Rh(III)-catalyzed redox-neutral C-H alkenylation of benzamides with *gem*-difluorohomoallylic silyl ethers *via* β-H elimination

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Supporting Information

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1. General Considerations

Unless otherwise noted, all reactions were carried out under an atmosphere of nitrogen in dried glassware. If reaction was not carried out at room temperature, reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The dry solvents used were purchased from commercial sources (Bide Pharmatech, Energy Chemical, J&K Chemic, TCI, Fluka, Acros, SCRC, Aladdin) and used without further purification unless otherwise stated.

Analytical thin layer chromatography was performed on GF_{254} plates from Qingdao Marine Chemical Co., Ltd. Visualization was accomplished with short wave UV light, or $KMnO_4$ staining solutions followed by heating. Flash chromatography was performed on silica gel (200-300 mesh) by standard technique.

^1H were recorded on a Bruker AV 500 in solvents as indicate. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; d_6-DMSO: δ_H = 2.50 ppm, δ_C = 39.52 ppm; d_4-MeOD: δ_H = 3.31 ppm, δ_C = 49.00 ppm). The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet. Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C NMR spectra were recorded on 101 MHz spectrometers. Chemical shifts were reported in parts per million relative to tetramethylsilane (δ = 0). High-resolution mass spectra (HRMS) were recorded using electrospray ionization (ESI) and time-offlight (TOF) mass analysis.

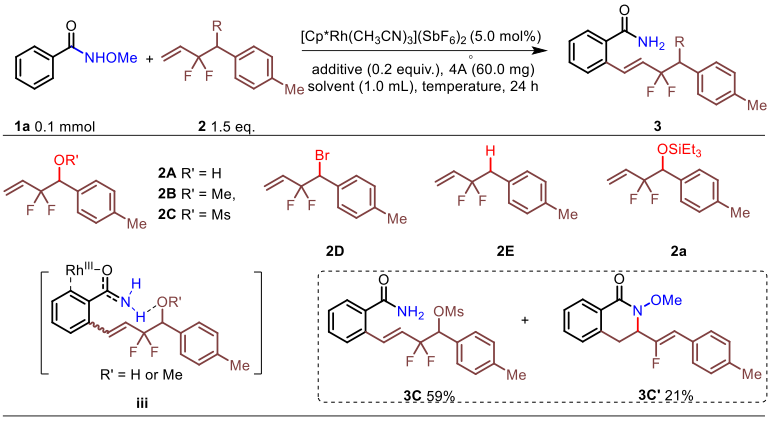
No attempts were made to optimize yields for substrate synthesis.

2. Optimization of the reaction conditions

We commenced our investigation by employing *N*-methoxybenzamide (**1a**) and 2,2-difluoro-1-(p-tolyl)but-3-en-1-ol (**2A**) as model reaction. Initially, the reaction proceeded in a 0.1 mmol scale with 1.5 equiv. **2A** in MeOH under base (CsOAc, 1.0 equiv.) and air conditions. Interestingly, the conversion of the reaction was high and mainly led to dialkenylation product in low *E/Z* ratios (detected by ^{1}H NMR), resulting in complex ^{1}H NMR spectra. Though several conditions were screened, we failed to obtain a single product in high stereo-selectivity. The use of 1-(2,2-difluoro-1-methoxybut-3-en-1-yl)-methylbenzene (**2B**) as a coupling partner gave the same result. We hypothesize that the high electron cloud density of oxygen atom in mono-alkenylation intermediate (Table 1, **iii**) may form hydrogen bond with the directing group which may increase the coordination ability of amide and results in dialkenylation. When an electron withdrawing group substituted difluorinated synthon (**2C**) was used as a coupling partner, it did result in monoalkenylated product **3C** in 59% along with 21% of annulated product **3C'** via β-F elimination/SN_2' reaction under the conditions of Cp*Rh$(CH_3CN)_3$]$(SbF_6)_2$ (5 mol%), $NaHCO_3$ (20 mol%), 4Å molecular sieve (60 mg) in DMF (0.1 M) at 70 ºC for 24 h. Unfortunately, the reaction was still unable to produce single product although different conditions were screened. We next continue to investigate the effect of the substituent groups on the *gem*-difluorinated synthons. When the substitution switched to Br (**2D**) or no substitution at homoallylic position of difluorinated synthon (**2E**), no product was formed under the same conditions. Delightedly, when the coupling partner was changed to a difluorinated building block (**2a**) with appropriate electrical property and steric hindrance effect, the β-H eliminated product **3aa** was detected in a 75% yield after 24 h (**Table 1**, entry 1). However, the absence of a base or replacement with PivOH resulted in low yields (entries 2 and 3). Solvent screening showed that DMF was the most favorable (entries 1 and 4). It should be noted that increasing the amount of $NaHCO_3$ to 50 mol% has no effect on the yield of **3aa** (entry 5). Moreover, either lowering or increasing the reaction temperature do not improve of the yield (entries 6 and 7). Removing the molecular sieve or decreasing the amount of catalyst resulted in a decrease in the

yields (entries 8 and 9). Control experiments showed that Cp*Rh(III) was essential for the reaction as its absence led to no formation of the desired product (entry 10).

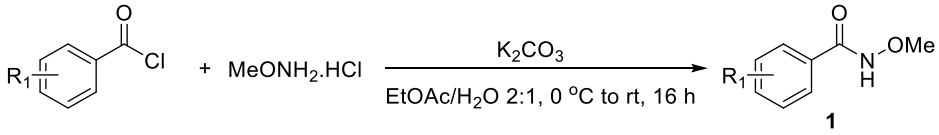
Table 1. Optimization of the reaction conditions[a]



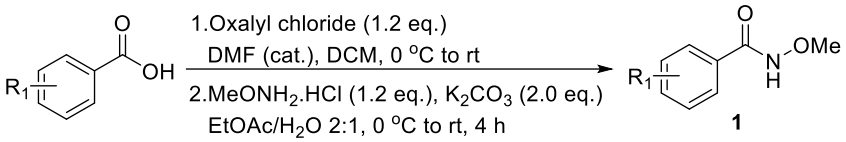
Entry	Additive	Solvent	T [°C]	Yield
1	$NaHCO_3$	DMF	70	75%
2	PivOH	MeOH	70	50%
3	-	MeOH	70	50%
4	$NaHCO_3$	MeOH	70	58%
5[b]	$NaHCO_3$	DMF	70	70%
6	$NaHCO_3$	DMF	80	72%
7	$NaHCO_3$	DMF	60	69%
8[c]	$NaHCO_3$	DMF	70	54%
9[d]	$NaHCO_3$	DMF	70	35%
10[e]	$NaHCO_3$	DMF	70	nr

[a] NMR yield with 4-Iodoanisole as an internal standard. [b] 0.5 equiv. $NaHCO_3$ was used. [c] 2.5 mol% of catalyst was used. [d] Without molecular sieve. [e] Without catalyst. nr: no reaction.

3. Preparation of *N*-methoxybenzamide

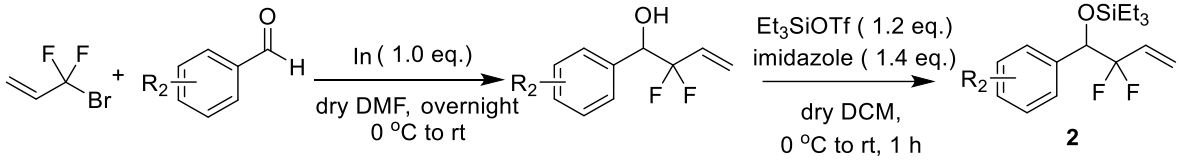


The title compounds were prepared according to a known procedure.[1]



The title compounds were prepared according to a known procedure.[1]

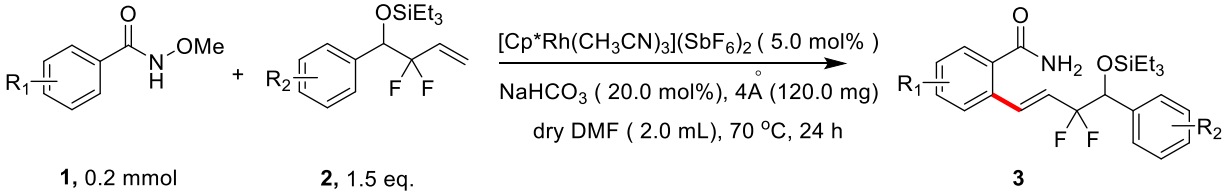
4. Preparation of *gem*-difluorohomoallylic silyl ethers



The title compounds was prepared according to a known procedure.[2]

5. General Procedure

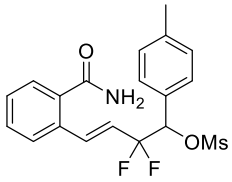
General Procedure:



A 15 mL-schlenk tube charged with a stirring bar, was added *N*-methoxybenzamide **1** (0.2 mmol, 1 equiv) and **2** (0.3 mmol, 1.5 equiv)、$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (8.3 mg, 0.01 mmol, 5.0 mol%)、$NaHCO_3$ (3.4 mg, 0.04 mmol, 20.0mol%) and 4Å molecular sieves (120.0 mg) , dry DMF (2.0 mL) were added subsequently into the reaction vessel. The reaction was allowed to stir at 70 °C for 24 hours. The reaction mixture was then diluted with EtOAc (20 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **3**.

6. Characterization of Products 3

(*E*)-4-(2-carbamoylphenyl)-2,2-difluoro-1-(p-tolyl)but-3-en-1-yl methanesulfon -ate (3C)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatorgraph (PE/EA = 1/1), **3C** was obtained as a white solid (46.6 mg, 0.118 mmol, 59 %). R_f = 0.40 (PE/EA = 1/1).

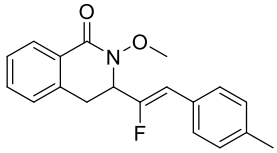
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.46 (ddd, *J* = 13.0, 7.6, 1.3 Hz, 2H), 7.42 – 7.34 (m, 4H), 7.22 (d, *J* = 7.9 Hz, 2H), 6.34 (s, 1H), 6.08 (ddd, *J* = 16.1, 12.6, 10.7 Hz, 1H), 5.86 (s, 1H), 5.67 (t, *J* = 9.6 Hz, 1H), 2.89 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 140.3, 135.3, 135.2, 135.2, 135.17, 133.2, 131.0, 129.6, 129.3, 128.8, 128.4, 128.1, 127.3, 121.9 (t, *J* = 24.9 Hz), 118.1 (t, *J* = 241.2 Hz), 82.5 (t, *J* = 32.7 Hz), 39.4, 21.4.

^{19}F NMR (471 MHz, $CDCl_3$) δ -103.31 (dt, *J* = 249.3, 9.9 Hz), -107.12 (dt, *J* = 248.7, 11.6 Hz).

ESI-MS: calculated for $C_{19}H_{19}F_2NO_4S[M+Na]^+$:418.0895, found: 418.0898.

(*Z*)-3-(1-fluoro-2-(p-tolyl)vinyl)-2-methoxy-3,4-dihydroisoquinolin-1(2H)-one (3C')



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatorgraph (PE/EA = 32/1), **3C'** was obtained as a white solid (13.1 mg, 0.042 mmol, 21 %). R_f = 0.20 (PE/EA = 32/1).

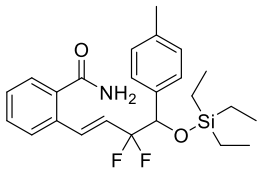
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.36 (td, *J* = 7.5, 1.3 Hz, 1H), 7.28 (td, *J* = 7.5, 7.9 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 2H), 5.89 (d, *J* = 38.8 Hz, 1H), 4.90 (ddd, *J* = 13.6, 10.0, 3.3 Hz, 1H), 3.95 (d, *J* = 19.9 Hz, 3H), 3.32 (dd, *J* = 16.1, 9.9 Hz, 1H), 3.10 (dd, *J* = 16.1, 3.4 Hz, 1H), 2.34 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.7, 138.0, 133.4, 131.8, 130.4, 129.6, 129.5, 129.4, 129.2 (d, *J* = 7.3 Hz), 128.5, 128.4, 128.0, 127.6, 125.5, 125.0, 109.8 (d, *J* = 6.2 Hz), 75.2 (d, *J* = 31.9 Hz), 63.0, 31.4, 21.5.

^{19}F NMR (471 MHz, $CDCl_3$) δ -118.55 (dd, *J* = 38.7, 14.5 Hz).

ESI-MS: calculated for $C_{19}H_{18}FNO_2[M+Na]^+$:334.1213, found: 334.1217.

(*E*)-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3aa)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatorgraph (PE/EA = 4/1), **3aa** was obtained as a white solid (62.1 mg, 0.144 mmol, 72 %). R_f = 0.16 (PE/EA = 4/1).

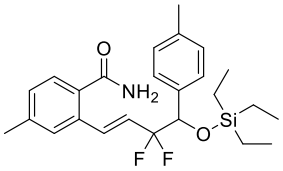
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (dt, *J* = 7.4, 1.0 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 2H), 7.38 – 7.33 (m, 1H), 7.29 (d, *J* = 7.7 Hz, 2H), 7.15 – 7.07 (m, 3H), 6.15 (ddd, *J* = 16.1, 14.0, 9.5 Hz, 1H), 5.73 (s, 1H), 5.33 (s, 1H), 4.93 (dd, *J* = 8.9, 7.0 Hz, 1H), 2.33 (s, 3H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.63-0.55 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 138.2, 135.2 (d, *J* = 5.2 Hz), 134.7, 133.8, 133.3 (t, *J* = 9.2 Hz), 131.1, 128.9, 128.8, 128.6, 127.7, 127.3, 123.8 (t, *J* = 25.9 Hz), 120.1 (t, *J* = 246.0 Hz), 76.7 (dd, *J* = 33.6, 29.0 Hz), 21.3, 6.8, 4.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -101.89 (dt, *J* = 241.8, 9.6 Hz), -107.99 (ddd, *J* = 241.8, 13.9, 6.9 Hz).

ESI-MS: calculated for $C_{24}H_{31}F_2NO_2Si[M+Na]^+$: 454.1984, found: 454.1985.

(*E*)-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)-4-methylbenzamide (3ba)



The title compound was prepared *via* the general procedure **C**, after purification by silica gel column chromatorgraph (PE/EA = 4/1), **3ba** was obtained as a white solid (64.0 mg, 0.144 mmol, 72 %). R_f = 0.13 (PE/EA = 4/1).

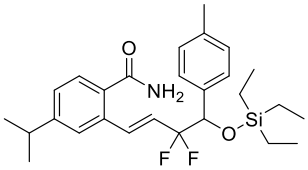
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.24 – 7.21 (m, 1H), 7.16 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.14 – 7.08 (m, 3H), 6.17 – 6.09 (m, 1H), 5.89 (s, 1H), 5.31 (s, 1H), 4.94 (dd, *J* = 8.9, 7.1 Hz, 1H), 2.38 (s, 3H), 2.33 (s, 3H), 0.91 (t, *J* = 7.9 Hz, 9H), 0.65-0.55 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 141.3, 138.2, 135.2 (d, *J* = 5.2 Hz), 133.9, 133.6 (t, *J* = 9.2 Hz), 131.9, 129.6, 128.8, 127.9, 127.7, 123.5 (t, *J* = 25.0 Hz), 120.1 (dd, *J* = 244.6, 245.8 Hz), 76.7 (dd, *J* = 33.6, 29.3 Hz), 21.5, 21.3, 6.8, 4.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -101.98 (dt, *J* = 240.6, 9.1 Hz), -107.83 (dd, *J* = 240.6, 12.8 Hz).

ESI-MS: calculated for $C_{25}H_{33}F_2NO_2Si[M+Na]^+$:468.2140, found: 468.2136.

(*E*)-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)-4-isopropylbenzamide (3ca)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatorgraph (PE/EA = 4/1), **3ca** was obtained as a white solid (73.9 mg, 0.156 mmol, 78 %). R_f = 0.19 (PE/EA = 4/1).

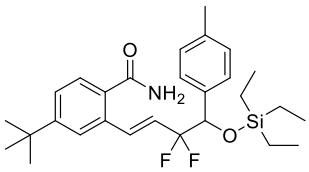
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.26 (t, *J* = 1.7 Hz, 1H), 7.23 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.16 (d, *J* = 16.1 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 2H), 6.15 (ddd, *J* = 16.1, 13.7, 9.9 Hz, 1H), 5.99 (s, 1H), 5.36 (s, 1H), 4.94 (t, *J* = 8.2 Hz, 1H), 2.94 (p, *J* = 6.9 Hz, 1H), 2.34 (s, 3H), 1.27 (s, 3H), 1.26 (s, 3H), 0.91 (t, *J* = 7.9 Hz, 9H), 0.66-0.54 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 152.2, 138.2, 135.2 (d, *J* = 4.7 Hz), 134.0, 133.7 (t, *J* = 9.2 Hz), 132.2, 128.9, 128.8, 127.8, 127.0, 125.5, 123.6 (t, *J* = 25.1 Hz), 120.1 (t, *J* = 245.7 Hz), 76.8 (dd, *J* = 33.2, 29.6 Hz), 34.2, 23.9, 23.8, 21.3, 6.8, 4.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.32 (dt, *J* = 242.0, 9.8 Hz), -107.90 (ddd, *J* = 242.0, 14.1, 8.2 Hz).

ESI-MS: calculated for $C_{27}H_{37}F_2NO_2Si[M+Na]^+$:496.2453, found: 496.2447.

(*E*)-4-(tert-butyl)-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3da)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatorgraph (PE/EA = 4/1), **3da** was obtained as a colourless oil (31.3 mg, 0.064 mmol, 32 %). R_f = 0.20 (PE/EA = 4/1).

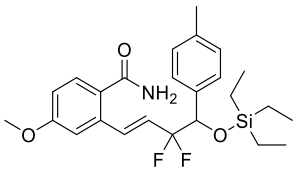
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.8 Hz, 1H), 7.40 (s, 1H), 7.39(d, *J* = 8.8 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 3H), 7.14 (d, *J* = 16.2 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 6.13 (ddd, *J* = 16.2, 13.6, 9.8 Hz, 1H), 5.65 (s, 1H), 5.33 (s, 1H), 4.93 (t, *J* = 8.2 Hz, 1H), 2.33 (s, 3H), 1.34 (s, 9H), 0.90 (t, *J* = 8.0 Hz, 11H), 0.65-0.53 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 154.5, 138.3, 135.2 (d, *J* = 4.7 Hz), 134.0 (t, *J* = 9.1 Hz), 133.8, 131.7, 128.8, 128.7, 127.8, 126.1, 124.4, 123.7 (t, *J* = 25.1 Hz), 120.1 (dd, *J* = 244.8, 246.0 Hz), 76.8 (dd, *J* = 33.2, 29.8 Hz), 35.1, 31.2, 21.3, 6.8, 4.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.45 (dt, *J* = 241.0, 9.5 Hz), -108.00 (ddd, *J* = 241.0, 13.9, 7.9 Hz).

ESI-MS: calculated for $C_{28}H_{39}F_2NO_2Si[M+Na]^+$: 510.2610, found: 510.2605.

(*E*)-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)-4-methoxybenzamide (3ea)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatography (PE/EA = 4/1), **3ea** was obtained as a colourless oil (63.3 mg, 0.137 mmol, 69 %). R_f =

0.13 (PE/EA = 4/1).

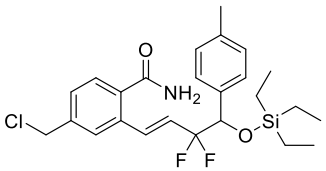
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (dt, *J* = 8.8, 1.2 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 16.0 Hz, 1H), 6.88-6.86 (m, 2H), 6.12 (ddd, *J* = 16.0, 14.0, 9.4 Hz, 1H), 5.65 (s, 1H), 5.25 (s, 1H), 4.93 (t, *J* = 8.2 Hz, 1H), 3.84 (s, 3H), 2.33 (s, 3H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.65-0.53 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 161.6, 138.3, 136.0, 135.2 (d, *J* = 5.3 Hz), 133.8 (t, *J* = 9.2 Hz), 130.9, 128.8, 127.7, 126.9, 124.0 (t, *J* = 25.0 Hz), 120.0 (dd, *J* = 245.5, 244.9 Hz), 114.1, 112.7, 76.7 (dd, *J* = 23.7, 29.2 Hz), 55.6, 21.3, 6.8, 4.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.04 (d, *J* = 241.9 Hz), -108.07 (ddd, *J* = 242.0, 13.8, 7.0 Hz).

ESI-MS: calculated for $C_{25}H_{33}F_2NO_3Si[M+Na]^+$: 484.2090, found: 484.2084.

(*E*)-4-(chloromethyl)-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl) benzamide (3fa)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatorgraph (PE/EA = 4/1), **3fa** was obtained as a colourless oil (39.0 mg, 0.081 mmol, 41 %). R_f = 0.10 (PE/EA = 4/1).

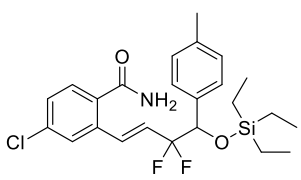
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 1H), 7.43 (s, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 16.1 Hz, 1H), 6.17 (ddd, *J* = 16.1, 13.9, 9.4 Hz, 1H), 5.56 (s, 1H), 5.26 (s, 1H), 4.94 (dd, *J* = 8.8, 7.2 Hz, 1H), 4.59 (s, 2H), 2.34 (s, 3H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.65-0.54 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 140.5, 138.3, 135.1 (d, *J* = 5.3 Hz), 134.5, 134.4, 132.9 (t, *J* = 9.2 Hz), 129.3, 128.9, 128.9, 127.8, 127.4, 124.5 (t, *J* = 25.2 Hz), 120.0 (dd, *J* = 241.7, 246.3 Hz), 76.7 (dd, *J* = 24.1, 28.7 Hz), 45.4, 21.3, 6.8, 4.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.11 (dd, *J* = 242.2, 9.2 Hz), -106.40 – -109.30 (m).

ESI-MS: calculated for $C_{25}H_{32}ClF_2NO_2Si[M+Na]^+$: 502.1751, found: 502.1745.

(*E*)-4-chloro-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3ga)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatorgraph (PE/EA = 4/1), **3ga** was obtained as a colourless oil (65.2 mg, 0.140 mmol, 70 %). R_f = 0.13 (PE/EA = 4/1).

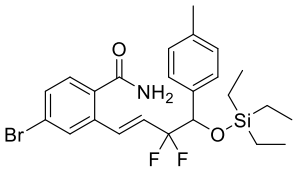
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 1H), 7.39 (d, *J* = 2.1 Hz, 1H), 7.33 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.05 – 7.00 (m, 1H), 6.15 (ddd, *J* = 16.2, 13.9, 9.2 Hz, 1H), 5.68 (s, 1H), 5.26 (s, 1H), 4.93 (dd, *J* = 8.8, 7.0 Hz, 1H), 2.33 (s, 3H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.65-0.52 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.3, 138.4, 137.2, 135.6, 135.1 (d, *J* = 5.4 Hz), 132.9, 132.3 (t, *J* = 9.2 Hz), 130.3, 128.9, 128.9, 127.7, 127.3, 125.1 (t, *J* = 25.1 Hz), 119.8 (dd, *J* = 244.9, 245.1 Hz), 76.6 (dd, *J* = 33.7, 29.0 Hz), 21.3, 6.8, 4.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.12 (dt, *J* = 242.9, 9.3 Hz), -108.23 (ddd, *J* = 242.9, 13.9, 7.0 Hz).

ESI-MS: calculated for $C_{24}H_{30}ClF_2NO_2Si[M+Na]^+$: 488.1594, found: 488.1594.

(*E*)-4-bromo-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3ha)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatography (PE/EA = 4/1), **3ha** was obtained as a white solid (66.2 mg, 0.130 mmol, 65 %). R_f = 0.23 (PE/EA = 4/1).

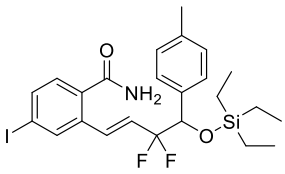
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 1.5 Hz, 1H), 7.47 (t, *J* = 1.5 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.02 (dt, *J* = 16.0, 2.2 Hz, 1H), 6.15 (ddd, *J* = 16.0, 13.8, 9.4 Hz, 1H), 5.96 (s, 1H), 5.34 (s, 1H), 4.93 (dd, *J* = 8.8, 7.1 Hz, 1H), 2.33 (s, 3H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.65-0.54 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 138.4, 135.7, 135.0 (d, J = 5.2 Hz), 133.4, 132.1 (t, J = 9.2 Hz), 132.0, 131.8, 130.2, 130.2, 128.9, 127.7, 125.4, 125.0 (t, *J* = 25.0 Hz), 119.9 (dd, J = 244.8, 245.7 Hz), 76.6 (dd, J = 33.7, 29.2 Hz), 21.3, 6.8, 4.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.18 (dd, *J* = 242.4, 10.0 Hz), -108.15 (ddd, *J* = 242.5, 13.5, 7.8 Hz).

ESI-MS: calculated for $C_{24}H_{30}BrF_2NO_2Si[M+Na]^+$: 532.1089, found: 532.1084.

(*E*)-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)-4-iodobenzamide (3ia)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatorgraph (PE/EA = 4/1), **3ia** was obtained as a white solid (55.5 mg, 0.100 mmol, 50 %). R_f = 0.16 (PE/EA = 4/1).

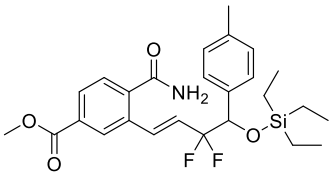
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 1.6 Hz, 1H), 7.69 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.98 (dt, *J* = 16.1, 2.3 Hz, 1H), 6.13 (ddd, *J* = 16.1, 13.8, 9.4 Hz, 1H), 5.84 (s, 1H), 5.29 (s, 1H), 4.93 (dd, *J* = 8.7, 7.2 Hz, 1H), 2.33 (s, 3H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.65-0.55 (m, 6H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.32 (dt, *J* = 242.6, 9.7 Hz), -108.17 (ddd, *J* = 242.6, 14.4, 7.7 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 138.4, 137.8, 136.2, 135.6, 135.1 (d, *J* = 5.1 Hz), 133.9, 132.0 (t, *J* = 9.2 Hz), 130.2, 128.9, 127.7, 125.0 (t, *J* = 25.1 Hz), 119.9 (dd, *J* = 244.8, 245.4 Hz), 97.6, 76.6 (dd, *J* = 29.4, 29.1 Hz), 21.3, 6.8, 4.8.

ESI-MS: calculated for $C_{24}H_{30}F_2INO_2Si[M+Na]^+$: 580.0950, found: 580.0944.

Methyl (*E*)-4-carbamoyl-3-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl) benzoate (3ja)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatorgraph (PE/EA = 4/1), **3ja** was obtained as a colourless oil (69.4 mg, 0.142 mmol, 71 %). R_f = 0.13 (PE/EA = 4/1).

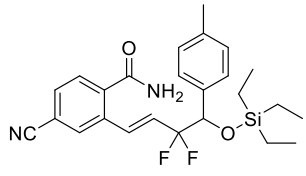
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 1.6 Hz, 1H), 7.99 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.05 (dt, *J* = 16.2, 2.3 Hz, 1H), 6.25 (ddd, *J* = 16.2, 13.7, 9.5 Hz, 1H), 5.71 (s, 1H), 5.36 (s, 1H), 4.93 (t, *J* = 8.1 Hz, 1H), 3.95 (s, 3H), 2.33 (s, 3H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.64-0.55 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 166.2, 138.4, 138.30, 135.1 (d, *J* = 4.8 Hz), 133.9, 132.4, 132.3 (dd, *J* = 19.9, 10.6 Hz), 129.7, 128.8, 128.8, 128.5, 127.8, 125.1 (t, *J* = 25.0 Hz), 120.0 (t, *J* = 246.0 Hz), 76.7 (dd, *J* = 21.3, 29.3 Hz), 52.7, 21.3, 6.8, 4.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.34 (dd, *J* = 243.0, 8.8 Hz), -108.22 (ddd, *J* = 243.0, 13.8, 7.6 Hz).

ESI-MS: calculated for $C_{26}H_{33}F_2NO_4Si[M+Na]^+$: 512.2039, found: 512.2032.

(*E*)-4-cyano-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3ka)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatography (PE/EA = 4/1), **3ka** was obtained as a white solid (54.3 mg, 0.119 mmol, 60 %). R_f = 0.07 (PE/EA = 4/1).

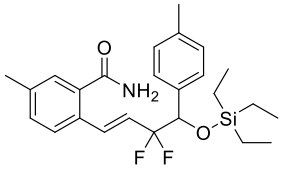
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 2H), 7.63 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.00 (dt, *J* = 16.1, 2.3 Hz, 1H), 6.21 (ddd, *J* = 16.1, 13.8, 9.0 Hz, 1H), 5.89 (s, 1H), 5.37 (s, 1H), 4.94 (dd, *J* = 8.8, 6.8 Hz, 1H), 2.33 (s, 3H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.64-0.56 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 138.5, 134.9 (d, *J* = 5.5 Hz), 134.9, 132.0, 131.2 (t, *J* = 9.2 Hz), 130.9, 129.4, 128.9, 127.6, 126.2 (t, *J* = 25.2 Hz), 119.7 (dd, *J* = 244.9, 245.5 Hz), 117.8, 115.0, 76.5 (dd, *J* = 33.5, 28.7 Hz), 21.3, 6.8, 4.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.02 (dt, *J* = 244.0, 9.3 Hz), -108.34 (ddd, *J* = 244.0, 13.8, 6.8 Hz).

ESI-MS: calculated for $C_{25}H_{30}F_2N_2O_2Si[M+Na]^+$: 479.1936, found: 479.1937.

(*E*)-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)-5-methyl benzamide (3la)



The title compound was prepared *via* the general procedure , after purification by silica gel column chromatography (PE/EA = 4/1), **3la**was obtained as a colourless oil (65.6 mg, 0.147 mmol, 74 %). R_f = 0.18 (PE/EA = 4/1).

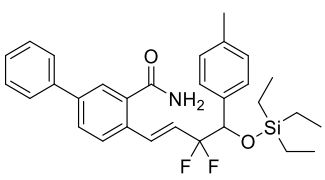
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.24 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.05 (dt, *J* = 16.1, 2.4 Hz, 1H), 6.12 (ddd, *J* = 16.1, 14.0, 9.6 Hz, 1H), 5.89 (s, 1H), 5.33 (s, 1H), 4.92 (dd, *J* = 8.9, 7.1 Hz, 1H), 2.36 (s, 3H), 2.33 (s, 3H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.65-0.53 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 139.1, 138.2, 135.2 (d, *J* = 4.8 Hz), 134.6, 133.1 (t, *J* = 9.3 Hz), 131.8, 130.9, 129.1, 128.8, 127.7, 127.1, 122.8 (t, *J* = 25.0 Hz), 120.2 (t, *J* = 245.2 Hz), 76.8 (dd, *J* = 33.9, 29.4 Hz), 21.3, 21.2, 6.8, 4.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -101.85 (dt, *J* = 241.2, 9.9 Hz), -107.83 (ddd, *J* = 241.2, 14.6, 7.2 Hz).

ESI-MS: calculated for $C_{25}H_{33}F_2NO_2Si[M+Na]^+$: 468.2140, found: 468.2136.

(*E*)-4-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)-[1,1'-biphenyl]-3-carboxa mide (3ma)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatography (PE/EA = 4/1), **3ma** was obtained as a colourless oil (65.0 mg, 0.128 mmol, 65 %). R_f =

0.24 (PE/EA = 4/1).

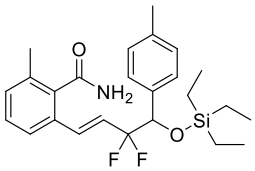
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 2.0 Hz, 1H), 7.67 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.36 (m, 1H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.15 – 7.10 (m, 3H), 6.21 (ddd, *J* = 16.0, 13.9, 9.5 Hz, 1H), 5.92 (s, 1H), 5.42 (s, 1H), 4.96 (dd, *J* = 8.8, 7.0 Hz, 1H), 2.34 (s, 3H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.67-0.55 (m, 6H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.6, 141.8, 139.6, 138.2, 135.3, 135.2 (d, *J* = 5.4 Hz), 132.8 (t, *J* = 9.2 Hz), 132.5, 129.5, 129.1, 128.8, 128.2, 127.8, 127.7, 127.1, 123.6 (t, *J* = 24.9 Hz), 120.2 (t, *J* = 245.5 Hz), 76.8 (dd, *J* = 33.8, 29.3 Hz), 21.3, 6.8, 4.8.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -101.81 (dt, *J* = 242.0, 9.8 Hz), -107.84 (ddd, *J* = 242.0, 14.1, 6.9 Hz).

ESI-MS: calculated for $C_{30}H_{35}F_2NO_2Si[M+Na]^+$: 530.2297, found: 530.2297.

(*E*)-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)-6-methylbenzamide (3na)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatorgraph (PE/EA = 4/1), **3na** was obtained as a colourless oil (12.0 mg, 0.027 mmol, 15 %). R_f = 0.19 (PE/EA = 4/1).

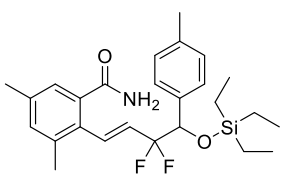
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 4H), 7.16 (d, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 2H), 6.85 (dt, *J* = 16.0, 2.4 Hz, 1H), 6.16 (ddd, *J* = 16.0, 13.7, 9.8 Hz, 1H), 5.60 (s, 1H), 5.29 (s, 1H), 4.89 (dd, *J* = 9.0, 7.2 Hz, 1H), 2.37 (s, 3H), 2.33 (s, 3H), 0.89 (t, *J* = 7.9 Hz, 9H), 0.63-0.52 (m, 6H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -101.80 (dd, *J* = 241.9, 10.0 Hz), -107.62 (ddd, *J* = 241.9, 14.1, 7.4 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0 , 138.1 , 136.1 , 135.3 , 135.3 (d, *J* = 4.9 Hz) , 132.5 (t, *J* = 9.2 Hz) , 132.3 , 130.8 , 129.4 , 128.7 , 127.8 , 123.6 , 123.2 (t, *J* = 24.9 Hz) , 120.2 (dd, *J* = 244.5, 244.0 Hz) , 76.8 (dd, *J* = 33.7, 29.6 Hz) , 21.4 , 19.4 , 6.8 , 4.8 .

ESI-MS: calculated for $C_{25}H_{33}F_2NO_2Si[M+Na]^+$: 468.2140, found: 468.2138.

(*E*)-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)-3,5-dimethylbenzamide (3oa)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatography (PE/EA = 4/1), **3oa** was obtained as a white solid (78.9 mg, 0.172 mmol, 86 %). R_f = 0.29

(PE/EA = 4/1).

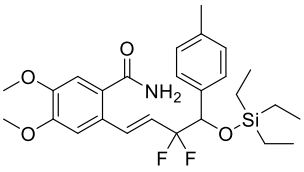
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.8 Hz, 2H), 7.26 (s, 1H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.07 (s, 1H), 6.89 (dt, *J* = 16.5, 2.6 Hz, 1H), 5.88 (ddd, *J* = 16.5, 13.3, 10.0 Hz, 1H), 5.59 (s, 1H), 5.44 (s, 1H), 4.93 (dd, *J* = 9.8, 6.0 Hz, 1H), 2.32 (s, 3H), 2.30 (s, 3H), 2.20 (s, 3H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.65-0.52 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4, 138.2, 137.9, 136.7, 135.0 (d, *J* = 7.3 Hz), 133.4, 132.5 (t, *J* = 9.3 Hz), 130.0, 128.8, 127.7, 127.0, 126.3 (t, *J* = 24.0 Hz), 119.9 (dd, *J* = 247.0, 243.8 Hz), 76.5 (dd, *J* = 33.7, 28.5 Hz), 21.3, 21.0, 20.7, 6.8, 4.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -101.58 (dt, *J* = 243.0, 10.2 Hz), -107.03 (ddd, *J* = 243.0, 14.3, 6.0 Hz).

ESI-MS: calculated for $C_{26}H_{35}F_2NO_2Si[M+Na]^+$: 482.2297, found: 482.2293.

(*E*)-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)-4,5-dimethoxybenzamide (3pa)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatography (PE/EA = 4/1), **3pa** was obtained as a yellow solid (39.4 mg, 0.080 mmol, 40 %). R_f = 0.08 (PE/EA = 4/1).

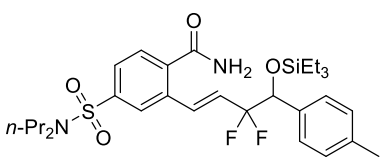
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.7 Hz, 2H), 7.21 (s, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 16.1 Hz, 1H), 6.82 (s, 1H), 6.10 – 5.97 (m, 1H), 5.39 (s, 1H), 5.13 (s, 1H), 4.94 (t, *J* = 7.8 Hz, 1H), 3.93 (s, 2H), 3.91 (s, 2H), 2.33 (s, 2H), 0.90 (td, *J* = 7.9, 2.8 Hz, 9H), 0.64-0.55 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 151.1, 149.5, 138.3, 135.3 (d, *J* = 5.0 Hz), 133.6 (t, *J* = 9.3 Hz), 128.8, 127.8, 127.3, 127.0, 122.7 (t, *J* = 24.9 Hz), 118.2 (dd, *J* = 247.3, 246.1 Hz), 111.7, 109.7, 76.7 (dd, *J* = 21.1, 29.3 Hz), 56.3, 56.2, 21.3, 6.8, 4.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -101.88 (d, *J* = 241.0 Hz), -107.80 (m).

ESI-MS: calculated for $C_{26}H_{35}F_2NO_4Si[M+Na]^+$: 514.2195, found: 514.2193.

(*E*)-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)-4-(*N*,*N*-dipropylsulfamoyl) benzamide (3qa)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatorgraph (PE/EA = 2/1),

3qa was obtained as a colorless oil (79.7 mg, 0.133 mmol, 67 %). R_f = 0.18 (PE/EA = 2/1).

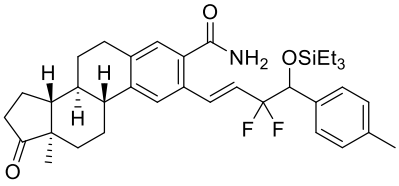
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 1.7 Hz, 1H), 7.73 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.05 (dt, *J* = 16.1, 2.2 Hz, 1H), 6.24 (ddd, *J* = 16.1, 13.7, 9.2 Hz, 1H), 5.98 (s, 1H), 5.44 (s, 1H), 4.93 (t, *J* = 7.9 Hz, 1H), 3.08 (t, *J* = 7.7 Hz, 4H), 2.32 (s, 3H), 1.55 (h, *J* = 7.4 Hz, 4H), 0.88 (dt, *J* = 8.8, 7.8 Hz, 16H), 0.59 (qd, *J* = 7.8, 5.4 Hz, 6H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 169.2 , 142.6 , 138.4 , 138.0 , 135.0 (d, *J* = 4.8 Hz), 134.7 , 131.8 (d, *J* = 9.1 Hz), 129.3 , 128.9 , 127.7 , 126.9 , 125.8 (d, *J* = 25.0 Hz), 125.6 , 119.8 (t, *J* = 244.3 Hz) , 76.6 (d, *J* = 4.6 Hz), 50.2 , 22.2 , 21.3 , 11.3 , 6.8 , 4.8 .

^{19}F NMR (471 MHz, Chloroform-*d*) δ -102.37 (dt, *J* = 243.0, 9.5 Hz), -108.47 (ddd, *J* = 243.0, 14.1, 7.7 Hz).

ESI-MS: calculated for $C_{30}H_{44}F_2N_2O_4SSi[M+Na]^+$:617.2651, found: 617.2646.

(8S,9R,13R,14R)-2-((E)-3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-3-carboxamide (3ra)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatorgraph (PE/EA = 2/1), **3ra** was obtained as a colorless oil (79.4 mg, 0.131 mmol, 65 %). R_f = 0.14 (PE/EA = 2/1).

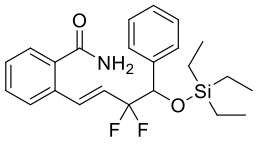
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 (s, 1H), 7.31 (d, *J* = 3.6 Hz, 1H), 7.28 (dd, *J* = 8.1, 2.5 Hz, 2H), 7.14 – 7.03 (m, 3H), 6.05 (dddd, *J* = 16.3, 13.6, 9.9, 6.8 Hz, 1H), 5.84 (s, 1H), 5.31 (d, *J* = 9.9 Hz, 1H), 4.91 (t, *J* = 8.0 Hz, 1H), 2.96 – 2.87 (m, 2H), 2.52 (dd, *J* = 19.0, 8.7 Hz, 1H), 2.45 (dd, *J* = 12.8, 4.8 Hz, 1H), 2.32 (m, 4H), 2.16 (dt, *J* = 18.6, 8.8 Hz, 1H), 2.06 (ddd, *J* = 16.6, 12.3, 6.7 Hz, 3H), 1.62 (ddd, *J* = 22.3, 11.6, 3.3 Hz, 2H), 1.59 – 1.47 (m, 3H), 1.49 – 1.38 (m, 1H), 0.95 – 0.86 (m, 12H), 0.58 (qd, *J* = 7.9, 5.7 Hz, 6H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.4 , 143.1 , 138.2 , 137.8 , 135.2 (d, *J* = 4.8 Hz) , 133.7 (d, *J* = 6.7 Hz) , 131.9 , 131.4 (d, *J* = 9.4 Hz) , 129.4 , 128.8 , 127.7 , 124.5 (d, *J* = 12.7 Hz) , 123.2 (d, *J* = 25.0 Hz) , 120.1 (t, *J* = 244.1 Hz) , 76.7 (m) , 50.6 , 48.0 , 44.5 , 44.5 , 37.9 (d, *J* = 3.4 Hz), 35.9 , 31.6 , 29.1 (d, *J* = 5.2 Hz), 26.3 , 25.7 , 21.7 , 21.3 , 13.9 , 6.8 , 4.8 .

^{19}F NMR (471 MHz, Chloroform-*d*) δ -102.52 (dd, *J* = 240.8, 9.1 Hz), -105.69 – -110.96 (m).

ESI-MS: calculated for $C_{36}H_{47}F_2NO_3Si[M+Na]^+$:630.3185, found: 630.3181.

(*E*)-2-(3,3-difluoro-4-phenyl-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3ab)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatography (PE/EA = 4/1), **3ab** was obtained as a white solid (61.7 mg, 0.148 mmol, 74 %). R_f = 0.13 (PE/EA = 4/1).

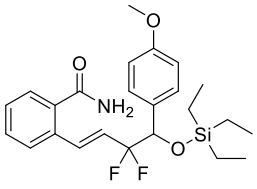
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 7.6 Hz, 1H), 7.45 – 7.40 (m, 4H), 7.37 – 7.29 (m, 4H), 7.10 (d, *J* = 16.1 Hz, 1H), 6.16 (ddd, *J* = 16.1, 14.1, 9.5 Hz, 1H), 5.98 (s, 1H), 5.36 (s, 1H), 4.97 (dd, *J* = 8.9, 7.0 Hz, 1H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.64-0,56 (m, 6H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.6, 138.2 (d, *J* = 5.2 Hz), 134.8, 133.7, 133.3 (t, *J* = 9.2 Hz), 131.0, 128.9, 128.5, 128.5, 128.1, 127.8, 127.2, 123.5 (t, *J* = 24.8 Hz), 120.1 (dd, *J* = 245.8, 246.4 Hz), 76.9 (dd, *J* = 33.7, 29.4 Hz), 6.8, 4.8.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -101.67 (dt, *J* = 242.0, 9.5 Hz), -107.89 (ddd, *J* = 242.0, 14.7, 7.5 Hz).

ESI-MS: calculated for $C_{23}H_{29}F_2NO_2Si[M+Na]^+$: 440.1827, found: 440.1827.

(*E*)-2-(3,3-difluoro-4-(4-methoxyphenyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3ac)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatorgraph (PE/EA = 4/1), **3ac** was obtained as a white solid (55.0 mg, 0.123 mmol, 74 %). R_f = 0.08 (PE/EA = 4/1).

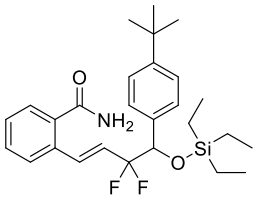
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.8Hz, 1H), 7.45-7.41 (m, 2H), 7.38 – 7.33 (m, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.12 (dt, *J* = 16.2, 2.4 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.15 (ddd, *J* = 16.2, 13.8, 9.7 Hz, 1H), 6.02 (s, 1H), 5.48 (s, 1H), 4.91 (dd, *J* = 8.8, 7.3 Hz, 1H), 3.79 (s, 3H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.63-0.54 (m, 6H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.5, 159.7, 134.7, 133.8, 133.2 (t, *J* = 9.2 Hz), 131.0, 130.2 (d, *J* = 5.5 Hz), 129.0, 128.9, 128.5, 127.2, 123.8 (t, *J* = 25.1 Hz), 120.1 (dd, *J* = 245.1, 244.6 Hz), 113.5, 76.5 (dd, *J* = 33.9, 29.5 Hz), 55.4, 6.8, 4.8.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -102.10 (dt, *J* = 242.0, 9.4 Hz), -107.81 (ddd, *J* = 242.0, 15.1, 8.3 Hz).

ESI-MS: calculated for $C_{24}H_{31}F_2NO_3Si[M+Na]^+$: 470.1933, found: 470.1932.

(*E*)-2-(4-(4-(tert-butyl)phenyl)-3,3-difluoro-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3ad)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatography (PE/EA = 4/1), **3ad** was obtained as a colourless oil (78.1 mg, 0.165 mmol, 82 %). R_f = 0.17 (PE/EA = 4/1).

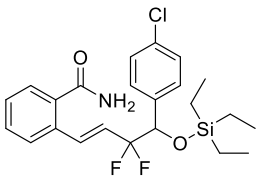
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 7.6, 1H), 7.46 – 7.41 (m, 2H), 7.39 – 7.29 (m, 5H), 7.12 (dt, *J* = 16.2, 2.8 Hz, 1H), 6.17 (ddd, *J* = 16.2, 13.9, 9.6 Hz, 1H), 5.72 (s, 1H), 5.34 (s, 1H), 4.94 (dd, *J* = 9.1, 7.0 Hz, 1H), 1.30 (s, 9H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.65-0.53 (m, 6H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.4, 151.4, 135.1 (d, *J* = 5.5 Hz), 134.6, 133.8, 133.3 (t, *J* = 9.2 Hz), 131.1, 128.9, 128.7, 127.5, 127.5, 127.3, 125.0, 123.9 (t, *J* = 24.8 Hz), 120.1 (dd, *J* = 245.0, 246.4 Hz), 76.7 (dd, *J* = 30.5, 29.1 Hz), 34.7, 31.5, 6.8, 4.8.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -101.55 (dt, *J* = 242.3, 9.7 Hz), -107.90 (ddd, *J* = 242.3, 14.0, 7.0 Hz).

ESI-MS: calculated for $C_{27}H_{37}F_2NO_2Si[M+Na]^+$: 496.2453, found: 496.2453.

(*E*)-2-(4-(4-chlorophenyl)-3,3-difluoro-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3ae)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatography (PE/EA = 4/1), **3ae** was obtained as a colourless oil (70.7 mg, 0.156 mmol, 78 %). R_f = 0.17 (PE/EA = 4/1).

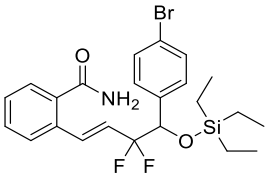
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.1 Hz, 1H), 7.49 – 7.39 (m, 2H), 7.36-7.34 (m, 3H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.15 (dt, *J* = 16.2, 2.4 Hz, 1H), 6.12 (ddd, *J* = 16.2, 13.5, 10.1 Hz, 1H), 6.07 (s, 1H), 5.58 (s, 1H), 4.93 (t, *J* = 8.0 Hz, 1H), 0.89 (t, *J* = 8.0 Hz, 8H), 0.65-0.55 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 136.7 (d, *J* = 4.7 Hz), 134.9, 134.4, 133.6, 133.4 (t, *J* = 9.2 Hz), 131.0, 129.2, 128.9, 128.3, 128.2, 127.1, 123.0 (t, *J* = 25.0 Hz), 119.9 (dd, *J* = 247.0, 244.6 Hz), 76.4 (dd, *J* = 33.8, 30.4 Hz), 6.7, 4.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -101.87 (dt, *J* = 243.2, 9.8 Hz), -107.51 (ddd, *J* = 243.2, 13.9, 8.0 Hz).

ESI-MS: calculated for $C_{23}H_{28}ClF_2NO_2Si[M+Na]^+$: 474.1438, found: 474.1439.

(*E*)-2-(4-(4-bromophenyl)-3,3-difluoro-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3af)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatography (PE/EA = 4/1), **3af** was obtained as a white solid (74.1 mg, 0.149 mmol, 75 %). R_f = 0.16 (PE/EA = 4/1).

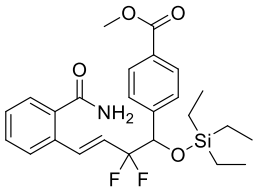
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 1H), 7.48 – 7.40 (m, 4H), 7.35 (ddd, *J* = 7.6, 6.3, 2.3 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.15 (dt, *J* = 16.1, 2.4 Hz, 1H), 6.11 (ddd, *J* = 16.1, 13.5, 10.1 Hz, 1H), 6.06 (s, 1H), 5.57 (s, 1H), 4.91 (t, *J* = 8.0 Hz, 2H), 0.89 (t, *J* = 7.9 Hz, 9H), 0.65-0.53 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 137.2 (d, *J* = 4.8 Hz), 135.0, 133.6, 133.5 (t, *J* = 9.2 Hz), 131.3, 131.0, 129.6, 129.0, 128.2, 127.1, 123.0 (t, *J* = 25.2 Hz), 122.6, 119.8 (dd, *J* = 247.5, 245.8 Hz), 76.4 (dd, *J* = 33.7, 30.3 Hz), 6.7, 4.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -101.85 (dt, *J* = 244.0, 9.3 Hz), -107.51 (ddd, *J* = 244.0, 14.5, 8.3 Hz).

ESI-MS: calculated for $C_{23}H_{28}BrF_2NO_2Si[M+Na]^+$: 518.0933, found: 518.0932.

Methyl (*E*)-4-(4-(2-carbamoylphenyl)-2,2-difluoro-1-((triethylsilyl)oxy)but-3-en-1-yl) benzoate (3ag)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatography (PE/EA = 4/1), **3ag** was obtained as a white solid (75.0 mg, 0.158 mmol, 79 %). R_f = 0.09 (PE/EA = 4/1).

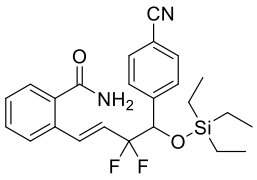
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.55 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.45 – 7.40 (m, 2H), 7.35 (m, 1H), 7.14 (dt, *J* = 16.2, 2.5 Hz, 1H), 6.11 (ddd, *J* = 16.2, 13.6, 10.0 Hz, 1H), 5.94 (s, 1H), 5.56 (s, 1H), 5.00 (t, *J* = 7.9 Hz, 1H), 3.89 (s, 3H), 0.89 (t, *J* = 8.0 Hz, 9H), 0.65-0.53 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 167.1, 143.2 (d, *J* = 5.0 Hz), 134.8, 133.6, 133.5 (t, *J* = 9.2 Hz), 131.0, 130.3, 129.4, 129.0, 128.2, 127.9, 127.1, 123.0 (t, *J* = 25.2 Hz), 119.8 (dd, *J* = 245.7, 246.5 Hz), 76.7 (dd, *J* = 29.5, 29.8 Hz), 52.3, 6.7, 4.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -101.54 (dt, *J* = 243.1, 9.8 Hz), -107.24 (ddd, *J* = 243.1, 13.8, 7.6 Hz).

ESI-MS: calculated for $C_{25}H_{31}F_2NO_4Si[M+Na]^+$: 498.1882, found: 498.1881.

(*E*)-2-(4-(4-cyanophenyl)-3,3-difluoro-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3ah)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatorgraph (PE/EA = 4/1), **3ah** was obtained as a white solid (52.2 mg, 0.118 mmol, 59 %). R_f = 0.09 (PE/EA = 4/1).

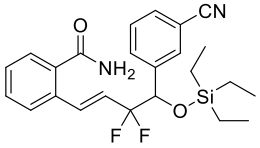
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.57 – 7.52 (m, 3H), 7.46 – 7.41 (m, 2H), 7.36 (ddd, *J* = 8.6, 6.3, 2.4 Hz, 1H), 7.21 (dt, *J* = 16.2, 2.4 Hz, 1H), 6.16 (s, 1H), 6.10 (ddd, *J* = 16.2, 13.2, 10.5 Hz, 1H), 5.75 (s, 1H), 4.98 (t, *J* = 8.1 Hz, 1H), 0.88 (t, *J* = 8.0 Hz, 9H), 0.65-0.53 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 143.3 (d, *J* = 4.5 Hz), 135.0, 133.7 (t, *J* = 9.3 Hz), 133.5, 132.0, 131.0, 129.1, 128.6, 128.0, 127.0, 122.4 (t, *J* = 25.2 Hz), 119.7 (t, *J* = 246.3 Hz), 118.8, 112.4, 76.5 (t, *J* = 32.5 Hz), 6.7, 4.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -101.32 (d, *J* = 245.0 Hz), -107.11 (d, *J* = 245.0 Hz).

ESI-MS: calculated for $C_{24}H_{28}F_2N_2O_2Si[M+Na]^+$: 465.1780, found: 465.1781.

(*E*)-2-(4-(3-cyanophenyl)-3,3-difluoro-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3ai)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatorgraph (PE/EA = 4/1), **3ai** was obtained as a white solid (69.3 mg, 0.157 mmol, 78 %). R_f = 0.06 (PE/EA = 4/1).

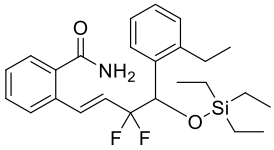
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.48-7.42 (m, 3H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 16.2 Hz, 1H), 6.22 (s, 1H), 6.11 (ddd, *J* = 16.2, 13.4, 10.2 Hz, 1H), 5.74 (s, 1H), 4.96 (t, *J* = 8.0 Hz, 1H), 0.89 (t, *J* = 8.0 Hz, 9H), 0.65-0.53 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 139.7 (d, *J* = 5.0 Hz), 134.9 , 133.8 (t, *J* = 9.2 Hz), 133.5, 132.4, 132.3, 131.4, 131.0, 129.1, 129.0, 129.0, 127.9, 127.0, 122.4 (t, *J* = 25.1 Hz), 119.7 (t, *J* = 246.2 Hz), 118.9, 112.3, 76.2 (t, *J* = 32.3 Hz), 6.7, 4.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -101.14 (dt, *J* = 245.0, 9.7 Hz), -107.44 (ddd, *J* = 245.0, 13.9 , 8.67 Hz).

ESI-MS: calculated for $C_{24}H_{28}F_2N_2O_2Si[M+Na]^+$: 465.1780, found: 465.1781.

(*E*)-2-(4-(2-ethylphenyl)-3,3-difluoro-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3aj)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatography (PE/EA = 4/1), **3aj** was obtained as a white solid (67.9 mg, 0.152 mmol, 76 %). R_f = 0.13 (PE/EA = 4/1).

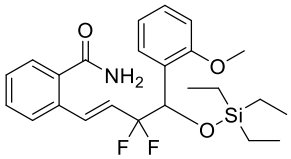
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.44 (td, *J* = 7.5, 1.4 Hz, 1H), 7.36 (td, *J* = 7.5, 1.4 Hz, 1H), 7.26 – 7.18 (m, 2H), 7.16 – 7.08 (m, 2H), 6.25 (ddd, *J* = 16.1, 14.2, 9.4 Hz, 1H), 5.93 (s, 1H), 5.44 (s, 1H), 5.33 (dd, *J* = 9.3, 5.4 Hz, 1H), 2.84 (dq, *J* = 15.0, 7.6 Hz, 1H), 2.70 (dq, *J* = 15.0, 7.6 Hz, 1H), 1.25 (t, *J* = 7.6 Hz, 3H), 0.88 (t, *J* = 7.9 Hz, 9H), 0.57 (m, 6H).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -98.31 – -101.13 (m), -108.49 (dd, *J* = 241.8, 14.5 Hz).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.6, 142.4, 135.7 (d, *J* = 4.8 Hz), 134.9, 133.7, 133.2 (t, *J* = 9.3 Hz), 131.0, 128.9, 128.5, 128.4, 128.4, 127.1, 125.4, 123.6 (t, *J* = 24.8 Hz), 120.8 (dd, *J* = 246.0, 247.0 Hz), 72.5 (dd, *J* = 34.1, 30.5 Hz), 25.1 (d, *J* = 3.7 Hz), 15.2, 6.7, 4.8.

ESI-MS: calculated for $C_{25}H_{33}F_2NO_2Si[M+Na]^+$: 468.2140, found: 468.2140.

(*E*)-2-(3,3-difluoro-4-(2-methoxyphenyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3ak)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatography (PE/EA = 4/1), **3ak** was obtained as a white solid (56.0 mg, 0.125 mmol, 63 %). R_f = 0.08 (PE/EA = 4/1).

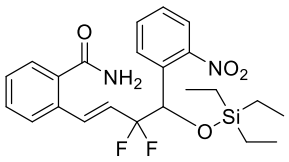
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.49 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.35 (td, *J* = 7.3, 1.7 Hz, 1H), 7.26 (td, *J* = 7.3, 1.8 Hz, 1H), 7.11 (dt, *J* = 16.1, 2.4 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.22 (ddd, *J* = 16.1, 12.7, 10.6 Hz, 1H), 5.89 (s, 1H), 5.53 (dd, *J* = 11.5, 6.0 Hz, 1H), 5.44 (s, 1H), 3.81 (s, 3H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.62-0.50 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 157.0, 134.8, 133.8, 132.7 (t, *J* = 9.4 Hz), 131.0 , 129.5, 129.2, 128.8, 128.6, 127.1, 126.9 (d, *J* = 3.6 Hz), 124.4 (t, *J* = 25.1 Hz), 120.4 (dd, *J* = 247.5, 245.3 Hz), 120.4, 110.7, 69.4 (dd, *J* = 32.8, 29.6 Hz), 55.8, 6.7, 4.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -105.46 (dt, *J* = 239.0, 11.1 Hz), -108.40 (ddd, *J* = 239.0, 12.9, 5.6 Hz).

ESI-MS: calculated for $C_{24}H_{31}F_2NO_3Si[M+Na]^+$: 470.1933, found: 470.1933.

(E)-2-(3,3-difluoro-4-(2-nitrophenyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3al)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatography (PE/EA = 4/1), **3al** was obtained as a white solid (78.2 mg, 0.169 mmol, 85 %). R_f = 0.07 (PE/EA = 4/1).

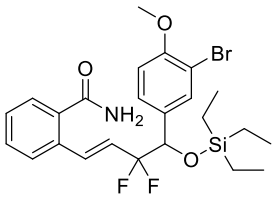
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.9 Hz, 1H), 7.84 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.61 (td, *J* = 7.6, 1.3 Hz, 1H), 7.53 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.48 – 7.41 (m, 3H), 7.35 (td, *J* = 7.3, 1.8 Hz, 1H), 7.15 (dt, *J* = 16.1, 2.4 Hz, 1H), 6.31 (s, 1H), 6.12 (ddd, *J* = 16.2, 12.9, 10.8 Hz, 1H), 6.06 (d, *J* = 8.5 Hz, 1H), 5.74 (s, 1H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.69- 0.57 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 148.9, 135.1, 133.5 (t, *J* = 9.3 Hz), 133.2, 132.6, 132.2 (d, *J* = 3.4 Hz), 130.8, 130.1, 129.3, 128.9, 127.9, 126.8, 124.3, 122.6 (t, *J* = 25.2 Hz), 119.6 (t, *J* = 247.0 Hz), 70.4 (t, *J* = 32.3 Hz), 6.5 , 4.5.

^{19}F NMR (471 MHz, $CDCl_3$) δ -103.17 (dt, *J* = 244.5, 10.4 Hz), -108.64 (ddd, *J* = 244.5, 12.1, 8.9 Hz).

ESI-MS: calculated for $C_{23}H_{28}F_2N_2O_4Si[M+Na]^+$: 485.1678, found: 485.1678.

(*E*)-2-(4-(3-bromo-4-methoxyphenyl)-3,3-difluoro-4-((triethylsilyl)oxy)but-1-en-1-yl)benza mide (3am)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatography (PE/EA = 4/1), **3am** was obtained as a colourless oil (79.1 mg, 0.150 mmol, 75 %). R_f = 0.08 (PE/EA = 4/1).

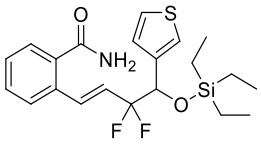
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 1.9 Hz, 1H), 7.56 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.35 (td, *J* = 7.4, 1.9 Hz, 1H), 7.31 (d, *J* = 8.5 Hz, 1H), 7.16 (dt, *J* = 16.2, 2.4 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 1H), 6.13 (ddd, *J* = 16.2, 13.5, 10.0 Hz, 1H), 6.06 (s, 1H), 5.62 (s, 1H), 4.87 (t, *J* = 8.0 Hz, 1H), 3.88 (s, 3H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.64-0.53 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 155.9, 134.9, 133.7, 133.4 (t, *J* = 9.2 Hz), 132.6, 131.6 (d, *J* = 5.5 Hz), 131.0, 128.9, 128.2, 128.0, 127.2, 123.3 (t, *J* = 25.1 Hz), 119.9 (t, *J* = 245.3 Hz), 111.4, 111.2, 76.0 (dd, *J* = 33.3, 30.5 Hz), 56.4, 6.8, 4.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -101.84 (dt, *J* = 243.0, 9.4 Hz), -107.56 (ddd, *J* = 243.0, 13.8, 8.2 Hz).

ESI-MS: calculated for $C_{24}H_{30}BrF_2NO_3Si[M+Na]^+$: 548.1038, found: 548.1038.

(*E*)-2-(3,3-difluoro-4-(thiophen-3-yl)-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3an)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatography (PE/EA = 4/1), **3an** was obtained as a colourless oil (71.4 mg, 0.169 mmol, 84 %). R_f = 0.11 (PE/EA = 4/1).

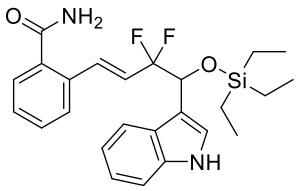
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.2 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.35 (ddd, *J* = 7.6, 6.1, 2.4 Hz, 1H), 7.29 (d, *J* = 3.0 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.18 (dt, *J* = 16.1, 2.5 Hz, 1H), 7.11 (d, *J* = 5.0 Hz, 1H), 6.16 (ddd, *J* = 16.1, 13.9, 9.6 Hz, 1H), 6.04 (s, 1H), 5.52 (s, 1H),5.06 (t, *J* = 7.8 Hz 1H), 0.91 (t, *J* = 7.9 Hz, 9H), 0.66-0.55 (m, 6H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.02 (dt, *J* = 243.2, 9.4 Hz), -107.55 (ddd, *J* = 243.2, 14.1, 7.1 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 139.8 (d, *J* = 5.9 Hz), 134.8, 133.7, 133.3 (t, *J* = 9.1 Hz), 131.0, 128.9, 128.4, 127.2, 127.1, 127.1, 125.6, 123.6, 123.5 (t, *J* = 25.0 Hz), 119.8 (dd, *J* = 245.1, 246.2 Hz), 73.9 (dd, *J* = 35.0, 30.8 Hz), 6.8, 4.8.

ESI-MS: calculated for $C_{21}H_{27}F_2NO_2SSi[M+Na]^+$: 446.1392, found: 446.1390.

(*E*)-2-(3,3-difluoro-4-(1H-indol-3-yl)-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3ao)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatography (PE/EA = 4/1), **3ao** was obtained as a yellow solid (77.8 mg, 0.170 mmol, 85 %). R_f = 0.04 (PE/EA = 4/1).

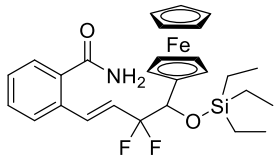
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.45 – 7.37 (m, 2H), 7.35 – 7.28 (m, 2H), 7.19 (d, *J* = 2.3 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.06 – 6.99 (m, 2H), 6.29 (ddd, *J* = 16.0, 14.2, 9.2 Hz, 1H), 5.74 (s, 1H), 5.30 (dd, *J* = 9.6, 6.1 Hz, 1H), 4.92 (s, 1H), 0.89 (t, *J* = 7.9 Hz, 9H), 0.66-0.54 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 136.3, 134.7, 133.8, 132.9 (t, *J* = 9.1 Hz), 131.0, 128.8, 128.4, 127.3, 126.2, 124.3 (dd, *J* = 24.6, 24.4 Hz), 124.1, 122.3, 120.8, 120.6 (t, *J* = 245.2 Hz), 119.9, 113.7 (d, *J* = 5.9 Hz), 111.4, 72.5 (dd, *J* = 36.0, 30.3 Hz), 6.8, 4.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -102.34 (dt, *J* = 239.5, 9.9 Hz), -106.88 (ddd, *J* = 239.5, 14.1, 6.4 Hz).

ESI-MS: calculated for $C_{25}H_{30}F_2N_2O_2Si[M+Na]^+$: 479.1937, found: 479.1937.

(*E*)-2-(3,3-difluoro-4-ferrocene)-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3ap)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatography (PE/EA = 4/1), **3ap** was obtained as a red solid (37.9 mg, 0.072 mmol, 36 %). R_f = 0.09 (PE/EA = 4/1).

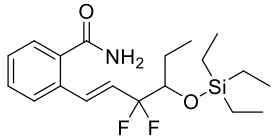
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.41 (td, *J* = 7.5, 1.4 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.09 (dd, *J* = 16.0, 2.1 Hz, 1H), 6.01 (td, *J* = 16.0, 8.4 Hz, 1H), 5.77 (s, 1H), 5.31 (s, 1H), 4.89 (t, *J* = 6.6 Hz, 1H), 4.32 (d, *J* = 7.0 Hz, 2H), 4.19 (s, 5H), 4.17 (s, 1H), 4.10 (s, 1H), 1.08 (t, *J* = 7.9 Hz, 9H), 0.85-0.74 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 134.6, 133.9, 133.3 (t, *J* = 9.1 Hz), 131.1, 128.9, 128.7, 127.4, 123.5 (dd, *J* = 25.7, 23.2 Hz), 119.9 (t, *J* = 245.7 Hz), 74.7 (dd, *J* = 35.2, 28.8 Hz), 69.1, 68.4, 67.3, 7.2, 5.5.

^{19}F NMR (471 MHz, $CDCl_3$) δ -97.33 – -99.66 (m), -106.51 (dd, *J* = 244.8, 15.3 Hz).

ESI-MS: calculated for $C_{27}H_{33}F_2FeNO_2Si[M+Na]^+$: 548.1490, found: 548.1489.

(*E*)-2-(3,3-difluoro-4-((triethylsilyl)oxy)hex-1-en-1-yl)benzamide (3aq)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatography (PE/EA = 4/1), **3aq** was obtained as a colourless oil (40.5 mg, 0.110 mmol, 55 %). R_f = 0.16 (PE/EA = 4/1).

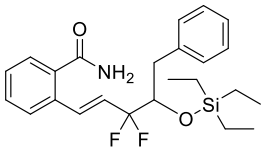
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.46 (td, *J* = 7.6, 1.4 Hz, 1H), 7.41 – 7.35 (m, 2H), 6.24 (ddd, *J* = 16.2, 14.6, 9.2 Hz, 1H), 5.91 (s, 1H), 5.80 (s, 1H), 3.85-3.80 (m, 1H), 1. 71-1.64 (m, 1H), 1.49-1.40 (m, 1H), 0.98 (t, *J* = 7.9 Hz, 12H), 0.66 (qd, *J* = 7.9, 2.2 Hz, 6H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -98.52 – -100.79 (m), -107.50 – -109.61 (m).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 134.9, 134.0, 132.6 (t, *J* = 9.3 Hz), 131.0, 128.9, 128.1, 127.3, 123.8 (t, *J* = 24.7 Hz), 121.1 (t, *J* = 243.9 Hz), 76.4 (dd, *J* = 33.0, 26.7 Hz), 25.4 (d, *J* = 4.6 Hz), 10.4, 7.0, 5.1.

ESI-MS: calculated for $C_{19}H_{29}F_2NO_2Si[M+Na]^+$: 392.1828, found: 392.1827.

(*E*)-2-(3,3-difluoro-5-phenyl-4-((triethylsilyl)oxy)pent-1-en-1-yl)benzamide (3ar)



The title compound was prepared *via* the general procedure, after purification by silica gel column chromatography (PE/EA = 4/1), **3ar** was obtained as a white solid (46.9 mg, 0.109 mmol, 53 %). R_f = 0.12 (PE/EA = 4/1).

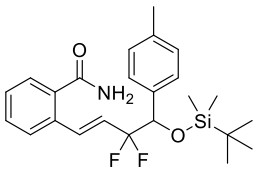
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dt, *J* = 7.7, 1.4 Hz, 2H), 7.49 – 7.43 (m, 2H), 7.38 (td, *J* = 7.5, 1.2 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.23 – 7.18 (m, 3H), 6.28 (m, 2H), 5.88 (s, 1H), 4.13 (tdd, *J* = 10.1, 4.7, 2.8 Hz, 1H), 2.99 (dt, *J* = 13.7, 2.5 Hz, 1H), 2.62 (dd, *J* = 13.7, 9.8 Hz, 1H), 0.79 (t, *J* = 7.9 Hz, 9H), 0.45 – 0.28 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 137.9, 135.1, 133.9, 133.1 (t, *J* = 9.6 Hz), 130.9, 130.0, 128.9, 128.4, 127.9, 127.2, 126.7, 123.3 (t, *J* = 25.0 Hz), 120.8 (t, *J* = 244.8 Hz), 76.7 (dd, *J* = 33.0, 27.3 Hz), 38.9 (d, *J* = 4.7 Hz), 6.8, 4.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -99.70 (dt, *J* = 246.2, 10.2 Hz), -108.26 (dd, *J* = 246.2, 13.9 Hz).

ESI-MS: calculated for $C_{24}H_{31}F_2NO_2Si[M+Na]^+$: 454.1984, found: 454.1976.

(E)-2-(4-((tert-butyldimethylsilyl)oxy)-3,3-difluoro-4-(p-tolyl)but-1-en-1-yl)benzamide (3as)



The title compound was prepared via the general procedure C, after purification by silica gel column chromatography (PE/EA = 4/1), **3as** was obtained as a yellow solid (54.0 mg, 0.125 mmol, 63 %). R_f = 0.18 (PE/EA = 4/1).

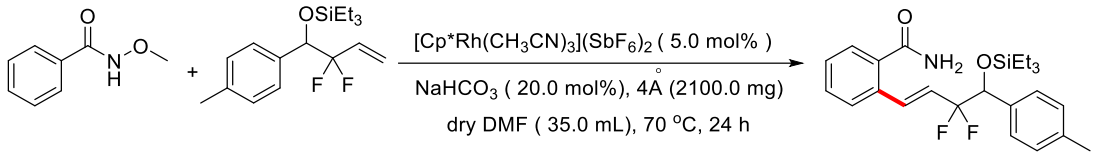
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.38 – 7.34 (m, 1H), 7.28 (d, *J* = 7.7 Hz, 2H), 7.12 (d, *J* = 7.7 Hz, 2H), 7.11 – 7.06 (m, 1H), 6.14 (ddd, *J* = 16.2, 14.1, 9.5 Hz, 1H), 5.79 (s, 1H), 5.31 (s, 1H), 4.92 (dd, *J* = 8.8, 7.0 Hz, 1H), 2.33 (s, 3H), 0.90 (s, 9H), 0.11 (s, 3H), -0.03 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.6 , 138.2 , 135.0 (d, *J* = 5.1 Hz) , 134.7 , 133.7 , 133.2 (t, *J* = 9.2 Hz) , 131.1 , 128.9 , 128.8 , 128.6 , 127.8 , 127.2 , 123.7 (t, *J* = 25.0 Hz) , 120.1 (t, *J* = 245.5 Hz) , 76.8 (d, *J* = 29.3 Hz) , 25.9 , 21.3 , 18.4 , -4.8 , -4.9 .

^{19}F NMR (471 MHz, Chloroform-*d*) δ -101.66 (dd, *J* = 242.0, 10.1 Hz), -108.12 (ddd, *J* = 242.0, 14.3, 6.9 Hz).

ESI-MS: calculated for $C_{24}H_{31}F_2NO_2Si[M+Na]^+$: 454.1984, found: 454.1984.

7. Large Scale Reaction

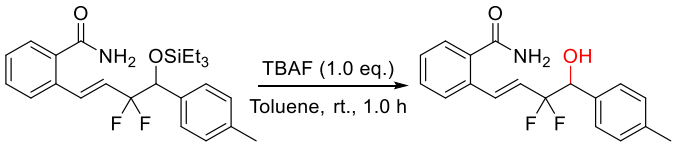


1a, 3.5 mmol **2a,** 1.5 eq. **3aa,** 71%, 1.07 g

A 50 mL-round bottom flask charged with a stirring bar, was added *N*-methoxybenzamide **1a** (3.5 mmol, 1 equiv) and **2a** (5.3 mmol, 1.5 equiv). $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (145.6 mg, 0.18 mmol, 5.0 mol%), $NaHCO_3$ (58.8 mg, 0.04 mmol, 20.0 mol%) and 4Å molecular sieves (2100.0 mg), dry DMF (35.0 mL) were added subsequently into the reaction vessel. The reaction was allowed to stir at 70 °C for 24 hours. The reaction mixture was then diluted with EtOAc (20 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **3aa** (71 %).

8. Derivatization of 3aa

(a) Synthetic Transformation of **3aa** to **4**



3aa **4** **Y =99%**

A 15 mL-schlenk tube was charged with **3aa** (0.2 mmol) in toluene (0.5 mL), then tetrabutylammonium fluoride (TBAF, 0.2 mmol, 1.0 mol/L in Tetrahydrofuran) was added dropwise and the mixture was stirred at room temperature until the complete consumption of **3aa** as monitored by TLC analysis (about 1.0 hour). The reaction mixture was then diluted with EtOAc (5.0 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The mixture was concentrated in vacuo and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding product (63.0 mg, 99 % yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.4 Hz, 1H), 7.46 – 7.37 (m, 2H), 7.34 (td, *J* = 7.1, 2.1 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 3H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.35 (s, 1H), 6.01 (dt, *J* = 16.2, 11.6 Hz, 1H), 5.91 (s, 1H), 4.89 (t, *J* = 9.2 Hz, 1H), 3.87 (s, 1H), 2.33 (s, 3H).

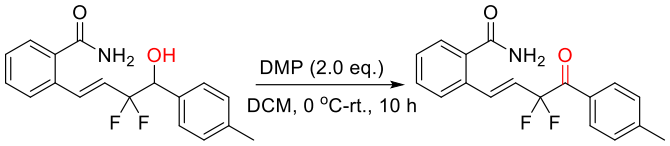
^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2 , 138.5 , 134.5 (t, *J* = 9.3 Hz) , 134.4 , 134.2 , 133.6 (d, *J* = 3.7 Hz) , 131.2 , 129.1 , 128.9 , 128.2 , 127.7 , 127.5 , 123.7 (t, *J* = 25.8 Hz) , 120.2 (t, *J* = 245.5 Hz) , 75.9 (t, *J* = 30.5 Hz) , 21.3 .

^{19}F NMR (471 MHz, $CDCl_3$) δ -104.34 (dt, *J* = 245.3, 10.5 Hz), -108.10 (dt, *J* = 245.3, 10.5 Hz).

ESI-MS: calculated for $C_{18}H_{17}F_2NO_2[M+Na]^+$:340.1119, found: 340.1118.

The compound was prepared according to a known procedure.[3]

(b) Synthetic Transformation of **4** to **5**



4 **5**

Y = 62%

The compound was prepared according to a known procedure.[4]

A 15 mL-schlenk tube was charged with **4** (0.2 mmol) in DCM (2.0 mL), then cooled to 0 °C and DessMartin periodinane (170 mg, 0.4 mmol) was added. The mixture was left to warm to room temperature for 10.0 h. The reaction mixture was then diluted with DCM (5.0 mL) and washed with brine. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine, dried over Na_2SO_4. The mixture was concentrated in vacuo and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding product (39.1 mg, 62 % yield).

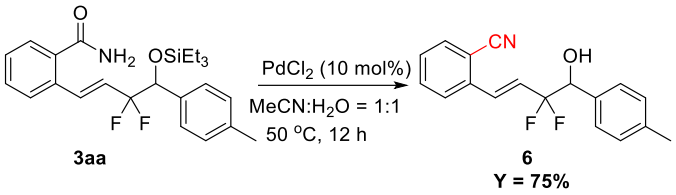
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.64 – 7.52 (m, 3H), 7.45 (td, *J* = 7.6, 1.3 Hz, 1H), 7.38 (td, *J* = 7.6, 1.3 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.40 (dt, *J* = 16.1, 11.4 Hz, 1H), 6.19 (s, 1H), 5.93 (s, 1H), 2.42 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ188.6 (t, *J* = 31.0 Hz), 170.8, 145.9, 135.1, 134.9 (t, *J* = 9.7 Hz), 133.3, 131.1, 130.6 (d, *J* = 5.4 Hz), 130.6, 129.6, 129.5, 129.4, 128.0, 127.4, 122.8 (t, *J* = 24.7 Hz), 116.1 (t, *J* = 251.3 Hz), 22.0 .

^{19}F NMR (471 MHz, $CDCl_3$) δ -97.78 (d, *J* = 10.5 Hz).

ESI-MS: calculated for $C_{18}H_{15}F_2NO_2[M+Na]^+$: 338.0963, found: 338.0962.

(c) Synthetic Transformation of **3aa** to **6**



The compound was prepared according to a known procedure. [5]

A 15 mL-schlenk tube was charged with **3aa** (0.2 mmol) in MeCN/H_2O (1:1) , then was treated with $PdCl_2$ (10 mol %, 3.5 mg) and the mixture was stirred at 50 °C until the complete consumption of **3aa** as monitored by TLC analysis (typically 12.0 hour) . The reaction mixture was then diluted with EtOAc (5.0 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine, and dried over Na_2SO_4. The mixture was concentrated in vacuo and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding product (45.1 mg, 75 % yield).

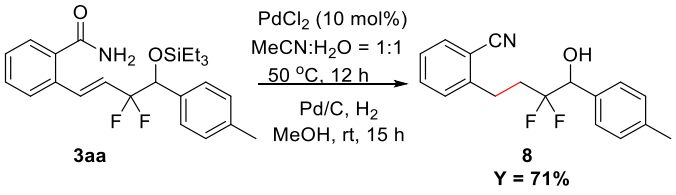
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.58 – 7.54 (m, 2H), 7.40 (ddd, *J* = 7.8, 5.3, 3.4 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.20 – 7.14 (m, 3H), 6.37 (dt, *J* = 16.1, 11.6 Hz, 1H), 4.98 (t, *J* = 9.4 Hz, 1H), 2.83 (s, 1H), 2.35 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9, 138.1, 133.4, 133.1, 133.0, 131.4 (t, *J* = 9.2 Hz), 129.2, 127.6, 126.6, 125.3 (t, *J* = 25.5 Hz), 119.9 (t, *J* = 245.3 Hz), 117.4, 112.0, 76.1 (t, *J* = 29.8 Hz), 21.4.

^{19}F NMR (471 MHz, $CDCl_3$) δ -105.46 (dt, *J* = 247.2, 10.5 Hz), -107.53 (dt, *J* = 247.2, 10.5 Hz).

ESI-MS: calculated for $C_{18}H_{15}F_2NO[M+Na]^+$: 322.1014, found: 322.1014.

(d) Synthetic Transformation of **3aa** to **7**



The compound was prepared according to a known procedure. [6]

A 15 mL-schlenk tube was charged with **3aa** (0.2 mmol) in MeCN/H_2O (1:1), then $PdCl_2$ (10 mol %, 3.5 mg) was added, and the mixture was stirred at 50 °C until the complete consumption of **3aa** as monitored by TLC analysis (typically 12.0 hour). The reaction mixture was then diluted

with EtOAc (5.0 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine, and dried over Na_2SO_4. The mixture was concentrated in vacuo and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the intermediate product (45.1 mg, 0.15 mmol). Then the intermediate product in methanol (2.0 ml) was hydrogenated at room temperature under room pressure in the presence of Pd/C (20 mol %, 3.2 mg) for 15 h. Upon completion, the solvent was then removed under vacuum. The residue was performed by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding product (43.4 mg, 72 % yield).

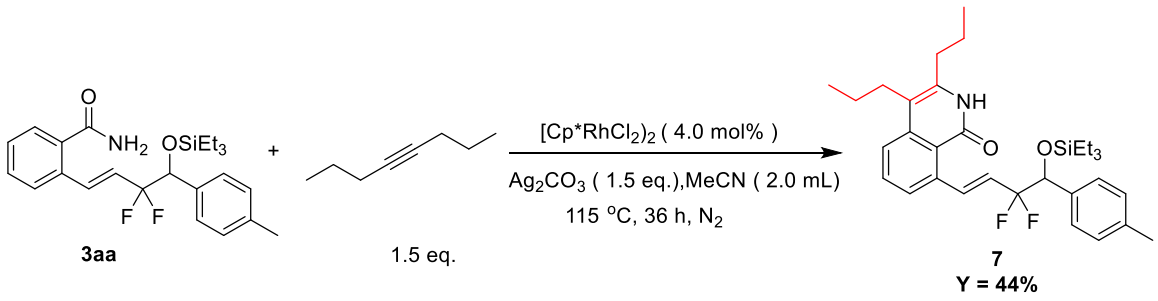
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.50 (td, *J* = 7.7, 1.4 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 4.89 (t, *J* = 10.2 Hz, 1H), 3.12 – 3.05 (m, 1H), 3.11-2.99 (m, 1H), 2.55 (s, 1H), 2.35 (s, 3H), 2.31 – 2.22 (m, 1H), 2.14 – 2.04 (m, 1H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -109.58 (dt, *J* = 22.5, 10.8 Hz), -109.76 (dt, *J* = 22.5, 10.8 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.8 , 138.8 , 133.4 , 133.1 , 129.8 , 129.3 , 127.4 , 127.1 , 123.0 (t, *J* = 246.9 Hz) , 117.9 , 112.6 , 75.4 (t, *J* = 28.6 Hz) , 33.1 (t, *J* = 24.1 Hz) , 26.7 (t, *J* = 5.0 Hz) , 21.4 .

ESI-MS: calculated for $C_{18}H_{17}F_2NO[M+Na]^+$: 324.1170, found: 324.1175.

(e) Synthetic Transformation of **3aa** to **8**



The compound was prepared according to a known procedure. [7]

A 15 mL-schlenk tube was charged with **3aa** (0.2 mmol), 4-Octyne (33.0 mg, 0.3 mmol, 1.5 equiv), Ag_2CO_3 (82.7 mg, 0.3 mmol, 1.5 equiv), and $[Cp^*RhCl_2]_2$ (5.0 mg, 4.0 mol%), and MeCN (2.0 mL) was added. After purged with nitrogen, the mixture was stirred at 115 °C for 36 h. The mixture was then diluted with CH_2Cl_2 and filtered through celite. All volatiles were removed under reduced pressure. The purification was performed by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding product (47.4 mg, 44 % yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.51 (s, 1H), 8.36 – 8.29 (m, 1H), 7.63 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.59 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 2H), 5.94 – 5.86 (m, 1H), 4.93 (t, *J* = 8.8 Hz, 1H), 2.71 – 2.64 (m, 2H), 2.62 (t, *J* = 7.5 Hz, 2H), 2.31 (s, 3H), 1.69 (q, *J* = 7.4 Hz, 2H), 1.59 – 1.55 (m, 2H), 1.03 (t, *J* = 7.3 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.9 Hz, 9H), 0.58 (qd, *J* = 7.9, 6.3 Hz, 6H).

^{19}F NMR (471 MHz, $CDCl_3$) δ -98.19 – -103.87 (m), -104.51 – -110.19 (m).

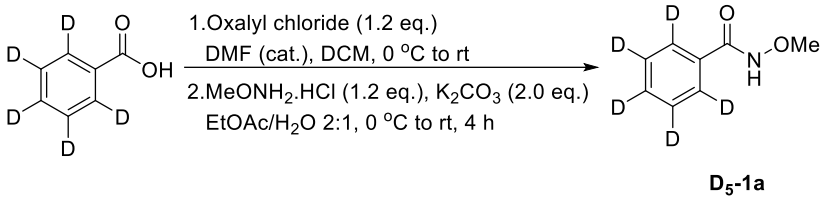
^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8, 140.0, 139.6, 138.6, 138.0, 137.7 (t, *J* = 9.3 Hz), 131.9 , 128.7, 128.0, 125.6, 123.7, 122.5, 121.8 (dd, *J* = 247.4, 253.9 Hz), 112.8, 76.8 (dd, *J* = 12.5, 14.2 Hz), 32.6, 29.1, 23.6, 22.6, 21.4, 14.5, 13.7, 6.8, 4.9.

ESI-MS: calculated for $C_{32}H_{43}F_2NO_2Si[M+Na]^+$: 562.2923, found: 562.2927.

9. Mechanistic Studies

9.1 Deuteration experiment

Synthesis of deuterated substrate (D_5-1a)

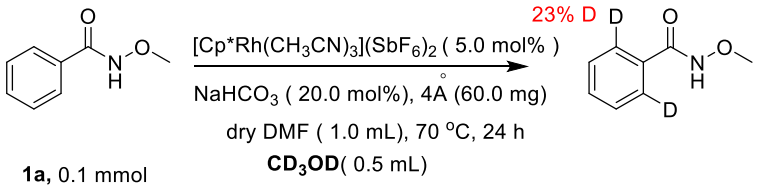


The **D_5-1a** was prepared accoding to the known procedure.[1]

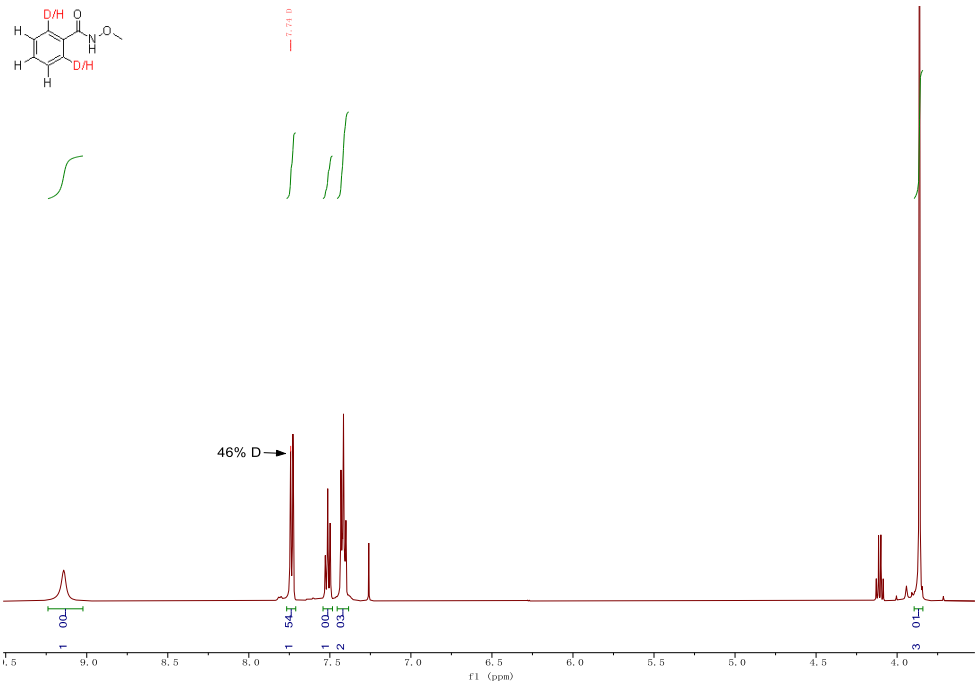
1) To a solution of the pentadeuterated benzoic acid (636 mg, 5.0 mmol, 1.0 eq.) in dry CH_2Cl_2 (15 mL) at 0°C under N_2 was added dropwise oxalyl chloride (0.6 mL, 6.0 mmol, 1.2 eq.) followed by a catalytic amount of dry DMF (1 drops). The reaction was allowed to stir at rt for 4h. The solvent was then removed under reduce pressure to afford the corresponding crude pentadeuterated benzoyl chloride.

2) Methoxyamine hydrochloride (501 mg, 6.0 mmol, 1.2 eq.) was added to a biphasic mixture of K_2CO_3 (1.380 g, 10.0 mmol, 2.0 eq.) in a 2:1 mixture of EtOAc (30 mL) and H_2O (15 mL). The resulting solution was cooled to 0°C followed by dropwise addition of the unpurified pentadeuterated benzoyl chloride dissolved in a minimum amount of EtOAc (3 mL). The flask containing the pentadeuterated benzoyl chloride was then rinsed with additional EtOAc. The reaction was allowed to stir for 4h while reaching rt. Afterwards, the phases were separated and the aqueous phase was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered and evaporated under reduced pressure. The pure product was purified by flash column chromatography on silica gel to afford the pure product **D_5-1a** as a yellow oil (687 mg, 4.4 mmol, 88 %).

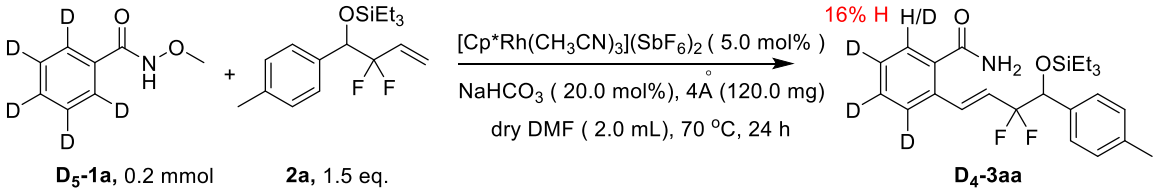
9.2 H/D exchange of the substrate



A 15 mL-schlenk tube charged with a stirring bar, was added *N*-methoxybenzamide **1a** (0.1 mmol, 1 equiv). Then the catalyst $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (4.2 mg, 0.005 mmol, 5.0 mol%)、$NaHCO_3$ (1.7 mg, 0.02 mmol, 20.0 mol%) and 4A molecular sieves (60.0 mg), dry DMF (1.0 mL) were added subsequently into the reaction vessel. The mixture was dissolved in CD_3OD (0.5 mL, 0.2 M) stirred . After 24 h an aliquot of the reaction mixture was removed and NMR determined the degree of deuterium incorporation.

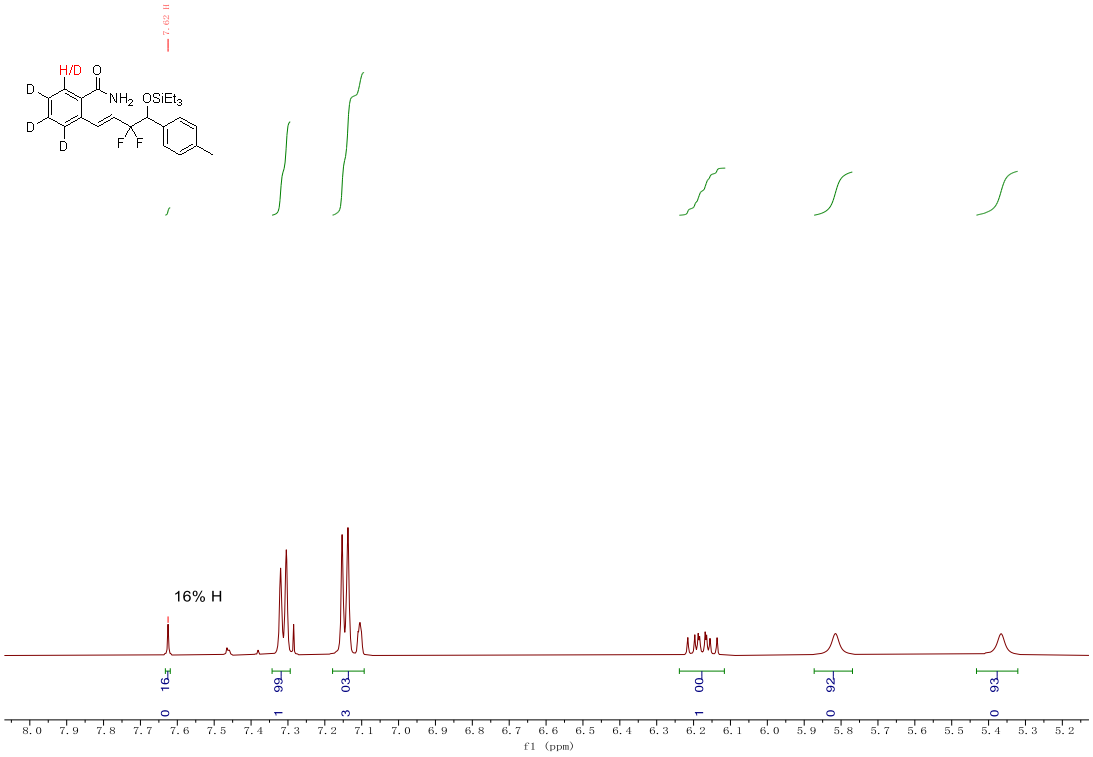


9.3 H/D exchange of the substrate



A 15 mL-schlenk tube charged with a stirring bar, was added D_5-N-methoxybenzamide **D_5-1a** (0.2 mmol, 1 equiv) and **2a** (0.3 mmol, 1.5 equiv)、$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (8.3 mg, 0.01 mmol, 5.0 mol%)、$NaHCO_3$ (3.4 mg, 0.04 mmol, 20.0mol%) and 4A molecular sieves (120.0 mg) , dry DMF (2.0 mL) were added subsequently into the reaction vessel. After 24 h of reaction at 70 ℃, the reaction mixture was then diluted with EtOAc (5.0 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine and

dried over Na_2SO_4. The mixture was concentrated in vacuo and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding product.



9.4 Determination of Intermolecular Kinetic Isotope Effect (KIE)

To probe the mechanism of the C-H activation step, the parallel experiments were showed that the kinetic isotope effect (KIE) was measured as k_H/k_D = 1.26

The procedures to measure KIE were as follows:

A 15 mL-schlenk tube charged with a stirring bar, was added *N*-methoxybenzamide **1a** (0.2 mmol, 1 equiv) and **2a** (0.3 mmol, 1.5 equiv)、$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (8.3 mg, 0.01 mmol, 5.0 mol%)、$NaHCO_3$ (3.4 mg, 0.04 mmol, 20.0mol%) and 4Å molecular sieves (120.0 mg) , dry DMF (2.0 mL) were added subsequently into the reaction vessel. In another reaction vessel, D_5-*N*-methoxybenzamide **D_5-1a** (0.2 mmol, 1 equiv), and **2a** (0.3 mmol, 1.5 equiv)、$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (8.3 mg, 0.01 mmol, 5.0 mol%)、$NaHCO_3$ (3.4 mg, 0.04 mmol, 20.0mol%) and 4Å molecular sieves (120.0 mg) , dry DMF (2.0 mL) were added subsequently into the reaction vessel. After a certain time of reaction at 70 ℃, an appropriate amount of water was added to quench these two reactions at the same time. To the reaction mixture was added P-iodoanisole (46.8 mg, 0.2 mmol, 1.0 equiv) as internal standard. The reaction flask and internal

standard solution was filtered with EtOAc in a short silica gel. The filtrate was evaporated under reduced pressure, and the yield was determined by NMR by integration of the product peaks relative to the P-iodoanisole.

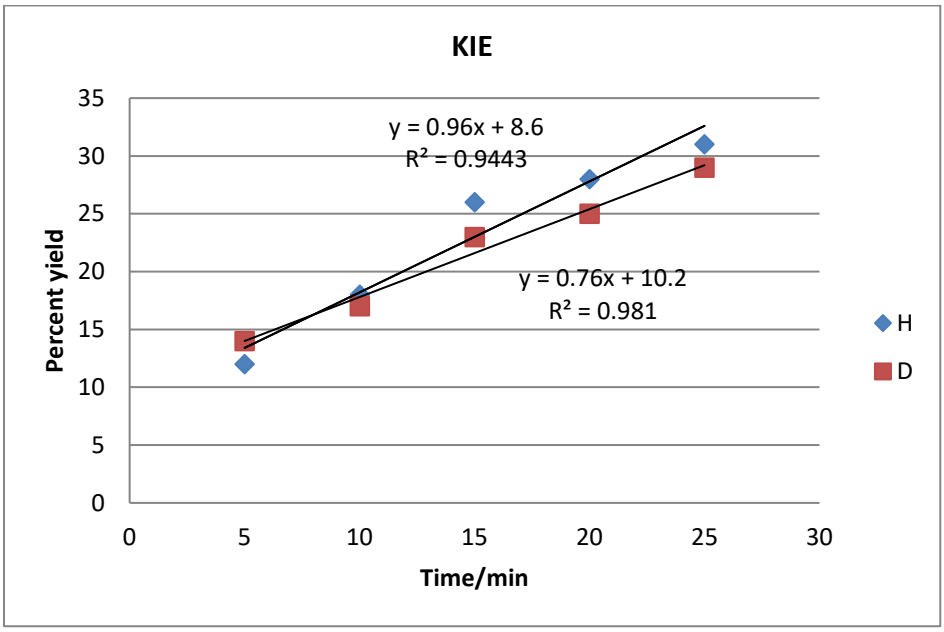
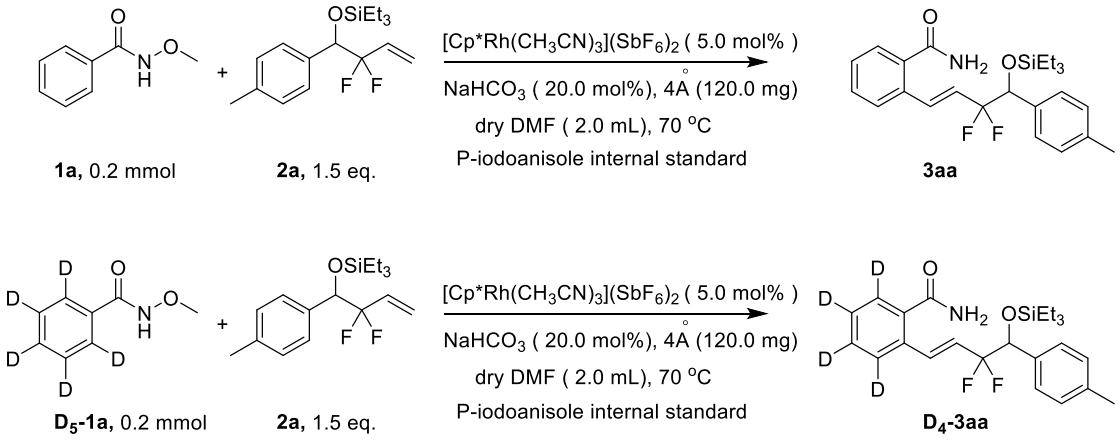
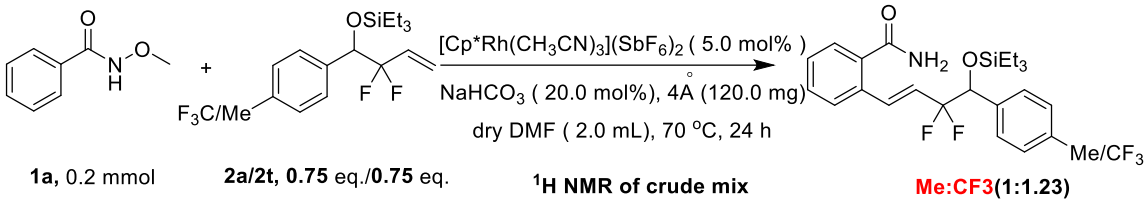


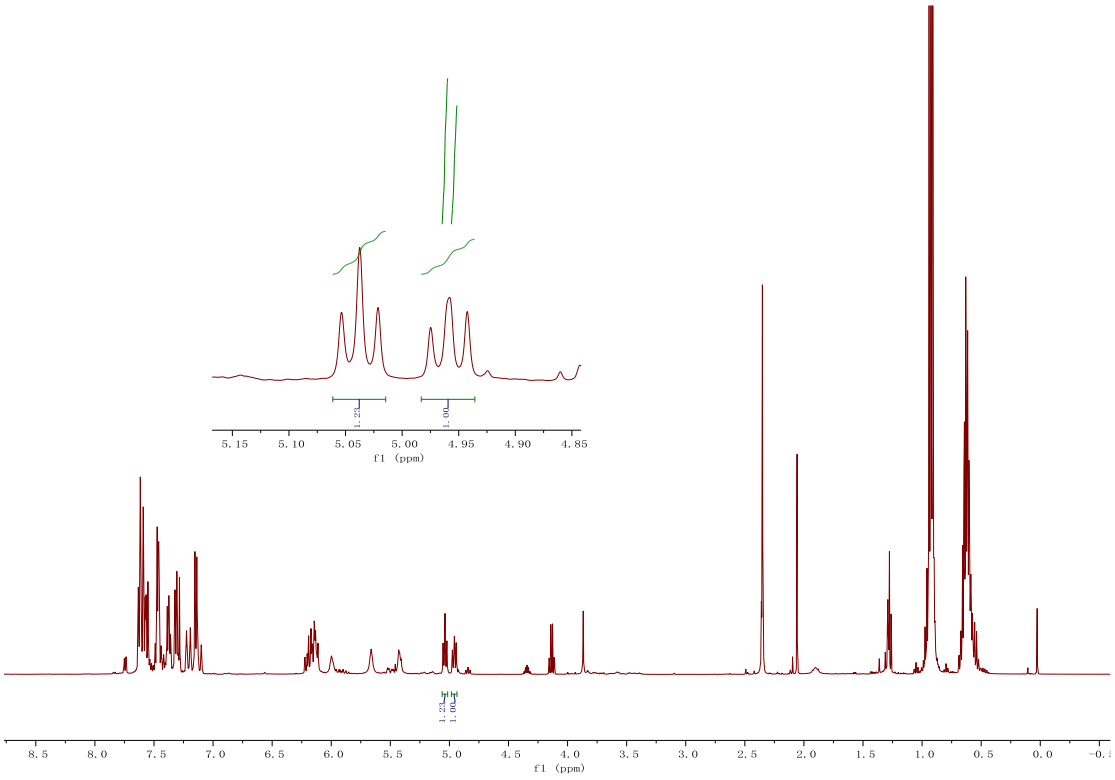
Figure 1. NMR yield mechanism diagram

With *N*-methoxybenzamide as raw material, the yield of every 5 minutes is 12，18，26，28，31%. And with deuterium *N*-methoxybenzamide as raw material, the yield of every 5 minute is 14, 17, 23, 25, 29%.

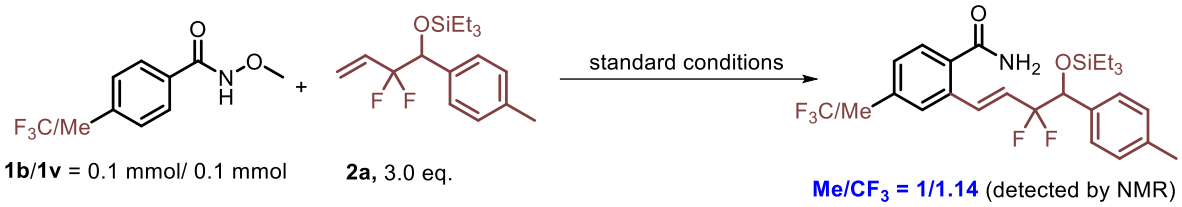


9.5 Competition Experiments





A 15 mL-schlenk tube charged with a stirring bar, was added *N*-methoxybenzamide **1a** (0.2 mmol, 1 equiv) 、 **2a** (0.15 mmol, 0.75 equiv)、 **2t** (0.15 mmol, 0.75 equiv)、 $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (8.3 mg, 0.01 mmol, 5.0 mol%)、$NaHCO_3$ (3.4 mg, 0.04 mmol, 20.0mol%) and 4Å molecular sieves (120.0 mg) , dry DMF (2.0 mL) were added subsequently into the reaction vessel. After 24 h of reaction at 70 ℃, the reaction mixture was then diluted with EtOAc (5.0 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine, and dried over Na_2SO_4. The mixture was concentrated in vacuo and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the crude mixture. The final ratio of the two products was determined by NMR.



A 15 mL-schlenk tube charged with a stirring bar, was added *N*-dimethoxybenzamide **1b** (0.1 mmol, 1 equiv)、4-bromo-*N*-methoxybenzamide **1v** (0.1 mmol, 1 equiv) and **2a** (0.3 mmol, 3.0 equiv)、 $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (8.3 mg, 0.01 mmol, 10.0 mol%)、$NaHCO_3$ (3.4 mg, 0.04 mmol, 40.0mol%) and 4Å molecular sieves (120.0 mg), dry DMF (2.0 mL) were added subsequently into the reaction vessel. After 24 h of reaction at 70 ℃, the reaction mixture was then diluted with EtOAc (5.0 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine, and dried over Na_2SO_4. The mixture was concentrated in vacuo and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the crude mixture. The final ratio of the two products was determined by NMR..

10. References

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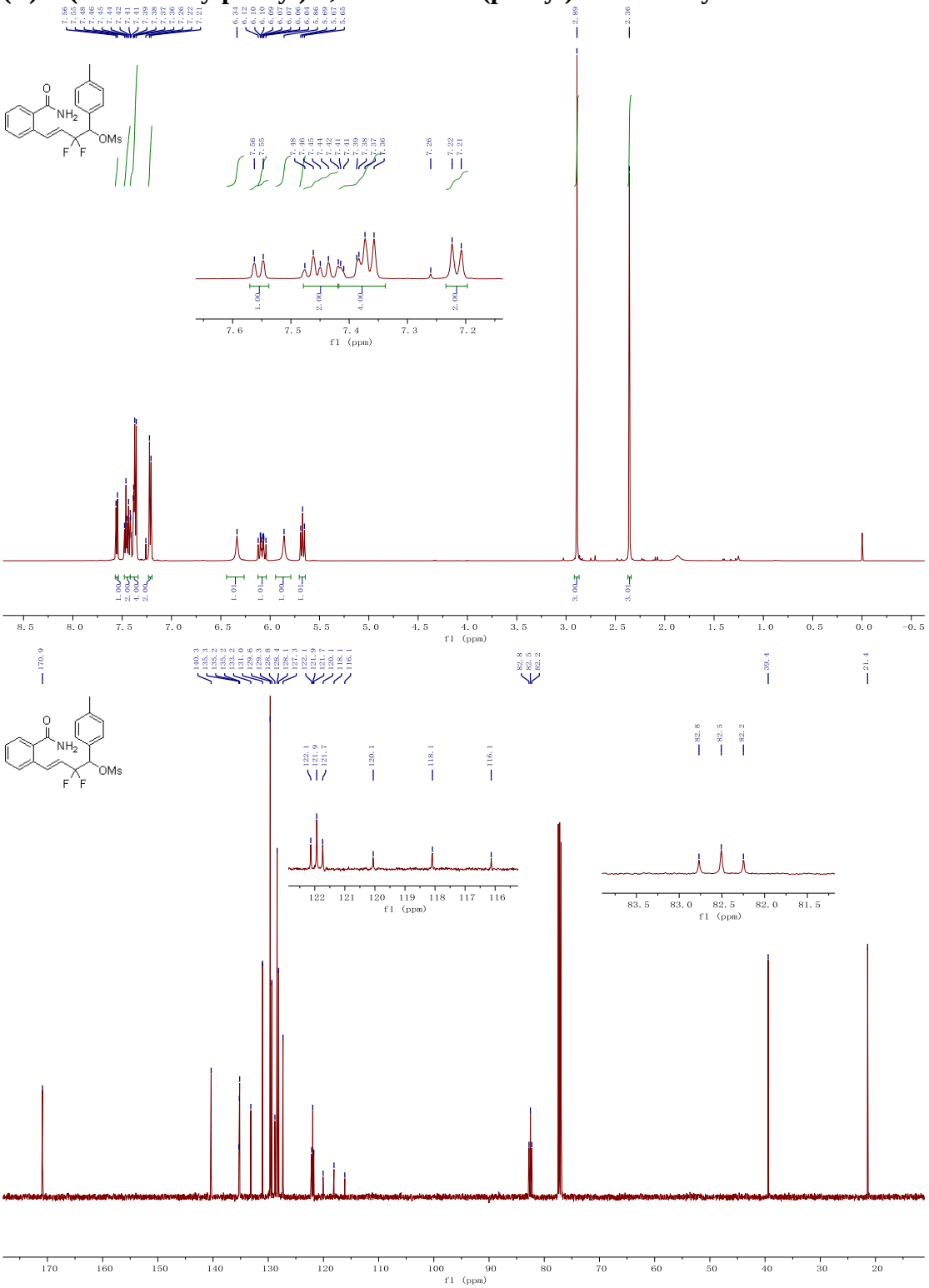
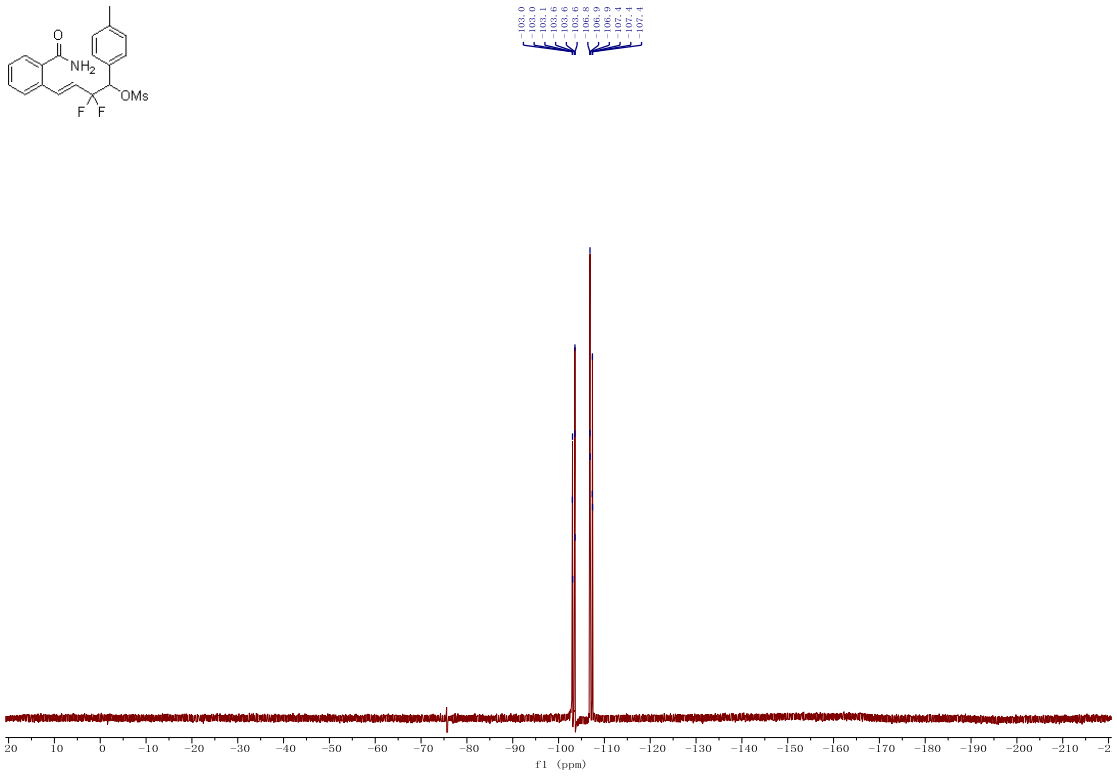
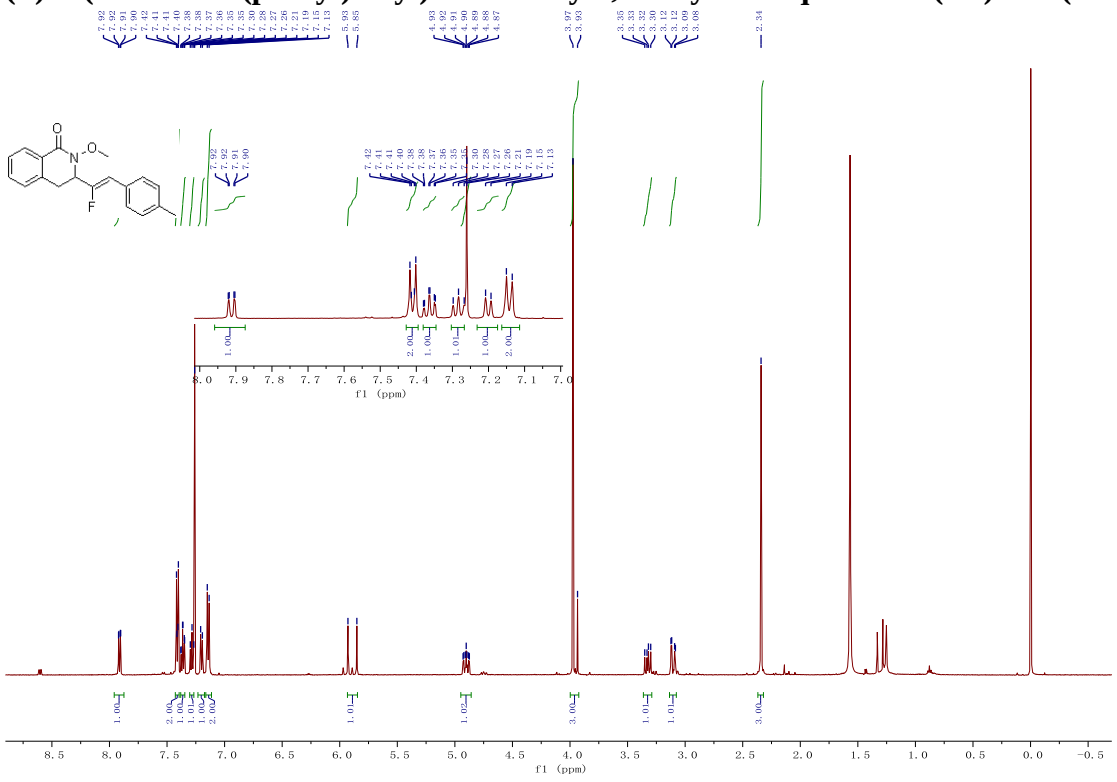
11. ^{1}H NMR 、^{19}F NMR and ^{13}C NMR spectra of Products

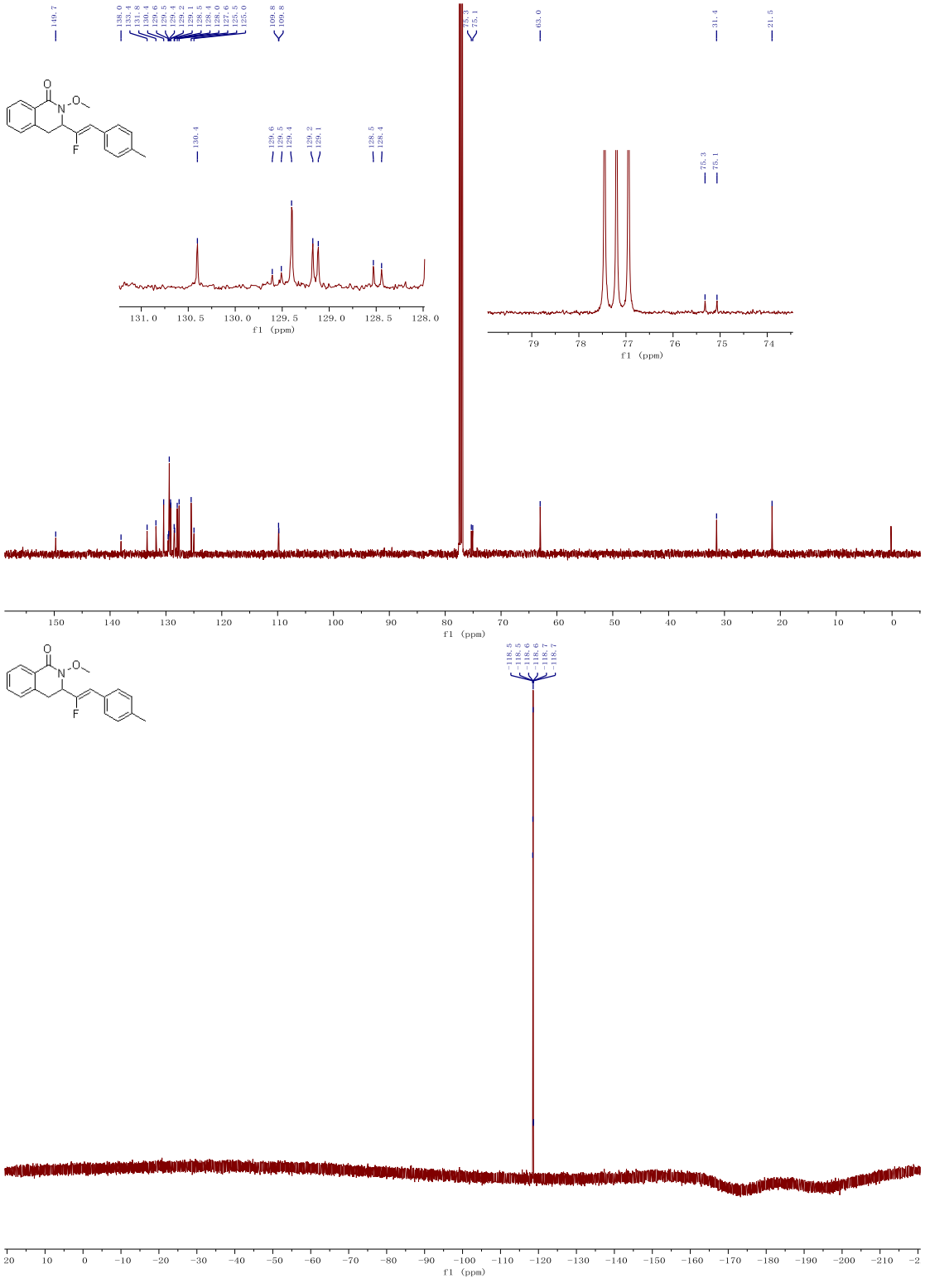
(*E*)-4-(2-carbamoylphenyl)-2,2-difluoro-1-(p-tolyl)but-3-en-1-yl methanesulfonate (3C)



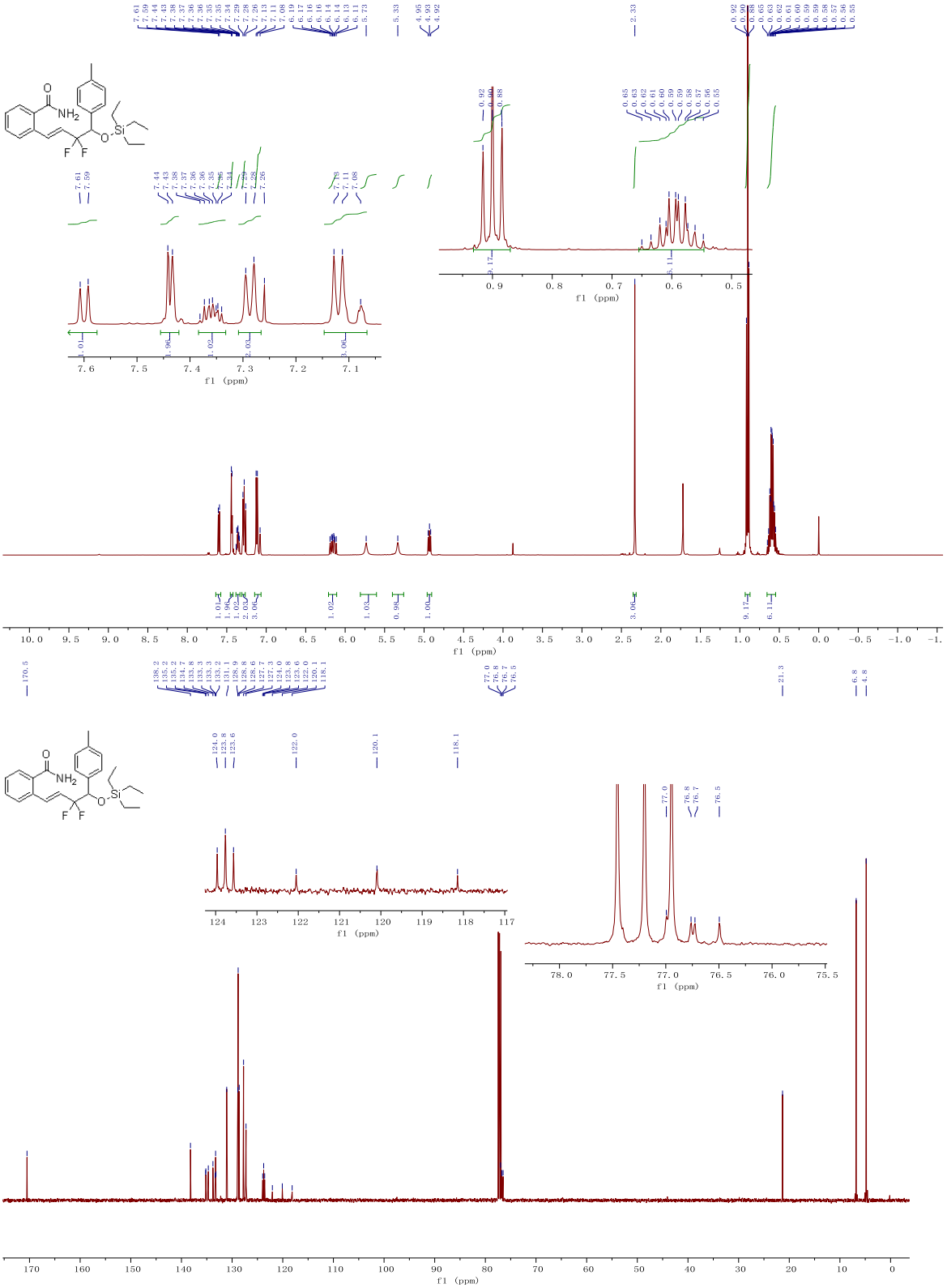


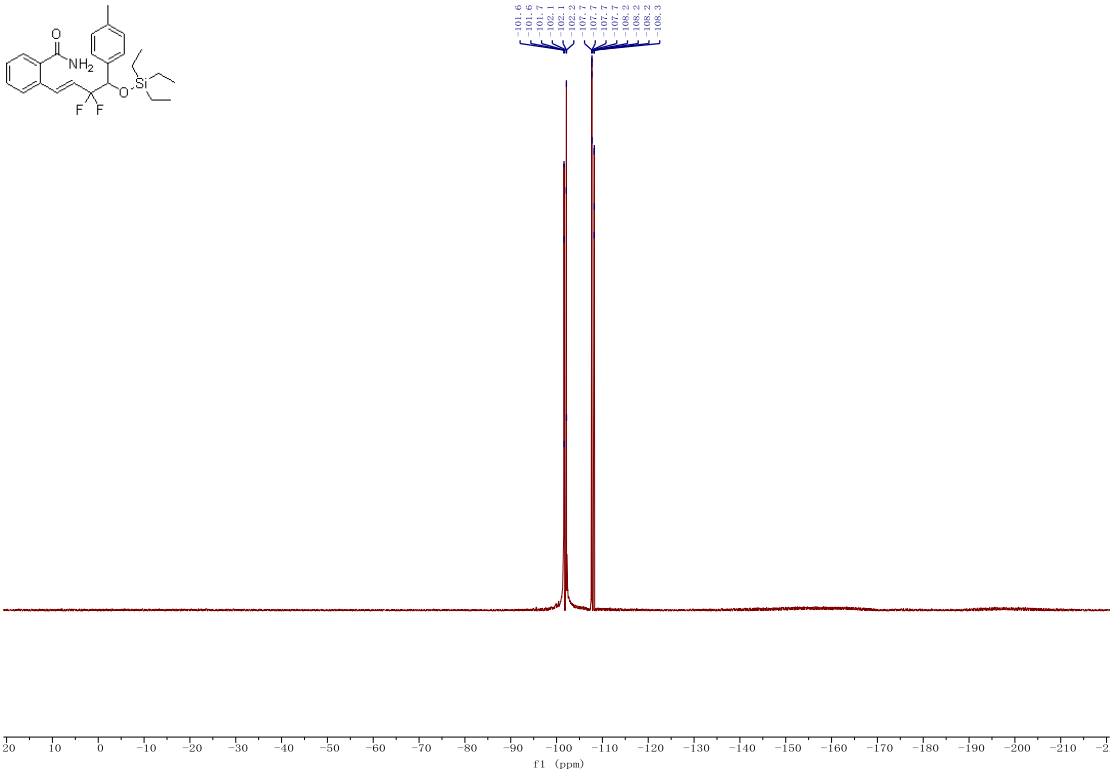
(*Z*)-3-(1-fluoro-2-(p-tolyl)vinyl)-2-methoxy-3,4-dihydroisoquinolin-1(2H)-one (3C’)



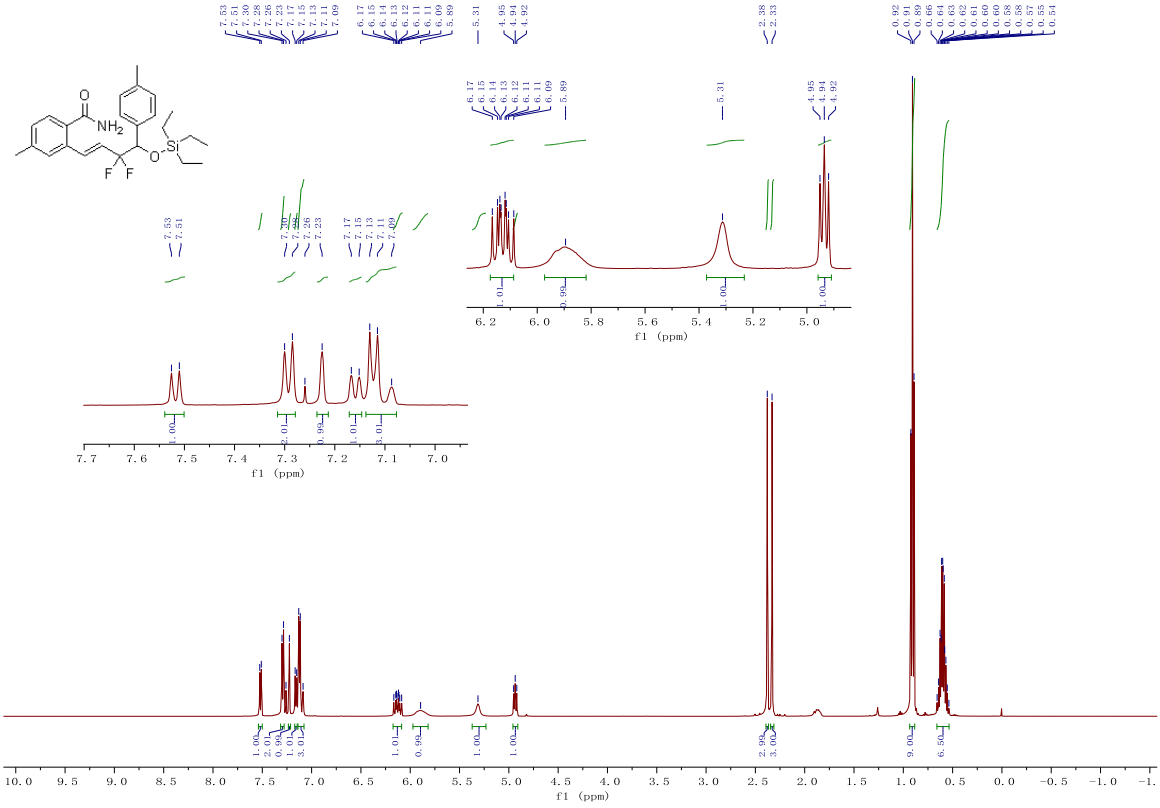

149.7
138.0
133.4
131.8
130.4
129.6
129.5
129.4
129.2
129.1
128.5
128.4
128.0
127.6
125.5
125.0
109.8
109.8
75.3
75.1
63.0
31.4
21.5
130.4
129.6
129.5
129.4
129.2
129.1
128.5
128.4
131.0
130.5
130.0
129.5
129.0
128.5
128.0
f1 (ppm)
75.3
75.1
79
78
77
76
75
74
f1 (ppm)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O
N
O
F
-118.5
-118.5
-118.6
-118.6
-118.7
-118.7
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-2
f1 (ppm)

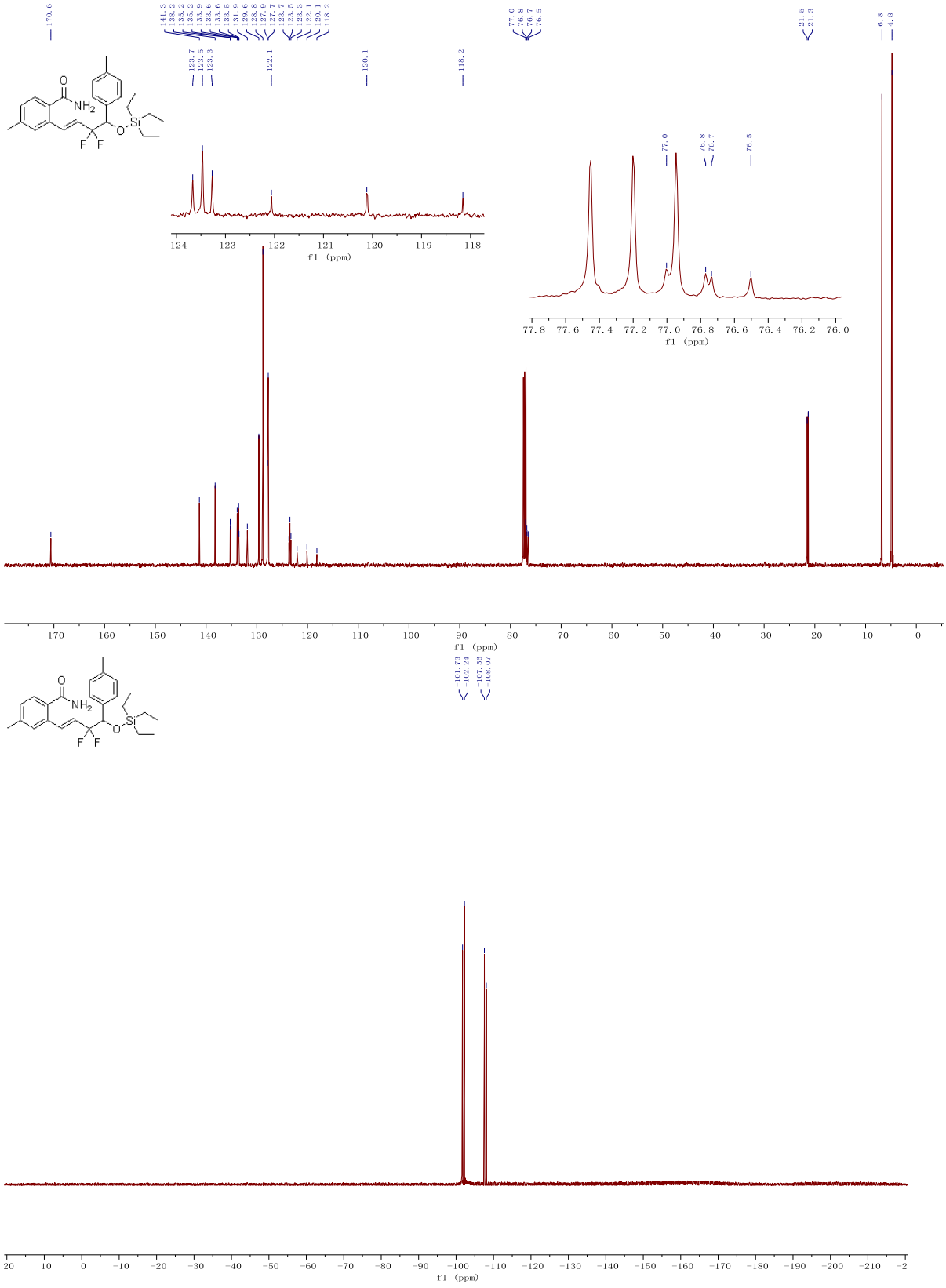
(*E*)-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3aa)





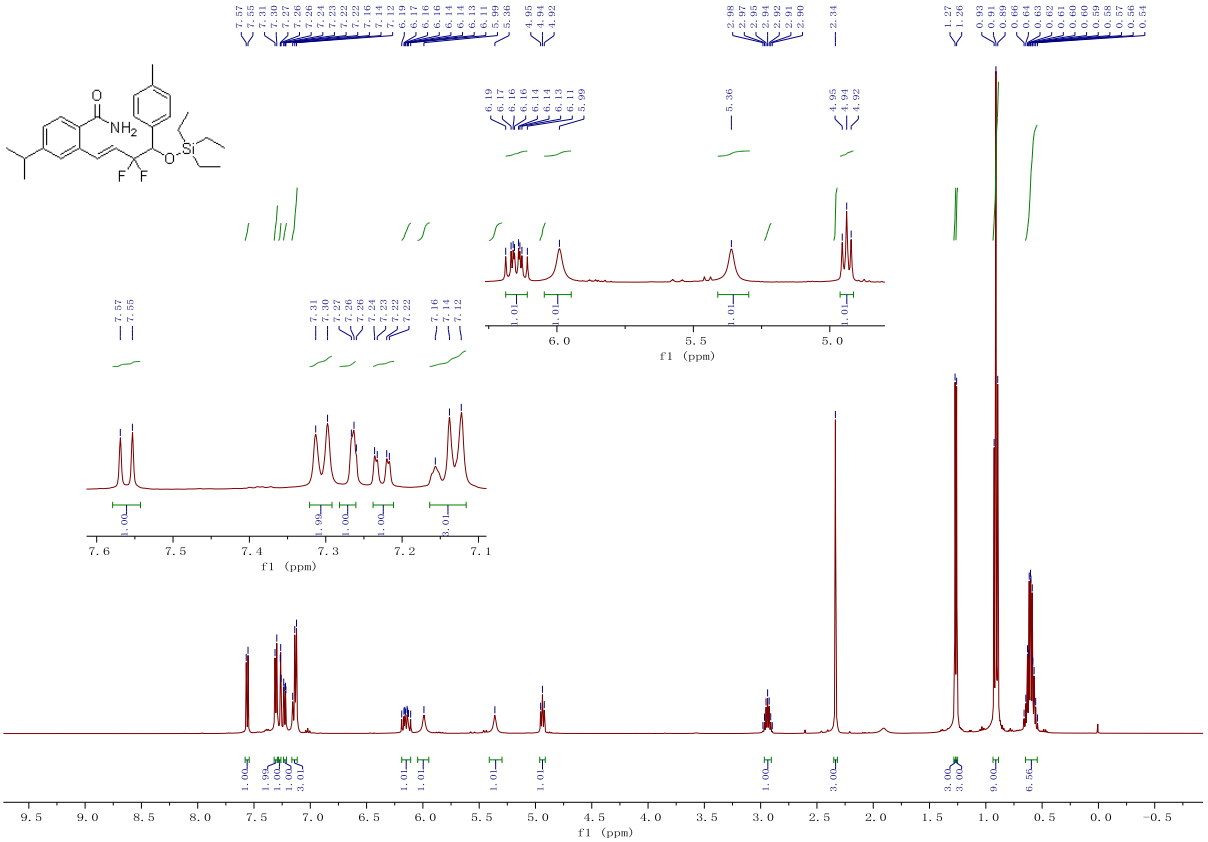
(*E*)-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)-4-methylbenzamide (3ba)

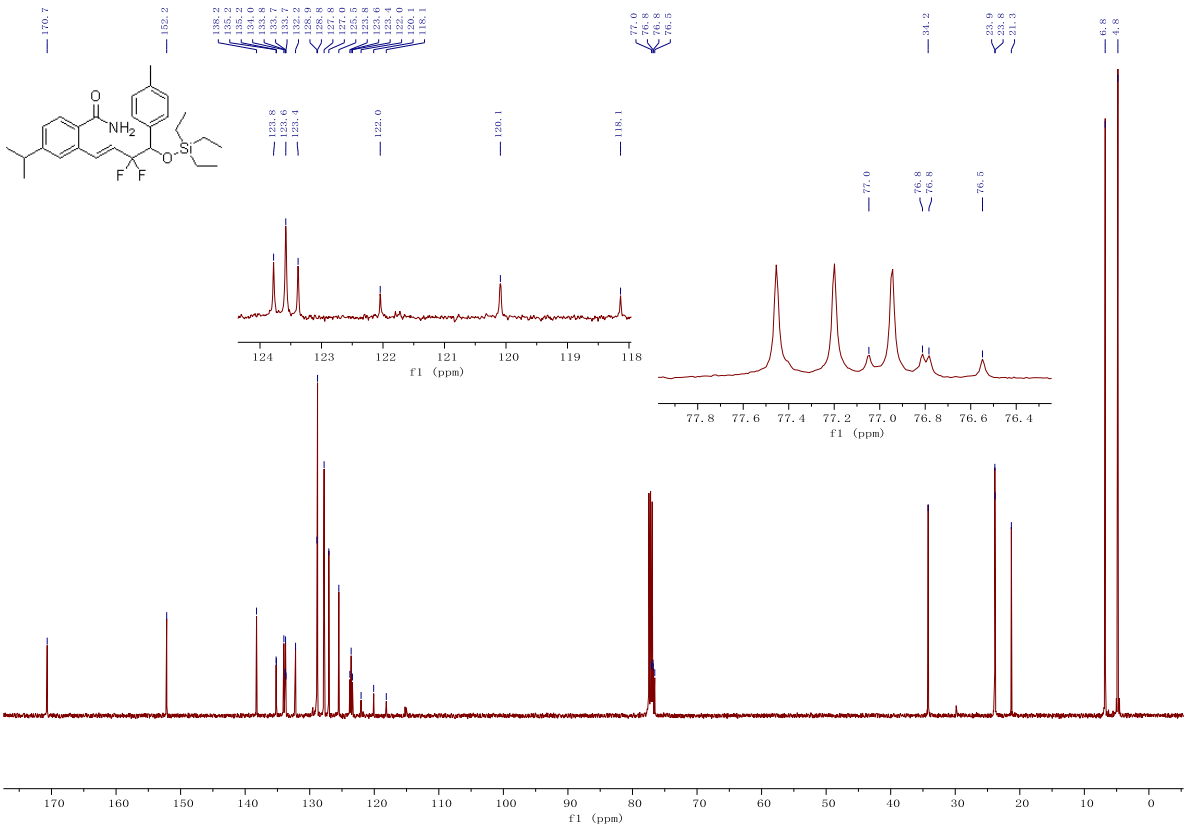


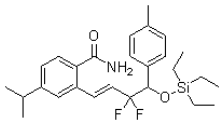

170.6
141.3
138.2
135.2
133.9
133.6
133.5
131.9
129.6
128.8
127.9
127.7
123.5
123.3
122.1
120.1
118.2
77.0
76.8
76.7
76.5
21.5
21.3
6.8
4.8
f1 (ppm)

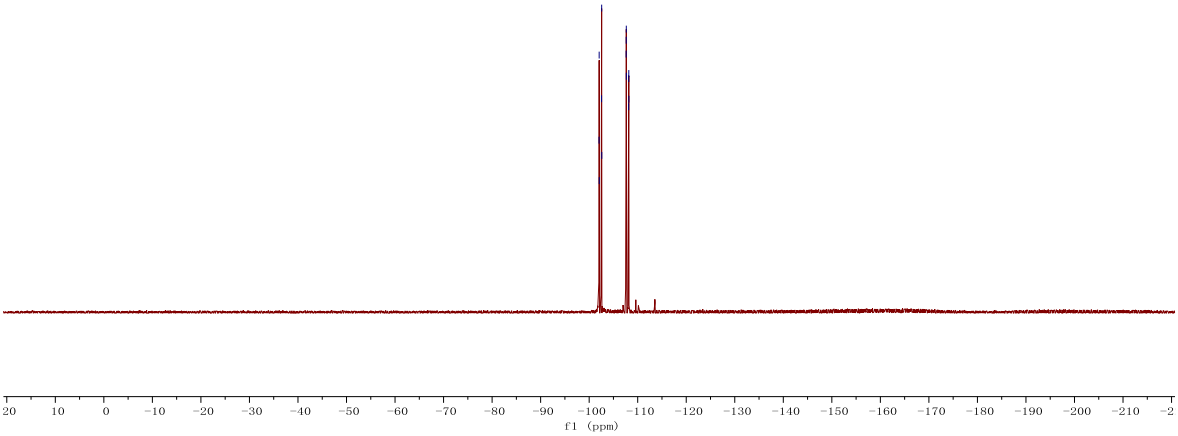
-101.73
-102.24
-107.56
-108.07
f1 (ppm)

(*E*)-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)-4-isopropylbenzamide (3ca)

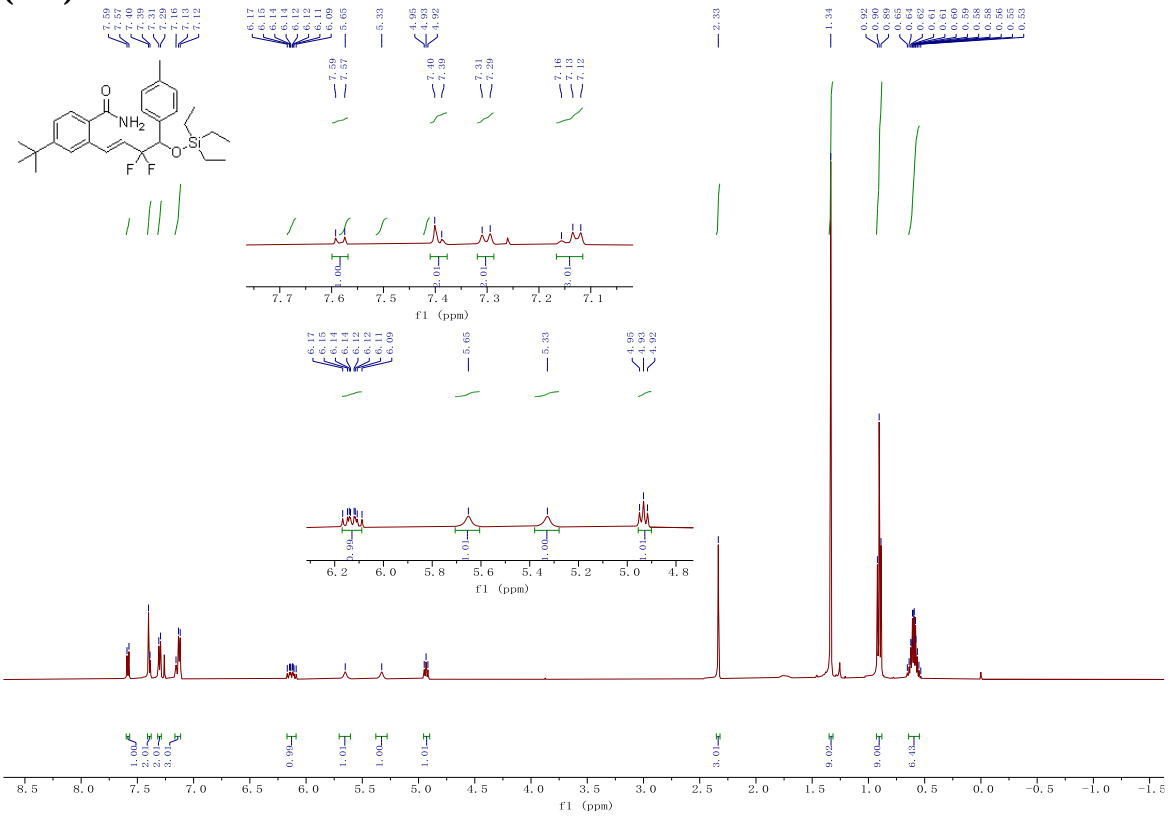


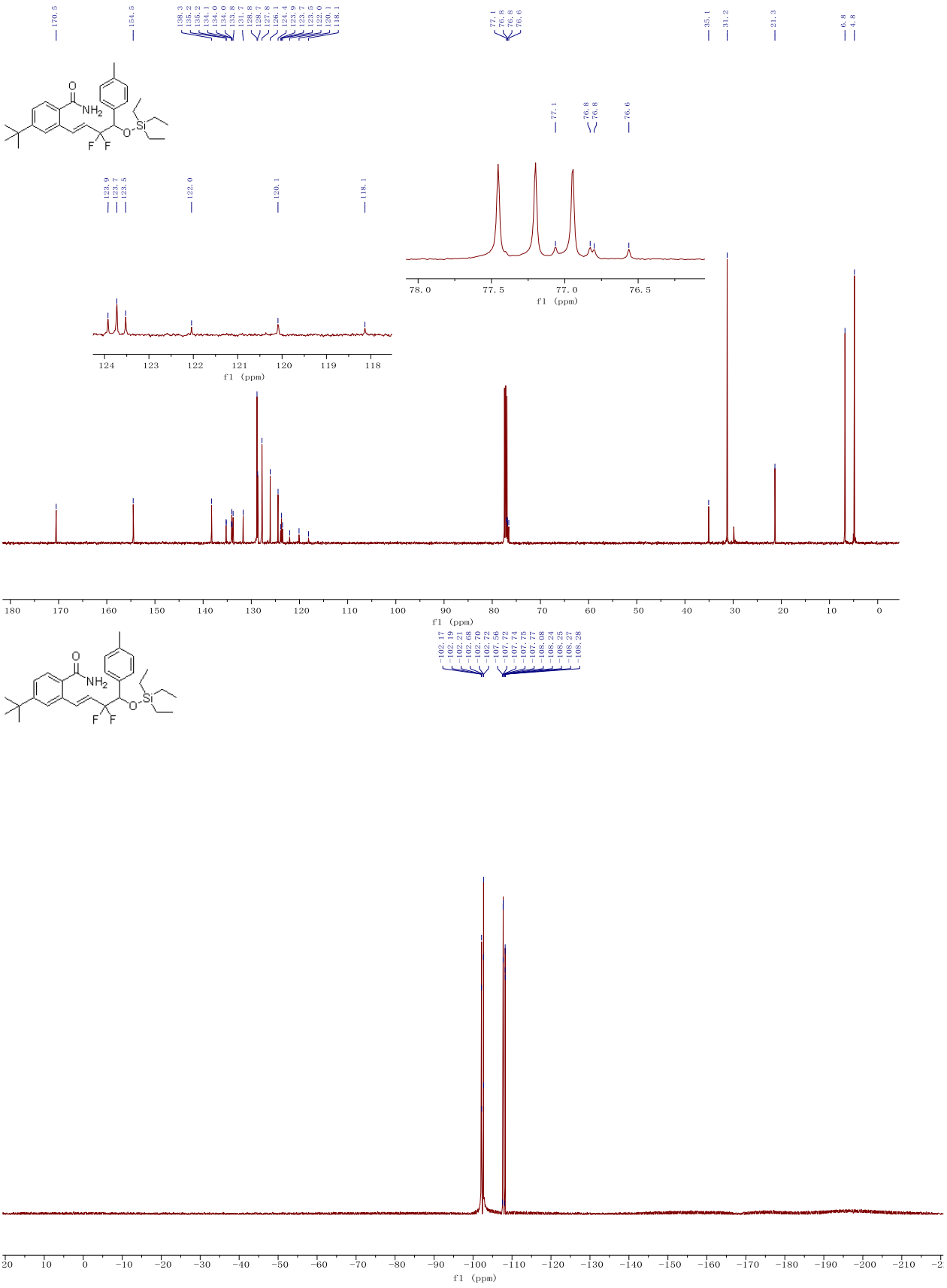






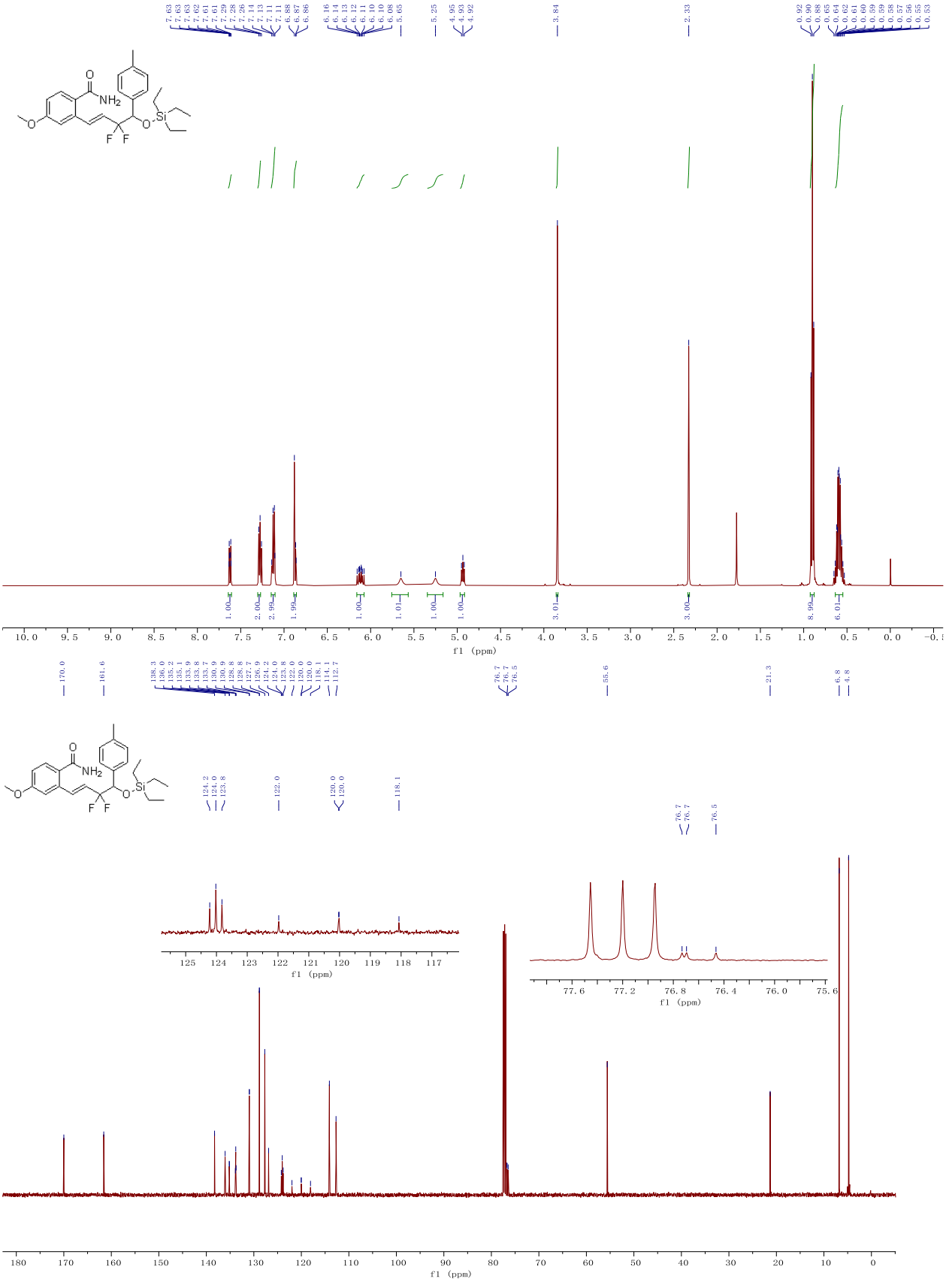
(*E*)-4-(tert-butyl)-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3da)

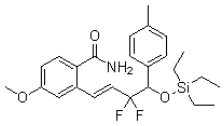


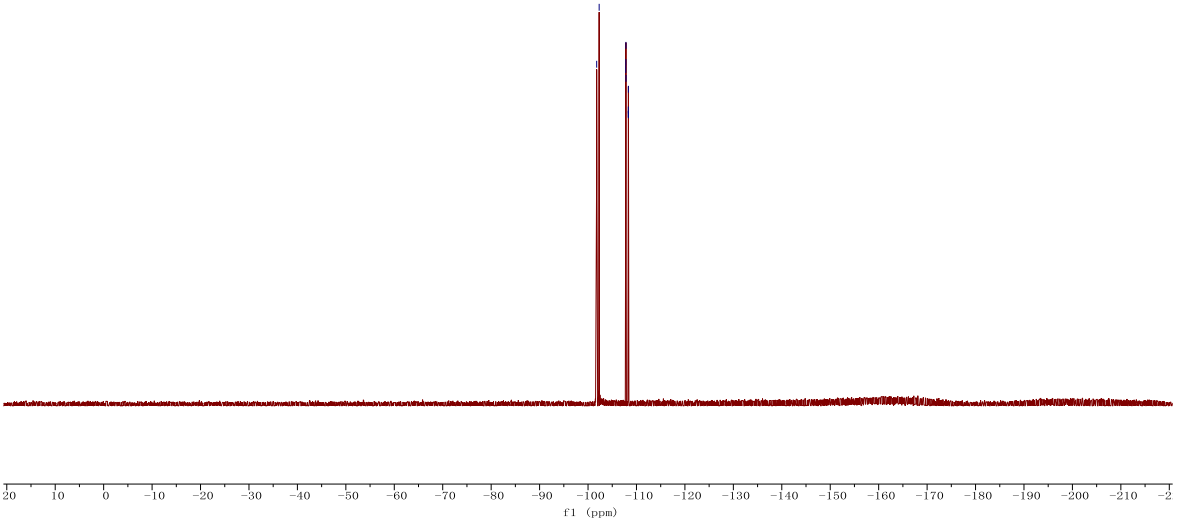

170.5
164.5
138.3
135.2
133.2
134.1
134.0
133.8
131.7
128.8
128.7
127.8
126.1
124.4
123.9
123.7
123.5
122.0
120.1
118.1
77.1
76.8
76.8
76.6
35.1
31.2
21.3
6.8
4.8
O
NH2
Si
F F
f1 (ppm)

-102.17
-102.19
-102.21
-102.68
-102.70
-102.72
-107.56
-107.72
-107.74
-107.75
-107.77
-108.08
-108.24
-108.25
-108.27
-108.28
O
NH2
Si
F F
f1 (ppm)

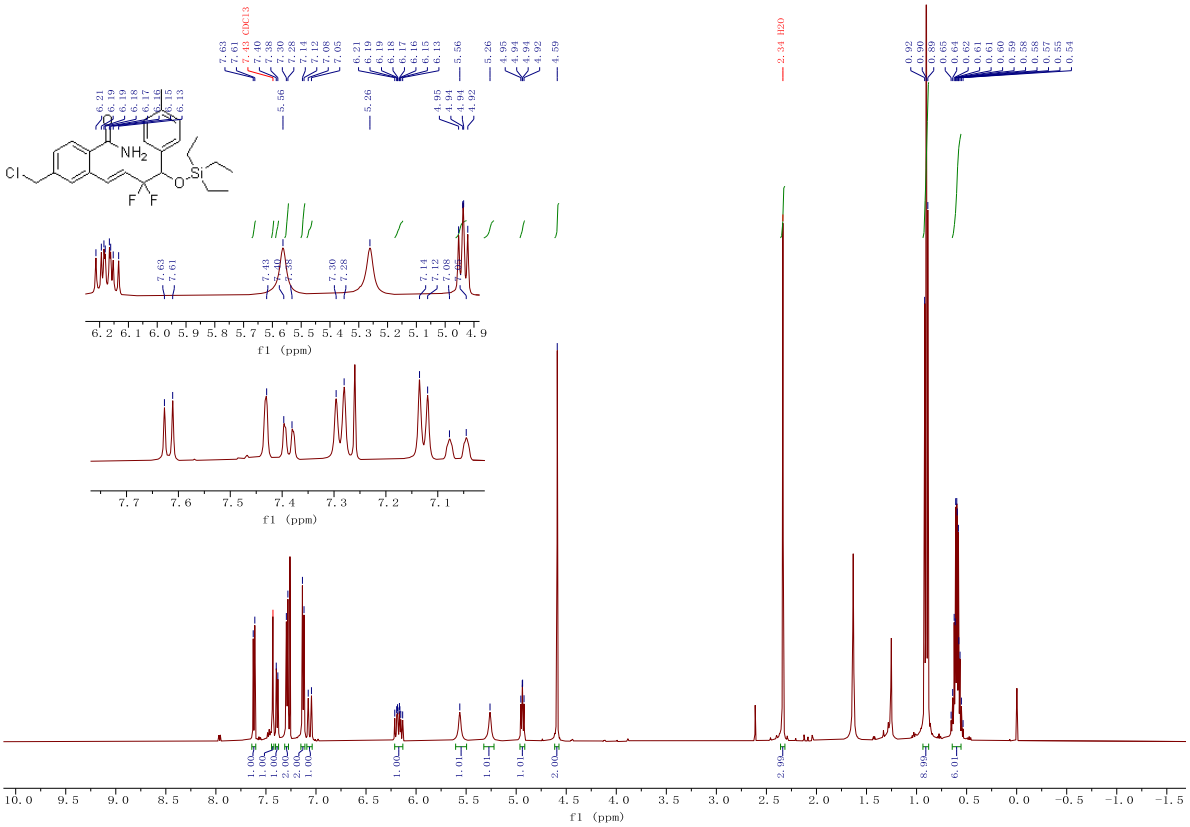
(*E*)-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)-4-methoxybenzamide (3ea)

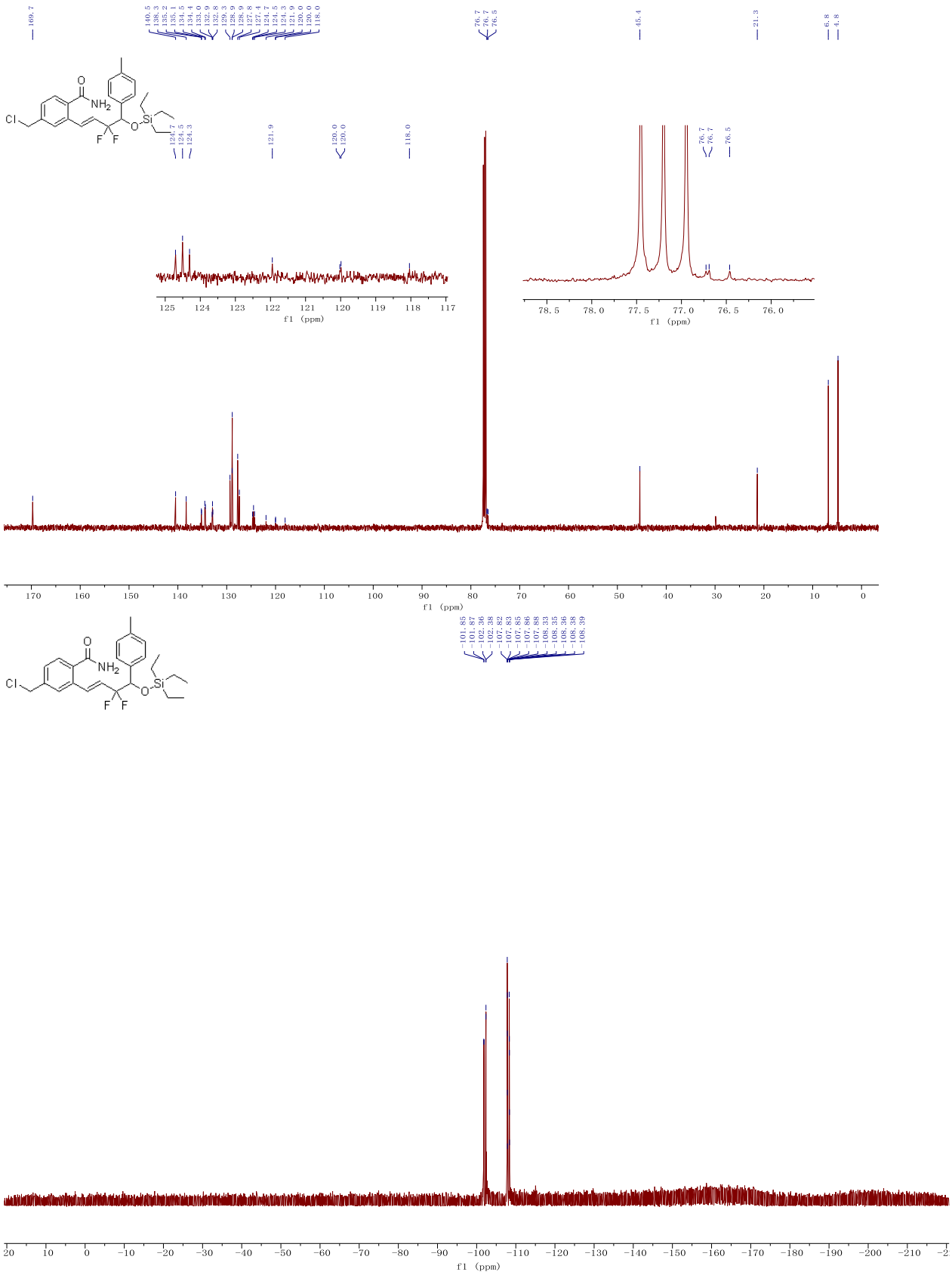




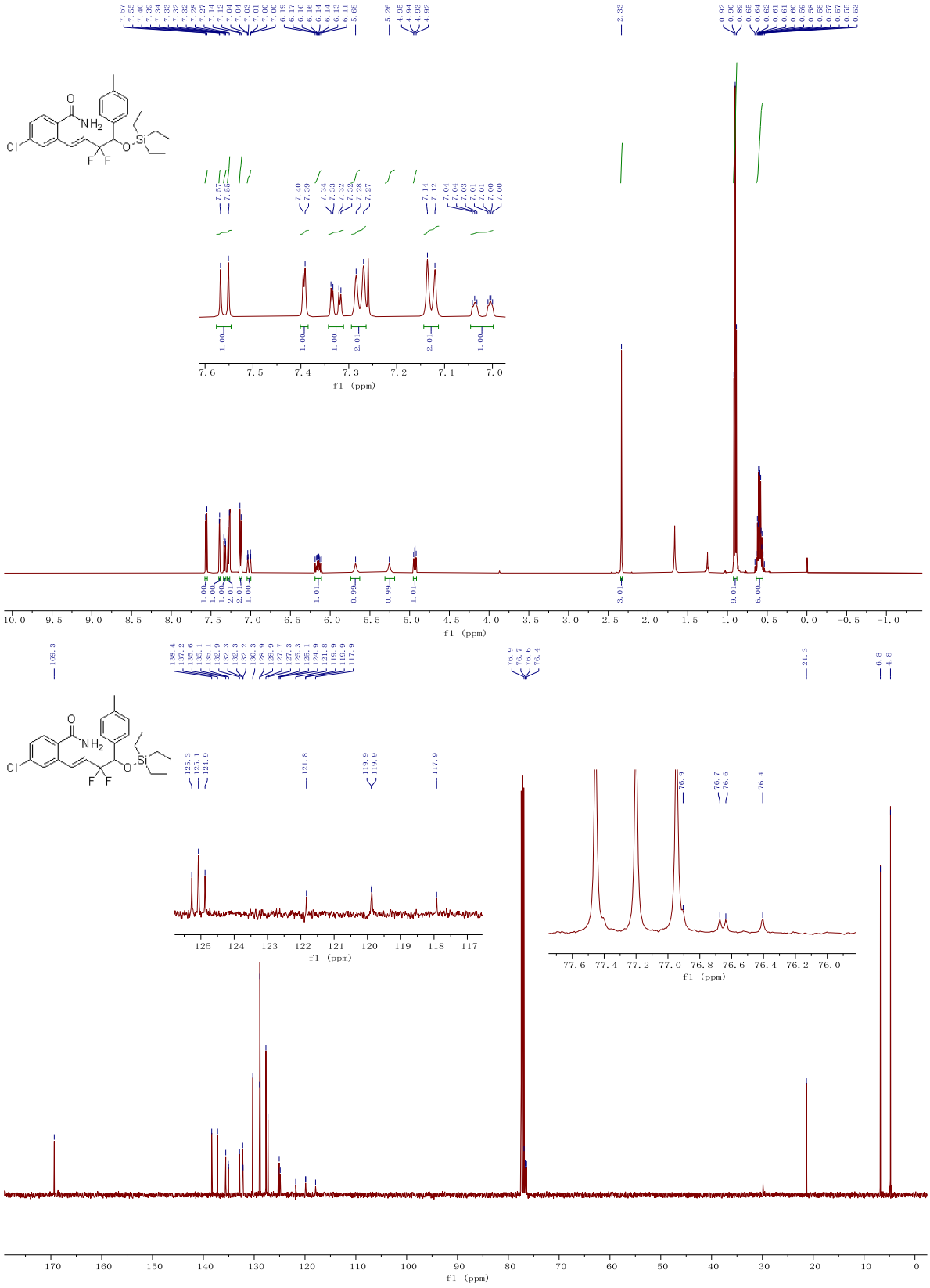


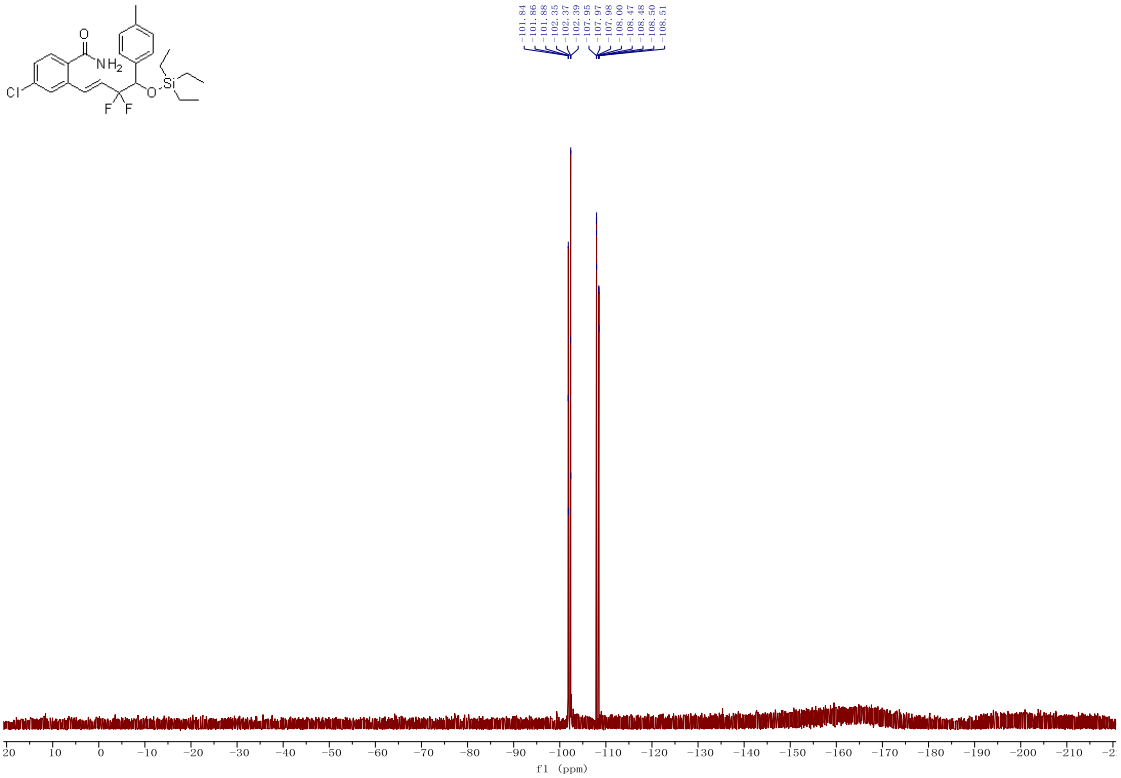
(*E*)-4-chloromethyl-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3fa)



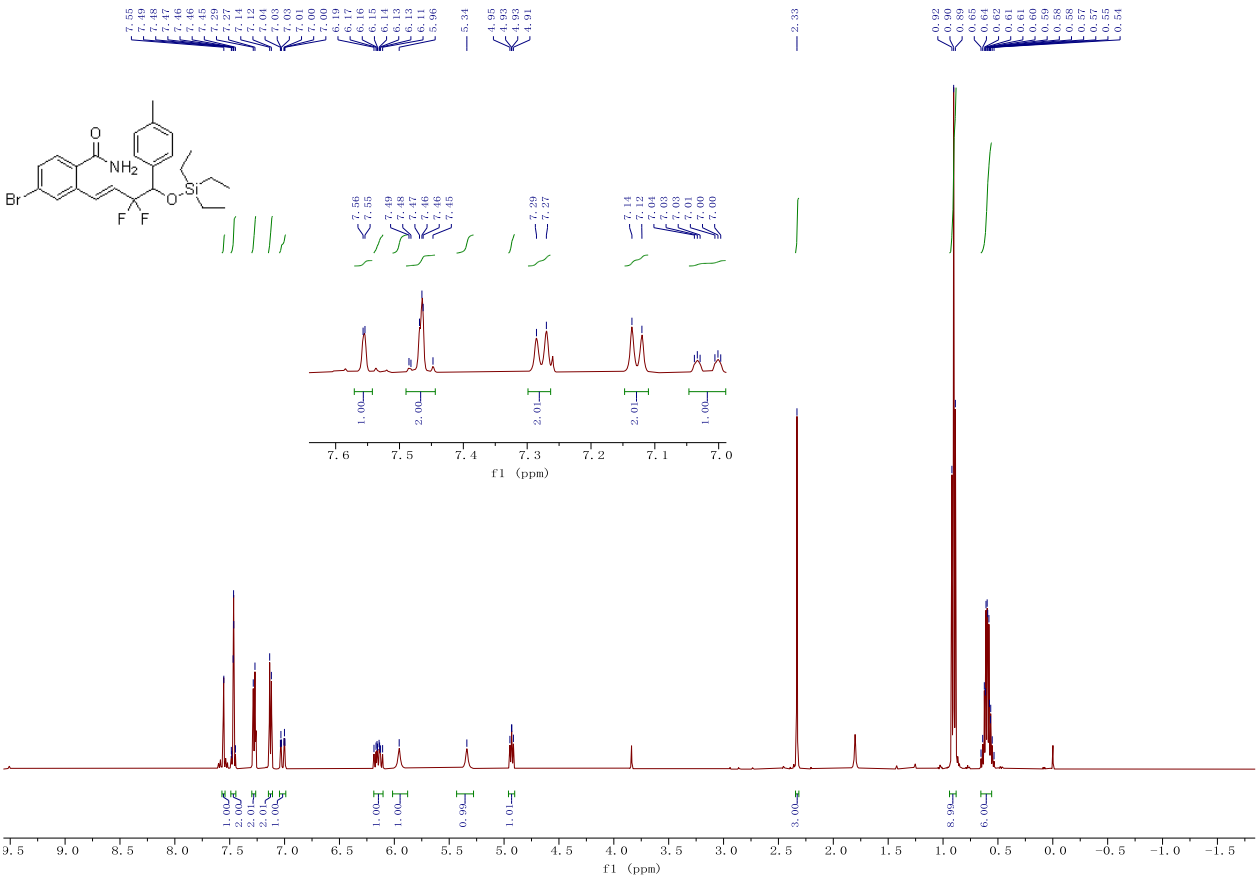

169.7
140.5
138.3
135.2
135.1
134.5
134.4
133.0
132.9
132.8
129.3
128.9
128.9
127.8
127.4
124.7
124.5
124.3
121.9
120.0
120.0
118.0
76.7
76.7
76.5
45.4
21.3
6.8
4.8
Cl
O
NH2
O
Si
F
F
124.7
124.5
124.3
121.9
120.0
120.0
118.0
76.7
76.7
76.5
f1 (ppm)
f1 (ppm)
f1 (ppm)
-101.85
-101.87
-102.36
-102.38
-107.82
-107.83
-107.85
-107.86
-107.88
-108.33
-108.35
-108.36
-108.38
-108.39
f1 (ppm)

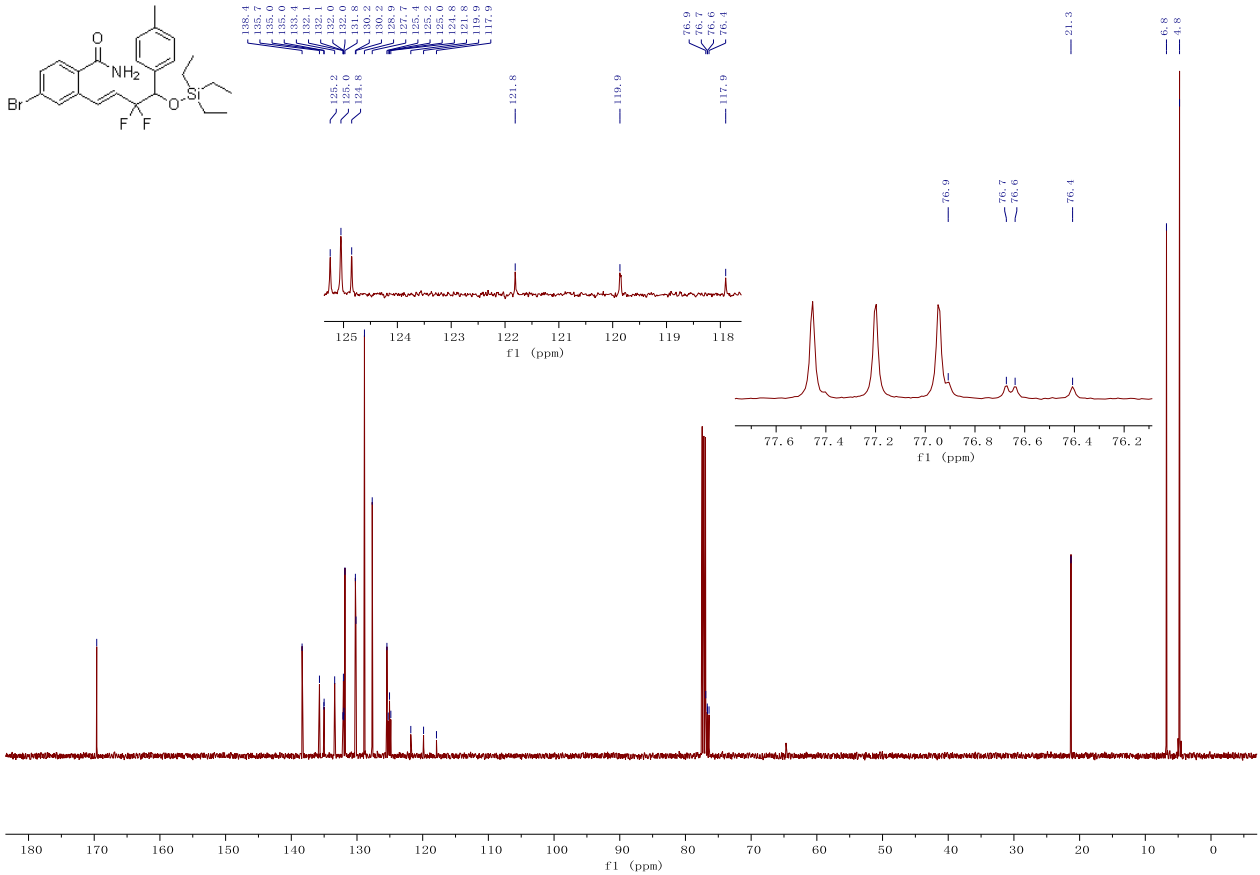
(*E*)-4-chloro-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3ga)

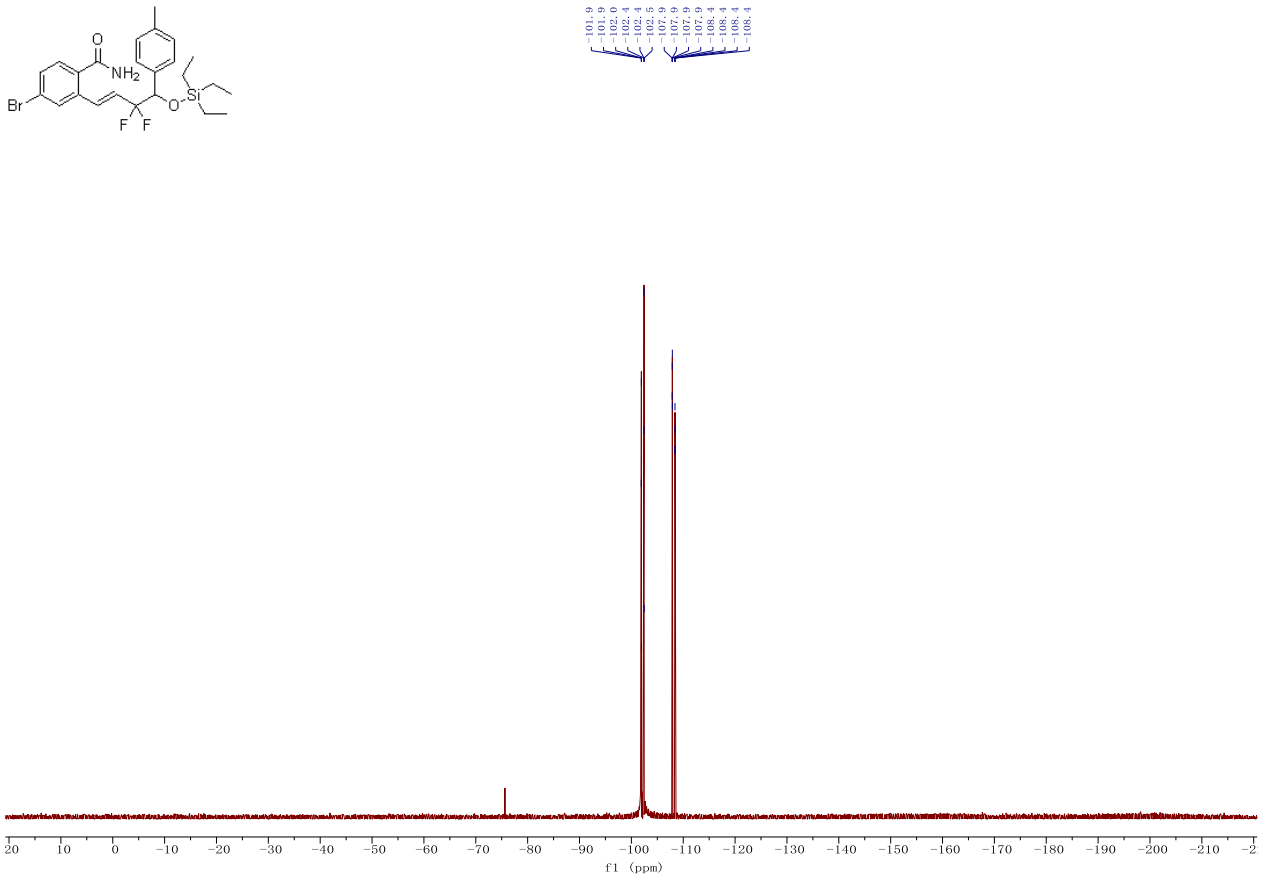




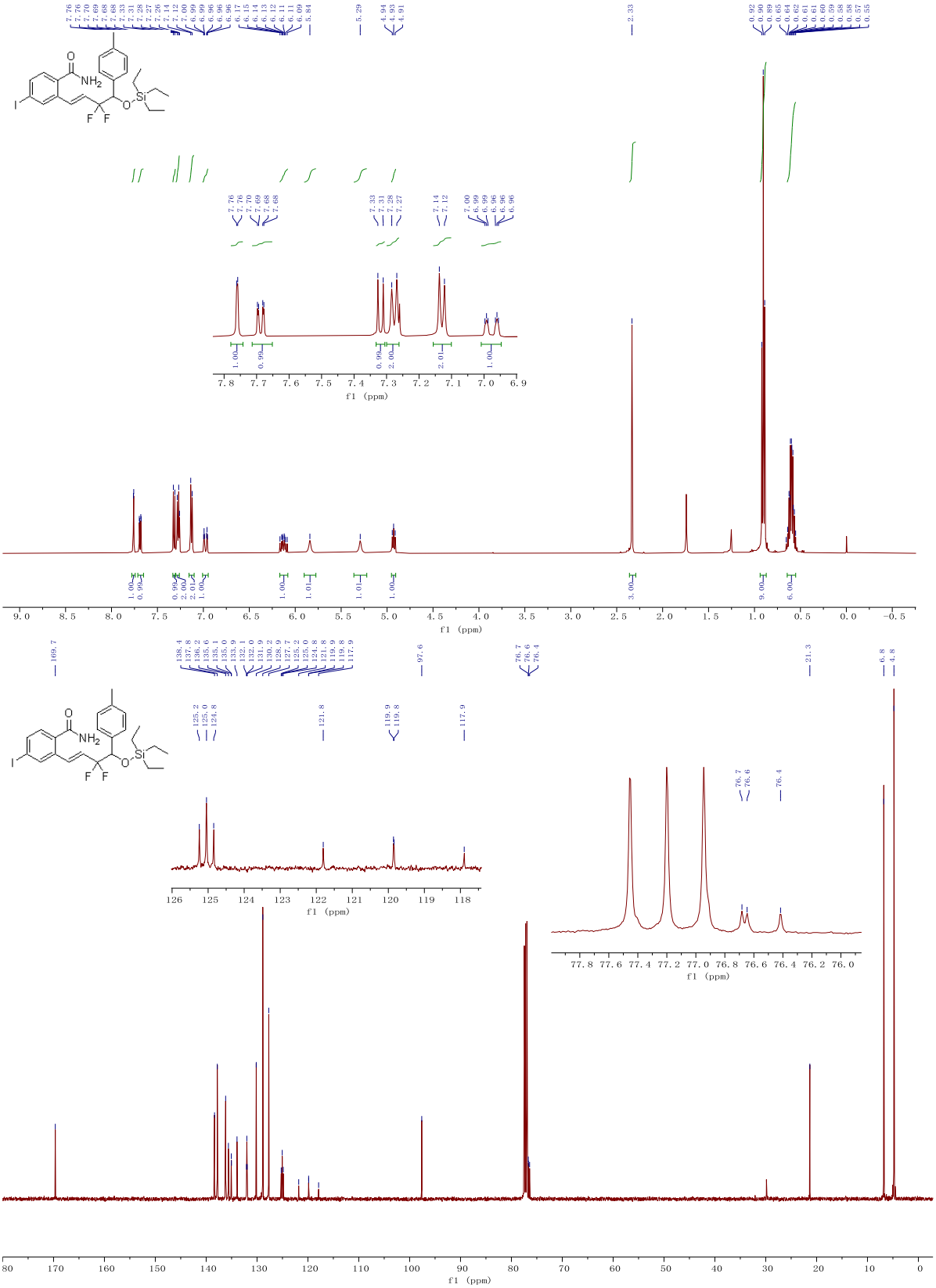
(*E*)-4-bromo-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3ha)

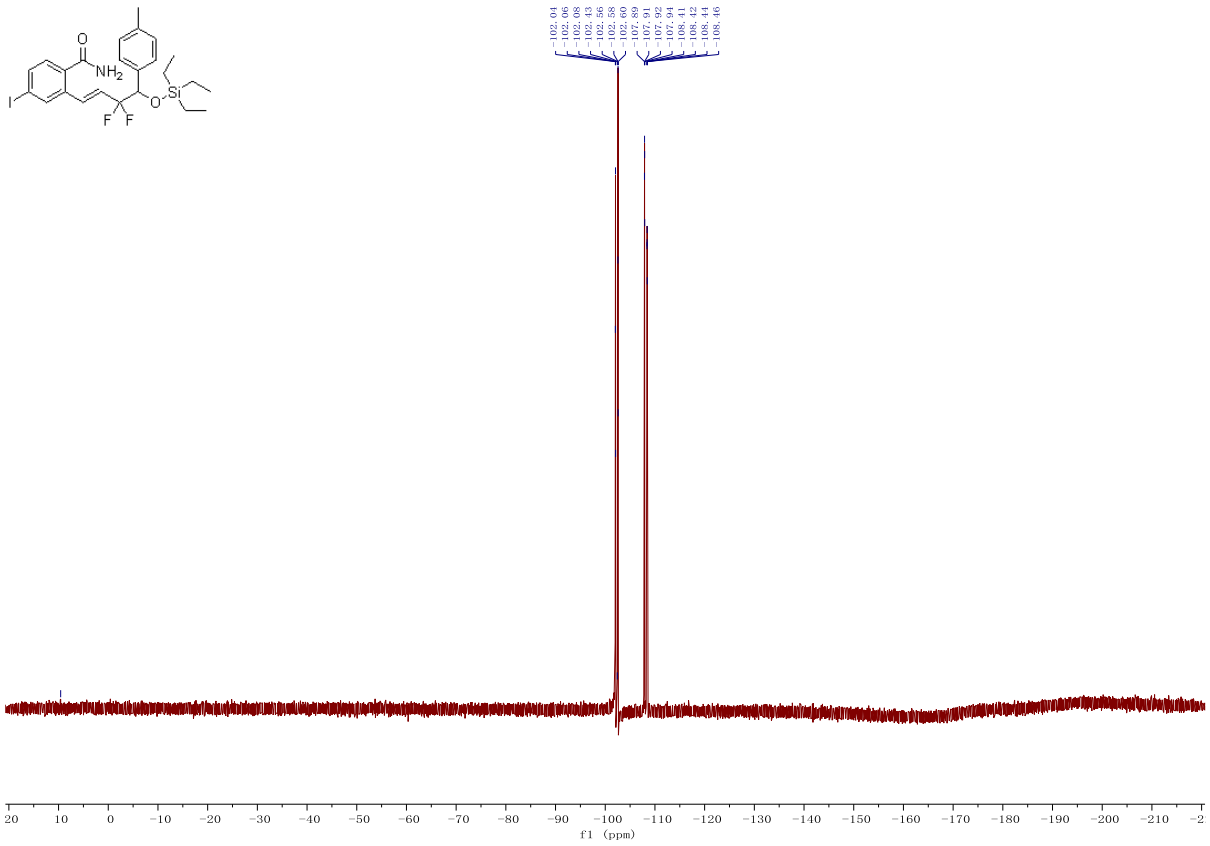



Br
O
NH2
F F
O
Si
f1 (ppm)

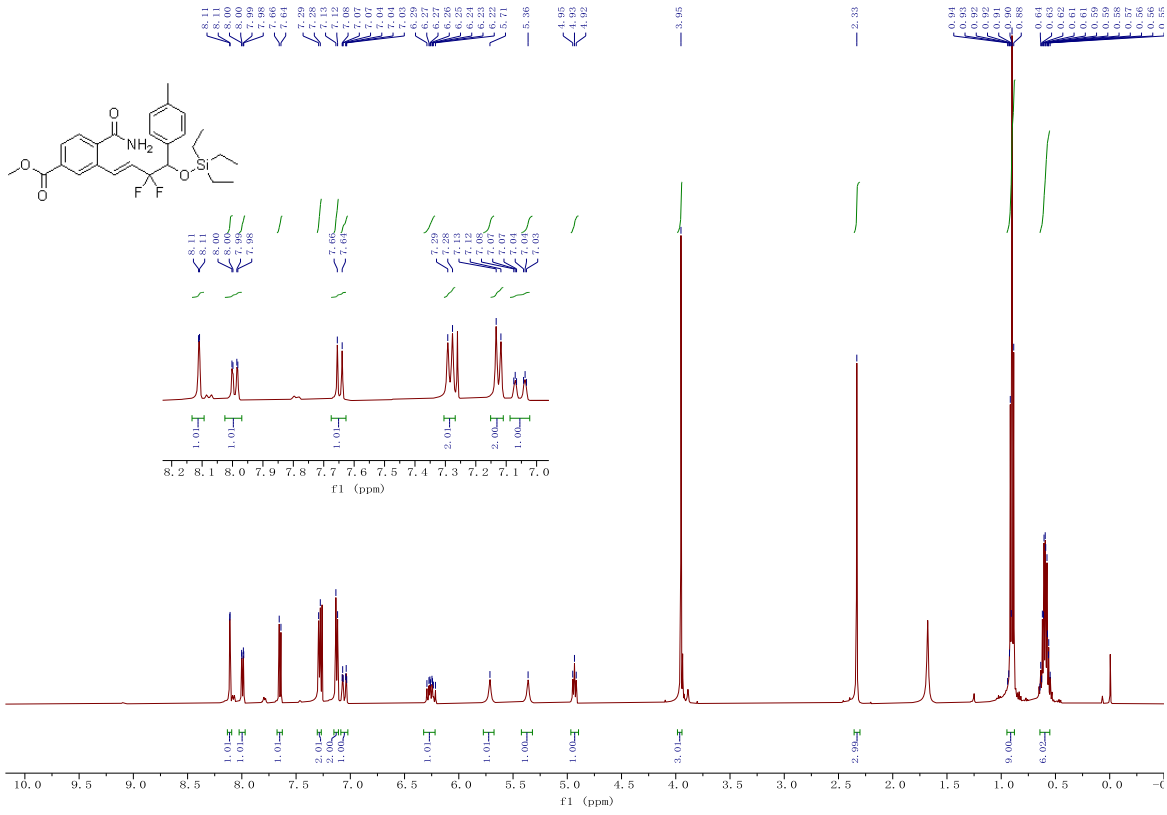

Br
O
NH2
F F
O
Si
f1 (ppm)

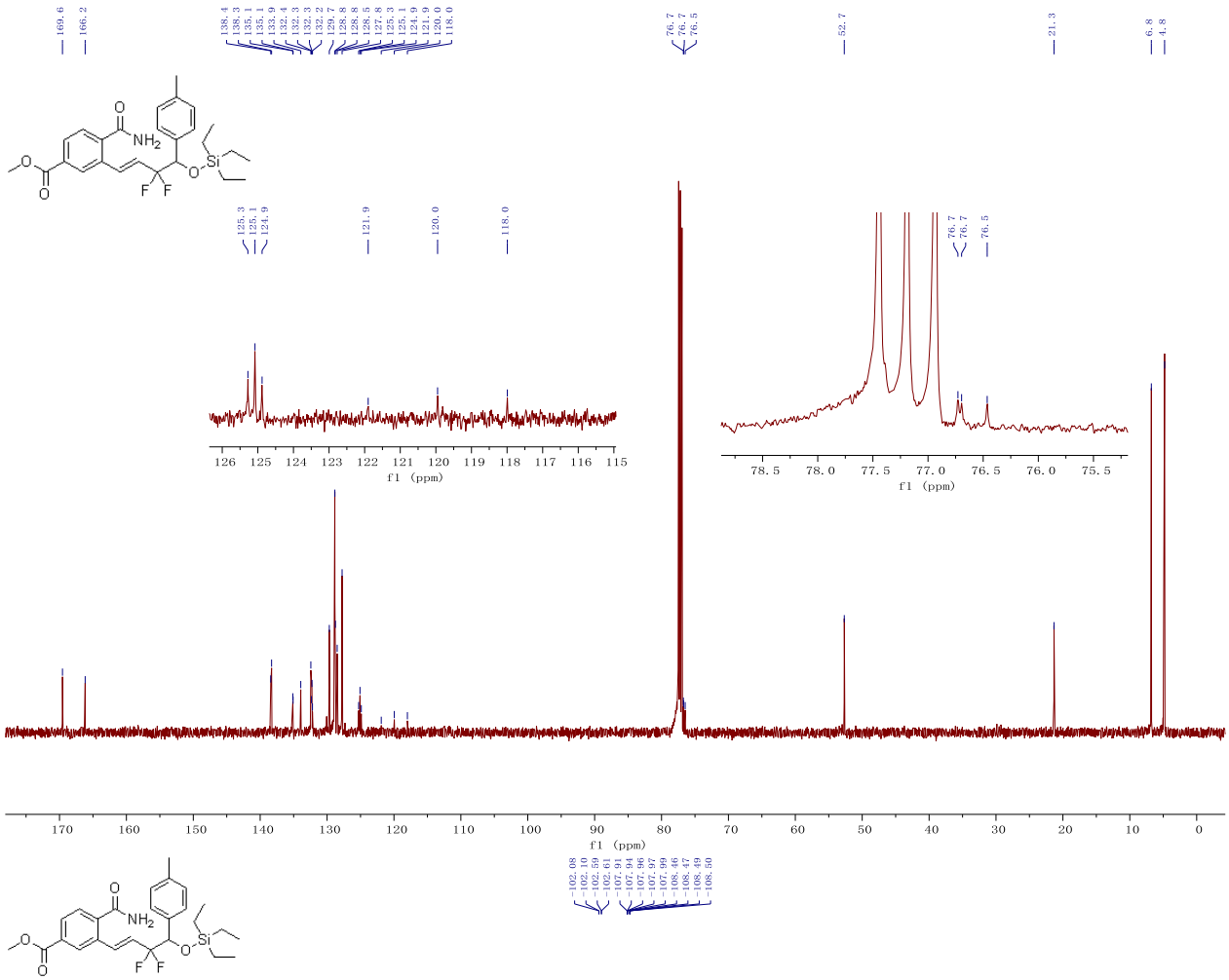
(*E*)-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)-4-iodobenzamide (3ia)

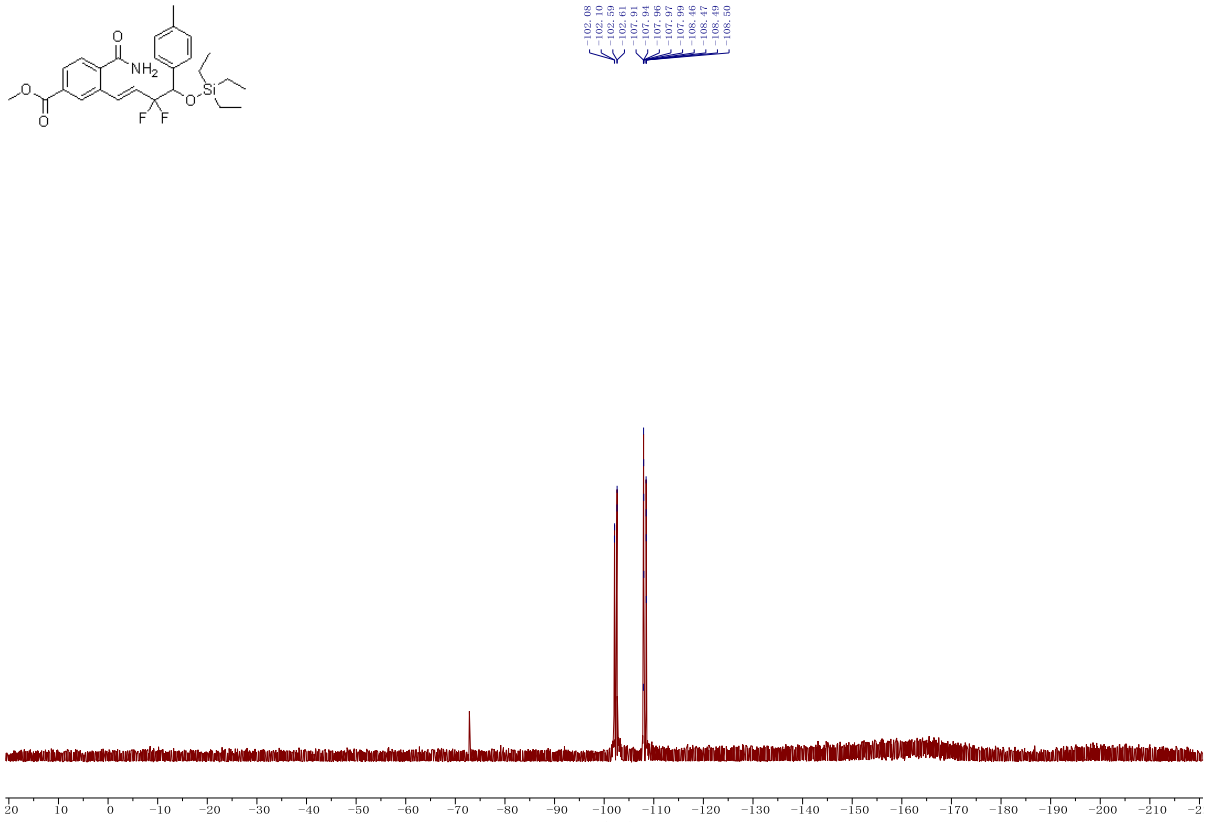




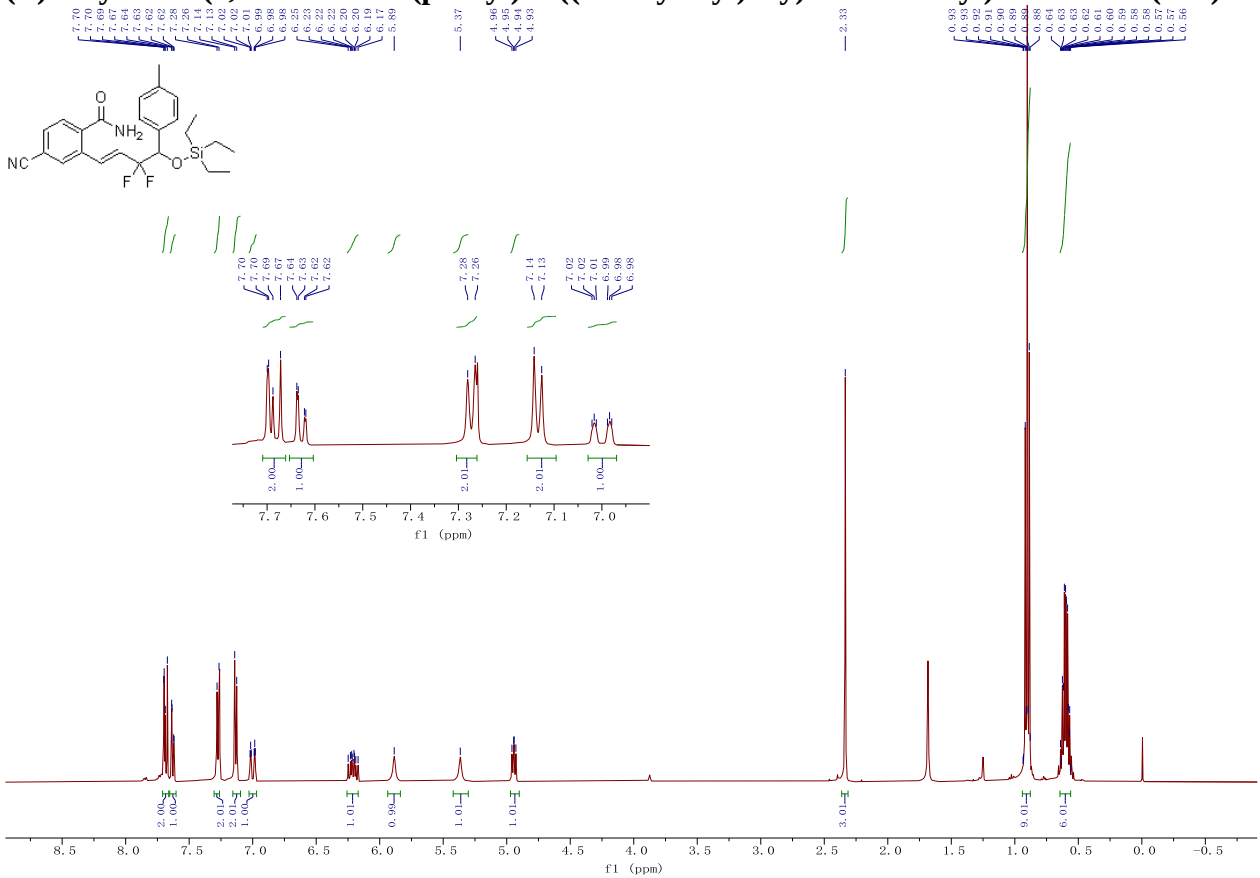
Methyl (*E*)-4-carbamoyl-3-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl) benzoate (3ja)

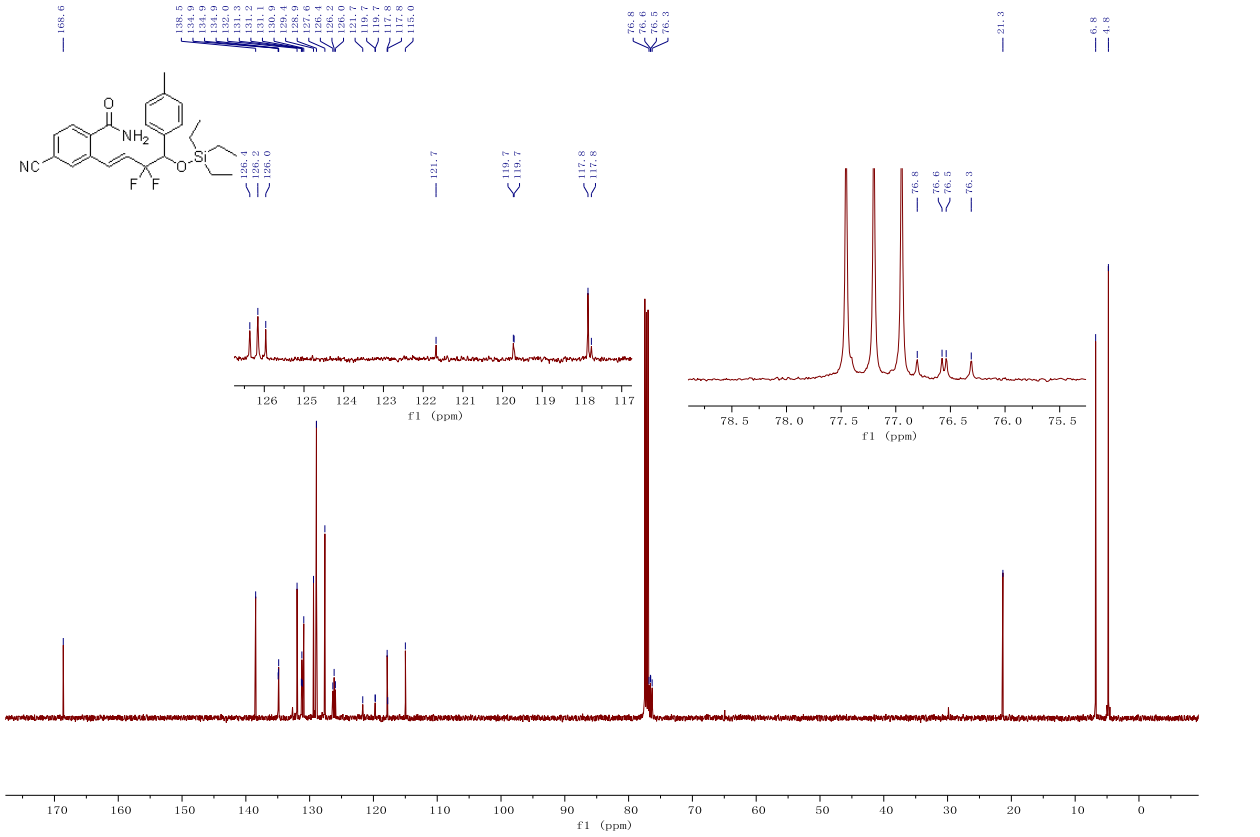


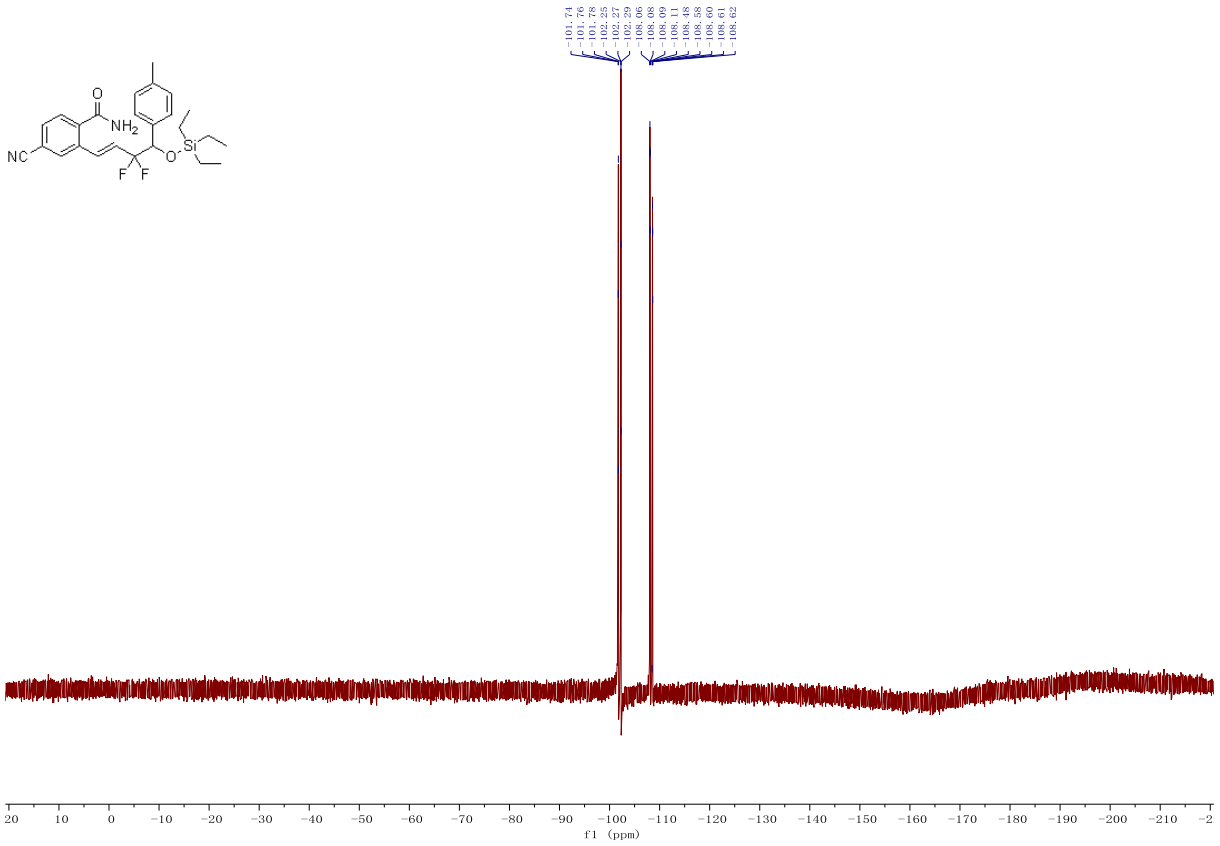

169.6
166.2
138.4
138.3
135.1
135.1
133.9
132.4
132.3
132.3
132.2
129.7
128.8
128.8
128.5
127.8
125.3
125.1
124.9
121.9
120.0
118.0
76.7
76.7
76.5
52.7
21.3
6.8
4.8
O
NH2
O
O
Si
F F
125.3
125.1
124.9
121.9
120.0
118.0
126 125 124 123 122 121 120 119 118 117 116 115
f1 (ppm)
76.7
76.7
76.5
78.5 78.0 77.5 77.0 76.5 76.0 75.5
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-102.08
-102.10
-102.59
-102.61
-107.91
-107.94
-107.96
-107.98
-107.99
-108.46
-108.47
-108.49
-108.50
O
NH2
O
O
Si
F F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

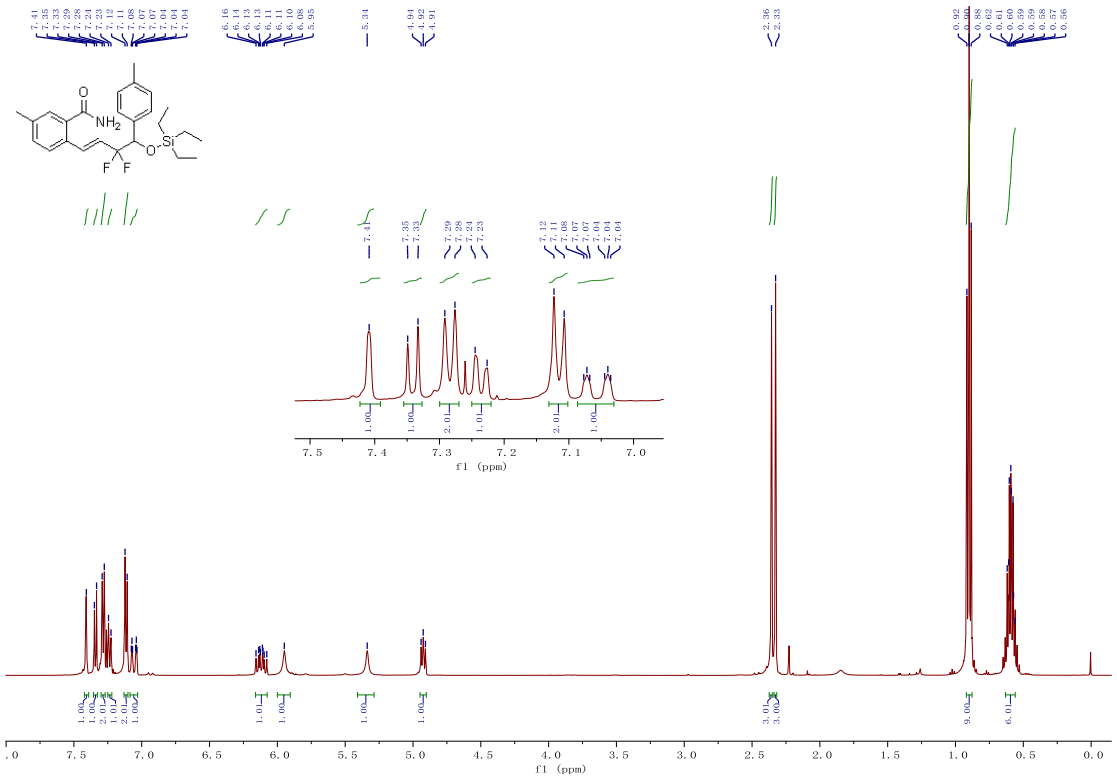
(*E*)-4-cyano-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3ka)

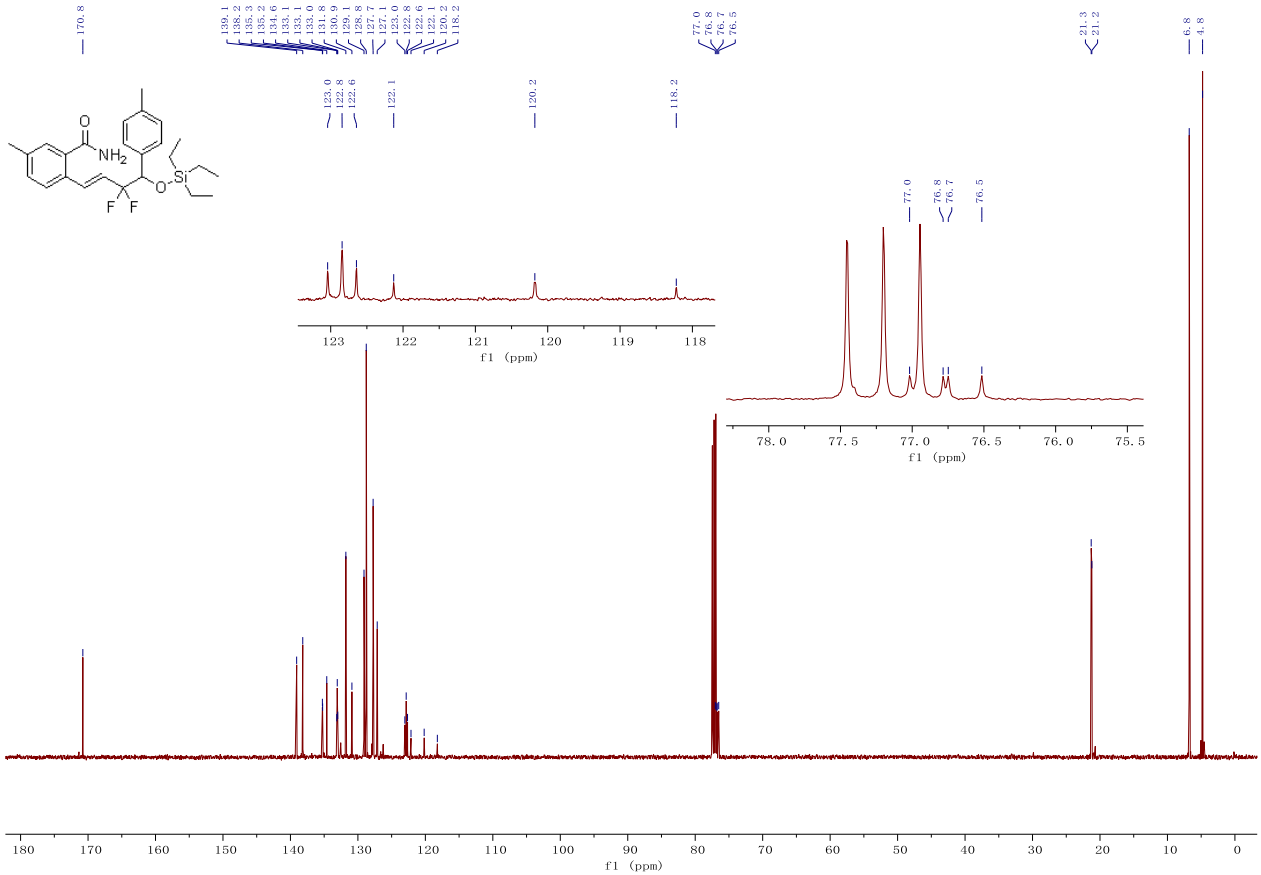


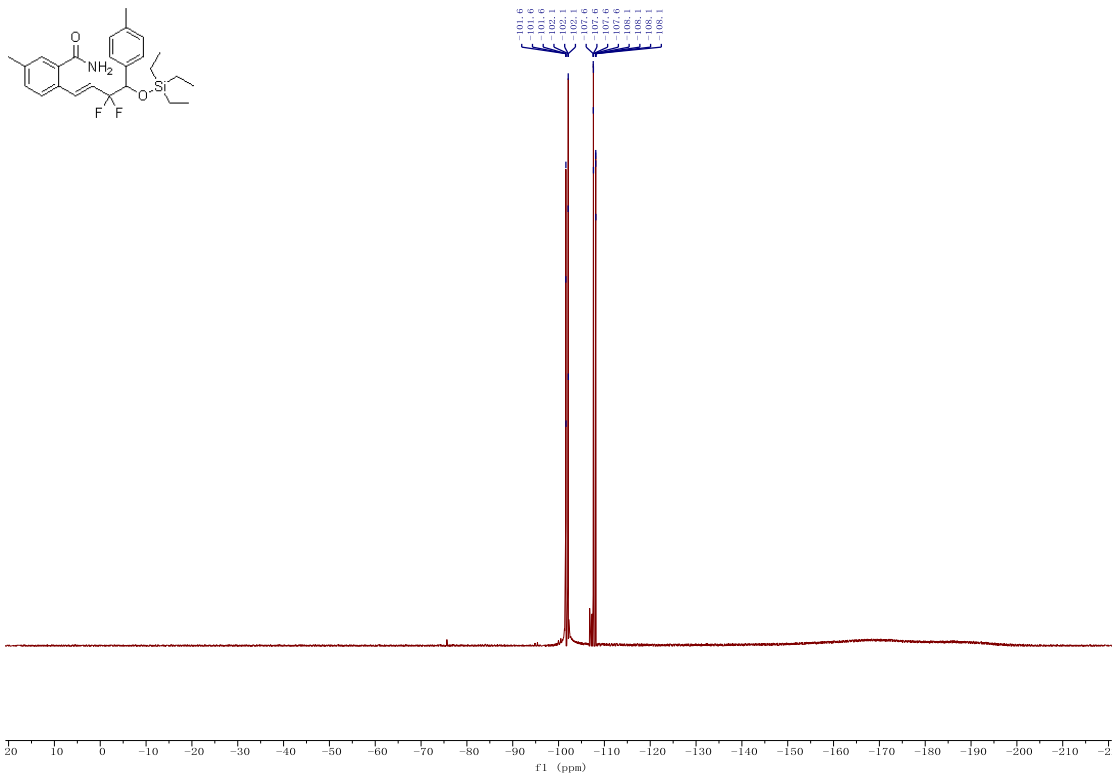




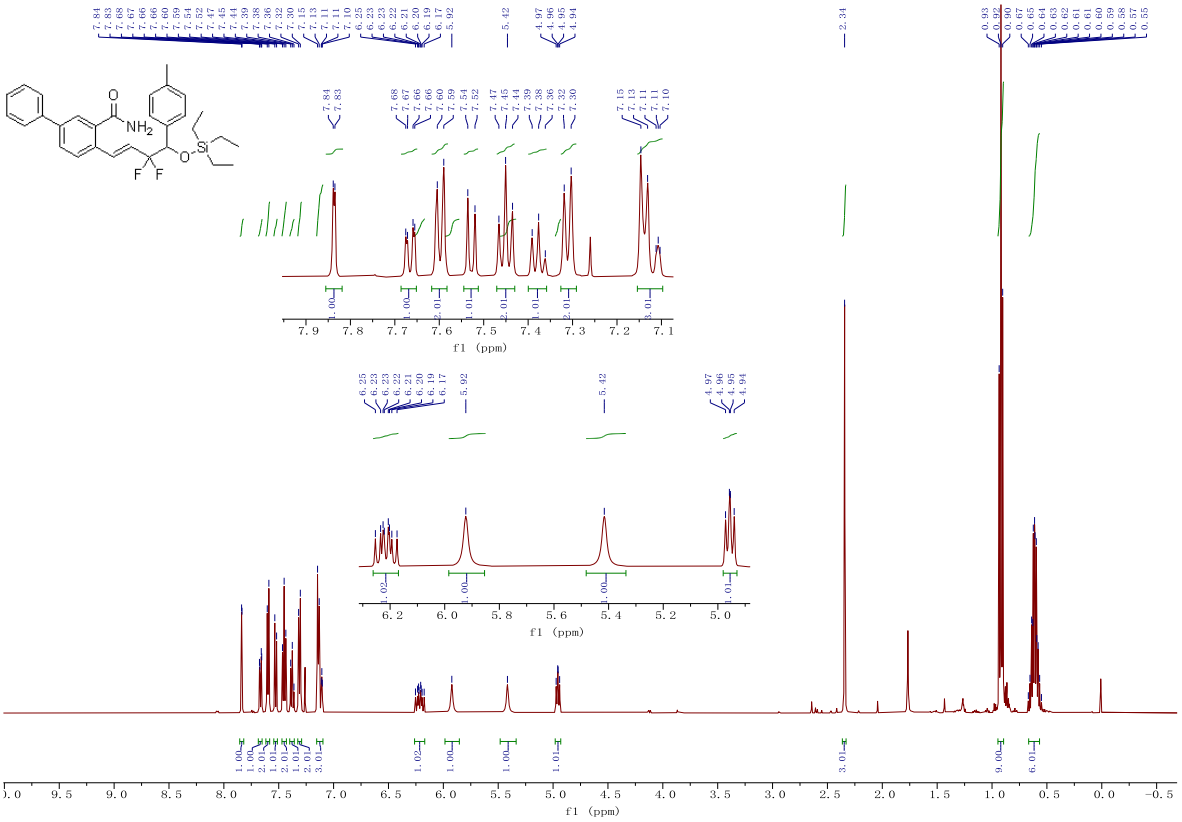
(*E*)-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)-5-methyl benzamide (3la)

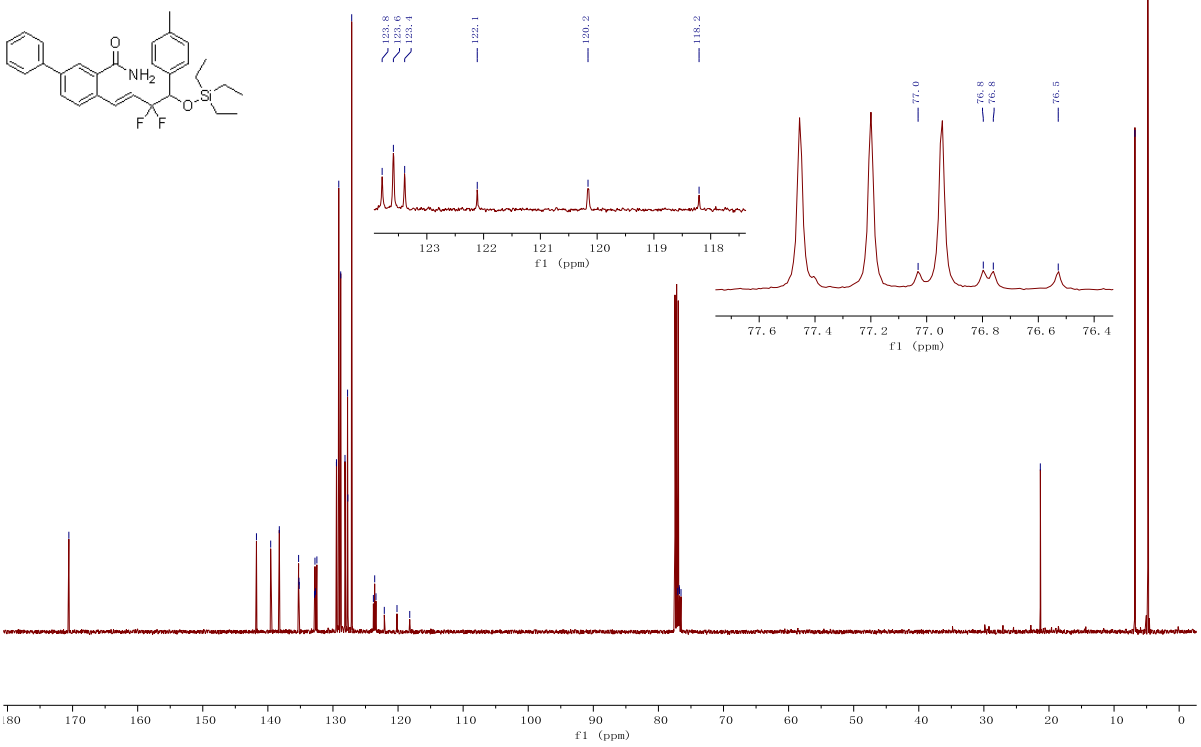


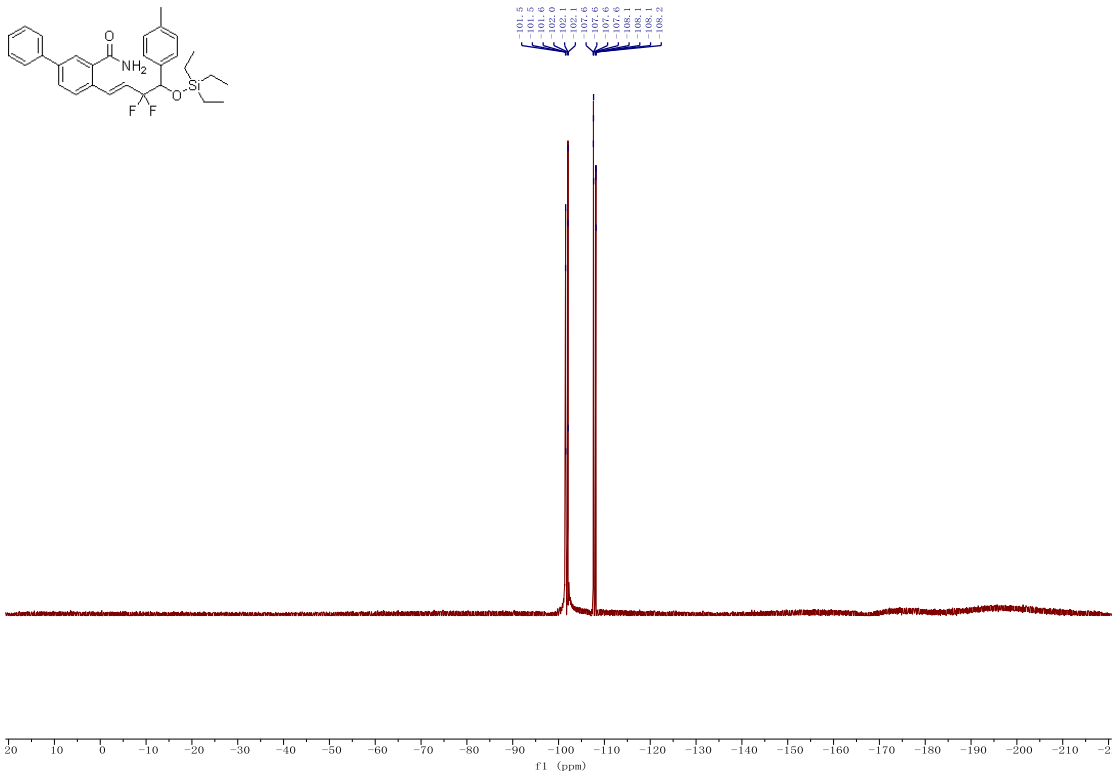

170.8
139.1
138.2
135.3
135.2
134.6
133.1
133.0
131.8
130.9
129.1
128.8
127.7
127.1
123.0
122.8
122.6
122.1
120.2
118.2
77.0
76.8
76.7
76.5
21.3
21.2
6.8
4.8
O
NH2
Si
F F
f1 (ppm)


-101.6
-101.6
-101.6
-102.1
-102.1
-102.1
-107.6
-107.6
-107.6
-107.6
-108.1
-108.1
-108.1
-108.1
O
NH2
Si
F F
f1 (ppm)

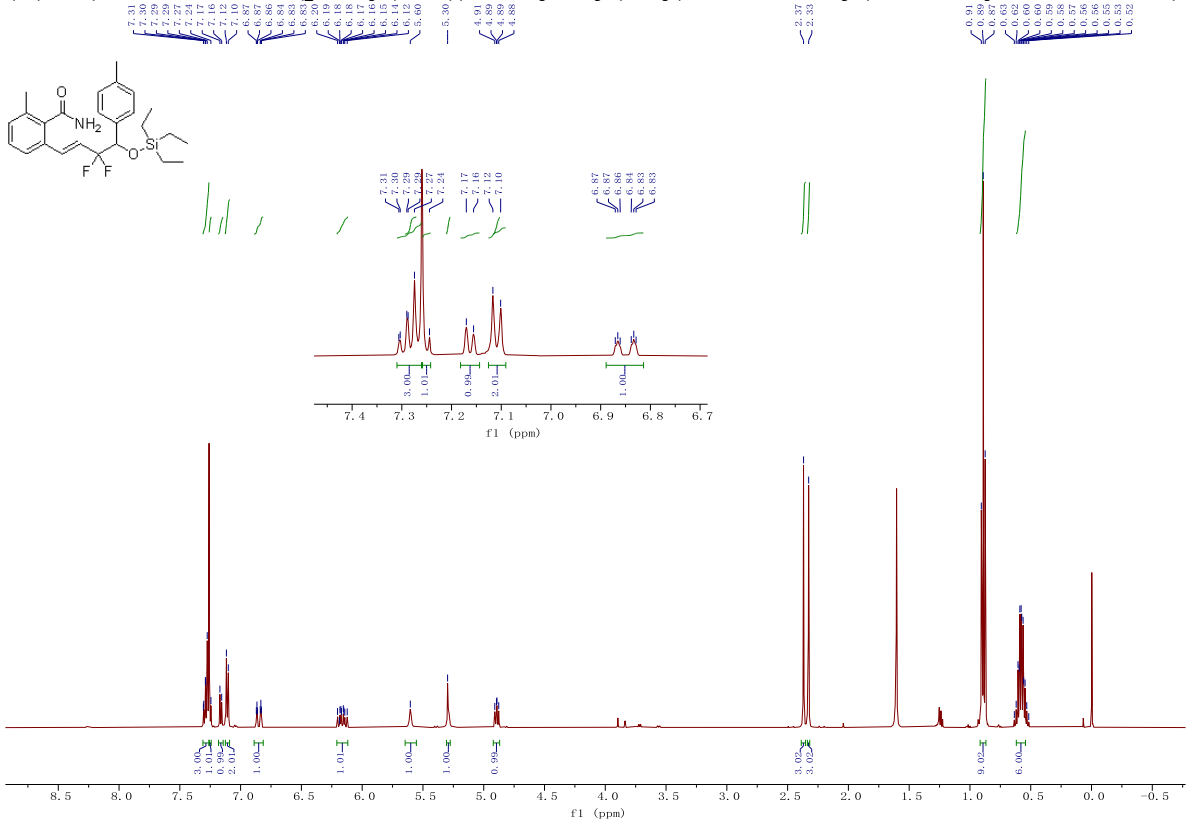
(*E*)-4-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)-[1,1'-biphenyl]-3-carboxamide (3ma)

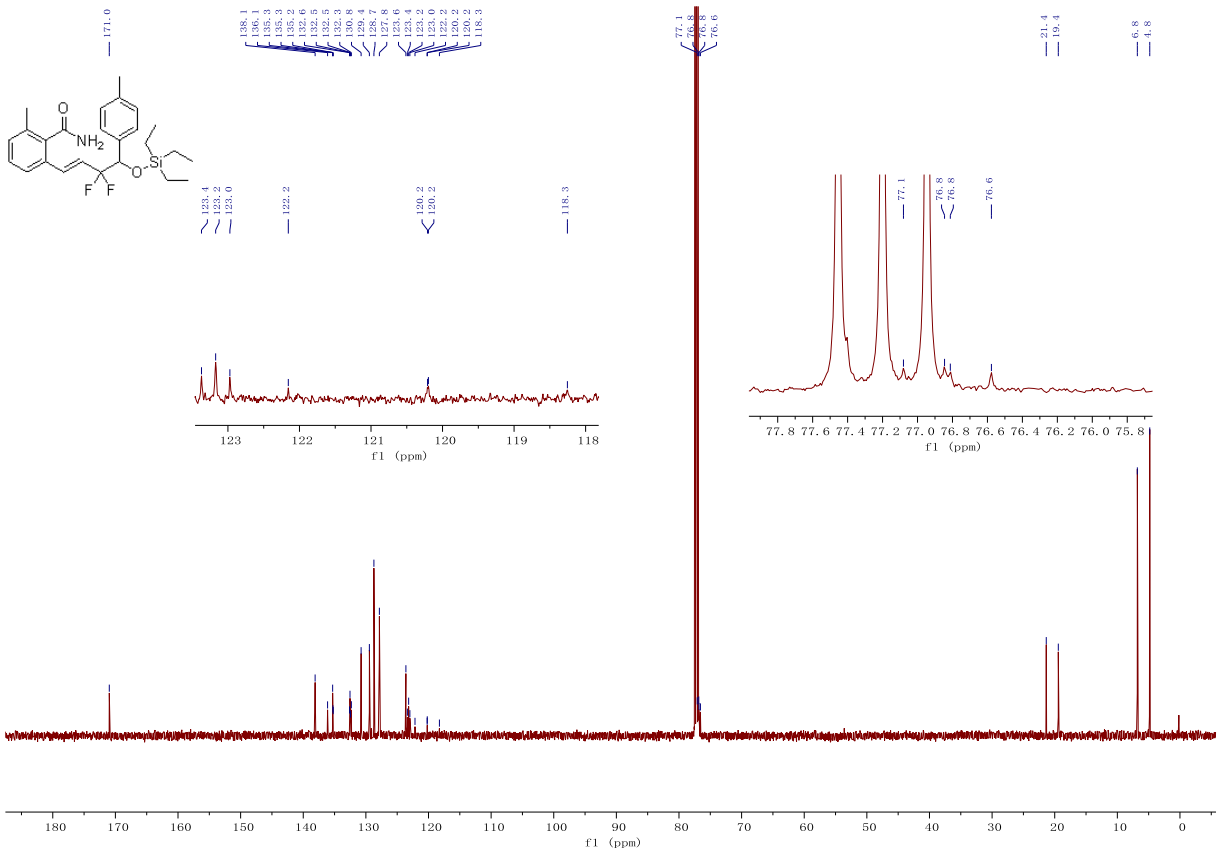


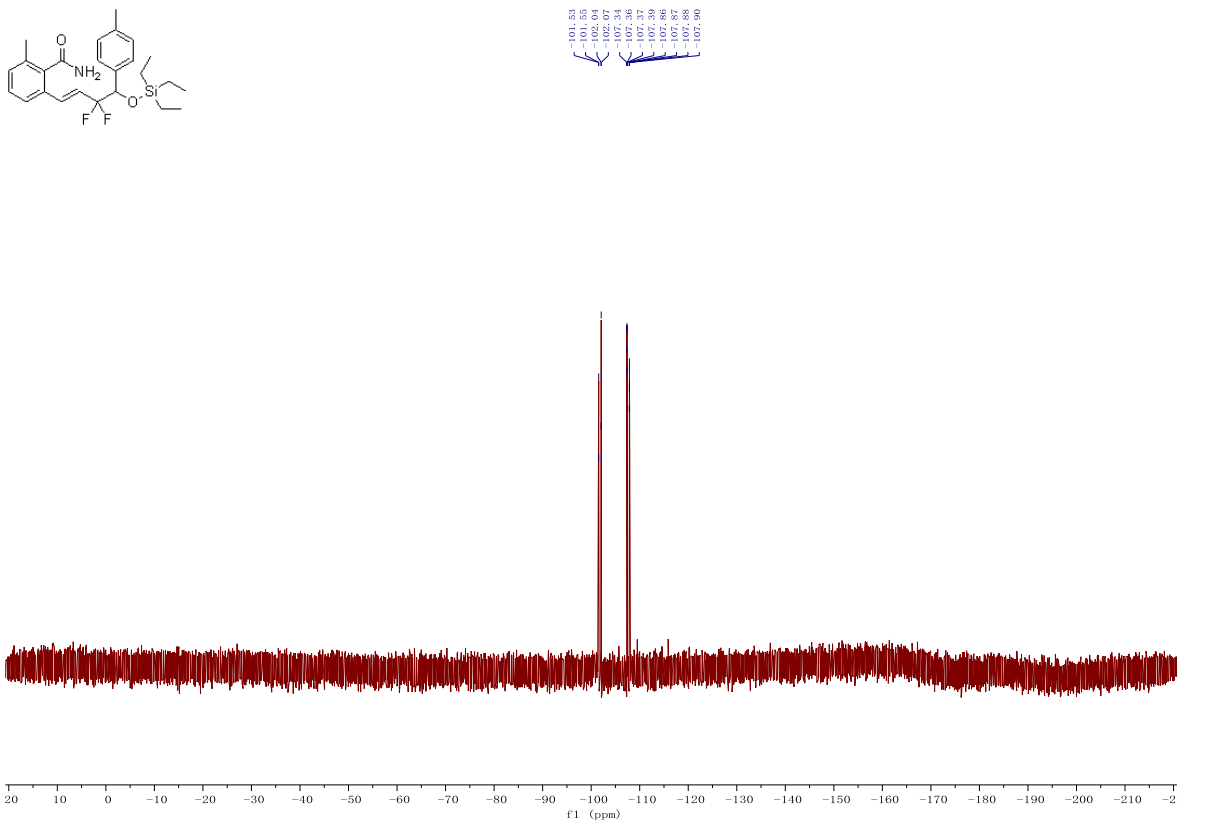




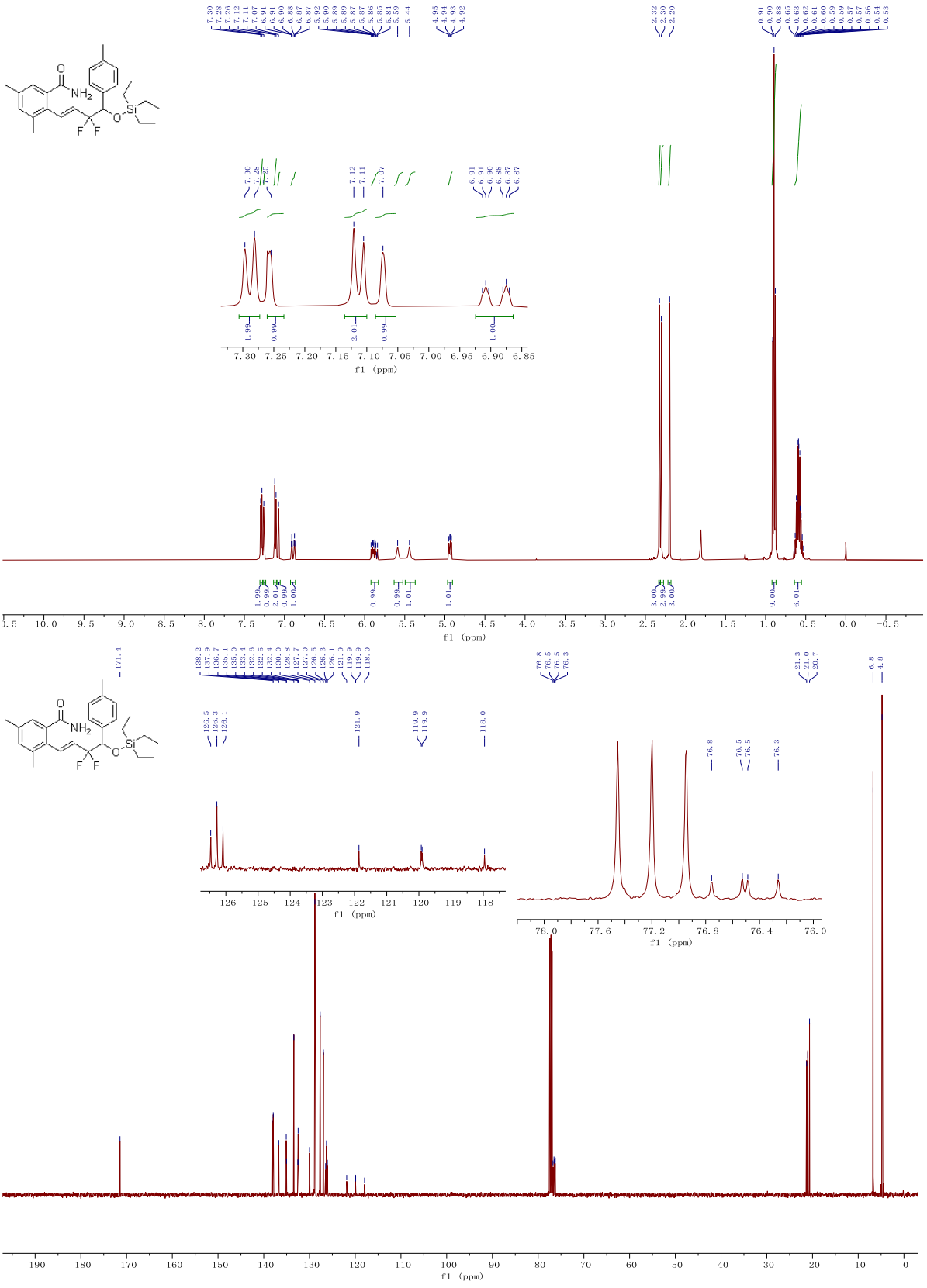
(*E*)-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)-6-methylbenzamide (3na)

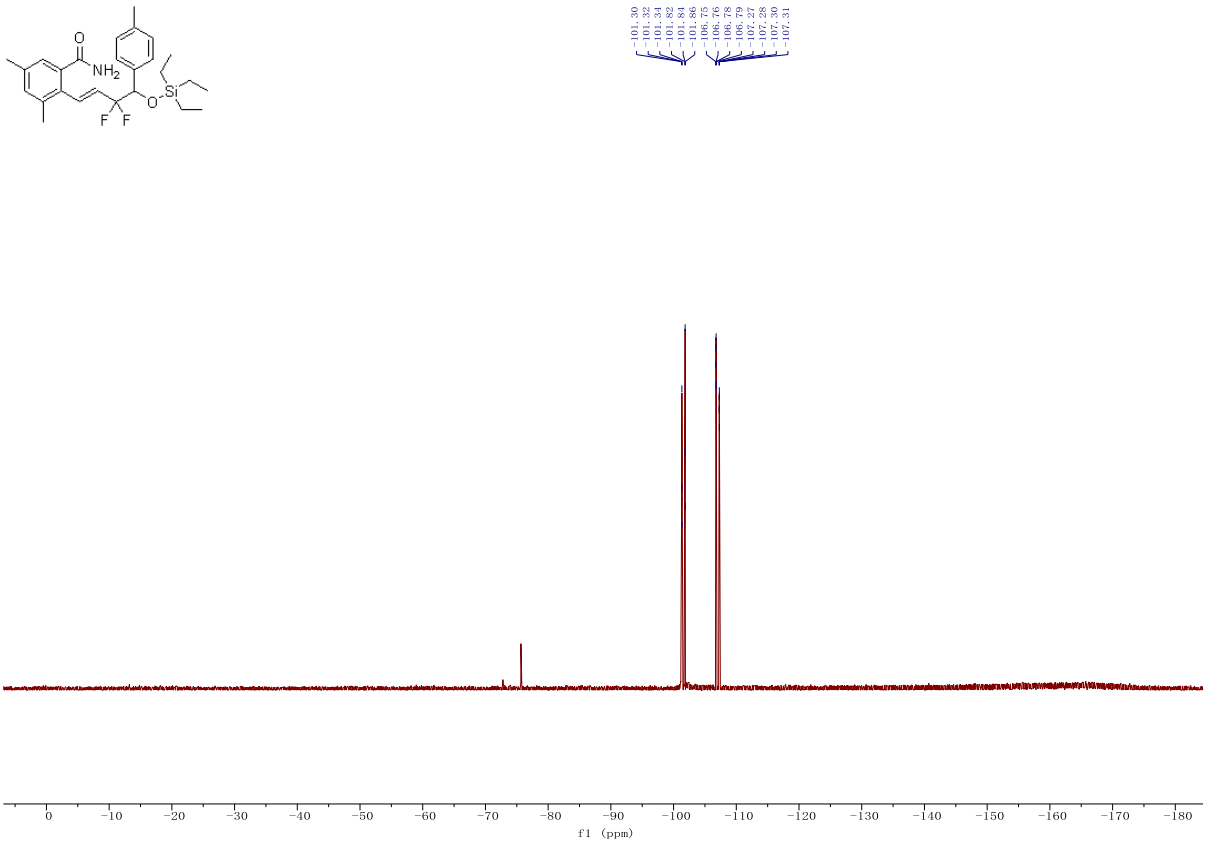



171.0
138.1
136.1
135.3
135.2
132.6
132.5
132.3
130.8
129.4
128.7
127.8
123.6
123.4
123.2
123.0
122.2
120.2
120.2
118.3
77.1
76.8
76.6
21.4
19.4
6.8
4.8
f1 (ppm)

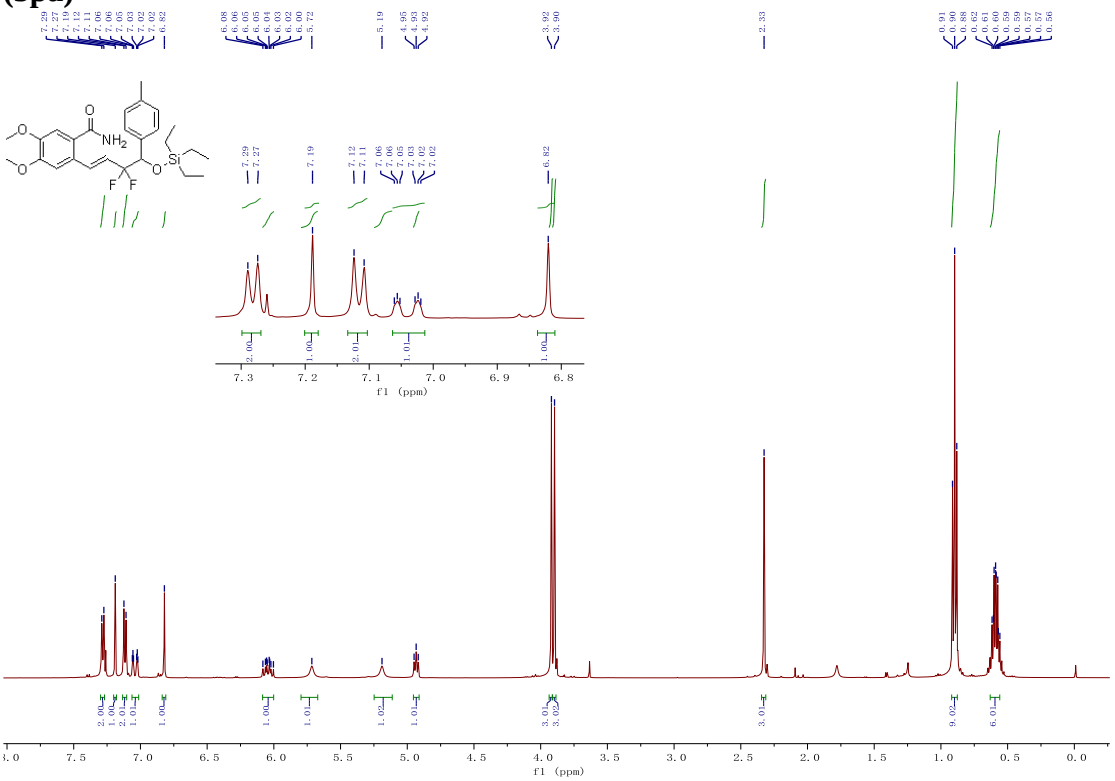

f1 (ppm)

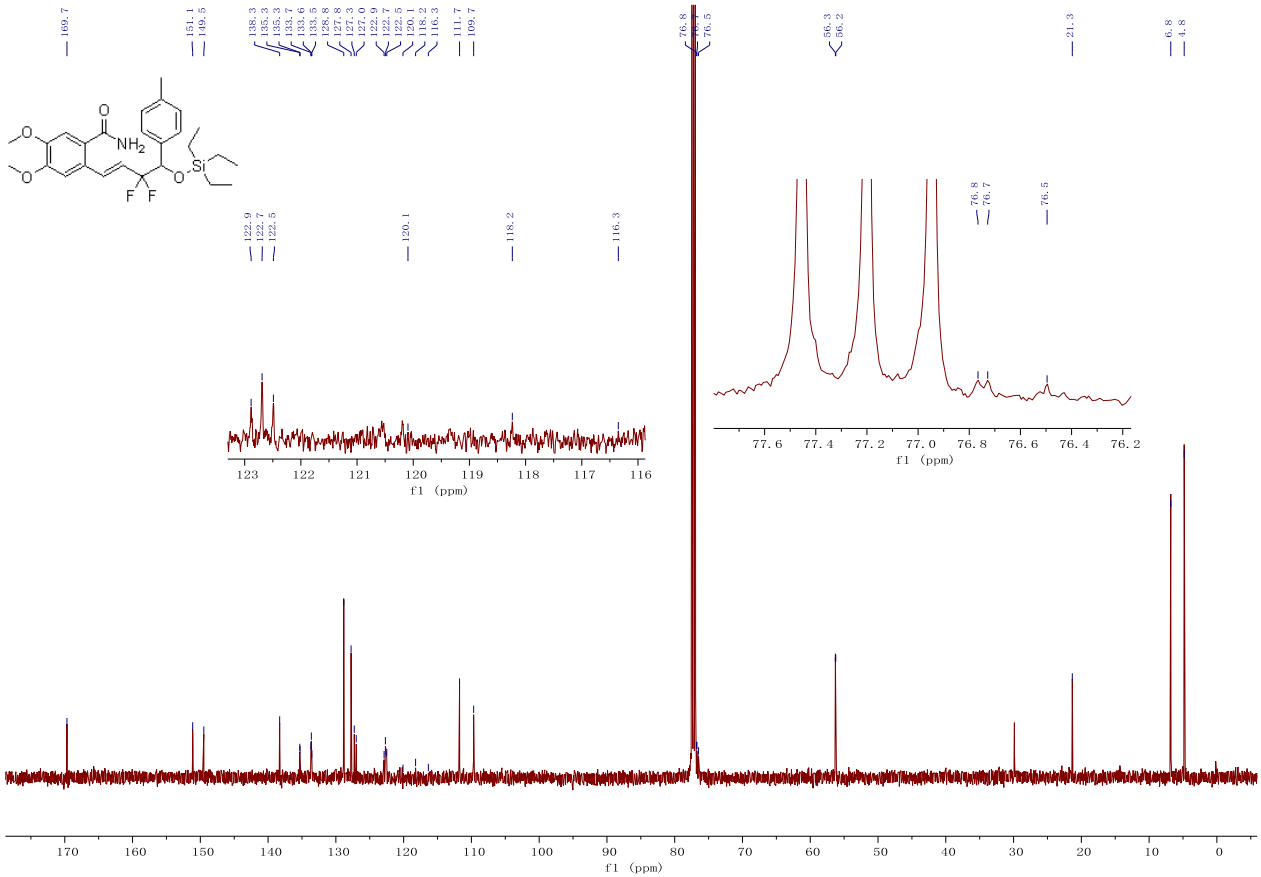
(*E*)-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)-3,5-dimethylbenzamide (3oa)

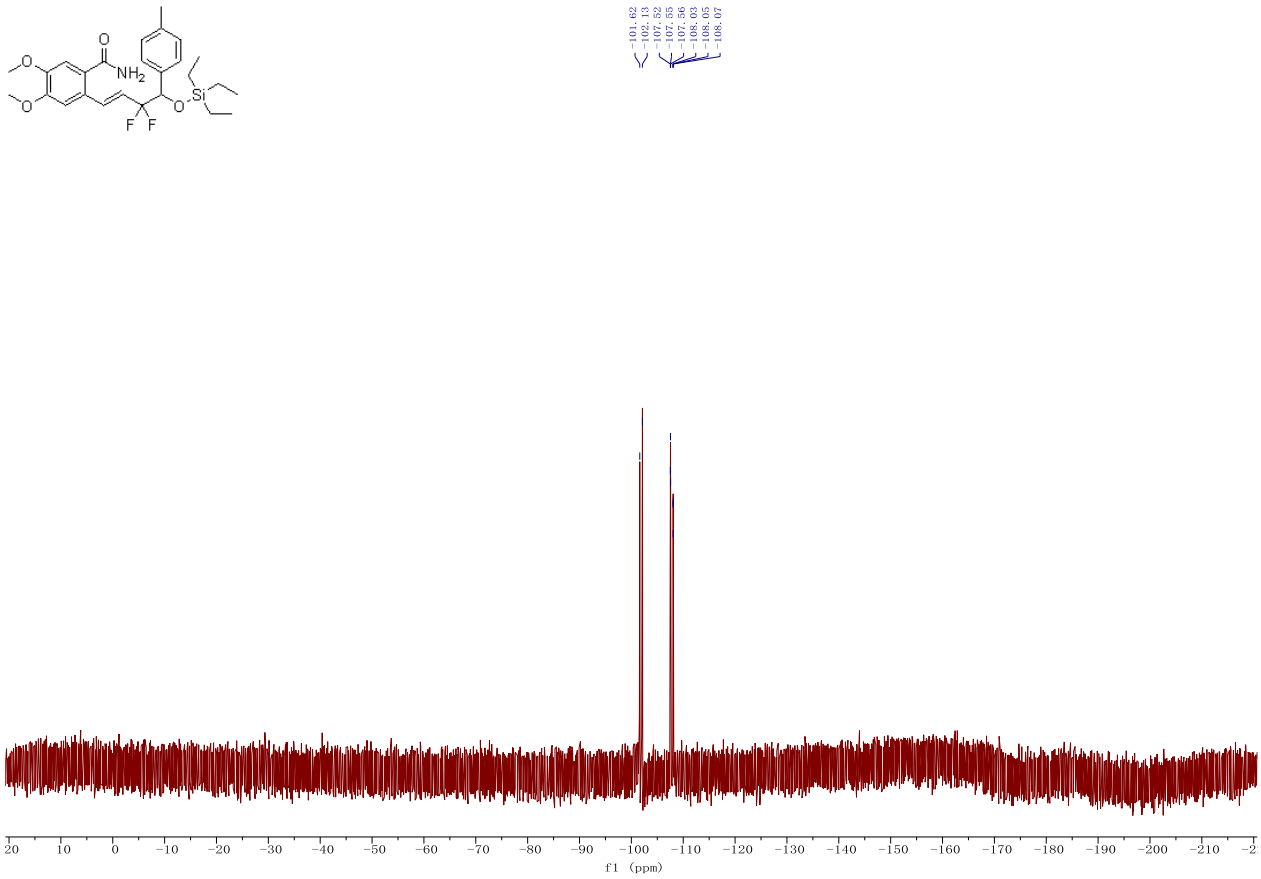




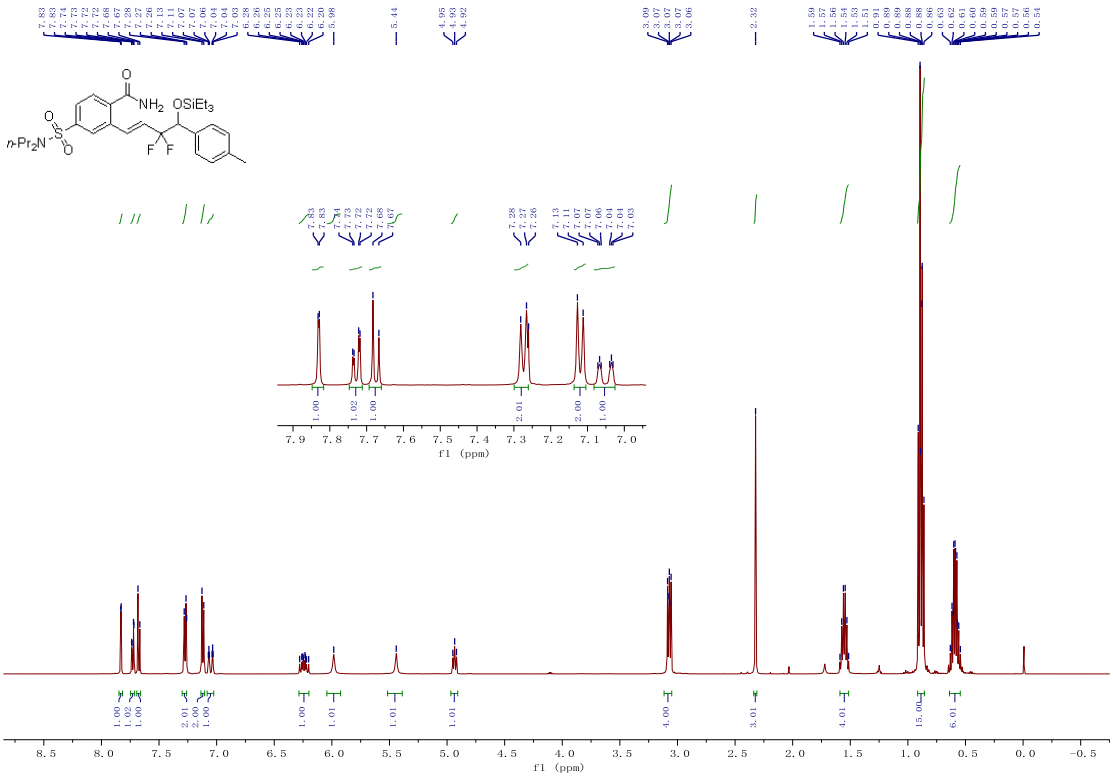
(*E*)-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)-4,5-dimethoxybenzamide (3pa)

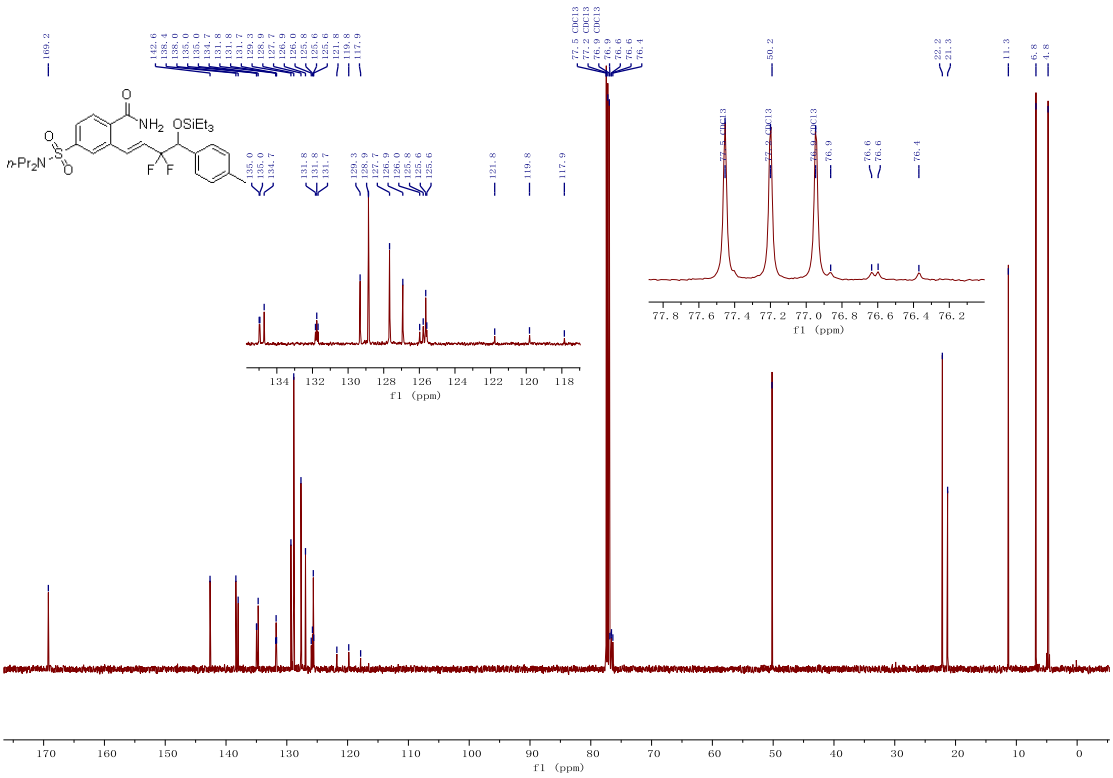


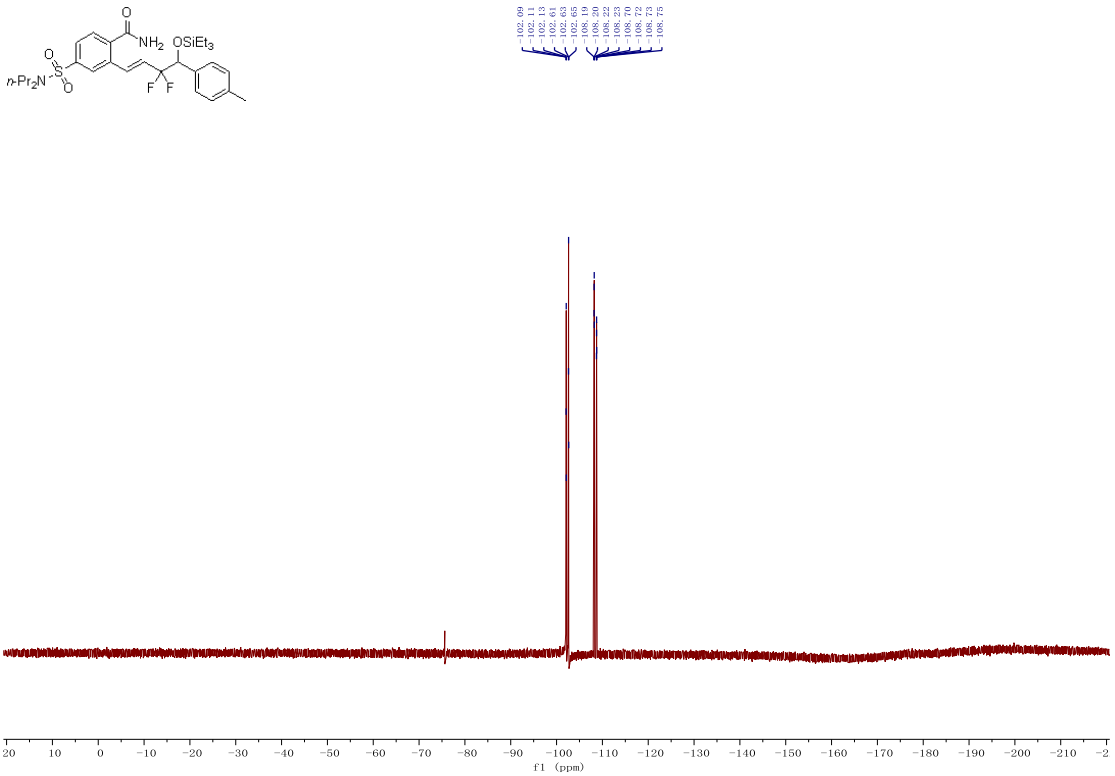

169.7
151.1
149.5
138.3
135.3
135.3
133.7
133.6
133.5
128.8
127.8
127.3
127.0
122.9
122.7
122.5
120.1
118.2
116.3
111.7
109.7
76.8
76.5
56.3
56.2
21.3
6.8
4.8
O
NH2
O
O
Si
F F
122.9
122.7
122.5
120.1
118.2
116.3
f1 (ppm)
76.8
76.7
76.5
f1 (ppm)
f1 (ppm)


-101.62
-102.13
-107.52
-107.55
-107.56
-108.03
-108.05
-108.07
O
NH2
O
O
Si
F F
f1 (ppm)

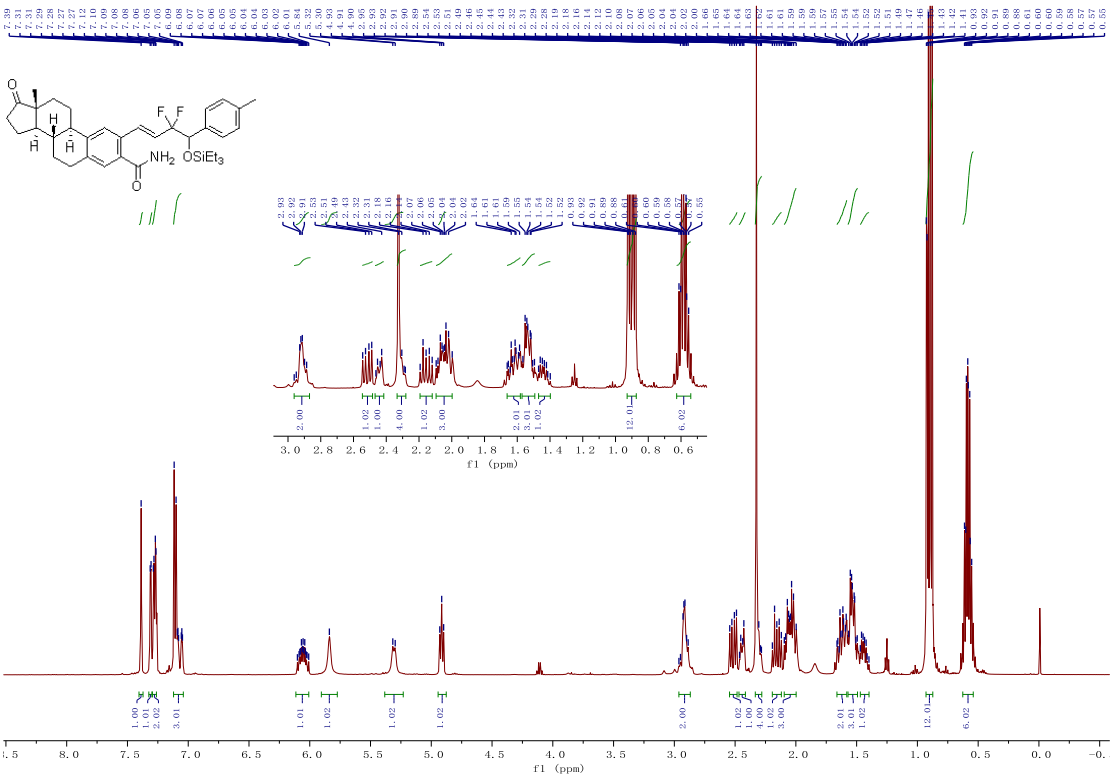
(*E*)-2-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)-4-(*N*,*N*-dipropylsulfamoyl) benzamide (3qa)

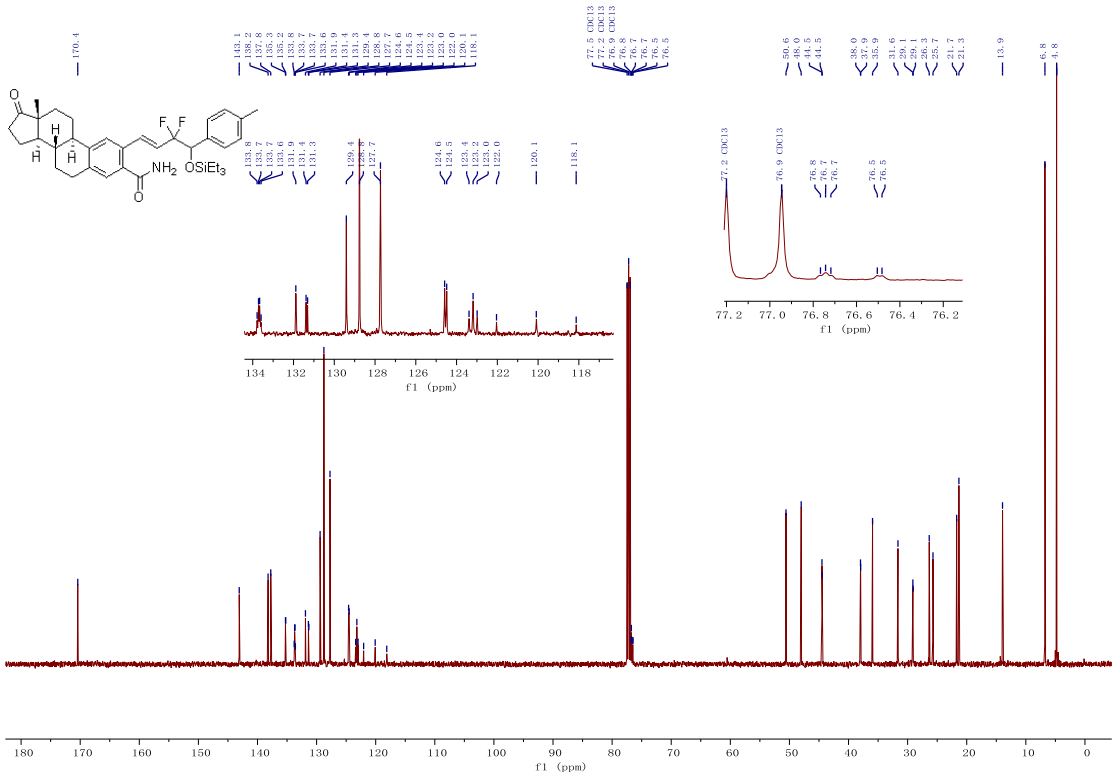


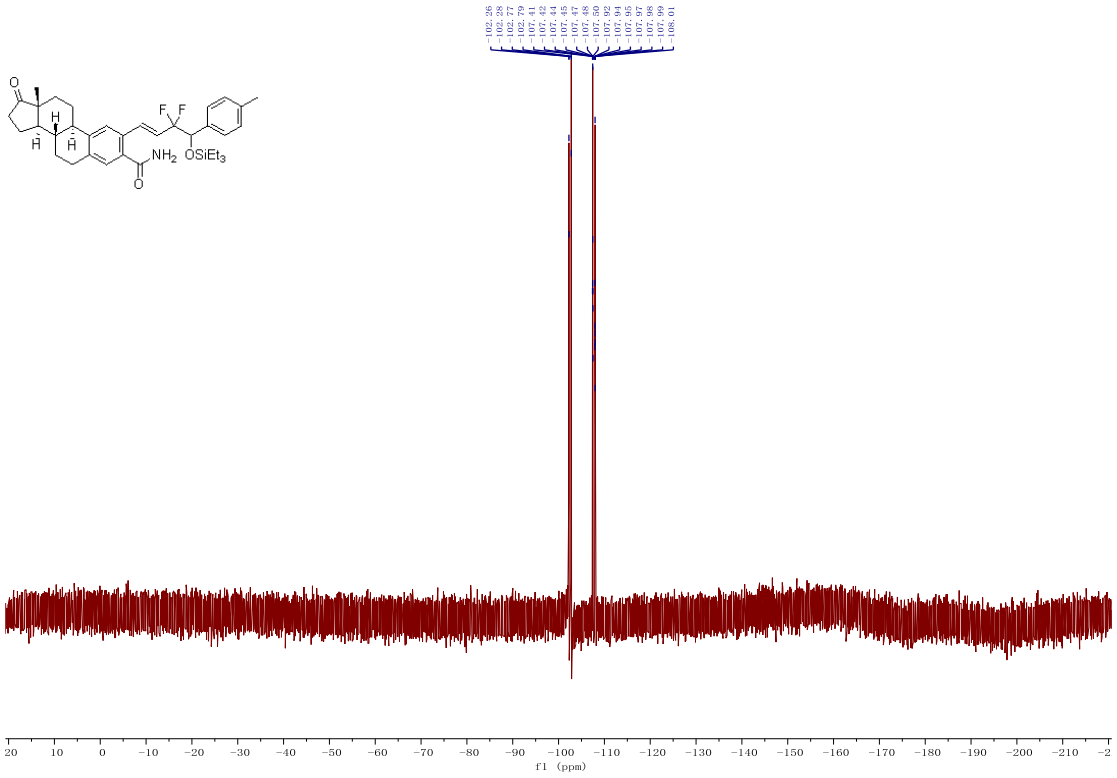




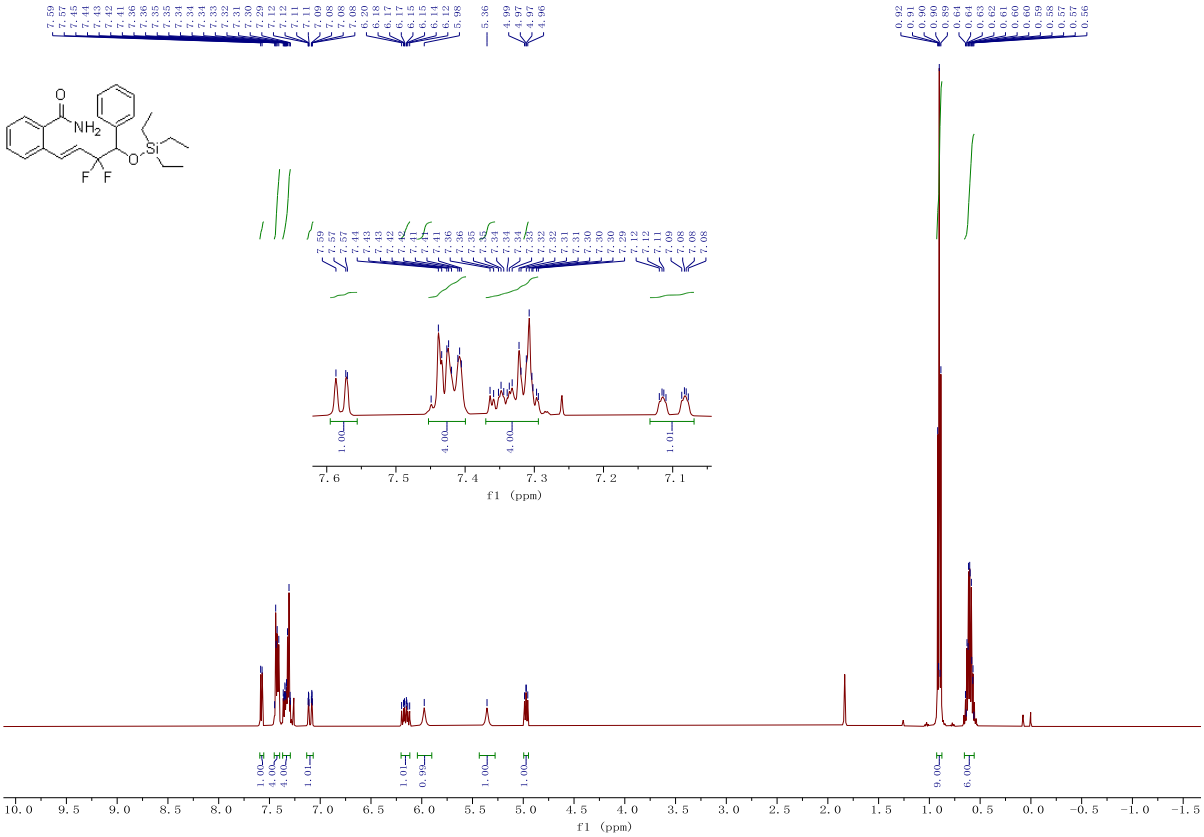
(8S,9R,13R,14R)-2-((*E*)-3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-3-carboxamide (3ra)

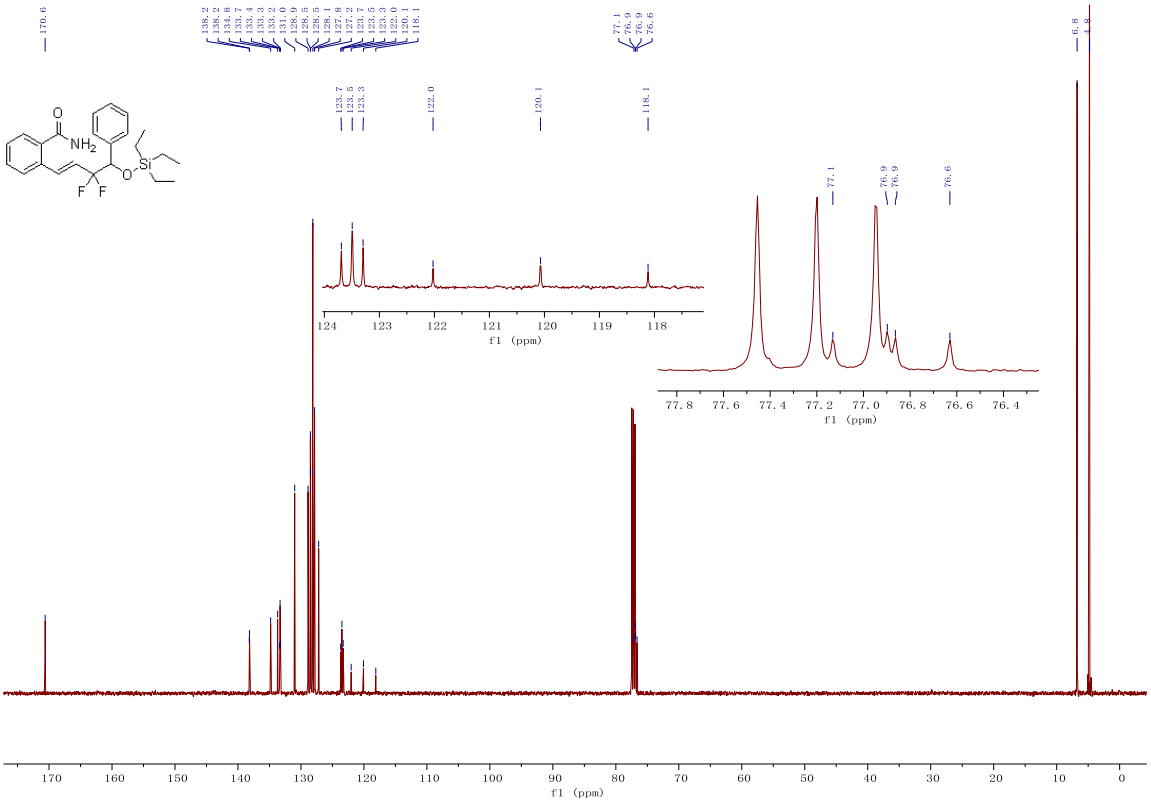


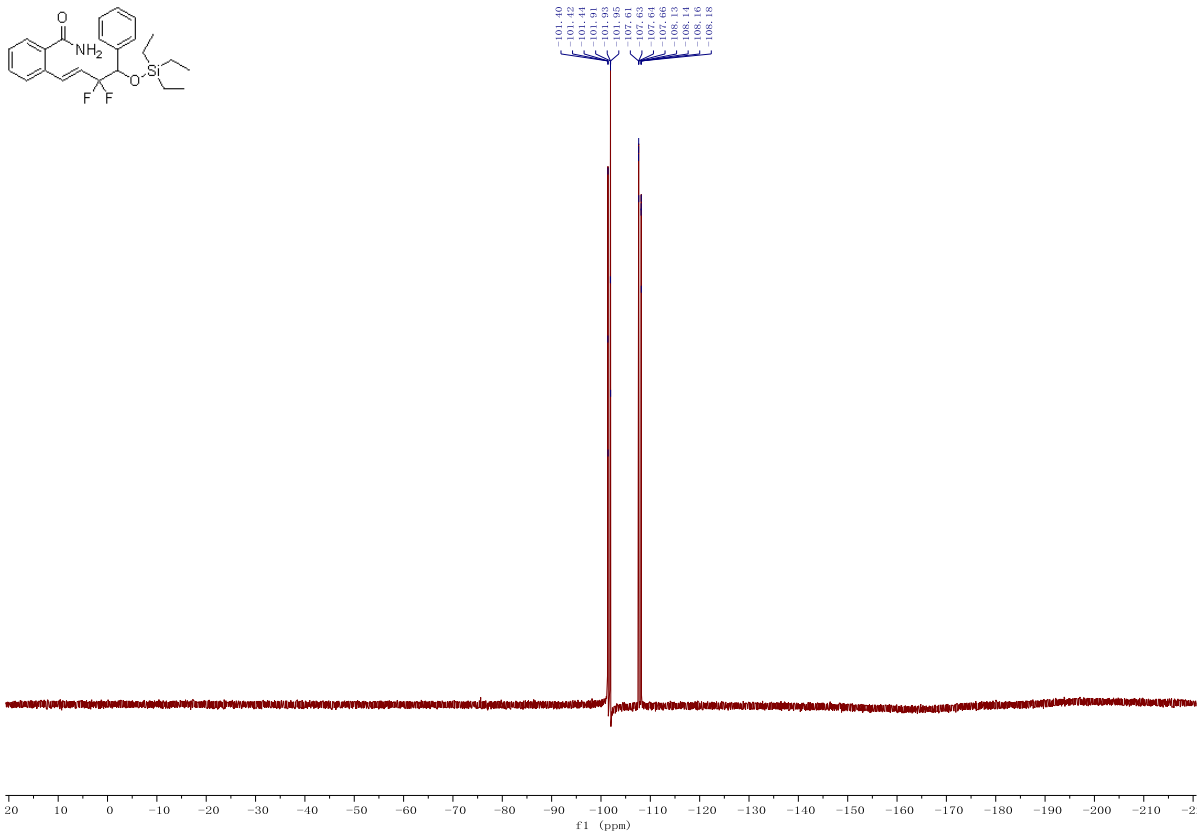

f1 (ppm)


f1 (ppm)

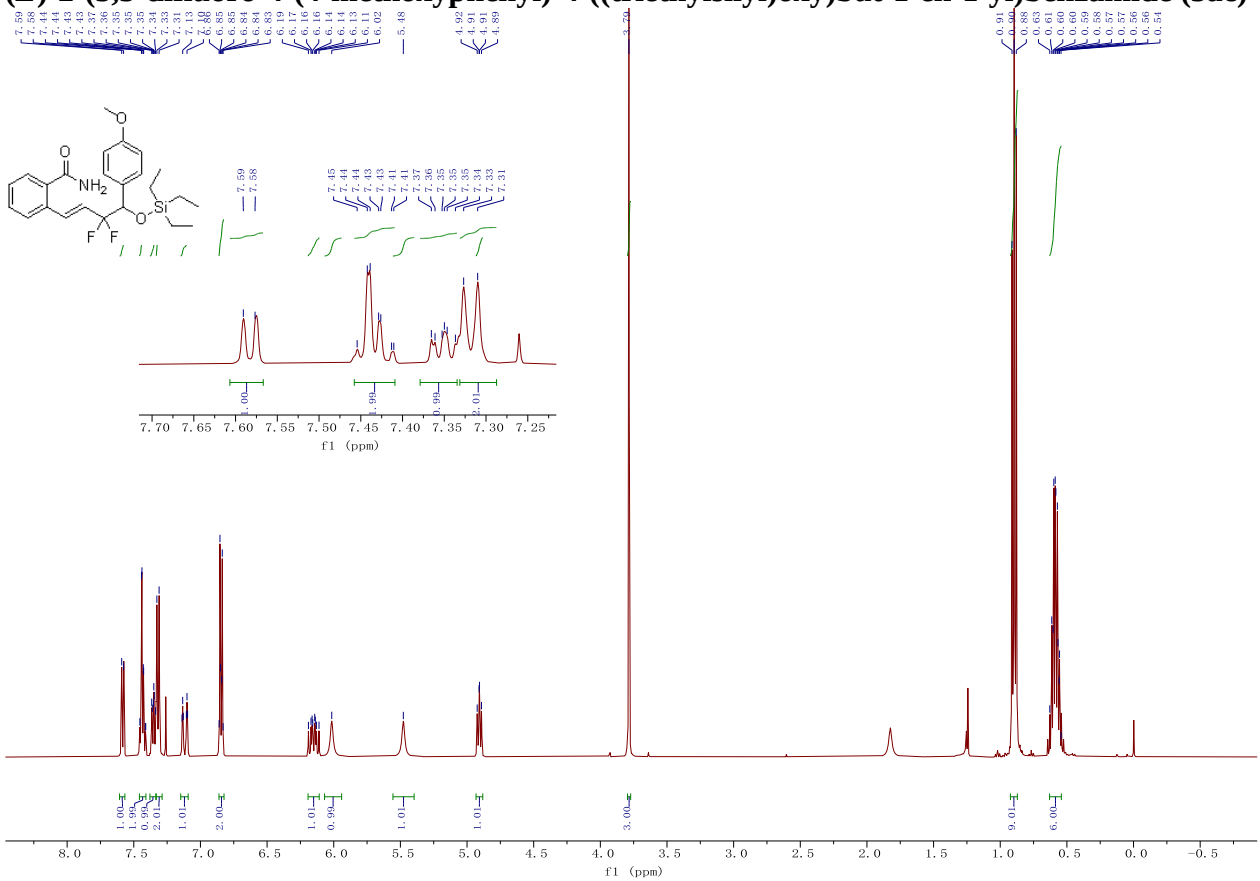
(*E*)-2-(3,3-difluoro-4-phenyl-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3ab)

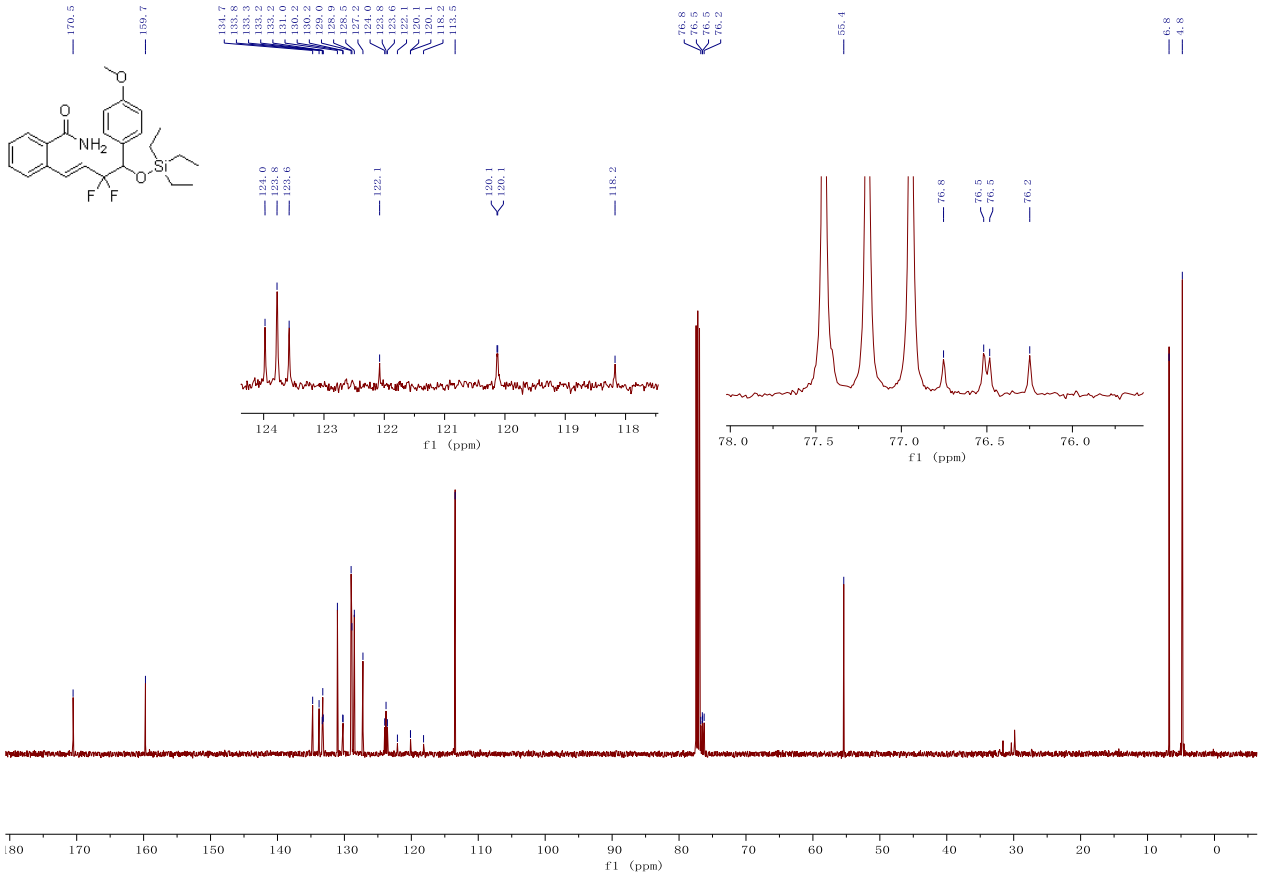


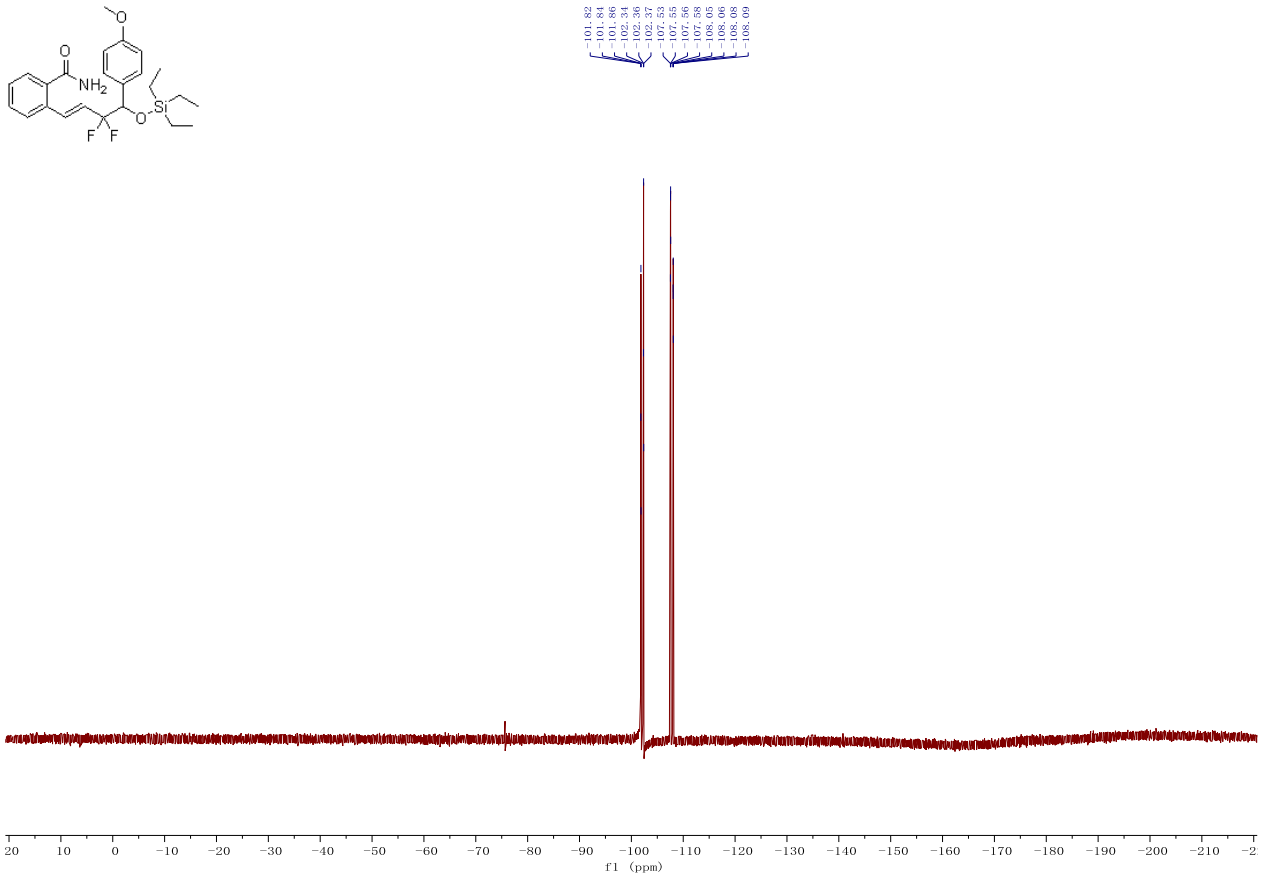




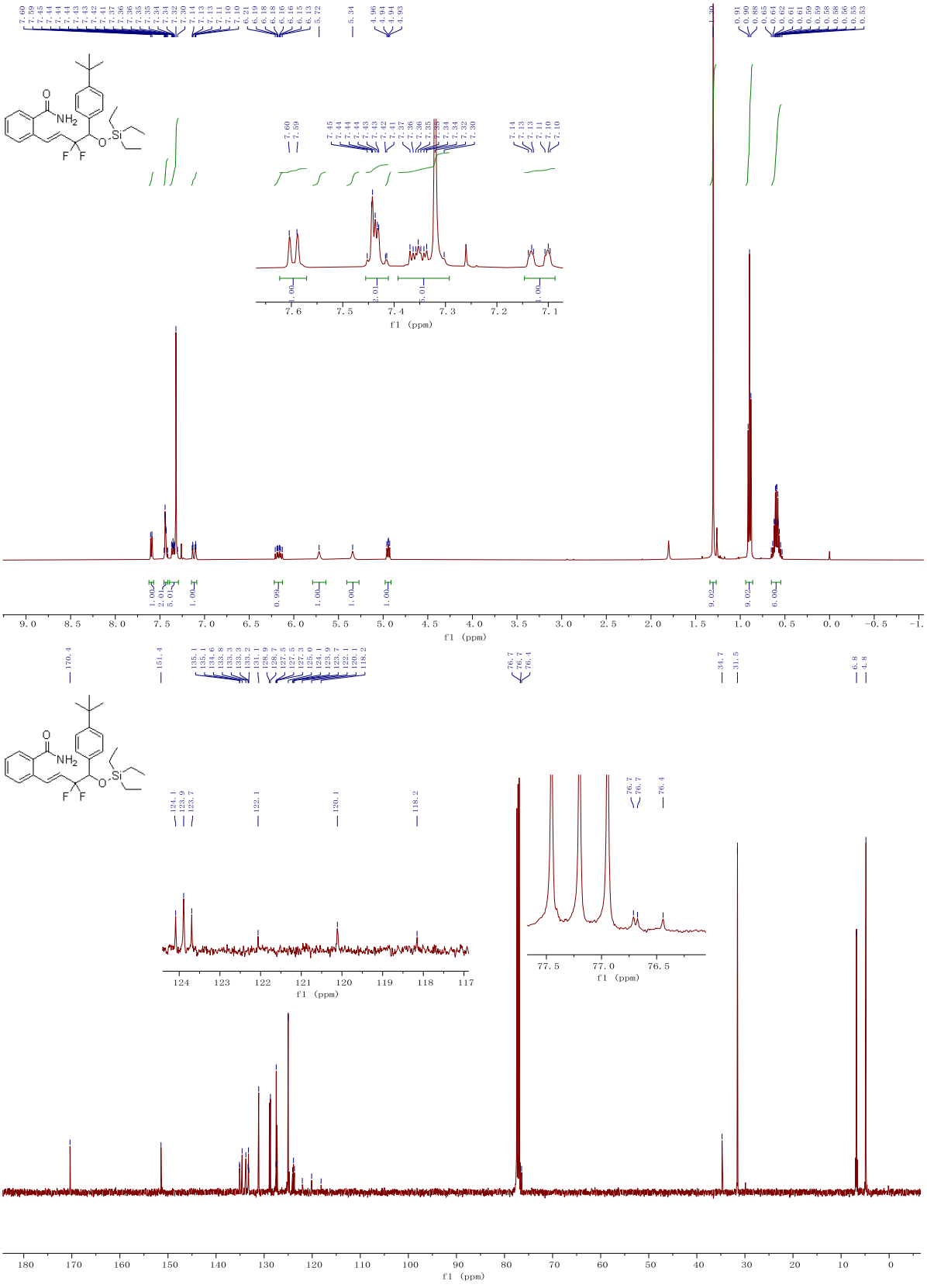
(*E*)-2-(3,3-difluoro-4-(4-methoxyphenyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3ac)

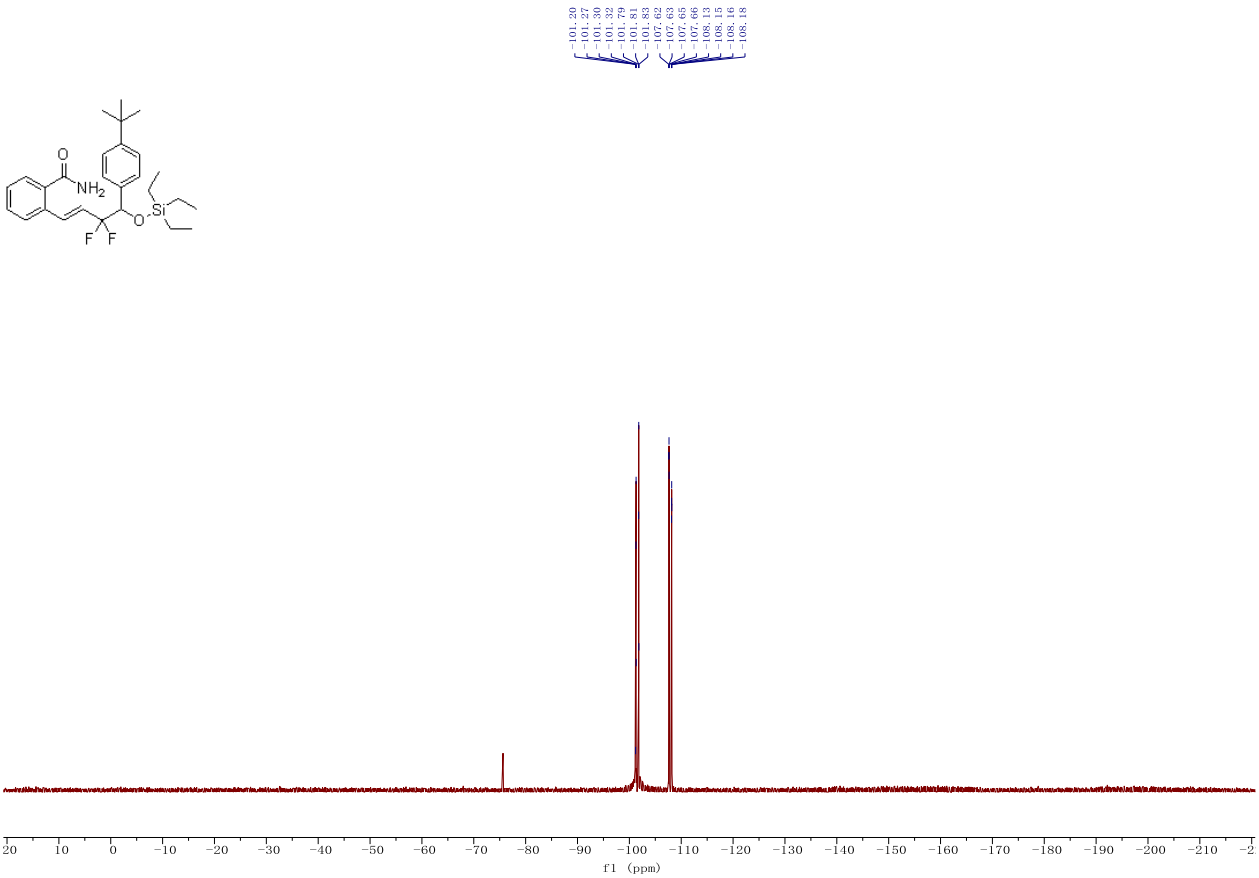



170.5
159.7
134.7
133.8
133.3
133.2
133.2
131.0
130.2
130.2
129.0
128.9
128.5
127.2
124.0
123.8
123.6
122.1
122.1
120.1
120.1
118.2
118.1
113.5
76.8
76.5
76.5
76.2
55.4
6.8
4.8
O
NH2
Si
F F
f1 (ppm)

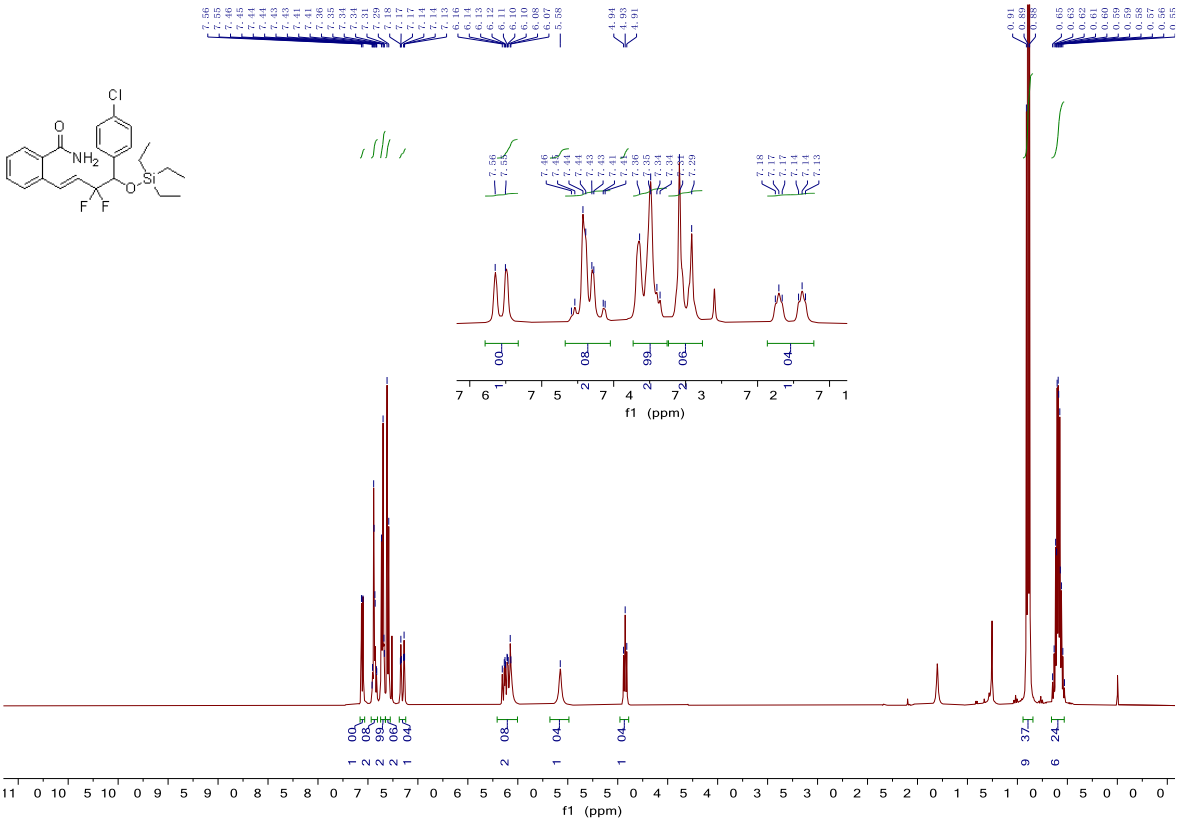

101.82
101.84
101.86
102.34
102.36
102.37
107.53
107.55
107.56
107.58
108.05
108.06
108.08
108.09
O
NH2
Si
F F
f1 (ppm)

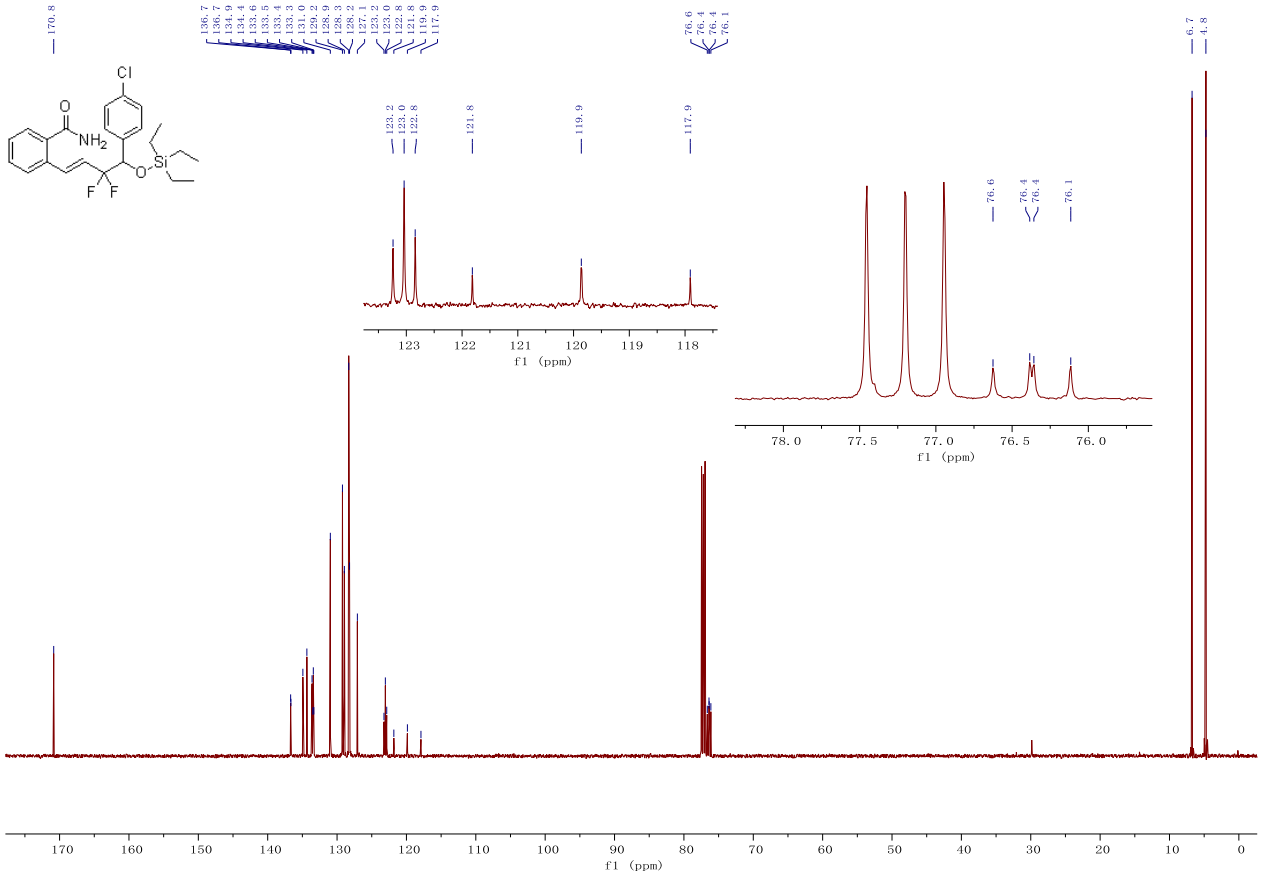
(*E*)-2-(4-(4-(tert-butyl)phenyl)-3,3-difluoro-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3ad)

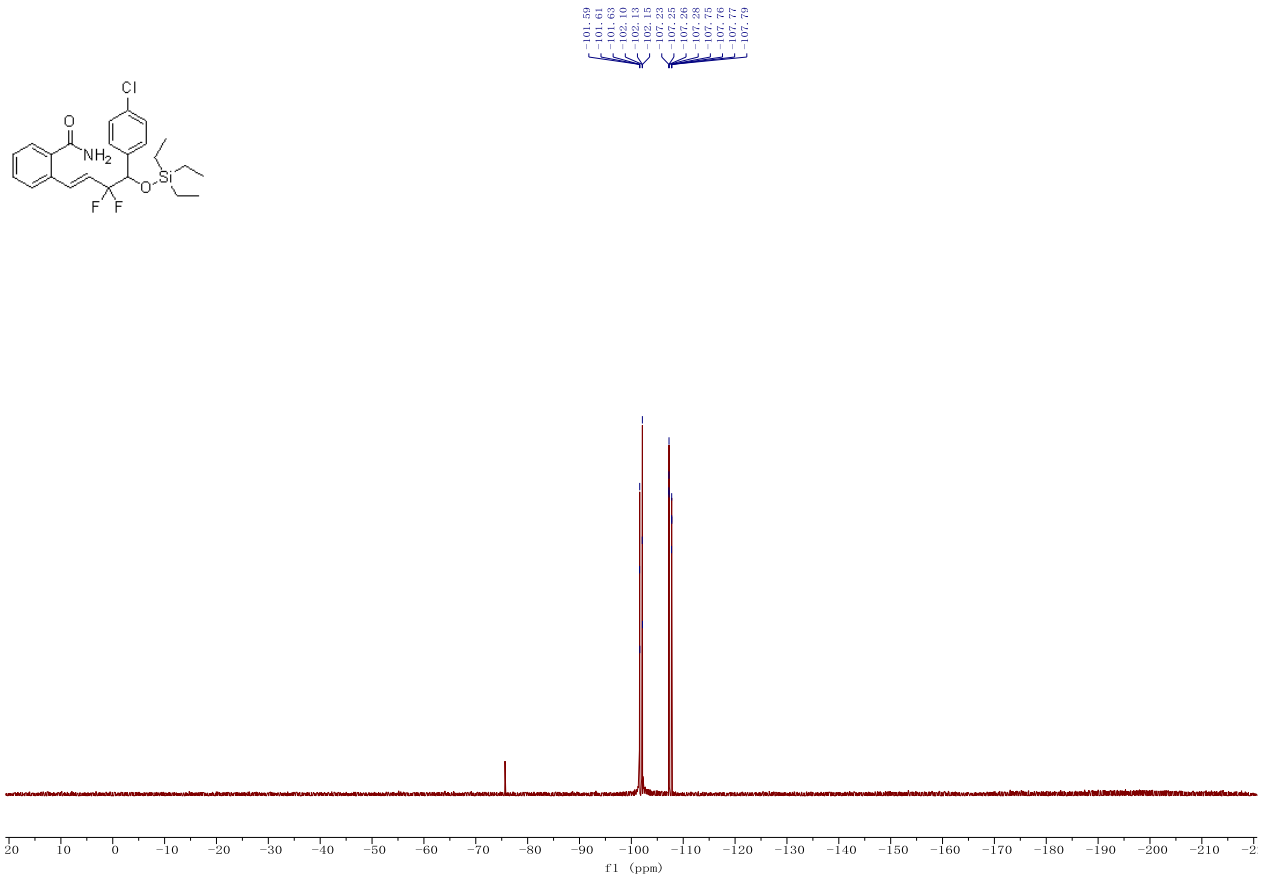




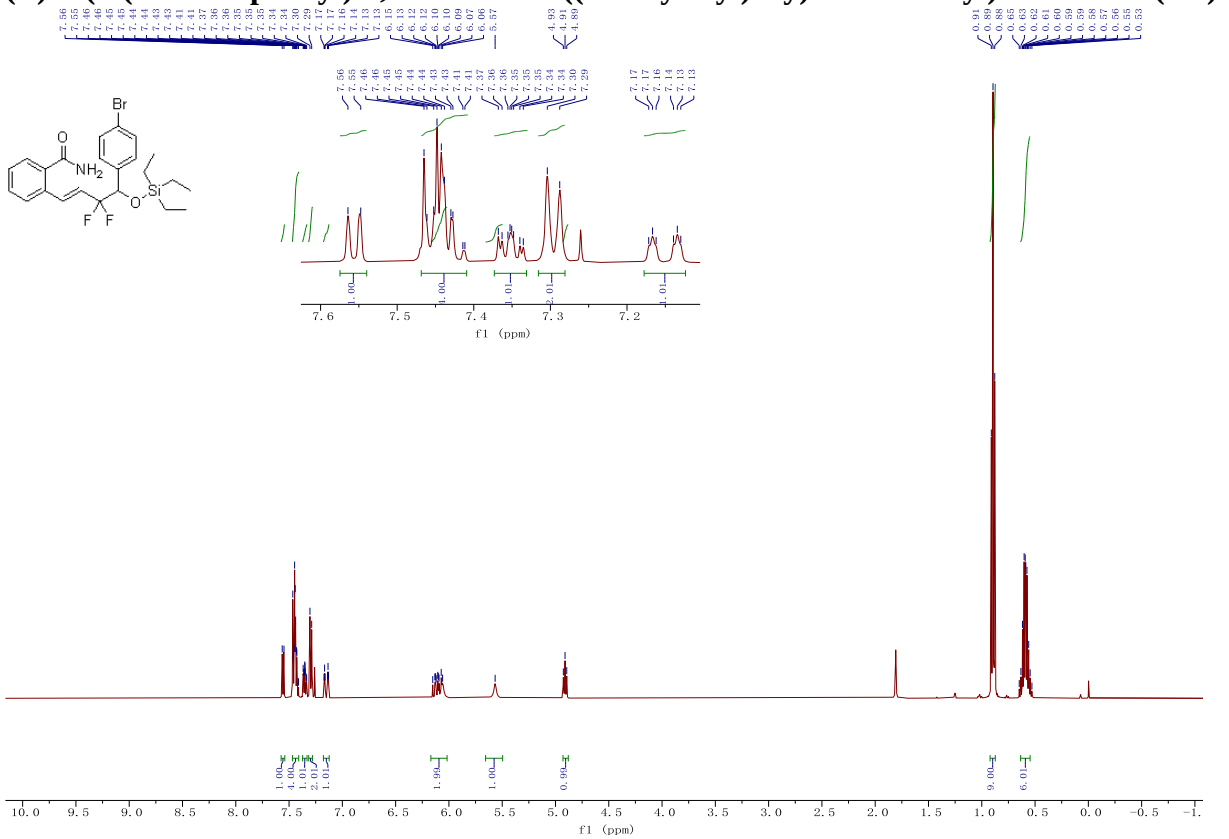
(*E*)-2-(4-(4-chlorophenyl)-3,3-difluoro-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3ae)

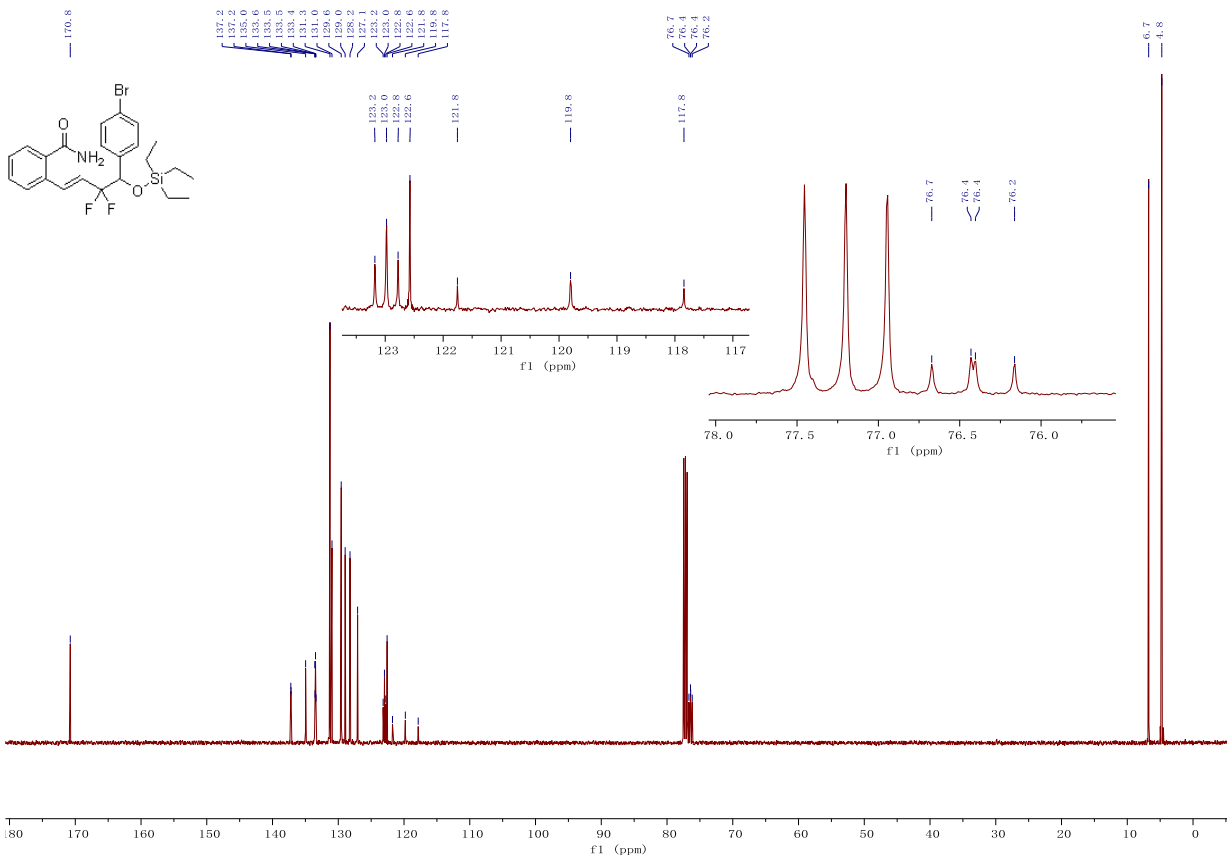


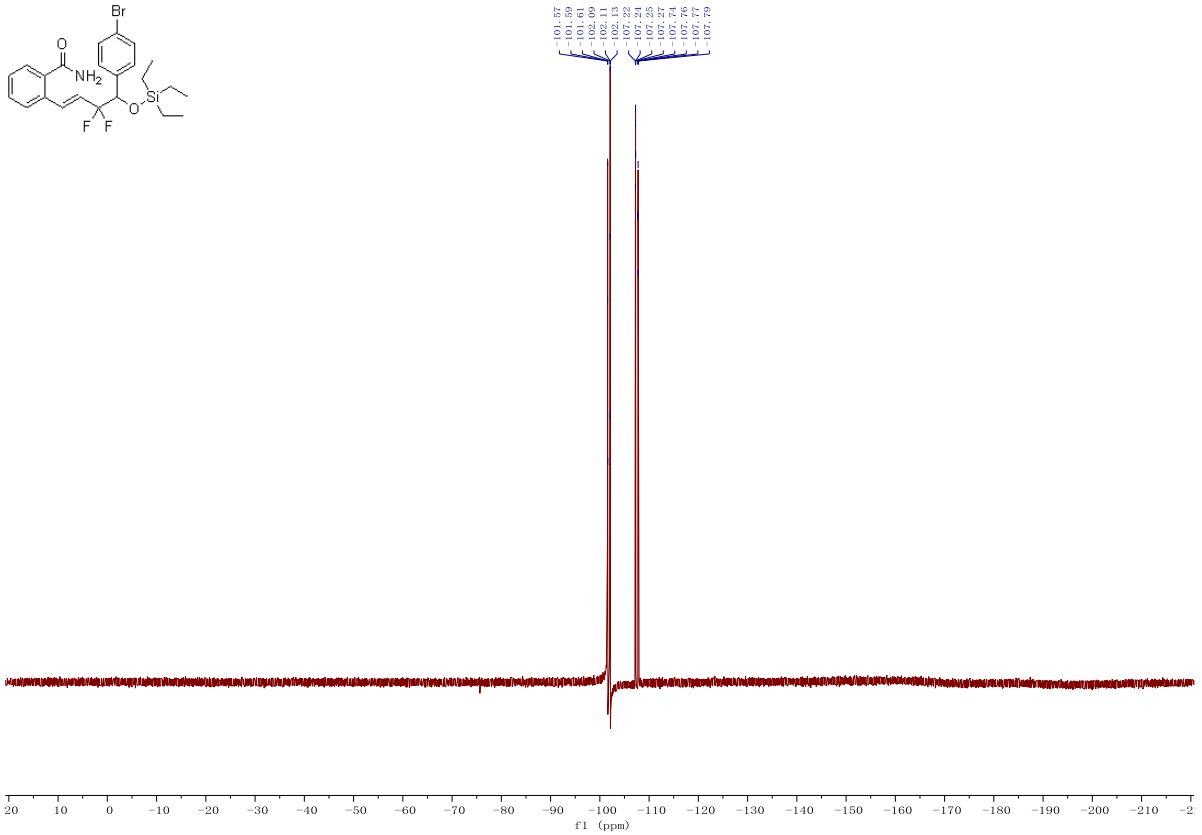

170.8
136.7
136.7
134.9
134.4
133.6
133.5
133.4
133.3
131.0
129.2
128.9
128.3
128.2
127.1
123.2
123.0
122.8
121.8
119.9
117.9
76.6
76.4
76.4
76.1
6.7
4.8
Cl
O
NH2
Si
F F
f1 (ppm)


-101.59
-101.61
-101.63
-102.10
-102.13
-102.15
-107.23
-107.25
-107.36
-107.38
-107.75
-107.76
-107.77
-107.79
Cl
O
NH2
Si
F F
f1 (ppm)

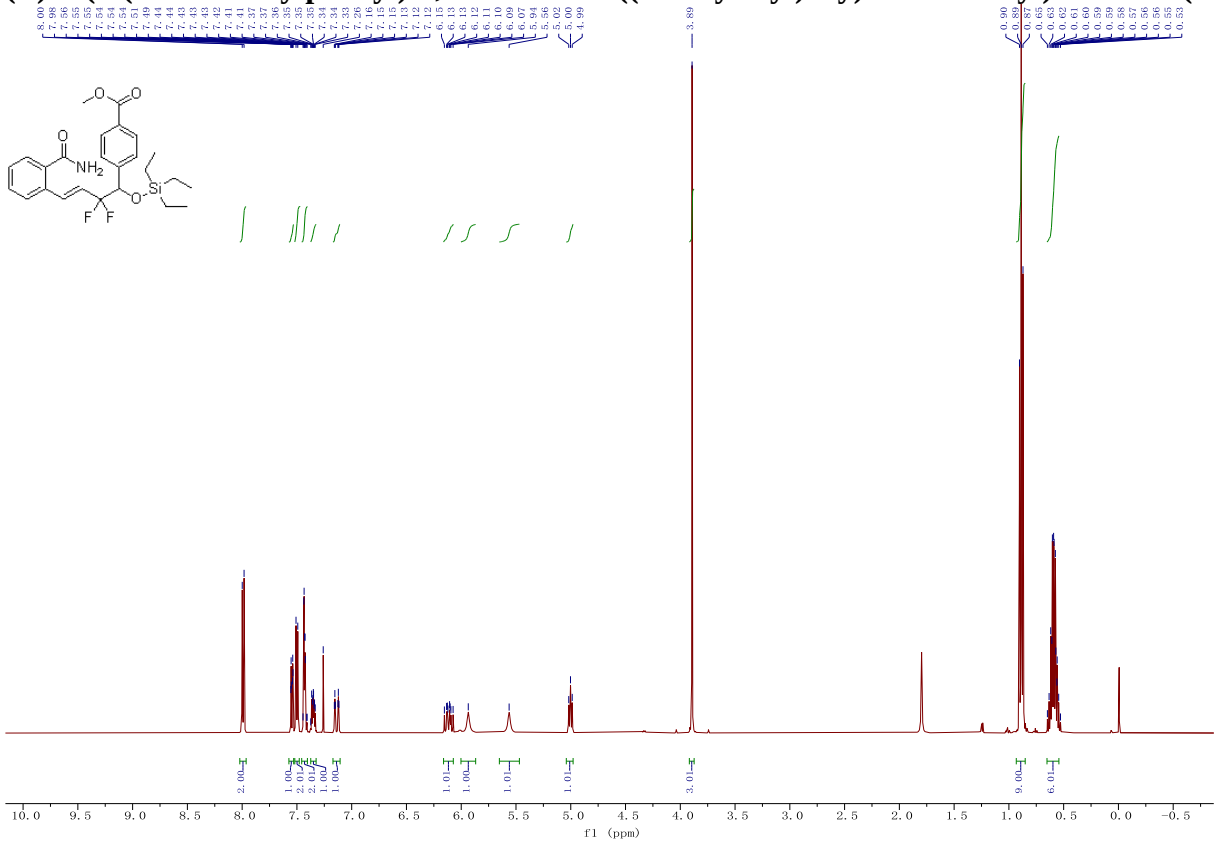
(*E*)-2-(4-(4-bromophenyl)-3,3-difluoro-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3af)

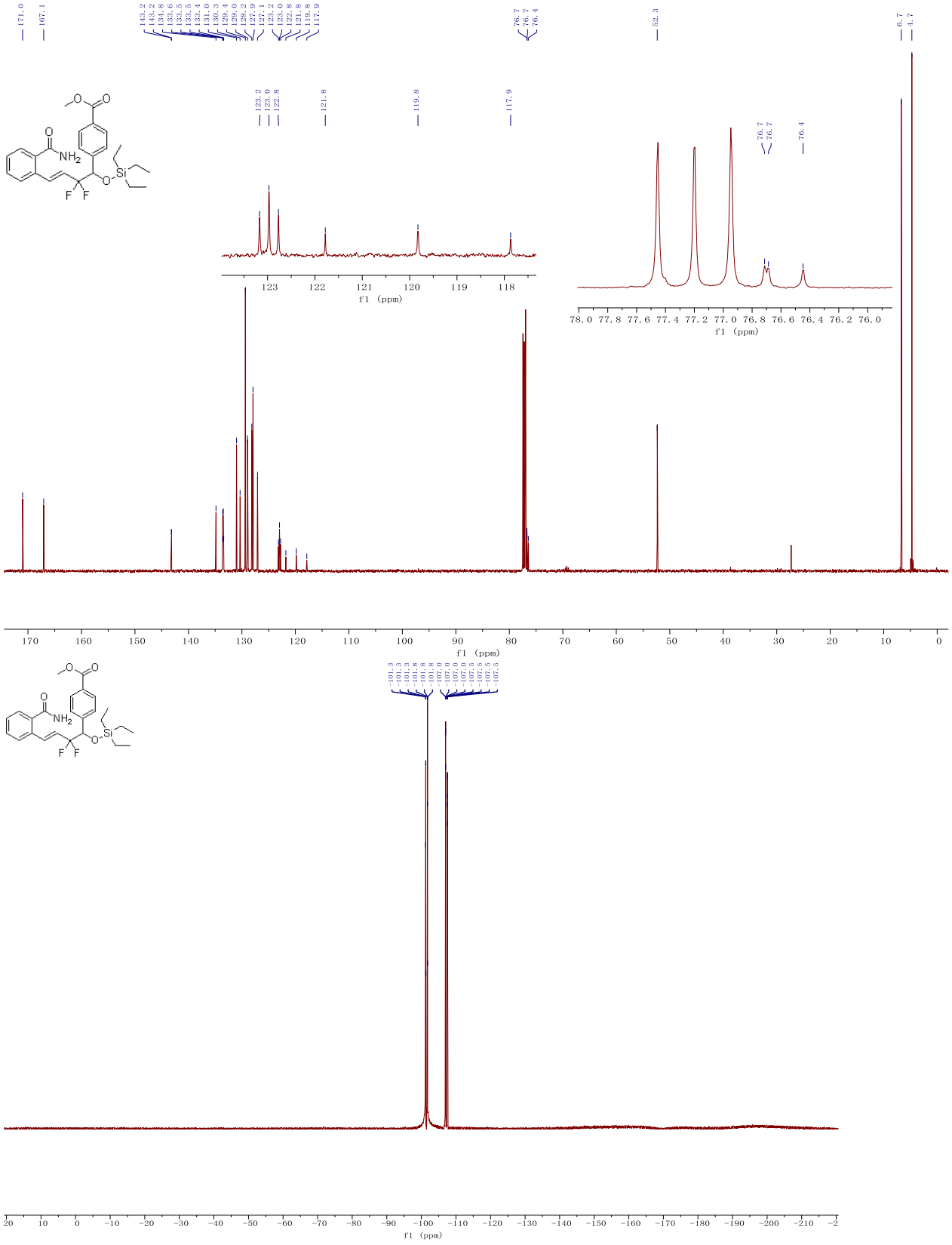




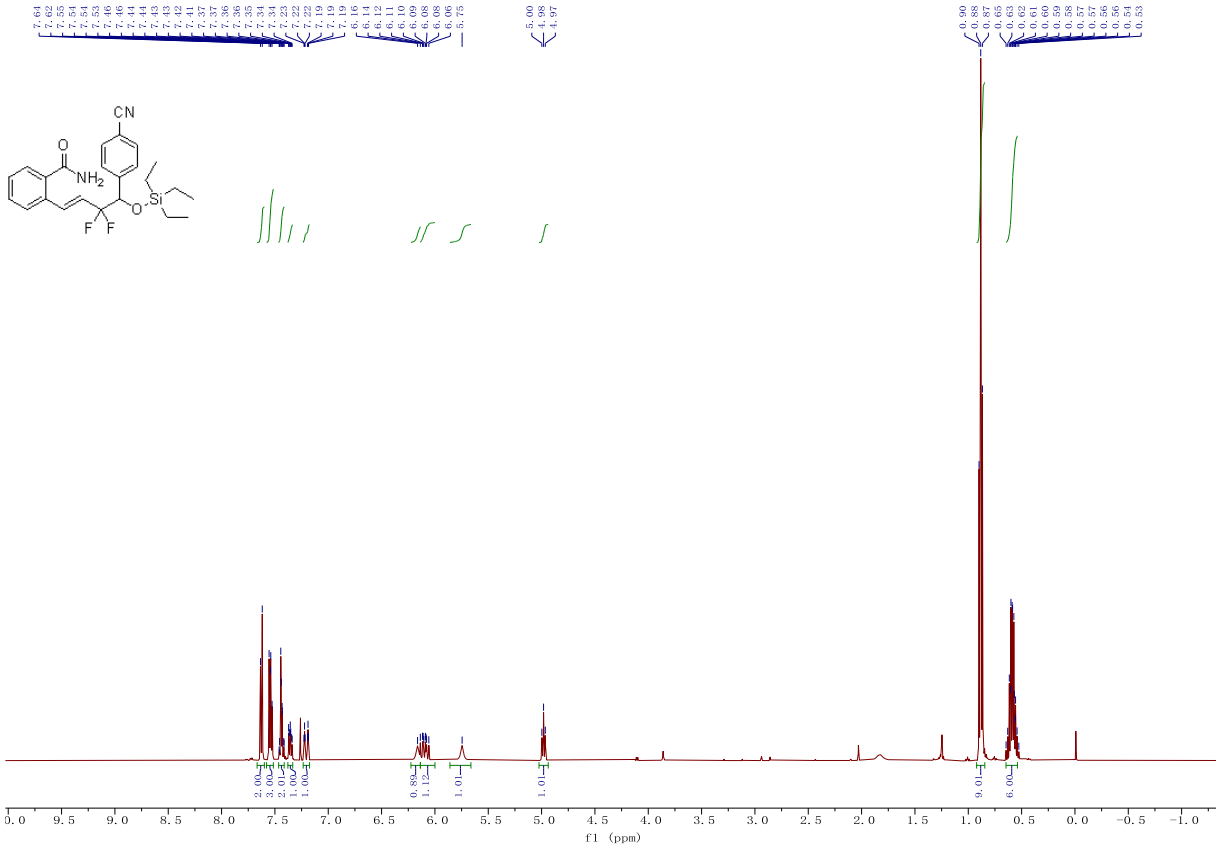


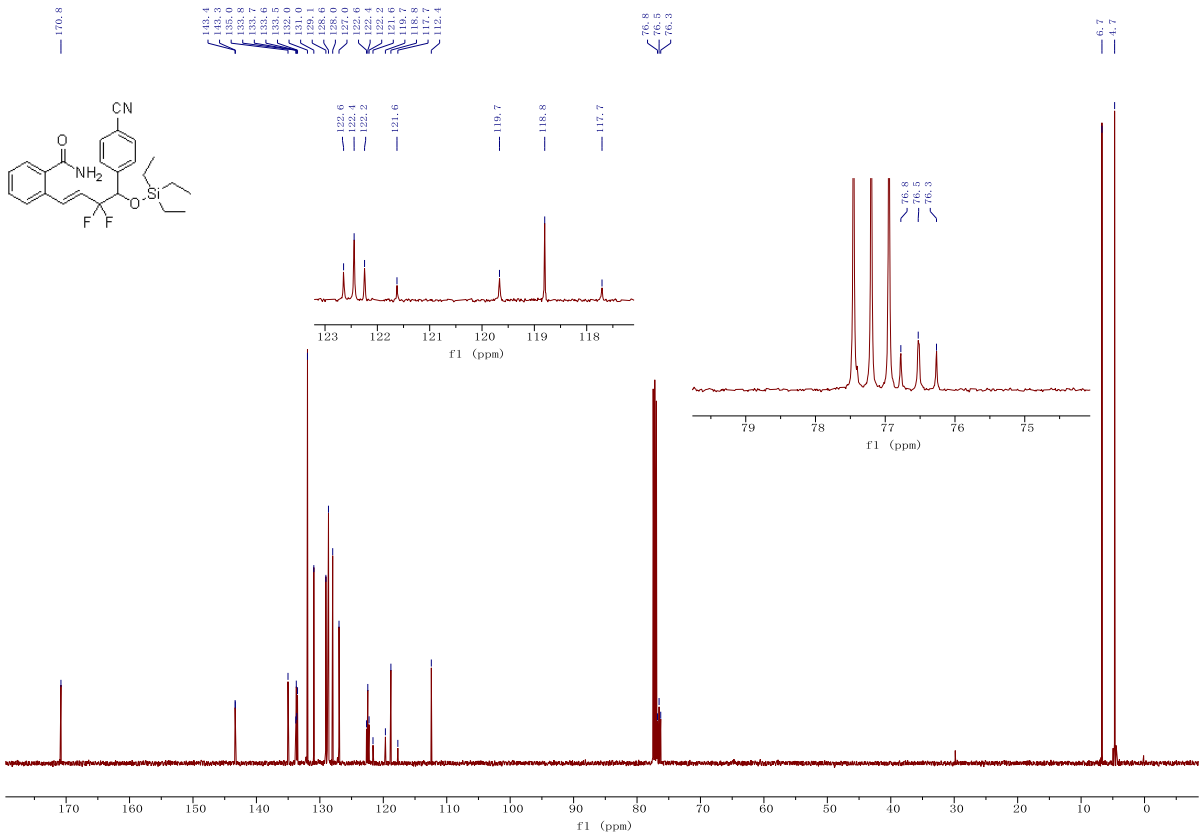
Methyl (*E*)-4-(4-(2-carbamoylphenyl)-2,2-difluoro-1-((triethylsilyl)oxy)but-3-en-1-yl)benzoate (3ag)

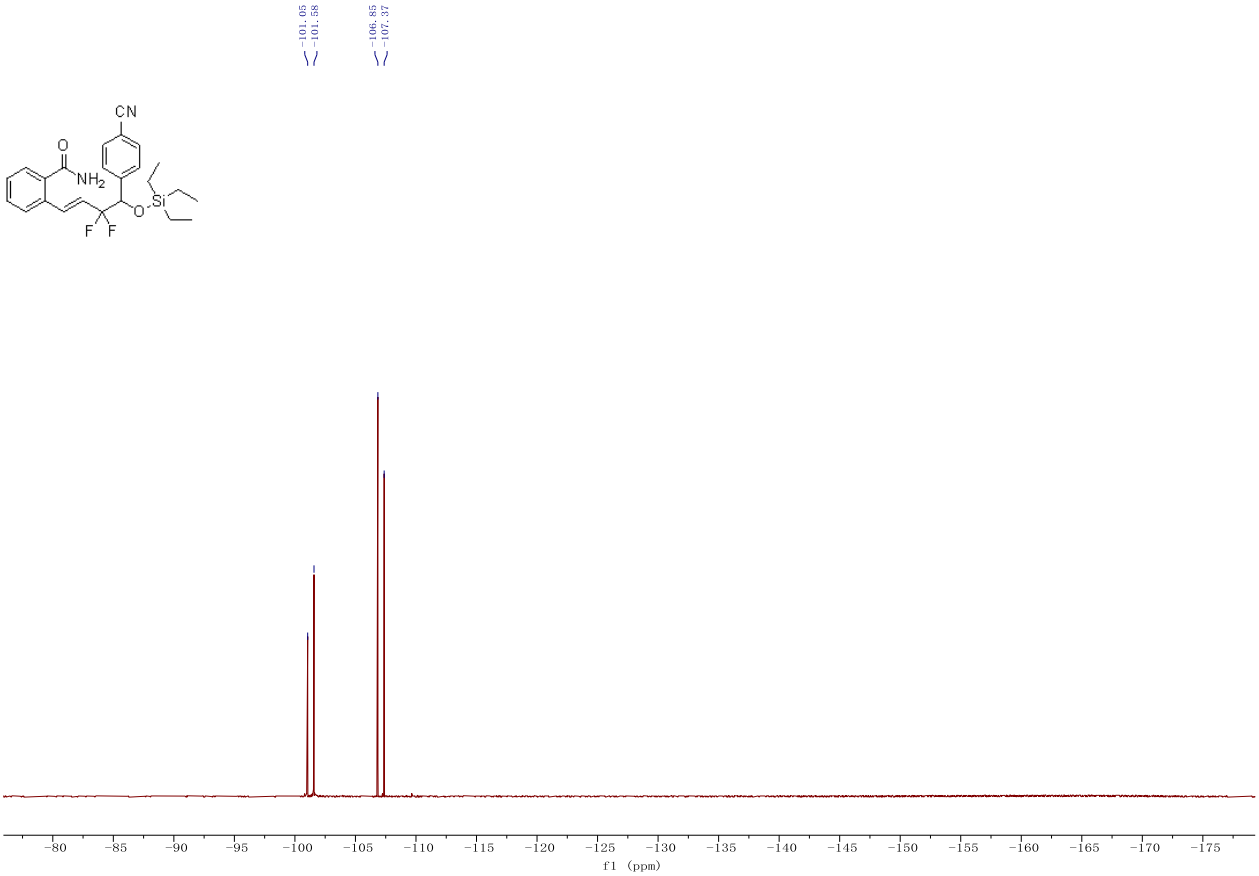



171.0
167.1
143.2
143.2
134.8
133.6
133.5
133.5
133.4
131.0
130.3
129.4
129.0
128.2
127.9
127.1
123.2
123.0
122.8
121.8
119.8
117.9
76.7
76.7
76.4
52.3
6.7
4.7
f1 (ppm)
f1 (ppm)
f1 (ppm)

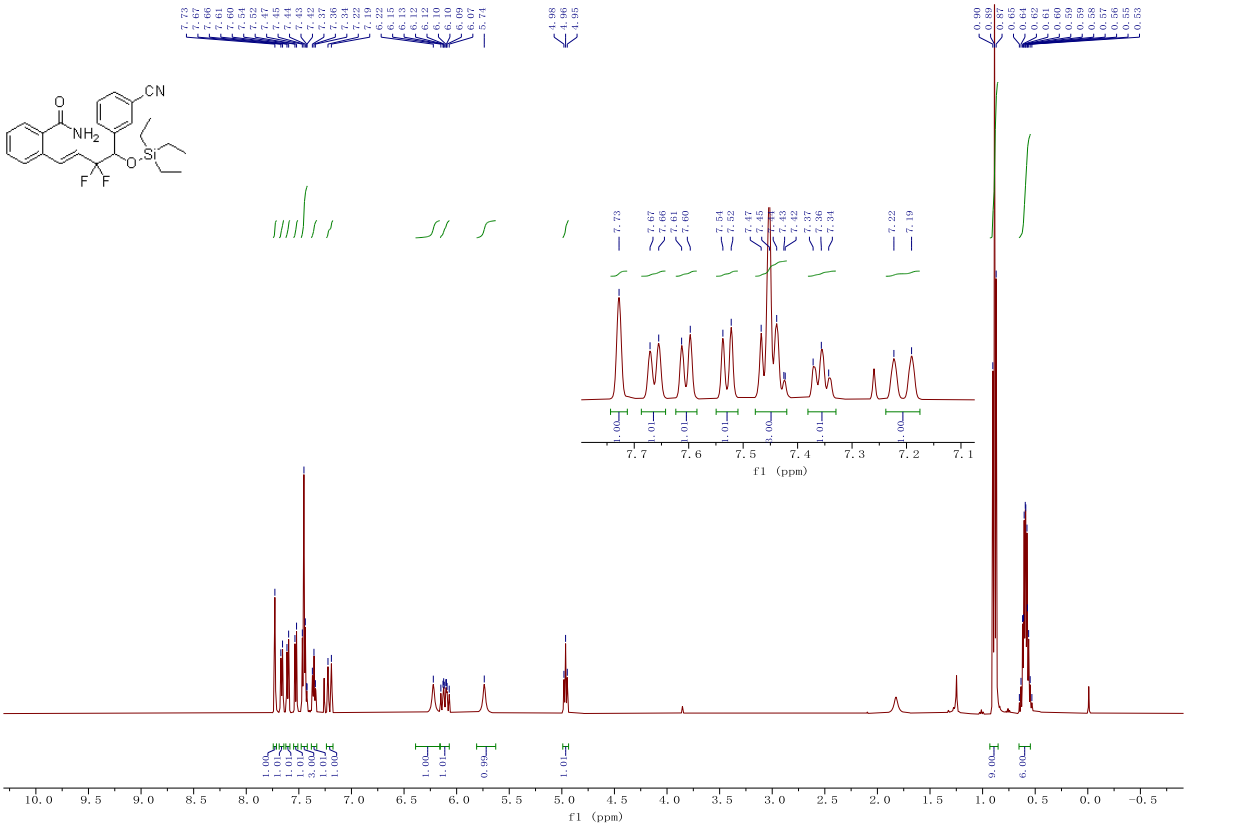
(*E*)-2-(4-(4-cyanophenyl)-3,3-difluoro-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3ah)

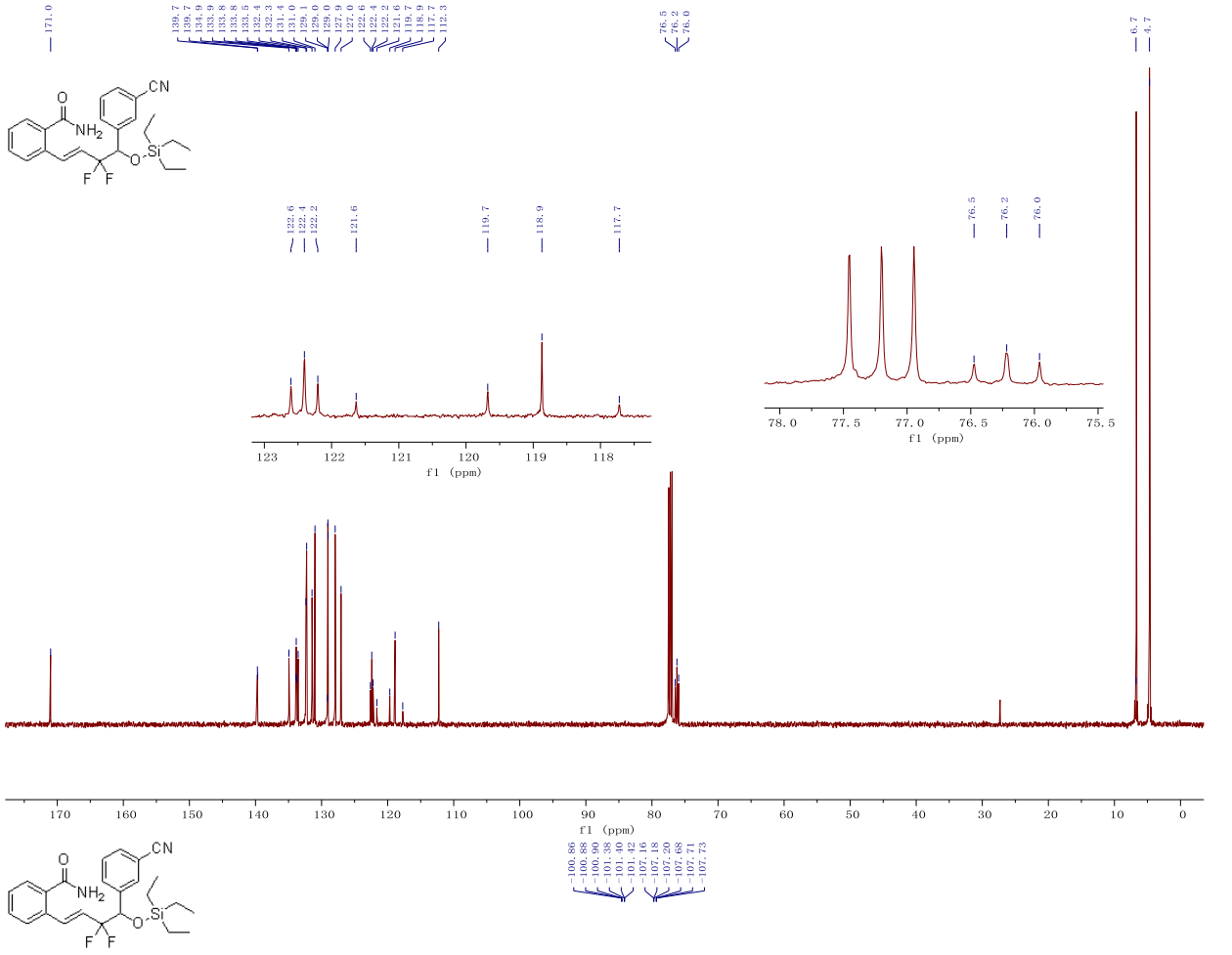


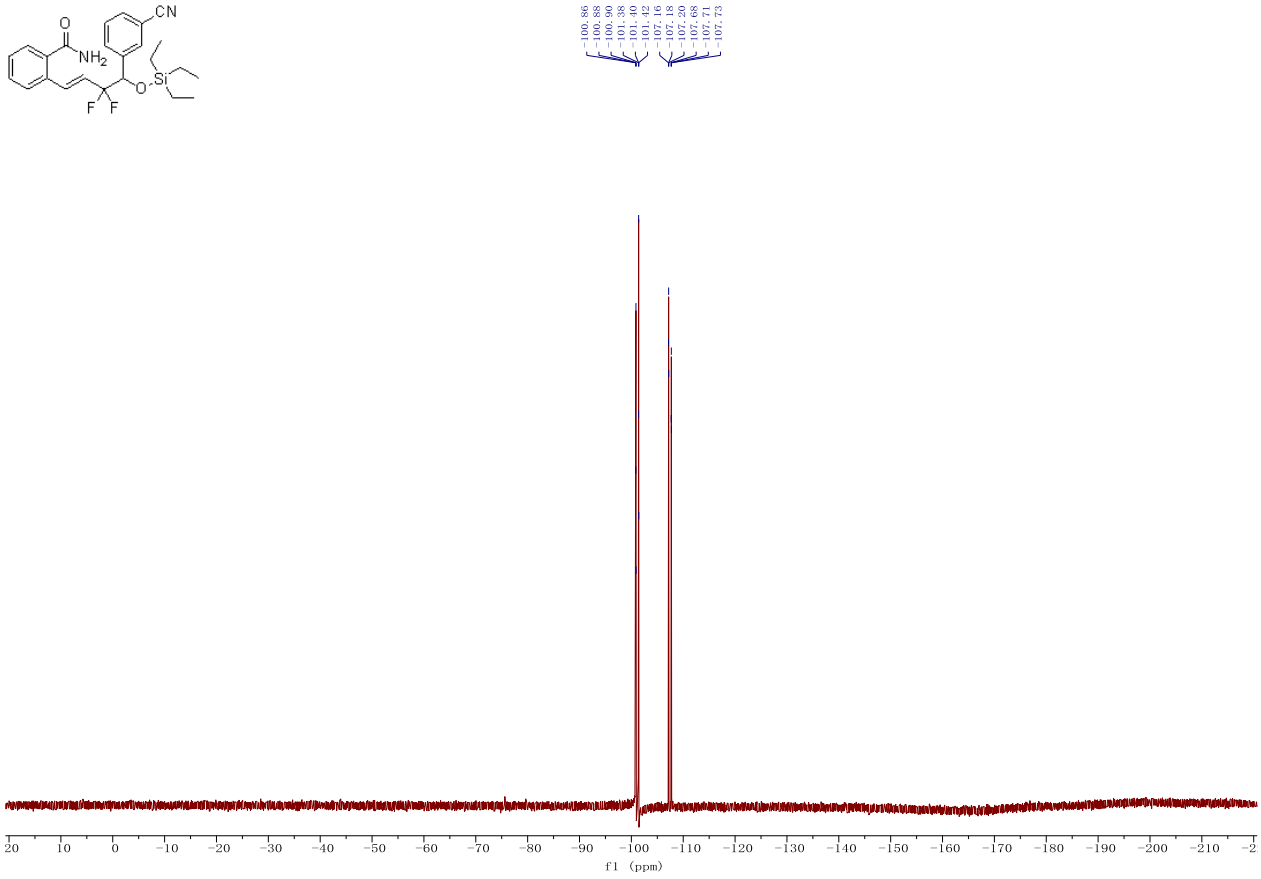




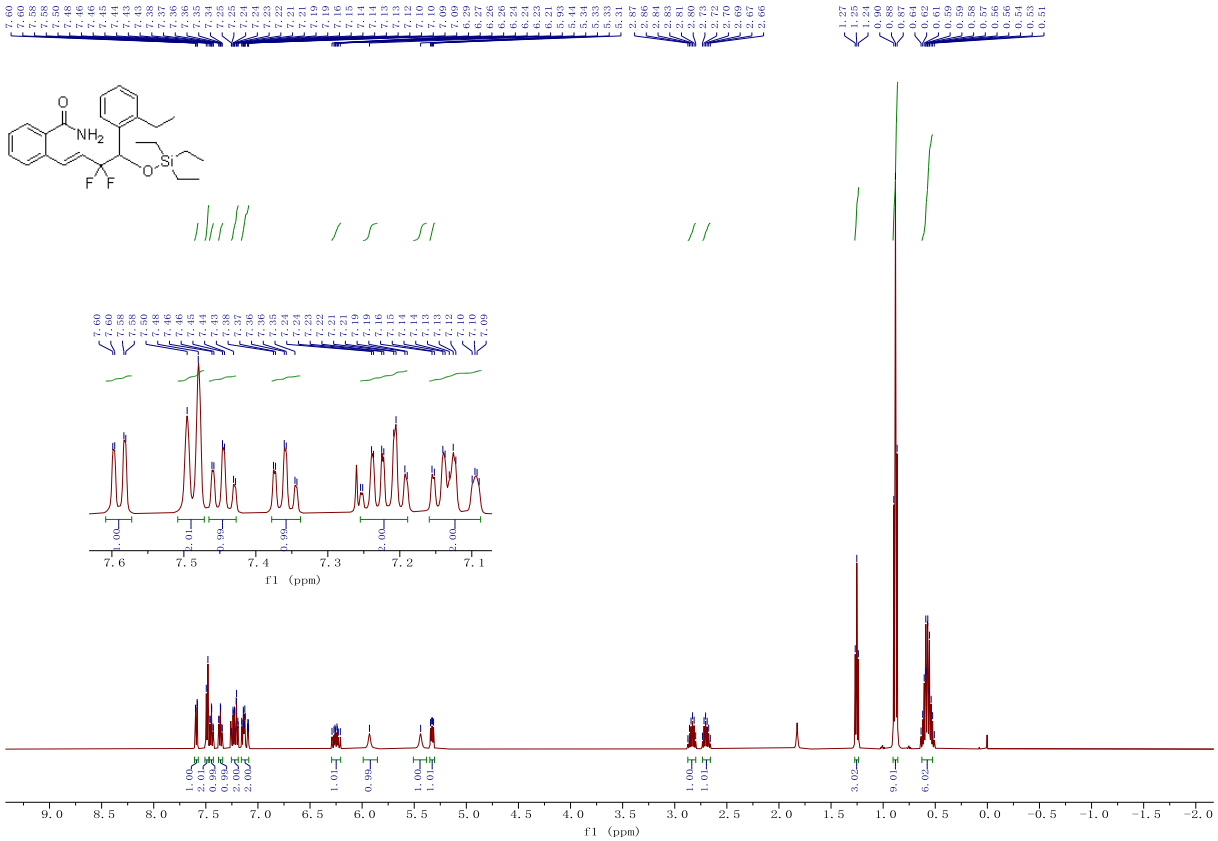
(*E*)-2-(4-(3-cyanophenyl)-3,3-difluoro-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3ai)

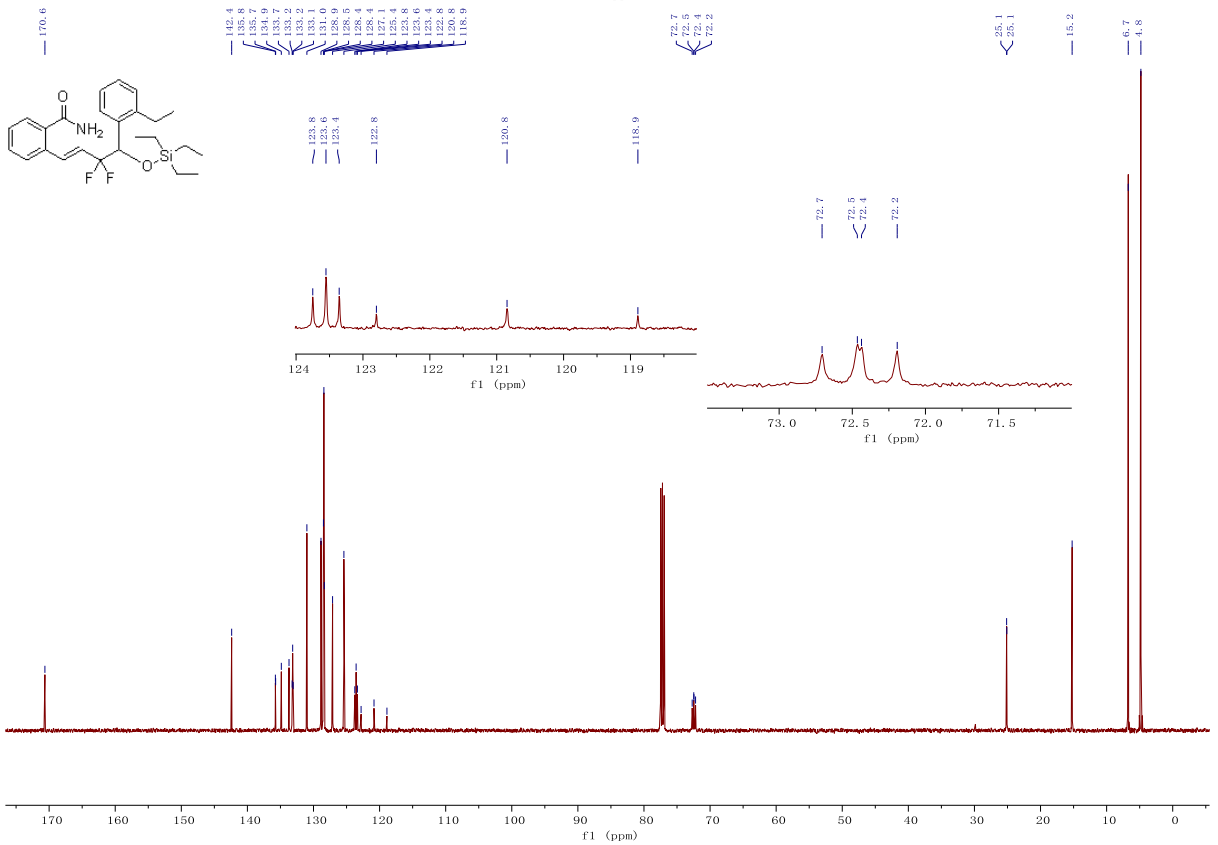


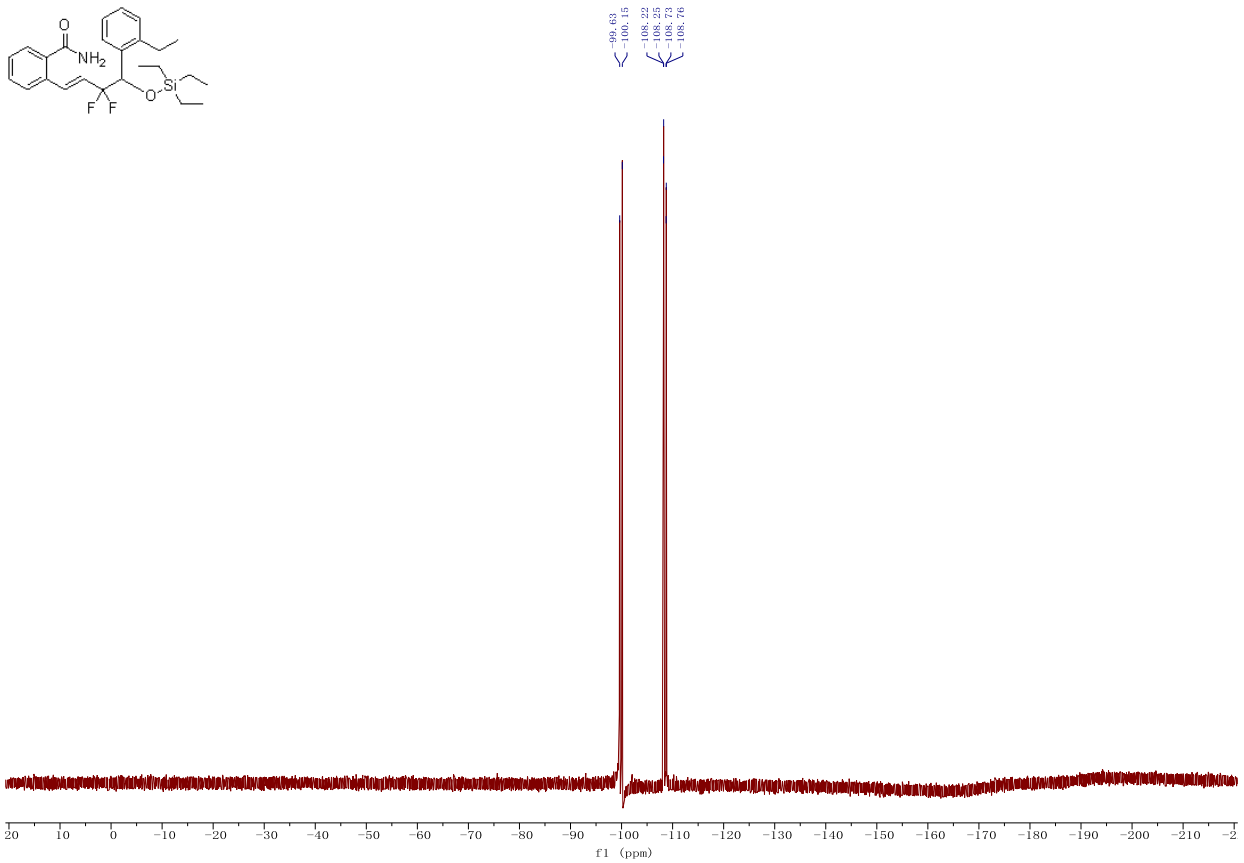

171.0
139.7
139.7
134.9
133.9
133.8
133.5
132.4
132.3
131.4
131.0
129.1
129.0
128.9
127.9
127.0
122.6
122.4
122.2
121.6
119.7
118.9
117.7
112.3
76.5
76.2
76.0
6.7
4.7
CN
O
NH2
O
Si
F
F
f1 (ppm)


100.86
100.88
100.90
101.38
101.40
101.42
107.16
107.18
107.20
107.68
107.71
107.73
CN
O
NH2
O
Si
F
F
f1 (ppm)

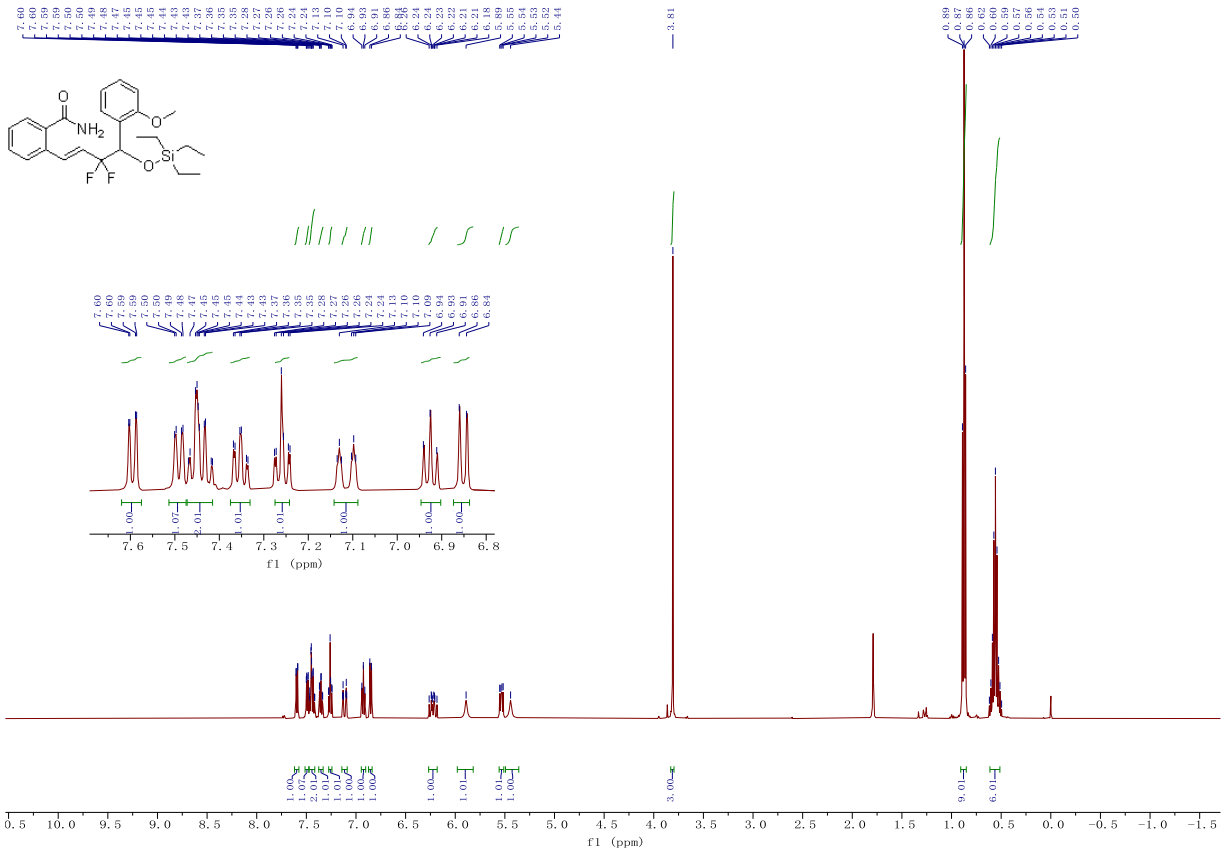
(*E*)-2-(4-(2-ethylphenyl)-3,3-difluoro-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3aj)

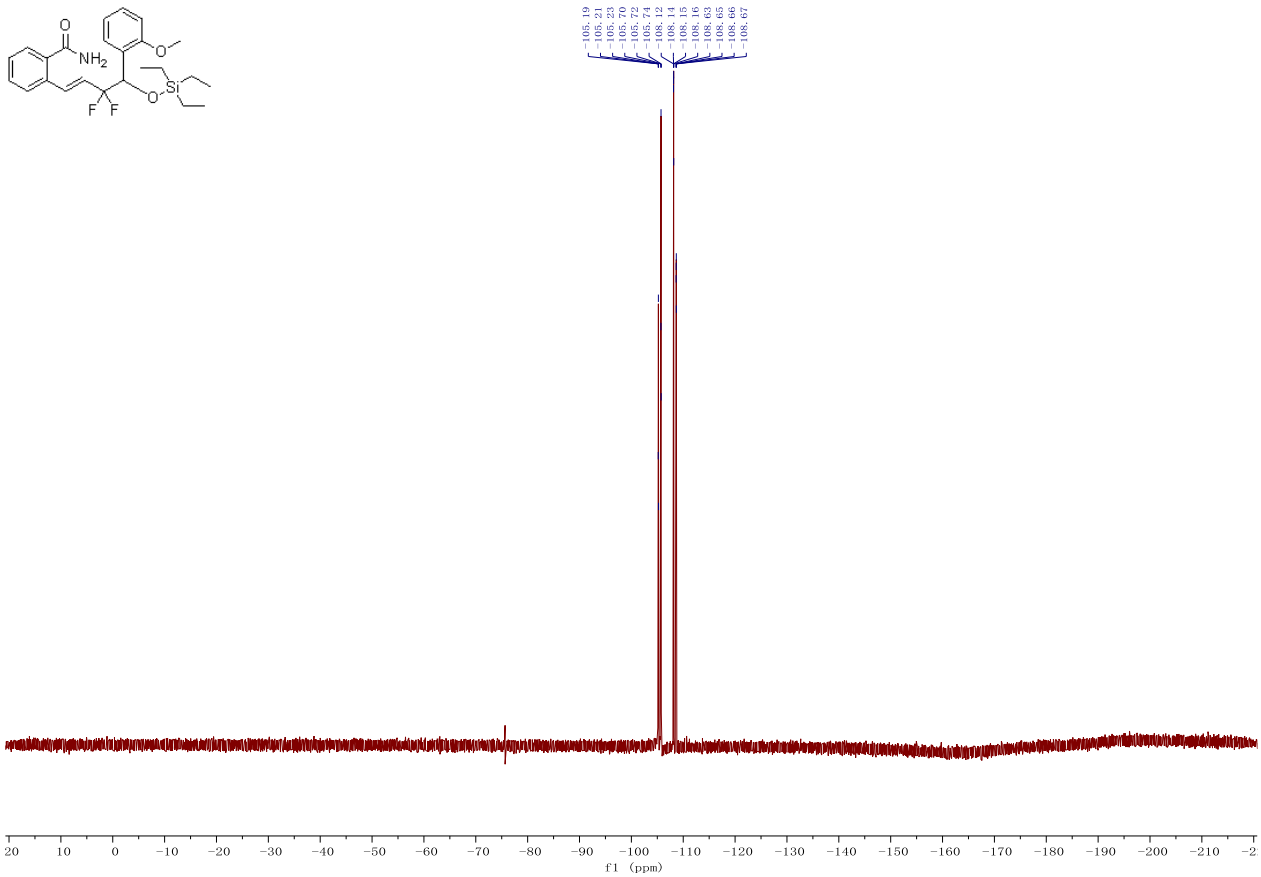


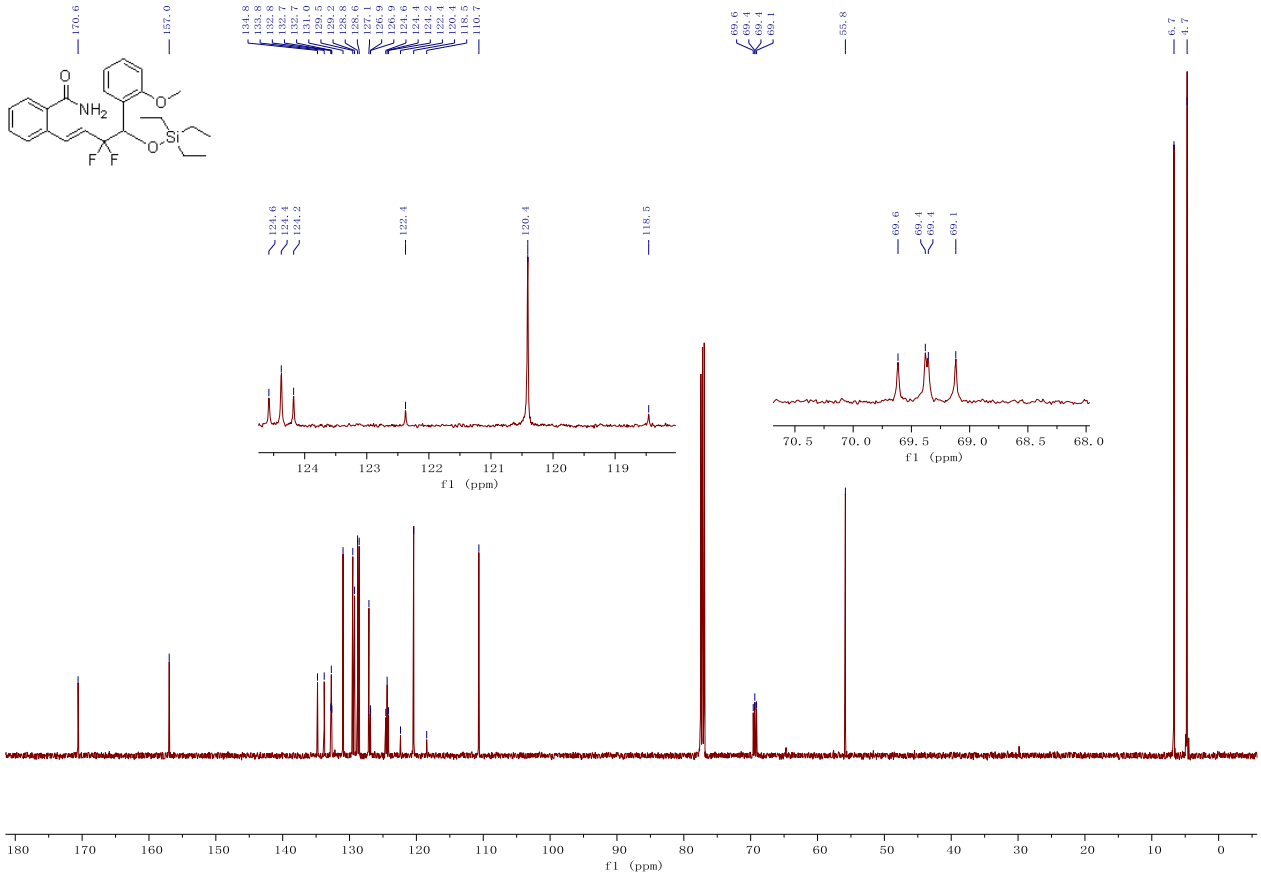




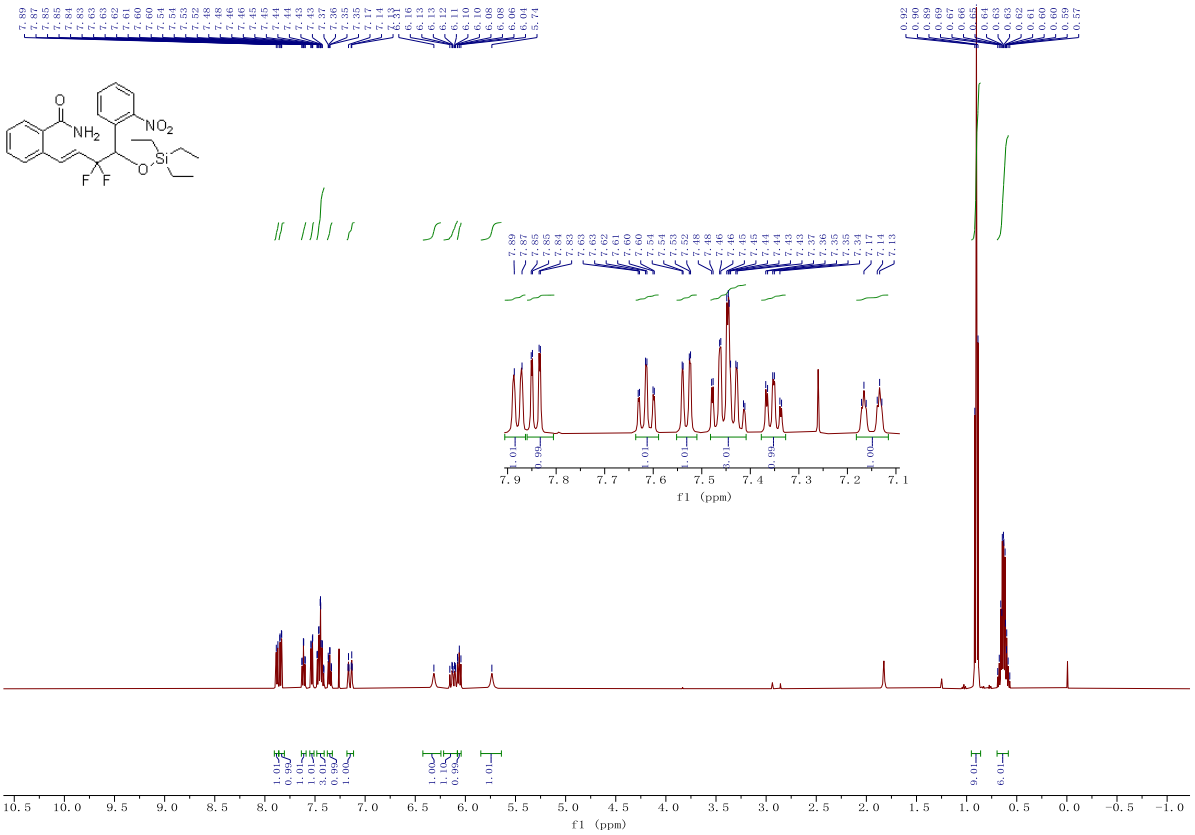
(*E*)-2-(3,3-difluoro-4-(2-methoxyphenyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3ak)

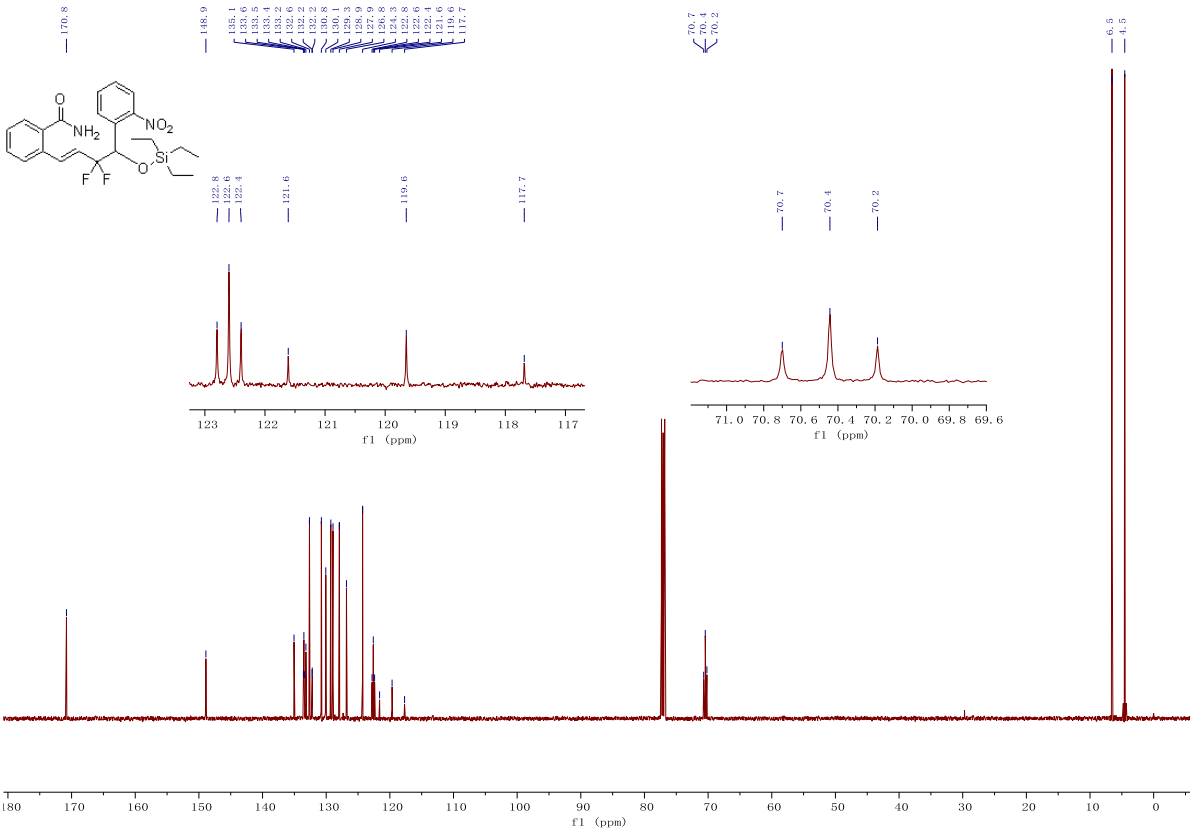


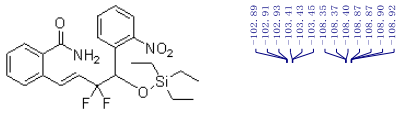

O
NH2
O
Si
O
F F
-105.19
-105.21
-105.23
-105.70
-105.72
-105.74
-108.12
-108.14
-108.15
-108.16
-108.63
-108.65
-108.66
-108.67
f1 (ppm)

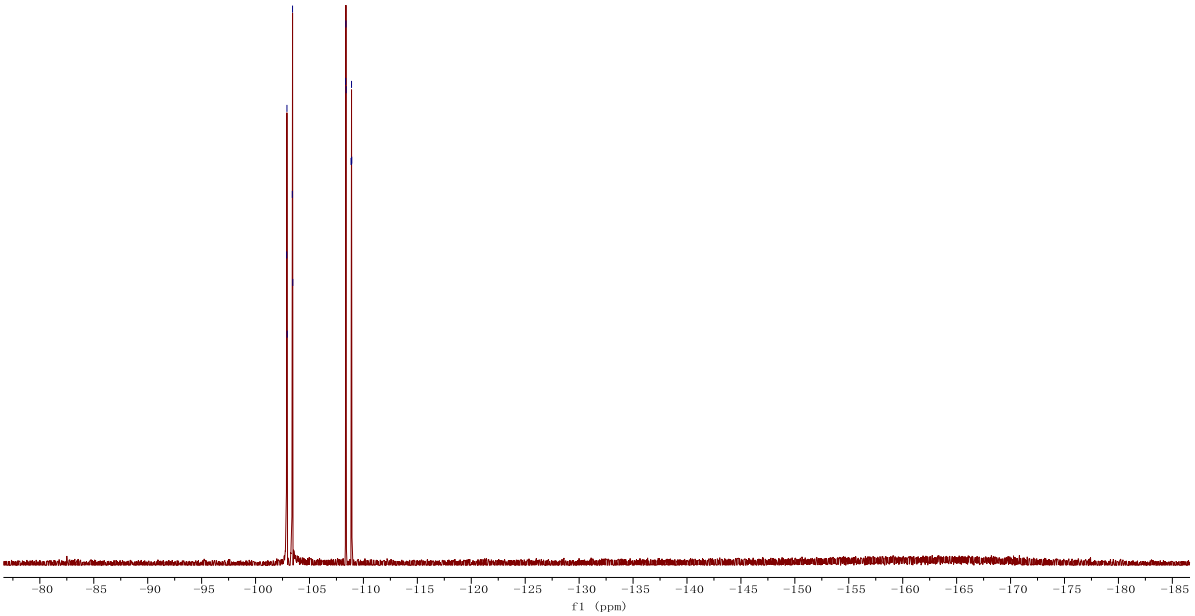

O
NH2
O
Si
O
F F
170.6
157.0
134.8
133.8
132.8
132.7
132.7
131.0
130.5
129.2
128.8
128.6
127.1
126.9
126.6
124.4
124.2
122.4
120.4
118.5
110.7
69.6
69.4
69.4
69.1
55.8
6.7
4.7
124.6
124.4
124.2
122.4
120.4
118.5
69.6
69.4
69.4
69.1
f1 (ppm)
f1 (ppm)
f1 (ppm)

(*E*)-2-(3,3-difluoro-4-(2-nitrophenyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3al)

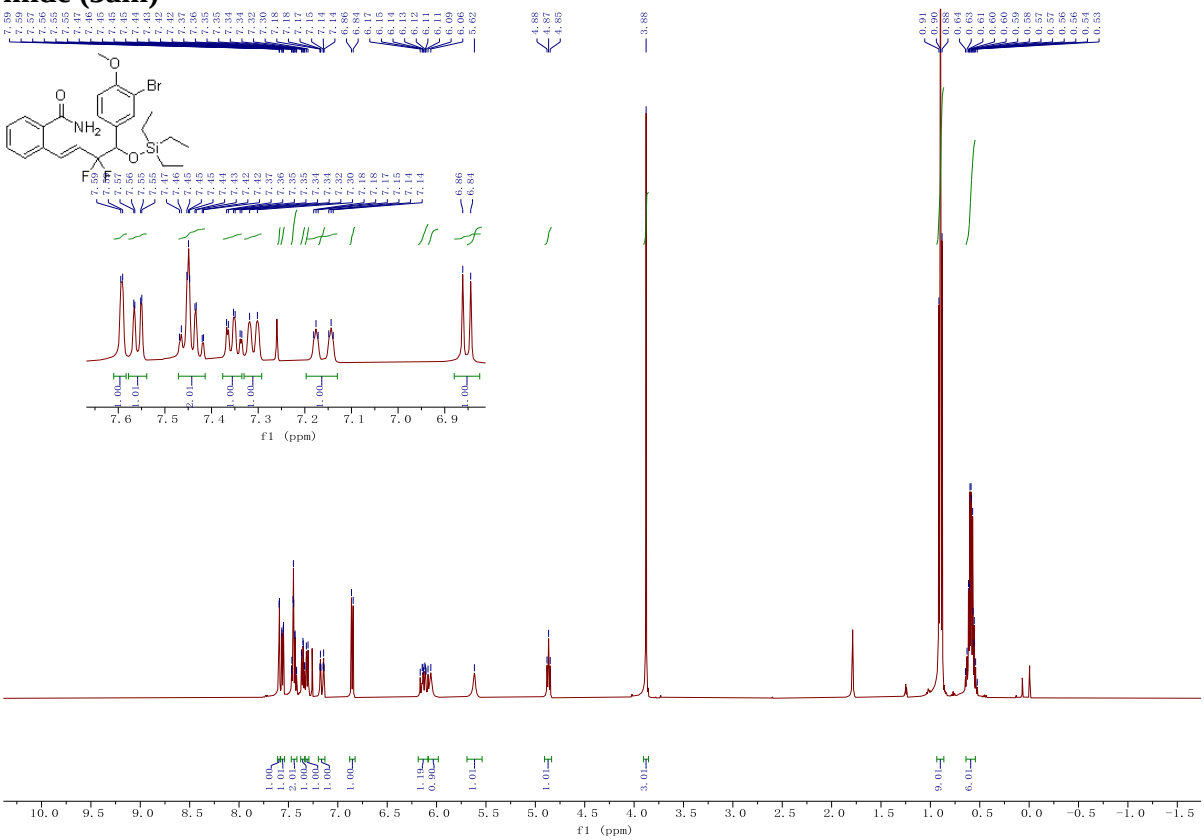


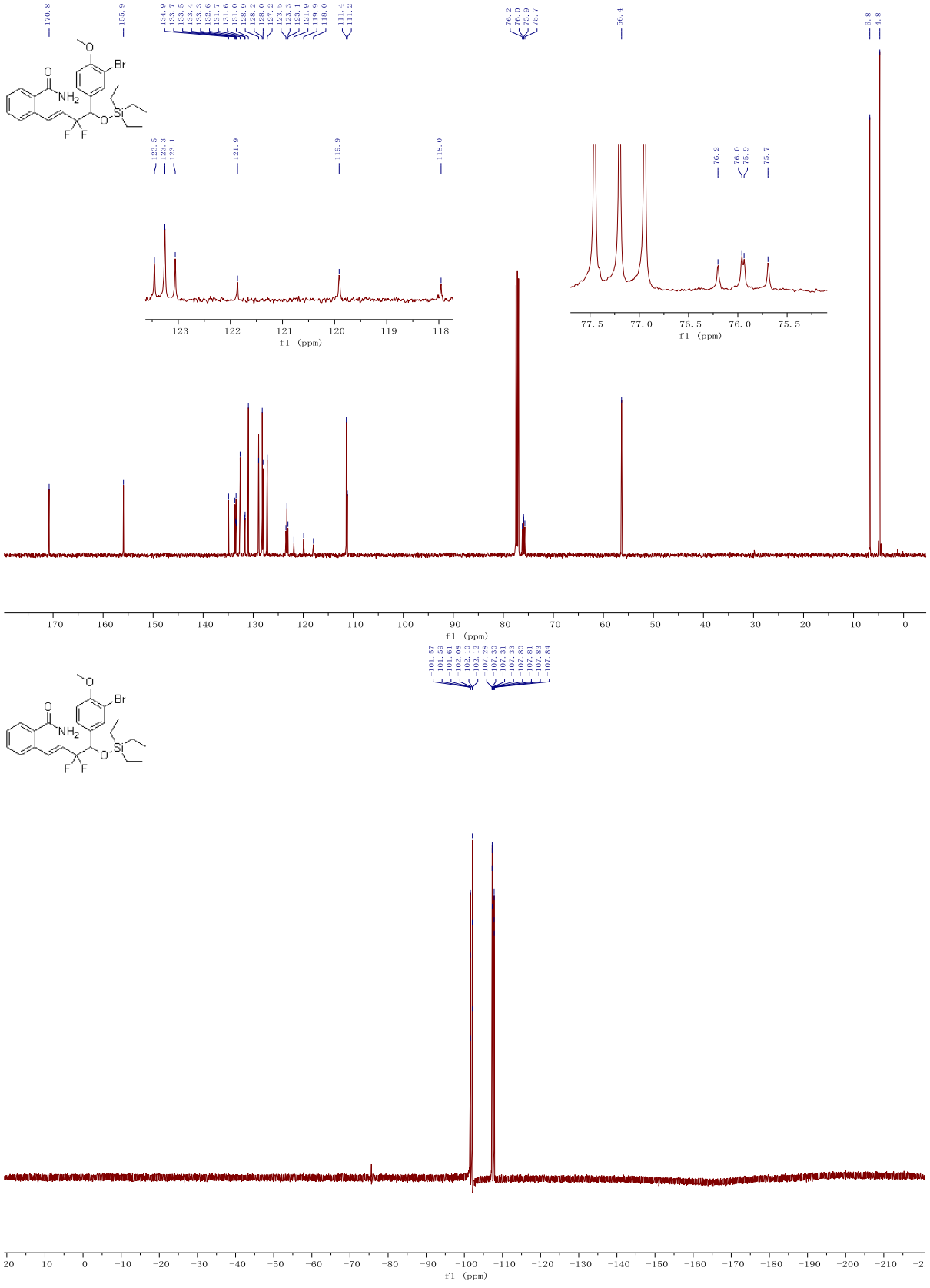






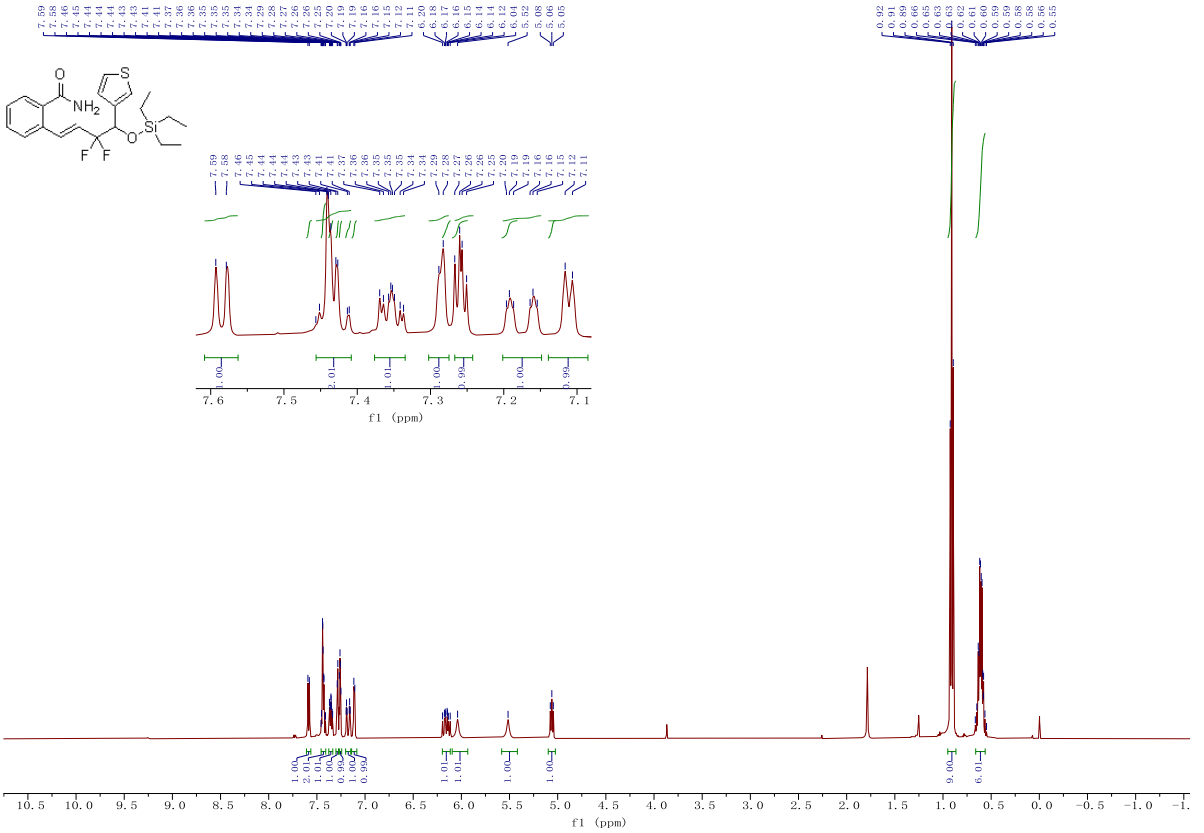
(E)-2-(4-(3-bromo-4-methoxyphenyl)-3,3-difluoro-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3am)

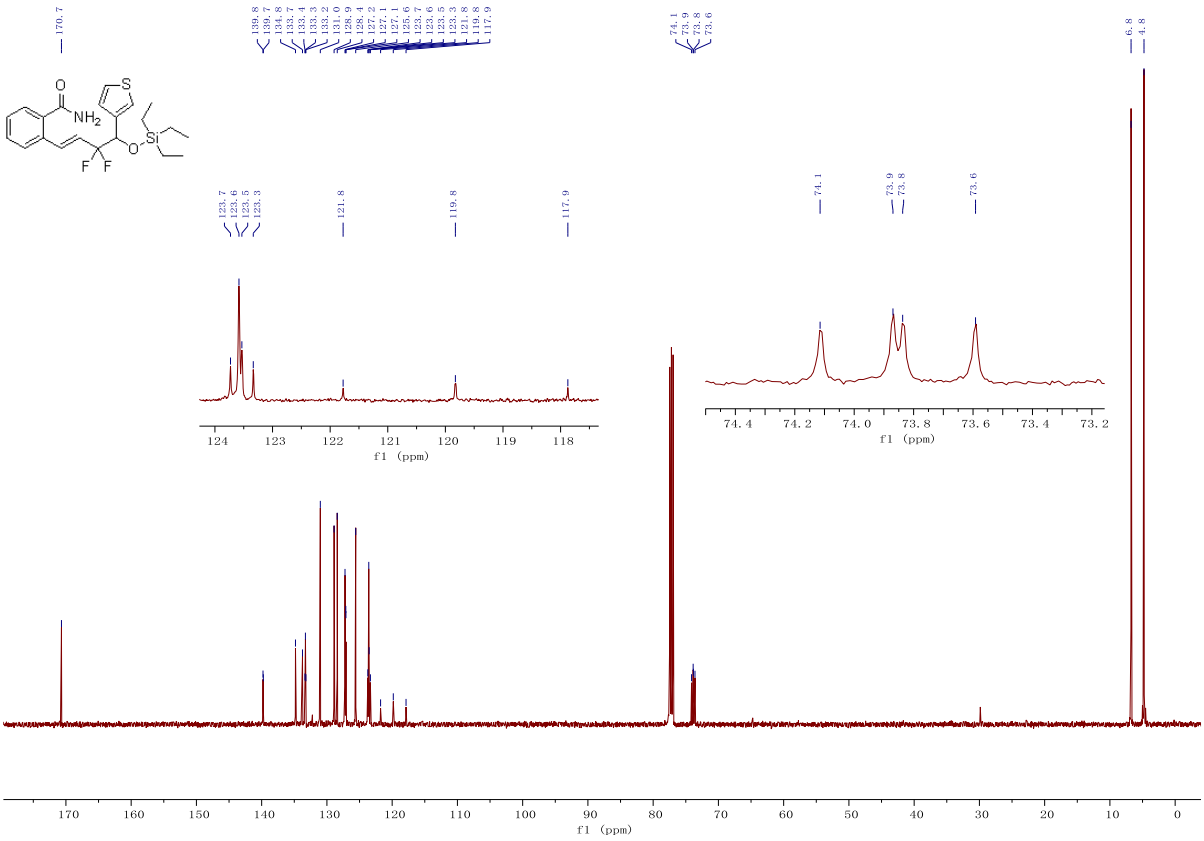


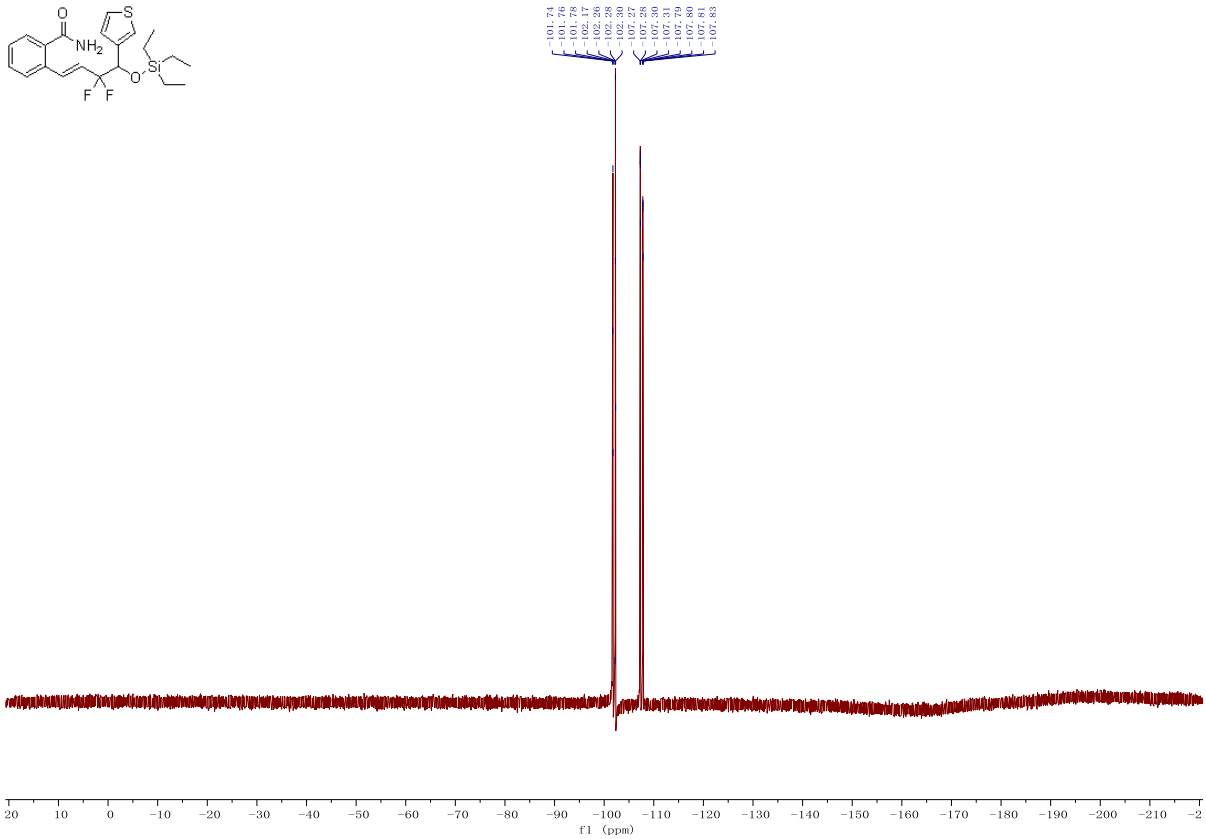

170.8
155.9
134.9
133.7
133.5
133.4
133.3
132.6
131.7
131.6
131.0
128.9
128.2
128.0
127.2
123.5
123.3
123.1
121.9
119.9
118.0
111.4
111.2
76.2
76.0
75.9
75.7
56.4
6.8
4.8
O
Br
NH2
O
Si
F F
f1 (ppm)

101.57
101.69
101.81
102.08
102.10
102.12
107.28
107.30
107.31
107.33
107.80
107.81
107.83
107.84
O
Br
NH2
O
Si
F F
f1 (ppm)

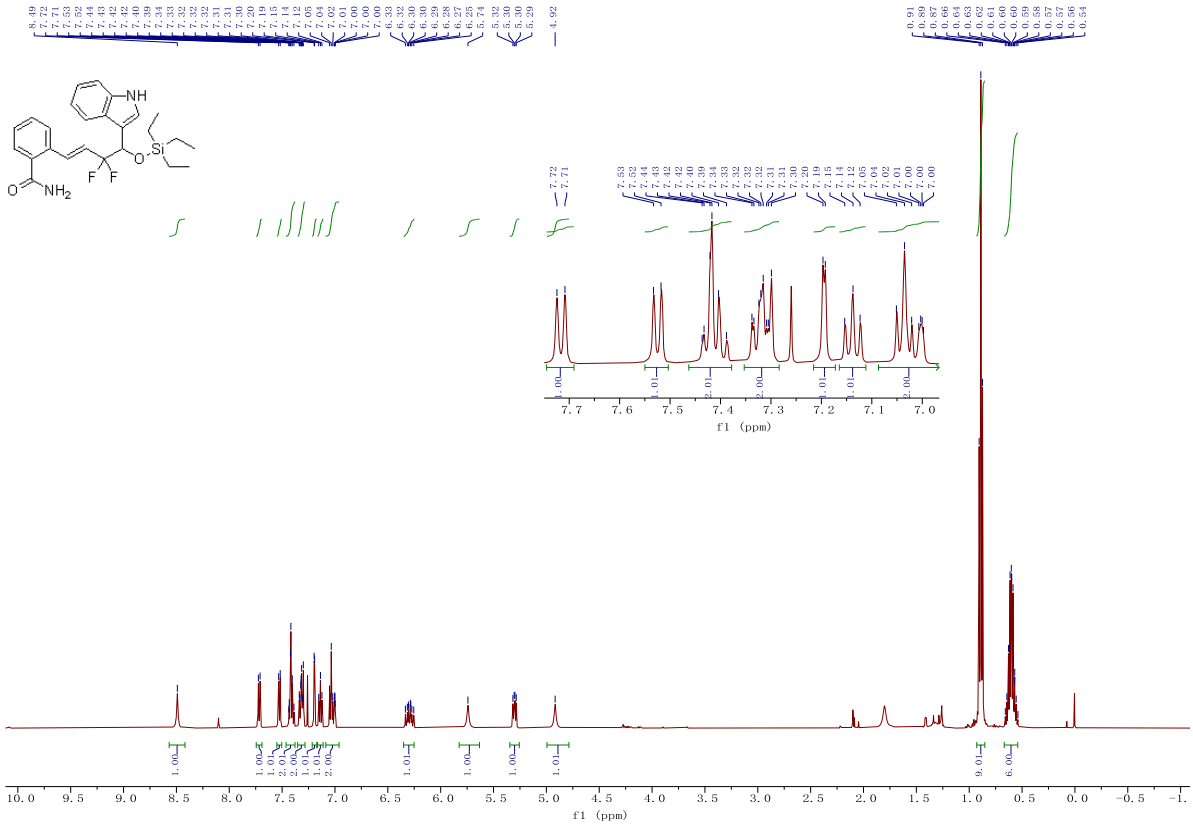
(*E*)-2-(3,3-difluoro-4-(thiophen-3-yl)-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3an)

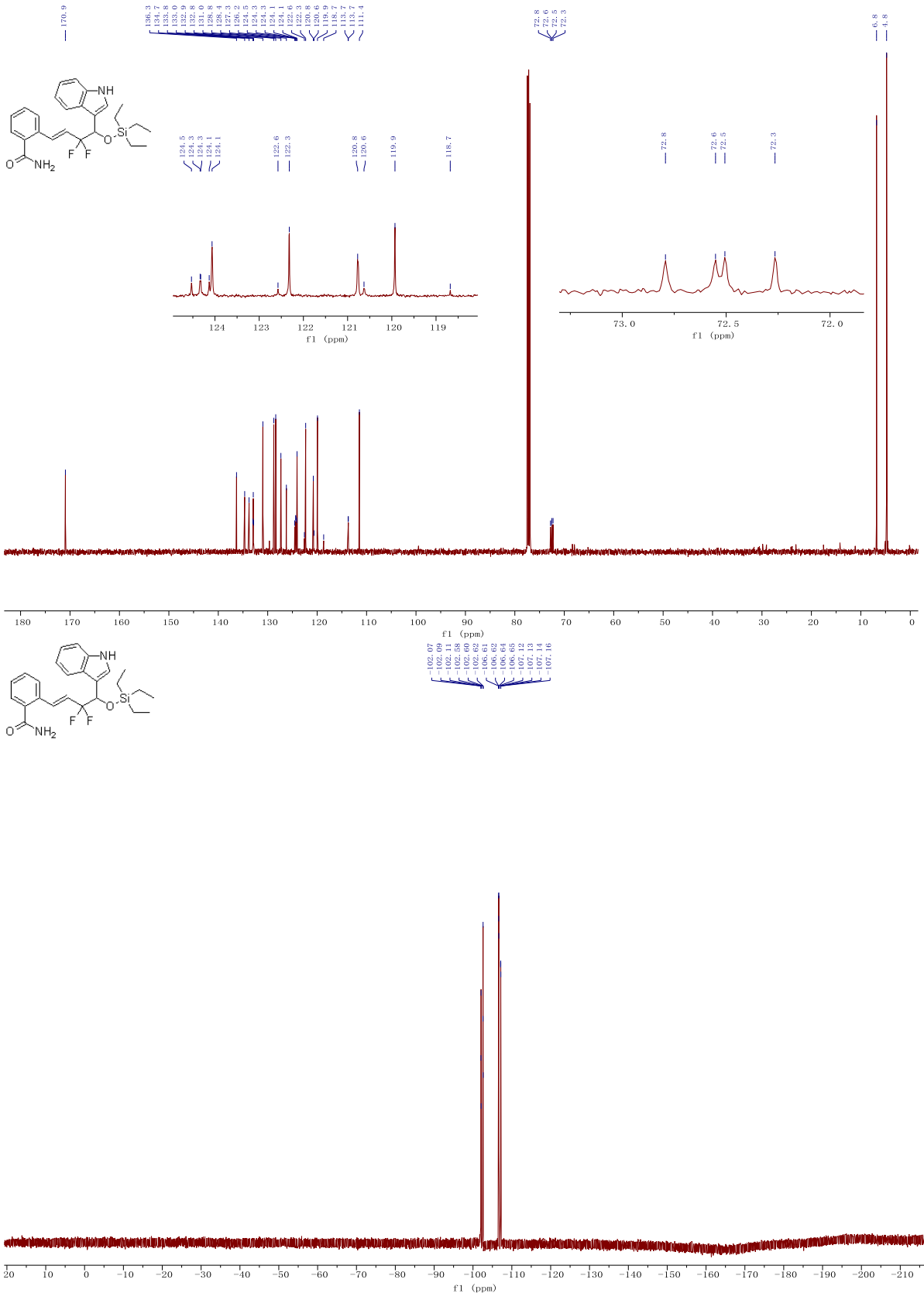






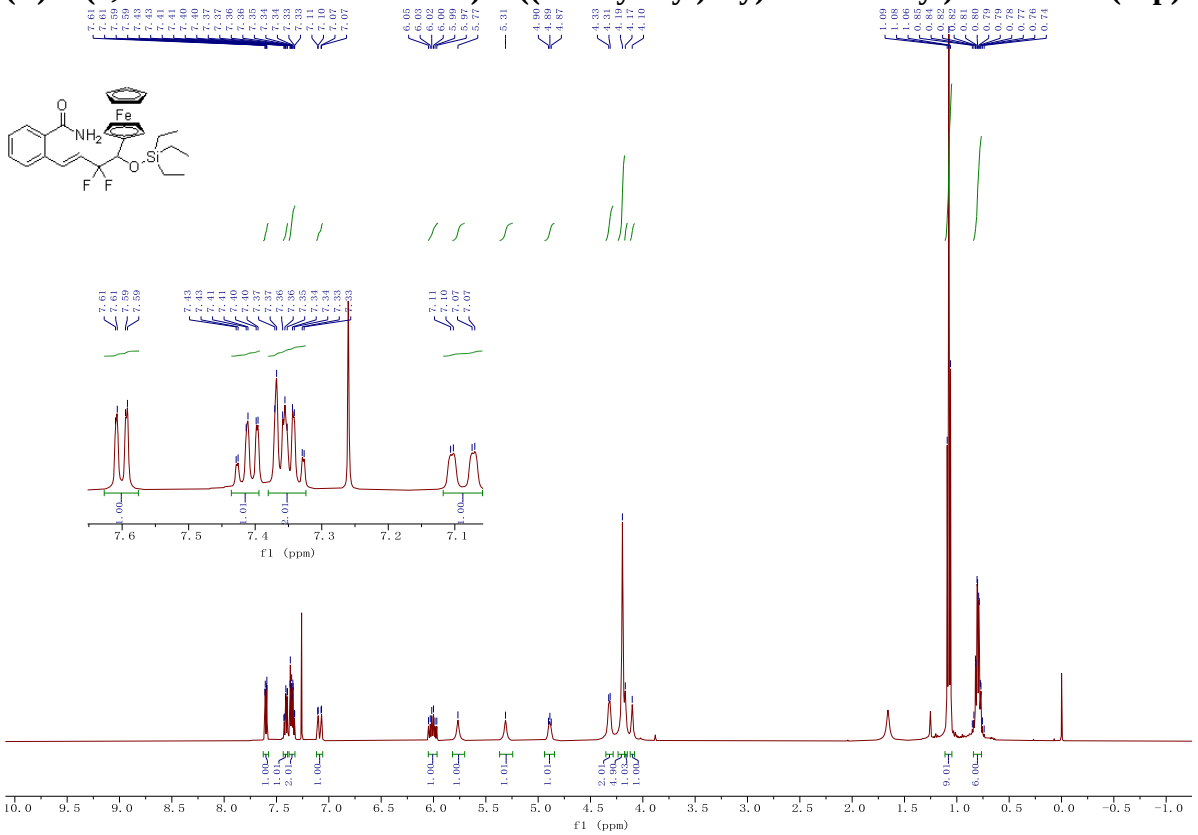
(*E*)-2-(3,3-difluoro-4-(1H-indol-3-yl)-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3ao)

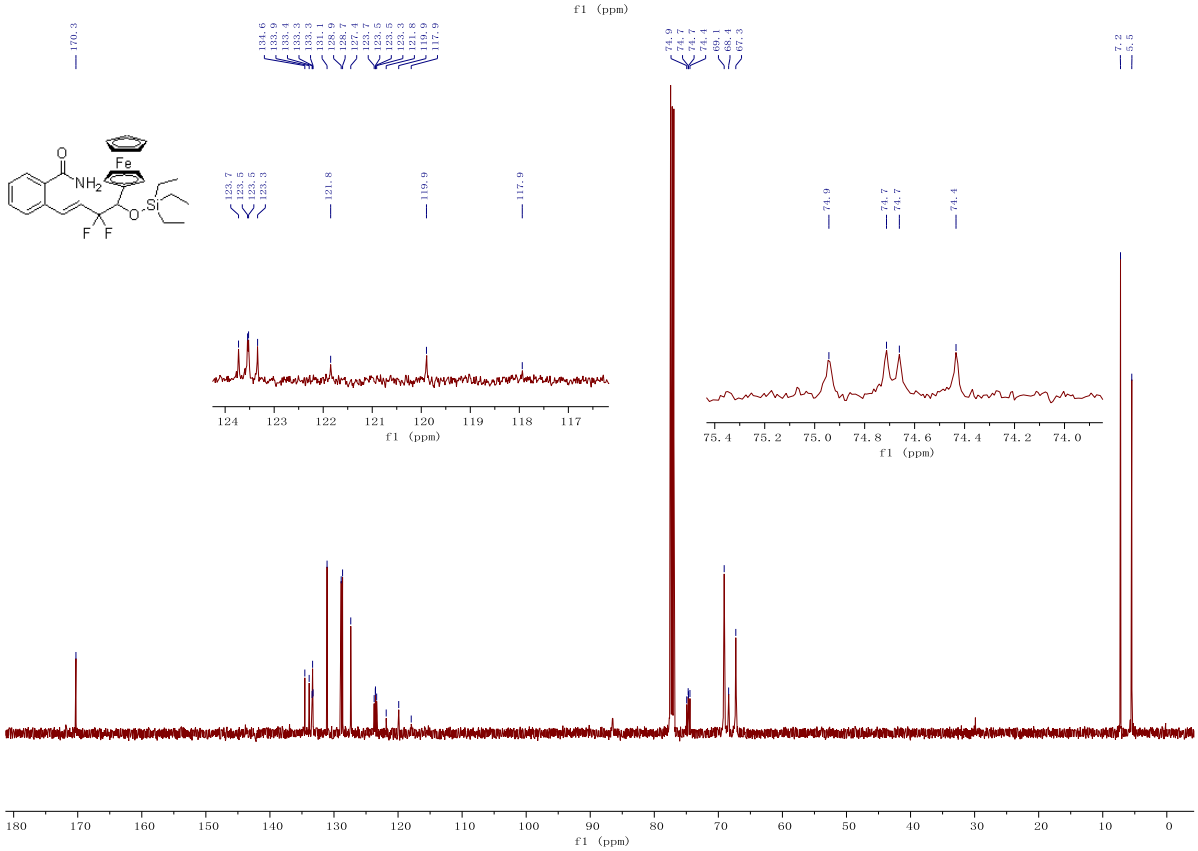


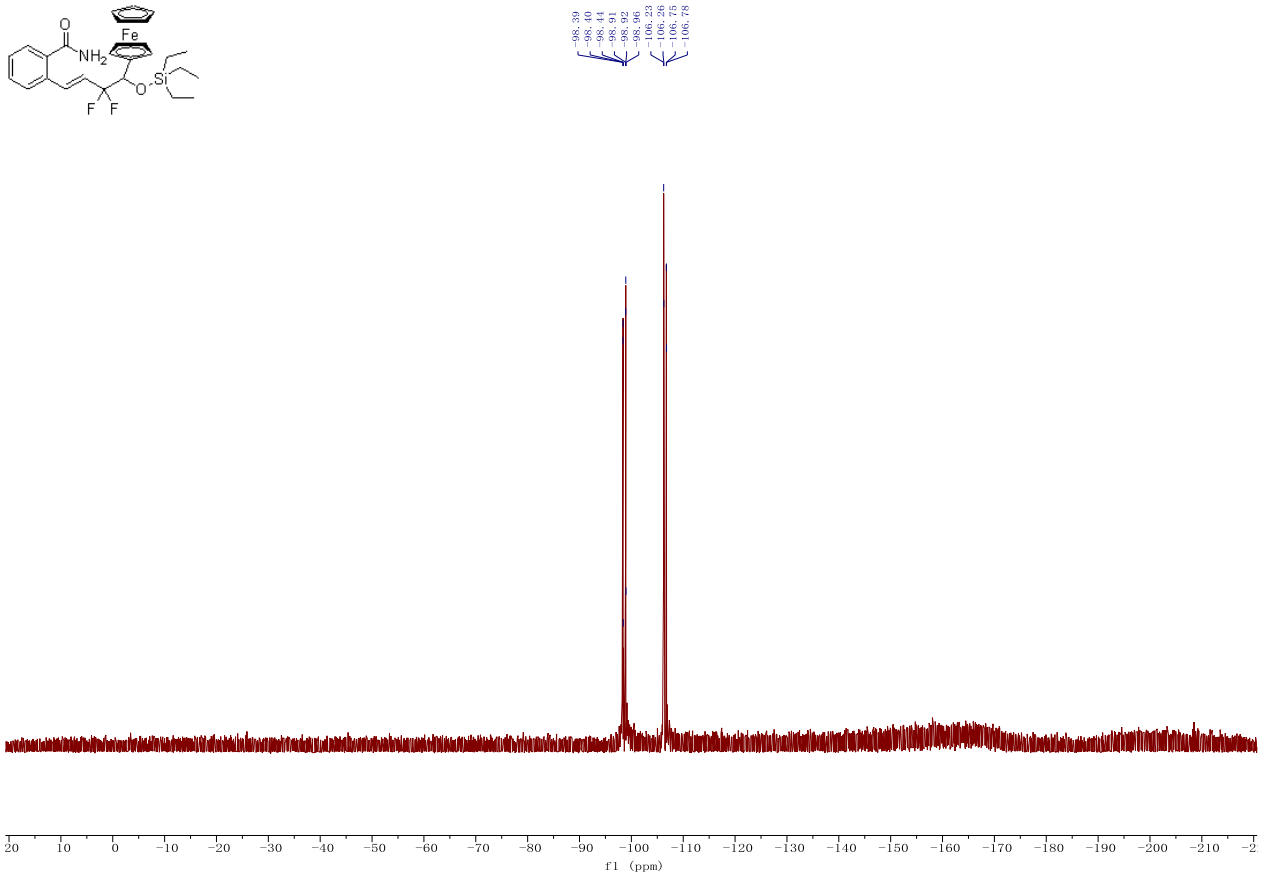

NH
O
Si
F F
O NH2
f1 (ppm)

f1 (ppm)

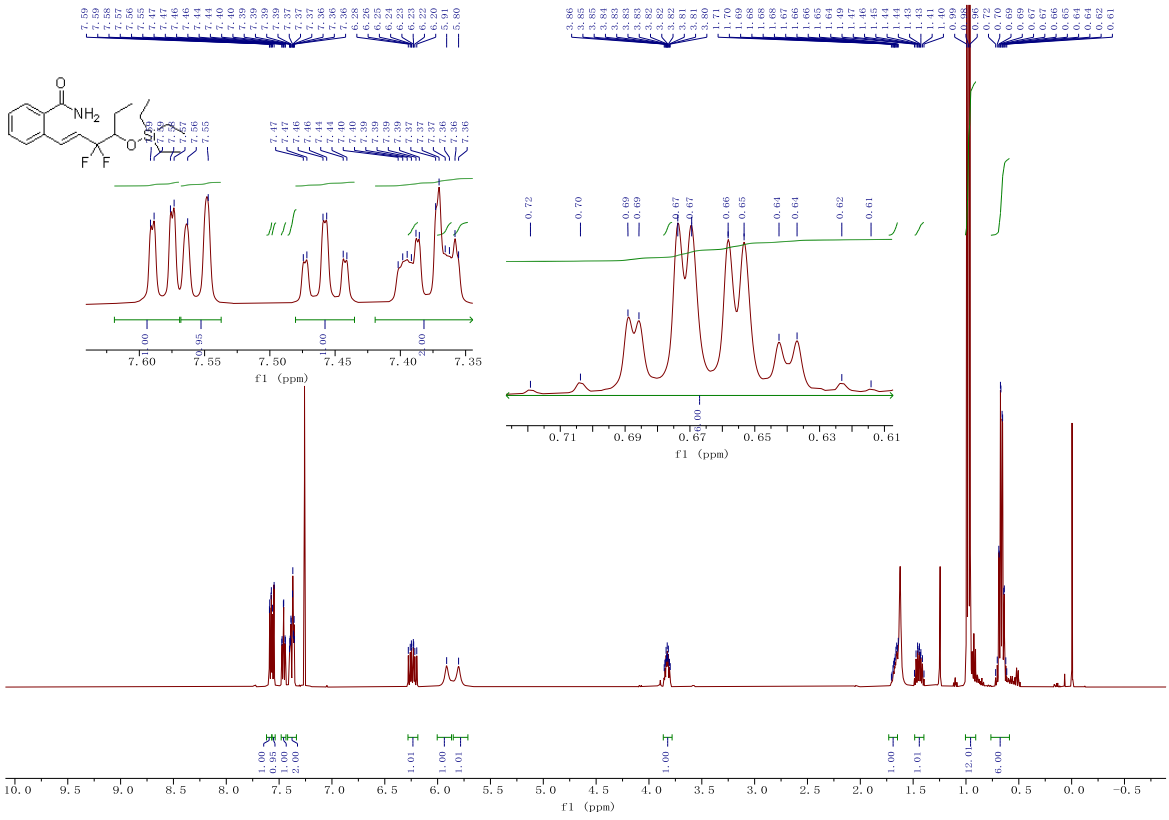
(*E*)-2-(3,3-difluoro-4- ferrocene)-4-((triethylsilyl)oxy)but-1-en-1-yl)benzamide (3ap)

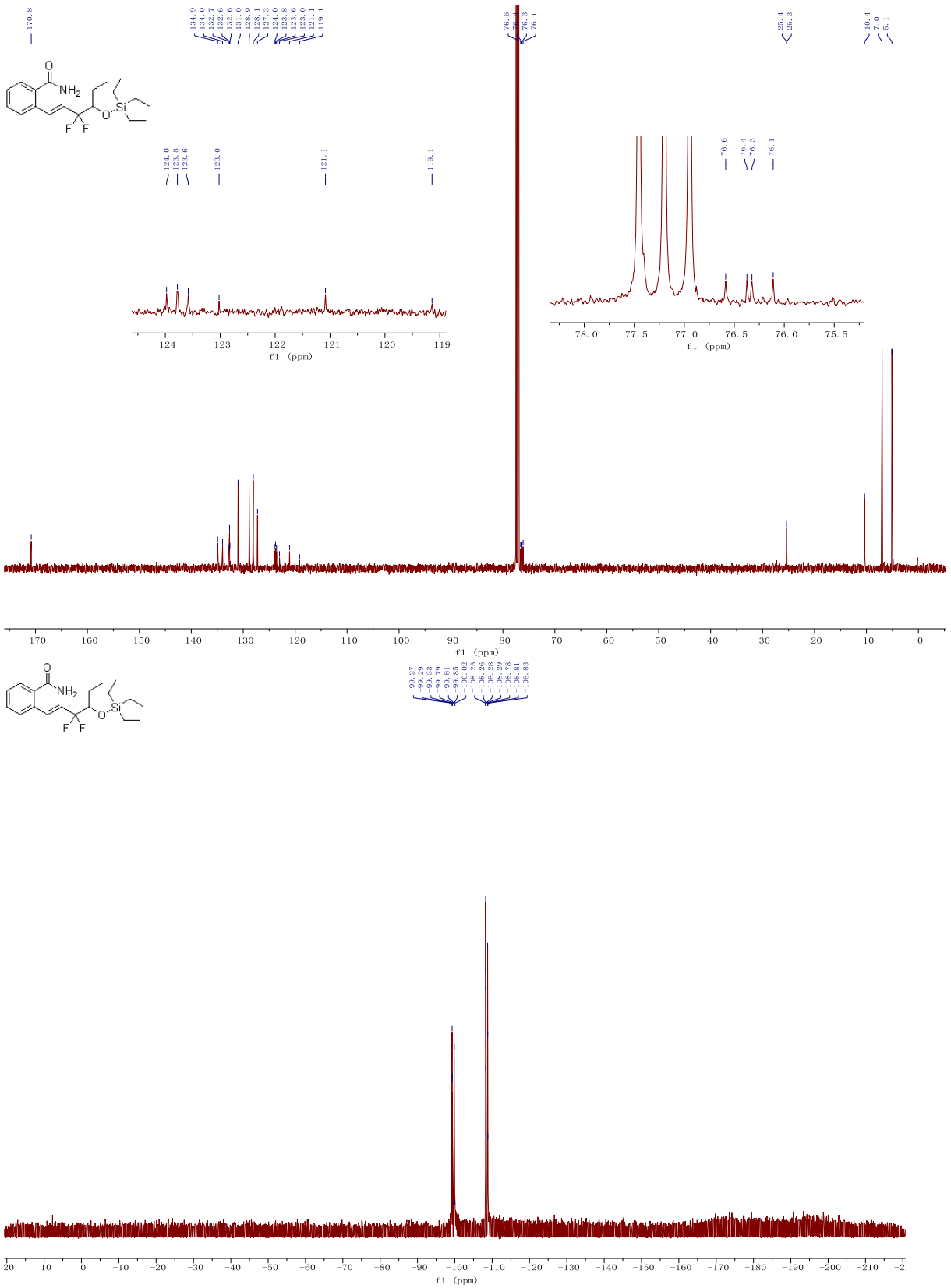




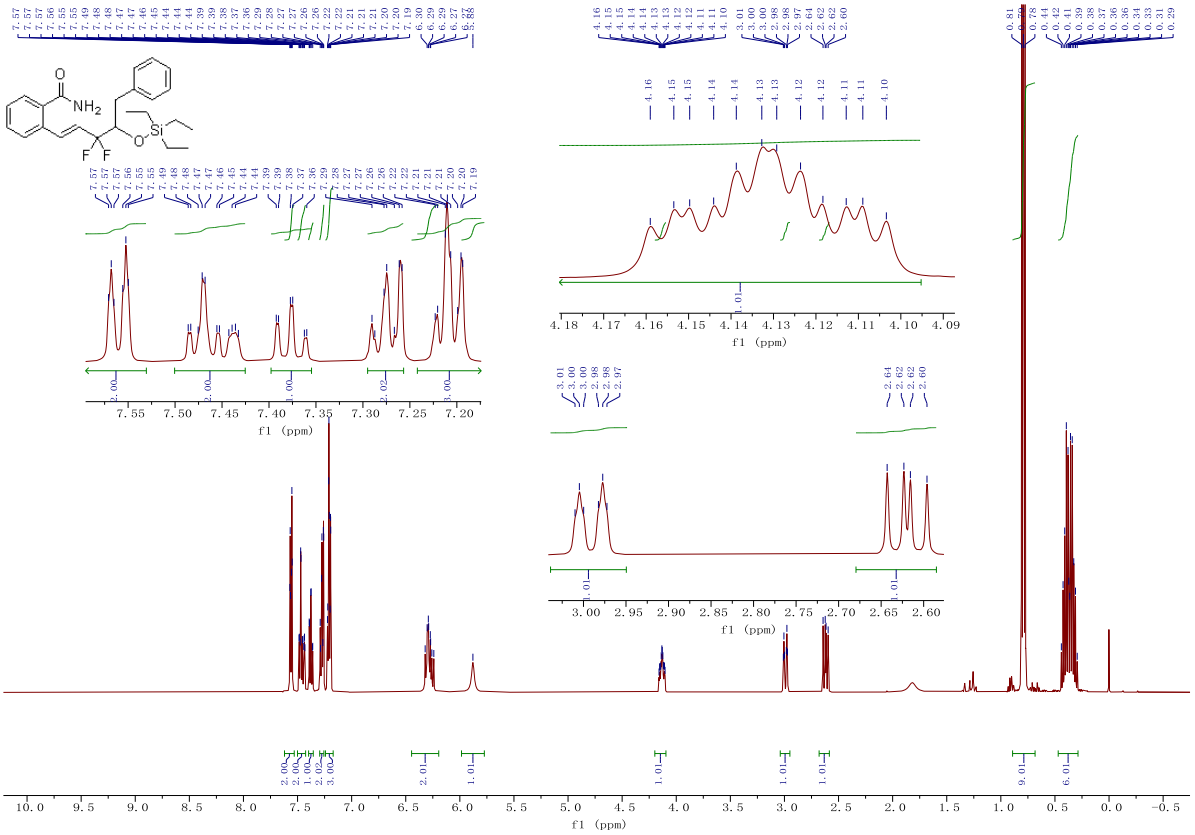


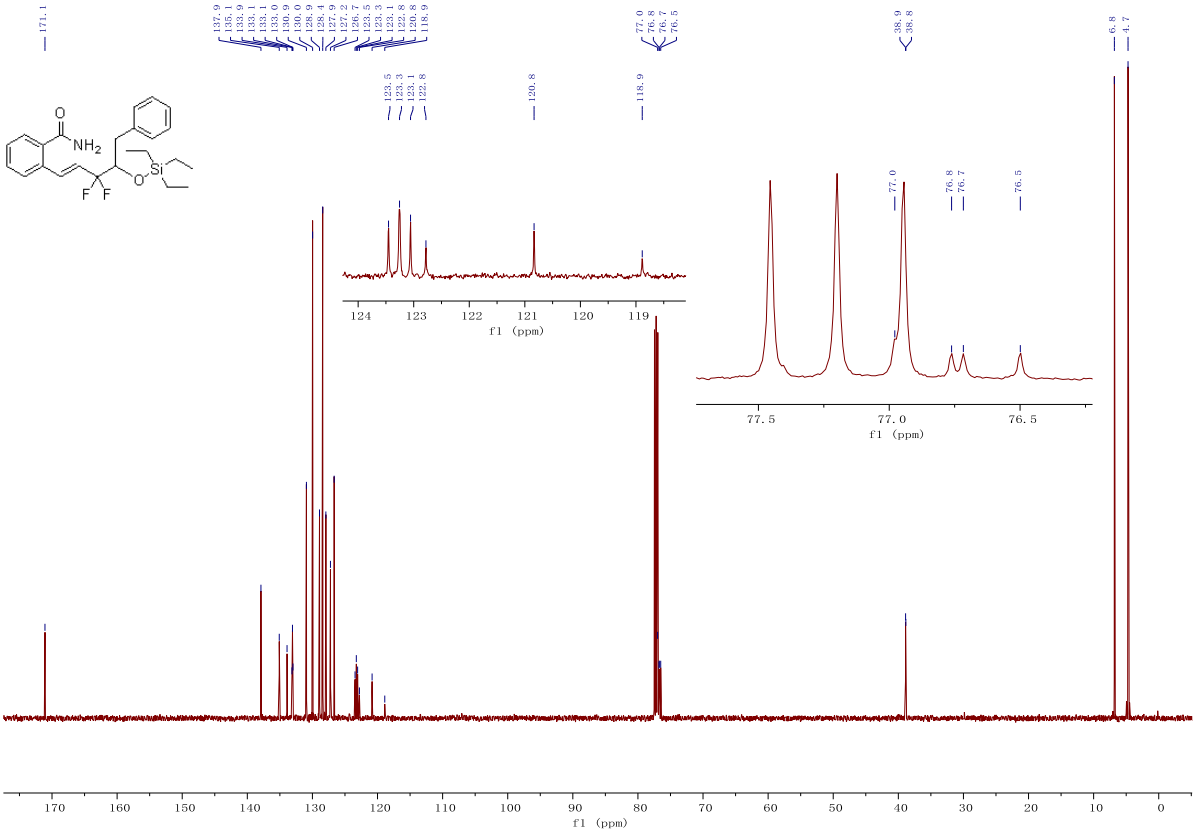
(*E*)-2-(3,3-difluoro-4-((triethylsilyl)oxy)hex-1-en-1-yl)benzamide (3aq)

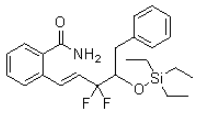


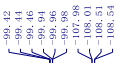

O
NH2
Si
O
F F
170.8
134.9
134.0
132.7
132.6
132.6
131.0
128.9
128.1
127.3
124.0
123.8
123.6
123.0
121.1
119.1
76.6
76.4
76.3
76.1
25.4
25.3
10.4
7.0
5.1
124.0
123.8
123.6
123.0
121.1
119.1
76.6
76.4
76.3
76.1
f1 (ppm)
f1 (ppm)
f1 (ppm)
-99.27
-99.29
-99.33
-99.79
-99.81
-99.85
-100.02
-108.25
-108.26
-108.28
-108.29
-108.78
-108.81
-108.83
f1 (ppm)

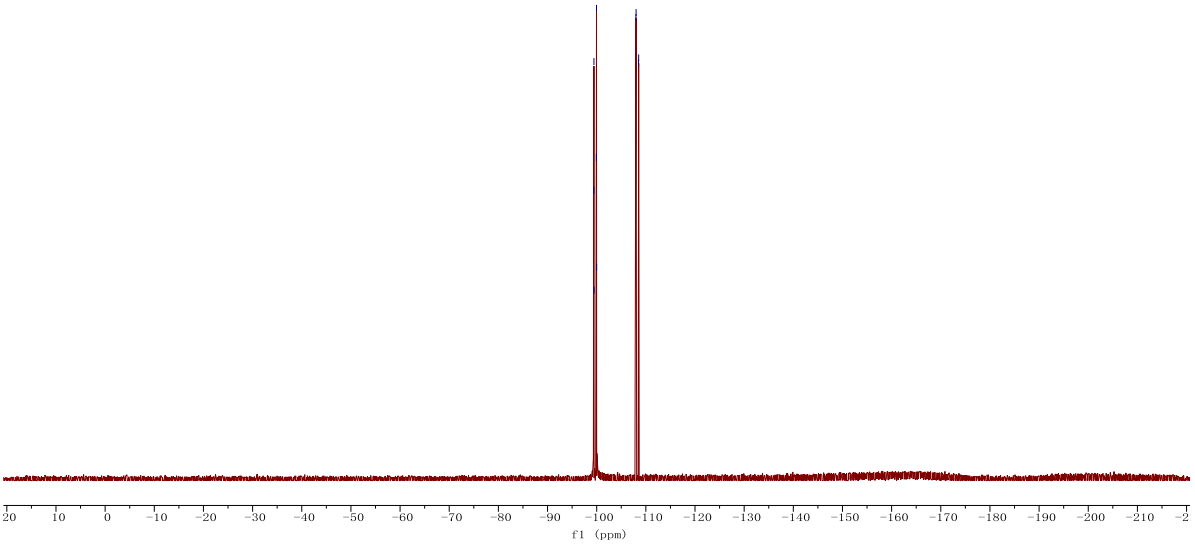
(E)-2-(3,3-difluoro-5-phenyl-4-((triethylsilyl)oxy)pent-1-en-1-yl)benzamide (3ar)



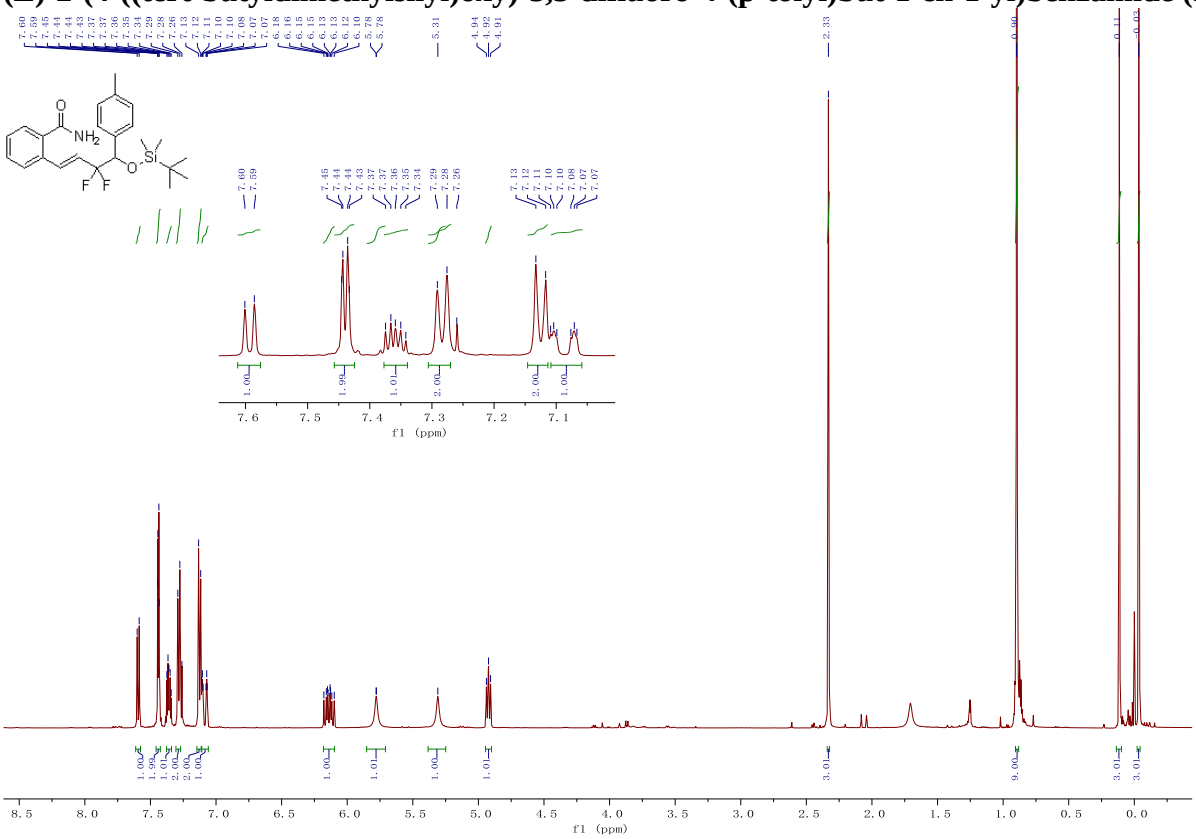


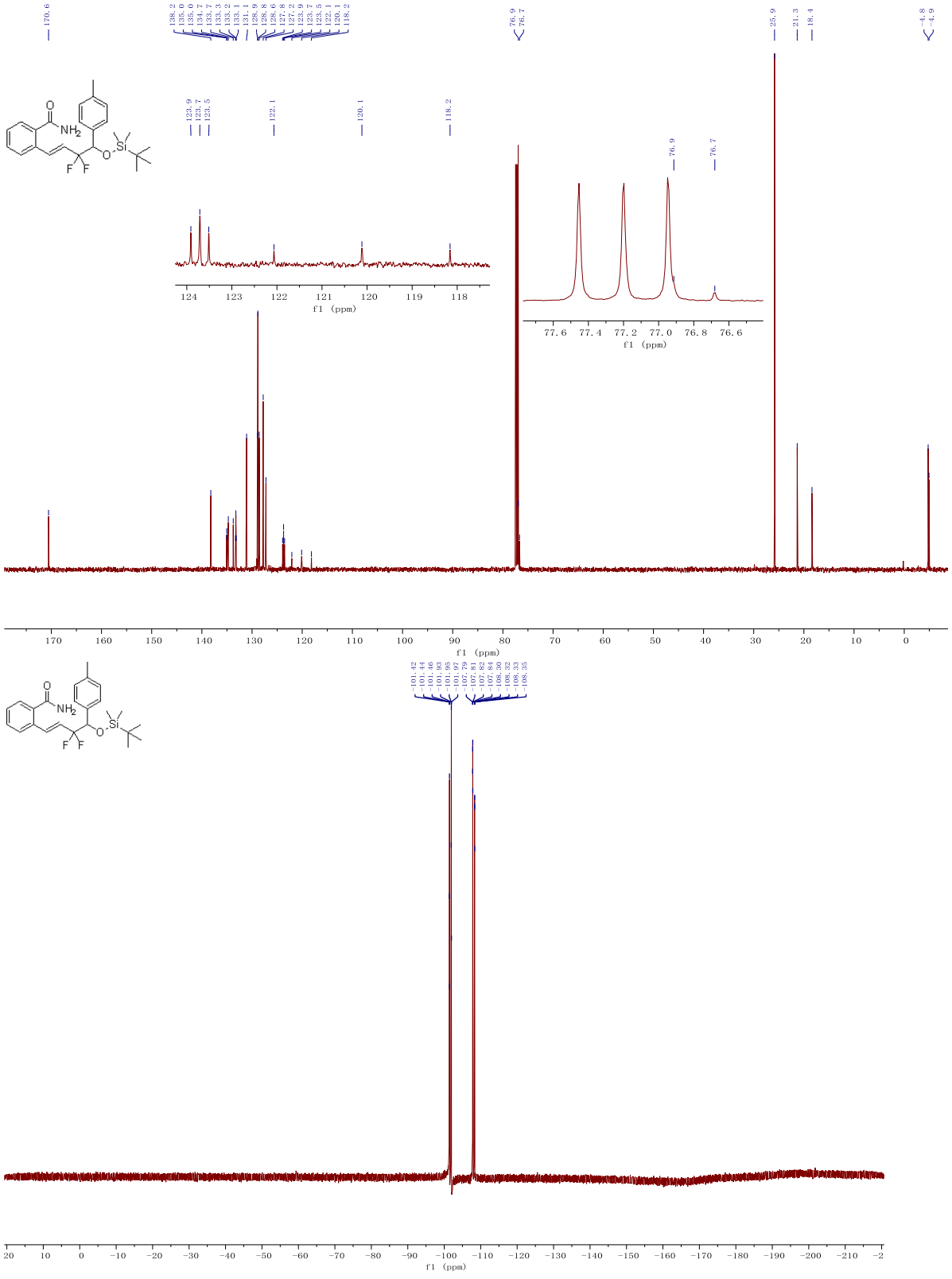






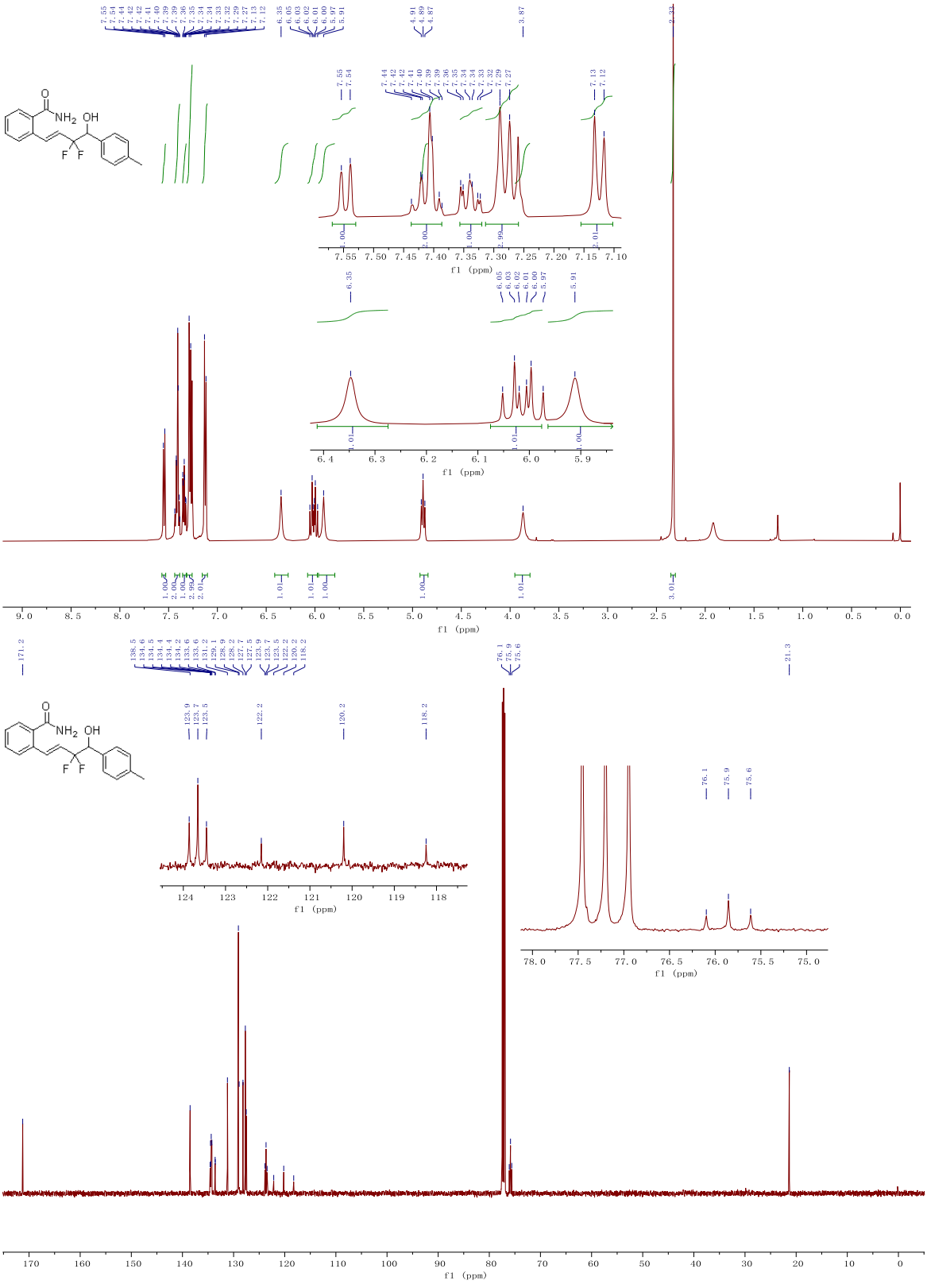
(E)-2-(4-((tert-butyldimethylsilyl)oxy)-3,3-difluoro-4-(p-tolyl)but-1-en-1-yl)benzamide (3as)

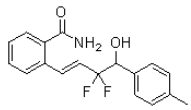


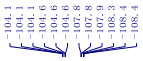

170.6
138.2
135.0
134.7
133.3
133.2
133.1
131.1
128.9
128.6
127.8
127.2
123.9
123.7
123.5
122.1
120.1
118.2
76.9
76.7
25.9
21.3
18.4
-4.8
-4.9
O
NH2
Si
F F
f1 (ppm)
-101.42
-101.44
-101.46
-101.93
-101.95
-101.99
-107.79
-107.81
-107.82
-107.84
-108.30
-108.32
-108.33
-108.35

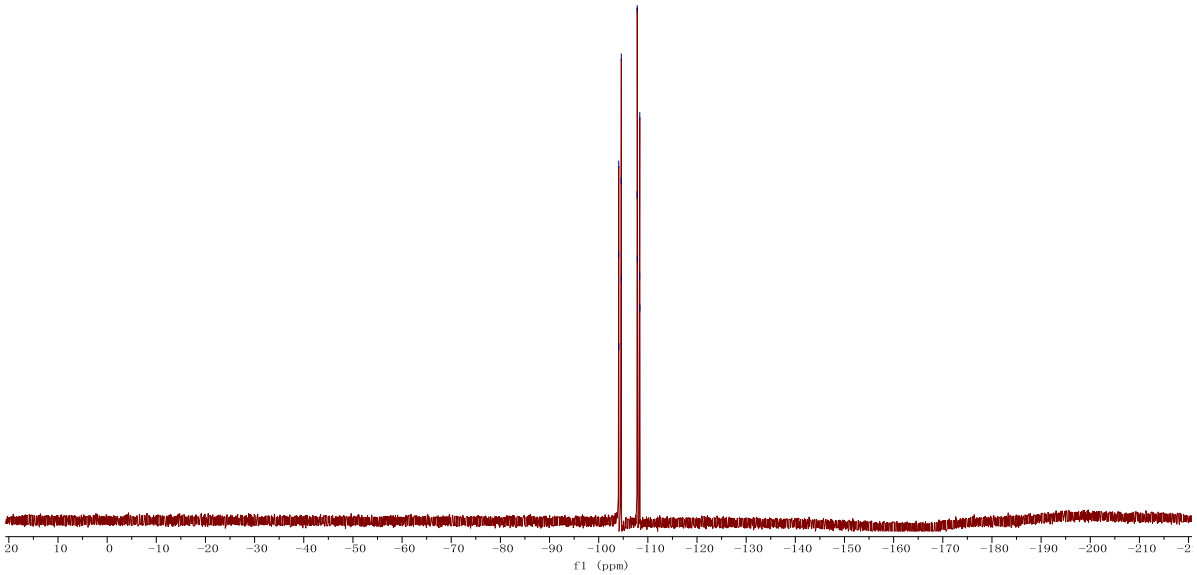
The ^{1}H NMR, ^{13}C NMR, ^{19}F NMR of compounds 4-8

(*E*)-2-(3,3-difluoro-4-hydroxy-4-(p-tolyl)but-1-en-1-yl)benzamide (4)

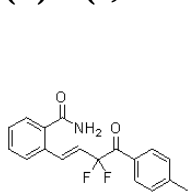


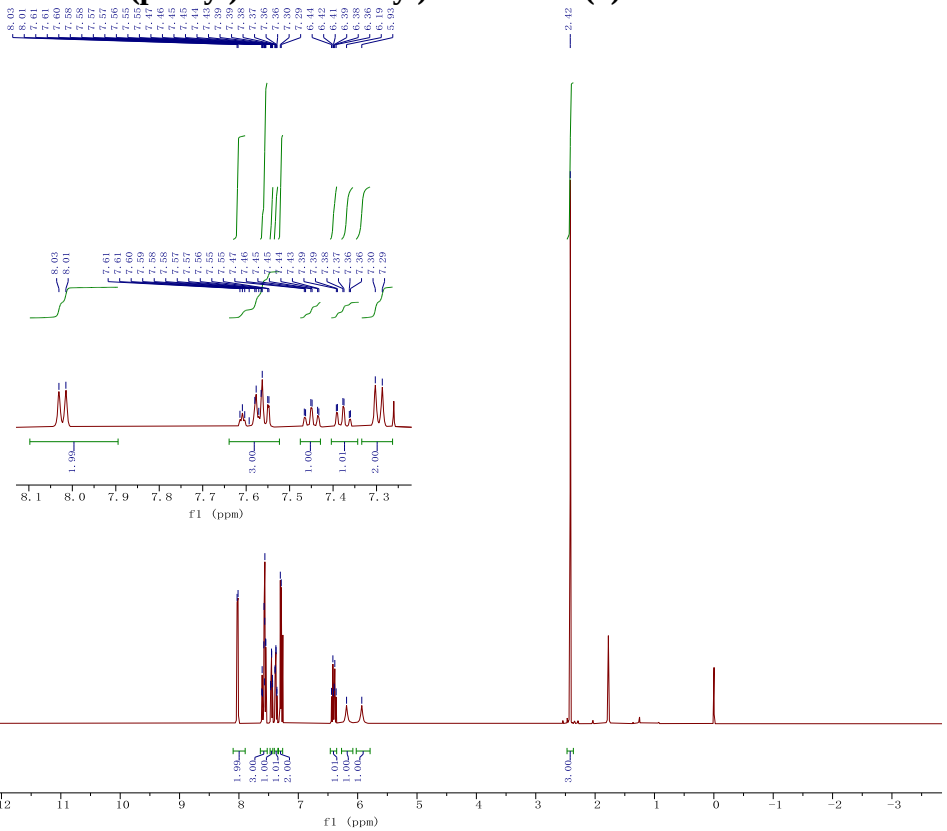


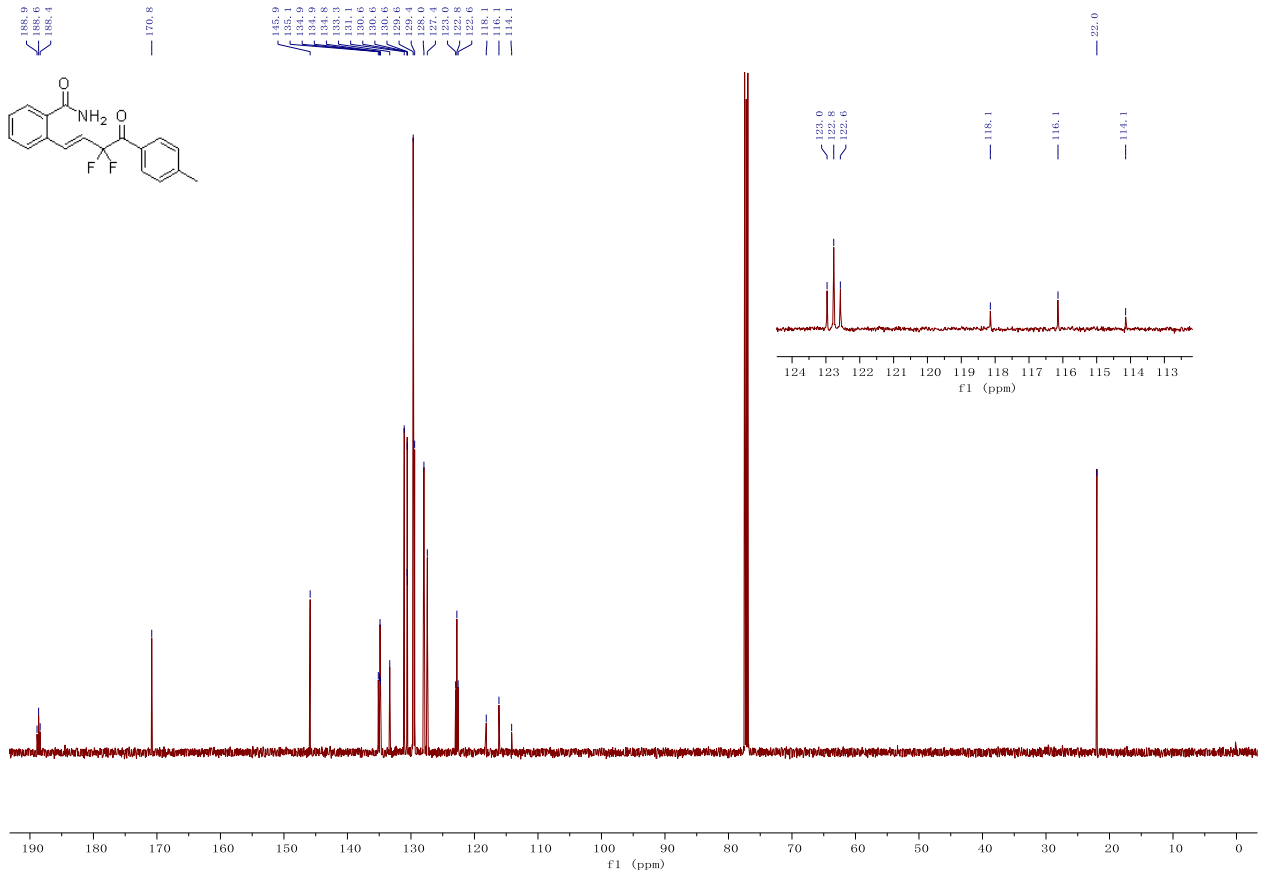


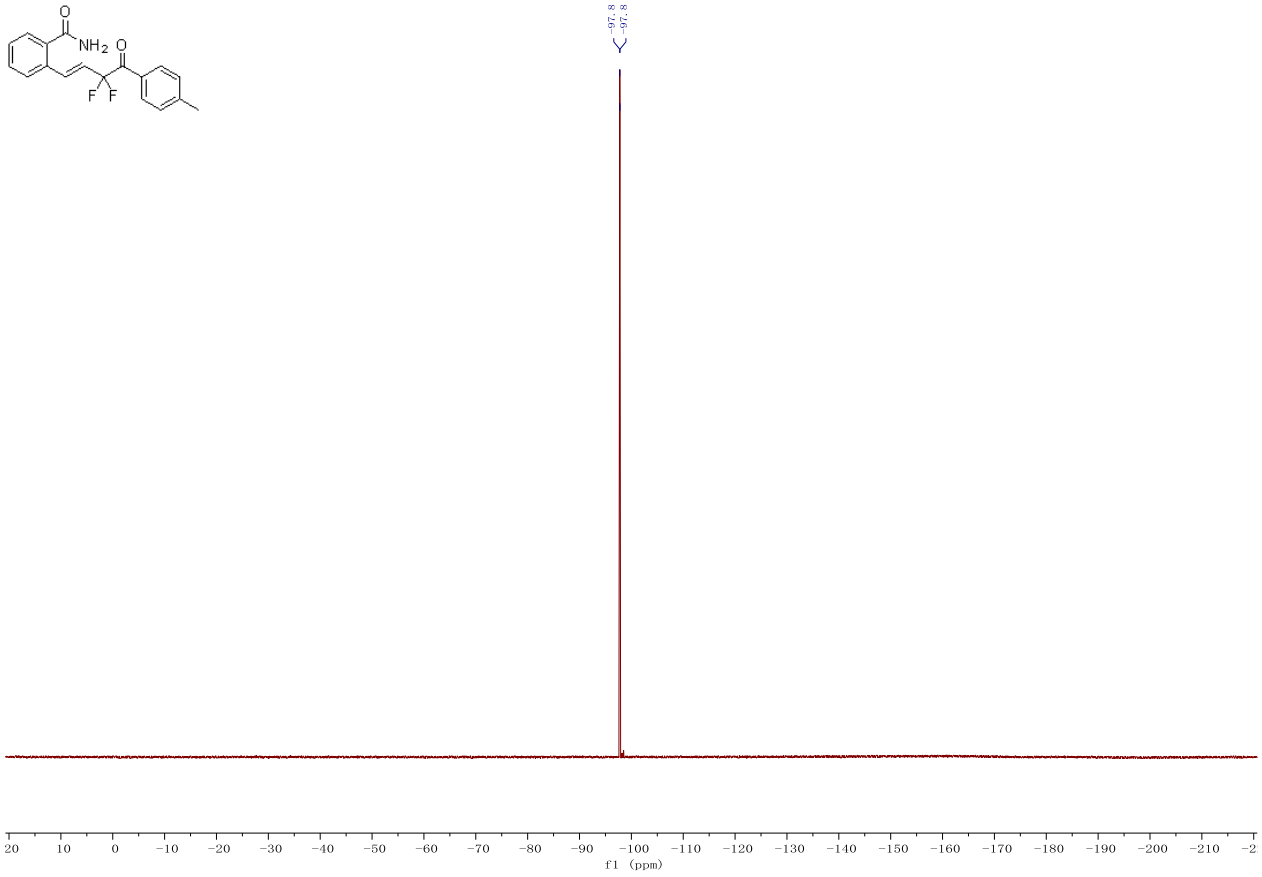


(*E*)-2-(3,3-difluoro-4-oxo-4-(p-tolyl)but-1-en-1-yl)benzamide (5)

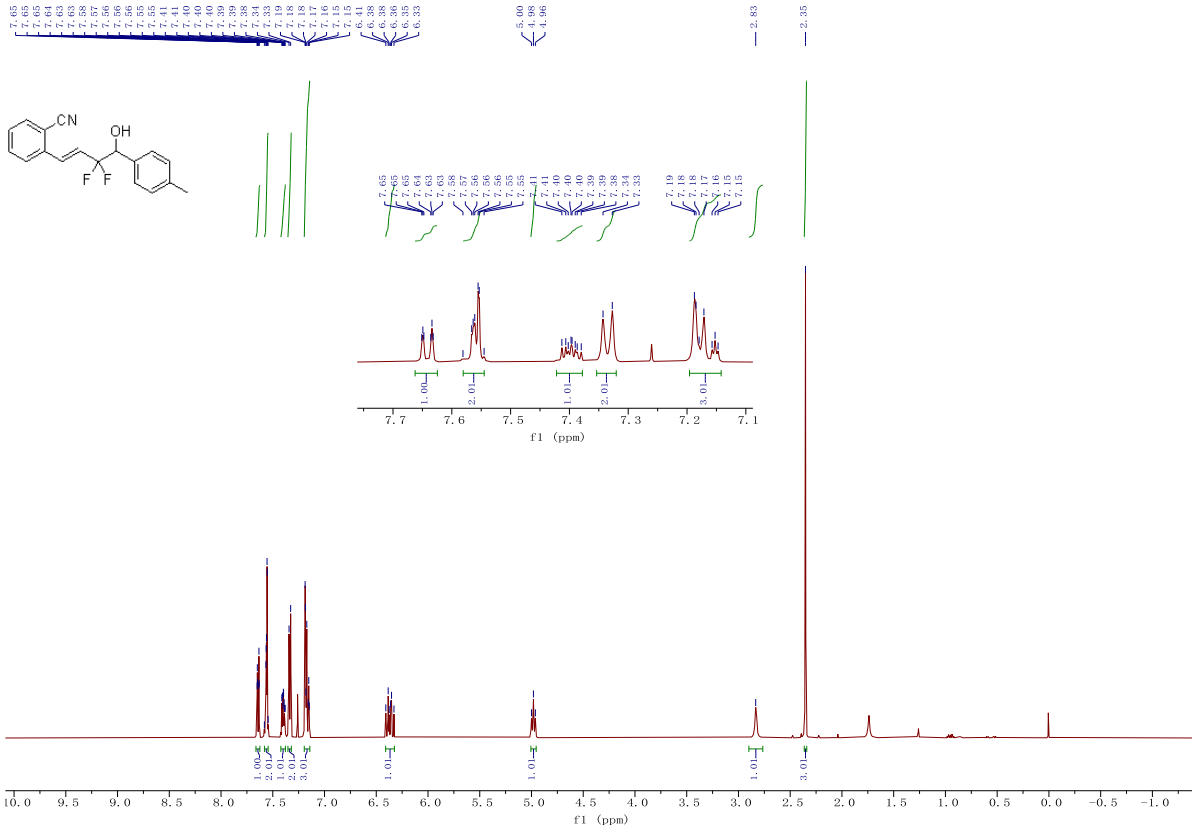


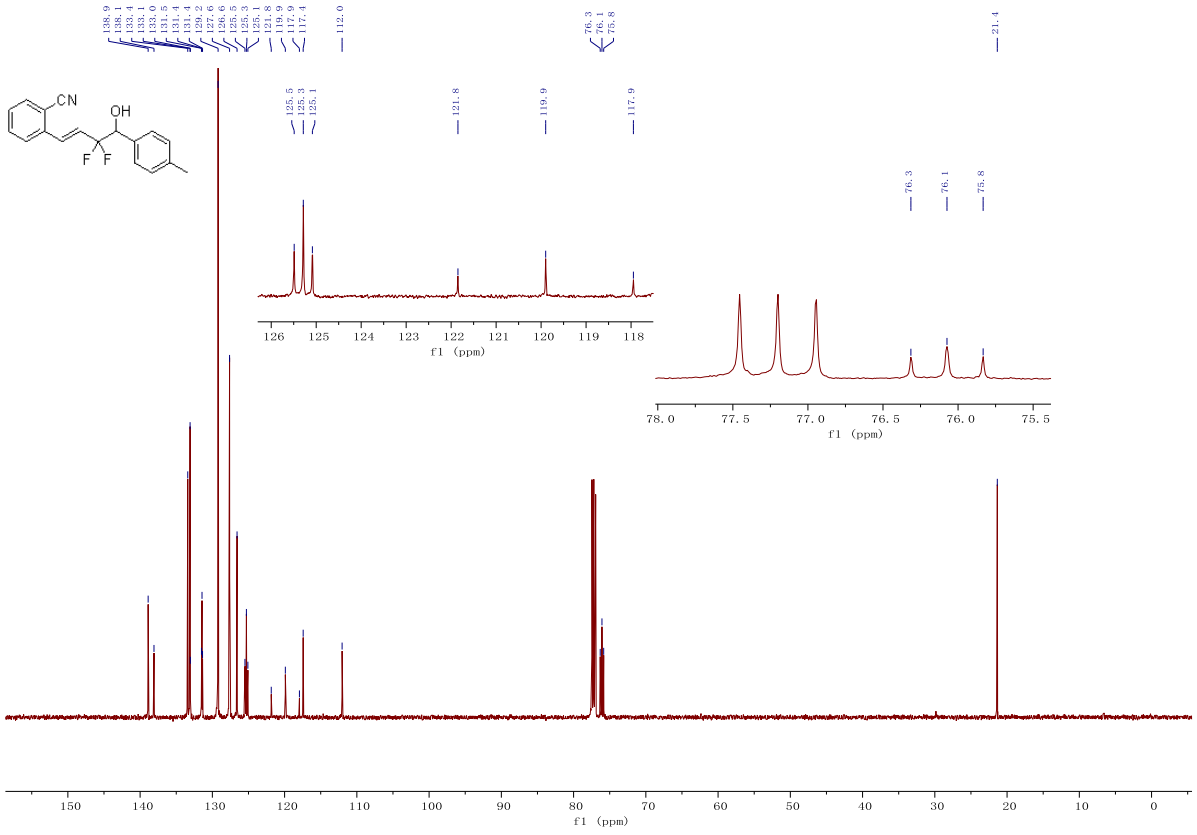


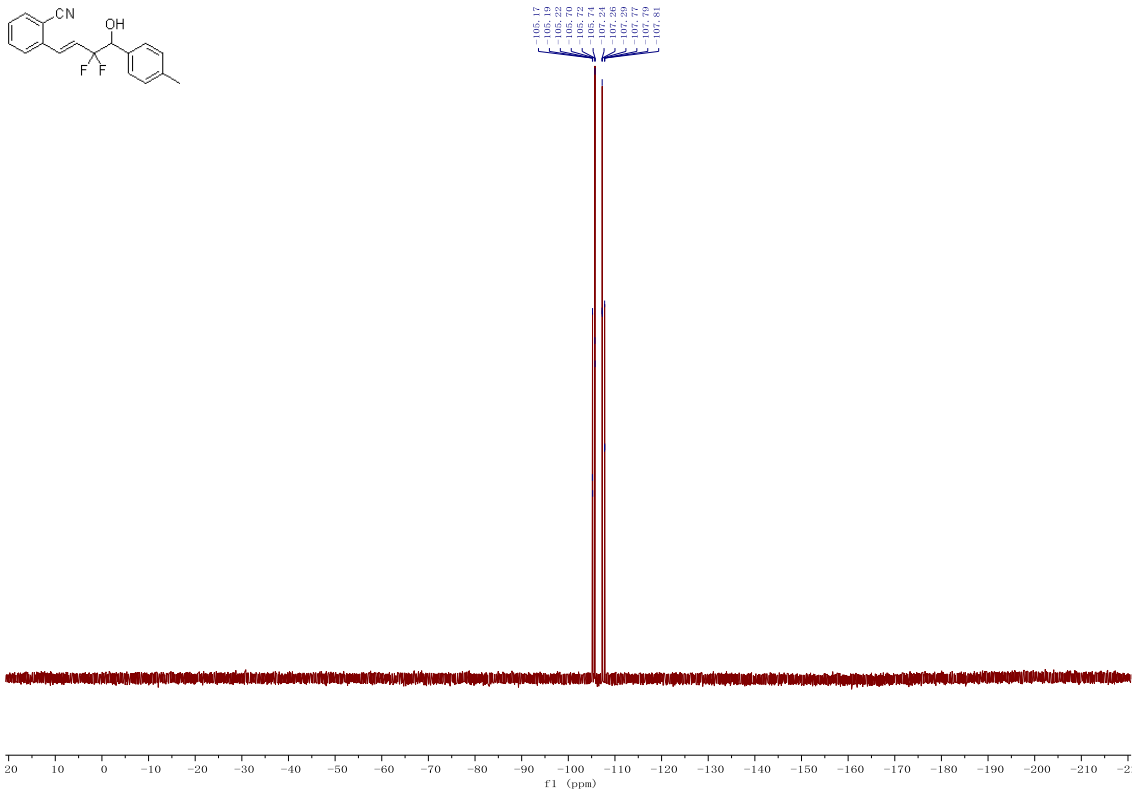

188.9
188.6
188.4
170.8
145.9
135.1
134.9
134.9
134.8
133.3
131.1
130.6
130.6
130.6
129.6
129.4
128.0
127.4
123.0
122.8
122.6
118.1
116.1
114.1
22.0
123.0
122.8
122.6
118.1
116.1
114.1
O
NH2
O
F
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
124 123 122 121 120 119 118 117 116 115 114 113
f1 (ppm)


-97.8
-97.8
O
NH2
O
F
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

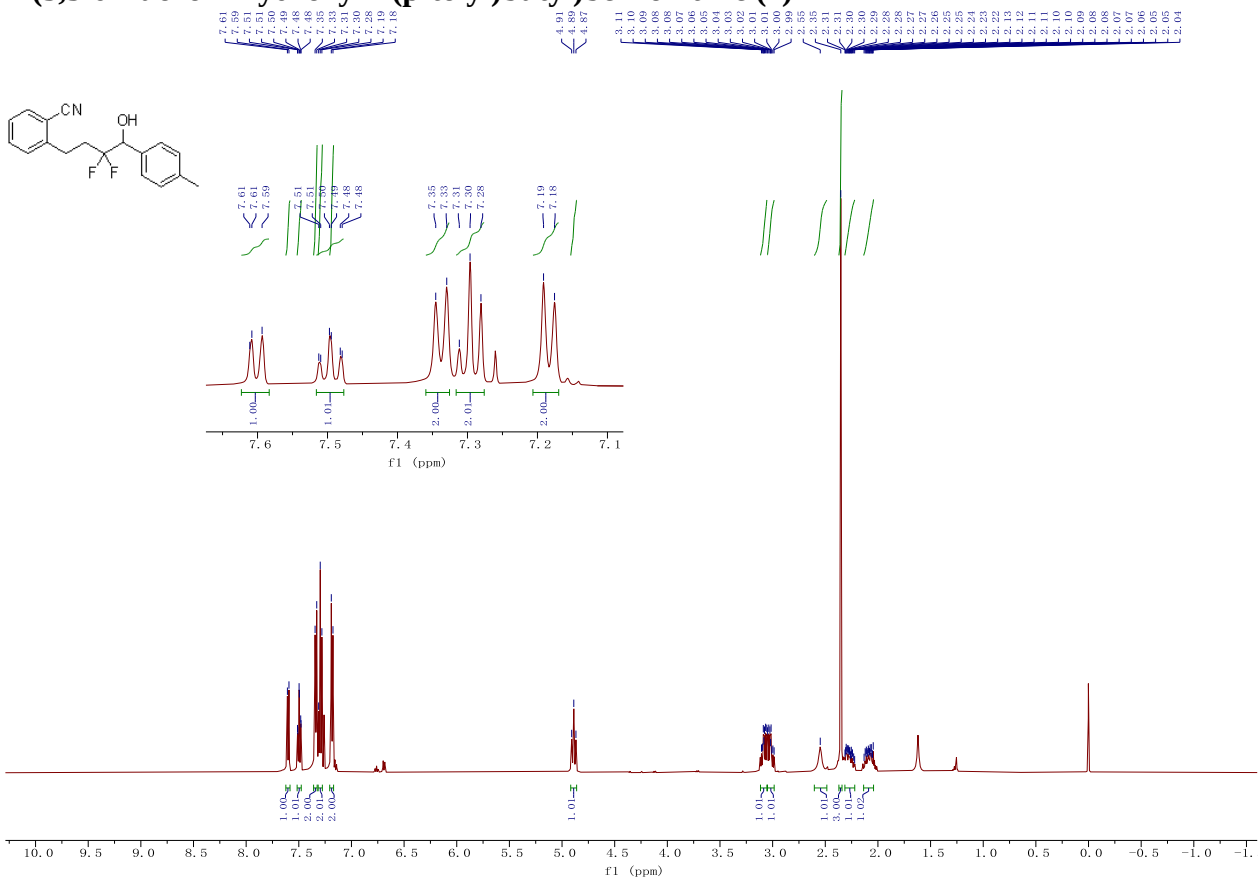
(*E*)-2-(3,3-difluoro-4-hydroxy-4-(p-tolyl)but-1-en-1-yl)benzonitrile (6)

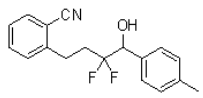


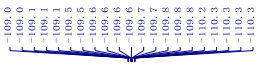


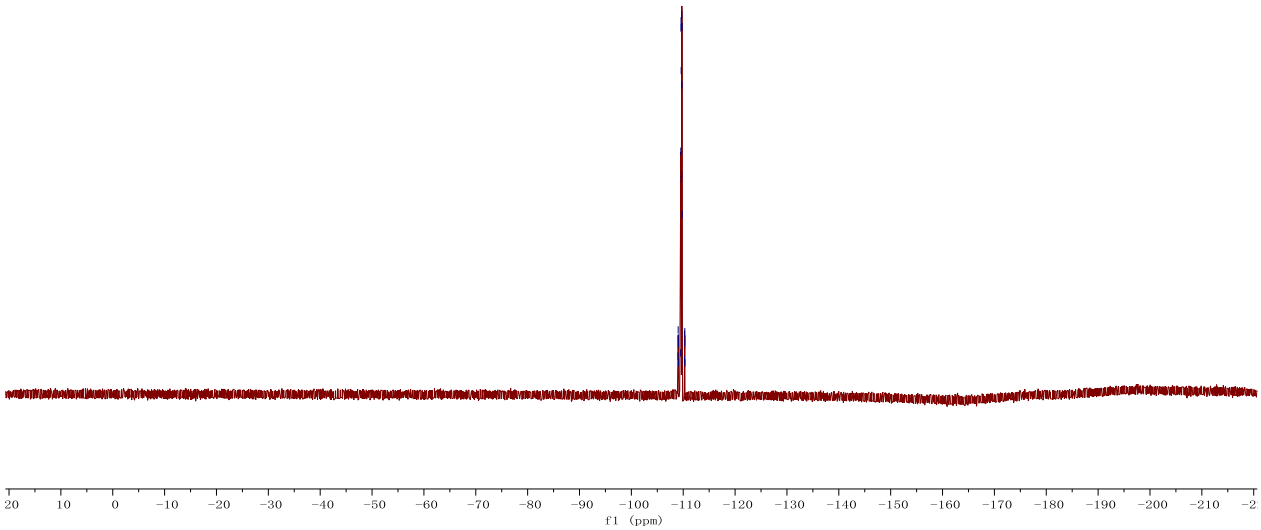


2-(3,3-difluoro-4-hydroxy-4-(p-tolyl)butyl)benzonitrile (7)

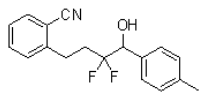


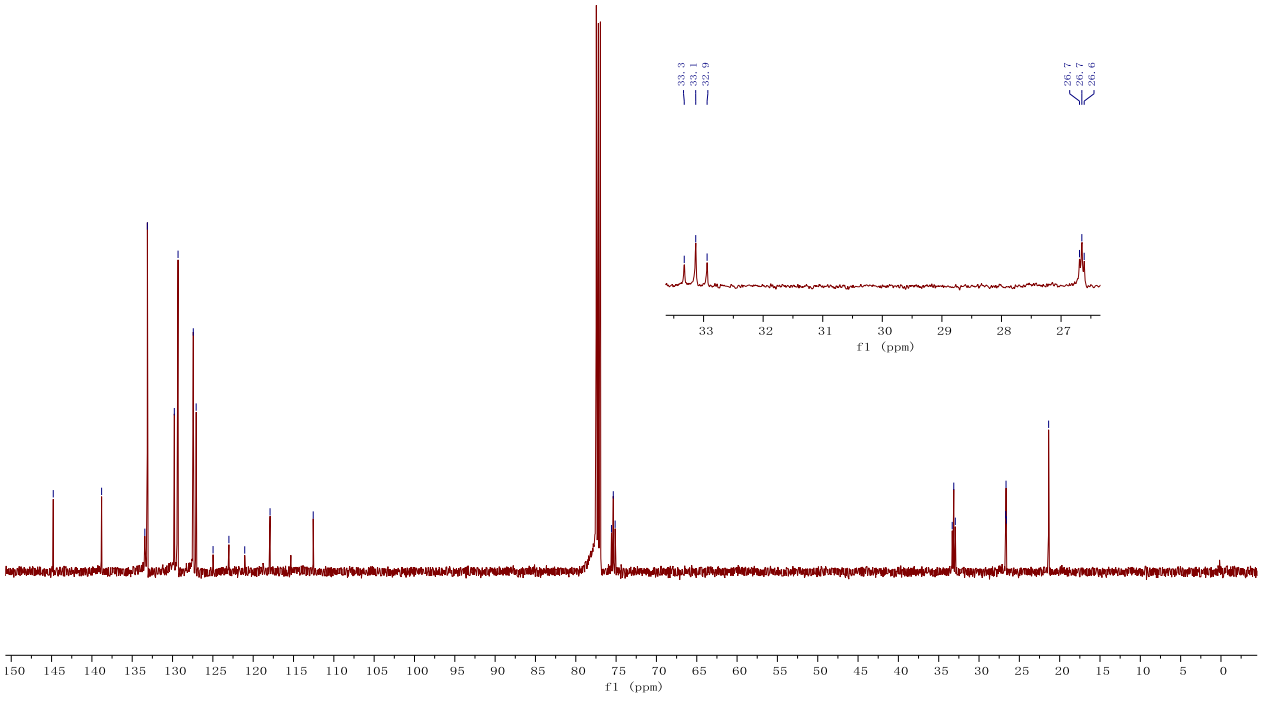

CN
OH
F
F


-109.0
-109.0
-109.1
-109.1
-109.1
-109.5
-109.5
-109.6
-109.6
-109.6
-109.6
-109.7
-109.7
-109.8
-109.8
-109.8
-110.2
-110.3
-110.3
-110.3
-110.3

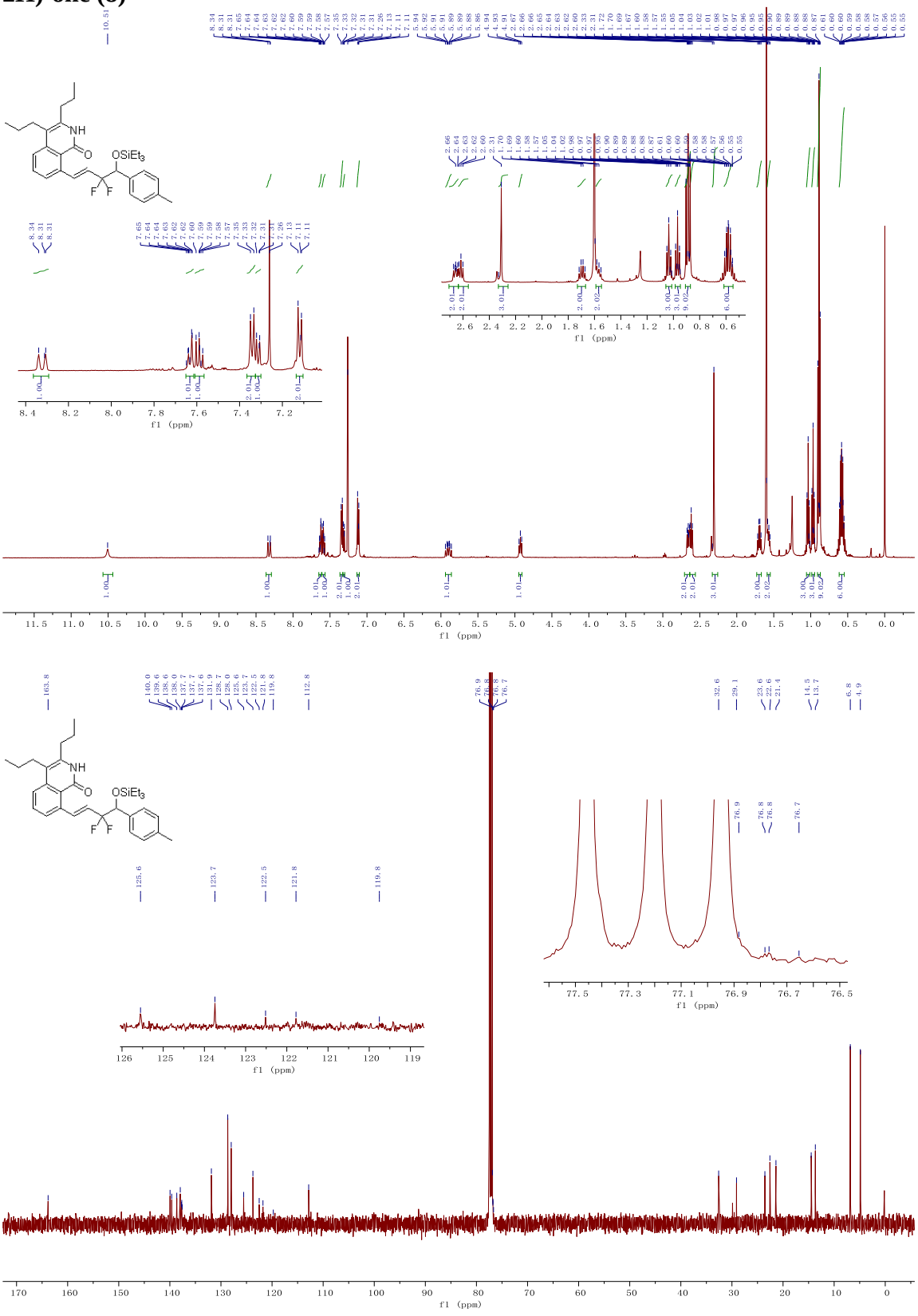

20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

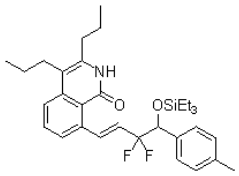

144.8
138.8
133.4
133.1
129.8
129.3
127.4
127.1
125.0
123.0
121.1
117.9
112.6
75.6
75.4
75.1
33.3
33.1
32.9
26.7
26.7
26.6
21.4

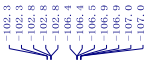

CN
OH
F
F

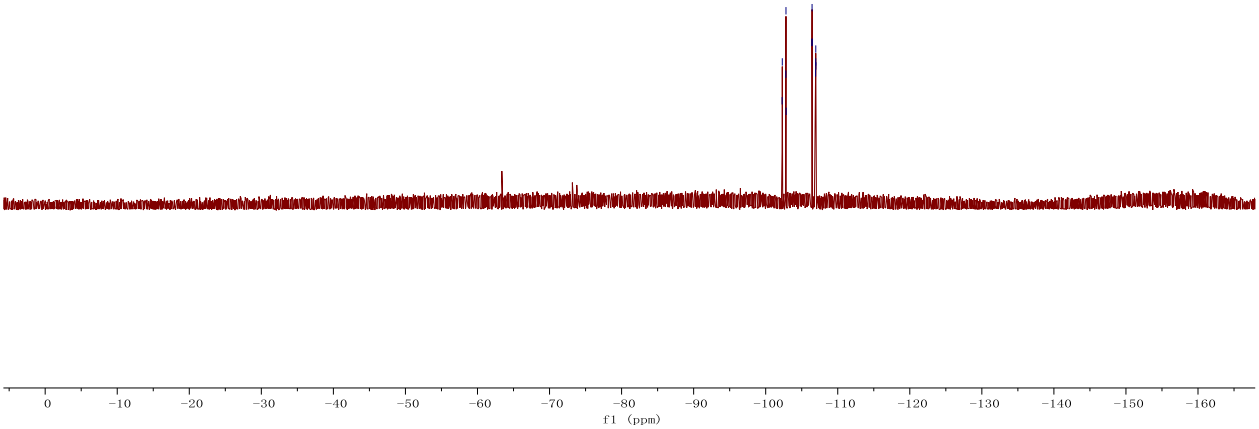

33.3
33.1
32.9
26.7
26.7
26.6
33 32 31 30 29 28 27
f1 (ppm)
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

(*E*)-8-(3,3-difluoro-4-(p-tolyl)-4-((triethylsilyl)oxy)but-1-en-1-yl)-3,4-dipropylisoquinolin-1(2H)-one (8)




NH
O
OSiEt3
F
F


-102.3
-102.3
-102.8
-102.8
-102.8
-106.4
-106.4
-106.5
-106.9
-106.9
-107.0
-107.0


0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)