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# Supporting Information

for

# *gem*-Difluorination of carbon–carbon triple bonds using Brønsted acid/$Bu_4NBF_4$ or electrogenerated acid

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## Experimental procedure, characterization data of compounds and copies of spectra of $^1$H NMR and $^{13}$C NMR

**General remarks.**

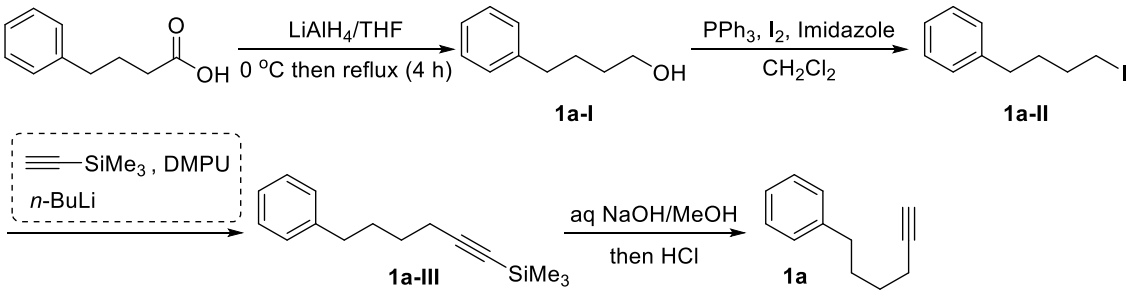
$^1$H and $^{13}$C NMR spectra were measured by using a MERCURY 300 ($^1$H, 300 MHz; $^{13}$C, 75 MHz), and a JEOL JNM-ECS 400 ($^1$H, 400 MHz; $^{13}$C, 100 MHz; $^{19}$F, 376 MHz) spectrometer. Unless otherwise noted, $CDCl_3$ was used as NMR solvent. The chemical shifts of $^1$H NMR in $CDCl_3$ are reported using 7.26 ppm from the residual $CHCl_3$ or 0.00 ppm from tetramethylsilane ($Me_4Si$) as an internal standard. The chemical shifts of $^{13}$C NMR in $CDCl_3$ are reported using 77.0 ppm. The chemical shifts of $^{19}$F NMR in $CDCl_3$ are reported using −62.7 ppm of trifluorotoluene ($CF_3C_6H_5$) as an internal standard. After the preparation of the crude product, $^{19}$F NMR spectrum was measured in the presence of trifluorotoluene ($CF_3C_6H_5$) as an internal standard. After the isolation and purification, the isolated material was also measured by $^{19}$F NMR to confirm the purity and absence of trifluorotoluene ($CF_3C_6H_5$) of an internal standard. In this supporting information, $^{19}$F NMR spectra at the crude product were shown below, unless mentioned. $^1$H and $^{13}$C NMR spectra were also showed, which were after the isolation and purification.

Mass spectra (HRMS) were measured by a Thermo Fisher Scientific EXACTIVE Plus spectrometer. GC analysis was carried out by using a Shimadzu GC 2014 apparatus, equipped with a capillary column and FID. GC–MS (EI) analysis was carried out by using an Agilent 6890N apparatus, equipped with an Agilent 5973N Mass Selective Detector and/or an Agilent 7890A Mass Selective Detector, equipped with an Agilent 5975C inert XL MSD with Triple Axis Detector. Merck pre-coated silica gel $F_{254}$ plates (thickness 0.25 mm) were used for the TLC analysis. A silica gel column (Kanto Chem. Co., Silica Gel N, spherical, neutral, 40–100 μm) was used for the flash chromatography by using an air pump. Preparative GPC separation was carried out by using LC-9201, LC-9210 NEXT, or LC-9110 NEXT equipped with JAIGEL-1H and JAIGEL-2H, in which $CHCl_3$ was used as an eluent. All reactions were carried out under $N_2$ atmosphere, unless mentioned.

**Materials.**

$CH_2Cl_2$ containing a small amount of MeOH as the stabilizer was purchased from SASAKI Chemical Co. and Sigma-Aldrich Japan. Dried and pure $CH_2Cl_2$ was prepared according to reported procedure.[1] $Bu_4NBF_4$ was purchased from commercial suppliers, and dried at 50 °C under 1 mmHg overnight to remove a small amount of water. The substrates such as but-3-yn-1-ylbenzene (**1b**), diphenylacetylene (**1c**), dec-1-yne (**1d**), octadec-1-yne (**1e**), dec-9-yn-1-ol (**1f**), 2-(pent-4-yn-1-yl)isoindoline-1,3-dione (**1h**), and dodec-6-yne (**1j**) were purchased from commercial suppliers and used without further purification. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification.

**Synthesis of hex-5-yn-1-ylbenzene (1a).**




To the suspension of $LiAlH_4$ (1.54 g, 40.6 mmol) in THF (100 mL) at 0 °C was slowly added a solution of 4-phenylbutanoic acid (6.58 g, 40.1 mmol)/THF (32 mL), and reaction temperature was increased to room temperature. Then, the solution was refluxed for 4 h. After the reaction, temperature was cooled to 0 °C, and $H_2O$ (1.5 mL), aqueous 15% NaOH (1.5 mL), and $H_2O$ (4.5 mL) were added to quench the reaction. After the celite filtration of the solution, the water in the solution was removed by $MgSO_4$, which was filtered and concentrated under reduced pressure to give 4-phenylbutan-1-ol (**1a-I**, 4.76 g, 31.7 mmol, 79% crude yield) as the crude material. This compound was identified by

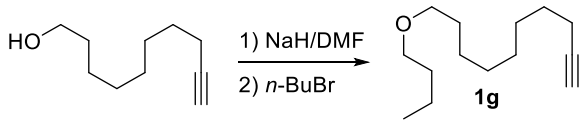
the comparison of the reported spectroscopic data.[2] Because the purity of the crude material was high, synthesized 4-phenylbutan-1-ol (**1a-I**) was used in the next step without the further purification.

To the solution of $PPh_3$ (11.80 g, 45.0 mmol), $I_2$ (11.43 g, 45.0 mmol), and imidazole (4.44 g, 65.2 mmol) in $CH_2Cl_2$ (100 mL), was slowly added 4-phenylbutan-1-ol (**1a-I**, 4.47 g, ca. 29.8 mmol) at room temperature. The reaction mixture was stirred for 2 h. After quenching the reaction by the addition of saturated aqueous $Na_2S_2O_3$ (100 mL), the additional $CH_2Cl_2$ (50 mL) and brine (100 mL) were added and separated. The aqueous phase was extracted by $CH_2Cl_2$ (50 mL × 2), and the combined organic extract was washed by saturated aqueous $NH_4Cl$ (100 mL), followed by dried over $MgSO_4$. After the filtration and the concentration under reduced pressure, the crude product thus obtained was purified by the flash chromatography (hexane/AcOEt = 3:1) to give (4-iodobutyl)benzene (**1a-II**, 7.55 g, 29.0 mmol, 97% yield). This compound was identified by the comparison of the reported spectroscopic data.[3]

To the solution of ethynyltrimethylsilane (4.86 g, 49.5 mmol) and DMPU (*N*,*N*'-dimethylpropyleneurea, 6.36 g, 49.6 mmol) in THF (50 mL) at -78 °C, was slowly added *n*-BuLi (1.57 M, 31 mL, ca. 48.7 mmol). The solution was stirred for 1 h at the same temperature. Then, a solution of (4-iodobutyl)benzene (**1a-II**, 7.12 g, 27.4 mmol) in THF (50 mL) was slowly added to the reaction mixture at −78 °C, and stirred for 0.5 h at −78 °C. Then, the mixture was additionally stirred at room temperature overnight. The reaction was quenched by the addition of saturated aqueous $NH_4Cl$ (100 mL). The additional $Et_2O$ (50 mL) was added and separated. The aqueous phase was extracted by $Et_2O$ (50 mL x 2), and the combined organic extract was washed by brine (50 mL), followed by dried over $Na_2SO_4$. After the filtration and concentration under reduced pressure, the crude product was purified by the flash chromatography (hexane/AcOEt = 10:1) to give trimethyl(6-phenylhex-1-yn-1-yl)silane (**1a-III**, 5.49 g, 23.8 mmol, 87% yield). This compound was identified by the comparison of the reported spectroscopic data.[3]

Trimethyl(6-phenylhex-1-yn-1-yl)silane (**1a-III**, 5.47 g, 23.7 mmol) was added to the round flask. MeOH (100 mL) and aqueous 2 M NaOH (24 mL) was added, and then the solution was stirred at room temperature overnight. The reaction was quenched by the addition of aqueous 2M HCl (24 mL). The brine (50 mL) and $Et_2O$ (100 mL) were added and separated. The aqueous phase was extracted by $Et_2O$ (100 mL × 2), and the combined organic extract was washed by brine (100 mL), followed by dried over $Na_2SO_4$. After the filtration and concentration under reduced pressure, the crude product was purified by the flash chromatography (hexane/AcOEt = 60:1) to give hex-5-yn-1-ylbenzene (**1a**, 3.26 g, 20.6 mmol, 87% yield). This compound was identified by the comparison of the reported spectroscopic data.[3]

**Synthesis of 10-butoxydec-1-yne (1g).**




To the suspension of NaH (ca. 55% in mineral, 0.60 g, 13.8 mmol) in DMF (40 mL) at 0 °C, was slowly added dec-9-yn-1-ol (0.86 g, 5.6 mmol). Then, *n*-BuBr (1.28 g, 9.3 mmol) was added, and the reaction temperature was increased to room temperature. Then, the reaction mixture was stirred overnight. The reaction was quenched by the addition of $H_2O$ (50 mL). $CH_2Cl_2$ (20 mL) and saturated aqueous $NH_4Cl$ (20 mL) were added to the solution, and separated. The aqueous phase was extracted by $CH_2Cl_2$ (20 mL × 2), and the combined organic extract was washed by brine (80 mL × 2), followed by dried over $MgSO_4$. After the filtration and concentration under reduced pressure, the residue was filtered through a short column (9.4 × 3.2 cm) of silica gel by $Et_2O$ to remove wastes to obtain the crude product. The crude product was purified by the first flash chromatography (hexane/AcOEt = 20:1) and second flash chromatography (hexane/AcOEt = 50:1) to give 10-butoxydec-1-yne (**1g**, 0.74 g, 3.5 mmol, 63% yield).

| **10-butoxydec-1-yne (1g)** | **Unknown compound**; $^1$H NMR (400 MHz, $CDCl_3$) δ 3.39 (t, *J* = 6.8 Hz, 2H), 3.34 (t, *J* = 6.4 Hz, 2H), 2.17 (td, *J* = 7.2, 2.8 Hz, 2H), 1.93 (t, *J* = 2.8 Hz, 1H), 1.62-1.47 (m, 7H), 1.44-1.18 (m, 9H), 0.91 (t, *J* = 7.6 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 84.8, 70.9, 70.6, 68.0, 31.8, 29.7, 29.3, 29.0, 28.7, 28.4, 26.1, 19.4, 18.4, 13.9 ppm; HRMS (ESI) calcd for $C_{14}H_{27}O$ ($[M+H]^+$): 211.2056, found: 211.2044. |
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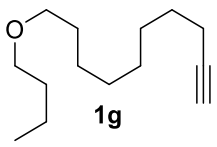
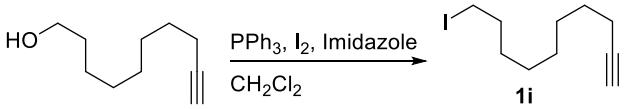



**Synthesis of 10-iododec-1-yne (1i).**




To the solution of $PPh_3$ (1.55 g, 5.9 mmol), $I_2$ (1.52 g, 6.0 mmol), and imidazole (0.67 g, 9.8 mmol) in $CH_2Cl_2$ (30 mL), was slowly added dec-9-yn-1-ol (0.66 g, 4.3 mmol) at room temperature. The solution was stirred at room temperature for 2 h. Then, the solution was refluxed for 1 h. The reaction was quenched by the addition of the saturated aqueous $Na_2S_2O_3$ (30 mL). $CH_2Cl_2$ (30 mL) was added to the solution and separated. The aqueous phase was extracted by $CH_2Cl_2$ (30 mL x 2), and the combined organic extract was washed by brine (30 mL), followed by dried over $MgSO_4$. After the filtration and the concentration under reduced pressure, the crude product was purified by the flash chromatography (hexane/AcOEt = 30:1) to give 10-iododec-1-yne (**1i**, 0.94 g, 3.6 mmol, 84% yield). This compound was identified by the comparison of the reported spectroscopic data.[4]

**Typical procedure for the *gem*-difluorination in method A (Table 1, entry 2).**

To the solution of $Bu_4NBF_4$ (823.0 mg, 2.5 mmol) in $CH_2Cl_2$ (4.0 mL), were added hex-5-yn-1-ylbenzene (**1a**, 78.6 mg, 0.497 mmol) and $Tf_2NH$ (694.4 mg, 2.5 mmol). The reaction was stirred for 16 h at room temperature. Then, the reaction mixture was cooled to 0 °C and $Et_3N$ (1.0 mL) was added to quench the reaction. After the concentration of the solution under reduced pressure, the residue was quickly filtered through a short column (9.4 × 3.2 cm) of silica gel by $Et_2O$ to remove $Bu_4NBF_4$ and others. The silica gel was washed with $Et_2O$. The crude product was evaluated by $^{19}$F NMR using trifluorotoluene ($CF_3C_6H_5$) (34.5 mg, 0.236 mmol) as an internal standard, indicating (5,5-difluorohexyl)benzene (**2a**) was obtained in 83% yield. Then, the crude product was purified via the flash chromatography (hexane) to give (5,5-difluorohexyl)benzene (**2a**, 71.1 mg, 0.359 mmol, 72% yield). In this step, $^{19}$F NMR was also measured to confirm the absence of trifluorotoluene. This compound was identified by the comparison of the reported spectroscopic data.[5]

Other entries in Tables 1 and 2 were conducted according to the above procedure. If necessary, the preparative GPC separation was carried out for the crude products to purify and isolate the desired products.

**Typical procedure for the *gem*-difluorination in method B (Scheme 1, 16 mA).**

The electrochemical oxidation was carried out in an H-type divided cell (4G glass filter), which was equipped with a carbon felt anode and a platinum plate cathode (20 mm × 20 mm). In the cathodic and anodic chambers, 0.3 M $Bu_4NBF_4/CH_2Cl_2$ (8.0 mL × 2) was added. Then, hex-5-yn-1-ylbenzene (**1a**, 79.4 mg, 0.502 mmol) was added to the anodic solution. The constant current electrolysis (16 mA, 3.0 F/mol based on **1a**) at room temperature was conducted. After the consumption of the electricity, $Et_3N$ (1.0 mL × 2) was added to both chambers to quench the reaction. After the concentration of the solution under reduced pressure, the residue was quickly filtered through a short column (9.4 × 3.2 cm) of silica gel by $Et_2O$ to remove $Bu_4NBF_4$ and others. The crude product was evaluated by $^{19}$F NMR using trifluorotoluene ($CF_3C_6H_5$) (33.4 mg, 0.229 mmol) as an internal standard, indicating (5,5-difluorohexyl)benzene (**2a**) was obtained in 42% yield. Then, the obtained crude product was purified

by the preparative GPC separation to give (5,5-difluorohexyl)benzene (**2a**, 29.0 mg, 0.146 mmol, 29% yield). In this step, $^{19}$F NMR was also measured to confirm the absence of trifluorotoluene. This compound was identified by the comparison of the reported spectroscopic data.[5]

(3,3-Difluorobutyl)benzene (**2b**)[6] and 2-(4,4-difluoropentyl)isoindoline-1,3-dione (**2h**)[7] were fully identified by the comparison of the reported spectroscopic data.

The identification of other compounds such as 2,2-difluorodecane (**2d**), 2,2-difluorooctadecane (**2e**), 9,9-difluorodecan-1-ol (**2f**), 1-butoxy-9,9-difluorodecane (**2g**), 9,9-difluoro-1-iododecane (**2i**), and 6,6-difluorododecane (**2j**) are described below. These compounds are either new compounds or known compounds but their spectra are not fully reported. Therefore, we report them in this paper. The analysis of $^{13}$C NMR of these compounds was according to the literature, in which the analysis of $^{13}$C NMR of 2,2-difluorotridecane is described.[8]

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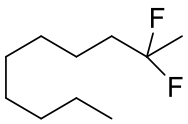
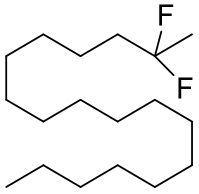
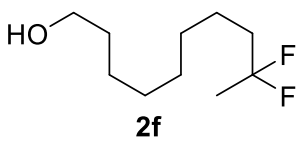
| **2,2-difluorodecane (2d)**<br>  <br>**2d** | **Known compound, but insufficient report for identification in some literatures (Table 2, ref 54)**; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 1.90-1.74 (m, 2H), 1.58 (t, *J* = 18.4 Hz, 3H), 1.50-1.40 (m, 2H), 1.38-1.18 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 124.5 (t, *J* = 236.5 Hz), 37.9 (t, *J* = 25.7 Hz), 31.8, 29.3, 29.3 (overlapping), 29.1, 23.2 (t, *J* = 28.6 Hz), 22.7 (t, *J* = 4.8 Hz), 22.6, 14.1 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$) δ from -90.17 to -90.43 (m, 2F) ppm; GC-MS (EI) m/z (%) = 158 (1) ([M-HF]$^+$), 138 (6), 65 (61), 43 (100). This compound was not detected by HRMS (ESI). The related aliphatic difluorinated compound such as 2,2-difluorododecane was detected by GC-MS in the literature,[9] in which [M-HF]$^+$ was confirmed. Because of the reason, we also carried out the analysis of GC-MS for **2d**, as described above. |
| **2,2-difluorooctadecane (2e)**<br>  <br>**2e** | **Unknown compound (Table 2, entry 8)**; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 1.89-1.71 (m, 2H), 1.57 (t, *J* = 18.2 Hz, 3H), 1.50-1.38 (m, 2H), 1.37-1.18 (m, 26H), 0.88 (t, *J* = 6.8 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 124.4 (t, *J* = 236.5 Hz), 38.0 (t, *J* = 24.8 Hz), 31.9, 29.7, 29.6, 29.5, 29.41, 29.38, 29.36, 23.2 (t, *J* = 27.6 Hz), 22.8 (t, *J* = 4.7 Hz), 22.7, 14.1 ppm. Some signals of $^{13}$C NMR seemed to be overlapping. $^{19}$F NMR (376 MHz, $CDCl_3$) δ from -90.15 to -90.42 (m, 2F) ppm; GC-MS (EI) m/z (%) = 270 (3) ([M-HF]$^+$), 250 (39), 71 (67), 57 (100), 43 (70). This compound was not detected by HRMS (ESI). The related aliphatic difluorinated compound such as 2,2-difluorododecane was detected by GC-MS in the literature,[9] in which [M-HF]$^+$ was confirmed. Because of the reason, we also carried out the analysis of GC-MS for **2e**, as described above. |
| **9,9-difluorodecan-1-ol (2f)**<br>  <br>**2f** | **Unknown compound (Table 2, entry 10)**; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 3.64 (t, *J* = 6.4 Hz, 2H), 1.90-1.74 (m, 2H), 1.64-1.51 (m, 5H), 1.51-1.41 (m, 2H), 1.41-1.26 (m, 9H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 124.4 (t, *J* = 235.5 Hz), 63.0, 37.9 (t, *J* = 24.8 Hz), 32.7, 29.3, 29.2, 29.2 (overlapping), 25.7, 23.2 (t, *J* = 28.6 Hz), 22.7 (t, *J* = 4.8 Hz) ppm; $^{19}$F NMR (376 MHz, $CDCl_3$) δ from -90.18 to -90.45 (m, 2F) ppm; HRMS (ESI) calcd for $C_{10}H_{20}OF_2Na$ ([M+Na]$^+$): 217.1374, found: 217.1369. |

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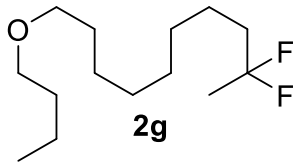
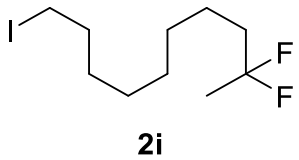
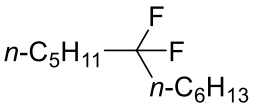
| **1-butoxy-9,9-difluorodecane (2g)**<br>  <br>**2g** | **Unknown compound (Table 2, entry 12)**; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 3.40 (t, *J* = 6.4 Hz, 2H), 3.39 (t, *J* = 6.4 Hz, 2H), 1.90-1.74 (m, 2H), 1.63-1.51 (m, 7H), 1.50-1.25 (m, 12H), 0.92 (t, *J* = 7.2 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 124.4 (t, *J* = 236.5 Hz), 70.8, 70.6, 37.9 (t, *J* = 24.8 Hz), 31.8, 29.7, 29.29, 29.26, 29.22, 26.1, 23.1 (t, *J* = 27.7 Hz), 22.7 (t, *J* = 4.8 Hz), 19.3, 13.9 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$) δ from -90.18 to -90.46 (m, 2F) ppm; HRMS (ESI) calcd for $C_{14}H_{28}OF_2Na$ ($[M+Na]^+$): 273.2000, found: 273.1996. |
| **9,9-difluoro-1-iododecane (2i)**<br>  <br>**2i** | **Unknown compound (Table 2, entry 16)**; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 3.19 (t, *J* = 6.8 Hz, 2H), 1.90-1.75 (m, 4H), 1.58 (t, *J* = 18.0 Hz, 3H), 1.51-1.27 (m, 10H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 124.4 (t, *J* = 236.5 Hz), 37.9 (t, *J* = 24.8 Hz), 33.4, 30.4, 29.19, 29.16, 28.3, 23.2 (t, *J* = 28.6 Hz), 22.7 (t, *J* = 4.8 Hz), 7.3 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$) δ from -90.24 to -90.50 (m, 2F) ppm; HRMS (ESI) calcd for $C_{10}H_{19}F_2INa$ ($[M+Na]^+$): 327.0392, found: 327.0389. |
| **6,6-difluorododecane (2j)**<br>  <br>**2j** | **Known compound, but insufficient report for identification in the literature[10] (Table 2, entry 18)**;$^{1}$H NMR (400 MHz, $CDCl_3$) δ 1.87-1.71 (m, 4H), 1.50-1.40 (m, 4H), 1.38-1.21 (m, 10H), 0.94-0.85 (m, 6H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 125.5 (t, *J* = 238.4 Hz), 36.29 (t, *J* = 25.7 Hz), 36.26 (t, *J* = 25.7 Hz), 31.6 (overlapping), 29.1, 22.5, 22.4, 22.3 (t, *J* = 4.7 Hz), 22.0 (t, *J* = 4.7 Hz), 14.0, 13.9 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -97.58 (quintet, *J* = 16.6 Hz, 2F) ppm; HRMS (ESI) calcd for $C_{12}H_{23}F_2$ ($[M-H]^-$): 205.1773, found: 205.1793. |

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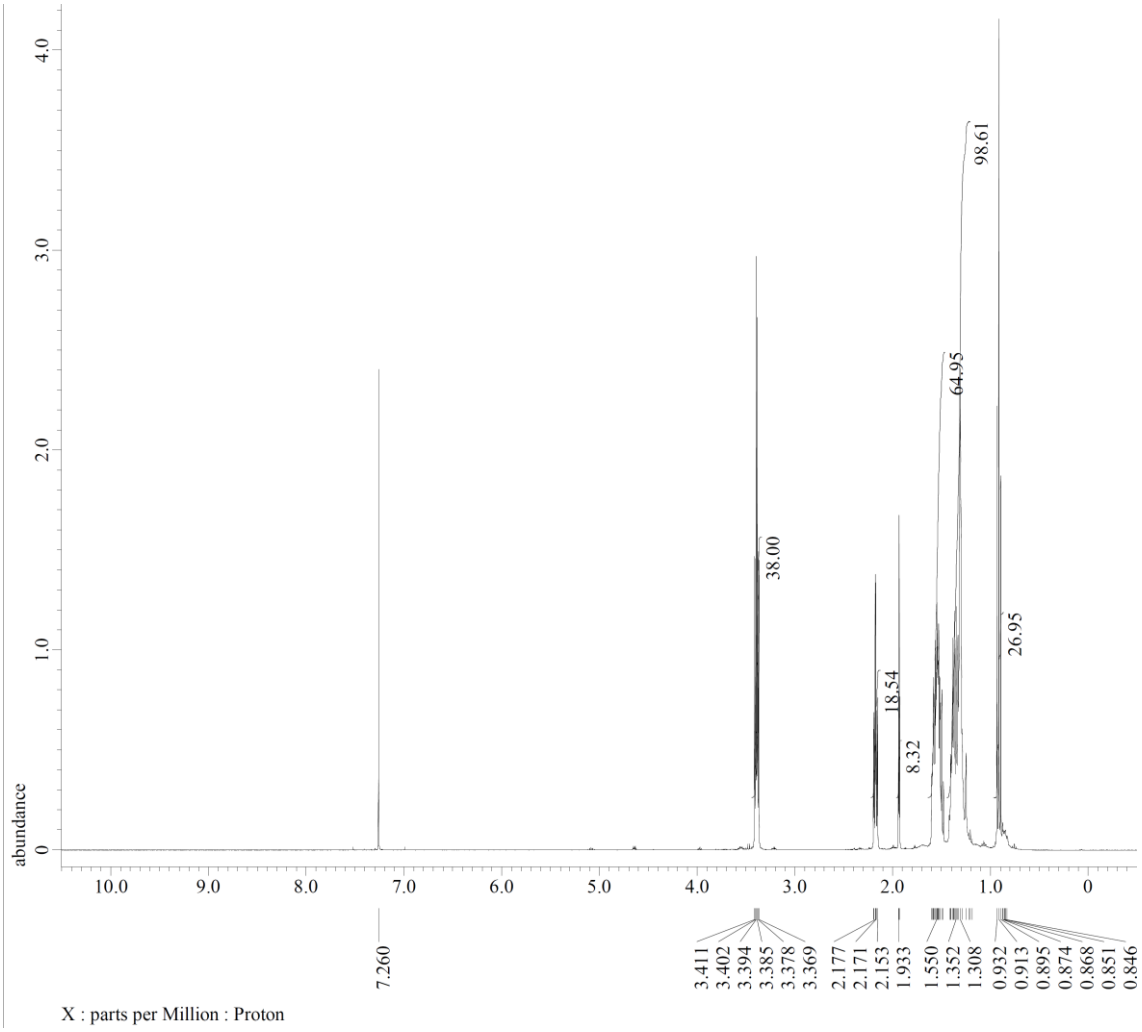
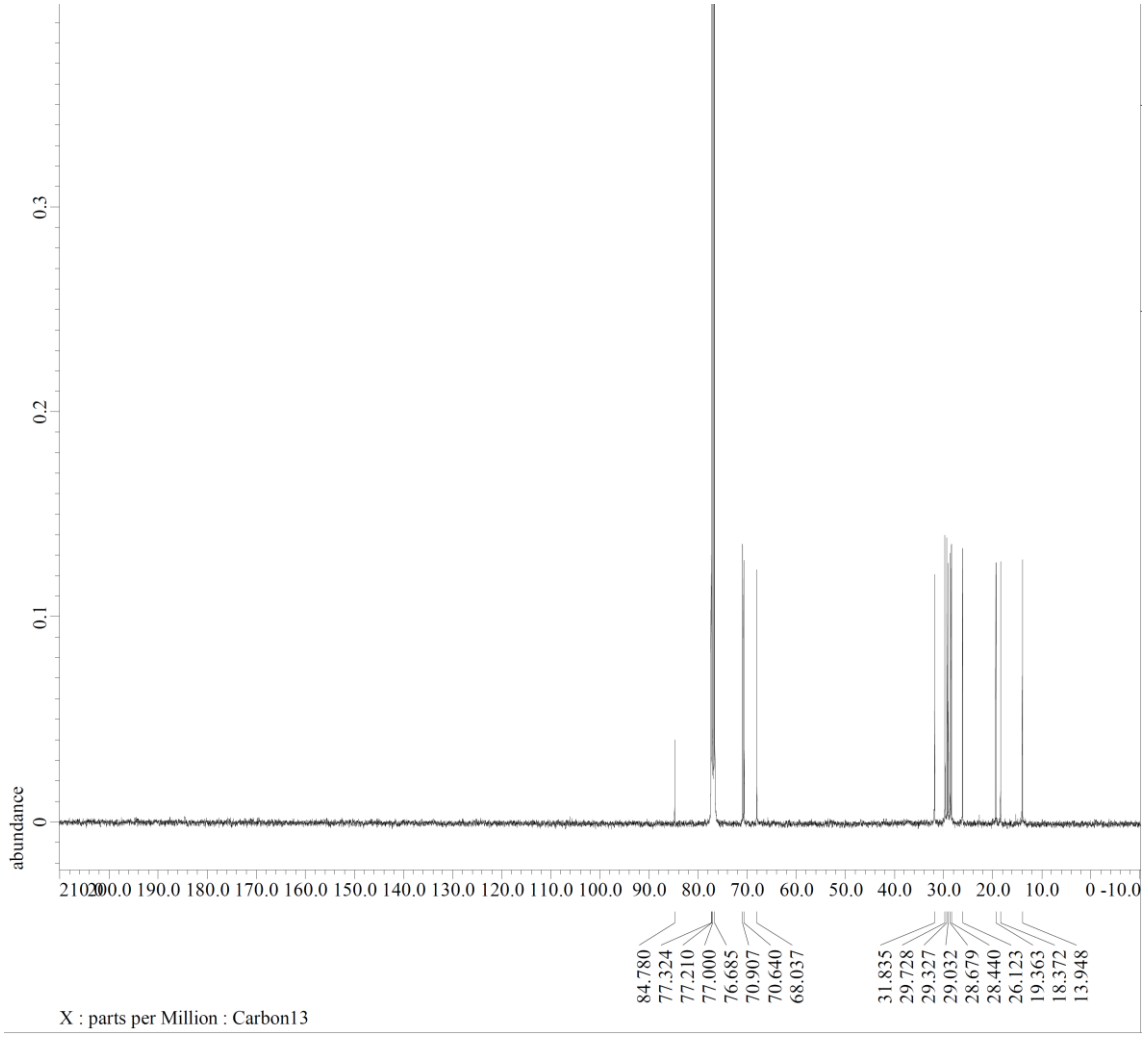
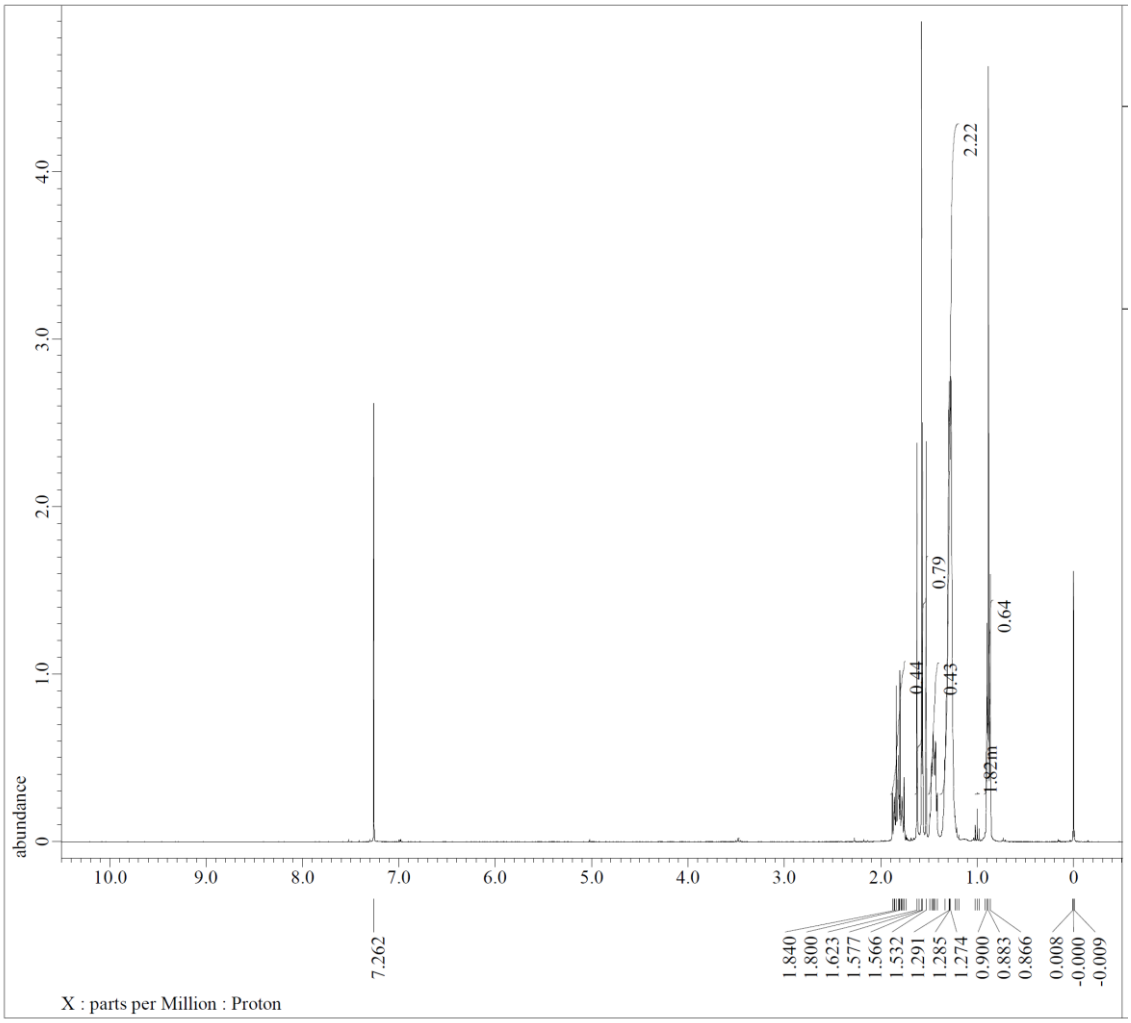


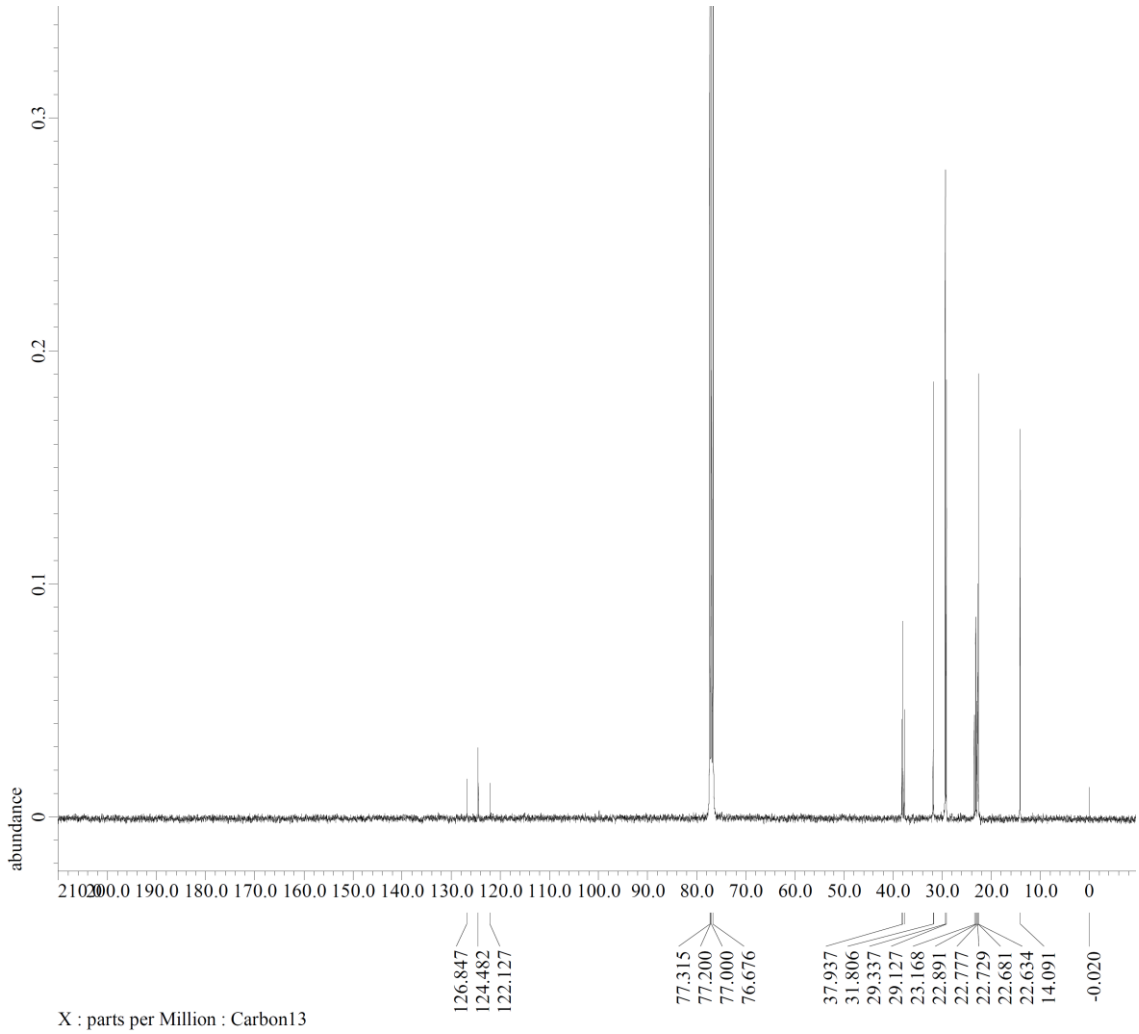

$^{1}$H NMR of 10-butoxydec-1-yne (**1g**).



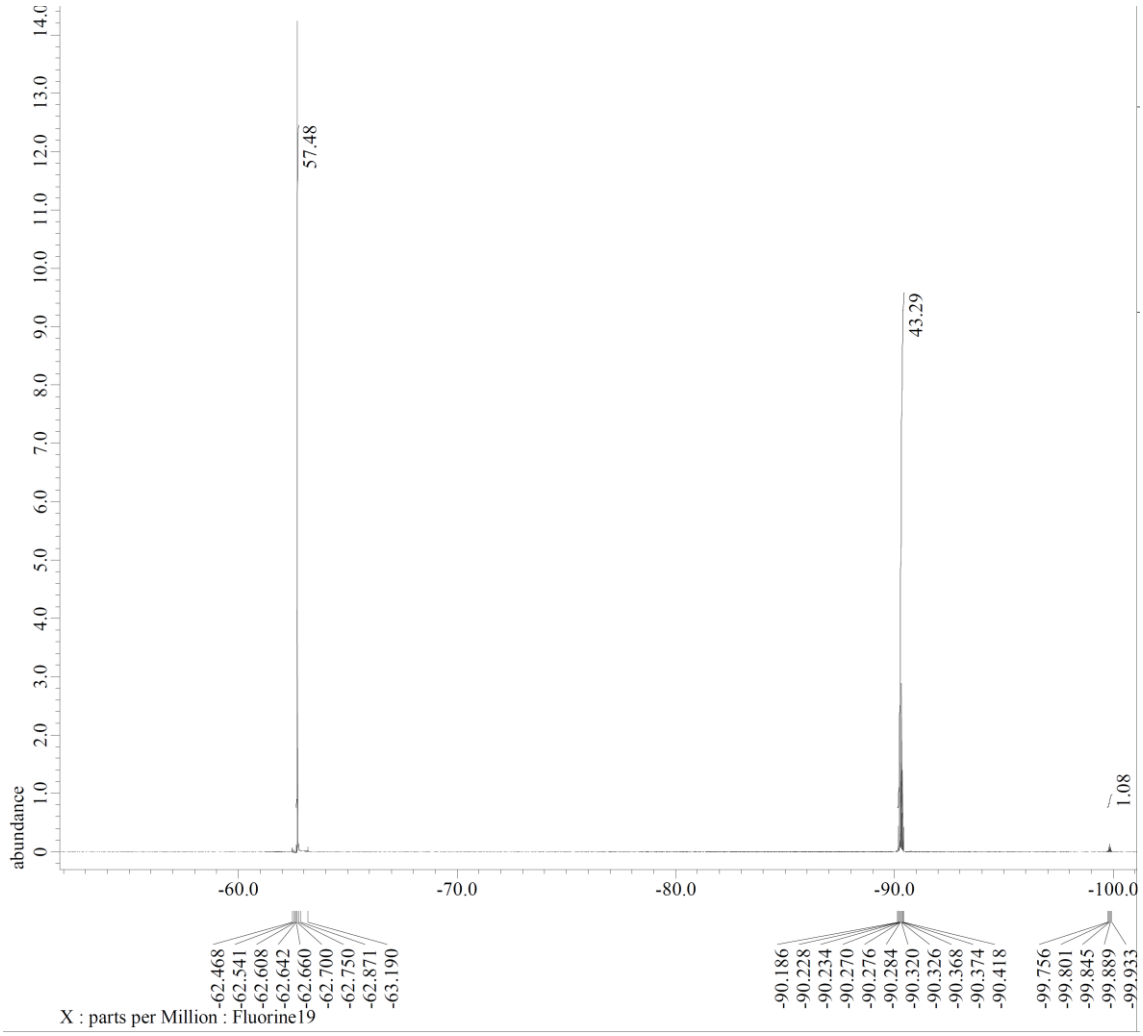

$^{13}$C NMR of 10-butoxydec-1-yne (**1g**).



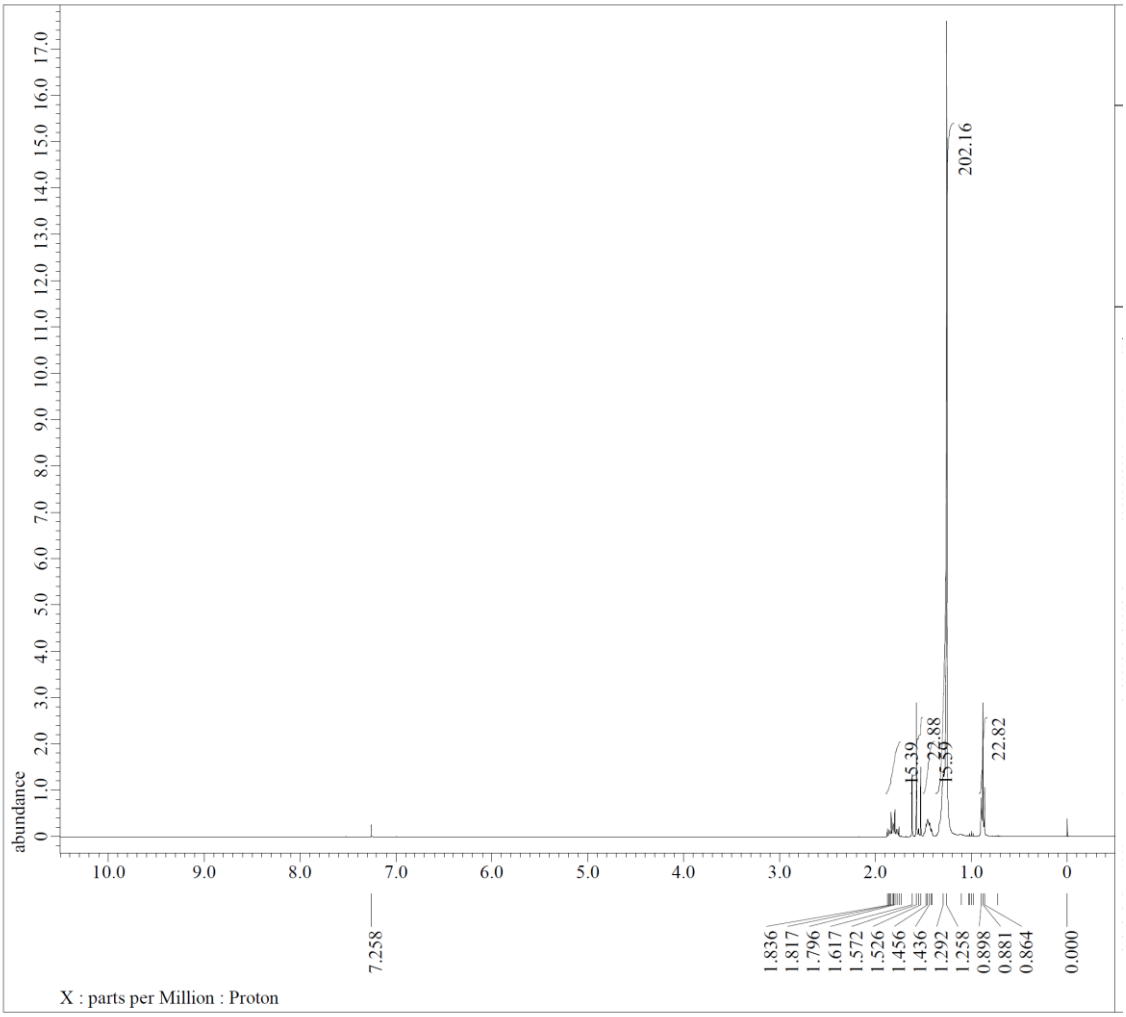

$^{1}$H NMR of 2,2-difluorodecane (**2d**).



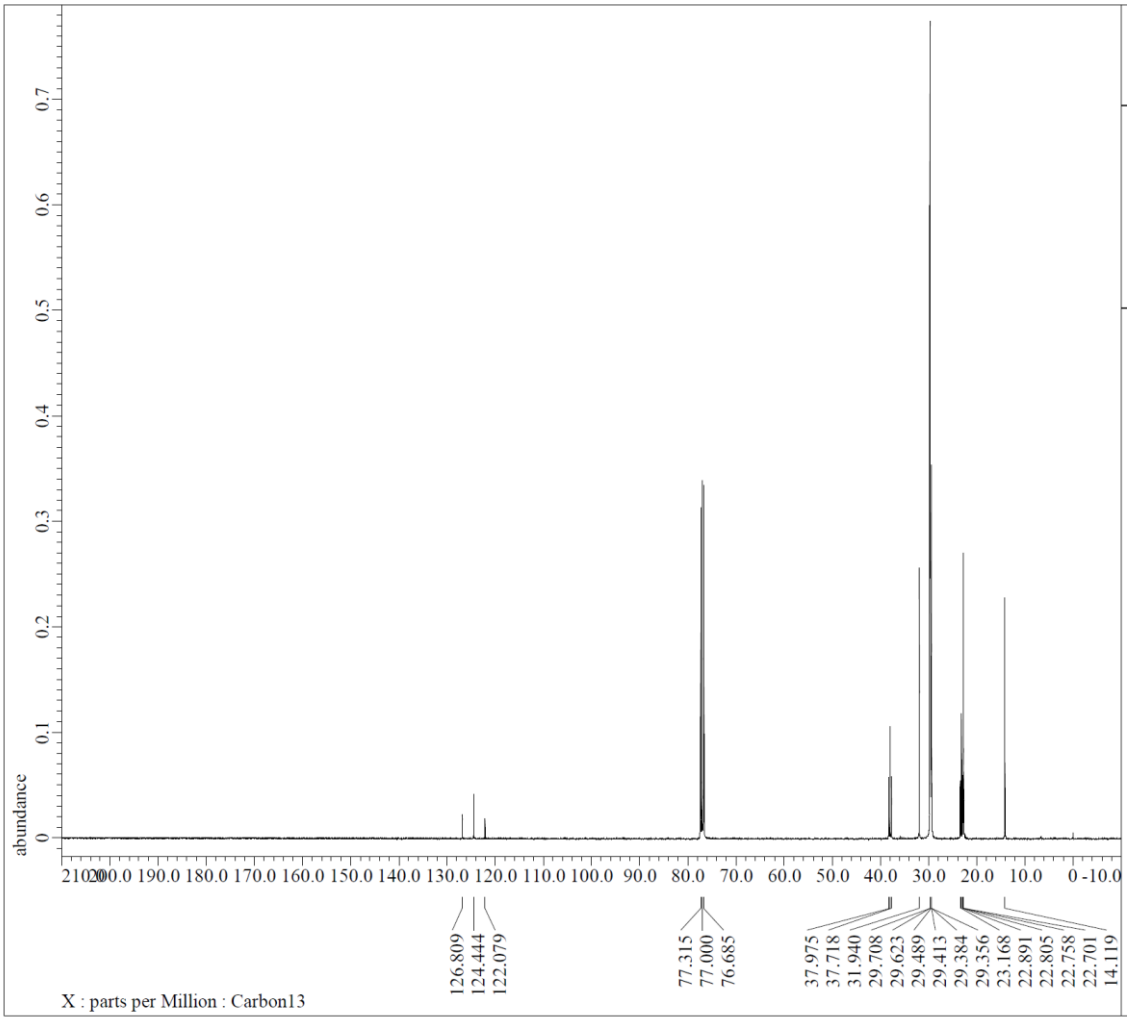

$^{13}$C NMR of 2,2-difluorodecane (**2d**).



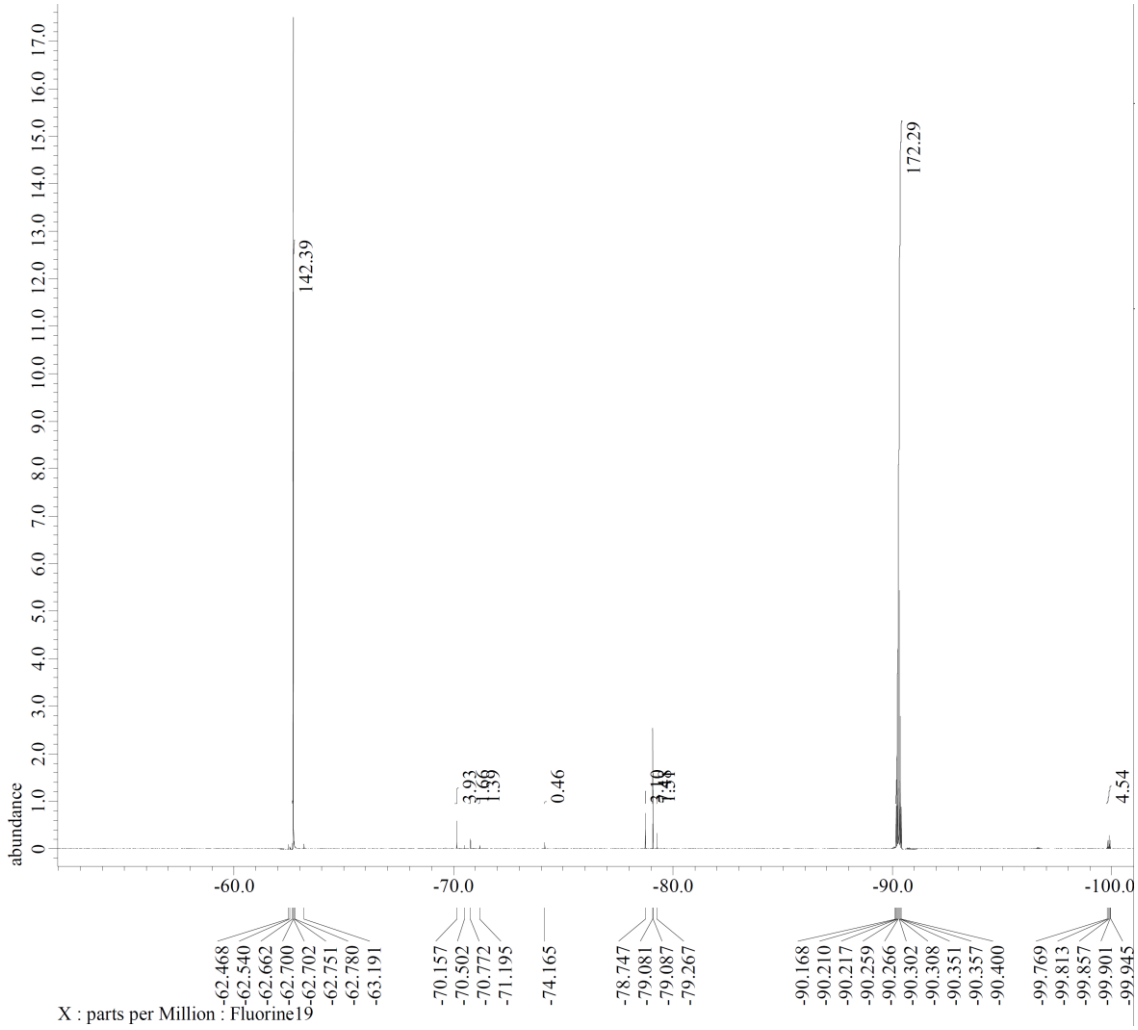

$^{19}F$ NMR of 2,2-difluorodecane (**2d**) in the presence of $CF_3C_6H_5$ as an internal standard. This $^{19}F$ NMR spectrum was measured after the purification and isolation, adding $CF_3C_6H_5$.



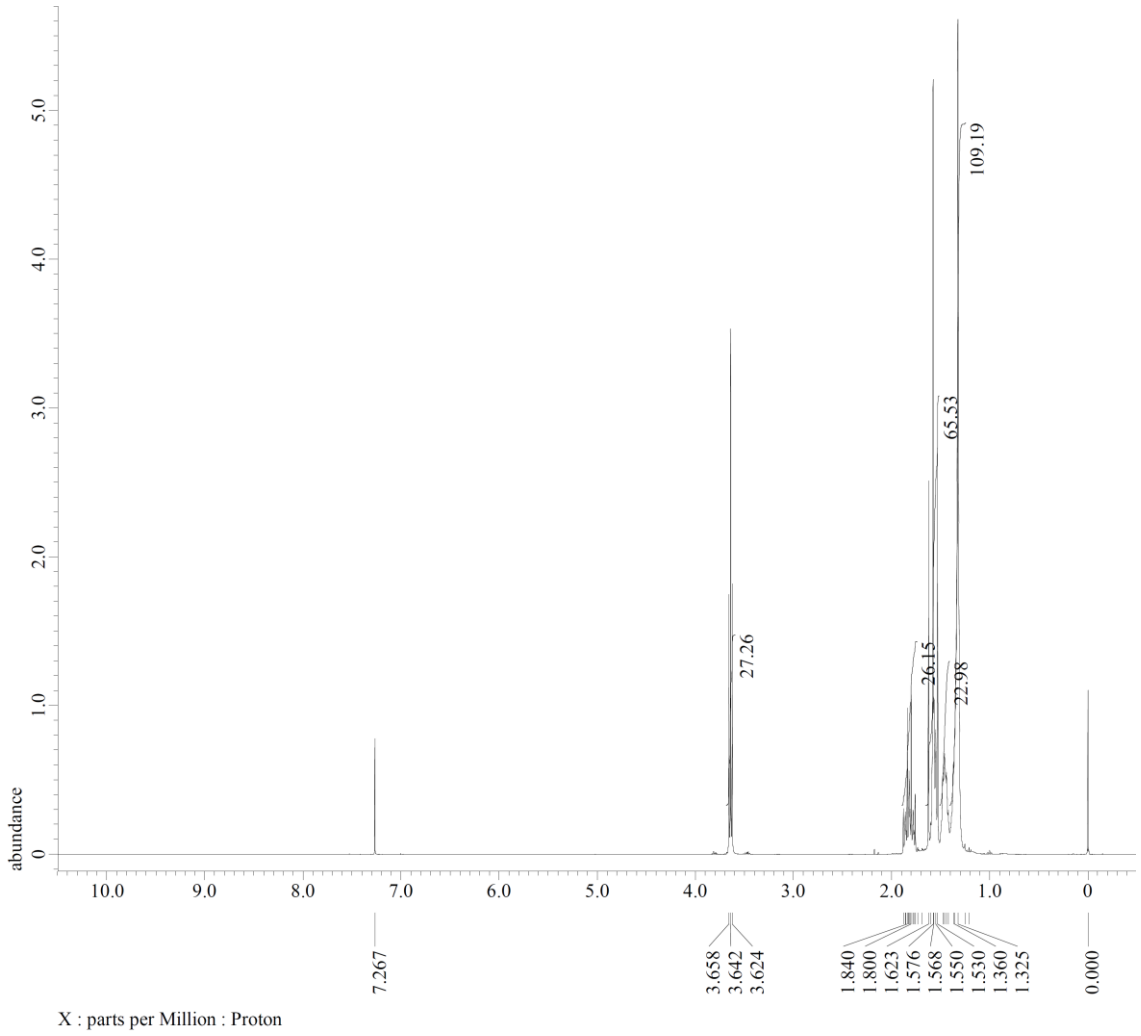

$^{1}$H NMR of 2,2-difluorooctadecane (**2e**).



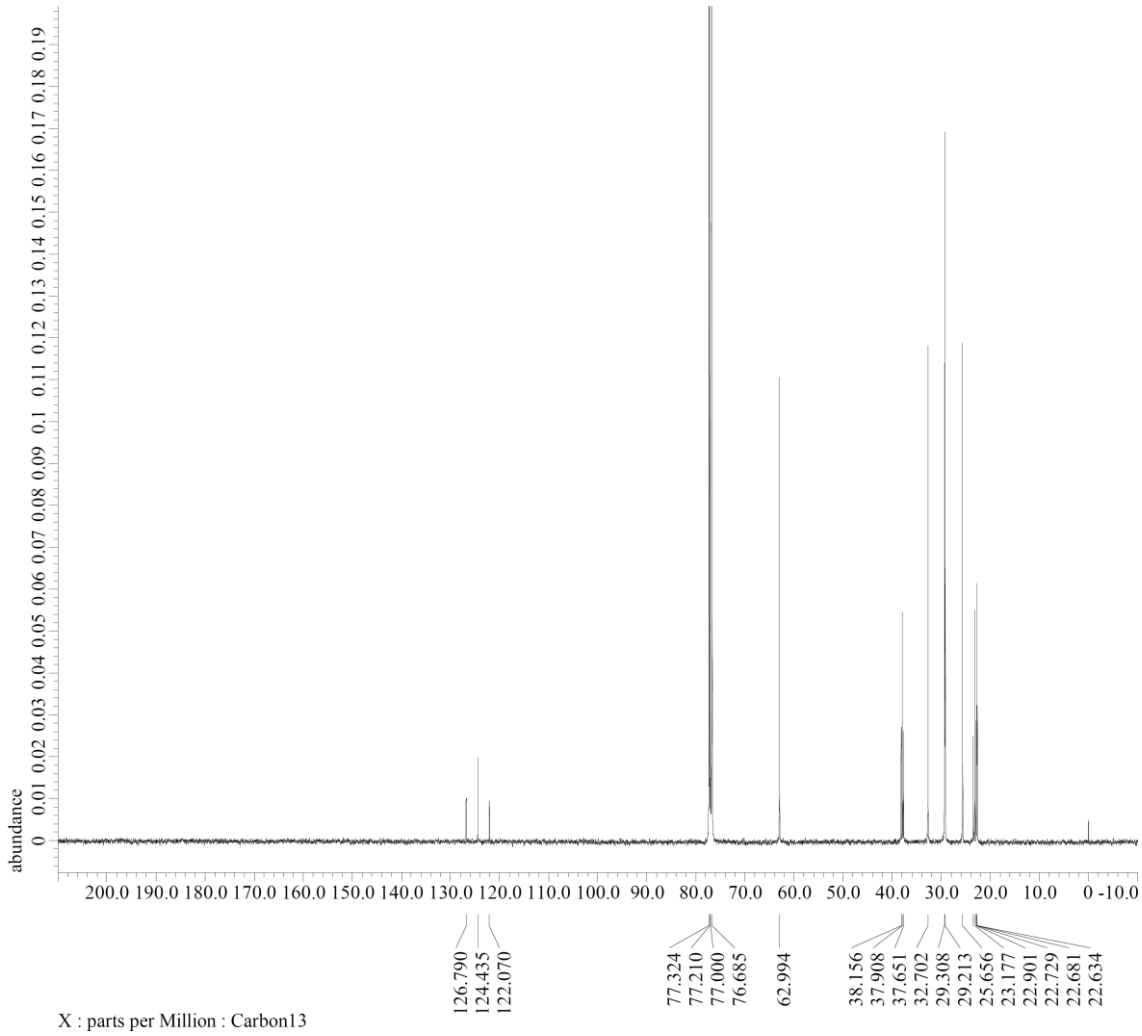

$^{13}$C NMR of 2,2-difluorooctadecane (**2e**).



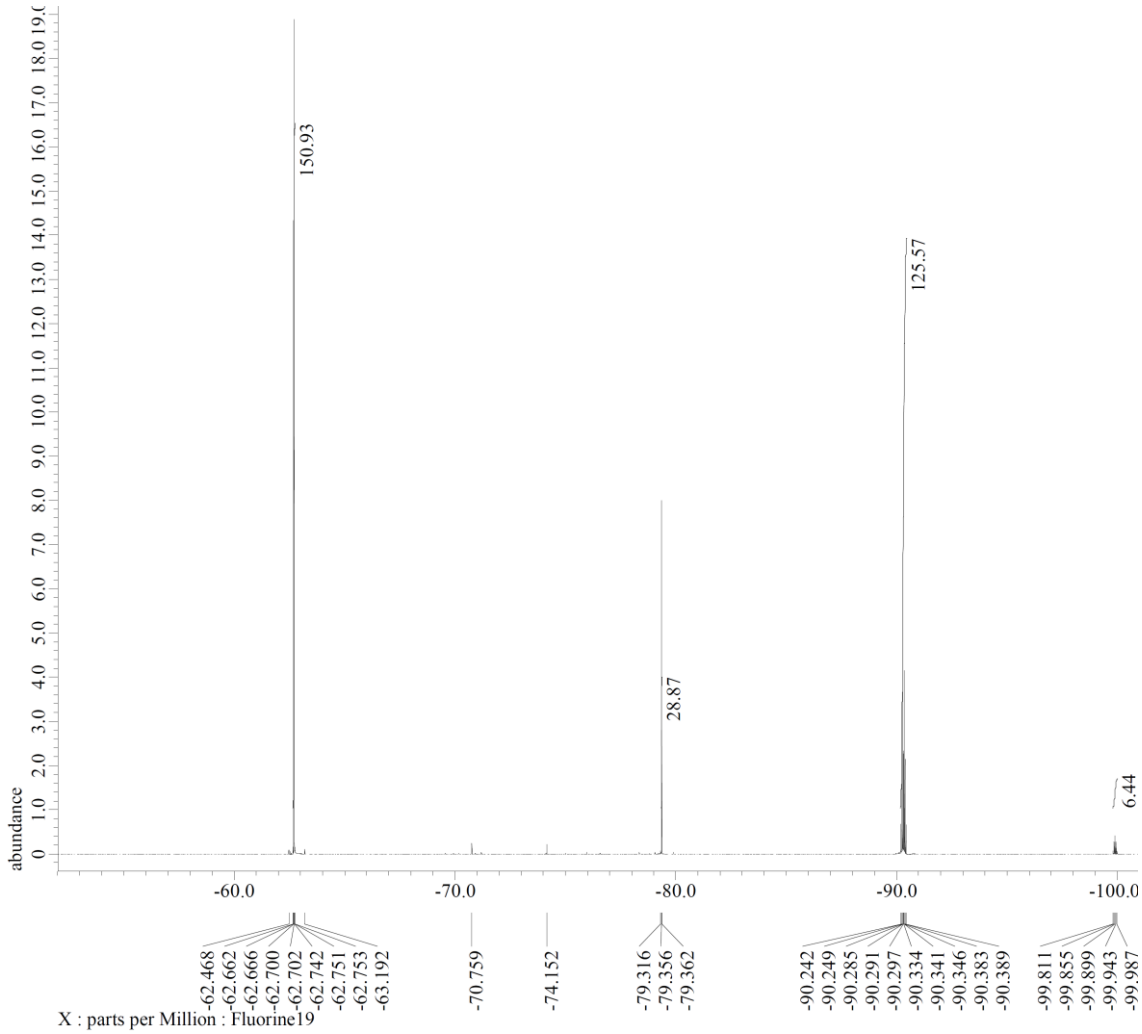

$^{19}F$ NMR of 2,2-difluorooctadecane (**2e**) in the presence of $CF_3C_6H_5$ as an internal standard. This $^{19}F$ NMR spectrum was measured at the crude product.



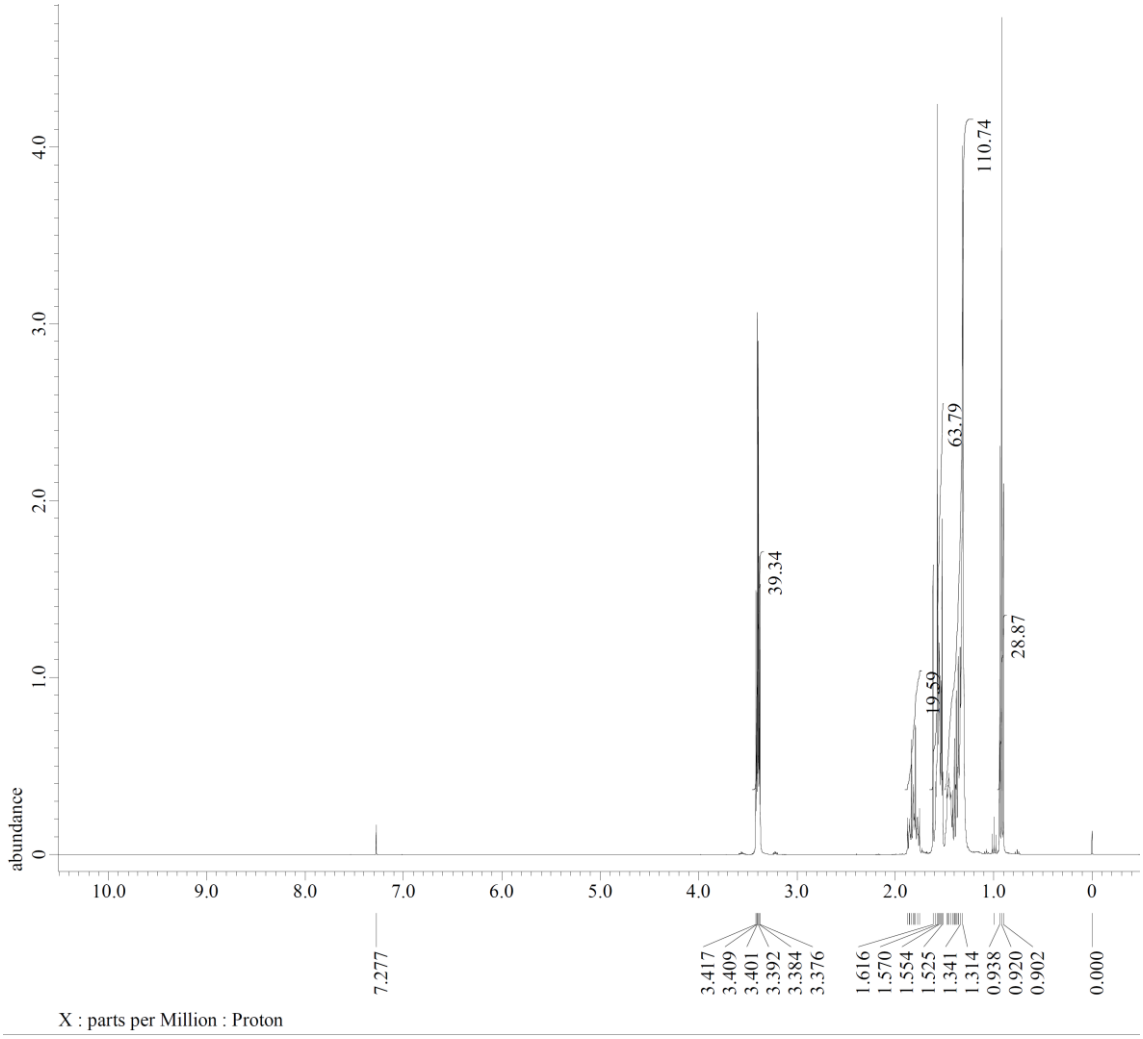

$^{1}$H NMR of 9,9-difluorodecan-1-ol (**2f**).



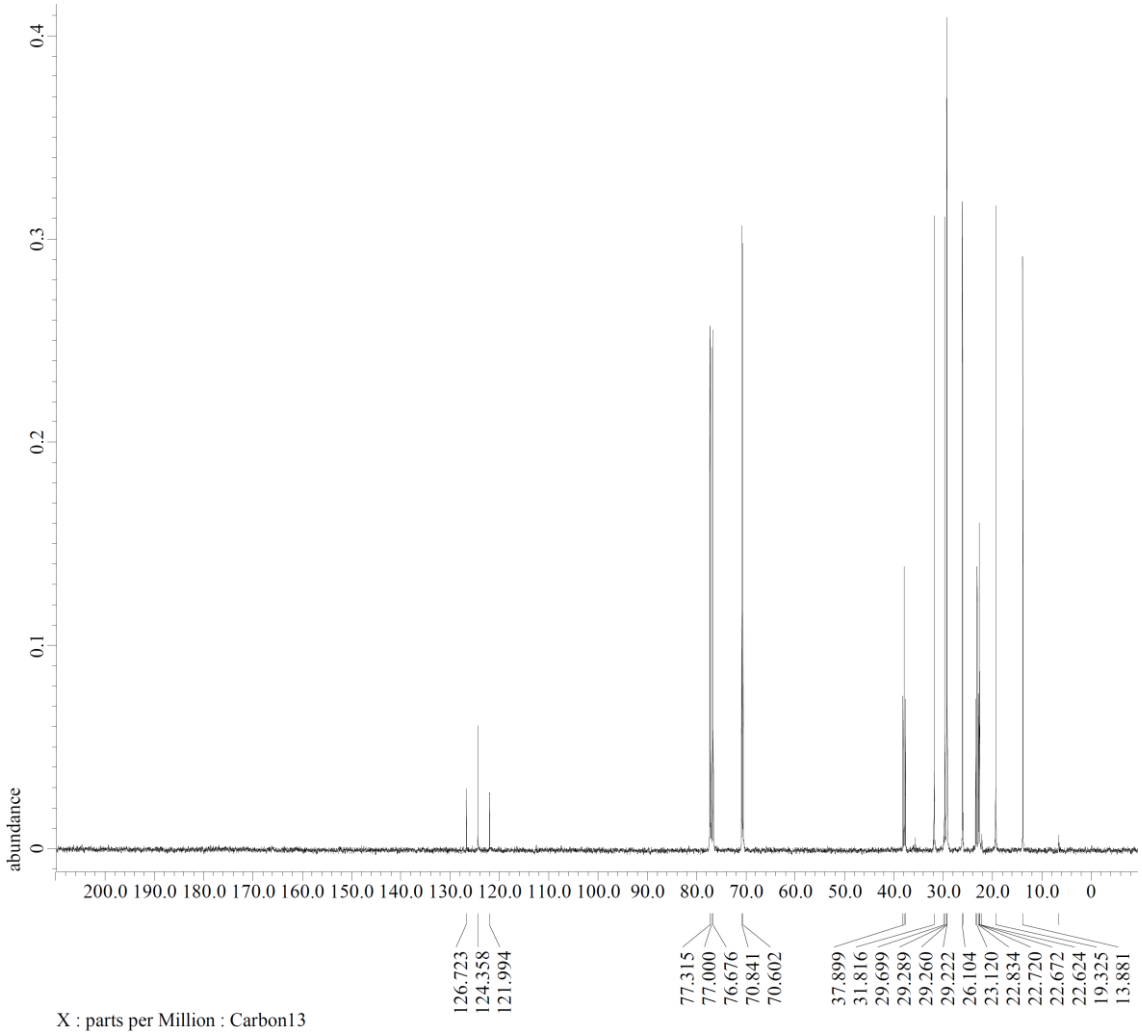

$^{13}$C NMR of 9,9-difluorodecan-1-ol (**2f**).



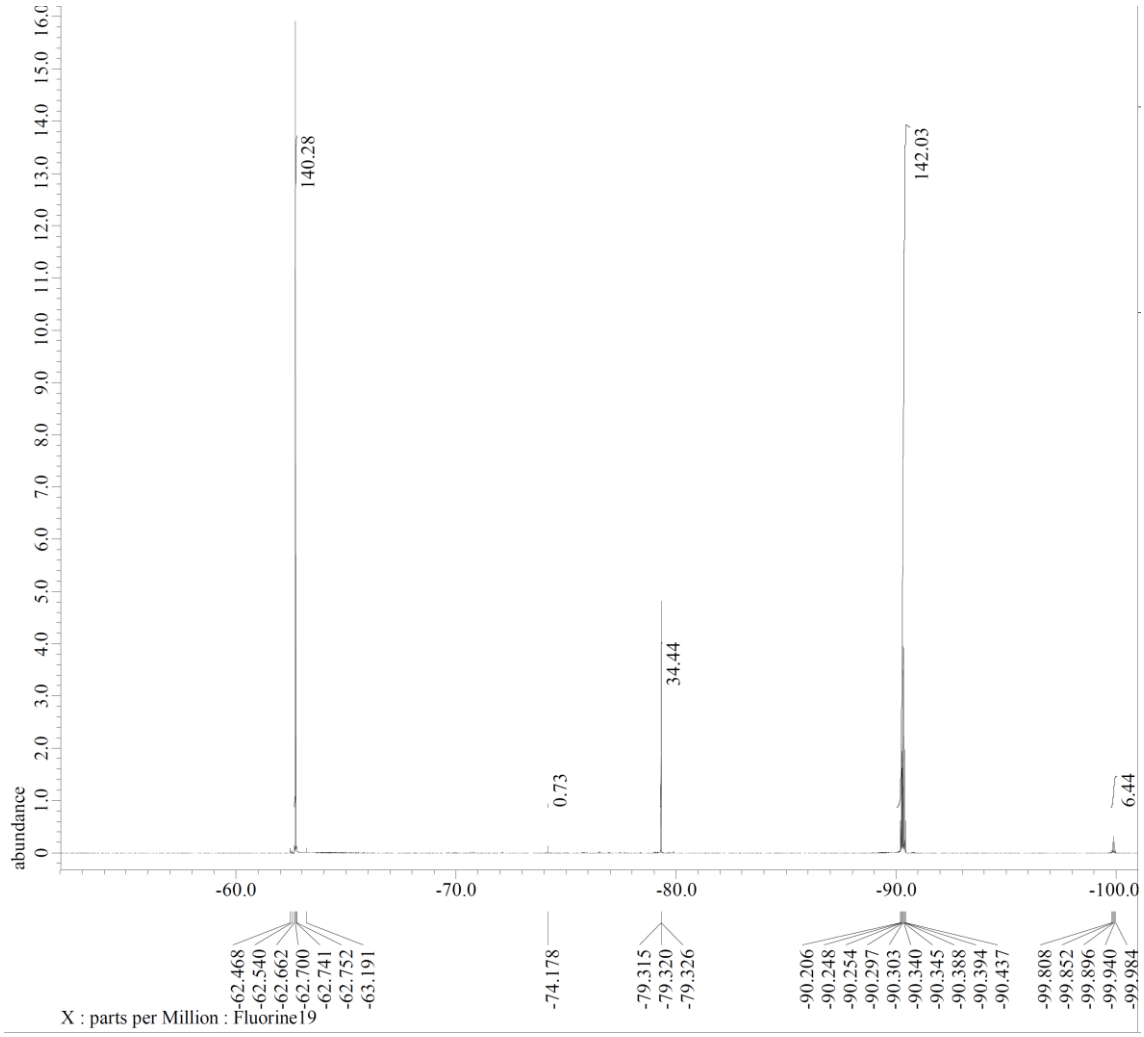

$^{19}F$ NMR of 9,9-difluorodecan-1-ol (**2f**) in the presence of $CF_3C_6H_5$ as an internal standard. This $^{19}F$ NMR spectrum was measured at the crude product.



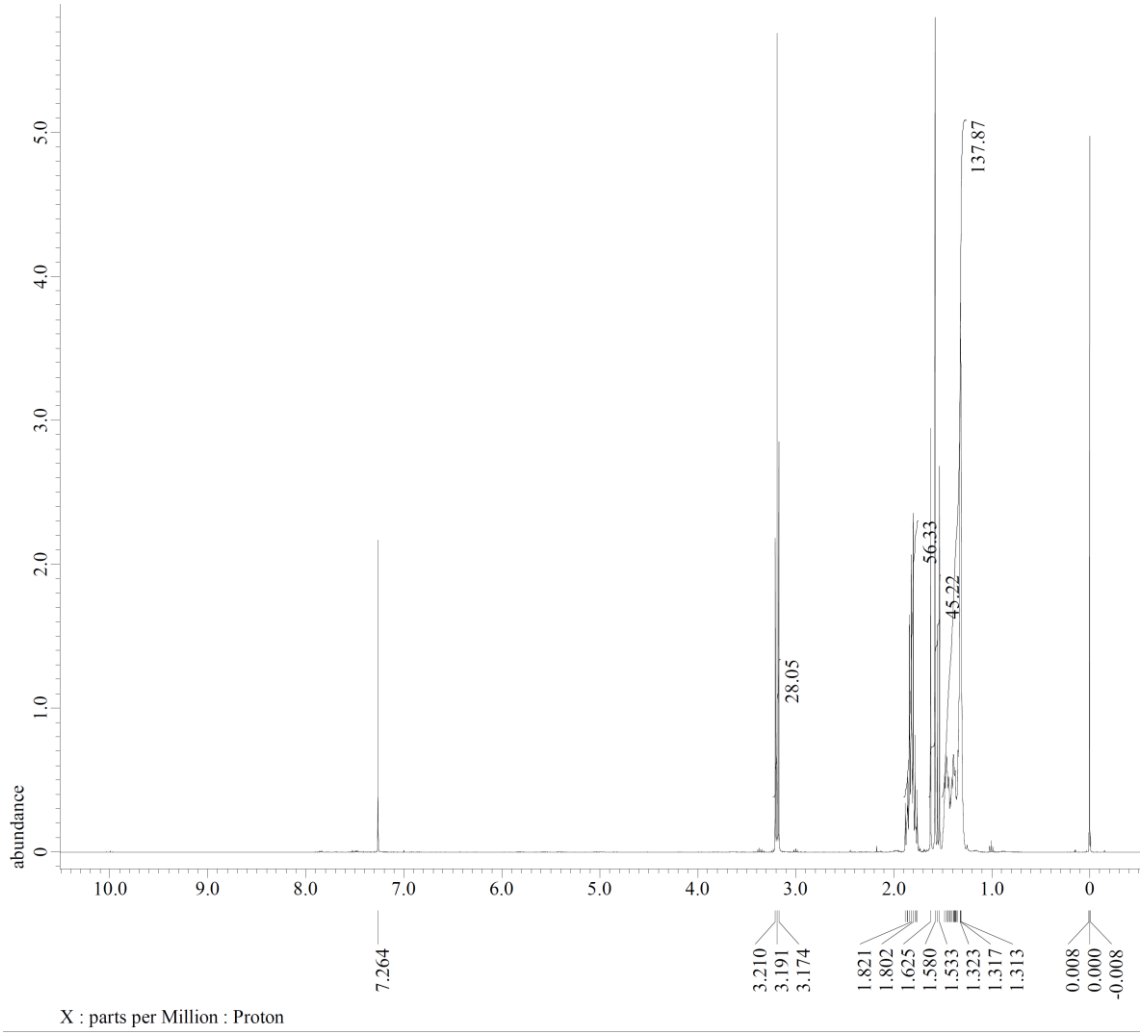

$^{1}$H NMR of 1-butoxy-9,9-difluorodecane (**2g**).



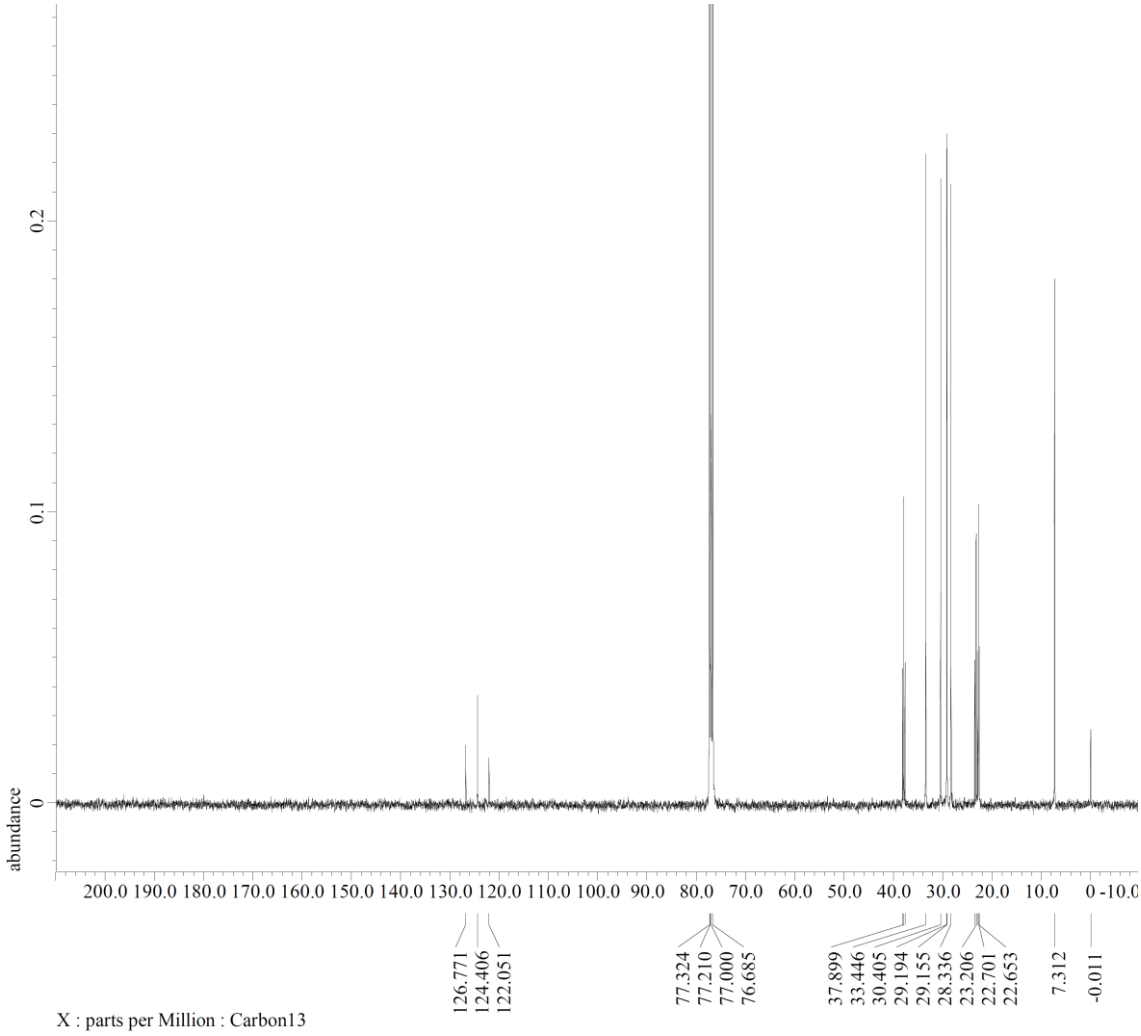

$^{13}$C NMR of 1-butoxy-9,9-difluorodecane (**2g**).



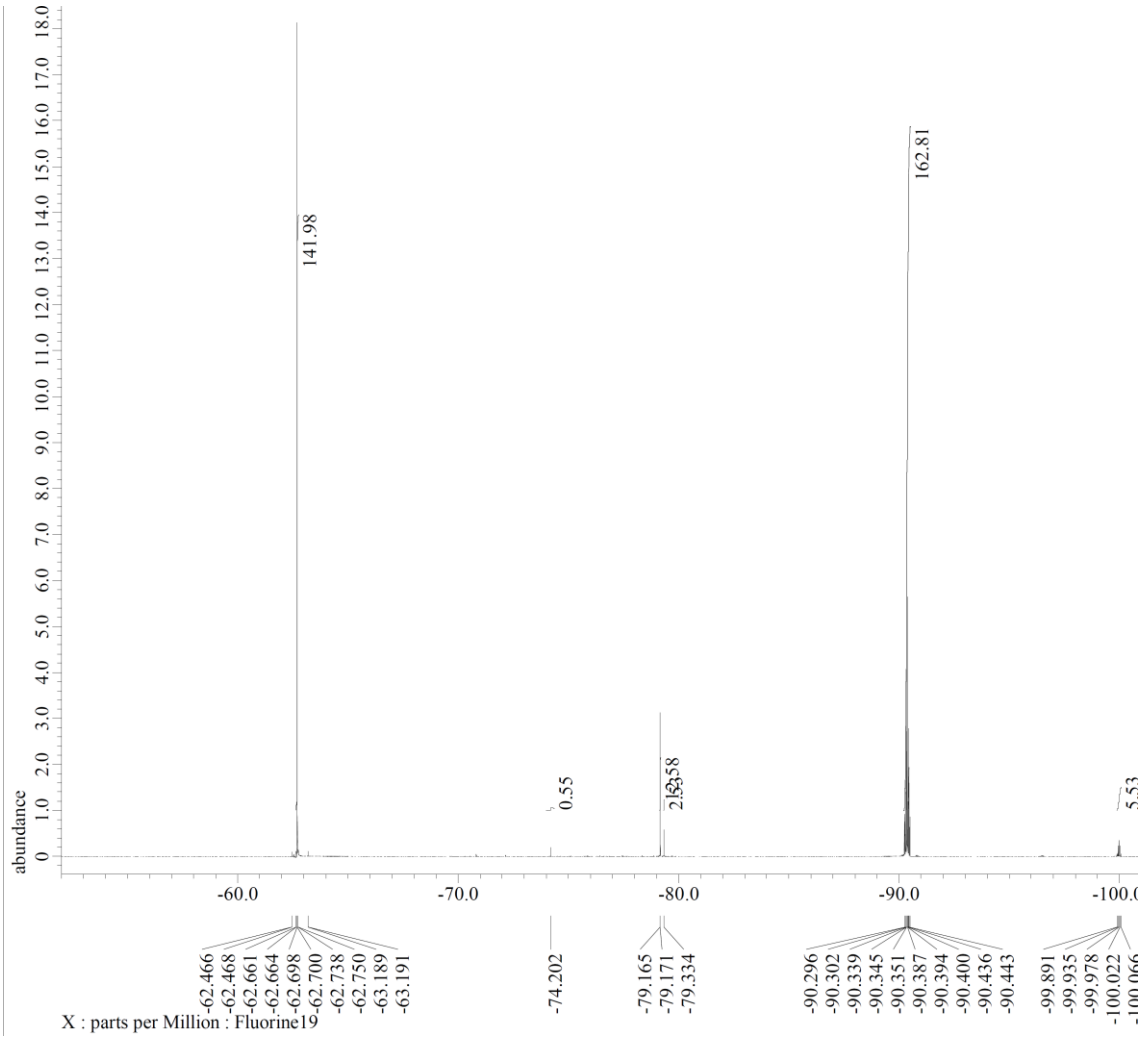

$^{19}F$ NMR of 1-butoxy-9,9-difluorodecane (**2g**) in the presence of $CF_3C_6H_5$ as an internal standard. This $^{19}F$ NMR spectrum was measured at the crude product.



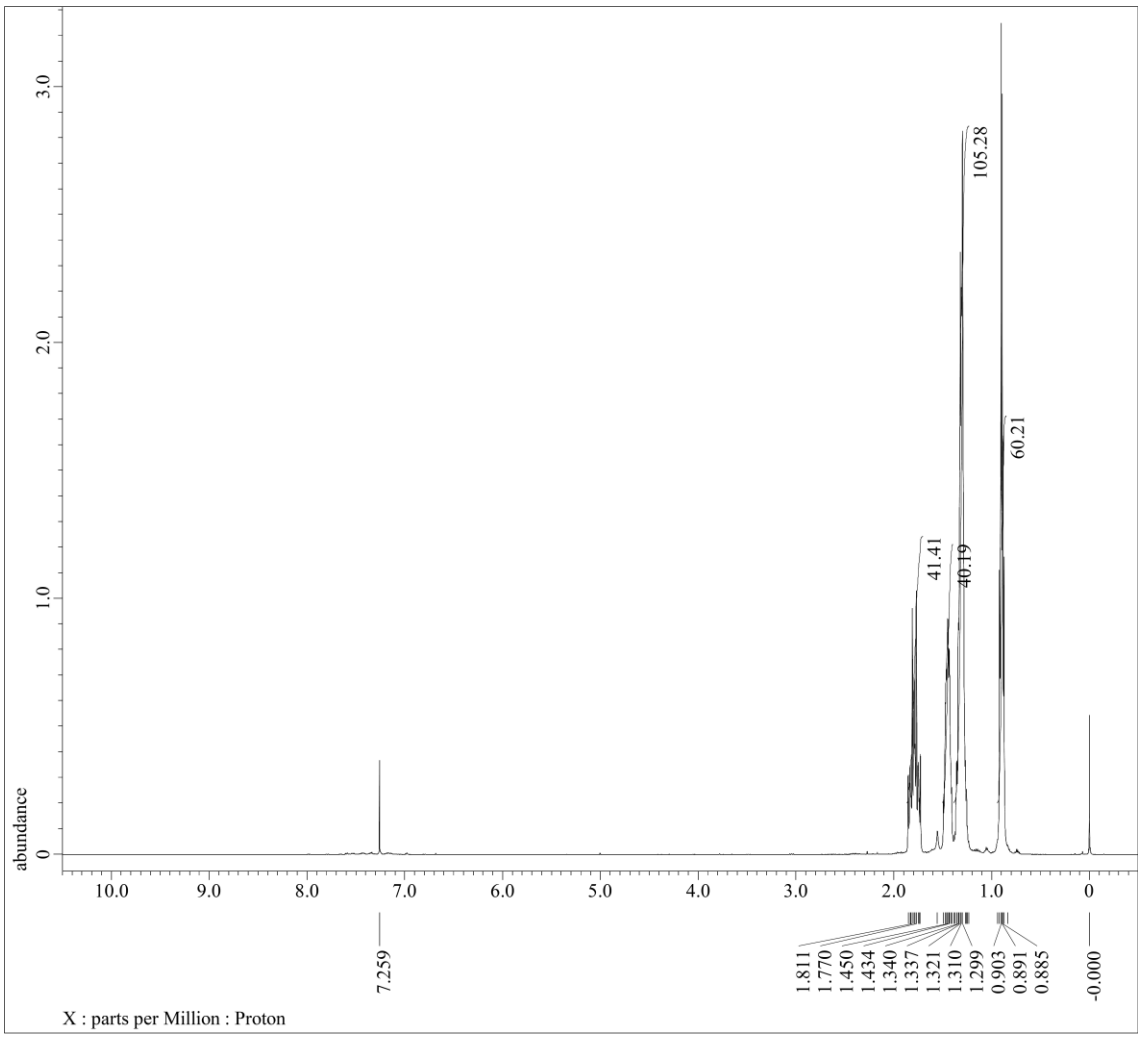

$^{1}$H NMR of 9,9-difluoro-1-iododecane (**2i**).



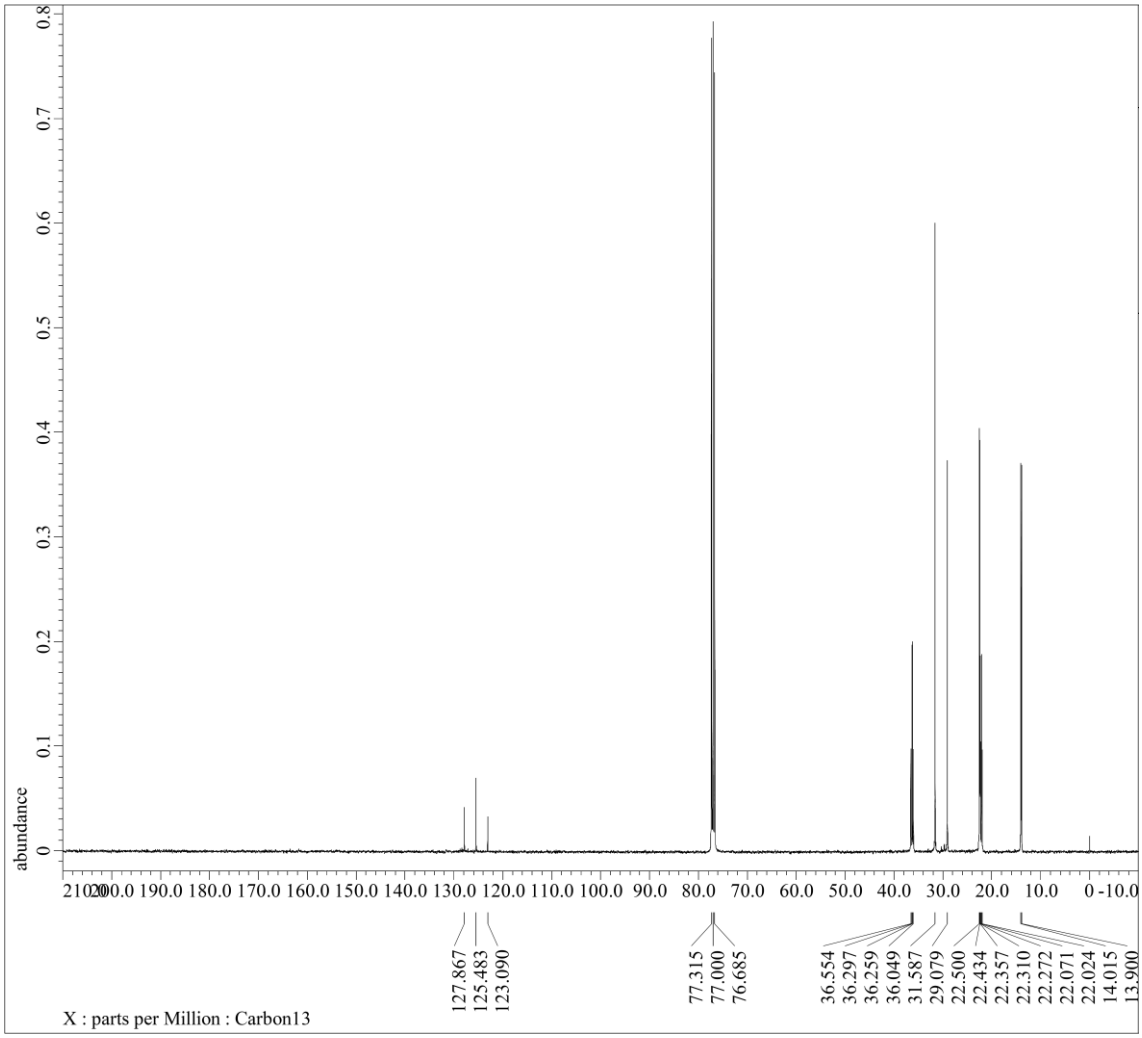

$^{13}$C NMR of 9,9-difluoro-1-iododecane (**2i**).



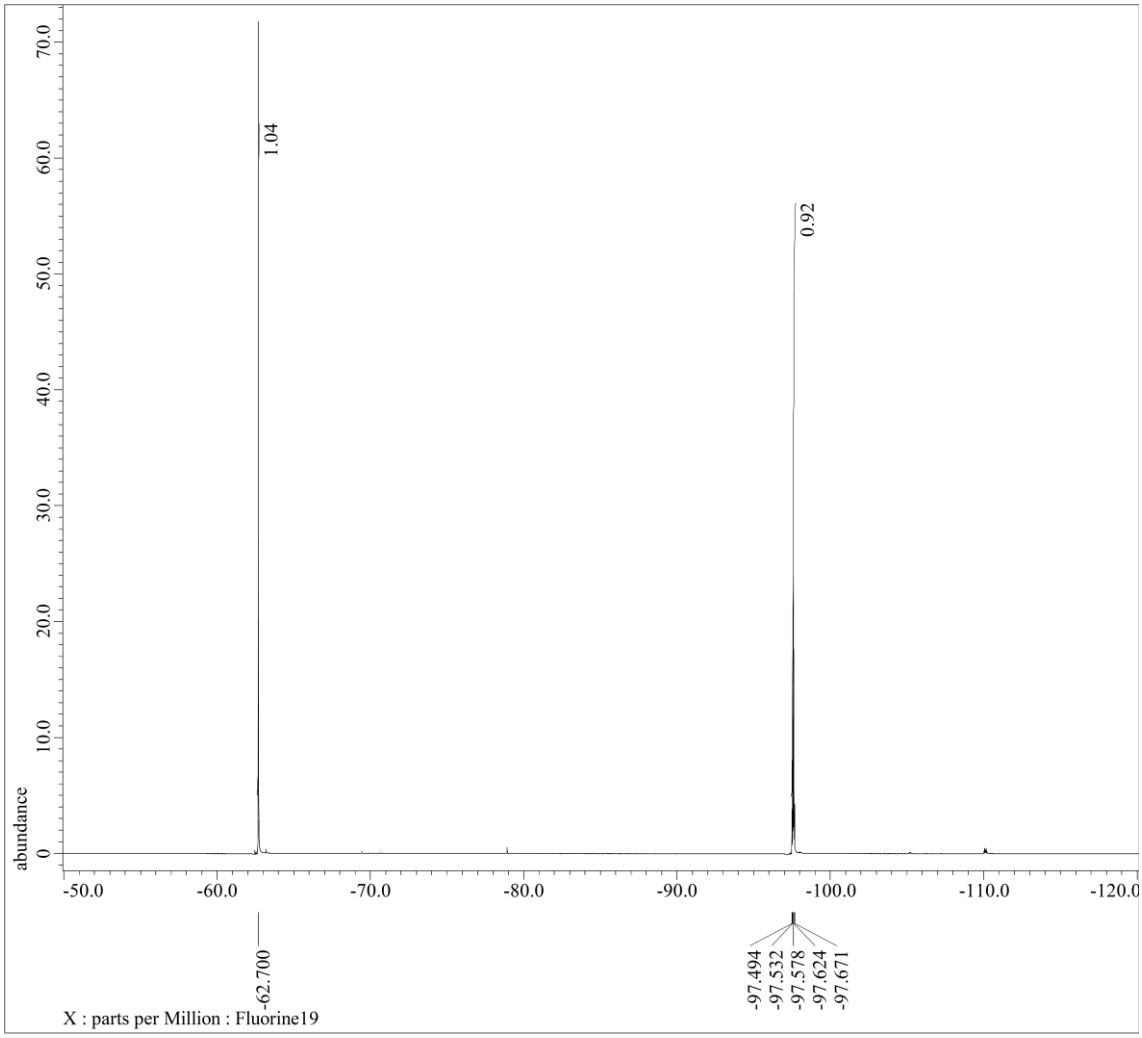

$^{19}F$ NMR of 9,9-difluoro-1-iododecane (**2i**) in the presence of $CF_3C_6H_5$ as an internal standard. This $^{19}F$ NMR spectrum was measured at the crude product.




$^{1}$H NMR of 6,6-difluorododecane (**2j**).




$^{13}$C NMR of 6,6-difluorododecane (**2j**).




$^{19}F$ NMR of 6,6-difluorododecane (**2j**) in the presence of $CF_3C_6H_5$ as an internal standard. This $^{19}F$ NMR spectrum was measured at the crude product.