Supporting Information

Visible-light organophotoredox-catalyzed fluoroalkyl aminoxylation of unactivated and activated alkenes

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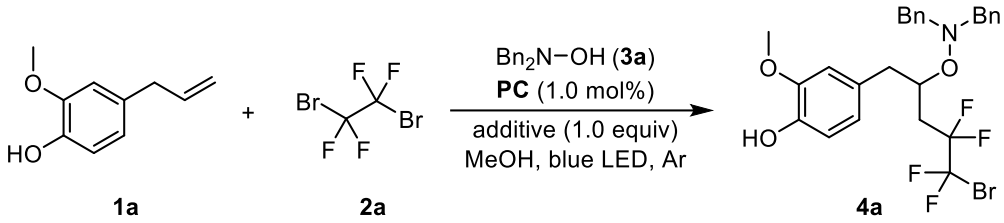
1. General Information

The reactions via general procedure were carried out under an atmosphere of argon unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker-AV (400, 100 and 376 MHz, respectively) instrument internally referenced to tetramethylsilane (TMS) or chloroform signals. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, tt = triplet of triplets, dq = doublet of quartets, dqd = doublet of quartet of doublets, ddd = doublet of double doublets, m = multiplet or unresolved, br = broad signal), coupling constant (J) in Hz, integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High-resolution mass spectra (ESI) were obtained with the Thermo Scientific LTQ Orbitrap XL mass spectrometer. Melting points were measured with a YUHUA X-5 melting point instrument and were uncorrected. The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and HRMS data with those in literatures. All reactions were performed in an oil bath when heating was required.

2. Detailed Optimization of Reaction Conditions

Table S1 Optimization of reaction conditions [a]



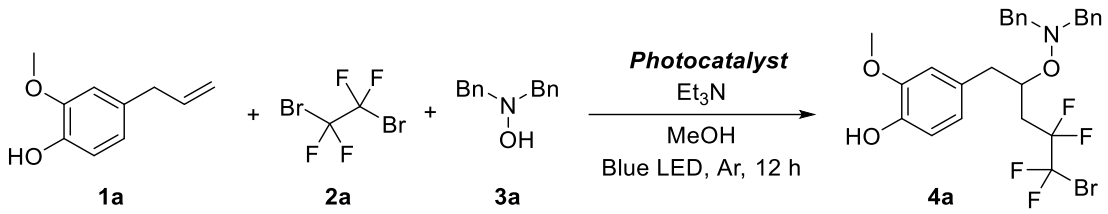
Entry	[PC]	Additive	Yield (%) [b]
1	$Ru(bpy)_3Cl\cdot 6H_2O$	Et_3N	12
2	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	Et_3N	43
3	Eosin B	Et_3N	trace
4	Rose bengal	Et_3N	trace
5	4CzIPN	Et_3N	76
6	4CzIPN	Et_3N	N.D.[c]
7	-	Et_3N	N.D.
8	4CzIPN	-	75
9	4CzIPN	H_2O	67
10	4CzIPN	Cs_2CO_3	64
11	4CzIPN	*i*-Pr_2NEt	89
12	4CzIPN	*i*-Pr_2NEt	87(81)[d]

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), **3a** (0.3 mmol), photocatalyst (1 mol %), additive (1.0 equiv) in MeOH (2.0 mL) at room temperature, Ar, 12 h, irradiation with 35W blue LED strips (λ_{max} = 460 nm). [b] Determined by ^{19}F NMR analysis of the crude reaction mixture using $PhCF_3$ as internal standard (isolated yield in parentheses). [c] No light. [d] **1a** (0.2 mmol), **2a** (1.5 equiv), **3a** (1.2 equiv), 6 h. N.D. = not detected.

Initially, we employed biomass eugenol (**1a**), commercial coolant 1,2-dibromotetrafluoroethane (**2a**) and *N*,*N*-dibenzylhydroxylamine (**3a**) as model substrates to evaluate the reaction parameters, such as the photocatalysts, solvent, and

additives (Table S1). As participated, the desired product **4a** was obtained in 12% yield when the reaction was carried out in the presence of $Ru(bpy)_3Cl\cdot 6H_2O$ and Et_3N in MeOH with irradiation of blue LED for 12 h (entry 1). Subsequently, various photocatalysts, including Ir-complex, Eosin B, Rose bengal and 4CzIPN were also explored (entries 2−5). Among them, 4CzIPN exhibited a better catalytic efficiency, and the yield of **4a** could be dramatically increased to 76% (entry 5). The photochemical nature of this transformation was confirmed when control experiments in the absence of light irradiation or the photocatalyst showed no conversion to product **4a** (entries 6-7). To our delight, the yield of **4a** was increased to 89% when the *i*-Pr_2NEt was employed as an additive (entries 8-11). The further optimization for the ratio of substrates was also tested, and the process did not affect when the ratio of **1a**, **2a** and **3a** was adjusted to 1:1.5:1.2 at a shortened time of 6 hours (entry 12).

Table S2. Optimization of photocatalyst [a]



Entry	Photocatalyst	Yield (%) [b]
1	None	0
2	5CzBN	75
3	4CzIPN	76
4	4CzTPN	14
5	4CzPN	trace
6	3DPACIIPN	14
7	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	43
8	$Ru(bpy)_3Cl\cdot 6H_2O$	12
9	Mes-Acr-Me^+ ClO_4^-	trace
10	Eosin B	trace
11	Eosin Y	trace
12	Rose bengal	trace

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv), **3a** (1.5 equiv), photocatalyst (1.0 mol%), Et_3N (1.0 equiv) in MeOH (2.0 mL) at room temperature, Ar, 12 h, irradiation with blue LED strips (λ_{max} = 460 nm). [b] Determined by ^{19}F NMR analysis of the crude reaction mixture using $PhCF_3$ as internal standard.

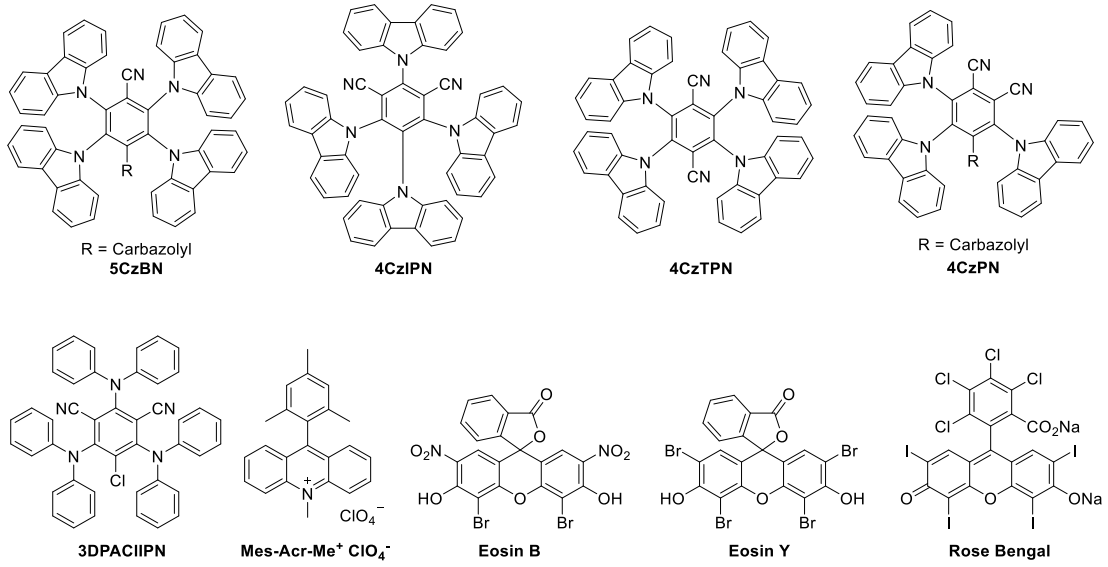
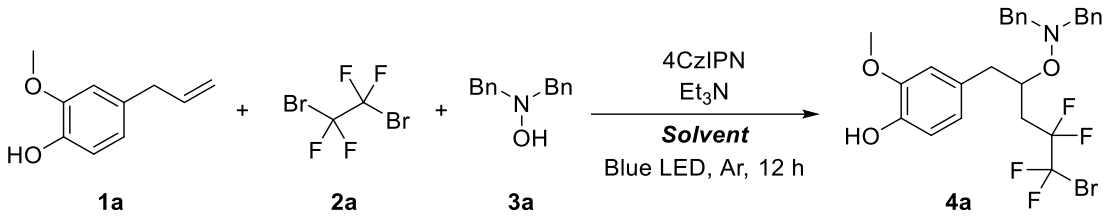


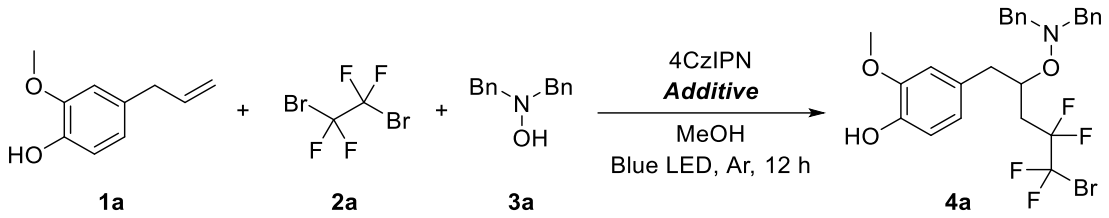
Table S3. Optimization of solvent [a]



Entry	Solvent	Yield (%) [b]
1	MeOH	76
2	MeCN	32
3	THF	38
4	EtOH	30
5	EtOAc	36
6	DMF	44
7	DMSO	50
8	CH_2Cl_2	28
9	CF_3CH_2OH	18
10	*i*-PrOH	42
11	*t*-BuOH	20

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv), **3a** (1.5 equiv), 4CzIPN (1.0 mol%), Et_3N (1.0 equiv) in corresponding solvents (2.0 mL) at room temperature, Ar, 12 h, irradiation with blue LED strips (λ_{max} = 460 nm). [b] Determined by ^{19}F NMR analysis of the crude reaction mixture using $PhCF_3$ as internal standard.

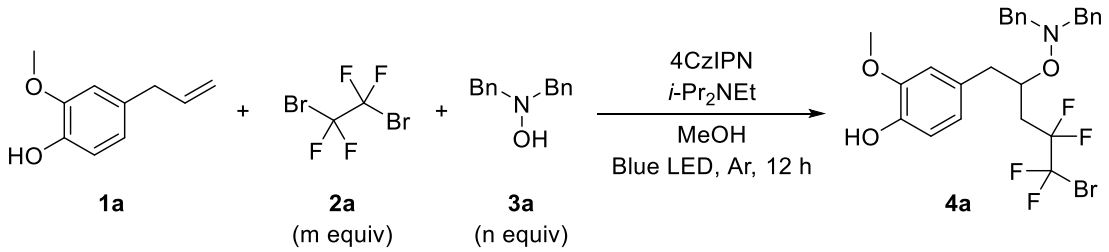
Table S4. Optimization of additives [a]



Entry	Additive	Yield (%) [b]
1	-	75
2	Et_3N	76
3	Et_2NH	70
4	LiO*t*-Bu	54
5	CS_2CO_3	64
6	H_2O	67
7	*i*-Pr_2NEt	89
8	NH_4Br	68
9	$(NBu_4)Br$	76

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv), **3a** (1.5 equiv), 4CzIPN (1.0 mol%), additive (1.0 equiv) in MeOH (2.0 mL) at room temperature, Ar, 12 h, irradiation with blue LED strips (λ_{max} = 460 nm). [b] Determined by ^{19}F NMR analysis of the crude reaction mixture using $PhCF_3$ as internal standard.

Table S5. Optimization of equivalent of substrates [a]

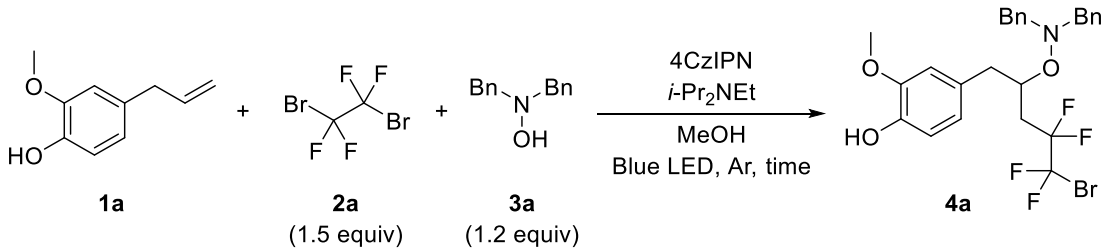


1a **2a** (m equiv) **3a** (n equiv) **4a**

Entry	m	n	Yield (%) [b]
1	1.5	1.2	88(81)
2	1.5	1.5	89
3	1.5	2.0	81
4	1.5	2.5	81
5	1.2	1.2	75
6	2.0	1.2	88

[a] Reaction Conditions: **1a** (0.1 mmol), **2a** (m equiv), **3a** (n equiv), 4CzIPN (1.0 mol%), *i*-Pr_2NEt (1.0 equiv) in MeOH (2.0 mL) at room temperature, Ar, 12 h, irradiation with blue LED strips (λ_{max} = 460 nm). [b] Determined by ^{19}F NMR analysis of the crude reaction mixture using $PhCF_3$ as internal standard (isolated yield in parentheses).

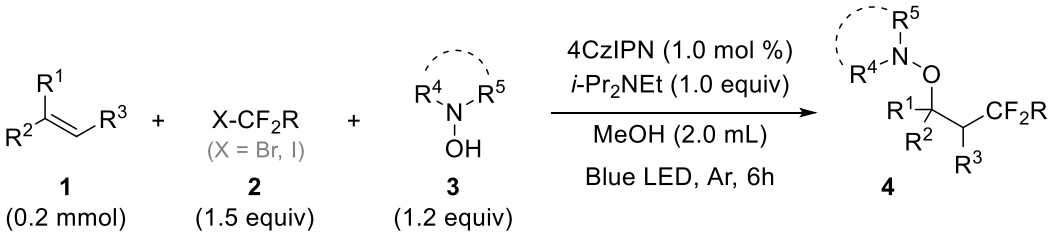
Table S6. Optimization of reaction time [a]



Entry	Time	Yield (%) [b]
1	3 h	60
2	6 h	87(81)
3	12 h	88(81)

[a] Reaction Conditions: **1a** (0.1 mmol), **2a** (1.5 equiv), **3a** (1.2 equiv), 4CzIPN (1.0 mol%), *i*-Pr_2NEt (1.0 equiv) in MeOH (2.0 mL) at room temperature, Ar, irradiation with blue LED strips (λ_{max} = 460 nm). [b] Determined by ^{19}F NMR analysis of the crude reaction mixture using $PhCF_3$ as internal standard (isolated yield in parentheses).

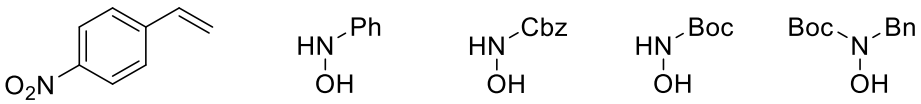
3. General Procedure for the Organophotoredox-Catalyzed Fluoroalkyl Aminoxylation of Alkenes



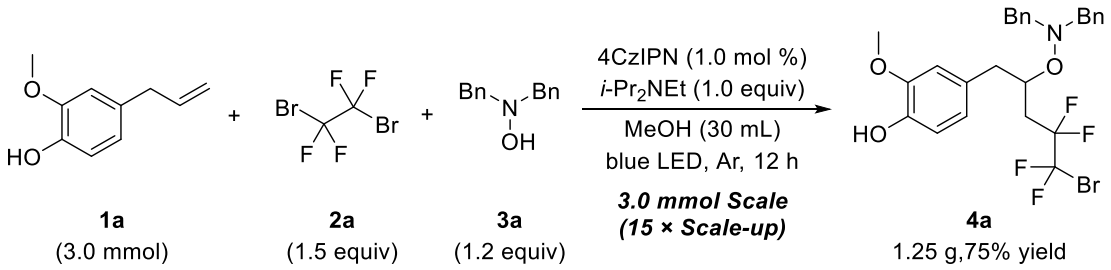
Under argon atmosphere, to a flame-dried 10 mL Schlenk tube were added **1** (0.2 mmol), **2** (0.3 mmol, 1.5 equiv), **3** (0.24 mmol, 1.2 equiv), 4CzIPN (1.6 mg, 0.002 mmol, 1.0 mol%), *i*-Pr_2NEt (35 μL, 0.2 mmol, 1.0 equiv) and MeOH (2.0 mL), then the tube was sealed. The mixture was stirred under the irradiation of blue LED strips (light-emitting diode, λ_{max} = 460 nm) at room temperature under Ar atmosphere for 6 h. After complete consumption of **1** (determined by TLC), the reaction mixture was concentrated under vacuum to afford the crude mixture. The diastereoisomeric ratio was determined by ^{19}F NMR analysis of the crude reaction mixture using $PhCF_3$ as an internal standard. The residue was purified by silica gel flash column chromatography (typically using petroleum ether to PE/EtOAc = 20:1 as elution) or prepared thin layer chromatography to afford the target products **4**.

Unsuccessful substrates:

alkene ---------- hydroxylamines ----------



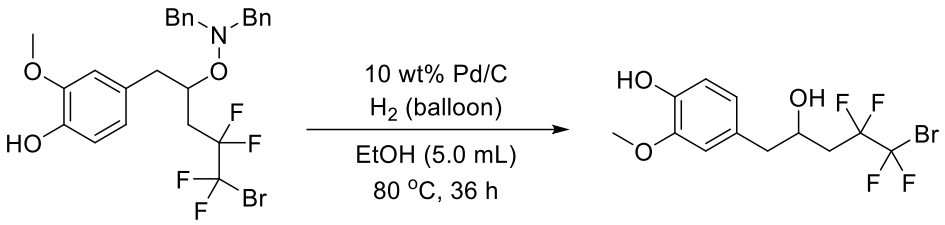
4. Gram-Scale Reaction on the Synthesis of 4a



A 100 mL Schlenk tube was flame-dried and cooled down under Ar atmosphere. To the Schlenk tube were added **1a** (3.0 mmol, 493 mg, 1.0 equiv), **2a** (4.5 mmol, 1.17 g, 1.5 equiv), **3a** (3.6 mmol, 768 mg, 1.2 equiv), 4CzIPN (0.03 mmol, 23.7 mg, 1.0 mol%), *i*-Pr_2NEt (3.0 mmol, 522 μL, 1.0 equiv) and MeOH (30 mL), then sealed. The mixture was stirred under the irradiation of blue LED strips (light-emitting diode, λ_{max} = 460 nm) at room temperature under Ar atmosphere for 12 h. After complete consumption of **1a** (determined by TLC), the reaction mixture was filtered over a short pad of silica gel, washed with ethyl acetate and concentrated under vacuum to afford the crude mixture. The residue was purified by silica gel column chromatography (petroleum ether) to afford the pure product **4a** as a colorless viscous oil (1.25 g, 75% yield).

5. Derivatizations of Products

5.1 Cleavage the N-O bond of 4a for the synthesis of free alcohol 5 [1]

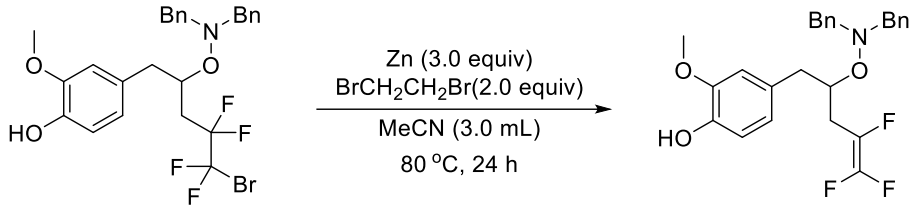


4a
(0.2 mmol)

5
72% yield

To a 10 mL Schlenk tube, 10 w.t.% Pd/C (30 mg) was added to a solution of **4a** (0.2 mmol, 111.3 mg) in EtOH (5.0 mL). The mixture was stirred under a hydrogen atmosphere (balloon) at 80 °C for 36 hours. After complete consumption of **4a** (determined by TLC), the reaction mixture was filtered over a short pad of silica gel, washed with MeOH (3 × 5 mL) and concentrated under vacuum to afford the crude mixture. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford free alcohol **5** as a colorless viscous oil (52.0 mg, 72% yield).

5.2 E1cb elimination reaction for the synthesis of trifluorovinyl compound 6 [2]



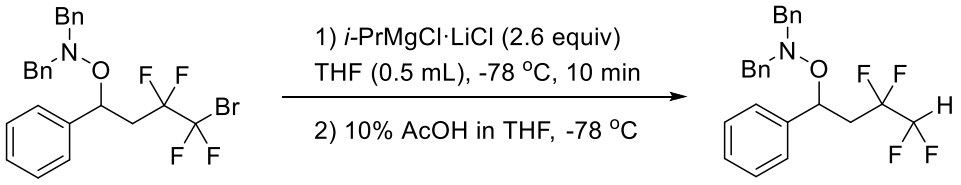
4a
(0.2 mmol)

6
60% yield

Under Ar atmosphere, to a flame-dried 10 mL Schlenk tube were added the starting material **4a** (0.2 mmol, 111.3 mg), activated zinc powder (0.6 mmol, 19.5 mg) and MeCN (3.0 mL). Subsequently, 1,2-dibromoethane compound was added via syringe (0,4 mmol, 2 equiv). The reaction mixture was reflux at 80 ºC for 24 hours. After complete consumption of **1a** (determined by TLC), the reaction mixture was filtered over a short pad of silica gel, washed with ethyl acetate and concentrated under vacuum to afford the crude mixture. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford trifluorovinyl compound **6** as a colorless viscous oil (54.8 mg, 60% yield).

5.3 Metalation of the bromide 4l and sequential capture with electrophiles [3]

(1) Synthesis of -CF_2CF_2H moiety-containing compounds 7

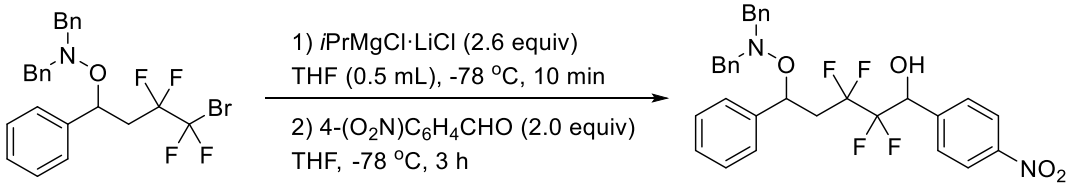


4l
(0.1 mmol)

7
90% yield

Product **4l** (0.1 mmol, 49.6 mg) was dissolved in anhydrous THF (0.5 mL) and cooled to –78 °C. A solution of *i*-PrMgCl·LiCl (Turbo Grignard) in THF (0.2 mmol, 1.3 M, 200 μL) was added dropwise. After stirred 10 min at –78 °C, the reaction was quenched by the addition of 10% AcOH in THF (1.0 mL). Saturated aqueous NH_4Cl (5.0 mL) was added, the product was extracted with CH_2Cl_2 (3 × 4 mL), dried with $MgSO_4$, then filtered over Celite, and concentrated under vacuum. The crude product was purified by silica gel column chromatography (petroleum ether/dichloromethane = 10: 1) to afford **7** as a colorless oil (37.5 mg, 90% yield).

(2) Organomagnesium intermediate trapped by aldehyde



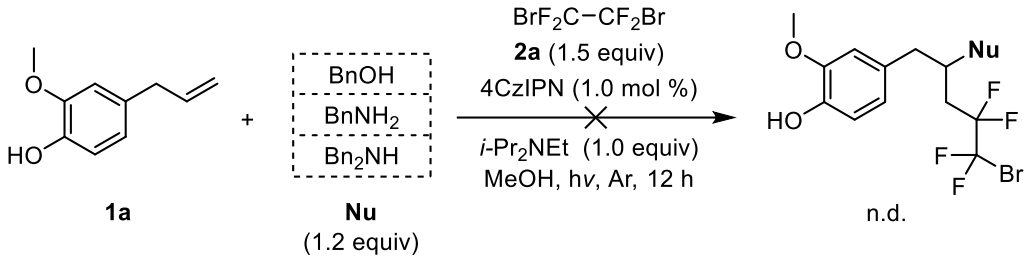
4l
(0.1 mmol)

8
61% yield

Product **4l** (0.1 mmol, 49.6 mg) was dissolved in anhydrous THF (0.5 mL) and cooled to –78 °C. A solution of *i*-PrMgCl·LiCl (Turbo Grignard) in THF (0.26 mmol, 1.3 M, 200 μL) was added dropwise. After stirred 10 min at –78 °C, a solution of 4-nitrobenzaldehyde (0.2 mmol, 30.3 mg) in THF (0.3 mL) was introduced, and the mixture was stirred for 3 hours while warming up to rt. Then quenched by saturated aqueous NH_4Cl (5.0 mL). The mixture was extracted with CH_2Cl_2 (3 × 4 mL), dried with $MgSO_4$, then filtered over Celite, and concentrated under vacuum. The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5: 1) to afford **8** as a colorless oil (34.5 mg, 61% yield, 1:1 dr).

6. Mechanistic Studies

6.1 Attempts using other nucleophiles

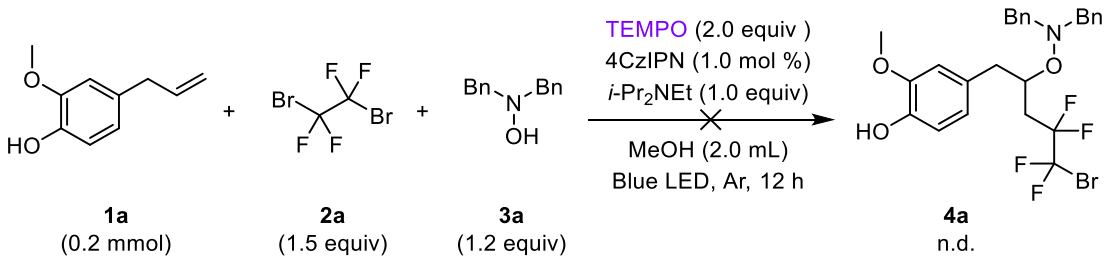


Under argon atmosphere, to a flame-dried 10 mL Schlenk tube were added **1a** (0.2 mmol), **2a** (0.3 mmol, 1.5 equiv), BnOH or $BnNH_2$/Bn_2NH (0.24 mmol, 1.2 equiv), 4CzIPN (1.6 mg, 0.002 mmol, 1.0 mol%), *i*-Pr_2NEt (35 μL, 0.2 mmol, 1.0 equiv), and MeOH (2.0 mL), then the tube was sealed. The mixture was stirred under the irradiation of blue LED strips (light-emitting diode, λ_{max} = 460 nm) at room temperature under Ar atmosphere for 6 h. None of difunctionalized products could be detected by TLC and ^{1}H NMR and ^{19}F NMR analysis.

Replacement of hydroxylamine with other alcohol or amine nucleophiles, however, none of difunctionalized products could be detected under the standard conditions, but with recovery of starting material **1a**. These attempts could rule out the carbo-cation intermediate involved in this photocatalytic cycle.

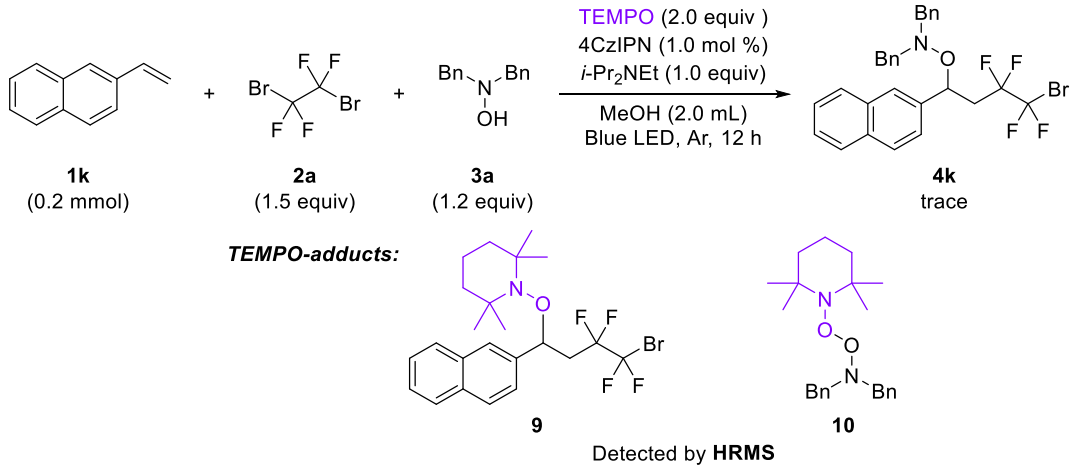
6.2 Radical trapping experiments

6.2.1 TEMPO trapping experiments



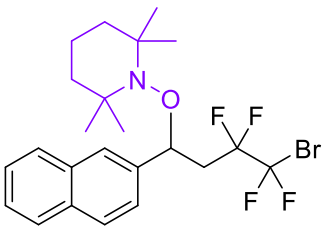
Under argon atmosphere, to a flame-dried 10 mL Schlenk tube were added **1a** (0.2 mmol), **2a** (0.3 mmol, 1.5 equiv), **3a** (0.24 mmol, 1.2 equiv), 4CzIPN (1.6 mg, 0.002 mmol, 1.0 mol%), *i*-Pr_2NEt (35 μL, 0.2 mmol, 1.0 equiv), 2,2,6,6-tetramethyl-1-

piperidinyloxy (**TEMPO**) (62.8 mg, 0.4 mmol, 2.0 equiv) and MeOH (2.0 mL), then the tube was sealed. The mixture was stirred under the irradiation of blue LED strips (light-emitting diode, λ_{max} = 460 nm) at room temperature under Ar atmosphere for 6 h. No production of **4a** was determined by TLC and ^{19}F NMR analysis, with starting material remained. *However, no TEMPO-adduct was detected, probably due to the less stability of the carbo-radical intermediate (intermediate **B** in Scheme 5d).*

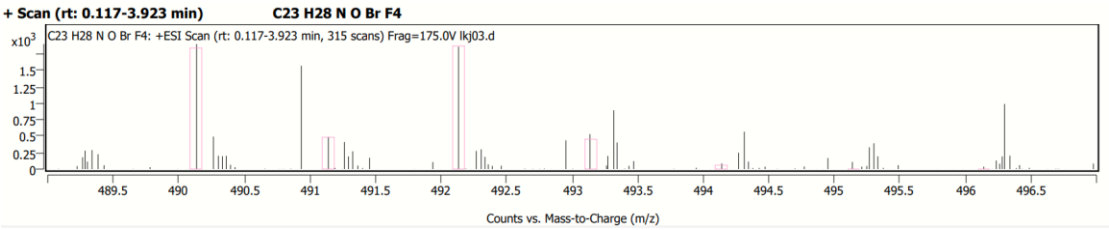


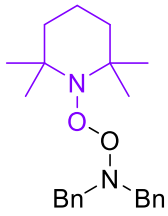
Under argon atmosphere, to a flame-dried 10 mL Schlenk tube were added **1k** (0.2 mmol), **2a** (0.3 mmol, 1.5 equiv), **3a** (0.24 mmol, 1.2 equiv), 4CzIPN (1.6 mg, 0.002 mmol, 1.0 mol%), *i*-Pr$_2$NEt (35 μL, 0.2 mmol, 1.0 equiv), 2,2,6,6-tetramethyl-1-piperidinyloxy (**TEMPO**) (62.8 mg, 0.4 mmol, 2.0 equiv) and MeOH (2.0 mL), then the tube was sealed. The mixture was stirred under the irradiation of blue LED strips (light-emitting diode, λ_{max} = 460 nm) at room temperature under Ar atmosphere for 12 h. The reaction was determined by HRMS and ^{19}F NMR analysis. Trace amount of product **4k** was determined by TLC and ^{19}F NMR analysis. *However, in this case, TEMPO-adducts could be detected by HRMS, probably due to the more stability of the benzylic carbo-radical intermediate (intermediate **B** in Scheme 5d).*

HRMS detection for reaction

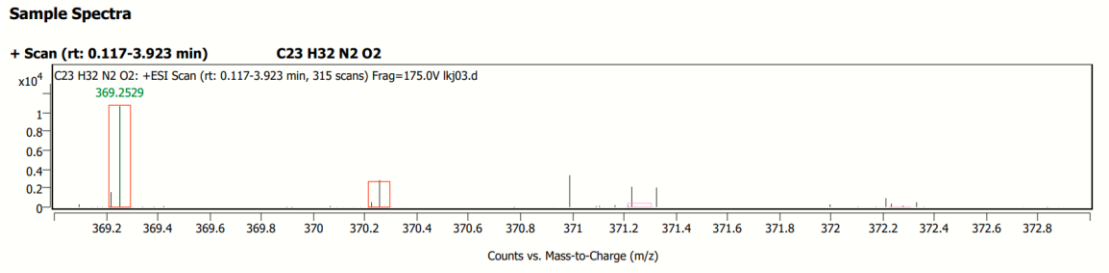


HRMS (ESI$^+$): calculated $[M+H]^+$ for $C_{23}H_{29}BrF_4NO^+$: 490.1363; found: 490.1356.

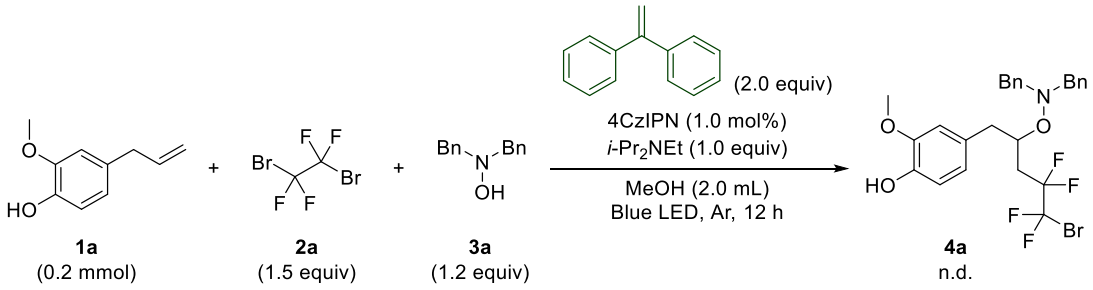


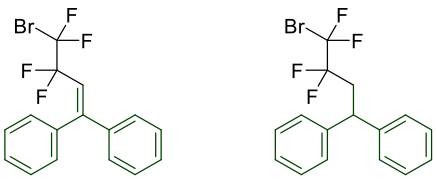


HRMS (ESI$^+$): calculated $[M+H]^+$ for $C_{23}H_{33}N_2O_2^+$: 369.2537; found: 369.2529.



6.2.2 1,1-Diphenylethylene trapping experiment





Detected by **GC-MS**

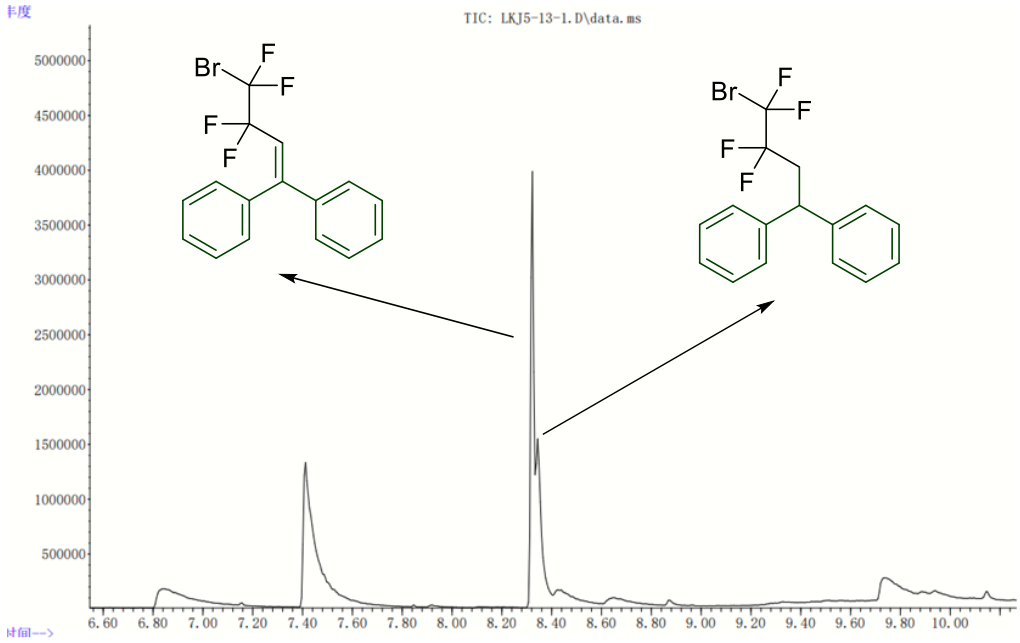
Under argon atmosphere, to a flame-dried 10 mL Schlenk tube were added **1a** (0.2 mmol), **2a** (0.3 mmol, 1.5 equiv), **3a** (0.24 mmol, 1.2 equiv), 4CzIPN (1.6 mg, 0.002 mmol, 1.0 mol%), *i*-Pr$_2$NEt (35 μL, 0.2 mmol, 1.0 equiv), 1,1-diphenylethylene (72.1 mg, 0.4 mmol, 2.0 equiv) and MeOH (2.0 mL), then the tube was sealed. The mixture

was stirred under the irradiation of blue LED strips (light-emitting diode, λ_{max} = 460 nm) at room temperature under Ar atmosphere for 12 h. No production of **4a** was determined by TLC and ^{19}F NMR analysis. *However, in this case, the adducts between fluoroalkyl radical and 1,1-diphenylethylene could be detected by GC-MS.*

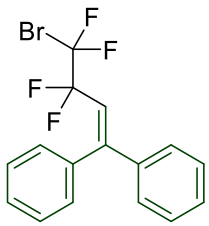
Fluoroalkyl radical (·CF_2R) could be captured by 1,1-diphenylethylene, which was supported by GC-MS spectroscopy. These experiments indicated a radical pathway should be participated in this process.

GC-MS detection for reaction

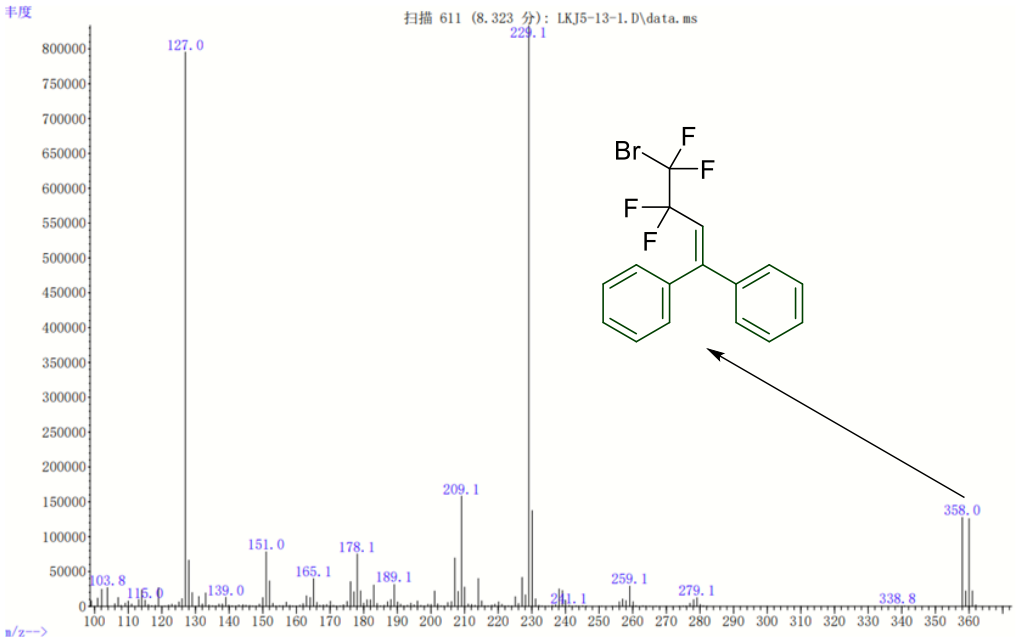
GC spectrum:

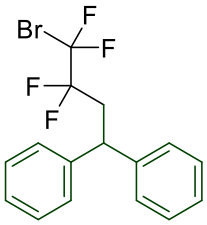


MS spectra:

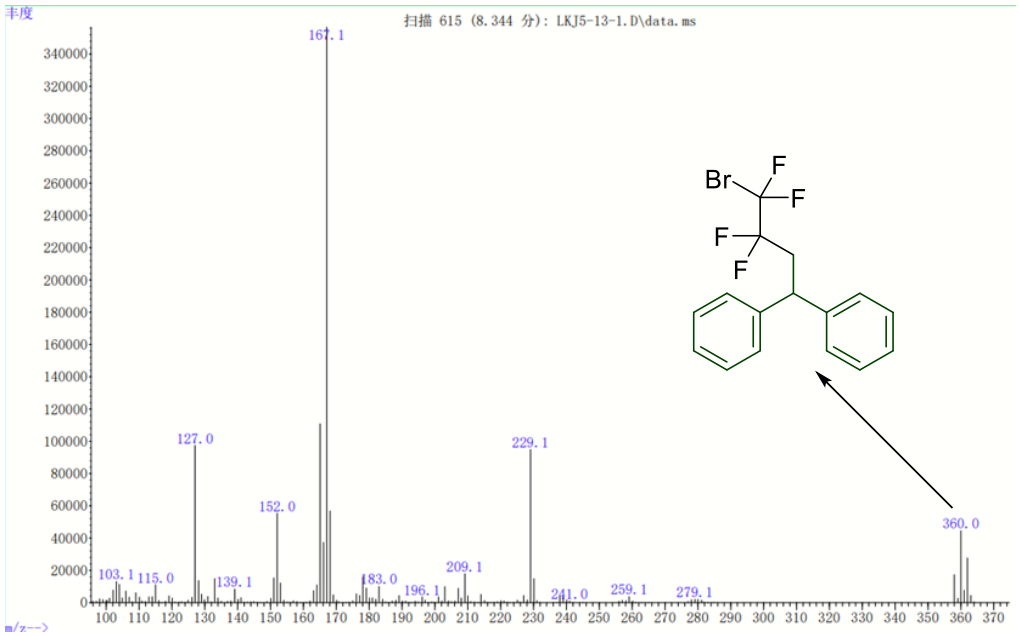


GCMS: calcd [M] for $C_{16}H_{11}BrF_4$: 357.9980; found 358.0 : 360.0 = 1 : 1





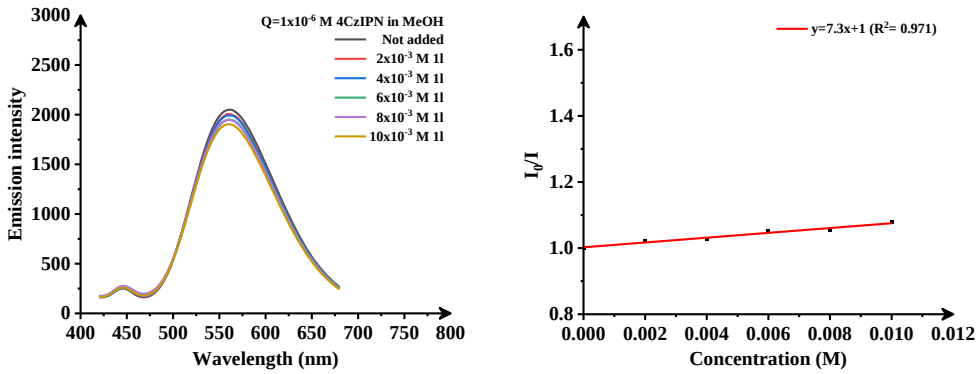
GCMS: calcd [M] for $C_{16}H_{13}BrF_4$: 360.0137; found 360.0 : 362.0 = 3 : 2



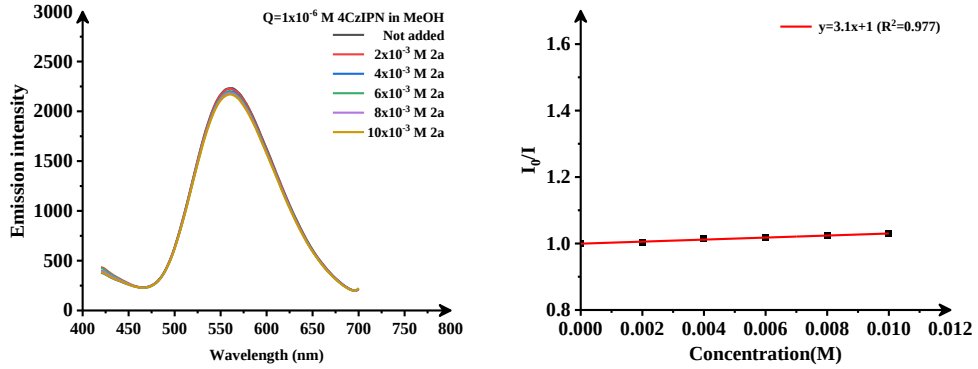
6.3 Stern–Volmer quenching

Formulation solution: Styrene (**1l**, 115 μL, 1.0 mmol) was dissolved in MeOH in a 5 mL volumetric flask to set the concentration to be 0.2 M. 1,2-dibromotetrafluoroethane (**2a**, 120 μL, 1.0 mmol) was dissolved in MeOH in a 5 mL volumetric flask to set the concentration to be 0.2 M. *Due to the poor solubility of N,N-dibenzylhydroxylamine in methanol*, *N*,*N*-dibenzylhydroxylamine (**3a**, 213.3 mg, 1.0 mmol) was dissolved in DMF in a 5 mL volumetric flask to set the concentration to be 0.2 M. DIPEA (174 μL, 1.0 mmol) was dissolved in MeOH in a 5 mL volumetric flask to set the concentration to be 0.2 M. Photocatalyst 4CzIPN (2 mg, 0.0025 mmol) was dissolved in MeOH or DMF (25.0 mL) to set the concentration to be 0.1 mM.

Experimental procedure: The resulting 0.1 mM solution of catalyst (20 μL) was added to cuvette, then diluted to a volume of 2.0 mL by adding MeOH or DMF to prepare a 1.0 μM solution. The resulting mixture was sparged with argon for 2 minutes and then irradiated at 360 nm. Fluorescence emission spectra were recorded. Into this solution, corresponding amount solution of each reaction reagent (**1l**, **2a**, **3a** or DIPEA) was successively added in a gradient of 20 μL and uniformly stirred, and the resulting mixture was bubbled with argon for 2 minutes and irradiated at 360 nm. Fluorescence intensity of 0 μL, 20.0 μL, 40.0 μL, 60.0 μL, 80.0 μL for each component was recorded. Follow this method and make changes to the amount to obtain the Stern–Volmer relationship in turn. The results were shown in the following figures.

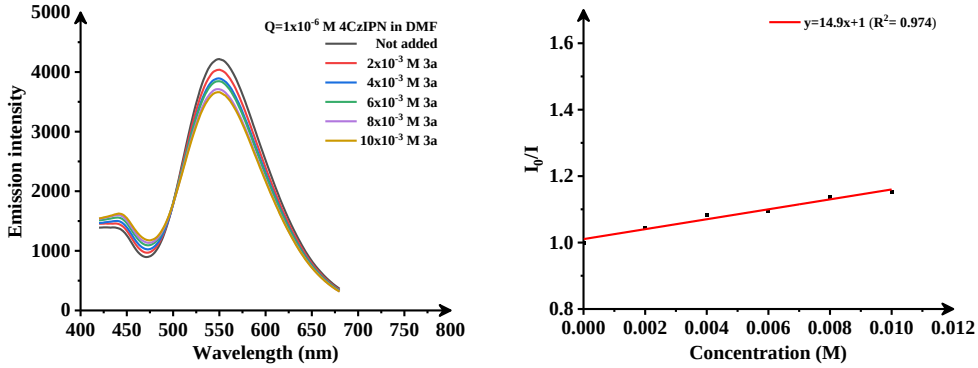


Emission quenching of 4CzIPN with styrene (**1l**) in MeOH

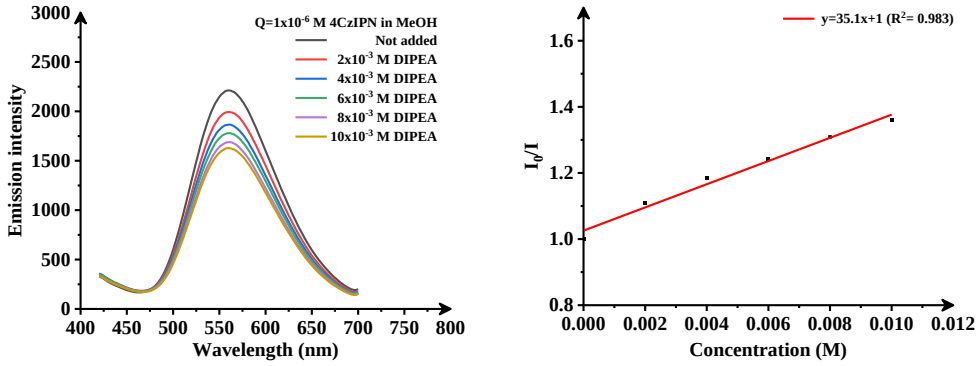


Emission quenching of 4CzIPN with 1,2-dibromotetrafluoroethane (**2a**) in MeOH

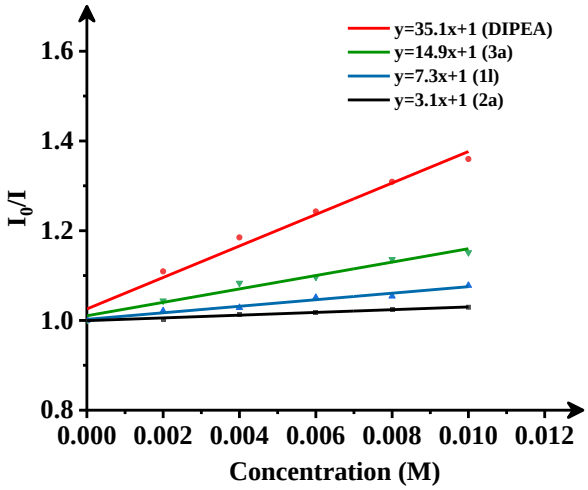
*Due to the poor solubility of N,N-dibenzylhydroxylamine (**3a**) in MeOH, fluorescence quenching experiment by N,N-dibenzylhydroxylamine (**3a**) was conducted in DMF.*



Emission quenching of 4CzIPN with *N*,*N*-Dibenzylhydroxylamine (**3a**) in DMF



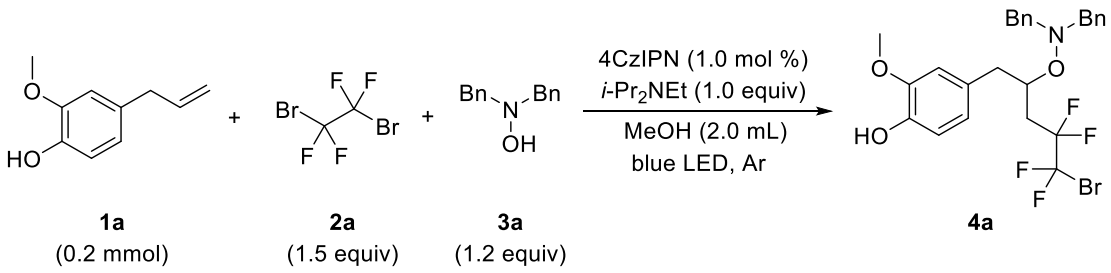
Emission quenching of 4CzIPN with **DIPEA** in MeOH



Stern-Volmer plot

The Stern−Volmer plot suggests that a strong interaction exists between excited photocatalyst and *i*-Pr_2NEt, revealing a direct energy transfer between them. However, in the absence of tertiary amine, hydroxylamine **3a** could also act as a reductive quencher for excited-state 4CzIPN.

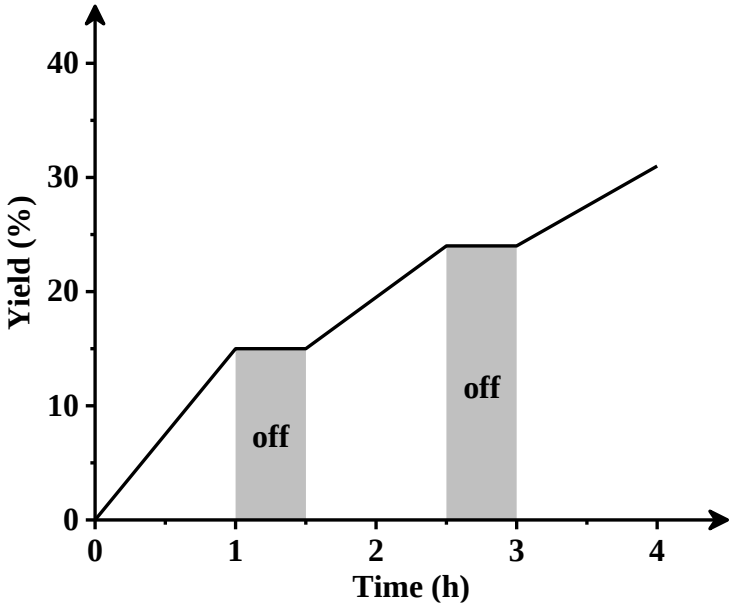
6.4 Light on/off experiment

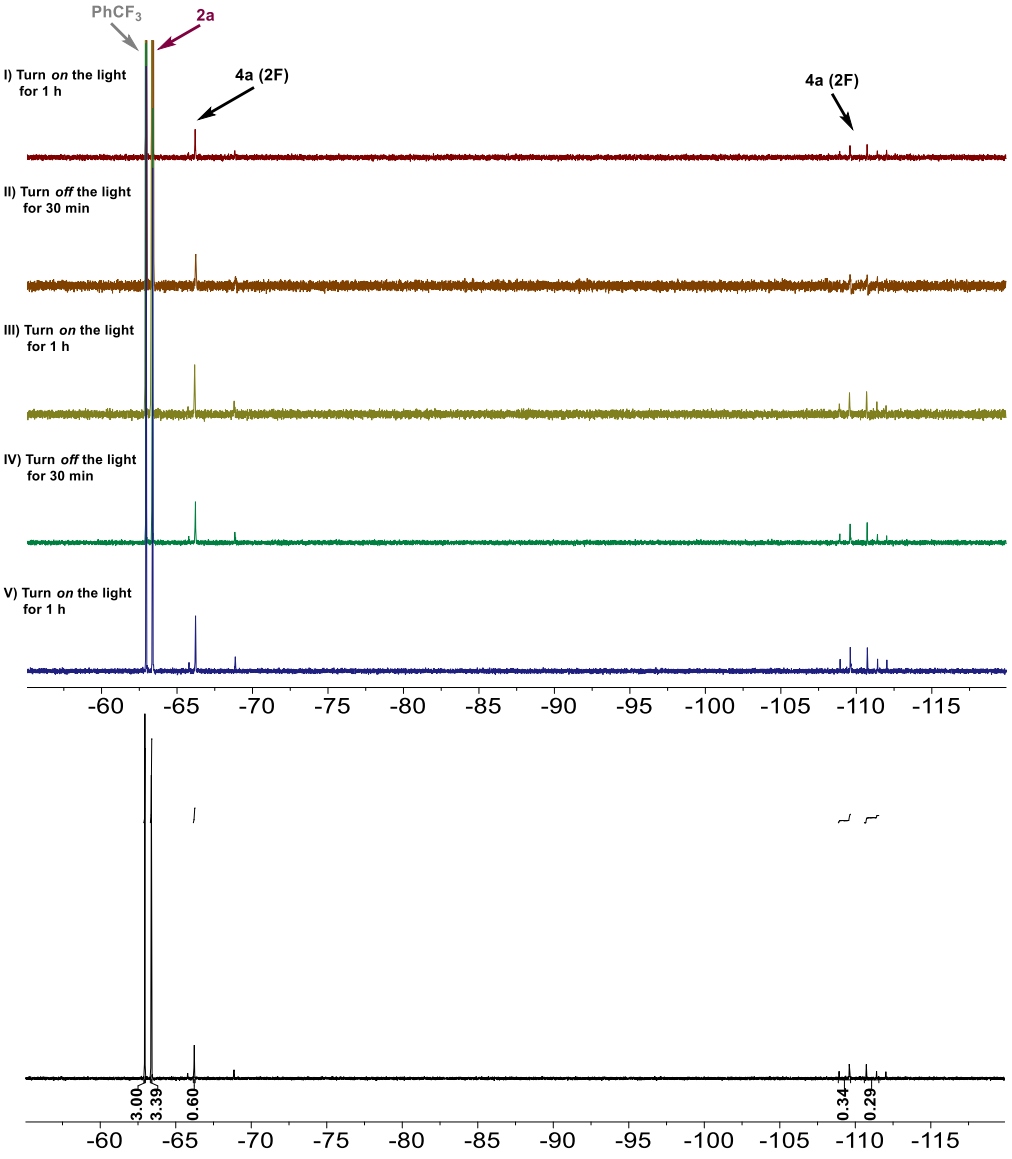


1a (0.2 mmol) + **2a** (1.5 equiv) + **3a** (1.2 equiv) → **4a**

Under argon atmosphere, to a flame-dried 10 mL Schlenk tube were added **1a** (0.2 mmol), **2a** (0.3 mmol, 1.5 equiv), **3a** (0.24 mmol, 1.2 equiv), 4CzIPN (1.6 mg, 0.002 mmol, 1.0 mol%), *i*-Pr_2NEt (35 μL, 0.2 mmol, 1.0 equiv), $PhCF_3$ (0.2 mmol, 1.0 equiv) and MeOH (2.0 mL), then the tube was sealed. Subsequent samples (each 80 μL) were taken at fixed time and determined by ^{19}F NMR analysis of the crude reaction mixture using $PhCF_3$ as internal standard.

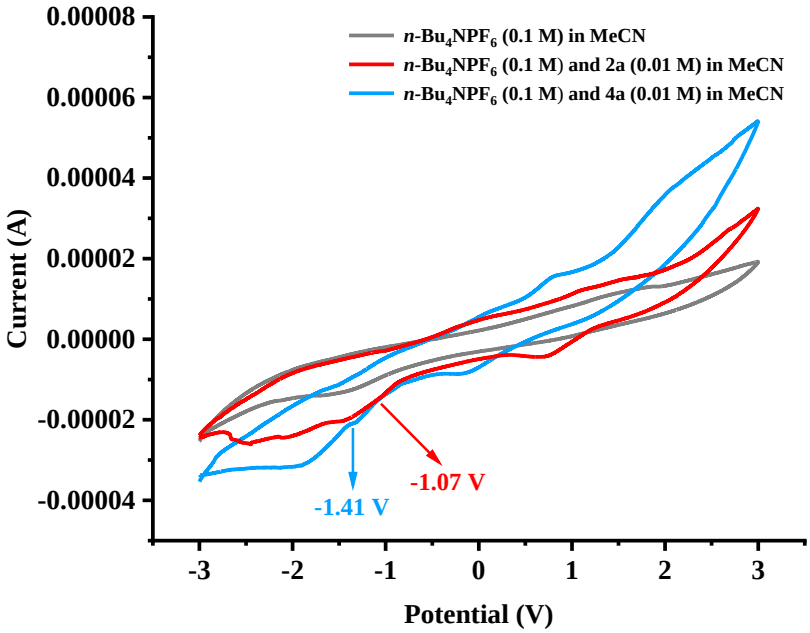
The light on/off experiment demonstrates the continuous irradiation is essential for this transformation, thus excluding the mechanism of atom transfer radical addition (ATRA) process.


Yield (%)
Time (h)
off
off


PhCF3
2a
I) Turn on the light for 1 h
4a (2F)
4a (2F)
II) Turn off the light for 30 min
III) Turn on the light for 1 h
IV) Turn off the light for 30 min
V) Turn on the light for 1 h
3.00
3.39
0.60
0.34
0.29

6.5 Cyclic voltammetry experiments

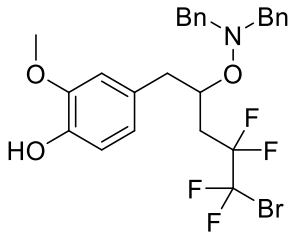
Cyclic voltammetry (CV) experiments were conducted in a 20 mL glass vial fitted with a glassy carbon working electrode, a silver/silver chloride electrode (Ag/AgCl) submerged in saturated aqueous KCl solution reference electrode, and a platinum wire counter electrode (CE). All measurements were carried out in 20 mL anhydrous MeCN, using a scan rate of 100 mV/s.



The cyclic voltammetry (CV) experiments of dibromoperfluoroalkane **2a** and product **4a** was performed. Two weak reductive peaks could be observed at -1.07 V (for **2a**) and -1.41 V (for **4a**), respectively. From literature report,[4] we could know that 4CzIPN possess a -1.21 V reduction potential [$E_{1/2}$ (PC/PC$^{\bullet-}$)]. Based on these data, it could be figured out why the radical anion of 4CzIPN is unable to further reduce products **4** to produce the double substitution of 1,2-dibromotetrafluoroethane **2a**.

7. Characterization Data of Compounds

4-(5-bromo-2-((dibenzylamino)oxy)-4,4,5,5-tetrafluoropentyl)-2-methoxyphenol (4a)



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford **4a** as a colorless viscous oil (90.1 mg, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.31 – 7.19 (m, 10H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.61 (d, *J* = 8.1 Hz, 1H), 6.57 (s, 1H), 5.54 (s, 1H), 3.84 – 3.70 (m, 8H), 2.64 (dd, *J* = 14.3, 7.2 Hz, 1H), 2.54 (dd, *J* = 14.3, 4.9 Hz, 1H), 2.20 – 2.05 (m, 1H), 1.65 – 1.54 (m, 1H).

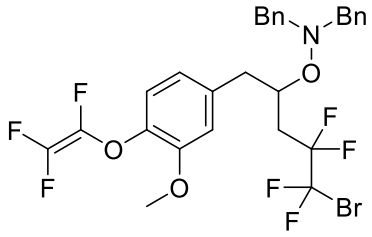
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 146.1, 144.1, 137.3, 129.8, 129.7, 128.2, 127.3, 122.5, 117.6 (tt, *J* = 310.2, 39.6 Hz), 117.0 (tt, *J* = 253.5, 31.0 Hz), 114.0, 112.1, 75.4, 62.2, 55.8, 39.6, 32.3 (t, *J* = 20.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -65.9 (s, 2F), -108.9 (dt, *J* = 255.5, 3.7 Hz, 1F), -110.8 (dt, *J* = 255.7, 3.9 Hz, 1F).

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{26}H_{26}BrF_4NO_3Na^+$: 578.0924; found: 578.0929.

IR (neat) ν (cm^{-1}): 3031, 2925, 2846, 1736, 1514, 1453, 1372, 1237, 1146, 1083, 1035, 905, 743, 698, 636, 590, 565.

***N*,*N*-dibenzyl-*O*-(5-bromo-4,4,5,5-tetrafluoro-1-(3-methoxy-4-((1,2,2-trifluorovinyl)oxy)phenyl)pentan-2-yl)hydroxylamine (4b)**



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford **4b** as a colorless viscous oil (57.3 mg, 45% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.22 – 7.10 (m, 10H), 6.88 (d, *J* = 8.6 Hz, 1H), 6.58 (d, *J* = 6.1 Hz, 2H), 3.79 – 3.64 (m, 8H), 2.54 (d, *J* = 5.9 Hz, 2H), 2.22 – 2.02 (m, 1H), 1.51 – 1.39 (m, 1H).

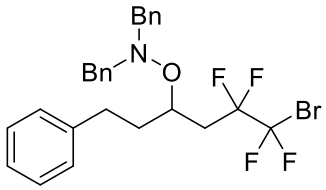
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 149.0, 146.7 (ddd, *J* = 277.7, 272.8, 62.1 Hz), 142.4, 137.1, 135.6, 134.1 (ddd, *J* = 262.1, 47.1, 41.7 Hz), 129.7, 128.2, 127.4, 121.9, 117.5 (tt, *J* = 310.0, 39.6 Hz), 117.0 (tt, *J* = 253.4, 31.2 Hz), 116.0, 114.4, 75.1, 62.4, 56.0, 39.7, 32.2 (t, *J* = 20.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -66.0 (s, 2F), -108.7 (dt, *J* = 255.5, 3.6 Hz, 1F), -111.0 (dt, *J* = 255.7, 4.0 Hz, 1F), -120.6 (dd, *J* = 98.8, 58.0 Hz, 1F), -126.9 (dd, *J* = 109.4, 98.9 Hz, 1F), -134.1 (dd, *J* = 109.4, 58.1 Hz, 1F).

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{28}H_{25}BrF_7NO_3Na^+$: 658.0798; found: 658.0824.

IR (neat) ν (cm^{-1}): 2931, 1604, 1510, 1454, 1421, 1269, 1200, 1084, 1036, 906, 741, 618, 588, 538.

***N*,*N*-dibenzyl-O-(6-bromo-5,5,6,6-tetrafluoro-1-phenylhexan-3-yl)hydroxylamine (4c)**



Purified by prepared thin layer chromatography (petroleum ether/ethyl acetate =20:1) to afford **4c** as a colorless viscous oil (63.9 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.42 – 7.12 (m, 15H), 4.14 – 3.64 (m, 5H), 2.80 – 2.67 (m, 1H), 2.54 – 2.41 (m, 1H), 2.38 – 2.19 (m, 1H), 1.87 – 1.76 (m, 1H), 1.76 – 1.64 (m, 1H), 1.63 – 1.49 (m, 1H).

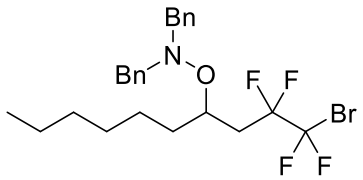
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) =141.8, 137.4, 129.8, 128.3, 128.3, 127.5, 125.8, 117.6 (tt, *J* = 310.0, 39.7 Hz), 117.0 (tt, *J* = 253.0, 31.0.0 Hz), 73.8, 62.3, 35.4, 32.9 (t, *J* = 20.9 Hz), 31.3

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -65.9 (s, 2F), -108.7 (dt, *J* = 255.6, 3.5 Hz, 1F), -111.8 (dt, *J* = 255.8, 4.0 Hz, 1F).

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{26}H_{26}BrF_4NONa^+$: 546.1026; found: 546.1040.

IR (neat) ν (cm^{-1}): .3029, 2927, 1603, 1495, 1454, 1208, 1144, 1119, 1028, 903, 744, 687, 569, 537.

***N*,*N*-dibenzyl-*O*-(1-bromo-1,1,2,2-tetrafluorodecan-4-yl)hydroxylamine (4d)**



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40:1) to afford **4d** as a colorless viscous oil (68.5 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.39 – 7.25 (m, 10H), 4.05 – 3.60 (m, 5H), 2.30 – 2.11 (m, 1H), 1.61 – 1.14 (m, 11H), 0.90 (t, *J* = 7.0 Hz, 3H).

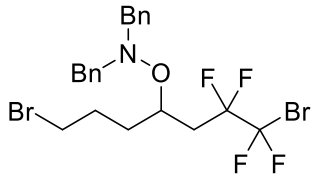
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 137.5, 129.7, 128.2, 127.4, 117.7 (tt, *J* = 310.2, 39.7 Hz), 117.0 (tt, *J* = 253.0, 30.9 Hz), 74.3, 62.3, 33.8, 33.0 (t, *J* = 20.9 Hz), 31.7, 29.2, 25.0, 22.6, 14.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -65.8 (s, 2F), -109.0 (dt, *J* = 255.5, 3.6 Hz, 1F), -111.7 (dt, *J* = 255.7, 3.8 Hz, 1F).

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{24}H_{30}BrF_4NONa^+$: 526.1339; found: 526.1354.

IR (neat) ν (cm^{-1}): 3032, 2926, 2854, 1495, 1454, 1208, 1144, 1077, 1029, 904, 746, 697, 649, 556.

***N*,*N*-dibenzyl-*O*-(1,7-dibromo-1,1,2,2-tetrafluoroheptan-4-yl)hydroxylamine (4e)**



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40:1) to afford **4e** as a colorless viscous oil (73.6 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.40 – 7.26 (m, 10H), 4.00 – 3.65 (m, 5H), 3.21 (td, *J* = 6.8, 1.8 Hz, 2H), 2.40 – 2.18 (m, 1H), 1.91 – 1.80 (m, 1H), 1.66 – 1.41 (m, 4H).

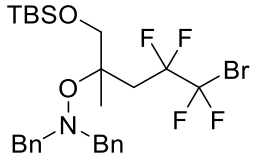
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 137.3, 129.7, 128.3, 127.5, 117.5 (tt, *J* = 310.1, 39.6 Hz), 116.9 (tt, *J* = 253.2, 30.8 Hz), 73.6, 62.5, 33.4, 32.8 (t, *J* = 20.9 Hz), 32.5, 28.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -66.0 (s, 2F), -108.9 (dt, *J* = 255.8, 3.4 Hz, 1F), -111.8 (dt, *J* = 255.5, 3.5 Hz, 1F).

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{21}H_{23}Br_2F_4NONa^+$: 561.9975; found: 561.9992.

IR (neat) ν (cm^{-1}): 2922, 1496, 1454, 1255,1208, 1143, 1079, 1030, 905, 745, 698, 647, 585.

***N*,*N*-dibenzyl-*O*-(5-bromo-1-((tert-butyldimethylsilyl)oxy)-4,4,5,5-tetrafluoro-2-methylpentan-2-yl)hydroxylamine (4f)**



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford **4f** as a colorless viscous oil (60.2 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = δ 7.38 – 7.23 (m, 10H), 4.00 – 3.75 (m, 4H), 3.60 – 3.18 (m, 2H), 2.44 – 2.25 (m, 1H), 2.19 – 2.00 (m, 1H), 0.88 (s, 9H), 0.00 (s, 6H).

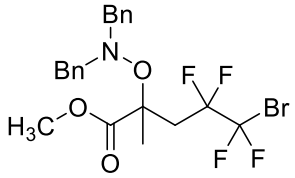
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 137.4, 129.8, 128.2, 127.4, 118.0 (tt, J = 310.9, 40.0 Hz), 117.4 (tt, J = 255.1, 30.6 Hz), 80.8, 66.6, 62.4, 33.5 (t, J = 20.3 Hz), 25.8, 20.2, 18.1, -5.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -65.7 (s, 2F), -108.7 (s, 1F), -108.8 (s, 1F).

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{27}H_{36}BrF_4NO_2SiNa^+$: 600.1527; found: 600.1552.

IR (neat) ν (cm^{-1}): 2929, 1455, 1361, 1251, 1210, 1146, 1098, 1072, 905, 835, 775, 737, 697, 670, 563, 538.

Methyl 5-bromo-2-((dibenzylamino)oxy)-4,4,5,5-tetrafluoro-2-methylpentanoate (4g)



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford **4g** as a colorless viscous oil (57.1 mg, 58% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.36 – 7.22 (m, 10H), 3.99 – 3.78 (m, 4H), 3.72 (s, 3H), 2.86 – 2.70 (m, 1H), 2.12 – 1.90 (m, 1H), 1.47 (s, 3H).

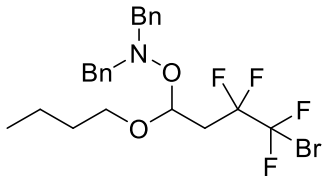
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 171.4, 136.7, 129.9, 128.3, 127.5, 117.3 (tt, *J* = 310.3, 39.4 Hz), 116.3 (tt, *J* = 254.9, 31.2 Hz), 80.3, 62.0, 52.3, 36.7 (t, *J* = 20.1 Hz), 20.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -66.41 (s, 2F), -106.1 (dd, *J* = 257.5, 5.0 Hz, 1F), -110.8 (dd, *J* = 257.5, 5.1 Hz, 1F).

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{21}H_{22}BrF_4NO_3Na^+$: 514.0611; found: 514.0642.

IR (neat) ν (cm^{-1}): 2952, 1742, 1495, 1454, 1315,1248, 1204, 1147, 1113, 1073, 985, 908, 749, 697, 583, 544.

***N*,*N*-dibenzyl-*O*-(4-bromo-1-butoxy-3,3,4,4-tetrafluorobutyl)hydroxylamine (4h)**



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40:1) to afford **4h** as a colorless viscous oil (43.4 mg, 44% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.38 – 7.27 (m, 10H), 4.67 (dd, *J* = 7.8, 2.8 Hz, 1H), 4.11 – 3.78 (m, 5H), 3.39 (dt, *J* = 9.4, 6.8 Hz, 1H), 2.21 – 2.05 (m, 1H), 1.95 – 1.80 (m, 1H), 1.52 – 1.43 (m, 2H), 1.35 – 1.29 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H).

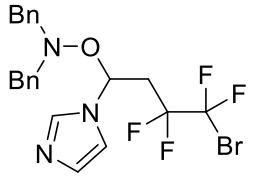
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 137.1, 129.6, 128.3, 127.6, 117.4 (tt, *J* = 310.2, 39.4 Hz), 115.9 (tt, *J* = 253.4, 31.2 Hz), 101.1, 69.6, 62.9, 34.6 (t, *J* = 20.8 Hz), 31.7, 19.1, 13.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -66.2 (s, 2F), -109.8 (dt, *J* = 257.6, 3.5 Hz, 1F), -111.8 (dt, *J* = 258.1, 4.1 Hz, 1F).

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{22}H_{26}BrF_4NO_2Na^+$: 514.0975; found: 514.0993.

IR (neat) ν (cm^{-1}): 3031, 2930, 1454, 1379, 1143,1086, 962, 907, 747, 698, 615, 579, 554.

***N*,*N*-dibenzyl-*O*-(4-bromo-3,3,4,4-tetrafluoro-1-(1H-imidazol-1-yl)butyl)hydroxylamine (4i)**



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3:1) to afford **4i** as a white solid (71.0 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.46 (s, 1H), 7.32 – 7.06 (m, 10H), 6.96 (s, 1H), 6.84 (s, 1H), 5.05 (dd, *J* = 7.1, 5.3 Hz, 1H), 3.81 – 3.47 (m, 4H), 2.48 – 2.29 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 137.2, 136.3, 130.2, 129.6, 128.5, 127.8, 116.7 (tt, *J* = 309.6, 38.5 Hz), 115.7, 114.9 (tt, *J* = 255.4, 31.9 Hz), 82.6, 64.5, 34.3 (t, *J* = 21.5 Hz).

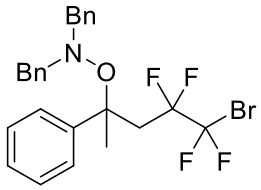
^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -66.7 (s, 2F), -111.5 (dt, *J* = 14.3, 3.7 Hz, 2F).

m.p. = 52-54 °C

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{21}H_{20}BrF_4N_3ONa^+$: 508.0618; found: 508.0640.

IR (neat) ν (cm^{-1}): 2924, 2850, 1493, 1454, 1384, 1304, 1252, 1223, 1140, 1103, 1030, 977, 914, 860, 806, 751, 737, 696, 660, 561, 544.

***N*,*N*-dibenzyl-*O*-(5-bromo-4,4,5,5-tetrafluoro-2-phenylpentan-2-yl)hydroxylamine (4j)**



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 80:1) to afford **4j** as a colorless viscous oil (62.0 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.49 (d, *J* = 7.5 Hz, 2H), 7.40 – 7.12 (m, 13H), 4.02 – 3.47 (m, 4H), 2.48 – 2.18 (m, 2H), 1.78 (s, 3H).

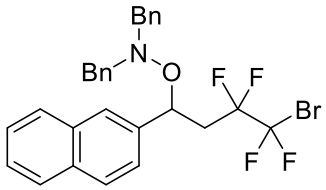
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 142.5, 137.4, 130.2, 128.3, 127.9, 127.9, 127.5, 126.6, 117.8 (tt, *J* = 310.7, 40.1 Hz), 116.5 (tt, *J* = 256.3, 30.8 Hz), 80.0, 63.6, 62.3, 38.9 (t, *J* = 19.8 Hz), 22.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -65.9 (s, 2F), -106.3 (dt, *J* = 254.5, 4.2 Hz, 1F), -109.3 (dt, *J* = 252.5, 3.0 Hz, 1F).

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{25}H_{24}BrF_4NONa^+$: 532.0870; found: 532.0888.

IR (neat) ν (cm^{-1}): 3031, 2926, 1495, 1452, 1356, 1228, 1144, 1097, 1078, 1030, 901, 749, 695, 616, 536.

***N*,*N*-dibenzyl-*O*-(4-bromo-3,3,4,4-tetrafluoro-1-(naphthalen-2-yl)butyl)hydroxylamine (4k)**



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40:1) to afford **4k** as a white solid (57.9 mg, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.84 – 7.79 (m, 2H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.54 (s, 1H), 7.51 – 7.46 (m, 2H), 7.39 – 7.17 (m, 11H), 4.68 (dd, *J* = 8.0, 5.1 Hz, 1H), 3.91 – 3.78 (m, 4H), 2.71 – 2.56 (m, 1H), 2.15 – 2.00 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 137.4, 137.3, 133.2, 133.0, 129.8, 128.2, 128.14, 128.07, 127.6, 127.4, 127.0, 126.1, 126.0, 124.7, 117.5 (tt, *J* = 310.0, 39.2 Hz), 116.2 (tt, *J* = 254.0, 31.1 Hz), 77.7, 62.6, 34.8 (t, *J* = 20.8 Hz).

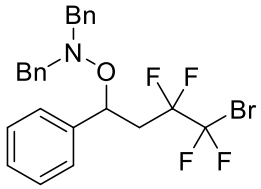
^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -66.0 (s, 2F), -109.1 (dt, *J* = 256.3, 3.6 Hz, 1F), -110.9 (dt, *J* = 256.4, 3.8 Hz, 1F).

m.p. = 88-90 °C

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{28}H_{24}BrF_4NONa^+$: 568.0770; found: 532.0790.

IR (neat) ν (cm^{-1}): 3056, 3032, 2997, 2918,2871, 2849, 1493, 1393, 1345, 1236, 1145, 1079, 1038, 973, 906, 867, 837, 810, 741, 697, 649, 588, 548.

***N*,*N*-dibenzyl-*O*-(4-bromo-3,3,4,4-tetrafluoro-1-phenylbutyl)hydroxylamine (4l)**



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40:1) to afford **4l** as a white solid (55.5 mg, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.41 – 7.19 (m, 13H), 7.14 (dd, *J* = 6.7, 2.9 Hz, 2H), 4.49 (dd, *J* = 8.0, 5.0 Hz, 1H), 4.01 – 3.60 (m, 4H), 2.66 – 2.48 (m, 1H), 2.05 – 1.87 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 140.1, 137.3, 129.8, 128.3, 128.23, 128.21, 127.5, 127.4, 117.5 (tt, *J* = 310.0, 39.4 Hz), 116.2 (tt, *J* = 254.2, 31.4 Hz), 77.52, 62.59, 34.8 (t, *J* = 20.7 Hz).

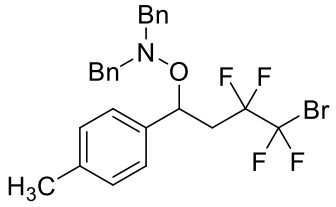
^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -66.0 (s, 2F), -109.3 (dt, *J* = 256.6, 3.6 Hz, 1F), -110.9 (dt, *J* = 256.5, 3.9 Hz, 1F).

m.p. = 44-46 °C

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{24}H_{22}BrF_4NONa^+$: 518.0713; found: 518.0733.

IR (neat) ν (cm^{-1}): 3033, 2925,, 1496, 1456, 1383, 1319, 1237, 1144, 1079, 905, 864, 838, 742, 694, 611, 557, 540.

***N*,*N*-dibenzyl-*O*-(4-bromo-3,3,4,4-tetrafluoro-1-(*p*-tolyl)butyl)hydroxylamine (4m)**



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40:1) to afford **4m** as a white solid (48.9 mg, 48% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.35 – 7.20 (m, 10H), 7.08 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 4.43 (dd, *J* = 8.2, 4.9 Hz, 1H), 3.88 – 3.70 (m, 4H), 2.61 – 2.47 (m, 1H), 2.31 (s, 3H), 2.00 – 1.82 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 137.9, 137.4, 137.1, 129.8, 129.0, 128.2, 127.42, 127.39, 117.5 (tt, *J* = 310.0, 39.4 Hz), 116.3 (tt, *J* = 254.2, 31.2 Hz), 77.3, 62.6, 34.6 (t, *J* = 20.7 Hz), 21.2.

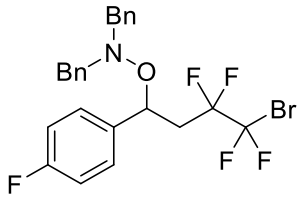
^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -66.0 (s, 2F), -109.2 (dt, *J* = 256.2, 3.6 Hz, 1F), -111.0 (dt, *J* = 256.6, 3.9 Hz, 1F).

m.p. = 41-43 ºC

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{25}H_{24}BrF_4NONa^+$: 532.0870; found: 532.0889.

IR (neat) ν (cm^{-1}): 3036, 2920, 1496, 1455, 1207, 1143, 1078, 1037, 972, 902, 866, 848, 803, 752, 742, 698, 574.

***N*,*N*-dibenzyl-*O*-(4-bromo-3,3,4,4-tetrafluoro-1-(4-fluorophenyl)butyl)hydroxylamine (4n)**



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40:1) to afford **4n** as a white solid (61.7 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.40 – 7.18 (m, 10H), 7.06 – 7.00 (m, 2H), 6.97 – 6.90 (m, 2H), 4.41 (dd, *J* = 8.3, 5.0 Hz, 1H), 3.90 – 3.67 (m, 4H), 2.62 – 2.44 (m, 1H), 1.96 – 1.77 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 162.5 (d, *J* = 246.5 Hz), 137.2, 135.9 (d, *J* = 3.3 Hz), 129.7, 129.1 (d, *J* = 8.3 Hz), 128.3, 127.5, 117.4 (tt, *J* = 310.0, 39.3 Hz), 116.2 (tt, *J* = 254.1, 31.2 Hz), 115.1 (d, *J* = 21.4 Hz), 76.7, 62.7, 34.83 (t, *J* = 20.7 Hz).

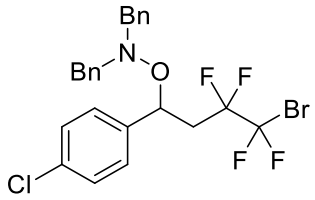
^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -66.1 (s, 2F), -109.3 (dt, *J* = 256.5, 3.5 Hz, 1F), -111.0 (dt, *J* = 256.2, 3.8 Hz, 1F), -113.9 (s, 1F).

m.p. = 61-63 °C

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{24}H_{21}BrF_5NONa^+$: 536.0619; found: 536.0642.

IR (neat) ν (cm^{-1}): 3036, 2917, 1605, 1512, 1456, 1257, 1225, 1144, 1077, 975, 904, 867, 851, 817, 754, 725, 698, 651, 596.

***N*,*N*-dibenzyl-*O*-(4-bromo-1-(4-chlorophenyl)-3,3,4,4-tetrafluorobutyl)hydroxylamine (4o)**



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40:1) to afford **4o** as a colorless viscous oil (49.8 mg, 47% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.34 – 7.17 (m, 12H), 6.97 (d, *J* = 8.2 Hz, 2H), 4.41 (dd, *J* = 8.1, 5.1 Hz, 1H), 3.86 – 3.72 (m, 4H), 2.60 – 2.41 (m, 1H), 1.97 – 1.78 (m, 1H).

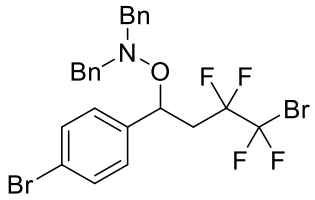
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 138.6, 137.2, 133.9, 129.7, 128.8, 128.4, 128.3, 127.5, 117.4 (tt, *J* = 310.1, 39.2 Hz), 116.1 (tt, *J* = 254.1, 31.3 Hz), 76.8, 62.8, 34.8 (t, *J* = 20.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -66.1 (s, 2F), -109.0 (dt, *J* = 256.7, 3.5 Hz, 1F), -110.9 (dt, *J* = 256.7, 3.9 Hz, 1F).

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{24}H_{21}BrClF_4NONa^+$: 552.0323; found: 552.0335.

IR (neat) ν (cm^{-1}): 3036, 2925, 1600, 1493, 1455, 1236, 1207, 1145, 1080, 1030, 1012, 974, 902, 864, 850, 811, 746, 699, 650, 578.

***N*,*N*-dibenzyl-*O*-(4-bromo-1-(4-bromophenyl)-3,3,4,4-tetrafluorobutyl)hydroxylamine (4p)**



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40:1) to afford **4o** as a colorless viscous oil (71.3 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.35 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.15 (m, 10H), 6.91 (d, *J* = 8.2 Hz, 2H), 4.40 (dd, *J* = 8.1, 5.1 Hz, 1H), 3.87 – 3.72 (m, 4H), 2.57 – 2.43 (m, 1H), 1.96 – 1.80 (m, 1H).

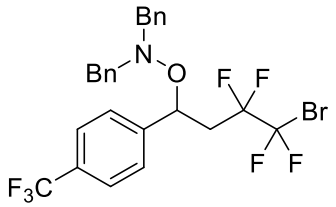
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 139.2, 137.2, 131.4, 129.7, 129.1, 128.3, 127.5, 122.1, 117.4 (tt, *J* = 310.2, 39.2 Hz), 116.1 (tt, *J* = 256.3, 31.4 Hz), 76.8, 62.7, 34.8 (t, *J* = 20.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -66.1 (s, 2F), -109.0 (dt, *J* = 256.6, 3.5 Hz, 1F), -110.9 (dt, *J* = 256.6, 3.9 Hz, 1F).

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{24}H_{21}Br_2F_4NONa^+$: 595.9818; found: 595.9836.

IR (neat) ν (cm^{-1}): 3031, 2926, 1488, 1454, 1205, 1143, 1080, 1010, 903, 850, 741, 697, 623, 580, 547, 539.

***N*,*N*-dibenzyl-*O*-(4-bromo-3,3,4,4-tetrafluoro-1-(4-(trifluoromethyl)phenyl)butyl) hydroxylamine (4q)**



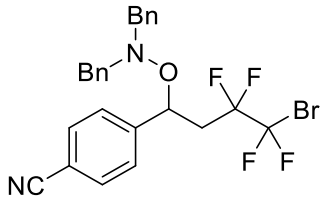
Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40:1) to afford **4q** as a colorless viscous oil (68.6 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.47 (d, *J* = 7.9 Hz, 2H), 7.38 – 7.07 (m, 12H), 4.50 (dd, *J* = 7.9, 5.3 Hz, 1H), 3.82 (s, 4H), 2.62 – 2.43 (m, 1H), 1.98 – 1.83 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 144.1, 137.1, 130.1 (q, *J* = 32.4 Hz), 129.6, 128.3, 127.7, 127.6, 125.2 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.1 Hz). 117.3 (tt, *J* = 309.5, 39.0 Hz), 116.1 (tt, *J* = 253,7, 31.4 Hz), 76.8, 62.8, 34.9 (t, *J* = 20.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -62.6 (s, 3F), -66.2 (s, 2F), -109.1 (dt, *J* = 256.0, 3.6 Hz, 1F), -110.8 (dt, *J* = 256.6, 4.0 Hz, 1F).

4-(4-bromo-1-((dibenzylamino)oxy)-3,3,4,4-tetrafluorobutyl)benzonitrile (4r)



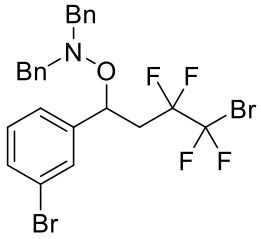
Purified by silica gel column chromatography (petroleum ether/dichloromethane = 10:1) to afford **4r** as a colorless viscous oil (57.6 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.50 (d, *J* = 8.0 Hz, 2H), 7.47 – 6.99 (m, 12H), 4.47 (dd, *J* = 8.0, 5.2 Hz, 1H), 3.83 (s, 4H), 2.59 – 2.41 (m, 1H), 1.96 – 1.81 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 145.3, 137.0, 132.0, 129.6, 128.3, 128.0, 127.6, 118.6, 117.1 (tt, *J* = 309.8, 39.0 Hz), 116.0 (tt, *J* = 254.4, 31.4 Hz), 111.8, 76.8, 62.9, 34.9 (t, *J* = 20.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -66.2 (s, 2F), -108.8 (dt, *J* = 256.7, 3.6 Hz, 1F), -110.8 (dt, *J* = 256.6, 3.8 Hz, 1F).

***N*,*N*-dibenzyl-*O*-(4-bromo-1-(3-bromophenyl)-3,3,4,4-tetrafluorobutyl)hydroxylamine (4s)**



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40:1) to afford **4s** as a colorless viscous oil (66.7 mg, 58% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.37 (d, *J* = 7.9 Hz, 1H), 7.35 – 7.17 (m, 11H), 7.12 (t, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.7 Hz, 1H), 4.38 (dd, *J* = 8.0, 5.1 Hz, 1H), 3.87 – 3.74 (m, 4H), 2.57 – 2.42 (m, 1H), 1.97 – 1.81 (m, 1H).

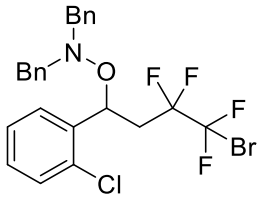
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 142.4, 137.1, 131.3, 130.7, 129.8, 129.7, 128.3, 127.6, 126.0, 122.3, 117.3 (tt, *J* = 310.0, 39.3 Hz), 116.1 (tt, *J* = 254.1, 31.4 Hz), 77.2, 62.8, 34.8 (t, *J* = 20.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -66.1 (s, 2F), -109.0 (dt, *J* = 256.8, 3.6 Hz, 1F), -110.8 (dt, *J* = 256.6, 3.8 Hz, 1F).

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{24}H_{21}Br_2F_4NONa^+$: 595.9818; found: 595.9836.

IR (neat) ν (cm^{-1}): 3031, 2926, 1571, 1494, 1431,1200, 1143, 1080, 1028, 903, 783, 745, 696, 617, 581, 554.

***N*,*N*-dibenzyl-*O*-(4-bromo-1-(2-chlorophenyl)-3,3,4,4-tetrafluorobutyl)hydroxylamine (4t)**



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40:1) to afford **4t** as a colorless viscous oil (72.2 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.24 – 7.01 (m, 14H), 5.24 (t, *J* = 6.5 Hz, 1H), 3.86 – 3.63 (m, 4H), 2.49 – 2.33 (m, 1H), 2.10 – 1.95 (m, 1H).

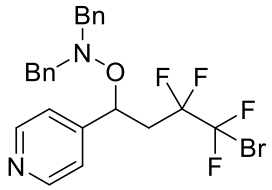
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 137.9, 137.2, 133.2, 129.6, 129.5, 129.1, 128.8, 128.2, 127.4, 126.8, 117.5 (tt, *J* = 310.0, 39.3 Hz), 116.1 (tt, *J* = 254.5, 31.2 Hz), 73.4, 62.2, 34.6 (t, *J* = 21.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -66.0 (s, 2F), -110.1 (s, 1F), -110.5 (s, 1F).

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{24}H_{21}BrClF_4NONa^+$: 552.0323; found: 552.0355.

IR (neat) ν (cm^{-1}): 3031, 2848, 1596, 1495, 1454,1240, 1141, 1081, 904, 870, 745, 697, 574, 547.

***N*,*N*-dibenzyl-*O*-(4-bromo-3,3,4,4-tetrafluoro-1-(pyridin-4-yl)butyl)hydroxylamine (4u)**



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) to afford **4u** as a white solid (71.6 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.40 (d, *J* = 6.1 Hz, 2H), 7.34 – 7.00 (m, 10H), 6.86 (d, *J* = 6.1 Hz, 2H), 4.34 (dd, *J* = 7.8, 5.2 Hz, 1H), 3.84 – 3.68 (m, 4H), 2.49 – 2.30 (m, 1H), 1.92 – 1.73 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 149.7, 148.8, 137.0, 129.7, 128.3, 127.6, 122.2, 117.1 (tt, *J* = 309.8, 39.0 Hz), 115.9 (tt, *J* = 254.3, 31.1 Hz), 76.4, 62.8, 34.8 (t, *J* = 21.0 Hz).

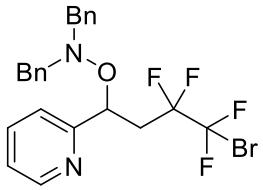
^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -66.2 (s, 2F), -108.9 (dt, *J* = 256.9, 3.5 Hz, 1F), -110.9 (dt, *J* = 256.6, 3.6 Hz, 1F).

m.p. = 69-71 °C

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{23}H_{21}BrF_4N_2ONa^+$: 519.0666; found: 519.0685.

IR (neat) ν (cm^{-1}): 2920, 1602, 1566, 1497, 1415, 1259, 1144, 1106, 1078, 906, 868, 852, 740, 700, 652, 592, 561, 549.

***N*,*N*-dibenzyl-*O*-(4-bromo-3,3,4,4-tetrafluoro-1-(pyridin-2-yl)butyl)hydroxylamine (4v)**



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) to afford **4v** as a colorless viscous oil (74.6 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.46 (d, *J* = 4.2 Hz, 1H), 7.47 (td, *J* = 7.7, 1.8 Hz, 1H), 7.25 – 7.04 (m, 11H), 6.89 (d, *J* = 7.7 Hz, 1H), 4.58 (dd, *J* = 7.3, 5.4 Hz, 1H), 4.02 – 3.32 (m, 5H), 2.54 – 2.36 (m, 2H).

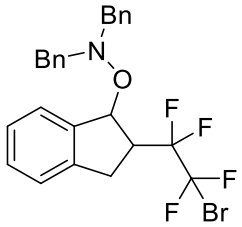
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 158.6, 149.4, 137.3, 136.1, 129.6, 128.2, 127.3, 123.4, 123.0, 117.5 (tt, *J* = 310.3, 39.0 Hz), 116.3 (tt, *J* = 254.1, 31.1 Hz), 78.5, 62.4, 33.6 (t, *J* = 21.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -66.0 (s, 2F), -109.8 (q, *J* = 3.5 Hz, 2F).

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{23}H_{21}BrF_4N_2ONa^+$: 519.0666; found: 519.0655.

IR (neat) ν (cm^{-1}): 2937, 1770, 1592, 1496, 1441, 1210, 1143, 1075, 905, 864, 849, 741, 699, 650, 587, 555.

***N*,*N*-dibenzyl-*O*-(2-(2-bromo-1,1,2,2-tetrafluoroethyl)-2,3-dihydro-1H-inden-1-yl)hydroxylamine (4w)**



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **4w** as a colorless viscous oil (61.0 mg, 60% yield, > 19:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.31 – 7.14 (m, 12H), 7.12 – 7.03 (m, 2H), 5.17 (s, 1H), 4.03 – 3.58 (m, 4H), 2.85 – 2.69 (m, 3H).

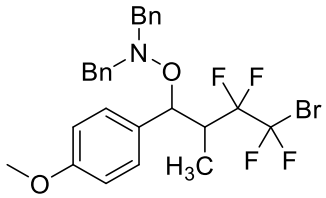
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 142.5, 139.3, 137.2, 129.9, 129.2, 128.3, 127.5, 126.8, 125.9, 124.3, 118.5 (tt, *J* = 311.4, 41.4 Hz), 117.1 (tt, *J* = 255.4, 30.6 Hz), 84.2, 62.4, 45.3 (t, *J* = 20.8 Hz), 30.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -61.7 (dd, *J* = 178.4, 5.5 Hz, 1F), -62.6 (dd, *J* = 178.3, 8.0 Hz, 1F), -108.0 (dd, *J* = 264.7, 5.4 Hz, 1F), -115.0 (dd, *J* = 264.6, 7.9 Hz, 1F).

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{25}H_{22}BrF_4NONa^+$: 530.0713; found: 530.0725.

IR (neat) ν (cm^{-1}): 3031, 2933, 1495, 1454, 1331, 1220, 1142, 1112, 1075, 1028, 958, 891, 827, 748, 697, 621, 582, 561.

***N*,*N*-dibenzyl-*O*-(4-bromo-3,3,4,4-tetrafluoro-1-(4-methoxyphenyl)-2-methylbutyl)hydroxylamine (4x)**



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40:1) to afford **4x** as a colorless viscous oil (78.9 mg, 73% yield, 13:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.30 – 7.12 (m, 10H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 8.3 Hz, 2H), 4.78 (d, *J* = 4.4 Hz, 1H), 3.90 – 3.68 (m, 8H), 2.73 – 2.37 (m, 1H), 1.06 (d, *J* = 7.2 Hz, 3H).

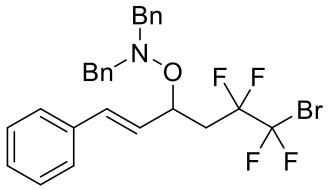
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 158.9, 137.5, 133.1, 129.5, 128.6, 128.0, 127.1, 118.8 (tt, *J* = 310.7, 39.9 Hz), 117.3 (tt, *J* = 255.7, 31.2 Hz), 113.2, 80.5, 61.5, 55.2, 41.6 (t, *J* = 19.8 Hz), 8.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -61.3 (dd, *J* = 176.2, 9.8 Hz, 1F), -62.4 (dd, *J* = 175.9, 3.9 Hz, 1F), -105.2 (dd, *J* = 263.0, 4.0 Hz, 1F), -115.8 (dd, *J* = 263.0, 9.9 Hz, 1F).

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{26}H_{26}BrF_4NO_2Na^+$: 562.0975; found: 562.1000.

IR (neat) ν (cm^{-1}): 2999, 2933, 1612, 1512, 1454, 1248, 1142, 1067, 1031, 913, 837, 739, 698, 603, 561, 543.

(*E*)-*N*,*N*-dibenzyl-*O*-(6-bromo-5,5,6,6-tetrafluoro-1-phenylhex-1-en-3-yl) hydroxylamine (4y)



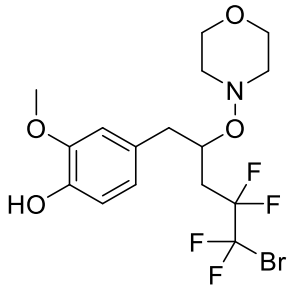
Purified by silica gel column chromatography (hexane/dichloromethane = 10:1) to afford **4y** as a colorless viscous oil (59.9 mg, 57% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.34 – 7.23 (m, 15H), 6.34 (d, *J* = 15.8 Hz, 1H), 5.72 (dd, *J* = 15.9, 8.4 Hz, 1H), 4.15 (td, *J* = 8.0, 4.9 Hz, 1H), 3.87 (q, *J* = 13.0 Hz, 4H), 2.38 – 2.20 (m, 1H), 1.90 – 1.73 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 137.4, 136.3, 133.2, 129.8, 128.4, 128.2, 128.0, 127.8, 127.4, 126.7, 117.5 (tt, *J* = 310.2, 39.4 Hz), 116.3 (tt, *J* = 254.1, 31.4 Hz),76.3, 62.8, 34.3 (t, *J* = 20.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -66.0 (s, 2F), -108.7 (dt, *J* = 256.8, 3.5 Hz, 1F), -110.8 (dt, *J* = 257.1, 3.8 Hz, 1F).

4-(5-bromo-4,4,5,5-tetrafluoro-2-(morpholinooxy)pentyl)-2-methoxyphenol (4aa)



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford **4aa** as a colorless viscous oil (36.6 mg, 41% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 6.84 (d, *J* = 7.9 Hz, 1H), 6.74 – 6.68 (m, 2H), 5.57 (s, 1H), 4.25 – 4.18 (m, 1H), 3.91 – 3.81 (m, 5H), 3.64 – 3.51 (m, 2H), 3.12 (d, *J* = 10.9 Hz, 1H), 3.00 – 2.90 (m, 2H), 2.80 – 2.69 (m, 2H), 2.66 – 2.56 (m, 1H), 2.45 – 2.29 (m, 1H), 2.25 – 2.10 (m, 1H).

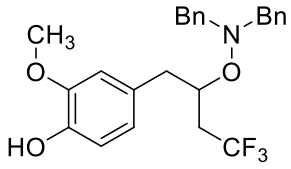
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 146.3, 144.2, 129.4, 122.2, 117.6 (tt, *J* = 309.7, 39.7 Hz), 116.9 (tt, *J* = 253.8, 31.4 Hz), 114.3, 112.0, 75.6, 66.0, 56.6, 55.9, 40.0, 33.1 (t, *J* = 21.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -66.0 (t, *J* = 3.7 Hz, 2F), -109.8 (t, *J* = 3.6 Hz, 2F).

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{16}H_{20}BrF_4NO_4Na^+$: 468.0404; found: 468.0426.

IR (neat) ν (cm^{-1}): 2927, 2852, 1603, 1515, 1461, 1431, 1376, 1267, 1237, 1206, 1143, 1103, 1082, 1034, 908, 855, 819, 749, 618, 575.

4-(2-((dibenzylamino)oxy)-4,4,4-trifluorobutyl)-2-methoxyphenol (4ab)



Using trifluoroiodomethane (CF_3I) as radical precursor. Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford **4ab** as a colorless viscous oil (57.9 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.32 – 7.22 (m, 10H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.56 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.51 (d, *J* = 1.9 Hz, 1H), 5.50 (s, 1H), 3.91 – 3.86 (m, 1H), 3.83 (s, 3H), 3.80 – 3.71 (m, 4H), 2.72 (dd, *J* = 14.1, 6.6 Hz, 1H), 2.36 (dd, *J* = 14.1, 6.1 Hz, 1H), 2.15 – 2.05 (m, 1H), 1.80 – 1.68 (m, 1H).

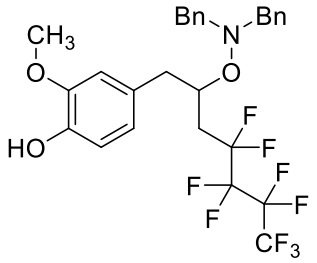
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 146.2, 144.1, 137.3, 129.8, 129.6, 128.2, 127.4, 126.2 (q, *J* = 275.4 Hz), 122.3, 114.1, 111.9, 76.2, 62.2, 55.9, 39.0, 36.1 (q, *J* = 27.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -62.6.

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{25}H_{26}F_3NO_3Na^+$: 468.1757; found: 468.1780.

IR (neat) ν (cm^{-1}): 2933, 1759, 1603, 1515, 1454, 1431, 1386, 1331, 1252, 1125, 1031, 887, 819, 742, 698, 590, 561.

4-(2-((dibenzylamino)oxy)-4,4,5,5,6,6,7,7,7-nonafluoroheptyl)-2-methoxyphenol (4ac)



Using perfluorobutyl iodide (C_4F_9I) as radical precursor. Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford **4ac** as a colorless viscous oil (69.1 mg, 58% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.31 – 7.20 (m, 10H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.56 (s, 1H), 5.50 (s, 1H), 3.87 – 3.69 (m, 8H), 2.66 (dd, *J* = 14.3, 7.2 Hz, 1H), 2.52 (dd, *J* = 14.3, 4.9 Hz, 1H), 2.17 – 2.01 (m, 1H), 1.67 – 1.57 (m, 1H).

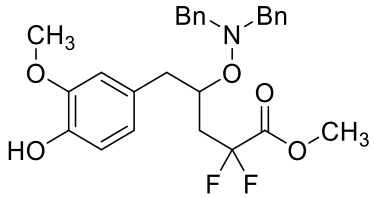
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 146.2, 144.1, 137.3, 129.8, 129.6, 128.2, 127.4, 122.5, 114.1, 112.1, 75.0, 62.2, 55.9, 39.7, 32.7 (t, *J* = 20.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -81.1 (s, 3F), -111.7 (dt, *J* = 270.8, 13.7 Hz, 1F), -113.2 (dt, *J* = 270.0, 12.9 Hz, 1F), -124.6 (d, *J* = 9.7 Hz, 2F), -125.9 (s, 2F).

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{28}H_{26}F_9NO_3Na^+$: 618.1661; found: 618.1694.

IR (neat) ν (cm^{-1}): 2924, 1605, 1515, 1454, 1432, 1356, 1216, 1132, 1037, 881, 817, 737, 718, 621, 575, 546.

Methyl 4-((dibenzylamino)oxy)-2,2-difluoro-5-(4-hydroxy-3-methoxyphenyl)pentanoate (4ad)



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **4ad** as a colorless viscous oil (53.4 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.27 – 7.15 (m, 10H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.44 (dd, *J* = 8.0, 1.9 Hz, 1H), 6.38 (d, *J* = 1.9 Hz, 1H), 5.41 (s, 1H), 3.81 – 3.71 (m, 8H), 3.67 – 3.59 (m, 3H), 2.88 – 2.79 (m, 1H), 2.12 – 1.94 (m, 2H), 1.81 – 1.65 (m, 1H).

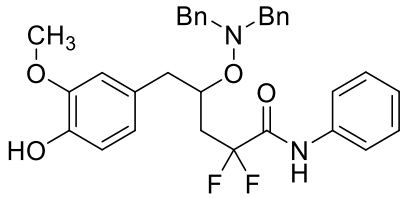
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 164.6 (t, *J* = 32.4 Hz), 146.3, 144.0, 137.4, 129.8, 129.7, 128.1, 127.3, 122.1, 115.3 (t, *J* = 250.8 Hz), 114.1, 112.8, 111.7, 76.1, 62.0, 55.9, 53.0, 39.1, 37.1 (t, *J* = 23.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -100.7 (d, *J* = 262.2 Hz, 1F), -107.6 (d, *J* = 261.9 Hz, 1F).

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{27}H_{29}F_2NO_5Na^+$: 508.1906; found: 508.1928.

IR (neat) ν (cm^{-1}): 3519, 3028, 2932, 1767, 1604, 1514, 1495, 1453, 1342, 1267, 1205, 1122, 1075, 1030, 885, 822, 742, 698, 634, 560.

4-((dibenzylamino)oxy)-2,2-difluoro-5-(4-hydroxy-3-methoxyphenyl)-N-phenylpentanamide (4ae)



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) to afford **4ae** as a colorless viscous oil (54.7 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.29 – 7.20 (m, 10H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 8.1 Hz, 1H), 6.50 (s, 1H), 5.50 (s, 1H), 3.86 – 3.68 (m, 8H), 2.91 (dd, *J* = 13.9, 5.8 Hz, 1H), 2.35 – 2.18 (m, 2H), 1.98 – 1.84 (m, 1H).

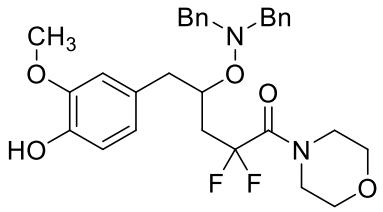
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 161.9 (t, *J* = 28.6 Hz), 146.2, 144.0, 137.3, 136.2, 129.8, 129.7, 129.2, 128.1, 127.3, 125.4, 122.1, 120.0, 117.2 (t, *J* = 251.9 Hz), 114.1, 111.8, 76.4, 62.1, 55.8, 39.4, 36.6 (t, *J* = 22.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -100.7 (d, *J* = 255.2 Hz, 1F), -106.4 (d, *J* = 255.1 Hz, 1F).

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{32}H_{32}F_2N_2O_4Na^+$: 569.2222; found: 508.2252.

IR (neat) ν (cm^{-1}): 2935, 1697, 1601, 1543, 1514, 1448, 1372, 1238, 1155, 1122, 1074, 1028, 885, 751, 698, 560.

4-((dibenzylamino)oxy)-2,2-difluoro-5-(4-hydroxy-3-methoxyphenyl)-1-morpholinopentan-1-one (4af)



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) to afford **4af** as a colorless viscous oil (50.8 mg, 47% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.32 – 7.23 (m, 10H), 6.79 (d, *J* = 7.9 Hz, 1H), 6.61 – 6.53 (m, 2H), 5.55 (s, 1H), 3.94 – 3.85 (m, 2H), 3.83 (s, 3H), 3.79 – 3.54 (m, 11H), 2.80 (dd, *J* = 14.0, 6.2 Hz, 1H), 2.34 (dd, *J* = 14.0, 6.5 Hz, 1H), 2.28 – 2.12 (m, 1H), 1.98 – 1.82 (m, 1H).

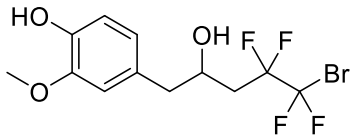
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 162.0 (t, *J* = 29.4 Hz), 146.1, 143.9, 137.4, 130.1, 129.8, 128.1, 127.2, 122.2, 118.2 (t, *J* = 252.0 Hz), 114.0, 112.0, 76.0, 66.6, 61.9, 55.8, 46.4, 43.2, 39.5, 37.0 (t, *J* = 21.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -97.6.

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{30}H_{34}F_2N_2O_5Na^+$: 563.2328; found: 563.2359.

IR (neat) ν (cm^{-1}): 2923, 2850, 1736, 1665, 1602, 1515, 1451, 1371, 1268, 1237, 1201, 1115, 1068, 1032, 995, 934, 887, 840, 744, 698, 634, 580, 560.

4-(5-bromo-4,4,5,5-tetrafluoro-2-hydroxypentyl)-2-methoxyphenol (5)



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford **5** as a colorless viscous oil (52.0 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 6.88 (d, *J* = 9.0 Hz, 1H), 6.76 – 6.68 (m, 2H), 5.56 (s, 1H), 4.34 – 4.26 (m, 1H), 3.89 (s, 3H), 2.85 (dd, *J* = 13.8, 4.5 Hz, 1H), 2.72 (dd, *J* = 13.7, 8.5 Hz, 1H), 2.40 – 2.25 (m, 2H), 1.90 (s, 1H).

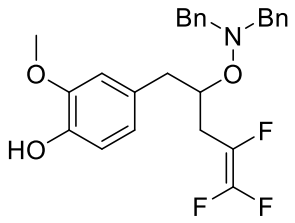
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 146.7, 144.7, 128.5, 122.1, 117.5 (tt, *J* = 309.6, 39.2 Hz), 117.1 (tt, *J* = 253.5, 31.0 Hz), 114.6, 111.8, 66.5, 55.9, 43.6, 36.8, (t, *J* = 21.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -66.2 (s, 2F), -109.9 (dt, *J* = 257.6, 3.5 Hz, 1F), -110.9 (dt, *J* = 257.5, 4.0 Hz, 1F).

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{12}H_{13}BrF_4O_3Na^+$: 382.9876; found: 382.9871.

IR (neat) ν (cm^{-1}): 2919, 2848, 1518, 1453, 1272, 1084, 1021, 910, 642, 613, 567, 551.

4-(2-((dibenzylamino)oxy)-4,5,5-trifluoropent-4-en-1-yl)-2-methoxyphenol (6)



Purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to afford **6** as a colorless viscous oil (54.9 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.32 – 7.24 (m, 10H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.52 (dd, *J* = 8.0, 1.9 Hz, 1H), 6.46 (d, *J* = 1.9 Hz, 1H), 5.47 (s, 1H), 3.87 – 3.75 (m, 7H), 3.64 – 3.56 (m, 1H), 2.71 (dd, *J* = 13.9, 6.2 Hz, 1H), 2.35 – 2.22 (m, 2H), 2.04 – 1.93 (m, 1H).

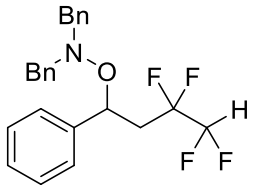
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 146.2, 144.0, 137.4, 129.9, 129.7, 128.1, 127.3, 122.1, 114.0, 111.8, 79.1, 62.5, 55.8, 38.9, 29.1 (dd, *J* = 20.7, 2.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -104.4 (dd, *J* = 86.1, 32.1 Hz, 1F), -123.6 (dd, *J* = 113.8, 86.0 Hz, 1F), -171.5 (dd, *J* = 113.8, 32.0 Hz, 1F).

HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{26}H_{26}F_3NO_3Na^+$: 480.1757; found: 480.1785.

IR (neat) ν (cm^{-1}): 2931, 1796, 1605, 1514, 1454, 1431, 1367, 1266, 1235, 1152, 1122, 1032, 817, 742, 698, 615, 577, 553.

***N*,*N*-dibenzyl-*O*-(3,3,4,4-tetrafluoro-1-phenylbutyl)hydroxylamine (7)**



Purified by silica gel column chromatography (petroleum ether/dichloromethane = 10:1) to afford **7** as a colorless oil (37.5 mg, 90% yield).

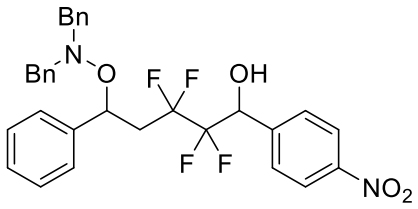
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.35 – 7.10 (m, 15H), 5.44 (tdd, $^{3}J_{H\text{-}F}$ = 53.8 Hz, $J_{H\text{-}H}$ = 5.4, 2.9 Hz, 1H), 4.48 (t, *J* = 6.7 Hz, 1H), 3.82 (d, *J* = 13.0 Hz, 2H), 3.68 (d, *J* = 13.0 Hz, 2H), 2.57 – 2.36 (m, 1H), 2.03 – 1.84 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 140.4, 137.3, 129.6, 128.4, 128.3, 128.2, 127.7, 127.4, 116.6 (tt, *J* = 247.0, 28.0 Hz), 110.1 (tt, *J* = 248.0, 38.0 Hz), 77.9 (t, *J* = 4.0 Hz), 62.4, 35.9 (t, *J* = 21.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -114.7 (dt, *J* = 270.0, 4.2 Hz, 1F), -115.9 (d, *J* = 269.9 Hz, 1F), -136.9 (dt, *J* = 297.6, 2.8 Hz, 1F), -137.7 (dt, *J* = 297.4, 4.3 Hz, 1F).

HRMS (ESI^+): calculated $[M+H]^+$ for $C_{24}H_{24}F_4NO^+$: 418.1789; found: 418.1785.

5-((dibenzylamino)oxy)-2,2,3,3-tetrafluoro-1-(4-nitrophenyl)-5-phenylpentan-1-ol (8)



Purified by silica gel column chromatography (petroleum ether/ ethyl acetate = 5:1) to afford **8** as a colorless oil (34.5 mg, 61% yield, 1:1 dr).

For the mixture of two diastereoisomers: **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 8.27 – 8.18 (m, 2H), 7.61 – 7.52 (m, 2H), 7.31 – 7.12 (m, 15H), 5.18 – 5.05 (m, 1H), 4.55 – 4.45 (m, 1H), 3.87 – 3.79 (m, 2H), 3.76 – 3.67 (m, 2H), 2.78 – 2.44 (m, 1H), 2.12 – 1.92 (m, 1H).

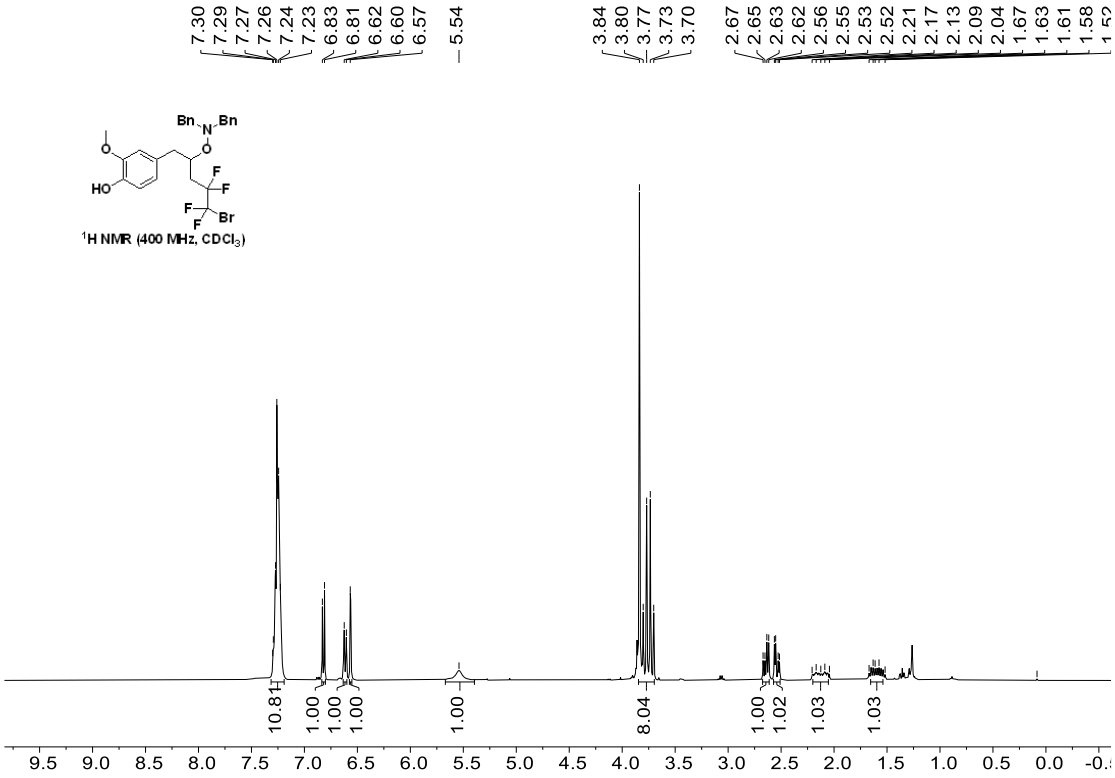
For the mixture of two diastereoisomers: **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 148.3 (*two diastereoisomers*), 141.7 (*two diastereoisomers*), 140.5 (*two diastereoisomers*), 137.3, 129.73, 129.70, 129.0, 128.3, 128.2, 127.5 (*two diastereoisomers*), 127.4, 123.3 (*two diastereoisomers*), 118.8 (tt, *J* = 254.0, 34.0 Hz), 114.8 (tt), 77.6 (*two diastereoisomers*), 70.8 (*two diastereoisomers*), 62.5, 35.5 (td, *J* = 20.9, 8.8 Hz).

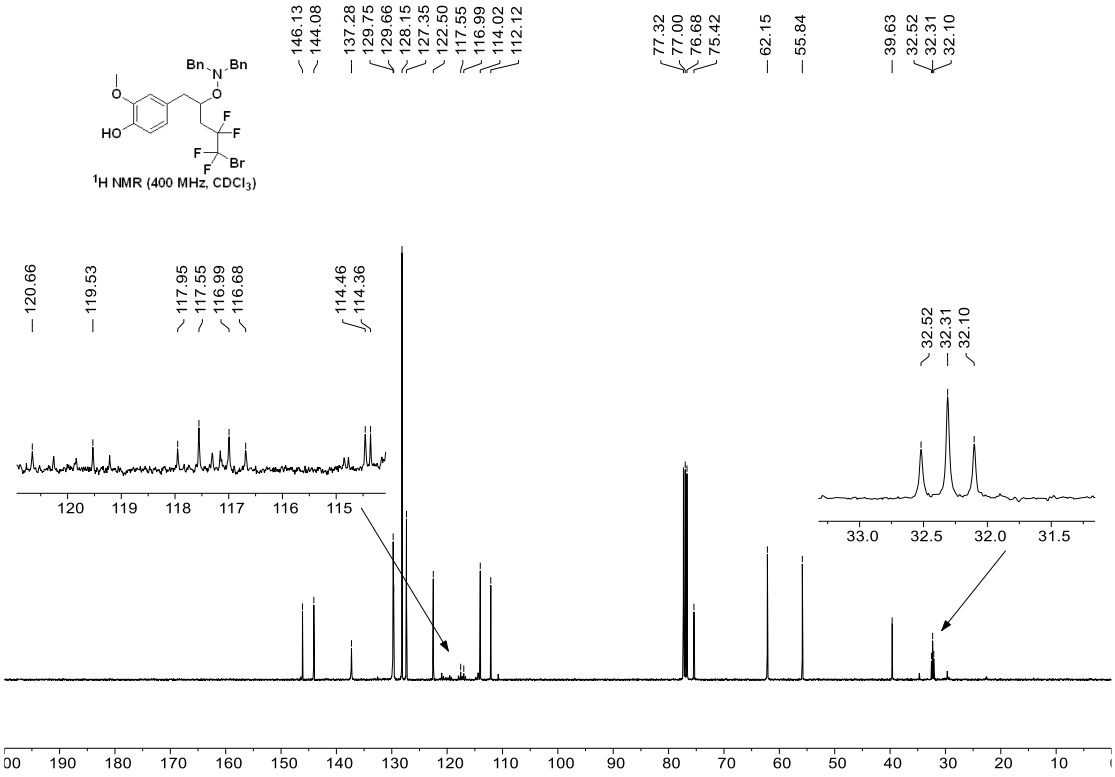
For the mixture of two diastereoisomers: **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -109.11 – -111.91 (*two diastereoisomers*: m, 2F), -118.8 (*two diastereoisomers*: dd, *J* = 274.5, 3.8 Hz, 1F), -127.2 (*two diastereoisomers*: dd, *J* = 278.2, 3.8 Hz, 1F).

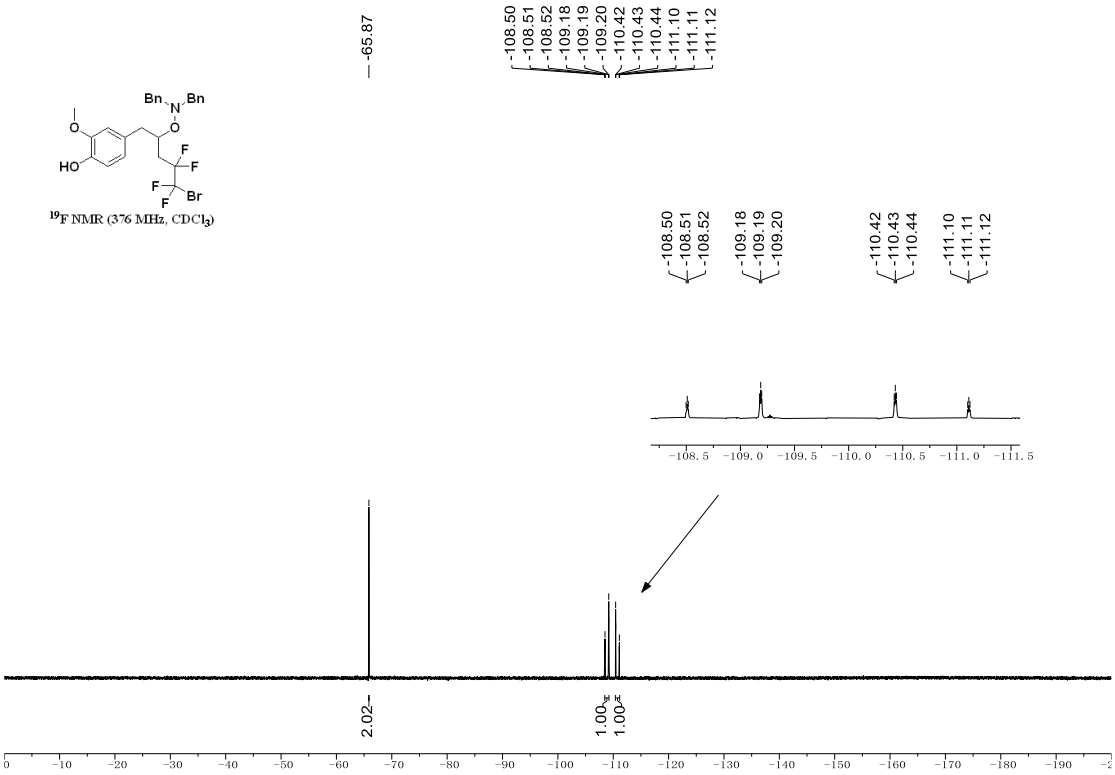
HRMS (ESI^+): calculated $[M+Na]^+$ for $C_{31}H_{28}F_4N_2O_4Na^+$: 591.1877; found: 591.1874.

8. Copies of NMR Spectra of All Products

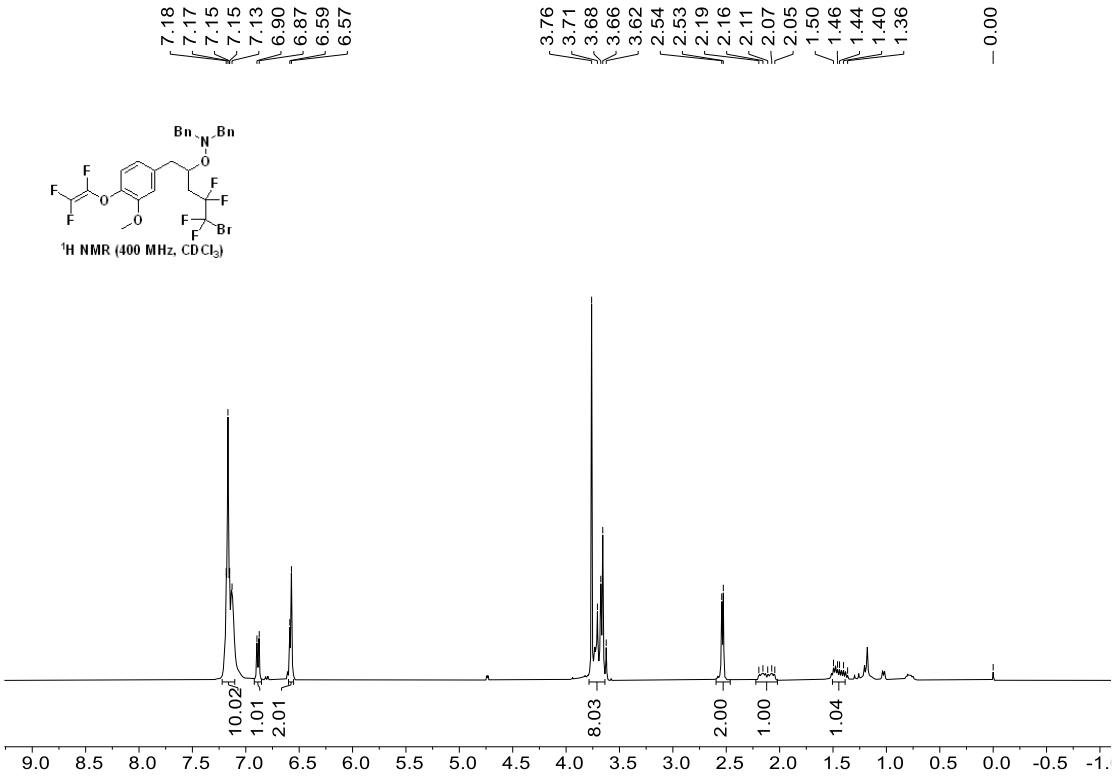
4-(5-bromo-2-((dibenzylamino)oxy)-4,4,5,5-tetrafluoropentyl)-2-methoxyphenol (4a)

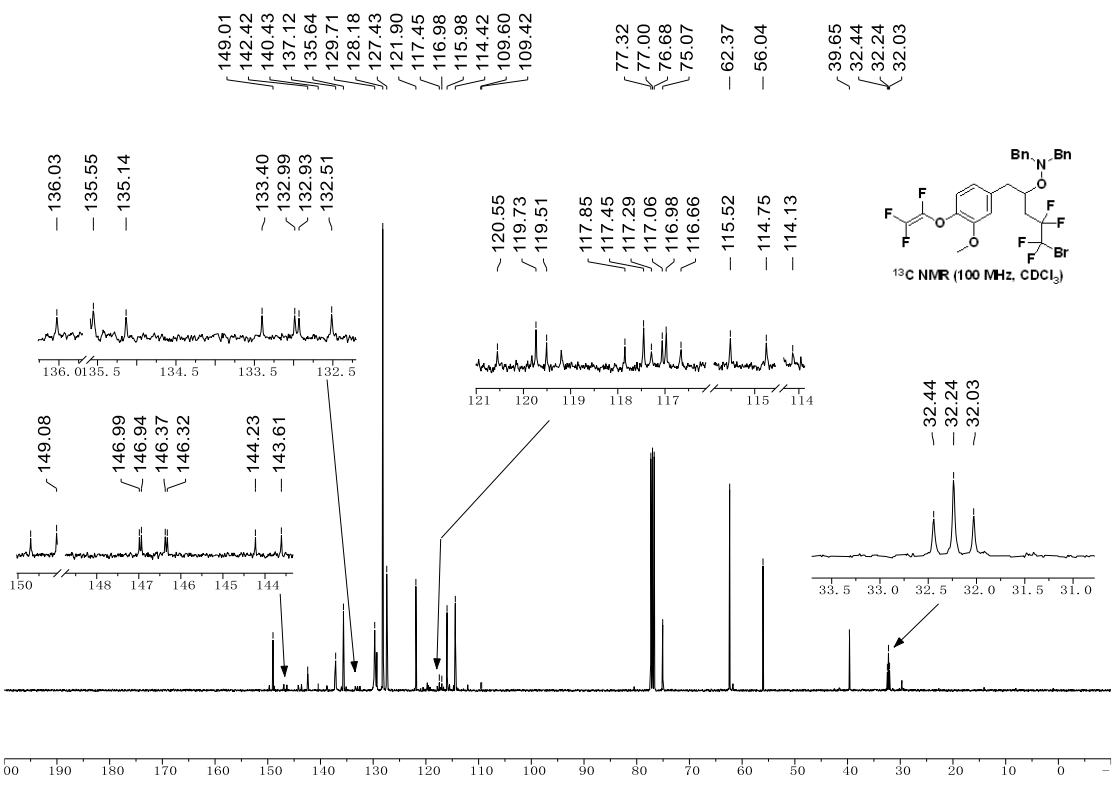


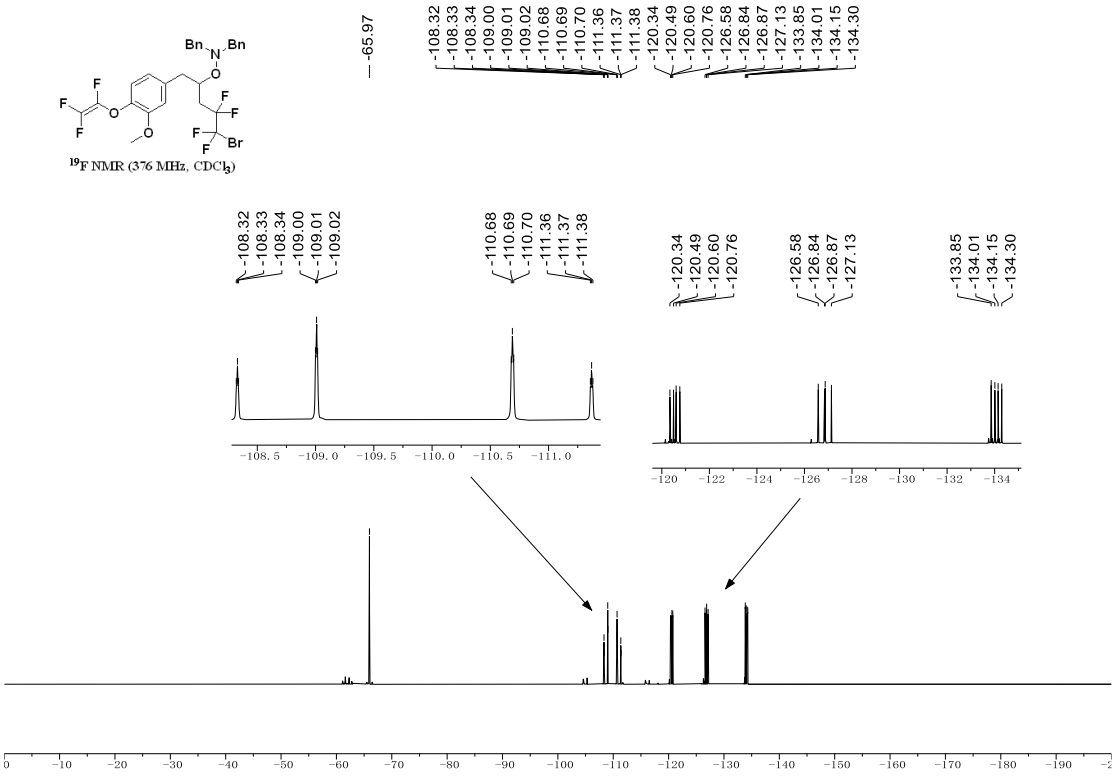



-65.87
-108.50
-108.51
-108.52
-109.18
-109.19
-109.20
-110.42
-110.43
-110.44
-111.10
-111.11
-111.12
Bn
N
Bn
O
O
HO
F
F
F
F
Br
^{19}F NMR (376 MHz, CDCl$_3$)
2.02
1.00
1.00
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−108.5
−109.0
−109.5
−110.0
−110.5
−111.0
−111.5

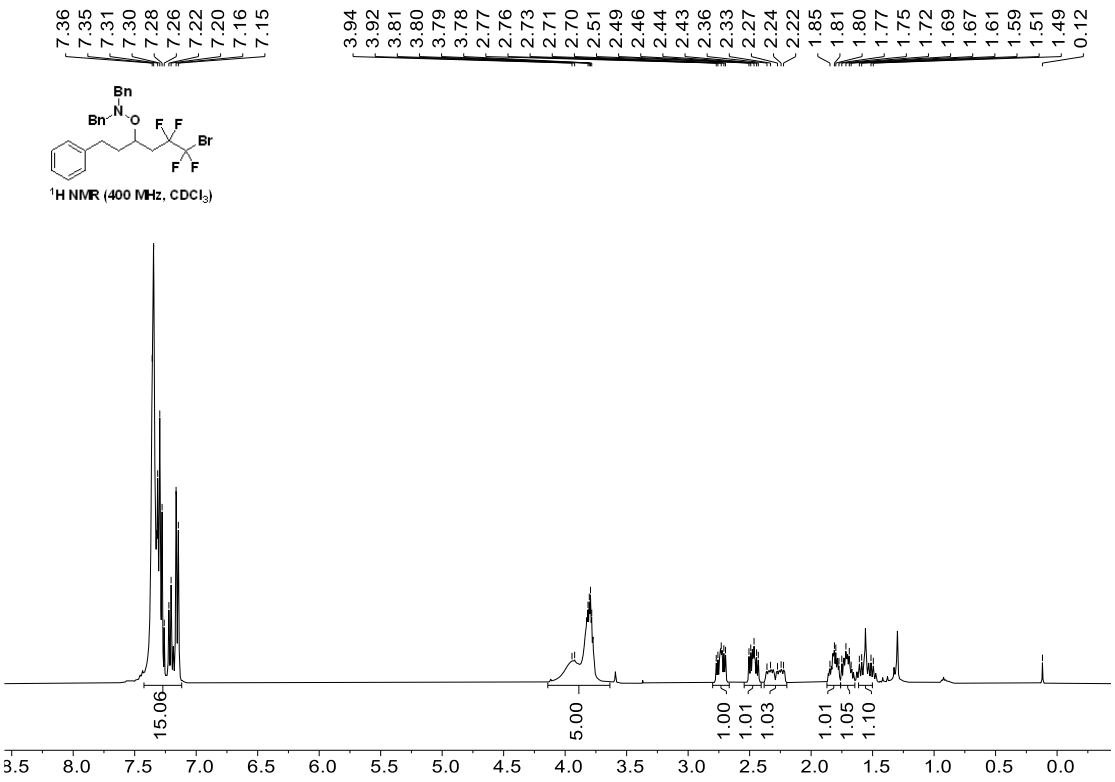
_N_,_N_-dibenzyl-_O_-(5-bromo-4,4,5,5-tetrafluoro-1-(3-methoxy-4-((1,2,2-trifluorovinyl)oxy)phenyl)pentan-2-yl)hydroxylamine (4b)

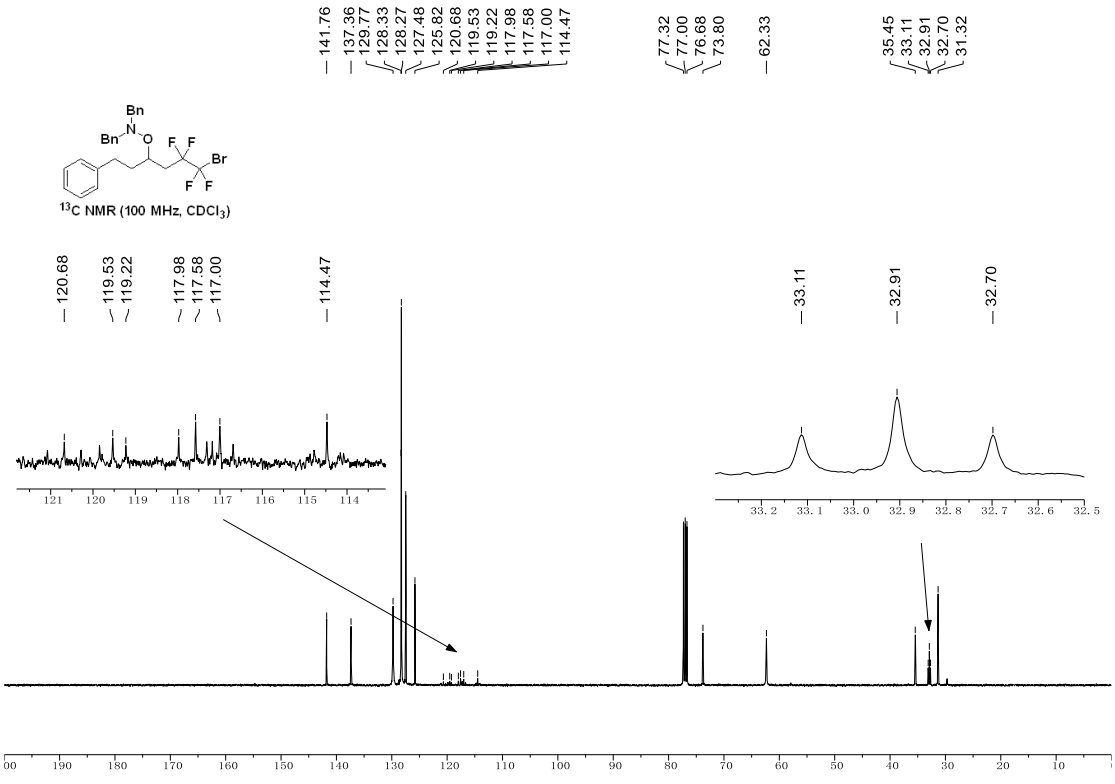


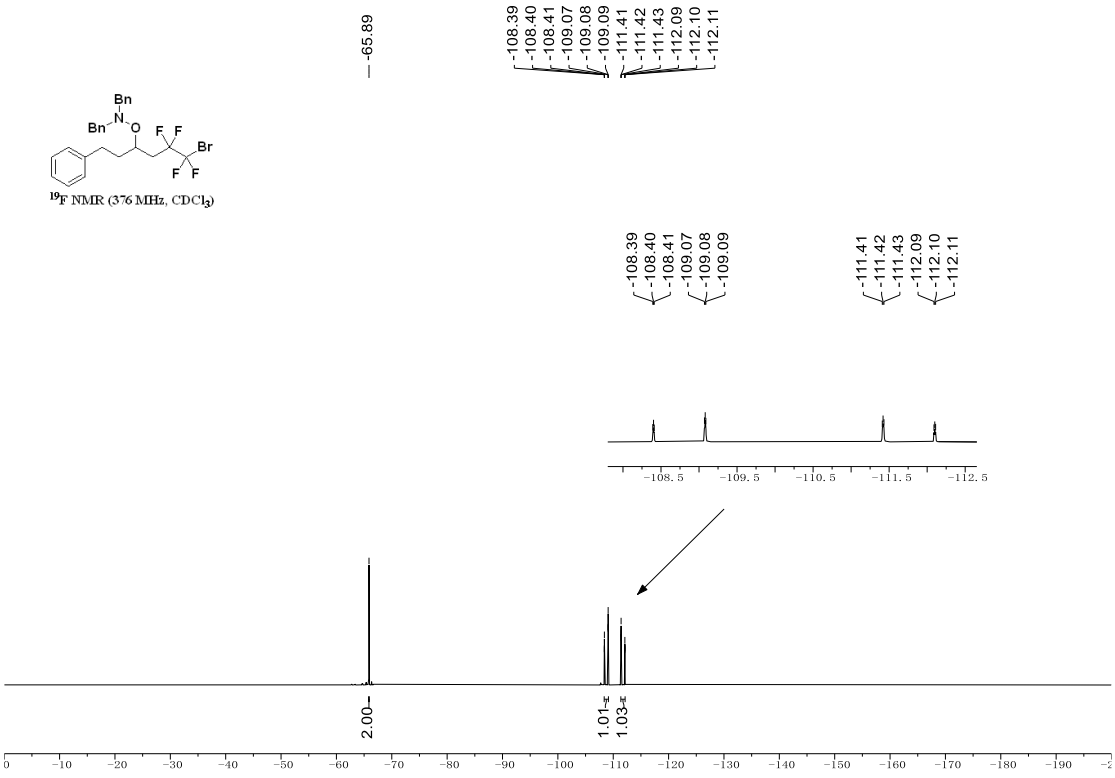



Bn
N
Bn
O
F
F
F
O
F
F
F
F
Br
O
19F NMR (376 MHz, CDCl3)
-65.97
-108.32
-108.33
-108.34
-109.00
-109.01
-109.02
-110.68
-110.69
-110.70
-111.36
-111.37
-111.38
-120.34
-120.49
-120.60
-120.76
-126.58
-126.84
-126.87
-127.13
-133.85
-134.01
-134.15
-134.30
-108.5
-109.0
-109.5
-110.0
-110.5
-111.0
-120
-122
-124
-126
-128
-130
-132
-134
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190

***N*,*N*-dibenzyl-O-(6-bromo-5,5,6,6-tetrafluoro-1-phenylhexan-3-yl)hydroxylamine (4c)**

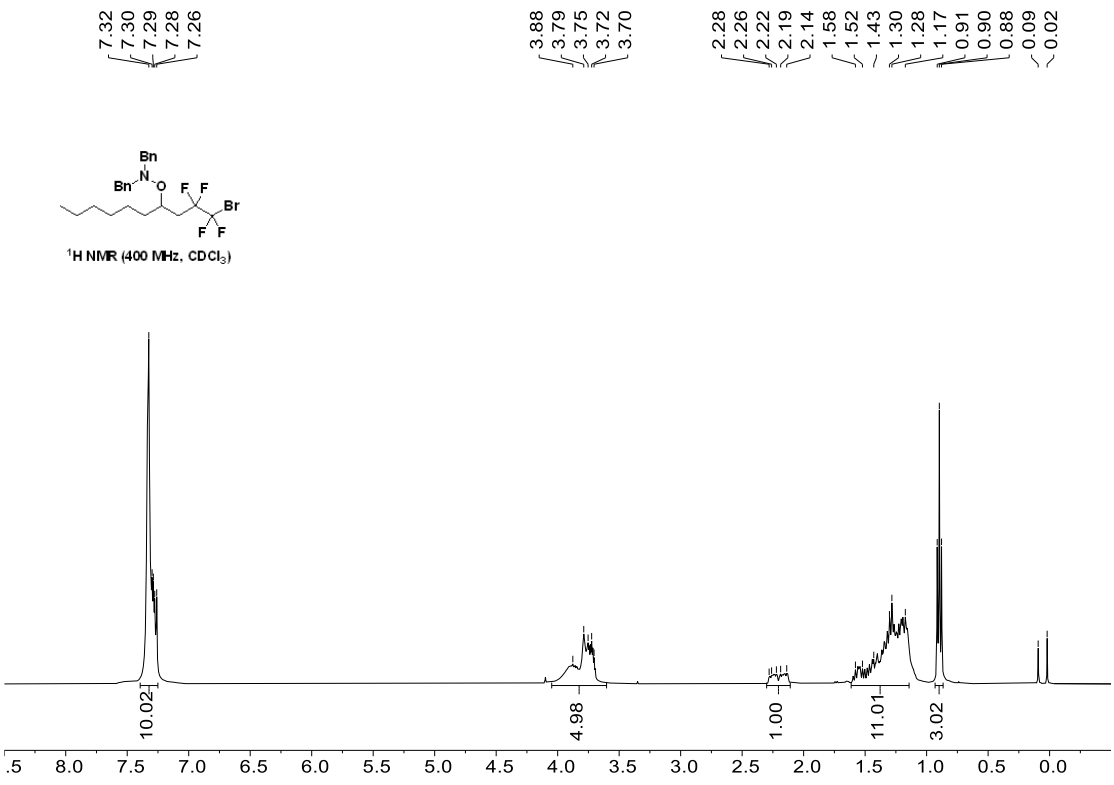


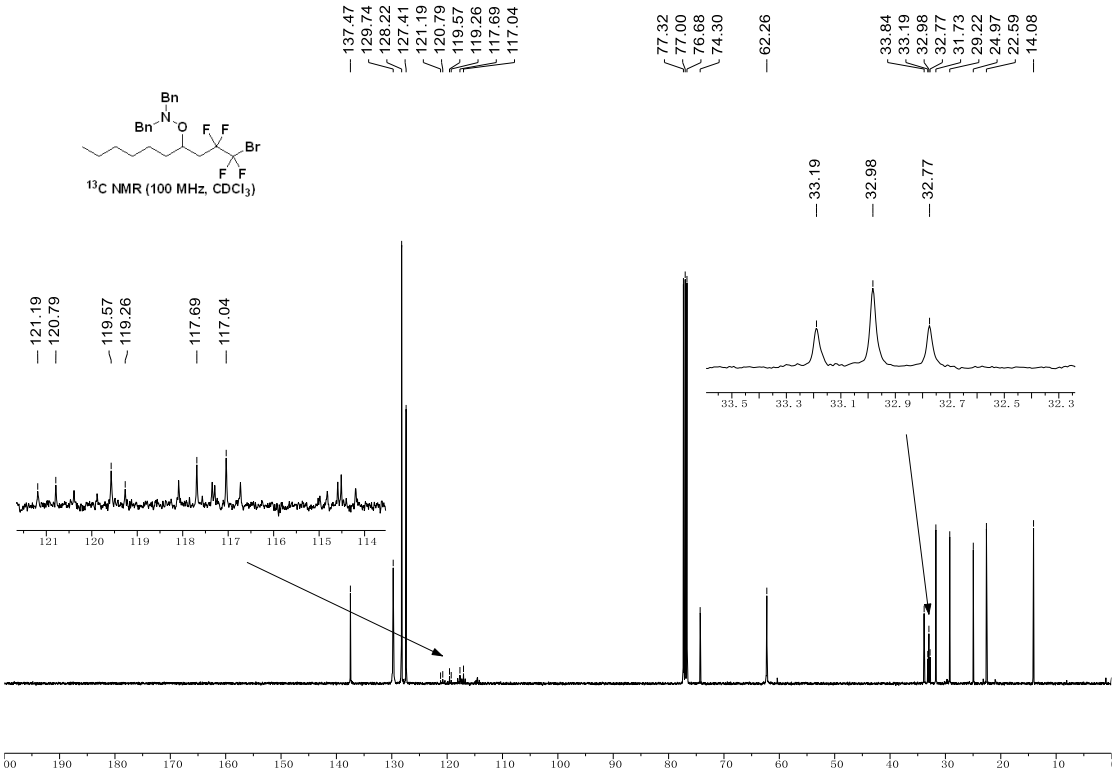


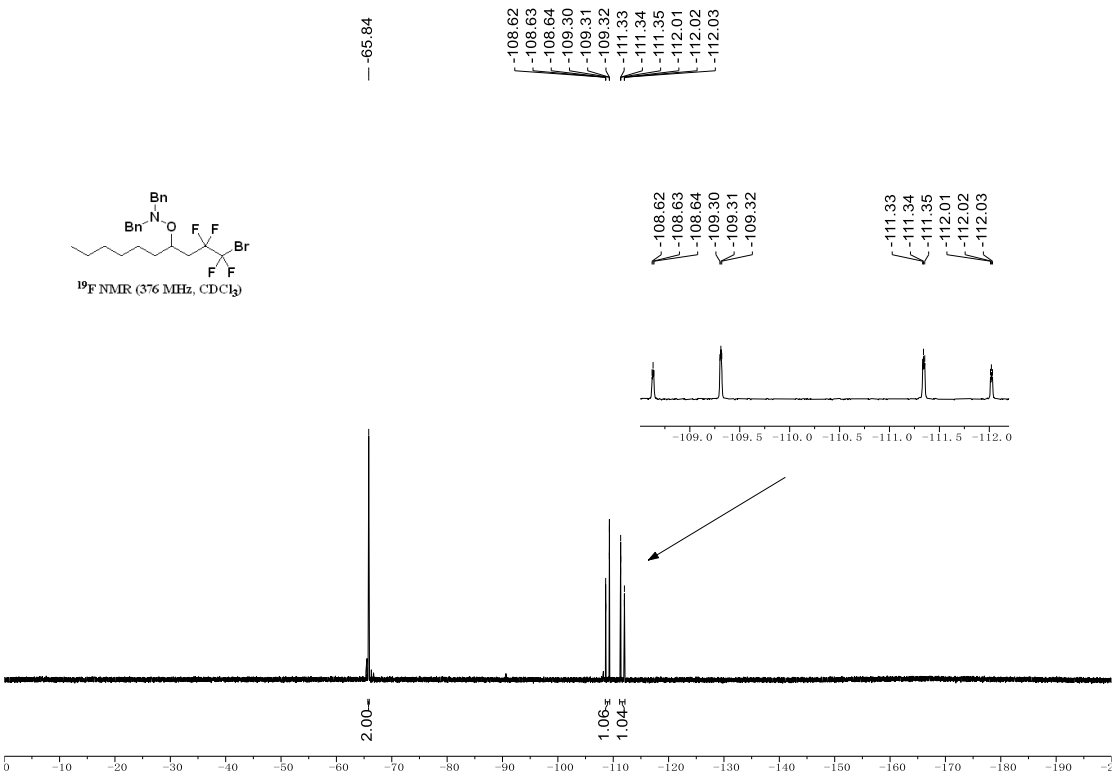


^{19}F NMR (376 MHz, $CDCl_3$)

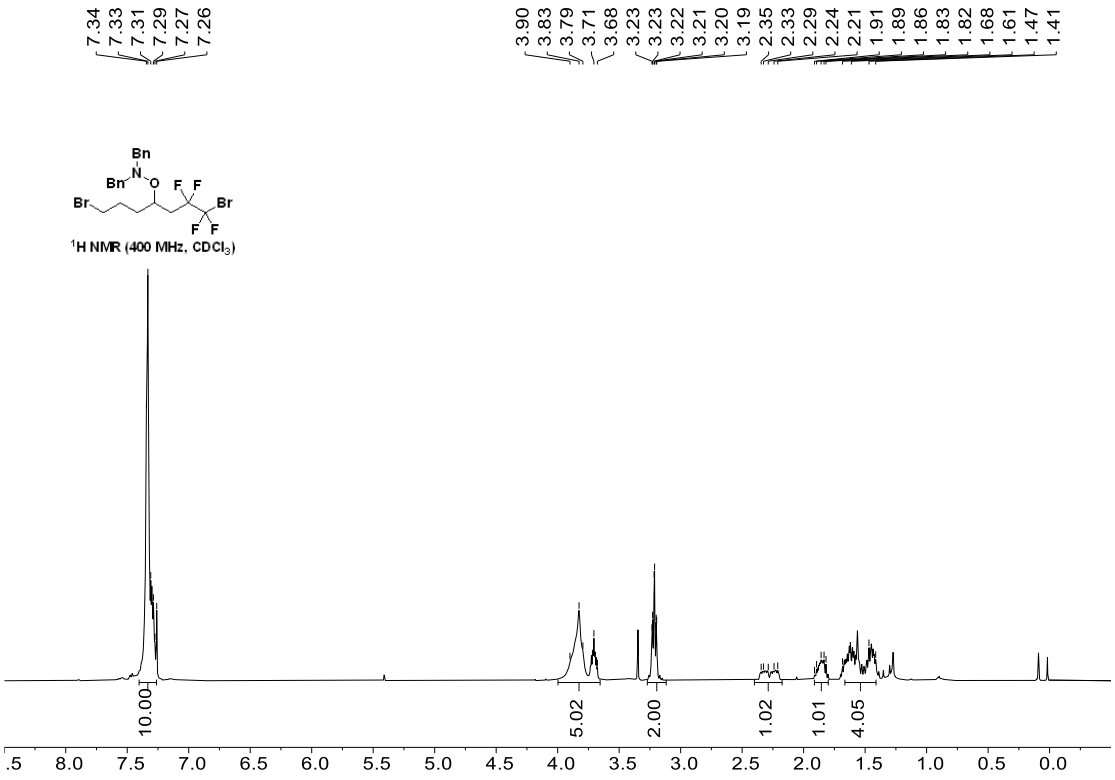
N,*N*-dibenzyl-*O*-(1-bromo-1,1,2,2-tetrafluorodecan-4-yl)hydroxylamine (4d)

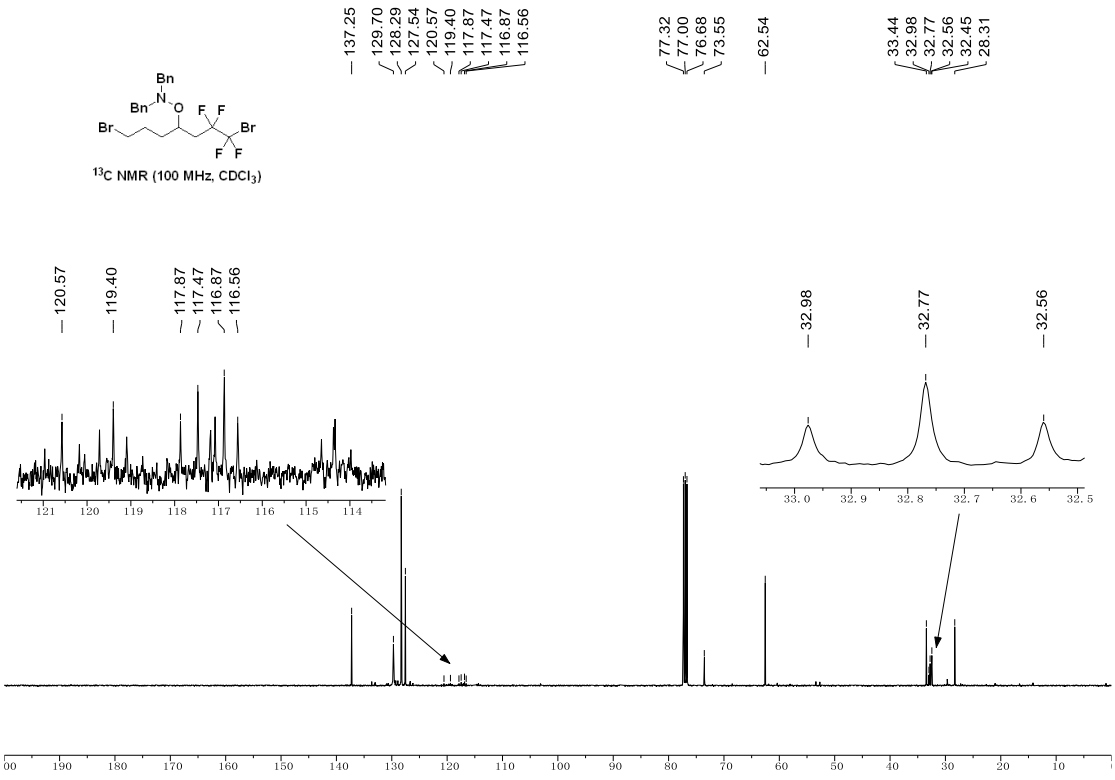


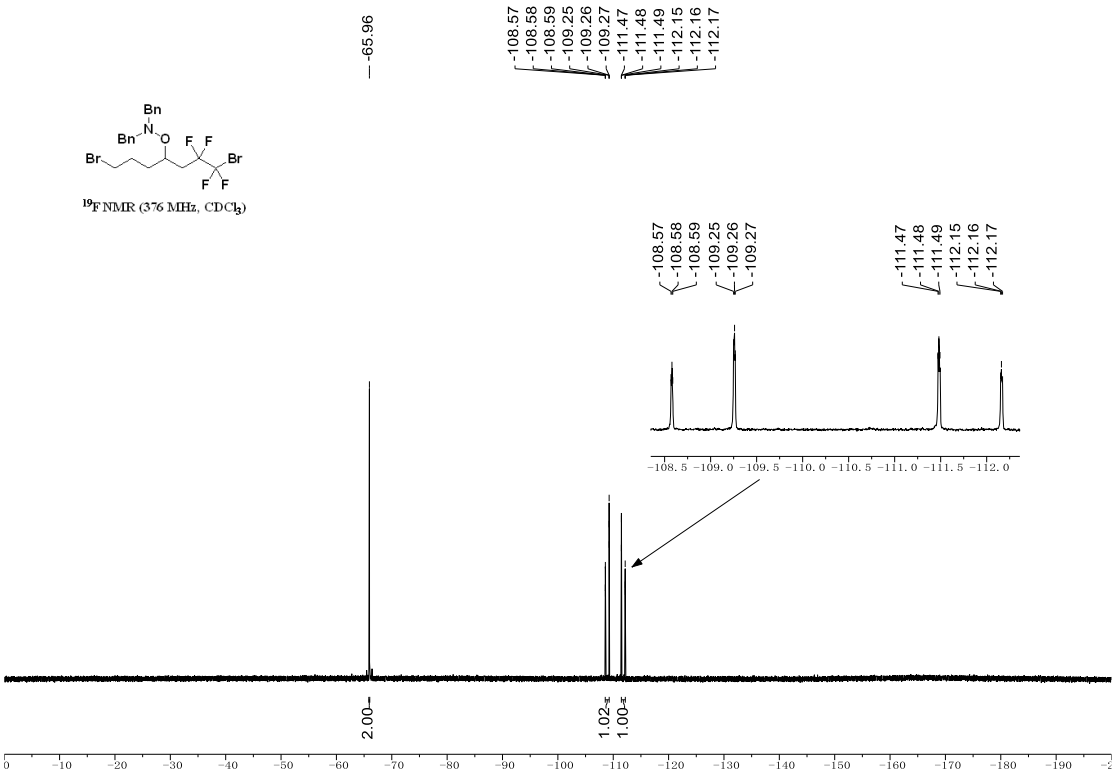



-65.84
-108.62
-108.63
-108.64
-109.30
-109.31
-109.32
-111.33
-111.34
-111.35
-112.01
-112.02
-112.03
Bn
Bn
N
O
F F
Br
F F
19F NMR (376 MHz, CDCl3)
2.00
1.06
1.04

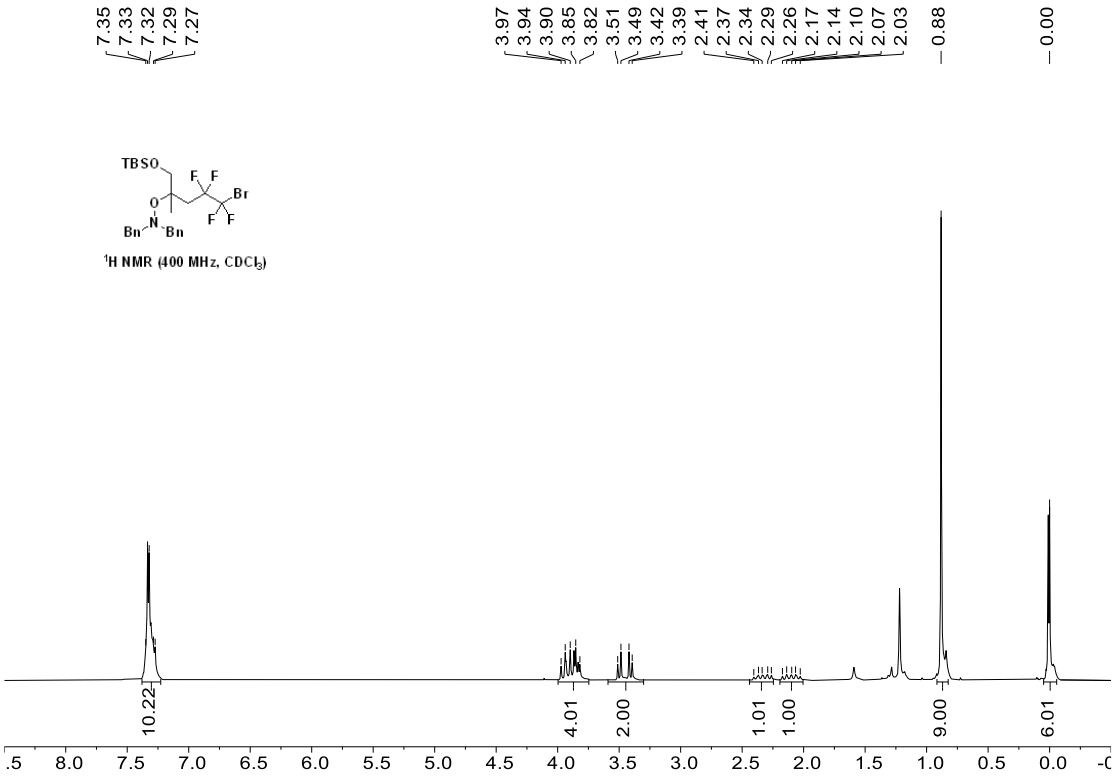
N,*N*-dibenzyl-*O*-(1,7-dibromo-1,1,2,2-tetrafluoroheptan-4-yl)hydroxylamine (4e)

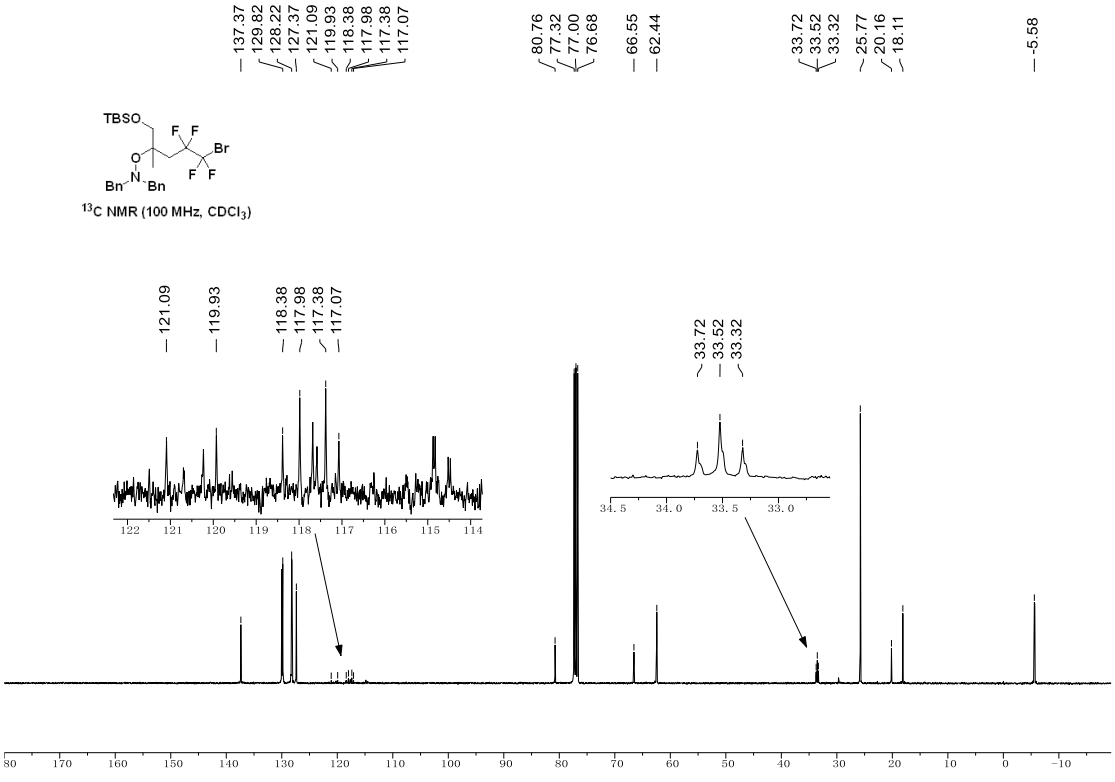


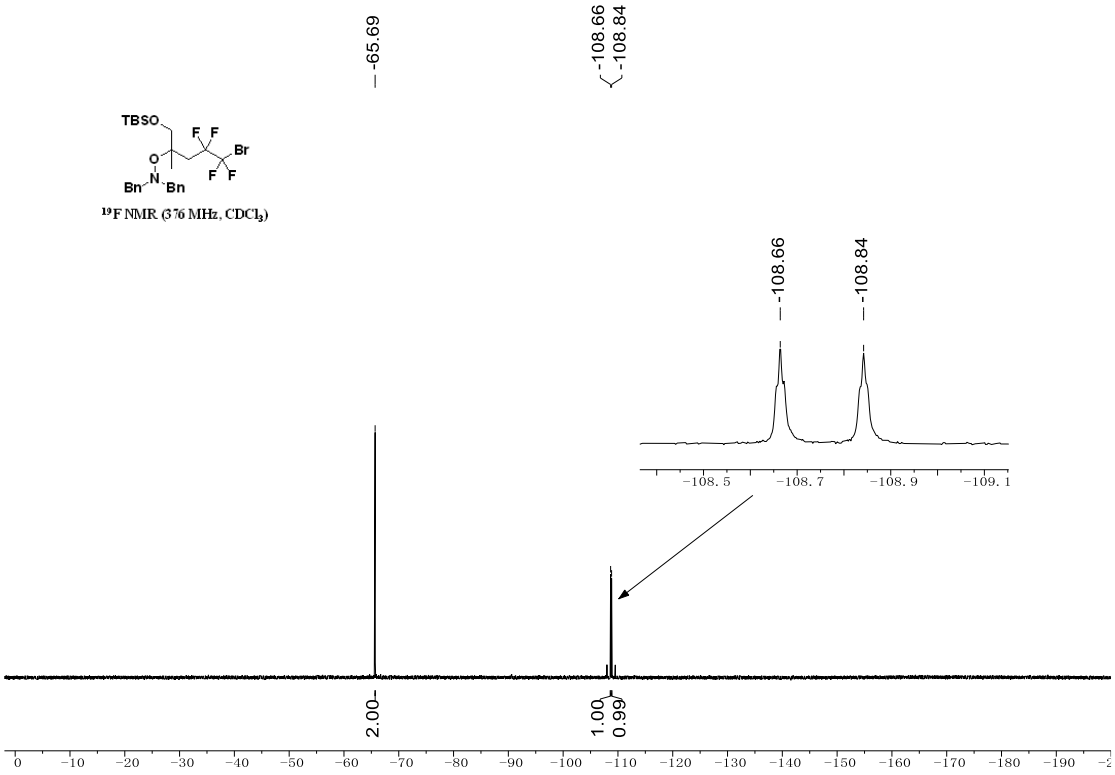



-65.96
-108.57
-108.58
-108.59
-109.25
-109.26
-109.27
-111.47
-111.48
-111.49
-112.15
-112.16
-112.17
Bn
Bn
N
O
F F
Br
Br
F F
19F NMR (376 MHz, CDCl3)
2.00
1.02
1.00

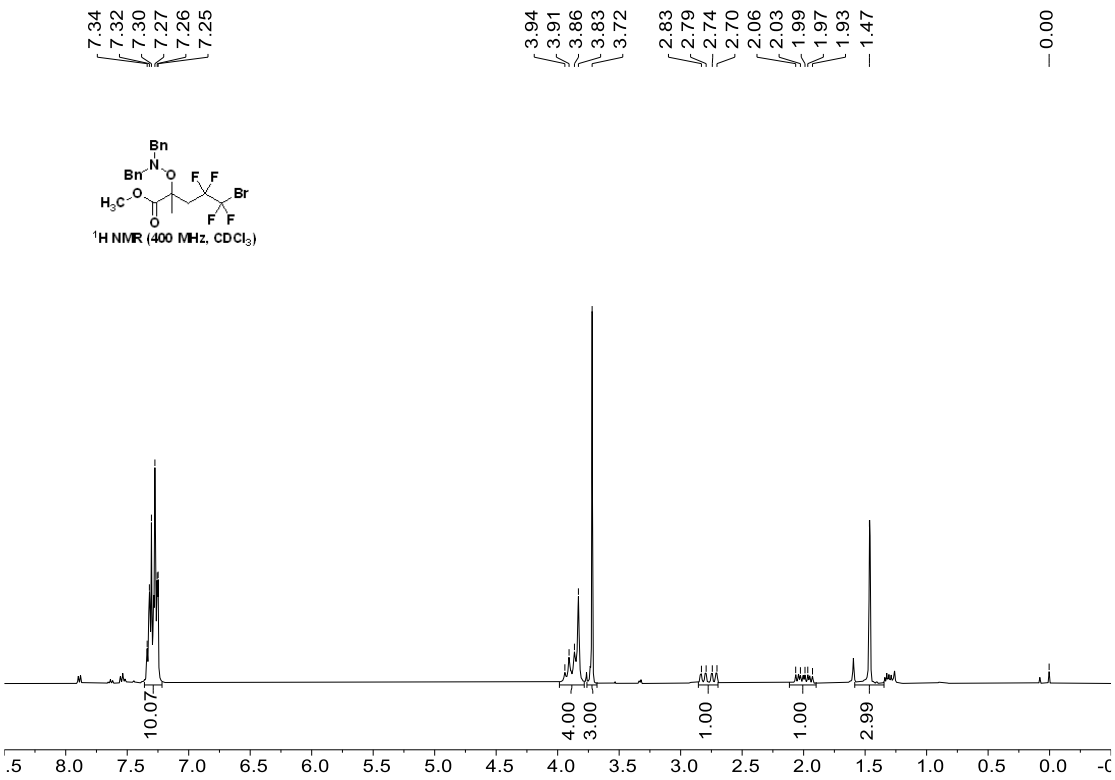
***N*,*N*-dibenzyl-*O*-(5-bromo-1-((tert-butyldimethylsilyl)oxy)-4,4,5,5-tetrafluoro-2-methylpentan-2-yl)hydroxylamine (4f)**

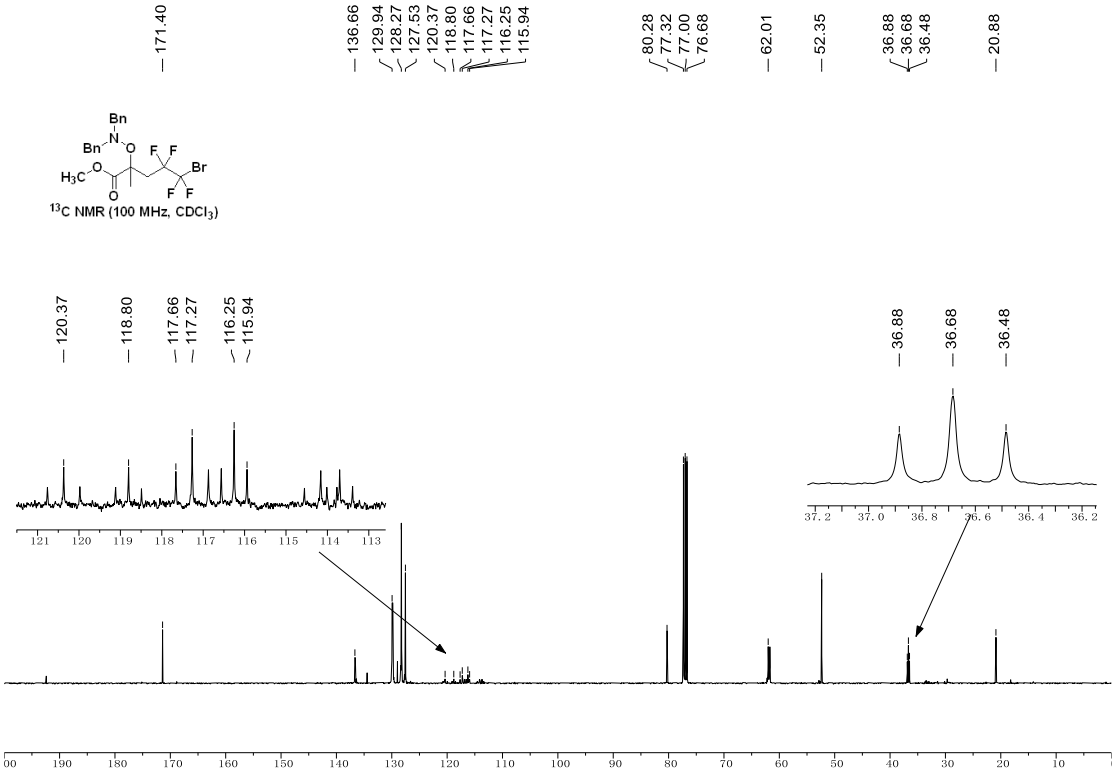


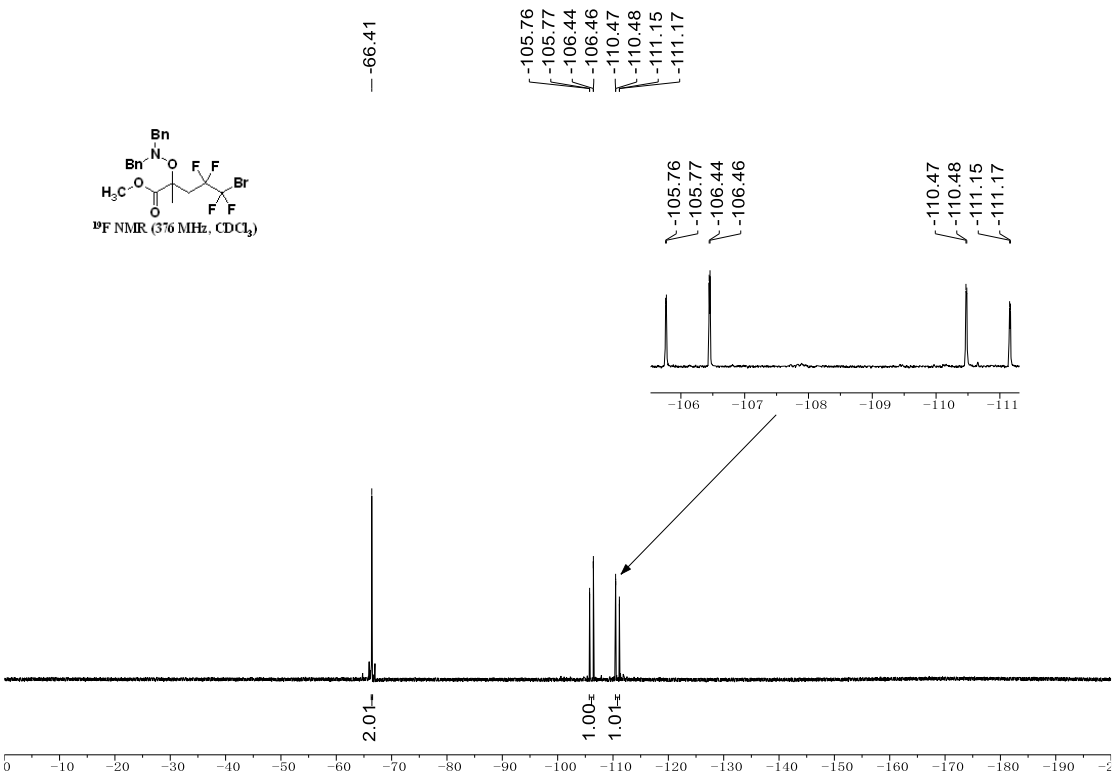



-65.69
-108.66
-108.84
TBSO
F F
Br
O
N
Bn Bn
F F
19F NMR (376 MHz, CDCl3)
-108.66
-108.84
-108.5
-108.7
-108.9
-109.1
2.00
1.00
0.99
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190

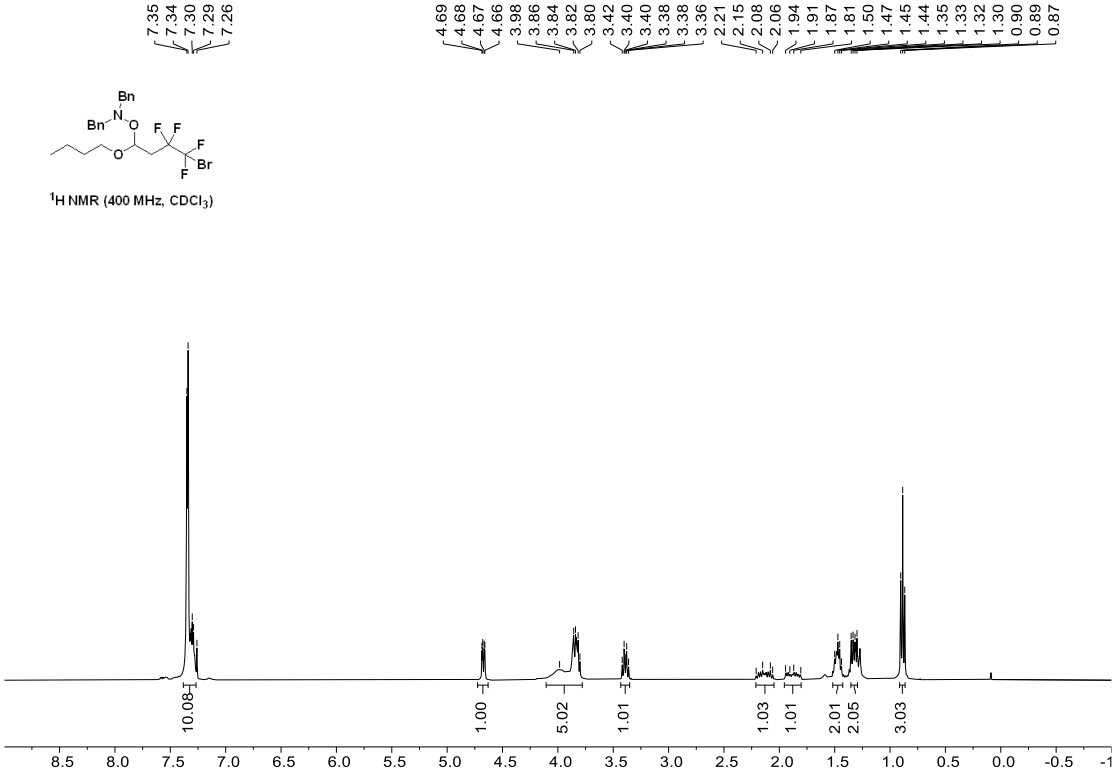
Methyl 5-bromo-2-((dibenzylamino)oxy)-4,4,5,5-tetrafluoro-2-methylpentanoate (4g)

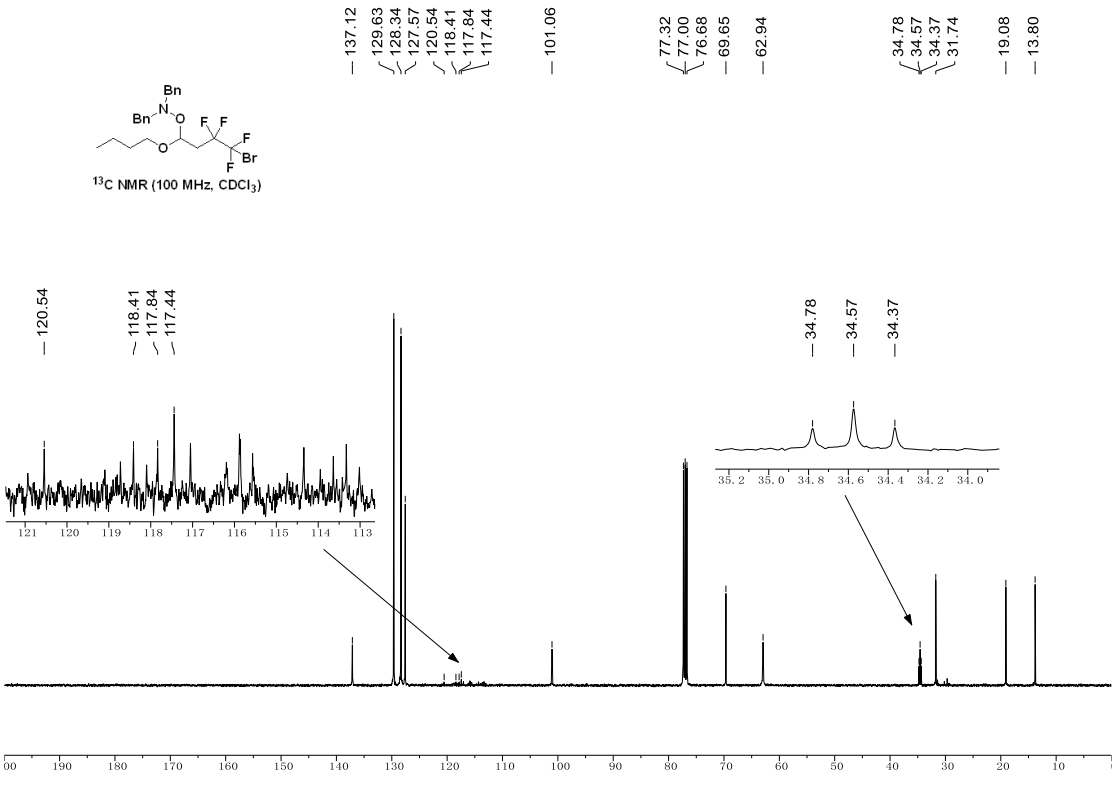


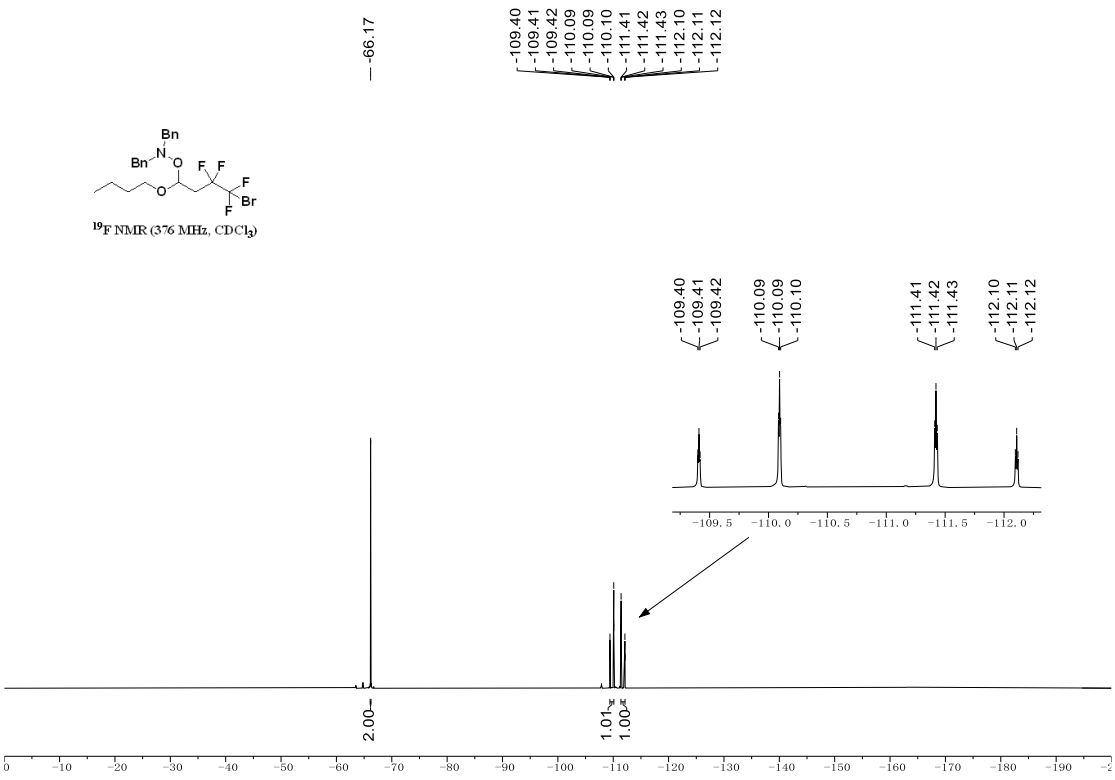



-66.41
-105.76
-105.77
-106.44
-106.46
-110.47
-110.48
-111.15
-111.17
Bn
Bn
N
O
F F
Br
H3C
O
O
F F
19F NMR (376 MHz, CDCl3)
2.01
1.00
1.01
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−106
−107
−108
−109
−110
−111

N,*N*-dibenzyl-*O*-(4-bromo-1-butoxy-3,3,4,4-tetrafluorobutyl)hydroxylamine (4h)

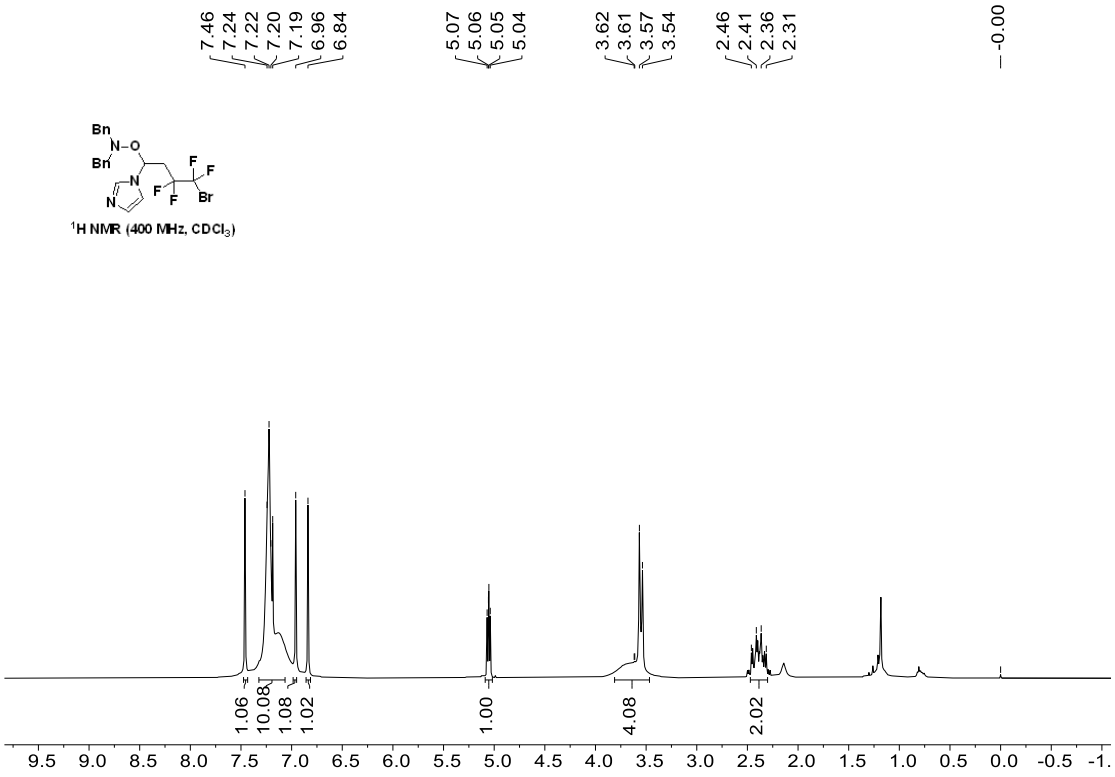


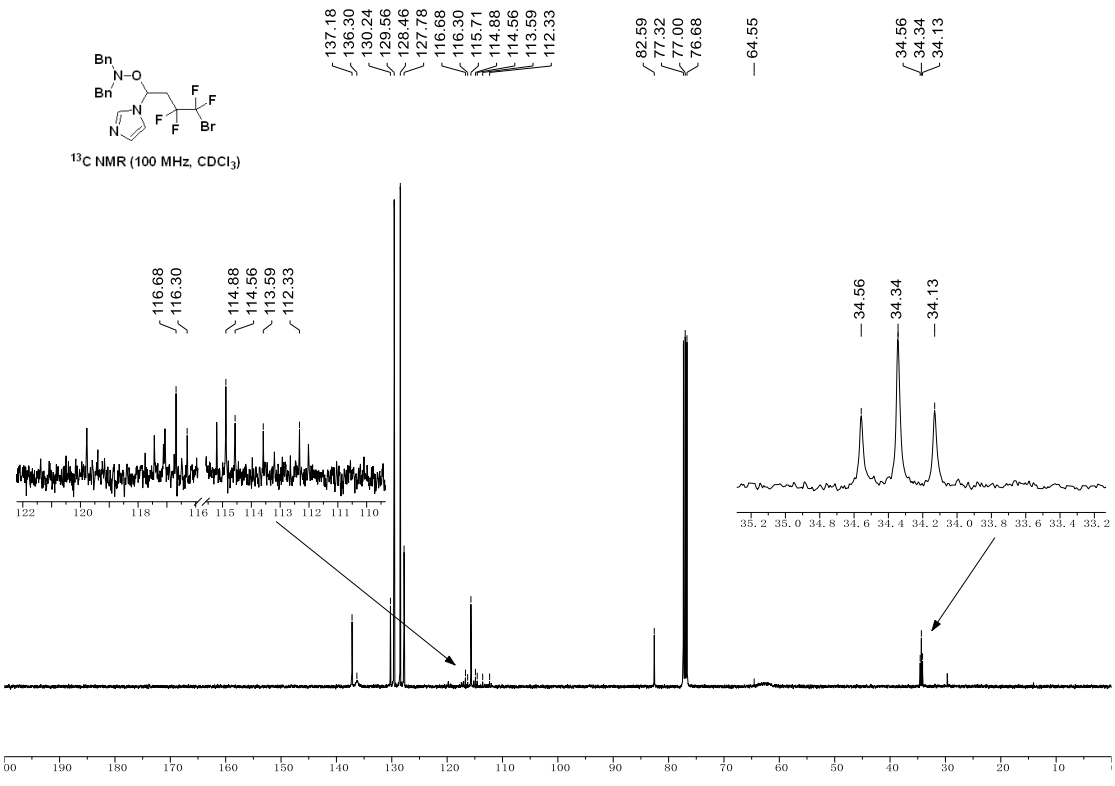


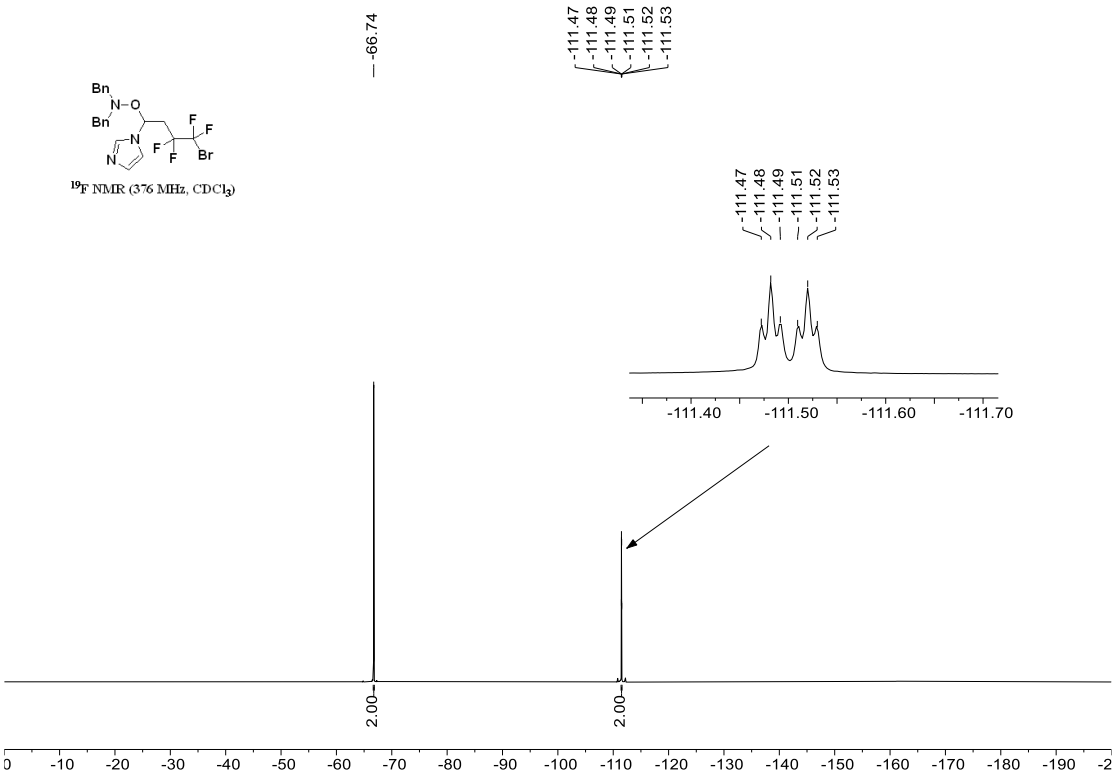


^{19}F NMR (376 MHz, $CDCl_3$)

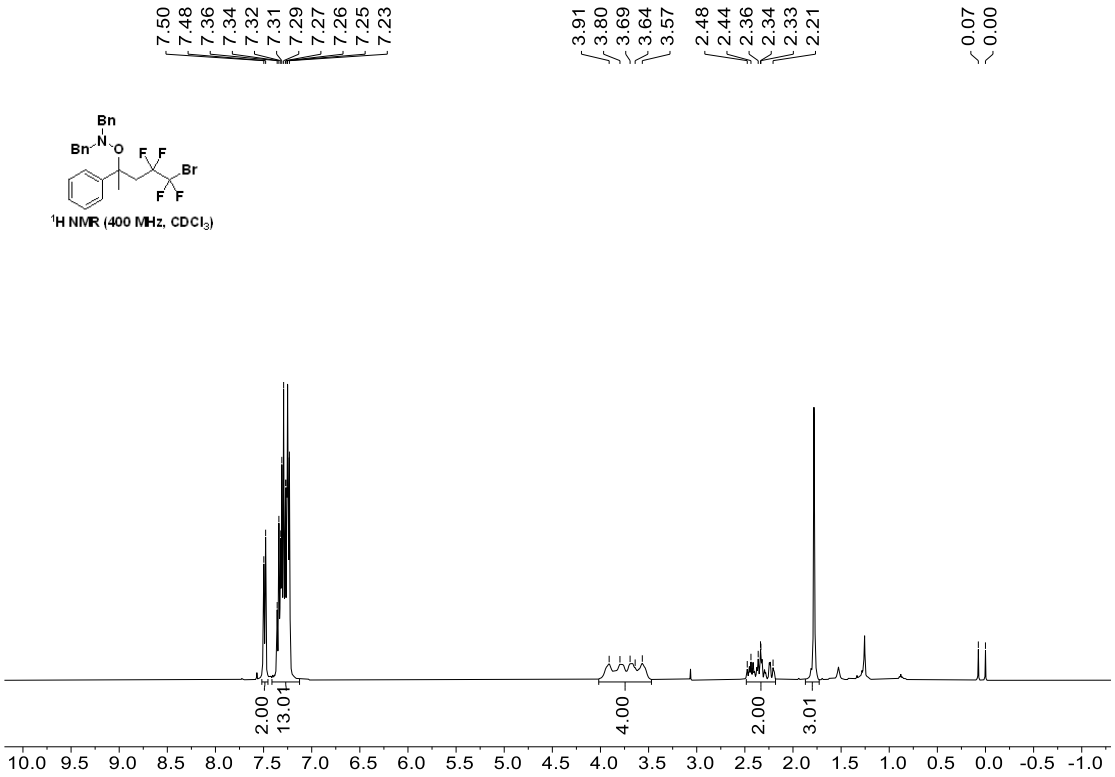
N,*N*-dibenzyl-*O*-(4-bromo-3,3,4,4-tetrafluoro-1-(1H-imidazol-1-yl)butyl)hydroxylamine (4i)

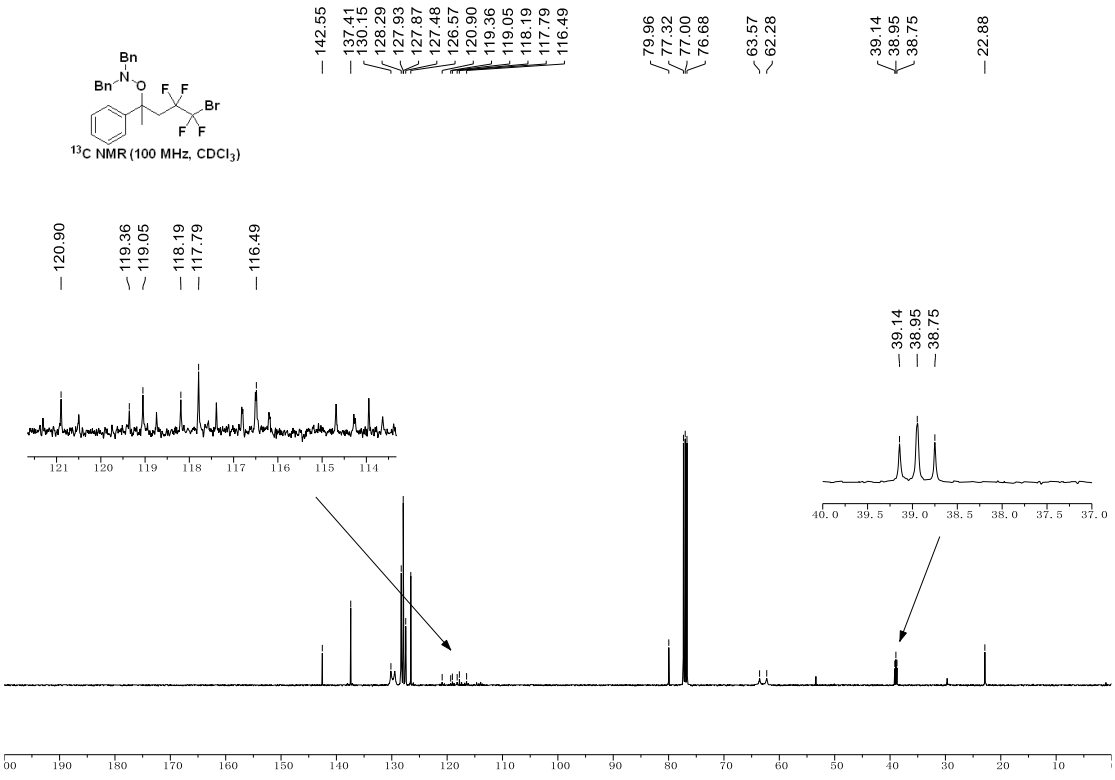


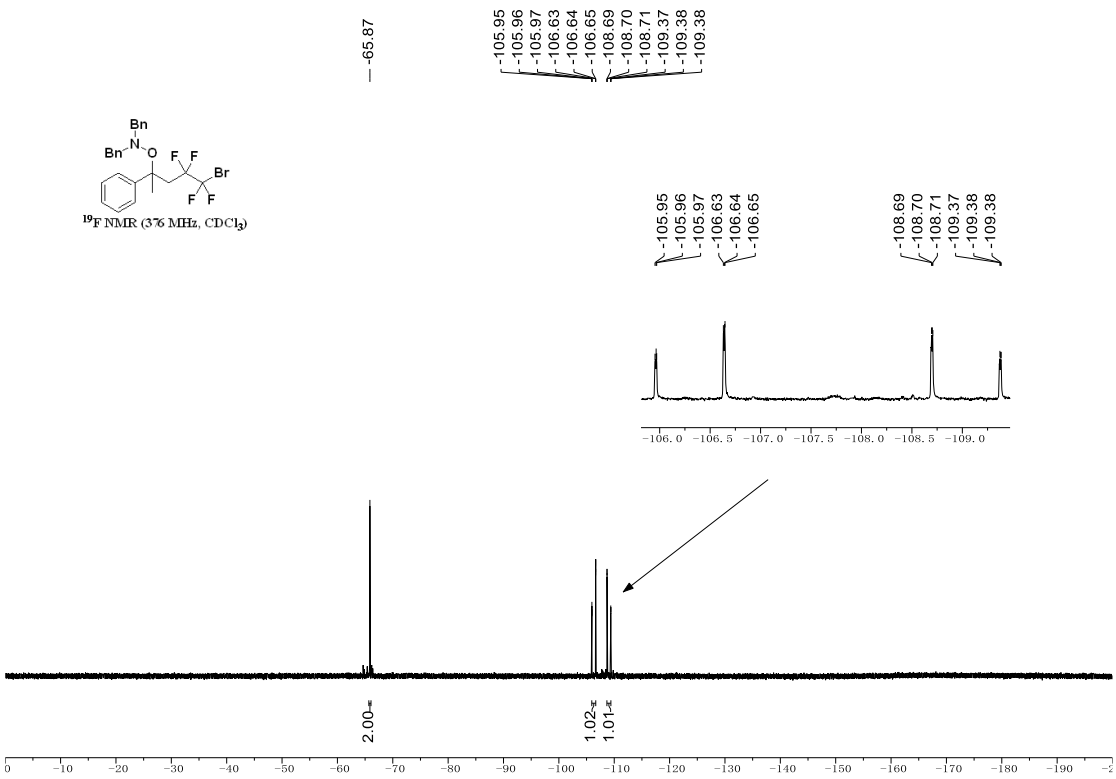



Bn
N
O
Bn
N
N
F
F
F
F
Br
^{19}F NMR (376 MHz, CDCl$_3$)
-66.74
-111.47
-111.48
-111.49
-111.51
-111.52
-111.53
-111.40
-111.50
-111.60
-111.70
2.00
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2

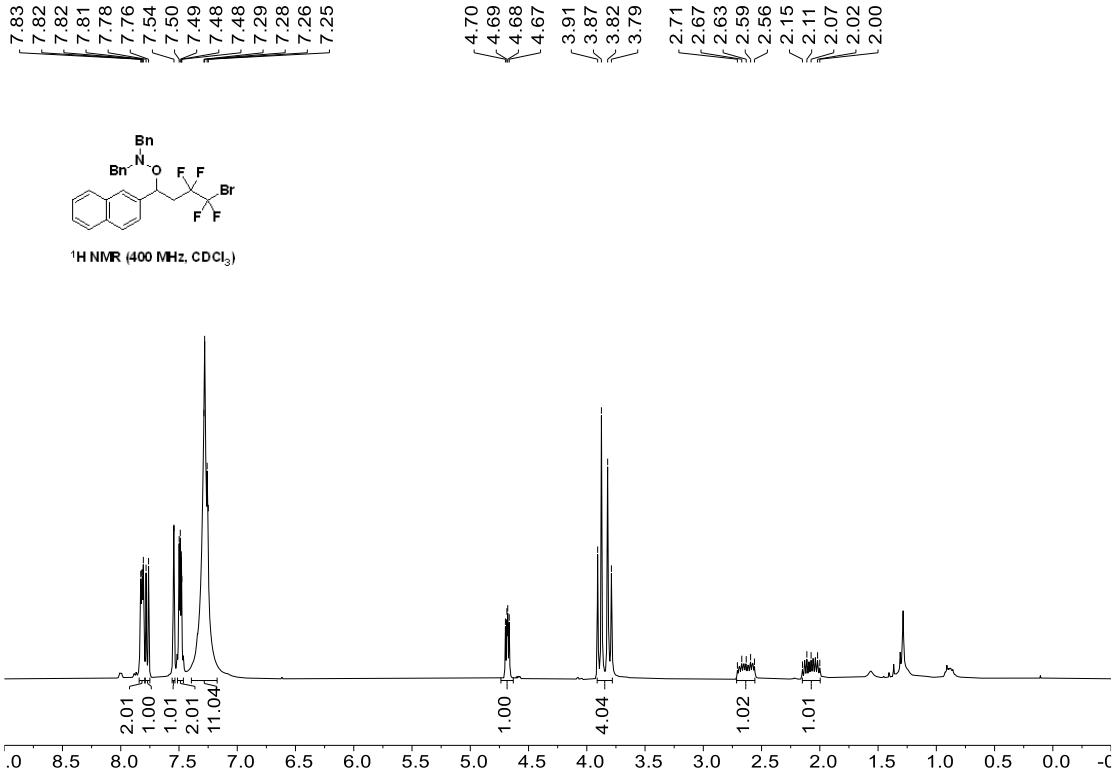
N,*N*-dibenzyl-*O*-(5-bromo-4,4,5,5-tetrafluoro-2-phenylpentan-2-yl)hydroxylamine (4j)

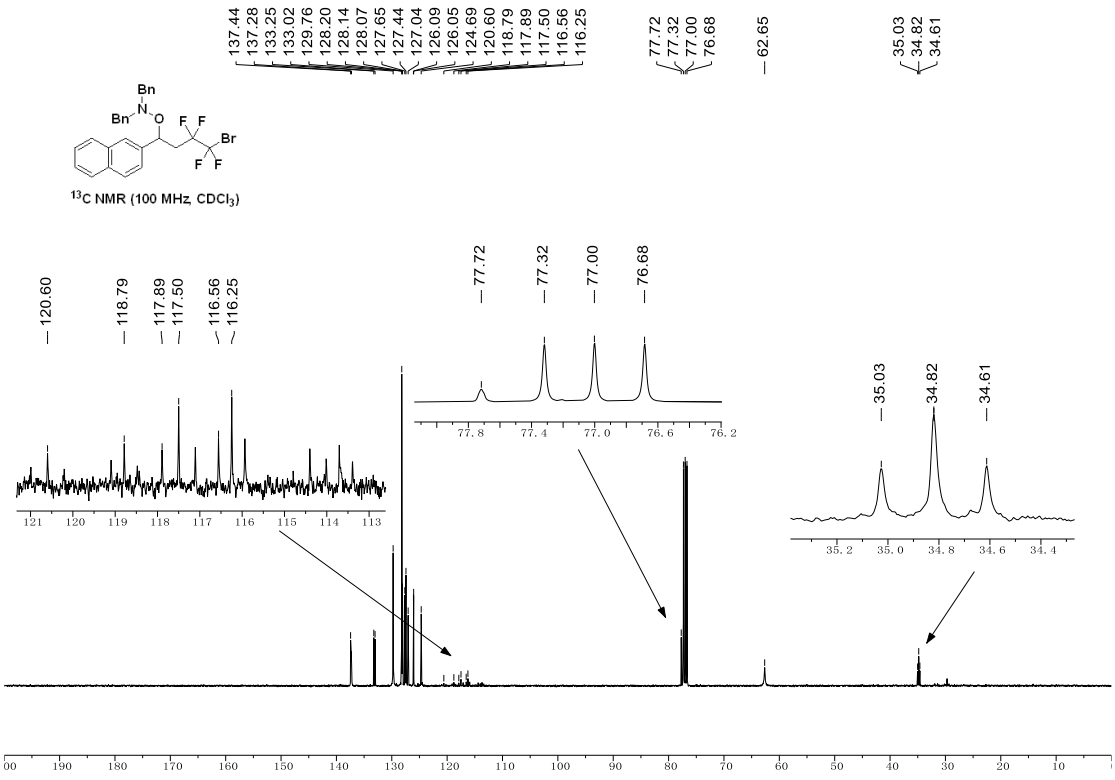


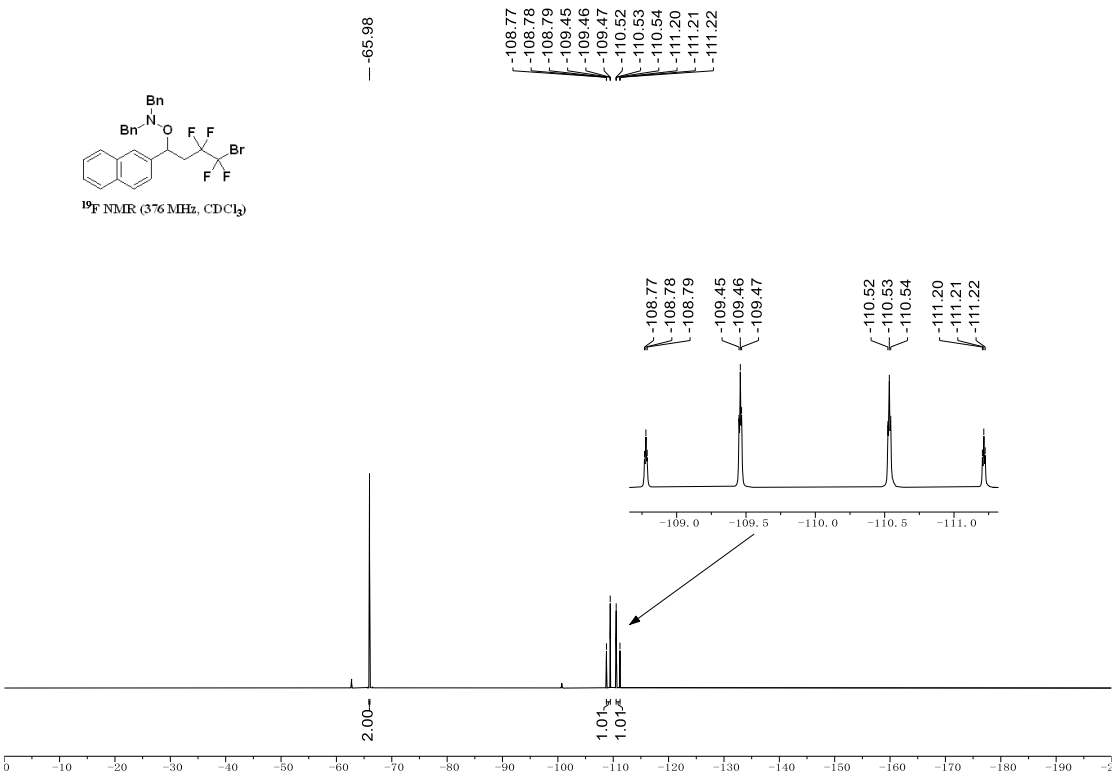



-65.87
-105.95
-105.96
-105.97
-106.63
-106.64
-106.65
-108.69
-108.70
-108.71
-109.37
-109.38
-109.38
Bn
Bn
N
O
F F
Br
F F
19F NMR (376 MHz, CDCl3)
-105.95
-105.96
-105.97
-106.63
-106.64
-106.65
-108.69
-108.70
-108.71
-109.37
-109.38
-109.38
-106.0 -106.5 -107.0 -107.5 -108.0 -108.5 -109.0
2.00
1.02
1.01
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190

N,*N*-dibenzyl-*O*-(4-bromo-3,3,4,4-tetrafluoro-1-(naphthalen-2-yl)butyl)hydroxylamine (4k)

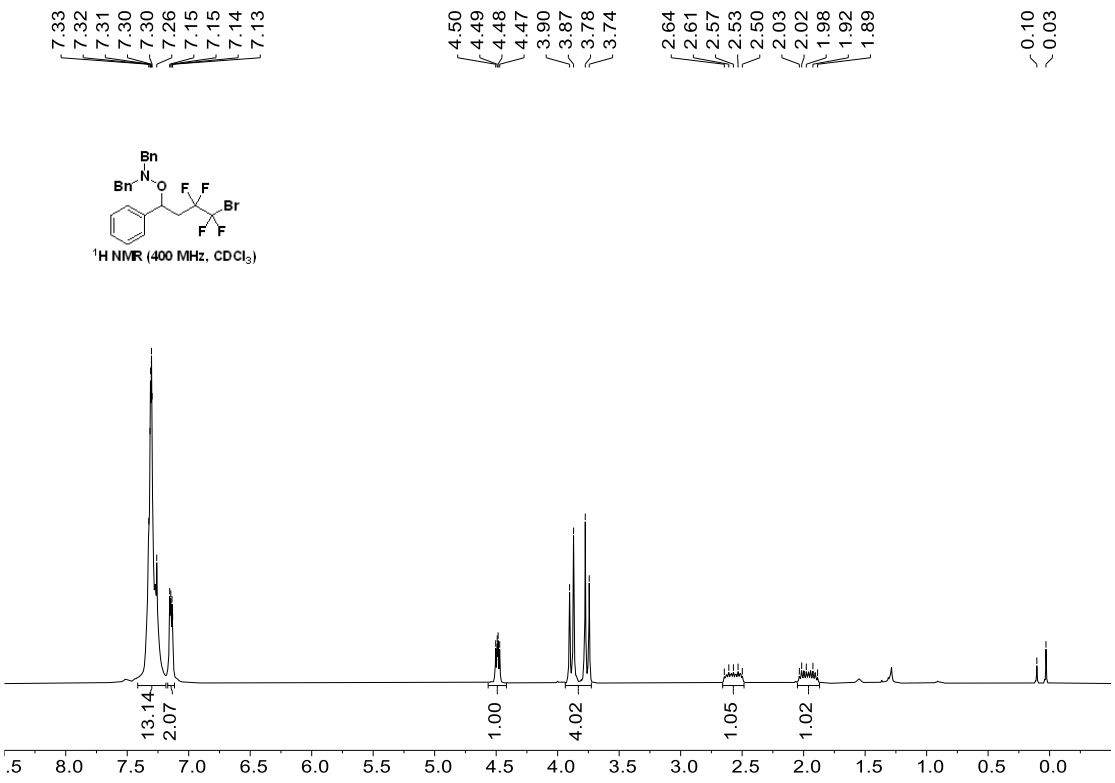


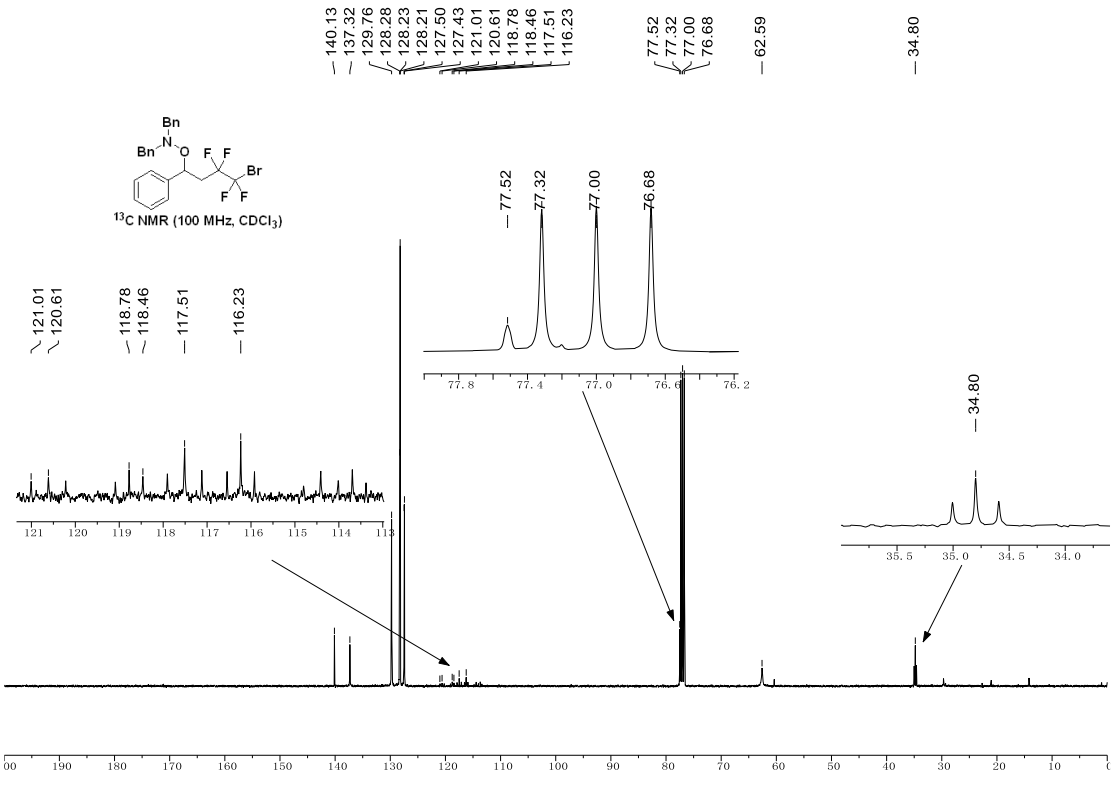


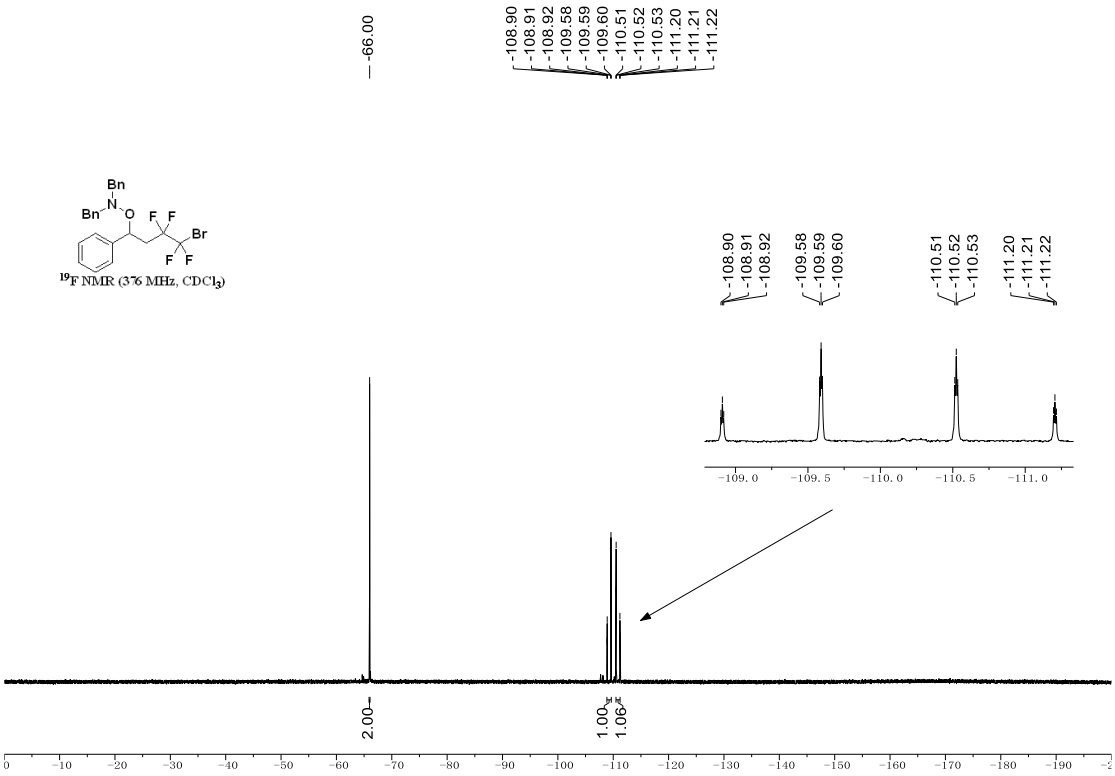


^{19}F NMR (376 MHz, $CDCl_3$)

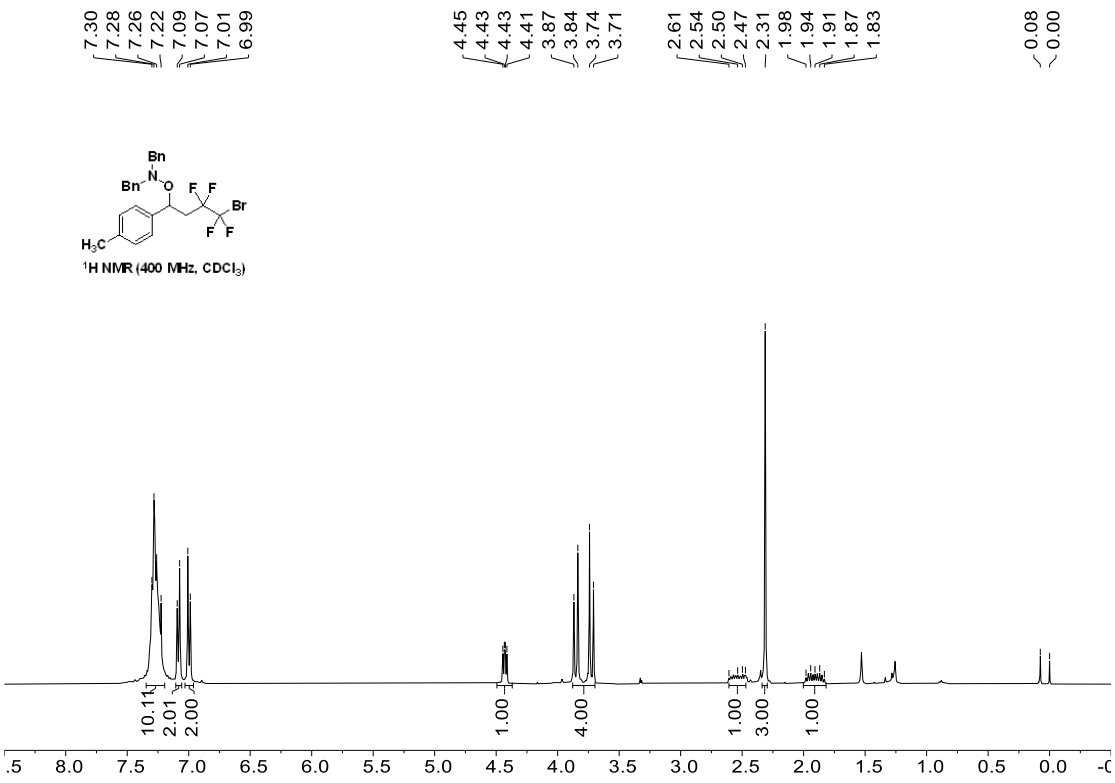
N,*N*-dibenzyl-*O*-(4-bromo-3,3,4,4-tetrafluoro-1-phenylbutyl)hydroxylamine (4l)

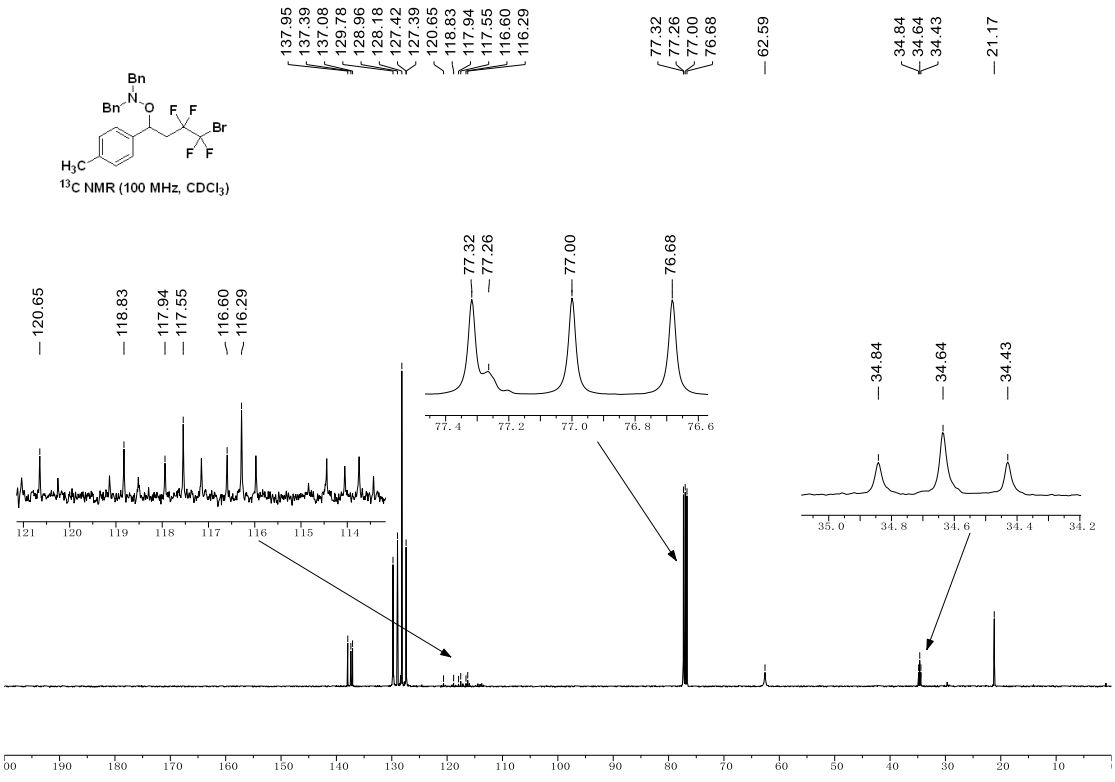


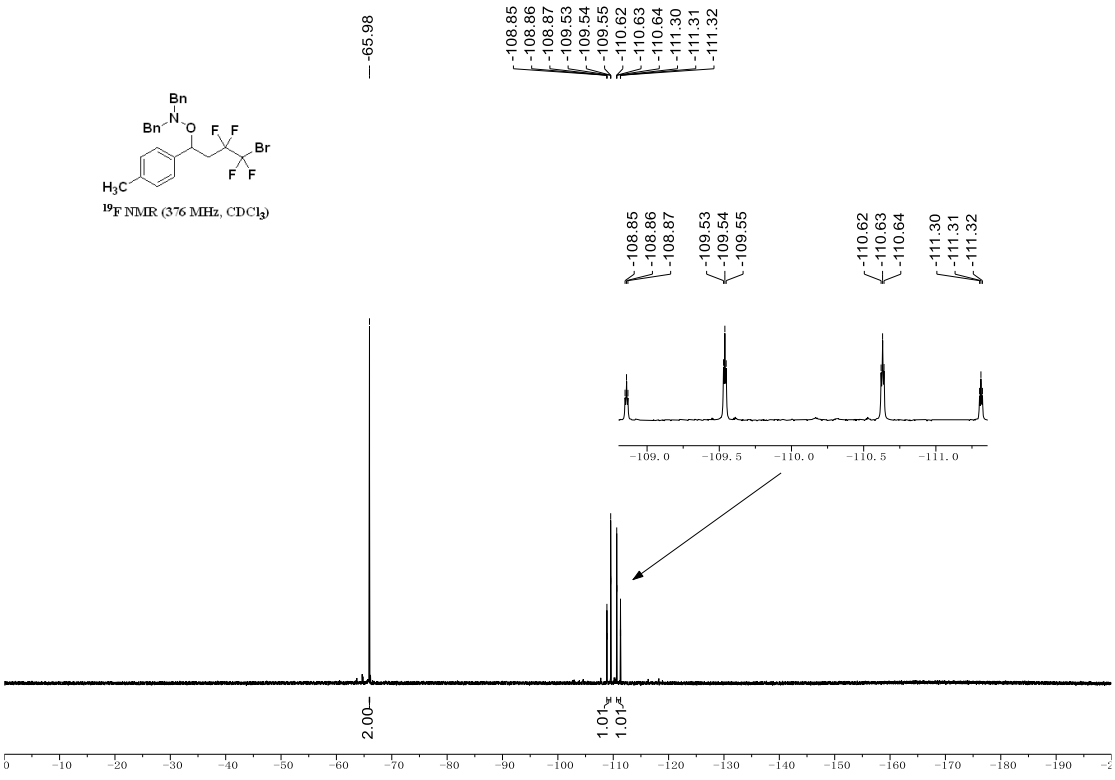



-66.00
-108.90
-108.91
-108.92
-109.58
-109.59
-109.60
-110.51
-110.52
-110.53
-111.20
-111.21
-111.22
Bn
N
Bn
O
F F
Br
F F
19F NMR (376 MHz, CDCl3)
2.00
1.00
1.06
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-109.0
-109.5
-110.0
-110.5
-111.0

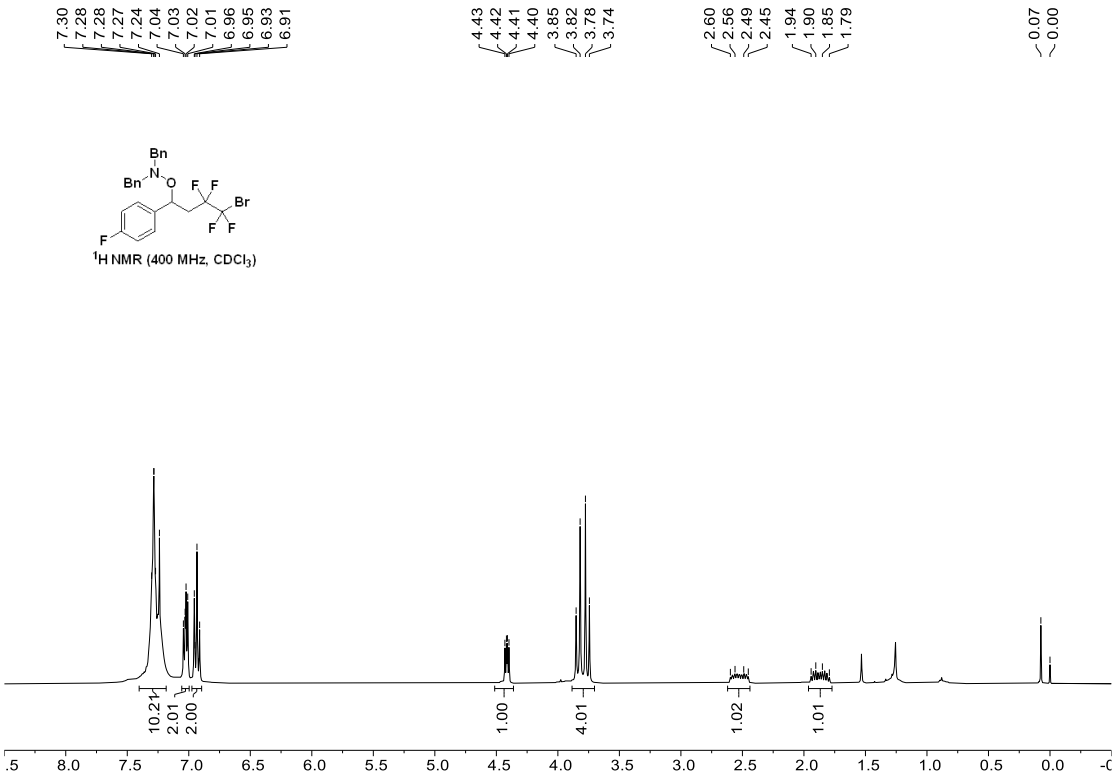
N,*N*-dibenzyl-*O*-(4-bromo-3,3,4,4-tetrafluoro-1-(p-tolyl)butyl)hydroxylamine (4m)

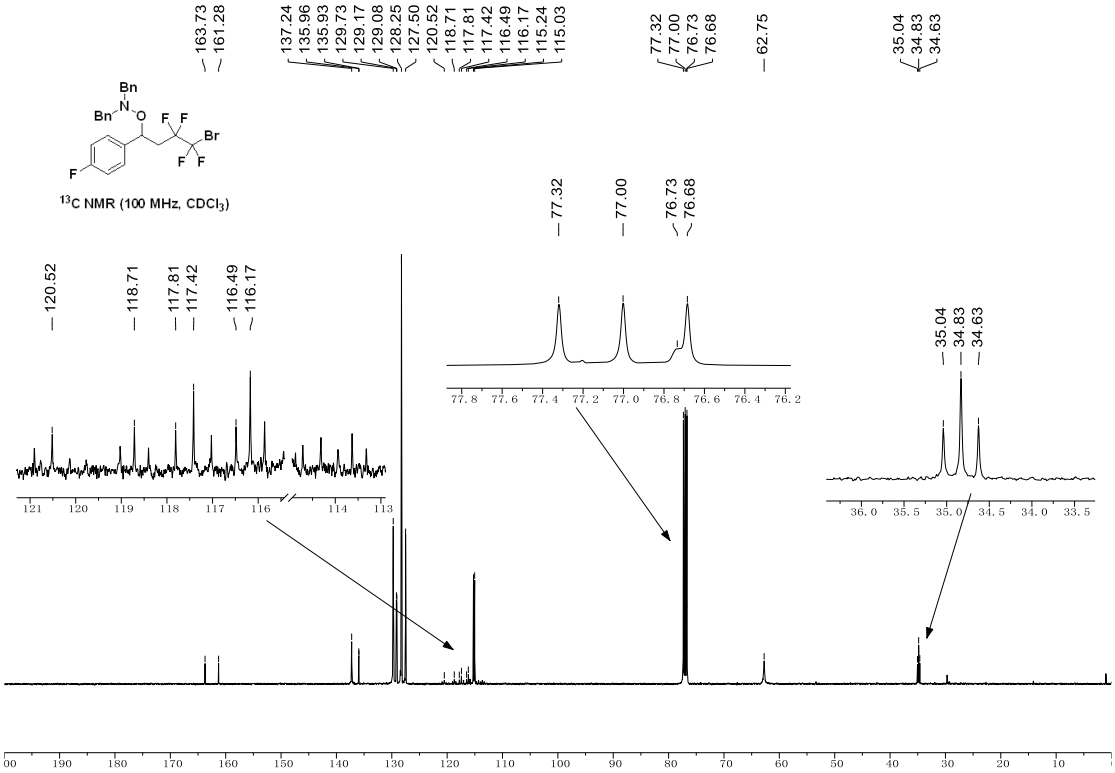


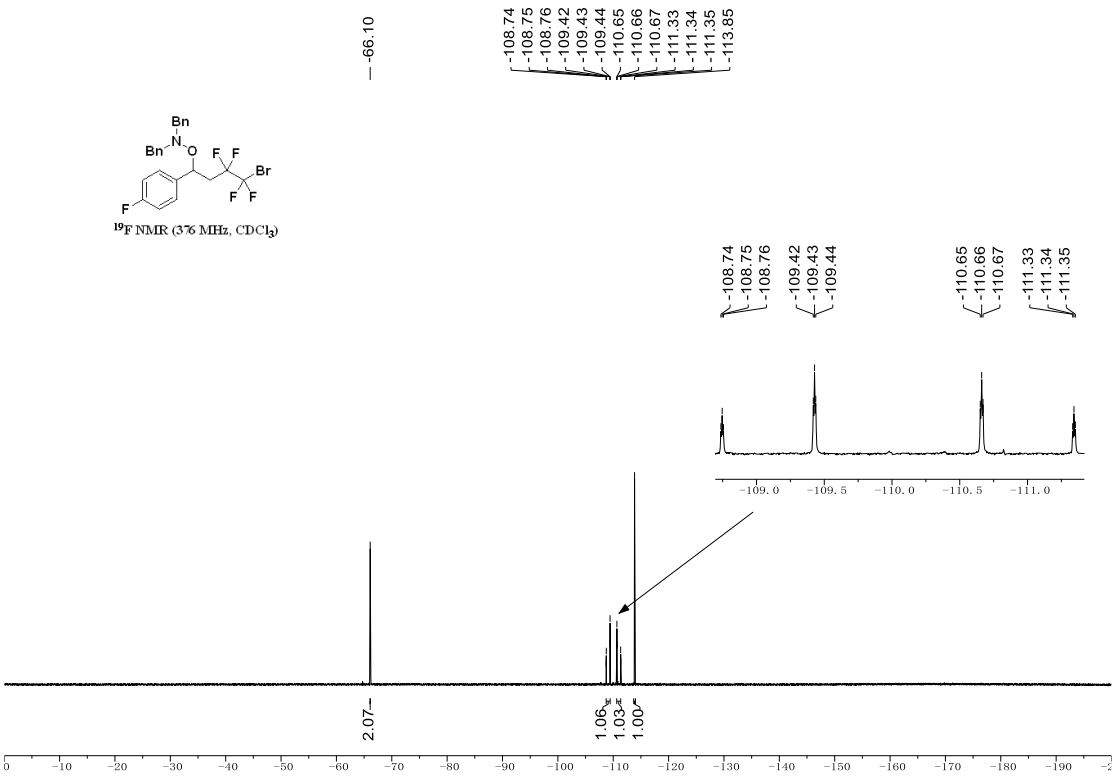



-65.98
-108.85
-108.86
-108.87
-109.53
-109.54
-109.55
-110.62
-110.63
-110.64
-111.30
-111.31
-111.32
Bn
Bn
N
O
F F
F F
Br
H3C
19F NMR (376 MHz, CDCl3)
-109.0
-109.5
-110.0
-110.5
-111.0
2.00
1.01
1.01
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190

N,*N*-dibenzyl-*O*-(4-bromo-3,3,4,4-tetrafluoro-1-(4-fluorophenyl)butyl)hydroxylamine (4n)

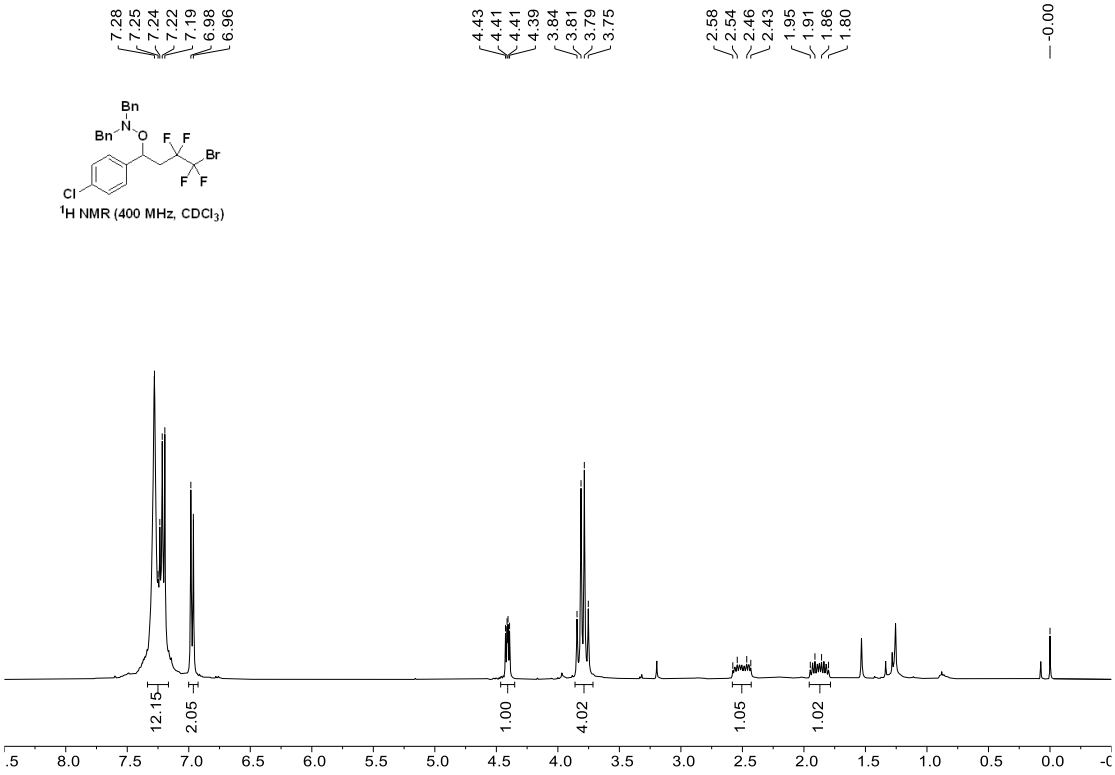


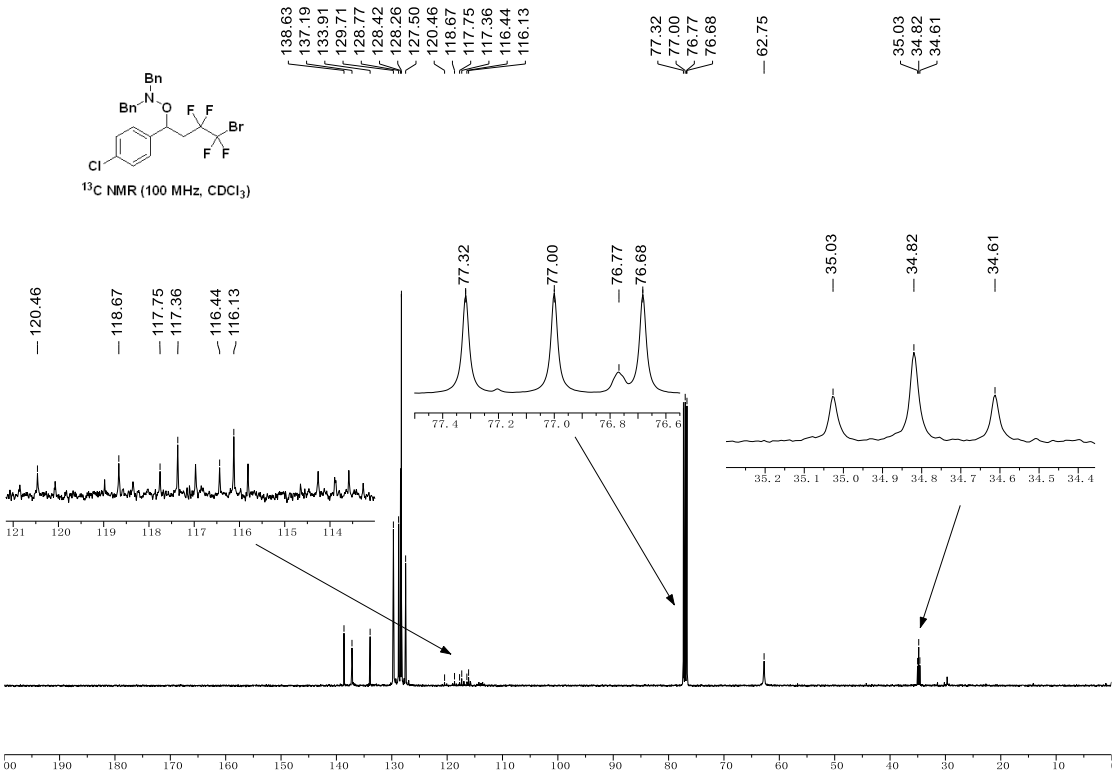


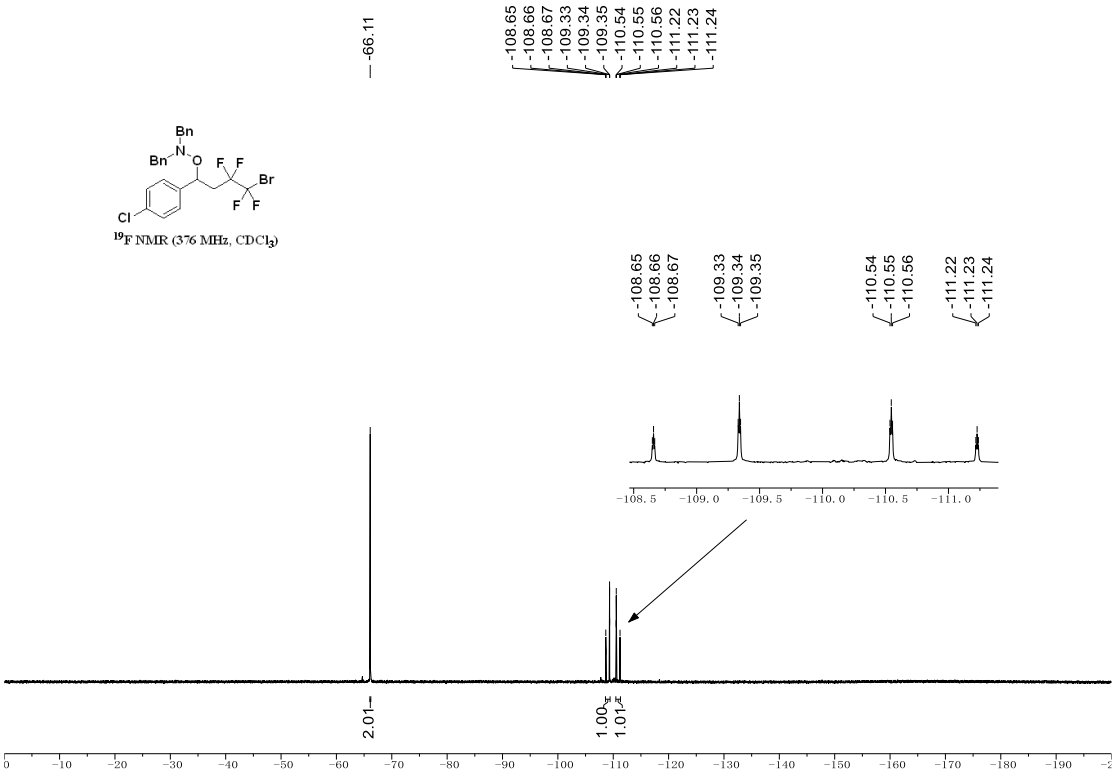


^{19}F NMR (376 MHz, $CDCl_3$)

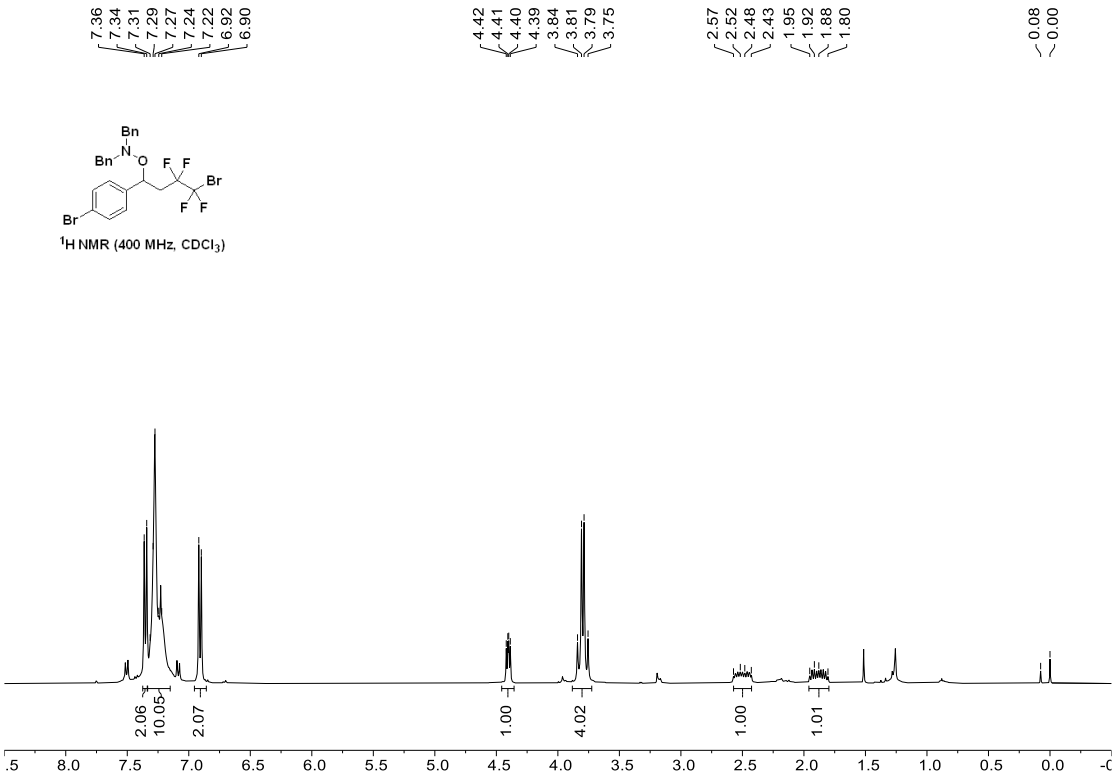
N,*N*-dibenzyl-*O*-(4-bromo-1-(4-chlorophenyl)-3,3,4,4-tetrafluorobutyl)hydroxylamine (4o)

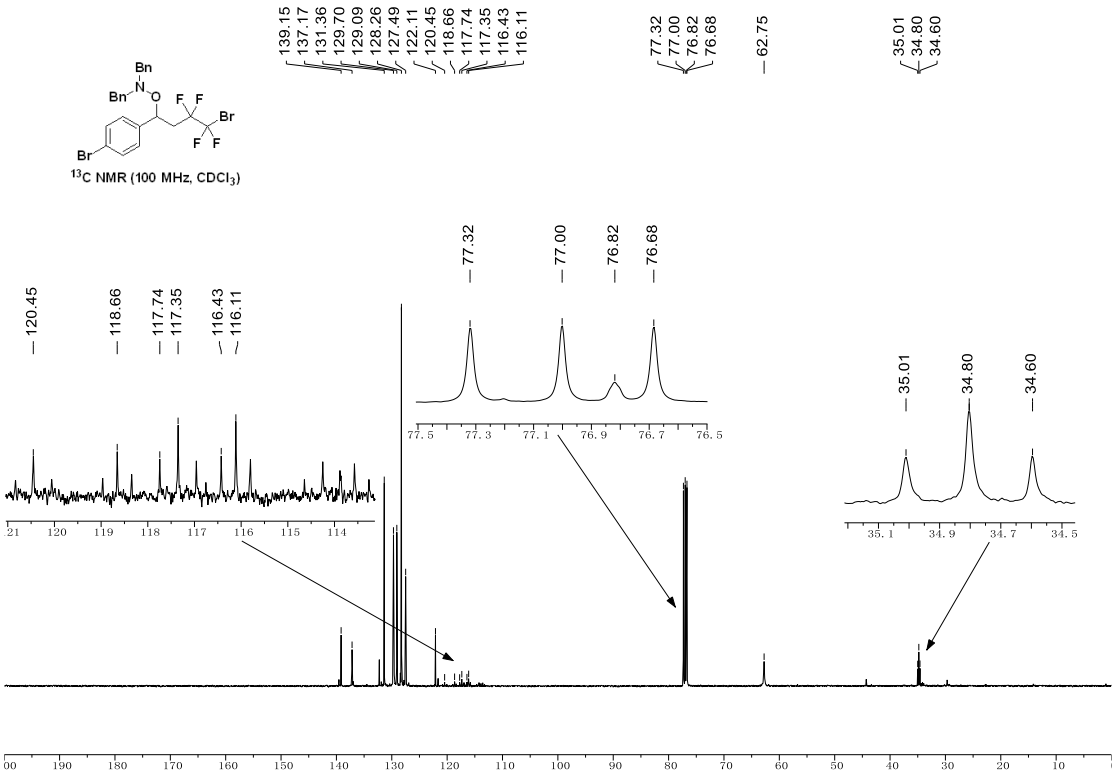


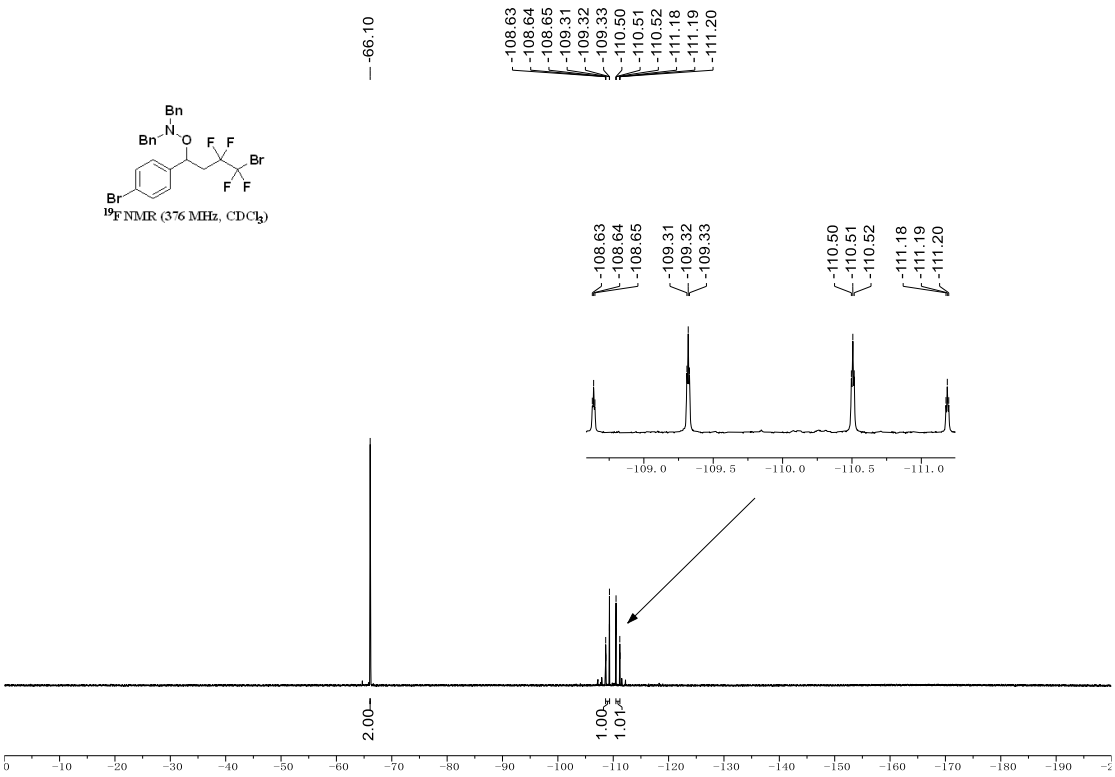



-66.11
-108.65
-108.66
-108.67
-109.33
-109.34
-109.35
-110.54
-110.55
-110.56
-111.22
-111.23
-111.24
Bn
Bn
N
O
F
F
Br
F
F
Cl
^{19}F NMR (376 MHz, CDCl$_3$)
2.01
1.00
1.01

N,*N*-dibenzyl-*O*-(4-bromo-1-(4-bromophenyl)-3,3,4,4-tetrafluorobutyl)hydroxylamine (4p)

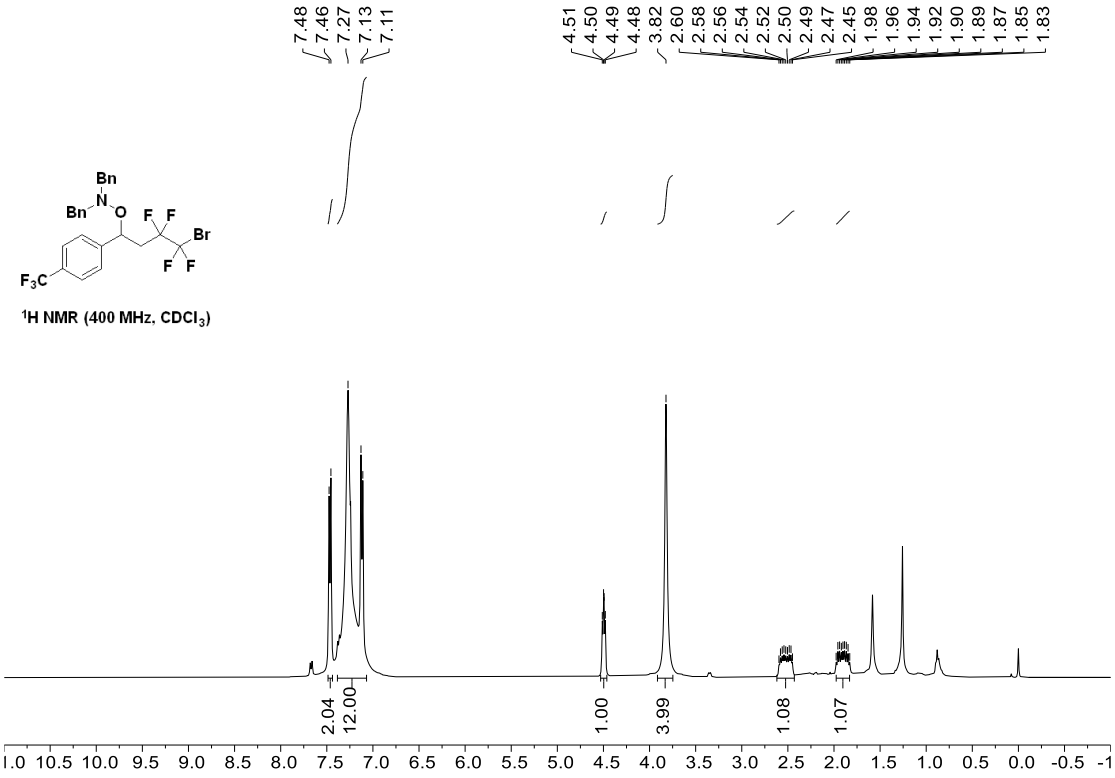


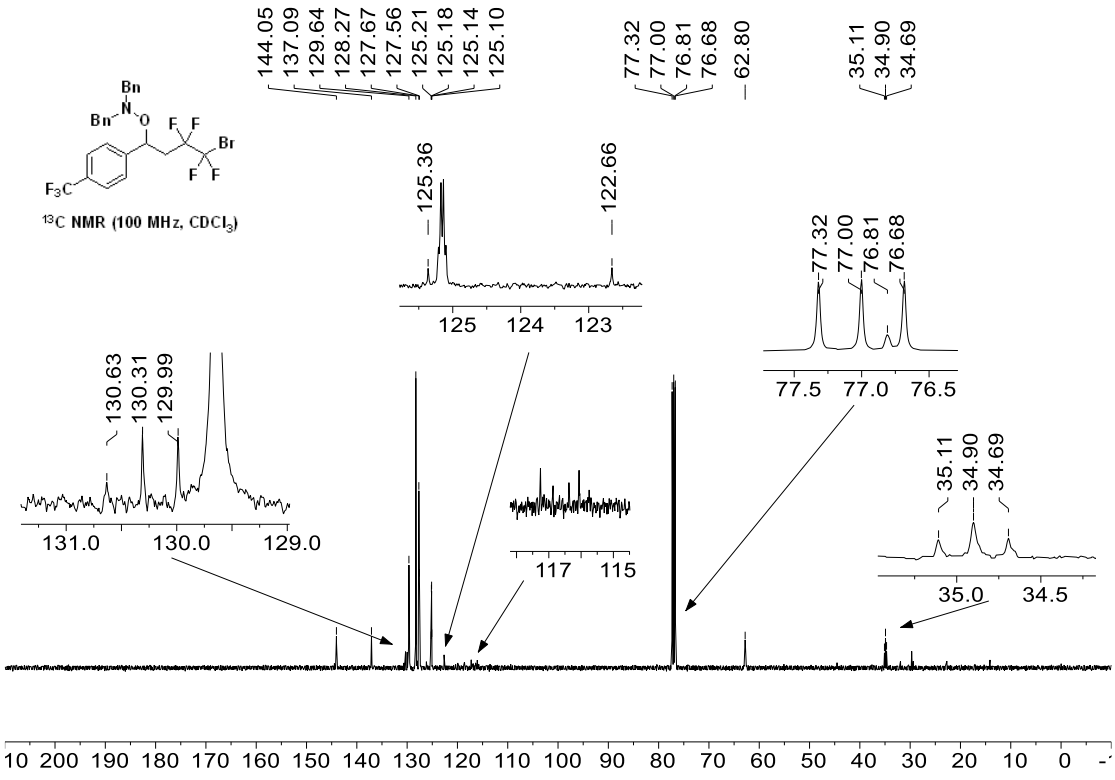


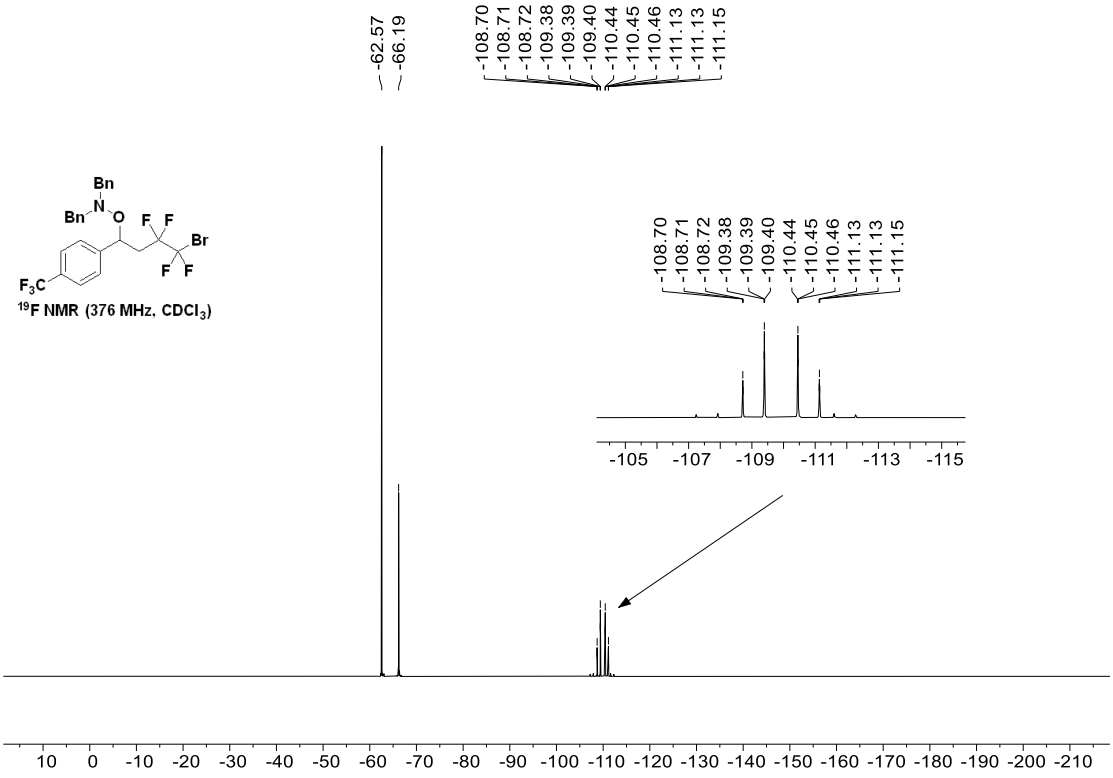


^{19}F NMR (376 MHz, $CDCl_3$)

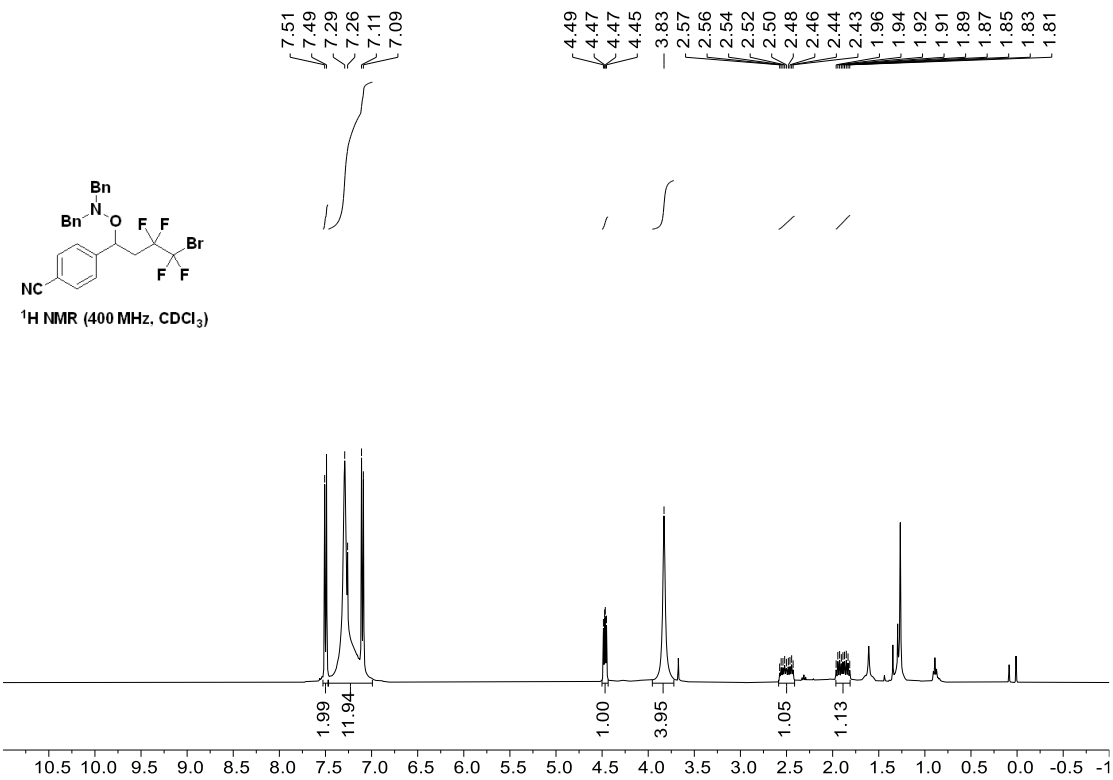
***N*,*N*-dibenzyl-*O*-(4-bromo-3,3,4,4-tetrafluoro-1-(4-(trifluoromethyl)phenyl)butyl) hydroxylamine (4q)**

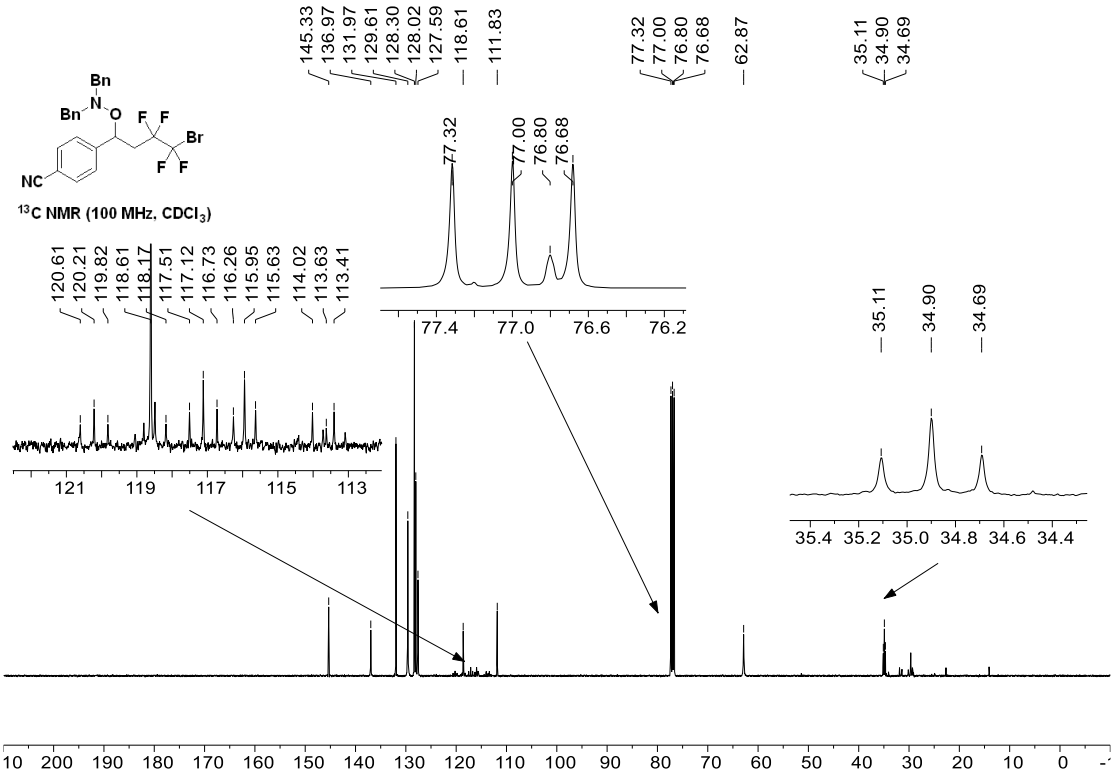


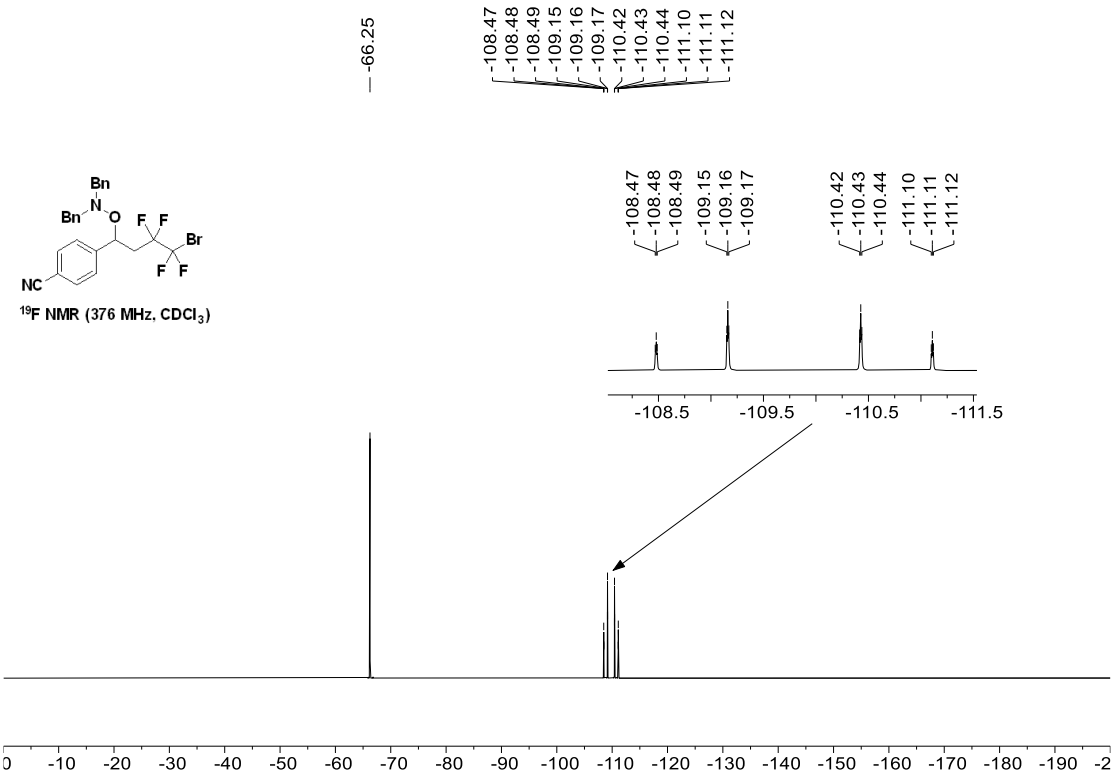



-62.57
-66.19
-108.70
-108.71
-108.72
-109.38
-109.39
-109.40
-110.44
-110.45
-110.46
-111.13
-111.13
-111.15
Bn
N
Bn
O
F F
Br
F F
F3C
19F NMR (376 MHz, CDCl3)
-105 -107 -109 -111 -113 -115
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

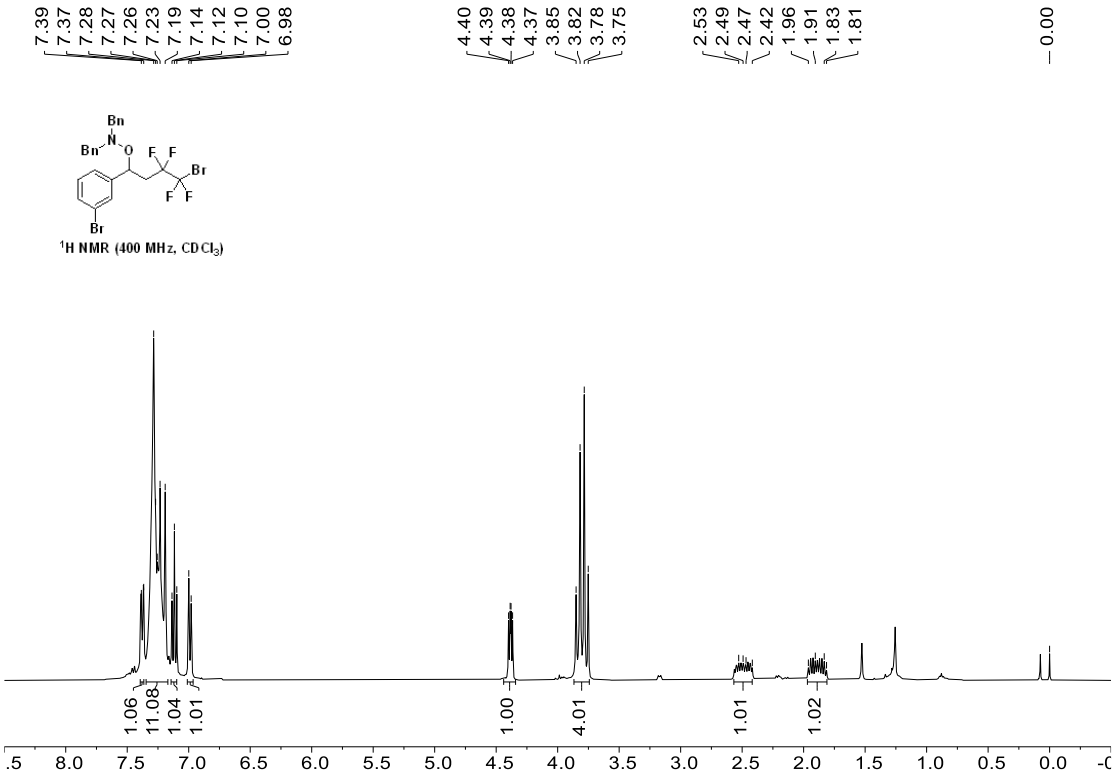
4-(4-bromo-1-((dibenzylamino)oxy)-3,3,4,4-tetrafluorobutyl)benzonitrile (4r)

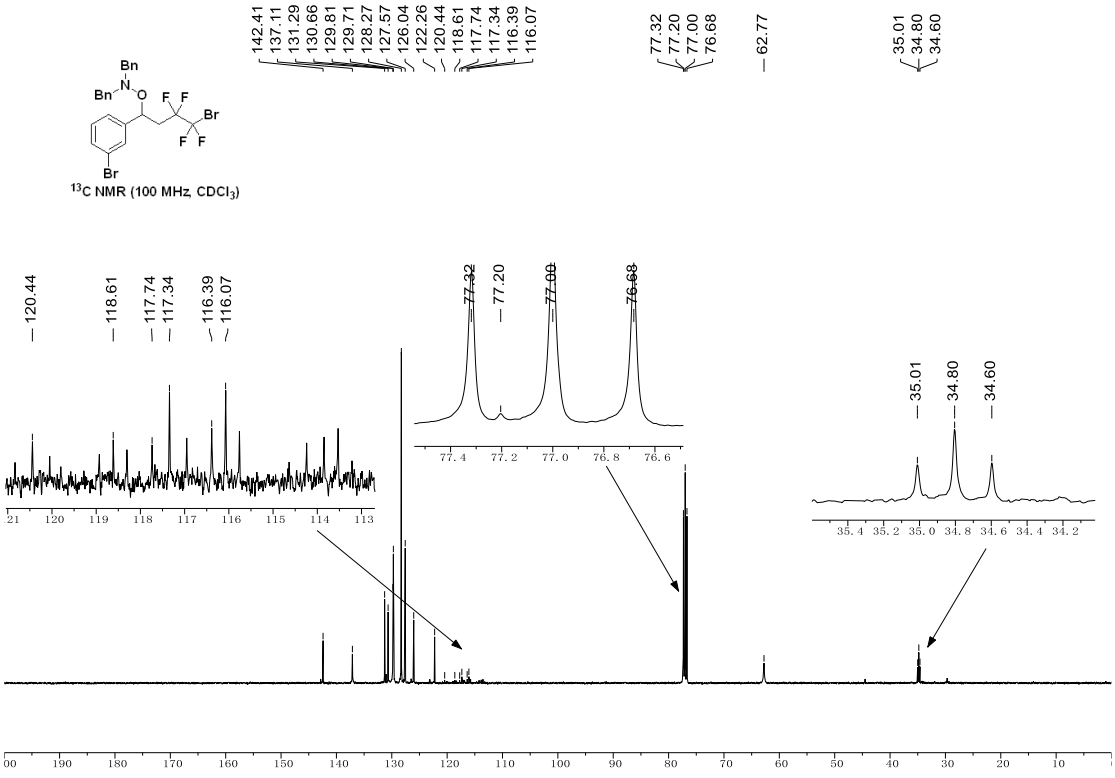


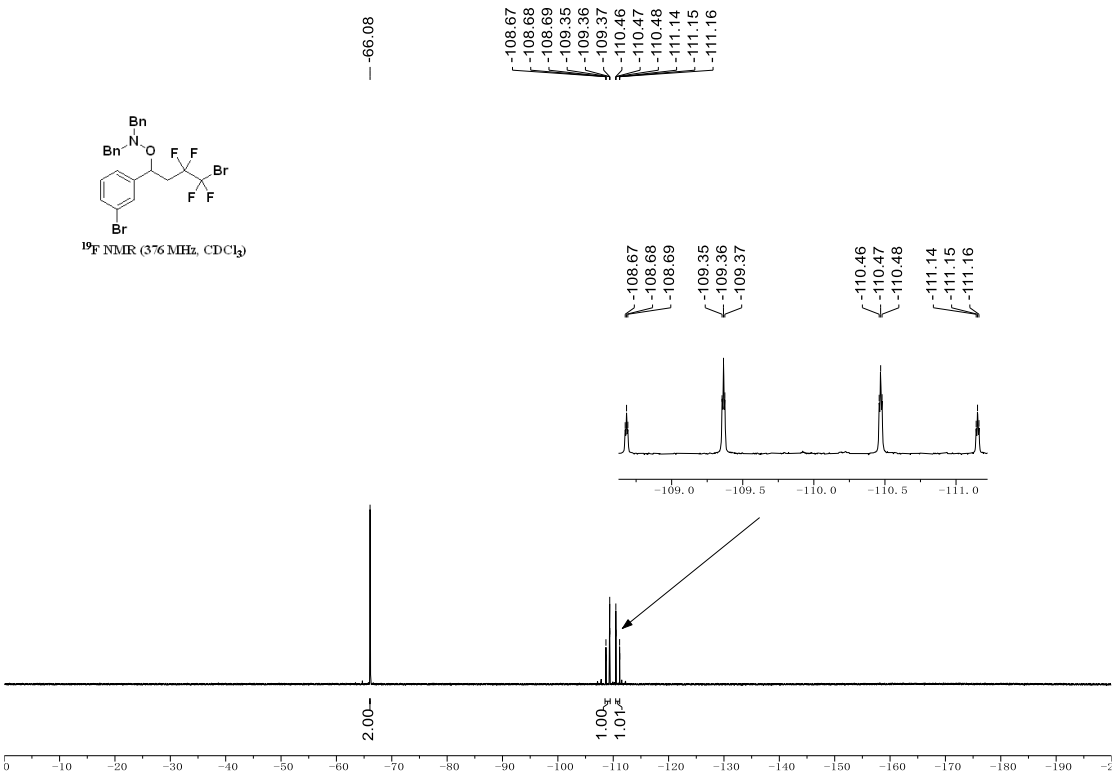



-66.25
-108.47
-108.48
-108.49
-109.15
-109.16
-109.17
-110.42
-110.43
-110.44
-111.10
-111.11
-111.12
Bn
Bn
N
O
F F
Br
F F
NC
19F NMR (376 MHz, CDCl3)
-108.5
-109.5
-110.5
-111.5
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2

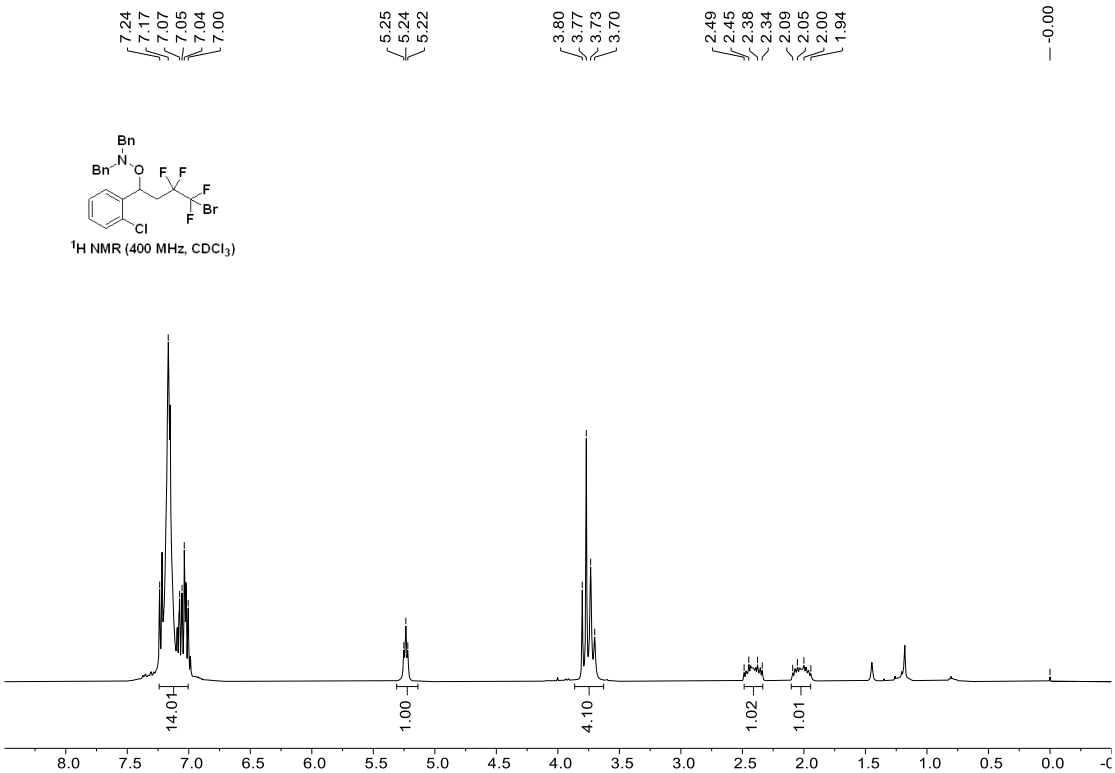
***N*,*N*-dibenzyl-*O*-(4-bromo-1-(3-bromophenyl)-3,3,4,4-tetrafluorobutyl)hydroxylamine (4s)**

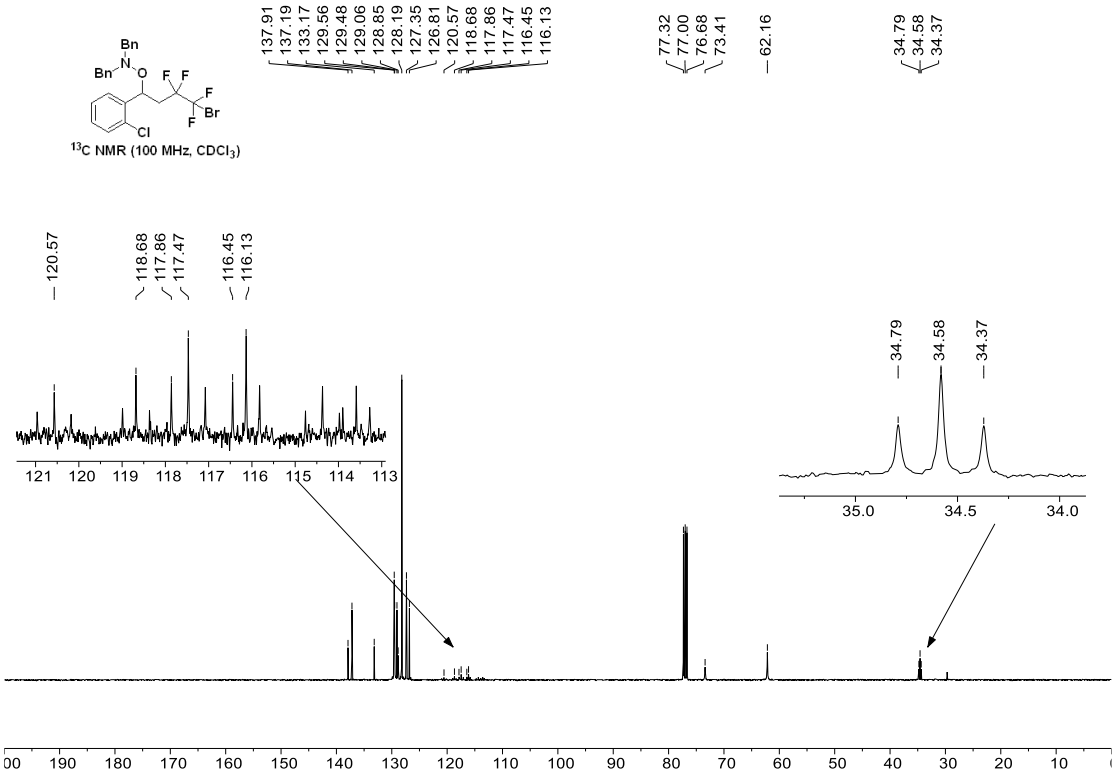


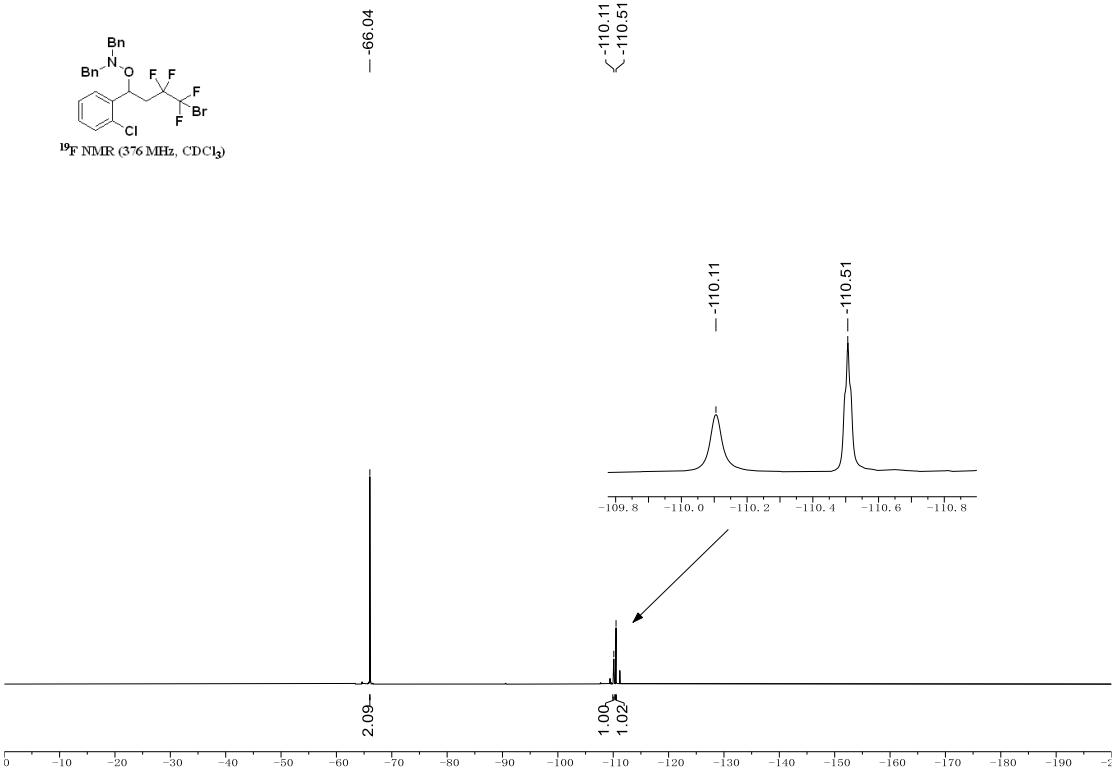



-66.08
-108.67
-108.68
-108.69
-109.35
-109.36
-109.37
-110.46
-110.47
-110.48
-111.14
-111.15
-111.16
Bn
Bn
N
O
F F
Br
F F
Br
19F NMR (376 MHz, CDCl3)
-109.0
-109.5
-110.0
-110.5
-111.0
2.00
1.00
1.01
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190

N,*N*-dibenzyl-*O*-(4-bromo-1-(2-chlorophenyl)-3,3,4,4-tetrafluorobutyl)hydroxylamine (4t)

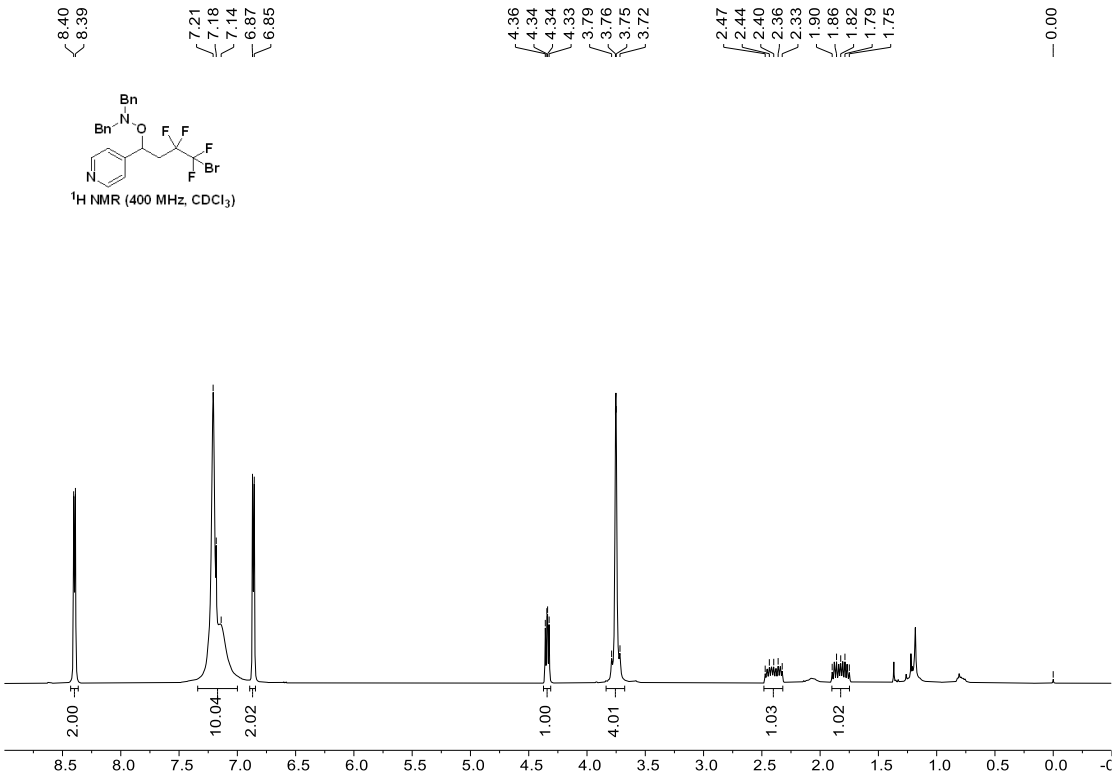


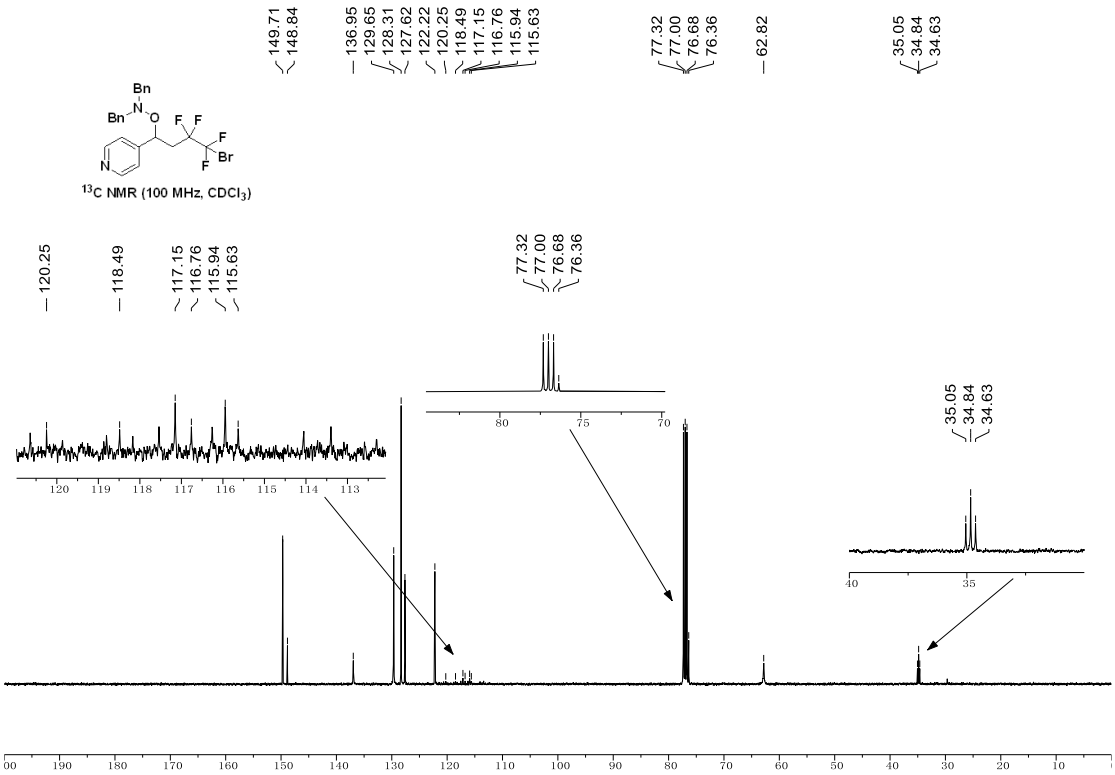


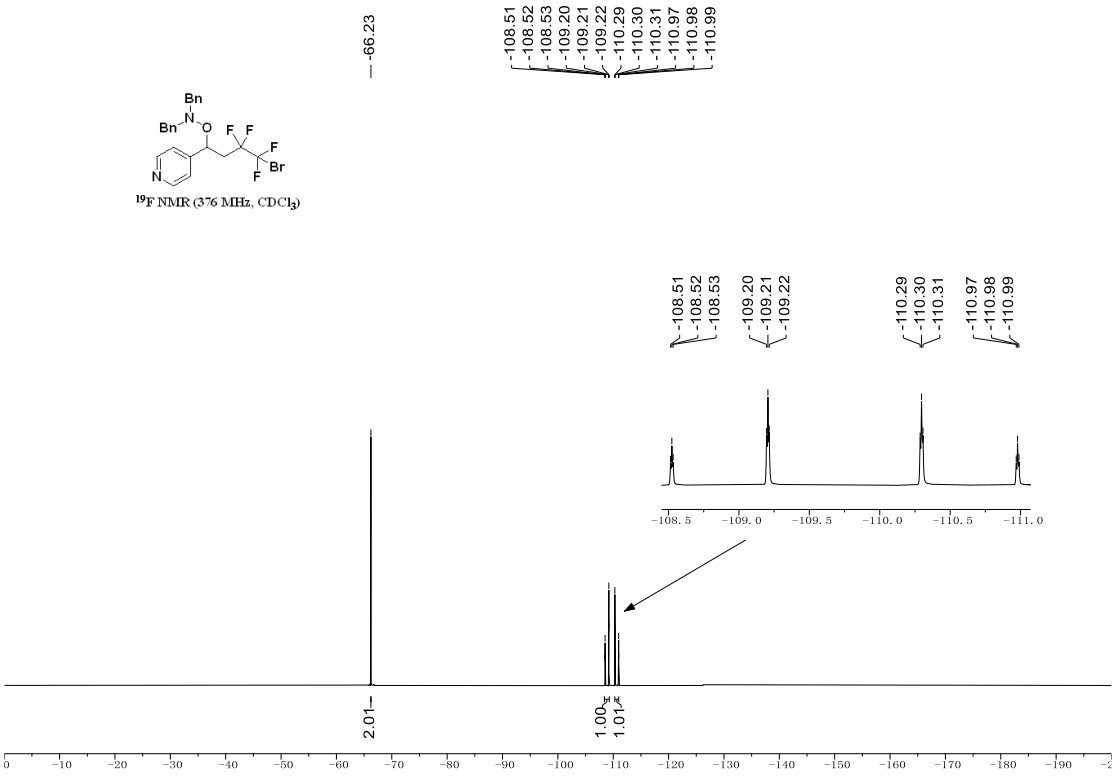


^{19}F NMR (376 MHz, $CDCl_3$)

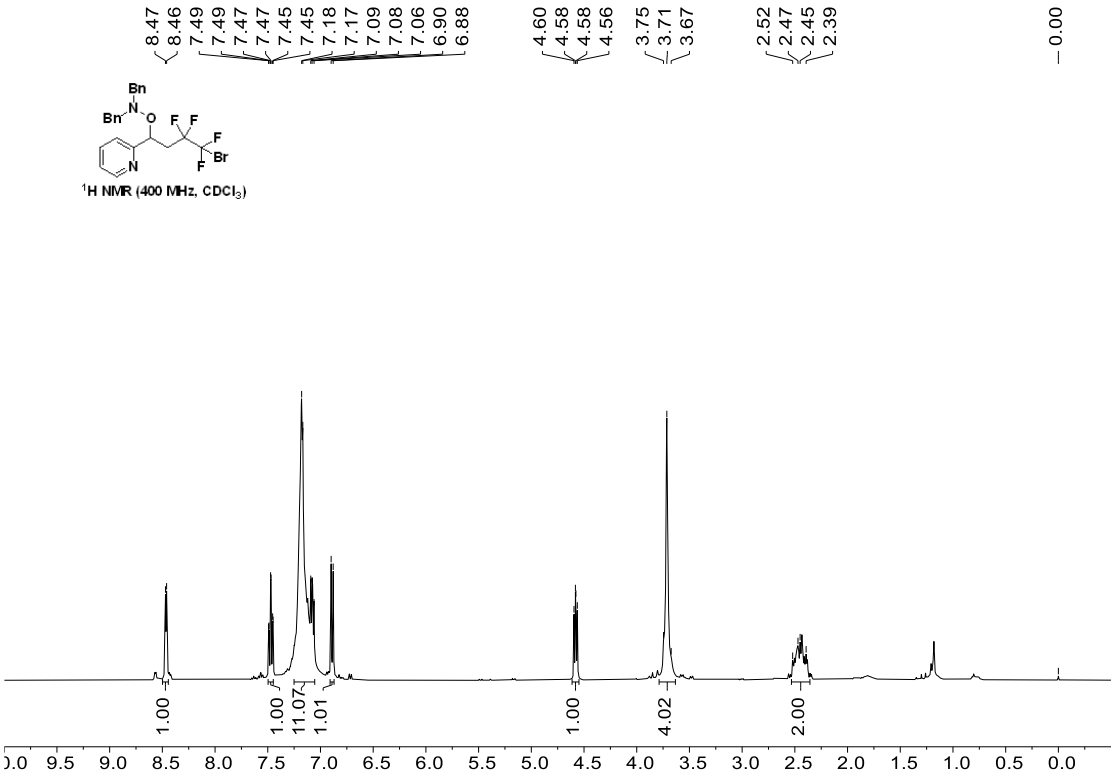
N,*N*-dibenzyl-*O*-(4-bromo-3,3,4,4-tetrafluoro-1-(pyridin-4-yl)butyl)hydroxylamine (4u)

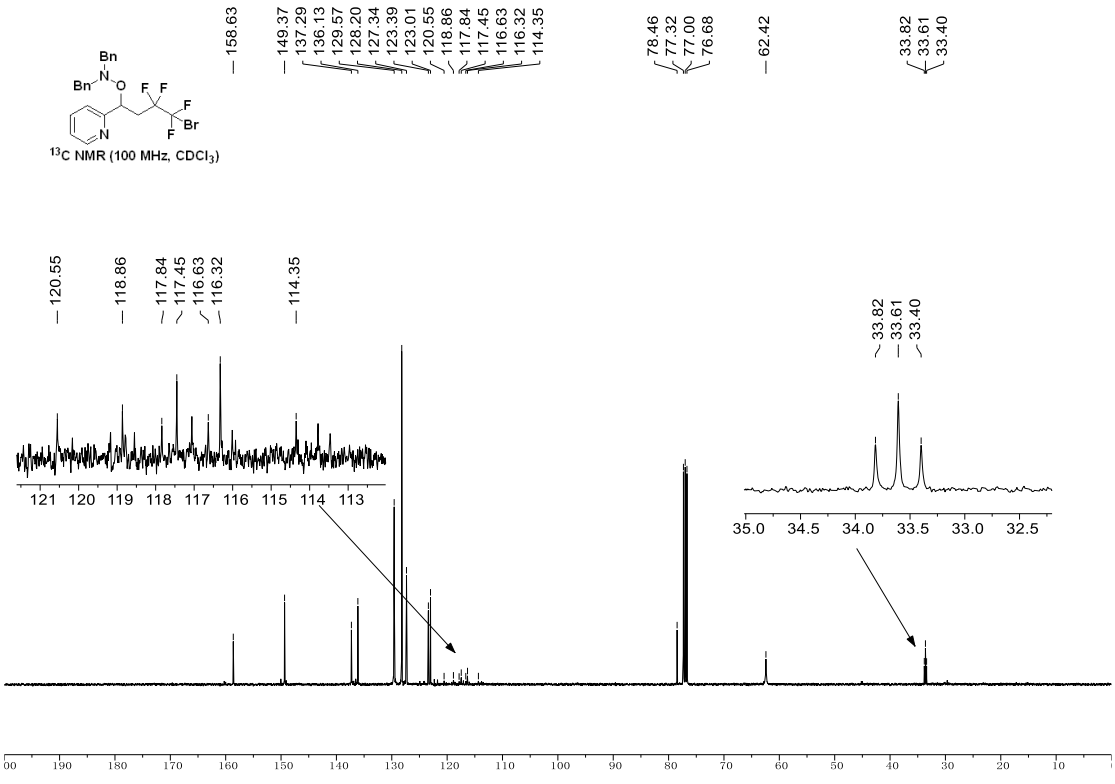


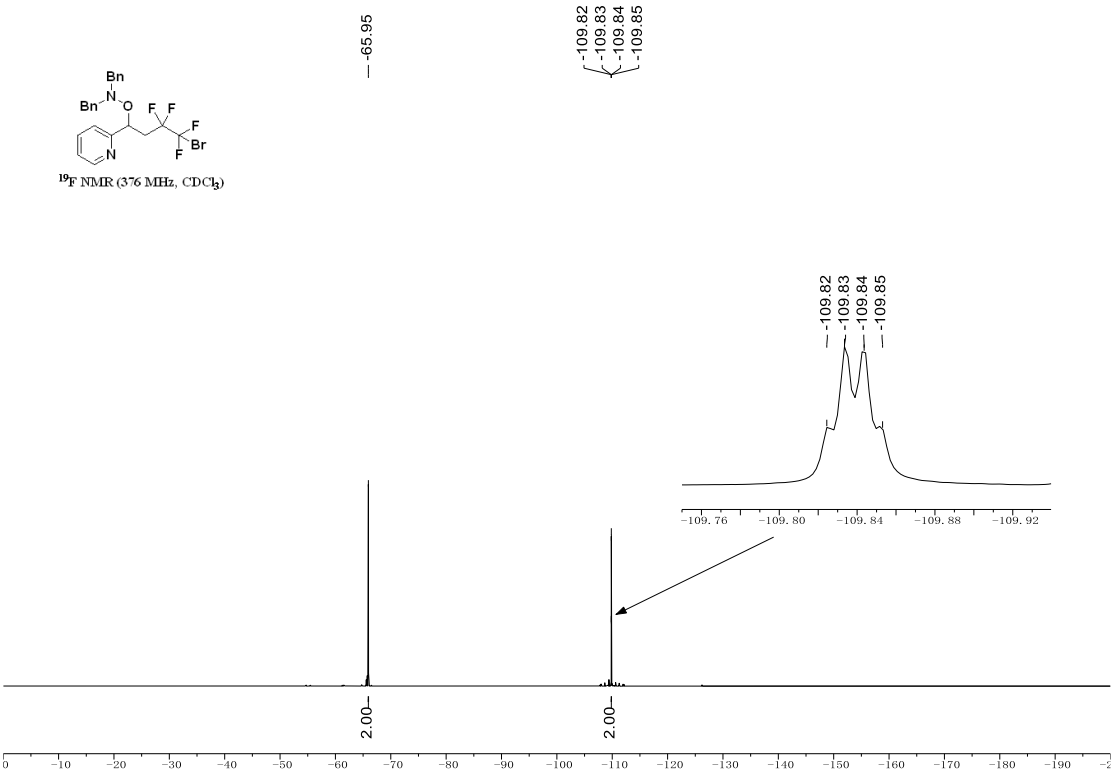



-66.23
-108.51
-108.52
-108.53
-109.20
-109.21
-109.22
-110.29
-110.30
-110.31
-110.97
-110.98
-110.99
Bn
Bn
N
O
F F
F
F
Br
N
19F NMR (376 MHz, CDCl3)
2.01
1.00
1.01
-108.5
-109.0
-109.5
-110.0
-110.5
-111.0

N,*N*-dibenzyl-*O*-(4-bromo-3,3,4,4-tetrafluoro-1-(pyridin-2-yl)butyl)hydroxylamine (4v)

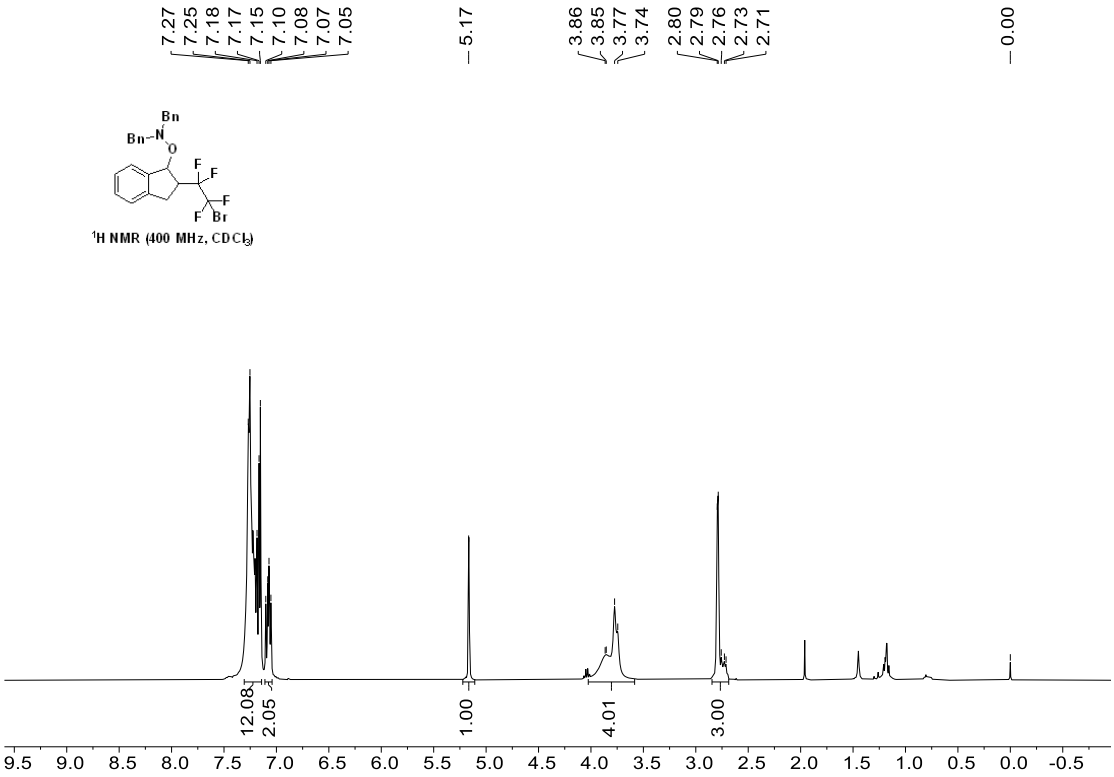


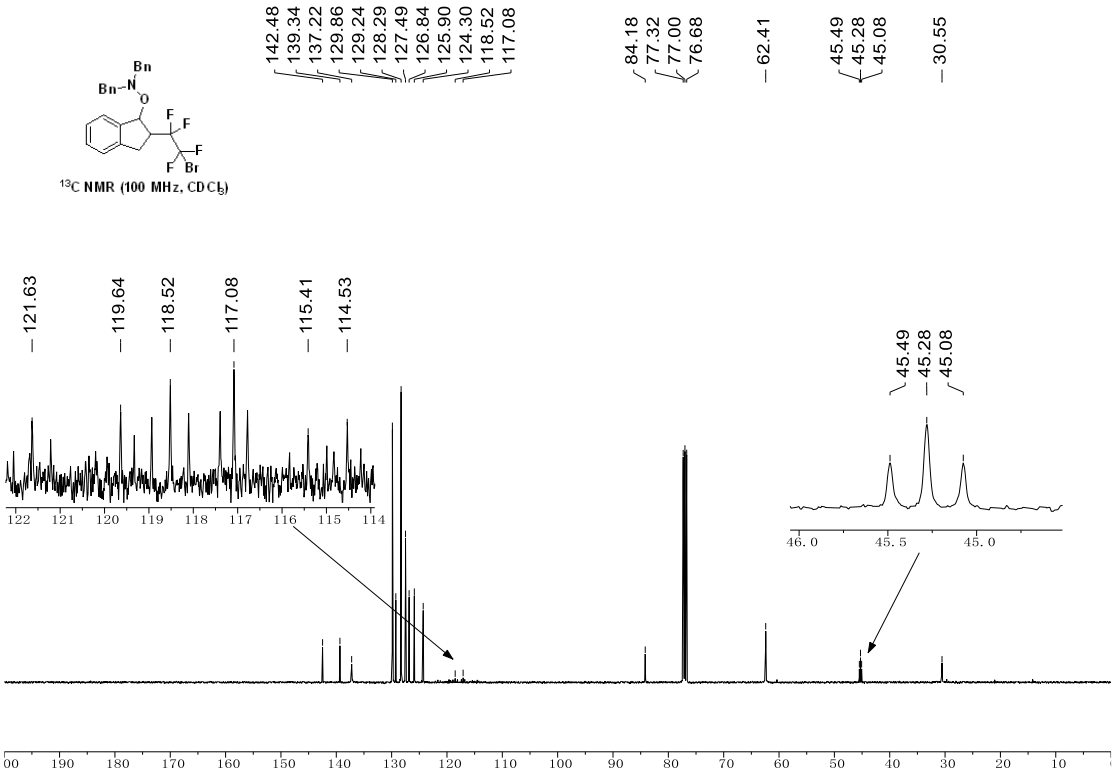


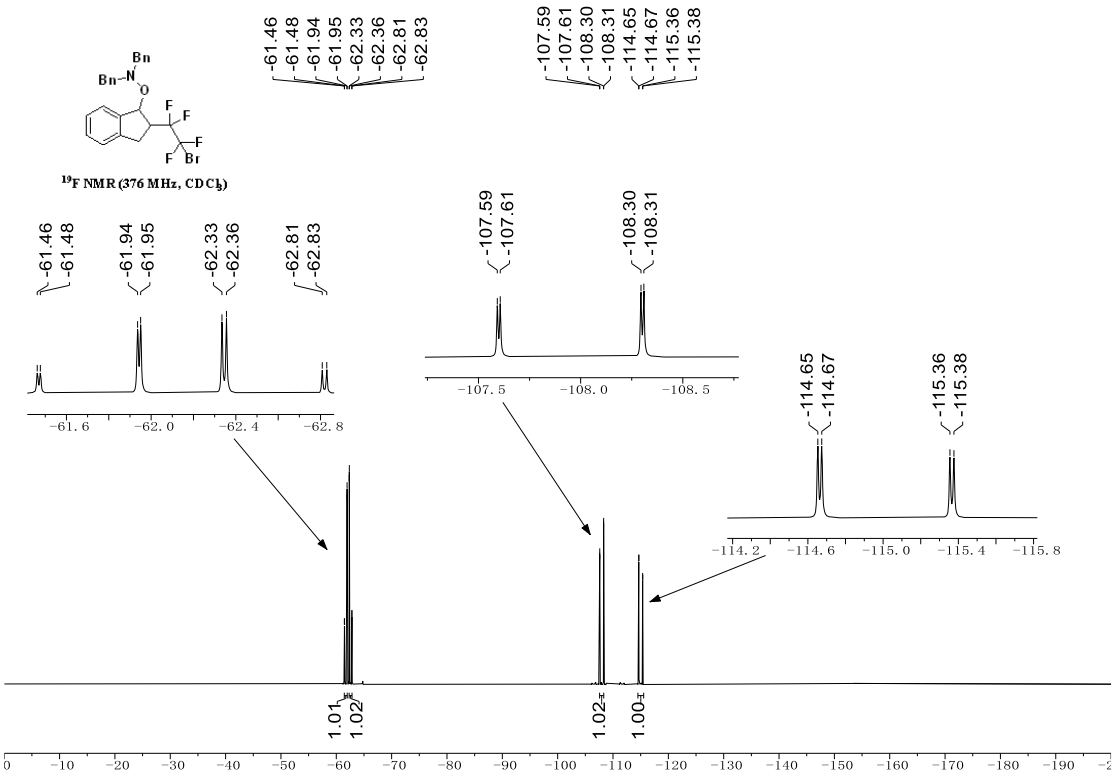


^{19}F NMR (376 MHz, $CDCl_3$)

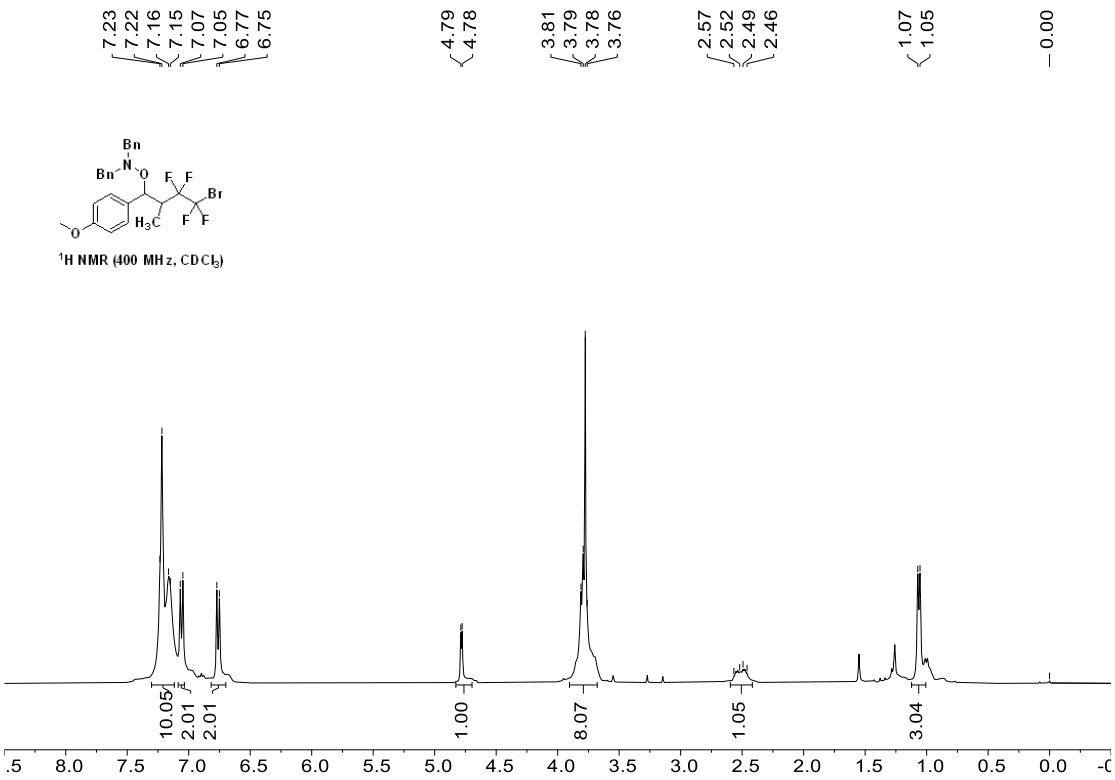
***N*,*N*-dibenzyl-*O*-(2-(2-bromo-1,1,2,2-tetrafluoroethyl)-2,3-dihydro-1H-inden-1-yl)hydroxylamine (4w)**

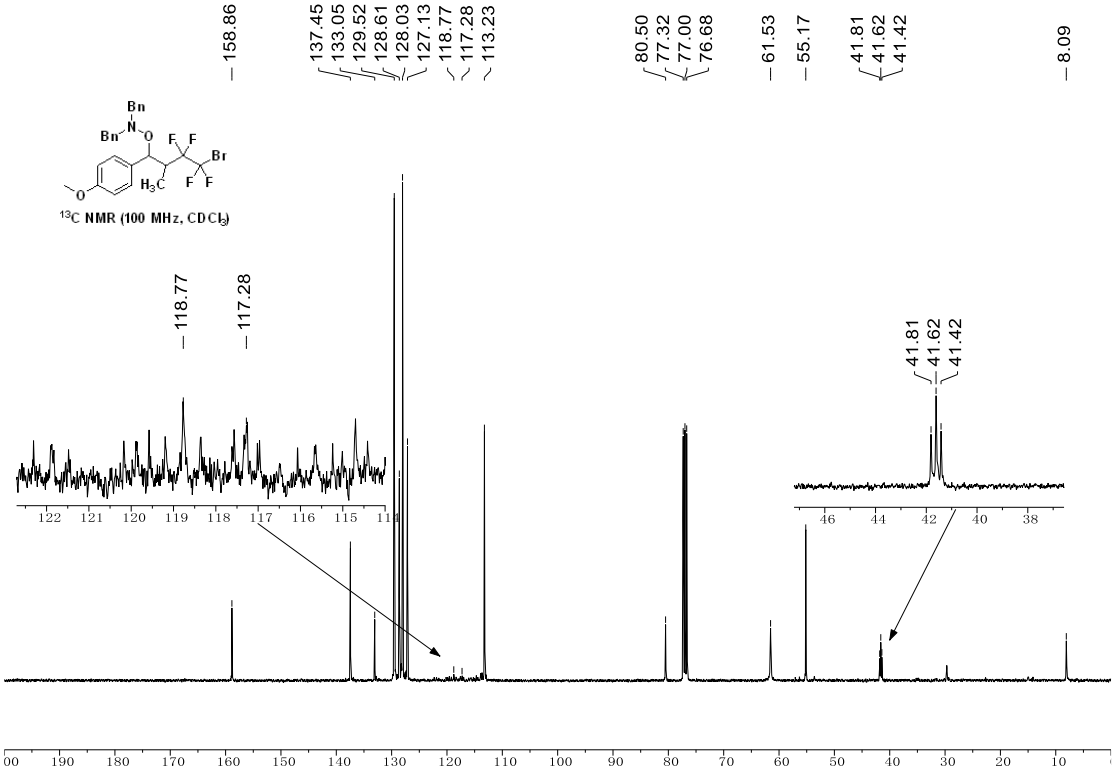


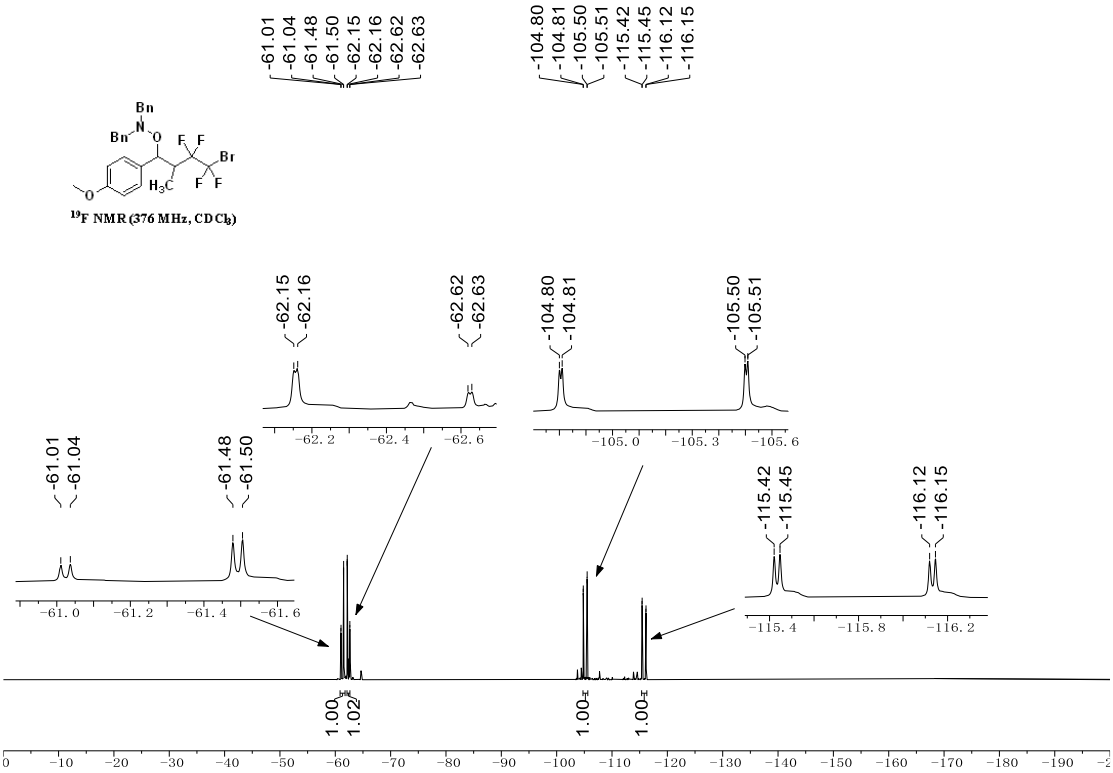



-61.46
-61.48
-61.94
-61.95
-62.33
-62.36
-62.81
-62.83
-107.59
-107.61
-108.30
-108.31
-114.65
-114.67
-115.36
-115.38
Bn
Bn–N
O
F
F
F
F
Br
19F NMR (376 MHz, CDCl3)
-61.6
-62.0
-62.4
-62.8
-107.5
-108.0
-108.5
-114.2
-114.6
-115.0
-115.4
-115.8
1.01
1.02
1.02
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190

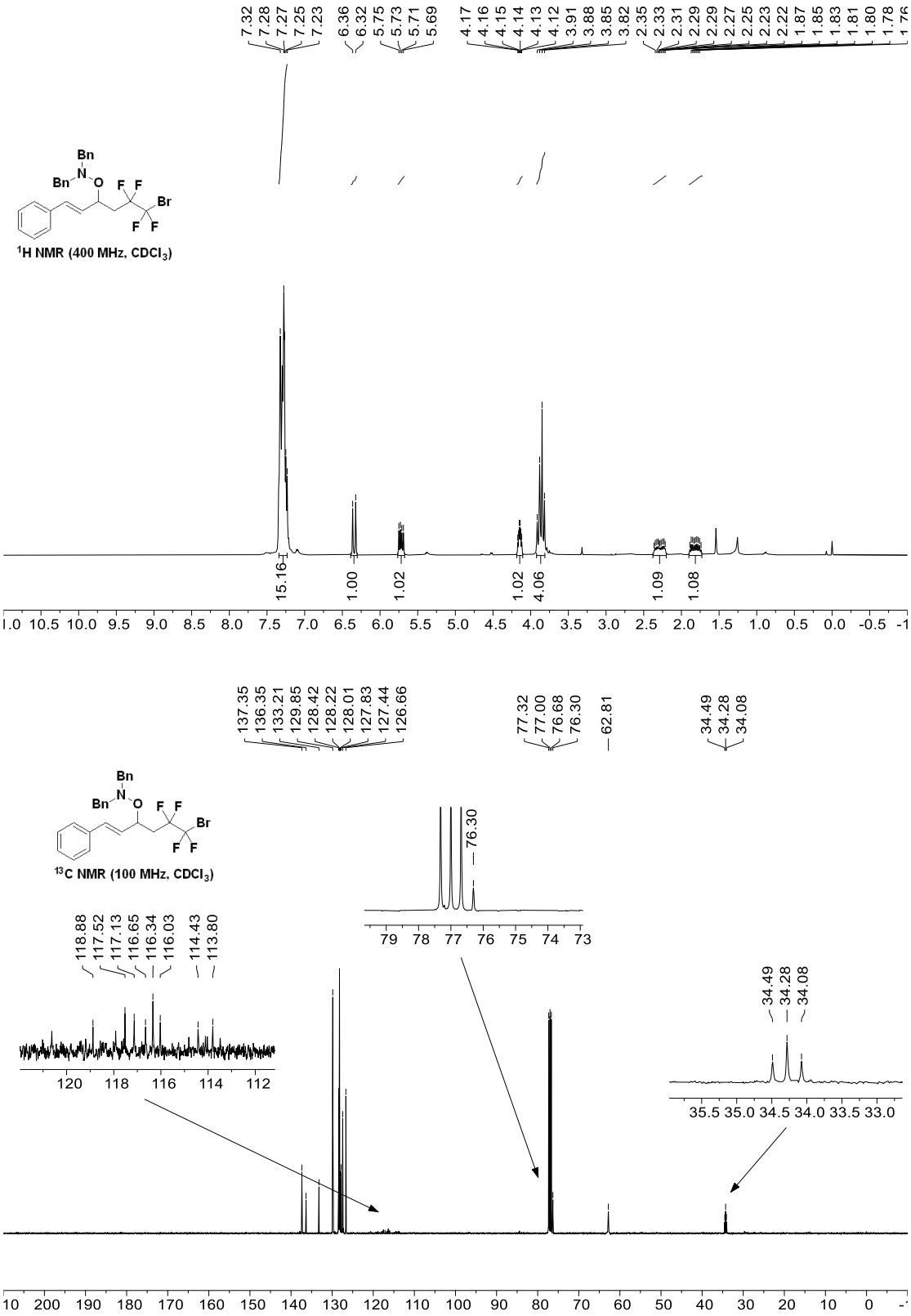
***N*,*N*-dibenzyl-*O*-(4-bromo-3,3,4,4-tetrafluoro-1-(4-methoxyphenyl)-2-methylbutyl)hydroxylamine (4x)**

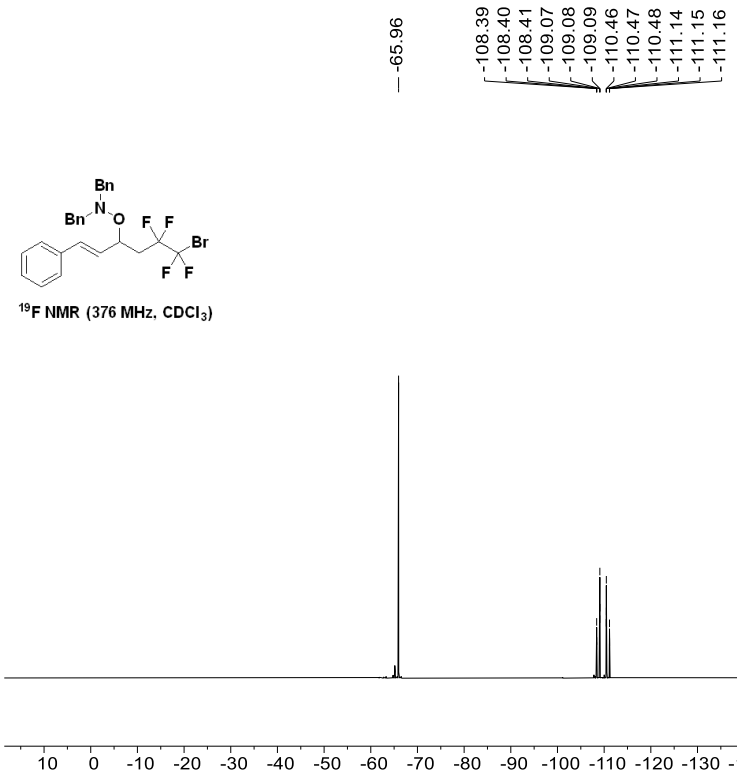





-61.01
-61.04
-61.48
-61.50
-62.15
-62.16
-62.62
-62.63
-104.80
-104.81
-105.50
-105.51
-115.42
-115.45
-116.12
-116.15
Bn
Bn
N
O
F F
Br
F F
H3C
O
19F NMR (376 MHz, CDCl3)
1.00
1.02
1.00
1.00

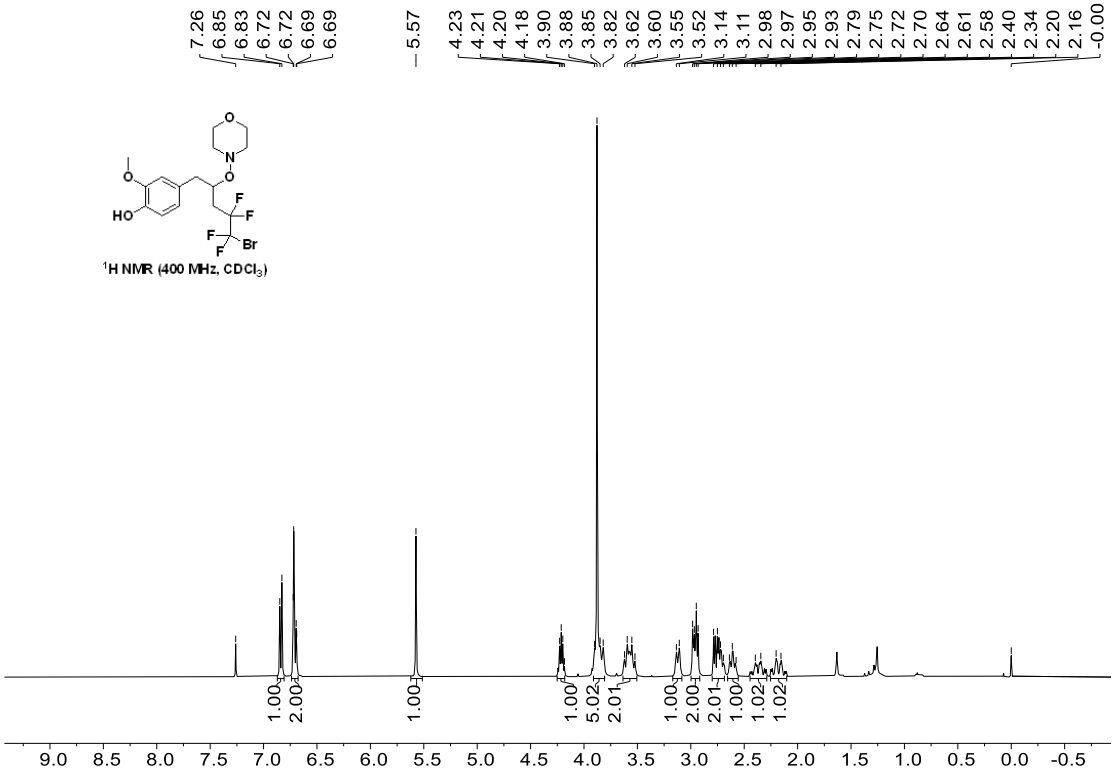
(*E*)-*N*,*N*-dibenzyl-*O*-(6-bromo-5,5,6,6-tetrafluoro-1-phenylhex-1-en-3-yl) hydroxylamine (4y)

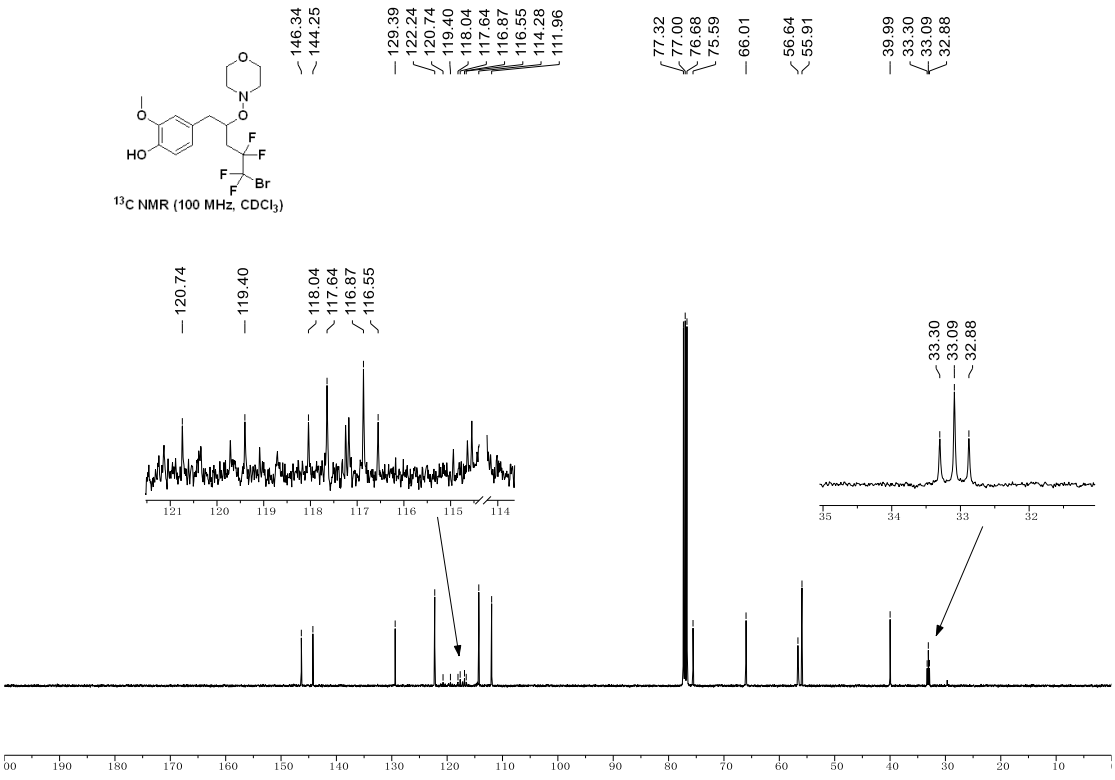


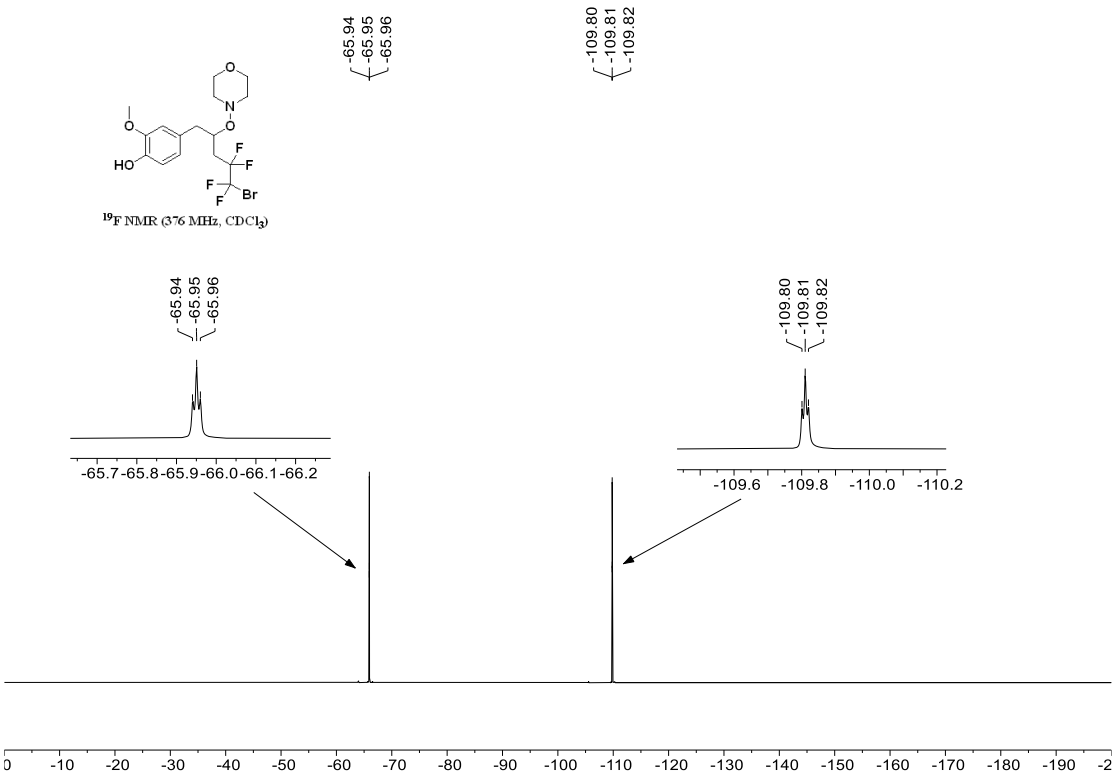


^{19}F NMR (376 MHz, $CDCl_3$)

4-(5-bromo-4,4,5,5-tetrafluoro-2-(morpholinooxy)pentyl)-2-methoxyphenol (4aa)

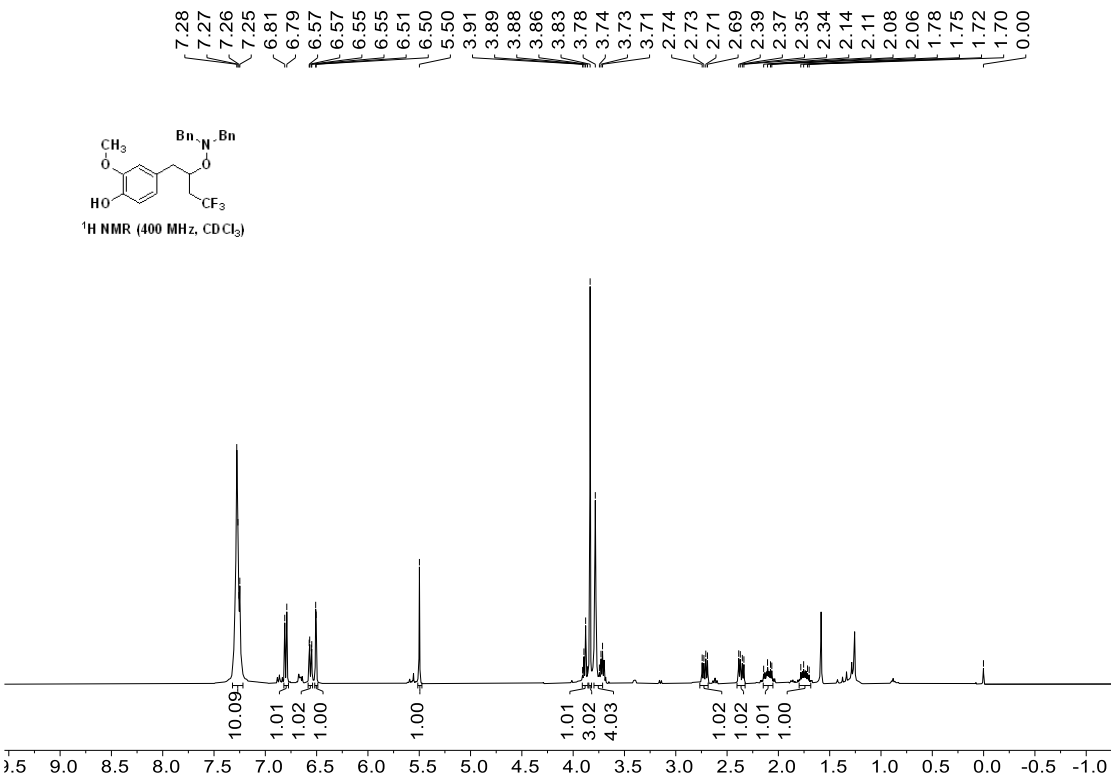


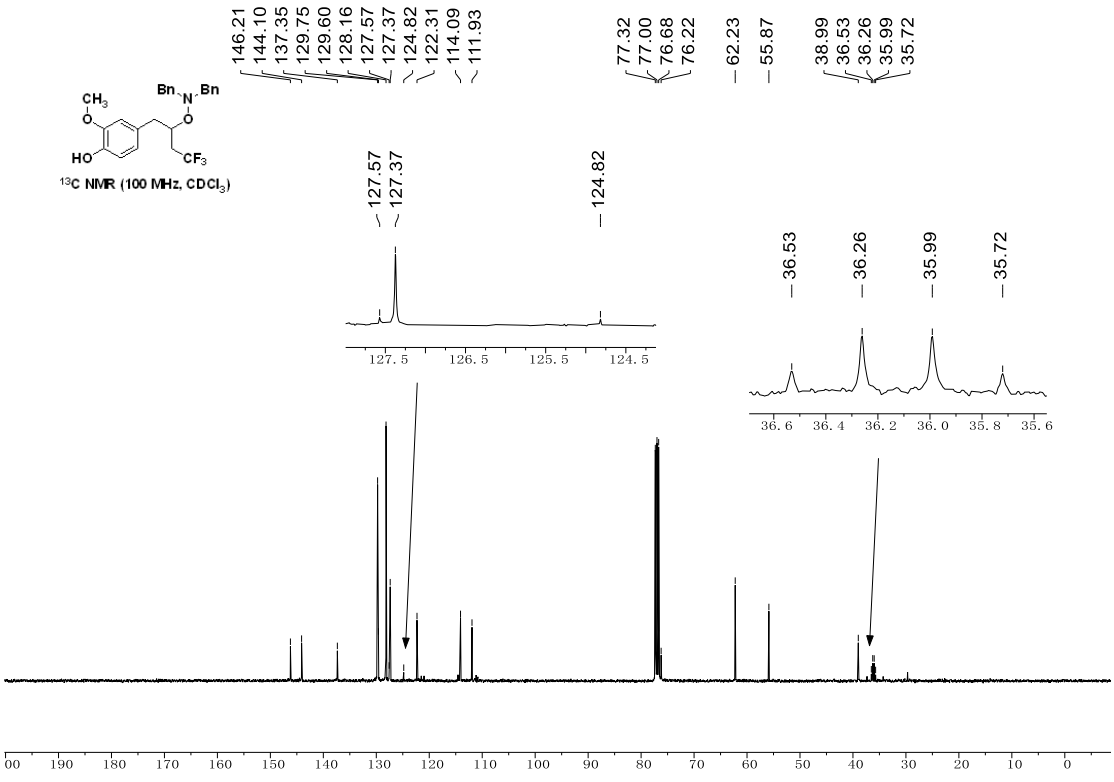


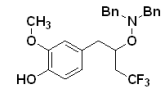


^{19}F NMR (376 MHz, $CDCl_3$)

4-(2-((dibenzylamino)oxy)-4,4,4-trifluorobutyl)-2-methoxyphenol (4ab)

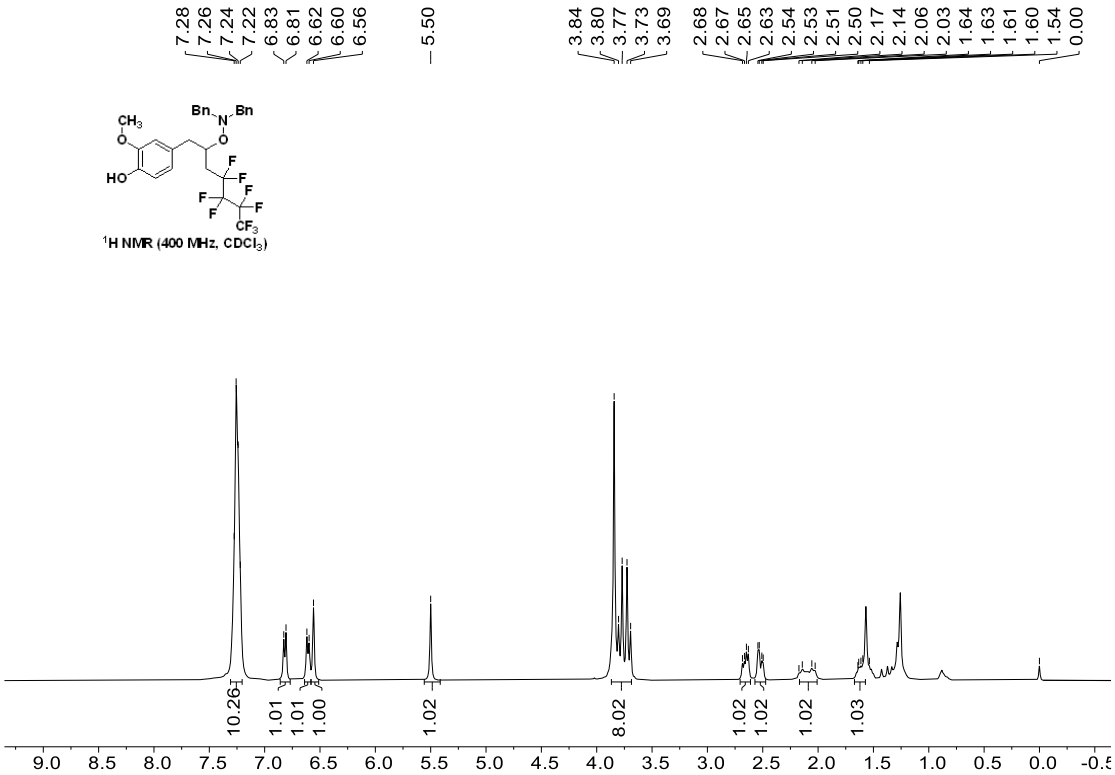


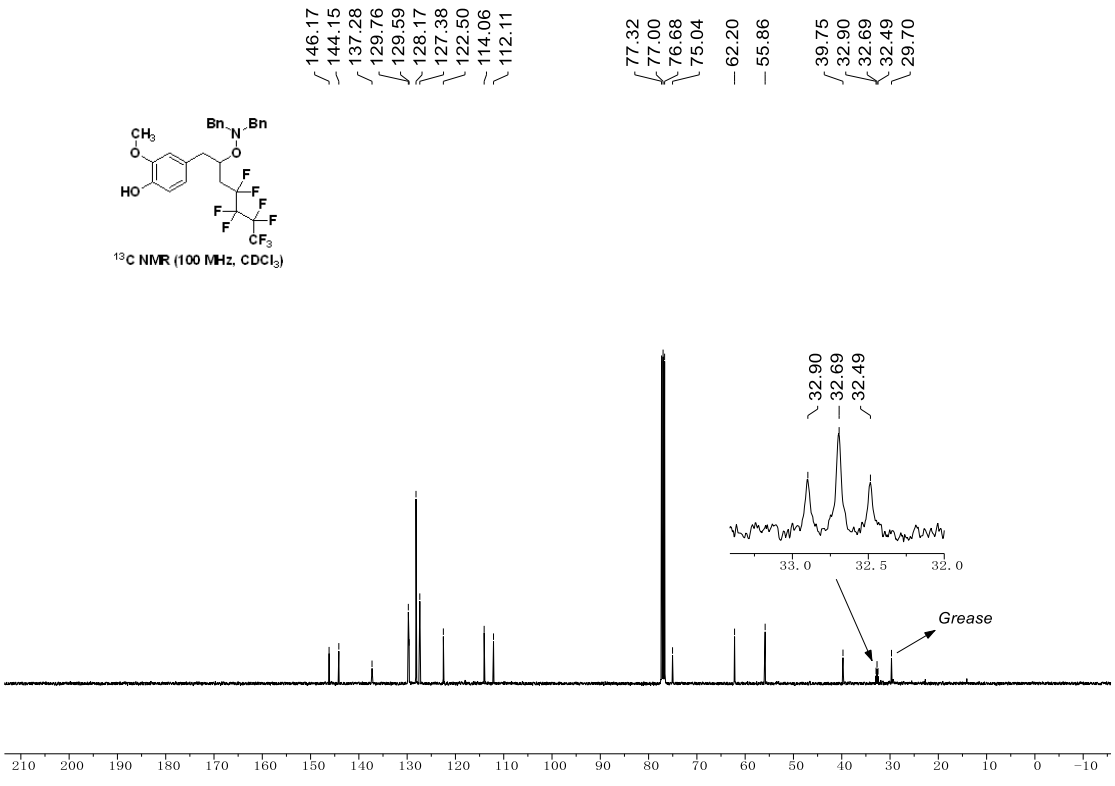


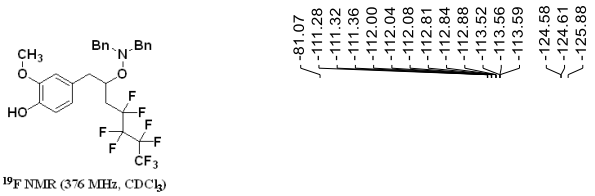


^{19}F NMR (376 MHz, $CDCl_3$)

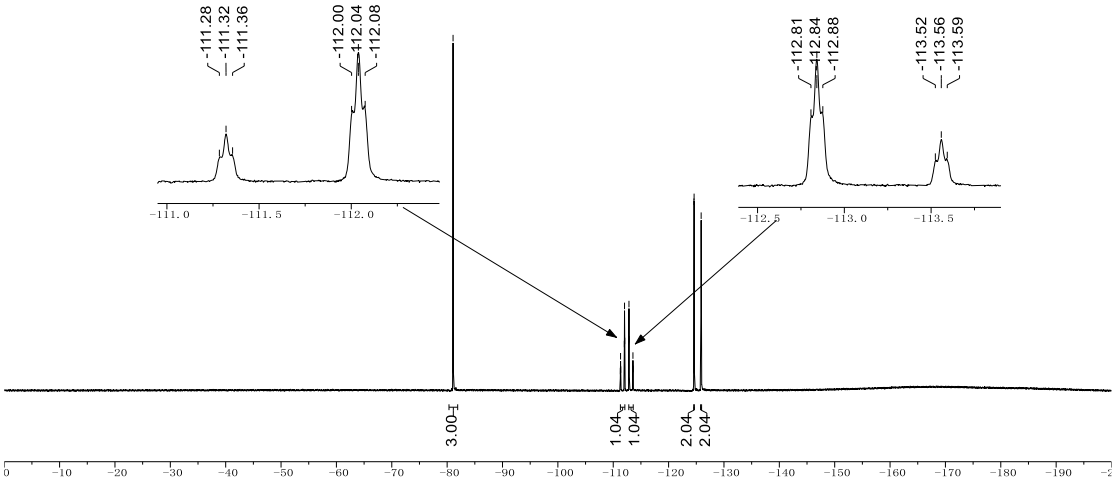
4-(2-((dibenzylamino)oxy)-4,4,5,5,6,6,7,7,7-nonafluoroheptyl)-2-methoxyphenol (4ac)



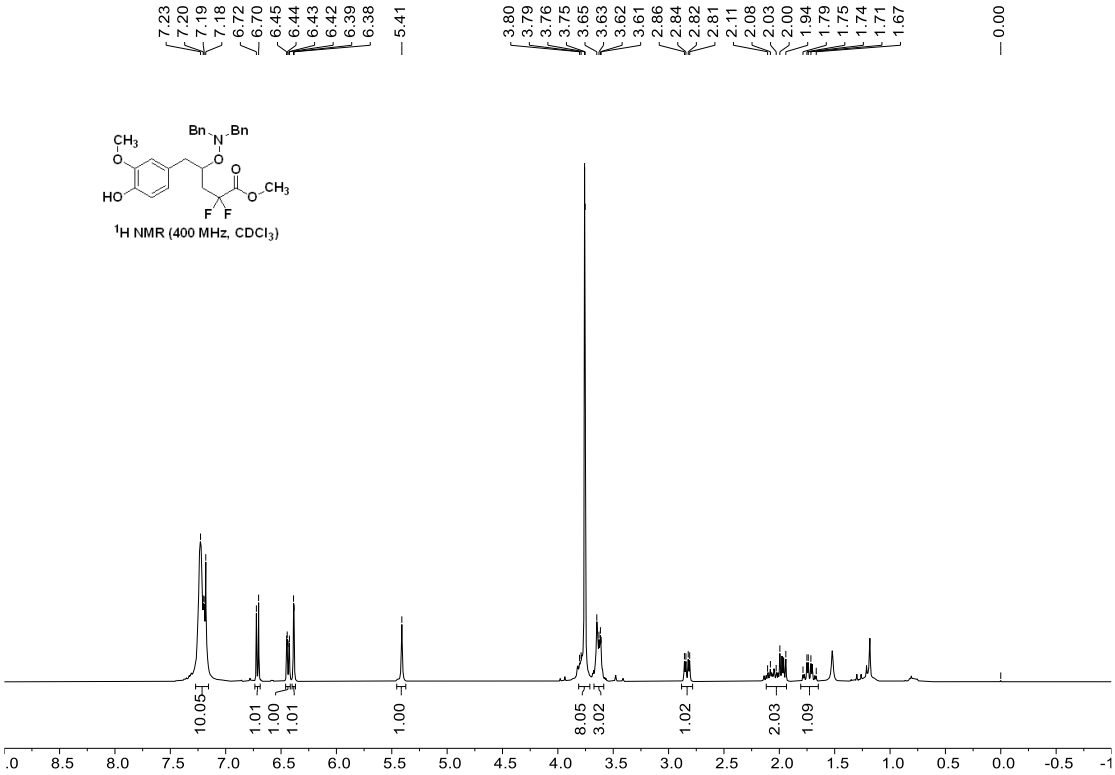


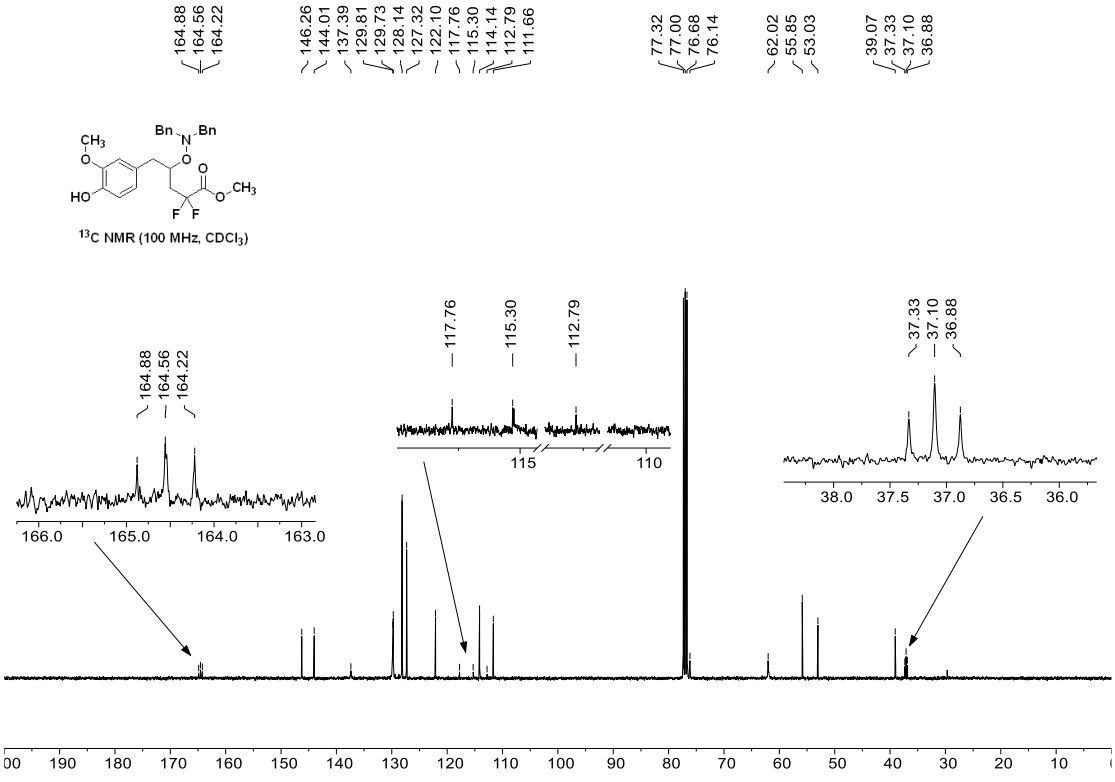


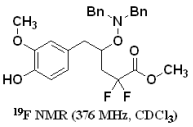
^{19}F NMR (376 MHz, CDCl$_3$)



Methyl 4-((dibenzylamino)oxy)-2,2-difluoro-5-(4-hydroxy-3-methoxyphenyl)pentanoate (4ad)

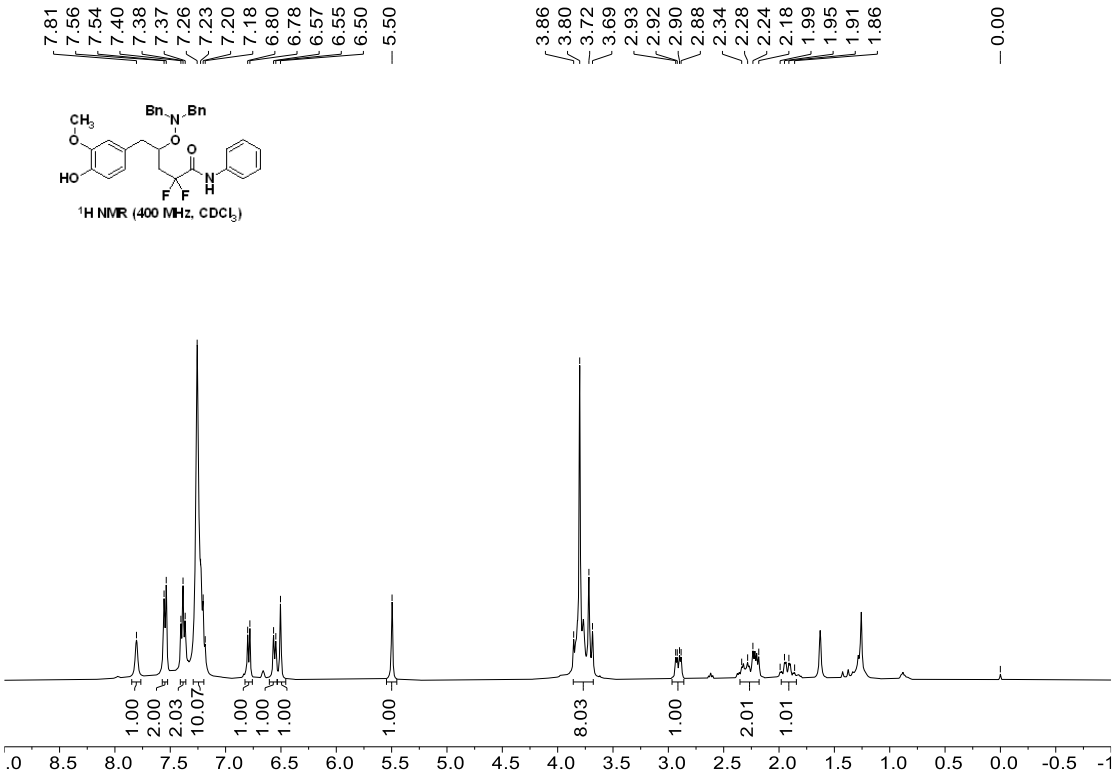


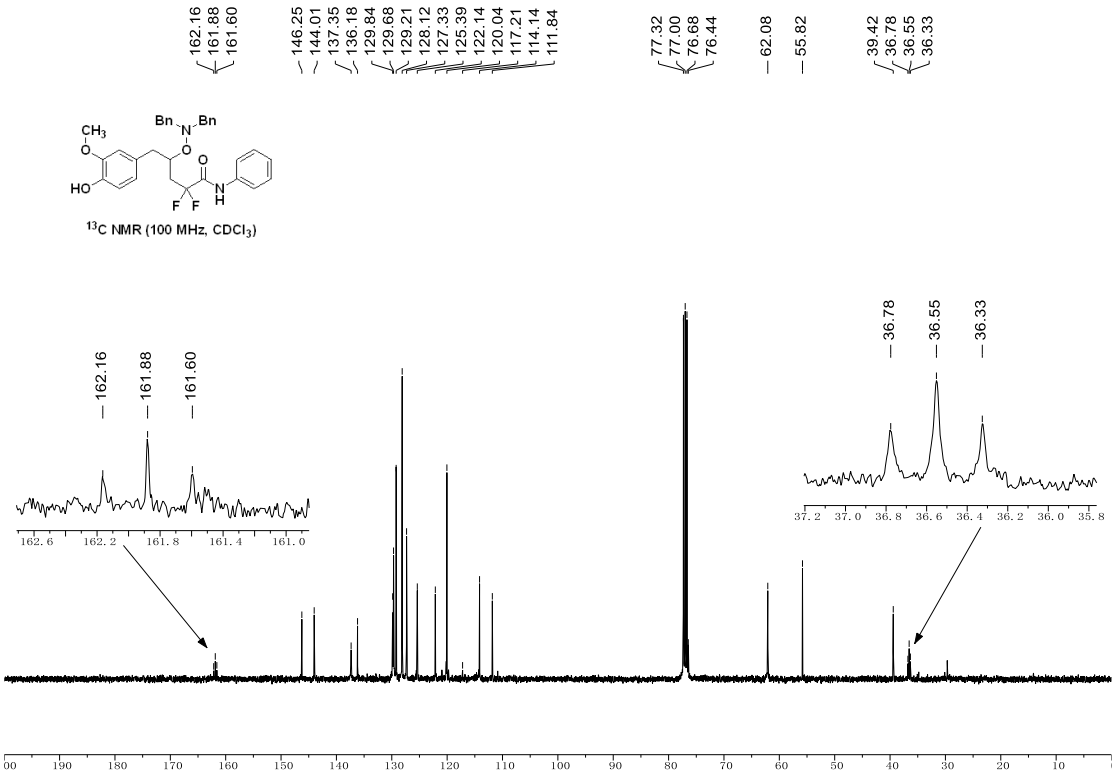


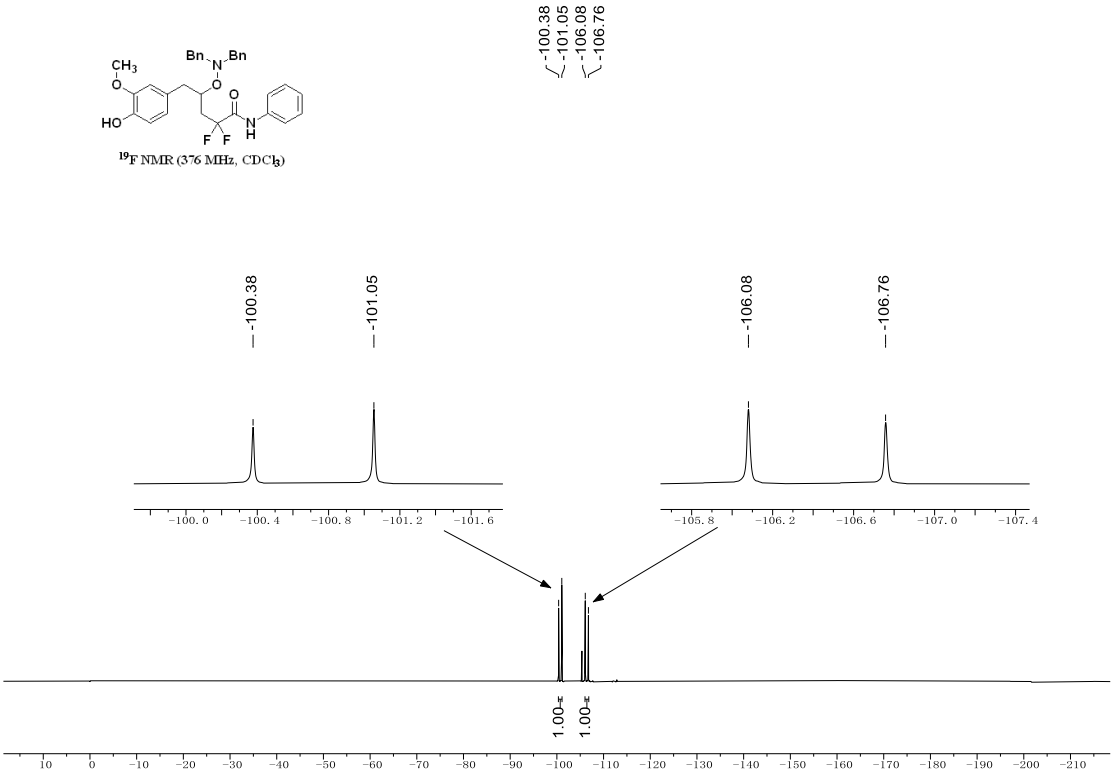


^{19}F NMR (376 MHz, $CDCl_3$)

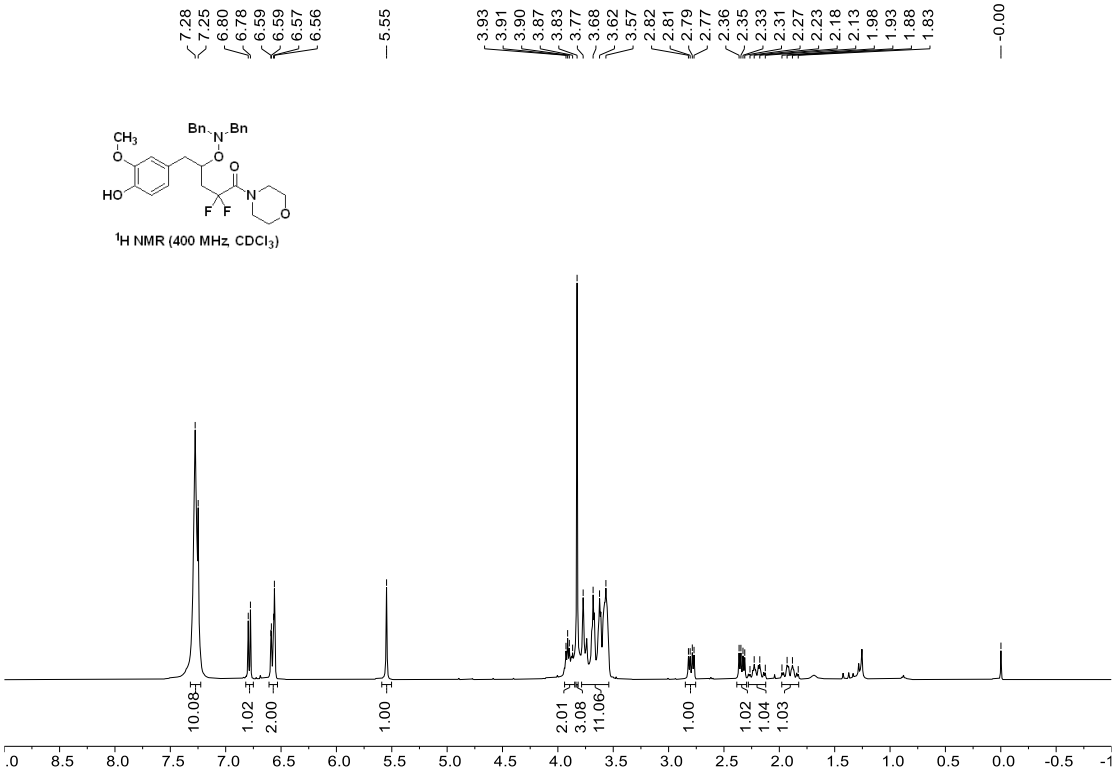
4-((dibenzylamino)oxy)-2,2-difluoro-5-(4-hydroxy-3-methoxyphenyl)-N-phenylpentanamide (4ae)

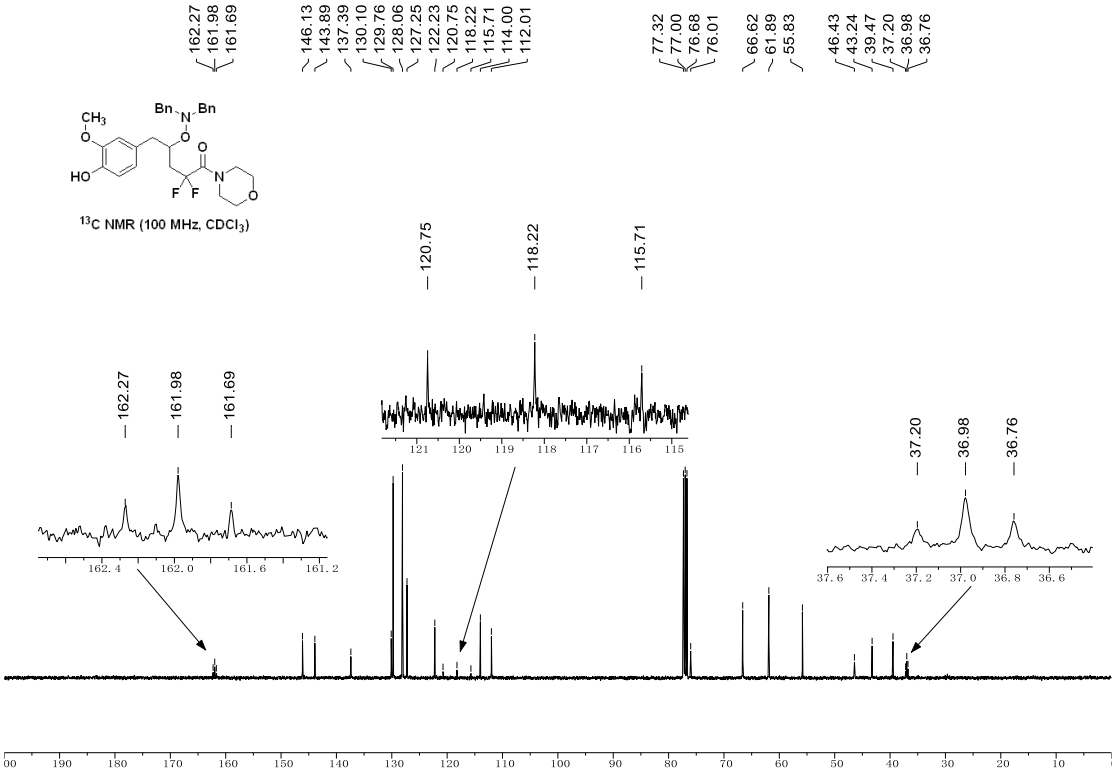


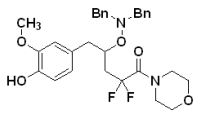



-100.38
-101.05
-106.08
-106.76
Bn
N
Bn
CH3
O
O
O
HO
N
H
F F
19F NMR (376 MHz, CDCl3)
-100.38
-101.05
-106.08
-106.76
-100.0
-100.4
-100.8
-101.2
-101.6
-105.8
-106.2
-106.6
-107.0
-107.4
1.00
1.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210

4-((dibenzylamino)oxy)-2,2-difluoro-5-(4-hydroxy-3-methoxyphenyl)-1-morpholinopentan-1-one (4af)

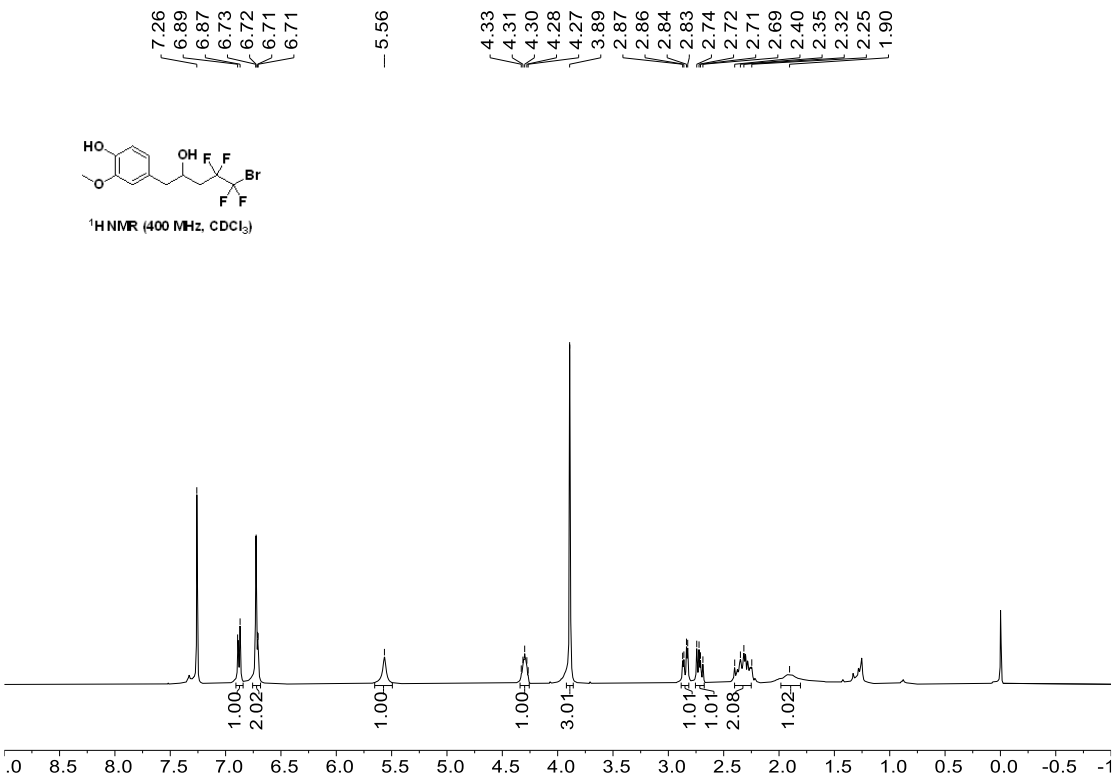


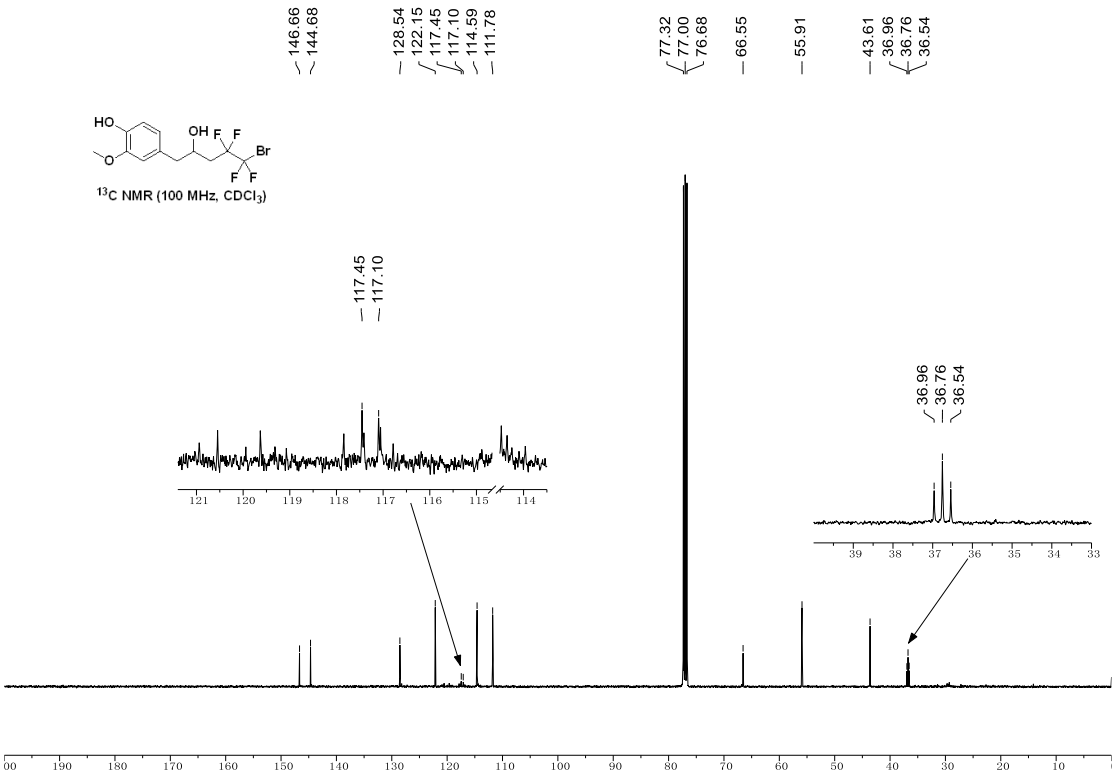


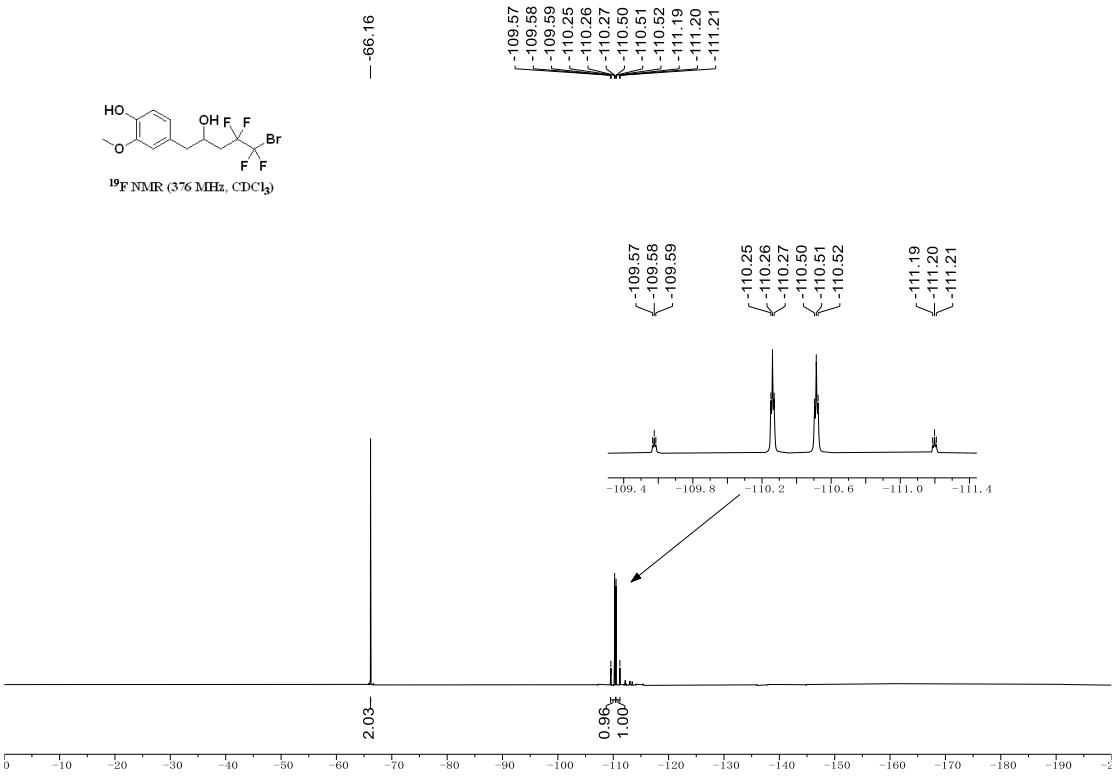


^{19}F NMR (376 MHz, $CDCl_3$)

4-(5-bromo-4,4,5,5-tetrafluoro-2-hydroxypentyl)-2-methoxyphenol (5)

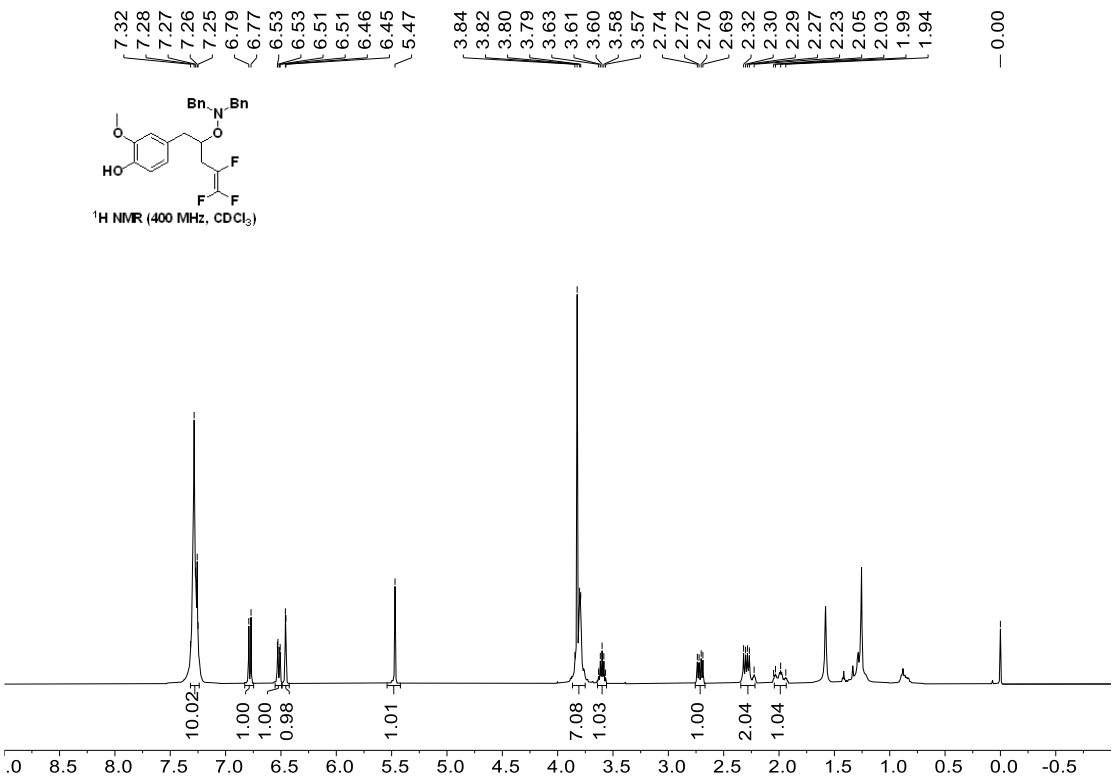


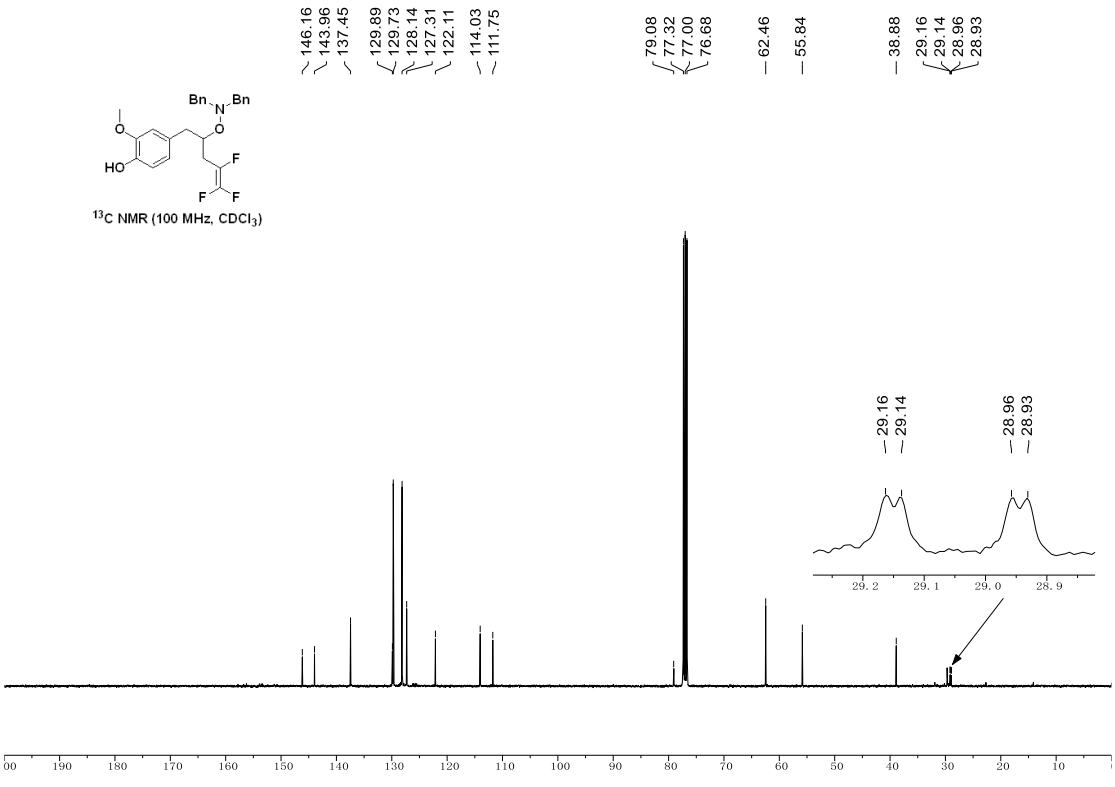


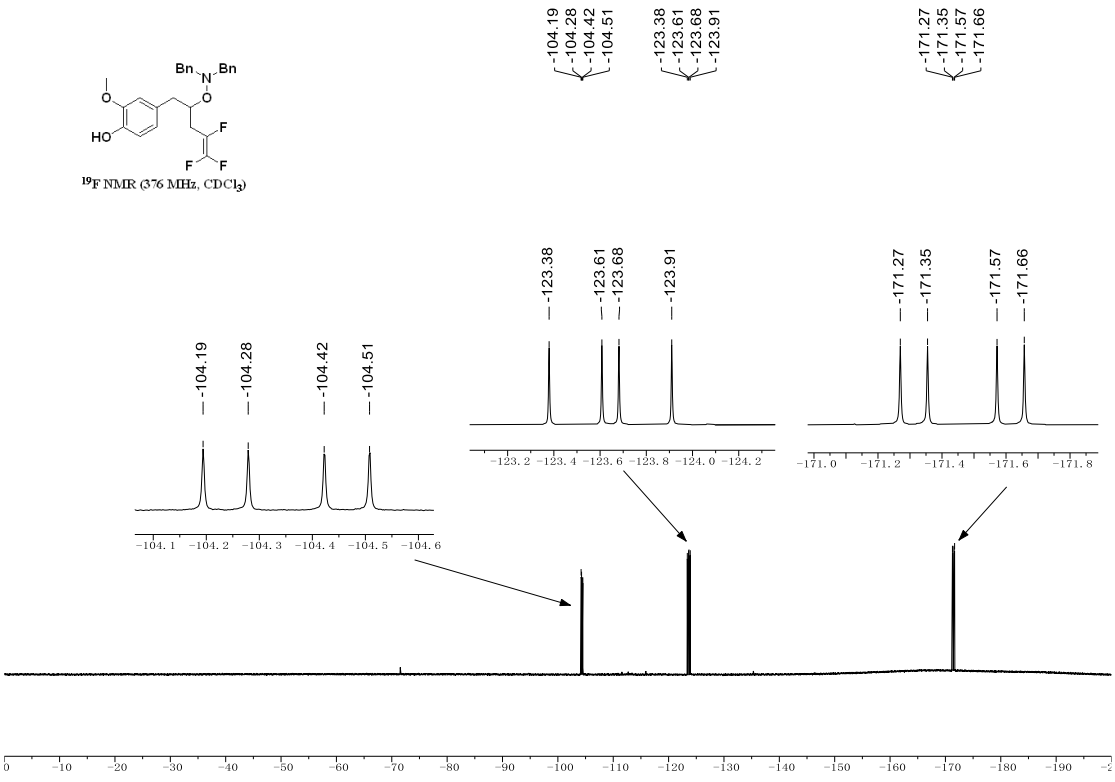


^{19}F NMR (376 MHz, $CDCl_3$)

4-(2-((dibenzylamino)oxy)-4,5,5-trifluoropent-4-en-1-yl)-2-methoxyphenol (6)

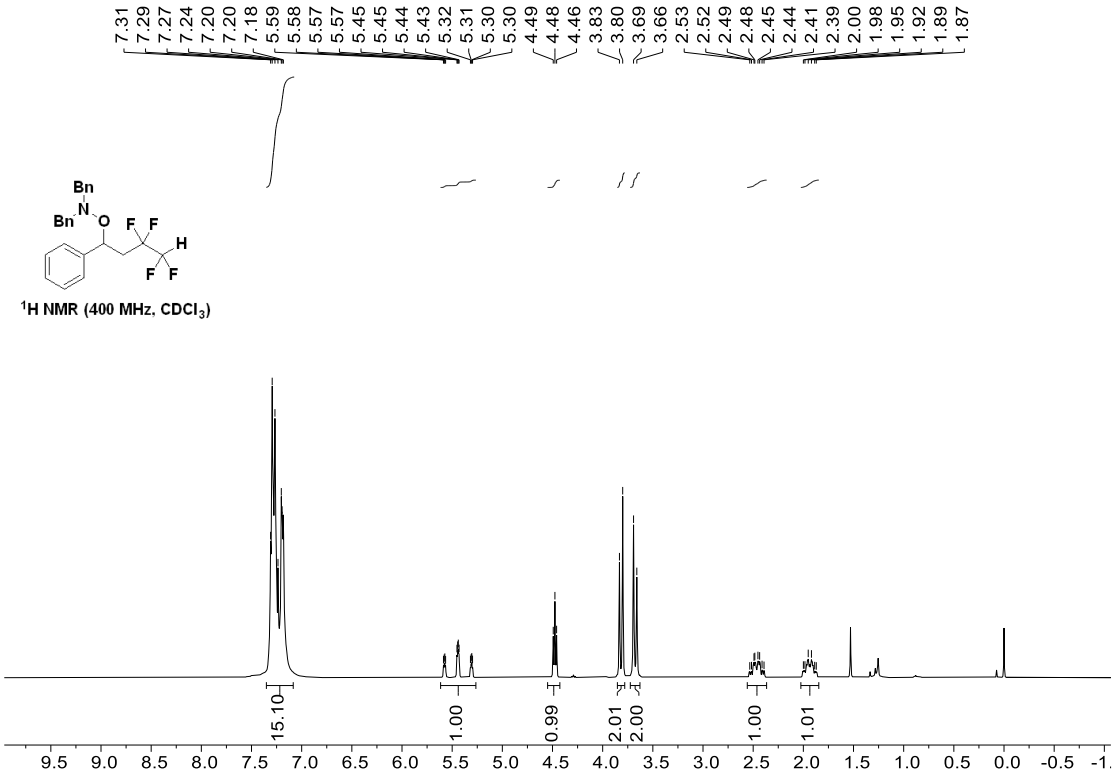




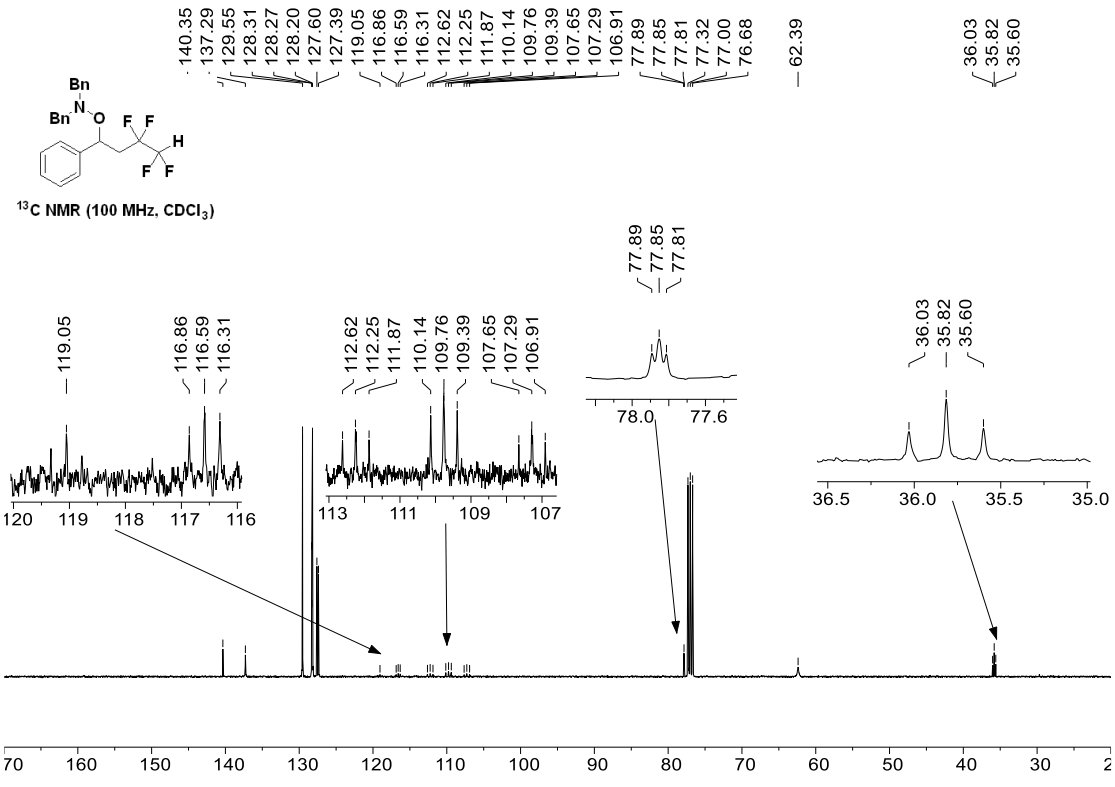


^{19}F NMR (376 MHz, $CDCl_3$)

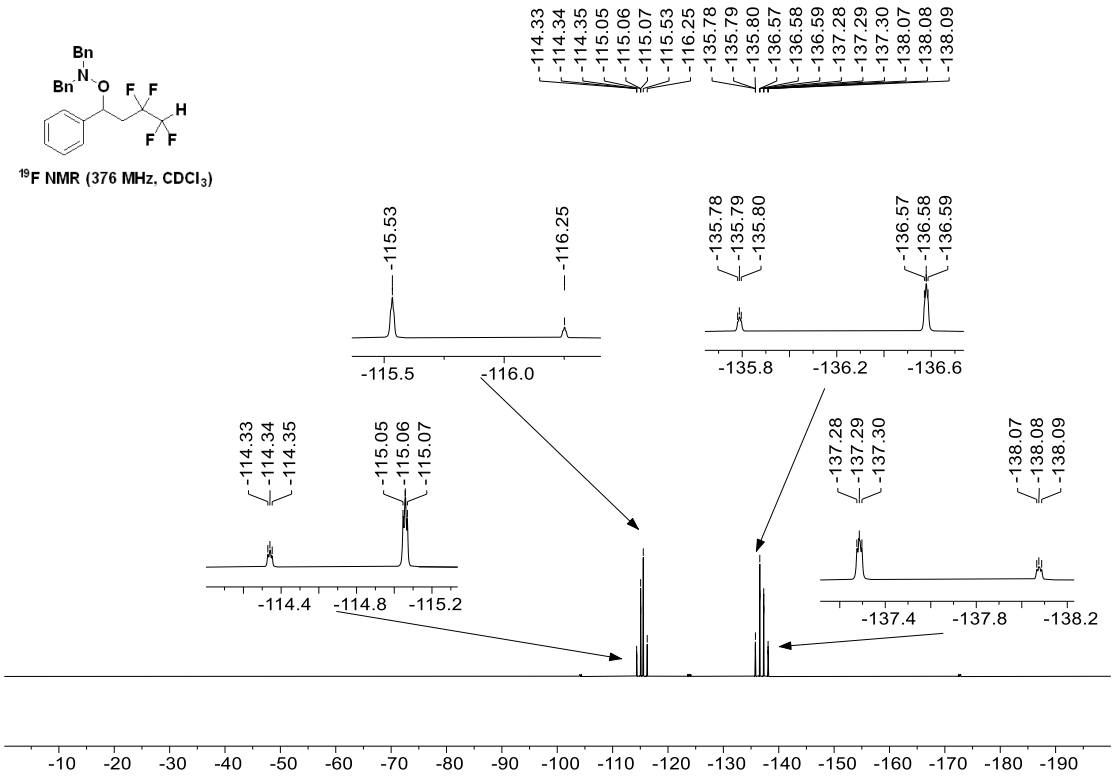
N,*N*-dibenzyl-*O*-(3,3,4,4-tetrafluoro-1-phenylbutyl)hydroxylamine (7)



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

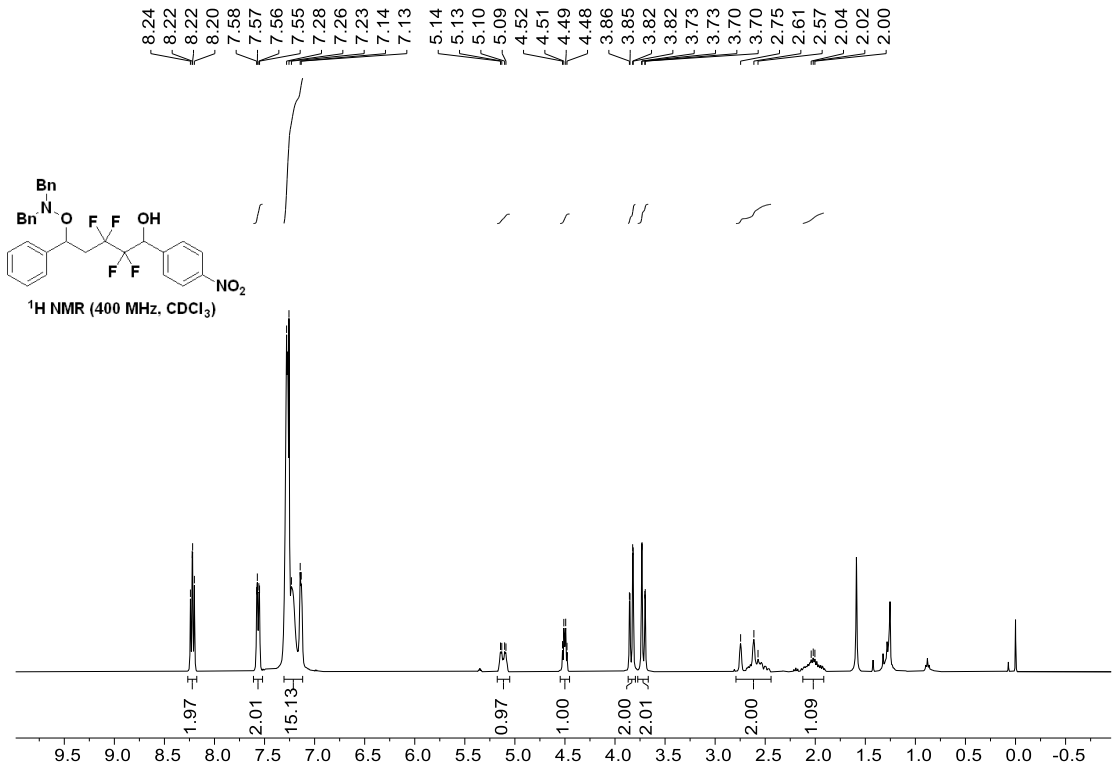


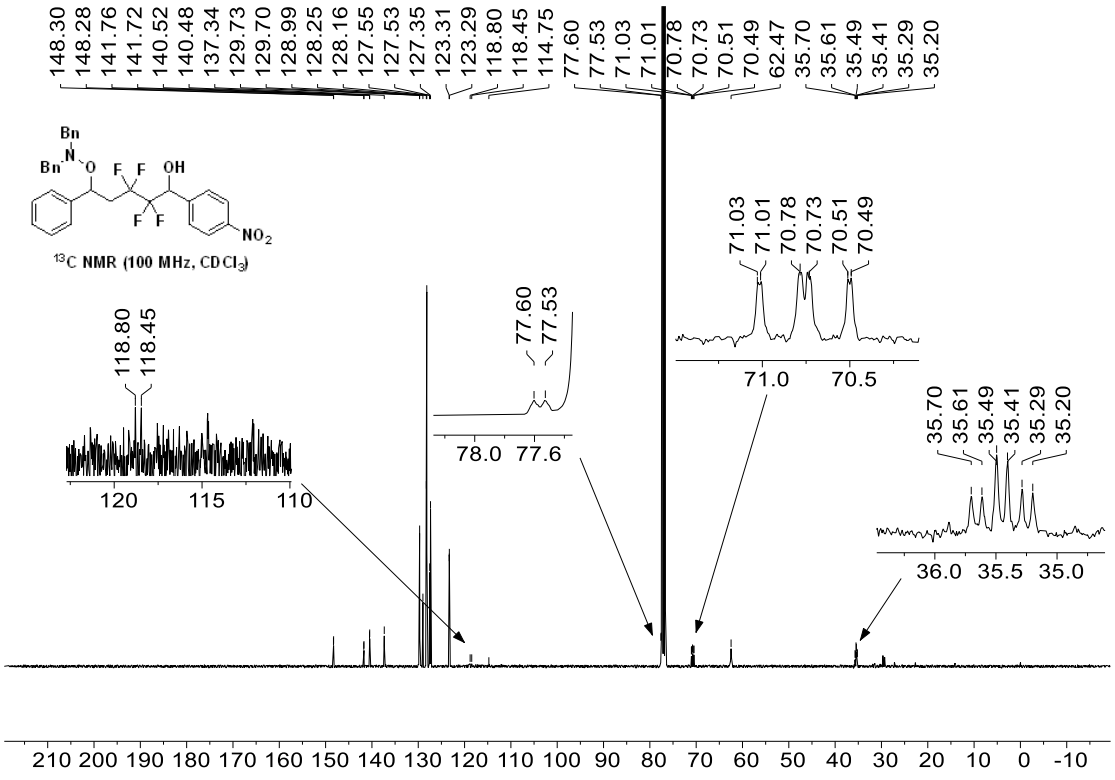
^{13}C NMR (100 MHz, $CDCl_3$)

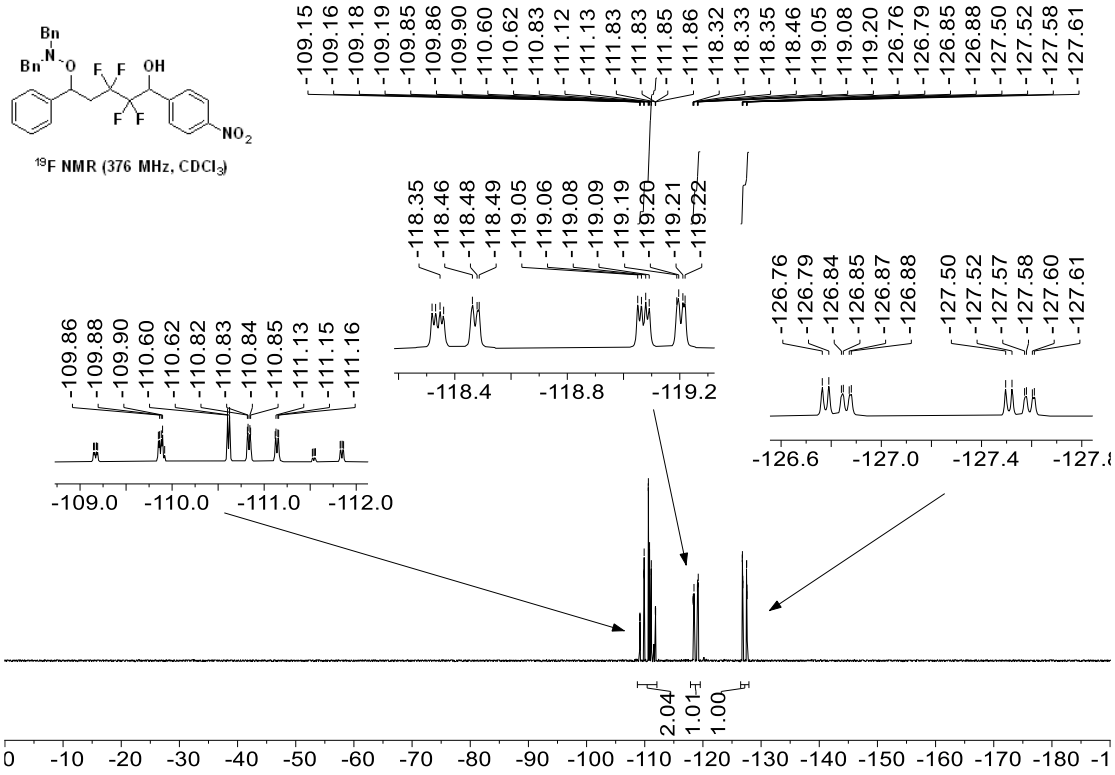


^{19}F NMR (376 MHz, $CDCl_3$)

5-((dibenzylamino)oxy)-2,2,3,3-tetrafluoro-1-(4-nitrophenyl)-5-phenylpentan-1-ol (8)






Bn
Bn
N
O
F F
OH
F F
NO2
19F NMR (376 MHz, CDCl3)
-109.15
-109.16
-109.18
-109.19
-109.85
-109.86
-109.90
-110.60
-110.62
-110.83
-111.12
-111.13
-111.83
-111.83
-111.85
-111.86
-118.32
-118.33
-118.35
-118.46
-119.05
-119.08
-119.20
-126.76
-126.79
-126.85
-126.88
-127.50
-127.52
-127.58
-127.61
-118.35
-118.46
-118.48
-118.49
-119.05
-119.06
-119.08
-119.09
-119.19
-119.20
-119.21
-119.22
-118.4
-118.8
-119.2
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-126.79
-126.84
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-127.57
-127.58
-127.60
-127.61
-126.6
-127.0
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-109.90
-110.60
-110.62
-110.82
-110.83
-110.84
-110.85
-111.13
-111.15
-111.16
-109.0
-110.0
-111.0
-112.0
2.04
1.01
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180

9. References

[1] M. Yang, W. Shao, L. Zuo, J. Wang, Y. Xu, G. Mao and G. J. Deng, Site-Selective Radical Trifluoromethylaminoxylation of Olefins for the Modular Synthesisof Diverse β-Trifluoromethyl Trisubstituted Hydroxylamines and Beyond. *Org. Lett.*, 2023, **25**, 2728-2732.

[2] Q. Wu, W. Zhang, W. Shao, Y. Pei and J. Wang, Partially Bio-Based and Fluorinated Polysiloxane with High Transparency and Low Dielectric Constant. *Eur. Polym. J.*, 2023, **194,** 112136.

[3] A. Budinská, J. Václavík, V. Matoušek and P. Beier, Nucleophilic Tetrafluoroethylation Employing in Situ Formed Organomagnesium Reagents. *Org. Lett.*, 2016, **18**, 5844−5847.

[4] J. Luo and J. Zhang, Donor–Acceptor Fluorophores for Visible-Light-Promoted Organic Synthesis: Photoredox/Ni Dual Catalytic $C(sp^3)$–$C(sp^2)$ Cross-Coupling. *ACS Catal.*, 2016, **6**, 873–877. (Correction: *ACS Catal.*, 2020, **10**, 14302–14303)