Supplementary Information for

Gold catalyzed hydrofluorination of propargyl alcohols promoted by fluorine-hydrogen bonding

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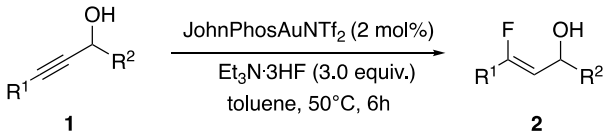
General Informations

Unless stated otherwise, all reactions were carried out under an air atmosphere. All commercial reagents were used without additional purification. Flash chromatography was carried out with silica gel (200-300 mesh). ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded with 400 MHz, 101 MHz and 377 MHz spectrometers in $CDCl_3$ by using tetramethylsilane (TMS) as the internal standard, respectively. High-resolution mass spectra (HRMS) were recorded using a positive-ion electrospray ionization (ESI+) source.

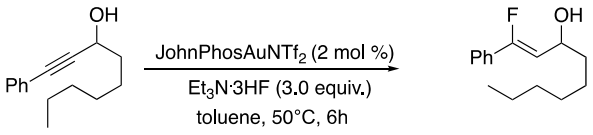
General Procedure of Hydrofluorination



1 **2**

Following the standard procedure, a dried 5 mL Teflon tube was charged with propargyl alcohols **1** (0.2 mmol, 1.0 equiv.), JohnPhosAuNTf$_2$ (0.004 mmol, 5 mol%) and Et$_3$N·3HF (97 mg, 0.6 mmol, 3.0 equiv.) in 2.0 mL of dried toluene at 50°C (oil bath) under an air atmosphere. After 6 hours, the reaction was quenched with a saturated solution of NaOH (10 mL), then extracted with ethyl acetate (3×30 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by column chromatography on silica gel to give the product **2.**

Gram-scale synthesis of fluoroallyl alcohol

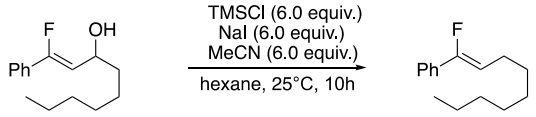


1a (10 mmol)

2a
1.54 g, 65% yield

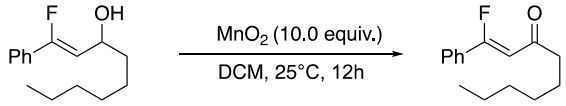
A 50 mL teflon tube was charged with propargyl alcohol **1a** (2.16 g, 10 mmol, 1.0 equiv.), JohnPhosAuNTf$_2$ (155 mg, 0.2 mmol, 2 mol%) and Et$_3$N·3HF (4.85 g, 30 mmol, 3.0 equiv.) in toluene (20 mL) at 50 °C (oil bath) under an air atmosphere. After 6 hours, the reaction was quenched with a saturated solution of NaOH (10 mL), then extracted with ethyl acetate (3×30 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by column chromatography on silica gel to give the product **2a**.

General Procedure of Derivatization



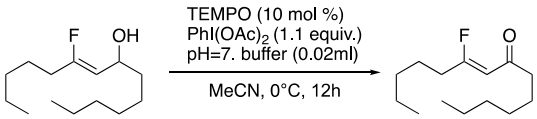
2a **4**

General Procedure A[1]**.** A dried 8 mL tube was charged with fluorine-substituted allyl alcohol **2a** (0.2 mmol, 1.0 equiv.), TMSCl (1.2 mmol, 6.0 equiv.), NaI (1.2 mmol, 6.0 equiv.) and MeCN (1.2 mmol, 6.0equiv.) in 2.0 mL of hexane at r.t. under an air atmosphere. After 10 hours, the reaction was extracted with ethyl acetate (3×15 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by column chromatography on silica gel to give the products **4**.



2a **5**

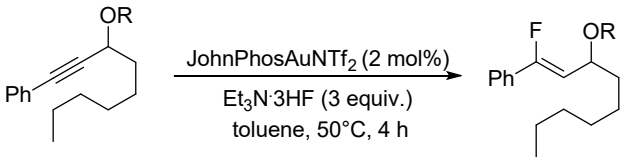
General Procedure B[2]**.** A dried 8 mL tube was charged with fluorine-substituted allyl alcohol **2a** (0.2 mmol, 1.0 equiv.) and MnO_2 (1.0 mmol, 5.0 equiv.) in 2.0 mL of DCM at r.t. under an air atmosphere. After 6 hours, the MnO_2 was filtered out and new MnO_2 (1.0 mmol, 5.0 equiv.) was added. After 6 hours, the mixture was filtered and extracted with ethyl acetate (3×15 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by column chromatography on silica gel to give the product **5.**



2j **6**

General Procedure C[3]**.** A dried 8 mL tube was charged with fluorine-substituted allyl alcohol **2j** (0.2 mmol, 1.0 equiv.) and TEMPO (0.2 mmol, 10 mol%), $PhI(OAc)_2$ (0.02 mmol, 1.1 equiv.), buffer (pH = 7, 0.02 ml) in 2.0 mL of MeCN at 0°C under an air atmosphere. The reaction was stirred at r.t. for 24 hours, the mixture was extracted with ethyl acetate (3×15 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by column chromatography on silica gel to give the product **6**.

Control experiment

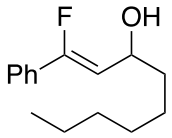


1a (R = H)
7 (R = Me)

2a (R = H) , 68%
8 (R = Me), 11%

A dried 5 mL Teflon tube A was charged with propargyl alcohols **1** (0.2 mmol, 1.0 equiv.) and B was charged with **7** (0.2 mmol, 1.0 equiv.), JohnPhosAuNTf$_2$ (0.004 mmol, 5 mol%) and Et$_3$N·3HF (97 mg, 0.6 mmol, 3.0 equiv.) in 2.0 mL of dried toluene at 50°C (oil bath) under an air atmosphere. After 4 hours, the reactions were quenched with a saturated solution of NaOH (10 mL), then extracted with ethyl acetate (3×30 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, filtered. 80mg mesitylene was added to the two crude products as the reference material, and the reaction was determined by the ^{1}H NMR.

Characterization of Products



(Z)-1-fluoro-1-phenylnon-1-en-3-ol (2a)

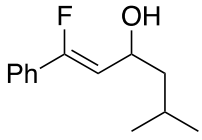
Compound **2a** was prepared following the general procedure. The reaction of **1a** (43 mg, 0.2 mmol) give **2a** as a yellow oil (38 mg, 80%); R_f=0.40 (petroleum ether/ethyl acetate 10: 1);

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.58 – 7.52 (m, 2H), 7.44 – 7.33 (m, 3H), 5.49 (dd, *J* = 37.0, 8.7 Hz, 1H), 4.82 (dt, *J* = 8.8, 6.7 Hz, 1H), 2.00 (s, 1H), 1.80 – 1.54 (m, 2H), 1.43 – 1.25 (m, 8H), 0.96 – 0.88 (m, 3H);

^{13}C NMR (101 MHz, CDCl$_3$) δ 157.3 (d, $J_{C\text{-}F}$ = 250.5 Hz), 131.9 (d, $J_{C\text{-}F}$ = 28.3 Hz), 129.2, 128.5 (d, $J_{C\text{-}F}$ = 2.0 Hz), 124.4 (d, $J_{C\text{-}F}$ = 8.1 Hz), 109.2 (d, $J_{C\text{-}F}$ = 15.2 Hz), 67.0 (d, $J_{C\text{-}F}$ = 6.1 Hz), 37.5 (d, $J_{C\text{-}F}$ = 1.0 Hz), 31.8, 29.2, 25.3, 22.6, 14.1;

^{19}F NMR (377MHz, CDCl$_3$) δ -117.1;

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{21}FNaO^+$ 259.1469, found 259.1468.



(Z)-1-fluoro-5-methyl-1-phenylhex-1-en-3-ol （2b）

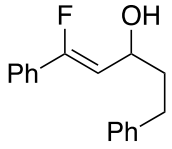
Compound **2b** was prepared following the general procedure. The reaction of **1b** (38 mg, 0.2 mmol) give **2a** as a yellow oil (19 mg, 45%); R_f=0.45 (petroleum ether/ethyl acetate 10:1);

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59 – 7.53 (m, 2H), 7.43 – 7.34 (m, 3H), 5.60 – 5.43 (m, 1H), 4.68 (dt, *J* = 8.9, 5.9 Hz, 1H), 1.78 (s, 1H), 1.72 – 1.56 (m, 2H), 1.30 – 1.14 (m, 1H), 1.04 – 0.94 (m, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7 (dd, J_{C-F} = 251.5 Hz), 131.9 (d, J_{C-F} = 29.23 Hz), 129.2 (d, J_{C-F} = 2.0 Hz), 128.5 (d, J_{C-F} = 2.0 Hz), 124.4 (dd, J_{C-F} = 7.1 Hz), 107.3 (dd, J_{C-F} = 67.7 Hz), 69.5 (dd, J_{C-F} = 23.2 Hz), 41.0 (dd, J_{C-F} = 18.2 Hz), 25.3, 25.0 (d, J_{C-F} = 20.2 Hz), 13.0 (dd, J_{C-F} = 281.8 Hz);

^{19}F NMR (377MHz, $CDCl_3$) δ -117.3 (d, J = 101.1 Hz);

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{17}FNaO^+$ 231.1156, found 231.1155.



(Z)-1-fluoro-1,5-diphenylpent-1-en-3-ol (2c)

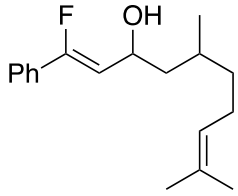
Compound **2c** was prepared following the general procedure. The reaction of **1c** (47 mg, 0.2 mmol) give **2c** as a yellow oil (35 mg, 68%); R_f=0.50 (petroleum ether/ethyl acetate 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 2H), 7.45 – 7.39 (m, 3H), 7.37 – 7.31 (m, 2H), 7.29 – 7.21 (m, 3H), 5.55 (dd, J = 36.9, 8.6 Hz, 1H), 4.94 – 4.80 (m, 1H), 2.90 – 2.69 (m, 2H), 2.15 – 2.03 (m, 1H), 1.96 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5 (d, J_{C-F} = 251.5 Hz), 141.7, 131.7 (d, J_{C-F} = 28.3 Hz), 129.3, 128.6 (d, J_{C-F} = 2.0 Hz), 128.5 (d, J_{C-F} = 3.0 Hz), 125.9, 124.4 (d, J_{C-F} = 7.1 Hz), 108.8 (d, J_{C-F} = 15.2 Hz), 65.5 (d, J_{C-F} = 6.1 Hz), 38.91 (d, J_{C-F} = 2.0 Hz), 31.7;

^{19}F NMR (377MHz, $CDCl_3$) δ -117.1;

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{17}FNaO^+$ 279.1156, found 279.1155.



(Z)-1-fluoro-5,9-dimethyl-1-phenyldeca-1,8-dien-3-ol (2d)

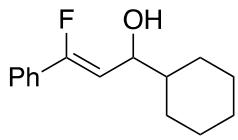
Compound **2d** was prepared following the general procedure. The reaction of **1d** (51 mg, 0.2 mmol) give **2d** as a yellow oil (36 mg, 64%); R_f=0.37 (petroleum ether/ethyl acetate 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dt, J = 7.7, 1.7 Hz, 2H), 7.41 – 7.35 (m, 3H), 5.47 (m, 1H), 5.12 (m, 1H), 4.97 – 4.87 (m, 1H), 2.02 (m, 2H), 1.85 – 1.72 (m, 2H), 1.68 (t, J = 1.4 Hz, 3H), 1.62 (d, J = 1.3 Hz, 3H), 1.60 – 1.57 (m, 1H), 1.47 – 1.34 (m, 2H), 1.26 – 1.19 (m, 1H), 0.98 (t, J = 6.3 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2 (dd, J_{C-F} = 251.5 Hz), 131.9 (dd, J_{C-F} = 29.3 Hz), 131.3, 129.2 (d, J_{C-F} = 4.0 Hz), 128.5 (d, J_{C-F} = 2.0 Hz), 124.7, 124.4 (dd, J_{C-F} = 7.1 Hz), 109.4 (dd, J_{C-F} = 37.4 Hz), 64.1 (d, J_{C-F} = 17.2 Hz), 44.7 (d, J_{C-F} = 13.1 Hz), 37.3 (d, J_{C-F} = 8.1 Hz), 29.1 (d, J_{C-F} = 32.3 Hz), 25.7, 25.4 (d, J_{C-F} = 6.1 Hz), 19.7 (d, J_{C-F} = 50.5 Hz), 17.7(d, J_{C-F} = 2.0 Hz);

^{19}F NMR (377MHz, $CDCl_3$) δ -118.0 (d, J = 16.9);

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{25}FNaO^+$ 299.1782, found 299.1785.



(Z)-1-cyclohexyl-3-fluoro-3-phenylprop-2-en-1-ol (2e)

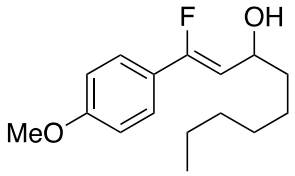
Compound **2e** was prepared following the general procedure. The reaction of **1e** (43 mg, 0.2 mmol) give **2e** as a yellow oil (22 mg, 46%); R_f=0.52 (petroleum ether/ethyl acetate 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 2H), 7.43 – 7.34 (m, 3H), 5.50 (dd, *J* = 37.0, 9.0 Hz, 1H), 4.56 (t, *J* = 7.9 Hz, 1H), 1.99 (d, *J* = 12.7 Hz, 1H), 1.84 – 1.68 (m, 5H), 1.53 (m, 1H), 1.31 – 1.05 (m, 5H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7 (d, $J_{C\text{-}F}$ = 250.5 Hz), 131.9 (d, $J_{C\text{-}F}$ = 28.3 Hz), 129.2, 128.5 (d, $J_{C\text{-}F}$ = 1.0 Hz), 124.4 (d, $J_{C\text{-}F}$ = 7.1 Hz), 107.6 (d, $J_{C\text{-}F}$ = 5.1 Hz), 70.2 (d, $J_{C\text{-}F}$ = 5.1 Hz), 44.1 (d, $J_{C\text{-}F}$ = 1.1 Hz), 28.6 (d, $J_{C\text{-}F}$ = 32.3 Hz), 26.5, 26.0 (d, $J_{C\text{-}F}$ = 10.1 Hz);

^{19}F NMR (377MHz, $CDCl_3$) δ -117.5;

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{19}FNaO^+$ 257.1312, found 257.1318.



(Z)-1-fluoro-1-(4-methoxyphenyl)non-1-en-3-ol (2f)

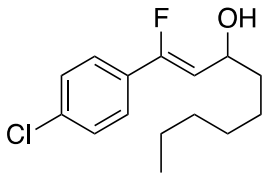
Compound **2f** was prepared following the general procedure. The reaction of **1f** (49 mg, 0.2 mmol) give **2f** as a yellow oil (30 mg, 57%); R_f=0.43 (petroleum ether/ethyl acetate 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.44 (m, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 5.34 (dd, *J* = 37.2, 8.7 Hz, 1H), 4.85 – 4.73 (m, 1H), 3.84 (s, 3H), 1.87 (s, 1H), 1.72 (m, 1H), 1.63 – 1.52 (m, 1H), 1.42 – 1.24 (m, 8H), 0.89 (d, *J* = 6.9 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 157.4 (d, $J_{C\text{-}F}$ = 250.5 Hz), 125.9 (d, $J_{C\text{-}F}$ = 7.1 Hz), 124.5 (d, $J_{C\text{-}F}$ = 29.3 Hz), 113.9 (d, $J_{C\text{-}F}$ = 2.0 Hz), 107.2 (d, $J_{C\text{-}F}$ = 15.2 Hz), 66.0 (d, $J_{C\text{-}F}$ = 5.1 Hz), 55.3, 37.5 (d, $J_{C\text{-}F}$ = 1.0 Hz), 31.8, 29.2, 25.4, 22.6, 14.1;

^{19}F NMR (377MHz, $CDCl_3$) δ -117.1;

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{23}FNaO_2^+$ 289.1574, found 289.1573.



(Z)-1-(4-chlorophenyl)-1-fluorononon-1-en-3-ol (2g)

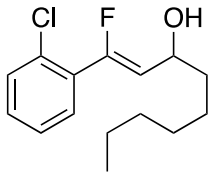
Compound **2g** was prepared following the general procedure. The reaction of **1g** (50 mg, 0.2 mmol) give **2g** as a yellow oil (36 mg, 66%); *Z*/*E* = 100:3; R_f=0.43 (petroleum ether/ethyl acetate 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 5.47 (dd, *J* = 36.8, 8.6 Hz, 1H), 4.79 (q, *J* = 7.1 Hz, 1H), 1.91 (s, 1H), 1.71 (d, *J* = 16.6 Hz, 2H), 1.58 (dt, *J* = 19.1, 5.9 Hz, 1H), 1.36 – 1.27 (m, 8H), 0.93 – 0.87 (m, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3 (d, $J_{C\text{-}F}$ = 251.5 Hz), 135.1, 130.4 (d, $J_{C\text{-}F}$ = 30.3 Hz), 128.8 (d, $J_{C\text{-}F}$ = 2.0 Hz), 125.7 (d, $J_{C\text{-}F}$ = 7.1 Hz), 109.7 (d, $J_{C\text{-}F}$ = 15.2 Hz), 65.9 (d, $J_{C\text{-}F}$ = 5.1 Hz), 37.4, 31.8, 29.2, 25.3, 22.6, 14.1;

^{19}F NMR (377MHz, $CDCl_3$) δ -117.9;

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{20}ClFNaO^+$ 293.1079, found 293.1075.



(Z)-1-(2-chlorophenyl)-1-fluorononon-1-en-3-ol (2h)

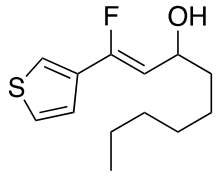
Compound **2h** was prepared following the general procedure. The reaction of **1h** (50 mg, 0.2 mmol) give **2h** as a yellow oil (35 mg, 66%); *Z/E* = 50:3; R_f =0.43 (petroleum ether/ethyl acetate 10:1);

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.52 (d, *J* = 2.1 Hz, 1H), 7.42 (dt, *J* = 6.6, 2.0 Hz, 1H), 7.35 – 7.29 (m, 2H), 5.50 (dd, *J* = 36.8, 8.6 Hz, 1H), 4.84 – 4.75 (m, 1H), 1.94 (s, 1H), 1.77 – 1.69 (m, 1H), 1.64 – 1.52 (m, 1H), 1.43 – 1.24 (m, 8H), 0.95 – 0.84 (m, 3H);

^{13}C NMR (101 MHz, CDCl$_3$) δ 155.9 (d, $J_{C\text{-}F}$ = 250.5 Hz), 134.7 (d, $J_{C\text{-}F}$ = 2.0 Hz), 133.6 (d, $J_{C\text{-}F}$ = 29.3 Hz), 129.8 (d, $J_{C\text{-}F}$ = 2.0 Hz), 129.2, 124.5 (d, $J_{C\text{-}F}$ = 7.1 Hz), 122.5, 122.4 (d, $J_{C\text{-}F}$ = 7.1 Hz), 110.4 (d, $J_{C\text{-}F}$ = 15.2 Hz), 65.9 (d, $J_{C\text{-}F}$ = 6.1 Hz), 37.4 (d, $J_{C\text{-}F}$ = 1.0 Hz), 31.8, 29.2, 25.3, 22.6, 14.1;

^{19}F NMR (377MHz, CDCl$_3$) δ -118.1;

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{20}ClFNaO^+$ 293.1079, found 293.1080.



(Z)-1-fluoro-1-(thiophen-3-yl)non-1-en-3-ol (2i)

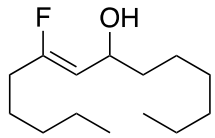
Compound **2i** was prepared following the general procedure. The reaction of **1i** (45 mg, 0.2 mmol) give **2i** as a yellow oil (37 mg, 76%); *Z/E* = 20:1; R_f =0.33 (petroleum ether/ethyl acetate 10:1);

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.45 (d, *J* = 1.9 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.17 (dt, *J* = 5.1, 1.3 Hz, 1H), 5.31 (dd, *J* = 37.0, 8.8 Hz, 1H), 4.81 – 4.72 (m, 1H), 1.86 (s, 1H), 1.76 – 1.68 (m, 1H), 1.63 – 1.52 (m, 1H), 1.39 – 1.25 (m, 8H), 0.93 – 0.88 (m, 3H);

^{13}C NMR (101 MHz, CDCl$_3$) δ 154.3 (d, $J_{C\text{-}F}$ = 246.0 Hz), 134.0 (d, $J_{C\text{-}F}$ = 32.3 Hz), 126.6 (d, $J_{C\text{-}F}$ = 2.0 Hz), 124.2 (d, $J_{C\text{-}F}$ = 7.1 Hz), 122.1 (d, $J_{C\text{-}F}$ = 5.1 Hz), 108.7 (d, $J_{C\text{-}F}$ = 14.1 Hz), 65.8 (d, $J_{C\text{-}F}$ = 6.1 Hz), 37.4 (d, $J_{C\text{-}F}$ = 1.0 Hz), 31.8, 29.2, 25.3, 22.6, 14.1;

^{19}F NMR (377MHz, CDCl$_3$) δ -114.5;

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{19}FNaOS^+$ 265.1033, found 265.1034.



(Z)-9-fluorotetradec-8-en-7-ol (2j)

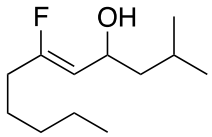
Compound **2j** was prepared following the general procedure. The reaction of **1j** (42 mg, 0.2 mmol) give **2j** as a yellow oil (32 mg, 70%); *Z/E* = 100:9; R_f =0.45 (petroleum ether/ethyl acetate 10:1);

^{1}H NMR (400 MHz, CDCl$_3$) δ 4.70 – 4.55 (m, 2H), 2.22 – 2.11 (m, 2H), 1.68 – 1.58 (m, 2H), 1.54 – 1.49 (m, 2H), 1.45 (td, *J* = 6.0, 3.4 Hz, 1H), 1.32 (td, *J* = 10.6, 9.0, 3.7 Hz, 14H), 0.90 (d, *J* = 6.9 Hz, 6H);

^{13}C NMR (101 MHz, CDCl$_3$) δ 161.2 (d, $J_{C\text{-}F}$ = 258.6 Hz), 108.9 (d, $J_{C\text{-}F}$ = 13.1 Hz), 65.6 (d, $J_{C\text{-}F}$ = 6.1 Hz), 37.4 (d, $J_{C\text{-}F}$ = 2.0 Hz), 31.8 (d, $J_{C\text{-}F}$ = 27.3 Hz), 31.8, 31.1, 29.2, 25.7 (d, $J_{C\text{-}F}$ = 1.0 Hz), 25.3, 22.6, 22.4, 14.1, 13.9;

^{19}F NMR (377MHz, $CDCl_3$) δ -105.5;

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{14}H_{21}FNaO^+$ 253.1938, found 253.1934.



(Z)-6-fluoro-2-methylundec-5-en-4-ol (2k)

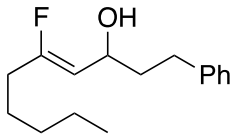
Compound **2k** was prepared following the general procedure. The reaction of **1k** (36 mg, 0.2 mmol) give **2k** as a yellow oil (23 mg, 58%); *Z/E* = 100:7; R_f =0.40 (petroleum ether/ethyl acetate 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.62 (dt, *J* = 37.1, 8.6 Hz, 1H), 4.43 (dt, *J* = 8.8, 5.9 Hz, 1H), 2.16 (dt, *J* = 16.7, 7.4 Hz, 2H), 1.57 – 1.47 (m, 4H), 1.31 (m, 4H), 1.11 (m, 1H), 0.90 (m, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7 (dd, $J_{C\text{-}F}$ = 258.6 Hz), 106.9 (dd, $J_{C\text{-}F}$ = 63.6 Hz), 69.3 (dd, $J_{C\text{-}F}$ = 28.3 Hz), 40.8 (dd, $J_{C\text{-}F}$ = 21.2 Hz), 32.1 (d, $J_{C\text{-}F}$ = 27.3 Hz), 31.2, 25.9, 25.8, 25.4, 25.0, 22.5, 14.4 (d, $J_{C\text{-}F}$ = 29.3 Hz), 14.1, 11.7 (d, $J_{C\text{-}F}$ = 23.2 Hz);

^{19}F NMR (377MHz, $CDCl_3$) δ-105.1 (d, *J* = 77.5 Hz);

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_{23}FNaO^+$ 225.1625, found 225.1625.



(Z)-5-fluoro-1-phenyldec-4-en-3-ol (2l)

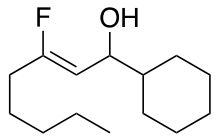
Compound **2l** was prepared following the general procedure. The reaction of **1l** (46 mg, 0.2 mmol) give **2l** as a yellow oil (37 mg, 73%); *Z/E* = 100:17; R_f =0.47 (petroleum ether/ethyl acetate 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 2H), 7.23 (dt, *J* = 8.1, 2.6 Hz, 3H), 4.77 – 4.61 (m, 2H), 2.79 – 2.65 (m, 2H), 2.19 (dt, *J* = 17.6, 7.7 Hz, 2H), 1.95 (m, 1H), 1.88 – 1.77 (m, 1H), 1.71 (s, 1H), 1.59 – 1.49 (m, 2H), 1.35 (m, 4H), 0.96 – 0.91 (m, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5 (d, $J_{C\text{-}F}$ = 259.6 Hz), 141.9, 128.4 (d, $J_{C\text{-}F}$ = 5.1 Hz), 125.8, 108.6 (d, $J_{C\text{-}F}$ = 13.1 Hz), 65.2 (d, $J_{C\text{-}F}$ = 5.1 Hz), 39.0 (d, $J_{C\text{-}F}$ = 1.0 Hz), 32.0, 31.8, 31.7, 31.1, 25.7 (d, $J_{C\text{-}F}$ = 2.0 Hz), 22.4, 14.0.;

^{19}F NMR (377MHz, $CDCl_3$) δ -104.5;

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{23}FNaO^+$ 273.1625, found 273.1624.



(Z)-1-cyclohexyl-3-fluorooct-2-en-1-ol (2m)

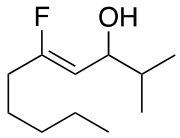
Compound **2m** was prepared following the general procedure. The reaction of **1m** (42 mg, 0.2 mmol) give **2m** as a yellow oil (30 mg, 66%); *Z/E* = 25:1; R_f =0.50 (petroleum ether/ethyl acetate 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.61 (dd, *J* = 37.3, 9.0 Hz, 1H), 4.31 (dd, *J* = 9.0, 6.9 Hz, 1H), 2.24 – 2.11 (m, 2H), 1.89 (m, 1H), 1.74 (m, 2H), 1.69 – 1.62 (m, 2H), 1.50 (m, 3H), 1.31 (dd, *J* = 7.5, 3.8 Hz, 5H), 0.92 – 0.87 (m, 3H).;

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4 (d, J_{C-F} = 258.6 Hz), 106.9 (d, J_{C-F} = 13.1 Hz), 69.6 (d, J_{C-F} = 5.1 Hz), 43.7 (d, J_{C-F} = 2.0 Hz), 31.7 (d, J_{C-F} = 27.3 Hz), 31.0, 28.3 (d, J_{C-F} = 40.4 Hz), 26.4, 25.8 (d, J_{C-F} = 10.1 Hz), 25.6 (d, J_{C-F} = 2.0 Hz), 22.2, 13.8;

^{19}F NMR (377MHz, $CDCl_3$) δ -105.4;

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{14}H_{25}FNaO^+$ 251.1782, found 251.1783.



(Z)-5-fluoro-2-methyldec-4-en-3-ol (2n)

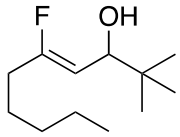
Compound **2n** was prepared following the general procedure. The reaction of **1n** (34 mg, 0.2 mmol) give **2n** as a yellow oil (24 mg, 65%); *Z/E* = 25:1; R_f =0.55 (petroleum ether/ethyl acetate 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.63 (dd, *J* = 37.2, 9.0 Hz, 1H), 4.33 (dd, *J* = 9.0, 6.5 Hz, 1H), 2.24 – 2.13 (m, 2H), 1.71 (m, 2H), 1.52 (p, *J* = 7.4 Hz, 2H), 1.33 (tt, *J* = 4.9, 2.0 Hz, 4H), 0.96 (d, *J* = 6.7 Hz, 3H), 0.90 (dd, *J* = 7.0, 3.0 Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6 (d, J_{C-F} = 258.6 Hz), 106.8 (d, J_{C-F} = 13.1 Hz), 70.5 (d, J_{C-F} = 4.0 Hz), 34.0 (d, J_{C-F} = 1.0 Hz), 31.9 (d, J_{C-F} = 27.3 Hz), 31.1, 25.7 (d, J_{C-F} = 2.0 Hz), 22.3, 18.2, 17.8, 14.0;

^{19}F NMR (377MHz, $CDCl_3$) δ -105.0;

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{11}H_{21}FNaO^+$ 211.1469, found 211.1466.



(Z)-5-fluoro-2,2-dimethyldec-4-en-3-ol (2o)

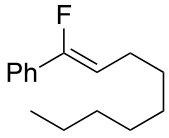
Compound **2o** was prepared following the general procedure. The reaction of **1o** (36 mg, 0.2 mmol) give **2o** as a yellow oil (22 mg, 66%); R_f =0.35 (petroleum ether/ethyl acetate 10:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.66 (dd, *J* = 37.0, 9.3 Hz, 1H), 4.27 (d, *J* = 9.2 Hz, 1H), 2.28 – 2.12 (m, 2H), 1.39 – 1.26 (m, 6H), 0.92 (s, 12H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 160.3 (d, J_{C-F} = 258.6 Hz), 105.5 (d, J_{C-F} = 13.1 Hz), 73.0 (d, J_{C-F} = 5.1 Hz), 35.0 (d, J_{C-F} = 2.0 Hz), 32.0 (d, J_{C-F} = 27.3 Hz), 31.1, 28.7, 25.8 (d, J_{C-F} = 2.0 Hz), 25.3, 22.3, 14.0;

^{19}F NMR (377MHz, $CDCl_3$) δ -104.6;

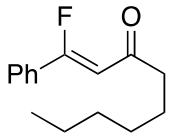
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_{23}FNaO^+$ 225.1625, found 225.1628.



(Z)-(1-fluorononon-1-en-1-yl)benzene (4)[4]

Compound **4** was prepared following the general procedure A. The reaction of **2a** (47 mg, 0.2 mmol) give **4** as a lightyellow oil (35 mg, 66%); R_f =0.7 (petroleum ether/ethyl acetate 50:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 2H), 7.43 – 7.32 (m, 3H), 5.43 (dt, *J* = 37.6, 7.6 Hz, 1H), 2.31 (m, 2H), 1.53 – 1.44 (m, 2H), 1.37 – 1.26 (m, 8H), 0.95 – 0.90 (m, 3H).



(Z)-1-fluoro-1-phenylnon-1-en-3-one (5)

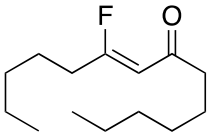
Compound **5** was prepared following the general procedure B. The reaction of **2a** (47mg, 0.2 mmol) give **5** as a lightyellow oil (33 mg, 70%); R_f =0.75 (petroleum ether/ethyl acetate 30:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 2H), 7.51 – 7.41 (m, 3H), 6.07 (d, *J* = 39.1 Hz, 1H), 2.79 (td, *J* = 7.4, 2.4 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.37 – 1.28 (m, 6H), 0.92 – 0.86 (m, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0 (d, $J_{C\text{-}F}$ = 2.0 Hz), 164.7 (d, $J_{C\text{-}F}$ = 275.7 Hz), 131.3, 130.6, 130.3 (d, $J_{C\text{-}F}$ = 27.3 Hz), 128.7 (d, $J_{C\text{-}F}$ = 20.2 Hz), 125.6 (d, $J_{C\text{-}F}$ = 8.1 Hz), 106.3 (d, $J_{C\text{-}F}$ = 10.1 Hz), 43.7 (d, $J_{C\text{-}F}$ = 5.1 Hz), 31.5, 28.8, 23.9 (d, $J_{C\text{-}F}$ = 2.0 Hz), 22.4, 13.9;

^{19}F NMR (377MHz, $CDCl_3$) δ -96.5;

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{19}FNaO^+$ 257.1312, found 257.1315.



(Z)-9-fluorotetradec-8-en-7-one (6)

Compound **6** was prepared following the general procedure C. The reaction of **2j** (46 mg, 0.2 mmol) give **6** as a lightyellow oil (40 mg, 87%); R_f =0.8 (petroleum ether/ethyl acetate 30:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.33 (d, *J* = 39.0 Hz, 1H), 2.65 (td, *J* = 7.4, 2.3 Hz, 2H), 2.30 (dt, *J* = 17.3, 7.5 Hz, 2H), 1.63 – 1.56 (m, 4H), 1.37 – 1.30 (m, 10H), 0.94 – 0.88 (m, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1 (d, $J_{C\text{-}F}$ = 3.0 Hz), 172.6 (d, $J_{C\text{-}F}$ = 283.8 Hz), 108.3 (d, $J_{C\text{-}F}$ = 8.1 Hz), 43.3 (d, $J_{C\text{-}F}$ = 6.1 Hz), 32.7 (d, $J_{C\text{-}F}$ = 25.3 Hz), 31.5, 30.8, 28.8, 25.2 (d, $J_{C\text{-}F}$ = 2.0 Hz), 23.8 (d, $J_{C\text{-}F}$ = 1.0 Hz), 22.4, 22.1, 13.9, 13.7;

^{19}F NMR (377MHz, $CDCl_3$) δ -79.6;

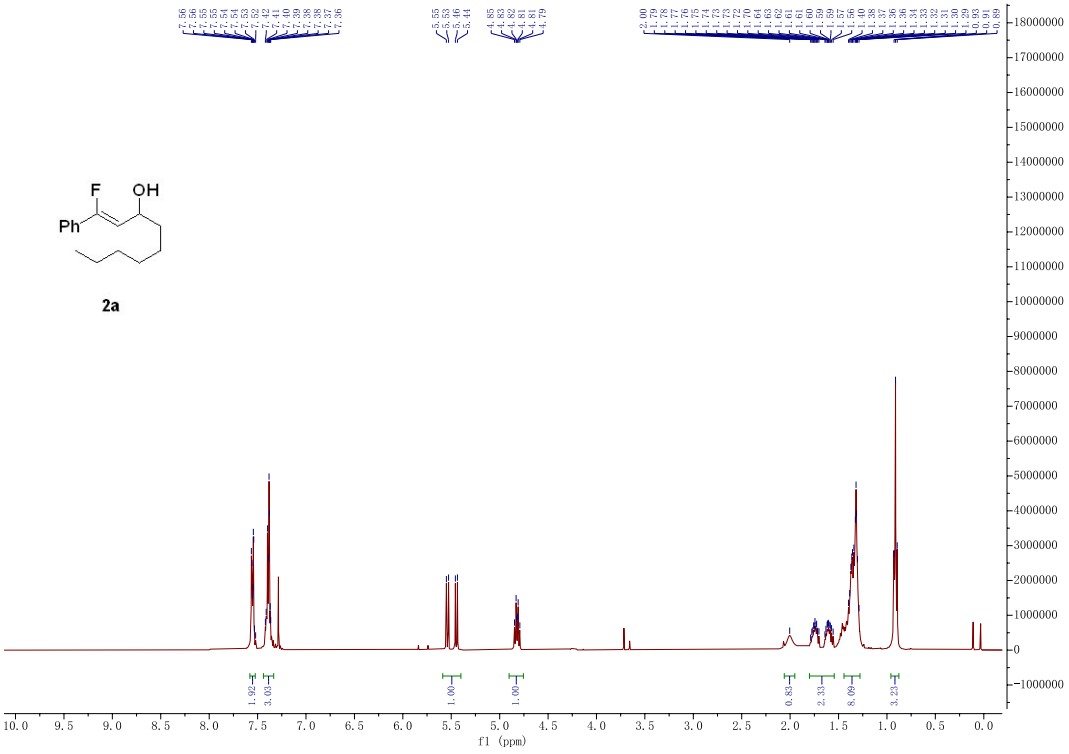
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{14}H_{25}FNaO^+$ 251.1782, found 251.1784.

References

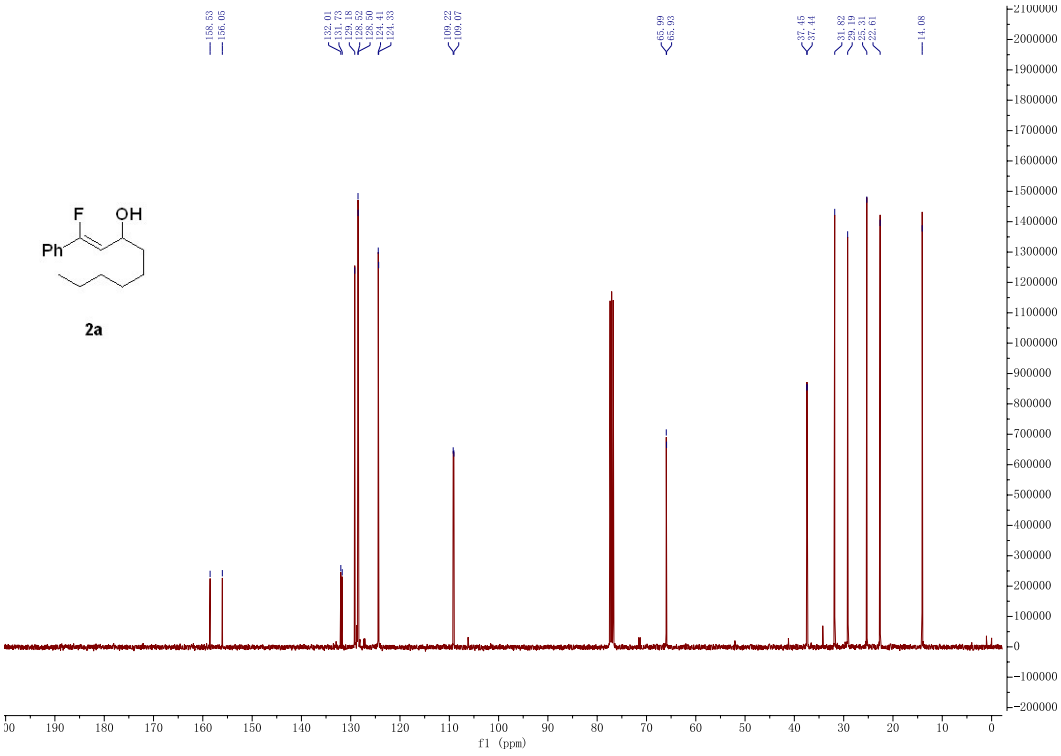
1. T. Sakai, K. Miyata, M. Utaka, M. Utaka and A. Takeda, *Tetrahedron Lett.*, 1987, **28(33)**, 3817-3818.
2. A. J. Fatiadi, *Synthesis*, 1976, **65**, 133-167.
3. G. Piancatelli and F. Leonelli, *Org. Synth.*, 2006, **83**, 18-23.
4. M.-H. Yang, S. S. Matikonda and R. A. Altman, *Org. Lett.*, 2013, **15(15)**, 3894-3897.

NMR Spectrum

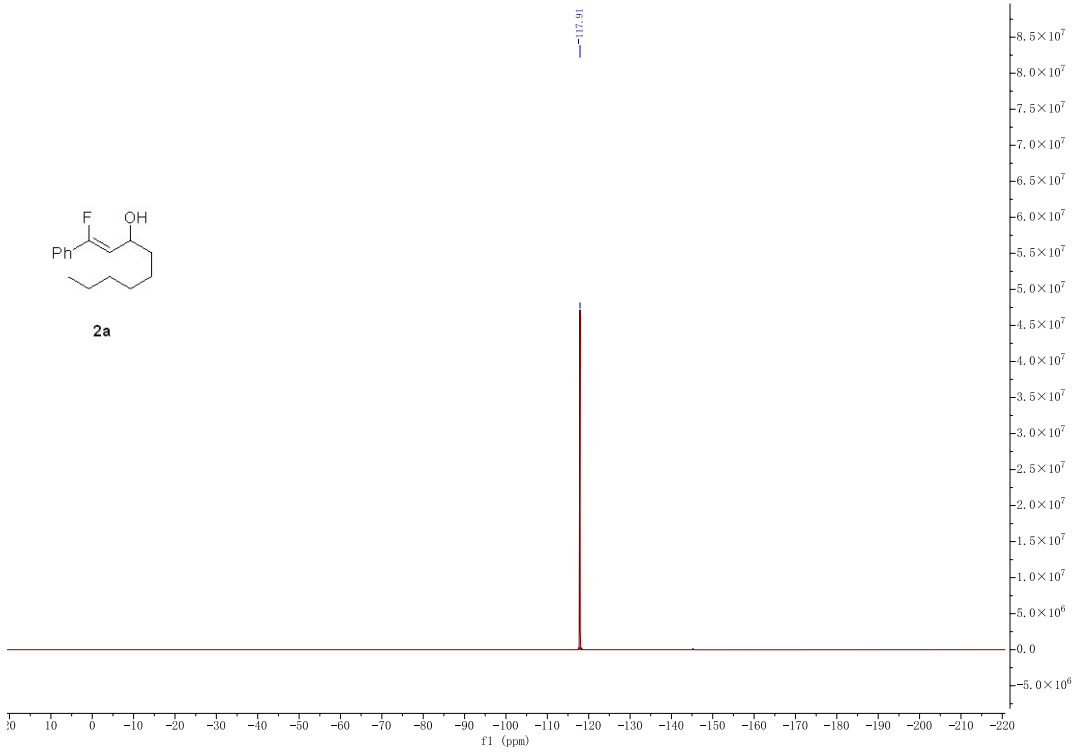
^{1}H NMR (400 MHz, $CDCl_3$)



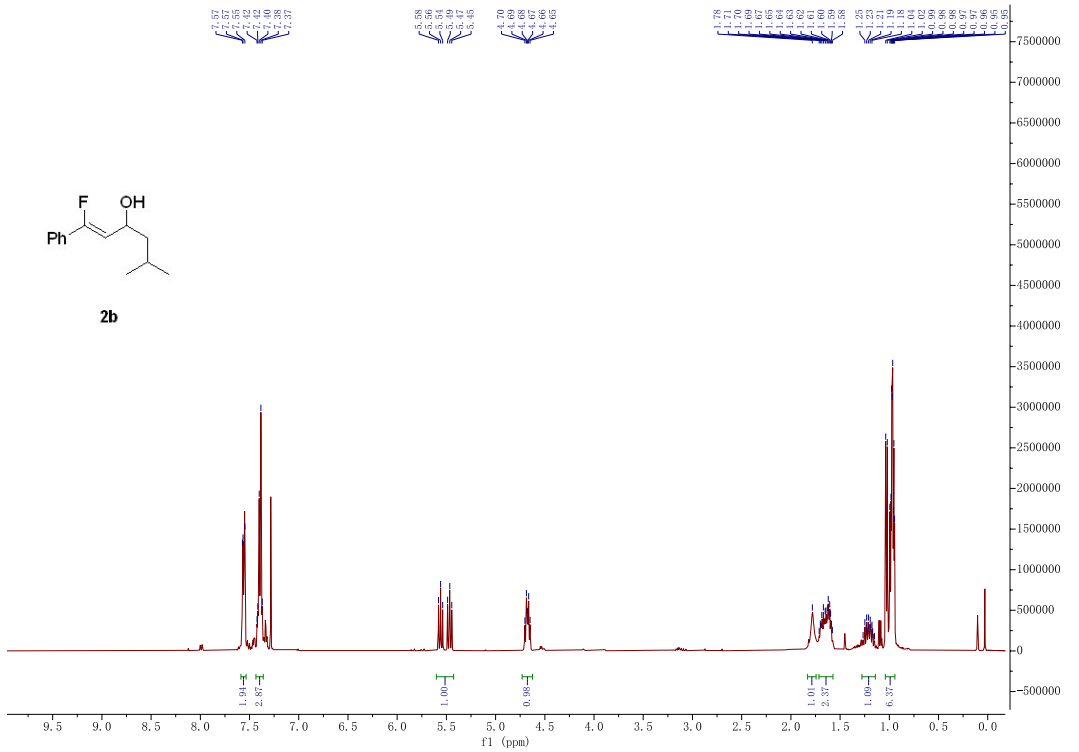
^{13}C NMR (101 MHz, $CDCl_3$)



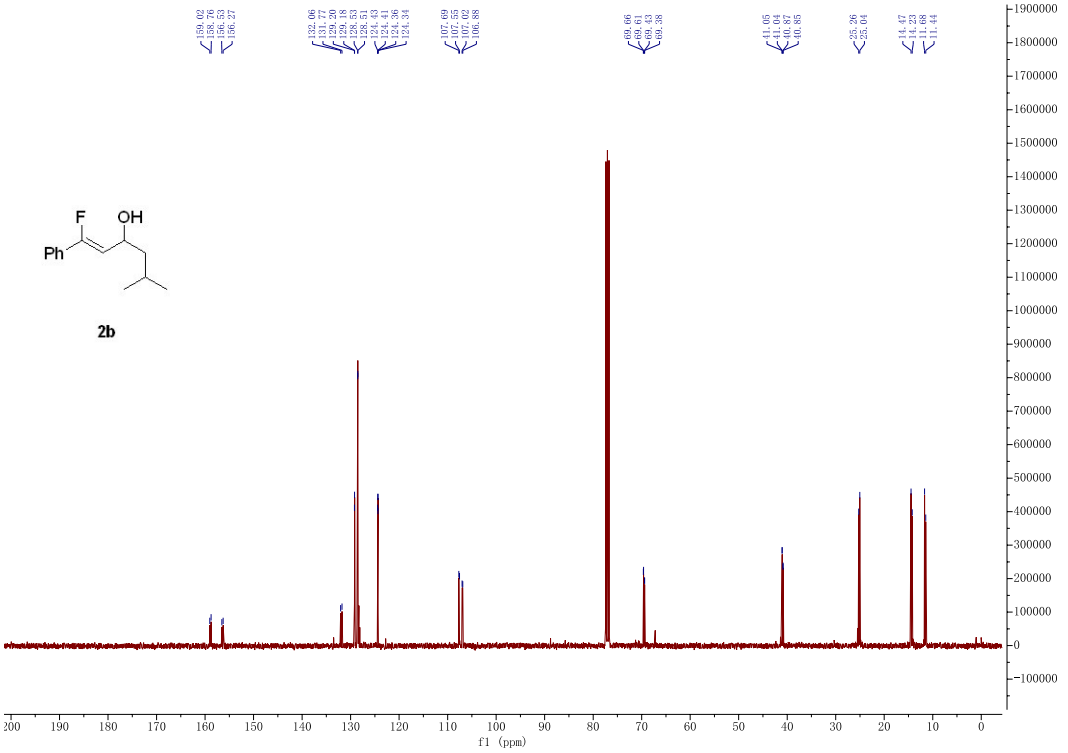
^{19}F NMR (337 MHz, $CDCl_3$)



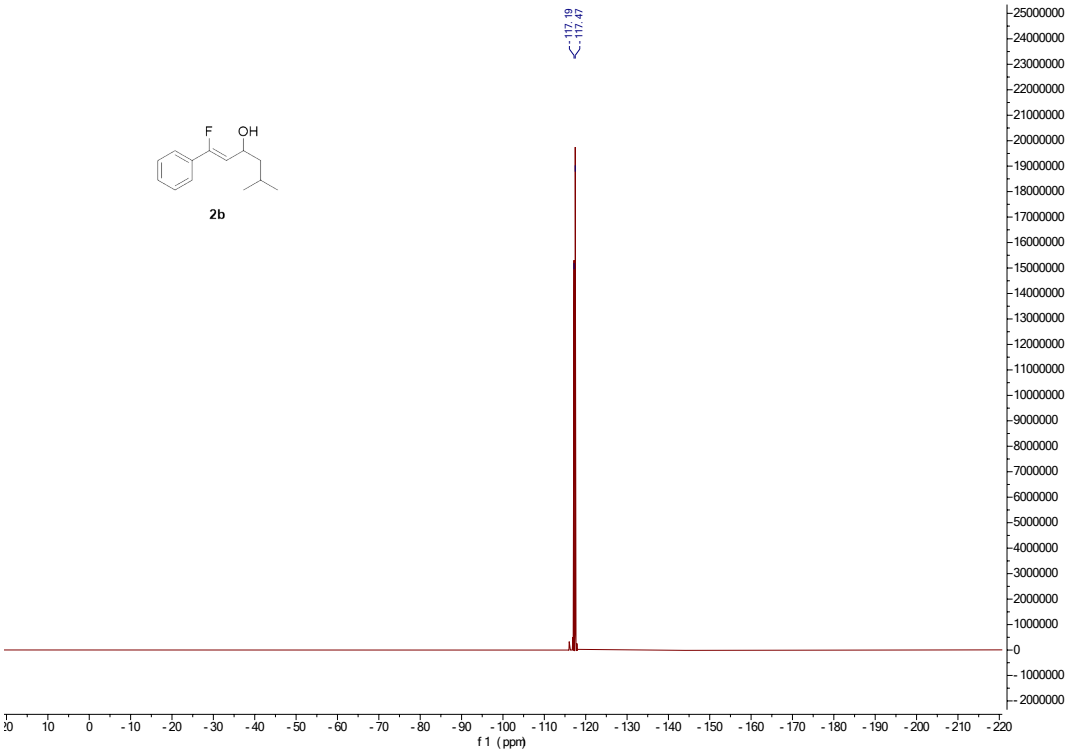
^{1}H NMR (400 MHz, $CDCl_3$)



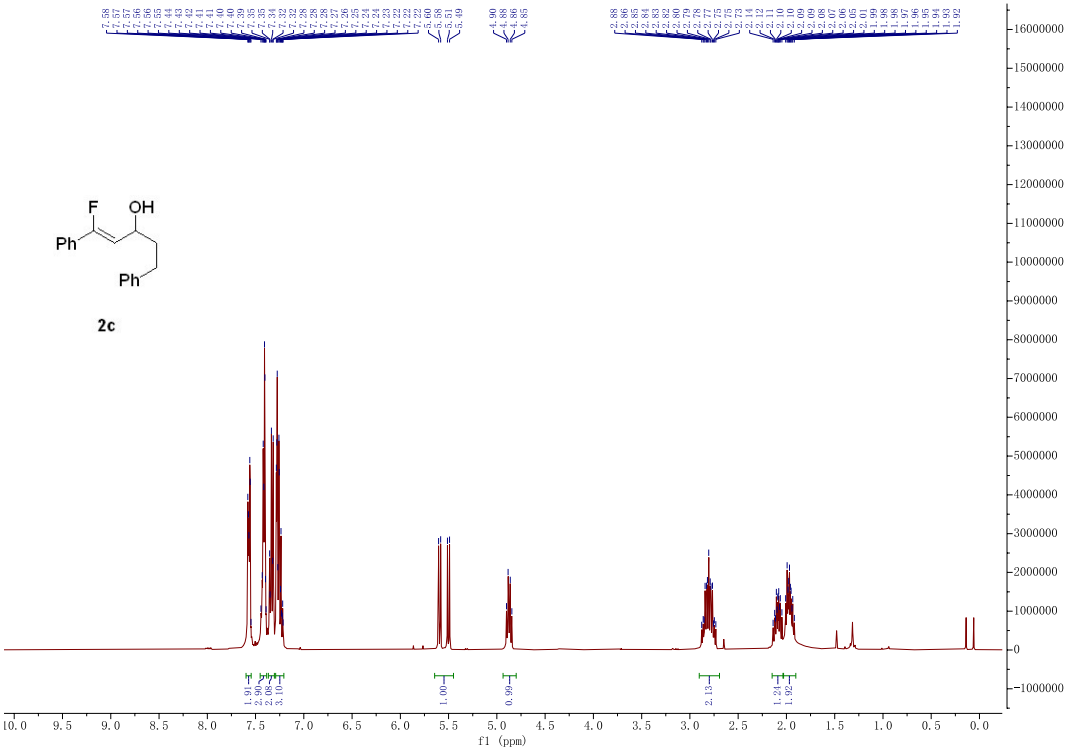
^{13}C NMR (101 MHz, $CDCl_3$)



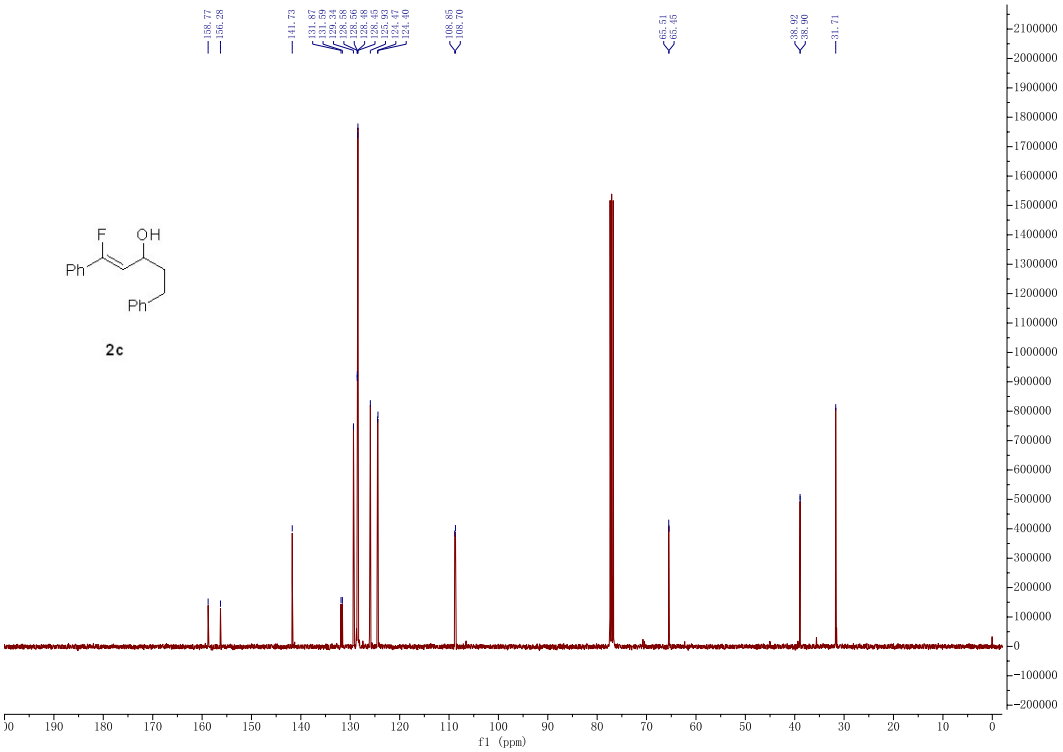
^{19}F NMR (337 MHz, $CDCl_3$)



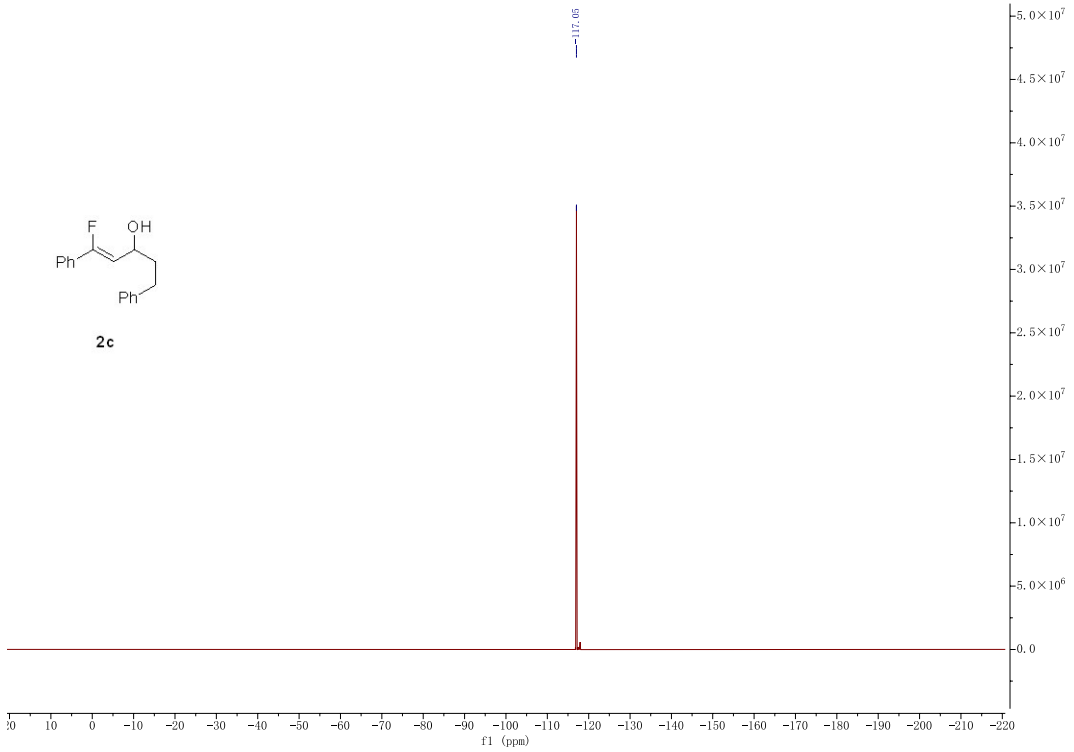
^{1}H NMR (400 MHz, $CDCl_3$)



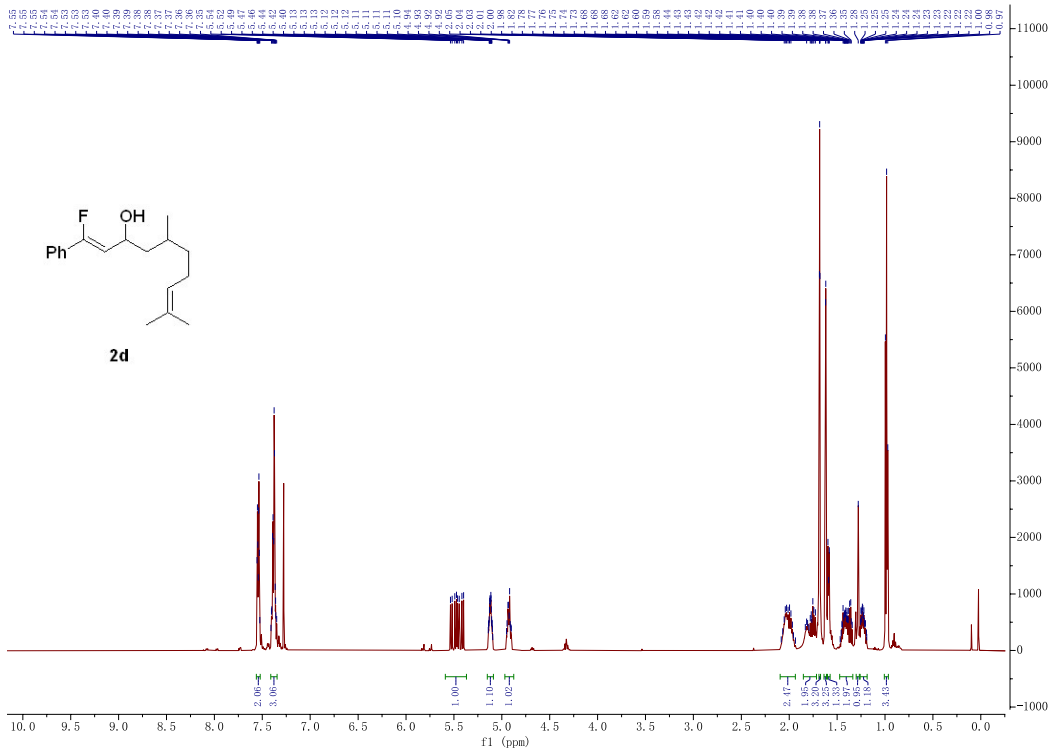
^{13}C NMR (101 MHz, $CDCl_3$)



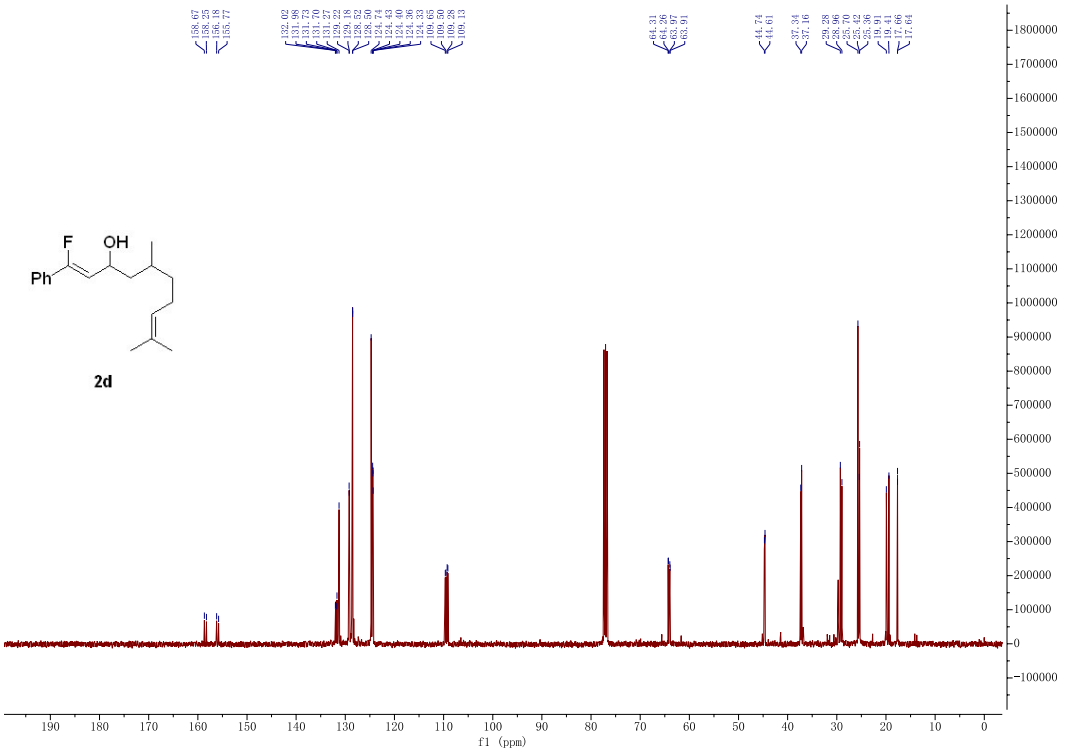
^{19}F NMR (337 MHz, $CDCl_3$)



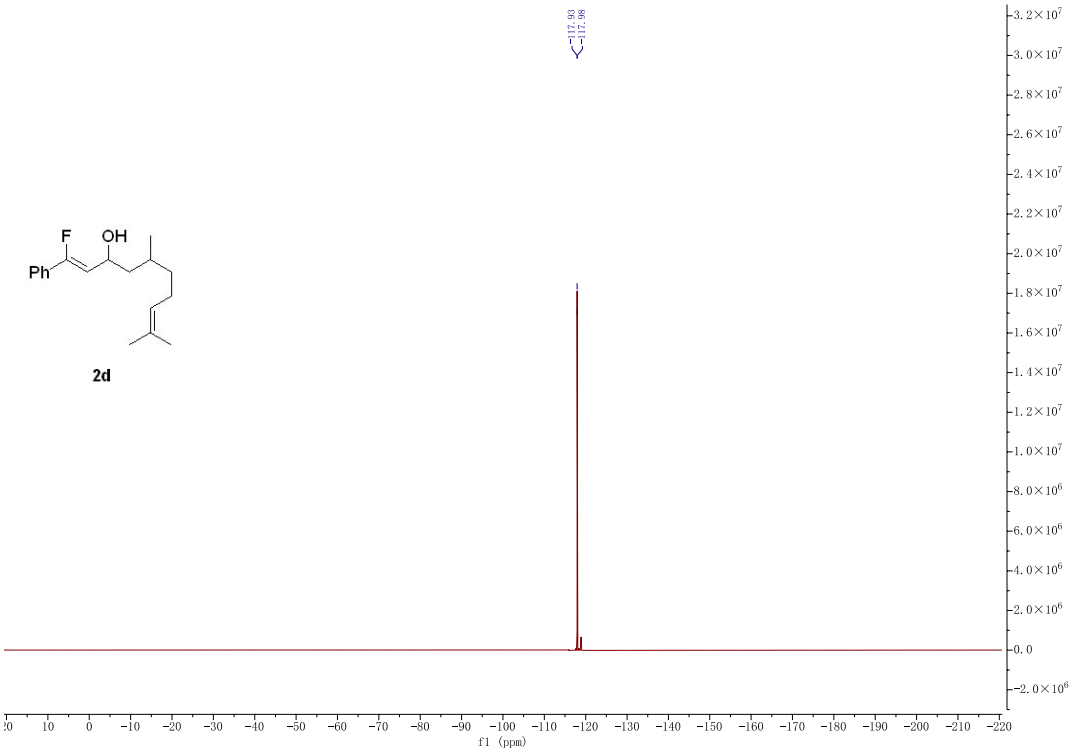
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (337 MHz, $CDCl_3$)



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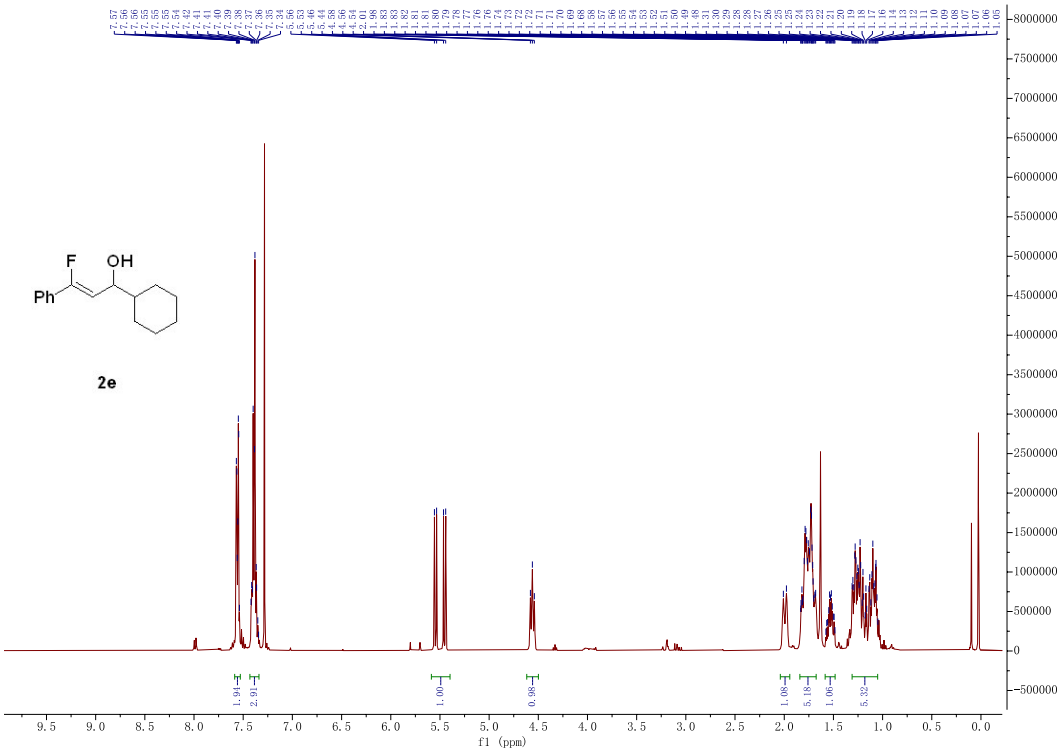
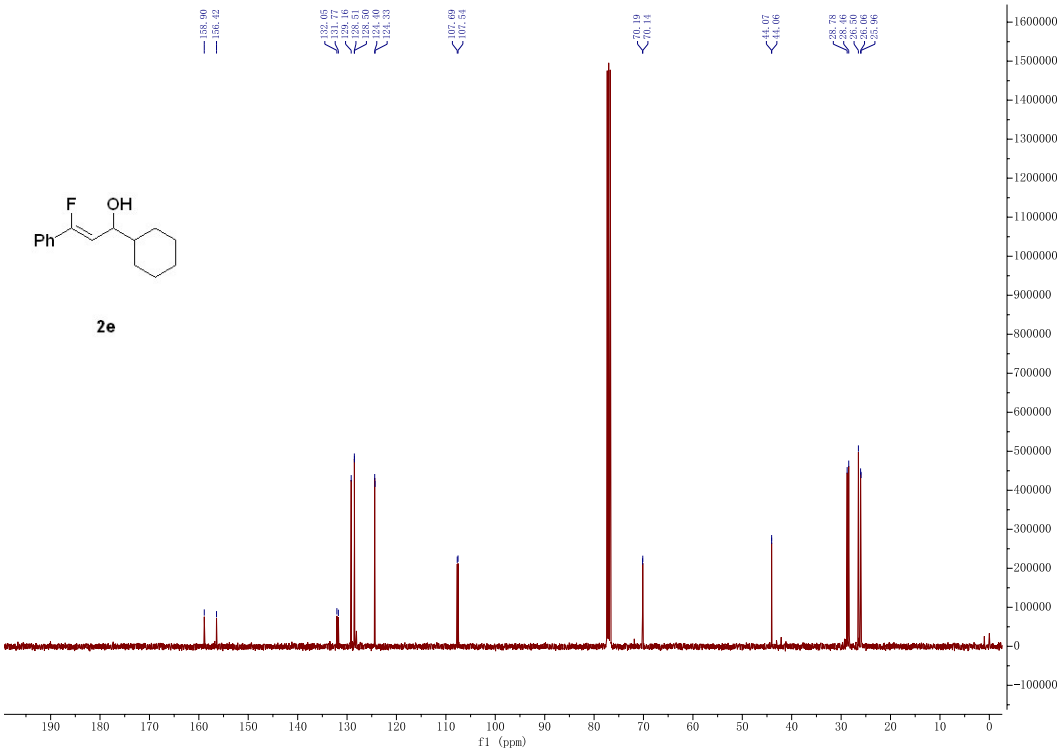


^{13}C NMR (101 MHz, $CDCl_3$)



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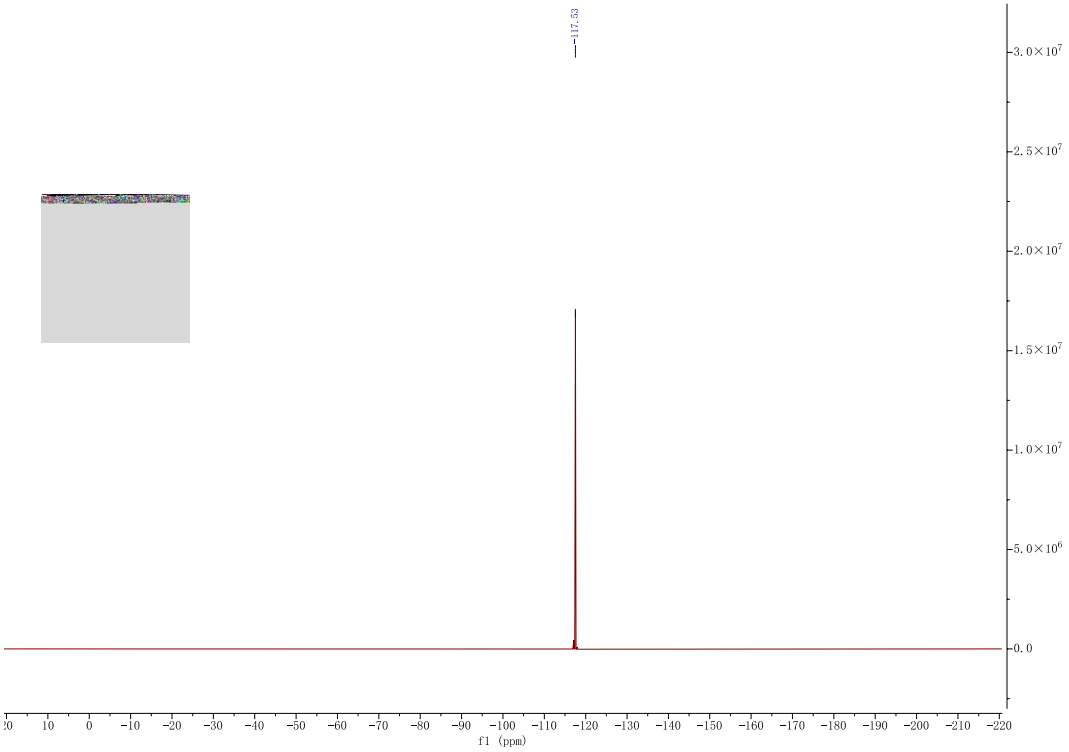
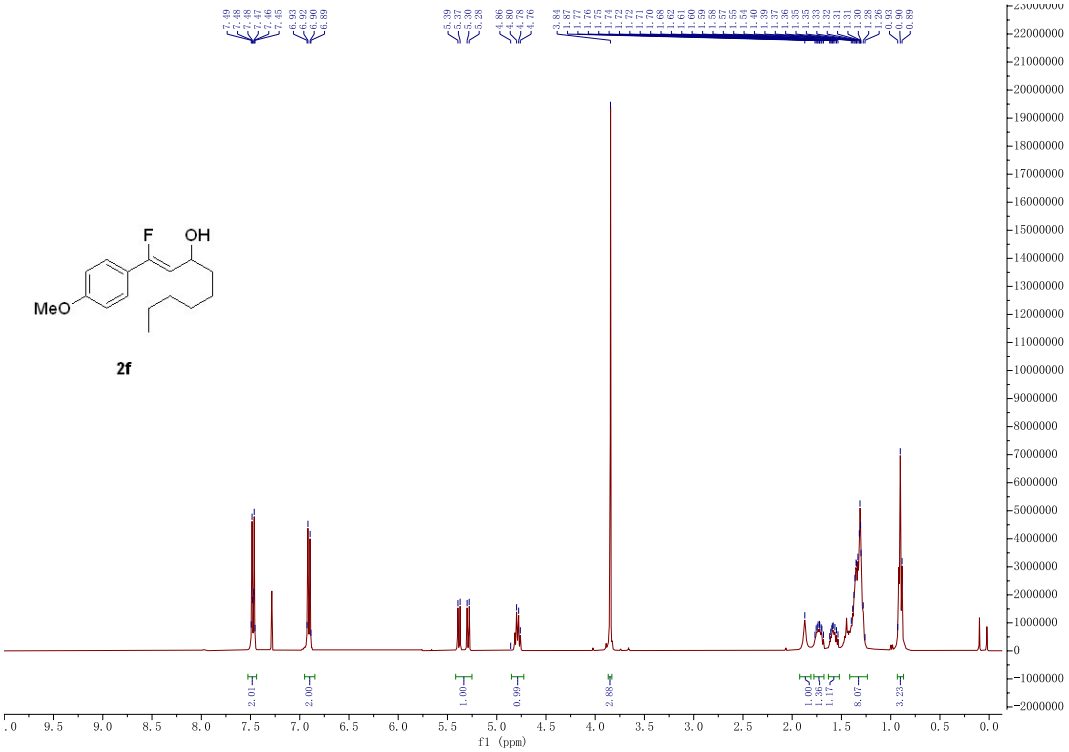
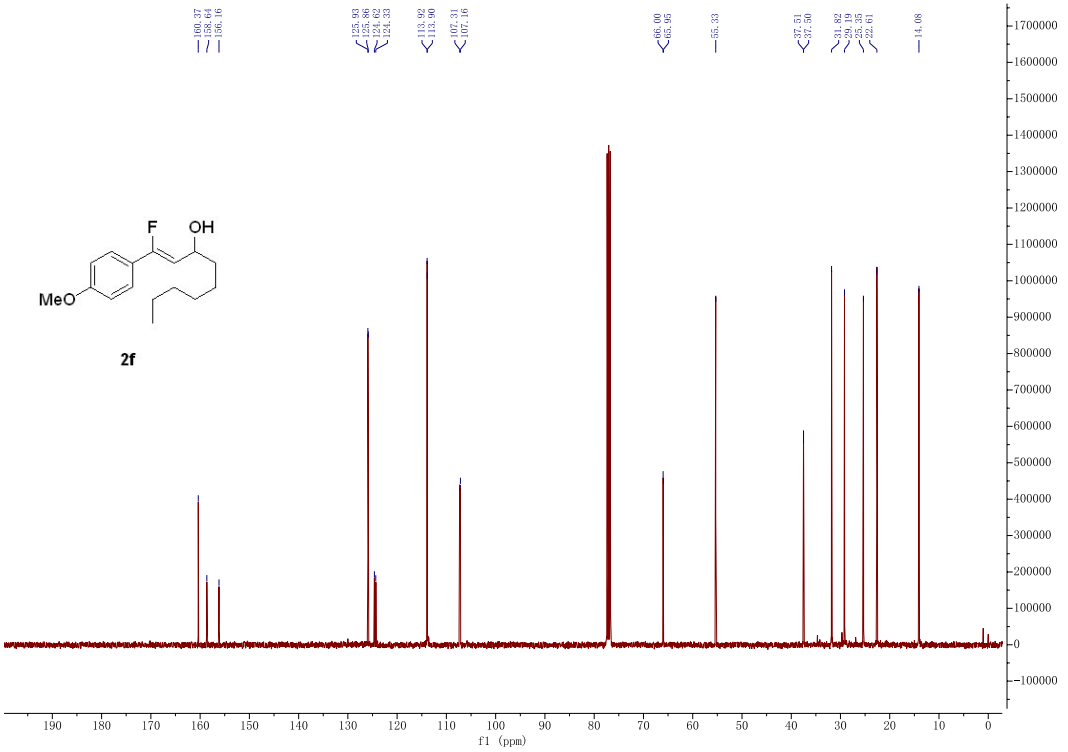


^{1}H NMR (400 MHz, $CDCl_3$)

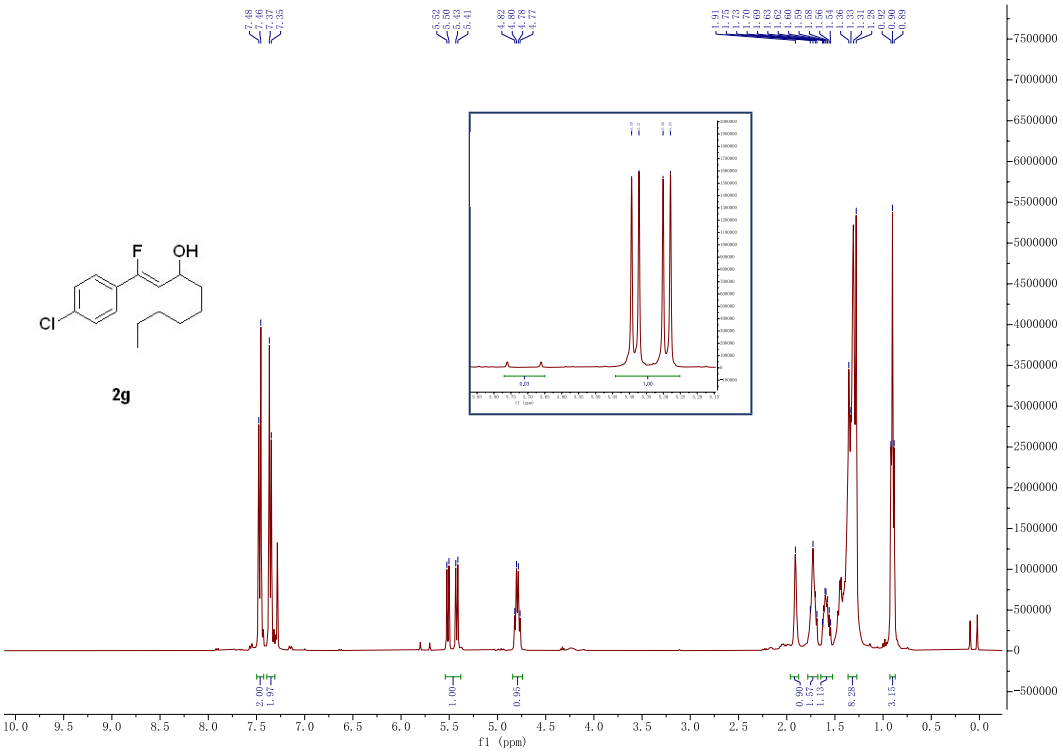


^{13}C NMR (101 MHz, $CDCl_3$)

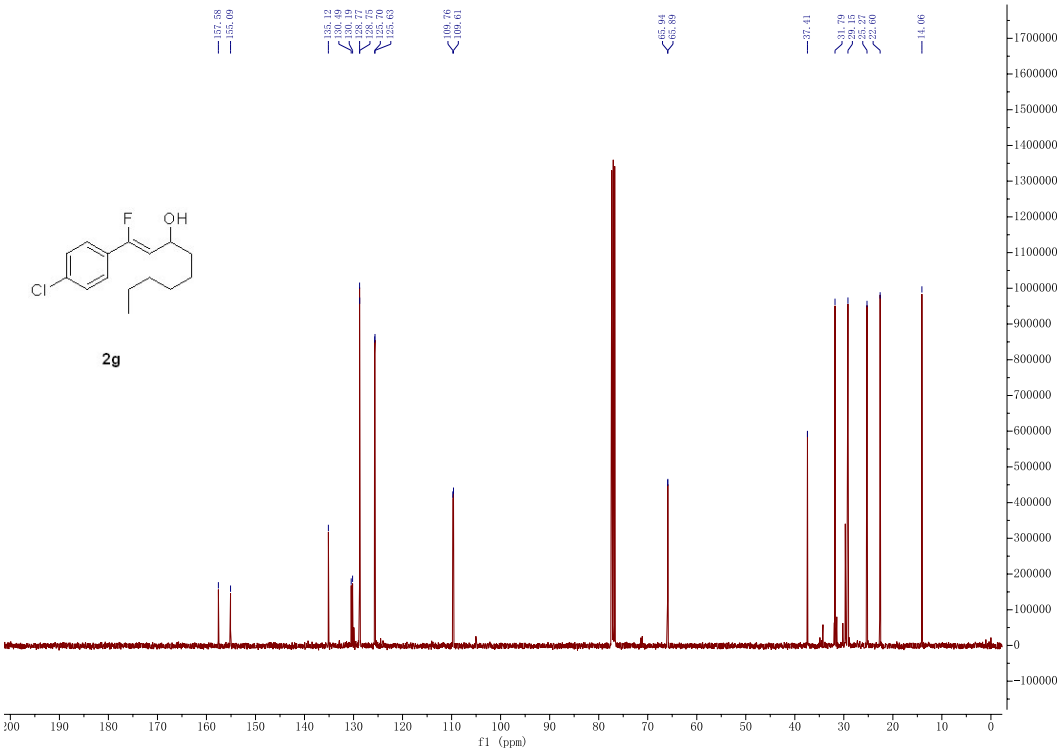


^{19}F NMR (337 MHz, $CDCl_3$)

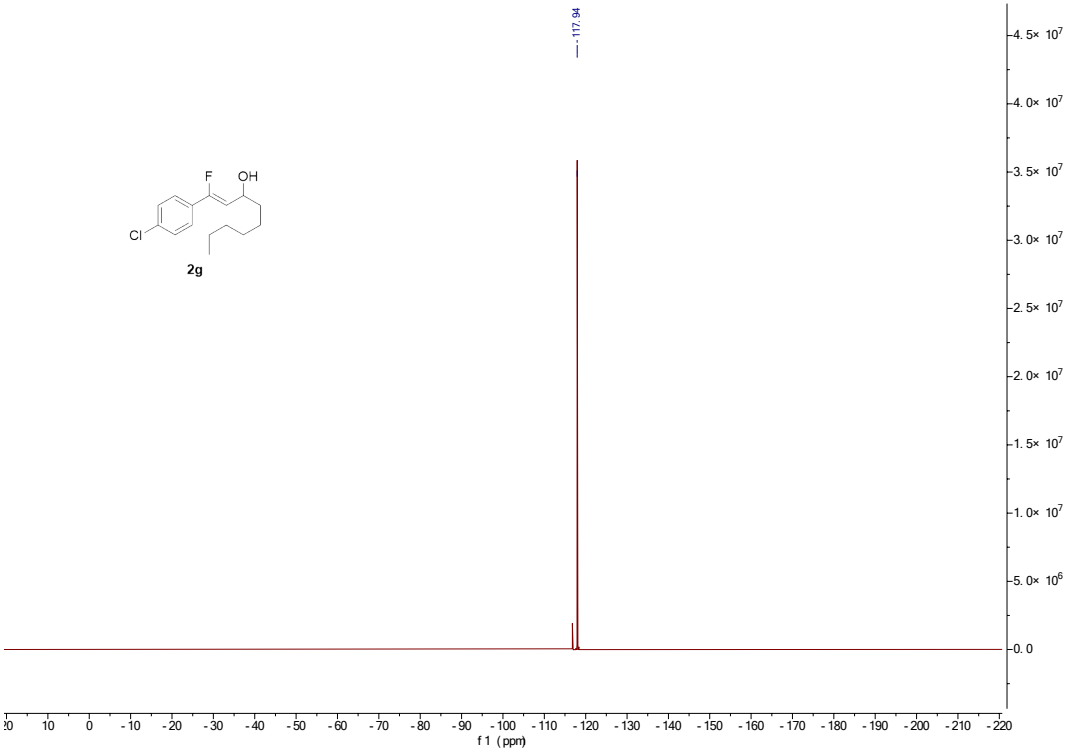
^{1}H NMR (400 MHz, $CDCl_3$)



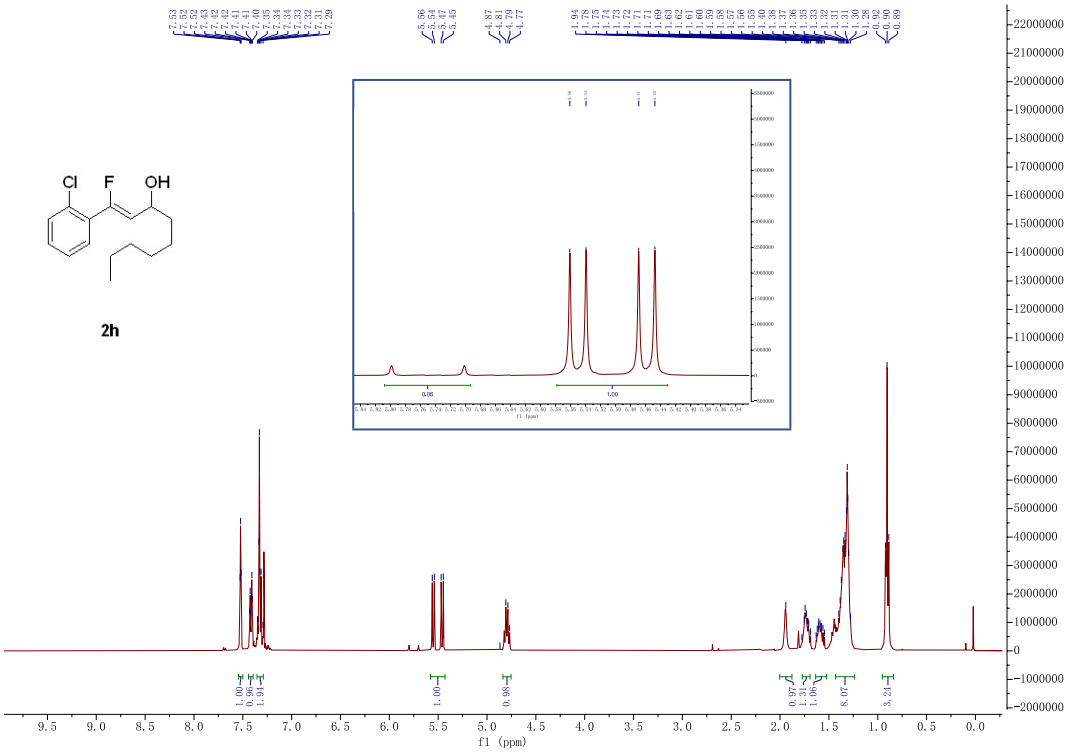
^{13}C NMR (101 MHz, $CDCl_3$)



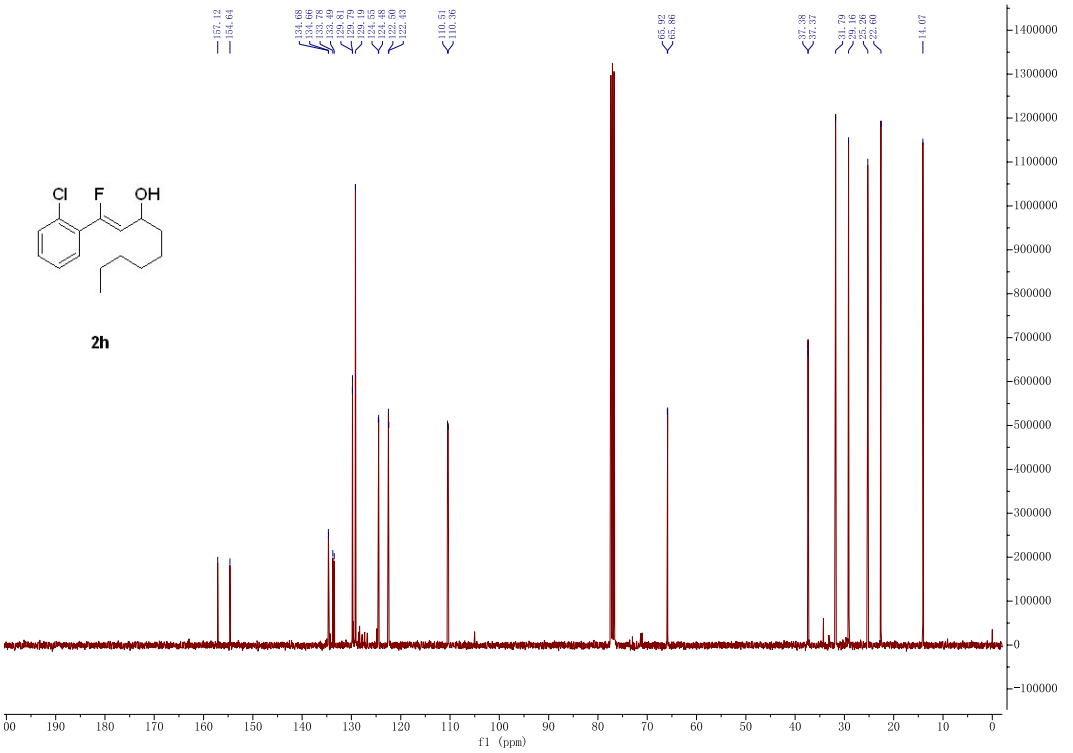
^{19}F NMR (337 MHz, $CDCl_3$)



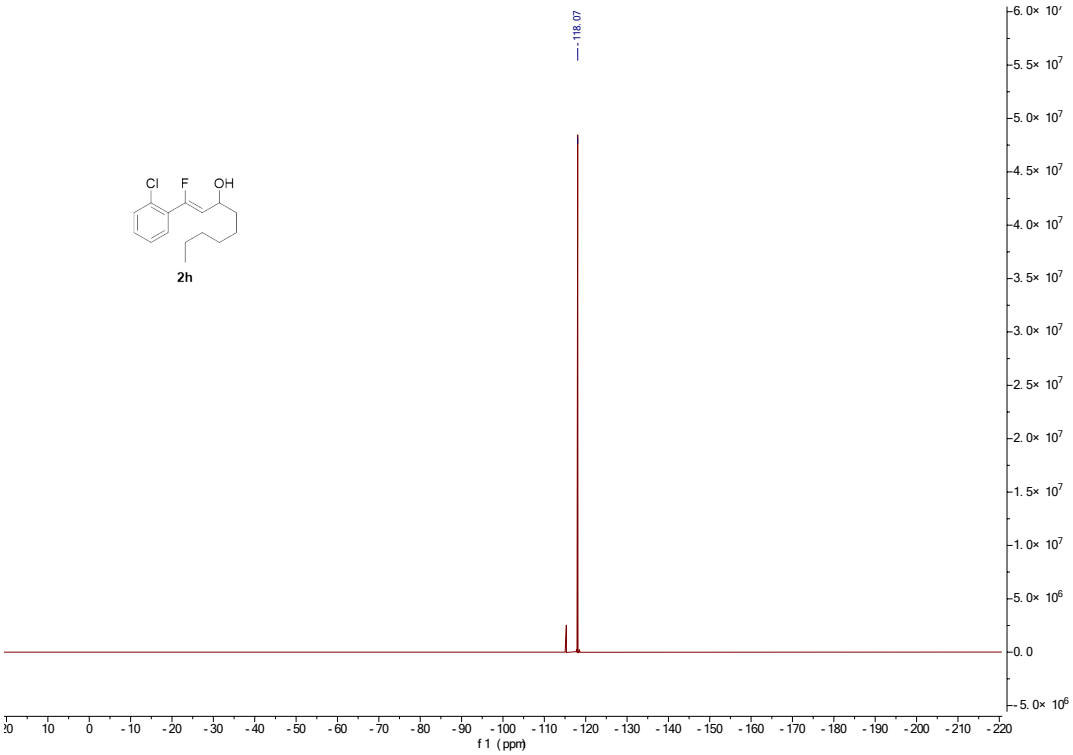
^{1}H NMR (400 MHz, $CDCl_3$)



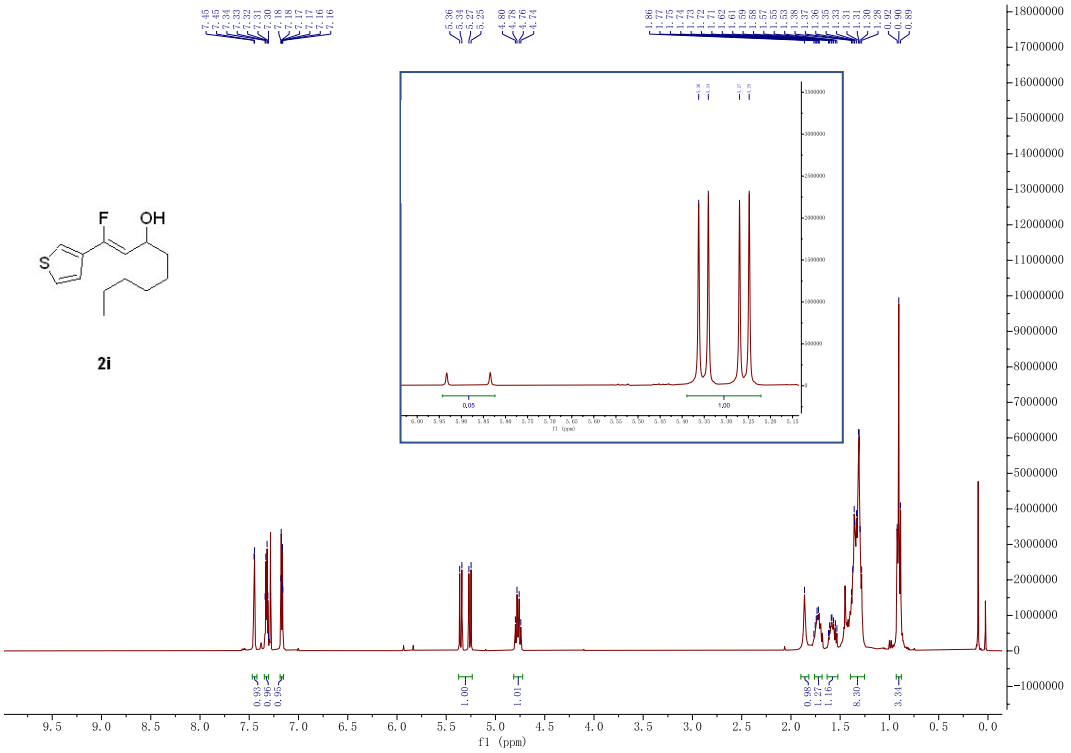
^{13}C NMR (101 MHz, $CDCl_3$)



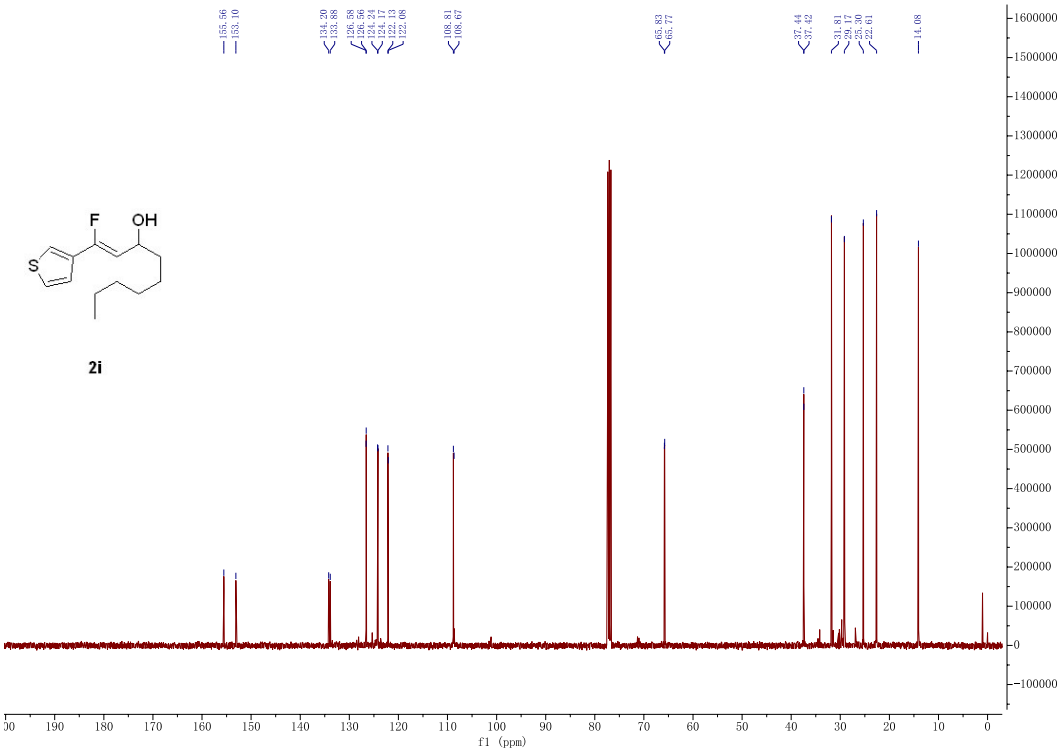
^{19}F NMR (337 MHz, $CDCl_3$)



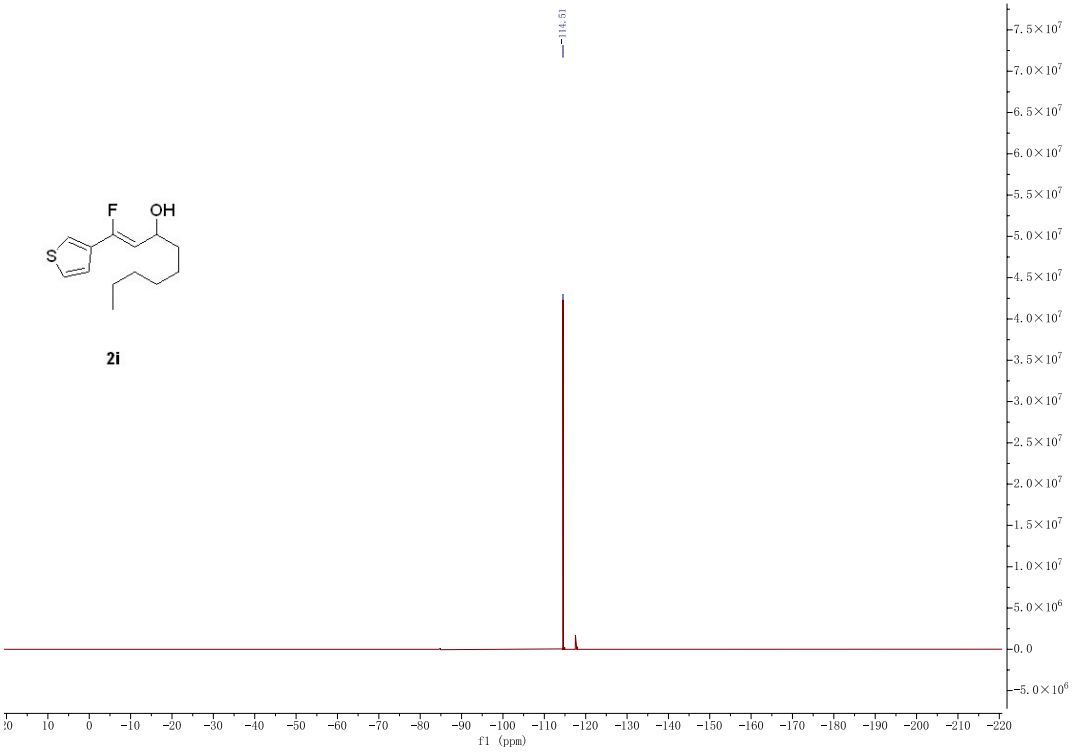
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (337 MHz, $CDCl_3$)



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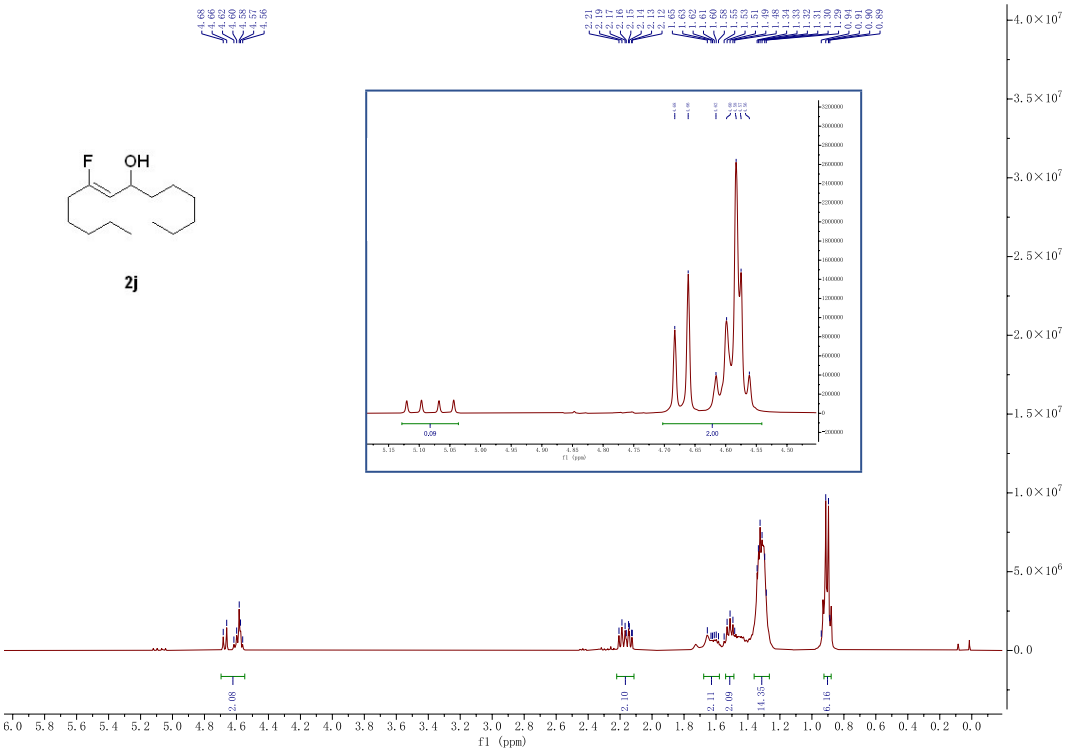

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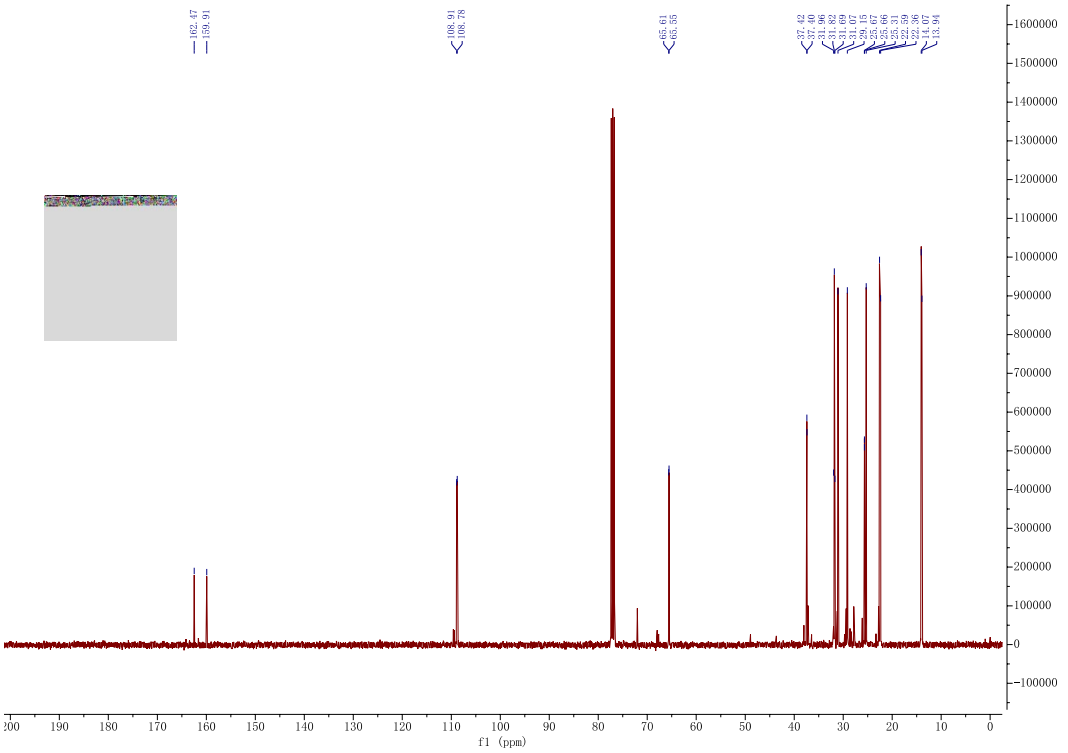

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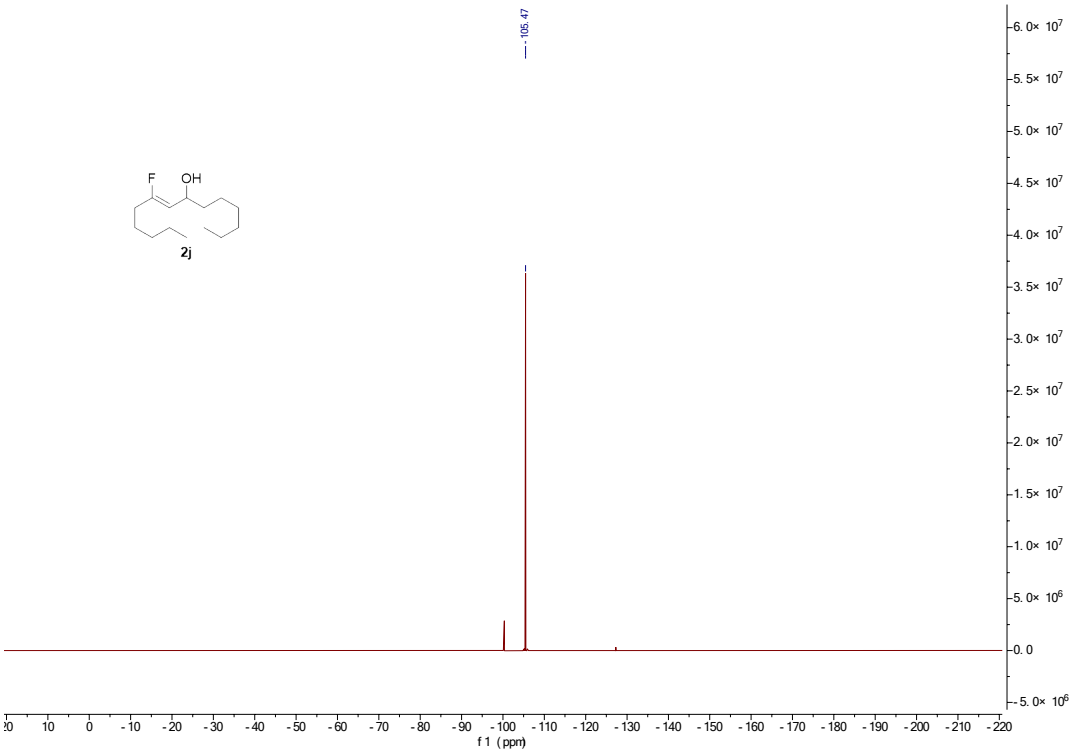

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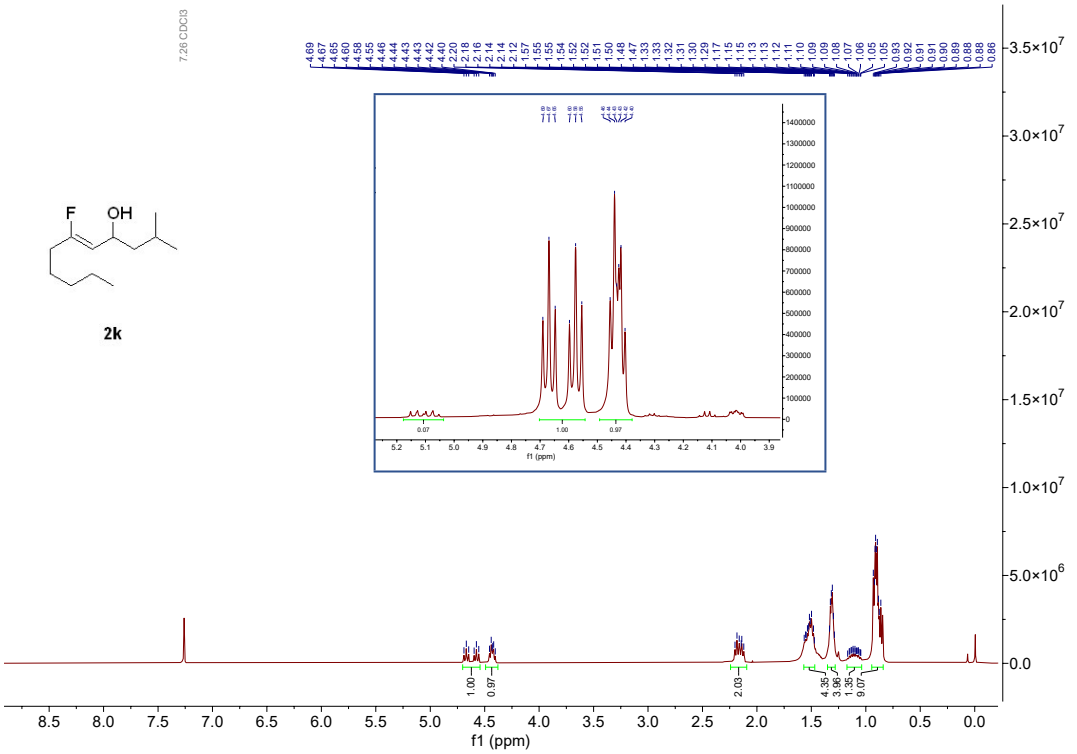

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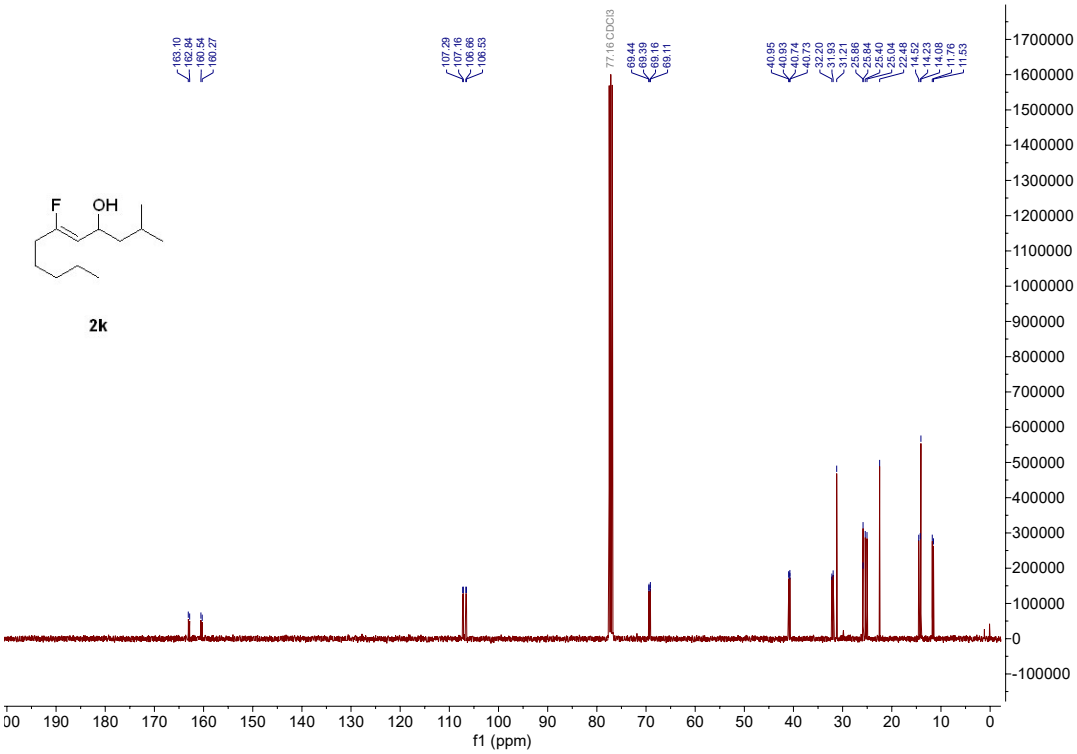

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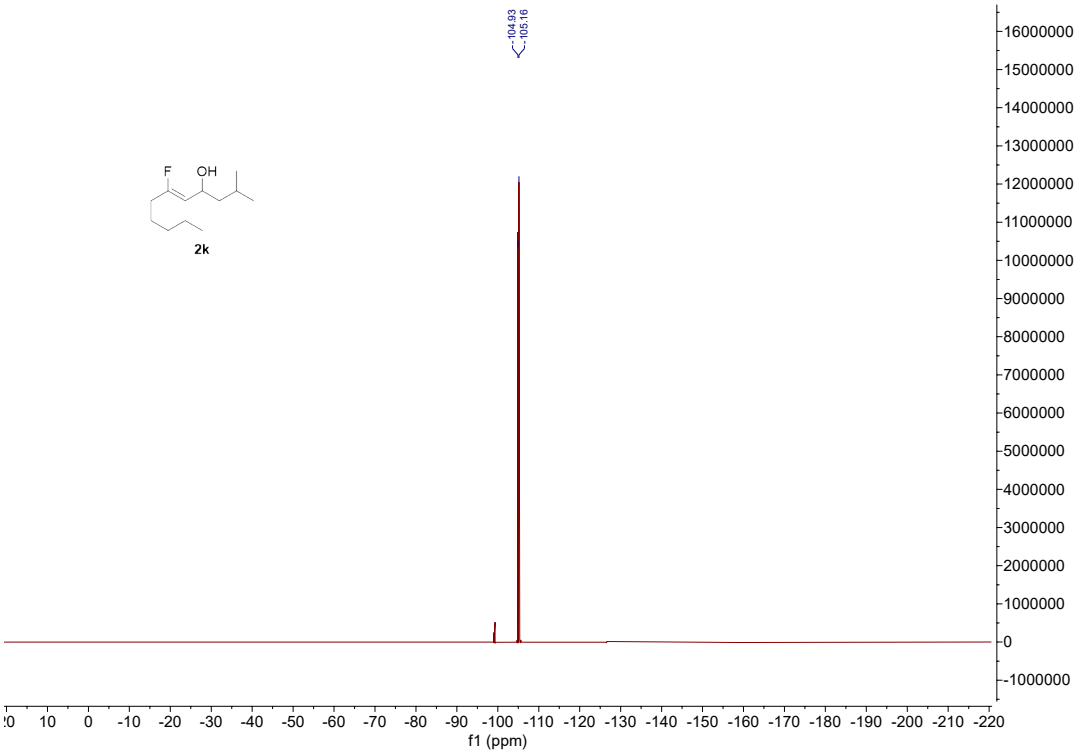

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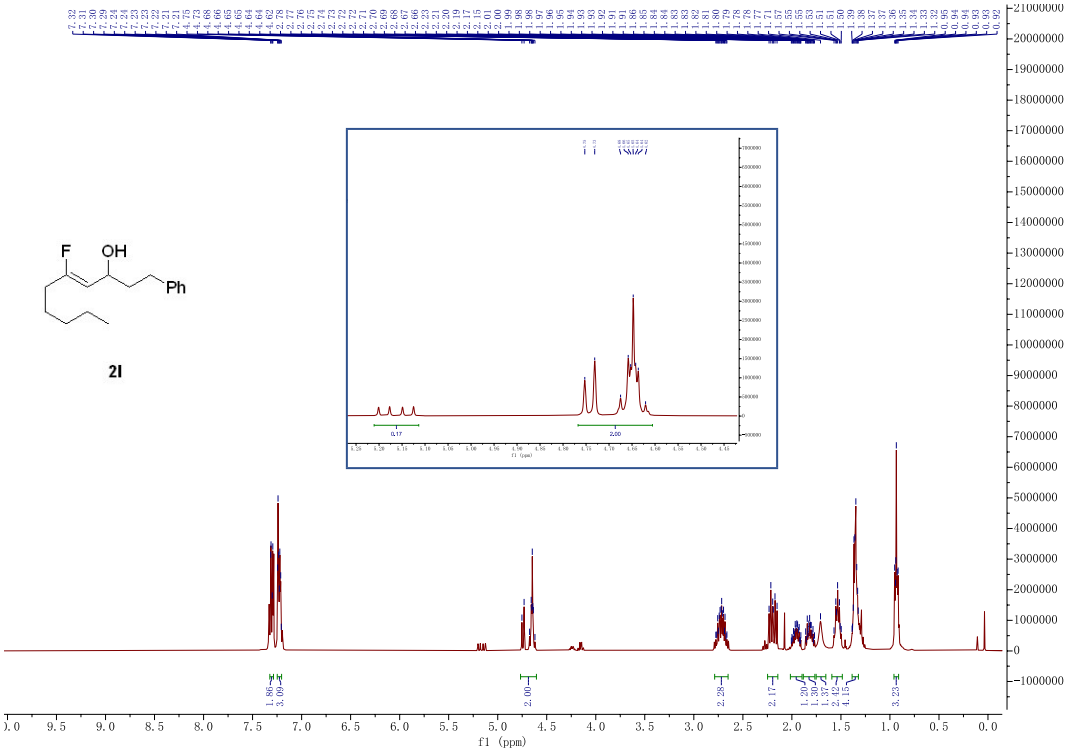
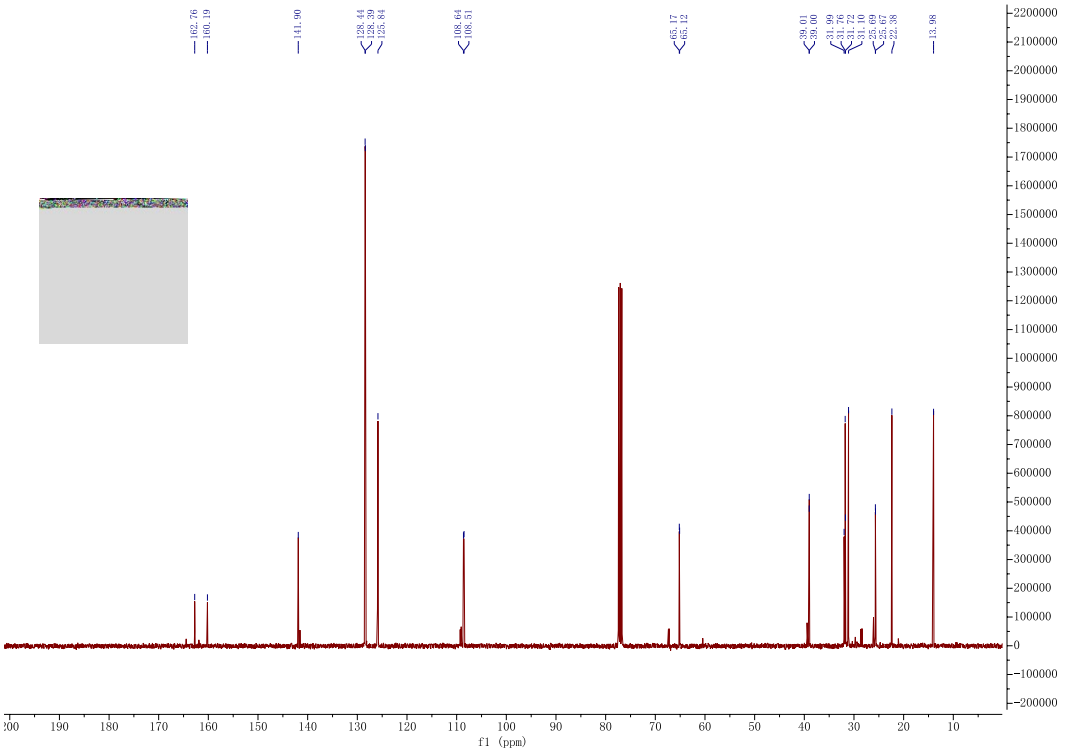


^{13}C NMR (101 MHz, $CDCl_3$)



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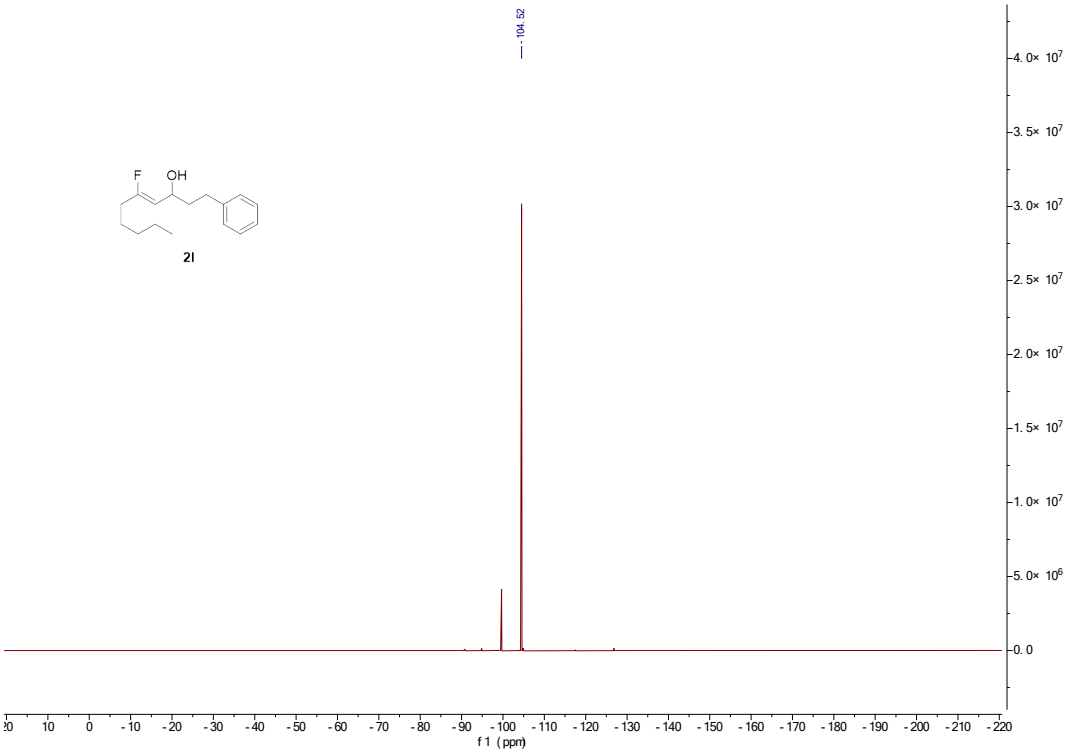

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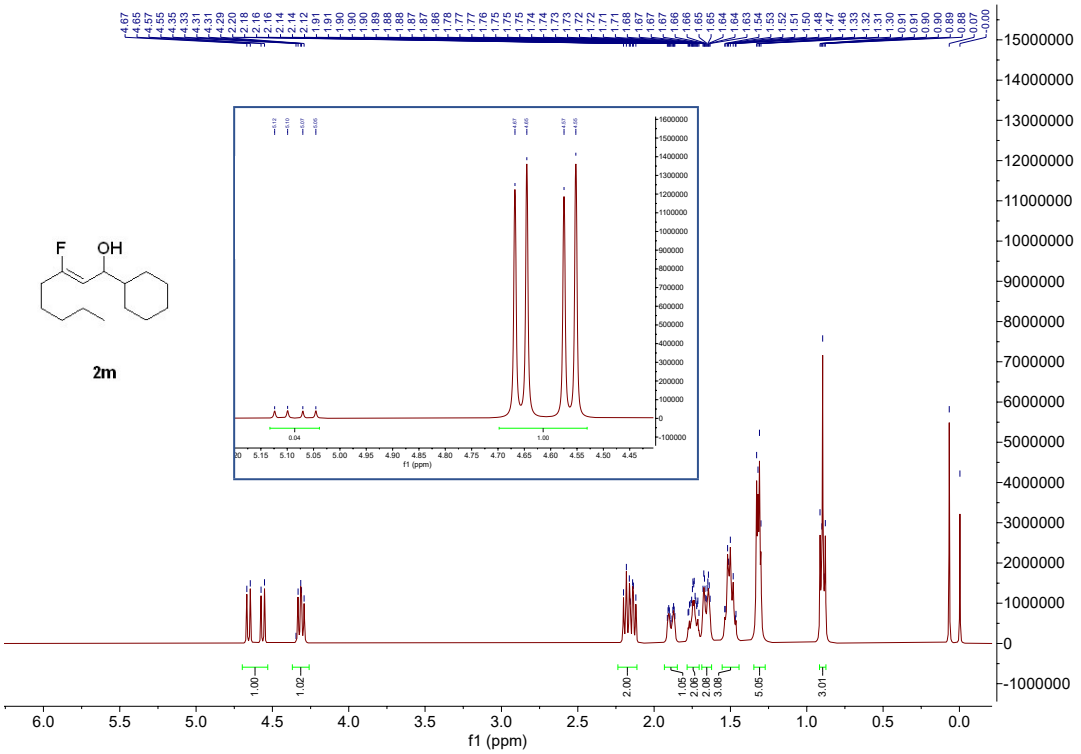

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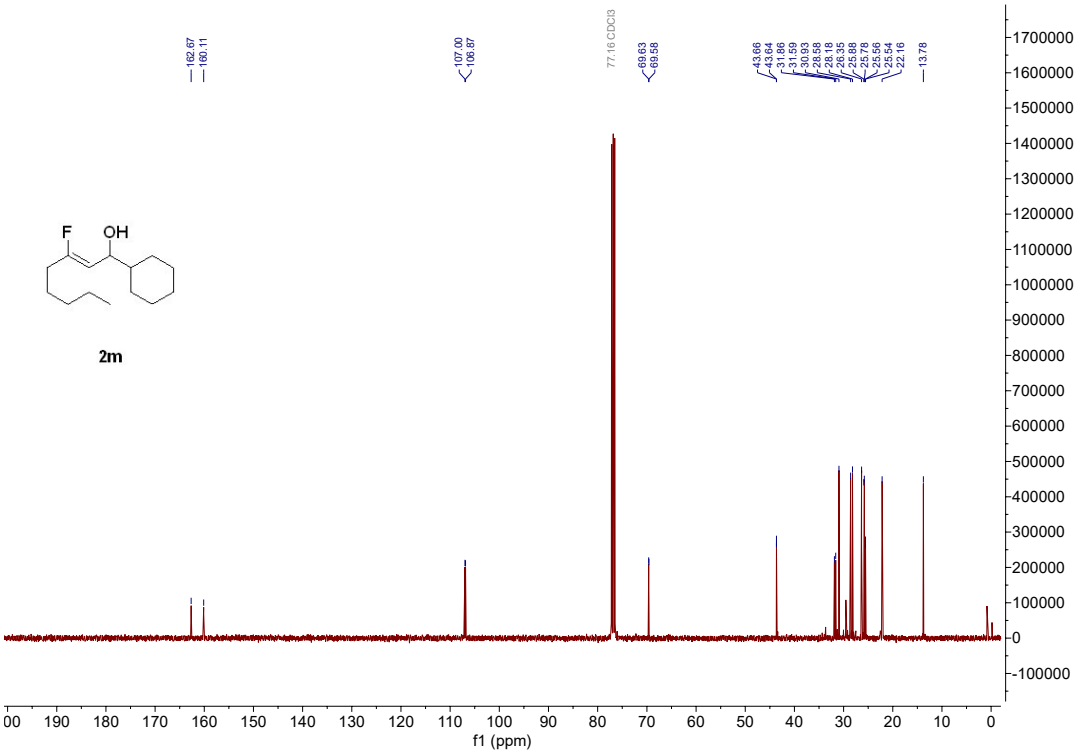

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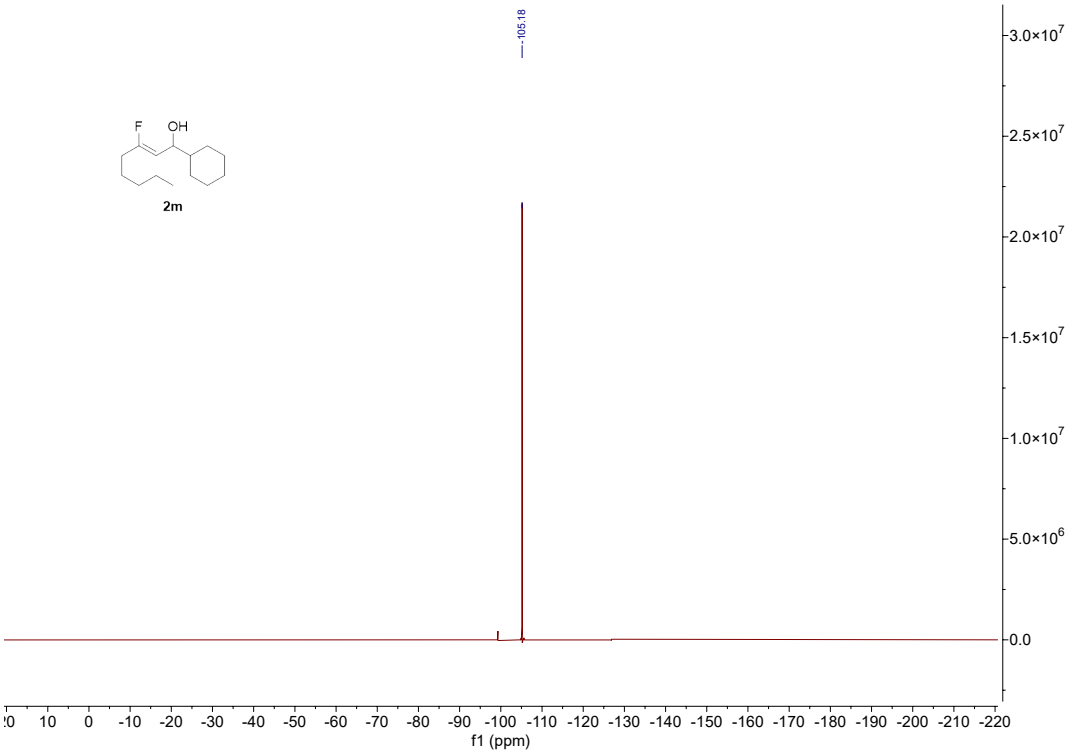

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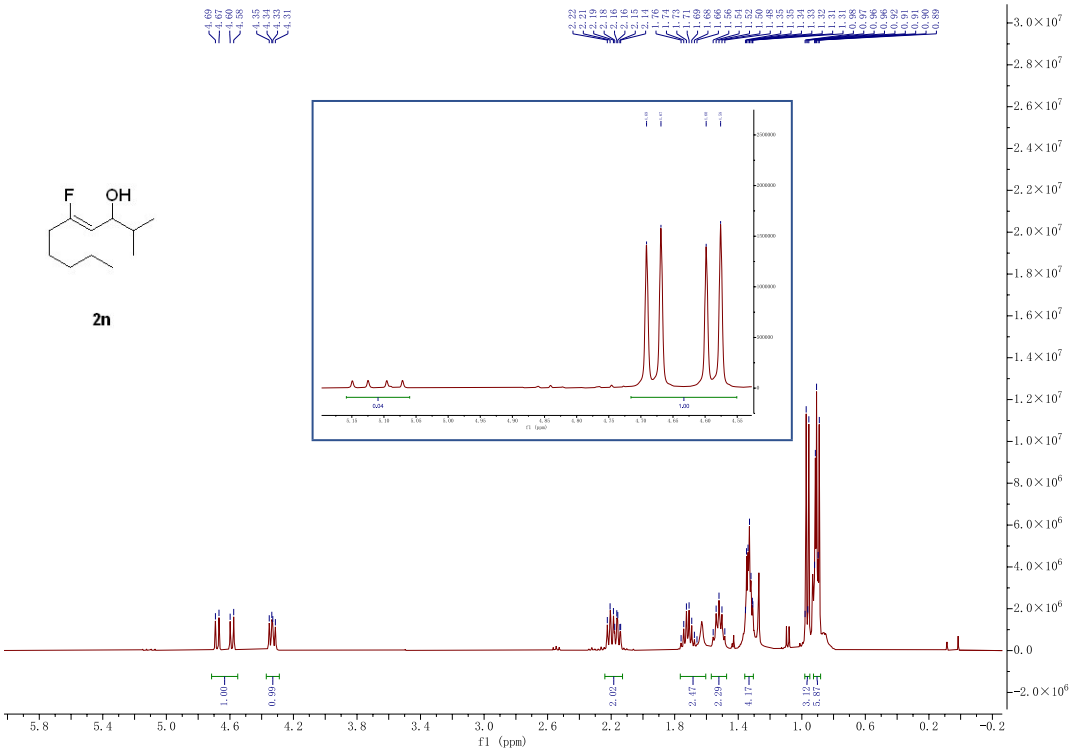

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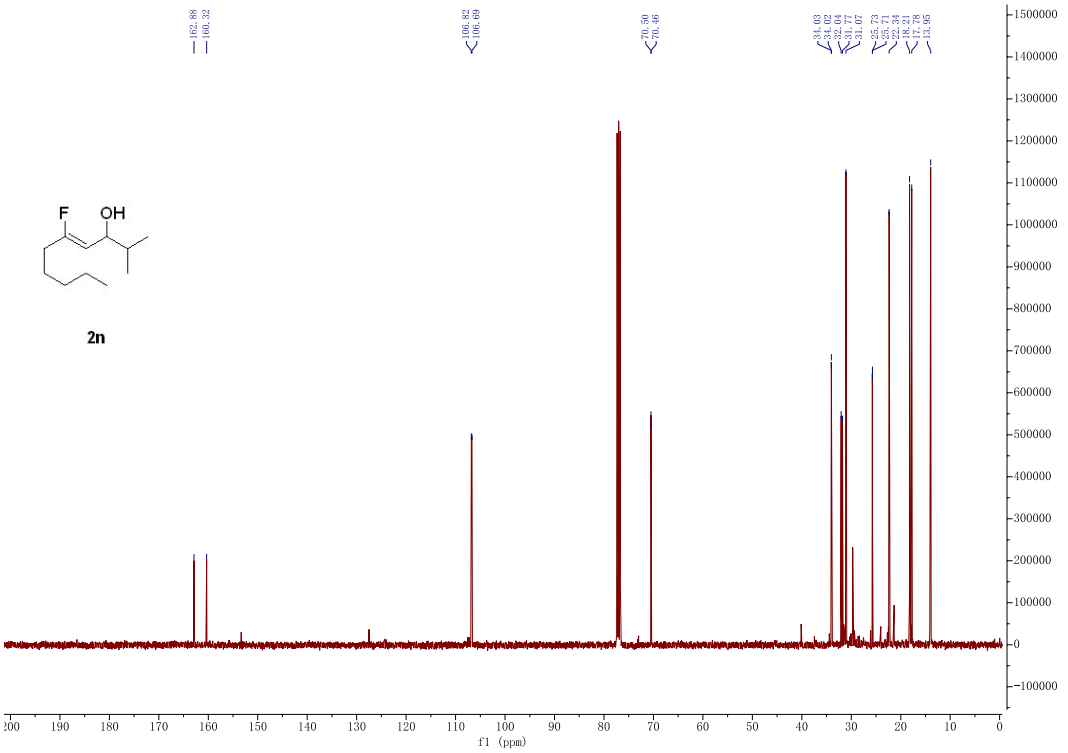

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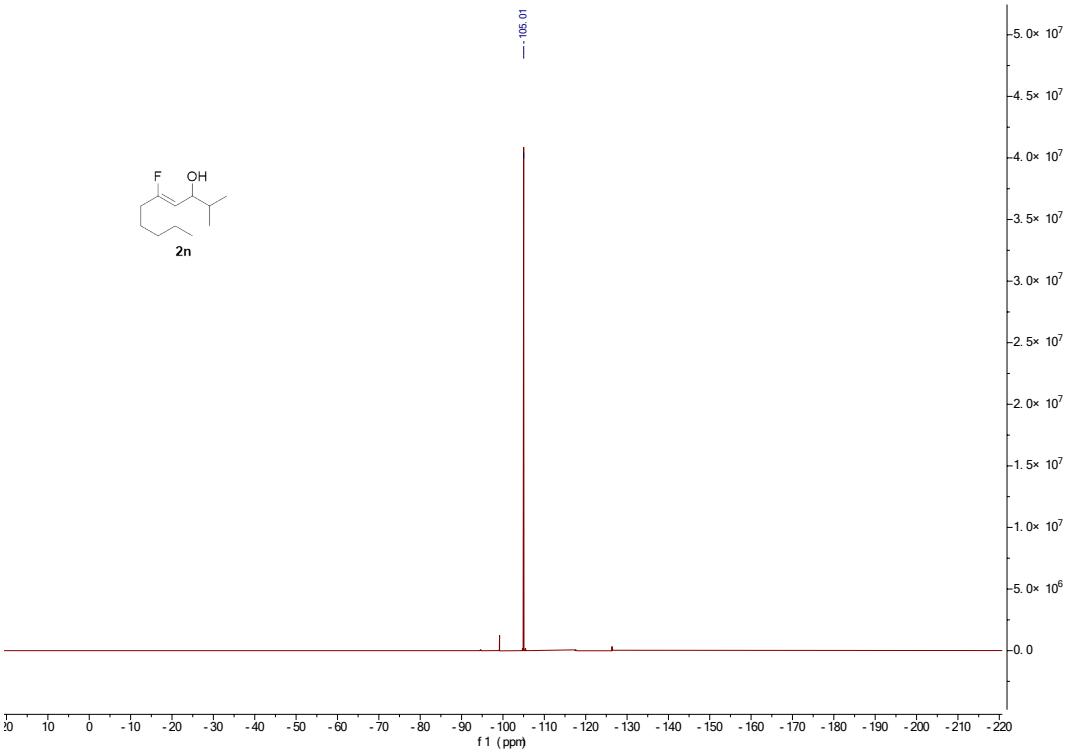

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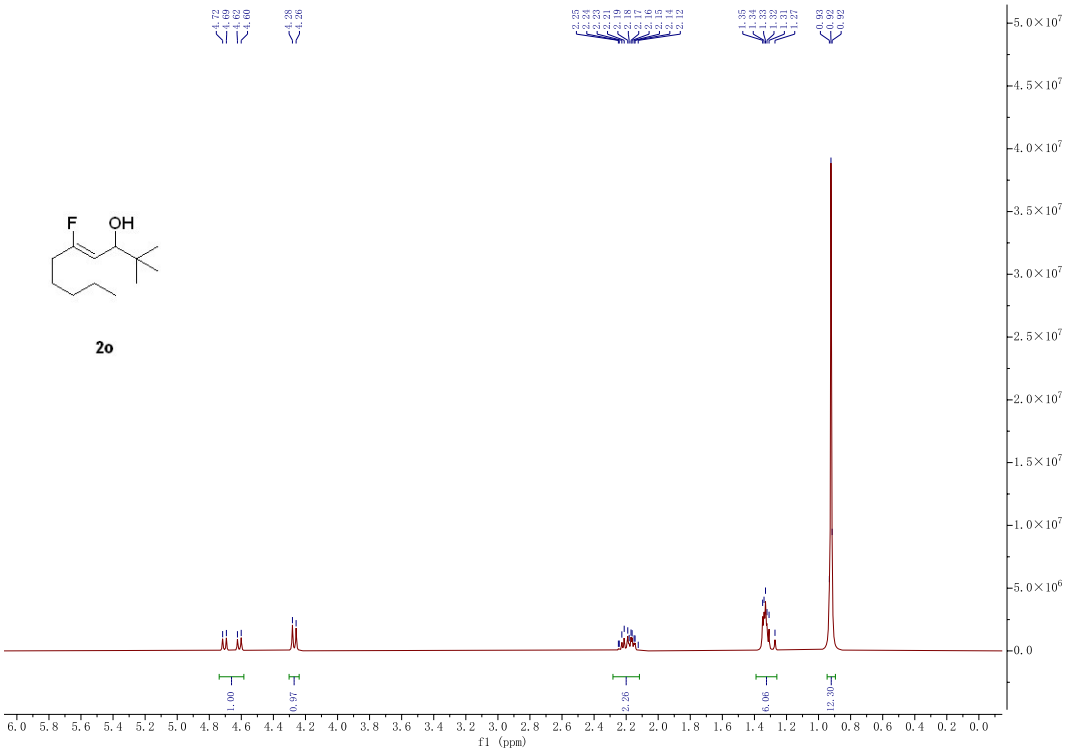

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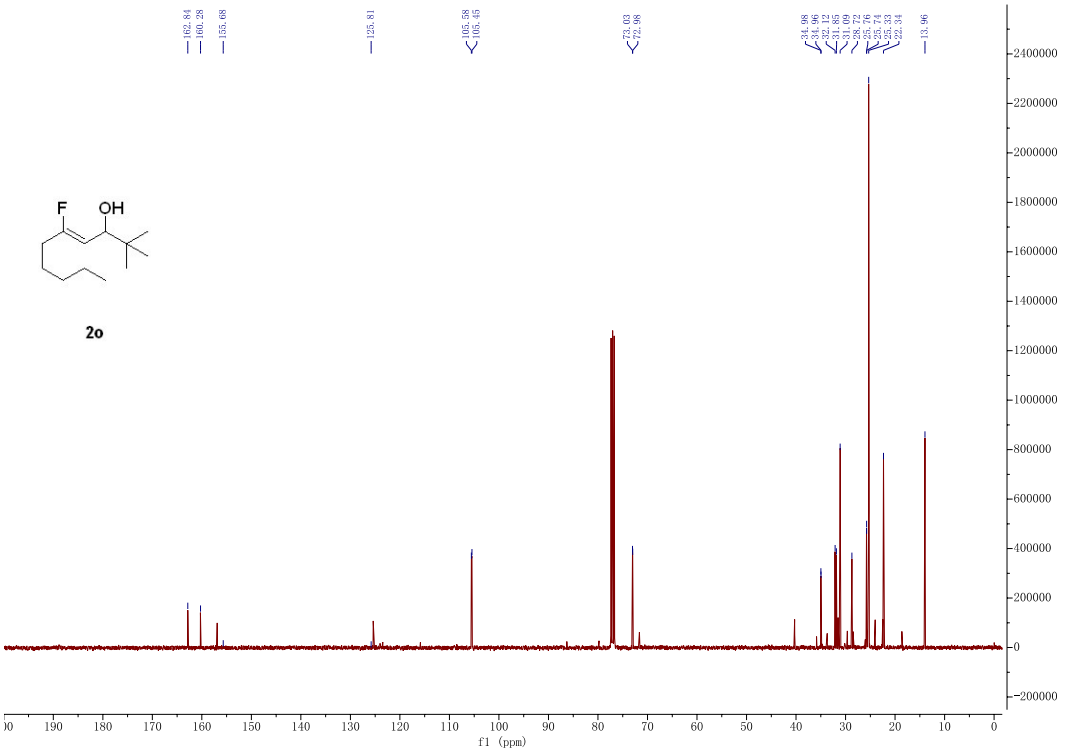

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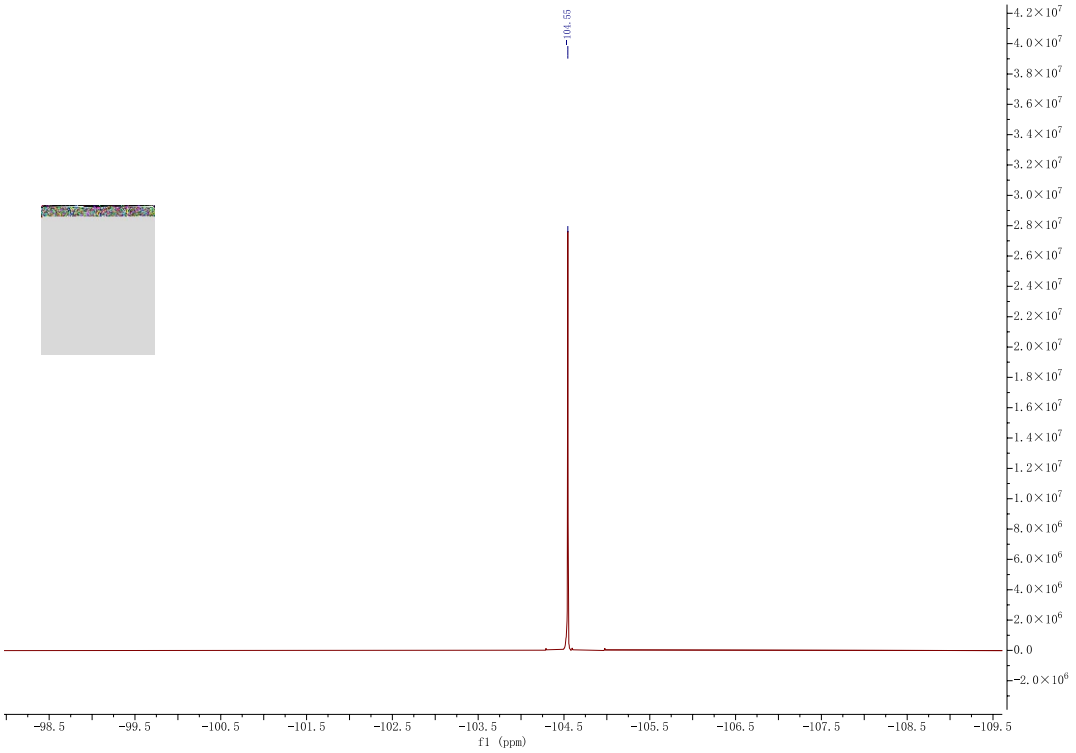

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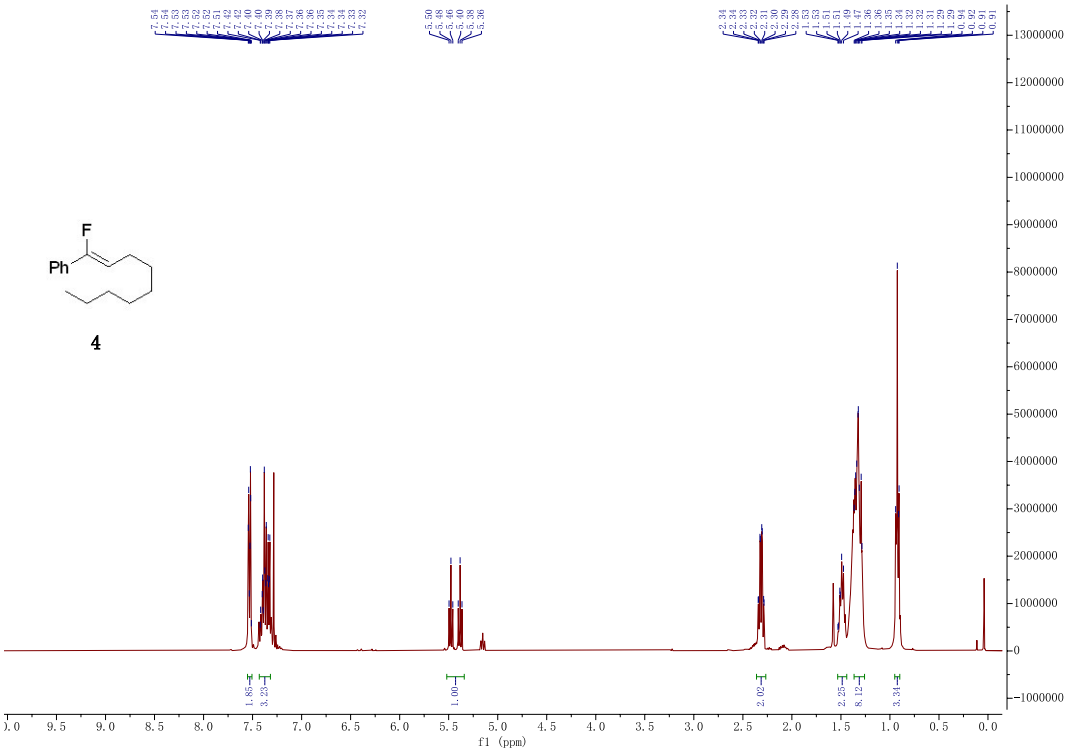

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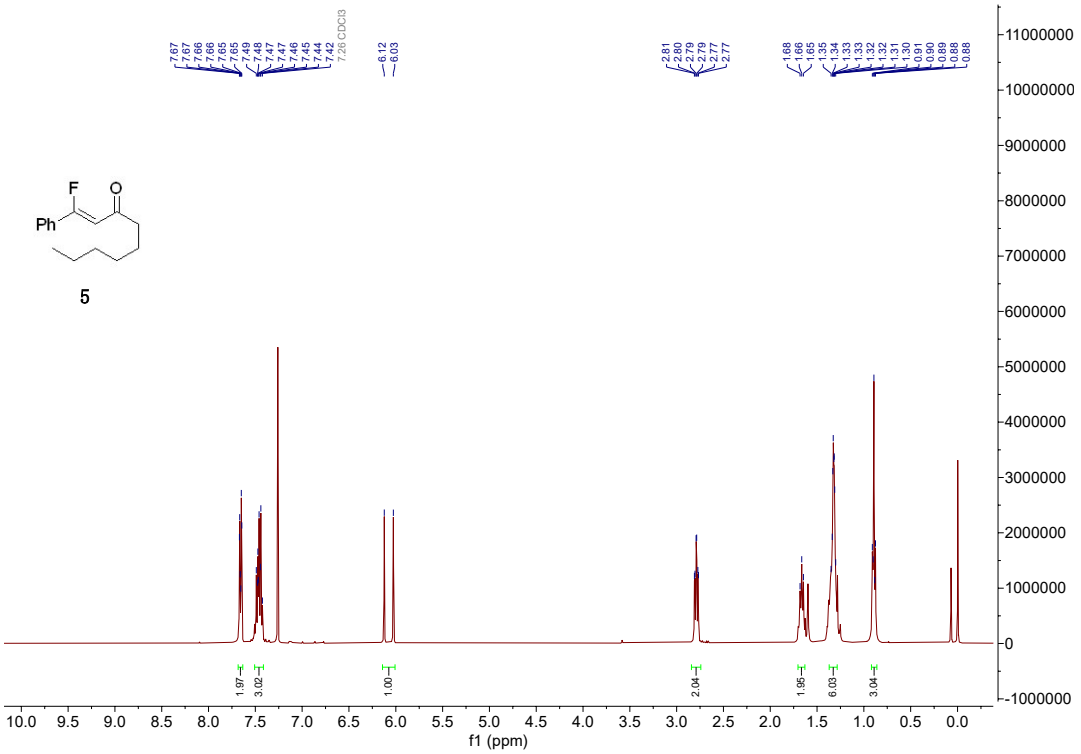

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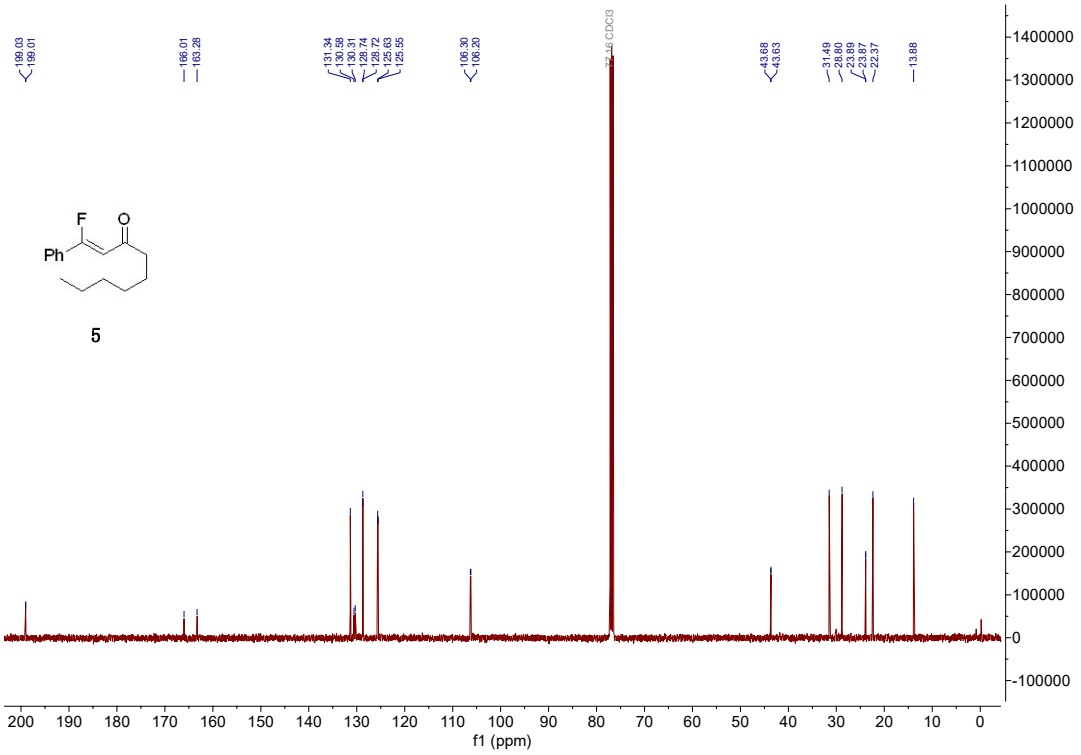

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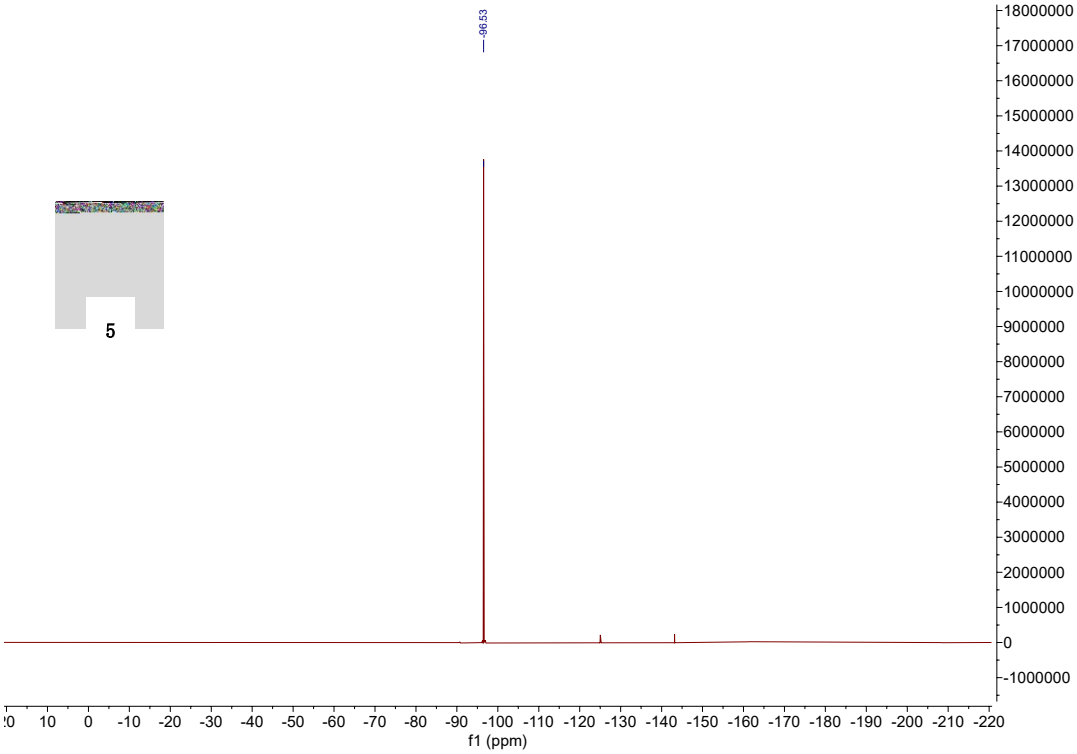

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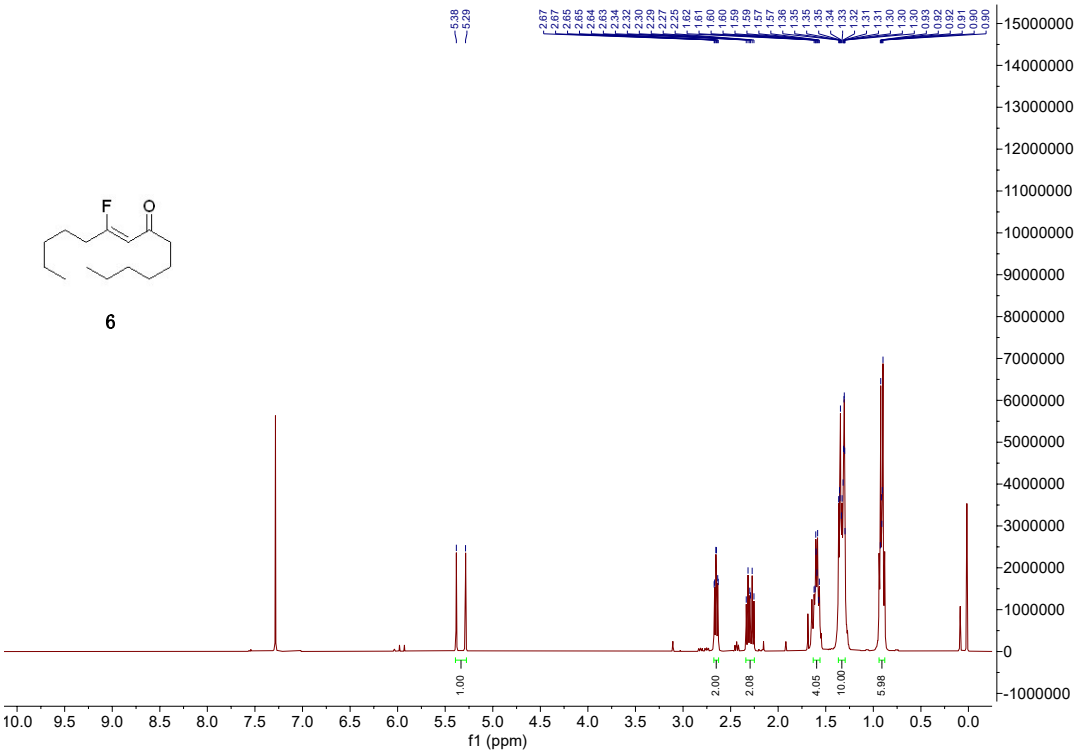

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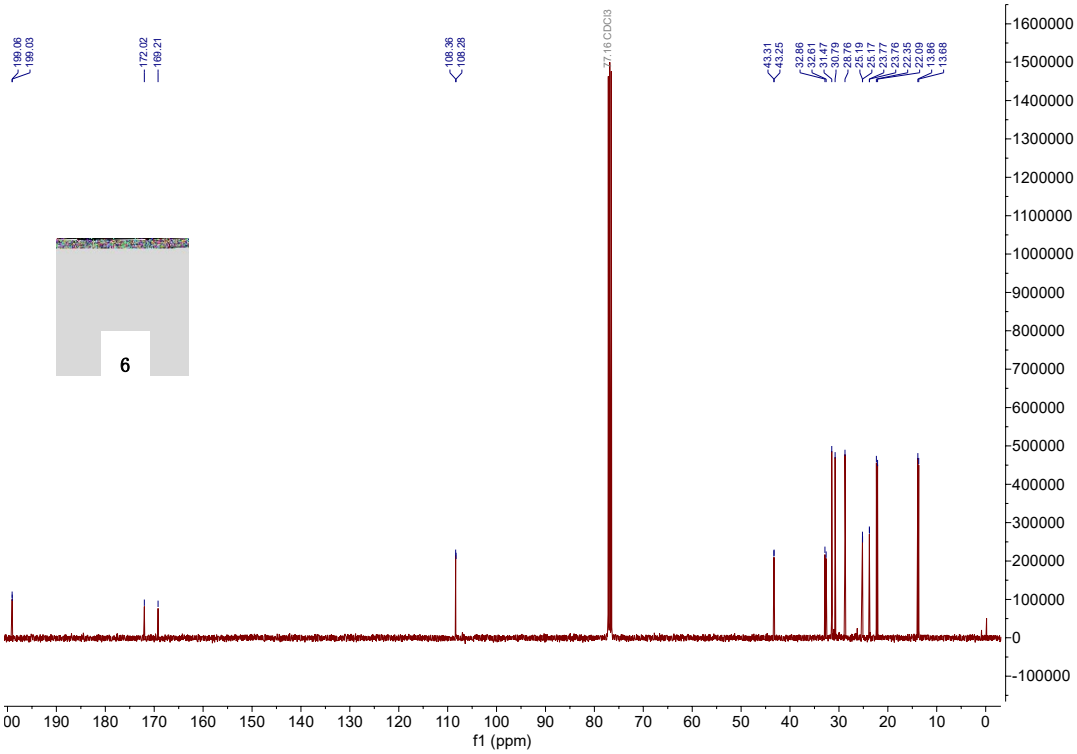

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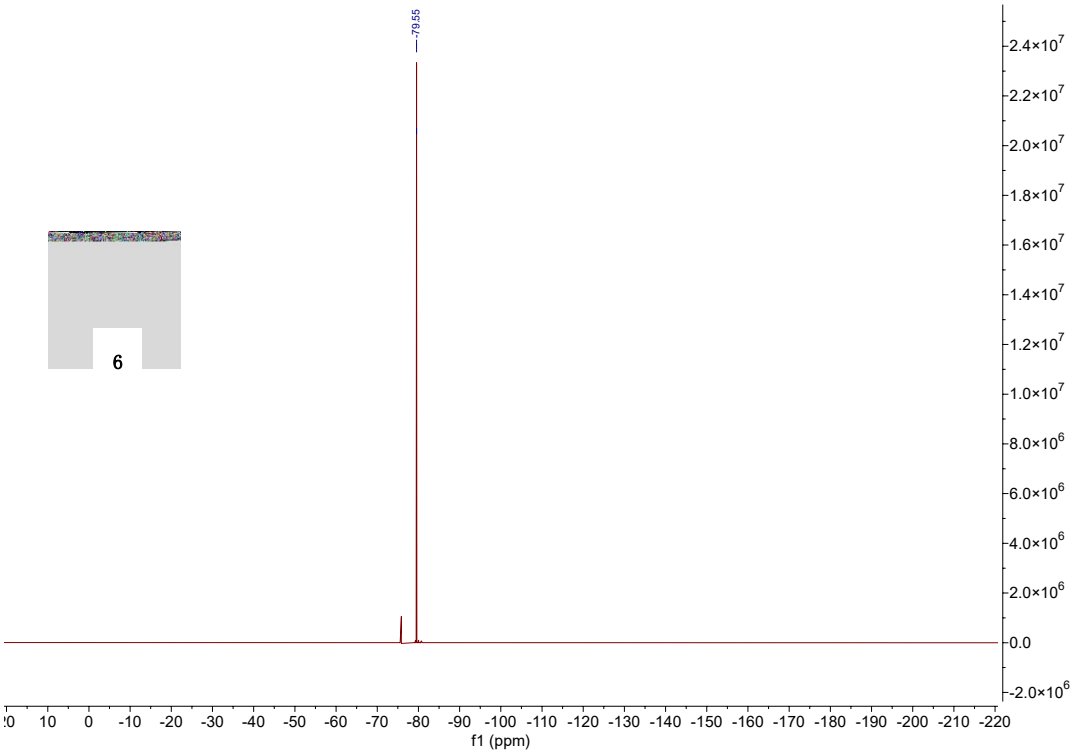

NMR Yield determination