Supporting Information

for

Visible-Light-Induced Thiotrifluoromethylation of Terminal Alkenes with Sodium Triflinate and Benzenesulfonothioates

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1) General Information

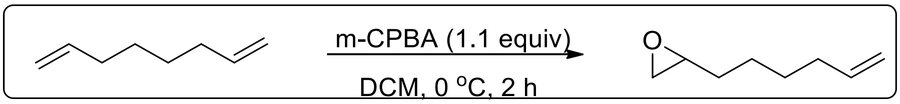
Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene, THF and dioxane were dried over Na with benzophenone-ketyl intermediate as an indicator. DCM, MeCN were distilled from CaH_2. DMF, DMSO were distilled from CaH_2 under reduced pressure. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ^{1}H NMR spectra were recorded on a Bruker AVIII-500 MHz spectrometers. Chemical shifts (in ppm) were referenced to $CDCl_3$ (δ = 7.26 ppm) as an internal standard. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm). ^{19}F NMR spectra were also obtained on the same NMR spectrometer. The following abbreviations are used to illuminate the diversities: δ, chemical shift; J, coupling constant; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High resolution mass spectra were recorded using a Waters Micromass GCT Premier. A Hitachi F-7000 fluorescence spectrophotometer with a 150 W Xe lamp as the light source and a Shimadzu UV-2600 UV-VIS spectrophotometer were used for the quantum yield measurement.

2) Preparation

Photoredox catalysts Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 **(1)** and Ir[dF(CF_3)ppy]$_2$(bpy)PF6 **(2)** were synthesized according to reported literatures.[1]

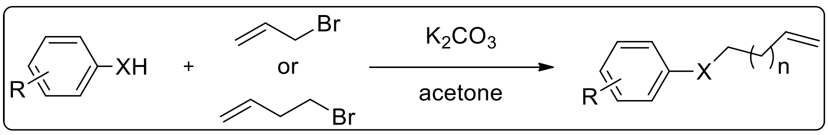
Olefins **1a-1f, 1s, 1u** were purchased from commercial source, and used without further purification. The other olefins are all known compounds and were synthesized according to the reported literatures. The general procedures to them were listed as bellow.

General Procedure for Preparation of 1g.[2]



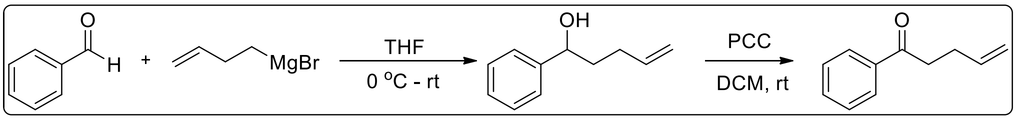
To a solution of 1,7- octadiene (5 mmol) in CH_2Cl_2 (20 mL) was added m-CPBA (5.5 mmol) The mixture was stirred at 0 ℃ for 2 h. The mixture was quenched with 1 M aqueous NaOH and then partitioned between brine and CH_2Cl_2. The organic extracts were dried (Na_2SO_4) and concentrated. The residue was then chromatographed to yield the mono epoxide **1g** (90% yield) as a clear oil.

General Procedure for Preparation of 1h-1r, 1t.[3]



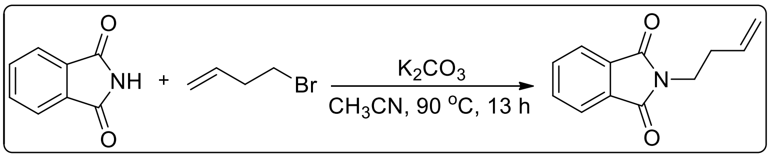
Allyl bromide (6.0 mmol) or 4-bromo-1-butene (6.0 mmol) was added to a suspension of the related phenol (5 mmol) or phenthiol derivate (5 mmol) and potassium carbonate (10 mmol) in acetone (15 mL). The reaction mixture was heated to 66 ℃ for 12 h, cooled to room temperature, diluted with ether, and quenched with water. The organic layer was separated, and the aqueous layer was extracted twice with ether. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The crude mixture was purified by column chromatography using petroleum ether and ethyl acetate as eluent.

General Procedure for Preparation of 1v.[4]



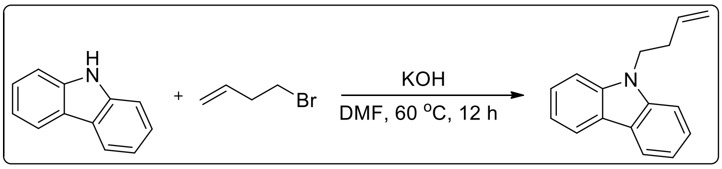
3-butenylmagnesium bromide (15.0 mmol) was added to a solution of benzaldehyde (10 mmol) in dry THF (30 mL) dropwise at 0 °C under N_2, the mixture was stirred at rt for 13 h. The mixture was poured into saturated aqueous NH_4Cl (100 mL). The aqueous layer was extracted with Et_2O (4 × 80 mL). The combined organic layers were dried over anhydrous $MgSO_4$, and the solvent was evaporated under vacuum and the resulting residue was purified by silica gel flash chromatography to provide the alcohol. To a solution of this alcohol (3.0 mmol) in CH_2Cl_2 (10 mL) was added PCC (3.9 mmol) in portions at 0 °C. The mixture was stirred at rt for 4 h, and then the solution was decanted from the black precipitate. The precipitate was extracted with Et_2O (4 × 10 mL). The combined organic solutions were concentrated *in vacuo*, and resulting residue was purified by silica gel flash chromatography to furnish **1v** as a yellow liquid.

The Preparation of 1w.[5]



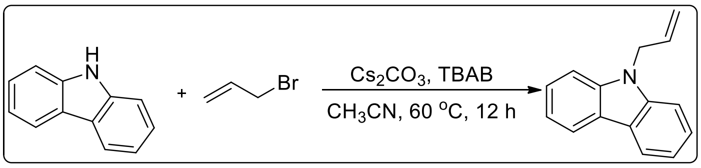
To a mixture of phthalimide (3.6 mmol) and potassium carbonate (9.0 mmol) in acetonitrile (10 mL), 4-bromo-1-butene (3.0 mmol) was added at room temperature. The resulting reaction mixture was stirred at 90 ℃ for 13 h. After the reaction was completed, the reaction mixture was filtered through a plug of Celite. Concentrated *in vacuo*, and the crude reaction mixture was purified by column chromatography on silica gel using petroleum ether and ethyl acetate (20:1) as eluent to afford a white solid.

The Preparation of 1x. [6]



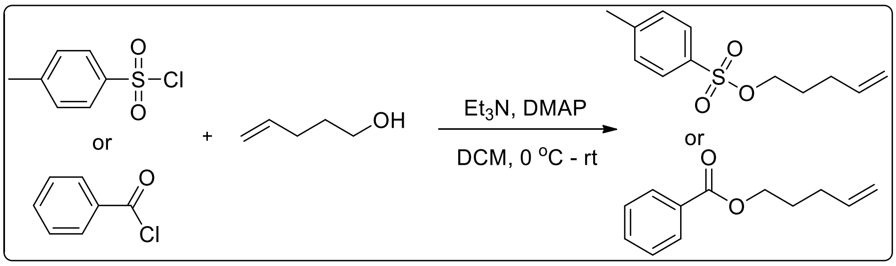
In a flame dried flask carbazole (3.0 mmol) was dissolved in a suspension of potassium hydroxide (3.0 mmol) and dry DMF (3.0 mL). To it 4-Bromo-1-butene (6.0 mmol) was added slowly and the reaction was stirred overnight at 60 ° C. The reaction was quenched with water, extracted with ethyl acetate and washed with brine. Concentrated *in vacuo*, and the crude reaction mixture was purified by column chromatography on silica gel using petroleum ether and ethyl acetate (40:1) as eluent to afford product.

The Preparation of 1y.[7]



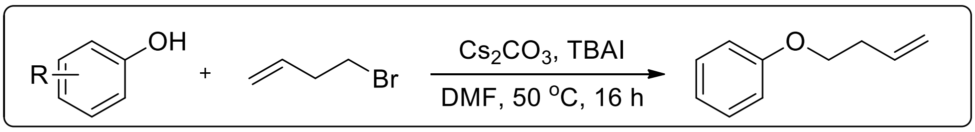
To a solution of carbazole (3.0 mmol) and Cs_2CO_3 (3.6 mmol) in 15 mL of dry acetonitrile was added allyl bromide (3.3 mmol) and TBAB (0.3 mmol). The reaction mixture was stirred at 60 °C for 12 h. After that, the inorganic salts were filtered off. Concentrated *in vacuo*, and the crude reaction mixture was purified by column chromatography on silica gel using petroleum ether and ethyl acetate (40:1) as eluent to afford product.

The Preparation of 1z, 1£[8]



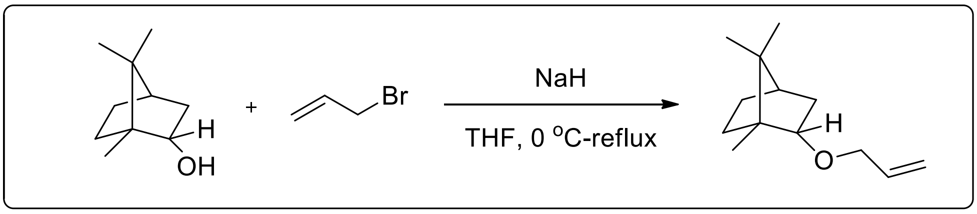
To a solution of hex-5-en-1-ol (5.0 mmol), Et_3N (10 mmol), DMAP (10% mol) in CH_2Cl_2 (15 mL) was added dropwise with the corresponding sulfochloride (15 mmol) or acyl chloride (15 mmol) dissolved in CH_2Cl_2 at 0 °C. The resulted mixture was vigorously stirred at room temperature. The reaction was monitored by TLC. The reaction mixture was treated with saturated aqueous $NaHCO_3$ (10 mL). After stirring at room temperature for 20 min, ethyl acetate (20 mL) was added. The organic layer was separated, and washed with water (3×100 mL). The combined organic extracts were washed with brine (50 mL), and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by chromatography on silica gel to give the product.

The Preparation of 1§ and 1&.[8]



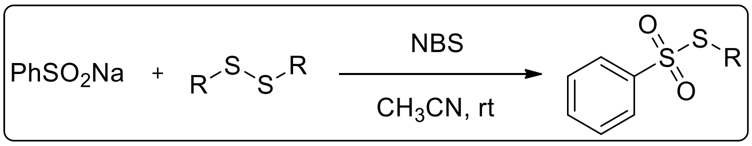
Aromatic alcohol (3.6 mmol) was dissolved in DMF (10 mL) and cessium carbonate (3.9 mmol) was added followed by the addition of 4-bromo-1-butene (3 mmol) and tetrabutylammonium iodide (0.3 mmol). The mixture is heated to 50 °C for 16 h. The reaction was then splitted between water and *tert*-butyl methyl ether, and the organic layer was washed with dilute sodium hydroxide solution, water, and brine, dried over sodium sulfate, and concentrated *in vacuo*. The resulting residue was purified by silica gel flash chromatography to provide the products.

The Preparation of 1ß[9]

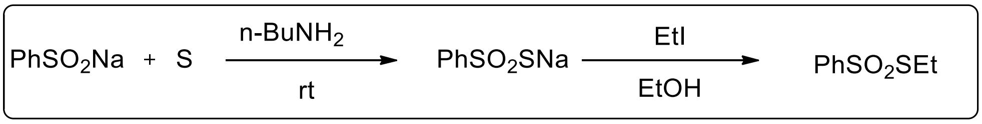


The (-)-borneol (1 equiv) was dissolved in dry THF under an atmosphere of nitrogen at 0 °C. To this solution was added sodium hydride (1.3 equiv) and was allowed to stir for 10 minutes at 0 °C. After adding allyl bromide (1.3 equiv), the solution was then allowed to stir at room temperature for 30 minutes and reflux overnight. The reaction was quenched by the addition of sat. NH_4Cl. The mixture was then extracted with diethyl ether three times and the organic phase was washed with water, brine and dried over $NaSO_4$. The solvent was removed by rotary evaporation and purification was performed by flash chromatography.

General Procedure for Preparation of Benzenesulfonothioates.[10]

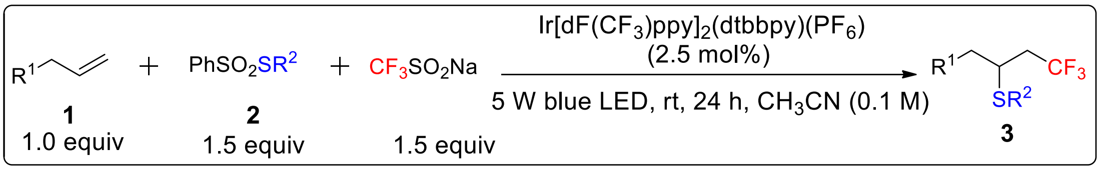


A mixture of sodium sulfinate (4.0 mmol), disulfide (1.0 mmol) and *N*-bromosuccinimide (2.0 mmol) in acetonitrile (15.0 mL) was stirred at room temperature for 15 h. Subsequently, the solvent was evaporated, the residue was redisolved in EtOAc, washed with water and extracted with EtOAc (3 x 15 mL). The combined organic phases were dried over $MgSO_4$. After filtration and concentration, the residue was purified by flash chromatography.



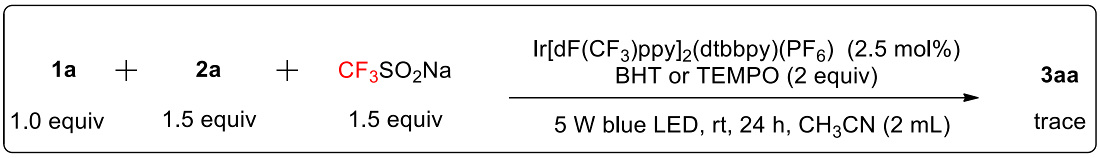
A mixture of $PhSO_2Na$ (1.0 equiv) and S (1.0 equiv) in *n*-$BuNH_2$ (1.0 mmol/mL) was stirred at room temperature for 0.5 h. After removal of the solvent under reduced pressure, the residue was washed by Et_2O to obtain a white solid $PhSO_2SNa$. Then $PhSO_2SNa$ was dissolved in EtOH (1.0 mmol/mL), then C_2H_5I (2.0 equiv) was added to the solution. The reaction mixture was stirred at 40-45 °C for 24 h. After removal of the solvent under reduced pressure, the reaction mixture was poured on a solution of $Na_2S_2O_3$ and CH_2Cl_2. The precipitate was filtered and dried by anhydrous Na_2SO_4, the residue was purified through column chromatography afforded the desired product as a yellow oil.

3) Procedure for Visible-Light-Induced Thiotrifluoromethylation of Terminal Alkenes.

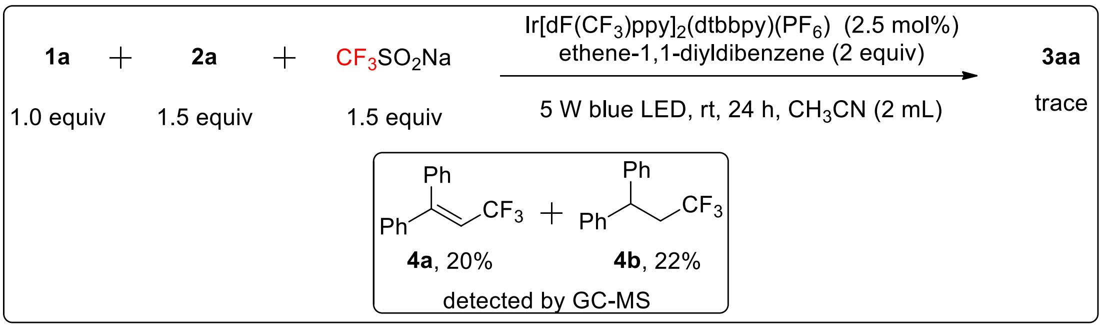


To a flame dried transparent Schlenk tube equipped with a stirring bar was added benzenesulfonothioates (0.3 mmol), Ir[dF(CF_3)ppy]$_2$(dtbpy)PF_6 (2.5 mol%), and CF_3SO_2Na (0.3 mmol). Then olefins (0.2 mmol) and dry CH_3CN (2 mL) was added under N_2. The reaction mixture was stirred under the irradiation of a 5 W blue LEDs at room temperature for 18 h. After that, the mixture was quenched with water and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel.

4) Experiments on Mechanism



To a flame dried transparent Schlenk tube equipped with a stirring bar was added **2a** (0.3 mmol), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.5 mol%), CF_3SO_2Na (0.3 mmol) and BHT or TEMPO (2 equiv). Then olefin **1a** (0.2 mmol) and dry CH_3CN (2 mL) was added under N_2. The reaction mixture was stirred under the irradiation of a 5 W blue LEDs at room temperature for 18 h. After that, the mixture was diluted with ethyl acetate. The amount of **3aa** was detected by TLC and GC-MS.



To a flame dried transparent Schlenk tube equipped with a stirring bar was added **2a** (0.3 mmol), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.5 mol%), CF_3SO_2Na (0.3 mmol) and ethene-1,1-diyldibenzene (2 equiv). Then olefin **1a** (0.2 mmol) and dry CH_3CN (2 mL) was added under N_2. The reaction mixture was stirred under the irradiation of a 5 W blue LEDs at room temperature for 18 h. After that, the mixture was diluted with ethyl acetate. The amount of **4a**, **4b** and **3aa** was detected by

TLC and GC-MS.

1a (1.0 equiv) + PhSSPh (1.5 equiv) + CF_3SO_2Na (1.5 equiv) —[Ir[dF(CF_3)ppy]$_2$(dtbbpy)(PF_6) (2.5 mol%); 5 W blue LED, rt, 24 h, CH_3CN (2 mL)]→ **3aa** trace

To a flame dried transparent Schlenk tube equipped with a stirring bar was added **2a** (0.3 mmol), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.5 mol%) and 1, 2-diphenyldisulfane (0.3 mmol). Then olefin **1a** (0.2 mmol) and dry CH_3CN (2 mL) was added under N_2. The reaction mixture was stirred under the irradiation of a 5 W blue LEDs at room temperature for 18 h. After that, the mixture was diluted with ethyl acetate. The amount of **3aa** was detected by TLC and GC-MS.

Quantum yield measurement

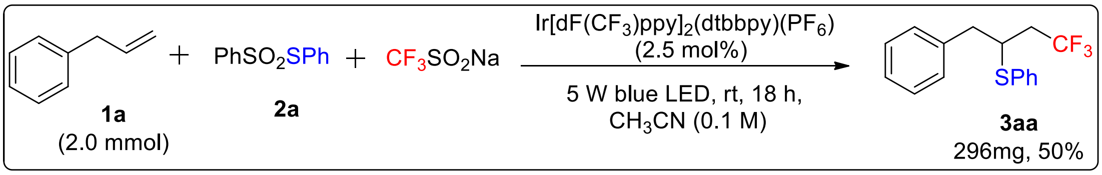
The quantum yield was measured according to a published procedure.[11] A Hitachi F-7000 fluorescence spectrophotometer with 150 W Xe lamp was used as the light source with 420 ±5 nm bandpass filter. Photo flux of this spectrophotometer was determined as 8.54 × 10^{-10} E/S using standard ferrioxalate actinometry.

A cuvette was charged with **2a** (0.3 mmol), Ir[dF(CF_3)ppy]$_2$(dtbpy)PF_6 (2.5 mol%), and CF_3SO_2Na (0.3 mmol). Then olefins **1a** (0.2 mmol) and dry CH_3CN (2 mL) was added under the blowing of N_2 and the cuvette was capped with a PTFE stopper. The sample was stirred and irradiated at 420 ±5 nm for 14400 s (4 h). After irradiation, the mixture was diluted with DCM and added with dodecane (0.2 mmol, 45μL). The amount of **3aa** was measured using GC analysis with dodecane as the internal standard. Finally, the amount of **3aa** was measured as 1.75 × 10^{-6} mol.

$$\Phi = \frac{\text{mol product}}{\text{flux} \cdot \text{t} \cdot \text{f}} = \frac{1.75 \times 10^{-6}\ \text{mol}}{8.54 \times 10^{-10}\ \text{mol s}^{-1} \times 14400\ \text{s} \times 1} = 0.142$$

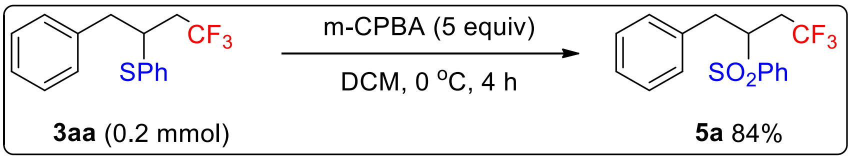
5) Synthetic Utility

Scaled-up Reaction



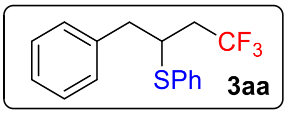
To a flame dried transparent Schlenk tube equipped with a stirring bar was added **2a** (3 mmol), Ir[dF(CF_3)ppy]$_2$(dtbpy)PF_6 (2.5 mol%), and CF_3SO_2Na (3 mmol). Then allylbenzene **1a** (2 mmol) and dry CH_3CN (20 mL) was added under N_2. The reaction mixture was stirred under the irradiation of a 10 W blue LEDs at room temperature for 18 h. After that, the mixture was quenched with water and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated *in vacuo*. The crude product was purified by chromatography on silica gel to give **3aa** in 50% yield.

Procedure for Oxidizing 3aa into Its Sulphone Derivative 5a

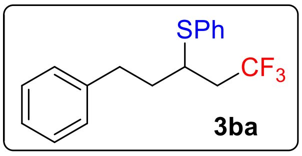


To a solution of **3aa** (0.2 mmol) in dry CH_2Cl_2 (3 mL) was added m-CPBA (5 equiv) at 0 °C, the solution was stirred for 4 h at this temperature. After that, the mixture was diluted with DCM (5 mL) and washed with sat. $NaHCO_3$ (3 x 5 mL). The organic layers were combined and concentrated under vacuo. The residue was purified by flash column chromatography on silica gel sing petroleum ether and ethyl acetate (5:1) as eluent to afford **5a** as colorless oil.

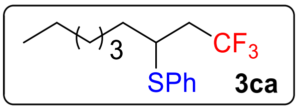
6) Characterization Data of Products



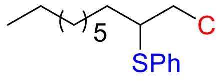
Phenyl(4,4,4-trifluoro-1-phenylbutan-2-yl)sulfane. Colorless oil (45 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 2H), 7.37 – 7.27 (m, 6H), 7.25 – 7.17 (m, 2H), 3.68 – 3.53 (m, 1H), 3.13 – 3.02 (m, 1H), 2.95 (ddd, J = 14.1, 7.5, 2.7 Hz, 1H), 2.59 – 2.23 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.73, 133.52, 132.76, 129.40, 129.21, 128.56, 127.79, 126.95, 126.15 (q, J = 278.5 Hz), 43.73 (d, J = 2.2 Hz), 40.61, 38.10 (q, J = 27.7 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.03. HRMS (EI) calcd for: $C_{16}H_{15}F_3S$ 296.0847; found: 296.0841.



Phenyl(1,1,1-trifluoro-5-phenylpentan-3-yl)sulfane. Colorless oil (43 mg, 69%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.37 – 7.28 (m, 5H), 7.25 – 7.16 (m, 3H), 3.34 (tt, J = 8.8, 4.4 Hz, 1H), 2.96 (ddd, J = 14.7, 9.9, 5.1 Hz, 1H), 2.85 (ddd, J = 13.8, 9.7, 6.7 Hz, 1H), 2.58 – 2.42 (m, 1H), 2.42 – 2.27 (m, 1H), 2.23 – 2.02 (m, 1H), 2.02 – 1.78 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.94, 133.20, 132.84, 129.23, 128.53, 128.47, 127.83, 126.17, 126.00 (q, J = 278.5 Hz), 41.79 (d, J = 2.3 Hz), 39.21 (q, J = 27.5 Hz) 35.33, 32.58; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.28. HRMS (EI) calcd for: $C_{17}H_{17}F_3S$ 310.1003; found: 310.1011.

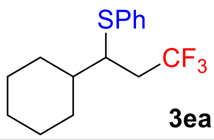


Phenyl(1,1,1-trifluorononan-3-yl)sulfane. Colorless oil (45 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (dd, J = 8.3, 1.3 Hz, 2H), 7.36 – 7.30 (m, 2H), 7.30 – 7.26 (m, 1H), 3.45 – 3.20 (m, 1H), 2.37 (dddd, J = 15.3, 13.4, 10.9, 6.6 Hz, 2H), 1.88 – 1.71 (m, 1H), 1.68 – 1.54 (m, 2H), 1.53 – 1.41 (m, 1H), 1.36 – 1.27 (m, 6H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.65, 132.65, 129.13, 127.61, 126.10 (q, J = 278.5 Hz), 42.41 (d, J = 2.3 Hz), 39.13 (q, J = 27.4 Hz), 33.78, 31.64, 28.94, 26.31, 22.59, 14.07; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.45. HRMS (EI) calcd for: $C_{15}H_{21}F_3S$ 290.1316; found: 290.1314.



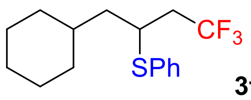
3da

Phenyl(1,1,1-trifluoroundecan-3-yl)sulfane. Pale yellow oil (53 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.35 (dtd, J = 5.2, 3.5, 1.3 Hz, 2H), 7.33 – 7.29 (m, 1H), 3.48 – 3.23 (m, 1H), 2.58 – 2.26 (m, 2H), 1.82 (ddd, J = 15.8, 10.4, 5.6 Hz, 1H), 1.63 (ddd, J = 15.0, 8.4, 4.3 Hz, 2H), 1.52 (dd, J = 10.0, 6.6 Hz, 1H), 1.33 (dd, J = 13.9, 4.9 Hz, 10H), 0.92 (t, J = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.66, 132.65, 129.13, 127.61, 126.11 (q, J = 278.5 Hz), 42.41 (d, J = 2.3 Hz), 39.13 (q, J = 27.4 Hz), 33.78, 31.87, 29.41, 29.28, 29.24, 26.35, 22.68, 14.12; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.44. HRMS (EI) calcd for: $C_{17}H_{25}F_3S$ 318.1629; found: 318.1631.



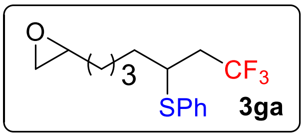
3ea

(1-cyclohexyl-3,3,3-trifluoropropyl)(phenyl)sulfane. Yellow oil (42 mg, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.38 – 7.33 (m, 2H), 7.33 – 7.29 (m, 1H), 3.42 (tt, J = 8.8, 4.3 Hz, 1H), 2.56 – 2.40 (m, 1H), 2.36 – 2.19 (m, 1H), 1.86 (d, J = 12.8 Hz, 1H), 1.77 – 1.66 (m, 5H), 1.48 (ddd, J = 14.1, 10.1, 3.9 Hz, 1H), 1.29 (dd, J = 14.3, 10.9 Hz, 1H), 1.23 – 1.12 (m, 1H), 0.93 (ddt, J = 15.9, 12.7, 6.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.52, 132.63, 129.14, 127.60, 126.50 (q, J = 278.5 Hz), 41.87, 40.06 (q, J = 27.0 Hz), 39.59 (d, J = 2.3 Hz), 34.79, 33.85, 32.16, 26.51, 26.24, 26.02; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.19. HRMS (EI) calcd for: $C_{15}H_{19}F_3S$ 288.1160; found: 288.1153.

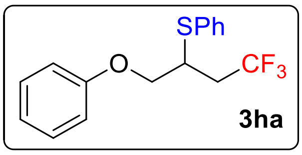


3fa

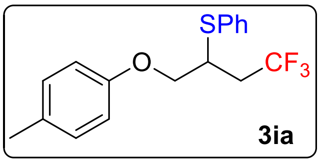
(1-cyclohexyl-4,4,4-trifluorobutan-2-yl)(phenyl)sulfane. Yellow oil (44 mg, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (dt, J = 3.3, 1.9 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.28 – 7.22 (m, 1H), 3.29 (td, J = 6.7, 2.9 Hz, 1H), 2.63 – 2.45 (m, 1H), 2.43 – 2.26 (m, 1H), 1.89 – 1.64 (m, 6H), 1.51 – 1.36 (m, 1H), 1.36 – 1.07 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.20, 131.92, 129.11, 127.19, 126.50 (q, J = 278.5 Hz), 49.31, 49.29, 41.34, 36.89 (q, J = 27.4 Hz), 30.47, 28.27, 26.35, 26.30 (d, J = 3.4 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.65. HRMS (EI) calcd for: $C_{16}H_{21}F_3S$ 302.1316; found: 302.1307.



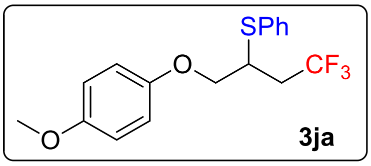
2-(5,5,5-trifluoro-3-(phenylthio)pentyl)oxirane. Colorless oil (38 mg, 62%).[1]H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.36 – 7.30 (m, 2H), 7.30 – 7.26 (m, 1H), 3.33 (tt, *J* = 8.5, 4.4 Hz, 1H), 2.95 – 2.86 (m, 1H), 2.79 – 2.68 (m, 1H), 2.51 – 2.38 (m, 2H), 2.38 – 2.24 (m, 1H), 1.88 – 1.74 (m, 1H), 1.69 – 1.43 (m, 7H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.43, 132.68 (d, J = 1.3 Hz), 129.19, 127.72, 126.05 (q, J = 278.7 Hz), 52.18, 47.08 (d, J = 4.0 Hz), 42.29 (m), 39.12 (q, J = 27.3 Hz), 33.63, 32.26, 26.16 (d, *J* = 1.6 Hz), 25.67; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.43, -63.43. HRMS (ESI) calcd for: $C_{15}H_{20}F_3OS^+$ $[M+H]^+$ 305.1181; found: 305.1182.



Phenyl(4,4,4-trifluoro-1-phenoxybutan-2-yl)sulfane. Colorless oil (38 mg, 61%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 2H), 7.42 – 7.35 (m, 3H), 7.31 (dd, J = 11.8, 4.2 Hz, 2H), 7.01 (td, J = 7.4, 0.9 Hz, 1H), 6.89 (dd, J = 7.9, 0.8 Hz, 2H), 4.20 (dd, J = 9.8, 4.5 Hz, 1H), 4.06 (dd, J = 9.7, 6.9 Hz, 1H), 3.78 – 3.56 (m, 1H), 2.85 (ddd, J = 16.7, 10.8, 5.7 Hz, 1H), 2.61 – 2.31 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.13, 133.31, 132.65, 129.57, 129.32, 128.28, 128.20 (q, J = 278.5 Hz), 121.42, 114.64, 68.84, 41.72 (d, J = 2.5 Hz), 35.69 (q, J = 28.7 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.44. HRMS (EI) calcd for: $C_{16}H_{15}F_3OS$ 312.0796; found: 312.0801.

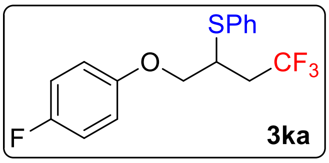


Phenyl(4,4,4-trifluoro-1-(p-tolyloxy)butan-2-yl)sulfane1. Colorless oil (35 mg, 54%).. H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.46 (m, 2H), 7.09 (t, *J* = 11.1 Hz, 3H), 6.82 – 6.69 (m, 2H), 4.14 (dd, *J* = 9.8, 4.5 Hz, 2H), 4.02 (ddd, *J* = 16.7, 9.7, 6.8 Hz, 1H), 3.74 – 3.56 (m, 1H), 2.92 – 2.72 (m, 1H), 2.54 – 2.35 (m, 1H), 2.31 (d, *J* = 16.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.03, 133.28, 132.68, 130.71, 129.99, 129.30, 129.09 (q, J = 278.5 Hz),128.23, 114.53, 69.04, 41.70 (d, J = 2.4 Hz), 35.64 (dd, J = 57.4, 28.6 Hz), 20.51; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.43. HRMS (EI) calcd for: $C_{17}H_{17}F_3OS$ 326.0952; found: 326.0956.

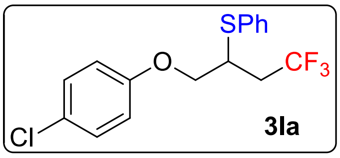


Phenyl(4,4,4-trifluoro-1-(4-methoxyphenoxy)butan-2-yl)sulfane. Pale yellow oil (37 mg, 54%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 2H), 7.40 – 7.30 (m, 3H), 6.91 – 6.72 (m, 4H), 4.12

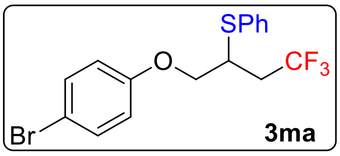
(dd, J = 9.8, 4.6 Hz, 1H), 4.02 – 3.94 (m, 1H), 3.77 (s, 3H), 3.66 – 3.54 (m, 1H), 2.89 – 2.74 (m, 1H), 2.43 (ddd, J = 15.5, 10.7, 6.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.32, 152.27, 133.24, 132.70, 129.30, 128.22, 126.50 (q, J = 278.5 Hz), 115.80, 114.69, 69.74, 55.71, 41.72 (d, J = 2.4 Hz), 35.64 (q, J = 28.7 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.44. HRMS (EI) calcd for: $C_{17}H_{17}F_3O_2S$ 342.0901; found: 342.0914.



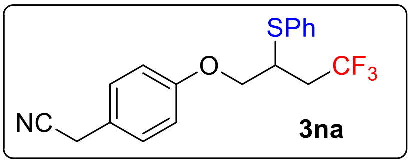
Phenyl(4,4,4-trifluoro-1-(4-fluorophenoxy)butan-2-yl)sulfane. Colorless oil (33 mg, 50%).. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2H), 7.41 – 7.30 (m, 3H), 7.02 – 6.93 (m, 2H), 6.84 – 6.76 (m, 2H), 4.12 (dd, *J* = 9.8, 4.5 Hz, 1H), 3.99 (dd, *J* = 9.7, 6.6 Hz, 1H), 3.68 – 3.55 (m, 1H), 2.87 – 2.68 (m, 1H), 2.55 – 2.34 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ157.60 (d, *J* = 239.2 Hz), 154.24 (d, J = 2.1 Hz), 133.31, 132.55, 129.34, 128.34, 126.02 (q, J = 278.5 Hz), 115.95 (d, J = 23.2 Hz), 115.75 (d, J = 8.0 Hz), 69.55, 41.70 (d, *J* = 2.4 Hz), 35.64 (q, *J* = 28.9 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.48, -122.99. HRMS (EI) calcd for: $C_{16}H_{14}F_4OS$ 330.0702; found: 330.0699.



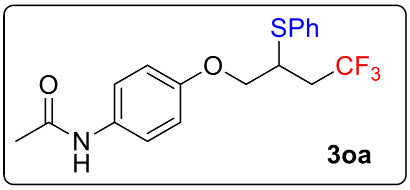
(1-(4-chlorophenoxy)-4,4,4-trifluorobutan-2-yl)(phenyl)sulfane. Yellow oil (37 mg, 54%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 2H), 7.39 – 7.31 (m, 3H), 7.26 – 7.20 (m, 2H), 6.83 – 6.74 (m, 2H), 4.13 (dd, *J* = 9.8, 4.6 Hz, 1H), 4.00 (dd, *J* = 9.8, 6.6 Hz, 1H), 3.67 – 3.55 (m, 1H), 2.78 (dqd, *J* = 21.5, 10.7, 6.5 Hz, 1H), 2.55 – 2.32 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.71, 133.38, 132.46, 129.44, 129.37, 128.40, 126.34, 126.00 (q, J = 278.5 Hz), 115.92, 69.13, 41.65 (d, *J* = 2.4 Hz), 35.65 (q, *J* = 28.8 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.47. HRMS (EI) calcd for: $C_{16}H_{14}ClF_3OS$ 346.0406; found: 346.0401.



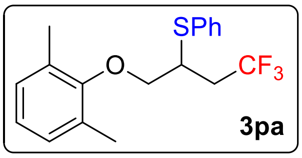
(1-(4-bromophenoxy)-4,4,4-trifluorobutan-2-yl)(phenyl)sulfane. Yellow oil (39 mg, 50%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.45 (m, 1H), 7.40 – 7.29 (m, 2H), 6.78 – 6.69 (m, 1H), 4.12 (dd, *J* = 9.8, 4.6 Hz, 1H), 3.99 (dd, *J* = 9.8, 6.6 Hz, 1H), 3.67 – 3.52 (m, 1H), 2.88 – 2.65 (m, 1H), 2.56 – 2.27 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.22, 133.39, 132.44, 132.38, 129.37, 128.41, 125.97 (q, J = 278.5 Hz), 116.42, 113.65, 69.04, 41.64 (d, *J* = 2.4 Hz), 35.65 (q, *J* = 28.8 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.47. HRMS (EI) calcd for: $C_{16}H_{14}BrF_3OS$ 389.9901; found: 389.9897.



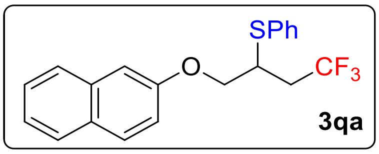
2-(4-(4,4,4-trifluoro-2-(phenylthio)butoxy)phenyl)acetonitrile. Colorless oil (34 mg, 51%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (td, *J* = 7.6, 3.3 Hz, 2H), 7.39 – 7.32 (m, 3H), 7.25 – 7.18 (m, 2H), 6.85 (t, *J* = 8.7 Hz, 2H), 4.16 (dd, *J* = 9.8, 4.5 Hz, 1H), 4.02 (dt, *J* = 10.7, 5.4 Hz, 1H), 2.79 (dqd, *J* = 21.5, 10.7, 6.5 Hz, 1H), 2.53 – 2.37 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.90, 133.38, 132.48, 129.36, 129.20, 128.40, 126.00 (q, J = 278.2 Hz), 122.61, 118.09, 115.23, 115.03, 68.95, 41.67 (d, J = 2.4 Hz), 35.67 (q, J = 28.7 Hz). 22.85. HRMS (ESI) calcd for: $C_{18}H_{16}F_3NOSNa^+$ $[M+Na]^+$ 374.0797; found: 374.0799.



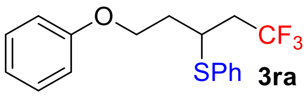
N-(4-(4,4,4-trifluoro-2-(phenylthio)butoxy)phenyl)acetamide. White viscous liquid (40 mg, 54%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.52 – 7.44 (m, 2H), 7.38 (d, J = 9.0 Hz, 2H), 7.36 – 7.28 (m, 3H), 6.82 – 6.73 (m, 2H), 4.12 (dd, J = 9.9, 4.5 Hz, 1H), 3.98 (dd, J = 9.7, 6.7 Hz, 1H), 3.69 – 3.41 (m, 1H), 2.78 (dqd, J = 21.5, 10.7, 6.4 Hz, 1H), 2.55 – 2.32 (m, 1H), 2.12 (s, 3H); ^{13}C NMR (126 MHz, CDCl3) δ 168.59, 154.89, 133.32, 132.53, 131.76, 129.33, 128.32, 126.05 (q, J = 278.5 Hz), 121.93, 114.97, 69.20, 41.68 (d, J = 2.4 Hz), 35.63 (q, J = 28.7 Hz), 24.27; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.42. HRMS (EI) calcd for: $C_{18}H_{18}F_3NO_2S$ 369.1010; found: 369.1013.



(1-(2,6-dimethylphenoxy)-4,4,4-trifluorobutan-2-yl)(phenyl)sulfane. Pale yellow oil (21 mg, 31%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.44 (m, 2H), 7.38 – 7.29 (m, 3H), 7.00 (d, J = 7.3 Hz, 2H), 6.93 (dd, J = 8.2, 6.6 Hz, 1H), 3.93 (ddd, J = 16.1, 9.8, 5.6 Hz, 2H), 3.70 (dd, J = 6.3, 4.9 Hz, 1H), 3.00 (ddd, J = 15.5, 10.8, 6.3 Hz, 1H), 2.56 – 2.37 (m, 1H), 2.24 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.80, 133.11, 132.61, 130.78, 129.29, 129.00, 127.98, 126.10 (q, J = 278.5 Hz), 124.27, 72.23, 42.55 (d, J = 2.3 Hz), 35.56 (q, J = 28.5 Hz), 16.31; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.49. HRMS (EI) calcd for: $C_{18}H_{19}F_3OS$ 340.1109; found: 340.1115.

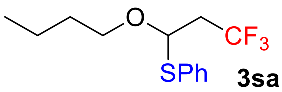


Phenyl(4,4,4-trifluoro-1-(naphthalen-2-yloxy)butan-2-yl)sulfane. White viscous liquid (24 mg, 33%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dd, J = 10.9, 8.7 Hz, 2H), 7.69 (d, J = 8.2 Hz, 1H), 7.54 (dd, J = 6.7, 1.3 Hz, 2H), 7.45 (t, J = 7.5 Hz, 1H), 7.40 – 7.33 (m, 4H), 7.14 (dd, J = 8.9, 2.4 Hz, 1H), 7.04 (d, J = 2.3 Hz, 1H), 4.30 (dd, J = 9.9, 4.5 Hz, 1H), 4.16 (dd, J = 9.8, 6.8 Hz, 1H), 3.75 – 3.62 (m, 1H), 2.98 – 2.78 (m, 1H), 2.58 – 2.34 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.04, 134.35, 133.39, 132.68, 129.63, 129.37, 129.24, 128.35, 127.69, 126.78, 126.52, 126.10 (q, J = 278.5 Hz), 123.96, 118.67, 106.94, 68.86, 41.69 (d, J = 2.4 Hz), 35.81 (q, J = 28.6 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.41. HRMS (EI) calcd for: $C_{20}H_{17}F_3OS$ 362.0952; found: 362.0953.



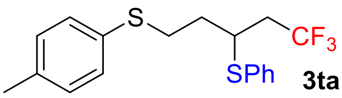
3ra

Phenyl(1,1,1-trifluoro-5-phenoxypentan-3-yl)sulfane. Colorless oil (43 mg, 66%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.37 – 7.28 (m, 5H), 7.03 – 6.96 (m, 1H), 6.96 – 6.91 (m, 2H), 4.28 (ddd, J = 9.3, 8.2, 5.2 Hz, 1H), 4.24 – 4.15 (m, 2H), 3.65 (tt, J = 9.2, 4.7 Hz, 1H), 2.51 (dddd, J = 18.7, 15.3, 10.4, 7.1 Hz, 2H), 2.40 – 2.30 (m, 1H), 2.02 (dq, J = 9.8, 5.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.67, 133.04, 132.96, 129.52, 129.26, 127.94, 126.10 (q, J = 278.5 Hz), 120.96, 114.61, 64.68, 39.69 (d, J = 2.4 Hz), 39.62 (q, J = 27.7 Hz), 33.64; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.14, -63.14. HRMS (EI) calcd for: $C_{17}H_{17}F_3OS$ 326.0952; found: 326.0967.



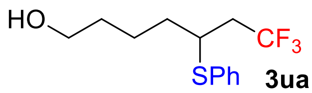
3sa

(1-butoxy-3,3,3-trifluoropropyl)(phenyl)sulfane. Yellow oil (22 mg, 40%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.43 (m, 2H), 7.34 (dd, J = 4.2, 2.4 Hz, 3H), 4.92 (dd, J = 8.8, 3.7 Hz, 1H), 4.00 (dt, J = 9.3, 6.4 Hz, 1H), 3.67 – 3.27 (m, 1H), 2.75 – 2.32 (m, 2H), 1.66 – 1.57 (m, 2H), 1.47 – 1.36 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.61, 130.92, 129.02, 128.45, 125.35 (q, J = 279.7 Hz), 81.77 (d, J = 3.4 Hz), 68.81, 40.96 (dd, J = 56.4, 28.3 Hz), 31.20, 19.29, 13.81; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.84. HRMS (EI) calcd for: $C_{13}H_{17}F_3OS$ 278.0952; found: 278.0954.



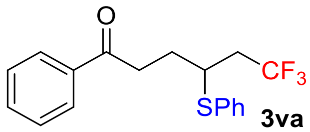
3ta

Phenyl(1,1,1-trifluoro-5-(p-tolylthio)pentan-3-yl)sulfane. Colorless oil (43 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 2H), 7.35 – 7.27 (m, 5H), 7.11 (d, J = 8.0 Hz, 2H), 3.52 (tt, J = 8.8, 4.3 Hz, 1H), 3.26 – 2.95 (m, 2H), 2.56 – 2.40 (m, 1H), 2.34 (s, 3H), 2.32 – 2.20 (m, 1H), 2.07 (tdd, J = 11.8, 7.9, 3.9 Hz, 1H), 1.90 – 1.74 (m, 1H); ^{13}C NMR (126 MHz, CDCl3) δ 136.69, 133.13, 132.70, 131.65, 130.90, 129.78, 129.24, 127.99, 125.86 (q, J = 278.5 Hz),41.38 (d, J = 2.3 Hz), 39.40 (q, J = 27.6 Hz), 33.27, 31.90, 21.07; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.28. HRMS (EI) calcd for: $C_{18}H_{19}F_3S_2$ 356.0880; found: 356.0874.



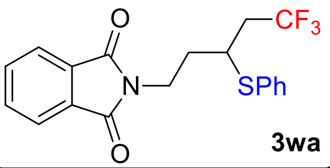
3ua

7,7,7-trifluoro-5-(phenylthio)heptan-1-ol. Colorless oil (45 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 2H), 7.33 (ddd, J = 7.4, 4.6, 1.4 Hz, 2H), 7.30 – 7.26 (m, 1H), 3.65 (t, J = 6.2 Hz, 2H), 3.34 (tt, J = 8.5, 4.4 Hz, 1H), 2.55 – 2.21 (m, 2H), 1.91 – 1.75 (m, 1H), 1.74 – 1.56 (m, 5H), 1.25 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.37, 132.75, 129.19, 127.76, 126.06 (q, J = 278.5 Hz), 62.59, 42.39 (d, J = 2.4 Hz), 39.11 (q, J = 27.5 Hz), 33.48, 32.27, 22.65; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.43. HRMS (EI) calcd for: $C_{13}H_{17}F_3OS$ 278.0952; found: 278.0955.



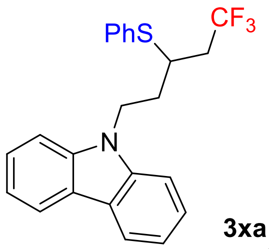
3va

6,6,6-trifluoro-1-phenyl-4-(phenylthio)hexan-1-one. Pale yellow oil (54 mg, 65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (t, J = 7.6 Hz, 2H), 7.62 – 7.53 (m, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.42 (d, J = 7.1 Hz, 2H), 7.30 (ddd, J = 10.8, 9.8, 5.2 Hz, 3H), 3.56 – 3.42 (m, 1H), 3.38 – 3.27 (m, 2H), 2.62 – 2.47 (m, 1H), 2.46 – 2.30 (m, 2H), 2.02 – 1.88 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.98, 136.71, 133.24, 132.89, 132.76, 129.31, 128.67, 128.04, 127.98, 126.06 (q, J = 278.5 Hz), 42.07 (d, J = 2.3 Hz), 39.59 (q, J = 27.7 Hz), 35.49, 28.01; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.27. HRMS (EI) calcd for: $C_{18}H_{17}F_3OS$ 338.0952; found: 338.0960.



3wa

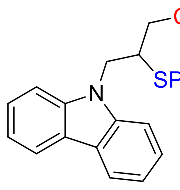
2-(5,5,5-trifluoro-3-(phenylthio)pentyl)isoindoline-1,3-dione. White solid, mp 66.3-69.1 °C, (63 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, J = 5.4, 3.0 Hz, 2H), 7.70 (dd, J = 5.5, 3.0 Hz, 2H), 7.59 – 7.42 (m, 2H), 7.38 – 7.28 (m, 3H), 4.01 (ddd, J = 14.0, 8.2, 5.9 Hz, 1H), 3.96 – 3.85 (m, 1H), 3.32 (dq, J = 13.2, 4.4 Hz, 1H), 2.58 – 2.42 (m, 1H), 2.34 (dqd, J = 15.4, 10.4, 8.6 Hz, 1H), 2.23 – 2.08 (m, 1H), 1.91 (dtd, J = 14.5, 8.6, 6.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.22, 134.01, 133.92, 132.06, 129.25, 128.35, 125.84 (q, J = 278.5 Hz), 123.29, 40.51 (d, J = 2.4 Hz), 39.14 (q, J = 27.6 Hz), 35.69, 32.35; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.27. HRMS (EI) calcd for: $C_{19}H_{16}F_3NO_2S$ 379.0854; found: 379.0851.



3xa

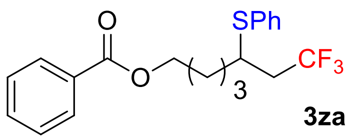
9-(5,5,5-trifluoro-3-(phenylthio)pentyl)-9H-carbazole. Pale yellow oil (42 mg, 53%). ^{1}H NMR

(500 MHz, $CDCl_3$) δ 8.21 – 8.10 (m, 2H), 7.57 – 7.44 (m, 6H), 7.42 – 7.34 (m, 3H), 7.30 (ddd, J = 4.6, 4.0, 1.1 Hz, 2H), 4.63 (dd, J = 16.0, 8.9 Hz, 2H), 3.60 – 3.26 (m, 1H), 2.62 – 2.44 (m, 2H), 2.43 – 2.29 (m, 1H), 2.19 – 1.99 (m, 1H); ^{13}C NMR (126 MHz, CDCl3) δ 140.21, 132.71, 132.64, 129.44, 128.15, 125.85, 125.76 (q, J = 278.5 Hz),123.06, 120.47, 119.15, 108.59, 40.29, 40.12 (d, J = 2.3 Hz), 39.32 (q, J = 27.7 Hz), 32.36; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.27. HRMS (EI) calcd for: $C_{23}H_{20}F_3NS$ 399.1269; found: 399.1265.



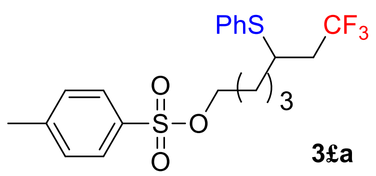
3ya

9-(4,4,4-trifluoro-2-(phenylthio)butyl)-9H-carbazole. Yellow viscous liquid (47 mg, 61%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (dd, J = 21.1, 11.5 Hz, 2H), 7.46 (dt, J = 8.2, 2.3 Hz, 2H), 7.41 – 7.36 (m, 2H), 7.35 – 7.25 (m, 5H), 7.22 (dd, J = 8.7, 5.1 Hz, 2H), 4.63 – 4.42 (m, 2H), 4.08 – 3.81 (m, 1H), 2.67 – 2.36 (m, 2H); ^{13}C NMR (126 MHz, CDCl3) δ 140.29, 133.52, 132.26, 129.25, 128.40, 126.95, 125.83 (q, J = 278.5 Hz), 123.11, 120.50, 119.51, 108.43, 47.37, 42.48 (d, J = 2.1 Hz), 36.91 (q, J = 28.9 Hz); ^{19}F NMR (471 MHz, CDCl3) δ -62.82. HRMS (EI) calcd for: $C_{22}H_{18}F_3NS$ 385.1112; found: 385.1103.



3za

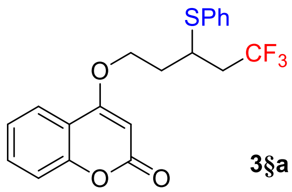
7,7,7-trifluoro-5-(phenylthio)heptyl benzoate. Colorless oil (60 mg, 79%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.01 (m, 2H), 7.61 – 7.53 (m, 1H), 7.49 – 7.40 (m, 4H), 7.35 – 7.28 (m, 3H), 4.34 (dd, J = 7.7, 4.5 Hz, 2H), 3.36 (tt, J = 8.5, 4.4 Hz, 1H), 2.60 – 2.24 (m, 2H), 1.93 – 1.73 (m, 4H), 1.71 – 1.63 (m, 2H); ^{13}C NMR (126 MHz, CDCl3) δ 166.62, 133.24, 132.91, 132.85, 130.36, 129.57, 129.21, 128.37, 127.83, 126.03 (q, J = 278.5 Hz), 64.62, 42.36 (d, J = 2.4 Hz), 39.19 (q, J = 27.4 Hz), 33.36, 28.43, 23.00; ^{19}F NMR (471 MHz, CDCl3) δ -63.38. HRMS (EI) calcd for: $C_{20}H_{21}F_3O_2S$ 382.1214; found: 382.1210.



3£a

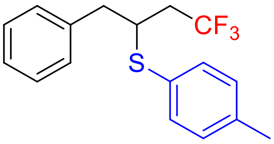
7,7,7-trifluoro-5-(phenylthio)heptyl 4-methylbenzenesulfonate. Pale yellow oil (74 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.77 (m, 2H), 7.46 – 7.39 (m, 2H), 7.39 – 7.29 (m, 4H), 4.17 – 3.94 (m, 2H), 3.27 (tt, J = 8.5, 4.4 Hz, 1H), 2.46 (s, 3H), 2.41 (ddd, J = 15.8, 10.0, 4.5 Hz, 1H), 2.35 – 2.20 (m, 1H), 1.81 – 1.71 (m, 1H), 1.71 – 1.60 (m, 3H), 1.59 – 1.45 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.81, 133.11, 133.07, 132.83, 129.88, 129.85, 129.24, 127.89, 126.00 (q, J

= 278.5 Hz), 70.15, 42.24, 42.22, 39.40, 39.18, 38.97, 38.79, 33.04, 28.52, 22.41, 21.64; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.42. HRMS (EI) calcd for: $C_{20}H_{23}F_3O_3S_2$ 432.1041; found: 432.1051.



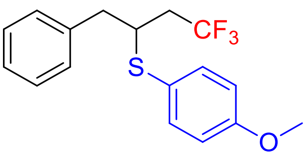
3§a

4-((5,5,5-trifluoro-3-(phenylthio)pentyl)oxy)-2H-chromen-2-one. Colorless oil (44 mg, 56%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (dd, J = 7.9, 1.5 Hz, 1H), 7.58 (ddd, J = 8.7, 7.3, 1.6 Hz, 1H), 7.47 – 7.39 (m, 2H), 7.34 (dd, J = 8.4, 0.7 Hz, 1H), 7.33 – 7.25 (m, 4H), 5.69 (s, 1H), 4.45 (td, J = 9.3, 4.5 Hz, 1H), 4.34 (dt, J = 9.9, 5.0 Hz, 1H), 3.73 – 3.49 (m, 1H), 2.74 – 2.57 (m, 1H), 2.57 – 2.38 (m, 2H), 2.11 (qd, J = 9.6, 4.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.22, 162.73, 153.31, 133.06, 132.48, 132.44, 129.40, 128.29, 125.81 (q, J = 278.5 Hz), 123.99, 122.78, 116.83, 115.52, 90.83, 66.16, 39.90 (q, J = 24.9 Hz), 39.68, 33.02; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.24. HRMS (EI) calcd for: $C_{20}H_{17}F_3O_3S$ 394.0851; found: 394.0843.



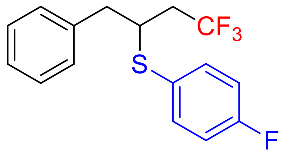
3ab

p-tolyl(4,4,4-trifluoro-1-phenylbutan-2-yl)sulfane. Colorless oil (44 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (dd, J = 15.2, 7.6 Hz, 4H), 7.27 (dd, J = 8.4, 6.2 Hz, 1H), 7.22 (d, J = 7.3 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 3.52 (p, J = 6.7 Hz, 1H), 3.03 (dd, J = 14.3, 6.4 Hz, 1H), 2.94 (dd, J = 14.3, 7.5 Hz, 1H), 2.43 – 2.36 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.15, 137.86, 133.52, 129.97, 129.56, 129.38, 128.52, 126.88, 126.16 (q, J = 278.5 Hz), 44.01 (d, J = 2.1 Hz), 40.59, 37.99 (q, J = 27.7 Hz), 21.16; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.99. HRMS (EI) calcd for: $C_{17}H_{17}F_3S$ 310.1003; found: 310.1013.

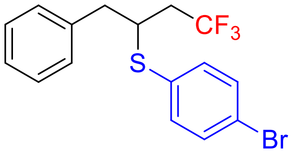


3ac

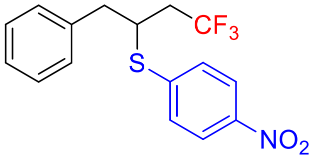
(4-methoxyphenyl)(4,4,4-trifluoro-1-phenylbutan-2-yl)sulfane. Pale yellow oil (47 mg, 72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J = 8.3 Hz, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.28 (d, J = 7.1 Hz, 1H), 7.22 (d, J = 7.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 3.82 (s, 3H), 3.42 (p, J = 6.7 Hz, 1H), 2.97 (ddd, J = 21.7, 14.3, 7.0 Hz, 2H), 2.47 – 2.25 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.01, 137.98, 136.22, 129.36, 128.54, 126.86, 126.20 (q, J = 278.5 Hz), 123.32, 114.75, 55.34, 44.67 (d, J = 2.1 Hz), 40.71, 37.89 (q, J = 27.7 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.92. HRMS (EI) calcd for: $C_{17}H_{17}F_3OS$ 326.0952; found: 326.0947.


3ad

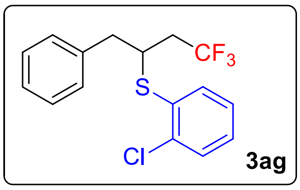
(4-fluorophenyl)(4,4,4-trifluoro-1-phenylbutan-2-yl)sulfane. Pale yellow oil (40 mg, 63%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.33 (dd, J = 9.5, 5.5 Hz, 2H), 7.28 (d, J = 7.0 Hz, 1H), 7.19 (t, J = 10.1 Hz, 2H), 7.08 – 6.97 (m, 2H), 3.47 (p, J = 6.7 Hz, 1H), 3.08 – 2.99 (m, 1H), 2.93 (dt, J = 14.3, 7.2 Hz, 1H), 2.47 – 2.28 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.78 (d, J = 248.6 Hz), 137.65, 135.76 (d, J = 8.3 Hz), 132.74, 129.34, 128.58, 126.99, 126.20 (q, J = 278.5 Hz), 116.34 (d, J = 21.9 Hz), 44.75 (d, J = 0.8 Hz), 40.81, 38.09 (q, J = 27.9 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.02, -112.93. HRMS (EI) calcd for: $C_{16}H_{14}F_4S$ 314.0752; found: 314.0742.


3ae

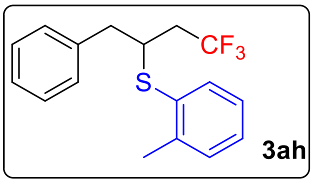
(4-bromophenyl)(4,4,4-trifluoro-1-phenylbutan-2-yl)sulfane. Pale yellow oil (48 mg, 64%). ^{1}H NMR (500 MHz, CDCl3) δ 7.46 – 7.42 (m, 2H), 7.36 – 7.31 (m, 2H), 7.30 – 7.25 (m, 1H), 7.25 – 7.23 (m, 1H), 7.23 – 7.19 (m, 3H), 3.64 – 3.43 (m, 1H), 3.06 (dd, J = 14.3, 6.2 Hz, 1H), 2.92 (dd, J = 14.3, 7.7 Hz, 1H), 2.47 – 2.30 (m, 2H); ^{13}C NMR (126 MHz, CDCl3) δ 137.45, 134.20, 132.75, 132.30, 129.36, 128.60, 127.05, 126.00 (q, J = 278.5 Hz), 122.04, 44.06 (d, J = 2.2 Hz), 40.71, 38.15 (q, J = 27.9 Hz); ^{19}F NMR (471 MHz, CDCl3) δ -63.03. HRMS (EI) calcd for: $C_{16}H_{14}BrF_3S$ 373.9952; found: 373.9945.


3af

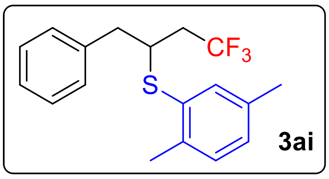
(4-nitrophenyl)(4,4,4-trifluoro-1-phenylbutan-2-yl)sulfane. Brown oil (31 mg, 46%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 – 8.07 (m, 2H), 7.34 (tdd, J = 7.5, 5.4, 1.9 Hz, 4H), 7.29 – 7.25 (m, 1H), 7.24 – 7.21 (m, 2H), 3.86 – 3.74 (m, 1H), 3.19 (dd, J = 14.4, 5.7 Hz, 1H), 2.97 (dd, J = 14.4, 8.0 Hz, 1H), 2.63 – 2.36 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.03, 144.46, 136.79, 129.39, 129.02, 128.71, 127.33, 125.80 (q, J = 278.5 Hz), 124.69, 124.14, 42.67 (d, J = 2.1 Hz), 40.65, 38.43 (q, J = 28.1 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.15. HRMS (EI) calcd for: $C_{16}H_{14}F_3NO_2S$ 341.0697; found: 341.0696.



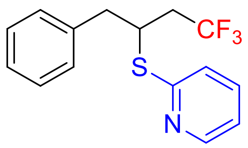
(2-chlorophenyl)(4,4,4-trifluoro-1-phenylbutan-2-yl)sulfane. Colorless oil (43 mg, 65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.35 (t, J = 7.4 Hz, 2H), 7.31 – 7.22 (m, 5H), 3.95 – 3.70 (m, 1H), 3.15 (dd, J = 14.4, 6.2 Hz, 1H), 2.98 (dd, J = 14.4, 7.6 Hz, 1H), 2.65 – 2.28 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.42, 136.69, 133.09, 133.05, 130.27, 129.37, 128.67, 128.55, 127.13, 127.01, 126.20 (q, J = 278.5 Hz), 42.53 (d, J = 2.1 Hz), 40.43, 38.14 (q, J = 28.0 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.08. HRMS (EI) calcd for: $C_{16}H_{14}ClF_3S$ 330.0457; found: 330.0453.



o-tolyl(4,4,4-trifluoro-1-phenylbutan-2-yl)sulfane. Colorless oil (42 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 1H), 7.33 (t, J = 7.3 Hz, 2H), 7.27 (d, J = 7.1 Hz, 1H), 7.25 – 7.20 (m, 3H), 7.20 – 7.14 (m, 1H), 3.66 – 3.44 (m, 1H), 3.10 (dd, J = 14.3, 6.2 Hz, 1H), 2.93 (dd, J = 14.3, 7.6 Hz, 1H), 2.41 (ddd, J = 13.0, 10.5, 6.5 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.33, 137.81, 133.08, 132.42, 130.67, 129.43, 128.50, 127.69, 126.90, 126.61, 126.07 (q, J = 279.7 Hz), 43.05 (d, J = 2.1 Hz), 40.51, 38.16 (q, J = 27.8 Hz), 20.66; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.07. HRMS (EI) calcd for: $C_{17}H_{17}F_3S$ 310.1003; found: 310.1004.

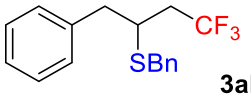


(2,5-dimethylphenyl)(4,4,4-trifluoro-1-phenylbutan-2-yl)sulfane. Pale yellow oil (35 mg, 54%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, J = 7.4 Hz, 2H), 7.24 (dd, J = 17.7, 11.0 Hz, 3H), 7.16 (s, 1H), 7.09 (t, J = 6.3 Hz, 1H), 6.99 (d, J = 7.5 Hz, 1H), 3.60 – 3.46 (m, 1H), 3.10 (dd, J = 14.3, 6.0 Hz, 1H), 2.92 (dd, J = 14.3, 7.7 Hz, 1H), 2.49 – 2.34 (m, 2H), 2.31 (d, J = 5.6 Hz, 6H); ^{13}C NMR (126 MHz, CDCl3) δ 137.88, 137.13, 136.14, 133.04, 132.63, 130.46, 129.37, 128.54, 128.48, 126.87, 126.16 (q, J = 279.7 Hz), 38.20 (q, J = 27.8 Hz), 40.54, 38.20 (q, J = 27.8 Hz), 20.86, 20.14; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.09. HRMS (EI) calcd for: $C_{18}H_{19}F_3S$ 324.1160; found: 324.1162.



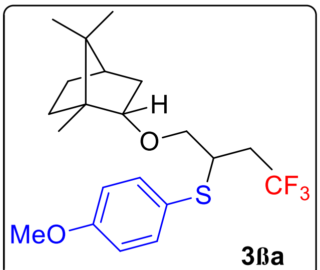
3aj

2-((4,4,4-trifluoro-1-phenylbutan-2-yl)thio)pyridine. Yellow oli (27 mg, 45%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (dd, J = 4.9, 0.8 Hz, 1H), 7.46 (ddd, J = 8.0, 7.5, 1.9 Hz, 1H), 7.34 – 7.27 (m, 4H), 7.26 – 7.22 (m, 1H), 7.13 (t, J = 8.3 Hz, 1H), 6.99 (ddd, J = 7.3, 4.9, 1.0 Hz, 1H), 4.45 (p, J = 6.8 Hz, 1H), 3.21 – 3.05 (m, 2H), 2.72 – 2.46 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ149.59, 138.08, 136.01, 129.59, 129.47, 128.42, 126.81, 126.27 (q, J = 279.7 Hz), 122.88, 119.74, 40.12, 39.25 (d, J = 2.3 Hz), 37.66 (q, J = 27.7 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.63. HRMS (EI) calcd for: $C_{15}H_{14}F_3NS$ 297.0799; found: 297.0793.



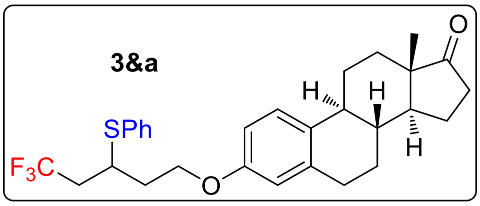
3ak

Benzyl(4,4,4-trifluoro-1-phenylbutan-2-yl)sulfane. Colorless oil (15 mg, 24%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 4H), 7.28 (dd, *J* = 7.5, 5.5 Hz, 4H), 7.16 (dd, *J* = 5.1, 3.2 Hz, 2H), 3.67 (d, *J* = 10.6 Hz, 2H), 3.10 – 2.95 (m, 2H), 2.95 – 2.84 (m, 1H), 2.49 – 2.30 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.90, 137.43, 129.48, 128.95, 128.57, 128.45, 127.24, 126.80, 126.11 (q, J = 278.5 Hz), 41.33, 39.48 (d, *J* = 2.2 Hz), 38.88 (q, *J* = 27.6 Hz), 36.06; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.14. HRMS (EI) calcd for: $C_{17}H_{17}F_3S$ 310.1003; found: 310.1011.

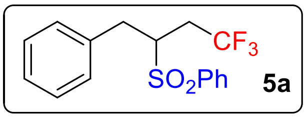


3ßa

(4-methoxyphenyl)(4,4,4-trifluoro-1-(((1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)butan-2-yl)sulfane. Colorless oil (35 mg, 44%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (t, *J* = 5.8 Hz, 2H), 6.90 – 6.81 (m, 2H), 3.81 (s, 3H), 3.70 – 3.50 (m, 2H), 3.42 (ddd, *J* = 53.7, 9.7, 6.6 Hz, 1H), 3.30 – 3.20 (m, 1H), 2.83 – 2.51 (m, 1H), 2.39 – 2.16 (m, 1H), 2.13 – 2.01 (m, 1H), 2.01 – 1.90 (m, 1H), 1.76 – 1.65 (m, 1H), 1.63 (dd, *J* = 8.7, 4.4 Hz, 1H), 1.25 – 1.15 (m, 2H), 1.03 – 0.93 (m, 1H), 0.89 – 0.86 (m, 1H), 0.85 – 0.78 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.96, 136.16, 126.34 (q, J = 277.7 Hz), 123.42, 114.64, 85.15 (d, J = 58.9 Hz), 70.78 (d, J = 45.4 Hz), 55.34, 48.57 (dd, J = 196.2, 10.7 Hz), 43.28 (d, J = 39.4 Hz), 35.83 (d, J = 5.6 Hz), 35.35 (d, J = 28.2 Hz), 29.96 (d, J = 61.2 Hz), 27.42 (dd, J = 196.2, 4.0 Hz), 19.73, 18.84,13.94 (d, J = 17.9 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.39, -63.45. HRMS (EI) calcd for: $C_{21}H_{29}F_3O_2S$ 402.1840; found: 402.1834.



(8R,9S,13S,14S)-13-methyl-3-((5,5,5-trifluoro-3-(phenylthio)pentyl)oxy)-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one. Brown oil (41 mg, 41%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (ddd, *J* = 10.0, 5.4, 3.0 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.19 (dd, *J* = 14.5, 5.7 Hz, 1H), 6.73 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.65 (t, *J* = 4.5 Hz, 1H), 4.29 – 4.19 (m, 1H), 4.16 (td, *J* = 9.3, 5.4 Hz, 1H), 3.61 (tt, *J* = 9.2, 4.7 Hz, 1H), 2.97 – 2.84 (m, 2H), 2.52 (ddt, *J* = 13.5, 12.1, 5.3 Hz, 2H), 2.46 – 2.37 (m, 2H), 2.34 – 2.22 (m, 2H), 2.20 – 2.12 (m, 1H), 2.10 – 1.93 (m, 4H), 1.70 – 1.58 (m, 3H), 1.51 (ddt, *J* = 11.5, 9.6, 6.3 Hz, 3H), 0.92 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 221.03, 156.69, 137.80, 132.96, 132.95, 132.31, 129.23, 127.91, 126.38, 125.97 (q, J = 279.7 Hz),114.62, 112.22, 64.72, 50.41, 48.04, 44.01, 39.63, 39.52 (q, J = 27.7 Hz) 38.37, 35.91, 33.56, 31.59, 29.67, 26.57, 25.95, 21.61, 13.88; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.15. HRMS (DART Positive) calcd for: $C_{29}H_{34}F_3O_2S$ 503.2232; found: 503.2226.



((4,4,4-trifluoro-1-phenylbutan-2-yl)sulfonyl)benzene. Colorless oil (55 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.84 (m, 2H), 7.72 – 7.63 (m, 1H), 7.60 – 7.52 (m, 2H), 7.31 – 7.19 (m, 3H), 7.17 – 7.07 (m, 2H), 3.62 (ddd, *J* = 13.2, 7.2, 3.8 Hz, 1H), 3.36 (dd, *J* = 14.7, 5.8 Hz, 1H), 3.03 (dd, *J* = 14.7, 7.5 Hz, 1H), 2.99 – 2.84 (m, 1H), 2.56 – 2.33 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.15, 135.62, 134.22, 129.43, 129.15, 128.82, 128.72, 127.22, 125.42 (q, J = 278.5 Hz), 60.15 (d, *J* = 1.9 Hz), 34.81, 32.35 (q, *J* = 30.5 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.78. HRMS (EI) calcd for: $C_{16}H_{15}F_3O_2S$ 328.0745; found: 328.0752.

7) References

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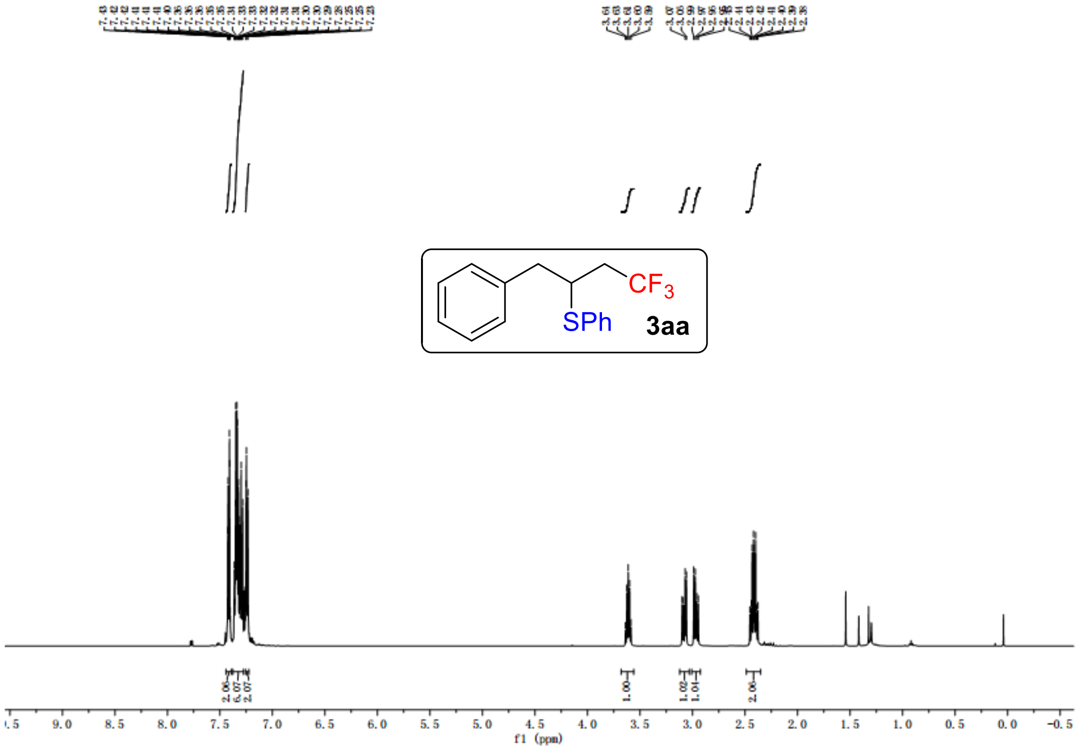
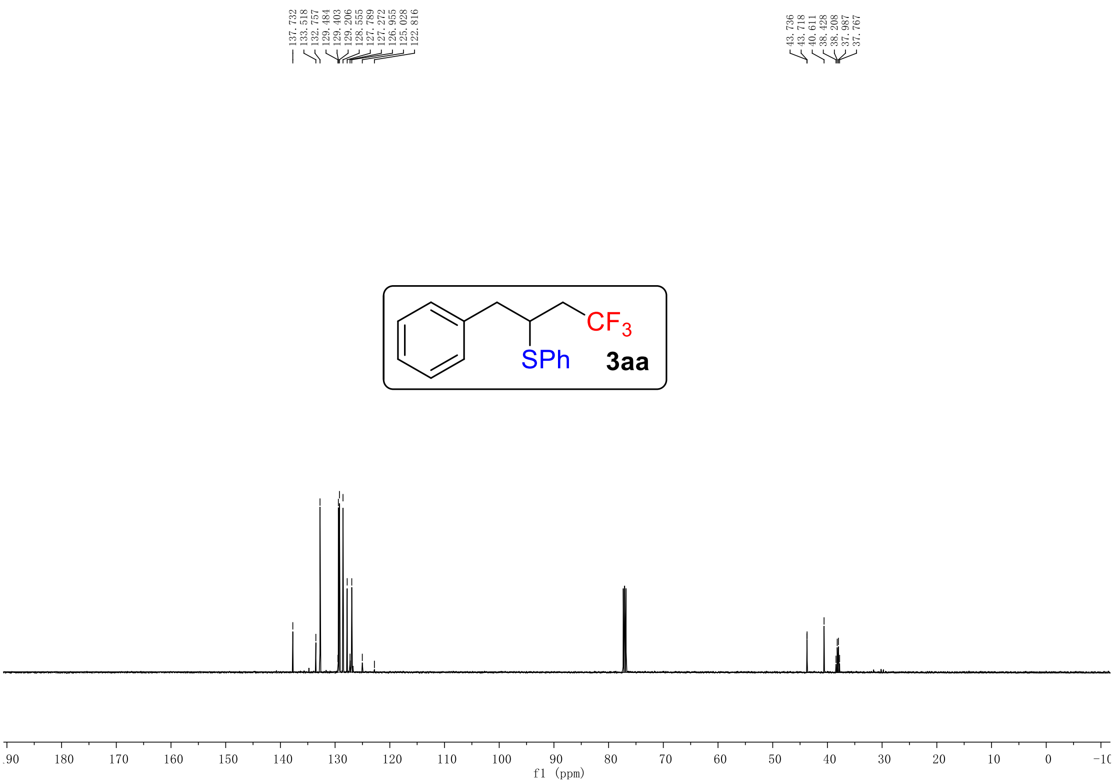
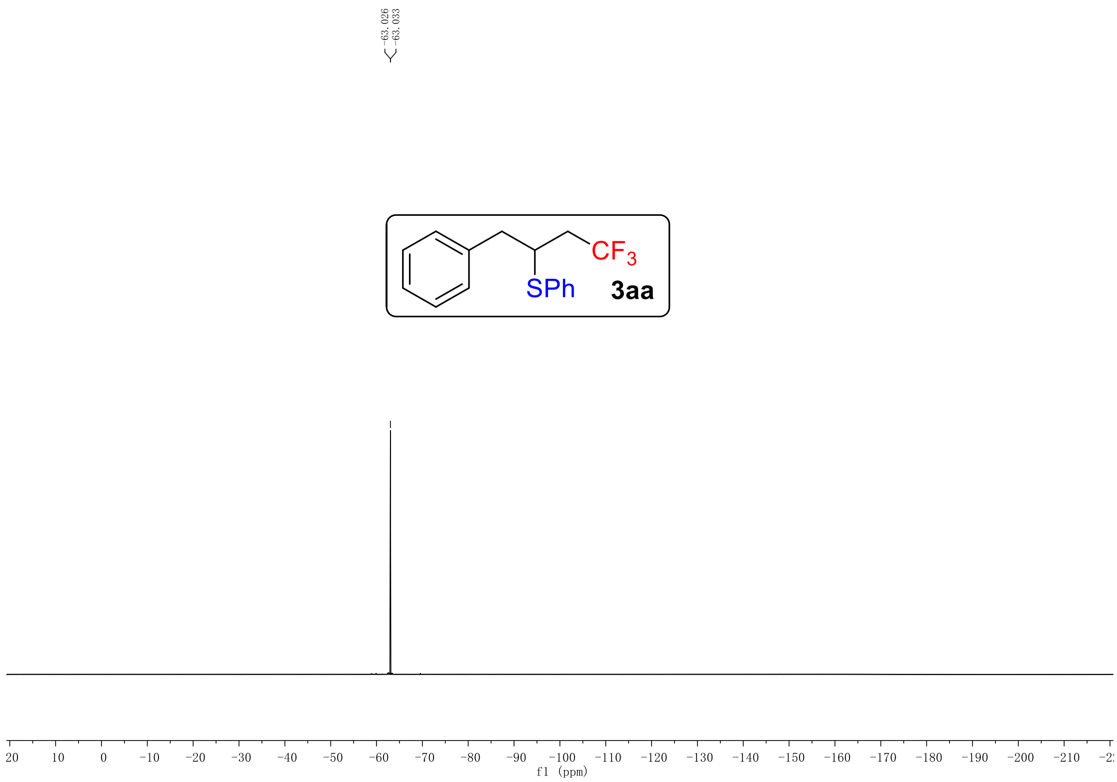
8) NMR Spectra



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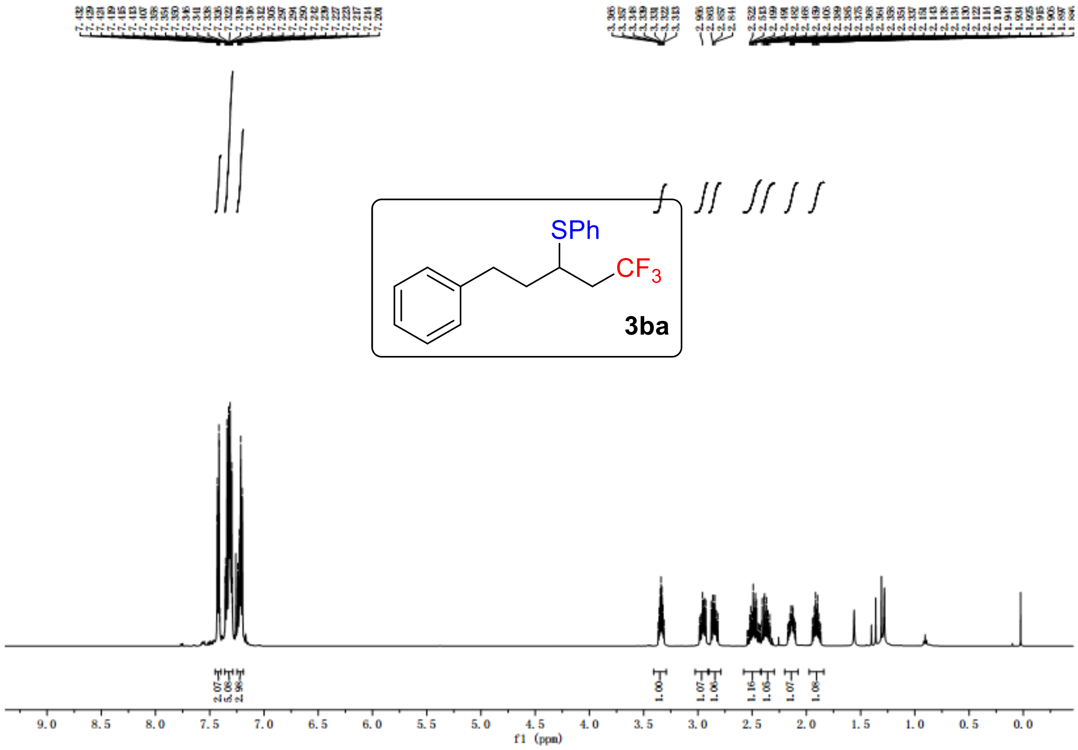
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CF3
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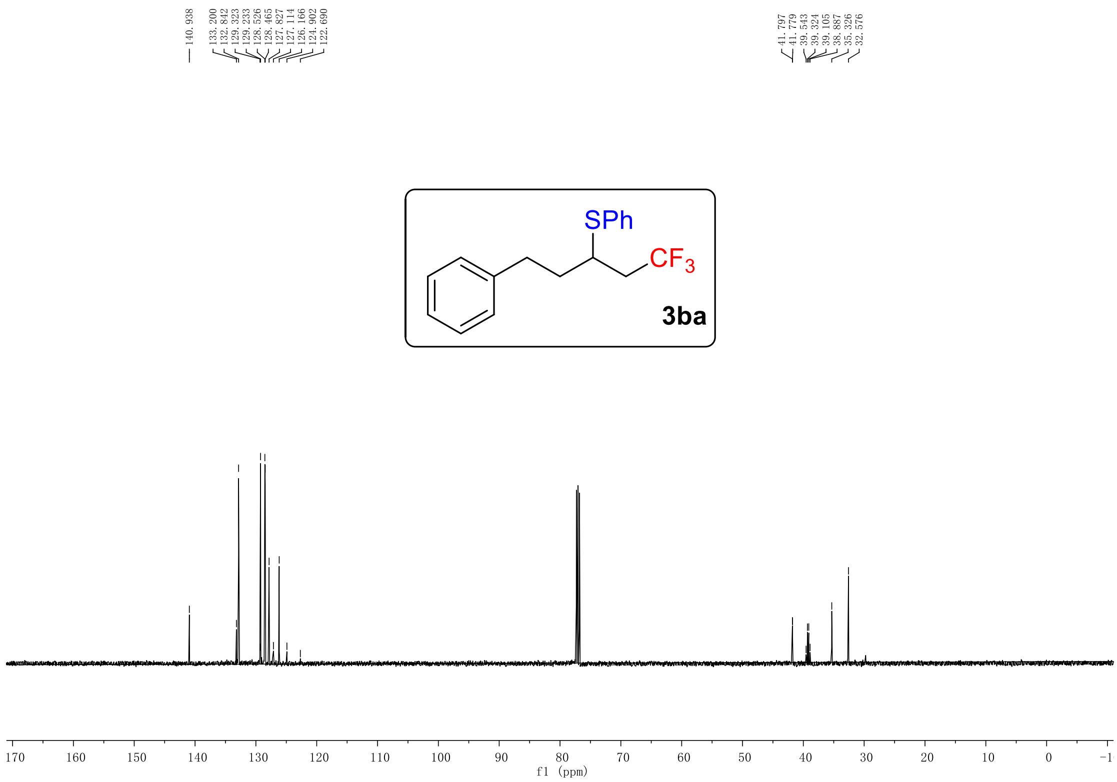
f1 (ppm)



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133.200
132.842
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129.233
128.526
128.465
127.827
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126.166
124.902
122.690
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39.543
39.324
39.105
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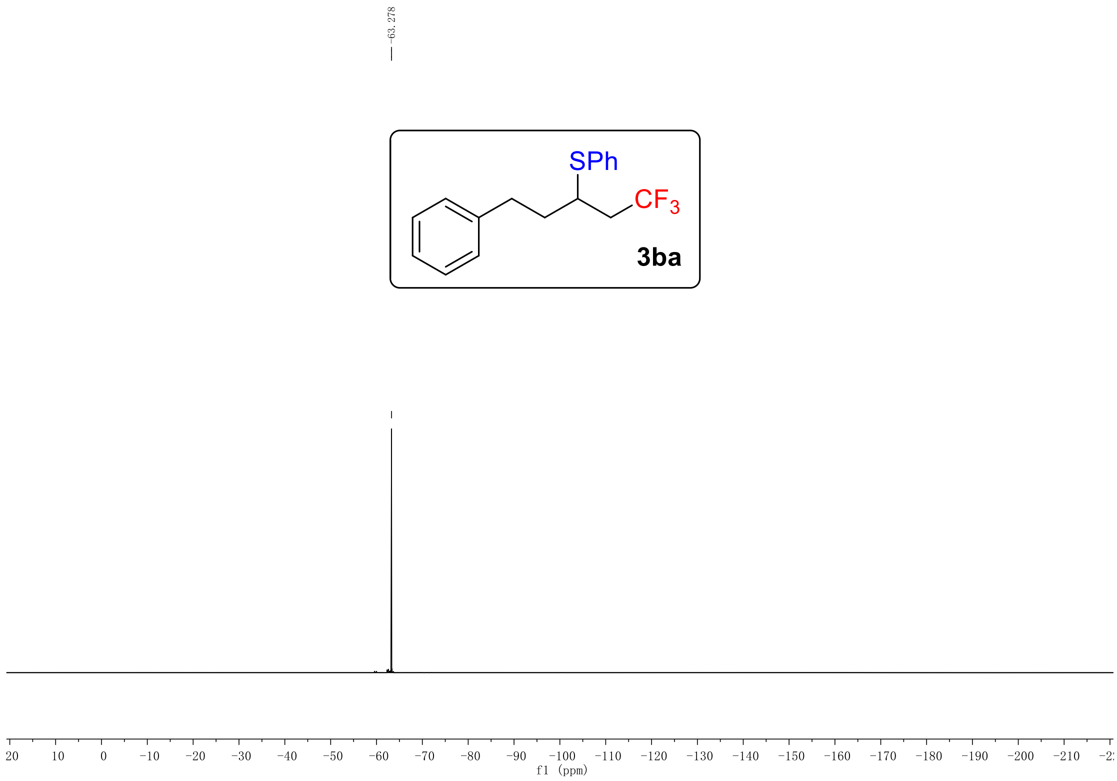
SPh
CF3
3ba
f1 (ppm)



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CF3
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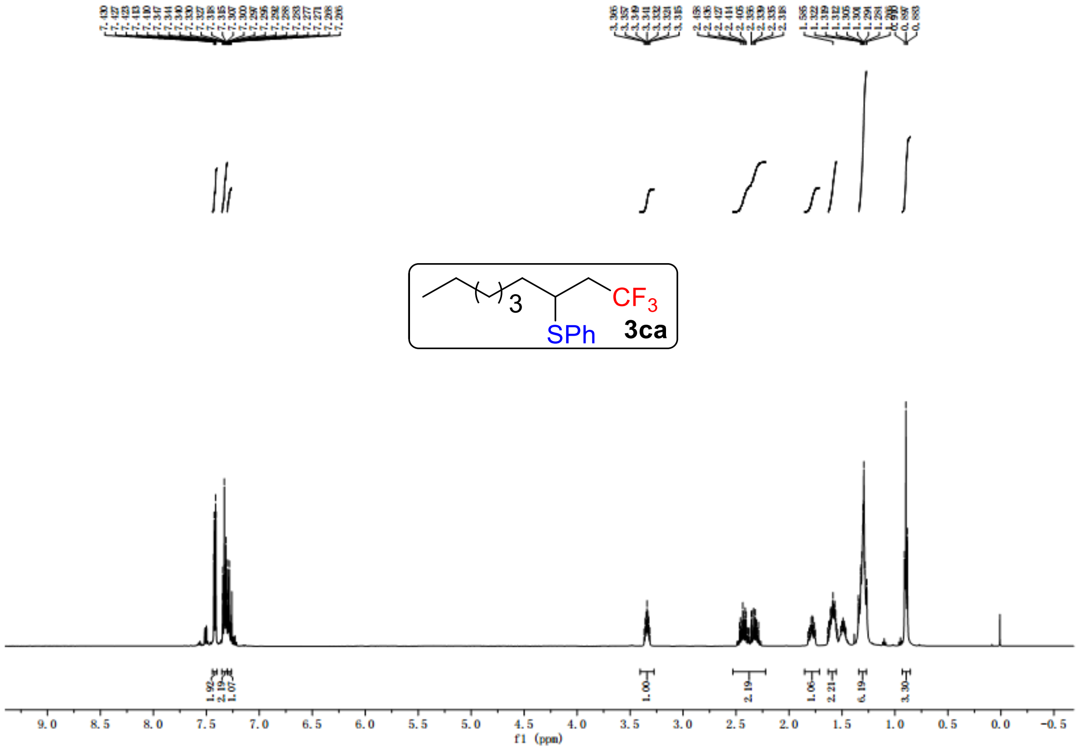
f1 (ppm)



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SPh
3ca
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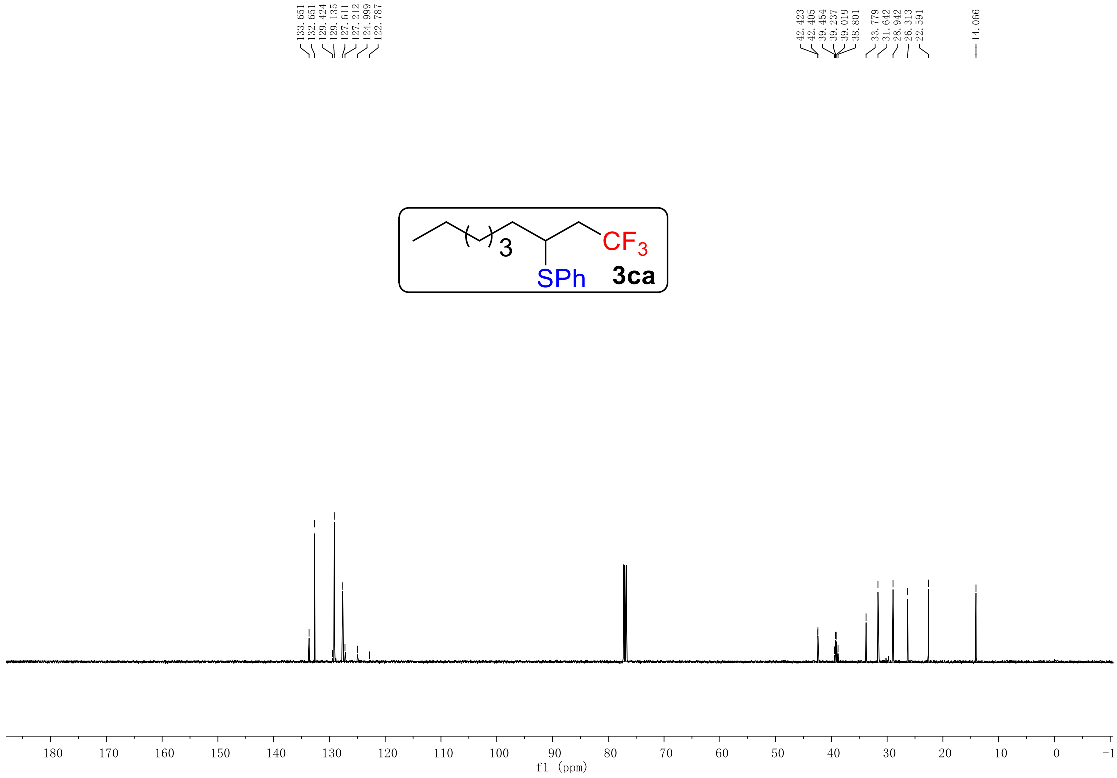
2.19
1.07
1.00
2.19
1.06
2.21
6.19
3.30
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



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122.787
42.423
42.405
39.454
39.237
39.019
38.801
33.779
31.642
28.942
26.313
22.591
14.066
CF3
SPh
3ca
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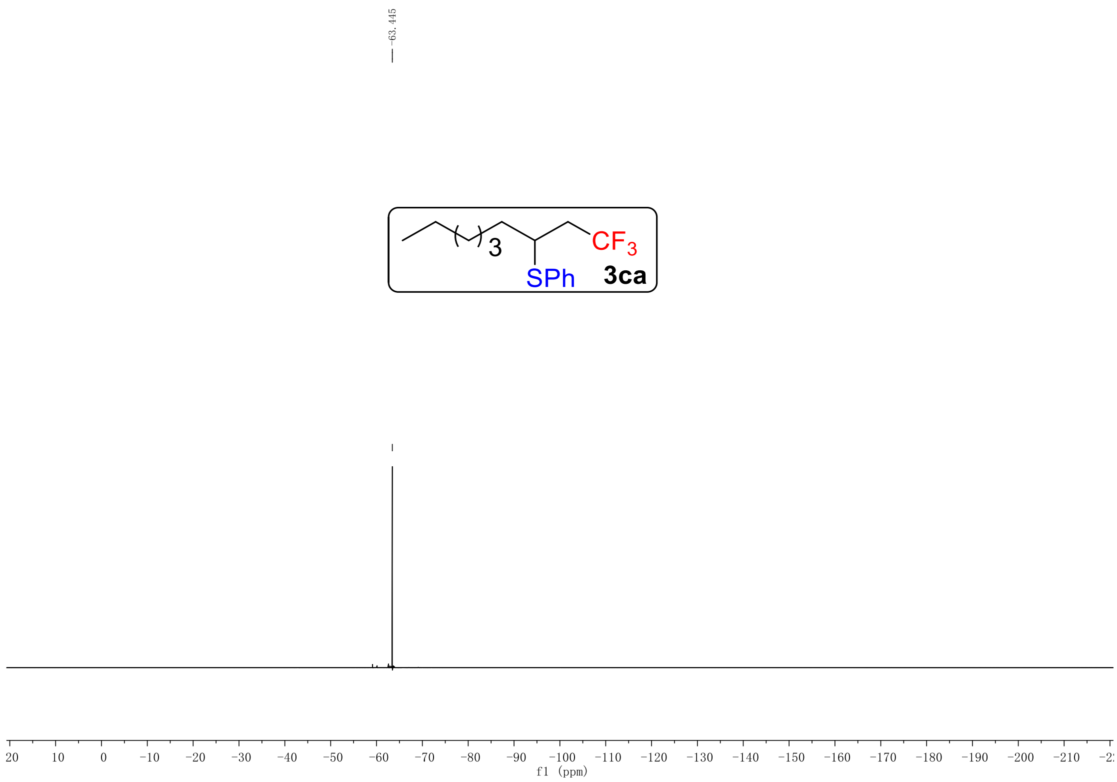
f1 (ppm)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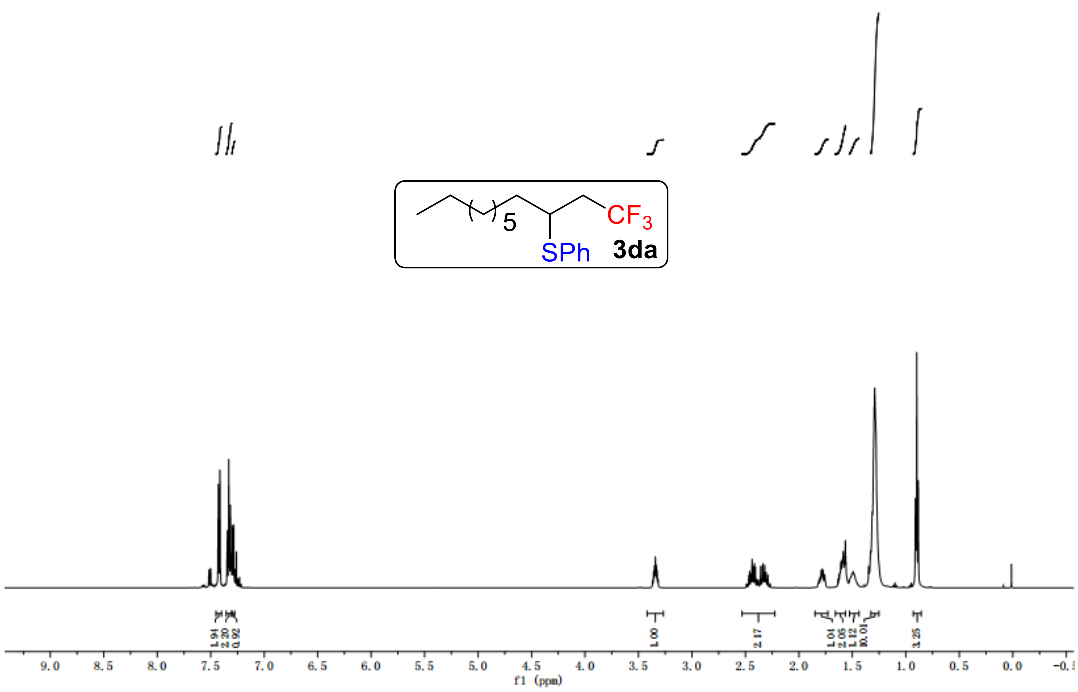
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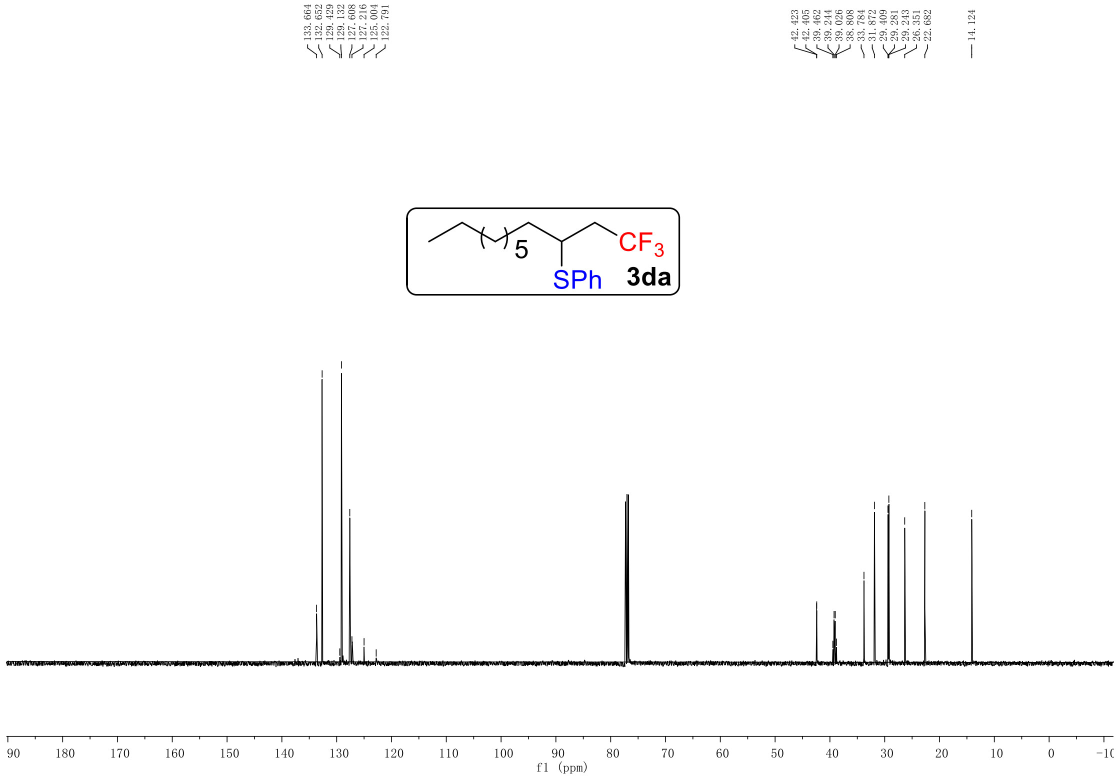
10.01
3.25
f1 (ppm)



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42.405
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39.026
38.808
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5
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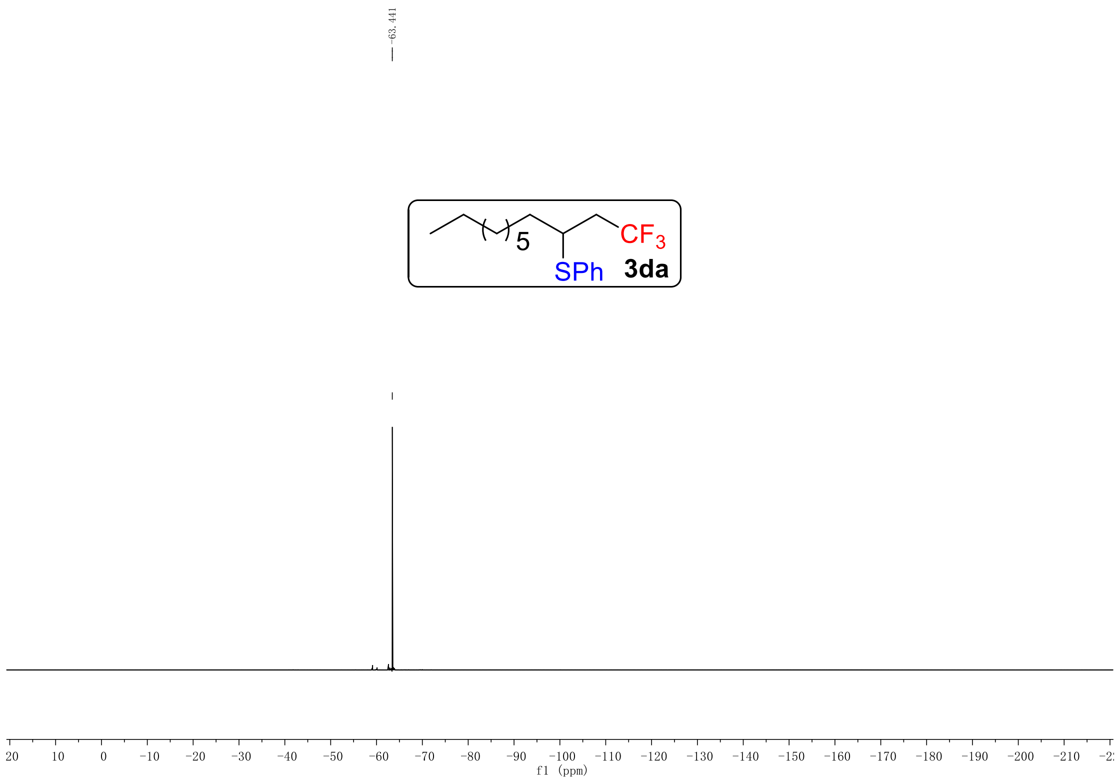
SPh
3da
f1 (ppm)



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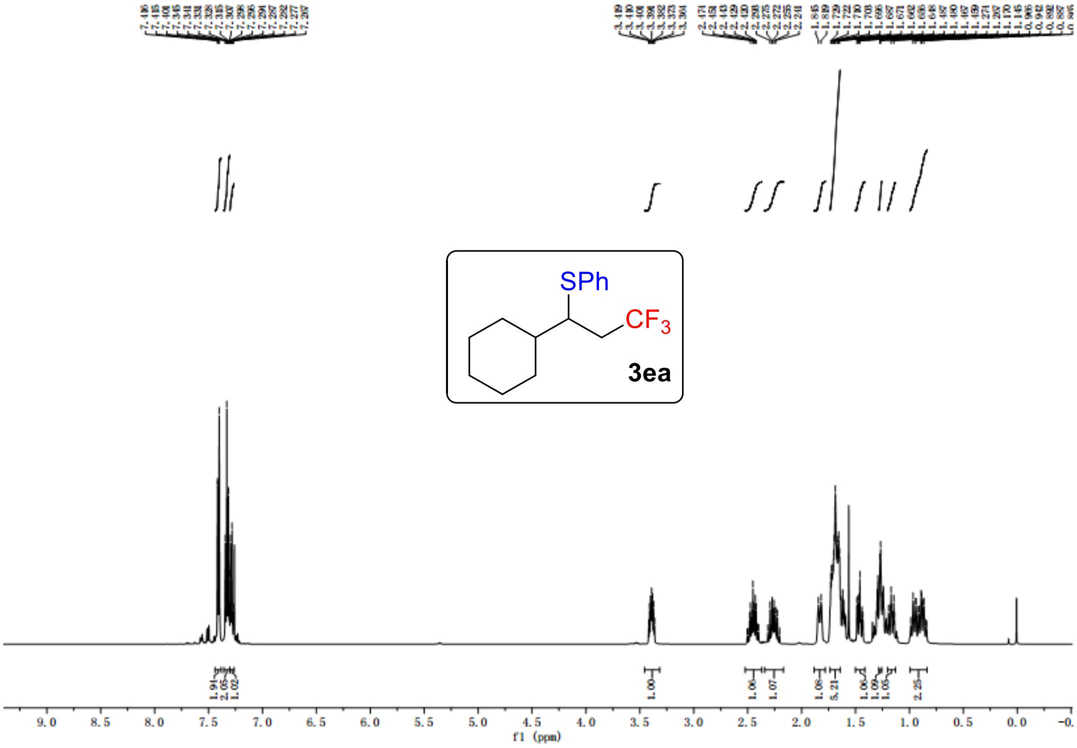

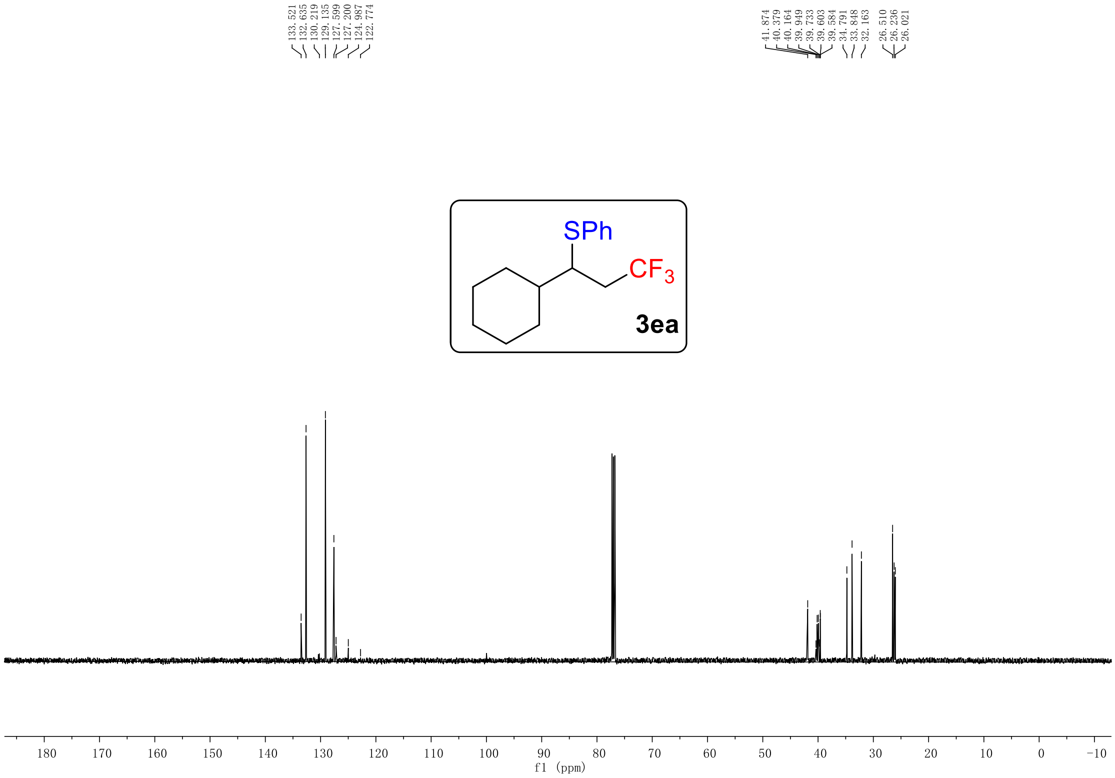

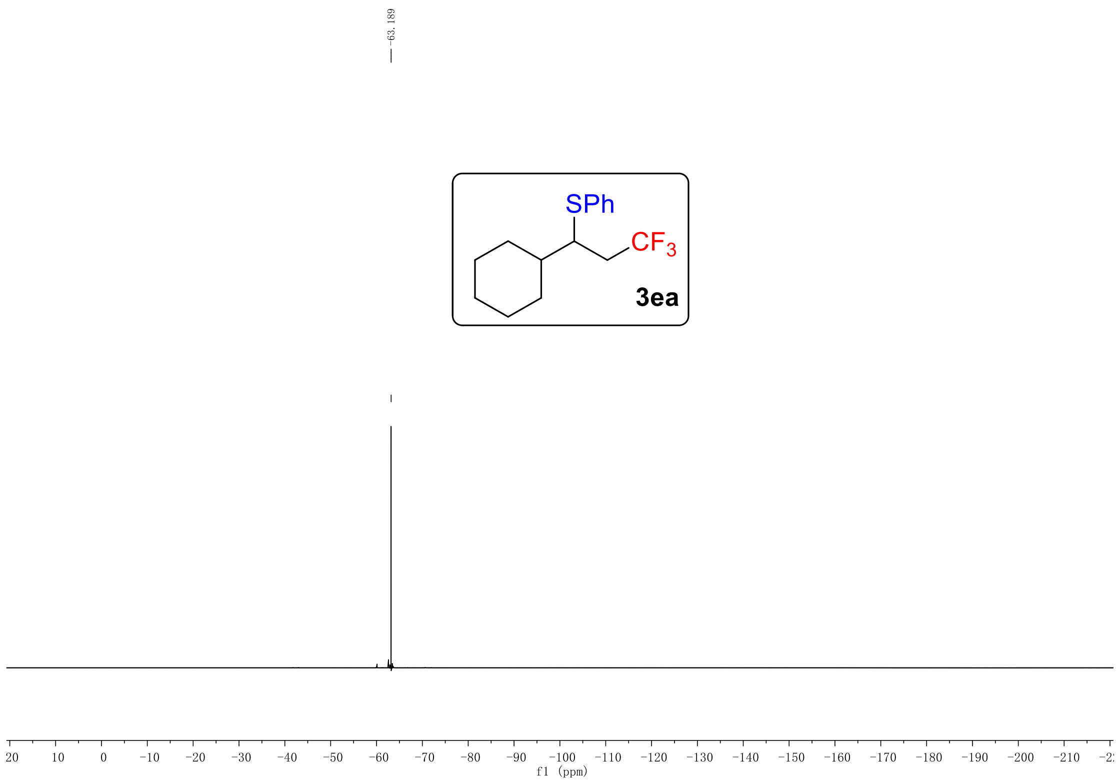
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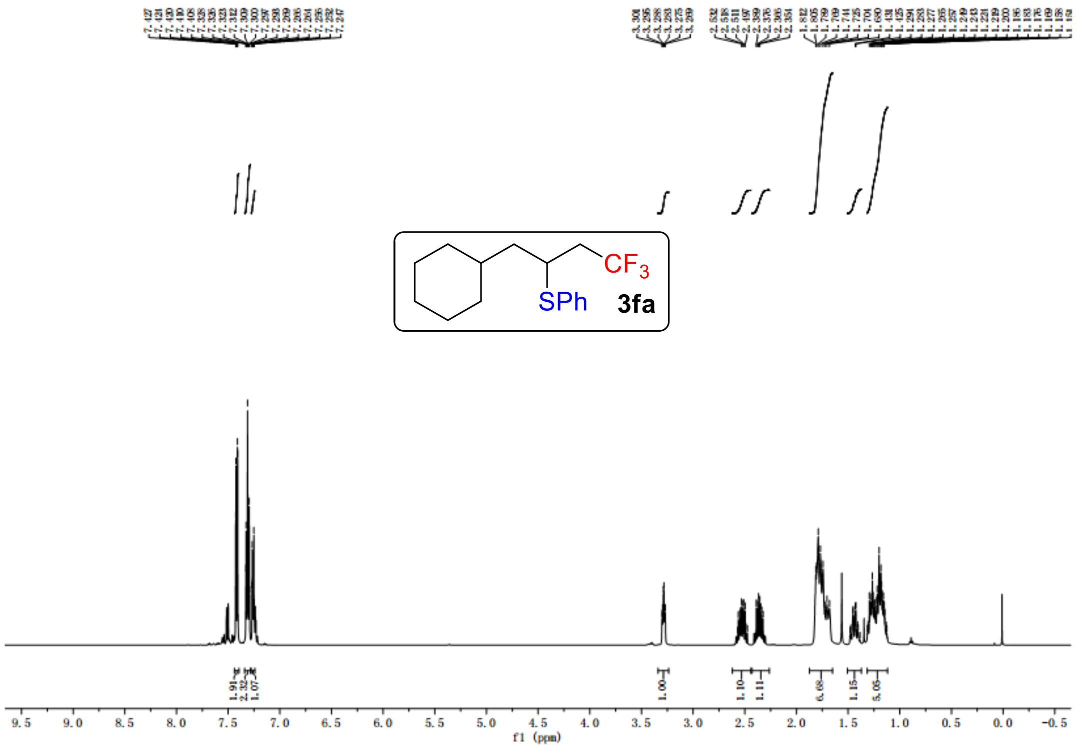
f1 (ppm)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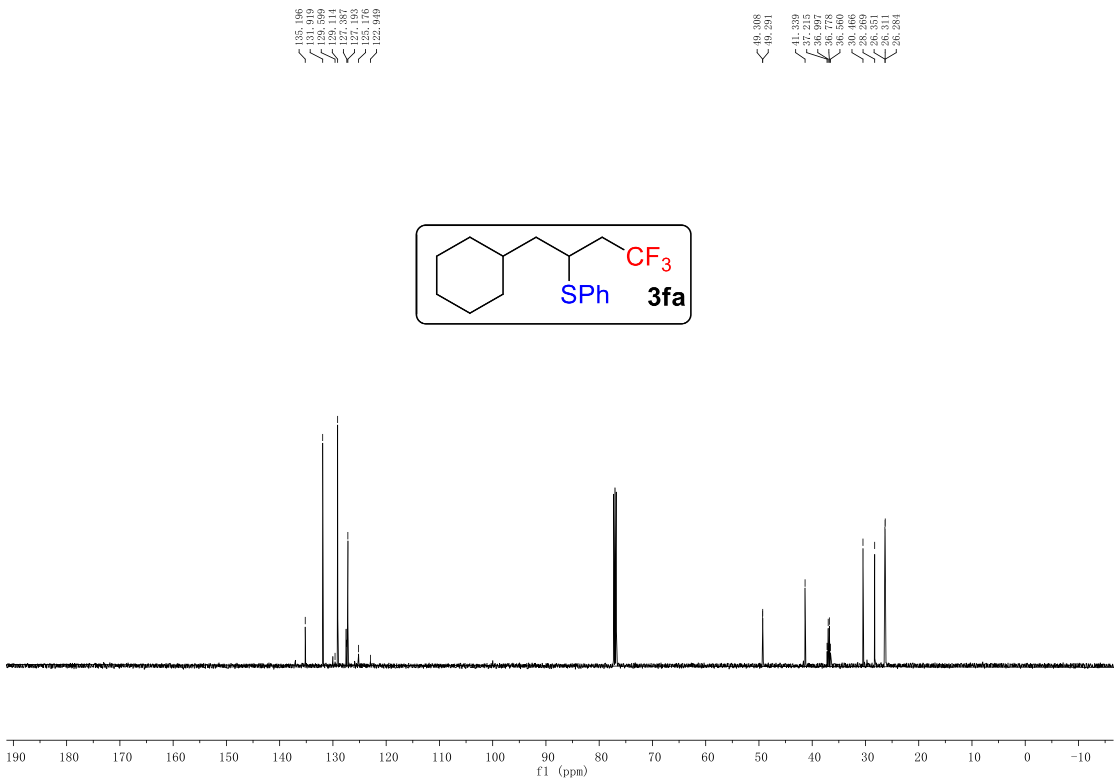
3fa
f1 (ppm)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36.560
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28.269
26.351
26.311
26.284
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SPh
3fa
190
180
170
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30
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10
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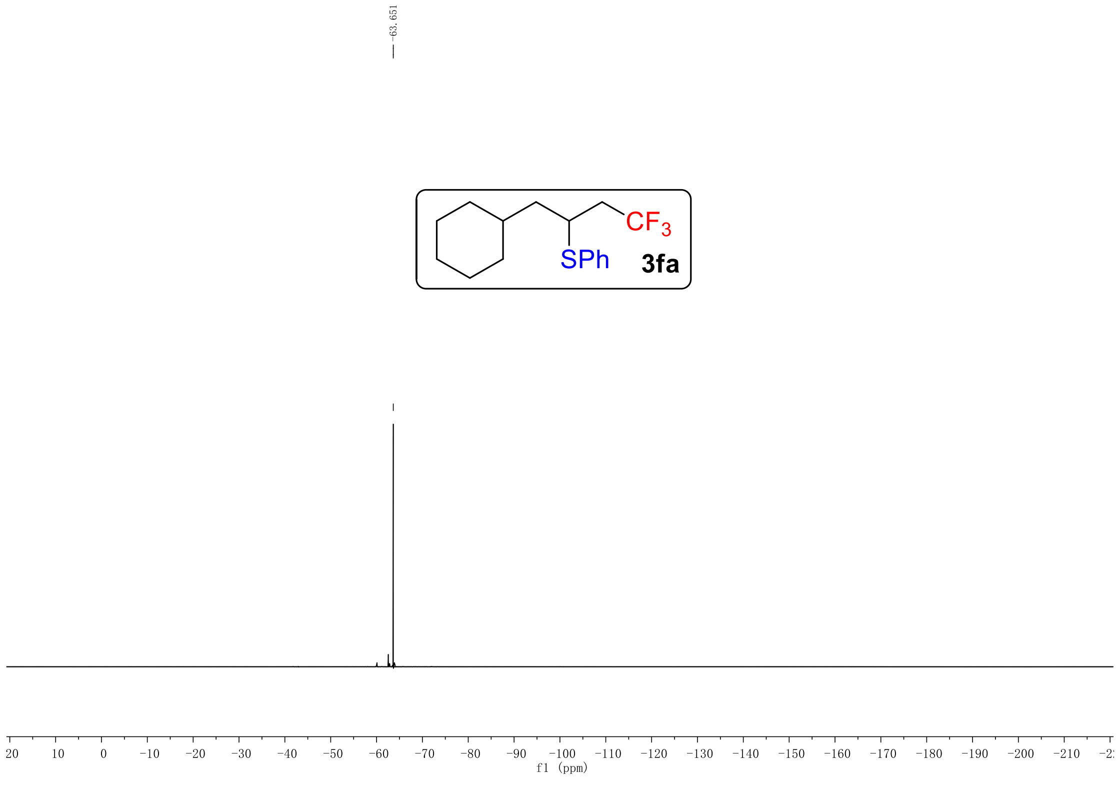
−10
f1 (ppm)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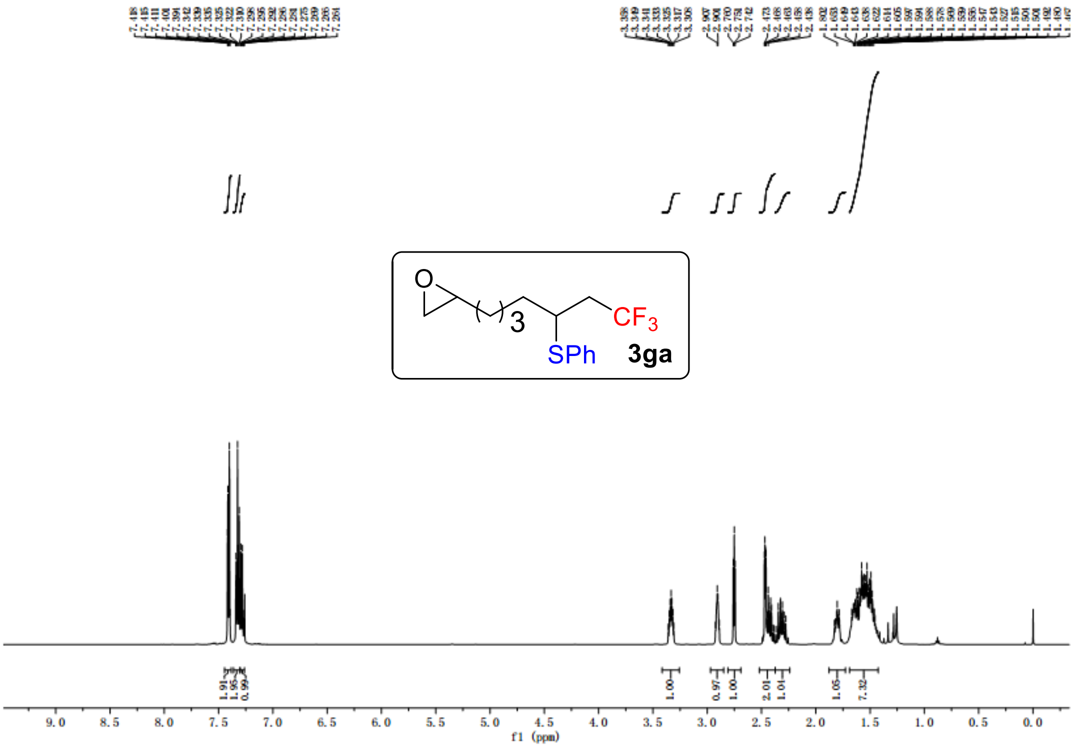

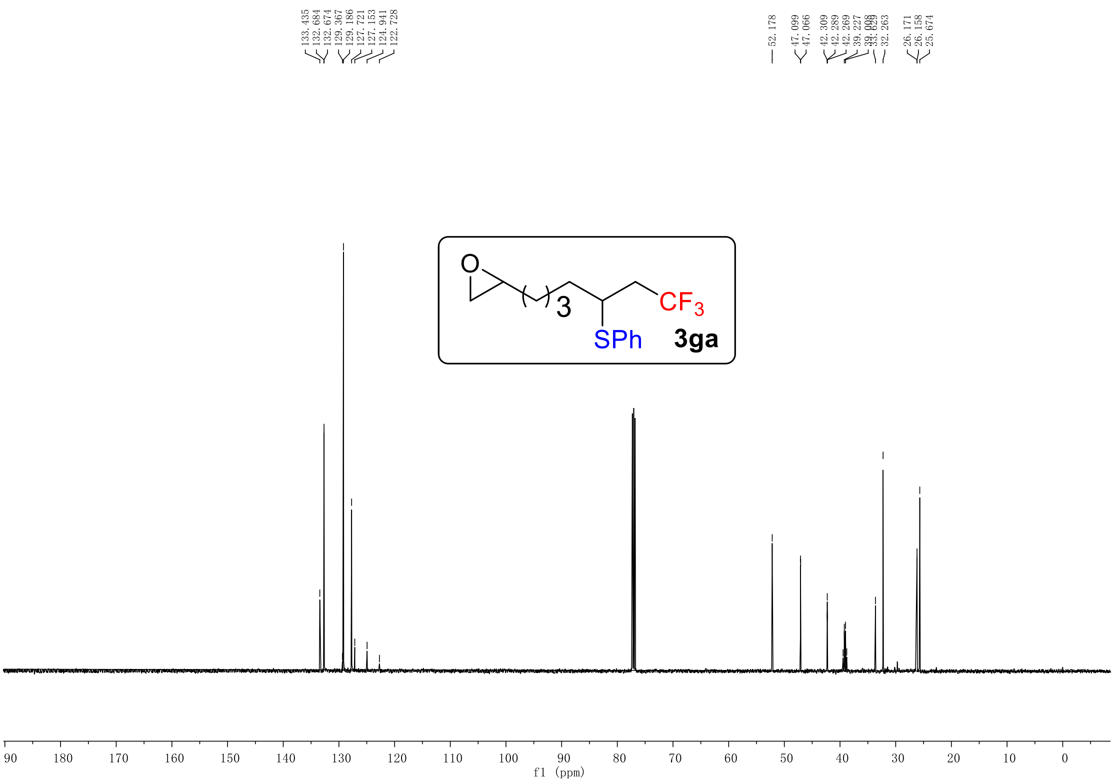

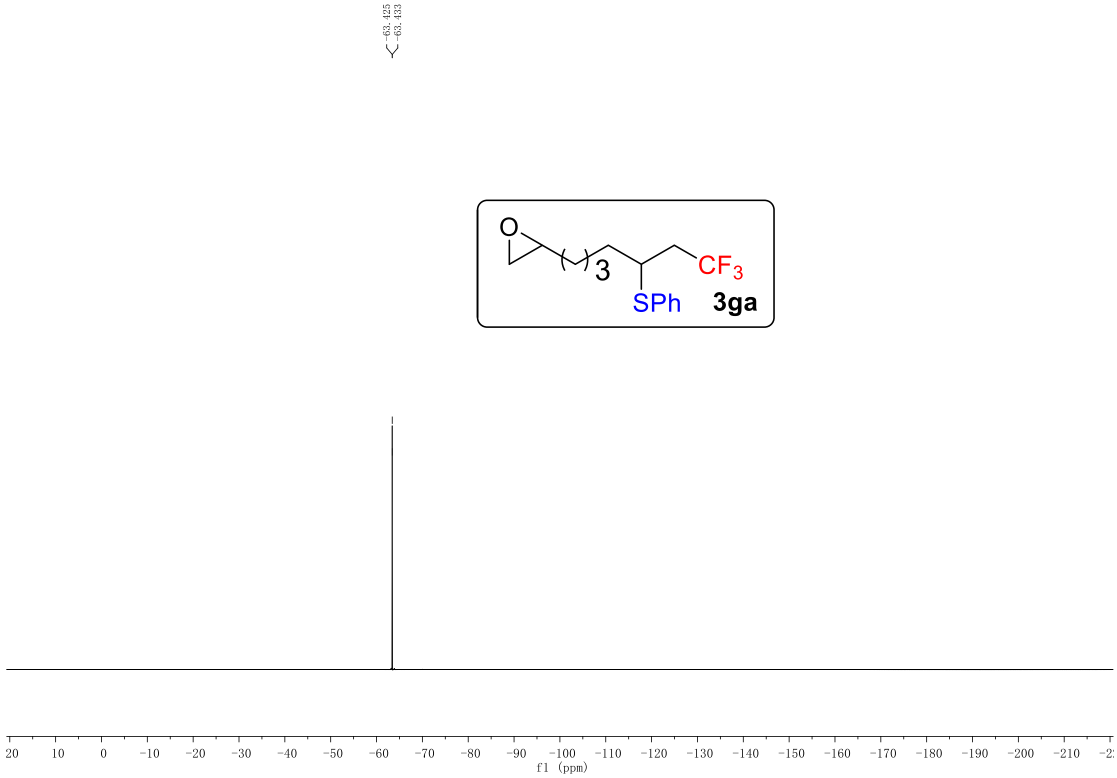
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SPh
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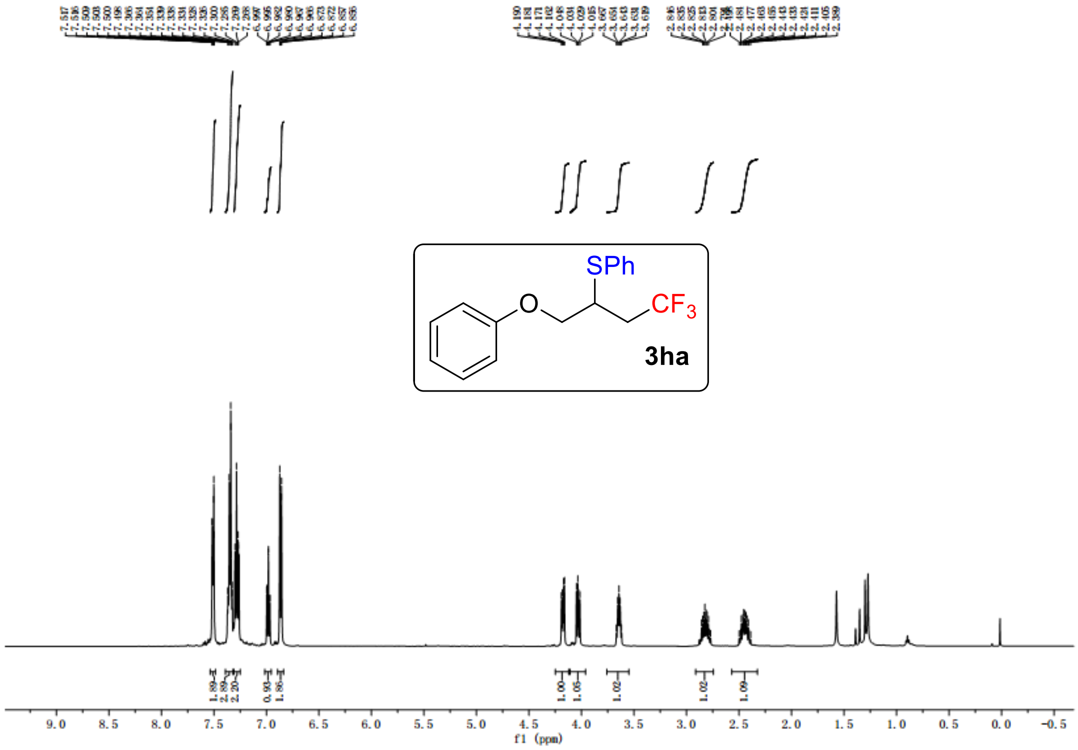
f1 (ppm)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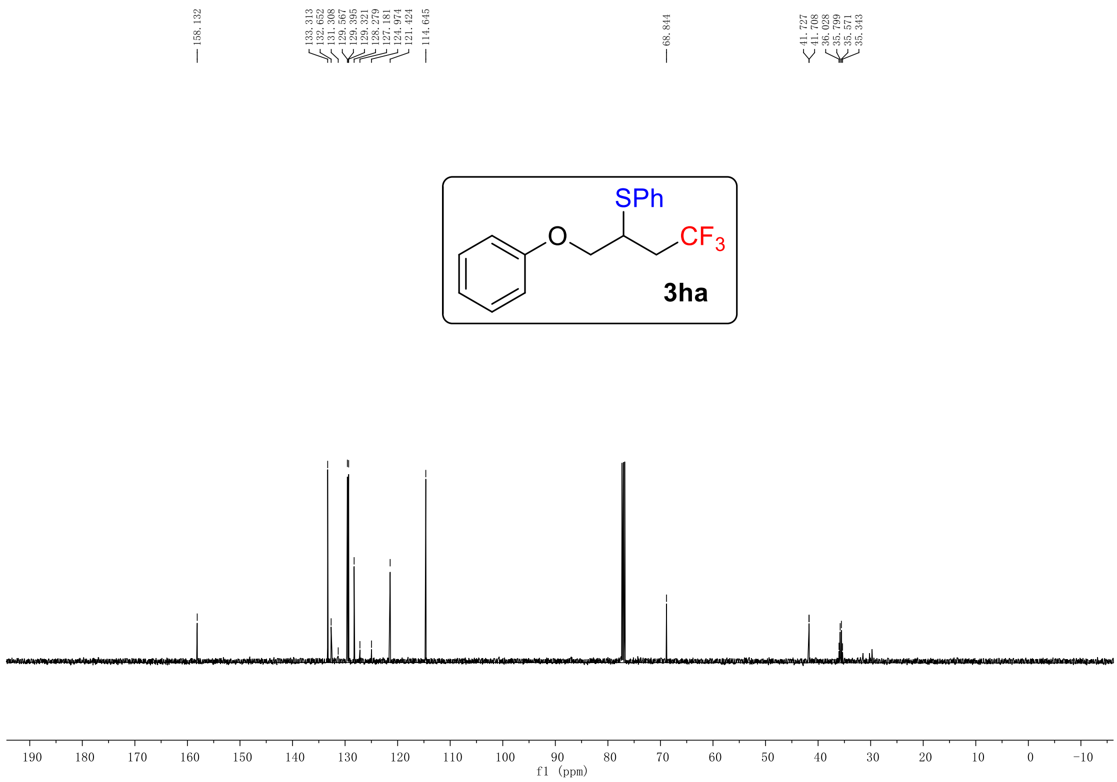
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CF3
3ha
190
180
170
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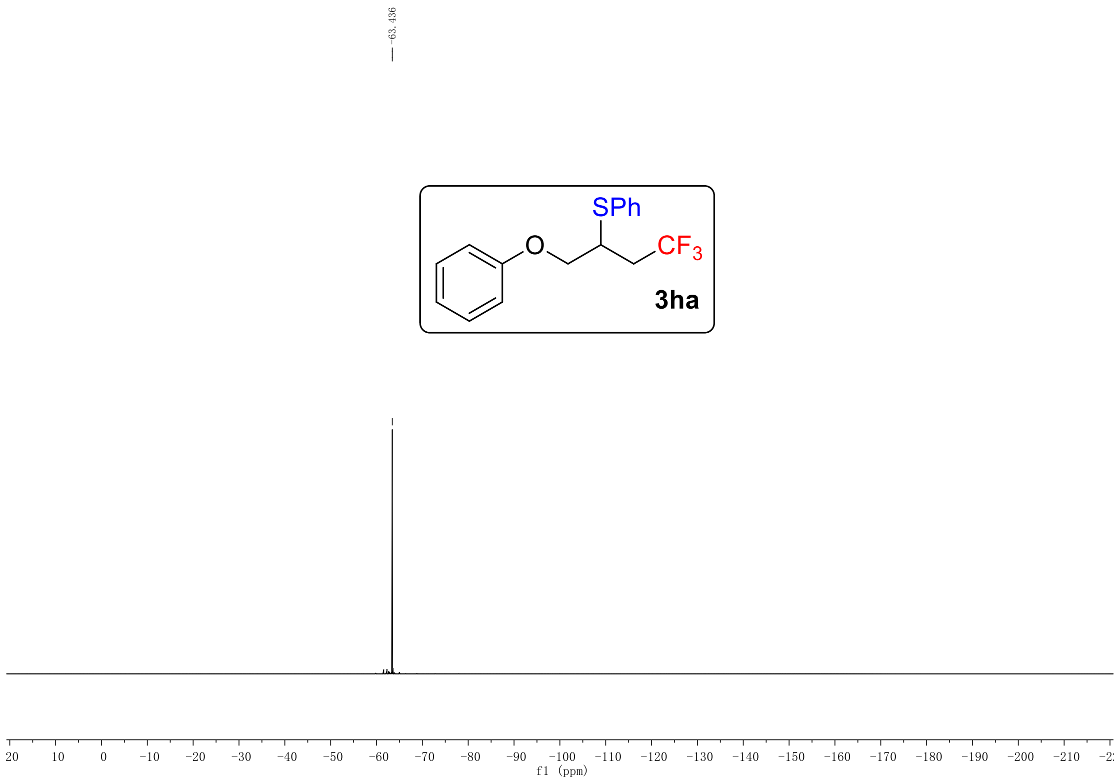
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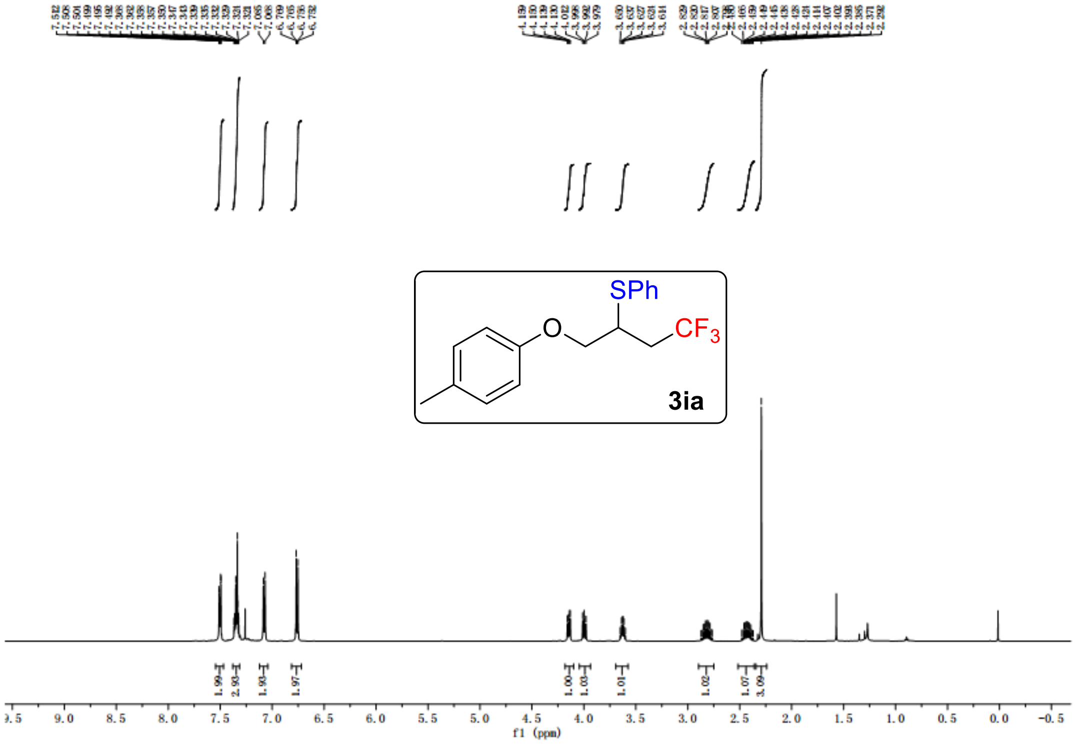
f1 (ppm)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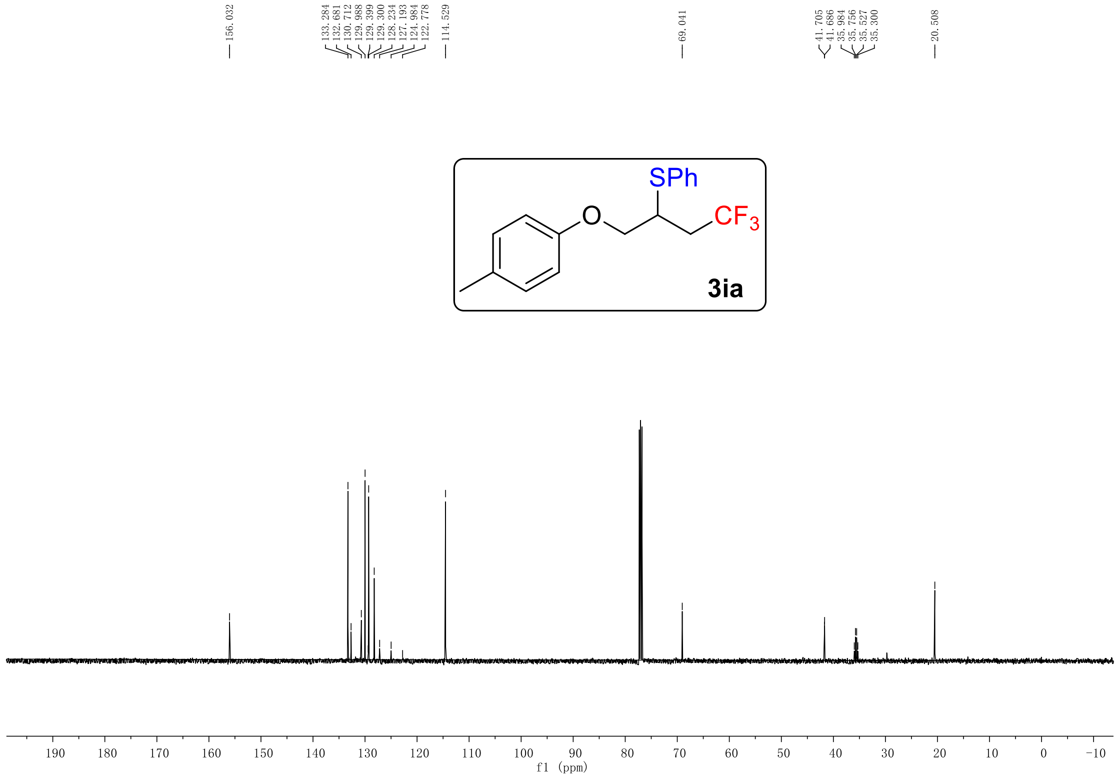
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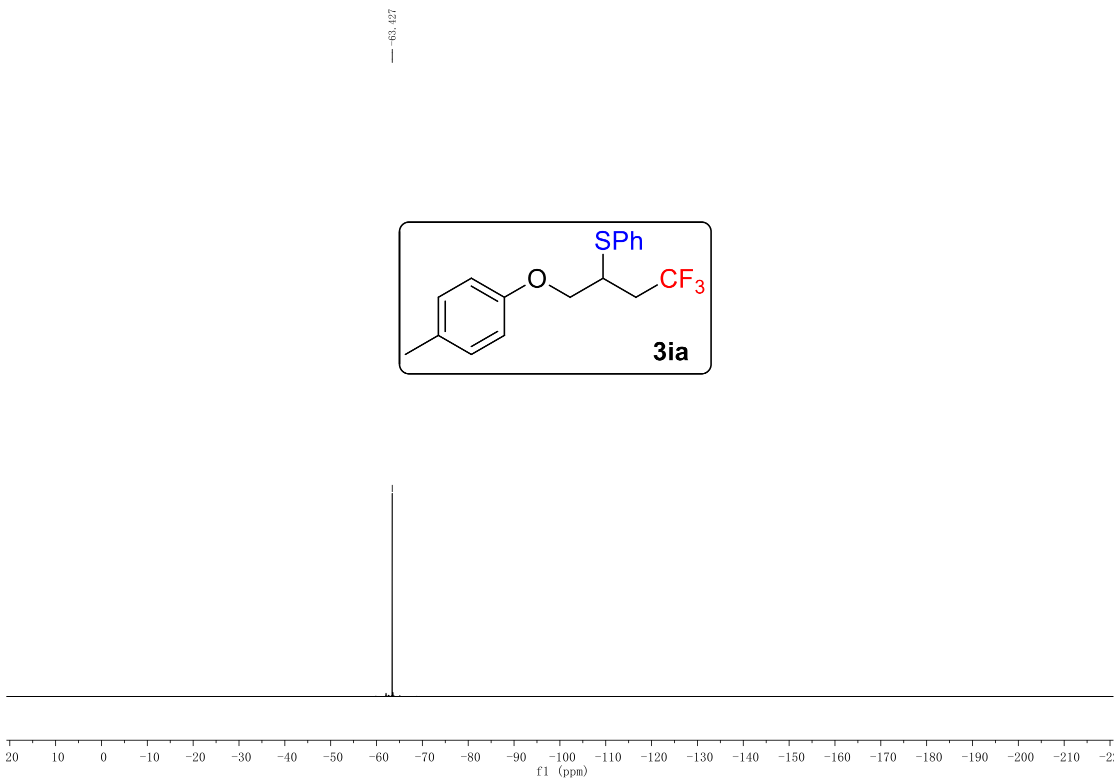
f1 (ppm)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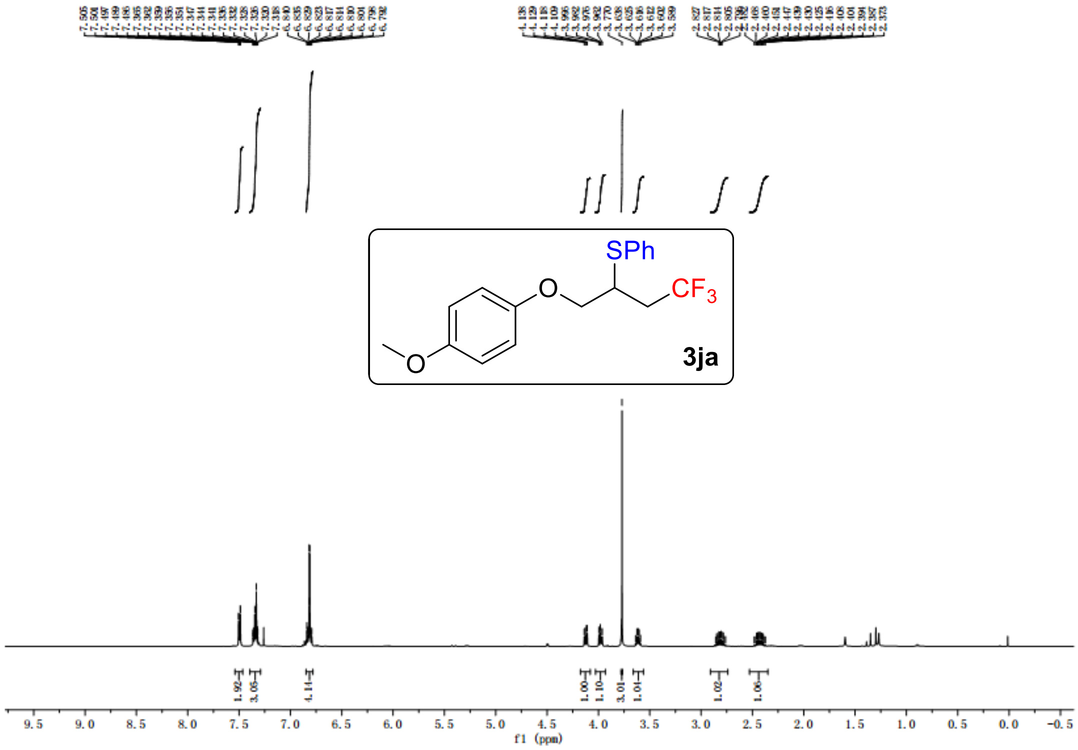
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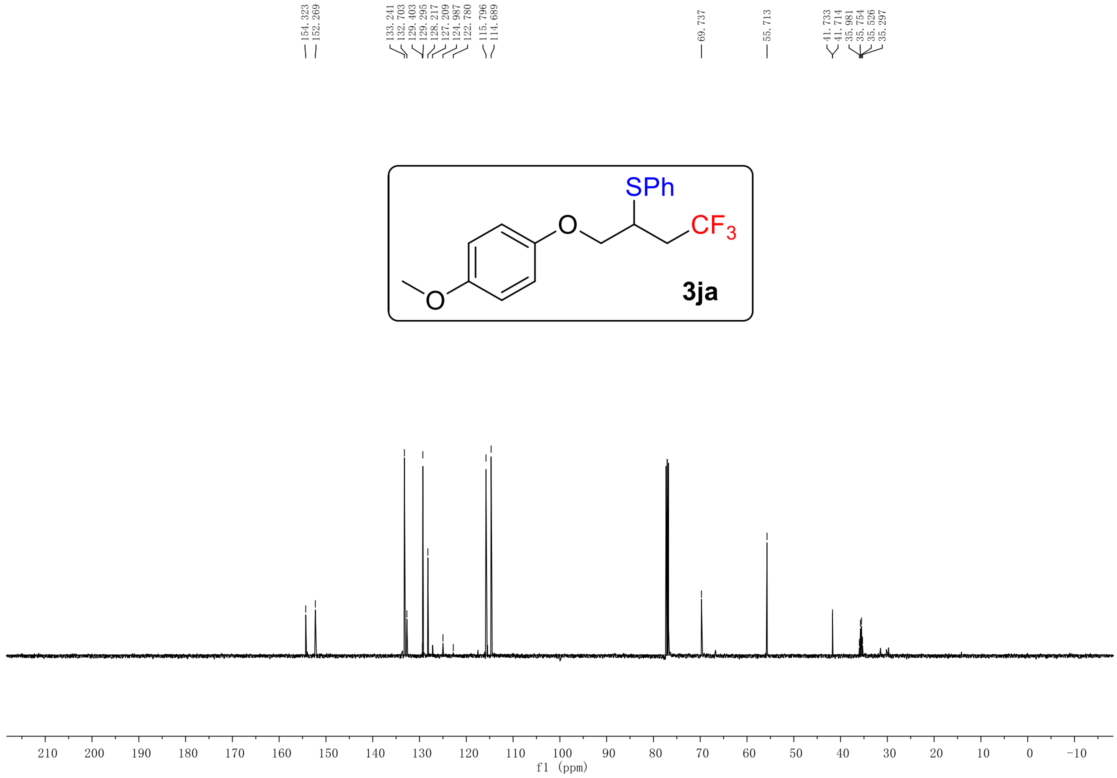
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55.713
41.733
41.714
35.981
35.754
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O
CF3
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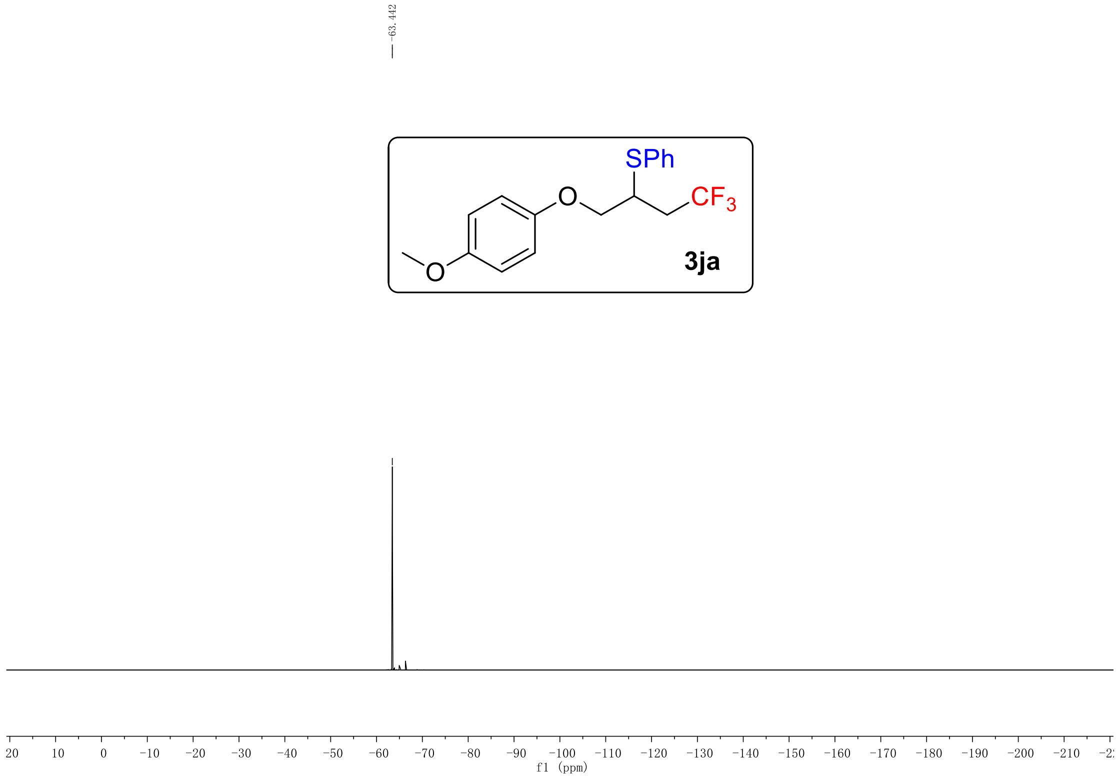
f1 (ppm)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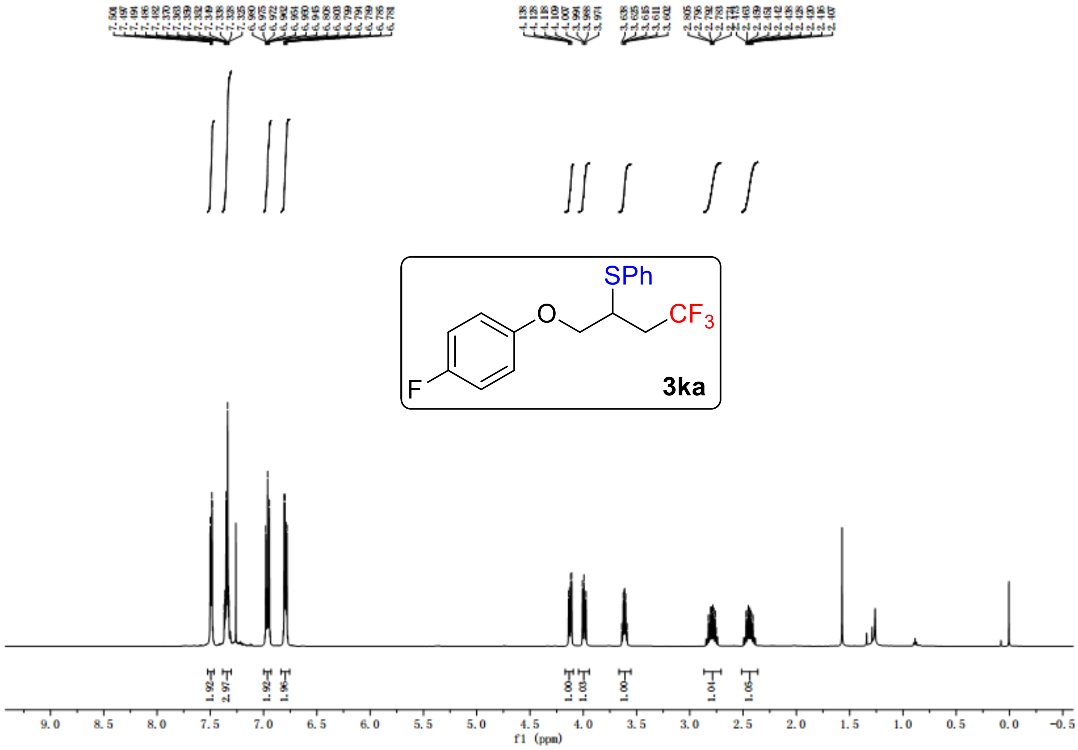
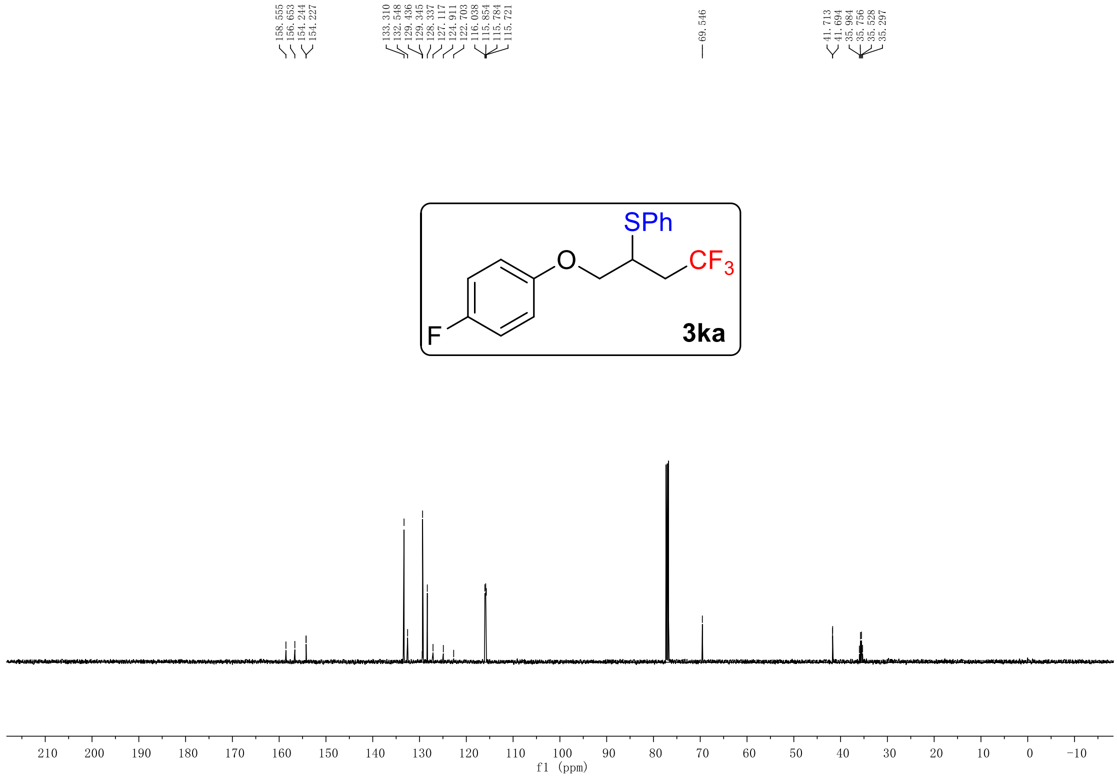
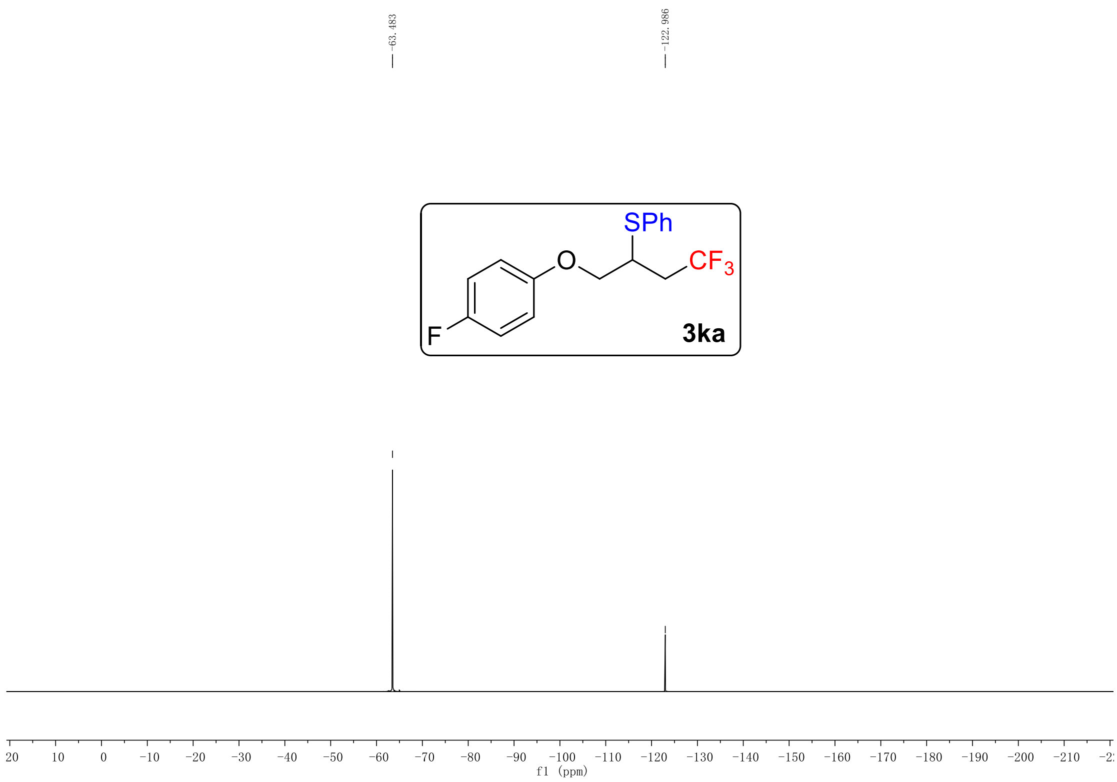
f1 (ppm)







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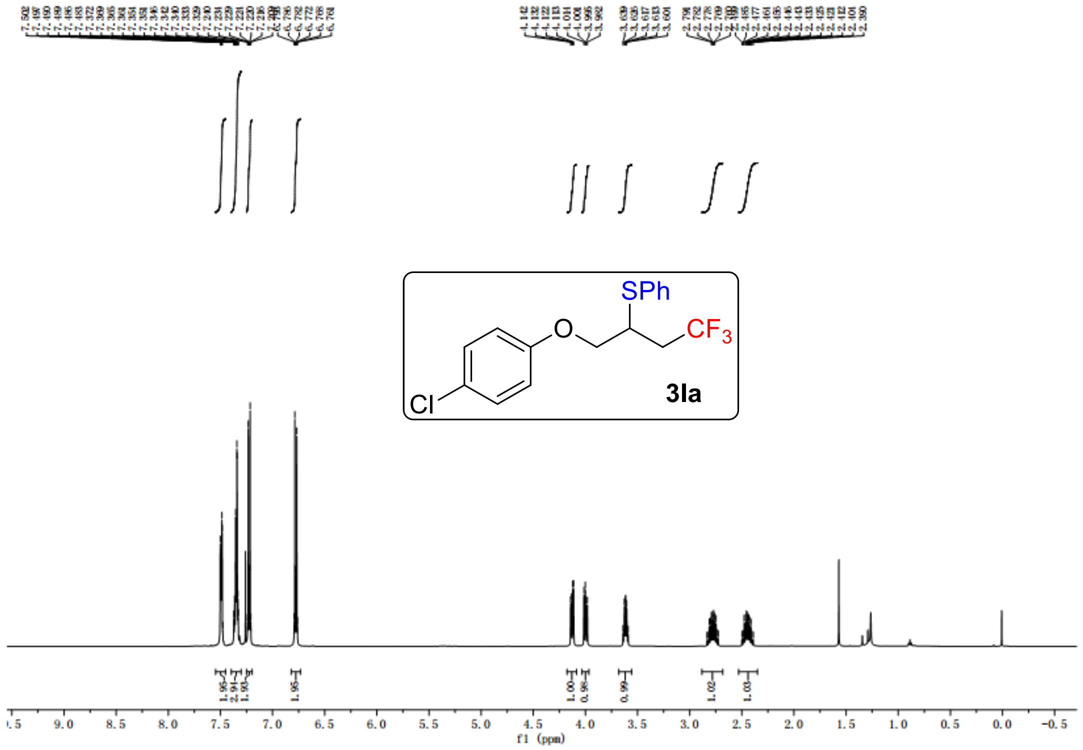
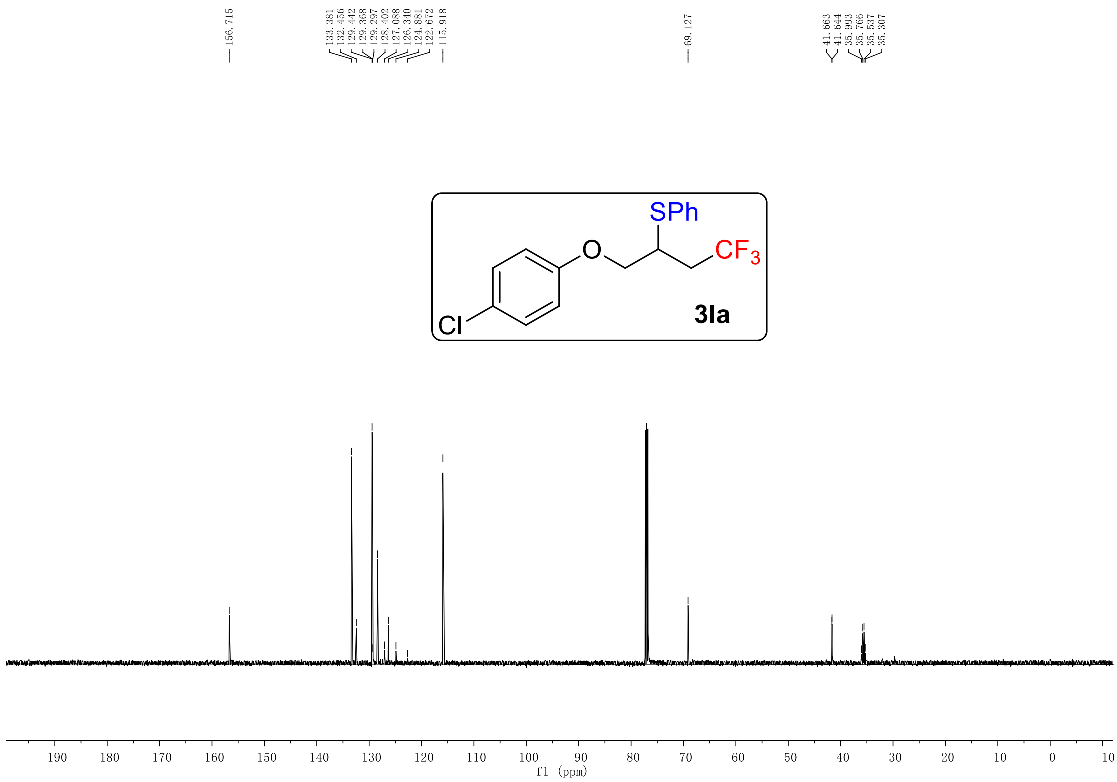


SPh
O
CF3
Cl
3la
f1 (ppm)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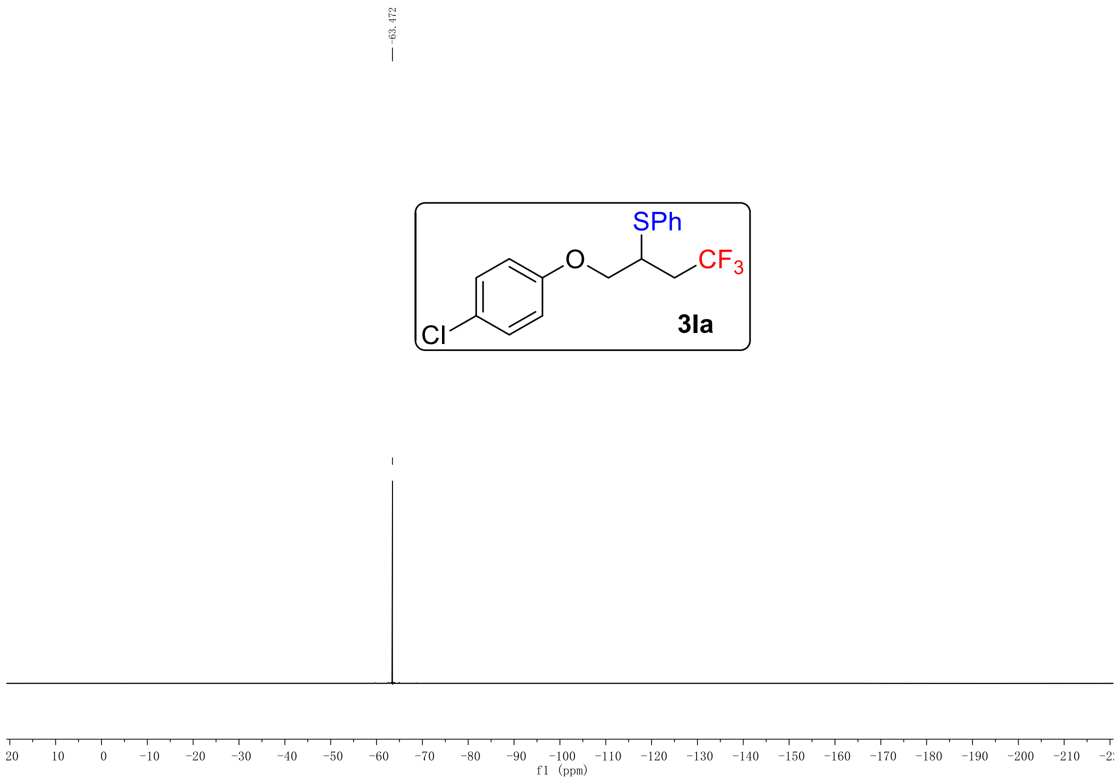
129.368
129.297
128.402
127.088
126.340
124.881
122.672
115.918
69.127
41.663
41.644
35.993
35.766
35.537
35.307
SPh
O
CF3
Cl
3la
f1 (ppm)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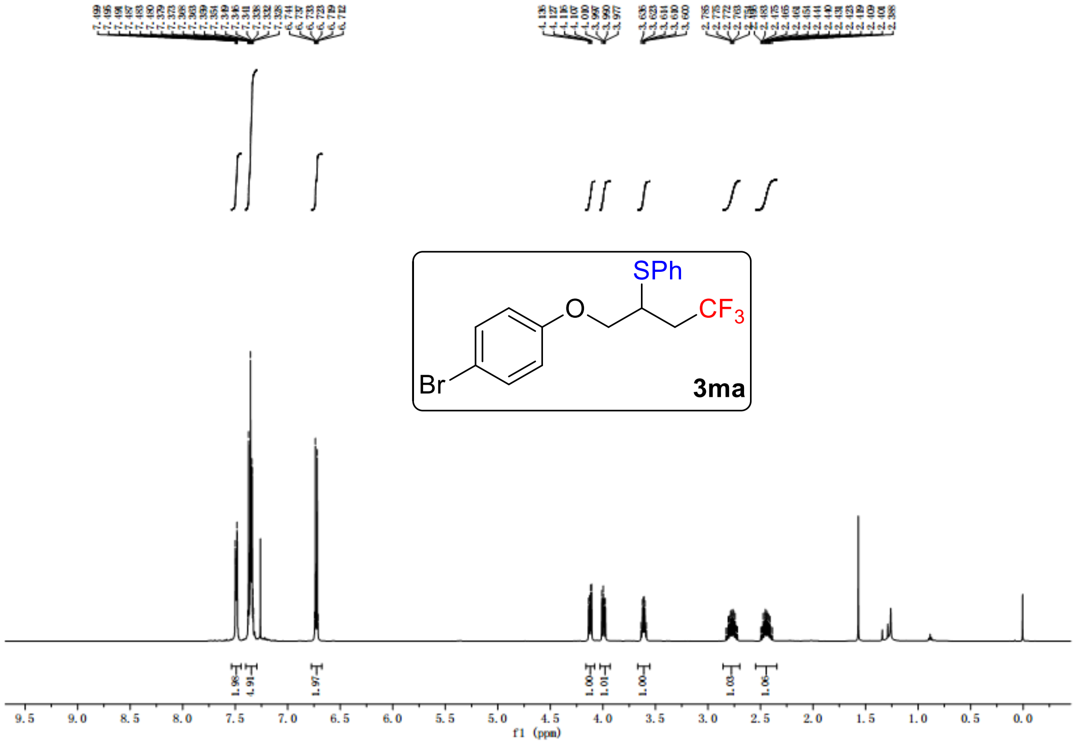
Cl
3la
f1 (ppm)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O
CF3
Br
3ma
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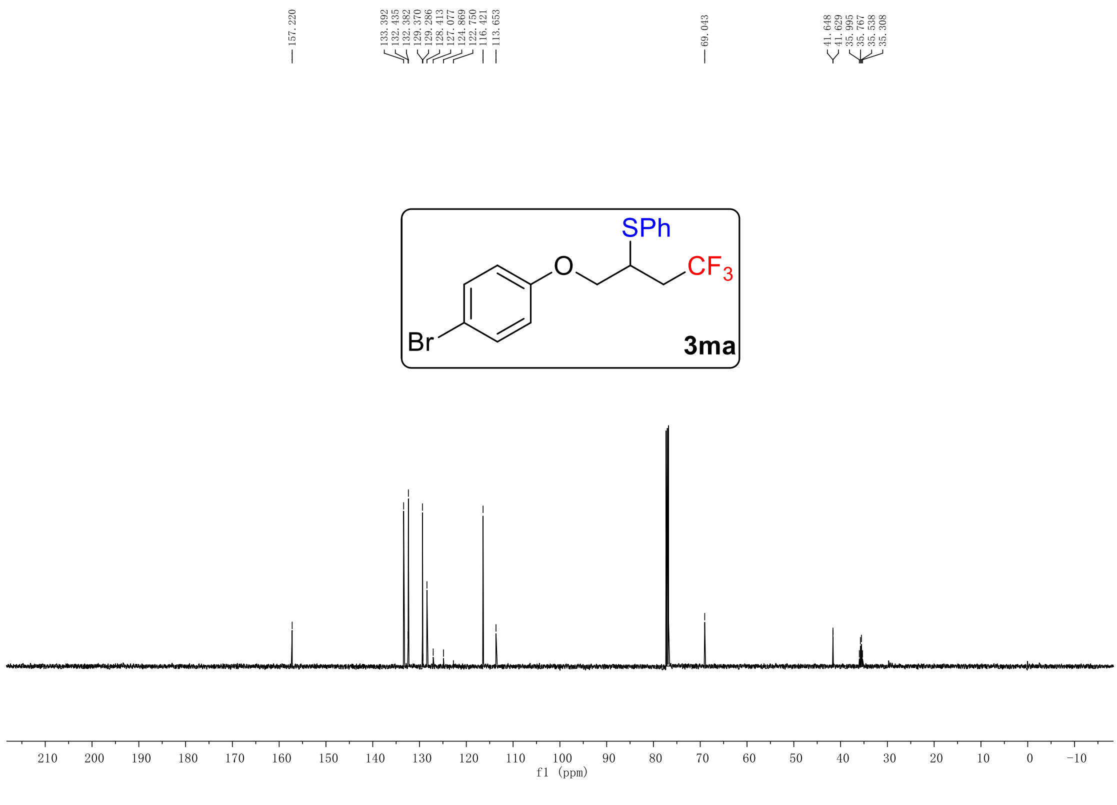
4.91
1.97
1.00
1.01
1.00
1.03
1.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.286
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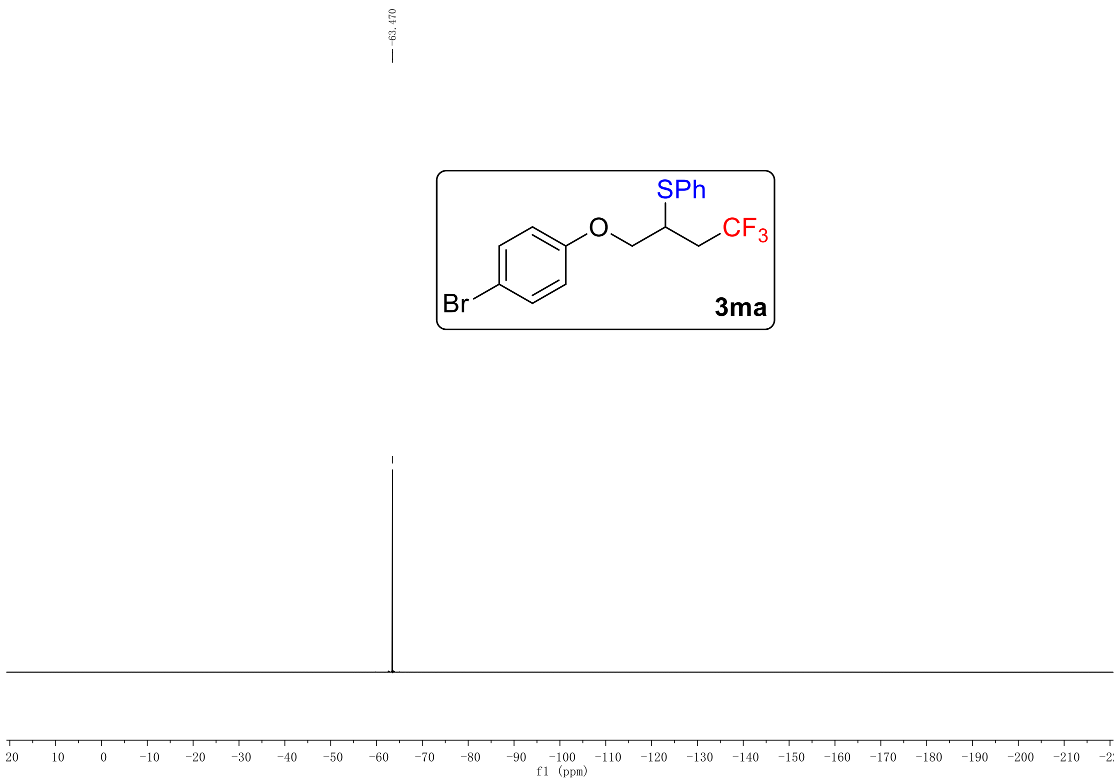
127.077
124.869
122.750
116.421
113.653
69.043
41.648
41.629
35.995
35.767
35.538
35.308
SPh
O
CF3
Br
3ma
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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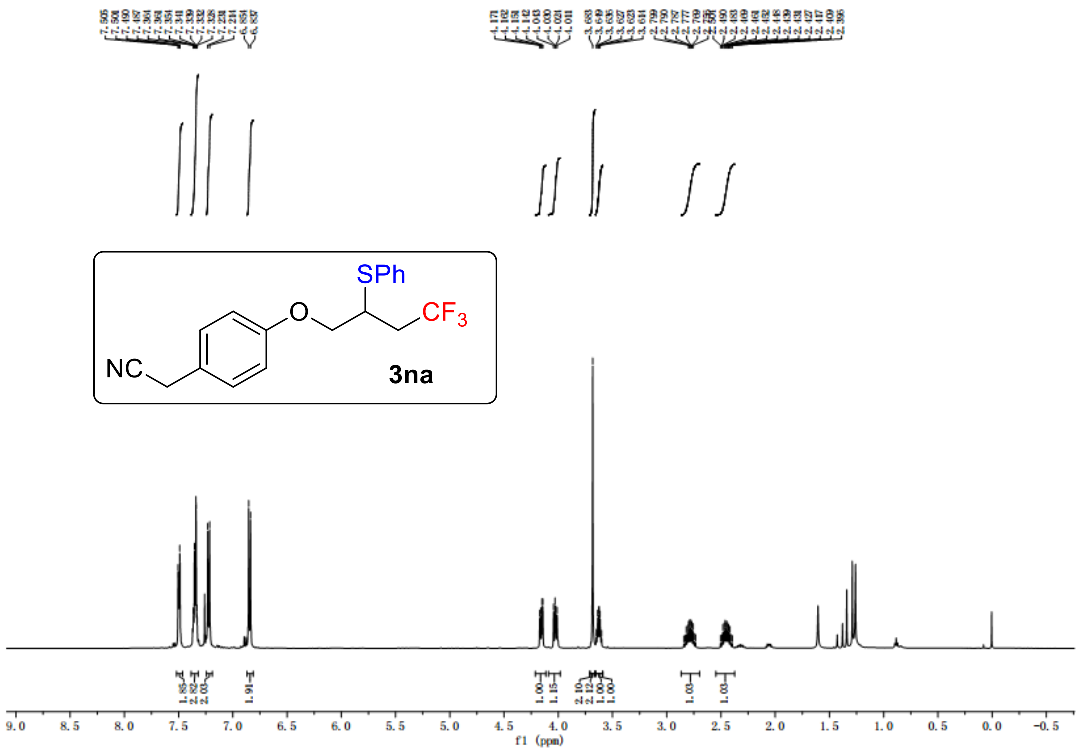
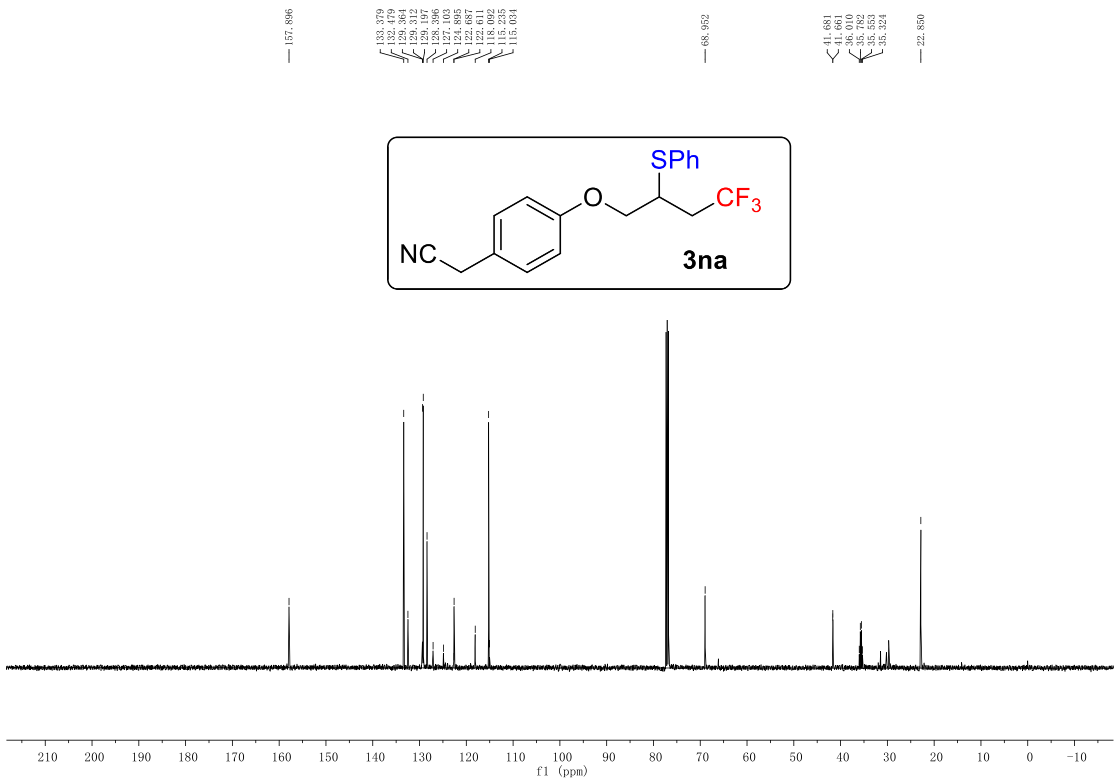
f1 (ppm)


SPh
O
CF3
NC
3na
f1 (ppm)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115.235
115.034
68.952
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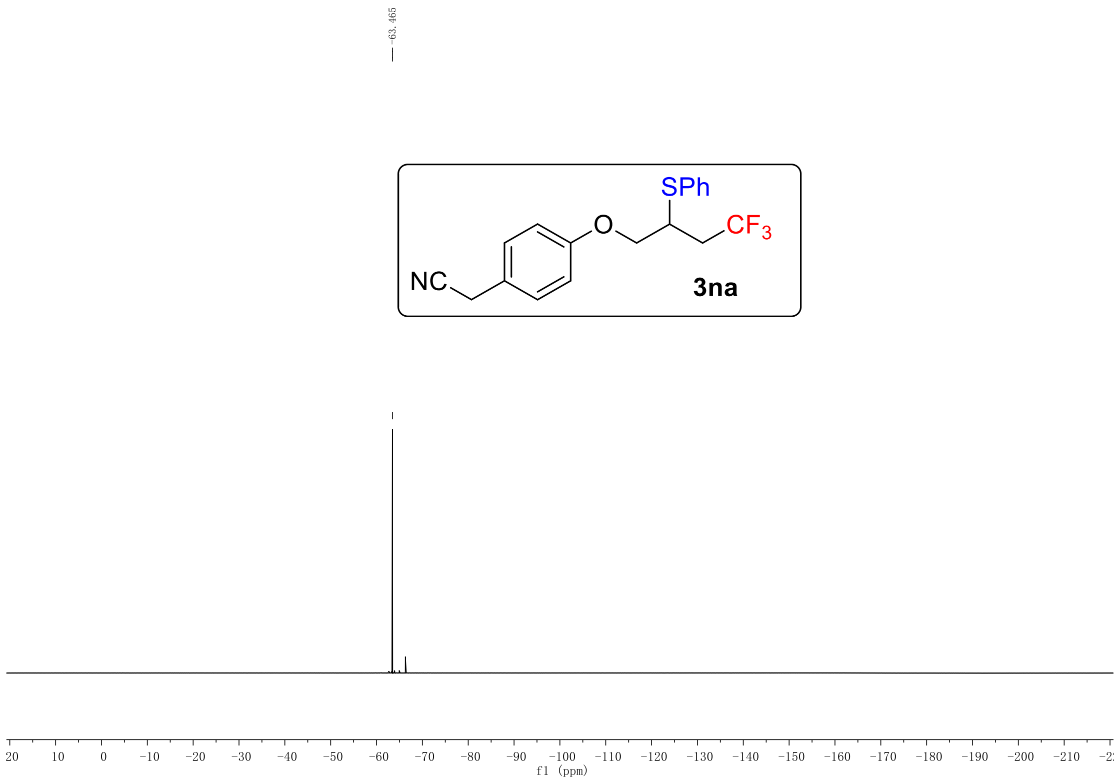
SPh
O
CF3
NC
3na
f1 (ppm)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CF3
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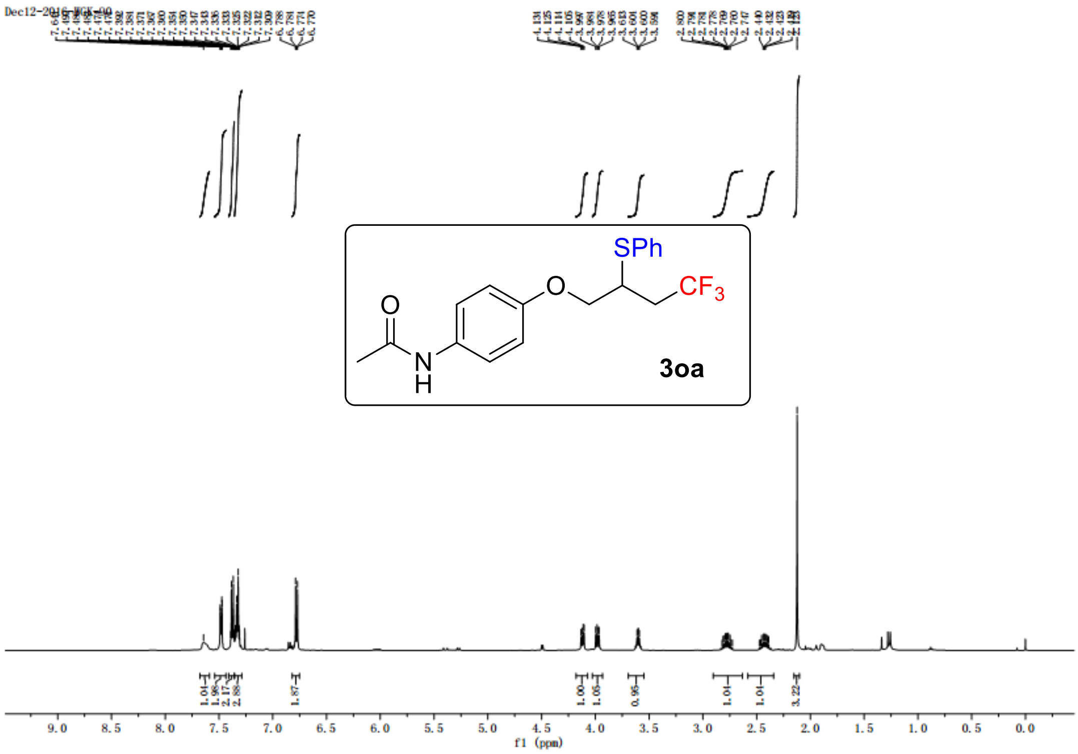
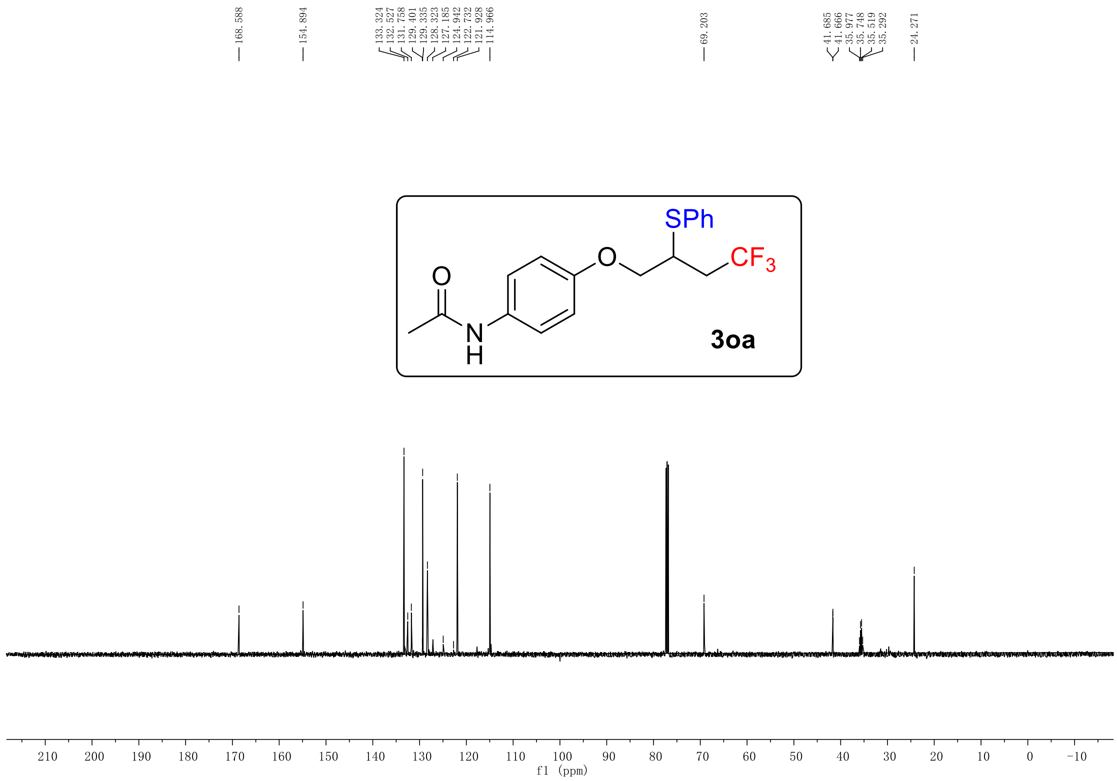
f1 (ppm)


SPh
O
CF3
O
N
H
3oa
1.04
1.98
2.17
2.88
1.87
1.00
1.05
0.95
1.04
1.04
3.22
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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122.732
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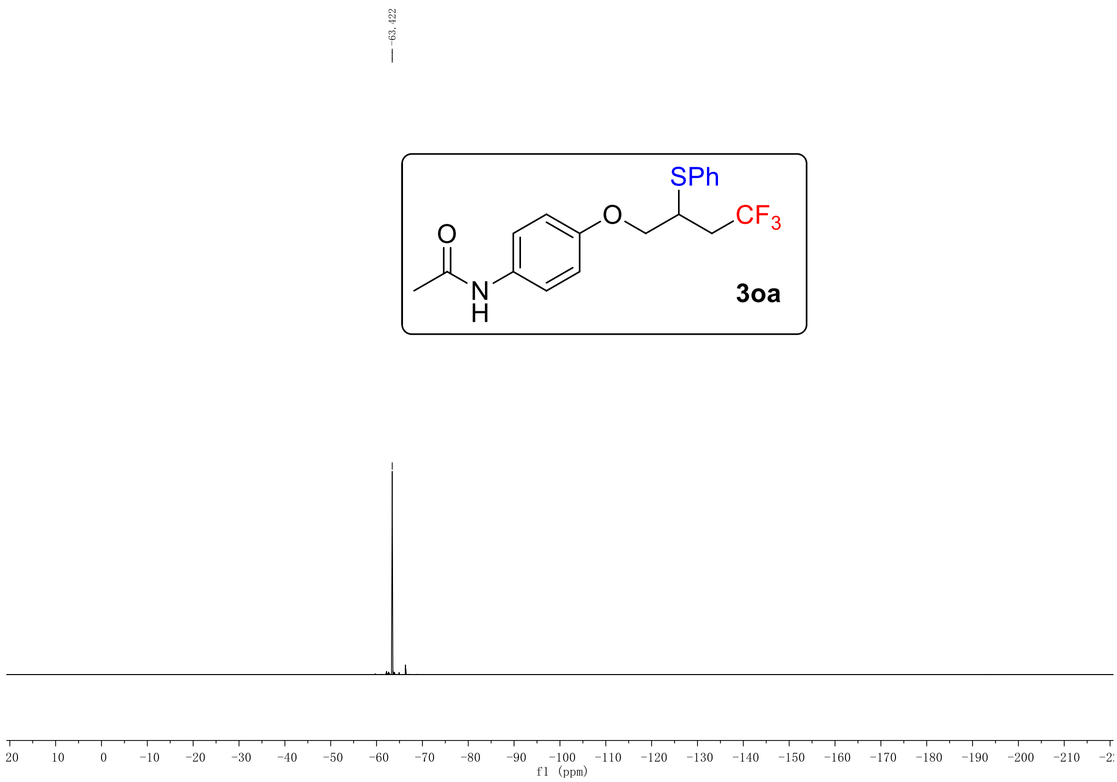
114.966
69.203
41.685
41.666
35.977
35.748
35.519
35.292
24.271
SPh
O
CF3
O
N
H
3oa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



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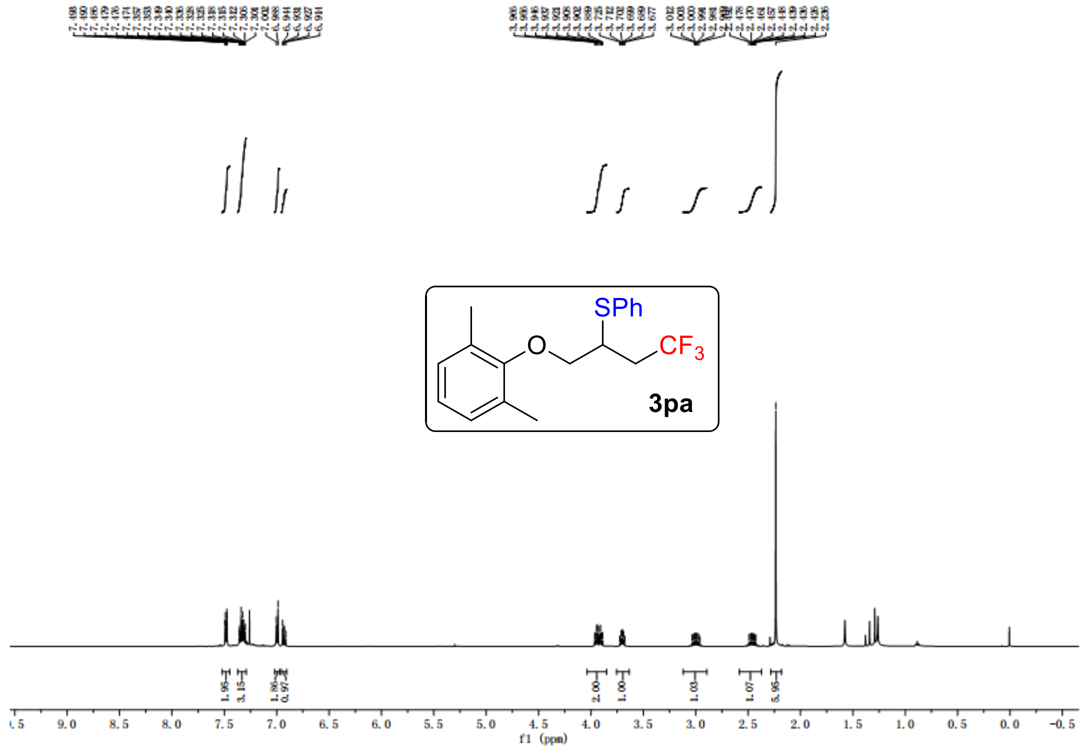
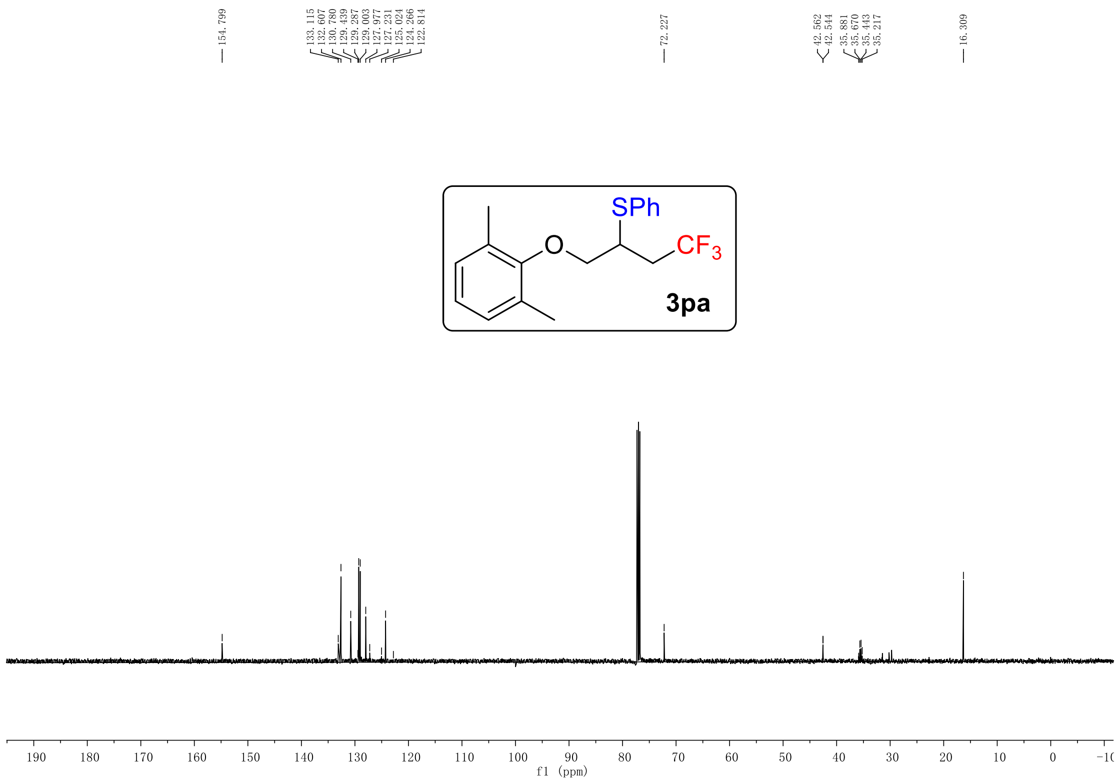
O
CF3
O
N
H
3oa
f1 (ppm)



SPh
O
CF3
3pa
f1 (ppm)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132.607
130.780
129.439
129.287
129.003
127.977
127.231
125.024
124.266
122.814
72.227
42.562
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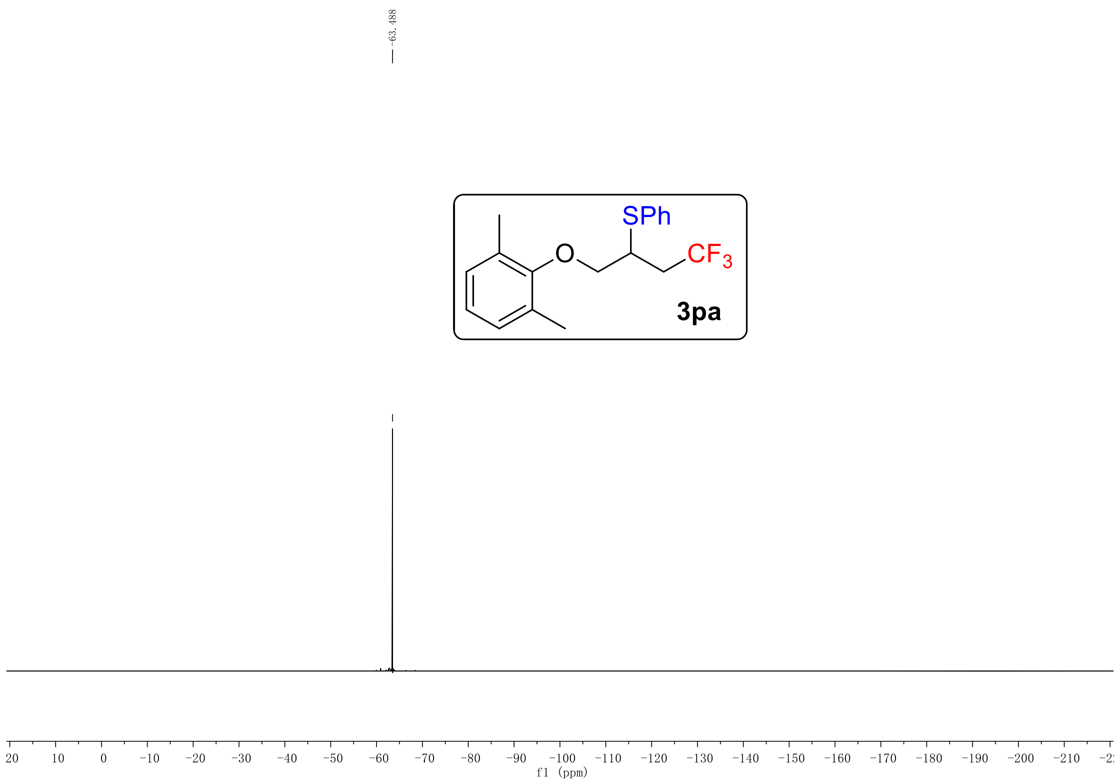
35.881
35.670
35.443
35.217
16.309
SPh
O
CF_3
3pa
f1 (ppm)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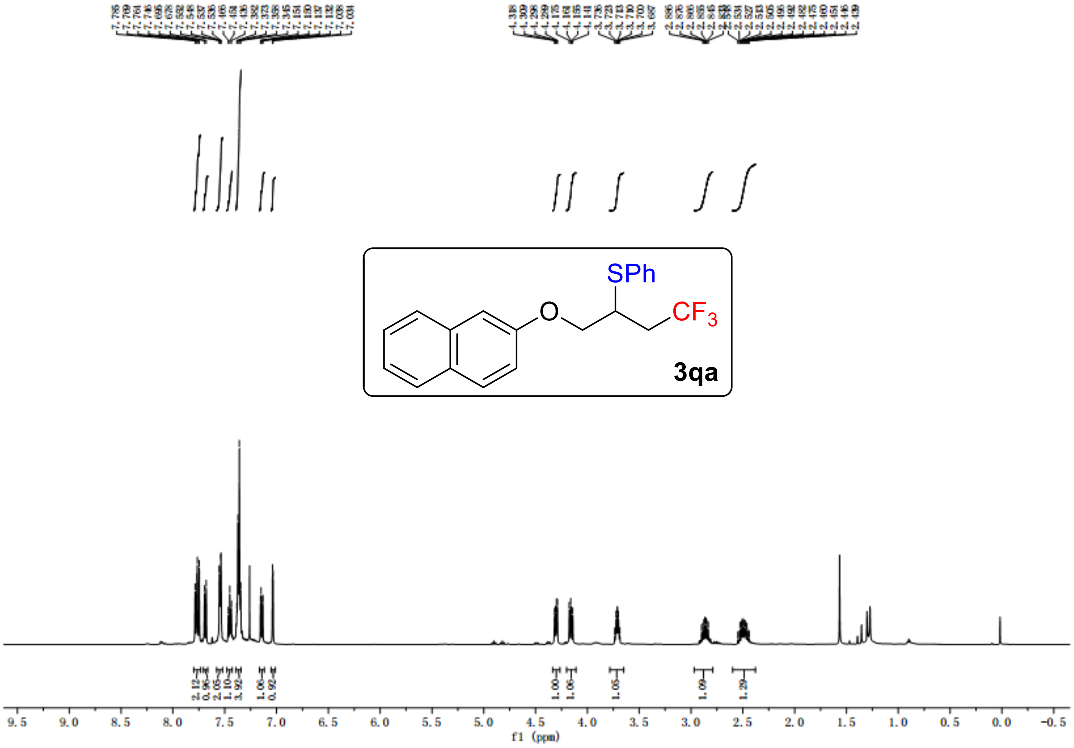
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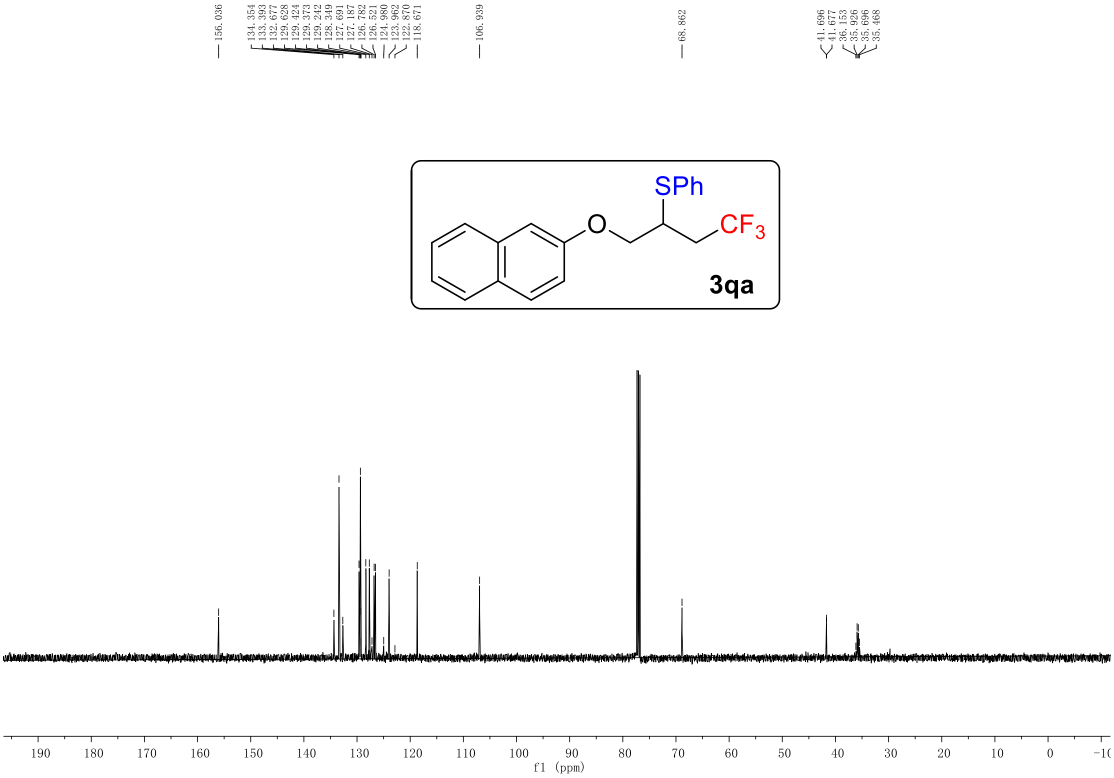
O
CF3
3qa
f1 (ppm)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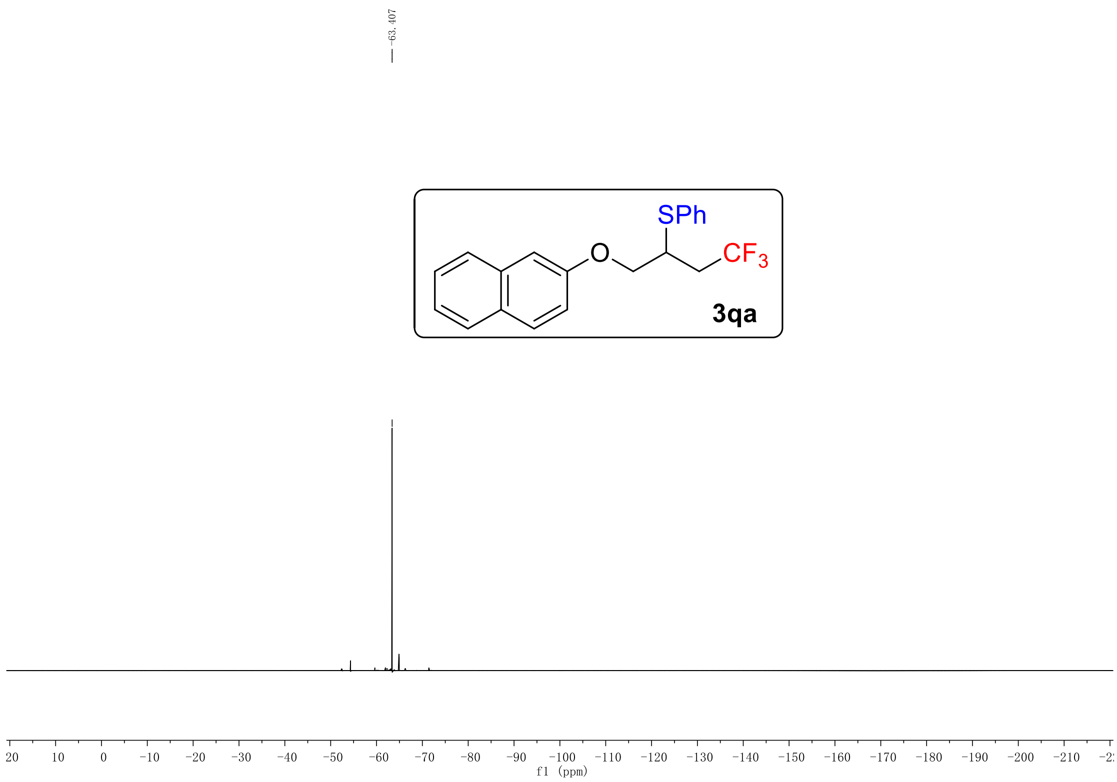
CF3
3qa
f1 (ppm)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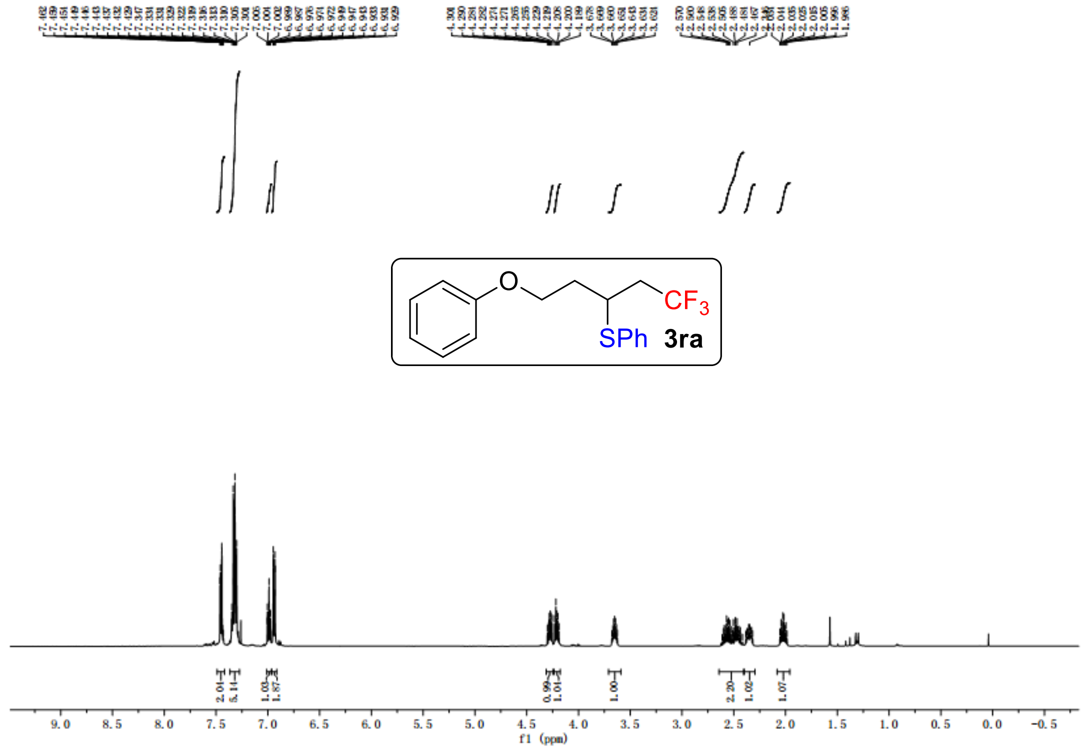
CF3
3qa
f1 (ppm)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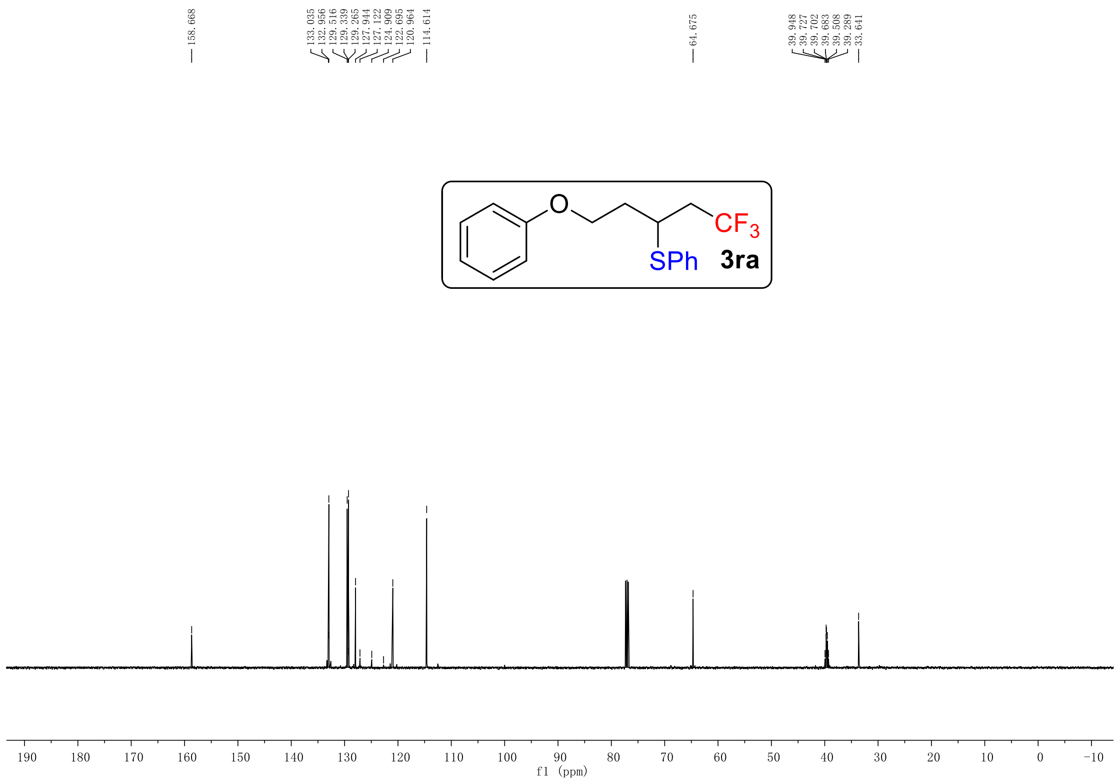
CF3
SPh
3ra
f1 (ppm)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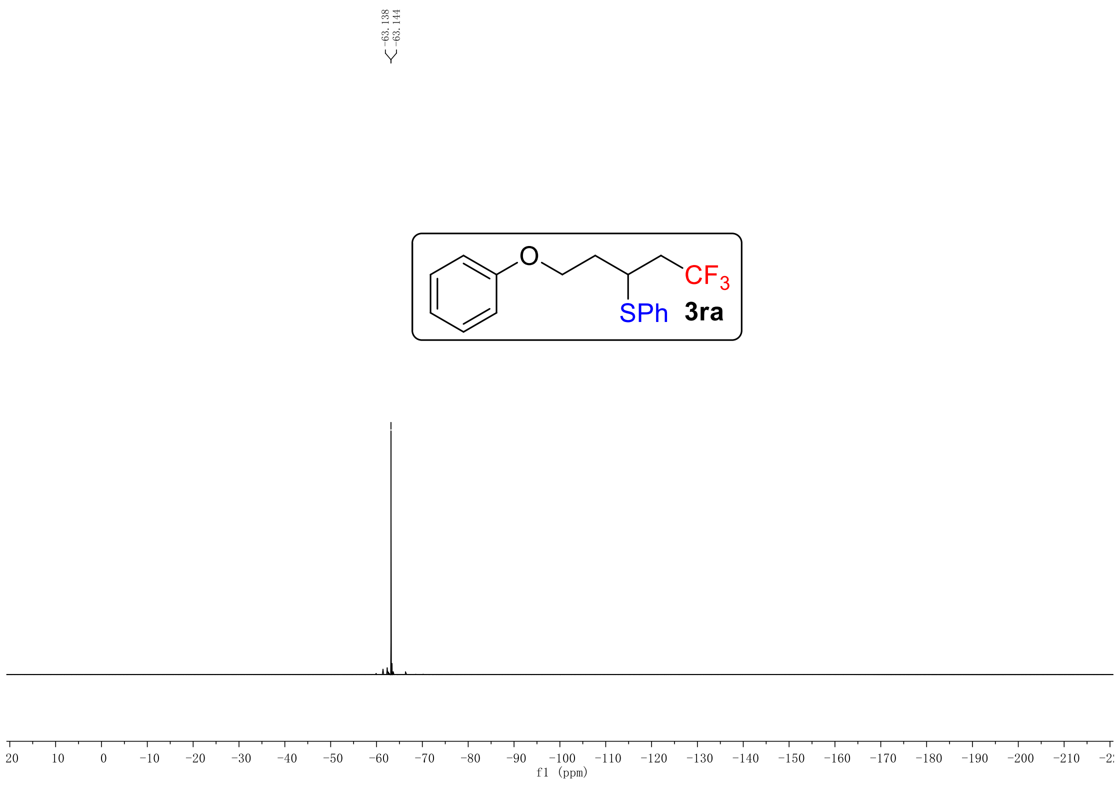
f1 (ppm)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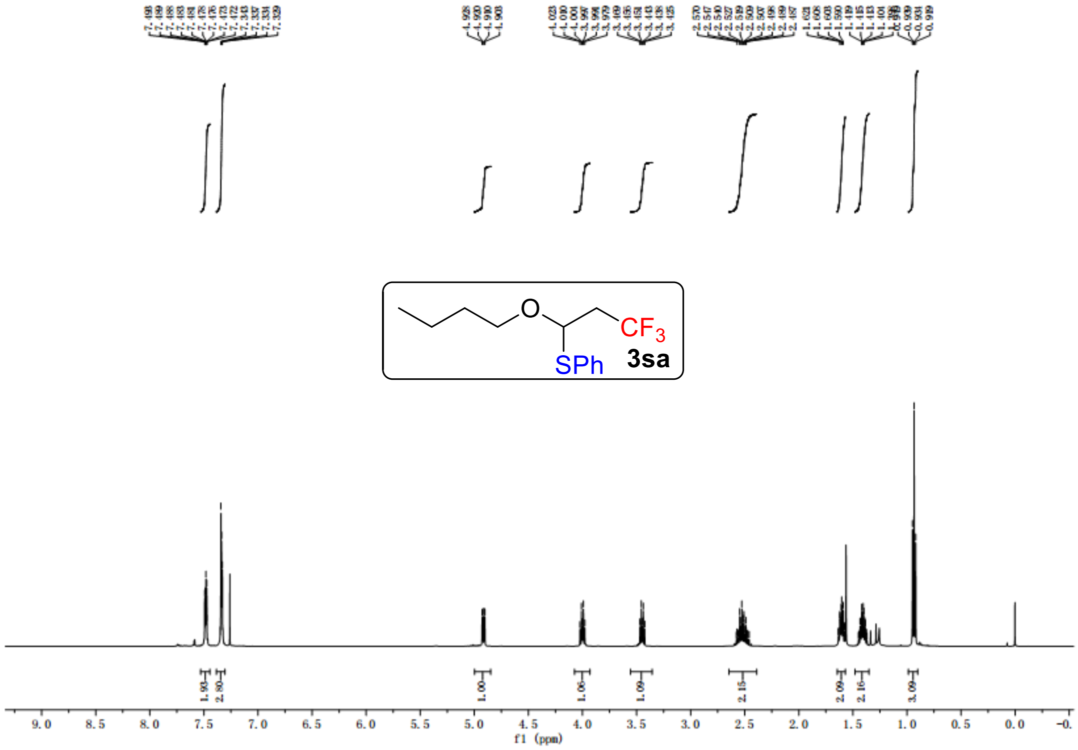

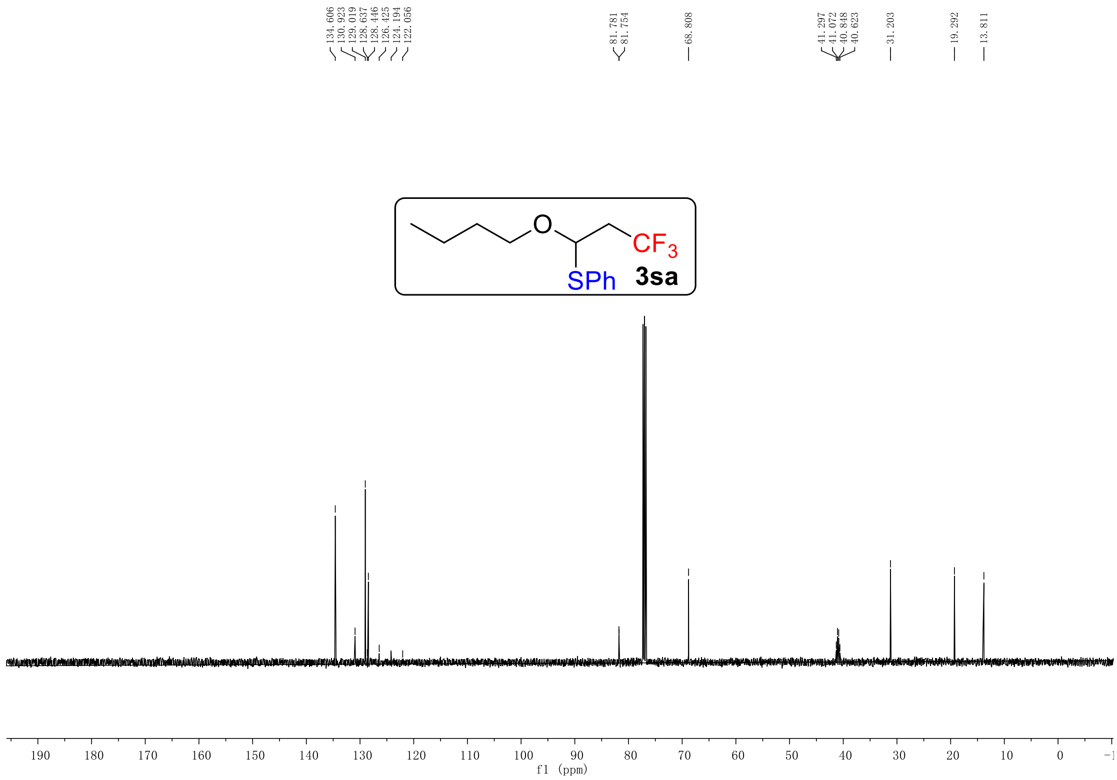

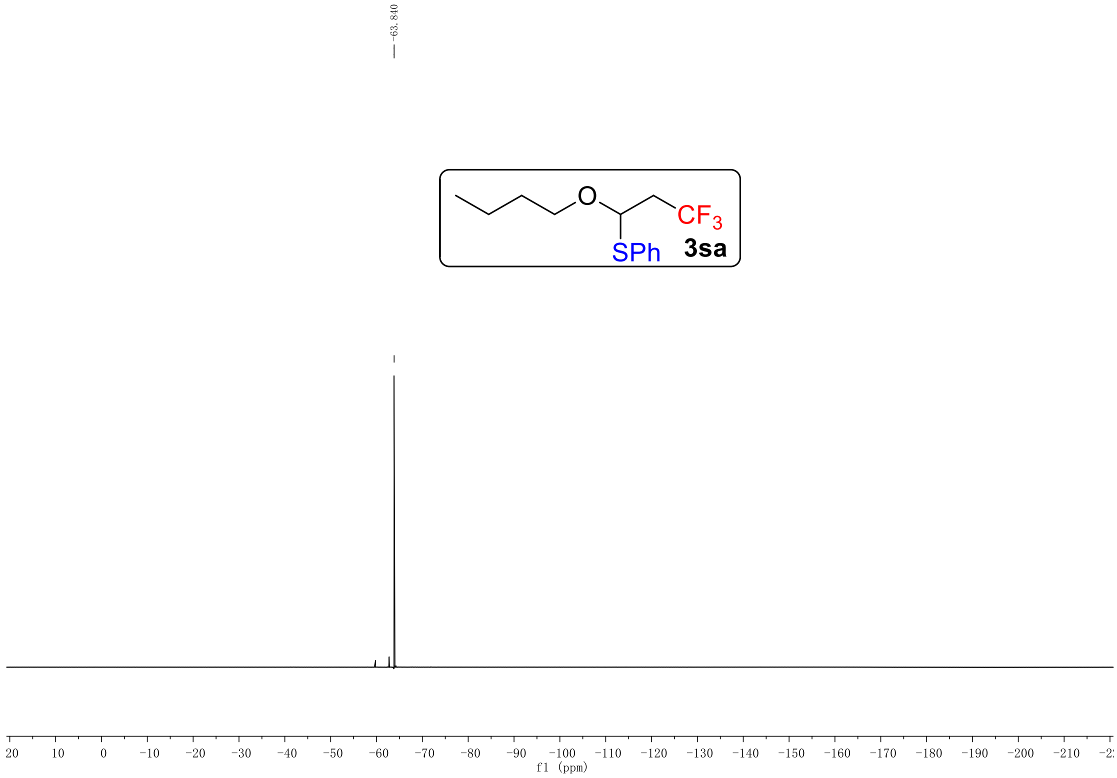
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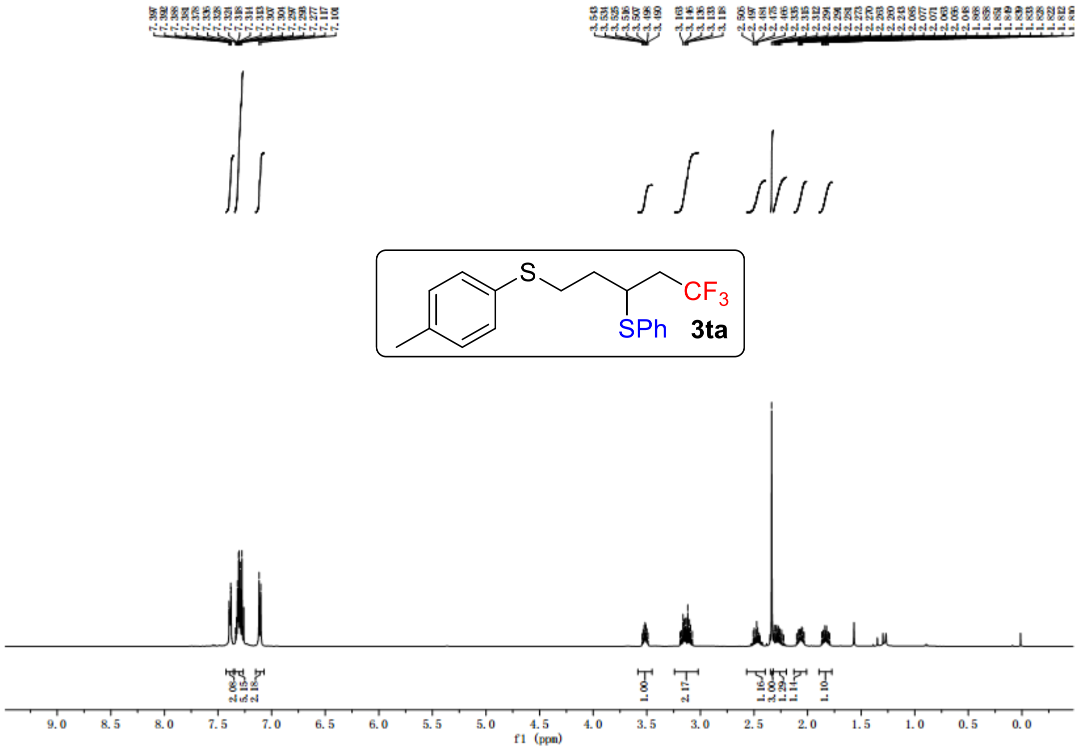
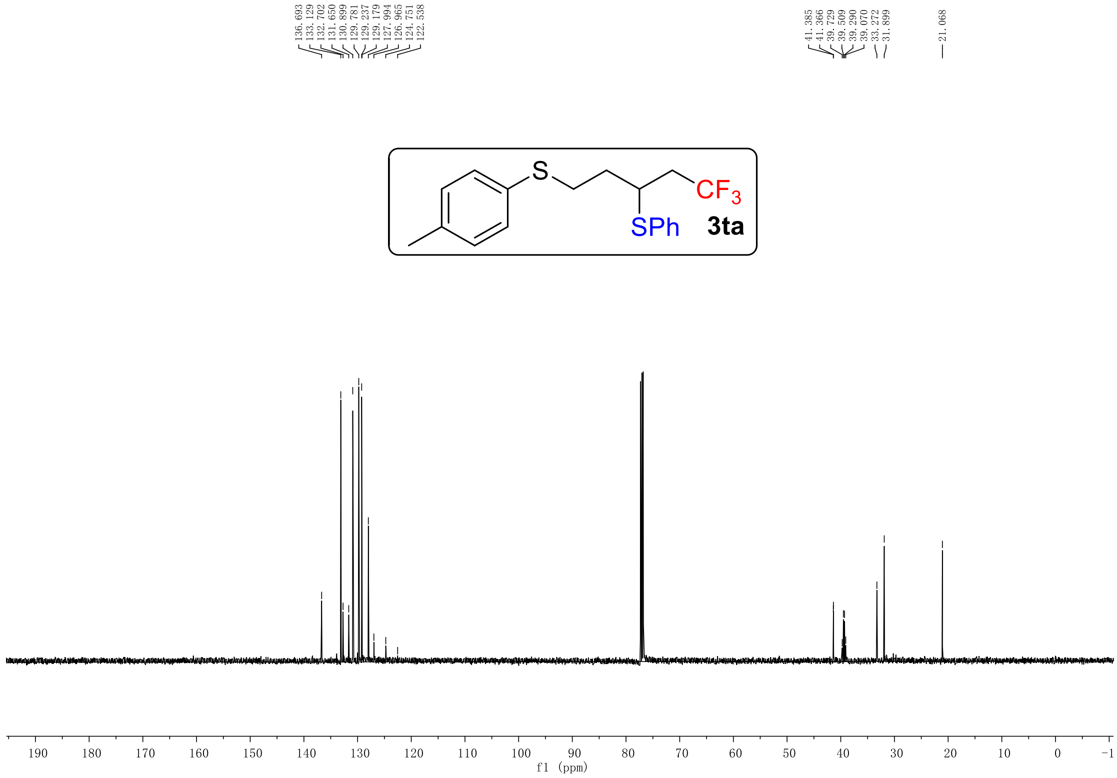
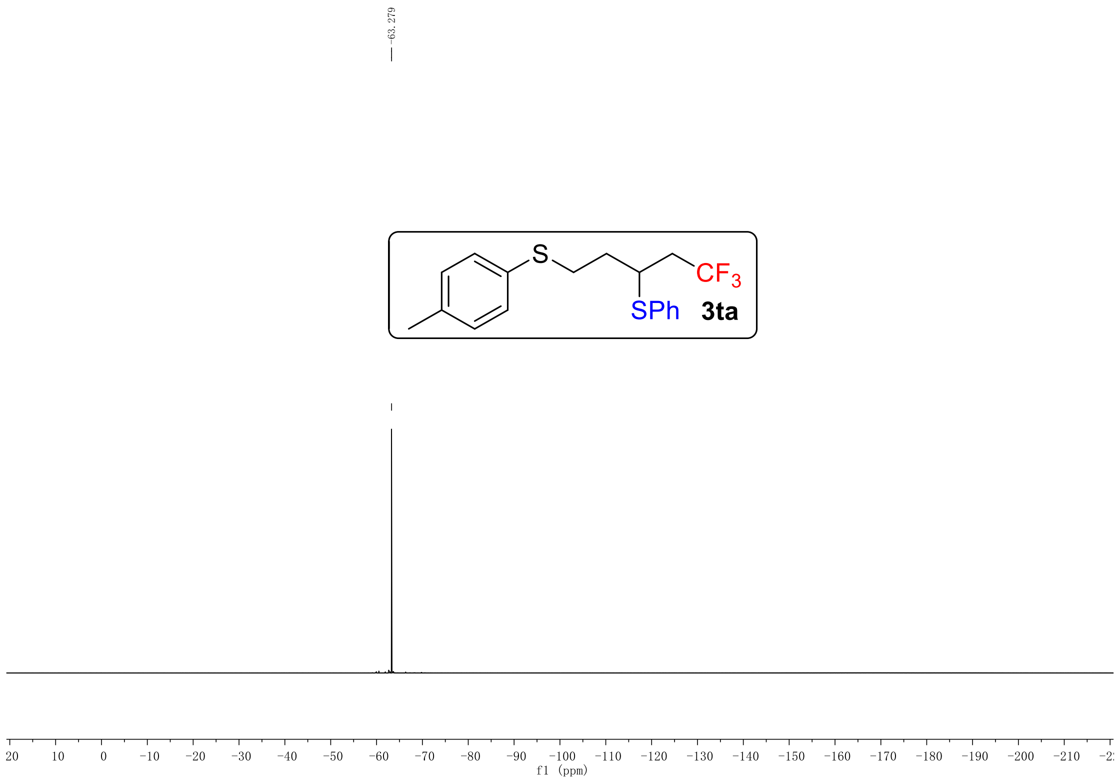
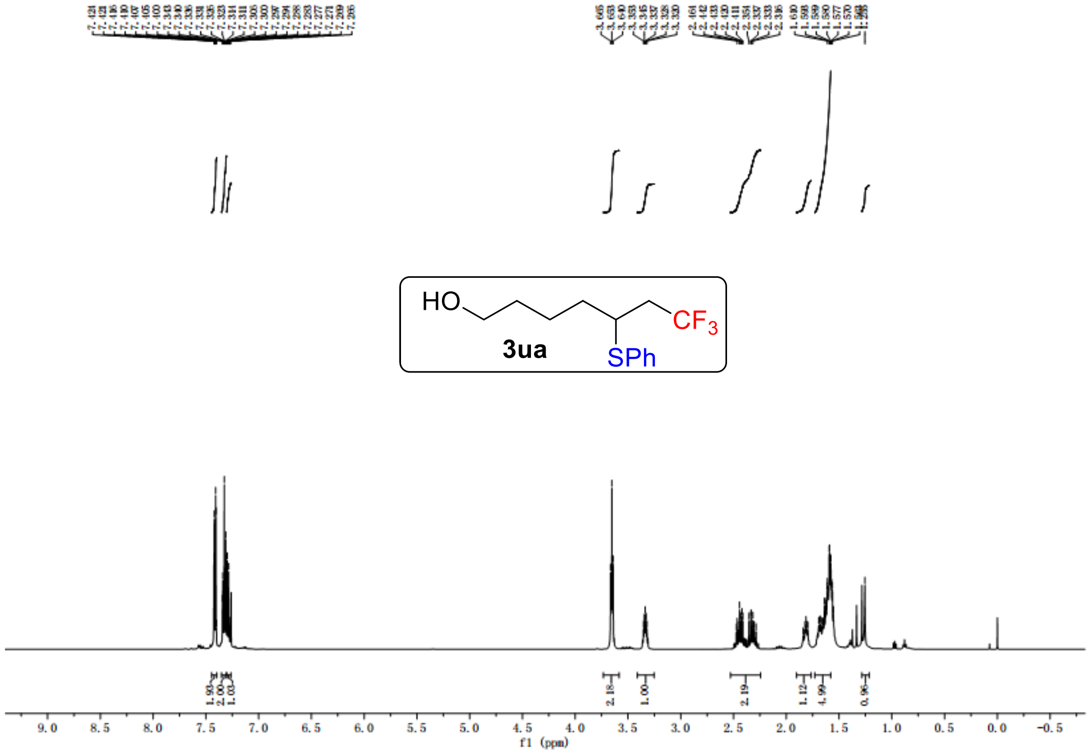
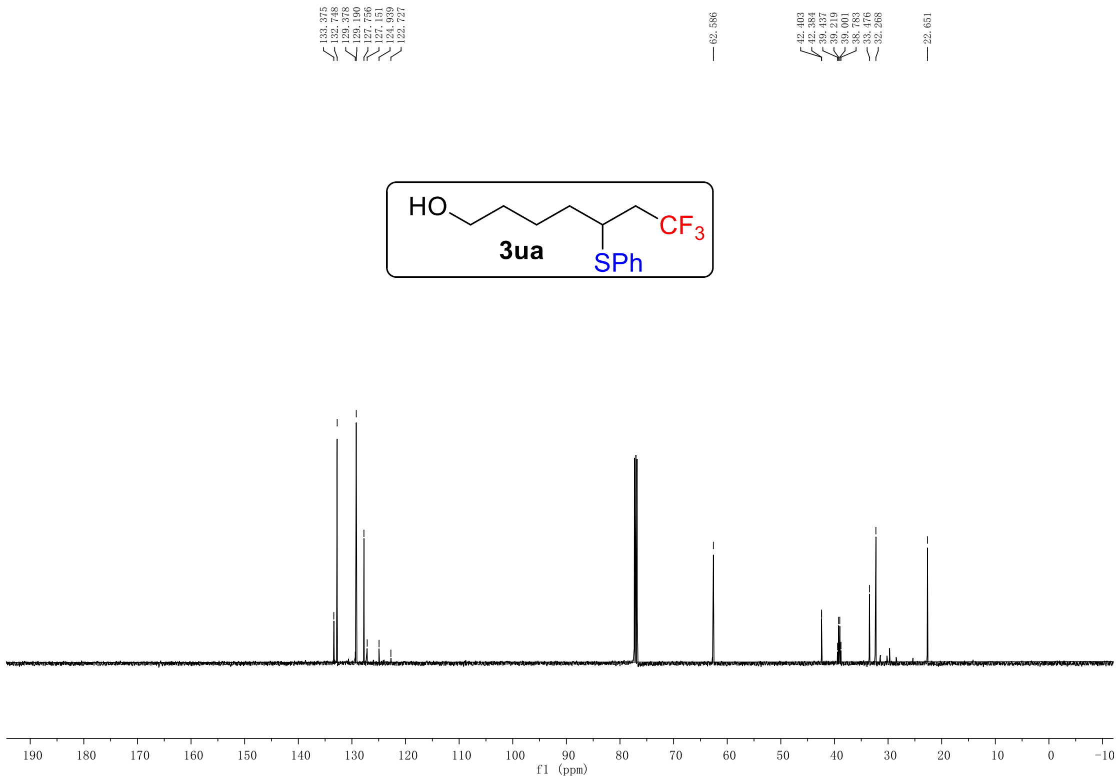
CF3
SPh
3sa
f1 (ppm)


S
CF3
SPh
3ta
f1 (ppm)






HO
CF3
3ua
SPh
f1 (ppm)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122.727
62.586
42.403
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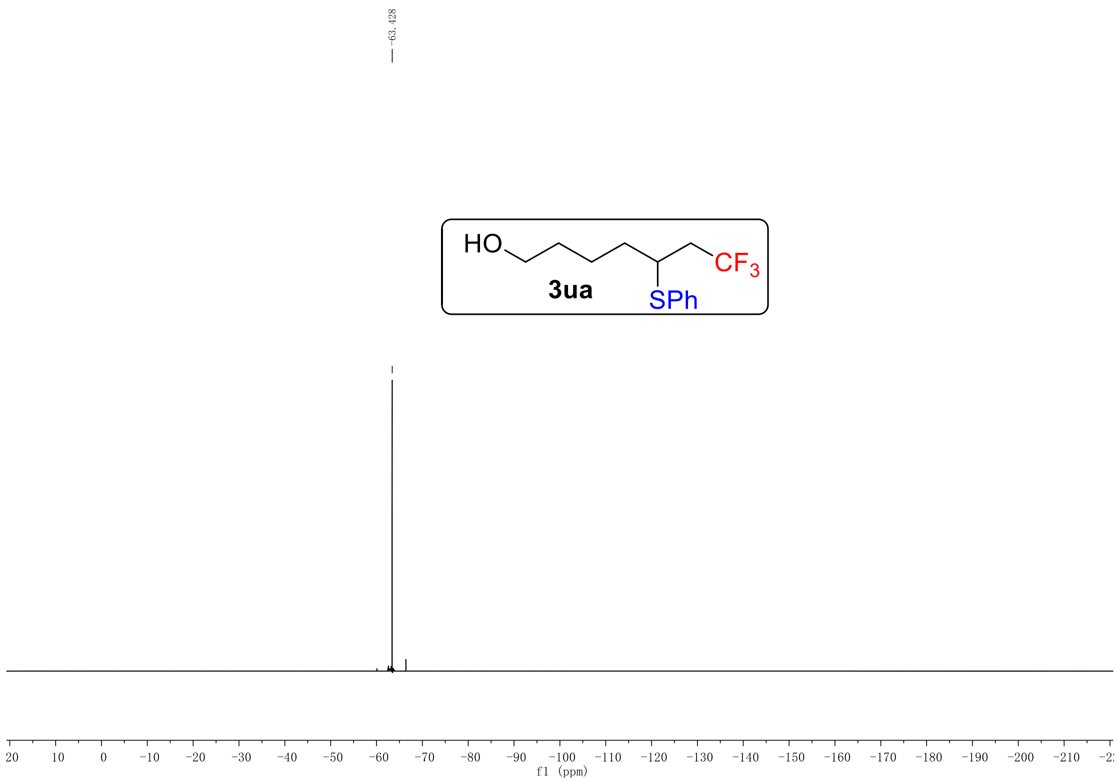
39.219
39.001
38.783
33.476
32.268
22.651
HO
CF3
3ua
SPh
f1 (ppm)



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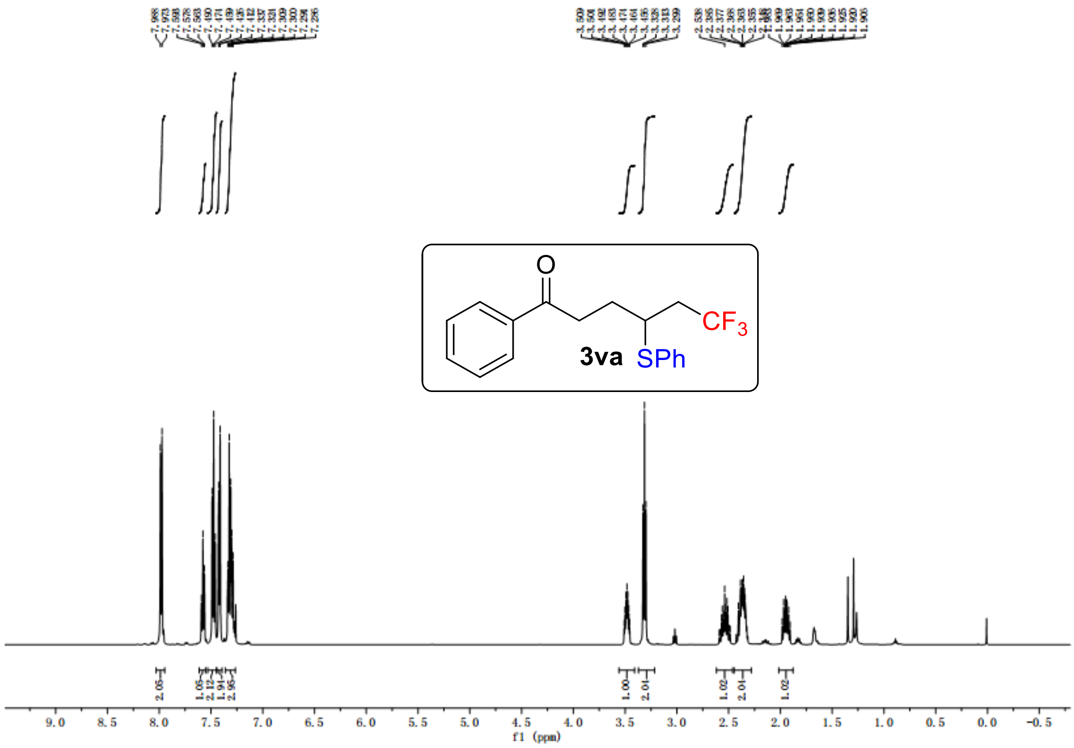
3ua
SPh
f1 (ppm)



O
CF3
3va
SPh
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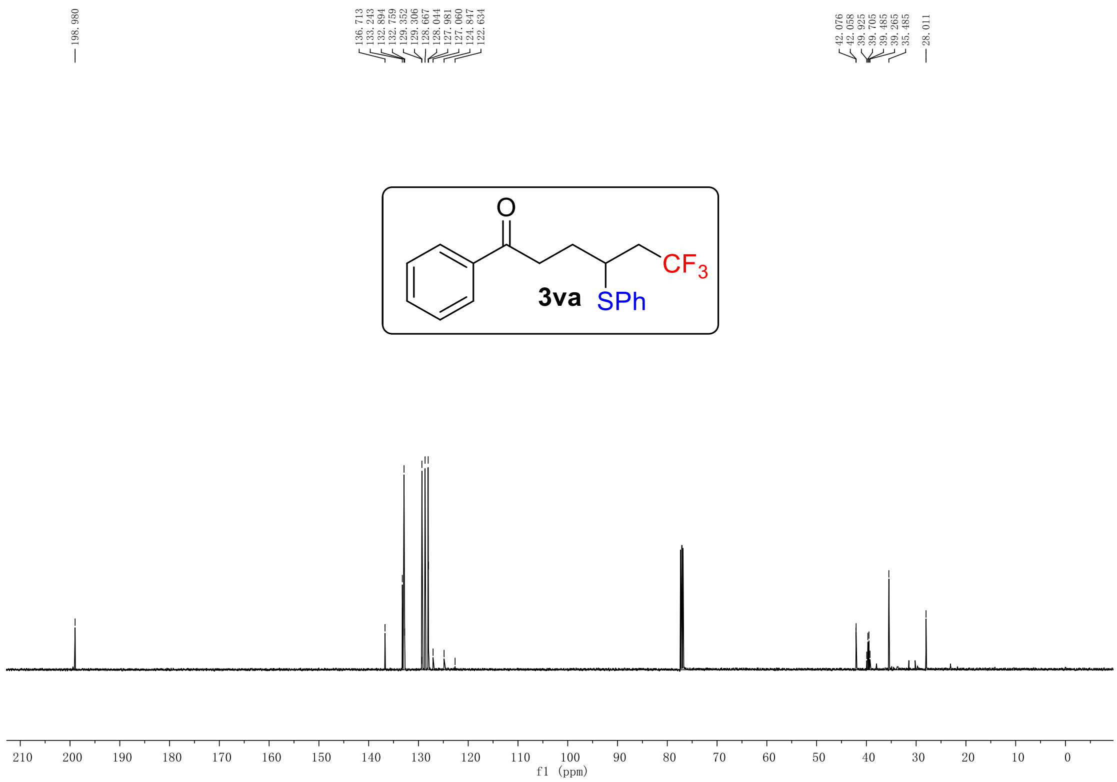
2.01
1.02
2.04
1.02
f1 (ppm)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129.306
128.667
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127.981
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124.847
122.634
42.076
42.058
39.925
39.765
39.485
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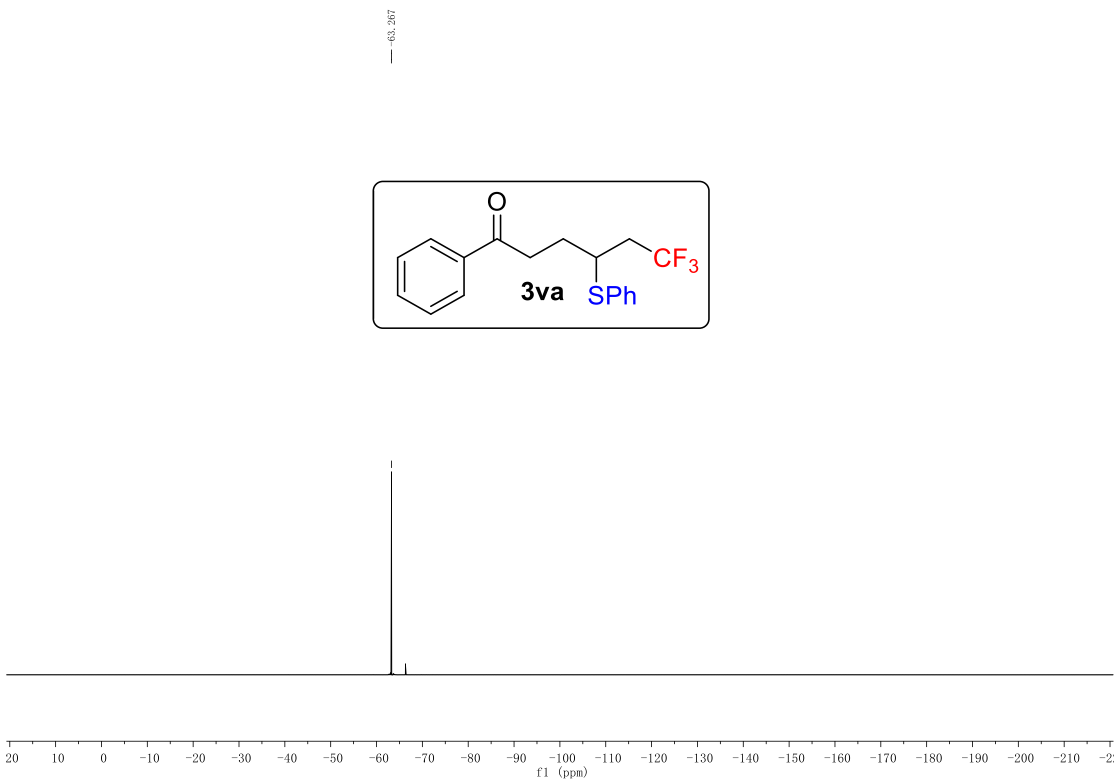
28.011
O
CF3
3va
SPh
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-63.267
O
CF3
3va
SPh
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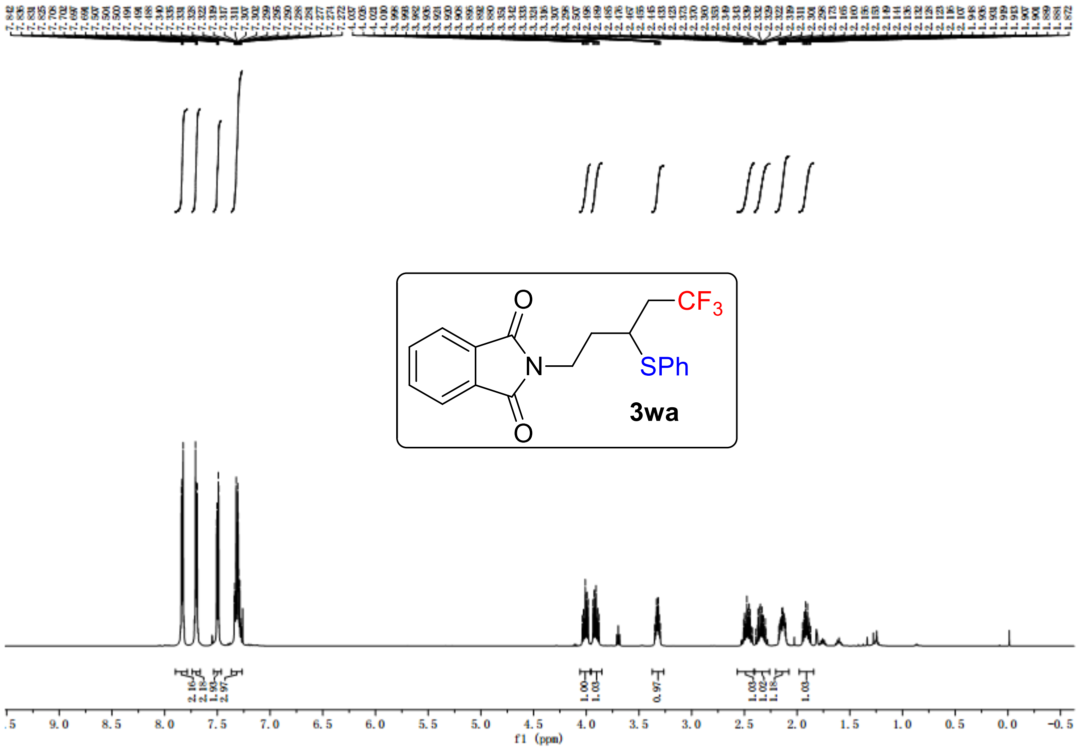
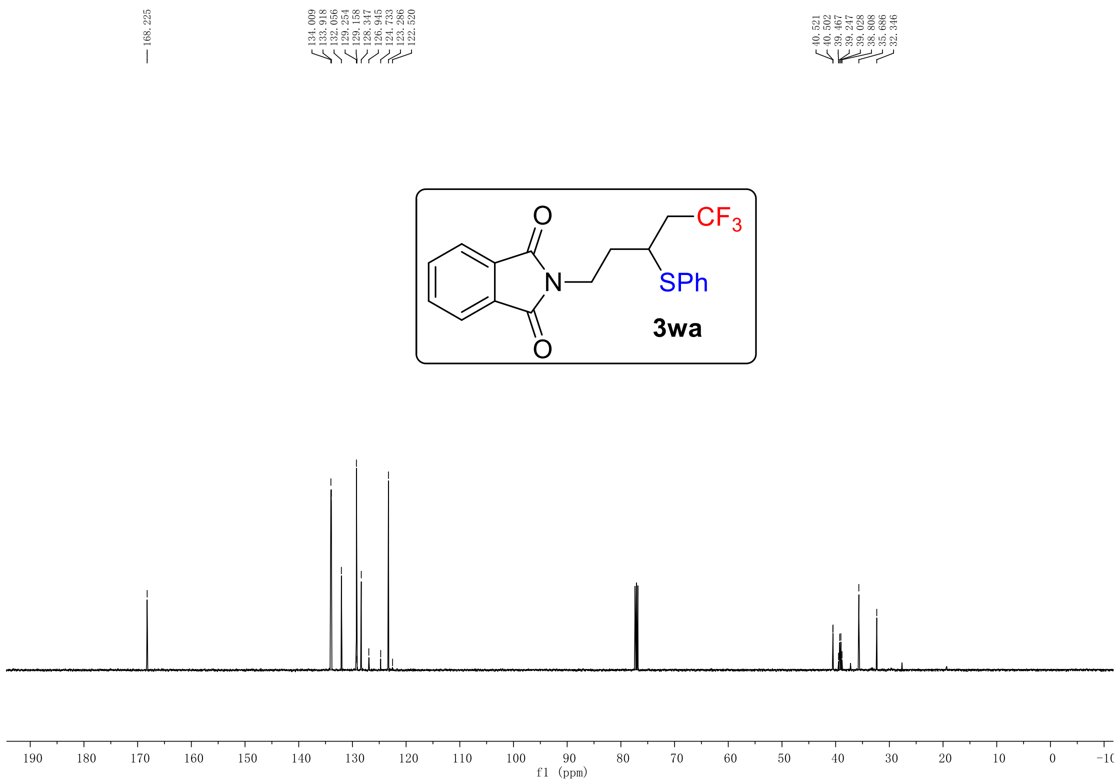
f1 (ppm)



CF3
SPh
3wa
f1 (ppm)



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129.254
129.158
128.347
126.945
124.733
123.286
122.520
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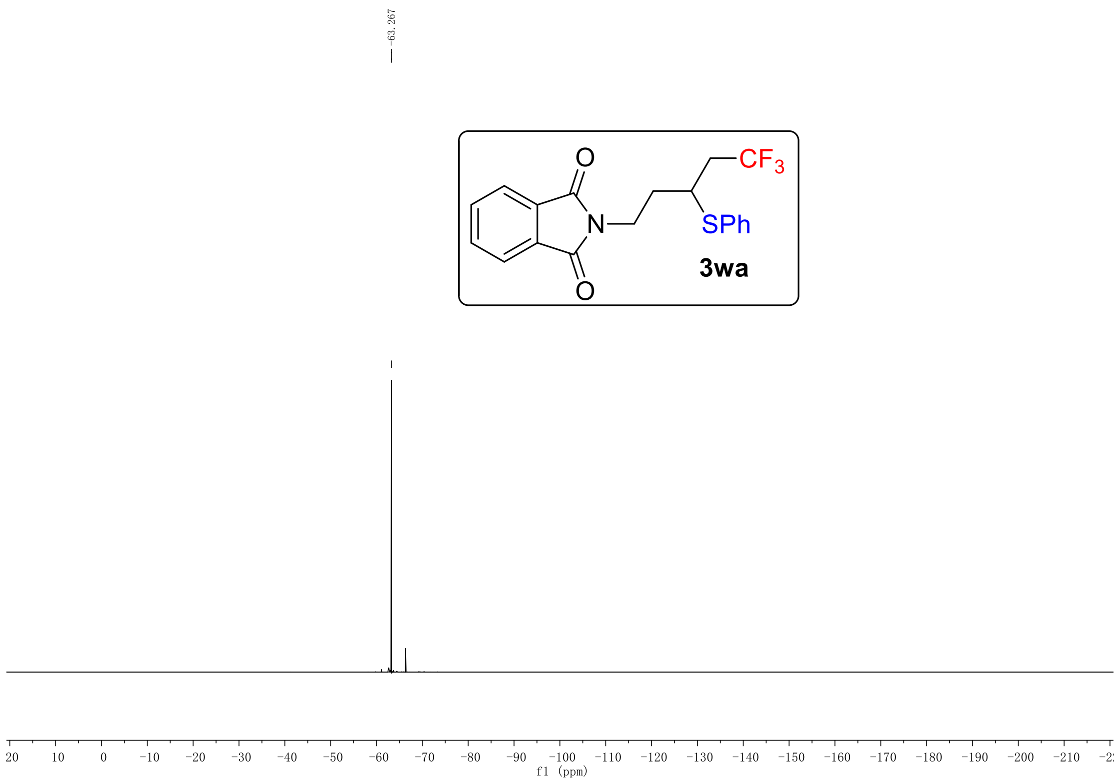
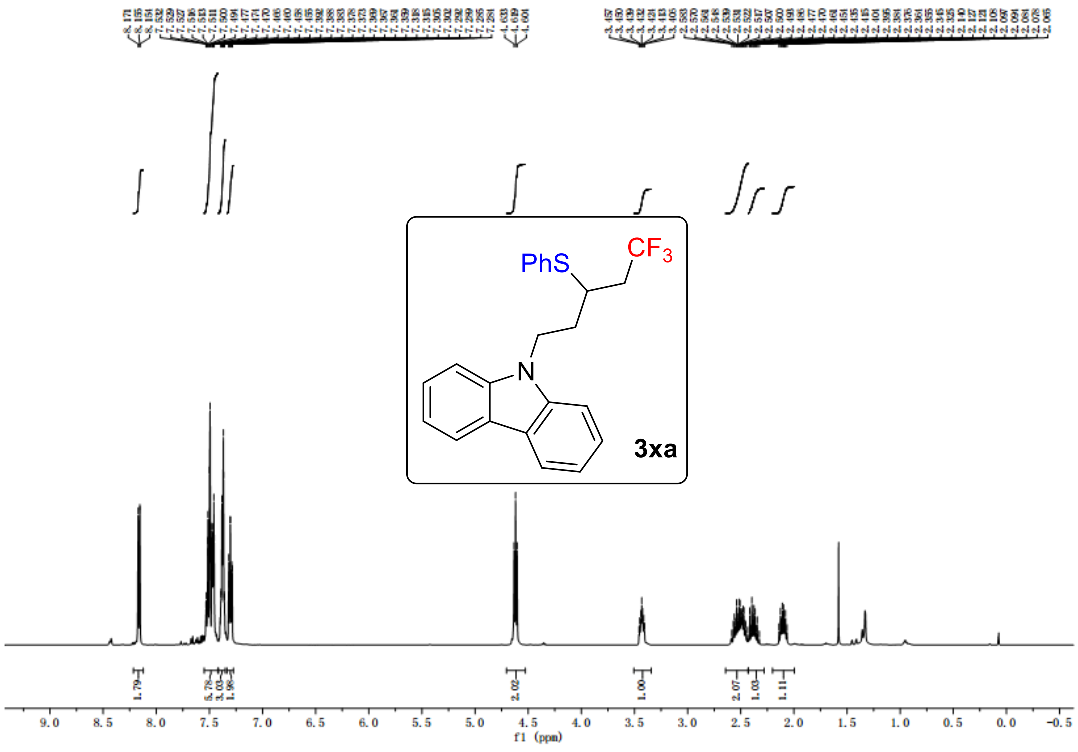
39.247
39.028
38.808
35.686
32.346
CF3
SPh
3wa
f1 (ppm)


—-63.267
CF3
SPh
3wa
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


PhS
CF3
N
3xa
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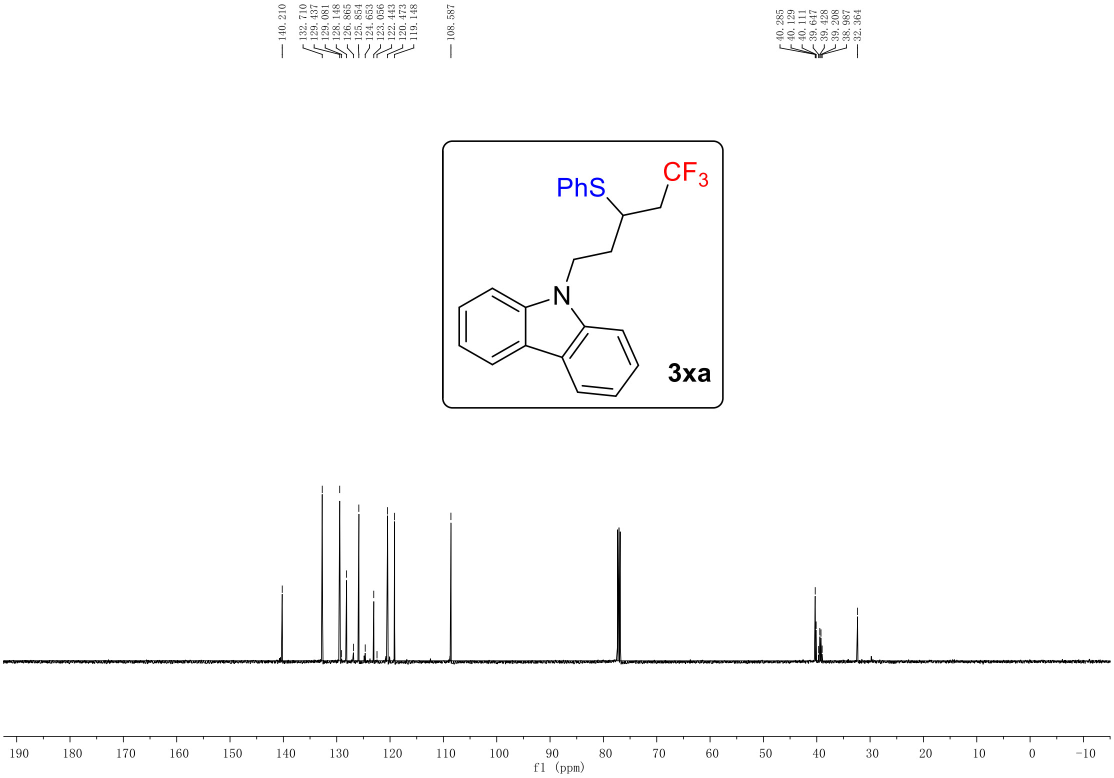
3.03
1.98
2.02
1.00
2.07
1.03
1.11
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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124.653
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120.473
119.148
108.587
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39.647
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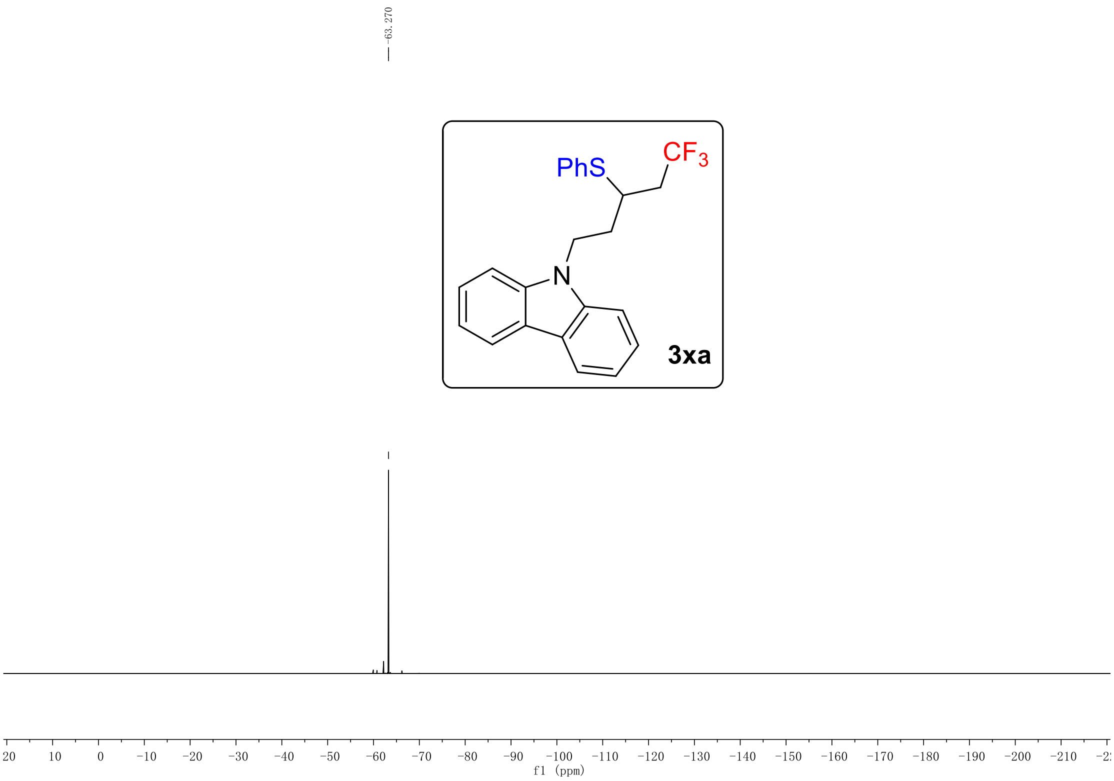
39.208
38.987
32.364
PhS
CF3
N
3xa
f1 (ppm)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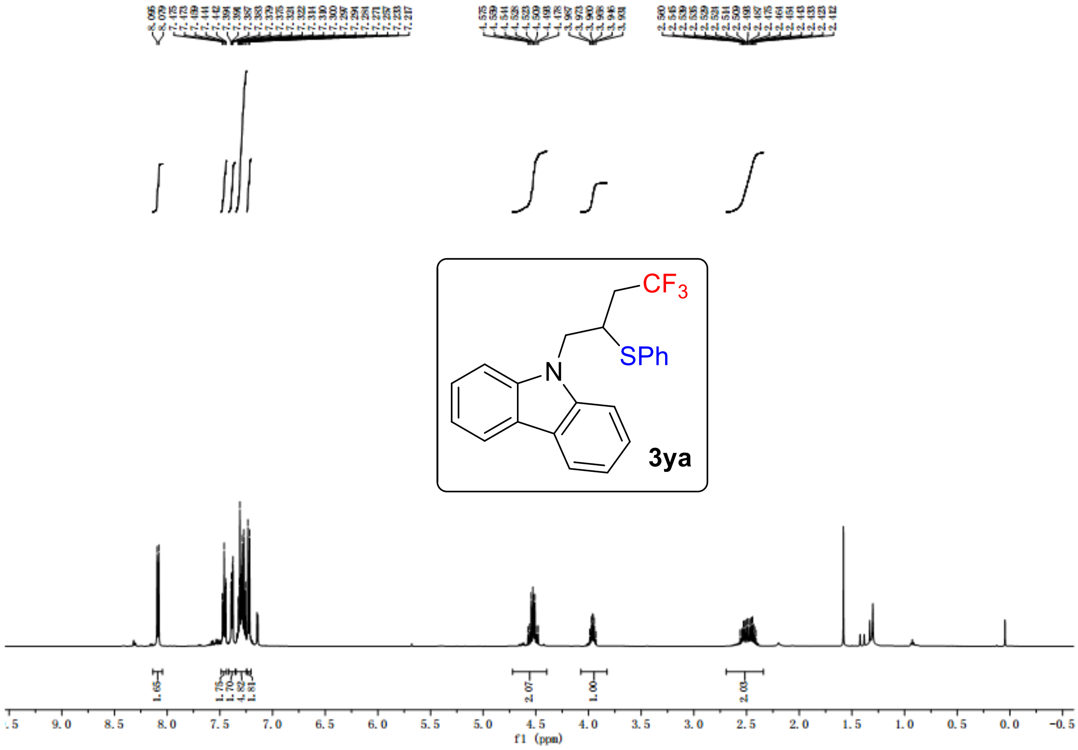
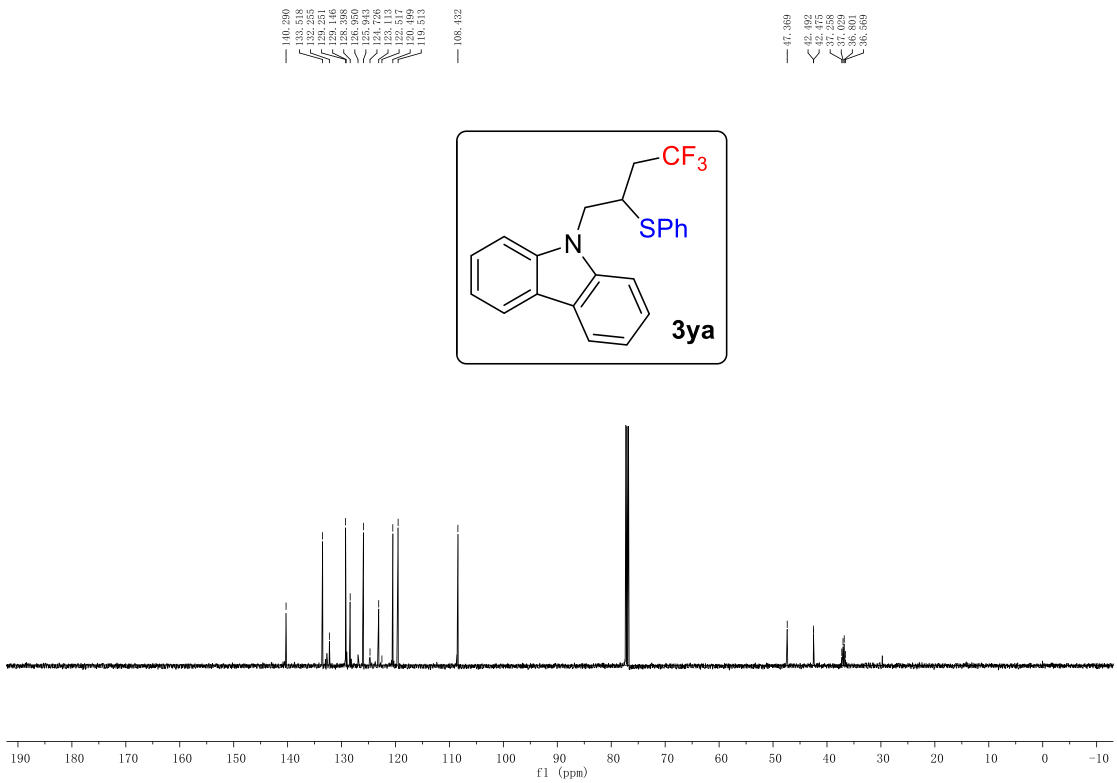
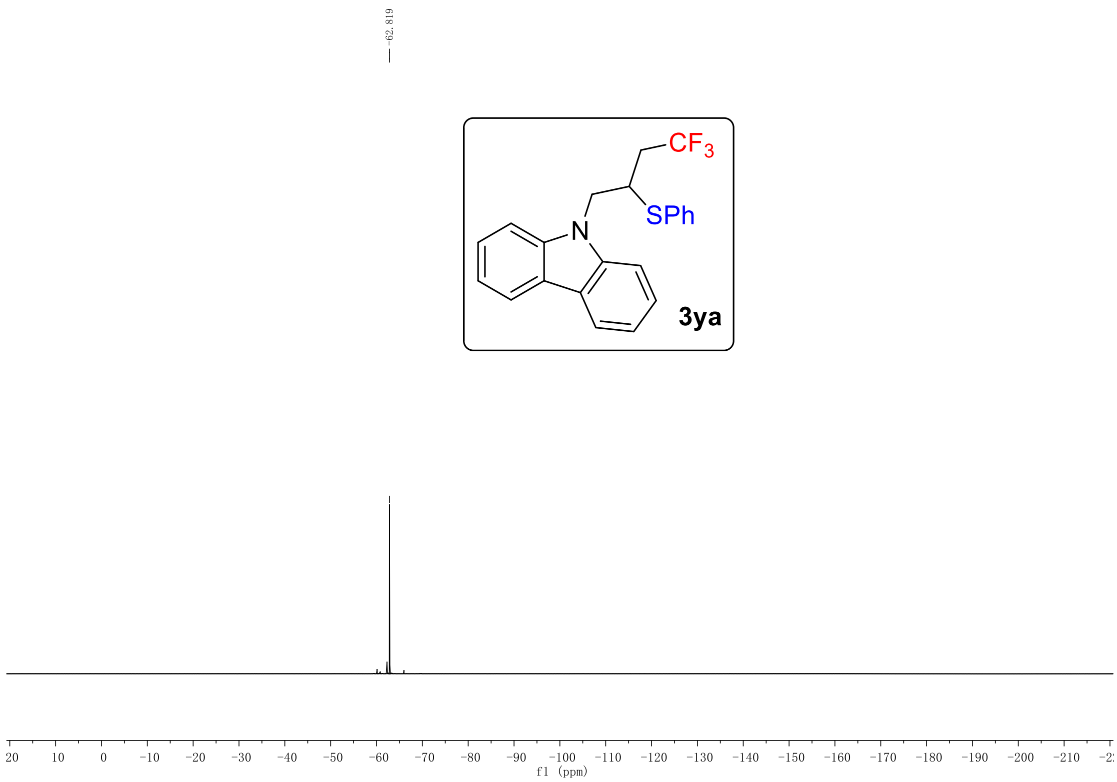
N
3xa
f1 (ppm)







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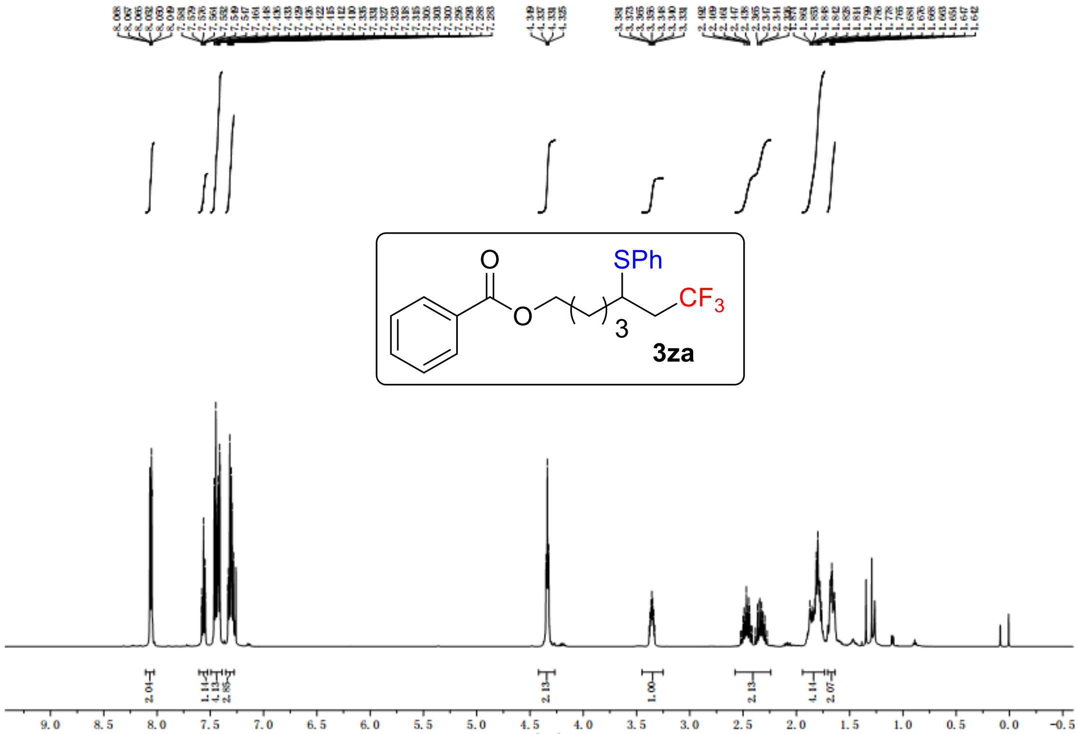
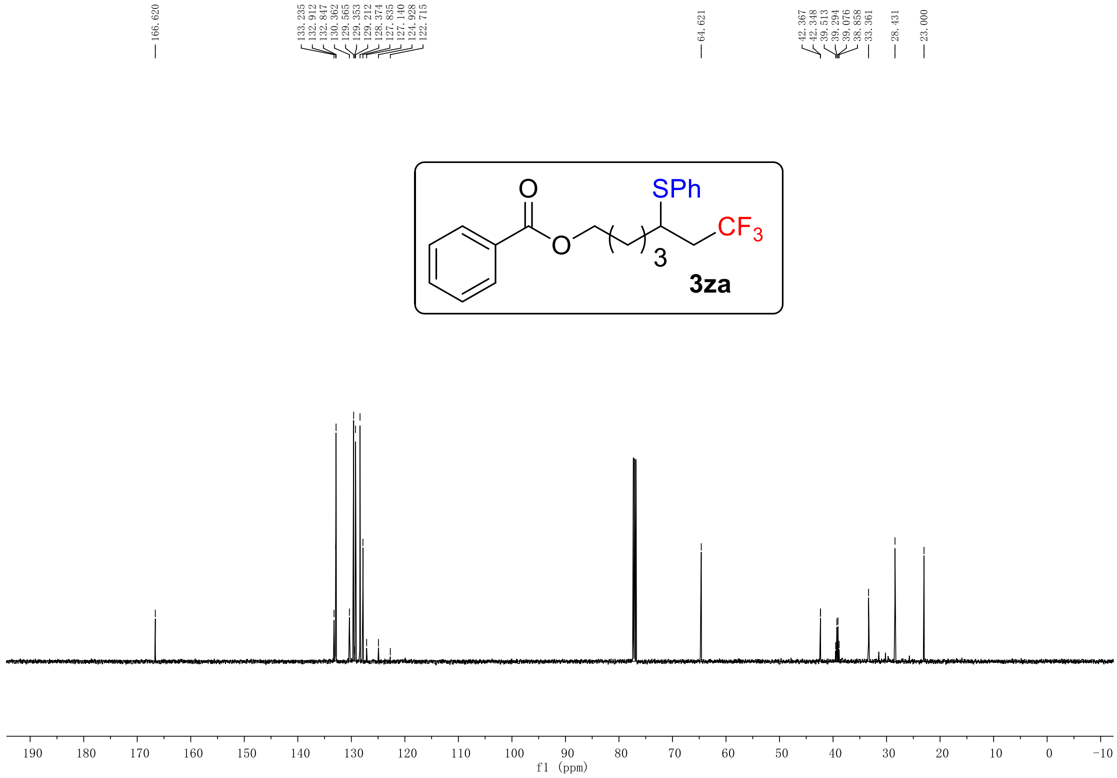
CF3
SPh
N
3ya
f1 (ppm)



O
SPh
CF3
3
3za
f1 (ppm)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129.212
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127.140
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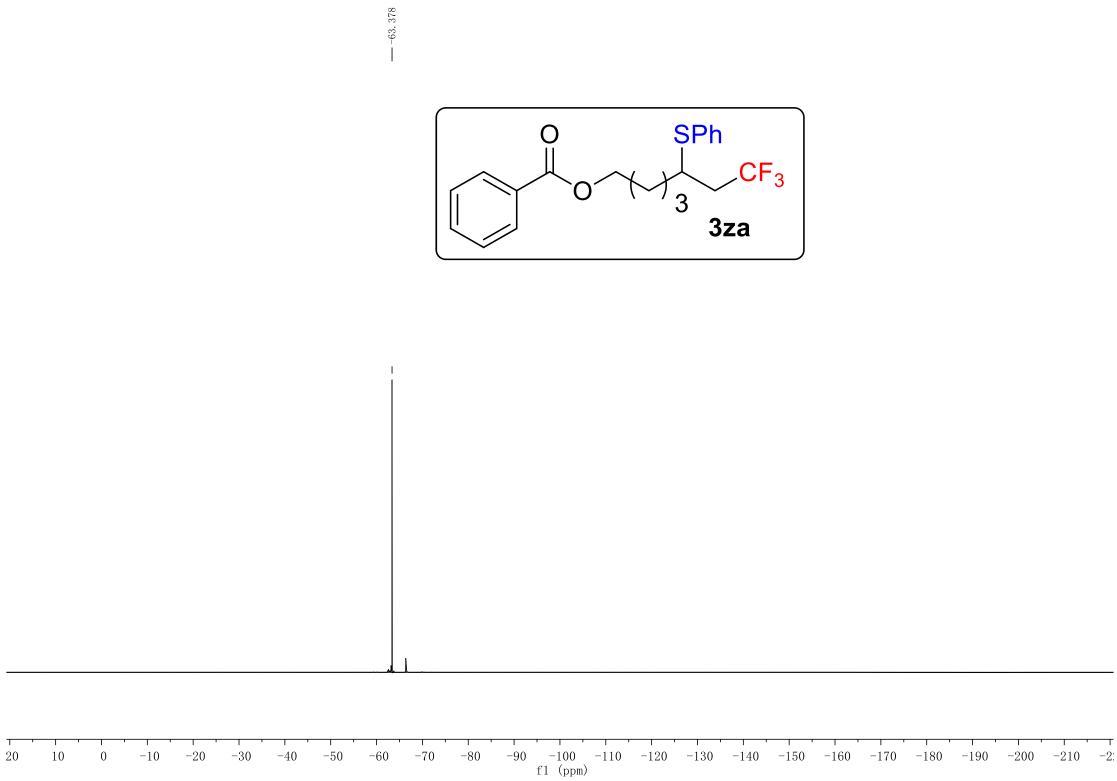
122.715
64.621
42.367
42.348
39.513
39.294
39.076
38.858
33.361
28.431
23.000
O
O
SPh
CF3
3
3za
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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O
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CF3
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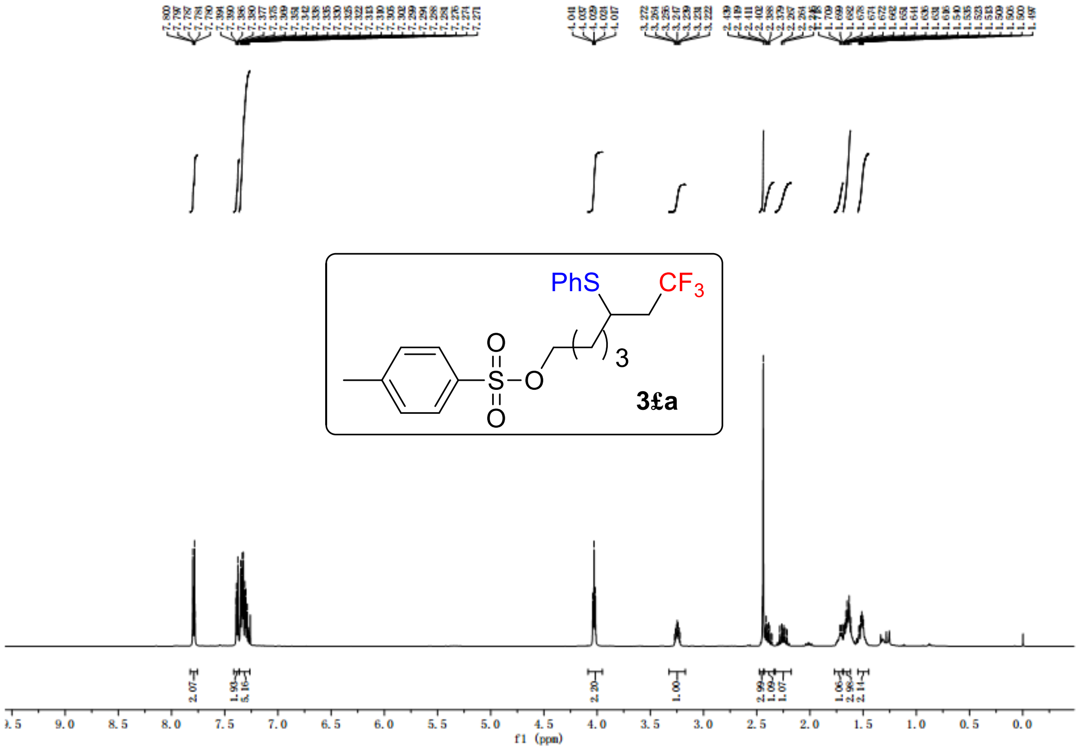
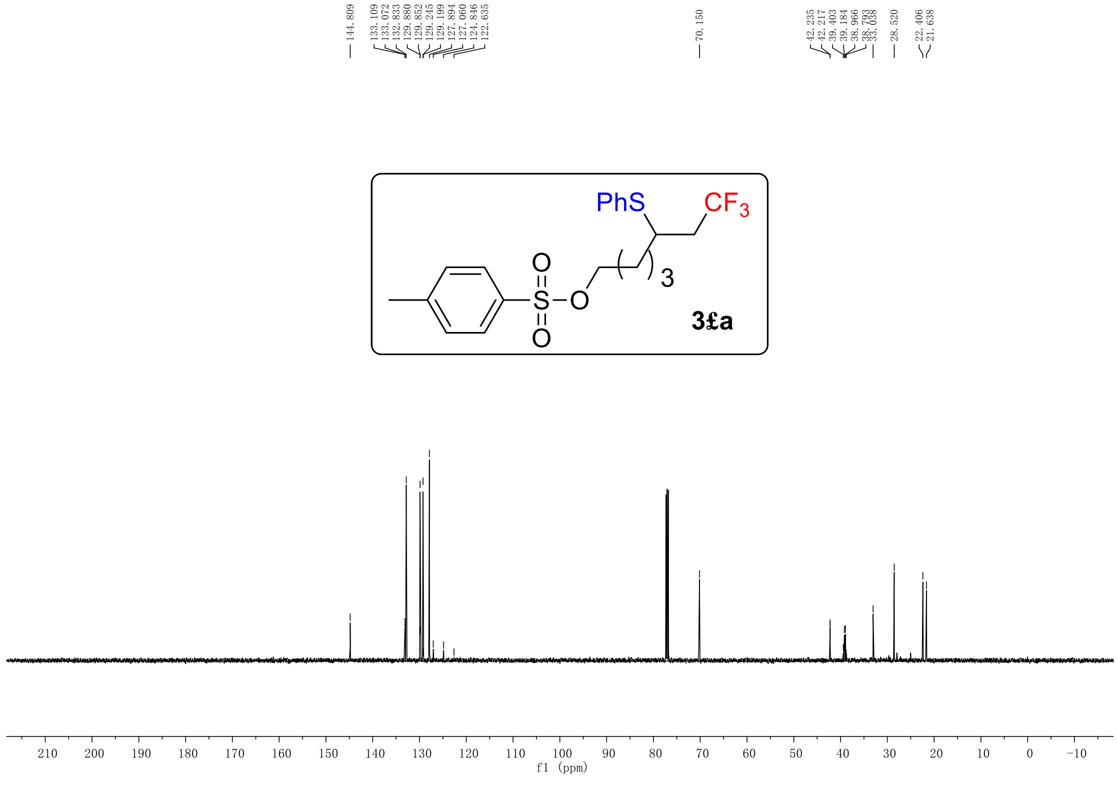
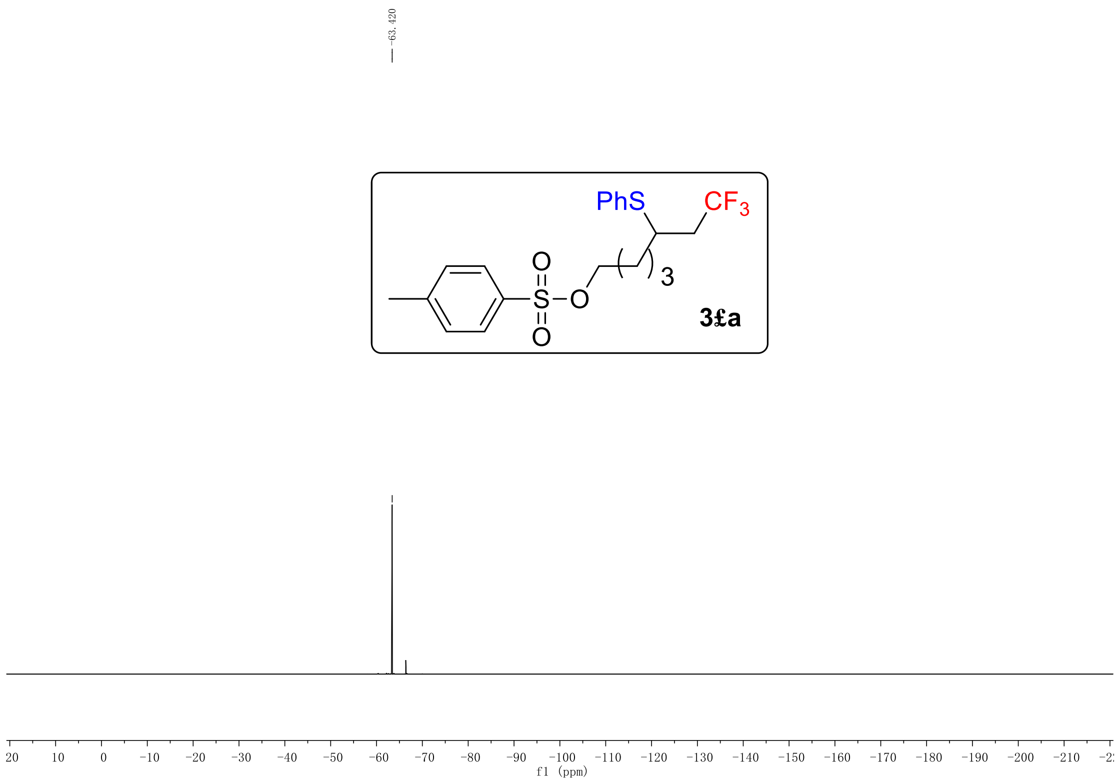
f1 (ppm)



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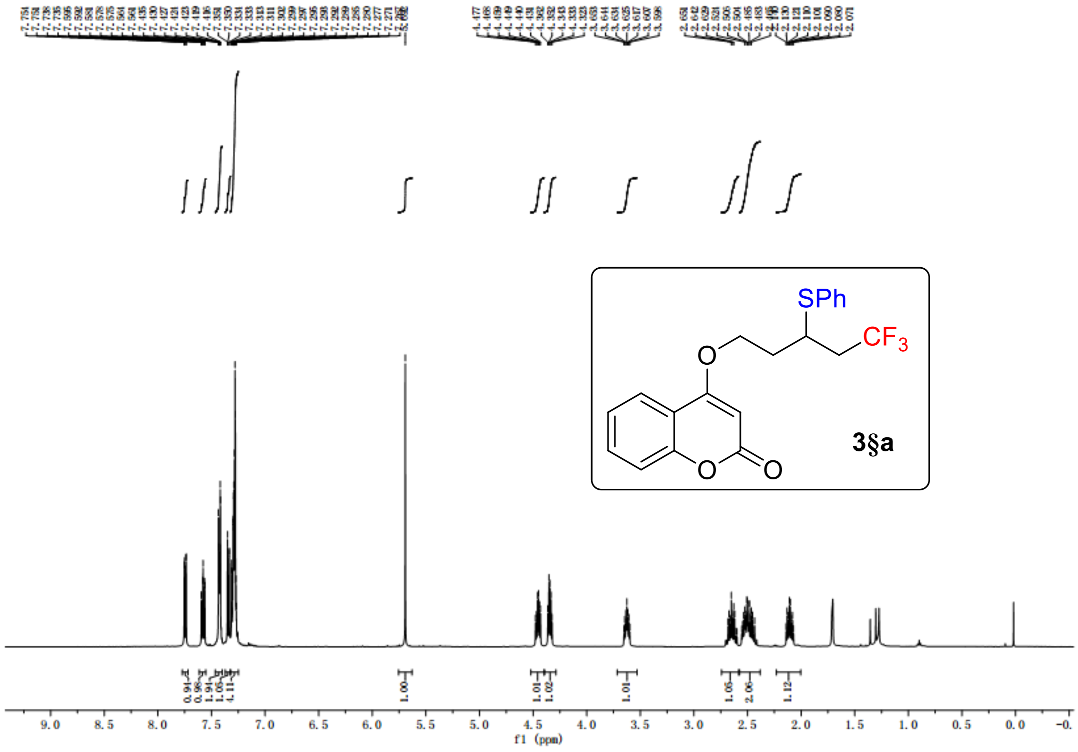
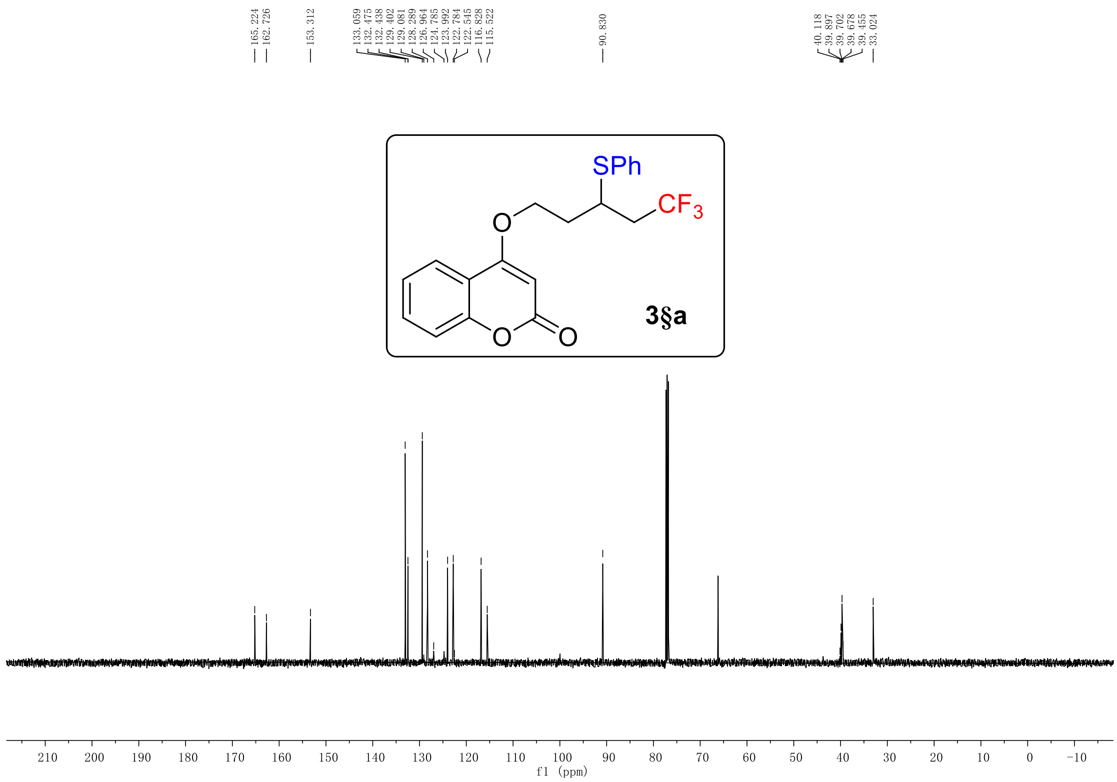
CF3
3
3£a
f1 (ppm)


SPh
CF3
3§a
f1 (ppm)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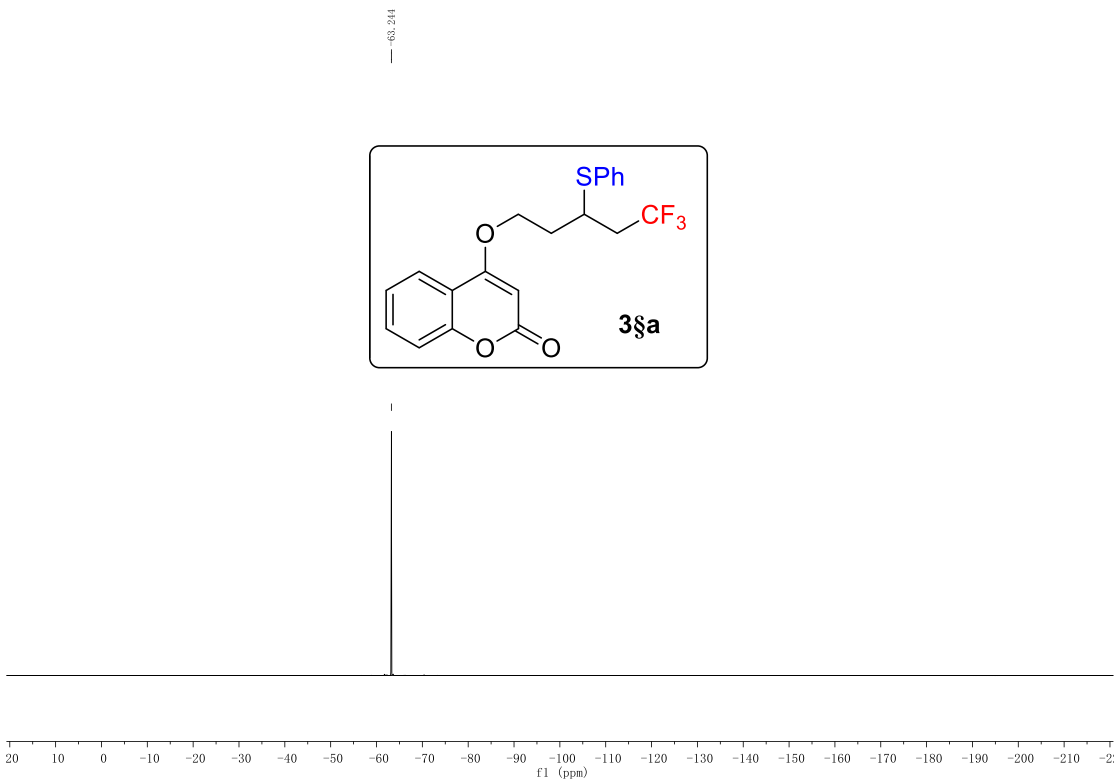
CF3
O
O
O
3§a
f1 (ppm)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O
3§a
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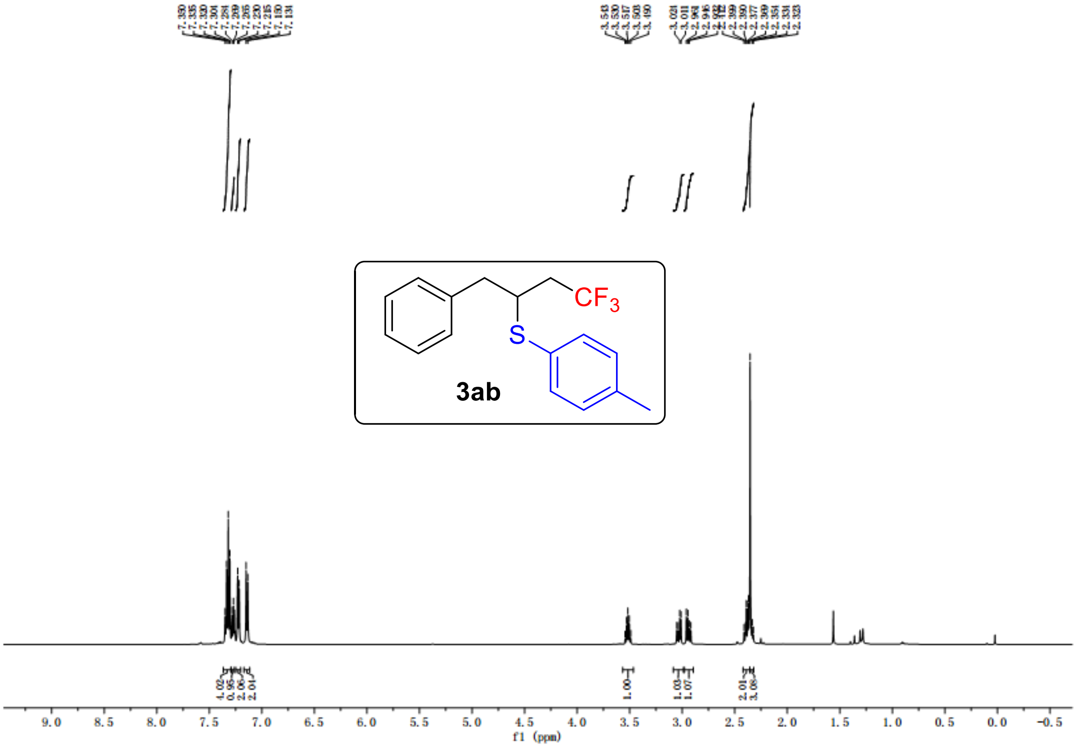
CF3
S
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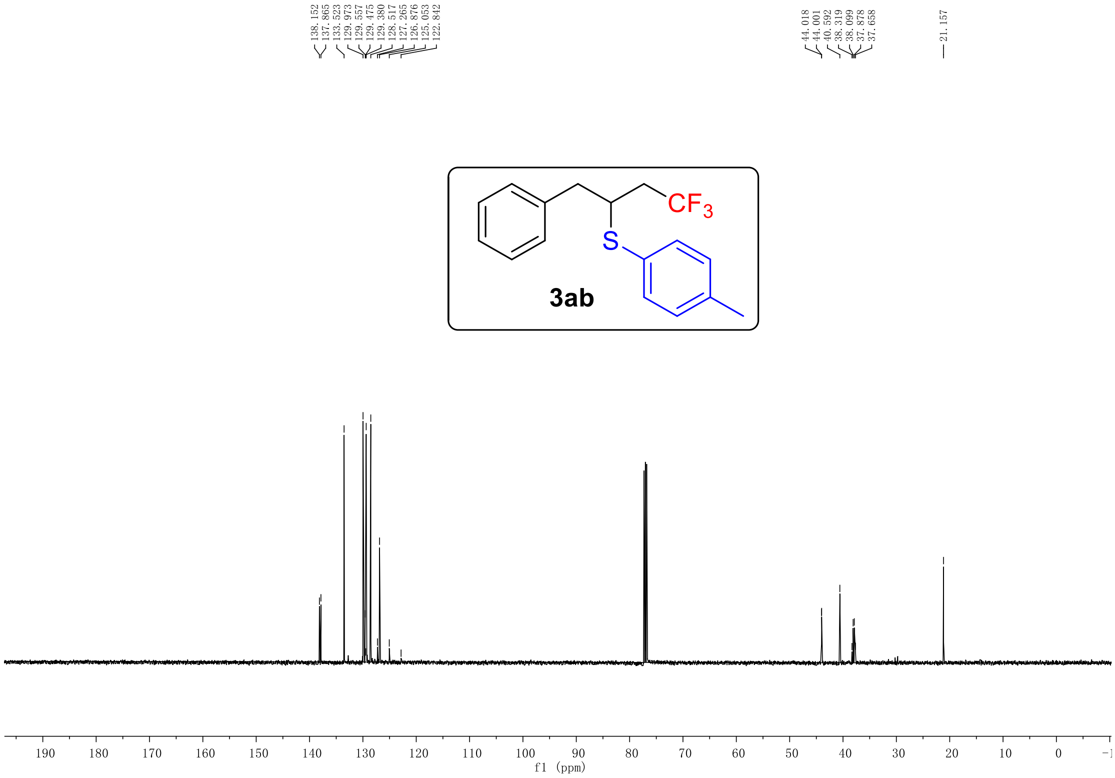
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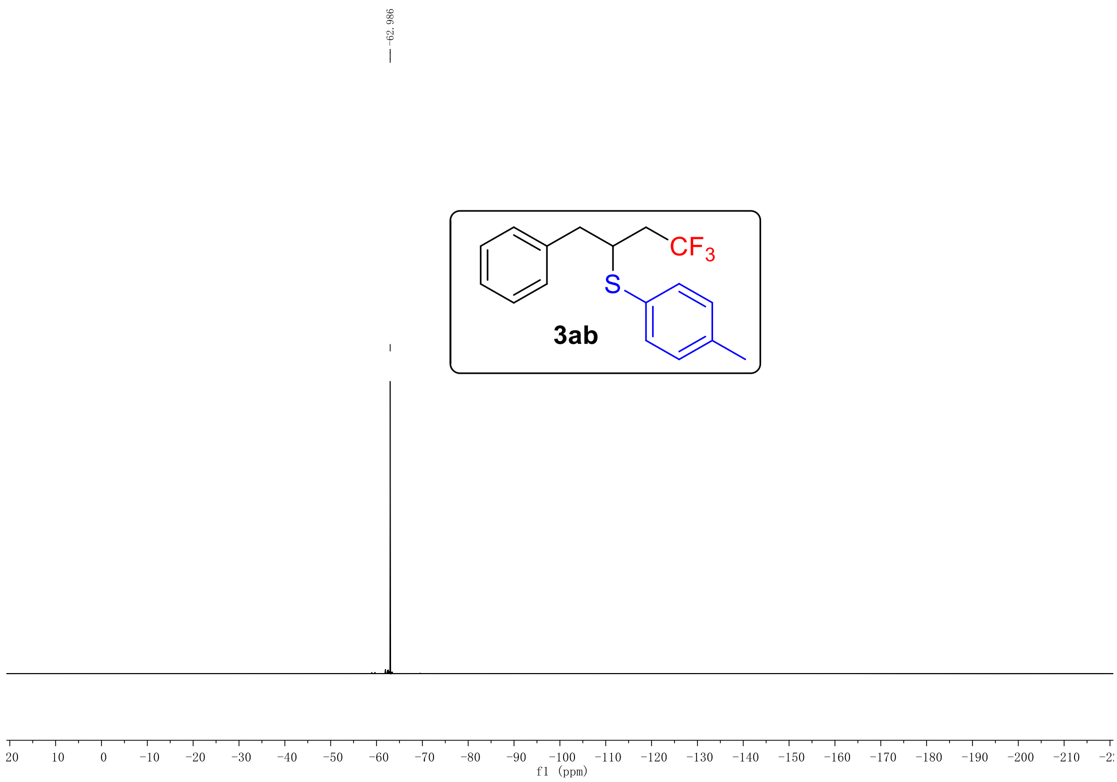
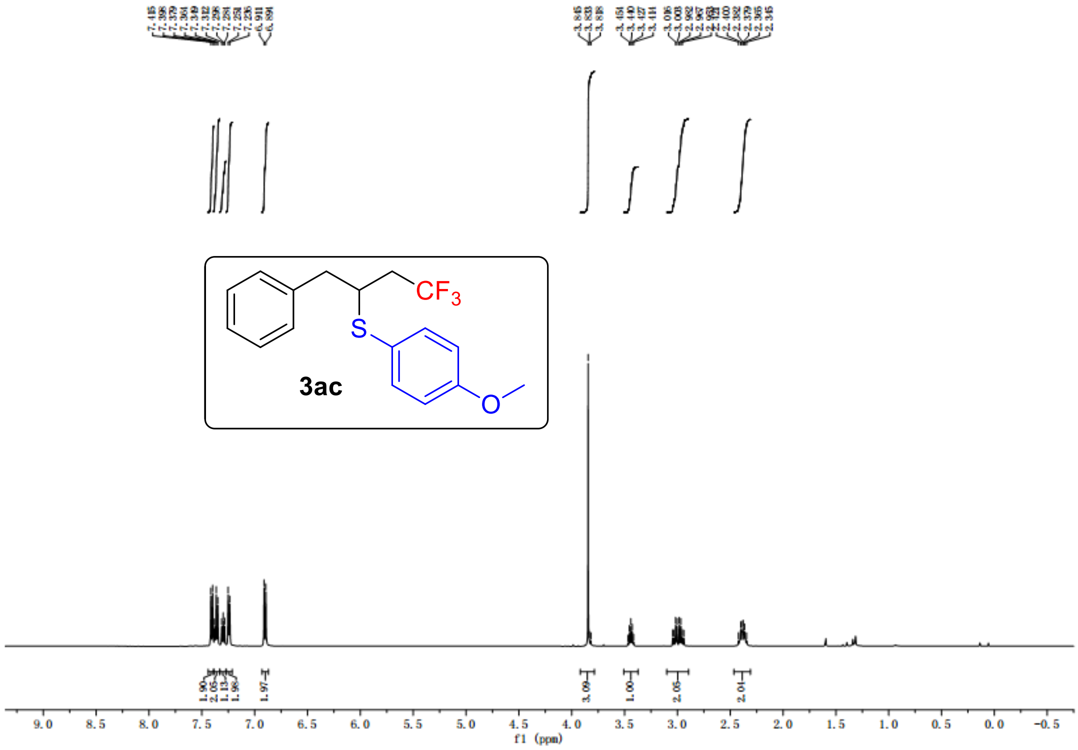
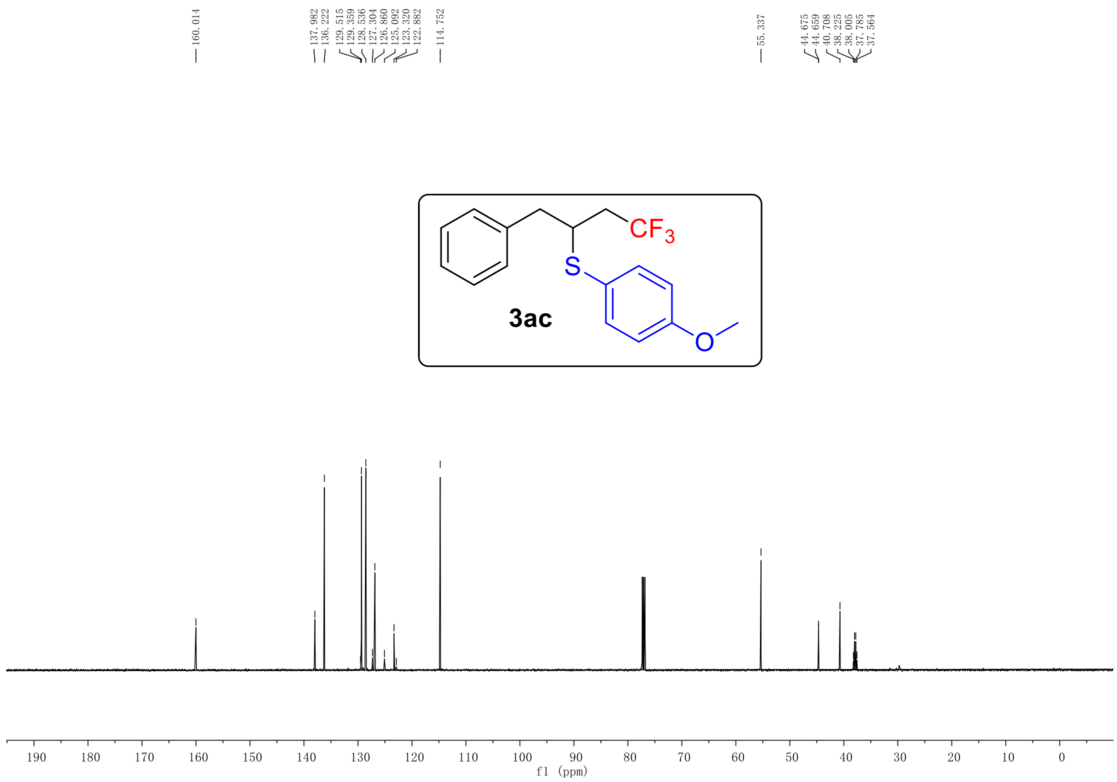
137.865
133.523
129.973
129.557
129.475
129.380
128.517
127.265
126.876
125.053
122.842
44.018
44.001
40.592
38.319
38.099
37.878
37.658
21.157
CF3
S
3ab
f1 (ppm)

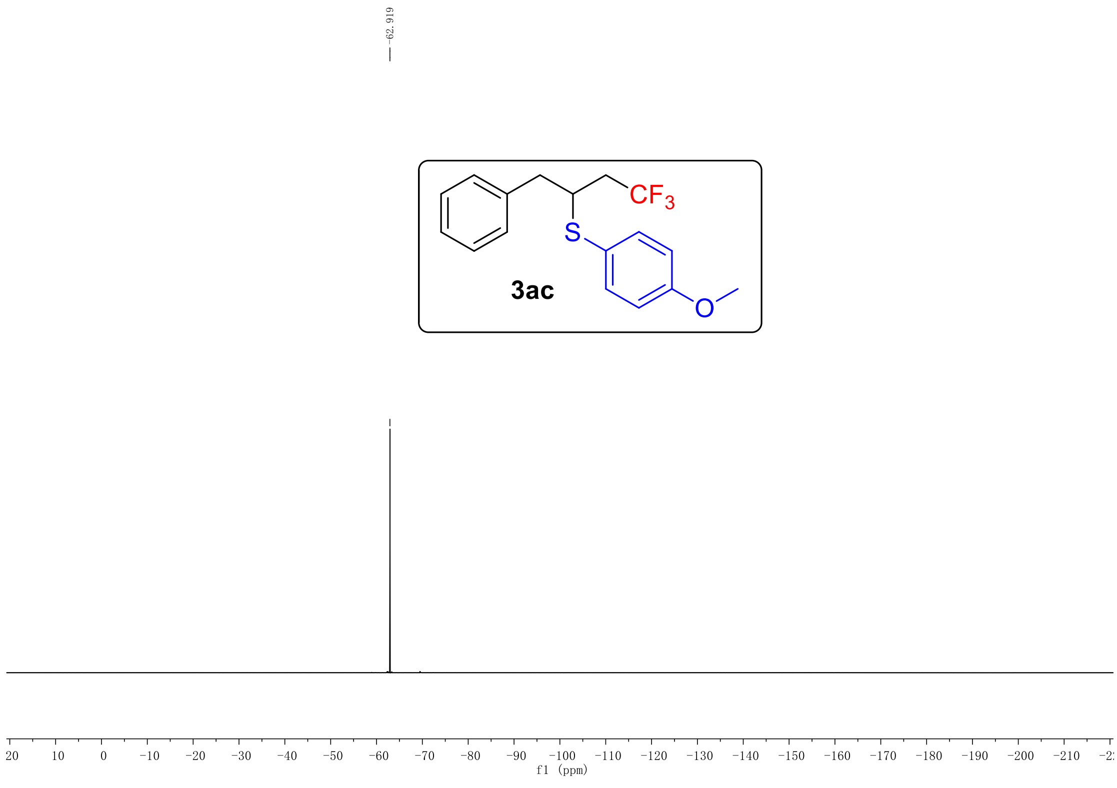


-62.986
CF3
S
3ab
f1 (ppm)



CF3
S
O
3ac
f1 (ppm)


160.014
137.982
136.222
129.515
129.359
128.536
127.304
126.860
125.092
123.320
122.882
114.752
55.337
44.675
44.659
40.708
38.225
38.005
37.785
37.564
CF3
S
O
3ac
f1 (ppm)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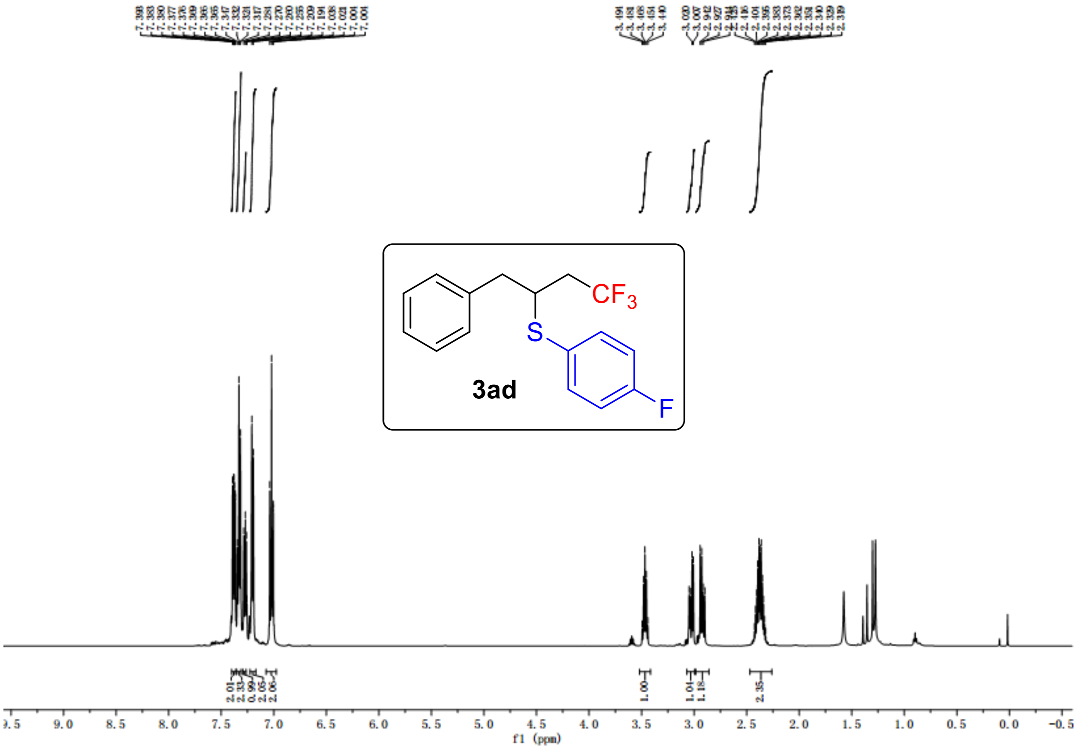
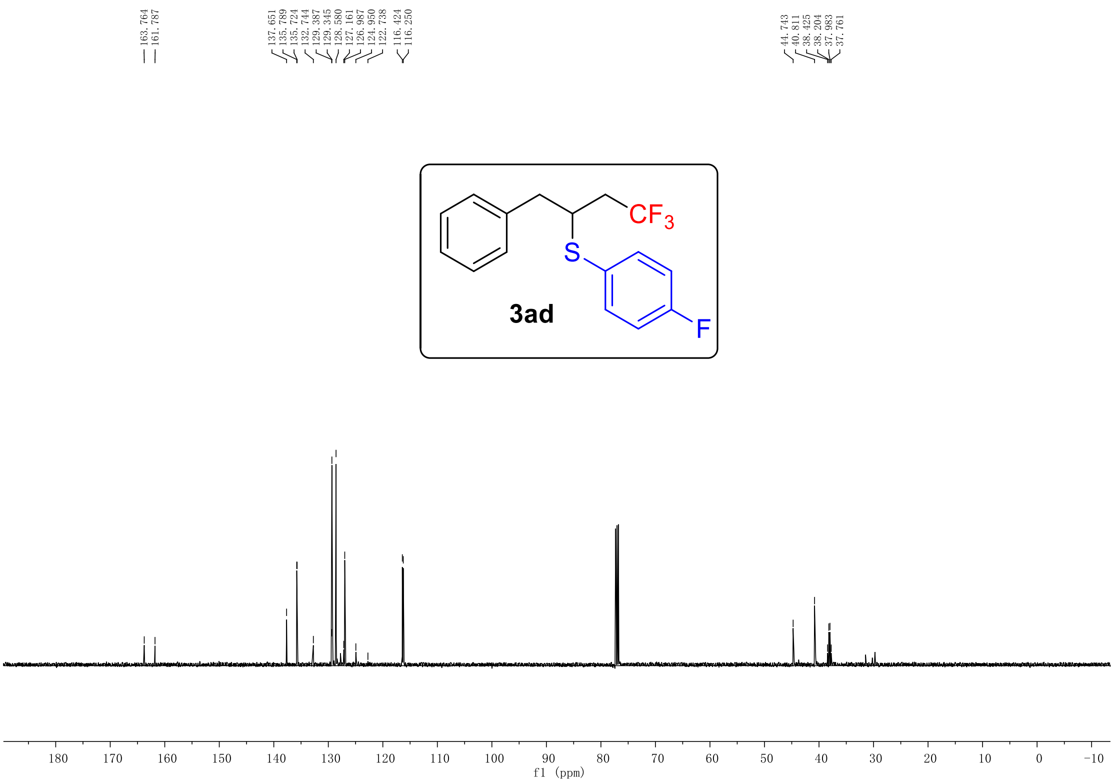
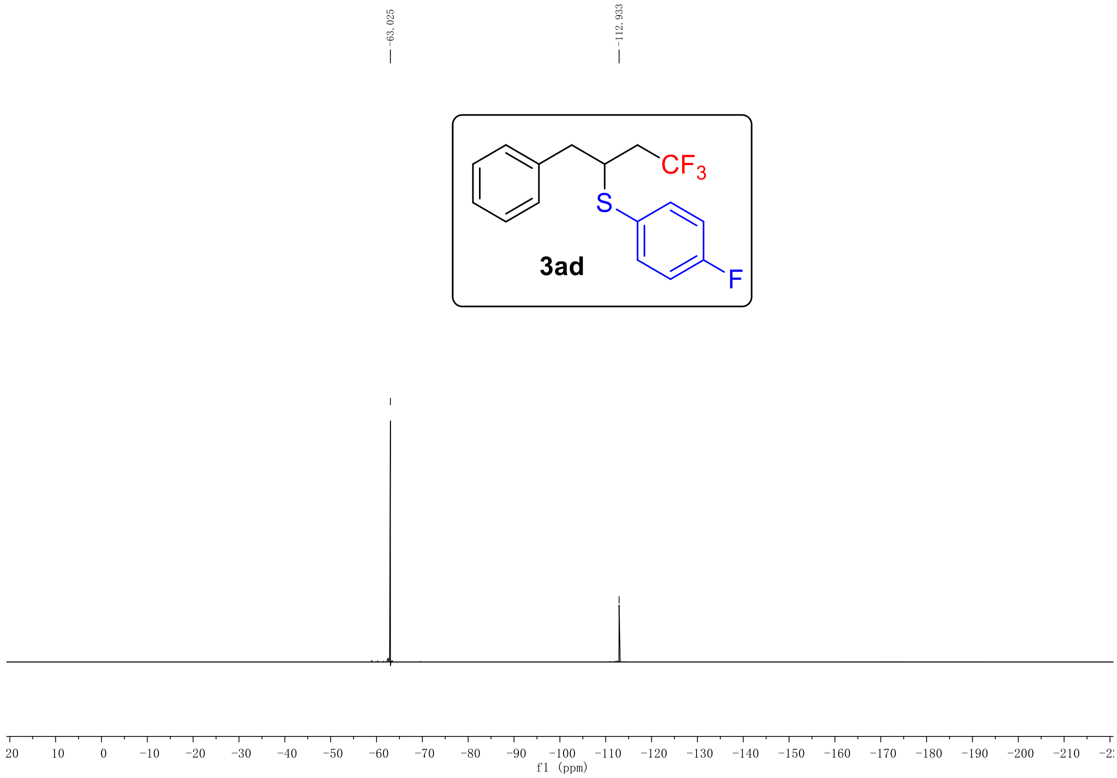
CF3
S
O
3ac
f1 (ppm)

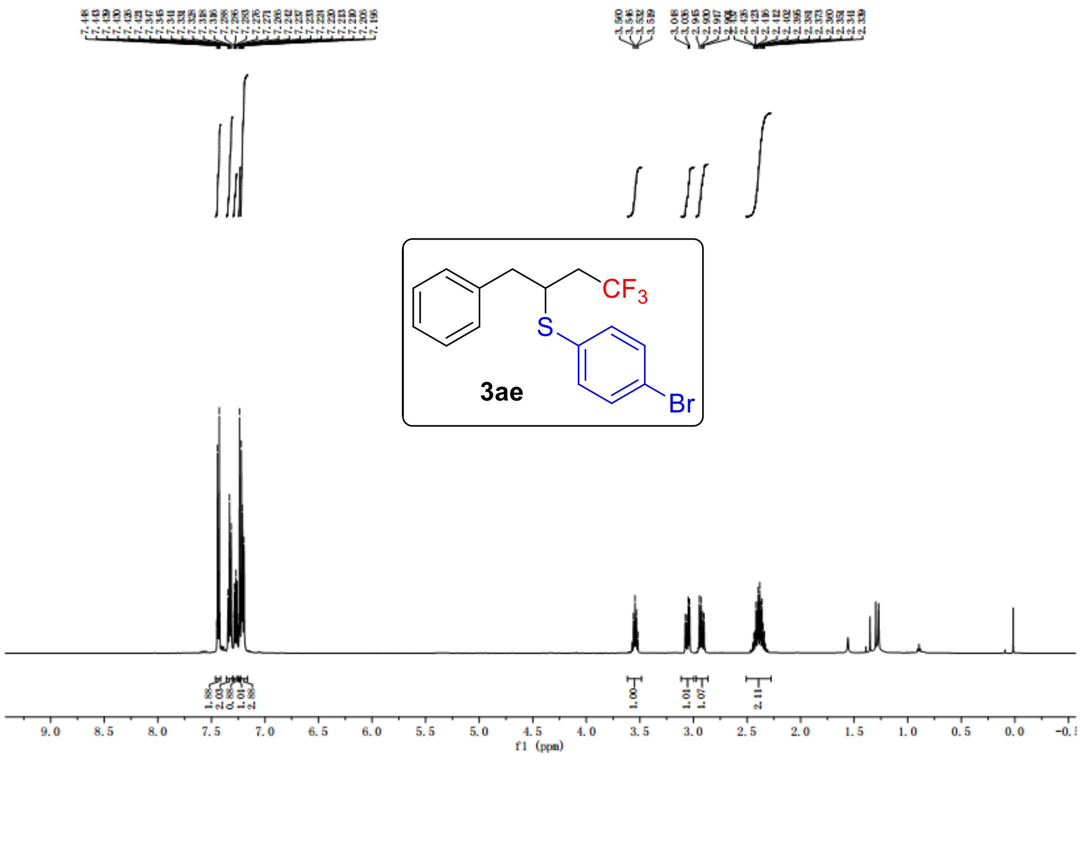


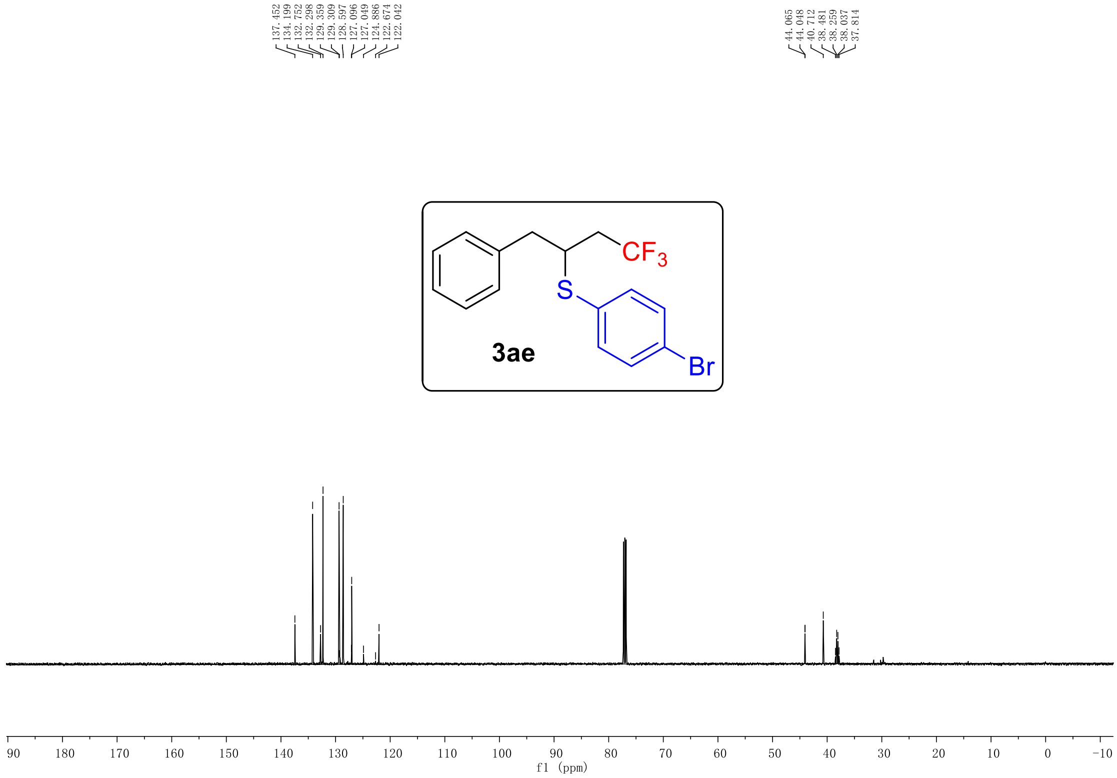
CF3
S
3ad
F
f1 (ppm)

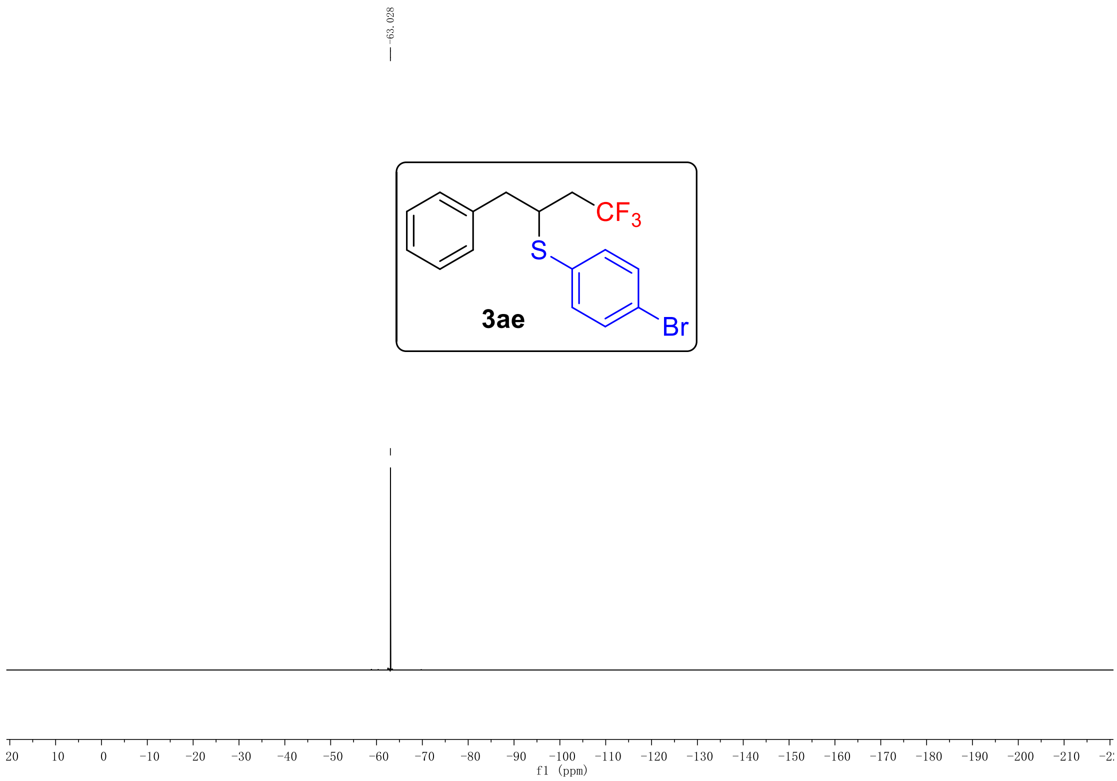


163.764
161.787
137.651
135.789
135.724
132.744
129.387
129.345
128.580
127.161
126.987
124.950
122.738
116.424
116.250
44.743
40.811
38.425
38.204
37.983
37.761
CF3
S
3ad
F
f1 (ppm)


-63.025
-112.933
CF3
S
3ad
F
f1 (ppm)


CF3
S
3ae
Br
f1 (ppm)


137.452
134.199
132.752
132.298
129.359
129.309
128.597
127.096
127.049
124.886
122.674
122.042
44.065
44.048
40.712
38.481
38.259
38.037
37.814
CF3
S
Br
3ae
f1 (ppm)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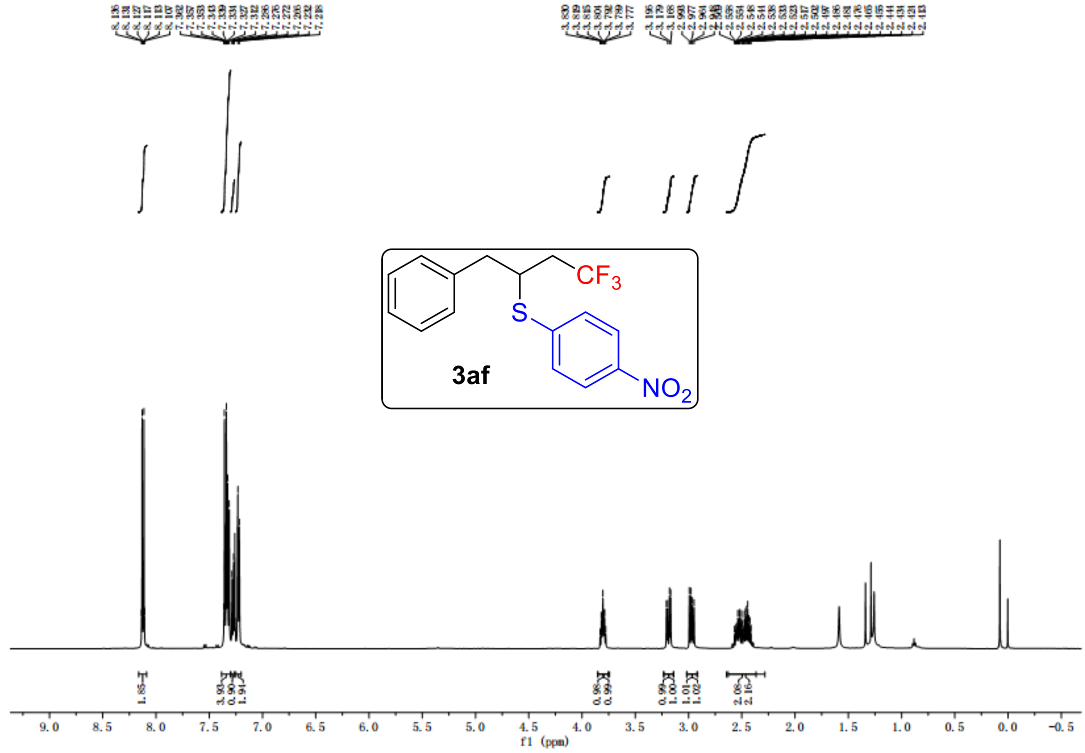
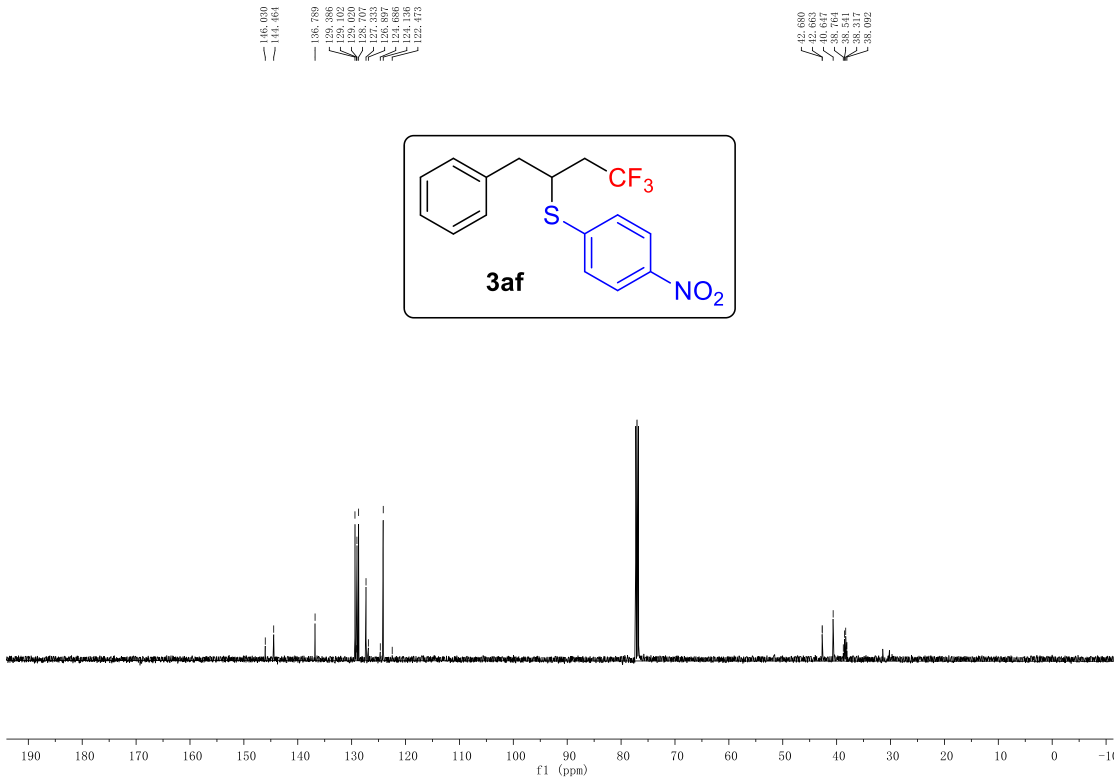
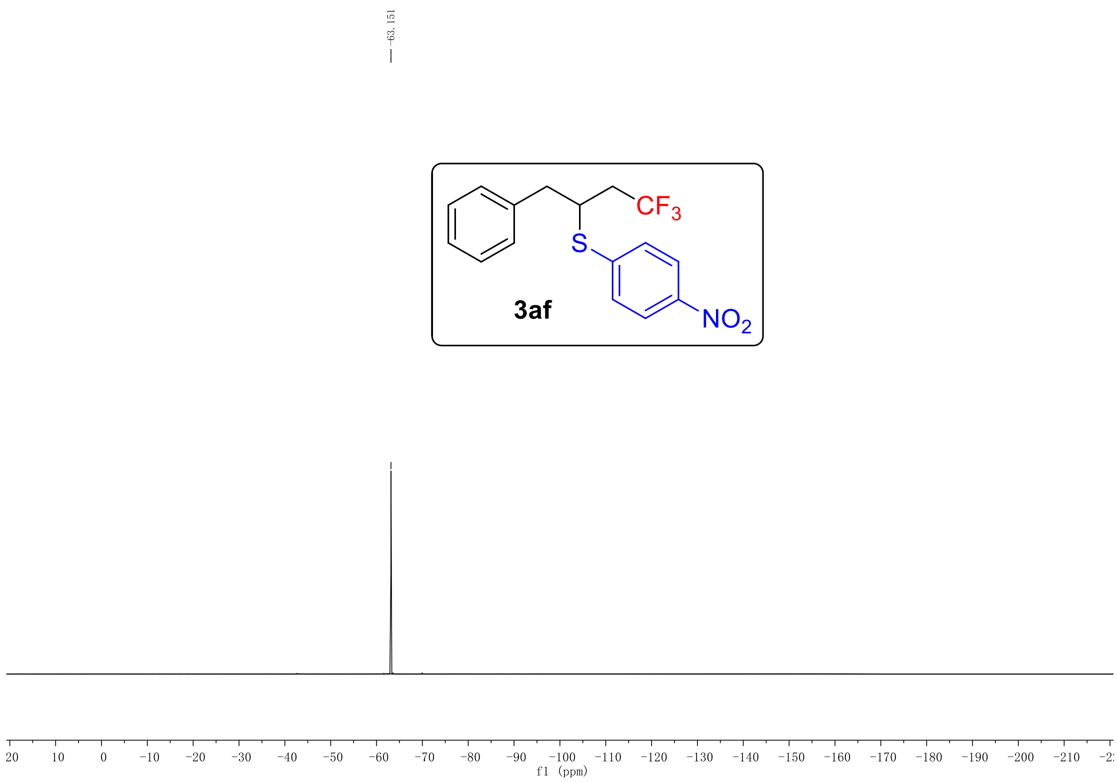
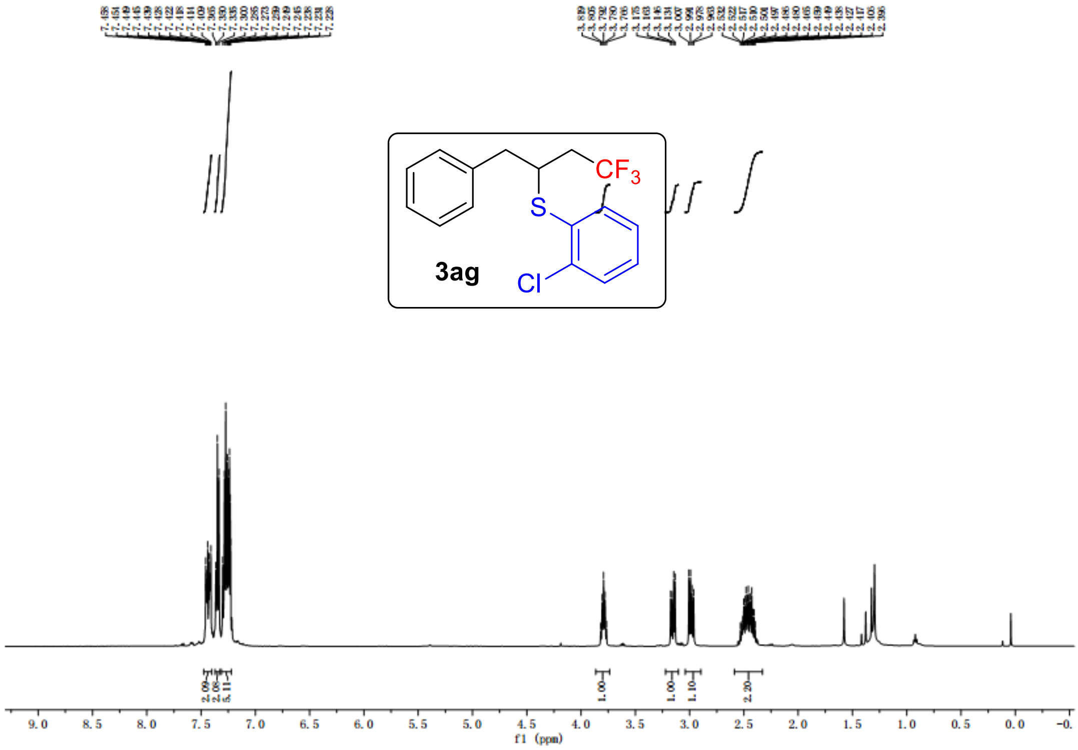
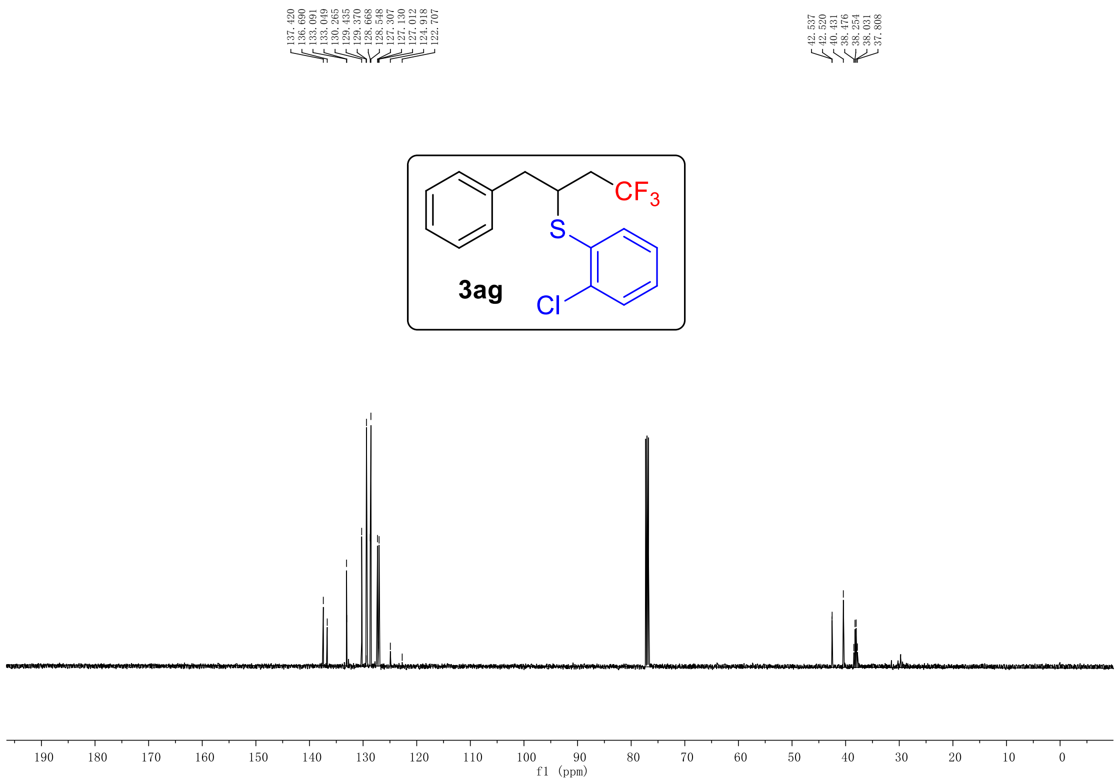
CF3
S
Br
3ae
f1 (ppm)


CF3
S
3af
NO2
f1 (ppm)


CF3
S
3af
NO2
f1 (ppm)


-63.151
3af
CF3
S
NO2
f1 (ppm)


3ag
CF3
S
Cl
f1 (ppm)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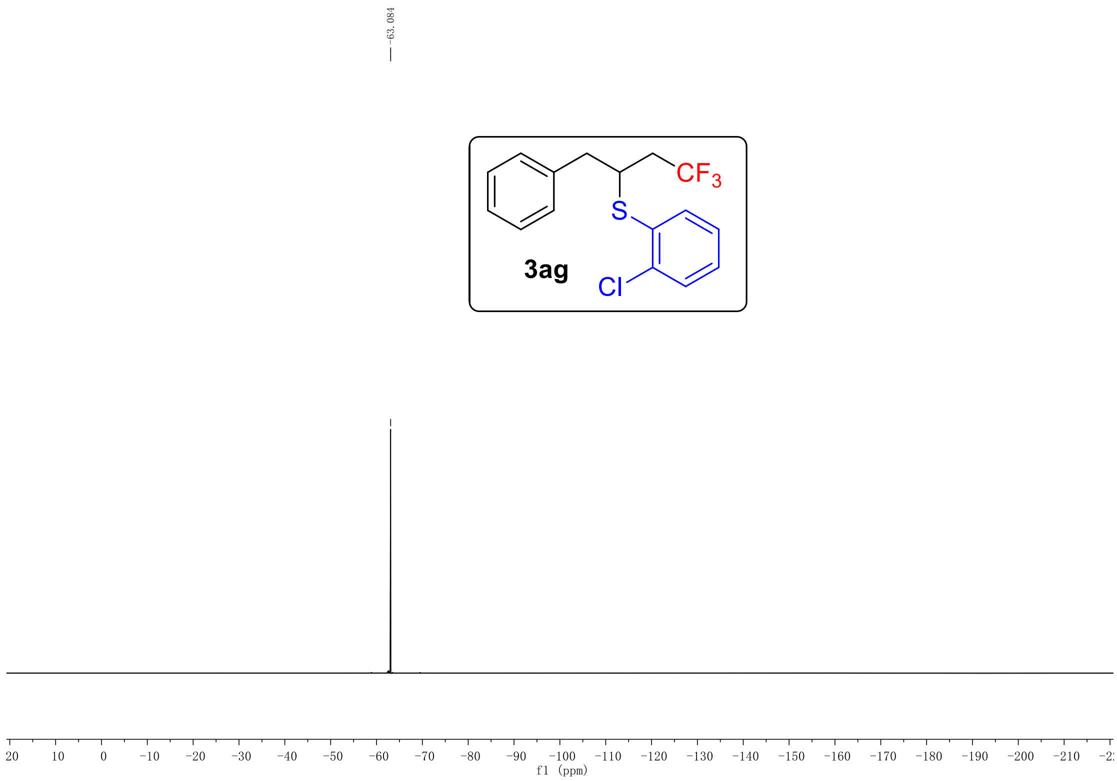
136.690
133.091
133.049
130.265
129.435
129.370
128.668
128.548
127.307
127.130
127.012
124.918
122.707
42.537
42.520
40.431
38.476
38.254
38.031
37.808
CF3
S
Cl
3ag
f1 (ppm)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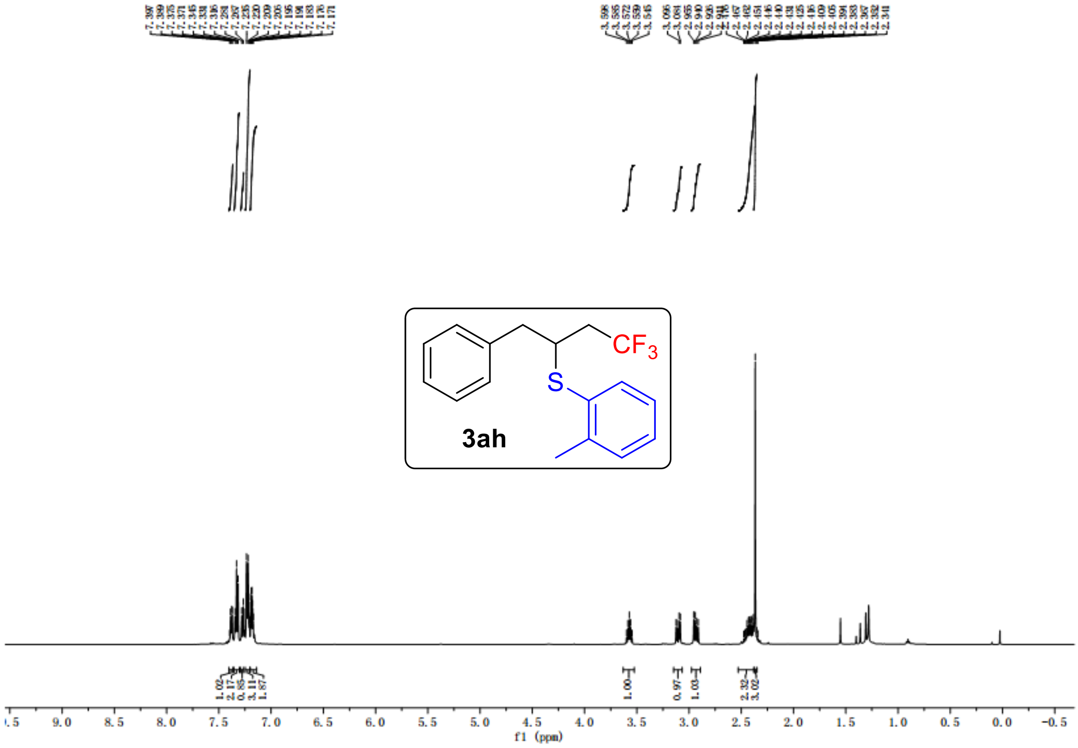
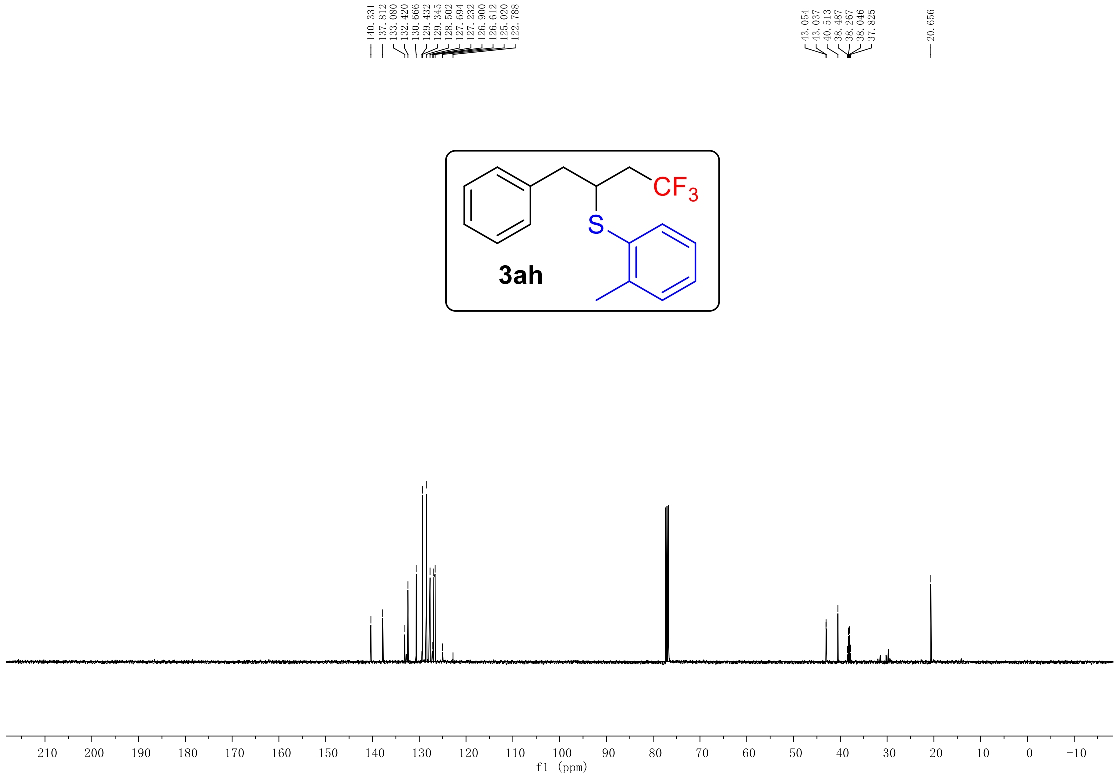
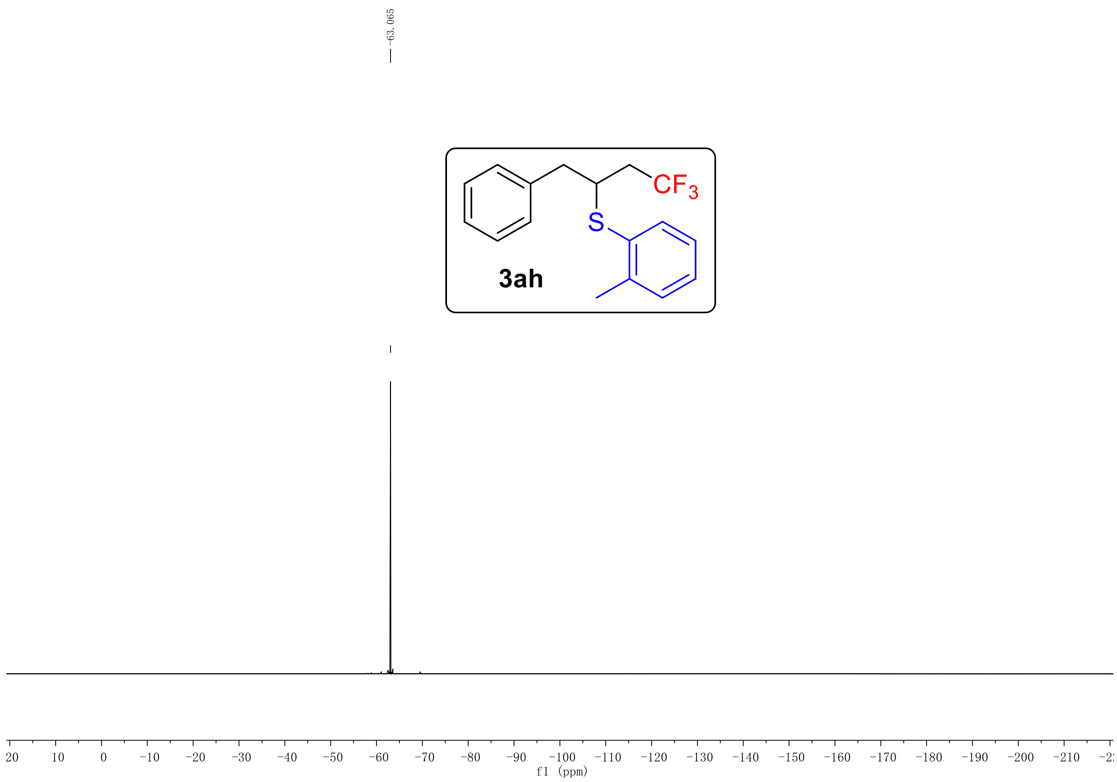
CF3
S
Cl
3ag
f1 (ppm)


CF3
S
3ah
1.02
2.17
0.85
3.11
1.87
1.00
0.97
1.03
2.32
3.02
f1 (ppm)


140.331
137.812
133.080
132.420
130.666
129.432
129.345
128.502
127.694
127.232
126.900
126.612
125.020
122.788
43.054
43.037
40.513
38.487
38.267
38.046
37.825
20.656
CF3
S
3ah
f1 (ppm)


-63.065
CF3
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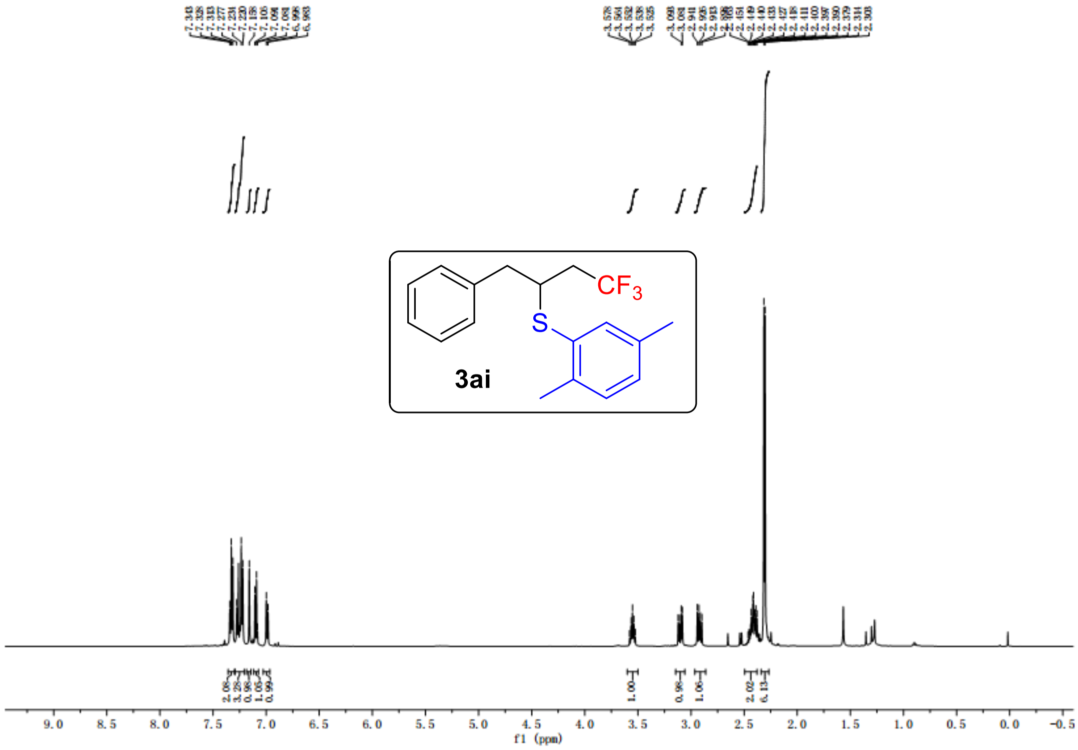
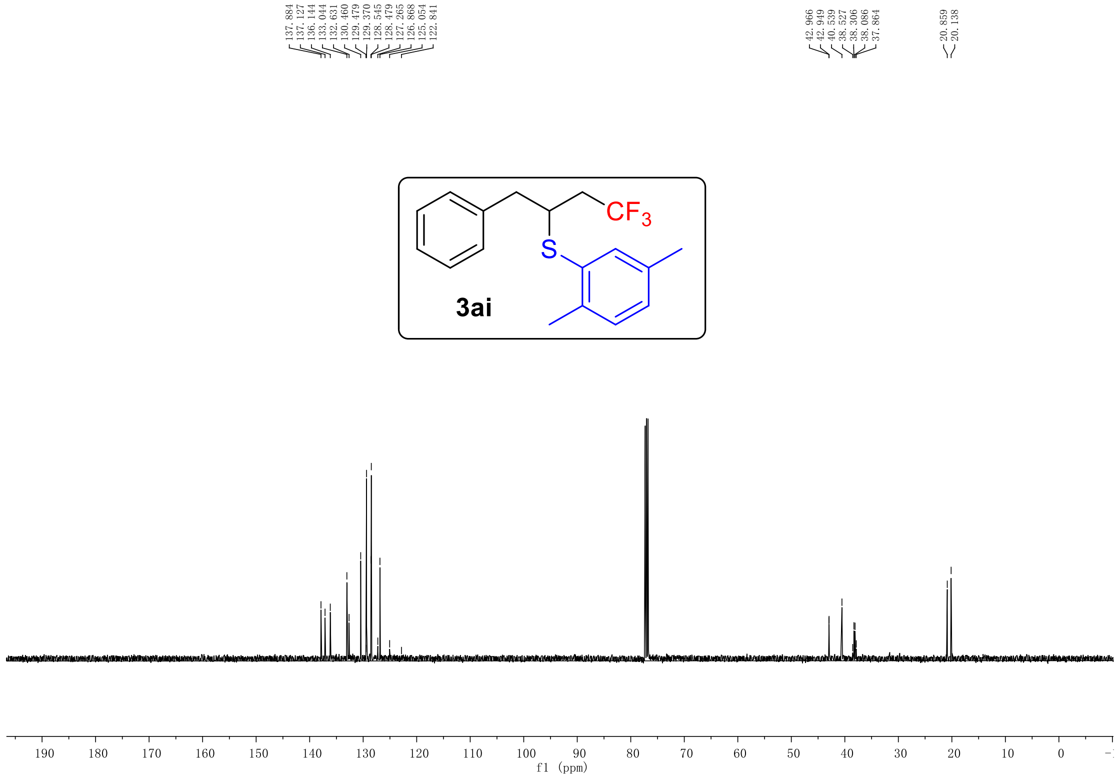
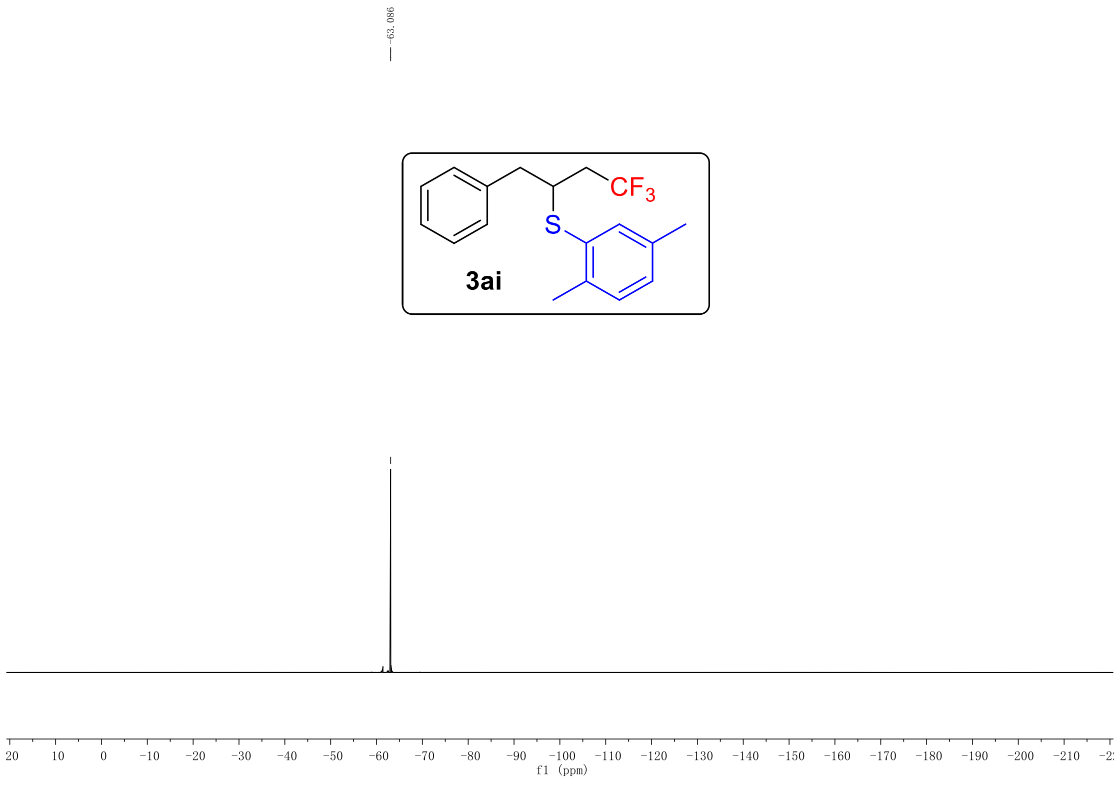
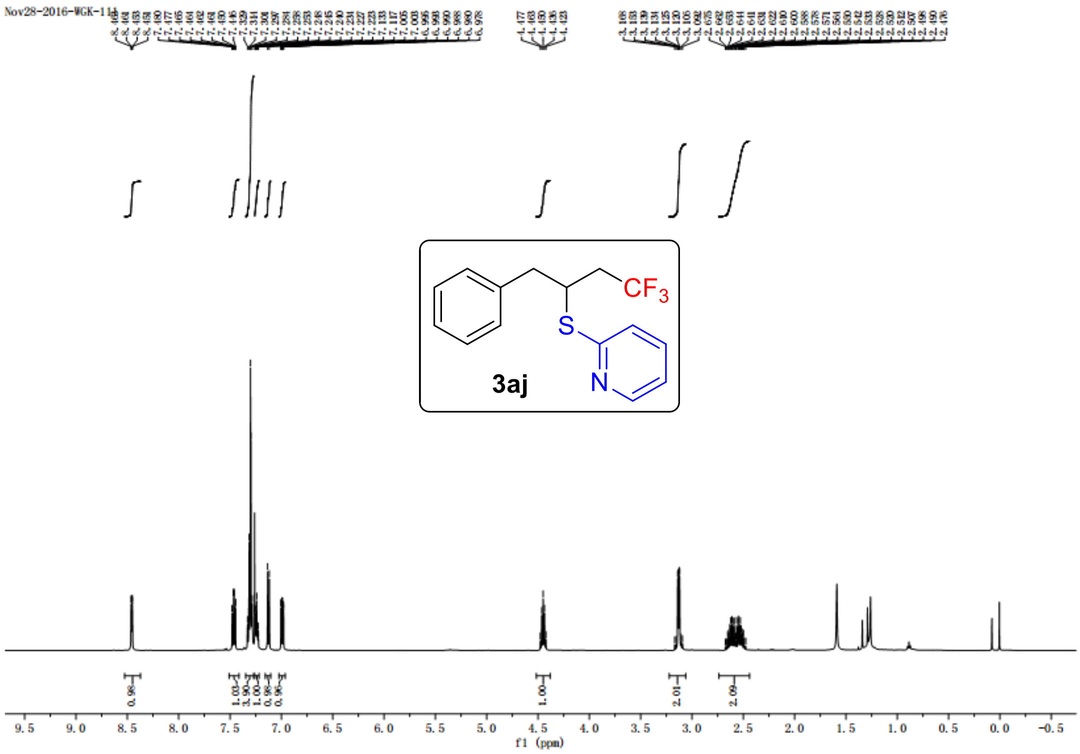
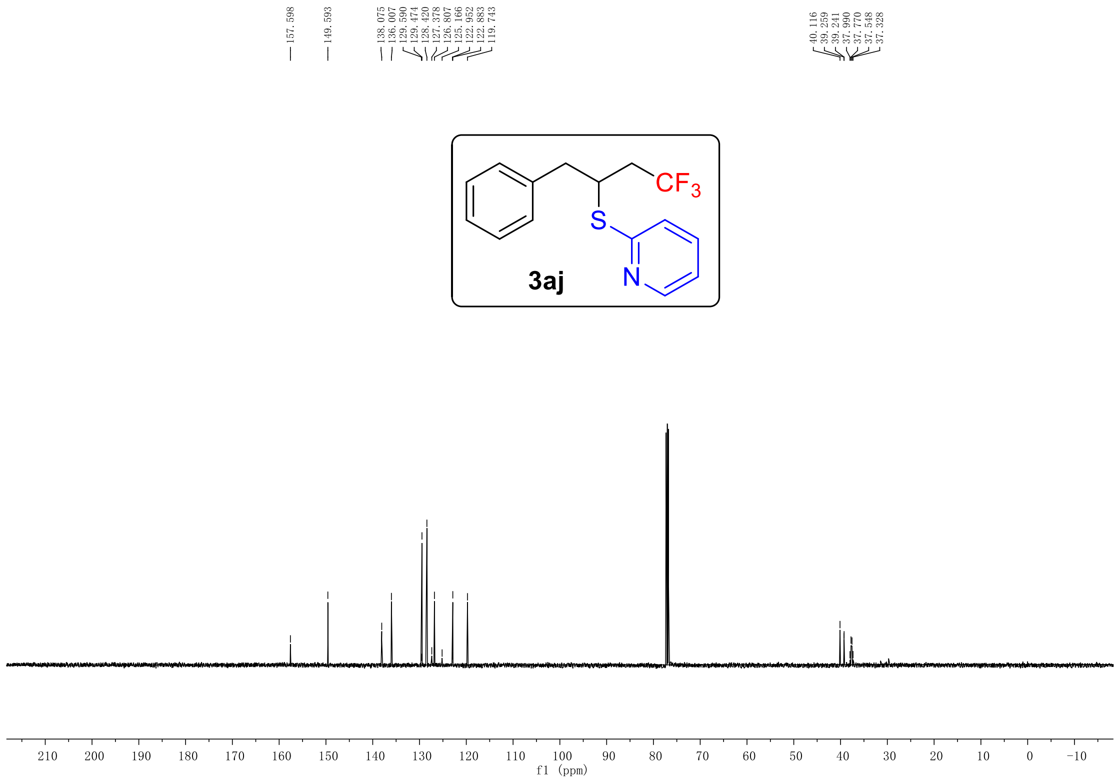
3ah
f1 (ppm)

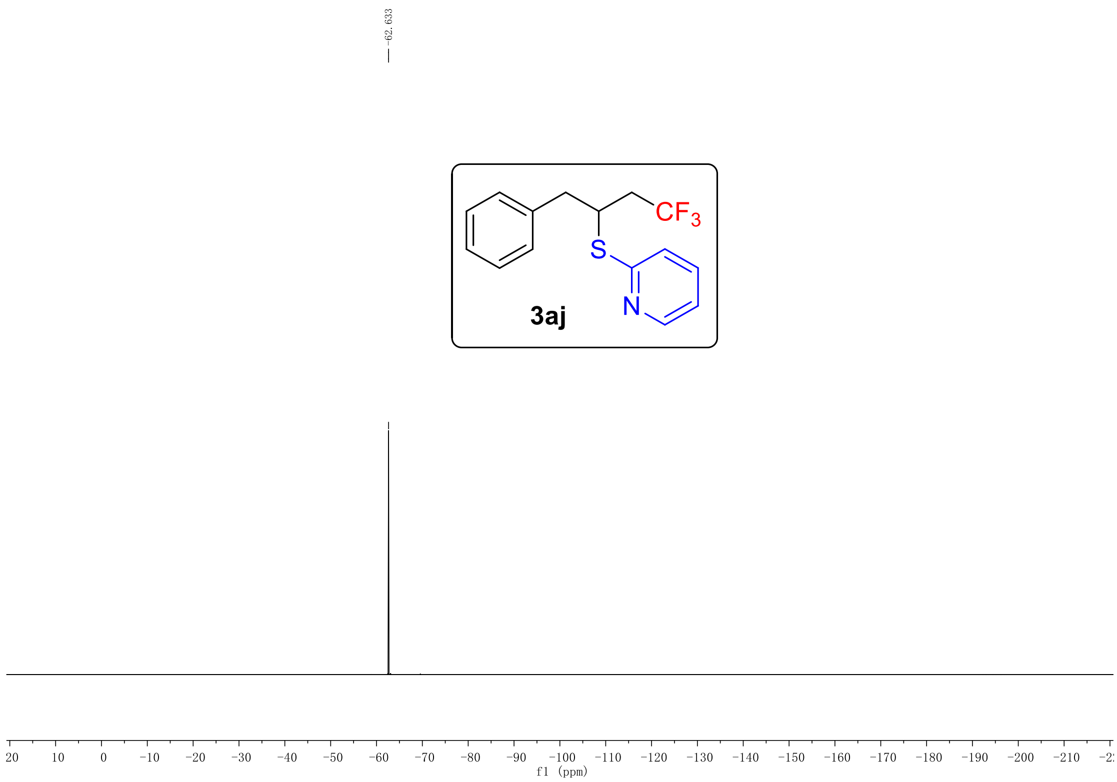

CF3
S
3ai
f1 (ppm)

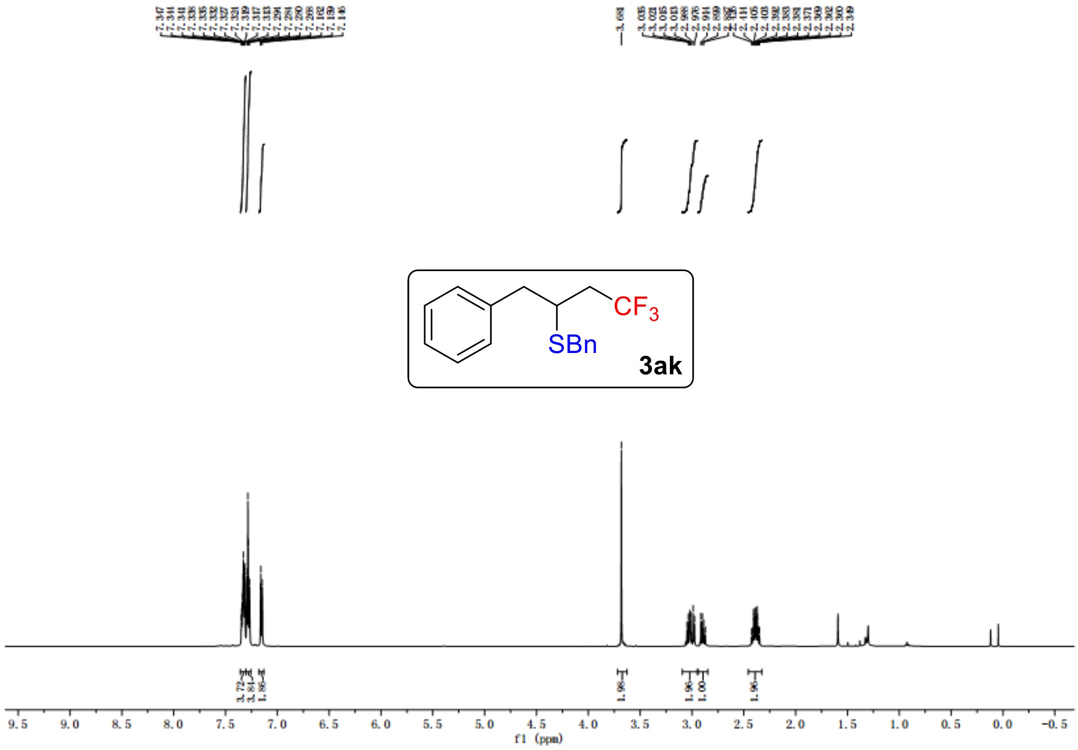


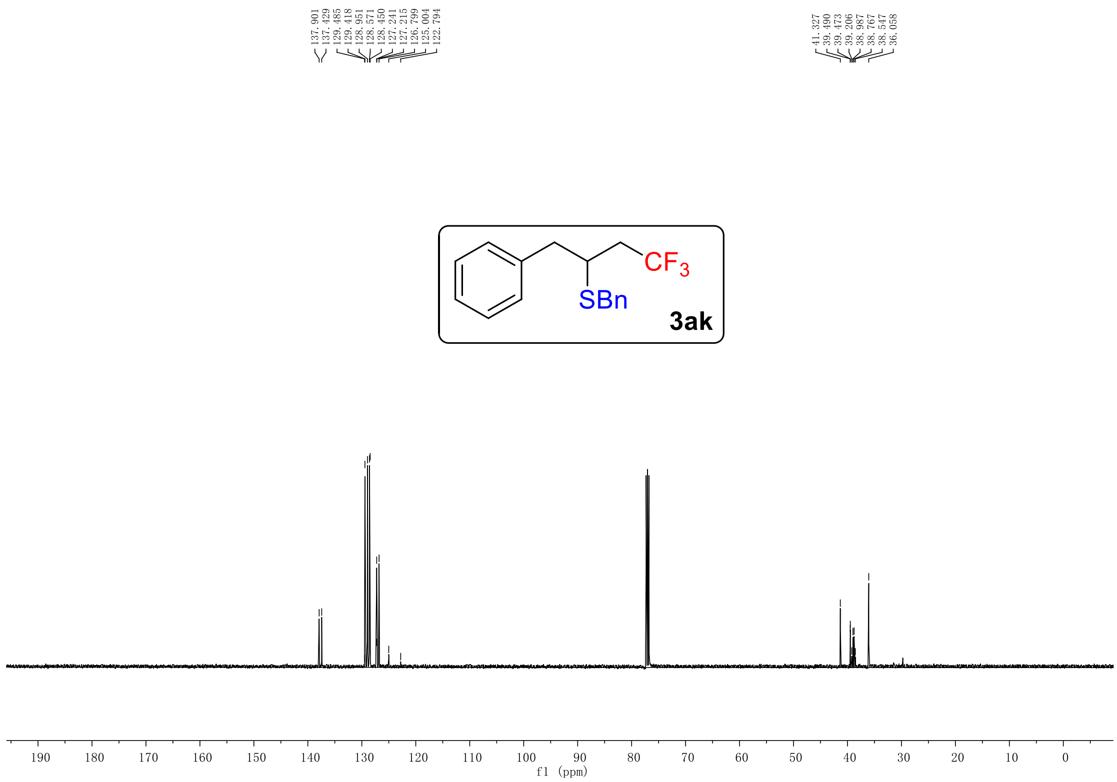







-62.633
CF3
S
N
3aj
f1 (ppm)


CF3
SBn
3ak
f1 (ppm)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137.429
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129.418
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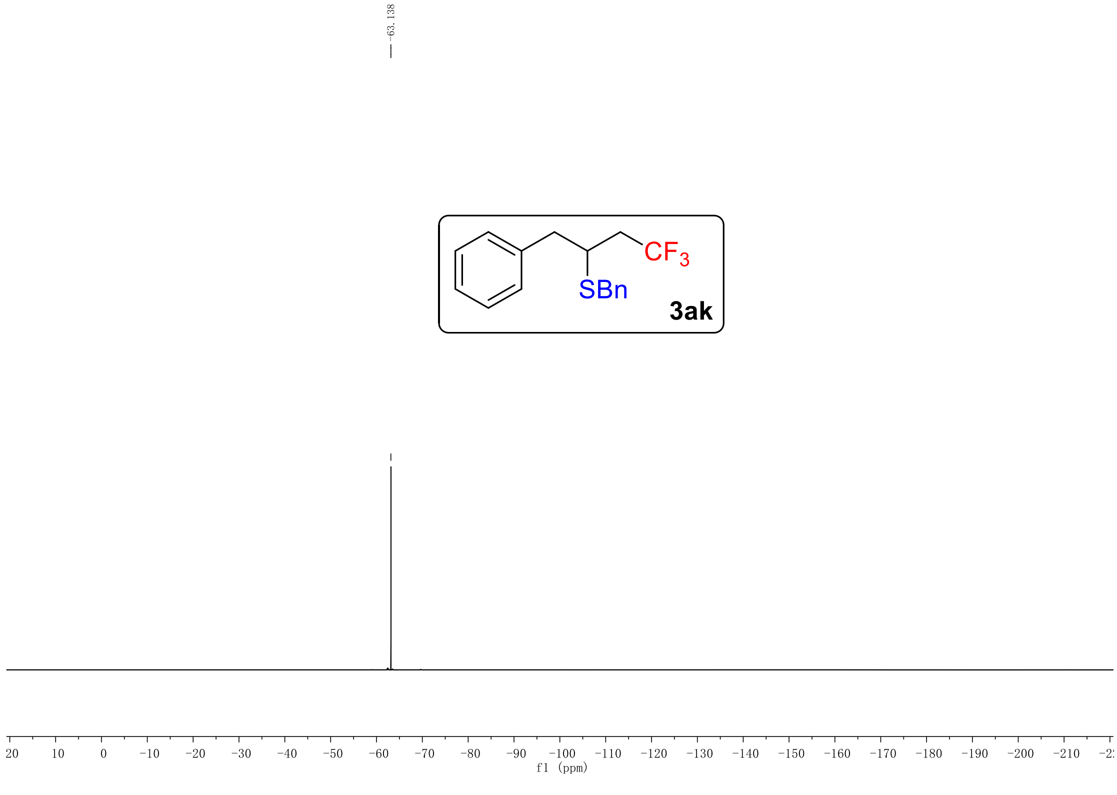
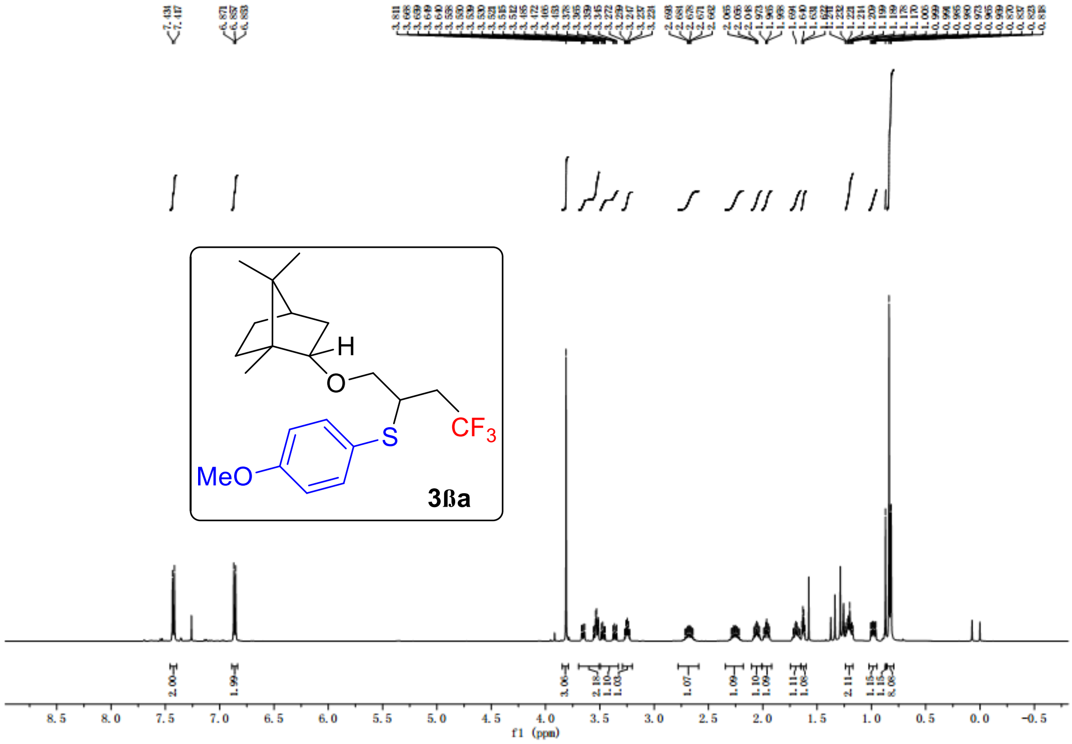
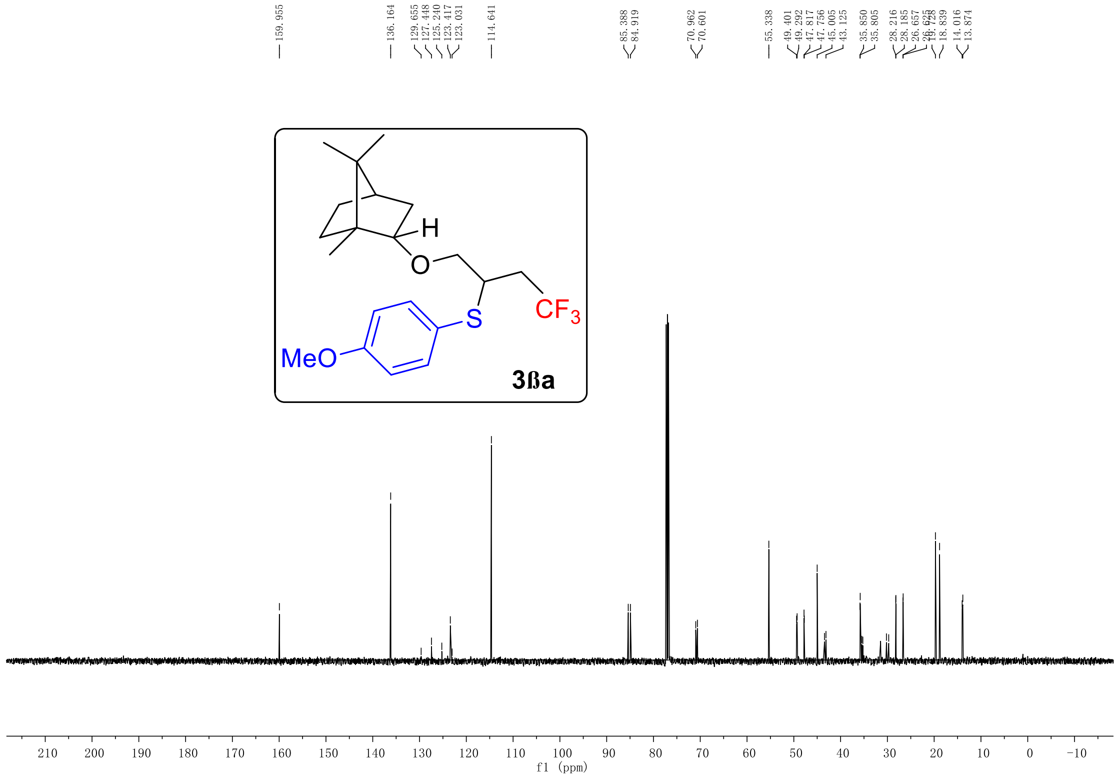
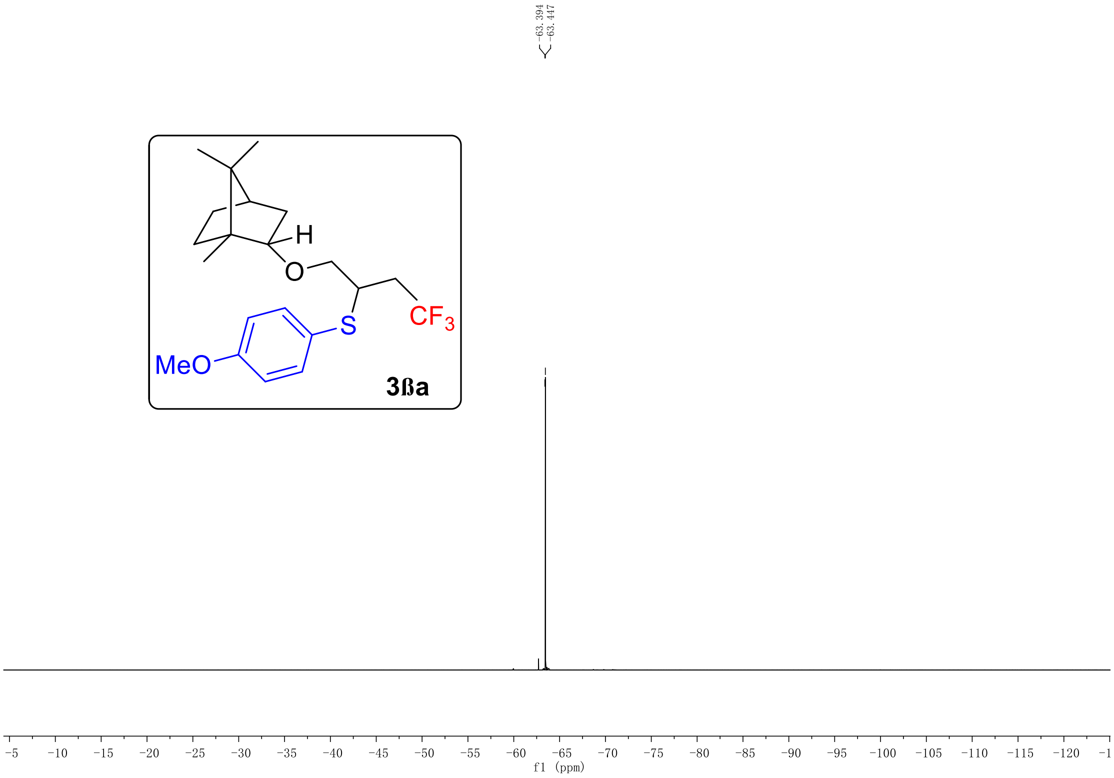
127.241
127.215
126.799
125.004
122.794
41.327
39.490
39.473
39.206
38.987
38.767
38.547
36.058
CF3
SBn
3ak
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-63.138
CF3
SBn
3ak
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


H
O
S
CF3
MeO
3ßa
f1 (ppm)


H
O
S
CF3
MeO
3ßa
f1 (ppm)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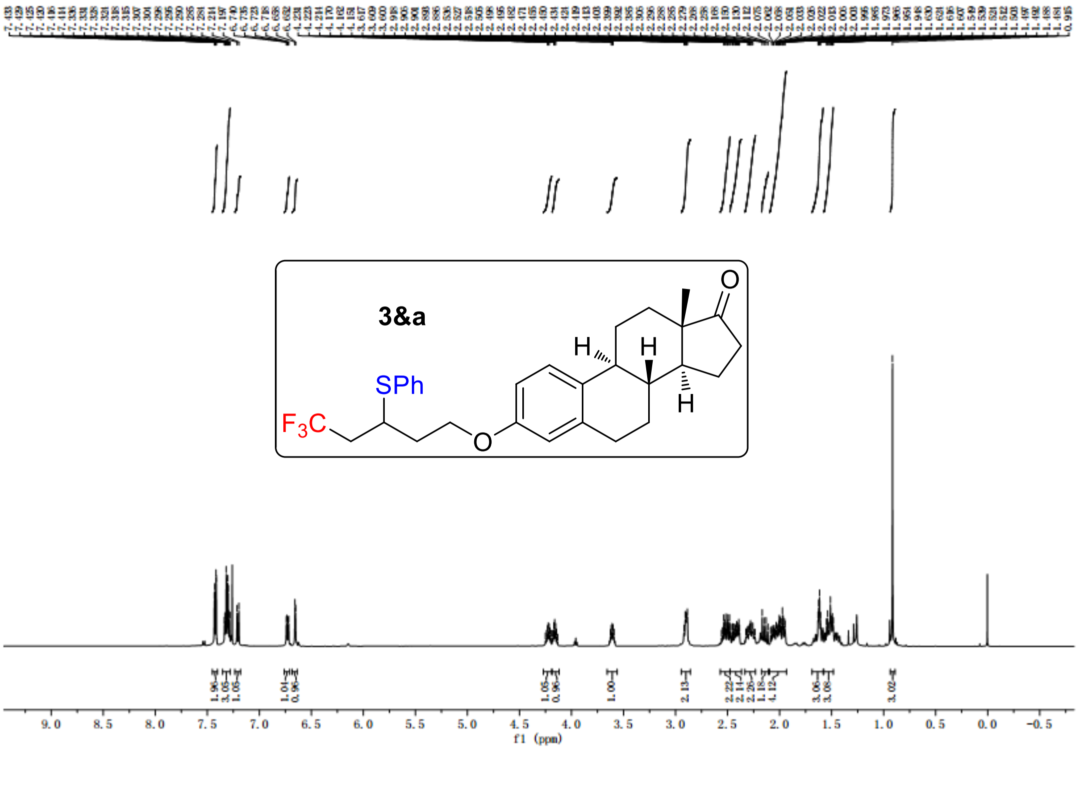
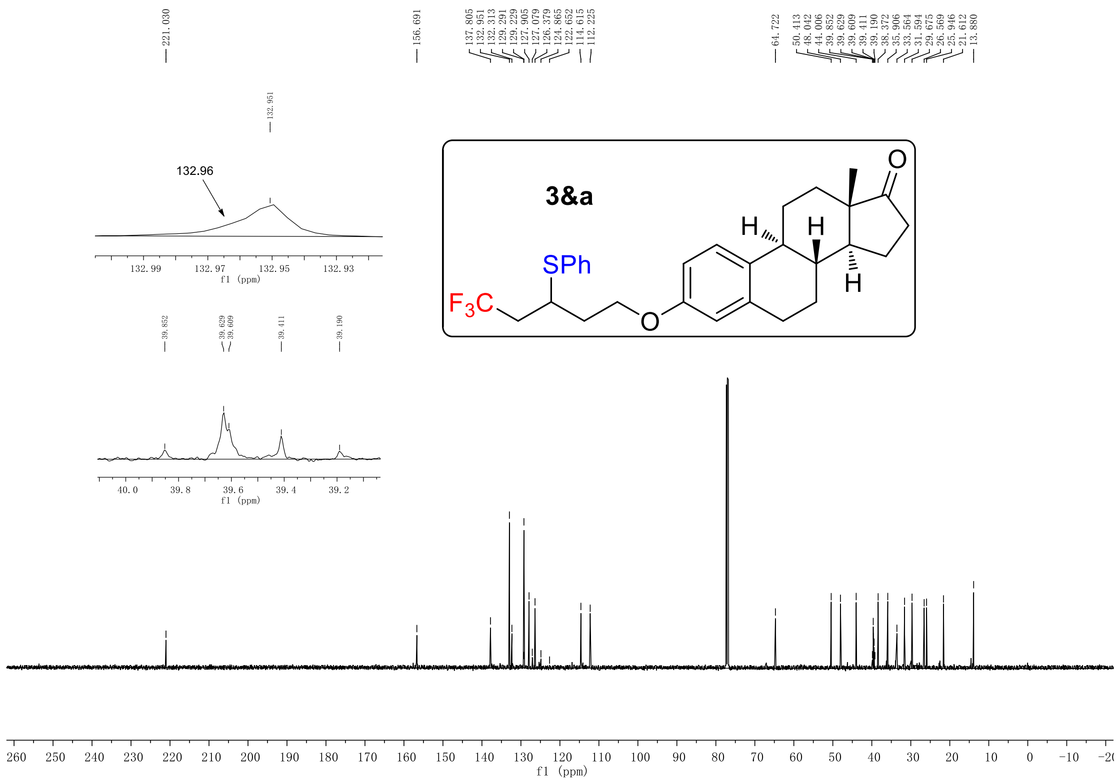
-63.447
MeO
S
O
H
CF3
3ßa
f1 (ppm)


3&a
SPh
F3C
O
H
H
H
O
f1 (ppm)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132.313
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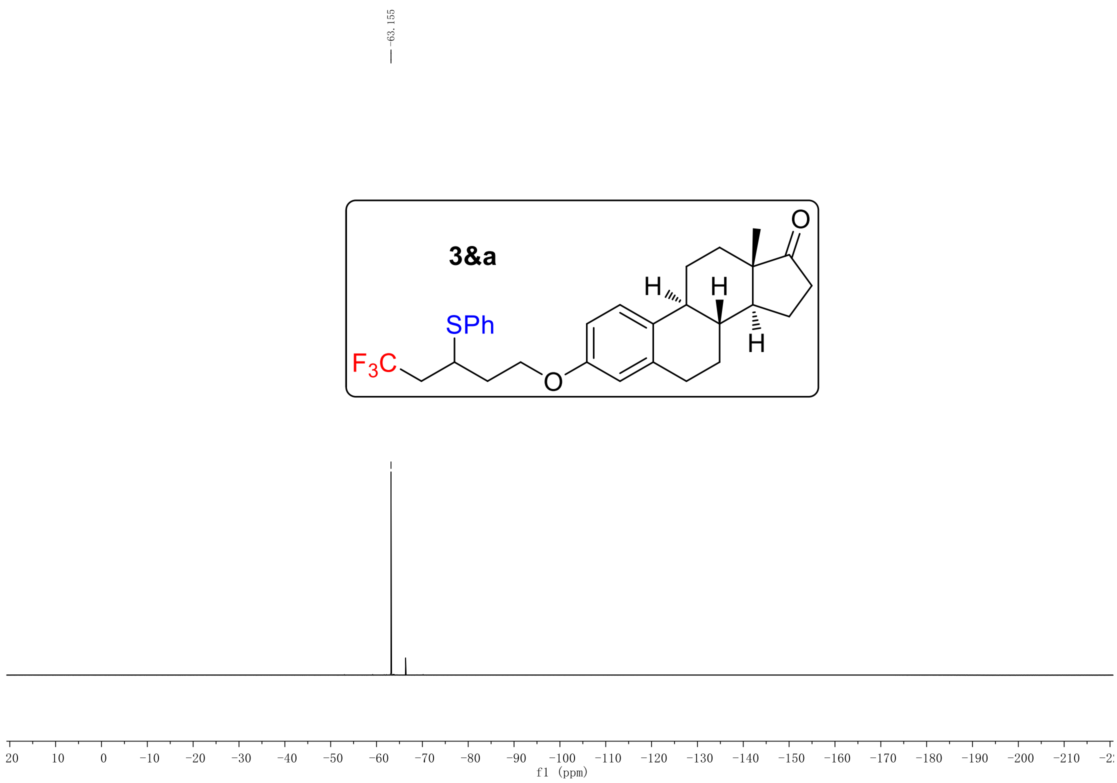
129.229
127.905
127.079
126.379
124.865
122.652
114.615
112.225
64.722
50.413
48.042
44.066
39.852
39.629
39.609
39.411
39.190
38.372
35.906
33.564
31.594
29.675
26.569
25.946
21.612
13.880
132.96
3&a
SPh
F3C
O
H
H
H
f1 (ppm)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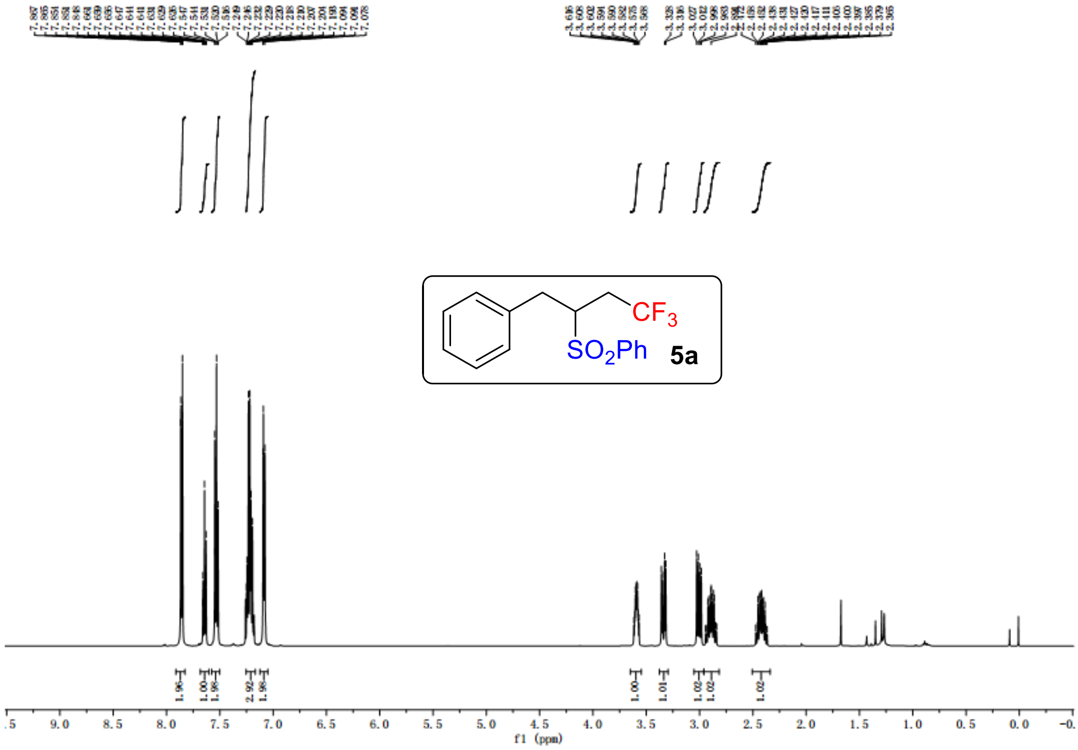
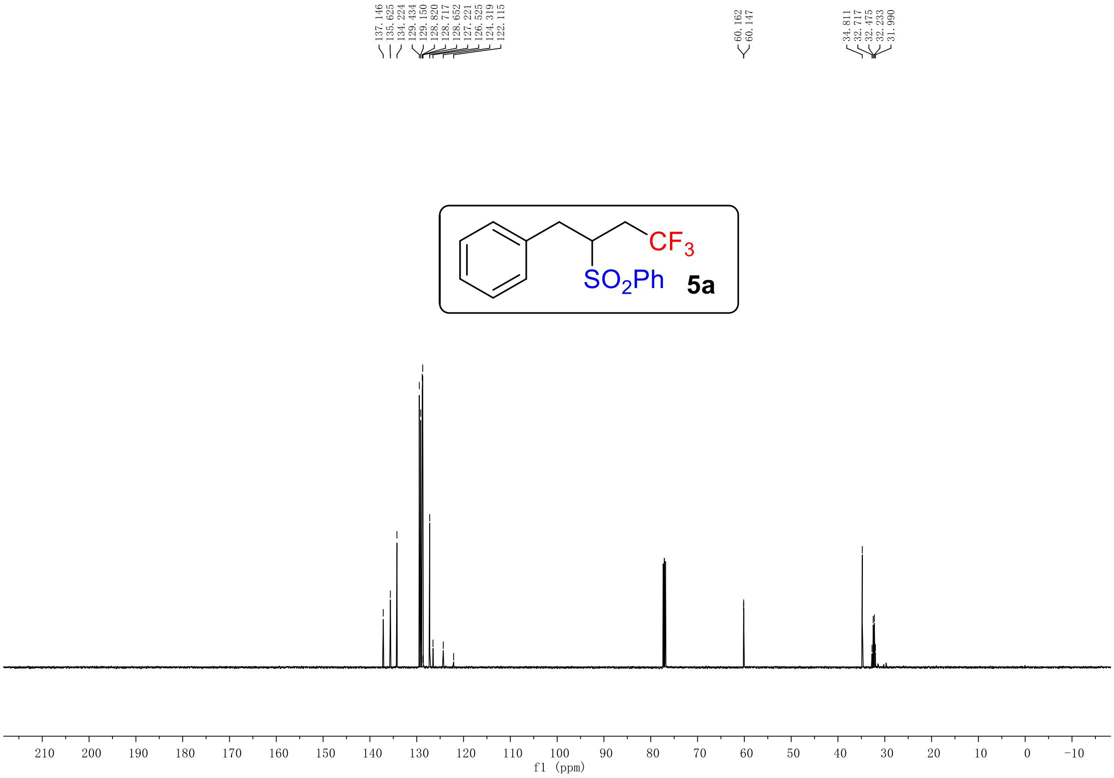
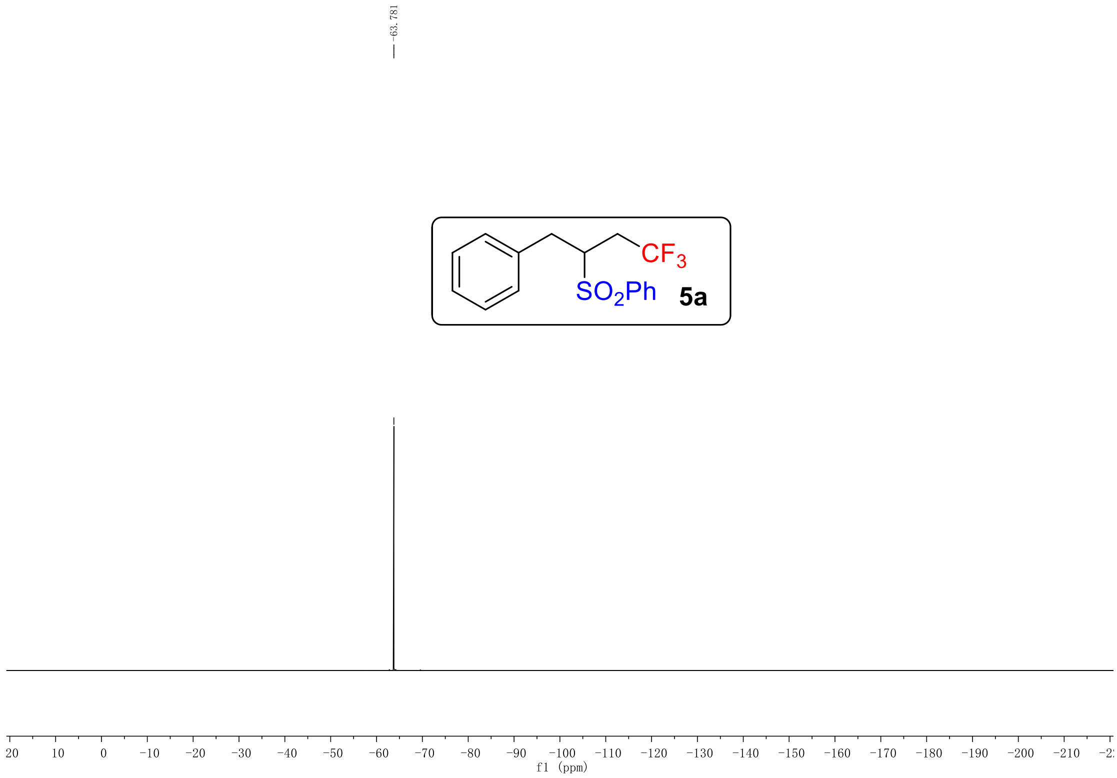
F3C
O
H
H
H
f1 (ppm)


CF3
SO2Ph
5a
f1 (ppm)


CF3
SO2Ph
5a
f1 (ppm)


-63.781
CF3
SO2Ph
5a
f1 (ppm)