Supporting information

Organocatalytic direct difluoromethylation of aldehydes and ketones with $TMSCF_2H$

Guang-Fen Du,[a,b] Ying Wang,[b] Cheng-Zhi Gu,[b] Bin Dai*[b] and Lin He*[b]

[a]*School of Chemical Engineering and Technology, Tianjin University. Tianjin 300072, P. R. of China*

[b]*School of Chemistry and Chemical Engineering, Shihezi University, Xinjiang Uygur Autonomous Region, 832000, China. Fax: (+86) 993-2057270*

E-mail: db_tea@shzu.edu.cn; helin@shzu.edu.cn

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General Methods

Unless otherwise indicated, all reactions were conducted under nitrogen atmosphere in an oven-dried glassware with magnetic stirring bar. Column chromatograph was performed with silica gel (200~300 mesh) and analytical TLC on silica gel 60-F254. ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$) spectra were recorded on a Bruker-DMX 400 spectrometer in $CDCl_3$, with tetramethylsilane as an internal standard and reported in ppm (δ). N-heterocyclic carbenes **4a** and **4b** were prepared according to literature.[1] N-heterocyclic carbenes **4c** and **4d,** phosphazene bases *t*-Bu-P4 (**5a**), *t*-Bu-P2 (**5b**) and *t*-Bu-P1 (**5c**) were purchased from Sigma-Aldrich. $TMSCF_2H$ **1** was purchased from TCI. All other chemicals were obtained from commercial supplies and used as received. Anhydrous THF and toluene, were distilled from sodium and benzophenone. DMF, CH_2Cl_2 and CH_3CN were distilled from calcium hydride.

General procedure for *t*-Bu-P4-catalyzed direct difluoromethylation reaction of aldehydes

A solution of *t*-Bu-P4 in hexane (25 μL, 10 mol%) was added to a stirred solution of $TMSCF_2H$ **1** (45 μL, 0.45 mmol, 1.5 equiv.) and aldehyde **2** (0.2 mmol) in dry DMF (0.5 mL) under nitrogen. The resulting mixture was stirred at room temperature until full consume of the starting aldehyde indicated by TLC. Then HCl (1.0 mL, 1.0 mol/L) or TBAF (0.4 mmol, 2.0

equiv.) was added to the mixture and stirred for 30 mins at room temperature. The mixture was extrated with Et_2O (10 mL×3) and the combined organic phase was washed subsequently by sat. aq. $NaHCO_3$ and water, dried over anhyd. Na_2SO_4, filtered, and concentrated. The crude product was purified by flash column chromatography on silica gel (PE-EtOAc, 15:1~10:1) to give the desired product.

Experimental Data:

1-(4-chlorophenyl)-2,2-difluoroethanol (3a)[2]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.30 (m, 4H), 5.73 (td, *J* = 55.9, 4.7 Hz, 1H), 4.82 (td, *J* = 10.0, 4.7 Hz, 1H), 2.47 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.9, 134.1, 128.88, 128.4 (t, *J* = 1.0 Hz),115.5 (t, J = 244.0 Hz), 73.03 (t, J = 24.0 Hz); ^{19}F NMR (376 MHz,$CDCl_3$) δ -127.6 (dd, J = 301.7, 285.5 Hz, 2F).

2,2-difluoro-1-(4-fluorophenyl)ethanol (3b)[3]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.35 (m, 2H), 7.20 – 7.02 (m, 2H), 5.73 (td, *J* = 56.0, 4.8 Hz, 1H), 4.83 (td, *J* = 9.9, 4.7 Hz, 1H), 2.41 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.32, 161.85, 131.52 (q, J = 3.9 Hz), 128.9 (dt, J = 8.0, 1.0 Hz), 115.66 (td, J = 244.0, 1.0 Hz), 73.05(t, J = 25.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.69 (s, 1F), -127.67 (d, *J* = 13.2 Hz, 2F).

1-(4-bromophenyl)-2,2-difluoroethanol (3c)[4]

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 6.97 (m, 4H), 5.74 (td, *J* =

55.9, 4.7 Hz, 1H), 4.81 (td, *J* = 10.1, 4.7 Hz, 1H), 2.64 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.65 (t, J = 3.0 Hz), 131.83, 128.76 (t, J = 1.0 Hz), 123.16, 115.46 (t, J = 244.0 Hz), 73.07 (t, J = 24.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.20 (d, J = 284.9 Hz, 1F), -128.0 (d, J = 284.9 Hz, 1F).

2,2-difluoro-1-phenylethanol (3d)[5]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.33 (m, 5H), 5.79 (td, J = 55.8, 4.72Hz, 1H), 4.84 (ddd, *J* = 10.7, 9.7, 4.7 Hz, 1H), 2.48 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.82 (t, J = 4.0 Hz), 129.0, 128.7, 127.10, 115.82 (td, J = 244, 2.0 Hz), 73.68 (t, J = 25.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.6 (dd, J = 307.8, 283.8 Hz, 2F).

2,2-difluoro-1-p-tolylethanol (3e)[6]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.04 (m, 4H), 5.78 (td, *J* = 56.1, 4.8 Hz, 1H), 4.81 (td, *J* = 10.1, 4.8 Hz, 1H), 2.40 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.95, 132.90, 129.39, 127.02, 115.88 (t, J = 244.0 Hz), 99.98, 73.55 (t, J = 24.0 Hz), 21.20; ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.5 (dd, J = 297.0, 282.0 Hz, 2F).

2,2-difluoro-1-(4-methoxyphenyl)ethanol (3f)[4]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.30 (m, 2H), 7.08-6.85 (m, 2H), 5.76 (td, *J* = 56.1, 4.8 Hz, 1H), 4.77 (td, *J* = 10.2, 4.8 Hz, 1H), 3.84 (s, 3H), 2.59 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.08, 128.44 (t, J = 1.0 Hz) 128.02 (t, J = 4.0 Hz), 118.32, 115.89, 114.11, 113.45, 73.27 (t, J = 25.0 Hz), 55.31; ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.53 (s, 2F).

1-(2-chlorophenyl)-2,2-difluoroethanol (3g)[4]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.50-7.30 (m, 3H), 5.96 (ddd, *J* = 55.6, 54.9, 3.3 Hz, 1H), 5.42 (ddd, *J* = 15.4, 6.5, 3.1 Hz, 1H), 2.61 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.48 (t, J = 3.0 Hz), 132.80, 130.03, 129.5, 128.64, 127.32, 114.70 (t, J = 244 Hz), 70.04 (dd, J = 25.0, 23.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -126.7 (d, J = 280.9 Hz, 1F), -132.1 (d, J = 280.9 Hz, 1F).

1-(3-chlorophenyl)-2,2-difluoroethanol (3h)[4]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.44 (m, 1H), 7.43 – 7.30 (m, 3H), 5.76 (td, *J* = 55.9, 4.7 Hz, 1H), 4.83 (td, *J* = 10.0, 4.7 Hz, 1H), 2.58 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.65, 134.68, 129.93, 129.20, 129.19, 127.26 (t, J = 4.0 Hz), 125.28 (t, J = 4.0 Hz), 115.47 (t, J = 244.0 Hz), 73.04 (t, J = 24.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.56 (d, *J* = 1.9 Hz, 2F).

1-(3-bromophenyl)-2,2-difluoroethanol (3i)[7]

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.48 (m, 2H), 7.47 – 7.21 (m, 2H), 5.76 (td, *J* = 55.8, 4.7 Hz, 1H), 4.82 (td, *J* = 10.0, 4.7 Hz, 1H), 2.71 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.89 (t, J = 3.0 Hz), 132.1, 130.21, 130.15 (t, J = 1.0 Hz), 125.77 (t, J = 1.0 Hz), 122.78, 115.46 (t, J = 245.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.53 (d, J = 1.40 Hz, 2F).

2,2-difluoro-1-(2-methoxyphenyl)ethanol (3j)[4]

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.31 (m, 2H), 7.04 (td, *J* = 7.48, 1.0 Hz, 1H), 6.95 (d, J = 8.28 Hz, 1H), 5.99 (ddd, *J* = 56.7, 55.5, 4.1 Hz, 1H), 5.05 (ddd, *J* = 14.8, 7.4, 4.1 Hz, 1H), 3.90 (d, *J* = 4.0 Hz, 3H), 3.12 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.80, 129.97 (d, J = 2.0 Hz), 128.84, 124.03, 121.14 (d, J = 2.0 Hz), 115.05 (t, J = 244.0 Hz), 110.75 (d, J = 2.0 Hz), 71.11 (t, J = 24.0 Hz), 55.50 (d, J = 1.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -125.6 (d, J = 280.7 Hz, 1F), -130.2 (d, J = 280.7 Hz, 1F).

2,2-difluoro-1-(3-methoxyphenyl)ethanol (3k)[7]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 11.8, 4.2 Hz, 1H), 7.12 – 6.85 (m, 3H), 5.78 (ddd, *J* = 56.3, 55.6, 4.7 Hz, 1H), 4.81 (ddd, *J* = 11.1, 9.2, 4.7 Hz, 1H), 3.84 (s, 3H), 2.64 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.81, 137.41 (q, J = 2.0 Hz), 129.75, 119.33 (t, J = 1.0 Hz), 118.20, 115.76, 114.56, 113.32, 112.60 (t, J = 1.0 Hz), 73.58 (dd, J = 25.0, 25.0 Hz), 55.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -126.97 (d, J = 285.7Hz, 1F), -127.93 (d, J = 285.7 Hz, 1F).

2,2-difluoro-1-(naphthalen-1-yl)ethanol (3l)[2]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.2 Hz, 1H), 7.93 (td, *J* = 7.8, 4.9 Hz, 2H), 7.74 (d, *J* = 7.0 Hz, 1H), 7.66-7.46 (m, 3H), 6.05 (ddd, *J* = 56.5, 55.1, 4.6 Hz, 1H), 5.66 (ddd, *J* = 12.2, 7.3, 4.6 Hz, 1H), 2.64 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.80, 131.75 (q, J = 2.0 Hz), 130.99, 129.65, 129.05, 126.69, 125.94, 125.32, 125.23 (t, J = 1.0 Hz), 122.90 (d, J = 1.0 Hz), 118.32, 115.87 (t, J = 245.0 Hz), 70.62 (t, J = 23.0 Hz);

-126.97 (d, J = 285.7 Hz, 1F), -127.93 (d, J = 285.7 Hz, 1F).

2,2-difluoro-1-(naphthalen-2-yl)ethanol (3m)[4]

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.85 (m, 4H), 7.70-7.40 (m, 3H), 5.89 (td, *J* = 56.0, 4.68 Hz, 1H), 5.02 (td, *J* = 10.1, 4.7 Hz, 1H), 5.02 (td, *J* = 10.1, 4.7 Hz, 1H), 2.61 (s, 1H), 2.61 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.56, 133.20 (t, J = 4.0 Hz), 133.09, 128.55, 128.15, 127.77, 126.64, 126.61, 126.50, 124.32, 115.88, (t, J = 244.0 Hz) 113.44, 73.83 (t, J = 25.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.3 (dd, J = 323.7, 284.0 Hz, 2F).

1-(benzo[d][1,3]dioxol-5-yl)-2,2-difluoroethanol (3n)[7]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95-6.75 (m, 3H), 5.96 (s, 2H), 5.71 (td, *J* = 56.0, 4.8 Hz, 1H), 4.71 (td, *J* = 10.0, 4.7 Hz, 1H), 2.51 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.14, 147.98, 129.6 (t, J = 4.0 Hz), 120.90 (t, J = 1.0 Hz), 115.75 (t, J = 243.0 Hz) 108.3, 107.45 (t, J = 1.0 Hz), 101.3, 73.45 (t, J = 250.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.53 (dd, J = 7.1, 3.5 Hz, 2F).

2,2-difluoro-1-(furan-2-yl)ethanol (3o)[7]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 1.8, 0.7 Hz, 1H), 6.72 – 6.30 (m, 2H), 5.99 (ddd, *J* = 55.9, 55.3, 4.3 Hz, 1H), 2.41(s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.39, 116.64, 114.20, 111.76, 110.62, 109.50 (t, J = 2.0 Hz), 68.10, 67.84 (dd, J = 27.0, 26.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -128.4 (dd, J = 532.5, 286.4Hz, 2F).

2,2-difluoro-1-(thiophen-2-yl)ethan-1-ol (3p)[7]

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.17 (d, *J* = 3.5 Hz, 1H), 7.07 (dd, *J* = 5.1, 3.6 Hz, 1H), 5.85 (td, *J* = 55.9, 4.5 Hz, 1H), 5.11 (ddd, *J* = 7.0, 5.0, 2.5 Hz, 1H), 2.53 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.24 (t, J = 3.0 Hz), 127.10, 126.55, 126.53, 117.49, 115.0 (t, J = 245.0 Hz), 70.09 (t, J = 25.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.42 (dd, J = 297.0, 285.8 Hz, 2F).

2,2-difluoro-1-(1-methyl-1H-pyrrol-2-yl)ethan-1-ol (3q)

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69 (s, 1H), 6.32-6.05 (m, *2*H), 6.00 (td, J = 53.8, 3.9 Hz, 1H), 4.94 – 4.78 (m, 1H), 3.71 (s, 3H), 2.07 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 127.08, 124.3, 115.1 (t, J = 241.0 Hz), 108.4, 107.4, 66.6 (tm, J = 26.0 Hz), 34.18; ^{19}F NMR (376 MHz, $CDCl_3$) δ -125.3 (d, J = 282.0 Hz, 1F), -128.0 (d, J = 285.7 Hz, 1F); GC-MS (EI): M/z 161.1 (M^+).

2,2-difluoro-1-(1-methyl-1H-indol-4-yl)ethan-1-ol (3r)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 1H), 7.29 (dd, *J* = 9.6, 5.6 Hz, 1H), 7.24 (d, *J* = 6.9 Hz, 1H), 7.15 (d, *J* = 3.1 Hz, 1H), 6.64 (d, *J* = 3.1 Hz, 1H), 6.02 (ddd, *J* = 56.8, 55.4, 4.9 Hz, 1H), 5.23 (ddd, J = 12.5, 7.96, 4.92 Hz, 1H), 2.45 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.95, 129.46, 127.80, 126.59, 121.54, 117.95, 115.7 (dd, J = 245.0, 243.0 Hz), 110.18, 99.21, 73.0 (dd, J = 27.0, 23.0 Hz), 33.00; GC-MS (EI): M/z 211.1 (M^+).

2,2-difluoro-1-(isoquinolin-5-yl)ethan-1-ol (3s)[7]

White solid. ^{1}H NMR (400 MHz, DMSO) δ 9.47 – 9.23 (m, 1H), 8.54 (dd, *J* = 6.3, 2.6 Hz, 1H), 8.20 – 8.04 (m, 2H), 8.03 – 7.86 (m, 1H), 7.74 (td, *J* = 8.3, 2.7 Hz, 1H), 6.51 (dd, *J* = 5.3, 2.1 Hz, 1H), 6.26 (dddd, *J* = 55.4, 50.8, 4.4, 2.4 Hz, 1H), 5.66 – 5.46 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 143.5, 130.5, 128.8, 128.7, 127.3, 117.4, 116.7 (t, J = 242.0 Hz), 99.9, 68.8 (t, J = 24.0 Hz); ^{19}F NMR (376 MHz, DMSO) δ -125.7 (dd, J = 661.7, 278.2 Hz, 2F).

1-(2,3-dihydrobenzofuran-5-yl)-2,2-difluoroethan-1-ol (3t)[7]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 5.76 (td, *J* = 56.1, 4.8 Hz, 1H), 4.76 (td, *J* = 10.1, 4.8 Hz, 1H), 4.61 (t, *J* = 8.8 Hz, 2H), 3.24 (t, *J* = 8.7 Hz, 2H), 2.43 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.74, 127.94, 127.69, 127.34, 123.82, 115.95 (t, J = 244.0 Hz), 109.35, 73.57 (t, J = 25.0 Hz), 71.51, 29.56; ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.43 (d, J = 3.76 Hz, 2F).

(E)-1,1-difluoro-4-phenylbut-3-en-2-ol (3u)[4]

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.29 (m, 5H), 6.84 (d, *J* = 16.0 Hz, 1H), 6.24 (ddd, J = 16.0, 6.2, 0.7 Hz, 1H), 5.75 (td, J = 56.0, 5.3 Hz, 1H), 4.58 – 4.42 (m, 1H), 2.13 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 134.8, 128.6, 128.43, 126.7, 122.4 (dd, J = 4.0, 3.0 Hz), 115.47 (t, J = 244.0 Hz), 72.24 (t, J = 24.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -128.6 (dd, J = 130.6, 90.3 Hz, 2F).

1,1-difluoro-4-phenylbutan-2-ol (3v)[4]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.14 (m, 5H), 5.64 (tt, *J* = 56.1, 3.7 Hz, 1H), 3.85-3.60 (m, 1H), 3.02 – 2.66 (m, 2H), 2.05 – 1.75 (m, 2H), 1.96 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.89, 128.57, 128.47, 126.20, 116.29 (t, J = 243.0 Hz), 70.30 (t, J = 24.0 Hz), 31.50, 30.94; ^{19}F NMR (376 MHz, $CDCl_3$) δ -129.6 (s, 2F).

1,1-bis(4-chlorophenyl)-2,2-difluoroethanol (8a)[4]

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, J = 1.8, 0.7 Hz, 1H), 6.53-6.35 (m, 2H), 5.99 (td, *J* = 55.2, 4.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.46 (t, J = 1.0 Hz), 134.61, 128.67, 128.55 (t, J = 2.0 Hz), 77.52 (t, J = 21.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.2 (s, 2F).

9-(difluoromethyl)-9H-fluoren-9-ol (8b)[4]

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.21 (m, 8H), 5.89 (td, *J* = 55.4, 2.5 Hz, 1H), 2.65 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.15 (t, J = 1.0 Hz), 140.80, 130.40, 128.28, 125.37 (t, J = 2.0 Hz), 120.34, 115.67 (t, J = 248.0 Hz), 81.33 (22.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -128.9 (s, 2F).

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7. **3i**, cas: 1540018-38-9; **3k**, cas: 1515191-06-6; **3n**, cas: 1379336-81-8; **3o**, cas: 1378582-48-9 ; **3p**, cas :1379271-50-7 ; **3s**, cas : 1564865-41-3 ; **3t**, cas : 1379365-06-6.

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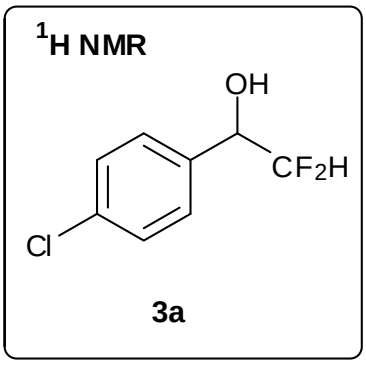

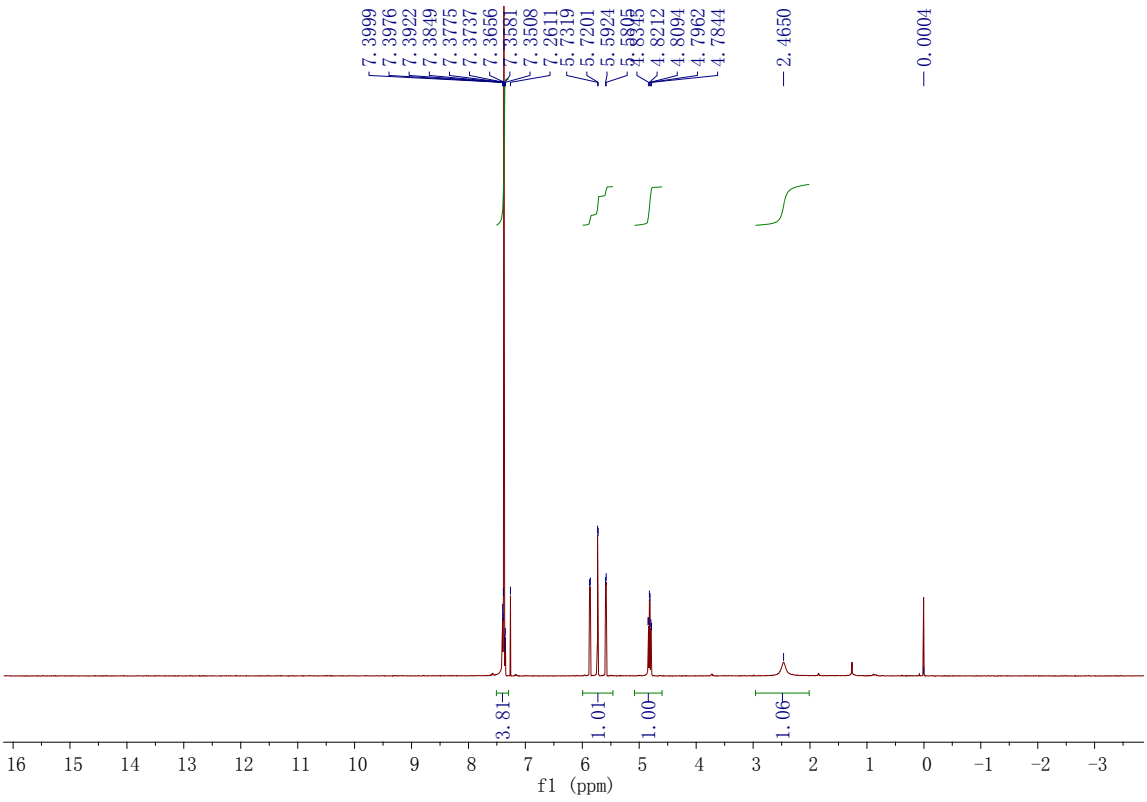

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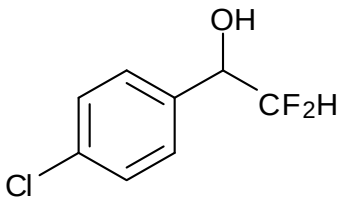
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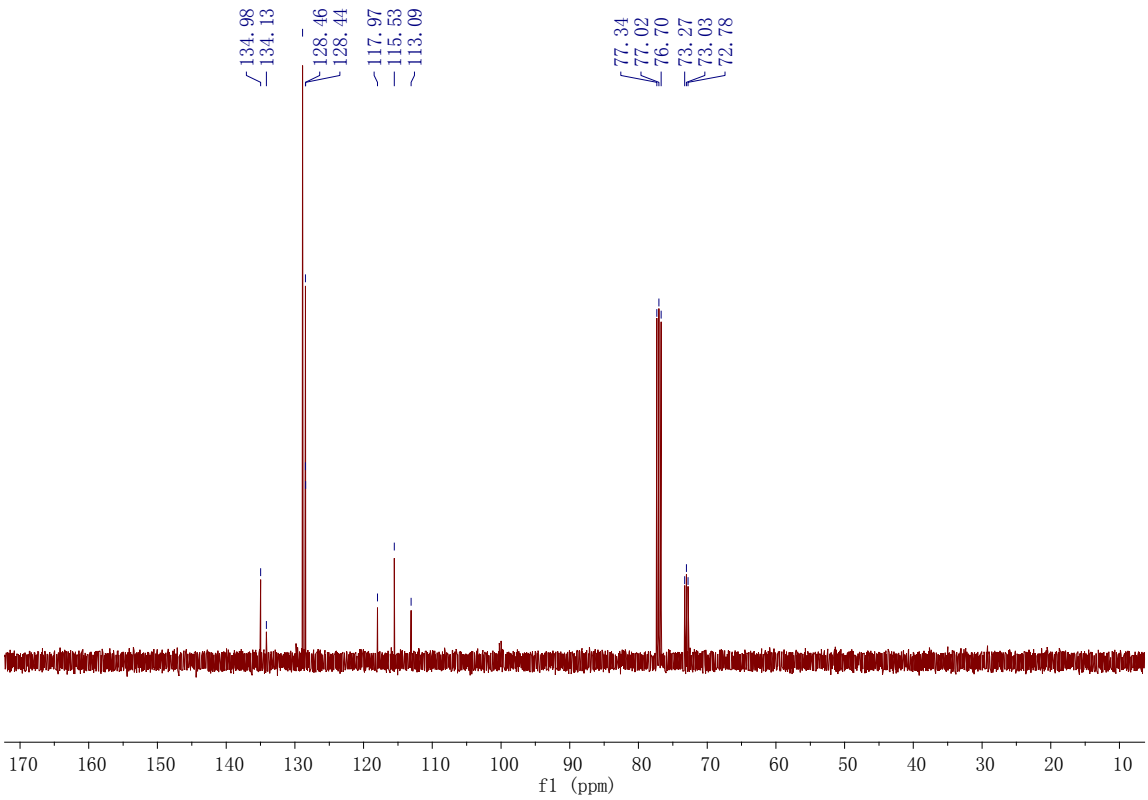
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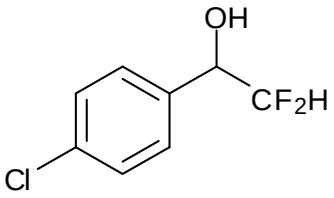
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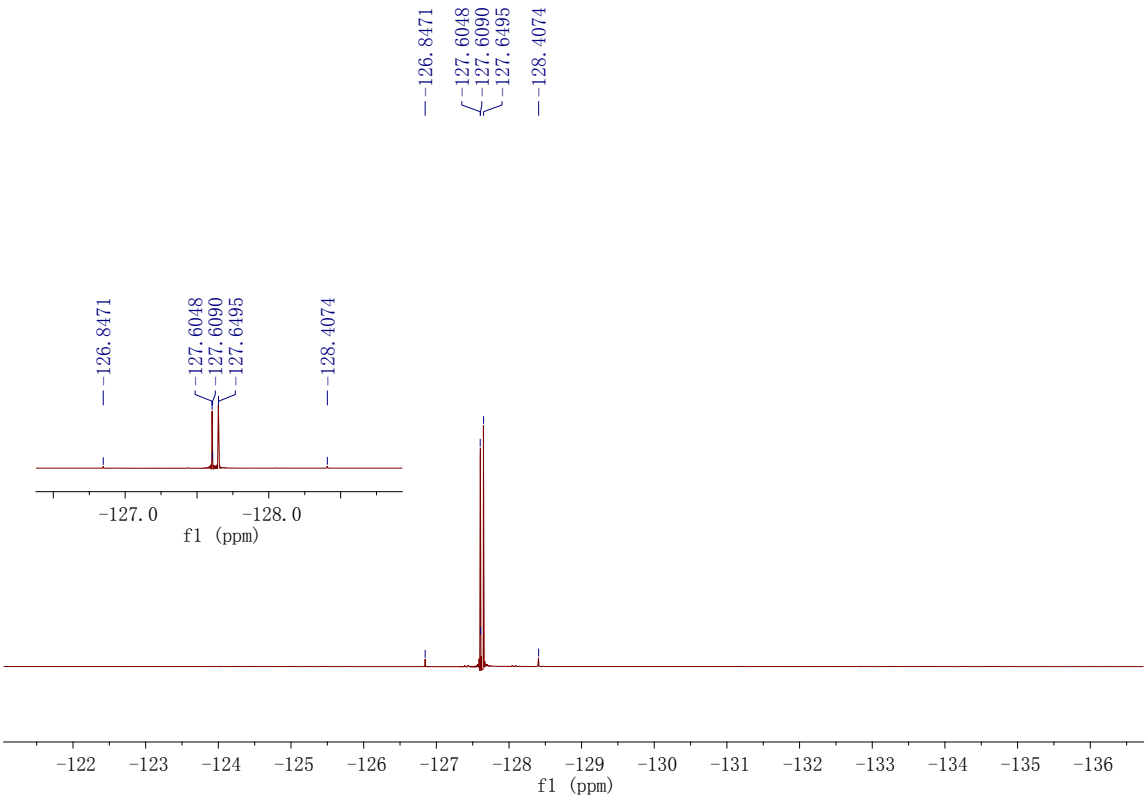
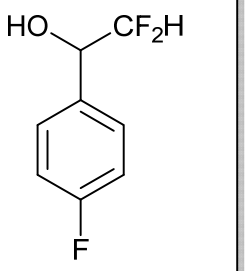
Cl

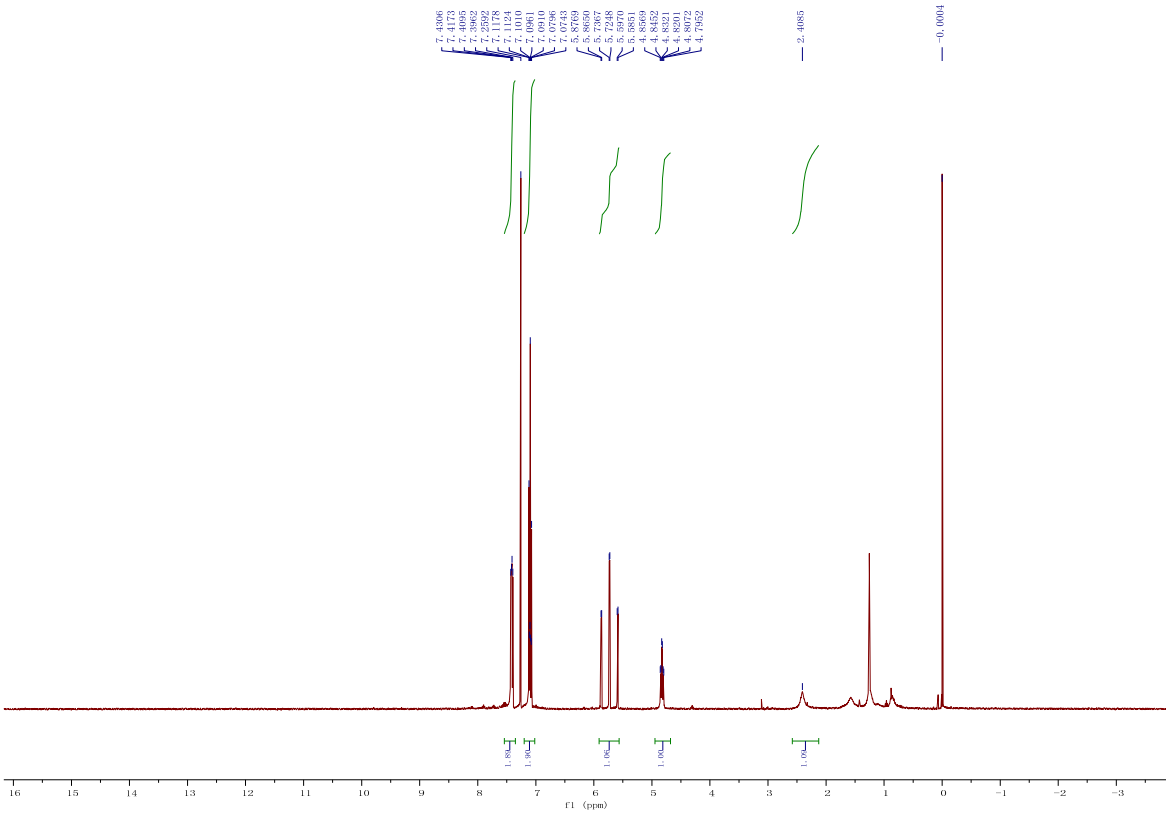
3a

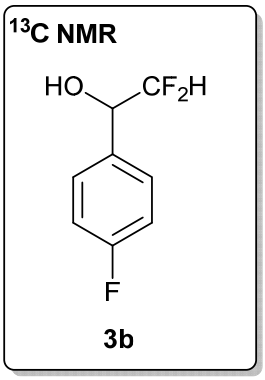

-126.8471
-127.6048
-127.6090
-127.6495
-128.4074
-127.0
-128.0
f1 (ppm)
-122
-123
-124
-125
-126
-127
-128
-129
-130
-131
-132
-133
-134
-135
-136
f1 (ppm)

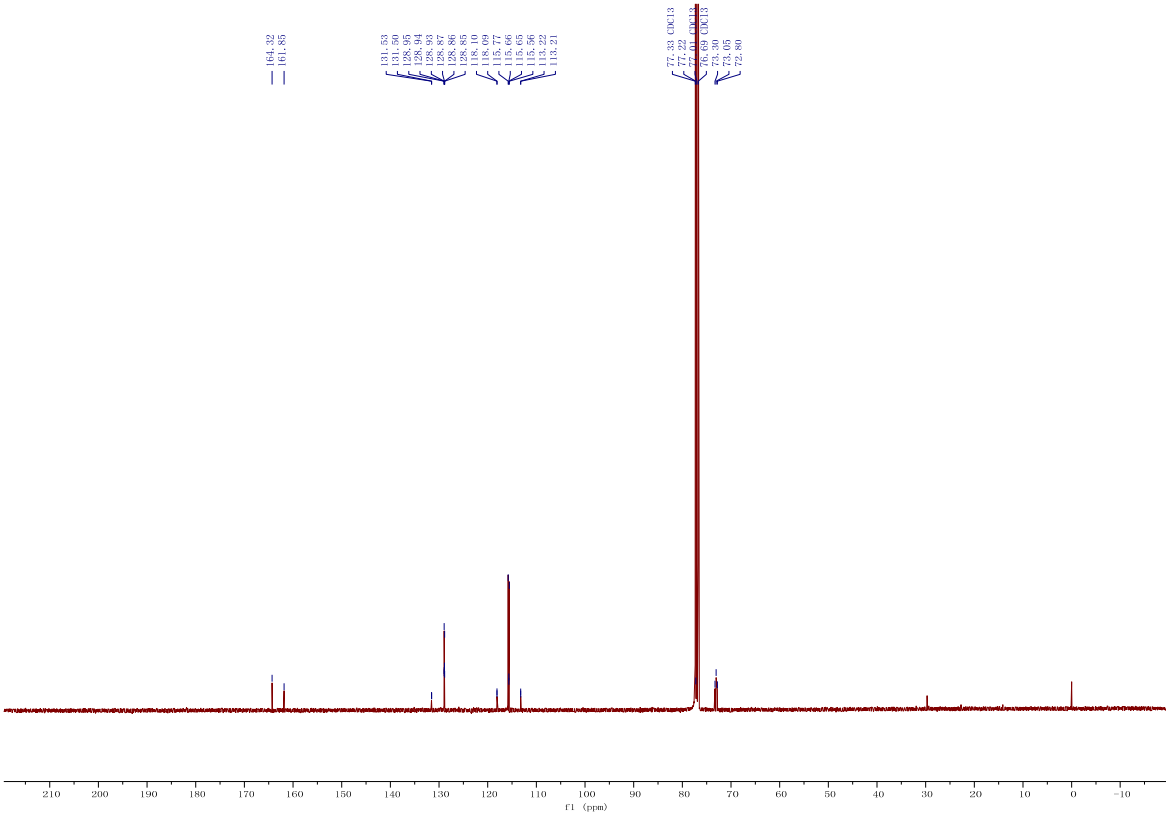
^{1}H NMR


HO
CF2H
F

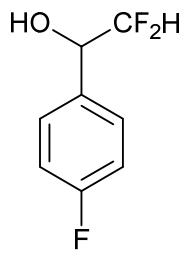
3b


7.4306
7.4173
7.4066
7.3962
7.2592
7.1178
7.1124
7.1041
7.0961
7.0910
7.0796
7.0743
5.8759
5.8650
5.7367
5.7248
5.5970
5.5853
4.8566
4.8452
4.8321
4.8201
4.7972
4.7952
2.4885
-0.0004
1.84
1.90
1.96
1.96
1.00
f1 (ppm)

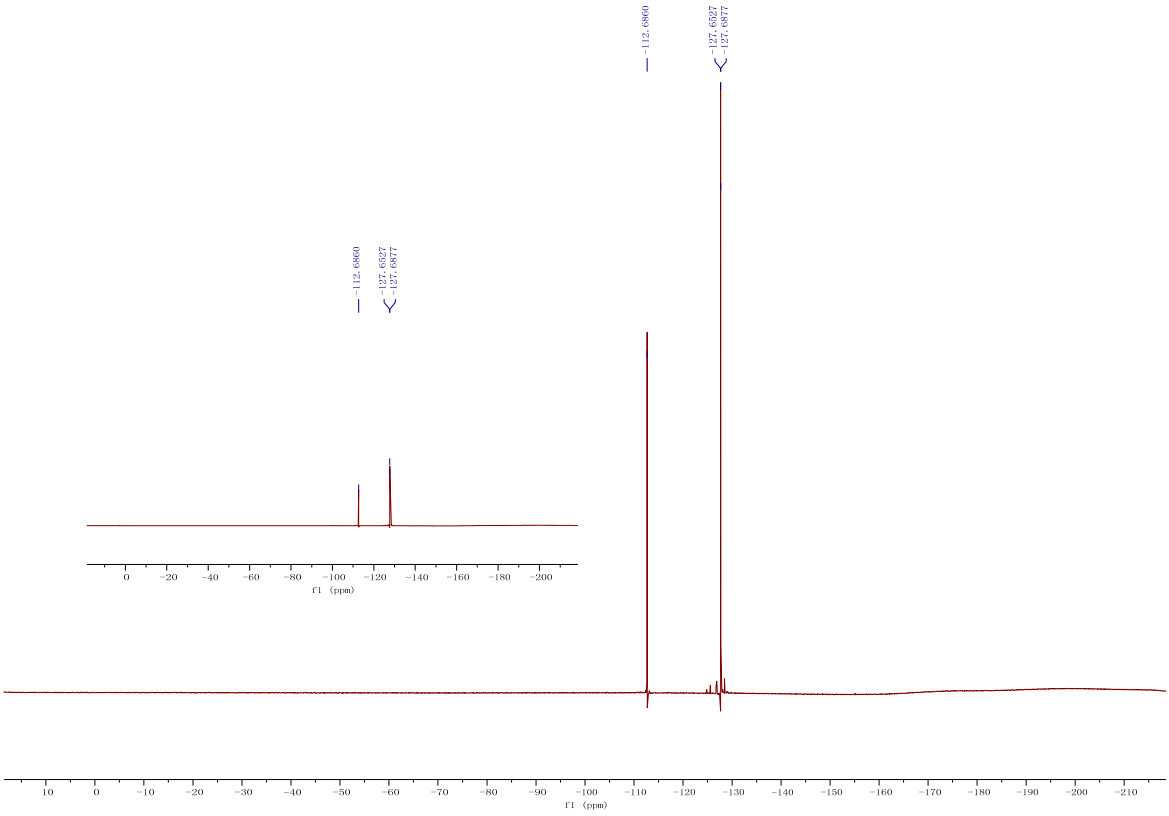

13C NMR
HO
CF2H
F
3b


164.32
161.85
131.53
131.50
128.95
128.94
128.93
128.87
128.86
128.85
118.10
118.09
115.77
115.66
115.65
115.56
113.22
113.21
77.33 CDCl3
77.22
77.01 CDCl3
76.69 CDCl3
73.10
73.05
72.80
f1 (ppm)

^{19}F NMR



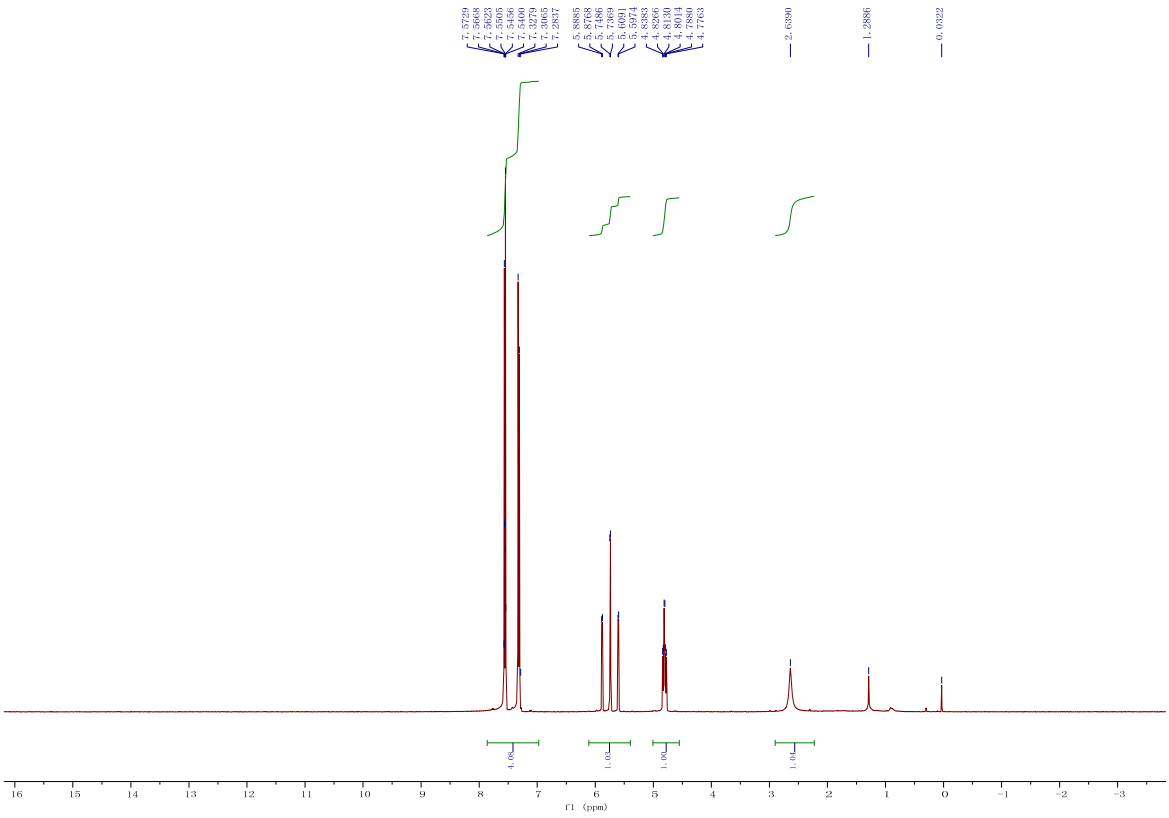
3b



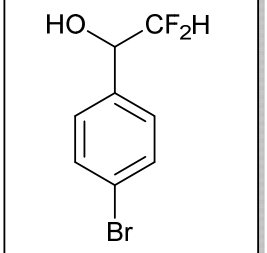
^{1}H NMR


HO
CF2H
Br

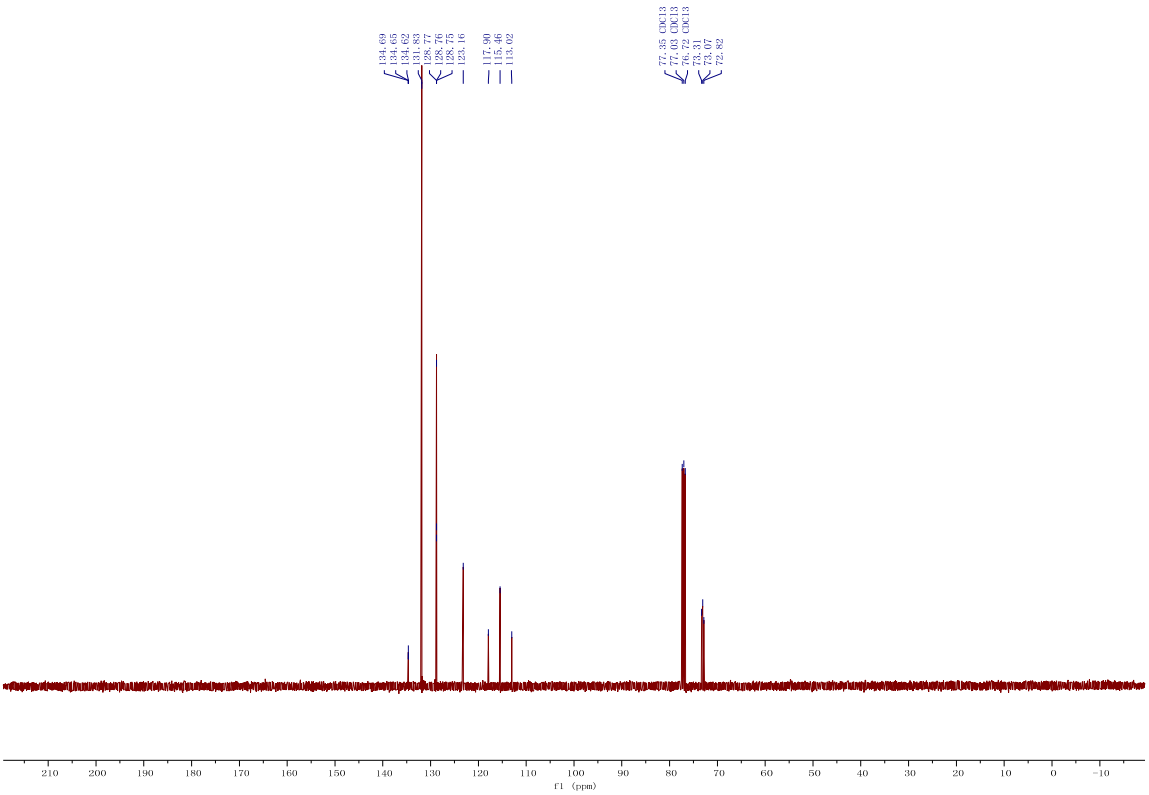
3c


7.5729
7.5668
7.5623
7.5505
7.5456
7.5400
7.5379
7.5065
7.2837
5.8885
5.8788
5.7486
5.7369
5.6991
5.5974
4.8265
4.8266
4.8130
4.8014
4.7880
4.7763
2.6390
1.2886
0.0322
4.08
1.03
1.00
1.04
f1 (ppm)

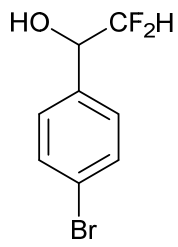
^{13}C NMR


HO
CF2H
Br

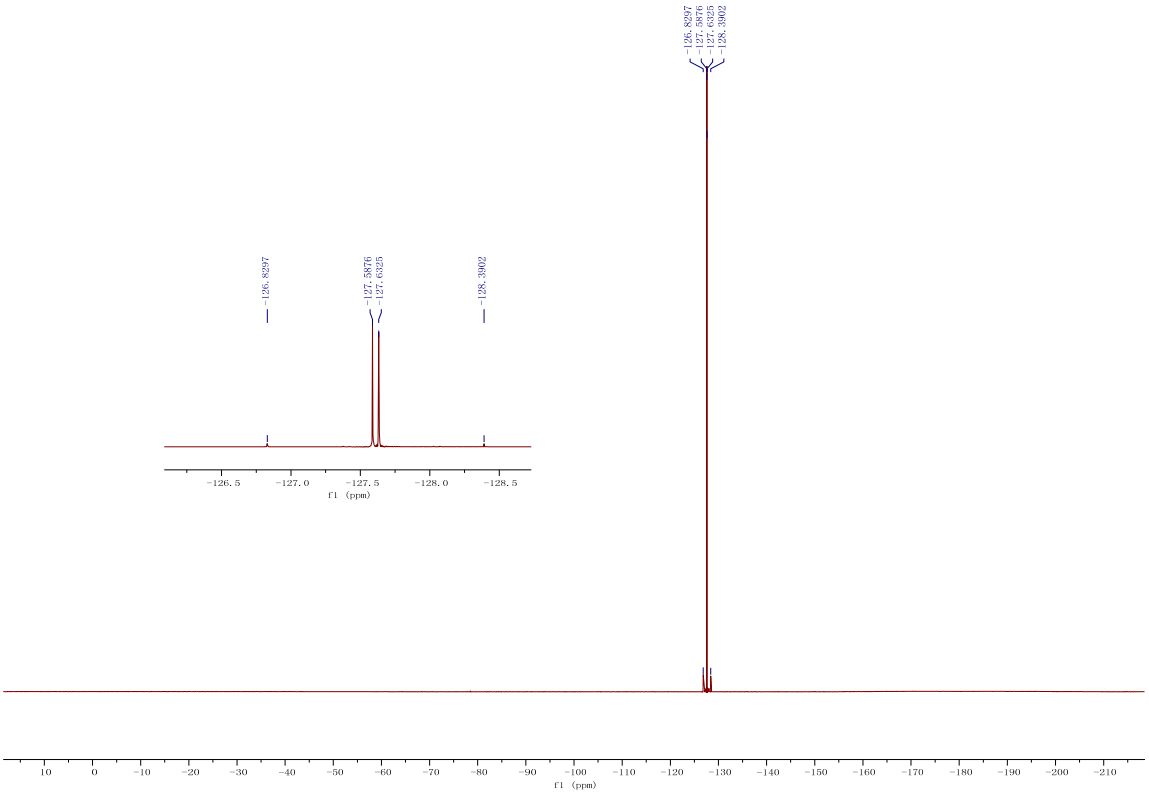
3c


134.69
134.65
134.62
131.83
128.77
128.76
128.75
123.16
117.90
115.46
113.02
77.35 CDCl3
77.03 CDCl3
76.72 CDCl3
73.31
73.07
72.82
f1 (ppm)

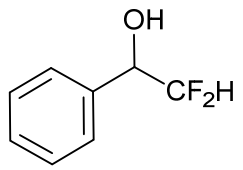
^{19}F NMR



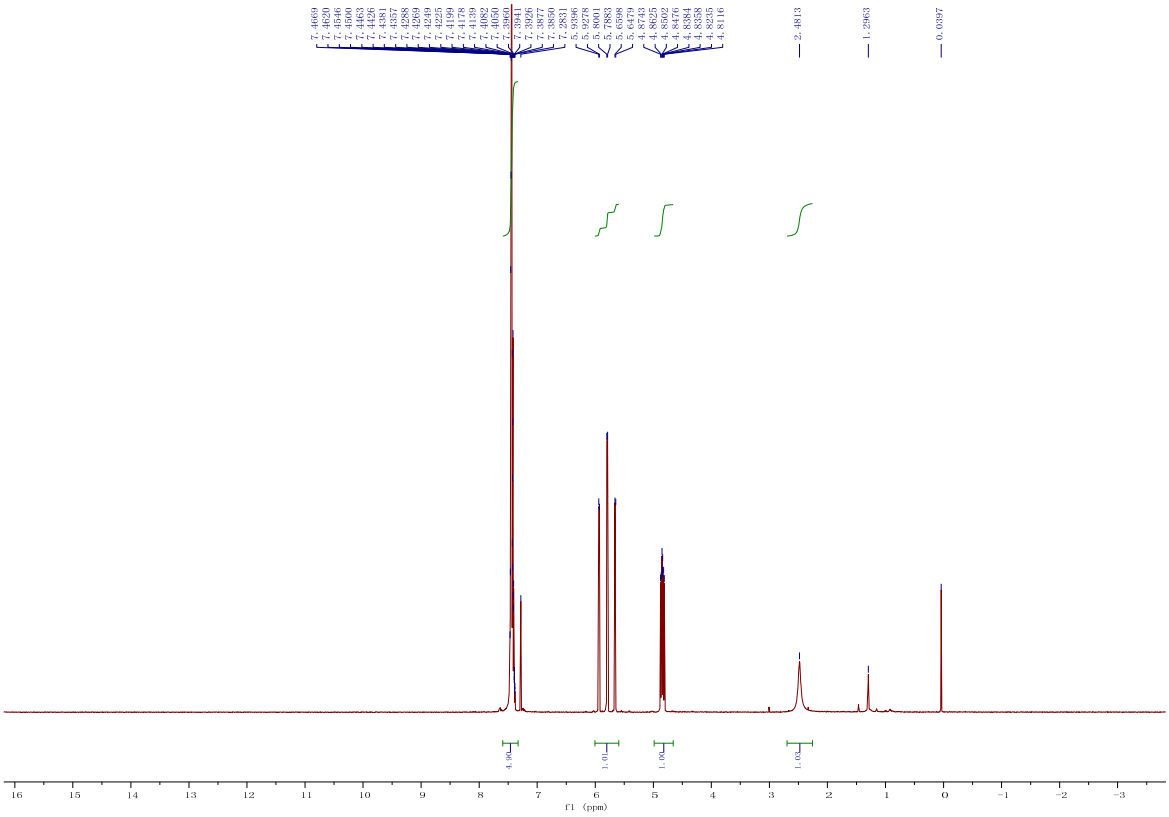
3c



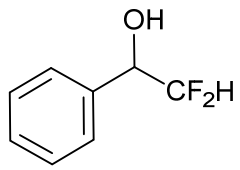
^{1}H NMR


OH
CF2H

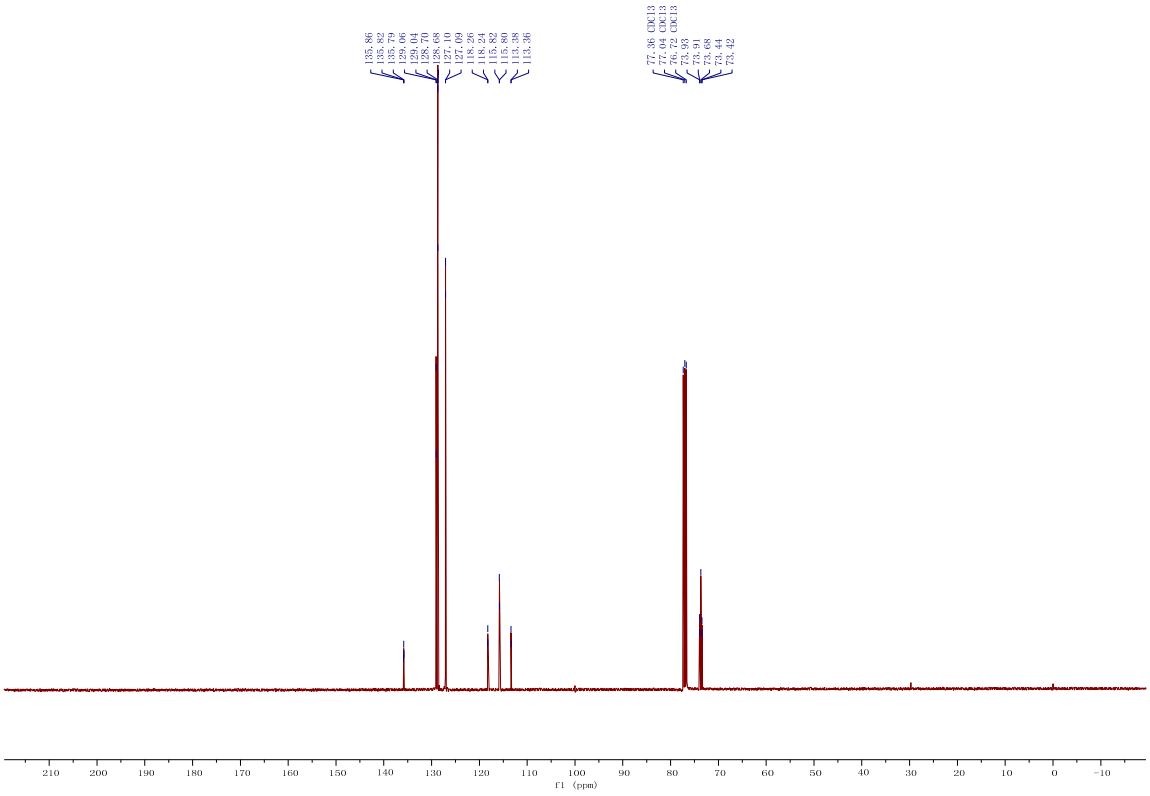
3d


7.4669
7.4620
7.4566
7.4500
7.4463
7.4426
7.4381
7.4357
7.4288
7.4269
7.4249
7.4225
7.4189
7.4178
7.4139
7.4082
7.4050
7.3993
7.3941
7.3926
7.3877
7.3850
7.3831
7.3696
5.9278
5.8001
5.7883
5.6398
5.6274
4.8743
4.8625
4.8502
4.8476
4.8384
4.8358
4.8235
4.8116
2.4813
1.2963
0.6397
4.96
1.01
1.96
1.03
f1 (ppm)

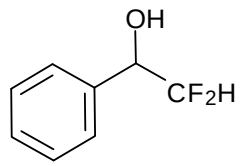
^{13}C NMR


OH
CF2H

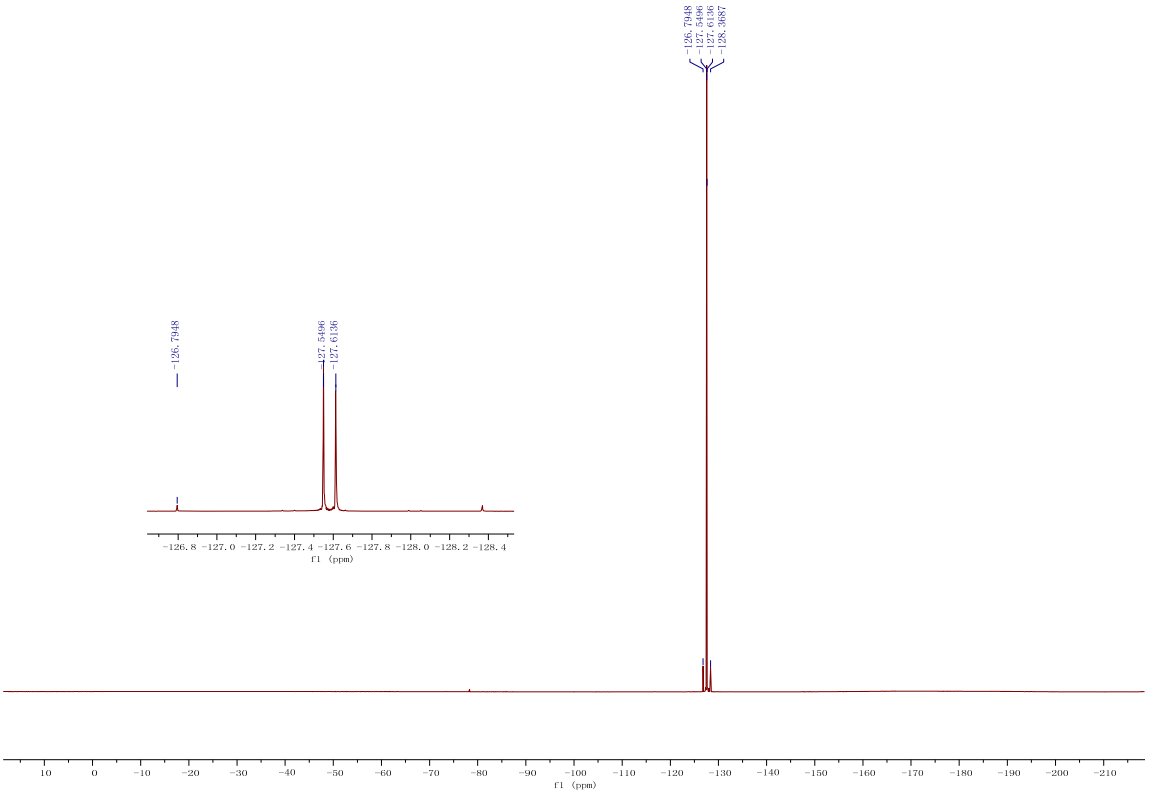
3d


135.86
135.82
135.79
129.06
128.04
128.70
128.68
127.10
127.09
118.26
118.24
115.82
115.80
113.38
113.36
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
73.93
73.91
73.68
73.44
73.42
f1 (ppm)

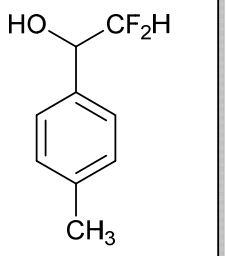
^{19}F NMR


OH
CF2H

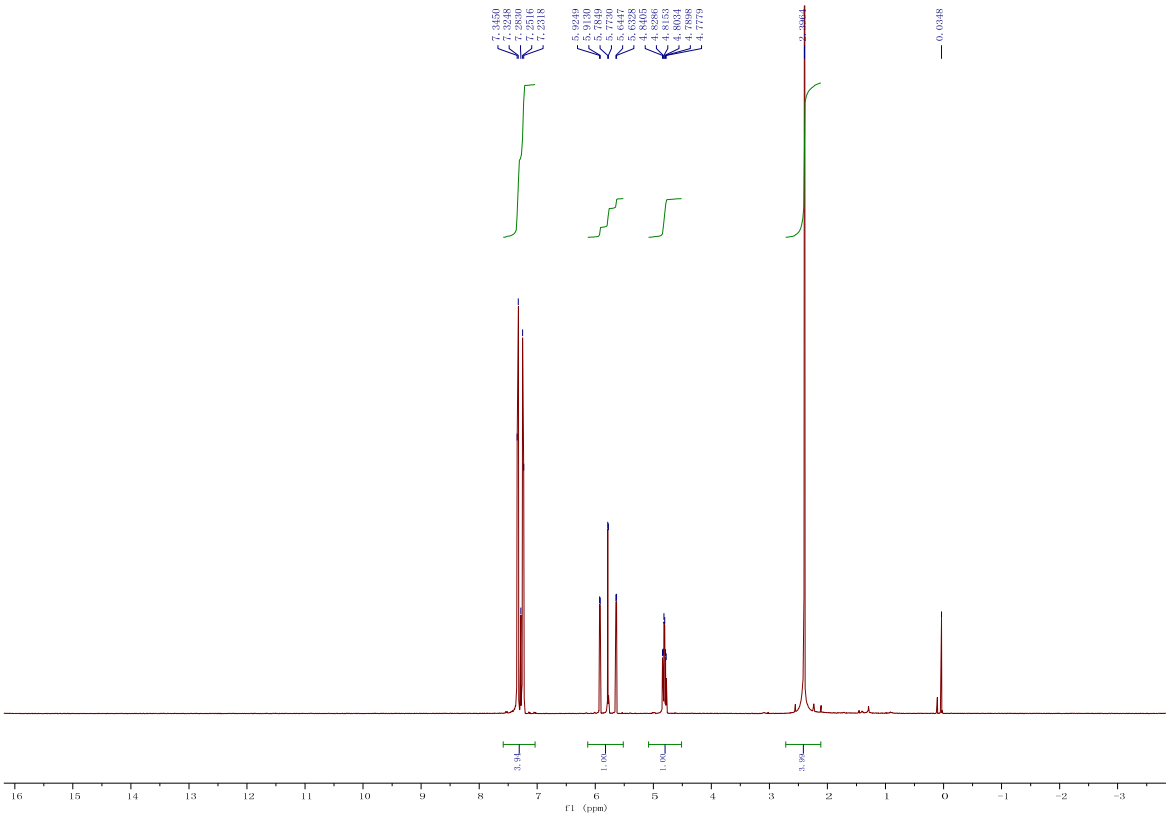
3d


-126.7948
-127.5496
-127.6136
-128.3687
-126.7948
-127.5496
-127.6136
-126.8 -127.0 -127.2 -127.4 -127.6 -127.8 -128.0 -128.2 -128.4
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

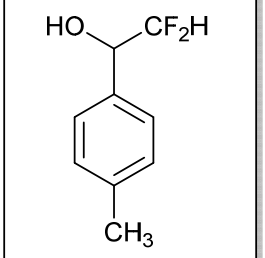
^{1}H NMR


HO
CF2H
CH3

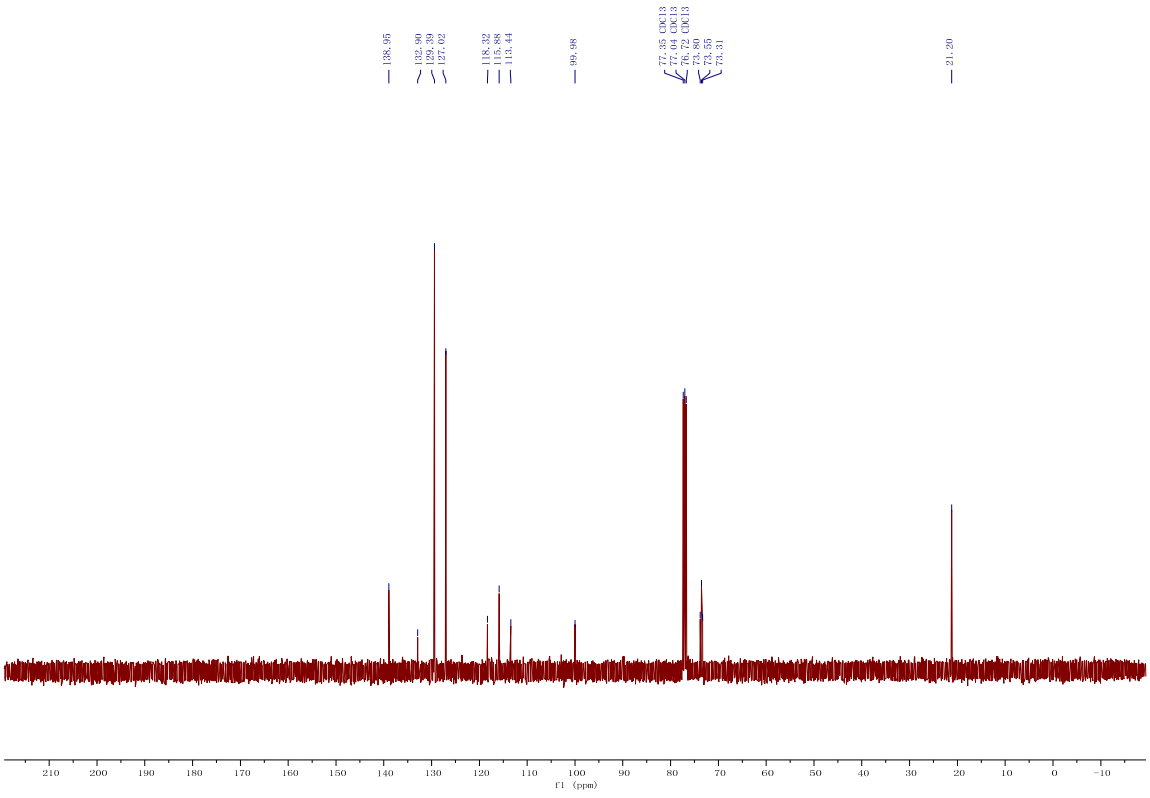
3e


7.3450
7.3248
7.2990
7.2516
7.2318
5.9249
5.9130
5.7849
5.7730
5.6447
5.6328
4.8465
4.8296
4.8163
4.8034
4.7898
4.7779
2.2964
0.0348
3.94
1.00
1.00
2.99
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)

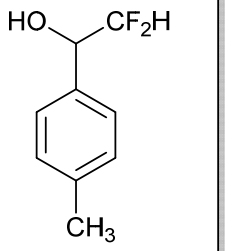
^{13}C NMR


HO
CF2H
CH3

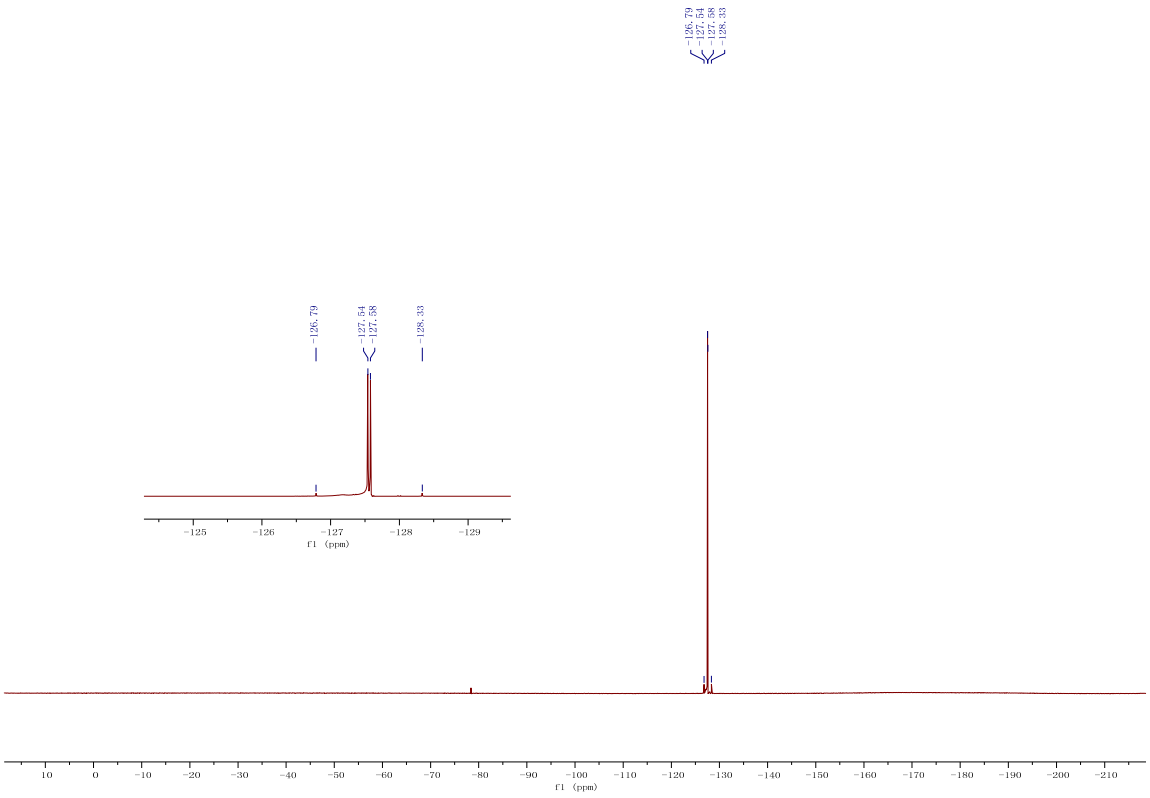
3e


138.95
132.90
129.39
127.02
118.32
115.98
113.44
99.98
77.35 CDCl3
77.04 CDCl3
76.72 CDCl3
73.80
73.35
72.31
21.20
f1 (ppm)

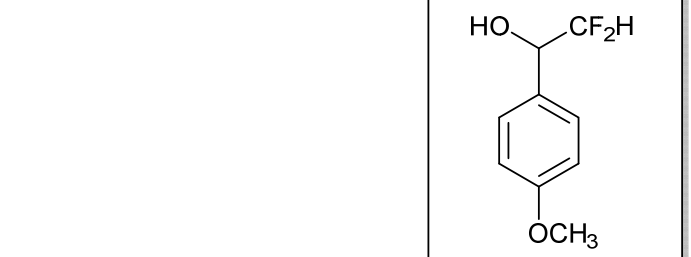
^{19}F NMR


HO
CF2H
CH3

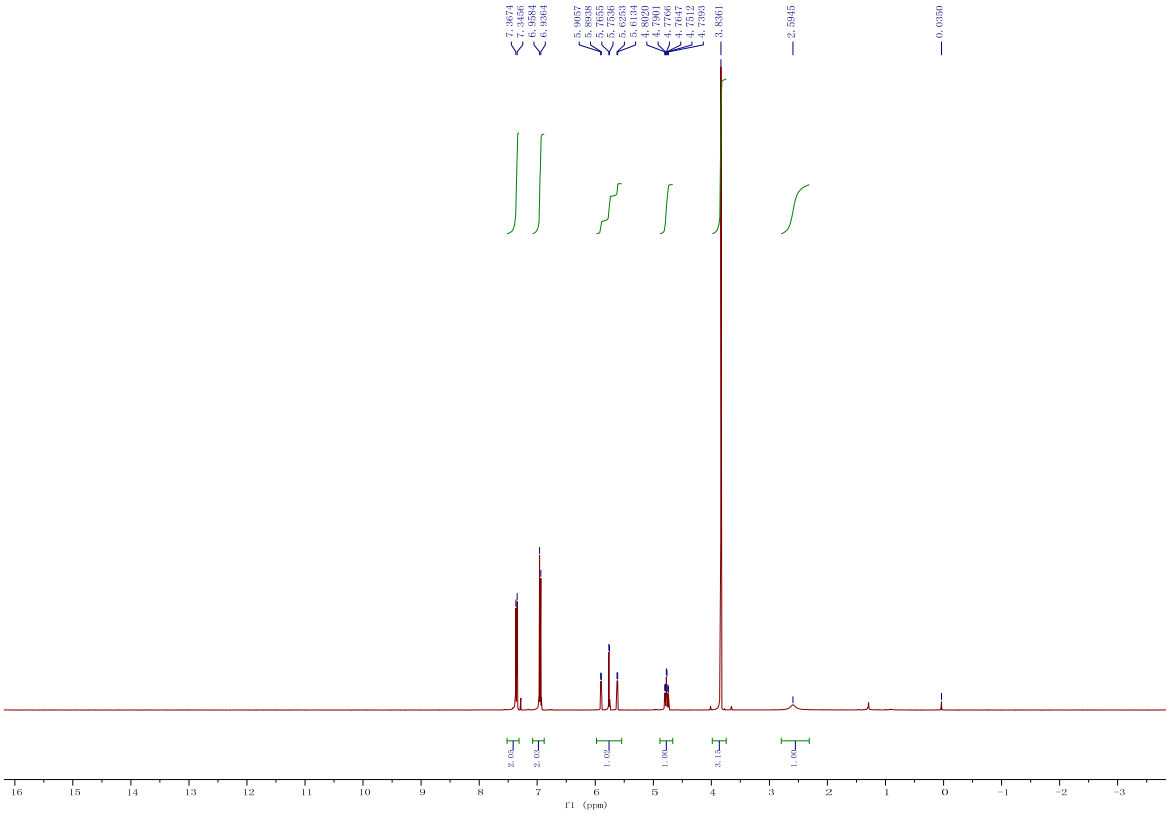
3e

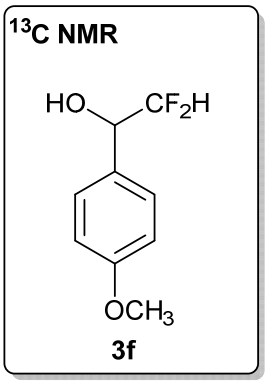

-126.79
-127.54
-127.58
-128.33
-125
-126
-127
-128
-129
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

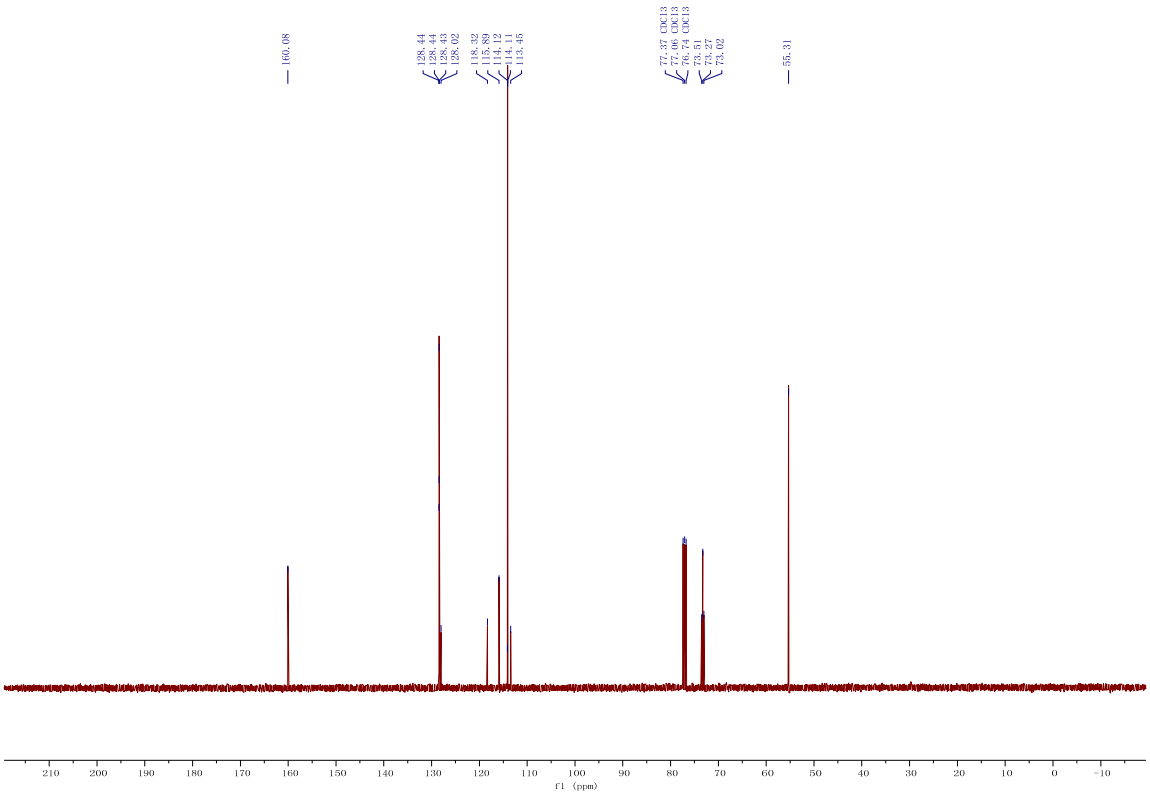
^{1}H NMR


HO
CF2H
OCH3

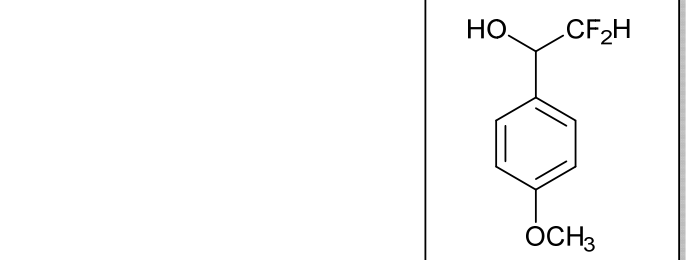
3f


7.3674
7.3456
6.4884
6.4364
5.8957
5.8698
5.7655
5.7536
5.6253
5.6134
4.8000
4.7901
4.7766
4.7647
4.7512
4.7393
3.8861
2.5945
0.0350
2.00
2.00
1.00
1.06
3.14
1.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)

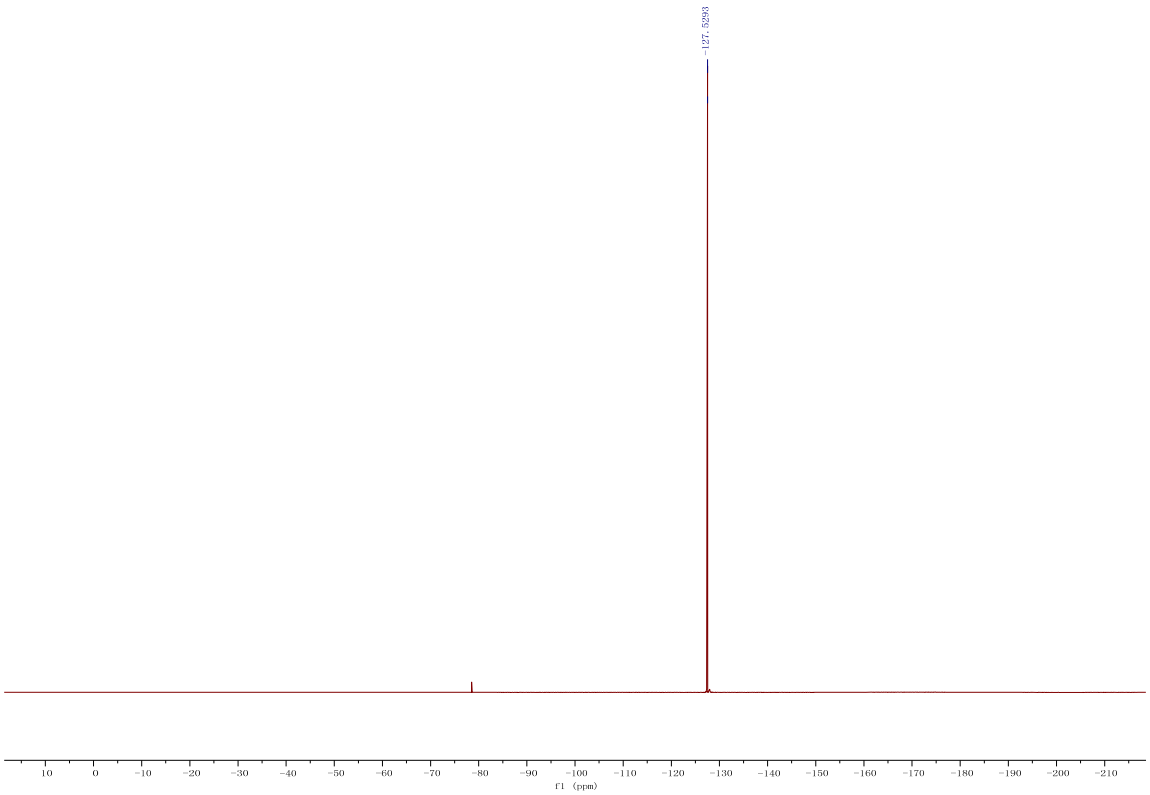

13C NMR
HO
CF2H
OCH3
3f


160.08
128.44
128.44
128.43
128.02
118.32
115.89
114.12
114.11
113.45
77.37 CDCl3
77.06 CDCl3
76.74 CDCl3
73.51
73.27
73.02
55.31
f1 (ppm)

^{19}F NMR


HO
CF2H
OCH3

3f


-127.5283
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
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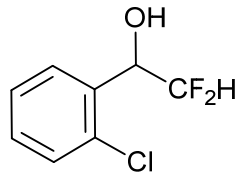
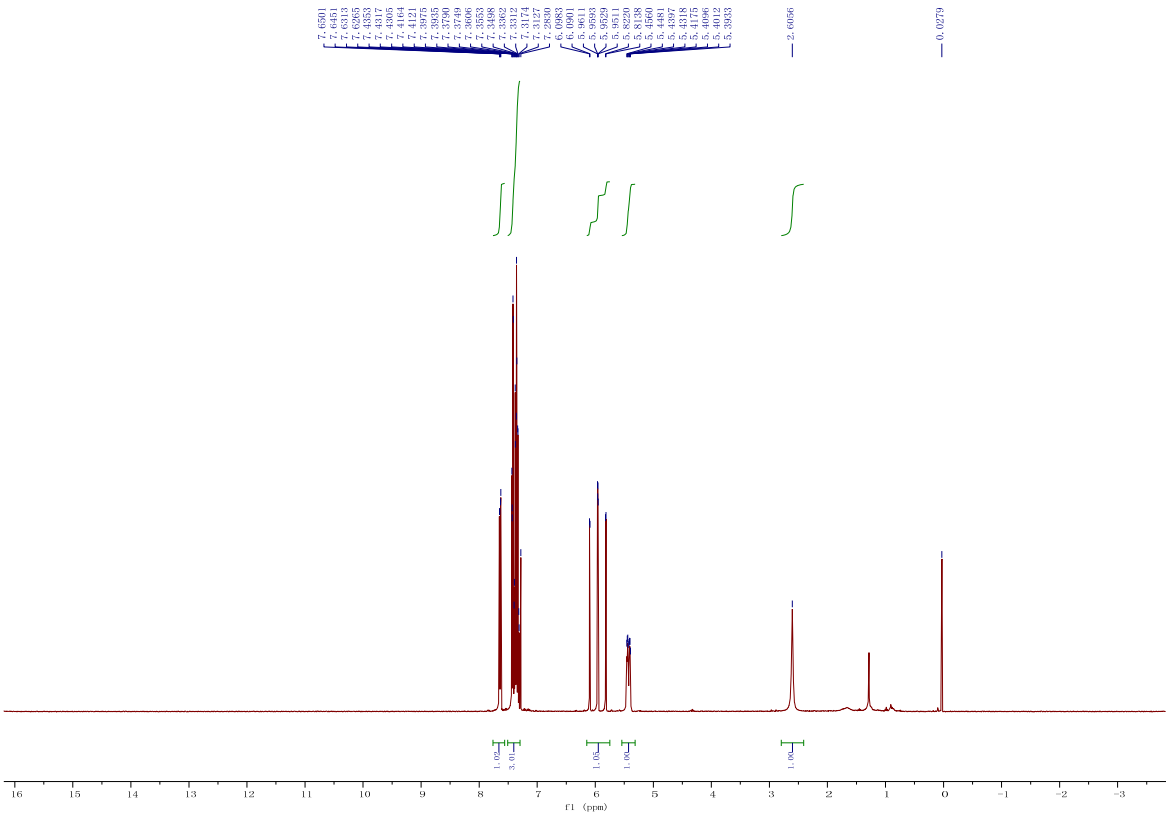
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

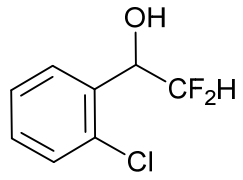
^{1}H NMR



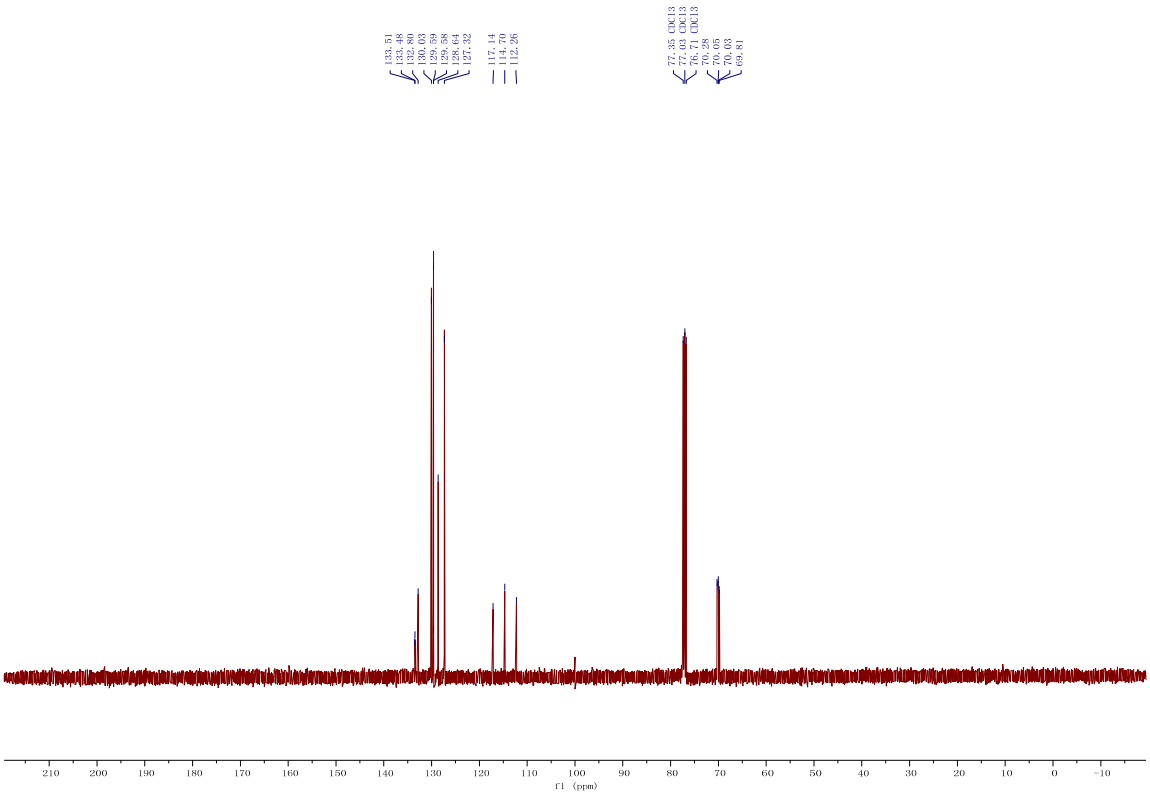
3g



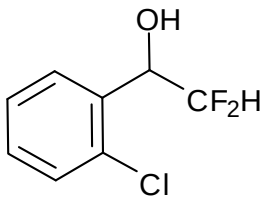
^{13}C NMR


OH
CF2H
Cl

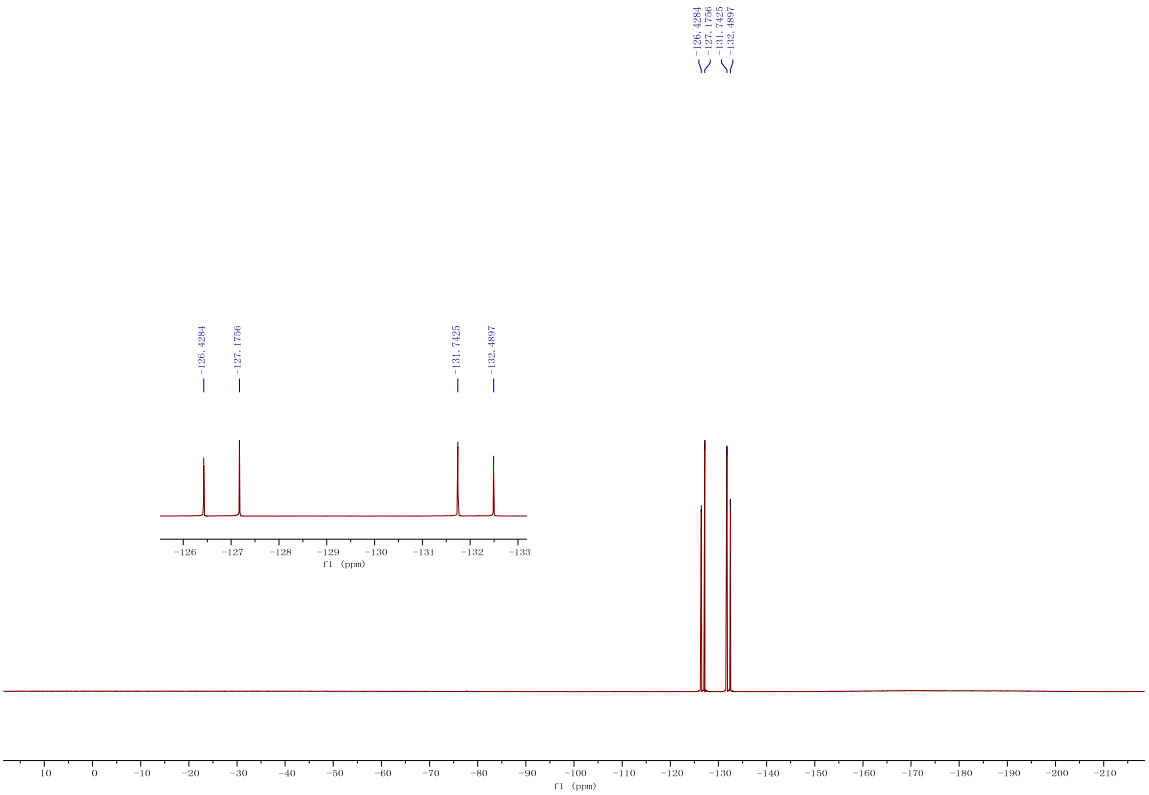
3g


133.51
133.48
132.86
130.03
129.59
129.58
128.64
127.52
117.14
114.70
112.26
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
70.28
70.05
70.03
69.81
f1 (ppm)

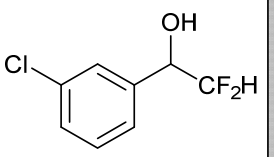
^{19}F NMR



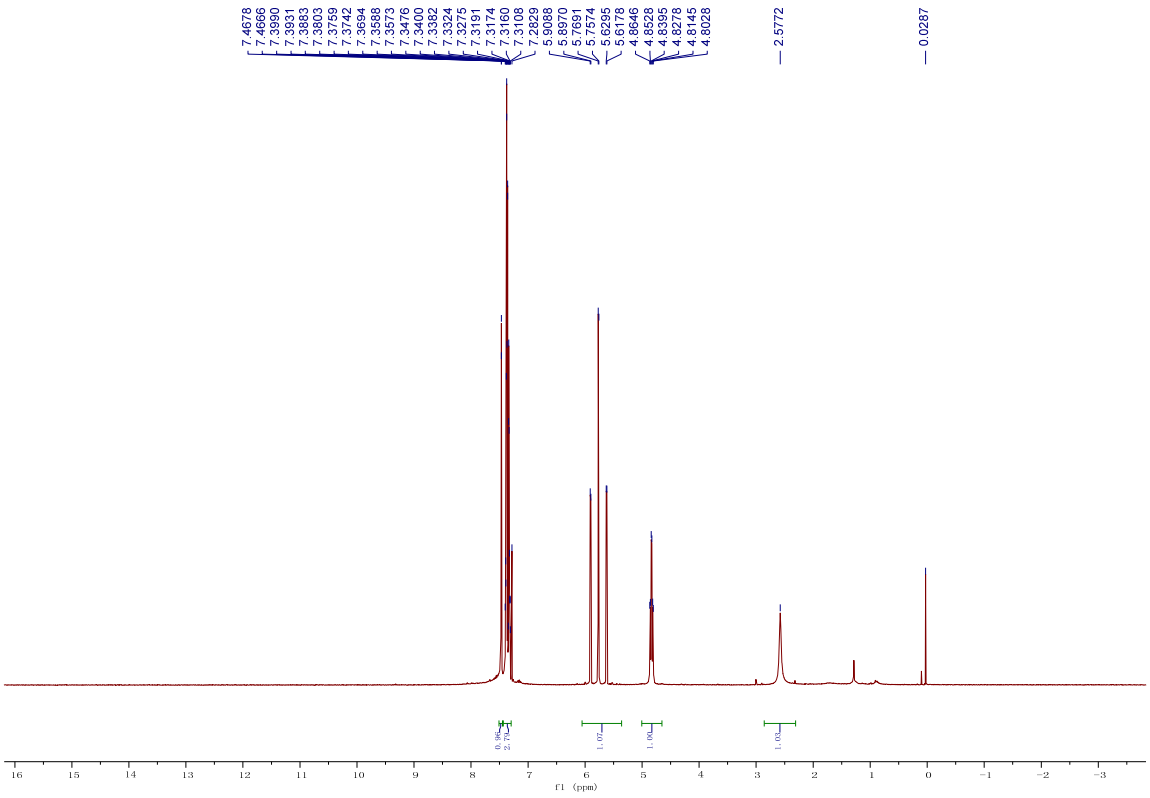
3g



^{1}H NMR


OH
Cl
CF2H

3h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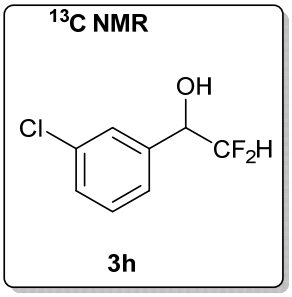
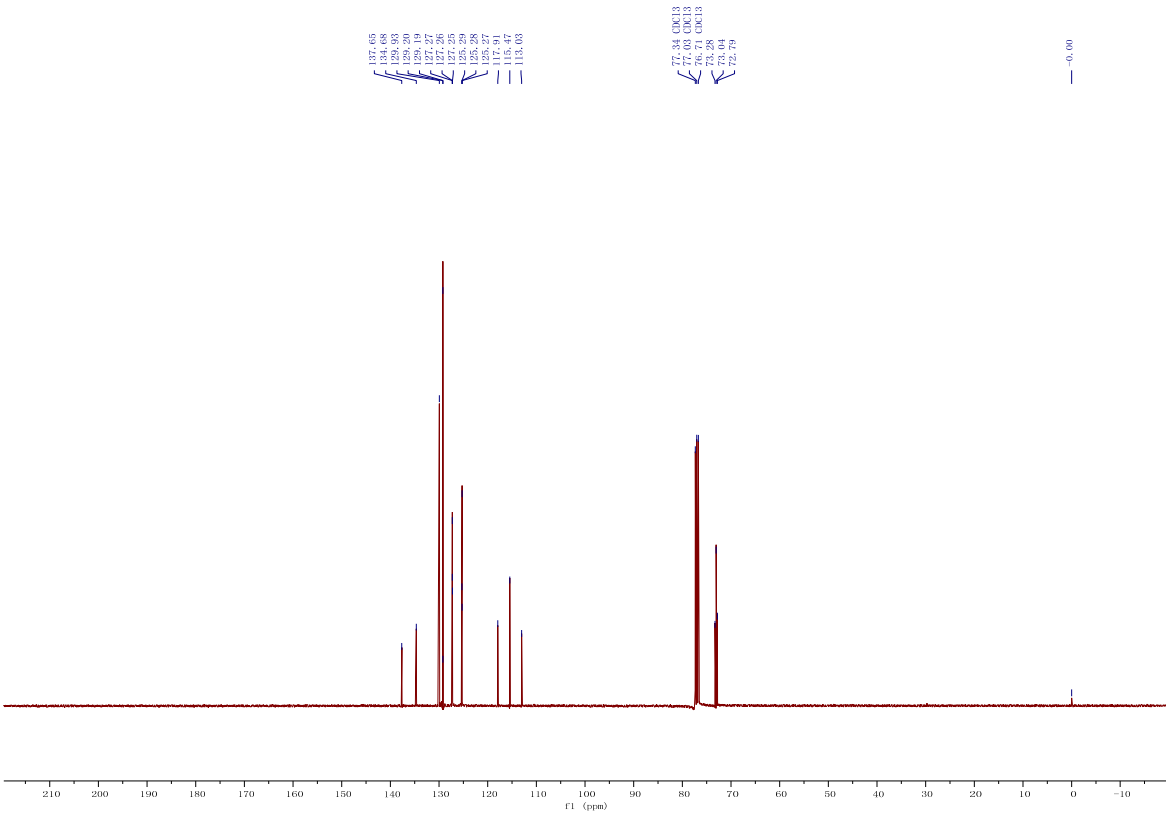
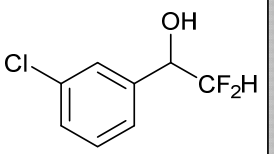
7.4666
7.3990
7.3931
7.3883
7.3803
7.3759
7.3742
7.3694
7.3588
7.3573
7.3476
7.3400
7.3382
7.3324
7.3275
7.3191
7.3174
7.3160
7.3108
7.2829
5.9088
5.8970
5.7691
5.7574
5.6295
5.6178
4.8646
4.8528
4.8395
4.8278
4.8145
4.8028
2.5772
0.0287
f1 (ppm)

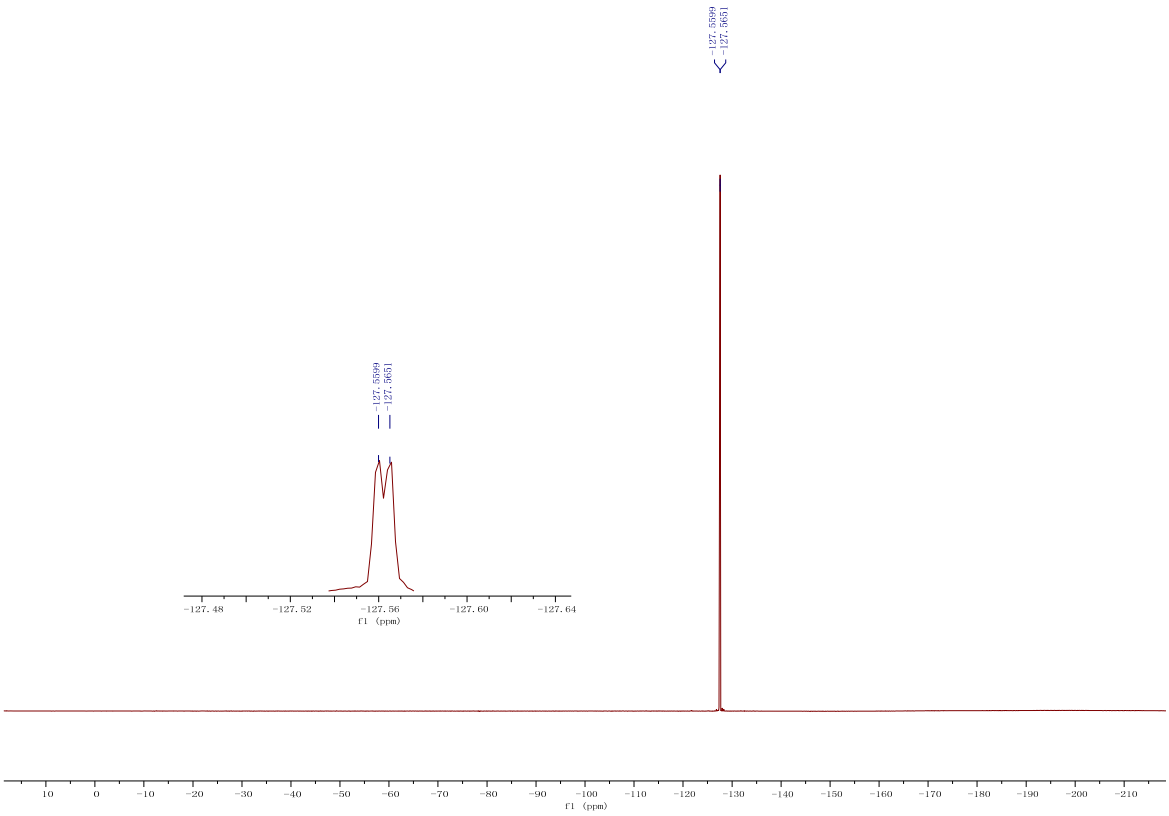

13C NMR
OH
Cl
CF2H
3h


137.65
134.68
129.93
129.30
129.19
127.27
127.26
127.25
125.29
125.28
125.27
117.91
115.47
115.03
77.34 CDCl3
77.00 CDCl3
76.71 CDCl3
73.28
73.04
72.79
0.00
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

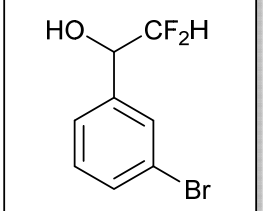
^{19}F NMR


OH
Cl
CF2H

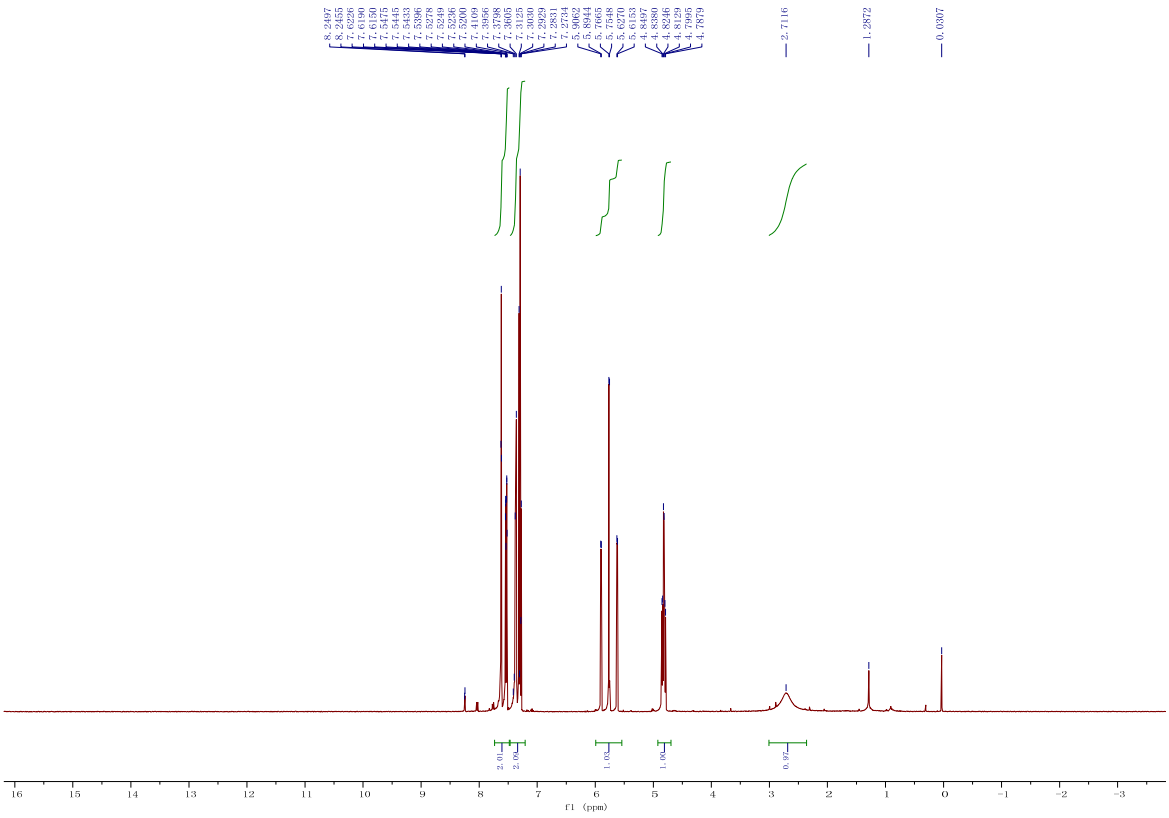
3h


-127.5599
-127.5651
-127.48
-127.52
-127.56
-127.60
-127.64
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

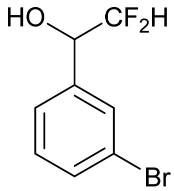
^{1}H NMR



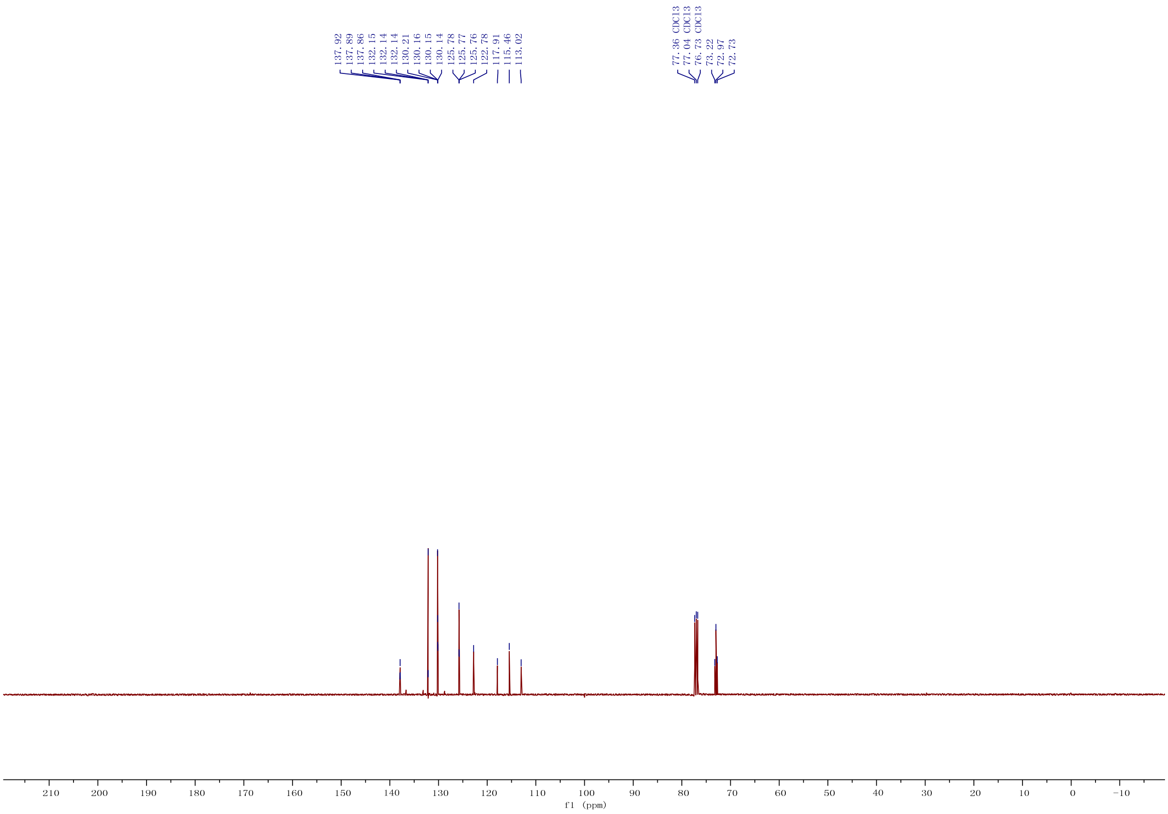
3i



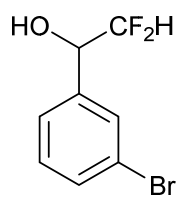
^{13}C NMR


HO
CF2H
Br

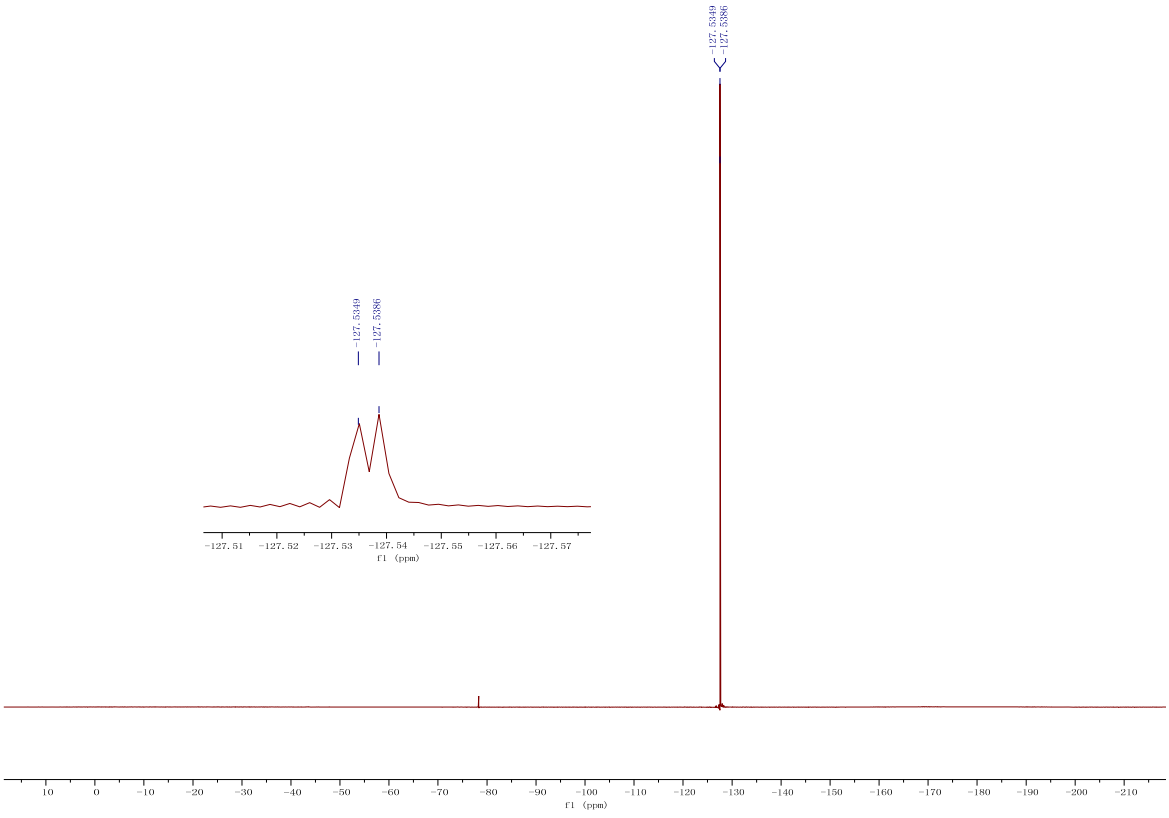
3i


137.92
137.89
137.86
132.15
132.14
132.14
130.21
130.16
130.15
130.14
125.78
125.77
125.76
122.78
117.91
115.46
113.02
77.36 CDCl3
77.04 CDCl3
76.73 CDCl3
73.22
72.97
72.73
f1 (ppm)

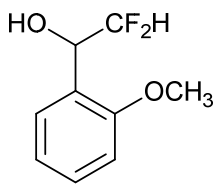
^{19}F NMR


HO
CF2H
Br

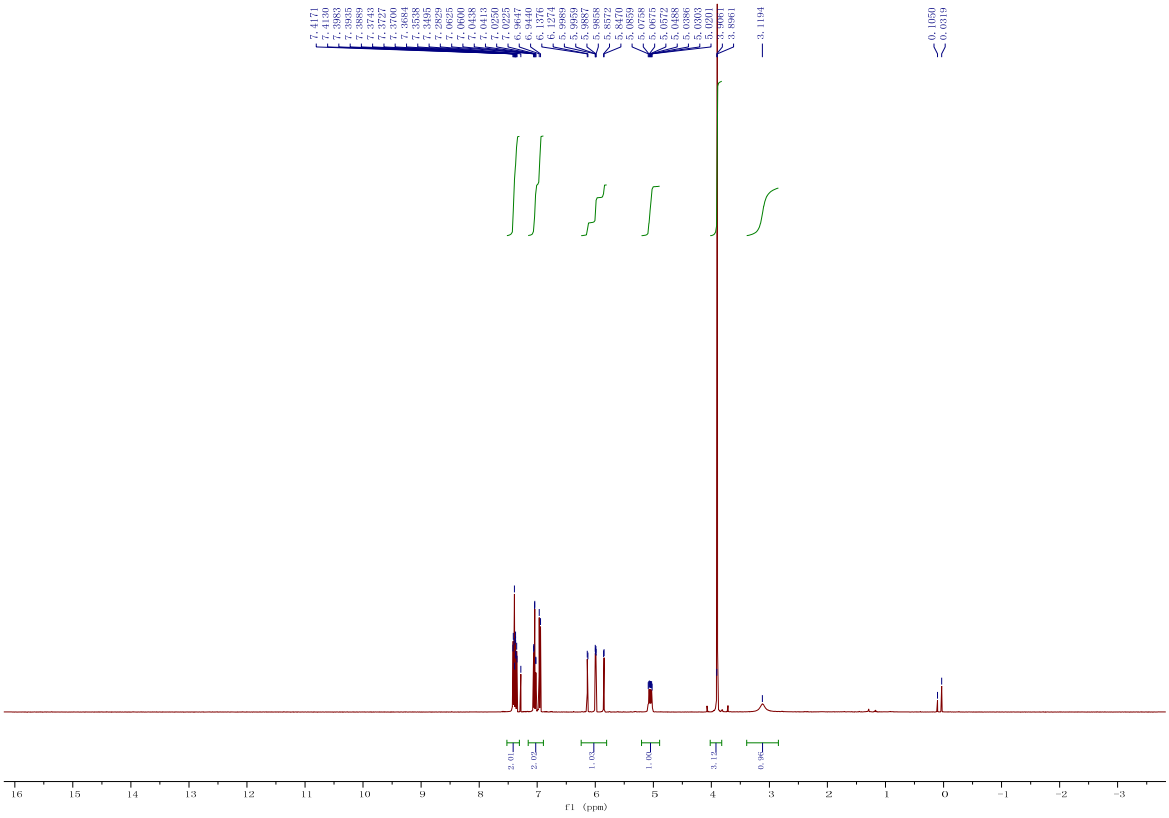
3i


-127.5349
-127.5386
-127.5349
-127.5386
-127.51
-127.52
-127.53
-127.54
-127.55
-127.56
-127.57
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

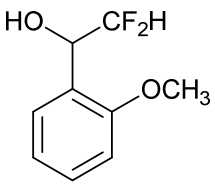
^{1}H NMR



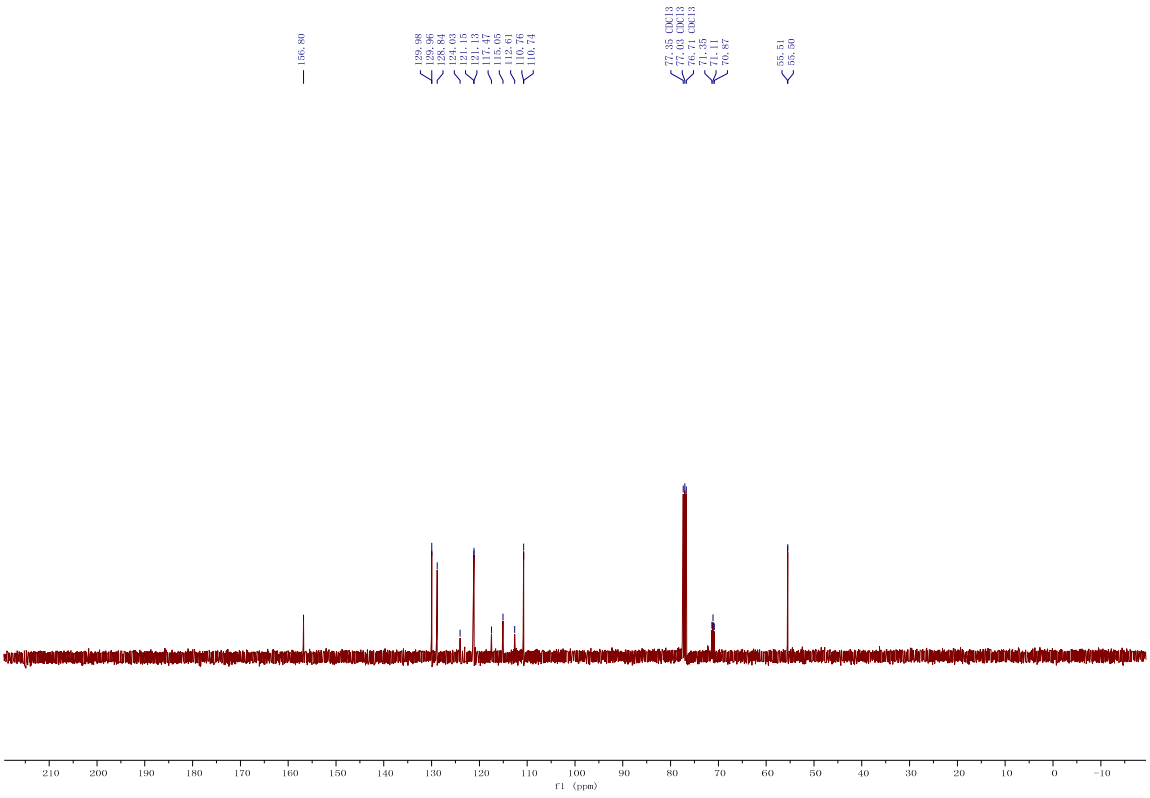
3j



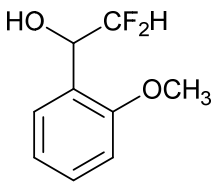
^{13}C NMR


HO
CF2H
OCH3

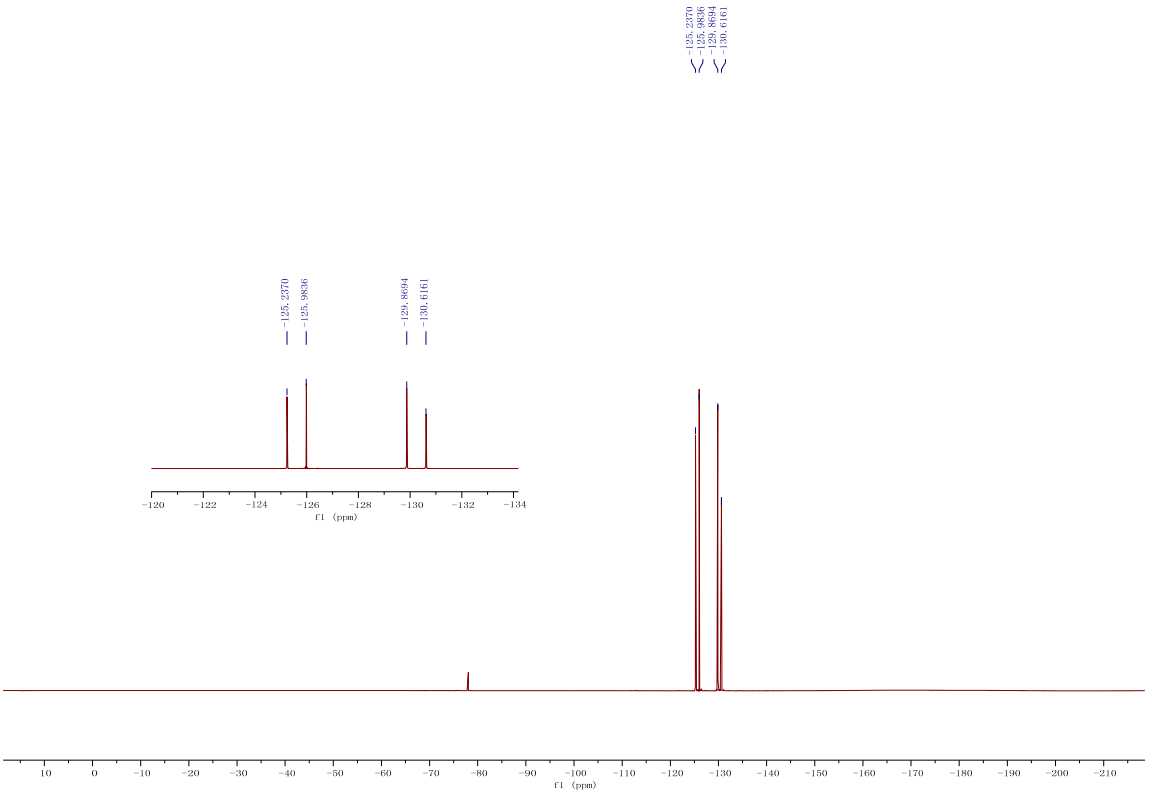
3j


156.80
129.98
129.96
128.84
124.65
121.15
121.13
117.47
115.65
112.61
110.76
110.74
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
71.35
71.11
70.87
55.51
55.50
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

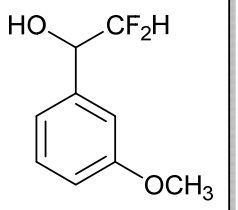
^{19}F NMR


HO
CF2H
OCH3

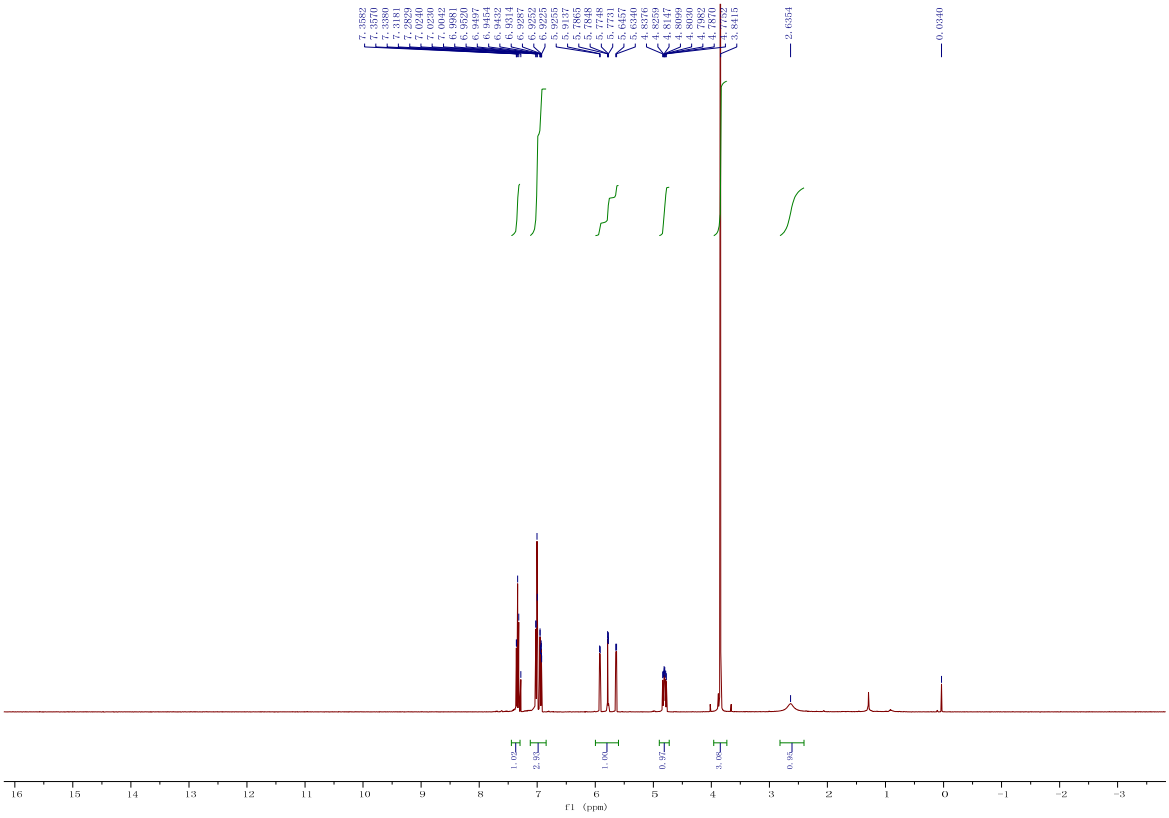
3j


-125.2370
-125.9836
-129.8694
-130.6161
-125.2370
-125.9836
-129.8694
-130.6161
f1 (ppm)
f1 (ppm)

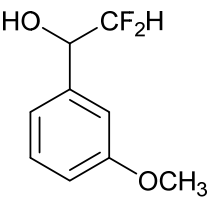
^{1}H NMR



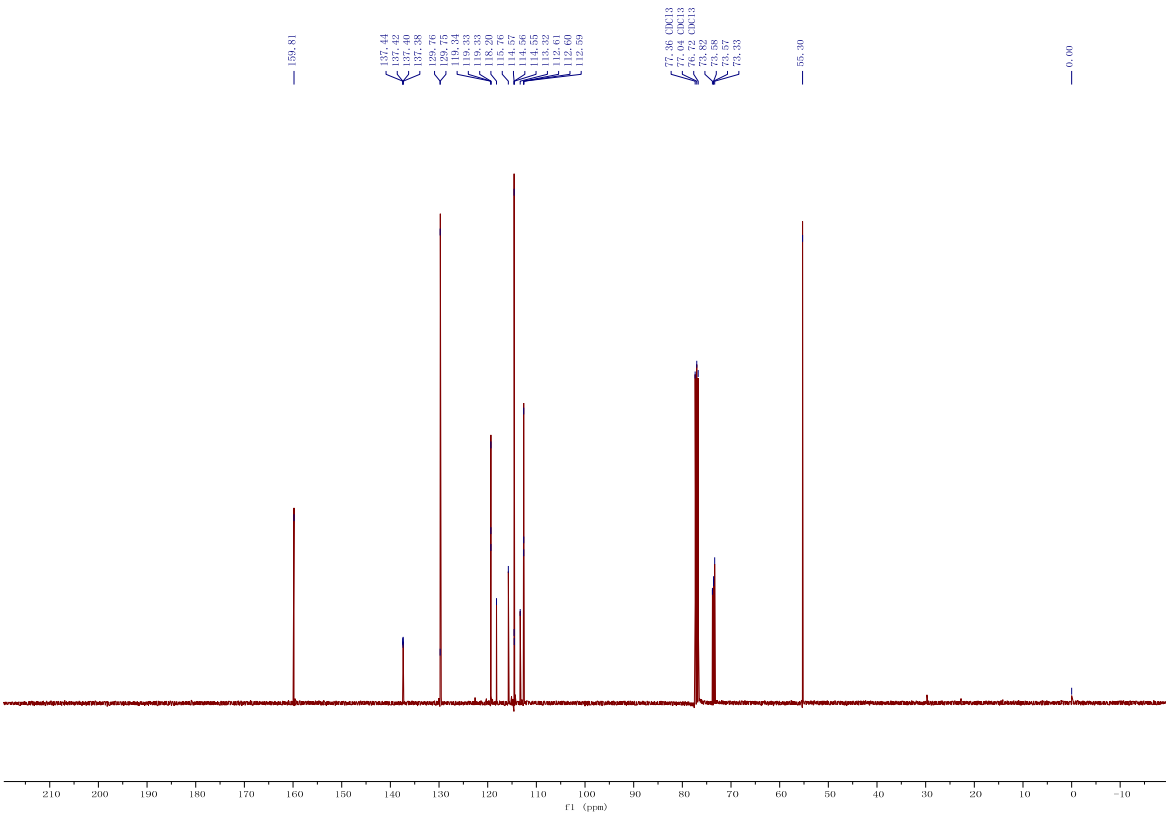
3k



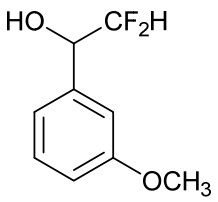
^{13}C NMR


HO
CF2H
OCH3

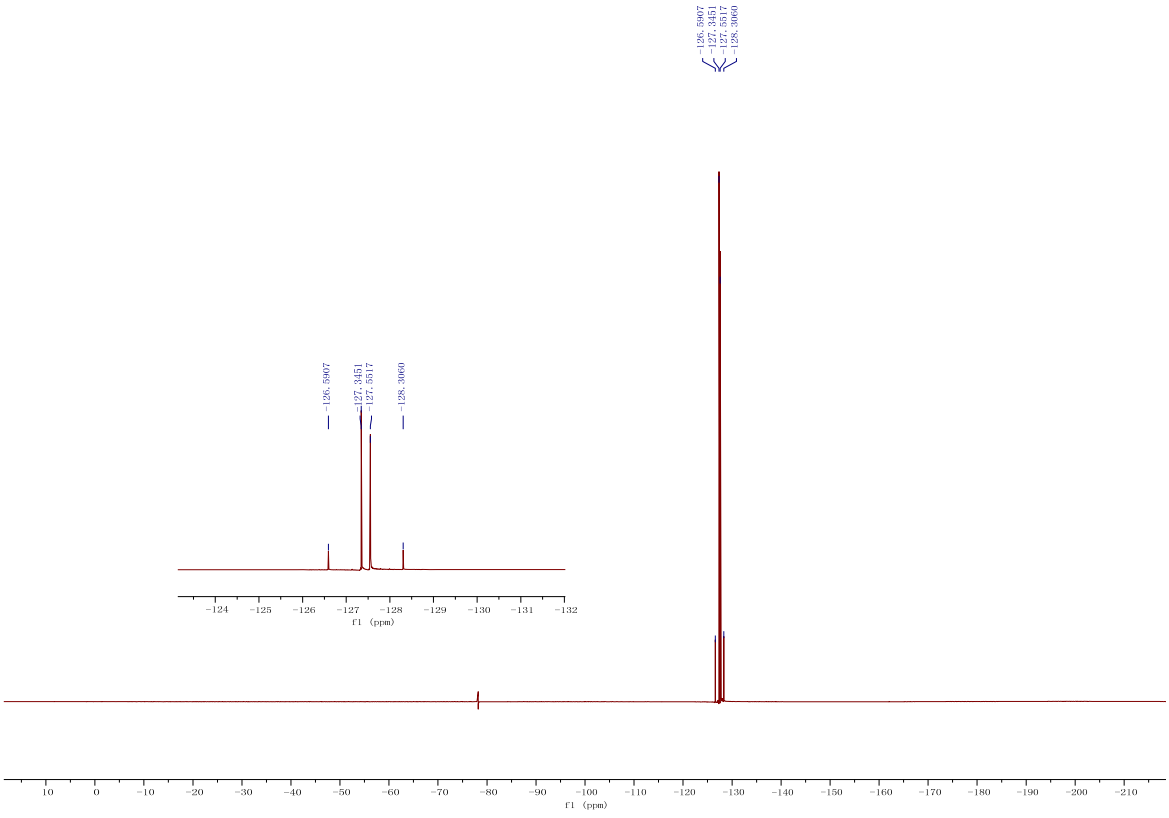
3k


159.81
137.44
137.42
137.40
137.38
129.76
129.75
119.34
115.33
115.23
115.20
115.76
114.57
114.56
114.55
114.32
112.61
112.60
112.59
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
73.82
73.68
73.57
73.33
55.30
0.00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

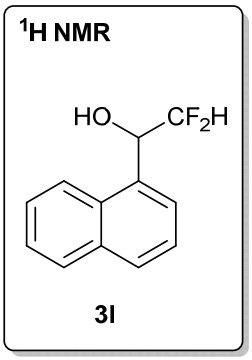
^{19}F NMR



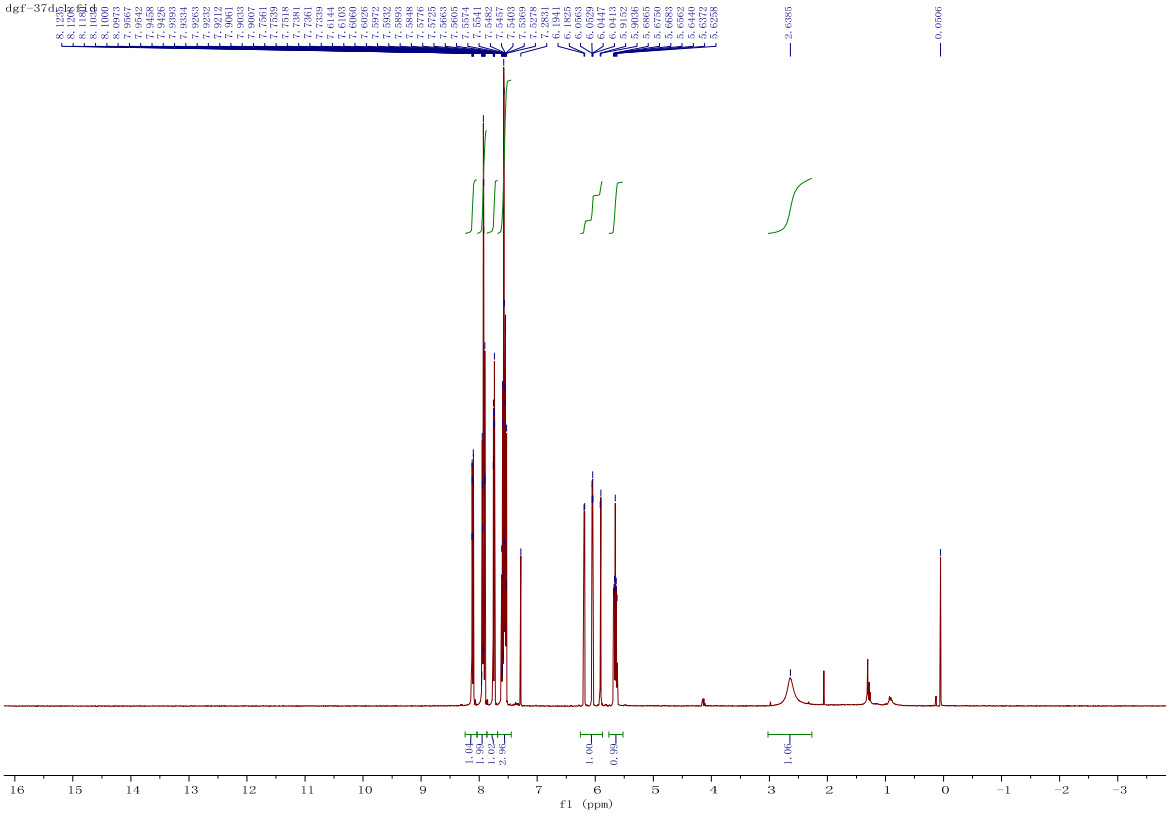
3k

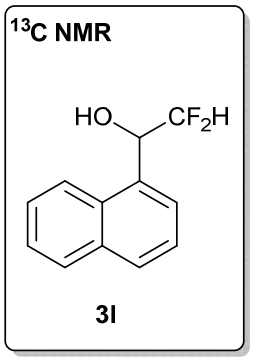


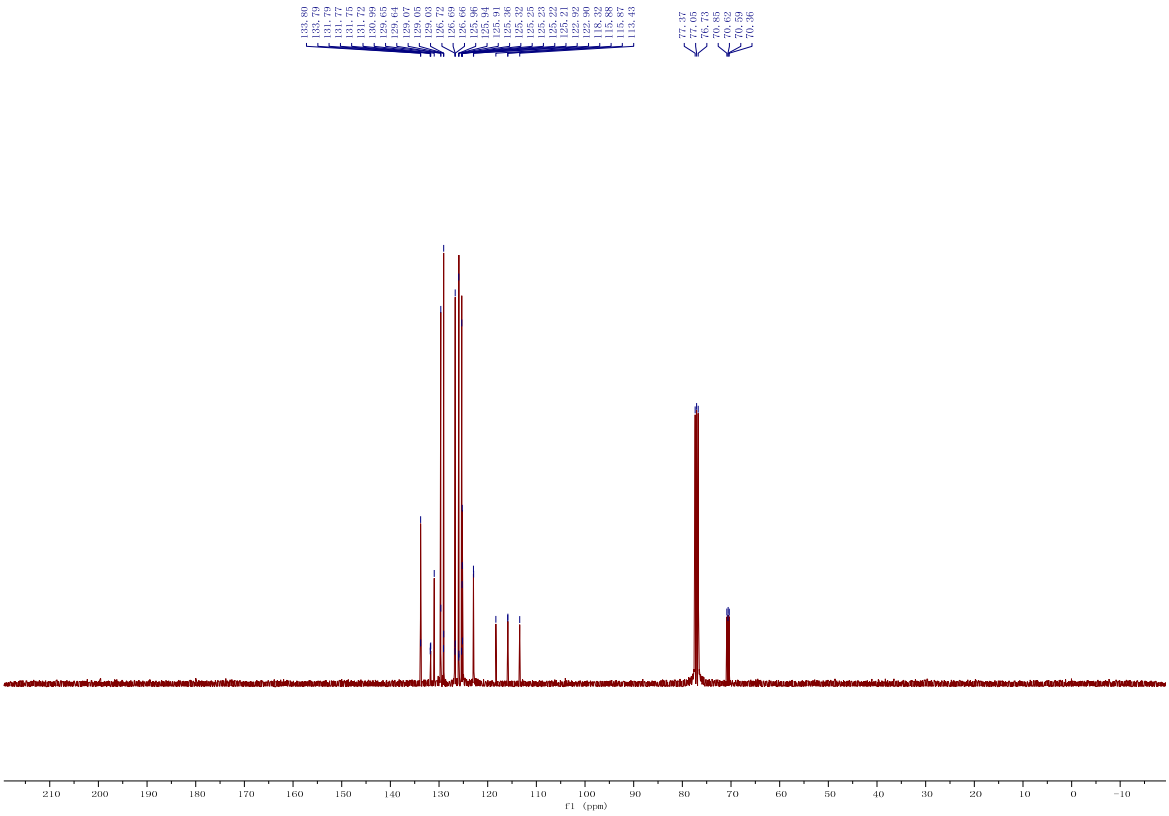
^{1}H NMR


HO
CF2H

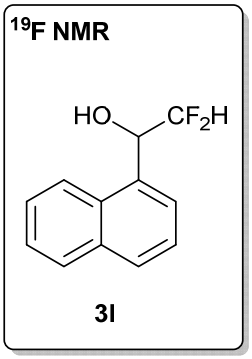
3l


2.6385
0.0586
1.04
1.99
1.12
2.98
1.00
0.99
1.06
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)

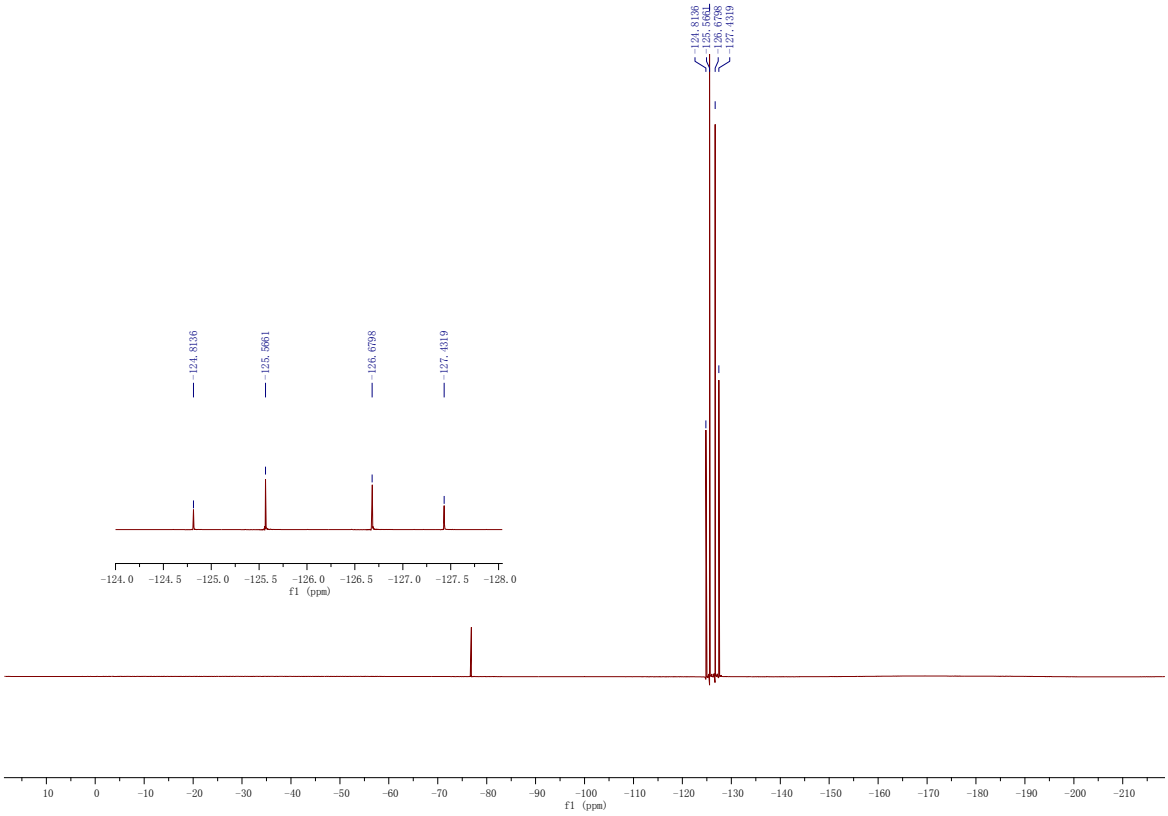

13C NMR
HO
CF2H
3l

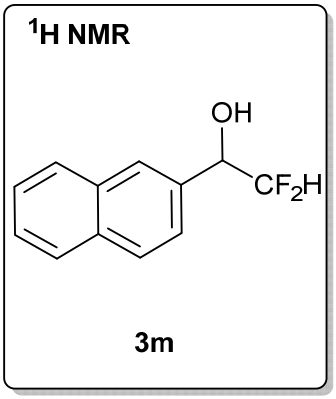

133.80
133.79
131.79
131.77
131.75
131.72
130.99
129.65
129.64
129.07
129.05
129.03
126.72
126.69
126.66
125.96
125.94
125.91
125.36
125.32
125.25
125.23
125.22
125.21
122.97
122.96
118.32
115.88
115.87
115.43
77.37
77.05
76.73
76.85
70.82
70.59
70.36
f1 (ppm)

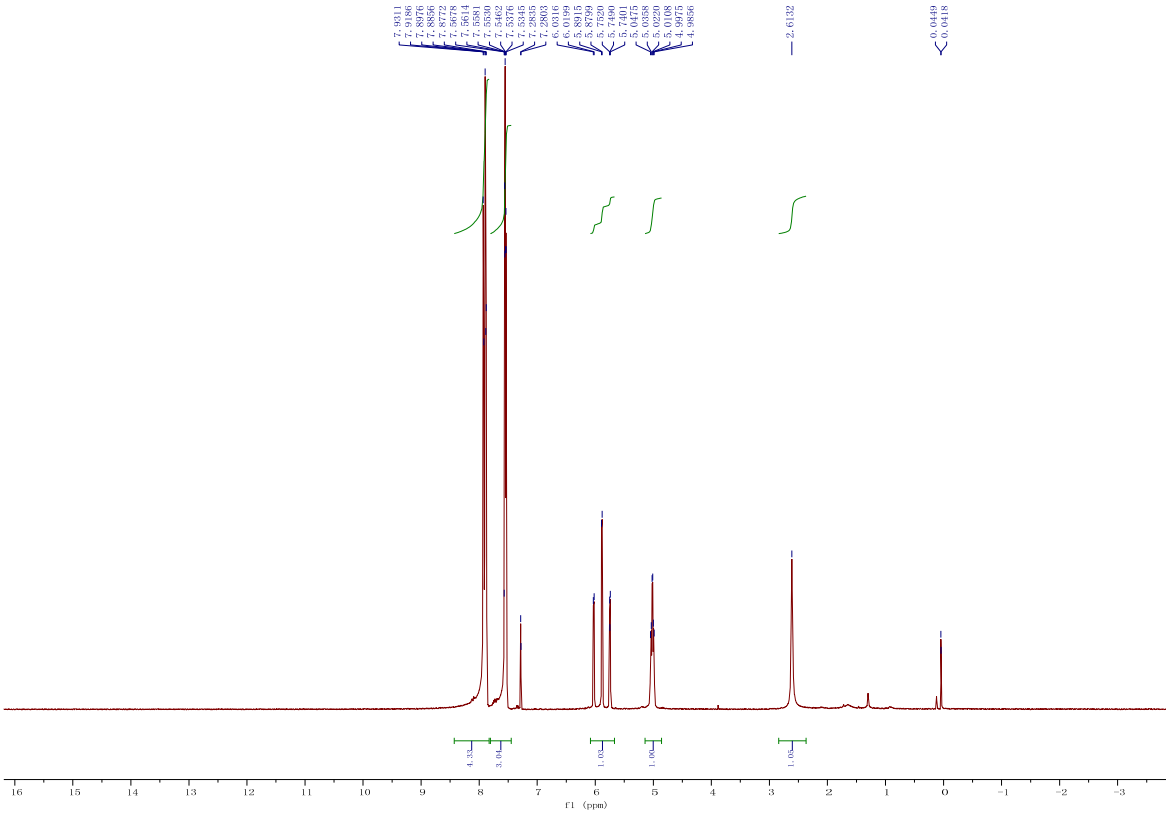
^{19}F NMR

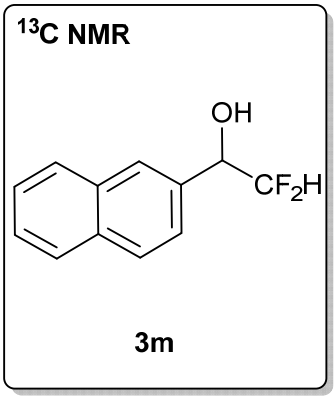

HO
CF2H

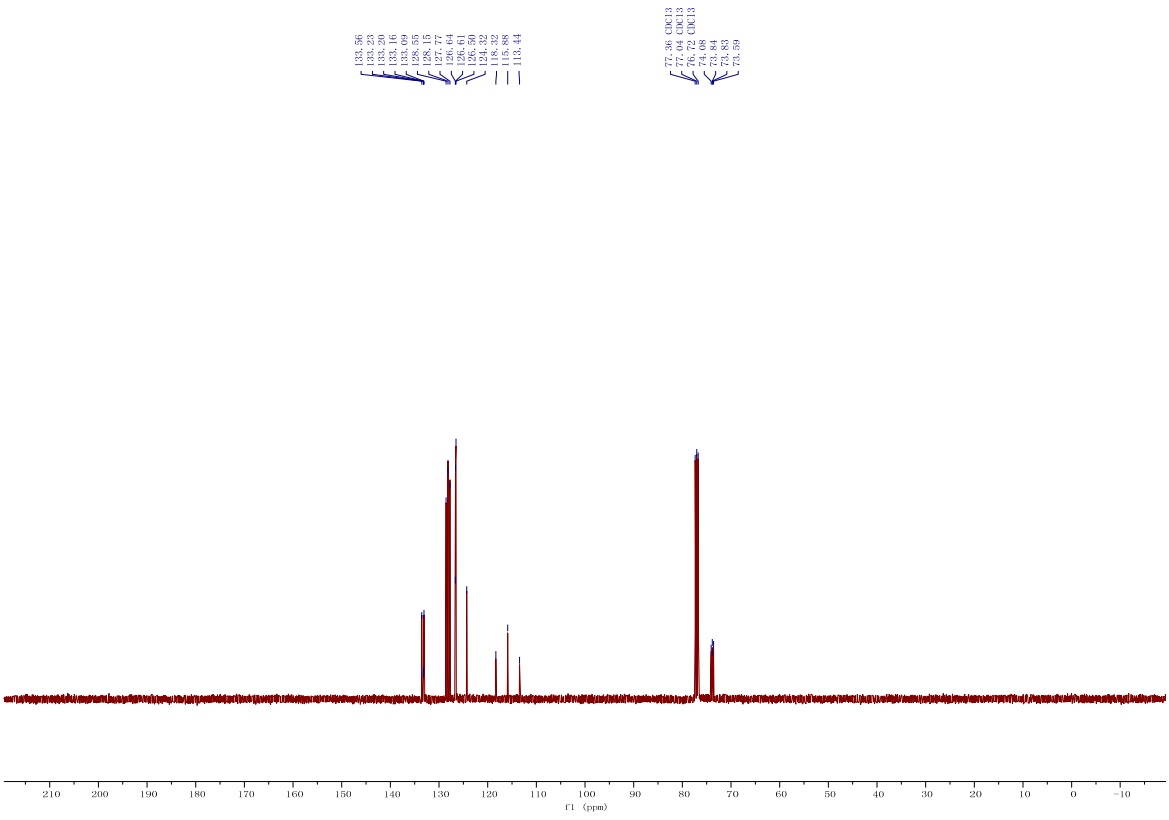
3l


-124.8136
-125.5661
-126.6798
-127.4319
-124.0
-124.5
-125.0
-125.5
-126.0
-126.5
-127.0
-127.5
-128.0
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

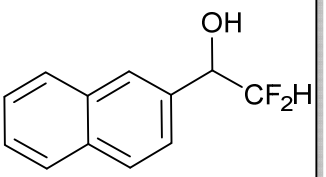

1H NMR
OH
CF2H
3m


7.9311
7.9196
7.8975
7.8856
7.8772
7.8678
7.8614
7.8561
7.5530
7.5462
7.5376
7.5345
7.2935
7.2803
6.0316
6.0199
5.8915
5.8799
5.7529
5.7490
5.7401
5.6475
5.6358
5.0229
5.0108
4.9975
4.9886
2.6132
0.0449
0.0418
4.33
3.04
1.03
1.00
1.00
f1 (ppm)

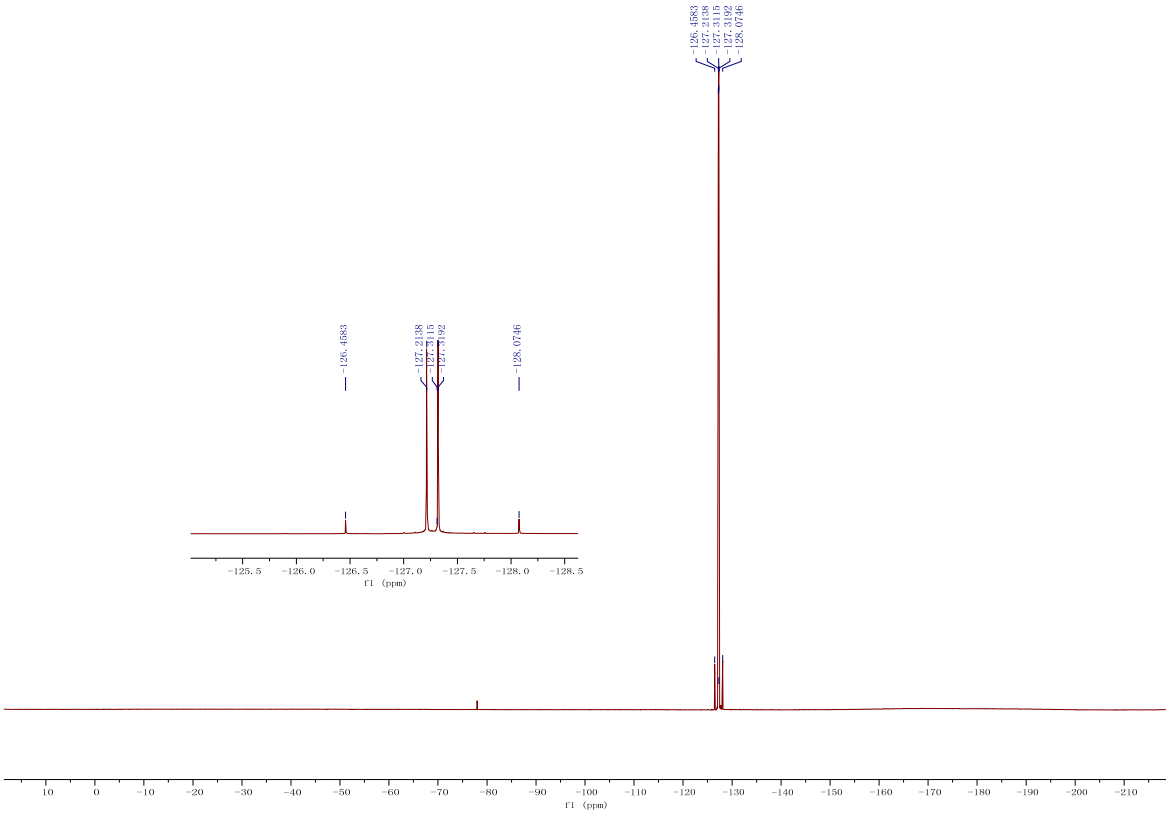

13C NMR
OH
CF2H
3m


133.56
133.23
133.20
132.45
131.09
128.55
128.15
127.77
126.64
126.61
126.50
124.32
118.32
115.98
113.44
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
74.08
73.84
73.83
73.59
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

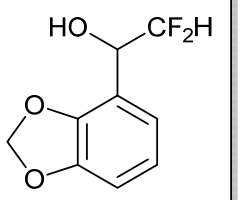
^{19}F NMR


OH
CF2H

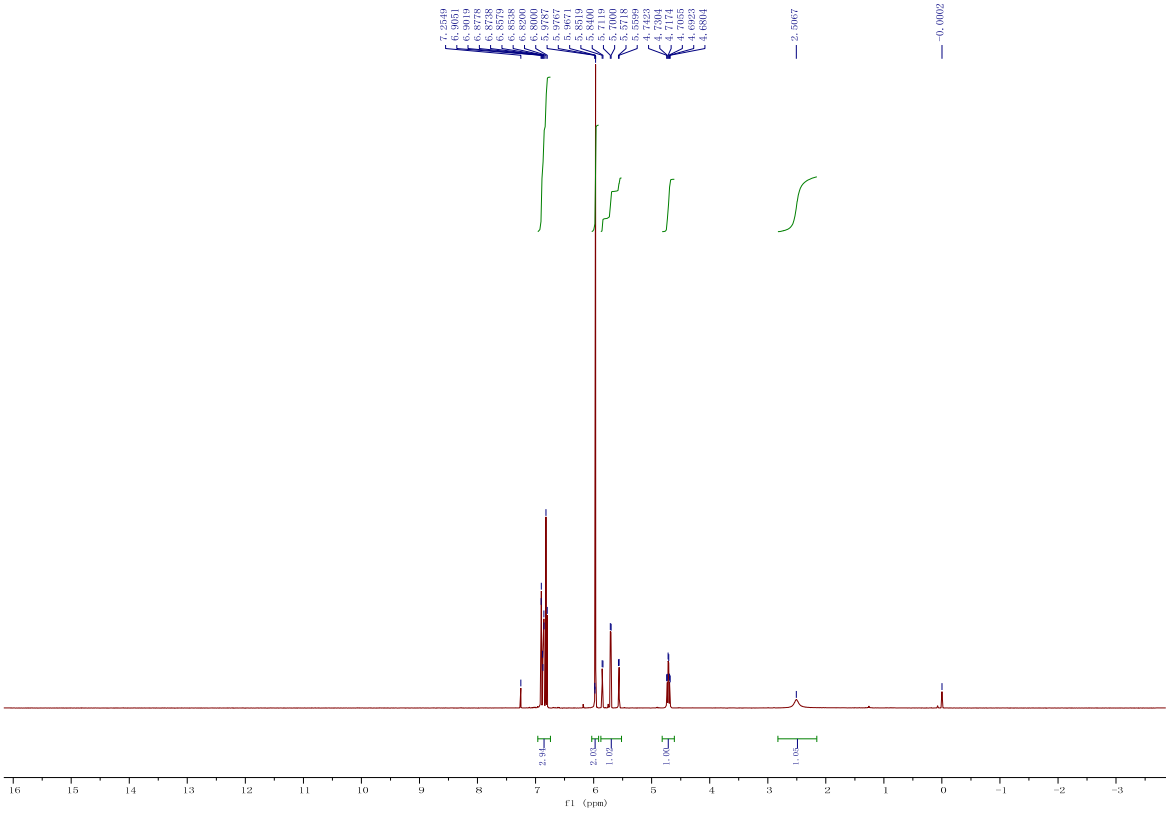
3m

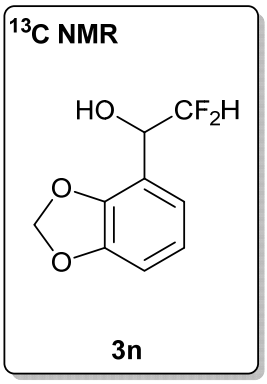

-126.4583
-127.2138
-127.3115
-127.3192
-128.0746
-125.5
-126.0
-126.5
-127.0
-127.5
-128.0
-128.5
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

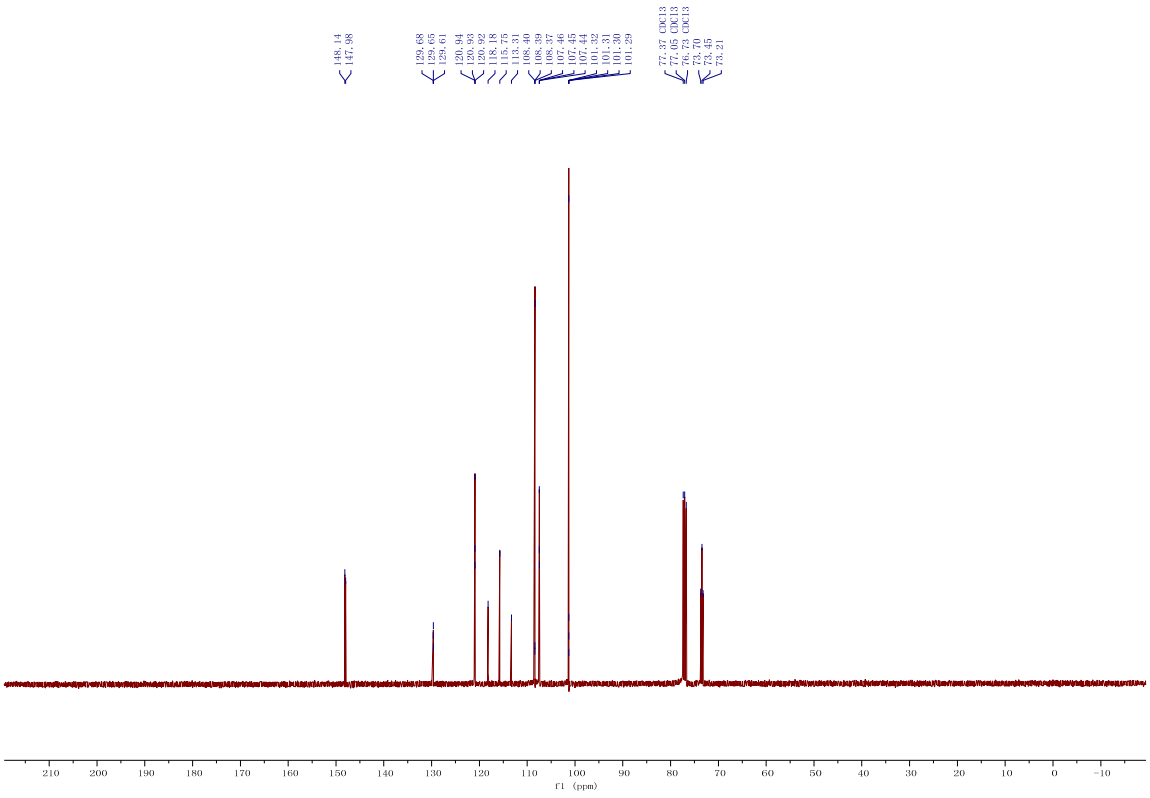
^{1}H NMR


HO
CF2H
O
O

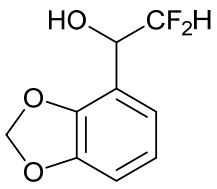
3n


7.2549
6.9051
6.9019
6.8778
6.8728
6.8579
6.8538
6.8200
6.8000
5.9787
5.9767
5.9671
5.8819
5.8400
5.7419
5.7000
5.5718
5.5399
4.7353
4.7204
4.7174
4.7055
4.6923
4.6804
2.5067
0.0002
2.94
2.02
1.02
1.00
1.05
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

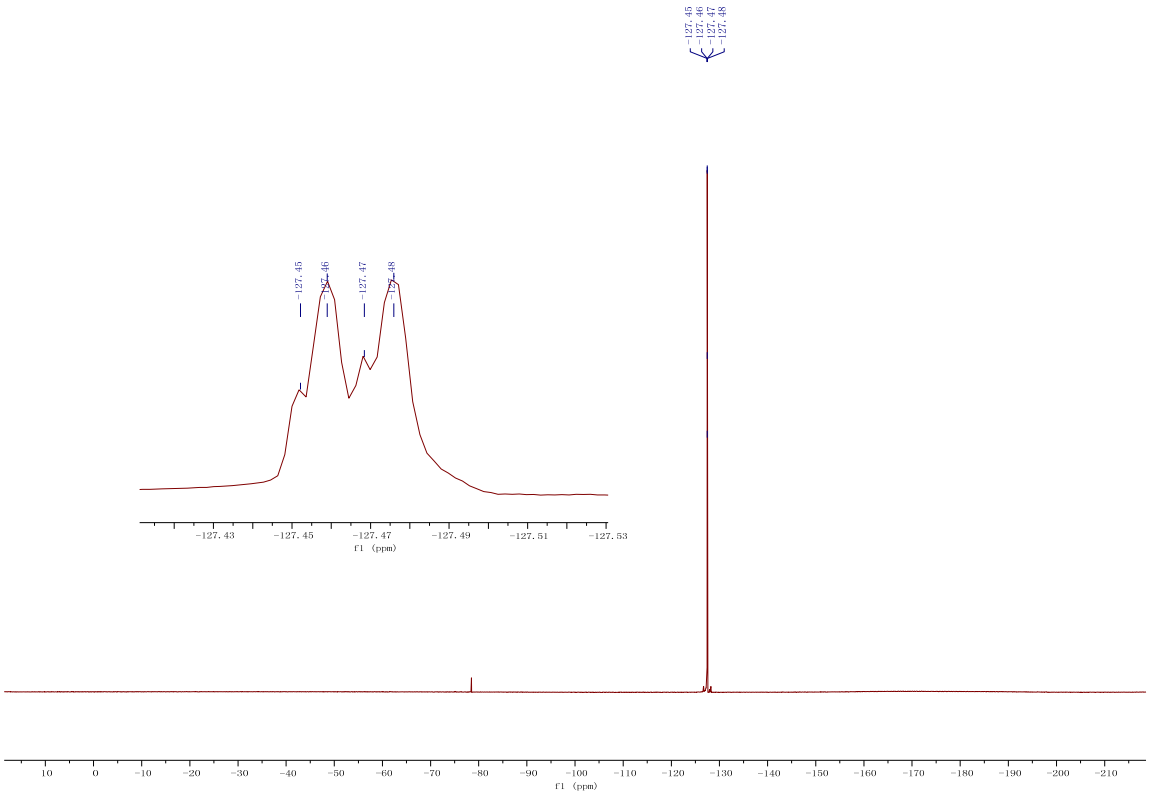

13C NMR
HO
CF2H
O
O
3n


148.14
147.98
129.68
129.65
129.61
120.94
120.93
120.92
118.18
115.75
113.31
108.40
108.39
108.37
107.46
107.45
107.44
101.32
101.31
101.30
101.29
77.37 CDCl3
77.05 CDCl3
76.73 CDCl3
73.70
73.45
72.21
f1 (ppm)

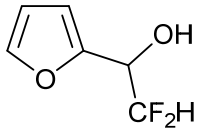
^{19}F NMR


HO
CF2H
O
O

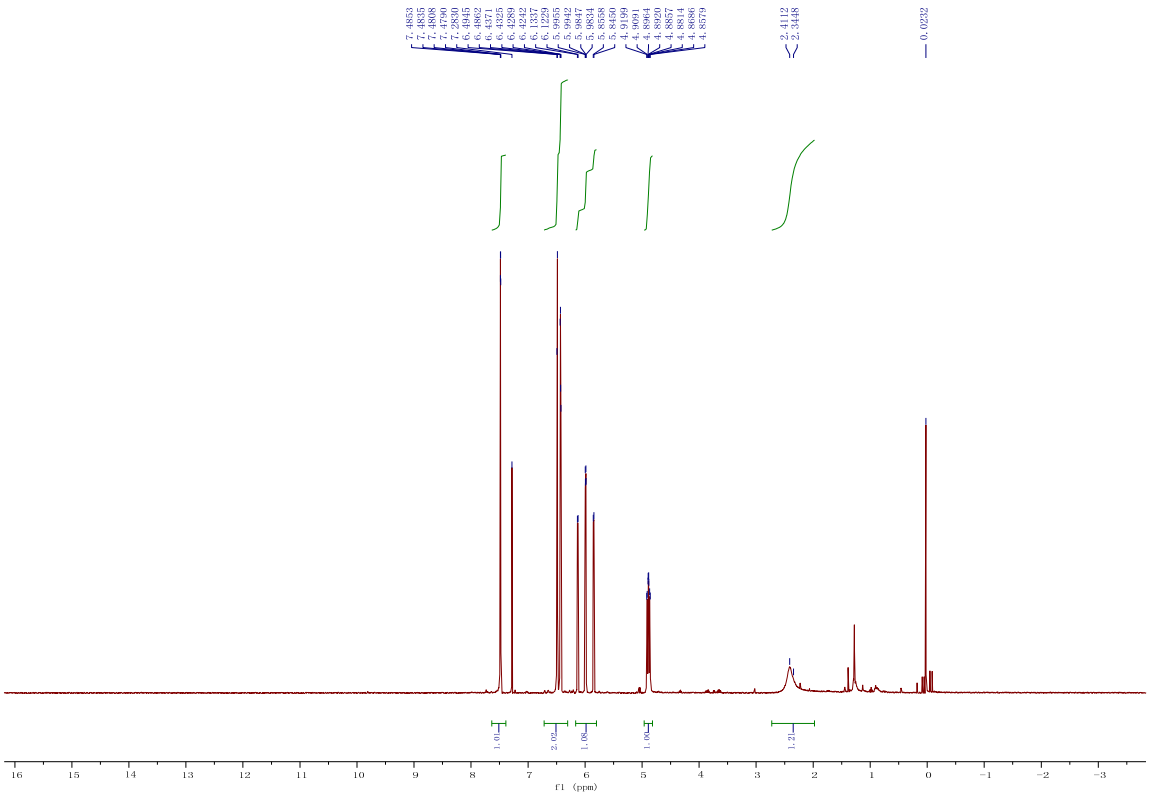
3n


-127.45
-127.46
-127.47
-127.48
-127.43
-127.45
-127.47
-127.49
-127.51
-127.53
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

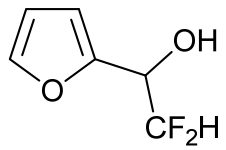
^{1}H NMR


OH
O
CF2H

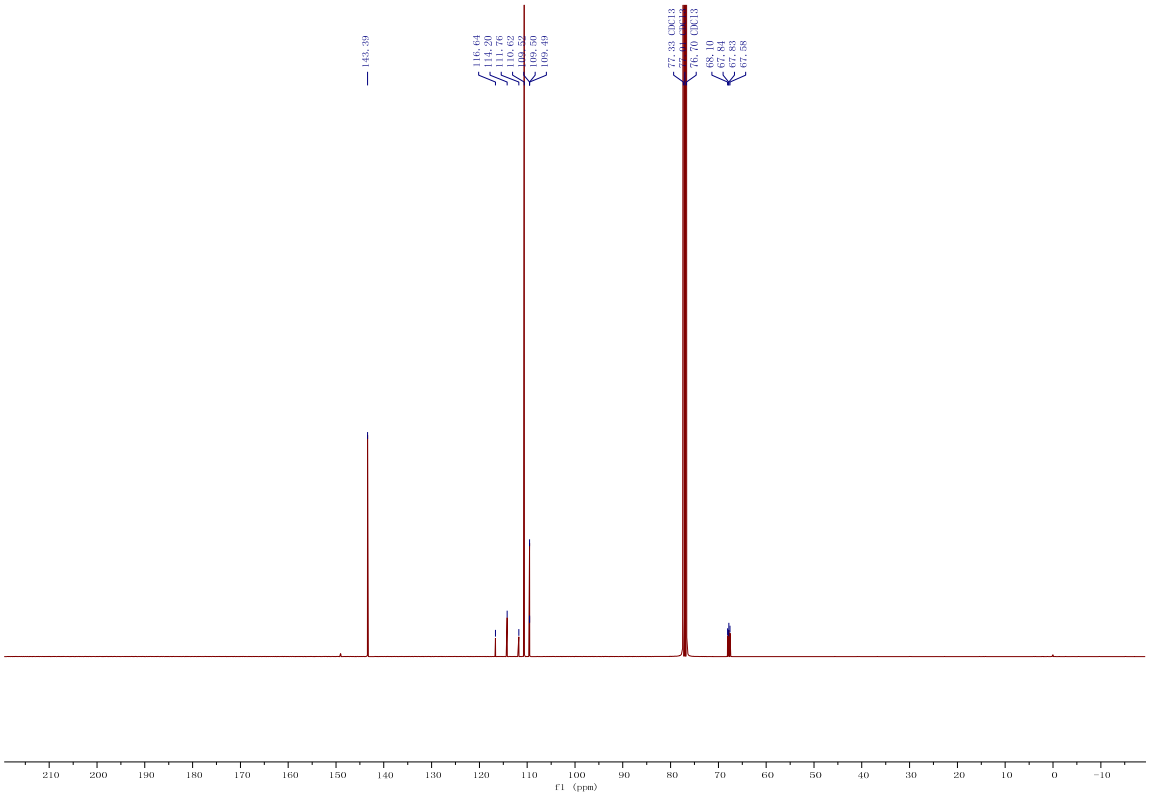
3o


7.4853
7.4835
7.4808
7.4790
7.4780
7.4745
6.4862
6.4371
6.4335
6.4289
6.4252
6.1337
6.1229
5.9955
5.9942
5.9847
5.9834
5.8558
5.8450
4.9199
4.9041
4.8964
4.8920
4.8857
4.8814
4.8696
4.8579
2.4112
2.3448
0.0232
1.01
2.02
1.08
1.04
1.21
f1 (ppm)

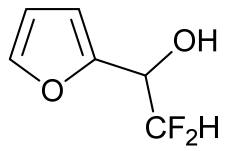
^{13}C NMR


OH
O
CF2H

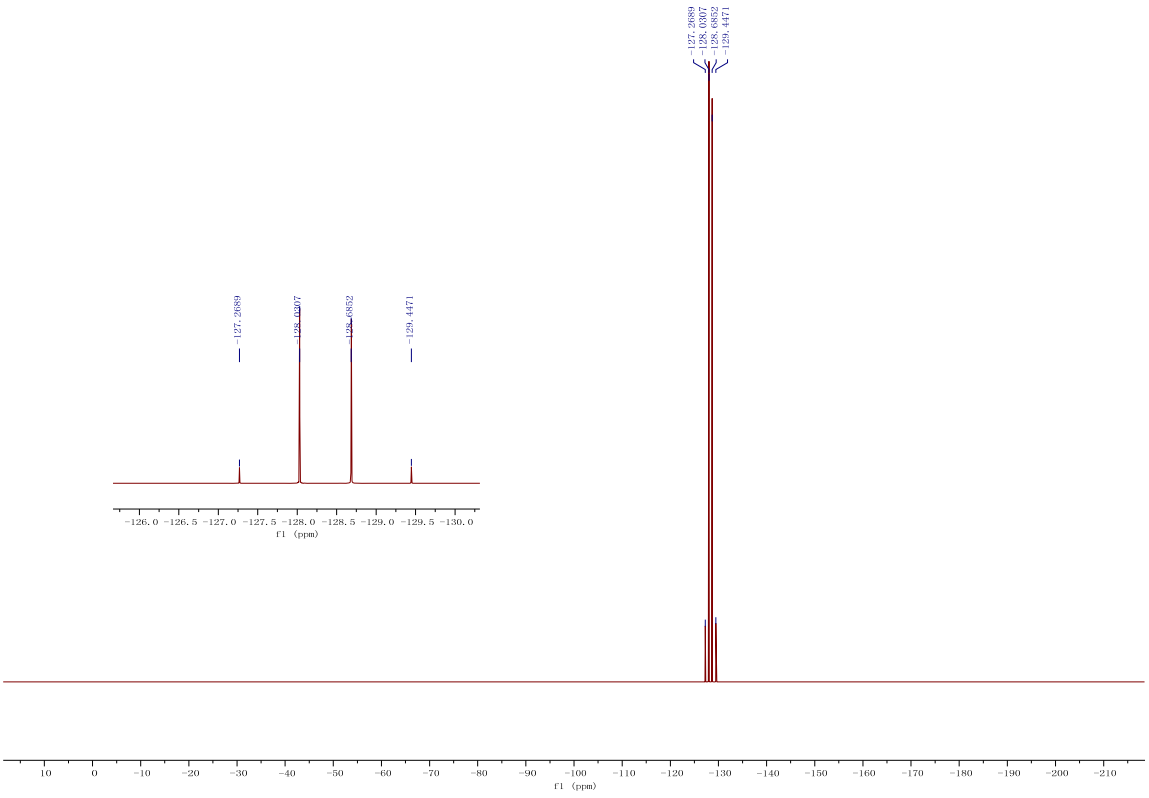
3o


143.39
116.64
114.20
111.76
110.62
109.50
109.49
77.33 CDCl3
76.70 CDCl3
68.10
67.84
67.83
67.58
f1 (ppm)

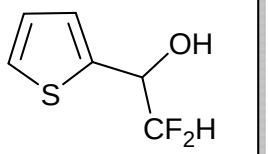
^{19}F NMR


OH
O
CF2H

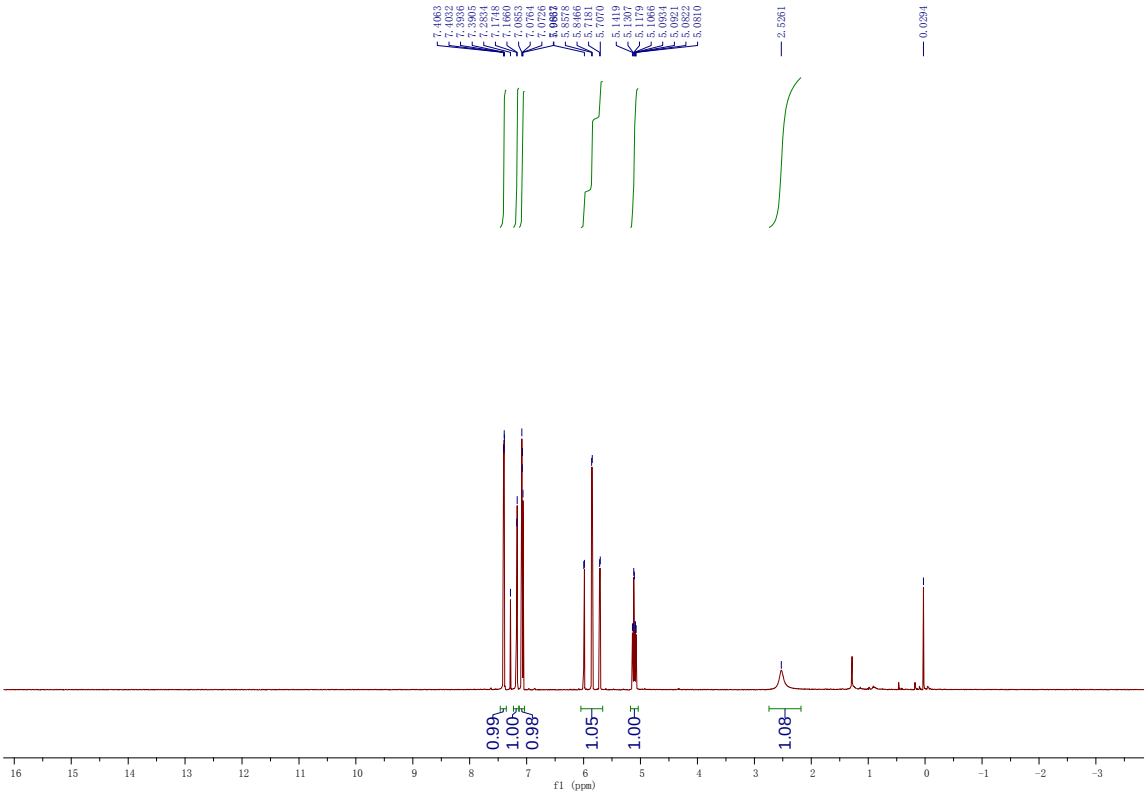
3o


-127.2689
-128.0307
-128.6852
-129.4471
-126.0 -126.5 -127.0 -127.5 -128.0 -128.5 -129.0 -129.5 -130.0
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

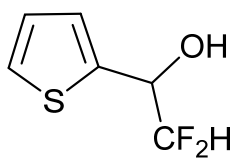
^{1}H NMR


OH
S
CF2H

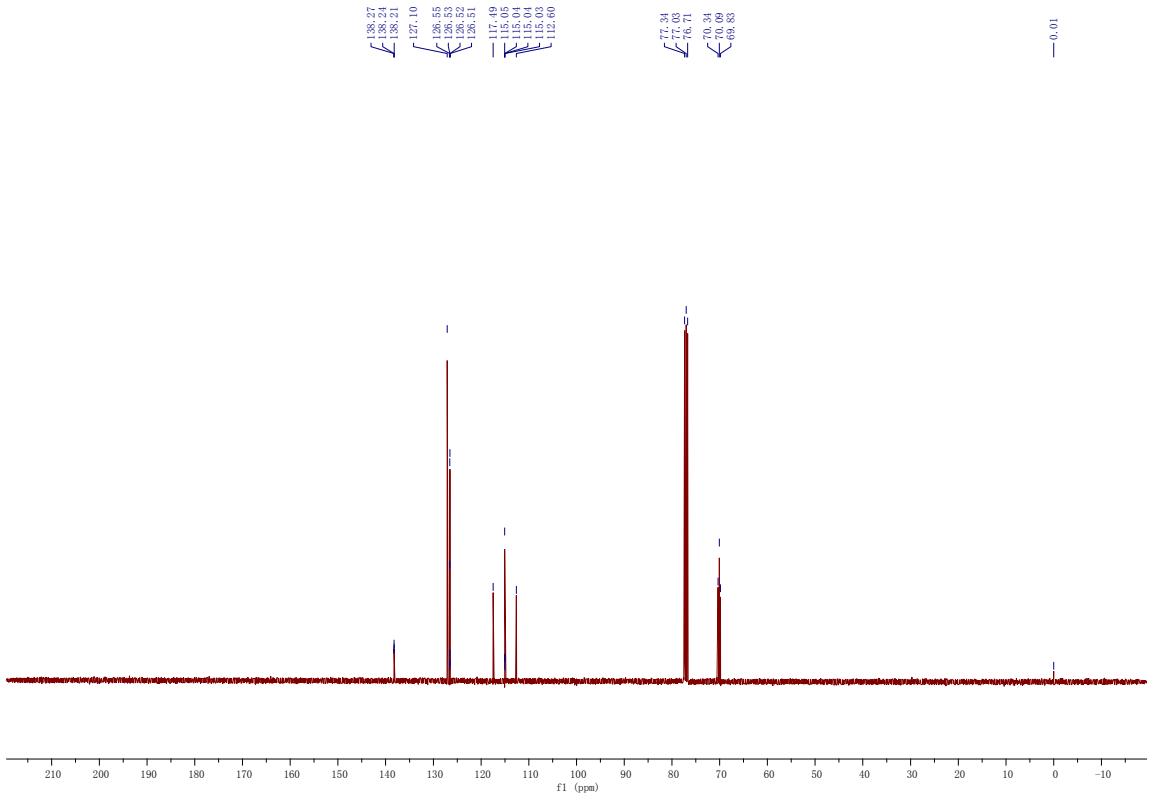
3p


7.4063
7.4032
7.3936
7.3905
7.2834
7.1748
7.1460
7.0853
7.0764
7.0726
5.8573
5.8496
5.7181
5.7070
5.1419
5.1307
5.1179
5.1066
5.0954
5.0921
5.0822
5.0810
2.5261
0.0294
0.99
1.00
0.98
1.05
1.00
1.08
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)

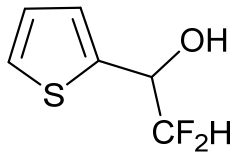
^{13}C NMR


OH
S
CF_2H

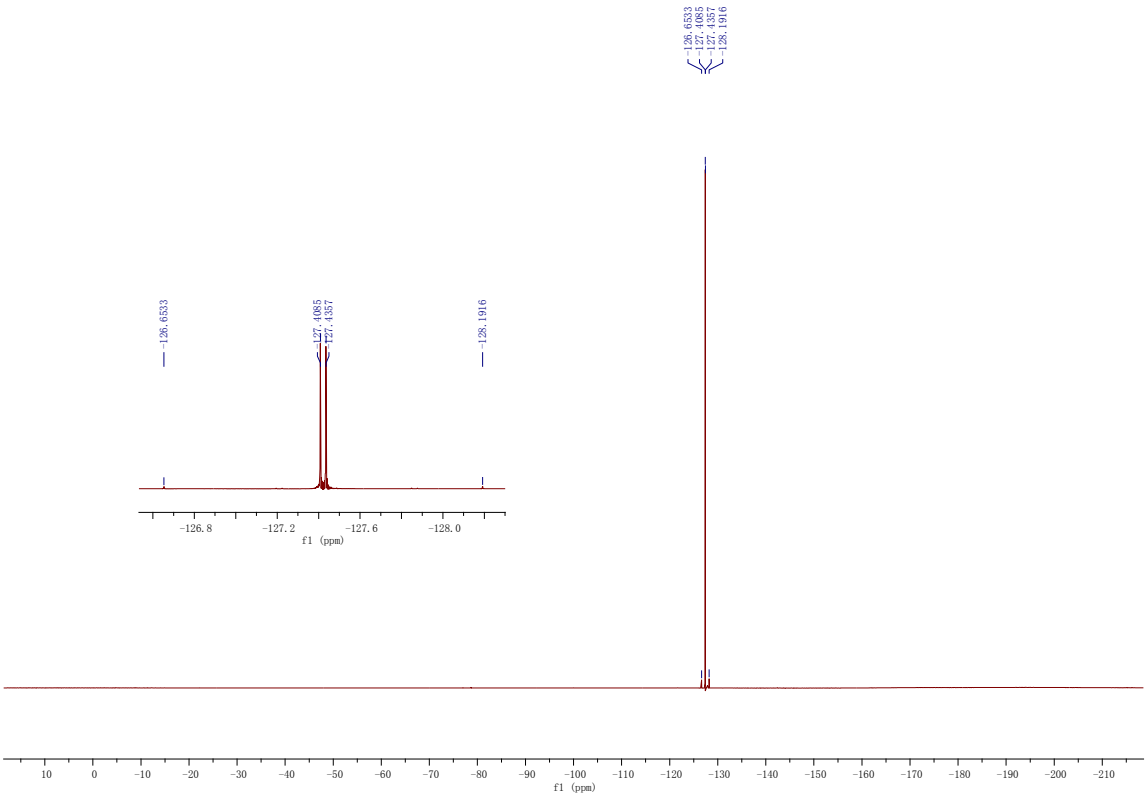
3p


138.27
138.24
138.21
127.10
126.55
126.53
126.52
126.51
117.49
115.05
115.04
115.03
112.60
77.34
77.03
76.71
70.34
70.09
69.83
0.01
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

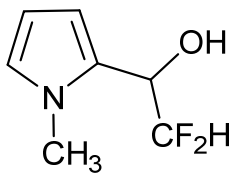
^{19}F NMR


OH
S
CF2H

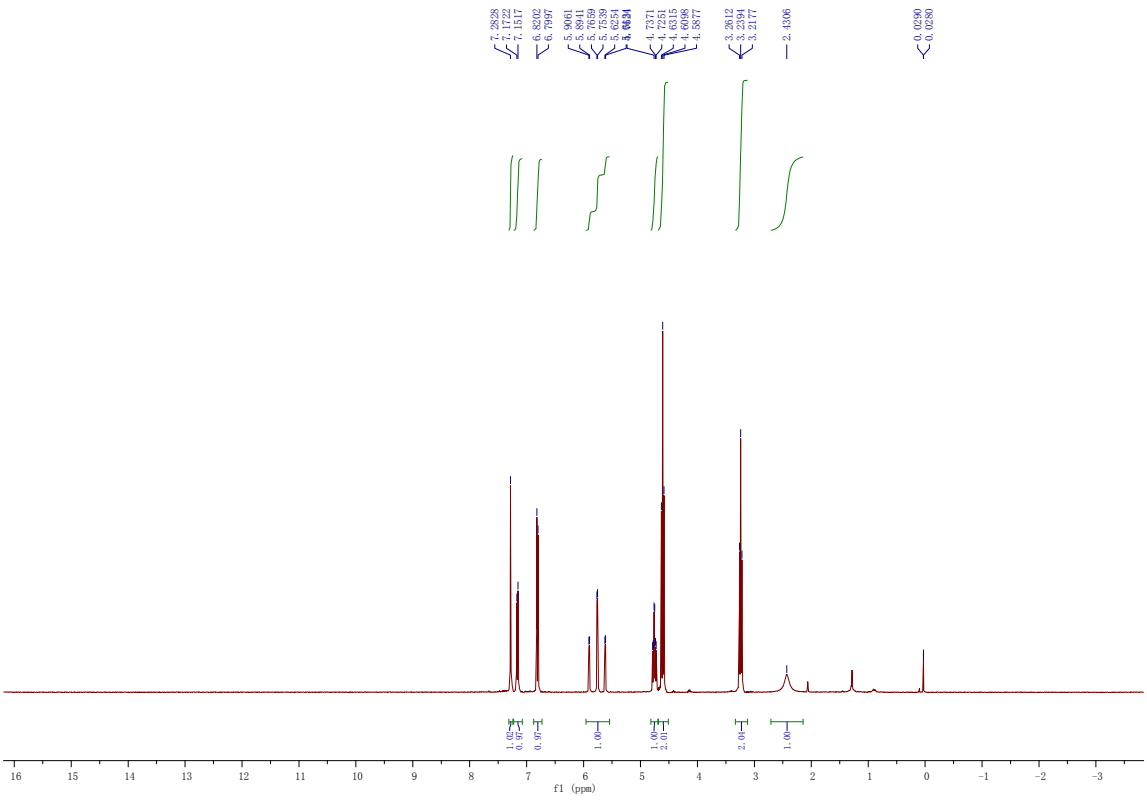
3p


-126.6533
-127.4085
-127.4357
-128.1916
-126.6533
-127.4085
-127.4357
-128.1916
-126.8
-127.2
-127.6
-128.0
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

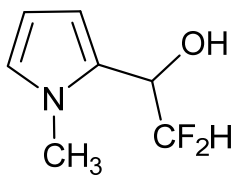
^{1}H NMR


OH
N
CH3
CF2H

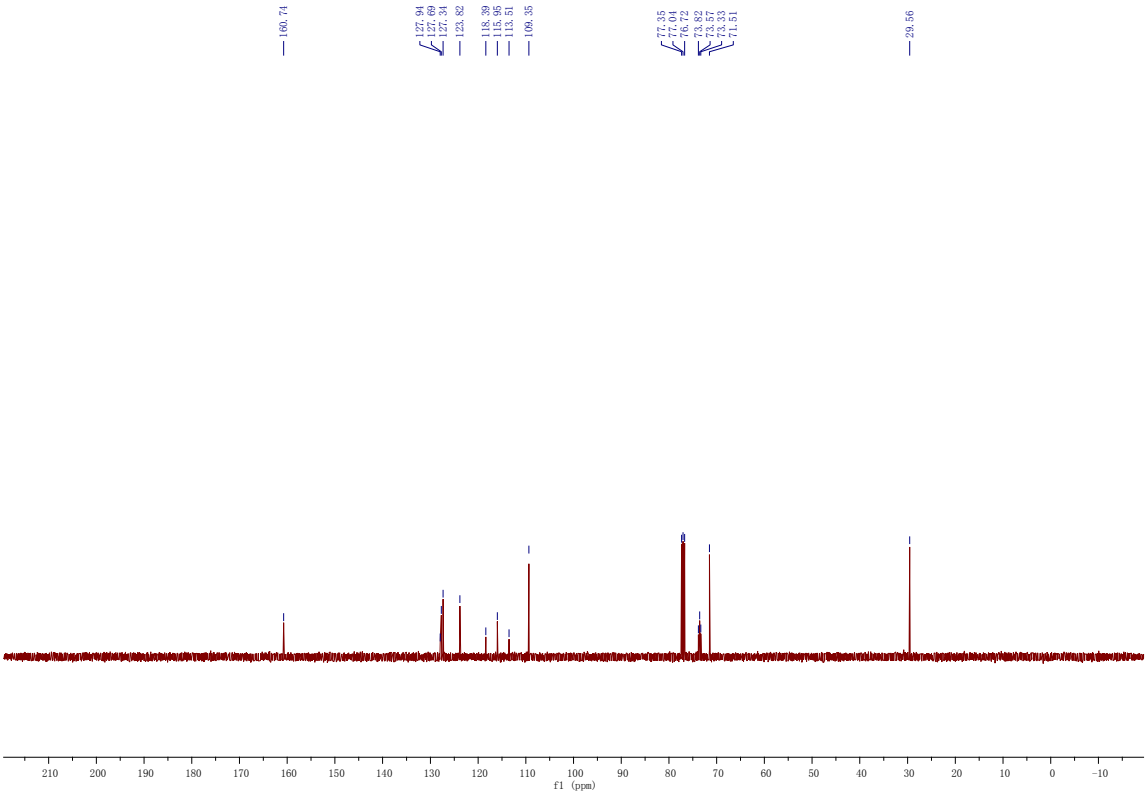
3q


7.2838
7.1722
7.1517
6.8202
6.7997
5.9061
5.8944
5.7678
5.7539
5.6254
4.7371
4.7251
4.6315
4.6098
4.5877
3.2612
3.2394
3.2177
2.4306
0.0290
0.0280
1.03
0.97
0.97
1.00
1.00
2.01
2.04
1.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)

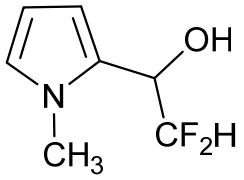
^{13}C NMR


OH
N
CH3
CF2H

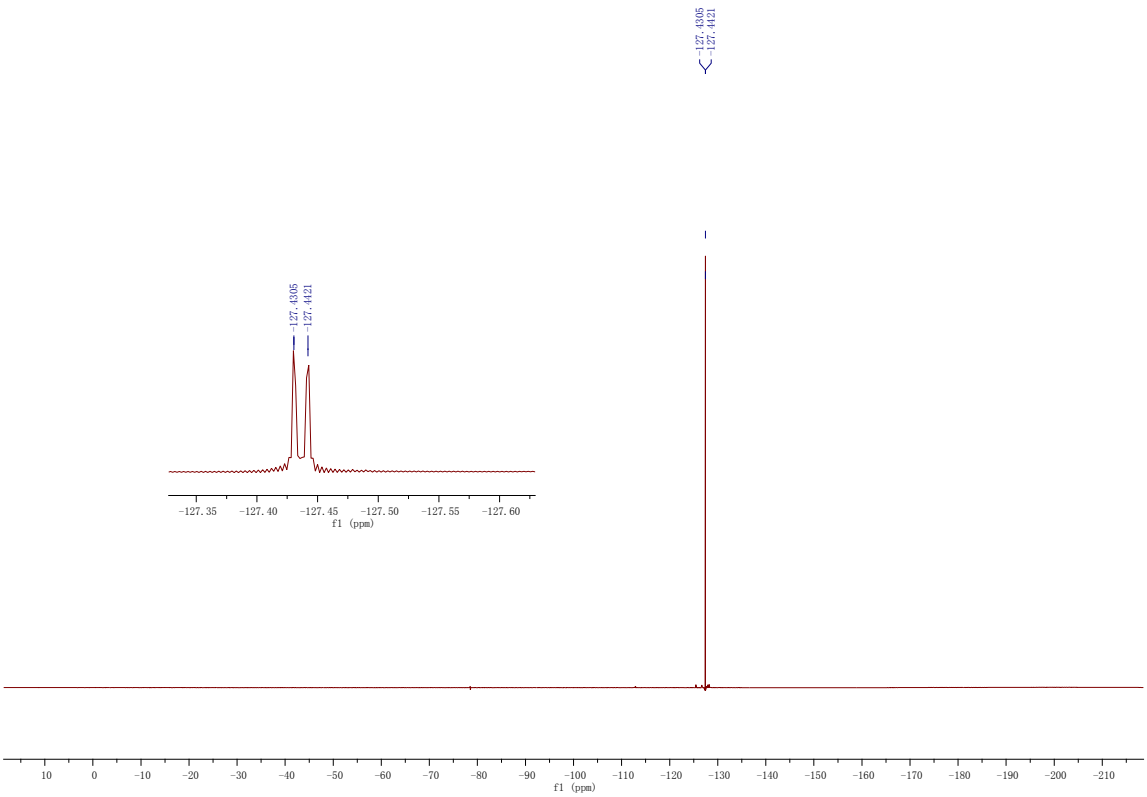
3q


160.74
127.94
127.69
127.34
123.82
118.39
115.95
113.51
109.35
77.35
77.04
76.72
73.82
73.57
73.33
71.51
29.56
f1 (ppm)

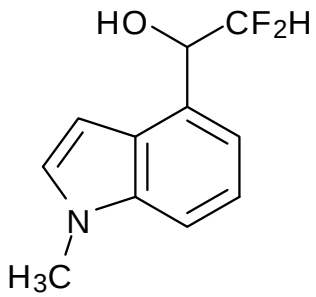
^{19}F NMR


OH
N
CH3
CF2H

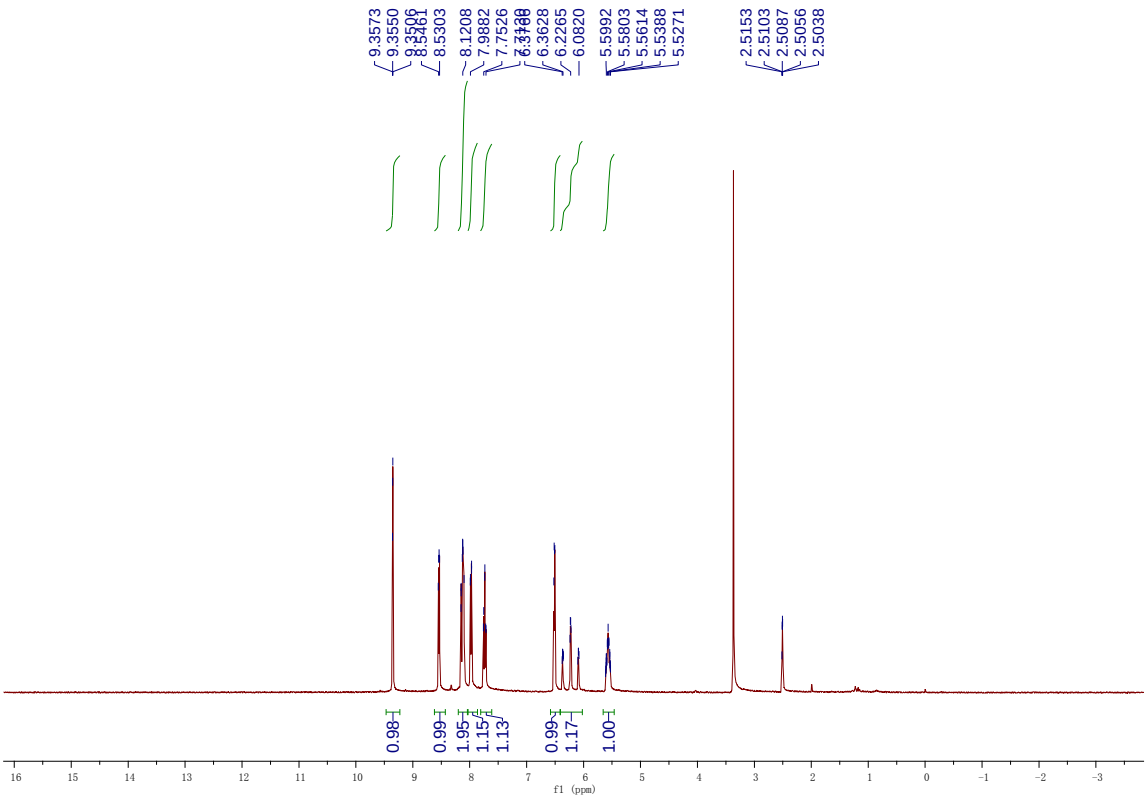
3q

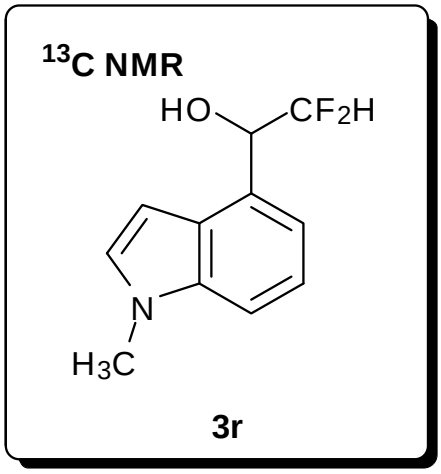

-127.4305
-127.4421
-127.4305
-127.4421
-127.35
-127.40
-127.45
-127.50
-127.55
-127.60
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

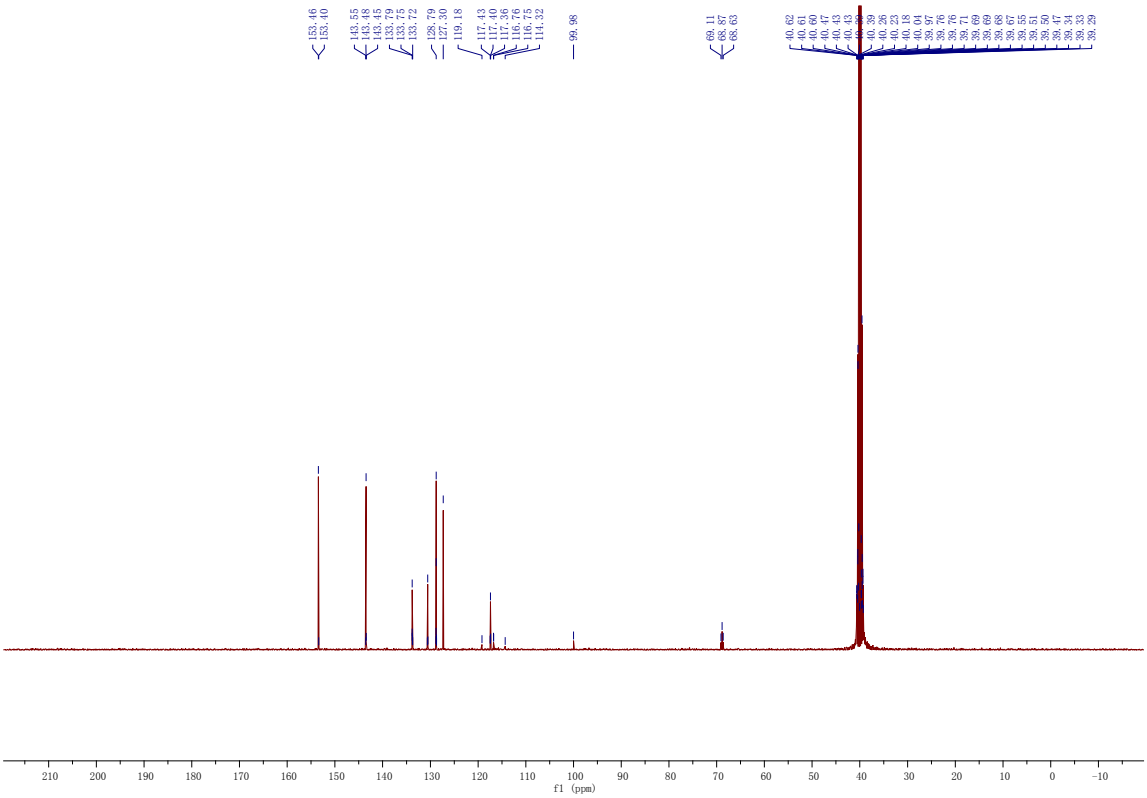
^{1}H NMR


HO
CF2H
N
H3C

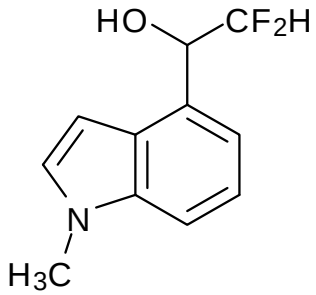
3r


9.3573
9.3550
8.5303
8.1208
7.9882
7.7526
6.3628
6.2265
6.0820
5.5992
5.5803
5.5614
5.5388
5.5271
2.5153
2.5103
2.5087
2.5056
2.5038
0.98
0.99
1.95
1.15
1.13
0.99
1.17
1.00
f1 (ppm)

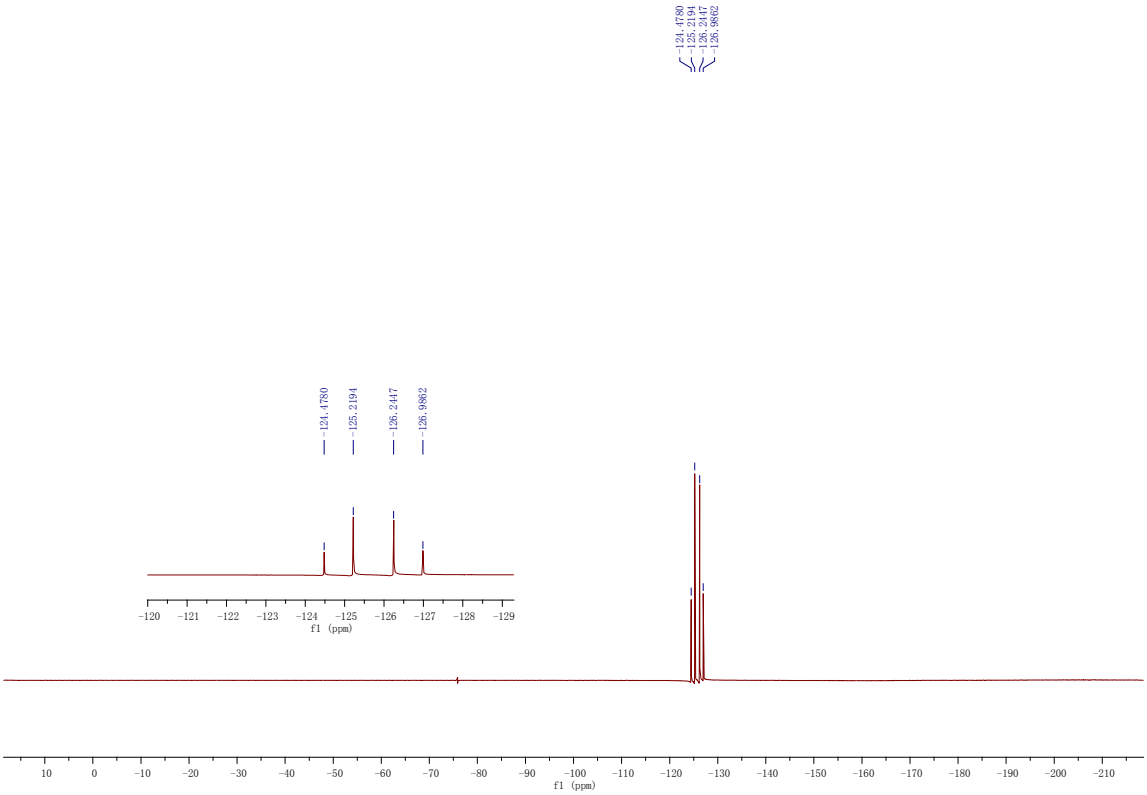

13C NMR
HO
CF2H
N
H3C
3r


153.46
153.40
143.55
143.48
143.45
133.79
133.75
133.72
128.79
127.30
119.18
117.43
117.40
117.36
116.76
116.75
114.32
99.98
69.11
68.87
68.63
40.62
40.61
40.60
40.47
40.43
40.39
40.26
40.23
40.18
40.04
39.97
39.76
39.76
39.71
39.69
39.69
39.68
39.67
39.55
39.51
39.50
39.47
39.34
39.33
39.29
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

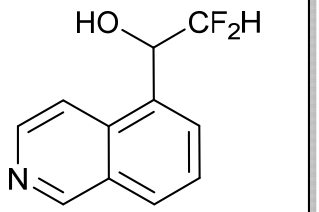
^{19}F NMR


HO
CF2H
N
H3C

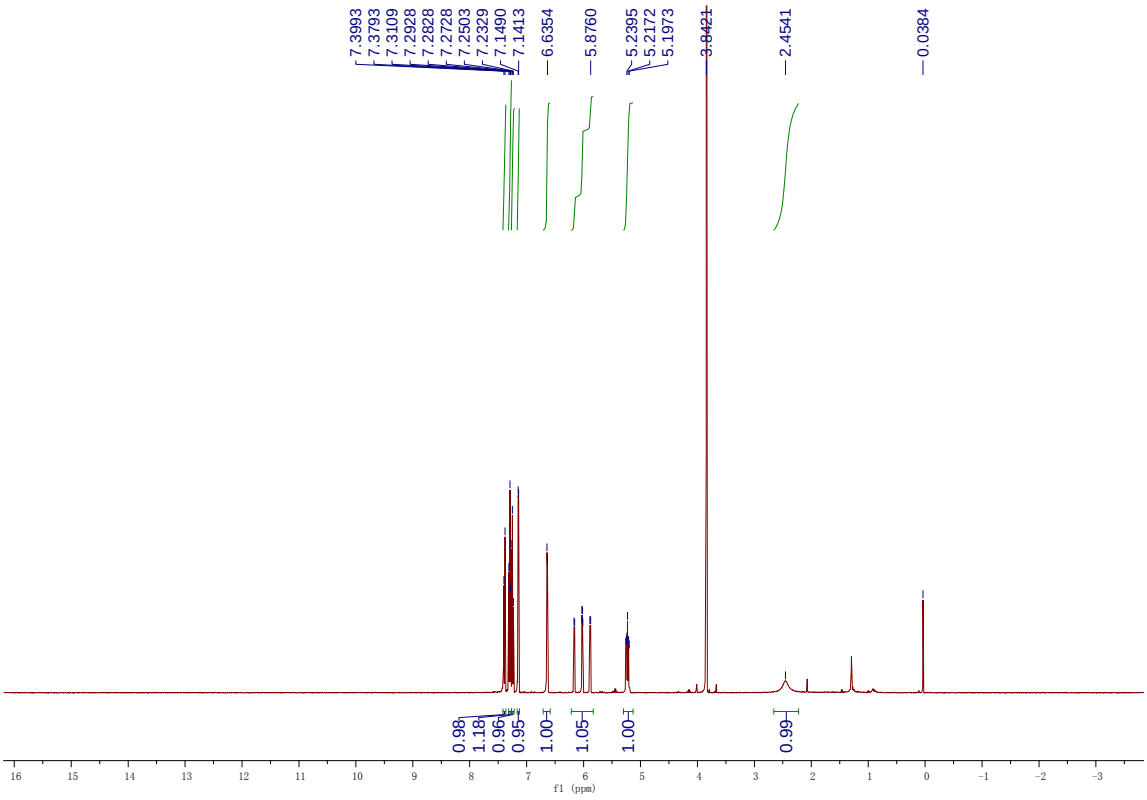
3r

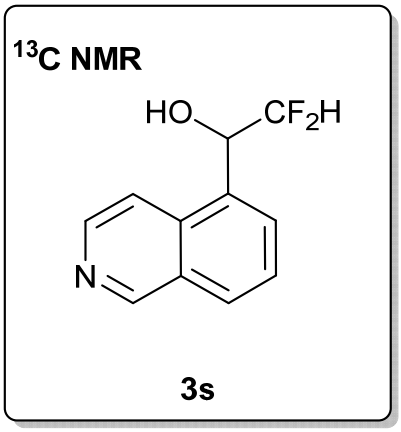

-124.4780
-125.2194
-126.2447
-126.9862
-120 -121 -122 -123 -124 -125 -126 -127 -128 -129
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

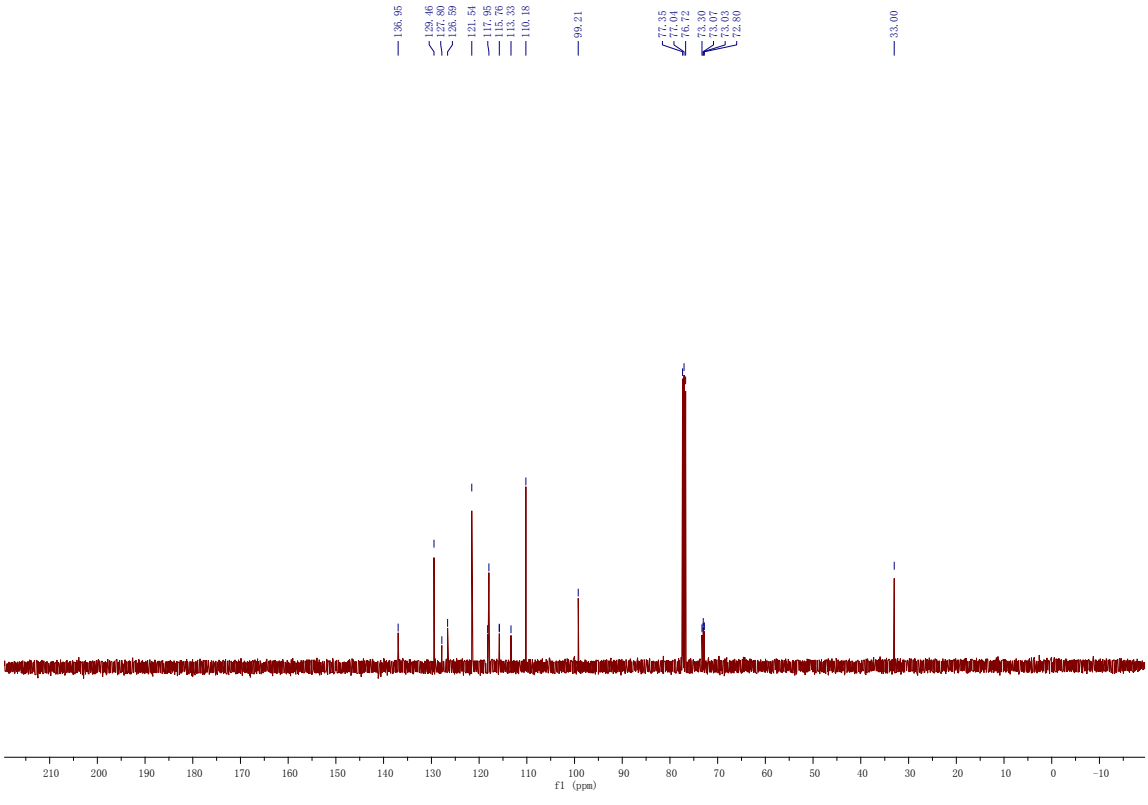
^{1}H NMR


HO
CF2H
N

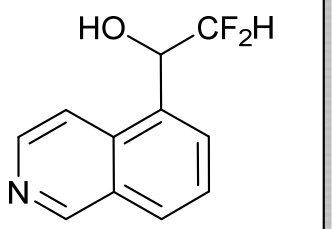
3s


7.3993
7.3793
7.3109
7.2928
7.2828
7.2728
7.2503
7.2329
7.1490
7.1413
6.6354
5.8760
5.2395
5.2172
5.1973
3.8421
2.4541
0.0384
0.98
1.18
0.96
0.95
1.00
1.05
1.00
0.99
f1 (ppm)

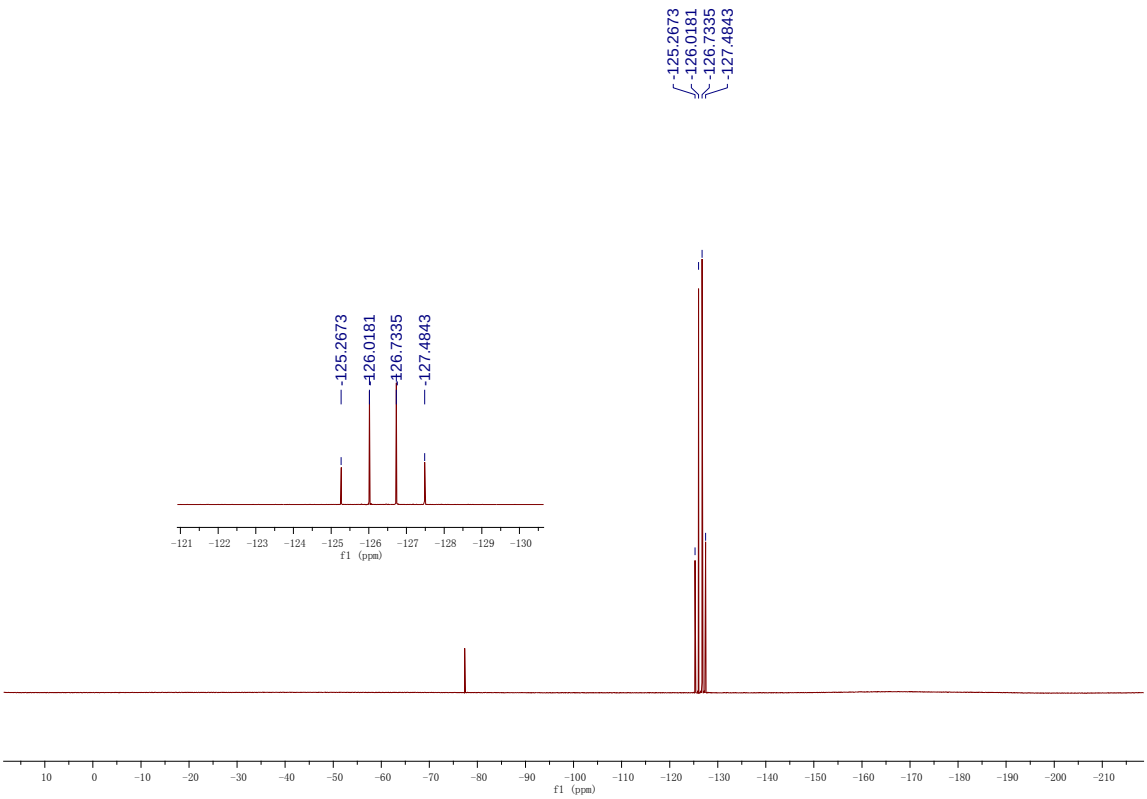

13C NMR
HO
CF2H
N
3s

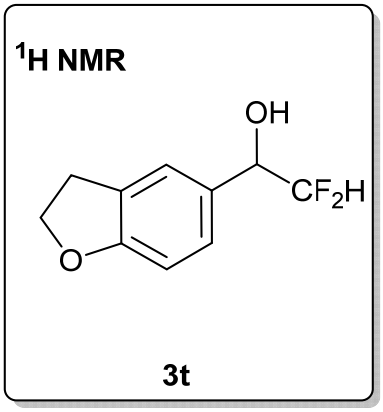

136.95
129.46
127.89
126.09
121.54
117.95
115.76
113.33
110.18
99.21
77.35
77.04
76.72
73.30
73.07
73.03
72.80
33.00
f1 (ppm)

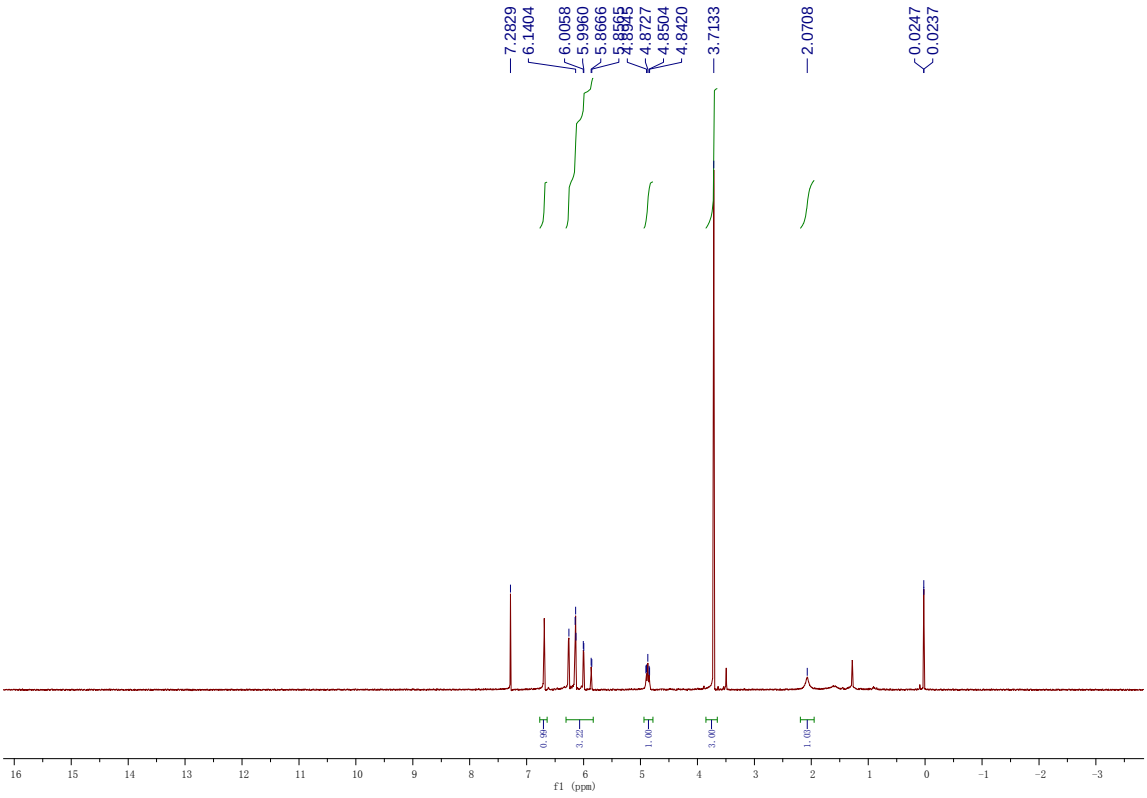
^{19}F NMR



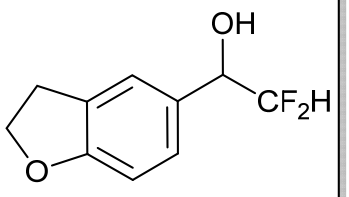
3s



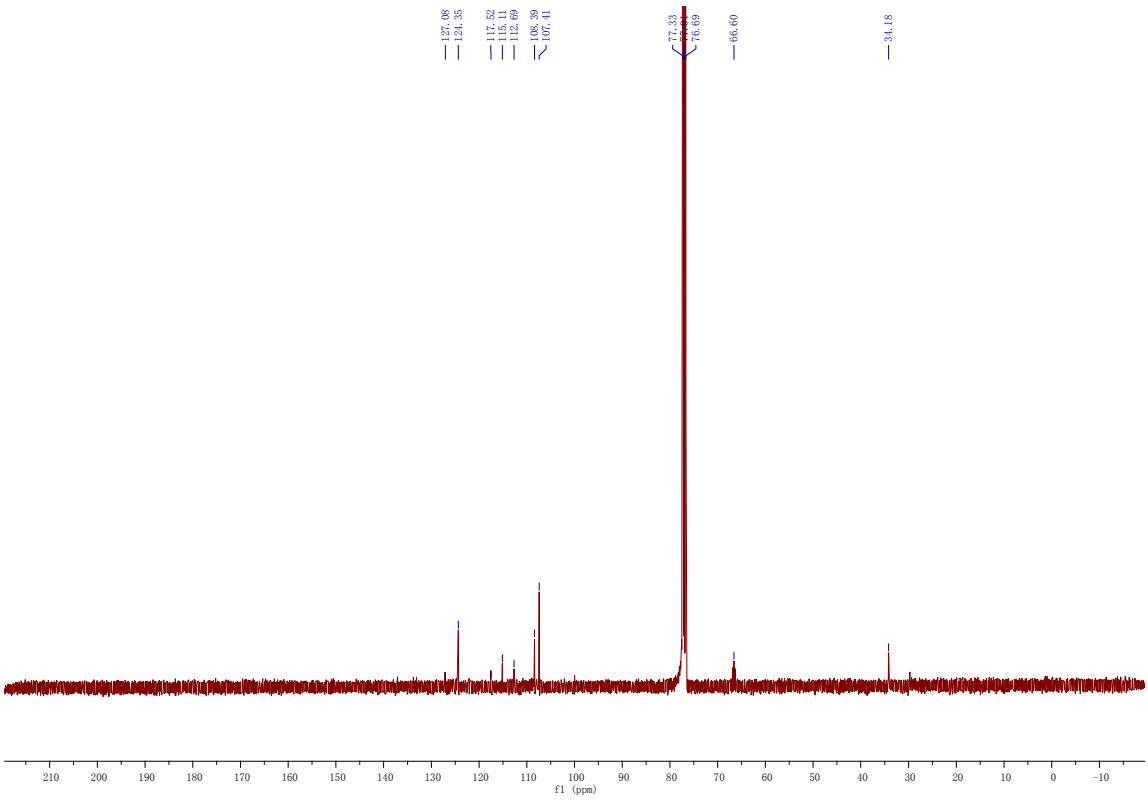

1H NMR
OH
CF2H
O
3t


7.2829
6.1404
6.0058
5.9960
5.8666
4.8727
4.8504
4.8420
3.7133
2.0708
0.0247
0.0237
0.99
3.22
1.00
3.00
1.03
f1 (ppm)

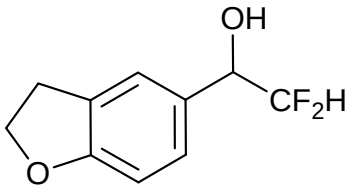
^{13}C NMR


OH
CF2H
O

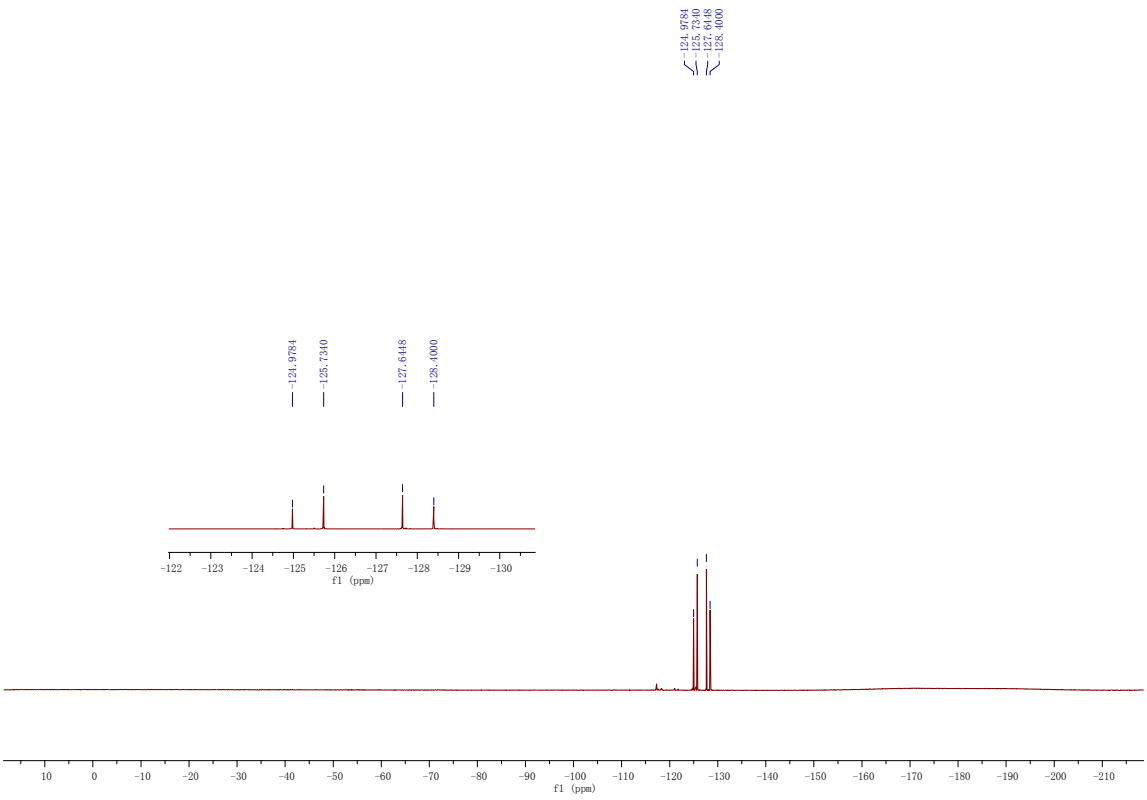
3t

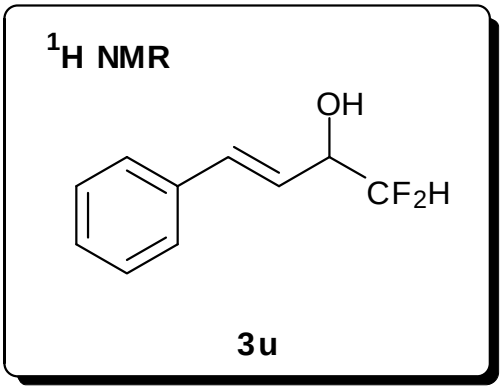

127.08
124.35
117.52
115.11
112.69
108.39
107.41
77.33
77.01
76.69
66.60
34.18
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

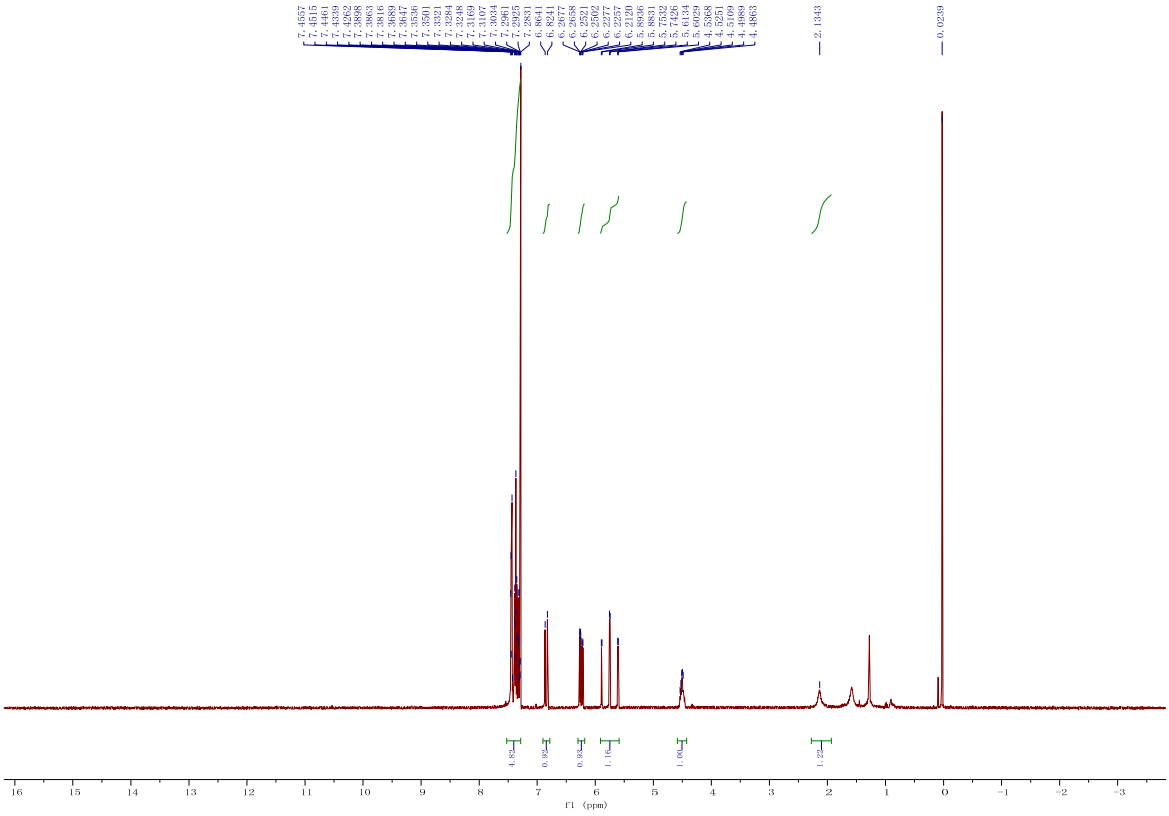
^{19}F NMR



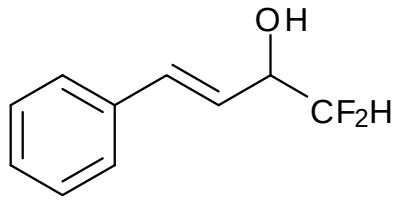
3t



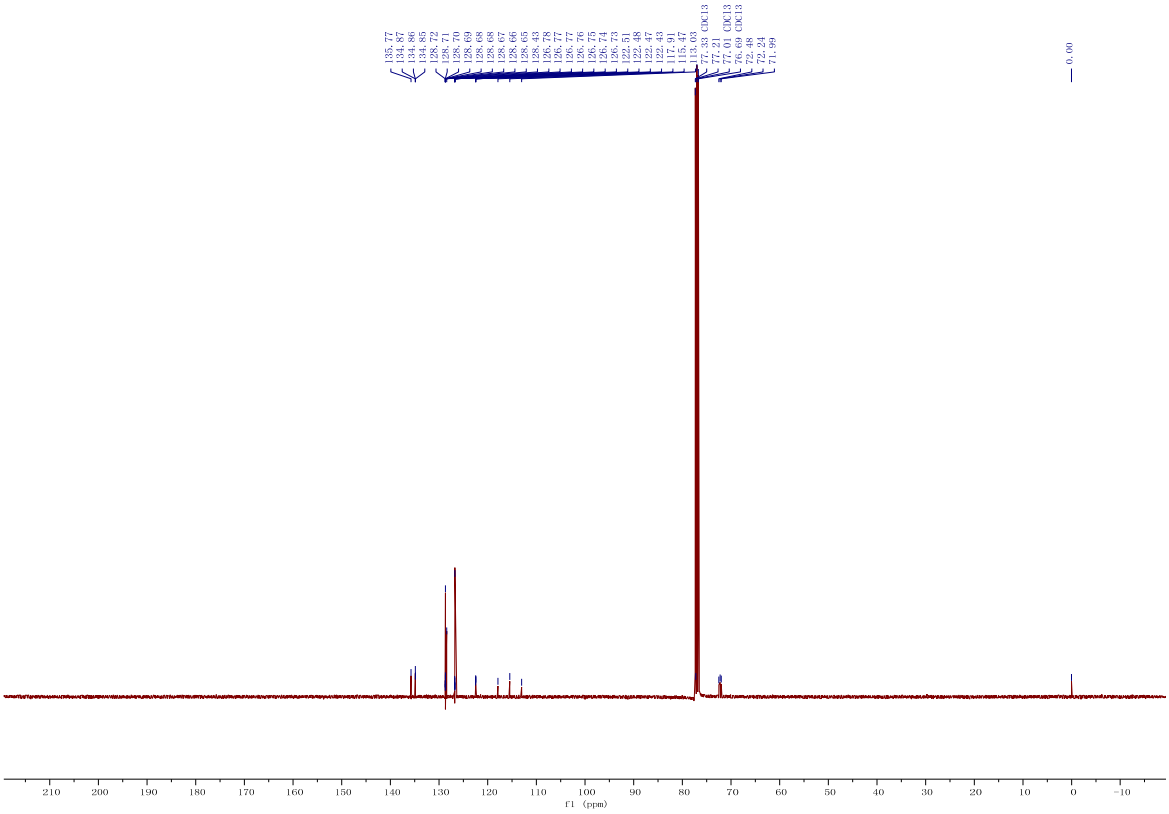

1H NMR
OH
CF2H
3u



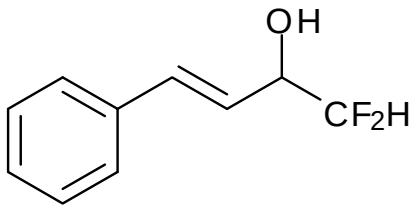
^{13}C NMR


OH
CF2H

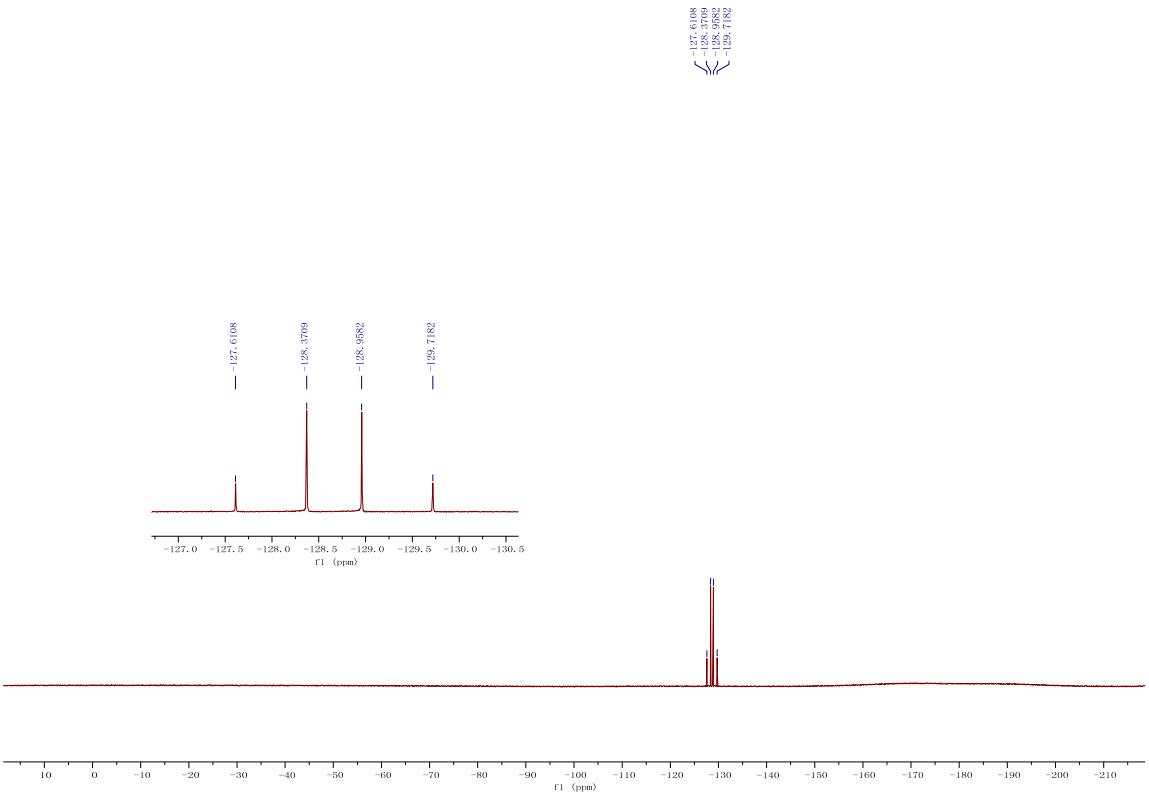
3u


135.77
134.87
134.86
134.85
134.72
128.71
128.70
128.69
128.68
128.66
128.67
128.66
128.65
128.43
126.78
126.77
126.77
126.76
126.75
126.74
126.73
122.51
122.48
122.47
122.43
117.91
115.47
113.03
77.33 CDCl3
77.01
77.01 CDCl3
76.69 CDCl3
72.48
72.24
71.99
0.00
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

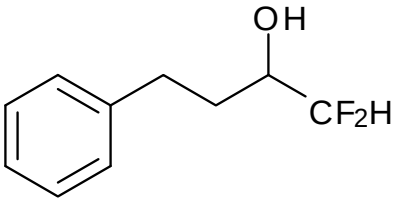
^{19}F NMR


OH
CF2H

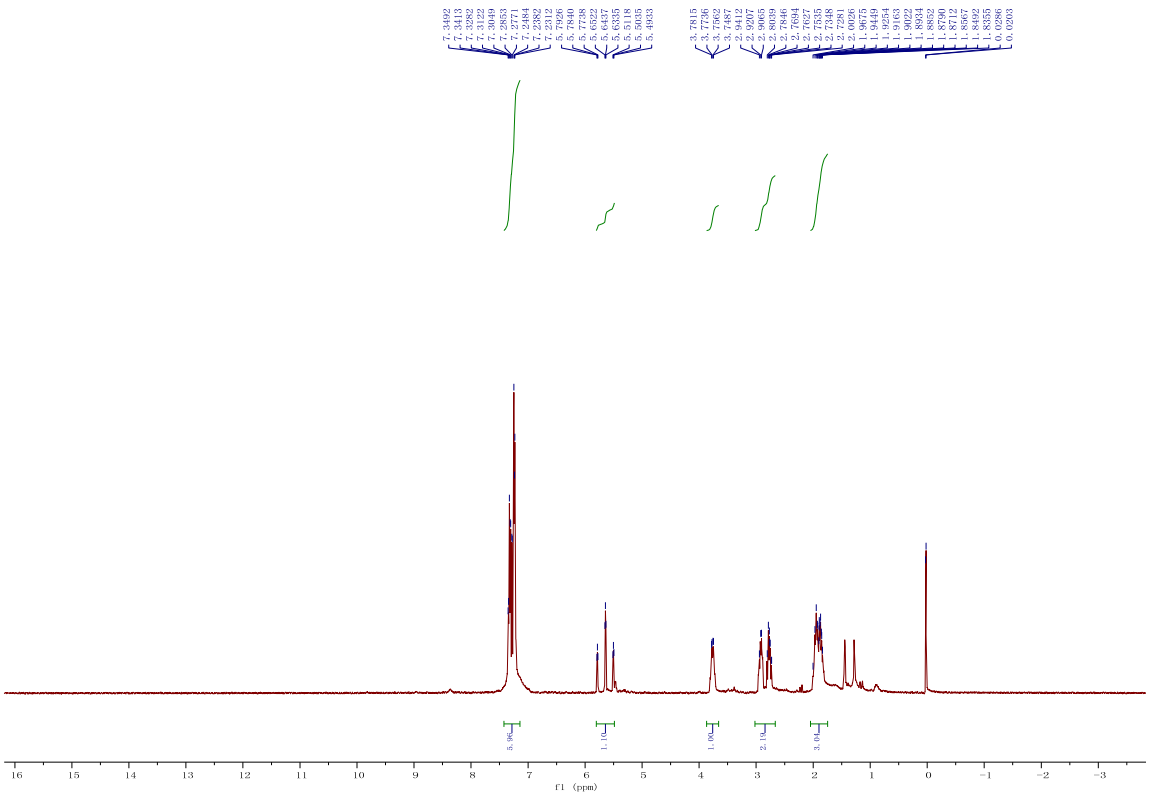
3u


-127.6108
-128.3709
-128.9582
-129.7182
-127.0
-127.5
-128.0
-128.5
-129.0
-129.5
-130.0
-130.5
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

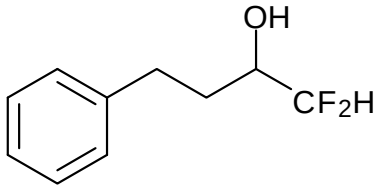
^{1}H NMR



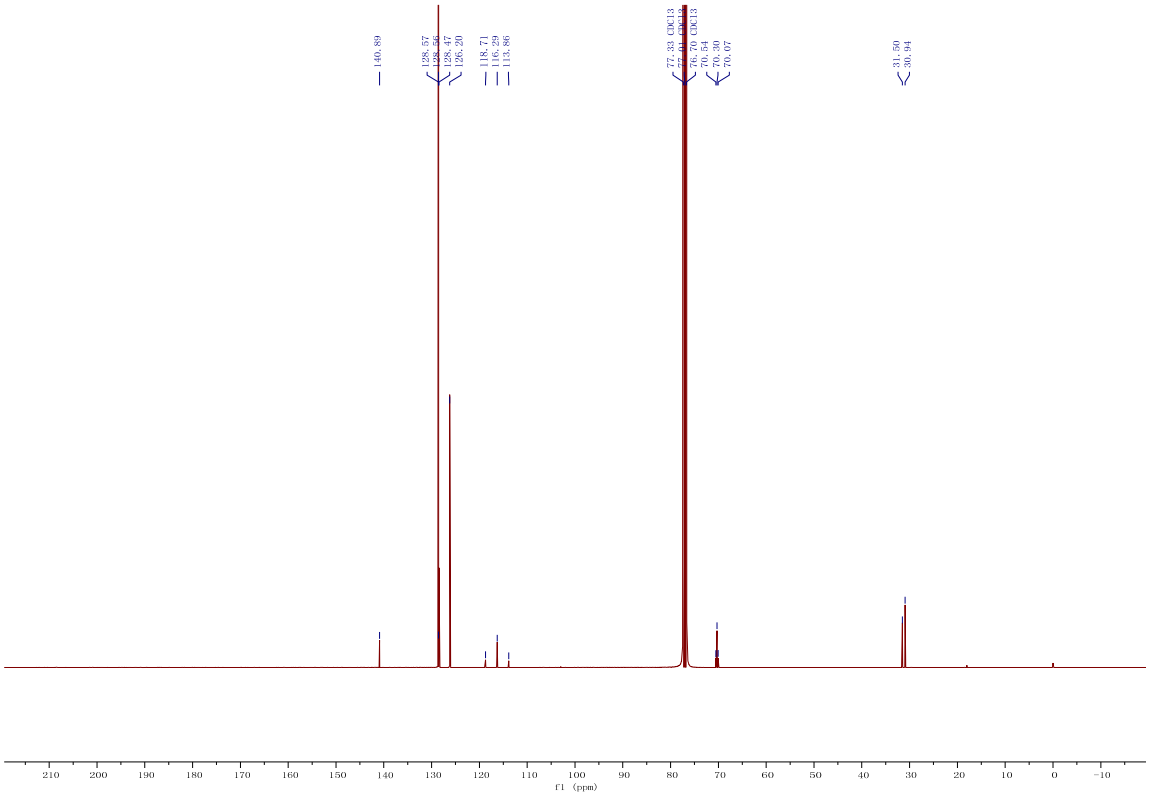
3v



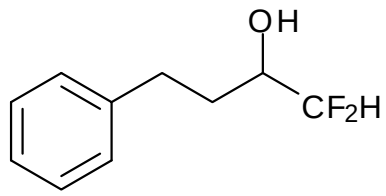
^{13}C NMR


OH
CF2H

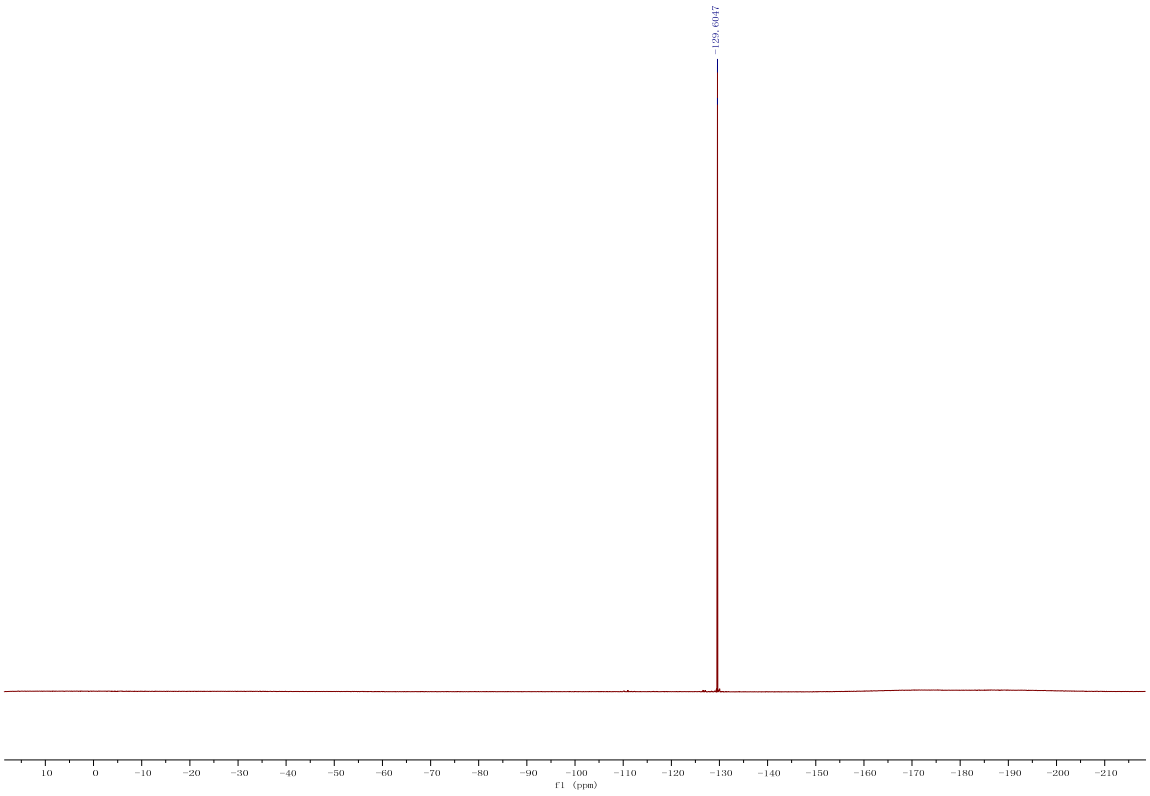
3v


140.89
128.57
128.56
128.47
126.20
118.71
116.39
113.86
77.33 CDCl3
77.16 CDCl3
76.70 CDCl3
70.54
70.30
70.07
31.50
30.94
f1 (ppm)

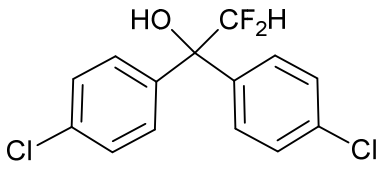
^{19}F NMR


OH
CF2H

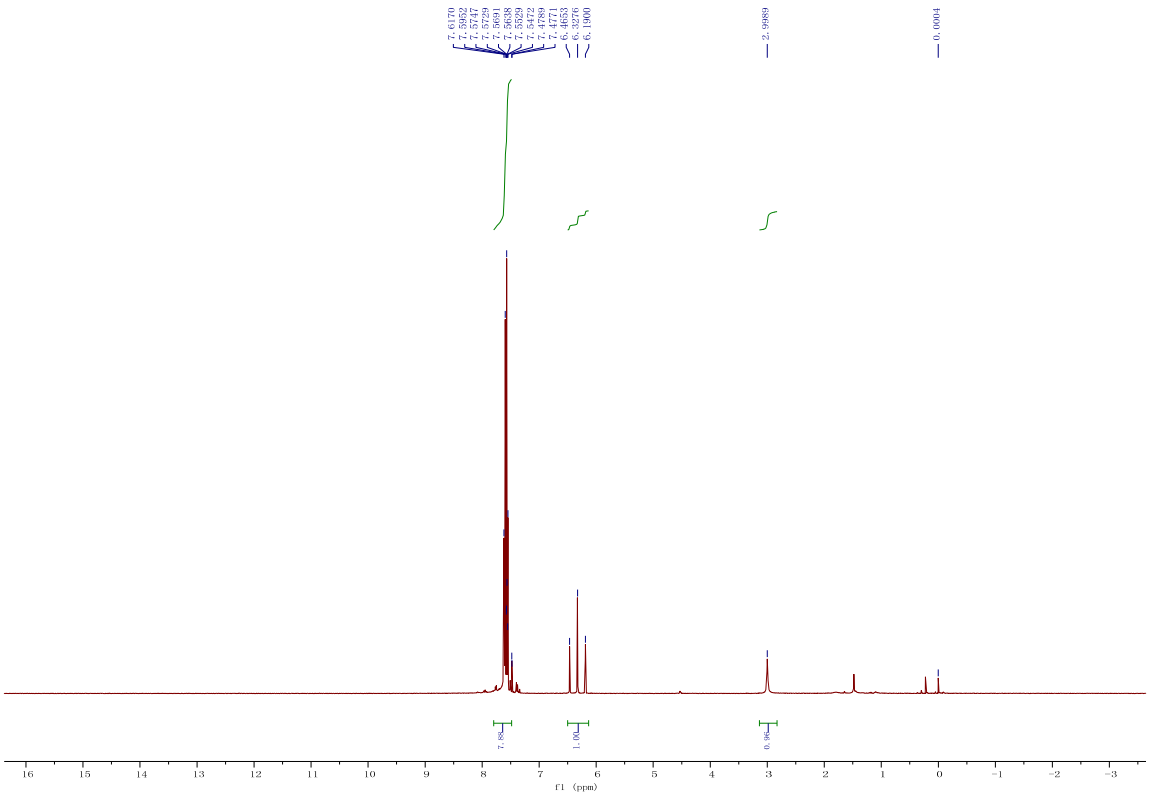
3v


-129.6047
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

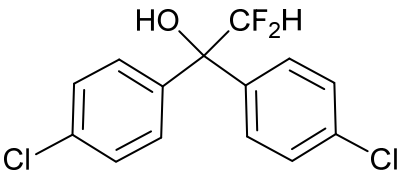
^{1}H NMR


HO
CF2H
Cl
Cl

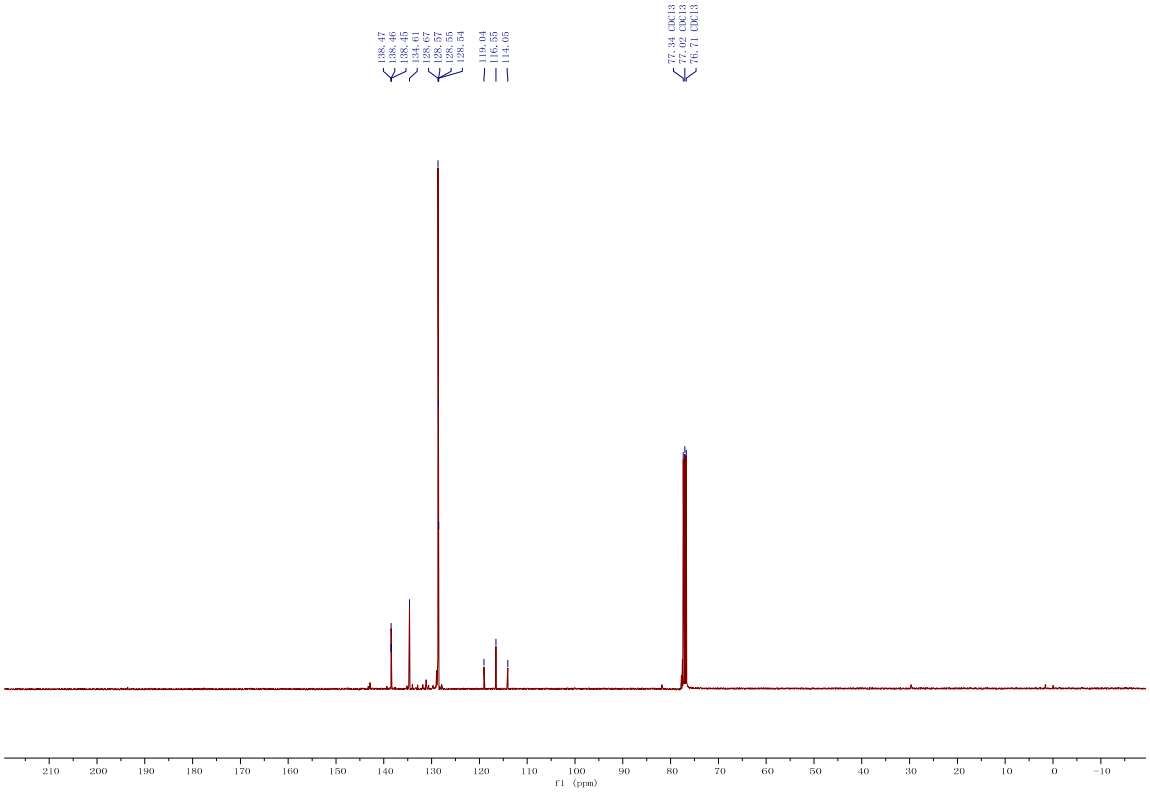
8a


7.6170
7.5952
7.5747
7.5729
7.5694
7.5658
7.5529
7.5472
7.4789
7.4771
6.4953
6.3276
6.1300
2.9989
0.0004
7.88
1.00
0.96
f1 (ppm)

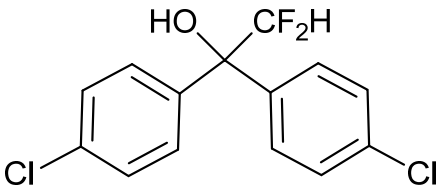
^{13}C NMR


HO
CF2H
Cl
Cl

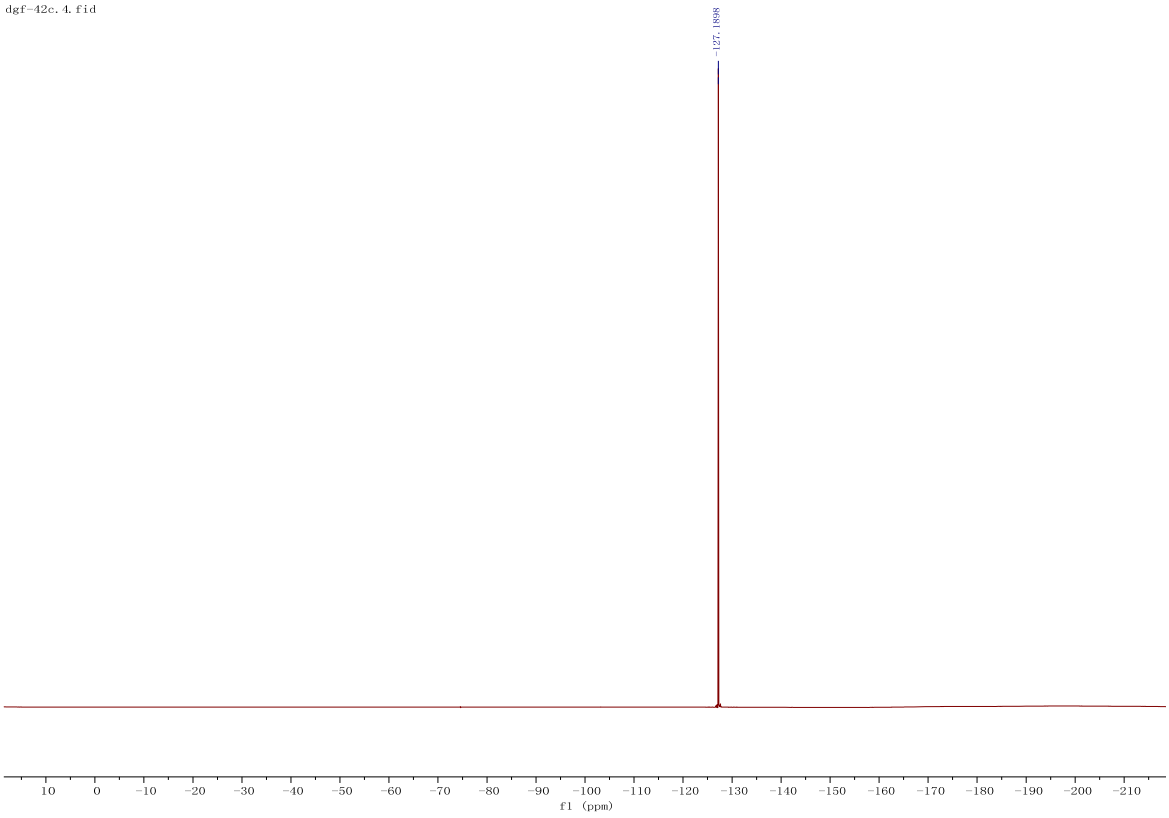
8a


138.47
138.46
138.45
134.61
128.57
128.53
128.55
128.54
119.04
116.55
114.05
77.34 CDCl3
77.02 CDCl3
76.71 CDCl3
f1 (ppm)

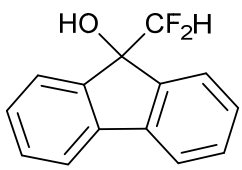
^{19}F NMR


HO
CF2H
Cl
Cl

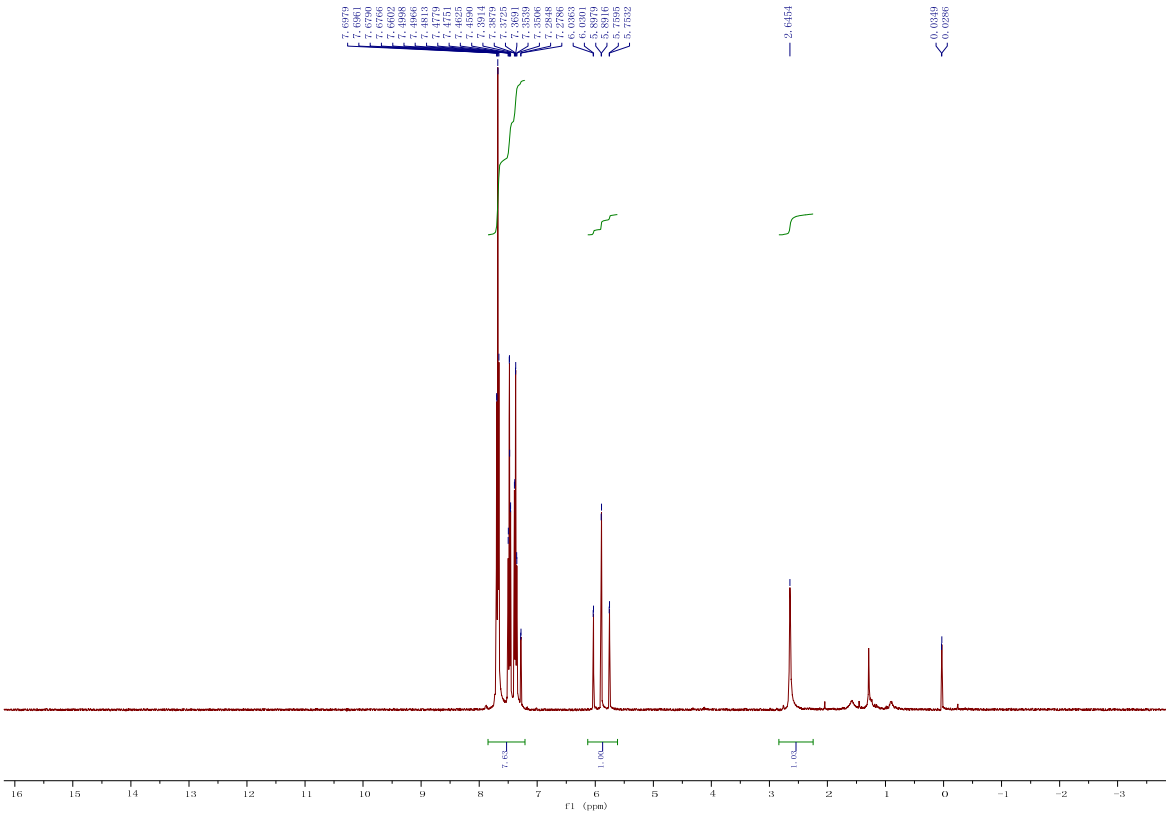
8a


dgf-42c.4.fid
-127.1898
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

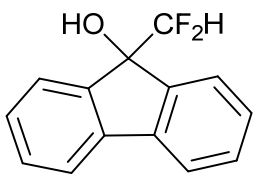
^{1}H NMR


HO
CF2H

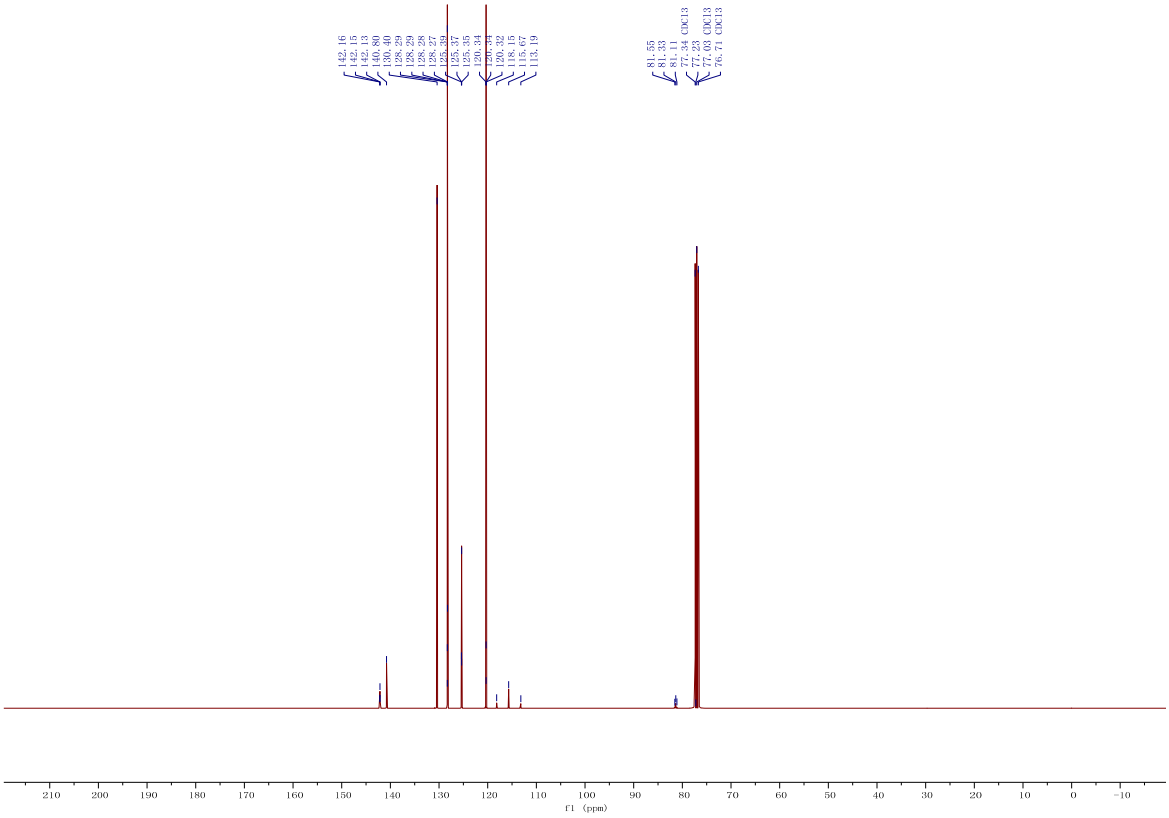
8b


7.6979
7.6961
7.6790
7.6766
7.6602
7.4998
7.4966
7.4813
7.4773
7.4751
7.4625
7.4590
7.3914
7.3873
7.3725
7.3691
7.3539
7.3506
7.2948
7.2786
6.0383
6.0301
5.8879
5.8816
5.7595
5.7532
2.6454
0.0349
0.0286
7.63
1.00
1.03
f1 (ppm)

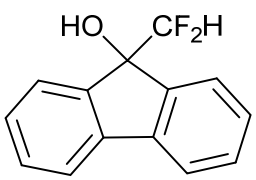
^{13}C NMR


HO
CF2H

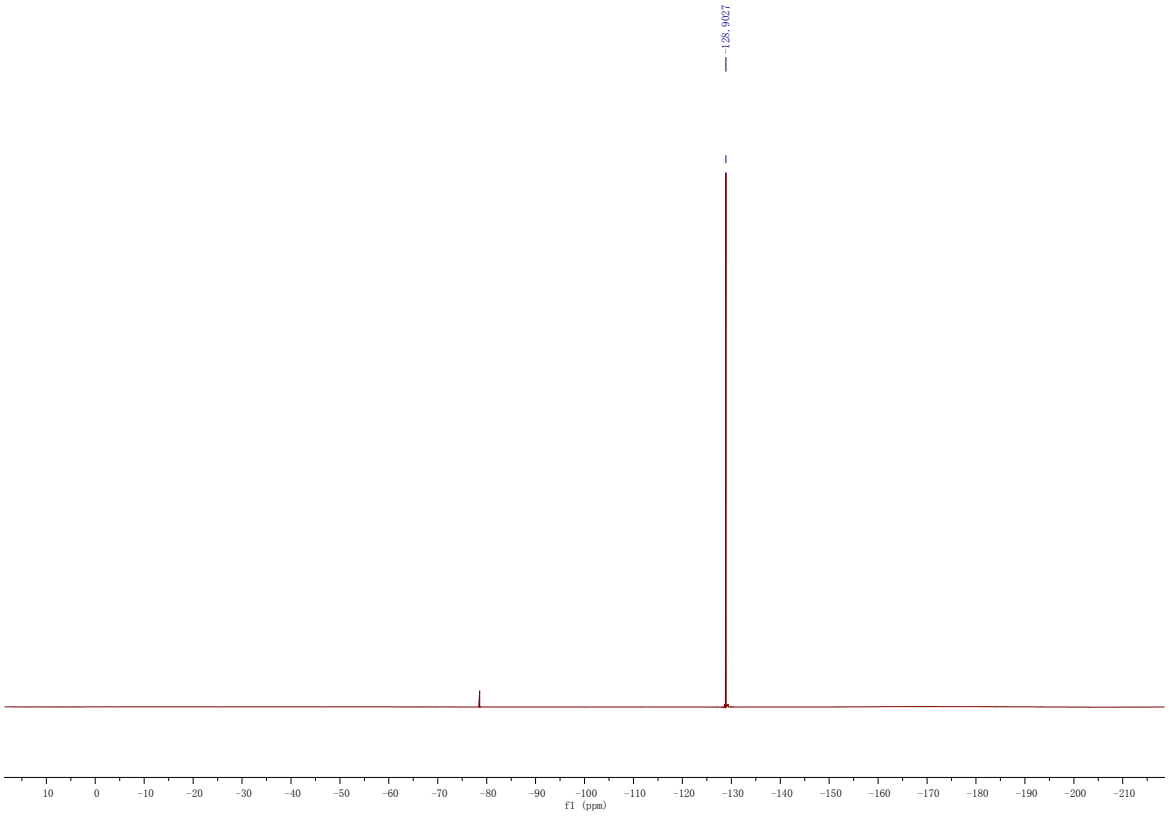
8b


142.16
142.15
142.13
140.80
130.40
128.29
128.29
128.28
128.27
125.39
125.37
125.35
120.34
120.34
120.32
118.15
115.67
115.19
81.55
81.33
81.11
77.34 CDCl3
77.23
77.03 CDCl3
76.71 CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

^{19}F NMR


HO
CF2H

8b


-128.9027
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)