Supplementary Information (SI) for ChemComm.
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Supporting Information

Direct C−H Difluoroallylation of α,β-Unsaturated Amides and Aryl Amides by Rhodium catalysis

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General Information S2

Preparation of Starting Materials S2

Characterization Data of Substrate **1** S6

General Procedure for the Synthesis of **3**. S6

Characterization Data of Products **3** S7

General procedure for the preparation of **4** S17

General Procedure for the Synthesis of **5** S18

Characterization Data of Products **5** S18

Gram-Scale Experiments S22

Transformation of products S22

Characterization Data of Products **6** S23

KIE Study S24

References S25

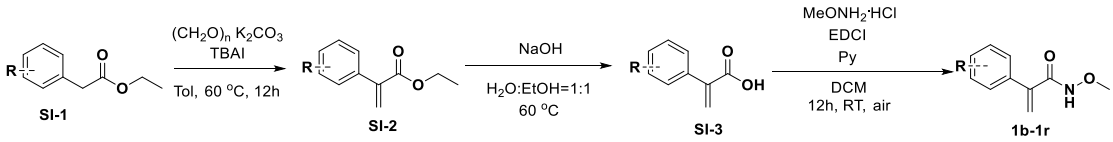
Copies of ^{1}H, ^{13}C NMR and ^{19}F NMR spectra S26

General Information

Unless otherwise specified, the chemical reagents were purchased from commercial sources and used directly without purification. Analytical thin-layer chromatography (TLC): HSGF 254 (0.15-0.2 mm thickness). Detection was conducted under UV light at 254 nm. Preparative thin layer chromatography was HSFG 254 (0.4-0.5 mm thickness). Yields refer to isolated compounds. ^{1}H, ^{13}C, and ^{19}F NMR spectra were collected on Brucker 500 MHz and 600 MHz instrument in chloroform-*d* or DMSO-d_6. Chemical shifts (δ) are expressed as parts per million (ppm). Proton coupling patterns were recorded as singlet (s), doublet (d), triplet (t), quartet (q), and multiple (m). HRMS (high-resolution mass spectrometry) were obtained by using a quadrupole mass analyzer with electrospray ionization (ESI) source.

Preparation of Starting Materials

General procedure A for preparation of 1b-1r[1-4]:

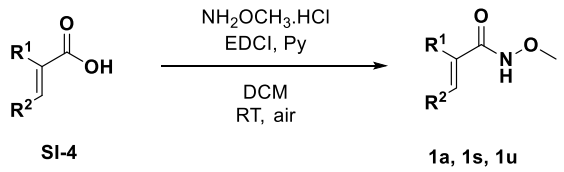


Step 1: Paraformaldehyde (0.90 g, 30.0 mmol, 3.0 equiv.), K_2CO_3 (4.15 g, 30.0 mmol, 3.0 equiv.), *n*-Bu_4NI (0.18 g, 0.5 mmol, 0.05 equiv.) were added to a solution of ester (10.0 mmol, 1.0 equiv.) in toluene (20.0 mL) at room temperature. The reaction mixture was heated to 60 °C for 12 h. After cooling to room temperature, H_2O (10.0 mL) was added and the aqueous layer was extracted with diethyl ether (20.0 mL × 3). The combined organic layer was dried over $MgSO_4$, concentrated in vacuo and purified by column chromatography to provide the corresponding acrylate **SI-2** as a colorless oil.

Step 2: A 50 mL round bottom flask was charged with ethyl 2-arylacrylate derivatives (1.0 equiv.), NaOH (5.0 equiv.), and H_2O/EtOH (1:1, 0.5 M). The reaction was stirred at 60 °C for overnight and then the reaction was cooled down to room temperature and acidified with 2N HCl. The aqueous phase was extracted with ethyl acetate (50.0 mL x 3). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (DCM/MeOH = 20/1, v/v) to give the corresponding unsaturated acid.

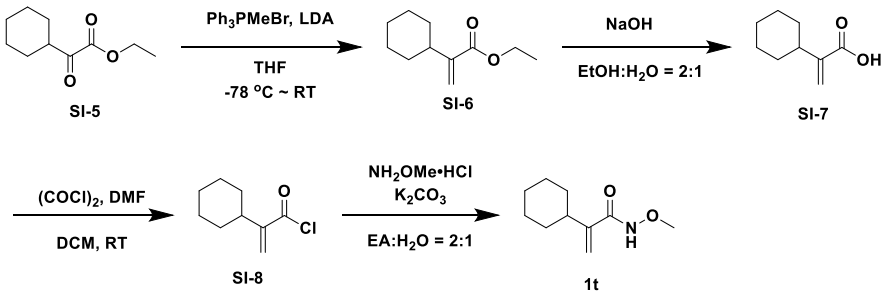
Step 3: To a solution of acrylic acid **SI-3** (2.0 mmol) in DCM (20.0 mL) was added pyridine (7.0 equiv.), EDCI (2.0 equiv.) and NH_2OCH_3·HCl (1.2 equiv.), and stirred at room temperature overnight. The mixture was washed with 2N HCl (20.0 mL), saturated aq. $NaHCO_3$ (20.0 mL) and brine (20.0 mL), dried over Na_2SO_4 and concentrated under reduced pressure to give the crude products, which was purified by column chromatography eluting with PE/EtOAc from 5:1 to 1:1.

General procedure B for preparation of 1a, 1s, 1u[1,4]:



To a solution of acrylic acid **SI-4** (2.0 mmol) in DCM (20.0 mL) was added pyridine (7.0 equiv.), EDCI (2.0 equiv.) and NH_2OCH_3·HCl (1.2 equiv.), and stirred at room temperature overnight. The mixture was washed with 2N HCl (20.0 mL), saturated aq. $NaHCO_3$ (20.0 mL) and brine (20.0 mL), dried over Na_2SO_4 and concentrated under reduced pressure to give the crude products, which was purified by column chromatography eluting with PE/EtOAc from 5:1 to 1:1.

Preparation of 1t[4]:



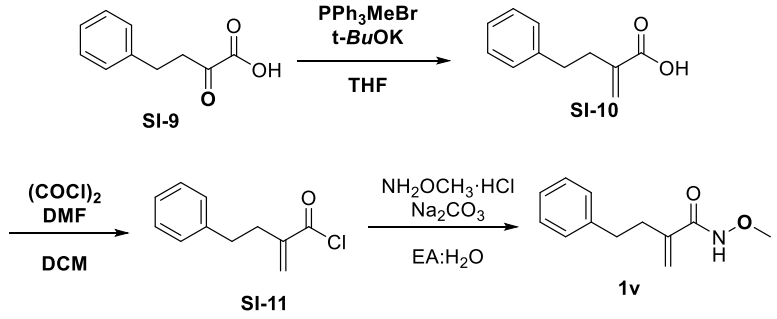
Step 1: An oven-dried 50 ml two-neck RBF was charged with methyl triphenyl phosphonium bromide (3.3 mmol) and dry THF (6.0 mL). The flask was cooled to -78 ℃ and LDA (3.0 mmol, 2M in THF) was dropwise added to the solution under N_2 atmosphere. After stirring 15 minutes, the mixture was warmed up to room temperature and stirred for 1 h, at which point the resulted yellow solution was re-cooled to -78℃ followed with the addition of crude *α*-ketoesters. After stirring for 1.0 h at -78 ℃, the mixture was warmed up to room temperature and the progress of the reaction was monitored using TLC. Once the reaction finished, 2N HCl (6.0 mL) was added followed by

extraction with ethyl acetate (2×10.0 ml), and dried over $MgSO_4$. The organic solvent was evaporated and the residue was purified by column chromatography on silica gel to deliver the *α*-substituted ethyl acrylate derivatives.

Step 2: A 50.0 mL round bottom flask was charged with ethyl 2-arylacrylate derivatives (1.0 equiv.), NaOH (5.0 equiv.), and H_2O/EtOH (1:2, 0.5 M). The reaction was stirred at 60 °C for overnight and then the reaction was cooled down to room temperature and acidified with 2N HCl. The aqueous phase was extracted with ethyl acetate (50.0 mL x 3). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (DCM/MeOH = 20/1, v/v) to give the corresponding unsaturated acid.

Step 3: To a solution of acrylic acid **SI-7** (2.0 mmol) in DCM (20.0 mL) was added pyridine (7.1 equiv.), EDCI (2.0 equiv.) and NH_2OCH_3·HCl (1.2 equiv.), and stirred at room temperature overnight. The mixture was washed with 2N HCl (20.0 mL), saturated aq. $NaHCO_3$ (20.0 mL) and brine (20.0 mL), dried over Na_2SO_4 and concentrated under reduced pressure to give the crude products, which was purified by column chromatography eluting with PE/EtOAc from 5:1 to 1:1.

Preparation of 1v:



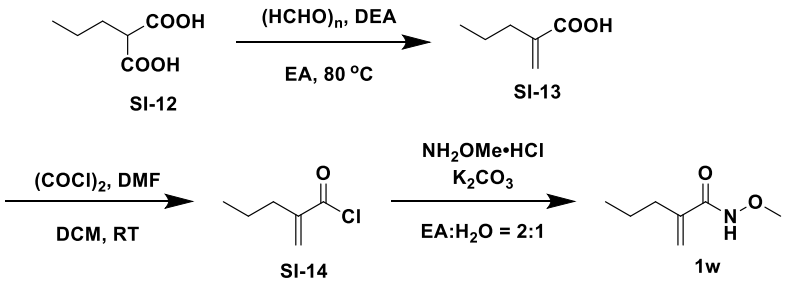
Step 1: Charge a flame-dried 100 mL round-bottom flask with methyltriphenylphosphonium bromide (3.0 g, 8.4 mmol, 5.0 equiv.) in dry THF (25 mL) at 0°C. Add t-BuOK (943mg, 8.4 mmol, 5.0 equiv.) to the mixture, then warm the sealed mixture to 22°C. Allow the mixture to stir at 22°C for 30 minutes. Add a solution of a-oxobenzenebutanoic acid (300 mg, 1.69 mmol, 1.0 equiv.) in dry THF (6 mL) to the mixture. Allow the resultant mixture to stir at 22°C for 3 hours. Acidify the mixture with aqueous HCl (2.0 M) to pH = 3-4, then remove the excess of THF under vacuum. Extract the resultant aqueous solution with EtOAc (3 x 30 mL). Wash the combined organic phases

with brine (30.0 mL). Dry the combined organic phases over anhydrous Na_2SO_4. Filter the mixture and concentrate under vacuum to get **SI-9**.

Step 2: To a solution of crude intermediate **SI-9** in anhydrous DCM (8.0 mL) was added $(COCl)_2$ (3.0 equiv.) over 30.0 min at 0 °C, then 2 drops of DMF was added. The resulting mixture was stirred at room temperature for 2.0 h. Then, the solution was concentrated to afford crude acyl chloride **SI-10** for the next step without further purification.

Step 3: The crude acyl chloride **SI-10** in EtOAc (5.0 mL) was added to a solution of methoxyamine hydrochloride (2.0 equiv.) and K_2CO_3 (2.0 equiv.) in EtOAc/H_2O =2/1 (9.0 mL) over 5.0 min at 0°C. The solution was stirred at room temperature for 12.0 h. Then the solution was extracted with EtOAc (40.0 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4, and evaporated to afford the residue. The residue was subject to column chromatography on silica gel (DCM/MeOH = 20/1) to afford the corresponding **1v**.

Preparation of 1w:

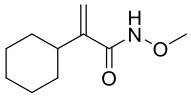


Step 1: To a solution of the diacid in EtOAc (0.75 M) at 0°c and subsequent addition of paraformaldehyde (1.5 equiv.). The reaction mixture was refluxed by oil bath for 2 h. After cooling to room temperature, H_2O (10.0 mL) was added and the aqueous layer was extracted with diethyl ether (20.0 mL × 3). The combined organic layer was dried over $MgSO_4$, concentrated in vacuo and purified the resulting crude acrylic acid **SI-13** as a colorless oil.

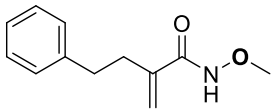
Step 2: To a solution of crude intermediate SI-10 in anhydrous DCM (8.0 mL) was added $(COCl)_2$ (3.0 equiv.) over 30.0 min at 0 °C, then 2 drops of DMF was added. The resulting mixture was stirred at room temperature for 2.0 h. Then, the solution was concentrated to afford crude acyl chloride **SI-14** for the next step without further purification.

Step 3: The crude acyl chloride **SI-14** in EtOAc (5.0 mL) was added to a solution of methoxyamine hydrochloride (2.0 equiv.) and K_2CO_3 (2.0 equiv.) in EtOAc/H_2O =2/1 (9.0 mL) over 5.0 min at 0°C. The solution was stirred at room temperature for 12.0 h. Then the solution was extracted with EtOAc (40.0 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4, and evaporated to afford the residue. The residue was subject to column chromatography on silica gel (DCM/MeOH = 20/1) to afford the corresponding **1w**.

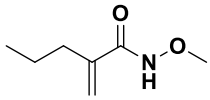
Characterization Data of Substrate 1t, 1v, 1w



2-cyclohexyl-*N*-methoxyacrylamide (1t): ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.29 (s, 1H), 5.39 (s, 1H), 5.20 (d, J = 1.5 Hz, 1H), 3.81 (s, 3H), 2.47 – 2.40 (m, 1H), 1.84 – 1.73 (m, 4H), 1.73 – 1.66 (m, 1H), 1.36 – 1.25 (m, 2H), 1.20 – 1.08 (m, 3H).



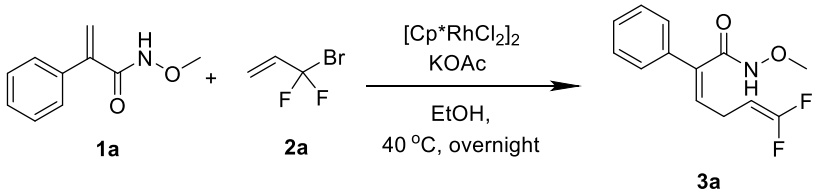
N-methoxy-2-methylene-4-phenylbutanamide (1v): ***^{1}H NMR (600 MHz, Chloroform-d)*** δ 8.30 (s, 1H), 7.28 (m, 2H), 7.18 (m, 3H), 5.54 (s, 1H), 5.28 (s, 1H), 3.79 (s, 3H), 2.80 (t, J = 7.8 Hz, 2H), 2.63 (t, J = 7.8 Hz, 2H).



N*-methoxy-2-methylenepentanamide (1w):** ***^{1}H NMR (600 MHz, Chloroform-d) δ 10.05 – 9.68 (m, 1H), 5.54 (s, 1H), 5.20 (s, 1H), 3.69 (s, 3H), 2.30 – 2.11 (m, 2H), 1.46 – 1.32 (m, J = 7.1, 6.0 Hz, 2H), 0.90 – 0.77 (m, 3H).

General Procedure for the Synthesis of 3.

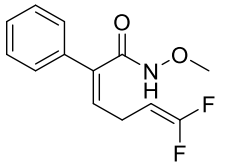
Representative Procedure for the Synthesis of **3a**



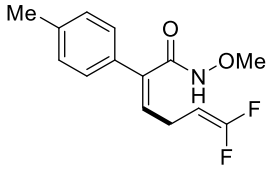
In a 10 mL reaction tube, to the mixture of **1a** (35.4 mg, 0.20 mmol, 1.0 eq), **2a** (47 mg, 0.3 mmol, 1.5 eq), $[Cp^*RhCl_2]_2$ (3.7 mg, 3.0 mol%) and KOAc (29.4 mg, 0.3 mmol, 1.5 eq) was added EtOH

(2.0 mL). Then the resulting mixture was stirred at 40 ℃ for 12.0 h. When the reaction was finished, the products are purified by preparative thin layer chromatography (DCM/MeOH = 20/1). The product **3a** was obtained as a yellow oil (40 mg, 79% yield). Other products **3** were prepared by a similar procedure.

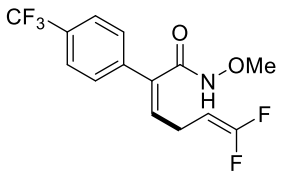
Characterization Data of Products 3



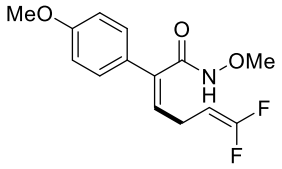
(*Z*)-6,6-difluoro-*N*-methoxy-2-phenylhexa-2,5-dienamide (3a): column solvent: DCM/MeOH = 20/1, yellow oil (40 mg, yield 79%); ***^{1}H NMR (500 MHz, DMSO-d$_6$)*** δ 11.51 (s, 1H), 7.40 – 7.34 (m, 4H), 7.32 – 7.28 (m, 1H), 6.12 (t, J = 7.6 Hz, 1H), 4.62 (dtd, J = 26.4, 7.8, 2.5 Hz, 1H), 3.71 (s, 3H), 2.92 – 2.87 (m, 2H). ***^{13}C NMR (126 MHz, DMSO-d$_6$)*** δ 164.07, 155.43 (t, J = 284.3 Hz), 136.14, 136.03, 128.64, 127.93, 127.90, 125.51, 76.94 (dd, J = 22.6, 18.8 Hz), 63.22, 22.59 (d, J = 4.9 Hz). ***^{19}F NMR (471 MHz, Chloroform-d)*** δ -87.73 (d, J = 43.0 Hz), -89.73 (d, J = 42.4 Hz). ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{13}H_{14}F_2NO_2$: 254.0987; Found: 254.0988.



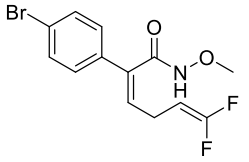
(*Z*)-6,6-difluoro-*N*-methoxy-2-(p-tolyl)hexa-2,5-dienamide (3b): column solvent: DCM/MeOH = 20/1, yellow oil (47 mg, yield 77%); ***^{1}H NMR (500 MHz, Chloroform-d)*** δ 8.19 (s, 1H), 7.23 (d, J = 7.9 Hz, 2H), 7.15 (d, J = 7.9 Hz, 2H), 5.97 (t, J = 7.6 Hz, 1H), 4.30 (dtd, J = 25.0, 7.8, 2.1 Hz, 1H), 3.84 (s, 3H), 3.12 – 3.06 (m, 2H), 2.34 (s, 3H). ***^{13}C NMR (126 MHz, Chloroform-d)*** δ 166.26, 159.07, 156.79, 154.50, 138.56, 135.31, 133.61, 132.80, 129.65, 126.68, 76.51, 76.34 (d, J = 3.4 Hz), 76.17, 64.73, 23.04, 23.00, 21.26. ***^{19}F NMR (471 MHz, Chloroform-d)*** δ -87.85 (d, J = 44.8 Hz), -89.83 (d, J = 44.5 Hz). ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{14}H_{16}F_2NO_2$: 268.1144; Found: 268.1138.



(*Z*)-6,6-difluoro-*N*-methoxy-2-(4-(trifluoromethyl)phenyl)hexa-2,5-dienamide (3c): column solvent: DCM/MeOH = 20/1, yellow oil (47 mg, yield 74%); ***^{1}H NMR (500 MHz, Chloroform-d)*** δ 8.23 (s, 1H), 7.60 (d, J = 8.2 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 6.11 (t, J = 7.7 Hz, 1H), 4.31 (dtd, J = 24.9, 7.9, 2.0 Hz, 1H), 3.86 (s, 3H), 3.14 – 3.03 (m, 2H). ***^{13}C NMR (151 MHz, Chloroform-d)*** δ 165.23, 158.67, 156.77, 154.86, 139.64, 134.51, 130.43 (d, J = 32.7 Hz), 126.73, 125.78 (d, J = 3.8 Hz), 124.81, 123.00, 75.84, 75.69 (d, J = 4.1 Hz), 75.55, 64.61, 23.07 (d, J = 4.8 Hz). ***^{19}F NMR (565 MHz, Chloroform-d)*** δ -62.77, -87.18 (d, J = 44.7 Hz), -89.26 (dd, J = 41.4, 24.0 Hz). ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{14}H_{13}F_5NO_2$: 322.0861; Found: 322.0853.

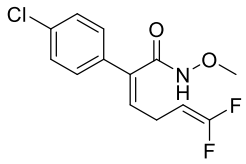


(*Z*)-6,6-difluoro-*N*-methoxy-2-(4-methoxyphenyl)hexa-2,5-dienamide (3d): column solvent: DCM/MeOH = 20/1, yellow oil (35 mg, yield 61%); ***^{1}H NMR (500 MHz, Chloroform-d)*** δ 8.16 (s, 1H), 7.27 (d, J = 11.4 Hz, 2H), 6.92 – 6.81 (m, 2H), 5.92 (t, J = 7.7 Hz, 1H), 4.30 (dtd, J = 25.0, 7.8, 2.1 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 3.11 – 3.05 (m, 2H). ***^{13}C NMR (126 MHz, Chloroform-d)*** δ 166.37, 159.92, 156.78 (t, J = 287.5 Hz), 134.95, 131.71, 128.91, 128.02, 114.35, 76.41 (dd, J = 23.0, 20.0 Hz), 64.75, 55.47, 23.01 (d, J = 5.2 Hz). ***^{19}F NMR (471 MHz, Chloroform-d)*** δ -87.90 (d, J = 43.6 Hz), -89.89 (dd, J = 44.1, 24.9 Hz). ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{14}H_{16}F_2NO_3$: 284.1093; Found: 284.1086.

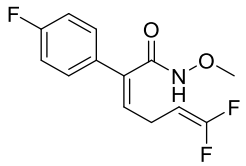


(*Z*)-2-(4-bromophenyl)-6,6-difluoro-*N*-methoxyhexa-2,5-dienamide (3e): column solvent: DCM/MeOH = 20:1, yellow oil (61 mg, yield 92%); ***^{1}H NMR (500 MHz, DMSO-d$_6$)*** δ 11.54 (s,

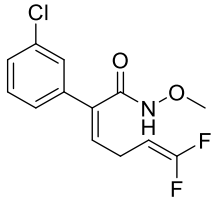
1H), 7.59 – 7.54 (m, 2H), 7.35 – 7.30 (m, 2H), 6.18 (t, *J* = 7.5 Hz, 1H), 4.61 (dtd, *J* = 26.4, 7.8, 2.5 Hz, 1H), 3.70 (s, 3H), 2.90 – 2.84 (m, 2H). ***^{13}C NMR (151 MHz, Chloroform-d)*** δ 165.59, 156.84 (t, *J* = 287.7 Hz), 135.25, 134.62, 133.47, 132.09, 128.21, 122.75, 76.14, 75.99 (dd, *J* = 23.6, 20.1 Hz), 64.76, 23.13 (d, *J* = 4.9 Hz). ***^{19}F NMR (471 MHz, Chloroform-d)*** δ -87.33 (d, *J* = 42.8 Hz), -89.37 (d, *J* = 43.0 Hz). ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{13}H_{13}BrF_2NO_2$: 332.0092, 334.0072; Found: 332.0088, 334.0063.



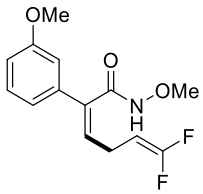
(*Z*)-2-(4-chlorophenyl)-6,6-difluoro-*N*-methoxyhexa-2,5-dienamide (3f): column solvent: DCM/MeOH = 20:1, yellow oil (46 mg, yield 80%); ***^{1}H NMR (500 MHz, Chloroform-d)*** δ 8.89 (s, 1H), 7.29 – 7.21 (m, 4H), 5.95 (t, *J* = 7.6 Hz, 1H), 4.26 (dtd, *J* = 25.0, 7.8, 2.0 Hz, 1H), 3.79 (s, 3H), 3.00 (t, *J* = 7.8 Hz, 2H). ***^{13}C NMR (151 MHz, Chloroform-d)*** δ 165.64, 156.76 (t, *J* = 287.8 Hz), 134.73, 134.55, 134.47, 132.87, 129.03, 127.78, 75.99 (dd, *J* = 23.7, 20.0 Hz), 64.56, 23.07 (d, *J* = 4.5 Hz). ***^{19}F NMR (471 MHz, Chloroform-d)*** δ -87.49 (d, *J* = 42.8 Hz), -89.56 (d, *J* = 44.0 Hz). ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{13}H_{13}ClF_2NO_2$: 288.0597; Found: 288.0591.



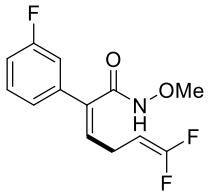
(*Z*)-6,6-difluoro-2-(4-fluorophenyl)-*N*-methoxyhexa-2,5-dienamide (3g): column solvent: DCM/MeOH = 20:1, yellow solid (29 mg, yield 54%); ***^{1}H NMR (500 MHz, Chloroform-d)*** δ 8.55 (s, 1H), 7.35 – 7.28 (m, 2H), 7.05 – 6.98 (m, 2H), 5.93 (t, *J* = 7.7 Hz, 1H), 4.28 (dtd, *J* = 25.0, 7.9, 2.1 Hz, 1H), 3.82 (s, 3H), 3.07 – 3.01 (m, 2H). ***^{13}C NMR (126 MHz, Chloroform-d)*** δ 165.86, 162.92 (d, *J* = 248.4 Hz), 156.83 (t, *J* = 287.8 Hz), 134.55, 133.06, 132.50 (d, *J* = 3.7 Hz), 128.47 (d, *J* = 8.2 Hz), 115.94 (d, *J* = 21.6 Hz), 76.14 (dd, *J* = 23.8, 20.0 Hz), 64.75, 23.07 (d, *J* = 5.0 Hz). ***^{19}F NMR (471 MHz, Chloroform-d)*** δ -87.56 (d, *J* = 44.8 Hz), -89.59 (d, *J* = 44.7 Hz), -113.06. ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{13}H_{13}F_3NO_2$: 272.0893; Found: 272.0887.



(*Z*)-2-(3-chlorophenyl)-6,6-difluoro-*N*-methoxyhexa-2,5-dienamide (3h): column solvent: DCM/MeOH = 20:1, yellow oil (18 mg, yield 31%); ***^{1}H NMR (500 MHz, Chloroform-d)*** δ 8.43 (s, 1H), 7.32 – 7.27 (m, 4H), 5.99 (t, J = 7.7 Hz, 1H), 4.28 (dtd, J = 25.0, 7.8, 2.0 Hz, 1H), 3.83 (s, 3H), 3.09 – 3.03 (m, 2H). ***^{13}C NMR (126 MHz, Chloroform-d)*** δ 165.43, 156.88 (t, J = 288.0 Hz), 138.13, 134.98, 134.43, 130.22, 130.09, 128.67, 126.81, 124.88, 75.98 (dd, J = 24.1, 19.7 Hz), 64.85, 23.13 (d, J = 4.8 Hz). ***^{19}F NMR (471 MHz, Chloroform-d)*** δ -87.30 (d, J = 43.5 Hz), -89.33 (d, J = 42.6 Hz). ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{13}H_{13}ClF_2NO_2$: 288.0597; Found: 288.0593.

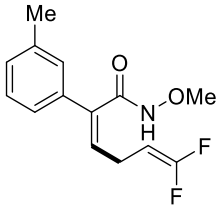


(*Z*)-6,6-difluoro-*N*-methoxy-2-(3-methoxyphenyl)hexa-2,5-dienamide (3i): column solvent: DCM/MeOH = 20/1, yellow oil (26 mg, yield 46%); ***^{1}H NMR (500 MHz, Chloroform-d)*** δ 8.60 (s, 1H), 7.39 – 7.18 (m, 1H), 7.18 – 6.62 (m, 3H), 5.97 (t, J = 7.6 Hz, 1H), 4.28 (dtd, J = 25.0, 7.8, 2.1 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.08 – 3.02 (m, 2H). ***^{13}C NMR (126 MHz, Chloroform-d)*** δ 165.92, 159.96, 156.79 (t, J = 287.6 Hz), 137.86, 135.31, 133.78, 129.98, 119.21, 114.07, 112.36, 76.22 (dd, J = 23.5, 19.7 Hz), 64.63, 55.40, 23.03 (d, J = 4.9 Hz). ***^{19}F NMR (471 MHz, Chloroform-d)*** δ -87.80 (d, J = 44.5 Hz), -89.82 (d, J = 44.6 Hz). ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{14}H_{16}F_2NO_3$: 284.1093; Found: 284.1086.

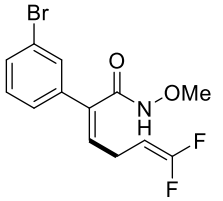


(*Z*)-6,6-difluoro-2-(3-fluorophenyl)-*N*-methoxyhexa-2,5-dienamide (3j): column solvent: DCM/MeOH = 20/1, yellow oil (35 mg, yield 65%); ***^{1}H NMR (500 MHz, Chloroform-d)*** δ 8.28 (s, 1H), 7.32 – 7.28 (m, 2H), 7.16 – 7.13 (m, 1H), 7.10 – 7.02 (m, 1H), 6.04 (t, J = 7.6 Hz, 1H), 4.31

(dtd, J = 25.1, 7.9, 2.1 Hz, 1H), 3.81 (s, 3H), 3.23 – 3.16 (m, 2H). ***^{13}C NMR (126 MHz, Chloroform-d)*** δ 165.52, 164.04, 162.08, 159.14, 156.85, 154.56, 138.45 (d, J = 7.9 Hz), 134.63, 133.84, 130.51 (d, J = 8.5 Hz), 122.31, 115.47 (d, J = 21.3 Hz), 113.56 (d, J = 22.4 Hz), 76.14, 75.96 (d, J = 4.3 Hz), 75.79, 64.73, 23.09 (d, J = 5.0 Hz). ***^{19}F NMR (471 MHz, Chloroform-d)*** δ -87.40 (d, J = 44.2 Hz), -89.44 (d, J = 43.7 Hz), -112.19. ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{13}H_{13}F_3NO_2$: 272.0893; Found: 272.0887.

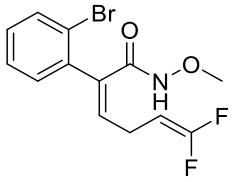


(*Z*)-6,6-difluoro-*N*-methoxy-2-(m-tolyl)hexa-2,5-dienamide (3k): column solvent: DCM/MeOH = 20/1, yellow oil (46 mg, yield 86%); ***^{1}H NMR (500 MHz, DMSO-d$_6$)*** δ 11.47 (s, 1H), 7.28 – 7.11 (m, 4H), 6.09 (t, J = 7.6 Hz, 1H), 4.61 (dtd, J = 26.4, 7.8, 2.5 Hz, 1H), 3.70 (s, 3H), 2.89 – 2.85 (m, 2H), 2.30 (s, 3H). ***^{13}C NMR (151 MHz, Chloroform-d)*** δ 166.14, 156.76 (t, J = 287.6 Hz), 138.64, 136.37, 135.53, 133.05, 129.26, 128.79, 127.38, 123.77, 76.28 (dd, J = 23.5, 20.0 Hz), 64.61, 23.01 (d, J = 4.8 Hz), 21.47. ***^{19}F NMR (471 MHz, DMSO-d$_6$)*** δ -89.02 (d, J = 45.5 Hz), -90.81 (d, J = 46.3 Hz). ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{14}H_{16}F_2NO_2$: 268.1144; Found: 286.1137.

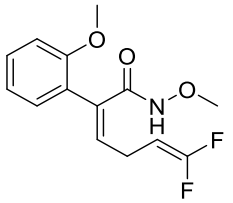


(*Z*)-2-(3-bromophenyl)-6,6-difluoro-*N*-methoxyhexa-2,5-dienamide (3l): column solvent: DCM/MeOH = 20/1, yellow oil (20 mg, yield 33%); ***^{1}H NMR (500 MHz, Chloroform-d)*** δ 8.36 (s, 1H), 7.50 (s, 1H), 7.44 (d, J = 7.9 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.21 (t, J = 7.9 Hz, 1H), 6.02 (t, J = 7.7 Hz, 1H), 4.29 (dtd, J = 25.0, 7.9, 2.0 Hz, 1H), 3.84 (s, 3H), 3.10 – 3.04 (m, 2H). ***^{13}C NMR (151 MHz, Chloroform-d)*** δ 165.40, 156.89 (t, J = 287.9 Hz), 138.41, 134.51, 134.36, 131.60, 130.47, 129.69, 125.35, 123.10, 75.97 (d, J = 24.4, 19.9 Hz), 64.85, 23.13 (d, J = 4.9 Hz). ***^{19}F NMR (471 MHz, Chloroform-d)*** δ -87.28 (d, J = 42.6 Hz), -89.31 (d, J = 42.6 Hz). ***HRMS (ESI-MS) m/z:***

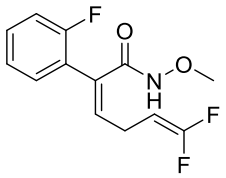
[M+H]$^+$ Calcd for $C_{13}H_{13}BrF_2NO_2$: 332.0092, 334.0072; Found: 332.0088, 334.0062.



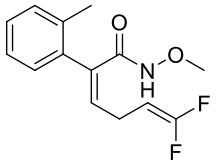
(*Z*)-2-(2-bromophenyl)-6,6-difluoro-*N*-methoxyhexa-2,5-dienamide (3m): column solvent: DCM/MeOH = 20:1, yellow oil (42 mg, yield 63%); ***^{1}H NMR (500 MHz, Chloroform-d)*** δ 7.96 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.24 (m, 2H), 7.21 – 7.16 (m, 1H), 5.86 (t, *J* = 7.4 Hz, 1H), 4.32 (dtd, *J* = 25.2, 7.9, 2.1 Hz, 1H), 3.74 (s, 3H), 3.37 – 3.31 (m, 2H). ***^{13}C NMR (151 MHz, Chloroform-d)*** δ 164.10, 156.91 (t, *J* = 289.3 Hz), 142.42, 138.60, 133.82, 133.30, 131.73, 130.26, 128.13, 123.81, 76.23 (dd, *J* = 23.6, 20.0 Hz), 64.48, 22.71 (d, *J* = 4.7 Hz). ***^{19}F NMR (471 MHz, DMSO-d$_6$)*** δ -92.69 (d, *J* = 42.9 Hz), -94.52 (d, *J* = 42.5 Hz). ***HRMS (ESI-MS) m/z:*** [M+H]$^+$ Calcd for $C_{13}H_{13}BrF_2NO_2$: 332.0092, 334.0072; Found: 332.0088, 334.0063.



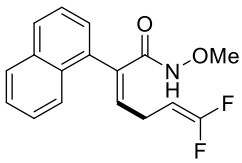
(*Z*)-6,6-difluoro-*N*-methoxy-2-(2-methoxyphenyl)hexa-2,5-dienamide (3n): column solvent: DCM/MeOH = 20:1, white solid (16 mg, yield 28%); ***^{1}H NMR (500 MHz, Chloroform-d)*** δ 8.14 (s, 1H), 7.36 – 7.29 (m, 1H), 7.21 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.00 – 6.91 (m, 1H), 6.91 – 6.86 (m, 2H), 5.89 (t, *J* = 7.5 Hz, 1H), 4.33 (dtd, *J* = 25.2, 7.9, 2.2 Hz, 1H), 3.83 (s, 3H), 3.77 (s, 3H), 3.23 (t, *J* = 7.7 Hz, 2H). ***^{13}C NMR (151 MHz, CDCl$_3$)*** δ 166.43, 158.70, 156.80, 156.70, 154.91, 138.28, 132.77, 130.85, 130.27, 127.12, 121.37, 111.08, 76.59 (dd, *J* = 23.1, 20.1 Hz), 64.44, 55.70, 22.78 (d, *J* = 5.1 Hz). ***^{19}F NMR (471 MHz, Chloroform-d)*** δ -88.24 (d, *J* = 43.0 Hz), -90.10 (d, *J* = 43.9 Hz). ***HRMS (ESI-MS) m/z:*** [M+H]$^+$ Calcd for $C_{14}H_{16}F_2NO_3$: 284.1093; Found: 284.1087.



(*Z*)-6,6-difluoro-2-(2-fluorophenyl)-*N*-methoxyhexa-2,5-dienamide (3o): column solvent: DCM/MeOH = 20:1, yellow oil (20 mg, yield 37%); ***^{1}H NMR (500 MHz, Chloroform-d)*** δ 8.09 (s, 1H), 7.36 – 7.27 (m, 2H), 7.15 (t, J = 7.5 Hz, 1H), 7.12 – 7.03 (m, 1H), 6.05 (t, J = 7.6 Hz, 1H), 4.33 (dtd, J = 25.0, 7.8, 2.0 Hz, 1H), 3.82 (s, 3H), 3.24 – 3.20 (m, 2H). ***^{13}C NMR (151 MHz, Chloroform-d)*** δ 165.19, 159.89 (d, J = 248.4 Hz), 156.88 (t, J = 287.7 Hz), 139.05, 130.55, 129.78, 125.09 (d, J = 13.9 Hz), 124.78, 116.19 (d, J = 21.7 Hz), 76.15 (dd, J = 23.8, 20.1 Hz), 64.56, 23.08 (d, J = 3.1 Hz). ***^{19}F NMR (471 MHz, Chloroform-d)*** δ -87.70 (d, J = 43.6 Hz), -89.62 (d, J = 44.3 Hz), -113.65. ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{13}H_{12}F_3NO_2$: 272.0893; Found: 272.0886.

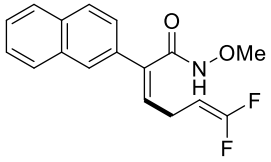


(*Z*)-6,6-difluoro-*N*-methoxy-2-(o-tolyl)hexa-2,5-dienamide (3p): column solvent: DCM/MeOH = 20:1, yellow oil (17 mg, yield 32%); ***^{1}H NMR (500 MHz, Chloroform-d)*** δ 7.88 (s, 1H), 7.31 – 7.23 (m, 1H), 7.23 – 7.19 (m, 2H), 7.16 – 7.09 (m, 1H), 5.84 (t, J = 7.4 Hz, 1H), 4.34 (dtd, J = 25.3, 7.9, 2.2 Hz, 1H), 3.74 (s, 3H), 3.43 – 3.37 (m, 2H), 2.26 (s, 3H). ***^{13}C NMR (126 MHz, Chloroform-d)*** δ 165.15, 156.91 (t, J = 288.2 Hz), 141.74, 137.41, 136.87, 133.63, 130.71, 130.11, 128.88, 126.57, 76.56 (dd, J = 23.7, 20.0 Hz), 64.54, 22.62 (d, J = 5.1 Hz), 19.83. ***^{19}F NMR (471 MHz, Chloroform-d)*** δ -88.26 (d, J = 44.8 Hz), -90.09 (d, J = 44.3 Hz). ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{14}H_{16}F_2NO_2$: 268.1144; Found: 268.1139.

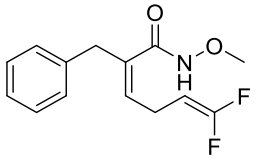


(*Z*)-6,6-difluoro-*N*-methoxy-2-(naphthalen-1-yl)hexa-2,5-dienamide (3q): column solvent: DCM/MeOH = 20/1, yellow oil (52 mg, yield 86%); ***^{1}H NMR (500 MHz, Chloroform-d)*** δ 7.90 – 7.84 (m, 4H), 7.55 – 7.49 (m, 2H), 7.48 – 7.44 (m, 1H), 7.37 (d, J = 6.8 Hz, 1H), 6.04 (t, J = 7.4 Hz,

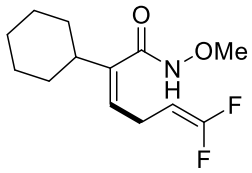
1H), 4.41 (dtd, *J* = 25.2, 7.9, 2.2 Hz, 1H), 3.63 (s, 3H), 3.52 – 3.46 (m, 2H). ***^{13}C NMR (126 MHz, Chloroform-d)*** δ 165.37, 156.96 (t, *J* = 286.5 Hz), 143.03, 135.36, 133.80, 132.74, 131.80, 129.37, 128.64, 127.83, 127.18, 126.65, 125.67, 125.13, 76.55 (dd, *J* = 23.7, 20.1 Hz), 64.45, 22.89 (d, *J* = 5.0 Hz). ***^{19}F NMR (471 MHz, Chloroform-d)*** δ -88.10 (d, *J* = 44.9 Hz), -89.94 (d, *J* = 45.1 Hz). ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{17}H_{16}F_2NO_2$: 304.1144; Found: 304.1138.



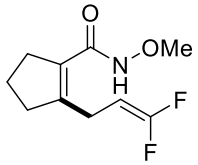
(*Z*)-6,6-difluoro-*N*-methoxy-2-(naphthalen-2-yl)hexa-2,5-dienamide (3r): column solvent: DCM/MeOH = 20/1, yellow oil (34 mg, yield 56%); ***^{1}H NMR (500 MHz, Chloroform-d)*** δ 8.36 (s, 1H), 7.95 – 7.70 (m, 4H), 7.62 – 7.42 (m, 3H), 6.13 (t, *J* = 7.6 Hz, 1H), 4.33 (dtd, *J* = 25.0, 7.9, 2.0 Hz, 1H), 3.86 (s, 3H), 3.16 – 3.11 (m, 2H). ***^{13}C NMR (126 MHz, Chloroform-d)*** δ 166.14, 156.84 (t, *J* = 288.9 Hz), 135.51, 133.61, 133.42, 133.14, 128.73, 128.34, 127.77, 126.77 (d, *J* = 9.4 Hz), 126.14, 124.08, 76.25 (dd, *J* = 23.8, 20.1 Hz), 64.79, 23.18 (d, *J* = 5.3 Hz). ***^{19}F NMR (471 MHz, Chloroform-d)*** δ -87.62 (d, *J* = 43.2 Hz), -89.62 (d, *J* = 44.5 Hz). ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{17}H_{16}F_2NO_2$: 304.1144; Found: 304.1145.



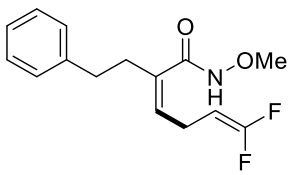
(*Z*)-2-benzyl-6,6-difluoro-*N*-methoxyhexa-2,5-dienamide (3s): column solvent: DCM/MeOH = 20:1, yellow solid (38 mg, yield 71%); ***^{1}H NMR (500 MHz, DMSO-d$_6$)*** δ 11.12 (s, 1H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.23 – 7.14 (m, 2H), 5.47 (t, *J* = 7.4 Hz, 1H), 4.55 (dtd, *J* = 26.7, 7.9, 2.6 Hz, 1H), 3.50 (s, 3H), 3.47 (s, 2H), 2.83 – 2.77 (m, 2H). ***^{13}C NMR (151 MHz, Chloroform-d)*** δ 166.74, 158.90, 156.62, 154.33, 137.85, 134.64, 132.09, 128.94, 127.06, 76.39 (dd, *J* = 23.7, 20.0 Hz), 64.44, 40.87, 22.76 (d, *J* = 4.9 Hz).***^{19}F NMR (471 MHz, DMSO-d$_6$)*** δ -89.33 (d, *J* = 45.3 Hz), -91.22 (d, *J* = 48.2 Hz). ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{14}H_{16}F_2NO_2$: 268.1144; Found: 268.1141.



(*Z*)-2-cyclohexyl-6,6-difluoro-*N*-methoxyhexa-2,5-dienamide (3t): column solvent: DCM/MeOH = 20/1, yellow oil (16 mg, yield 31%); ***^{1}H NMR (500 MHz, Chloroform-d)*** δ 8.19 (s, 1H), 5.38 (t, J = 7.6 Hz, 1H), 4.18 (dtd, J = 25.1, 7.8, 2.1 Hz, 1H), 3.83 (s, 3H), 2.79 (t, J = 7.8 Hz, 2H), 2.17 (t, J = 11.7 Hz, 1H), 1.84 – 1.62 (m, 6H), 1.31 – 1.21 (m, 2H), 1.20 – 1.08 (m, 2H). ***^{13}C NMR (151 MHz, Chloroform-d)*** δ 167.72, 156.54 (t, J = 287.3 Hz), 141.34, 126.63, 76.63 (m), 64.74, 41.96, 31.94, 26.43, 26.05, 22.68 (d, J = 4.9 Hz). ***^{19}F NMR (471 MHz, Chloroform-d)*** δ -88.09 (d, J = 45.2 Hz), -90.03 (d, J = 45.0 Hz). ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{13}H_{20}F_2NO_2$: 260.1457; Found: 260.1455.

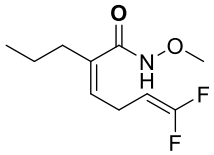


2-(3,3-difluoroallyl)-*N*-methoxycyclopent-1-ene-1-carboxamide (3u): column solvent: DCM/MeOH = 20/1, yellow oil (19 mg, yield 44%); ***^{1}H NMR (500 MHz, Chloroform-d)*** δ 8.29 (s, 1H), 4.26 (dtd, J = 25.1, 8.1, 2.3 Hz, 1H), 3.79 (s, 3H), 3.26 (d, J = 8.1 Hz, 2H), 2.51 (t, J = 7.4 Hz, 2H), 2.44 (t, J = 7.6 Hz, 2H), 1.91 – 1.84 (m, 2H). ***^{13}C NMR (151 MHz, Chloroform-d)*** δ 165.27, 156.97 (t, J = 285.9 Hz), 129.18, 128.37, 75.74 (dd, J = 23.7, 20.6 Hz), 64.75, 37.22, 33.20, 22.92 (d, J = 4.7 Hz), 21.81. ***^{19}F NMR (565 MHz, Chloroform-d)*** δ -88.44 (d, J = 46.1 Hz), -90.88 (dd, J = 45.2, 27.1 Hz). **HRMS (ESI-MS) *m/z:*** $[M+H]^+$ Calcd for $C_{10}H_{14}F_2NO_2$: 230.0987; Found: 230.0988.

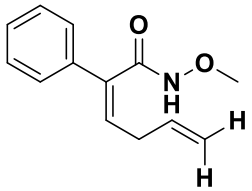


(*Z*)-6,6-difluoro-*N*-methoxy-2-phenethylhexa-2,5-dienamide (3v): column solvent: DCM/MeOH = 20/1, yellow soild (34 mg, yield 61%); ***^{1}H NMR (600 MHz, Chloroform-d)*** δ 8.05

(s, 1H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 2H), 5.46 (t, *J* = 7.7 Hz, 1H), 4.14 (dtd, *J* = 25.1, 7.8, 2.1 Hz, 1H), 3.79 (s, 3H), 2.82 (t, *J* = 7.8 Hz, 2H), 2.80 – 2.71 (m, 2H), 2.53 (t, *J* = 7.8 Hz, 2H). ***^{13}C NMR (151 MHz, Chloroform-d)*** δ 167.28, 158.47, 156.57, 154.66, 140.83, 134.61, 131.05, 128.63 (d, *J* = 4.9 Hz), 126.37, 76.51, 76.37 (d, *J* = 3.2 Hz), 76.22, 64.71, 36.14, 34.68, 22.70 (d, *J* = 5.2 Hz). ***^{19}F NMR (565 MHz, Chloroform-d)*** δ -88.00 (d, *J* = 44.9 Hz), -89.84 (dd, *J* = 45.1, 24.9 Hz). **HRMS (ESI-MS)** ***m/z:*** $[M+H]^+$ Calcd for $C_{15}H_{18}F_2NO_2$: 282.1300; Found: 282.1301.

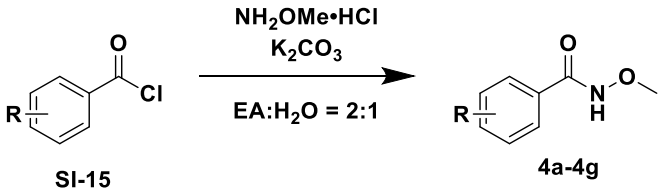


(Z)*-6,6-difluoro-*N*-methoxy-2-propylhexa-2,5-dienamide (3w):** column solvent: DCM/MeOH = 20/1, yellow oil (26 mg, yield 59%); ***^{1}H NMR (600 MHz, Chloroform-d) δ 8.51 (s, 1H), 5.46 (t, J = 7.6 Hz, 1H), 4.19 (dtd, J = 25.2, 7.8, 2.1 Hz, 1H), 3.81 (s, 3H), 2.84 (t, J = 7.5 Hz, 2H), 2.17 (t, J = 7.6 Hz, 2H), 1.53 – 1.36 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H). ***^{13}C NMR (151 MHz, Chloroform-d)*** δ 167.49, 158.46, 156.56, 154.65, 135.49, 130.03, 76.72, 76.57, 76.43, 64.64, 50.89, 36.70, 22.65 (d, J = 4.7 Hz), 21.36, 13.67. ***^{19}F NMR (565 MHz, Chloroform-d)*** δ -88.23 (d, J = 45.0 Hz), -90.16 (dd, J = 45.4, 25.2 Hz). **HRMS (ESI-MS)** ***m/z:*** $[M+H]^+$ Calcd for $C_{10}H_{16}F_2NO_2$: 220.1143; Found: 220.1145.



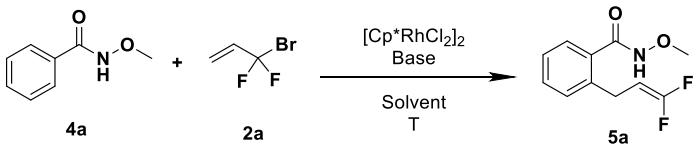
(*Z*)-N-methoxy-2-phenylhexa-2,5-dienamide (3x): column solvent: DCM/MeOH = 20/1, yellow soild (18 mg, yield 42%); ***^{1}H NMR (600 MHz, Chloroform-d)*** δ 8.41 (d, *J* = 21.9 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.35 – 7.27 (m, 3H), 6.13 (t, *J* = 7.6 Hz, 1H), 5.96 – 5.84 (m, 1H), 5.16 – 5.05 (m, 2H), 3.83 (s, 3H), 3.13 (t, *J* = 7.1 Hz, 2H). ***^{13}C NMR (151 MHz, Chloroform-d)*** δ 166.39, 136.61, 135.73, 132.96, 128.86, 128.32, 126.51, 126.14, 116.33, 64.69, 34.05. **HRMS (ESI-MS)** ***m/z:*** $[M+H]^+$ Calcd for $C_{13}H_{16}NO_2$: 218.1176; Found: 218.1178.

General procedure for the preparation of 4[5-6]:



The crude **SI-15** in EtOAc (5.0 mL) was added to a solution of methoxyamine hydrochloride (2.0 equiv.) and K_2CO_3, (2.0 equiv.) in EtOAc/H_2O = 2/1 (9.0 mL) over 5.0 min at 0°C. The solution was stirred at room temperature for 1.0 h. Then the solution was extracted with EtOAc (40.0 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4, and evaporated to afford the residue. The residue was subject to column chromatography on silica gel (DCM/MeOH = 20/1) to afford the corresponding **4a-4g**.

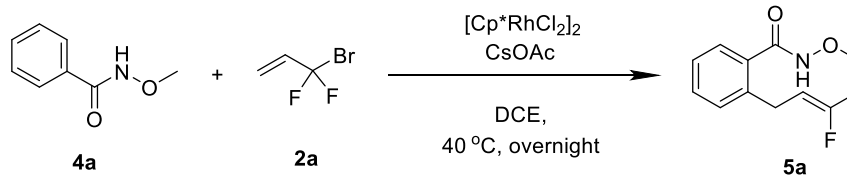
Table S1. Optimization of reaction conditions



Entry	Catalyst	Base	Solvent	T(°C)	Time (h)	Yield
1	$[Cp^*RhCl_2]_2$	KOAc	EtOH	40	12	44%
2	$[Cp^*RhCl_2]_2$	KOAc	DCE	40	12	53%
3	$[Cp^*RhCl_2]_2$	KOAc	Dioxane	40	12	NR
4	$[Cp^*RhCl_2]_2$	KOAc	TFE	40	12	NR
5	$[Cp^*RhCl_2]_2$	KOAc	DCE	60	12	trace
6	$[Cp^*RhCl_2]_2$	NaOAc	DCE	40	12	NR
7	**$[Cp^*RhCl_2]_2$**	**CsOAC**	**DCE**	**40**	**12**	**57%**
8	$[Cp^*RhCl_2]_2$	K_2CO_3	DCE	40	12	NR

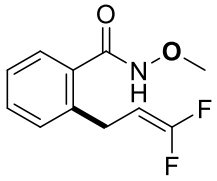
Reaction conditions: **4a** (0.2 mmol), **2a** (0.3 mmol), catalyst (3 mol%), base (0.2 mmol), under air, solvent (2.0 mL), 12 h. Isolated yields were reported. NR = no reaction.

General Procedure for the Synthesis of 5:

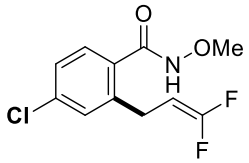


In a 10 mL reaction tube, to the mixture of **4a** (30.0 mg, 0.20 mmol, 1.0 eq), **2a** (47 mg, 0.3 mmol, 1.5 eq), $[Cp^*RhCl_2]_2$ (3.8 mg, 3.0 mol%) and CsOAc (38 mg, 0.1 mmol, 1 eq) was added DCE (2.0 mL). Then the resulting mixture was stirred at 40 ℃ for 12.0 h. When the reaction was finished, the products are purified by preparative thin layer chromatography (DCM/MeOH = 20/1). The product **5a** was obtained as a yellow solid (26 mg, 57% yield). Other products **5** were prepared by a similar procedure.

Characterization Data of Products 5

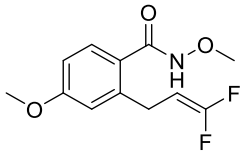


2-(3,3-difluoroallyl)-N-methoxybenzamide (5a): column solvent: DCM/MeOH = 20/1, yellow solid (26 mg, yield 57%); ***^{1}H NMR (500 MHz, Chloroform-d)*** δ 8.54 (s, 1H), 7.44 – 7.37 (m, 1H), 7.33 (d, J = 6.8 Hz, 1H), 7.29 (d, J = 7.7 Hz, 1H), 7.24 (d, J = 7.4 Hz, 1H), 4.45 (dtd, J = 25.0, 8.0, 2.2 Hz, 1H), 3.88 (s, 3H), 3.48 (d, J = 8.0 Hz, 2H). ***^{13}C NMR (151 MHz, Chloroform-d)*** δ 167.67, 158.56, 156.66, 154.75, 139.01, 132.27, 131.28, 130.23, 127.40, 126.73, 77.89, 77.74 (d, J = 4.3 Hz), 77.60, 64.80, 26.15, 26.12. ***^{19}F NMR (471 MHz, Chloroform-d)*** δ -88.42 (d, J = 44.9 Hz), -90.81 (d, J = 43.4 Hz). ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{11}H_{12}F_2NO_2$: 228.0831; Found: 228.0833.

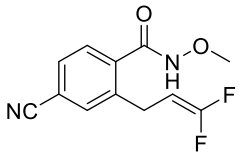


4-chloro-2-(3,3-difluoroallyl)-N-methoxybenzamide (5b): column solvent: DCM/MeOH = 20/1, white solid (15 mg, yield 29%); ***^{1}H NMR (600 MHz, Chloroform-d)*** δ 8.55 (s, 1H), 7.28 (t, J = 4.2

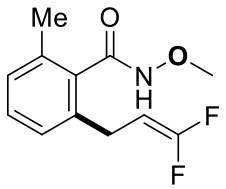
Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 1H), 4.43 (dtd, *J* = 24.7, 8.0, 2.0 Hz, 1H), 3.87 (s, 3H), 3.46 (d, *J* = 8.0 Hz, 2H). ***[13]C NMR (151 MHz, Chloroform-d)*** δ 166.78, 158.74, 156.84, 154.93, 141.13, 137.29, 130.61, 130.30, 128.76, 126.90, 77.08, 77.05, 64.84, 25.99 (d, *J* = 5.0 Hz). ***[19]F NMR (565 MHz, Chloroform-d)*** δ -87.46 (d, *J* = 44.8 Hz), -89.97 (dd, *J* = 42.3, 24.8 Hz). ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{11}H_{11}ClF_2NO_2$: 262.0441, 264.0411; Found: 262.0444, 264.0411.



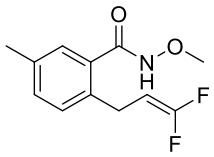
2-(3,3-difluoroallyl)-N,4-dimethoxybenzamide (5c): column solvent: DCM/MeOH = 20/1, yellow solid (12 mg, yield 23%); ***1H NMR (600 MHz, Chloroform-d)*** δ 8.45 (s, 1H), 7.31 (d, J = 8.4 Hz, 1H), 6.80 (s, 1H), 6.73 (dd, J = 8.5, 2.6 Hz, 1H), 4.46 (dtd, J = 25.1, 8.0, 1.9 Hz, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 3.48 (d, J = 5.8 Hz, 2H). ***[13]C NMR (151 MHz, Chloroform-d)*** δ 161.77, 158.62, 156.71, 154.81, 141.57, 129.19, 124.40, 116.15, 111.43, 77.84, 77.70 (d, J = 4.5 Hz), 77.55, 64.75, 55.49, 26.42 (d, J = 5.4 Hz). ***[19]F NMR (565 MHz, Chloroform-d)*** δ -88.35 (d, J = 42.1 Hz), -90.81 (dd, J = 44.7, 24.5 Hz). ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{12}H_{14}F_2NO_3$: 258.0936; Found: 258.0939.



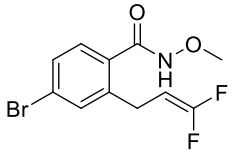
4-cyano-2-(3,3-difluoroallyl)-*N*-methoxybenzamide (5d): column solvent: DCM/MeOH = 20/1, yellow solid (14 mg, yield 28%); ***[1]H NMR (500 MHz, Chloroform-d)*** δ 8.86 (s, 1H), 7.55 (d, J = 16.3 Hz, 2H), 7.45 (d, J = 7.9 Hz, 1H), 4.42 (dtd, J = 24.6, 8.0, 1.9 Hz, 1H), 3.88 (s, 3H), 3.49 (d, J = 7.9 Hz, 2H). ***[13]C NMR (126 MHz, Chloroform-d)*** δ 165.75, 159.29, 156.99, 154.69, 140.50, 136.54, 133.46, 130.45, 128.22, 117.84, 114.98, 76.68, 76.51 (d, *J* = 5.6 Hz), 76.33, 64.90, 25.88 (d, *J* = 5.5 Hz). ***[19]F NMR (565 MHz, Chloroform-d)*** δ -86.56 (d, *J* = 40.7 Hz), -89.12 (dd, *J* = 40.6, 24.4 Hz). ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{12}H_{11}F_2N_2O_2$: 253.0783; Found: 253.0786.



2-(3,3-difluoroallyl)-N-methoxy-6-methylbenzamide (5e): column solvent: DCM/MeOH = 20/1, white solid (35 mg, yield 73%); ***[1]H NMR (600 MHz, Chloroform-d)*** δ 8.54 (s, 1H), 7.24 (t, J = 7.6 Hz, 1H), 7.06 (d, J = 7.7 Hz, 2H), 4.38 (dtd, J = 24.8, 8.0, 2.1 Hz, 1H), 3.89 (s, 3H), 3.31 (d, J = 8.0 Hz, 2H), 2.32 (s, 3H). ***[13]C NMR (151 MHz, Chloroform-d)*** δ 167.22, 158.46, 156.56, 154.65, 137.23 (t, J = 2.4 Hz), 135.73, 133.04, 130.14, 128.62, 126.45, 77.75, 77.60 (d, J = 4.1 Hz), 77.46, 64.65, 25.92 (d, J = 4.8 Hz), 19.15. ***[19]F NMR (565 MHz, Chloroform-d)*** δ -88.19 (d, J = 43.6 Hz), -90.75 (dd, J = 43.8, 24.6 Hz). ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{12}H_{14}F_2NO_2$: 242.0987; Found: 242.0988.



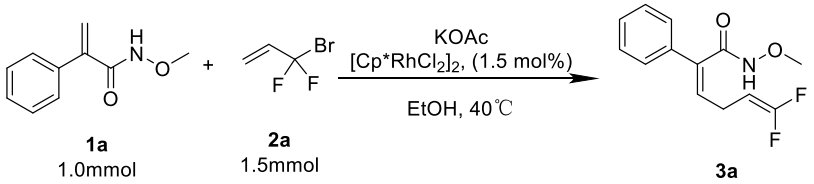
2-(3,3-difluoroallyl)-N-methoxy-5-methylbenzamide (5f): column solvent: DCM/MeOH = 20/1, white solid (34 mg, yield 70%); ***[1]H NMR (600 MHz, Chloroform-d)*** δ 8.43 (s, 1H), 7.21 (d, J = 6.2 Hz, 1H), 7.17 (d, J = 7.9 Hz, 1H), 7.15 (s, 1H), 4.43 (dtd, J = 25.2, 8.0, 2.2 Hz, 1H), 3.89 (s, 3H), 3.43 (d, J = 7.9 Hz, 2H), 2.32 (s, 3H). ***[13]C NMR (151 MHz, Chloroform-d)*** δ 167.83, 158.50, 156.60, 154.70, 136.54, 135.91, 131.93, 130.18, 127.99, 78.09, 77.95 (d, J = 4.3 Hz), 77.80, 64.81, 25.74 (d, J = 4.7 Hz), 20.93. ***[19]F NMR (471 MHz, Chloroform-d)*** δ -88.65 (d, J = 43.2 Hz), -91.02 (d, J = 44.8 Hz). ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{12}H_{14}F_2NO_2$: 242.0987; Found: 242.0989.



4-bromo-2-(3,3-difluoroallyl)-N-methoxybenzamide (5g): column solvent: DCM/MeOH = 20/1, white solid (14 mg, yield 23%); ***[1]H NMR (500 MHz, Chloroform-d)*** δ 8.54 (s, 1H), 7.44 (s, 1H), 7.39 (d, J = 8.2 Hz, 1H), 7.21 (d, J = 8.1 Hz, 1H), 4.43 (dt, J = 24.8, 8.0 Hz, 1H), 3.87 (s, 3H), 3.45 (d, J = 8.0 Hz, 2H). ***[13]C NMR (126 MHz, Chloroform-d)*** δ 157.96 (d, J = 288.9 Hz), 154.53, 141.25,

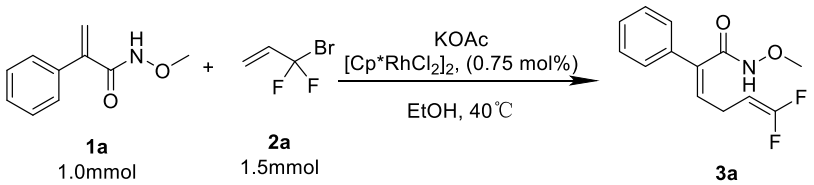
133.24, 131.08, 129.90, 128.87, 125.65, 77.26, 77.07, 64.88, 25.97 (d, J = 5.1 Hz). ***^{19}F NMR (565 MHz, Chloroform-d)*** δ -86.56 (d, J = 40.7 Hz), -89.12 (dd, J = 40.6, 24.4 Hz). ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{11}H_{11}BrF_2NO_2$: 305.9936, 307.9915; Found: 305.9935, 307.9915.

Gram-Scale Experiments



1a 1.0mmol　　**2a** 1.5mmol　　**3a**

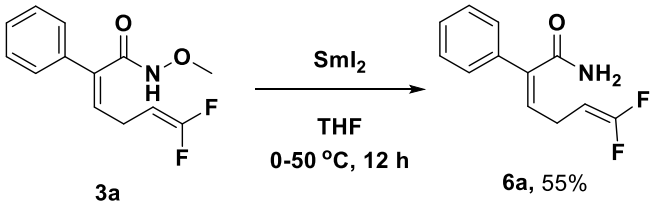
In a 100 mL reaction tube, the mixture of **1a** (177.1 mg, 1.0 mmol, 1.0 eq.), **2a** (235.4 mg, 1.5 mmol, 1.5 eq.), $[Cp^*RhCl_2]_2$ (1.5 mol%) and KOAc (1.0 eq.) was added EtOH (5.0 mL). Then the resulting mixture was stirred at 40 ℃ for 4.0 h. When the reaction was finished, the products are separated by thin layer chromatography plates (DCM/MeOH = 20/1). The product **3a** was obtained as a yellow oil (199 mg, 79% yield).



1a 1.0mmol　　**2a** 1.5mmol　　**3a**

In a 100 mL reaction tube, the mixture of **1a** (177.1 mg, 1.0 mmol, 1.0 eq.), **2a** (235.4 mg, 1.5 mmol, 1.5 eq.), $[Cp^*RhCl_2]_2$ (0.75 mol%) and KOAc (1.0 eq.) was added EtOH (5.0 mL). Then the resulting mixture was stirred at 40 ℃ for 4.0 h. When the reaction was finished, the products are separated by thin layer chromatography plates (DCM/MeOH = 20/1). The product **3a** was obtained as a yellow oil (176 mg, 70% yield).

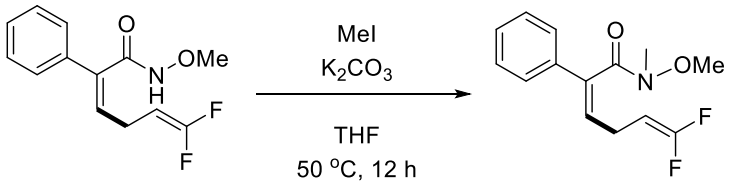
Transformation of products



3a　　**6a,** 55%

In a 10 mL reaction tube, a solution of SmI_2 (4.0 mL, 0.1 M in THF) was added dropwise to a solution of **3a** (23.5 mg, 0.1 mmol, 1.0 equiv.) in dry THF (2.0 mL) at 0 °C for 30 mins, then the mixture was warmed up to 50℃ and stirred for 12 h. And then saturated sodium carbonate solution (5.0 mL) was dropped to quench the reaction, and extracted with EtOAc (10.0 ml x 2) and the combined organic layers were washed with brine, then the combined organic layer was dried ($MgSO_4$) and concentrated. The products are separated by thin layer chromatography plates

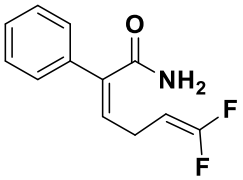
(DCM/MeOH = 20/1), the product **6a** was obtained as a white solid (12 mg, 55% yield). The product **6a** was directly used for ^{1}H-NMR analysis.



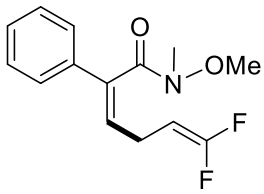
3a **6b**, 34%

To a solution of **3a** (0.2 mmol) in THF (2.0 mL) was added K_2CO_3 (2.0 equiv.) and MeI(3.0 equiv.), then the mixture was warmed up to 50℃ and stirred for 12 h. When the reaction was finished, THF was removed under vacuum, the residue was extracted with EtOAc (10.0 ml x 2) and the combined organic layers were washed with brine, then the combined organic layer was dried ($MgSO_4$) and concentrated. The products are separated by thin layer chromatography plates (DCM/MeOH = 40/1), the product **6b** was obtained as a white solid (18 mg, 34% yield). The product **6b** was directly used for ^{1}H-NMR analysis.

Characterization Data of Products 6



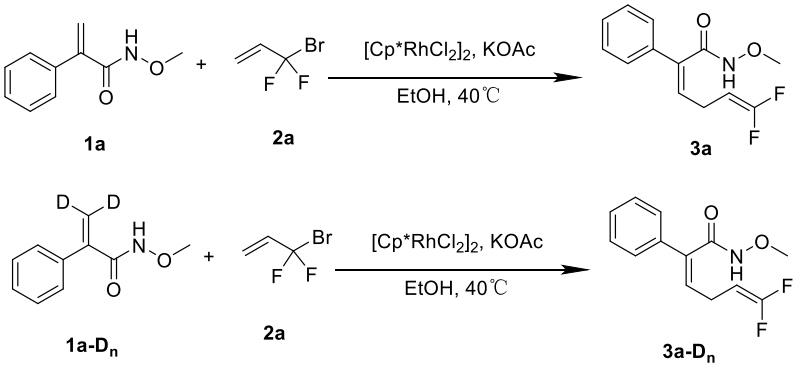
(*Z*)-6,6-difluoro-2-phenylhexa-2,5-dienamide (6a)： column solvent: DCM/MeOH = 20:1, white solid (12 mg, yield 55%); ***^{1}H NMR (600 MHz, DMSO-d_6)*** δ 7.69 (s, 1H), 7.49 (s, 1H), 7.43 – 7.38 (m, 2H), 7.38 – 7.32 (m, 2H), 7.31 – 7.25 (m, 1H), 5.93 (t, J = 7.5 Hz, 1H), 4.62 (dtd, J = 26.6, 7.7, 2.5 Hz, 1H), 2.90 (tt, J = 7.7, 1.8 Hz, 2H). ***^{13}C NMR (151 MHz, DMSO-d_6)*** δ 169.81, 157.28, 155.39 (d, J = 3.4 Hz), 153.50, 139.63, 136.59, 128.49, 127.62, 125.73, 124.84 (d, J = 2.5 Hz), 77.40, 77.26 (d, J = 3.6 Hz), 77.13, 22.61 (d, J = 4.9 Hz). ***^{19}F NMR (565 MHz, DMSO-d_6)*** δ -89.28 (d, J = 47.5 Hz), -91.07 (dd, J = 47.9, 26.5 Hz). ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{12}H_{12}F_2NO$: 224.0881; Found: 224.0883.



(*Z*)-6,6-difluoro-N-methoxy-N-methyl-2-phenylhexa-2,5-dienamide(6b): column solvent: DCM/MeOH = 40:1, white solid (18 mg, yield 34%); ***^{1}H NMR (500 MHz, Chloroform-d)*** δ 7.42 – 7.31 (m, 5H), 5.93 (t, J = 7.6 Hz, 1H), 4.29 (dtd, J = 25.1, 7.8, 2.1 Hz, 1H), 3.35 (s, 3H), 3.30 (s, 3H), 2.90 (t, J = 7.8 Hz, 2H). ***^{13}C NMR (151 MHz, Chloroform-d)*** δ 170.13, 158.43, 156.53, 154.62, 138.20, 136.58, 128.99, 128.65, 127.90, 127.12, 125.71, 76.40, 76.26, 76.12, 61.37, 32.14, 23.24 (d, J = 5.1 Hz). ***^{19}F NMR (471 MHz, Chloroform-d)*** δ -88.17 (d, J = 45.1 Hz), -90.25 (d, J = 43.1 Hz). ***HRMS (ESI-MS) m/z:*** $[M+H]^+$ Calcd for $C_{14}H_{16}F_2NO_2$: 268.1144; Found: 268.1145.

KIE Study

Two parallel reactions for KIE value measurement



To a mixture of **1a** (17.7 mg, 0.1 mmol, 1.0 eq.), **2a** (15.7 mg, 0.15 mmol, 1.5 eq.), $[Cp^*RhCl_2]_2$ (1.9 mg, 0.003 mmol, 3 mol%) and KOAc (14.7 mg, 0.15 mmol, 1.5 eq.), in a 10 mL reaction tube was added EtOH (2.0 mL). Then the resulting mixture was stirred at the temperature for 1.0 h. The reaction was finished to provide the product **3a** (18.0 mg, 72% yield).

To a mixture of **1a-D** (17.9 mg, 0.1 mmol, 1.0 eq.), **2a** (15.7 mg, 0.15 mmol, 1.5 eq.), $[Cp^*RhCl_2]_2$ (1.9 mg, 0.003 mmol, 3 mol%) and KOAc (14.7 mg, 0.15 mmol, 1.5 eq.), in a 10 mL reaction tube was added EtOH (2.0 mL). Then the resulting mixture was stirred at the temperature for 1.0 h. The reaction was finished to provide the product **3a-D$_n$** (12.0 mg, 48% yield). The ratio of **3a**/**3a-D$_n$** was 1.5 (18/12)

References

[1] Liu, Y.; Xie, F.; Jia, A.-Q.; Li, X. Cp*Co(iii)-catalyzed amidation of olefinic and aryl C–H bonds: highly selective synthesis of enamides and pyrimidones. *Chem. Commun.* **2018**, *54*, 4345-4348.

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[3] Li, W.; Zhou, H.; He, Y.; Zeng, G.; Zheng, Y.; Hu, Y.; Chen, Z.; Ge, J.-Y.; Lv, N.; Chen, J. Synthesis of Diverse γ-Lactams via Rh-Catalyzed C(sp^2)–H Addition to Aliphatic Nitriles. *Org. Lett.* **2022**, *24*, 5090-5094.

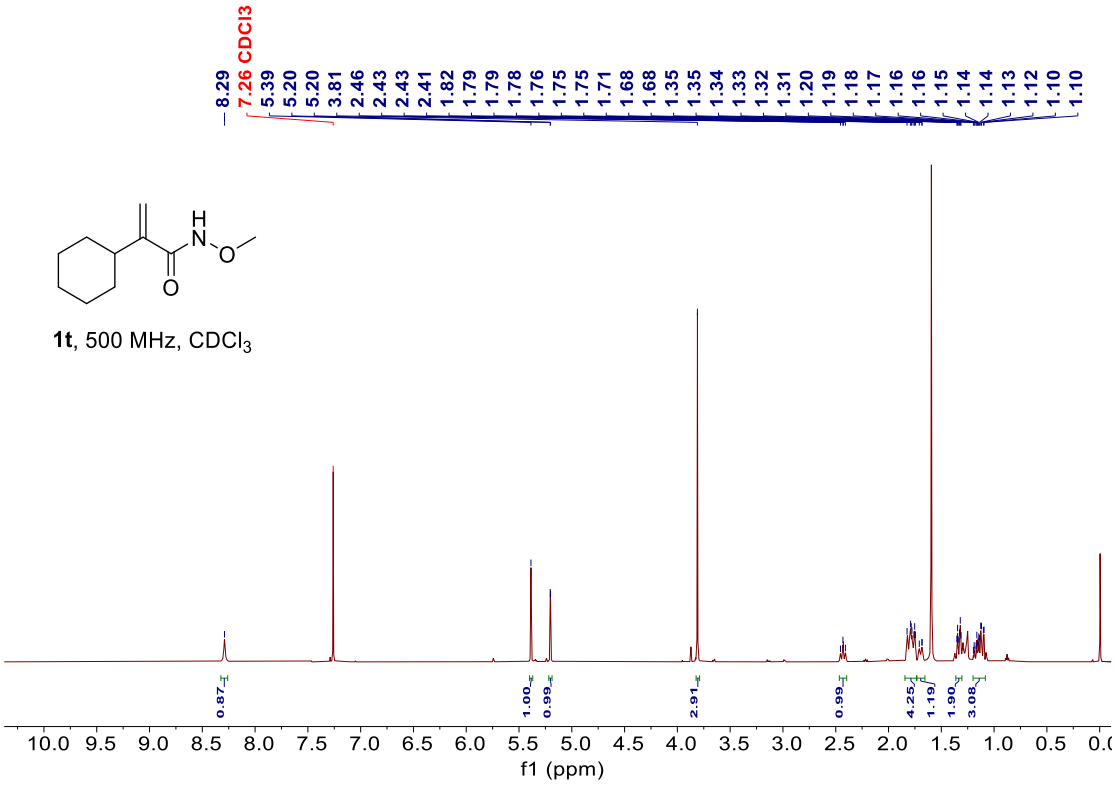
[4] Yu, C.; Li, F.; Zhang, J.; Zhong, G. A direct cross-coupling reaction of electron-deficient alkenes using an oxidizing directing group. *Chem. Commun.*, **2017**, *53*, 533-536.

[5] Li, X.; Cheng, H.; Shao, J.; Zhang, G.; Zhang, S. Rh(III)-Catalyzed [4+1] Annulation of Benzamides with Vinyl Cyclic Carbonates for the Synthesis of Isoindolinones. *Org. Lett.* **2024**, *26,* 1304-1309.

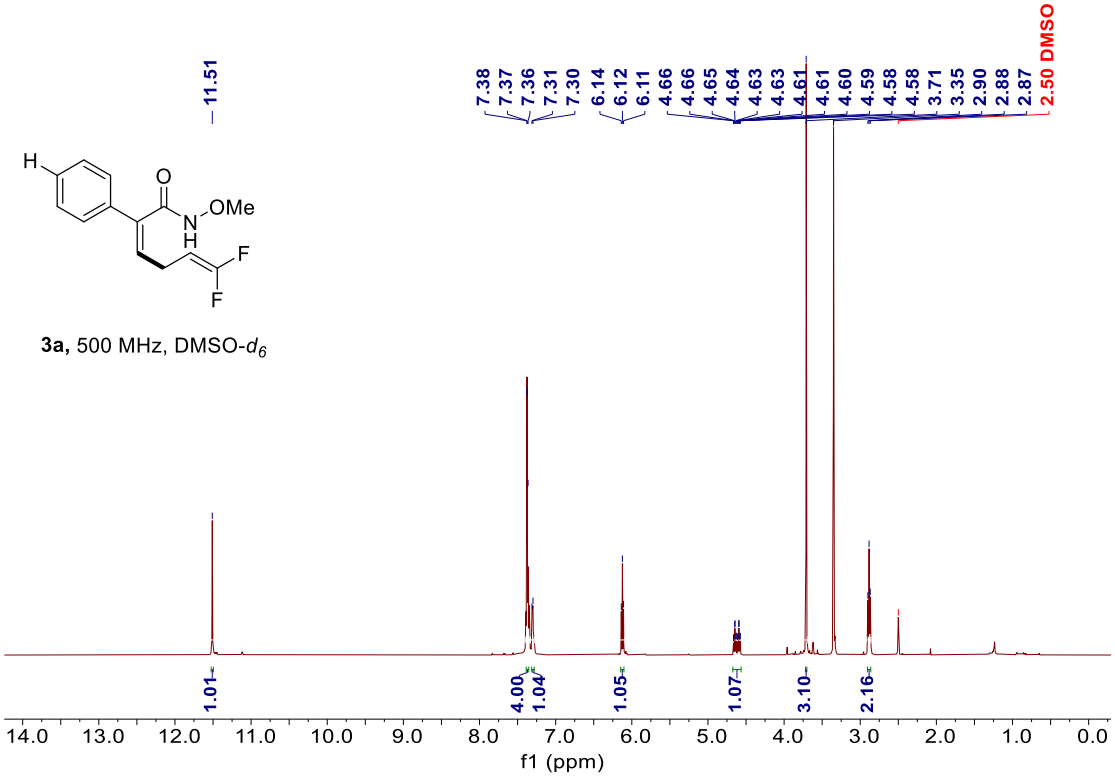
[6] Lei, J.; Li, M.; Zhang, Q.; Liu, S.; Li, H.; Shi, L.; Jiang, W.-F.; Duan, C.; Jin, Y. Visible light-induced radical cascade cross-coupling via C(sp3)–H activation and C–N/N–O cleavage: a feasible access to methylenebisamide derivatives. *Org. Lett.* **2023**, *25,* 2300-2305.

Copies of ^{1}H, ^{13}C NMR and ^{19}F NMR spectra

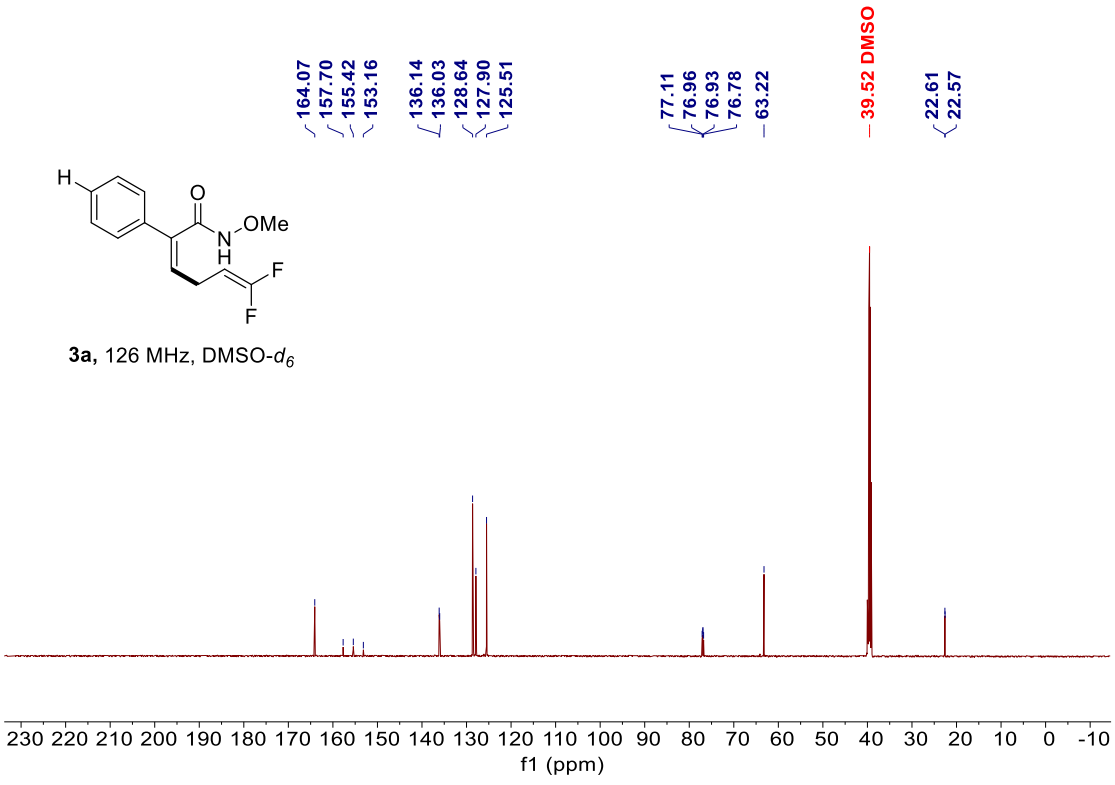
2-cyclohexyl-*N*-methoxyacrylamide(1t)



(*Z*)-6,6-difluoro-*N*-methoxy-2-phenylhexa-2,5-dienamide (3a)

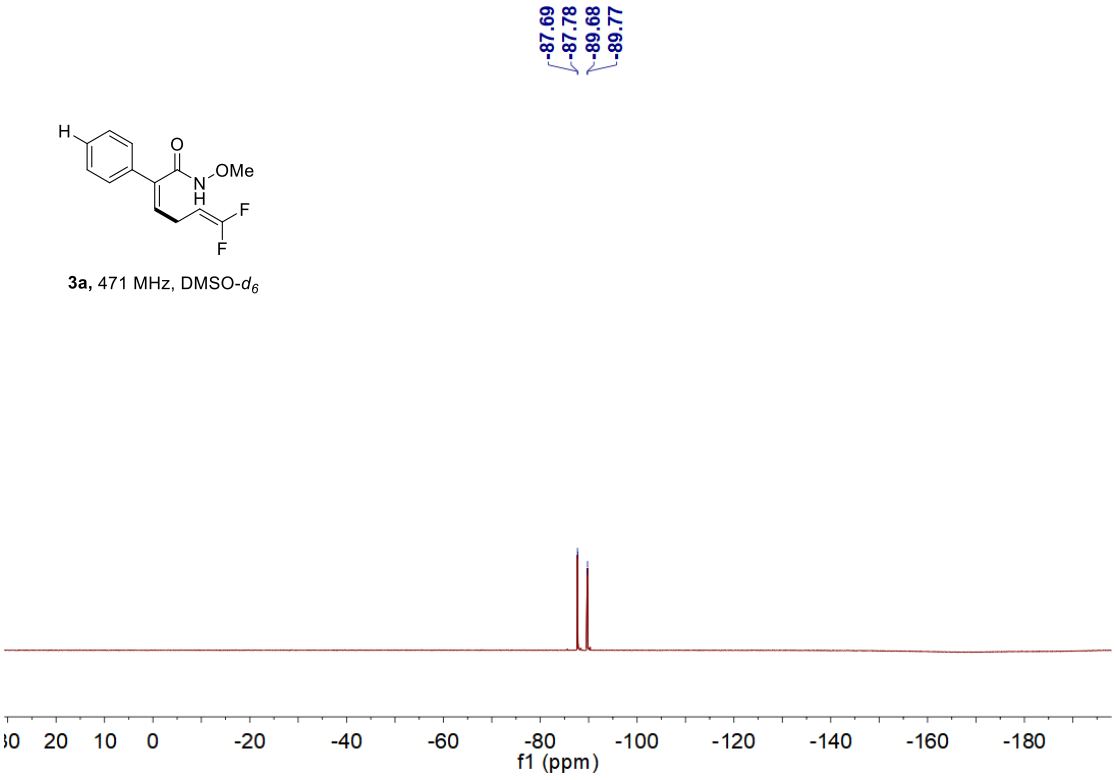


3a, 500 MHz, DMSO-d_6



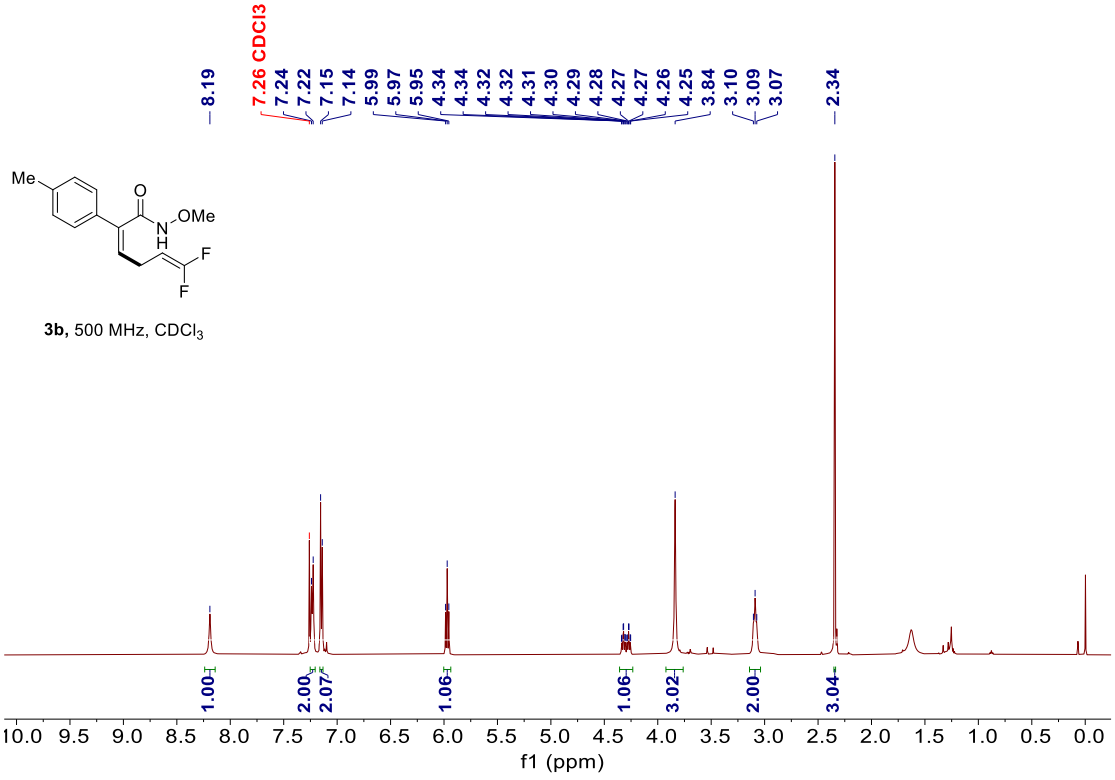
3a, 126 MHz, DMSO-d_6

^{19}F NMR spectrum for product 3a

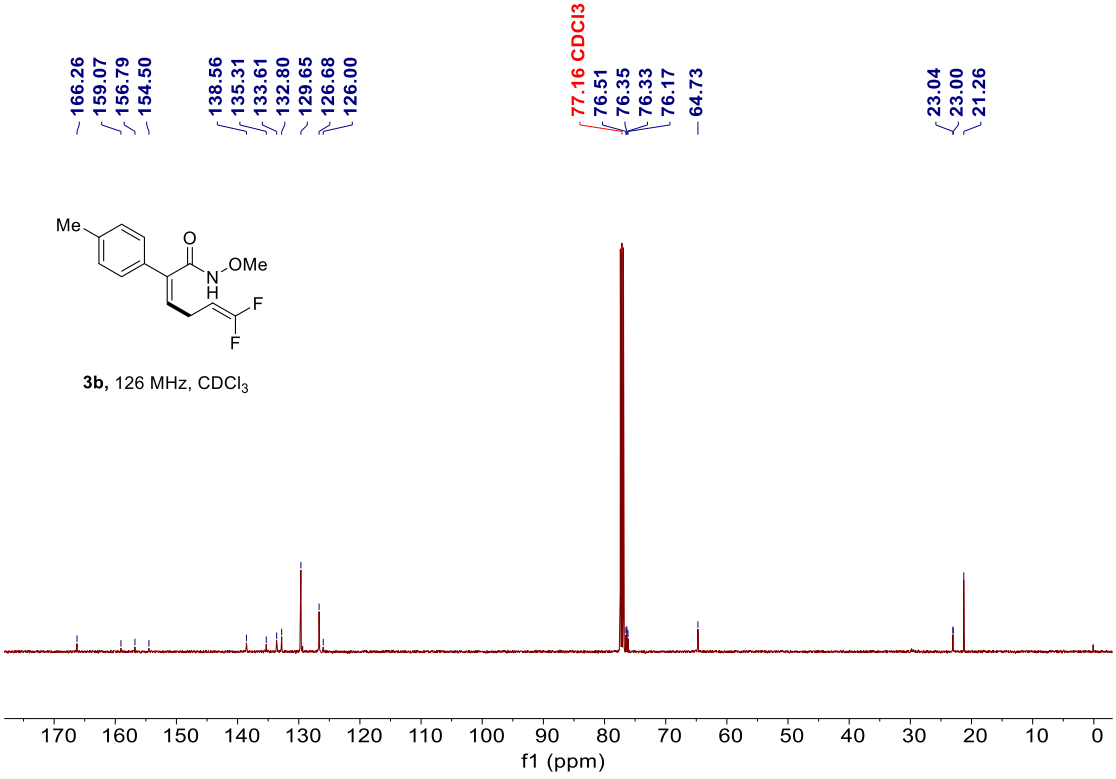


3a, 471 MHz, DMSO-d_6

(*Z*)-6,6-difluoro-*N*-methoxy-2-(p-tolyl)hexa-2,5-dienamide (3b)

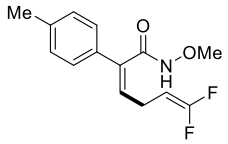


3b, 500 MHz, $CDCl_3$



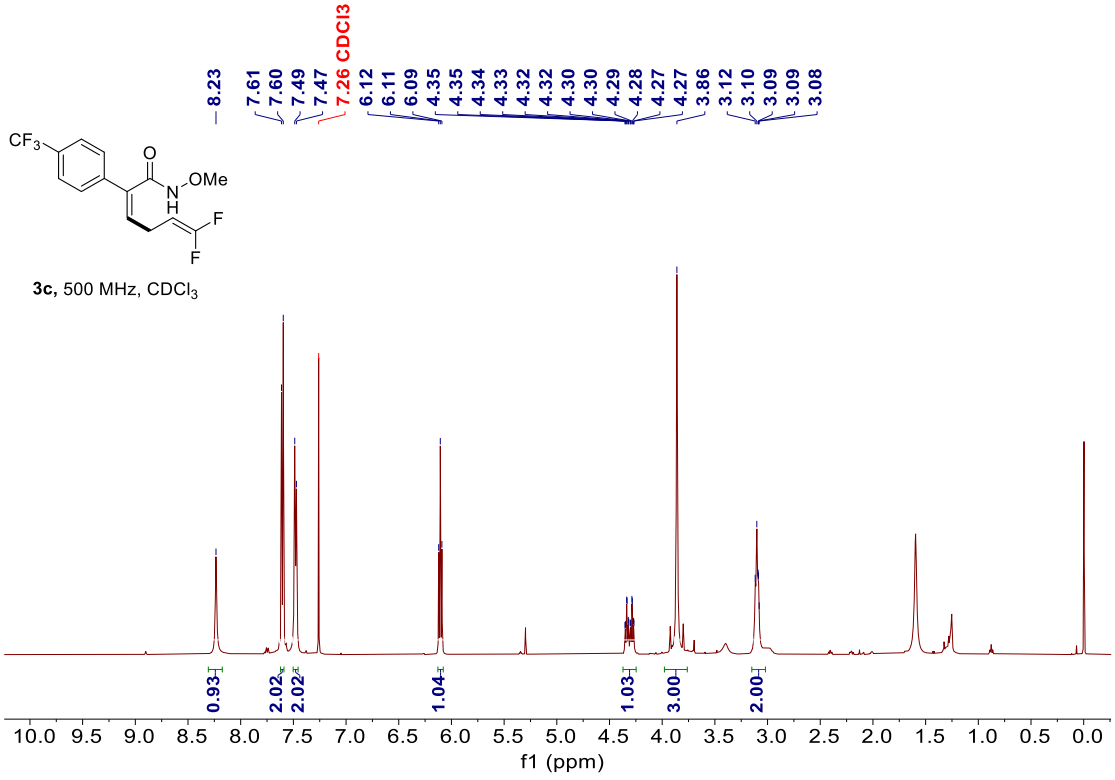
3b, 126 MHz, $CDCl_3$

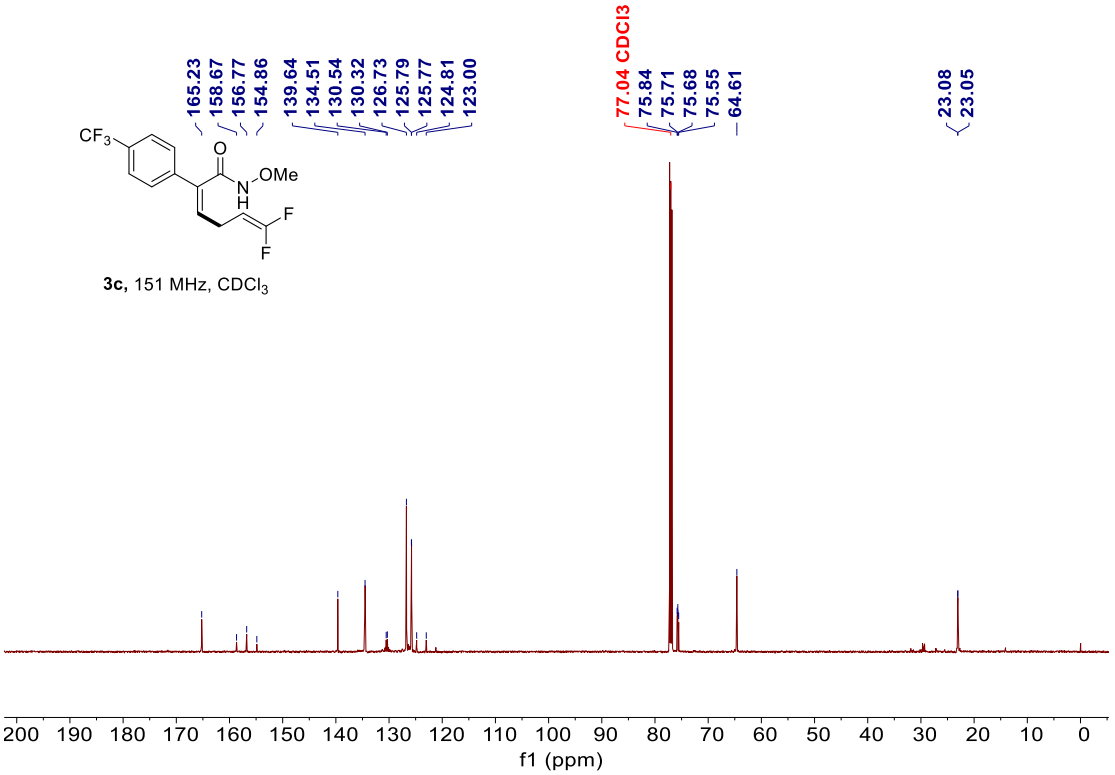
^{19}F NMR spectrum for product 3b



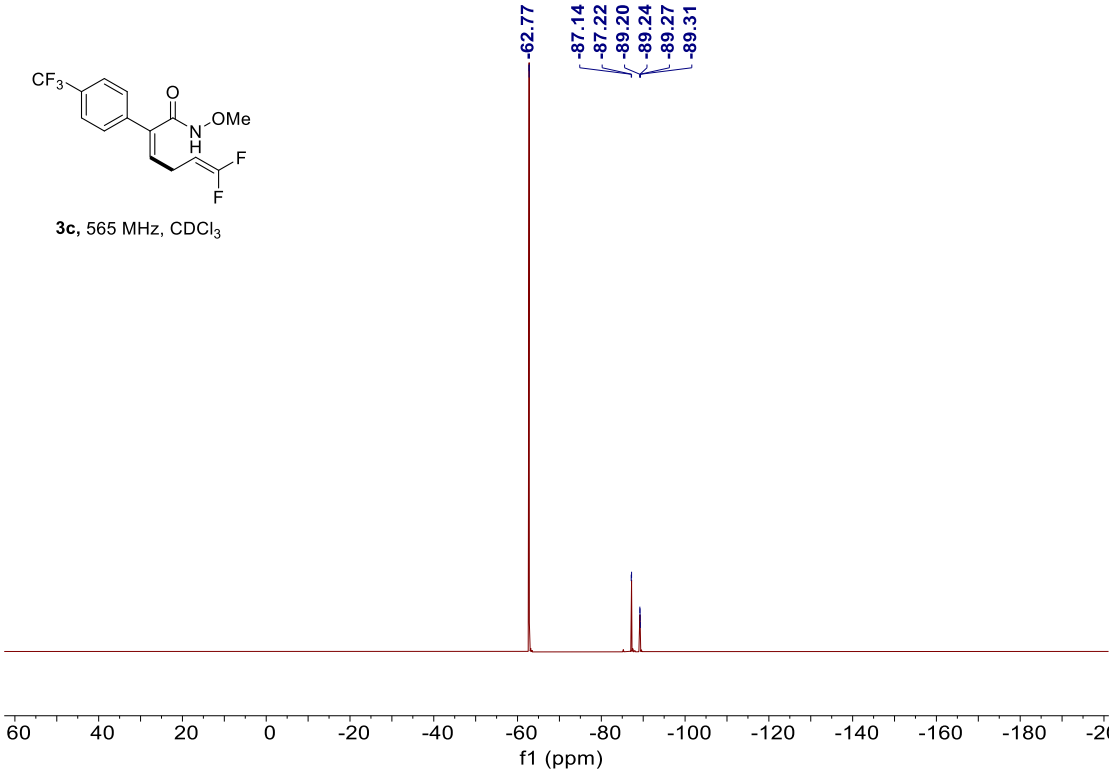
3b, 471 MHz, $CDCl_3$

(*Z*)-6,6-difluoro-*N*-methoxy-2-(4-(trifluoromethyl)phenyl)hexa-2,5-dienamide (3c)

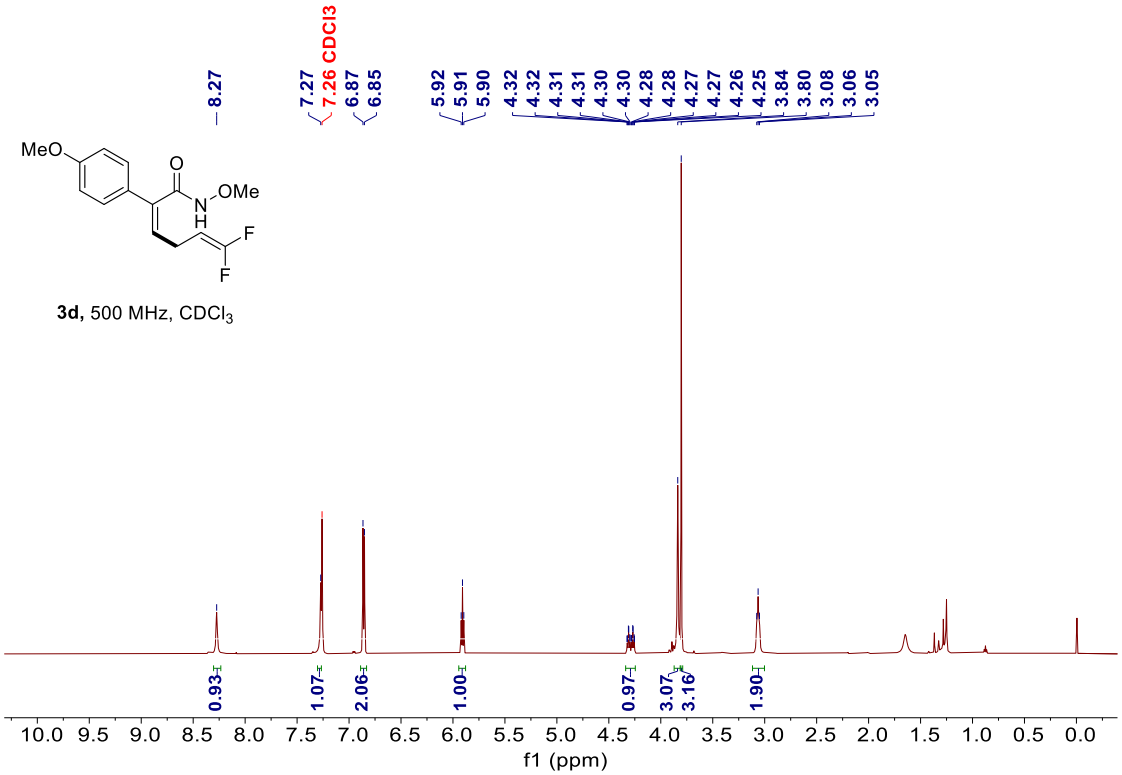




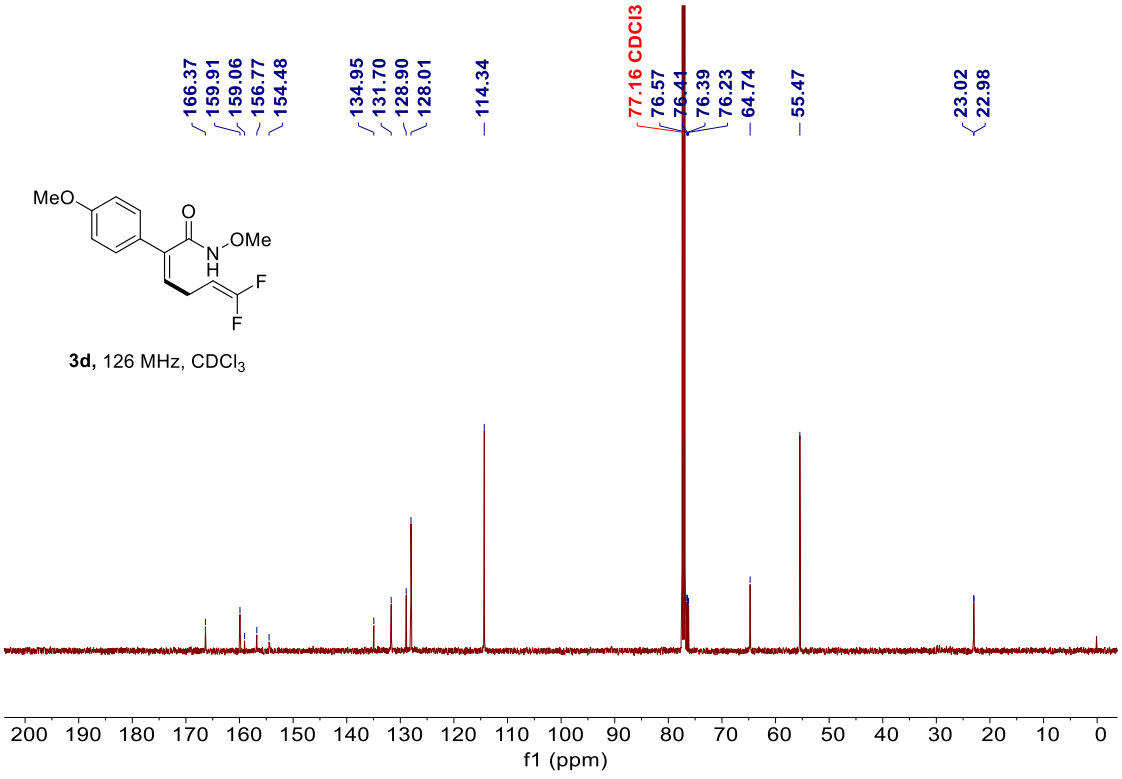
^{19}F NMR spectrum for product 3c



(*Z*)-6,6-difluoro-*N*-methoxy-2-(4-methoxyphenyl)hexa-2,5-dienamide (3d)

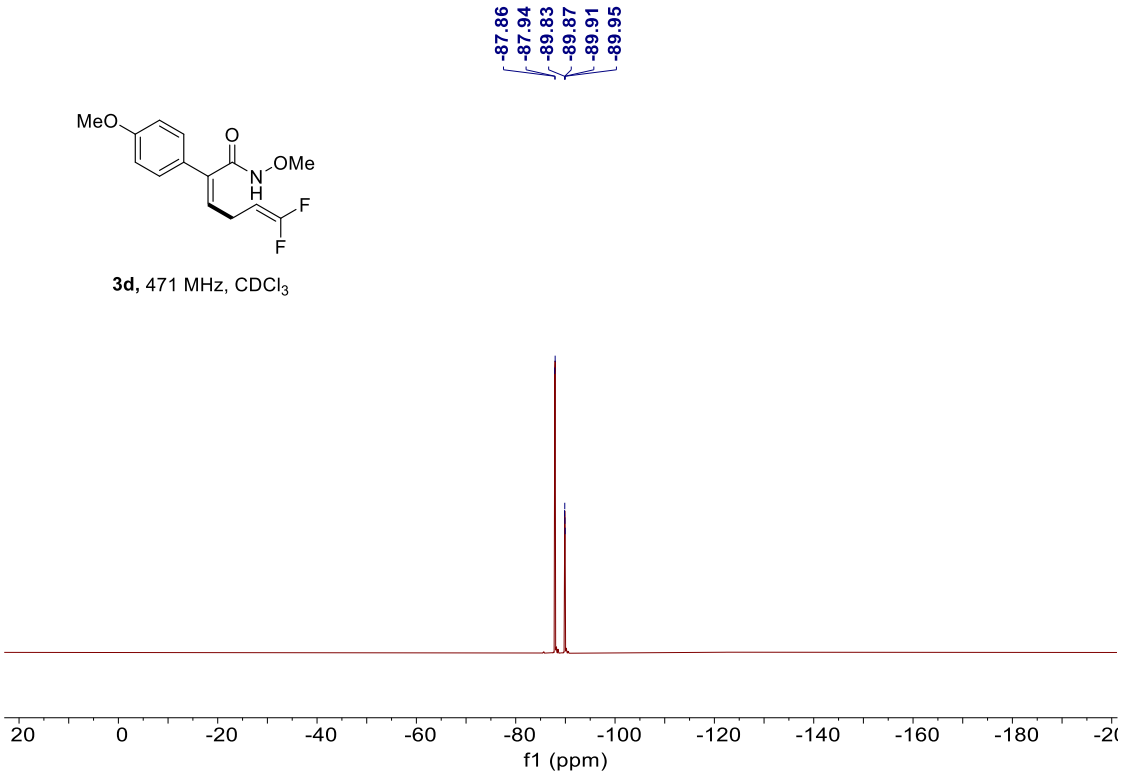


3d, 500 MHz, $CDCl_3$



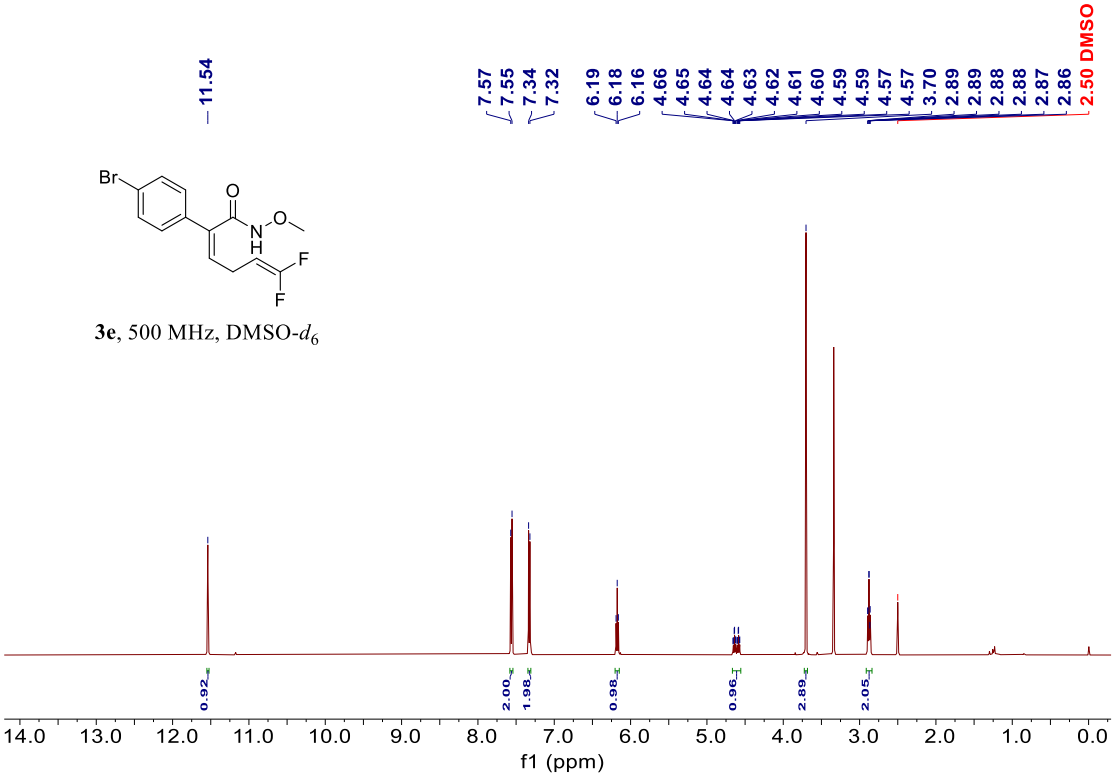
3d, 126 MHz, $CDCl_3$

^{19}F NMR spectrum for product 3d

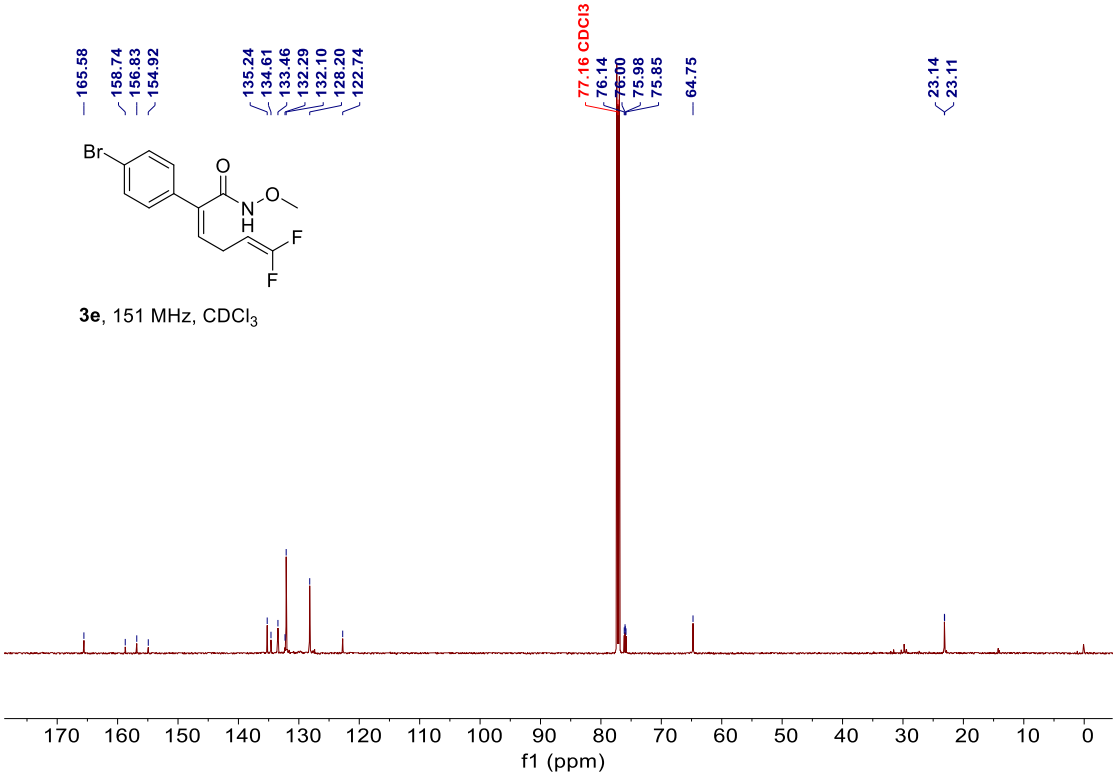


3d, 471 MHz, $CDCl_3$

(*Z*)-2-(4-bromophenyl)-6,6-difluoro-*N*-methoxyhexa-2,5-dienamide (3e)

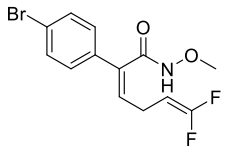


3e, 500 MHz, DMSO-d_6



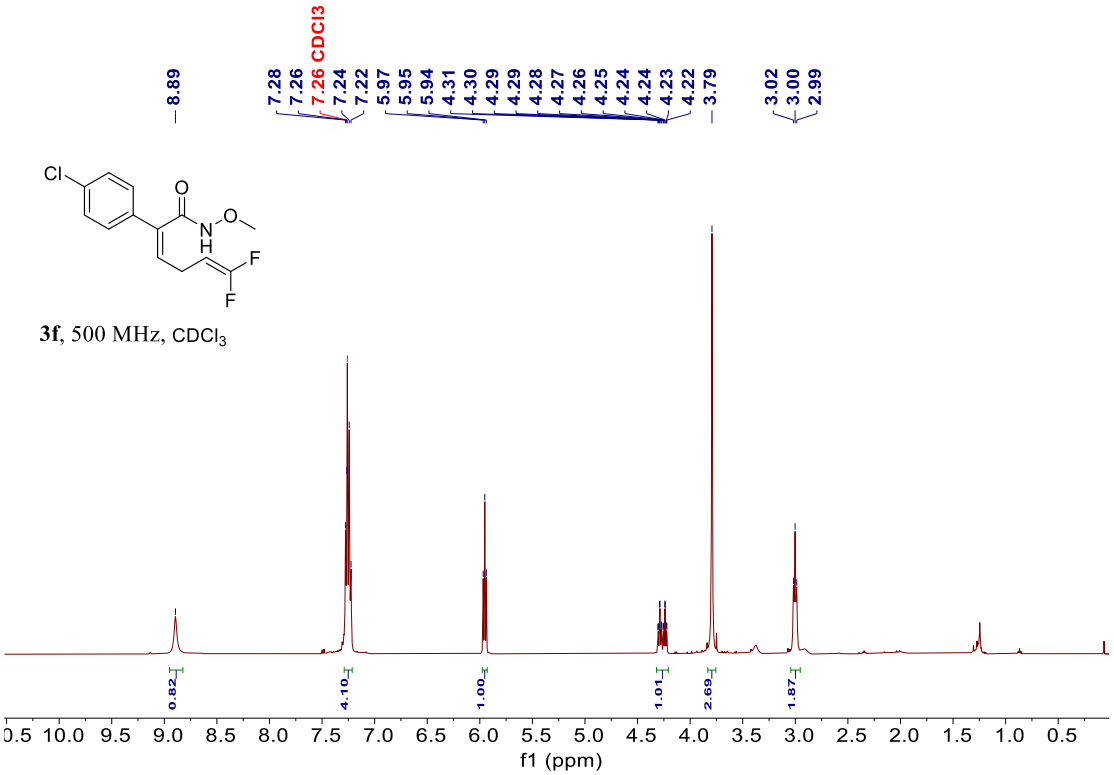
3e, 151 MHz, $CDCl_3$

^{19}F NMR spectrum for product 3e

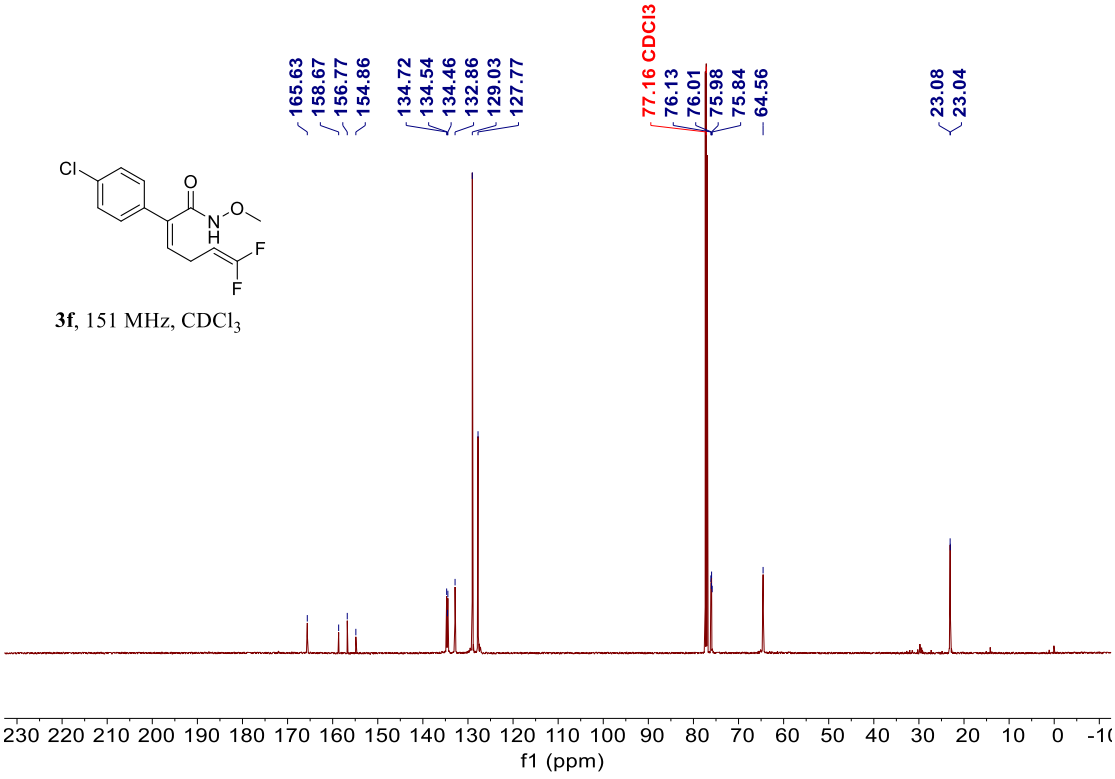


3e, 471 MHz, $CDCl_3$

(*Z*)-2-(4-chlorophenyl)-6,6-difluoro-*N*-methoxyhexa-2,5-dienamide (3f)

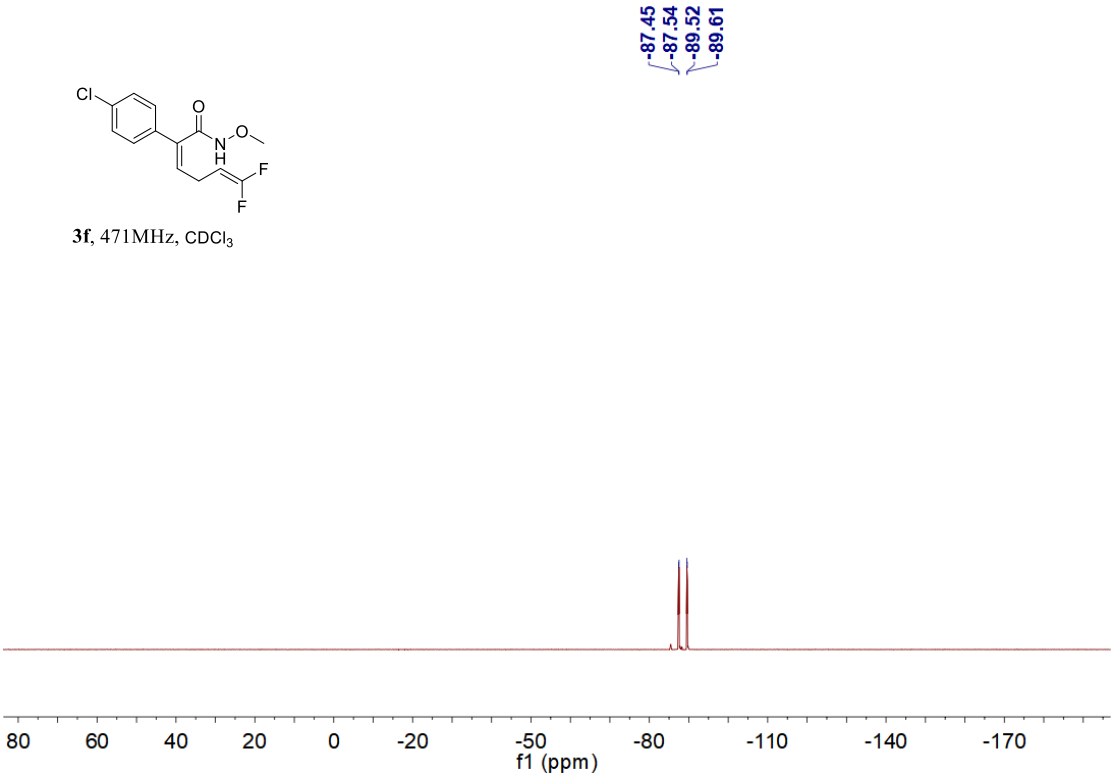


3f, 500 MHz, $CDCl_3$



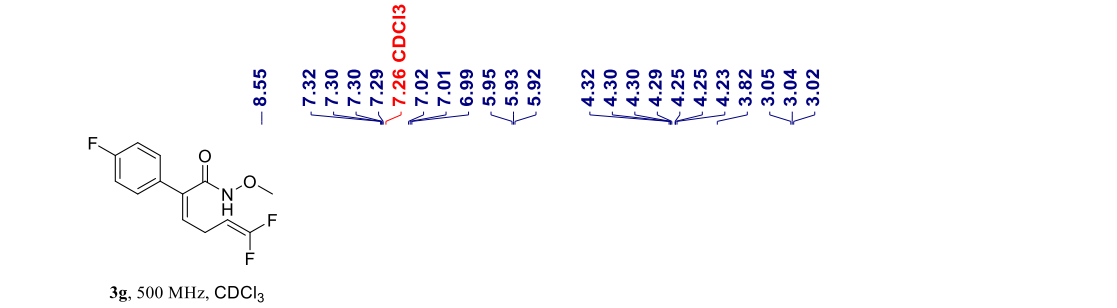
3f, 151 MHz, $CDCl_3$

^{19}F NMR spectrum for product 3f

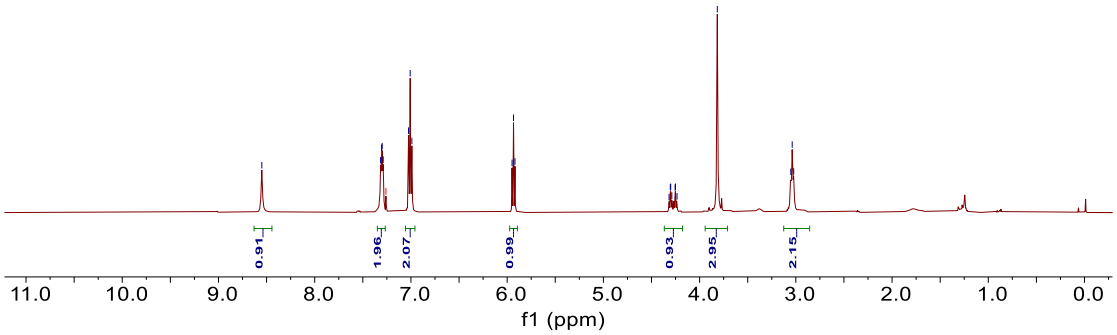


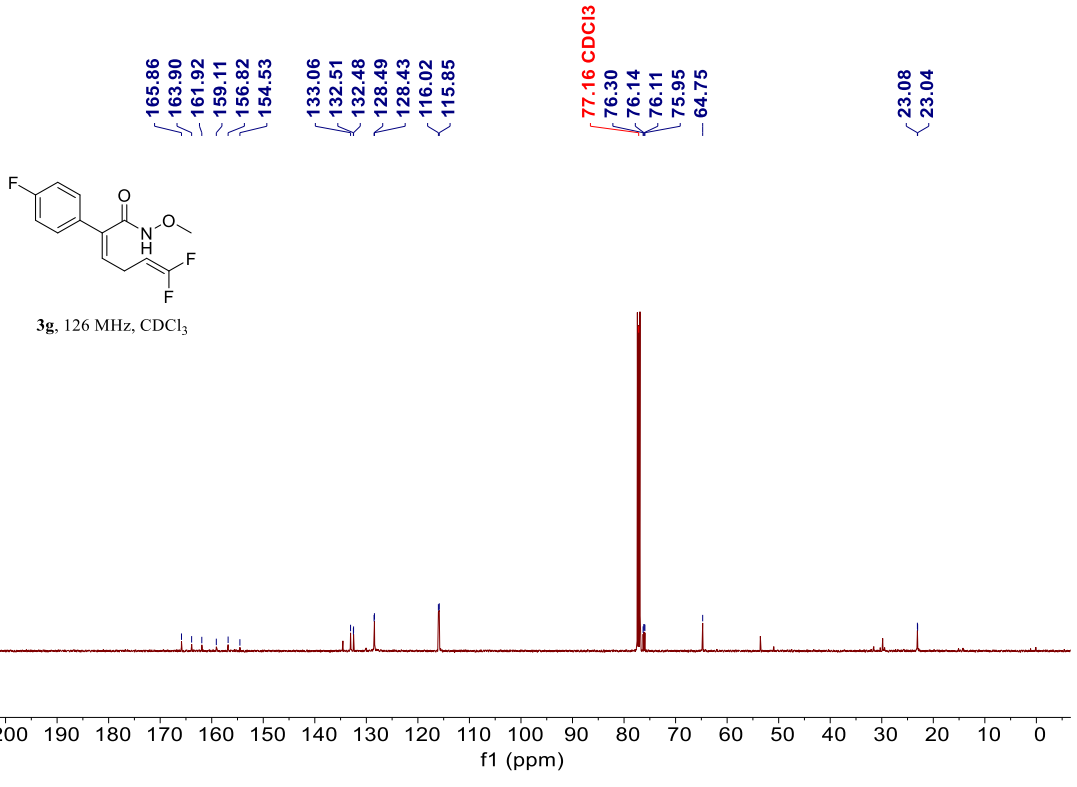
3f, 471MHz, $CDCl_3$

(*Z*)-6,6-difluoro-2-(4-fluorophenyl)-*N*-methoxyhexa-2,5-dienamide (3g)



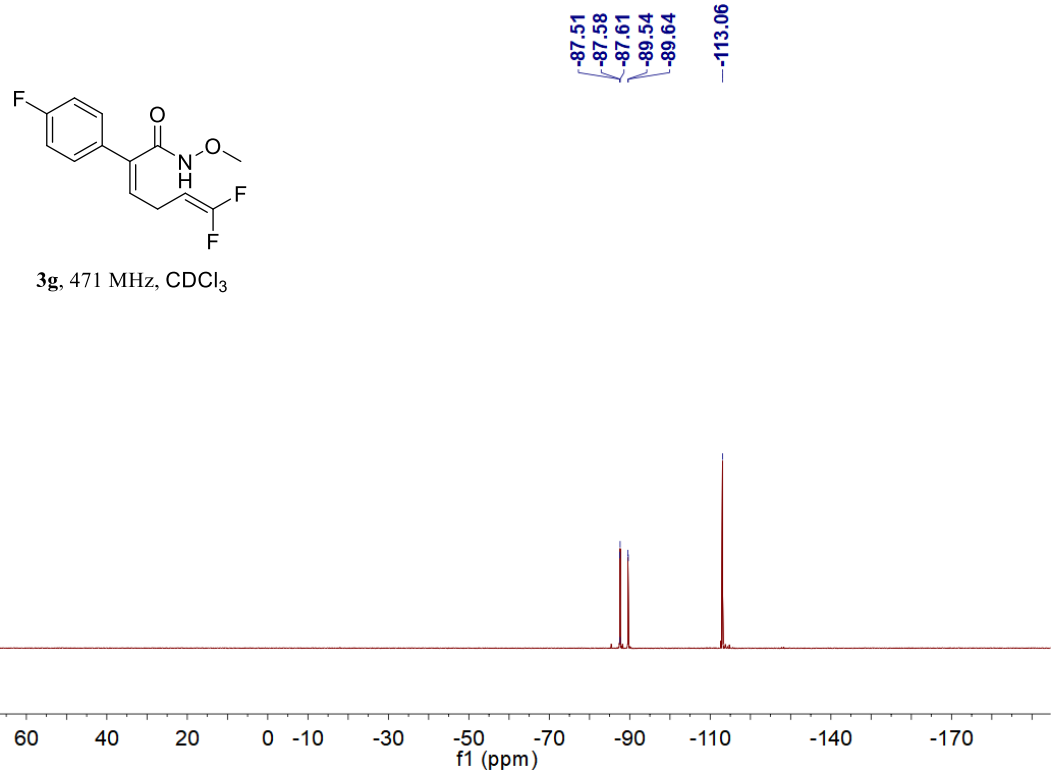
3g, 500 MHz, $CDCl_3$





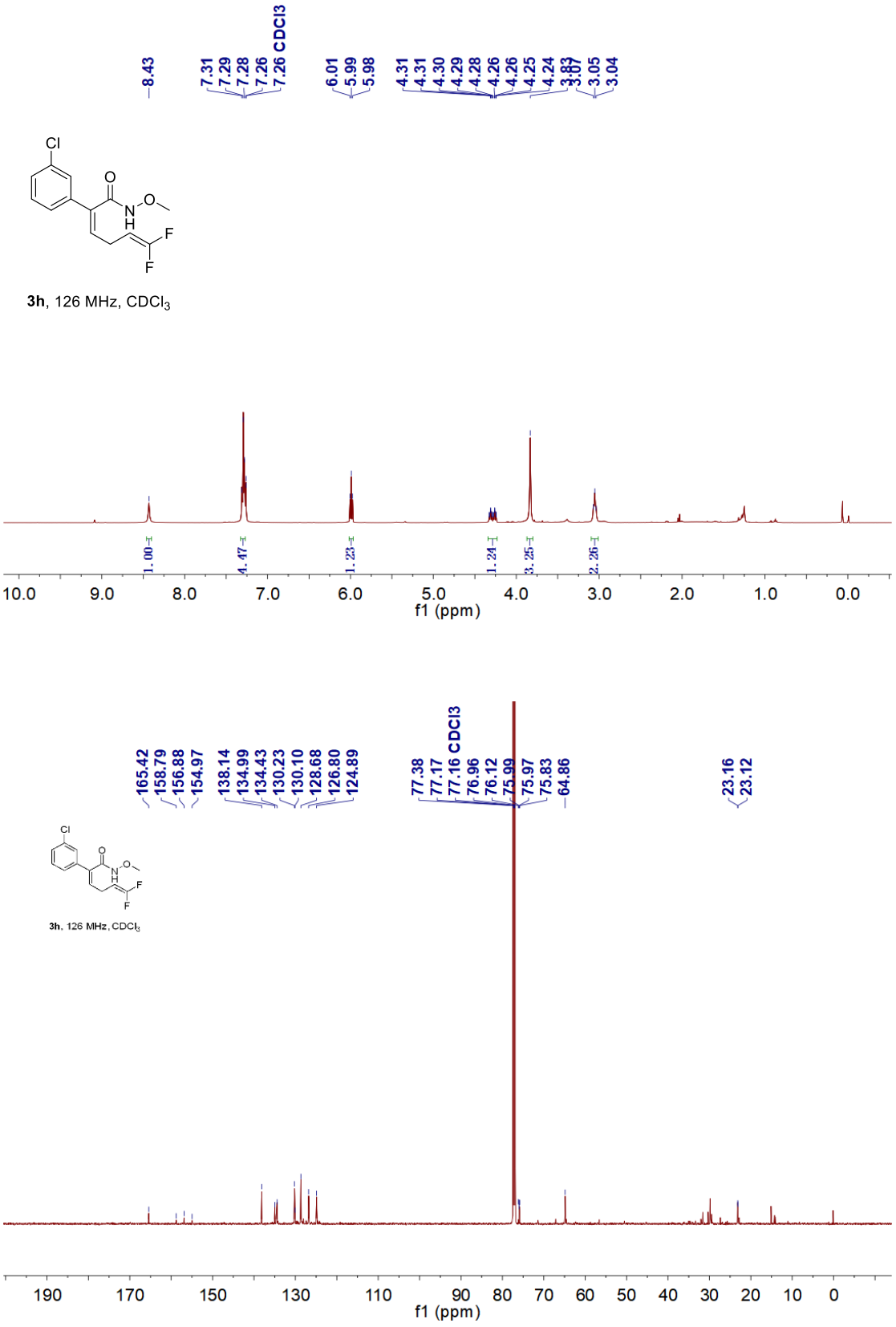
3g, 126 MHz, $CDCl_3$

^{19}F NMR spectrum for product 3g

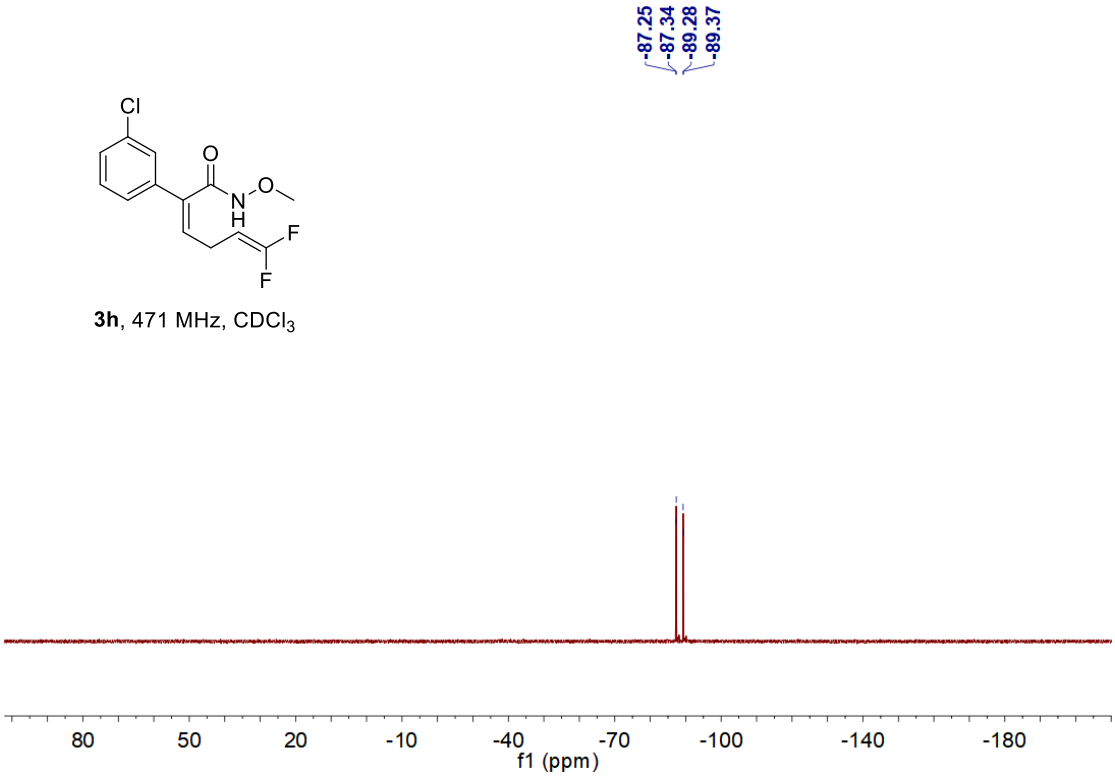


3g, 471 MHz, $CDCl_3$

(*Z*)-2-(3-chlorophenyl)-6,6-difluoro-*N*-methoxyhexa-2,5-dienamide (3h)

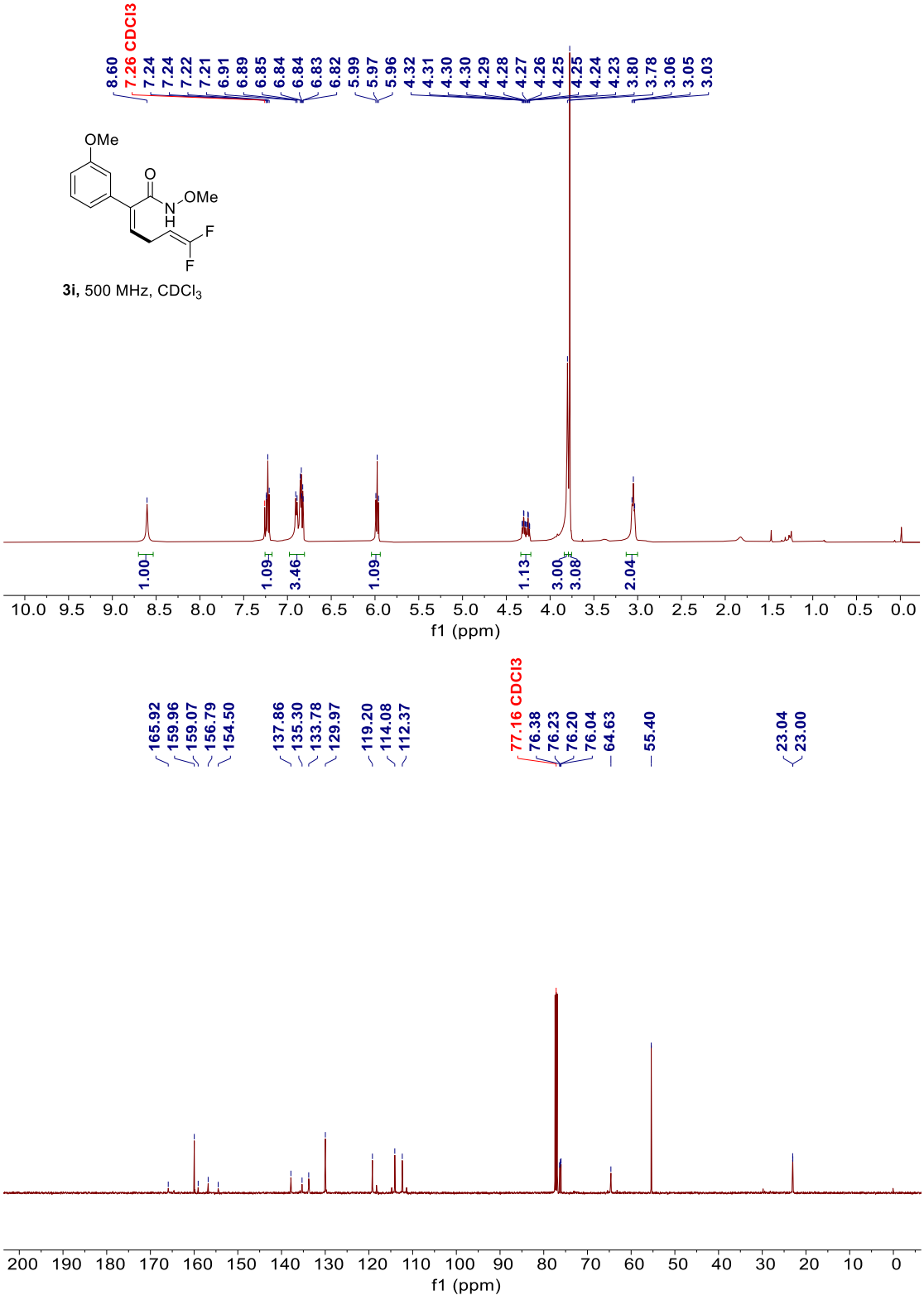


^{19}F NMR spectrum for product 3h

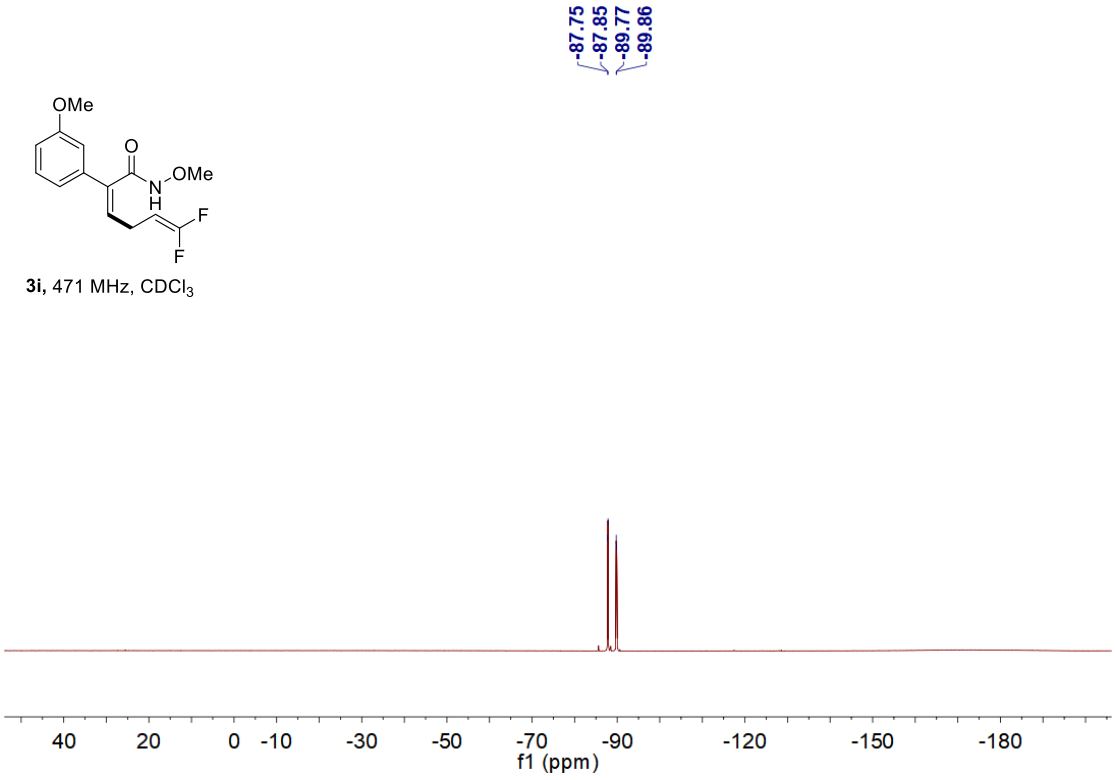


3h, 471 MHz, $CDCl_3$

(*Z*)-6,6-difluoro-*N*-methoxy-2-(3-methoxyphenyl)hexa-2,5-dienamide (3i)

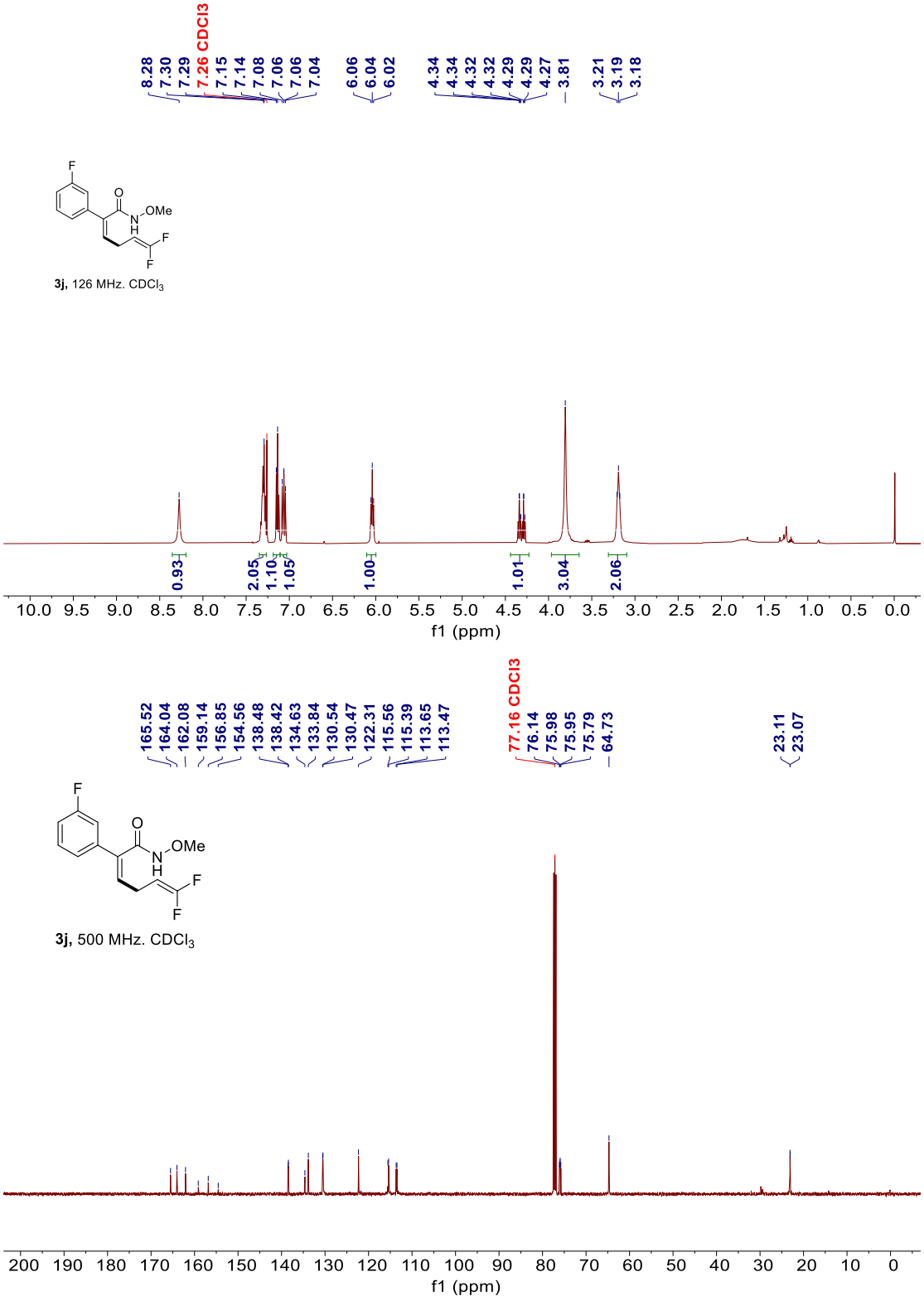


^{19}F NMR spectrum for product 3i

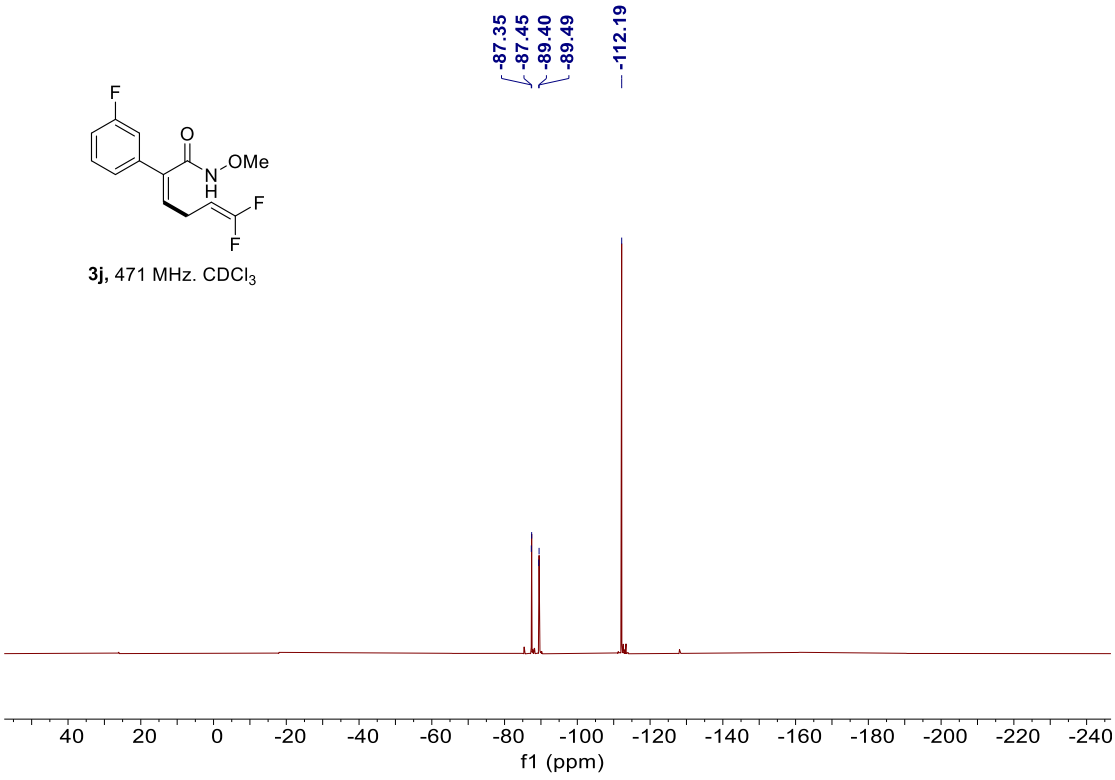


3i, 471 MHz, $CDCl_3$

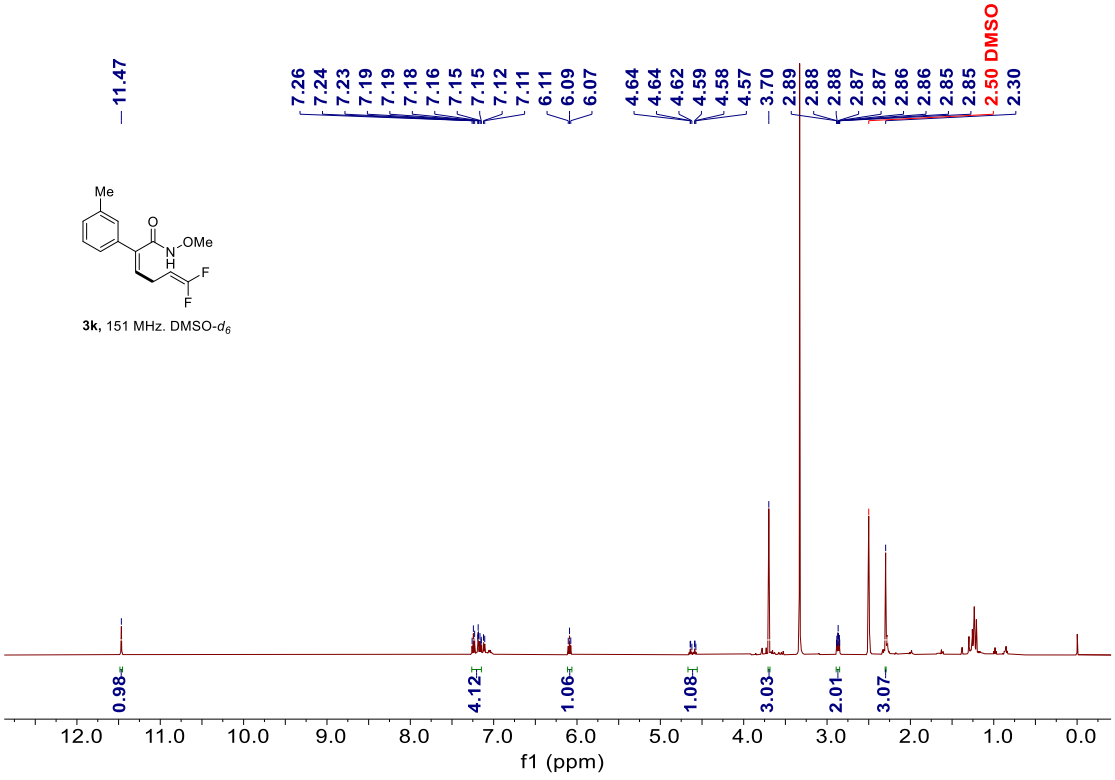
(*Z*)-6,6-difluoro-2-(3-fluorophenyl)-*N*-methoxyhexa-2,5-dienamide (3j)

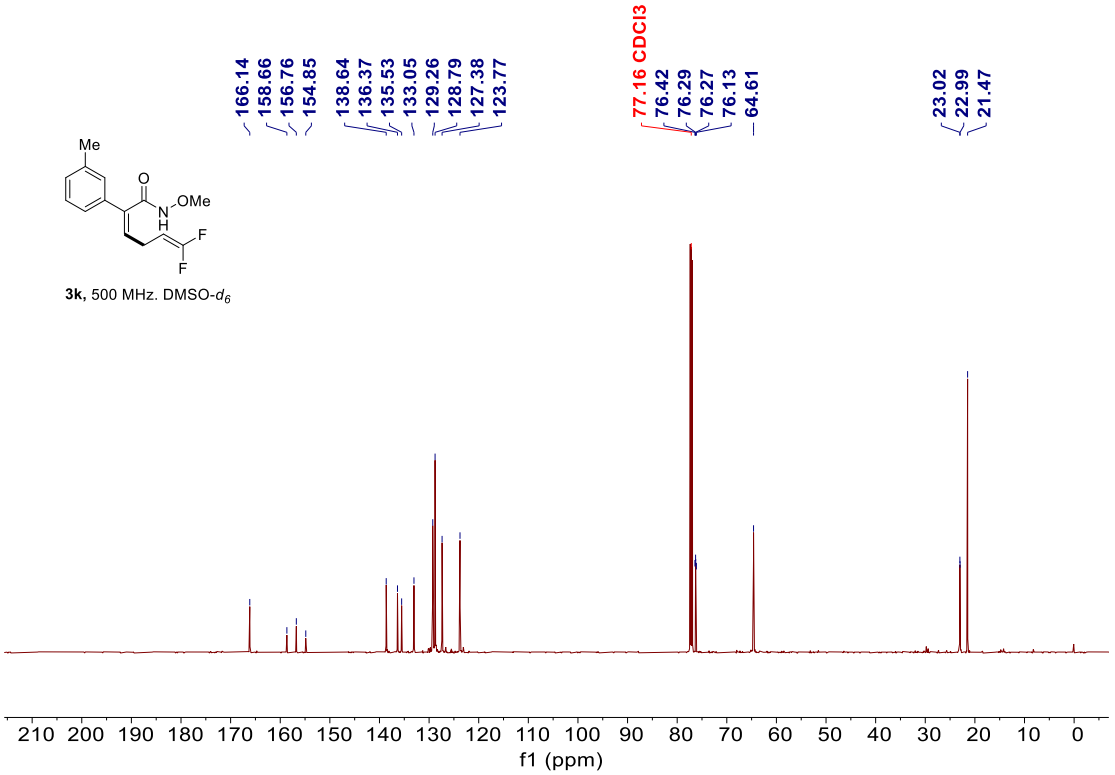


^{19}F NMR spectrum for product 3j

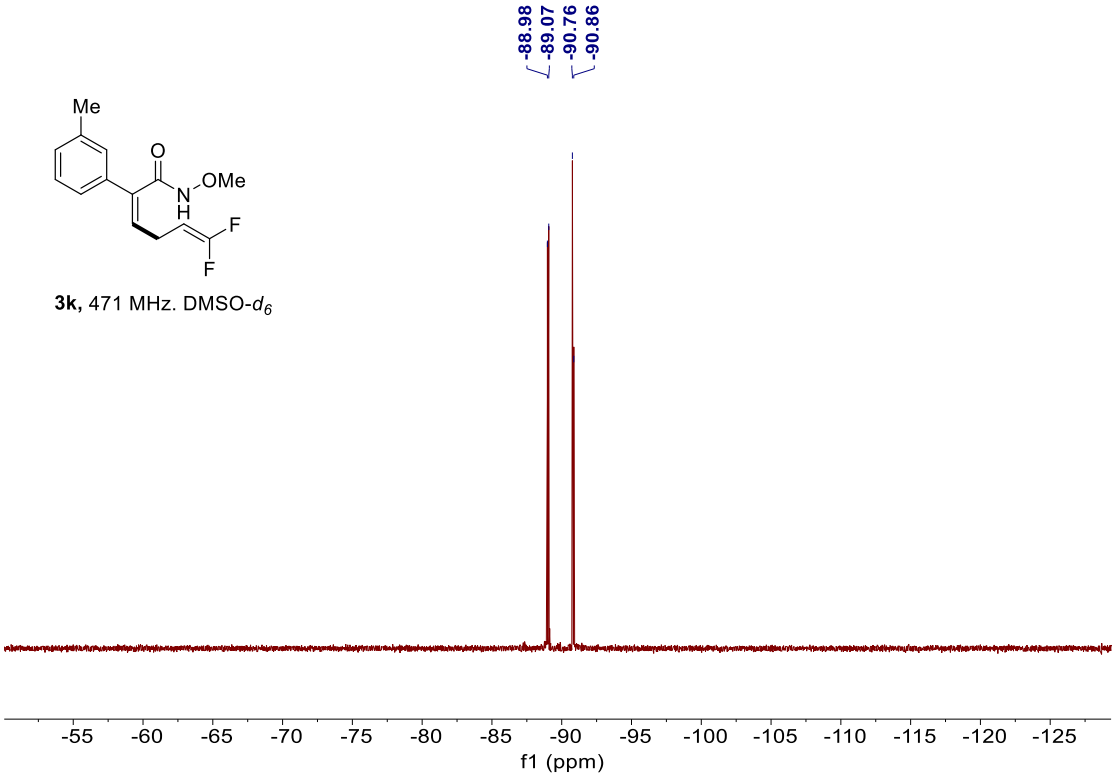


(*Z*)-6,6-difluoro-*N*-methoxy-2-(m-tolyl)hexa-2,5-dienamide (3k)



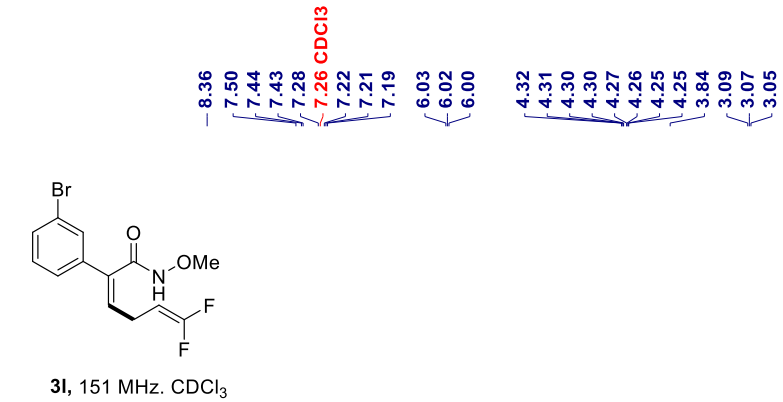


^{19}F NMR spectrum for product 3k

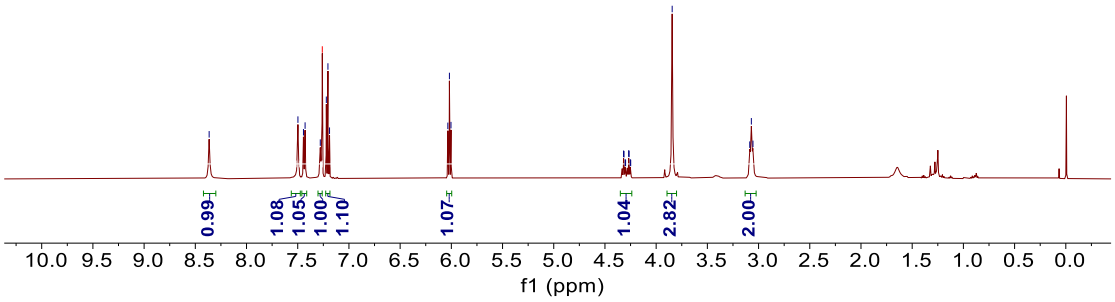


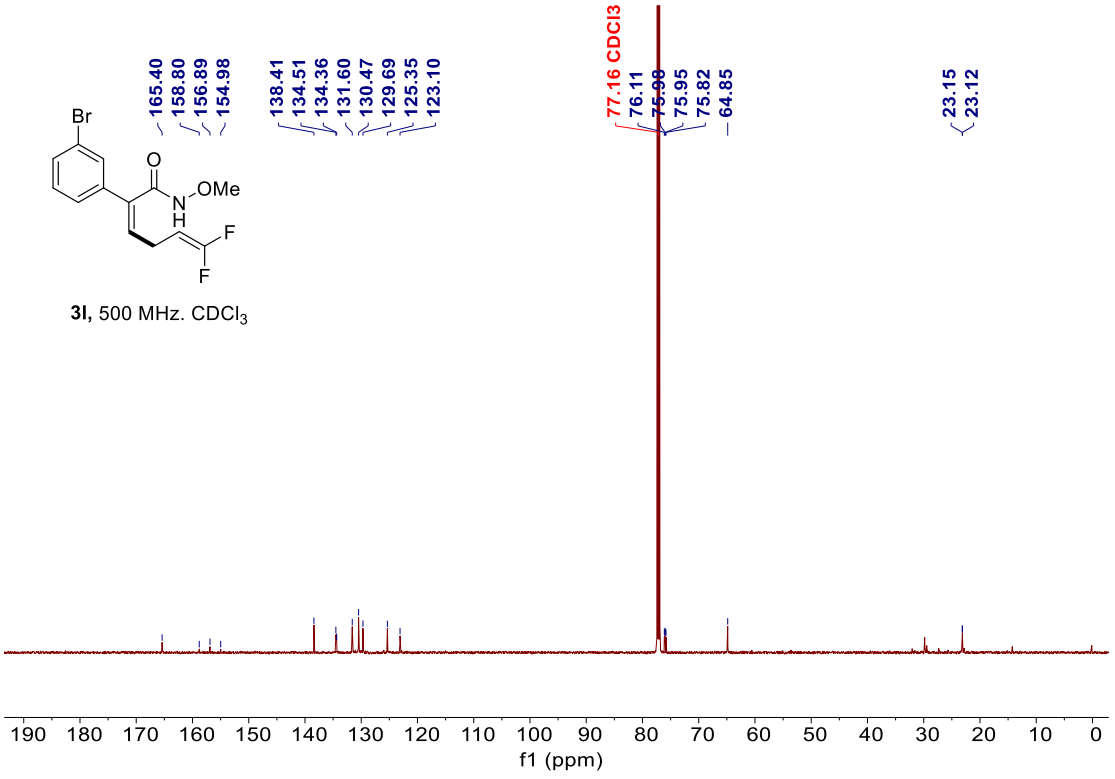
3k, 471 MHz. DMSO-d_6

(*Z*)-2-(3-bromophenyl)-6,6-difluoro-*N*-methoxyhexa-2,5-dienamide (3l)



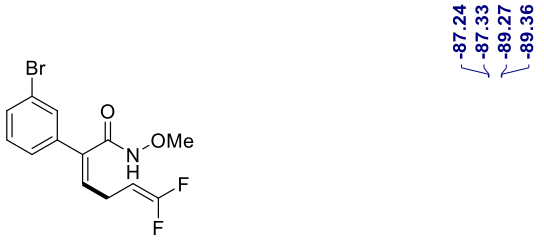
3l, 151 MHz. $CDCl_3$





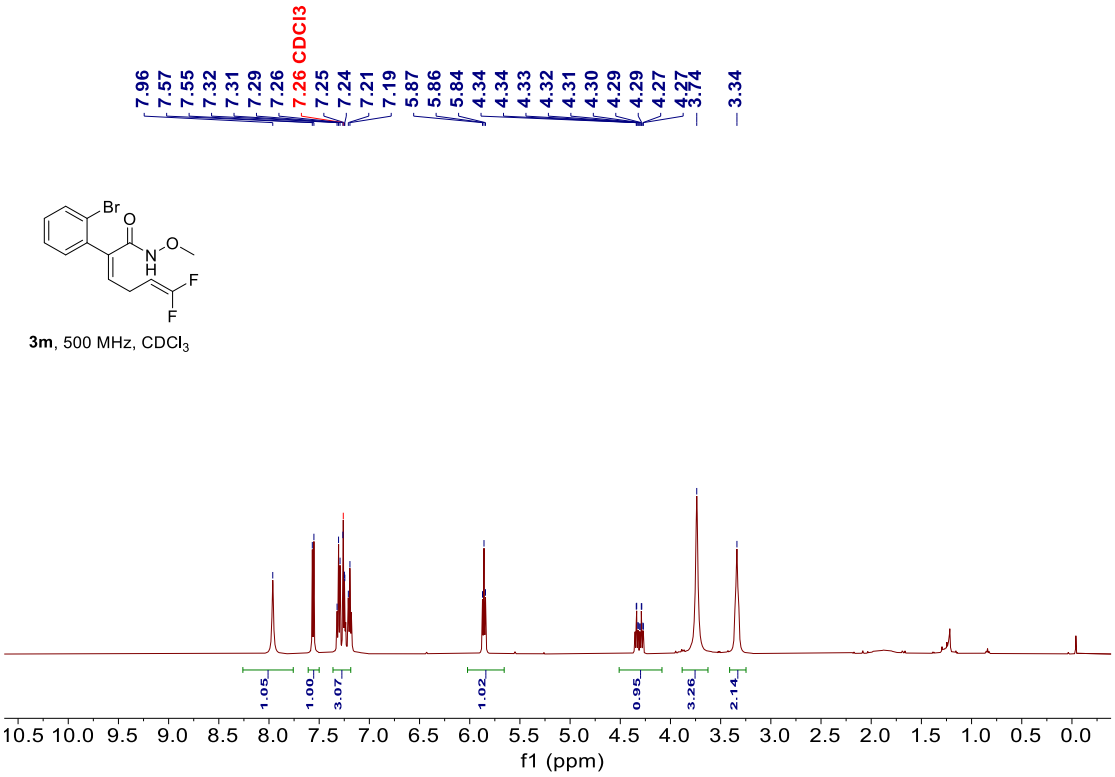
3l, 500 MHz. $CDCl_3$

^{19}F NMR spectrum for product 3l

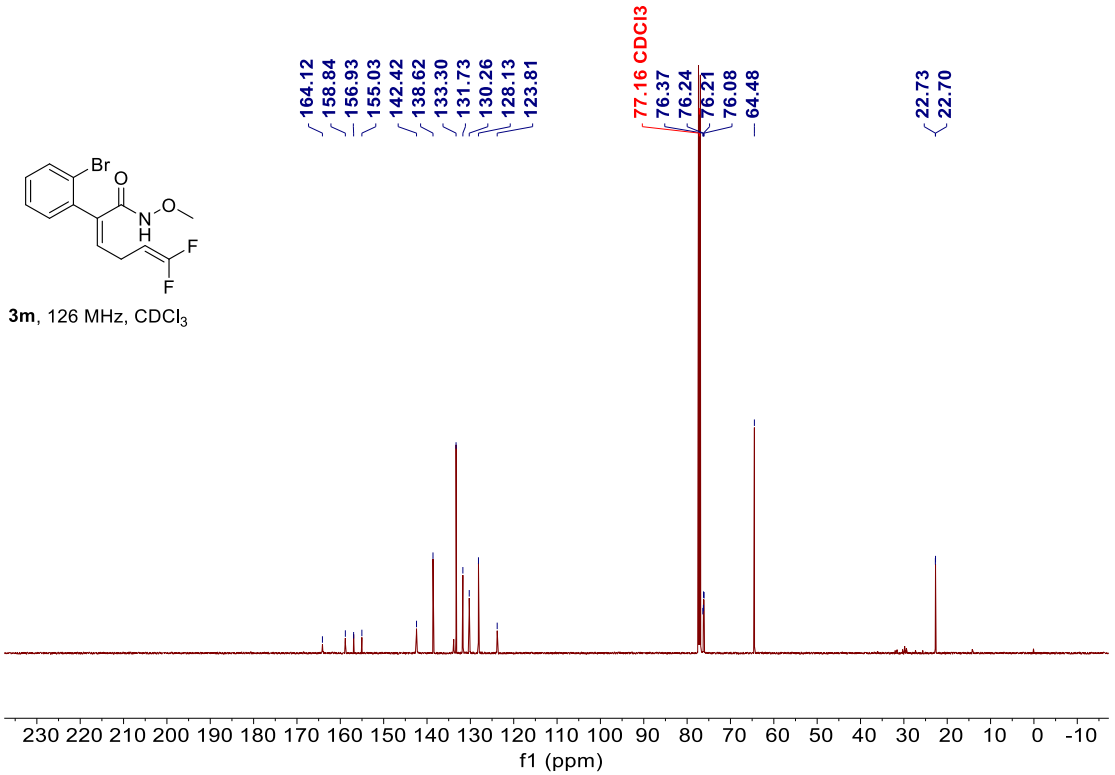


3l, 471 MHz. $CDCl_3$

(*Z*)-2-(2-bromophenyl)-6,6-difluoro-*N*-methoxyhexa-2,5-dienamide (3m)

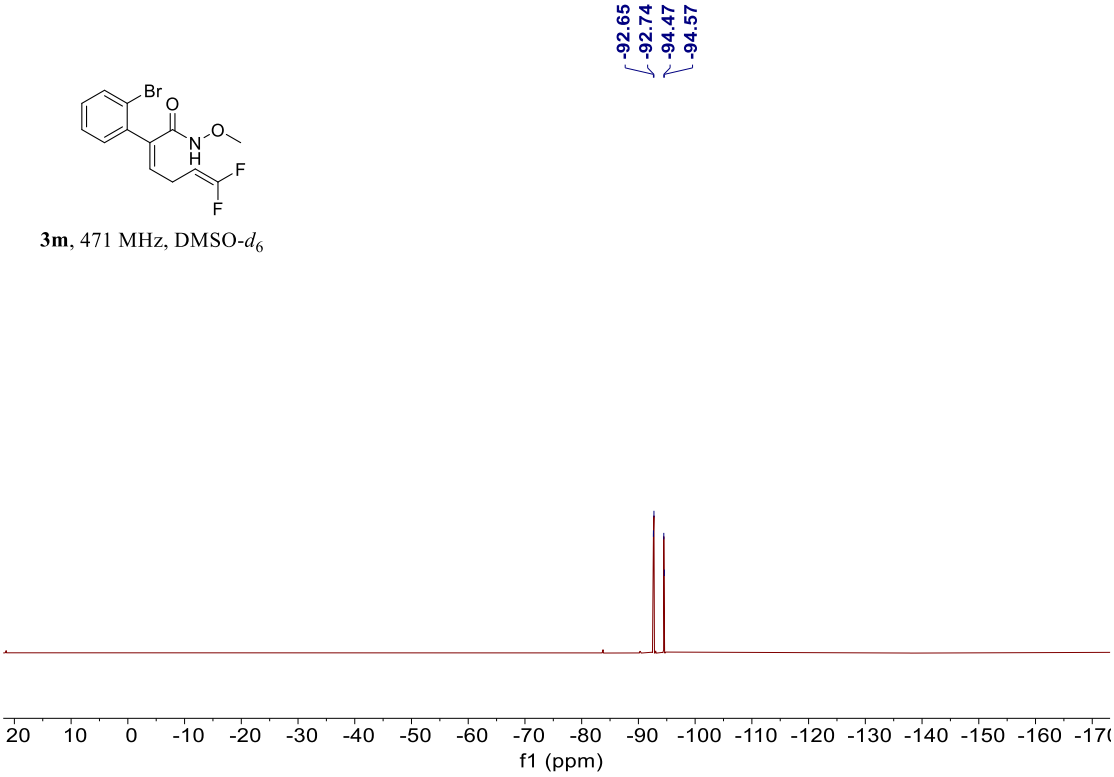


3m, 500 MHz, $CDCl_3$



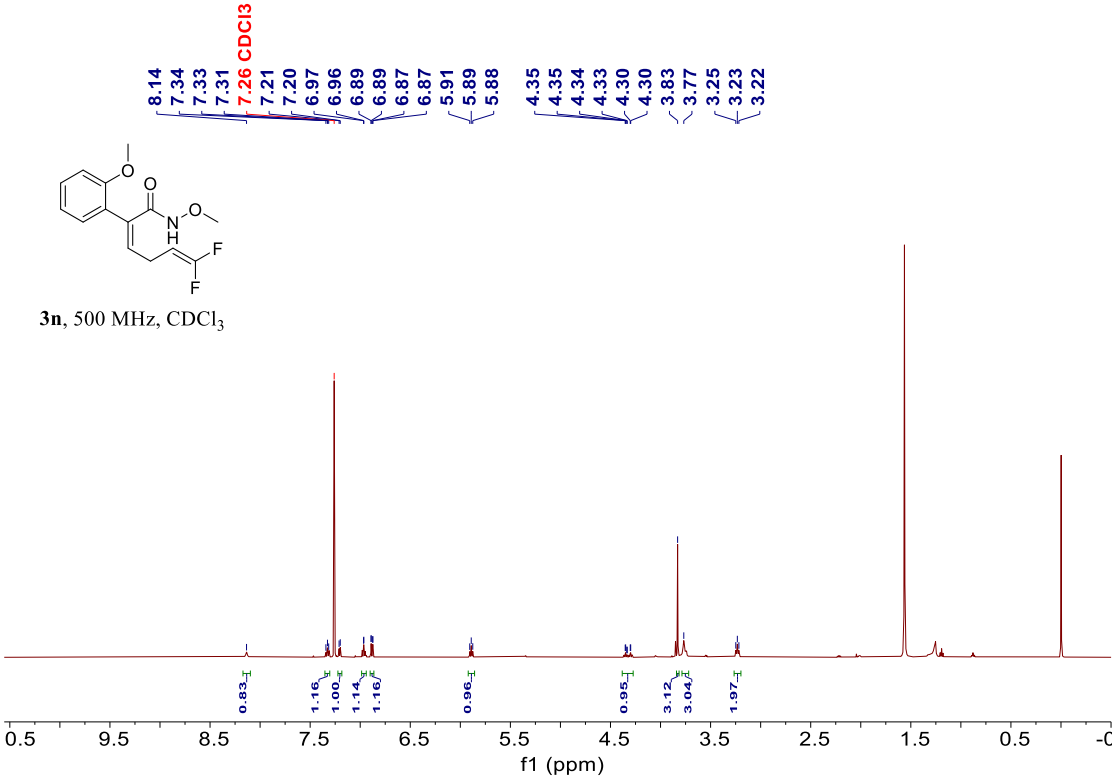
3m, 126 MHz, $CDCl_3$

^{19}F NMR spectrum for product 3m

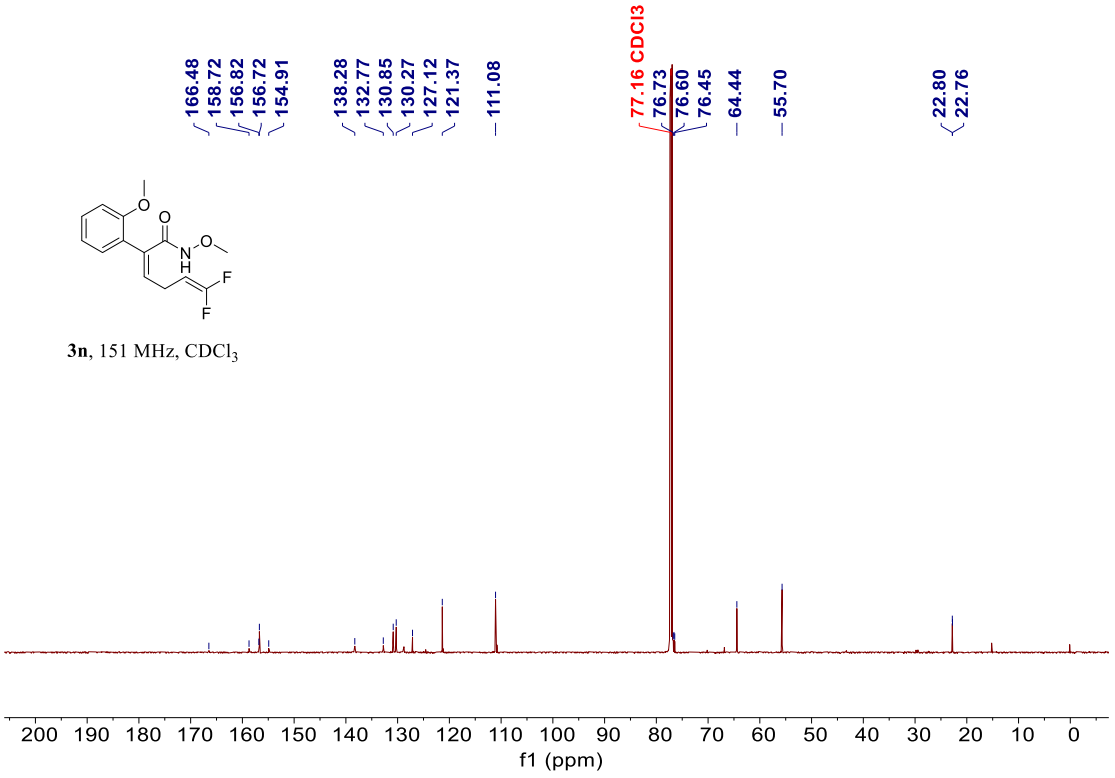


3m, 471 MHz, DMSO-d_6

(*Z*)-6,6-difluoro-*N*-methoxy-2-(2-methoxyphenyl)hexa-2,5-dienamide (3n)

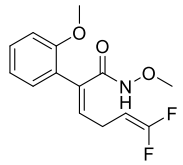


3n, 500 MHz, $CDCl_3$



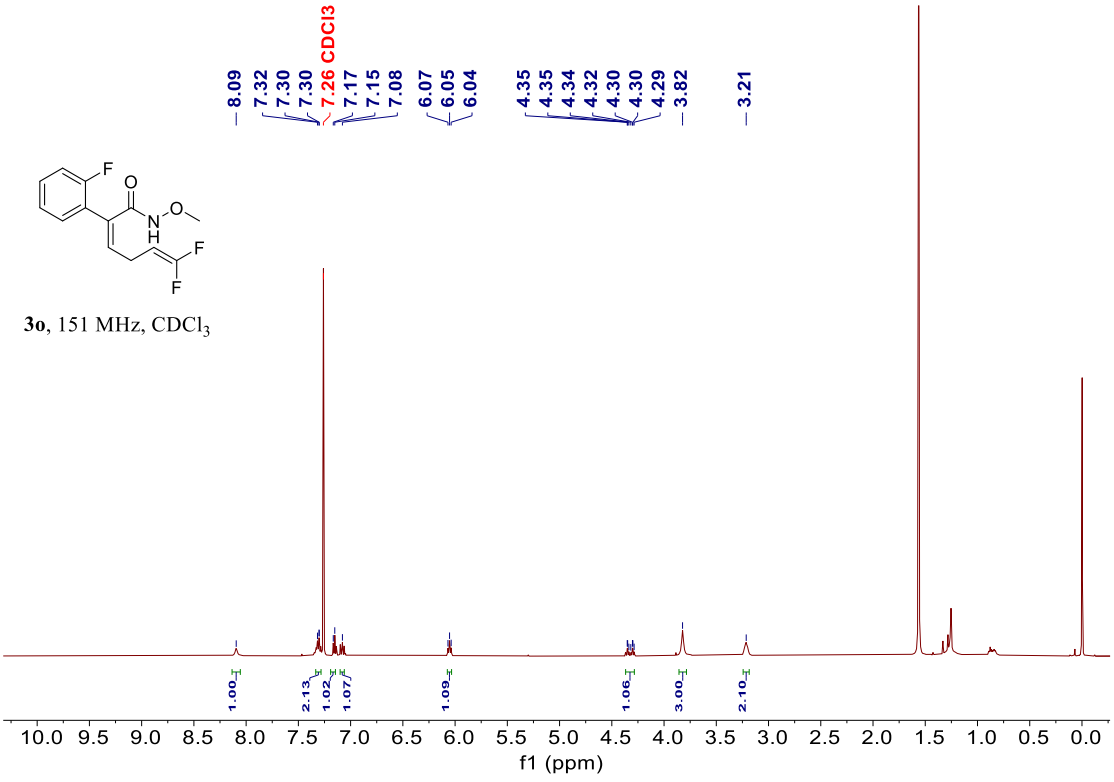
3n, 151 MHz, $CDCl_3$

^{19}F NMR spectrum for product 3n

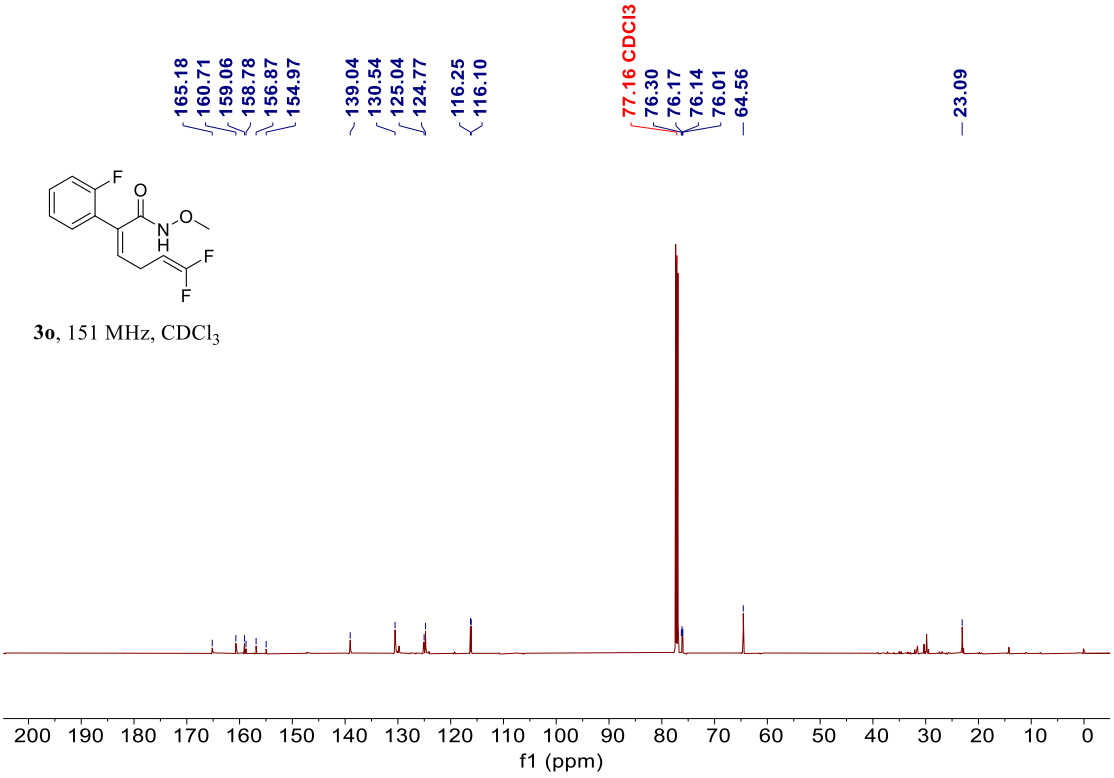


3n, 471 MHz, $CDCl_3$

(*Z*)-6,6-difluoro-2-(2-fluorophenyl)-*N*-methoxyhexa-2,5-dienamide (3o)

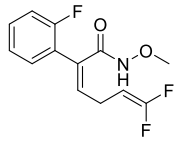


3o, 151 MHz, $CDCl_3$



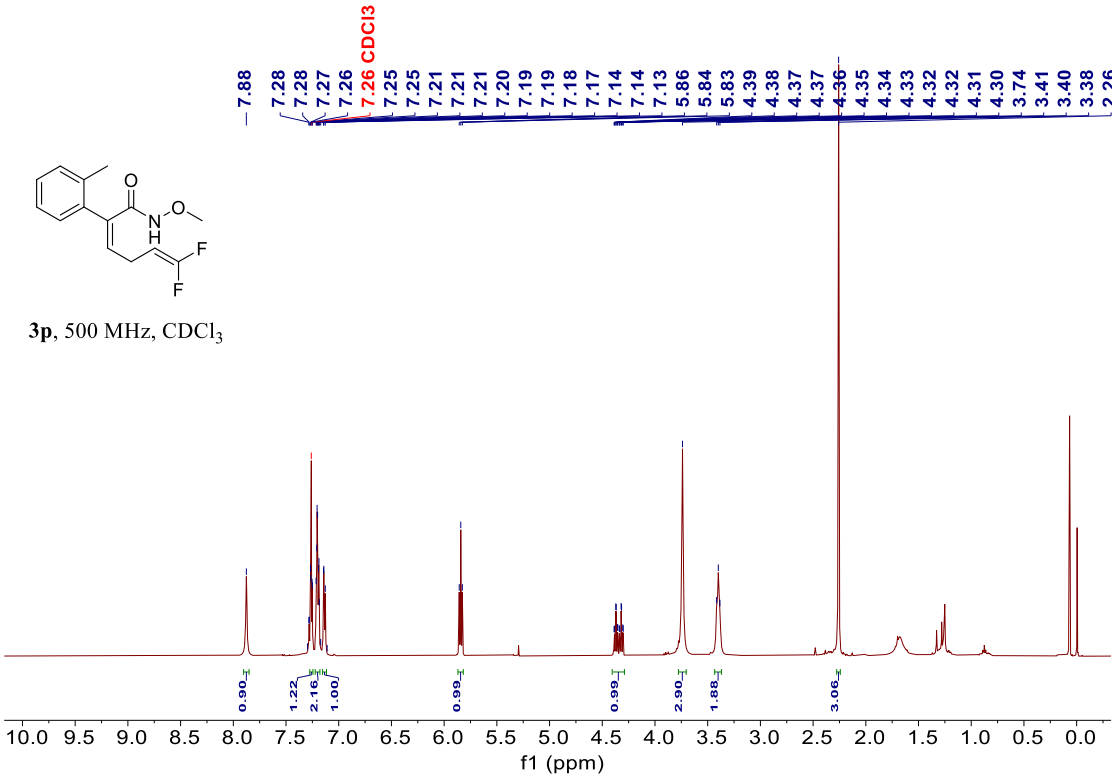
3o, 151 MHz, $CDCl_3$

^{19}F NMR spectrum for product 3o

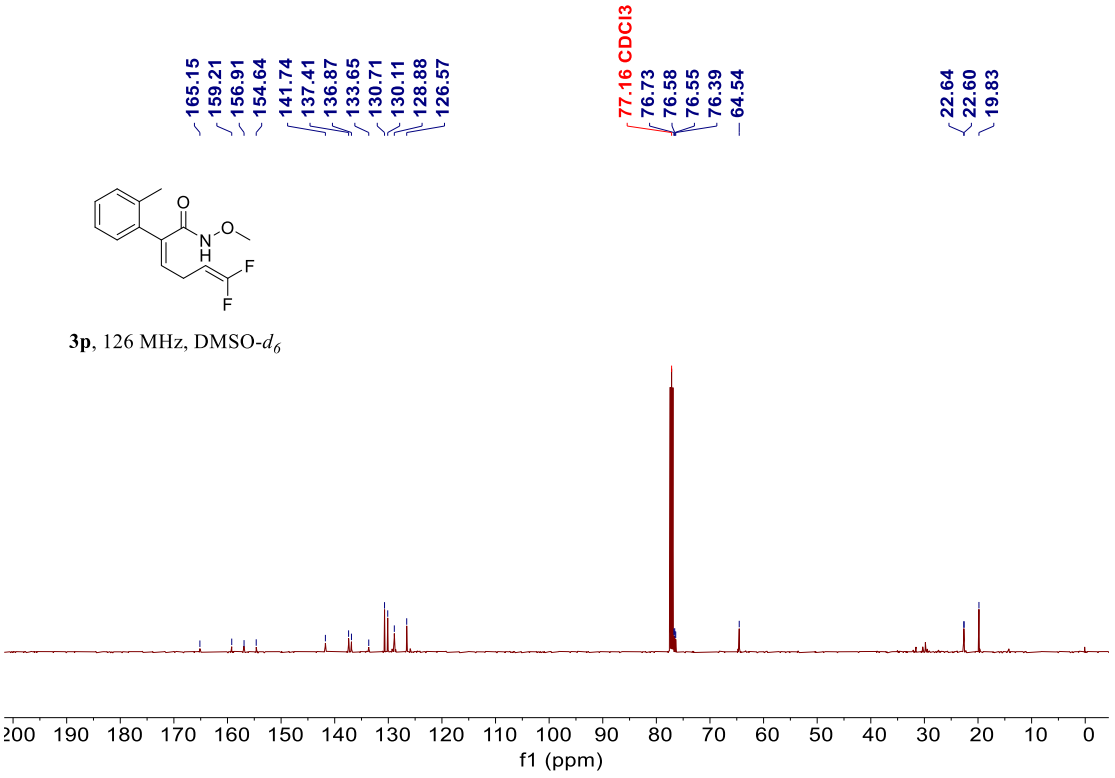


3o, 471 MHz, $CDCl_3$

(*Z*)-6,6-difluoro-*N*-methoxy-2-(o-tolyl)hexa-2,5-dienamide (3p)

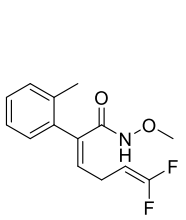


3p, 500 MHz, $CDCl_3$



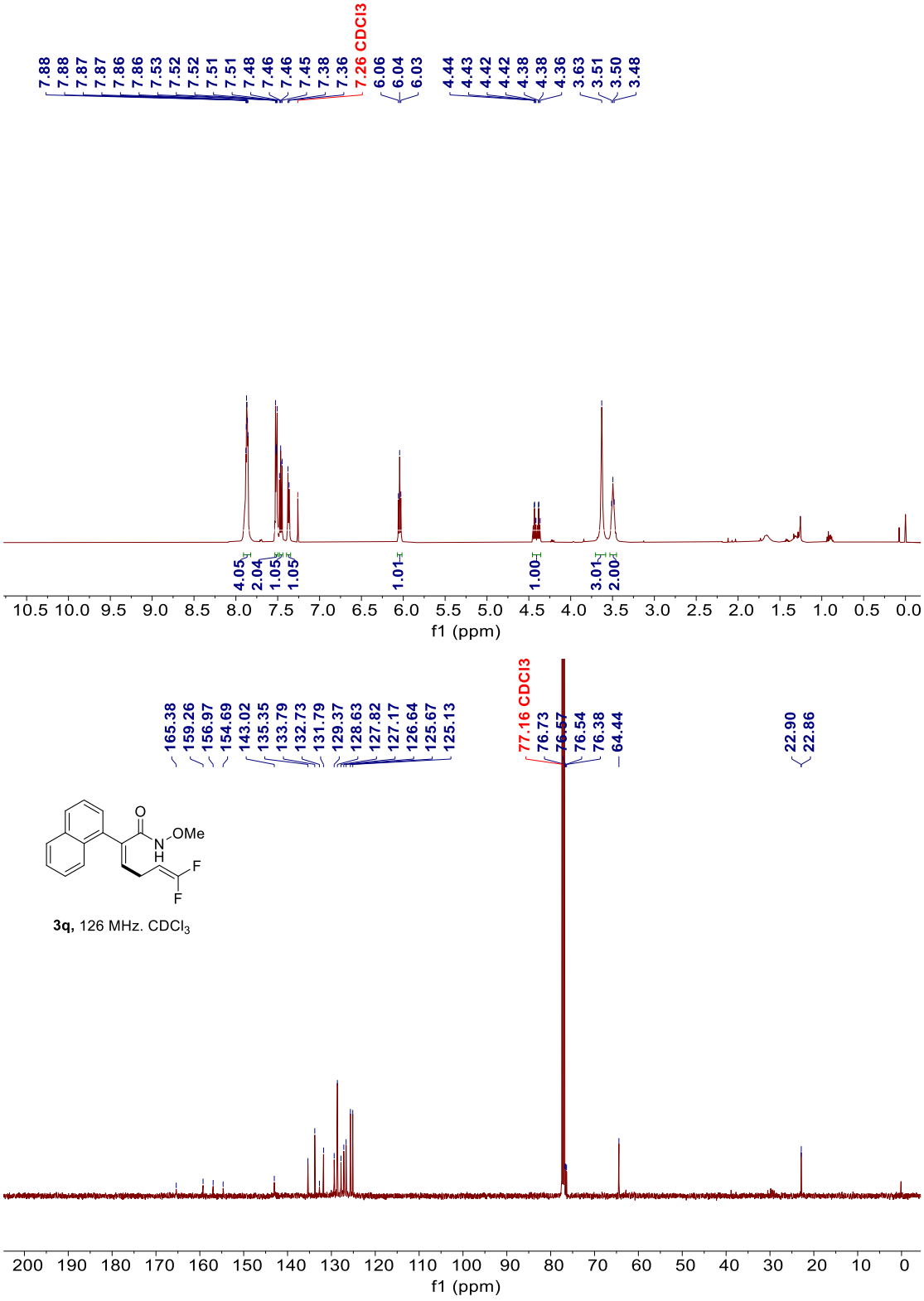
3p, 126 MHz, DMSO-d_6

^{19}F NMR spectrum for product 3p



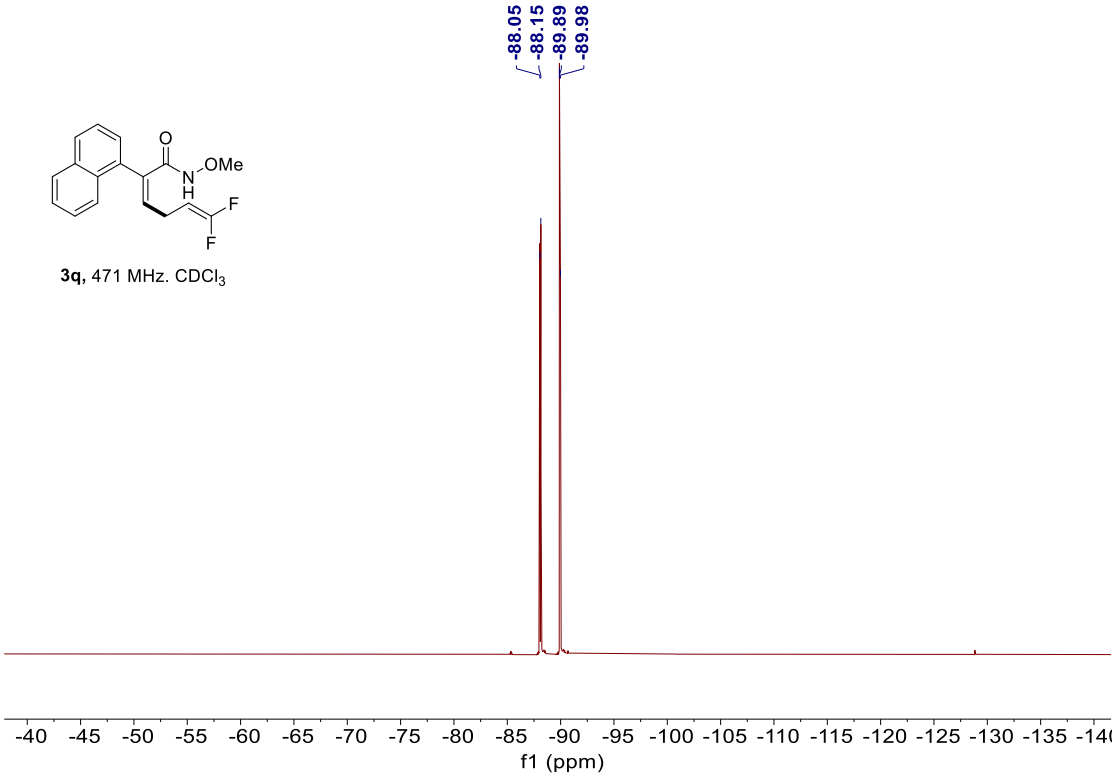
3p, 471 MHz, DMSO-d_6

(*Z*)-6,6-difluoro-*N*-methoxy-2-(naphthalen-1-yl)hexa-2,5-dienamide (3q)



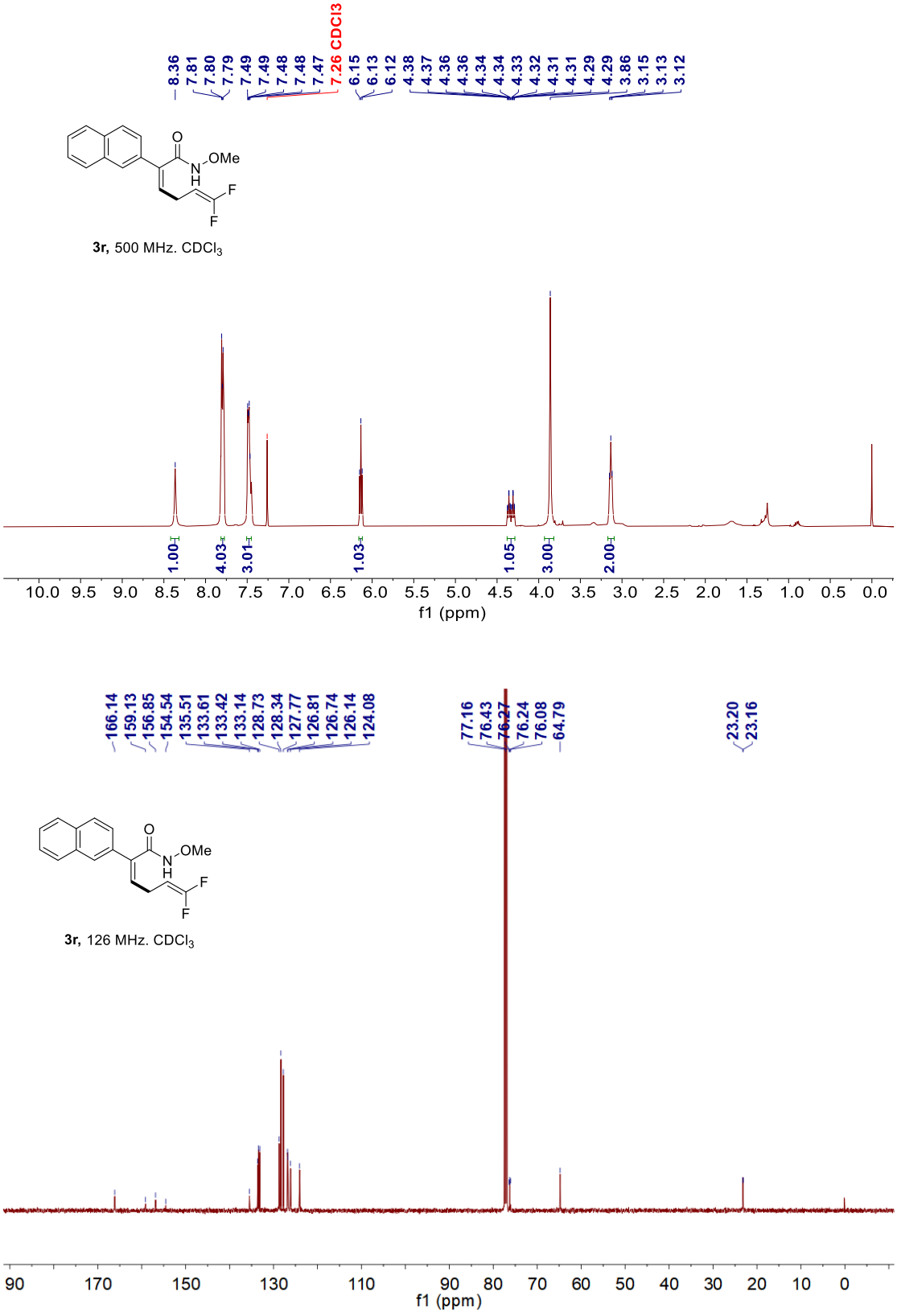
3q, 126 MHz. $CDCl_3$

^{19}F NMR spectrum for product 3q

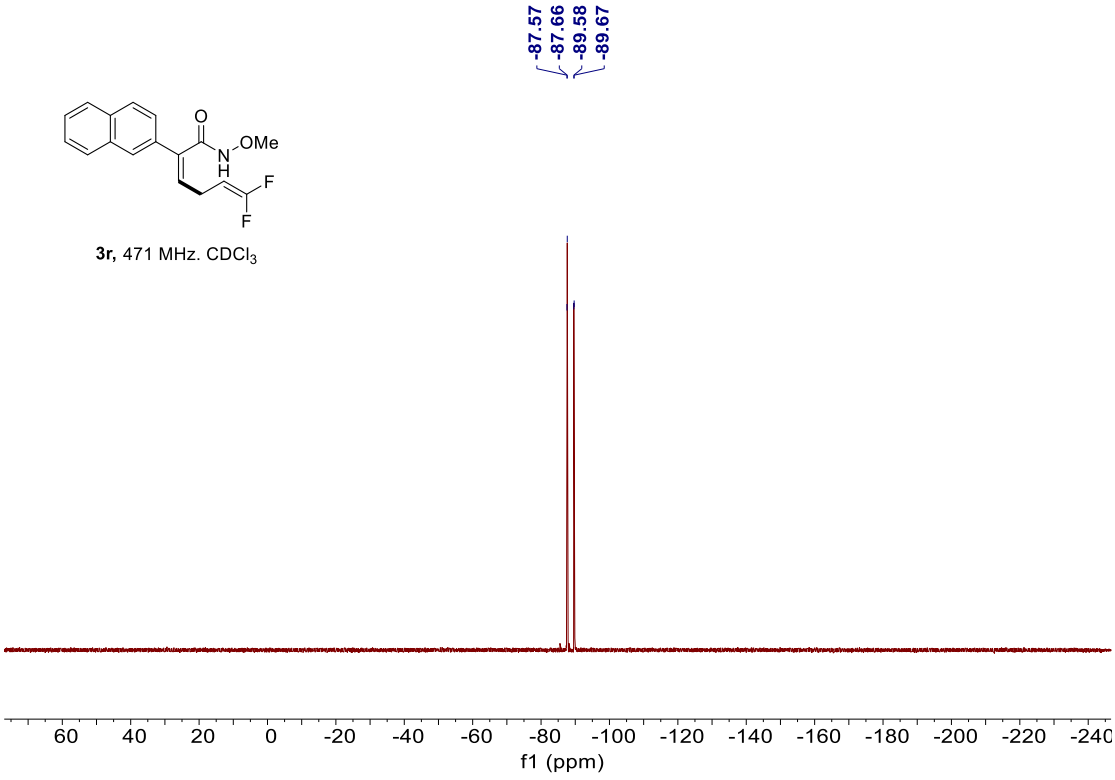


3q, 471 MHz. $CDCl_3$

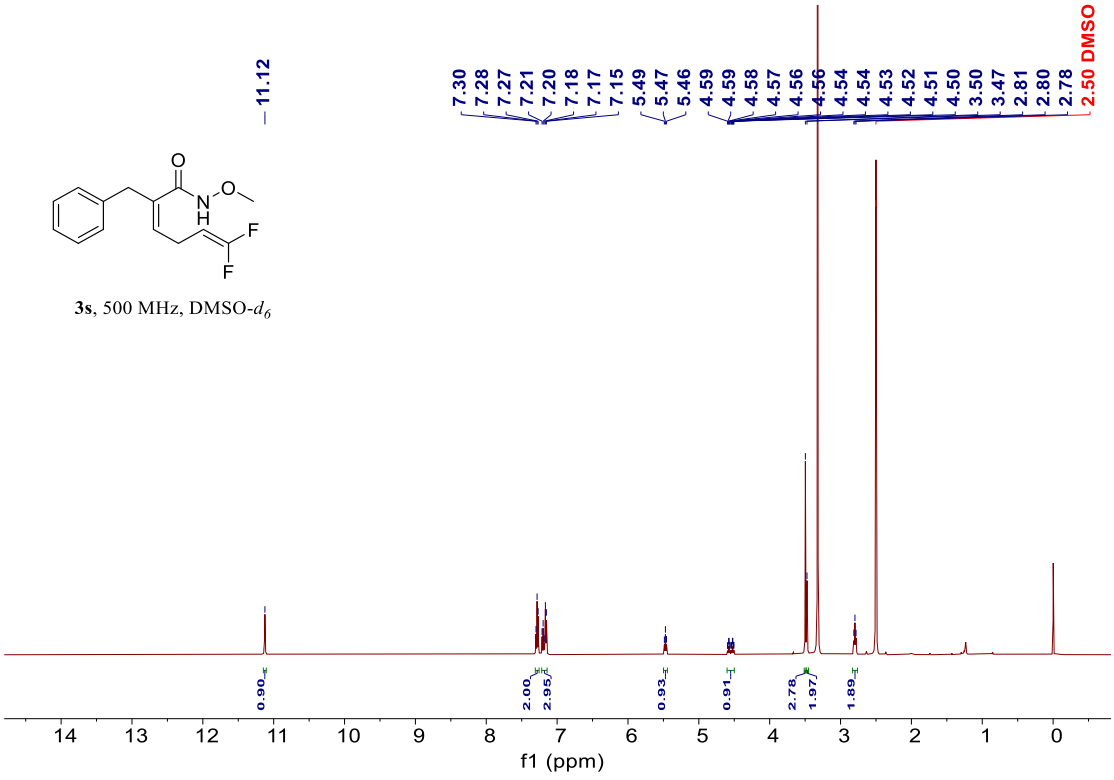
(*Z*)-6,6-difluoro-*N*-methoxy-2-(naphthalen-2-yl)hexa-2,5-dienamide (3r)



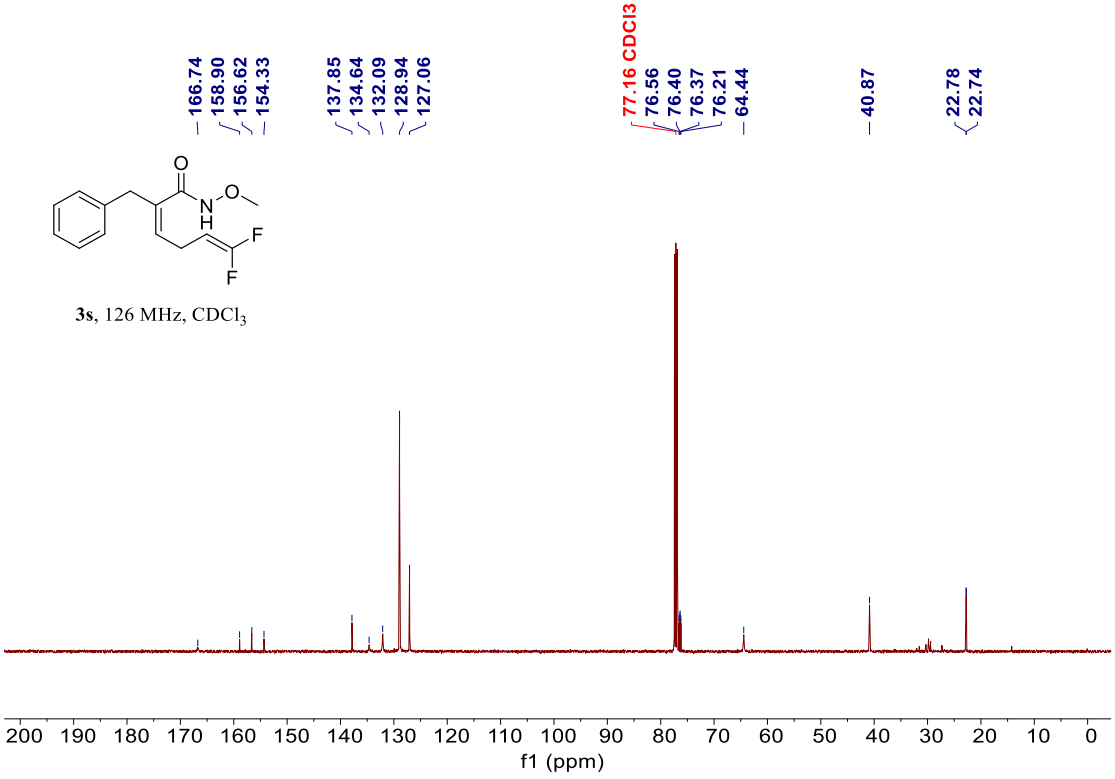
^{19}F NMR spectrum for product 3r



(*Z*)-2-benzyl-6,6-difluoro-*N*-methoxyhexa-2,5-dienamide (3s)

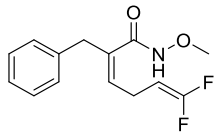


3s, 500 MHz, DMSO-d_6



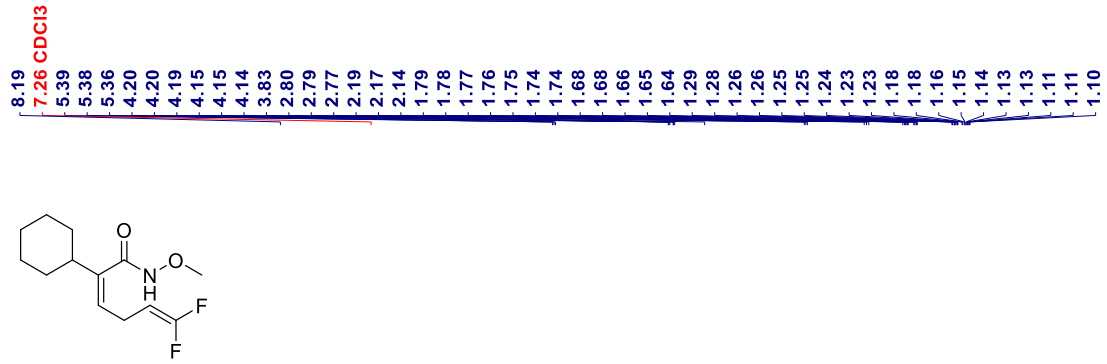
3s, 126 MHz, $CDCl_3$

^{19}F NMR spectrum for product 3s

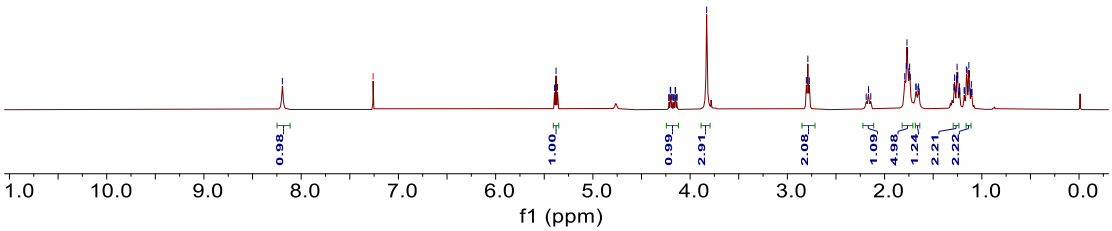


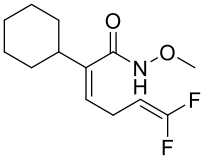
3s, 471 MHz, DMSO-d_6

(*Z*)-2-cyclohexyl-6,6-difluoro-*N*-methoxyhexa-2,5-dienamide (3t)



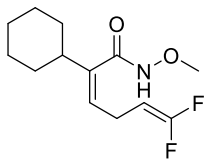
3t, 500 MHz, $CDCl_3$





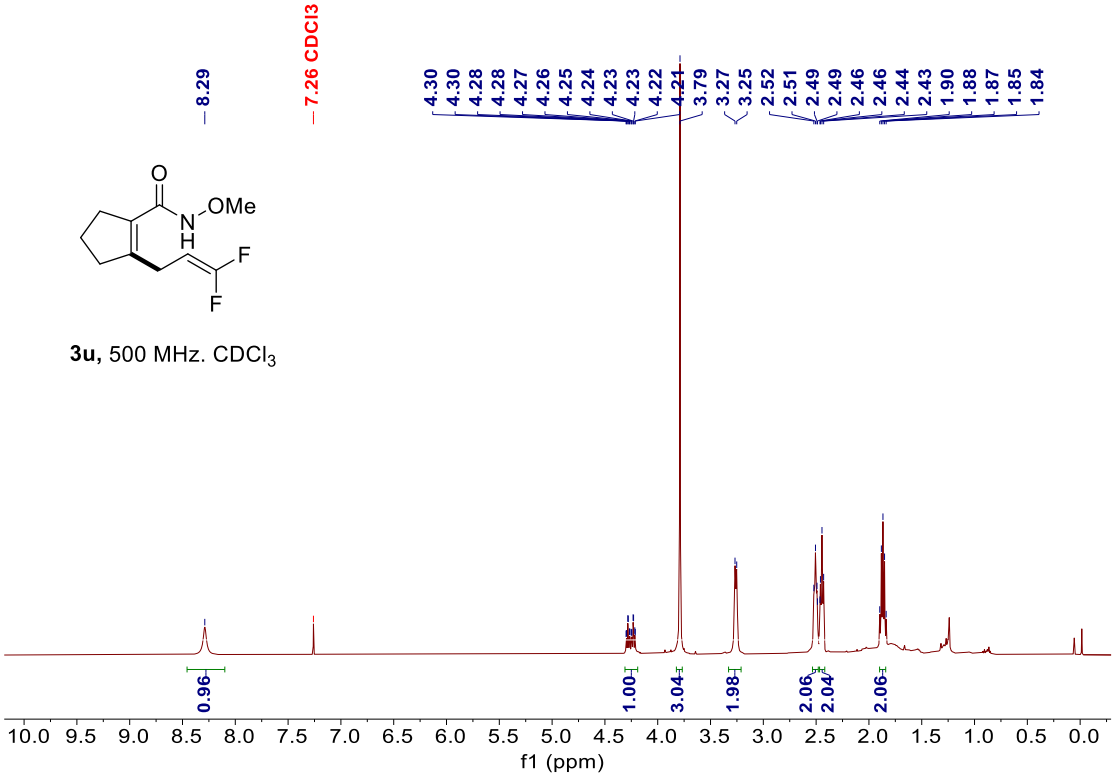
3t, 151 MHz, $CDCl_3$

^{19}F NMR spectrum for product 3t

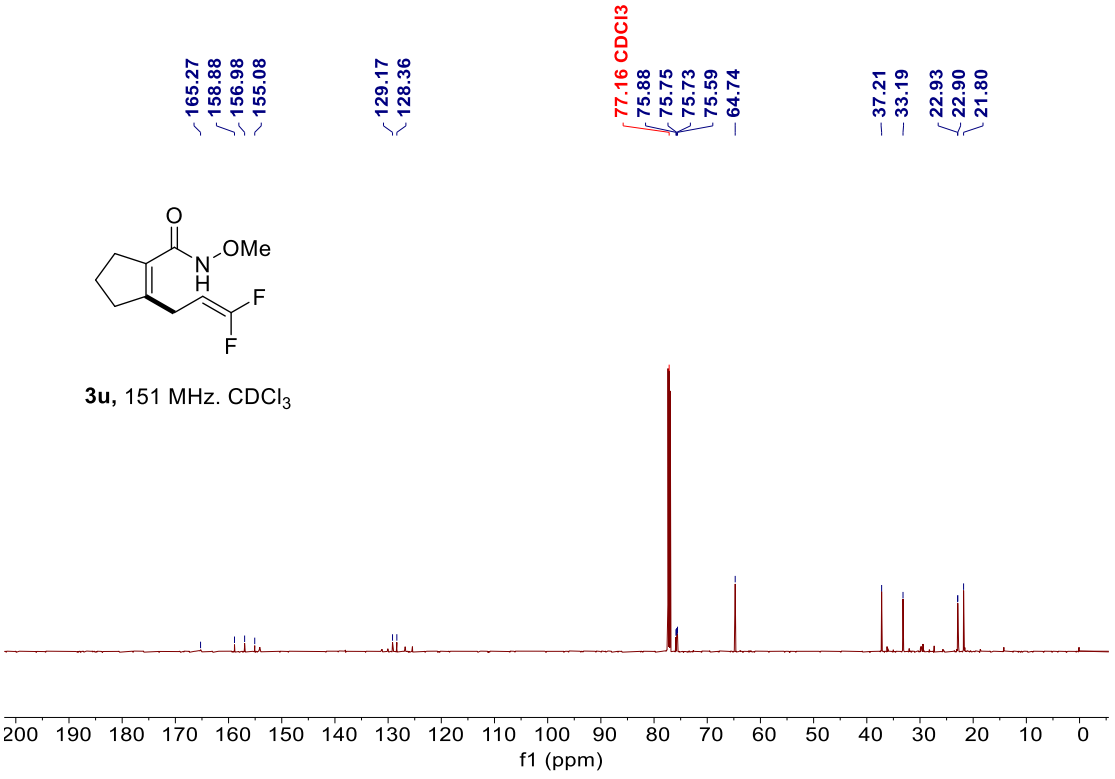


3t, 471 MHz, $CDCl_3$

2-(3,3-difluoroallyl)-*N*-methoxycyclopent-1-ene-1-carboxamide (3u)

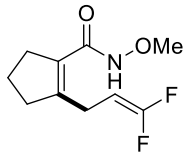


3u, 500 MHz. $CDCl_3$



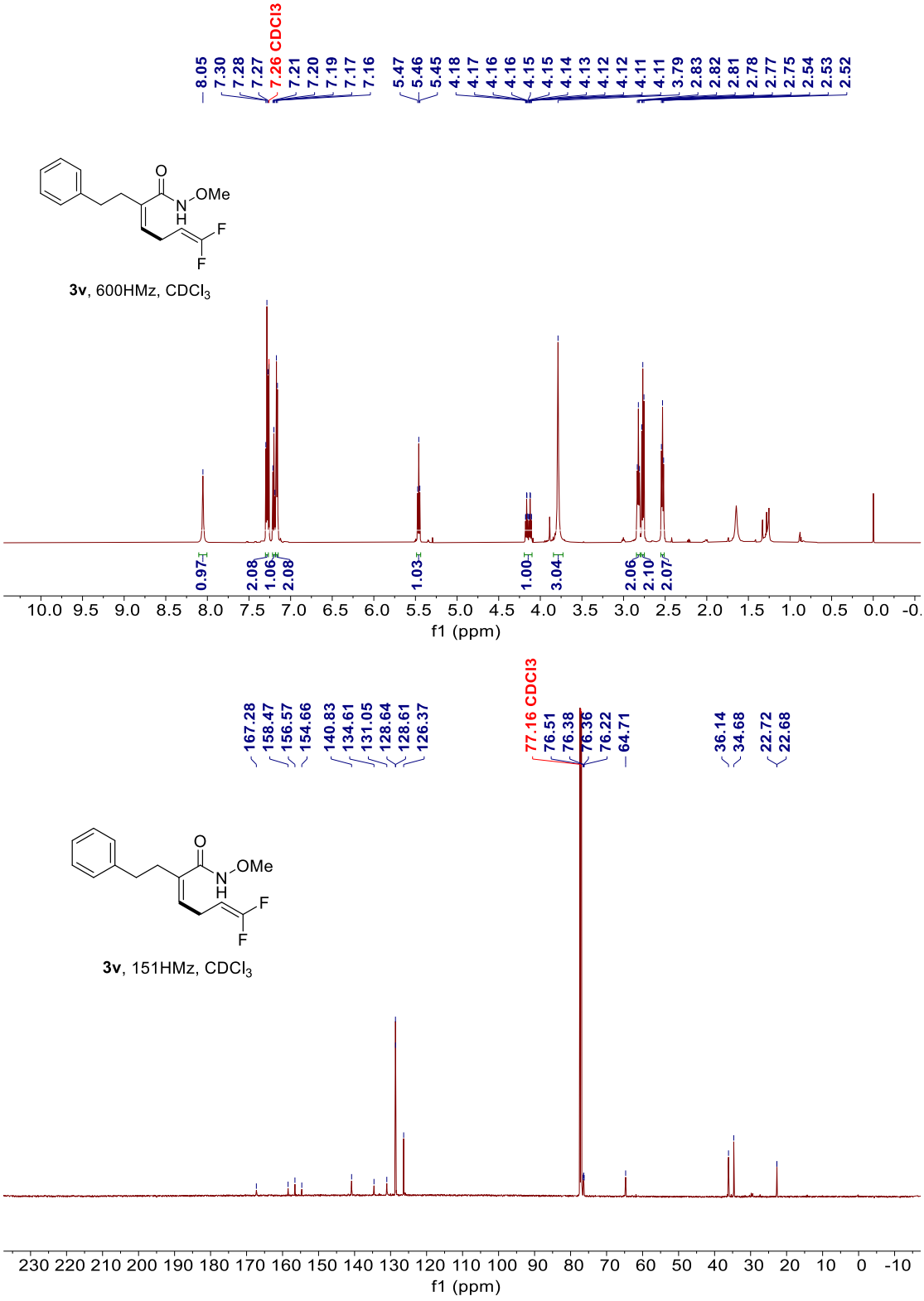
3u, 151 MHz. $CDCl_3$

^{19}F NMR spectrum for product 3u

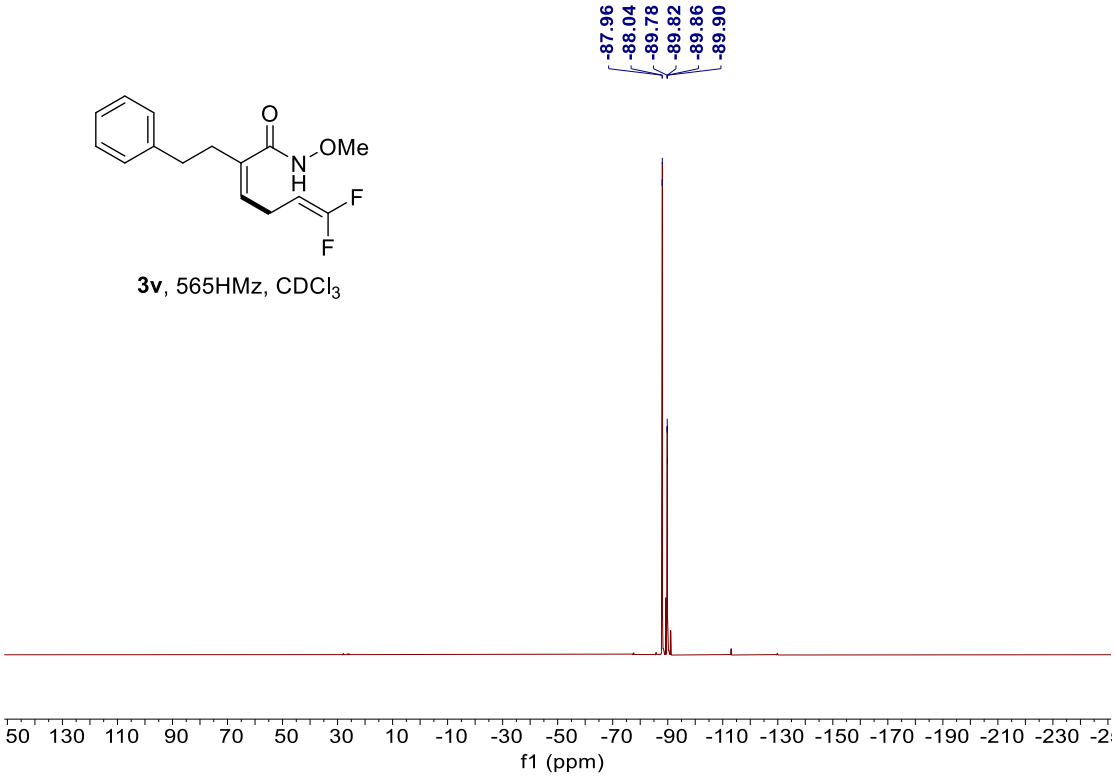


3u, 565 MHz. $CDCl_3$

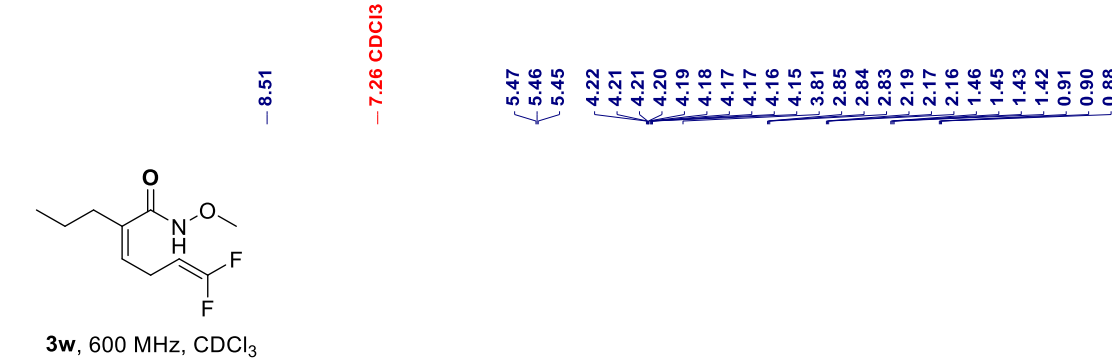
(*Z*)-6,6-difluoro-*N*-methoxy-2-phenethylhexa-2,5-dienamide (3v)



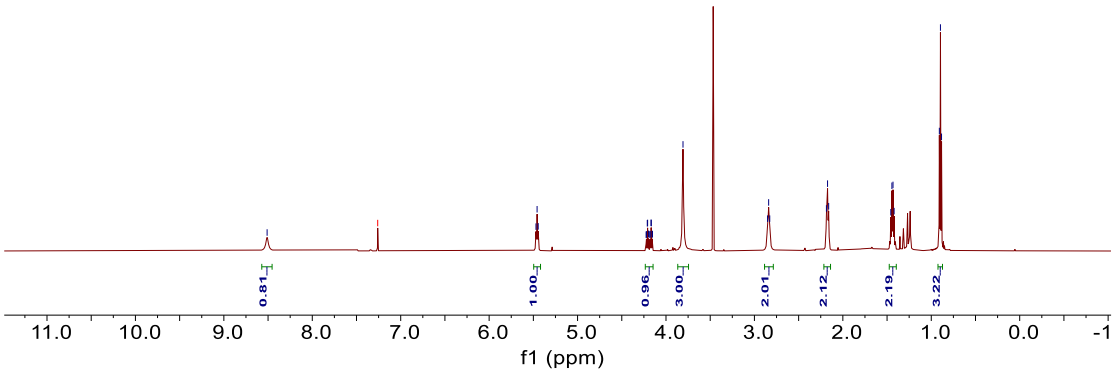
^{19}F NMR spectrum for product 3v

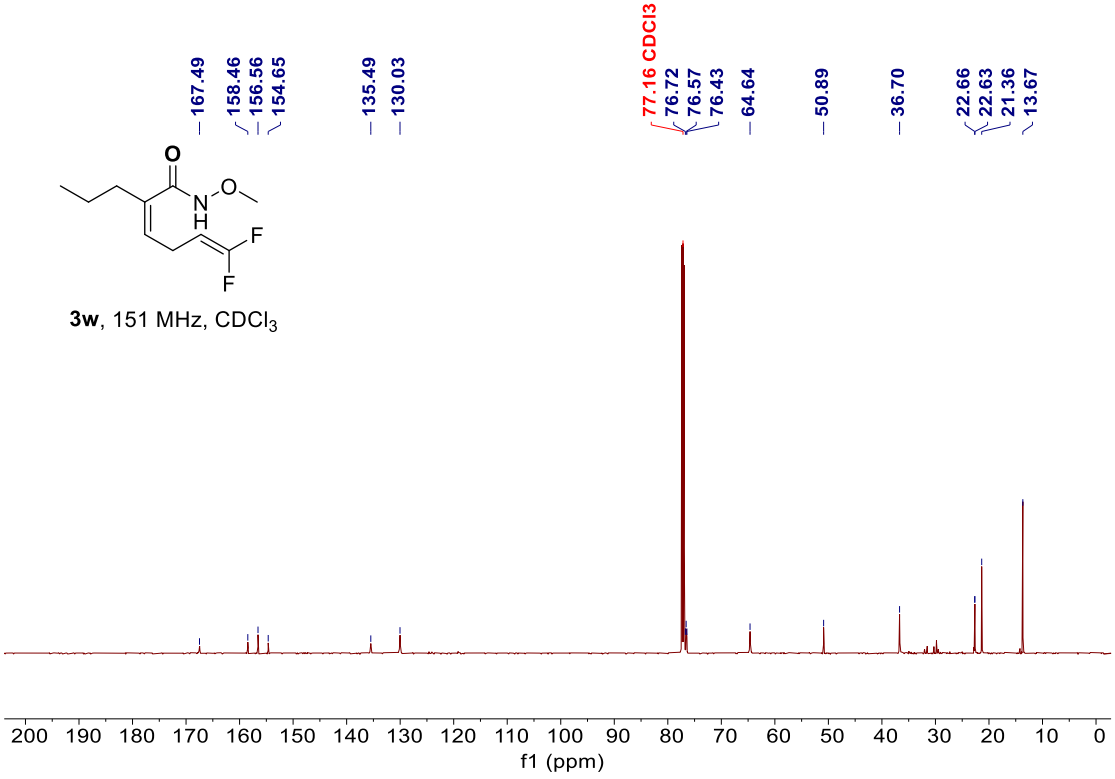


***(Z)*-6,6-difluoro-*N*-methoxy-2-propylhexa-2,5-dienamide (3w)**



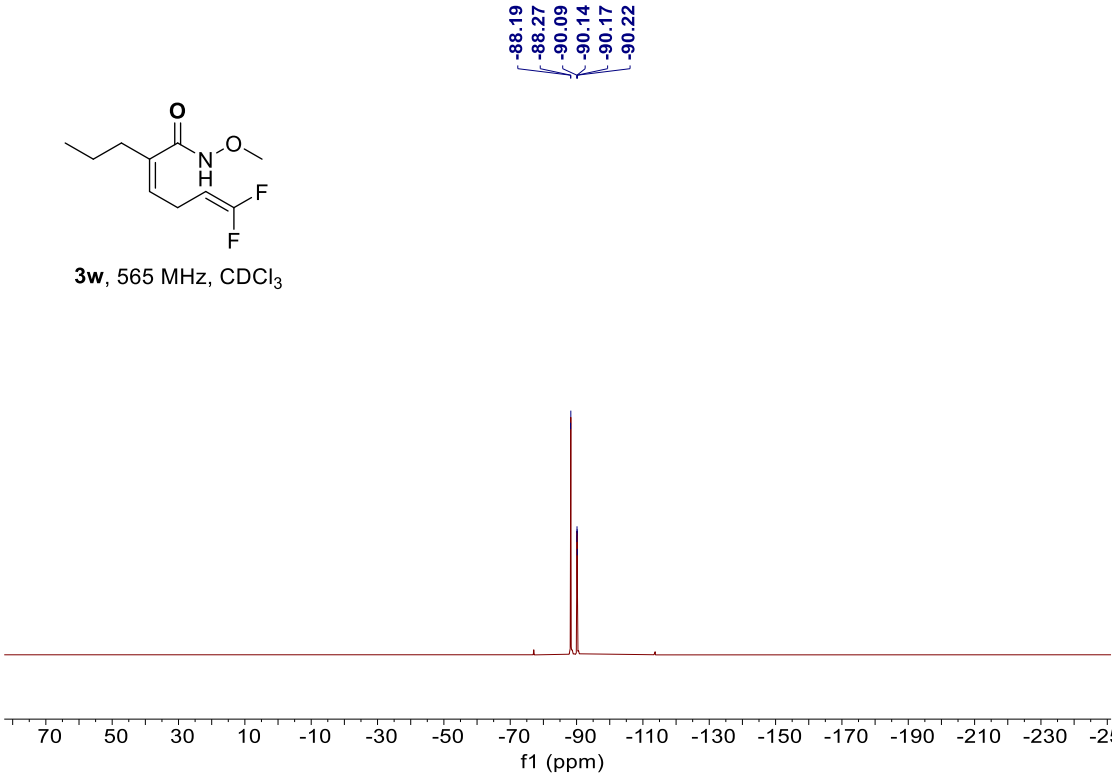
3w, 600 MHz, $CDCl_3$





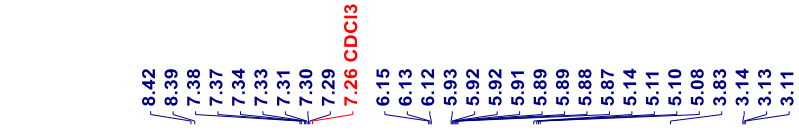
3w, 151 MHz, $CDCl_3$

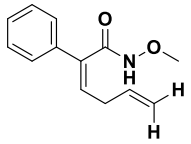
^{19}F NMR spectrum for product 3w



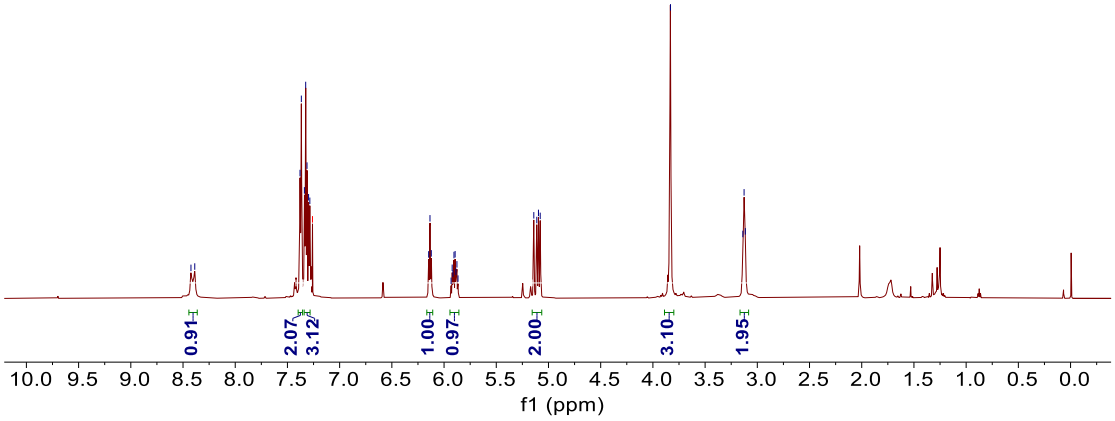
3w, 565 MHz, $CDCl_3$

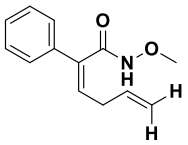
(*Z*)-*N*-methoxy-2-phenylhexa-2,5-dienamide (3x)



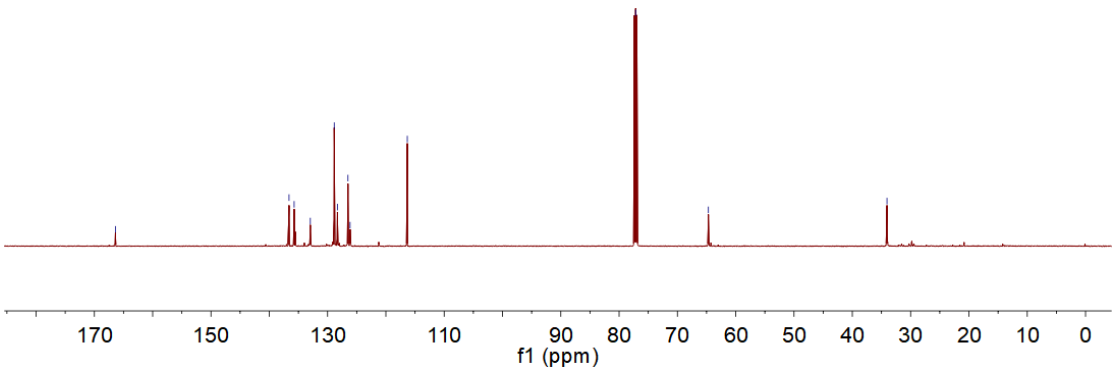


3x, 600MHz, $CDCl_3$

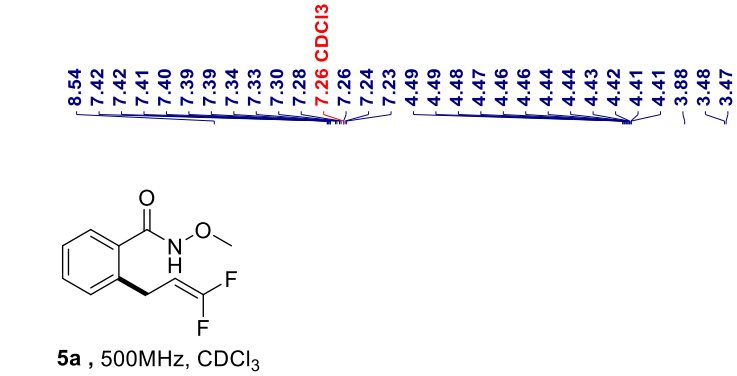




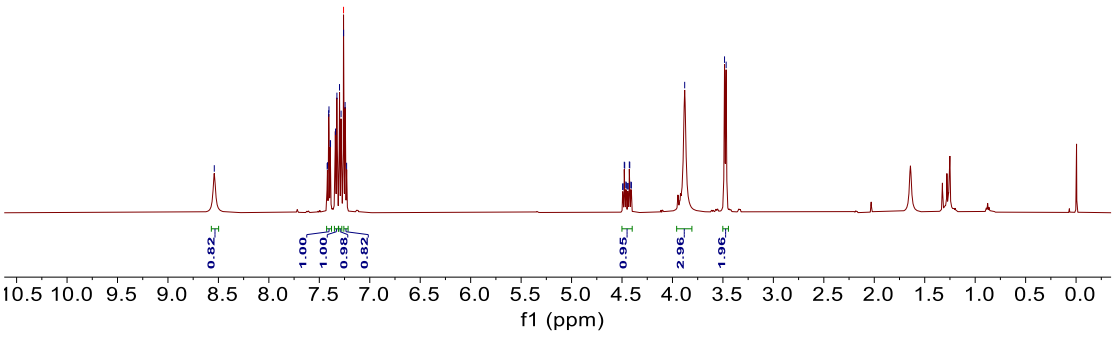
3x, 151MHz, $CDCl_3$

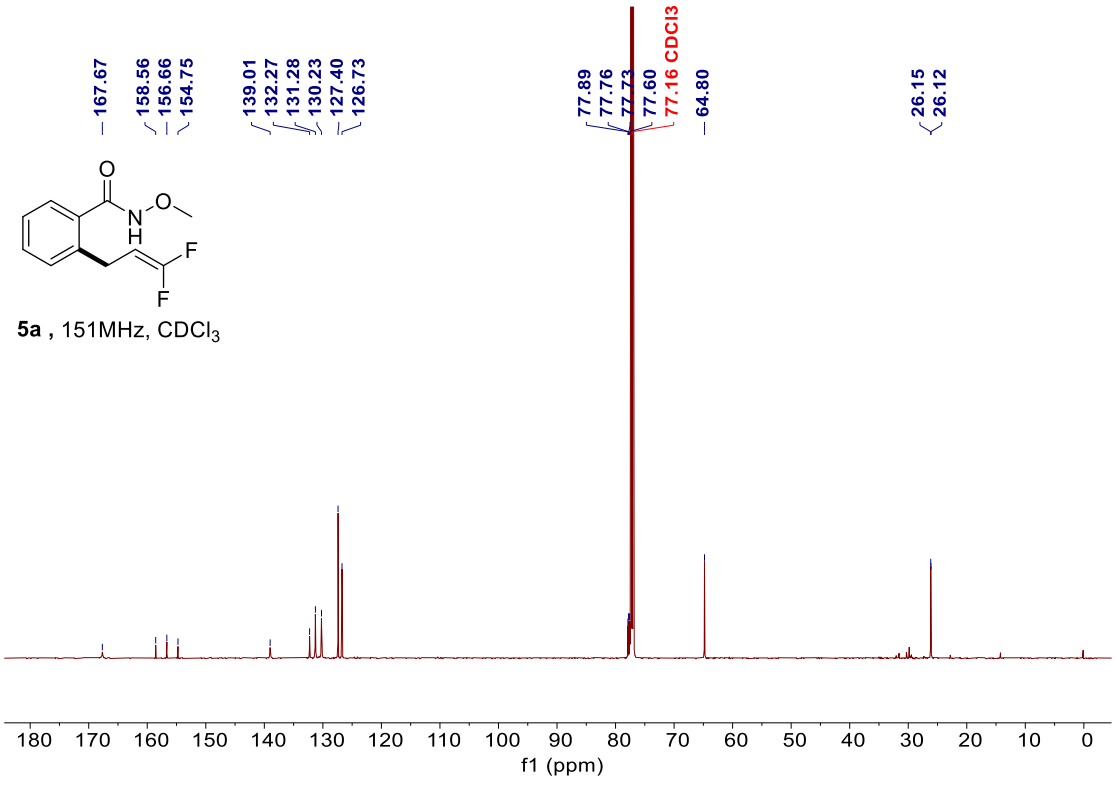


2-(3,3-difluoroallyl)-N-methoxybenzamide (5a)



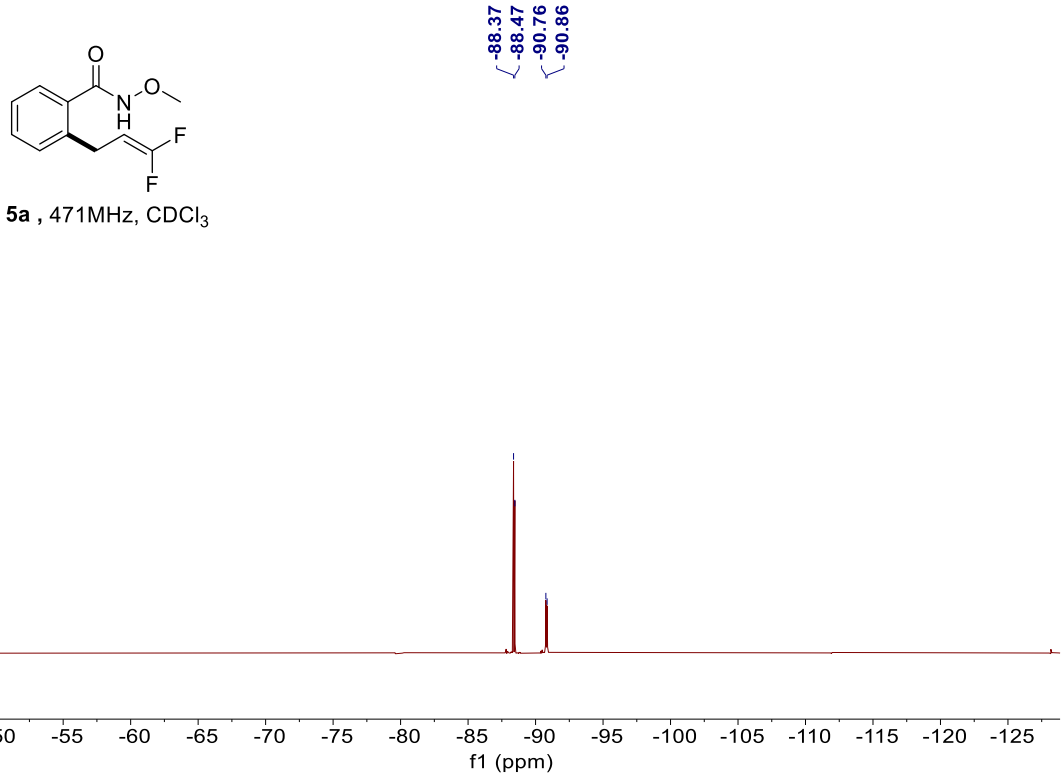
5a , 500MHz, $CDCl_3$





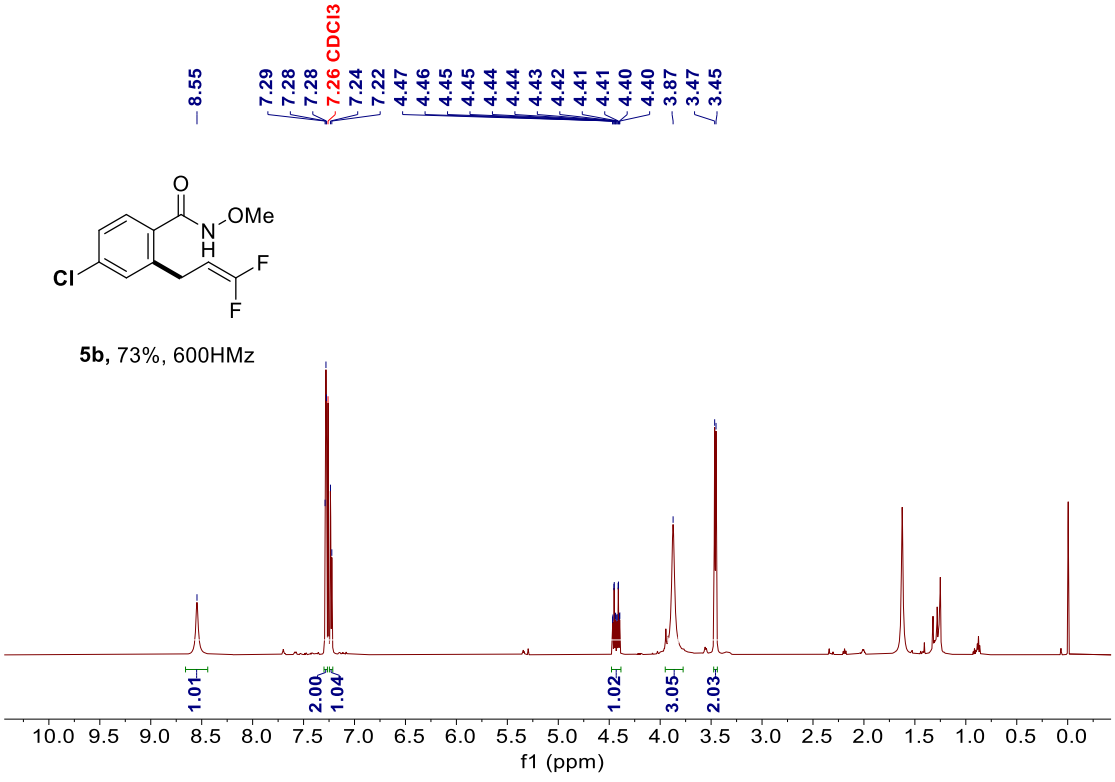
5a , 151MHz, $CDCl_3$

^{19}F NMR spectrum for product 5a

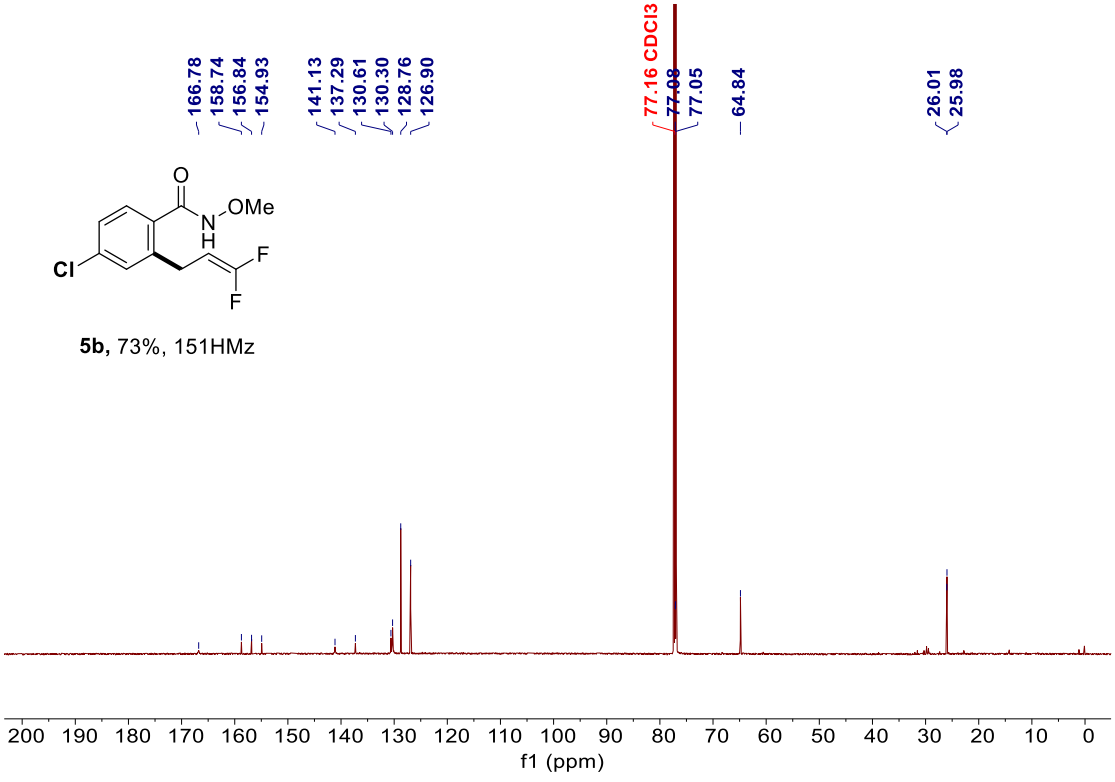


5a , 471MHz, $CDCl_3$

4-chloro-2-(3,3-difluoroallyl)-N-methoxybenzamide (5b)

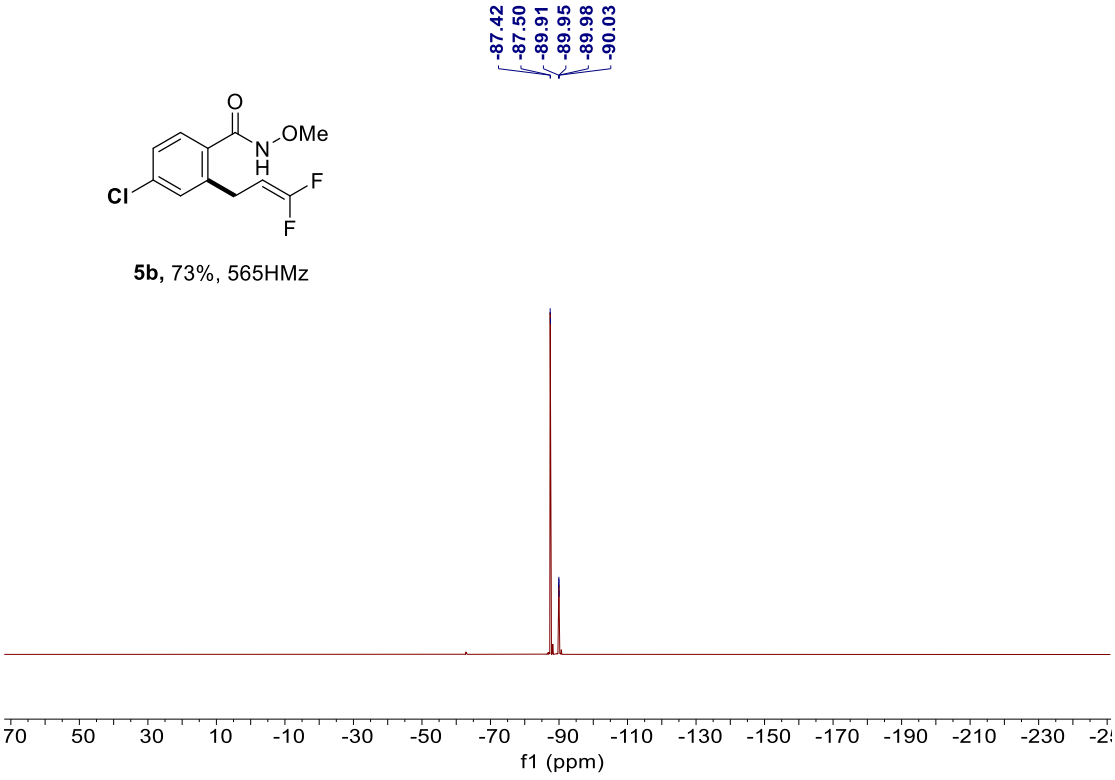


5b, 73%, 600HMz



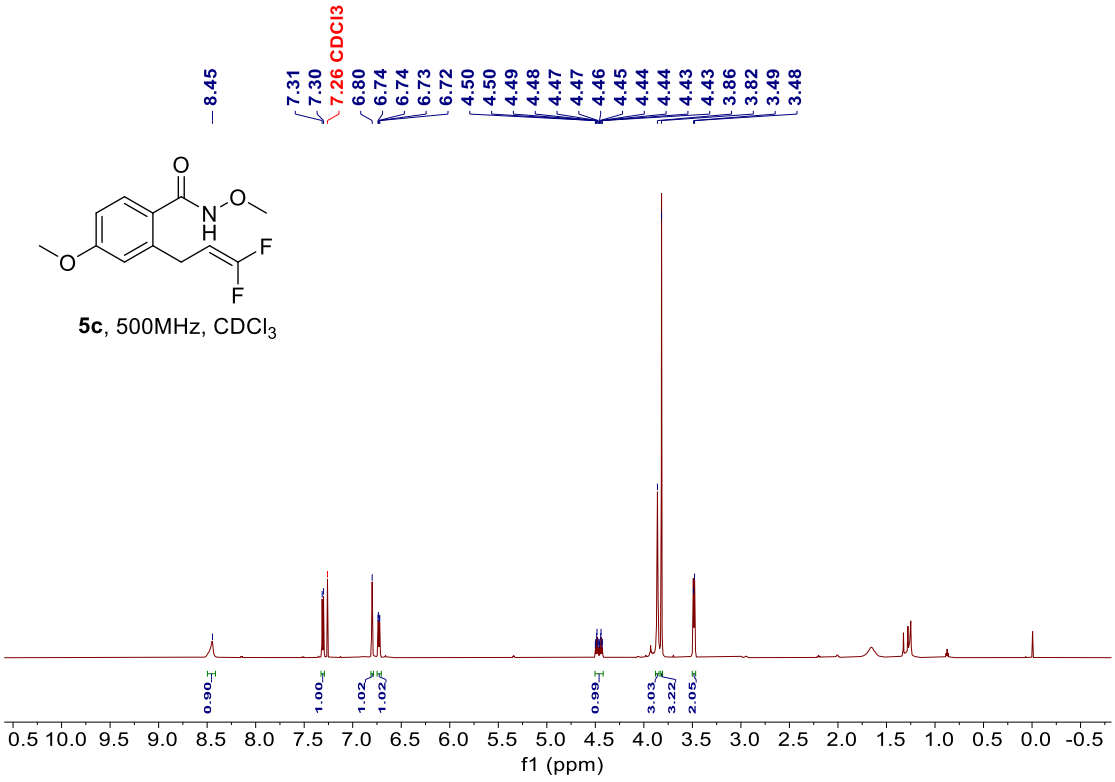
5b, 73%, 151HMz

^{19}F NMR spectrum for product 5b

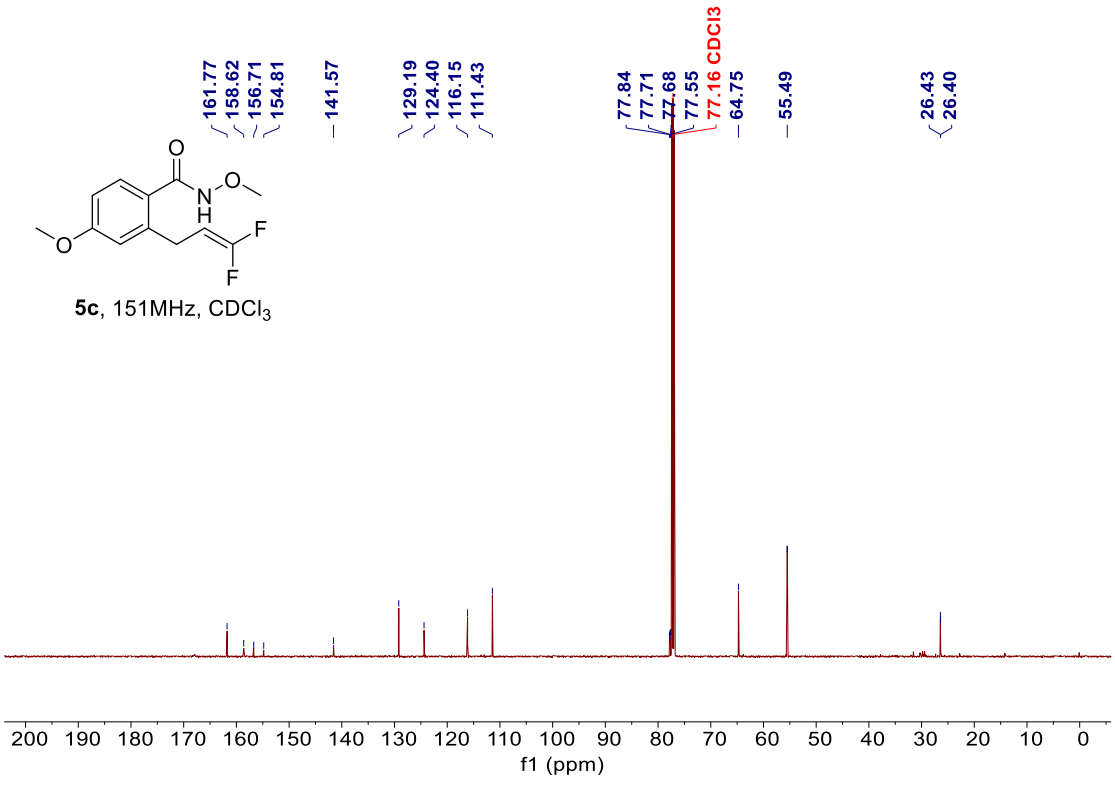


5b, 73%, 565HMz

2-(3,3-difluoroallyl)-N,4-dimethoxybenzamide (5c)

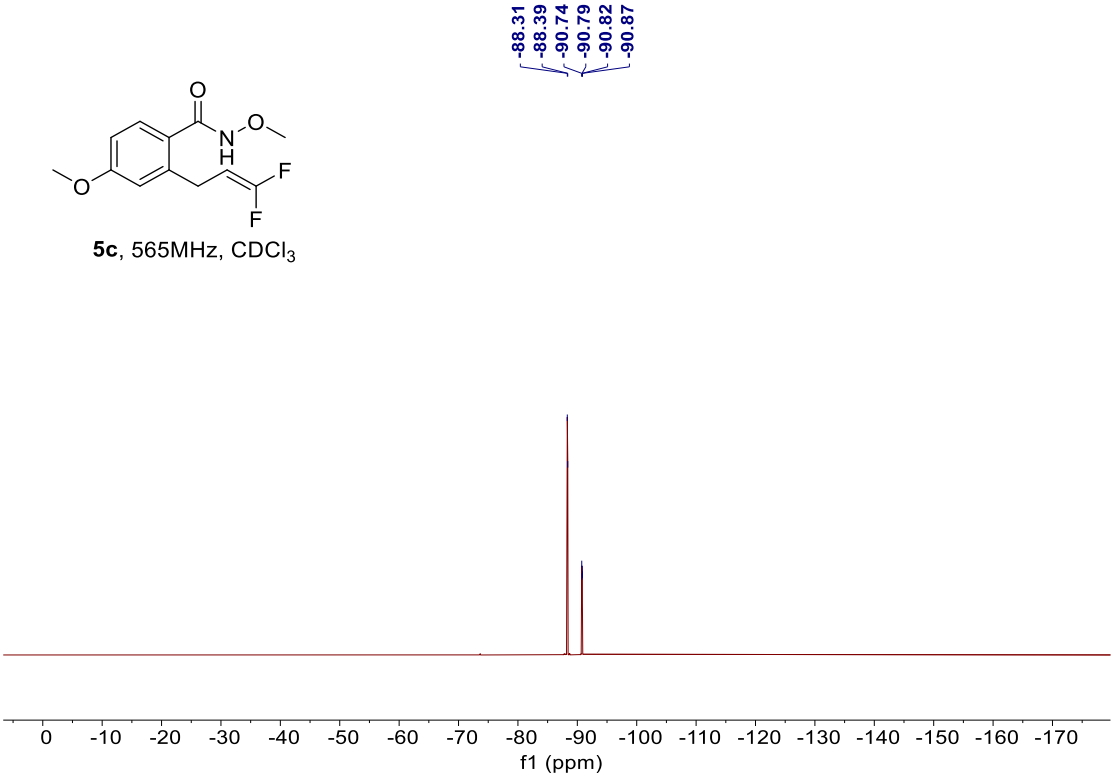


5c, 500MHz, $CDCl_3$



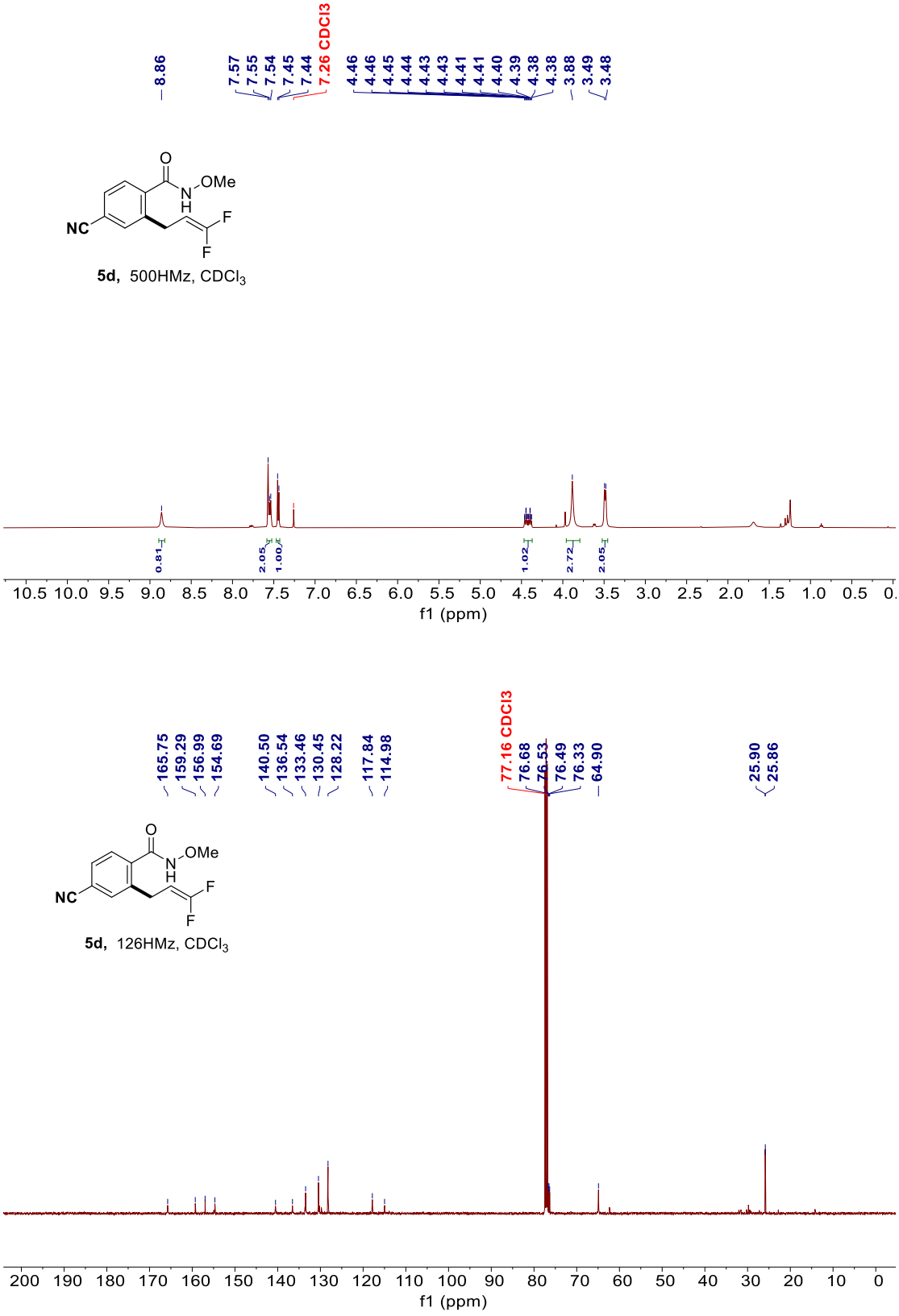
5c, 151MHz, $CDCl_3$

^{19}F NMR spectrum for product 5c



5c, 565MHz, $CDCl_3$

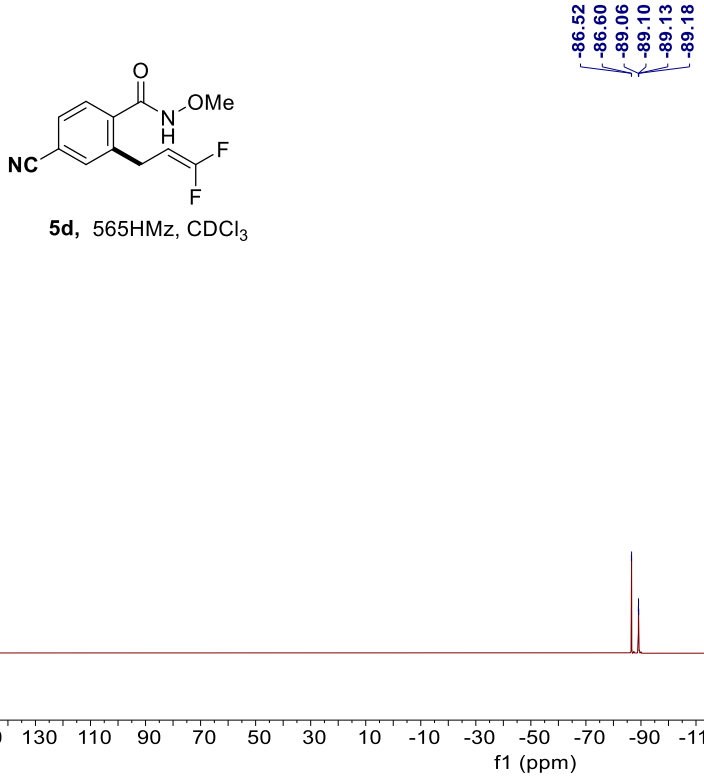
4-cyano-2-(3,3-difluoroallyl)-*N*-methoxybenzamide (5d)



5d, 500HMz, $CDCl_3$

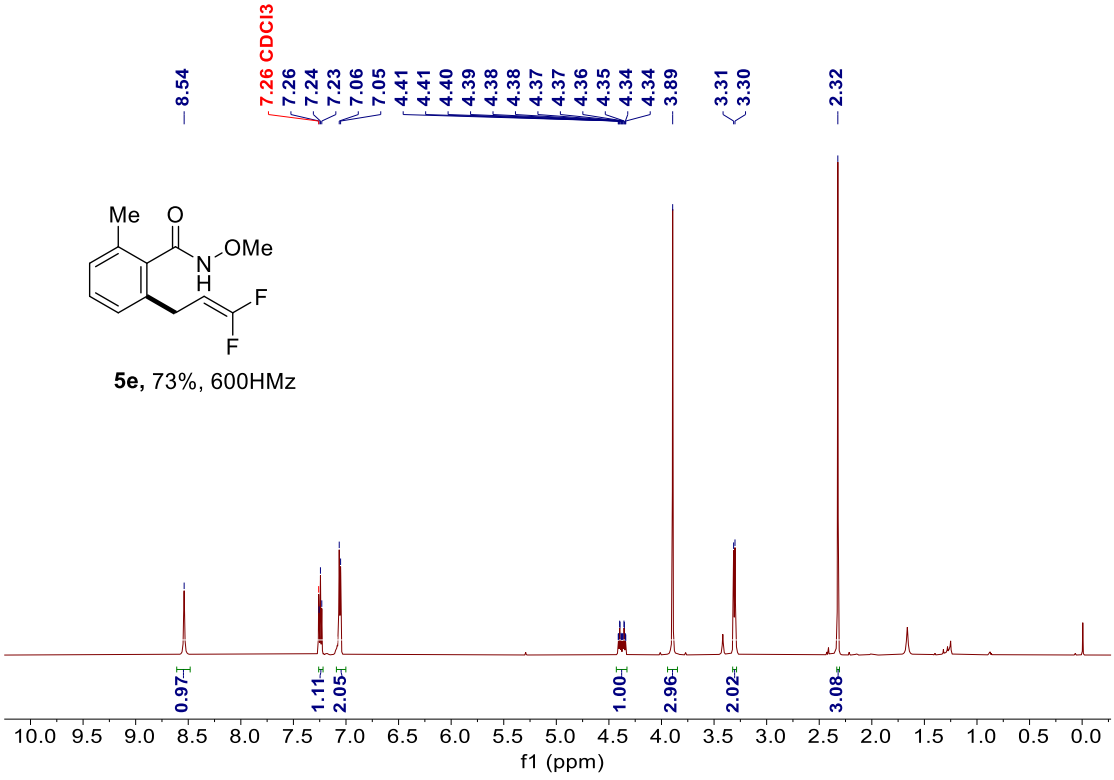
5d, 126HMz, $CDCl_3$

^{19}F NMR spectrum for product 5d

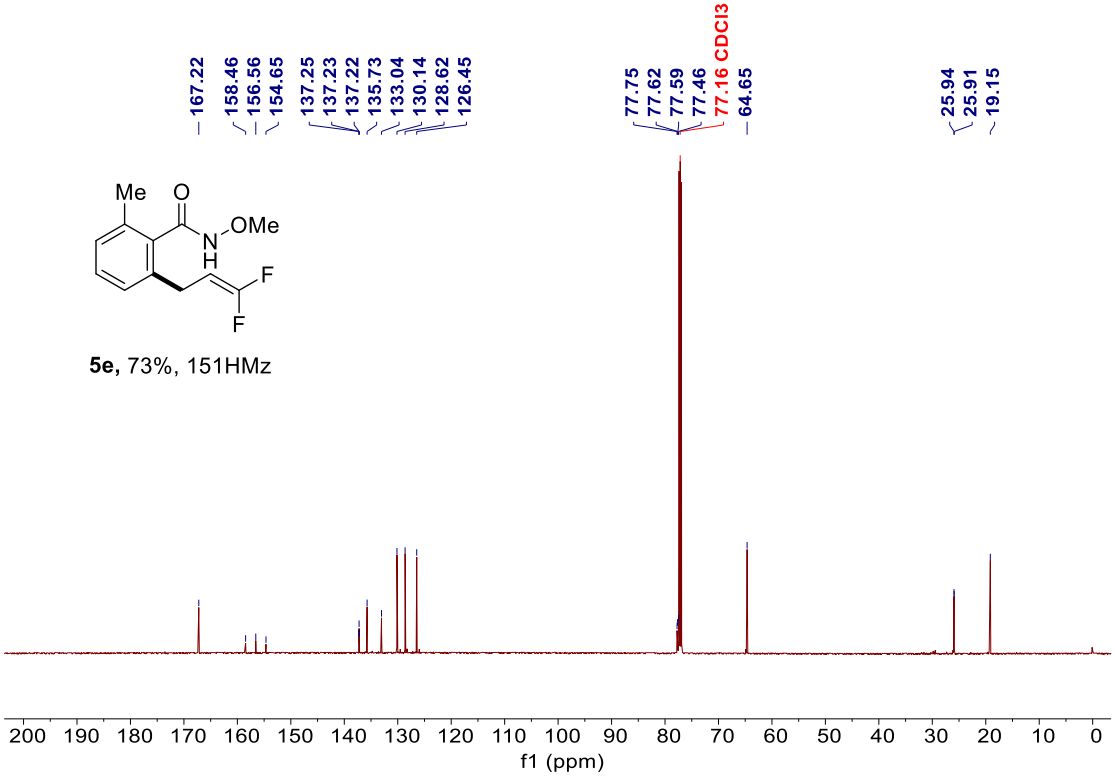


5d, 565HMz, $CDCl_3$

2-(3,3-difluoroallyl)-N-methoxy-6-methylbenzamide (5e)

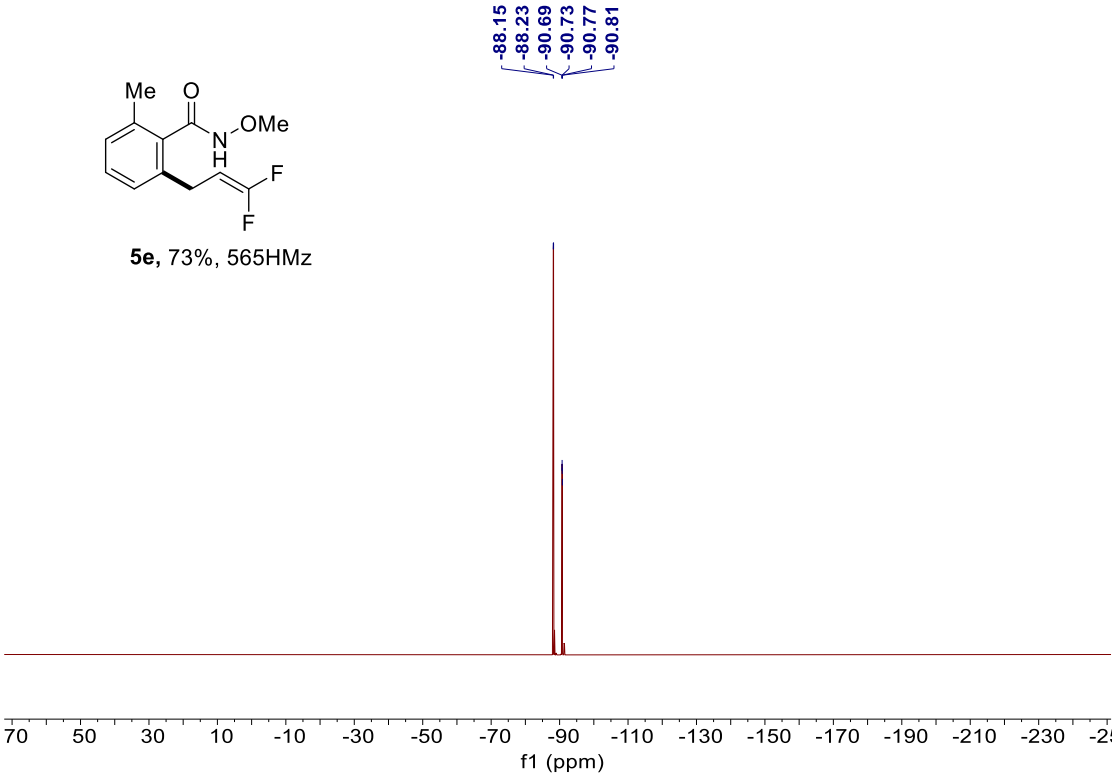


5e, 73%, 600HMz



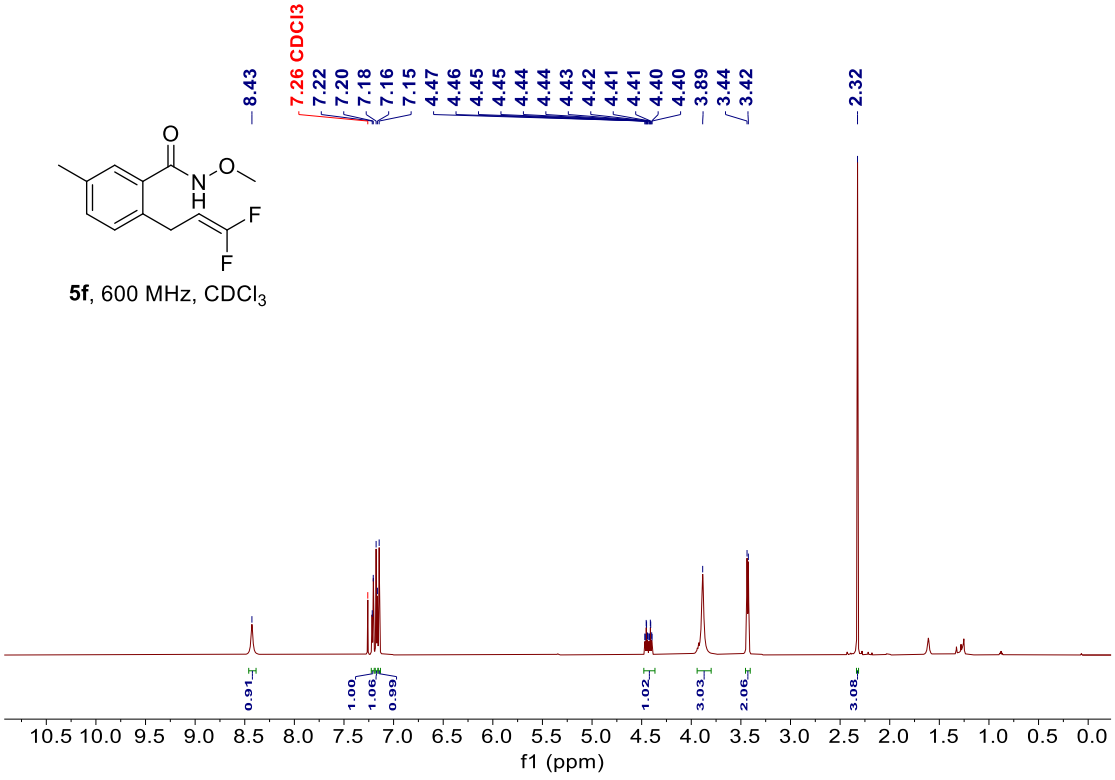
5e, 73%, 151HMz

^{19}F NMR spectrum for product 5e

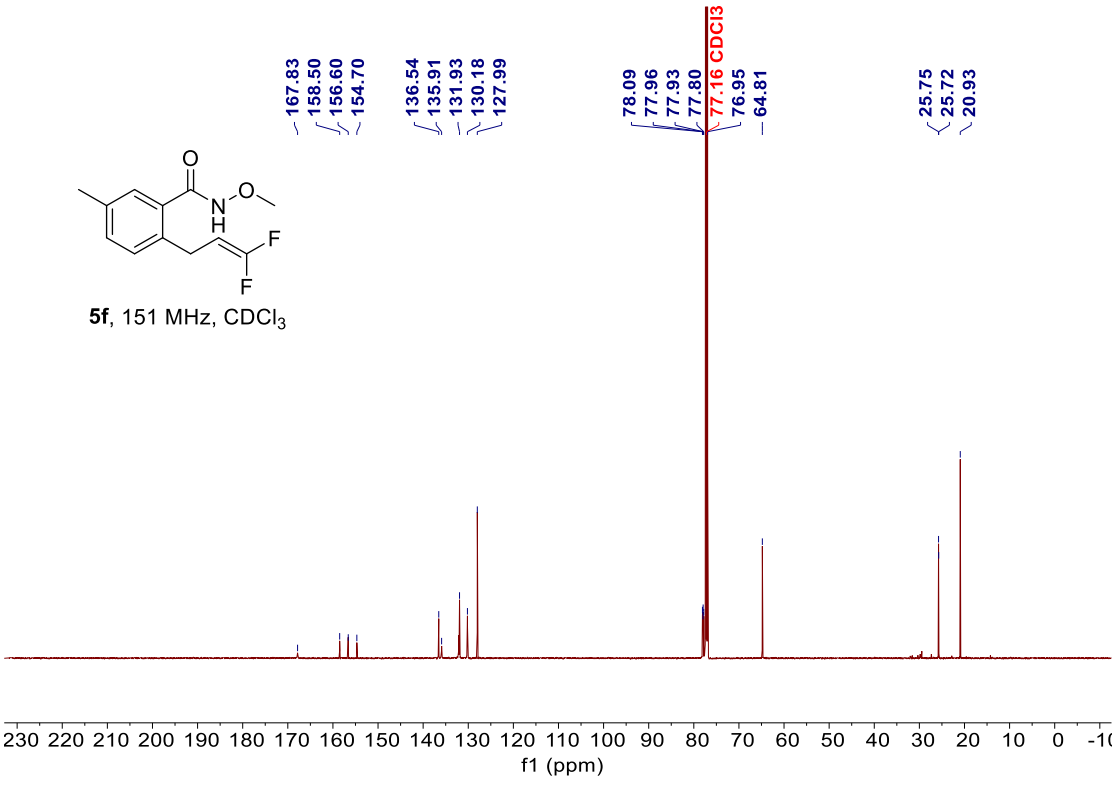


5e, 73%, 565HMz

2-(3,3-difluoroallyl)-N-methoxy-5-methylbenzamide (5f)

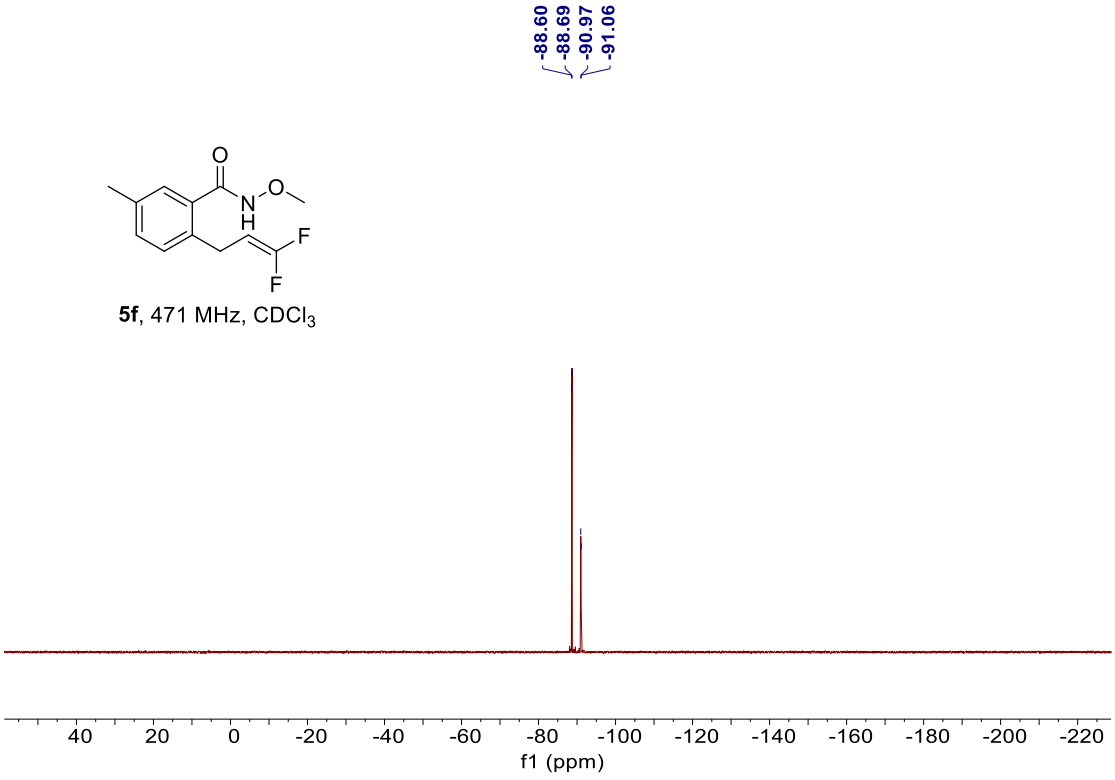


5f, 600 MHz, $CDCl_3$

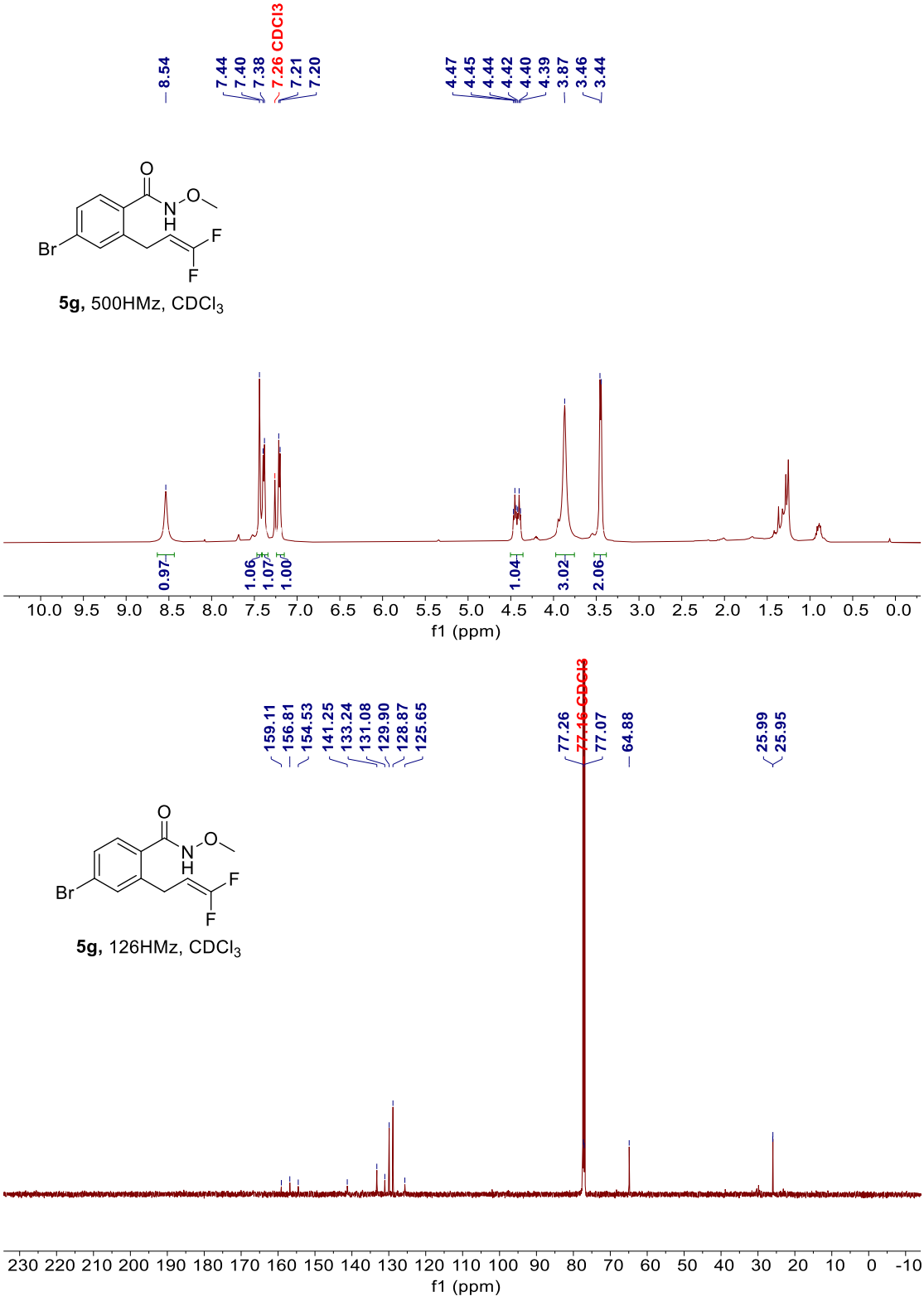


5f, 151 MHz, $CDCl_3$

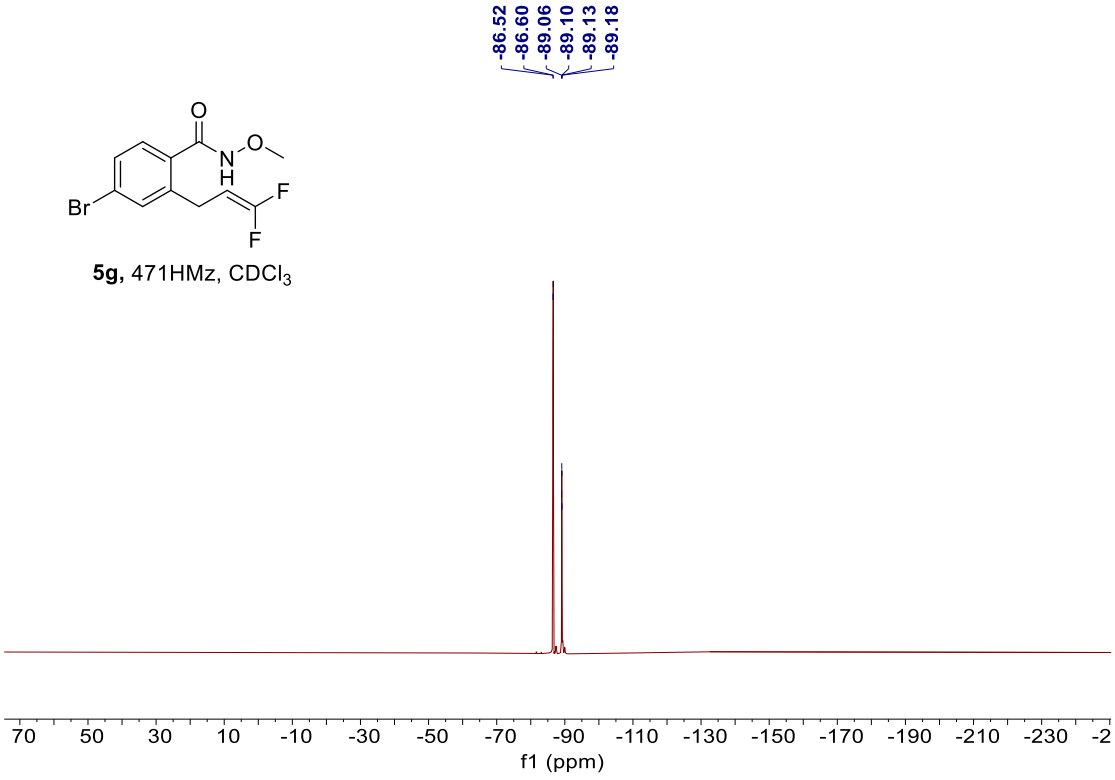
^{19}F NMR spectrum for product 5f



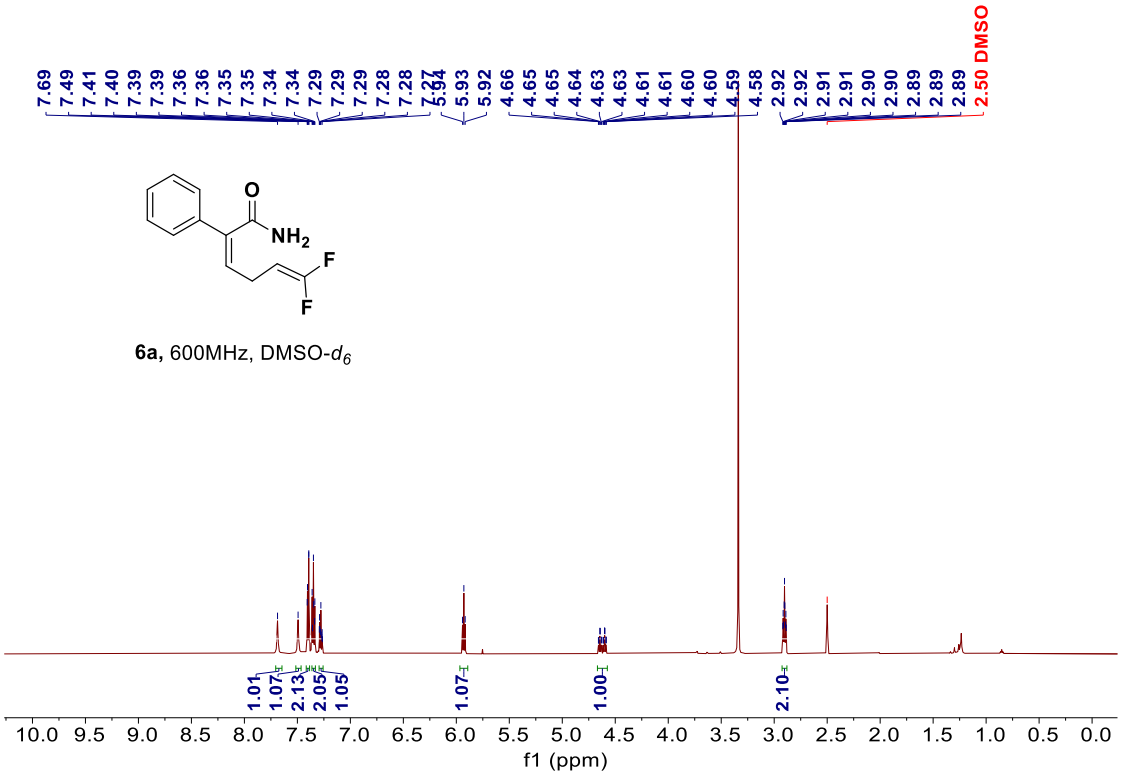
4-bromo-2-(3,3-difluoroallyl)-N-methoxybenzamide (5g)



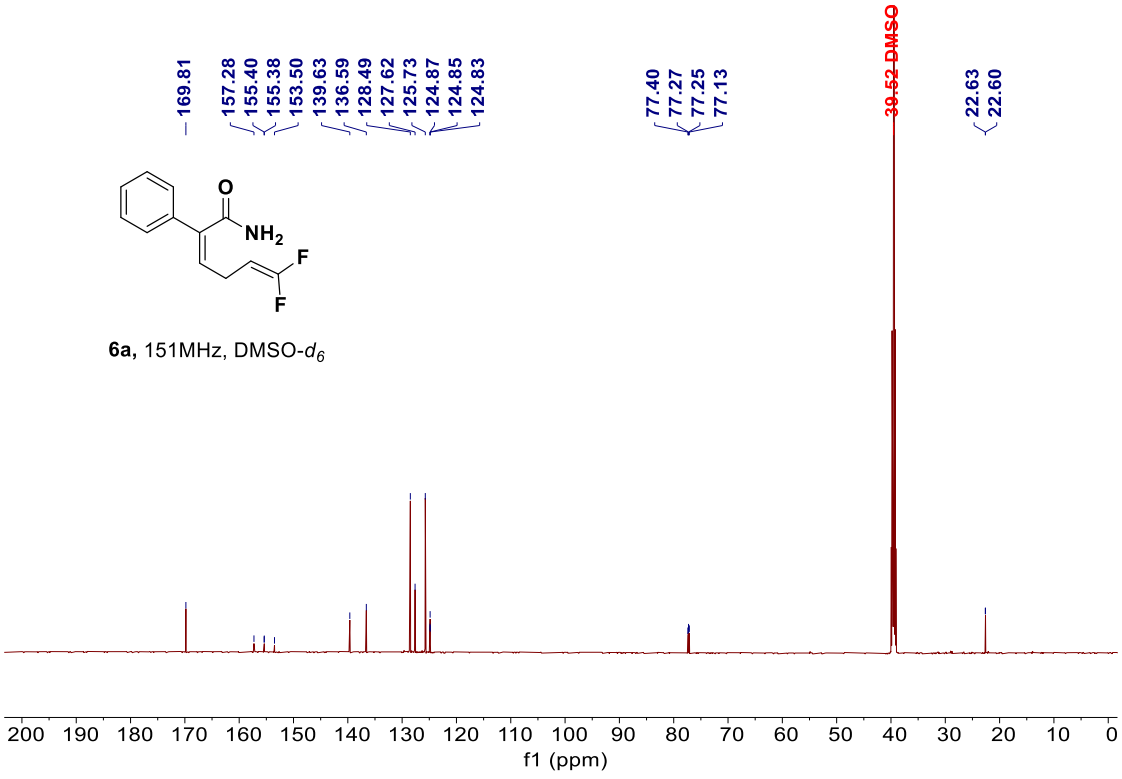
^{19}F NMR spectrum for product 5g



(*Z*)-6,6-difluoro-2-phenylhexa-2,5-dienamide (6a)

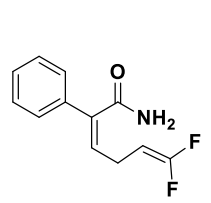


6a, 600MHz, DMSO-d_6



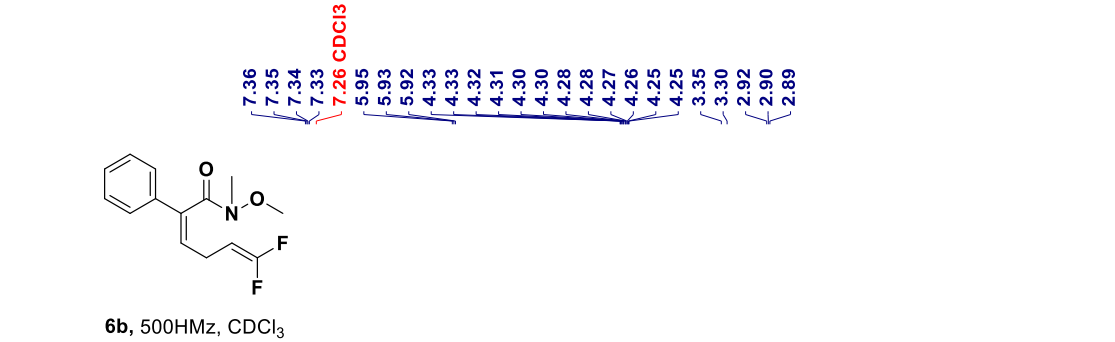
6a, 151MHz, DMSO-d_6

^{19}F NMR spectrum for product 6a

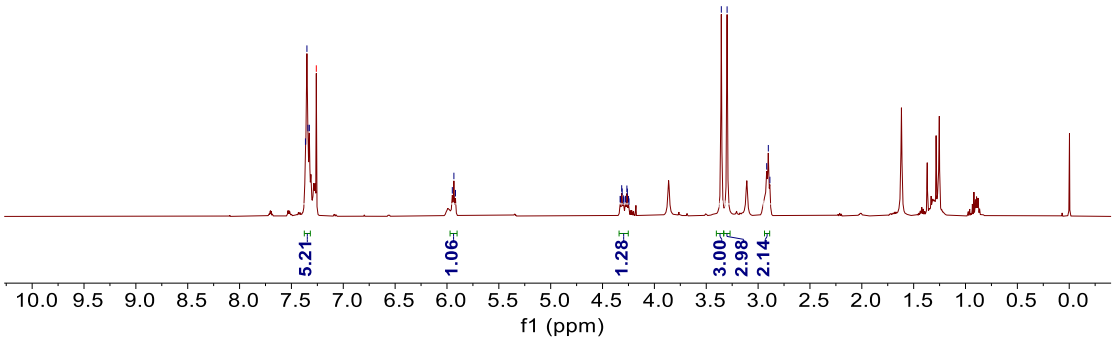


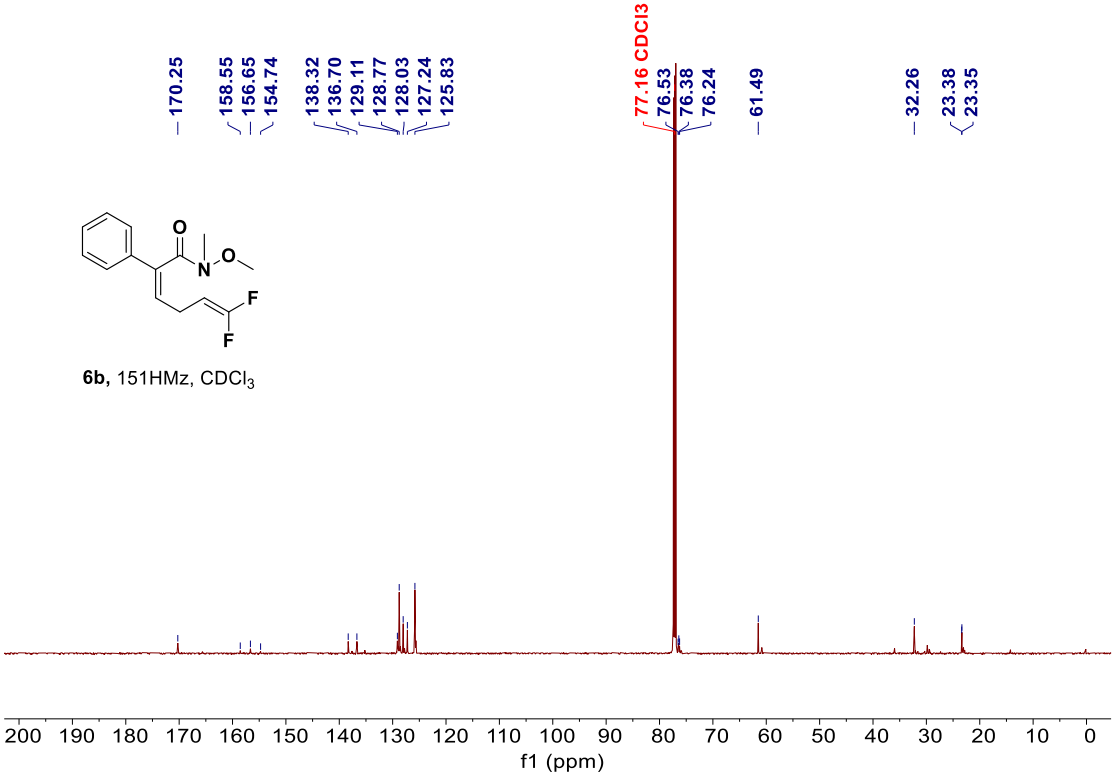
6a, 565MHz, DMSO-d_6

(*Z*)-6,6-difluoro-N-methoxy-*N*-methyl-2-phenylhexa-2,5-dienamide (6b)



6b, 500HMz, $CDCl_3$





6b, 151HMz, $CDCl_3$

^{19}F NMR spectrum for product 6b