Supporting Information

Synthesis and Decarboxylative Wittig Reaction of DifluoromethylenePhosphobetaine

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Contents

1. General information:

Solvents and reagents were purchased from commercial sources and used as received unless otherwise noted. The solvent NMP (*N*-methyl-2-pyrrolidinone) were distilled from CaH_2. ^{1}H, ^{13}C and ^{19}F NMR spectra were detected on a 500 MHz, 400 MHz or 300 MHz NMR spectrometer. Data for ^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, coupling constant (s) in Hz). Mass spectra were obtained on a GC-MS. High resolution mass data were recorded on a high resolution mass spectrometer in the EI or ESI mode.

2. Synthesis of phosphobetaine 1a and 1b:

Potassium bromodifluoroacetate ($BrCF_2CO_2K$): Into a solution of potassium hydroxide (11.2 g, 200 mmol) in MeOH (180 mL) was added $BrCF_2CO_2Et$ (41.0 g, 202 mmol) at 0 ºC. Upon addition, the mixture was warmed to room temperature and stirred for 16 h. The solvent was removed by concentration, and the residue was further dried under reduced pressure to give a white powder ($BrCF_2CO_2K$, 39.8 g, 93%). ^{19}F NMR (282 MHz, D_2O) δ -58.91 (s, 2F).

(Triphenylphosphonio)difluoroacetate (1a):

$$Ph_3P^+CF_2CO_2^-$$

To a 250 mL flask, triphenylphosphine (31.5 g, 120 mmol) and potassium bromodifluoroacetate (25.6 g, 120 mmol) was mixed with DMF (150 mL) at room temperature. The solution was stirred at room temperature for 15 h. The crude product and KBr were precipitated from the solution. After filtration, the solid was washed with DMF (10 mL × 2), H_2O (10 mL × 2) and Et_2O (20 mL × 3), then dried under reduced pressure to give the pure product as a white powder (28.7 g, 81 mmol, 67%). ^{1}H NMR (400 MHz, CD_3OD) δ 7.97 – 7.81 (m, 9H), 7.79 – 7.70 (m, 6H). ^{19}F NMR (376 MHz, CD_3OD) δ -96.01 (d, *J* = 96.7 Hz, 2F). ^{31}P NMR (162 MHz, CD_3OD) δ 27.05 (t, *J* = 96.7 Hz, 1P). ^{13}C NMR (101 MHz, CD_3OD) δ 161.28 (td, *J* = 22.0, 15.0 Hz), 135.58 (d, *J* = 3.2 Hz), 134.61 (d, *J* = 10.3 Hz), 130.07 (d, *J* = 13.2 Hz), 117.12 (td, *J* = 291.1, 79.8 Hz), 115.25 (d, *J* = 85.6Hz). IR (neat) ν = 1690, 1439, 1343, 1055, 712, 690, 540, 526 cm^{-1}. HRMS (ESI) Calcd. for $C_{20}H_{16}F_2O_2P$ $[M+H]^+$: 357.0850; found 357.0850. Anal.calcd. for $C_{20}H_{16}F_2O_2P$: C, 67.18; H, 4.47; found C, 67.14; H,4.42.

[Tris(dimethylamino)phosphonio]difluoroacetate (1b):

$$(Me_2N)_3P^+CF_2CO_2^-$$

To a 50 mL flask, tris(dimethylamino)phosphine (6.72 g, 41.2 mmol) and potassium bromodifluoroacetate (8.52 g, 40 mmol) were mixed with DMF (15 mL) at 18 ^{o}C. The solution was stirred at the same temperature for 29 h. White powder was precipitated from the solution. More white powder was precipitated after Et_2O (120 mL) was added into the mixture. After filtration, the residue was washed with Et_2O

(20 mL × 2) and then mixed with CH_2Cl_2 (150 mL). The dissolved solid is the expected product. The insoluble solid was removed by filtration. The CH_2Cl_2 solution was concentrated to give a solid, which was further dried under reduced pressure to give the pure product (4.4 g, 17.1 mmol, 43%). ^{1}H NMR (400 MHz, D_2O) δ 2.69 (d, *J* = 10.0 Hz, 18H). ^{19}F NMR (376 MHz, D_2O) δ -100.49 (d, *J* = 97.1 Hz, 2F). ^{31}P NMR (162 MHz, D_2O) δ 43.14 (t, *J* = 97.1 Hz, 1P). ^{13}C NMR (126 MHz, D_2O) δ 165.00 (td, *J* = 23.6, 16.7 Hz), 113.52 (td, *J* = 281.8, 149.4 Hz), 36.08 (d, *J* = 4.1 Hz). IR (neat) ν = 2934, 1690, 1346, 1314, 1073, 1005, 799, 659 cm^{-1}. HRMS (ESI) Calcd. for $C_8H_{19}F_2N_3O_2P$ $[M+H]^+$: 258.1177; found 258.1165.

3. The confirmation of Wittig reaction intermediate:

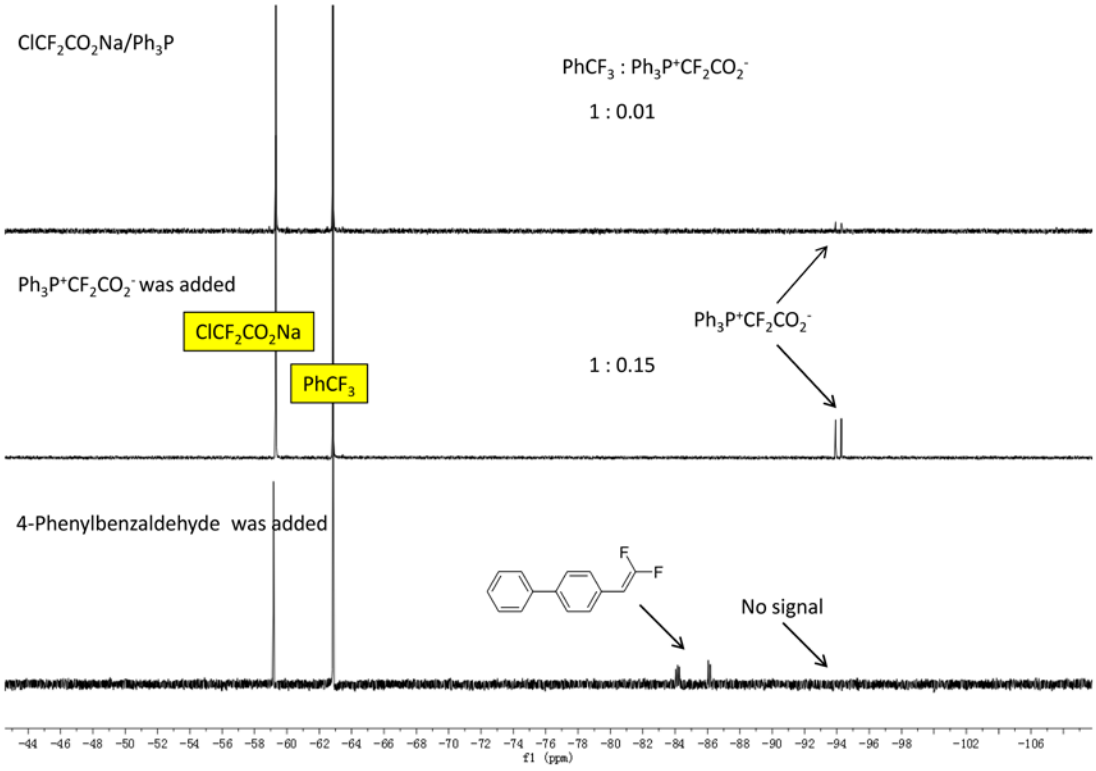


Figure 1. ^{19}F NMR of the trapping experiment.

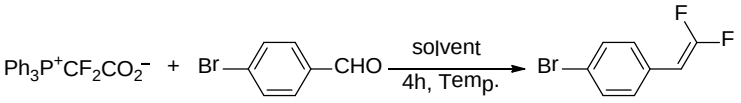
Into a NMR tube, triphenylphosphine (26.2 mg, 0.1 mmol) and sodium chlorodifluoroacetate (15.2 mg, 0.1 mmol), DMF (0.5 mL) was added successively. The solution was kept at 55 ^{o}C for 3.5 h. Then the tube was moved into a liquid nitrogen bath for 1 min and then warmed to room temperature. Trifluoromethylbenzene (7.3 mg, 0.05 mmol) was added as standard and then ^{19}F NMR was taken at room temperature. A weak doublet signal at -94.10 ppm (*J* = 100.3 Hz) in DMF was observed. The integration ratio of the trifluoromethylbenzene to the doublet signal area is 1:0.01. Then the prepared phosphobetaine **1a** (6 mg, 0.017 mmol) was added into the NMR tube. The phosphobetaine **1a** was partially dissolved in DMF. ^{19}F NMR showed that the intensity of this doublet signal at -94.10 ppm was significantly increased. The integration ratio of the two signals increased to 1:0.15. This result indicated that the reaction between triphenylphosphine and sodium

chlorodifluoroacetate really afforded the phosphobetaine **1a.** After the final addition of 4-phenylbenzaldehyde, the resulting solution was kept at 55 ºC for 1h. The doublet signal disappeared and the desired *gem*-difluoroolefination product was detected in ^{19}F NMR. The evidence clearly indicated that the phosphobetaine **1a** is the reaction intermediate of the Wittig reaction of aldehyde, triphenylphosphine and sodium chlorodifluoroacetate.

4. Screening of the reaction conditions of PDFA.

The stable reaction intermediate PDFA was then investigated its application as a ylide precursor in Wittig difluoroolefination. It was found that only low yield of the difluoroolefinated product was achieved in DMSO even though the PDFA was completely decomposed after being heated at 80 ºC for 4 h (entry1, Table 1). This might be caused by the side reaction between DMSO and the generated ylide.[10] The reaction was significantly improved when 1,4-dioxane, DMF or THF were used as the solvent (entries 2-4). Almost quantitative yield of the product could be obtained when the reaction was conducted in NMP (entry 5). Further screening of the temperature and the reactant ratio showed that 2:1 of phosphobetaine to aldehyde at 80 ºC in NMP were the optimal reaction conditions.

Table 1. Screening of the reaction conditions[a]

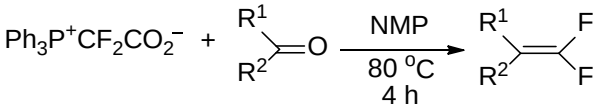


1a **2a** **3a**

Entry	Solv.	Temp. (°C)	1a:2a[b]	Yield (%)[c]
1	DMSO	80	2:1	12
2	1,4-Dioxane	80	2:1	81
3	DMF	80	2:1	83
4	THF	80	2:1	81
5	NMP	80	2:1	>99
6	NMP	60	2:1	69
7	NMP	100	2:1	96
8	NMP	80	1:1	77
9	NMP	80	3:1	95

[a]Performed on a 0.1 mmol scale based on **2a**. [b]Molar ratio. [c]Determined by ^{19}F NMR through the quantitative addition of trifluoro-methylbenzene as the standard.

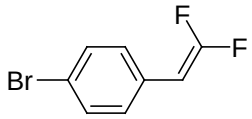
5. General procedure for the Wittig reaction of phosphobetaine 1a:



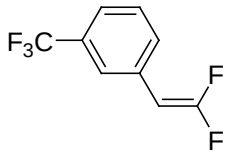
1a **3a-l, 4a-b**

Into a 25 mL Schlenk tube with a magnetic stirrer, **1a** (570 mg, 1.6 mmol) and 4-bromobenzaldehyde (148 mg, 0.8 mmol) were added. The mixture was degassed and then NMP (1.2 mL) was added under N_2. The reaction mixture was stirred at 80 ^oC for 4 h. After cooling to room temperature, the solution was subjected to flash column chromatography to afford pure product **3a**.

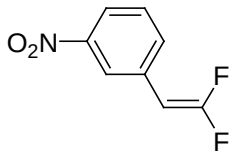
1-bromo-4-(2,2-difluorovinyl)benzene (3a)[1]: 89%; ^1H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J*= 8.5 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 5.19 (dd, *J* = 25.9, 3.6 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -81.30 (dd, *J* = 29.3, 25.9 Hz, 1F), -83.11 (dd, *J* = 29.3, 3.6 Hz, 1F). GC-MS (EI) calcd. for $C_8H_5BrF_2$ $[M]^+$ 218.0; found 217.9.



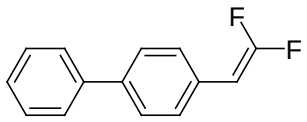
1-(2,2-difluorovinyl)-3-(trifluoromethyl)benzene (3b)[2]: 60%; ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.55-7.39 (m, 3H), 5.33 (dd, *J* = 26.4, 3.1 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.02 (s, 3F), -80.56 (t, *J* = 26.4Hz, 1F), -82.30 (dd, *J* = 26.4, 3.1 Hz, 1F). GC-MS (EI) calcd. for $C_9H_5F_5$ $[M]^+$ 208.0; found 208.0.



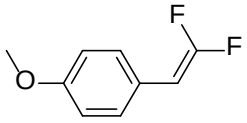
1-(2,2-difluorovinyl)-3-nitrobenzene (3c)[1]: 75%; ^1H NMR (300 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 5.39 (dd, *J* = 24.6, 3.1 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -79.05 (t, *J* = 24.6 Hz, 1F), -80.77 (dd, *J* = 24.6, 3.1 Hz, 1F). GC-MS (EI) calcd. for $C_8H_5F_2NO_2$ $[M]^+$ 185.0; found 185.0.



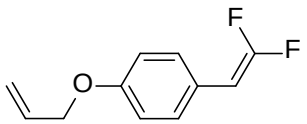
1-(2,2-difluorovinyl)-4-phenylbenzene (3d)[3]: 96%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73-7.60 (m, 4H), 7.56-7.39 (m, 5H), 5.38 (dd, *J* = 26.3, 3.7 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.91 (dd, *J* = 30.8, 26.3 Hz, 1F), -83.80 (dd, *J* = 30.8, 3.7 Hz, 1F)). GC-MS (EI) calcd. for $C_{14}H_{10}F_2$ $[M]^+$ 216.1; found 216.0.



1-(2,2-difluorovinyl)-4-methoxybenzene (3e)[1]: 85%; ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 5.21 (dd, *J* = 26.4, 3.3 Hz, 1H), 3.80 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -84.64 (dd, *J* = 36.8, 26.4 Hz, 1F), -86.45 (dd, *J* = 36.8, 3.3Hz, 1F).GC-MS (EI) calcd. for $C_9H_8F_2O$ $[M]^+$ 170.1; found 170.1.

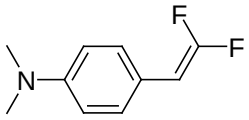


1-(allyloxy)-4-(2,2-difluorovinyl)benzene (3f): 87%; ^1H NMR (400 MHz,$CDCl_3$) δ 7.27 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.03-6.13 (m, 1H), 5.44 (d, *J* = 17.3 Hz, 1H), 5.32 (d, *J* = 10.5 Hz, 1H), 5.23 (dd, *J* = 26.4, 3.4 Hz, 1H), 4.55 (d, *J* = 4.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.68 (dd, *J* = 36.8, 26.4 Hz, 1F), -86.48 (dd, *J* = 36.8, 3.4 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.70

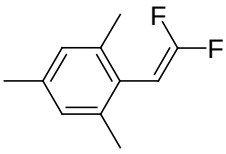


(t，J = 2.2 Hz), 155.96 (dd, J = 296.5, 286.6 Hz), 133.26 (s), 128.87 (dd, J = 6.3, 3.5 Hz), 122.84 (dd, J = 6.5, 5.9 Hz), 117.77 (s), 115.10 (s), 81.65 (dd, J = 29.2, 14.1 Hz), 68.90 (s). IR (neat) ν = 1732, 1613, 1514, 1294, 1246, 1183, 1167, 938 cm^{-1}. HRMS (EI) Calcd. for $C_{11}H_{10}F_2O[M]^+$: 196.0694; found 196.0695.

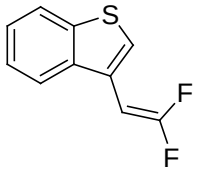
4-(2,2-difluorovinyl)-N,N-dimethylbenzenamine (3g)[1]: 85%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, J = 8.6 Hz, 2H), 6.68 (d, J = 8.6 Hz, 2H), 5.15 (dd, J = 26.9, 3.9 Hz, 1H), 2.93 (s, 6H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -85.86 (dd, J = 40.5, 26.9 Hz, 1F), -88.01 (dd, J = 40.5, 3.9 Hz, 1F). GC-MS (EI) calcd. for $C_{10}H_{11}F_2N$ $[M]^+$ 183.1; found 183.1.



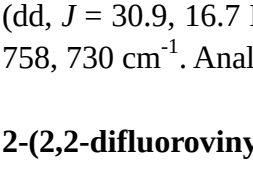
2-(2,2-difluorovinyl)-1,3,5-trimethylbenzene (3h)[4]: 77%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.95 (s, 2H), 5.24 (d, J = 27.4 Hz, 1H), 2.34 (s, 3H), 2.30 (s, 6H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -83.77 (dd, J = 33.9, 27.4 Hz, 1F), -87.45 (dd, J = 33.9, 1.6 Hz, 1F). GC-MS (EI) calcd. for $C_{11}H_{12}F_2$ $[M]^+$ 182.1; found 182.1.



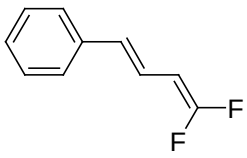
3-(2,2-difluorovinyl)benzo[b]thiophene (3i): 86%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, J = 7.8 Hz, 1H), 7.64 (d, J = 7.2 Hz, 1H), 7.39 (s, 1H), 7.37-7.28 (m, 2H), 5.53 (dd, J = 26.0, 2.2 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -80.64 (t, J = 26.0 Hz, 1F), -84.47 (dd, J = 26.0, 2.2 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.48 (dd, J = 296.7, 289.6 Hz), 139.61 (s), 137.82 (d, J = 3.6 Hz), 124.69 (s), 124.33 (d, J = 11.46 Hz), 124.33 (s), 123.08 (dd, J = 9.8, 3.3 Hz), 122.83 (s), 121.17 (s), 74.83 (dd, J = 30.9, 16.7 Hz). IR (neat) ν = 3070, 1857, 1730, 1428, 1320, 1200, 1102, 917, 758, 730 cm^{-1}. Anal. calcd. for $C_{10}H_6F_2S$: C, 61.21; H, 3.08. found C, 61.05; H,3.16.



2-(2,2-difluorovinyl)benzofuran (3j): 82%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, J = 7.0 Hz, 1H), 7.48 (d, J = 7.8 Hz, 1H), 7.35 – 7.19 (m, 2H), 6.70 (s, 1H), 5.48 (dd, J = 25.1, 1.4 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -76.01 (dd, J = 25.1, 16.5 Hz, 1F), -82.27 (dd, J = 16.5, 1.4 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.87 (dd, J = 300.0, 291.7 Hz), 154.53 (t, J = 1.8 Hz), 147.45 (dd, J = 8.7, 7.1 Hz), 128.69 (s), 124.26 (s), 123.05 (s), 120.65 (s), 110.97 (s), 104.53 (dd, J = 7.4, 6.5 Hz), 74.74 (dd, J = 34.9, 15.8 Hz). IR (neat) ν = 3064, 1734, 1615, 1478, 1453, 1353, 1254, 1074, 1012, 979, 964, 750 cm^{-1}. HRMS (EI) Calcd. for $C_{10}H_6F_2O$ $[M]^+$: 180.0381; found 180.0384.

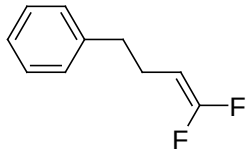


(*E*)-1-(4,4-difluorobuta-1,3-dienyl)benzene (3k)[1]: 81%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.3 Hz, 2H), 7.35 (t, J = 7.3 Hz, 2H), 7.27 (t, J = 7.3 Hz, 1H), 6.70 (dd, J = 15.9, 10.9 Hz, 1H), 6.50 (d, J = 15.9 Hz, 1H), 5.16 (ddd, J = 24.1, 10.9, 0.9 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.41 (dd, J = 26.4, 24.1 Hz, 1F), -87.13

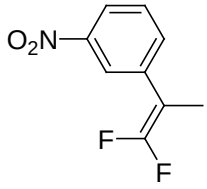


(d, *J* = 26.4 Hz, 1F). GC-MS (EI) calcd. for $C_{10}H_8F_2$ $[M]^+$ 166.1; found 166.0.

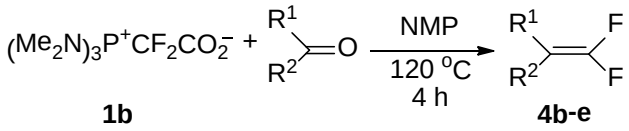
1-(4,4-difluorobut-3-enyl)benzene (3l)[1]: 69%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.23 – 7.13 (m, 3H), 4.14 (dt, *J* = 25.4, 7.8 Hz, 1H), 2.67 (t, *J* = 7.8 Hz, 2H), 2.34 – 2.23 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -89.38 (d, *J* = 47.3 Hz, 1F), -91.45 (dd, *J* = 47.3, 25.4 Hz, 1F). GC-MS (EI) calcd. for $C_{10}H_{10}F_2$ $[M]^+$ 168.1; found 168.0.



1-(1,1-difluoroprop-1-en-2-yl)-3-nitrobenzene (4a): 65%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 2.03 (t, *J* = 3.3 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -87.13 (dq, *J* = 37.3, 3.3 Hz, 1F), -87.99 (dq, *J* = 37.3, 3.3 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.99 (dd, *J* = 292.6, 288.3 Hz), 148.38 (s), 136.63 (t, *J* = 4.8 Hz), 133.38 (dd, *J* = 5.6, 3.2 Hz), 129.32 (s), 122.29 (dd, *J* = 4.6, 4.0 Hz), 121.94 (s), 86.50 (dd, *J* = 24.4, 13.4 Hz), 12.96 (t, *J* = 1.4 Hz). IR (neat) ν = 1725, 1532, 1354, 1242, 1136, 1105, 738, 684 cm^{-1}. HRMS (EI) Calcd. for $C_9H_7F_2NO_2$ $[M]^+$: 199.0445; found 199.0444.



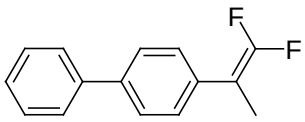
6. General procedure for the Wittig reaction of phosphobetaine 1b:



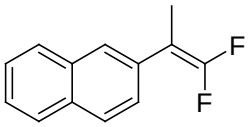
1b **4b-e**

Into a 25 mL Schlenk tube with a magnetic stirrer, phosphobetaine **1b** (309 mg, 1.2 mmol) and 4'-phenylacetophenone (118 mg, 0.6 mmol) were added. The system was degassed and then NMP (1.2 mL) was added under N_2. The reaction mixture was stirred at 120 °C for 4 h. After cooling to room temperature, the solution was subjected to flash column chromatography to afford pure product **4b**.

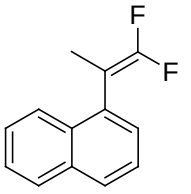
1-(1,1-difluoroprop-1-en-2-yl)-4-phenylbenzene (4b)[1]: 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 - 7.53 (m, 4H), 7.47 - 7.38 (m, 4H), 7.33 (t, *J* = 7.3 Hz, 1H), 1.99 (t, *J* = 3.3 Hz, 3H). ^{19}F NMR (376 MHz, , $CDCl_3$) δ -89.74 (dd, *J* = 42.7, 3.3 Hz, 1F), -90.13 (dd, *J* = 42.7, 3.3 Hz, 1F). GC-MS (EI) calcd. for $C_{15}H_{12}F_2[M]^+$ 230.1; found 230.1.



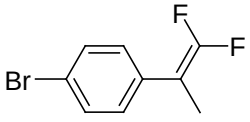
2-(1,1-difluoroprop-1-en-2-yl)naphthalene (4c)[5]: 56%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 - 7.71 (m, 4H), 7.53 - 7.39 (m, 3H), 2.04 (t, *J* = 3.3 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -89.61 (dd, *J* = 42.8, 3.3 Hz, 1F), -90.27 (d, *J* = 42.8 Hz, 1F). GC-MS (EI) calcd. for $C_{13}H_{10}F_2[M]^+$ 204.1; found 204.1.



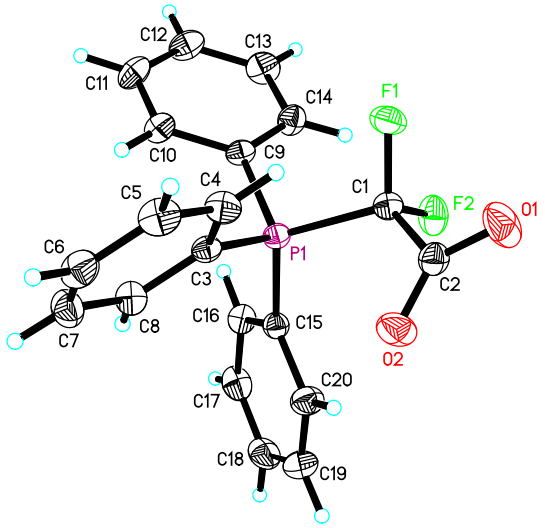
1-(1,1-difluoroprop-1-en-2-yl)naphthalene (4d): 53%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 – 7.80 (m, 3H), 7.58 – 7.43 (m, 3H), 7.38 (d, *J* = 7.0 Hz, 1H), 2.06 (t, *J* = 2.9 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -89.41 (dd, *J* = 45.4, 2.9 Hz, 1F), -93.68 (dd, *J* = 45.4, 2.9 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.93 (dd, *J* = 287.8, 284.5 Hz), 133.81 (s), 132.89 (dd, *J* = 4.9, 1.3 Hz), 131.24 (dd, *J* = 2.7, 1.2 Hz), 128.56 (s), 128.21 (s), 126.79 (dd, *J* = 3.4, 1.5 Hz), 126.32 (s), 125.93 (s), 125.44 (s), 124.83 (s), 86.00 (dd, *J* = 23.3, 20.0 Hz), 15.48 (d, *J* = 1.5 Hz). IR (neat) ν = 1784, 1508, 1302, 1255, 1240, 1133, 1117, 900, 800, 776, 509 cm^{-1}. GC-MS (EI) calcd. for $C_{13}H_{10}F_2[M]^+$ 204.1; found 204.1. HRMS (EI) Calcd. for $C_{13}H_{10}F_2$ $[M]^+$: 204.0751; found 204.0748.

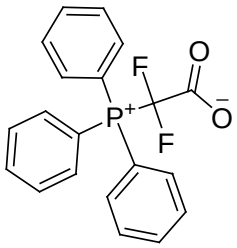


1-bromo-4-(1,1-difluoroprop-1-en-2-yl)benzene (4e)[1]: 61%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 1.94 (t, *J* = 3.0 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -89.27 (dd, *J* = 41.6, 3.0 Hz, 1F), -89.75 (dd, *J* = 41.6, 3.0 Hz, 1F). GC-MS (EI) calcd. for $C_9H_7BrF_2$ $[M]^+$ 232.0; found 232.0.



7. X-ray structure of 1a:

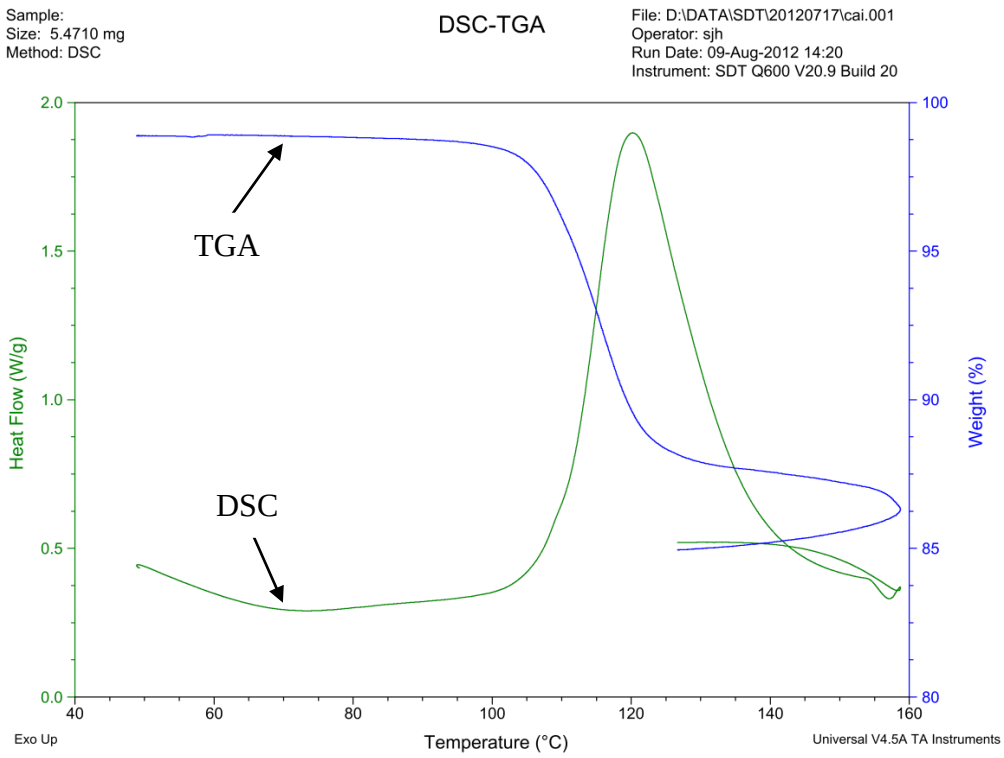




1a

Crystal data for **1a** (CCDC 929401): $C_{20}H_{15}F_2O_2P$, *M*=356.29, Monoclinic, space group P2(1)/n, a = 12.3883(14) Å, alpha = 90 deg, b = 10.0280(11) Å, beta = 93.014(2) deg, c = 13.0620(15) Å, gamma = 90 deg. *V* =1620.4(3) $Å^3$, *T*=293(2) K, *Z*=4, μ(Mo-Kα) =0.202 mm^{-1}, *R*1 = 0.0438, *wR*2 = 0.1117 (I > 2σ (I)); *R*1 = 0.0596, *wR*2 = 0.1205 (all data). Reflections collected / unique: 9528 / 3172 [R(int) = 0.0416].

8. DSC-TGA of 1a



TGA (thermal gravimetric analysis) and DSC (differential scanning calorimetry) analysis shows no decomposition below 105 ºC, and it commences to decompose before melting.

References

1 Y. Zhao,; W. Huang, L. Zhu, J. Hu, *Org. Lett.* 2010, **12**, 1444-1447.

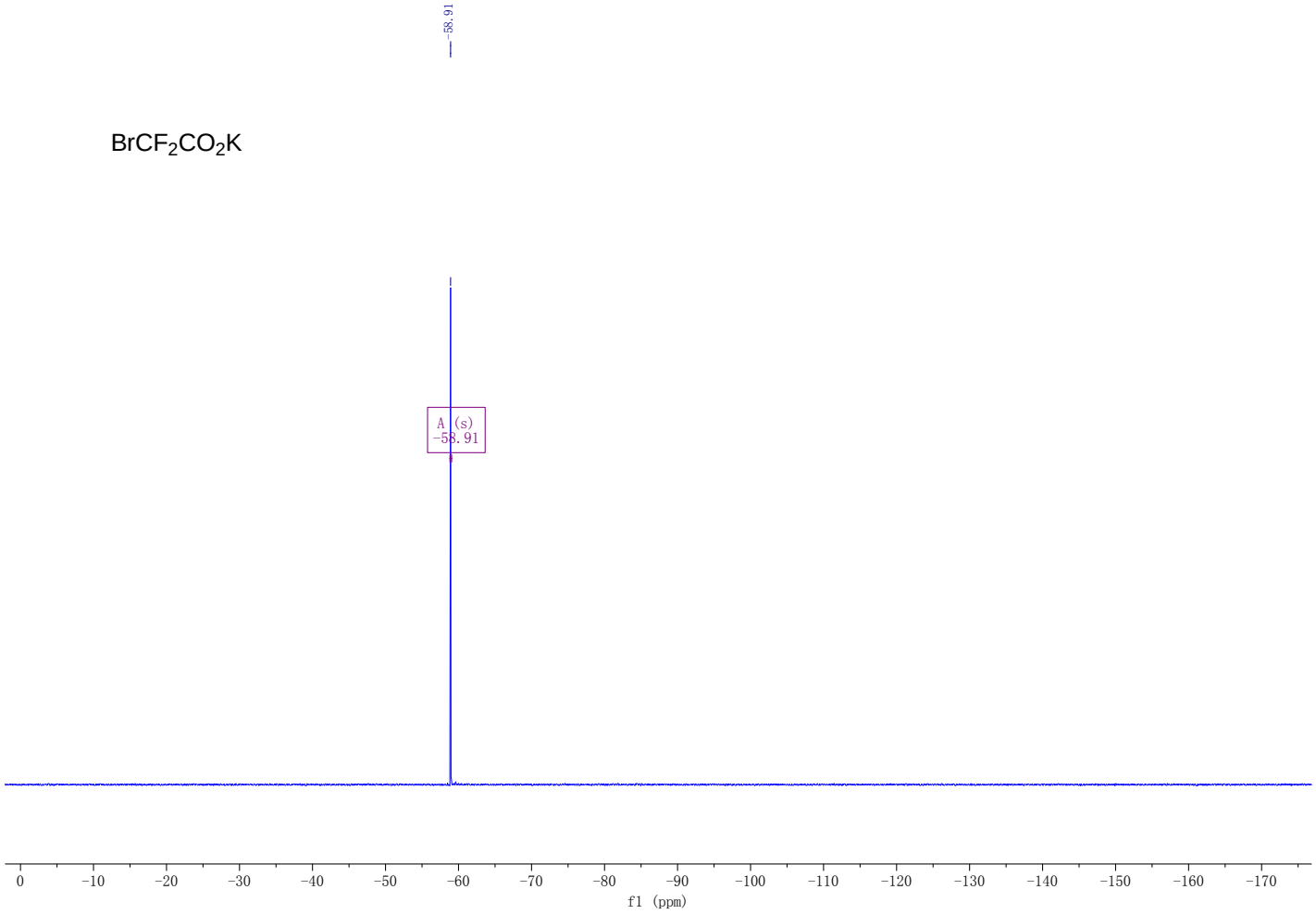
2 B. V. Nguyen, D. J. Burton, *J. Org. Chem.* 1997, **62**, 7758-7764.

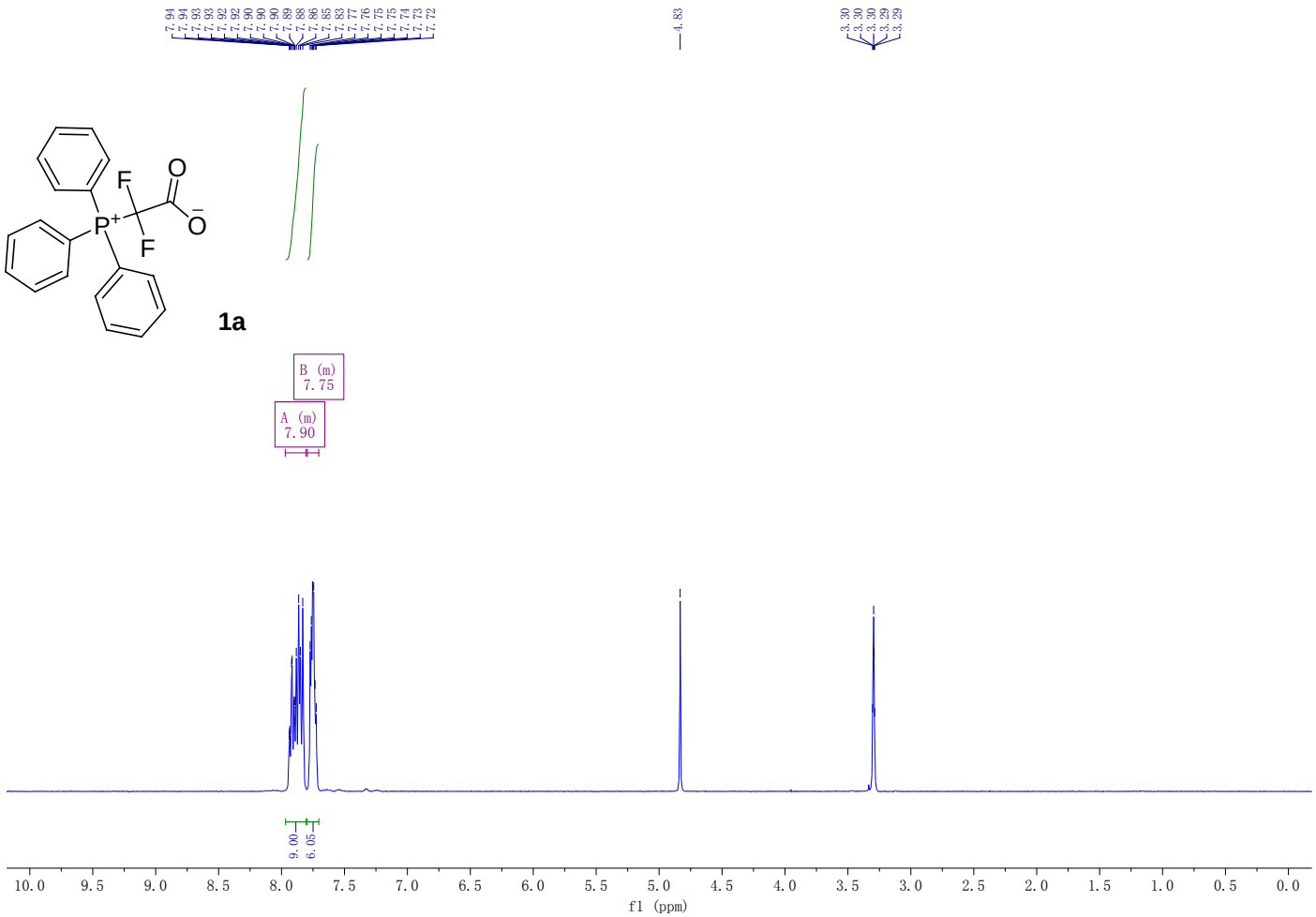
3 T. M. Gøgsig, L. S. Søbjerg, A. T. Lindhardt, K. L. Jensen, T. Skrydstrup, *J. Org. Chem.* 2008, **73**, 3404-3410.

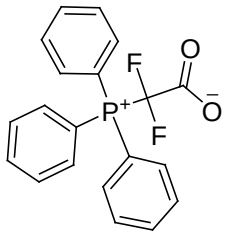
4 T. Fujita, T. Ichitsuka, K. Fuchibe, J. Ichikawa, *Chem. Lett.* 2011, **40**, 986-988.

5 I. Nowak, M. J. Robins, *Org. Lett.* 2005, **7**, 721-724.

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

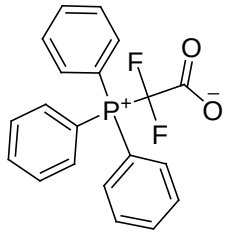



7.94
7.94
7.93
7.93
7.92
7.92
7.90
7.90
7.90
7.89
7.88
7.86
7.85
7.83
7.77
7.76
7.75
7.75
7.74
7.73
7.72
4.83
3.30
3.30
3.30
3.29
3.29
F
O
P+
F
O−
1a
B (m)
7.75
A (m)
7.90
9.00
6.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


F
O
P+
O
F

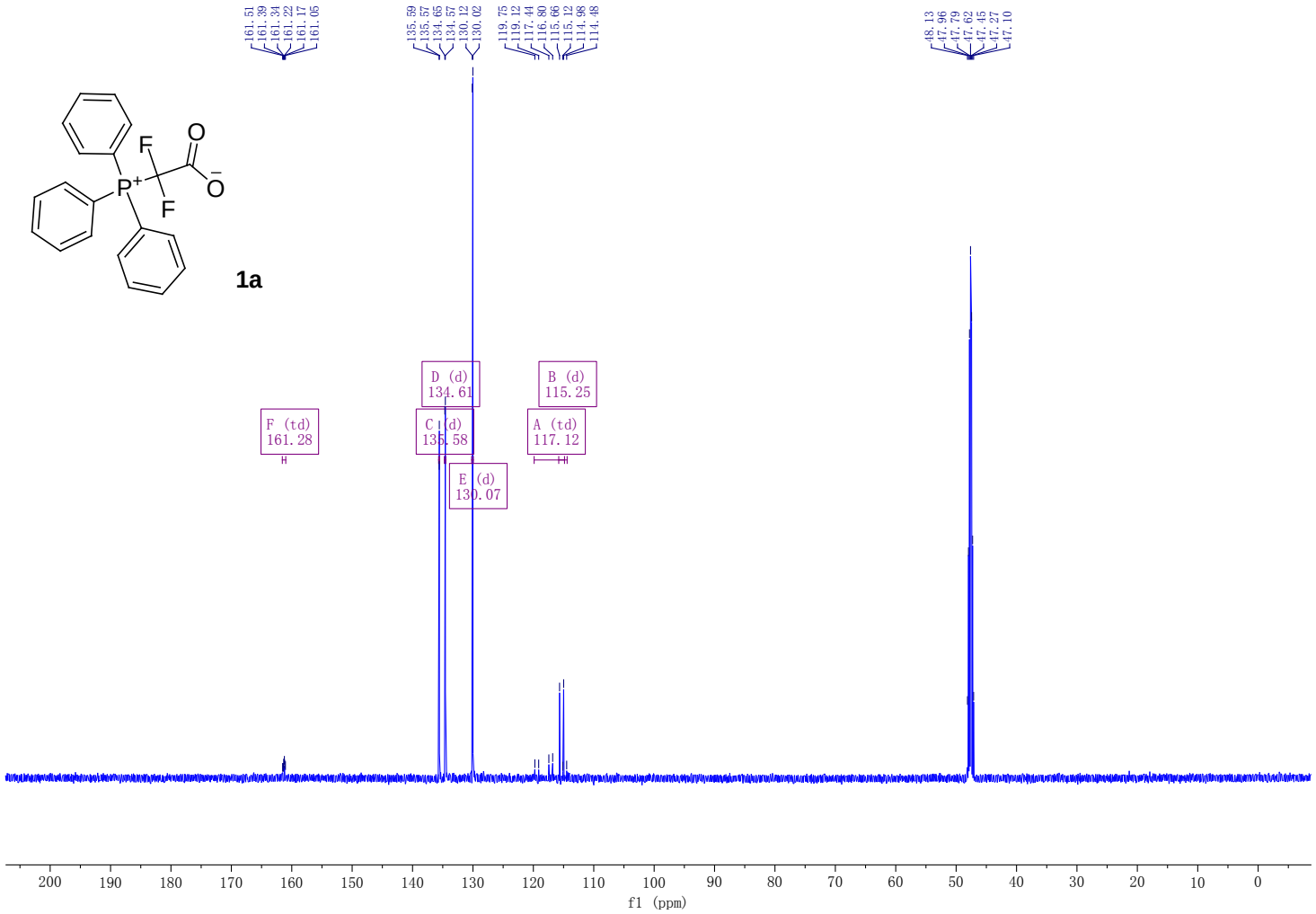
1a

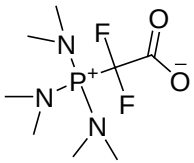
-95.88
-96.14
A (d)
-96.01
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)


F
O
P+
O−
F

1a

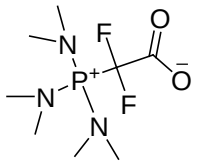
27.65
27.05
26.45
A (t)
27.05
1.00
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
f1 (ppm)


161.51
161.39
161.34
161.22
161.17
161.05
135.59
135.57
134.65
134.57
130.12
130.02
119.75
119.12
117.44
116.80
116.66
115.12
114.98
114.48
48.13
47.96
47.79
47.62
47.45
47.27
47.10
F
O
P+
F
O
1a
D (d)
134.61
B (d)
115.25
F (td)
161.28
C (d)
135.58
A (td)
117.12
E (d)
130.07
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
F
O
P+
O−
N
F
N

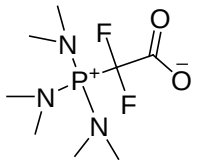
1b

4.64
2.71
2.68
A (d)
2.69
18.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


N
F
O
P+
O−
N
F
N

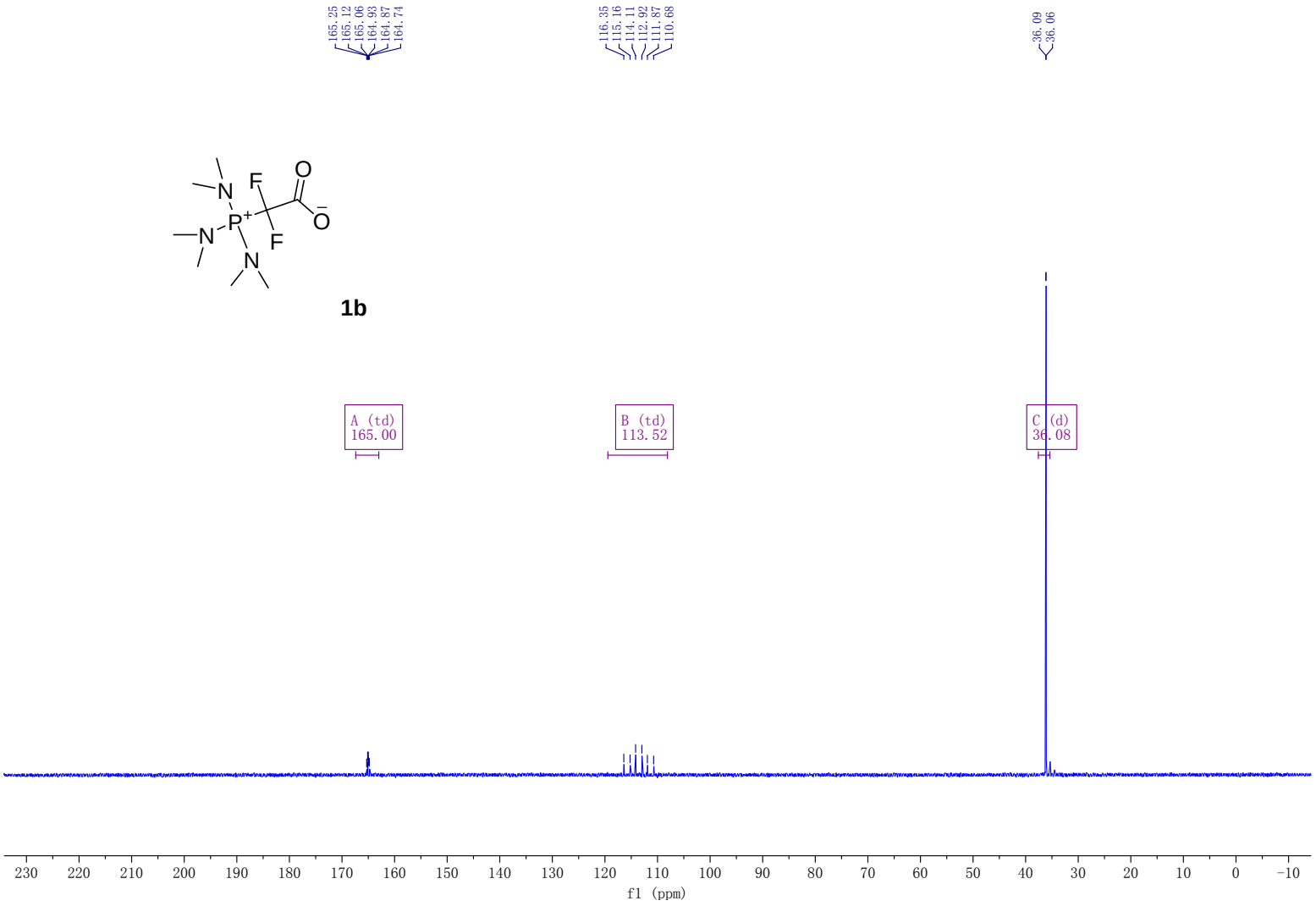
1b

-100.36
-100.62
A (d)
-100.49
H
2.00
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
f1 (ppm)


N
F
O
P+
O−
N
F
N

1b

43.74
43.14
42.54
A (t)
43.14
1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40
f1 (ppm)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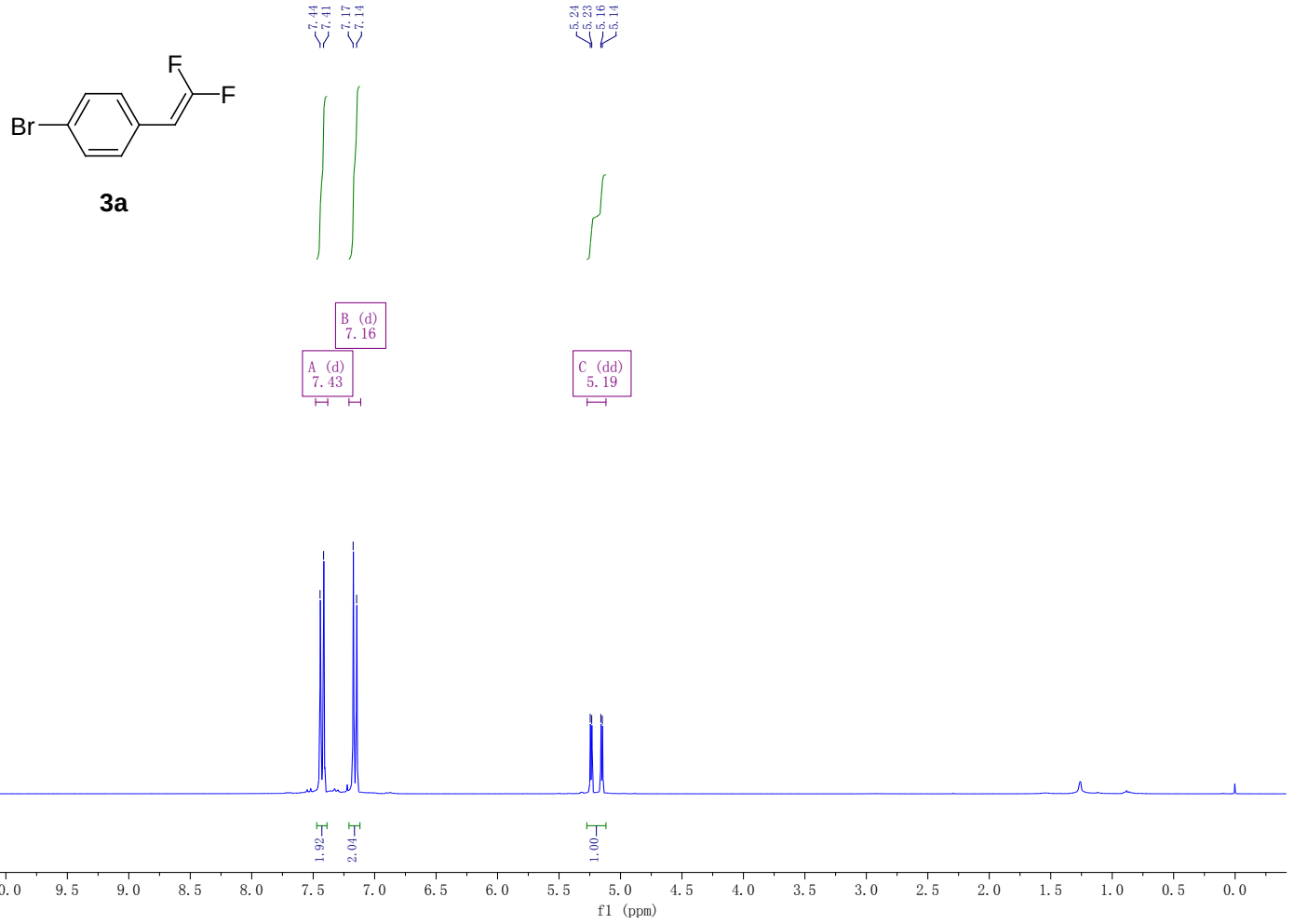
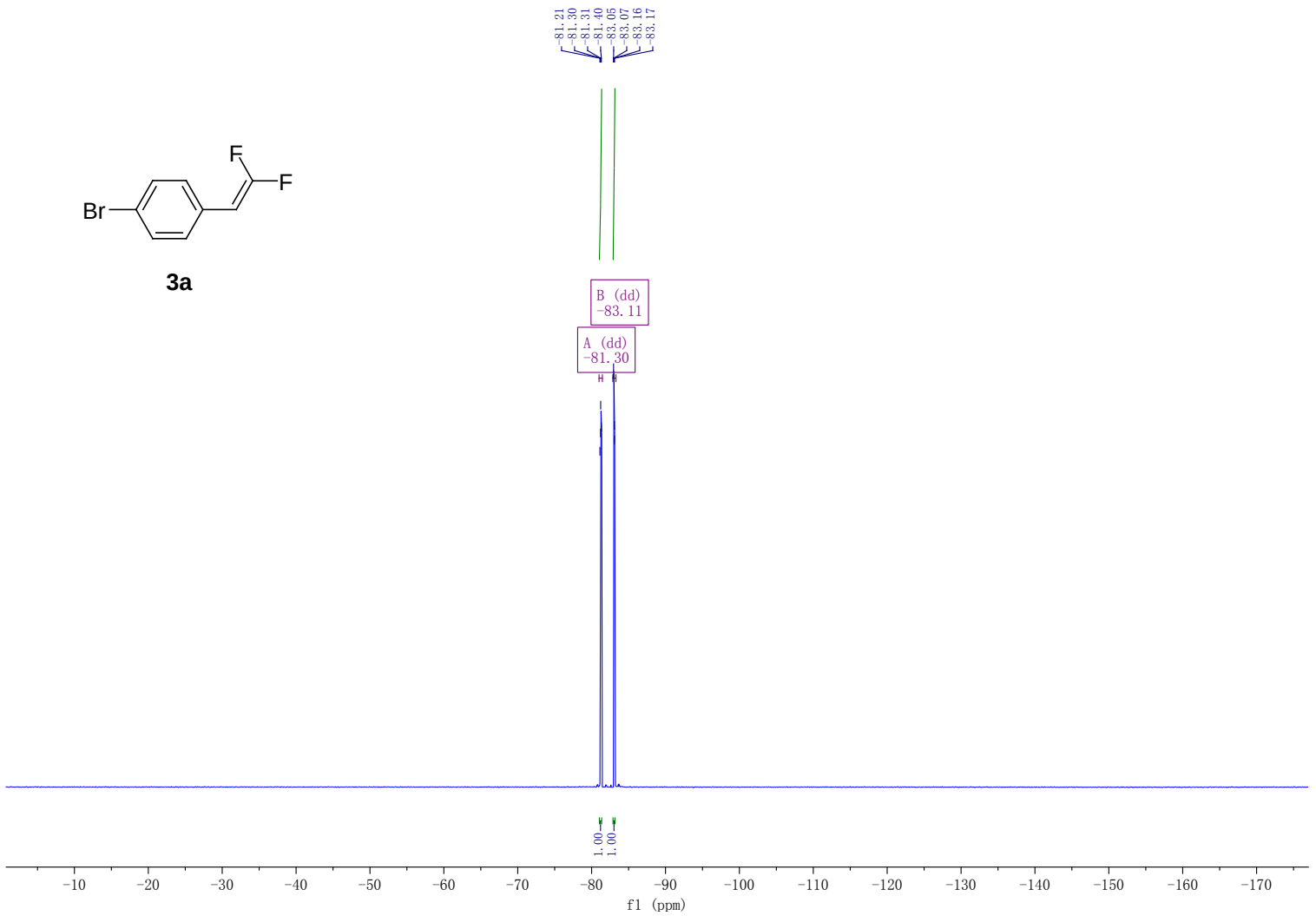
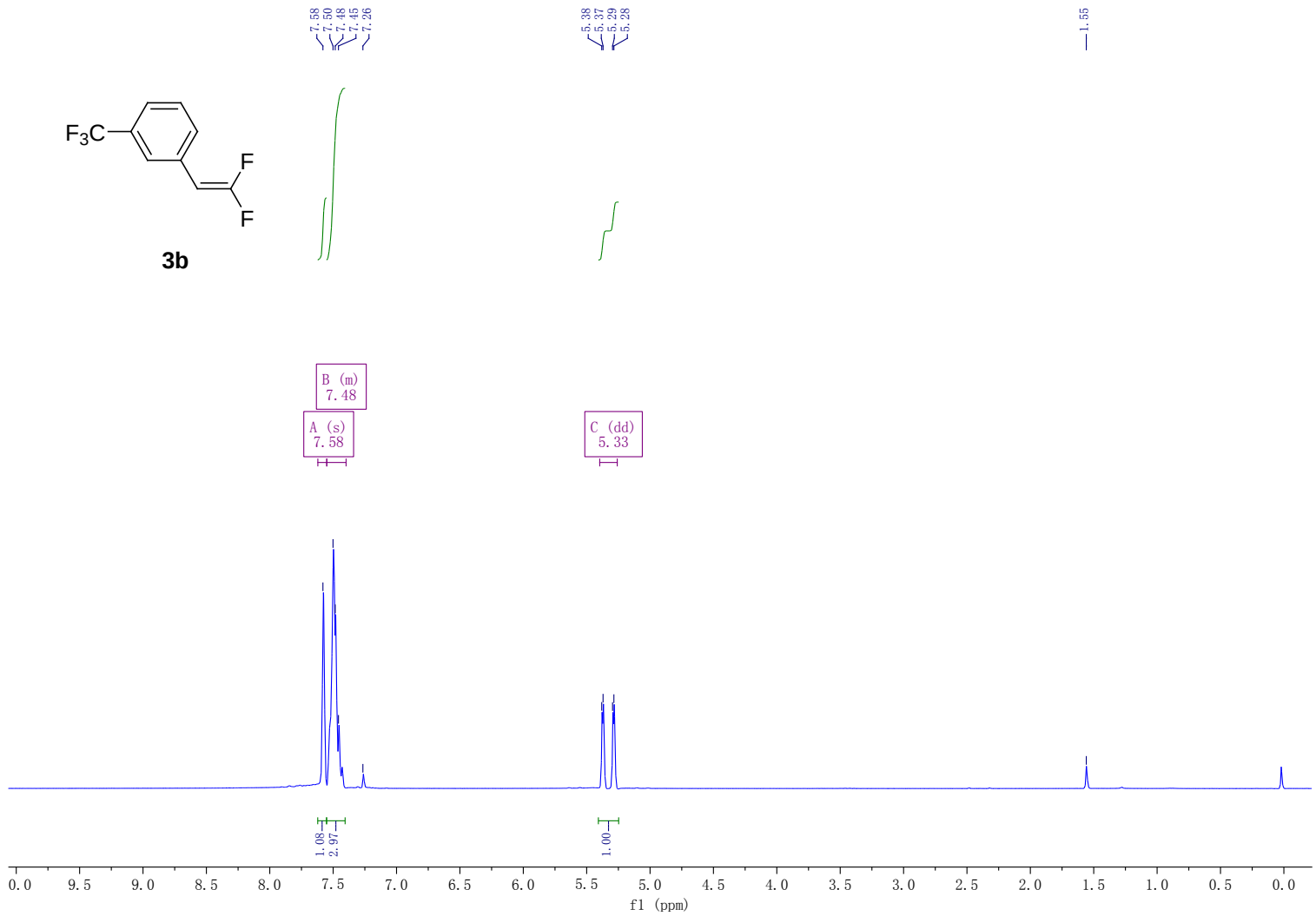
165.12
165.06
164.93
164.87
164.74
116.35
115.16
114.11
112.92
111.87
110.68
36.09
36.06
N
F
O
P+
F
O
N
N
1b
A (td)
165.00
B (td)
113.52
C (d)
36.08
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


F
F
Br
3a
7.44
7.41
7.17
7.14
5.24
5.23
5.16
5.14
B (d)
7.16
A (d)
7.43
C (dd)
5.19
1.92
2.04
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


F
F
Br
3a
-81.21
-81.30
-81.31
-81.40
-83.05
-83.07
-83.16
-83.17
B (dd)
-83.11
A (dd)
-81.30
1.00
1.00
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)


7.58
7.50
7.48
7.45
7.26
5.38
5.37
5.29
5.28
1.55
F3C
F
F
3b
B (m)
7.48
A (s)
7.58
C (dd)
5.33
1.08
2.97
1.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.5
2.0
1.5
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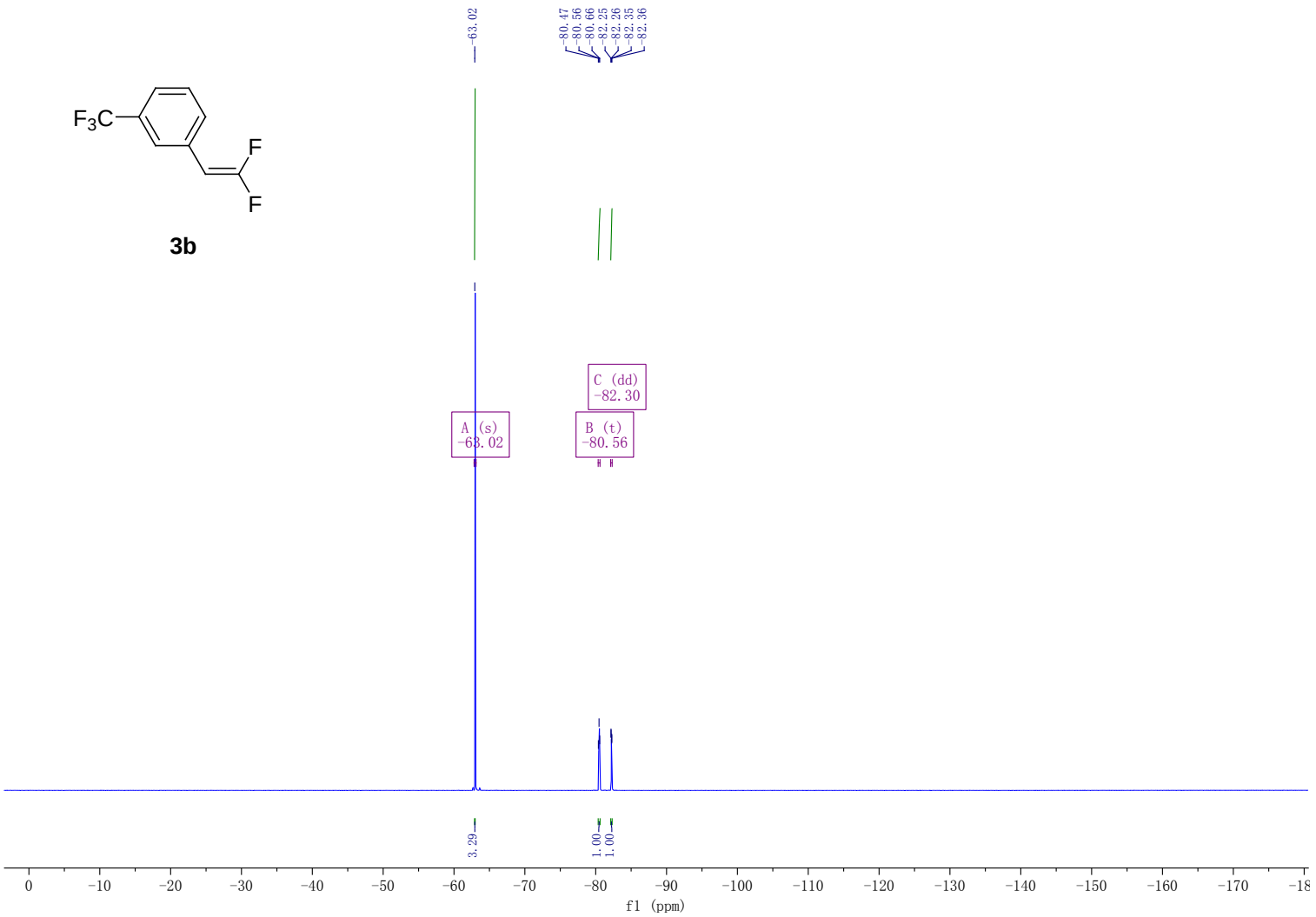
0.0
f1 (ppm)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F
F
3b
-63.02
-80.47
-80.56
-80.66
-82.25
-82.26
-82.35
-82.36
A (s)
-63.02
B (t)
-80.56
C (dd)
-82.30
3.29
1.00
1.00
0
-10
-20
-30
-40
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-60
-70
-80
-90
-100
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-140
-150
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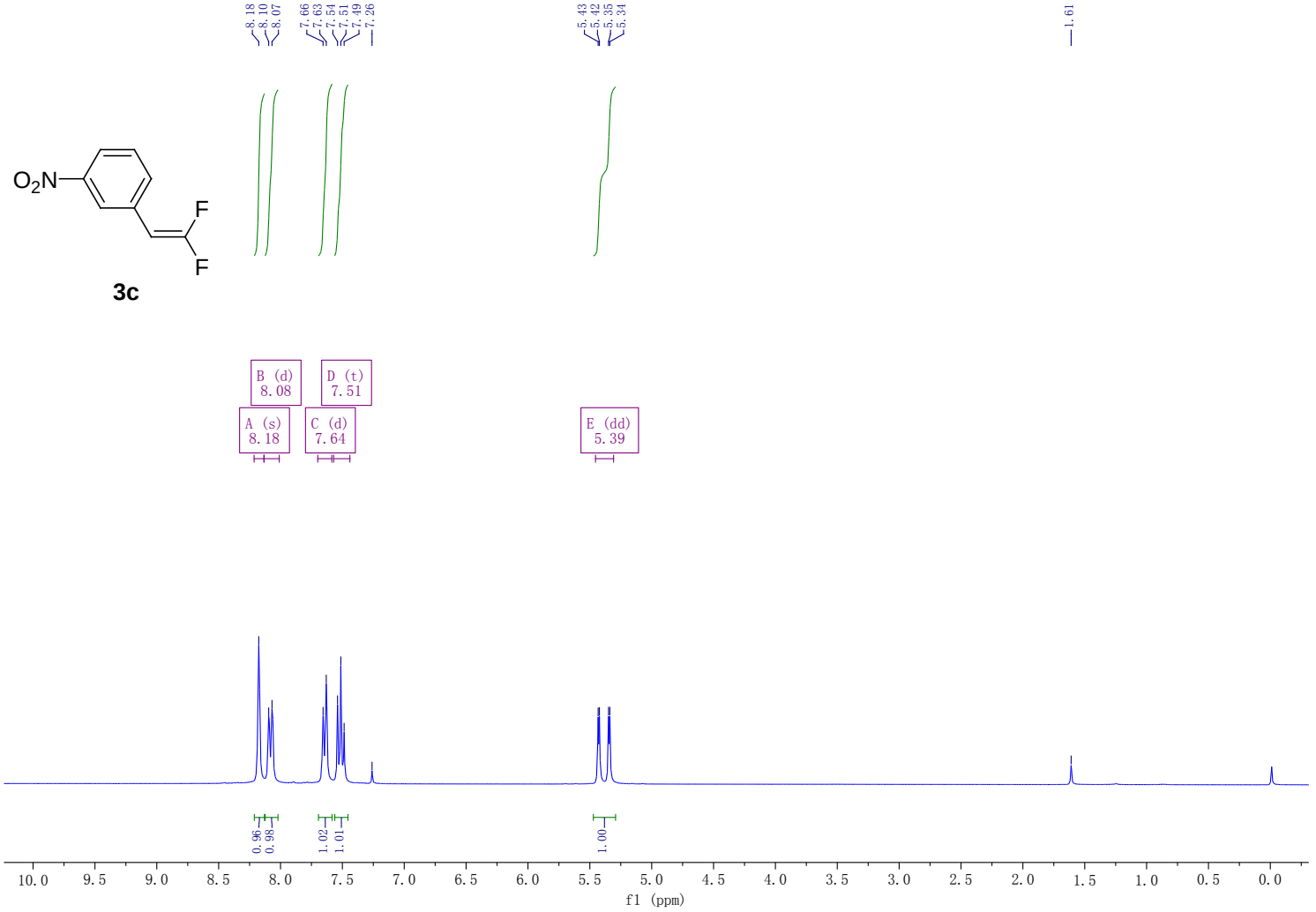
-170
f1 (ppm)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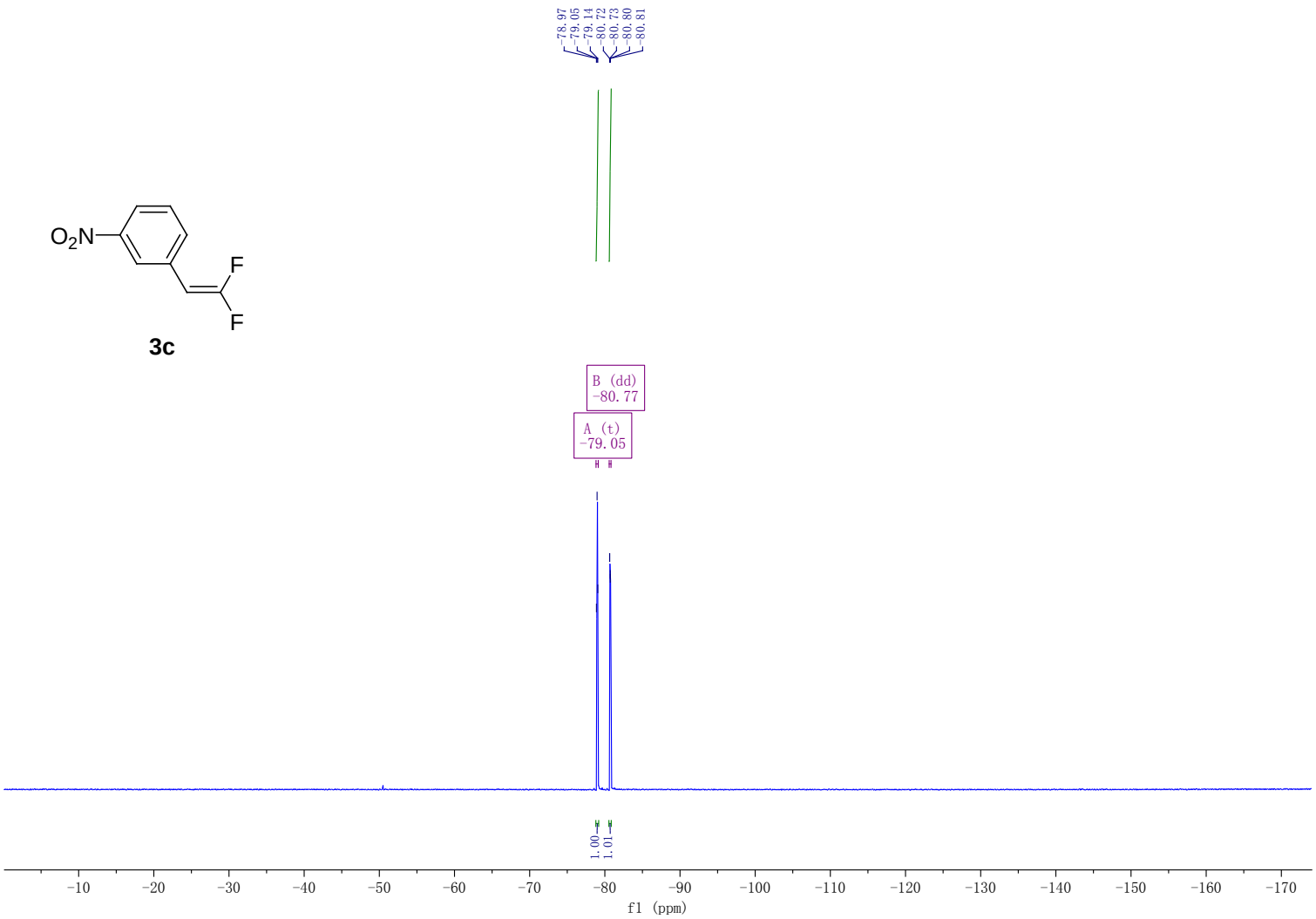
8.07
7.66
7.63
7.54
7.51
7.49
7.26
5.43
5.42
5.35
5.34
1.61
O2N
F
F
3c
B (d)
8.08
D (t)
7.51
A (s)
8.18
C (d)
7.64
E (dd)
5.39
0.96
0.98
1.02
1.01
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


-78.97
-79.05
-79.14
-80.72
-80.73
-80.80
-80.81
O2N
F
F
3c
B (dd)
-80.77
A (t)
-79.05
1.00
1.01
-10
-20
-30
-40
-50
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-70
-80
-90
-100
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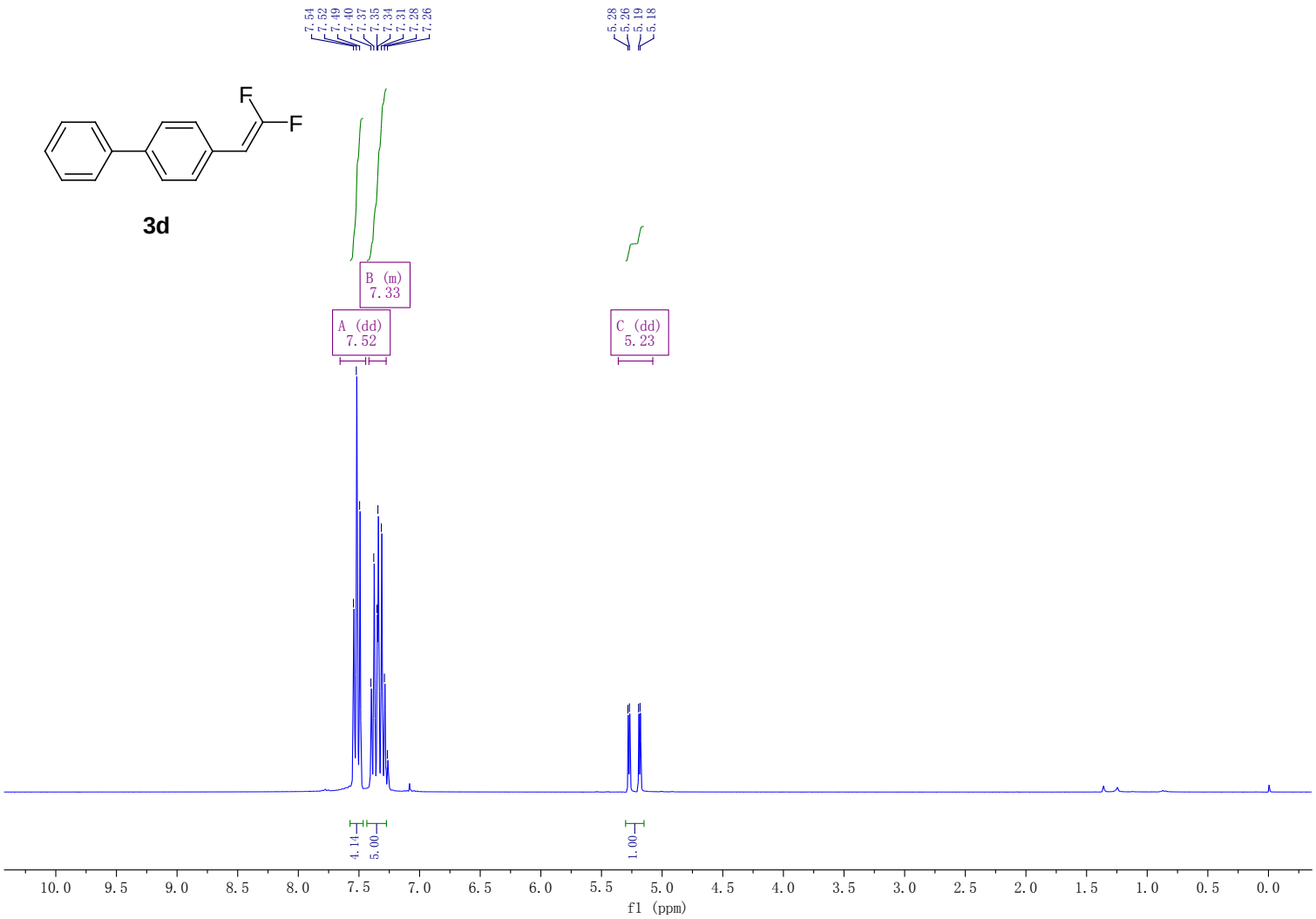
-120
-130
-140
-150
-160
-170
f1 (ppm)


7.54
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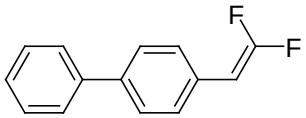
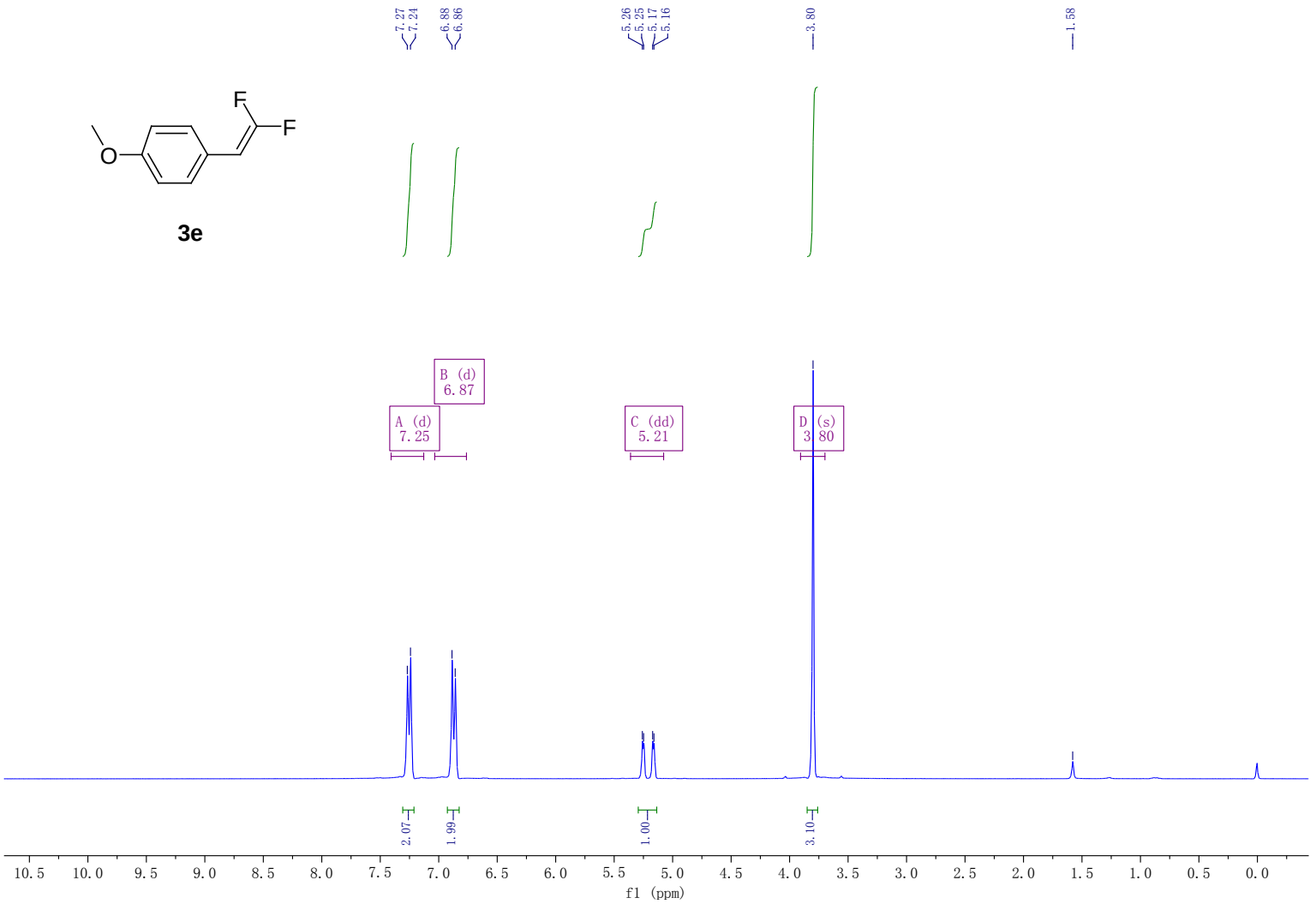
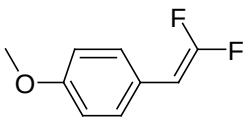
7.40
7.37
7.35
7.34
7.31
7.28
7.26
5.28
5.26
5.19
5.18
F
F
3d
B (m)
7.33
A (dd)
7.52
C (dd)
5.23
4.14
5.00
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


F
F

3d

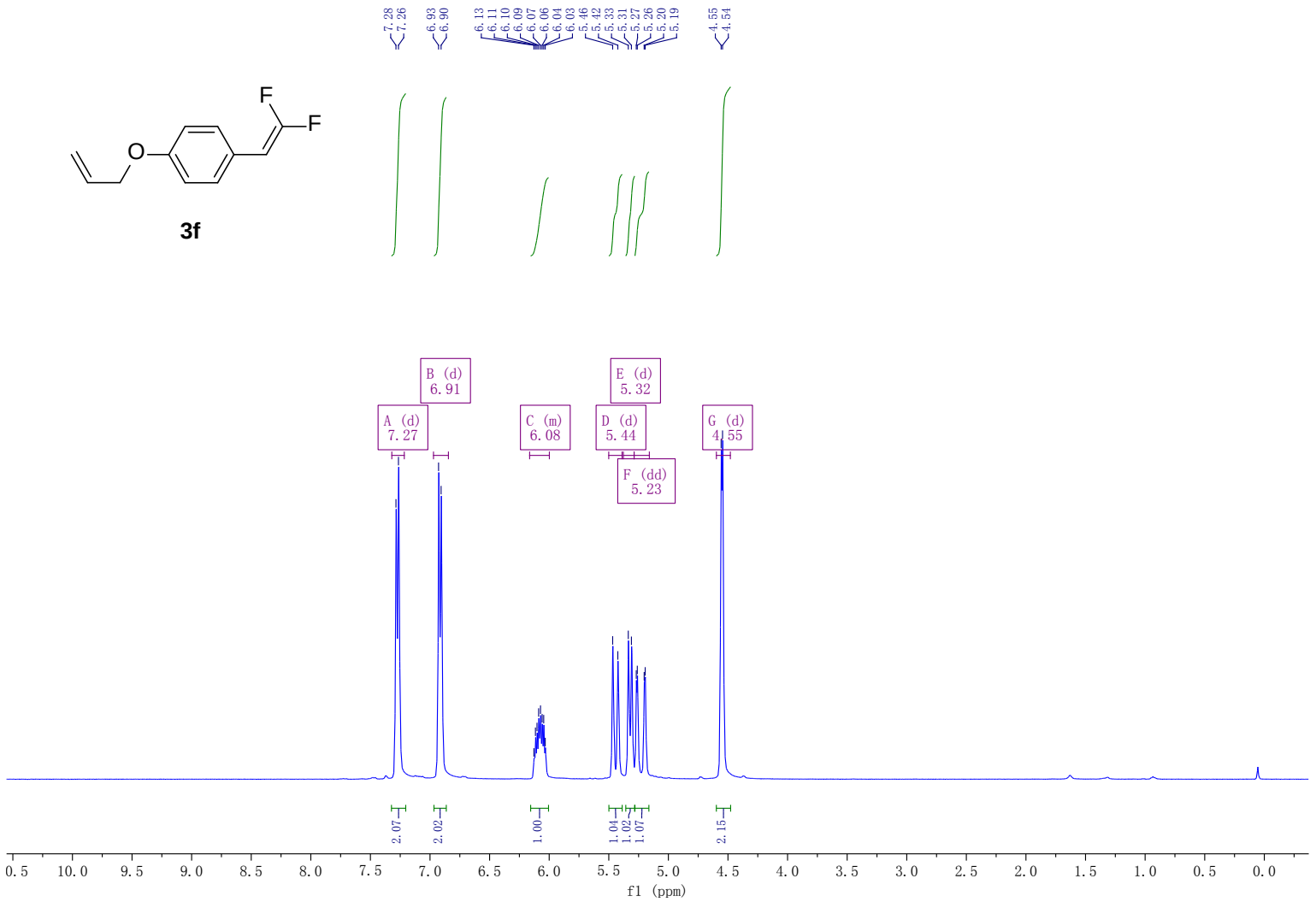
81.72
81.81
81.83
81.92
83.65
83.67
83.76
83.78
B (dd)
-83.71
A (dd)
-81.82
1.00
1.02
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

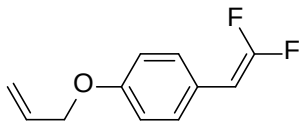

7.27
7.24
6.88
6.86
5.26
5.25
5.17
5.16
3.80
1.58
F
F
O
3e
B (d)
6.87
A (d)
7.25
C (dd)
5.21
D (s)
3.80
2.07
1.99
1.00
3.10
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


F
F
O

3e

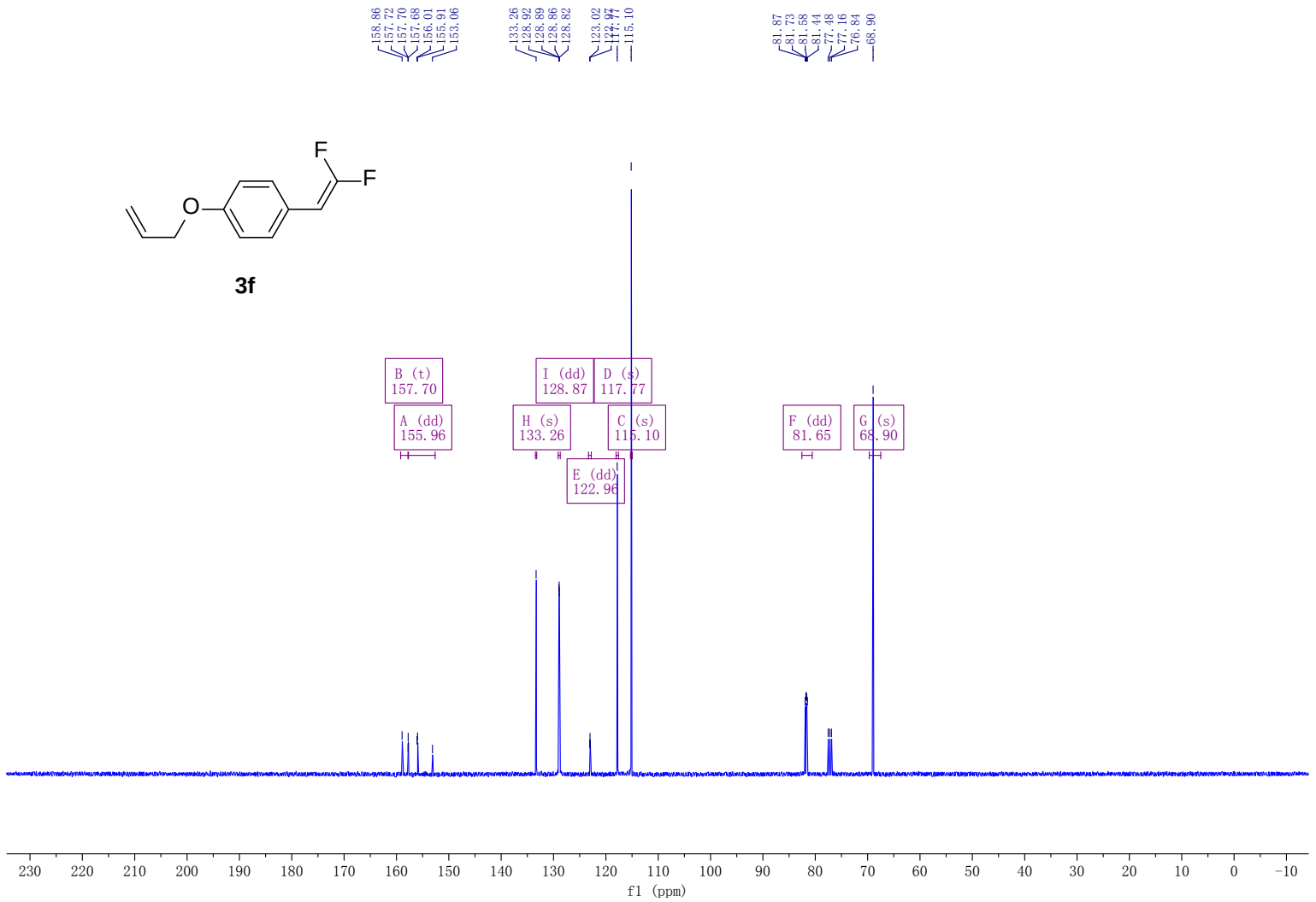
-84.53
-84.62
-84.66
-84.75
-86.37
-86.39
-86.51
-86.52
B (dd)
-86.45
A (dd)
-84.64
1.00
1.02
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

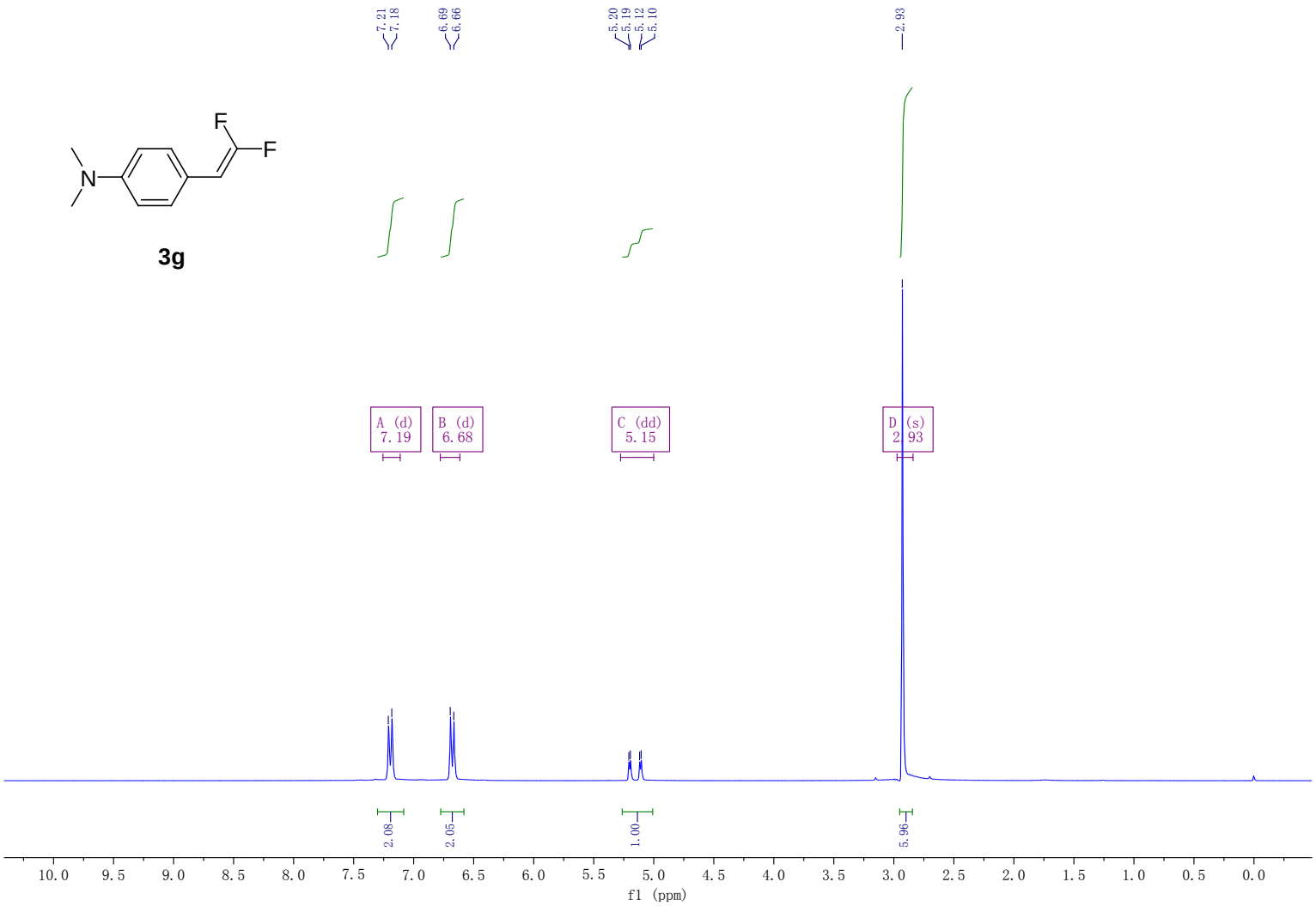

F
F
O
3f
7.28
7.26
6.93
6.90
6.13
6.11
6.10
6.09
6.07
6.06
6.04
6.03
5.46
5.42
5.33
5.31
5.27
5.26
5.20
5.19
4.55
4.54
A (d)
7.27
B (d)
6.91
C (m)
6.08
D (d)
5.44
E (d)
5.32
F (dd)
5.23
G (d)
4.55
2.07
2.02
1.00
1.04
1.02
1.07
2.15
f1 (ppm)

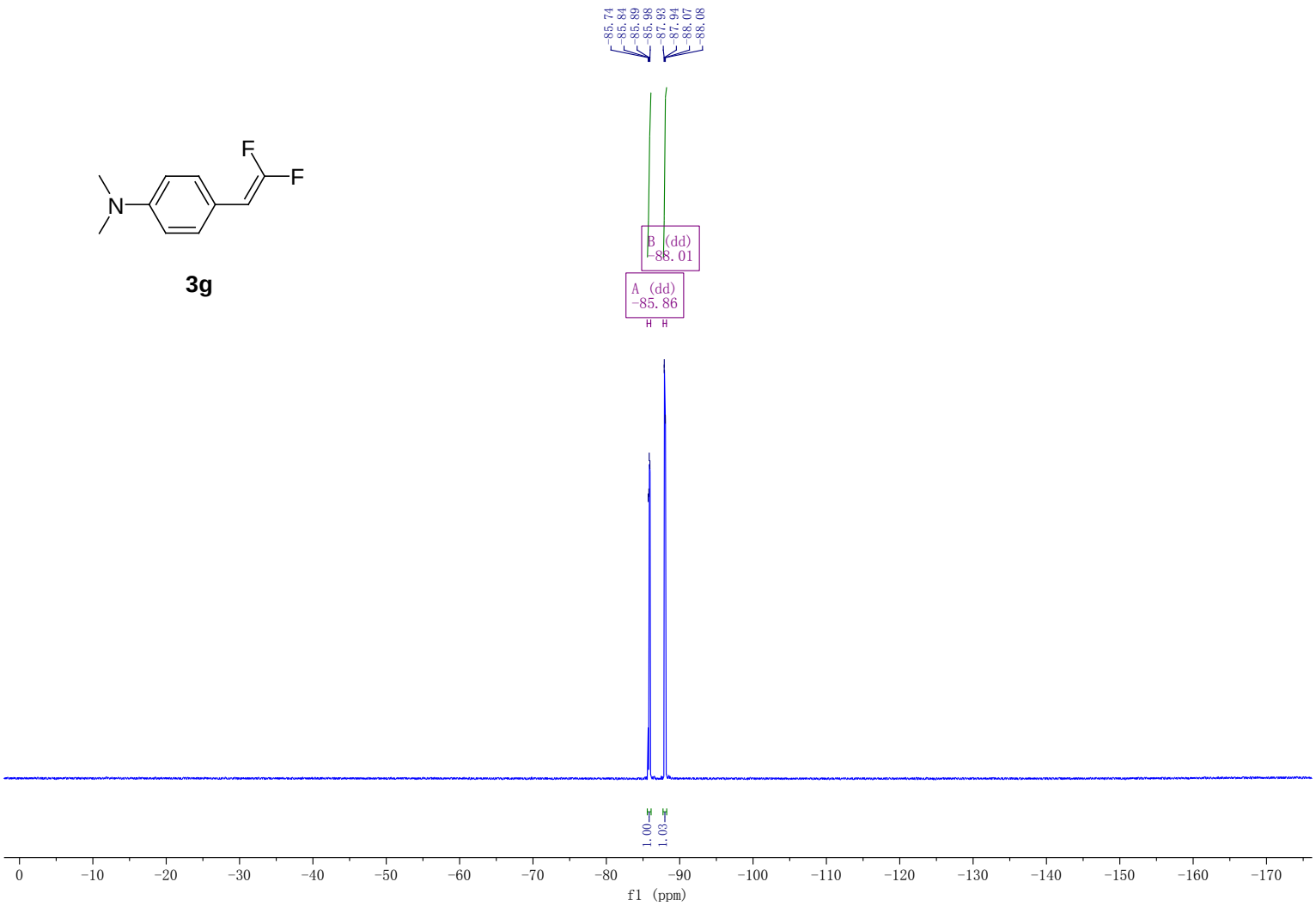

F
F
O

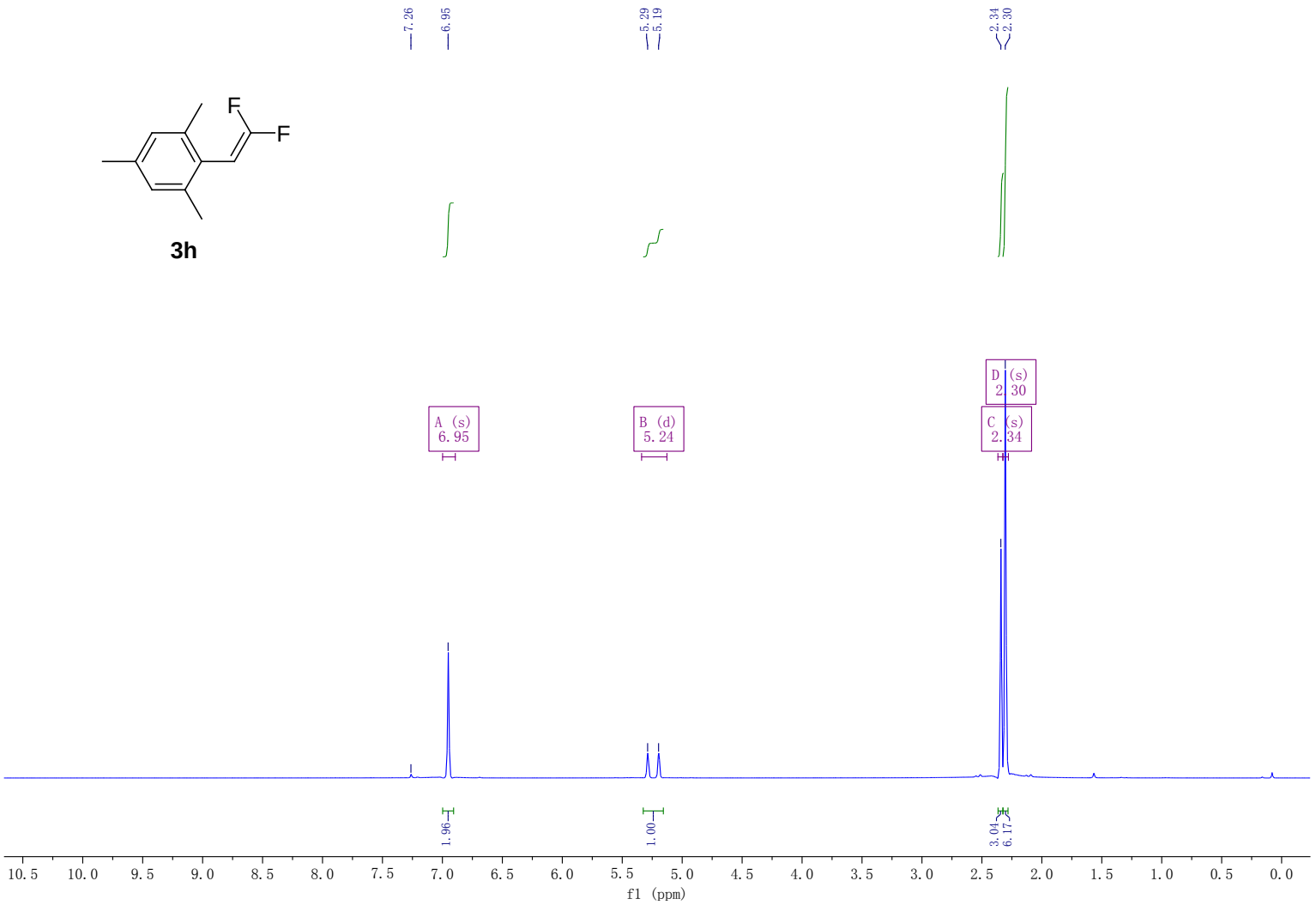
3f

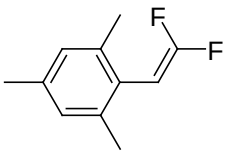
-84.59
-84.66
-84.69
-84.76
-86.43
-86.44
-86.52
-86.53
B (dd)
-86.48
A (dd)
-84.68
1.00
1.01
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)


158.86
157.72
157.70
157.68
156.01
155.91
153.06
133.26
128.92
128.89
128.86
128.82
123.02
115.10
81.87
81.73
81.58
81.44
77.48
77.16
76.84
68.90
F
F
O
3f
B (t)
157.70
A (dd)
155.96
I (dd)
128.87
D (s)
117.77
H (s)
133.26
C (s)
115.10
E (dd)
122.96
F (dd)
81.65
G (s)
68.90
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


F
F
N
3g
7.21
7.18
6.69
6.66
5.20
5.19
5.12
5.10
2.93
A (d)
7.19
B (d)
6.68
C (dd)
5.15
D (s)
2.93
2.08
2.05
1.00
5.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

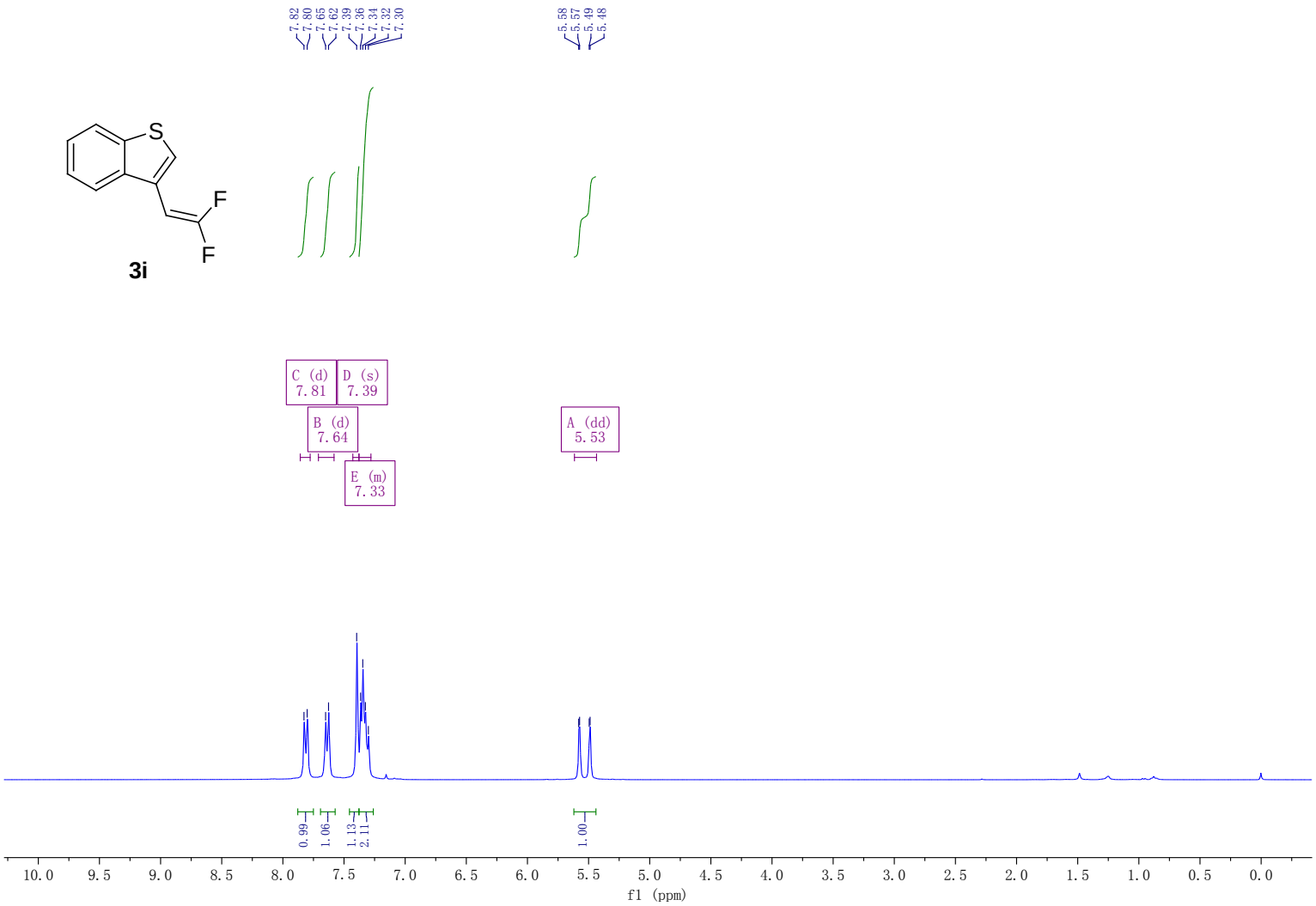

F
F
N
3g
-85.74
-85.84
-85.89
-85.98
-87.93
-87.94
-88.07
-88.08
B (dd)
-88.01
A (dd)
-85.86
H H
1.00
1.03
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

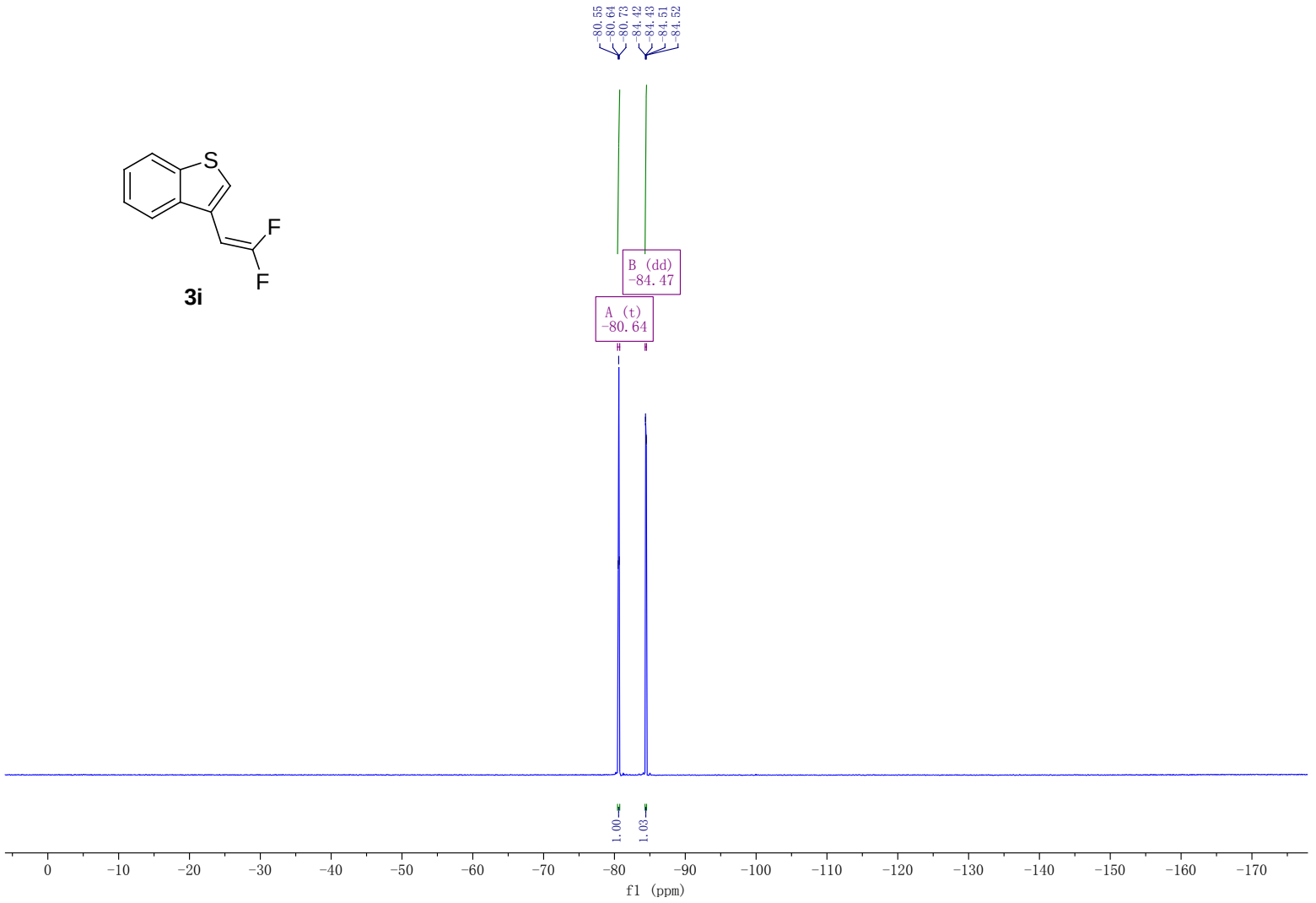

F
F
3h
7.26
6.95
5.29
5.19
2.34
2.30
A (s)
6.95
B (d)
5.24
D (s)
2.30
C (s)
2.34
1.96
1.00
3.04
6.17
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

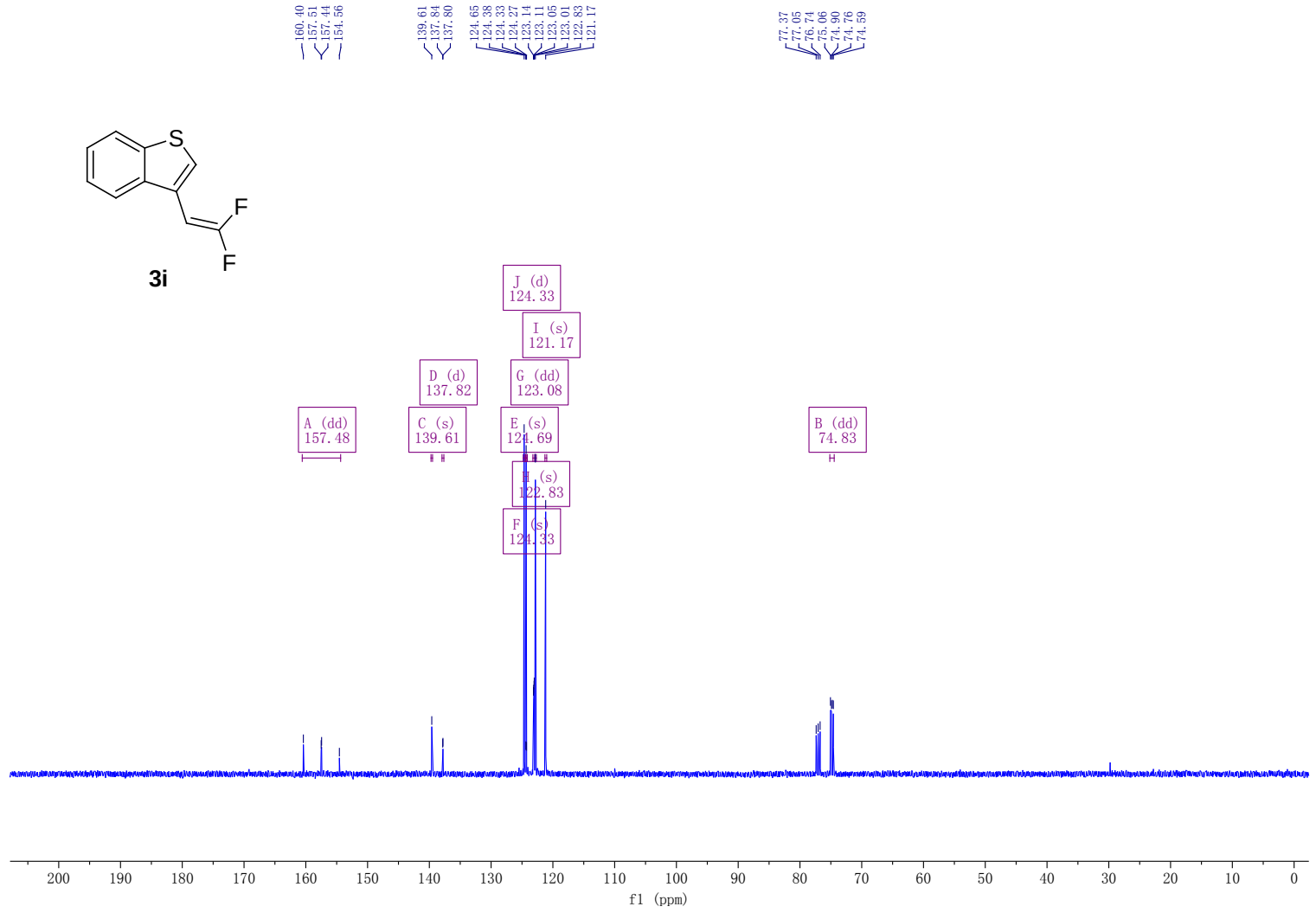

F
F

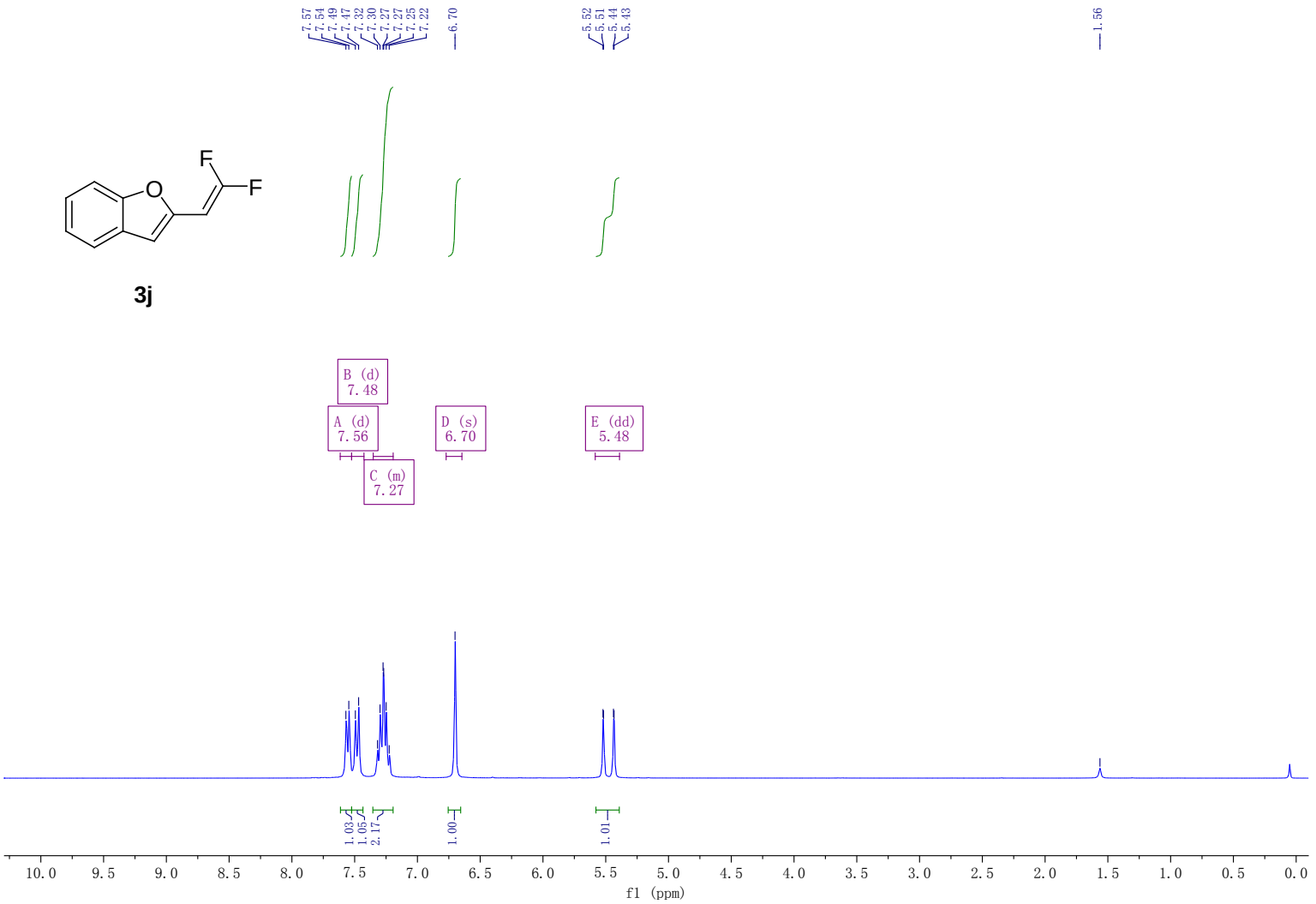
3h

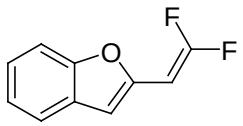
-83.66
-83.76
-83.78
-83.88
-87.38
-87.39
-87.50
-87.51
B (dd)
-87.45
A (dd)
-83.77
1.00
1.05
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)


7.82
7.80
7.65
7.62
7.39
7.36
7.34
7.32
7.30
5.58
5.57
5.49
5.48
S
F
F
3i
C (d)
7.81
D (s)
7.39
B (d)
7.64
E (m)
7.33
A (dd)
5.53
0.99
1.06
1.13
2.11
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


S
F
F
3i
-80.55
-80.64
-80.73
-84.42
-84.43
-84.51
-84.52
B (dd)
-84.47
A (t)
-80.64
1.00
1.03
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

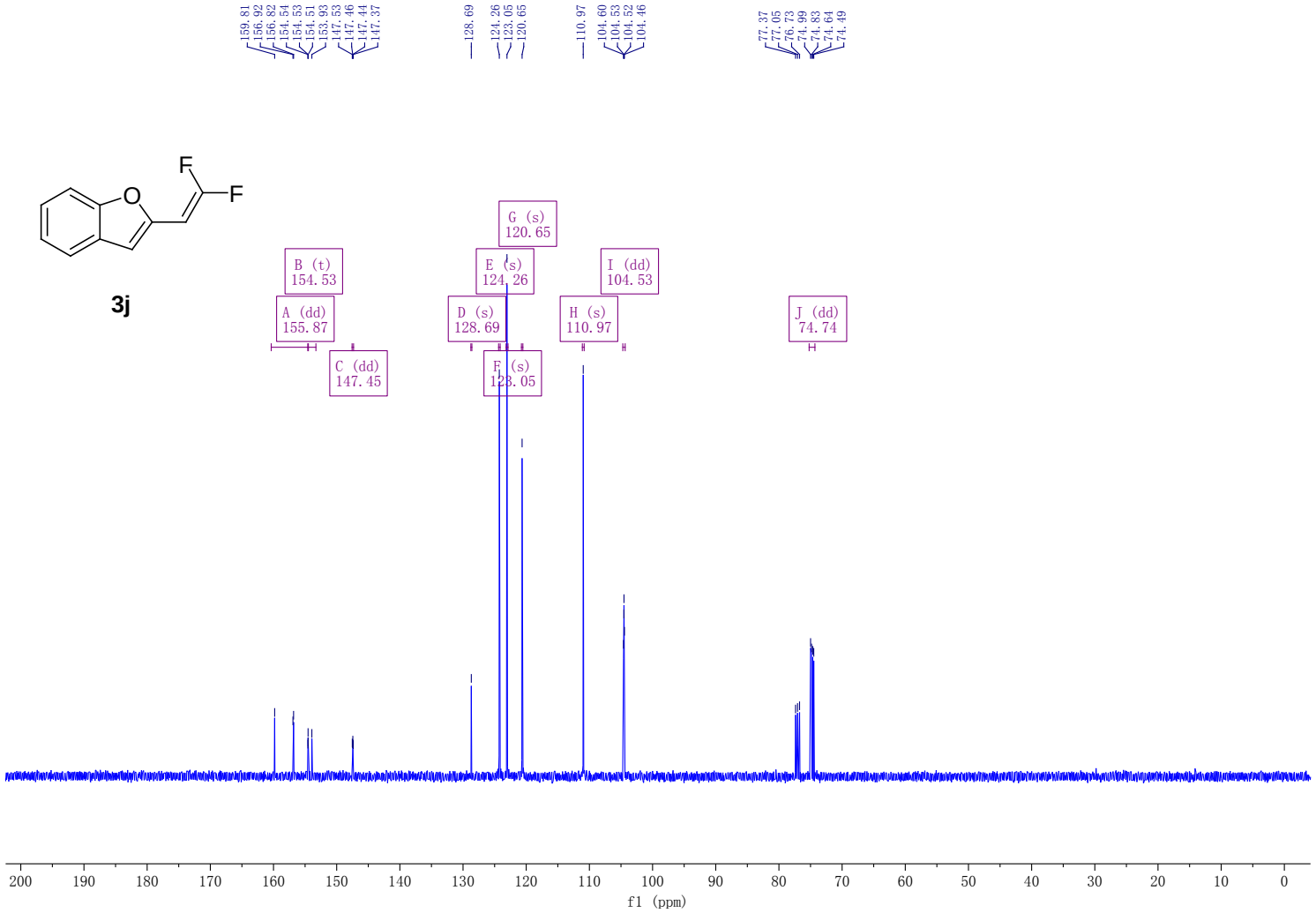

160.40
157.51
157.44
154.56
139.61
137.84
137.80
124.65
124.38
124.33
124.27
123.14
123.11
123.05
123.01
122.83
121.17
77.37
77.05
76.74
75.06
74.90
74.76
74.59
S
F
F
3i
J (d)
124.33
I (s)
121.17
D (d)
137.82
G (dd)
123.08
A (dd)
157.48
C (s)
139.61
E (s)
121.69
B (dd)
74.83
H
H (s)
122.83
F (s)
121.33
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.57
7.54
7.49
7.47
7.32
7.30
7.27
7.27
7.25
7.22
6.70
5.52
5.51
5.44
5.43
1.56
F
F
O
3j
B (d)
7.48
A (d)
7.56
C (m)
7.27
D (s)
6.70
E (dd)
5.48
1.03
1.05
2.17
1.00
1.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


F
O
F

3j

-75.86
-75.91
-75.94
-76.00
-82.16
-82.21
B (d)
-82.18
A (dd)
-75.93
1.00
1.02
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)


159.81
156.92
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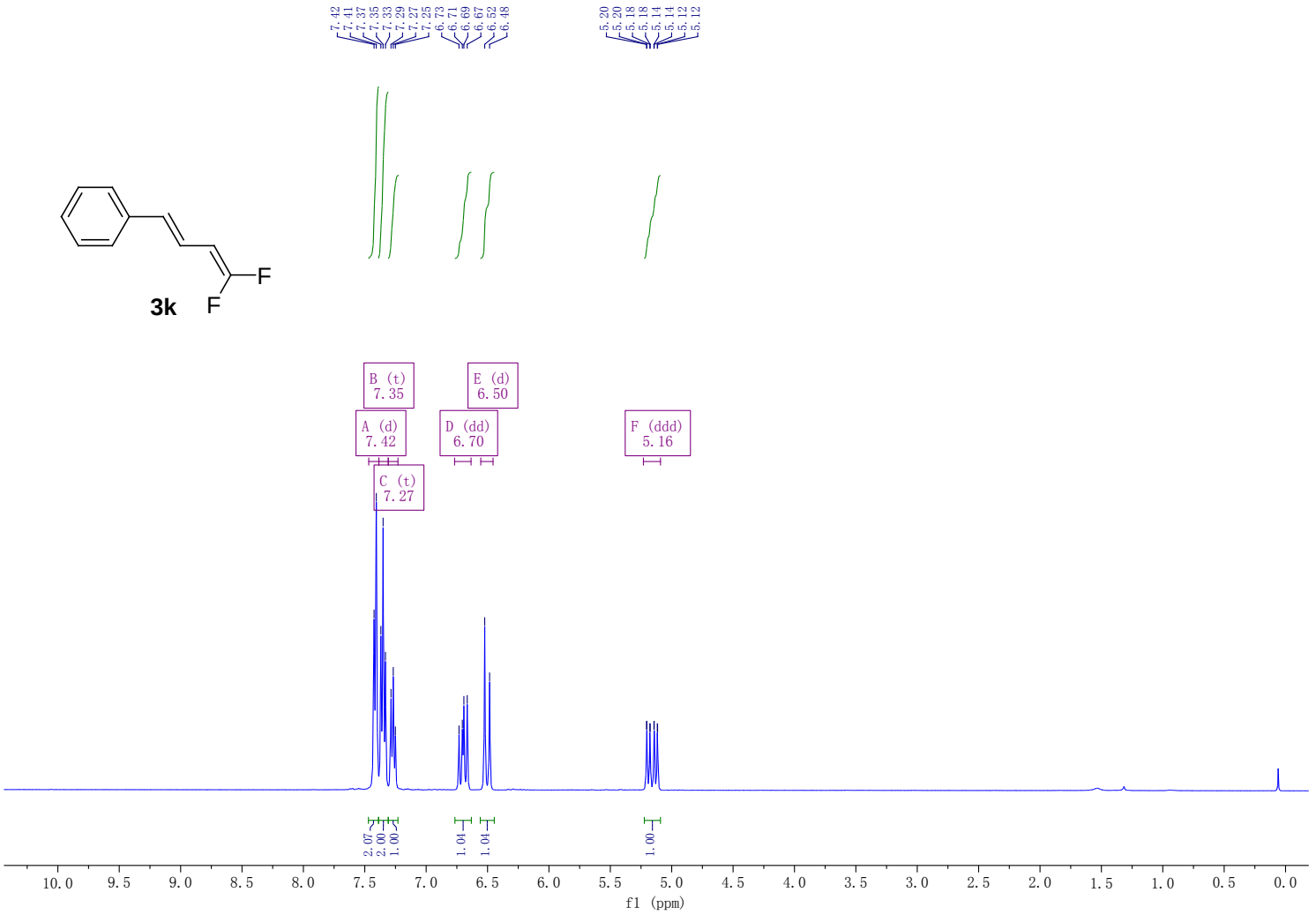
156.54
154.54
154.53
154.51
153.93
147.53
147.46
147.44
147.37
128.69
124.26
123.05
120.65
110.97
104.60
104.53
104.52
104.46
77.37
77.05
76.73
74.99
74.83
74.64
74.49
F
O
F
3j
B (t)
154.53
A (dd)
155.87
C (dd)
147.45
G (s)
120.65
E (s)
124.26
D (s)
128.69
F (s)
123.05
I (dd)
104.53
H (s)
110.97
J (dd)
74.74
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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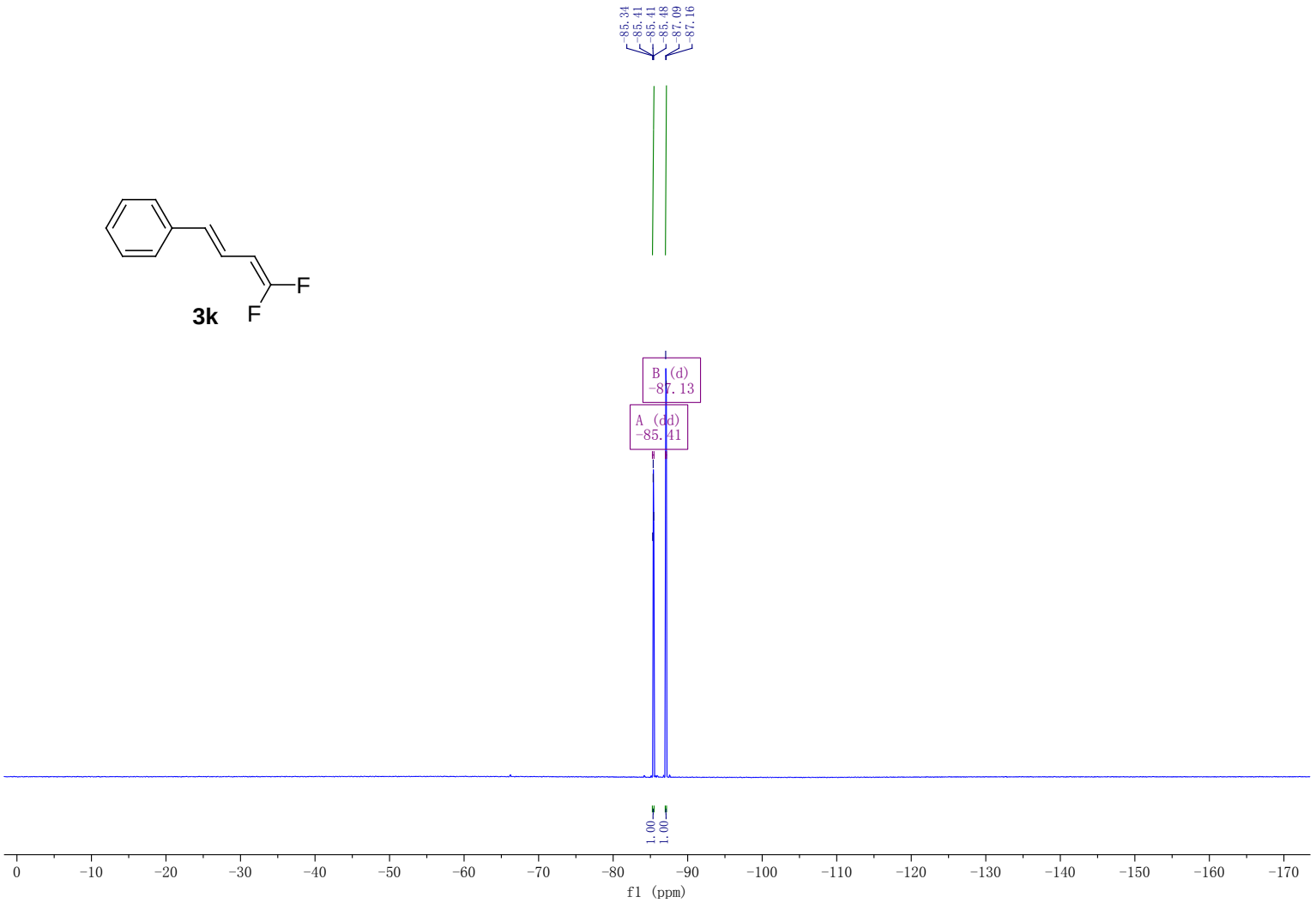
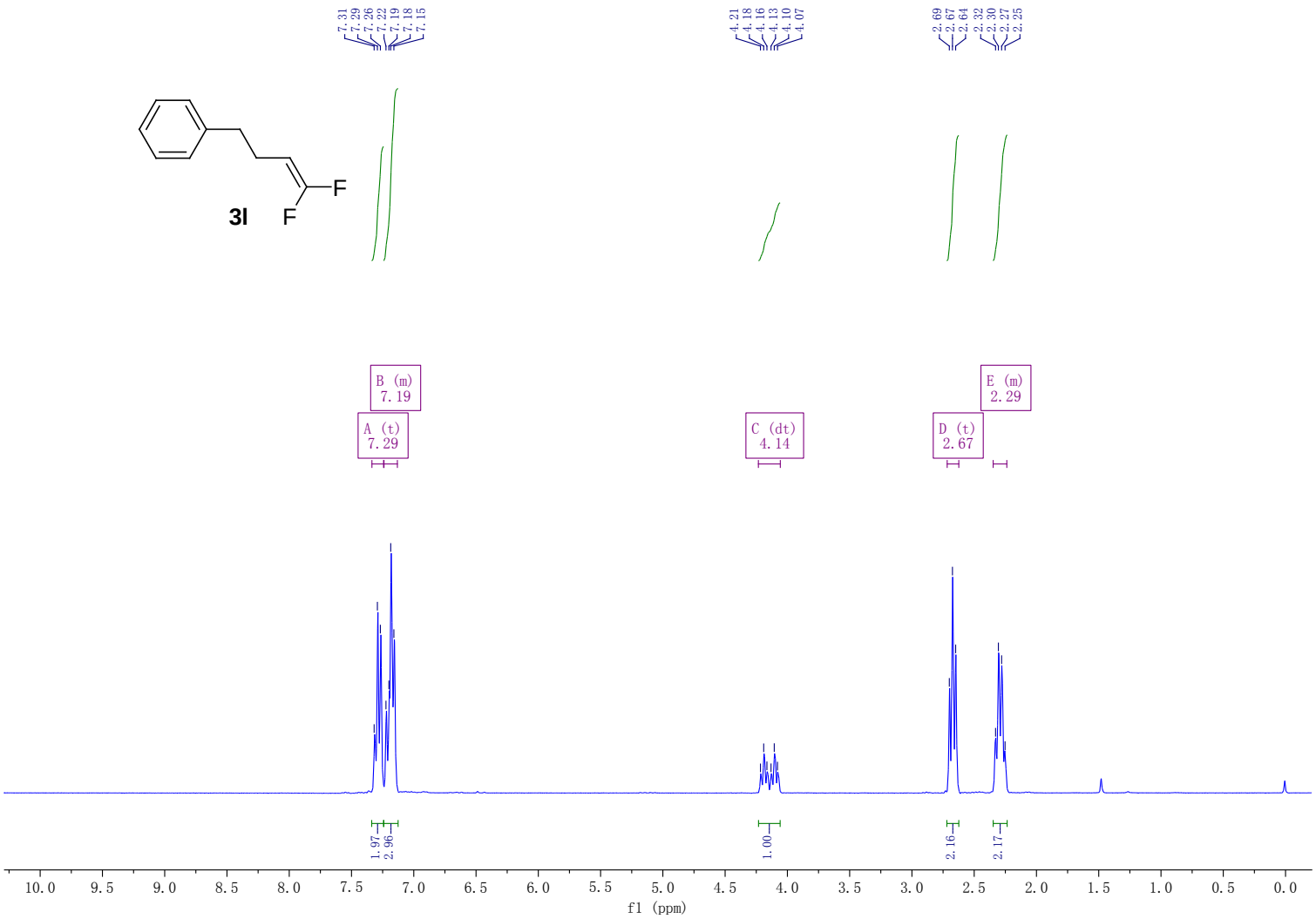
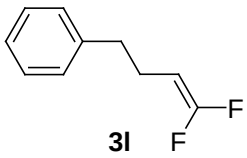
7.41
7.37
7.35
7.33
7.29
7.27
7.25
6.73
6.71
6.69
6.67
6.52
6.48
5.20
5.20
5.18
5.18
5.14
5.14
5.12
5.12
F
F
3k
B (t)
7.35
E (d)
6.50
A (d)
7.42
D (dd)
6.70
F (ddd)
5.16
C (t)
7.27
2.07
2.00
1.00
1.04
1.04
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

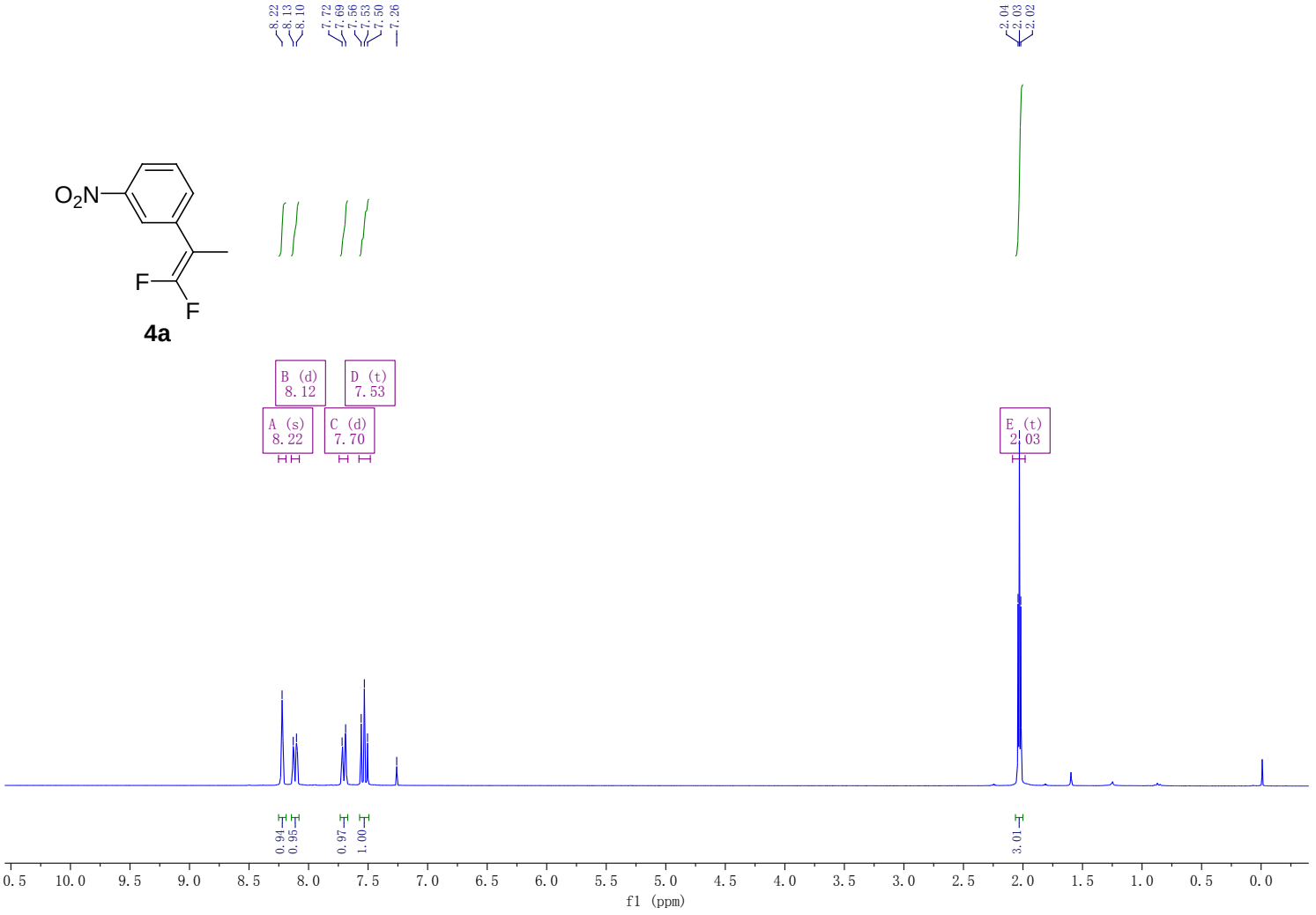

-85.34
-85.41
-85.41
-85.48
-87.09
-87.16
F
F
3k
B (d)
-87.13
A (dd)
-85.41
1.00
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

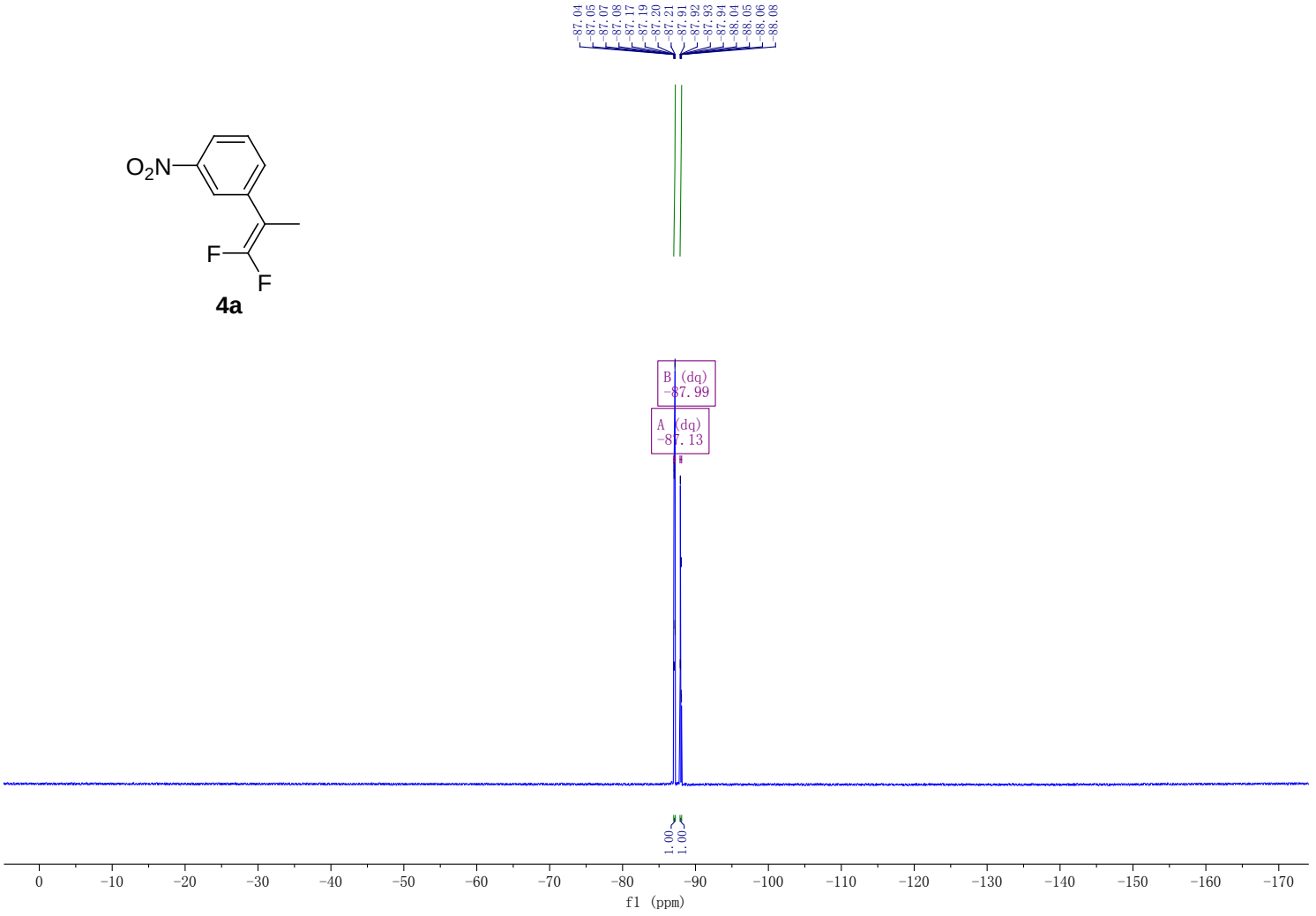

7.31
7.29
7.26
7.22
7.19
7.18
7.15
4.21
4.18
4.16
4.13
4.10
4.07
2.69
2.67
2.64
2.32
2.30
2.27
2.25
3l
F
F
B (m)
7.19
A (t)
7.29
C (dt)
4.14
E (m)
2.29
D (t)
2.67
1.97
2.96
1.00
2.16
2.17
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

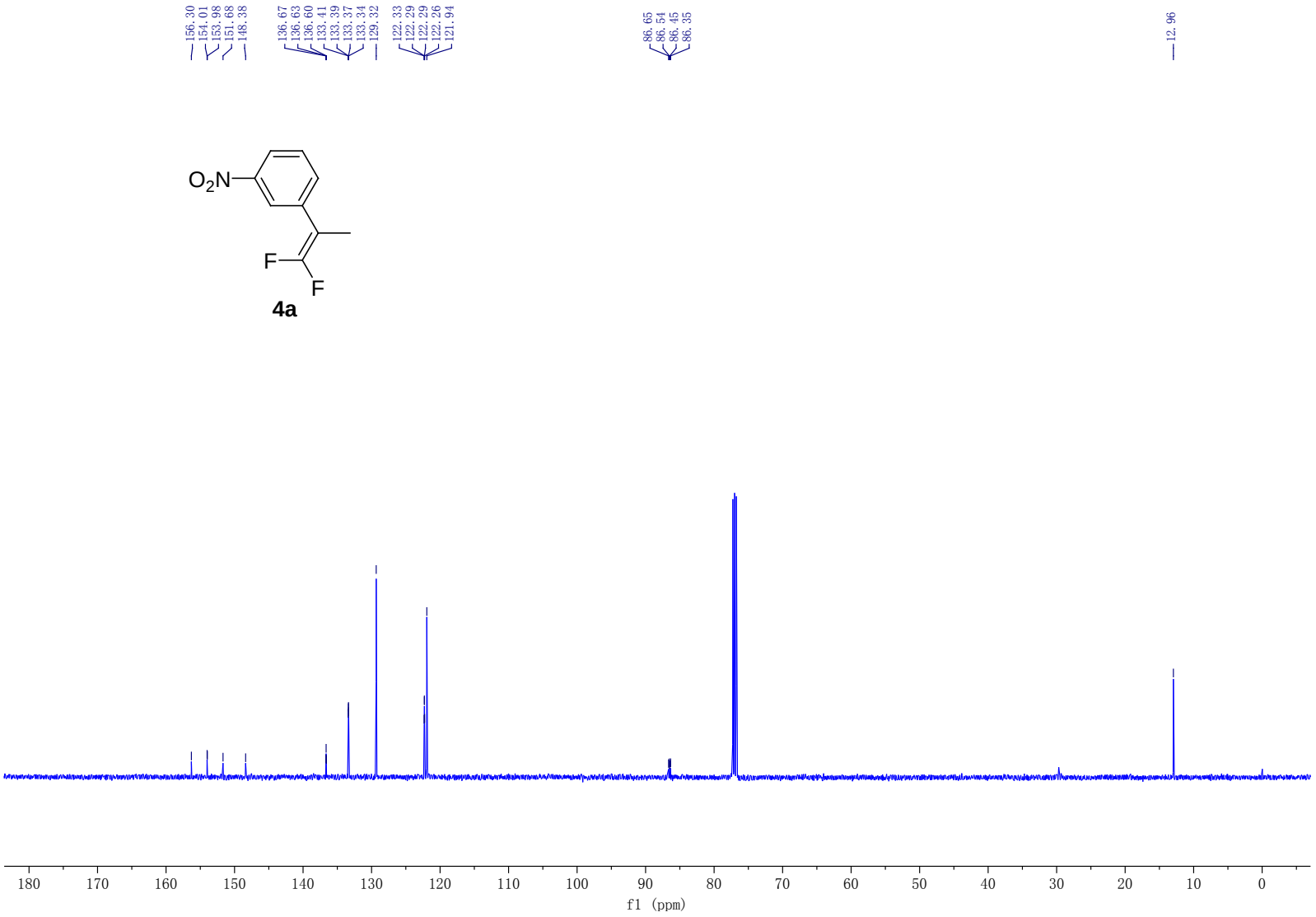

F
F

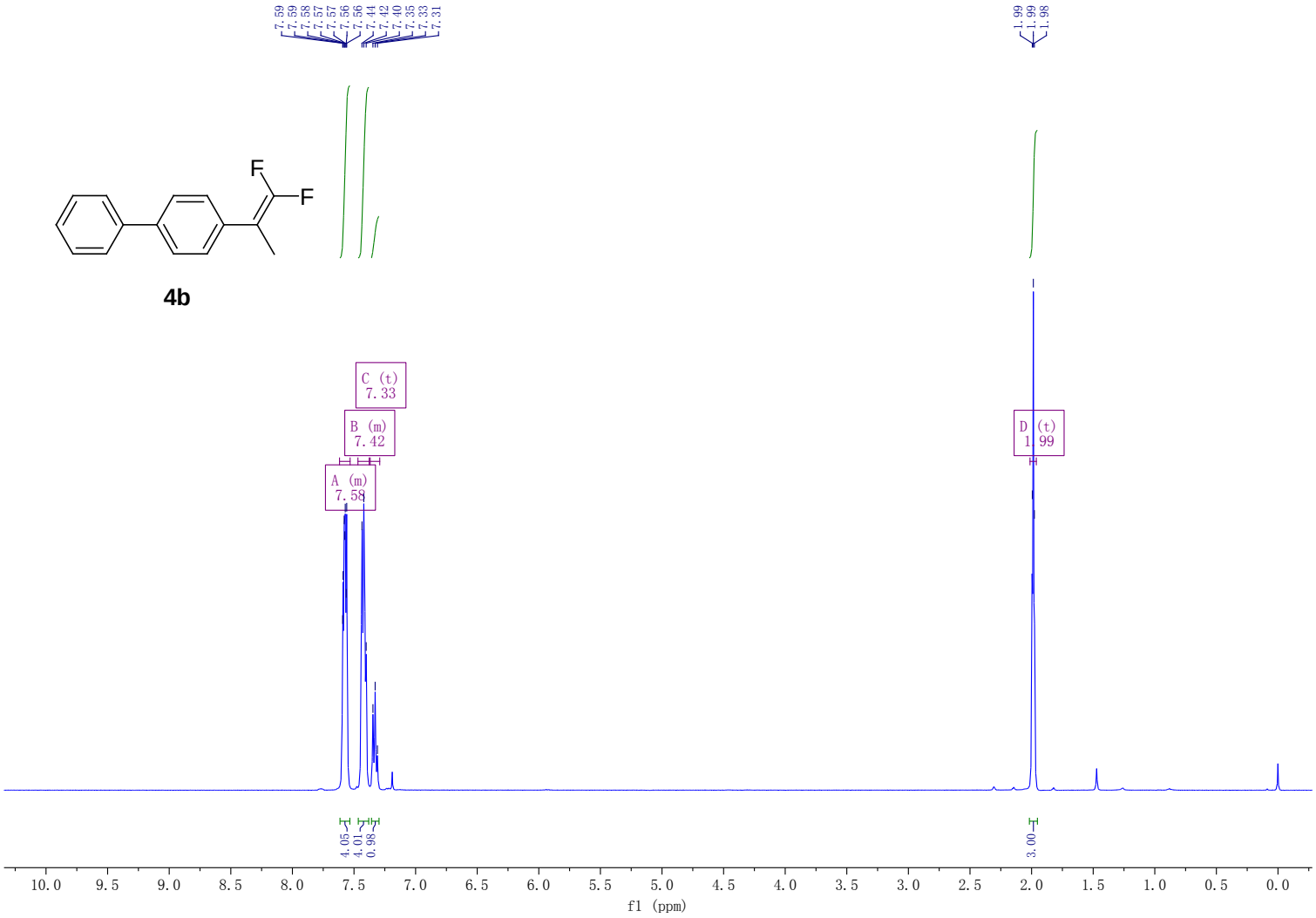
3l

-89.29
-89.46
-91.32
-91.41
-91.49
-91.58
B (dd)
-91.45
A (d)
-89.38
1.00
0.99
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

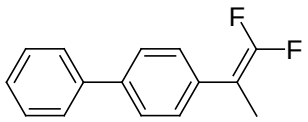

8.22
8.13
8.10
7.72
7.69
7.56
7.53
7.50
7.26
2.04
2.03
2.02
O2N
F
F
4a
B (d)
8.12
D (t)
7.53
A (s)
8.22
C (d)
7.70
E (t)
2.03
0.94
0.95
0.97
1.00
3.01
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


-87.04
-87.05
-87.07
-87.08
-87.17
-87.19
-87.20
-87.21
-87.91
-87.92
-87.93
-87.94
-88.04
-88.05
-88.06
-88.08
O2N
F
F
4a
B (dq)
-87.99
A (dq)
-87.13
1.00
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)


156.30
154.01
153.98
151.68
148.38
136.67
136.63
136.60
133.41
133.39
133.37
133.34
129.32
122.33
122.29
122.29
122.26
121.94
86.65
86.54
86.45
86.35
12.96
O2N
F
F
4a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

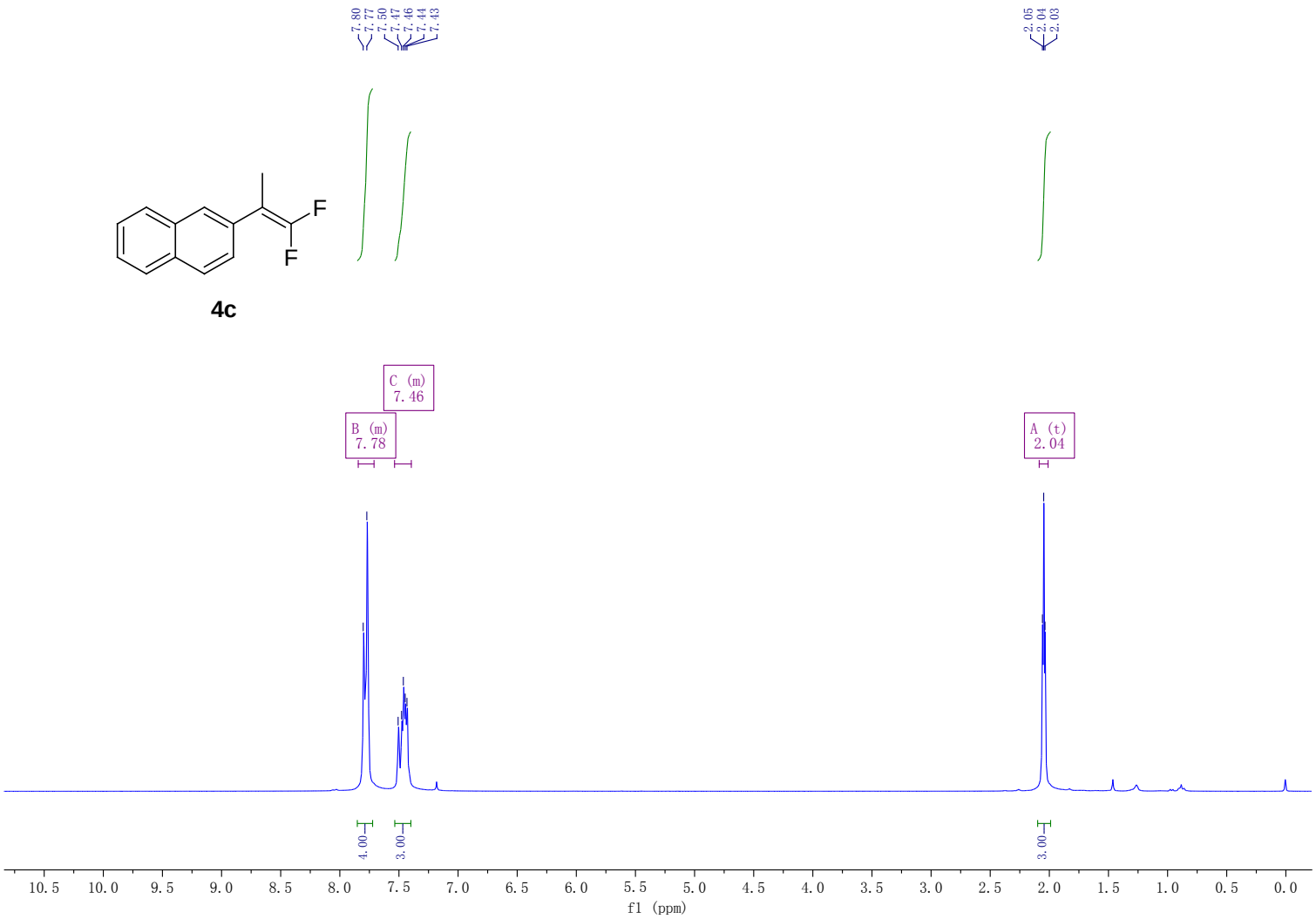

7.59
7.59
7.58
7.57
7.57
7.56
7.56
7.44
7.42
7.40
7.35
7.33
7.31
1.99
1.99
1.98
F
F
C (t)
7.33
B (m)
7.42
A (m)
7.58
D (t)
1.99
4.05
4.01
0.98
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

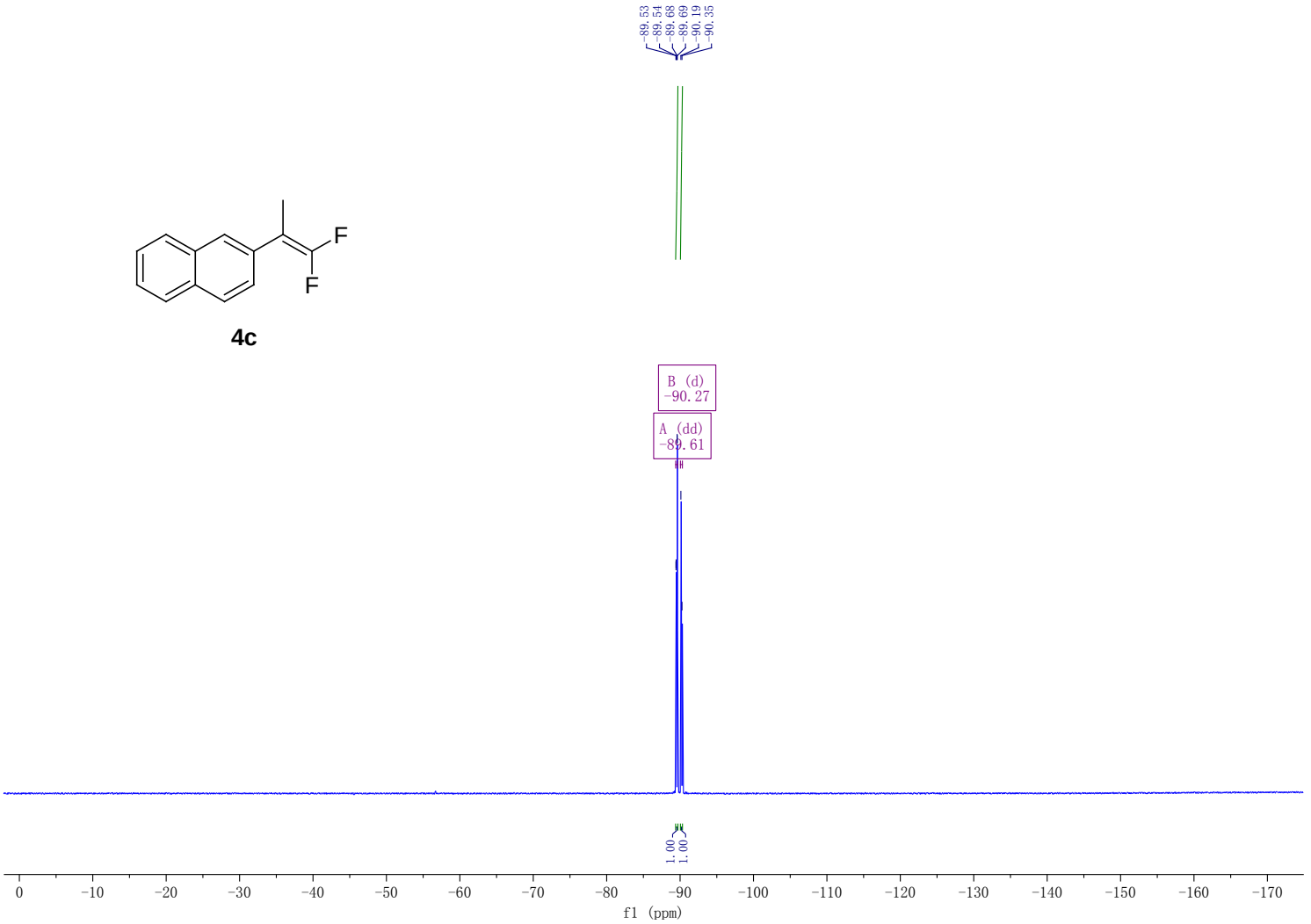
4b


F
F

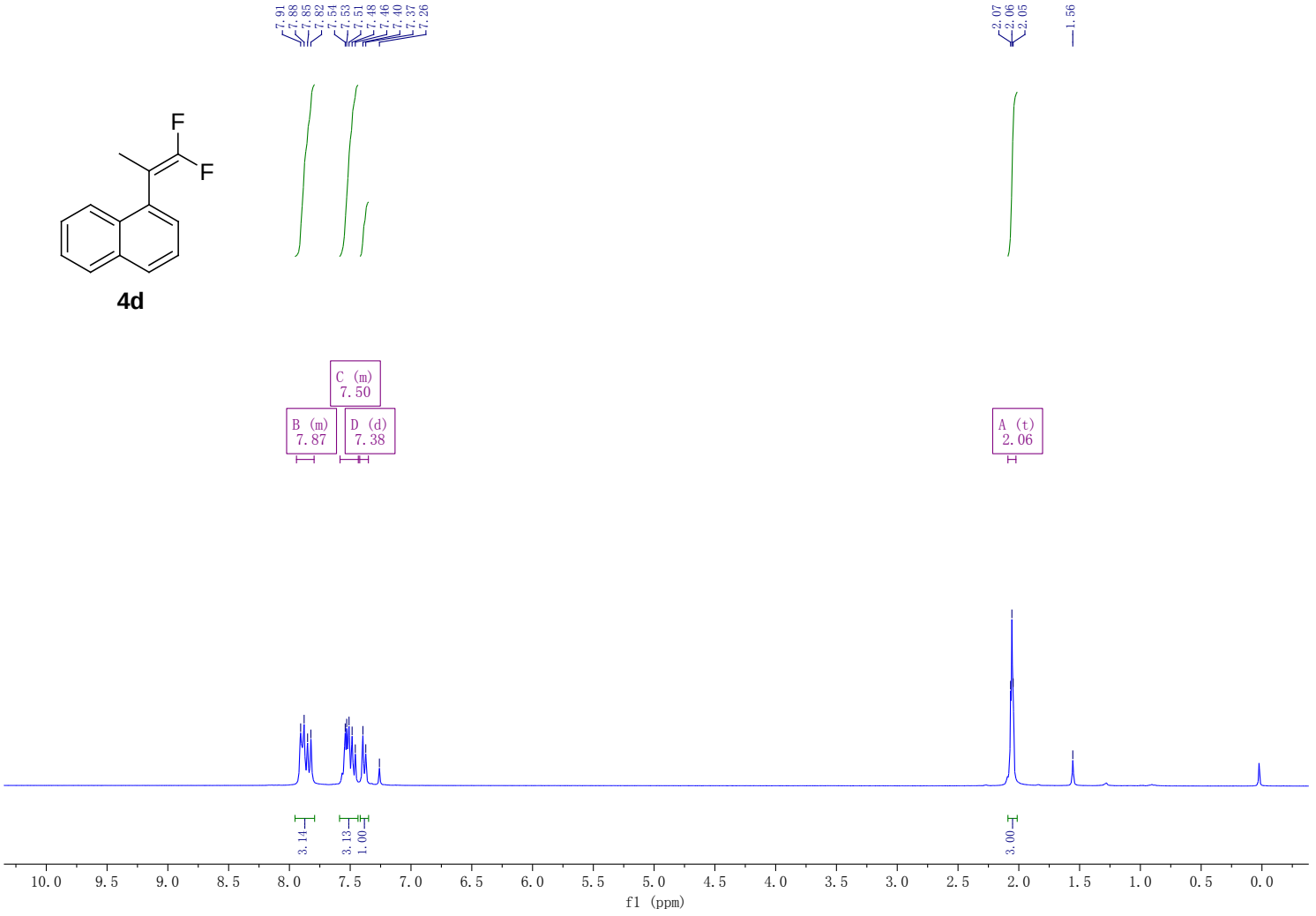
4b

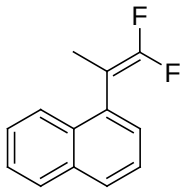
-89.67
-89.68
-89.69
-89.70
-89.78
-89.79
-89.80
-89.81
-90.07
-90.08
-90.18
-90.19
B (dd)
-90.13
A (dq)
-89.74
1.00
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)


7.80
7.77
7.50
7.47
7.46
7.44
7.43
2.05
2.04
2.03
F
F
4c
C (m)
7.46
B (m)
7.78
A (t)
2.04
4.00
3.00
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


-89.53
-89.54
-89.68
-89.69
-90.19
-90.35
F
F
B (d)
-90.27
A (dd)
-89.61
1.00
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

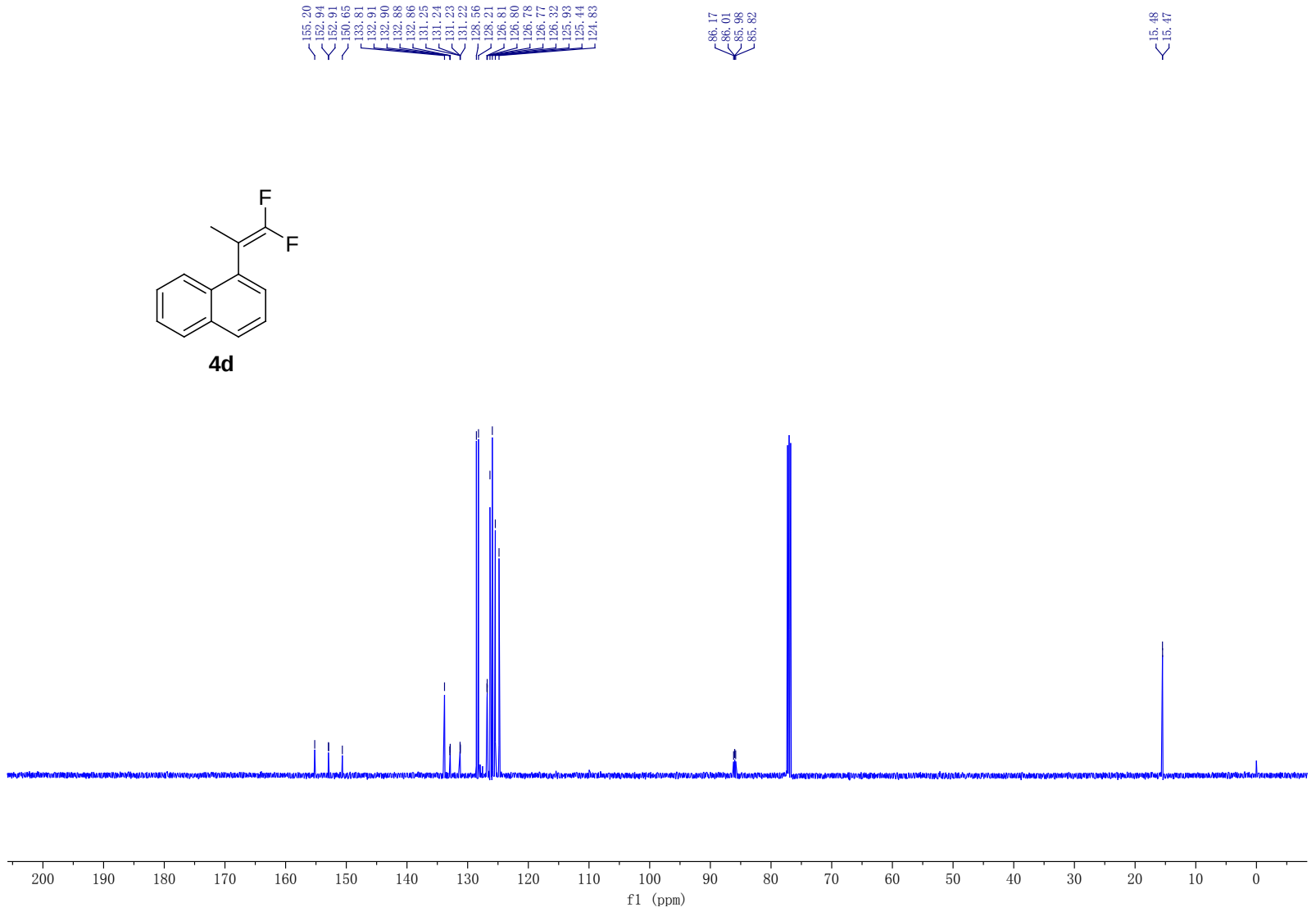
4c


7.91
7.88
7.85
7.82
7.54
7.53
7.51
7.48
7.46
7.40
7.37
7.26
2.07
2.06
2.05
1.56
F
F
4d
C (m)
7.50
B (m)
7.87
D (d)
7.38
A (t)
2.06
3.14
3.13
1.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

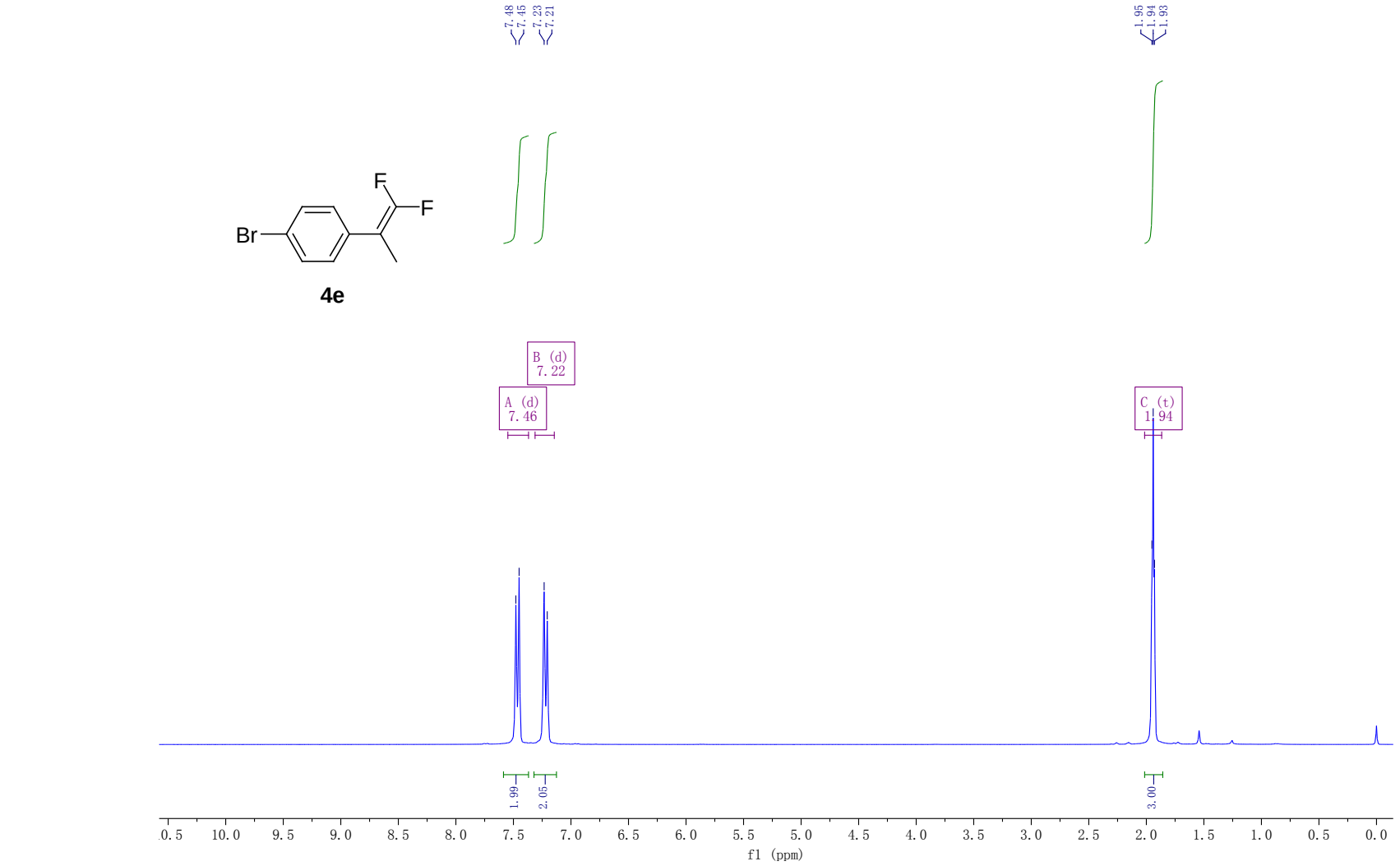

F
F

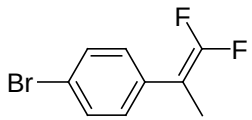
4d

-89.32
-89.33
-89.48
-89.49
-93.59
-93.61
-93.76
-93.77
B (dd)
-93.68
A (dd)
-89.41
H
H
1.00
1.01
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)


155.20
152.94
152.91
150.65
133.81
132.91
132.90
132.88
132.86
131.25
131.24
131.23
131.22
128.56
128.21
126.81
126.80
126.78
126.77
126.32
125.93
125.44
124.83
86.17
86.01
85.98
85.82
15.48
15.47
F
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4d


F
F
Br
4e
7.48
7.45
7.23
7.21
1.95
1.94
1.93
B (d)
7.22
A (d)
7.46
C (t)
1.94
1.99
2.05
3.00
f1 (ppm)


F
F
Br

4e

-89.19
-89.20
-89.34
-89.35
-89.67
-89.68
-89.82
-89.83
B (dd)
-89.75
A (dd)
-89.27
1.00
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)