Diethylzinc-Mediated Radical 1,2-Addition of Alkenes and Alkynes

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Supporting Information

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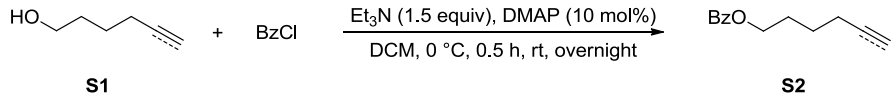
I. General Information

All air or moisture sensitive reactions were conducted in oven-dried glassware under nitrogen atmosphere. Ethyl iododifluoroacetate and diethylzinc (1.0 mol/L in hexane, EnergySeal) were purchased from *Energy Chemical* and used as received. Acetonitrile (99.9%, for HPLC) was purchased from *Sigma Aldrich* and used as received. Unless otherwise stated, chemicals and reagents were used as received. Flash column chromatography was performed over silica gel (200-300 mesh) purchased from *Qindao Bangkai Co., China*. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on a Bruker AV 500 MHz NMR spectrometer using residue solvent peaks as an internal standard (^{1}H NMR: $CHCl_3$ at 7.26 ppm, ^{13}C NMR: $CDCl_3$ at 77.0 ppm). HRMS were recorded on an Agilent 6545 Q-TOF LC/MS instrument with electrospray ionization (ESI) technique.

II. Preparation of Materials

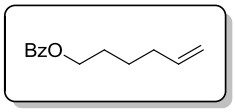
2.1. Synthesis of Benzoate Substrates



S1 **S2**

To a solution of **S1** (3.0 mmol)**,** DAMP (37 mg, 0.3 mmol, 0.1 equiv), and triethylamine (455 mg, 4.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 was added benzoyl chloride (525 mg, 3.75 mmol,1.25 equiv) dropwise at 0 °C. The resulting mixture was stirred at 0 °C for 0.5 hour, and then at room temperature overnight. After completion, the reaction was quenched with water and extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40/1) to afford the corresponding pure product.

Hex-5-en-1-yl benzoate (S2a)



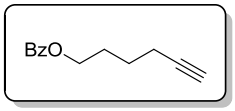
Colorless oil, 610 mg, 100% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 – 8.03 (m, 2H), 7.61 – 7.55 (m, 1H), 7.49 – 7.42 (m, 2H), 5.85 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 1H), 5.06 (dq, *J* = 17.1, 1.7 Hz, 1H), 5.01 (ddt, *J* = 10.2, 2.3, 1.3 Hz, 1H), 4.35 (t, *J* = 6.6 Hz, 2H), 2.21 – 2.12 (m, 2H), 1.81 (dq, *J* = 8.5, 6.6 Hz, 2H), 1.58 (tt, *J* = 9.9, 6.5 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 138.3, 132.8, 130.5, 129.5, 128.3, 114.8, 64.9, 33.3, 28.2, 25.3.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{16}O_2Na$: 227.1043; found: 227.1042.

Hex-5-yn-1-yl benzoate (S2b)



Colorless oil, 605 mg, 100% yield.

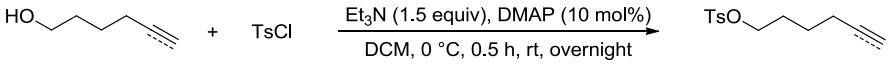
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.01 (m, 2H), 7.59 – 7.53 (m, 1H), 7.49 – 7.40 (m, 2H), 4.36 (t, *J* = 6.5 Hz, 2H), 2.29 (td, *J* = 7.0, 2.7 Hz,

2H), 2.00 (t, *J* = 2.6 Hz, 1H), 1.91 (ddt, *J* = 9.6, 8.2, 6.4 Hz, 2H), 1.77 – 1.66 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 132.8, 130.2, 129.4, 128.2, 83.7, 68.7, 64.3, 27.7, 25.0, 18.0.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{14}O_2Na$: 225.0886; found: 225.0883.

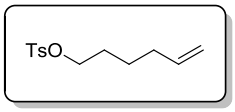
2.2 Synthesis of Tosylate Substrates



S1 **S3**

To a solution of **S1** (3.0 mmol)**,** DAMP (37 mg, 0.3 mmol, 0.1 equiv), and triethylamine (455 mg, 4.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 was added *p*-toluenesulfonyl chloride (715 mg, 3.75 mmol, 1.25 equiv) in potions at 0 °C. The resulting mixture was stirred at 0 °C for 0.5 hour, and then at room temperature overnight. After completion, the reaction was quenched with water and extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to afford the corresponding pure product.

Hex-5-en-1-yl 4-methylbenzenesulfonate (S3a)



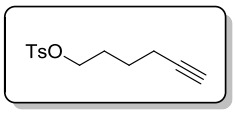
Colorless oil, 501 mg, 66% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 5.73 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.03 – 4.90 (m, 2H), 4.04 (t, *J* = 6.4 Hz, 2H), 2.46 (s, 3H), 2.06 – 1.97 (m, 2H), 1.66 (dq, *J* = 8.4, 6.5 Hz, 2H), 1.47 – 1.38 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 137.8, 133.2, 129.8, 127.8, 115.0, 70.4, 32.8, 28.1, 24.5, 21.6.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{18}O_3SNa$: 277.0869; found: 277.0867.

Hex-5-yn-1-yl 4-methylbenzenesulfonate (S3b)



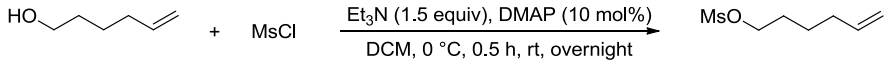
Colorless oil, 433 mg, 57% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 4.07 (t, *J* = 6.3 Hz, 2H), 2.47 (s, 3H), 2.18 (td, *J* = 6.9, 2.6 Hz, 2H), 1.94 (t, *J* = 2.7 Hz, 1H), 1.85 – 1.75 (m, 2H), 1.57 (p, *J* = 7.1 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 133.1, 129.8, 127.8, 83.4, 69.9, 68.9, 27.7, 24.2, 21.6, 17.7.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{16}O_3SNa$: 275.0712; found: 275.0711.

2.3 Synthesis of Mesylate Substrate

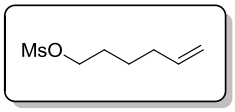


S1a **S4a**

To a solution of **S1a** (1000 mg, 10 mmol) **,** DAMP (122 mg, 1 mmol, 0.1 equiv), and triethylamine (1515 mg, 15 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 was added

methylsulfonyl chloride (1432 mg, 12.5 mmol, 1.25 equiv) dropwise at 0 °C. The resulting mixture was stirred at 0 °C for 0.5 hour, and then at room temperature overnight. After completion, the reaction was quenched with water and extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to afford the corresponding pure product.

Hex-5-en-1-yl methanesulfonate (S4a)



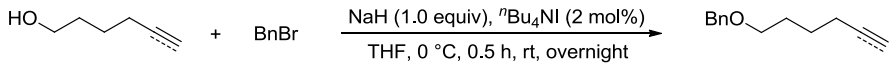
Pale yellow oil, 1770 mg, 99% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.12 – 4.96 (m, 2H), 4.25 (t, *J* = 6.5 Hz, 2H), 3.02 (s, 3H), 2.16 – 2.08 (m, 2H), 1.83 – 1.73 (m, 2H), 1.53 (tt, *J* = 10.1, 6.5 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 137.8, 115.2, 69.9, 37.3, 32.9, 28.5, 24.6.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_7H_{14}O_3SNa$: 201.0556; found: 201.0554.

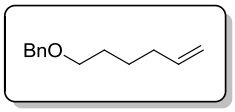
2.4 Synthesis of Benzyl-Protected Alcohol Substrates



S1 **S5**

To a solution of **S1** (2.2 mmol, 1.1 equiv) and ^{n}Bu$_4$NI (15 mg, 0.04 mmol, 0.02 equiv) in anhydrous THF was added NaH (80 mg, 2 mmol, 1.0 equiv) in potions at 0 °C. After stirring at 0 °C for 10 minutes, benzyl bromide (376 mg, 2.2 mmol, 1.1 equiv) was added dropwise. The resulting mixture was stirred at 0 °C for additional 20 minutes, and then at room temperature overnight. After completion, the reaction was quenched with saturated NH_4Cl and extracted with diethyl ether. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40/1) to afford the corresponding pure product.

((Hex-5-en-1-yloxy)methyl)benzene (S5a)



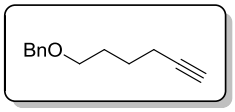
Colorless oil, 357 mg, 94 % yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 4H), 7.34 – 7.29 (m, 1H), 5.84 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.04 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.98 (ddt, *J* = 10.2, 2.3, 1.2 Hz, 1H), 4.54 (s, 2H), 3.51 (t, *J* = 6.6 Hz, 2H), 2.15 – 2.06 (m, 2H), 1.71 – 1.64 (m, 2H), 1.55 – 1.47 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 138.74, 138.66, 128.3, 127.6, 127.5, 114.5, 72.9, 70.2, 33.5, 29.2, 25.5.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{18}ONa$: 213.1250; found: 213.1245.

((Hex-5-yn-1-yloxy)methyl)benzene (S5b)



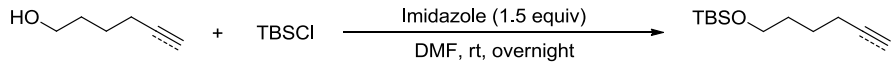
Colorless oil, 332 mg, 88% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 4H), 7.34 – 7.26 (m, 1H), 4.54 (s, 2H), 3.53 (t, *J* = 6.3 Hz, 2H), 2.25 (td, *J* = 7.0, 2.7 Hz, 2H), 1.98 (t, *J* = 2.7 Hz, 1H), 1.82 – 1.73 (m, 2H), 1.67 (tdd, *J* = 10.0, 4.8, 2.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5, 128.3, 127.6, 127.5, 84.3, 72.9, 69.7, 68.4, 28.7, 25.2, 18.2.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{16}ONa$: 211.1093; found: 211.1089.

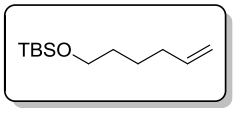
2.5 Synthesis of TBS-Protected Alcohol Substrates



S1 **S6**

To a solution of **S1**(3.0 mmol) and imidazole (306 mg, 4.5 mmol, 1.5 equiv) in anhydrous DMF was added TBSCl (543 mg, 3.6 mmol, 1.2 equiv) in one potion. After stirring at room temperature overnight, the reaction was quenched with water and extracted with diethyl ether. The combined organic layers were washed with saturated NH_4Cl for 5 times, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether) to afford the corresponding pure product.

***tert*-butyl(hex-5-en-1-yloxy)dimethylsilane (S6a)**



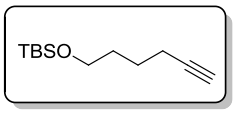
Colorless oil, 579 mg, 90% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 1H), 5.03 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.96 (ddt, *J* = 10.2, 2.3, 1.2 Hz, 1H), 2.11 – 2.06 (m, 2H), 1.59 – 1.52 (m, 2H), 1.49 – 1.41 (m, 2H), 0.92 (s, 9H), 0.07 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9, 114.3, 63.1, 33.5, 32.3, 26.0, 25.2, 18.4, -5.3.

HRMS (ESI) m/z: $[M+K]^+$ calcd for $C_{12}H_{26}OSiK$: 253.1385; found: 253.1405.

***tert*-butyl(hex-5-yn-1-yloxy)dimethylsilane (S6b)**



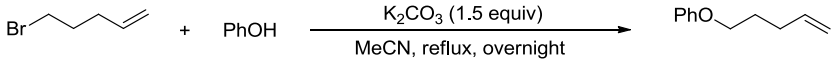
Colorless oil, 525 mg, 83% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.65 (t, *J* = 6.0 Hz, 2H), 2.23 (td, *J* = 6.8, 2.6 Hz, 2H), 1.96 (t, *J* = 2.7 Hz, 1H), 1.71 – 1.53 (m, 4H), 0.91 (s, 9H), 0.07 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 84.5, 68.2, 62.6, 31.8, 26.0, 25.0, 18.3, 18.2, -5.3.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_{24}OSiNa$: 235.1489; found: 235.1493.

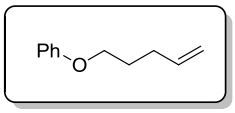
2.6 Synthesis of Phenyl Ether Substrate



S7 **S8**

A mixture of **S7** (581 mg, 3.9 mmol, 1.3 equiv), phenol (282 mg, 3 mmol, 1.0 equiv), and K_2CO_3 (621 mg, 4.5 mmol, 1.5 equiv) in anhydrous acetonitrile was heated to reflux in an oil bath. After refluxing overnight, the reaction mixture was cooled to room temperature, concentrated under reduced pressure, diluted with saturated NH_4Cl and extracted with ethyl acetate. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether) to afford the corresponding pure product.

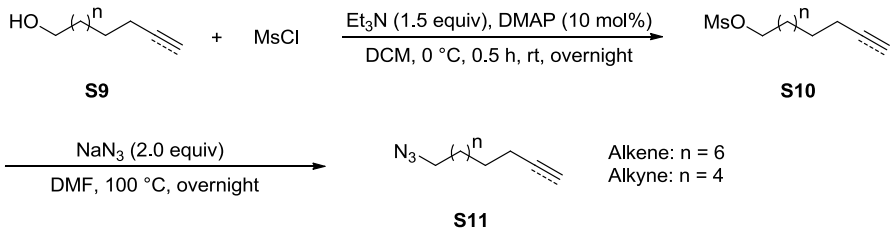
(pent-4-en-1-yloxy)benzene (S8)



Colorless oil, 403 mg, 83% yield.

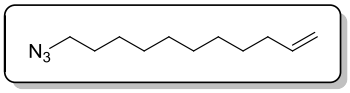
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 8.6, 7.2 Hz, 2H), 7.01 – 6.97 (m, 1H), 6.97 – 6.94 (m, 2H), 5.91 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 1H), 5.12 (dq, *J* = 17.1, 1.9 Hz, 1H), 5.06 (ddt, *J* = 10.2, 2.1, 1.2 Hz, 1H), 4.02 (t, *J* = 6.4 Hz, 2H), 2.37 – 2.23 (m, 2H), 1.99 – 1.90 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 137.8, 129.4, 120.5, 115.1, 114.5, 67.0, 30.1, 28.5.
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{11}H_{14}ONa$: 185.0937; found: 185.0935.

2.7 Synthesis of Azide Substrates



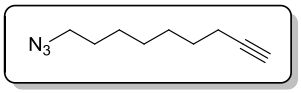
To a solution of **S9** (3.0 mmol)**,** DAMP (37 mg, 0.3 mmol, 0.1 equiv), and triethylamine (455 mg, 4.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 was added methylsulfonyl chloride (429 mg, 3.75 mmol, 1.25 equiv) dropwise at 0 °C. The resulting mixture was stirred at 0 °C for 0.5 hour, and then at room temperature overnight. After completion, the reaction was quenched with water and extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was used for the next step without further purification.
A mixture of **S10** and sodium azide (390 mg, 6 mmol, 2.0 equiv) in anhydrous DMF was heated at 100 °C in an oil bath overnight. After cooling to room temperature, the reaction was quenched with water and extracted with diethyl ether. The combined organic layers were washed with saturated NH_4Cl for 5 times, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether) to afford the corresponding pure product.

11-azidoundec-1-ene (S11a)



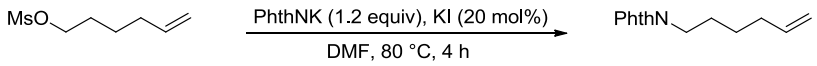
Colorless oil, 490 mg, 84% yield.
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.02 (dq, *J* = 17.2, 1.8 Hz, 1H), 4.95 (dq, *J* = 10.3, 1.4 Hz, 1H), 3.28 (t, *J* = 7.0 Hz, 2H), 2.12 – 2.01 (m, 2H), 1.68 – 1.56 (m, 2H), 1.46 – 1.25 (m, 12H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 139.1, 114.1, 51.5, 33.8, 29.4, 29.3, 29.1, 29.0, 28.9, 28.8, 26.7.
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{11}H_{21}N_3Na$: 218.1628; found: 218.1626.

9-azidonon-1-yne (S11b)



Colorless oil, 393 mg, 79% yield.
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.28 (t, *J* = 6.9 Hz, 2H), 2.21 (td, *J* = 7.3, 2.9 Hz, 2H), 1.96 (t, *J* = 2.6 Hz, 1H), 1.62 (p, *J* = 6.9 Hz, 2H), 1.55 (p, *J* = 7.0 Hz, 2H), 1.49 – 1.32 (m, 6H),
^{13}C NMR (125 MHz, $CDCl_3$) δ 84.5, 68.2, 51.4, 28.8, 28.6, 28.5, 28.3, 26.6, 18.3.
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_9H_{15}N_3Na$: 188.1158; found: 188.1155.

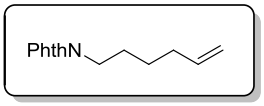
2.8 Synthesis of N-Phth-Protected Amine Substrate



S4a **S12**

A mixture of **S4a**(356 mg, 2 mmol, 2.0 mmol)**,** KI (33.2 mg, 0.2 mmol, 0.1 equiv), and potassium phthalimide (445 mg, 2.4 mmol, 1.2 equiv) in anhydrous DMF was heated at 80 °C in an oil bath for 4 hours. After cooling to room temperature, the reaction was quenched with water and extracted with diethyl ether. The combined organic layers were washed with saturated NH_4Cl for 5 times, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 8/1) to afford the corresponding pure product.

2-(hex-5-en-1-yl)isoindoline-1,3-dione (S12)



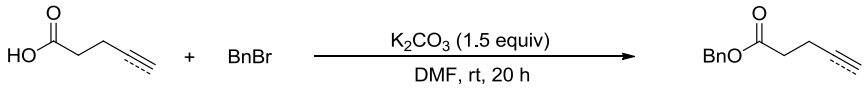
Colorless oil, 428 mg, 93% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H), 5.79 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.02 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.96 (ddt, *J* = 10.2, 2.3, 1.2 Hz, 1H), 3.70 (t, *J* = 7.3 Hz, 2H), 2.11 (dtd, *J* = 7.3, 5.9, 1.4 Hz, 2H), 1.81 – 1.66 (m, 2H), 1.52 – 1.41 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 138.2, 133.8, 132.1, 123.1, 114.8, 37.8, 33.2, 28.0, 26.1.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{14}H_{15}O_2Na$: 252.0995; found: 252.0994.

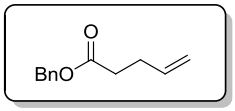
2.9 Synthesis of Azide Substrates



S13 **S14**

To a mixture of **S13** (3.0 mmol) and K_2CO_3 (621 mg, 4.5 mmol, 1.5 equiv) in anhydrous DMF was added benzyl bromide (616 mg, 3.6 mmol, 1.2 equiv) dropwise. After stirring at room temperature for 20 hours, the reaction was quenched with water and extracted with diethyl ether. The combined organic layers were washed with saturated NH_4Cl for 5 times, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40/1) to afford the corresponding pure product.

Benzyl pent-4-enoate (S14a)



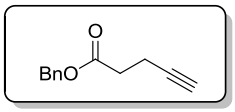
Pale yellow oil, 489 mg, 86% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 4H), 7.38 – 7.34 (m, 1H), 5.86 (ddt, *J* = 16.6, 10.2, 6.3 Hz, 1H), 5.16 (s, 2H), 5.09 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.04 (dq, *J* = 10.2, 1.4 Hz, 1H), 2.50 (ddd, *J* = 7.9, 6.6, 1.6 Hz, 2H), 2.47 – 2.40 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.7, 136.5, 136.0, 128.5, 128.1 (two peaks), 115.5, 66.1, 33.5, 28.8.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_{14}O_2Na$: 213.0886; found: 213.0881.

Benzyl pent-4-ynoate (S14b)



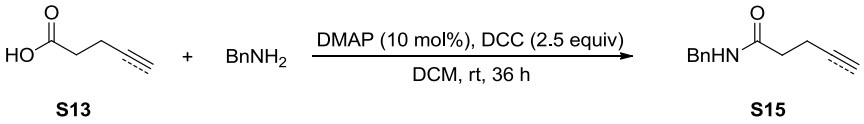
Colorless oil, 506 mg, 90% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.32 (m, 5H), 5.18 (s, 2H), 2.66 – 2.60 (m, 2H), 2.58 – 2.53 (m, 2H), 2.00 (t, *J* = 2.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5, 135.7, 128.5, 128.3, 128.2, 82.4, 69.1, 66.5, 33.3, 14.3.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_{12}O_2Na$: 211.0730; found: 211.0732.

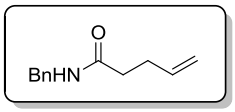
2.10 Synthesis of Azide Substrates



S13 **S15**

To a solution of **S13** (3.0 mmol, 1.5 equiv), DAMP (24 mg, 0.2 mmol, 0.1 equiv), and benzylamine (214 mg, 2 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 was added DCC (1030 mg, 5 mmol, 2.5 equiv) in one potion. After stirring at room temperature for 36 hours, the mixture was filtered through a pad of Celite, washed with CH_2Cl_2. The combined organic layers were washed with water, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1/1) to afford the corresponding pure product.

***N*-benzylpent-4-enamide (S15a)**



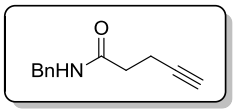
White amorphous solid, 483 mg, 85% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 8.4, 6.4 Hz, 2H), 7.31 – 7.25 (m, 3H), 6.01 (s, 1H), 5.84 (ddt, *J* = 16.8, 10.2, 6.4 Hz, 1H), 5.08 (dq, *J* = 17.1, 1.7 Hz, 1H), 5.02 (dt, *J* = 10.3, 1.5 Hz, 1H), 4.44 (d, *J* = 5.7 Hz, 2H), 2.47 – 2.38 (m, 2H), 2.35 – 2.27 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.0, 138.3, 137.0, 128.7, 127.8, 127.5, 115.6, 43.6, 35.9, 29.6.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_{15}NONa$: 212.1046; found: 212.1052.

***N*-benzylpent-4-ynamide (S15b)**



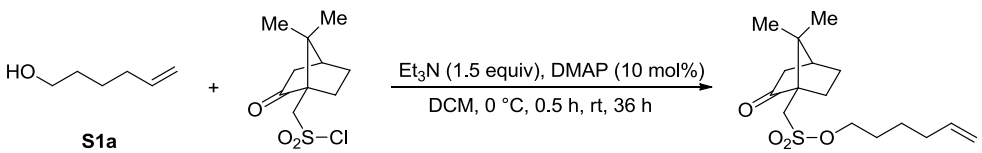
Pale yellow amorphous solid, 385 mg, 69% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 7.31 (dd, *J* = 7.2, 1.7 Hz, 3H), 5.97 (s, 1H), 4.69 – 4.17 (m, 2H), 2.59 (tt, *J* = 7.3, 6.4, 2.2 Hz, 2H), 2.46 (td, *J* = 7.1, 1.8 Hz, 2H), 2.01 (td, *J* = 2.6, 0.9 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 138.1, 128.7, 127.8, 127.5, 82.9, 69.4, 43.7, 35.4, 14.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_{13}NONa$: 210.0899; found: 210.0890.

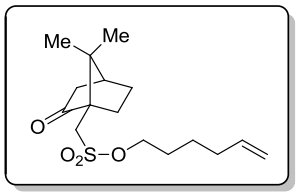
2.11. Synthesis of Camphorsulfonic Acid Derivative



S1a **S16** **S17**

To a solution of **S1a** (300 mg, 3.0 mmol), DAMP (37 mg, 0.3 mmol, 0.1 equiv), and triethylamine (455 mg, 4.5 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 was added camphorsulfonyl chloride (900 mg, 3.6 mmol, 1.2 equiv) in potions at 0 °C. The resulting mixture was stirred at 0 °C for 0.5 hour, and then at room temperature for 36 hours. After completion, the reaction was quenched with water and extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1) to afford the corresponding pure product as a colorless oil, 837 mg, 89% yield.

Hex-5-en-1-yl ((1*S*,4*S*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonate (S17)

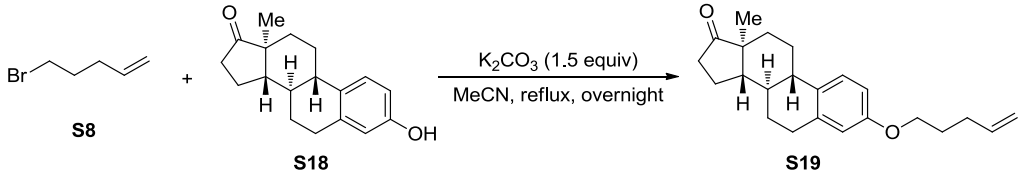


^{1}H NMR (500 MHz, $CDCl_3$) δ 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.03 (dq, *J* = 17.2, 1.7 Hz, 1H), 4.99 (dq, *J* = 10.2, 1.4 Hz, 1H), 4.30 (qt, *J* = 9.7, 6.6 Hz, 2H), 3.61 (d, *J* = 15.1 Hz, 1H), 3.00 (d, *J* = 15.1 Hz, 1H), 2.51 (ddd, *J* = 14.9, 11.8, 4.0 Hz, 1H), 2.40 (ddd, *J* = 18.5, 4.7, 3.3 Hz, 1H), 2.16 – 2.05 (m, 4H), 1.97 (d, *J* = 18.6 Hz, 1H), 1.77 (dt, *J* = 15.2, 6.7 Hz, 2H), 1.67 (ddd, *J* = 14.1, 9.4, 4.7 Hz, 1H), 1.57 – 1.50 (m, 2H), 1.46 (ddt, *J* = 13.1, 9.4, 4.4 Hz, 1H), 1.13 (s, 3H), 0.89 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 214.5, 137.9, 115.1, 70.4, 57.9, 47.9, 46.6, 42.7, 42.5, 33.0, 28.6, 26.8, 24.8, 24.6, 19.8, 19.7.

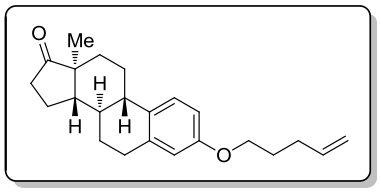
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{26}O_4SNa$: 337.1444; found: 337.1445.

2.12 Synthesis of Estrone Derivative



A mixture of **S8** (373 mg, 2.5 mmol, 1.25 equiv), Estrone (540 mg, 2 mmol, 1.0 equiv), and K_2CO_3 (414 mg, 3 mmol, 1.5 equiv) in anhydrous acetonitrile was heated to reflux in an oil bath. After refluxing overnight, the reaction mixture was cooled to room temperature, concentrated under reduced pressure, diluted with saturated NH_4Cl and extracted with ethyl acetate. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to afford the corresponding pure product as a white amorphous solid, 580 mg, 97% yield.

(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(pent-4-en-1-yloxy)-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[a]phenanthren-17(14*H*)-one (S19)



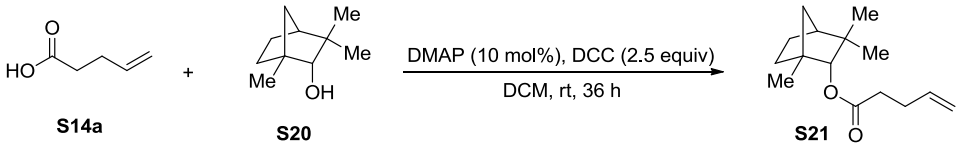
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 8.7, 1.1 Hz, 1H), 6.74 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.67 (d, *J* = 2.7 Hz, 1H), 5.88 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.09 (dq, *J* = 17.1, 1.7 Hz, 1H), 5.02 (ddt, *J* = 10.2, 2.2, 1.3 Hz, 1H), 3.97 (t, *J* = 6.4 Hz, 2H), 2.92 (td, *J* = 6.9, 2.0 Hz, 2H), 2.53 (ddd, *J* = 18.9,

8.8, 0.9 Hz, 1H), 2.45 – 2.38 (m, 1H), 2.32 – 2.22 (m, 3H), 2.22 – 2.14 (m, 1H), 2.12 – 1.94 (m, 3H), 1.93 – 1.85 (m, 2H), 1.71 – 1.41 (m, 6H), 0.93 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 157.1, 137.9, 137.7, 131.9, 126.3, 115.1, 114.6, 112.1, 67.1, 50.4, 48.0, 44.0, 38.4, 35.9, 31.6, 30.1, 29.6, 28.5, 26.6, 25.9, 21.6, 13.8.

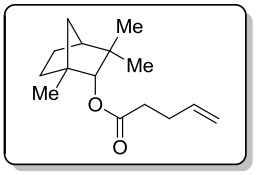
HRMS (ESI) m/z: $[M+K]^+$ calcd for $C_{23}H_{30}O_2K$: 377.1877; found: 377.1870.

2.13 Synthesis of (+)-Fenchol Derivative



To a solution of **S14a** (300 mg, 3 mmol, 1.5 equiv)**,** (+)-Fenchol (308 mg, 2 mmol, 1.0 equiv)**,** and DAMP (24 mg, 0.2 mmol, 0.1 equiv) in anhydrous CH_2Cl_2 was added DCC (1030 mg, 5 mmol, 2.5 equiv) in one potion. After stirring at room temperature for 36 hours, the mixture was filtered through a pad of Celite, washed with CH_2Cl_2. The combined organic layers were washed with water, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford the corresponding pure product as a yellow oil, 454 mg, 96% yield.

(1*S*,2*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl pent-4-enoate (S21)

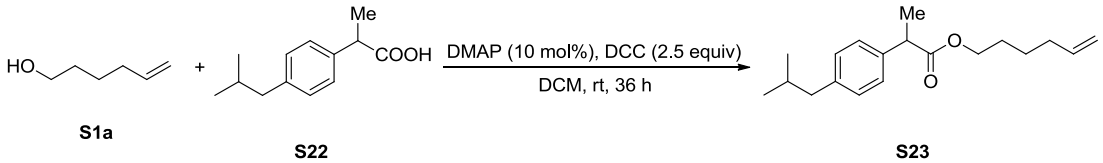


^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86 (ddt, *J* = 16.4, 10.2, 6.1 Hz, 1H), 5.09 (dq, *J* = 17.1, 1.6 Hz, 1H), 5.03 (dq, *J* = 10.3, 1.4 Hz, 1H), 4.39 (d, *J* = 1.9 Hz, 1H), 2.49 – 2.44 (m, 2H), 2.44 – 2.37 (m, 2H), 1.80 – 1.67 (m, 3H), 1.59 (dq, *J* = 10.3, 2.2 Hz, 1H), 1.52 – 1.42 (m, 1H), 1.20 (dd, *J* = 10.3, 1.6 Hz, 1H), 1.12 (s, 3H), 1.11 – 1.07 (m, 1H), 1.05 (s, 3H), 0.79 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 136.8, 115.4, 86.1, 48.3, 48.2, 41.4, 39.4, 33.7, 29.7, 29.0, 26.6, 25.8, 20.2, 19.4.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{24}O_2Na$: 259.1669; found: 259.1668.

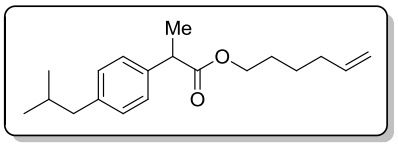
2.14. Synthesis of Ibuprofen Derivative



To a solution of **S1a** (300 mg, 3 mmol, 1.5 equiv)**,** Ibuprofen (412 mg, 2 mmol, 1.0 equiv)**,** and DAMP (24 mg, 0.2 mmol, 0.1 equiv) in anhydrous CH_2Cl_2 was added DCC (1030 mg, 5 mmol, 2.5 equiv) in one potion. After stirring at room temperature for 36 hours, the mixture was filtered through a pad of Celite, washed with CH_2Cl_2. The combined organic layers were washed with water, dried with Na_2SO_4, filtered, and concentrated under

reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30/1) to afford the corresponding pure product as a colorless oil, 510 mg, 895 yield.

Hex-5-en-1-yl 2-(4-isobutylphenyl)propanoate (S23)

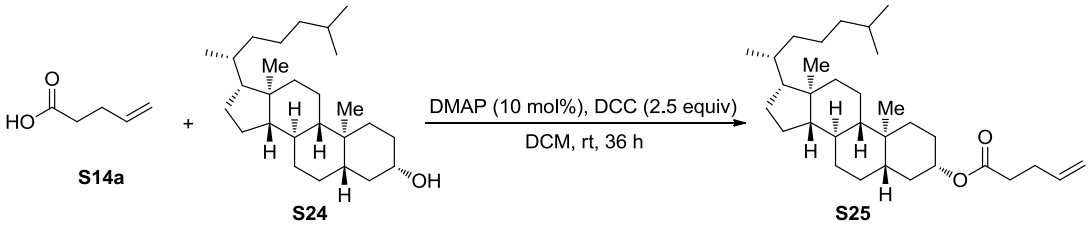


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 5.77 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 1H), 5.06 – 4.93 (m, 2H), 4.10 (td, *J* = 6.6, 1.8 Hz, 2H), 3.72 (q, *J* = 7.1 Hz, 1H), 2.49 (d, *J* = 7.2 Hz, 2H), 2.09 – 2.00 (m, 2H), 1.89 (dp, *J* = 13.5, 6.7 Hz, 1H), 1.68 – 1.57 (m, 2H), 1.53 (d, *J* = 7.2 Hz, 3H), 1.39 (tt, *J* = 9.8, 6.5 Hz, 2H), 0.94 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.7, 140.3, 138.2, 137.8, 129.2, 127.1, 114.6, 64.4, 45.1, 45.0, 33.1, 30.1, 27.9, 25.0, 22.3, 18.4.

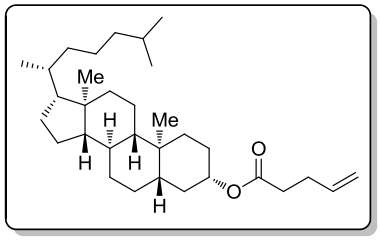
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{28}O_2Na$: 311.1982; found: 311.1986.

2.15 Synthesis of Dihydrocholesterol Derivative



To a solution of **S14a** (96 mg, 0.96 mmol, 1.5 equiv)**,** Dihydrocholesterol (250 mg, 0.64 mmol, 1.0 equiv)**,** and DAMP (8 mg, 0.06 mmol, 0.1 equiv) in anhydrous CH_2Cl_2 was added DCC (330 mg, 1.6 mmol, 2.5 equiv) in one potion. After stirring at room temperature for 36 hours, the mixture was filtered through a pad of Celite, washed with CH_2Cl_2. The combined organic layers were washed with water, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford the corresponding pure product as a pale yellow amorphous solid, 278 mg, 92% yield.

(3*S*,5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl pent-4-enoate (S25)

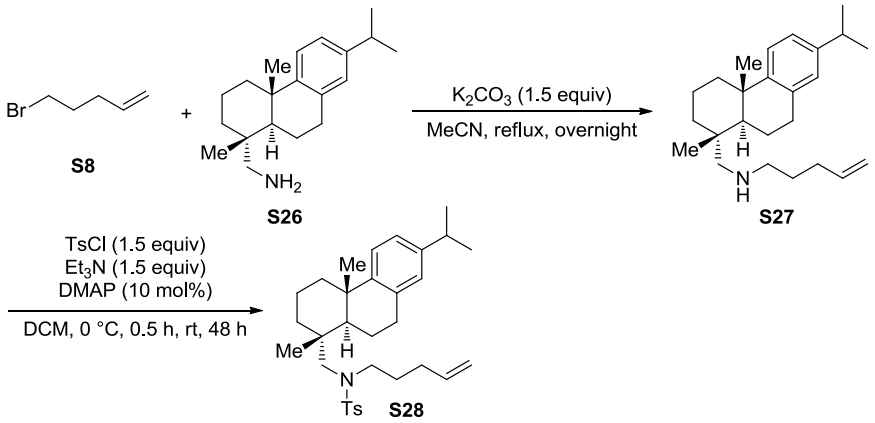


^{1}H NMR (500 MHz, $CDCl_3$) δ 5.84 (ddq, *J* = 16.6, 9.8, 3.3 Hz, 1H), 5.07 (dd, *J* = 17.0, 1.7 Hz, 1H), 5.01 (dd, *J* = 10.2, 1.7 Hz, 1H), 4.73 (tt, *J* = 11.3, 4.9 Hz, 1H), 2.42 – 2.34 (m, 1H), 2.39 (s, 3H), 1.98 (dt, *J* = 12.6, 3.4 Hz, 1H), 1.82 (tdd, *J* = 9.3, 5.9, 3.6 Hz, 2H), 1.74 (dt, *J* = 13.4, 3.7 Hz, 1H), 1.67 (dq, *J* = 13.0, 3.4 Hz, 1H), 1.63 – 1.45 (m, 6H), 1.42 – 1.22 (m, 10H), 1.22 – 0.96 (m, 12H), 0.95 – 0.80 (m, 2H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.89 (d, *J* = 2.4 Hz, 3H), 0.88 (d, *J* = 2.3 Hz, 3H), 0.84 (s, 3H), 0.67 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 136.8, 115.4, 73.7, 56.4, 56.3, 54.2, 44.7, 42.6, 40.0, 39.5, 36.8, 36.2, 35.8, 35.49, 35.46, 34.1, 33.9, 32.0, 29.0, 28.6, 28.2, 28.0, 27.5, 24.2, 23.8, 22.8, 22.6, 21.2, 18.7, 12.2, 12.1.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{32}H_{54}O_2Na$: 493.4016; found: 493.4017.

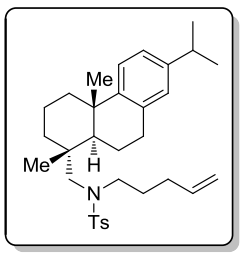
2.16 Synthesis of (+)-Dehydroabietylamine Derivative



A mixture of **S8** (551 mg, 3.75 mmol, 1.25 equiv), (+)-Dehydroabietylamine (856 mg, 3 mmol, 1.0 equiv), and K_2CO_3 (621 mg, 4.5 mmol, 1.5 equiv) in anhydrous acetonitrile was heated to reflux in an oil bath. After refluxing overnight, the reaction mixture was cooled to room temperature, concentrated under reduced pressure, diluted with saturated NH_4Cl and extracted with ethyl acetate. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford the corresponding pure product **S27** as a pale yellow oi, 966 mg, 91% yield.

To a solution of **S27** (530 mg, 1.5 mmol, 1.0 equiv)**,** DAMP (18 mg, 0.15 mmol, 0.1 equiv), and triethylamine (227 mg, 2.25 mmol, 1.5 equiv) in anhydrous CH_2Cl_2 was added *p*-toluenesulfonyl chloride (357 mg, 1.86 mmol, 1.25 equiv) in potions at 0 °C. The resulting mixture was stirred at 0 °C for 0.5 hour, and then at room temperature for 48 hours. After completion, the reaction was quenched with water and extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1) to afford the corresponding pure product as a pale yellow sticky oil, 636 mg, 84% yield.

***N*-(((1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-4-methyl-*N*-(pent-4-en-1-yl)benzenesulfonamide (S28)**



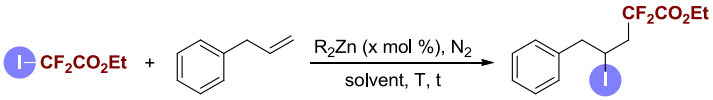
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 1H), 7.01 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.91 (d, *J* = 1.9 Hz, 1H), 5.76 – 5.59 (m, 1H), 4.96 (d, *J* = 1.5 Hz, 1H), 4.93 (dq, *J* = 6.0, 1.6 Hz, 1H), 3.17 (d, *J* = 14.5 Hz, 1H), 3.14 – 3.03 (m, 2H), 3.02 – 2.96 (m, 1H), 2.96 – 2.88 (m, 2H), 2.85 (p, *J* = 6.9 Hz, 1H), 2.44 (s, 3H), 2.31 (dq, *J* = 13.8, 2.6, 2.1 Hz, 1H), 1.96 – 1.84 (m, 3H), 1.85 – 1.67 (m, 4H), 1.66 – 1.57 (m, 2H), 1.51 (ddd, *J* = 13.3, 6.8, 3.5 Hz, 2H), 1.41 (td, *J* = 12.9, 4.4 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 6H), 1.25 (s, 3H), 1.02 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 147.4, 145.6, 143.1, 137.3, 136.7, 134.5, 129.5, 127.5, 126.8, 123.9, 123.8, 115.3, 59.8, 51.3, 45.5, 38.9, 38.2, 37.6, 37.2, 33.4, 31.2, 29.8, 27.3, 25.6, 24.0, 24.0, 21.5, 19.3, 18.9, 18.6.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{32}H_{45}NO_2SNa$: 530.3063; found: 530.3063.

III. Screening of Reaction Conditions

Table S1. Optimization of Reaction Conditions for Alkene

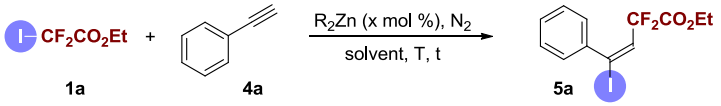


1a **2a** **3a**

entry	solvent	**T** (°C)	R_2Zn	(x mol%)	t (h)	yield (%)
1	THF	0	Me_2Zn	100	20	72
2	THF	-10	Me_2Zn	100	20	88
3	THF	-20	Me_2Zn	100	20	90
4	hexane	-20	Me_2Zn	100	20	73
5	MeCN	-20	Me_2Zn	100	20	96
6	DMF	-20	Me_2Zn	100	20	82
7	DCM	-20	Me_2Zn	100	20	93
8	MeCN	-20	Me_2Zn	50	20	97
9	MeCN	-20	Me_2Zn	20	20	51~97[a]
10	MeCN	-20	Me_2Zn	10	20	42
11	MeCN	-20	Me_2Zn	5	20	29
12	MeCN	-20	Et_2Zn	50	20	96
13	MeCN	-20	Et_2Zn	20	20	47~93[b]
14	MeCN	-20	Et_2Zn	10	20	27
15	MeCN	-20	Et_2Zn	5	20	15
16	MeCN	-20	Et_2Zn	50	16	99
17	MeCN	-20	Et_2Zn	50	8	79
18	MeCN	-20	Et_2Zn	50	4	69
19	MeCN	-20	Et_2Zn	50	2	51
20	MeCN	-30	Et_2Zn	50	16	95

a: The yields varied from 51% to 97% in 5 runs
b: The yields varied from 47% to 93% in 5 runs

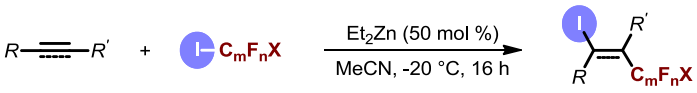
Table S2. Optimization of Reaction Conditions for Alkyne



1a 4a 5a

entry	solvent	T (°C)	R_2Zn	(x mol%)	t (h)	yield (%)
1	THF	-10	Me_2Zn	100	20	63
2	toluene	-10	Me_2Zn	100	20	< 10
3	MeCN	-10	Me_2Zn	100	20	66
4	DMF	-10	Me_2Zn	100	20	23
5	DCM	-10	Me_2Zn	100	20	< 5
6	MeCN	-20	Me_2Zn	100	20	73
7	MeCN	-20	Me_2Zn	100	16	74
8	MeCN	-20	Me_2Zn	100	8	73
9	MeCN	-20	Me_2Zn	100	4	42
10	MeCN	-20	Me_2Zn	50	16	65
11	MeCN	-20	Me_2Zn	50	8	57
12	MeCN	-20	Me_2Zn	50	4	47
13	MeCN	-20	Et_2Zn	100	16	85
14	MeCN	-20	Et_2Zn	100	8	87
15	MeCN	-20	Et_2Zn	50	16	93
16	MeCN	-20	Et_2Zn	50	8	99
17	MeCN	-20	Et_2Zn	20	8	51
18	MeCN	-20	Et_2Zn	10	8	21

IV. General Procedure for the 1,2-Addition of Perfluoroalkyl Iodides to Alkenes and Alkynes



For liquid substrates:

An oven-dried Schlenk tube was charged with a stir bar. The tube was degased and refilled with nitrogen for 3 times, and then a solution of alkenes or alkynes (0.2 mmol) and perfluoroalkyl iodides (0.2 mmol, 1.0 equiv) in acetonitrile (2 mL) was injected to the tube via a syringe. The reaction mixture was cooled to the temperature indicated. After stirring for 3 minutes, a solution of diethylzinc (1.0 mol/L in hexane, 0.1 mL, 0.5 equiv) was injected to the reaction mixture via a syringe. After stirring at the same temperature for the time indicated, the reaction was quenched with saturated NH_4Cl and extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried with Na_2SO_4, filtered through a short pad of silica gel, and concentrated under reduced pressure. The residue was pure enough to submit to NMR experiments or was purified by silica gel

column chromatography (petroleum ether/ethyl acetate) to afford the pure product if necessary.

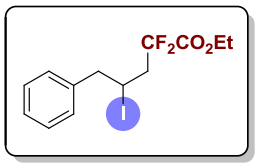
For solid substrates:

An oven-dried Schlenk tube was charged with alkenes or alkynes (0.2 mmol) and a stir bar. The tube was degased and refilled with nitrogen for 3 times, and then a solution of perfluoroalkyl iodides (0.2 mmol, 1.0 equiv) in acetonitrile (2 mL) was injected to the tube via a syringe. The following procedure was the same to that of liquid substrates.

*For a 1 mmol scale synthesis of **3a**:*

An oven-dried Schlenk tube was charged with a stir bar. The tube was degased and refilled with nitrogen for 3 times, and then a solution of **2a** (118.0 mg, 1.0 mmol) and ethyl iododifluoroacetate **1a** (249.9 mg, 1.0 mmol, 1.0 equiv) in acetonitrile (10 mL) was injected to the tube via a syringe. The reaction mixture was cooled to - 20 °C. After stirring for 3 minutes, a solution of diethylzinc (1.0 mol/L in hexane, 0.5 mL, 0.5 equiv) was injected to the reaction mixture via a syringe. After stirring at - 20 °C for 16 hours, the reaction was quenched with saturated NH_4Cl and extracted with ethyl acetate (3 × 100 mL). The combined organic layers were dried with Na_2SO_4, filtered through a short pad of silica gel, and concentrated under reduced pressure. The residue (colorless oil, 368.7 mg, 99% yield) was pure enough to submit to NMR experiments.

Ethyl 2,2-difluoro-4-iodo-5-phenylpentanoate (3a)



Colorless oil, 73.5 mg, 99% yield.

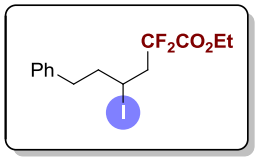
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 3H), 7.24 – 7.19 (m, 2H), 4.42 – 4.31 (m, 3H), 3.26 (qd, *J* = 14.5, 7.3 Hz, 2H), 2.94 (qd, *J* = 16.5, 7.3 Hz, 1H), 2.87 – 2.75 (m, 1H), 1.39 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -101.8 (d, *J* = 263.5 Hz), -106.4 (d, *J* = 263.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4 (t, $^2J_{C\text{-}F}$ = 32.3 Hz), 138.8, 129.0, 128.6, 127.2, 115.2 (dd, $^1J_{C\text{-}F}$ = 253.5, 251.7 Hz), 63.3, 47.2, 44.4 (t, $^2J_{C\text{-}F}$ = 23.5 Hz), 21.8 (t, $^3J_{C\text{-}F}$ = 3.9 Hz), 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{15}F_2IO_2Na$: 390.9977; found: 390.9979.

Ethyl 2,2-difluoro-4-iodo-6-phenylhexanoate (3b)



Colorless oil, 74.9 mg, 98% yield.

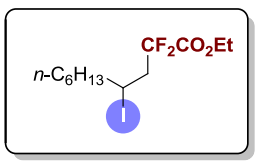
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.27 – 7.20 (m, 3H), 4.33 (q, *J* = 7.1 Hz, 2H), 4.19 (dtd, *J* = 9.9, 6.7, 3.9 Hz, 1H), 3.07 – 2.89 (m, 2H), 2.88 – 2.68 (m, 2H), 2.22 – 2.04 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -101.7 (d, *J* = 263.5 Hz), -106.4 (d, *J* = 263.1 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3 (t, $^2J_{C\text{-}F}$ = 32.3 Hz), 140.1, 128.51, 128.48, 126.3, 115.1 (dd, $^1J_{C\text{-}F}$ = 253.9, 252.6 Hz), 63.2, 45.3 (t, $^2J_{C\text{-}F}$ = 23.2 Hz), 41.8, 35.5, 22.4 (t, $^3J_{C\text{-}F}$ = 4.0 Hz), 13.8.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{14}H_{17}F_2IO_2Na$: 405.0134; found: 405.0130.

Ethyl 2,2-difluoro-4-iododecanoate (3c)



Colorless oil, 71.7 mg, 99% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.37 (q, *J* = 7.2 Hz, 2H), 4.24 (ddd, *J* = 11.2, 8.9, 5.6 Hz, 1H), 2.93 (dtd, *J* = 18.3, 16.0, 6.5 Hz, 1H), 2.76 (dddd, *J* = 17.8, 15.6, 12.5, 7.1 Hz, 1H), 1.83 (dtd, *J* = 14.3, 9.4, 4.8

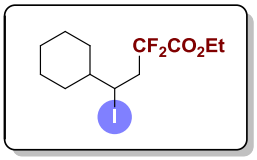
Hz, 1H), 1.75 (ddt, J = 14.7, 9.8, 4.9 Hz, 1H), 1.54 (dtt, J = 14.7, 10.4, 5.4 Hz, 1H), 1.47 – 1.24 (m, 7H), 1.39 (t, J = 7.2 Hz, 3H), 0.91 (t, J = 6.7 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.1 (d, J = 262.8 Hz), -106.8 (d, J = 262.8 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5 (t, $^2J_{C\text{-}F}$ = 32.3 Hz), 115.20 (dd, $^1J_{C\text{-}F}$ = 253.5, 252.2 Hz), 63.2, 45.4 (t, $^2J_{C\text{-}F}$ = 23.1 Hz), 40.5, 31.6, 29.4, 28.2, 23.3 (t, $^3J_{C\text{-}F}$ = 4.1 Hz), 22.5, 14.0, 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_{21}F_2IO_2Na$: 385.0447; found: 385.0444.

Ethyl 4-cyclohexyl-2,2-difluoro-4-iodobutanoate (3d)



Colorless oil, 69.8 mg, 97% yield.

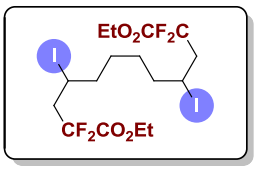
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.36 (q, J = 7.2 Hz, 2H), 4.28 – 4.21 (m, 1H), 2.96 – 2.70 (m, 2H), 1.86 – 1.63 (m, 5H), 1.39 (t, J = 7.2 Hz, 3H), 1.37 – 1.07 (m, 5H), 0.92 – 0.81 (m, 1H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.3 (d, J = 261.6 Hz), -107.3 (d, J = 261.6 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5 (t, $^2J_{C\text{-}F}$ = 32.4 Hz), 115.3 (dd, $^1J_{C\text{-}F}$ = 253.6, 251.3 Hz), 63.2, 44.5, 42.9 (t, $^2J_{C\text{-}F}$ = 23.3 Hz), 33.3, 32.8 (t, $^3J_{C\text{-}F}$ = 3.8 Hz), 29.9, 26.0, 25.8, 25.6, 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_{19}F_2IO_2Na$: 383.0290; found: 383.0289.

Diethyl 2,2,11,11-tetrafluoro-4,9-diiodododecanedioate (3e)



Colorless oil, 120.8 mg, 99% yield.

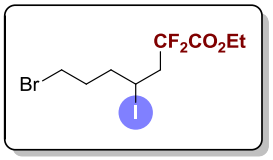
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.35 (q, J = 7.2 Hz, 4H), 4.26 – 4.18 (m, 2H), 3.00 – 2.84 (m, 2H), 2.74 (dddd, J = 18.2, 15.6, 12.2, 7.3 Hz, 2H), 1.79 (dqd, J = 28.7, 9.4, 4.7 Hz, 4H), 1.66 – 1.40 (m, 4H), 1.37 (t, J = 7.2 Hz, 6H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.12 (d, J = 263.8 Hz), -102.13 (d, J = 263.8 Hz), -106.73 (d, J = 263.8 Hz), -106.76 (d, J = 263.8 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3 (t, $^2J_{C\text{-}F}$ = 32.3 Hz), 115.1 (t, $^1J_{C\text{-}F}$ = 252.7 Hz), 63.2, 45.21 (t, $^2J_{C\text{-}F}$ = 23.1 Hz), 45.15 (t, $^2J_{C\text{-}F}$ = 23.1 Hz), 40.0, 39.9, 28.41, 28.38, 22.66 (t, $^3J_{C\text{-}F}$ = 4.3 Hz), 22.62 (t, $^3J_{C\text{-}F}$ = 4.3 Hz), 13.8.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{24}F_4I_2O_4Na$: 632.9592; found: 632.9589.

Ethyl 7-bromo-2,2-difluoro-4-iodoheptanoate (3f)



Colorless oil, 78.8 mg, 99% yield.

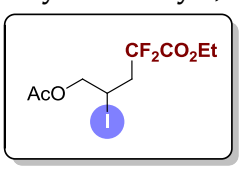
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.36 (q, J = 7.2 Hz, 2H), 4.29 – 4.20 (m, 1H), 3.45 (td, J = 5.7, 3.0 Hz, 2H), 2.95 (dtd, J = 19.0, 15.5, 6.3 Hz, 1H), 2.84 – 2.70 (m, 1H), 2.22 – 2.09 (m, 1H), 2.05 – 1.91 (m, 3H), 1.39 (t, J = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.3 (d, J = 263.7 Hz), -106.6 (d, J = 263.7 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3 (t, $^2J_{C\text{-}F}$ = 32.2 Hz), 115.0 (t, $^1J_{C\text{-}F}$ = 252.9 Hz), 63.3, 45.3 (t, $^2J_{C\text{-}F}$ = 23.2 Hz), 38.7, 32.5, 32.0, 21.1 (t, $^3J_{C\text{-}F}$ = 3.9 Hz), 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_9H_{14}BrF_2IO_2Na$: 420.9082; found: 420.9087.

Ethyl 5-acetoxy-2,2-difluoro-4-iodopentanoate (3g)



Colorless oil, 65.1 mg, 93% yield.

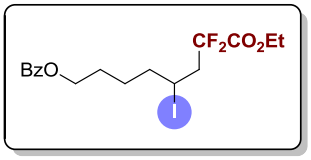
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.40 – 4.30 (m, 2H), 4.36 (q, J = 7.2 Hz, 2H), 4.29 – 4.23 (m, 1H), 2.95 – 2.74 (m, 2H), 2.12 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -103.1 (d, J = 265.7 Hz), -106.0 (d, J = 265.7 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 163.11 (t, $^2J_{C\text{-}F}$ = 32.2 Hz), 114.8 (t, $^1J_{C\text{-}F}$ = 252.7 Hz), 68.6, 63.3, 41.7 (t, $^2J_{C\text{-}F}$ = 23.7 Hz), 20.7, 14.5 (t, $^3J_{C\text{-}F}$ = 4.1 Hz), 13.8.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_9H_{13}F_2IO_4Na$: 372.9719; found: 372.9714.

8-Ethoxy-7,7-difluoro-5-iodo-8-oxooctyl benzoate (3h)



Colorless oil, 87.2 mg, 96% yield.

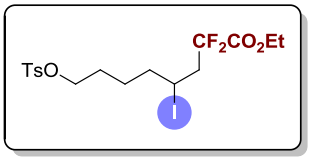
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.1 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 4.40 – 4.31 (m, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.27 (dtd, *J* = 10.7, 6.9, 4.1 Hz, 1H), 2.95 (dtd, *J* = 18.9, 15.7, 6.3 Hz, 1H), 2.77 (dddd, *J* = 18.7, 15.5, 12.1, 7.3 Hz, 1H), 1.93 – 1.72 (m, 5H), 1.66 – 1.54 (m, 1H), 1.38 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.1 (d, *J* = 263.0 Hz), -106.8 (d, *J* = 263.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 163.3 (t, $^2J_{C\text{-}F}$ = 32.2 Hz), 132.9, 130.3, 129.5, 128.3, 115.1 (t, $^1J_{C\text{-}F}$ = 253.2 Hz), 64.4, 63.2, 45.3 (t, $^2J_{C\text{-}F}$ = 23.1 Hz), 39.9, 27.7, 26.2, 22.5 (t, $^3J_{C\text{-}F}$ = 4.0 Hz), 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{21}F_2IO_4Na$: 477.0345; found: 477.0346.

Ethyl 2,2-difluoro-4-iodo-8-(tosyloxy)octanoate (3i)



Colorless oil, 93.7 mg, 93% yield.

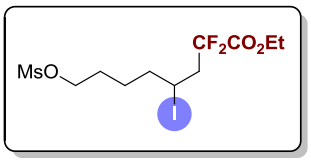
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 4.15 (dtd, *J* = 11.0, 6.9, 4.1 Hz, 1H), 4.05 (t, *J* = 6.3 Hz, 2H), 2.89 (dtd, *J* = 19.1, 15.7, 6.4 Hz, 1H), 2.69 (dddd, *J* = 18.8, 15.6, 12.0, 7.3 Hz, 1H), 2.46 (s, 3H), 1.79 – 1.63 (m, 4H), 1.56 (dtt, *J* = 20.1, 10.2, 5.3 Hz, 1H), 1.47 – 1.36 (m, 1H), 1.38 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.2 (d, *J* = 263.2 Hz), -106.9 (d, *J* = 263.2 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3 (t, $^2J_{C\text{-}F}$ = 32.3 Hz), 144.8, 133.0, 129.8, 127.8, 115.0 (t, $^1J_{C\text{-}F}$ = 252.7 Hz), 70.0, 63.2, 45.1 (t, $^2J_{C\text{-}F}$ = 23.1 Hz), 39.5, 27.8, 25.6, 22.0 (t, $^3J_{C\text{-}F}$ = 3.9 Hz), 21.6, 13.8.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{23}F_2IO_5SNa$: 527.0171; found: 527.0173.

Ethyl 2,2-difluoro-4-iodo-8-((methylsulfonyl)oxy)octanoate (3j)



Colorless oil, 74.7 mg, 92% yield.

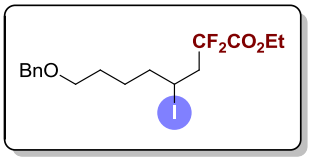
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.36 (q, *J* = 7.2 Hz, 2H), 4.29 – 4.20 (m, 1H), 4.25 (t, *J* = 6.3 Hz, 2H), 3.03 (s, 3H), 3.00 – 2.86 (m, 1H), 2.83 – 2.69 (m, 1H), 1.92 – 1.75 (m, 4H), 1.75 – 1.64 (m, 1H), 1.60 – 1.49 (m, 1H), 1.38 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.2 (d, *J* = 263.1 Hz), -106.8 (d, *J* = 263.1 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2 (t, $^2J_{C\text{-}F}$ = 32.2 Hz), 115.1 (t, $^1J_{C\text{-}F}$ = 252.8 Hz), 69.4, 63.3, 45.1 (t, $^2J_{C\text{-}F}$ = 23.1 Hz), 39.5, 37.3, 28.0, 25.6, 22.1 (t, $^3J_{C\text{-}F}$ = 3.9 Hz), 13.8.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_{20}F_2IO_5S$: 429.0033; found: 429.0033.

Ethyl 8-(benzyloxy)-2,2-difluoro-4-iodooctanoate (3k)



Colorless oil, 82.7 mg, 94% yield.

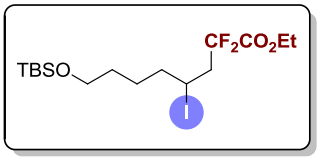
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 4H), 7.33 – 7.29 (m, 1H), 4.53 (s, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.25 (dtd, *J* = 8.8, 6.8, 4.3 Hz, 1H), 3.51 (t, *J* = 5.9 Hz, 2H), 2.94 (dtd, *J* = 18.4, 15.8, 6.5 Hz, 1H), 2.76 (dddd, *J* = 17.9, 15.6, 12.4, 7.0 Hz, 1H), 1.92 – 1.75 (m, 2H), 1.74 – 1.60 (m, 3H), 1.59 – 1.47 (m, 1H), 1.39 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.1 (d, J = 263.3 Hz), -106.8 (d, J = 263.3 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4 (t, $^2J_{C\text{-}F}$ = 32.2 Hz), 138.5, 128.3, 127.6, 127.5, 115.1 (t, $^1J_{C\text{-}F}$ = 252.6 Hz), 72.9, 69.9, 63.2, 45.3 (t, $^2J_{C\text{-}F}$ = 23.2 Hz), 40.2, 28.7, 26.3, 22.9 (t, $^3J_{C\text{-}F}$ = 4.0 Hz), 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{23}F_2IO_3Na$: 463.0552; found: 463.0551.

Ethyl 8-((tert-butyldimethylsilyl)oxy)-2,2-difluoro-4-iodooctanoate (3l)



Colorless oil, 84.9 mg, 96% yield.

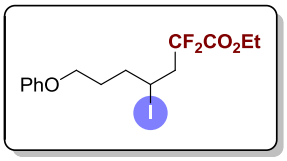
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.36 (q, J = 7.2 Hz, 2H), 4.24 (dtd, J = 8.7, 6.8, 4.2 Hz, 1H), 3.64 (t, J = 6.0 Hz, 2H), 2.93 (dtd, J = 18.4, 15.9, 6.5 Hz, 1H), 2.75 (dddd, J = 18.0, 15.6, 12.4, 7.0 Hz, 1H), 1.92 – 1.72 (m, 2H), 1.68 – 1.44 (m, 4H), 1.39 (t, J = 7.2 Hz, 3H), 0.91 (s, 9H), 0.07 (s, 6H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.1 (d, J = 263.2 Hz), -106.9 (d, J = 263.2 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4 (t, $^2J_{C\text{-}F}$ = 32.3 Hz), 115.2 (t, $^1J_{C\text{-}F}$ = 252.1 Hz), 63.2, 62.7, 45.4 (t, $^2J_{C\text{-}F}$ = 23.1 Hz), 40.2, 31.7, 26.0, 25.9, 23.1 (t, $^3J_{C\text{-}F}$ = 3.9 Hz), 18.3, 13.9, -5.3.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{32}F_2IO_3Si$: 465.1128; found: 465.1133.

Ethyl 2,2-difluoro-4-iodo-7-phenoxyheptanoate (3m)



Colorless oil, 74.2 mg, 90% yield.

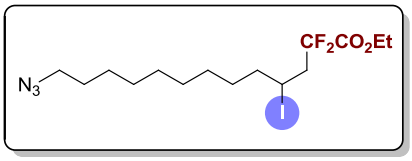
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.00 – 6.95 (m, 1H), 6.94 – 6.89 (m, 2H), 4.40 – 4.29 (m, 1H), 4.36 (q, J = 7.2 Hz, 2H), 4.02 (t, J = 5.8 Hz, 2H), 2.99 (dtd, J = 18.6, 15.8, 6.5 Hz, 1H), 2.81 (dddd, J = 17.9, 15.6, 12.4, 7.2 Hz, 1H), 2.13 – 1.97 (m, 3H), 1.97 – 1.88 (m, 1H), 1.39 (t, J = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.1 (d, J = 263.6 Hz), -106.7 (d, J = 263.6 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4 (t, $^2J_{C\text{-}F}$ = 32.2 Hz), 158.8, 129.4, 120.8, 115.1 (t, $^1J_{C\text{-}F}$ = 252.6 Hz), 114.5, 66.5, 63.3, 45.3 (t, $^2J_{C\text{-}F}$ = 23.2 Hz), 37.2, 29.5, 22.4 (t, $^3J_{C\text{-}F}$ = 3.9 Hz), 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{19}F_2IO_3Na$: 435.0239; found: 435.0235.

Ethyl 13-azido-2,2-difluoro-4-iodotridecanoate (3n)



Colorless oil, 87.6 mg, 95% yield.

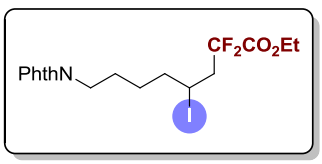
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.36 (q, J = 7.1 Hz, 2H), 4.23 (dtd, J = 10.9, 6.9, 4.2 Hz, 1H), 3.27 (t, J = 7.0 Hz, 2H), 2.93 (dtd, J = 18.5, 15.9, 6.5 Hz, 1H), 2.75 (dddd, J = 17.9, 15.6, 12.4, 7.1 Hz, 1H), 1.82 (dtd, J = 14.3, 9.4, 4.8 Hz, 1H), 1.74 (ddt, J = 14.7, 9.8, 4.9 Hz, 1H), 1.61 (p, J = 7.0 Hz, 2H), 1.53 (td, J = 8.4, 3.9 Hz, 1H), 1.44 – 1.26 (m, 11H), 1.39 (t, J = 7.1 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.1 (d, J = 262.8 Hz), -106.8 (d, J = 262.8 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4 (t, $^2J_{C\text{-}F}$ = 32.2 Hz), 115.2 (t, $^1J_{C\text{-}F}$ = 252.1 Hz), 63.2, 51.4, 45.3 (t, $^2J_{C\text{-}F}$ = 23.2 Hz), 40.4, 29.4, 29.3, 29.2, 29.0, 28.8, 28.4, 26.6, 23.2 (t, $^3J_{C\text{-}F}$ = 3.9 Hz), 13.8.

HRMS (ESI) m/z: $[M+K]^+$ calcd for $C_{15}H_{26}F_2IN_3K$: 484.0669; found: 484.0663.

Ethyl 8-(1,3-dioxoisoindolin-2-yl)-2,2-difluoro-4-iodooctanoate (3o)



Colorless oil, 93.0 mg, 97% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, J = 5.5, 3.0 Hz, 2H), 7.72 (dd, J = 5.5, 3.0 Hz, 2H), 4.34 (q, J = 7.2 Hz, 2H), 4.20 (dtd, J = 8.7, 6.8, 4.2 Hz, 1H), 3.70 (t, J = 7.2 Hz, 2H), 2.91 (dtd, J =

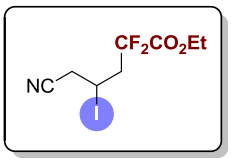
18.6, 15.9, 6.5 Hz, 1H), 2.73 (dddd, *J* = 18.1, 15.5, 12.3, 7.2 Hz, 1H), 1.90 – 1.55 (m, 5H), 1.46 (dddd, *J* = 15.6, 9.9, 8.2, 4.7 Hz, 1H), 1.37 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.1 (d, *J* = 263.3 Hz), -106.7 (d, *J* = 263.3 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 163.3 (t, $^2J_{C\text{-}F}$ = 32.2 Hz), 133.9, 132.0, 123.1, 115.1 (t, $^1J_{C\text{-}F}$ = 252.8 Hz), 63.2, 45.2 (t, $^2J_{C\text{-}F}$ = 23.2 Hz), 39.7, 37.5, 27.4, 26.8, 22.4 (t, $^1J_{C\text{-}F}$ = 3.9 Hz), 13.8.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{20}F_2INO_4Na$: 502.0297; found: 502.0297.

Ethyl 5-cyano-2,2-difluoro-4-iodopentanoate (3p)



Colorless oil, 62.8 mg, 99% yield.

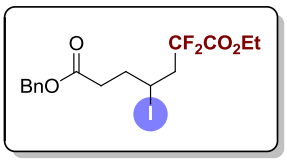
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.44 – 4.35 (m, 1H), 4.37 (t, *J* = 7.2 Hz, 2H), 3.27 (dd, *J* = 17.6, 6.3 Hz, 1H), 3.18 (dd, *J* = 17.6, 4.6 Hz, 1H), 3.04 – 2.83 (m, 2H), 1.39 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -103.2 (d, *J* = 265.4 Hz), -106.7 (d, *J* = 265.4 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6 (t, $^2J_{C\text{-}F}$ = 31.9 Hz), 116.8, 114.7 (t, $^1J_{C\text{-}F}$ = 253.6 Hz), 63.6, 44.0 (t, $^2J_{C\text{-}F}$ = 23.4 Hz), 30.2, 13.8, 7.7 (t, $^3J_{C\text{-}F}$ = 3.6 Hz).

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_8H_{10}F_2INO_2Na$: 339.9616; found: 339.9619.

7-Benzyl 1-ethyl 2,2-difluoro-4-iodoheptanedioate (3q)



Colorless oil, 81.8 mg, 93% yield.

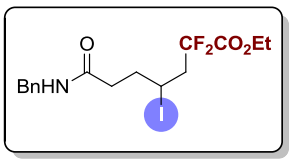
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 5H), 5.16 (s, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.30 (dtd, *J* = 10.3, 6.8, 3.8 Hz, 1H), 2.97 (dtd, *J* = 18.9, 15.5, 6.4 Hz, 1H), 2.77 (dddd, *J* = 18.1, 15.6, 12.1, 7.3 Hz, 1H), 2.66 (ddd, *J* = 16.8, 8.8, 5.4 Hz, 1H), 2.56 (ddd, *J* = 16.7, 8.9, 6.7 Hz, 1H), 2.19 (dddd, *J* = 15.3, 8.8, 6.6, 3.7 Hz, 1H), 2.10 (dtd, *J* = 14.9, 9.2, 5.4 Hz, 1H), 1.39 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.2 (d, *J* = 264.2 Hz), -106.5 (d, *J* = 264.2 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 171.8, 163.2 (t, $^2J_{C\text{-}F}$ = 32.2 Hz), 135.7, 128.5, 128.3, 128.2, 115.0 (t, $^1J_{C\text{-}F}$ = 252.7 Hz), 66.5, 63.3, 45.2 (t, $^2J_{C\text{-}F}$ = 23.3 Hz), 35.2, 34.4, 21.3 (t, $^3J_{C\text{-}F}$ = 4.0 Hz), 13.8.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{19}F_2IO_4Na$: 463.0188; found: 463.0186.

Ethyl 7-(benzylamino)-2,2-difluoro-4-iodo-7-oxoheptanoate (3r)



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1/1), pale yellow oil, 85.9 mg, 90% yield.

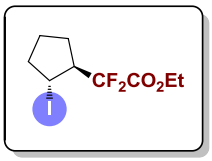
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 2H), 7.31 – 7.26 (m, 3H), 6.01 (t, *J* = 5.7 Hz, 1H), 4.44 (d, *J* = 5.7 Hz, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 4.28 (dtd, *J* = 10.3, 6.8, 3.7 Hz, 1H), 2.95 (dtd, *J* = 18.2, 15.6, 6.7 Hz, 1H), 2.77 (dddd, *J* = 17.8, 15.6, 12.5, 6.8 Hz, 1H), 2.49 (ddd, *J* = 14.3, 8.7, 5.2 Hz, 1H), 2.41 – 2.31 (m, 1H), 2.20 (dddd, *J* = 15.3, 8.6, 6.8, 3.6 Hz, 1H), 2.08 (dtd, *J* = 14.7, 9.2, 5.2 Hz, 1H), 1.38 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.1 (d, *J* = 264.3 Hz), -106.4 (d, *J* = 264.3 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 163.3 (t, $^2J_{C\text{-}F}$ = 32.2 Hz), 138.1, 128.7, 127.8, 127.5, 115.0 (t, $^1J_{C\text{-}F}$ = 252.2 Hz), 63.3, 45.3 (t, $^2J_{C\text{-}F}$ = 23.3 Hz), 43.7, 36.4, 35.9, 22.2 (t, $^3J_{C\text{-}F}$ = 4.1 Hz), 13.8.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{20}F_2INO_3Na$: 462.0348; found: 462.0345.

Ethyl 2,2-difluoro-2-(2-iodocyclopentyl)acetate (3s)



Colorless oil, 63.0 mg, 99% yield.

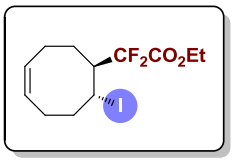
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.37 (q, *J* = 7.2 Hz, 2H), 4.32 (q, *J* = 6.0 Hz, 1H), 3.13 (dddd, *J* = 23.8, 11.6, 9.7, 5.9 Hz, 1H), 2.27 – 2.18 (m, 1H), 2.18 – 2.10 (m, 1H), 1.95 (tdd, *J* = 12.8, 6.8, 3.3 Hz, 1H), 1.86 (dt, *J* = 11.9, 6.8 Hz, 1H), 1.82 – 1.75 (m, 1H), 1.75 – 1.66 (m, 1H), 1.39 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -111.3 (d, *J* = 256.6 Hz), -113.3 (d, *J* = 256.6 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5 (t, $^2J_{C\text{-}F}$ = 32.7 Hz), 116.0 (t, $^1J_{C\text{-}F}$ = 253.0 Hz), 63.1, 55.1 (t, $^2J_{C\text{-}F}$ = 22.5 Hz), 41.2, 25.4 (dd, $^3J_{C\text{-}F}$ = 4.2, 2.6 Hz), 25.2, 19.5 (dd, $^3J_{C\text{-}F}$ = 5.3, 2.2 Hz), 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_9H_{13}F_2IO_2Na$: 340.9821; found: 340.9822.

Ethyl 2,2-difluoro-2-(8-iodocyclooct-4-en-1-yl)acetate (3t)



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 100/1), colorless oil, 63.7 mg, 89% yield.

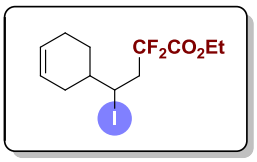
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.93 (dtd, *J* = 10.2, 7.7, 1.2 Hz, 1H), 5.63 (tdd, *J* = 10.2, 6.8, 1.6 Hz, 1H), 4.88 (t, *J* = 4.2 Hz, 1H), 4.36 (qq, *J* = 10.7, 7.1 Hz, 2H), 2.72 (tdd, *J* = 13.3, 10.3, 6.5 Hz, 1H), 2.56 – 2.45 (m, 1H), 2.32 (dddd, *J* = 14.9, 6.6, 4.7, 1.7 Hz, 1H), 2.16 – 1.99 (m, 3H), 1.93 – 1.85 (m, 1H), 1.83 – 1.69 (m, 2H), 1.39 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -107.2 (d, *J* = 253.2 Hz), -111.2 (d, *J* = 253.2 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7 (t, $^2J_{C\text{-}F}$ = 32.7 Hz), 131.5, 128.9, 117.0 (dd, $^1J_{C\text{-}F}$ = 256.7, 253.3 Hz), 63.1, 43.3 (t, $^2J_{C\text{-}F}$ = 20.7 Hz), 39.2, 31.7 (dd, $^3J_{C\text{-}F}$ = 3.8, 2.5 Hz), 30.1 (t, $^3J_{C\text{-}F}$ = 2.9 Hz), 25.2, 23.0, 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_{17}F_2IO_2Na$: 381.0134; found: 381.0130.

Ethyl 4-(cyclohex-3-en-1-yl)-2,2-difluoro-4-iodobutanoate (3u) (1:1 dr)



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 100/1), colorless oil, 67.2 mg, 94% yield.

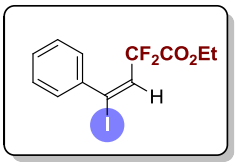
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.75 – 5.62 (m, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 4.40 – 4.29 (m, 1H), 3.04 – 2.72 (m, 2H), 2.20 – 1.88 (m, 4H), 1.83 – 1.64 (m, 1H), 1.54 – 1.33 (m, 1H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.17 (ddddd, *J* = 26.6, 10.8, 7.9, 5.2, 2.7 Hz, 1H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.2 (d, *J* = 261.8 Hz), -107.3 (d, *J* = 261.8 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5 (t, $^2J_{C\text{-}F}$ = 32.2 Hz), 127.0, 125.0, 115.3 (dd, $^1J_{C\text{-}F}$ = 251.8, 245.7 Hz), 63.2, 43.0 (t, $^2J_{C\text{-}F}$ = 23.3 Hz), 40.2, 32.7 (t, $^3J_{C\text{-}F}$ = 4.3 Hz), 30.3, 28.7, 25.0, 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_{17}F_2IO_2Na$: 381.0134; found: 381.0131.

Ethyl 2,2-difluoro-4-iodo-4-phenylbut-3-enoate (5a)



Colorless oil, 69.7 mg, 99% yield.

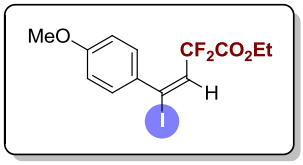
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 5H), 6.75 (t, *J* = 11.0 Hz, 1H), 3.99 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -93.8.

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5 (t, $^2J_{C\text{-}F}$ = 33.2 Hz), 140.7, 133.0 (t, $^2J_{C\text{-}F}$ = 28.4 Hz), 129.4, 128.1, 127.8 (t, $^4J_{C\text{-}F}$ = 2.0 Hz), 110.9 (t, $^1J_{C\text{-}F}$ = 250.2 Hz), 108.7 (t, $^3J_{C\text{-}F}$ = 10.1 Hz), 63.1, 13.6.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_{11}F_2IO_2Na$: 374.9664; found: 374.9660.

Ethyl 2,2-difluoro-4-iodo-4-(4-methoxyphenyl)but-3-enoate (5b)



Colorless oil, 75.7 mg, 99% yield.

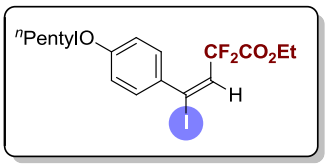
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.69 (t, *J* = 10.8 Hz, 1H), 4.01 (q, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -93.3.

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6 (t, $^2J_{C-F}$ = 33.3 Hz), 160.3, 133.0, 132.5 (t, $^2J_{C-F}$ = 28.4 Hz), 129.7 (t, $^4J_{C-F}$ = 2.1 Hz), 113.4, 110.9 (t, $^1J_{C-F}$ = 249.6 Hz), 109.4 (t, $^3J_{C-F}$ = 10.2 Hz), 63.1, 55.3, 13.7.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{13}F_2IO_3Na$: 404.9763; found: 404.9763.

Eethyl 2,2-difluoro-4-iodo-4-(4-(pentyloxy)phenyl)but-3-enoate (5c)



Colorless oil, 86.8 mg, 99% yield.

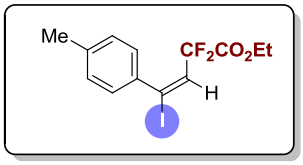
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.68 (t, *J* = 10.8 Hz, 1H), 4.00 (q, *J* = 7.1 Hz, 2H), 3.97 (q, *J* = 7.0 Hz, 2H), 1.80 (p, *J* = 6.7 Hz, 2H), 1.52 – 1.35 (m, 4H), 1.21 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.0 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -93.1.

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6 (t, $^2J_{C-F}$ = 33.3 Hz), 159.9, 132.7, 132.4 (t, $^2J_{C-F}$ = 28.5 Hz), 129.6 (t, $^4J_{C-F}$ = 2.0 Hz), 113.8, 110.9 (t, $^1J_{C-F}$ = 249.5 Hz), 109.5 (t, $^3J_{C-F}$ = 10.4 Hz), 68.1, 63.0, 28.8, 28.10, 22.4, 14.0, 13.7.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{21}F_2IO_3Na$: 461.0396; found: 461.0399.

Ethyl 2,2-difluoro-4-iodo-4-(p-tolyl)but-3-enoate (5d)



Colorless oil, 72.5 mg, 99% yield.

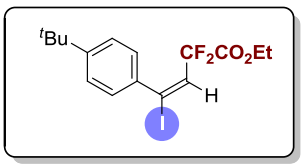
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.72 (t, *J* = 10.9 Hz, 1H), 4.00 (q, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -93.7.

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5 (t, $^2J_{C-F}$ = 33.3 Hz), 139.6, 137.8, 132.7 (t, $^2J_{C-F}$ = 28.4 Hz), 128.6, 127.8 (t, $^4J_{C-F}$ = 2.0 Hz), 110.8 (t, $^2J_{C-F}$ = 250.0 Hz), 109.2 (t, $^3J_{C-F}$ = 10.1 Hz), 63.0, 21.3, 13.6.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{13}F_2IO_2Na$: 388.9821; found: 388.9819.

Ethyl 4-(4-(tert-butyl)phenyl)-2,2-difluoro-4-iodobut-3-enoate (5e)



Colorless oil, 80.9 mg, 99% yield.

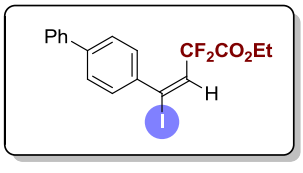
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 6.72 (t, *J* = 10.7 Hz, 1H), 3.92 (q, *J* = 7.2 Hz, 2H), 1.33 (s, 9H), 1.17 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -93.0.

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5 (t, $^2J_{C-F}$ = 33.2 Hz), 152.7, 137.6, 132.7 (t, $^2J_{C-F}$ = 28.8 Hz), 127.8 (t, $^4J_{C-F}$ = 1.9 Hz), 124.9, 110.8 (t, $^1J_{C-F}$ = 249.4 Hz), 109.3 (t, $^3J_{C-F}$ = 10.5 Hz), 62.9, 34.7, 31.1, 13.6.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{19}F_2IO_2Na$: 431.0290; found: 431.0287.

Ethyl 4-([1,1'-biphenyl]-4-yl)-2,2-difluoro-4-iodobut-3-enoate (5f)



Colorless oil, 83.7 mg, 98% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 4H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.44 – 7.38 (m, 3H), 6.79 (t, *J* = 11.0 Hz, 1H), 4.04 (q, *J* =

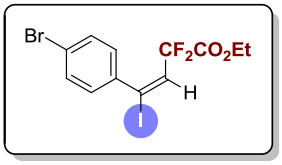
7.1 Hz, 2H), 1.22 (t, J = 7.1 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -93.7.

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6 (t, $^2J_{C\text{-}F}$ = 33.2 Hz), 142.3, 140.0, 139.6, 133.0 (t, $^2J_{C\text{-}F}$ = 28.3 Hz), 128.9, 128.4 (t, $^4J_{C\text{-}F}$ = 1.9 Hz), 127.9, 127.1, 126.7, 111.0 (t, $^1J_{C\text{-}F}$ = 250.4 Hz), 108.6 (t, $^3J_{C\text{-}F}$ = 10.0 Hz), 63.2, 13.7.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{15}F_2IO_2Na$: 450.9977; found: 450.9970.

Ethyl 4-(4-bromophenyl)-2,2-difluoro-4-iodobut-3-enoate (5g)



Colorless oil, 84.4 mg, 98% yield.

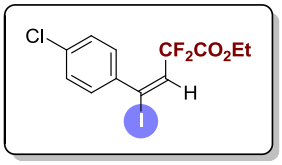
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 6.73 (t, J = 11.3 Hz, 1H), 4.10 (q, J = 7.2 Hz, 2H), 1.26 (t, J = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -94.7.

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5 (t, $^2J_{C\text{-}F}$ = 33.2 Hz), 139.7, 133.4 (t, $^2J_{C\text{-}F}$ = 27.7 Hz), 131.2, 129.3 (t, $^4J_{C\text{-}F}$ = 2.2 Hz), 123.6, 110.8 (t, $^1J_{C\text{-}F}$ = 251.2 Hz), 106.9 (t, $^3J_{C\text{-}F}$ = 9.4 Hz), 63.3, 13.7.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_{10}BrF_2IO_2Na$: 452.8769; found: 452.8773.

Ethyl 4-(4-chlorophenyl)-2,2-difluoro-4-iodobut-3-enoate (5h)



Colorless oil, 76.4 mg, 99% yield.

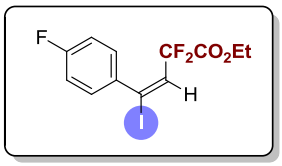
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, J = 8.6 Hz, 2H), 7.26 (d, J = 8.6 Hz, 2H), 6.73 (t, J = 11.3 Hz, 1H), 4.09 (q, J = 7.2 Hz, 2H), 1.25 (t, J = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -94.6.

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5 (t, $^2J_{C\text{-}F}$ = 33.3 Hz), 139.2, 135.4, 133.4 (t, $^2J_{C\text{-}F}$ = 27.7 Hz), 129.1 (t, $^4J_{C\text{-}F}$ = 2.2 Hz), 128.3, 110.8 (t, $^1J_{C\text{-}F}$ = 250.0 Hz), 106.9 (t, $^3J_{C\text{-}F}$ = 9.4 Hz), 63.3, 13.7.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_{10}ClF_2IO_2Na$: 408.9274; found: 408.9274.

Ethyl 2,2-difluoro-4-(4-fluorophenyl)-4-iodobut-3-enoate (5i)



Colorless oil, 73.2 mg, 99% yield.

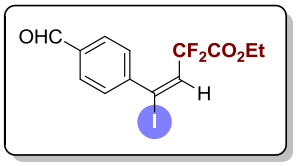
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (dd, J = 8.5, 5.2 Hz, 2H), 7.03 (t, J = 8.5 Hz, 2H), 6.74 (t, J = 11.2 Hz, 1H), 4.08 (q, J = 7.2 Hz, 2H), 1.25 (t, J = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -94.4, -110.6.

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8 (d, $^1J_{C\text{-}F}$ = 250.0 Hz), 162.5 (t, $^2J_{C\text{-}F}$ = 33.3 Hz), 136.8 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 133.4 (t, $^2J_{C\text{-}F}$ = 27.8 Hz), 129.9 (d, $^3J_{C\text{-}F}$ = 8.6 Hz), 115.1 (d, $^2J_{C\text{-}F}$ = 22.2 Hz), 110.8 (t, $^1J_{C\text{-}F}$ = 250.8 Hz), 107.3 (t, $^3J_{C\text{-}F}$ = 9.6 Hz), 63.2, 13.7.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_{10}F_3IO_2Na$: 392.9570; found: 392.9570.

Ethyl 2,2-difluoro-4-(4-formylphenyl)-4-iodobut-3-enoate (5j)



yellow amorphous solid, 70.5 mg, 93% yield.

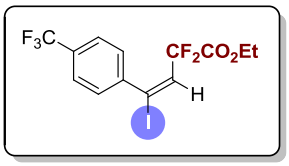
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.61 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 6.79 (t, J = 11.5 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -95.6.

^{13}C NMR (125 MHz, $CDCl_3$) δ 191.2, 162.4 (t, $^2J_{C\text{-}F}$ = 33.3 Hz), 146.5, 136.4, 133.6 (t, $^2J_{C\text{-}F}$ = 27.2 Hz), 129.3, 128.3 (t, $^4J_{C\text{-}F}$ = 2.1 Hz), 110.9 (t, $^1J_{C\text{-}F}$ = 252.0 Hz), 106.1 (t, $^3J_{C\text{-}F}$ = 8.8 Hz), 63.4, 13.8.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{11}F_2IO_3Na$: 402.9613; found: 402.9615.

Ethyl 2,2-difluoro-4-iodo-4-(4-(trifluoromethyl)phenyl)but-3-enoate (5k)



Colorless oil, 80.6 mg, 96% yield.

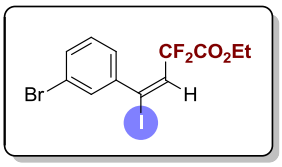
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 6.79 (t, *J* = 11.5 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -63.0, -95.3.

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4 (t, $^2J_{C-F}$ = 33.2 Hz), 144.3, 133.8 (t, $^2J_{C-F}$ = 27.3 Hz), 131.2 (q, $^2J_{C-F}$ = 32.8 Hz), 128.0 (t, $^4J_{C-F}$ = 2.2 Hz), 125.0 (q, $^3J_{C-F}$ = 3.8 Hz), 123.6 (q, $^1J_{C-F}$ = 272.4 Hz), 110.9 (t, $^1J_{C-F}$ = 251.9 Hz), 105.9 (t, $^3J_{C-F}$ = 9.0 Hz), 63.4, 13.7.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{10}F_5IO_2Na$: 442.9538; found: 442.9534.

Ethyl 4-(3-bromophenyl)-2,2-difluoro-4-iodobut-3-enoate (5l)



Colorless oil, 80.7 mg, 99% yield.

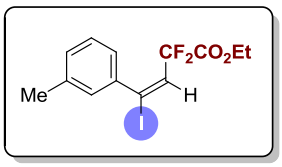
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.40 (m, 2H), 7.26 – 7.18 (m, 2H), 6.74 (t, *J* = 11.2 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -94.8.

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4 (t, $^2J_{C-F}$ = 33.2 Hz), 142.5, 133.7 (t, $^2J_{C-F}$ = 27.9 Hz), 132.3, 130.4 (t, $^4J_{C-F}$ = 2.0 Hz), 129.5, 126.3 (t, $^4J_{C-F}$ = 2.1 Hz), 121.7, 110.8 (t, $^1J_{C-F}$ = 251.2 Hz), 105.8 (t, $^3J_{C-F}$ = 9.5 Hz), 63.3, 13.7.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{11}BrF_2IO_2$: 430.8950; found: 430.8970.

Ethyl 2,2-difluoro-4-iodo-4-(m-tolyl)but-3-enoate (5m)



Colorless oil, 72.4 mg, 99% yield.

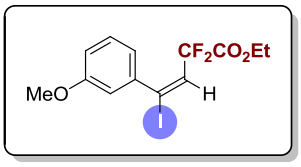
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.8 Hz, 1H), 7.17 – 7.10 (m, 3H), 6.72 (t, *J* = 10.8 Hz, 1H), 3.98 (q, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -93.6.

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5 (t, $^2J_{C-F}$ = 33.3 Hz), 140.5, 137.7, 132.8 (t, $^2J_{C-F}$ = 28.6 Hz), 130.2, 128.3, 127.9, 124.9 (t, $^4J_{C-F}$ = 2.1 Hz), 110.8 (t, $^1J_{C-F}$ = 249.8 Hz), 109.0 (t, $^3J_{C-F}$ = 10.3 Hz), 63.0, 21.2, 13.6.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{13}F_2IO_2Na$: 388.9821; found: 388.9815.

Ethyl 2,2-difluoro-4-iodo-4-(3-methoxyphenyl)but-3-enoate (5n)



Colorless oil, 75.6 mg, 99% yield.

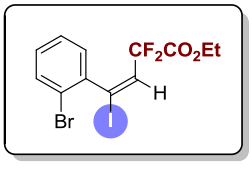
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.9 Hz, 1H), 6.91 (dt, *J* = 7.6, 1.3 Hz, 1H), 6.89 – 6.83 (m, 2H), 6.72 (t, *J* = 10.9 Hz, 1H), 4.01 (q, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -93.8.

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5 (t, $^2J_{C-F}$ = 33.3 Hz), 158.8, 141.7, 133.0 (t, $^2J_{C-F}$ = 28.6 Hz), 129.1, 120.3 (t, $^4J_{C-F}$ = 2.0 Hz), 115.4, 113.1, 110.8 (t, $^1J_{C-F}$ = 250.0 Hz), 108.4 (t, $^3J_{C-F}$ = 10.2 Hz), 63.1, 55.3, 13.6.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{13}F_2IO_3Na$: 404.9763; found: 404.9762.

Ethyl 4-(2-bromophenyl)-2,2-difluoro-4-iodobut-3-enoate (5o)



Colorless oil, 85.0 mg, 99% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.32 (td, *J* = 7.5, 1.2 Hz, 1H), 7.25 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.20 (td, *J* = 7.8, 1.8

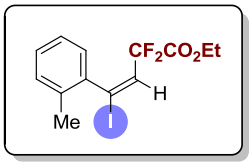
Hz, 1H), 6.78 (t, J = 11.5 Hz, 1H), 4.19 (qd, J = 7.2, 2.8 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -97.7 (d, J = 269.0 Hz), -98.5 (d, J = 269.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2 (t, $^2J_{C\text{-}F}$ = 33.2 Hz), 140.7, 134.2 (dd, $^2J_{C\text{-}F}$ = 28.6, 25.9 Hz), 133.0, 130.4, 128.8 (t, $^4J_{C\text{-}F}$ = 2.2 Hz), 127.1, 121.0, 110.8 (dd, $^1J_{C\text{-}F}$ = 253.3, 250.8 Hz), 105.5 (dd, $^3J_{C\text{-}F}$ = 10.1, 8.8 Hz), 63.3, 13.8.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_{10}BrF_2IO_2Na$: 452.8769; found: 452.8769.

Ethyl 2,2-difluoro-4-iodo-4-(o-tolyl)but-3-enoate (5p)



Colorless oil, 72.6 mg, 99% yield.

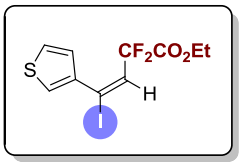
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.21 (m, 1H), 7.21 – 7.15 (m, 2H), 7.15 – 7.10 (m, 1H), 6.83 – 6.74 (m, 1H), 4.01 (qd, J = 7.2, 1.4 Hz, 2H), 2.30 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -95.8 (d, J = 273.1 Hz), -97.8 (d, J = 273.1 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5 (t, $^2J_{C\text{-}F}$ = 33.2 Hz), 139.7, 134.8, 133.7 (t, $^2J_{C\text{-}F}$ = 28.1 Hz), 130.3, 129.4, 127.2 (t, $^4J_{C\text{-}F}$ = 2.5 Hz), 125.5, 110.7 (t, $^1J_{C\text{-}F}$ = 250.9 Hz), 107.9 (t, $^3J_{C\text{-}F}$ = 9.9 Hz), 63.1, 19.4, 13.6.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{13}F_2IO_2Na$: 388.9821; found: 388.9816.

Ethyl 2,2-difluoro-4-iodo-4-(thiophen-3-yl)but-3-enoate (5q)



Yellow oil, 64.5 mg, 90% yield.

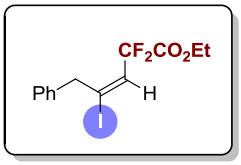
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, J = 3.0, 1.3 Hz, 1H), 7.31 (dd, J = 5.1, 3.0 Hz, 1H), 7.12 (dd, J = 5.1, 1.3 Hz, 1H), 6.71 (t, J = 10.6 Hz, 1H), 4.05 (q, J = 7.1 Hz, 2H), 1.22 (t, J = 7.1 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -92.6.

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4 (t, $^2J_{C\text{-}F}$ = 33.4 Hz), 140.1, 133.3 (t, $^2J_{C\text{-}F}$ = 29.0 Hz), 128.4, 125.9 (t, $^4J_{C\text{-}F}$ = 2.9 Hz), 125.6, 111.0 (t, $^1J_{C\text{-}F}$ = 249.3 Hz), 102.1 (t, $^3J_{C\text{-}F}$ = 10.6 Hz), 63.2, 13.7.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{10}H_9F_2IO_2SNa$: 380.9228; found: 380.9224.

Ethyl 2,2-difluoro-4-iodo-5-phenylpent-3-enoate (5r) (E/Z = 3:1)



Colorless oil, 69.6 mg, 95% yield.

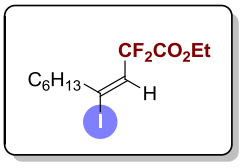
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.30 (m, 3H), 7.27 – 7.20 (m, 2H), 6.61 (t, J = 12.5 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 4.08 (s, 2H), 1.39 (t, J = 7.1 Hz, 3H) (major isomer).

^{19}F NMR (471 MHz, $CDCl_3$) δ -97.1 (major isomer).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1 (t, $^2J_{C\text{-}F}$ = 34.1 Hz), 137.0, 132.2 (t, $^2J_{C\text{-}F}$ = 26.9 Hz), 128.9, 128.6, 127.2, 116.7 (t, $^3J_{C\text{-}F}$ = 7.3 Hz), 111.6 (t, $^1J_{C\text{-}F}$ = 252.8 Hz), 63.5, 46.3 (t, $^4J_{C\text{-}F}$ = 2.3 Hz), 13.9 (major isomer).

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{13}F_2IO_2Na$: 388.9821; found: 388.9813.

Ethyl 2,2-difluoro-4-iododec-3-enoate (5s) (E/Z = 3.3:1 dr)



Colorless oil, 71.8 mg, 99% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.42 (t, J = 13.2 Hz, 1H), 4.35 (q, J = 7.2 Hz, 2H), 2.61 (t, J = 7.5 Hz, 2H), 1.63 – 1.50 (m, 2H), 1.37 (t, J = 7.2 Hz, 3H), 1.35 – 1.26 (m, 6H), 0.91 (t, J = 6.6 Hz, 3H) (major isomer).

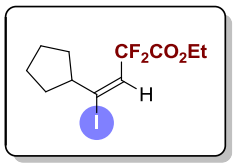
^{19}F NMR (471 MHz, $CDCl_3$) δ -97.7 (major isomer).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2 (t, $^2J_{C\text{-}F}$ = 34.4 Hz), 131.2 (t, $^2J_{C\text{-}F}$ = 27.0 Hz), 119.6 (t, $^3J_{C\text{-}F}$ = 7.6 Hz), 111.5 (t, $^1J_{C\text{-}F}$ = 252.3 Hz), 63.3, 40.7 (t, $^4J_{C\text{-}F}$ = 2.2 Hz), 31.5, 29.9, 28.0, 22.5, 14.0,

13.9 (major isomer).

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_{19}F_2IO_2Na$: 383.0290; found: 383.0283.

Ethyl 4-cyclopentyl-2,2-difluoro-4-iodobut-3-enoate (5t) (*E*/*Z* = 2:1)



Colorless oil, 68.2 mg, 99% yield.

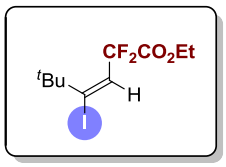
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.43 (t, *J* = 13.0 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 2.64 – 2.50 (m, 1H), 1.91 – 1.82 (m, 1H), 1.81 – 1.71 (m, 3H), 1.59 – 1.50 (m, 2H), 1.50 – 1.41 (m, 2H), 1.37 (t, *J* = 7.2 Hz, 3H) (major isomer).

^{19}F NMR (471 MHz, $CDCl_3$) δ -96.8 (major isomer).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4 (t, $^2J_{C\text{-}F}$ = 34.5 Hz), 131.1 (t, $^3J_{C\text{-}F}$ = 27.7 Hz), 126.4 (t, $^2J_{C\text{-}F}$ = 29.7 Hz), 111.7 (t, $^1J_{C\text{-}F}$ = 252.0 Hz), 63.3, 45.9, 34.8, 25.7, 13.9 (major isomer).

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{11}H_{15}F_2IO_2Na$: 366.9977; found: 366.9973.

Ethyl 2,2-difluoro-4-iodo-5,5-dimethylhex-3-enoate (5u) (*E*/*Z* > 20:1)



Colorless oil, 65.8 mg, 99% yield.

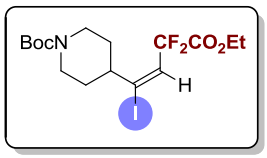
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.44 (t, *J* = 11.7 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.24 (s, 9H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -96.5.

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6 (t, $^2J_{C\text{-}F}$ = 34.3 Hz), 131.4 (t, $^3J_{C\text{-}F}$ = 9.7 Hz), 126.4 (t, $^2J_{C\text{-}F}$ = 30.5 Hz), 113.0 (t, $^1J_{C\text{-}F}$ = 246.8 Hz), 63.1, 41.4, 29.9, 13.8.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{10}H_{15}F_2IO_2Na$: 354.9977; found: 354.9981.

tert-butyl 4-(4-ethoxy-3,3-difluoro-1-iodo-4-oxobut-1-en-1-yl)piperidine-1-carboxylate (5v) (*E*/*Z* = 1:1)



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1), colorless oil, 66.0 mg, 72% yield.

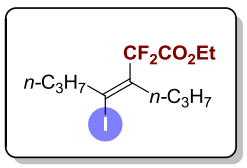
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.50 (t, *J* = 13.2 Hz, 1H), 4.36 (q, *J* = 7.3 Hz, 2H), 4.30 – 4.11 (m, 2H), 2.97 – 2.65 (m, 2H), 2.40 – 2.30 (m, 1H), 1.91 – 1.77 (m, 1H), 1.60 – 1.50 (m, 3H), 1.49 (s, 9H), 1.38 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -97.5.

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2 (t, $^2J_{C\text{-}F}$ = 34.2 Hz), 154.7, 131.3 (t, $^3J_{C\text{-}F}$ = 27.5 Hz), 127.4 (t, $^2J_{C\text{-}F}$ = 29.8 Hz), 112.3 (t, $^1J_{C\text{-}F}$ = 247.9 Hz), 79.7, 63.5, 50.9, 43.0 (t, $^4J_{C\text{-}F}$ = 2.3 Hz), 32.4, 28.4, 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{24}F_2INO_4Na$: 482.0610; found: 482.0614.

Ethyl 2,2-difluoro-4-iodo-3-propylhept-3-enoate (5w) (*E*/*Z* = 8:1)



Colorless oil, 49.8 mg, 69% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.33 (q, *J* = 7.1 Hz, 2H), 2.71 – 2.63 (m, 2H), 2.48 – 2.39 (m, 2H), 1.68 – 1.48 (m, 4H), 1.36 (t, *J* = 7.1 Hz, 3H), 0.99 (t, *J* = 7.4 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H).

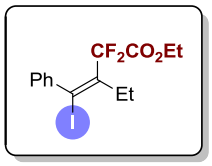
^{19}F NMR (471 MHz, $CDCl_3$) δ -96.5.

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7 (t, $^2J_{C\text{-}F}$ = 35.2 Hz), 136.8 (t, $^2J_{C\text{-}F}$ = 22.7 Hz), 119.8 (t, $^3J_{C\text{-}F}$ = 6.1 Hz), 111.9 (t, $^1J_{C\text{-}F}$ = 256.1 Hz), 63.2, 44.3 (t, $^4J_{C\text{-}F}$ = 2.4 Hz), 41.2 (t, $^3J_{C\text{-}F}$ = 3.7 Hz), 23.8, 21.5, 14.0, 13.9, 12.8.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_{19}F_2IO_2Na$: 383.0290; found: 383.0295.

Ethyl 2,2-difluoro-3-(iodo(phenyl)methylene)pentanoate (5x) (*E*/*Z* > 20:1)

Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 25/1),



colorless oil, 47.9 mg, 63% yield.

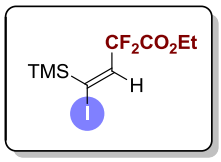
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 3H), 7.25 – 7.19 (m, 2H), 3.89 (q, *J* = 7.2 Hz, 2H), 2.77 – 2.65 (m, 2H), 1.25 (t, *J* = 7.5 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -92.6.

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9 (t, $^2J_{C\text{-}F}$ = 33.6 Hz), 142.6, 141.0 (t, $^2J_{C\text{-}F}$ = 23.2 Hz), 128.7, 128.5, 127.8, 110.8 (t, $^1J_{C\text{-}F}$ = 254.1 Hz), 108.3 (t, $^3J_{C\text{-}F}$ = 8.1 Hz), 62.8, 32.3 (t, $^3J_{C\text{-}F}$ = 3.2 Hz), 13.6, 12.3.

HRMS (ESI) m/z: [M+Na]$^+$ calcd for $C_{14}H_{15}F_2IO_2Na$: 402.9977; found: 402.9973.

Ethyl 2,2-difluoro-4-iodo-4-(trimethylsilyl)but-3-enoate (5y) (*E*/*Z* = 2:1)



Colorless oil, 69.0 mg, 99% yield.

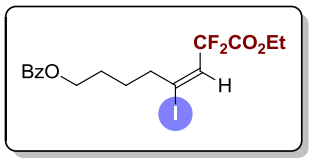
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (t, *J* = 14.7 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 0.33 (s, 9H) (major isomer).

^{19}F NMR (471 MHz, $CDCl_3$) δ -97.6 (major isomer).

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8 (t, $^2J_{C\text{-}F}$ = 33.3 Hz), 143.7 (t, $^2J_{C\text{-}F}$ = 25.8 Hz), 123.5 (t, $^3J_{C\text{-}F}$ = 7.0 Hz), 111.7 (t, $^1J_{C\text{-}F}$ = 252.0 Hz), 63.4, 13.9, -1.9 (major isomer).

HRMS (ESI) m/z: [M+Na]$^+$ calcd for $C_9H_{15}F_2IO_2SiNa$: 370.9746; found: 370.9740.

8-ethoxy-7,7-difluoro-5-iodo-8-oxooct-5-en-1-yl benzoate (5z) (*E*/*Z* = 5:1)



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 25/1), colorless oil, 74.1 mg, 82% yield.

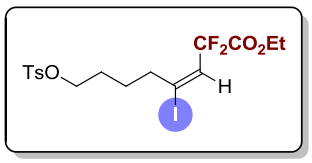
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 – 7.99 (m, 2H), 7.63 – 7.54 (m, 1H), 7.51 – 7.42 (m, 2H), 6.47 (t, *J* = 13.2 Hz, 1H), 4.39 – 4.33 (m, 2H), 4.34 (t, *J* = 7.2 Hz, 2H), 2.84 – 2.62 (m, 2H), 1.88 – 1.71 (m, 4H), 1.36 (t, *J* = 7.2 Hz, 3H) (major isomer).

^{19}F NMR (471 MHz, $CDCl_3$) δ -97.7 (major isomer).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 163.1 (t, $^2J_{C\text{-}F}$ = 34.4 Hz), 132.9, 131.9 (t, $^2J_{C\text{-}F}$ = 27.0 Hz), 130.3, 129.6, 128.3, 118.6 (t, $^3J_{C\text{-}F}$ = 7.5 Hz), 111.5 (t, $^1J_{C\text{-}F}$ = 252.5 Hz), 64.4, 63.4, 40.2 (t, $^4J_{C\text{-}F}$ = 2.1 Hz), 27.4, 26.4, 13.9 (major isomer).

HRMS (ESI) m/z: [M+Na]$^+$ calcd for $C_{17}H_{19}F_2IO_4Na$: 475.0188; found: 475.0192.

Ethyl 2,2-difluoro-4-iodo-8-(tosyloxy)oct-3-enoate (5aa) (*E*/*Z* = 4:1)



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1), colorless oil, 78.0 mg, 78% yield.

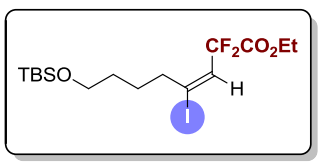
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 6.42 – 6.30 (m, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.07 (t, *J* = 5.8 Hz, 2H), 2.57 (td, *J* = 6.2, 5.2, 2.5 Hz, 2H), 2.48 (s, 3H), 1.75 – 1.55 (m, 4H), 1.39 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -98.1.

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5 (t, $^2J_{C\text{-}F}$ = 35.3 Hz), 144.9, 133.0, 129.9, 128.9 (t, $^2J_{C\text{-}F}$ = 29.5 Hz), 127.9, 113.3 (t, $^3J_{C\text{-}F}$ = 8.8 Hz), 111.9 (t, $^1J_{C\text{-}F}$ = 248.0 Hz), 69.8, 63.3, 45.8, 27.2, 24.9, 21.6, 13.9.

HRMS (ESI) m/z: [M+Na]$^+$ calcd for $C_{17}H_{21}F_2IO_5SNa$: 525.0015; found: 525.0017.

Ethyl 8-((tert-butyldimethylsilyl)oxy)-2,2-difluoro-4-iodooct-3-enoate (5ab) (*E*/*Z* = 3:1)



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 100/1), colorless oil, 66.0 mg, 69% yield.

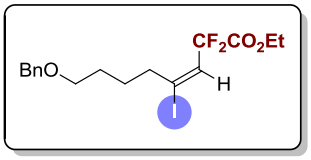
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.44 (t, *J* = 13.2 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.64 (t, *J* = 6.1 Hz, 2H), 2.76 – 2.58 (m, 2H), 1.71 – 1.58 (m, 4H), 1.38 (t, *J* = 7.1 Hz, 3H), 0.92 (s, 9H), 0.08 (s, 6H) (major isomer).

^{19}F NMR (471 MHz, $CDCl_3$) δ -97.7 (major isomer).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2 (t, $^2J_{C\text{-}F}$ = 34.3 Hz), 131.4 (t, $^2J_{C\text{-}F}$ = 27.0 Hz), 119.4 (t, $^3J_{C\text{-}F}$ = 7.4 Hz), 111.6 (t, $^1J_{C\text{-}F}$ = 252.4 Hz), 68.2, 62.6, 40.4, 31.5, 26.0, 25.0, 18.3, 13.9, -5.3 (major isomer).

HRMS (ESI) m/z: $[M+K]^+$ calcd for $C_{16}H_{29}F_2IO_3SiK$: 501.0530; found: 501.0538.

Ethyl 8-(benzyloxy)-2,2-difluoro-4-iodooct-3-enoate (5ac) (*E*/*Z* = 3:1)



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 25/1), colorless oil, 65.7 mg, 75% yield.

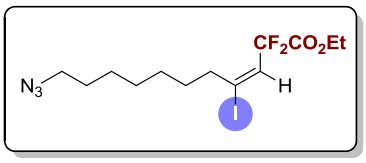
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 4H), 7.34 – 7.29 (m, 1H), 6.44 (t, *J* = 13.7 Hz, 1H), 4.53 (s, 2H), 4.34 (q, *J* = 7.2 Hz, 2H), 3.57 – 3.44 (m, 2H), 2.70 – 2.61 (m, 2H), 1.72 – 1.63 (m, 4H), 1.36 (t, *J* = 7.2 Hz, 3H) (major isomer).

^{19}F NMR (471 MHz, $CDCl_3$) δ -97.7 (major isomer).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2 (t, $^2J_{C\text{-}F}$ = 34.3 Hz), 138.5, 131.5 (t, $^2J_{C\text{-}F}$ = 27.0 Hz), 128.3, 127.6, 127.5, 119.1 (t, $^3J_{C\text{-}F}$ = 7.5 Hz), 111.5 (t, $^1J_{C\text{-}F}$ = 252.4 Hz), 72.9, 69.8, 63.4, 40.4 (t, $^4J_{C\text{-}F}$ = 2.2 Hz), 28.4, 26.7, 13.9 (major isomer).

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{21}F_2IO_3Na$: 461.0396; found: 461.0392.

Ethyl 11-azido-2,2-difluoro-4-iodoundec-3-enoate (5ad) (*E*/*Z* = 3:1)



Colorless oil, 78.0 mg, 94% yield.

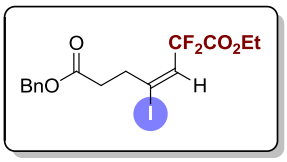
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.42 (t, *J* = 13.2 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 3.28 (t, *J* = 6.9 Hz, 2H), 2.66 – 2.57 (m, 2H), 1.67 – 1.54 (m, 4H), 1.44 – 1.31 (m, 6H), 1.38 (t, *J* = 7.2 Hz, 3H) (major isomer).

^{19}F NMR (471 MHz, $CDCl_3$) -97.7 (major isomer).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2 (t, $^2J_{C\text{-}F}$ = 34.3 Hz), 131.3 (t, $^2J_{C\text{-}F}$ = 27.0 Hz), 119.4 (t, $^3J_{C\text{-}F}$ = 7.6 Hz), 111.5 (t, $^1J_{C\text{-}F}$ = 252.4 Hz), 63.3, 51.4, 40.6 (t, $^4J_{C\text{-}F}$ = 2.2 Hz), 29.7, 28.8, 28.7, 28.1, 26.5, 13.9 (major isomer).

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{20}F_2IN_3O_2Na$: 438.0460; found: 438.0459.

7-benzyl 1-ethyl 2,2-difluoro-4-iodohept-3-enedioate (5ae) (*E*/*Z* = 3:1)



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 25/1), colorless oil, 62.9 mg, 72% yield.

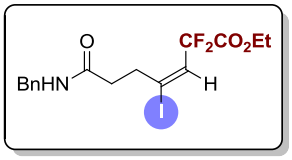
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.33 (m, 5H), 6.48 (t, *J* = 13.1 Hz, 1H), , 5.16 (s, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 3.12 – 2.90 (m, 2H), 2.66 (t, *J* = 7.5 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H) (major isomer).

^{19}F NMR (471 MHz, $CDCl_3$) δ -98.1 (major isomer).

^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 162.4 (t, $^2J_{C\text{-}F}$ = 34.1 Hz), 135.6, 129.6 (t, $^2J_{C\text{-}F}$ = 29.5 Hz), 128.6, 128.4, 128.3, 111.8 (t, $^1J_{C\text{-}F}$ = 248.2 Hz), 111.1 (t, $^3J_{C\text{-}F}$ = 9.8 Hz), 66.7, 63.3, 42.0, 33.9, 13.9 (major isomer).

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{17}F_2IO_4Na$: 461.0032; found: 461.0034.

Eethyl 7-(benzylamino)-2,2-difluoro-4-iodo-7-oxohept-3-enoate (5af) (*E*/*Z* = 3:1)



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1/1), colorless oil, 49.8 mg, 60% yield.

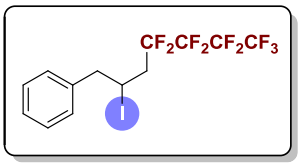
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.34 (m, 2H), 7.34 – 7.26 (m, 3H), 6.47 (t, *J* = 13.1 Hz, 1H), 5.82 (s, 1H), 4.47 (d, *J* = 5.7 Hz, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 3.14 – 2.88 (m, 2H), 2.59 – 2.35 (m, 2H), 1.37 (t, *J* = 7.2 Hz, 3H) (major isomer).

^{19}F NMR (471 MHz, $CDCl_3$) δ -98.0 (major isomer).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 163.0 (t, $^2J_{C\text{-}F}$ = 34.3 Hz), 138.0, 132.5 (t, $^2J_{C\text{-}F}$ = 27.3 Hz), 128.7, 127.9, 127.6, 116.2 (t, $^3J_{C\text{-}F}$ = 7.7 Hz), 111.6 (t, $^1J_{C\text{-}F}$ = 252.8 Hz), 63.6, 43.8, 36.9 (t, $^4J_{C\text{-}F}$ = 2.3 Hz), 36.4, 13.9 (major isomer).

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{18}F_2INO_3Na$: 438.0372; found: 438.0370.

(4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptyl)benzene (6a)



6a is a known product.[1] Purified by silica gel column chromatography (petroleum ether), colorless oil, 72.3 mg, 78% yield.

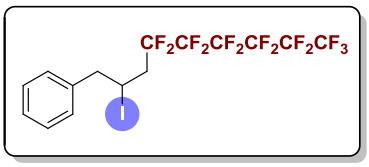
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.33 (m, 3H), 7.27 – 7.22 (m, 2H), 4.51 (dq, *J* = 8.9, 6.3 Hz, 1H), 3.34 (dd, *J* = 14.6, 5.8 Hz, 1H), 3.24 (dd, *J* = 14.6, 8.9 Hz, 1H), 3.06 – 2.81 (m, 2H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -81.1 (t, *J* = 9.4 Hz, 3F), -112.2 (dt, *J* = 269.4, 12.6 Hz, 1F), -114.1 (dt, *J* = 269.4, 12.6 Hz, 1F), -124.6 (m, 2F), -126.0 (m, 2F).

^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 128.9, 128.6, 127.3, 121 – 108 (m), 47.0, 40.8 (t, $^2J_{C\text{-}F}$ = 20.9 Hz), 19.2.

LRMS: m/z (EI) 337 (M-I), 148, 117, 103, 91, 77.

(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-iodononyl)benzene (6b)



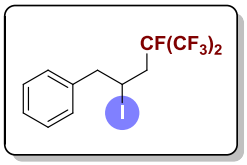
6b is a known product.[2] Purified by silica gel column chromatography (petroleum ether), colorless oil, 69.9 mg, 62% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 3H), 7.23 (dd, *J* = 6.7, 1.8 Hz, 2H), 4.53 – 4.43 (m, 1H), 3.33 (dd, *J* = 14.6, 5.8 Hz, 1H), 3.23 (dd, *J* = 14.6, 8.9 Hz, 1H), 3.03 – 2.78 (m, 2H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -80.8 (t, *J* = 10.2 Hz, 3F), -112.0 (dt, *J* = 269.8, 14.5 Hz, 1F), -113.8 (dt, *J* = 269.8, 14.3 Hz, 1F), -121.8 (m, 2F), -122.9 (m, 2F), -123.7 (m, 2F), -126.2 (m, 2F).

^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 128.9, 128.6, 127.3, 120 – 106 (m), 47.0, 40.8 (t, $^2J_{C\text{-}F}$ = 20.9 Hz), 19.3.

LRMS: m/z (EI) 437 (M-I), 178, 148, 117, 103, 91, 69.



(4,5,5,5-tetrafluoro-2-iodo-4-(trifluoromethyl)pentyl)benzene (6c)

6c is a known product.[3] Purified by silica gel column chromatography (petroleum ether), colorless oil, 49.6 mg, 60% yield.

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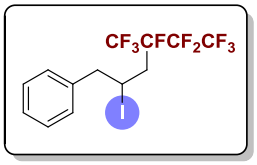
[1] Behrends, I.; Bähr, S.; Czekelius, C. *Chem. Eur. J.* **2016**, *22*, 17177–17181.

[2] Yajima, T.; Ikegami, M. *Eur. J. Org. Chem.* **2017**, 2126–2129.

[3] Yoshioka, E.; Kohtani, S.; Jichu, T.; Fukazawa, T.; Nagai, T.; Kawashima, A.; Takemoto, Y.; Miyabe, H. *J. Org. Chem.* **2016**, *81*, 7217–7229.

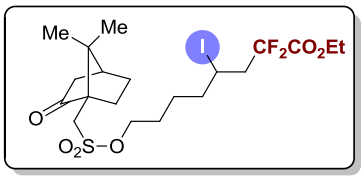
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 3H), 7.25 – 7.17 (m, 2H), 4.52 – 4.42 (m, 1H), 3.31 (dd, *J* = 14.6, 5.4 Hz, 1H), 3.17 (dd, *J* = 14.6, 9.2 Hz, 1H), 3.04 – 2.87 (m, 2H).
^{19}F NMR (471 MHz, $CDCl_3$) δ -76.2 (p, *J* = 7.1 Hz, 3F), -77.2 (p, *J* = 7.1 Hz, 3F), -185.4 (hept, *J* = 7.1 Hz, 1F).
^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 128.9, 128.6, 127.3, 122 – 119 (m), 93 – 90 (m), 47.5, 38.9 (d, $^2J_{C\text{-}F}$ = 18.3 Hz), 21.7.

(4,5,5,6,6,6-hexafluoro-2-iodo-4-(trifluoromethyl)hexyl)benzene (6d) (2.6:1 dr)



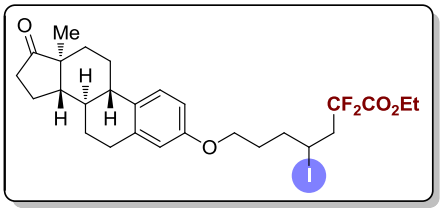
Purified by silica gel column chromatography (petroleum ether), colorless oil, 52.8 mg, 57% yield.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 3H), 7.26 – 7.17 (m, 2H), 4.46 (tt, *J* = 13.6, 5.9 Hz, 1H), 3.37 – 3.20 (m, 1H), 3.14 – 2.99 (m, 2H), 2.92 (td, *J* = 17.9, 17.4, 6.2 Hz, 1H).
^{19}F NMR (471 MHz, $CDCl_3$) δ -76.2 (tq, *J* = 14.1, 7.0 Hz, 3F), -80.0 (dq, *J* = 13.1, 6.9 Hz, 3F), -120.9 (pent, *J* = 7.8 Hz, 1F), -121.1 (qd, *J* = 11.5, 4.4 Hz, 1F), -186.0 (td, *J* = 13.2, 6.3 Hz, 1F).
^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 128.9, 128.6, 127.4, 48.0, 38.8 (d, $^2J_{C\text{-}F}$ = 18.9 Hz), 21.0.
LRMS: m/z (EI) 337 (M-I), 281, 253, 207, 191, 126, 97, 72 (100).

Eethyl 8-((((1S,4S)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)sulfonyl)oxy)-2,2-difluoro-4-iodooctanoate (7a) (1:1 dr)



Colorless oil, 111.7 mg, 99% yield.
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.35 (q, *J* = 7.1 Hz, 2H), 4.35 – 4.19 (m, 3H), 3.60 (d, *J* = 15.1 Hz, 1H), 3.00 (d, *J* = 15.1 Hz, 1H), 2.99 – 2.85 (m, 1H), 2.74 (dddd, *J* = 18.8, 15.6, 12.0, 7.3 Hz, 1H), 2.49 (ddd, *J* = 14.8, 11.9, 4.0 Hz, 1H), 2.39 (dt, *J* = 18.5, 4.1 Hz, 1H), 2.13 (t, *J* = 4.6 Hz, 1H), 2.07 (tp, *J* = 12.2, 4.2, 3.8 Hz, 1H), 1.97 (d, *J* = 18.5 Hz, 1H), 1.90 – 1.73 (m, 4H), 1.73 – 1.63 (m, 2H), 1.59 – 1.49 (m, 1H), 1.45 (ddd, *J* = 13.0, 9.4, 4.0 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.12 (s, 3H), 0.88 (s, 3H).
^{19}F NMR (471 MHz, $CDCl_3$) δ -102.1 (d, *J* = 263.2 Hz), -106.8 (d, *J* = 263.2, 3.4 Hz).
^{13}C NMR (125 MHz, $CDCl_3$) δ 214.6, 163.3 (t, $^2J_{C\text{-}F}$ = 32.2 Hz), 115.1 (7, $^1J_{C\text{-}F}$ = 253.1 Hz), 70.0, 63.3, 57.9, 48.0, 46.7, 45.2 (t, $^2J_{C\text{-}F}$ = 23.2 Hz), 42.7, 42.5, 39.6, 28.2, 26.8, 25.7, 24.8, 22.2, 19.7, 19.6, 13.9.
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{20}H_{31}F_2IO_6Na$: 587.0746; found: 587.0750.

Ethyl 2,2-difluoro-4-iodo-7-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)heptanoate (7b)

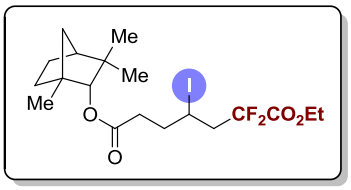


Colorless oil, 116.4 mg, 99% yield.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.6 Hz, 1H), 6.72 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.66 (d, *J* = 2.8 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.31 (dq, *J* = 6.9, 4.0 Hz, 1H), 3.98 (q, *J* = 6.4 Hz, 2H), 3.05 – 2.86 (m, 3H), 2.80 (dddd, *J* = 18.1, 15.7, 12.4, 7.1 Hz, 1H), 2.52 (dd, *J* = 19.0, 8.7 Hz, 1H), 2.44 – 2.39 (m, 1H), 2.27 (td, *J* = 10.8, 4.6 Hz, 1H), 2.16 (dt, *J* = 18.6, 8.9 Hz, 1H), 2.11 – 1.95 (m, 6H), 1.93 – 1.86 (m, 1H), 1.70 – 1.59 (m, 2H), 1.59 – 1.49 (m, 3H), 1.48 – 1.42 (m, 1H), 1.39 (t, *J* = 7.2 Hz, 3H), 0.93 (s, 3H).
^{19}F NMR (471 MHz, $CDCl_3$) δ -102.1 (d, *J* = 263.5 Hz), -106.8 (d, *J* = 263.5 Hz).
^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4 (t, $^2J_{C\text{-}F}$ = 32.3 Hz), 156.8, 137.7, 132.1, 126.3, 115.09 (t,

$^{1}J_{C\text{-}F}$ = 253.3 Hz), 115.06, 114.5, 112.1, 66.6, 63.2, 50.4, 48.0, 45.3 (t, $^{2}J_{C\text{-}F}$ = 23.2 Hz), 43.9, 38.3, 37.2, 35.8, 31.5, 29.6, 29.5, 26.5, 25.9, 22.4 (t, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 21.5, 13.9, 13.8.

HRMS (ESI) m/z: [M+H]$^{+}$ calcd for $C_{27}H_{36}F_2IO_4$: 589.1621; found: 589.1605.

1-Ethyl 7-((1S,2R,4S)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl) 2,2-difluoro-4-iodo-heptanedioate (7c) (1:1 dr)



Colorless oil, 96.3 mg, 99% yield.

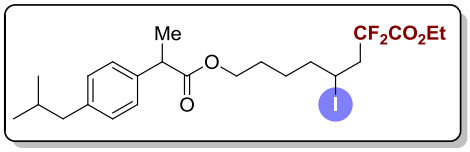
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.38 – 4.28 (m, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 3.06 – 2.89 (m, 1H), 2.77 (dddd, *J* = 18.7, 15.6, 12.1, 7.2 Hz, 1H), 2.67 – 2.57 (m, 1H), 2.53 (dddd, *J* = 16.2, 8.6, 6.8, 3.9 Hz, 1H), 2.15 (dddt, *J* = 12.6, 10.2, 5.7, 2.8 Hz, 1H), 2.11 – 2.02 (m, 1H), 1.84 – 1.67 (m, 4H), 1.59 (dt, *J* = 10.3, 2.1 Hz, 1H), 1.46 (tt, *J* = 12.3, 4.3 Hz, 1H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.20 (dd, *J* = 10.3, 1.5 Hz, 1H), 1.14 – 1.03 (m, 1H), 1.11 (s, 3H), 1.05 (s, 3H), 0.78 (s, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.0 (d, *J* = 264.2 Hz), -106.5 (d, *J* = 264.2 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 163.3 (t, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 115.0 (t, $^{1}J_{C\text{-}F}$ = 252.8 Hz), 86.6, 63.3, 48.3, 48.2, 45.3 (t, $^{2}J_{C\text{-}F}$ = 23.3 Hz), 41.3, 39.4, 35.5, 34.6, 29.6, 26.6, 25.7, 21.5 (t, $^{3}J_{C\text{-}F}$ = 4.1 Hz), 20.1, 19.3, 13.8.

HRMS (ESI) m/z: [M+K]$^{+}$ calcd for $C_{19}H_{29}F_2IO_4K$: 525.0710; found: 525.0677.

Ethyl 2,2-difluoro-4-iodo-8-((2-(4-isobutylphenyl)propanoyl)oxy)octanoate (7d)



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1), colorless oil, 86.1 mg, 82% yield.

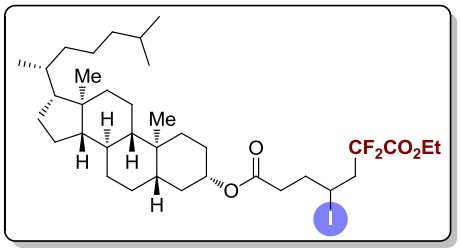
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 4.18 (dtd, *J* = 8.7, 6.8, 4.1 Hz, 1H), 4.12 – 4.07 (m, 2H), 3.71 (q, *J* = 7.2 Hz, 1H), 2.91 (dtdd, *J* = 18.8, 15.8, 6.4, 1.8 Hz, 1H), 2.79 – 2.64 (m, 1H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.87 (dp, *J* = 13.4, 6.6 Hz, 1H), 1.82 – 1.53 (m, 5H), 1.51 (d, *J* = 7.2 Hz, 3H), 1.45 – 1.32 (m, 1H), 1.40 (t, *J* = 7.2 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 6H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.0 (d, *J* = 263.2 Hz), -107.0 (d, *J* = 263.2 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.7, 163.4 (t, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 140.5, 137.8, 129.3, 127.1, 115.1 (t, $^{1}J_{C\text{-}F}$ = 252.7 Hz), 64.1, 63.2, 45.3 (t, $^{2}J_{C\text{-}F}$ = 23.2 Hz), 45.2, 45.0, 39.8, 30.2, 27.5, 26.0, 22.5 (t, $^{3}J_{C\text{-}F}$ = 3.5 Hz), 22.4, 18.4, 13.9.

HRMS (ESI) m/z: [M+K]$^{+}$ calcd for $C_{23}H_{33}F_2IO_4K$: 577.1023; found: 577.1045.

7-((3*S*,5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadeca hydro-1H-cyclopenta[a]phenanthren-3-yl) 1-ethyl 2,2-difluoro-4-iodoheptanedioate (7e) (1:1 dr)



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1), pale yellow amorphous solid, 36.6 mg, 51% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.73 (tt, *J* = 11.0, 4.9 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.30 (dtd, *J* = 10.4, 6.8, 3.7 Hz, 1H), 2.97 (dtd, *J* = 18.9, 15.5, 6.4 Hz, 1H), 2.77 (dddd, *J* = 18.8, 15.5, 12.2, 7.3 Hz, 1H), 2.56 (ddd, *J* = 16.5, 8.6, 5.5 Hz, 1H), 2.46 (dt, *J* = 16.2, 7.7 Hz, 1H), 2.15 (ddt, *J* = 15.1, 7.8, 3.8 Hz, 1H), 2.06 (ddt, *J* = 14.8, 9.6, 4.6 Hz, 1H), 1.98 (dt,

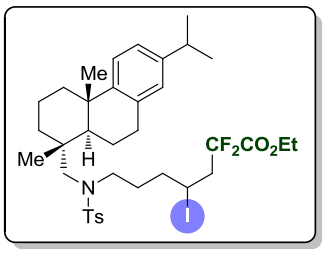
J = 12.6, 3.4 Hz, 1H), 1.84 (tdd, *J* = 14.9, 8.2, 4.3 Hz, 2H), 1.75 (dt, *J* = 13.3, 3.7 Hz, 1H), 1.67 (dq, *J* = 13.0, 3.4 Hz, 1H), 1.64 – 1.46 (m, 6H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.40 – 1.23 (m, 10H), 1.22 – 0.96 (m, 10H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.89 (d, *J* = 2.4 Hz, 3H), 0.88 (d, *J* = 2.4 Hz, 3H), 0.84 (s, 3H), 0.67 (s, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.2 (d, *J* = 264.2 Hz), -106.7 (d, *J* = 264.2 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 171.6, 163.3 (t, $^2J_{C\text{-}F}$ = 32.3 Hz), 115.0 (t, $^1J_{C\text{-}F}$ = 252.8 Hz), 74.2, 63.3, 56.4, 56.3, 54.2, 45.4 (t, $^2J_{C\text{-}F}$ = 23.3 Hz), 44.7, 42.6, 40.0, 39.5, 36.7, 36.2, 35.8, 35.52, 35.46, 34.9, 34.01, 33.98, 32.0, 28.6, 28.2, 28.0, 27.4, 24.2, 23.8, 22.8, 22.6, 21.5, 21.2, 18.7, 13.9, 12.2, 12.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{36}H_{60}F_2IO_4$: 721.3499; found: 721.3436.

Ethyl 2,2-difluoro-4-iodo-7-(N-(((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-4-methylphenylsulfonamido)heptanoate (7f) (1:1 dr)



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1), pale yellow amorphous solid, 131.7 mg, 87% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.91 (s, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.11 (p, *J* = 6.5 Hz, 1H), 3.27 – 2.75 (m, 8H), 2.62 (dddd, *J* = 18.4, 15.1, 11.6, 7.0 Hz, 1H), 2.44 (s, 3H), 2.31 (d, *J* = 12.8 Hz, 1H), 1.95 – 1.69 (m, 6H), 1.66 – 1.51 (m, 6H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.25 (d, *J* = 3.3 Hz, 6H), 1.24 (s, 3H), 1.03 (s, 3H).

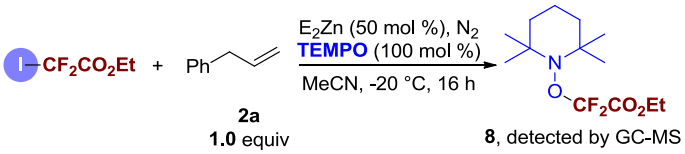
^{19}F NMR (471 MHz, $CDCl_3$) δ -102.1 (d, *J* = 263.0 Hz), -107.0 (d, *J* = 263.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3 (t, $^2J_{C\text{-}F}$ = 32.4 Hz), 147.3, 145.6, 143.3, 136.5, 134.4, 129.7, 127.5, 126.8, 123.9, 123.8, 115.0 (t, $^1J_{C\text{-}F}$ = 252.8 Hz), 63.3, 59.6, 50.5, 45.3, 44.9 (t, $^2J_{C\text{-}F}$ = 24.0 Hz), 39.0, 38.1, 37.8, 37.6, 37.2, 33.4, 29.8, 28.1, 25.6, 24.0, 21.5, 21.4 (t, $^4J_{C\text{-}F}$ = 4.2 Hz), 19.3, 18.9, 18.6, 13.9.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{36}H_{50}F_2INO_4S$: 758.2546; found: 758.2562.

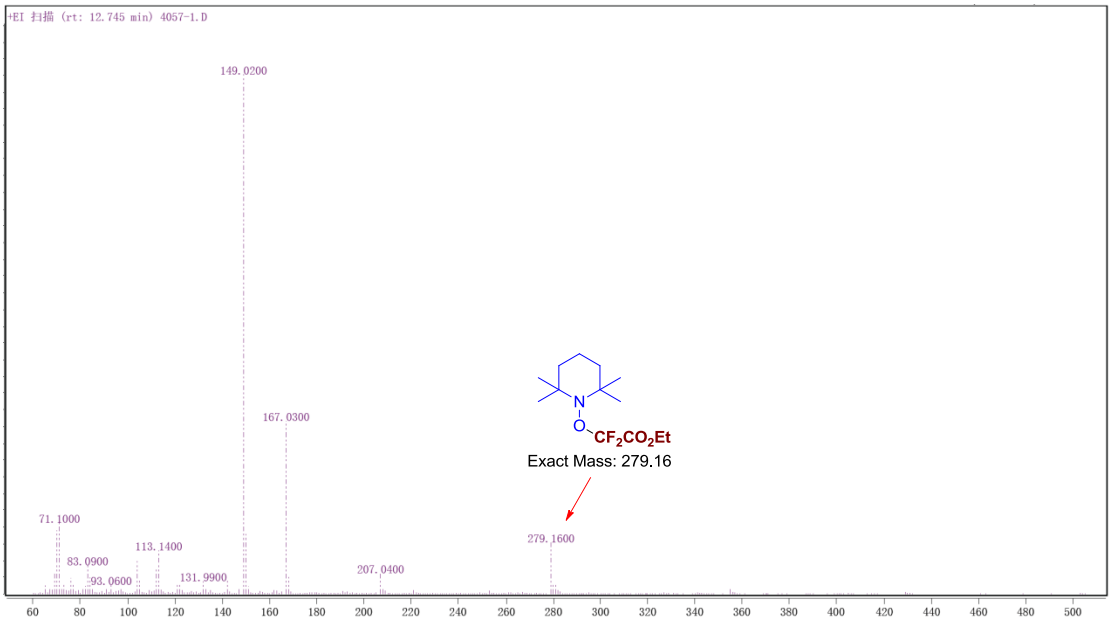
V. Mechanism Studies

5.1 TEMPO Capture Experiment

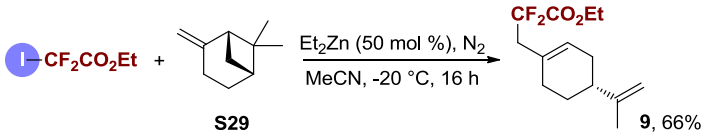


An oven-dried Schlenk tube was charged with a stir bar. The tube was degased and refilled with nitrogen for 3 times, and then a solution of **2a** (23.6 mg, 0.2 mmol), ethyl iododifluoroacetate **1a** (49.9 mg, 0.2 mmol, 1.0 equiv) and TEMPO (31.2 mg, 0.2 mmol, 1.0 equiv) in acetonitrile (2 mL) was injected to the tube via a syringe. The reaction mixture was cooled to - 20 °C. After stirring for 3 minutes, a solution of diethylzinc (1.0 mol/L in

hexane, 0.1 mL, 0.5 equiv) was injected to the reaction mixture via a syringe. After stirring at - 20 °C for 16 hours, the reaction was quenched with saturated NH_4Cl and extracted with ethyl acetate (3 × 100 mL). The combined organic layers were dried with Na_2SO_4, filtered through a short pad of silica gel, and concentrated under reduced pressure. The residue was submitted to GC-MS analysis.

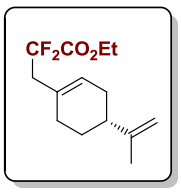


5.2 Radical Ring-Opening Experiment



An oven-dried Schlenk tube was charged with a stir bar. The tube was degased and refilled with nitrogen for 3 times, and then a solution of α-Pinene **S29** (27.2 mg, 0.2 mmol) and ethyl iododifluoroacetate **1a** (49.9 mg, 0.2 mmol, 1.0 equiv) in acetonitrile (2 mL) was injected to the tube via a syringe. The reaction mixture was cooled to - 20 °C. After stirring for 3 minutes, a solution of diethylzinc (1.0 mol/L in hexane, 0.1 mL, 0.5 equiv) was injected to the reaction mixture via a syringe. After stirring at - 20 °C for 16 hours, the reaction was quenched with saturated NH_4Cl and extracted with ethyl acetate (3 × 100 mL). The combined organic layers were dried with Na_2SO_4, filtered through a short pad of silica gel, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 100/1) to afford the corresponding pure product as a colorless oil, 33.9 mg, 66% yield.

(*R*)-ethyl 2,2-difluoro-3-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)propanoate (9)



^{1}H NMR (500 MHz, $CDCl_3$) δ 5.70 – 5.59 (m, 1H), 4.74 (t, *J* = 1.8 Hz, 1H), 4.71 (dt, *J* = 1.8, 0.9 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 2.74 (t, *J* = 16.6 Hz, 2H), 2.24 – 2.06 (m, 4H), 2.02 – 1.91 (m, 1H), 1.83 (ddt, *J* = 12.7, 5.2, 2.5 Hz, 1H), 1.74 (s, 3H), 1.53 – 1.41 (m, 1H), 1.36 (t, *J* = 7.1 Hz, 3H).

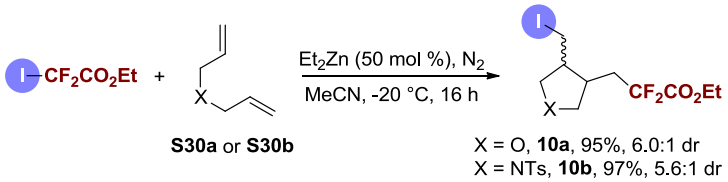
^{19}F NMR (471 MHz, $CDCl_3$) δ -102.8 (d, *J* = 254.0 Hz), -103.5 (d, *J* = 254.0

Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.2 (t, $^2J_{C\text{-}F}$ = 32.8 Hz), 149.5, 128.3, 128.2 (t, $^3J_{C\text{-}F}$ = 3.9 Hz), 116.1 (t, $^1J_{C\text{-}F}$ = 252.4 Hz), 108.7, 62.6, 42.7 (t, $^2J_{C\text{-}F}$ = 23.2 Hz), 40.4, 30.9, 29.5, 27.7, 20.7, 14.0.

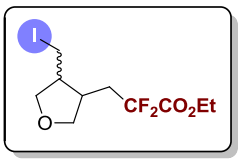
HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{21}F_2O_2$: 259.1504; found: 259.1502.

5.3 Radical Ring-Closure Experiment



An oven-dried Schlenk tube was charged with a stir bar. The tube was degased and refilled with nitrogen for 3 times, and then a solution of **S30** (27.2 mg, 0.2 mmol) and ethyl iododifluoroacetate **1a** (49.9 mg, 0.2 mmol, 1.0 equiv) in acetonitrile (2 mL) was injected to the tube via a syringe. The reaction mixture was cooled to - 20 °C. After stirring for 3 minutes, a solution of diethylzinc (1.0 mol/L in hexane, 0.1 mL, 0.5 equiv) was injected to the reaction mixture via a syringe. After stirring at - 20 °C for 16 hours, the reaction was quenched with saturated NH_4Cl and extracted with ethyl acetate (3 × 100 mL). The combined organic layers were dried with Na_2SO_4, filtered through a short pad of silica gel, and concentrated under reduced pressure. The residue was purified by silica gel column chromatographyto afford the corresponding pure product.

Ethyl 2,2-difluoro-3-(4-(iodomethyl)tetrahydrofuran-3-yl)propanoate (10a) (6:1 dr)



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1), colorless oil, 66.1 mg, 95% yield.

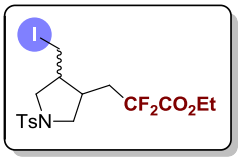
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.34 (q, *J* = 7.1 Hz, 2H), 4.03 – 3.93 (m, 2H), 3.73 (dd, *J* = 9.0, 4.5 Hz, 1H), 3.60 (t, *J* = 8.4 Hz, 1H), 3.23 (ddd, *J* = 9.8, 5.1, 1.1 Hz, 1H), 3.06 (dd, *J* = 10.8, 9.7 Hz, 1H), 2.76 (tdd, *J* = 11.1, 6.5, 4.9 Hz, 1H), 2.55 (dqd, *J* = 9.6, 7.4, 4.7 Hz, 1H), 2.30 (dtd, *J* = 22.7, 14.5, 4.7 Hz, 1H), 2.06 (dddd, *J* = 21.6, 14.8, 11.0, 9.5 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -104.2 (d, *J* = 261.0 Hz), -106.3 (d, *J* = 261.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7 (t, $^2J_{C\text{-}F}$ = 32.5 Hz), 115.5 (t, $^1J_{C\text{-}F}$ = 251.5 Hz), 73.4, 71.5 (t, $^3J_{C\text{-}F}$ = 2.1 Hz), 63.1, 45.1, 36.5, 31.8 (t, $^2J_{C\text{-}F}$ = 23.3 Hz), 13.9, 3.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{10}H_{15}F_2IO_3$: 349.0107; found: 349.0100.

Ethyl 2,2-difluoro-3-(4-(iodomethyl)-1-tosylpyrrolidin-3-yl)propanoate (10b) (5.6:1 dr)



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1), colorless oil, 97.3 mg, 97% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 3.48 – 3.40 (m, 2H), 3.36 (dd, *J* = 10.6, 3.9 Hz, 1H), 3.11 (dd, *J* = 10.2, 8.1 Hz, 1H), 3.08 – 3.04 (m, 1H), 2.62 (dd, *J* = 10.8, 9.3 Hz, 1H), 2.59 – 2.53 (m, 1H), 2.46 – 2.38 (m, 1H), 2.44 (s, 3H), 2.14 (dddd, *J* = 22.6, 14.9, 13.4, 5.0 Hz, 1H), 1.97 – 1.83 (m, 1H), 1.34 (t, *J* = 7.2 Hz, 3H).

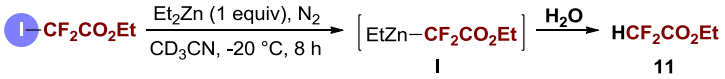
^{19}F NMR (471 MHz, $CDCl_3$) δ -104.3 (d, *J* = 262.4 Hz), -106.2 (d, *J* = 262.4 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4 (t, $^2J_{C\text{-}F}$ = 32.3 Hz), 143.7, 133.4, 129.8, 127.3, 115.2 (t,

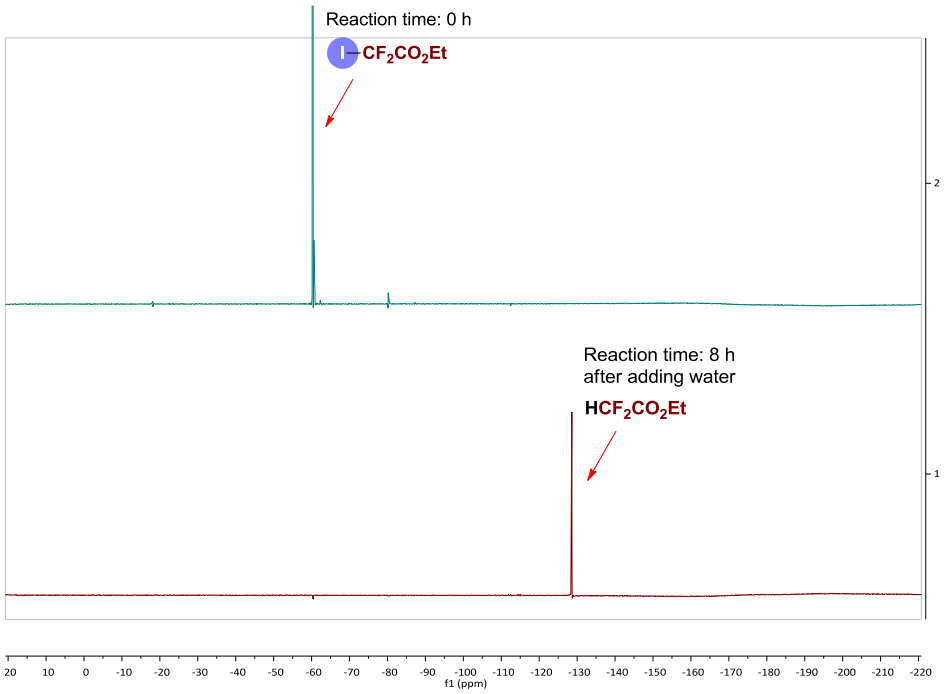
$^1J_{C\text{-}F}$ = 251.9 Hz), 63.2, 52.8, 50.9, 44.7, 35.6 (t, $^3J_{C\text{-}F}$ = 2.9 Hz), 31.9 (t, $^2J_{C\text{-}F}$ = 23.3 Hz), 21.5, 13.8, 2.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{23}F_2INO_4S$: 502.0355; found: 502.0354.

5.4 Crude ^{19}F-NMR Experiment

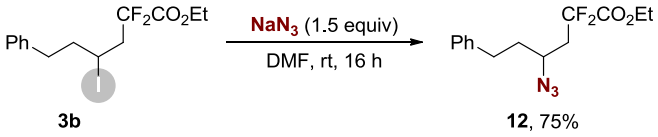


An oven-dried Schlenk tube was charged with a stir bar. The tube was degased and refilled with nitrogen for 3 times, and then a solution of ethyl iododifluoroacetate **1a** (12.5 mg, 0.05 mmol) in CD_3CN (0.5 mL) was injected to the tube via a syringe. The reaction mixture was cooled to - 20 °C. After stirring for 3 minutes, a solution of diethylzinc (1.0 mol/L in hexane, 0.05 mL, 1.0 equiv) was injected to the reaction mixture via a syringe. After stirring at - 20 °C for 8 hours, the reaction was quenched with water (2.7 mg, 3.0 equiv), and the solution was submitted to crude ^{19}F-NMR experiment.



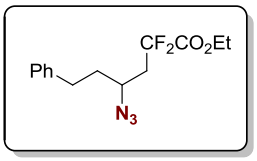
VI. Synthetic Applications

6.1 Intermolecular S_N2 Substitution



A mixture of **3b** (38.2 mg, 0.1 mmol) and sodium azide (9.8 mg, 0.15 mmol, 1.5 equiv) in anhydrous DMF was stirred at room temperature overnight. After completion, the reaction was quenched with water and extracted with diethyl ether. The combined organic layers were washed with saturated NH_4Cl for 5 times, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 25/1) to afford the corresponding pure product as a colorless oil, 22.3 mg, 75% yield.

Ethyl 4-azido-2,2-difluoro-6-phenylhexanoate (12)



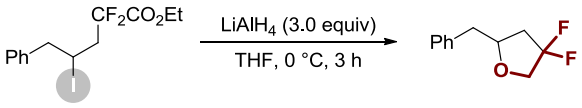
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 3.62 (dq, *J* = 9.3, 4.6 Hz, 1H), 2.89 – 2.80 (m, 1H), 2.74 (dt, *J* = 13.8, 8.2 Hz, 1H), 2.40 (dtd, *J* = 19.8, 14.1, 9.3 Hz, 1H), 2.27 (qd, *J* = 15.1, 3.6 Hz, 1H), 1.99 – 1.87 (m, 2H), 1.38 (t, *J* = 7.2 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.3 (d, *J* = 264.2 Hz), -107.2 (d, *J* = 264.2 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7 (t, $^2J_{C\text{-}F}$ = 32.2 Hz), 140.3, 128.6, 128.4, 126.3, 114.8 (dd, $^1J_{C\text{-}F}$ = 252.6, 249.7 Hz), 63.2, 56.1 (dd, $^3J_{C\text{-}F}$ = 6.1, 3.0 Hz), 39.4 (t, $^2J_{C\text{-}F}$ = 23.5 Hz), 36.7, 31.9, 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{14}H_{17}F_2N_3O_2Na$: 320.1181; found: 320.1182.

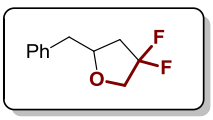
6.2 Reduction & Intramolecular S_N2 Substitution



3a **13**, 87%

To a solution of **3a** (36.8 mg, 0.1 mmol) in anhydrous THF was added $LiAlH_4$ (11.4 mg, 0.3 mmol, 3.0 equiv) at 0 °C. The resulting mixture was stirred at 0 °C for 3 hour. After completion, the reaction was quenched with saturated NH_4Cl and extracted with diethyl ether. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford the corresponding pure product as a colorless oil, 17.3 mg, 87% yield.

2-benzyl-4,4-difluorotetrahydrofuran (13)



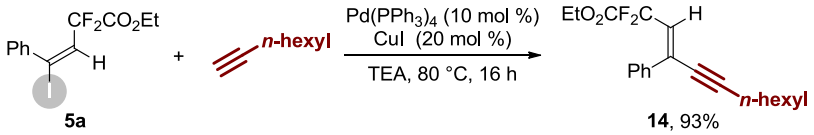
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 3H), 7.27 – 7.22 (m, 2H), 4.48 (dq, *J* = 8.9, 6.4 Hz, 1H), 3.90 – 3.71 (m, 2H), 3.33 (dd, *J* = 14.6, 5.8 Hz, 1H), 3.23 (dd, *J* = 14.6, 8.8 Hz, 1H), 2.92 – 2.64 (m, 2H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -104.2 (d, *J* = 253.1 Hz), -108.5 (d, *J* = 253.1 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 129.0, 128.5, 127.1, 122.4 (t, $^1J_{C\text{-}F}$ = 244.4 Hz), 64.2 (t, $^2J_{C\text{-}F}$ = 31.9 Hz), 47.4, 43.6 (t, $^2J_{C\text{-}F}$ = 23.7 Hz), 23.7 (t, $^3J_{C\text{-}F}$ = 3.5 Hz).

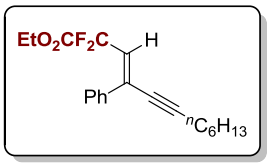
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{11}H_{12}F_2ONa$: 221.0748; found: 221.0759.

6.3 Palladium-Catalyzed Sonogashira Coupling



Compound **14** was synthesized according to a literature reported procedure.[4]

An oven-dried Schlenk tube was charged with $Pd(PPh_3)_4$ (16.4 mg, 0.014 mmol, 10 mmol%), CuI (5.4 mg, 0.028 mmol, 10 mmol%) and a stir bar. The tube was degased and refilled with nitrogen for 3 times, and then a solution of **5a** (50.0 mg, 0.14 mmol) and 1-octyne (35.8 mg, 0.325 mmol, 2.3 equiv) in a triethylamine (1 mL) was injected into the tube via a syringe. The resulting mixture was heated at 60 °C in an oil bath for 16 hours. After completion, the mixture was filtered through a pad of Celite, washed with diethyl ether. The combined organic layers were concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1) to afford the corresponding pure product as a colorless oil, 43.5 mg, 93% yield.



(*E*)-ethyl 2,2-difluoro-4-phenyldodec-3-en-5-ynoate (14)

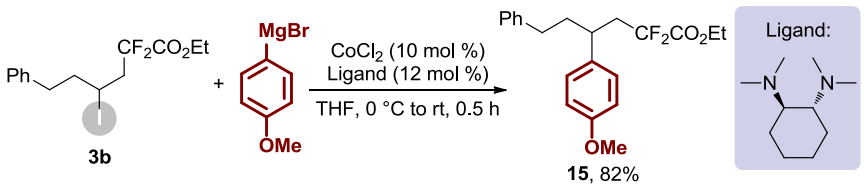
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.37 – 7.34 (m, 3H), 6.19 (t, J = 12.3 Hz, 1H), 3.91 (q, J = 7.2 Hz, 2H), 2.39 – 2.35 (m, 2H), 1.61 – 1.55 (m, 2H), 1.46 – 1.38 (m, 2H), 1.37 – 1.27 (m, 4H), 1.14 (t, J = 7.2 Hz, 3H), 0.91 (t, J = 7.0 Hz, 3H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -91.6.

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0 (t, $^2J_{C\text{-}F}$ = 33.6 Hz), 136.1, 134.3 (t, $^3J_{C\text{-}F}$ = 10.2 Hz), 128.9, 128.5 (t, $^4J_{C\text{-}F}$ = 2.3 Hz), 128.0, 125.9 (t, $^2J_{C\text{-}F}$ = 28.2 Hz), 112.0 (t, $^1J_{C\text{-}F}$ = 245.0 Hz), 95.8, 80.9 (t, $^4J_{C\text{-}F}$ = 2.7 Hz), 62.8, 31.2, 28.5, 28.3, 22.5, 19.5, 14.0, 13.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{25}F_2O_2$: 335.1817; found: 335.1824.

6.4 Cobalt-Catalyzed Kumada Coupling



Compound **15** was synthesized according to a literature reported procedure.[5]

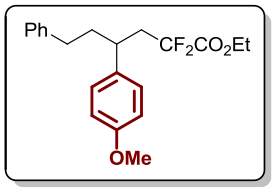
An oven-dried Schlenk tube was charged with anhydrous cobalt (II) chloride (1.3 mg, 0.01 mmol, 10 mol%) and a stir bar. The tube was heated with a hair-dryer in vacuo for 2 minutes. After the color of the cobalt salt became blue, a solution of (1*R*,2*R*)-*N*,*N*,*N*′,*N*′-tetramethylcyclohexane-1,2-diamine (2.2 mg, 0.012 mmol, 12 mol%) in anhydrous THF (1 mL) was injected into the tube via a syringe. The mixture was stirred for 3 minutes at room temperature. Then, **3b** (38.2 mg, 0.10 mmol) was added and

[4] T. Xu, C. W. Cheung, X. Hu, *Angew. Chem. Int. Ed.* **2014**, *53*, 4910–4914

[5] H. Ohmiya, H. Yorimitsu, K. Oshima, *J. Am. Chem. Soc.* **2006,** *128*, 1886–1889

the tube was placed to an ice-water bath. 4-Methoxyphenylmagnesium bromide (1.0 M THF solution, 0.12 mL, 0.12 mmol, 1.2 equiv) was injected into the tube via a syringe at 0 °C. After stirring at 0 °C for 5 minutes and at room temperature for 20 minutes, the reaction was quenched with saturated NH_4Cl and extracted with diethyl ether. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 15/1) to afford the corresponding pure product as a colorless oil, 29.4 mg, 82% yield.

Ethyl 2,2-difluoro-4-(4-methoxyphenyl)-6-phenylhexanoate (15)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 3H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.13 – 7.08 (m, 3H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.02 – 3.91 (m, 2H), 3.83 (s, 3H), 2.86 (tt, *J* = 9.9, 5.0 Hz, 1H), 2.59 – 2.34 (m, 4H), 2.04 (dtd, *J* = 16.9, 8.4, 7.9, 4.9 Hz, 1H), 1.92 (ddt, *J* = 13.6, 9.2, 7.0 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H).

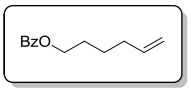
^{19}F NMR (471 MHz, $CDCl_3$) δ -100.1 (d, *J* = 259.9 Hz), -106.6 (d, *J* = 259.9 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9 (t, $^2J_{C\text{-}F}$ = 33.2 Hz), 158.4, 141.7, 134.7, 128.8, 128.4, 128.3, 125.8, 115.8 (t, $^1J_{C\text{-}F}$ = 251.9 Hz), 113.8, 62.6, 55.3, 41.6 (t, $^2J_{C\text{-}F}$ = 22.5 Hz), 38.9, 38.4 (t, $^3J_{C\text{-}F}$ = 3.2 Hz), 33.3, 13.7.

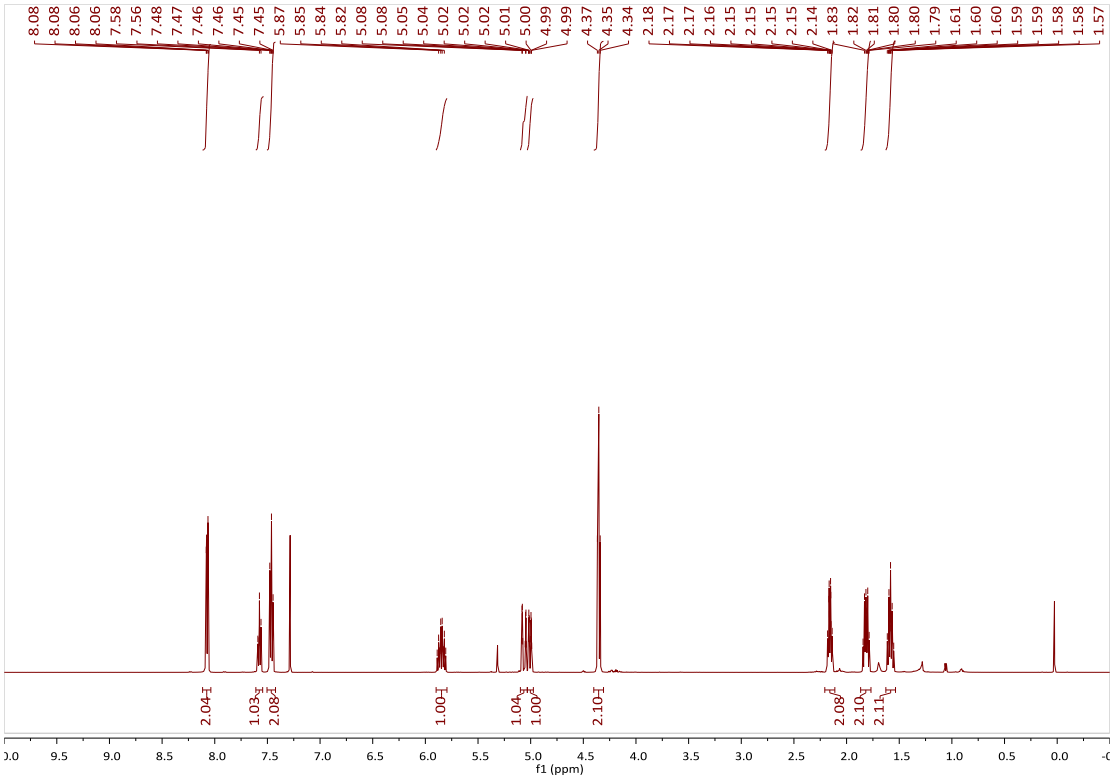
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{24}F_2O_3Na$: 385.1586; found: 385.1588.

VII. NMR Spectra

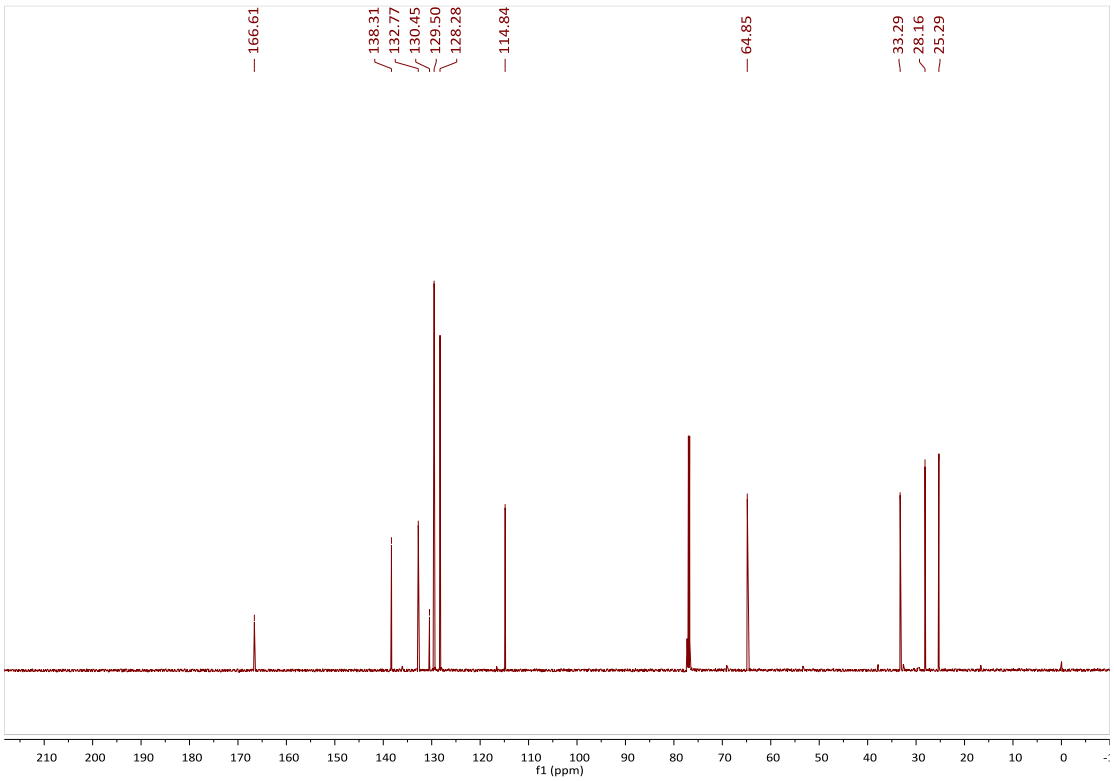
Please refer to next pages

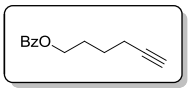


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **S2a**

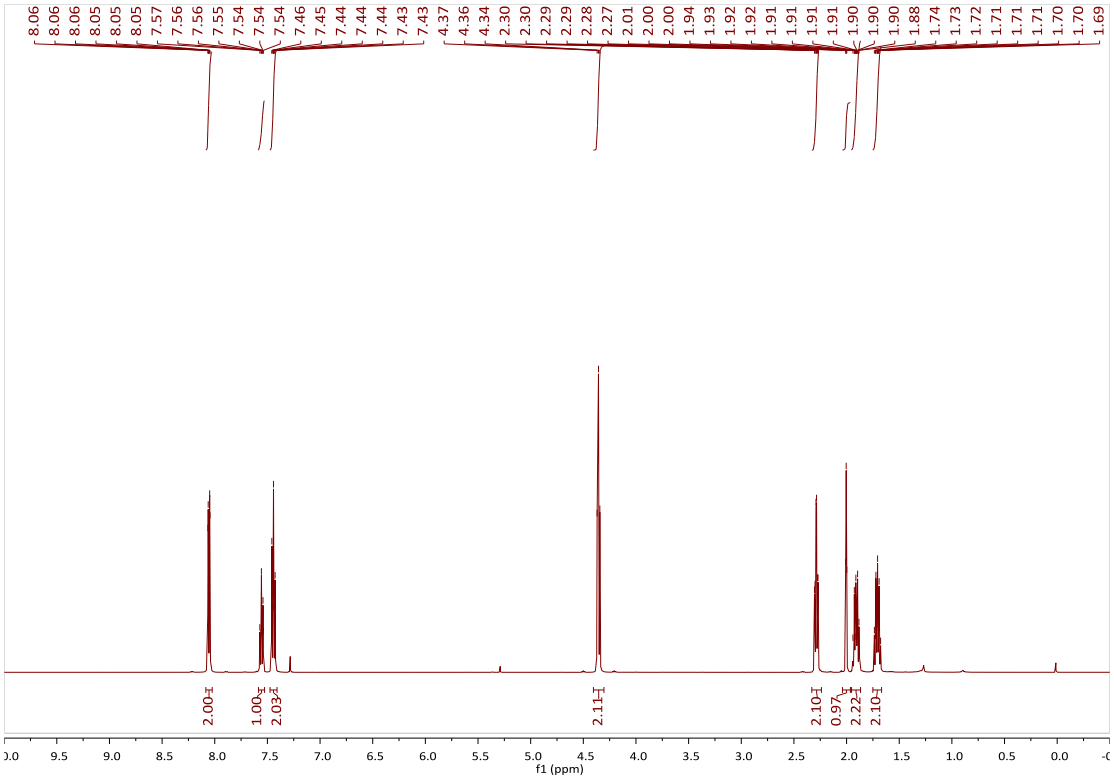


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **S2a**

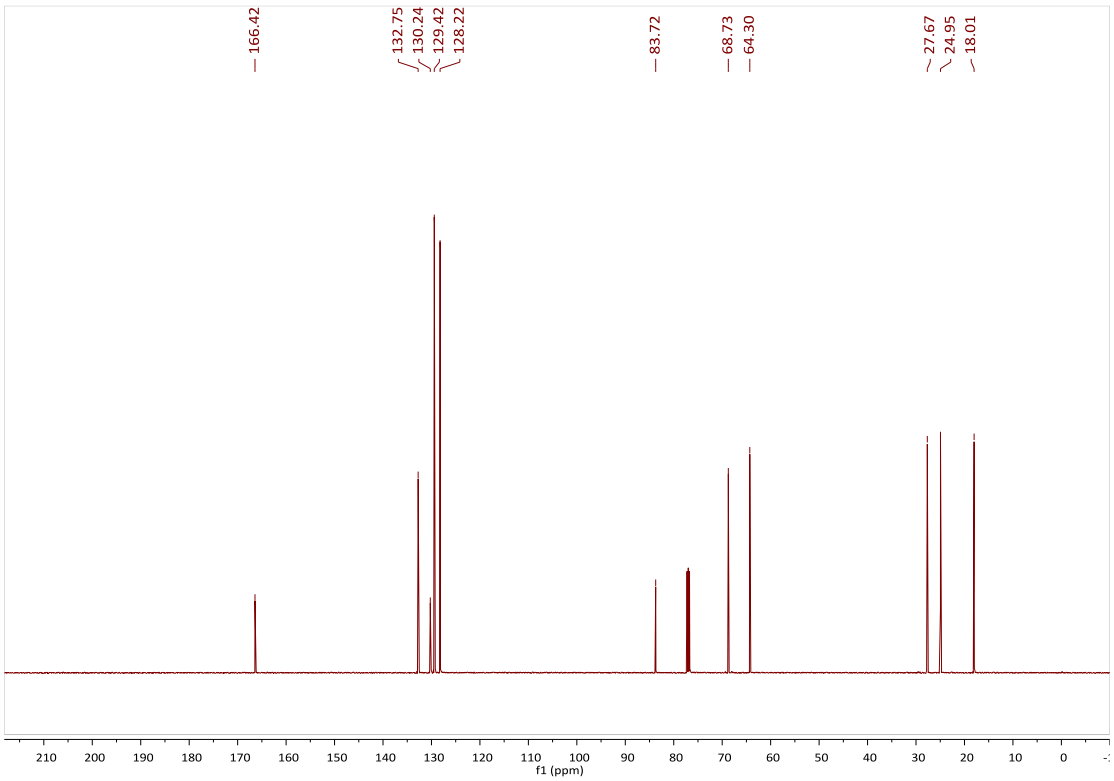


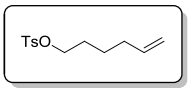


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **S2b**

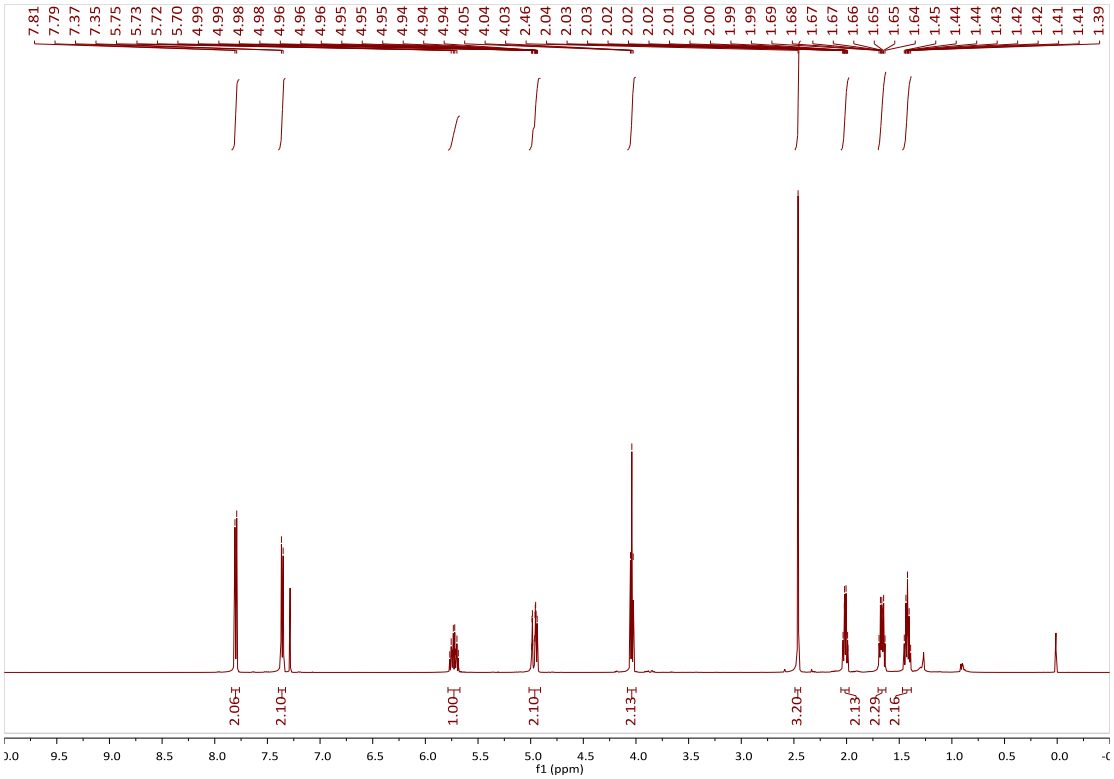


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **S2b**

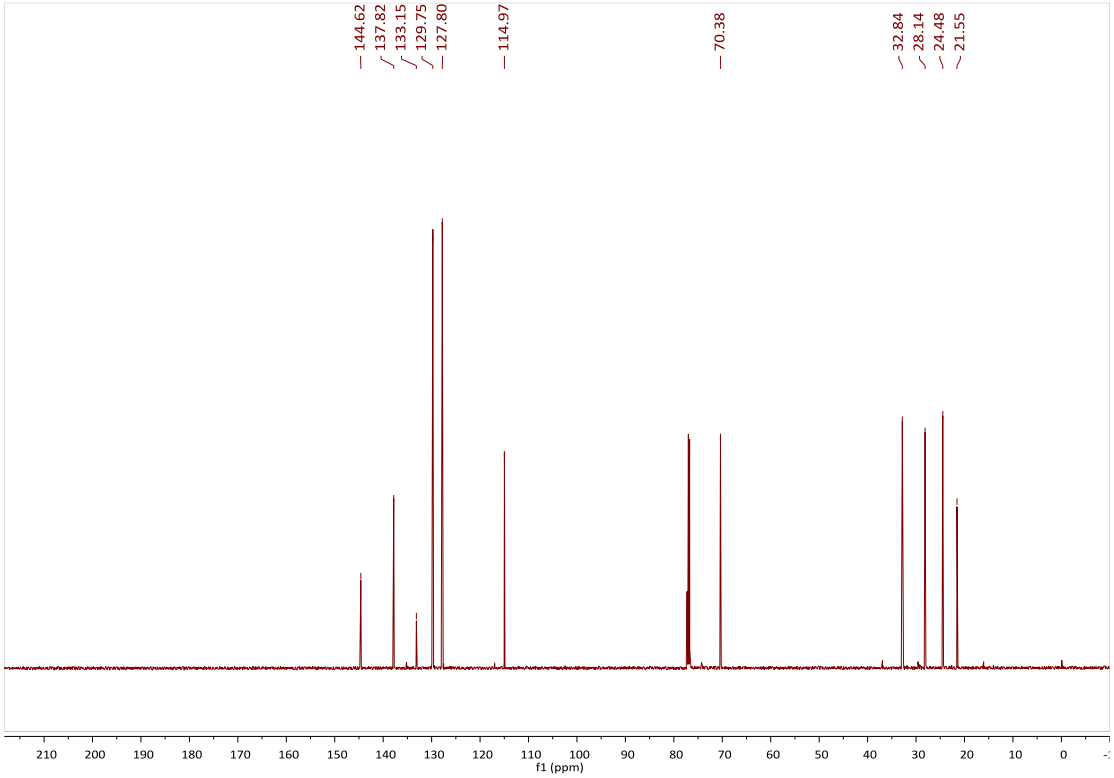


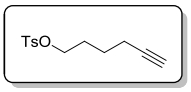


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **S3a**

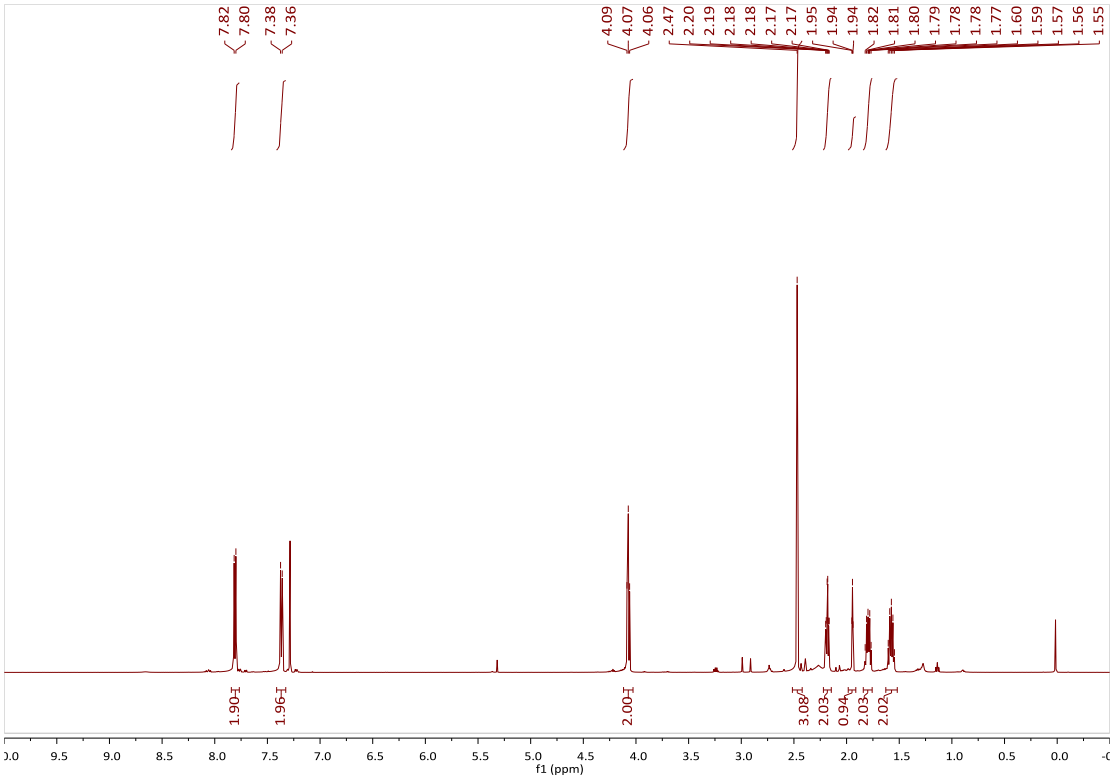


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **S3a**

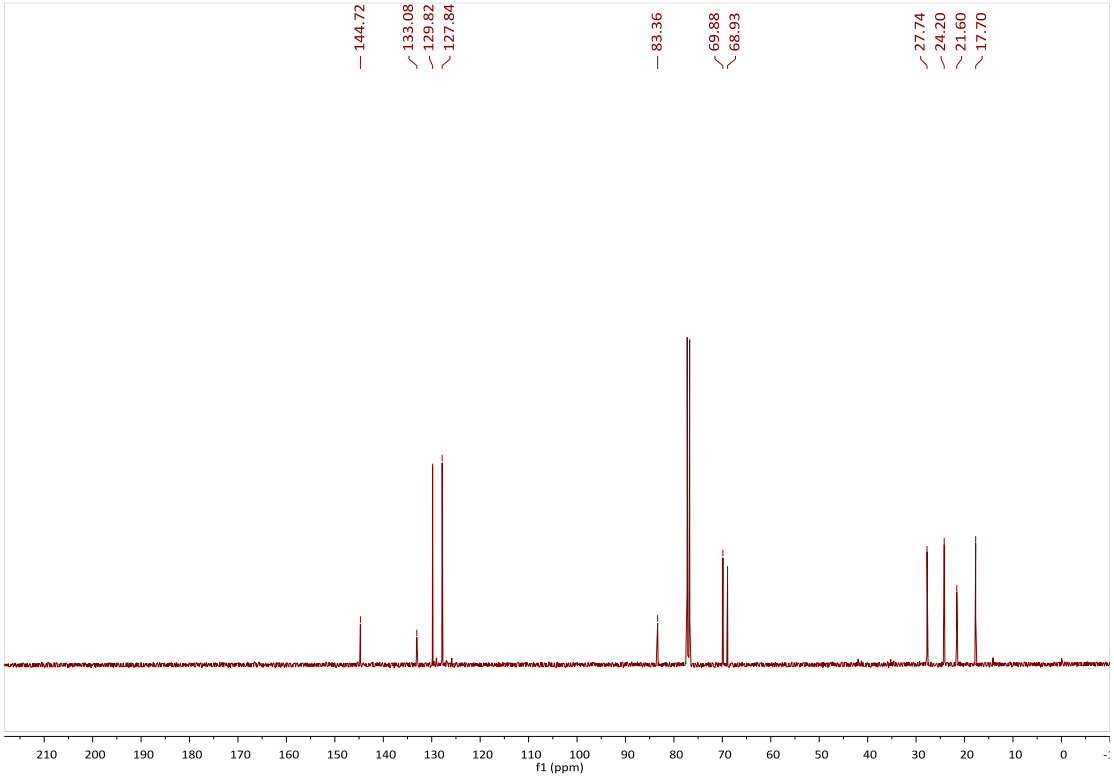


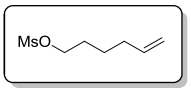


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **S3b**

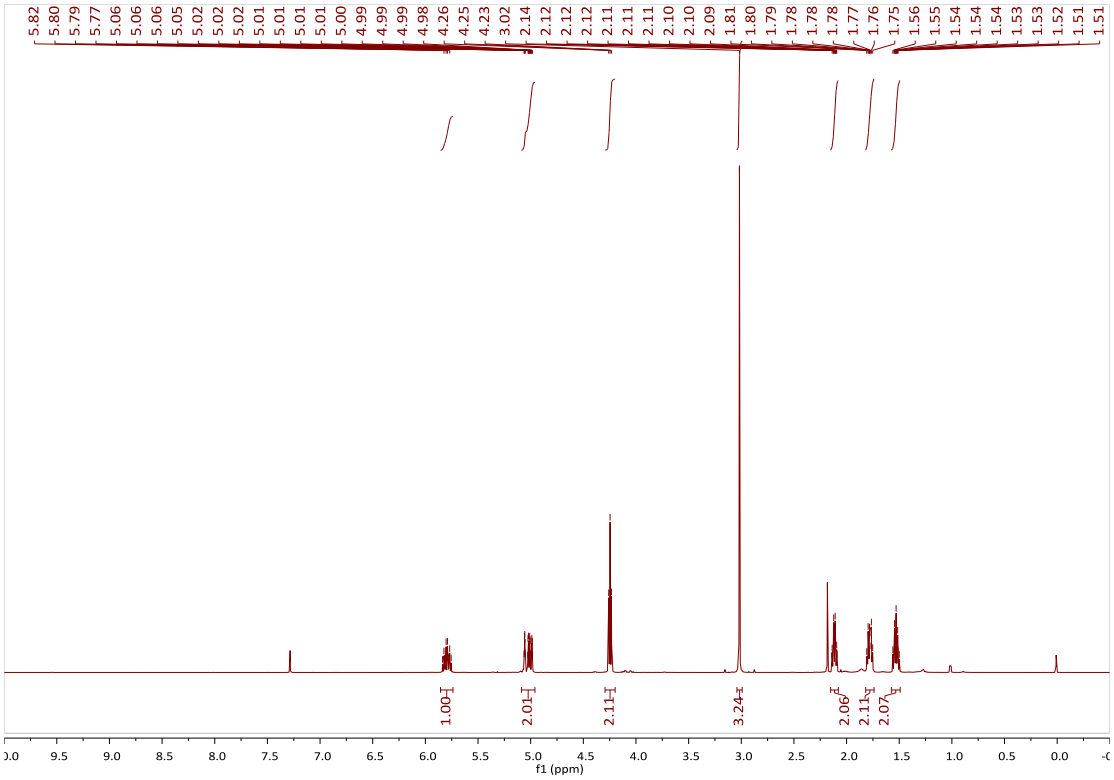


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **S3b**





^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **S4a**



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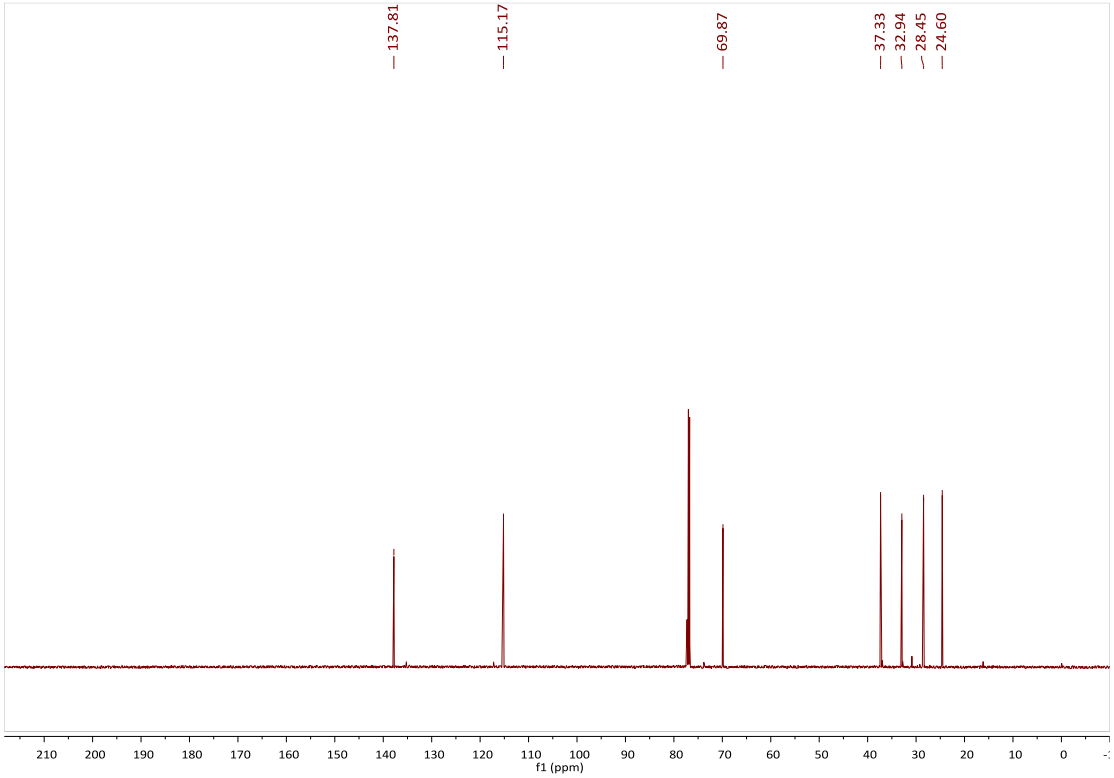
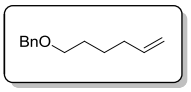
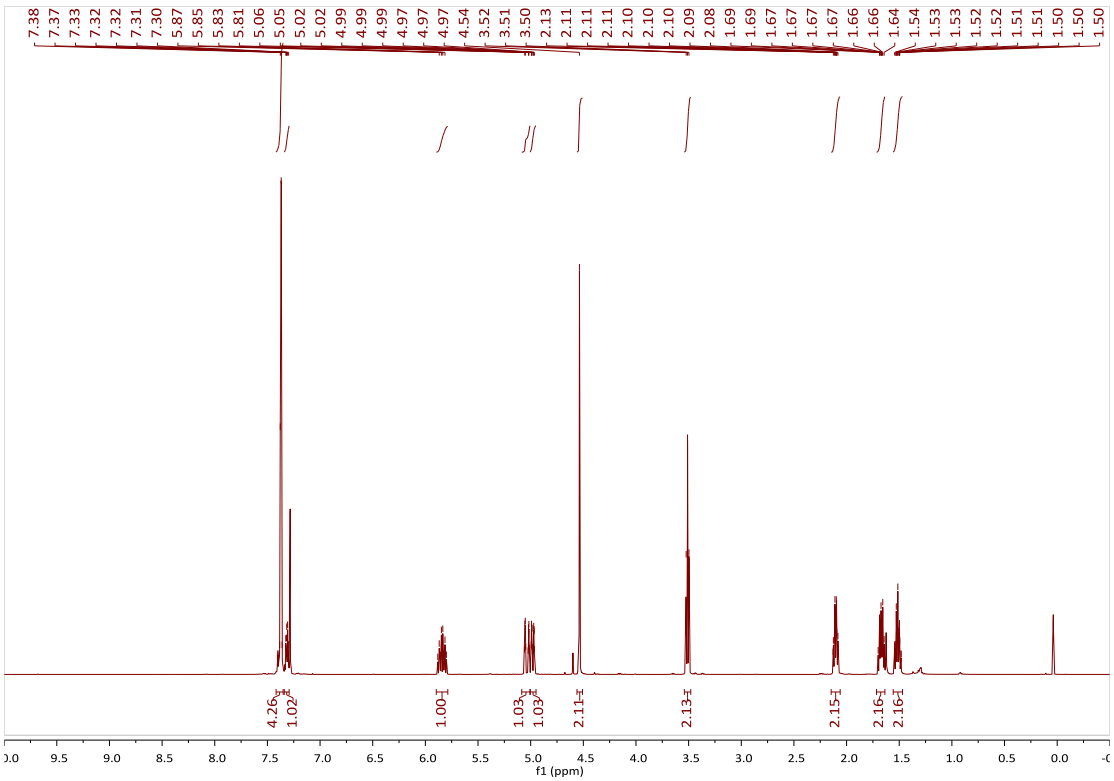




^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **S5a**



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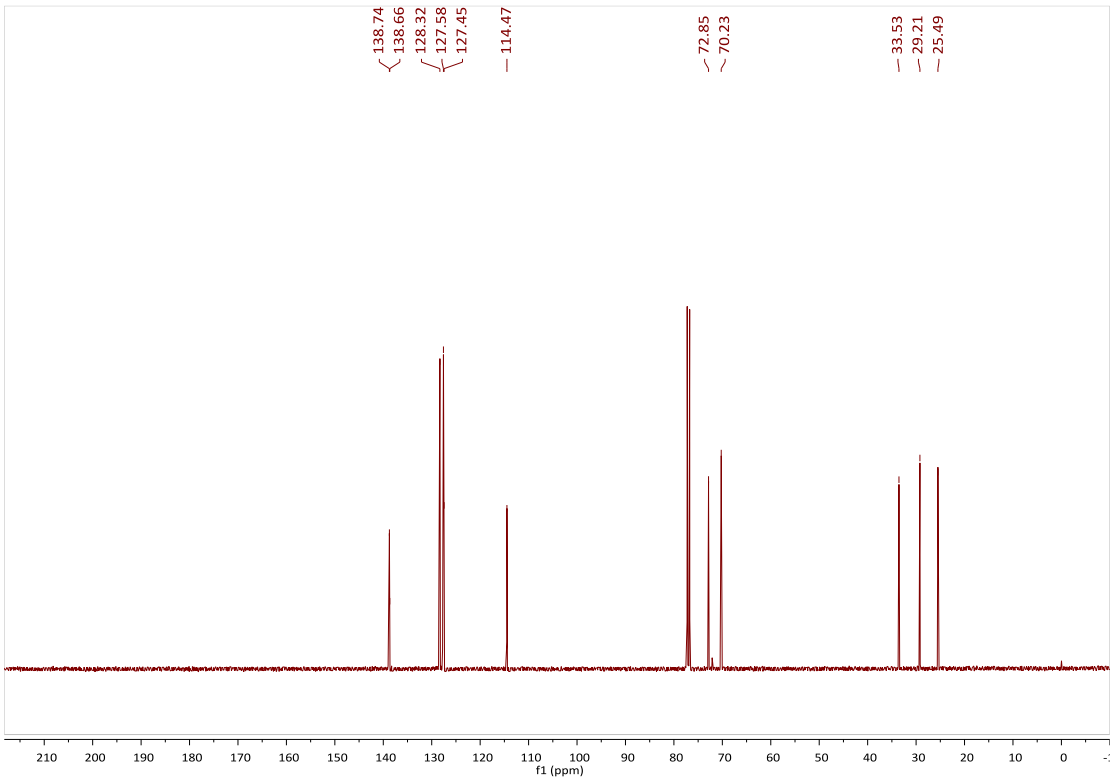
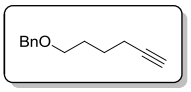
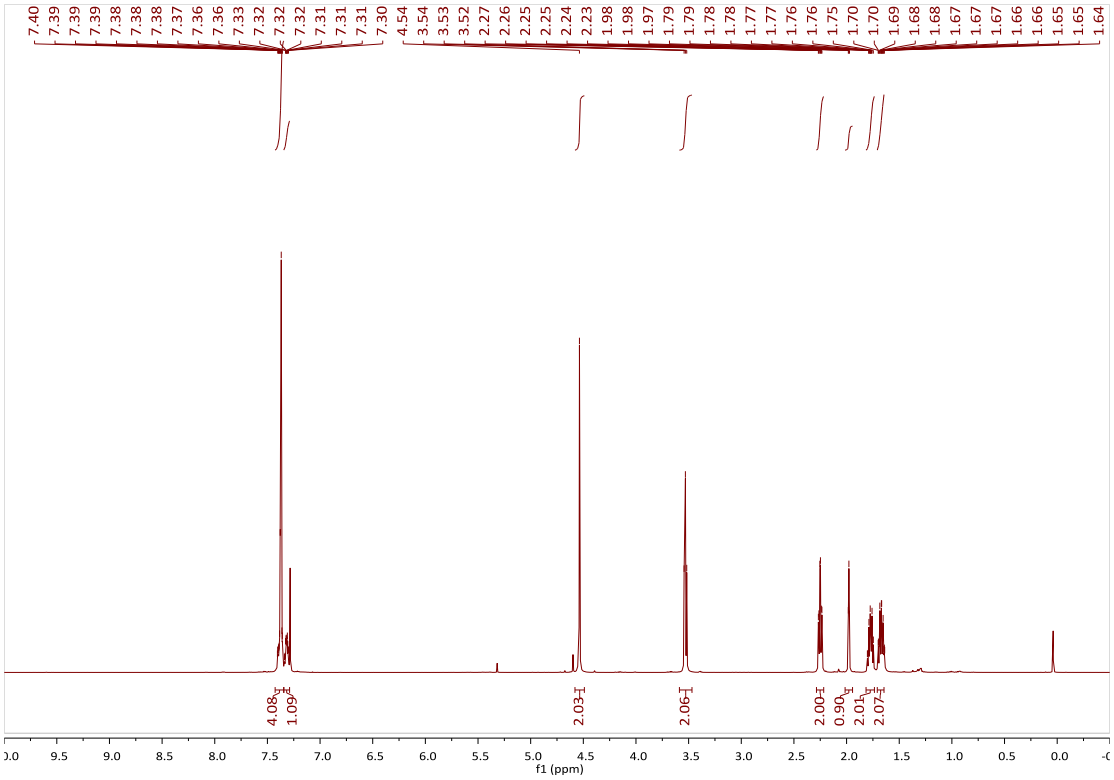




^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **S5b**



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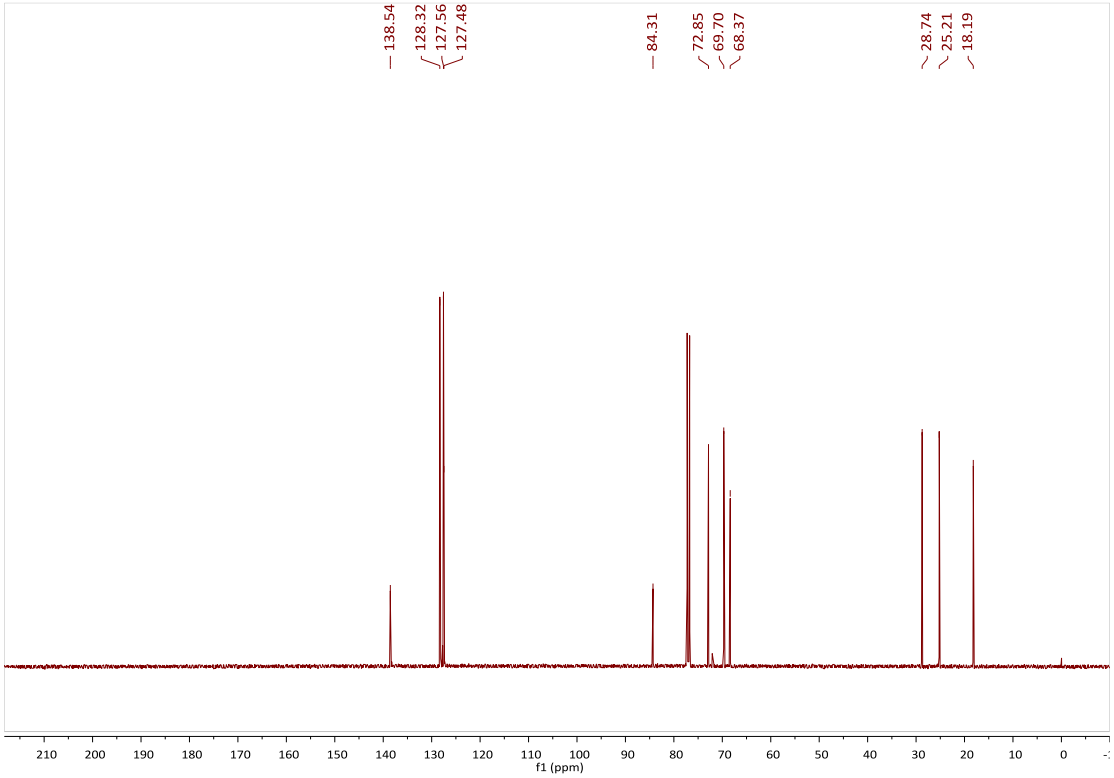
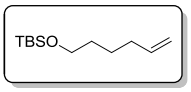
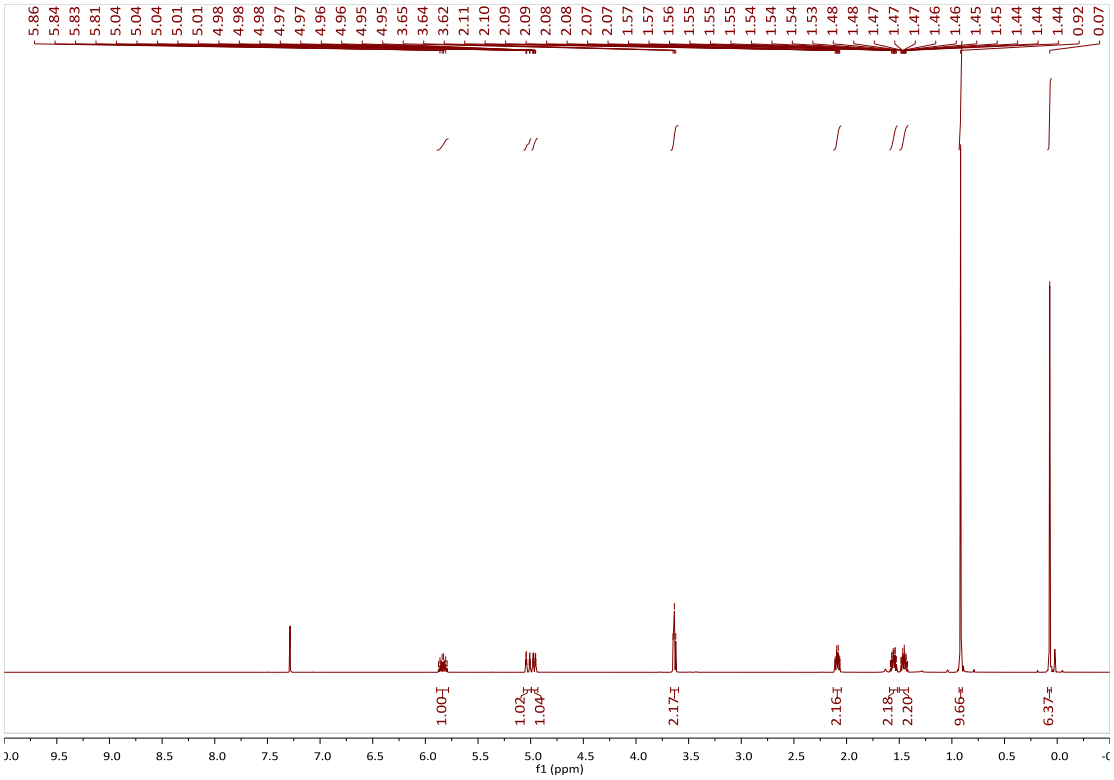




^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **S6a**



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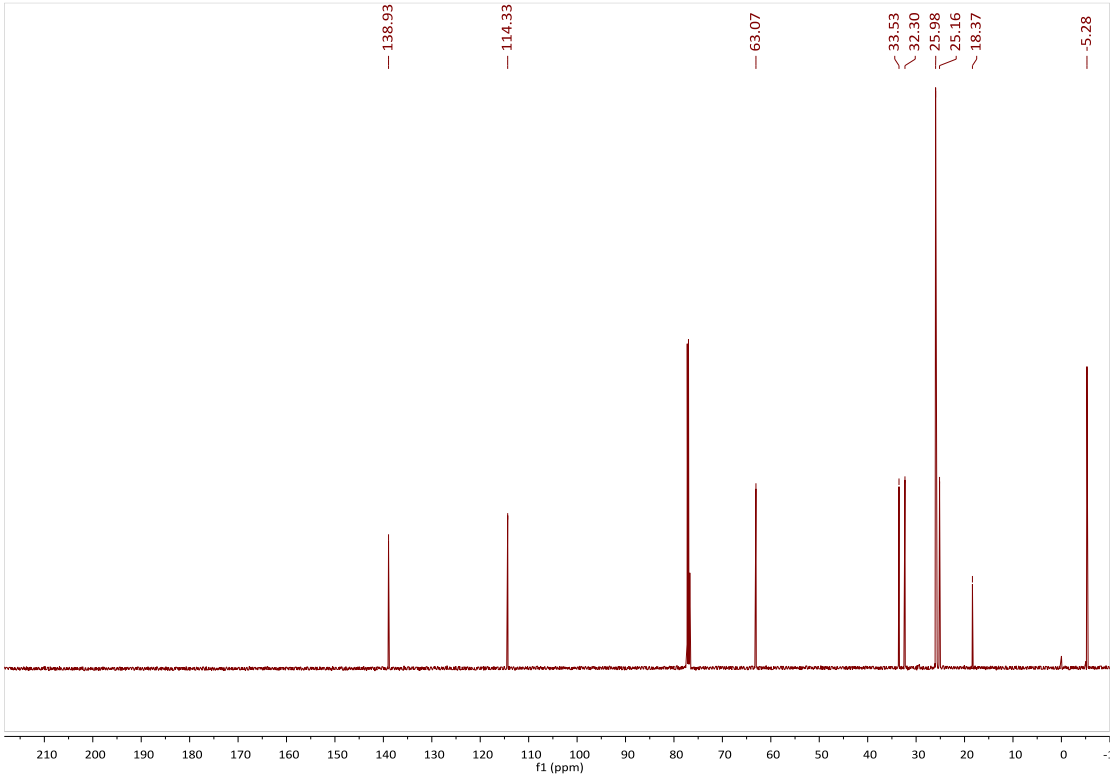

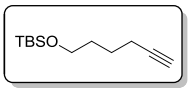

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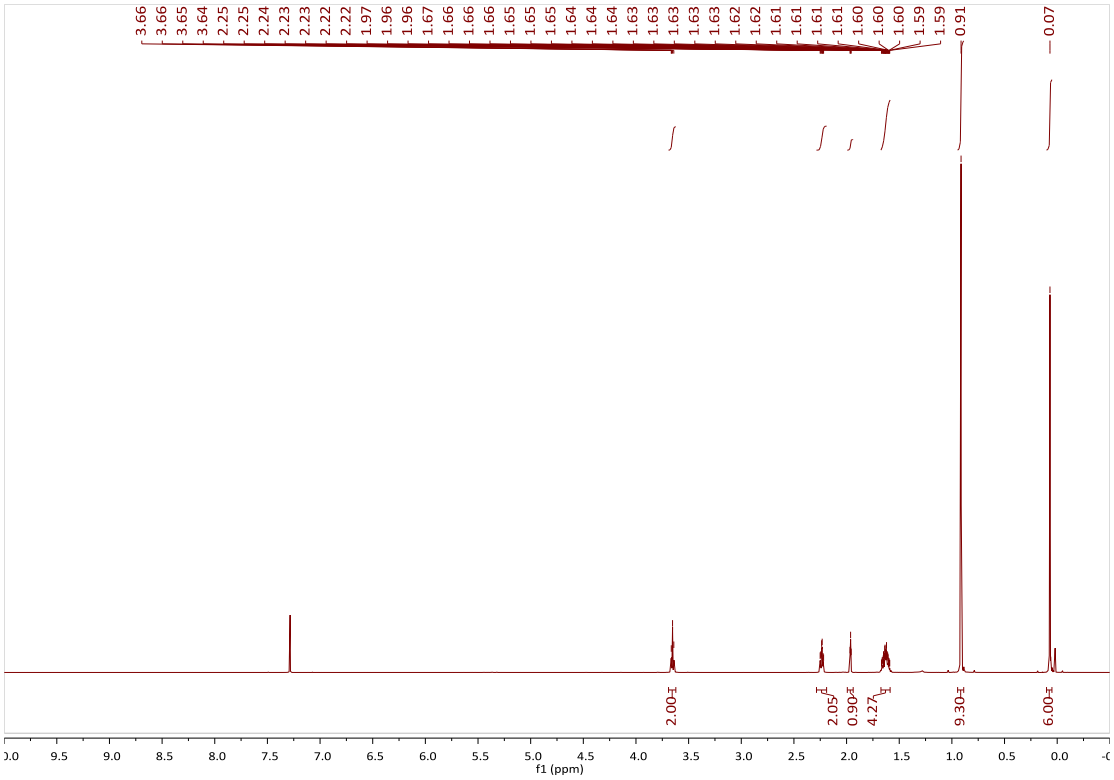

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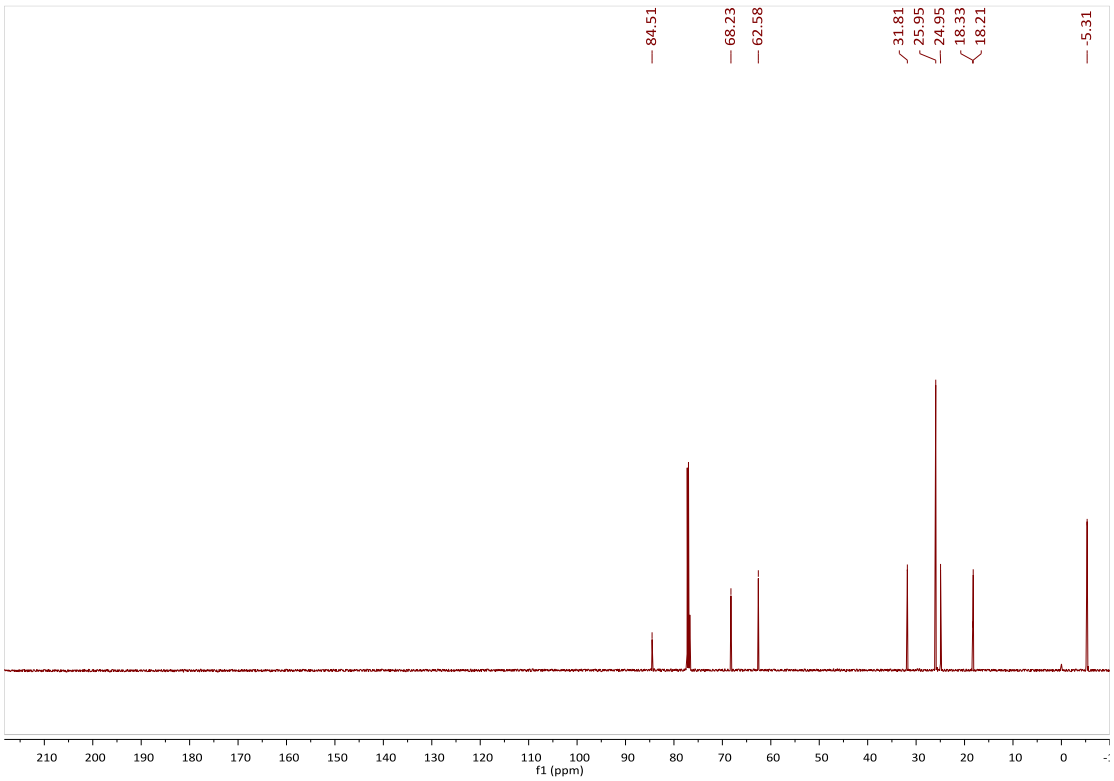
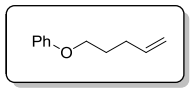
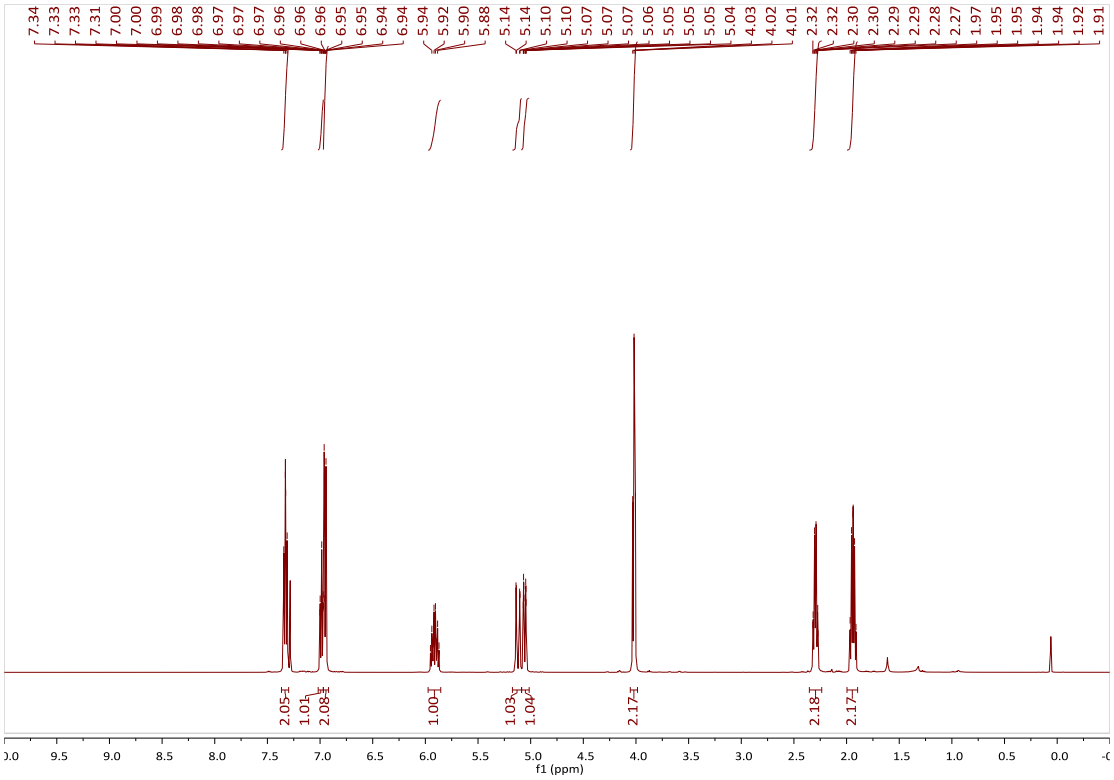
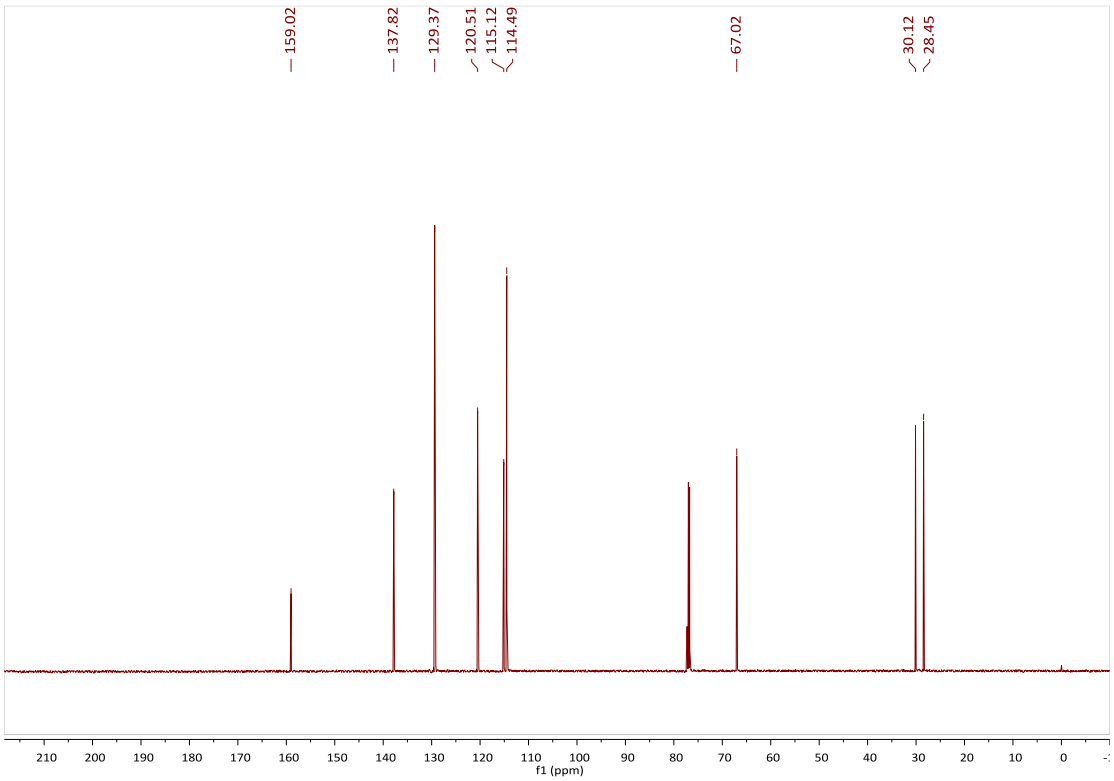


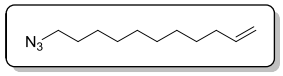


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **S8**

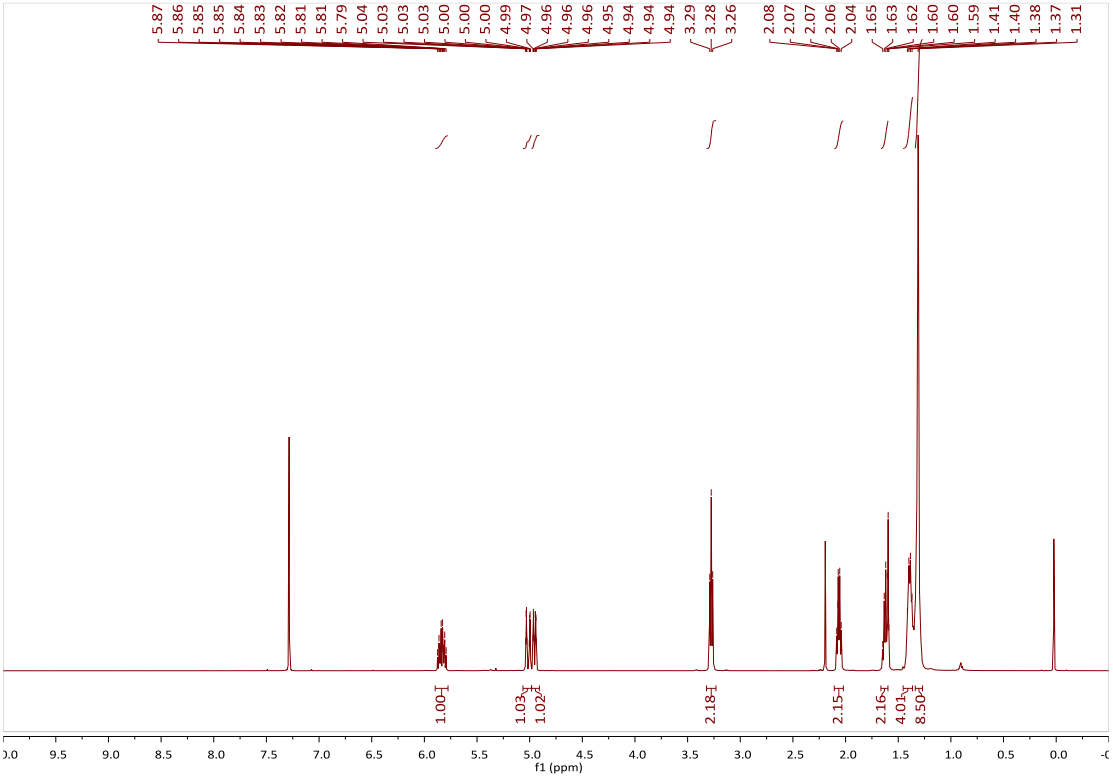


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **S8**





^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **S11a**



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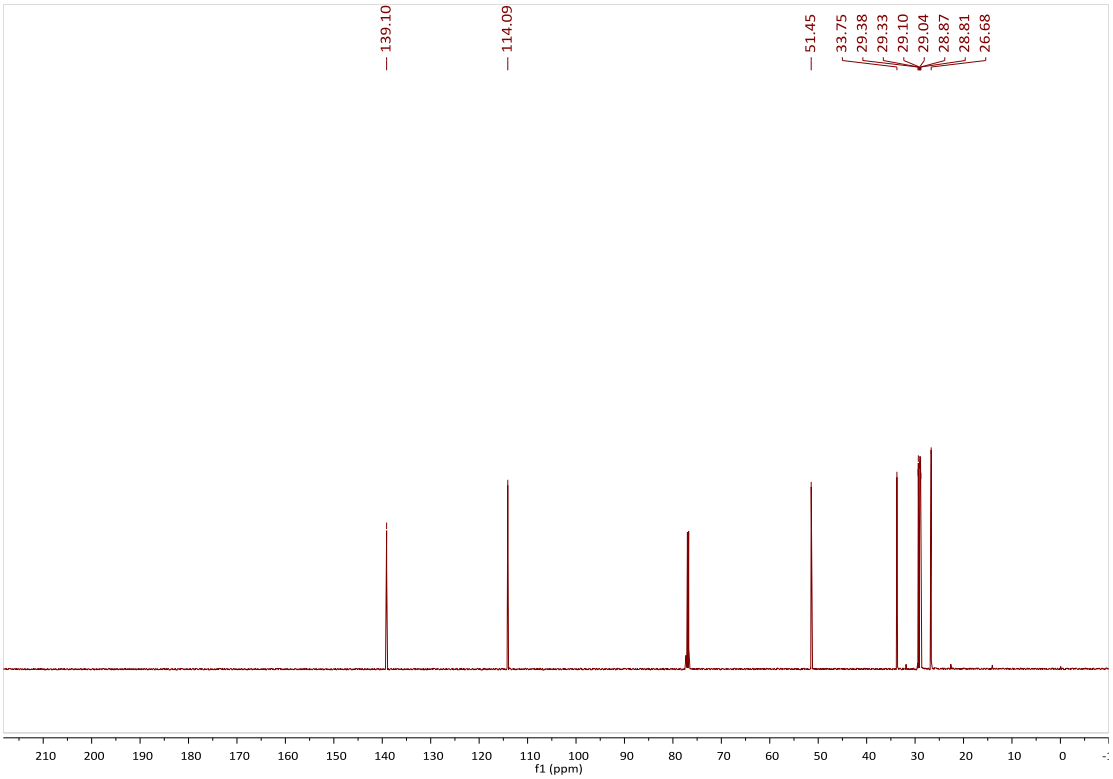

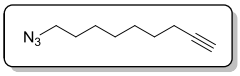

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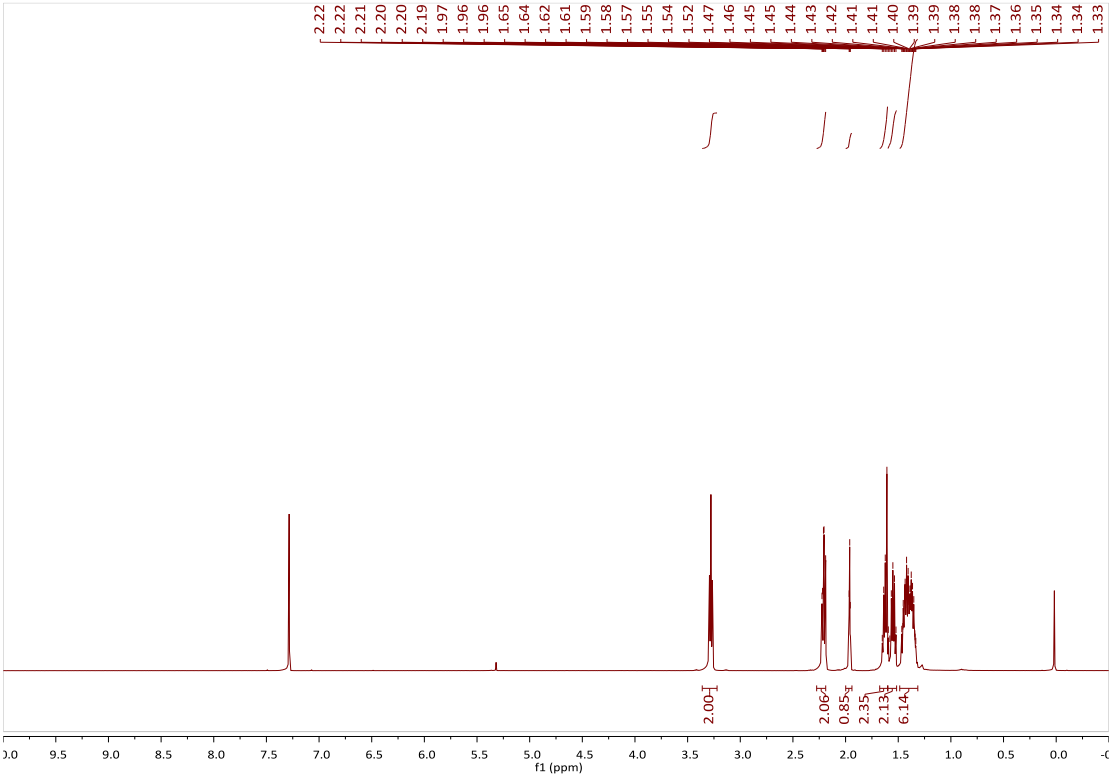

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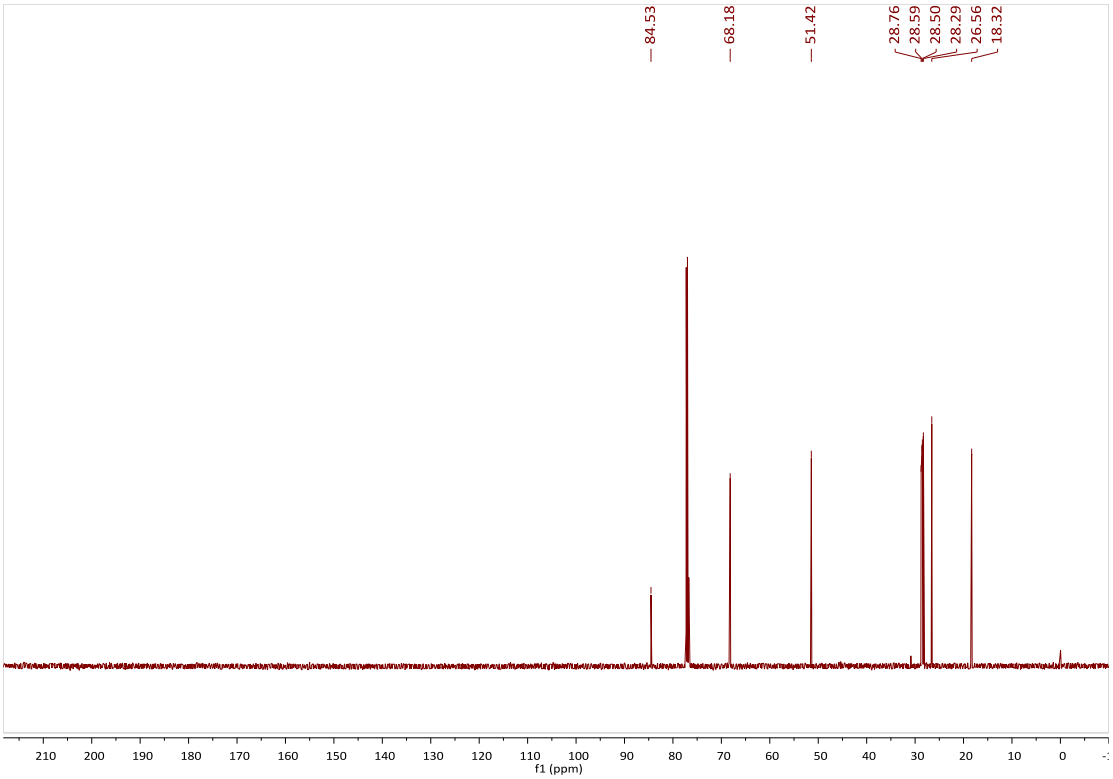

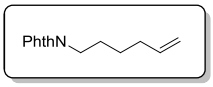

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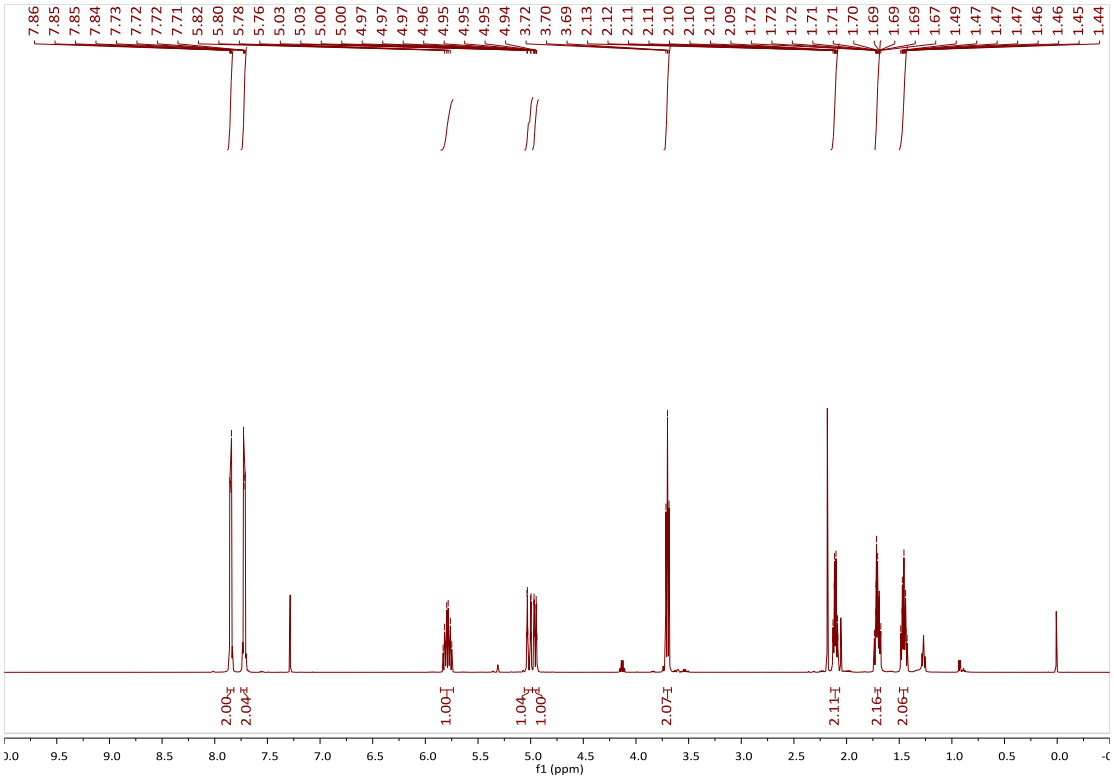

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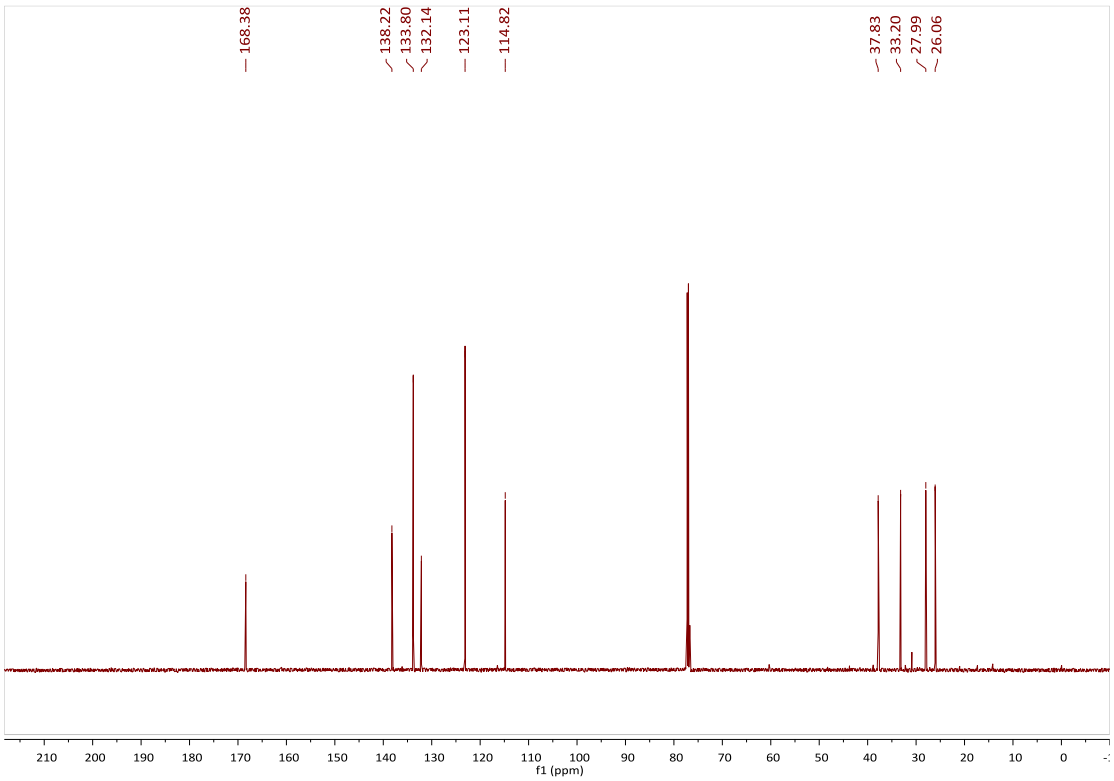
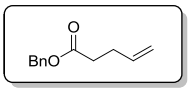
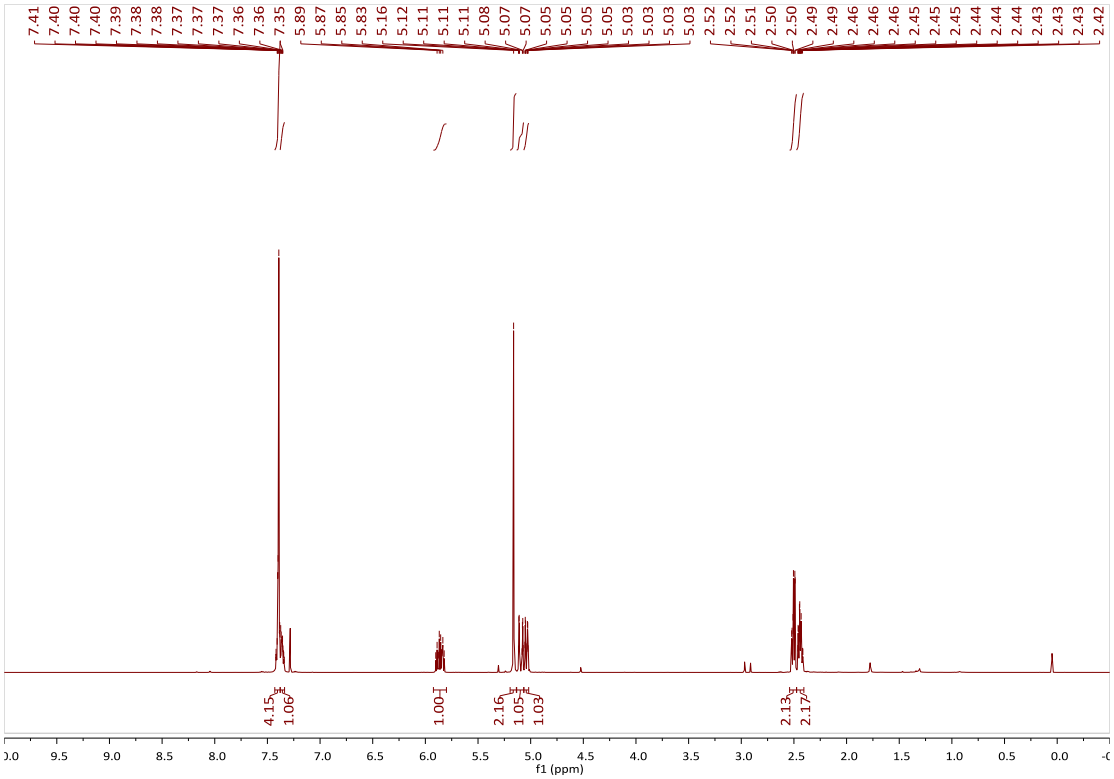
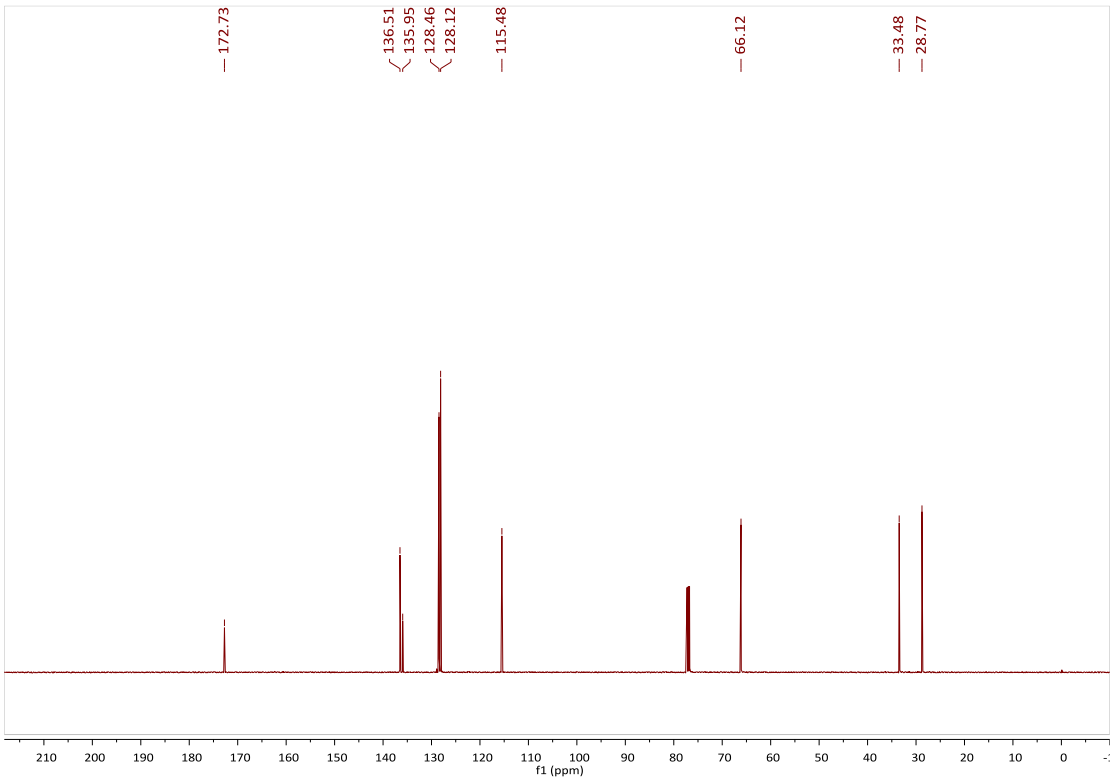


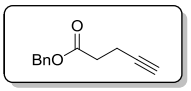


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **S14a**

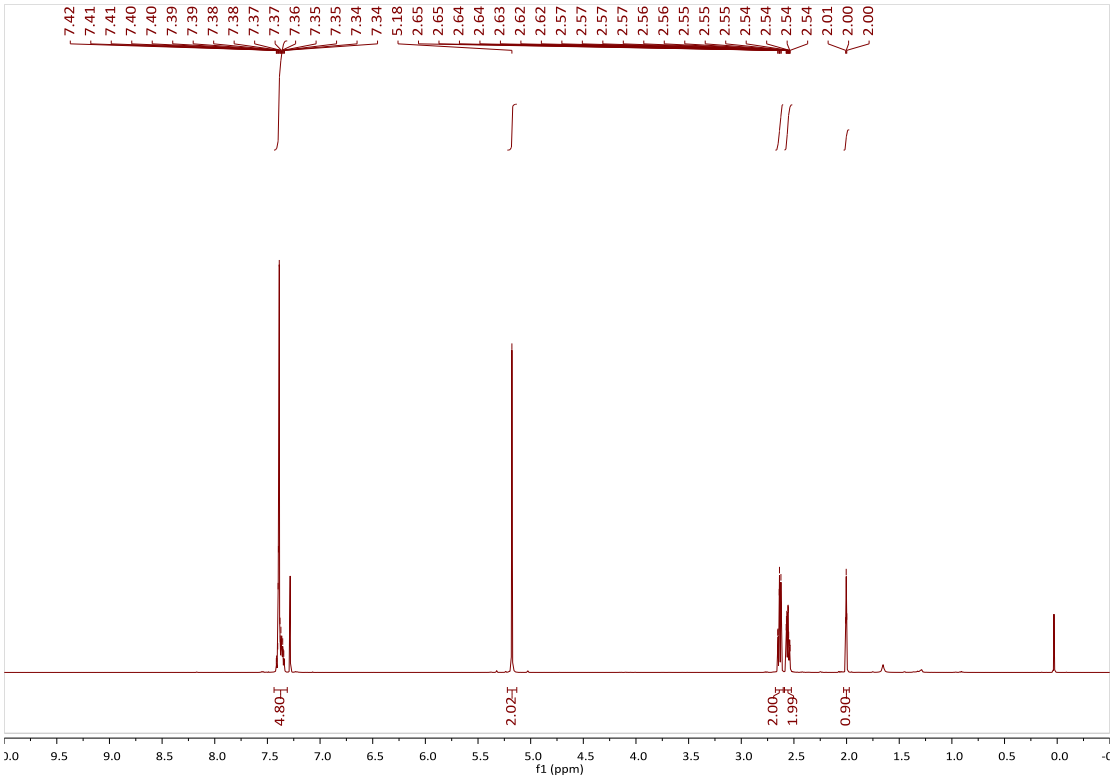


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **S14a**





^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **S14b**



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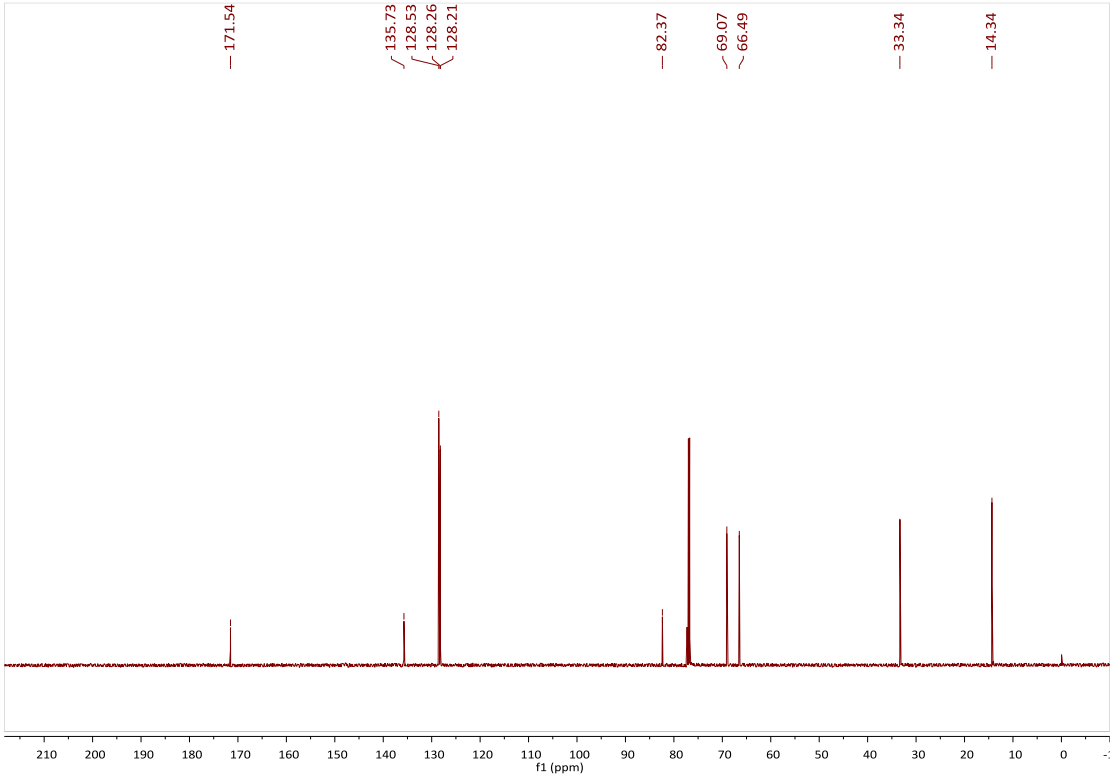
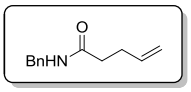
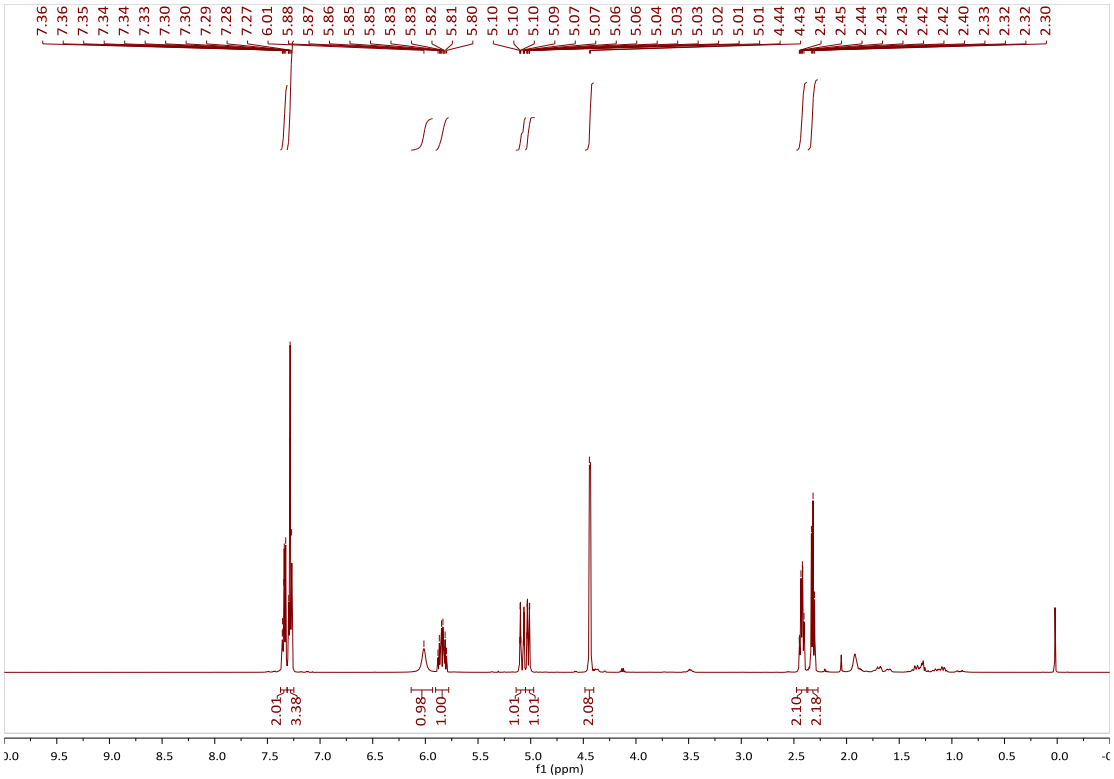
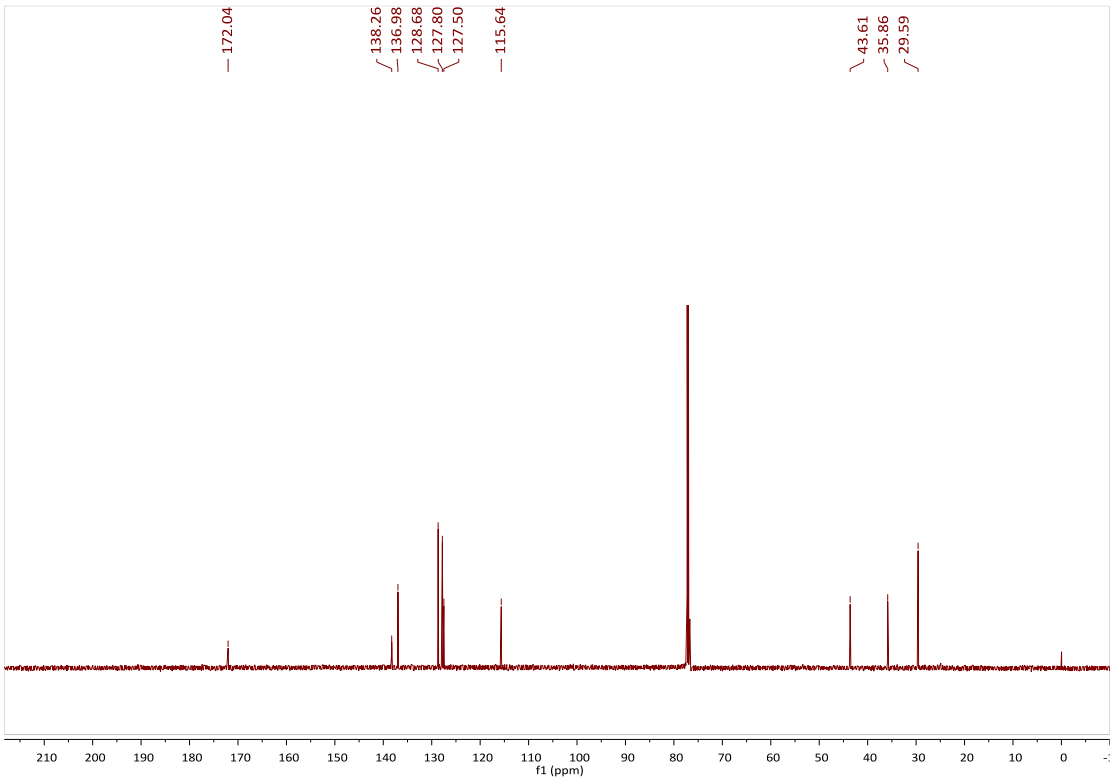


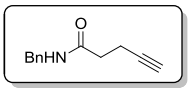


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **S15a**

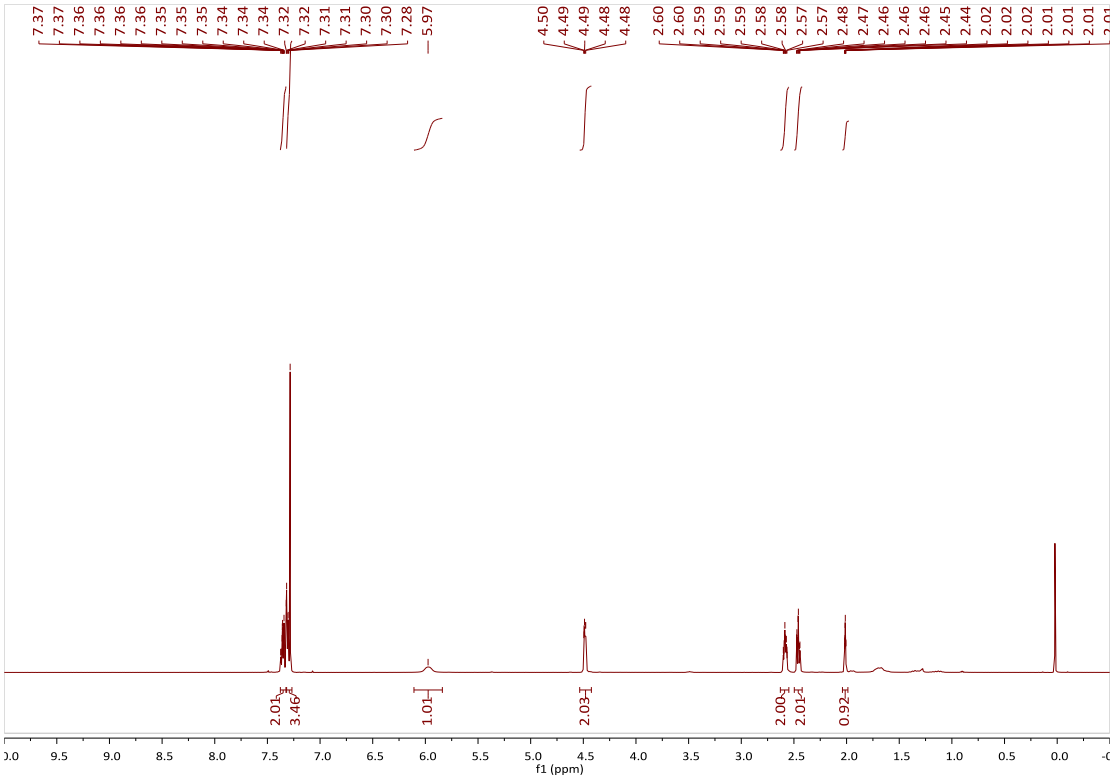


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **S15a**

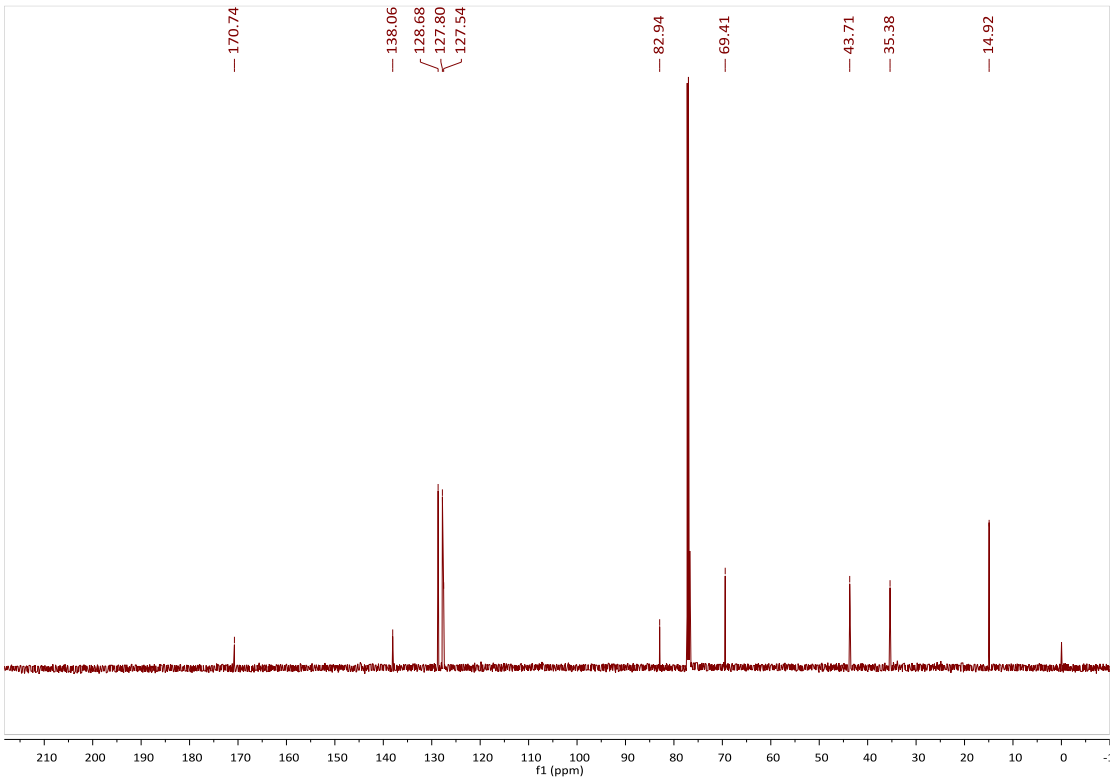


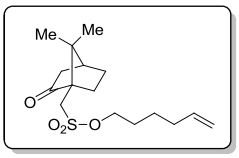


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **S15b**

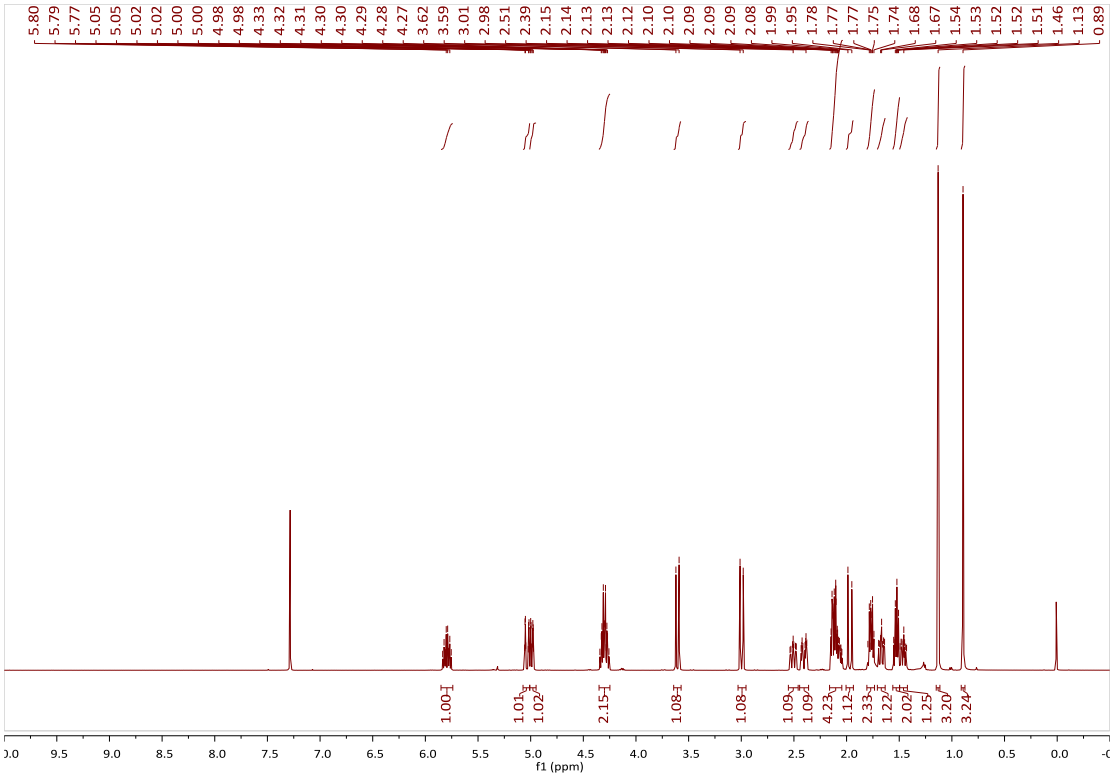


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **S15b**

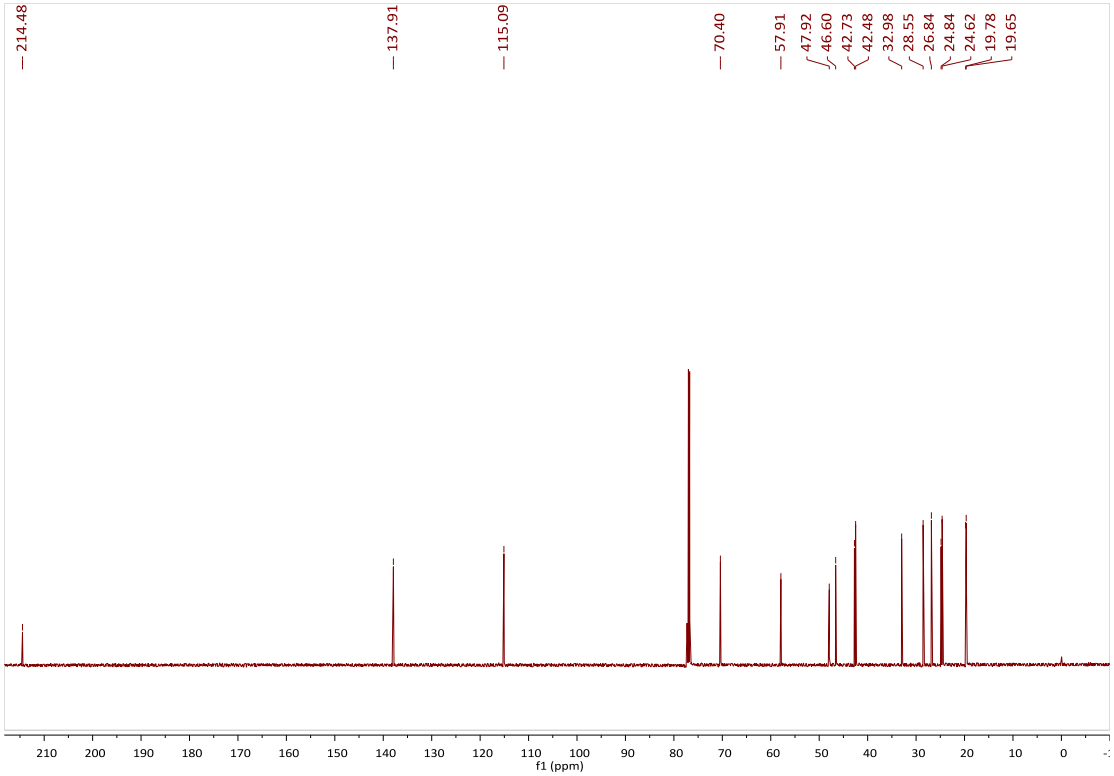


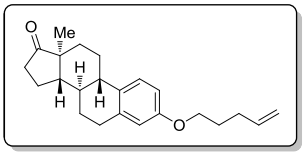


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **S17**

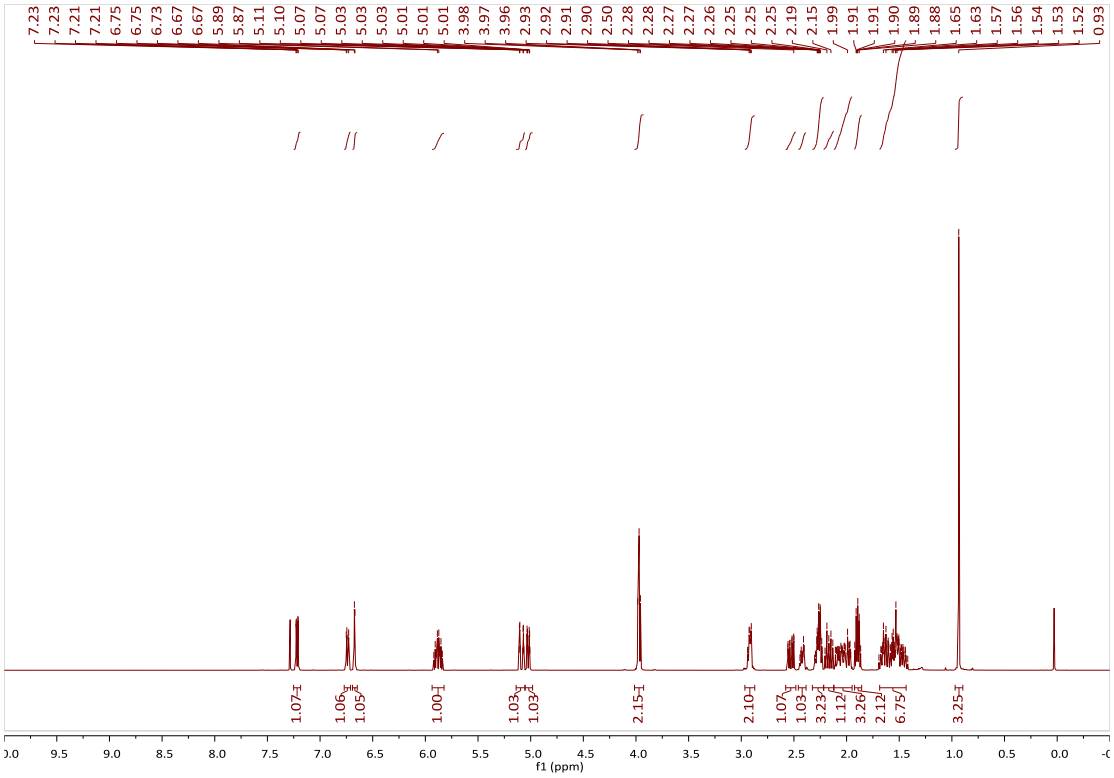


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **S17**

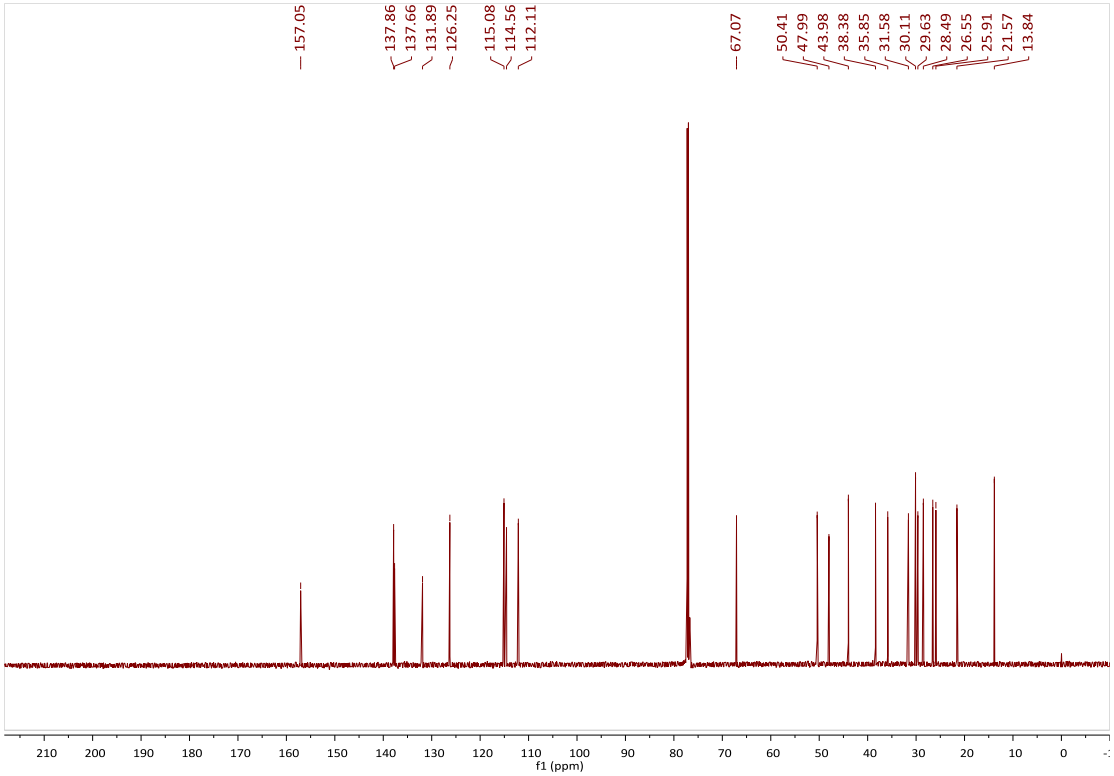


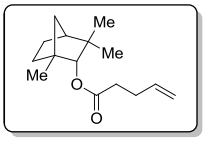


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **S19**

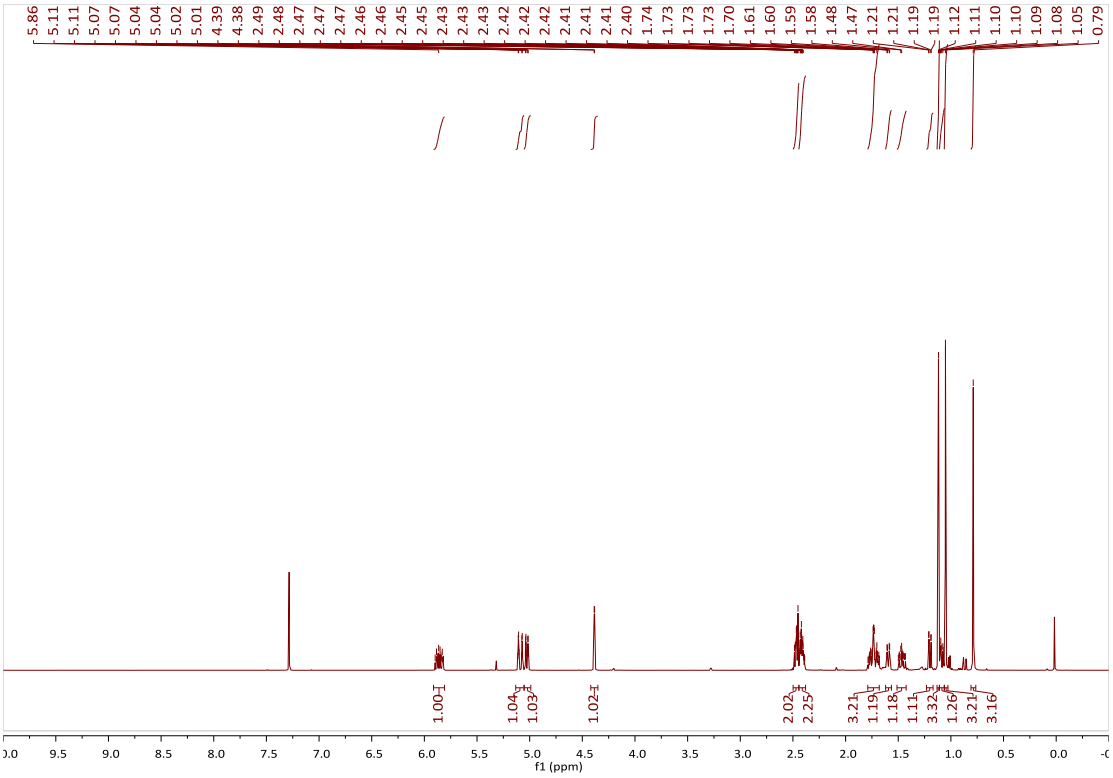


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **S19**

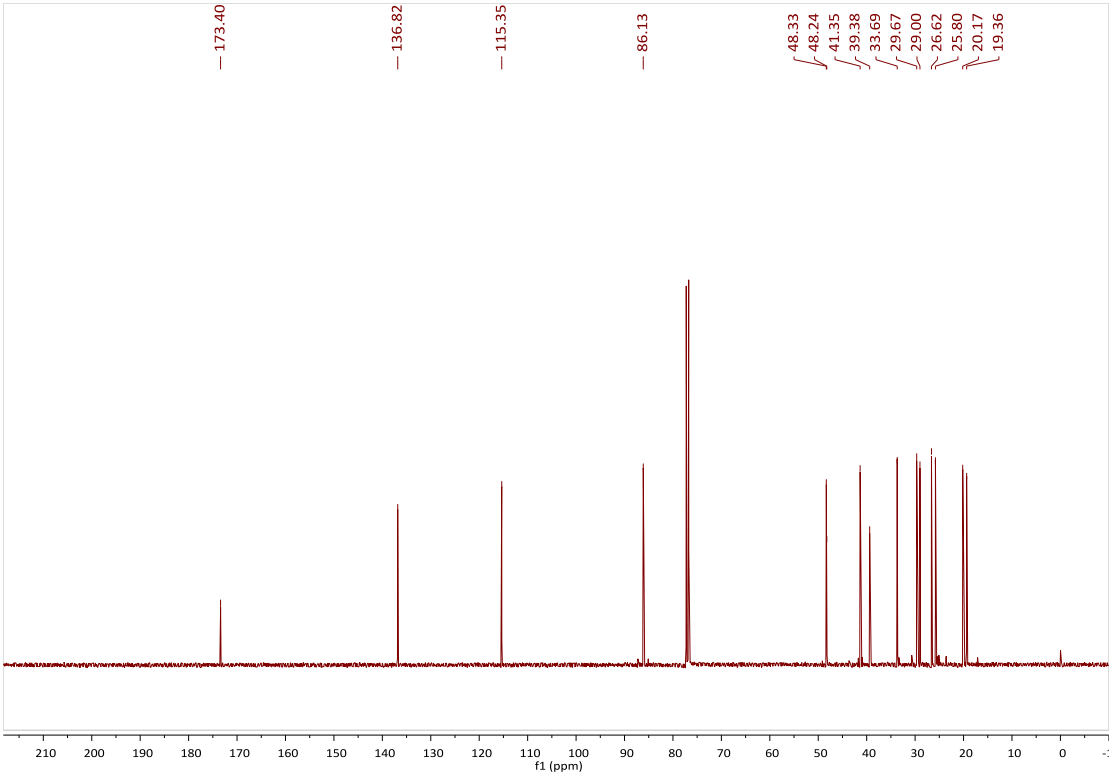


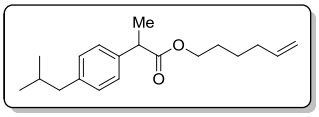


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **S21**

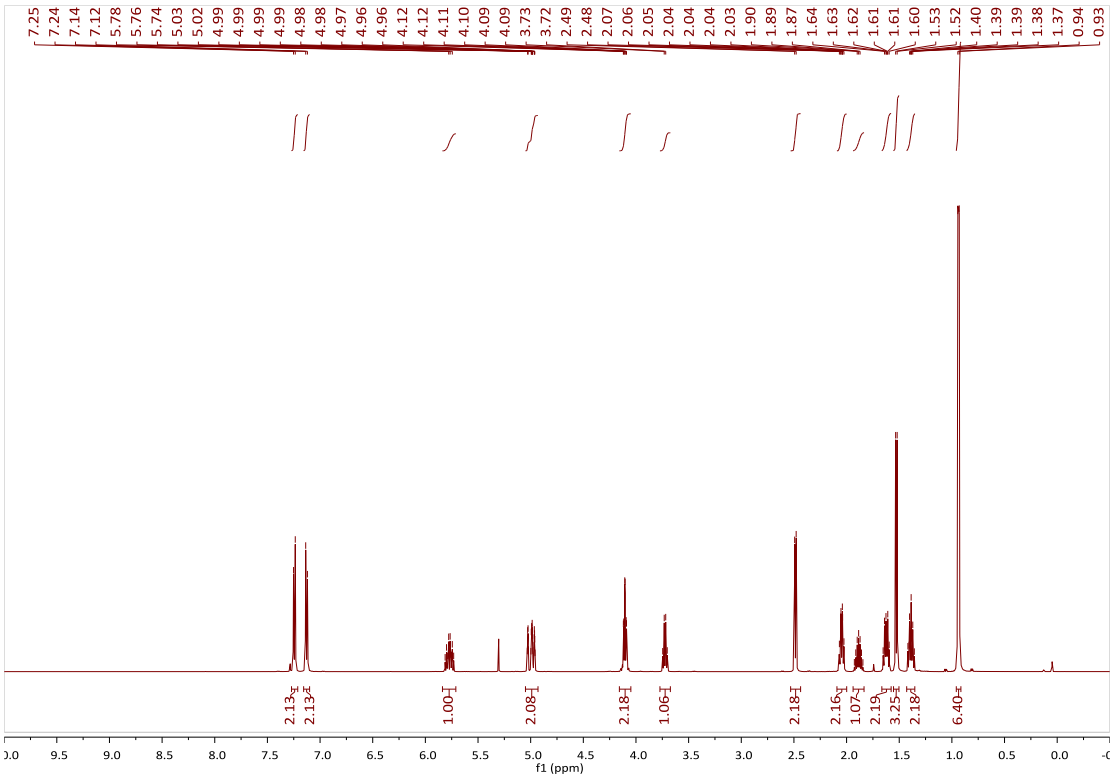


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **S21**

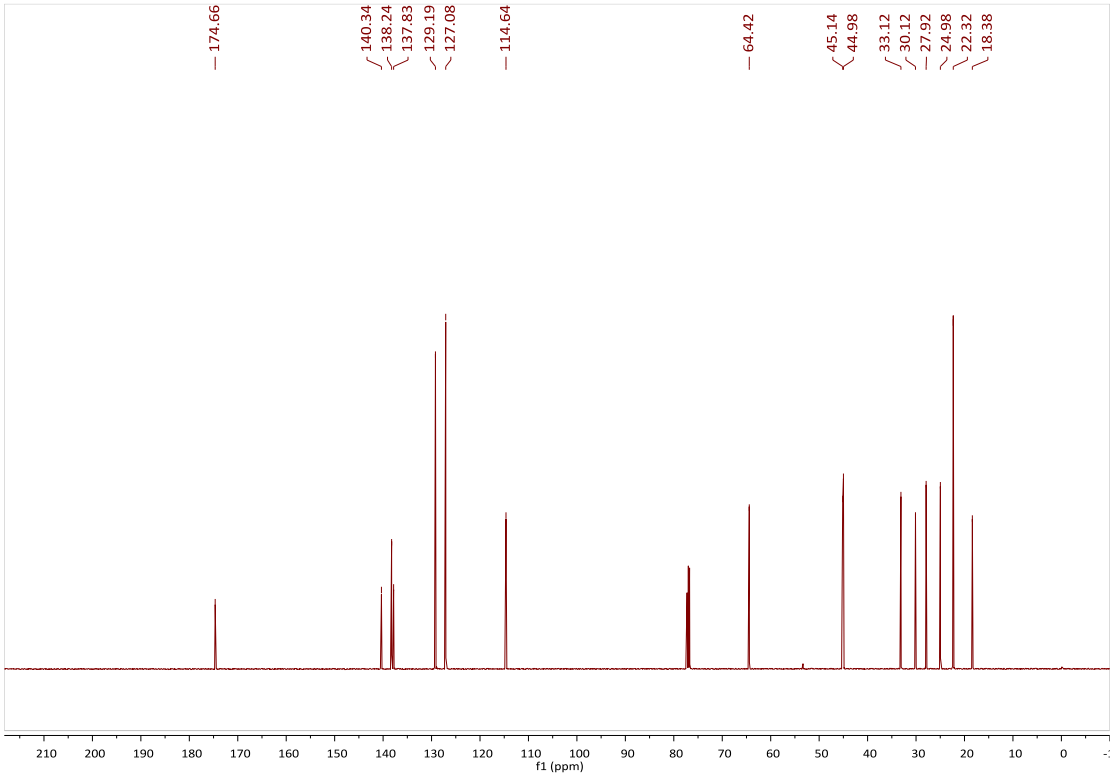


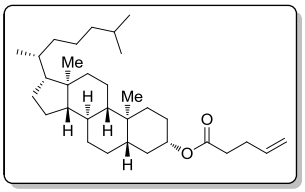


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **S23**

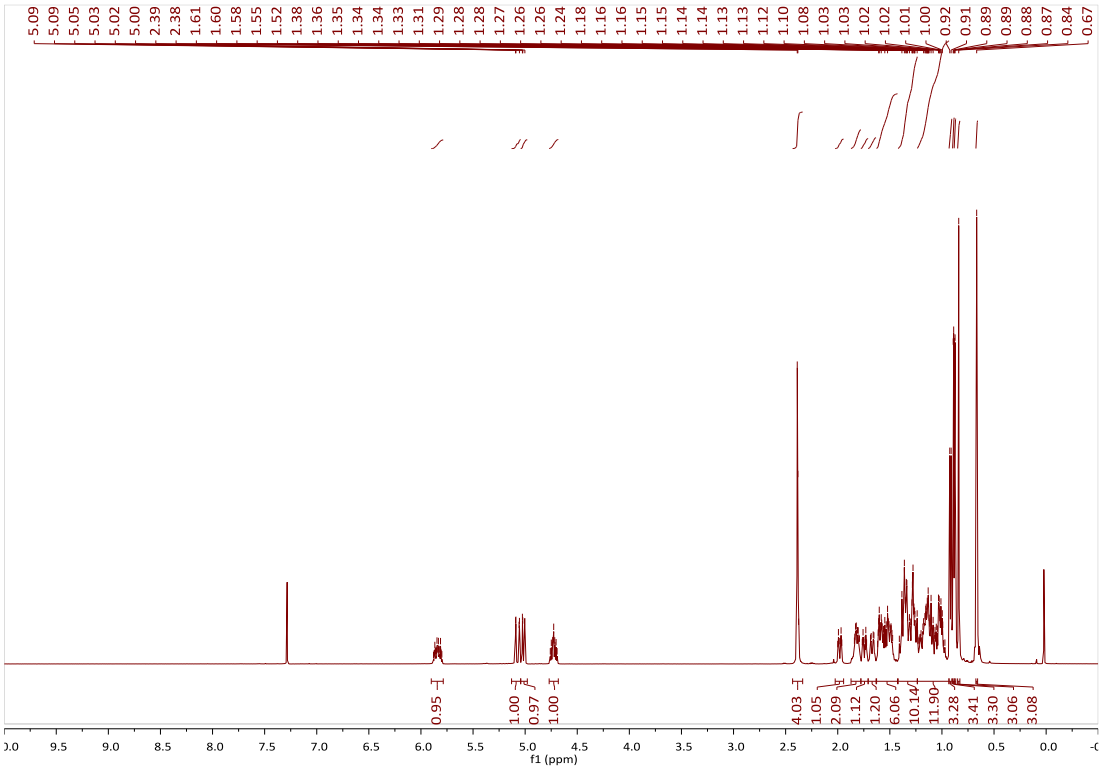


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **S23**

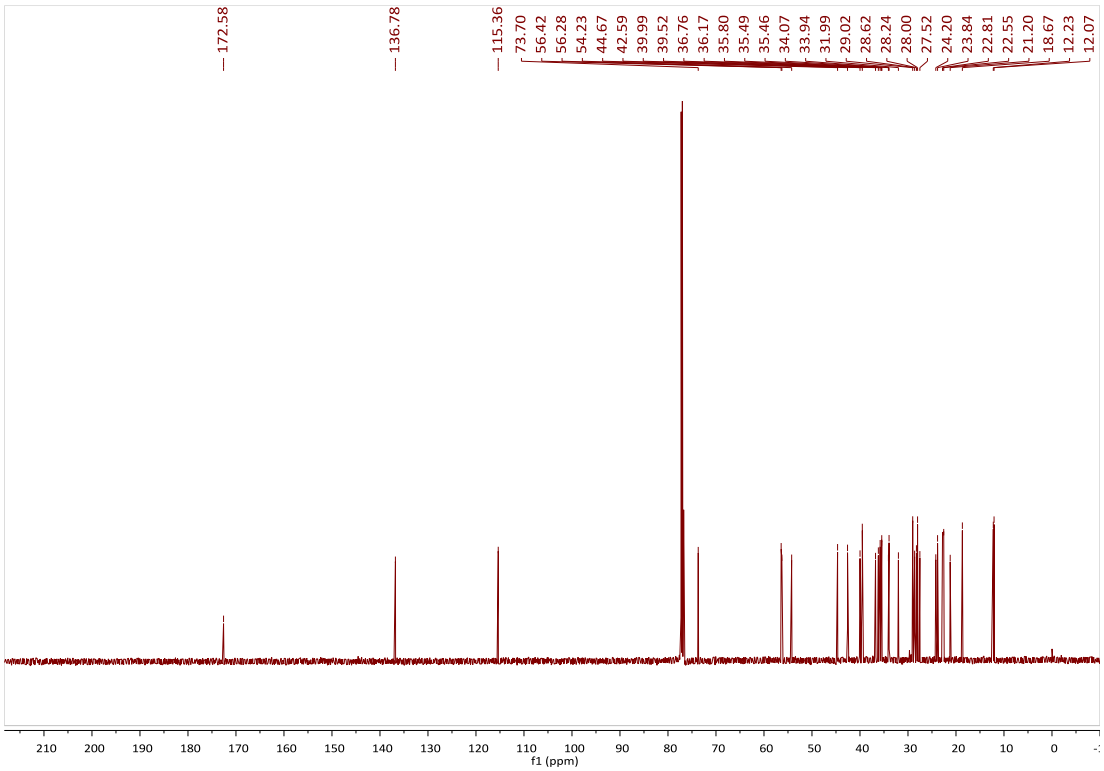


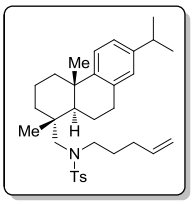


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **S25**

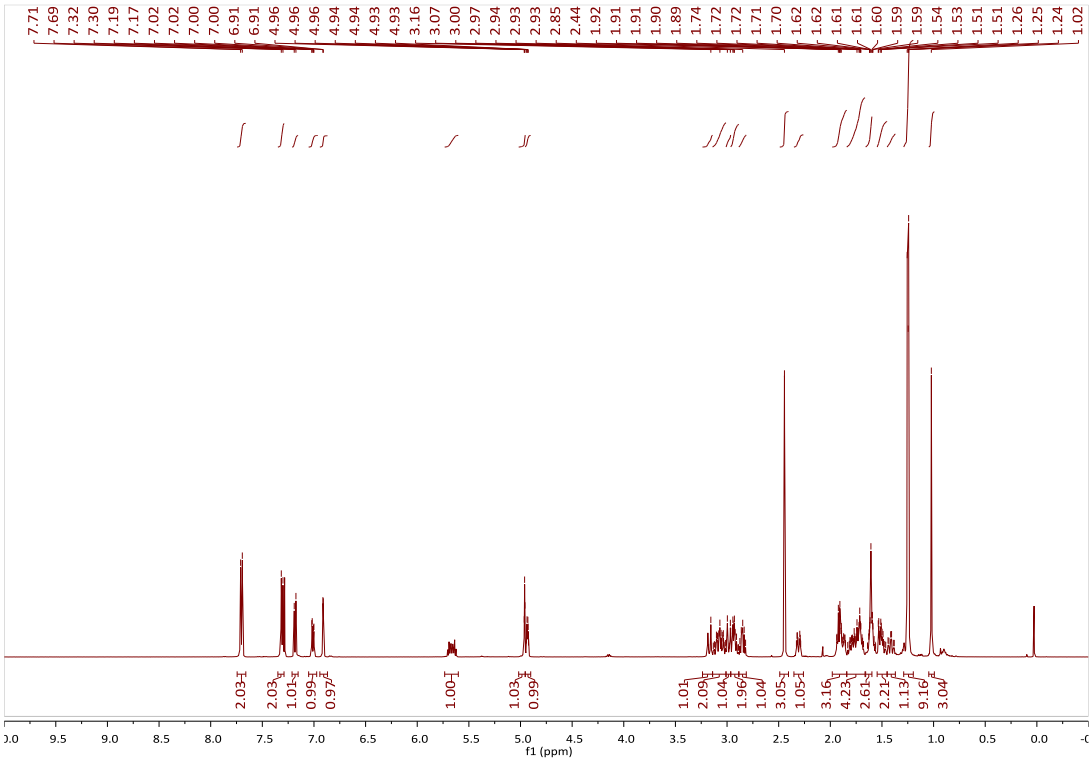


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **S25**

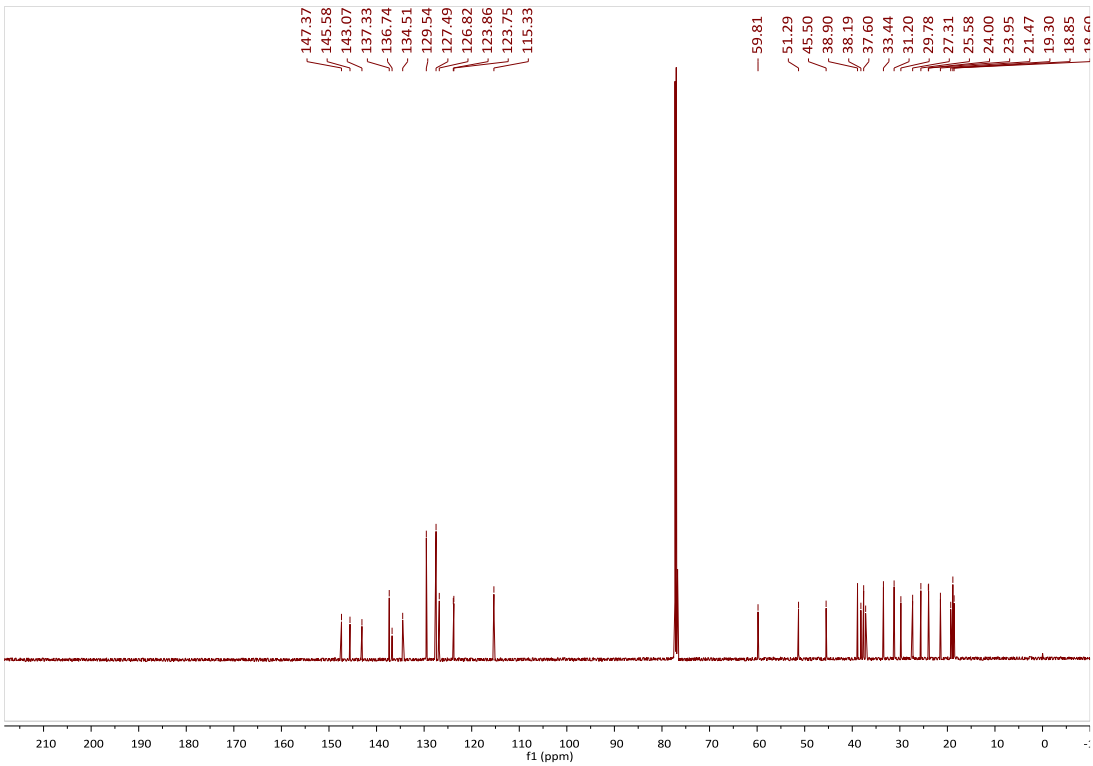


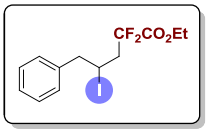


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **S28**

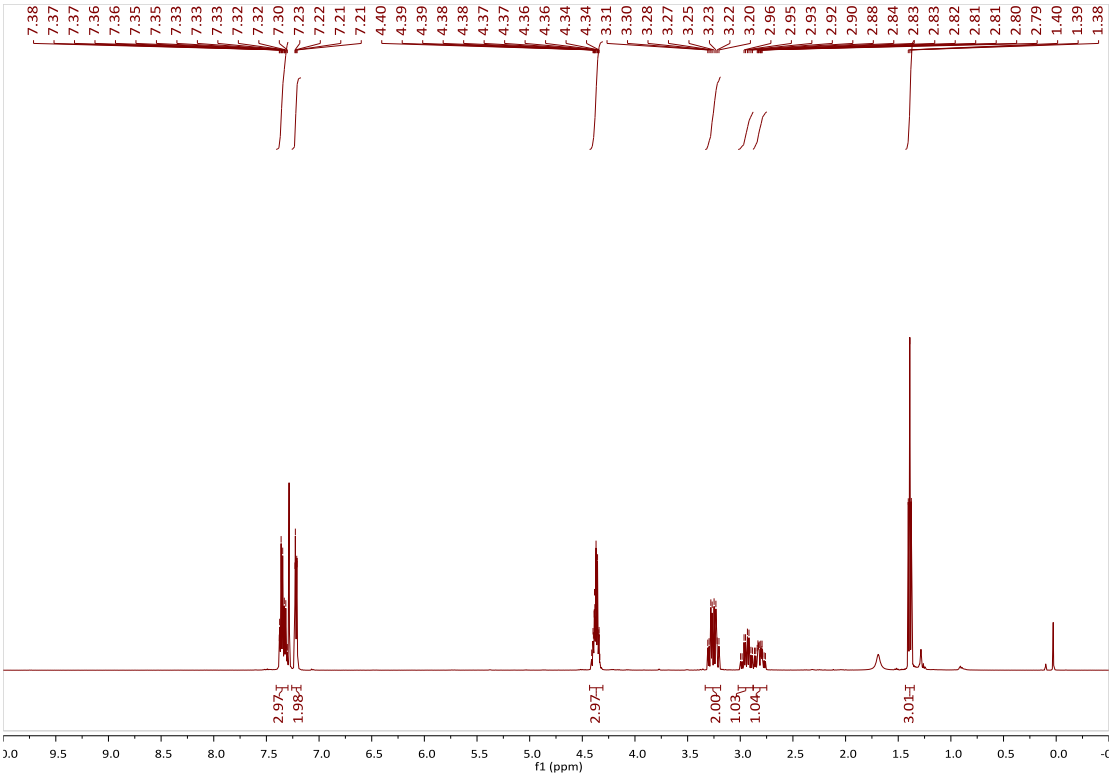


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **S28**

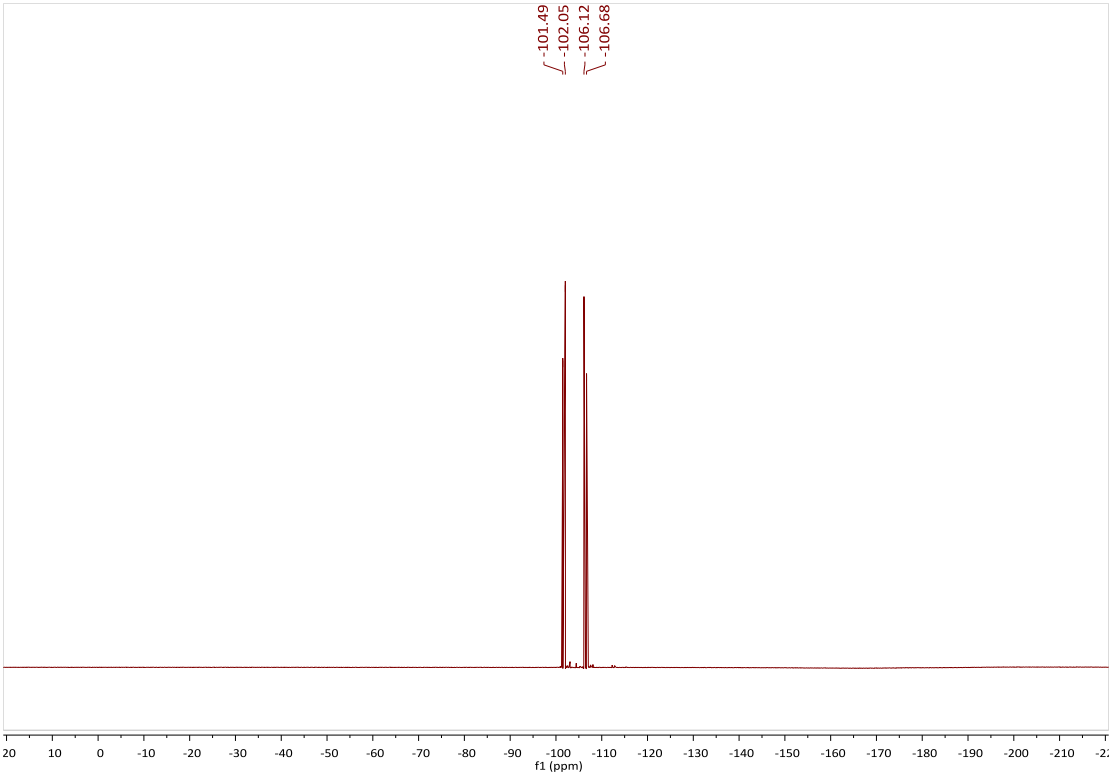


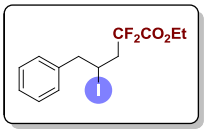


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3a**

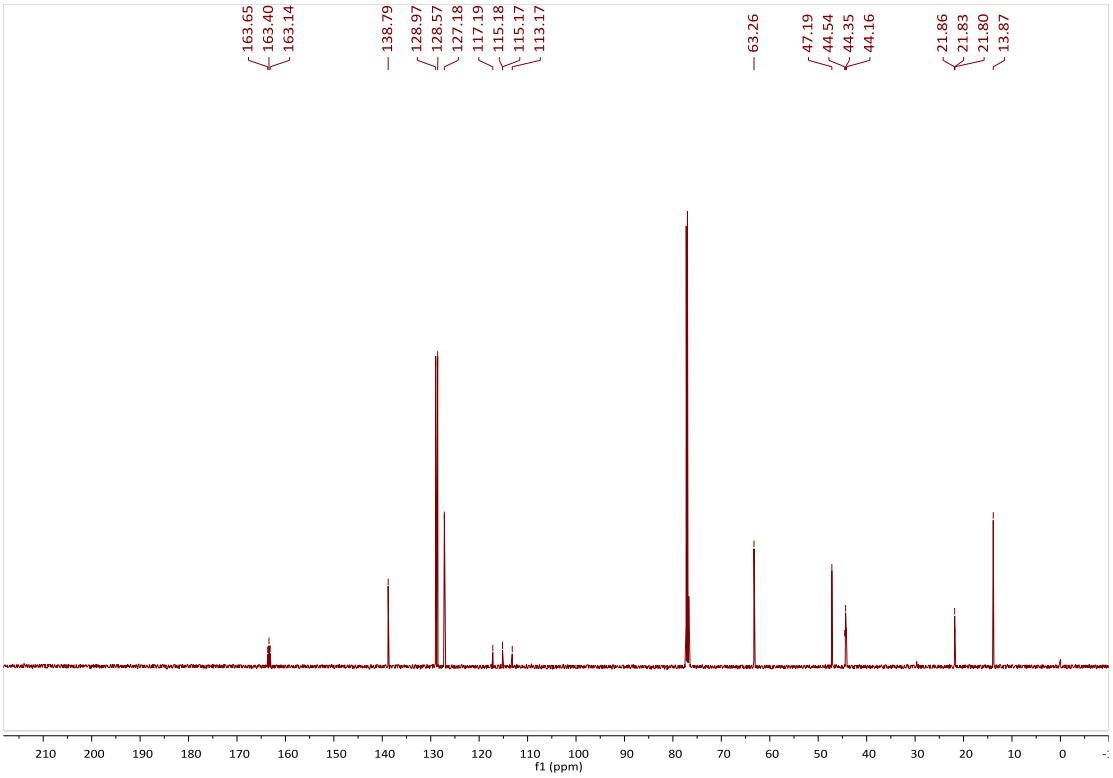


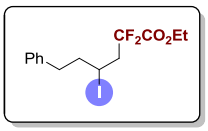
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3a**



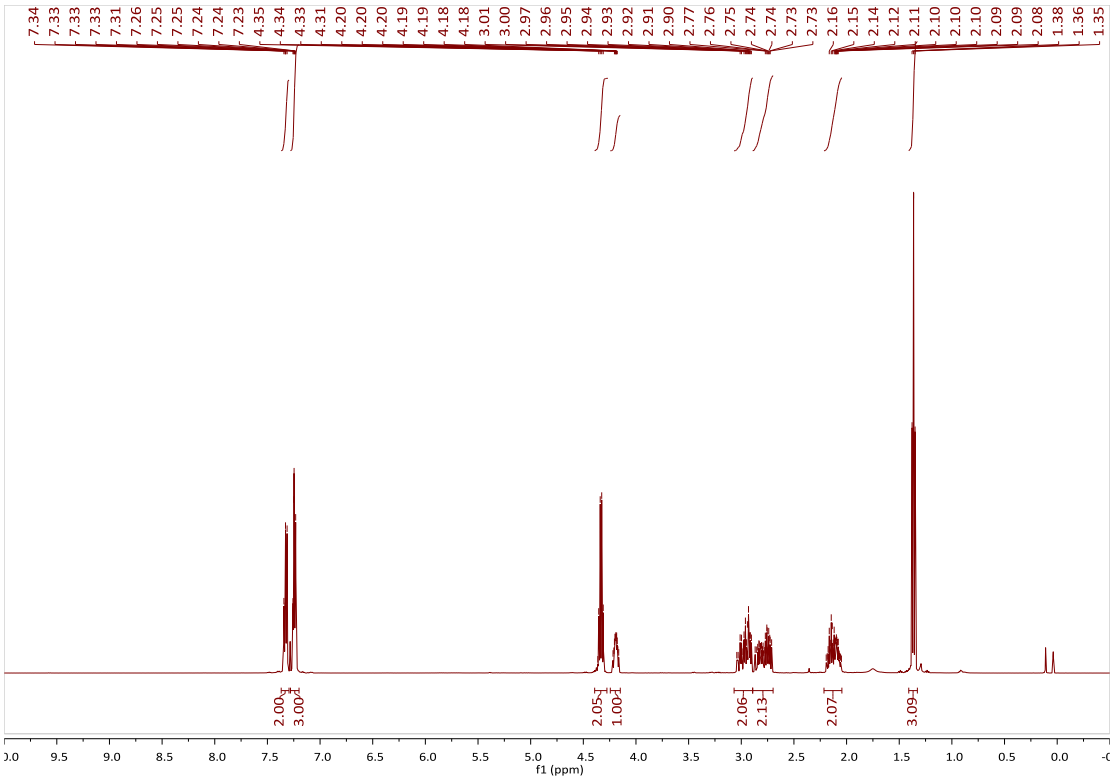


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3a**

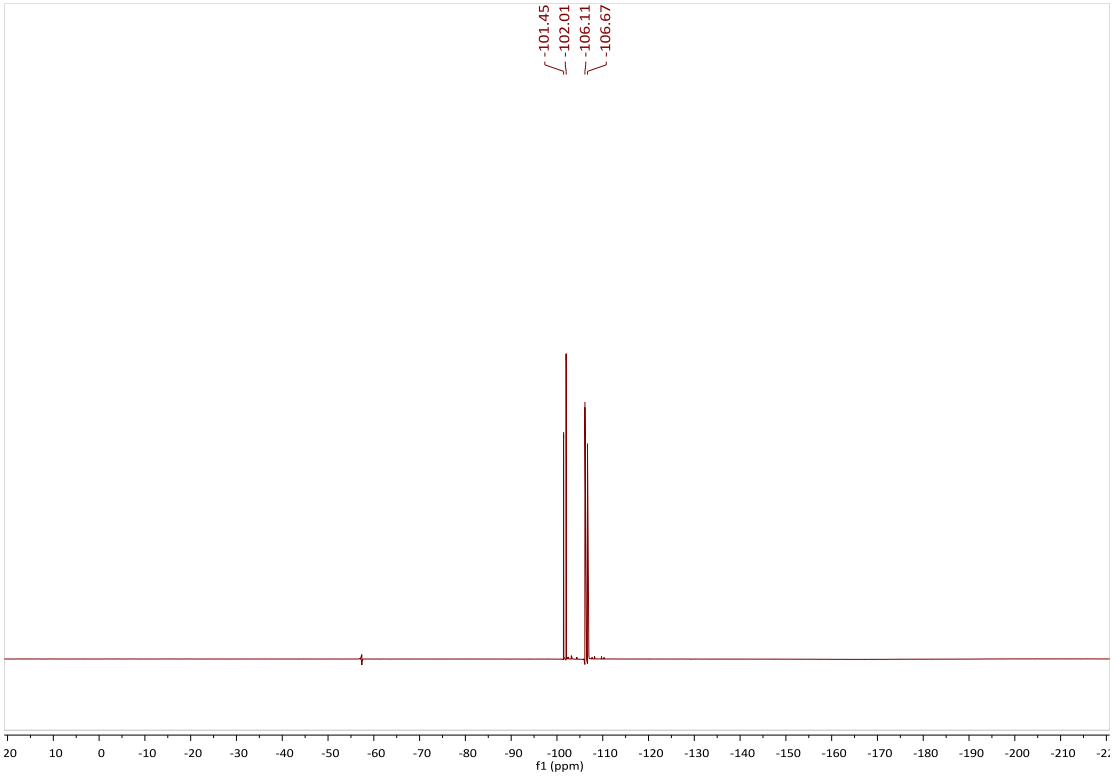


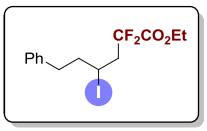


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3b**

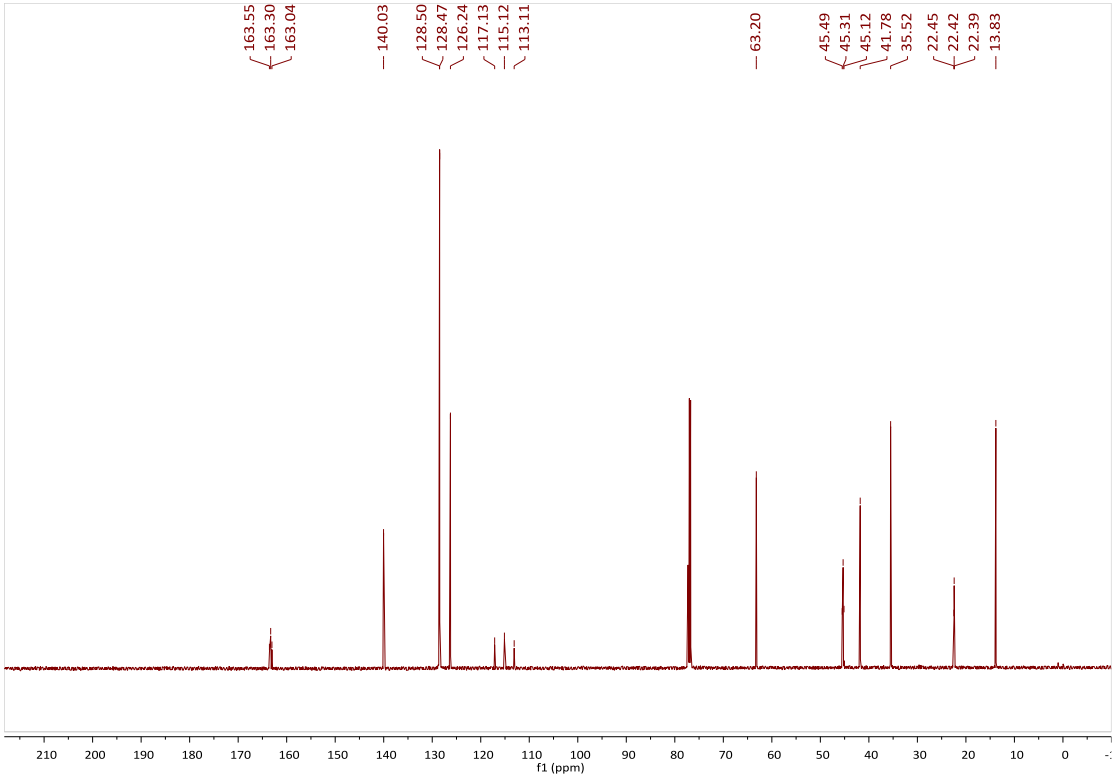


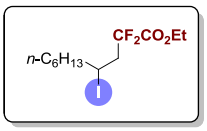
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3b**



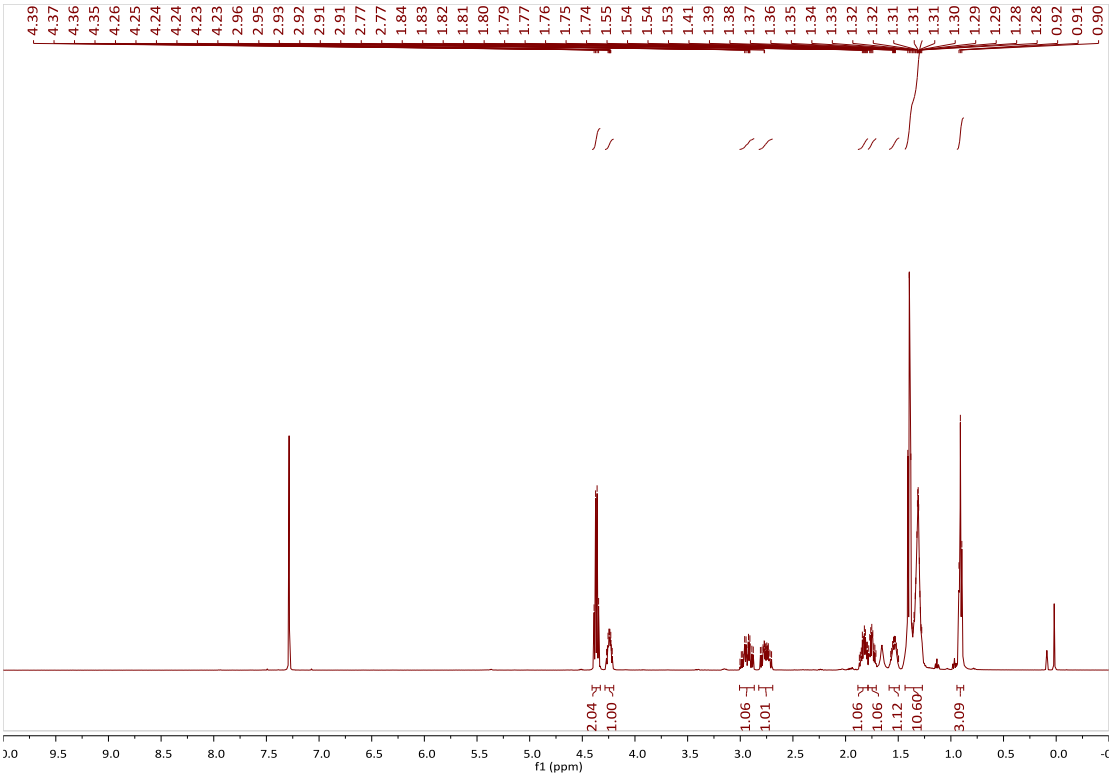


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3b**

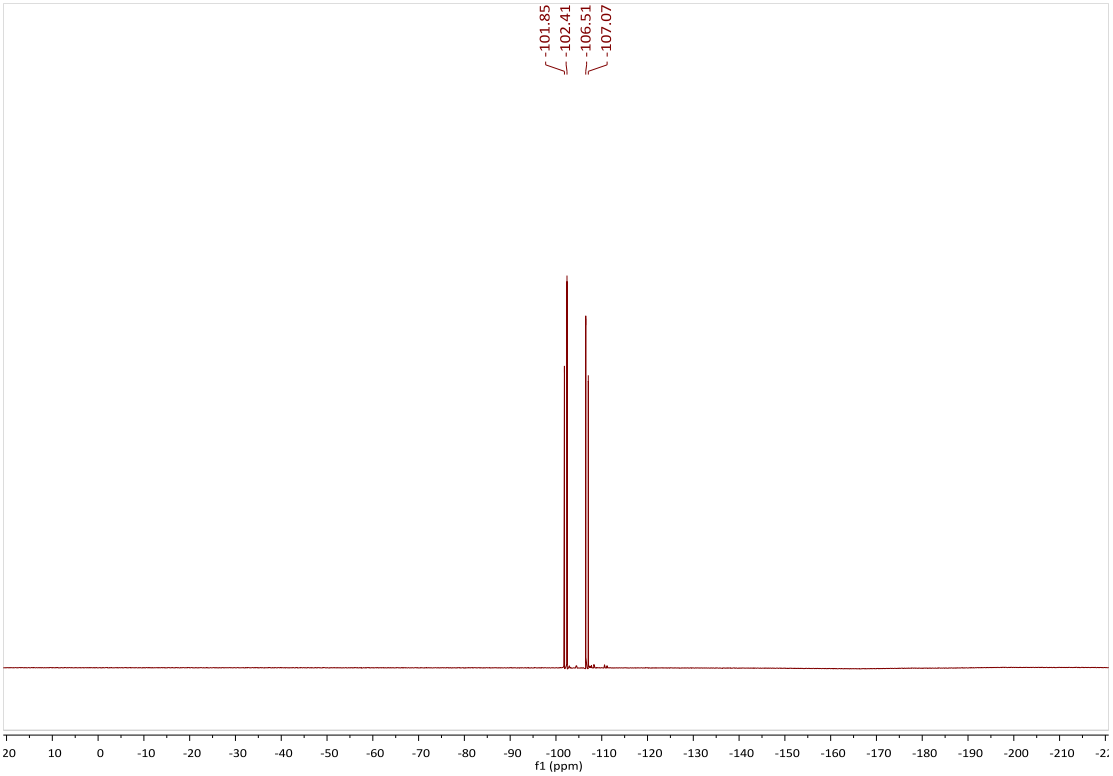


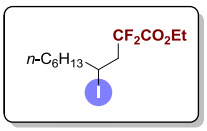


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3c**

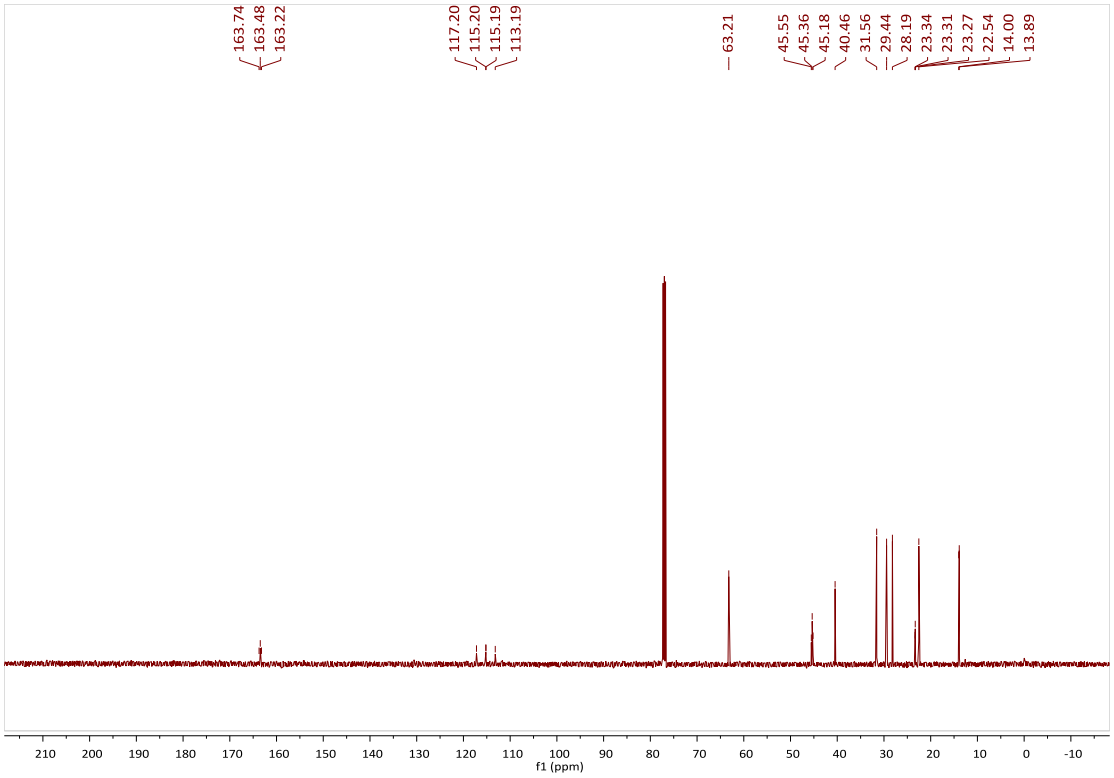


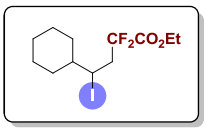
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3c**



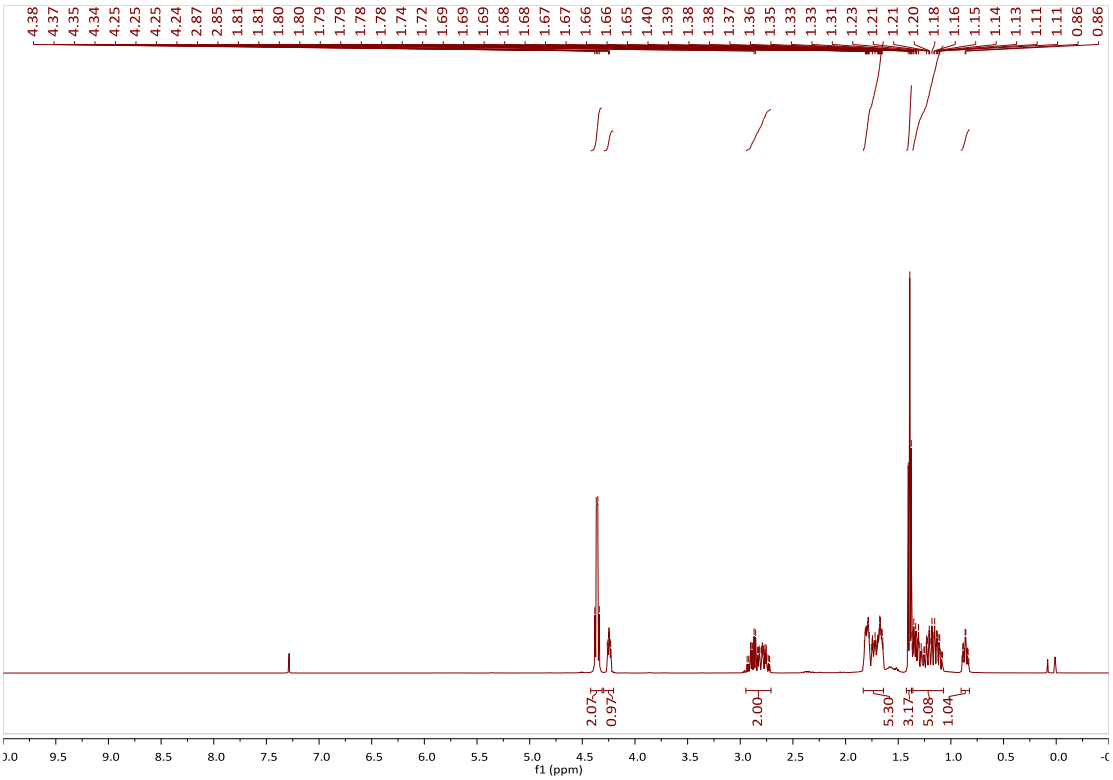


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3c**

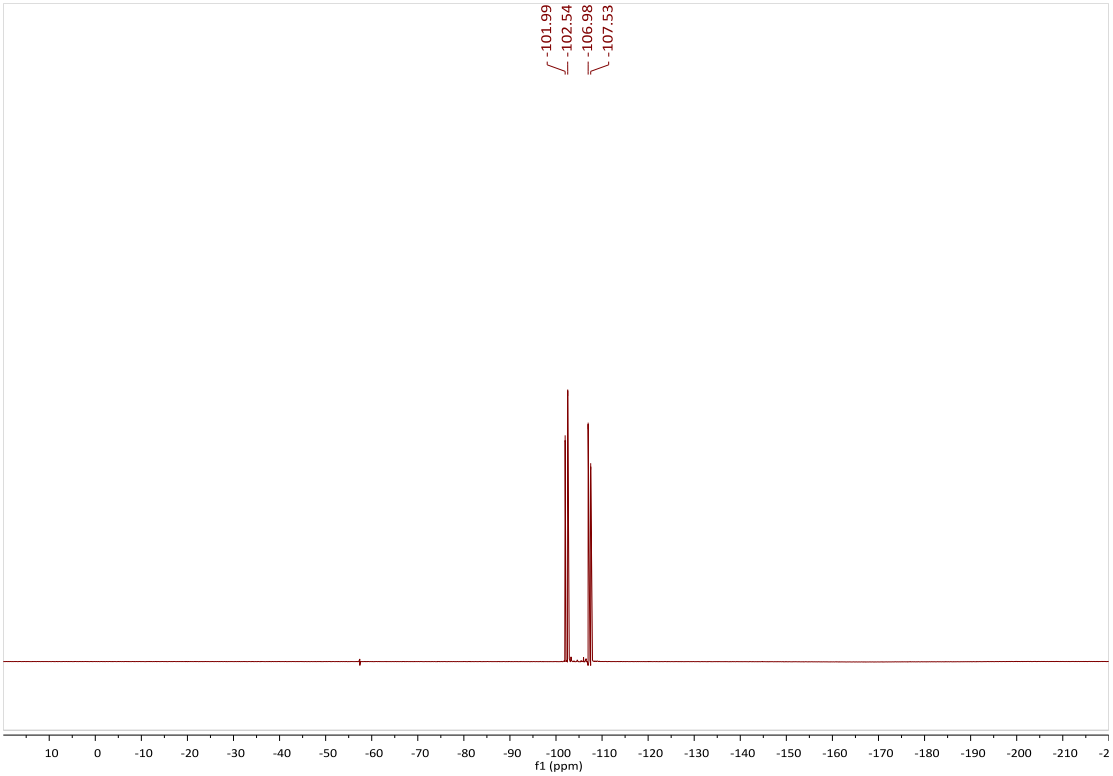


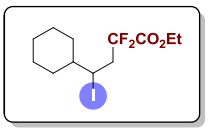


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3d**

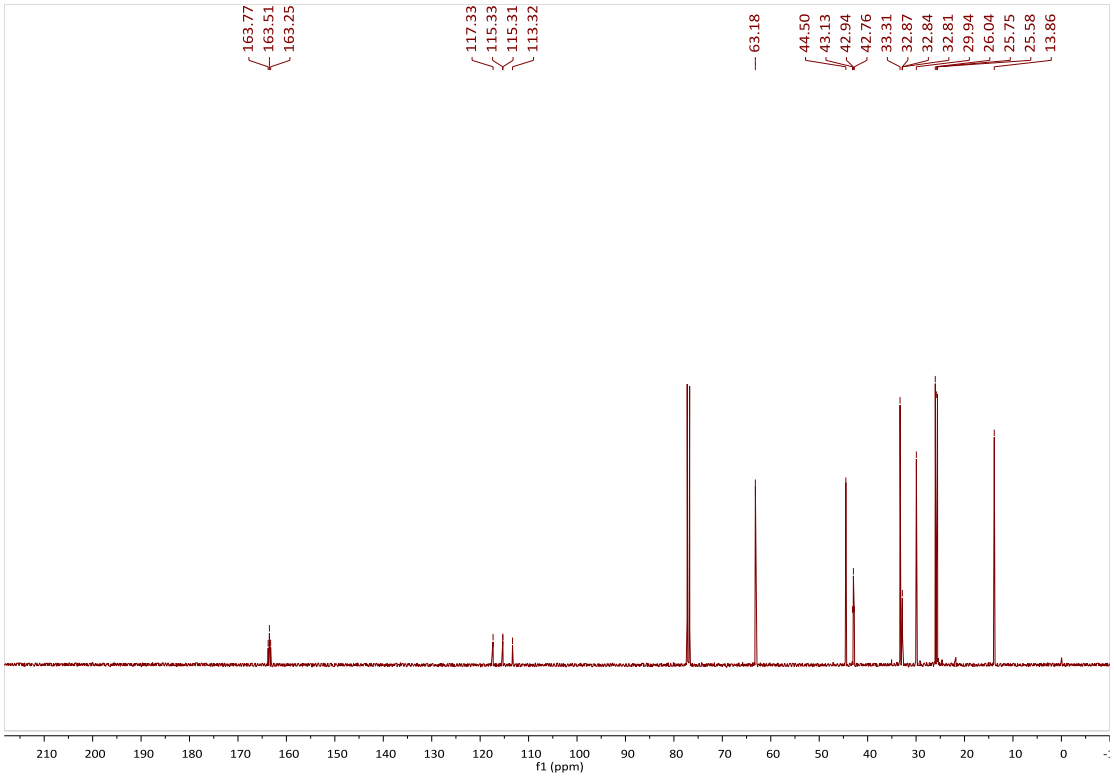


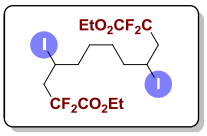
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3d**



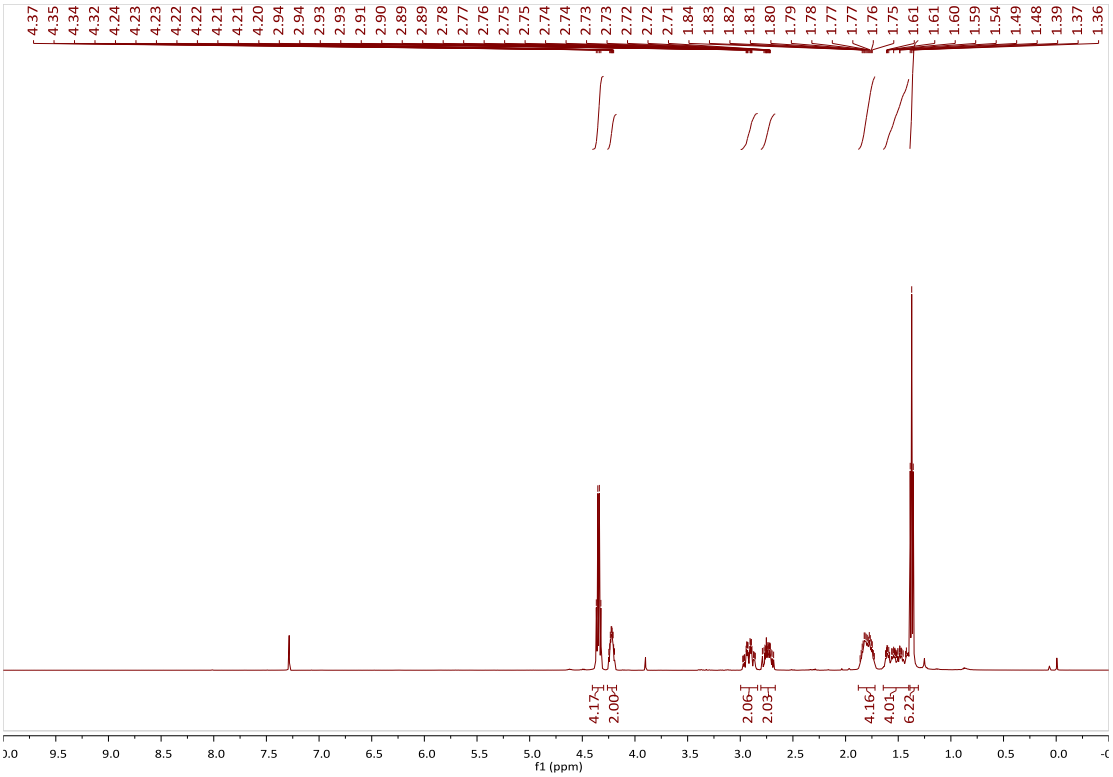


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3d**

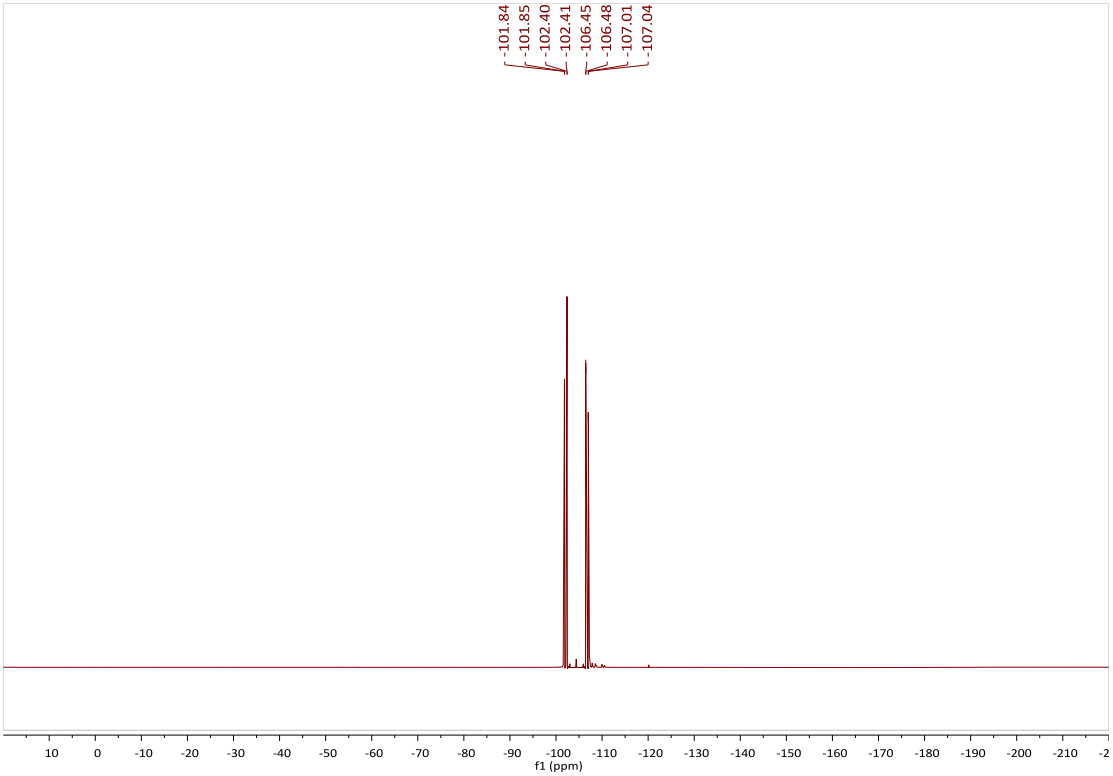


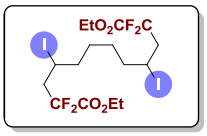


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3e**

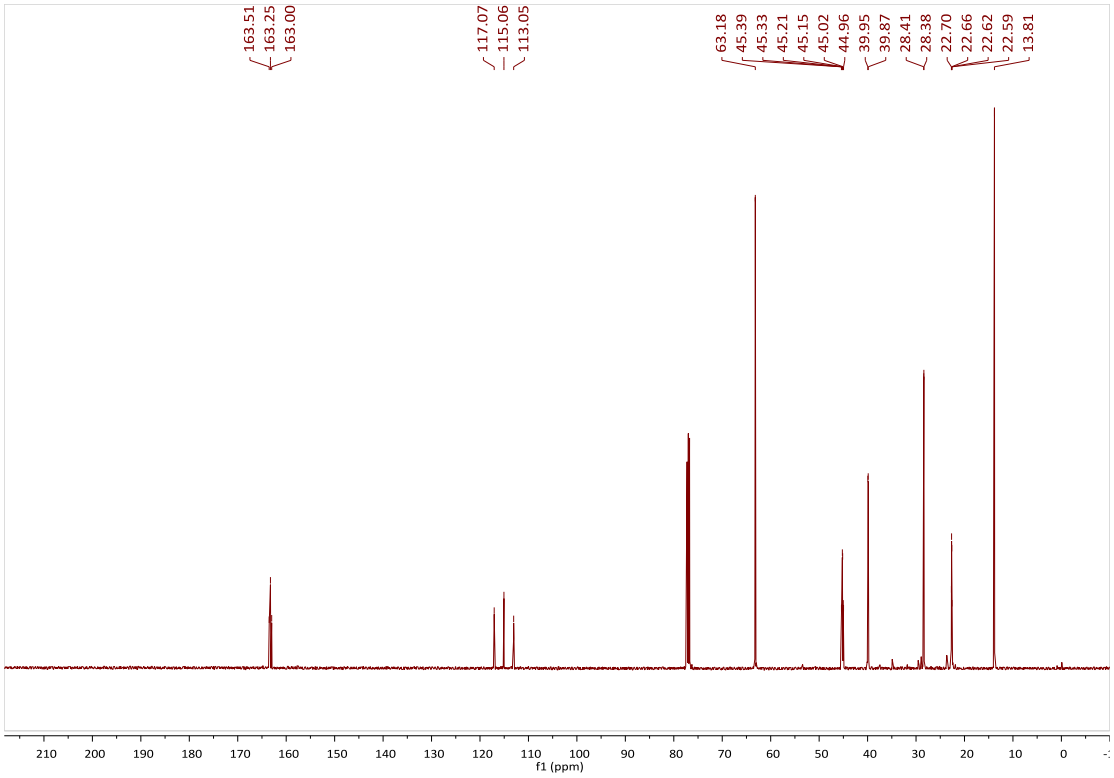


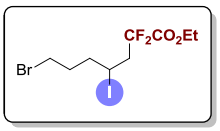
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3e**



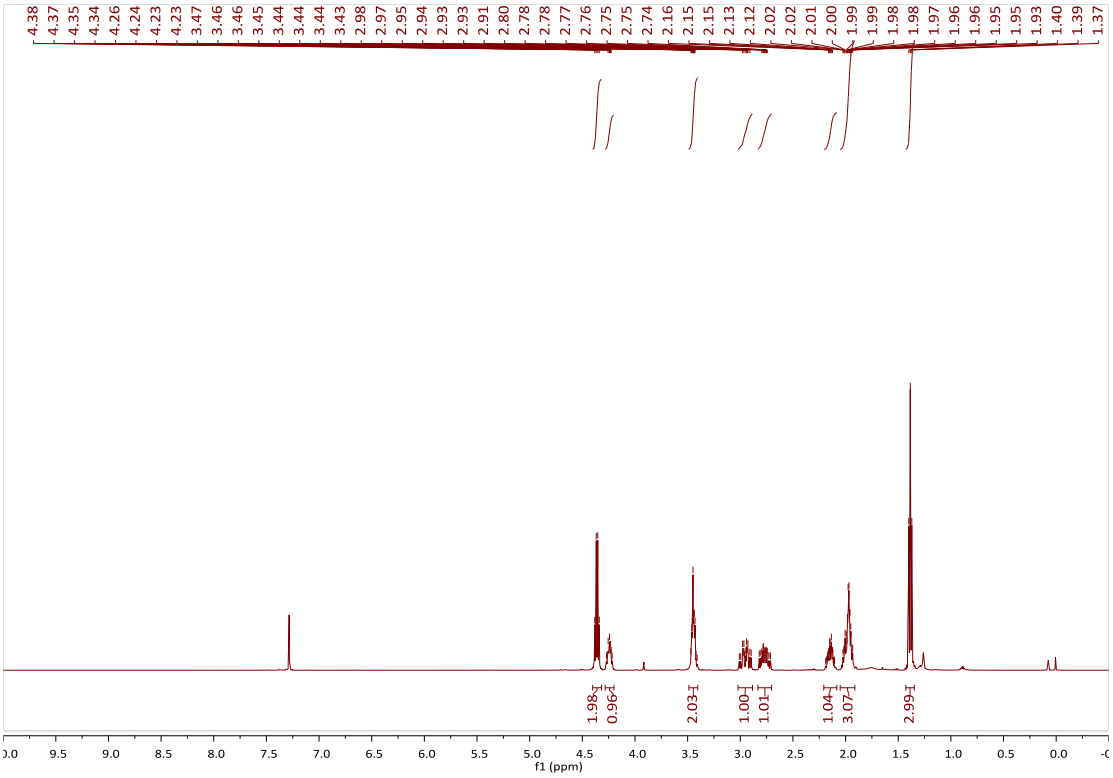


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3e**

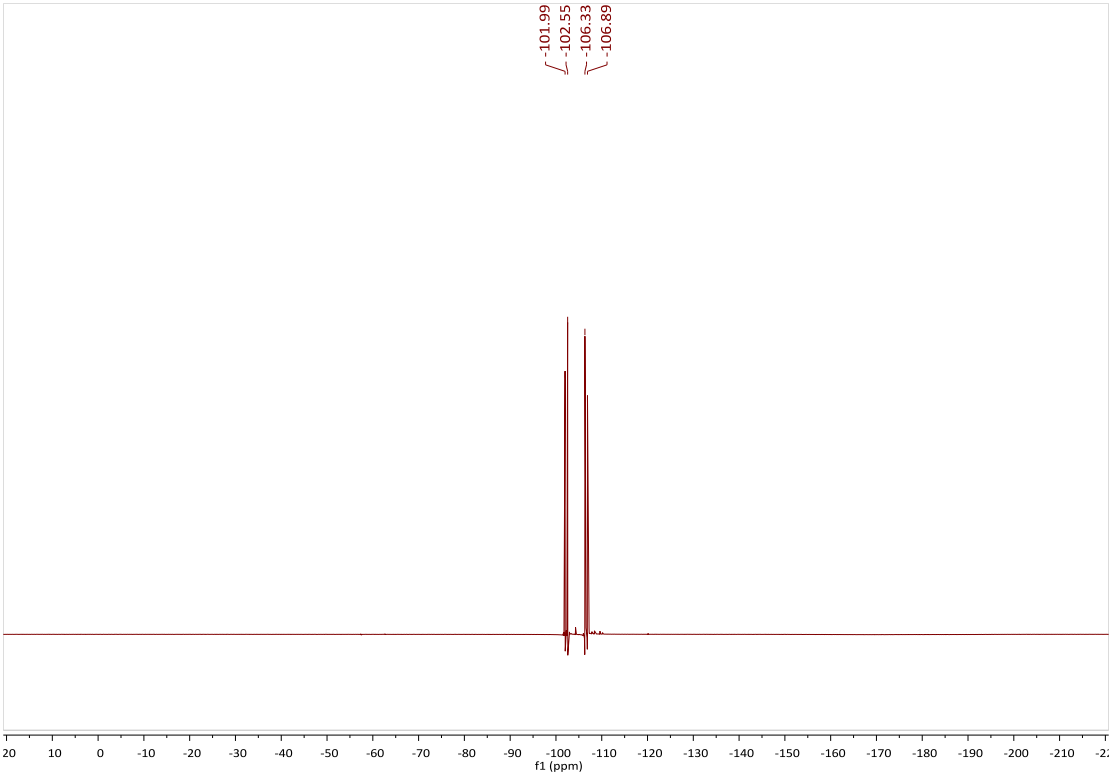


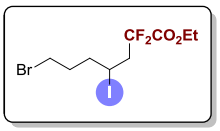


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3f**

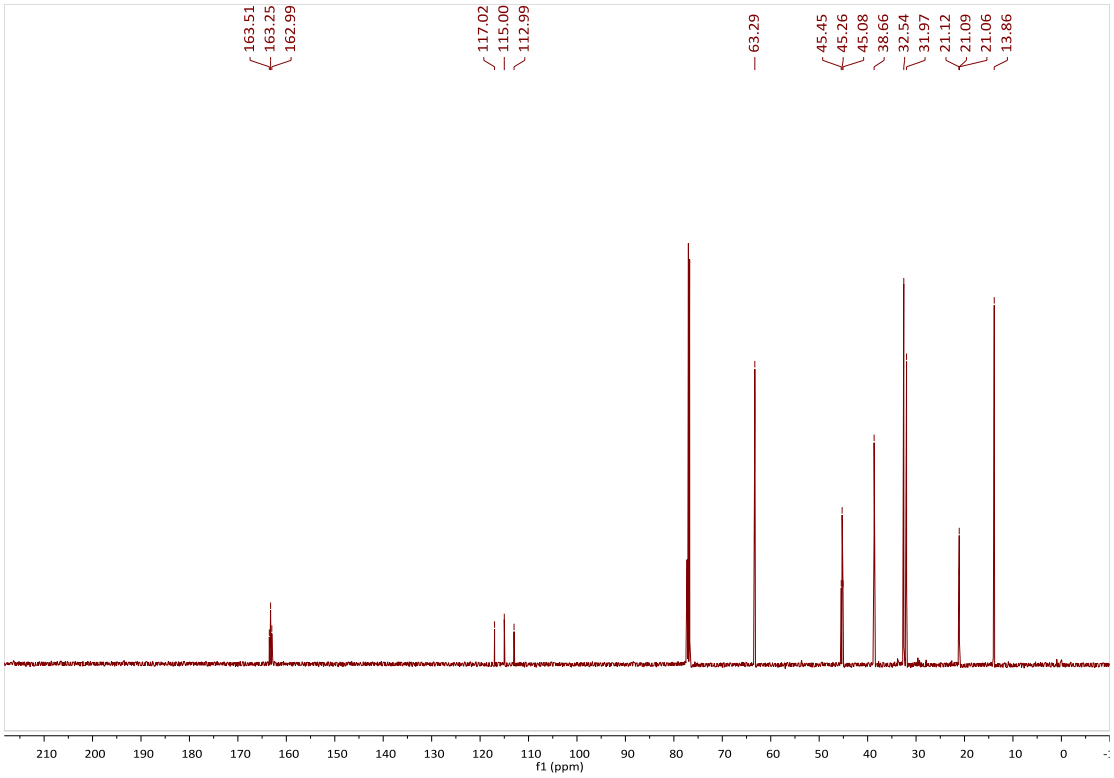


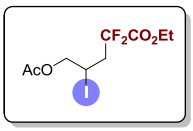
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3f**



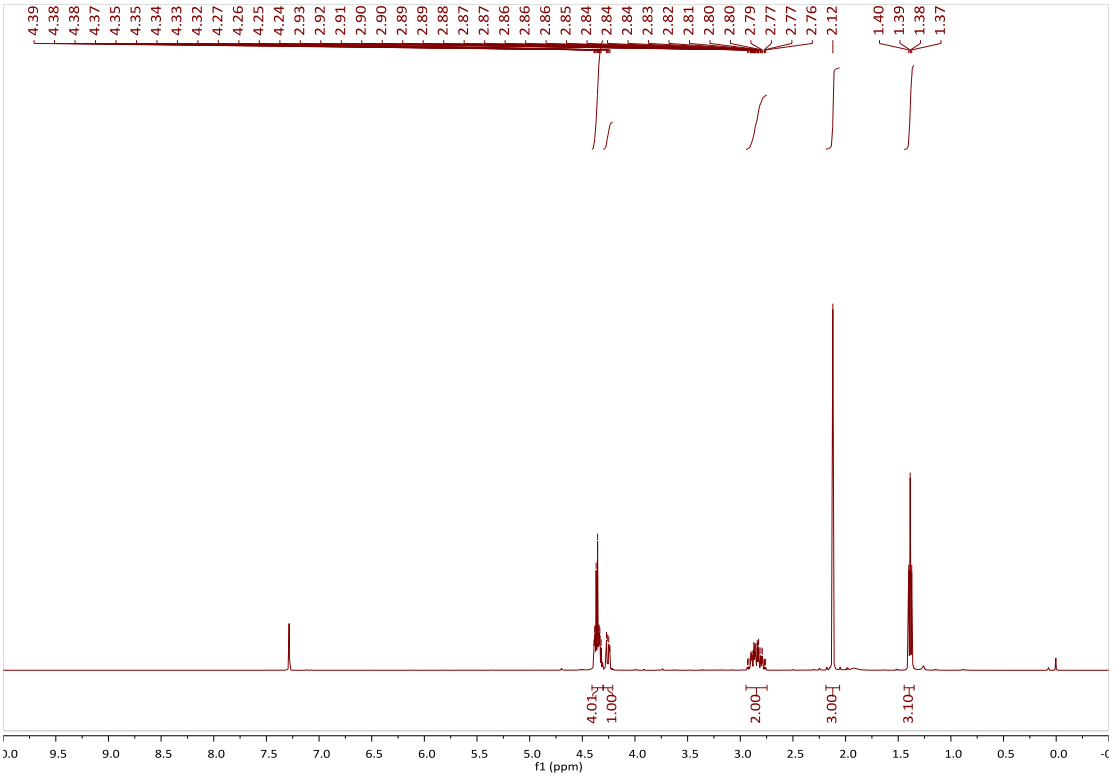


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3f**

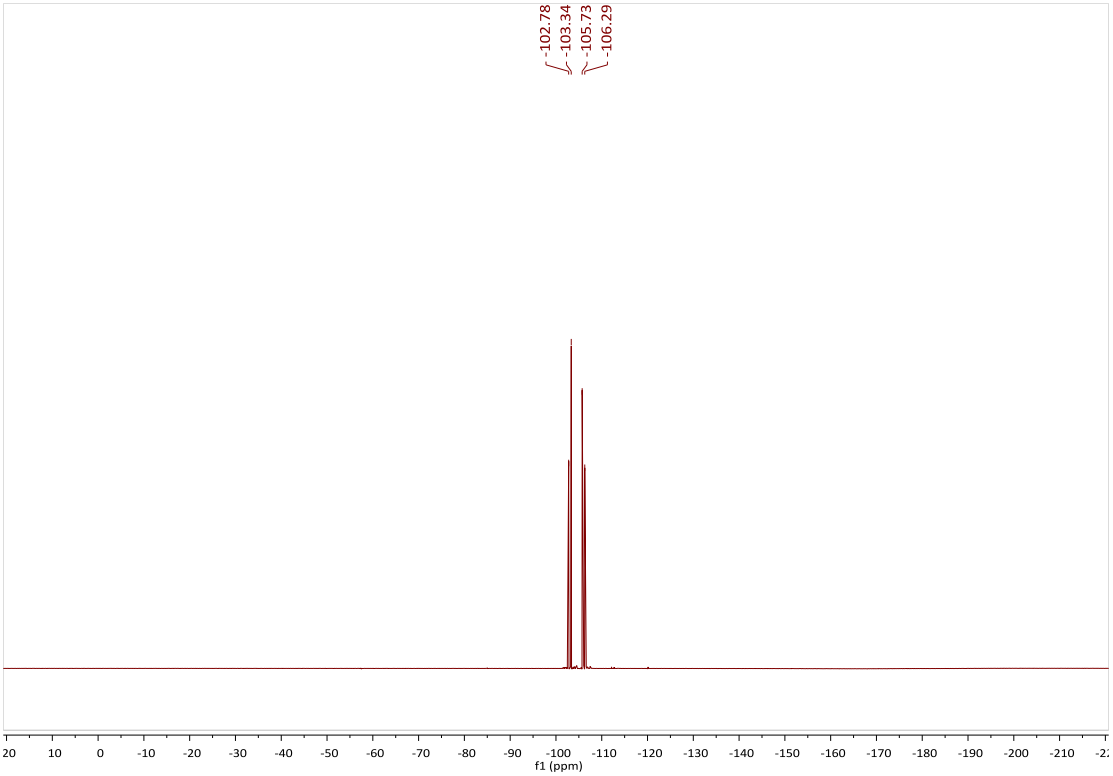


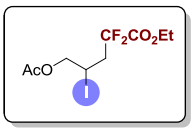


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3g**

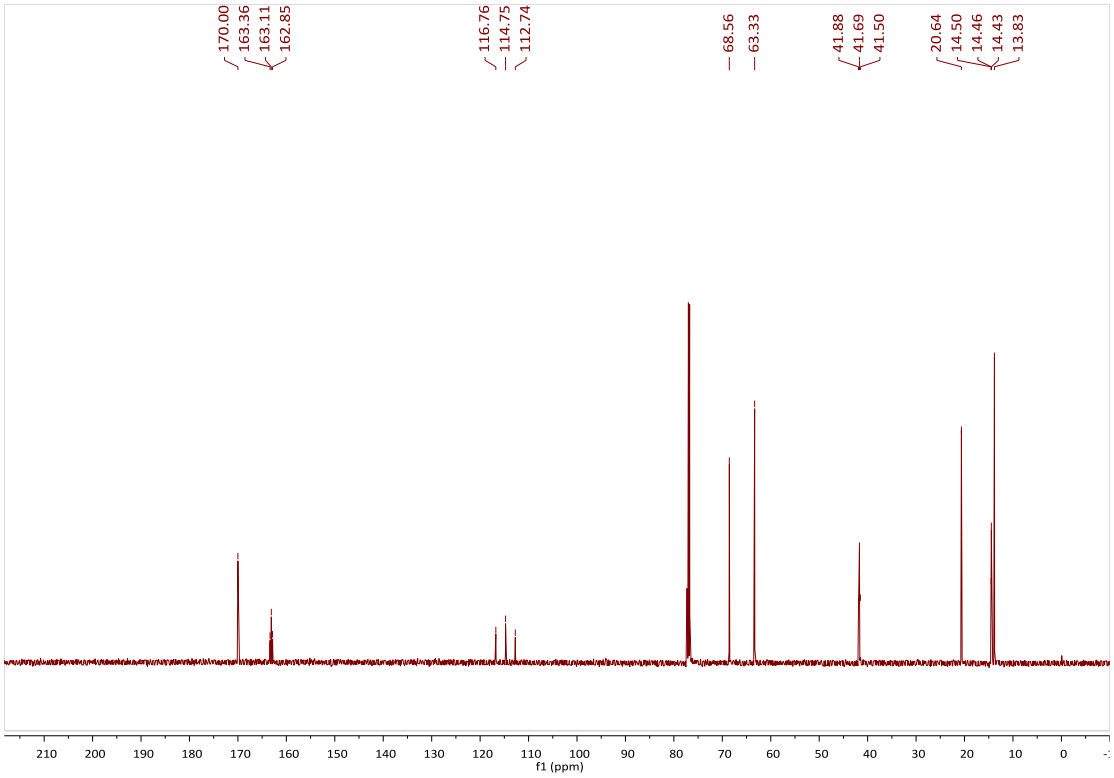


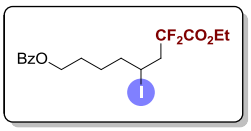
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3g**



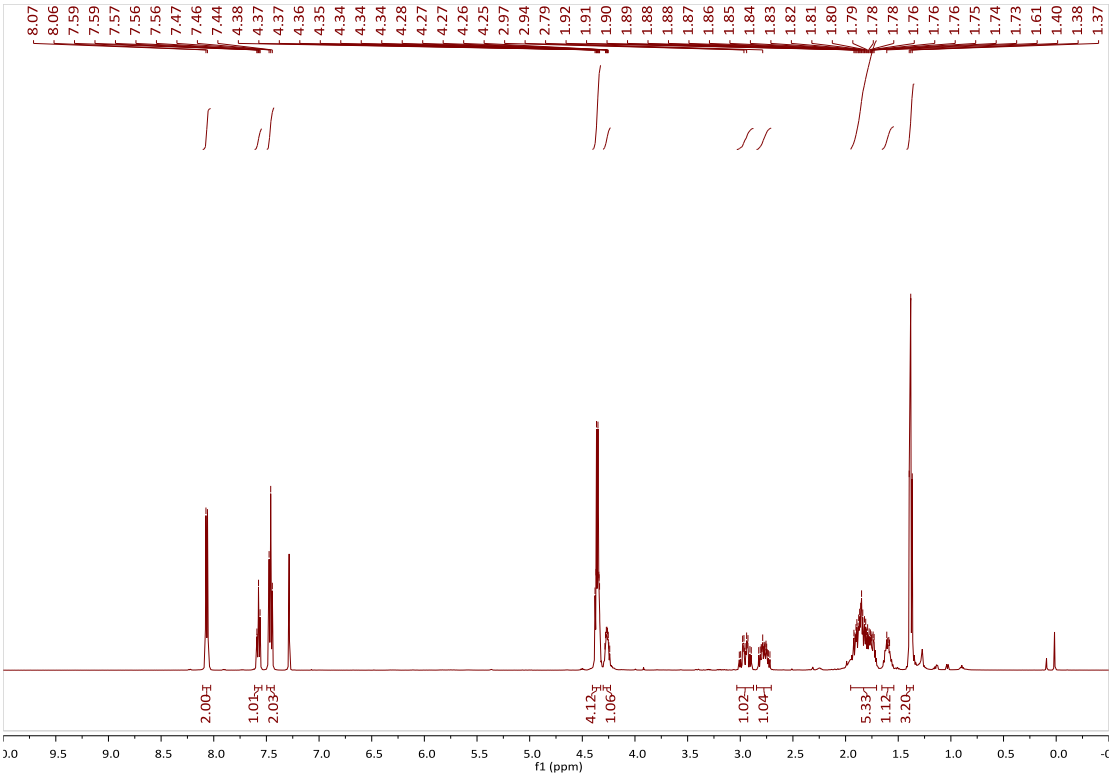


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3g**

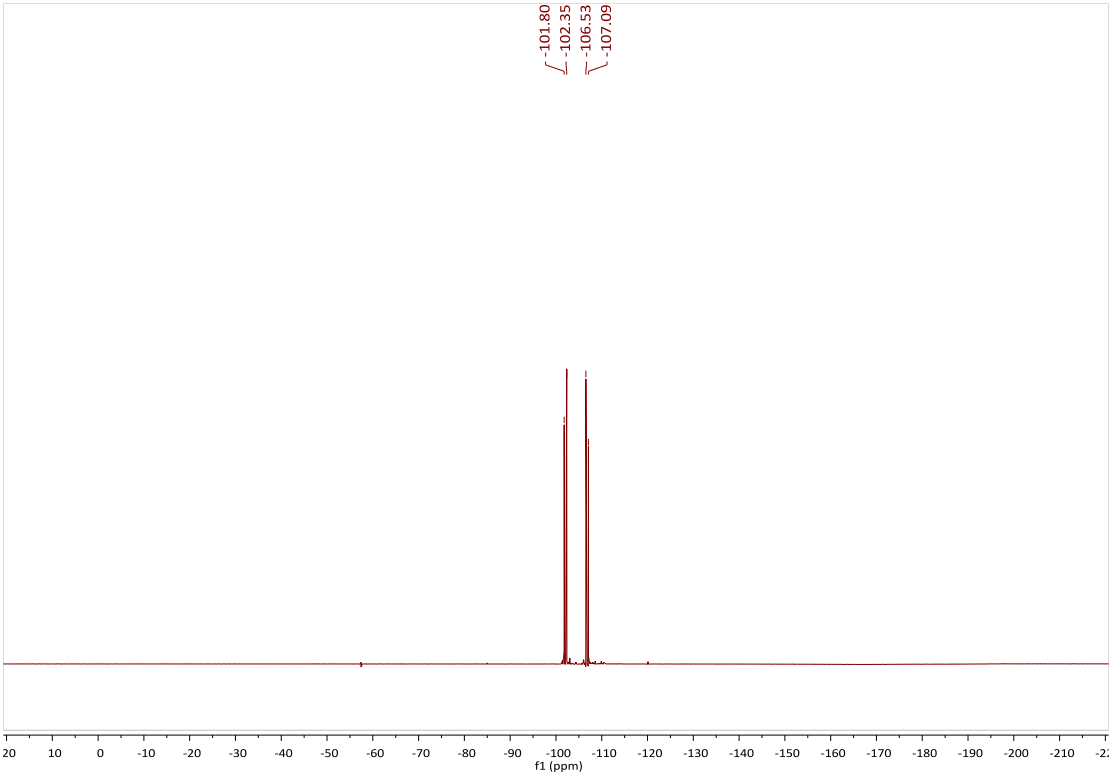


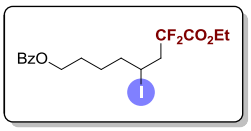


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3h**

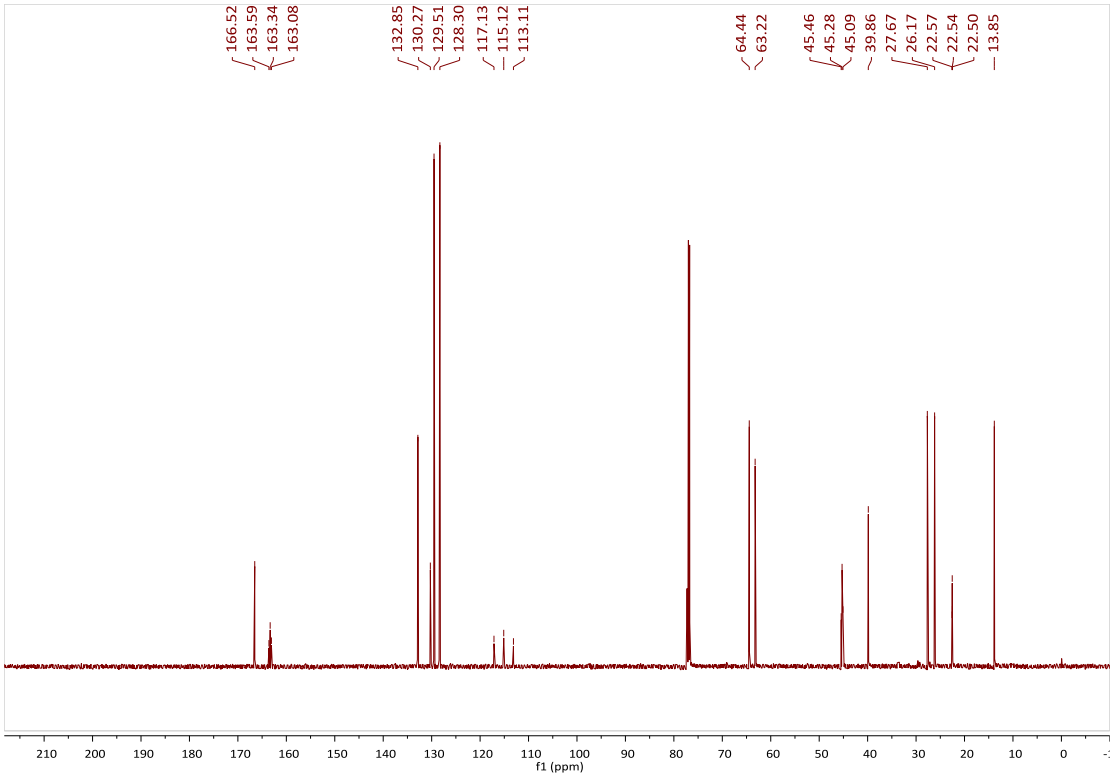


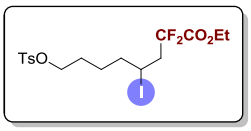
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3h**



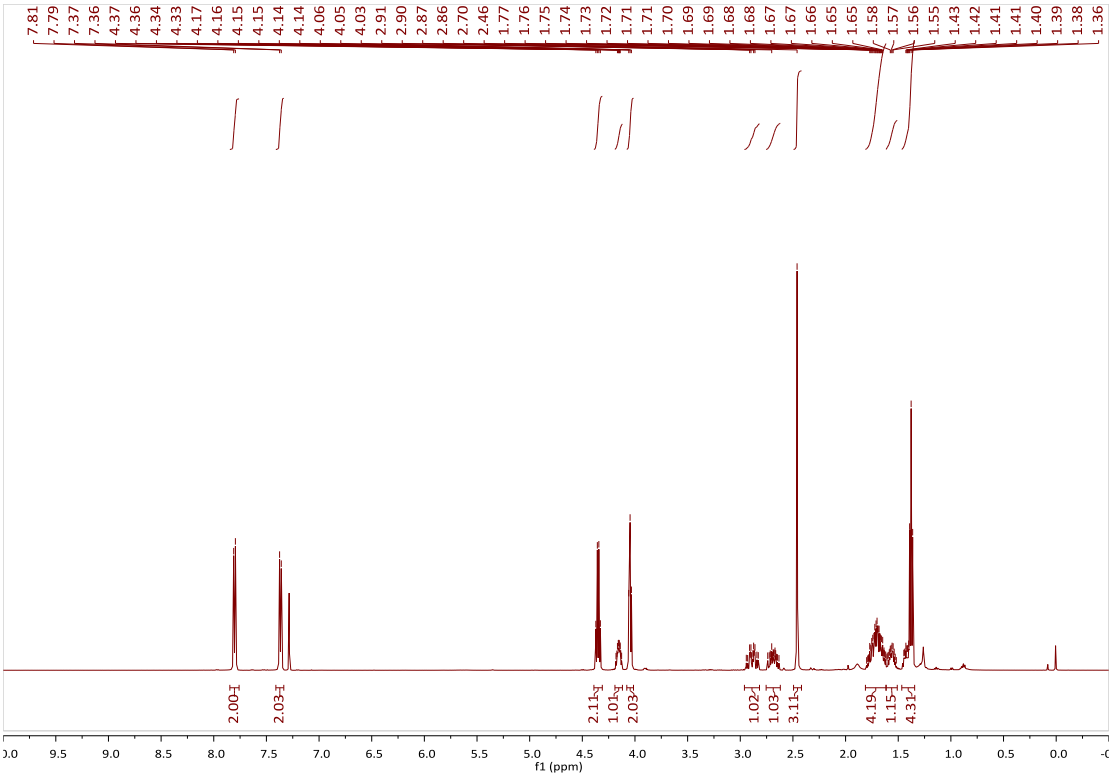


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3h**

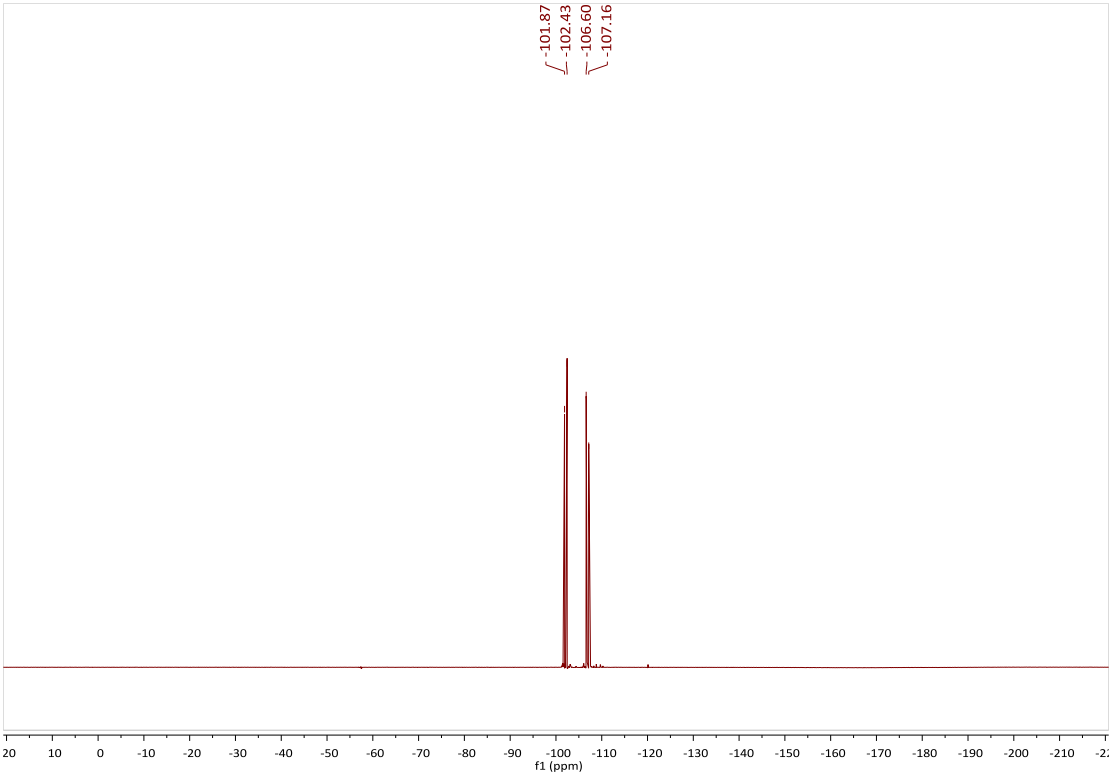


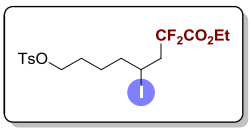


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3i**

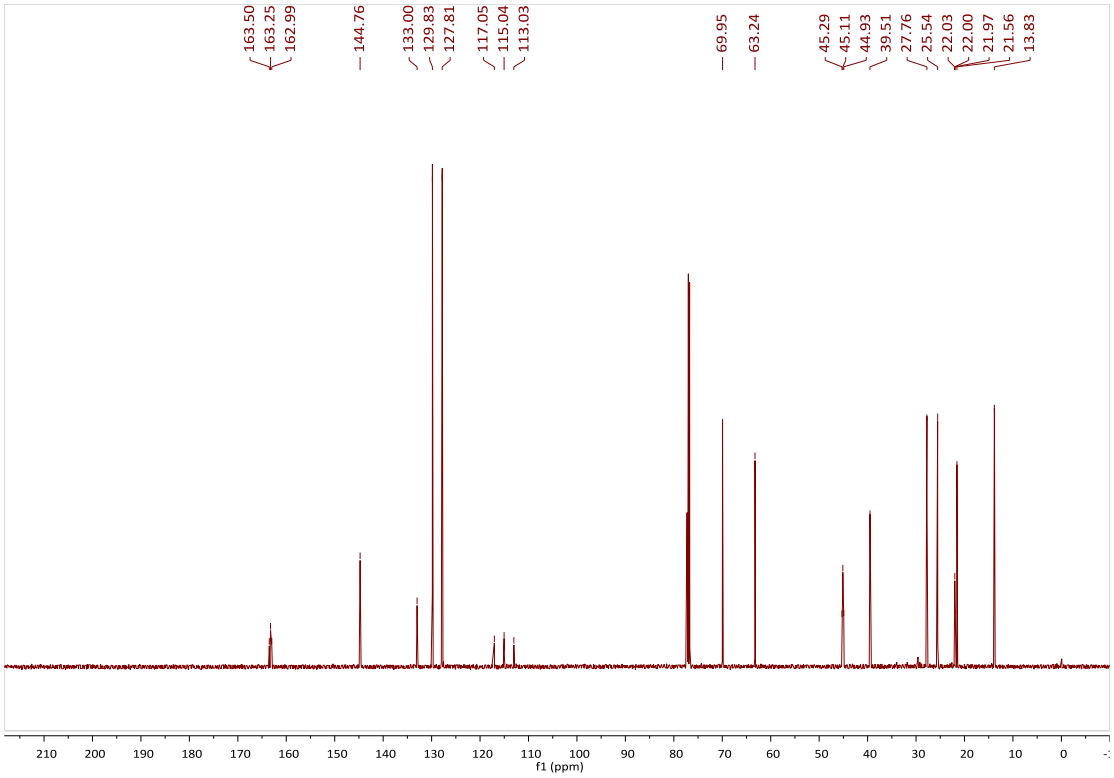


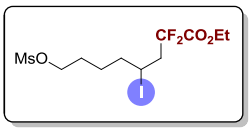
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3i**



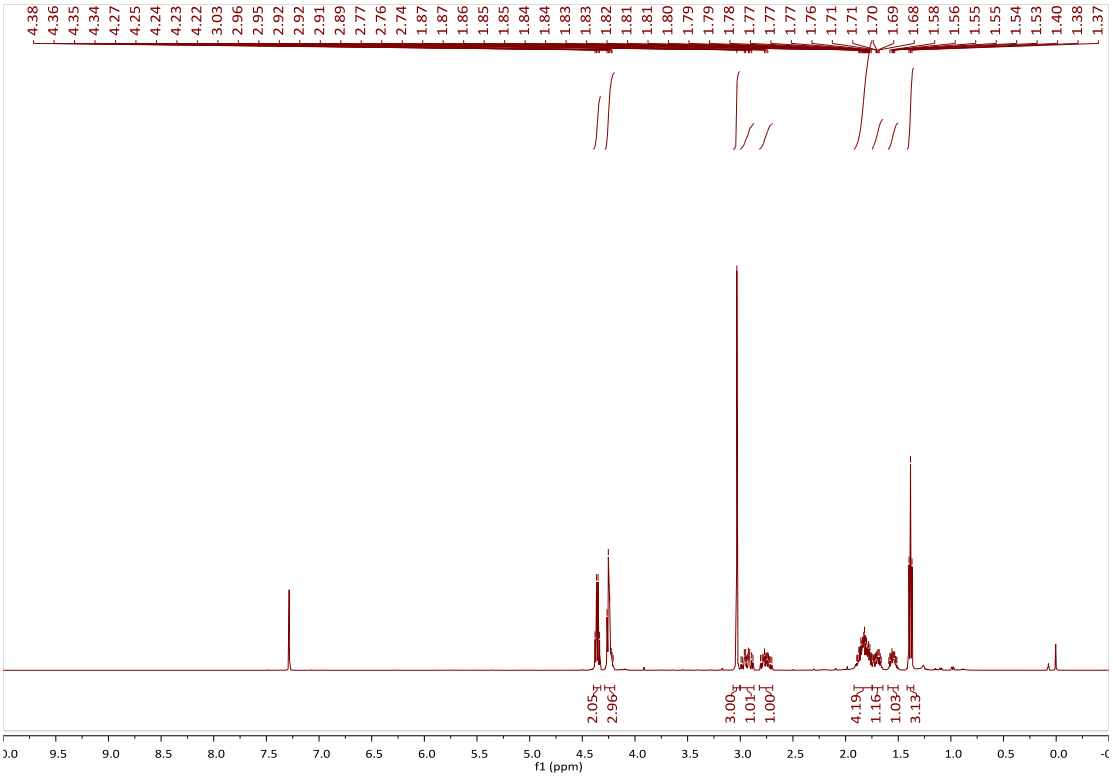


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3i**

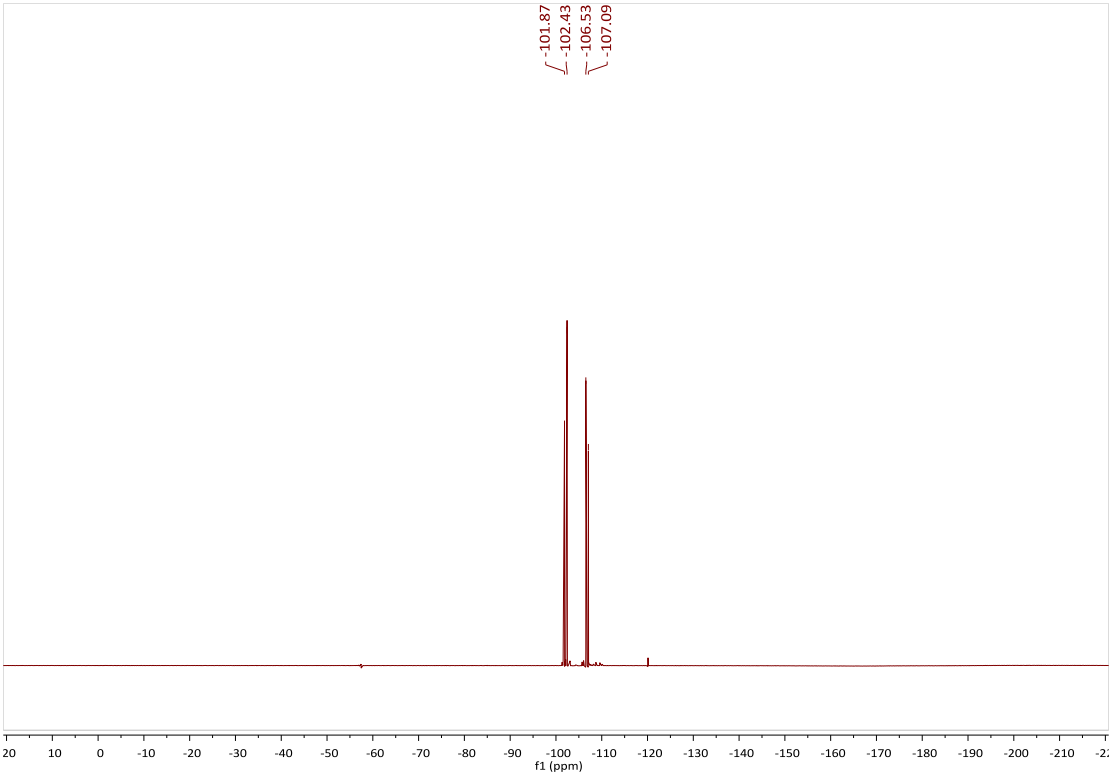


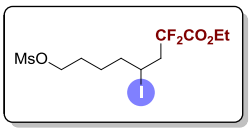


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3j**

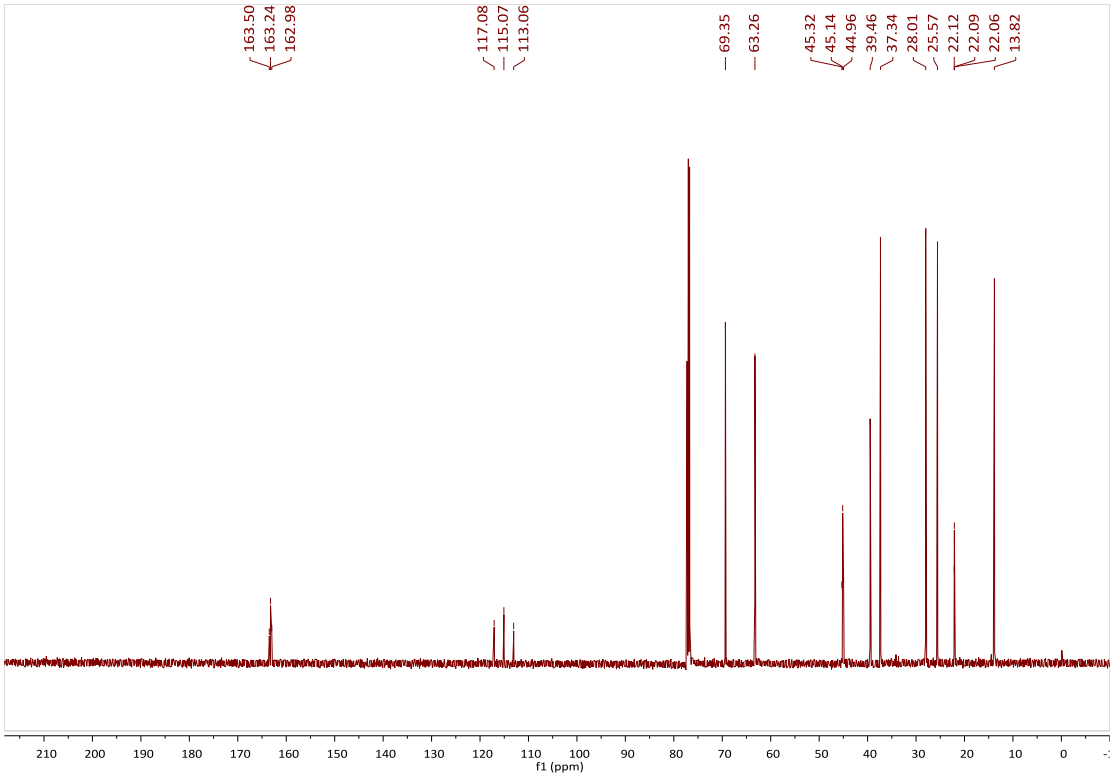


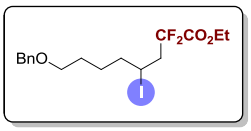
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3j**



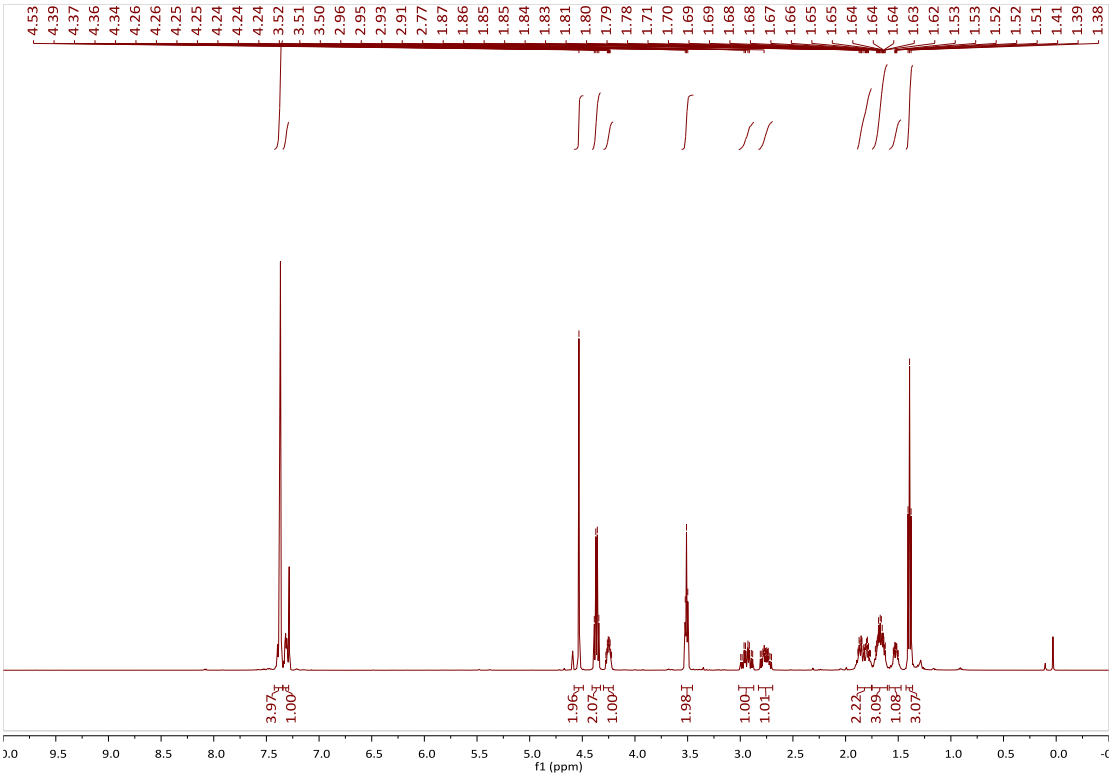


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3j**

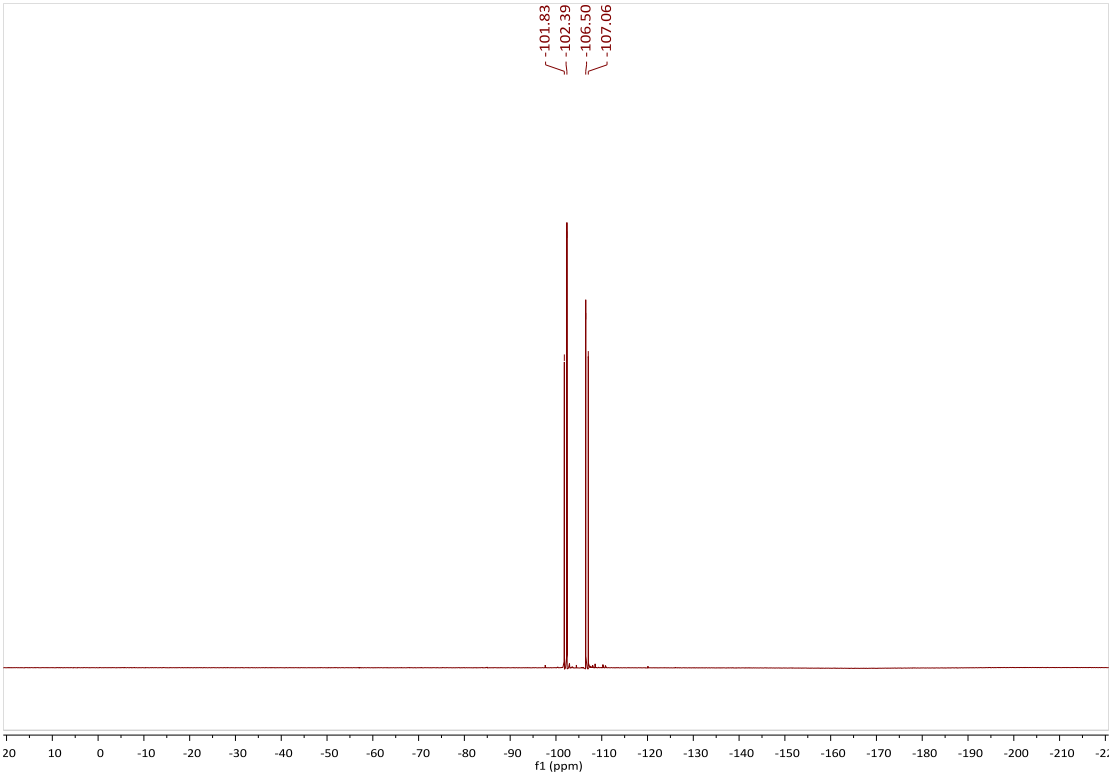


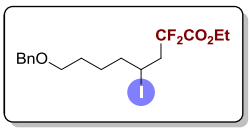


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3k**

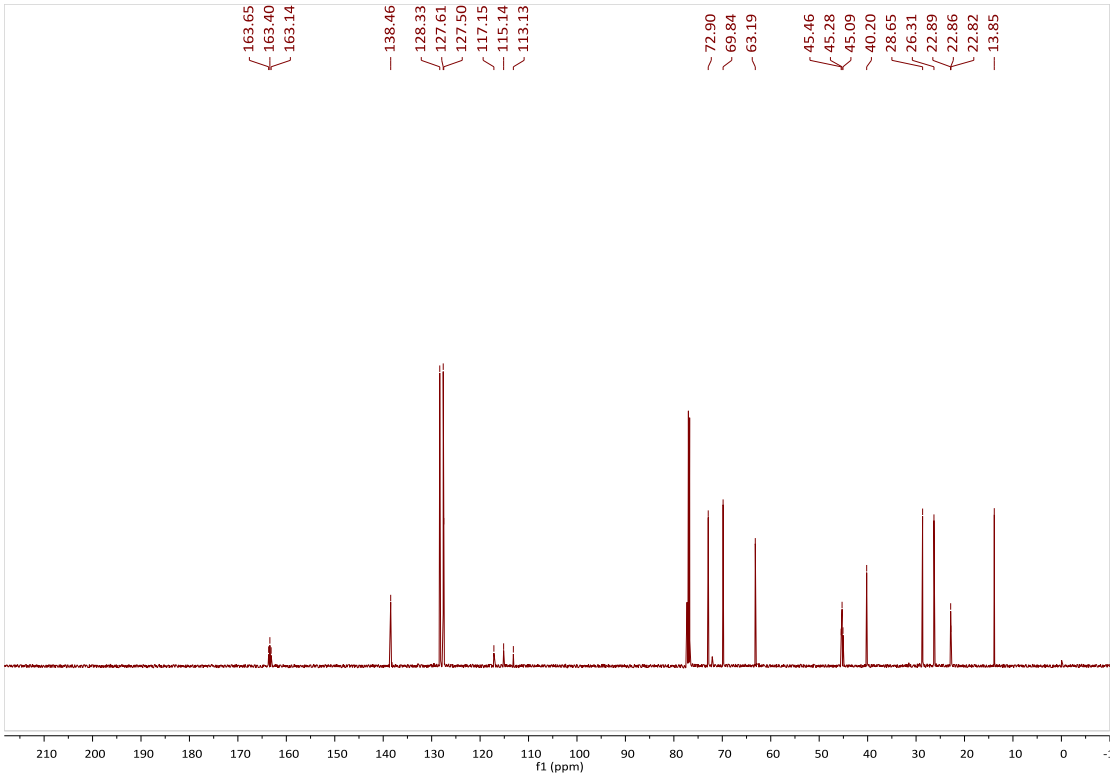


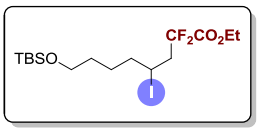
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3k**



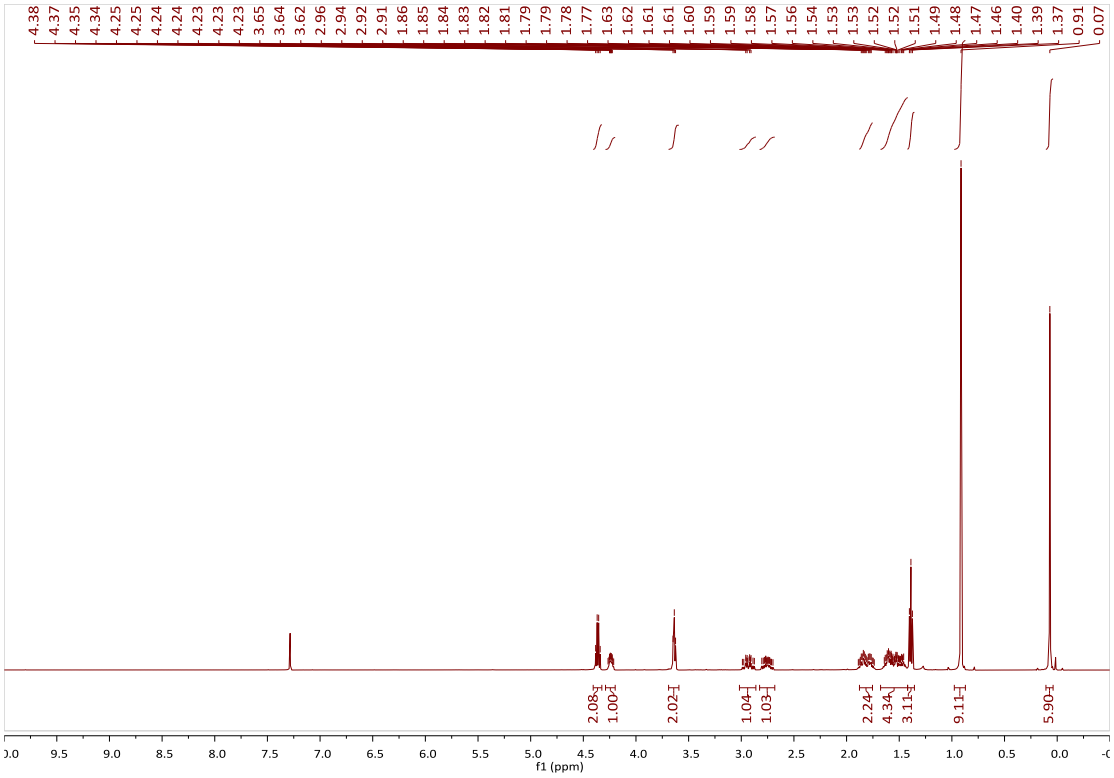


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3k**

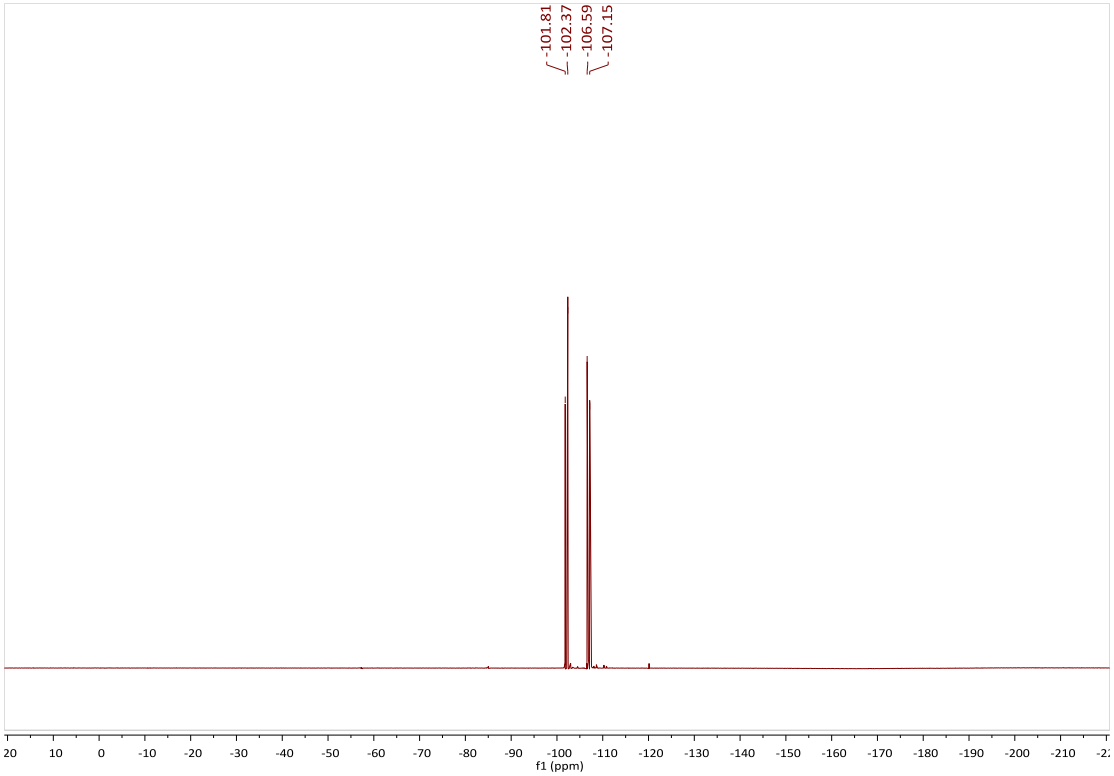


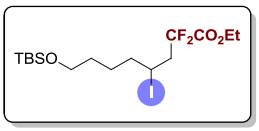


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3l**

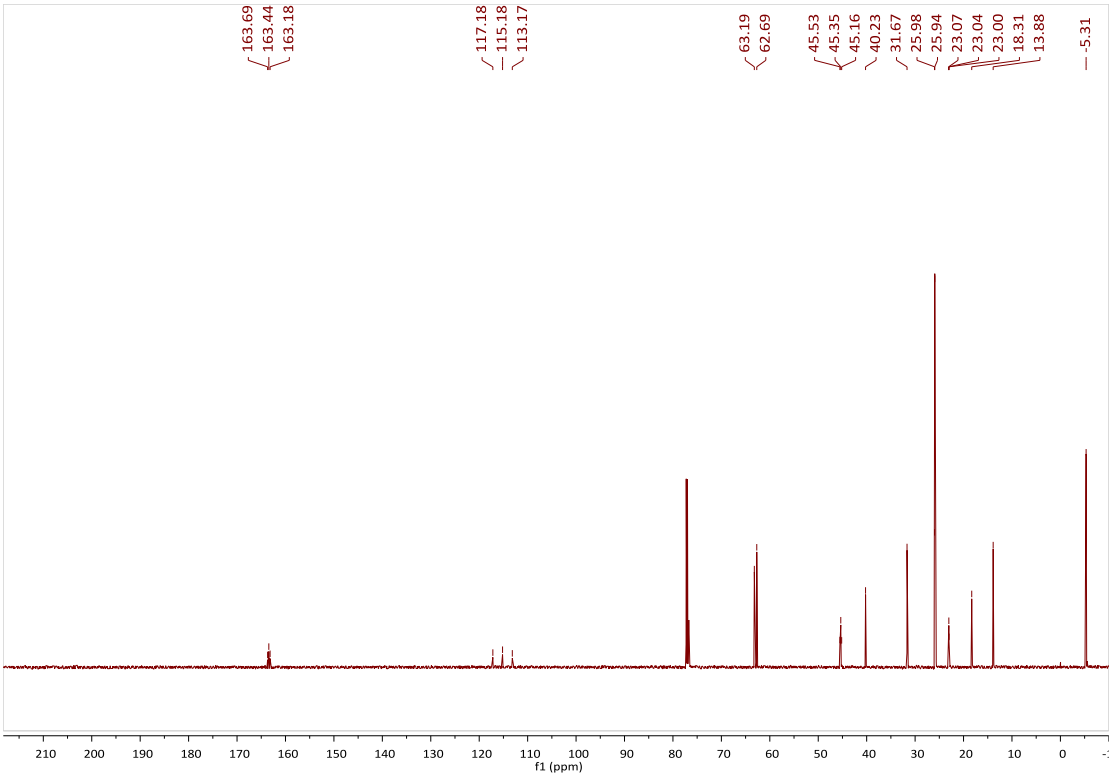


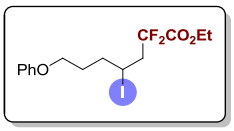
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3l**



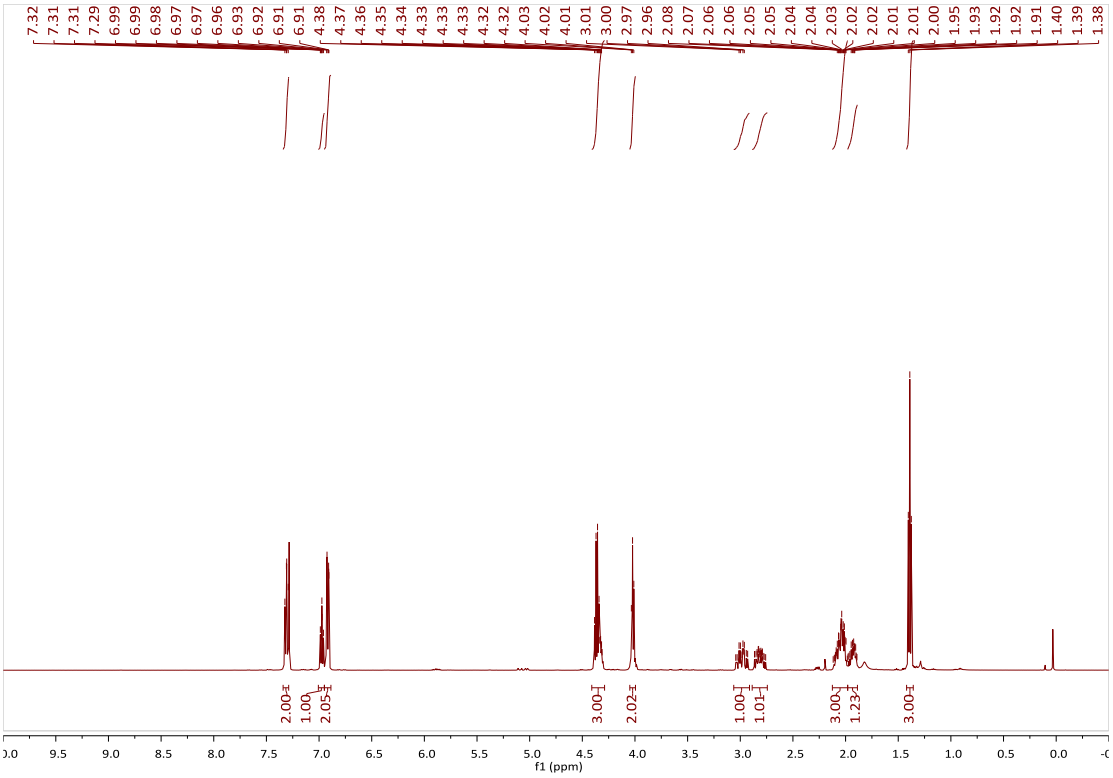


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3l**

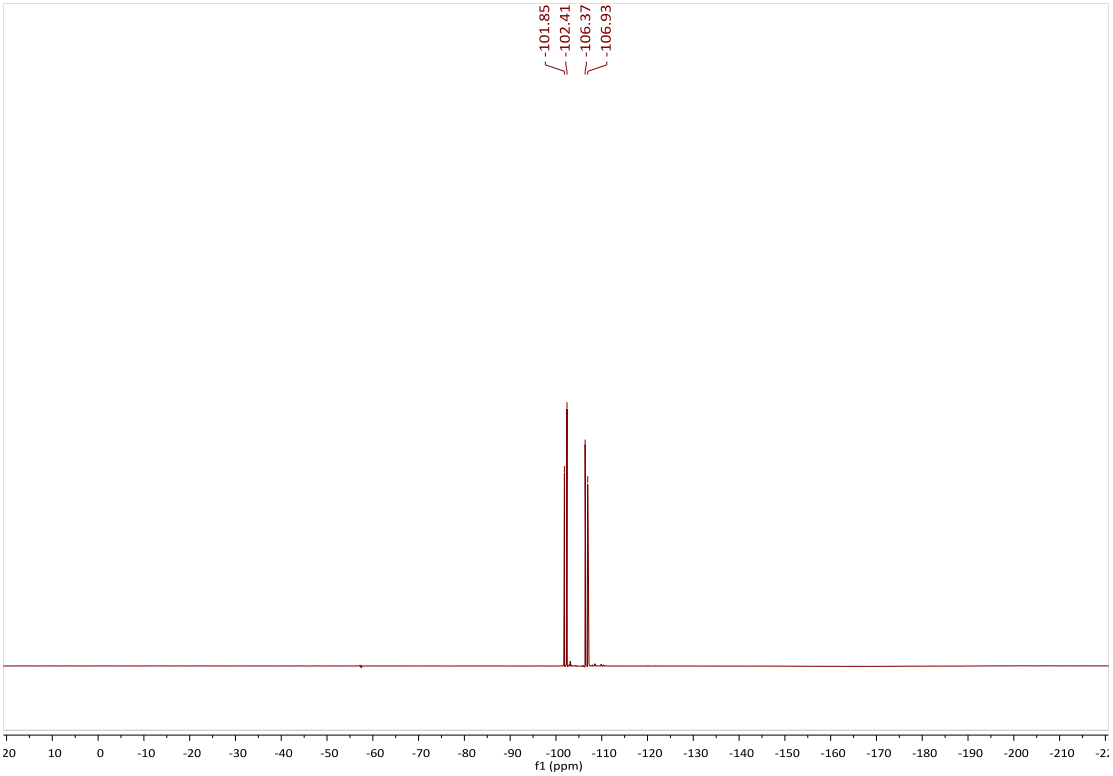


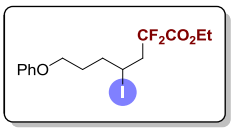


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3m**

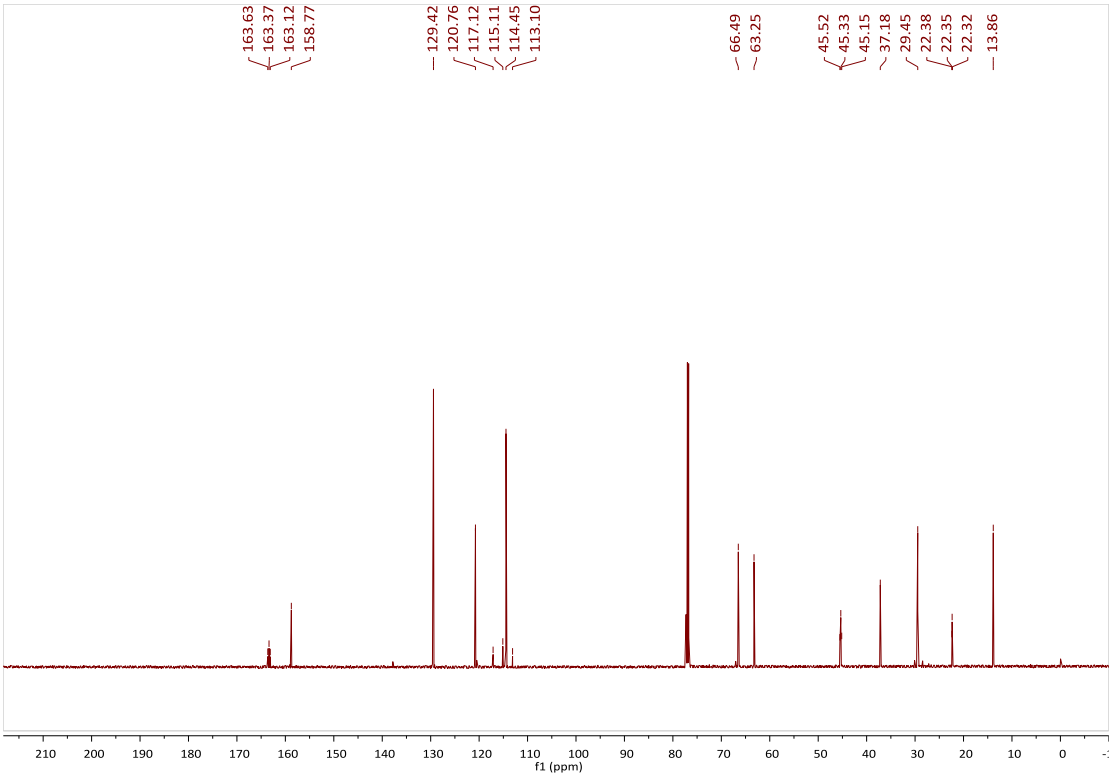


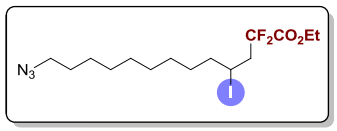
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3m**



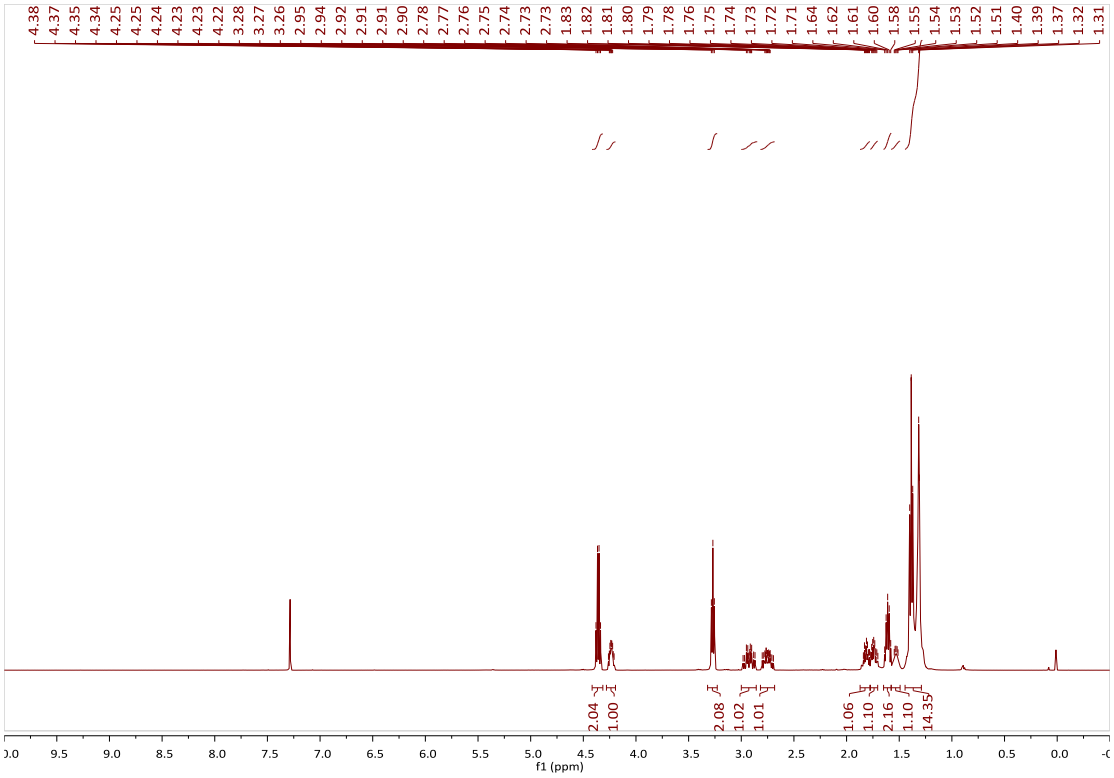


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3m**

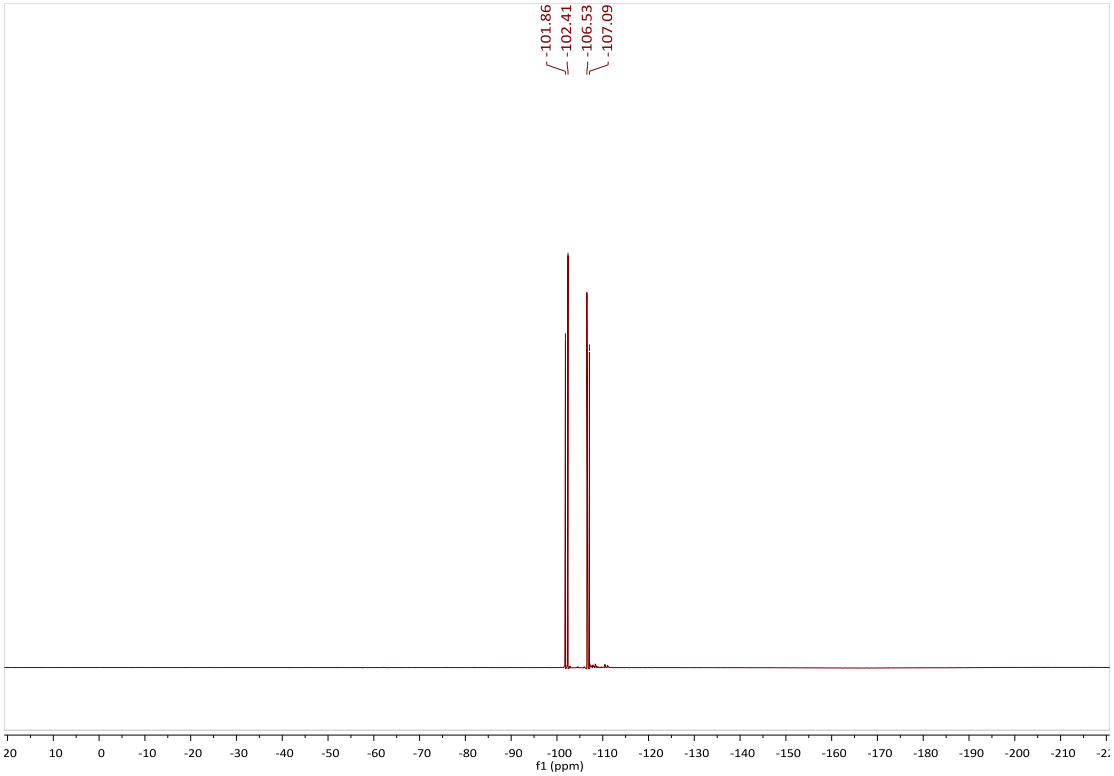


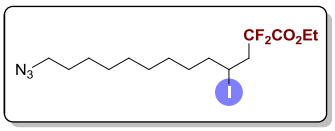


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3n**

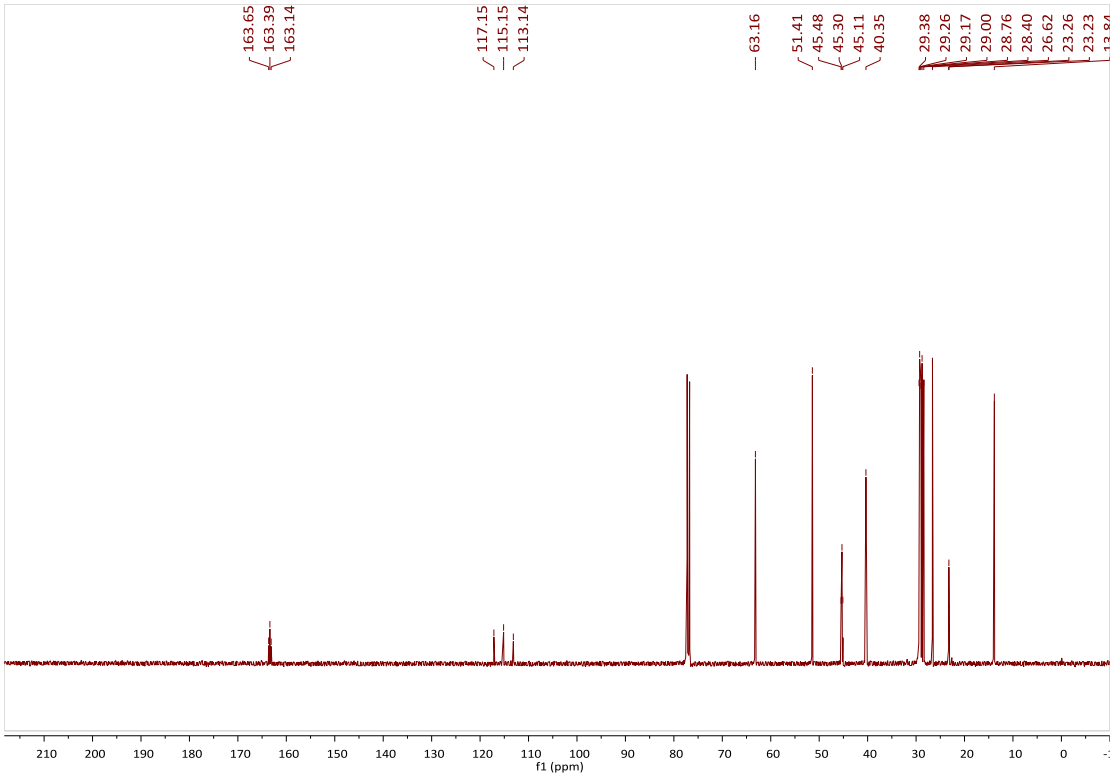


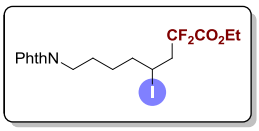
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3n**



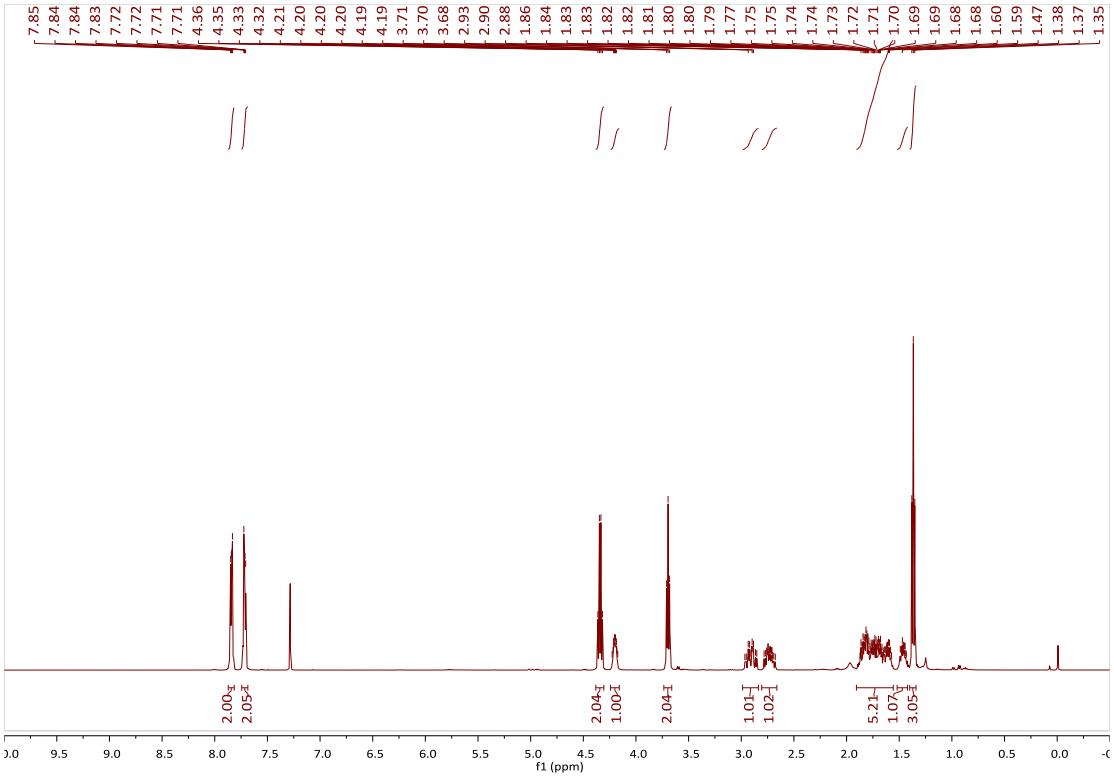


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3n**

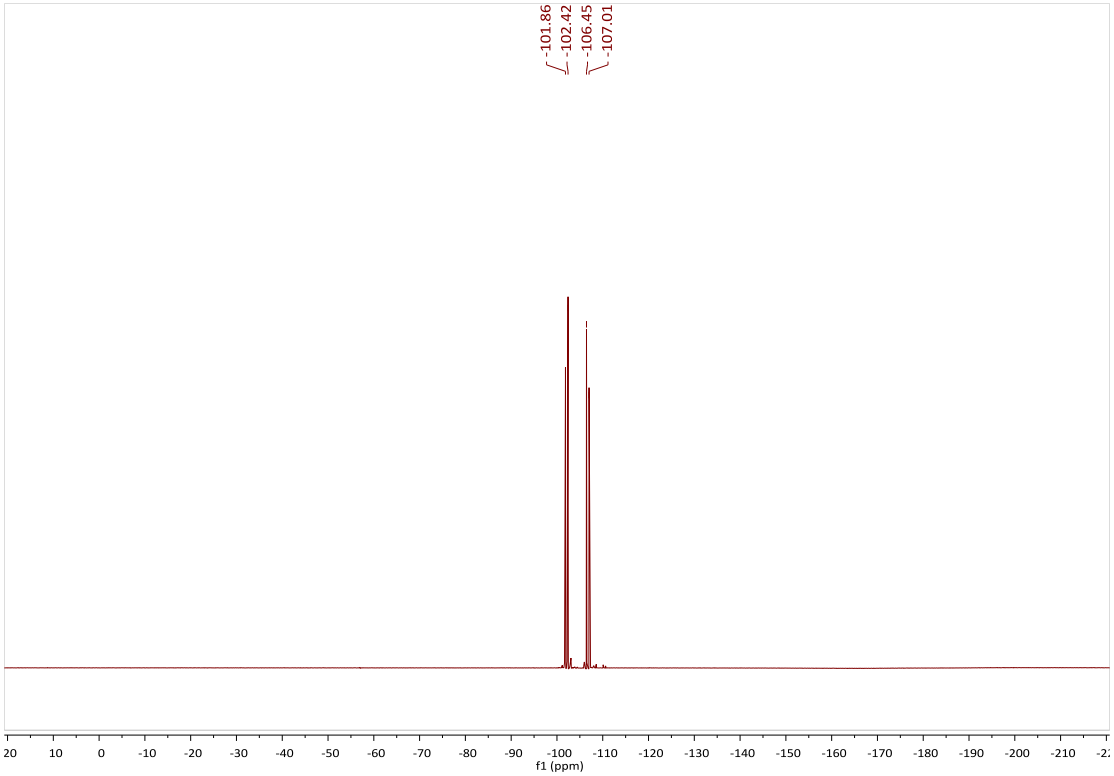


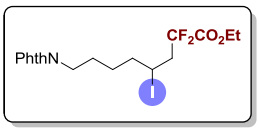


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3o**

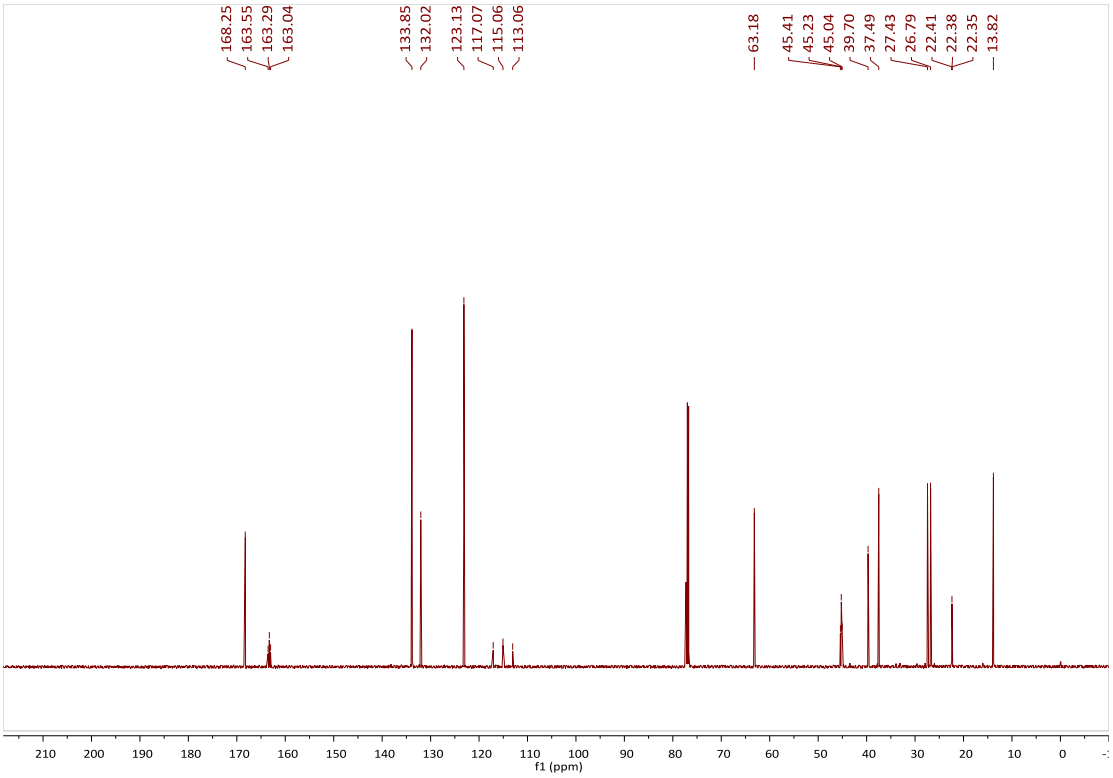


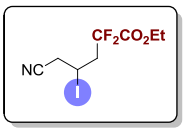
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3o**



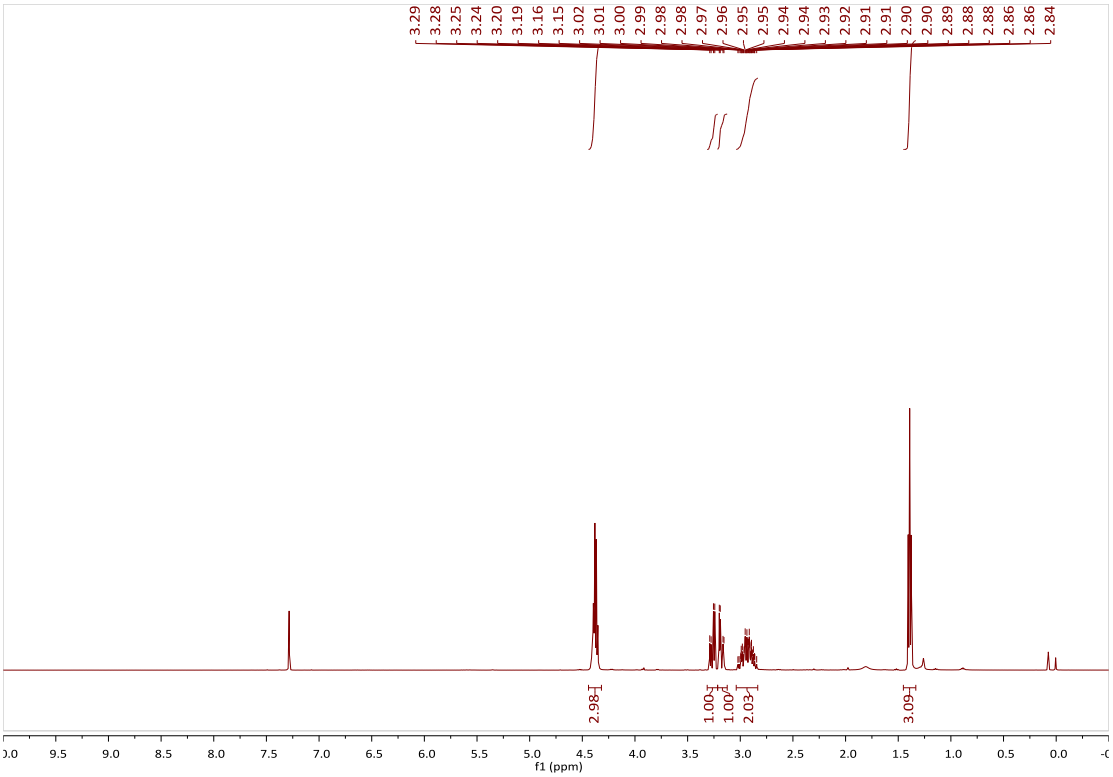


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3o**

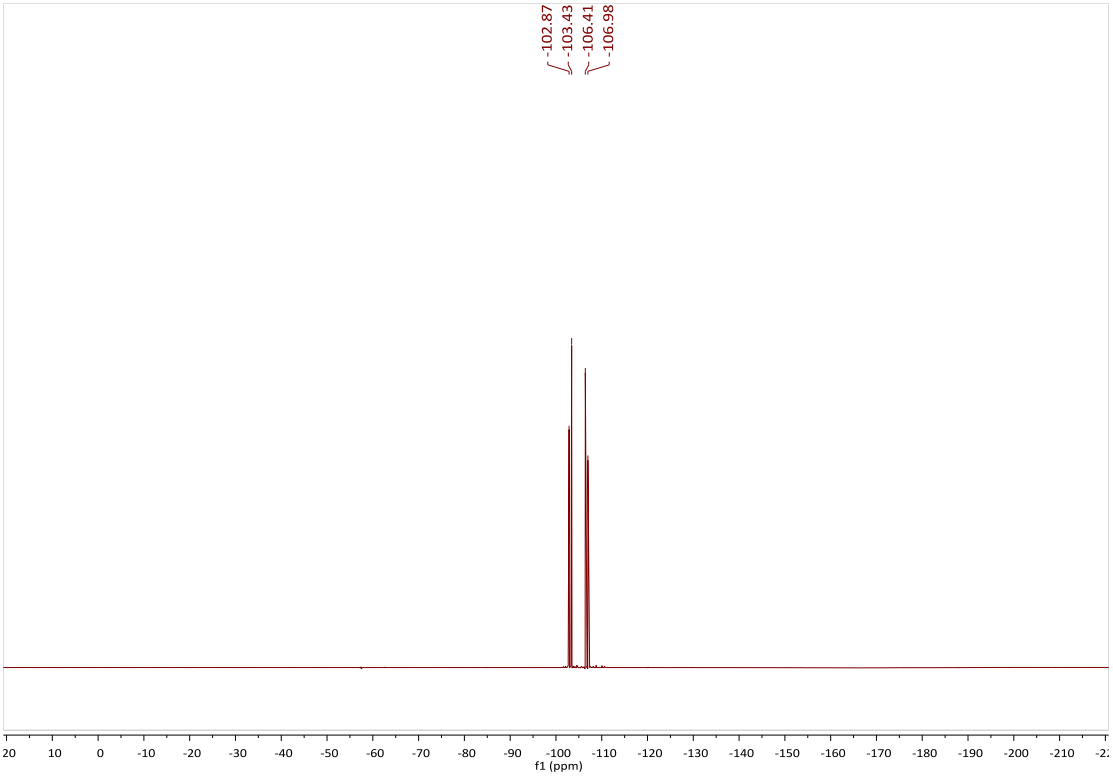


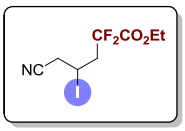


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3p**

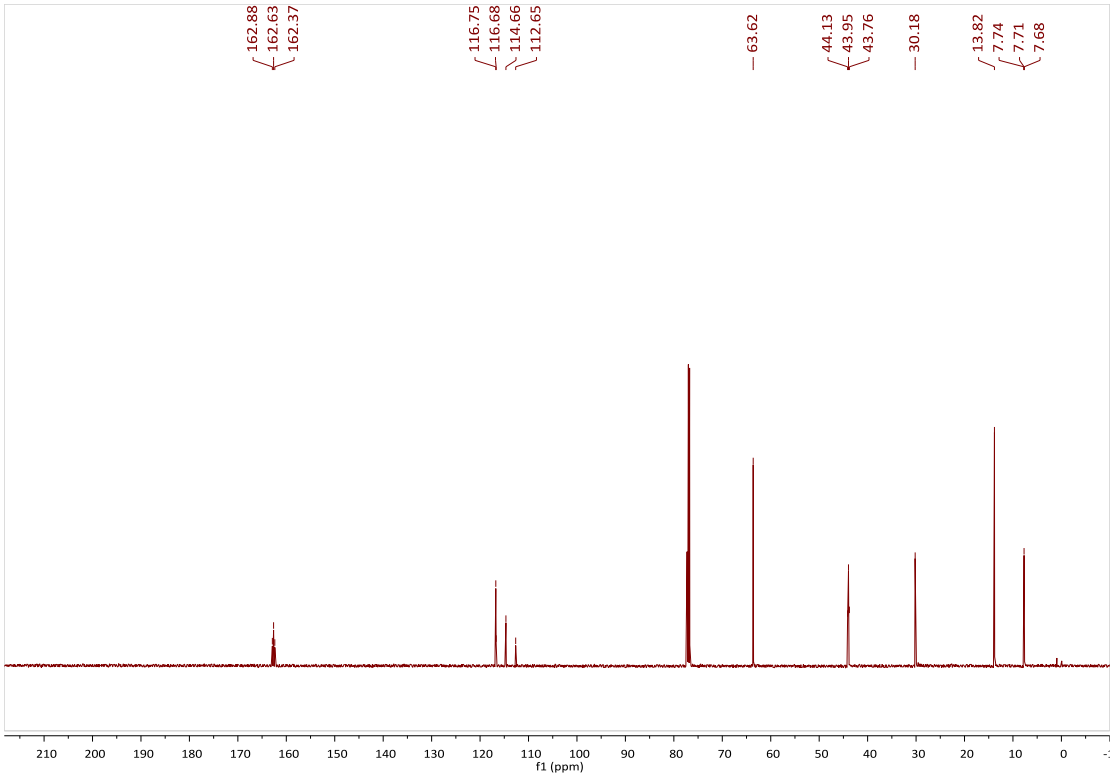


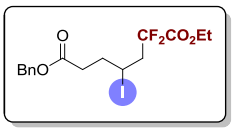
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3p**



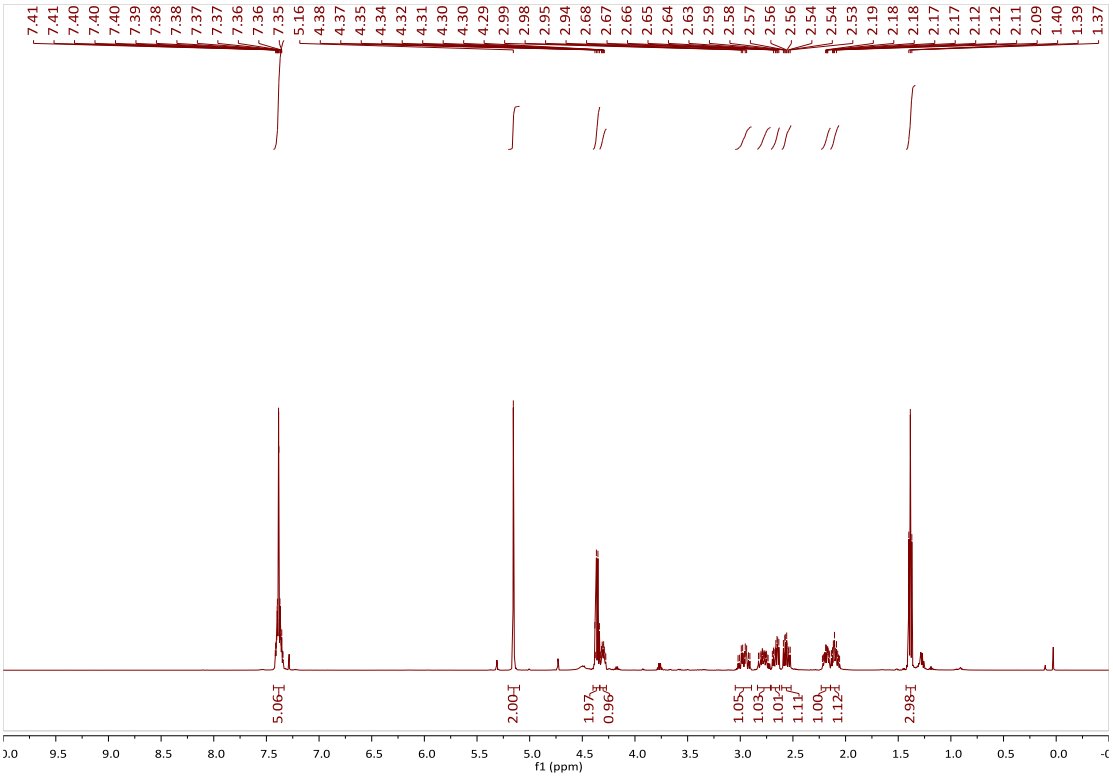


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3p**

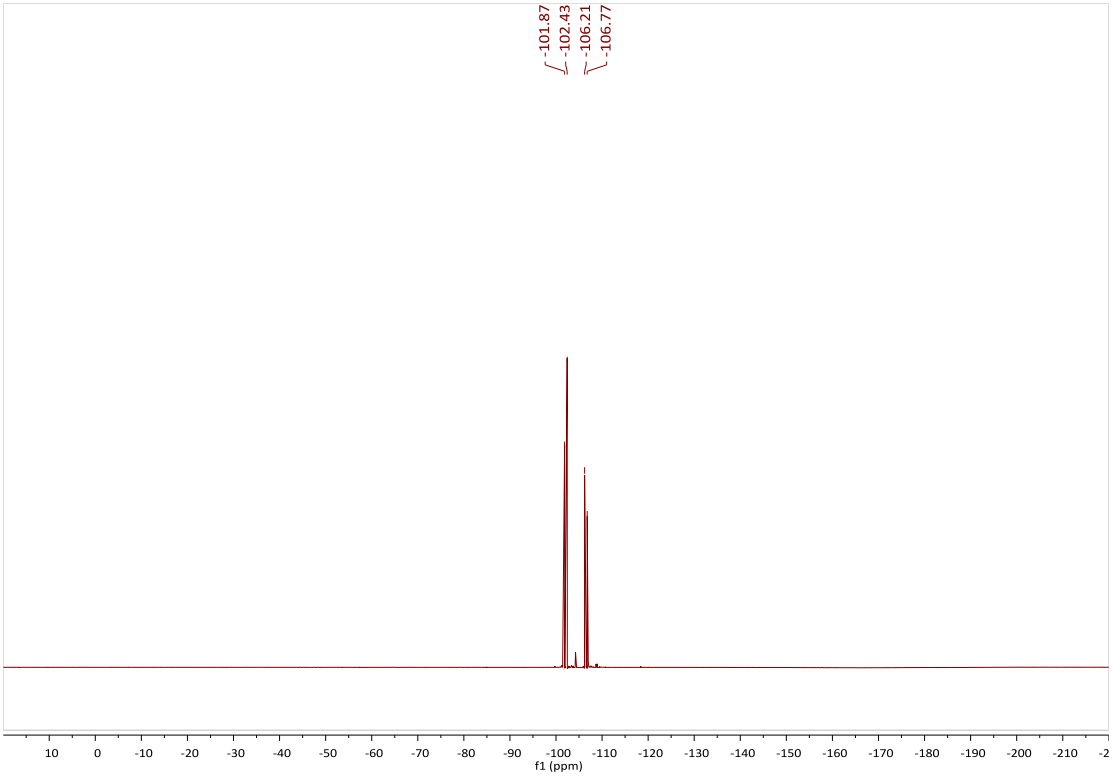


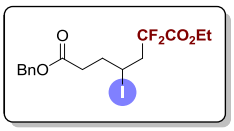


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3q**

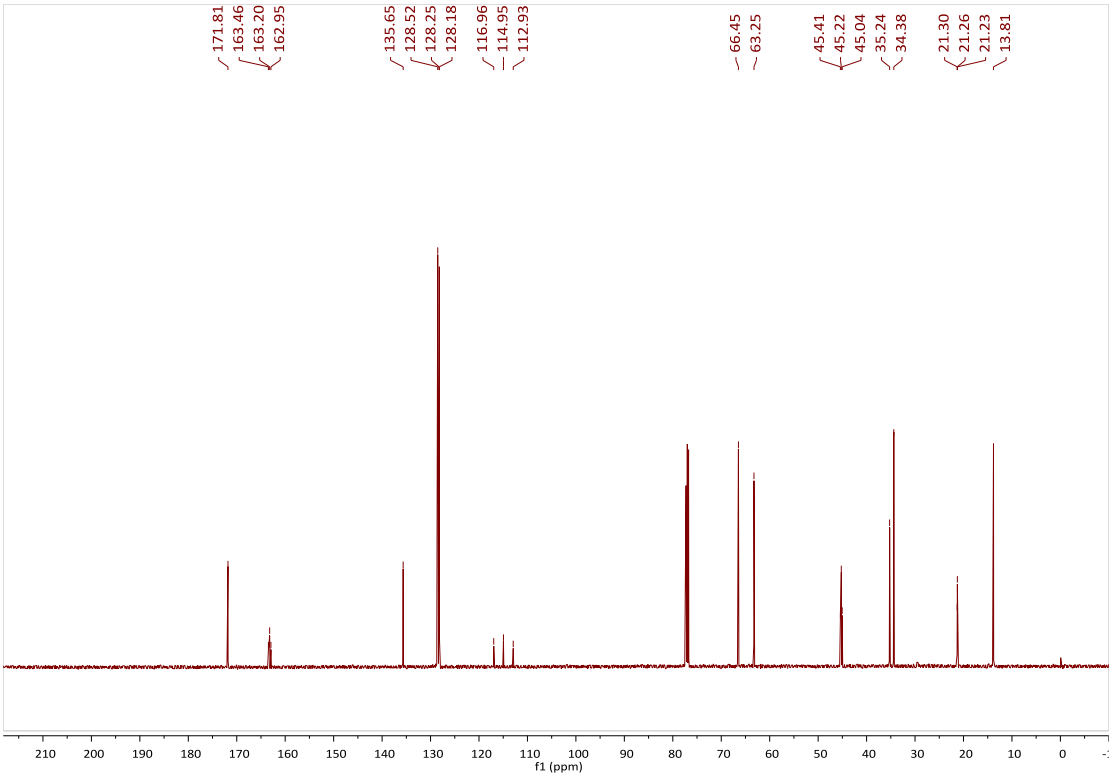


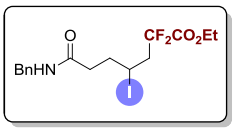
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3q**



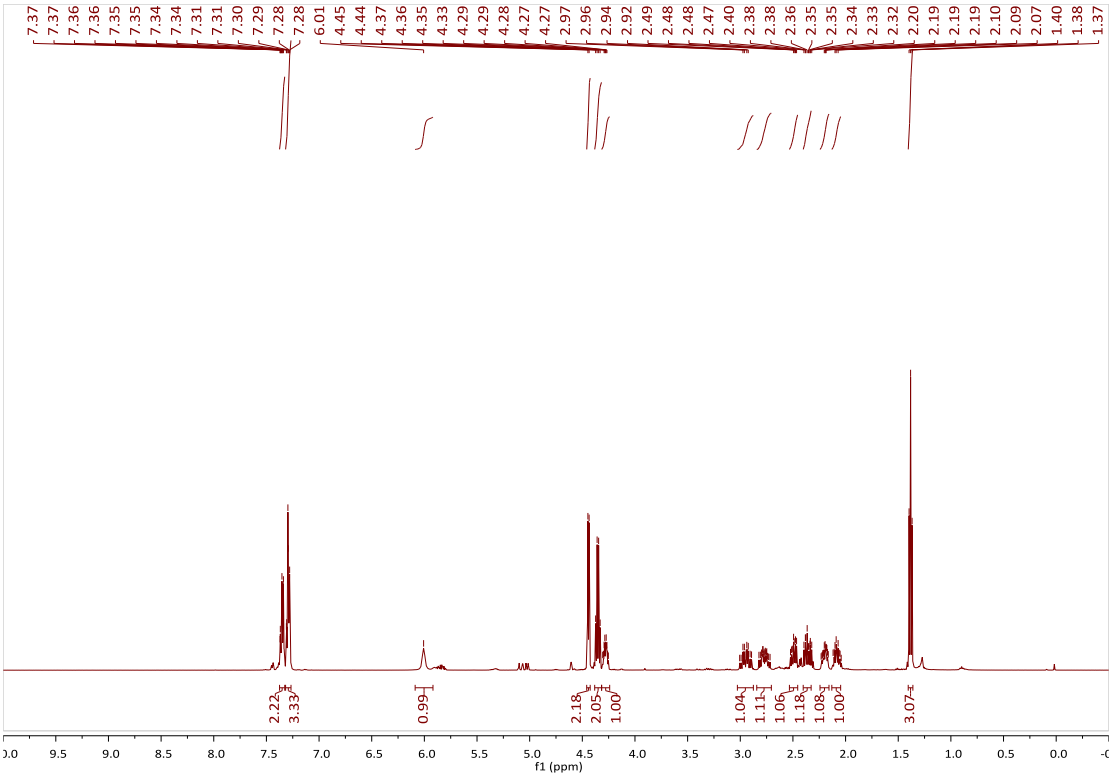


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3q**

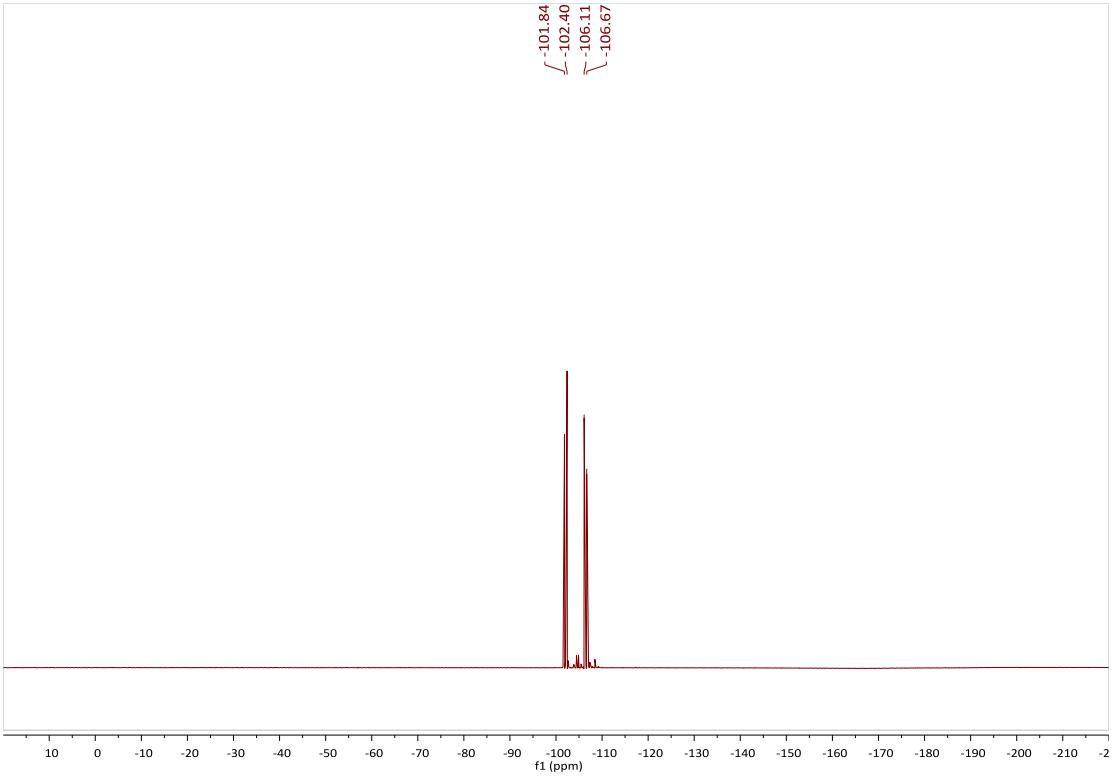


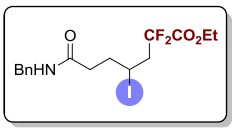


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3r**

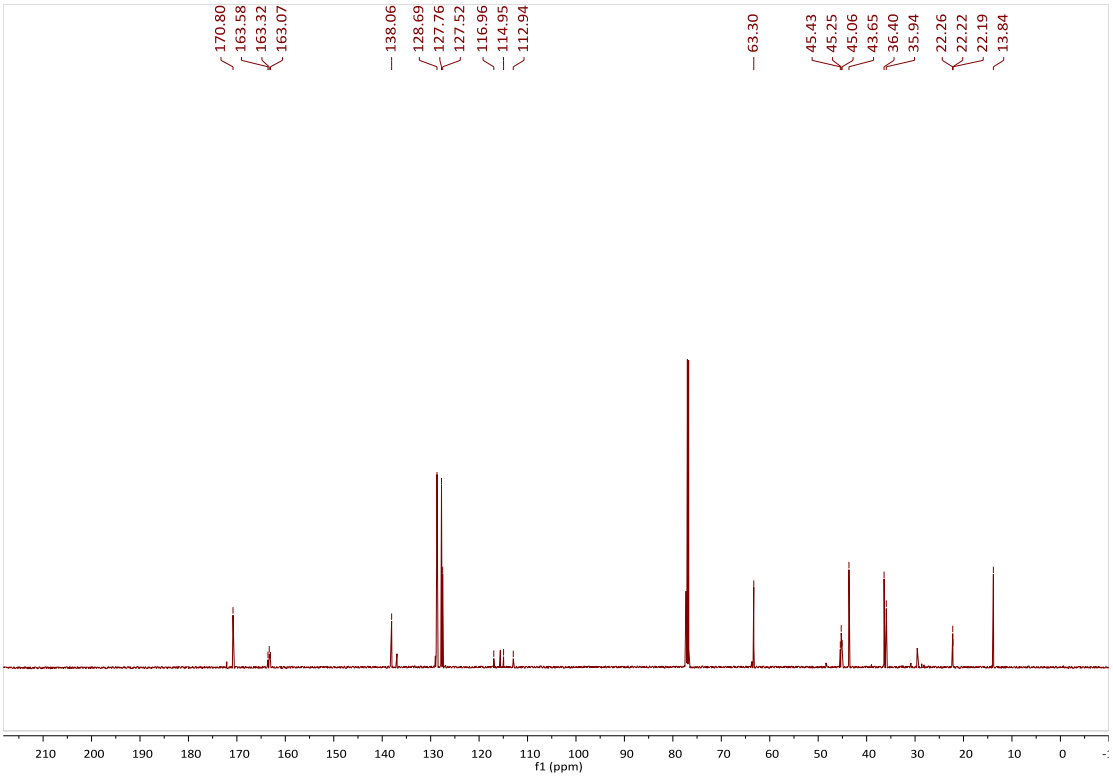


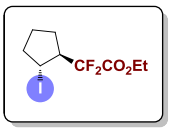
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3r**



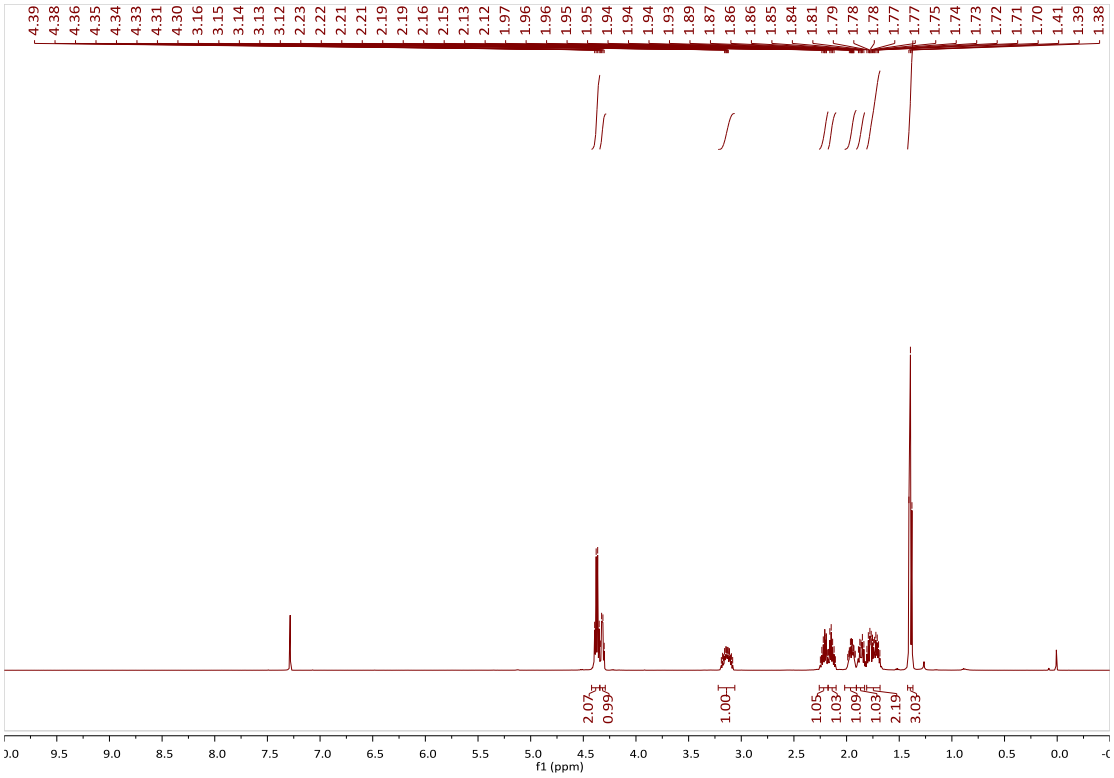


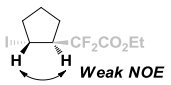
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3r**

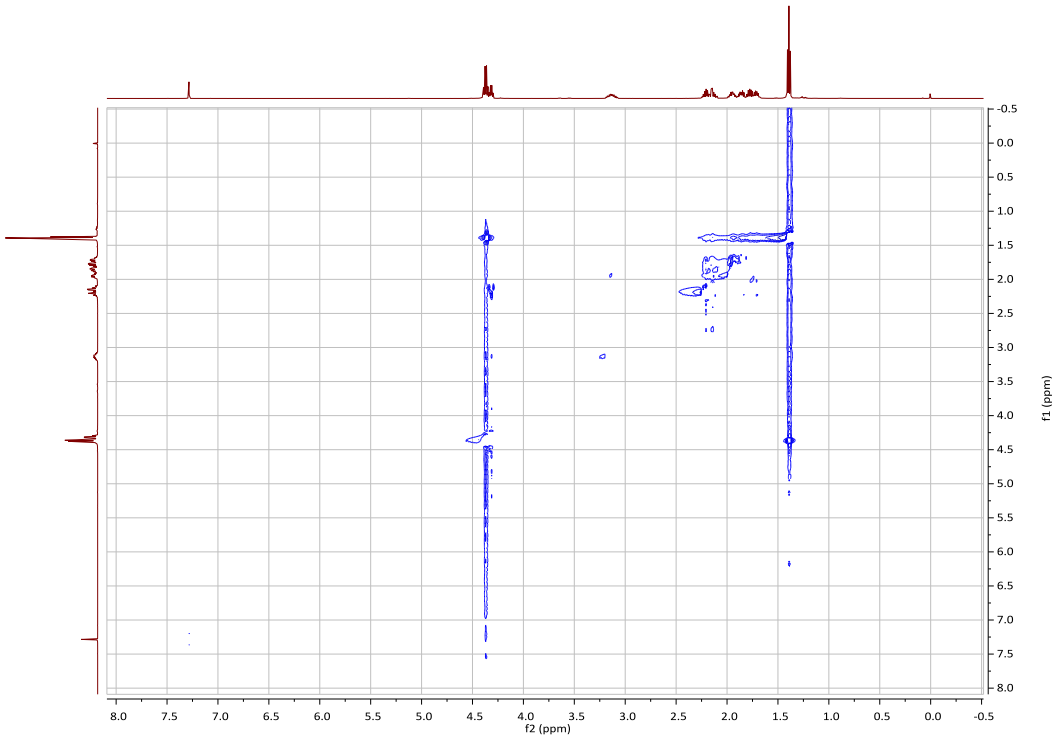


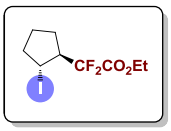


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3s**

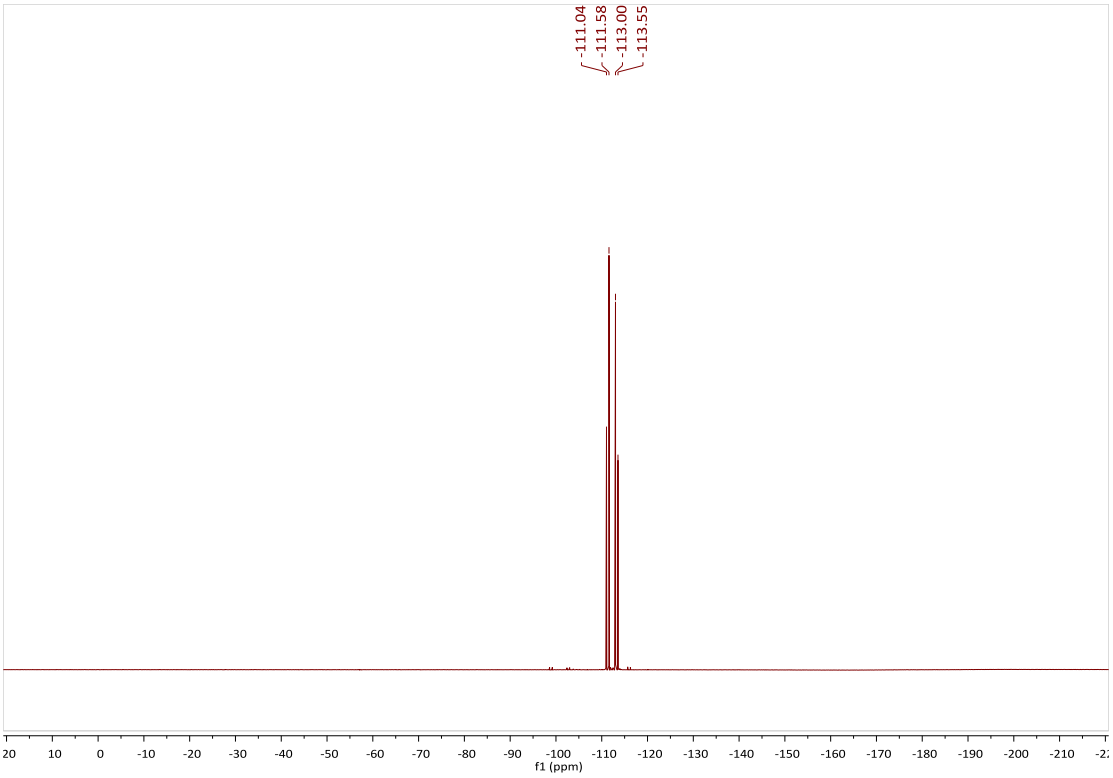




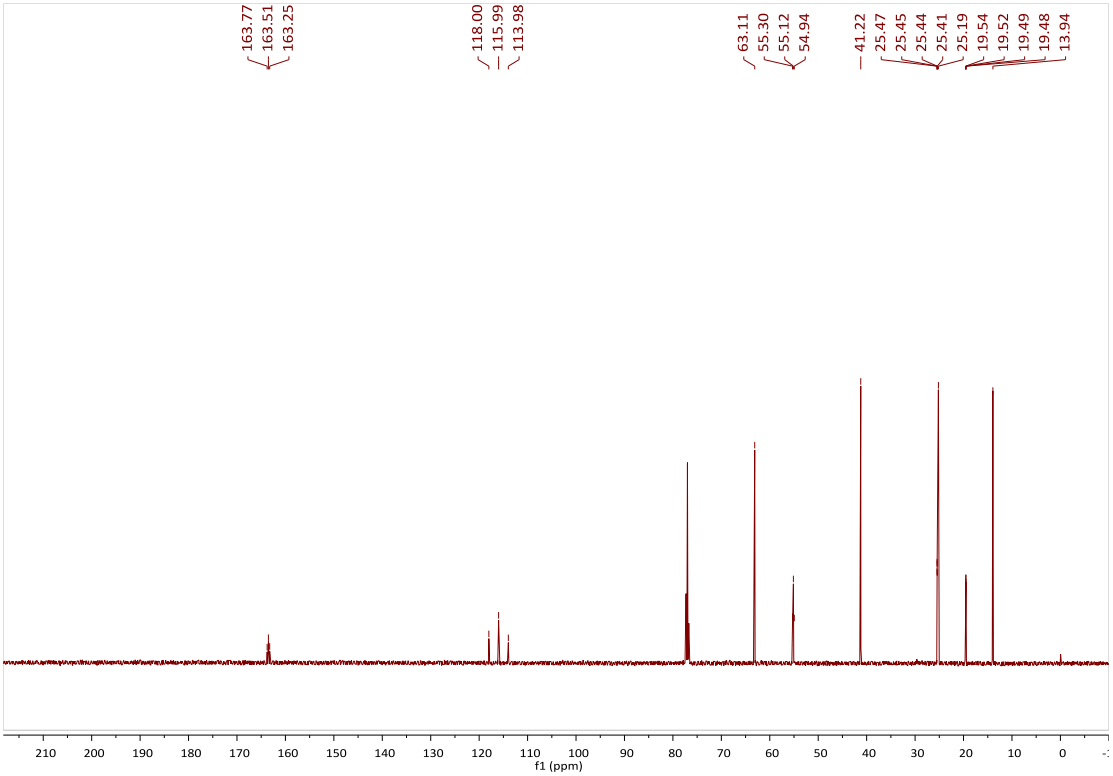


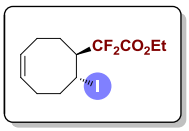


^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3s**

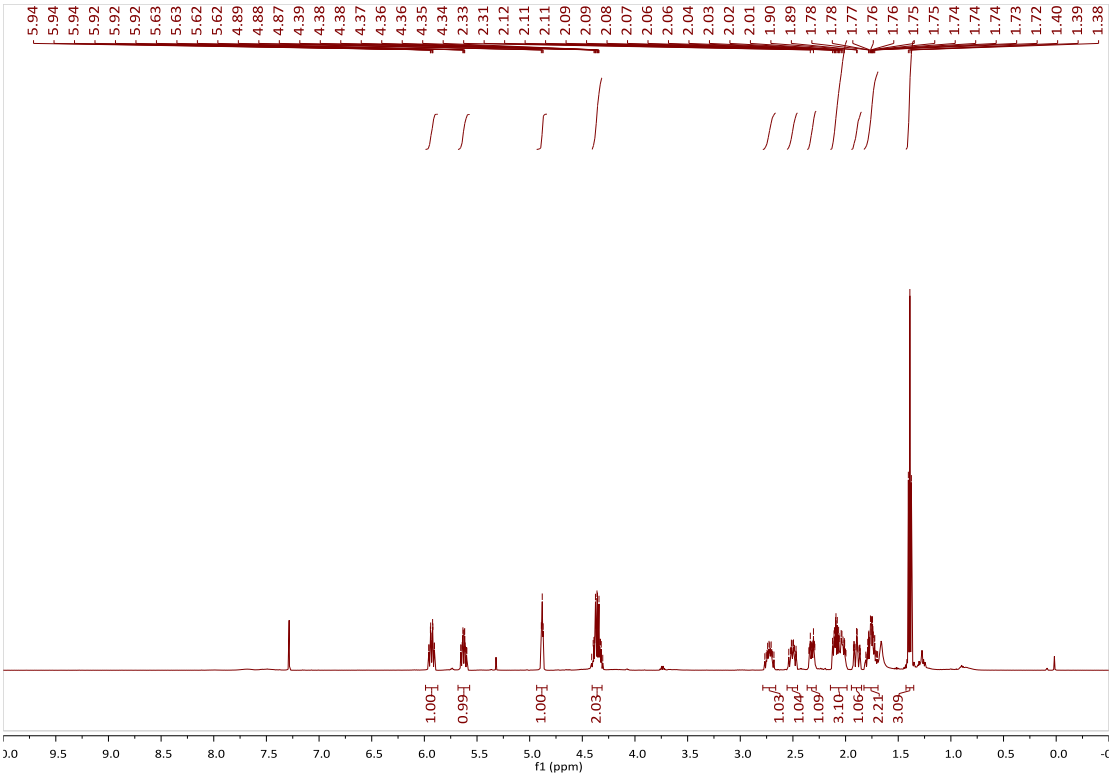


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3s**

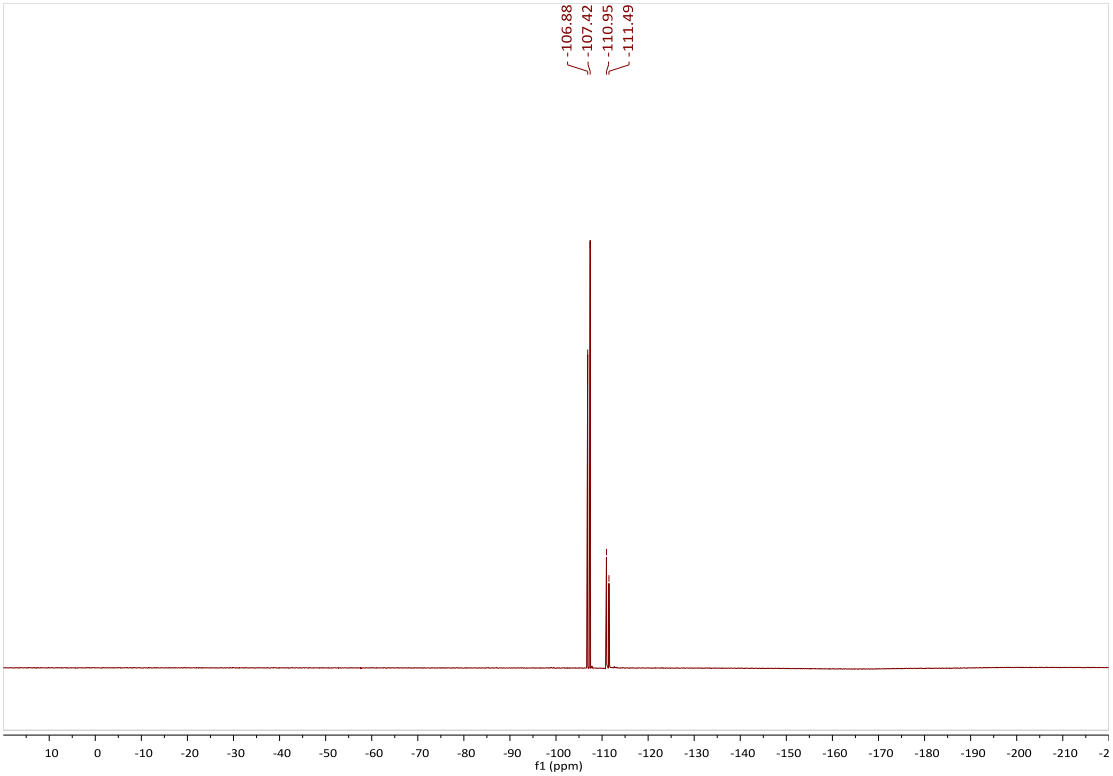


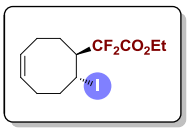


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3t**

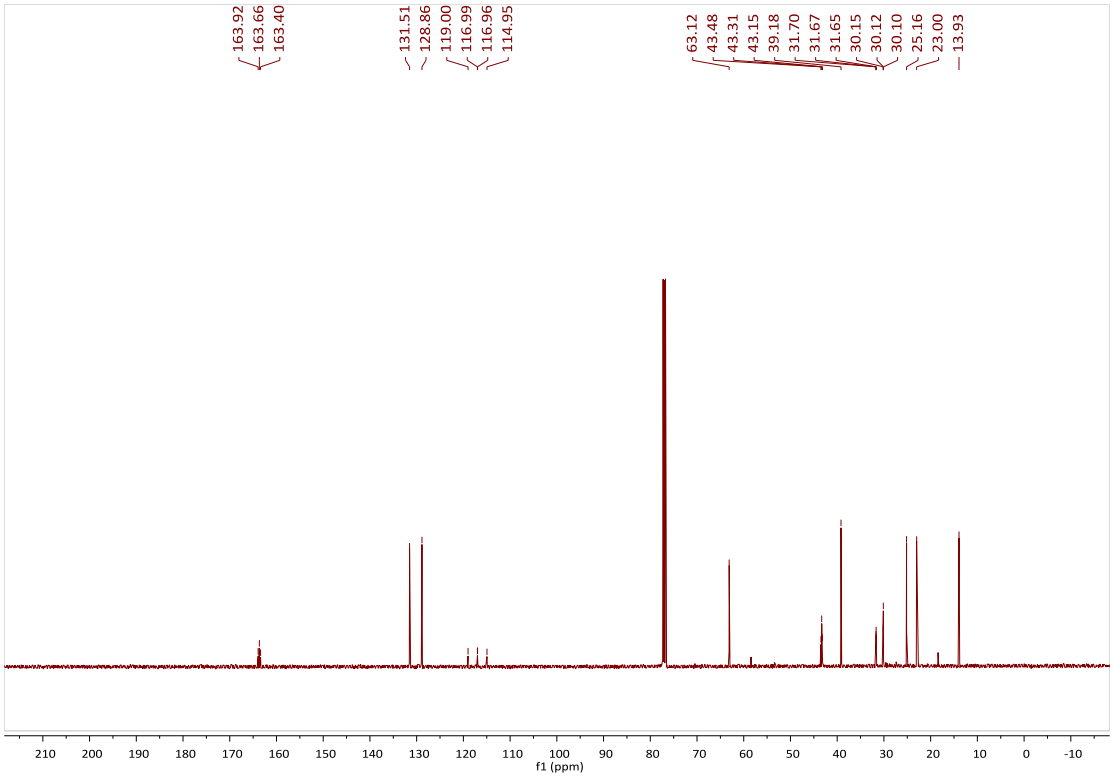


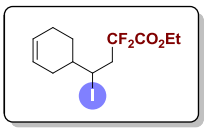
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3t**





^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3t**





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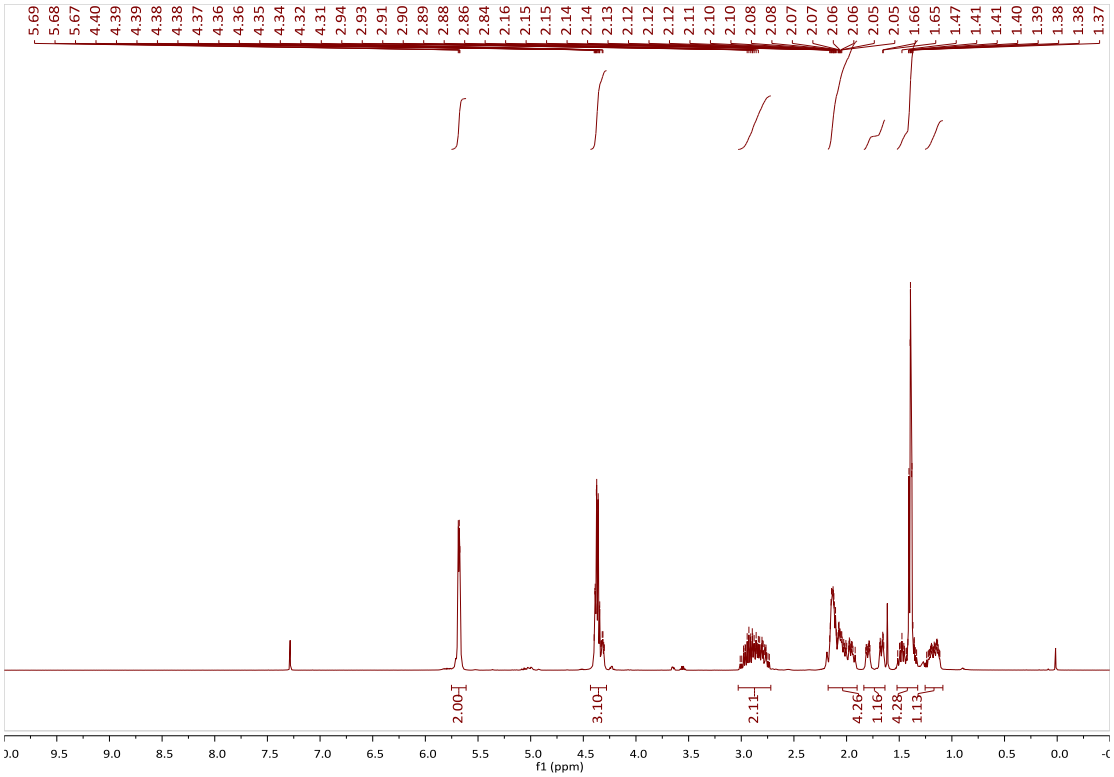
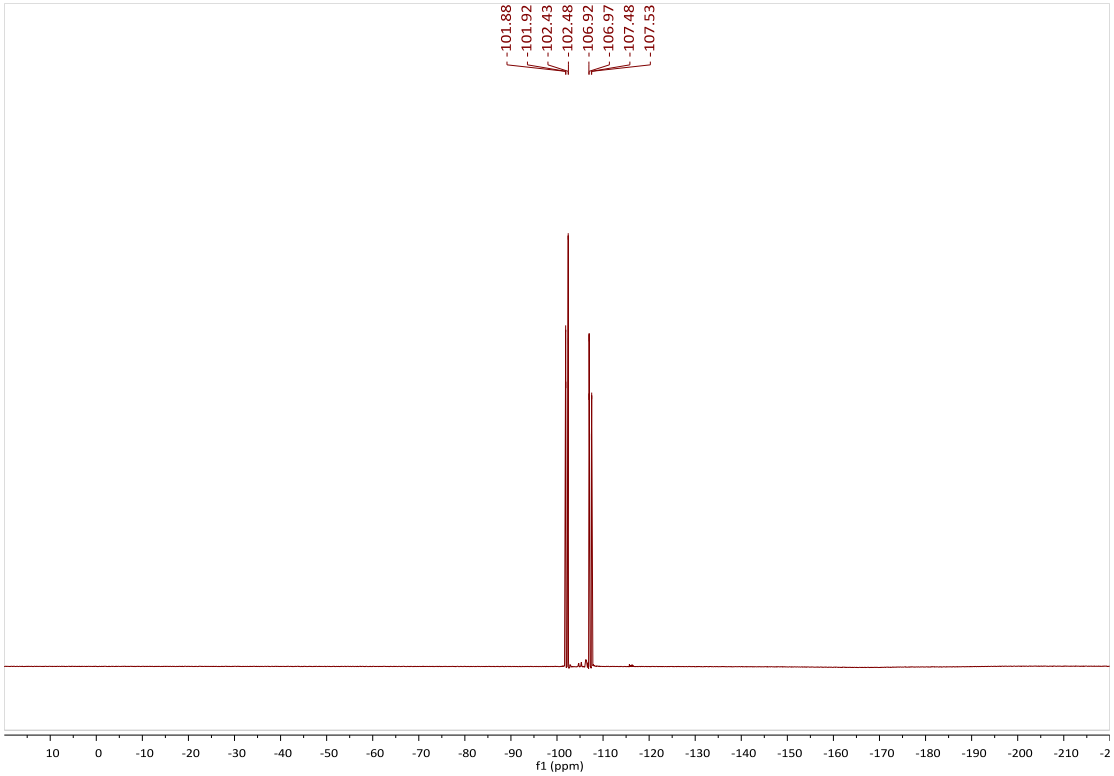
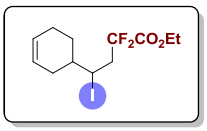
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3u**



^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **3u**





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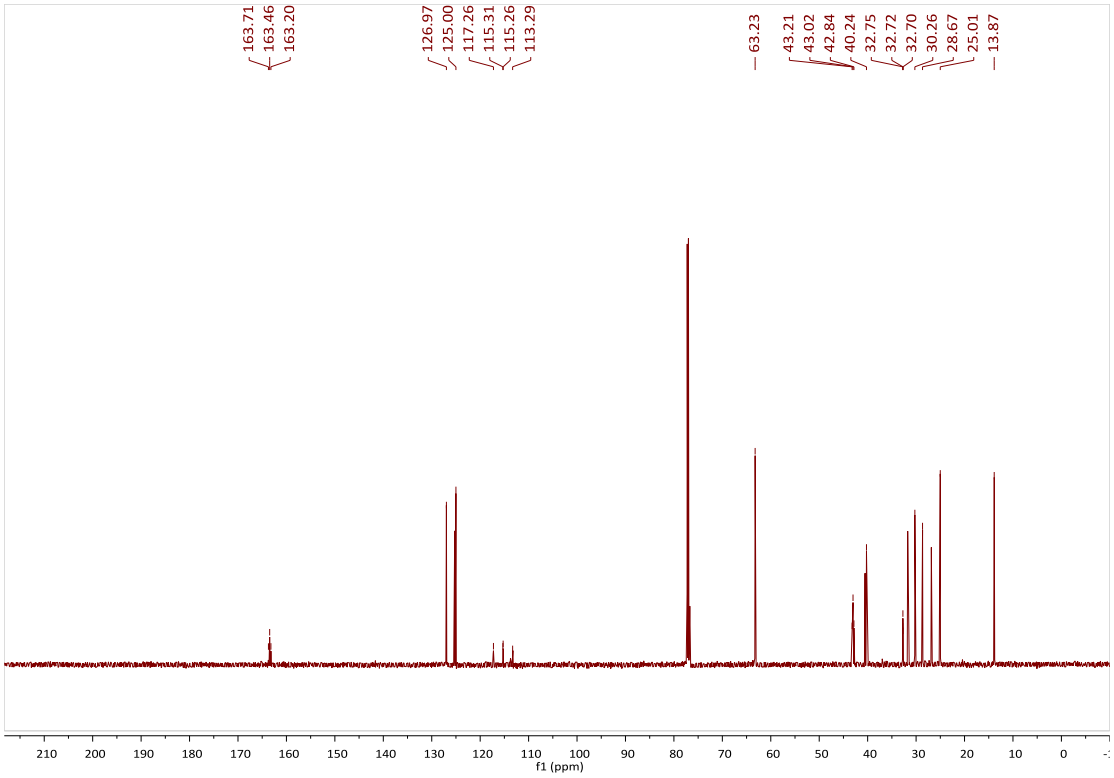
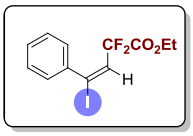
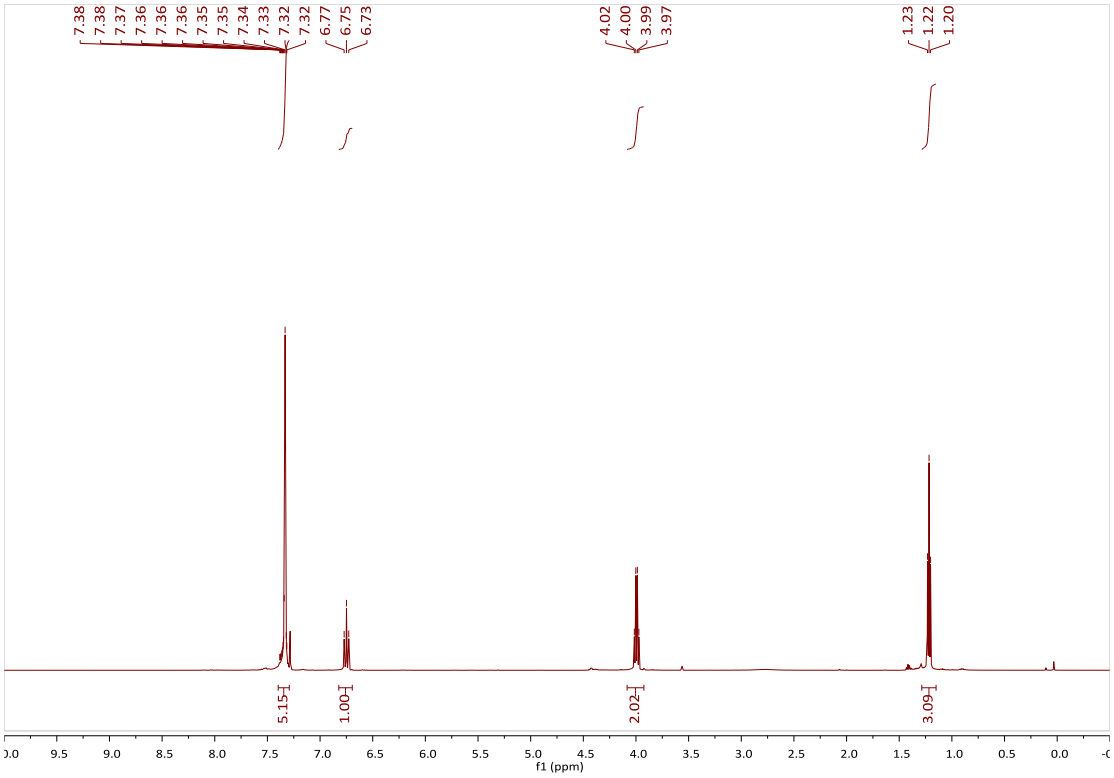
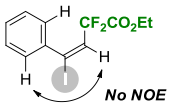
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **3u**

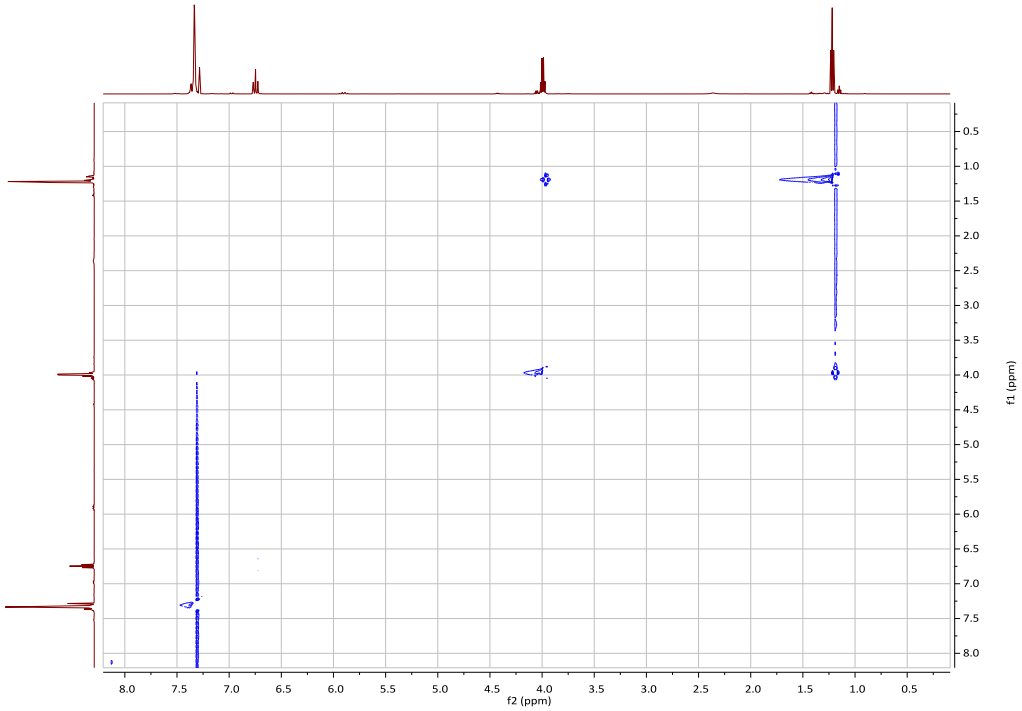


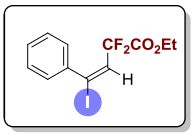


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5a**

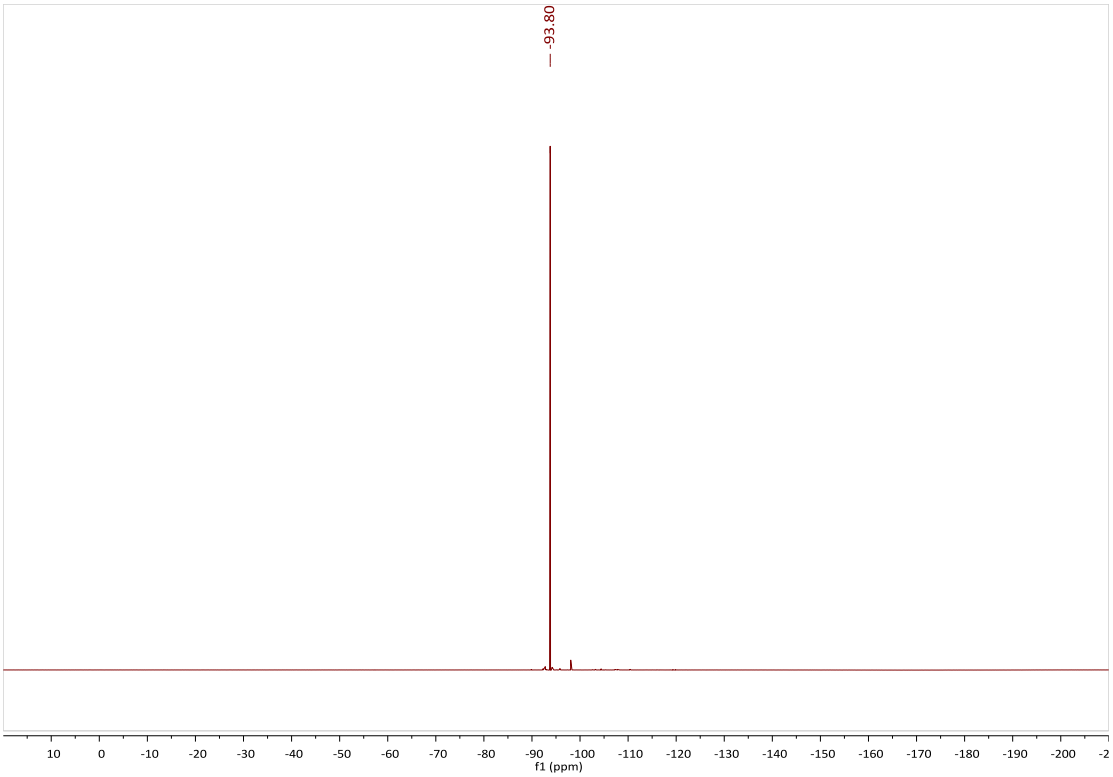




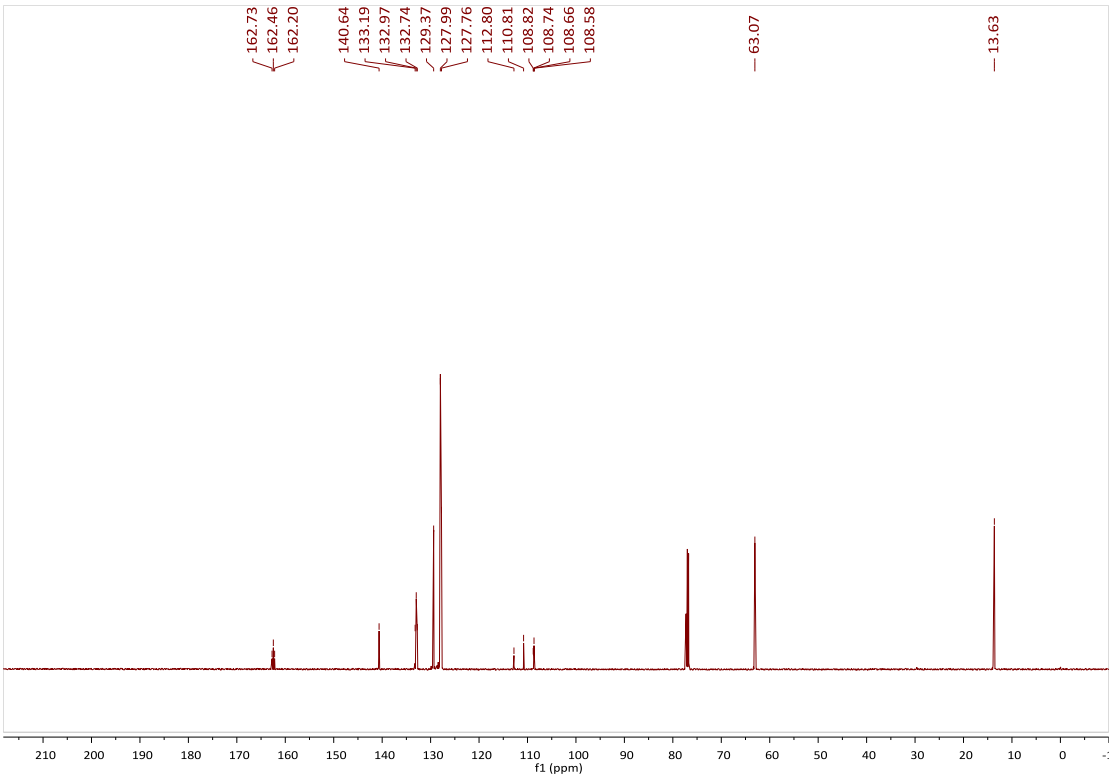


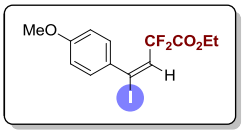


^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5a**

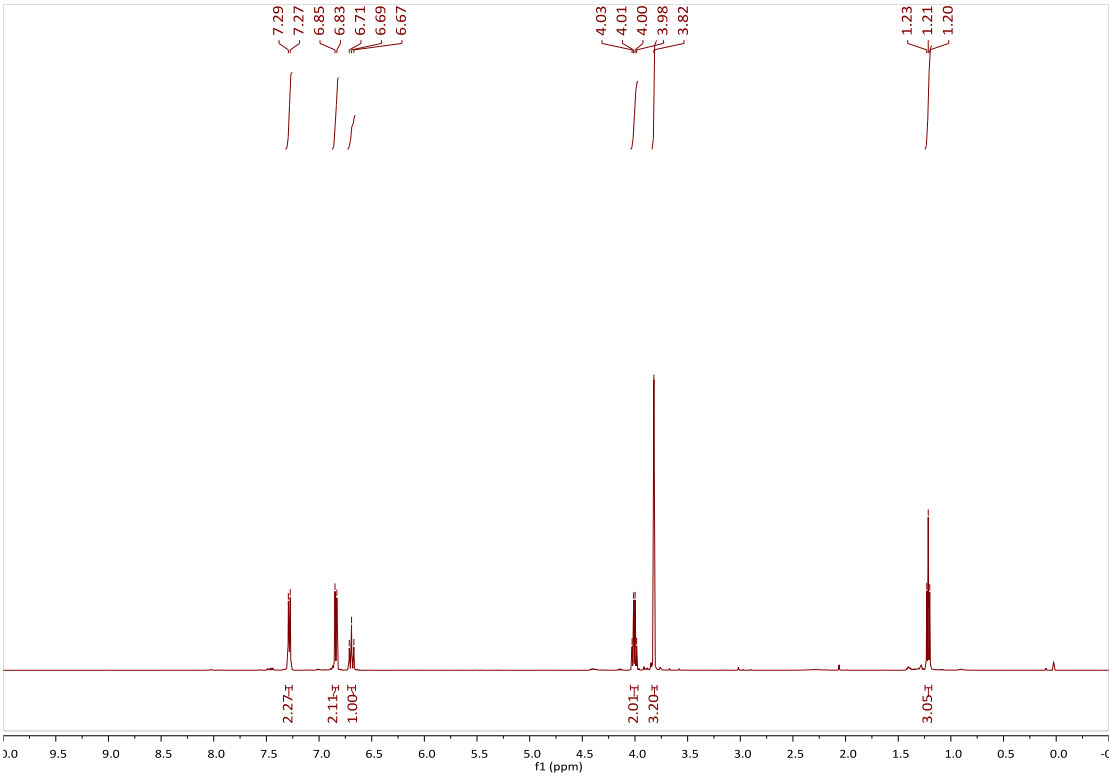


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5a**

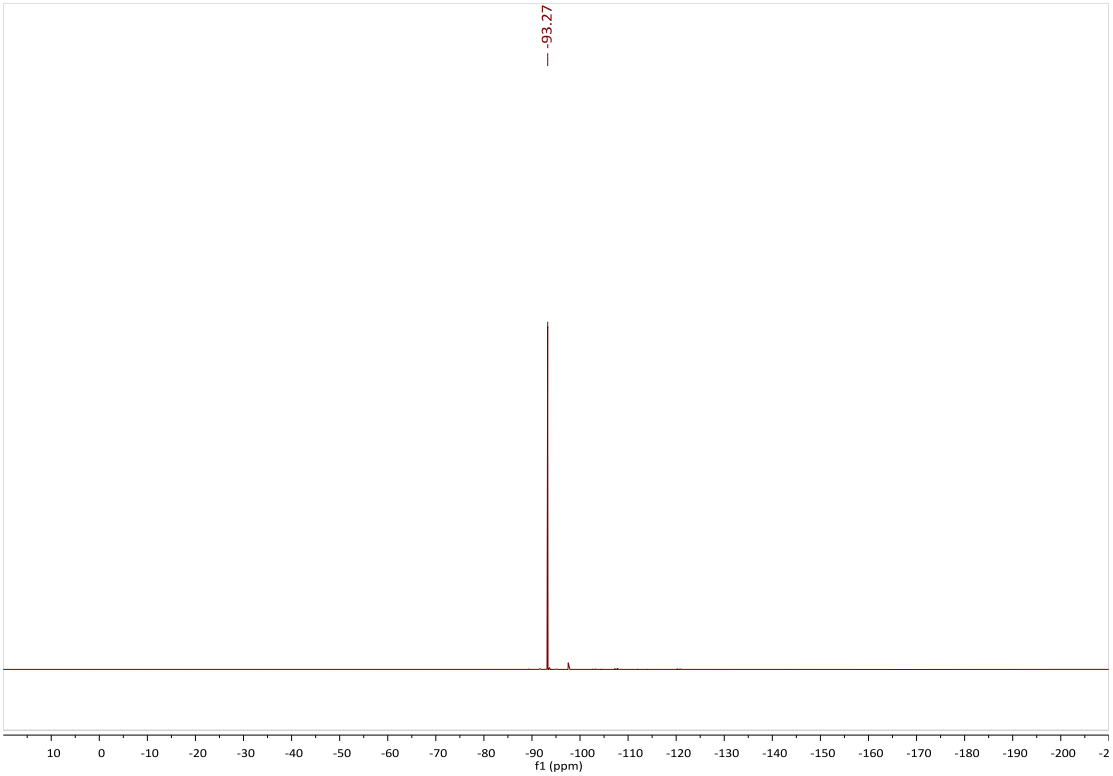


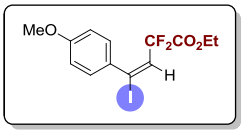


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5b**

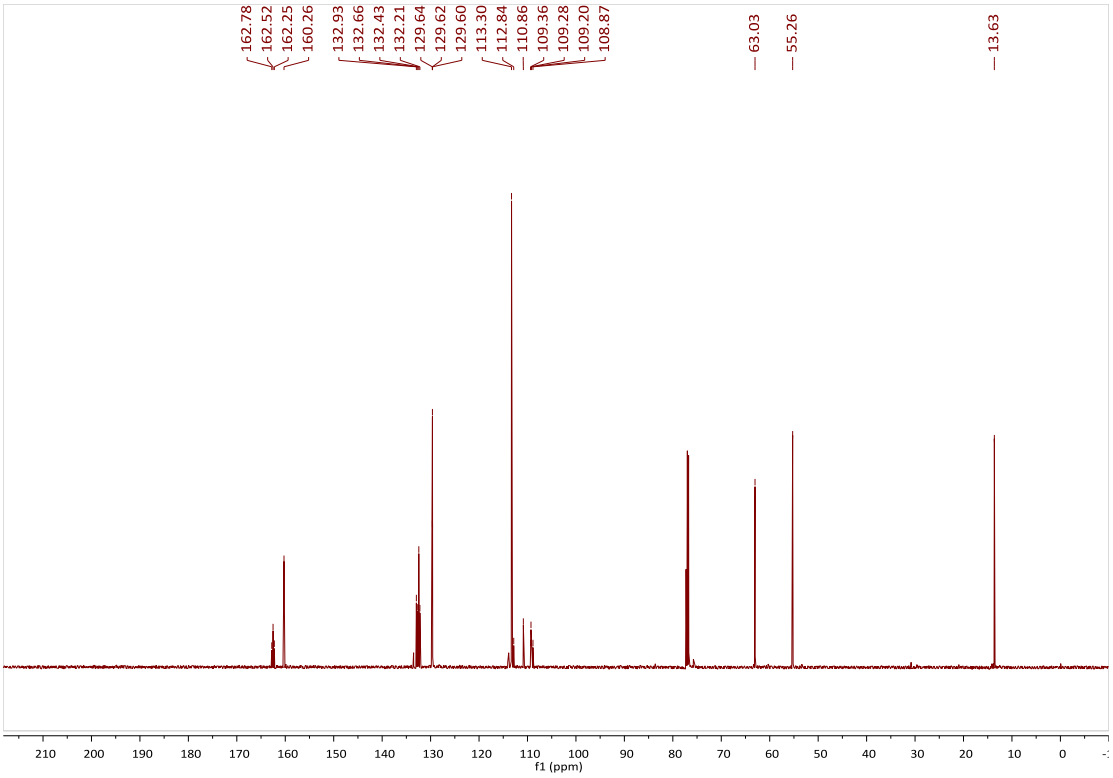


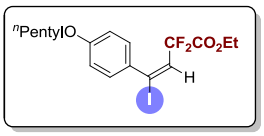
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5b**



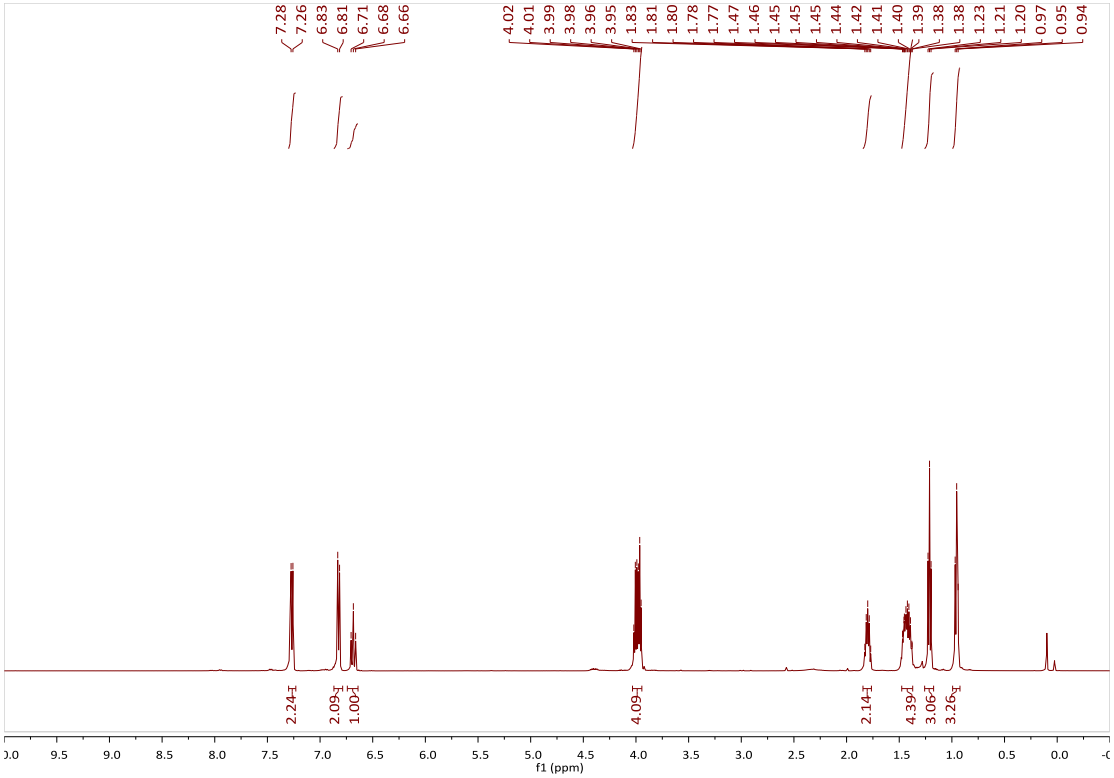


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5b**

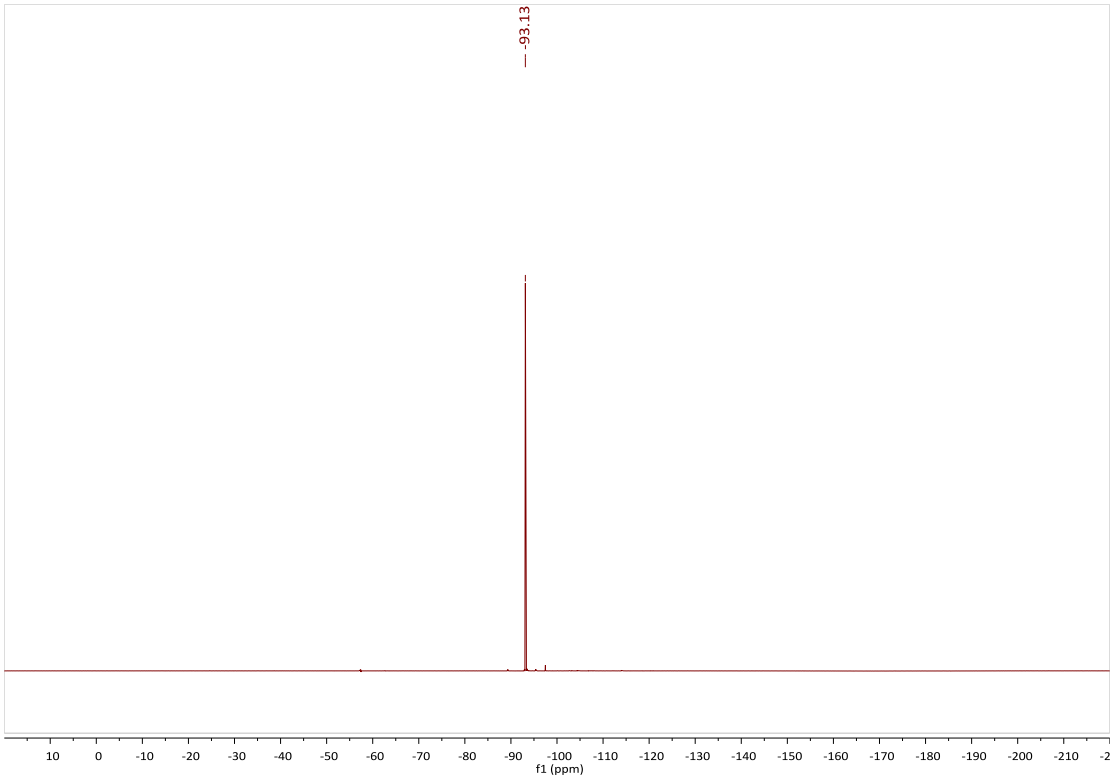


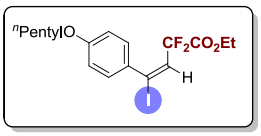


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5c**

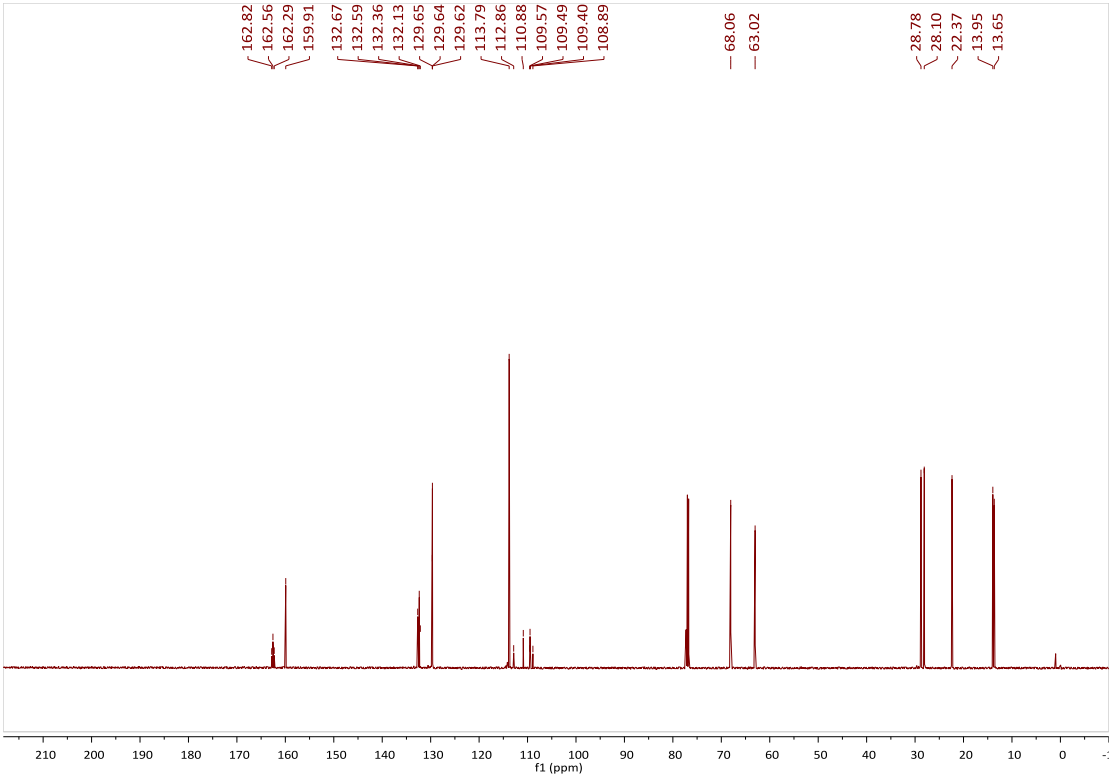


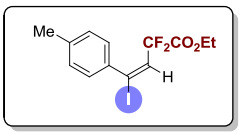
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5c**



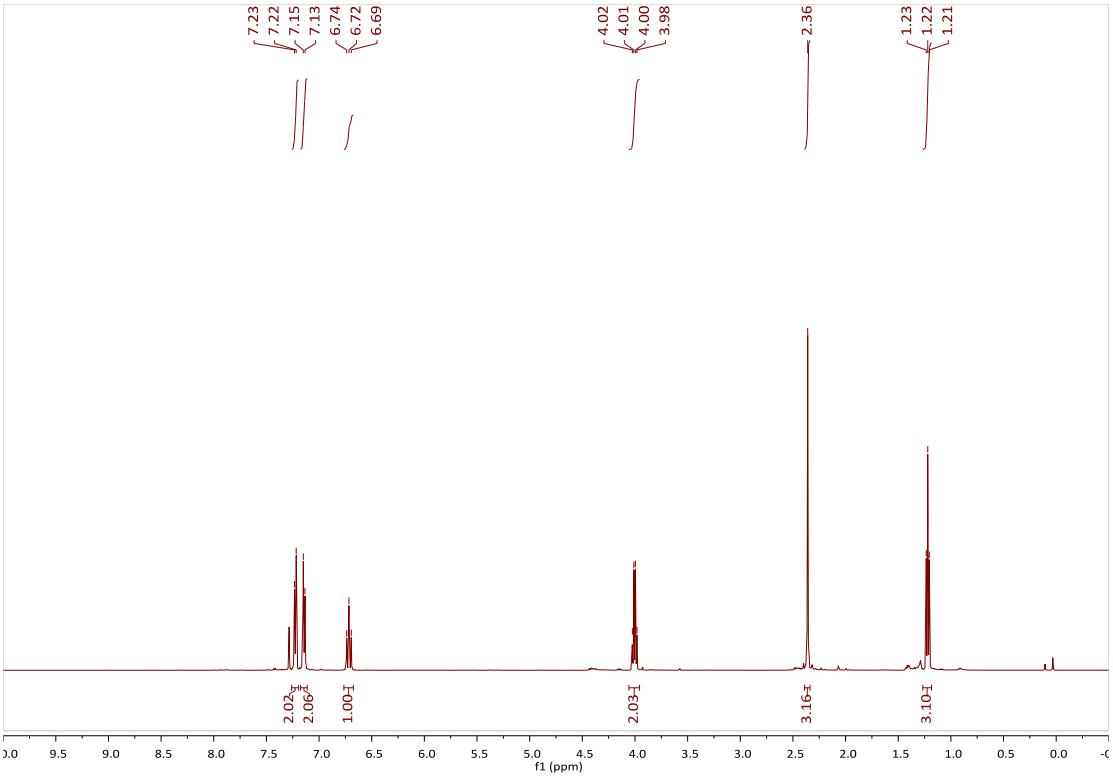


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5c**

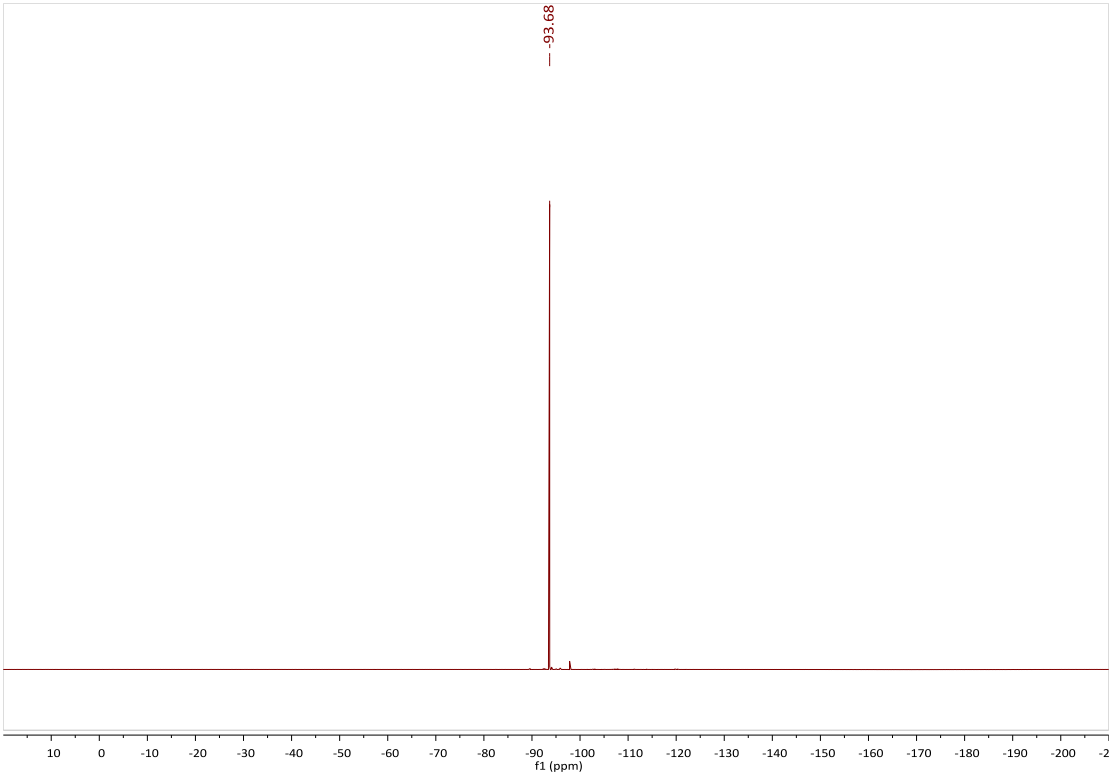


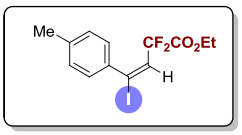


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5d**

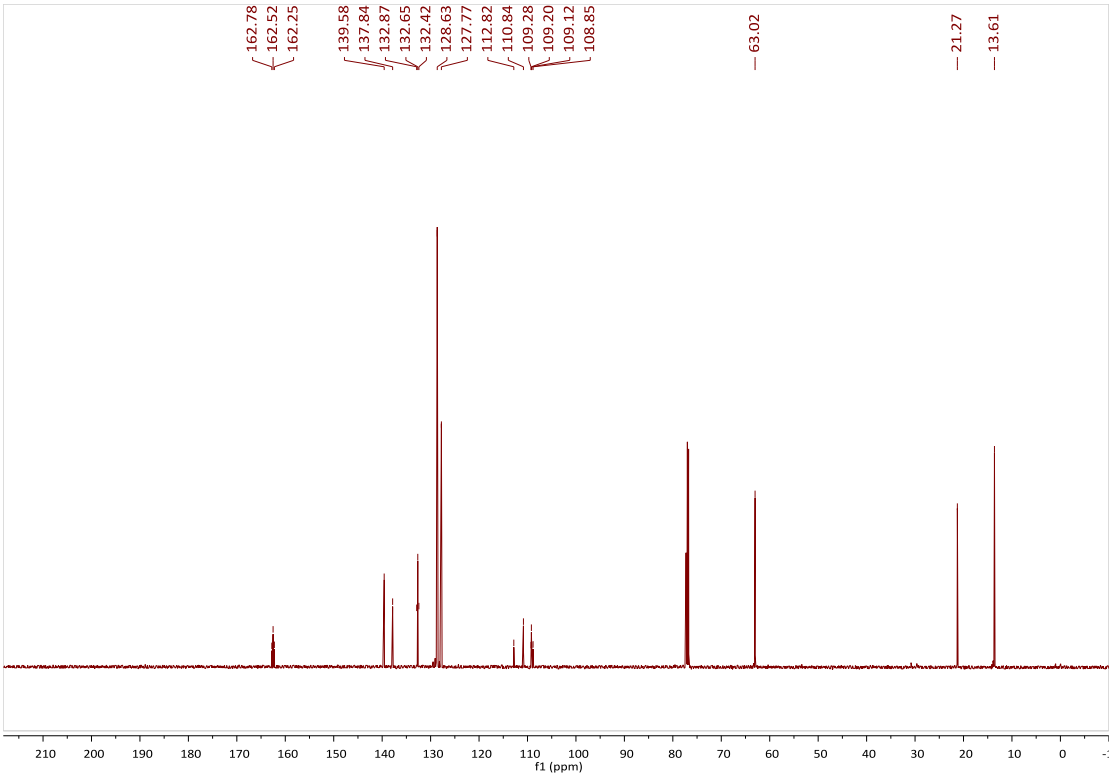


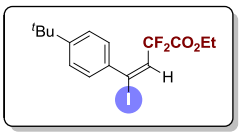
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5d**



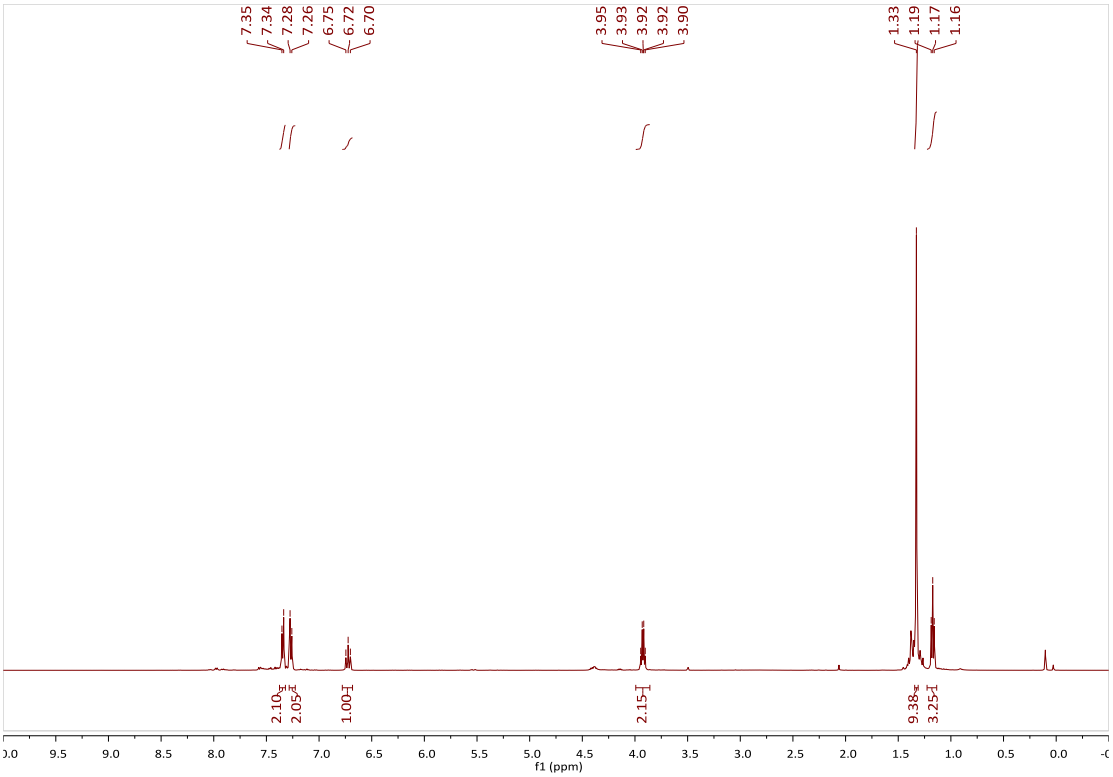


^{13}C **NMR**-spectrum (125 MHz, $CDCl_3$) of **5d**

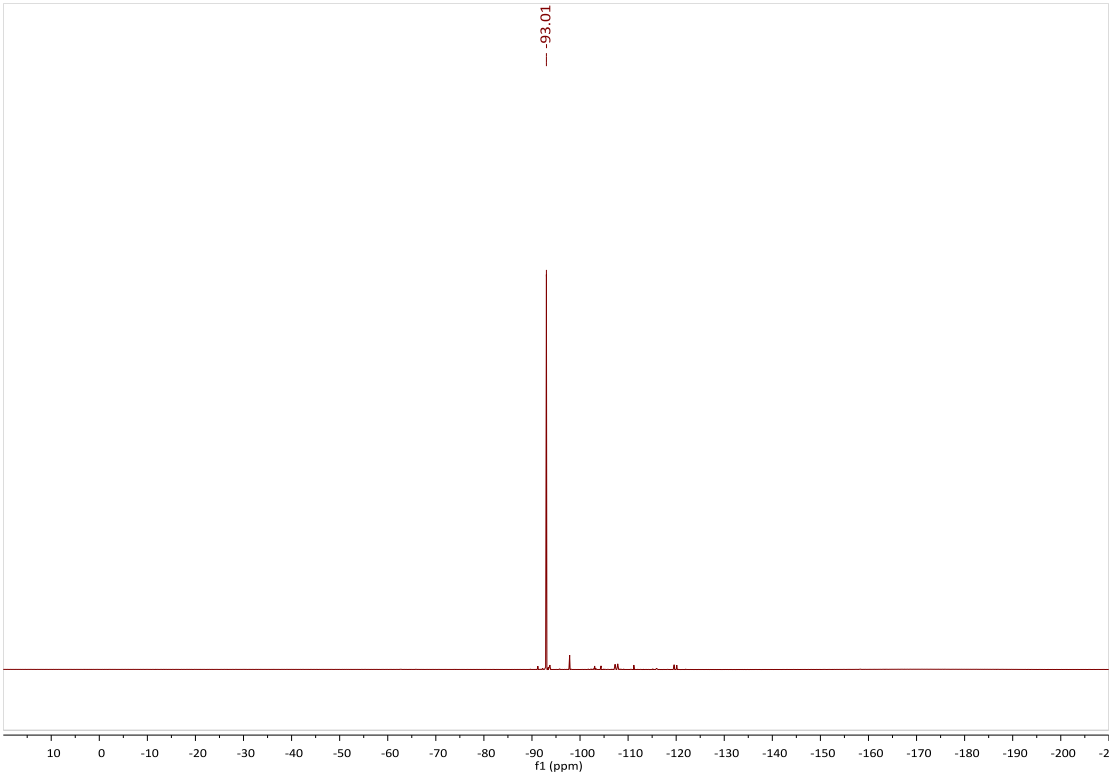


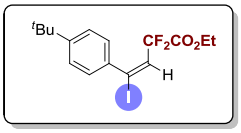


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5e**

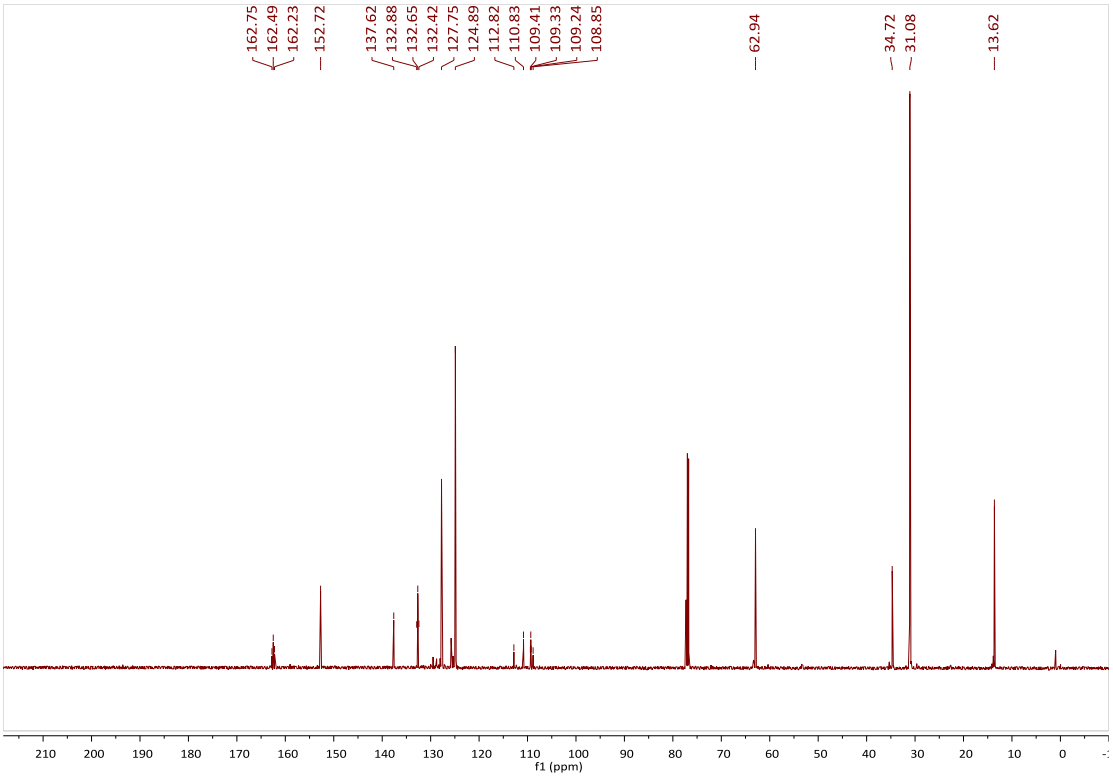


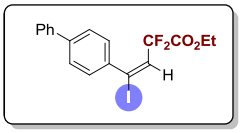
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5e**



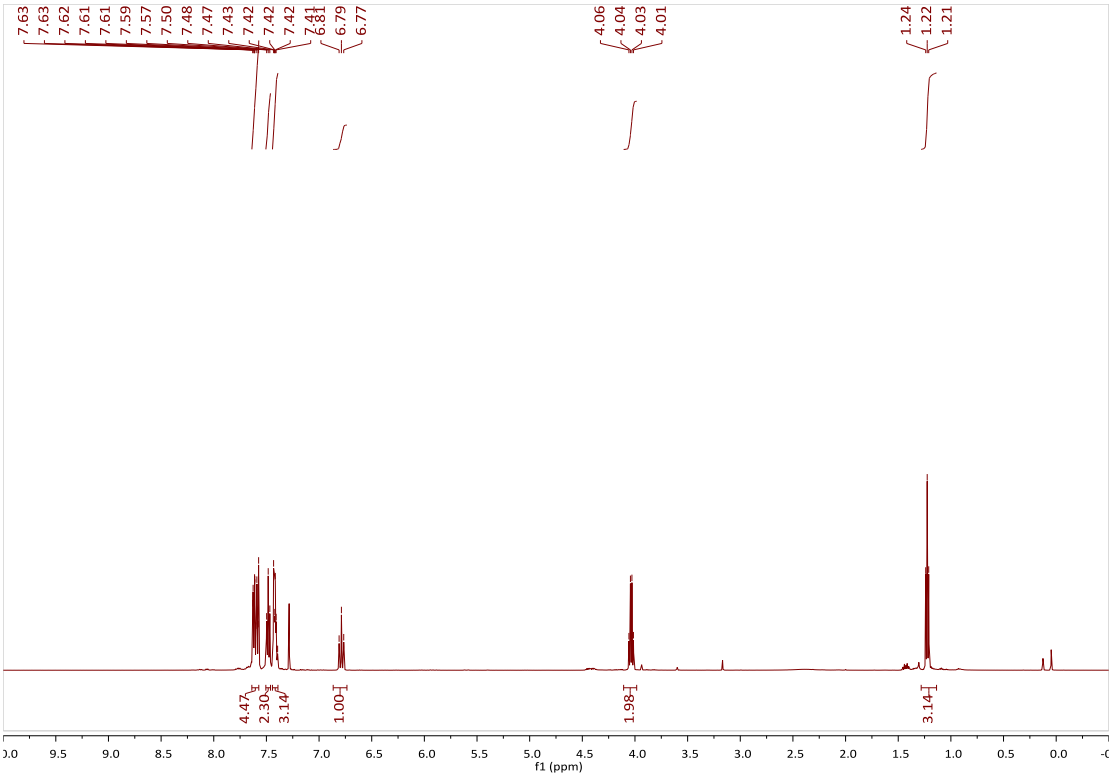


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5e**

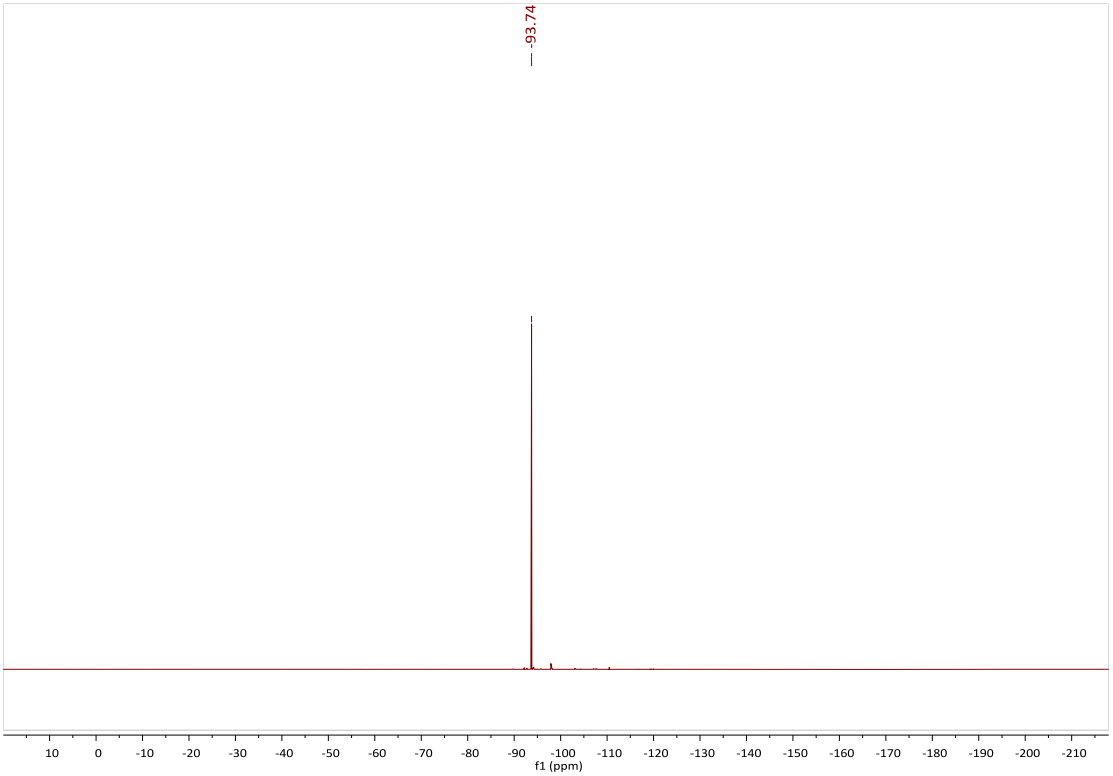


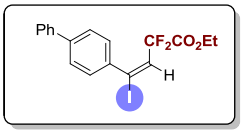


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5f**

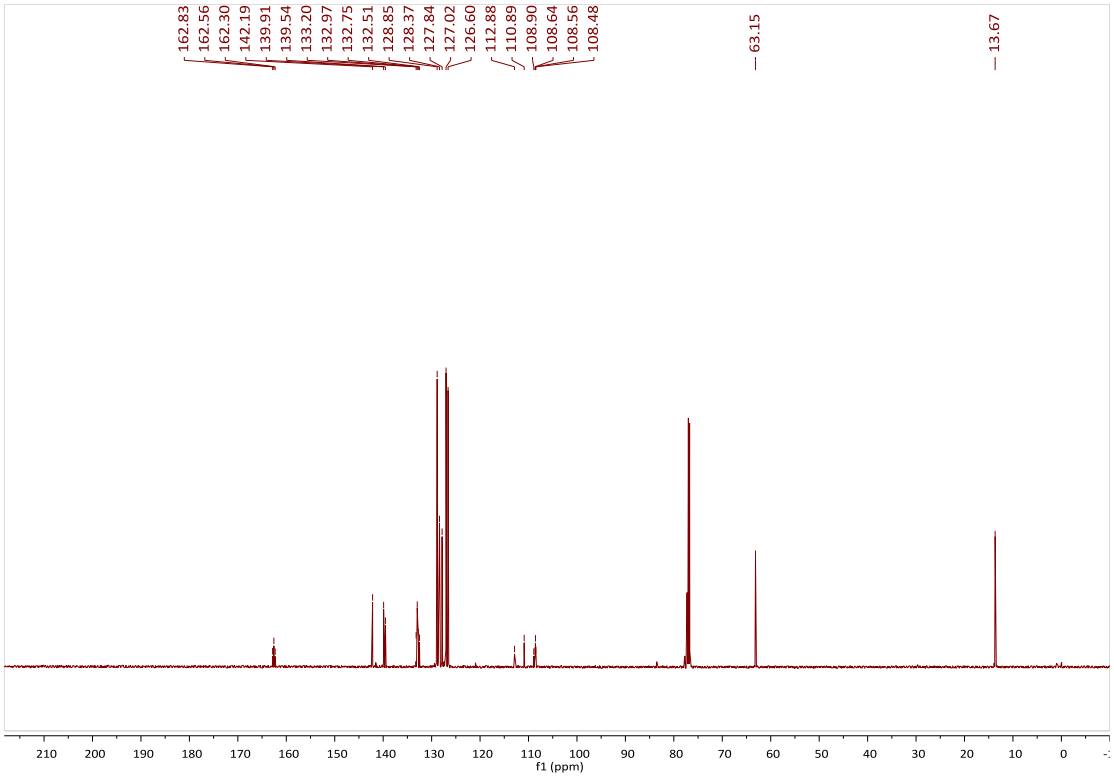


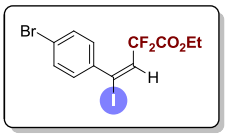
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5f**



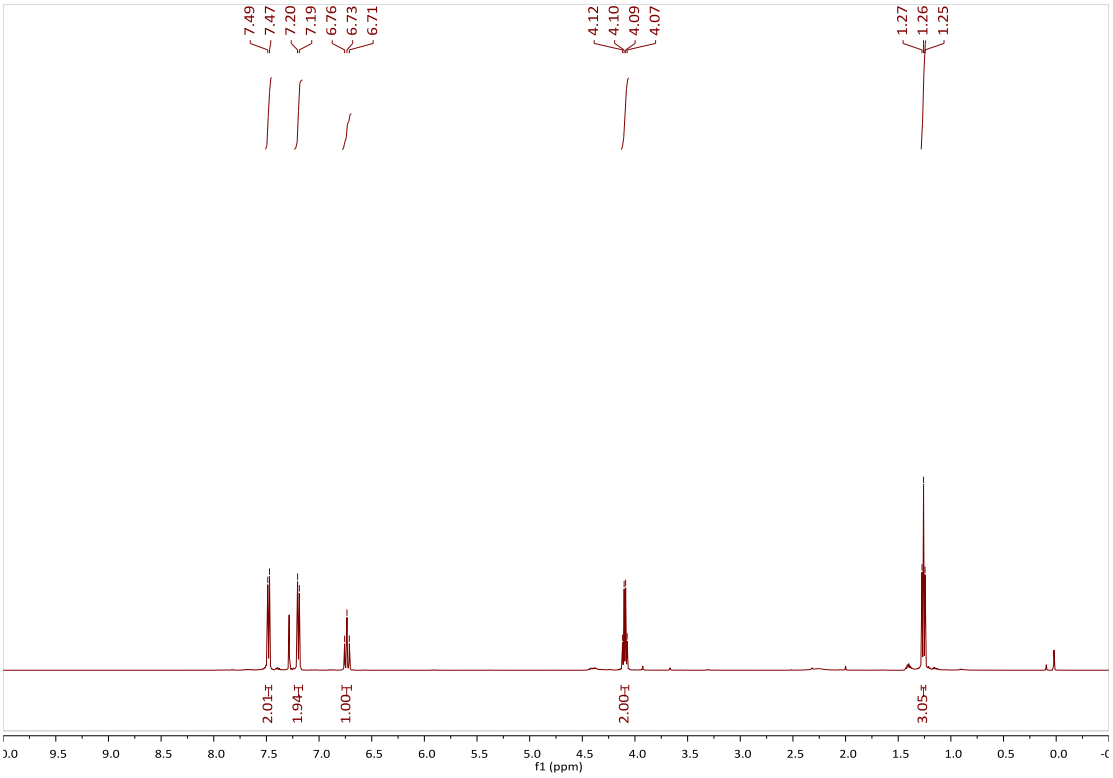


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5f**

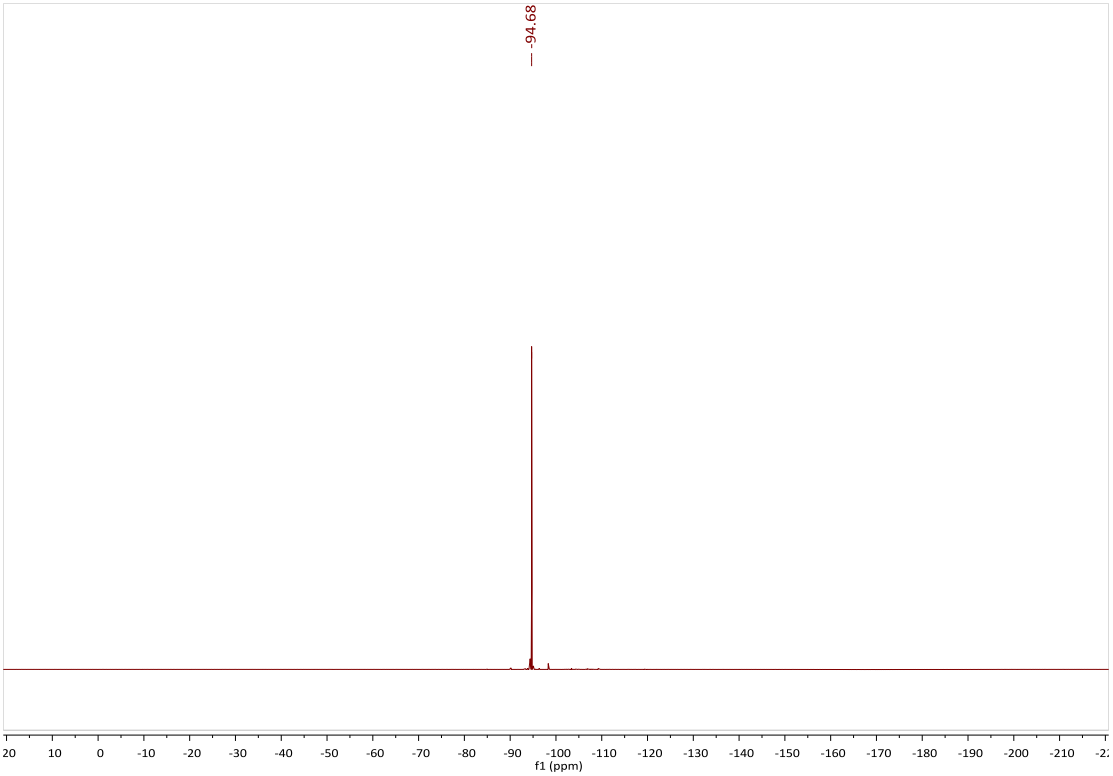


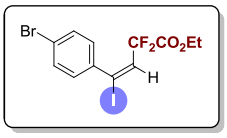


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5g**

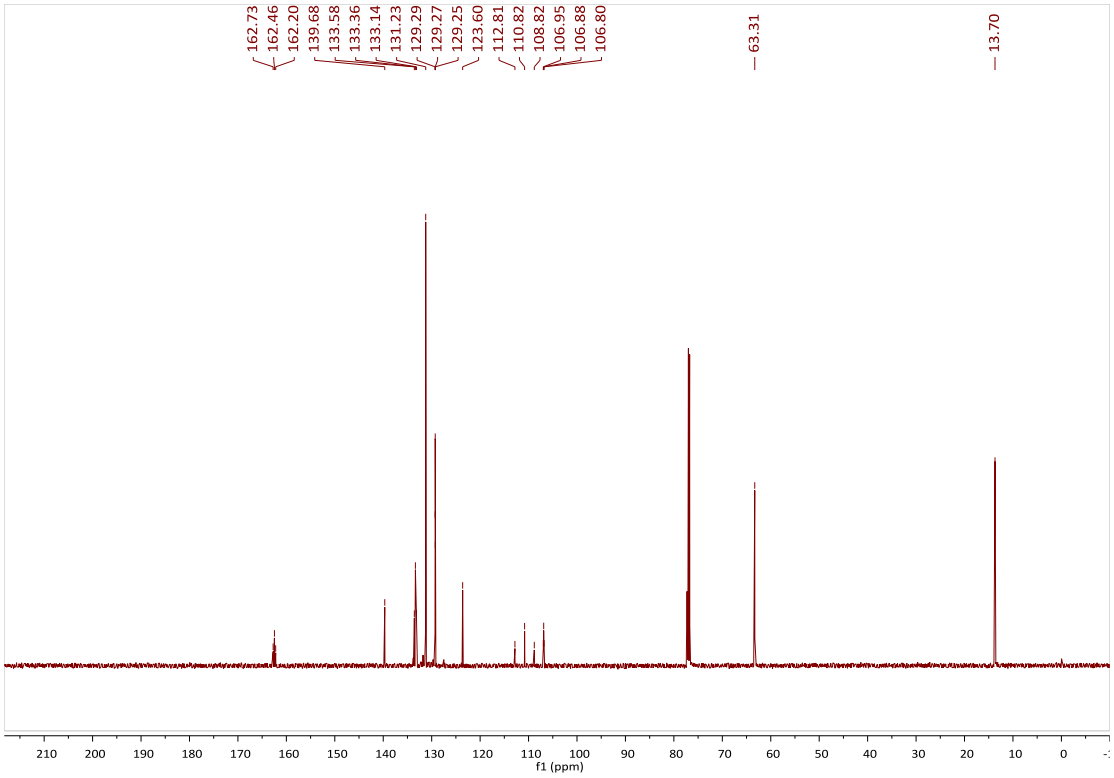


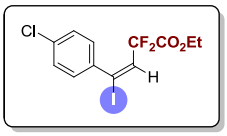
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5g**



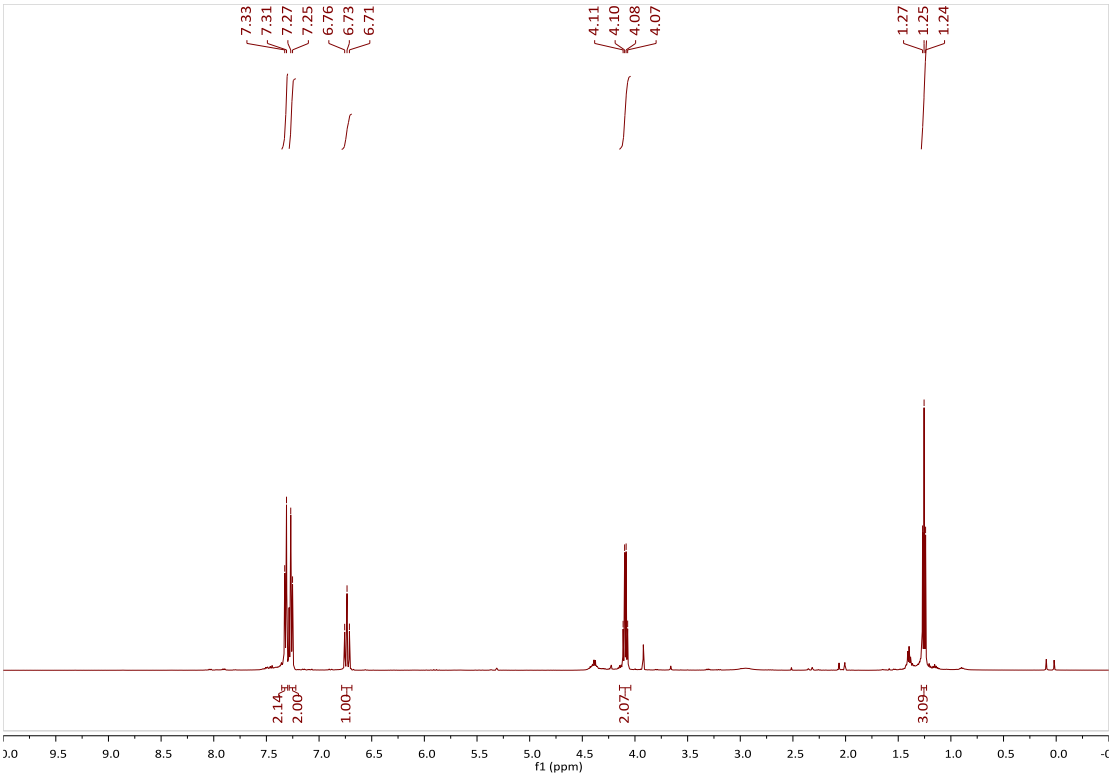


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5g**

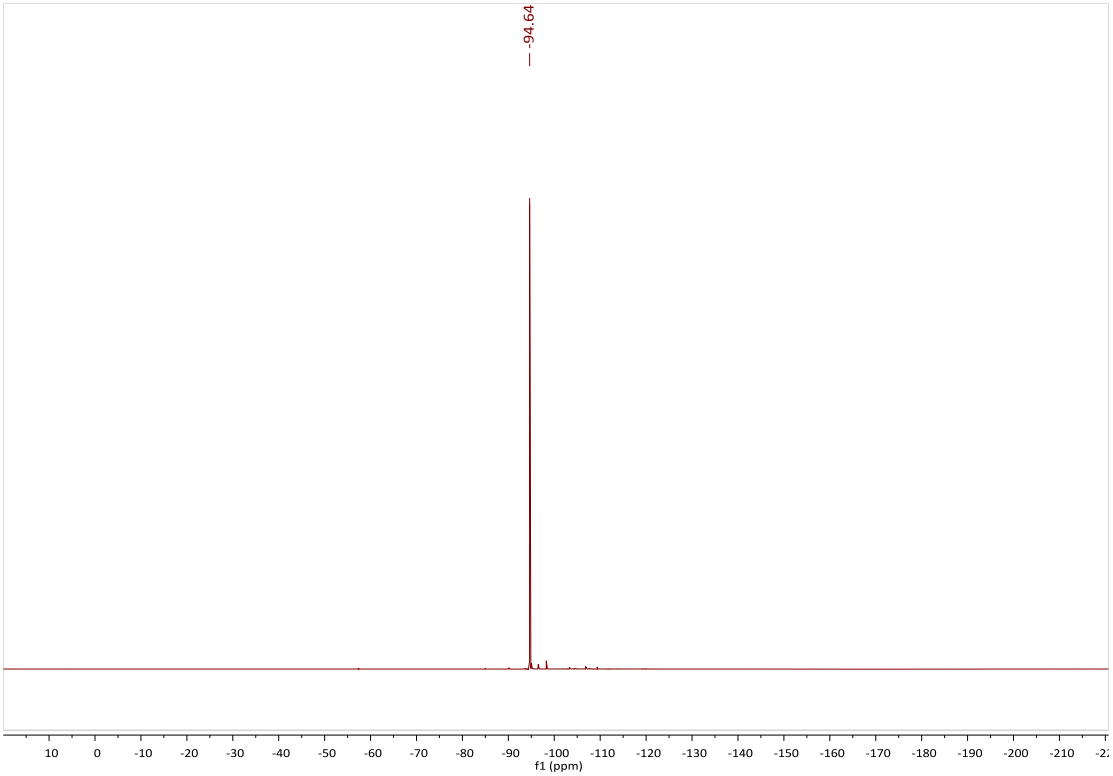


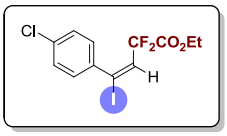


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5h**

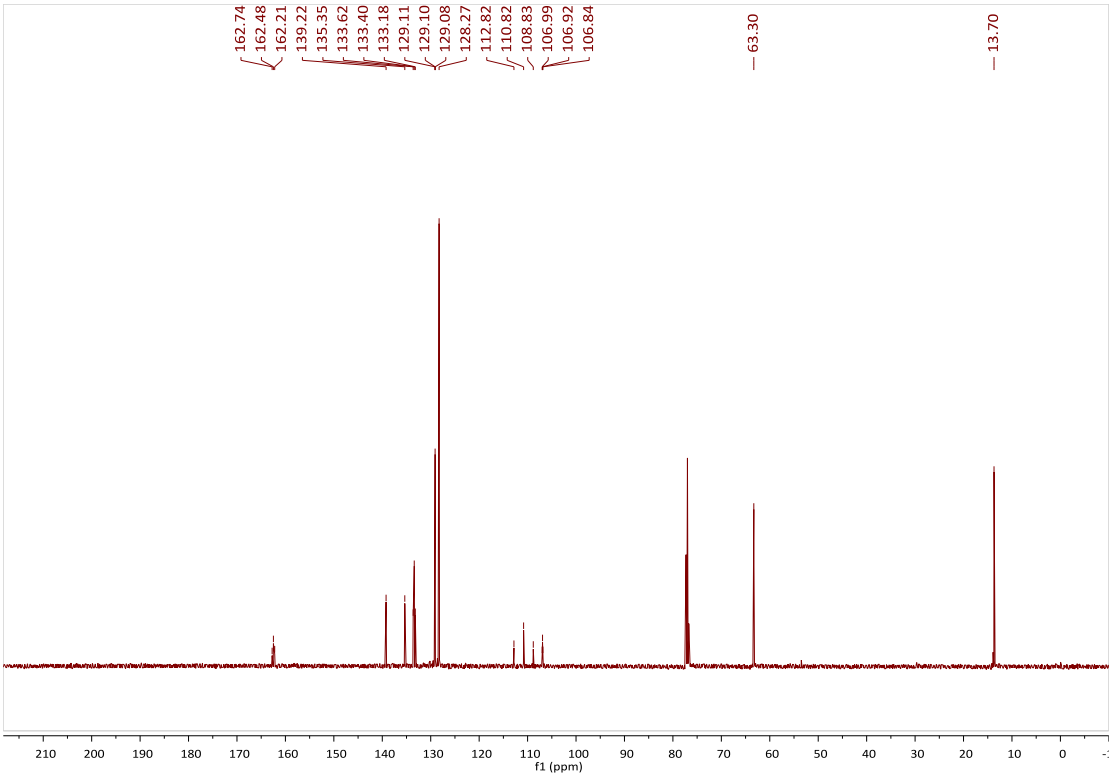


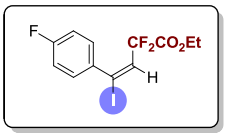
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5h**



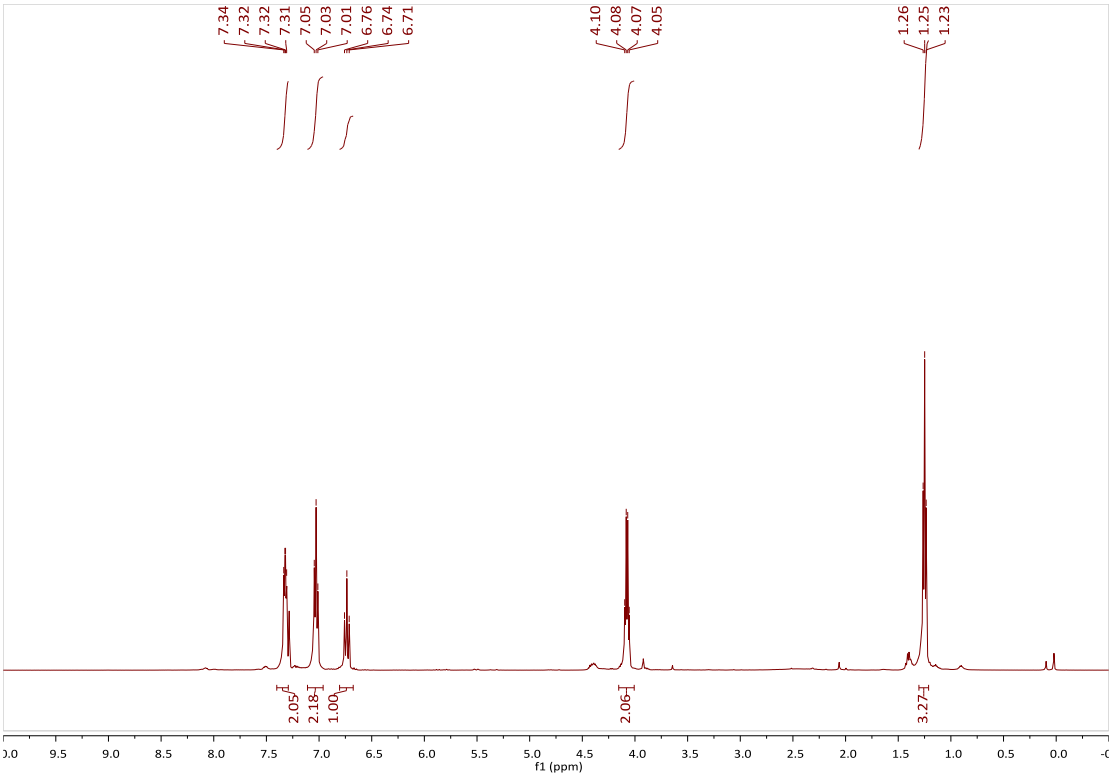


^{13}C **NMR**-spectrum (125 MHz, $CDCl_3$) of **5h**

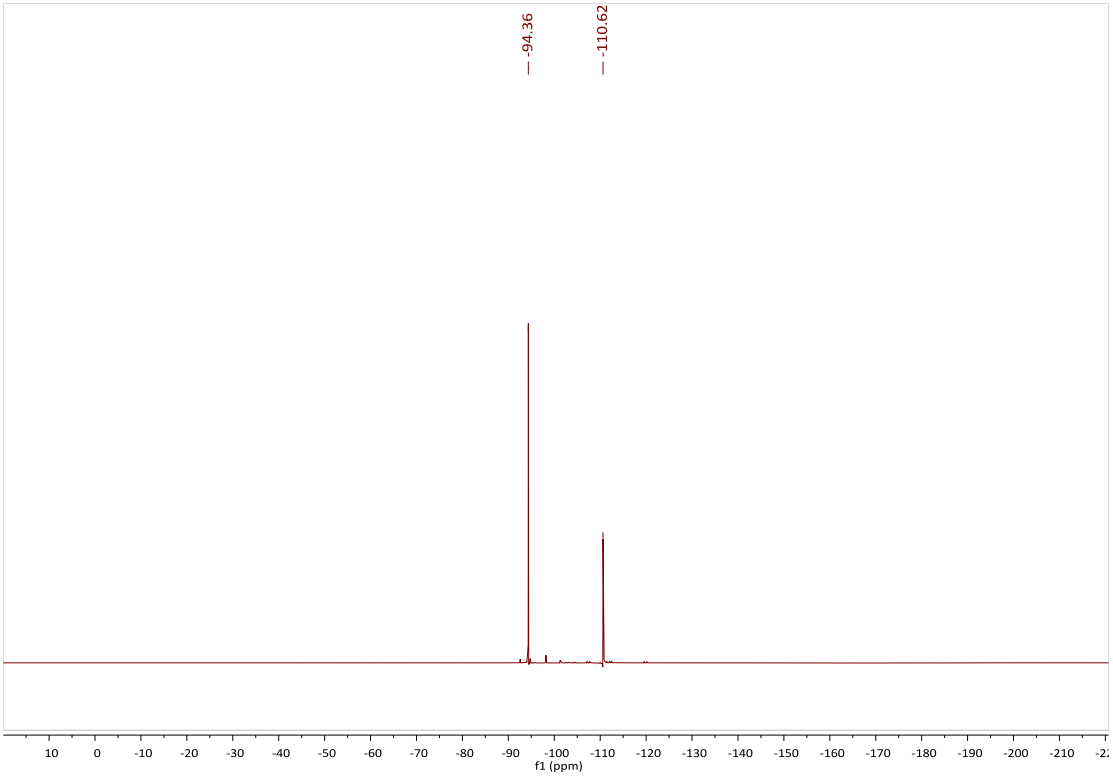


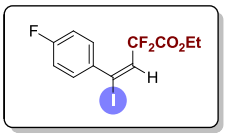


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5i**

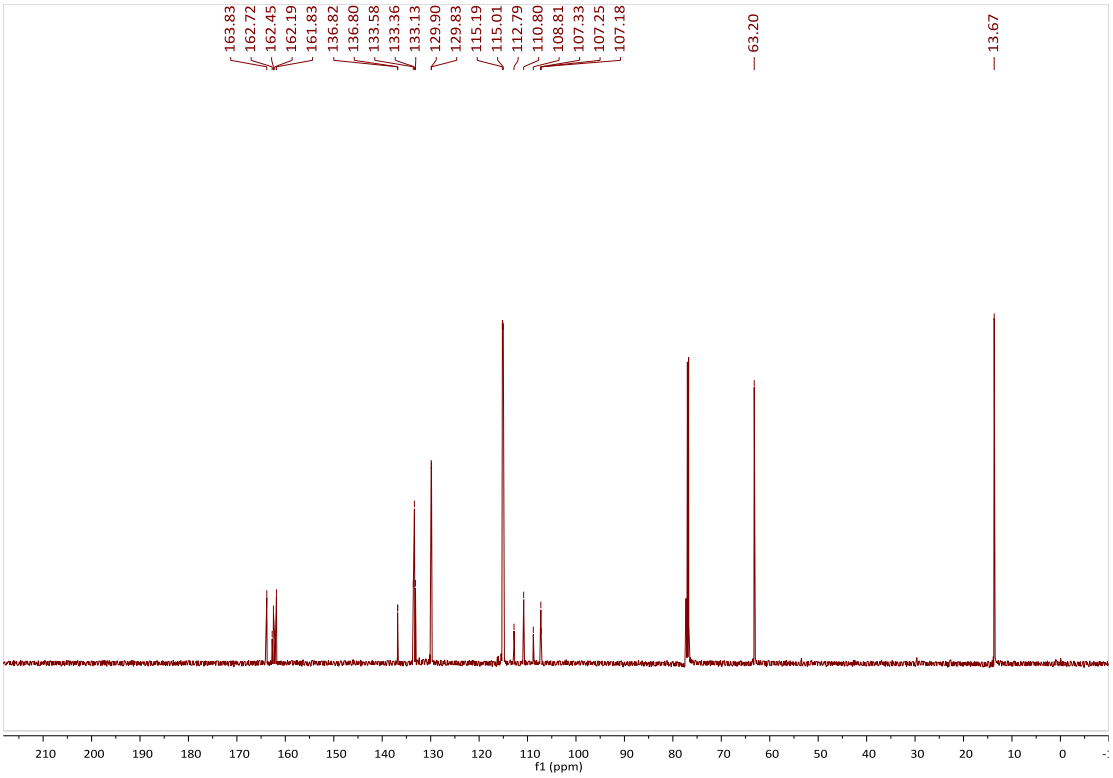


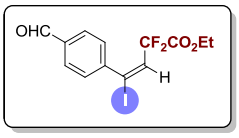
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5i**



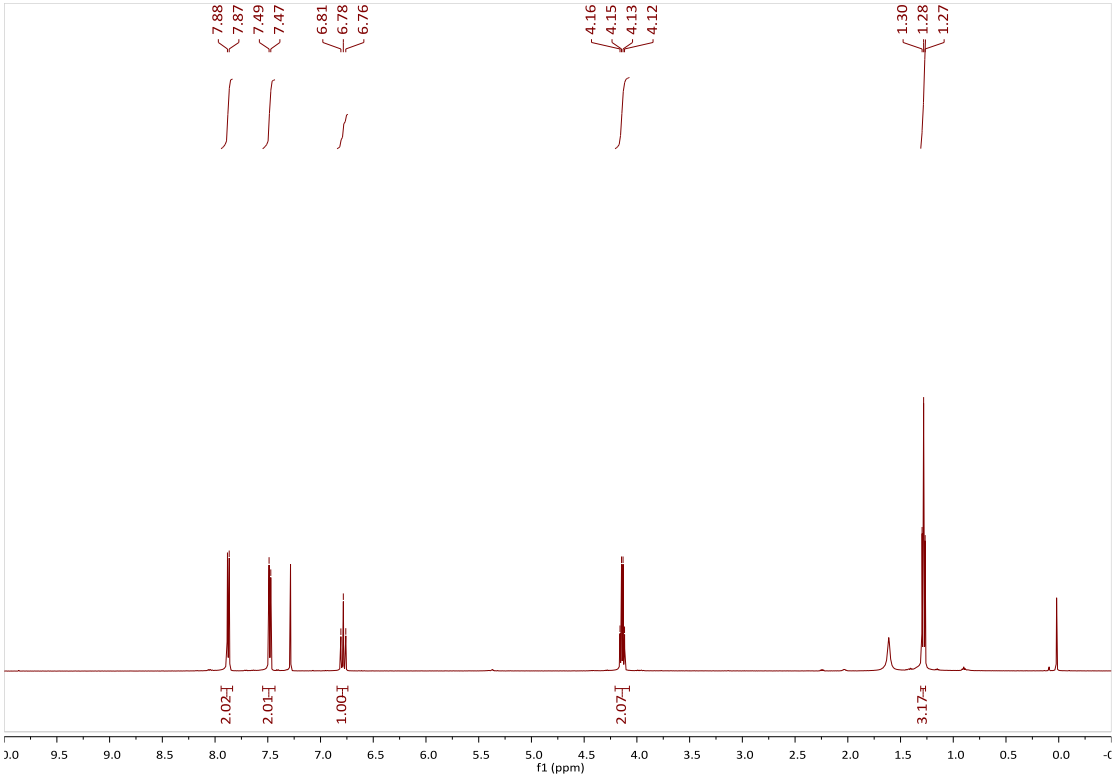


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5i**

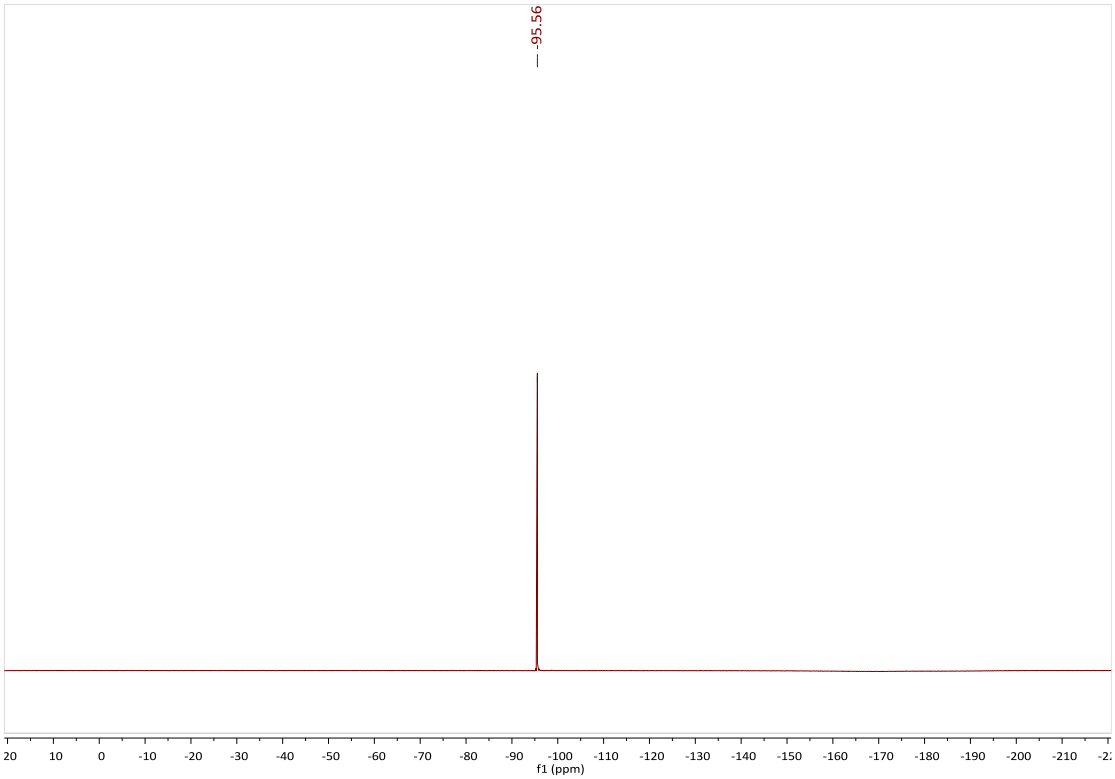


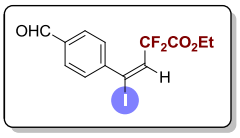


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5j**

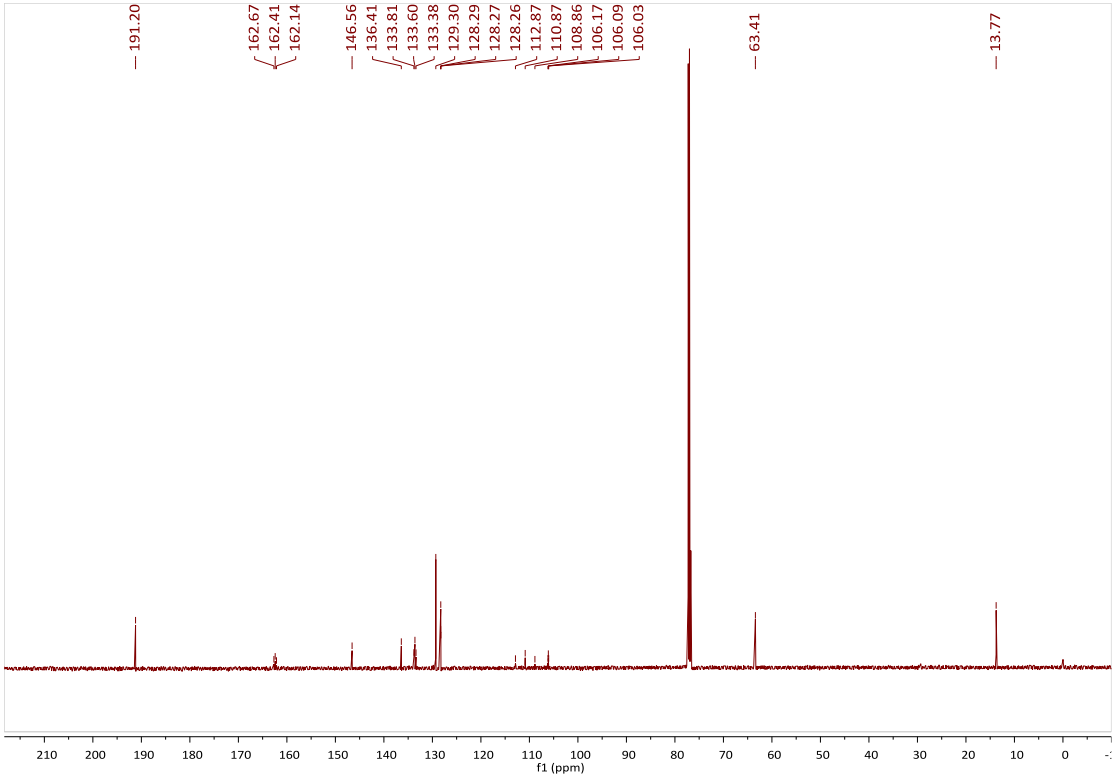


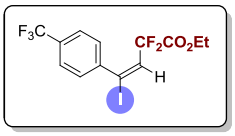
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5j**



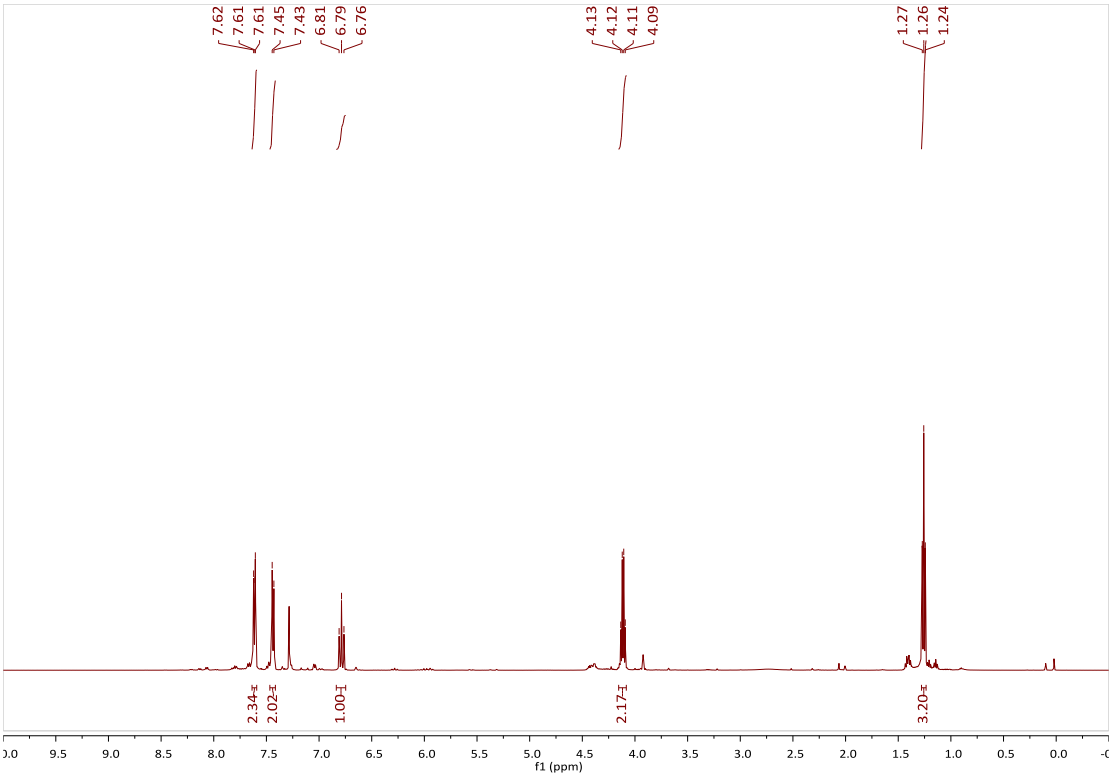


^{13}C **NMR**-spectrum (125 MHz, $CDCl_3$) of **5j**

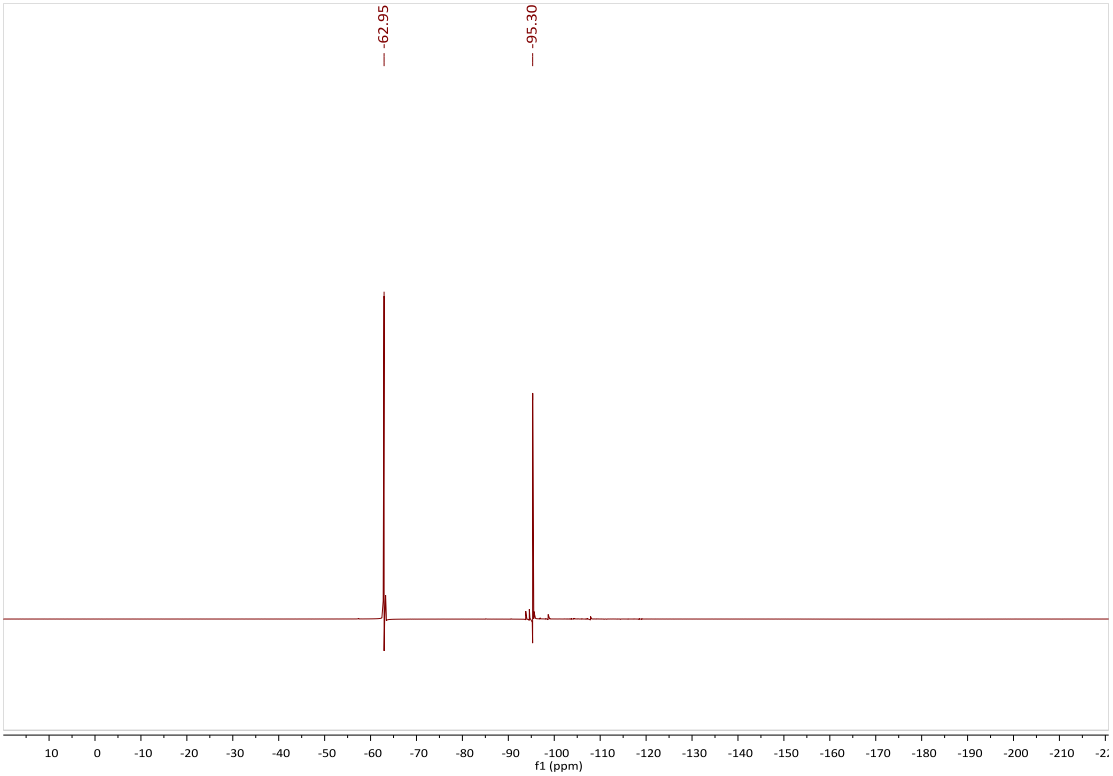


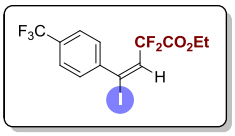


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5k**

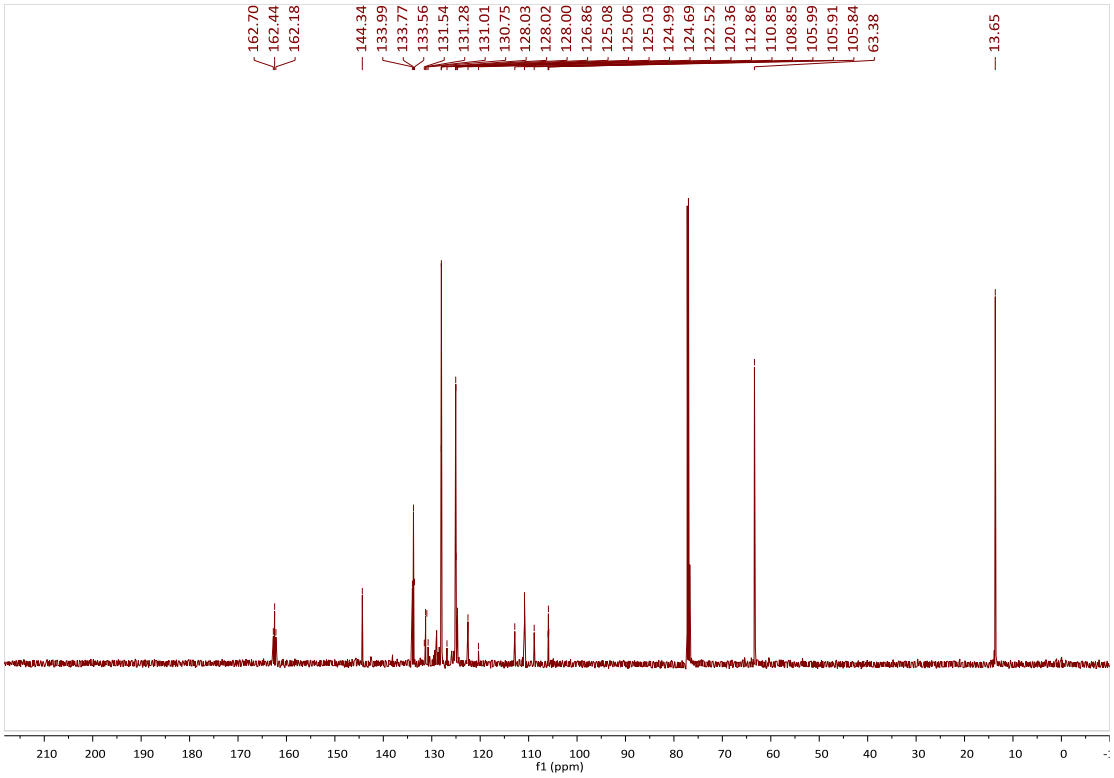


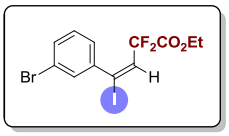
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5k**



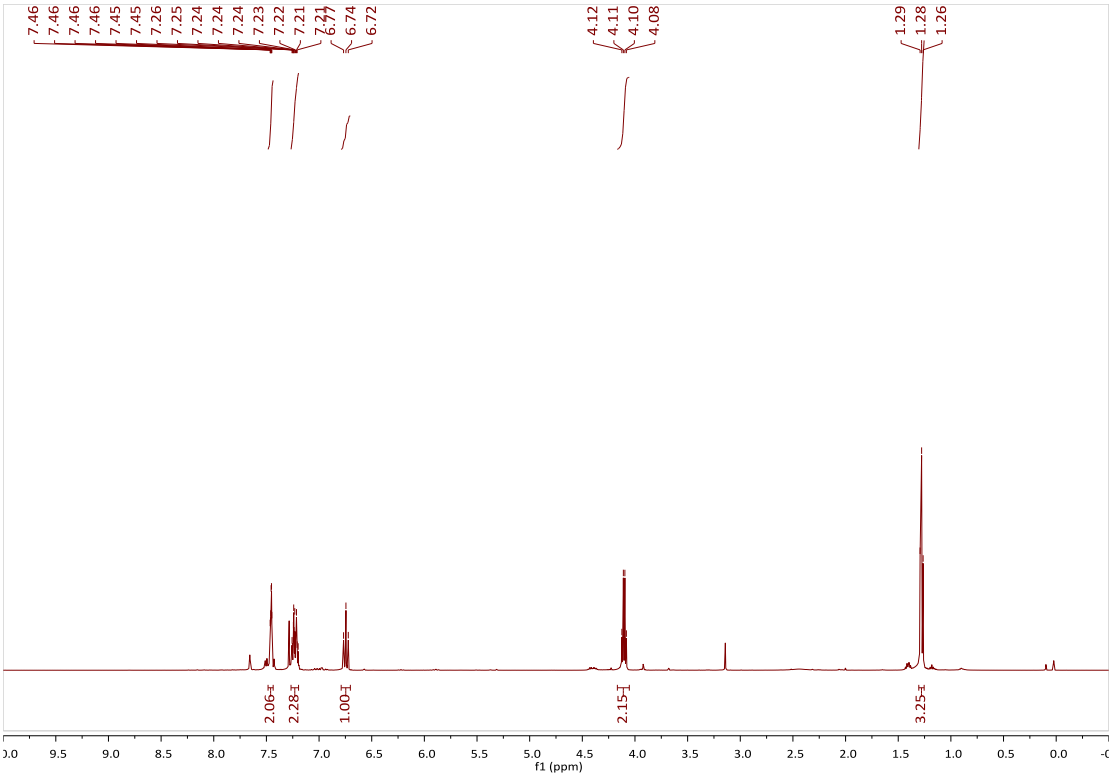


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5k**

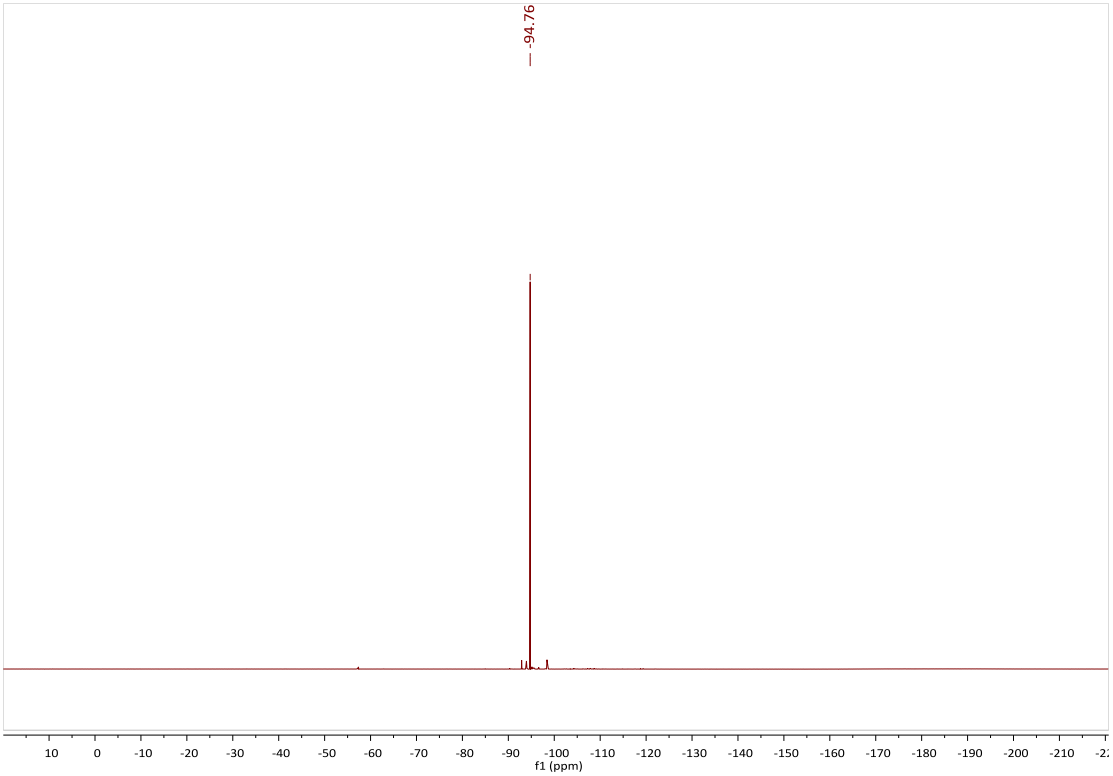


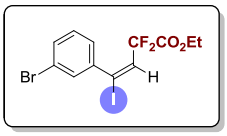


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5l**

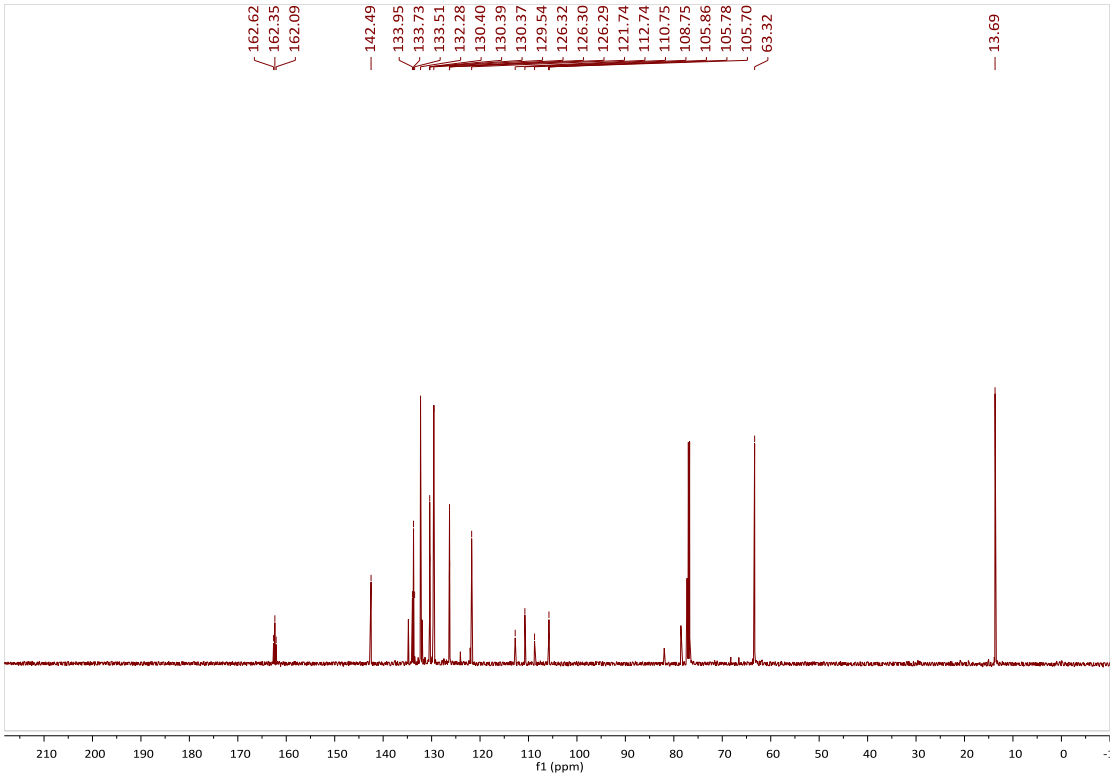


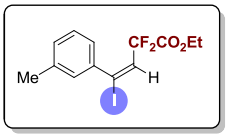
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5l**



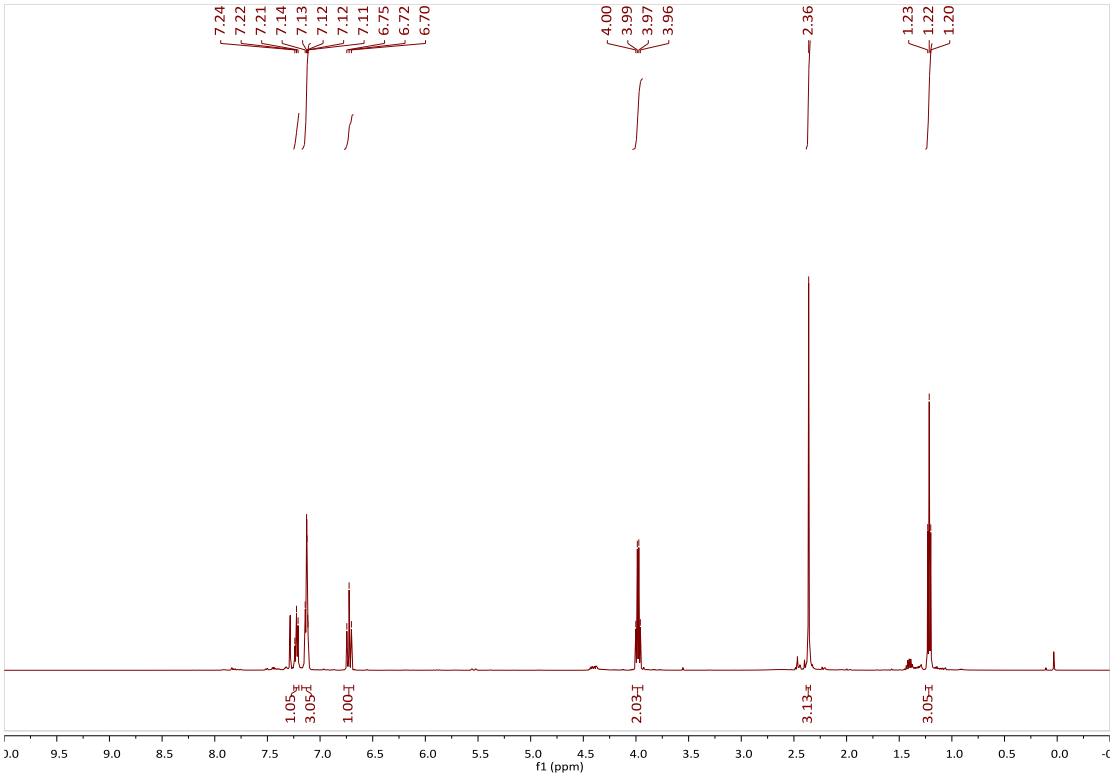


^{13}C **NMR**-spectrum (125 MHz, $CDCl_3$) of **5l**

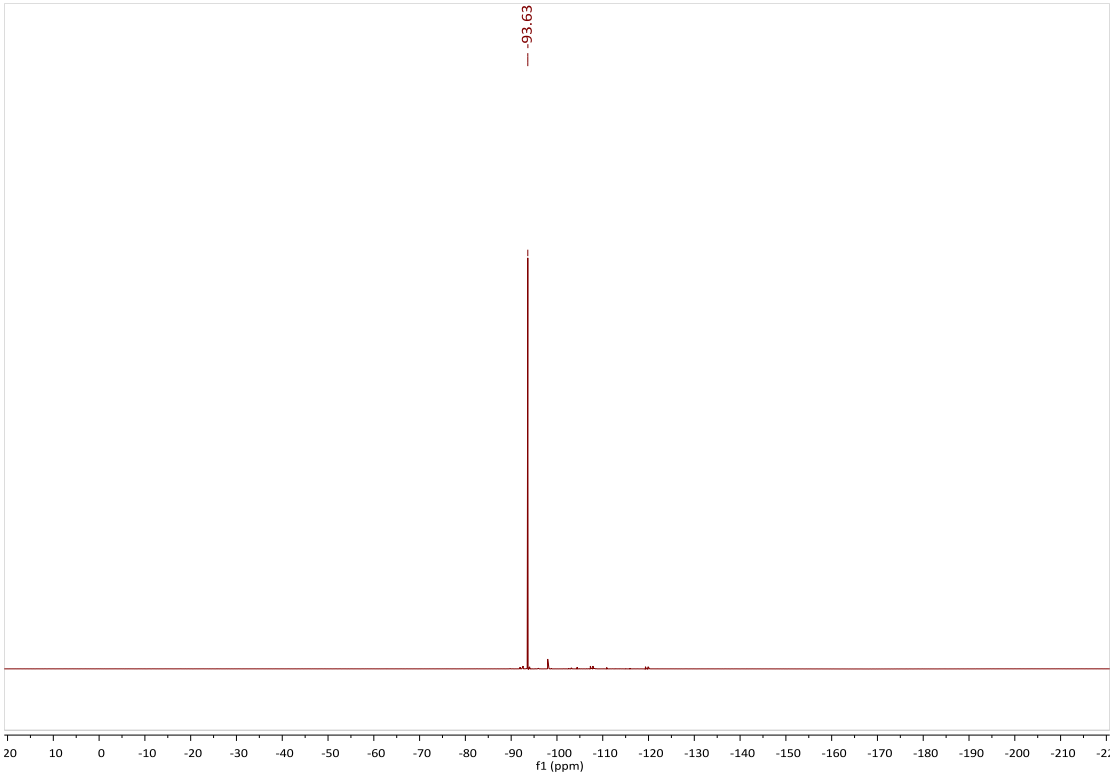


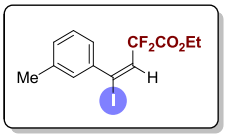


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5m**

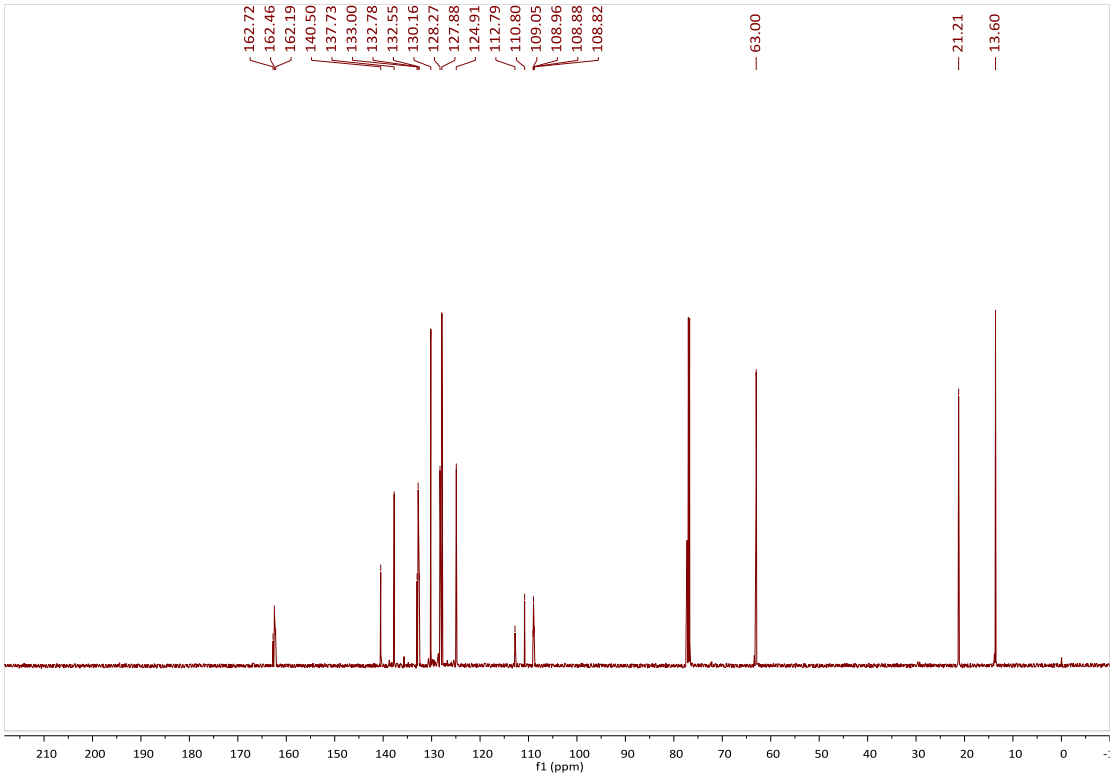


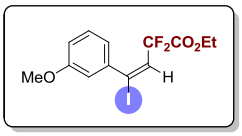
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5m**



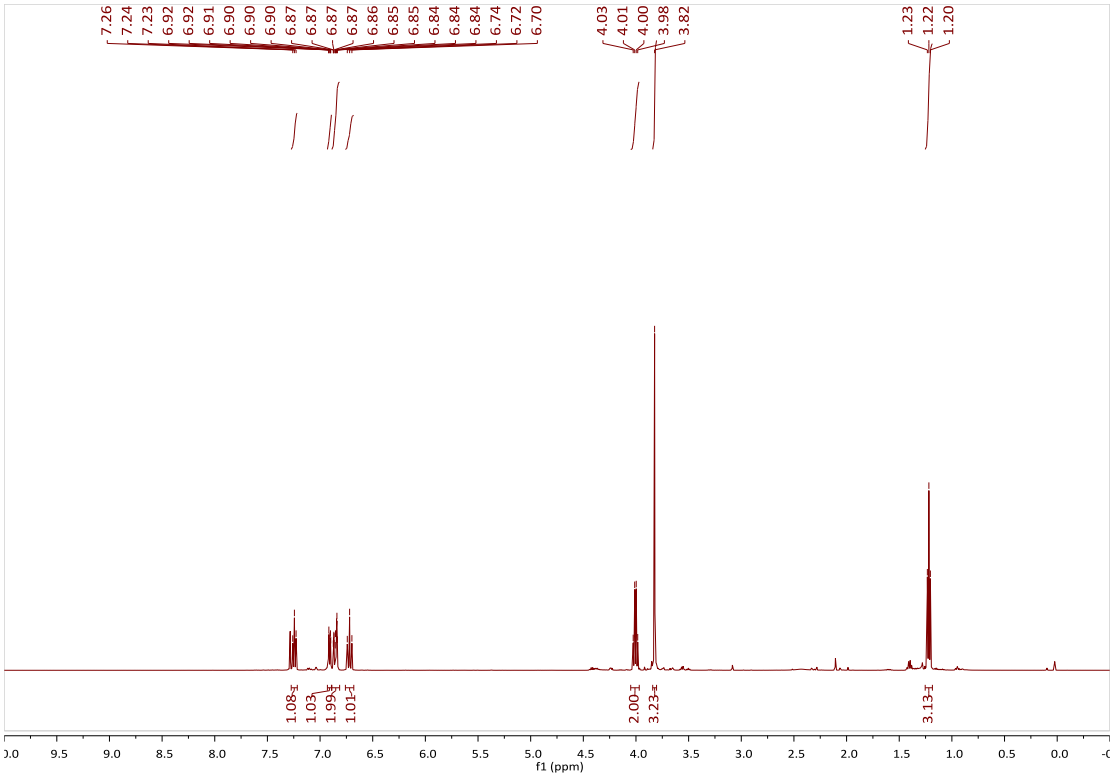


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5m**

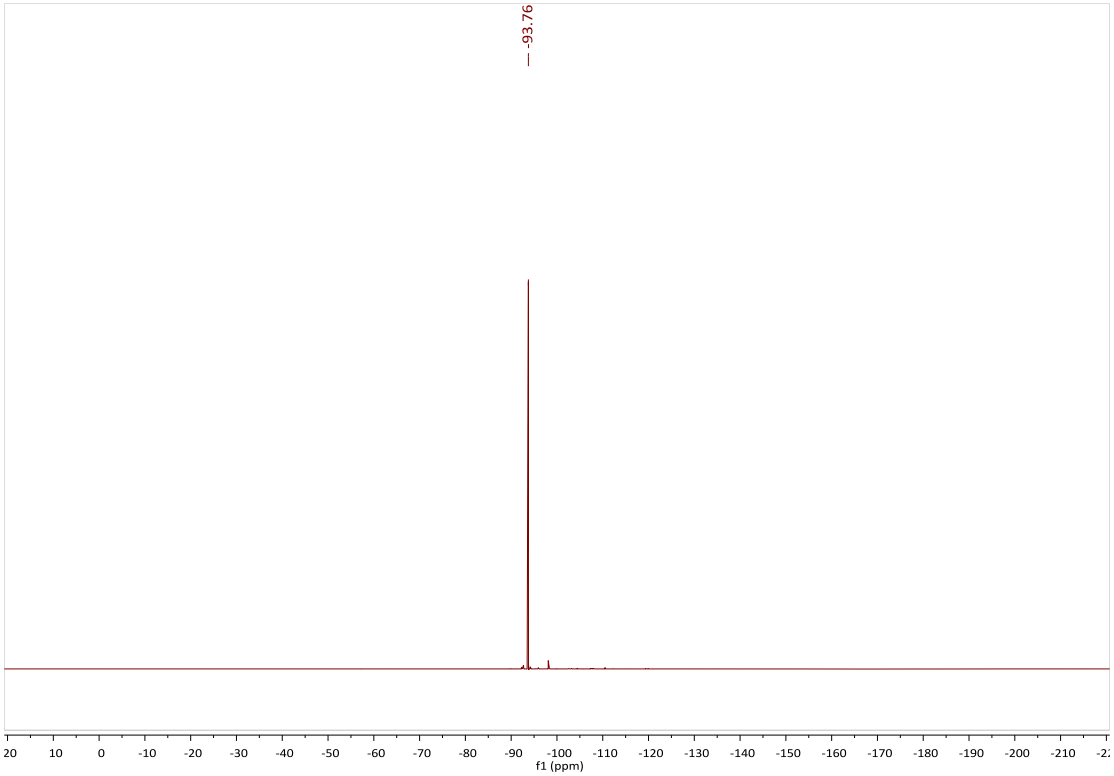


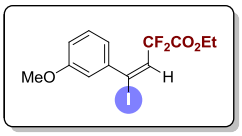


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5n**

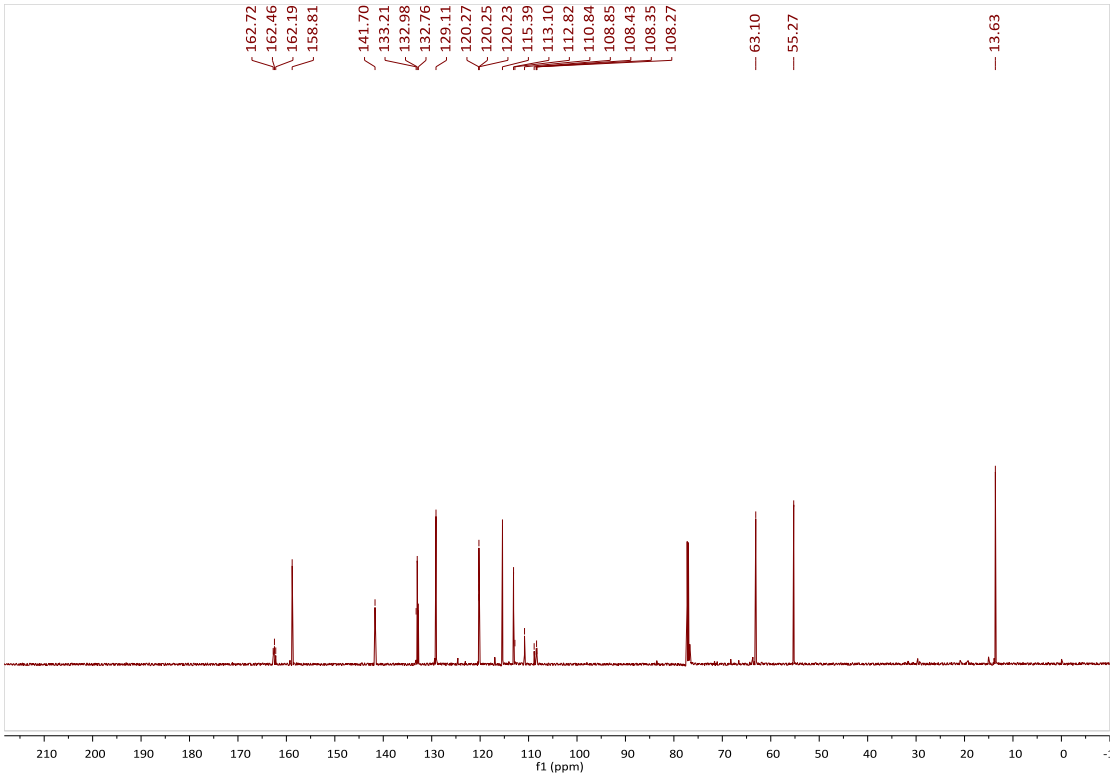


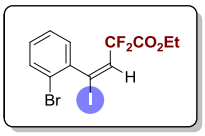
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5n**



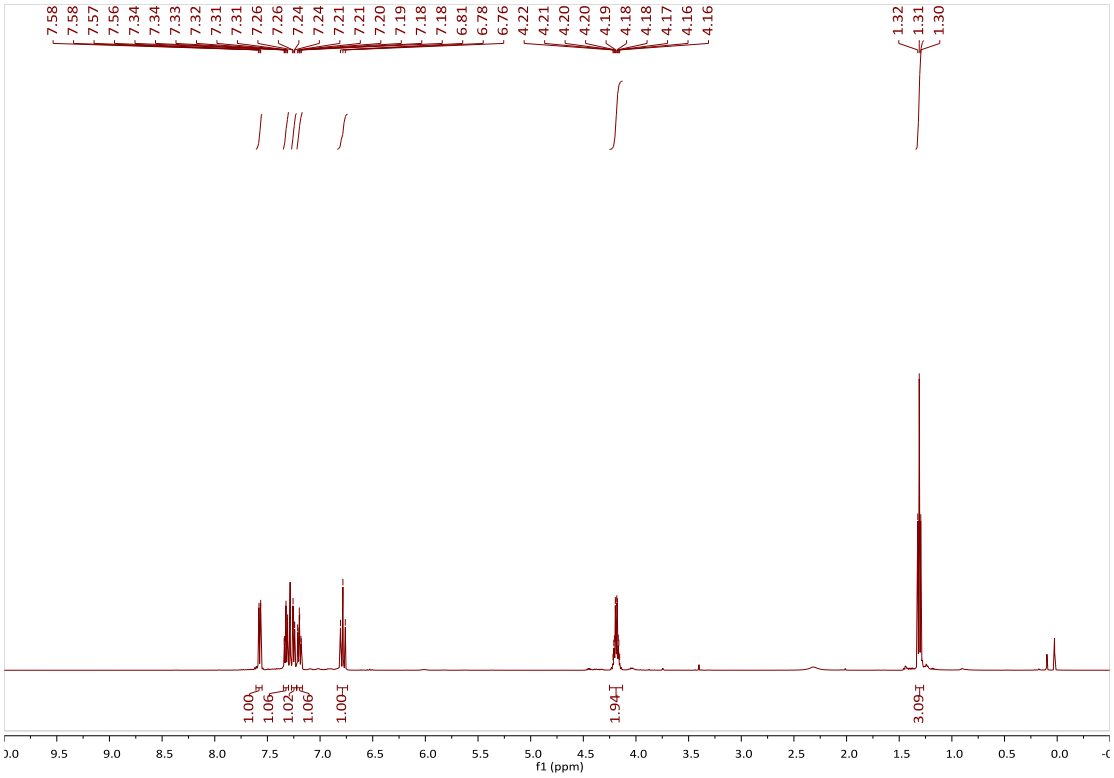


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5n**

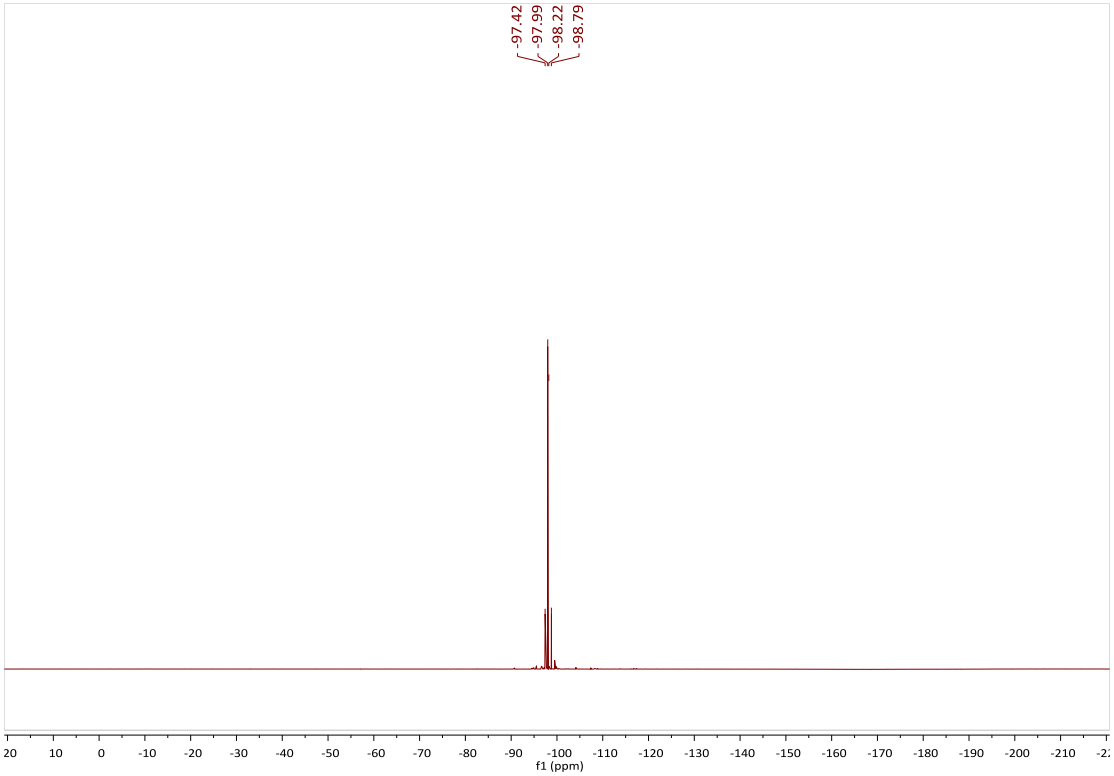


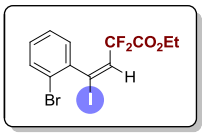


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5o**

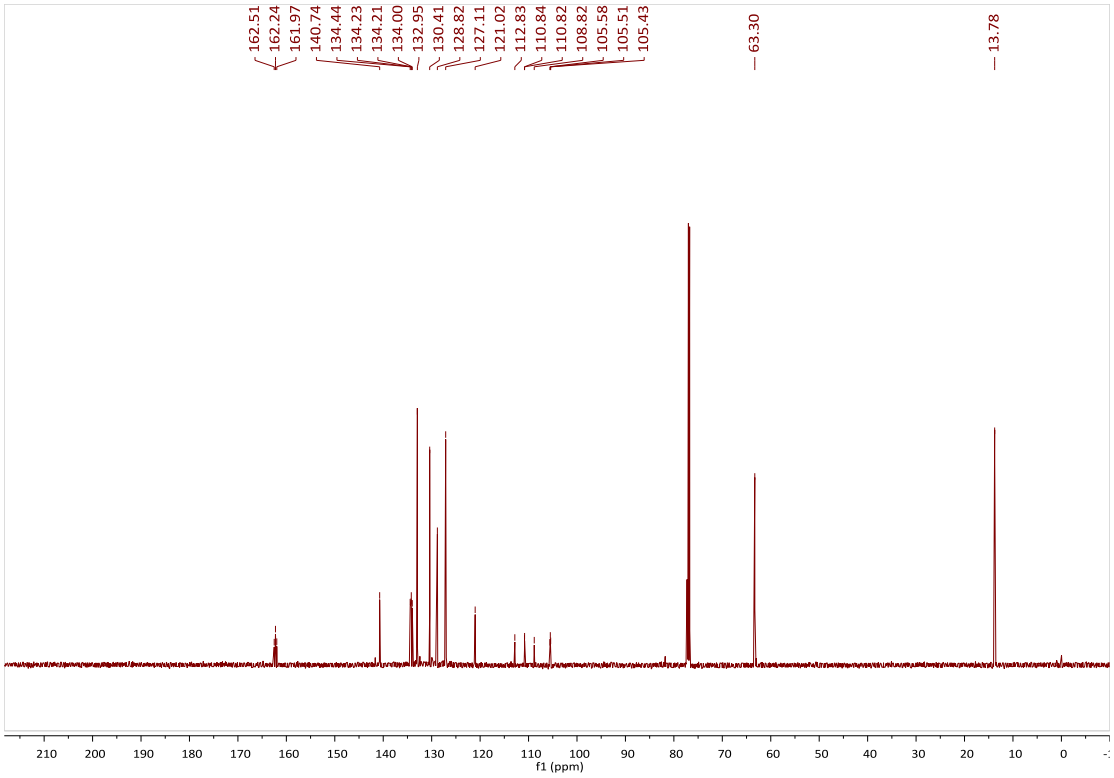


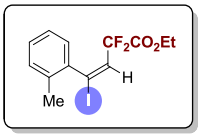
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5o**



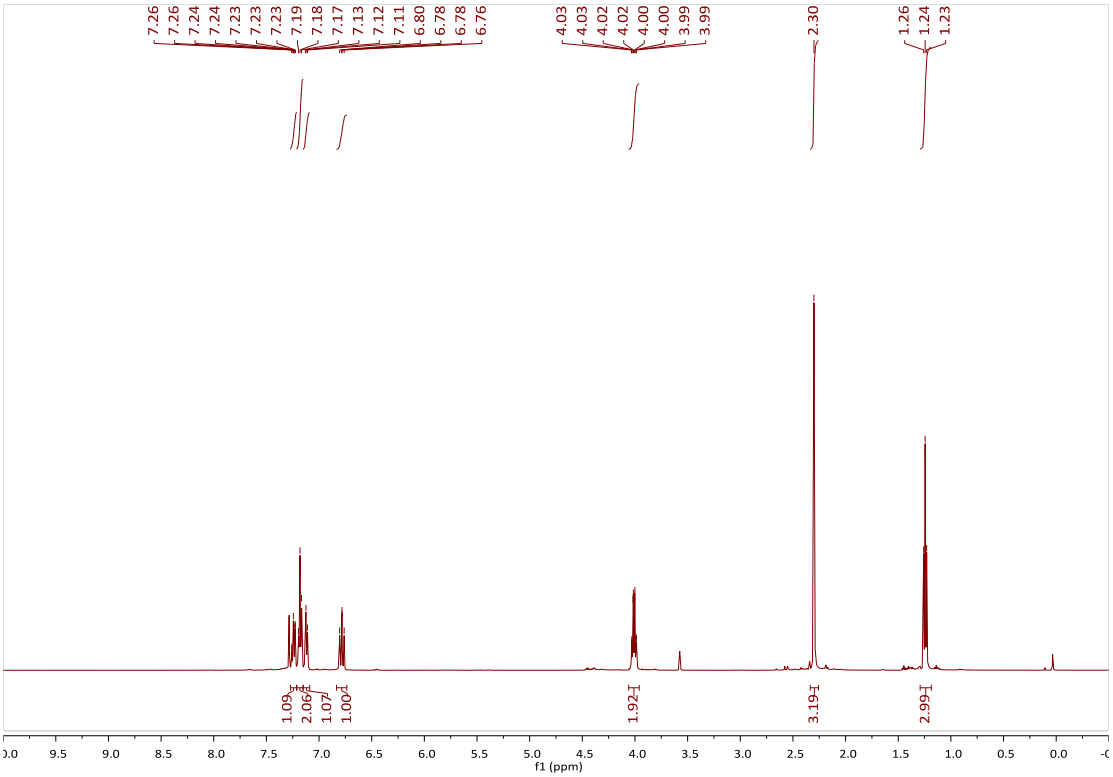


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5o**

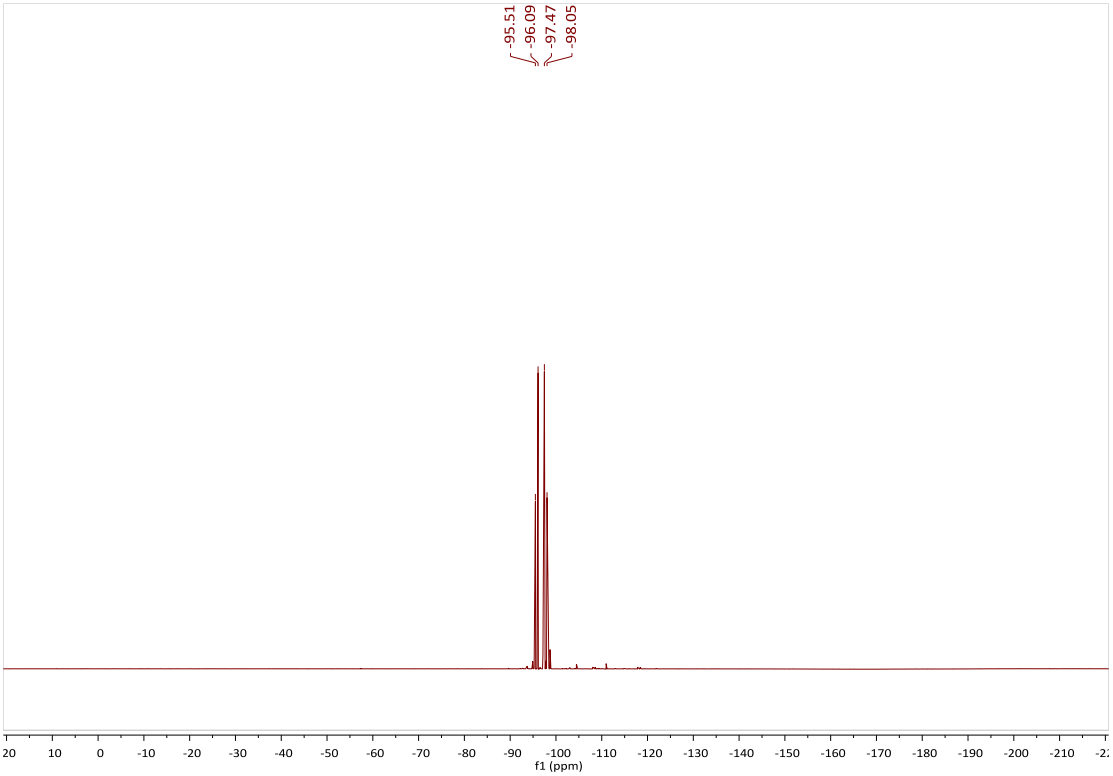


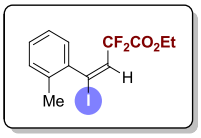


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5p**

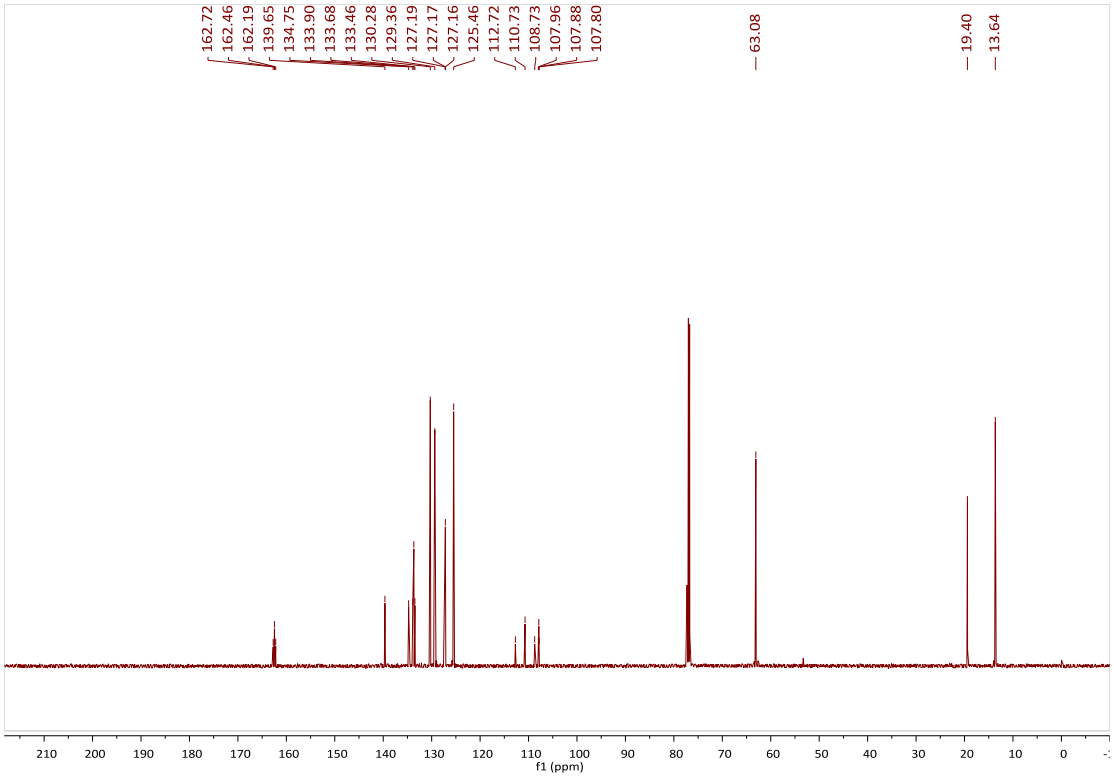


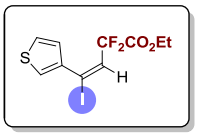
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5p**



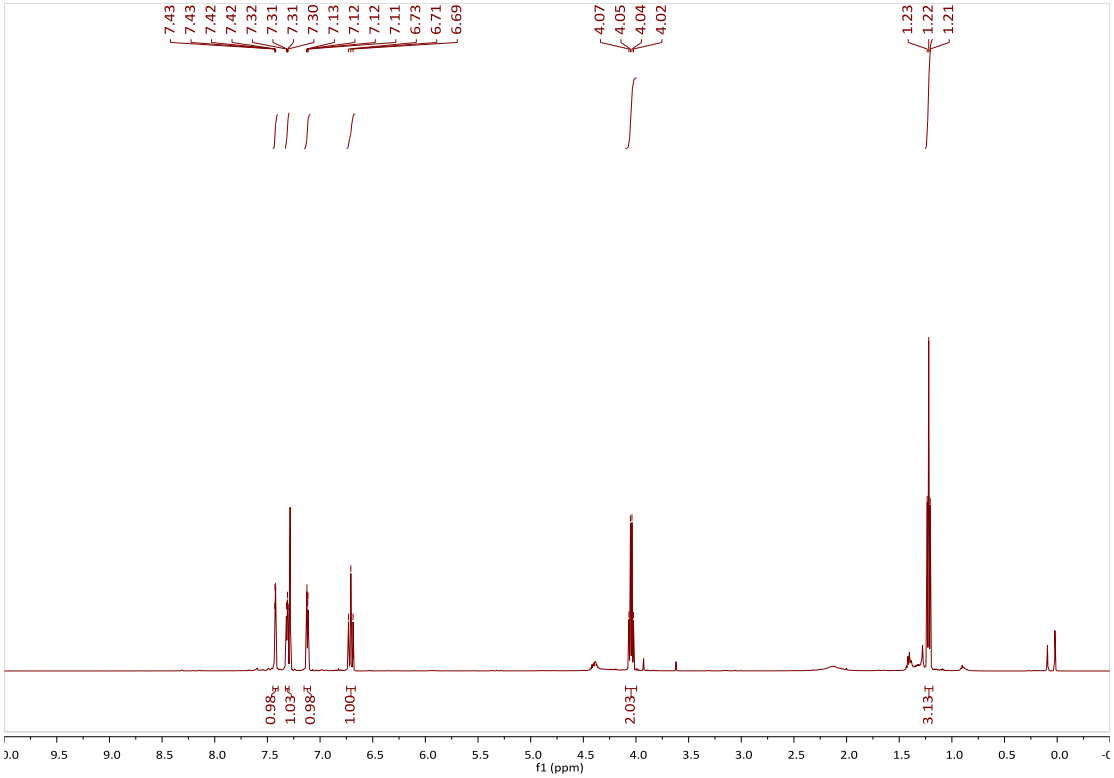


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5p**

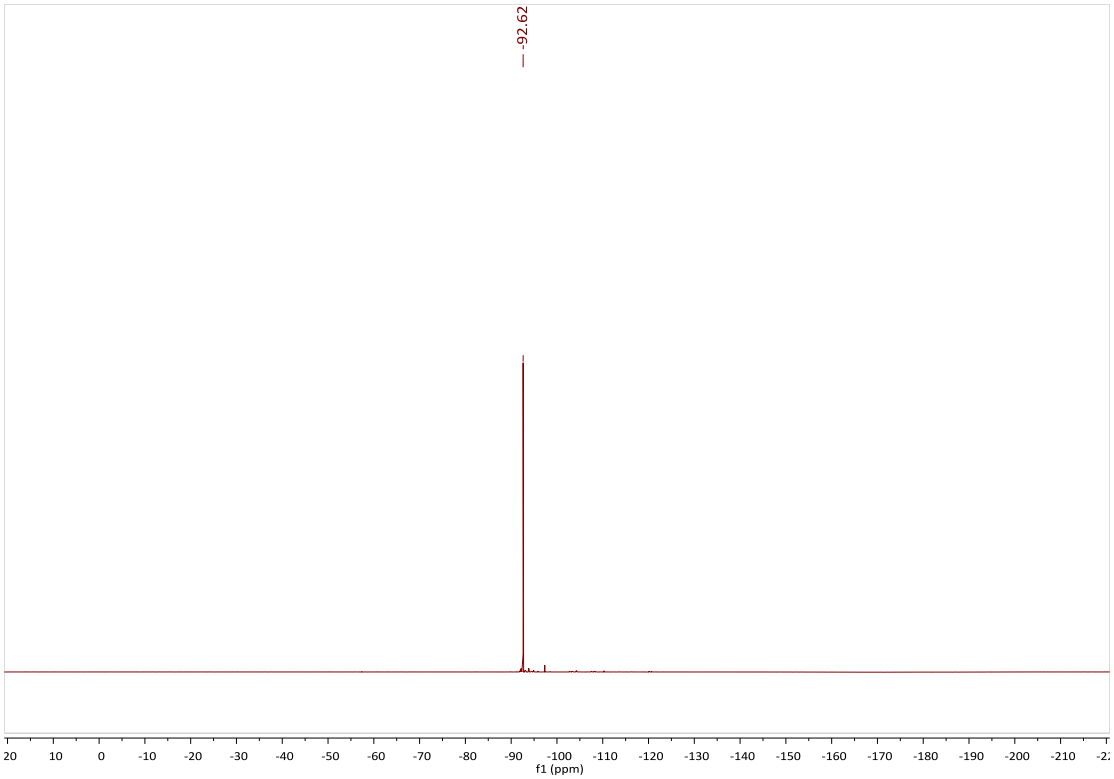


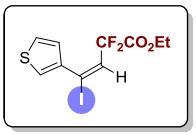


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5q**

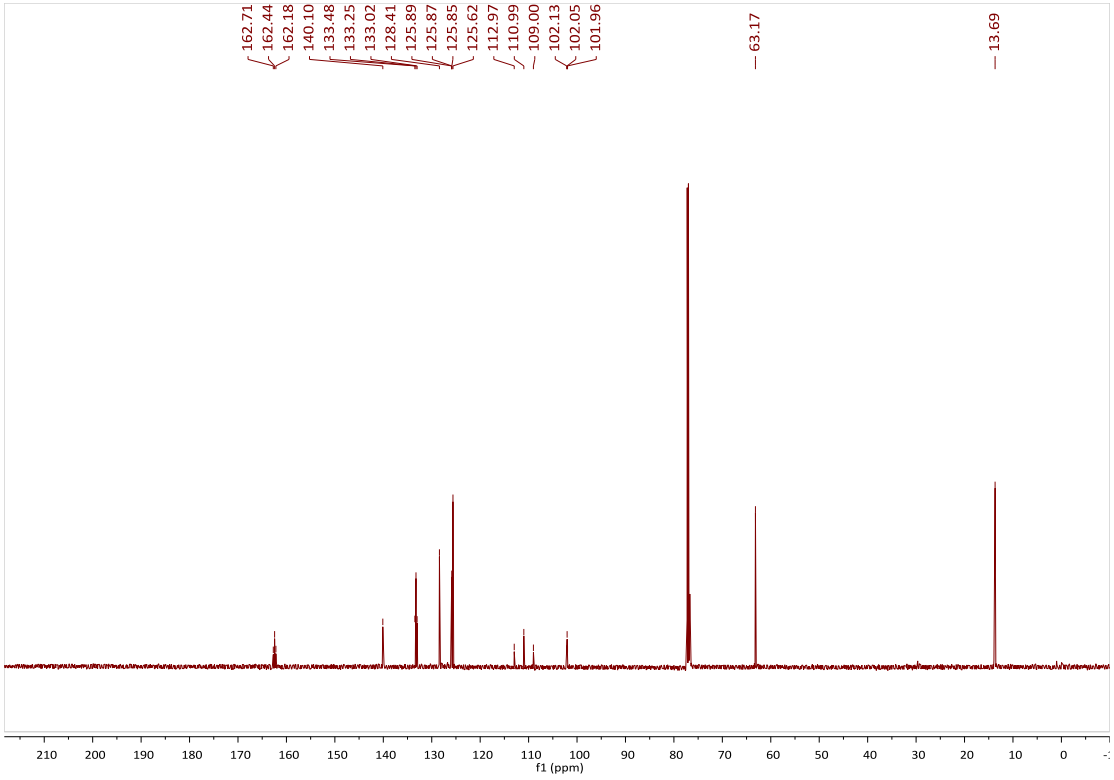


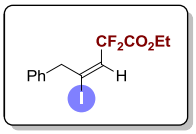
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5q**





^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5q**





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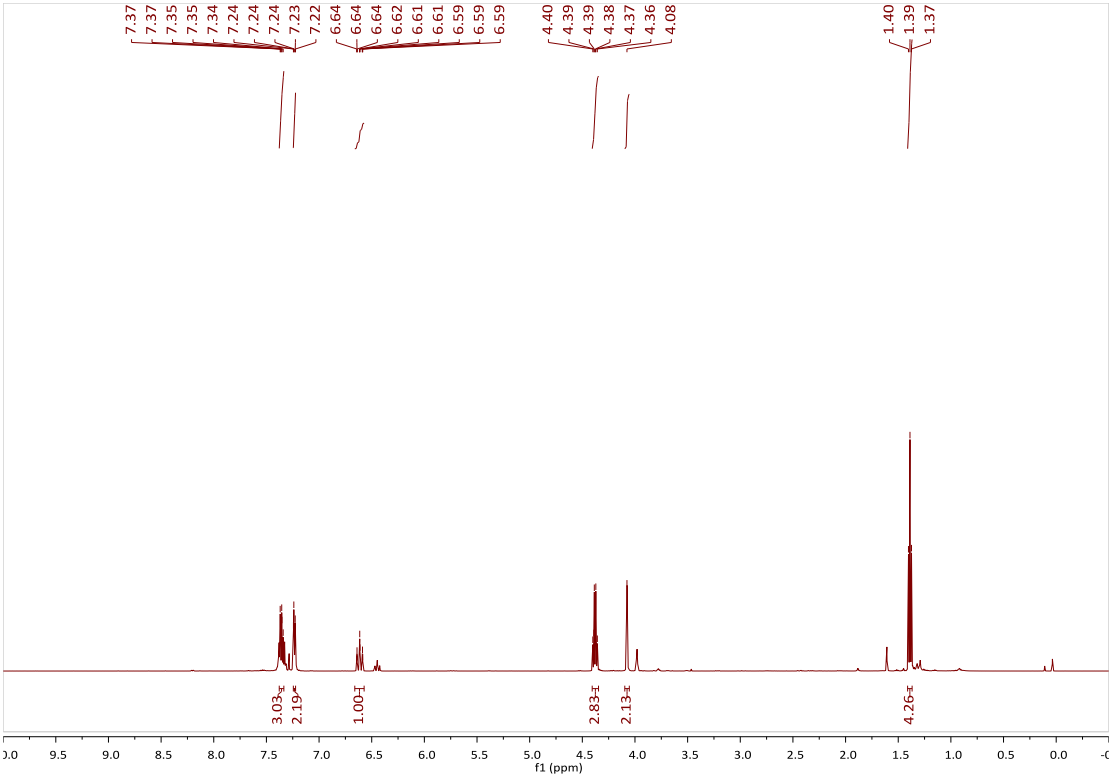
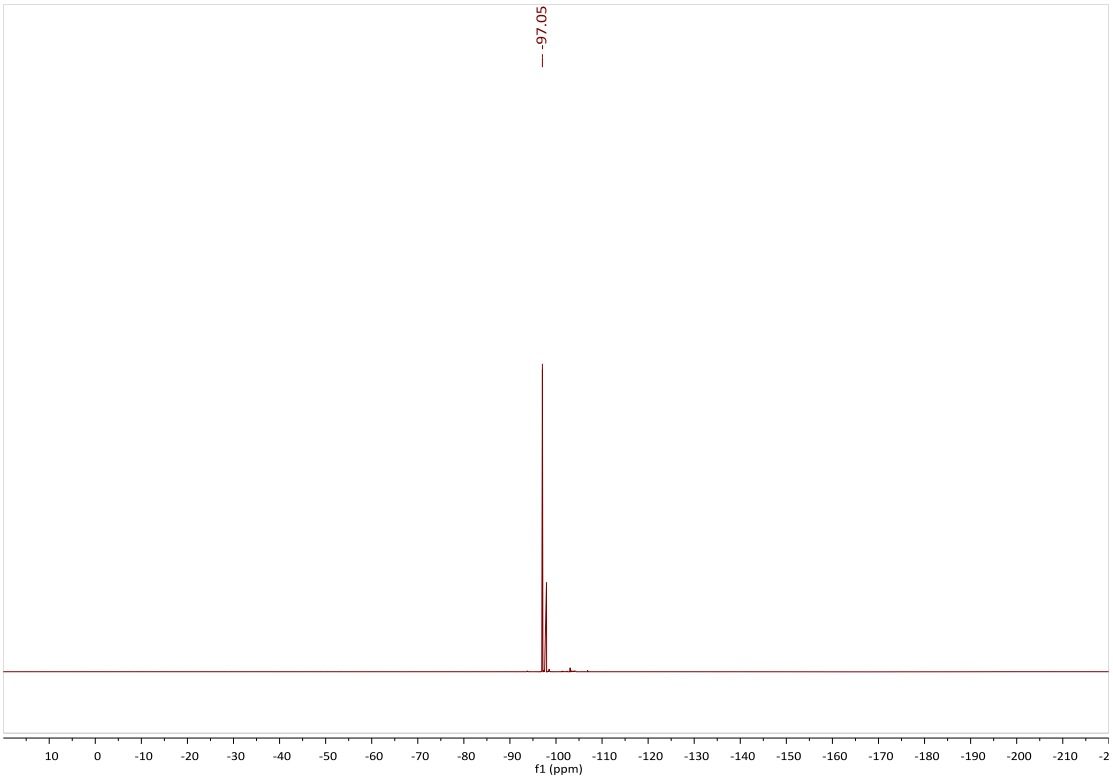
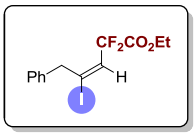
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5r**



^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5r**





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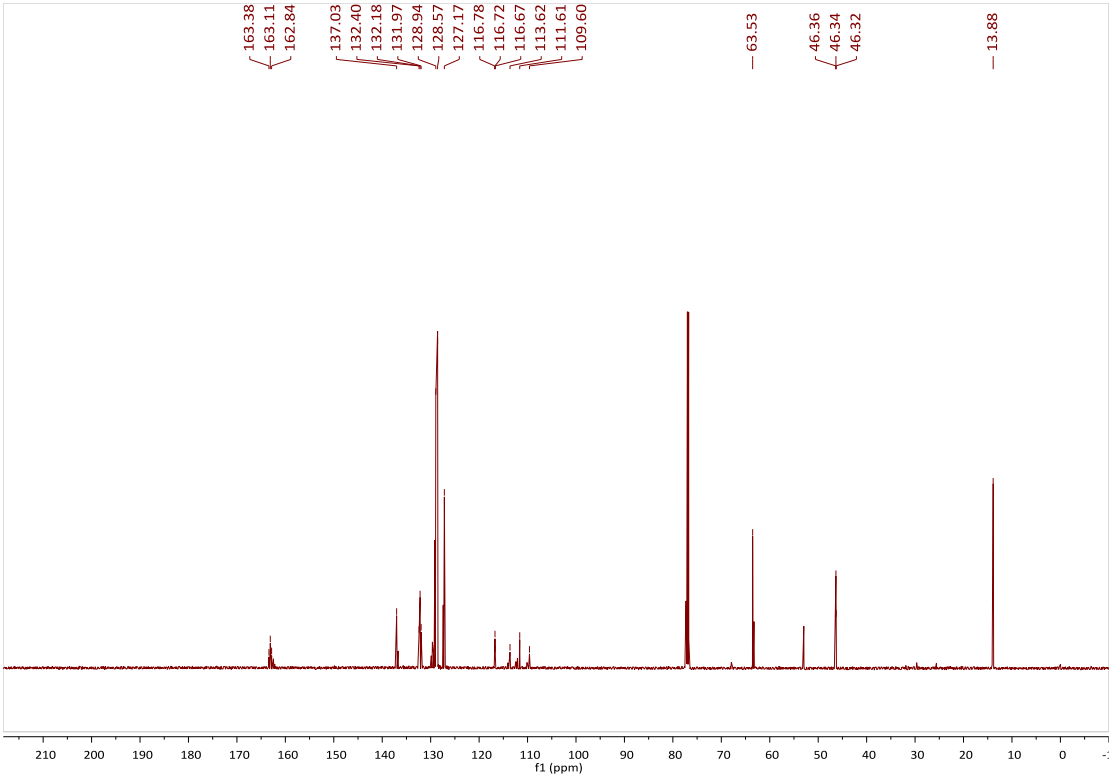
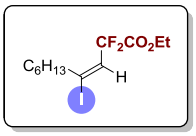
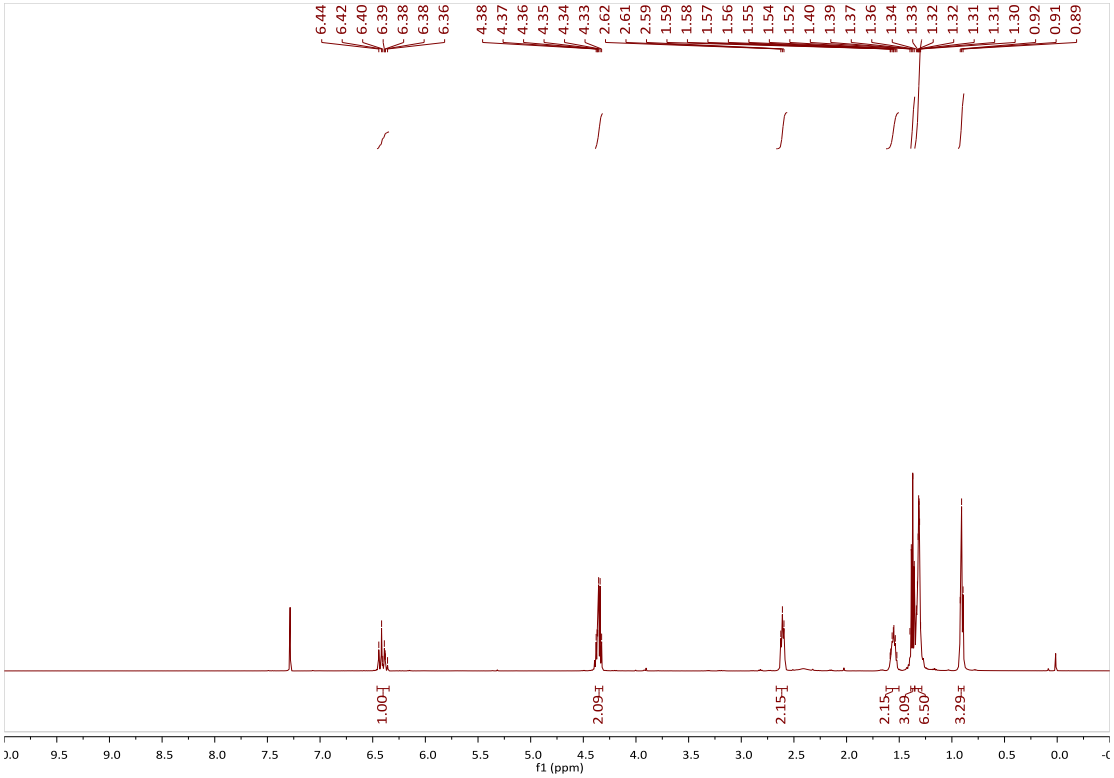
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5r**

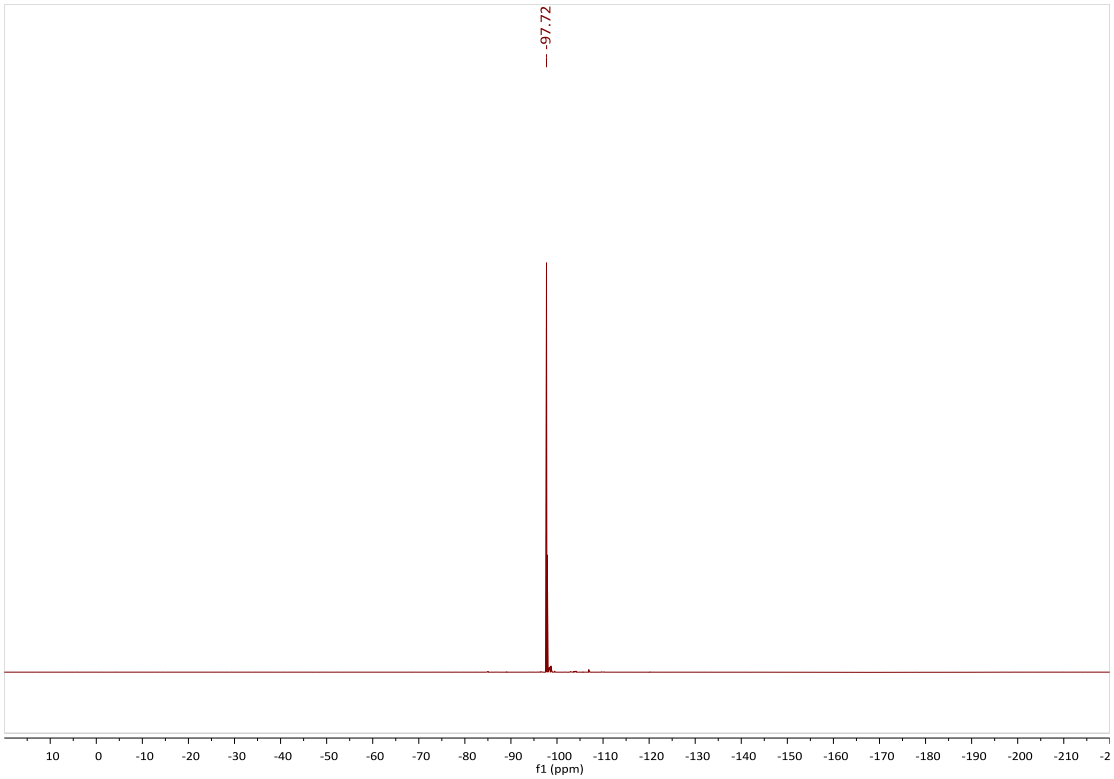


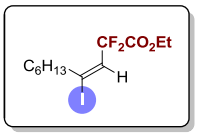


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5s**

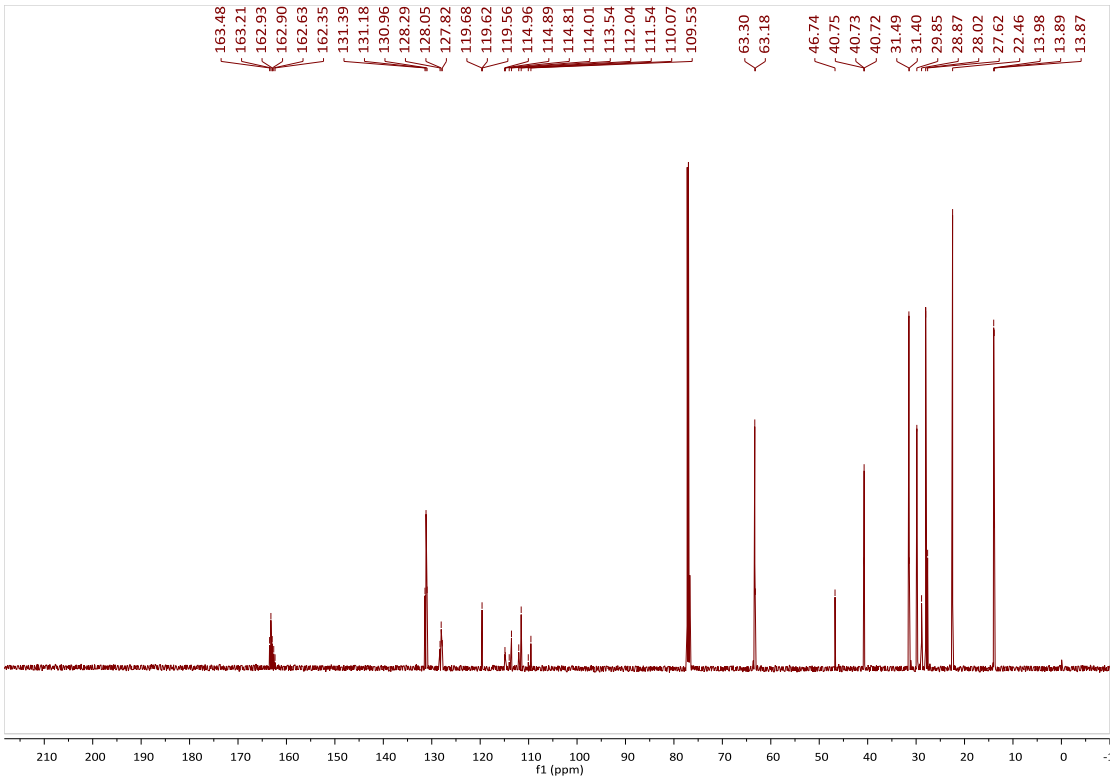


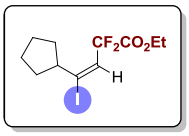
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5s**





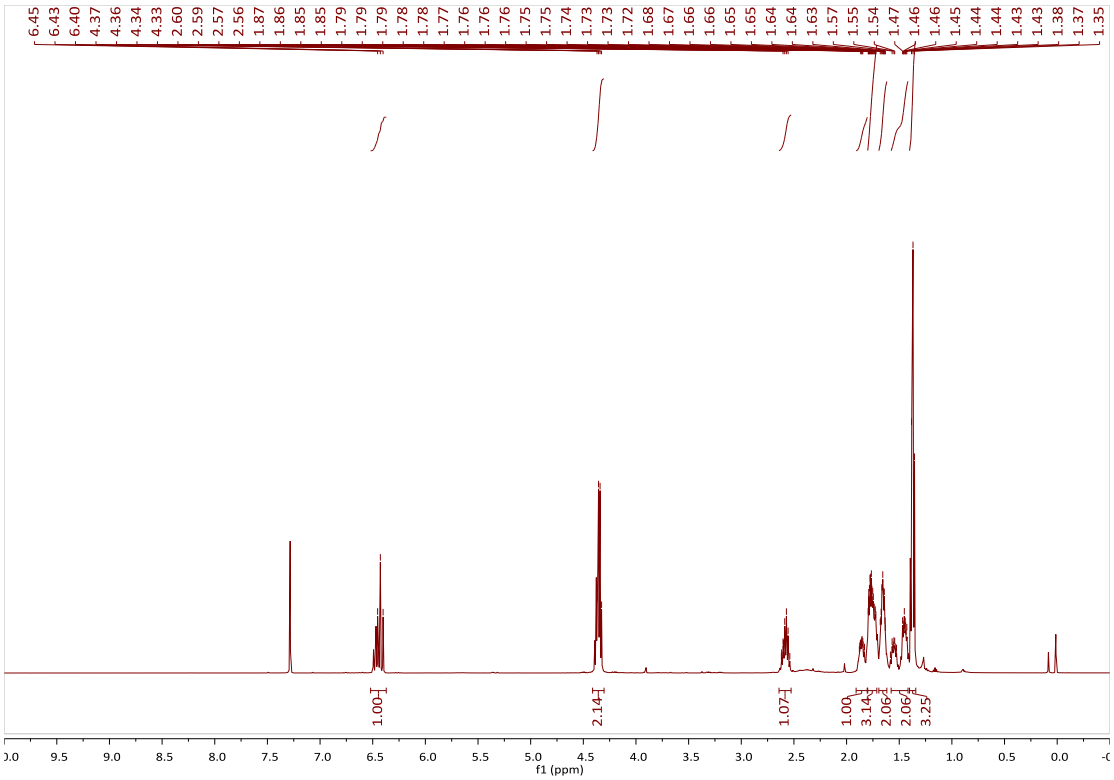
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5s**



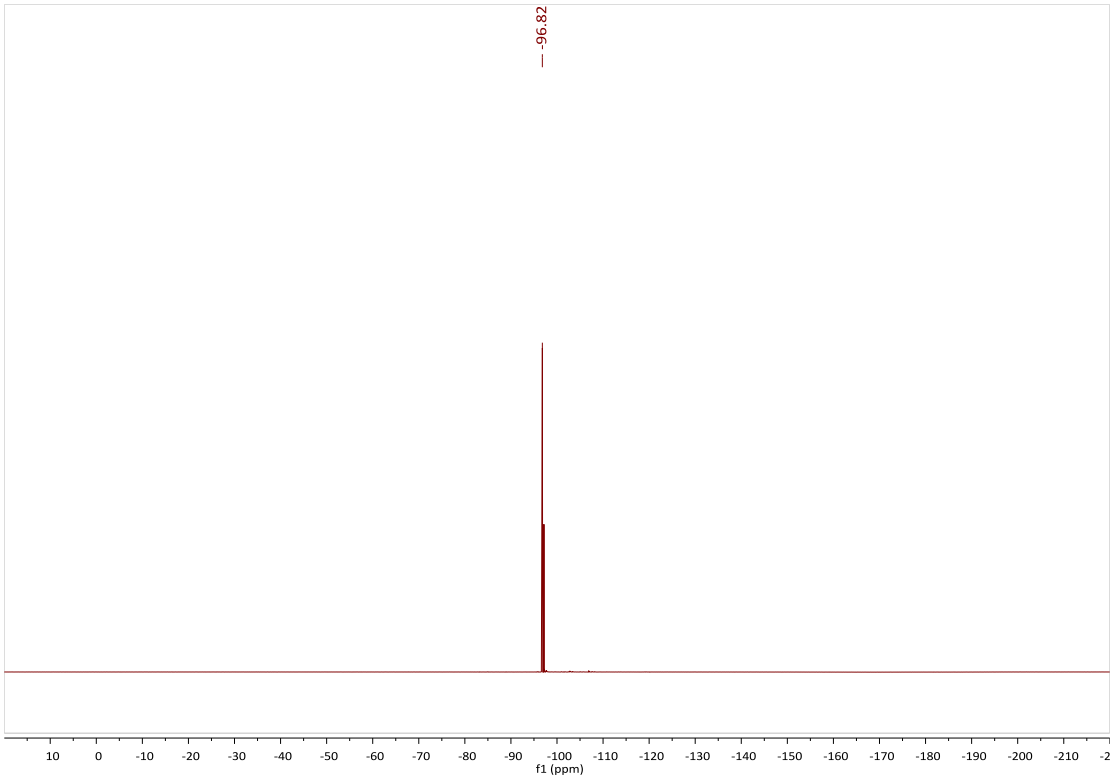


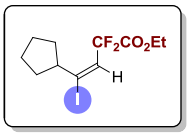
E/Z = 2.0:1

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5t**



^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5t**





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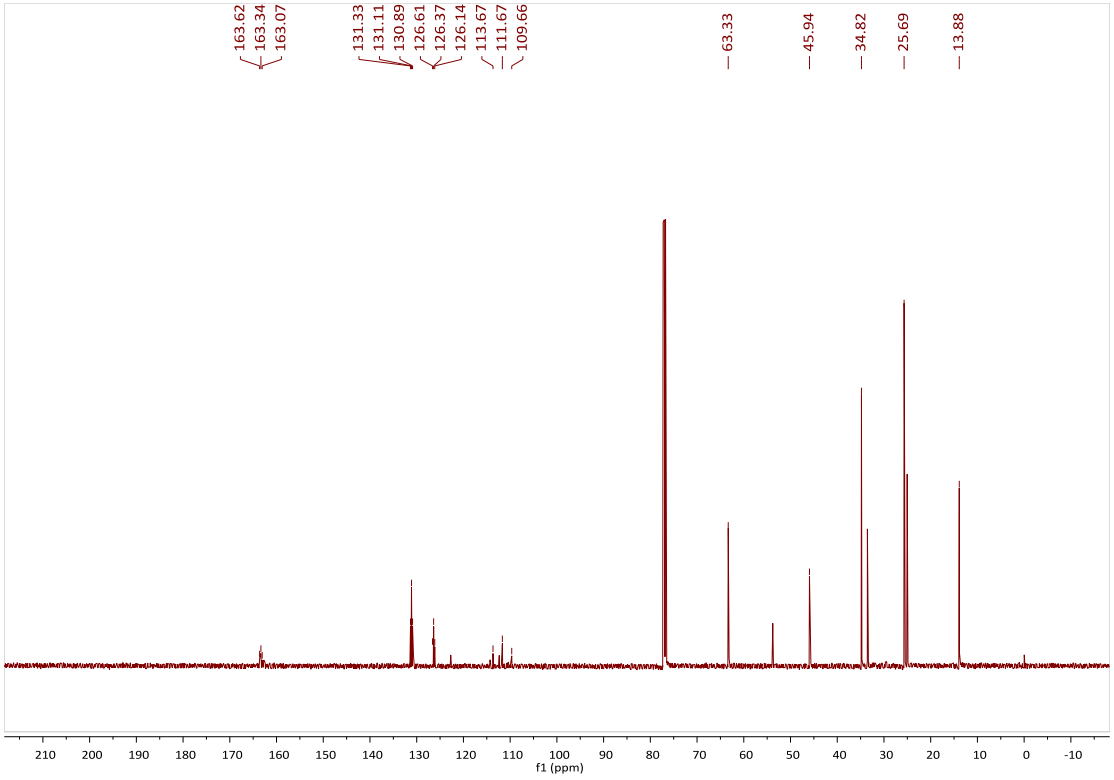
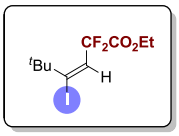
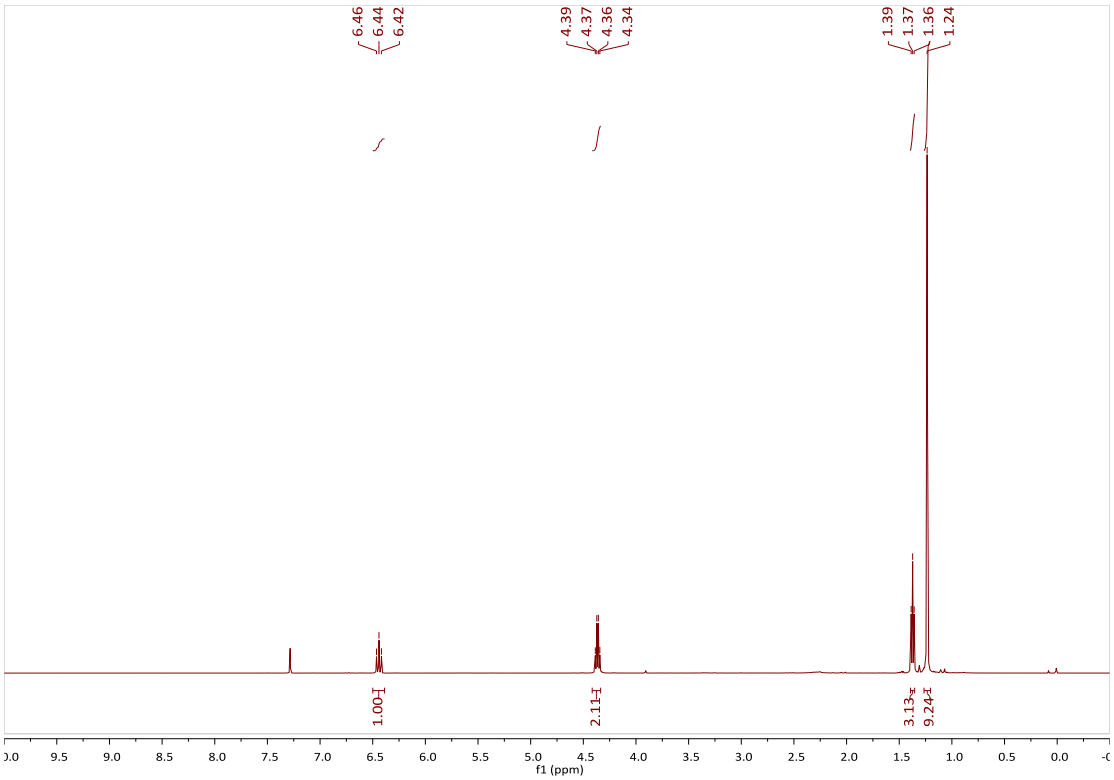
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5t**

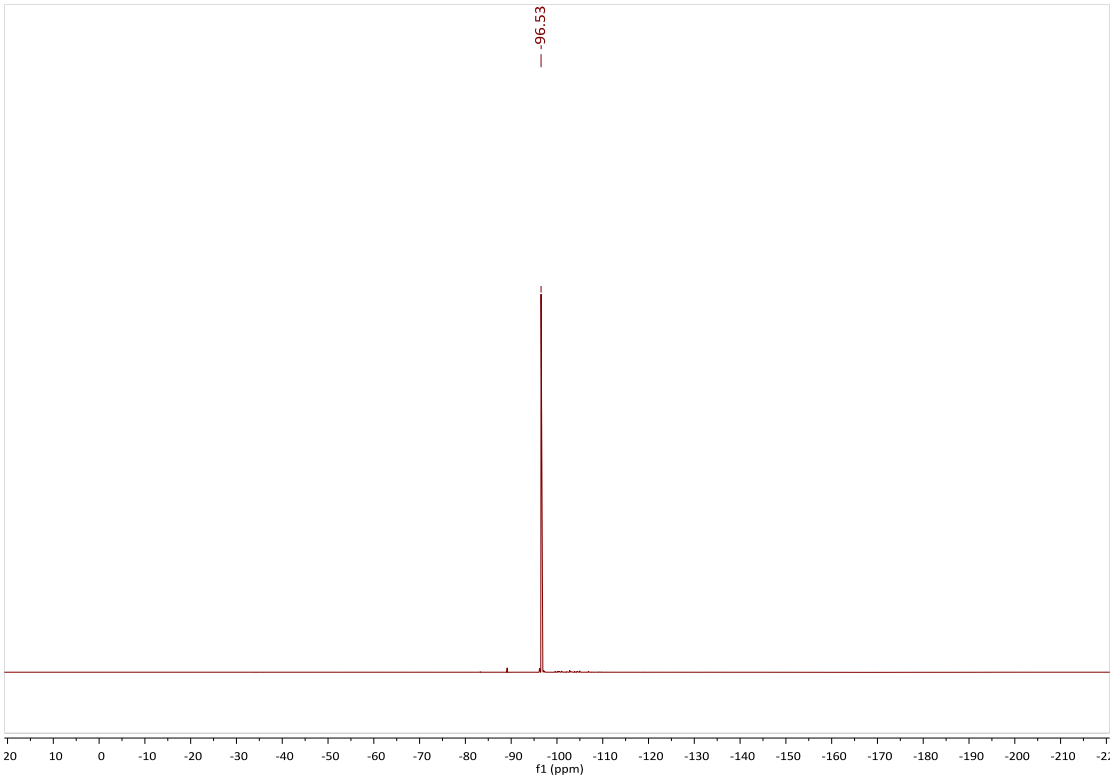


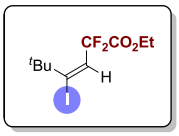


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5u**

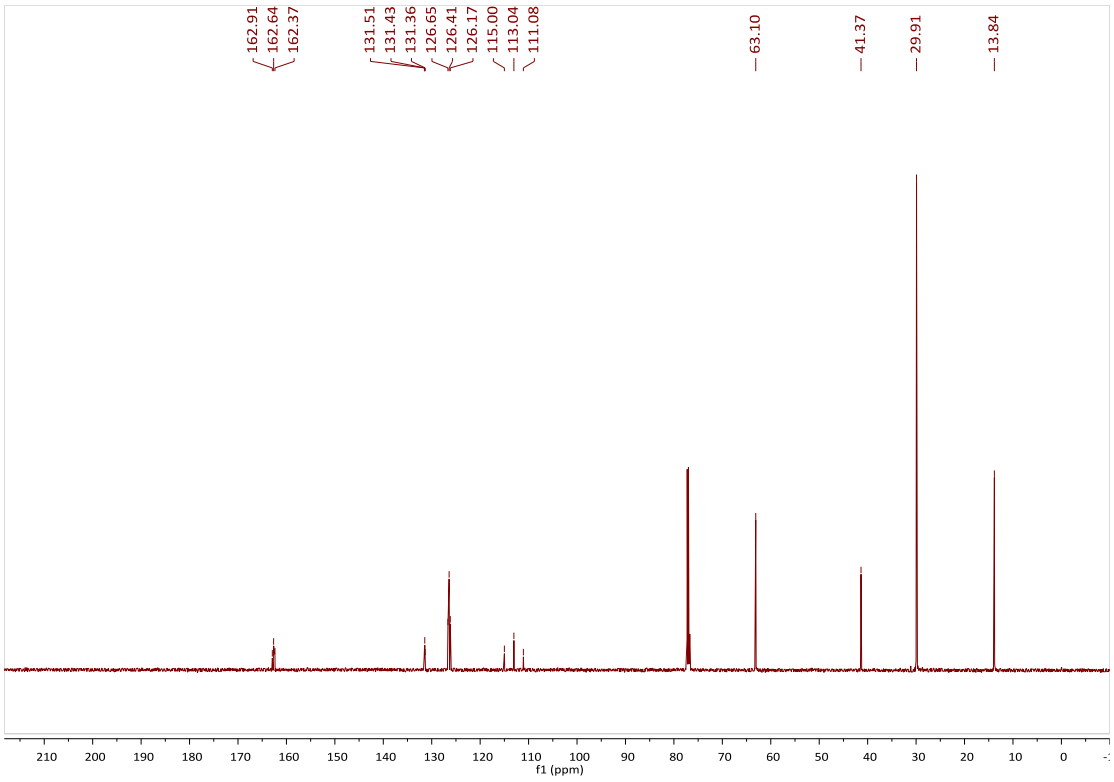


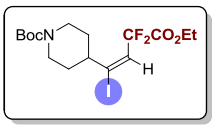
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5u**





^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5u**





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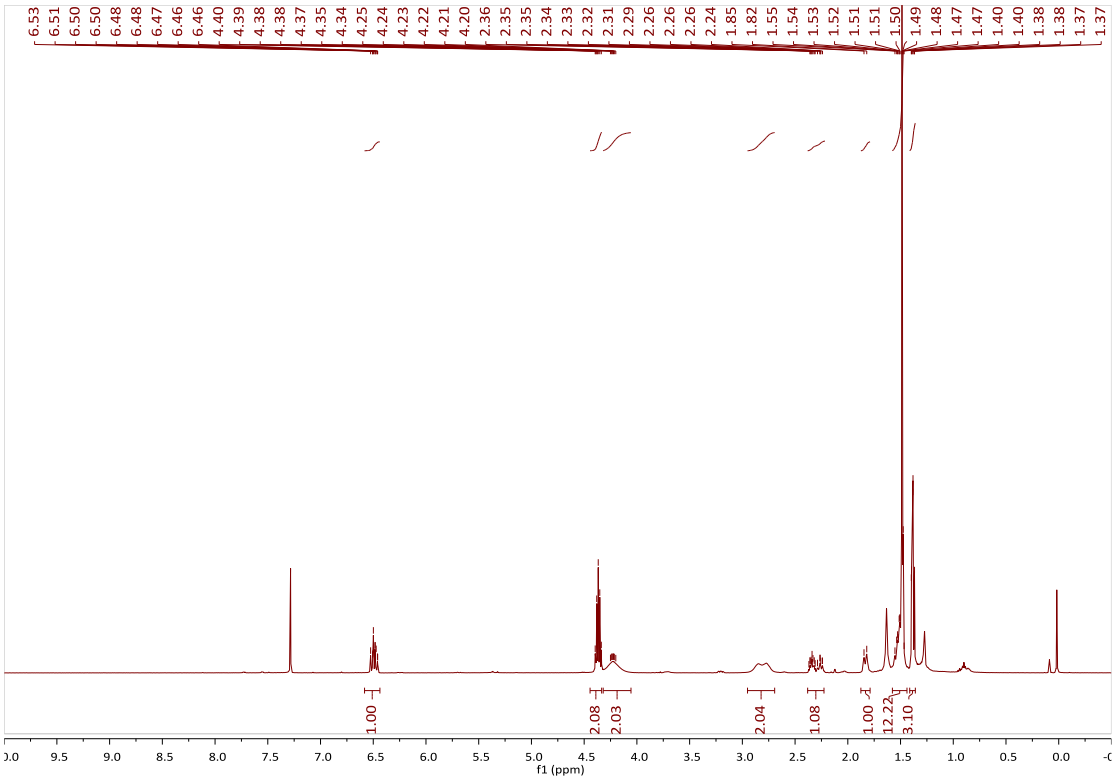
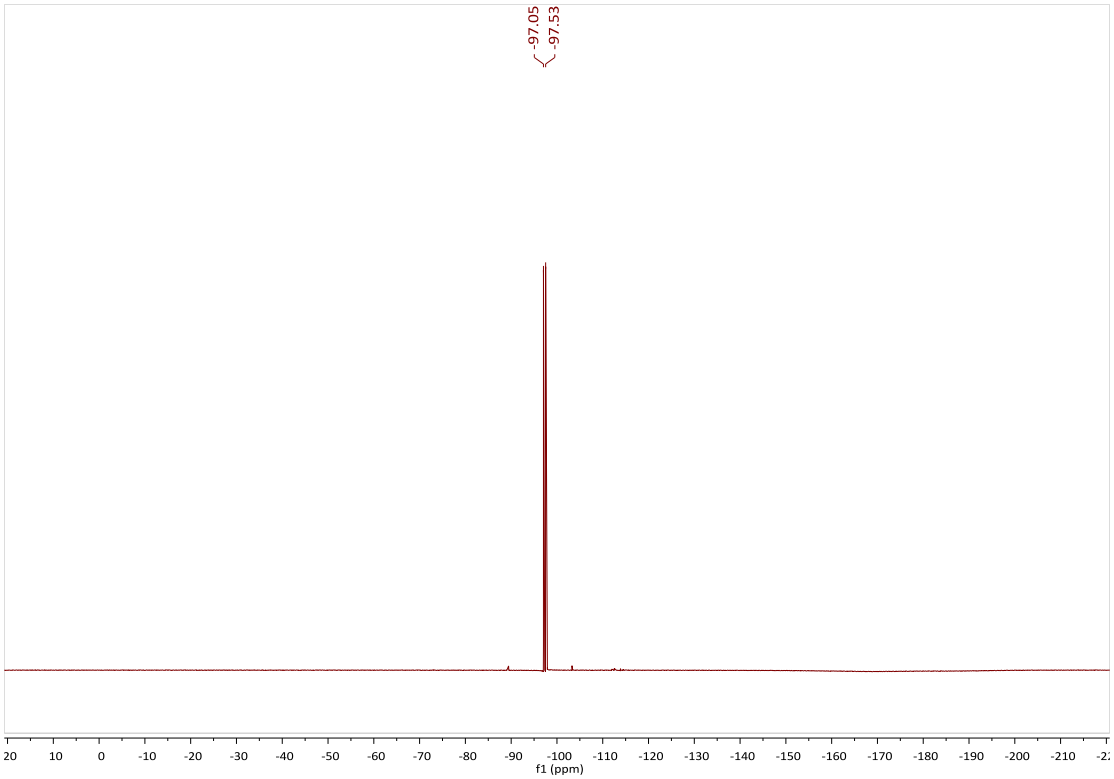
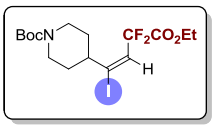
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5v**



^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5v**





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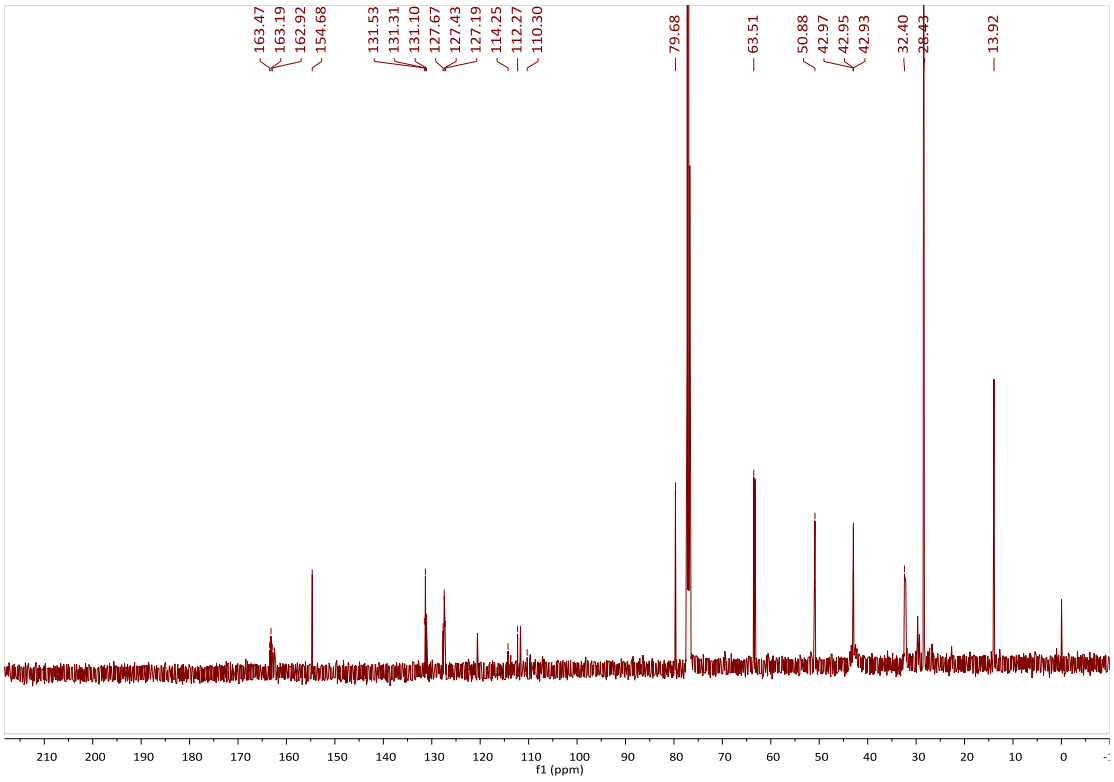
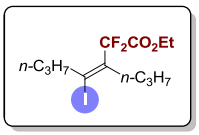
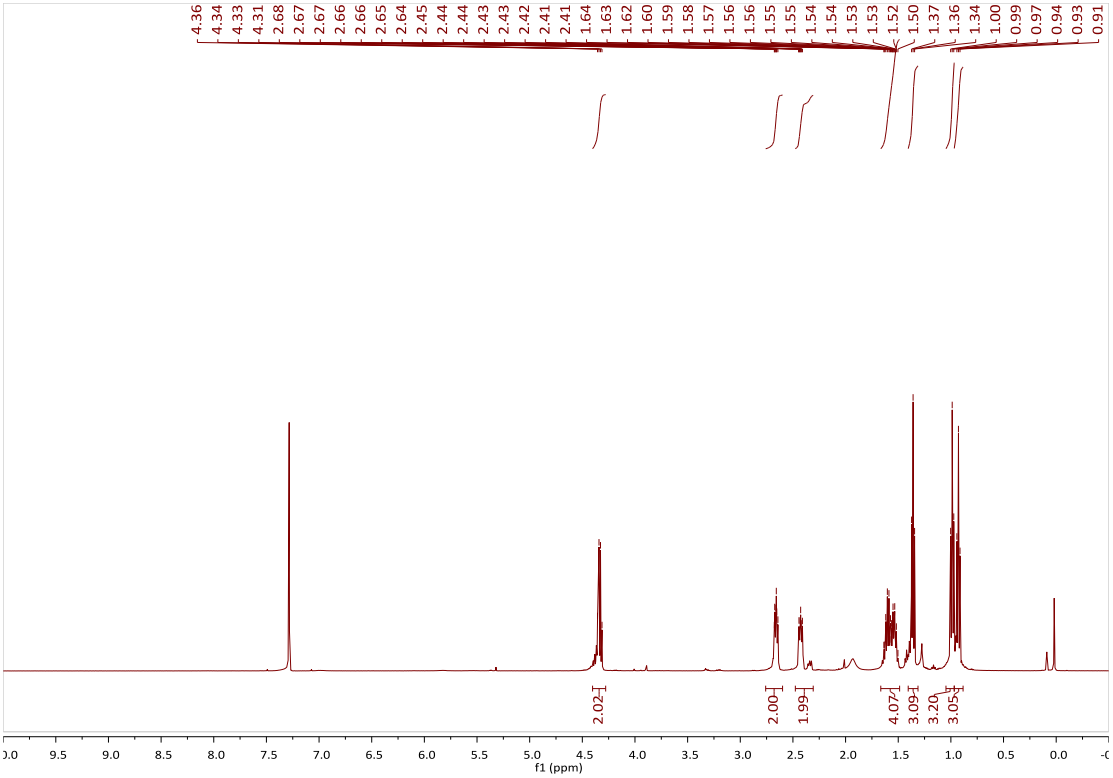
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5v**

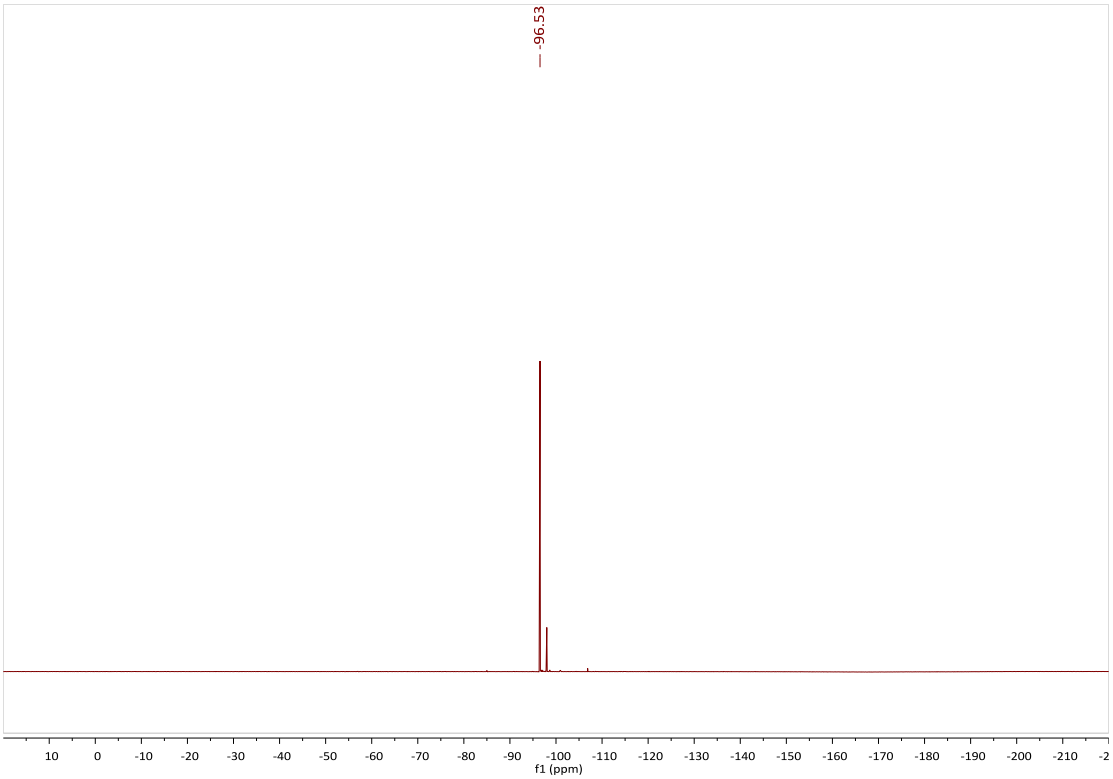


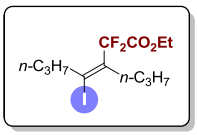


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5w**

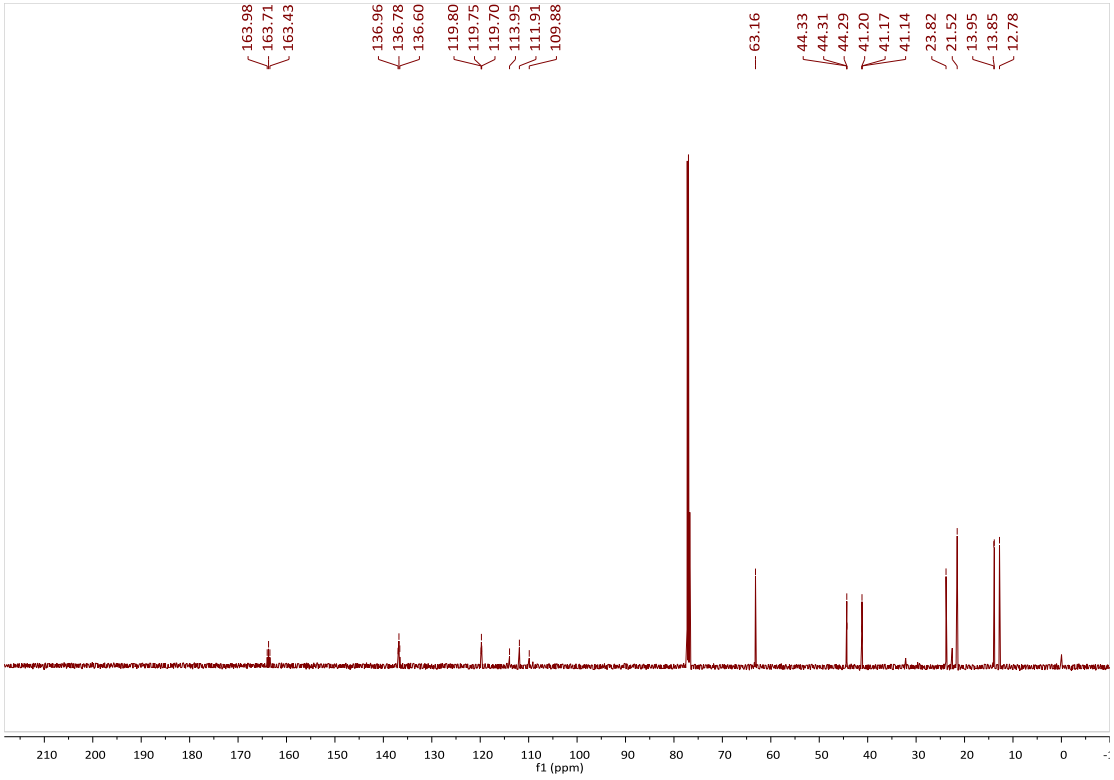


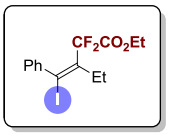
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5w**



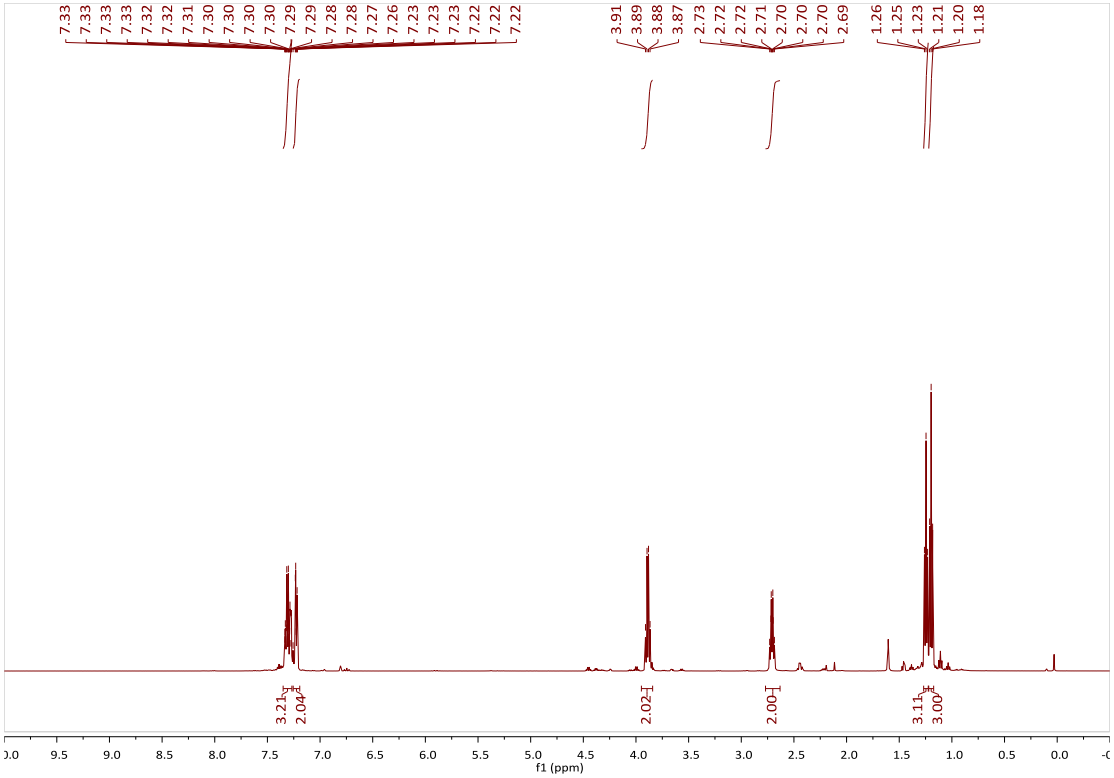


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5w**

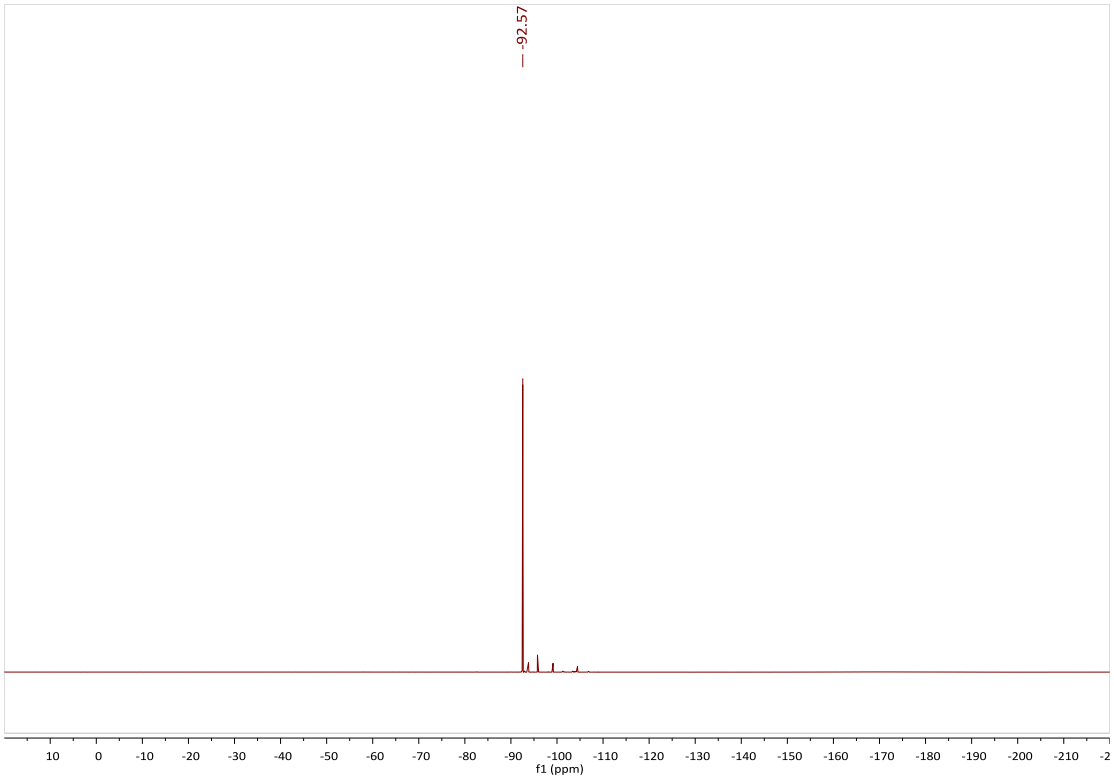


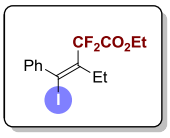


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5x**

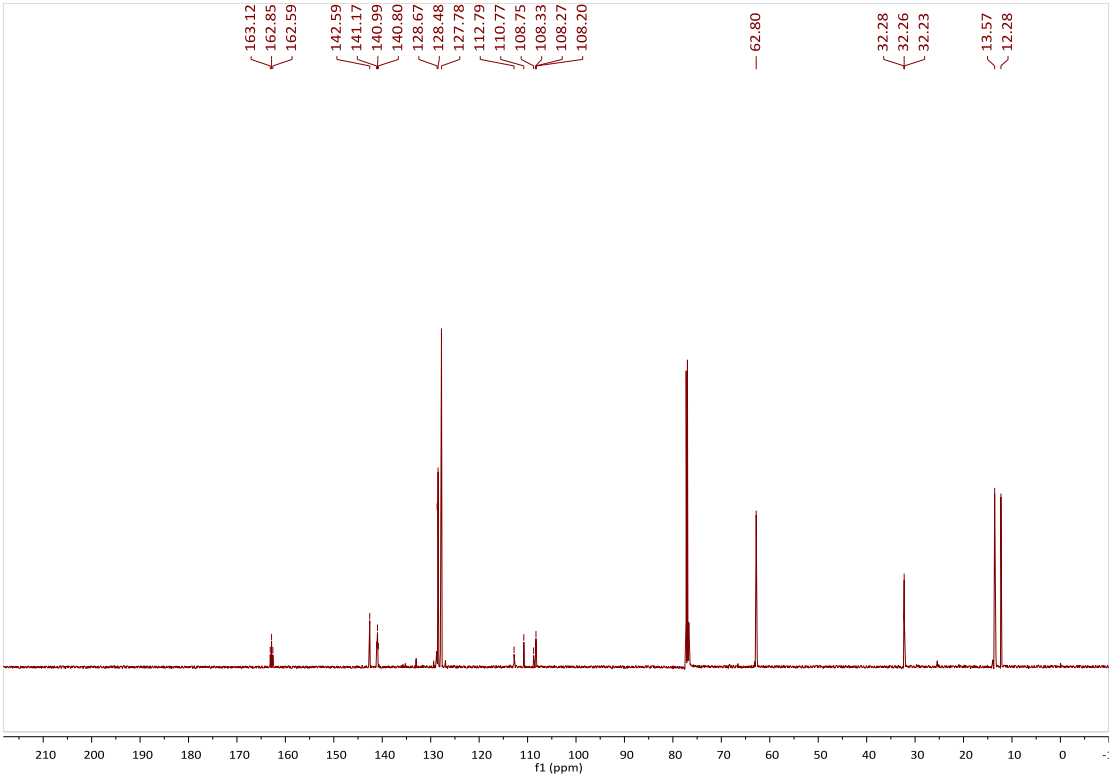


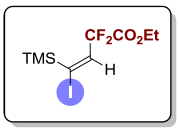
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5x**





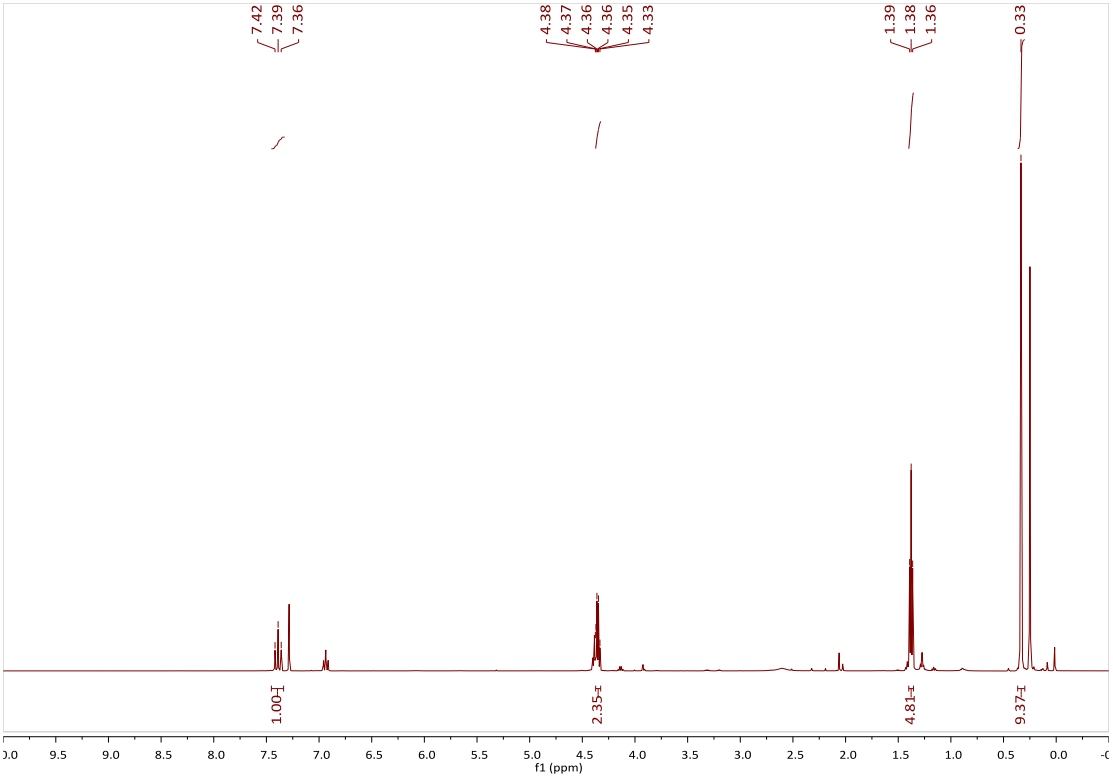
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5x**



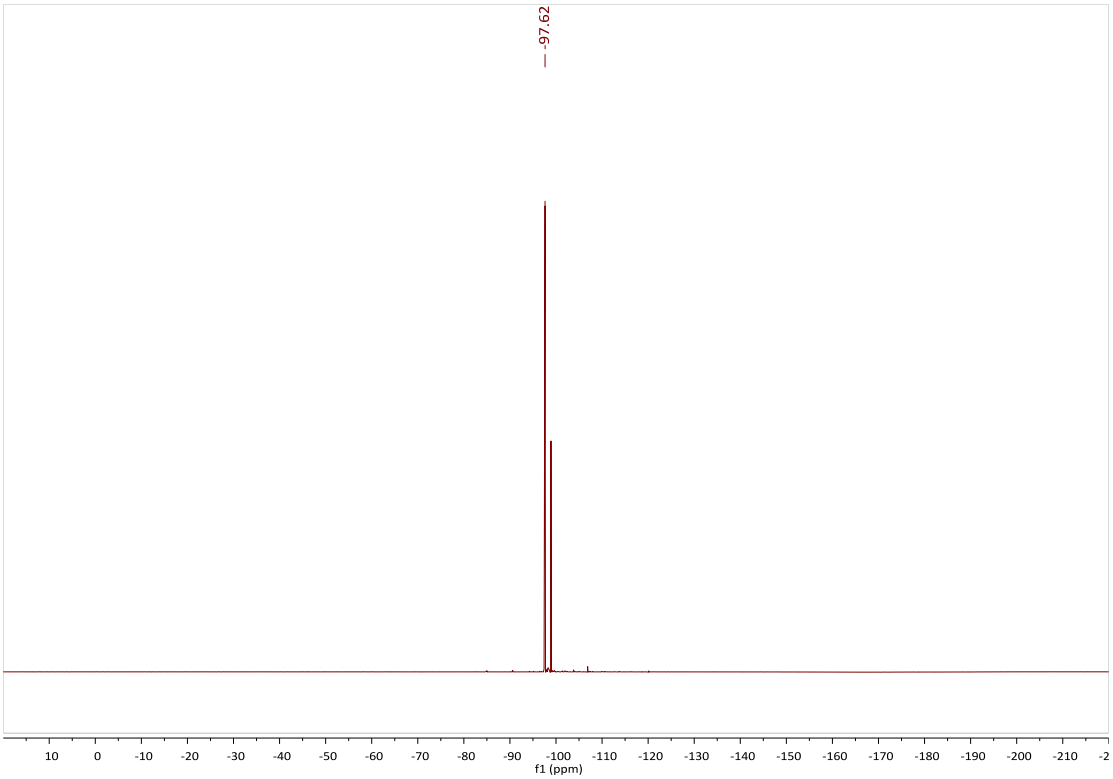


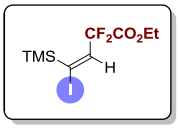
E/*Z* = 2:1

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5y**



^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5y**





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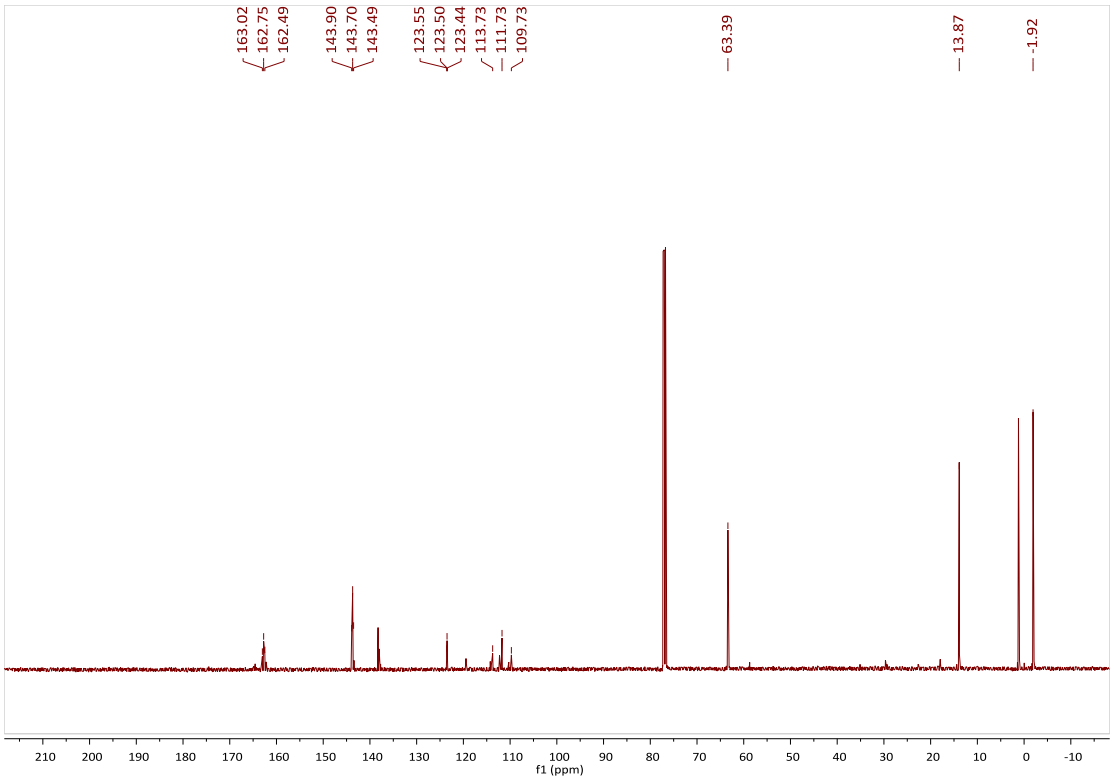
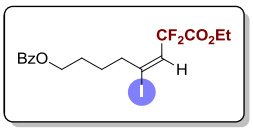
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5y**





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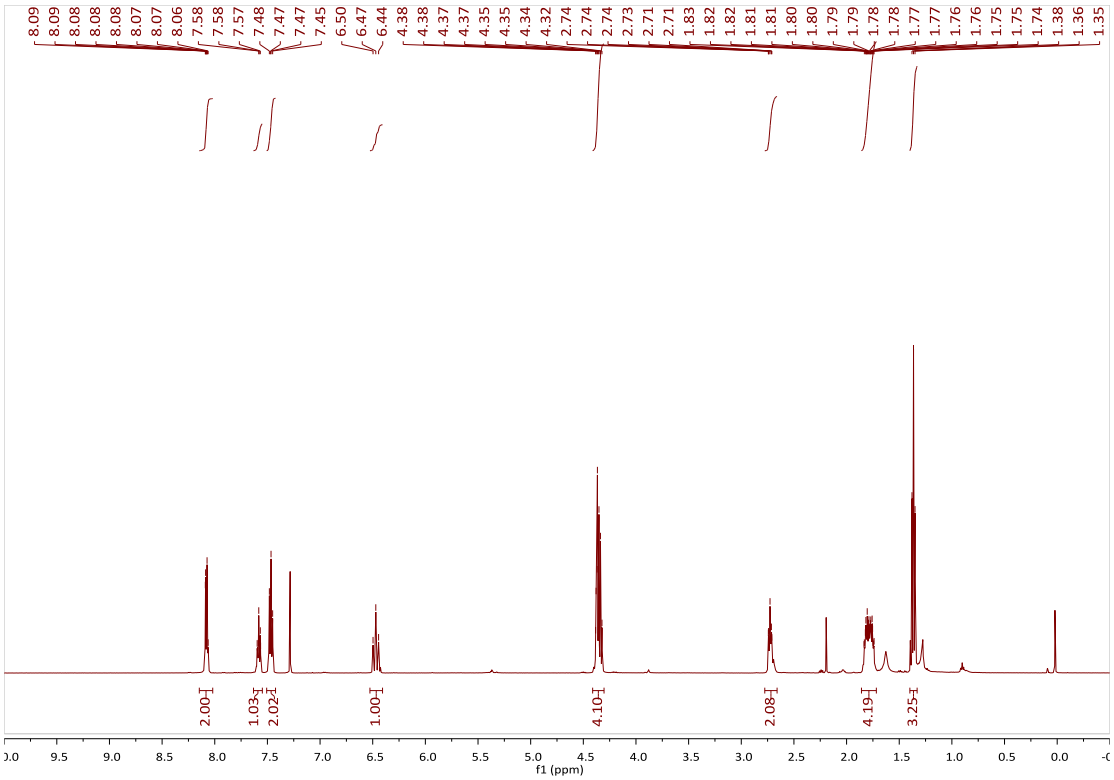
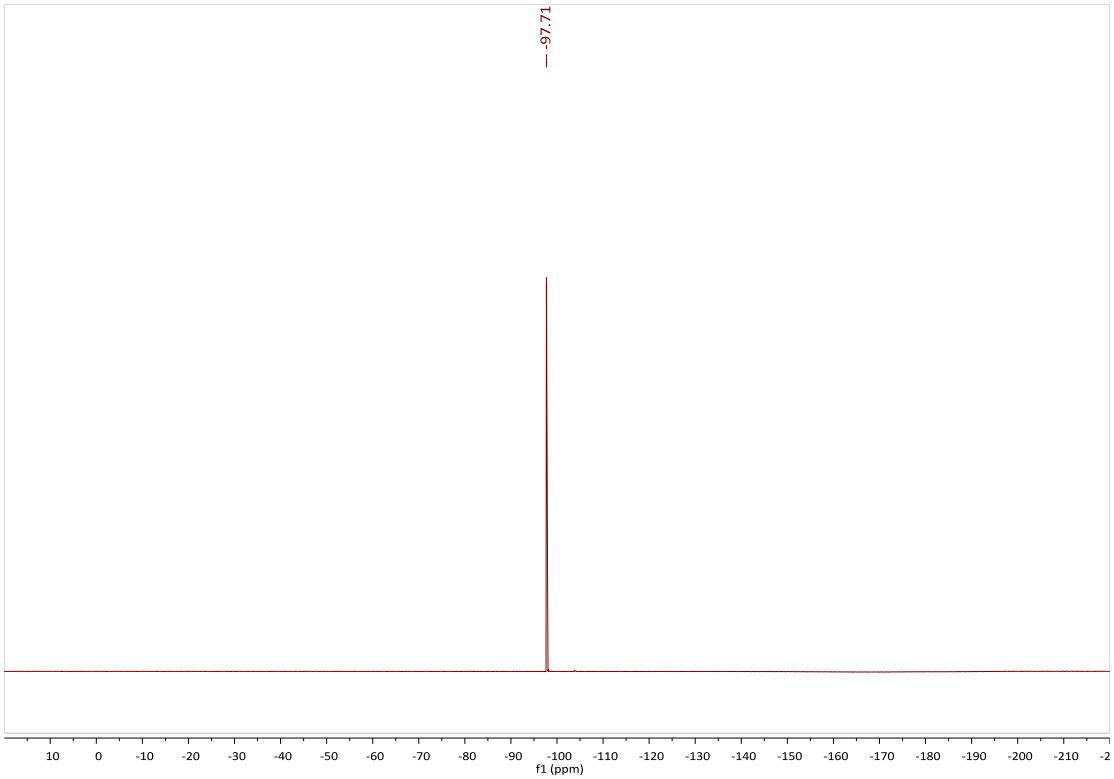
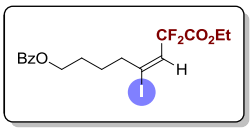
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5z**



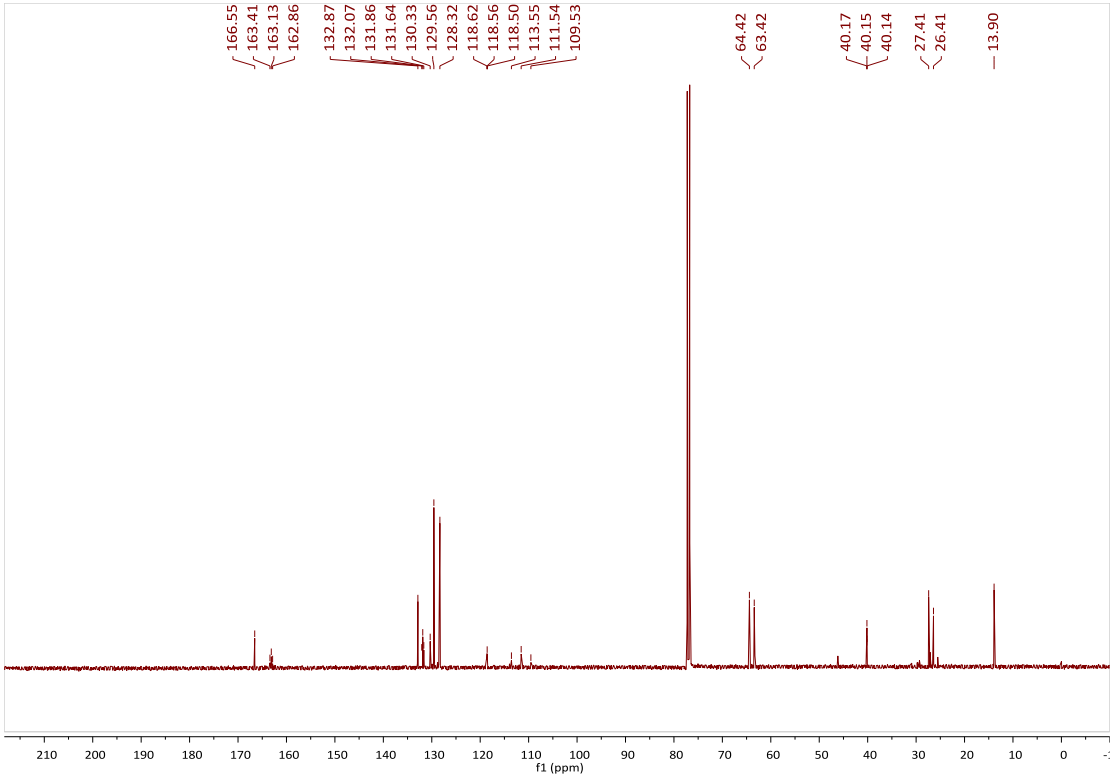
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5z**

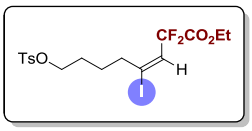




E/*Z* = 5:1

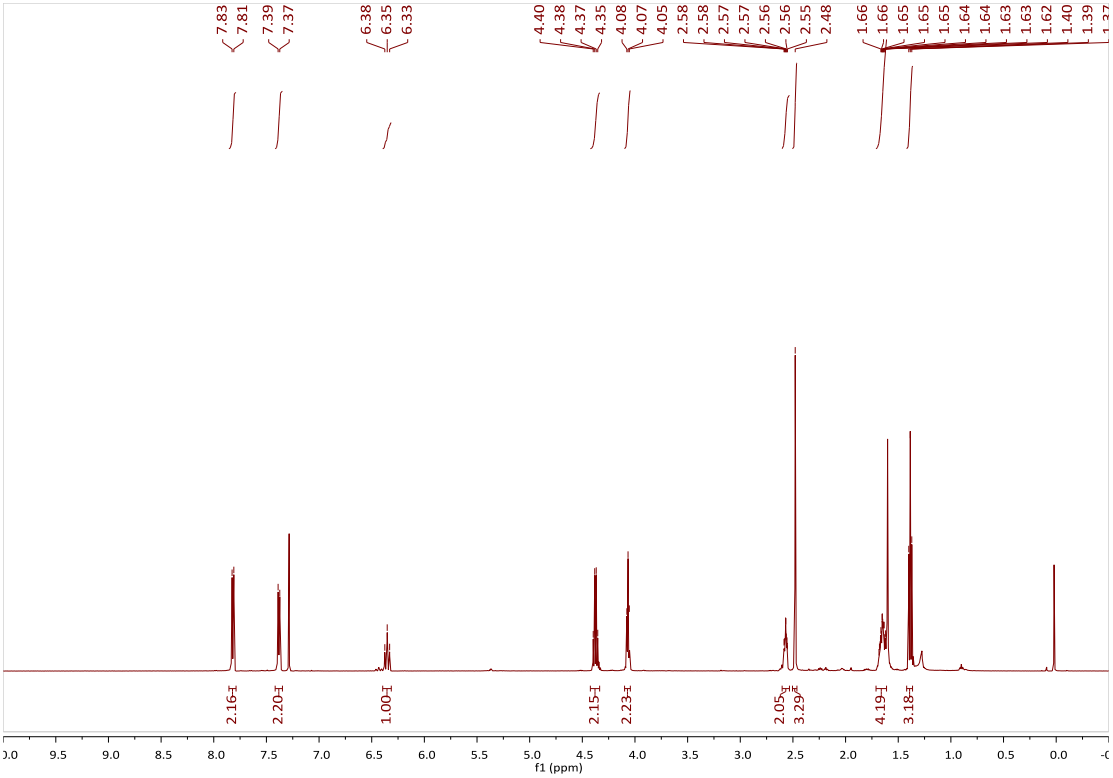
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5z**



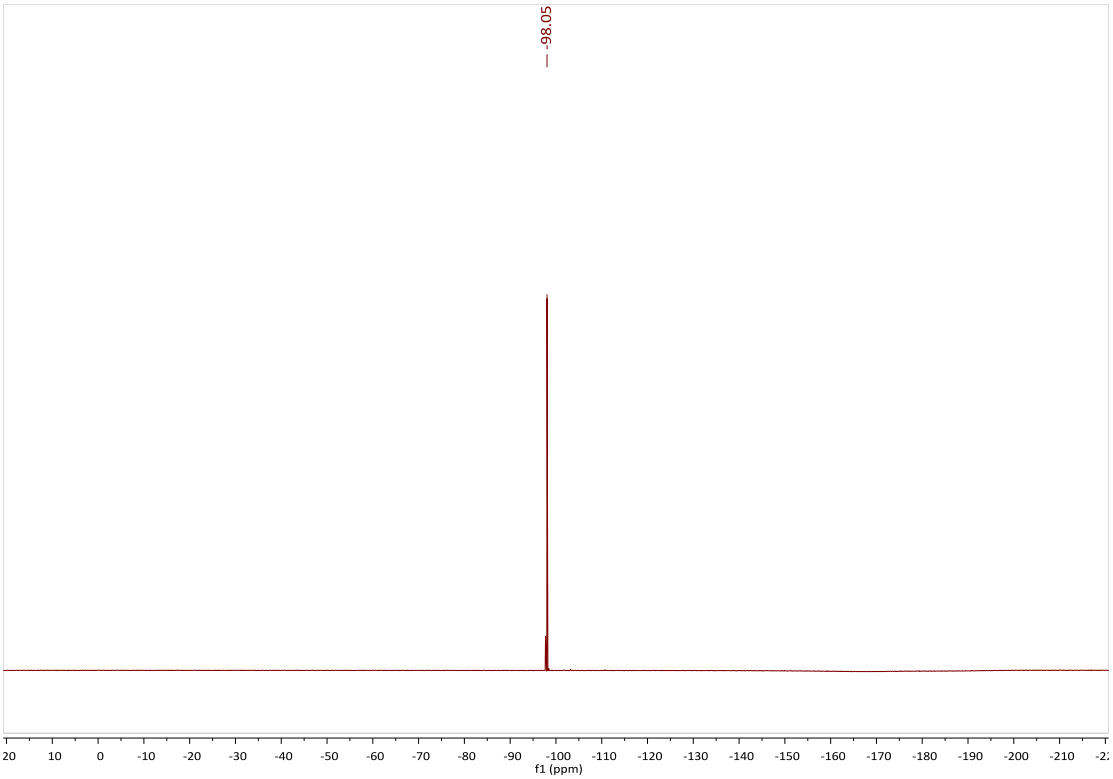


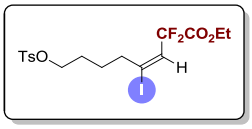
E/*Z* = 4:1

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5aa**



^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5aa**





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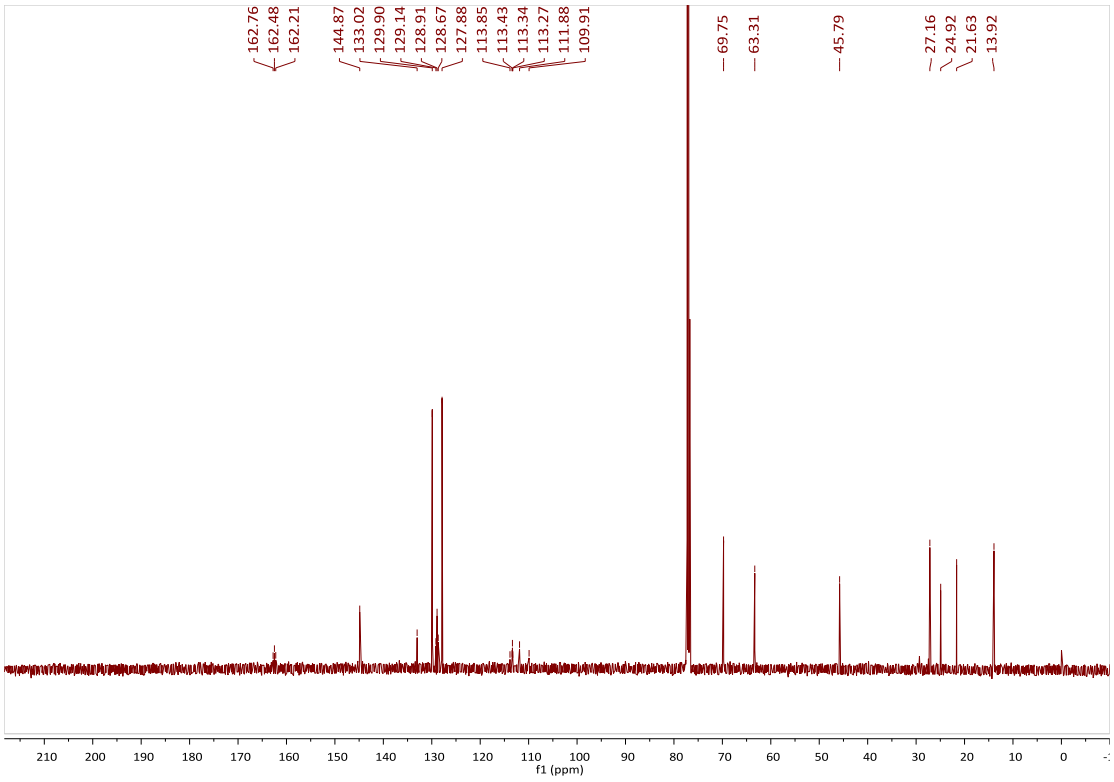
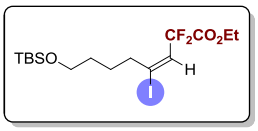
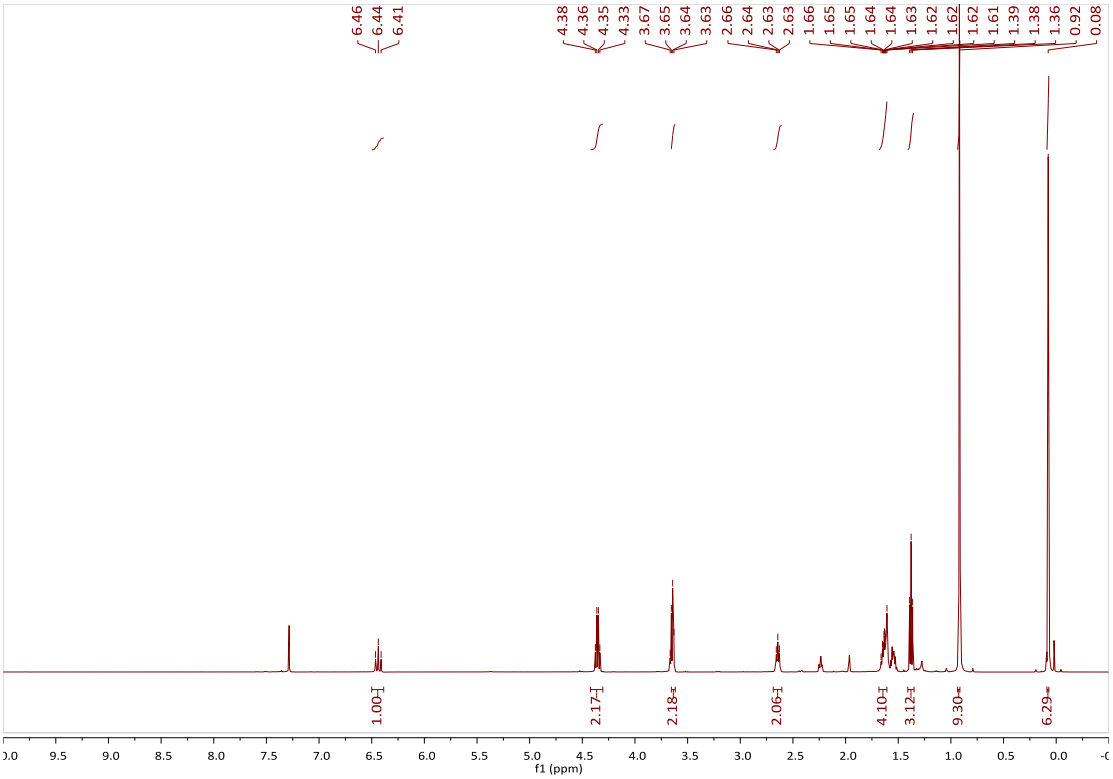
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5aa**



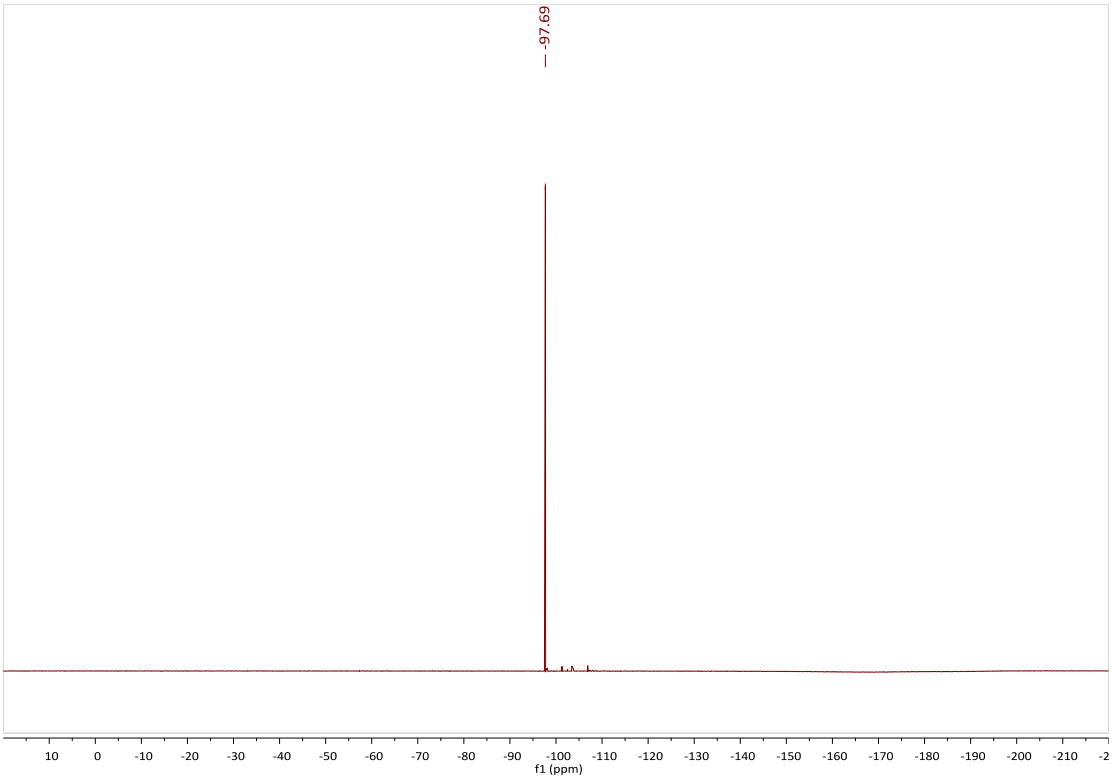


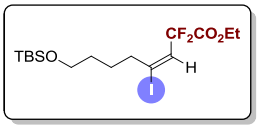
E/*Z* = 3:1

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5ab**



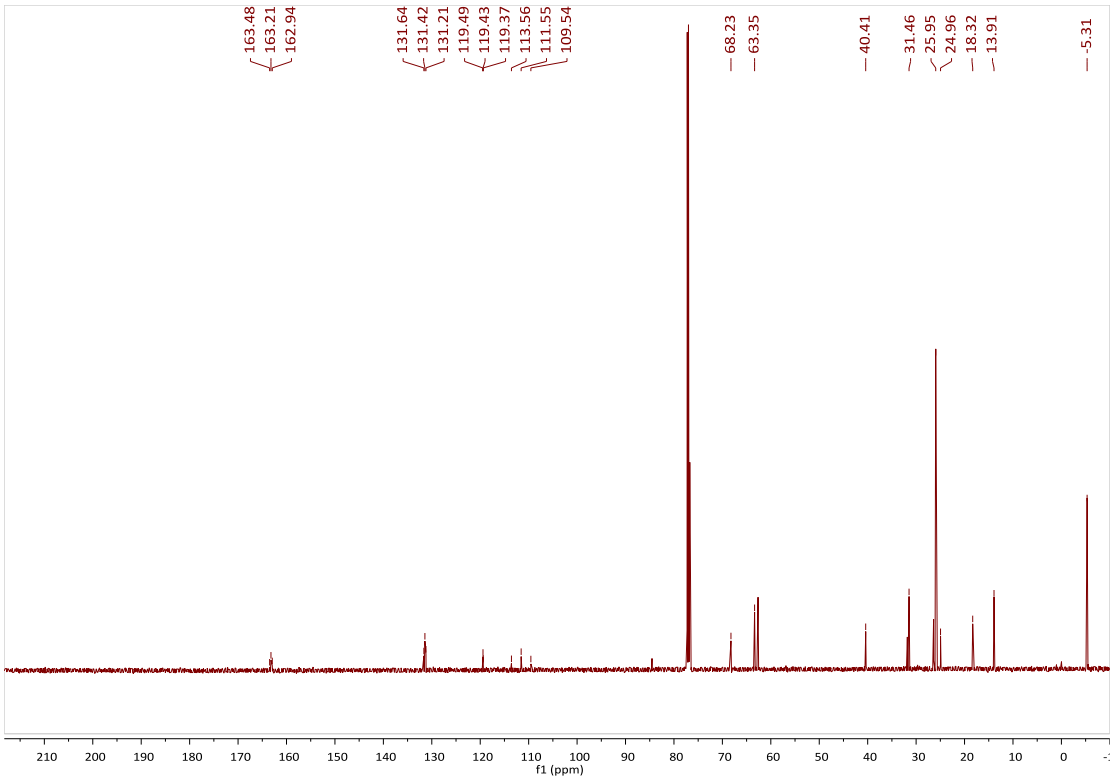
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5ab**

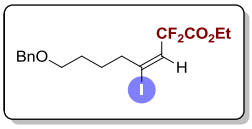




E/*Z* = 3:1

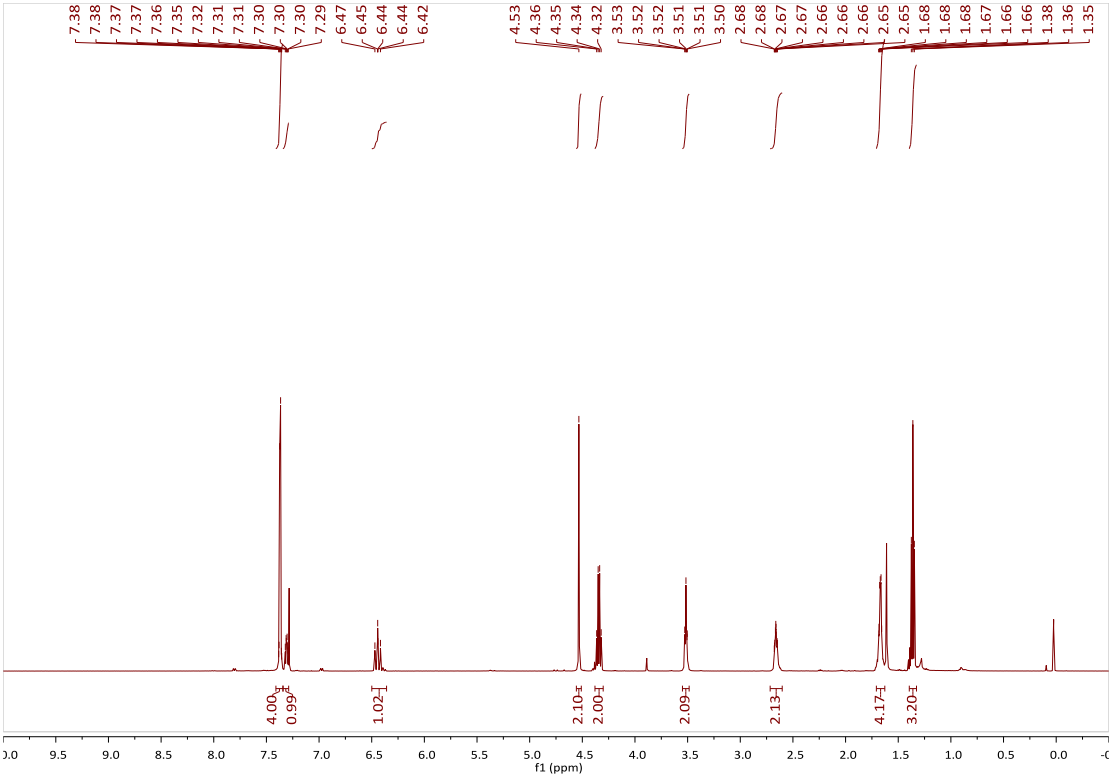
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5ab**



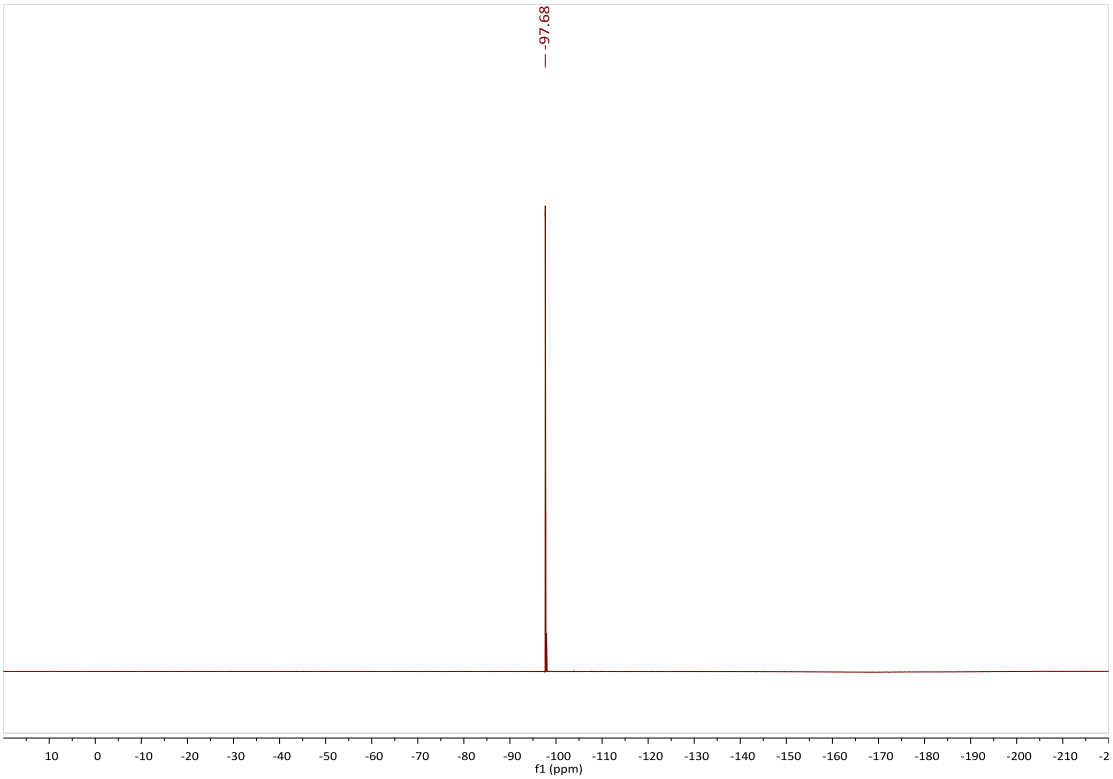


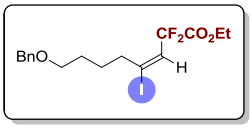
E/*Z* = 3:1

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5ac**



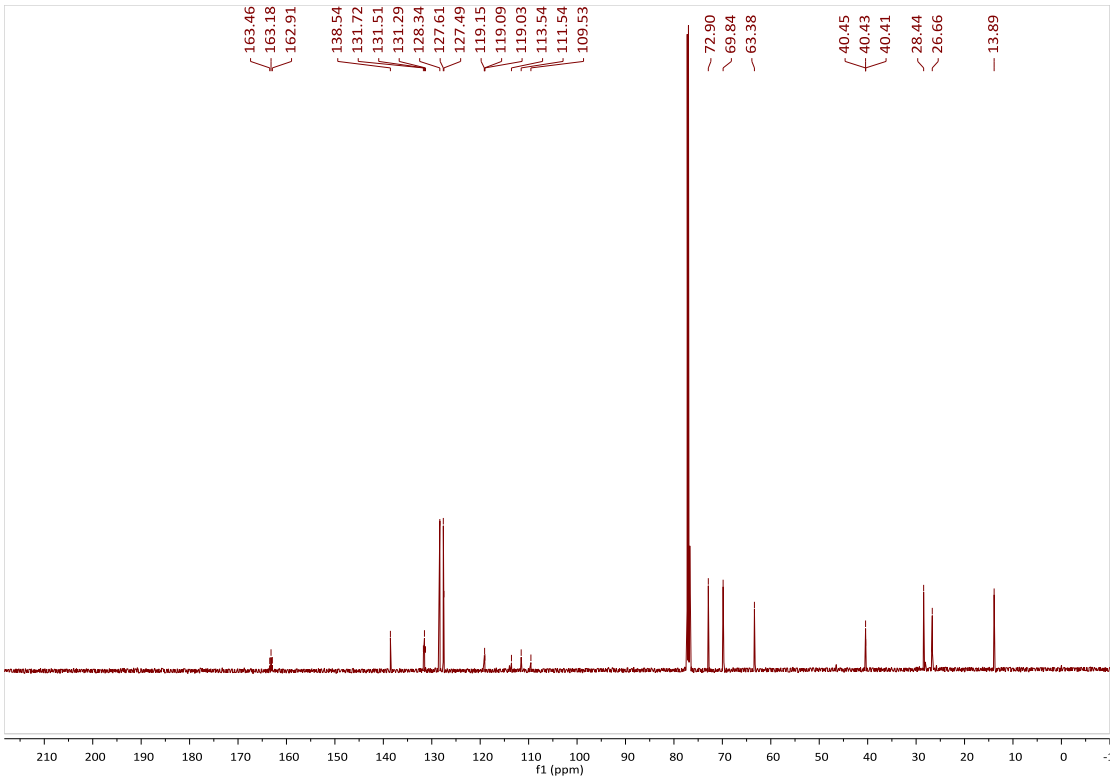
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5ac**

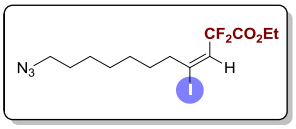




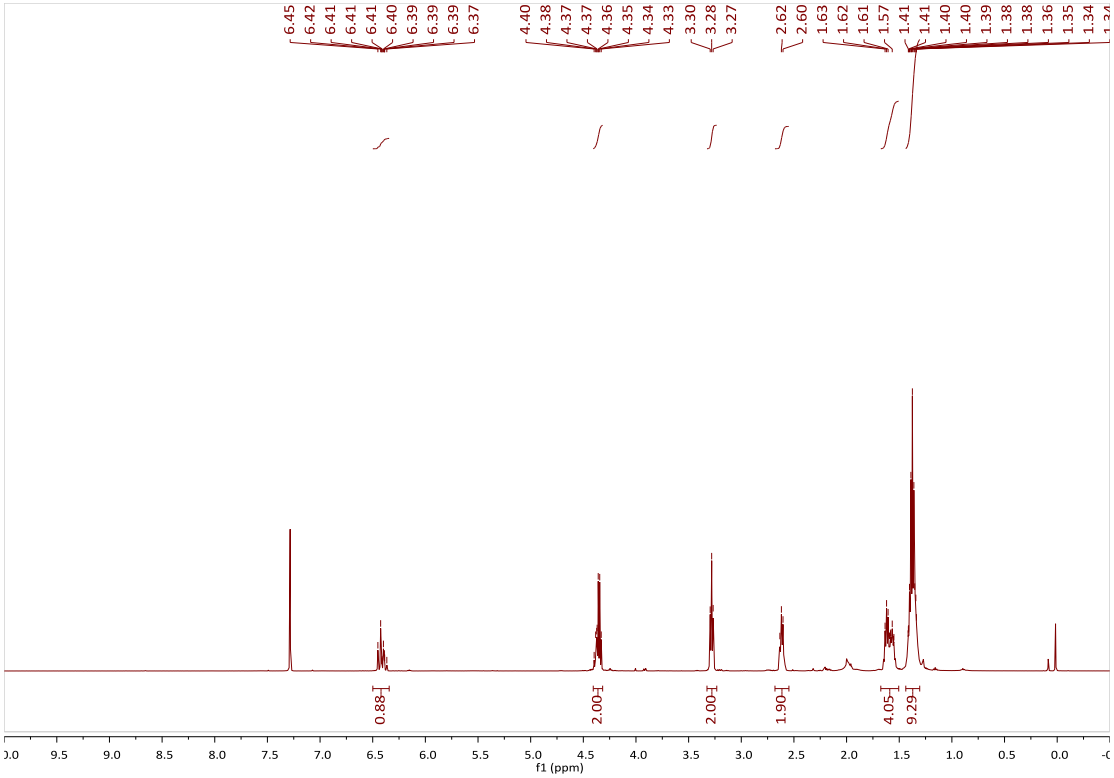
E/*Z* = 3:1

^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5ac**

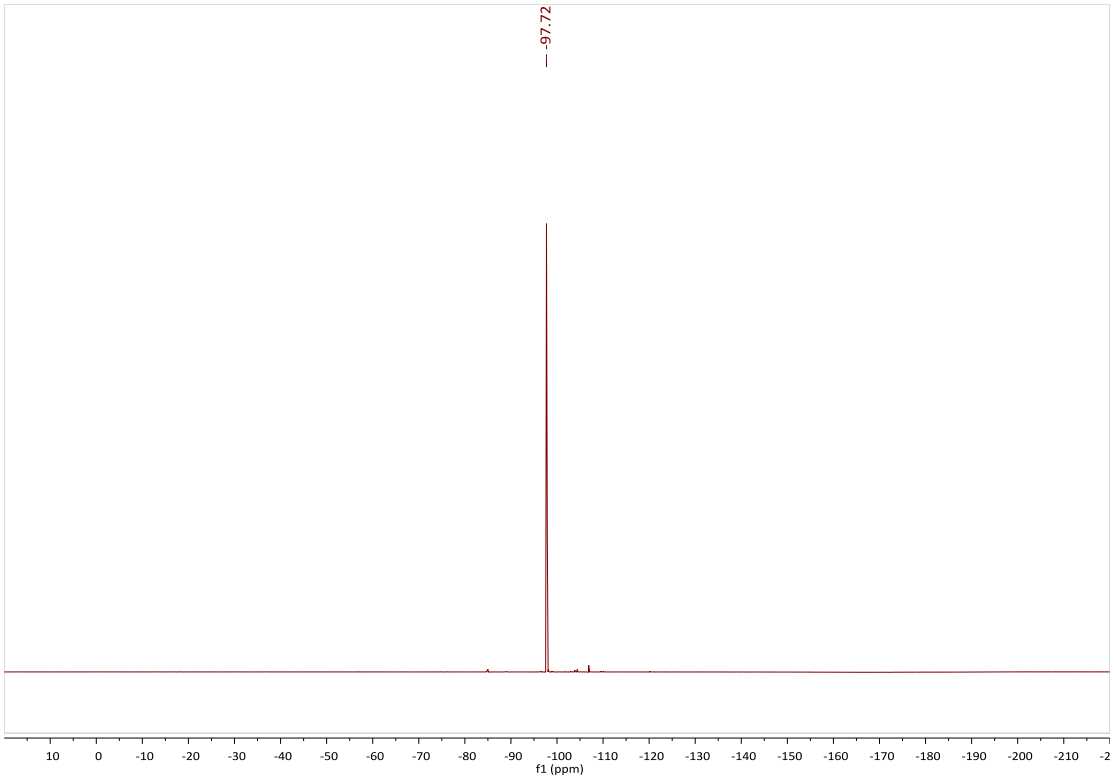


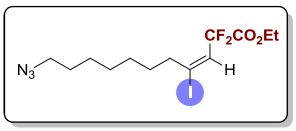


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5ad**

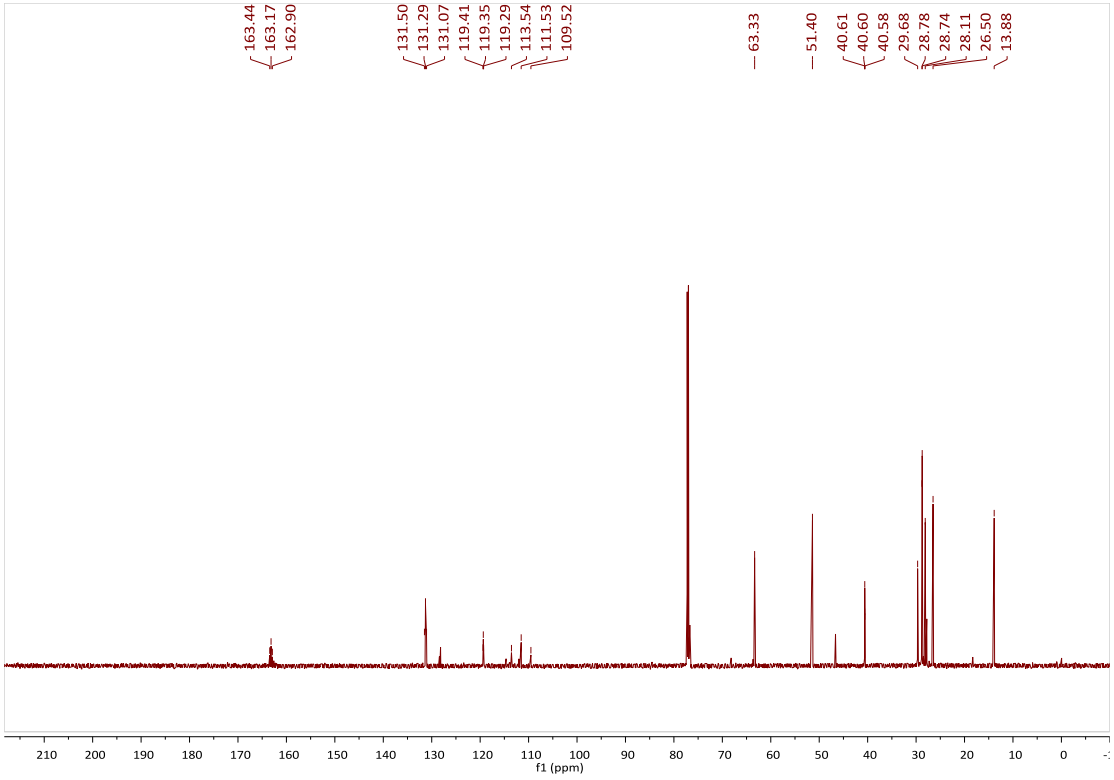


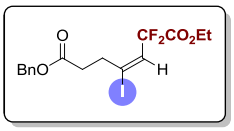
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5ad**





^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5ad**





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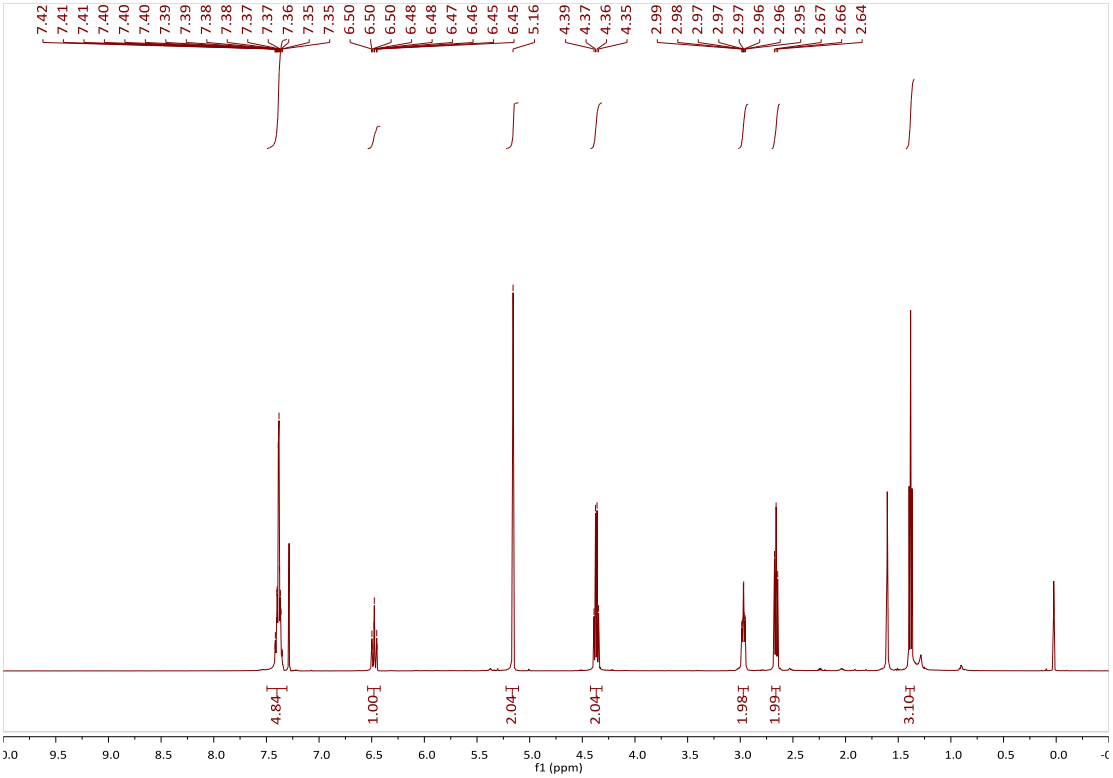
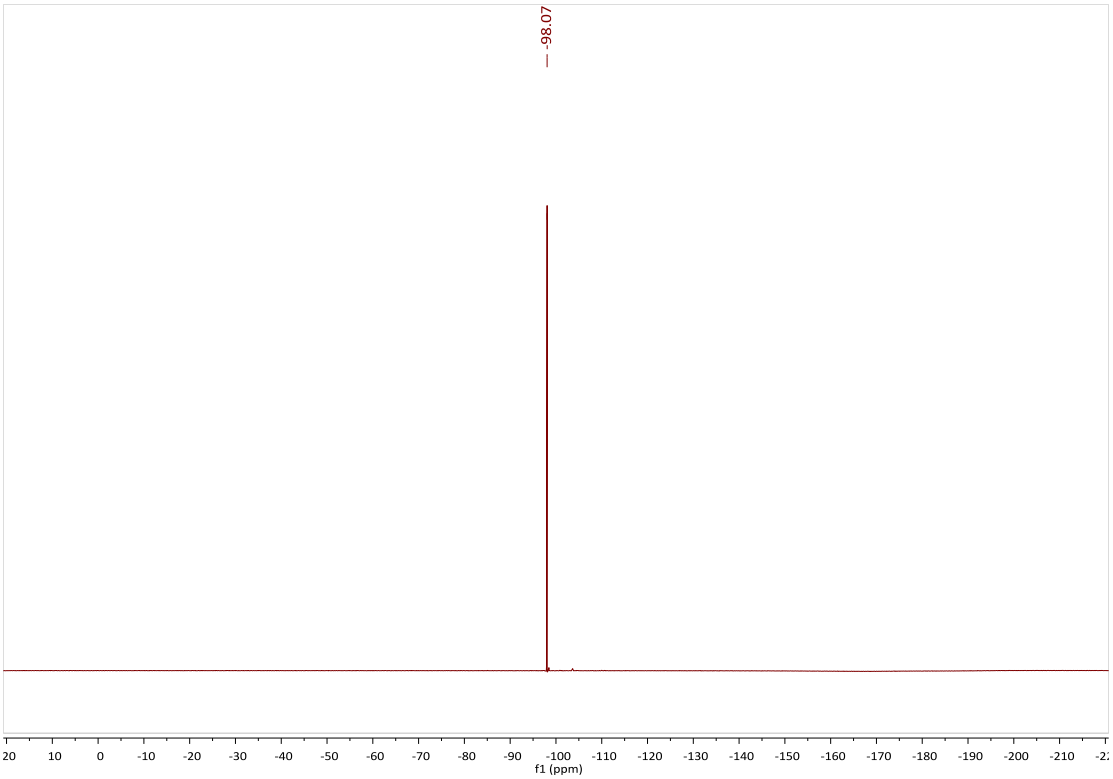
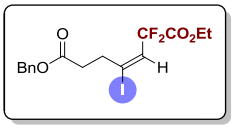
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5ae**



^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5ae**





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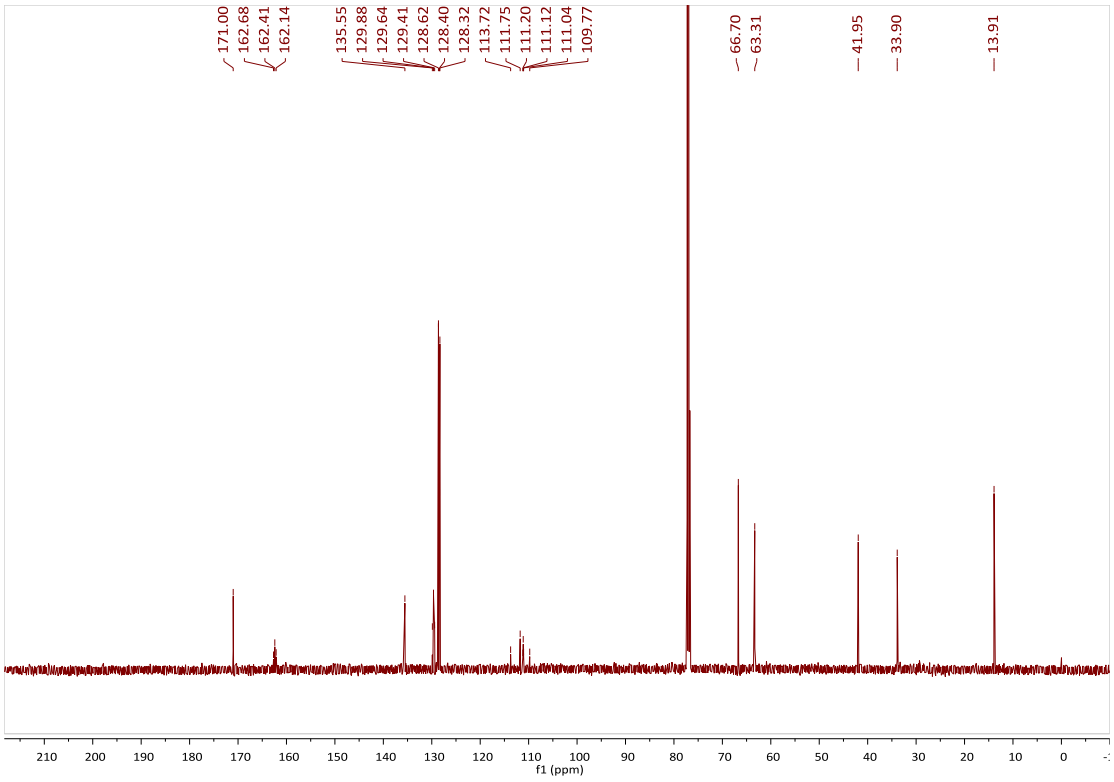
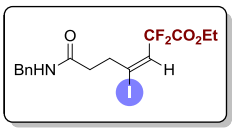
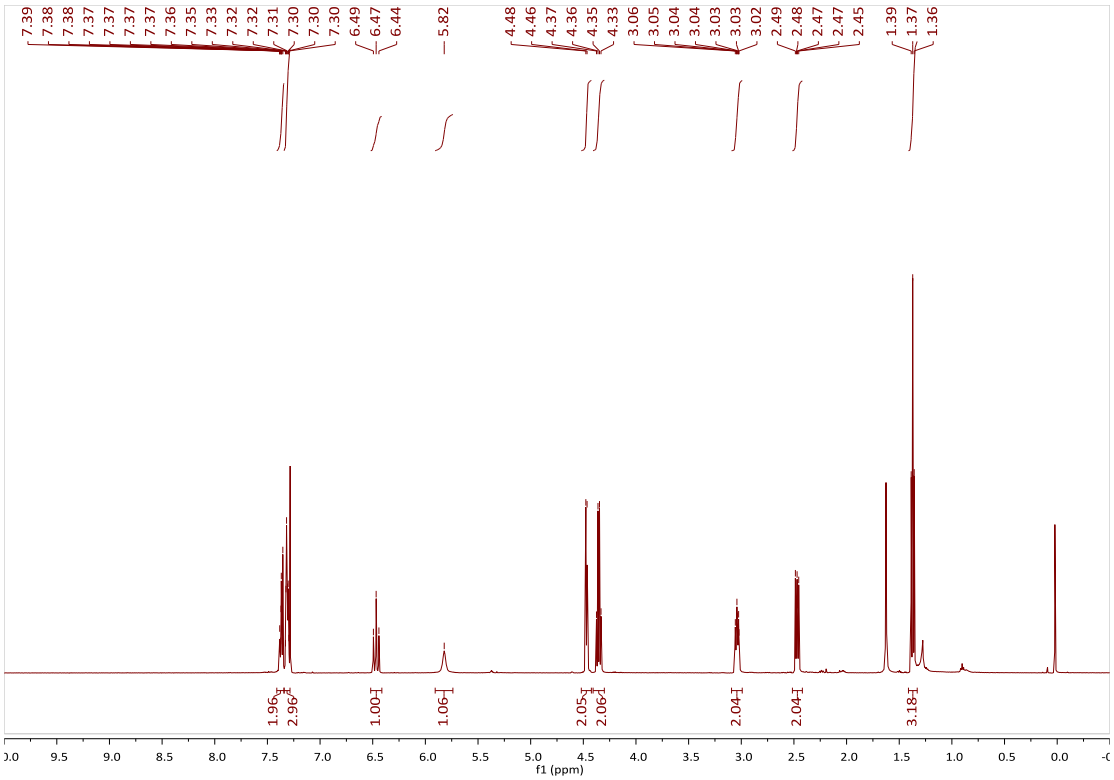
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5ae**

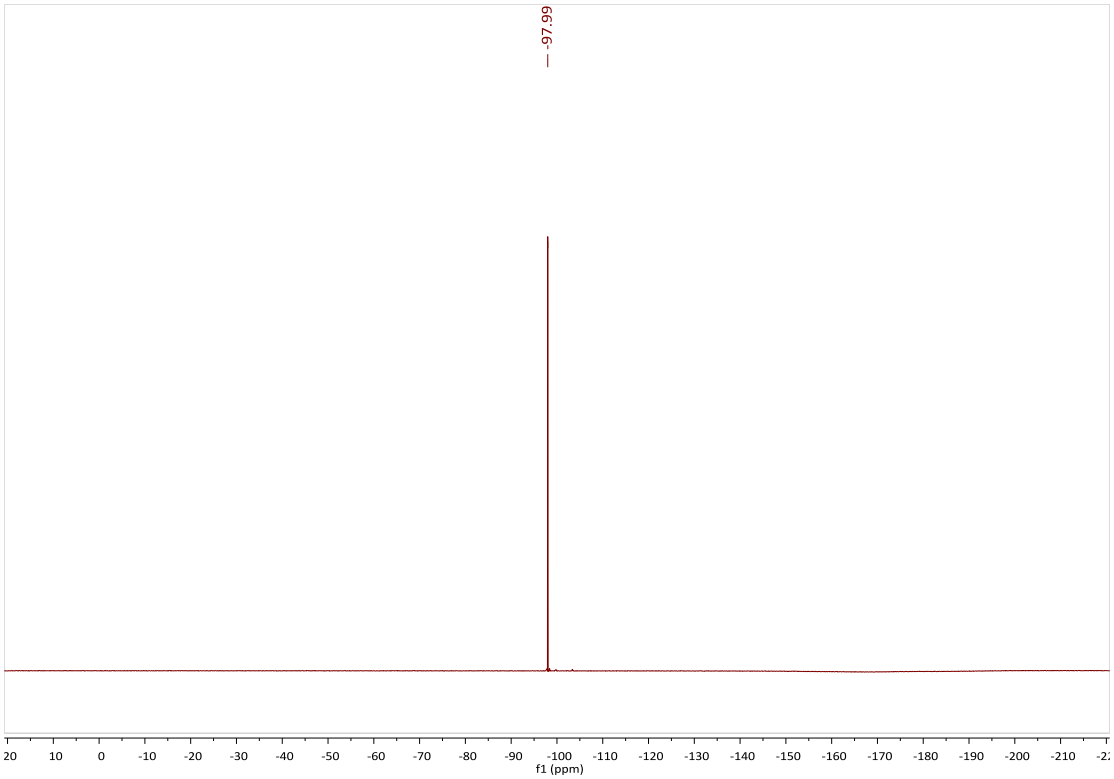


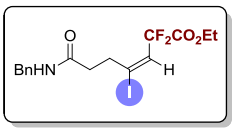


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **5af**

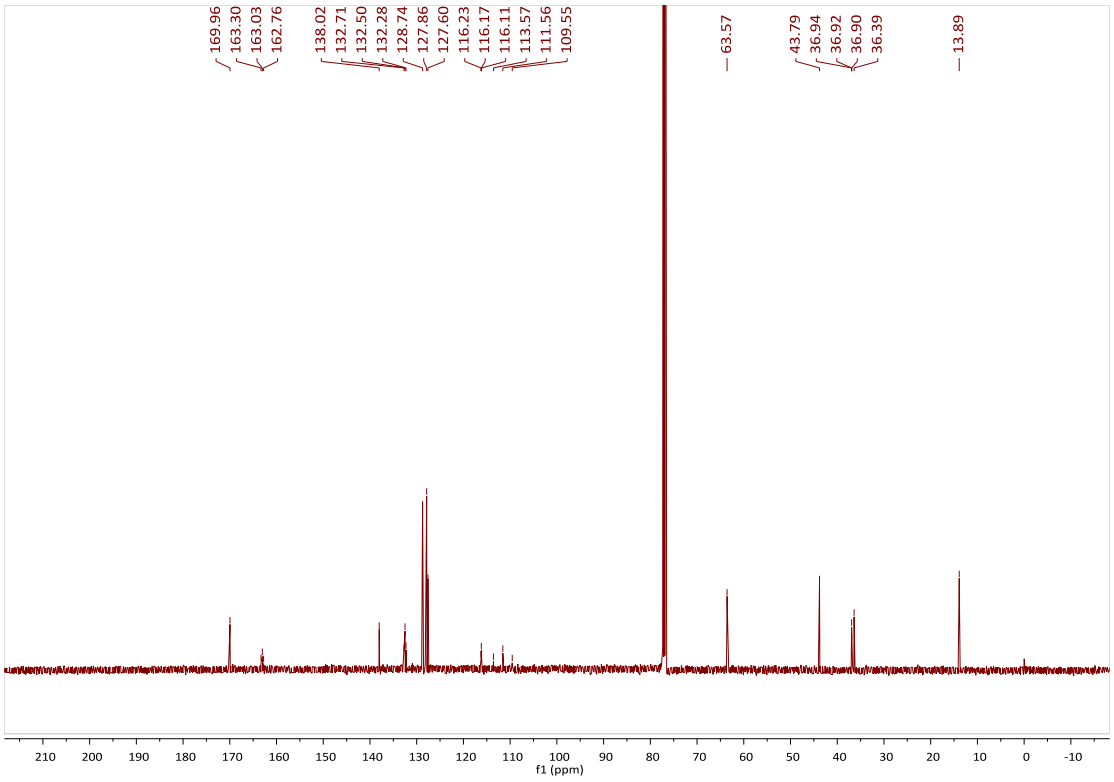


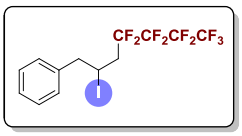
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **5af**



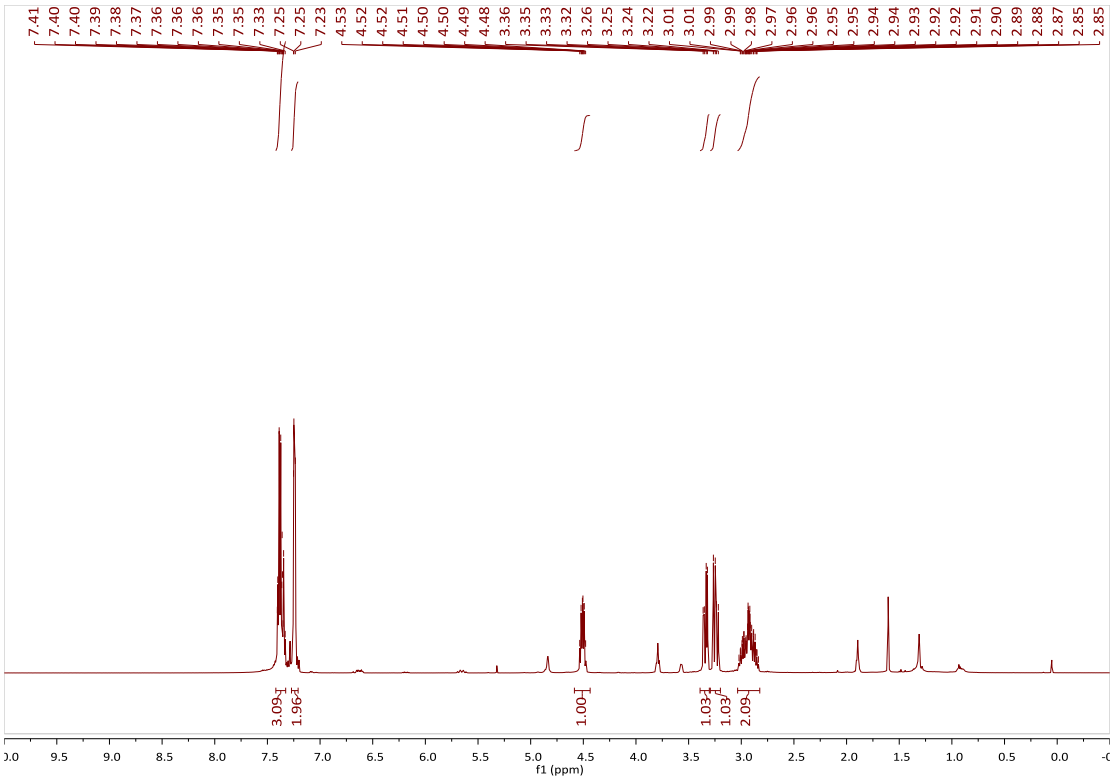


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **5af**

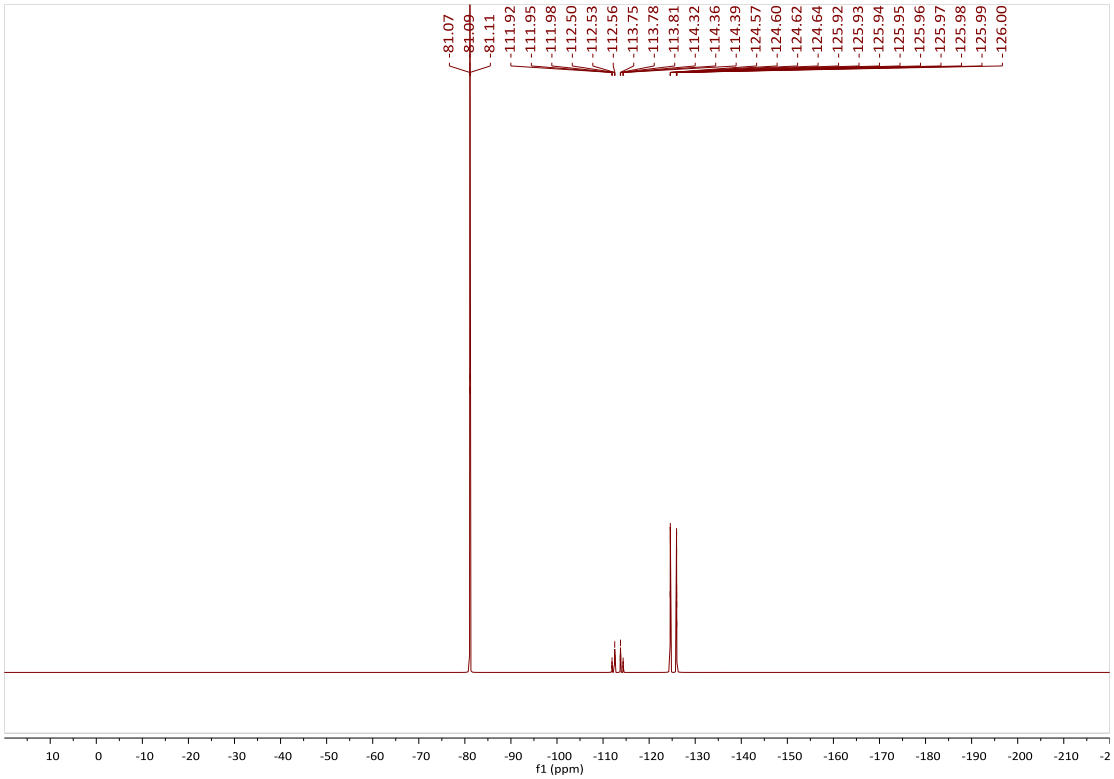


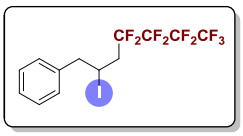


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **6a**

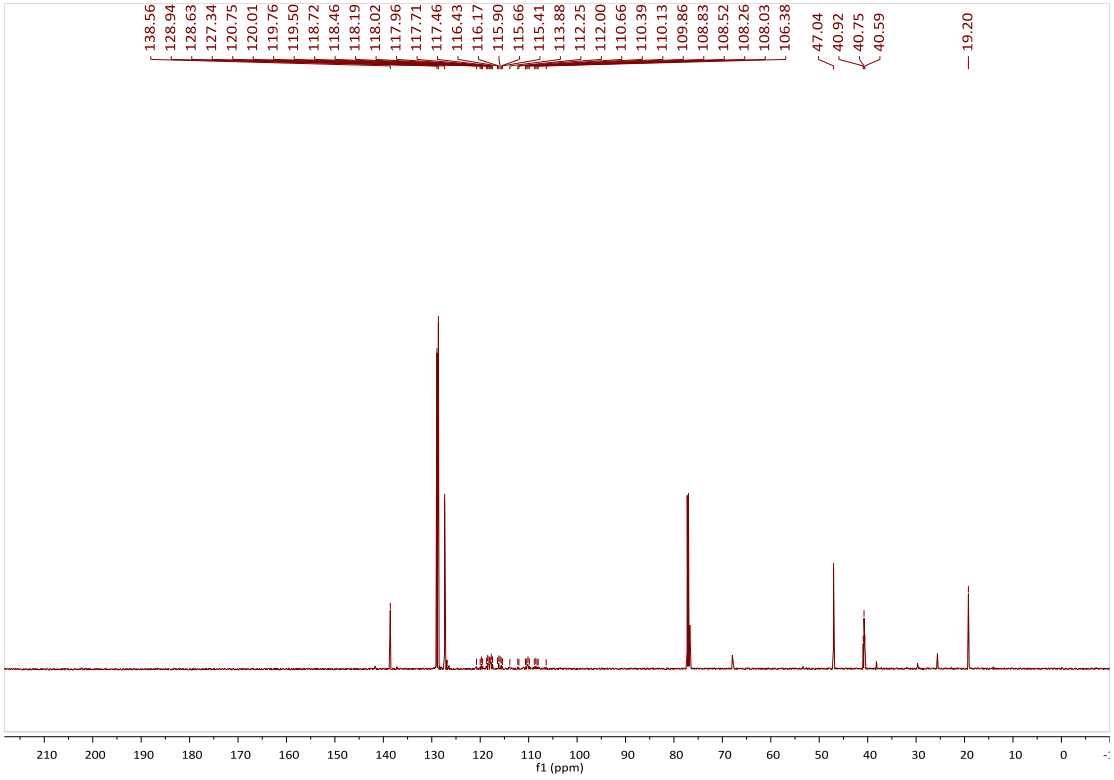


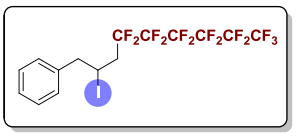
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **6a**



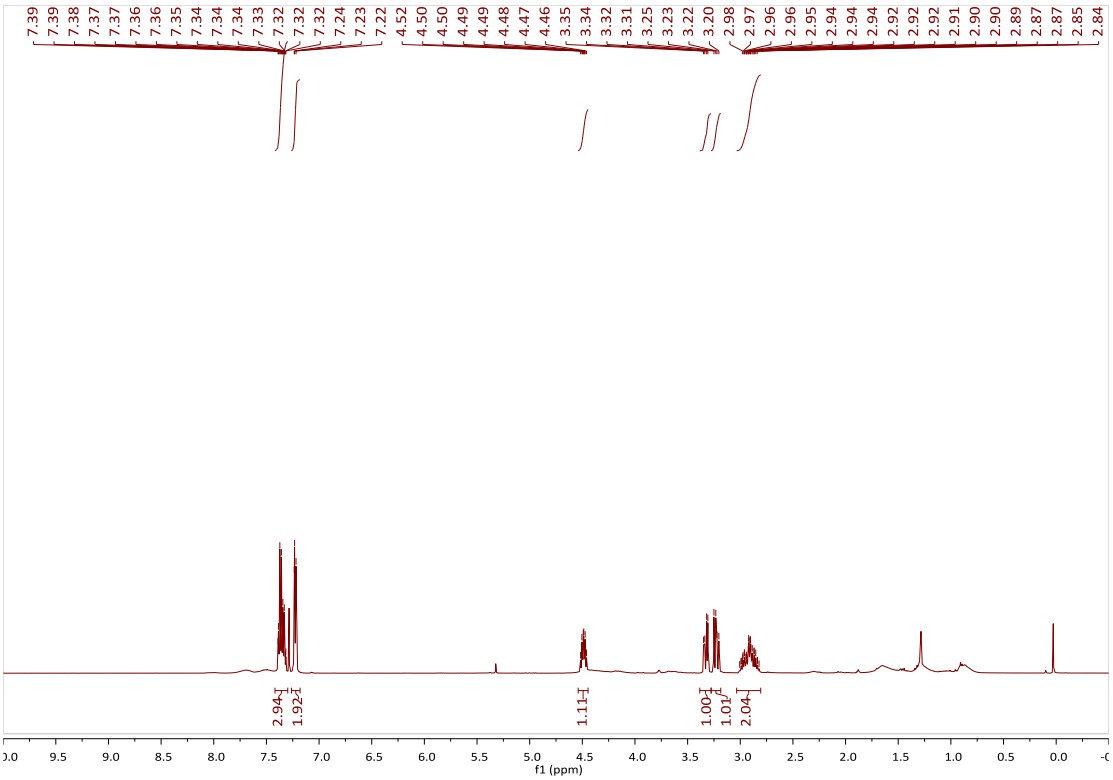


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **6a**

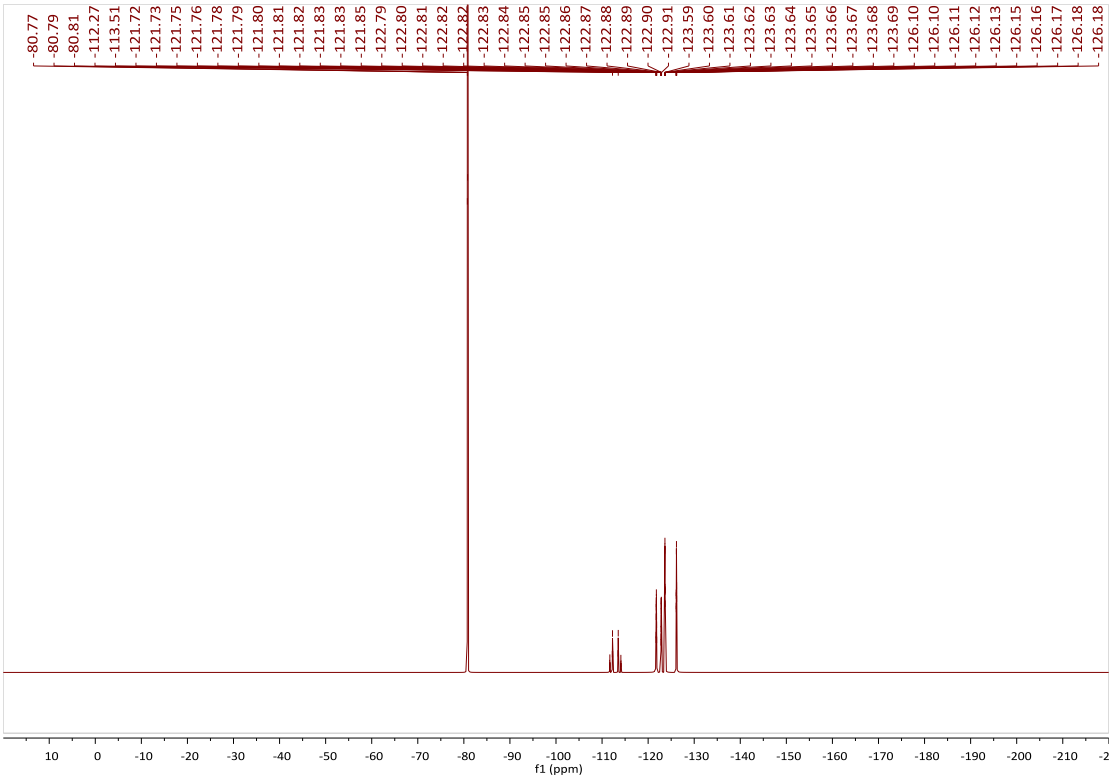


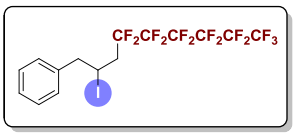


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **6b**

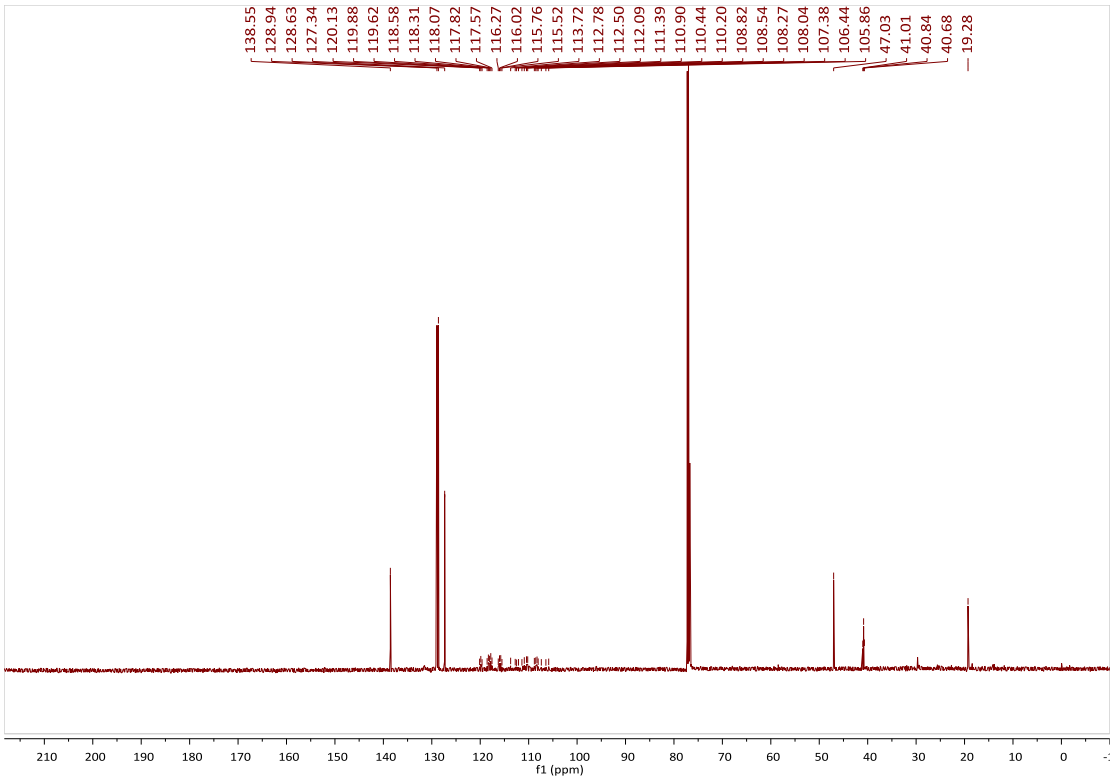


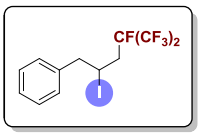
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **6b**



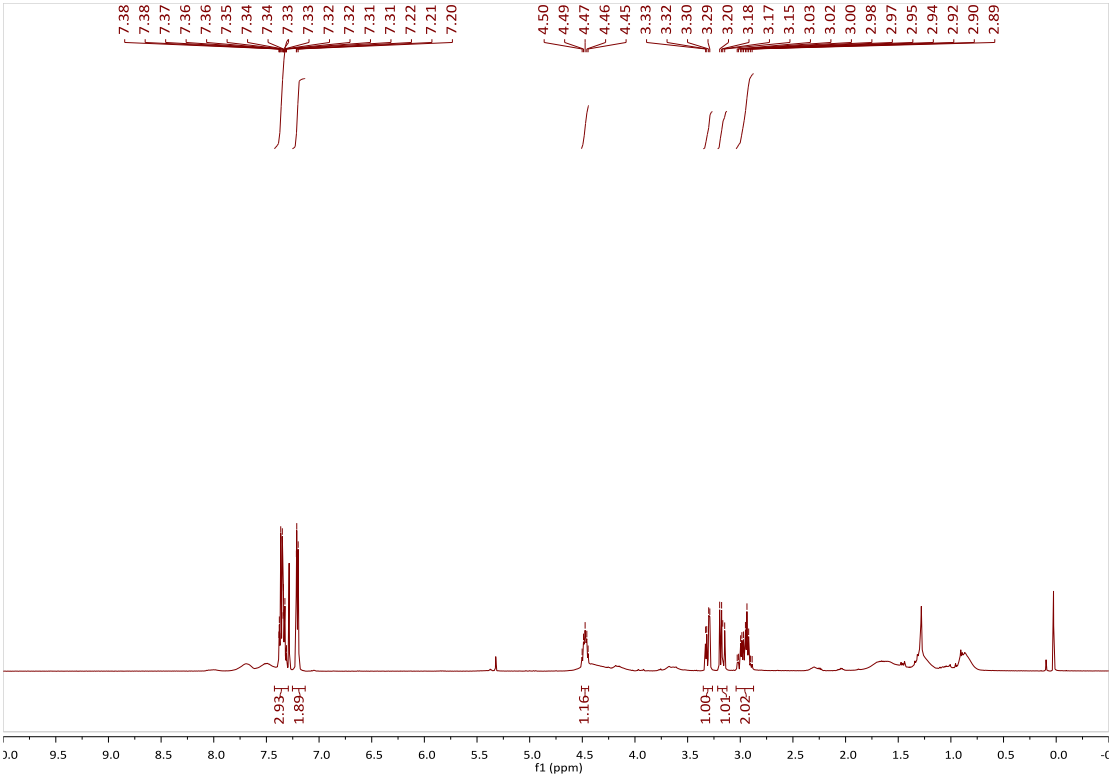


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **6b**

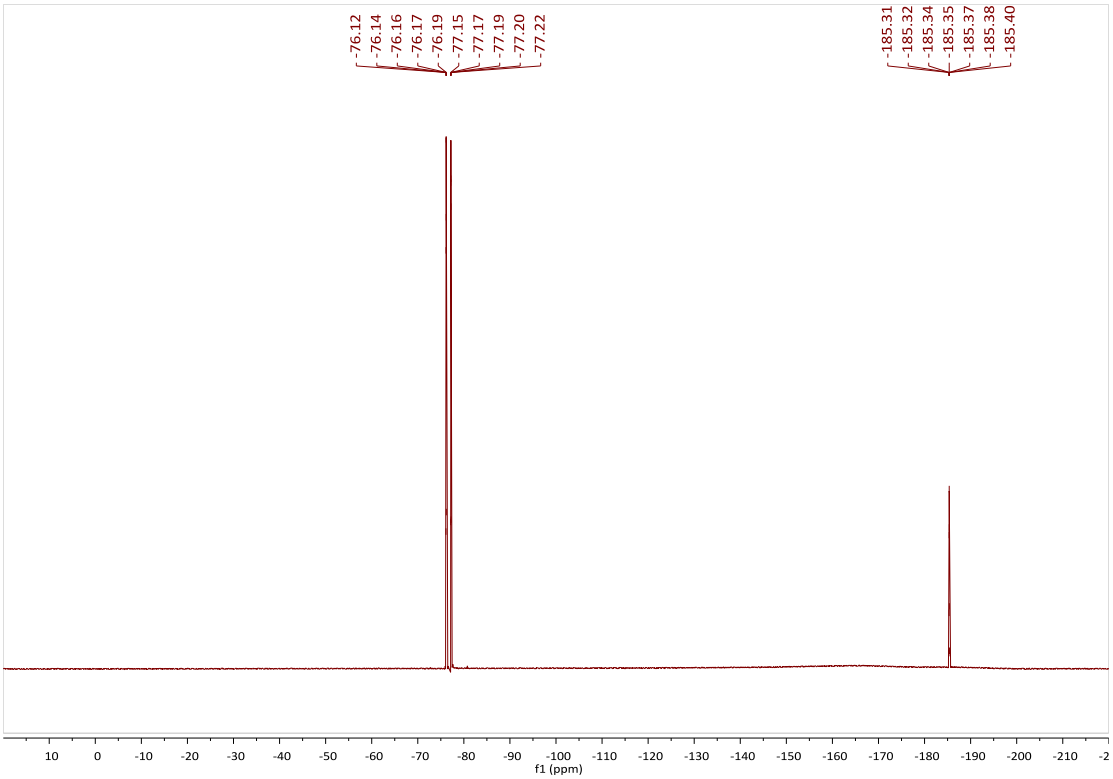


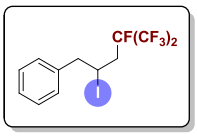


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **6c**

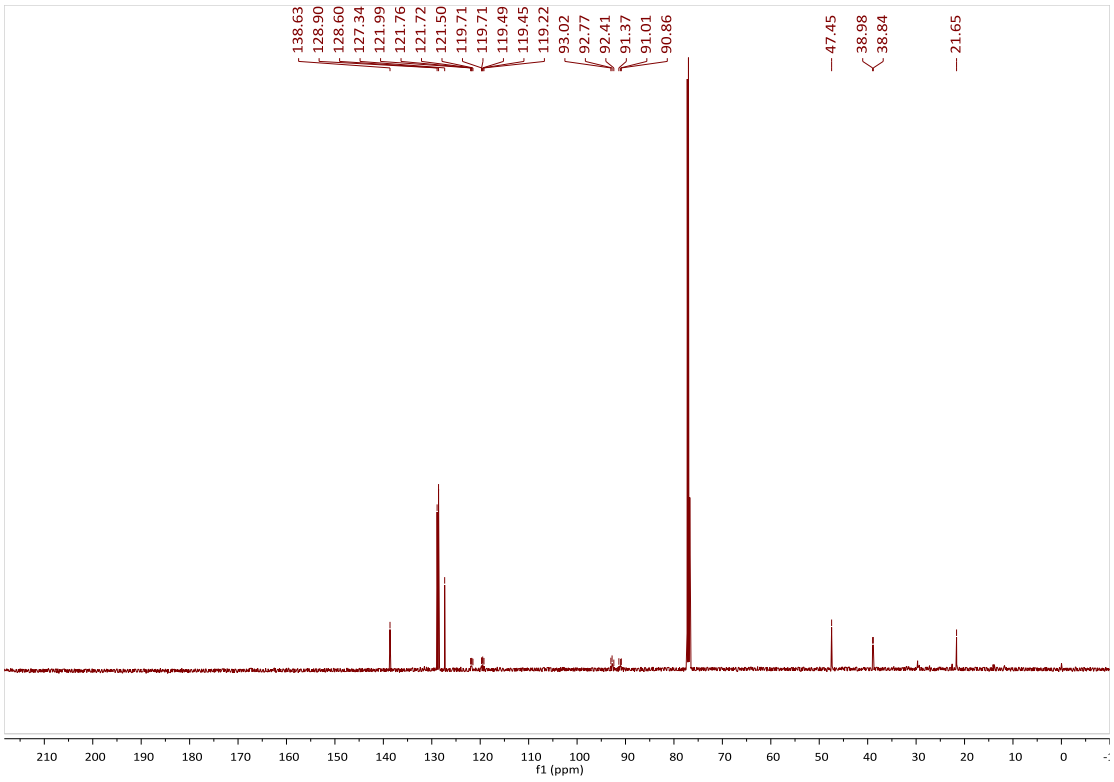


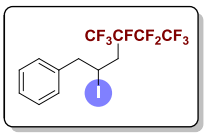
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **6c**



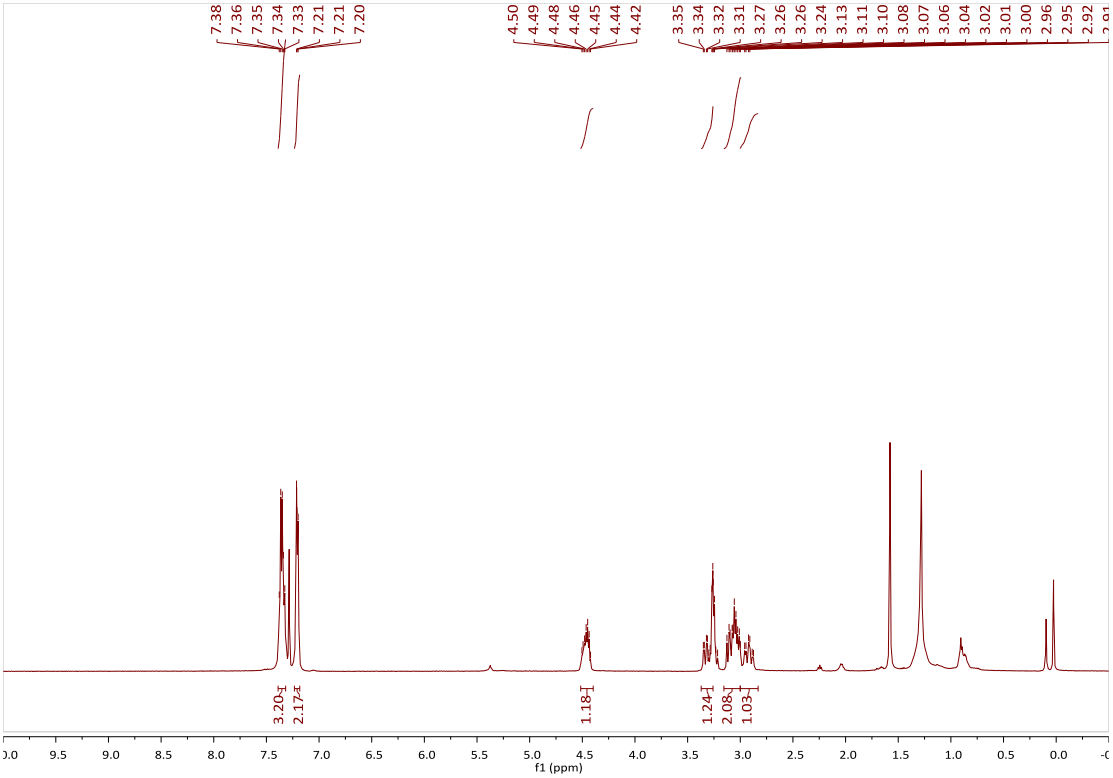


^{13}**C NMR**-spectrum (125 MHz, $CDCl_3$) of **6c**

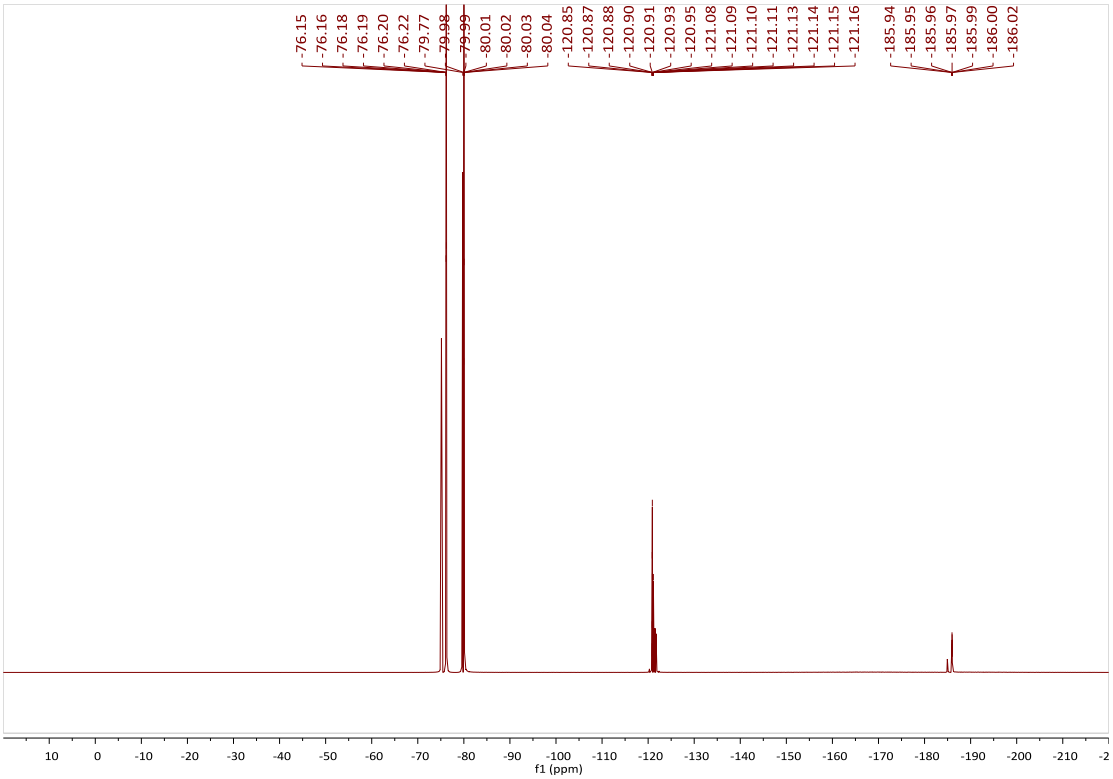


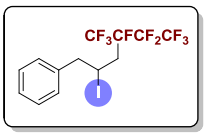


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **6d**

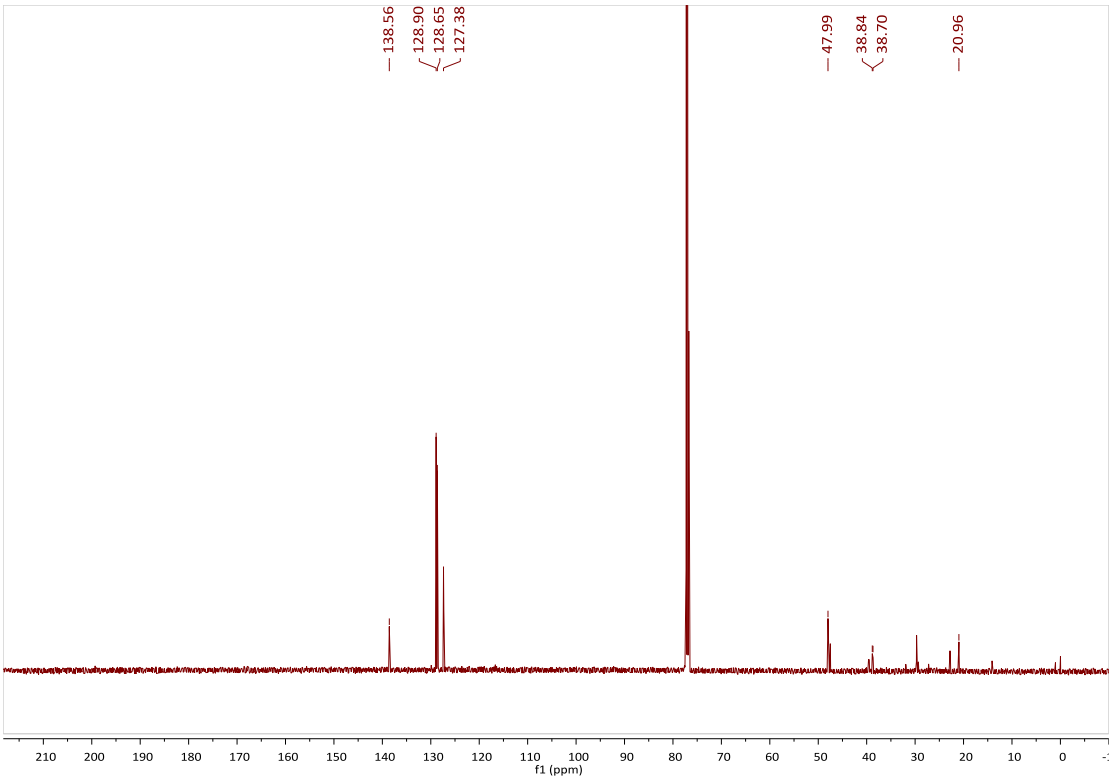


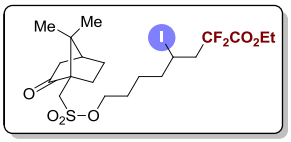
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **6d**





^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **6d**





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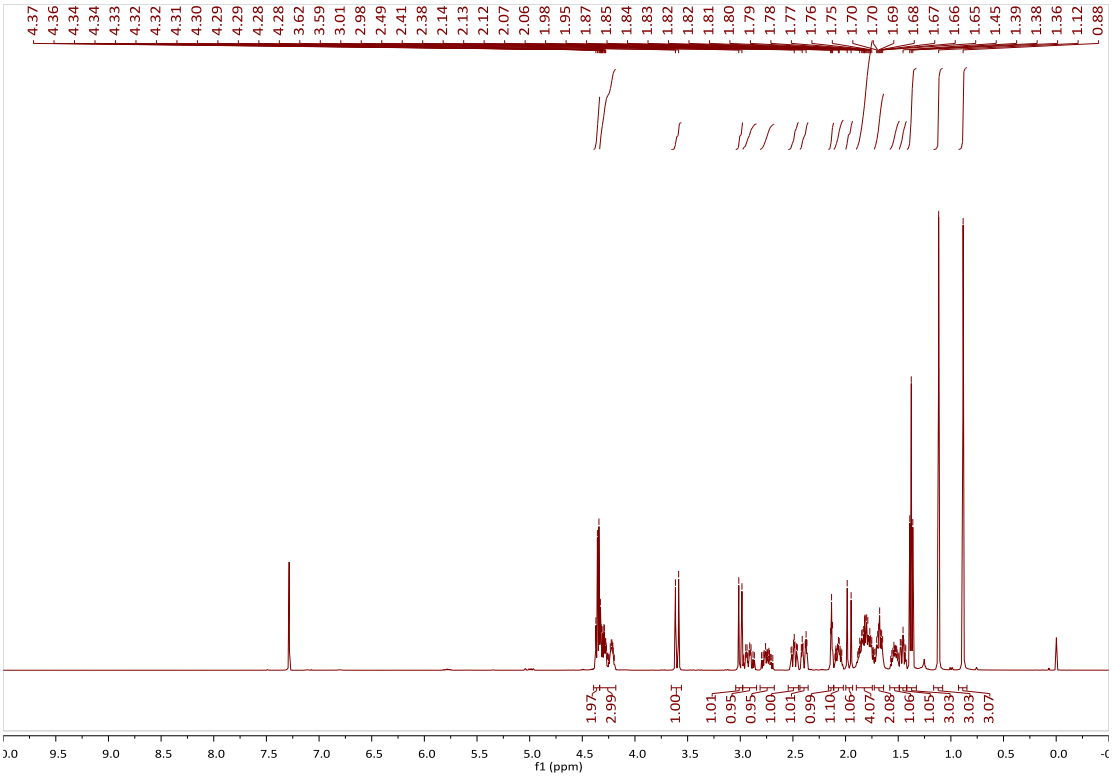
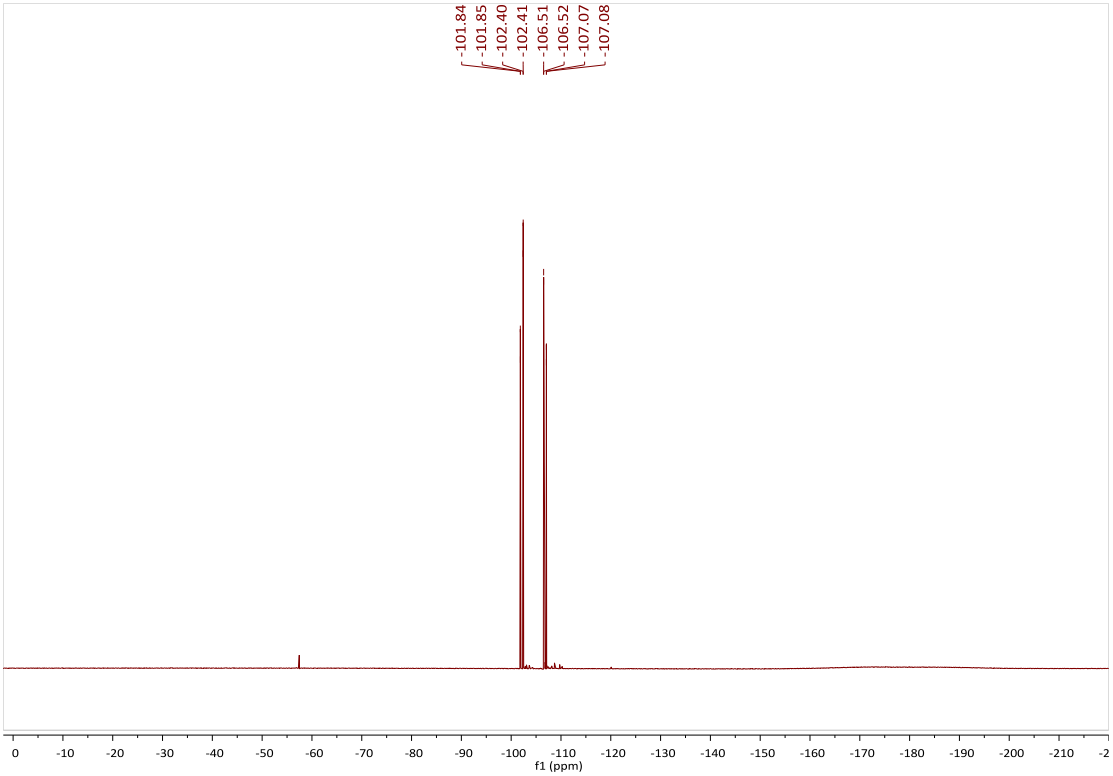
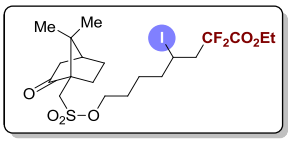
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **7a**



^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **7a**





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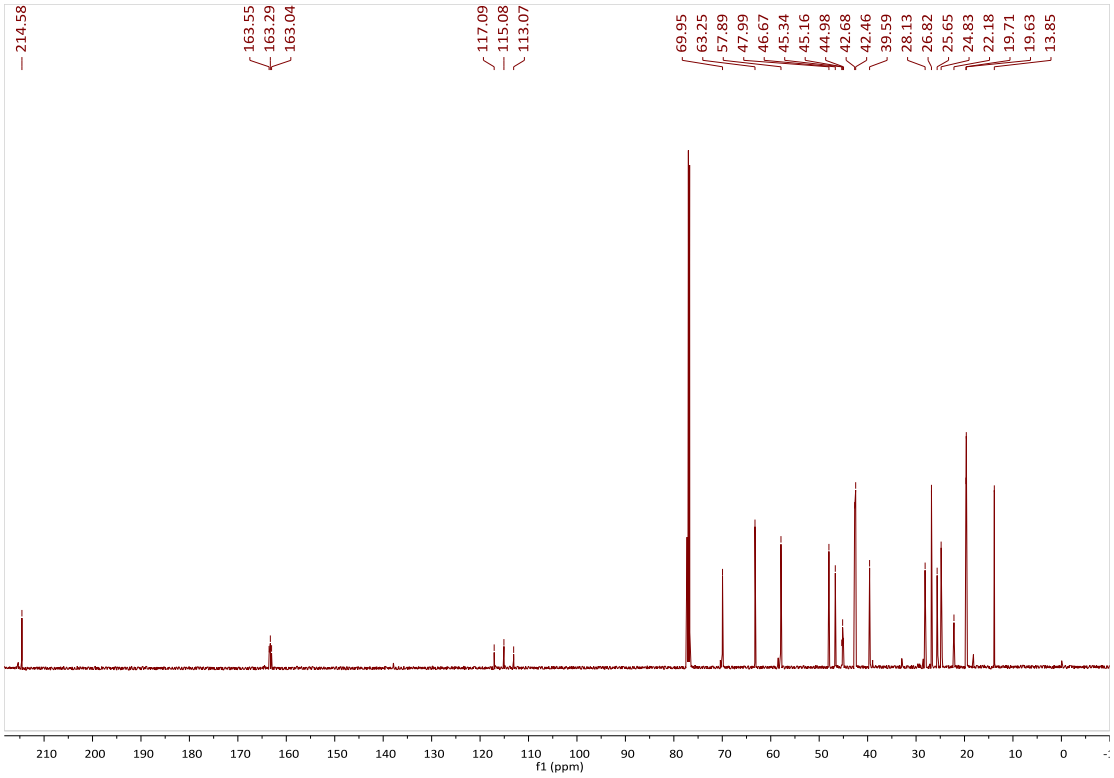
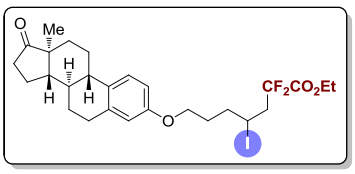
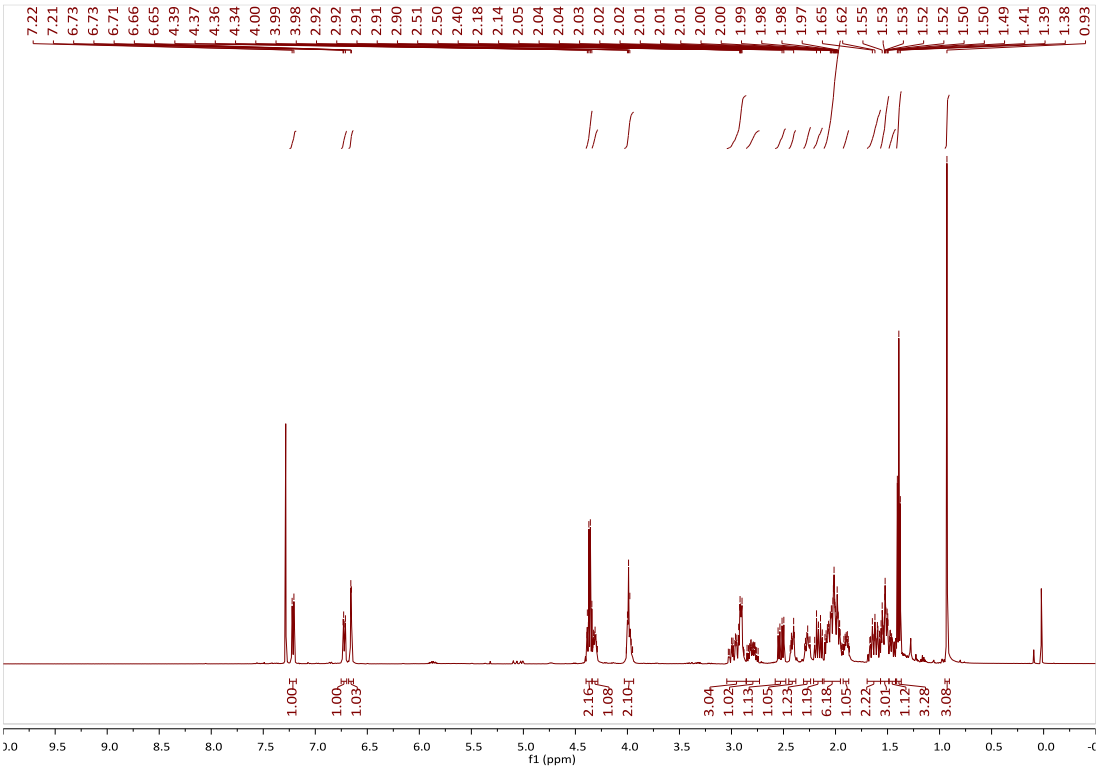
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **7a**

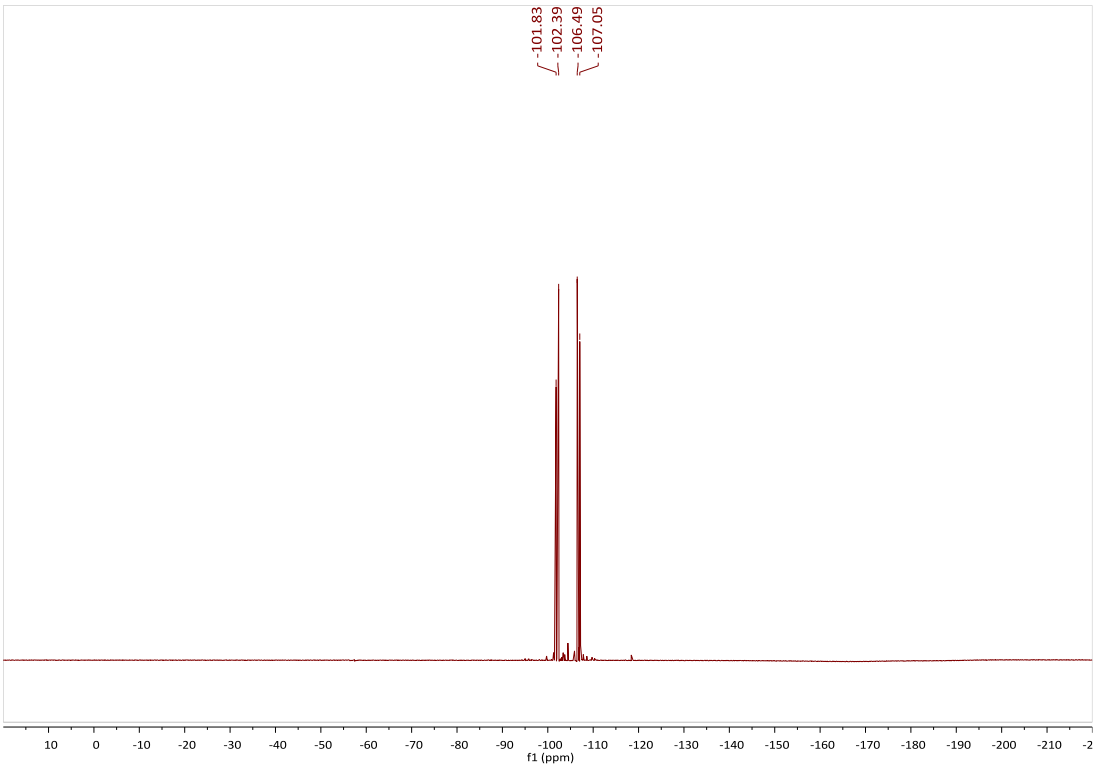


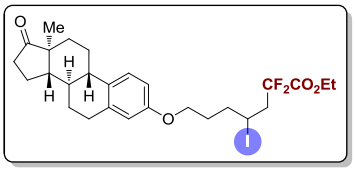


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **7b**

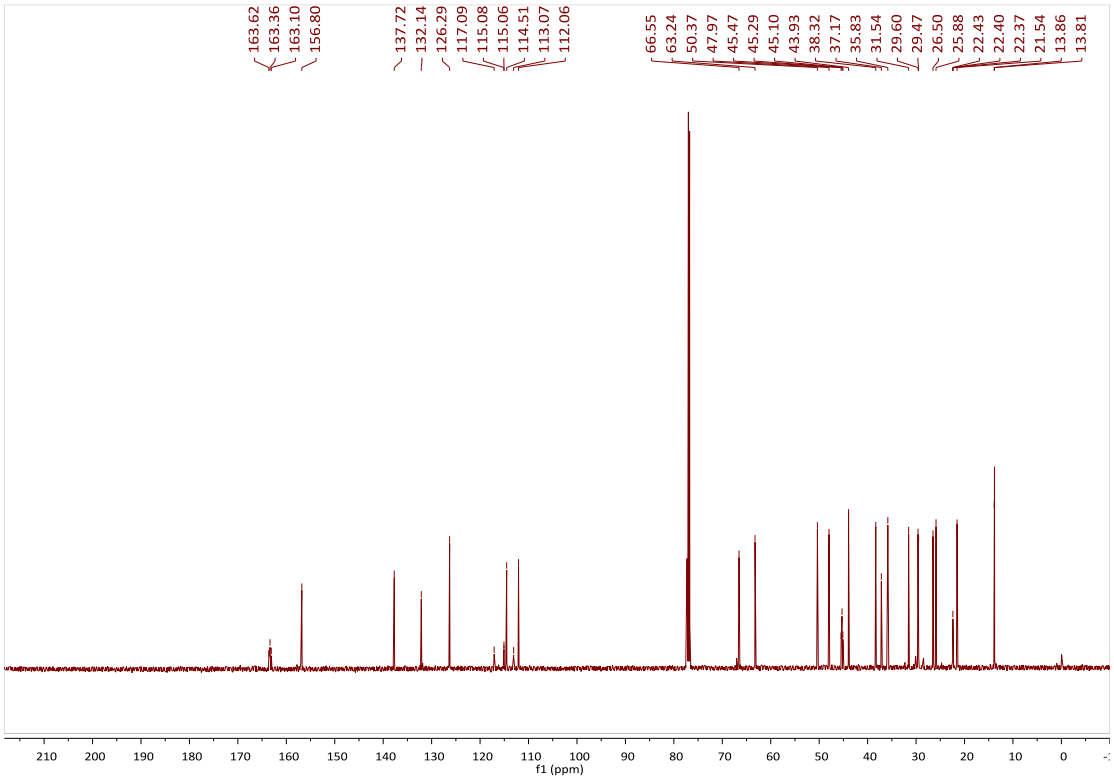


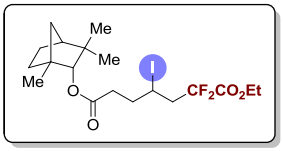
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **7b**





^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **7b**





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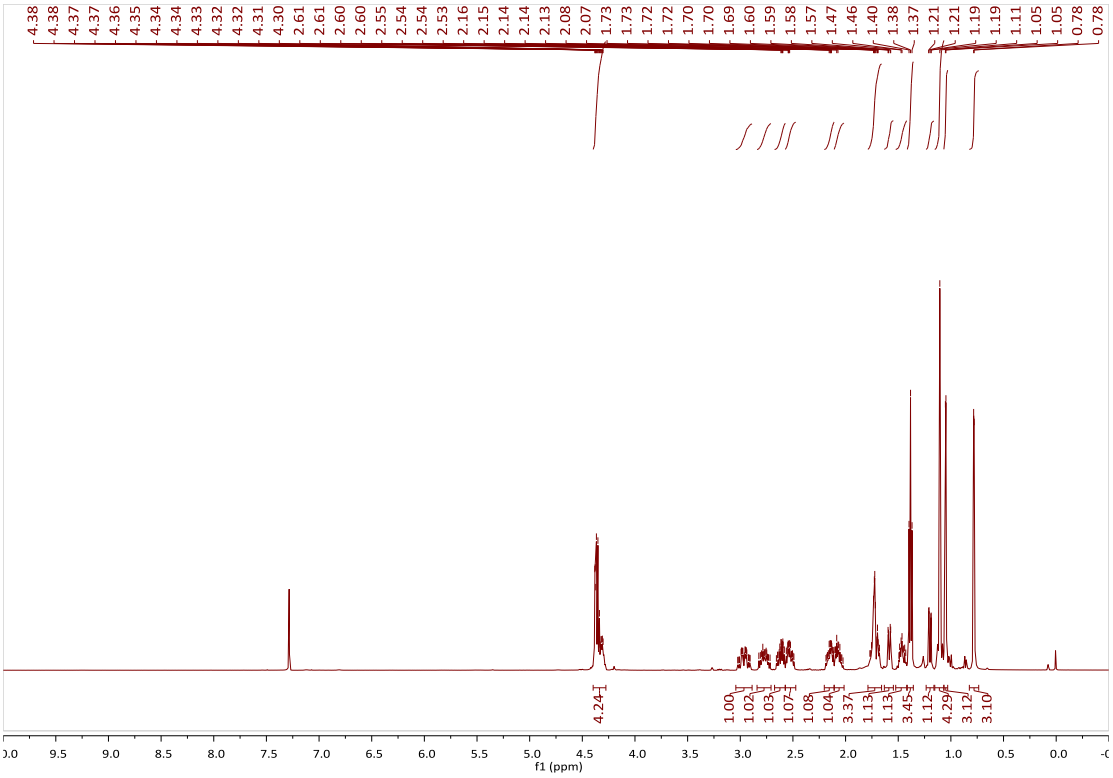
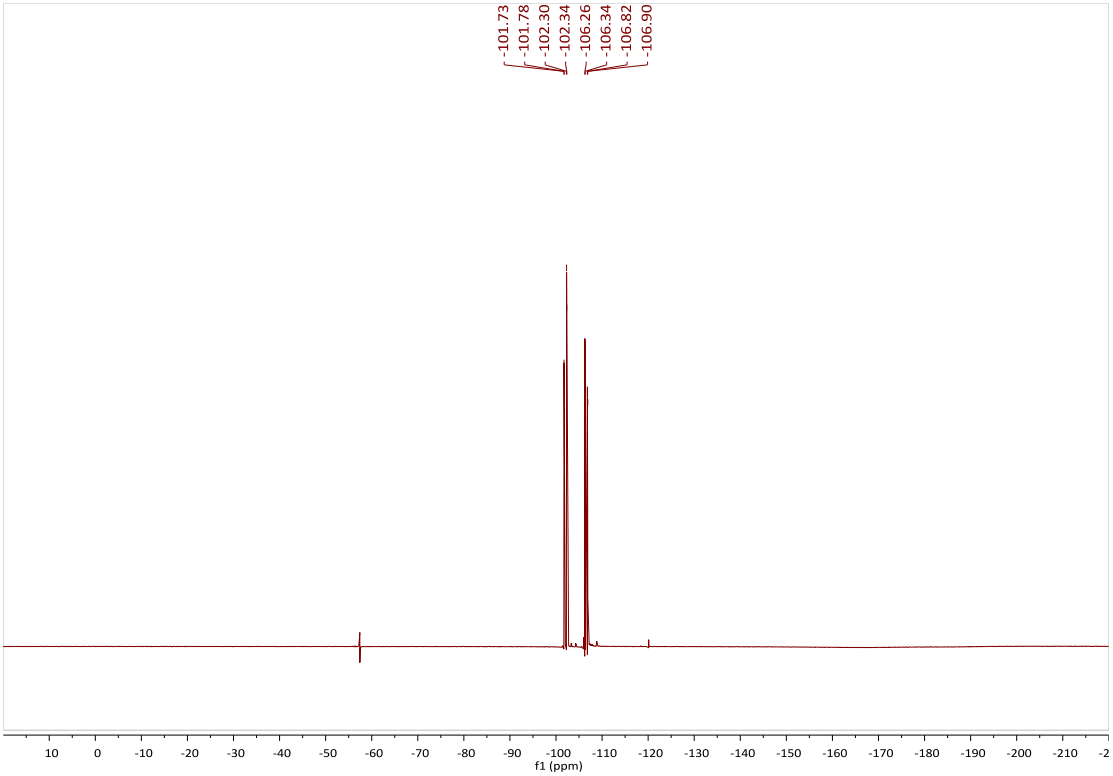
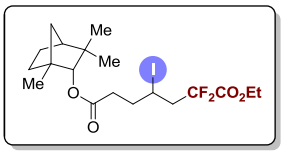
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **7c**



^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **7c**





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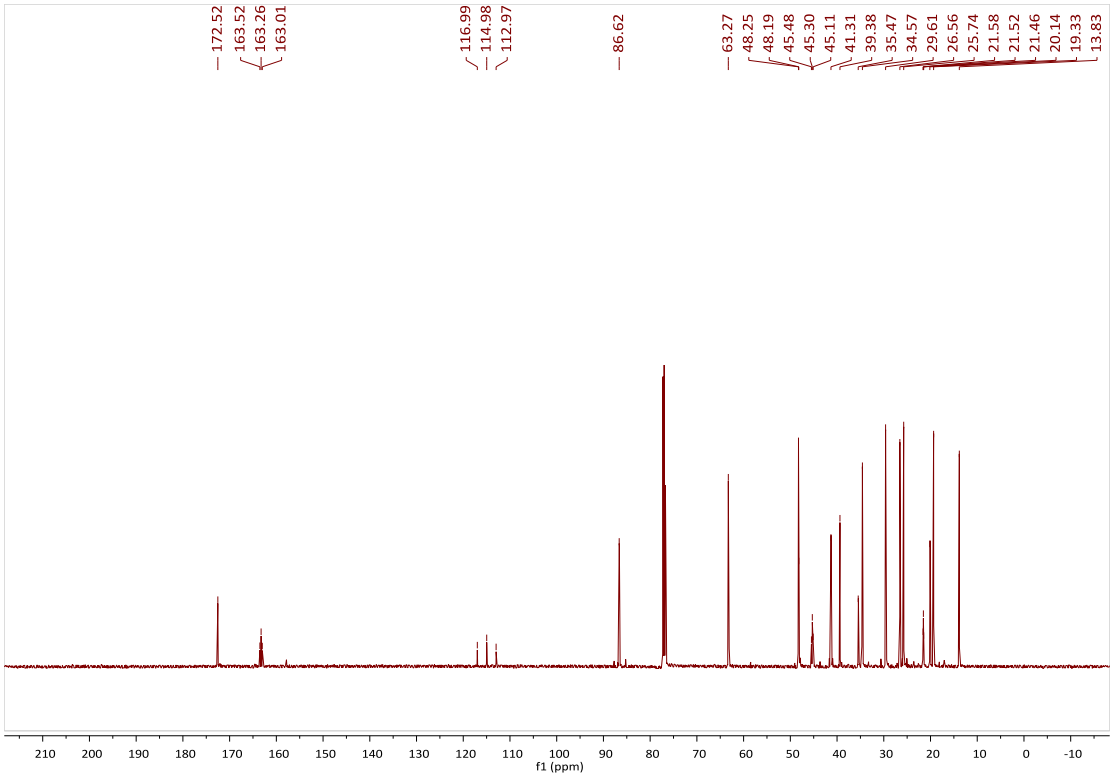
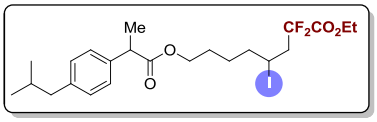
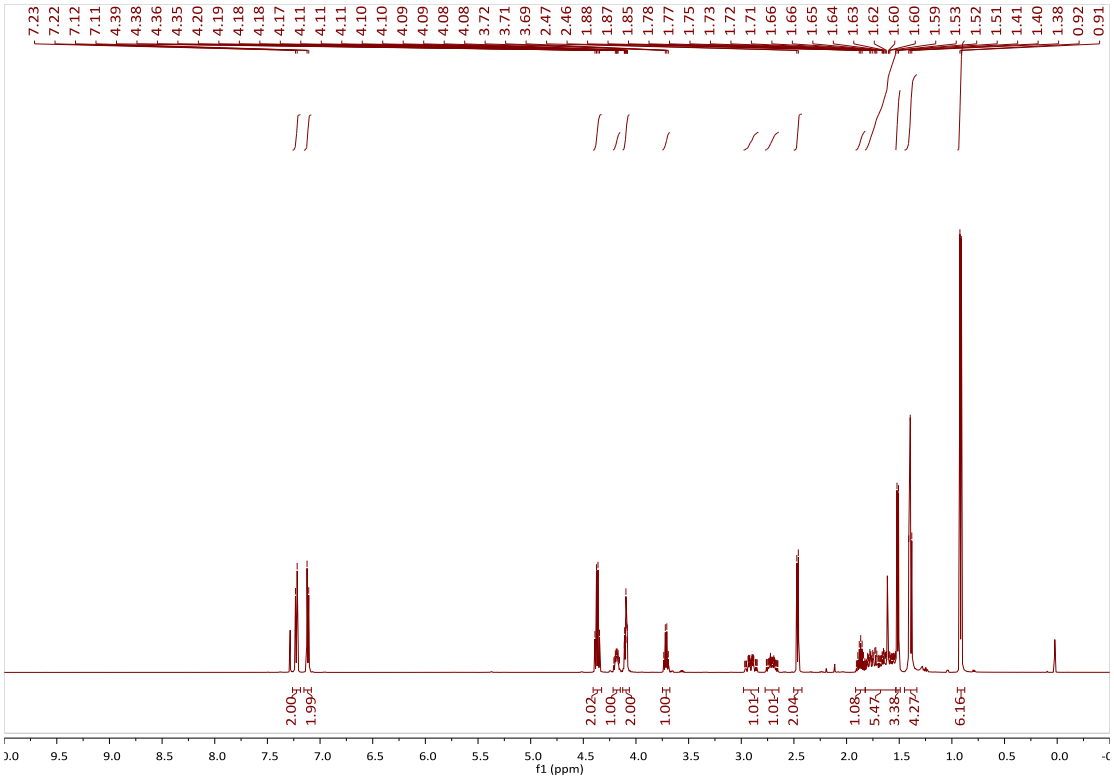
^{13}**C NMR**-spectrum (125 MHz, $CDCl_3$) of **7c**

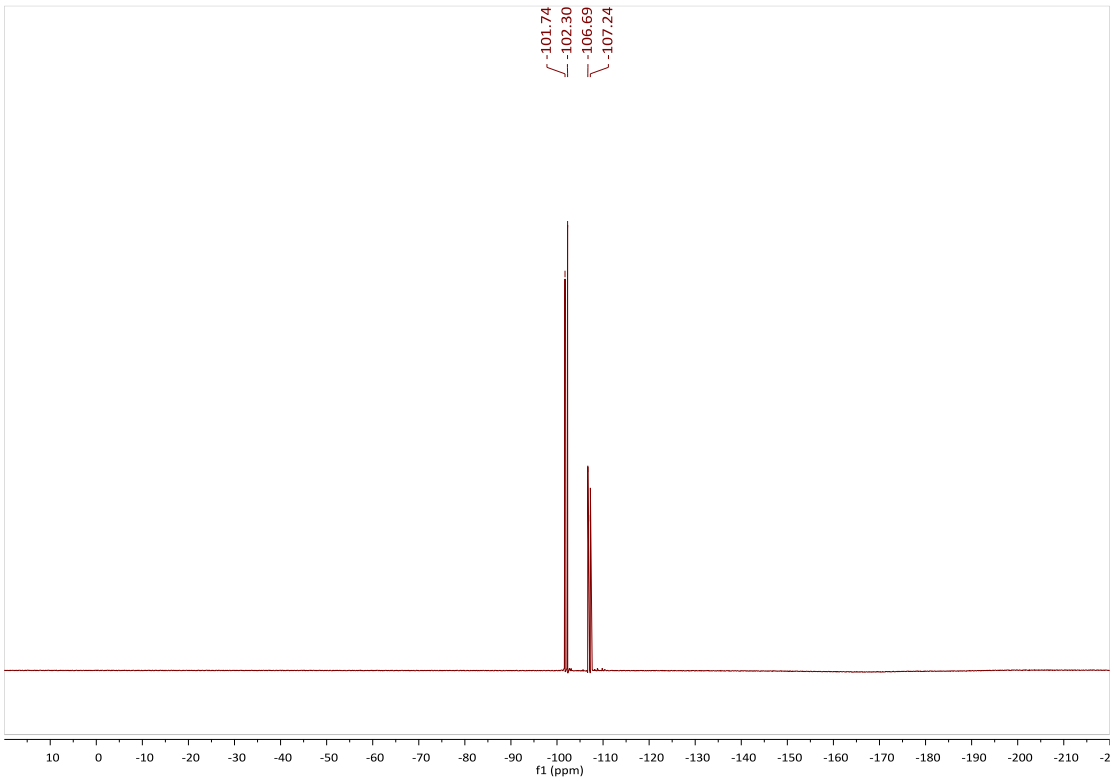


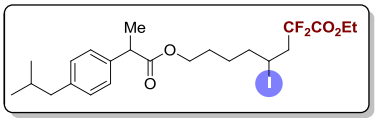


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **7d**

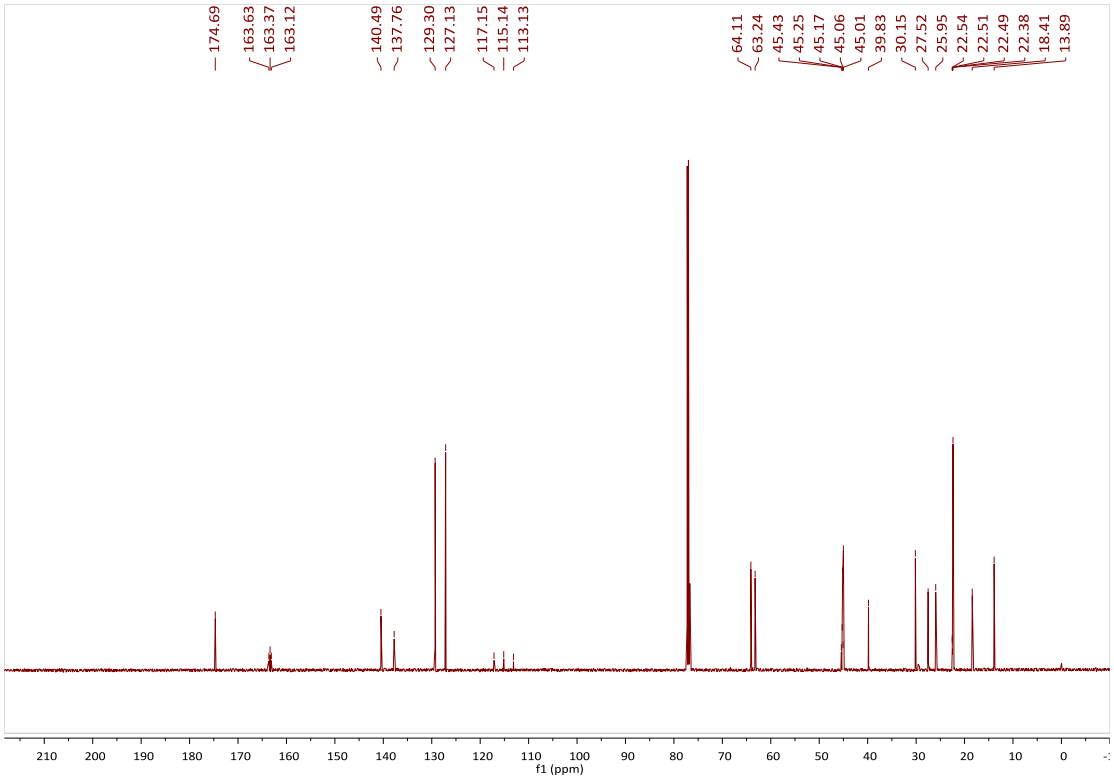


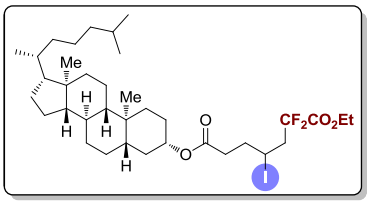
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **7d**



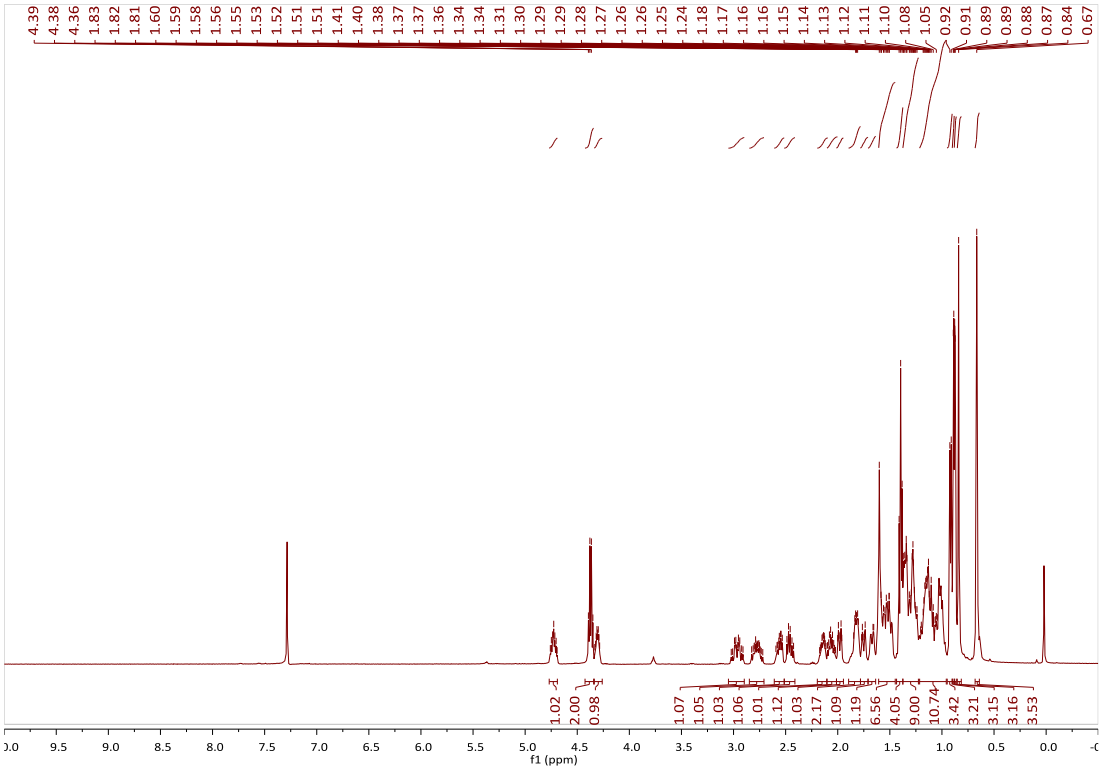


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **7d**

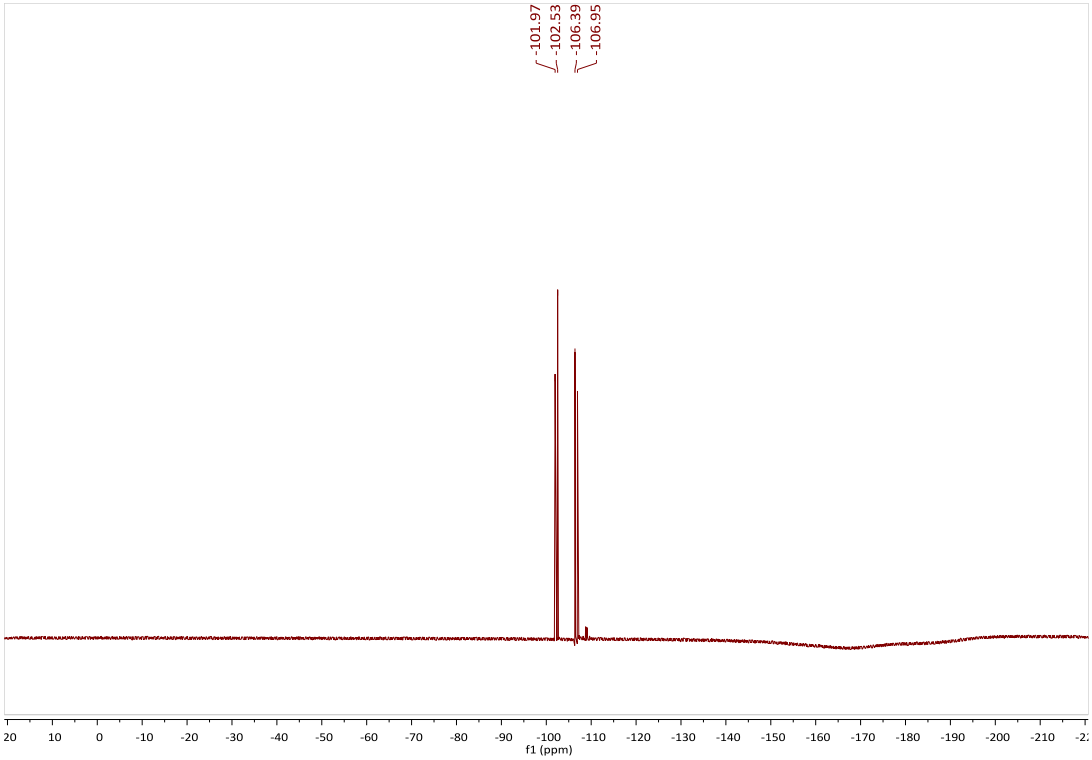


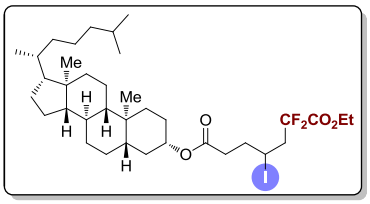


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **7e**

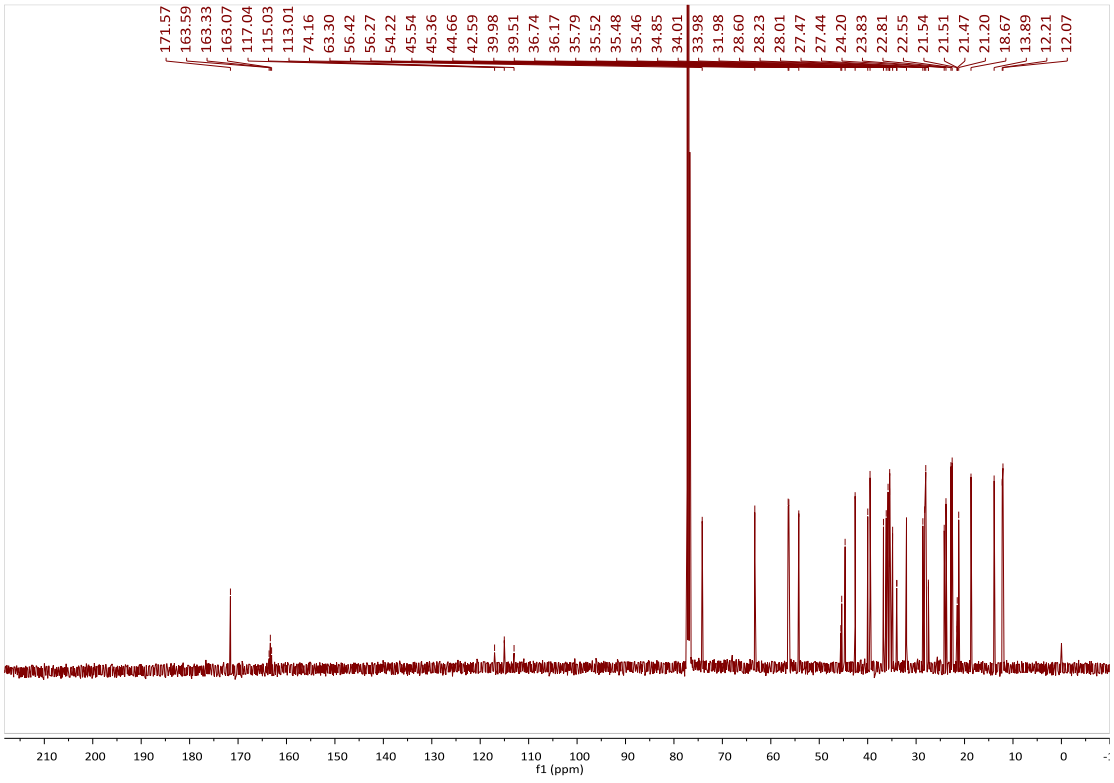


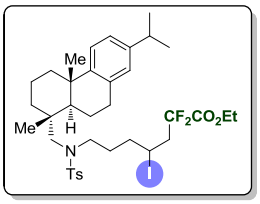
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **7e**



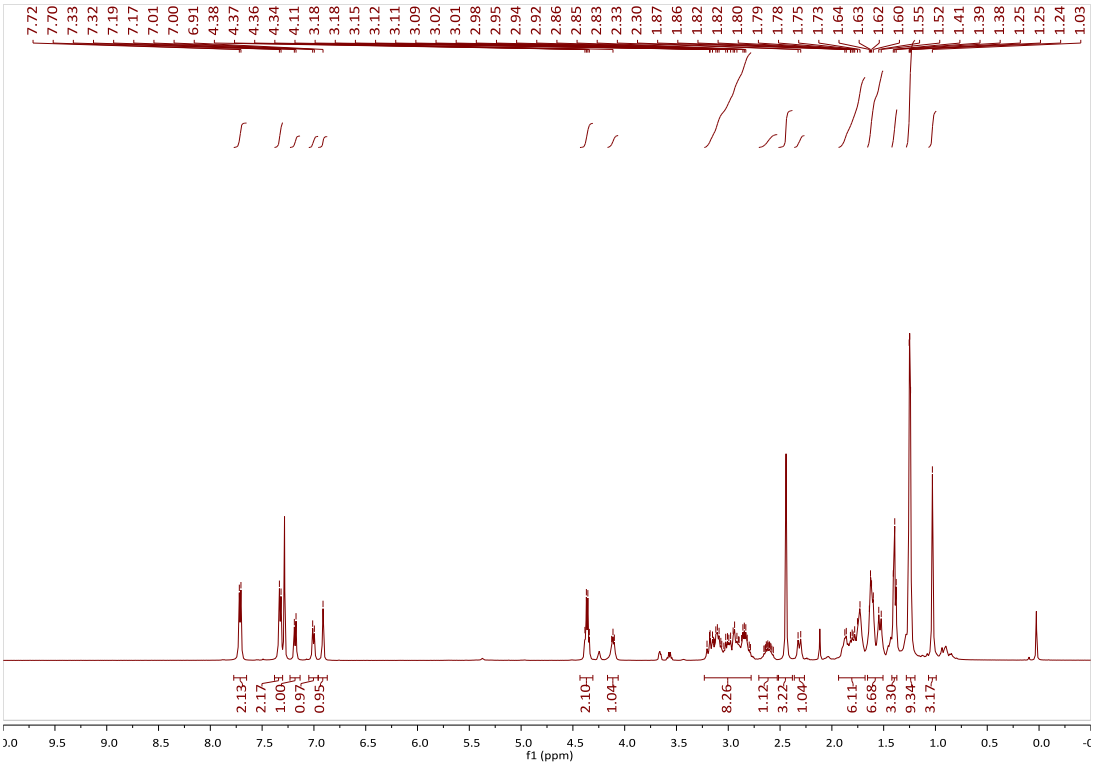


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **7e**

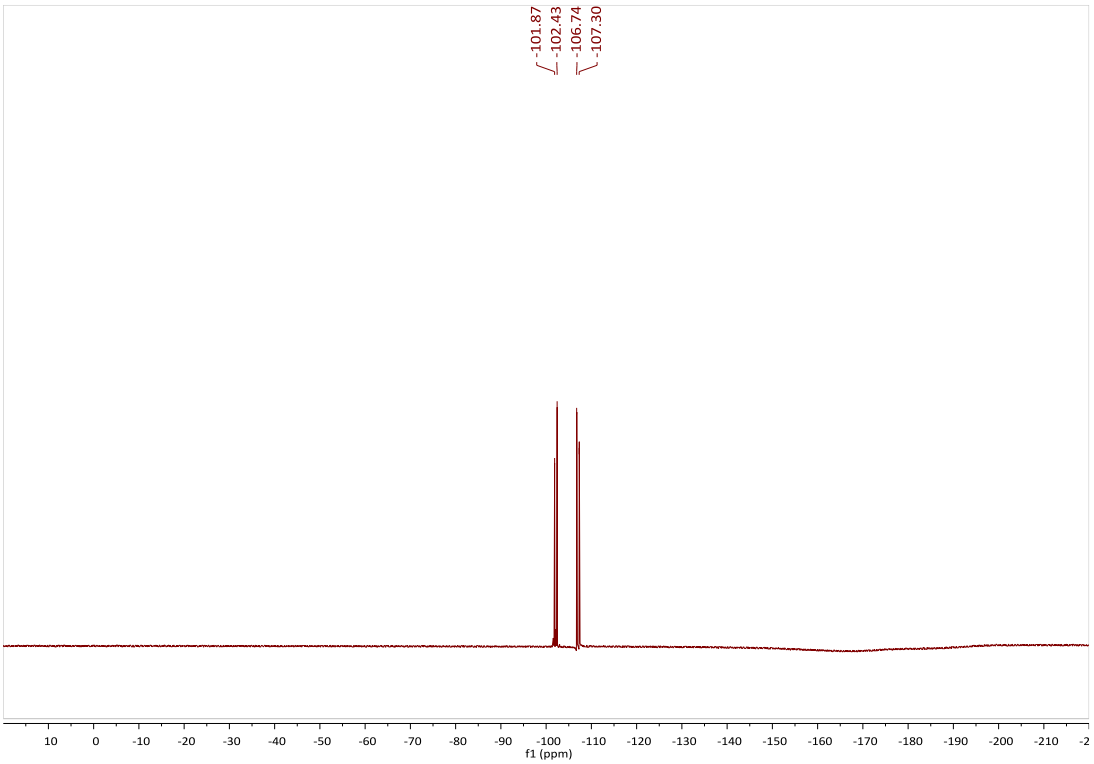


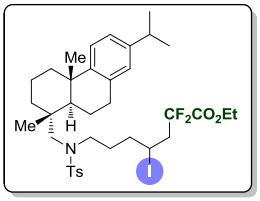


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **7f**

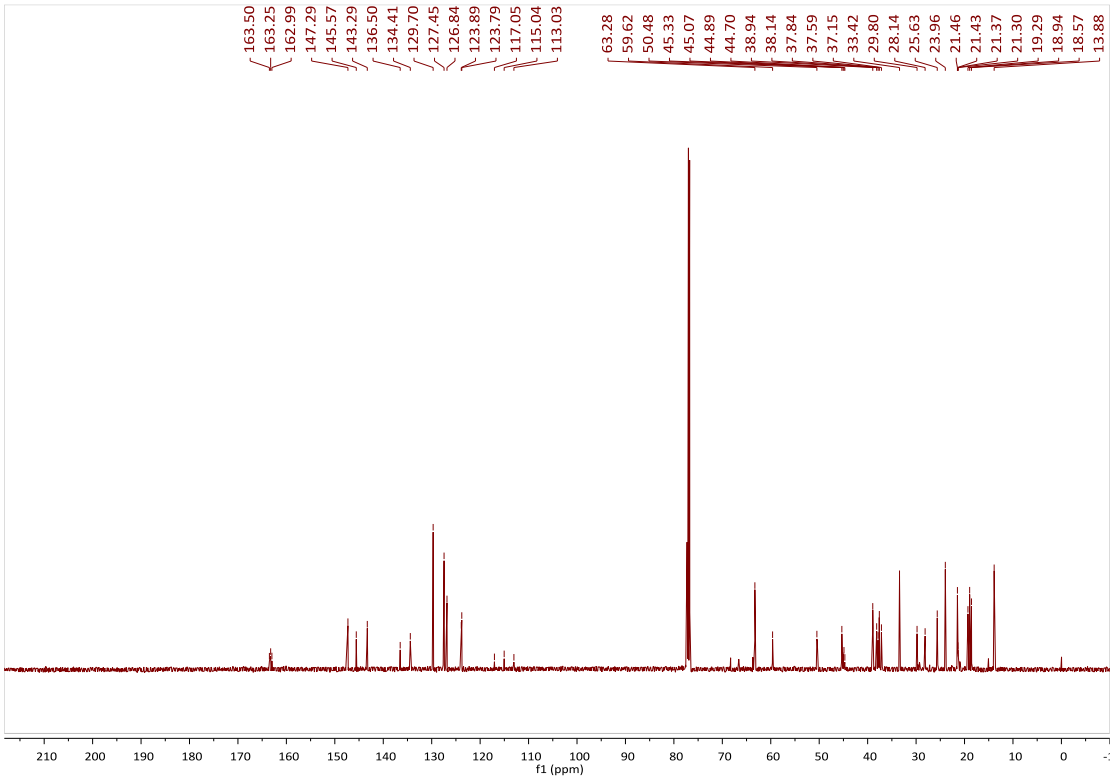


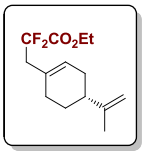
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **7f**



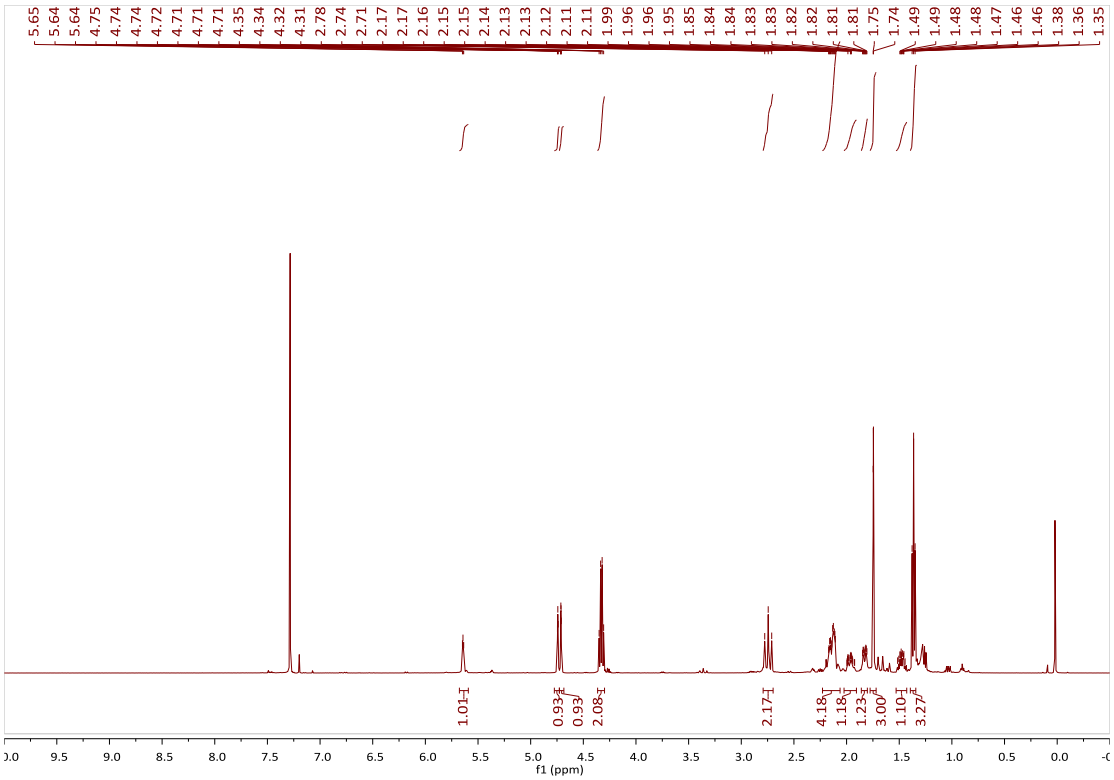


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **7f**

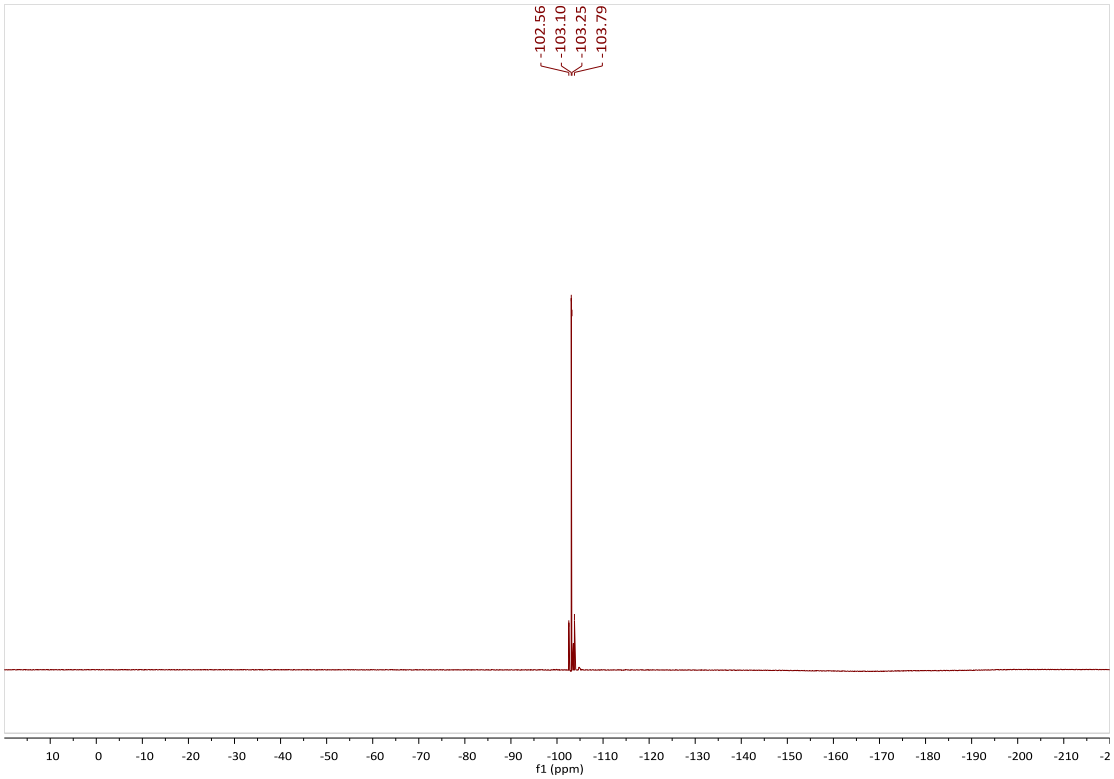


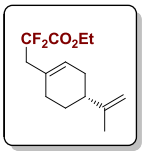


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **9**

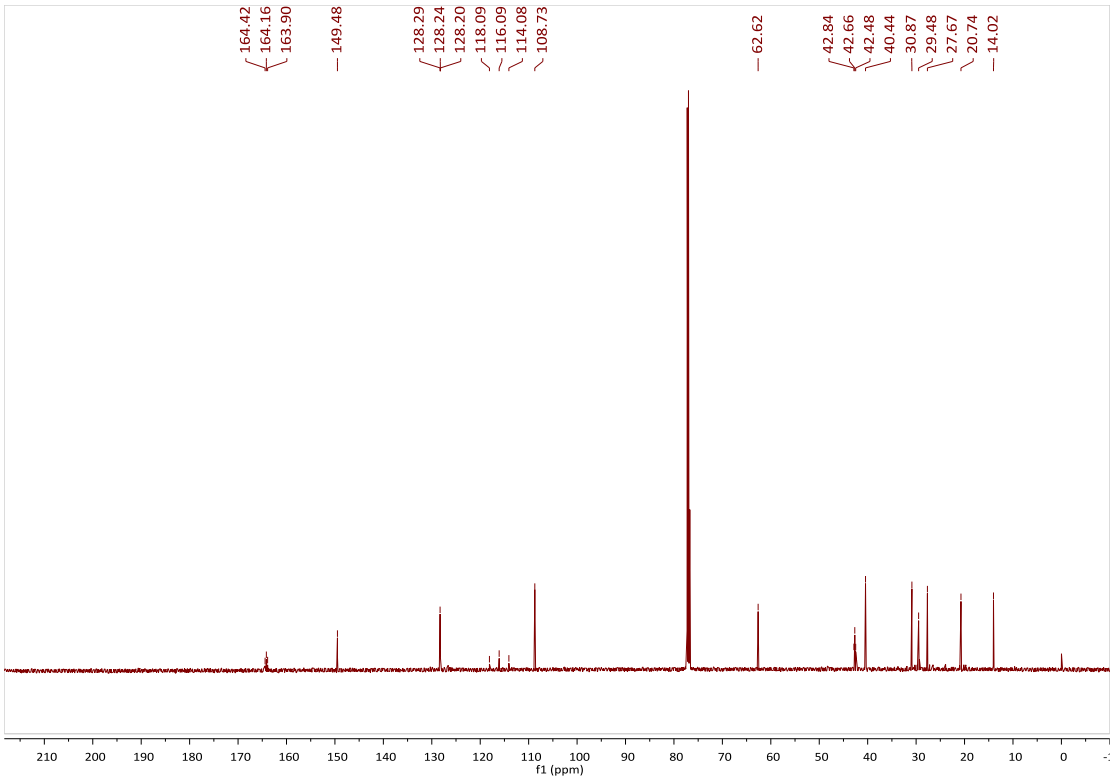


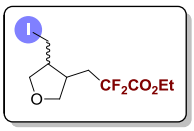
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **9**





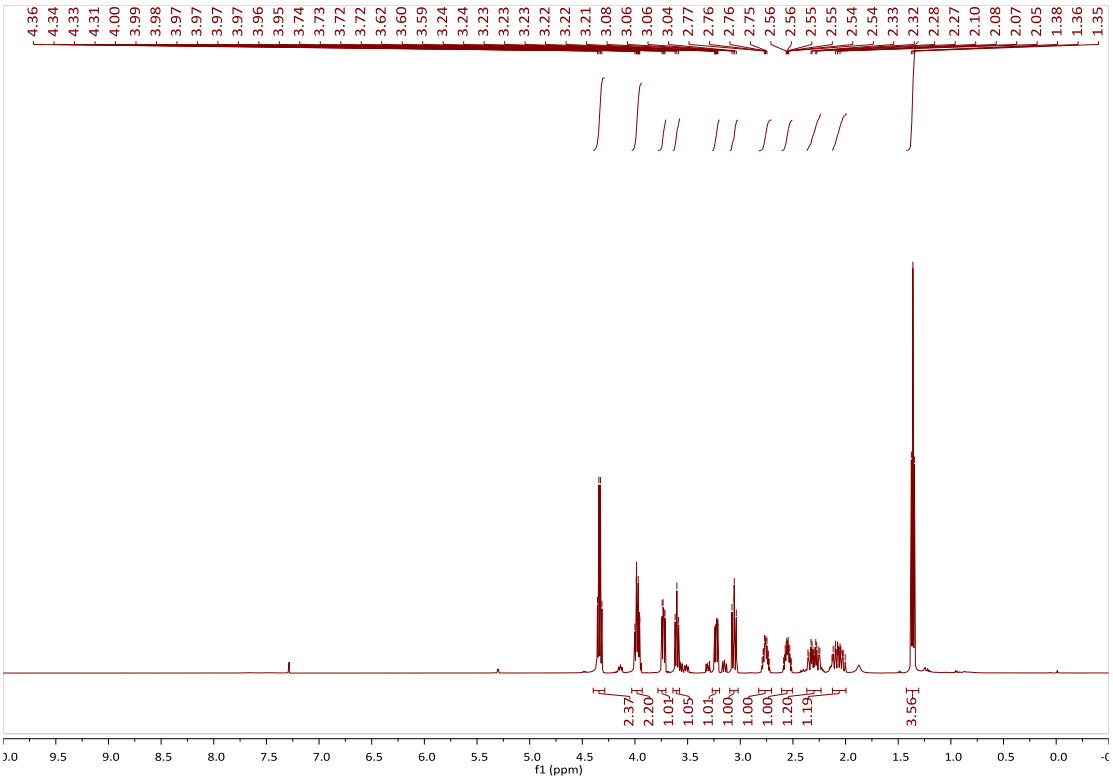
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **9**



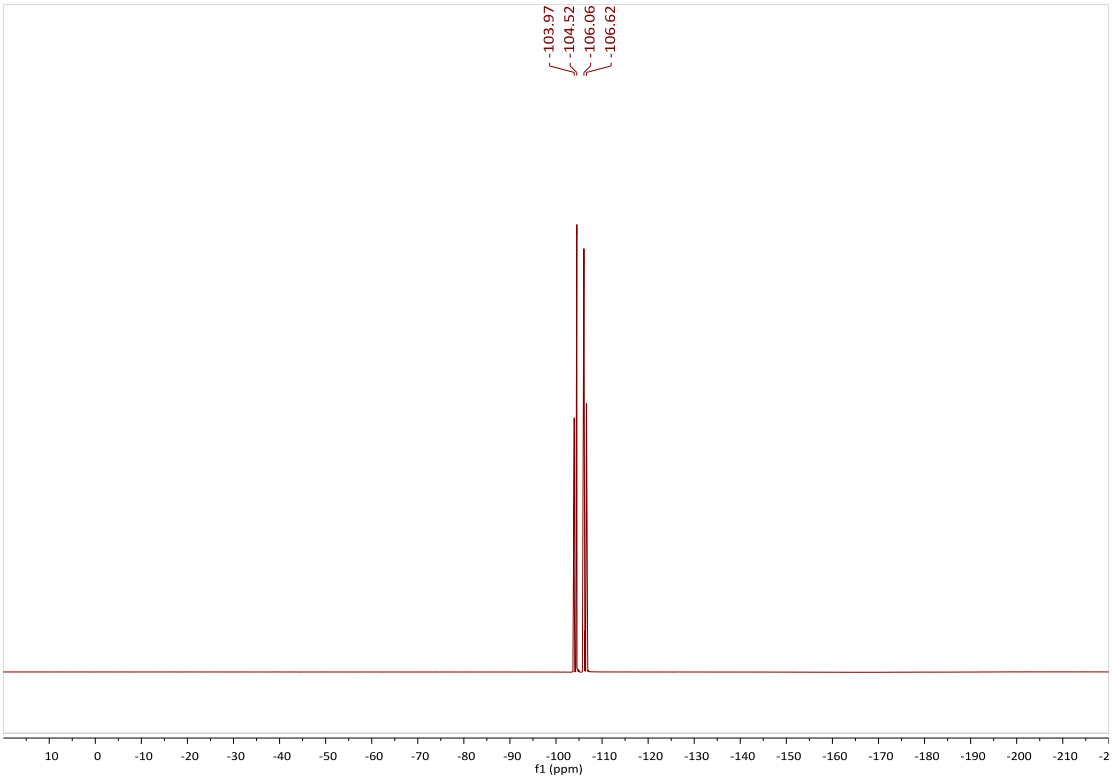


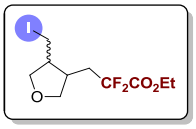
6:1 dr

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **10a**



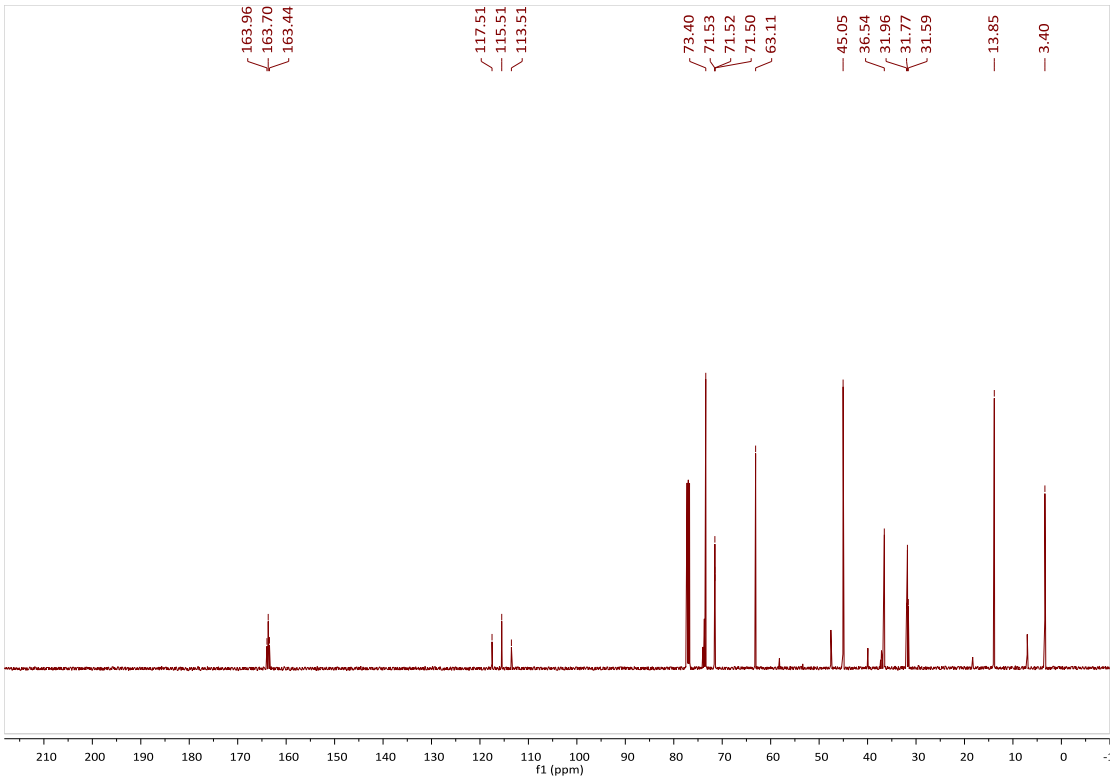
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **10a**

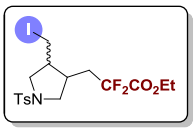




6:1 dr

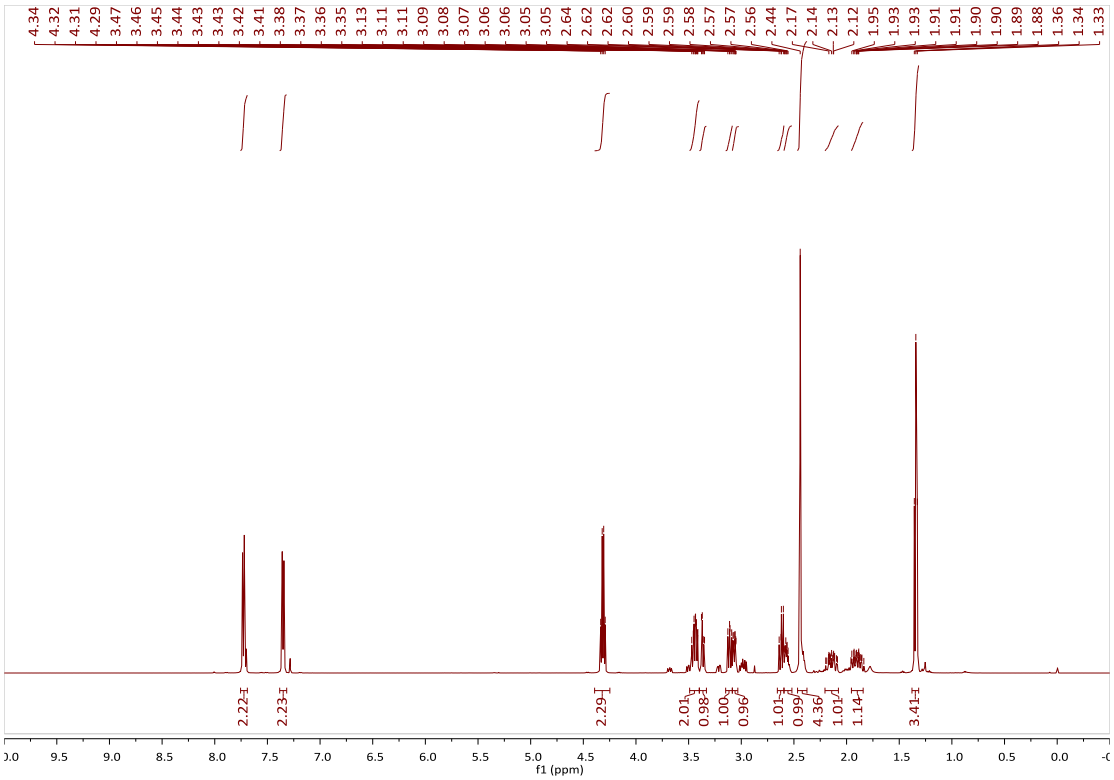
^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **10a**



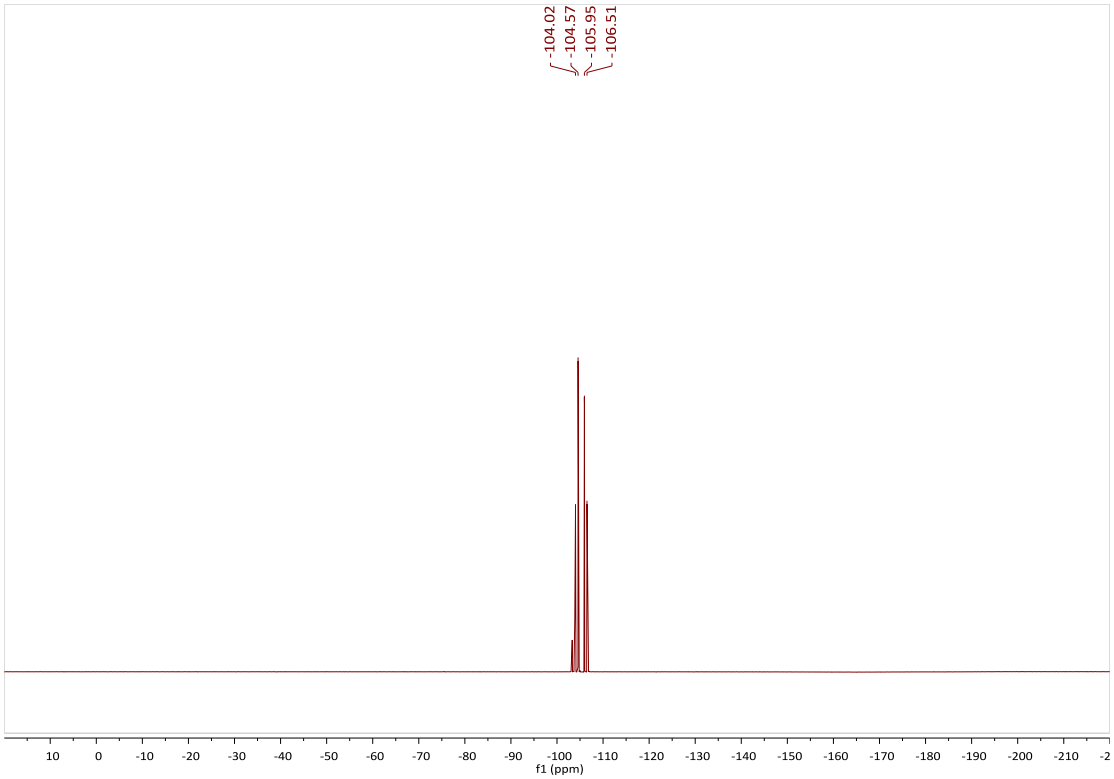


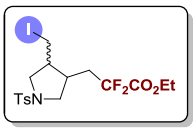
5.6:1 dr

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **10b**



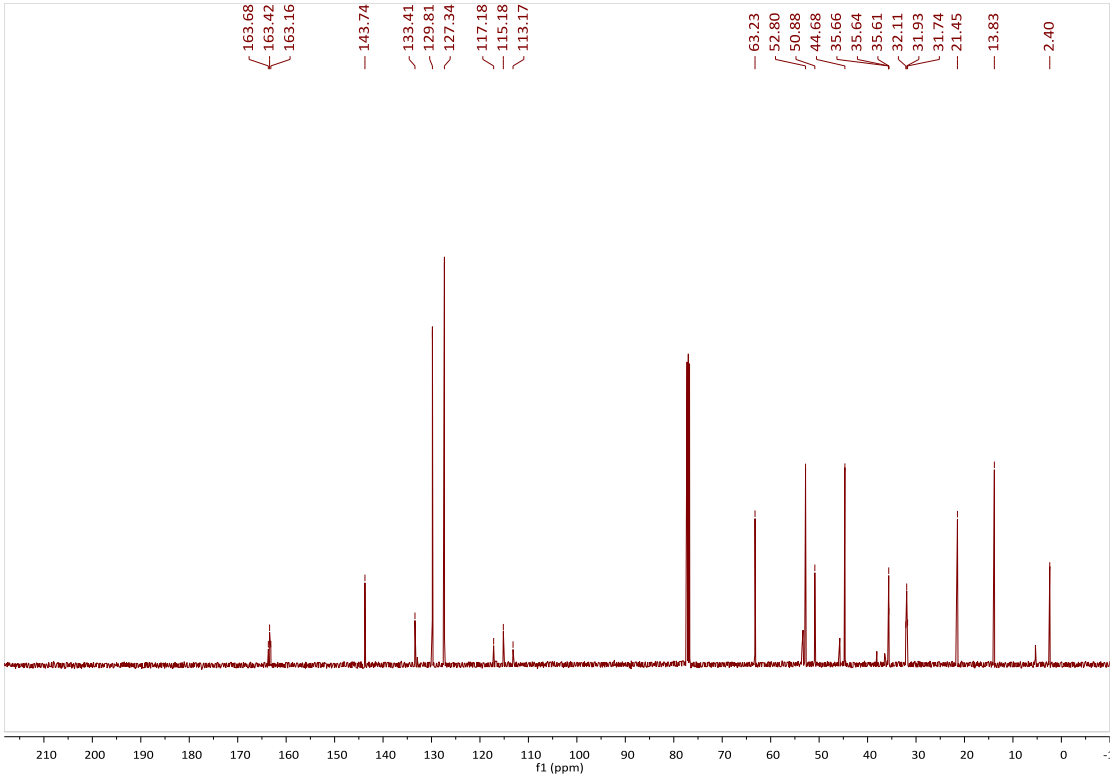
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **10b**

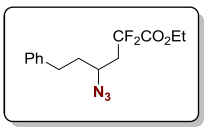




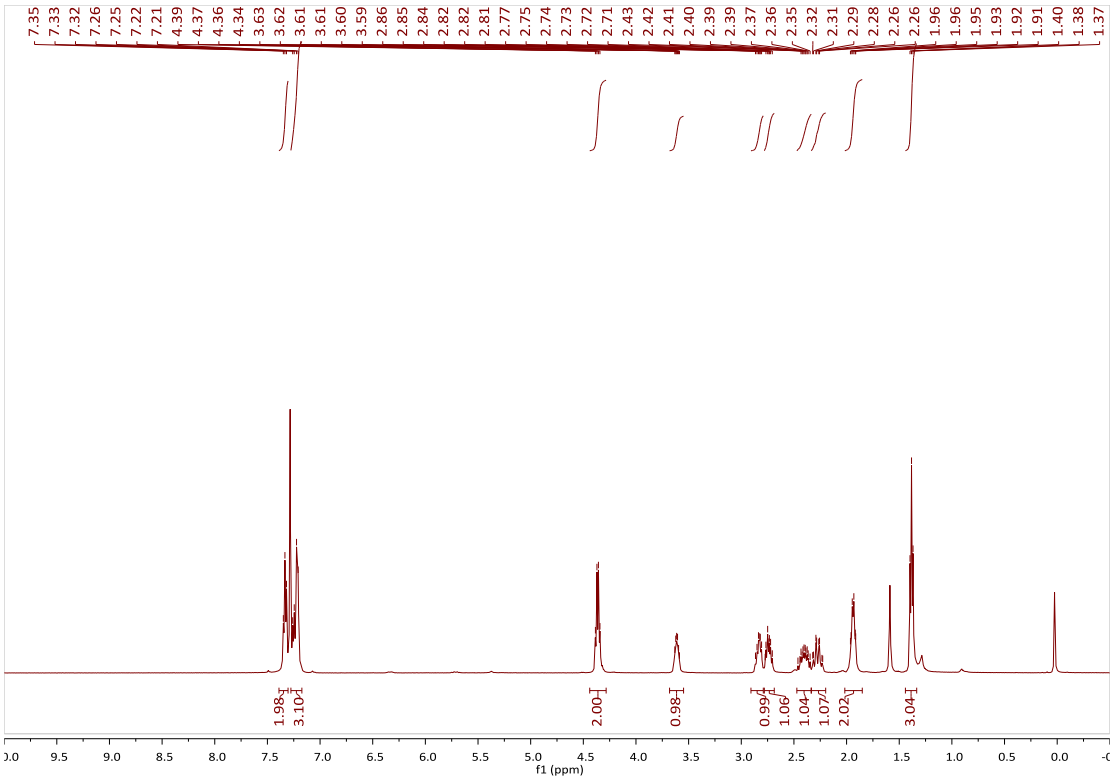
5.6:1 dr

^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **10b**

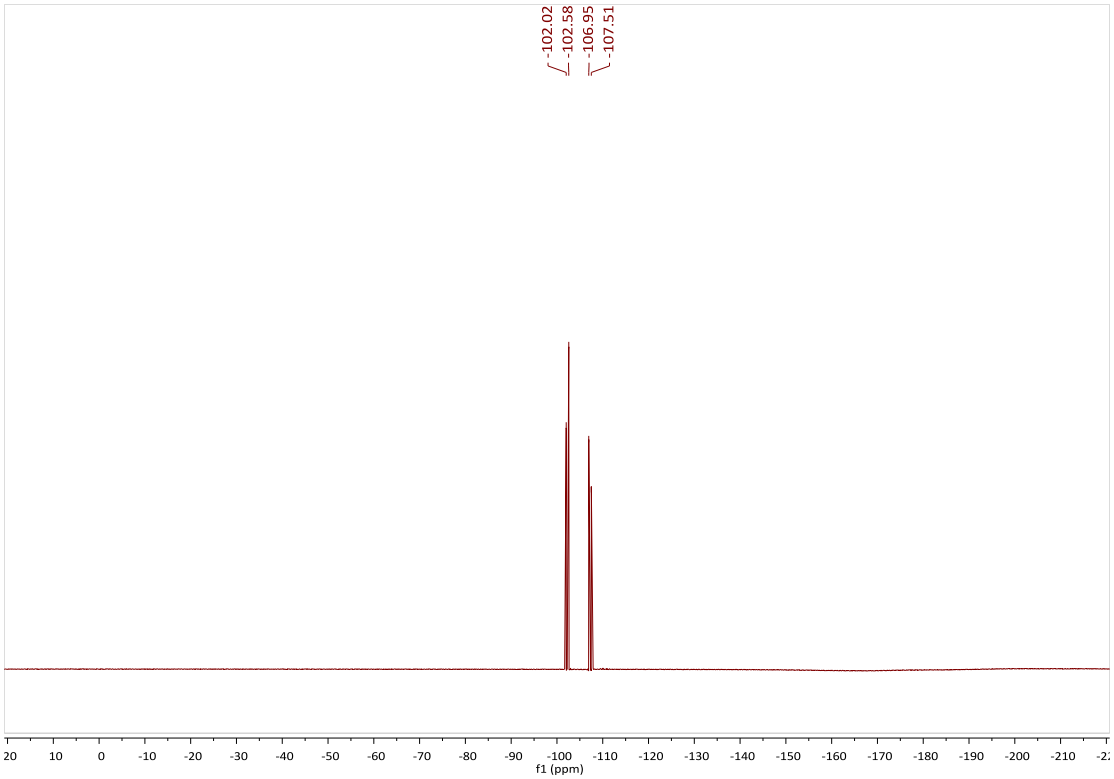


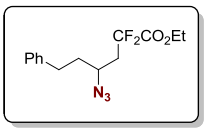


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **12**

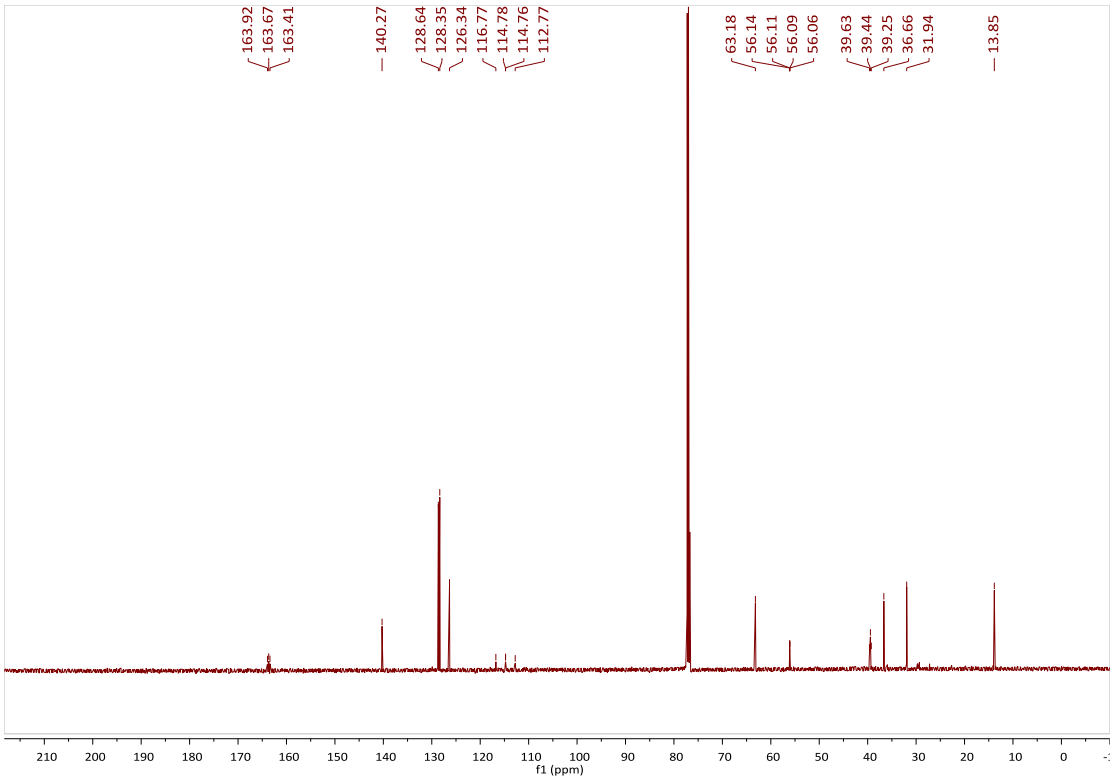


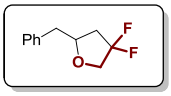
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **12**



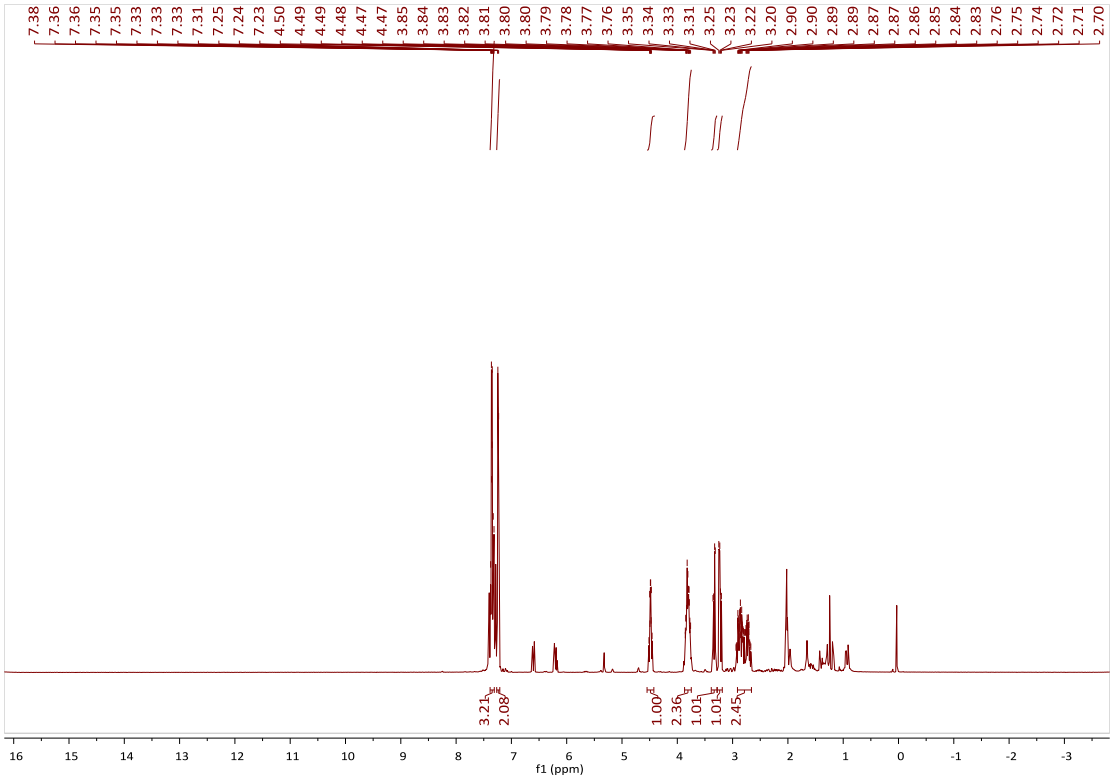


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **12**

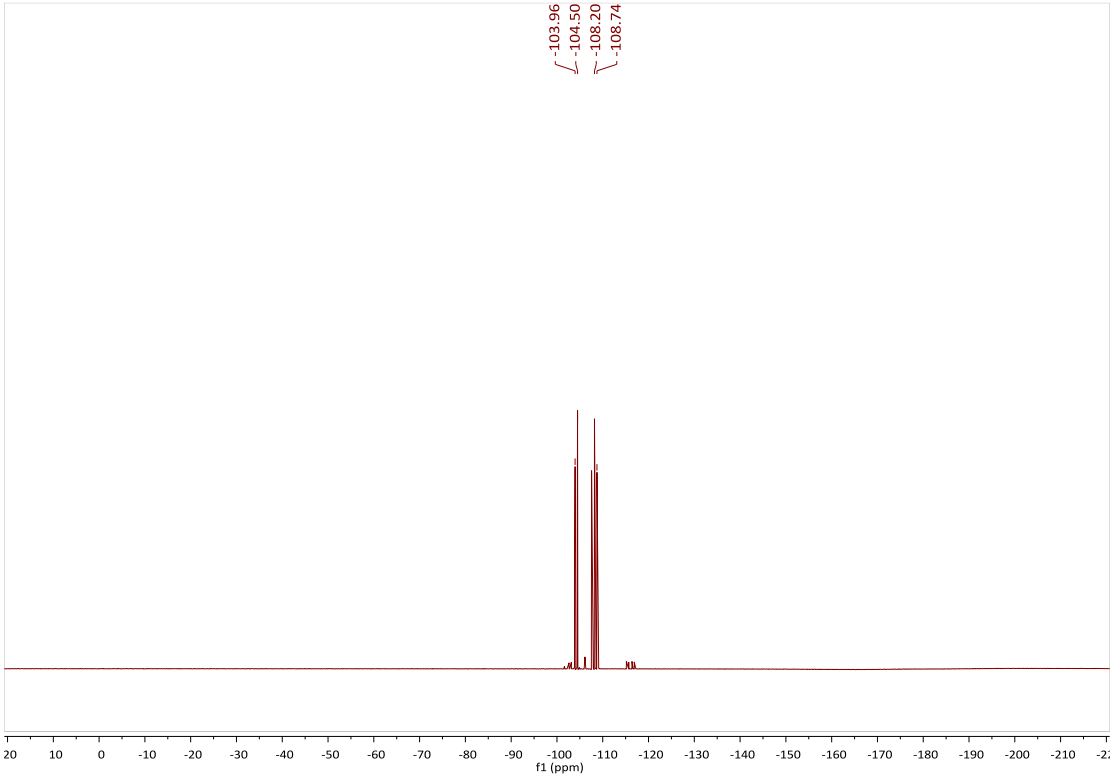


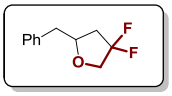


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **13**

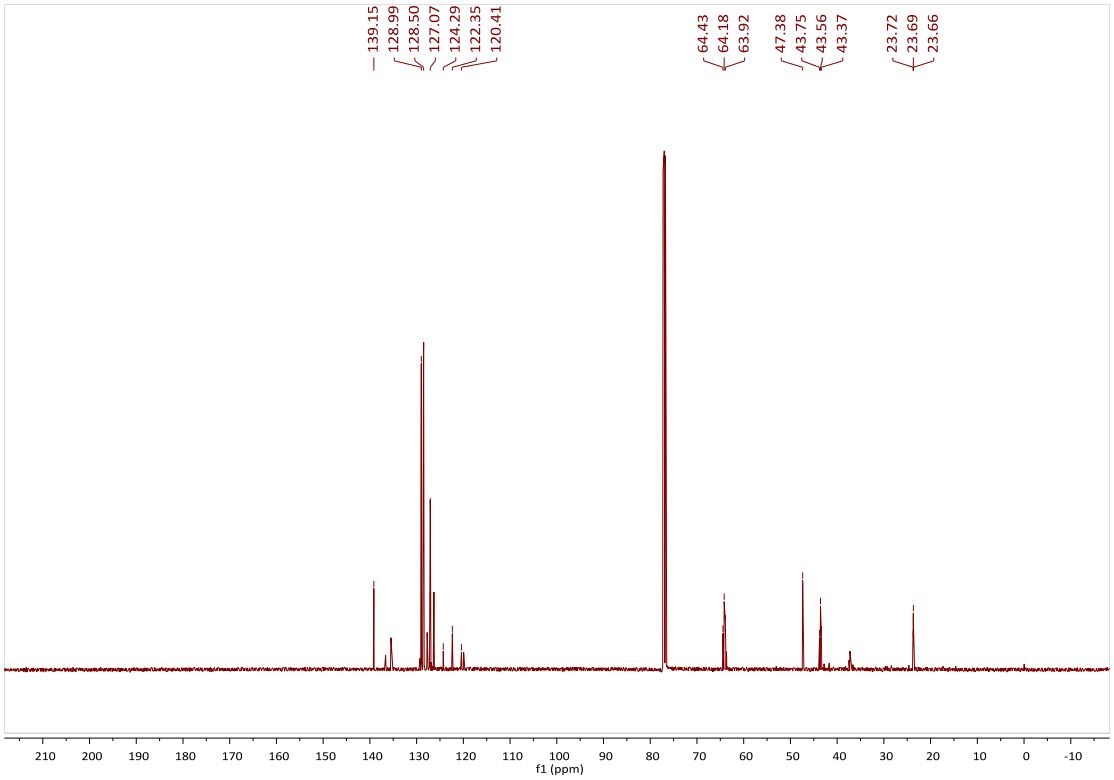


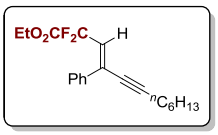
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **13**



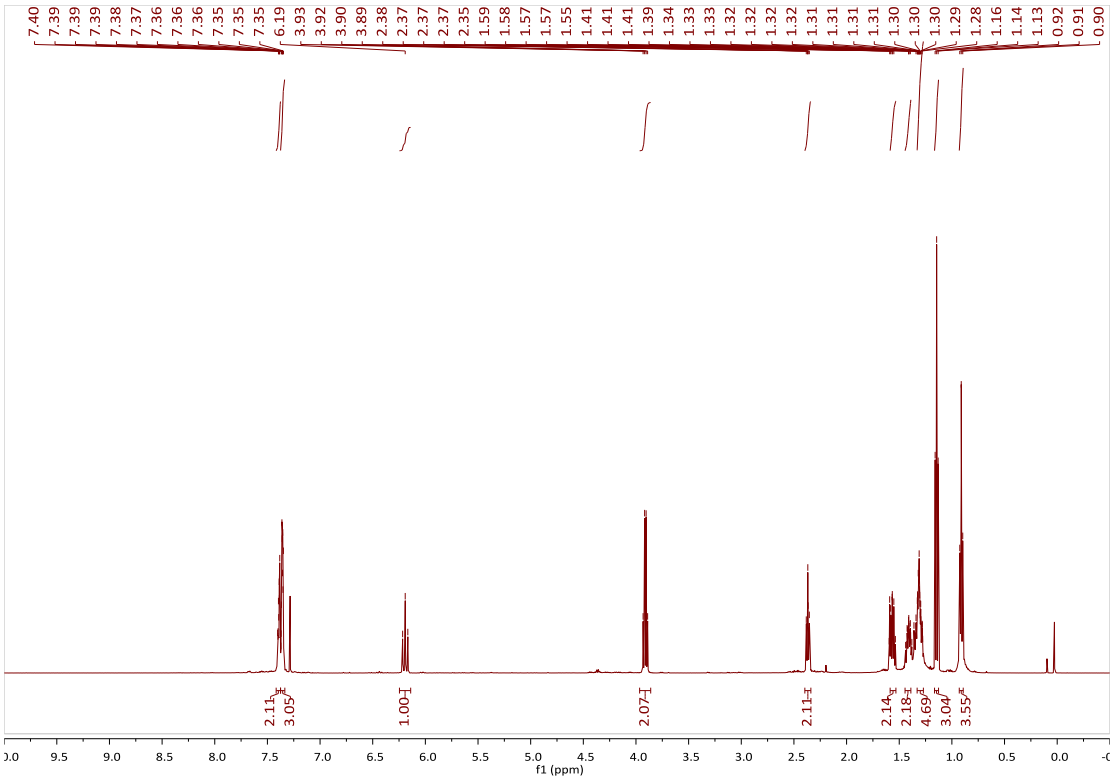


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **13**

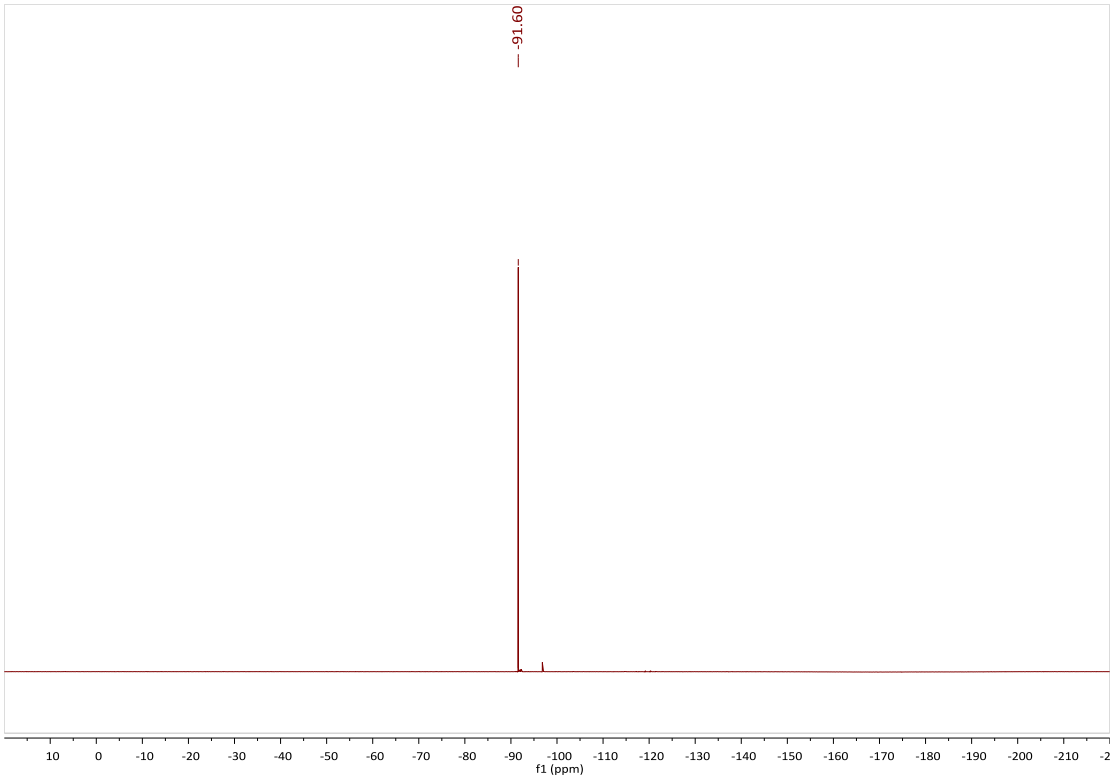


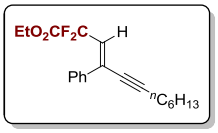


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **14**

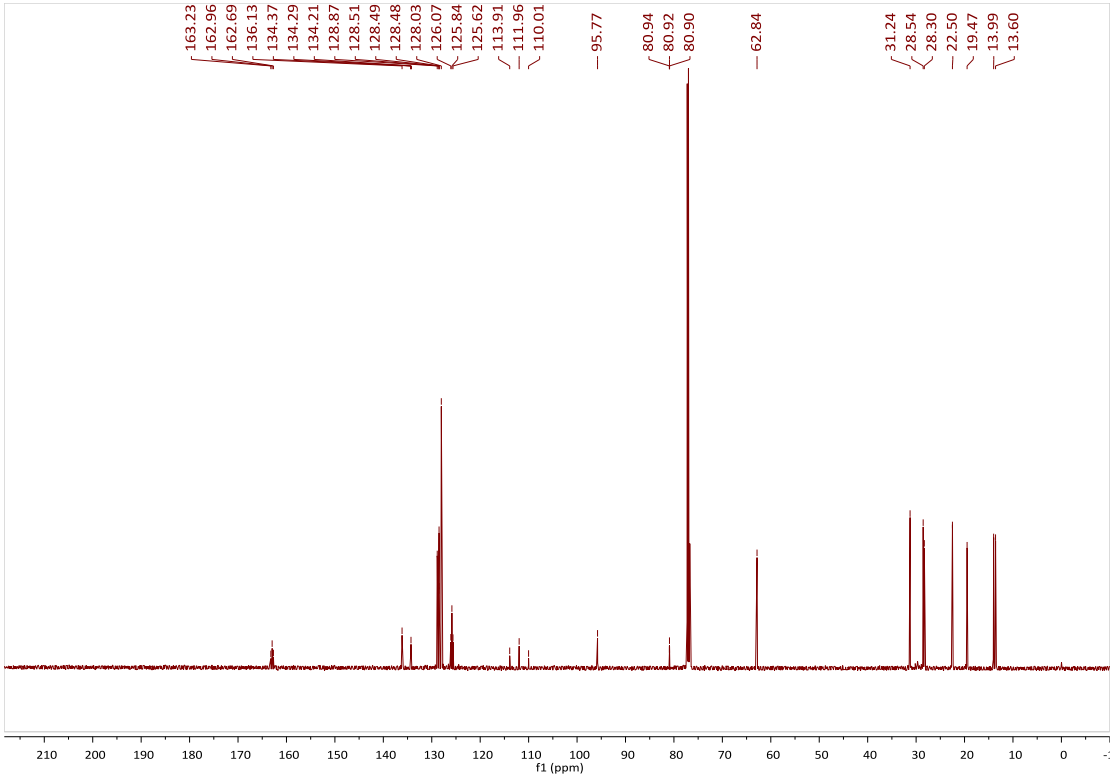


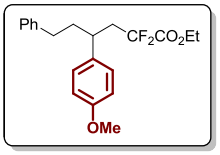
^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **14**



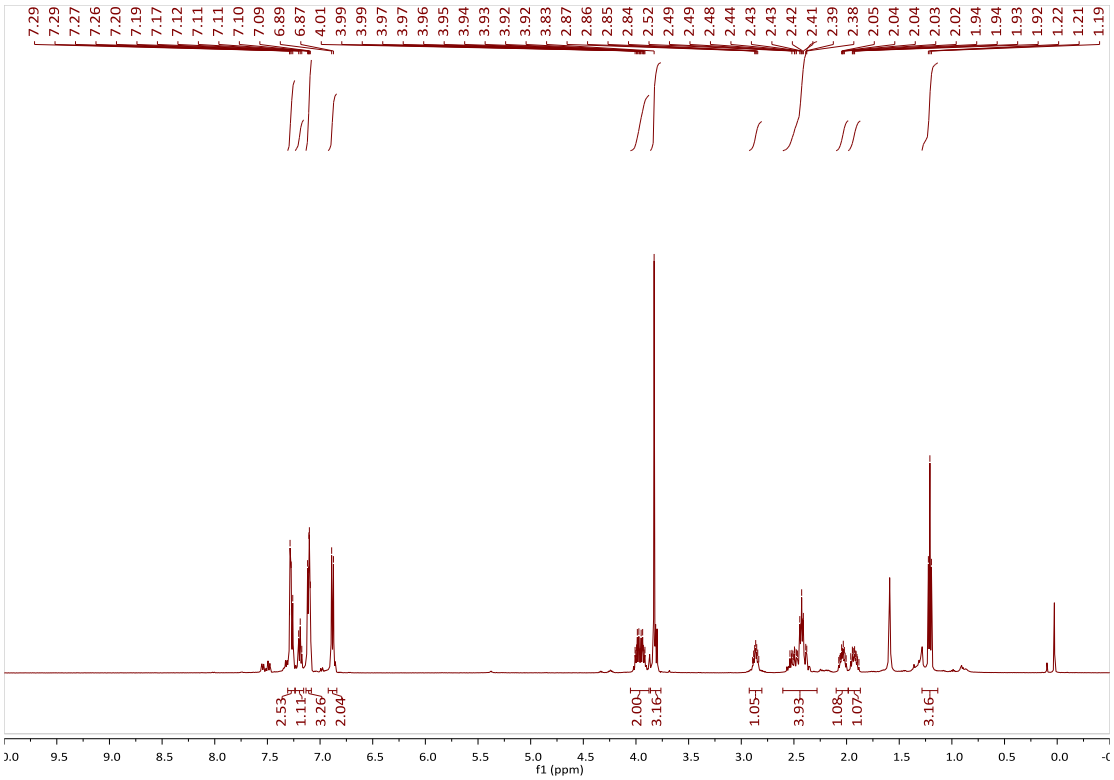


^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **14**

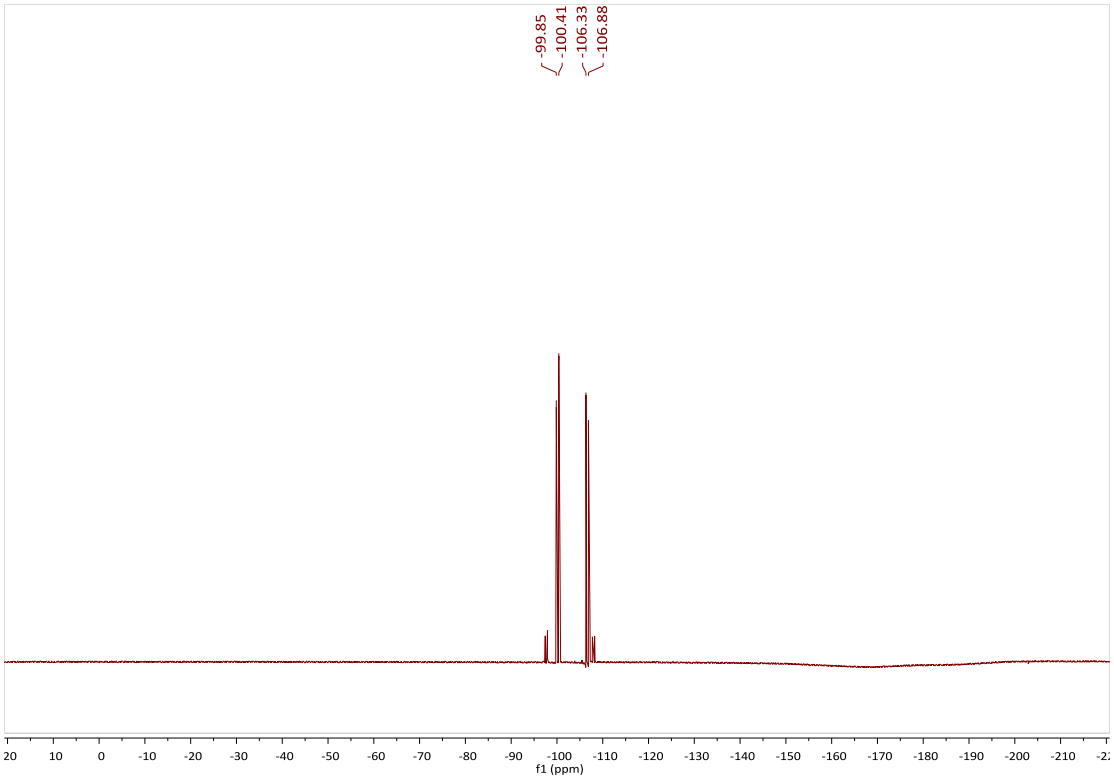


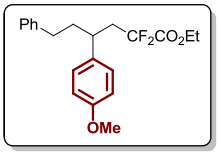


^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **15**



^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **15**





^{13}C NMR-spectrum (125 MHz, $CDCl_3$) of **15**