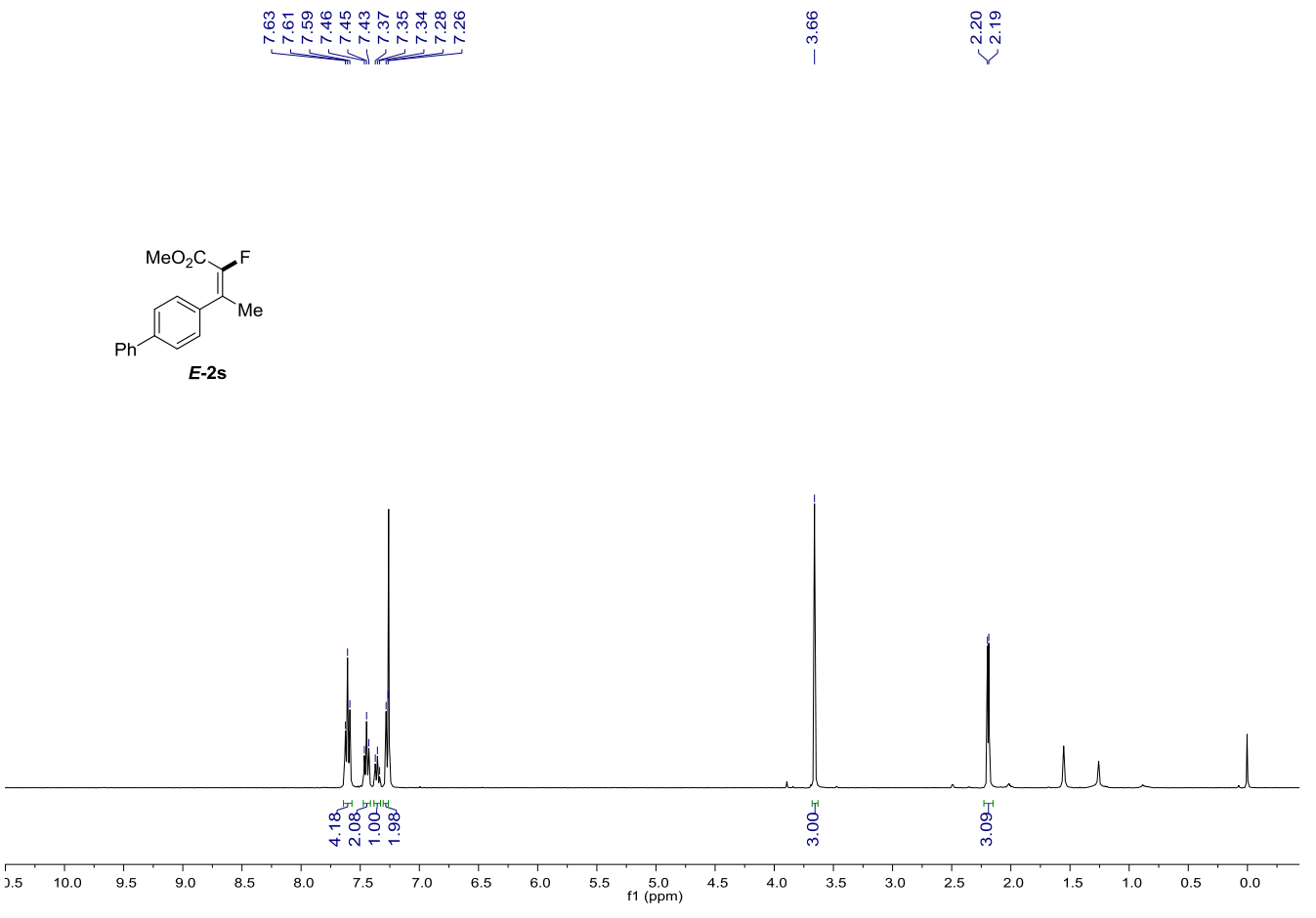
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7.26
3.66
2.20
2.19
MeO2C
F
Me
Ph
E-2s
4.18
2.08
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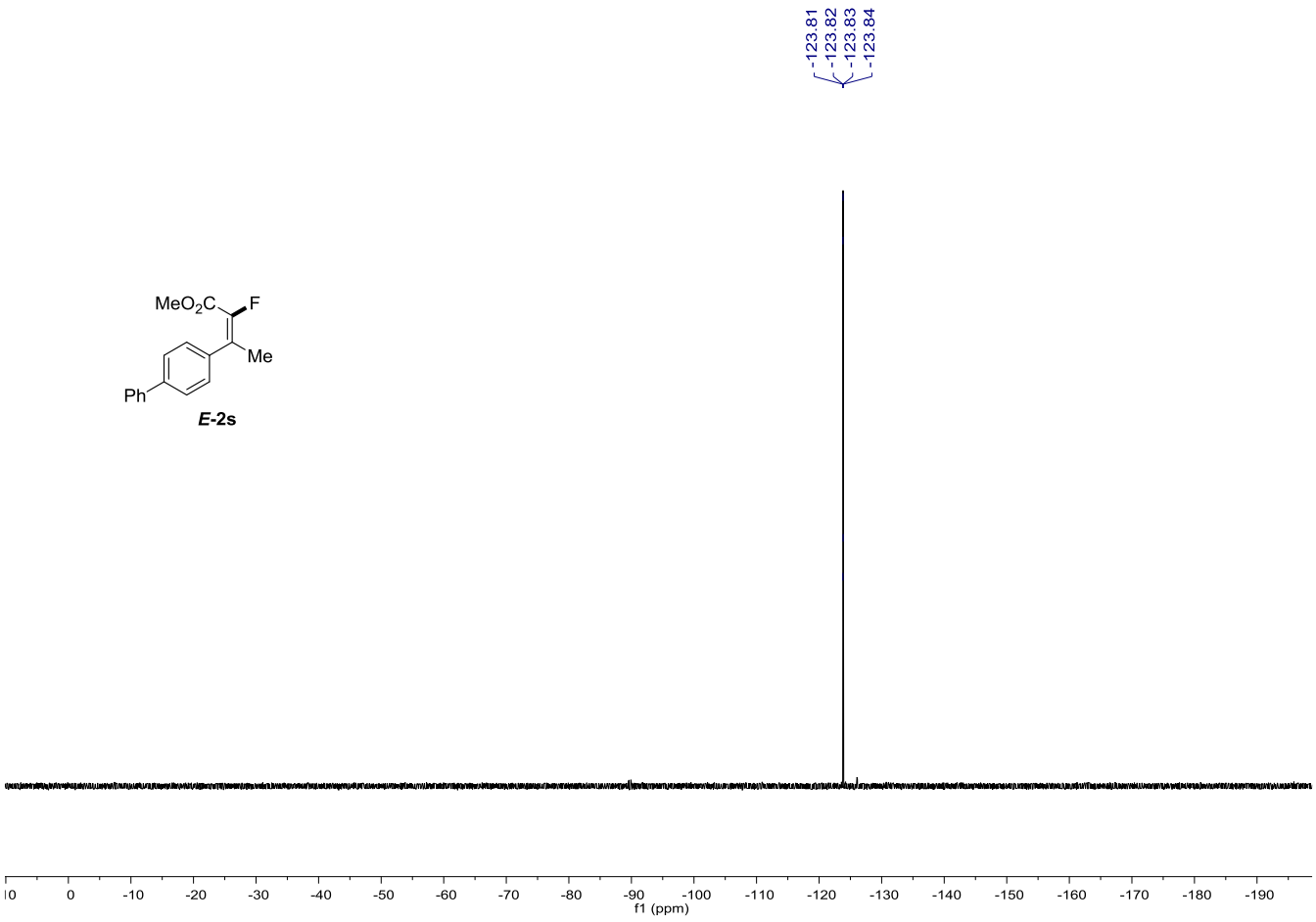
1.98
3.00
3.09
f1 (ppm)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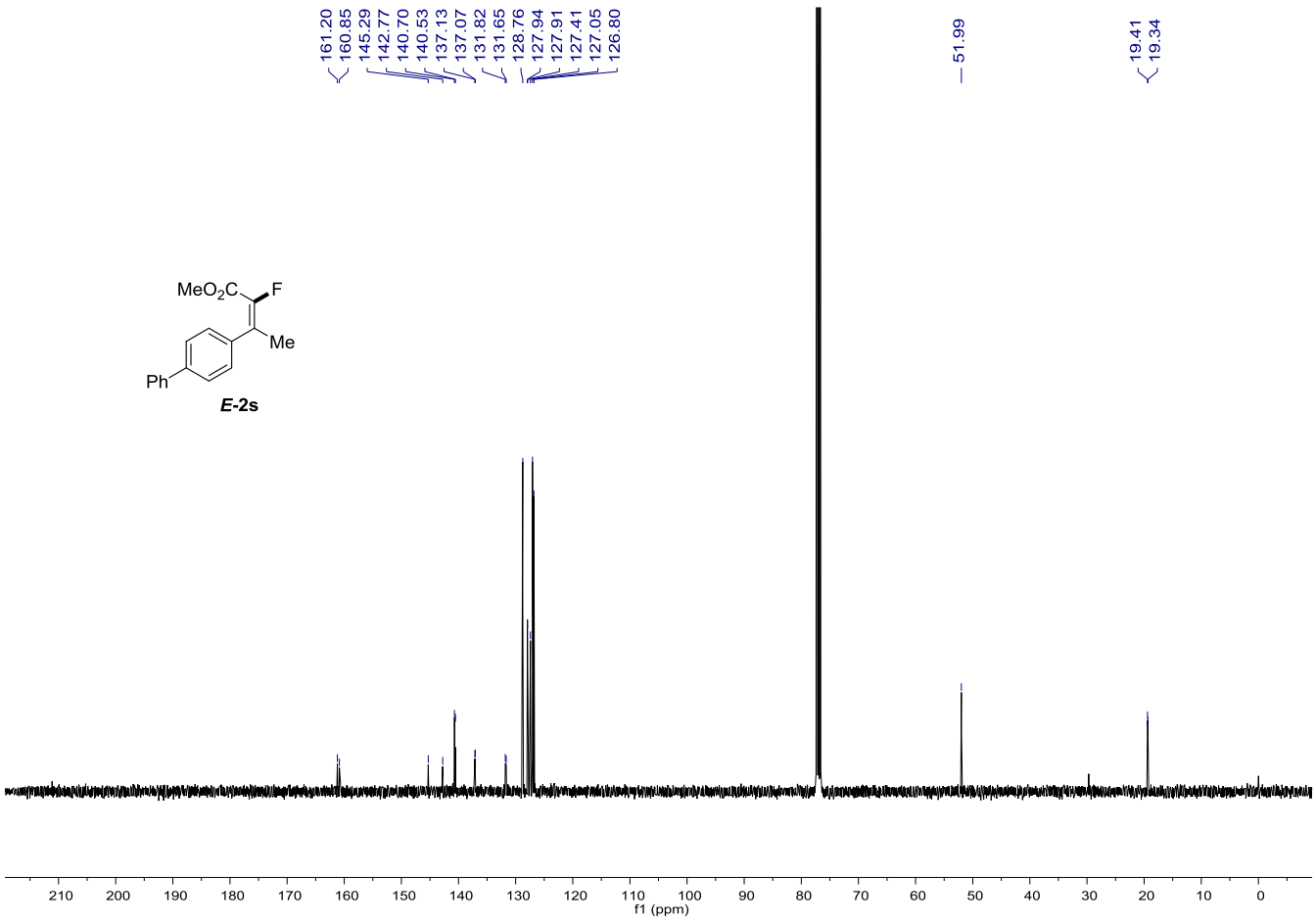
F
Me
Ph
E-2s
f1 (ppm)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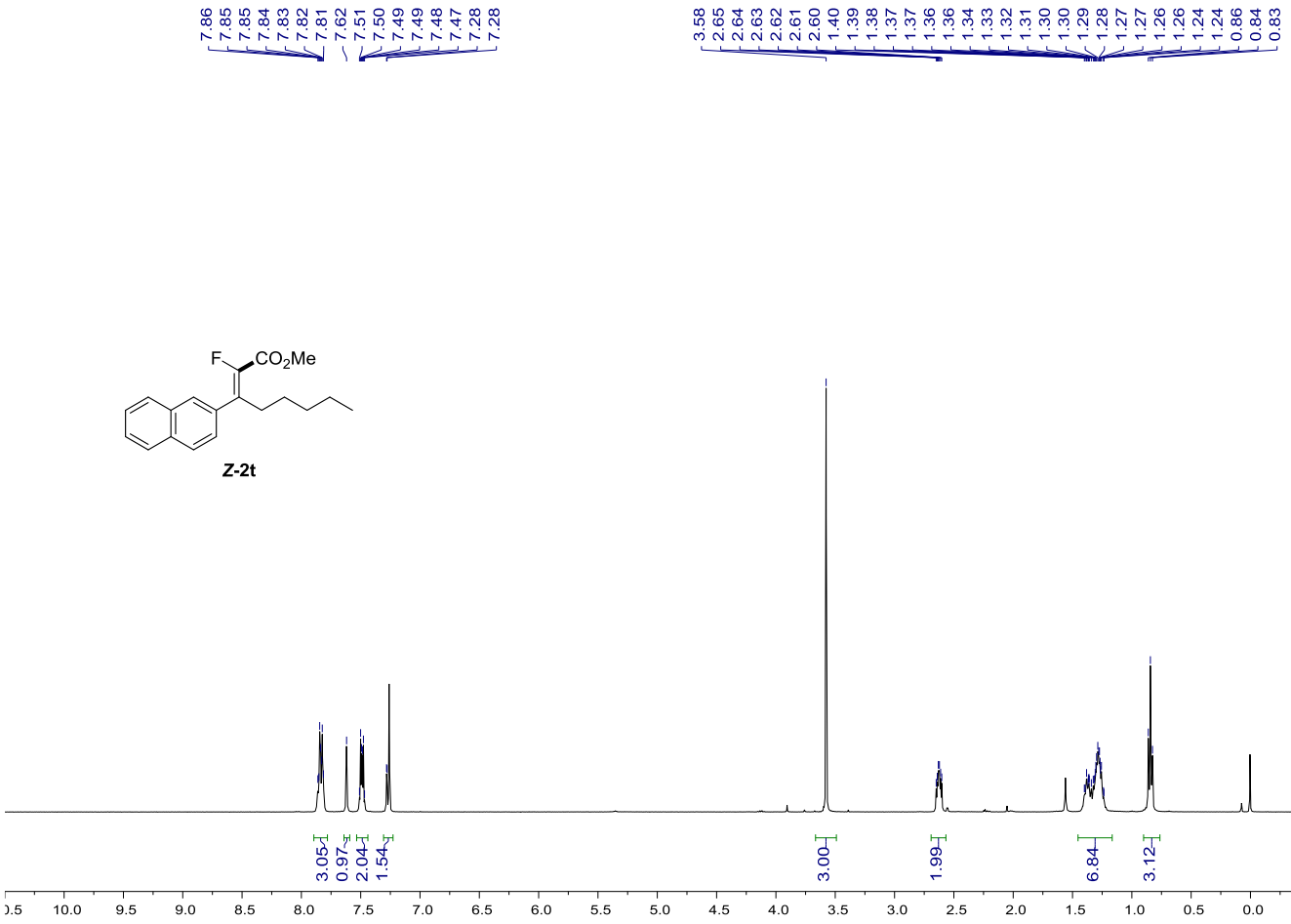
126.80
51.99
19.41
19.34
MeO2C
F
Me
Ph
E-2s
f1 (ppm)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7.48
7.47
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7.28
3.58
2.65
2.64
2.63
2.62
2.61
2.60
1.40
1.39
1.38
1.37
1.37
1.36
1.36
1.34
1.33
1.32
1.31
1.30
1.30
1.29
1.28
1.27
1.27
1.26
1.26
1.24
1.24
0.86
0.84
0.83
F
CO2Me
Z-2t
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1.54
3.00
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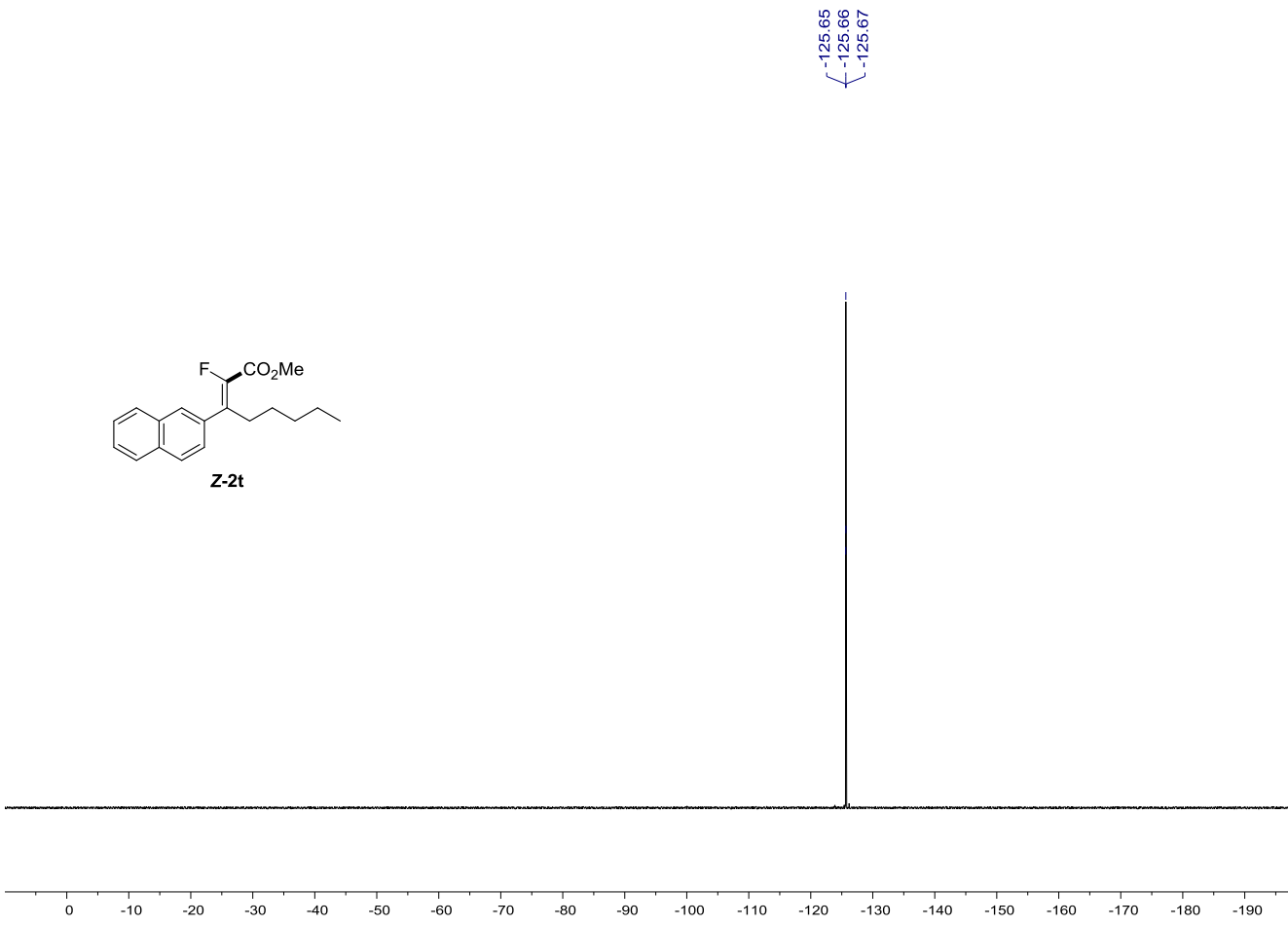
6.84
3.12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-125.66
-125.67
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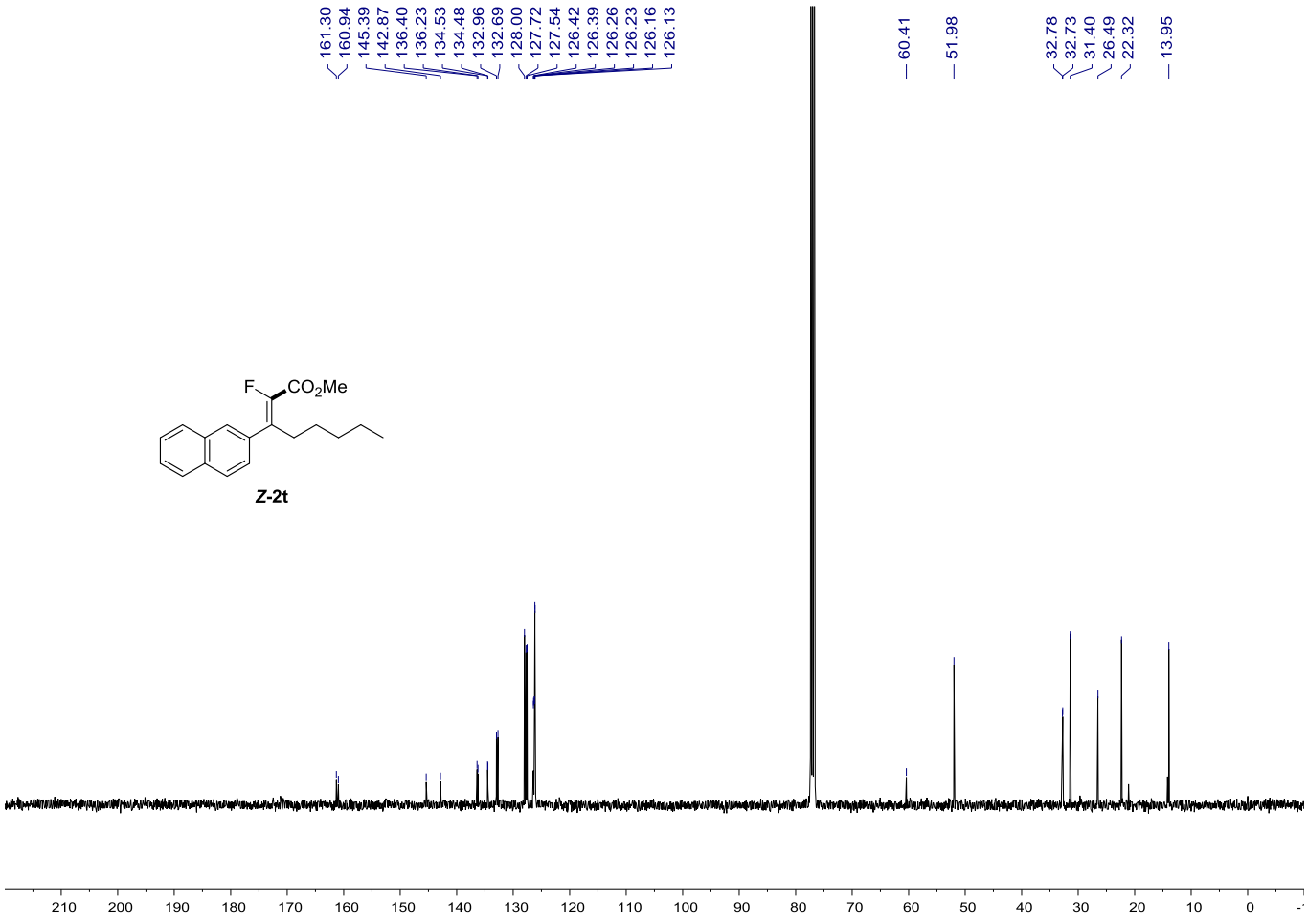
CO2Me
Z-2t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134.48
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132.69
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127.72
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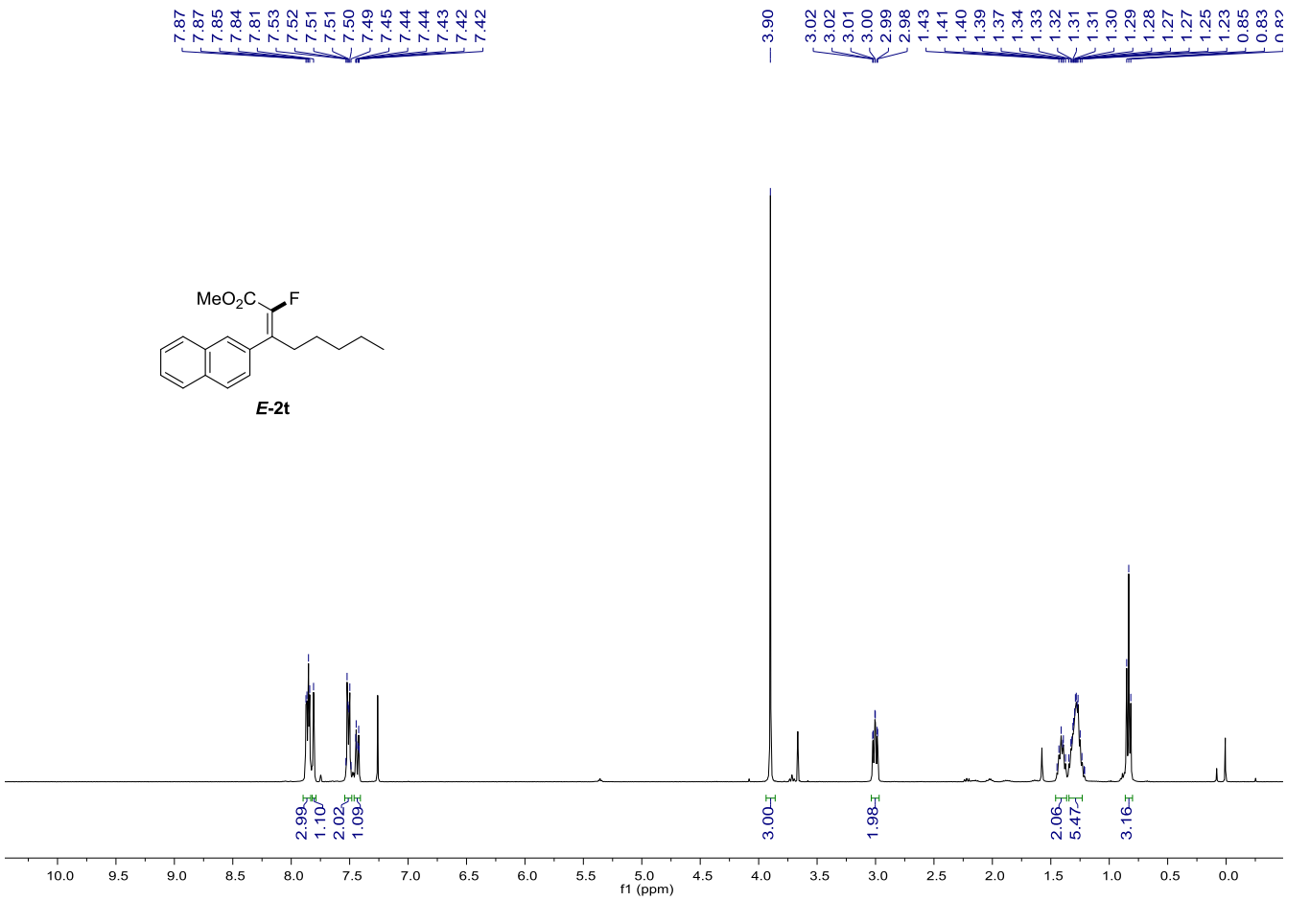
126.42
126.39
126.26
126.23
126.16
126.13
60.41
51.98
32.78
32.73
31.40
26.49
22.32
13.95
F
CO2Me
Z-2t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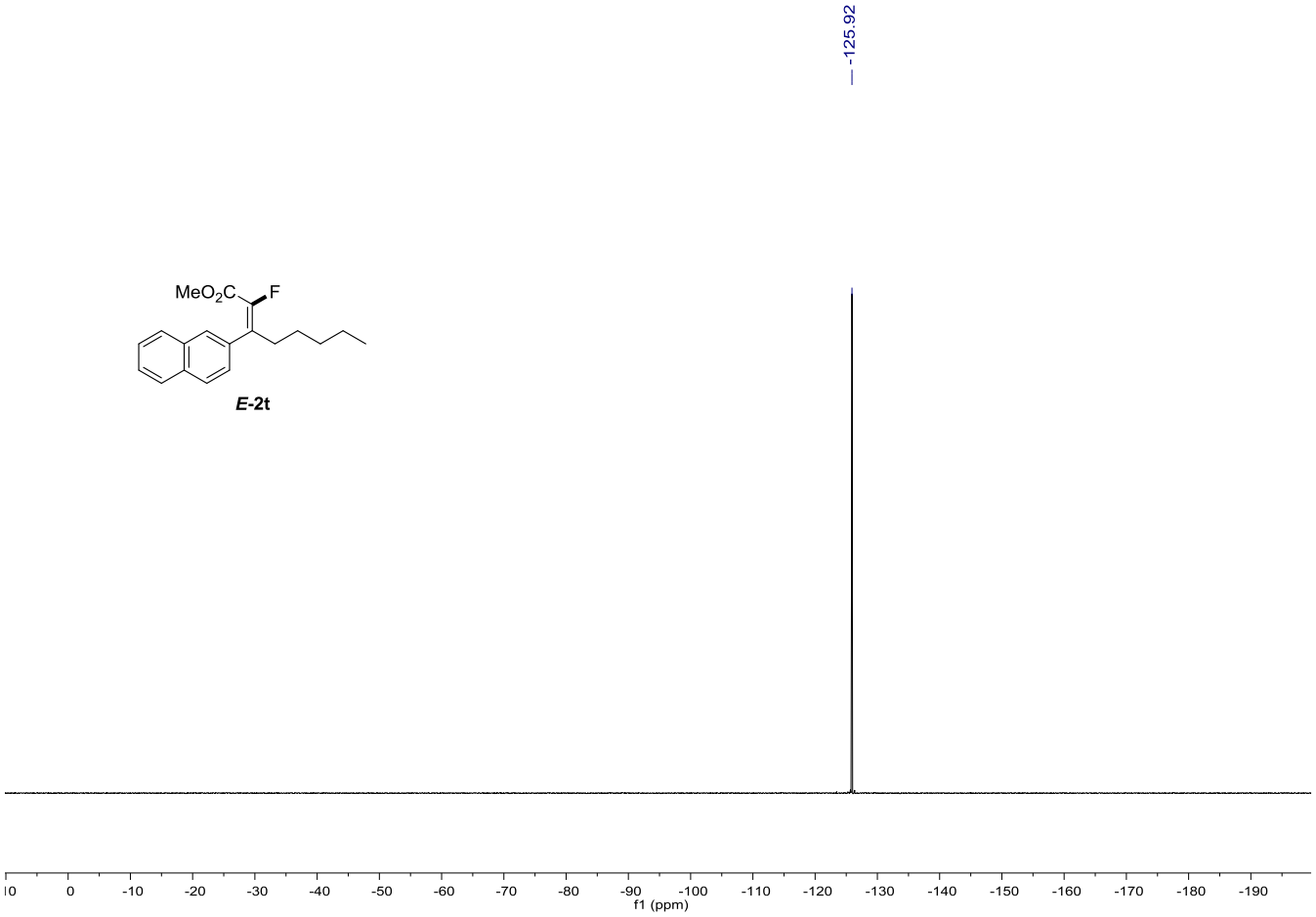
7.52
7.51
7.51
7.50
7.49
7.45
7.44
7.44
7.43
7.42
7.42
3.90
3.02
3.02
3.01
3.00
2.99
2.98
1.43
1.41
1.40
1.39
1.37
1.34
1.33
1.32
1.31
1.31
1.30
1.29
1.28
1.27
1.27
1.25
1.23
0.85
0.83
MeO2C
F
E-2t
2.99
1.10
2.02
1.09
3.00
1.98
2.06
5.47
3.16
f1 (ppm)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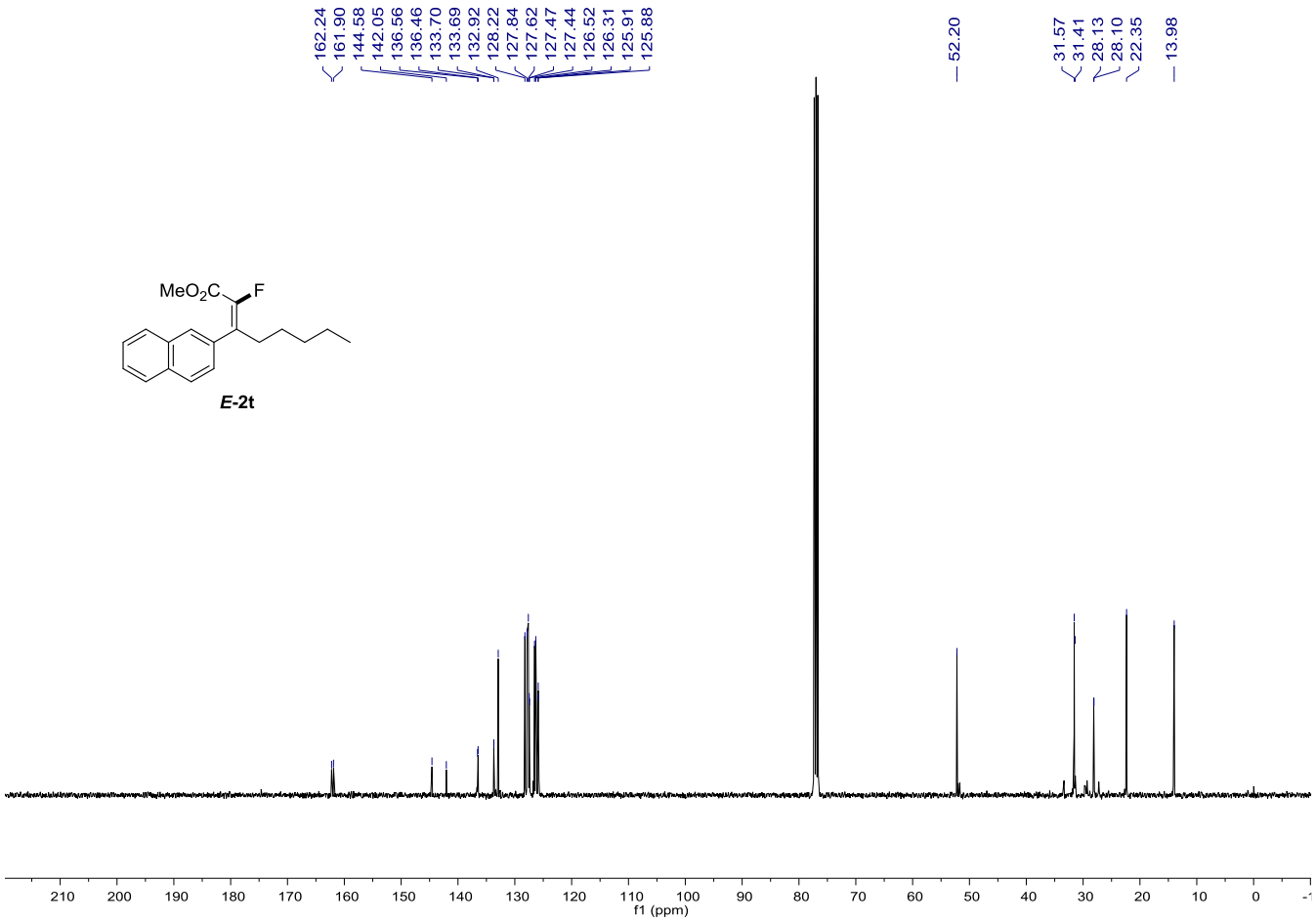
MeO2C
F
E-2t
f1 (ppm)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133.69
132.92
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127.84
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127.47
127.44
126.52
126.31
125.91
125.88
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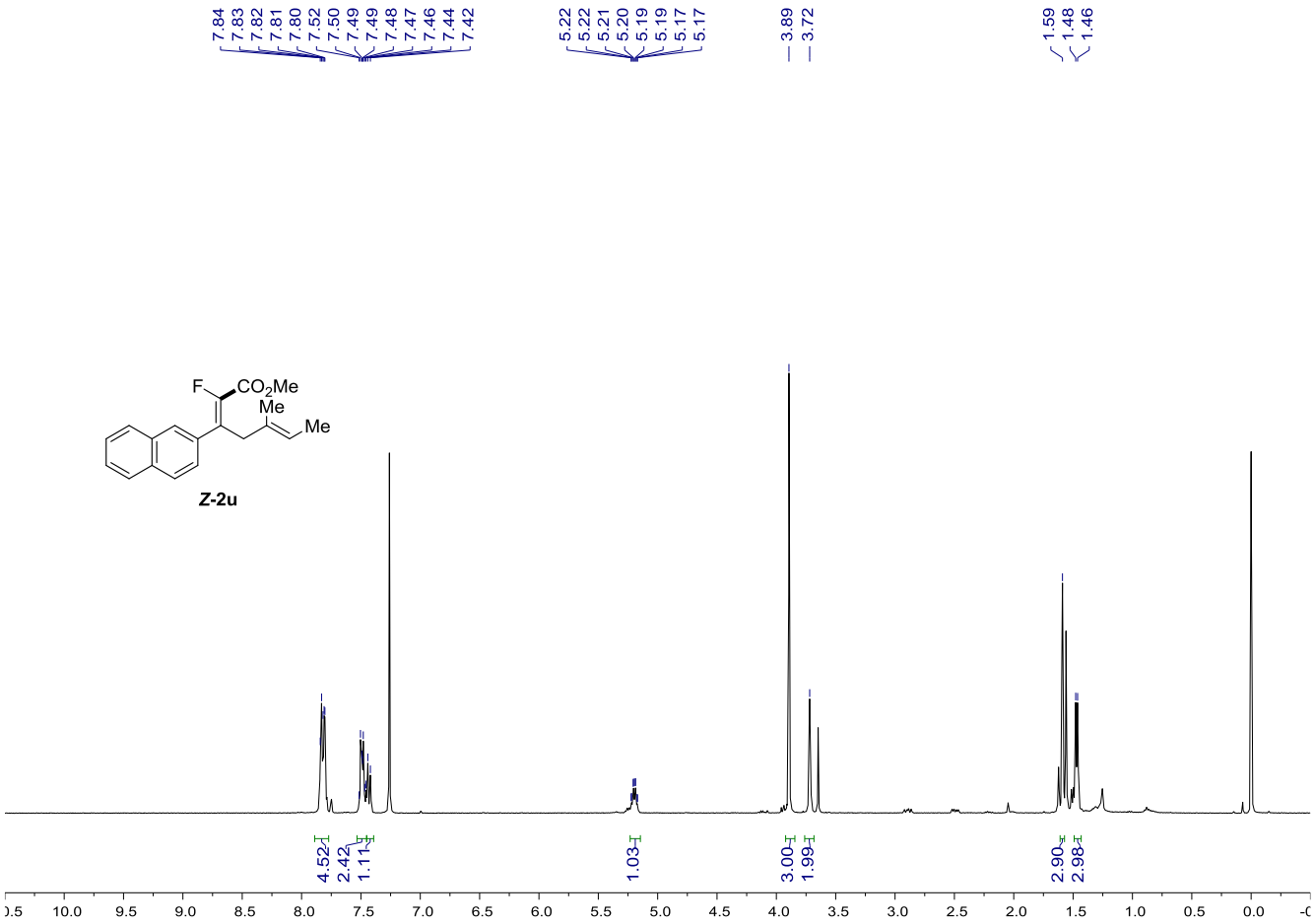
31.41
28.13
28.10
22.35
13.98
MeO2C
F
E-2t
f1 (ppm)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7.50
7.49
7.49
7.48
7.47
7.46
7.44
7.42
5.22
5.22
5.21
5.20
5.19
5.19
5.17
5.17
3.89
3.72
1.59
1.48
1.46
F
CO2Me
Me
Me
Z-2u
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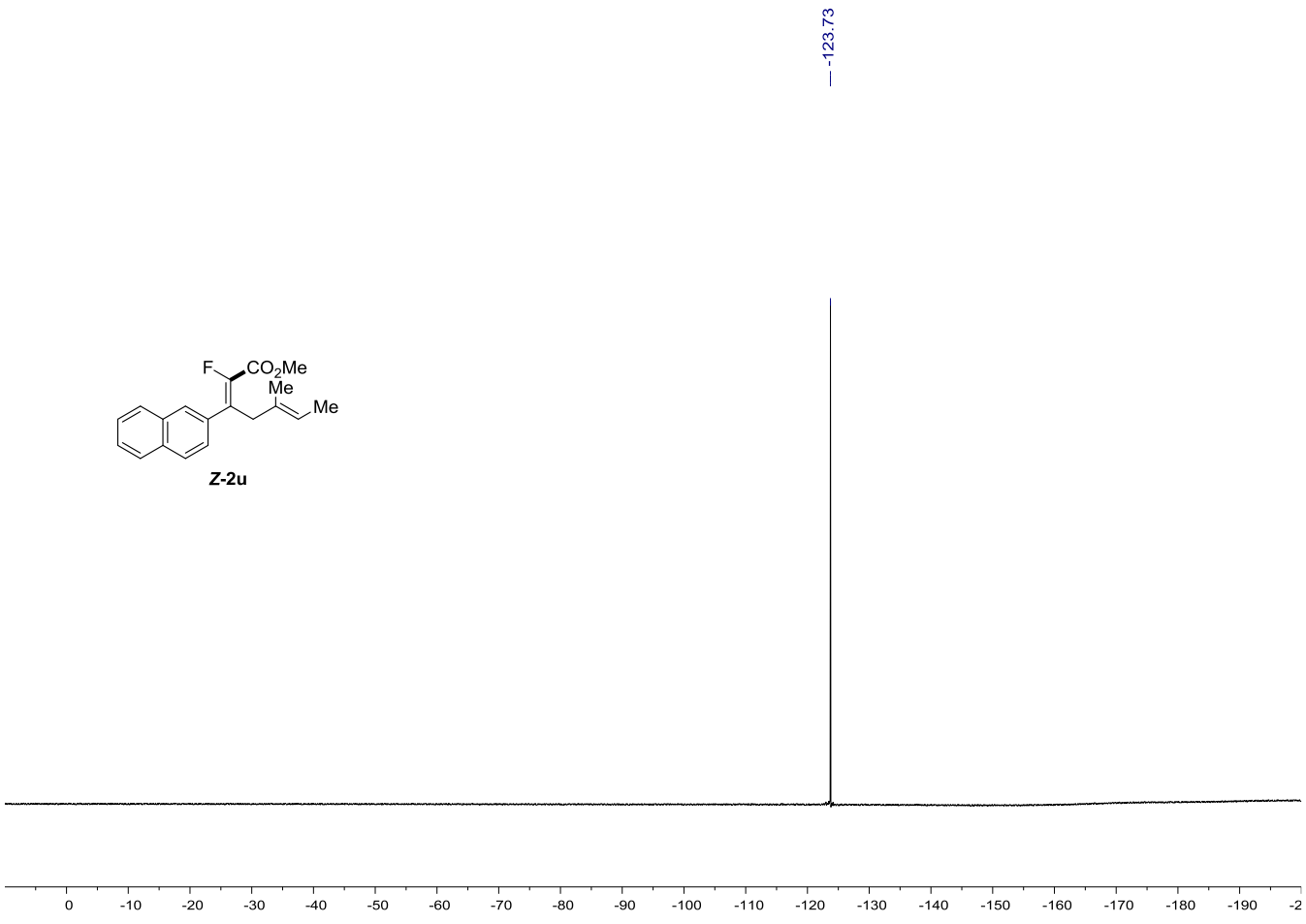
1.11
1.03
3.00
1.99
2.90
2.98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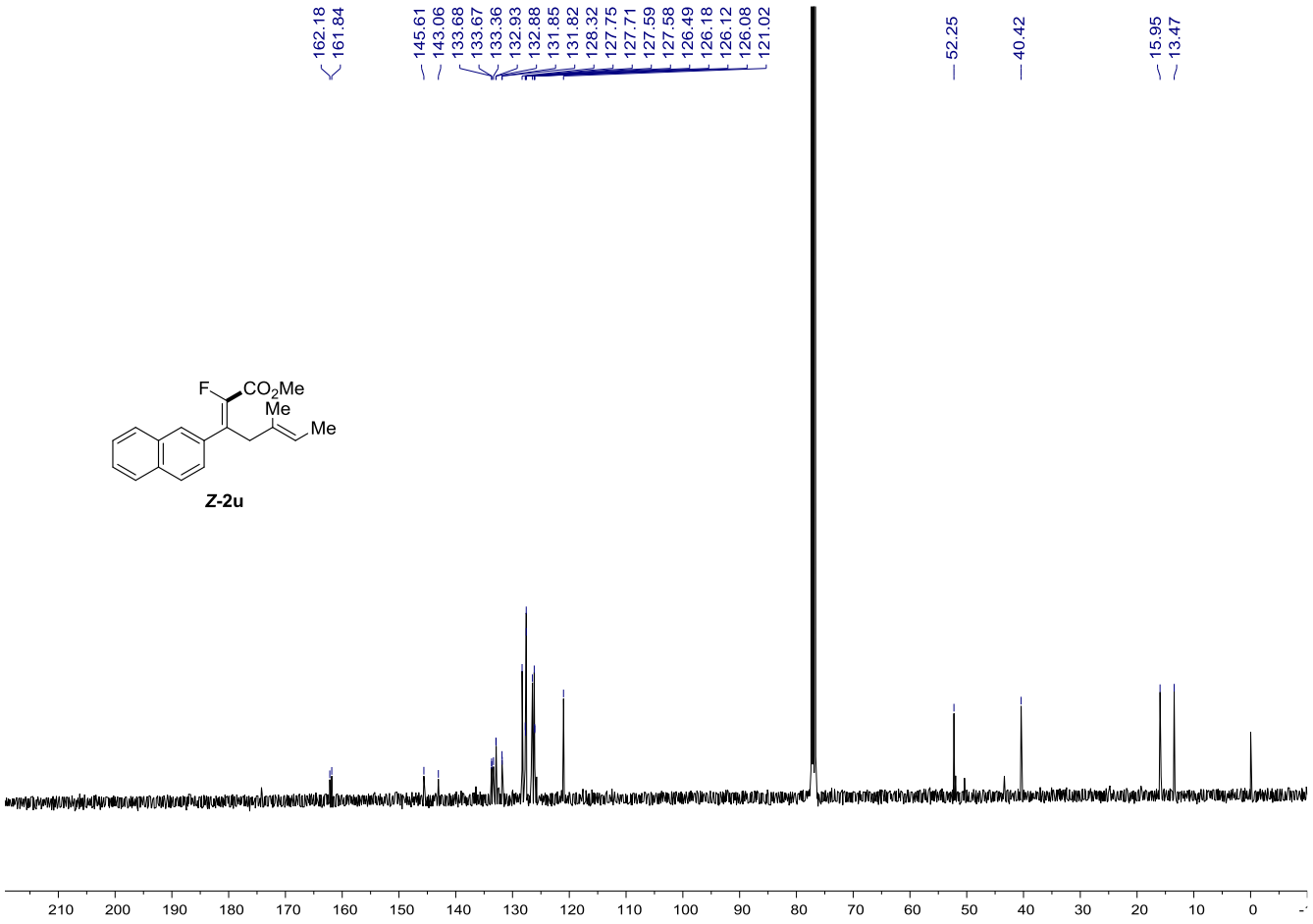
F
CO2Me
Me
Me
Z-2u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131.85
131.82
128.32
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127.71
127.59
127.58
126.49
126.18
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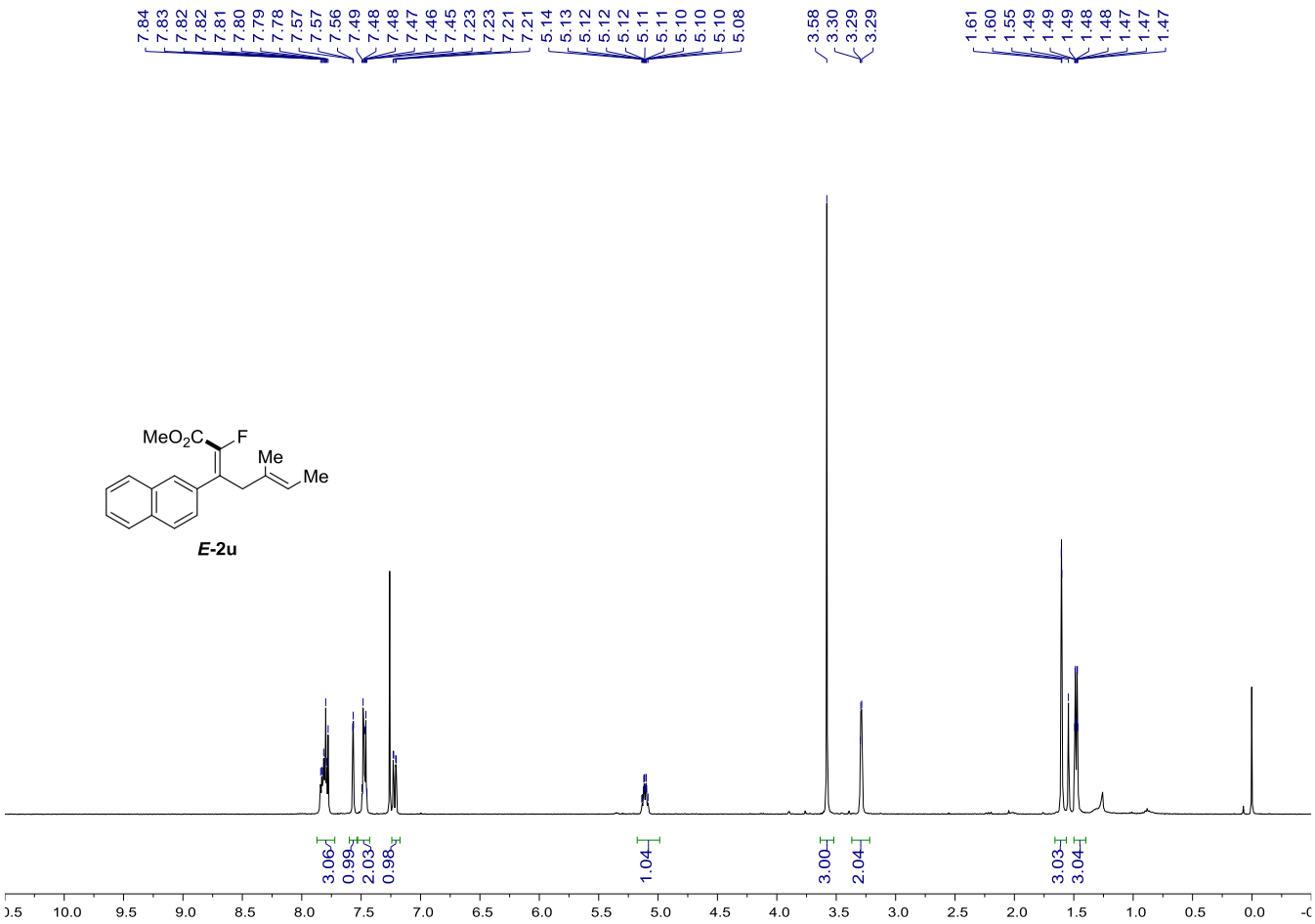
126.08
121.02
52.25
40.42
15.95
13.47
F
CO2Me
Me
Me
Z-2u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7.48
7.48
7.47
7.46
7.45
7.23
7.23
7.21
7.21
5.14
5.13
5.12
5.12
5.12
5.11
5.11
5.10
5.10
5.10
5.08
3.58
3.30
3.29
3.29
1.61
1.60
1.55
1.49
1.49
1.49
1.48
1.48
1.47
1.47
1.47
MeO2C
F
Me
Me
E-2u
3.06
0.99
2.03
0.98
1.04
3.00
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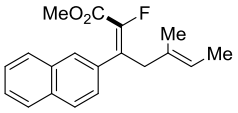
3.03
3.04


MeO2C
F
Me
Me

***E*-2u**

-124.08
-124.09
-124.10
0
-10
-20
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-40
-50
-60
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-80
-90
-100
-110
-120
-130
-140
-150
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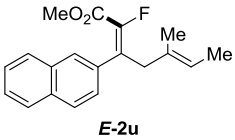
MeO2C
F
Me
Me

***E*-2u**

161.32
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143.29
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134.42
133.84
133.68
132.91
132.71
130.15
130.13
128.05
127.70
127.23
126.65
126.61
126.43
126.40
126.06
126.02
122.58
52.01
42.73
42.68
15.79
13.46
210
200
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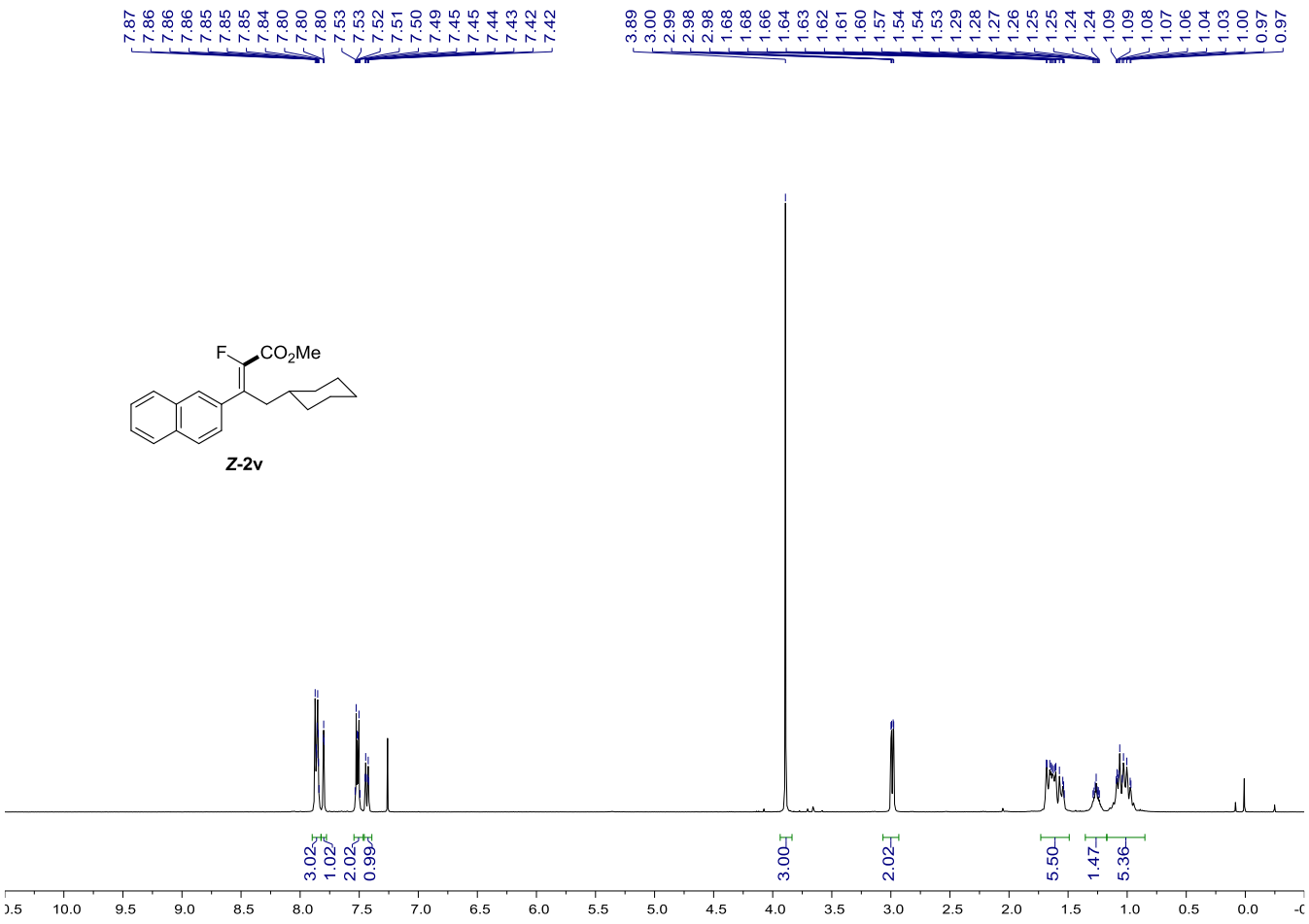
10
0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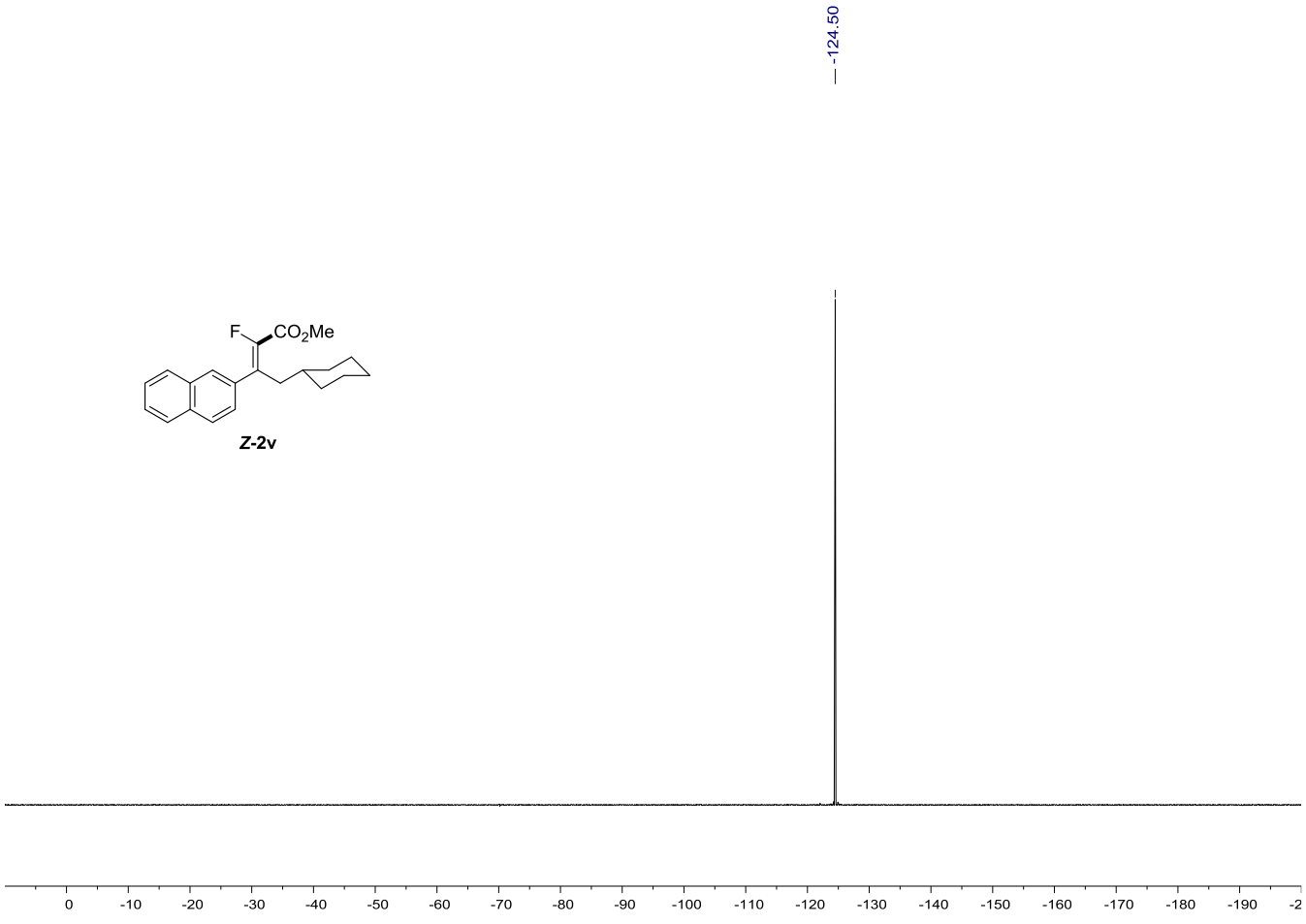
3.89 3.00 2.99 2.98 2.98 1.68 1.68 1.66 1.64 1.63 1.62 1.61 1.60 1.57 1.54 1.54 1.53 1.29 1.28 1.27 1.26 1.25 1.25 1.24 1.24 1.09 1.09 1.08 1.07 1.06 1.04 1.03 1.00 0.97 0.97
F
CO2Me
Z-2v
3.02
1.02
2.02
0.99
3.00
2.02
5.50
1.47
5.36
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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Z-2v
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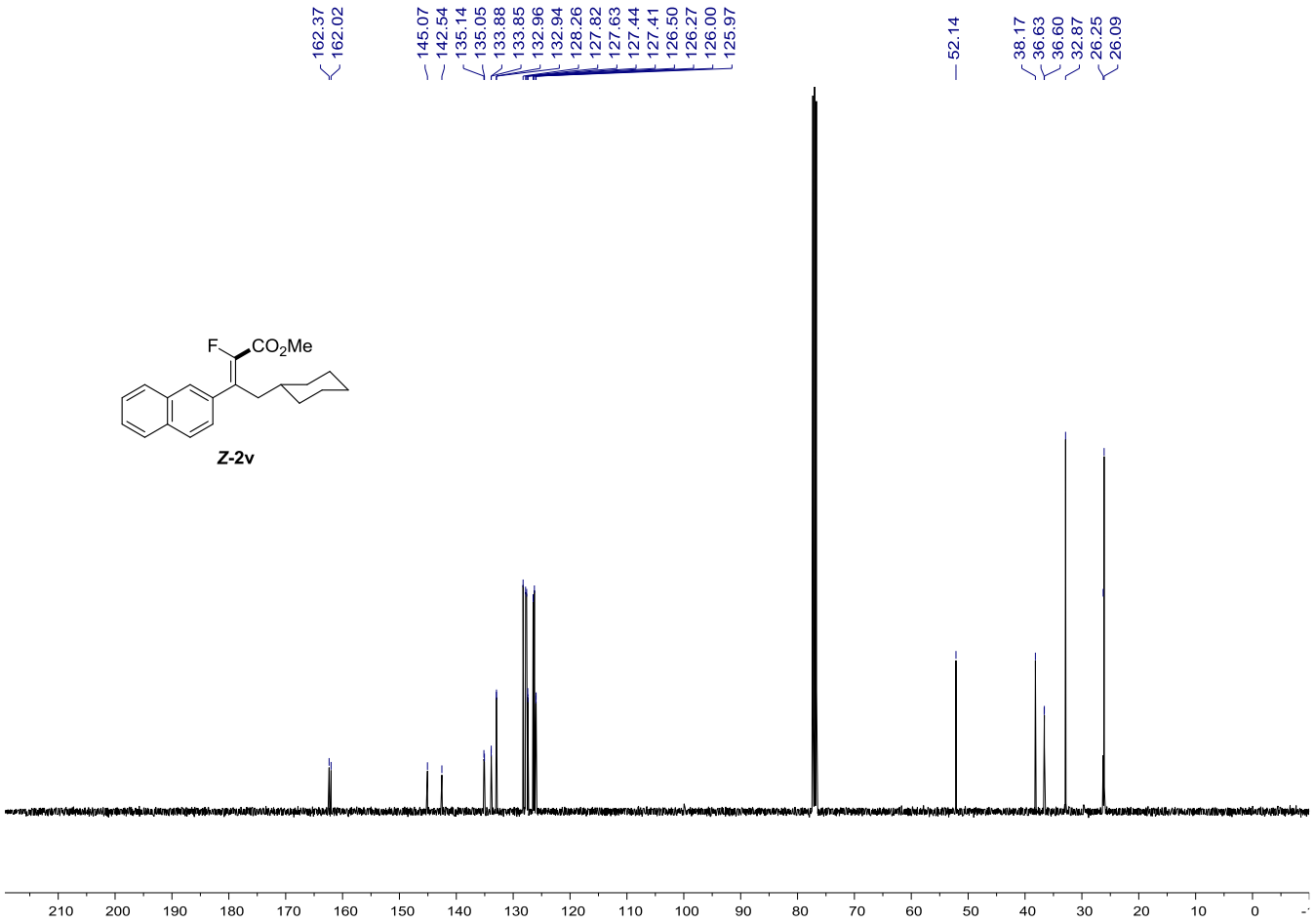
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132.94
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127.63
127.44
127.41
126.50
126.27
126.00
125.97
52.14
38.17
36.63
36.60
32.87
26.25
26.09
F
CO2Me
Z-2v


7.87
7.86
7.86
7.85
7.84
7.83
7.82
7.63
7.62
7.62
7.51
7.50
7.50
7.50
7.49
7.48
7.47
7.29
7.28
7.27
7.26


3.58
2.56
2.55
2.54
2.53
1.72
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1.68
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1.65
1.64
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1.26
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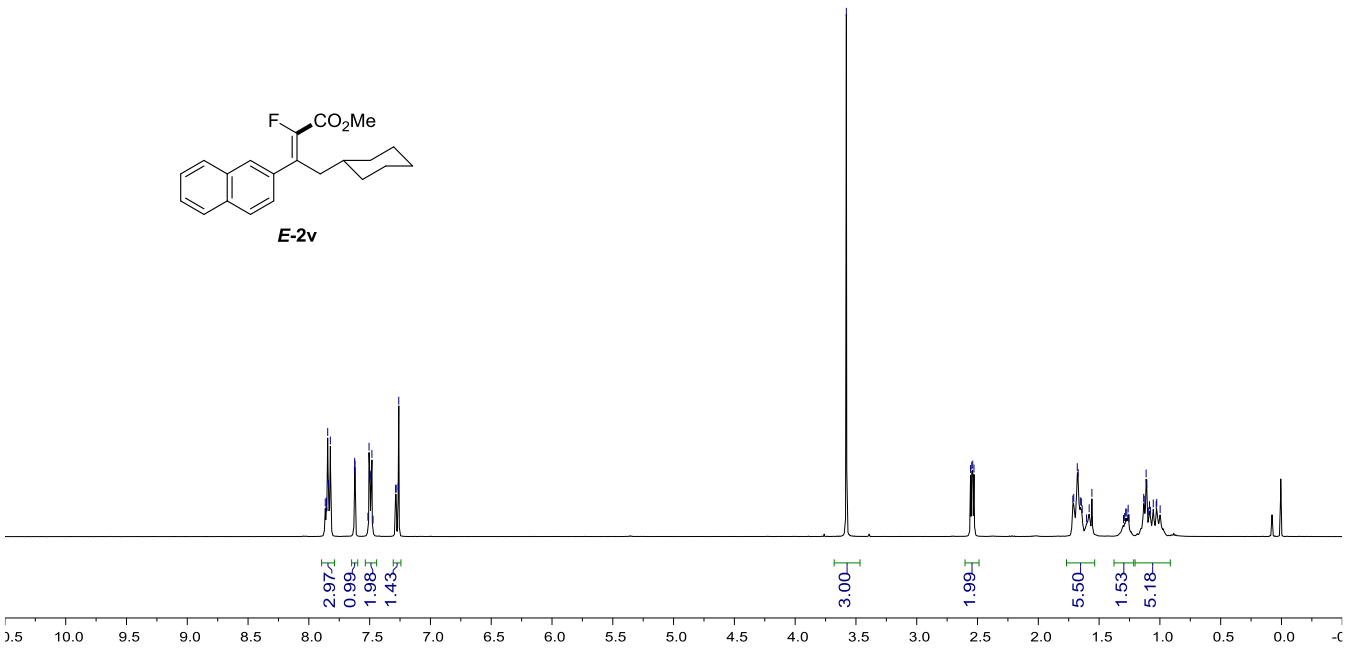
1.09
1.09
1.08
1.05
1.03
1.03
1.00


F
CO2Me
E-2v
2.97
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1.98
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1.99
5.50
1.53
5.18


-124.25
-124.26
-124.27
F
CO2Me
E-2v
0
-10
-20
-30
-40
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-90
-100
-110
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-140
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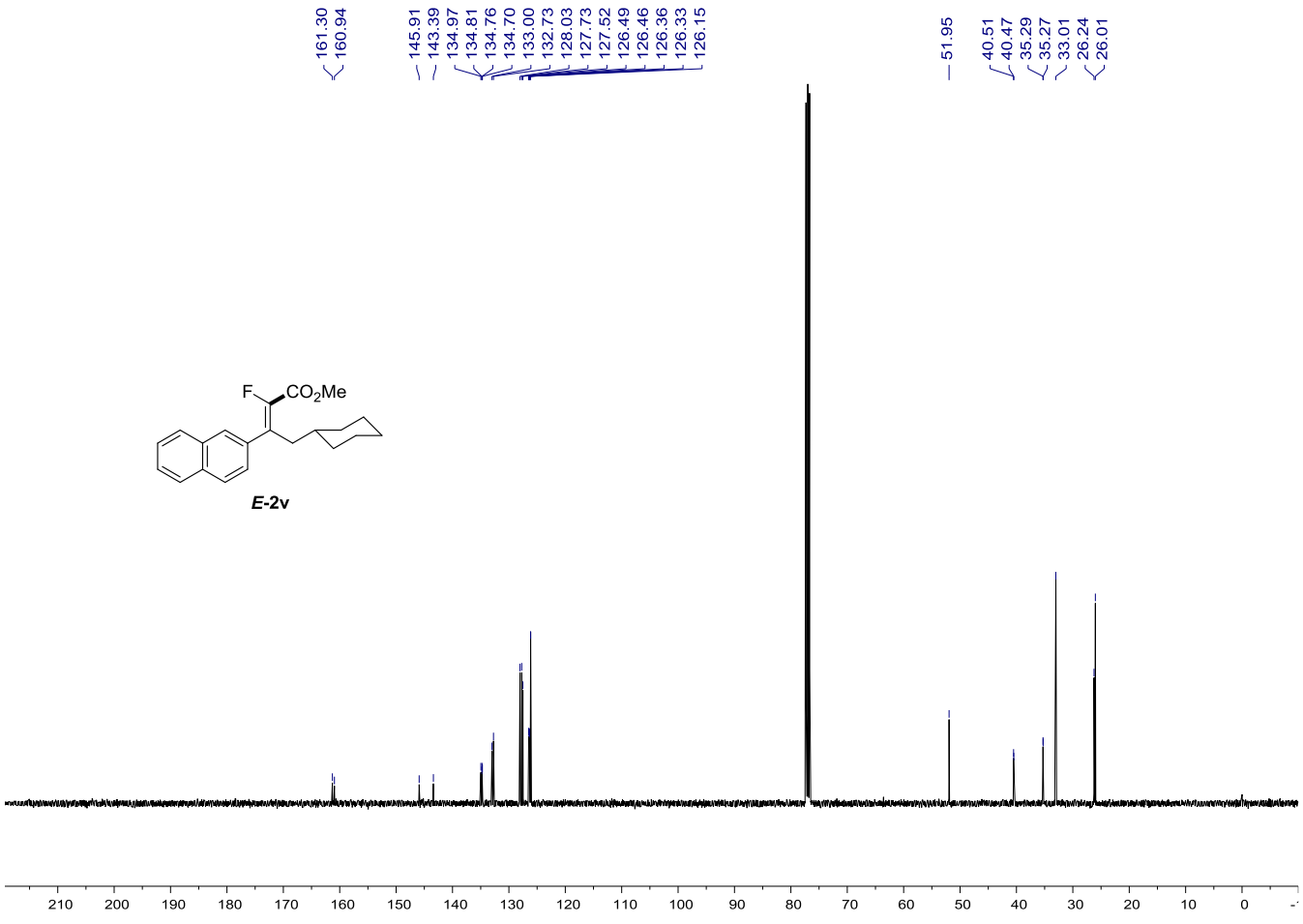
-170
-180
-190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126.46
126.36
126.33
126.15
51.95
40.51
40.47
35.29
35.27
33.01
26.24
26.01
F
CO2Me
E-2v
210
200
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10
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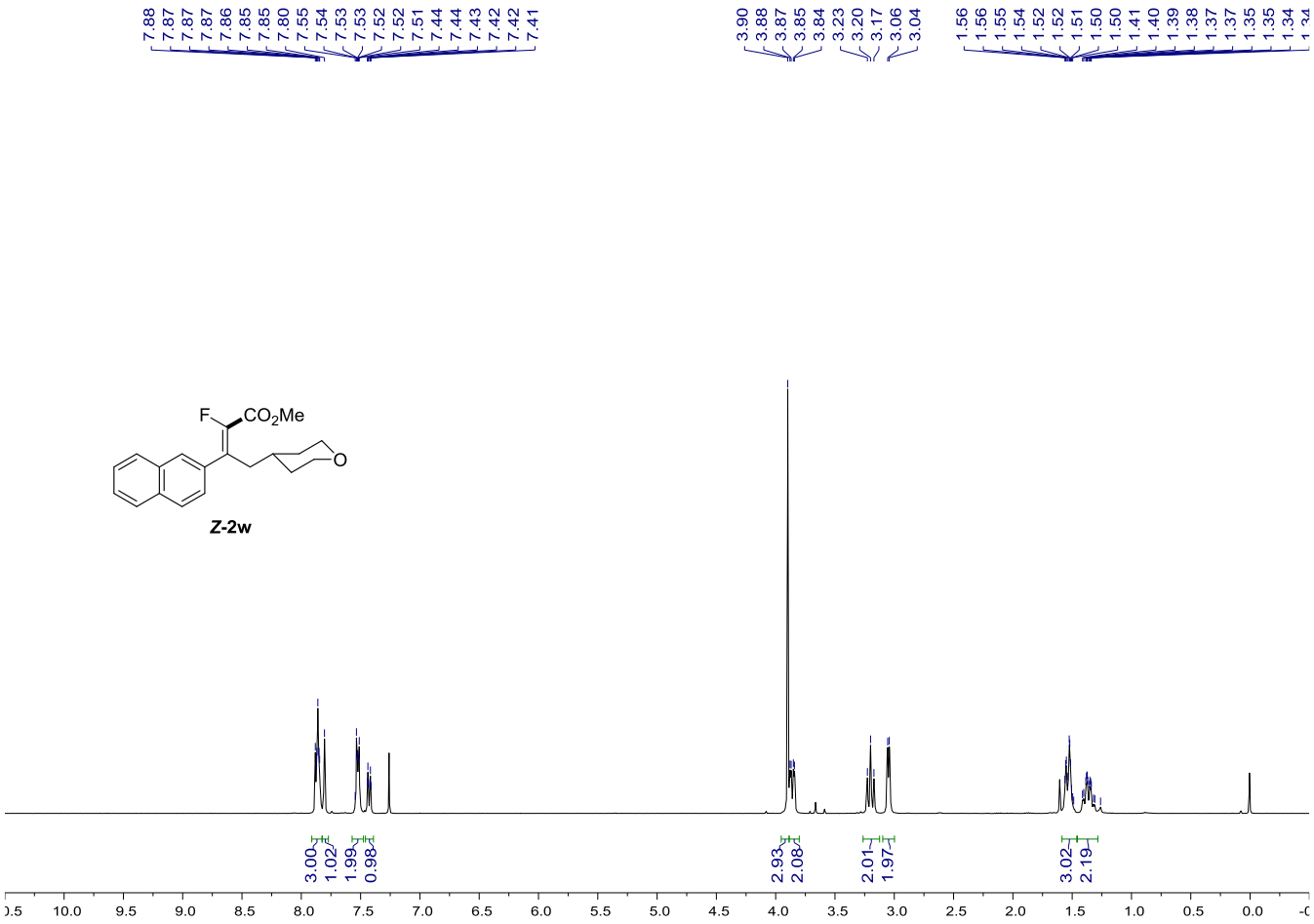
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7.51
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7.43
7.42
7.42
7.41
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3.88
3.87
3.85
3.84
3.23
3.20
3.17
3.06
3.04
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1.56
1.55
1.54
1.52
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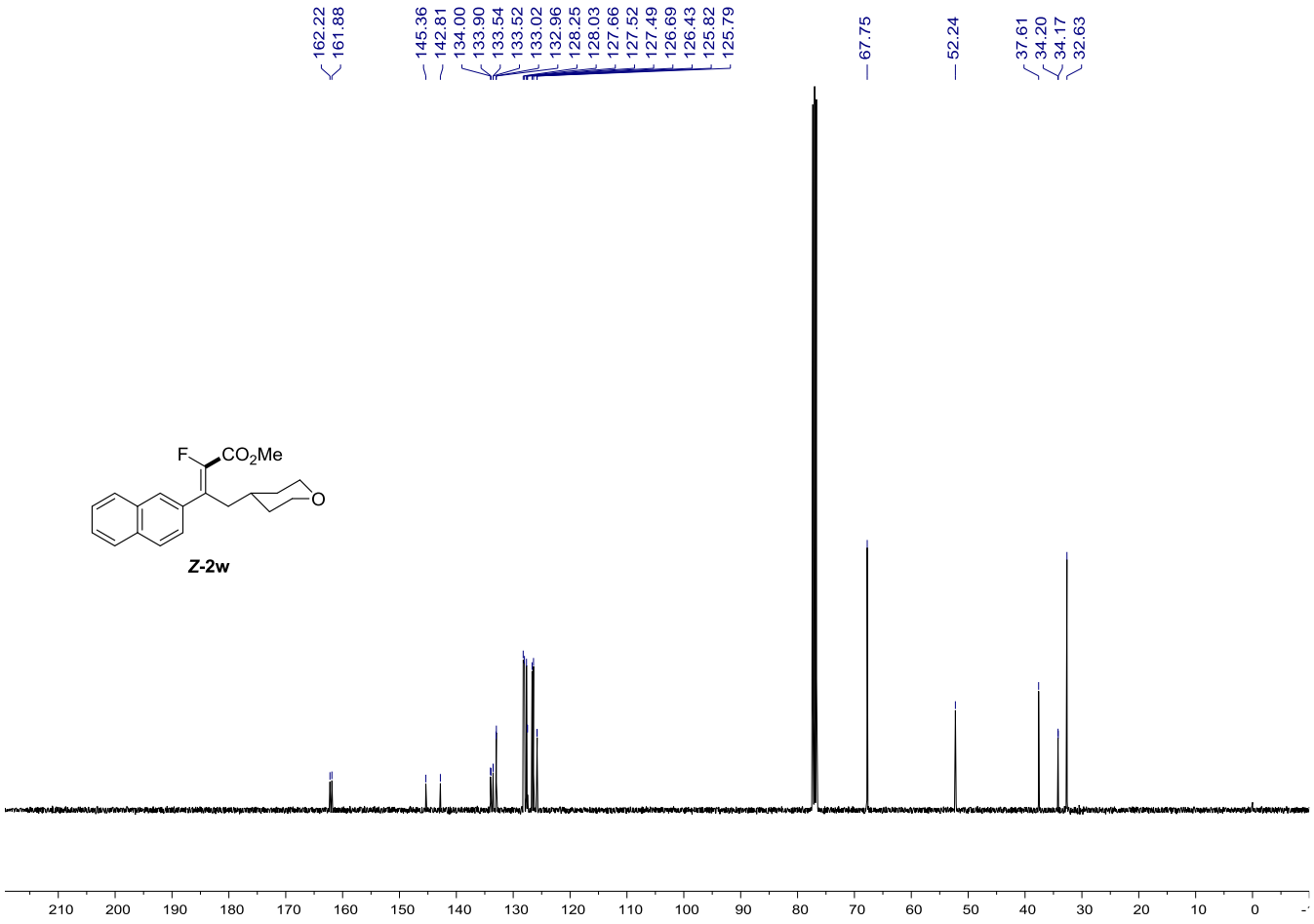
1.51
1.50
1.50
1.41
1.40
1.39
1.38
1.37
1.37
1.35
1.35
1.34
F
CO2Me
O
Z-2w
3.00
1.02
1.99
0.98
2.93
2.08
2.01
1.97
3.02
2.19


-123.14
-123.15
-123.16
F
CO2Me
O
Z-2w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127.66
127.52
127.49
126.69
126.43
125.82
125.79
67.75
52.24
37.61
34.20
34.17
32.63
F
CO2Me
O
Z-2w
210
200
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70
60
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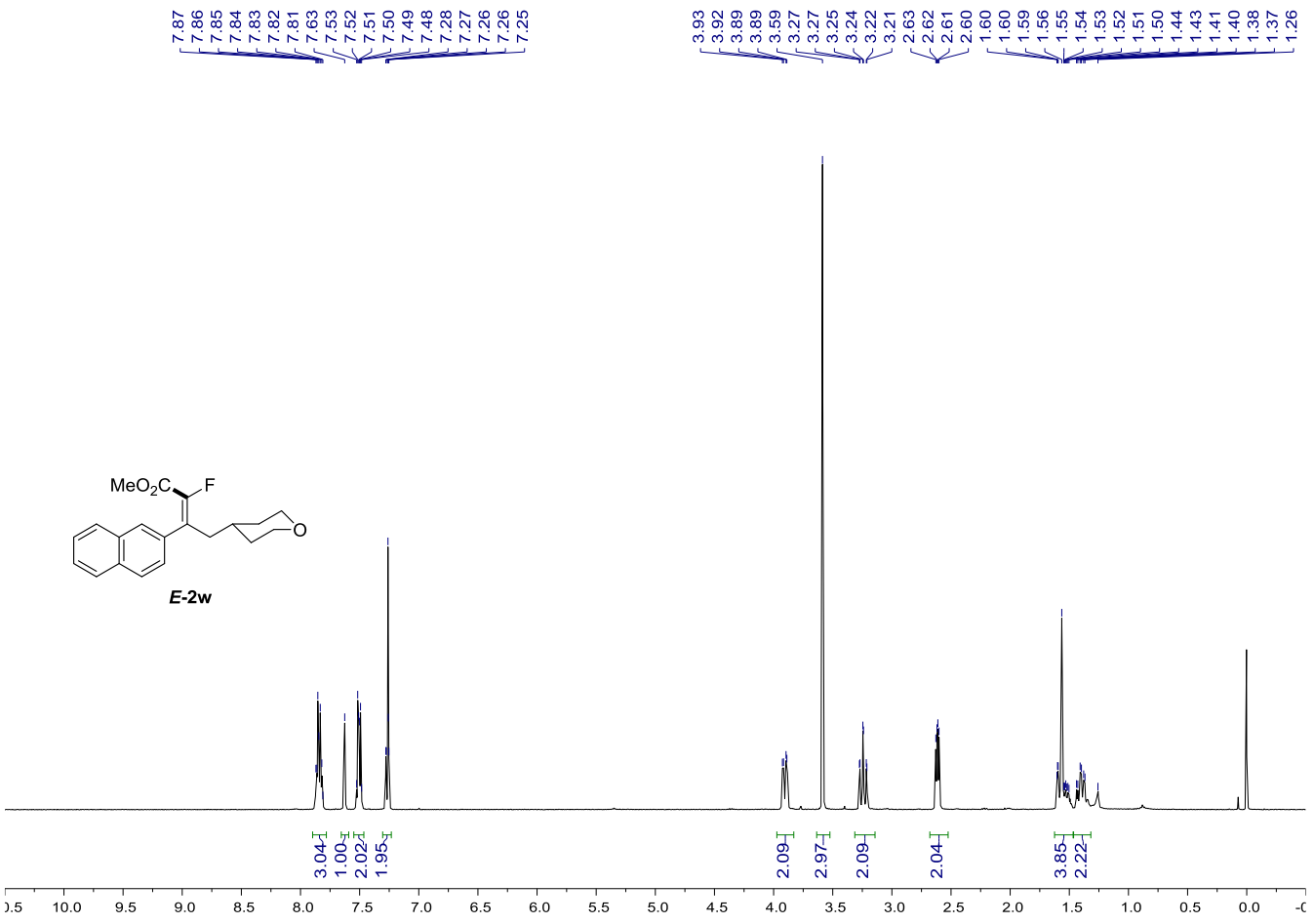
10
0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1.54
1.53
1.52
1.51
1.50
1.44
1.43
1.41
1.40
1.38
1.37
1.26
MeO2C
F
O
E-2w
3.04
1.00
2.02
1.95
2.09
2.97
2.09
2.04
3.85
2.22
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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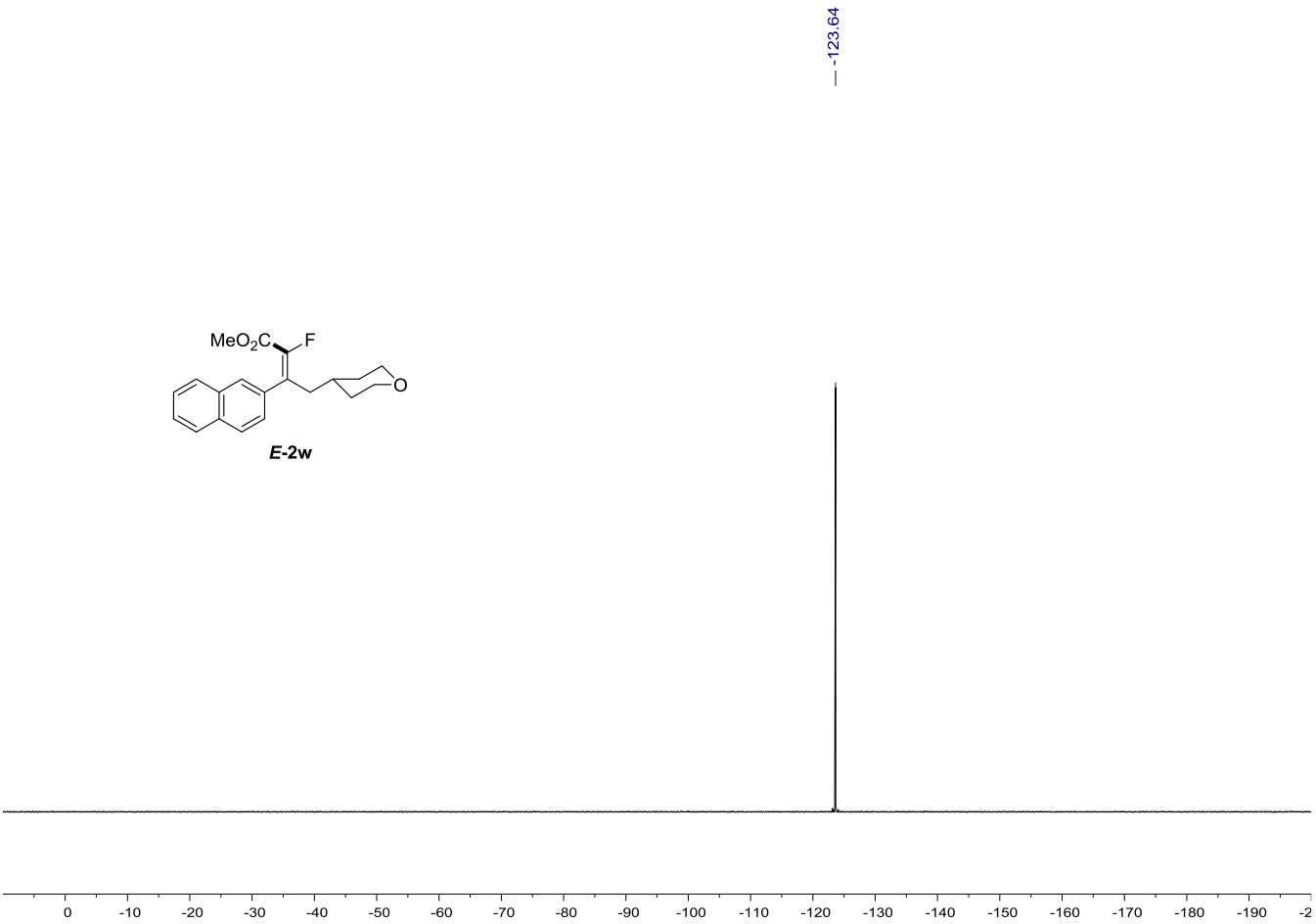
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MeO2C
F
O
E-2w
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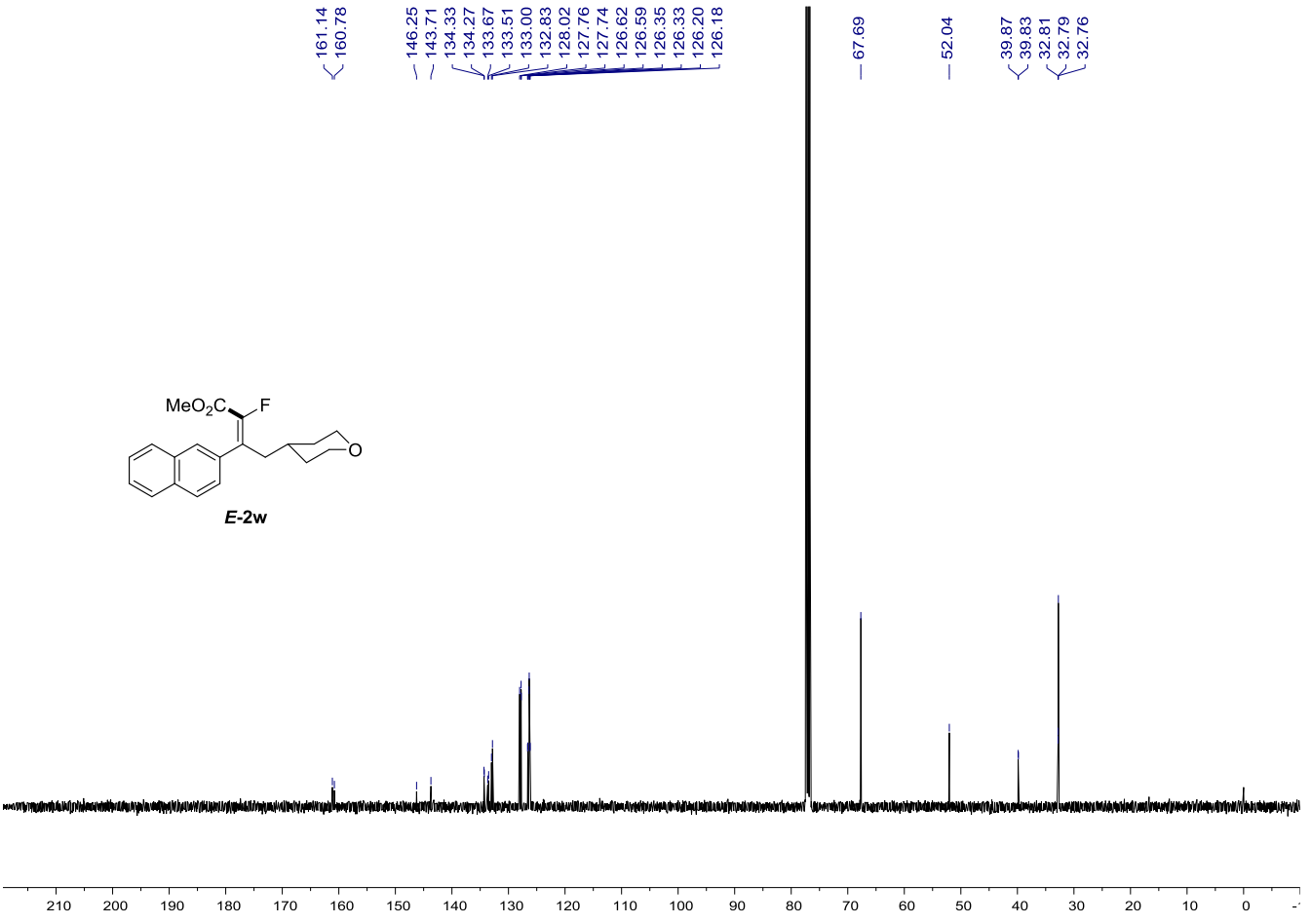
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190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39.83
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32.79
32.76
MeO2C
F
O
E-2w
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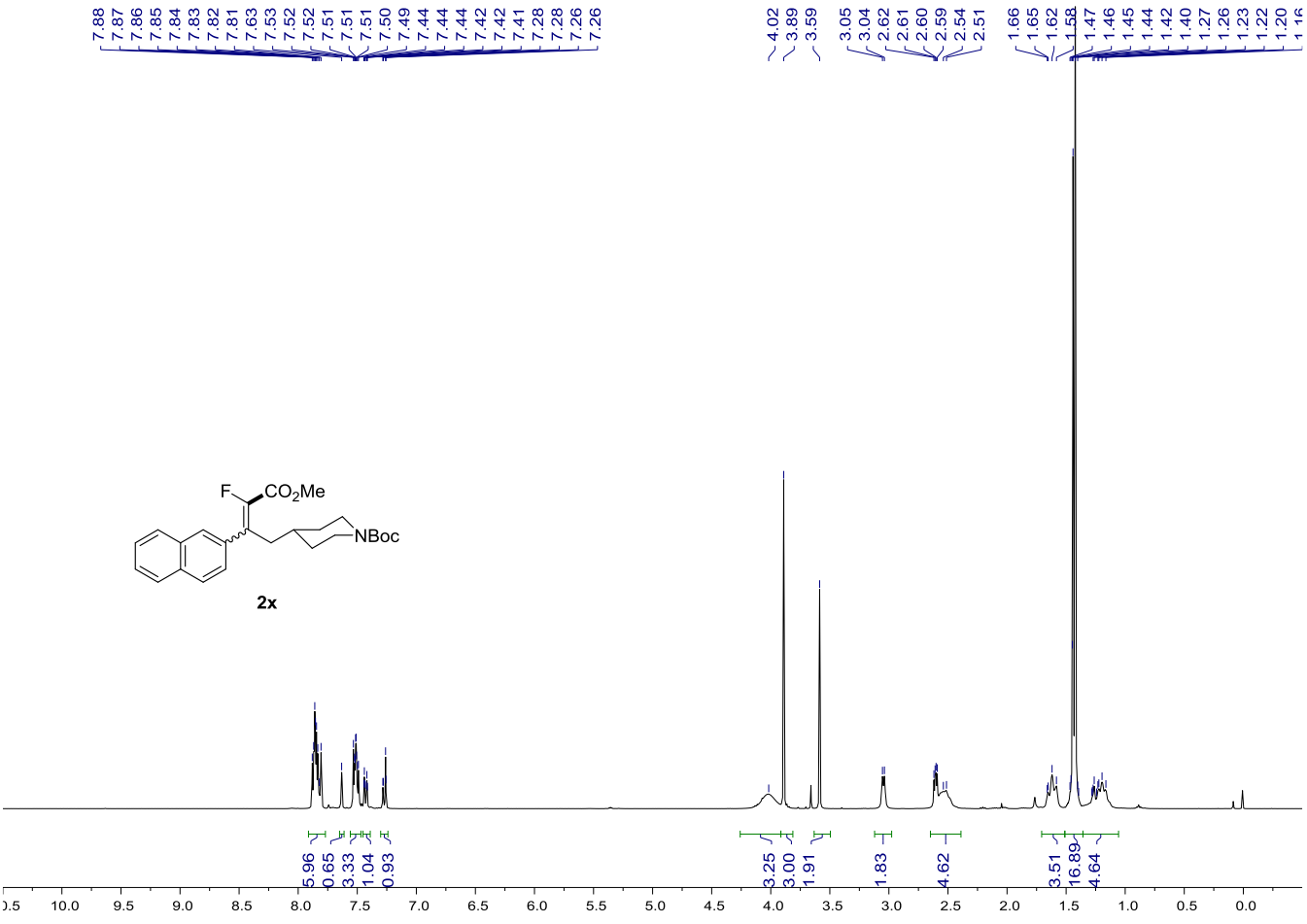
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CO2Me
NBoc
2x
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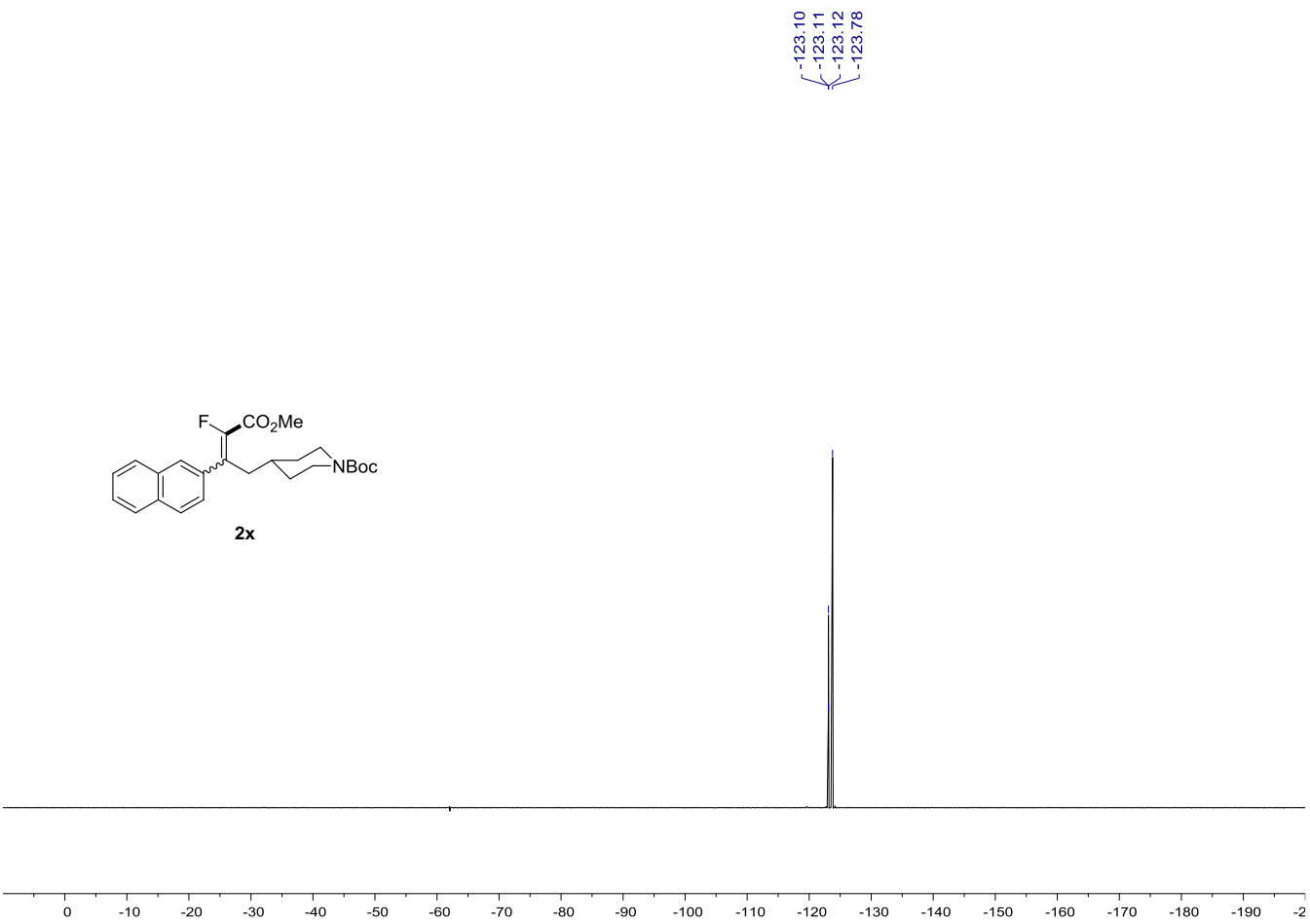
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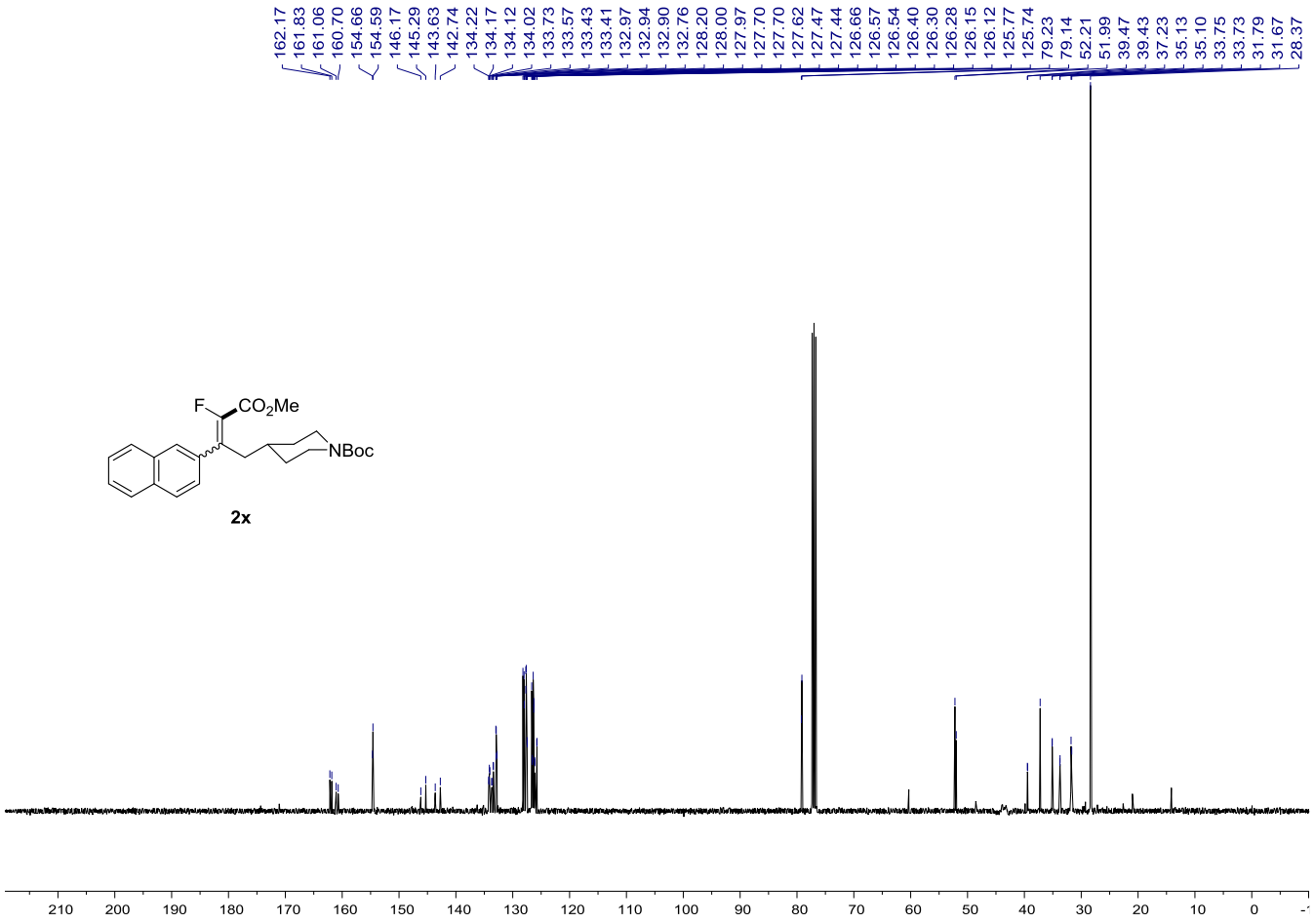
2x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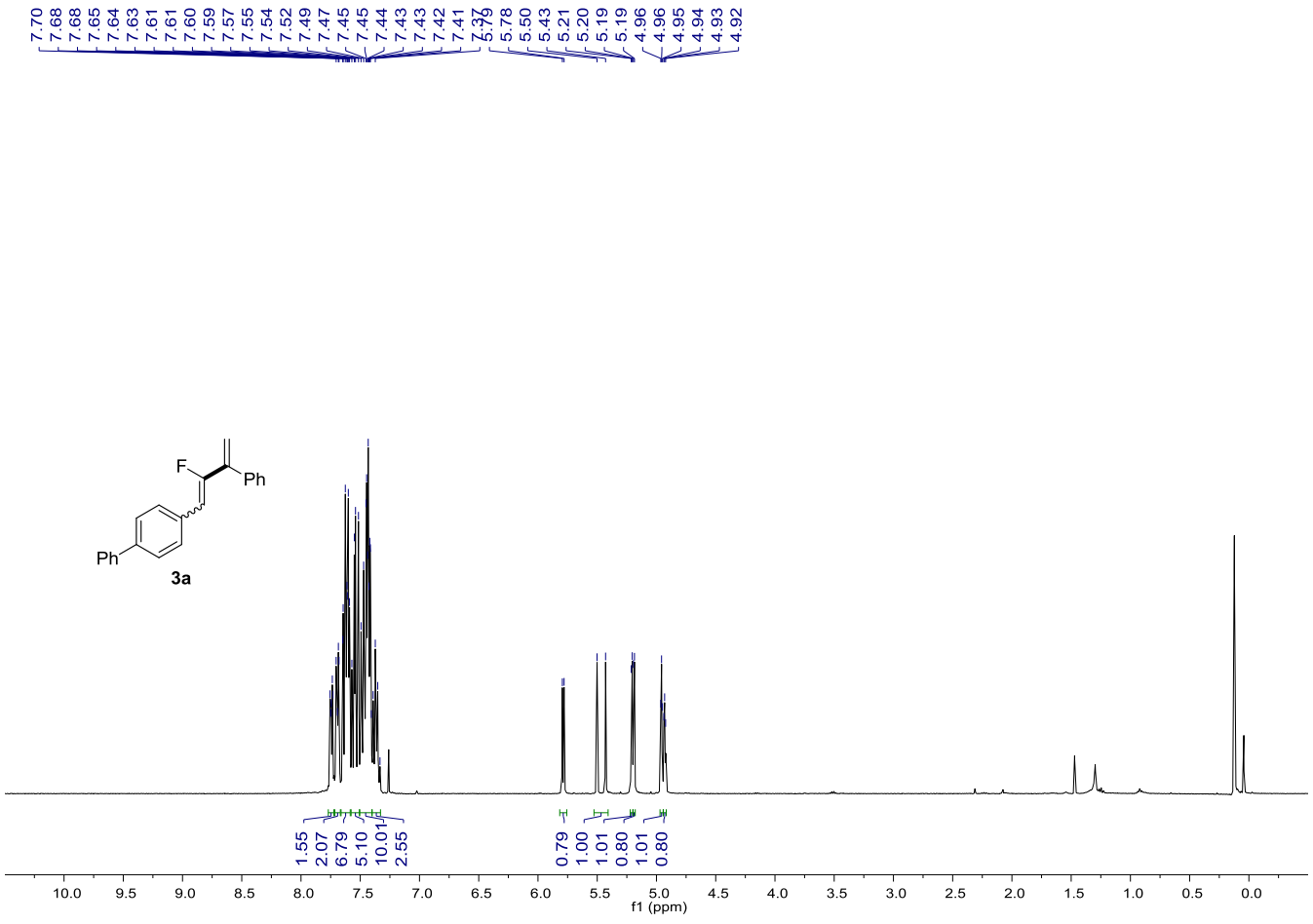
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Ph
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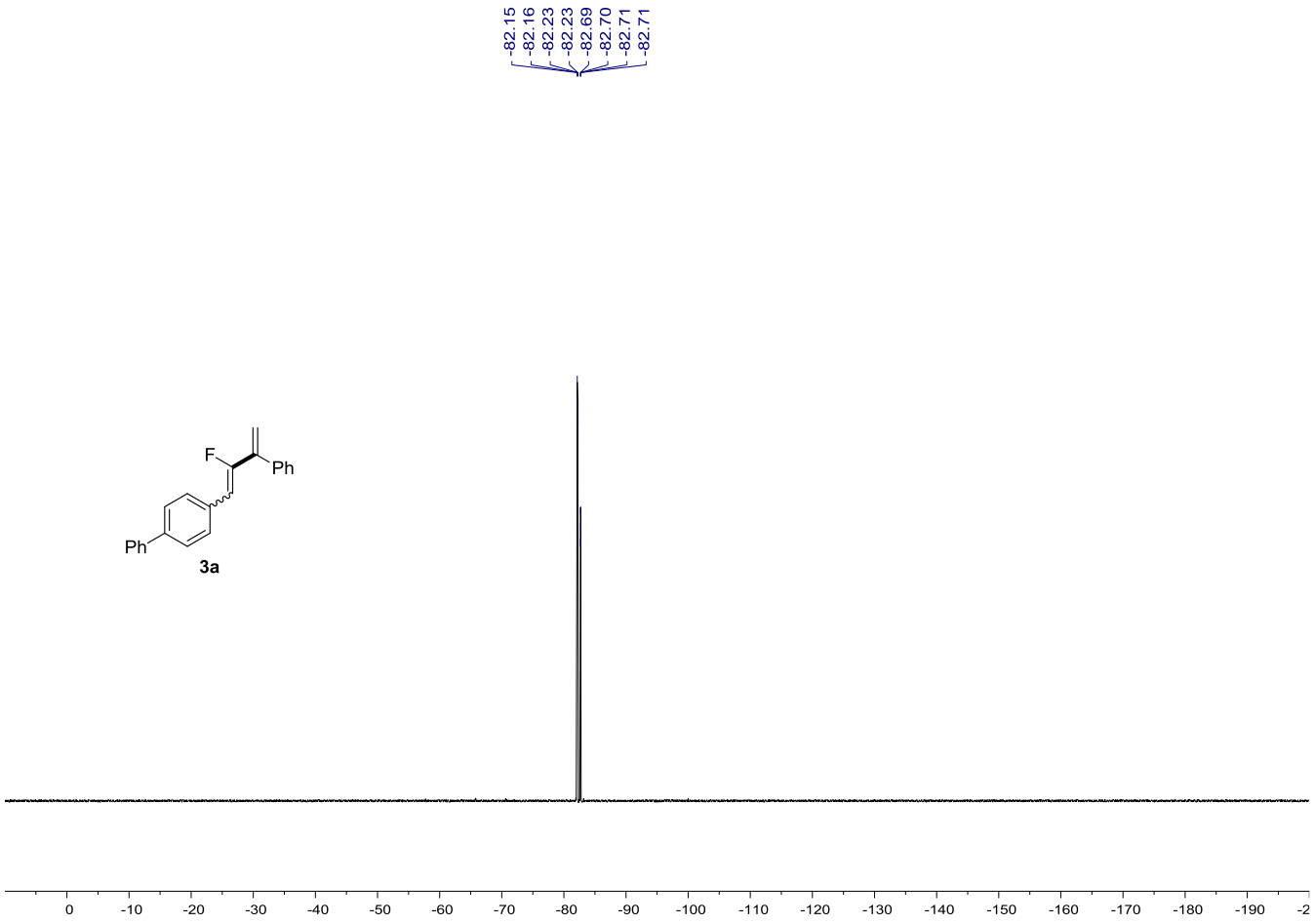
f1 (ppm)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Ph
Ph
3a
0
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-20
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-40
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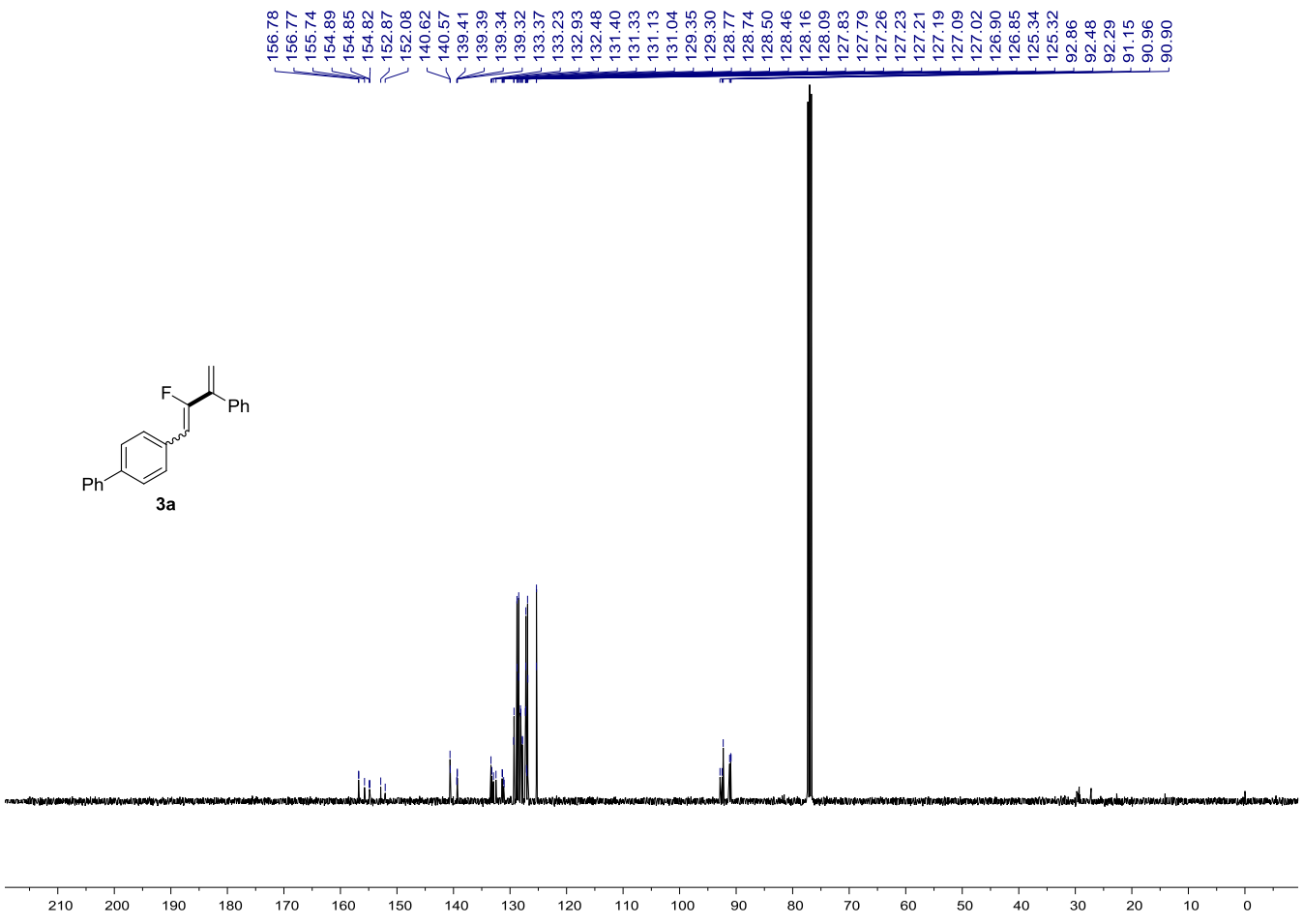
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F
Ph
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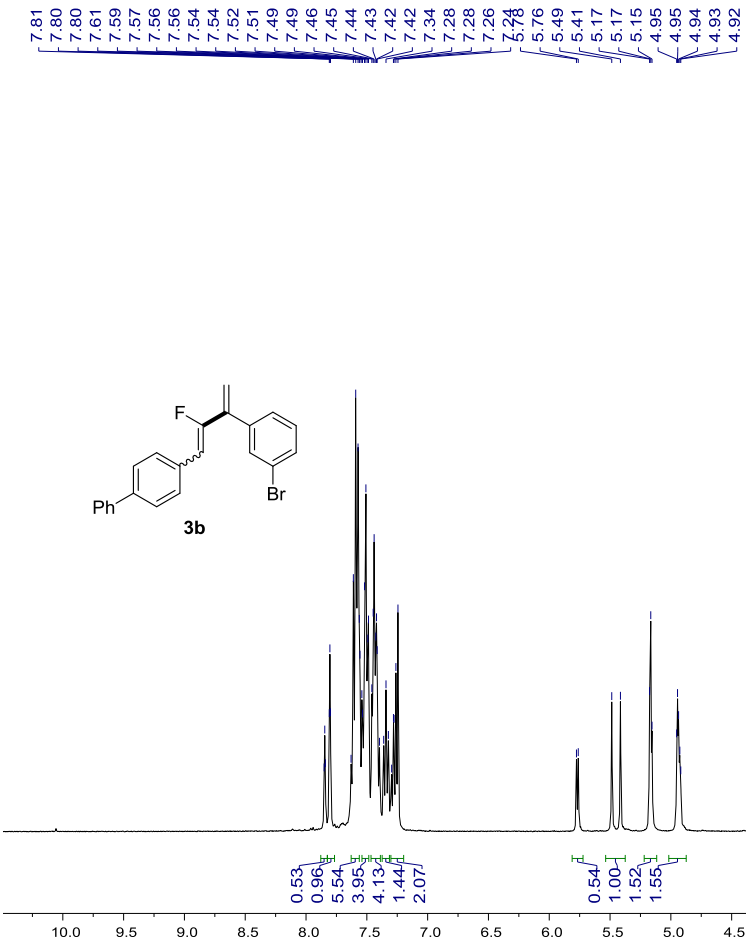
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4.95
4.94
4.93
4.92
F
Ph
Br
3b
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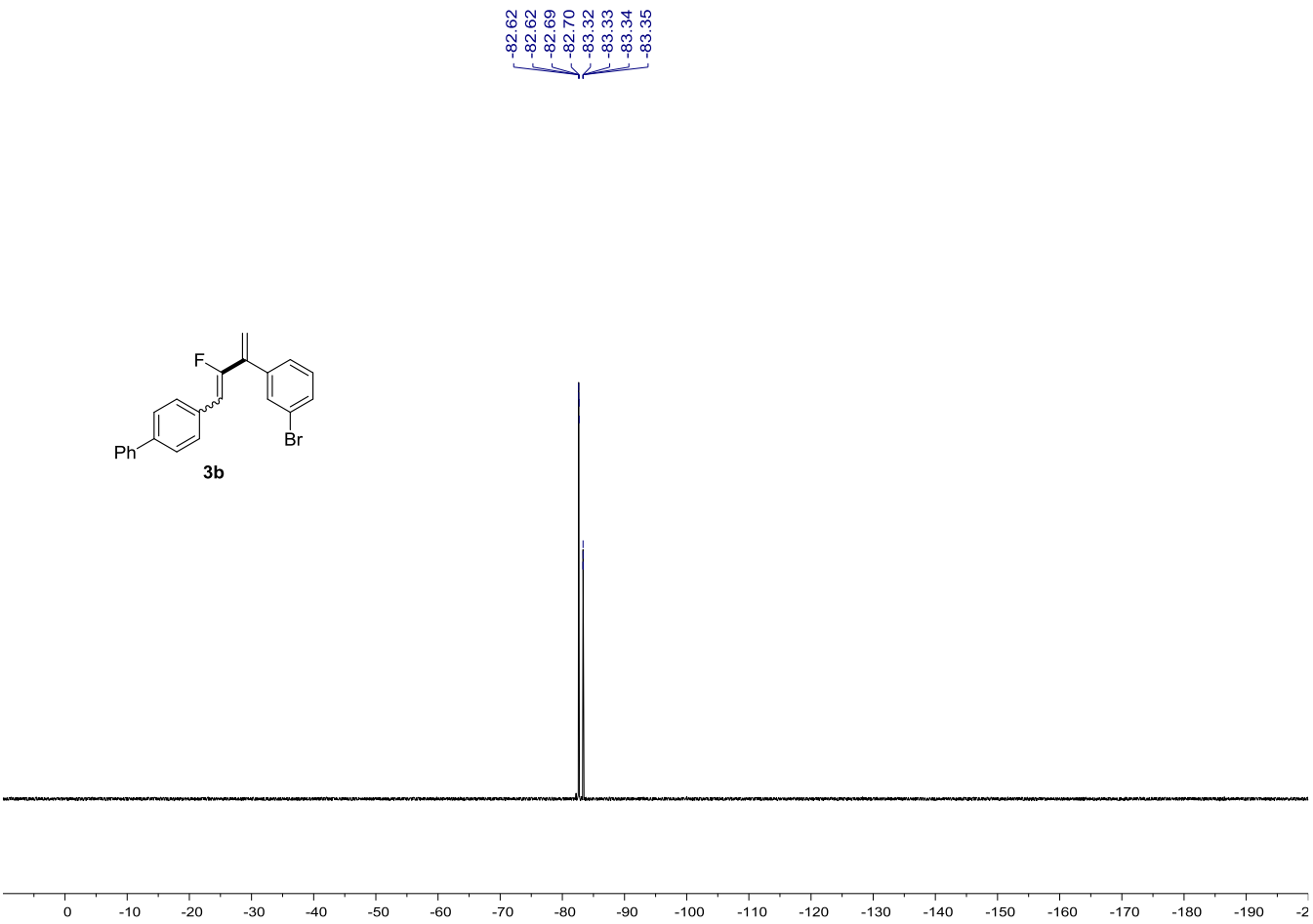
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Ph
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-10
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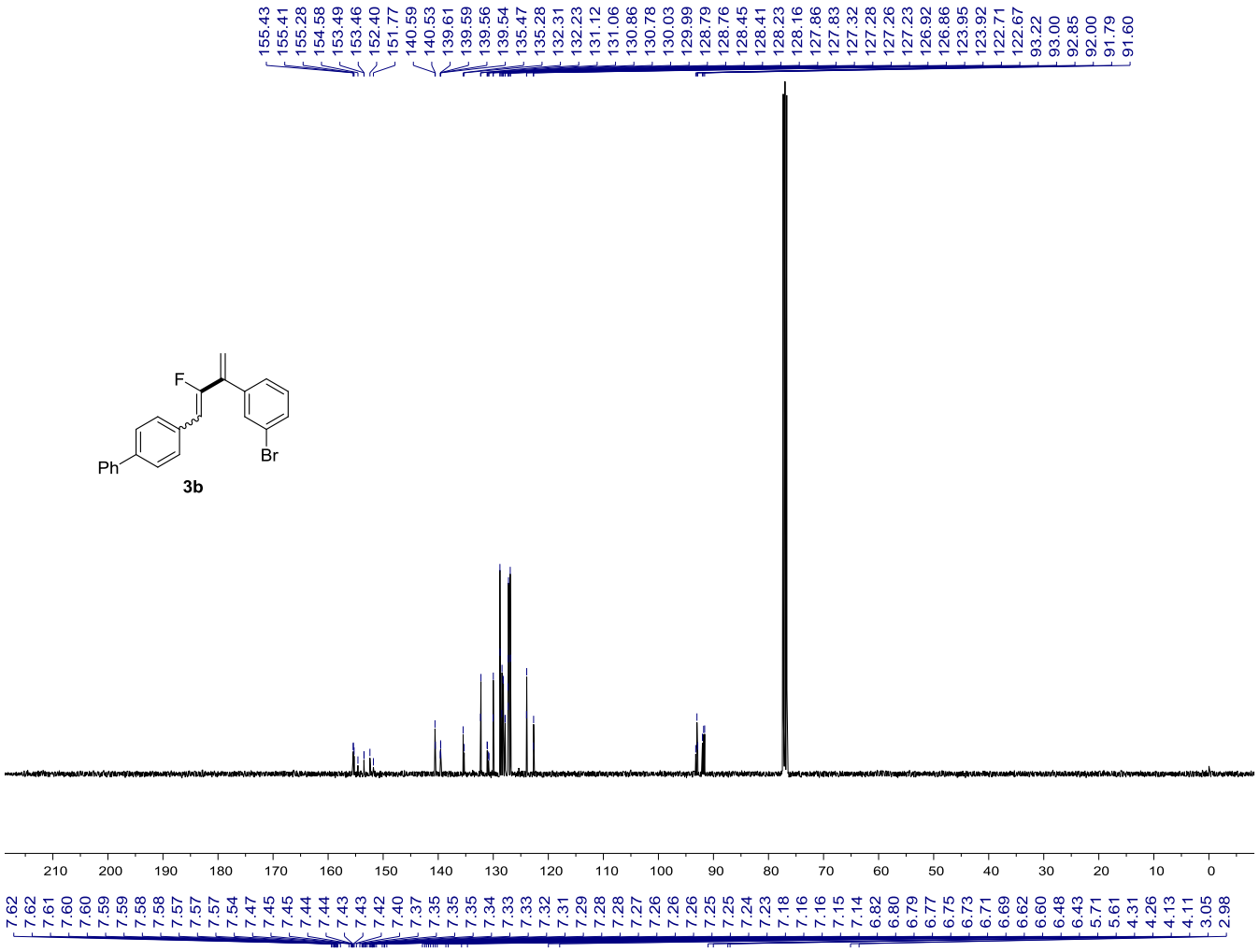
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91.60
F
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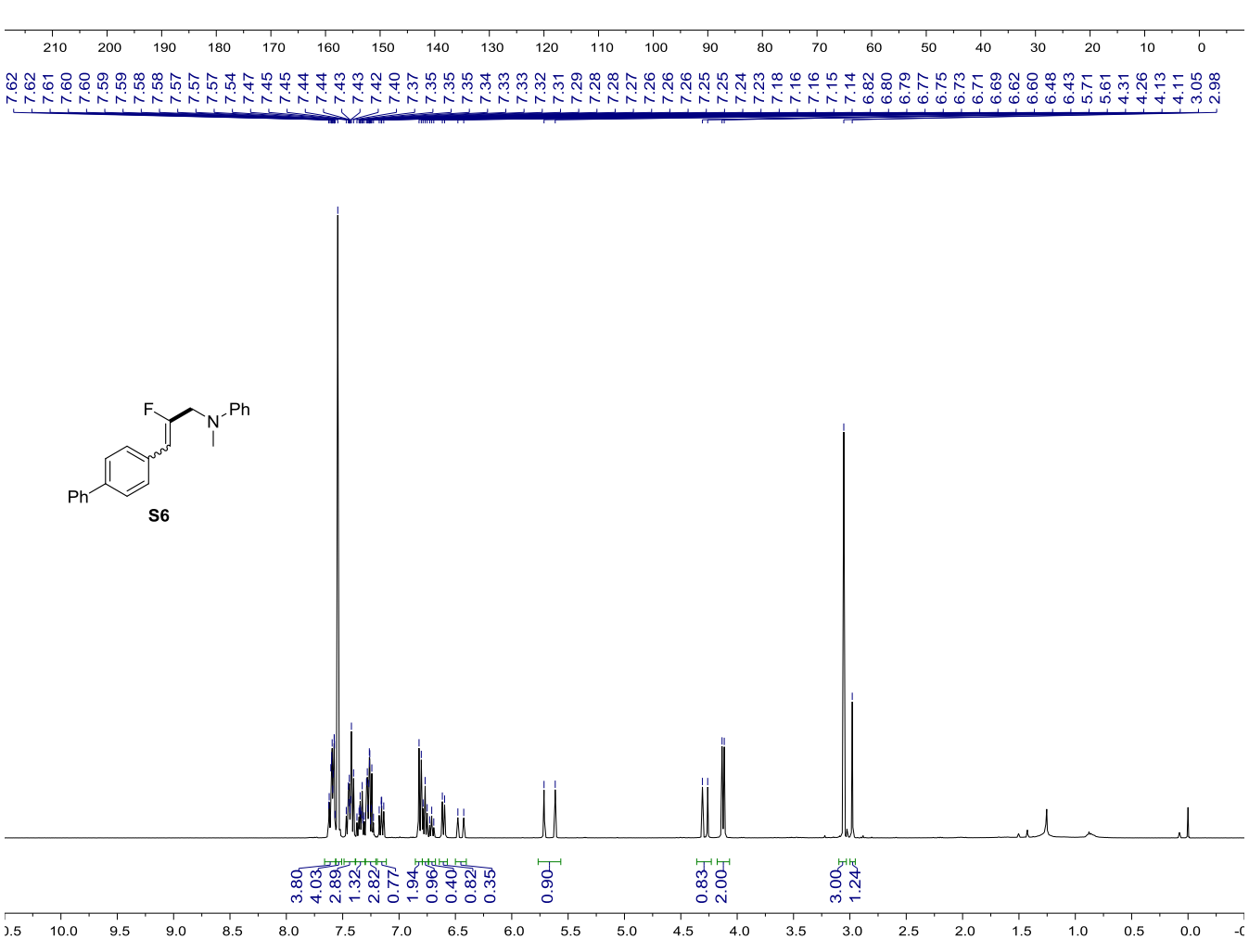
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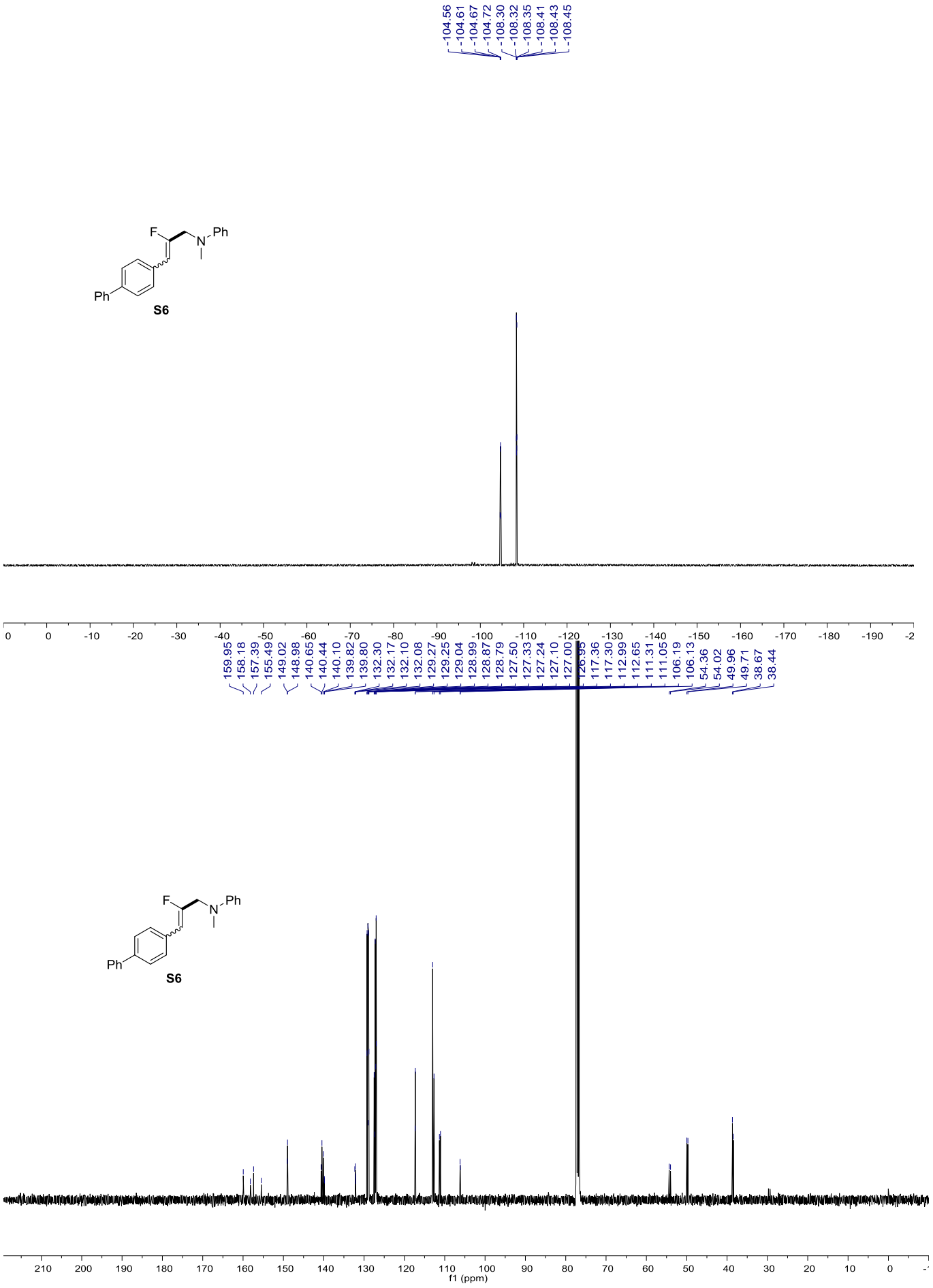
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f1 (ppm)