Supporting Information for

A General Platform for *S*-Stereogenic α-Fluoroalkyl S(IV/VI) Compounds via Enantioselective Radical Fluoroalkylation of Sulfenamides

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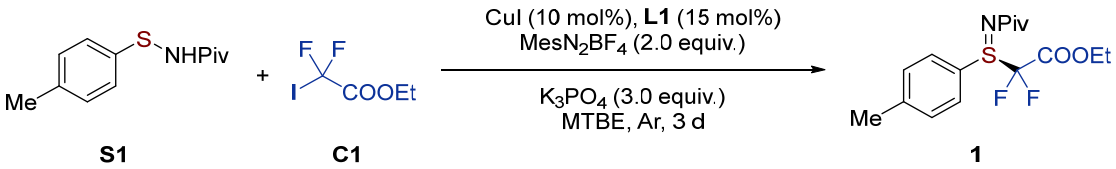
1. Supplementary tables for experiments

Table S1. Reaction condition optimization with **S1** and **C1**: Screening of temperature[a]

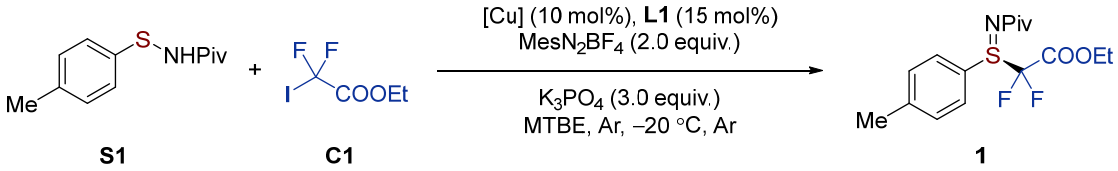


S1 **C1** **1**

Entry	Temperature (°C)	Yield (%)	ee (%)
1	− 30	30	98
2	− 20	95	98
3	− 10	76	89
4	0	85	78

[a] Reaction conditions: **S1** (0.20 mmol), **C1** (1.5 equiv.), CuI (10 mol%), **L1** (15 mol%), $MesN_2BF_4$ (2.0 equiv.) and K_3PO_4 (3.0 equiv.) in MTBE (4.0 mL) for 3 d under argon. Yield is based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. Ee values are based on chiral HPLC analysis. Piv, *tert*-butylcarbonyl; Mes, mesityl; MTBE, methyl *tert*-butyl ether.

Table S2. Reaction condition optimization with **S1** and **C1**: Screening of copper salts[a]

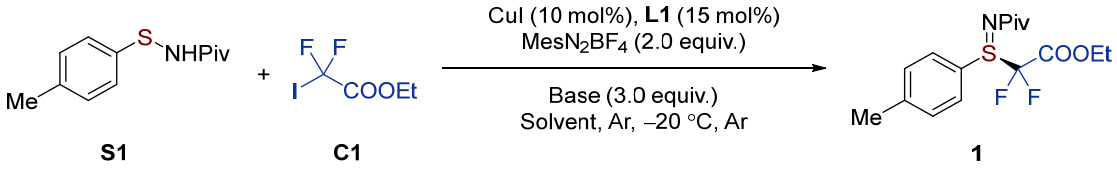


S1 **C1** **1**

Entry	[Cu]	Yield (%)	ee (%)
1	CuI	95	98
2	CuBr	74	97
3	$Cu(OTf)_2$	60	83
4	$Cu(Br)_2$	81	91
5	CuTc	90	97
6	$Cu(PPh_3)_2BH_4$	0	ND
7	$Cu(OAc)_2$	69	70

[a] Reaction conditions: **S1** (0.20 mmol), **C1** (1.5 equiv.), [Cu] (10 mol%), **L1** (15 mol%), $MesN_2BF_4$ (2.0 equiv.) and K_3PO_4 (3.0 equiv.) in MTBE (4.0 mL) at –20 °C for 3 d under argon. Yield is based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. Ee values are based on chiral HPLC analysis. ND, not detected.

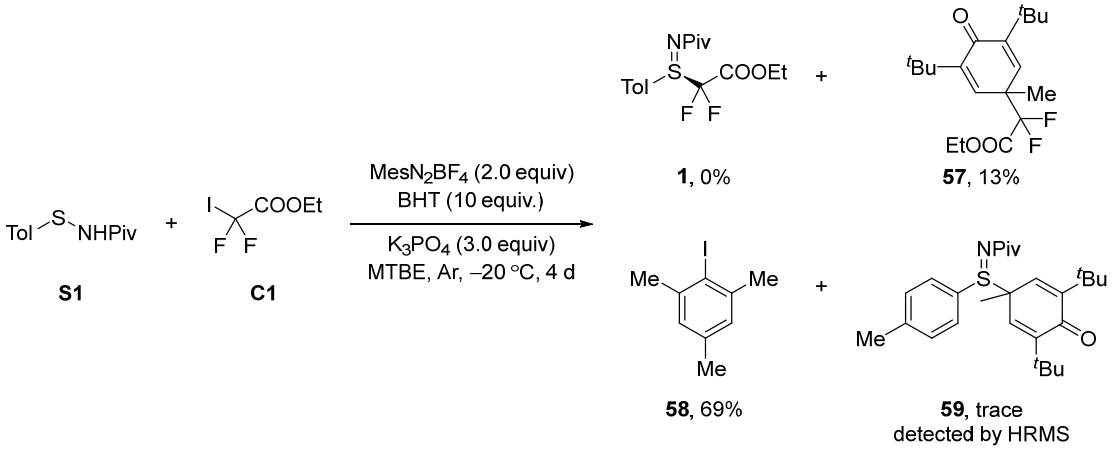
Table S3. Reaction condition optimization with **S1** and **C1**: Screening of solvents and bases[a]



Entry	Solvent	Base	Yield (%)	ee (%)
1	MTBE	K_3PO_4	95	98
2	MeCN	K_3PO_4	66	95
3	EtOAc	K_3PO_4	40	97
4	PhF	K_3PO_4	87	94
5	Cyclohexane	K_3PO_4	0	ND
6	$^{i}Pr_2O$	K_3PO_4	92	94
7	DME	K_3PO_4	72	78
8	THF	K_3PO_4	66	97
9	CH_2Cl_2	K_3PO_4	73	46
10	MTBE	KF	0	ND
11	MTBE	Li_2CO_3	0	ND
12	MTBE	$^{t}BuONa$	0	ND
13	MTBE	K_2HPO_4	30	68
14	MTBE	K_2CO_3	65	80
15	MTBE	Cs_2CO_3	83	90

[a] Reaction conditions: **S1** (0.20 mmol), **C1** (1.5 equiv.), CuI (10 mol%), **L1** (15 mol%), $MesN_2BF_4$ (2.0 equiv.) and base (3.0 equiv.) in solvent (4.0 mL) at –20 °C for 3 d under argon. Yield is based on ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. Ee values are based on chiral HPLC analysis.

2. Supplementary figures for experiments



HRMS (ESI) m/z calcd. for $C_{27}H_{39}NNaO_2S^+$ $[M + Na]^+$ 464.2594, found 464.2589.

Figure S1. Mechanistic studies of the background reaction. These results are consistent with a possible SET process between the aryl diazonium salt ($MesN_2BF_4$) and the *N*-acyl sulfenamide (**S1**) under basic conditions, generating an aryl radical and a sulfenamide-derived sulfur radical. The aryl radical may then undergo XAT with fluoroalkyl iodide **C1** to give the fluoroalkyl radical, which can subsequently couple with the sulfur radical to afford the racemic background product **1**.

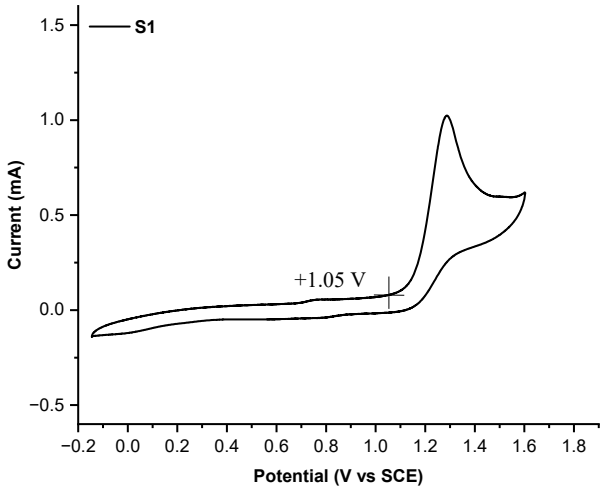


Figure S2. Cyclic voltammogram of **S1**. Under the standard electrochemical conditions, **S1** (0.10 mM) exhibited an irreversible oxidation peak with an onset oxidation potential of +1.05 V vs SCE, using ferrocene as the internal reference.

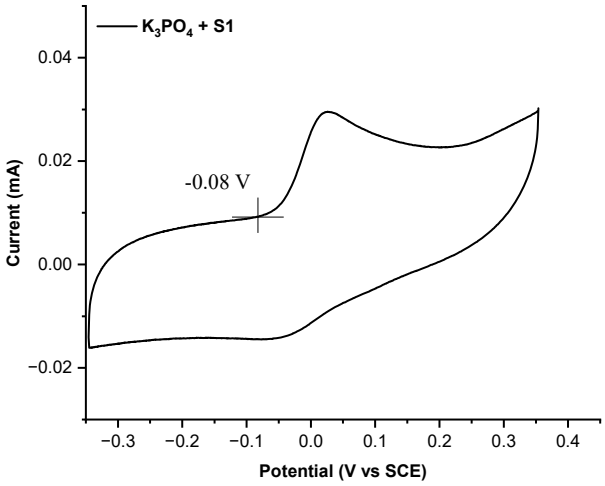


Figure S3. Cyclic voltammogram of **S1** in the presence of K_3PO_4. Under the standard electrochemical conditions, the **S1**/K_3PO_4 system (0.10 mM) exhibited an irreversible oxidation process with an onset oxidation potential of −0.08 V vs SCE, using ferrocene as an internal reference.

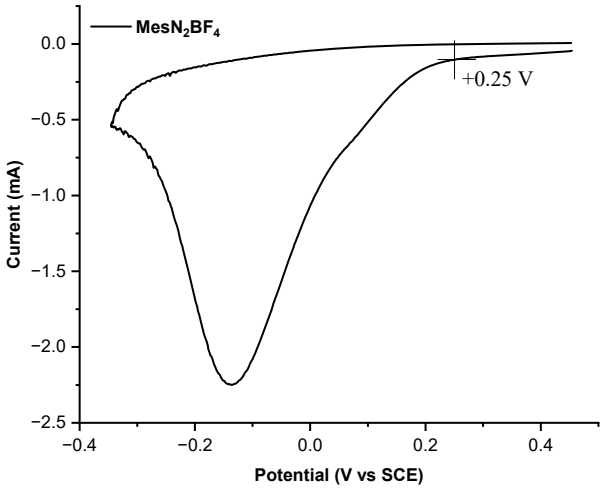


Figure S4. Cyclic voltammogram of $MesN_2BF_4$. Under the standard electrochemical conditions, $MesN_2BF_4$ (1.0 mM) exhibited an irreversible reduction process with an onset reduction potential of +0.25 V vs SCE, using ferrocene as an internal reference.

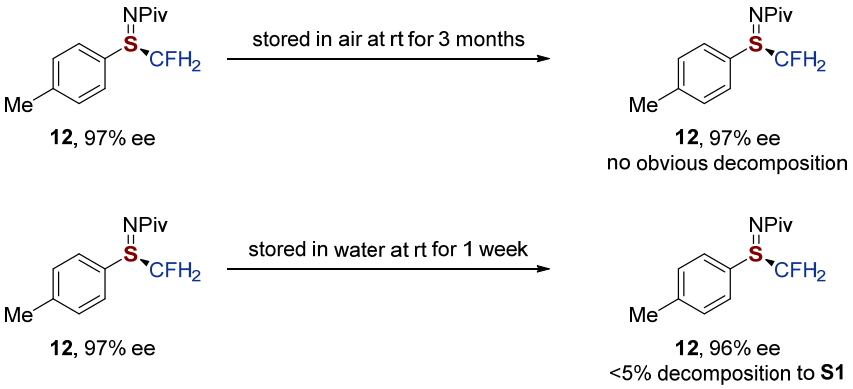


Figure S5. Storage stability test of **12**. Product **12** showed excellent stability under air at rt for three months, with no detectable decomposition or erosion of enantiomeric excess. Upon storage in water at rt for one week, minor decomposition to the corresponding starting material sulfenamide **S1** was observed (<5%), accompanied by a slight decrease in ee.

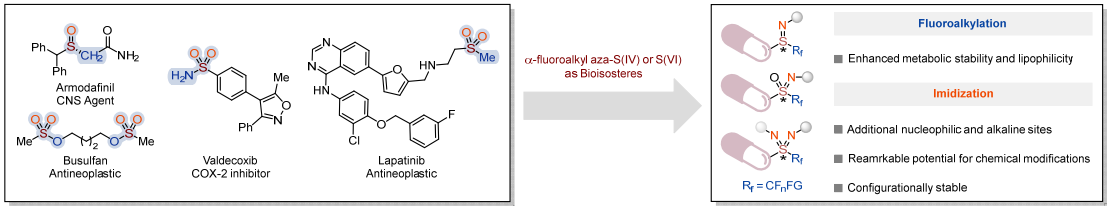
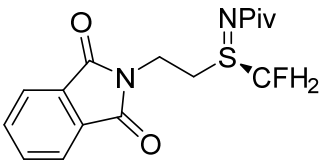


Figure S6. Drug of S(IV) and S(VI) and importance of α-fluoroalkyl aza-bioisosteres. Oxygen-to-nitrogen bioisosteric replacement in high-oxidation-state sulfur moieties [1–3] is a prevalent and critical single-site modification: it can introduce a configurationally stable *S*-chiral center, enhances hydrogen-bonding via nitrogen's lone pair, and creates versatile *N*-substitution sites for functionalization. These changes improve pharmacokinetic profiles and reduce toxic side effects, mitigating the stereodiversity deficit of unmodified sulfur scaffolds. Complementing this, α-fluoroalkyl groups—valued in medicinal chemistry for unique physicochemical properties—remedy limitations of aza-modifications in regulating lipophilicity and metabolic stability: their strong C–F bond dipole moment and hydrogen bond-mimicking ability enable precise modulation of these traits, serving as effective bioisosteres for methyl, amino, or carbonyl groups [4]. Integrating these modifications to construct α-fluoroalkyl S(IV/VI) architectures leverages their synergies, serving as ideal bifunctional surrogates for sulfur-based drug moieties (e.g., sulfones, sulfoxides, sulfonate esters, sulfonamides) and enabling precise structure-activity relationship (SAR) tuning.



54a

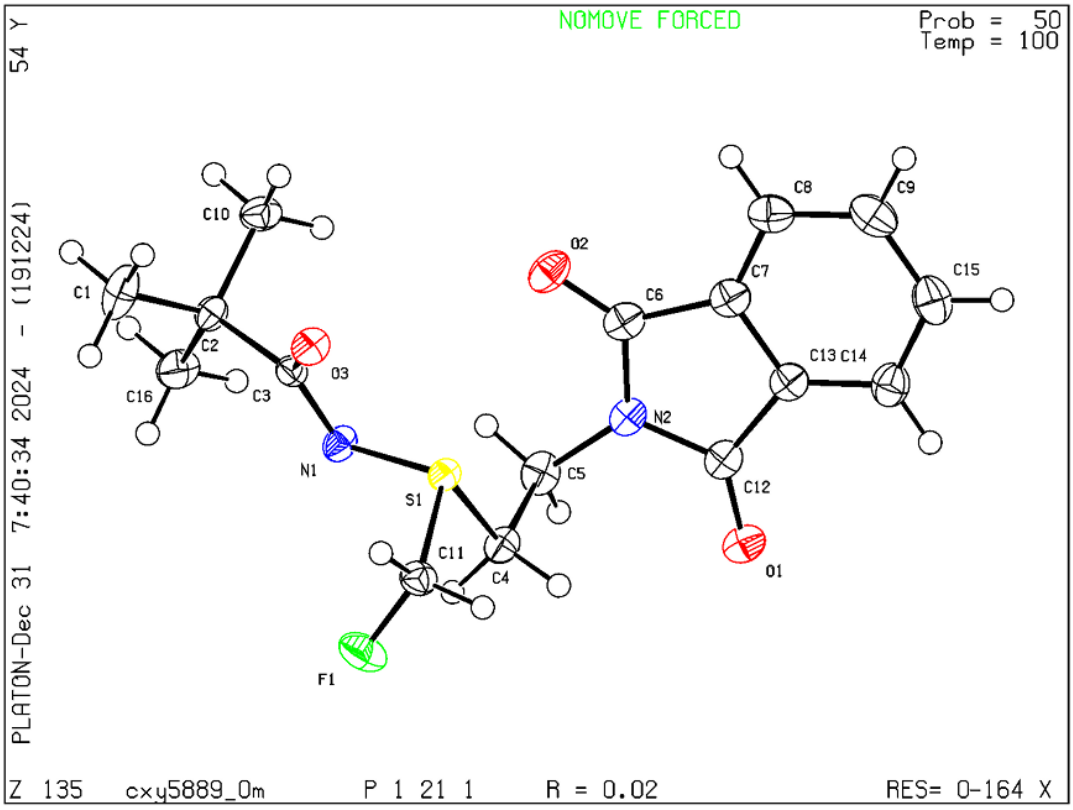
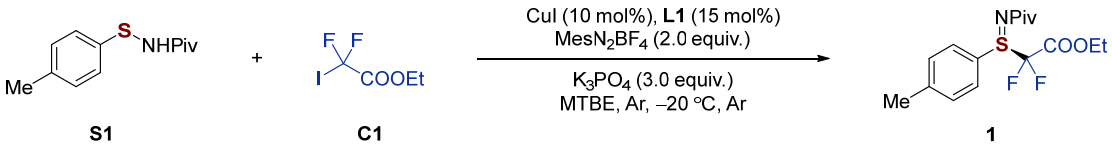
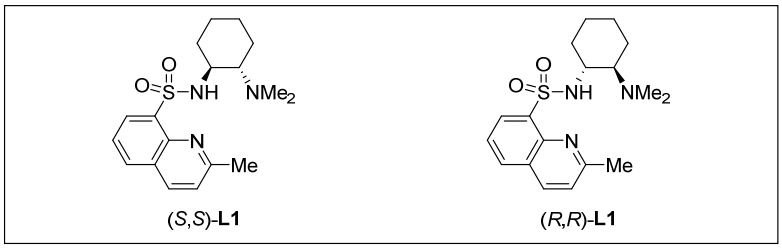


Figure S7. The X-ray structure of **54a** (CCDC 2479749, 50% probability ellipsoids).





Entry	Catalyst ee (%)	Product ee (%)
1	100	98
2	80	81
3	60	59
4	40	40
5	20	19
6	0	0

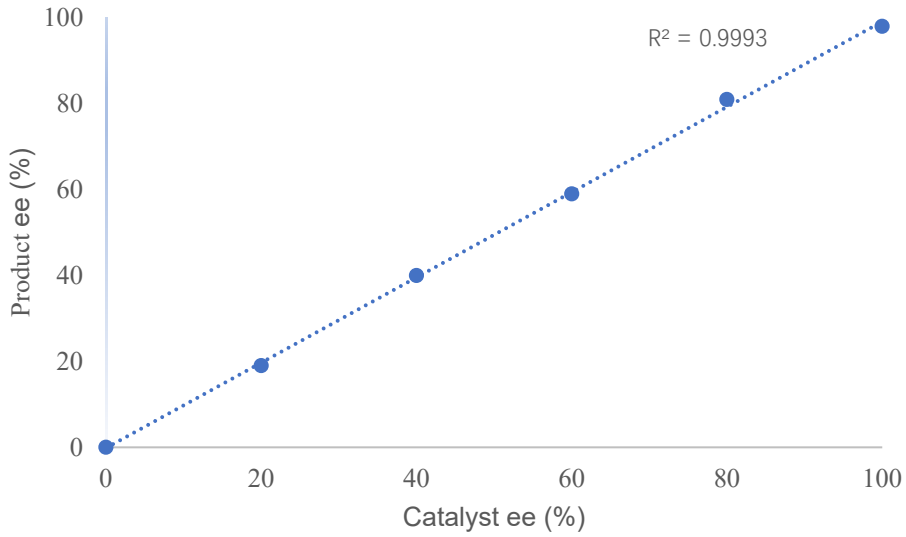


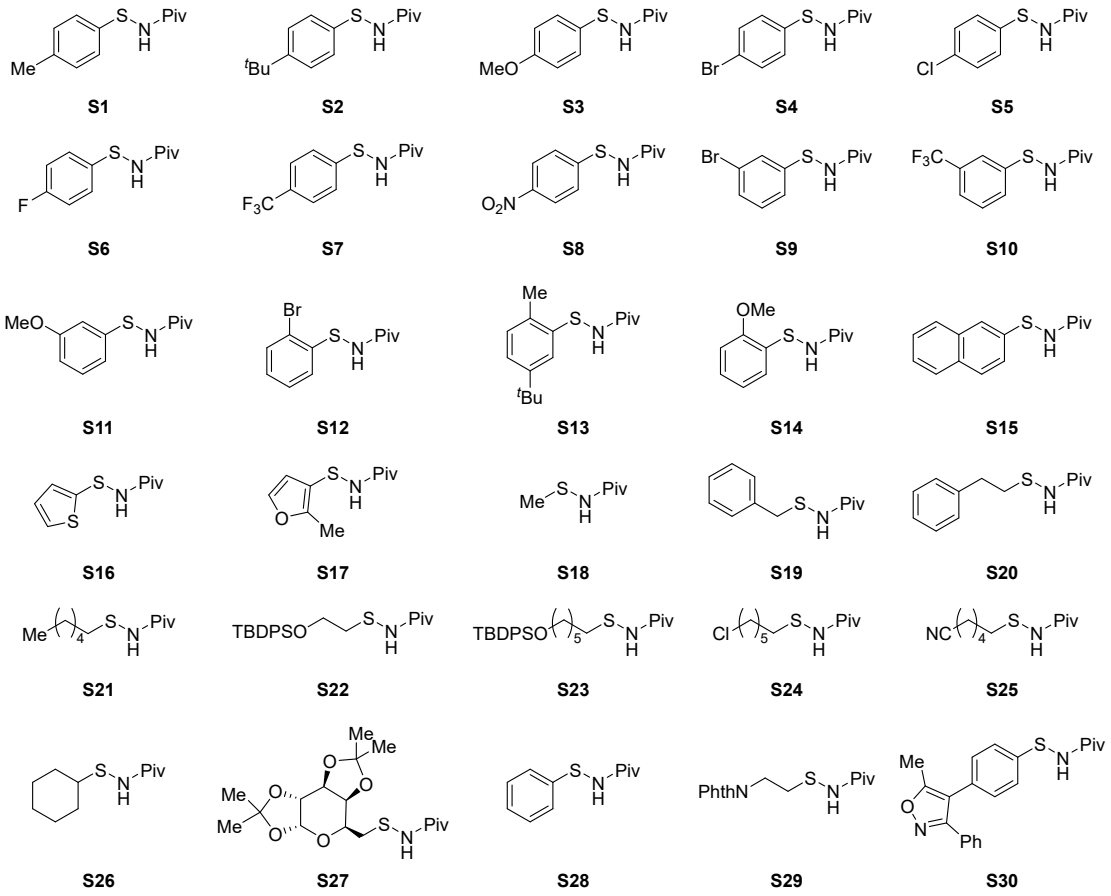
Figure S8. The non-linear effect. The control experiments indicated a linear relationship between ee values of products and corresponding catalysts.

3. General information

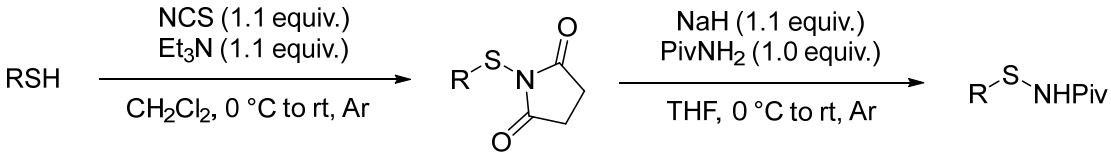
Most of the reactions were carried out under an argon atmosphere using Schlenk techniques. Reagents were purchased at the highest available commercial quality and used without further purification, unless otherwise stated. CuI and K_3PO_4 were purchased from Adamas and Bide Pharmatech Ltd. and used directly without further treatment. Other reagents were purchased from J&K, Energy, etc. Anhydrous MTBE was purchased from J&K. Analytical thin-layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). As eluents, the petroleum ether (PE), hexane, ethyl acetate (EtOAc), dichloromethane (CH_2Cl_2), and methanol were purchased from Shanghai Titan Scientific Co. Ltd. without further purification. Visualization on TLC was achieved by UV light (254 nm), iodine, or basic $KMnO_4$ indicator. NMR spectra were recorded on Bruker DRX-400 and DPX-600 spectrometers at 400 or 600 MHz for ^1H NMR and at 100 or 150 MHz for ^{13}C NMR, respectively, in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard. Chemical shifts are expressed in ppm, and coupling constants are given in Hz. Data for ^1H NMR are reported as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; dd, doublet of doublets; dt, doublet of triplets; ddd, doublet of doublet of doublets; t, triplet; q, quartet; m, multiplet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High-resolution mass spectrometry (HRMS) was performed on a Thermo Scientific Q Exactive mass spectrometer using an ESI ion source. Enantiomeric excess (ee) was determined using a SHIMADZU LC-20AD with an SPD-20AV detector. Column conditions are reported in the experimental section below. X-ray diffraction data were collected on a Bruker APEX-II CCD diffractometer with Cu–Kα radiation.

4. The preparation of substrates

General procedure for the synthesis of sulfenamides



S1–**S17** and **S19**–**S30** were synthesized according to **General Procedure 1**. **S18** were synthesized according to **General Procedure 2**. All the characterization data are consistent with those reported in the literature [5–7].

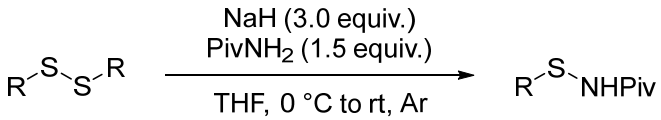


General Procedure 1:

According to a previously reported procedure [8] with slight modification, the following synthesis was performed: Under an argon atmosphere and in an ice bath, *N*-chlorosuccinimide (NCS, 11.0 mmol, 1.1 equiv.) was slowly added to a solution of thiol (10 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (0.2 M, 50 mL). The mixture was stirred at rt for 0.5 h. Triethylamine (11.0 mmol, 1.1 equiv.) was then added slowly under an ice bath, and the reaction mixture was stirred at rt overnight. Upon completion (monitored by TLC), the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was used directly in

the next step without further purification.

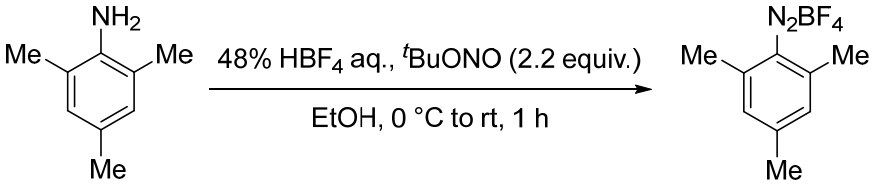
In the subsequent step, under an argon atmosphere and in an ice bath, sodium hydride (60% in mineral oil, 1.1 equiv.) was slowly added to a solution of amide (1.0 equiv.) in anhydrous THF (0.33 M). The reaction mixture was stirred at rt for 0.5 h, after which the intermediate product (1.0 equiv.) was added slowly under an ice bath. The reaction mixture was then stirred at rt overnight. Upon completion (monitored by TLC), the reaction was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude mixture was purified by column chromatography on silica gel to afford the desired product.



General Procedure 2:

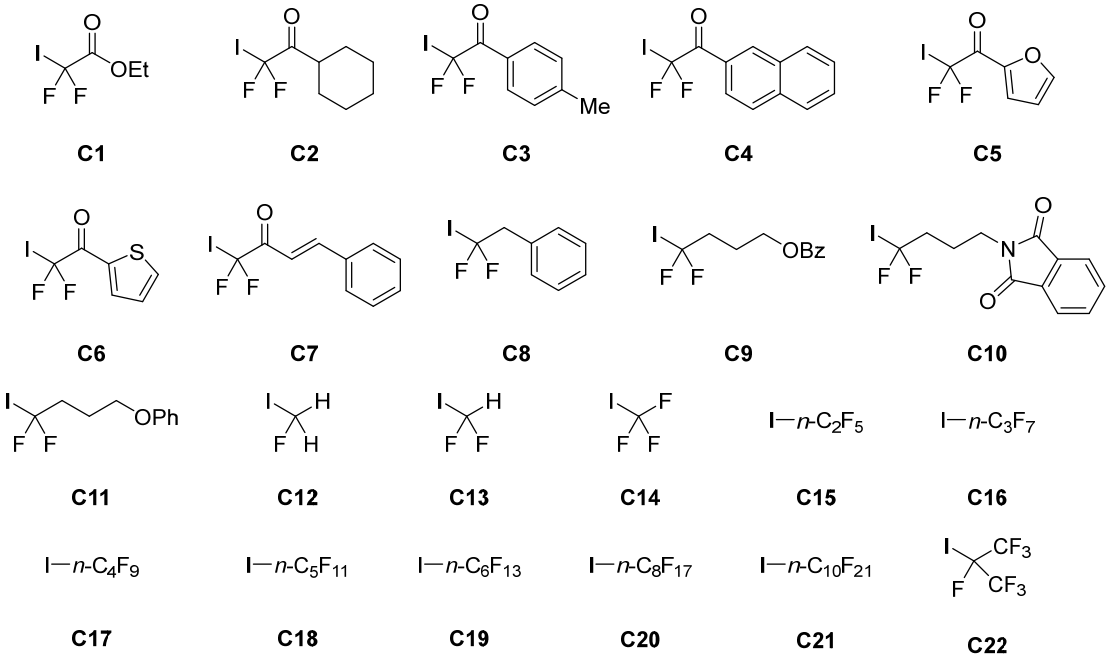
According to a previously reported procedure [9] with slight modification, the following synthesis was performed: Under an argon atmosphere and in an ice bath, sodium hydride (60% in mineral oil, 1.2 g, 30 mmol, 3.0 equiv.) was slowly added to a solution of benzamide (15.0 mmol, 1.5 equiv.) in anhydrous THF (100 mL). The reaction mixture was stirred at rt for 0.5 h. Disulfide (10 mmol, 1.0 equiv.) was then added slowly under an ice bath, and the reaction mixture was stirred at rt overnight. Upon completion (monitored by TLC), the reaction was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude mixture was purified by column chromatography on silica gel to afford the desired product.

General procedure for the synthesis of diazonium salts



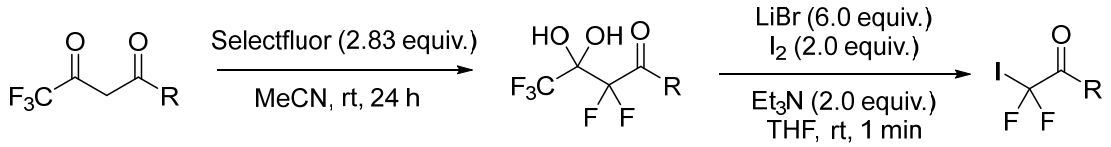
According to a previously reported procedure [10] with slight modification, the following synthesis was performed: In a 50 mL round-bottom flask, aniline (10 mmol) was dissolved in a mixture of absolute ethanol (3.0 mL) and aqueous HBF_4 solution (48%, 2.5 mL), followed by the dropwise addition of ^{t}BuONO (2.2 equiv.) at 0 °C. The reaction mixture was stirred at rt for 1 h, after which diethyl ether (20 mL) was added to precipitate the arenediazonium tetrafluoroborate. The precipitate was collected by filtration, washed with diethyl ether (3 × 10 mL), dried in vacuo for 10 min, and stored in a refrigerator under an argon atmosphere.

Summary of the Fluoroiodinated substrates



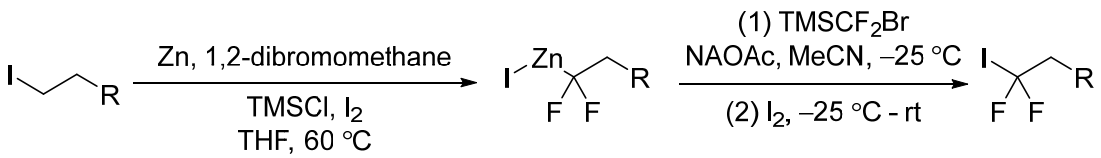
C12–**C22** were all purchased from commercial sources.

C1–**C7** was synthesized as follows.



According to a previously reported procedure [11] with slight modification, the following synthesis was performed: A solution of 4,4,4-trifluoro-butane-1,3-dione (65.0 mmol) in CH_3CN (250 mL) was treated with selectfluor (184.0 mmol, 2.83 equiv.) at rt. After 24 h, the reaction was diluted with EtOAc (50 mL) and filtered through Celite. The residue was concentrated in vacuo, dissolved in CH_2Cl_2 (150 mL), and washed with water (100 mL x 3). The combined organics were dried over with Na_2SO_4 and concentrated under reduced pressure to give 2,2,4,4,4-pentafluoro-3,3-dihydroxy-butan-1-one as an oil. To a solution of 2,2,4,4,4-pentafluoro-3,3-dihydroxy-butan-1-one (3.4 g, 12.50 mmol) in dry THF (120 mL) LiBr (80 mmol, 6.0 equiv.) and I_2 (26.0 mmol, 2.0 equiv.) were added sequentially. The reaction mixture was stirred for 1 min, and then Et_3N (250 mmol, 2.0 equiv.) was added. After stirring for 30 min at rt, the reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ (50 mL). The mixture was diluted with water (150 mL) and extracted in EtOAc (50 mL x 3), and the combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. Flash chromatography (PE/EtOAc= 25/1) afforded the 2-difluoro-2-iodo-ethan-1-one as a pale purple liquid.

C1–**C7** are known compounds, the NMR data are in agreement with those reported.



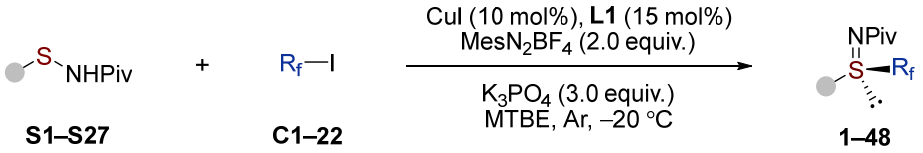
C8–**C11** was synthesized as follows.

Following a modified literature procedure [12], the synthesis was conducted as follows: To a stirred suspension of zinc dust (45.0 mmol, 1.5 equiv.) in THF (30 mL) was added one drop of 1,2-dibromoethane. After stirring at 60 °C, two drops of Me_3SiCl were added, and the mixture was stirred vigorously at 60 °C for 15 minutes —during which gas evolution was observed and zinc dust turned dark-grey fuzzy. Alkyl iodide (30 mmol, 1.0 equiv.) was slowly added. After the resulting mixture was stirred at 60 °C for 18 h, the unreacted zinc was allowed to settle down. The concentration of organozinc reagent was determined by iodometric titration. A freshly titrated THF solution of organozinc reagent (5.0 mmol, 1.0 equiv.) was concentrated under vacuum until the solid or viscous residue was formed. The residue was dissolved in freshly distilled MeCN (5.0 mL). To the resulting solution was added sodium acetate (6.0 mmol, 1.2 equiv.) at rt, the reaction flask was immersed in a cold bath at –25 °C, and the mixture was stirred for 10 minutes at –25 °C. Then, Me_3SiCF_2Br (6.0 mmol, 1.2 equiv.) was added dropwise at –25 °C, and the reaction mixture was stirred at this temperature for 18 h. Iodine (5.25 mmol, 1.05 equiv.) was added at –25 °C to the reaction mixture with vigorous stirring. After dissolution of iodine, the cooling bath was removed, the mixture was allowed to warm to rt and was stirred for additional 5.0 h. The resulting reddish-brown mixture was quenched by addition of aqueous 0.5 M solution of $Na_2S_2O_3$ until decoloration, diluted with water, and extracted with PE. The combined organic layers were filtered through Na_2SO_4, concentrated under vacuum. The residue was purified by column chromatography on silica gel.

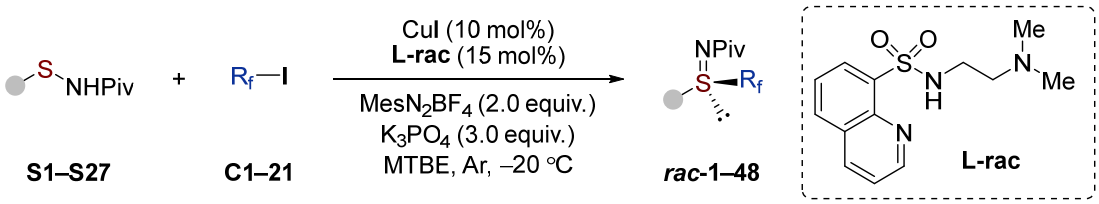
C8–**C11** are known compounds, the NMR data are in agreement with those reported.

5. General procedure for the synthesis of sulfilimines

General Procedure:

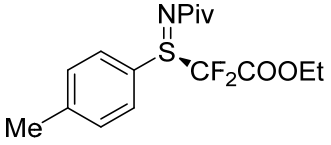


To a flame-dried Schlenk tube equipped with a magnetic stir bar was charged with CuI (3.8 mg, 0.020 mmol, 10 mol%), **L1** (10 mg, 0.030 mmol, 15 mol%), sulfenamide (0.20 mmol, 1.0 equiv.), fluoroalkyl iodide (0.30 mmol, 1.5 equiv.), $MesN_2BF_4$ (93.6 mg, 0.40 mmol, 2.0 equiv.), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times, followed by the addition of anhydrous MTBE (4.0 mL). The reaction mixture was stirred at –20 °C for 3–5 d. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.



To a flame-dried Schlenk tube equipped with a magnetic stir bar was charged with CuI (3.8 mg, 0.020 mmol, 10 mol%), **L-rac** (8.4 mg, 0.030 mmol, 15 mol%), sulfenamide (0.20 mmol, 1.0 equiv.), fluoroalkyl iodide (0.30 mmol, 1.5 equiv.), $MesN_2BF_4$ (93.6 mg, 0.40 mmol, 2.0 equiv.), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times, followed by the addition of anhydrous MTBE (4.0 mL). The reaction mixture was stirred at –20 °C for 3–5 d. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

Ethyl-(*R*)-2,2-difluoro-2-(*N*-pivaloyl-*S*-(*p*-tolyl)sulfinimidoyl)acetate (1)



According to **General Procedure** with *N*-(*p*-tolylthio)pivalamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 3 d at −20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/5) to yield the product as a yellow oil (65.6 mg, 95% yield, 98% ee).

HPLC analysis: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 233 nm), t_R (major) = 14.54 min, t_R (minor) = 10.65 min.

$[\alpha]_D^{27}$ = −58 (c 0.5, $CHCl_3$).

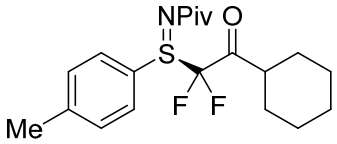
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 4.50 – 4.34 (m, 2H), 2.45 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.24 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 158.8 (dd, *J* = 30.4, 26.9 Hz), 145.0, 130.5, 129.0, 123.8, 116.8 (dd, *J* = 309.8, 291.2 Hz), 64.5, 40.2, 28.4, 21.7, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ −97.71 (d, *J* = 212.9 Hz), −105.41 (d, *J* = 212.4 Hz).

HRMS (ESI) m/z calcd. for $C_{16}H_{22}F_2NO_3S$ $[M + H]^+$ 346.1283, found 346.1285.

(*R*)-*N*-((2-Cyclohexyl-1,1-difluoro-2-oxoethyl)(*p*-tolyl)-λ^4-sulfaneylidene) pivalamide (2)



According to **General Procedure** with *N*-(*p*-tolylthio)pivalamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.) and 1-cyclohexyl-2,2-difluoro-2-iodoethan-1-one **C2** (86.4 mg, 0.30 mmol, 1.5 equiv.) for 4 d at 0 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a yellow liquid (74.4 mg, 97% yield, 97% ee).

HPLC analysis: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 240 nm), t_R (major) = 19.69 min, t_R (minor) = 14.55 min.

$[\alpha]_D^{27}$ = −33 (c 0.5, $CHCl_3$).

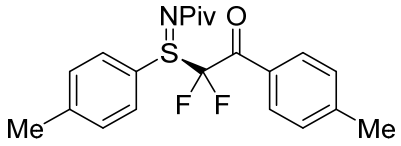
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 3.06 – 2.84 (m, 1H), 2.44 (s, 3H), 2.06 – 1.98 (m, 1H), 1.96 – 1.89 (m, 1H), 1.88 – 1.77 (m, 2H), 1.75 – 1.65 (m, 1H), 1.52 – 1.40 (m, 1H), 1.39 – 1.25 (m, 4H), 1.23 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7 (dd, *J* = 25.7, 20.2 Hz), 191.0, 144.8, 130.5, 129.0, 124.1, 118.6 (dd, *J* = 318.3, 296.1 Hz), 47.0, 40.1, 28.5, 28.0 (d, *J* = 1.8 Hz), 27.7, 25.6 (d, *J* = 13.9 Hz), 23.5 (d, *J* = 356.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ −96.02 (d, *J* = 210.7 Hz), −108.08 (d, *J* = 210.7 Hz).

HRMS (ESI) m/z calcd. for $C_{20}H_{28}F_2NO_2S$ $[M + H]^+$ 384.1803, found 384.1794.

(*R*)-*N*-((1,1-Difluoro-2-oxo-2-(*p*-tolyl)ethyl)(*p*-tolyl)-λ^4-sulfaneylidene)pivalamide (3)



According to **General Procedure** with *N*-(*p*-tolylthio)pivalamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.) and 2,2-difluoro-2-iodo-1-(*p*-tolyl)ethan-1-one **C3** (88.8 mg, 0.30 mmol, 1.5 equiv.) for 4 d at 0 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a colorless oil (74.4 mg, 95% yield, 97% ee).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 280 nm), t_R (major) = 23.25 min, t_R (minor) = 17.41 min.

$[\alpha]_D^{27}$ = −15 (c 0.5, $CHCl_3$).

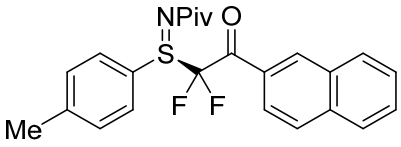
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 2.46 – 2.43 (m, 6H), 1.12 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 183.8 (dd, *J* =24.55, 22.52Hz), 146.5, 144.9, 130.7 – 130.3 (m, 2C), 129.8, 129.6, 129.0, 124.5(d, *J* = 1.62 Hz), 120.0 (dd, *J* = 314.6, 296.1 Hz), 40.2, 28.4, 22.0, 21.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ −92.21 (d, *J* = 215.7 Hz), −99.07 (d, *J* = 215.7 Hz).

HRMS (ESI) m/z calcd. for $C_{21}H_{24}F_2NO_2S$ $[M + H]^+$ 392.1490, found 392.1483.

(*R*)-*N*-((1,1-Difluoro-2-(naphthalen-2-yl)-2-oxoethyl)(*p*-tolyl)-λ^4-sulfaneylidene) pivalamide (4)



According to **General Procedure** with *N*-(*p*-tolylthio)pivalamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.) and 2,2-difluoro-2-iodo-1-(naphthalen-2-yl)ethan-1-one **C4** (99.6 mg, 0.30 mmol, 1.5 equiv.) for 4 d at 0 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a yellow liquid (82.1 mg, 96% yield, 94% ee).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 14.82 min, t_R (minor) = 6.20 min.

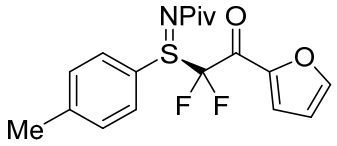
$[\alpha]_D^{27}$ = −10 (c 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.09 – 8.04 (m, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.95 – 7.85 (m, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.68 – 7.63 (m, 1H), 7.59 (tt, *J* = 6.8, 1.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H), 1.10 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 184.2 (dd, *J* = 24.8, 22.3 Hz), 144.9, 136.2, 133.4 (dd, *J* = 5.5, 3.3 Hz), 132.1, 130.5, 130.3, 129.8, 129.7, 128.9, 128.7, 127.9, 127.2,

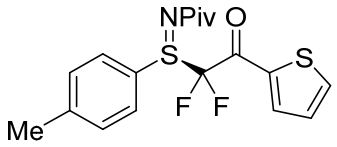
124.8 (d, J = 2.4 Hz), 124.4, 120.1 (dd, J = 314.5, 296.0 Hz), 40.1, 28.3, 21.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ −91.71 (d, J = 215.3 Hz), −98.42 (d, J = 215.6 Hz).
HRMS (ESI) m/z calcd. for $C_{24}H_{24}F_2NO_2S$ $[M + H]^+$ 428.1490, found 428.1487.

(*R*)-*N*-((1,1-Difluoro-2-(furan-2-yl)-2-oxoethyl)(*p*-tolyl)-λ^4-sulfaneylidene) pivalamide (5)



According to **General Procedure** with *N*-(*p*-tolylthio)pivalamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.) and 2,2-difluoro-1-(furan-2-yl)-2-iodoethan-1-one **C5** (81.6 mg, 0.30 mmol, 1.5 equiv.) for 2 d at 0 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a white solid (60.3 mg, 82% yield, 98% ee).
HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.6 mL/min, λ = 284 nm), t_R (major) =17.32 min, t_R (minor) = 14.67 min.
$[\alpha]_D^{27}$ = −66 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 1.6 Hz, 1H), 7.68 (d, J = 8.1 Hz, 2H), 7.56 (dt, J = 3.9, 1.9 Hz, 1H), 7.38 (d, J = 8.1 Hz, 2H), 6.67 (dd, J = 3.8, 1.7 Hz, 1H), 2.44 (s, 3H), 1.11 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 171.3 (dd, J = 26.5, 24.4 Hz), 149.7, 148.7, 145.0, 130.5, 128.9, 124.4 (dd, J = 6.6, 3.6 Hz), 124.0, 119.1 (dd, J = 312.0, 295.7 Hz), 113.2, 40.1, 28.3, 21.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ −95.43 (d, J = 214.5 Hz), −103.50 (d, J = 214.6 Hz).
HRMS (ESI) m/z calcd. for $C_{18}H_{20}F_2NO_3S$ $[M + H]^+$ 368.1126, found 368.1120.

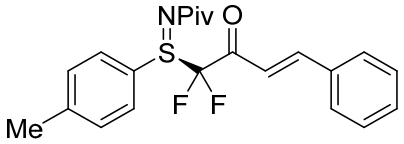
(*R*)-*N*-((1,1-Difluoro-2-oxo-2-(thiophen-2-yl)ethyl)(*p*-tolyl)-λ^4-sulfaneylidene) pivalamide (6)



According to **General Procedure** with *N*-(*p*-tolylthio)pivalamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.) and 2,2-difluoro-2-iodo-1-(thiophen-2-yl)ethan-1-one **C6** (86.4 mg, 0.30 mmol, 1.5 equiv.) for 2 d at 0 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a yellow liquid (73.7 mg, 96% yield, 97% ee).
HPLC analysis: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 289 nm), t_R (major) = 10.87 min, t_R (minor) = 8.63 min.
$[\alpha]_D^{27}$ = −76(c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.04 (m, 1H), 7.87 (dd, J = 4.9, 1.2 Hz, 1H), 7.68

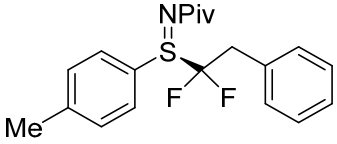
(d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.22 (dd, *J* = 4.9, 3.9 Hz, 1H), 2.43 (s, 3H), 1.10 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 176.6 (dd, *J* = 26.2, 23.8 Hz), 144.9, 138.5 (d, *J* = 2.1 Hz), 137.8, 137.0 (dd, *J* = 6.7, 3.9 Hz), 130.5, 129.0, 128.9, 124.2, 119.5 (dd, *J* = 313.2, 296.2 Hz), 40.1, 28.2, 21.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ −94.28 (d, *J* = 212.3 Hz), −100.74 (d, *J* = 216.0 Hz).
HRMS (ESI) m/z calcd. for $C_{18}H_{20}F_2NO_2S_2$ $[M + H]^+$ 384.0898, found 384.0890.

_N_-((_R_)-((_E_)-1,1-Difluoro-2-oxo-4-phenylbut-3-en-1-yl)(_p_-tolyl)-λ^4-sulfaneylidene) pivalamide (7)



According to **General Procedure** with *N*-(*p*-tolylthio)pivalamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.) and (*E*)-1,1-difluoro-1-iodo-4-phenylbut-3-en-2-one **C7** (92.4 mg, 0.30 mmol, 1.5 equiv.) for 2 d at 0 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a yellow liquid (68.6 mg, 85% yield, 96% ee).
HPLC analysis: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.7 mL/min, λ = 320 nm), t_R (major) = 48.87 min, t_R (minor) = 53.94 min.
$[\alpha]_D^{27}$ = −5 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 15.8 Hz, 1H), 7.70 – 7.60 (m, 4H), 7.51 – 7.40 (m, 3H), 7.40 – 7.33 (m, 2H), 7.24 – 7.14 (m, 1H), 2.43 (s, 3H), 1.19 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 183.1 (dd, *J* = 25.4, 22.9 Hz), 147.5, 144.8, 133.8, 132.0, 130.5, 129.2, 129.2, 128.7, 124.3, 119.2, 118.7 (dd, *J* = 311.4, 295.0 Hz), 40.1, 28.4, 21.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ −99.26 (dd, *J* = 209.8, 3.8 Hz), −106.61 (d, *J* = 209.9 Hz).
HRMS (ESI) m/z calcd. for $C_{22}H_{24}F_2NO_2S$ $[M + H]^+$ 404.1490, found 404.1482.

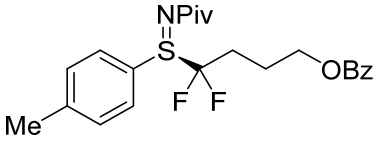
(_R_)-_N_-((1,1-Difluoro-2-phenylethyl)(_p_-tolyl)-λ^4-sulfaneylidene)pivalamide (8)



According to **General Procedure** with *N*-(*p*-tolylthio)pivalamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.) and (2,2-difluoro-2-iodoethyl)benzene **C8** (80.4 mg, 0.30 mmol, 1.5 equiv.) for 2 d at 0 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a colorless oil (68.3 mg, 94% yield, 97% ee).
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 85/15, flow rate 0.7 mL/min, λ = 230

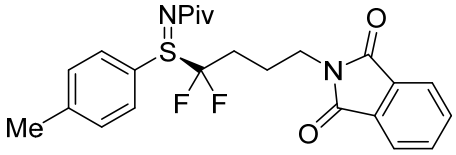
nm), t_R (major) = 13.62 min, t_R (minor) = 8.97 min.
$[\alpha]_D^{27}$ = −88 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.20 (m, 7H), 3.95 – 3.31 (m, 2H), 2.38 (s, 3H), 1.34 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 144.0, 130.8, 130.3, 129.7 (m), 128.8, 128.6, 128.3, 126.9 (dd, *J* = 298.4, 282.8 Hz), 124.8, 40.4, 39.2 (dd, *J* = 20.9, 19.4 Hz), 28.7, 21.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ −92.82 (dd, *J* = 208.7, 116.6 Hz).
HRMS (ESI) m/z calcd. for $C_{20}H_{24}F_2NOS$ $[M + H]^+$ 364.1541, found 364.1535.

(*R*)-4,4-Difluoro-4-(*N*-pivaloyl-*S*-(*p*-tolyl)sulfinimidoyl)butyl benzoate (9)



According to **General Procedure** with *N*-(*p*-tolylthio)pivalamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.) and 4,4-difluoro-4-iodobutyl benzoate **C9** (102.0 mg, 0.30 mmol, 1.5 equiv.) for 2 d at 0 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a yellow liquid (68.8 mg, 79% yield, 98% ee).
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 85/15, flow rate 0.7 mL/min, λ = 227 nm), t_R (major) = 48.61 min, t_R (minor) = 31.08 min.
$[\alpha]_D^{27}$ = −140 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 6.9 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.59 – 7.53 (m, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.37 (t, *J* = 6.2 Hz, 2H), 2.76 – 2.50 (m, 2H), 2.40 (s, 3H), 2.22 – 1.96 (m, 2H), 1.27 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 166.3, 144.1, 133.2, 130.4, 129.9, 129.6, 128.6, 128.4, 128.0 (dd, *J* = 297.6, 282.3 Hz), 124.8, 63.3, 29.8 (t, *J* = 20.4 Hz), 28.5, 21.6, 21.4 – 20.7 (m), 16.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ −93.03 (d, *J* = 209.9 Hz), −94.36 (d, *J* = 209.9 Hz).
HRMS (ESI) m/z calcd. for $C_{23}H_{28}F_2NO_3S$ $[M + H]^+$ 436.1752, found 436.1743.

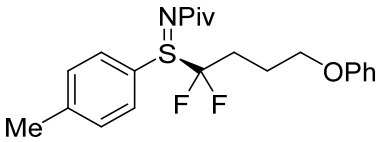
(*R*)-*N*-((4-(1,3-Dioxoisoindolin-2-yl)-1,1-difluorobutyl)(*p*-tolyl)-λ^4-sulfaneylidene) pivalamide (10)



According to **General Procedure** with *N*-(*p*-tolylthio)pivalamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.) and 2-(4,4-difluoro-4-iodobutyl)isoindoline-1,3-dione **C10** (109.5 mg, 0.30 mmol, 1.5 equiv.) for 2 d at 0 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the

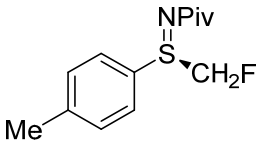
product as a yellow liquid (87.5 mg, 95% yield, 98% ee).
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 27.64 min, t_R (minor) = 21.58 min.
$[\alpha]_D^{27}$ = −133(c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 2H), 7.76 – 7.67 (m, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.75 (t, *J* = 6.9 Hz, 2H), 2.65 – 2.36 (m, 3H), 2.35 – 1.81 (m, 4H), 1.19 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 168.2, 144.1, 134.1, 132.0, 130.3, 128.5, 130.9 – 124.4 (m), 124.8, 123.4, 40.3, 36.9, 30.5 (t, *J* = 20.4 Hz), 28.4, 21.6, 21.2 – 20.4 (m).
^{19}F NMR (376 MHz, $CDCl_3$) δ –93.01 (d, *J* = 210.0 Hz), –94.04 (d, *J* = 210.2 Hz).
HRMS (ESI) m/z calcd. for $C_{24}H_{27}F_2N_2O_3S$ $[M + H]^+$ 461.1705, found 461.1714.

(*R*)-*N*-((1,1-Difluoro-4-phenoxybutyl)(*p*-tolyl)-λ^4-sulfaneylidene)pivalamide (11)



According to **General Procedure** with *N*-(*p*-tolylthio)pivalamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.) and (4,4-difluoro-4-iodobutoxy)benzene **C11** (93.6 mg, 0.30 mmol, 1.5 equiv.) for 2 d at 0 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a yellow liquid (61.9 mg, 76% yield, 98% ee).
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 85/15, flow rate 0.7 mL/min, λ = 240 nm), t_R (major) = 17.42 min, t_R (minor) = 11.31 min.
$[\alpha]_D^{27}$ = −56 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.21 (m, 2H), 6.99 – 6.91 (m, 1H), 6.89 – 6.80 (m, 2H), 3.99 (m, 2H), 2.71 – 2.33 (m, 5 h), 2.23 – 1.94 (m, 2H), 1.28 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 158.6, 144.1, 130.4, 129.5, 128.6, 128.2 (dd, *J* = 297.2, 282.7 Hz), 124.9, 121.0, 114.5, 66.1, 40.5, 29.9 (t, *J* = 20.2 Hz), 28.6, 22.0 – 21.88 (m), 21.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ –92.89 (d, *J* = 209.1 Hz), –93.91 (d, *J* = 209.1 Hz).
HRMS (ESI) m/z calcd. for $C_{22}H_{28}F_2NO_2S$ $[M + H]^+$ 408.1803, found 408.1792.

(*R*)-*N*-((Fluoromethyl)(*p*-tolyl)-λ^4-sulfaneylidene)pivalamide (12)



According to **General Procedure** with *N*-(*p*-tolylthio)pivalamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.) and fluoroiodomethane **C12** (48.0 mg, 0.30 mmol, 1.5 equiv.) for 4 d at 0 °C, the reaction mixture was purified by preparative thin-layer chromatography

on silica gel (EtOAc/PE = 1/10) to yield the product as a colorless oil (50.6 mg, 99% yield, 97% ee).

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 19.22 min, t_R (minor) = 13.19 min.

$[\alpha]_D^{27}$ = −13 (c 0.5, $CHCl_3$).

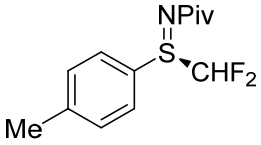
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 5.67 – 5.07 (m, 2H), 2.41 (s, 3H), 1.25 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 143.6, 130.7, 127.8, 127.5, 92.0 (d, *J* = 224.4 Hz), 40.1, 28.6, 21.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ −211.99.

HRMS (ESI) m/z calcd. for $C_{13}H_{19}FNOS$ $[M + H]^+$ 256.1166, found 256.1162.

(*R*)-*N*-((Difluoromethyl)(*p*-tolyl)-λ^4-sulfaneylidene)pivalamide (13)



According to **General Procedure** with *N*-(*p*-tolylthio)pivalamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.) and difluoroiodomethane **C13** (53.4 mg, 0.30 mmol, 1.5 equiv.) for 4 d at 0 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/2) to yield the product as a colorless liquid (49.2 mg, 90% yield, 97% ee).

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 8.02 min, t_R (minor) = 5.37 min.

$[\alpha]_D^{27}$ = −99 (c 0.5, $CHCl_3$).

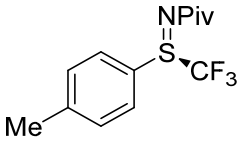
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 6.79 (dd, *J* = 56.8, 55.0 Hz, 1H), 2.45 (s, 3H), 1.28 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 144.6, 130.7, 128.7, 123.9, 117.9 (dd, *J* = 292.4, 285.8 Hz), 40.2, 28.5, 21.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ −110.77 (d, *J* = 3.6 Hz), −117.01 (d, *J* = 245.3 Hz).

HRMS (ESI) m/z calcd. for $C_{13}H_{18}F_2NOS$ $[M + H]^+$ 273.0999, found 274.1009.

(*R*)-*N*-(*p*-Tolyl(trifluoromethyl)-λ^4-sulfaneylidene)pivalamide (14)

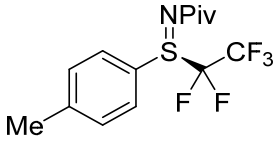


According to **General Procedure** with *N*-(*p*-tolylthio)pivalamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.) and trifluoroiodomethane **C14** (58.8 mg, 0.30 mmol, 1.5 equiv.) for 3 d at 0 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a colorless oil (36.7 mg, 63% yield, 97% ee).

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 20.38 min, t_R (minor) = 10.15 min.

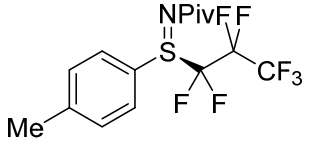
$[\alpha]_D^{27}$ = −126(c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 2.45 (s, 3H), 1.28 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 145.3, 130.8, 128.4, 124.5, 124.4 (q, *J* = 323.9 Hz), 40.4, 28.4, 21.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ −64.94.
HRMS (ESI) m/z calcd. for $C_{13}H_{17}F_3NOS$ $[M + H]^+$ 292.0977, found 292.0971.

(*R*)-*N*-((Perfluoroethyl)(*p*-tolyl)-λ^4-sulfaneylidene)pivalamide (15)



According to **General Procedure** with *N*-(*p*-tolylthio)pivalamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.) and perfluorooctyl iodide **C15** (73.8 mg, 0.30 mmol, 1.5 equiv.) for 3 d at 0 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a colorless oil (52.5 mg, 77% yield, 97% ee).
HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 21.22 min, t_R (minor) = 10.72 min.
$[\alpha]_D^{27}$ = −133 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 2.46 (s, 3H), 1.26 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 145.6, 130.8, 129.1, 123.2, 119.8-111.1 (m), 40.6, 28.3, 21.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ −78.23, −107.03 (d, *J* = 230.5 Hz), −114.20 (dd, *J* = 230.9, 2.4 Hz).
HRMS (ESI) m/z calcd. for $C_{14}H_{17}F_5NOS$ $[M + H]^+$ 342.0946, found 342.0937.

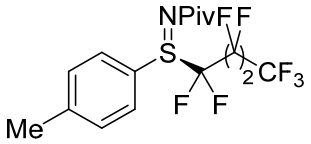
(*R*)-*N*-((3,3,3,3,3,3,3-Heptafluoro-3λ^8-prop-1-yn-1-yl)(*p*-tolyl)-λ^4-sulfaneylidene) pivalamide (16)



According to **General Procedure** with *N*-(*p*-tolylthio)pivalamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.), perfluoropropyl iodide **C16** (88.8 mg, 0.30 mmol, 1.5 equiv.) and **L2** (10 mg, 0.030 mmol, 15 mol%) for 2 d at −10 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the

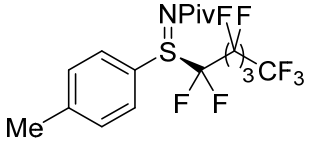
product as a colorless oil (72.0 mg, 92% yield, 95% ee).
HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 12.95 min, t_R (minor) = 8.00 min.
$[\alpha]_D^{27}$ = −154 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 2.45 (s, 3H), 1.27 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 145.6, 130., 129.31, 123.4, 122.2 – 99.8 (m), 40.6, 28.2, 21.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ −80.68 (dd, *J* = 10.5, 7.7 Hz), −102.59 – −116.36 (m), −120.41 – −126.37 (m).
HRMS (ESI) m/z calcd. for $C_{15}H_{17}F_7NOS$ $[M + H]^+$ 392.0914, found 392.0908.

(*R*)-*N*-((4,4,4,4,4,4,4,4,4-Nonafluoro-4λ^{12}-buta-1,3-diyn-1-yl)(*p*-tolyl)-λ^4-sulfaneylidene)pivalamide (17)



According to **General Procedure** with *N*-(*p*-tolylthio)pivalamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.), perfluorobutyl iodide **C17** (103.8 mg, 0.30 mmol, 1.5 equiv.) and **L2** (10 mg, 0.030 mmol, 15 mol%) for 2 d at −10 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a colorless oil (83.9 mg, 95% yield, 97% ee).
HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 11.35 min, t_R (minor) = 7.39 min.
$[\alpha]_D^{27}$ = −245 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 2.46 (s, 3H), 1.26 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 145.6, 130.7, 129.4, 123.4, 121.8 – 103.5 (m), 40.6, 28.2, 21.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ −80.69 (t, *J* = 9.6 Hz, 3F), −102.99 – −111.90 (m, 2F), −118.08 – −120.99 (m, 2F), −123.25 – −130.00 (m, 2F).
HRMS (ESI) m/z calcd. for $C_{16}H_{17}F_9NOS$ $[M + H]^+$ 442.0882, found 442.0873.

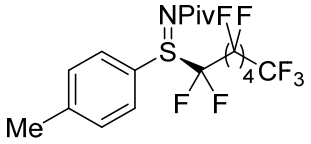
(*R*)-*N*-(*p*-Tolyl(5,5,5,5,5,5,5,5,5,5,5-undecafluoro-5λ^{12}-penta-1,3-diyn-1-yl)-λ^4-sulfaneylidene)pivalamide (18)



According to **General Procedure** with *N*-(*p*-tolylthio)pivalamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.), perfluoropentyl iodide **C18** (119.0 mg, 0.30 mmol, 1.5 equiv.) and

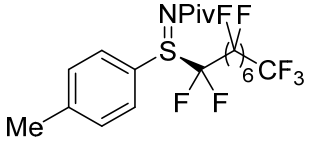
L2 (10 mg, 0.030 mmol, 15 mol%) for 2 d at −10 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a yellow liquid (78.6 mg, 80% yield, 95% ee).
HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 3.82 min, t_R (minor) = 3.13 min.
$[\alpha]_D^{27}$ = −230 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 2.46 (s, 3H), 1.27 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 145.6, 130.7, 129.4, 123.4, 122.4 – 106.2 (m), 40.7, 28.2, 21.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ −80.90, −102.39 – −111.63 (m), −117.72 – −119.88 (m), −121.39 – −124.14 (m), −124.98 – −127.75 (m).
HRMS (ESI) m/z calcd. for $C_{17}H_{17}F_{11}NOS$ $[M + H]^+$ 492.0850, found 492.0860.

(*R*)-*N*-(*p*-Tolyl(6,6,6,6,6,6,6,6,6,6,6,6,6-tridecafluoro-6λ^{16}-hexa-1,3,5-triyn-1-yl)-λ^4-sulfaneylidene)pivalamide (19)



According to **General Procedure** with *N*-(*p*-tolylthio)pivalamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.), perfluoro-1-iodohexane **C19** (133.8 mg, 0.30 mmol, 1.5 equiv.) and **L2** (10 mg, 0.030 mmol, 15 mol%) for 2 d at −10 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a colorless oil (88.8 mg, 82% yield, 92% ee).
HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 10.44 min, t_R (minor) = 6.97 min.
$[\alpha]_D^{27}$ = −309 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 2.46 (s, 3H), 1.26 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 190.6, 144.6, 129.7, 128.4, 122.5, 120.0 – 104.2 (m), 39.7, 27.2, 20.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ −80.71 – −80.95 (m, 3F), −103.62 – −104.57 (m, 2F), −108.73 – −109.73 (m, 2F), −117.40 – −119.72 (m, 2F), −120.33 – −123.82 (m, 2F), −125.02 – −127.33 (m, 2F).
HRMS (ESI) m/z calcd. for $C_{18}H_{17}F_{13}NOS$ $[M + H]^+$ 542.0818, found 542.0804.

(*R*)-*N*-((8,8,8,8,8,8,8,8,8,8,8,8,8,8,8,8,8-Heptadecafluoro-8λ^{20}-octa-1,3,5,7-tetrayn-1-yl)(*p*-tolyl)- λ^4-sulfaneylidene)pivalamide (20)



According to **General Procedure** with *N*-(*p*-tolylthio)pivalamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.), perfluorooctyl iodide **C20** (163.8 mg, 0.30 mmol, 1.5 equiv.) and **L2** (10 mg, 0.030 mmol, 15 mol%) for 5 d at −15 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a colorless oil (125.7 mg, 98% yield, 97% ee).

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 233 nm), t_R (major) = 15.42 min, t_R (minor) = 8.31 min.

$[\alpha]_D^{27}$ = −150 (c 0.5, $CHCl_3$).

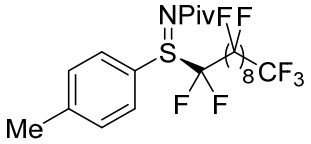
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 2.46 (s, 3H), 1.26 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 145.6, 130.7, 129.4, 123.5, 121.9 – 102.6 (m), 40.6, 28.2 (d, *J* = 2.5 Hz), 21.6 (d, *J* = 3.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ −80.05 – −85.18 (m, 3F), −101.91 – −112.86 (m, 2F), −117.09 – −119.78 (m, 2F), −120.52 – −124.01 (m, 8F), −126.16 (m, 2F).

HRMS (ESI) m/z calcd. for $C_{20}H_{17}F_{17}NOS$ $[M + H]^+$ 642.0754, found 642.0732.

(*R*)-*N*-((10,10,10,10,10,10,10,10,10,10,10,10,10,10,10,10,10,10,10,10,10-Henicosafluoro-10λ^{24}-deca-1,3,5,7,9-pentayn-1-yl)(*p*-tolyl)- λ^4-sulfaneylidene) pivalamide (21)



According to **General Procedure** with *N*-(*p*-tolylthio)pivalamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.), perfluorodecyl iodide **C21** (130.5 mg, 0.30 mmol, 1.5 equiv.) and **L2** (10 mg, 0.030 mmol, 15 mol%) for 2 d at −10 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a yellow solid (130.4 mg, 88% yield, 95% ee).

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 233 nm), t_R (major) = 12.08 min, t_R (minor) = 7.41 min.

$[\alpha]_D^{27}$ = −144 (c 0.5, $CHCl_3$).

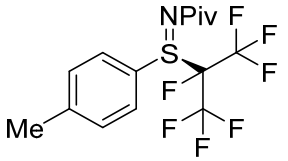
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 2.45 (s, 3H), 1.27 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 145.6, 130.7, 129.4, 123.5, 122.0 – 105.2 (m, 10C), 40.6, 28.2, 21.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ −80.76 – −81.44 (m), −104.26 (ddd, *J* = 229.3, 21.8, 11.3 Hz), −109.33 (dd, *J* = 231.8, 13.6 Hz), −117.16 – −119.99 (m), −120.54 – −123.54 (m), −126.41 (t, *J* = 27.2 Hz).

HRMS (ESI) m/z calcd. for $C_{22}H_{17}F_{21}NOS$ $[M + H]^+$ 742.0690, found 742.0682.

(*R*)-*N*-((Perfluoropropan-2-yl)(*p*-tolyl)- λ^4-sulfaneylidene)pivalamide (22)



According to **General Procedure** with *N*-(*p*-tolylthio)pivalamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.) and 1,1,1,2,3,3,3-heptafluoro-2-iodopropane **C22** (88.8 mg, 0.30 mmol, 1.5 equiv.) for 5 d at 0 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a colorless oil (72.0 mg, 92% yield, 97% ee).

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 15.51 min, t_R (minor) = 9.41 min.

$[\alpha]_D^{27}$ = −160 (c 0.5, $CHCl_3$).

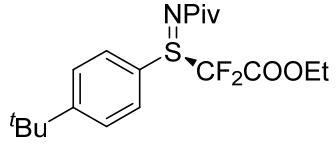
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 2.46 (s, 3H), 1.27 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 145.6, 130.5, 129.3, 123.6, 119.3 (qd, *J* = 289.3, 26.6, 15.8 Hz), 97.2 (dp, *J* = 253.3, 32.7 Hz), 40.8, 28.1, 21.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ −64.89 – −87.90 (m), −163.28 – −173.32 (m).

HRMS (ESI) m/z calcd. for $C_{15}H_{17}F_7NOS$ $[M + H]^+$ 392.0914, found 392.0906.

Ethyl (*R*)-2-(*S*-(4-(*tert*-butyl)phenyl)-*N*-pivaloylsulfinimidoyl)-2,2-difluoroacetate (23)



According to **General Procedure** with *N*-((4-(*tert*-butyl)phenyl)thio)pivalamide **S2** (53.1 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 2 d at −20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/5) to yield the product as a light yellow oil (65.1 mg, 84% yield, 96% ee).

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 234 nm), t_R (major) = 24.33 min, t_R (minor) = 13.60 min.

$[\alpha]_D^{27}$ = −25 (c 0.5, $CHCl_3$).

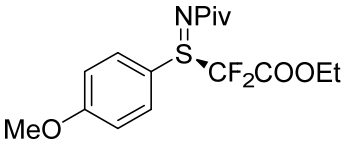
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 4.41 (dd, *J* = 7.2 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.34 (s, 9H), 1.24 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 158.8 (dd, *J* = 30.5, 26.9 Hz), 157.8, 128.8, 126.9, 123.6, 116.8 (dd, *J* = 309.7, 290.8 Hz), 64.5, 40.2, 35.3, 31.1, 28.4, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ −97.63 (d, *J* = 212.8 Hz), −105.36 (d, *J* = 212.8 Hz).

HRMS (ESI) m/z calcd. for $C_{19}H_{28}F_2NO_3S$ $[M + H]^+$ 388.1752, found 388.1750.

Ethyl (*R*)-2,2-difluoro-2-(*S*-(4-methoxyphenyl)-*N*-pivaloylsulfinimidoyl)acetate (24)



According to **General Procedure** with *N*-((4-methoxyphenyl)thio)pivalamide **S3** (47.9 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 3 d at −20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/5) to yield the product as a yellow oil (60.0 mg, 83% yield, 97% ee).

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 25.94 min, t_R (minor) = 15.49 min.

$[\alpha]_D^{27}$ = −5 (c 0.5, $CHCl_3$).

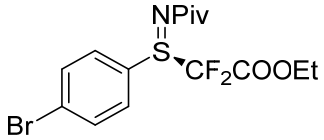
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.7 Hz, 2H), 7.05 (d, *J* = 8.9 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.24 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 164.3, 158.9 (dd, *J* = 30.4, 27.0 Hz), 131.1, 117.2, 116.8 (dd, *J* = 309.3, 291.1 Hz), 115.4, 64.5, 55.7, 40.2, 28.5, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ −97.82 (d, *J* = 212.3 Hz), −106.11 (d, *J* = 212.3 Hz).

HRMS (ESI) m/z calcd. for $C_{16}H_{22}F_2NO_4S$ $[M + H]^+$ 362.1232, found 362.1228.

Ethyl (*R*)-2-(*S*-(4-bromophenyl)-*N*-pivaloylsulfinimidoyl)-2,2-difluoroacetate (25)



According to **General Procedure** with *N*-((4-bromophenyl)thio)pivalamide **S4** (57.6 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 4 d at −20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/8) to yield the product as a light yellow solid (61.5 mg, 75% yield, 90% ee).

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 241 nm), t_R (major) = 34.04 min, t_R (minor) = 18.87 min.

$[\alpha]_D^{27}$ = −22 (c 0.5, $CHCl_3$).

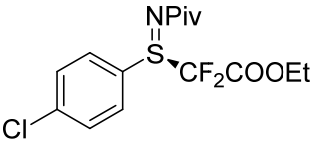
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.7 Hz, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.25 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 158.5 (dd, *J* = 30.2, 26.7 Hz), 133.1, 130.3, 129.2, 126.3 (d, *J* = 1.8 Hz), 116.7 (dd, *J* = 310.8, 292.4 Hz), 64.7, 40.2, 28.3, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ −97.19 (d, *J* = 212.4 Hz), −104.67 (d, *J* = 212.5 Hz).

HRMS (ESI) m/z calcd. for $C_{15}H_{19}BrF_2NO_3S$ $[M + H]^+$ 410.0232, found 410.0232.

Ethyl (*R*)-2-(*S*-(4-chlorophenyl)-*N*-pivaloylsulfinimidoyl)-2,2-difluoroacetate (26)



According to **General Procedure** with *N*-((4-fluorophenyl)thio)pivalamide **S5** (48.7 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 4 d at −20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/5) to yield the product as a yellow oil (47.6 mg, 65% yield, 97% ee).

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 240 nm), t_R (major) = 32.00 min, t_R (minor) = 18.10 min.

$[\alpha]_D^{27}$ = −15 (c 0.5, $CHCl_3$).

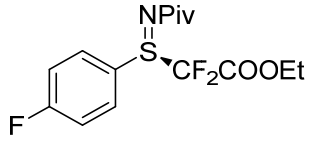
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.24 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 158.5 (dd, *J* = 30.3, 26.8 Hz), 140.7, 130.2, 130.2, 125.7, 116.8 (dd, *J* = 310.7, 292.3 Hz), 64.7, 40.2, 28.3, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ −97.22 (d, *J* = 212.1 Hz), −104.73 (d, *J* = 212.5 Hz).

HRMS (ESI) m/z calcd. for $C_{15}H_{19}ClF_2NO_3S$ $[M + H]^+$ 366.0737, found 366.0729.

Ethyl (*R*)-2,2-difluoro-2-(*S*-(4-fluorophenyl)-*N*-pivaloylsulfinimidoyl)acetate (27)



According to **General Procedure** with *N*-((4-fluorophenyl)thio)pivalamide **S6** (45.5 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 4 d at −20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/5) to yield the product as a yellow oil (46.8 mg, 67% yield, 95% ee).

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 26.21 min, t_R (minor) = 16.11 min.

$[\alpha]_D^{27}$ = −14 (c 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.7, 4.9 Hz, 2H), 7.35 – 7.20 (m, 2H), 4.43 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.24 (s, 9H).

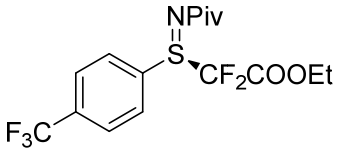
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 166.2 (d, *J* = 256.4 Hz), 158.6 (dd, *J* = 30.3, 26.8 Hz), 131.5 (d, *J* = 9.5 Hz), 122.6 (d, *J* = 2.8 Hz), 117.3 (d, *J* = 22.9 Hz), 116.7 (dd, *J* = 310.4, 292.0 Hz), 64.7, 40.2, 28.3, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ −97.39 (d, *J* = 212.5 Hz), −103.27, −105.24 (d, *J* = 212.6 Hz).

HRMS (ESI) m/z calcd. for $C_{15}H_{19}F_3NO_3S$ $[M + H]^+$ 350.1032, found 350.1024.

Ethyl (*R*)-2,2-difluoro-2-(*N*-pivaloyl-*S*-(4-(trifluoromethyl)phenyl)sulfinimidoyl)

acetate (28)



According to **General Procedure** with *N*-((4-(trifluoromethyl)phenyl)thio)pivalamide **S7** (55.5 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 3.5 d at –20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/5) to yield the product as a yellow oil (59.9 mg, 75% yield, 95% ee).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 269 nm), t_R (major) = 5.59 min, t_R (minor) = 4.52 min.

$[\alpha]_D^{27}$ = −14 (c 0.5, $CHCl_3$).

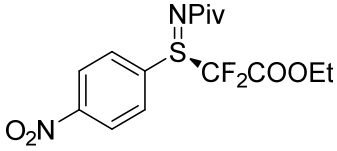
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 4.51 – 4.38 (m, 2H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.25 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 158.3 (dd, *J* = 30.1, 26.6 Hz), 135.5 (q, *J* = 33.2 Hz), 131.8, 129.4, 126.7 (q, *J* = 3.7 Hz), 123.1 (q, *J* = 273.1), 116.9 (dd, *J* = 311.5, 292.8 Hz), 64.8, 40.2, 28.3, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ –63.29, –96.90 (d, *J* = 212.8 Hz), –103.68 (d, *J* = 212.8 Hz).

HRMS (ESI) m/z calcd. for $C_{16}H_{19}F_5NO_3S$ $[M + H]^+$ 400.1000, found 400.0999.

Ethyl (*R*)-2,2-difluoro-2-(*S*-(4-nitrophenyl)-*N*-pivaloylsulfinimidoyl)acetate (29)



According to **General Procedure** with *N*-((4-nitrophenyl)thio)pivalamide **S8** (50.9 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 5 d at –20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/5) to yield the product as a yellow oil (60.2 mg, 80% yield, 98% ee).

HPLC analysis: Chiralcel ID (*n*-hexane/*i*-PrOH = 85/15, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 19.73 min, t_R (minor) = 18.12 min.

$[\alpha]_D^{27}$ = −8 (c 0.5, $CHCl_3$).

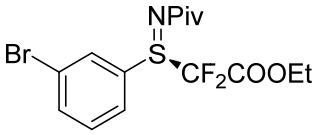
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.8 Hz, 2H), 7.99 (d, *J* = 8.7 Hz, 2H), 4.65 – 4.17 (m, 2H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.26 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 158.2 (dd, *J* = 29.9, 26.5 Hz), 151.2, 134.6, 130.1, 124.7, 117.1 (dd, *J* = 311.9, 293.8 Hz), 65.1, 40.3, 28.4, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ –96.47 (d, *J* = 212.3 Hz), –102.85 (d, *J* = 212.3 Hz).

HRMS (ESI) m/z calcd. for $C_{15}H_{19}F_2N_2O_5S$ $[M + H]^+$ 377.0977, found 377.0975.

Ethyl (*R*)-2-(*S*-(3-bromophenyl)-*N*-pivaloylsulfinimidoyl)-2,2-difluoroacetate (30)



According to **General Procedure** with *N*-((3-bromophenyl)thio)pivalamide **S9** (57.6 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 4 d at −20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/5) to yield the product as a yellow oil (65.6 mg, 80% yield, 93% ee).

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 224 nm), t_R (major) = 23.31 min, t_R (minor) = 18.85 min.

$[\alpha]_D^{27}$ = −5 (c 0.5, $CHCl_3$).

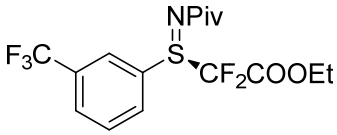
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.79 (d, *J* = 7.9, 1.6, 0.8 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 4.49 – 4.36 (m, 2H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.25 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 158.4 (dd, *J* = 30.3, 26.9 Hz), 136.9, 131.3, 131.0, 129.4, 127.6, 123.8, 116.9 (dd, *J* = 311.1, 292.3 Hz), 64.8, 40.2, 28.3, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ −96.99 (d, *J* = 212.6 Hz), −103.83 (d, *J* = 212.5 Hz).

HRMS (ESI) m/z calcd. for $C_{15}H_{19}BrF_2NO_3S$ $[M + H]^+$ 410.0232, found 410.0222.

Ethyl (*R*)-2,2-difluoro-2-(*N*-pivaloyl-*S*-(3-(trifluoromethyl)phenyl)sulfinimidoyl) acetate (31)



According to **General Procedure** with *N*-((3-(trifluoromethyl)phenyl)thio)pivalamide **S10** (55.5 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 4 d at −20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/5) to yield the product as a yellow oil (57.5 mg, 72% yield, 93% ee).

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 234 nm), t_R (major) = 20.05 min, t_R (minor) = 14.49 min.

$[\alpha]_D^{27}$ = −5 (c 0.5, $CHCl_3$).

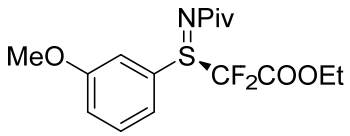
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.75 (t, *J* = 7.9 Hz, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.26 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 158.3 (dd, *J* = 30.0, 26.8 Hz), 132.5 (q, *J* = 33.7 Hz), 132.2, 130.5 (q, *J* = 3.51Hz), 130.4, 129.1 (d, *J* = 1.79 Hz), 125.6 (q, *J* = 3.86 Hz), 123.1 (q, *J* = 273.0 Hz), 117.0 (dd, *J* = 311.0, 292.3 Hz), 64.9, 40.2, 28.3, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ −63.04, −97.02 (d, *J* = 213.1 Hz), −103.53 (d, *J* = 213.1

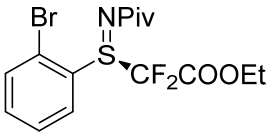
Hz).
HRMS (ESI) m/z calcd. for $C_{16}H_{19}F_5NO_3S$ $[M + H]^+$ 400.1000, found 400.0997.

Ethyl (*R*)-2,2-difluoro-2-(*S*-(3-methoxyphenyl)-*N*-pivaloylsulfinimidoyl)acetate (32)



According to **General Procedure** with *N*-((3-methoxyphenyl)thio)pivalamide **S11** (47.9 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 3 d at –20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/5) to yield the product as a light yellow oil (61.4 mg, 85% yield, 99% ee).
HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 225 nm), t_R (major) = 17.33 min, t_R (minor) = 15.86 min.
$[\alpha]_D^{27}$ = −10 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (t, *J* = 8.0 Hz, 1H), 7.38 – 7.32 (m, 1H), 7.32 – 7.27 (m, 1H), 7.21 – 7.14 (m, 1H), 4.42 (q, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.25 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 160.5, 158.7 (dd, *J* = 30.4, 26.7 Hz), 130.6, 128.3 (d, *J* = 1.8 Hz), 121.3, 120.4, 116.9 (dd, *J* = 310.5, 291.3 Hz), 112.9, 64.6, 55.6, 40.2, 28.4, 13.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ –97.45 (d, *J* = 212.2 Hz), –104.80 (d, *J* = 212.3 Hz).
HRMS (ESI) m/z calcd. for $C_{16}H_{22}F_2NO_4S$ $[M + H]^+$ 362.1232 found 362.1212.

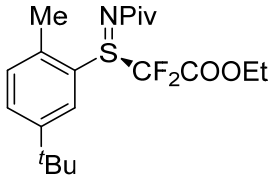
Ethyl (*R*)-2-(*S*-(2-bromophenyl)-*N*-pivaloylsulfinimidoyl)-2,2-difluoroacetate (33)



According to **General Procedure** with *N*-((2-bromophenyl)thio)pivalamide **S12** (57.6 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 3.5 d at –20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/5) to yield the product as a yellow oil (68.1 mg, 83% yield, 92% ee).
HPLC analysis: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 18.82 min, t_R (minor) = 16.37 min.
$[\alpha]_D^{27}$ = −15 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 1H), 7.81 – 7.73 (m, 1H), 7.66 – 7.49 (m, 2H), 4.53 (q, *J* = 7.2 Hz, 2H), 1.49 (t, *J* = 7.2 Hz, 3H), 1.31 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 158.4 (dd, *J* = 30.4, 26.7 Hz), 134.8, 134.0,

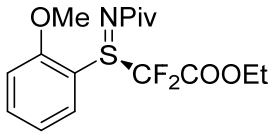
130.3, 128.8, 128.4, 125.2, 118.0 (dd, J = 311.1, 294.6 Hz), 64.6, 40.3, 28.30, 13.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ −95.64 (d, J = 209.6 Hz), −101.73 (d, J = 209.6 Hz).
HRMS (ESI) m/z calcd. for $C_{15}H_{19}BrF_2NO_3S$ $[M + H]^+$ 410.0232, found 410.0234.

Ethyl (*R*)-2-(*S*-(5-(*tert*-butyl)-2-methylphenyl)-*N*-pivaloylsulfinimidoyl)-2,2-difluoroacetate (34)



According to **General Procedure** with *N*-((5-(*tert*-butyl)-2-methylphenyl) thio)pivalamide **S13** (55.9 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 3.5 d at −20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/5) to yield the product as a yellow oil (72.3 mg, 90% yield, 99% ee).
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 14.08 min, t_R (minor) = 13.01 min.
$[\alpha]_D^{27}$ = −14 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.27 (d, J = 8.0 Hz, 1H), 4.52 – 4.33 (m, 2H), 2.61 (s, 3H), 1.41 (t, J = 7.2 Hz, 3H), 1.30 (s, 9H), 1.24 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 158.8 (dd, J = 31.21, 26.69 Hz), 150.5, 137.7, 131.3, 130.7, 125.5, 124.8, 117.8 (dd, J = 309.7, 288.1 Hz), 64.5, 40.0, 34.9, 31.1, 28.4, 18.5 (d, J = 2.25 Hz), 14.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ −97.19 (d, J = 214.5 Hz), −104.03 (d, J = 214.5 Hz).
HRMS (ESI) m/z calcd. for $C_{20}H_{30}F_2NO_3S$ $[M + H]^+$ 402.1909, found 402.1903.

Ethyl (*R*)-2,2-difluoro-2-(*S*-(2-methoxyphenyl)-*N*-pivaloylsulfinimidoyl)acetate (35)



According to **General Procedure** with *N*-((2-methoxyphenyl)thio)pivalamide **S14** (47.9 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 3.5 d at −20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/5) to yield the product as a yellow oil (65.8 mg, 91% yield, 95% ee).
HPLC analysis: Chiralcel ID (*n*-hexane/*i*-PrOH = 85/15, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 10.71 min, t_R (minor) = 12.67 min.

$[\alpha]_D^{27} = -13$ (c 0.5, $CHCl_3$).

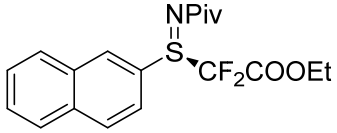
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.9 Hz, 1H), 7.62 – 7.54 (m, 1H), 7.18 – 7.10 (m, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 4.50 – 4.34 (m, 2H), 3.94 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.24 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 159.1, 158.8 (dd, *J* = 30.3, 27.2 Hz), 135.1, 129.1, 121.7, 117.9 (dd, *J* = 309.0, 293.7 Hz), 111.9, 64.3, 56.4, 40.2, 28.4, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ −98.02 (d, *J* = 209.4 Hz), −103.00 (d, *J* = 209.4 Hz).

HRMS (ESI) m/z calcd. for $C_{16}H_{22}F_2NO_4S$ $[M + H]^+$ 362.1232, found 362.1231.

Ethyl (*R*)-2,2-difluoro-2-(*S*-(naphthalen-2-yl)-*N*-pivaloylsulfinimidoyl)acetate (36)



According to **General Procedure** with *N*-(naphthalen-2-ylthio)pivalamide **S15** (51.9 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 3 d at −20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/5) to yield the product as a yellow oil (64.8 mg, 85% yield, 96% ee).

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 236 nm), t_R (major) = 39.90 min, t_R (minor) = 27.10 min.

$[\alpha]_D^{27} = -22$ (c 0.5, $CHCl_3$).

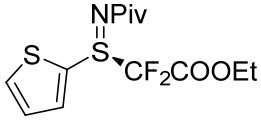
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.03 (d, *J* = 8.7 Hz, 1H), 7.99 – 7.90 (m, 2H), 7.79 (d, *J* = 8.6 Hz, 1H), 7.70 – 7.58 (m, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.28 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 158.8 (dd, *J* = 30.3, 26.8 Hz), 135.7, 132.7, 131.3, 129.9, 129.2, 128.9, 128.1, 127.7, 124.2, 123.0, 117.1 (dd, *J* = 310.5, 292.0 Hz), 64.6, 40.3, 28.4, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ −97.06 (d, *J* = 212.4 Hz), −104.67 (d, *J* = 212.4 Hz).

HRMS (ESI) m/z calcd. for $C_{19}H_{22}F_2NO_3S$ $[M + H]^+$ 382.1283, found 382.1279.

Ethyl (*S*)-2,2-difluoro-2-(*N*-pivaloylthiophene-2-sulfinimidoyl)acetate (37)



According to **General Procedure** with *N*-(thiophen-2-ylthio)pivalamide **S16** (43.1 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 4 d at −20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/5) to yield the product as a yellow oil (56.0 mg, 83% yield, 93% ee).

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 23.70 min, t_R (minor) = 17.33 min.

$[\alpha]_D^{27}$ = −25 (c 0.5, $CHCl_3$).

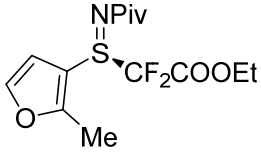
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.72 (dd, *J* = 3.9, 1.3 Hz, 1H), 7.25 (dd, *J* = 5.1, 3.8 Hz, 1H), 4.43 (q, *J* = 7.2 Hz, 2H), 1.44 – 1.37 (t, *J* = 7.2 Hz, 3H), 1.23 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 158.7 (dd, *J* = 29.7, 27.0 Hz), 136.0, 135.7, 128.3, 126.5, 116.1 (dd, *J* = 313.8, 296.1 Hz), 64.7, 40.1, 28.3, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ –97.54 (d, *J* = 205.3 Hz), –107.22 (d, *J* = 205.4 Hz).

HRMS (ESI) m/z calcd. for $C_{13}H_{18}F_2NO_3S_2$ $[M + H]^+$ 338.0691, found 338.0683.

Ethyl (*R*)-2,2-difluoro-2-(2-methyl-*N*-pivaloylfuran-3-sulfinimidoyl)acetate (38)



According to **General Procedure** with *N*-((2-methylfuran-3-yl)thio)pivalamide **S17** (42.7 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 3 d at –20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/5) to yield the product as a light yellow oil (44.9 mg, 67% yield, 99% ee).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min, λ = 240 nm), t_R (major) = 9.40 min, t_R (minor) = 8.01 min.

$[\alpha]_D^{27}$ = −11 (c 0.5, $CHCl_3$).

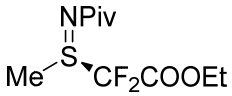
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 2.1 Hz, 1H), 6.71 (d, *J* = 1.9 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 2.56 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.19 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 160.2, 159.0 (dd, *J* = 30.0, 27.1 Hz), 142.8, 116.9 (dd, *J* = 311.3, 292.9 Hz), 109.8 (d, *J* = 1.7 Hz), 106.8 (d, *J* = 2.2 Hz), 64.6, 40.0, 28.3, 139, 12.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ –97.46 (d, *J* = 212.0 Hz), –106.09 (d, *J* = 211.6 Hz).

HRMS (ESI) m/z calcd. for $C_{14}H_{20}F_2NO_4S$ $[M + H]^+$ 336.1076, found 336.1067.

Ethyl (*R*)-2,2-difluoro-2-(*S*-methyl-*N*-pivaloylsulfinimidoyl)acetate (39)

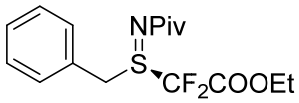


According to **General Procedure** with *N*-(methylthio)pivalamide **S18** (29.5 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 4 d at –20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a yellow oil (22.6 mg, 42% yield, 80% ee).

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 19.74 min, t_R (minor) = 17.71 min.

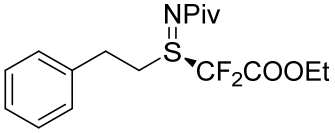
$[\alpha]_D^{27} = -8$ (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.53 – 4.33 (m, 2H), 2.86 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.17 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 160.4 – 156.3 (m), 117.0 (dd, *J* = 306.6, 292.9 Hz), 64.6, 39.7, 28.3, 26.2 – 26.0 (m), 13.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ −100.48 (d, *J* = 221.8 Hz), −107.41 (d, *J* = 221.5 Hz).
HRMS (ESI) m/z calcd. for $C_{10}H_{18}F_2NO_3S$ $[M + H]^+$ 270.0970, found 270.0966.

Ethyl (*R*)-2-(*S*-benzyl-*N*-pivaloylsulfinimidoyl)-2,2-difluoroacetate (40)



According to **General Procedure** with *N*-(benzylthio)pivalamide **S19** (44.7 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 4 d at −20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a yellow oil (59.4 mg, 86% yield, 96% ee).
HPLC analysis: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 23.54 min, t_R (minor) = 15.61 min.
$[\alpha]_D^{27} = -33$ (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.30 (m, 5 h), 4.69 – 4.32 (m, 4H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.15 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 158.7 (dd, *J* = 29.5, 27.0 Hz), 130.8, 129.3, 129.0, 127.9, 117.8 (dd, *J* = 306.4, 295.9 Hz), 64.6, 48.2 (dd, *J* = 3.9, 1.5 Hz), 40.1, 28.3, 13.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ −97.50 (d, *J* = 221.1 Hz), −103.48 (d, *J* = 221.4 Hz).
HRMS (ESI) m/z calcd. for $C_{16}H_{22}F_2NO_3S$ $[M + H]^+$ 346.1283, found 346.1280.

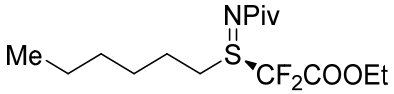
Ethyl (*R*)-2,2-difluoro-2-(*S*-phenethyl-*N*-pivaloylsulfinimidoyl)acetate (41)



According to **General Procedure** with *N*-(phenethylthio)pivalamide **S20** (47.5 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 4 d at −20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a yellow oil (55.4 mg, 77% yield, 97% ee).
HPLC analysis: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 214 nm), t_R (major) = 19.04 min, t_R (minor) = 16.03 min.
$[\alpha]_D^{27} = -88$ (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.17 (m, 5 h), 4.59 – 4.26 (m, 2H), 3.67 – 3.33

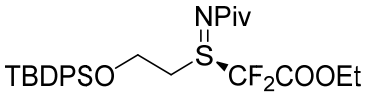
(m, 2H), 3.28 – 2.95 (m, 2H), 1.39 (t, J = 7.2 Hz, 3H), 1.20 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 157.7 (dd, J = 29.5, 26.9 Hz), 136.4, 128.0, 127.6, 126.3, 116.4 (dd, J = 307.9, 295.1 Hz), 63.6, 42.5 (d, J = 1.9 Hz), 39.1, 28.3, 27.4, 12.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ −98.50 (d, J = 220.3 Hz), −105.32 (d, J = 220.3 Hz).
HRMS (ESI) m/z calcd. for $C_{17}H_{24}F_2NO_3S$ $[M + H]^+$ 360.1439, found 360.1432.

Ethyl (*R*)-2,2-difluoro-2-(*S*-hexyl-*N*-pivaloylsulfinimidoyl)acetate (42)



According to **General Procedure** with *N*-(hexylthio)pivalamide **S21** (43.5 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 4 d at −20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a yellow oil (28.5 mg, 42% yield, 98% ee).
HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 22.14 min, t_R (minor) = 10.03 min.
$[\alpha]_D^{27}$ = −88 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.50 – 4.34 (m, 2H), 3.29 – 3.11 (m, 2H), 1.88 – 1.71 (m, 2H), 1.56 – 1.44 (m, 2H), 1.40 (t, J = 7.2 Hz, 3H), 1.36 – 1.28 (m, 4H), 1.17 (s, 9H), 0.98 – 0.85 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 158.8 (dd, J = 30.0, 27.1 Hz), 117.4 (dd, J = 307.4, 294.3 Hz), 64.6, 44.5 – 41.7 (m, 2C), 40.0, 31.1, 28.3, 28.2, 23.3, 22.3, 13.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ −98.63 (d, J = 220.7 Hz), −105.92 (d, J = 220.6 Hz).
HRMS (ESI) m/z calcd. for $C_{15}H_{28}F_2NO_3S$ $[M + H]^+$ 340.1752, found 340.1748.

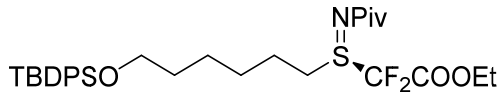
Ethyl (*R*)-2-(*S*-(2-((*tert*-butyldiphenylsilyl)oxy)ethyl)-*N*-pivaloylsulfinimidoyl)-2,2-difluoroacetate (43)



According to **General Procedure** with *N*-((2-((*tert*-butyldiphenylsilyl)oxy)ethyl)thio) pivalamide **S22** (83.1 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 4 d at −20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a light yellow solid (86.1 mg, 80% yield, 95% ee).
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 11.25 min, t_R (minor) = 9.36 min.
$[\alpha]_D^{27}$ = −44 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 4H), 7.48 – 7.34 (m, 6H), 4.51 – 4.35 (m, 2H), 4.21 – 4.10 (m, 1H), 4.05 – 3.96 (m, 1H), 3.48 – 3.29 (m, 2H), 1.39 (t, J = 7.1

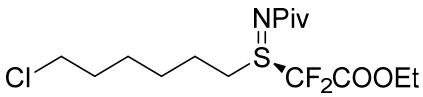
Hz, 3H), 1.15 (s, 9H), 1.06 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 158.9 (dd, *J* = 29.3, 27.1 Hz), 135.6, 135.5, 132.5 (d, *J* = 27.9 Hz), 130.1 (d, *J* = 1.2 Hz), 127.9, 117.0 (dd, *J* = 309.2, 297.5 Hz), 64.6, 57.4, 45.4 (d, *J* = 2.8 Hz), 40.0, 28.3, 26.7, 19.2, 13.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ −98.98 (d, *J* = 218.7 Hz), −105.84 (d, *J* = 218.6 Hz).
HRMS (ESI) m/z calcd. for $C_{27}H_{38}F_2NO_4SSi$ $[M + H]^+$ 538.2253, found 538.2257.

Ethyl (*R*)-2-(*S*-(7-((*tert*-butyldiphenylsilyl)oxy)heptyl)-*N*-pivaloylsulfinimidoyl)-2,2-difluoroacetate (44)



According to **General Procedure** with *N*-((6-((*tert*-butyldiphenylsilyl)oxy)hexyl)thio) pivalamide **S23** (94.4 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 4 d at −20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/5) to yield the product as a yellow oil (89.1 mg, 75% yield, 97% ee).
HPLC analysis: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min, λ = 230 nm), t_R (major) = 17.56 min, t_R (minor) = 9.74 min.
$[\alpha]_D^{27}$ = −67 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 6.7 Hz, 4H), 7.46 – 7.33 (m, 6H), 4.51 – 4.32 (m, 2H), 3.66 (t, *J* = 6.2 Hz, 2H), 3.27 – 3.08 (m, 2H), 1.88 – 1.69 (m, 2H), 1.61 – 1.52 (m, 2H), 1.49 – 1.36 (m, 7H), 1.17 (s, 9H), 1.05 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 158.8 (dd, *J* = 29.6, 27.0 Hz), 135.6, 134.0, 129.6, 127.6, 117.4 (dd, *J* = 307.5, 294.3 Hz), 64.6, 63.6, 42.1 (d, *J* = 3.50 Hz), 40.1, 32.1, 28.4, 28.3, 26.9, 25.2, 23.4, 19.2, 13.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ −98.60 (d, *J* = 220.5 Hz), −105.96 (d, *J* = 220.5 Hz).
HRMS (ESI) m/z calcd. for $C_{31}H_{46}F_2NO_4SSi$ $[M + H]^+$ 594.2879, found 594.2872.

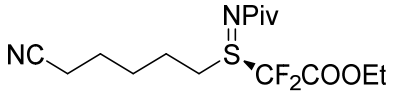
Ethyl (*R*)-2-(*S*-(6-chlorohexyl)-*N*-pivaloylsulfinimidoyl)-2,2-difluoroacetate (45)



According to **General Procedure** with *N*-((6-chlorohexyl)thio)pivalamide **S24** (50.4 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 4 d at −20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a yellow oil (41.1 mg, 55% yield, 96% ee).
HPLC analysis: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 210 nm), t_R (major) = 37.43 min, t_R (minor) = 14.60 min.
$[\alpha]_D^{27}$ = −50 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.48 – 4.37 (m, 2H), 3.54 (t, *J* = 6.6 Hz, 2H), 3.30 –

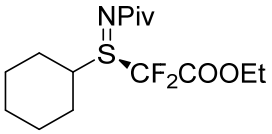
3.13 (m, 2H), 1.91 – 1.73 (m, 4H), 1.59 – 1.46 (m, 4H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.17 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 158.7 (dd, *J* = 29.9, 26.9 Hz), 117.5 (dd, *J* = 308.1, 294.7 Hz), 64.6, 44.7, 42.2, 40.0, 32.1, 28.3, 27.9, 26.3, 23.3, 13.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ −98.61 (d, *J* = 220.7 Hz), −105.71 (d, *J* = 220.7 Hz).
HRMS (ESI) m/z calcd. for $C_{15}H_{27}ClF_2NO_3S$ $[M + H]^+$ 374.1363, found 374.1353.

Ethyl (*R*)-2-(*S*-(5-cyanopentyl)-*N*-pivaloylsulfinimidoyl)-2,2-difluoroacetate (46)



According to **General Procedure** with *N*-((5-cyanopentyl)thio)pivalamide **S25** (45.7 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 4 d at −20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a yellow oil (42.1 mg, 60% yield, 94% ee).
HPLC analysis: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.7 mL/min, λ = 230 nm), t_R (major) = 15.42 min, t_R (minor) = 8.11 min.
$[\alpha]_D^{27}$ = −40 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.51 – 4.32 (m, 2H), 3.30 – 3.14 (m, 2H), 2.39 (t, *J* = 6.8 Hz, 2H), 1.97 – 1.80 (m, 2H), 1.80 – 1.61 (m, 4H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.17 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 158.6 (dd, *J* = 29.6, 27.0 Hz), 119.2, 117.5 (dd, *J* = 307.4, 294.6 Hz), 64.7, 42.2 – 42.0 (m), 40.0, 28.3, 27.6, 24.9, 22.7, 17.0, 13.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ −98.62 (d, *J* = 220.9 Hz), −105.34 (d, *J* = 221.0 Hz).
HRMS (ESI) m/z calcd. for $C_{15}H_{25}F_2N_2O_3S$ $[M + H]^+$ 351.1548, found 351.1534.

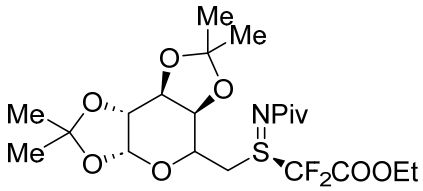
Ethyl (*R*)-2-(*S*-cyclohexyl-*N*-pivaloylsulfinimidoyl)-2,2-difluoroacetate (47)



According to **General Procedure** with *N*-(cyclohexylthio)pivalamide **S26** (43.1 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 4 d at −20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/10) to yield the product as a yellow oil (56.7 mg, 84% yield, 98% ee).
HPLC analysis: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.7 mL/min, λ = 230 nm), t_R (major) = 16.06 min, t_R (minor) = 11.47 min.
$[\alpha]_D^{27}$ = −35 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.50 – 4.28 (m, 2H), 3.57 (m, 1H), 2.13 (d, *J* = 12.4 Hz, 1H), 2.02 – 1.76 (m, 4H), 1.69 (m, 1H), 1.57 – 1.47 (m, 1H), 1.41 – 1.29 (m, 5 h), 1.29

– 1.22 (m, 1H) 1.22 – 1.08 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 158.8 (dd, *J* = 30.7, 27.5 Hz), 118.6 (dd, *J* = 307.4, 292.7 Hz), 64.5, 55.6 (d, *J* = 2.6 Hz), 40.3, 29.0, 28.5, 26.6 – 24.5 (m, 4C), 14.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ −95.06 (d, *J* = 220.4 Hz), −103.74 (d, *J* = 220.7 Hz).
HRMS (ESI) m/z calcd. for $C_{15}H_{26}F_2NO_3S$ $[M + H]^+$ 338.1596, found 338.1591.

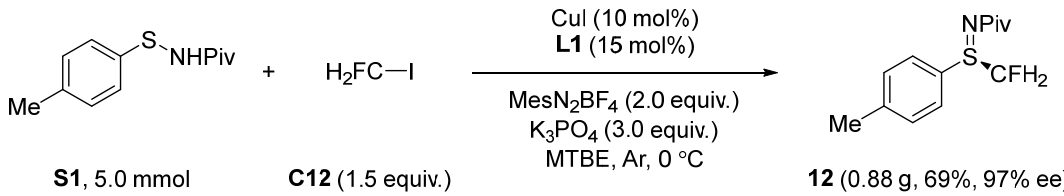
Ethyl 2,2-difluoro-2-((*R*)-*N*-pivaloyl-*S*-(((3a*R*,5a*R*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5 h-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl)sulfinimidoyl)acetate (48)



According to **General Procedure** with *N*-((3-methoxyphenyl)thio)pivalamide **S27** (75.0 mg, 0.20 mmol, 1.0 equiv.) and ethyl iododifluoroacetate **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.) for 4 d at −20 °C, the reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/5) to yield the product as a light yellow solid (89.6 mg, 90% yield, > 20:1 dr).
$[\alpha]_D^{27}$ = −74 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.50 (d, *J* = 4.9 Hz, 1H), 4.70 – 4.63 (m, 1H), 4.52 – 4.38 (m, 2H), 4.38 – 4.29 (m, 2H), 4.25 – 4.16 (m, 1H), 3.52 – 3.41 (m, 1H), 3.33 – 3.25 (m, 1H), 1.50 (d, *J* = 26.3 Hz, 6H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.33 (d, *J* = 14.8 Hz, 6H), 1.15 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 158.9 (dd, *J* = 29.6, 26.9 Hz), 116.5 (dd, *J* = 310.5, 299.8 Hz), 109.9, 109.2, 96.1, 72.2, 71.0, 70.3, 64.5, 62.8, 43.1 (t, *J* = 3.3 Hz), 39.8, 28.3, 26.1 (d, *J* = 28.8 Hz), 24.6 (d, *J* = 47.3 Hz), 13.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ −98.78 (d, *J* = 215.7 Hz), −107.60 (d, *J* = 215.7 Hz).
HRMS (ESI) m/z calcd. for $C_{21}H_{34}F_2NO_8S$ $[M + H]^+$ 498.1968 found 498.1954.

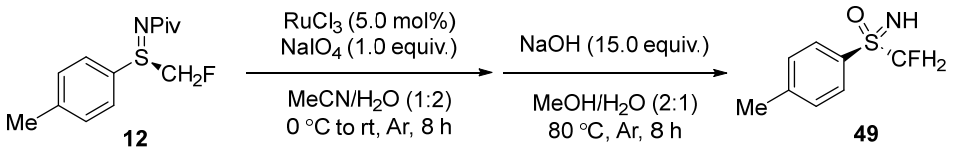
6. **Transformation**

Gram-scale reaction



S1, 5.0 mmol **C12** (1.5 equiv.) **12** (0.88 g, 69%, 97% ee)

To a flame-dried Schlenk tube equipped with a magnetic stir bar was charged with CuI (95.0 mg, 0.50 mmol, 10 mol%), **L1** (260.5 mg, 0.75 mmol, 15 mol%), sulfenamide **S1** (1.11 g, 5.0 mmol, 1.0 equiv.), fluoroalkyl iodide **C12** (1.20 g, 7.50 mmol, 1.5 equiv.), $MesN_2BF_4$ (2.34 g, 10 mmol, 2.0 equiv.), and K_3PO_4 (3.19 g, 15.0 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times, followed by the addition of anhydrous MTBE (50 mL). The reaction mixture was stirred at 0 °C for 7 d. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product **12** (0.88 g, 69% yield, 97% ee).

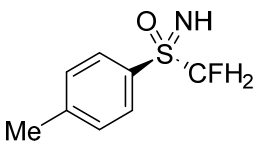


12 97% ee **49** 88% yield, 99% ee

According to a previously reported procedure [8] with slight modification. To a solution of sulfimide **12** (25.4 mg, 0.10 mmol, 1.0 equiv.) in MeCN (1.0 mL) was added a predissolved solution of $NaIO_4$ (21.6 mg, 0.10 mmol, 1.0 equiv.) in H_2O (2.0 mL). This solution was cooled to 0 °C, and then $RuCl_3$ hydrate (1.0 mg, 0.0050 mmol, 5.0 mol%) was added under argon. After stirring at 0 °C to rt for 8 h, the reaction mixture was extracted with CH_2Cl_2. The combined organic layers were dried over sodium sulfate and concentrated without further purification.

To the above concentrated organic layer in MeOH (1.0 mL) and H_2O (0.5 mL) was added NaOH (60 mg, 1.50 mmol, 15.0 equiv.) under argon. The reaction mixture was heated to 80 °C for 5 h. After cooling to rt, the reaction mixture was quenched with NH_4Cl and then extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated. Purification by silica gel chromatography afforded the product **49**.

(*R*)-Imino(λ^1-methyl)(*p*-tolyl)-λ^6-sulfanone-λ^2-fluorane (49)



The product mixture was purified by silica gel column chromatography (EtOAc/PE = 5/1) to afford **49** as colorless oil (16.5 mg, 88% yield, 97% ee).

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 24.82 min, t_R (minor) = 19.32 min.

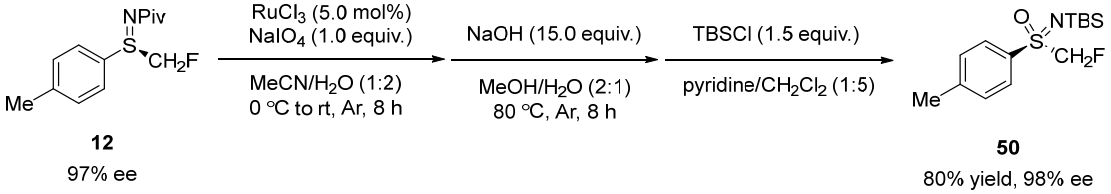
$[\alpha]_D^{27}$ = 4 (c 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.87 (m, 2H), 7.43 – 7.36 (m, 2H), 5.21 – 4.91 (m, 2H), 3.06 (s, 1H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 134.8, 130.1, 129.2, 92.8 (d, *J* = 222.0 Hz), 21.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ −203.78.

HRMS (ESI) m/z calcd. for $C_8H_{10}FNNaOS$ $[M + Na]^+$ 210.0359, found 210.0358.



12
97% ee

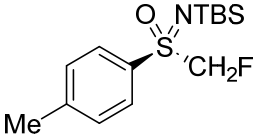
50
80% yield, 98% ee

According to a previously reported procedure [8] with slight modification. To a solution of sulfimide **12** (25.4 mg, 0.10 mmol, 1.0 equiv.) in MeCN (1.0 mL) was added a predissolved solution of $NaIO_4$ (21.6 mg, 0.10 mmol, 1.0 equiv.) in H_2O (2.0 mL). This solution was cooled to 0 °C, and then $RuCl_3$ hydrate (1.0 mg, 0.0050 mmol, 5.0 mol%) was added under argon. After stirring at 0 ºC to rt for 8 h, the reaction mixture was extracted with CH_2Cl_2. The combined organic layers were dried over sodium sulfate and concentrated without further purification.

To the above concentrated organic layer in MeOH (1.0 mL) and H_2O (0.5 mL) was added NaOH (60 mg, 1.50 mmol, 15.0 equiv.) under argon. The reaction mixture was heated to 80 °C for 5 h. After cooling to rt, the reaction mixture was quenched with NH_4Cl and then extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated without further purification.

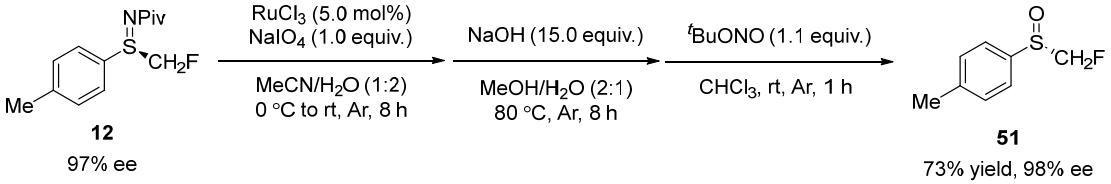
According to a previously reported procedure [13] with slight modification. To the above concentrated organic layer in pyridine (0.50 mL) and CH_2Cl_2 (1.0 mL) was added TBSCl (22.6 mg, 0.15 mmol, 1.5 equiv.) at 0 °C. The reaction mixture was stirred overnight. Then, the reaction mixture was extracted CH_2Cl_2. The combined organic layers were washed with brine, dried over sodium sulfate. Purification by silica gel chromatography afforded the product **50**.

(*S*)-((*tert*-Butyldimethylsilyl)imino)(fluoromethyl)(*p*-tolyl)-λ^6-sulfanone (50)



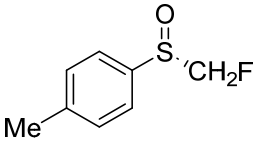
The product mixture was purified by silica gel column chromatography (EtOAc/PE = 1/10) to afford **50** as colorless oil (24.1 mg, 80% yield, 98% ee).

HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 11.08 min, t_R (minor) = 10.04 min.
$[\alpha]_D^{27}$ = 5 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 5.18 – 4.65 (m, 1H), 2.46 (s, 2H), 0.95 (s, 5 H), 0.13 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 137.6, 129.67, 128.6, 94.1 (d, *J* = 222.6 Hz), 25.9, 21.6, 17.9, –2.3.
^{19}F NMR (376 MHz, $CDCl_3$) δ –201.69.
HRMS (ESI) m/z calcd. for $C_{14}H_{25}FNOSSi$ $[M + H]^+$ 302.1405, found 302.1396.



According to a previously reported procedure [8] with slight modification. To a solution of sulfimide **12** (25.4 mg, 0.10 mmol, 1.0 equiv.) in MeCN (1.0 mL) was added a predissolved solution of $NaIO_4$ (21.6 mg, 0.10 mmol, 1.0 equiv.) in H_2O (2.0 mL). This solution was cooled to 0 °C, and then $RuCl_3$ hydrate (1.0 mg, 0.0050 mmol, 5.0 mol%) was added under argon. After stirring at 0 ºC to rt for 8 h, the reaction mixture was extracted with CH_2Cl_2. The combined organic layers were dried over sodium sulfate and concentrated without further purification.
To the above concentrated organic layer in MeOH (1.0 mL) and H_2O (0.50 mL) was added NaOH (60 mg, 1.50 mmol, 15.0 equiv.) under argon. The reaction mixture was heated to 80 °C for 5 h. After cooling to rt, the reaction mixture was quenched with NH_4Cl and then extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated without further purification.
According to a previously reported procedure [14] with slight modification. To the above concentrated organic layer in $CHCl_3$ (2.0 mL) was added ^{t}BuONO (11.4 mg, 0.11 mmol, 1.1 equiv.) under argon. The reaction mixture was stirred at rt for 1 h. Then, the reaction mixture was concentrated. Purification by silica gel chromatography afforded the product **51**.

(*S*)-1-((Fluoromethyl)sulfinyl)-4-methylbenzene (51)



The product mixture was purified by silica gel column chromatography (EtOAc/PE = 1/10) to afford **51** as colorless oil (12.6 mg, 73% yield, 98% ee).
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 42.57 min, t_R (minor) = 51.60 min.

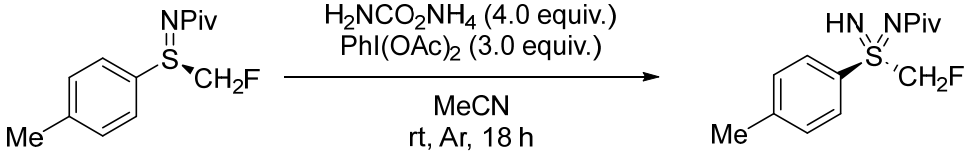
$[\alpha]_D^{27} = -5$ (c 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 5.24 – 4.80 (m, 1H), 2.44 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 135.3 (d, *J* = 6.4 Hz), 130.3, 124.7, 98.2 (d, *J* = 220.7 Hz), 21.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ –211.47.

HRMS (ESI) m/z calcd. for $C_8H_{10}FOS$ $[M + H]^+$ 173.0431, found 173.0432.

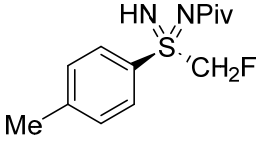


12 97% ee

52 22% yield, 97% ee

According to a previously reported procedure [15] with slight modification. To the sulfimide **12** (25.4 mg, 0.10 mmol) were added $PhI(OAc)_2$ (96.6 mg, 0.30 mmol), ammonium carbamate (31.2 mg, 0.40 mmol) and finally MeCN (0.40 mL). The mixture was stirred in an open flask at rt for 18 h and quenched by saturated $NaHCO_3$ aqueous solution. The mixture was extracted with EtOAc (5.0 mL × 3). The combined organic layer was dried by Na_2SO_4. Solvent was removed under reduced pressure and purified by flash chromatography (silica gel, EtOAc/methanol = 10/1 as eluent) to give **52** as white solid.

(*R*)-*N*-((Fluoromethyl)(imino)(*p*-tolyl)-λ^6-sulfaneylidene)pivalamide (52)



The product mixture was purified by silica gel column chromatography (EtOAc/PE = 1/1) to afford **52** as colorless oil (5.95 mg, 22% yield, 97% ee).

HPLC analysis: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 9.18 min, t_R (minor) = 7.37 min.

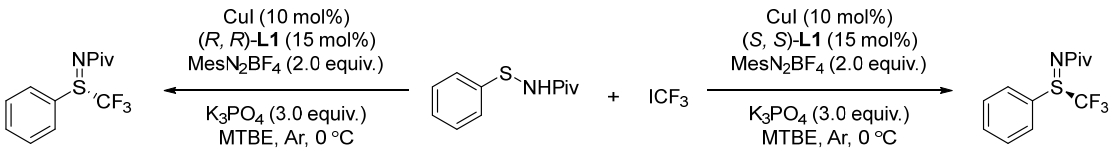
$[\alpha]_D^{27} = -18$ (c 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 5.40 (dd, *J* = 159.2, 47.2, 8.4 Hz, 1H), 2.47 (s, 2H), 1.25 (s, 7H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 145.3, 131.7, 130.2, 128.6, 92.5 (d, *J* = 230.6 Hz), 41.2, 27.9, 21.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ –202.25.

HRMS (ESI) m/z calcd. for $C_{13}H_{20}FN_2OS$ $[M + H]^+$ 271.1275, found 271.1275.



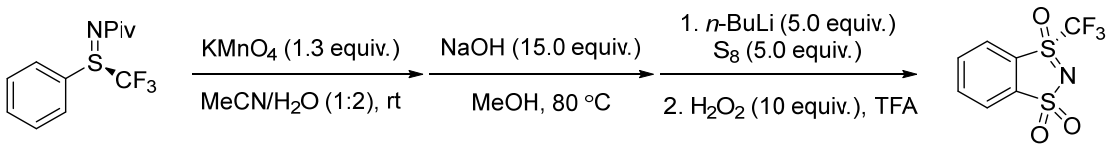
(*S*)-**53a**
86%, 99% ee

S28

C14

(*R*)-**53a**
83%, 98% ee

To a flame-dried Schlenk tube equipped with a magnetic stir bar was charged with CuI (3.8 mg, 0.020 mmol, 10 mol%), (*S, S*)-**L1** or (*R, R*)-**L1** (10 mg, 0.030 mmol, 15 mol%), sulfenamide **S28** (41.9 mg, 0.20 mmol, 1.0 equiv.), fluoroalkyl iodide **C14** (58.8 mg, 0.30 mmol, 1.5 equiv.), $MesN_2BF_4$ (93.6 mg, 0.40 mmol, 2.0 equiv.), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times, followed by the addition of anhydrous MTBE (4.0 mL). The reaction mixture was stirred at 0 °C for 5 d. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography (EtOAc/PE = 1/5) on silica gel to afford the desired product (*R*)-**53a** (46.0 mg, 83% yield, 98% ee) or (*S*)-**53a** (49.7 mg, 86% yield, 99 % ee) as a white solid.



(*R*)-**53a**
98% ee

(*S*)-**53**
58%, 99% ee

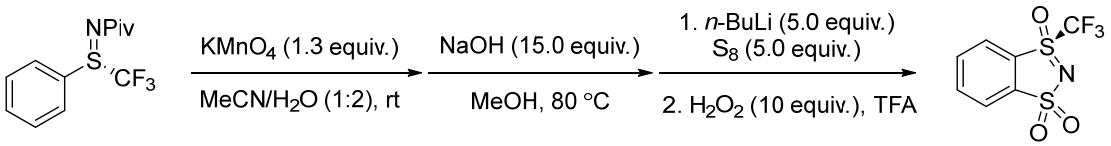
According to a previously reported procedure [16] with slight modification. To a solution of sulfimide (*R*)-**53a** (47.1 mg, 0.170 mmol, 1.0 equiv.) in MeCN (2.0 mL) was added a predissolved solution of $KMnO_4$ (34.1 mg, 0.220 mmol, 1.3 equiv.) in H_2O (2.0 mL). This solution stirred at rt overnight, the reaction mixture was extracted with CH_2Cl_2. The combined organic layers were dried over sodium sulfate and concentrated without further purification.

To the above concentrated organic layer in MeOH (2.0 mL) was added NaOH (72.0 mg, 15.0 equiv.), and the solution stirred at 80 °C for 5 h. The solution was quenched with NH_4Cl and then dried over sodium sulfate and concentrated without further purification.

According to a previously reported procedure [17] with slight modification. A round-bottomed flask was charged with the above concentrated organic layers in THF at 50 °C under Argon. *n*-BuLi in a 2.5 M solution in hexane (400 uL, 1.0 mmol, 5.0 equiv.) was added dropwise at −50 °C and the reaction medium stirred for 5 h at −30 °C. The temperature was then decreased to −50 °C again and solid elemental sulfur (32.0 mg, 1.0 mmol, 5.0 equiv.) was added by portion and carefully in order to stay under −30 °C. The resulting mixture was stirred for 1 h at rt and the reaction was quenched with aqueous NH_4Cl (sat.). The organic and aqueous phases were separated and the aqueous phase extracted with Et_2O. The combined organic phases were then washed with aqueous NaCl (sat.) and dried over sodium sulfate and concentrated under vacuum.

The resulting crude was then diluted in trifluoroacetic acid (2.0 mL) and H_2O_2 in a 10

M solution in water (200 uL, 10 equiv.) was carefully added by portion at 0 °C. The resulting mixture was stirred at rt for 4 h and then diluted with 10 mL of water. The reaction was then carefully quenched with a dilution aqueous $NaHCO_3$ (sat.) and the organic and aqueous phases were separated. The aqueous phase was extracted with CH_2Cl_2 and the combined organic phases washed with aqueous $NaHCO_3$ (sat.), dried over sodium sulfate and concentrated under vacuum. This crude was purified by column chromatography on silica gel (EtOAc/PE = 1/5) and (*S*)-**53** isolated as a white solid. (26.7 mg, 58% yield, 99% ee)



(*S*)-**53a**
99% ee

(*R*)-**53**
61%, 99% ee

According to a previously reported procedure [16] with slight modification. To a solution of sulfimide (*S*)-**53a** (47.1 mg, 0.170 mmol, 1.0 equiv.) in MeCN (2.0 mL) was added a predissolved solution of $KMnO_4$ (34.1 mg, 0.220 mmol, 1.3 equiv.) in H_2O (2.0 mL). This solution stirred at rt overnight, the reaction mixture was extracted with CH_2Cl_2. The combined organic layers were dried over sodium sulfate and concentrated without further purification.

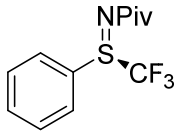
To the above concentrated organic layer in MeOH (2.0 mL) was added NaOH (72.0 mg, 15.0 equiv.), and the solution stirred at 80 °C for 5 h. The solution was quenched with NH_4Cl and then dried over sodium sulfate and concentrated without further purification.

According to a previously reported procedure [17] with slight modification. A round-bottomed flask was charged with the above concentrated organic layers in THF at 50 °C under Argon. *n*-BuLi in a 2.5 M solution in hexane (400 uL, 1.0 mmol, 5.0 equiv.) was added dropwise at −50 °C and the reaction medium stirred for 5 h at −30 °C. The temperature was then decreased to −50 °C again and solid elemental sulfur (32.0 mg, 1.0 mmol, 5.0 equiv.) was added by portion and carefully in order to stay under −30 °C. The resulting mixture was stirred for 1 h at rt and the reaction was quenched with aqueous NH_4Cl (sat.). The organic and aqueous phases were separated and the aqueous phase extracted with Et_20. The combined organic phases were then washed with aqueous NaCl (sat.) and dried over sodium sulfate and concentrated under vacuum.

The resulting crude was then diluted in trifluoroacetic acid (2.0 mL) and H_2O_2 in a 10 M solution in water (200 uL, 10 equiv.) was carefully added by portion at 0 °C. The resulting mixture was stirred at rt for 4 h and then diluted with 10 mL of water. The reaction was then carefully quenched with a dilution aqueous $NaHCO_3$ (sat.) and the organic and aqueous phases were separated. The aqueous phase was extracted with CH_2Cl_2 and the combined organic phases washed with aqueous $NaHCO_3$ (sat.), dried over sodium sulfate and concentrated under vacuum. This crude was purified by column chromatography on silica gel (EtOAc/PE = 1/5) and (*R*)-**53** isolated as a white solid.

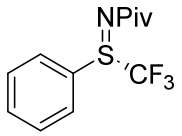
(28.1 mg, 61% yield, 99% ee)

(*R*)-*N*-(Phenyl(trifluoromethyl)- λ⁴-sulfaneylidene)pivalamide ((*R*)-53a)



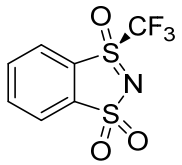
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 21.75 min, t_R (minor) = 13.94 min.
$[\alpha]_D^{27}$ = −140 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (m, 2H), 7.72 – 7.66 (m, 1H), 7.63 – 7.57 (m, 2H), 1.29 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 134.1, 130.1, 128.4, 128.0, 124.4 (q, *J* = 323.8 Hz), 40.5, 28.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ −64.54.
HRMS (ESI) m/z calcd. for $C_{12}H_{15}F_3NOS$ $[M + H]^+$ 278.0821, found 278.0821.

(*S*)-*N*-(Phenyl(trifluoromethyl)- λ⁴-sulfaneylidene)pivalamide ((*S*)-53a)



HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 14.37 min, t_R (minor) = 22.57 min.
$[\alpha]_D^{27}$ = 96 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.73 – 7.65 (m, 1H), 7.64 – 7.57 (m, 2H), 1.29 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 134.1, 130.1, 128.4, 128.0, 124.4 (q, *J* = 323.8 Hz), 40.5, 28.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ −64.53.
HRMS (ESI) m/z calcd. for $C_{12}H_{15}F_3NOS$ $[M + H]^+$ 278.0821, found 278.0816.

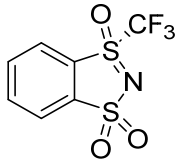
(*R*)-3-(Trifluoromethyl)-3λ⁴-benzo[d][1,3,2]dithiazole 1,1,3-trioxide ((*R*)-53)



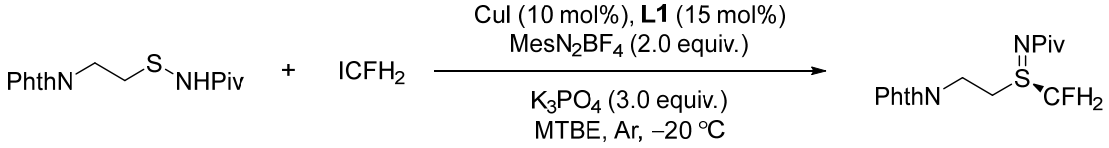
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 85/15, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 16.52 min, t_R (minor) = 17.78 min.
$[\alpha]_D^{27}$ = −15 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.18 (m, 3H), 8.18-8.12 (m, 2H), 8.12-8.00 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 138.9, 135.1, 126.8, 126.3, 124.1, 120.4 (q, *J* = 328.3 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ −74.03.
HRMS (ESI) m/z calcd. for $C_7H_4F_3NaNO_3S_2$ $[M + Na]^+$ 293.9477, found 293.9478.

(*S*)-3-(Trifluoromethyl)-3λ^4-benzo[d][1,3,2]dithiazole 1,1,3-trioxide ((*S*)-53)

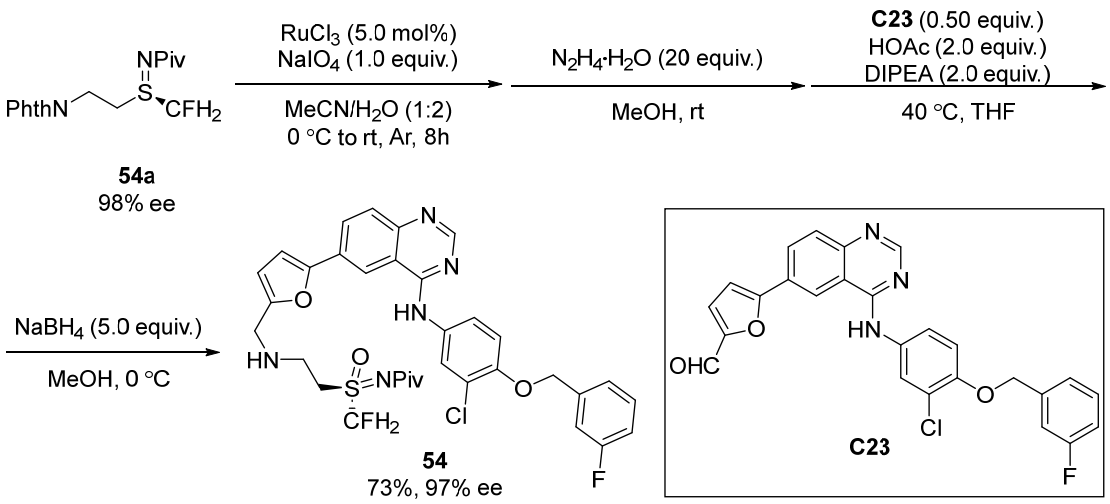


HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 85/15, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 17.68 min, t_R (minor) = 16.55 min.
$[\alpha]_D^{27}$ = 8 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.18 (m, 3H), 8.18 – 8.13 (m, 2H), 8.11 – 8.04 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 138.9, 135.1, 126.8, 126.3, 124.1, 120.4 (q, *J* = 328.3 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ −74.03.
HRMS (ESI) m/z calcd. for $C_7H_4F_3NNaO_3S_2$ $[M + Na]^+$ 293.9477, found 293.9476.



S29 **C12** **54a**
75%, 98% ee

To a flame-dried Schlenk tube equipped with a magnetic stir bar was charged with CuI (5.7 mg, 0.030 mmol, 10 mol%), **L1** (15 mg, 0.045 mmol, 15 mol%), *N*-((2-(1,3-dioxoisoindolin-2-yl)ethyl)thio)pivalamide **S29** (91.8 mg, 0.30 mmol, 1.0 equiv.), fluoroiodomethane **C12** (72.0 mg, 0.450 mmol, 1.5 equiv.), $MesN_2BF_4$ (140.4 mg, 0.60 mmol, 2.0 equiv.), and K_3PO_4 (191.1 mg, 0.90 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times, followed by the addition of anhydrous MTBE (6.0 mL). The reaction mixture was stirred at 0 °C for 4 d. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography (EtOAc/PE = 1/5) on silica gel to afford the desired product **54a** as a white solid (76.1 mg, 75% yield, 98% ee).

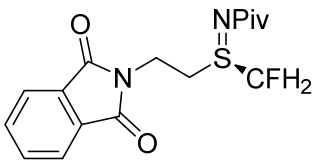


According to a previously reported procedure [8] with slight modification. To a solution of sulfimide **54a** (67.7 mg, 0.20 mmol, 1.0 equiv.) in MeCN (2.0 mL) was added a predissolved solution of $NaIO_4$ (21.6 mg, 0.20 mmol, 1.0 equiv.) in H_2O (4.0 mL). This solution was cooled to 0 °C, and then $RuCl_3$ hydrate (1.0 mg, 0.010 mmol, 5.0 mol%) was added under argon. After stirring at 0 ºC to rt for 8 h, the reaction mixture was extracted with CH_2Cl_2. The combined organic layers were dried over sodium sulfate and concentrated without further purification.

To the combined organic layer were added hydrazinium hydroxide solution (3.60 mmol, 180 mg) in MeOH (2.0 mL). The mixture was stirred at rt for 2 h. The mixture was quenched with NH_4Cl and extracted with CH_2Cl_2. The combined organic layers were dried with sodium sulfate. Solvent was removed under reduced pressure without further purification.

To the above concentrated organic layer in THF (2.0 mL) was added 5-(4-((3-chloro-4-((3-fluorobenzyl)oxy)phenyl)amino)quinazolin-6-yl)furan-2 carbaldehyde **C23** (0.10 mmol, 47.3 mg), HOAc (0.40 mmol, 24.0 mg), DIPEA (0.40 mmol, 52.0 mg) and finally THF (0.5 mL) under argon. The mixture was stirred at 40 °C for 2 h and then cooled to 0 °C. The mixture was added $NaBH_4$ (0.50 mmol, 19.0 mg) and stirred at 0 °C overnight. The mixture was quenched with NH_4Cl and then extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried with sodium sulfate. Solvent was removed under reduced pressure and purified by flash chromatography (silica gel, EtOAc/methanol = 1/1 as eluent) to give **54** as white solid (49.8 mg, 56% yield, 97% ee).

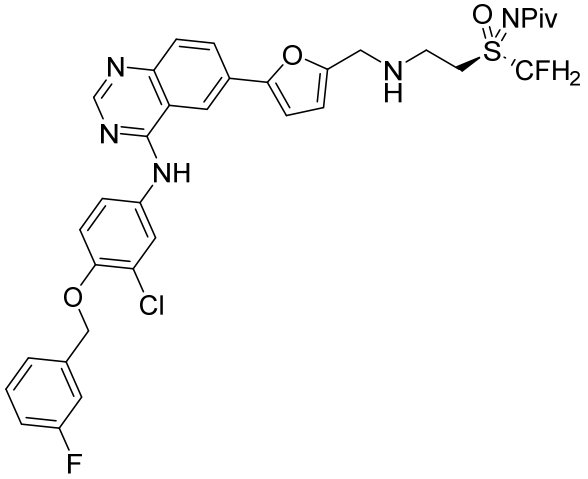
(*S*)-*N*-((2-(1,3-Dioxoisoindolin-2-yl)ethyl)(λ^1-methyl)-λ^4-sulfaneylidene) pivalamide-λ^2-fluorane (54a)



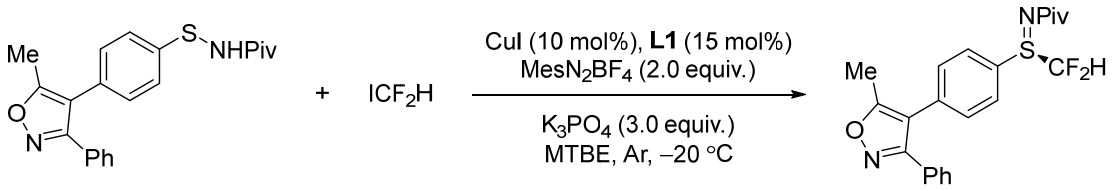
HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 217

nm), t_R (major) = 13.98 min, t_R (minor) = 18.99 min.
$[\alpha]_D^{27}$ = −55 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 2H), 7.80 – 7.71 (m, 2H), 5.93 – 5.32 (m, 2H), 4.38 – 3.89 (m, 2H), 3.56 – 3.44 (m, 2H), 1.14 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 167.7, 134.4, 131.8, 123.7, 88.1 (d, *J* = 227.1 Hz), 39.9, 39.7 (d, *J* = 3.8 Hz), 32.1, 28.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ −218.04.
HRMS (ESI) m/z calcd. for $C_{16}H_{20}FN_2O_3S$ $[M + H]^+$ 339.1173, found 339.1163.

(*R*)-*N*-((2-(((5-(4-((3-Chloro-4-((3-fluorobenzyl)oxy)phenyl)amino)quinazolin-6-yl)furan-2-yl)methyl)amino)ethyl)(λ^1-methyl)(oxo)-λ^6-sulfaneylidene)pivalamide--λ^2-fluorane (54)



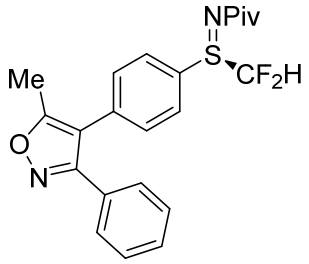
HPLC analysis: Chiralcel ADH (*n*-hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 15.99 min, t_R (minor) = 9.29 min.
$[\alpha]_D^{27}$ = −7 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.67 (s, 1H), 8.37 (d, *J* = 1.8 Hz, 1H), 7.97 – 7.78 (m, 3H), 7.51 (d, *J* = 8.8, 2.4 Hz, 1H), 7.39 – 7.30 (m, 1H), 7.24 – 7.15 (m, 2H), 7.05 – 6.95 (m, 1H), 6.90 (d, *J* = 9.0, 2.4 Hz, 1H), 6.64 (d, *J* = 3.3 Hz, 1H), 6.26 (d, *J* = 3.1 Hz, 1H), 6.06 – 5.59 (m, 2H), 5.09 (s, 2H), 3.82 (dd, *J* = 14.8, 2.8 Hz, 2H), 3.66 – 3.55 (m, 1H), 3.47 – 3.36 (m, 1H), 3.34 – 3.10 (m, 1H), 2.58 (s, 1H), 1.09 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 164.2, 161.6, 158.1, 154.7, 153.4, 152.6 (d, *J* = 1.5 Hz), 150.9, 149.2, 139.2 (d, *J* = 7.3 Hz), 132.6, 130.2 (d, *J* = 8.3 Hz), 129.0, 128.8, 128.7, 125.2, 123.2, 122.5 (d, *J* = 2.9 Hz), 122.3, 115.6, 115.3, 115.0, 114.8, 114.2, 114.1, 113.9, 110.0, 107.3, 92.6 (d, *J* = 222.6 Hz), 70.3 (d, *J* = 2.0 Hz), 49.7, 46.0, 42.2, 41.4, 27.5.
^{19}F NMR (376 MHz, $CDCl_3$) δ −112.60, −209.59.
HRMS (ESI) m/z calcd. for $C_{34}H_{35}ClF_2N_5O_4S$ $[M + H]^+$ 682.2061, found 682.2053.



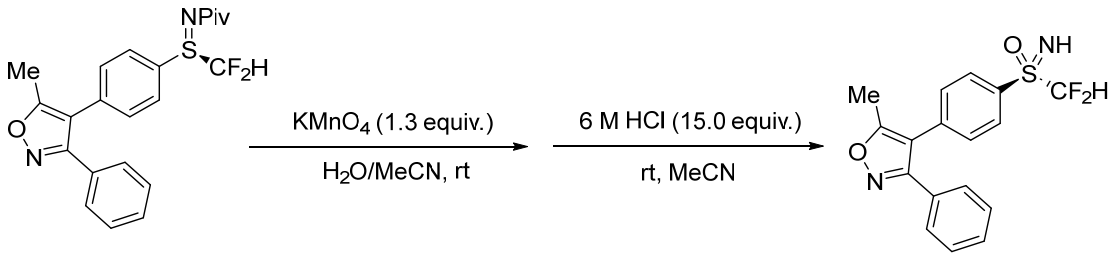
S30 **C13** **55a**
83%, 94% ee

To a flame-dried Schlenk tube equipped with a magnetic stir bar was charged with CuI (3.8 mg, 0.020 mmol, 10 mol%), **L1** (10 mg, 0.030 mmol, 15 mol%), *N*-((4-(5-methyl-3-phenylisoxazol-4-yl)phenyl)thio)pivalamide **S30** (72.0 mg, 0.20 mmol, 1.0 equiv.), difluoroiodomethane **C13** (53.4 mg, 0.30 mmol, 1.5 equiv.), $MesN_2BF_4$ (93.6 mg, 0.40 mmol, 2.0 equiv.), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times, followed by the addition of anhydrous MTBE (4.0 mL). The reaction mixture was stirred at 0 °C for 4 d. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography (EtOAc/PE = 1/5) on silica gel to afford the desired product **55a** as a white solid (69.1 mg, 83% yield, 94% ee).

(*R*)-*N*-((Difluoromethyl)(4-(5-methyl-3-phenylisoxazol-4-yl)phenyl)-λ^4-sulfaneylidene)pivalamide (55a)



HPLC analysis: Chiralcel IF (*n*-hexane/*i*-PrOH = 85/15, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 18.10 min, t_R (minor) = 14.92 min.
$[\alpha]_D^{27}$ = −60 (c 0.5, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.74 (m, 2H), 7.46 – 7.30 (m, 7H), 6.84 (dd, *J* = 56.8, 54.8 Hz, 1H), 2.51 (s, 3H), 1.28 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 167.5, 161.1, 136.2, 130.9, 129.8, 129.1, 128.8, 128.5, 128.4, 126.3, 117.9 (dd, *J* = 293.2, 286.5 Hz), 114.3, 40.3, 28.5, 11.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ −109.98 (d, *J* = 244.4 Hz), −116.29 (d, *J* = 244.4 Hz).
HRMS (ESI) m/z calcd. for $C_{22}H_{22}F_2N_2NaO_2S$ $[M + Na]^+$ 439.1262, found 439.1253.



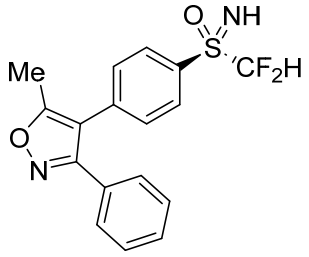
55a
98% ee

55
62%, 97% ee

To a solution of sulfimide **55a** (69.1 mg, 0.17 mmol, 1.0 equiv.) in MeCN (2.0 mL) was added a predissolved solution of $KMnO_4$ (34.1 mg, 0.22 mmol, 1.3 equiv.) in H_2O (2.0 mL). This solution stirred at rt overnight, the reaction mixture was extracted with CH_2Cl_2. The combined organic layers were dried over sodium sulfate and concentrated without further purification.

To the combined organic layer in MeCN (2.0 mL) was added 6 M HCl (0.42 mL, 15.0 equiv.). The solution stirred at rt overnight, the reaction mixture was extracted with CH_2Cl_2. The concentrated reaction mixture was purified by preparative thin-layer chromatography on silica gel (EtOAc/PE = 1/5) to yield the product **55** as a white solid (43.1 mg, 62% yield, 97% ee).

(*S*)-(Difluoromethyl)(imino)(4-(5-methyl-3-phenylisoxazol-4-yl)phenyl)-λ^6-sulfanone (55)



HPLC analysis: Chiralcel IF (*n*-hexane/*i*-PrOH = 85/15, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 33.83 min, t_R (minor) = 25.21 min.

$[\alpha]_D^{27}$ = 25 (c 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 2H), 7.48 – 7.31 (m, 7H), 6.37 – 6.00 (m, 1H), 2.52 (s, 3H).

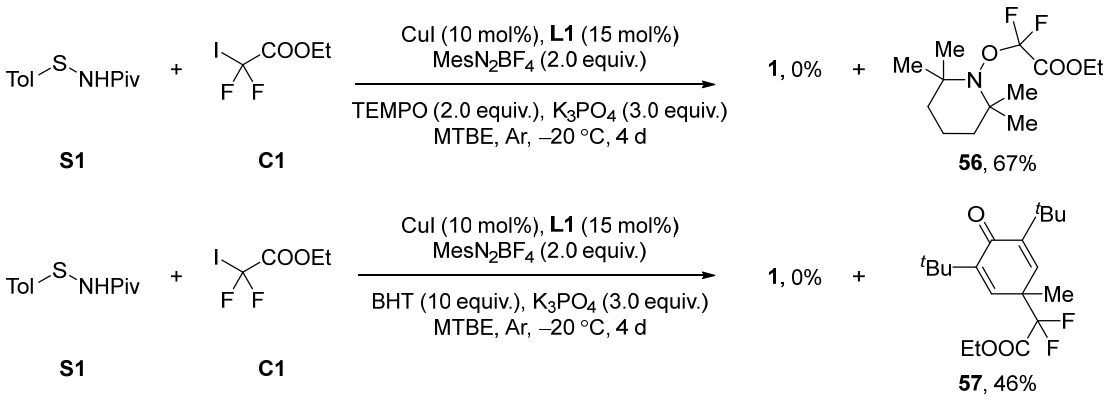
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 161.1, 137.7, 132.1, 130.9, 130.5, 129.9, 128.8, 128.5, 128.3, 115.3 (dd, *J* = 287.1 Hz), 114.2, 11.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ −118.48 (d, *J* = 258.4 Hz), −121.67 (d, *J* = 258.5 Hz).

HRMS (ESI) m/z calcd. for $C_{17}H_{15}F_2N_2O_2S$ $[M + H]^+$ 349.0817, found 349.0815.

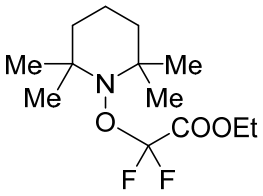
7. Mechanistic investigation

Radical inhibition experiments



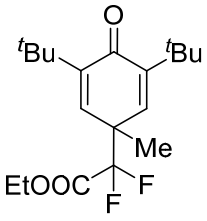
To a flame-dried Schlenk tube equipped with a magnetic stir bar was charged with CuI (3.8 mg, 0.020 mmol, 10 mol%), **L1** (10 mg, 0.030 mmol, 15 mol%), TEMPO (2,2,6,6-tetramethylpiperidinooxy, 63.0 mg, 0.40 mmol, 2.0 equiv.) or BHT (butylated hydroxytoluene, 441 mg, 2.0 mmol, 10 equiv.), sulfenamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.), fluoroalkyl iodide **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.), $MesN_2BF_4$ (93.6 mg, 0.40 mmol, 2.0 equiv.), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times, followed by the addition of anhydrous MTBE (4.0 mL). The reaction mixture was stirred at –20 ºC for 4 d. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product. Yield is based on ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. The yields of **56** and **57** were calculated based on **S1**, and their characterization data were consistent with those reported in the literature [18].

Ethyl 2,2-difluoro-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acetate (56)



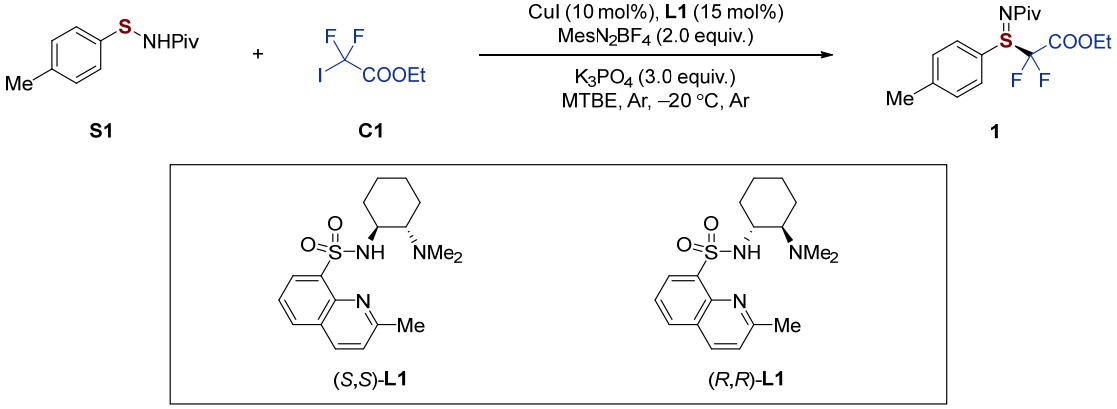
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.36 (q, *J* = 7.1 Hz, 2H), 1.65 – 1.51 (m, 6H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.20 (s, 6H), 1.17 (s, 6H).

Ethyl 2-(3,5-di-tert-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-2,2-difluoroacetate (57)



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.54 (s, 2H), 4.16 (q, J = 7.1 Hz, 2H), 1.40 (s, 3H), 1.27 – 1.21 (m, 21H).

The non-linear effect of catalysts:



To a flame-dried Schlenk tube equipped with a magnetic stir bar was charged with CuI (3.8 mg, 0.020 mmol, 10 mol%), **L1** (10 mg, 0.030 mmol, 15 mol%), sulfenamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.), fluoroalkyl iodide **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.), $MesN_2BF_4$ (93.6 mg, 0.40 mmol, 2.0 equiv.), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times, followed by the addition of anhydrous MTBE (4.0 mL). The reaction mixture was stirred at –20 °C for 4 d. Upon completion (monitored by TLC), product **1** was isolated by preparative TLC on silica gel. The ee value of product **1** was determined by HPLC, which indicated a linear relationship between the ee values of product **1** and those of the corresponding catalysts (for detailed data, see Figure S8 on page S13). Catalysts **L1** with different ee values were prepared by mixing (*S*,*S*)-**L1** (99% ee) and (*R*,*R*)-**L1** (99% ee) in appropriate ratios.

Storage stability test of 12.

The storage stability of product **12** was evaluated under air and in water at rt (for additional information, see Figure S5 on page 10). After storage under air for three months, no detectable decomposition was observed, and the ee value remained at 97% ee, indicating excellent stability under ambient conditions. When product **12** was stored in water at rt for one week, minor decomposition to the corresponding starting material sulfenamide **S1** was confirmed (<5%). The ee value decreased only slightly from 97% ee to 96% ee. These results demonstrate that product **12** is highly stable under air and maintains good stability in water, with only minor decomposition and minimal erosion of enantiopurity.

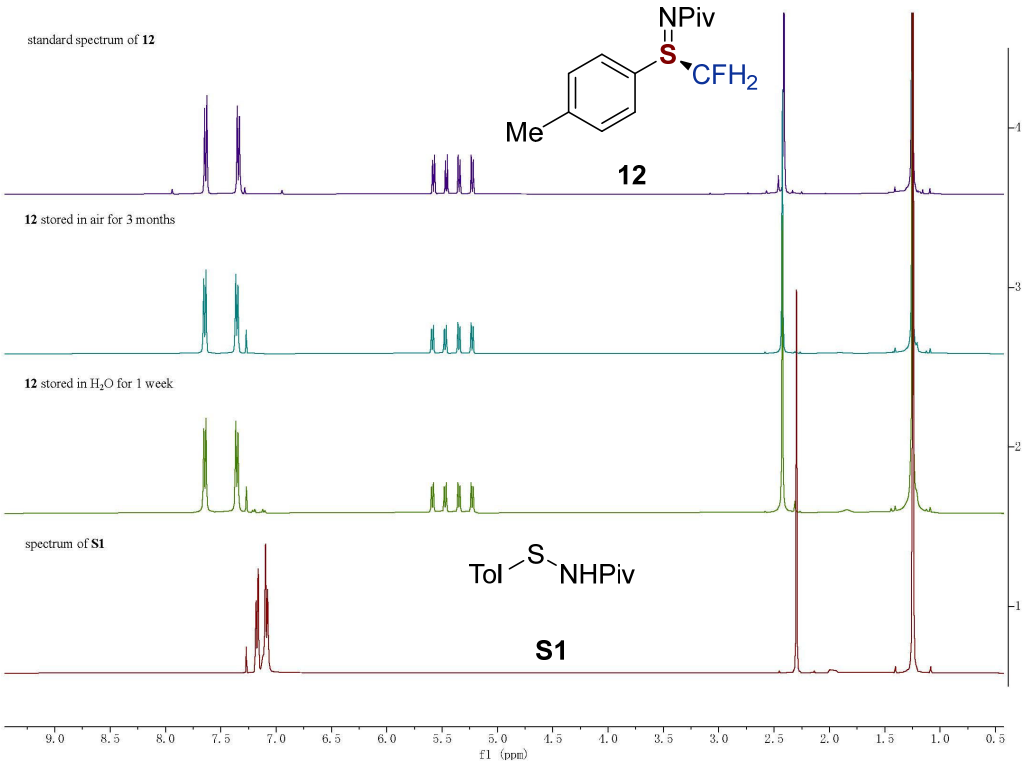
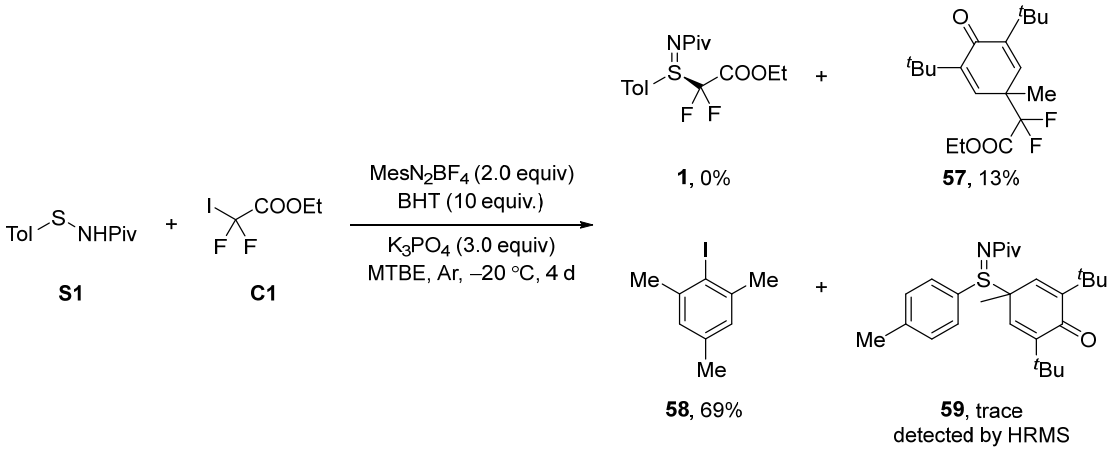


Figure S9. NMR spectral comparison of **12** for stability evaluation.

HPLC analysis with air condition: Chiralcel IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) =23.02 min, t_R (minor) = 14.77 min.

HPLC analysis with H_2O condition: Chiralcel IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) =23.02 min, t_R (minor) = 14.76 min.

Mechanistic studies of the background reaction.



HRMS (ESI) m/z calcd. for $C_{27}H_{39}NNaO_2S^+$ $[M + Na]^+$ 464.2594, found 464.2589.

To a flame-dried Schlenk tube equipped with a magnetic stir bar was charged with CuI (3.8 mg, 0.020 mmol, 10 mol%), **L1** (10 mg, 0.030 mmol, 15 mol%), BHT (butylated hydroxytoluene, 441 mg, 2.0 mmol, 10 equiv.), sulfenamide **S1** (44.7 mg, 0.20 mmol, 1.0 equiv.), fluoroalkyl iodide **C1** (75.0 mg, 0.30 mmol, 1.5 equiv.), $MesN_2BF_4$ (93.6 mg, 0.40 mmol, 2.0 equiv.), and K_3PO_4 (127.4 mg, 0.60 mmol, 3.0 equiv.). The tube was evacuated and backfilled with argon three times, followed by the addition of anhydrous MTBE (4.0 mL). The reaction mixture was stirred at –20 °C for 4 d. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product. Yield is based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. The yield of **57** was calculated based on $MesN_2BF_4$, while the yield of **58** was calculated based on **S1**. Compound **59** was observed by HRMS analysis. (For additional information and discussion, see Figure S1 on page S6.)

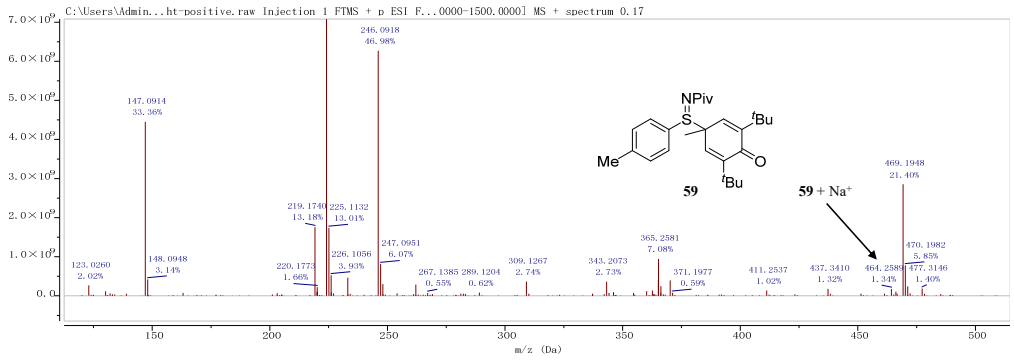
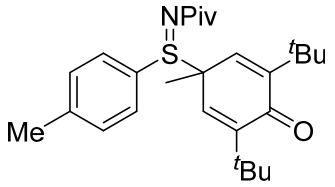


Figure S10. HRMS spectrum of **59**

N-((3,5-Di-*tert*-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)(p-tolyl)-l4-sulfaneylidene)pivalamide (**59**)



HRMS (ESI) m/z calcd. for $C_{27}H_{39}NNaO_2S+$ $[M + Na]^+$ 464.2594, found 464.2589.

Cyclic voltammograms

Cyclic voltammetry (CV) experiments were performed on a CHI 650E potentiostat using a standard three-electrode cell, consisting of a glassy carbon working electrode, an Ag/AgCl reference electrode, and a platinum counter electrode. The measurements were conducted in degassed CH_3CN containing 0.10 M $TBAClO_4$ as the supporting electrolyte at a scan rate of 0.10 V s^{-1}. Ferrocene was added at the end of each measurement as an internal reference, and the potentials were calibrated against the Fc/Fc^+ couple ($E_{1/2}$ = +0.40 V vs SCE). All potentials are reported versus SCE.

For the CV measurements, three samples were prepared under an argon atmosphere: **S1** (0.10 mM), **S1**/K_3PO_4 (**S1**, 0.10 mM; K_3PO_4, 0.30 mM), and $MesN_2BF_4$ (1.0 mM). The **S1**/K_3PO_4 mixture was prepared in degassed CH_3CN/0.10 M $TBAClO_4$ and stirred at 40 °C for 3 h under argon before the CV measurement. The **S1** and $MesN_2BF_4$ samples were prepared by directly dissolving the corresponding compound in degassed CH_3CN /0.10 M $TBAClO_4$ under argon and were used directly for CV analysis.

To probe the feasibility of direct electron transfer between **S1** and $MesN_2BF_4$, cyclic voltammetry experiments were conducted. **S1** alone exhibited an apparent oxidation potential of +1.05 V vs SCE (Figure S2 on page S7), whereas the **S1**/K_3PO_4 system showed a markedly lower apparent oxidation potential of −0.08 V vs SCE (Figure S3 on page S8). This comparison indicates that base activation substantially facilitates the oxidation of the sulfenamide-derived species. Since $MesN_2BF_4$ displayed an apparent reduction potential of +0.25 V vs SCE (Figure S4 on page S9), the SET from the base-activated **S1**-derived species to $MesN_2BF_4$ is thermodynamically feasible, with a positive potential difference of ca. 0.33 V. These CV results are consistent with a base-promoted direct SET process involved in the catalyst-free background reaction.

8. References

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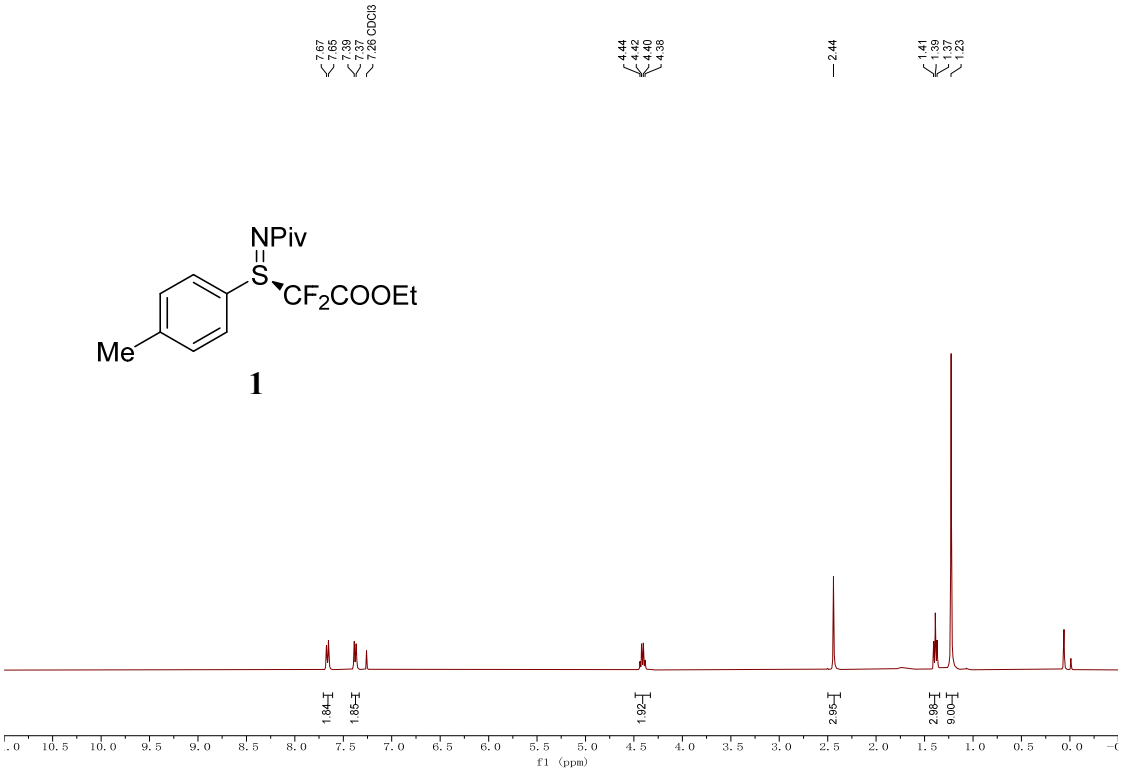
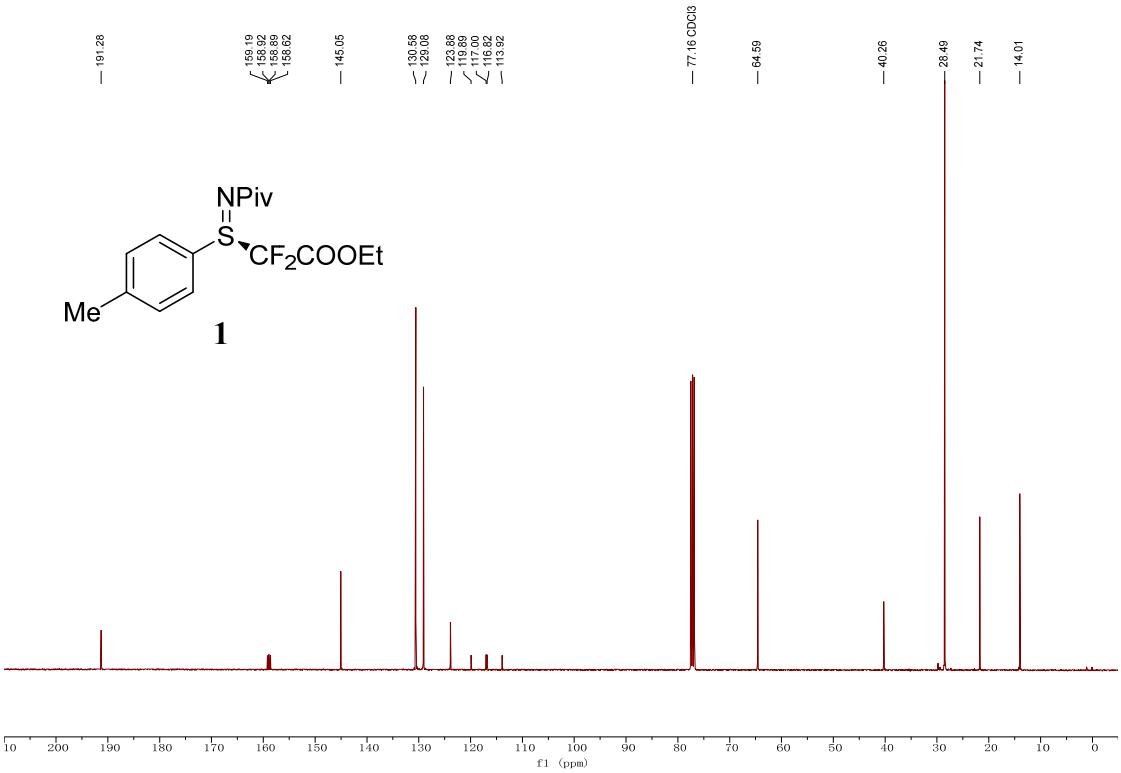
9. NMR spectra

Figure S11. NMR spectra of compound **1**.

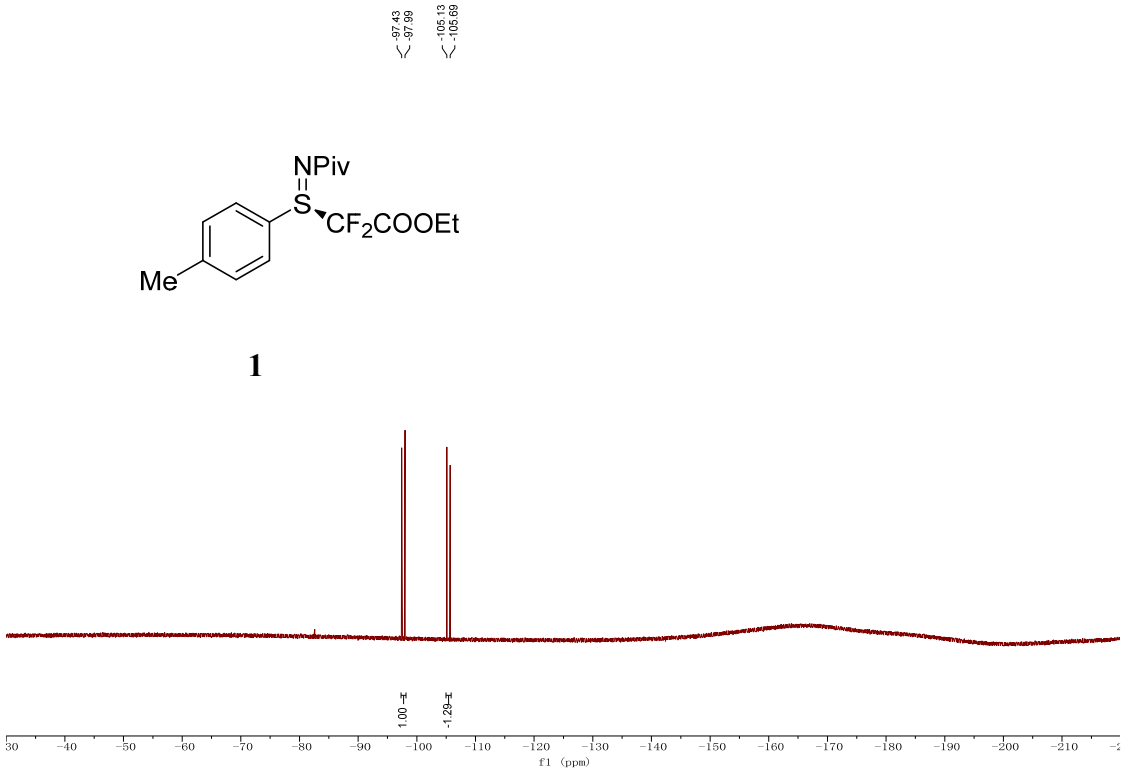
^{1}H NMR (400 MHz) spectrum of compound **1** ($CDCl_3$, 297.2 K)



^{13}C NMR (100 MHz) spectrum of compound **1** ($CDCl_3$, 299.6 K)



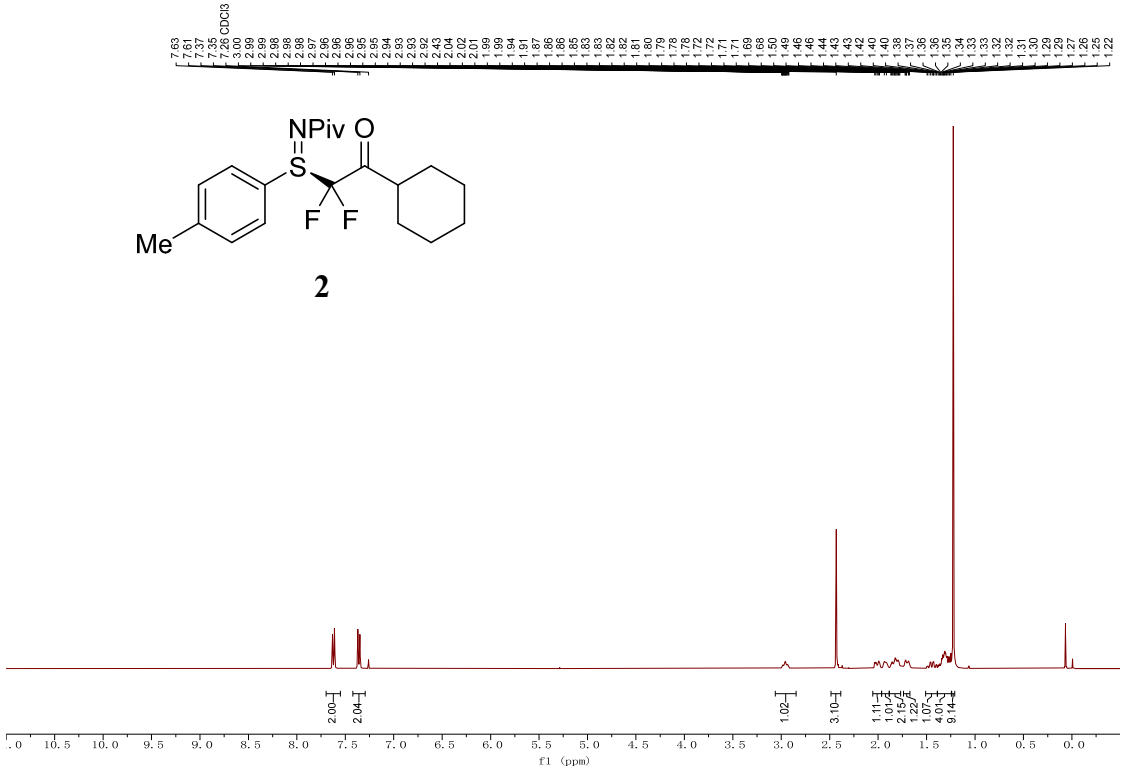
^{19}F NMR (376 MHz) spectrum of compound **1** ($CDCl_3$, 300.2 K)



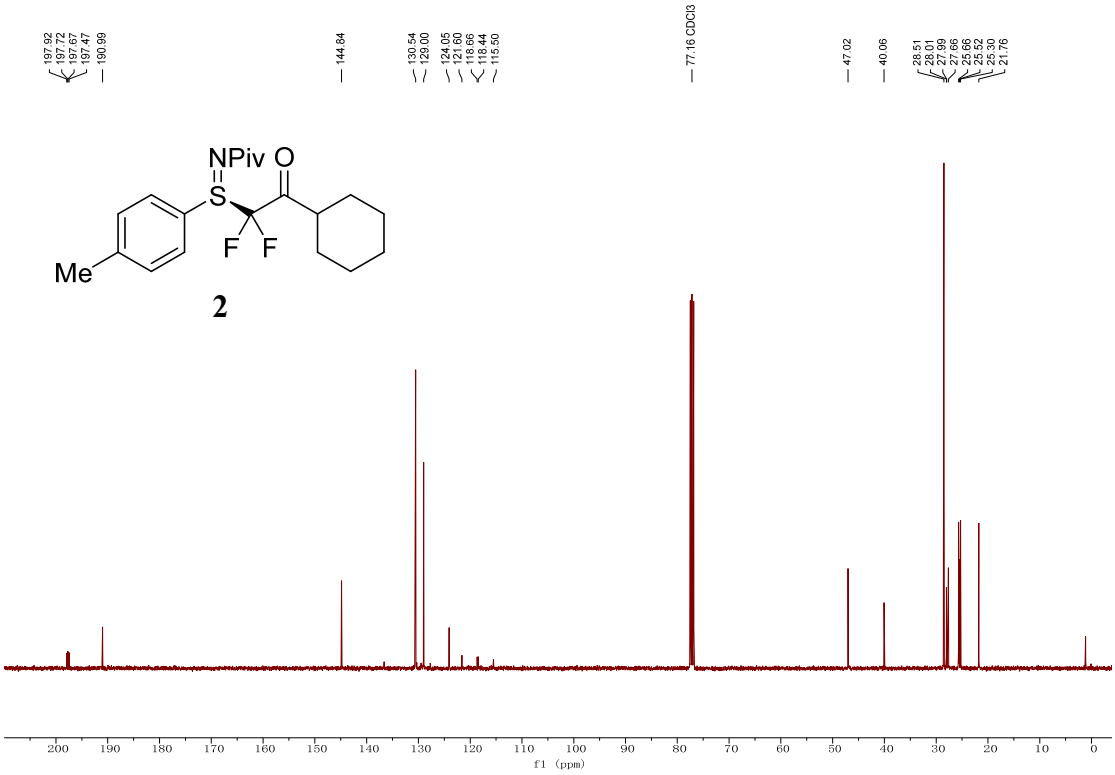
1

Figure S12. NMR spectra of compound **2**.

^{1}H NMR (400 MHz) spectrum of compound **2** ($CDCl_3$, 297.4 K)



^{13}C NMR (100 MHz) spectrum of compound **2** ($CDCl_3$, 297.8 K)



^{19}F NMR (376 MHz) spectrum of compound **2** ($CDCl_3$, 297.5 K)

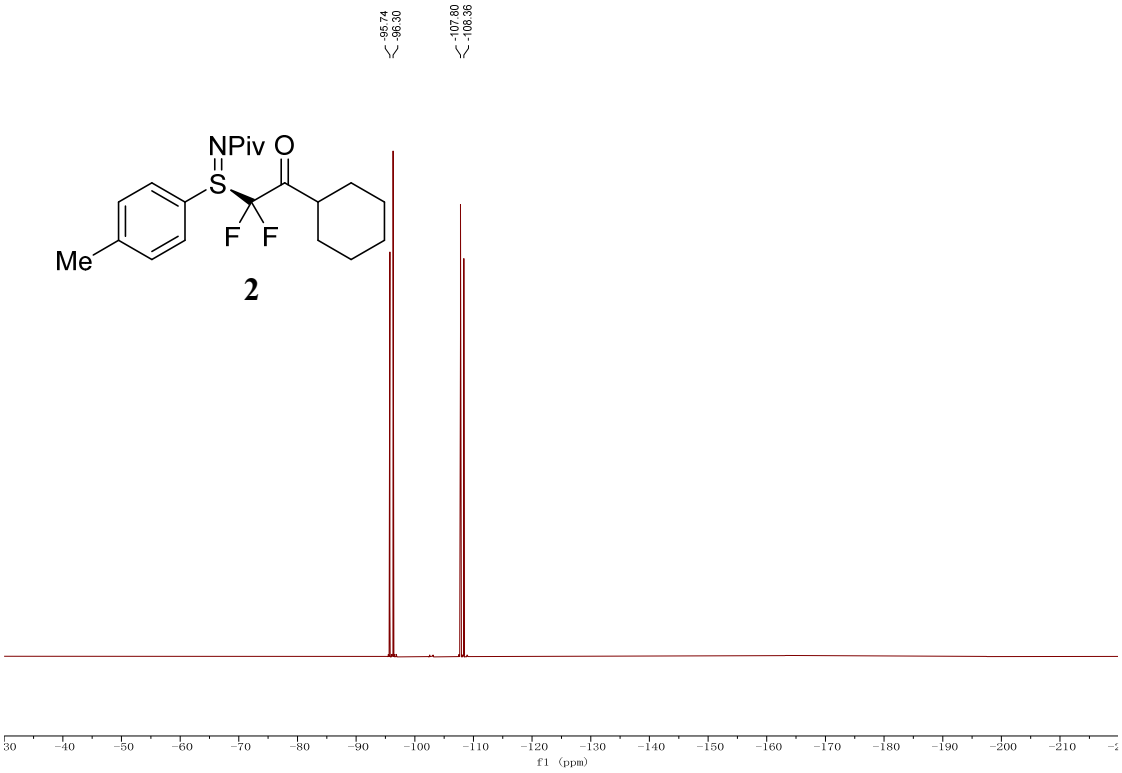
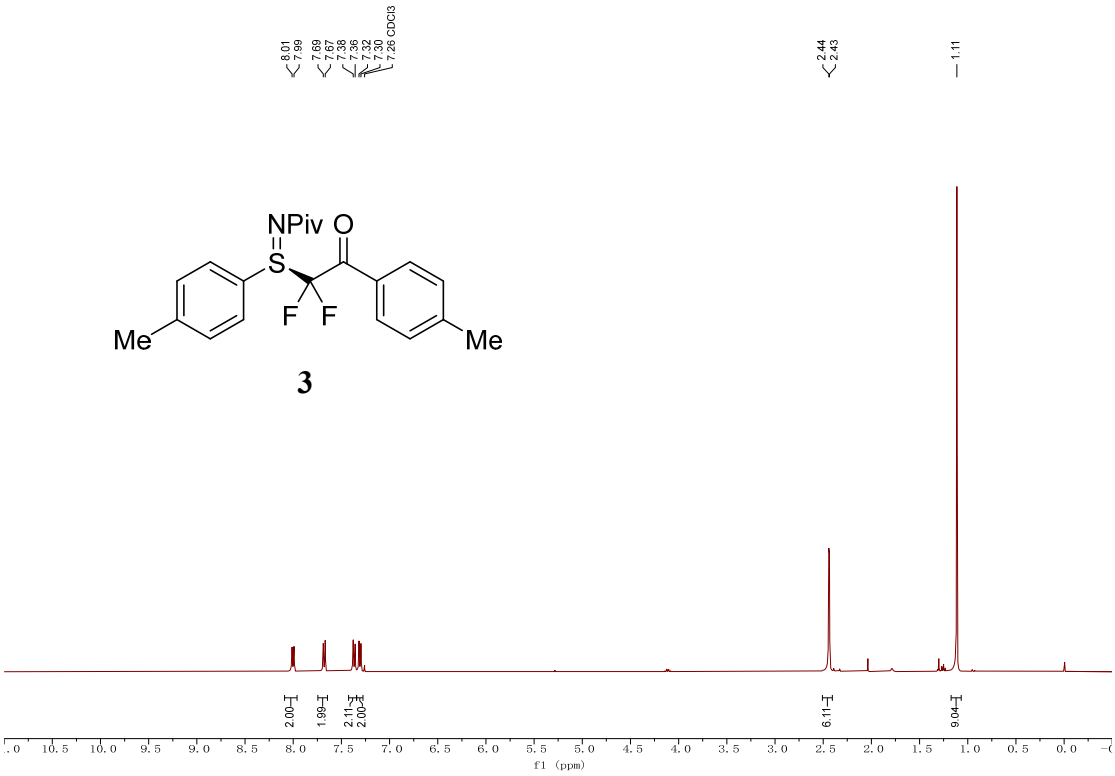
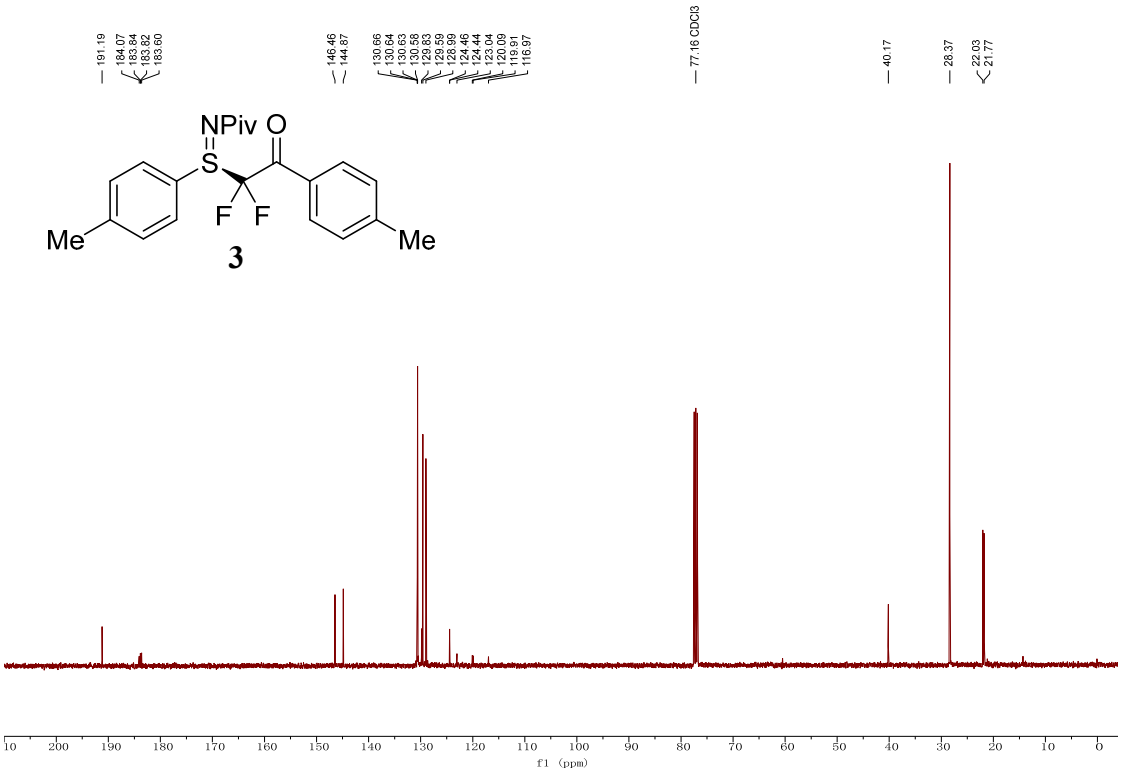


Figure S13. NMR spectra of compound **3**.

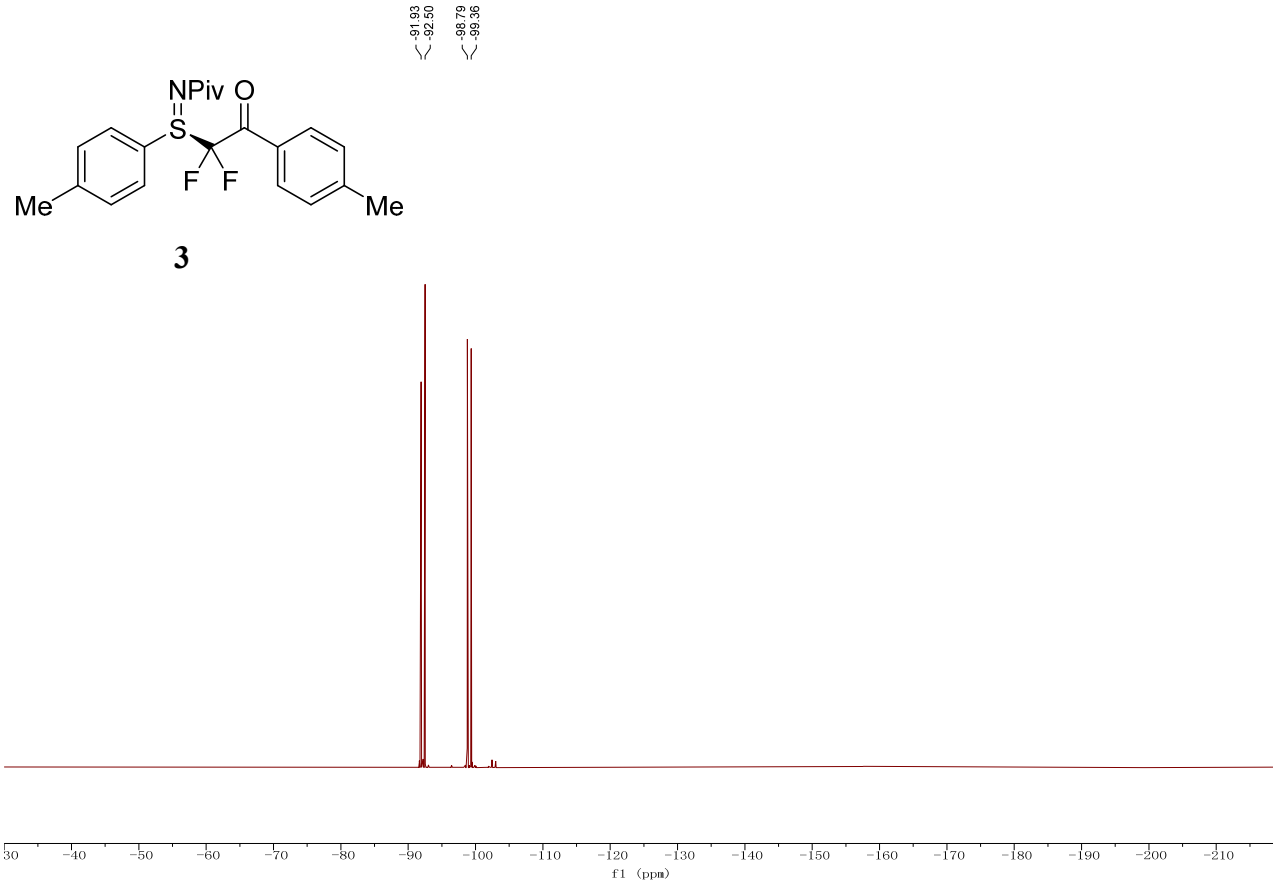
^{1}H NMR (400 MHz) spectrum of compound **3** ($CDCl_3$, 295.2 K)



^{13}C NMR (100 MHz) spectrum of compound **3** ($CDCl_3$, 295.4 K)



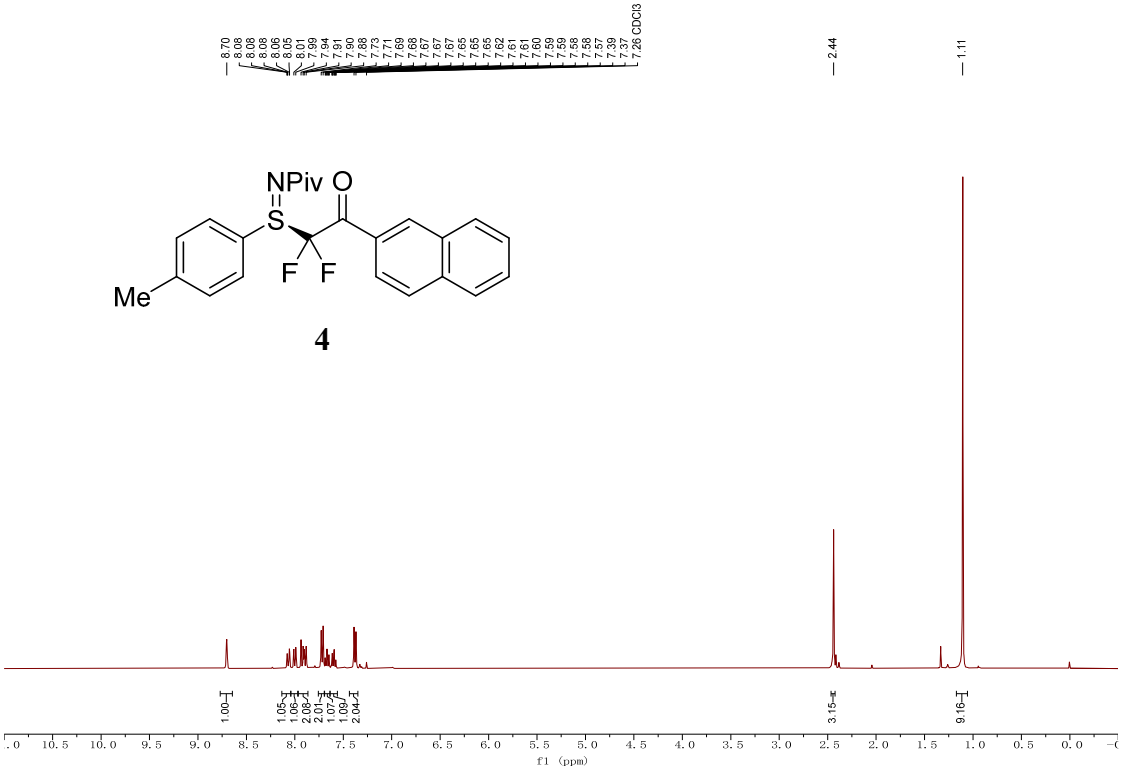
^{19}F NMR (376 MHz) spectrum of compound **3** ($CDCl_3$, 295.8 K)



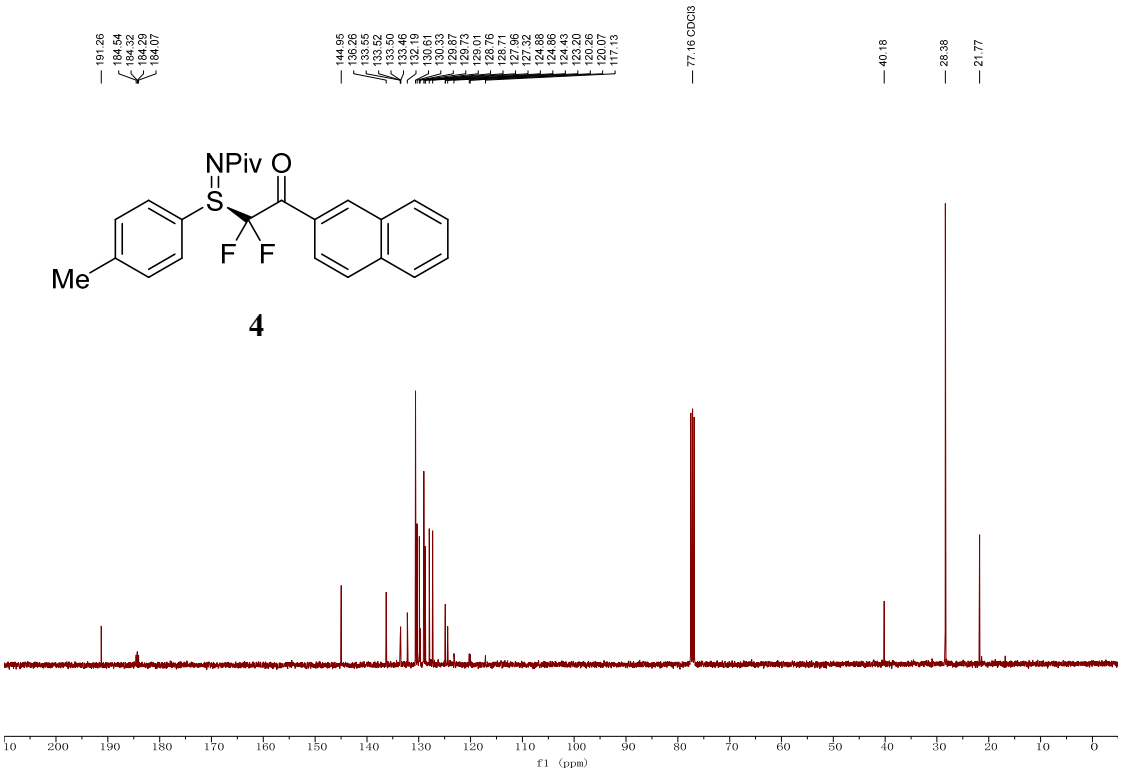
3

Figure S14. NMR spectra of compound **4**.

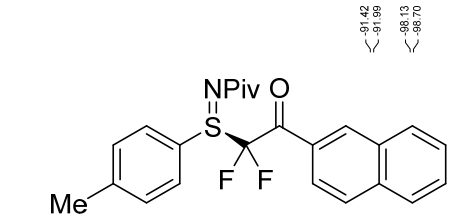
^{1}H NMR (400 MHz) spectrum of compound **4** ($CDCl_3$, 296.1 K)



^{13}C NMR (100 MHz) spectrum of compound **4** ($CDCl_3$, 296.1 K)



^{19}F NMR (376 MHz) spectrum of compound **4** ($CDCl_3$, 296.5 K)



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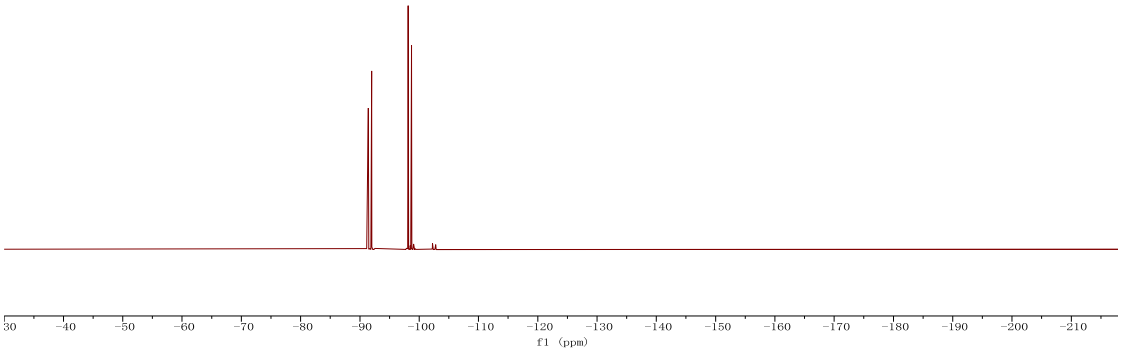
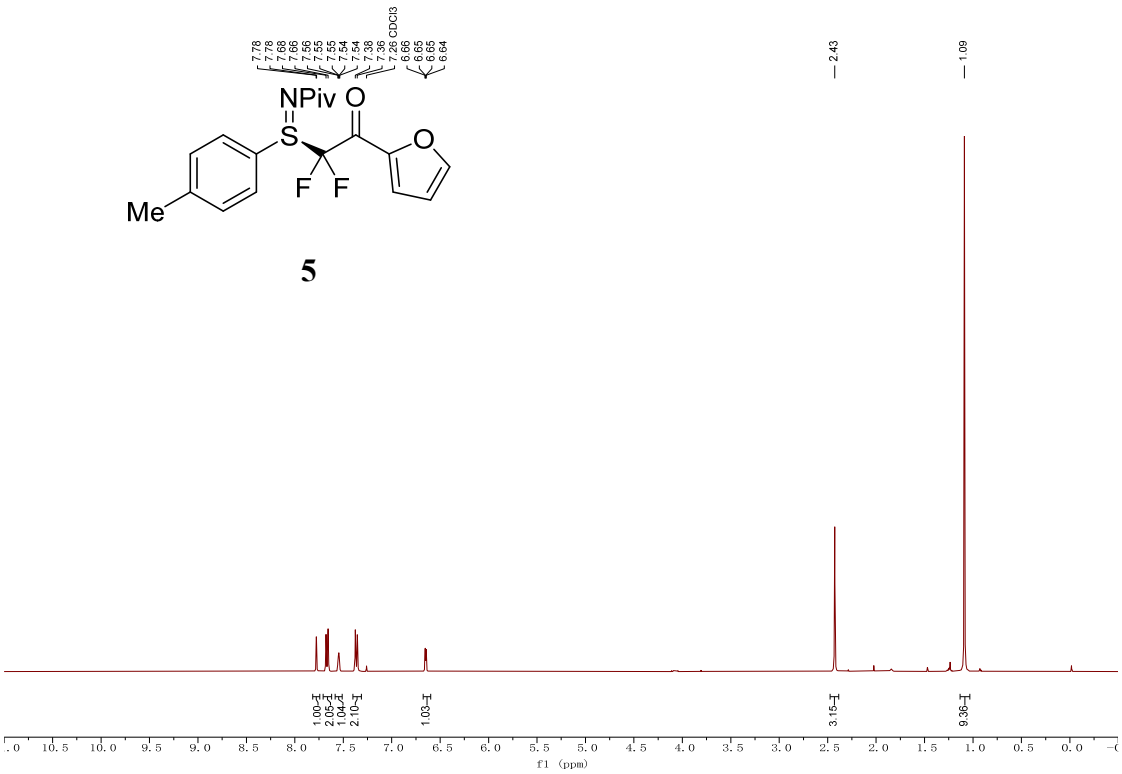
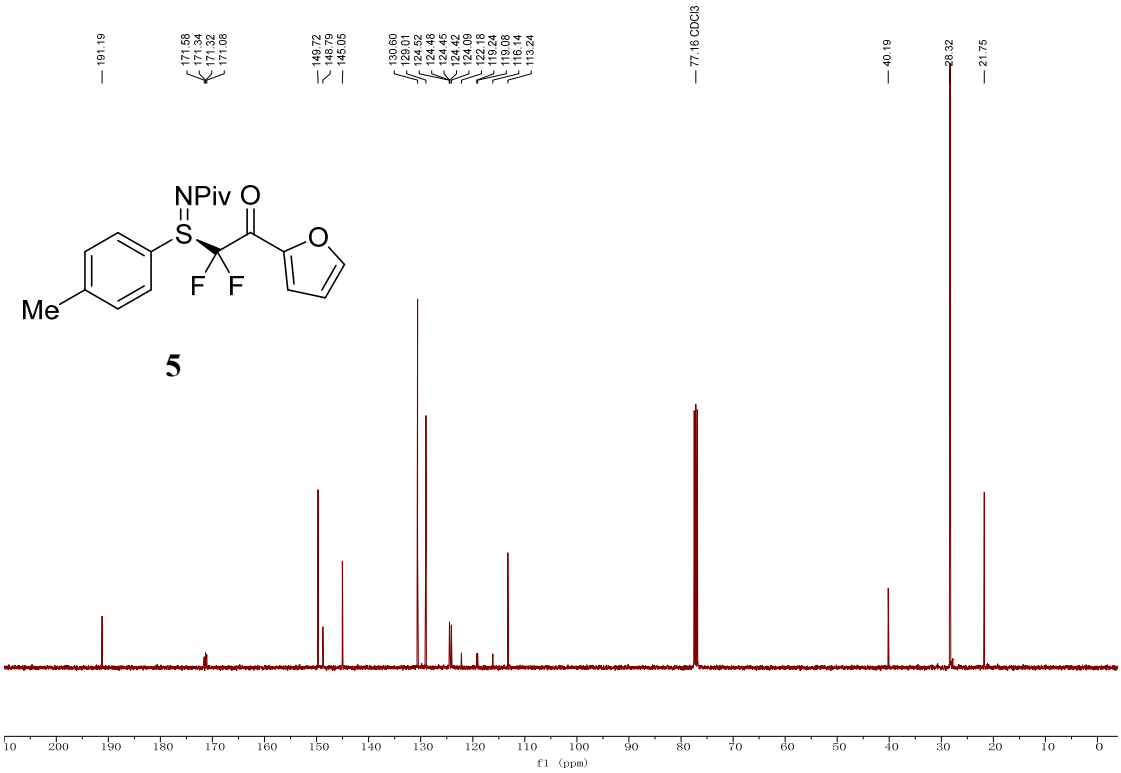


Figure S15. NMR spectra of compound **5**.

^{1}H NMR (400 MHz) spectrum of compound **5** ($CDCl_3$, 298.2 K)



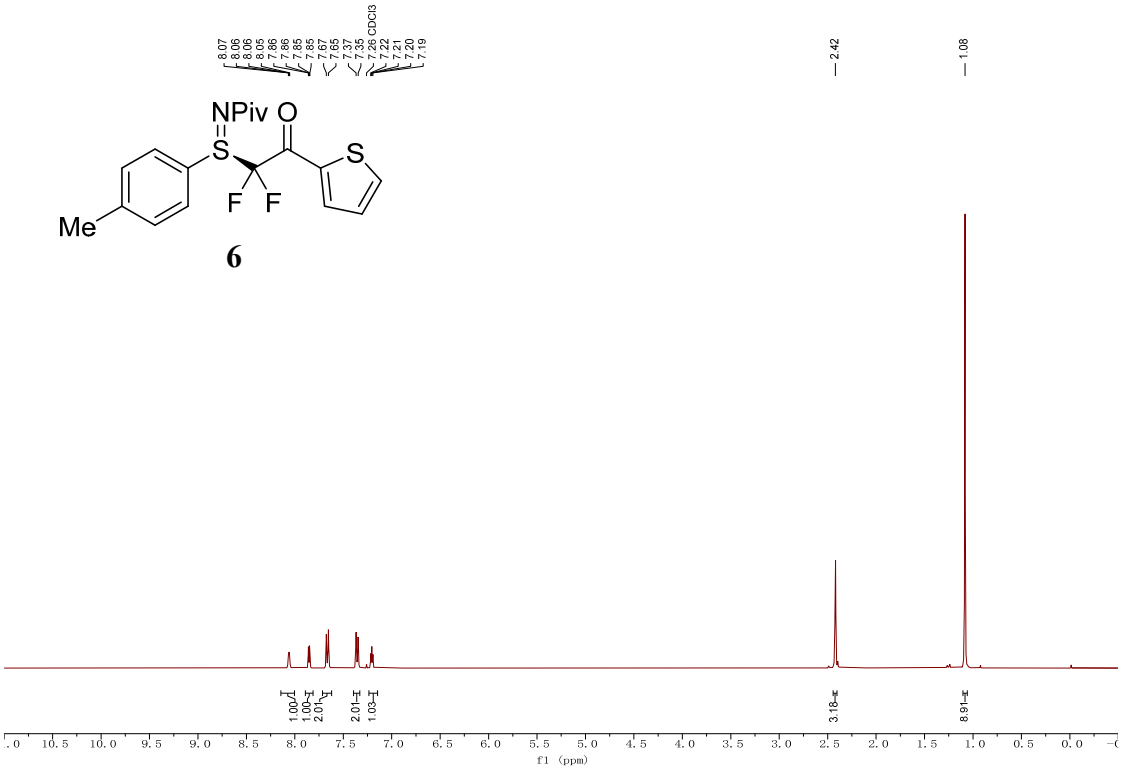
^{13}C NMR (100 MHz) spectrum of compound **5** ($CDCl_3$, 298.2 K)



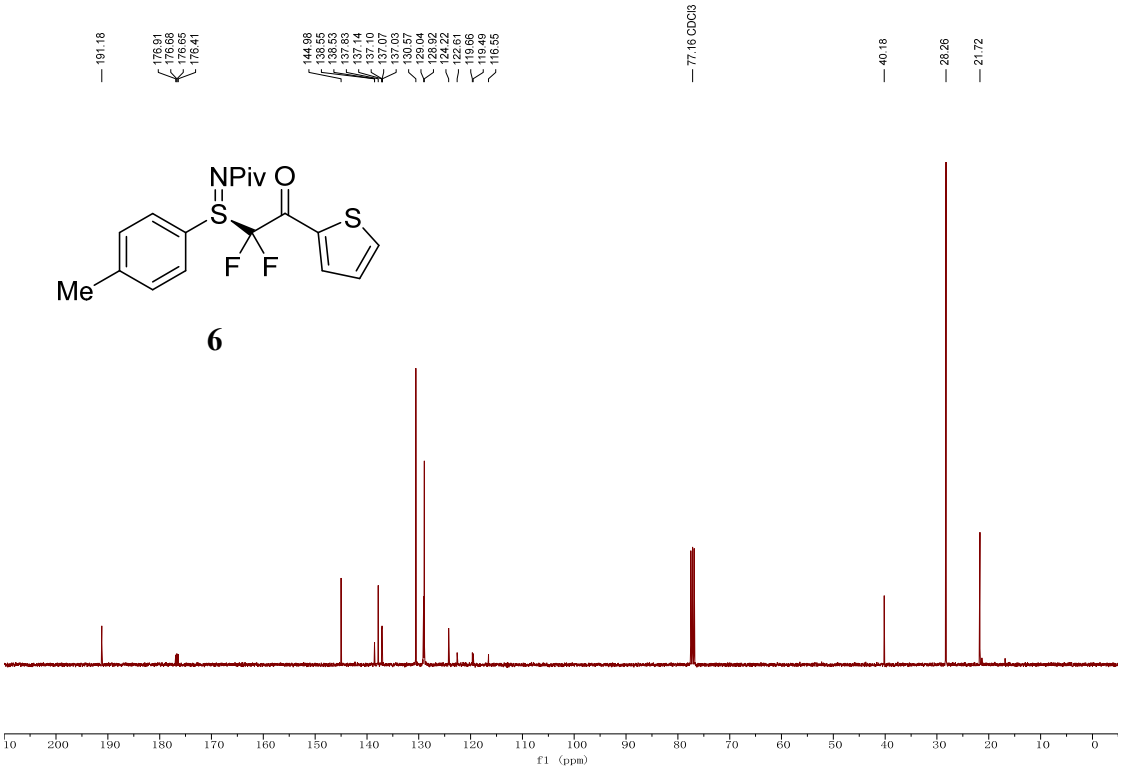
^{19}F NMR (376 MHz) spectrum of compound **5** ($CDCl_3$, 298.1 K)

Figure S16. NMR spectra of compound **6**.

^{1}H NMR (400 MHz) spectrum of compound **6** ($CDCl_3$, 298.1 K)



^{13}C NMR (100 MHz) spectrum of compound **6** ($CDCl_3$, 298.2 K)

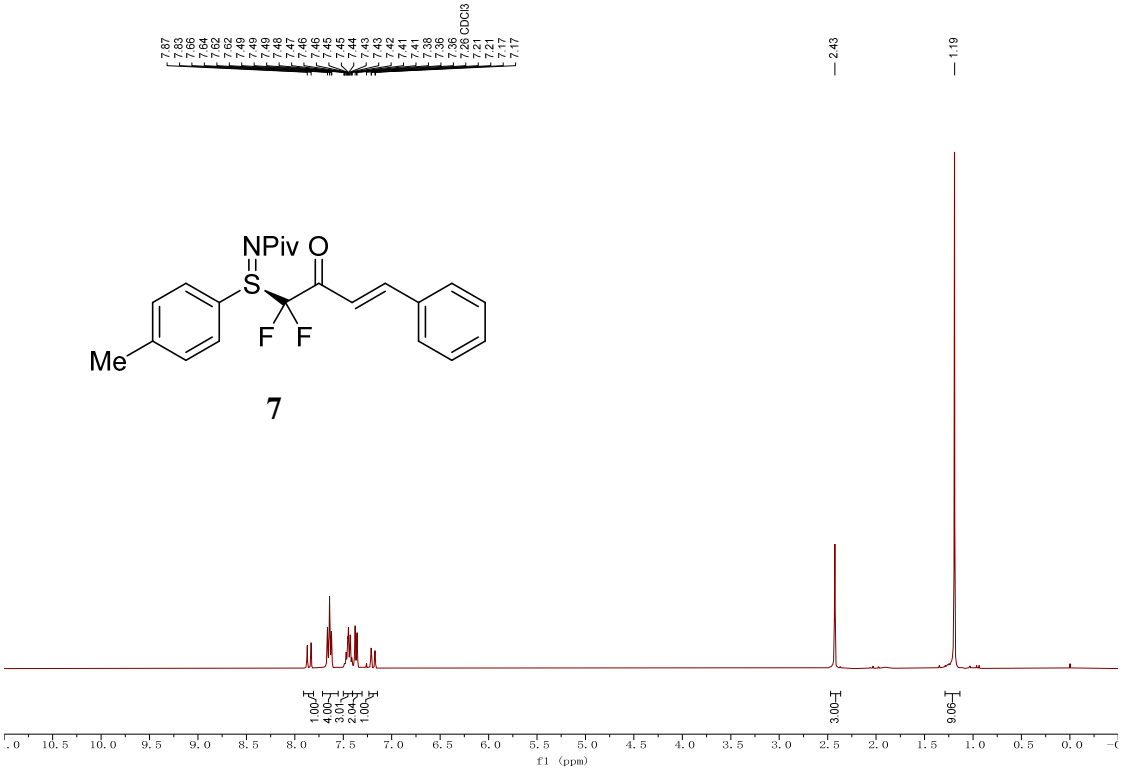


^{19}F NMR (376 MHz) spectrum of compound **6** ($CDCl_3$, 298.2 K)

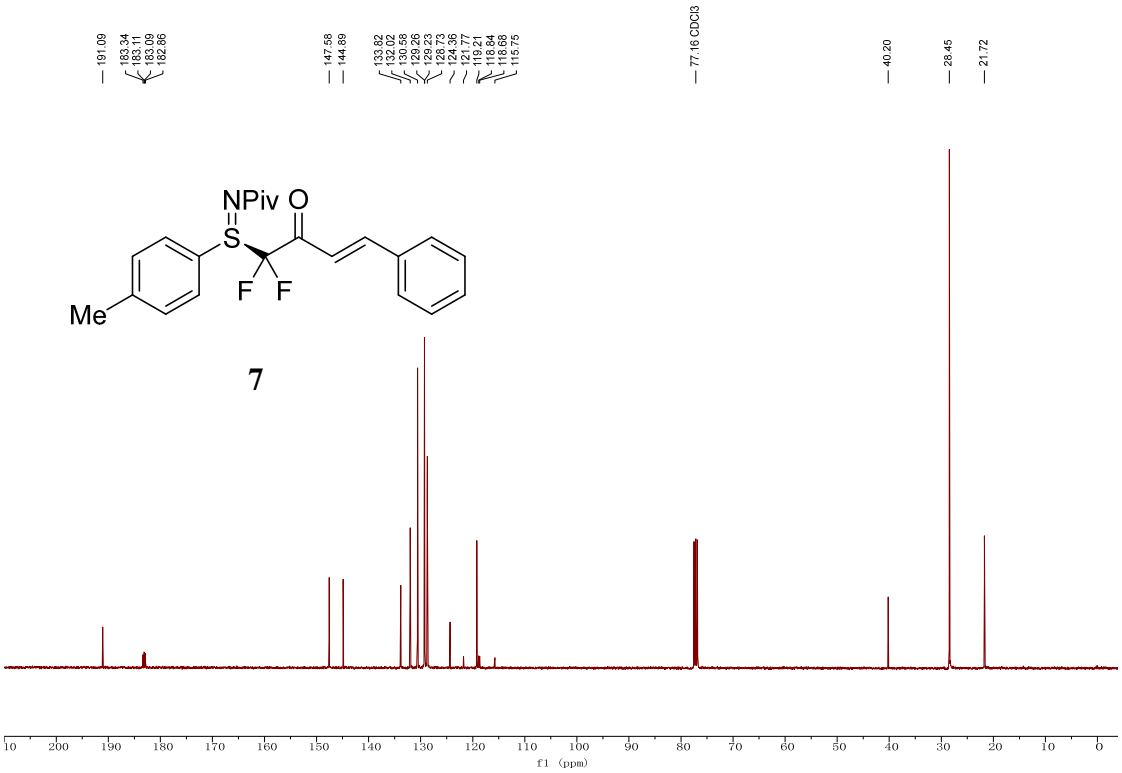
6

Figure S17. NMR spectra of compound **7**.

^{1}H NMR (400 MHz) spectrum of compound **7** ($CDCl_3$, 298.3 K)



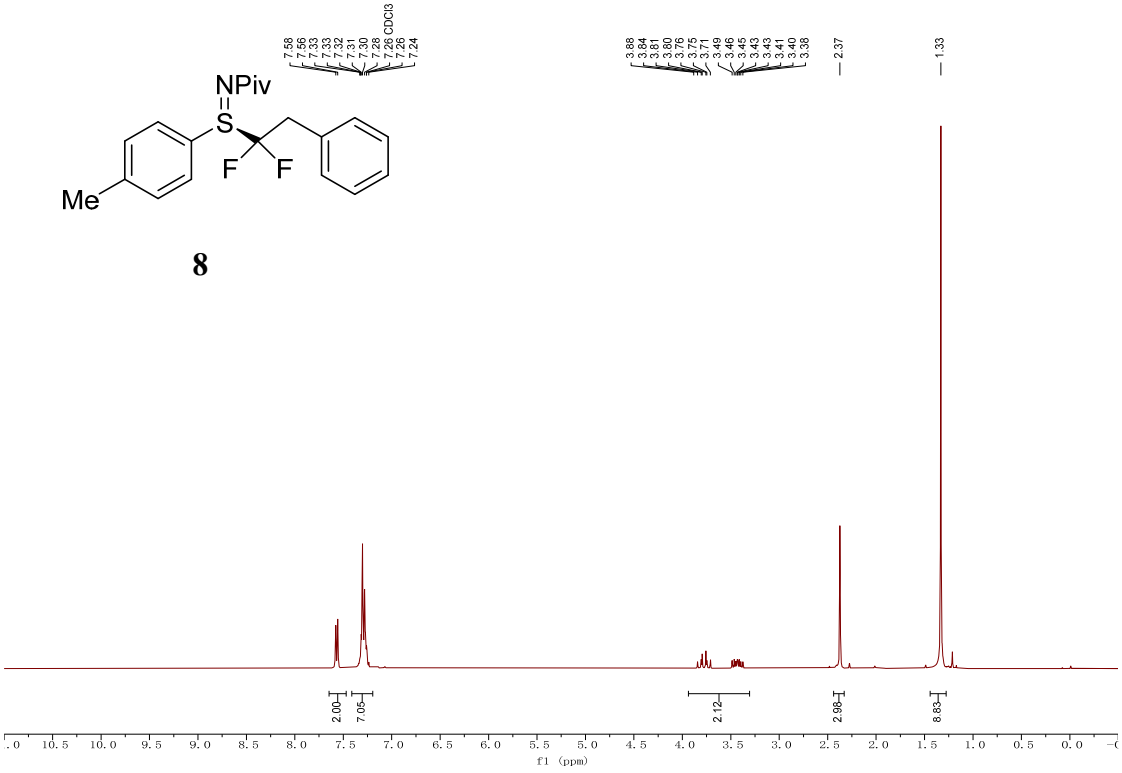
^{13}C NMR (100 MHz) spectrum of compound **7** ($CDCl_3$, 298.4 K)



^{19}F NMR (376 MHz) spectrum of compound **7** ($CDCl_3$, 298.7 K)

Figure S18. NMR spectra of compound **8**.

^{1}H NMR (400 MHz) spectrum of compound **8** ($CDCl_3$, 298.1 K)



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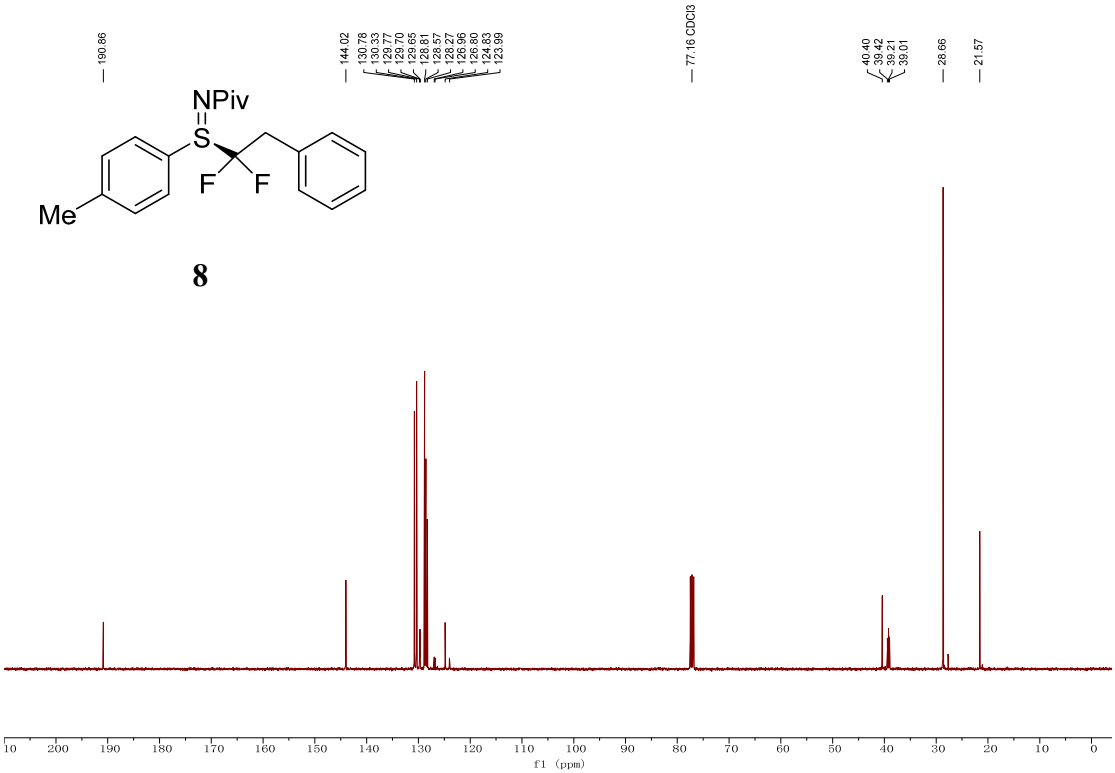
^{13}C NMR (100 MHz) spectrum of compound **8** ($CDCl_3$, 298.2 K)



8

^{19}F NMR (376 MHz) spectrum of compound **8** ($CDCl_3$, 298.1 K)

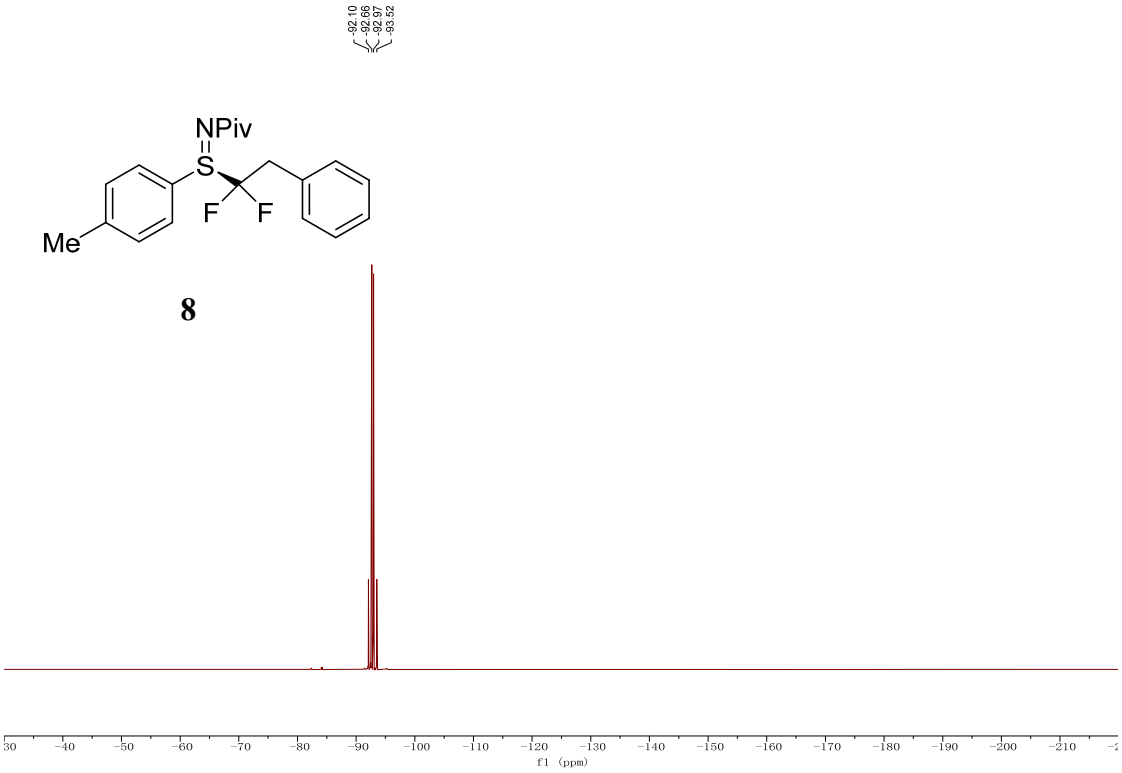
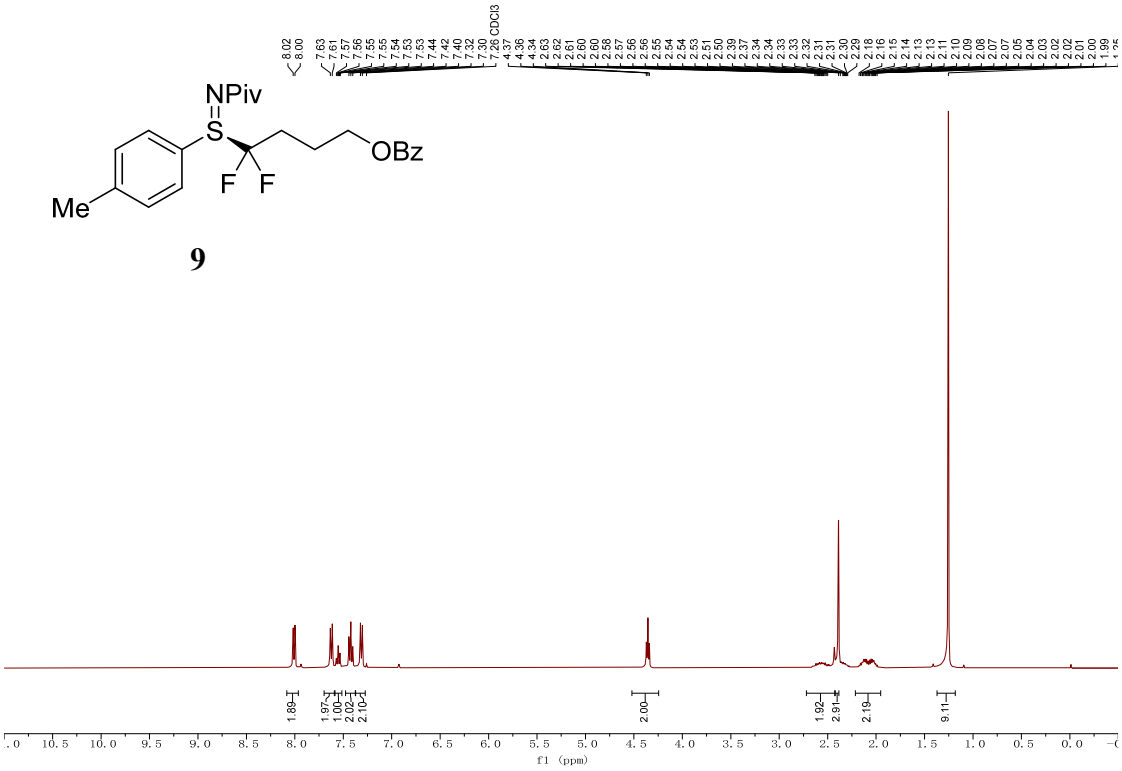
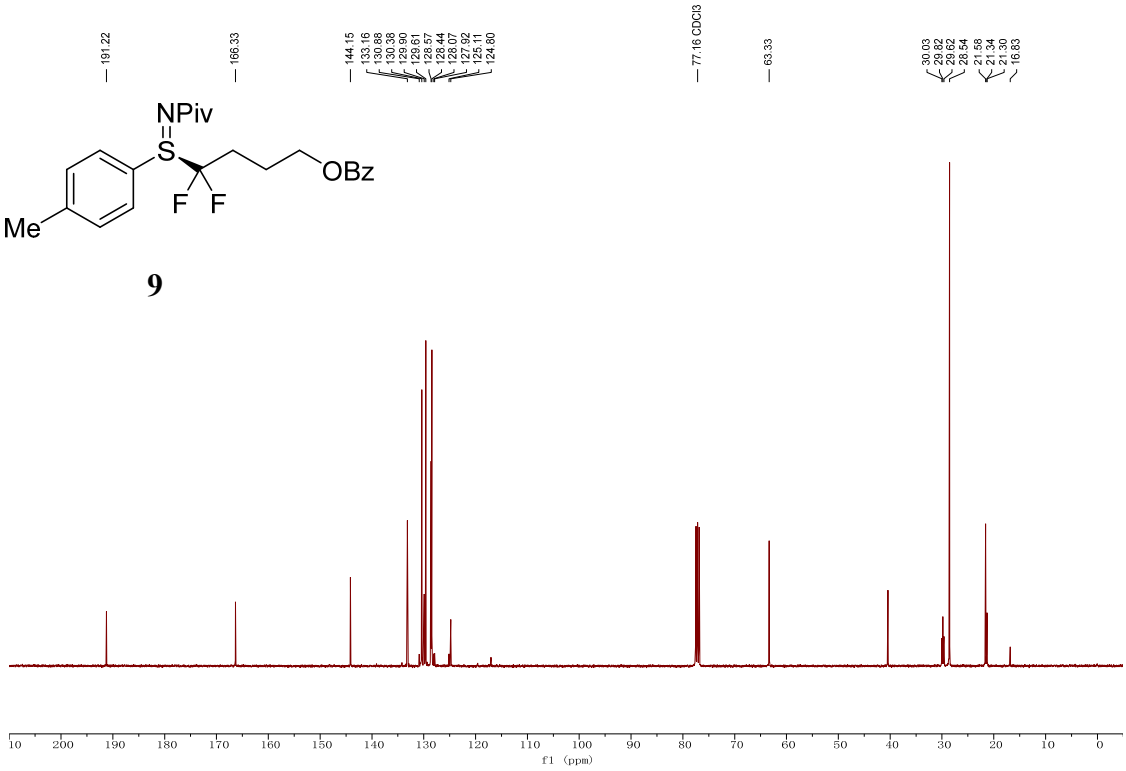


Figure S19. NMR spectra of compound **9**.

^{1}H NMR (400 MHz) spectrum of compound **9** ($CDCl_3$, 297.1 K)



^{13}C NMR (100 MHz) spectrum of compound **9** ($CDCl_3$, 297.3 K)



^{19}F NMR (376 MHz) spectrum of compound **9** ($CDCl_3$, 297.2 K)

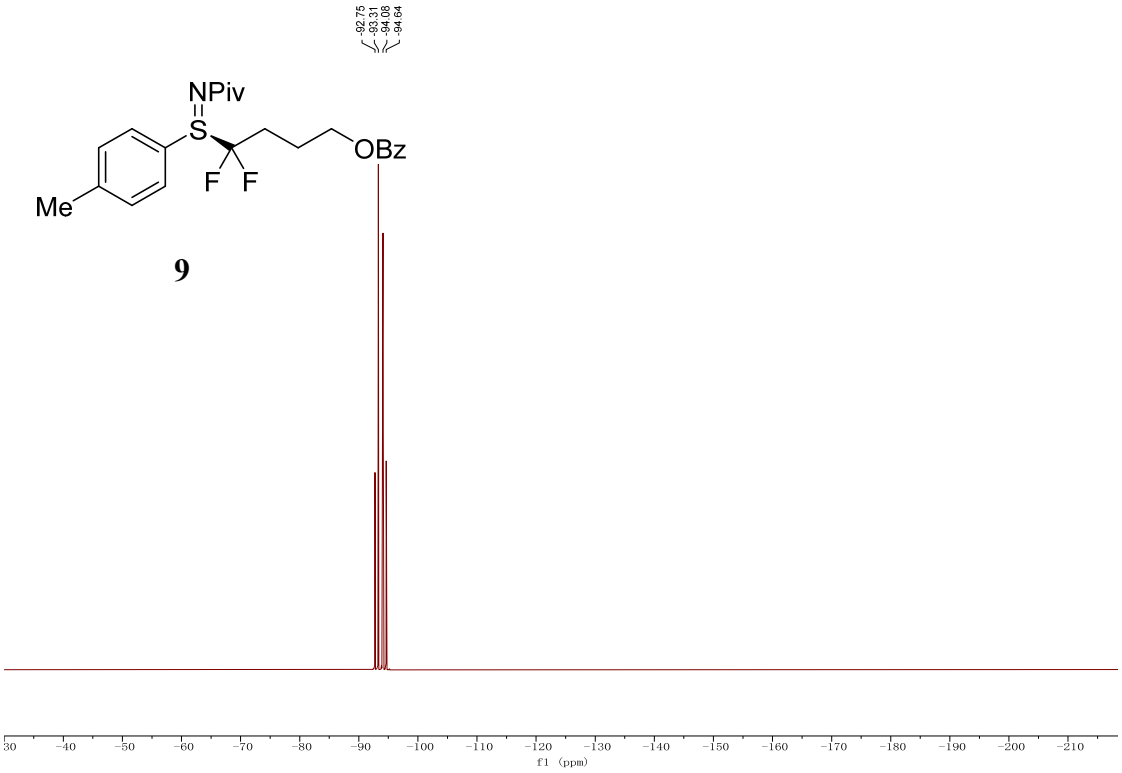
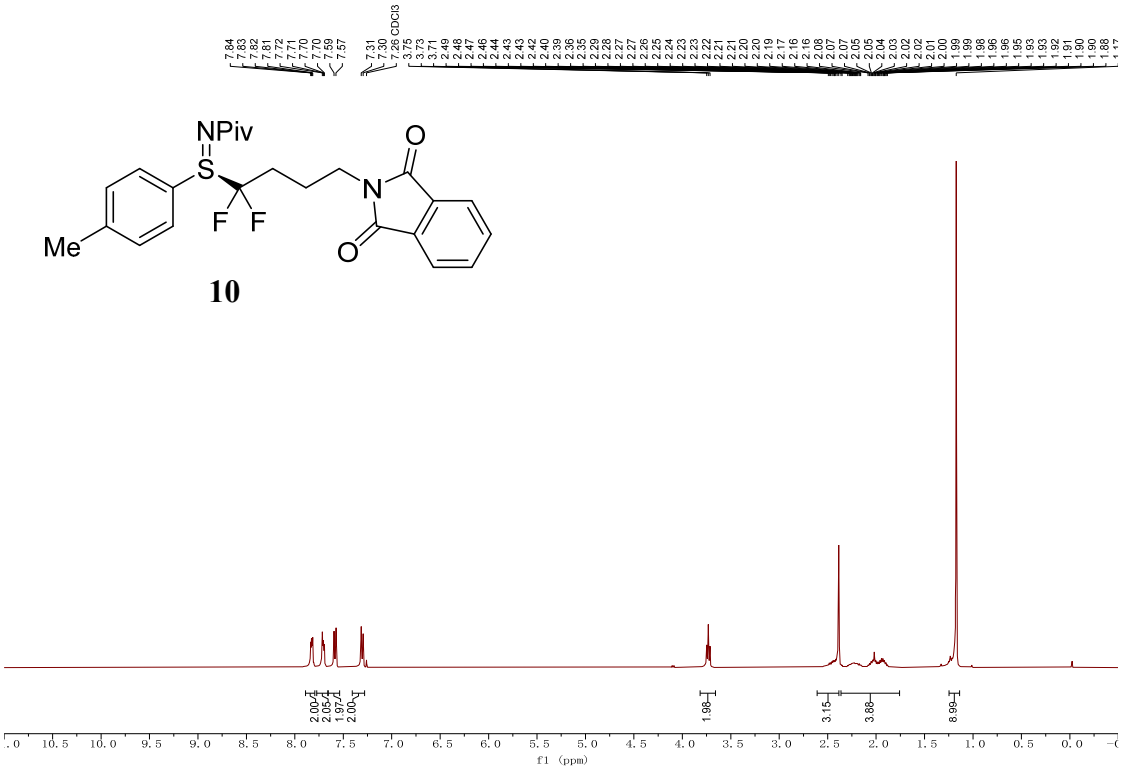
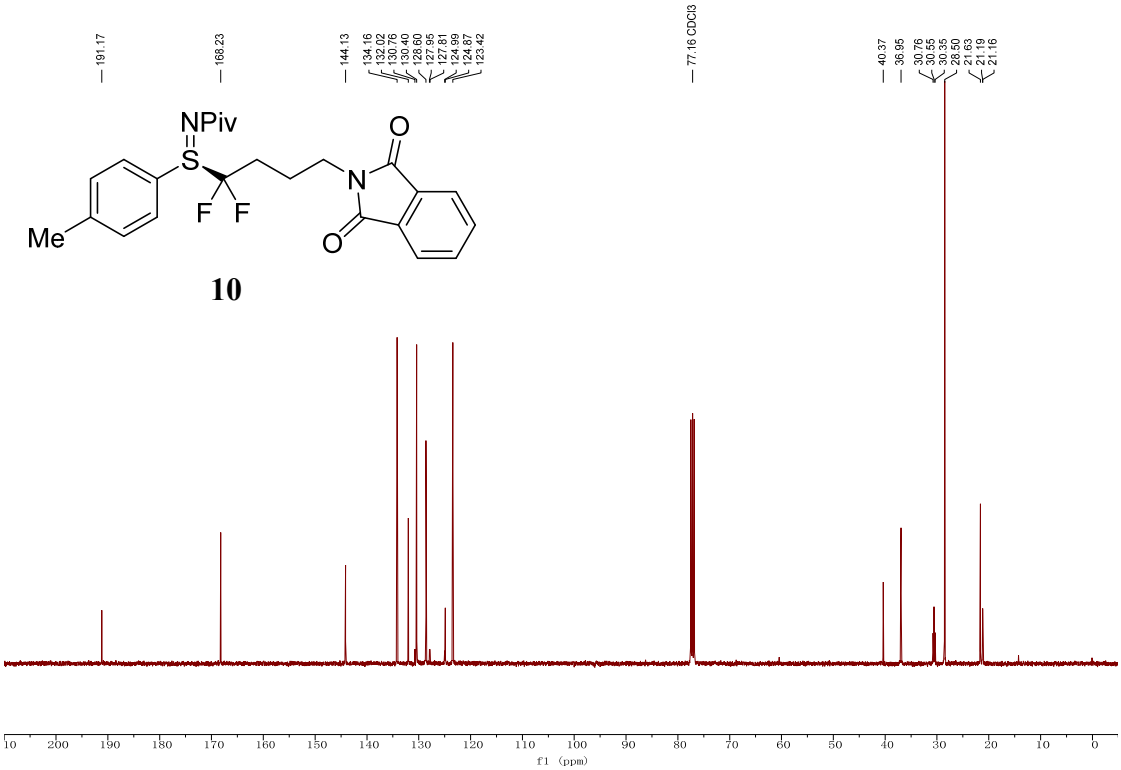


Figure S20. NMR spectra of compound **10**.

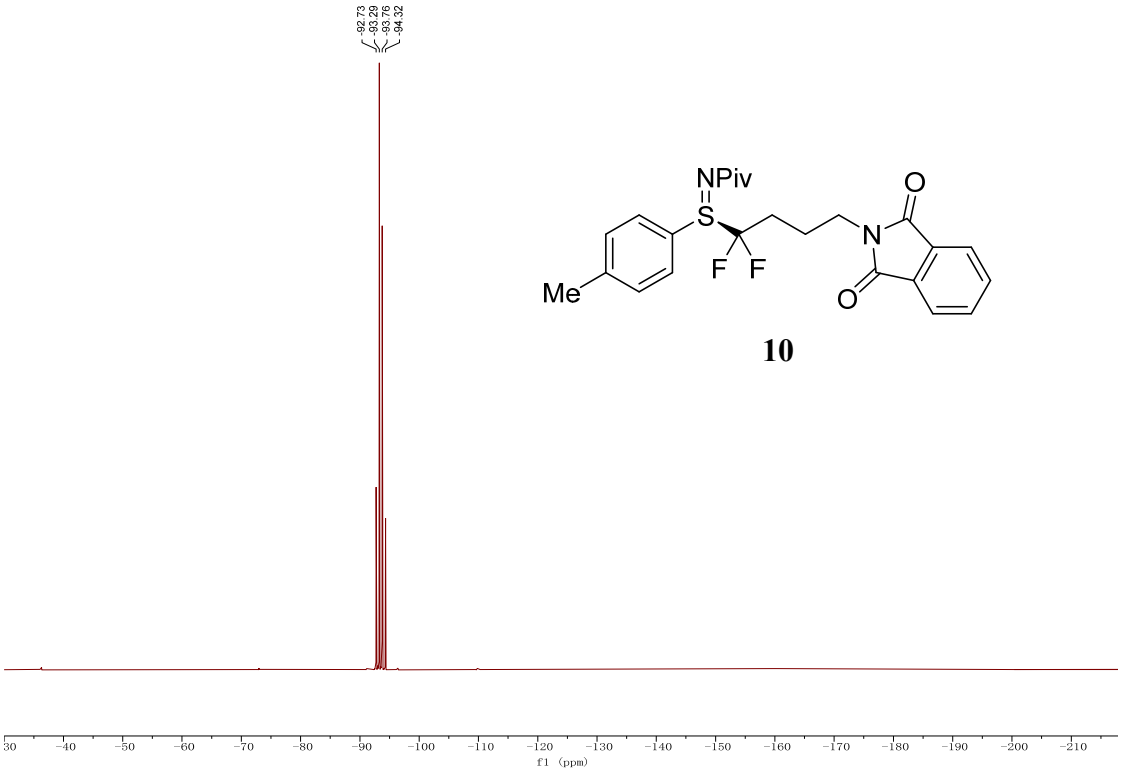
^{1}H NMR (400 MHz) spectrum of compound **10** ($CDCl_3$, 298.1 K)



^{13}C NMR (100 MHz) spectrum of compound **10** ($CDCl_3$, 297.6 K)



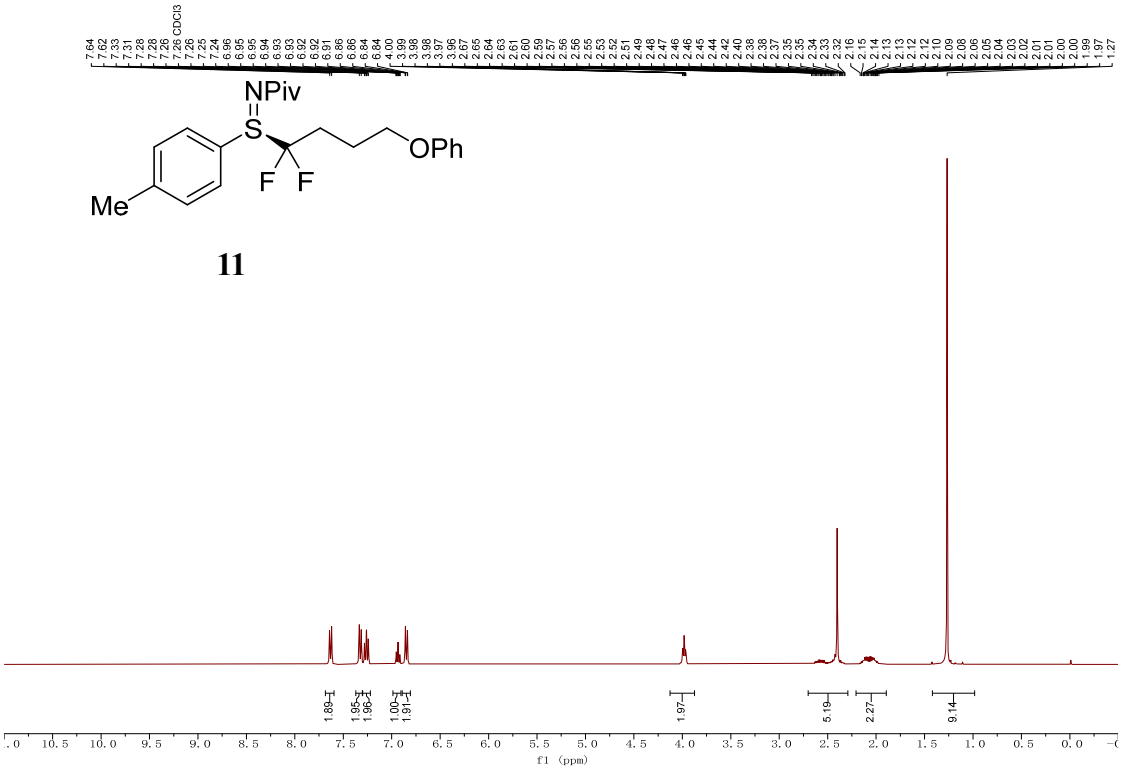
^{19}F NMR (376 MHz) spectrum of compound **10** ($CDCl_3$, 297.7 K)



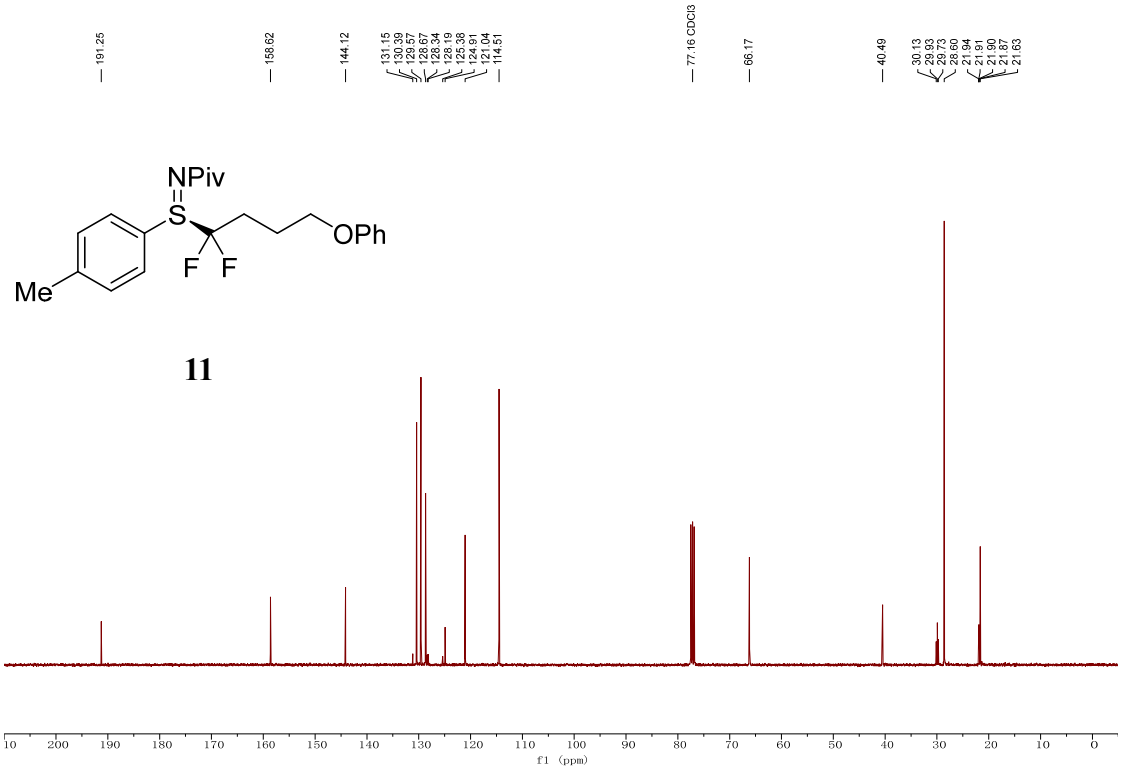
10

Figure S21. NMR spectra of compound **11**.

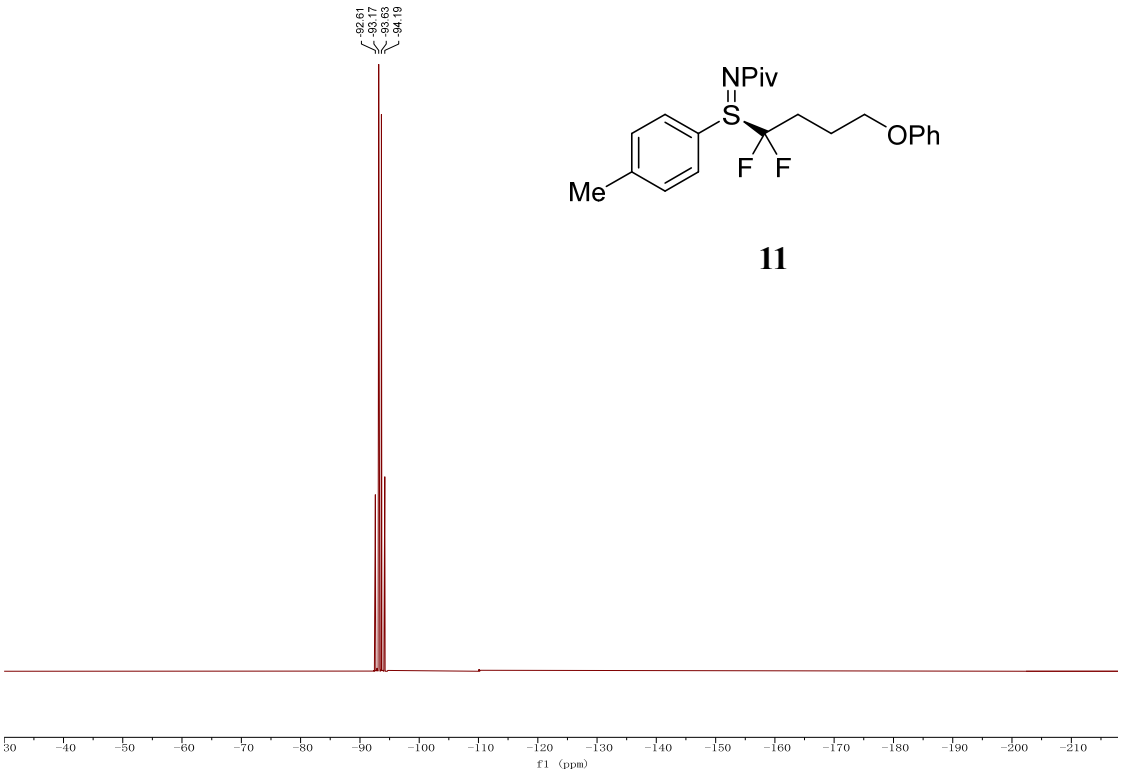
^{1}H NMR (400 MHz) spectrum of compound **11** ($CDCl_3$, 297.0 K)



^{13}C NMR (100 MHz) spectrum of compound **11** ($CDCl_3$, 297.6 K)



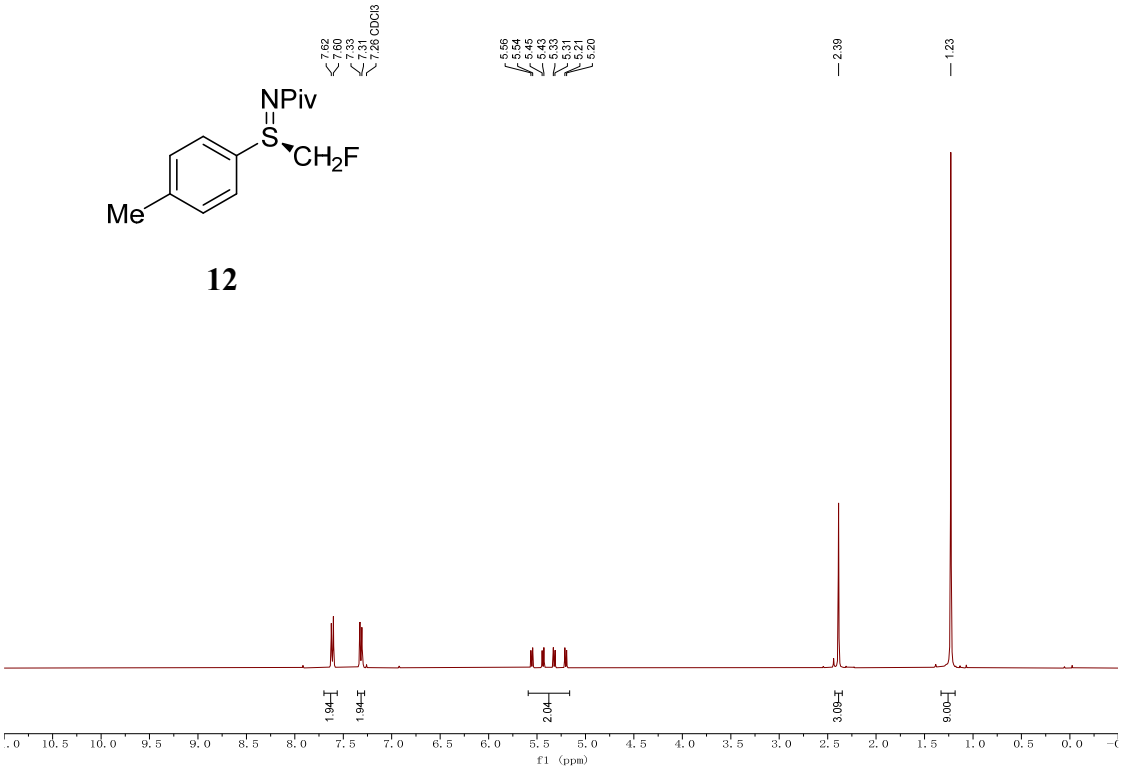
^{19}F NMR (376 MHz) spectrum of compound **11** ($CDCl_3$, 297.1 K)



11

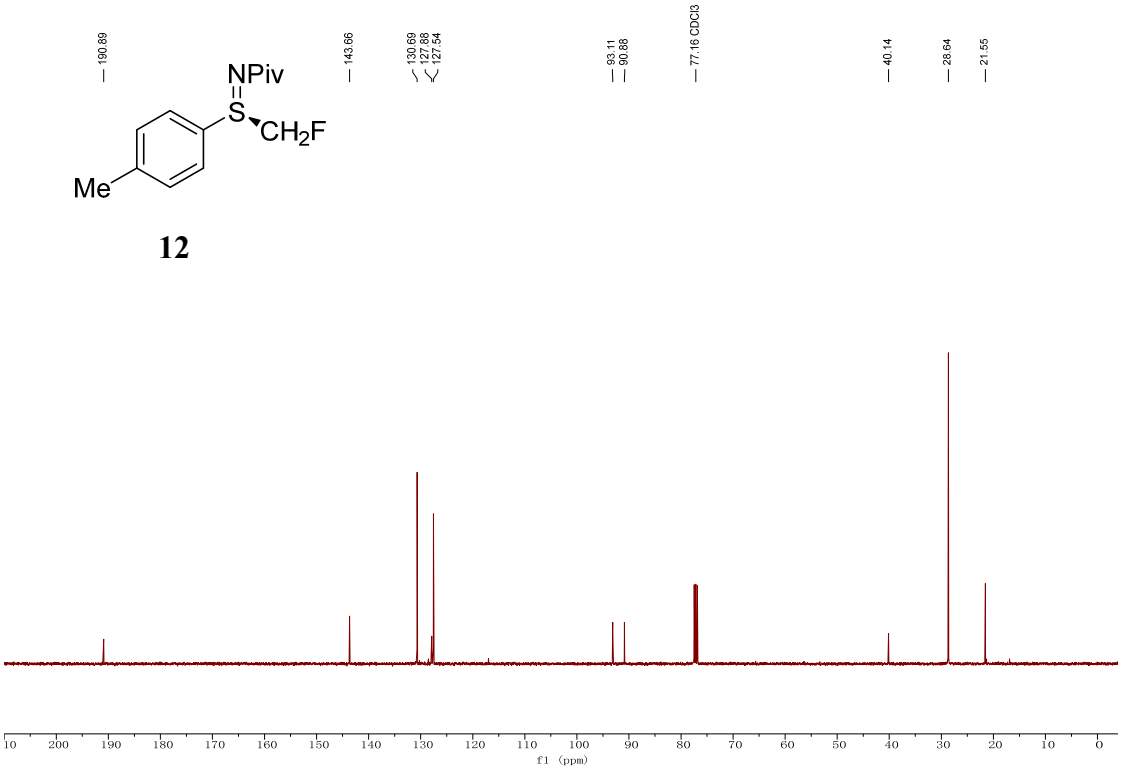
Figure S22. NMR spectra of compound **12**.

^{1}H NMR (400 MHz) spectrum of compound **12** ($CDCl_3$, 298.1 K)



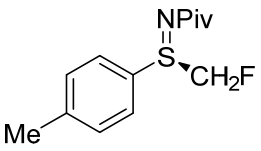
12

^{13}C NMR (100 MHz) spectrum of compound **12** ($CDCl_3$, 298.2 K)



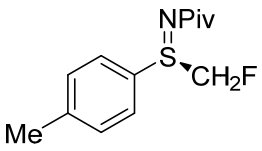
12

^{19}F NMR (376 MHz) spectrum of compound **12** ($CDCl_3$, 298.2 K)

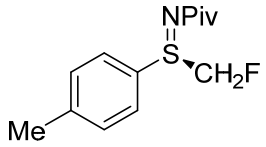


12

^{1}H NMR (400 MHz) spectrum of compound **12** ($CDCl_3$, 295.2 K)



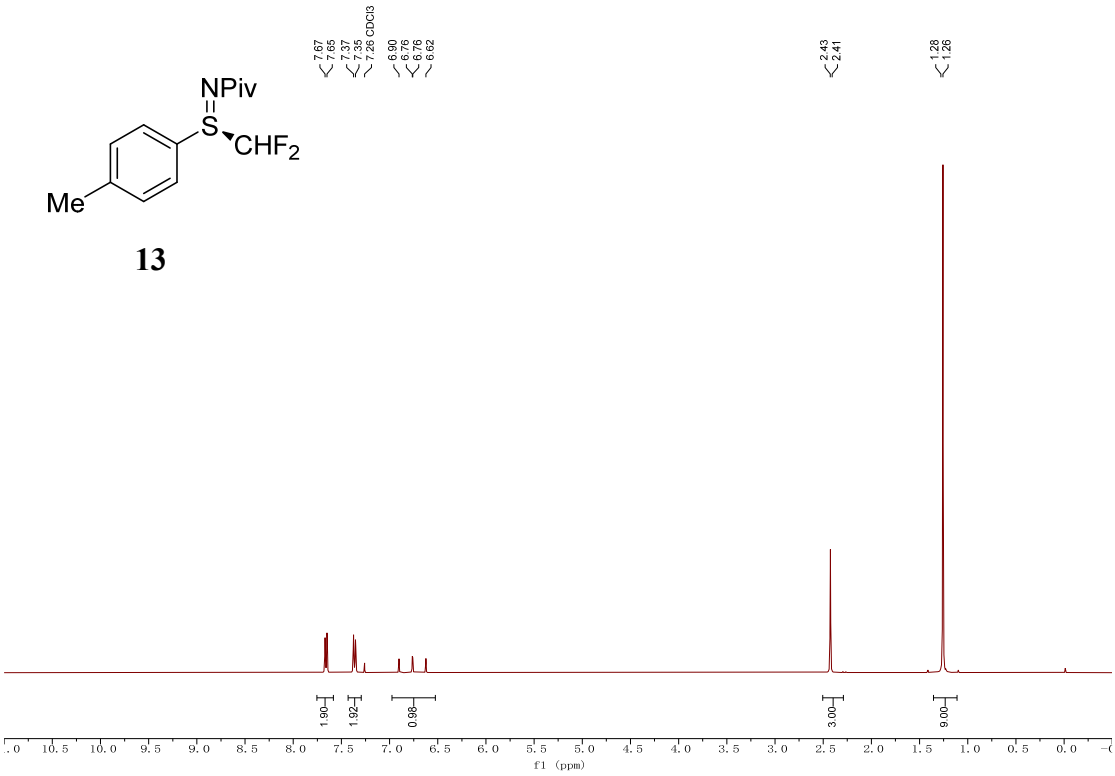
12 (stored in air for 3 months)



12 (stored in water for 1 week)

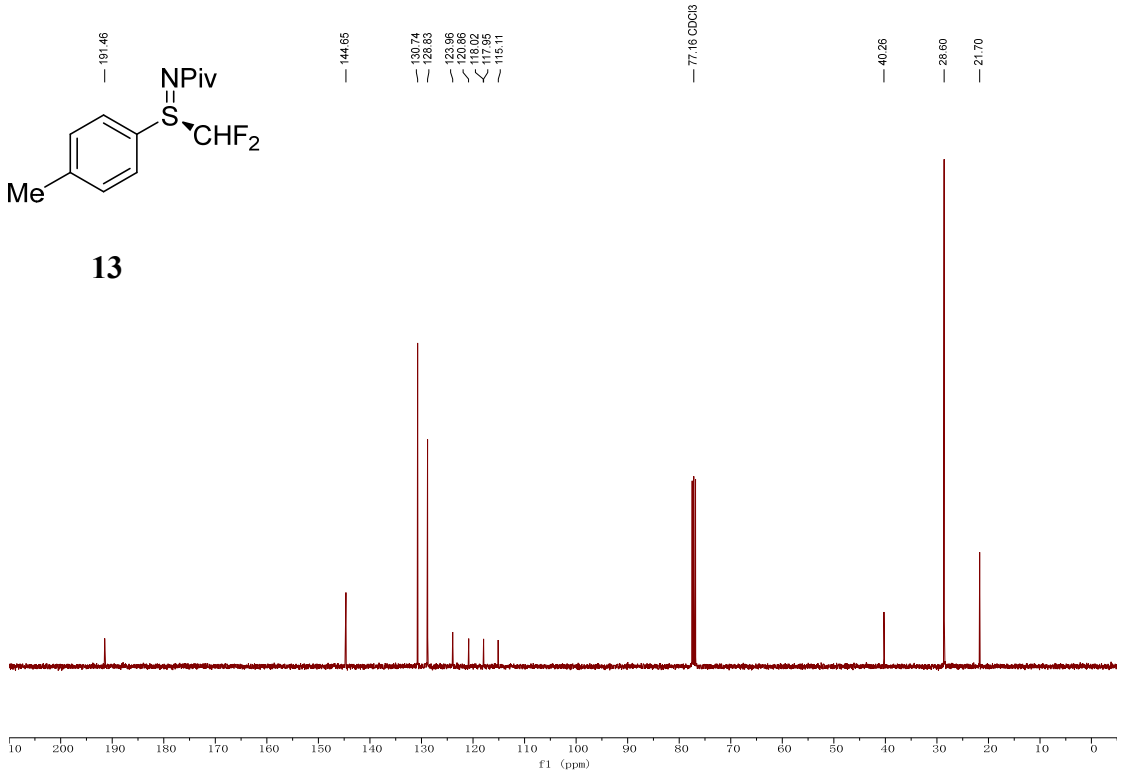
Figure S23. NMR spectra of compound **13**.

^{1}H NMR (400 MHz) spectrum of compound **13** ($CDCl_3$, 294.6 K)



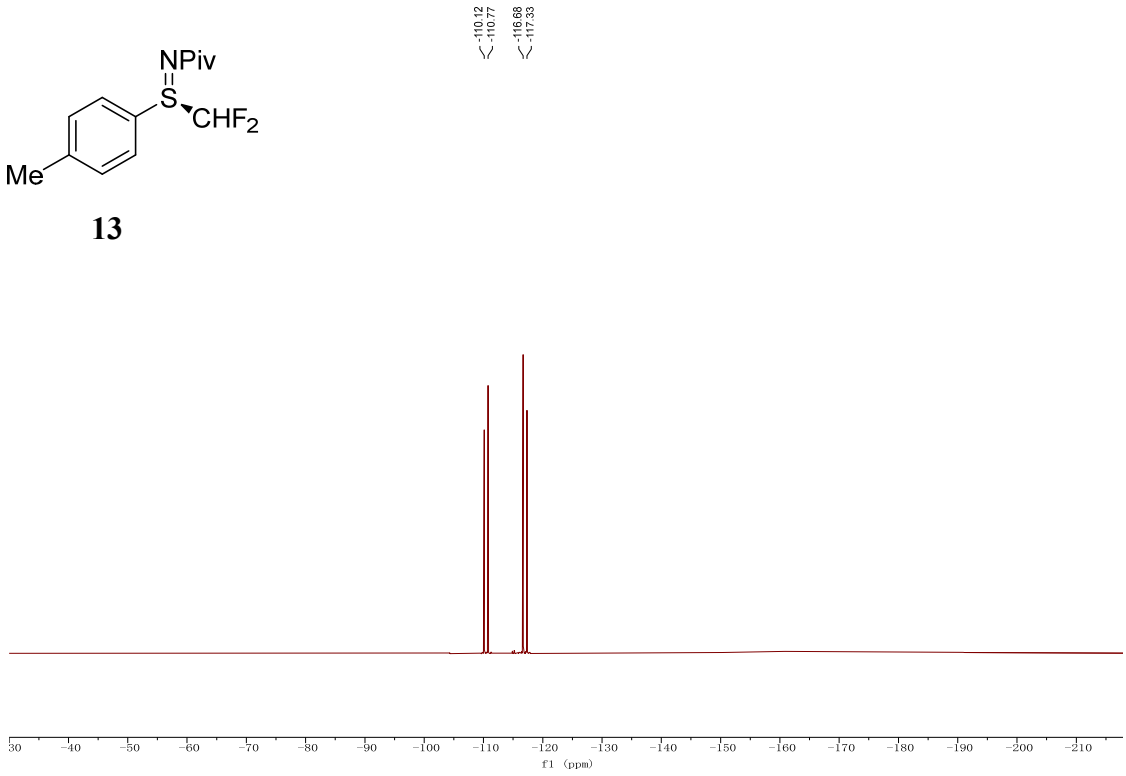
13

^{13}C NMR (100 MHz) spectrum of compound **13** ($CDCl_3$, 295.0 K)



13

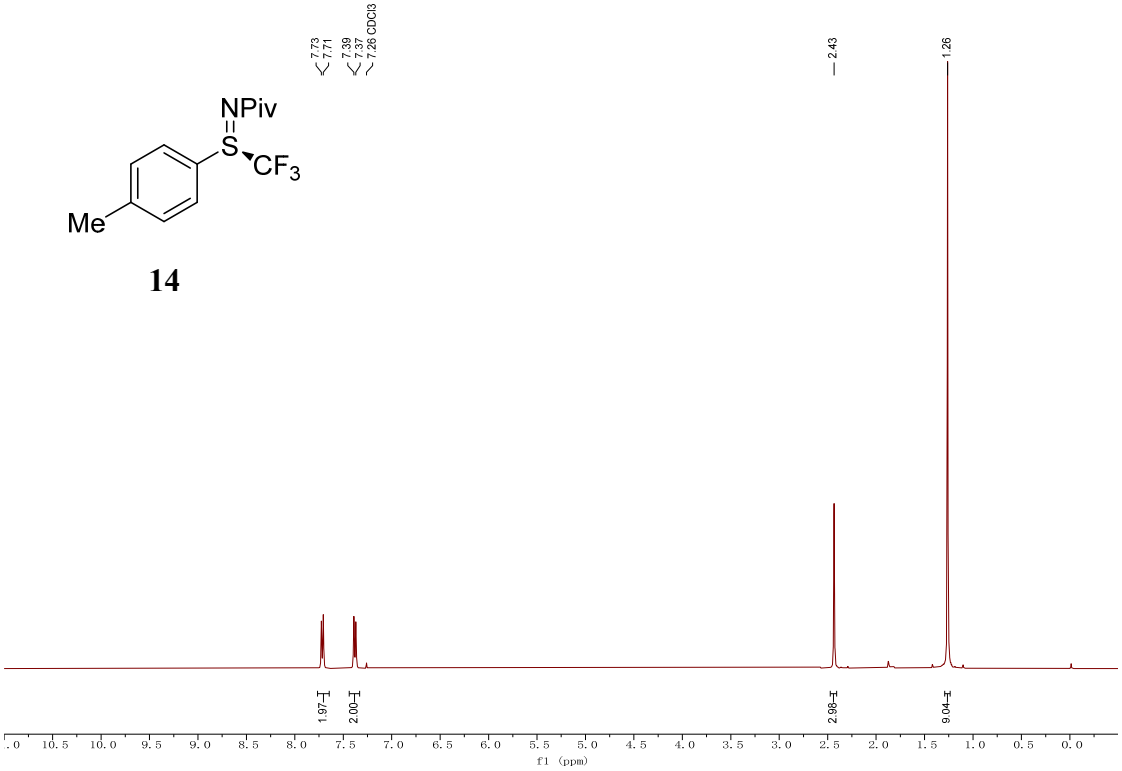
^{19}F NMR (376 MHz) spectrum of compound **13** ($CDCl_3$, 294.7 K)



13

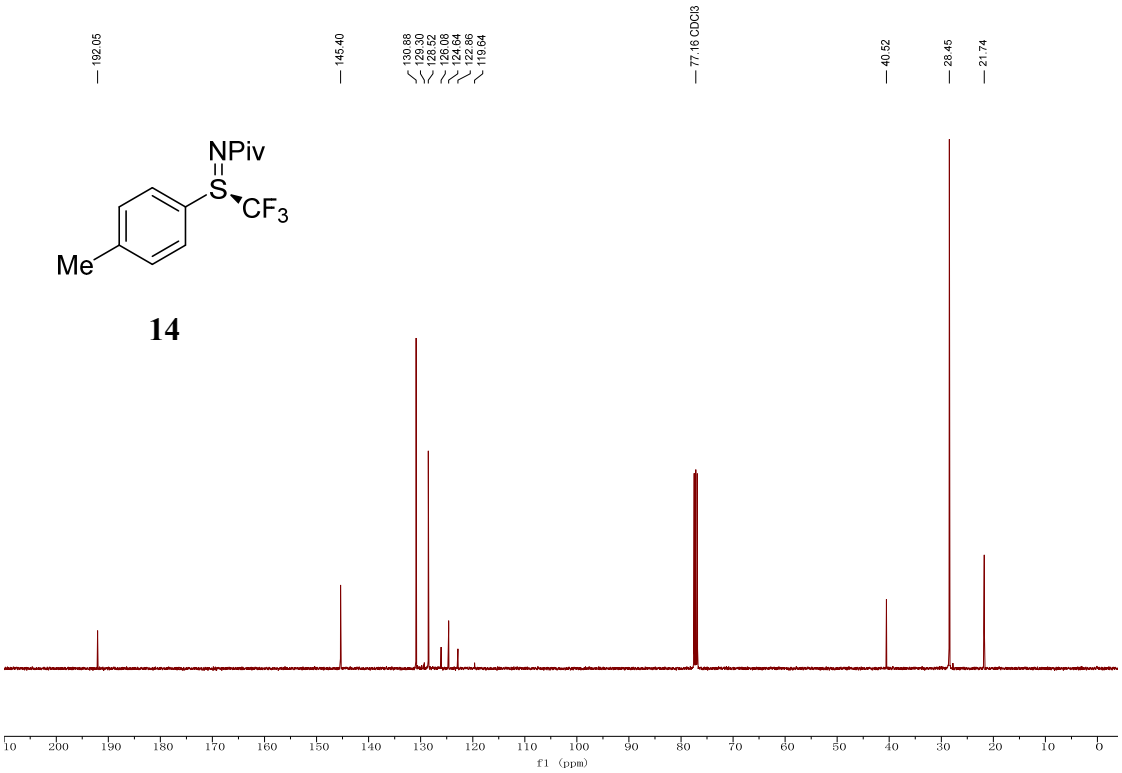
Figure S24. NMR spectra of compound **14**.

^{1}H NMR (400 MHz) spectrum of compound **14** ($CDCl_3$, 298.1 K)



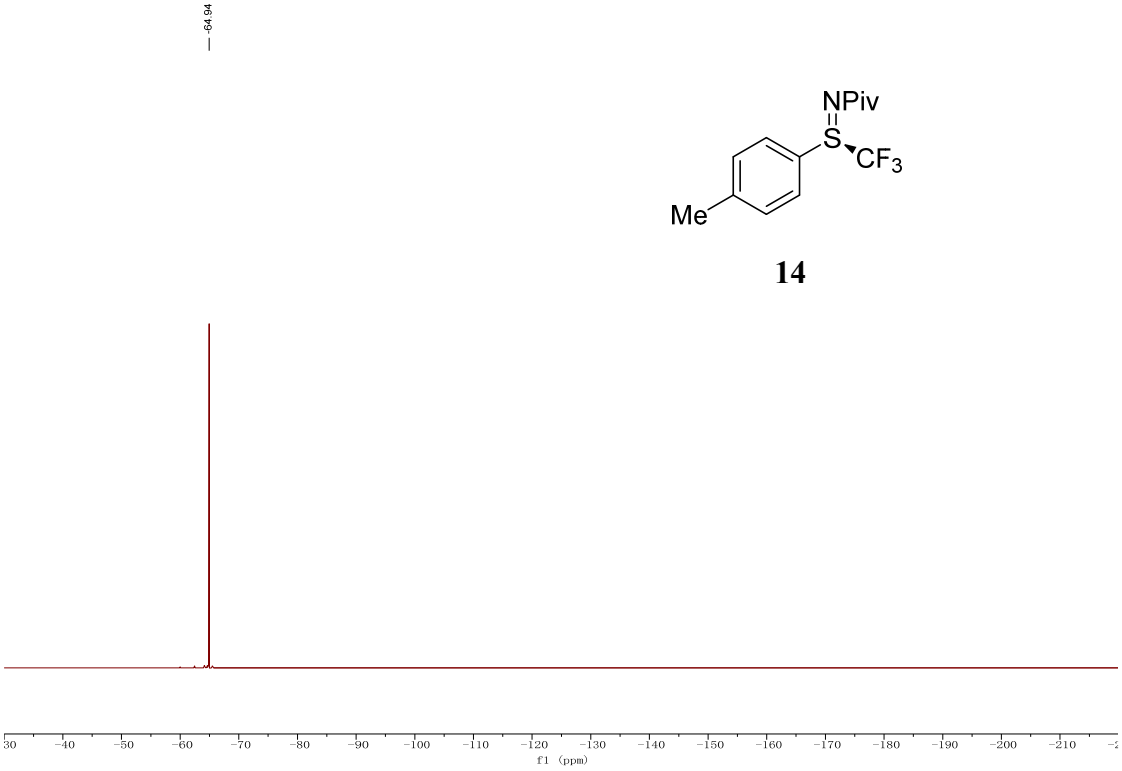
14

^{13}C NMR (100 MHz) spectrum of compound **14** ($CDCl_3$, 298.2 K)



14

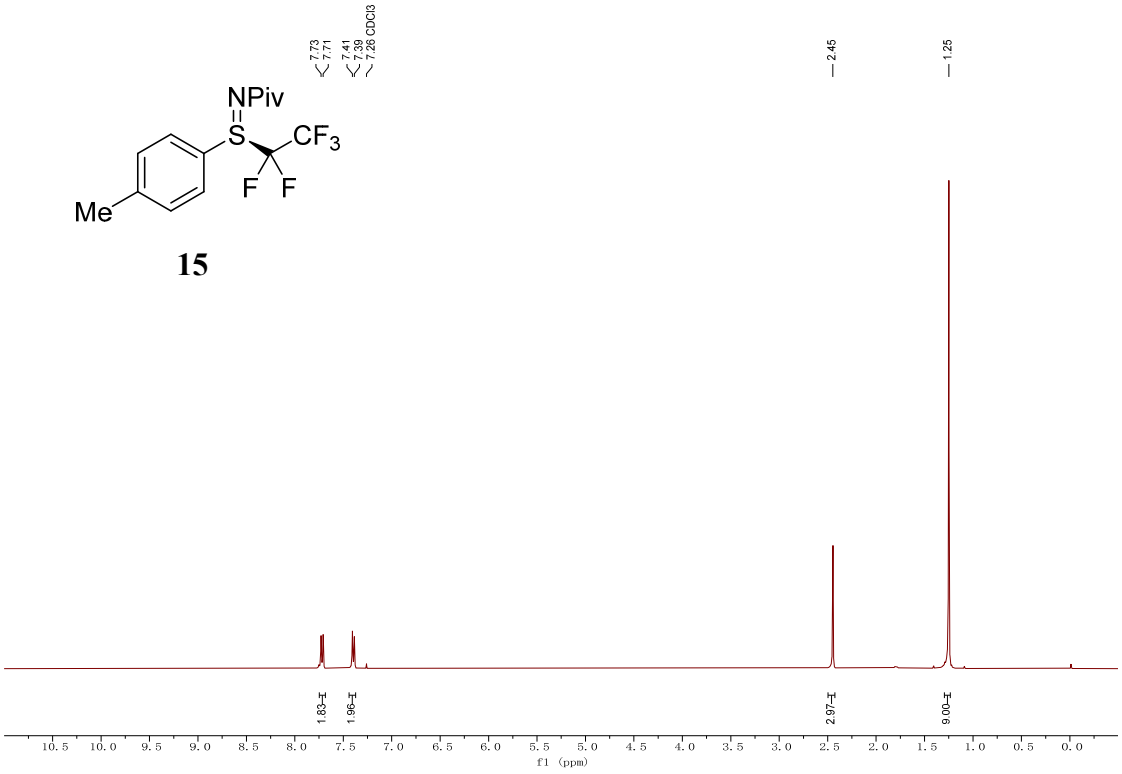
^{19}F NMR (376 MHz) spectrum of compound **14** ($CDCl_3$, 298.2 K)



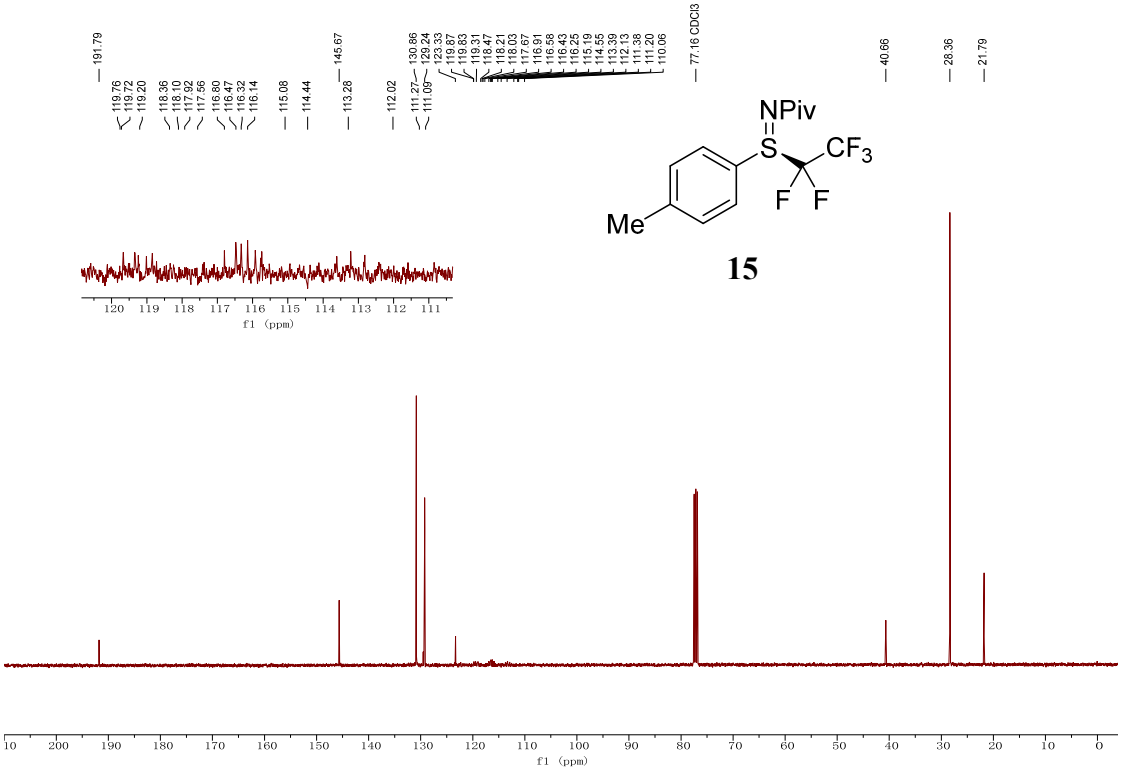
14

Figure S25. NMR spectra of compound **15**.

^{1}H NMR (400 MHz) spectrum of compound **15** ($CDCl_3$, 294.5 K)



^{13}C NMR (100 MHz) spectrum of compound **15** ($CDCl_3$, 295.0 K)



^{19}F NMR (376 MHz) spectrum of compound **15** ($CDCl_3$, 294.6 K)

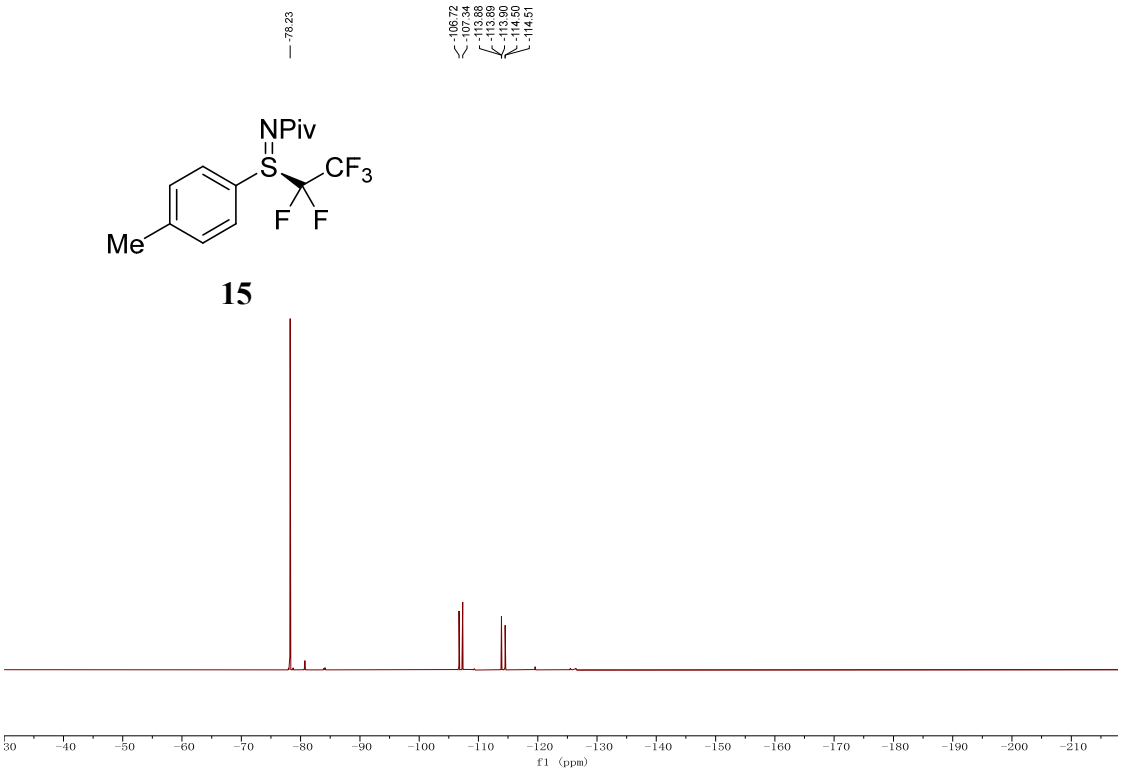
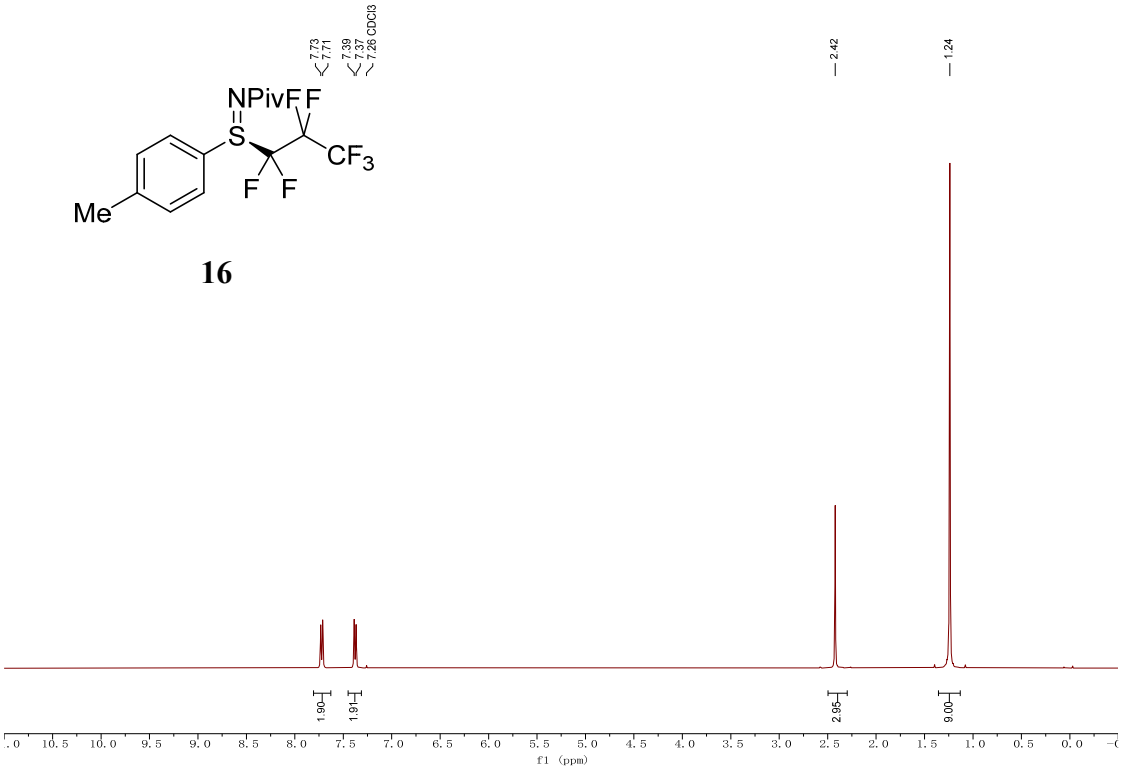
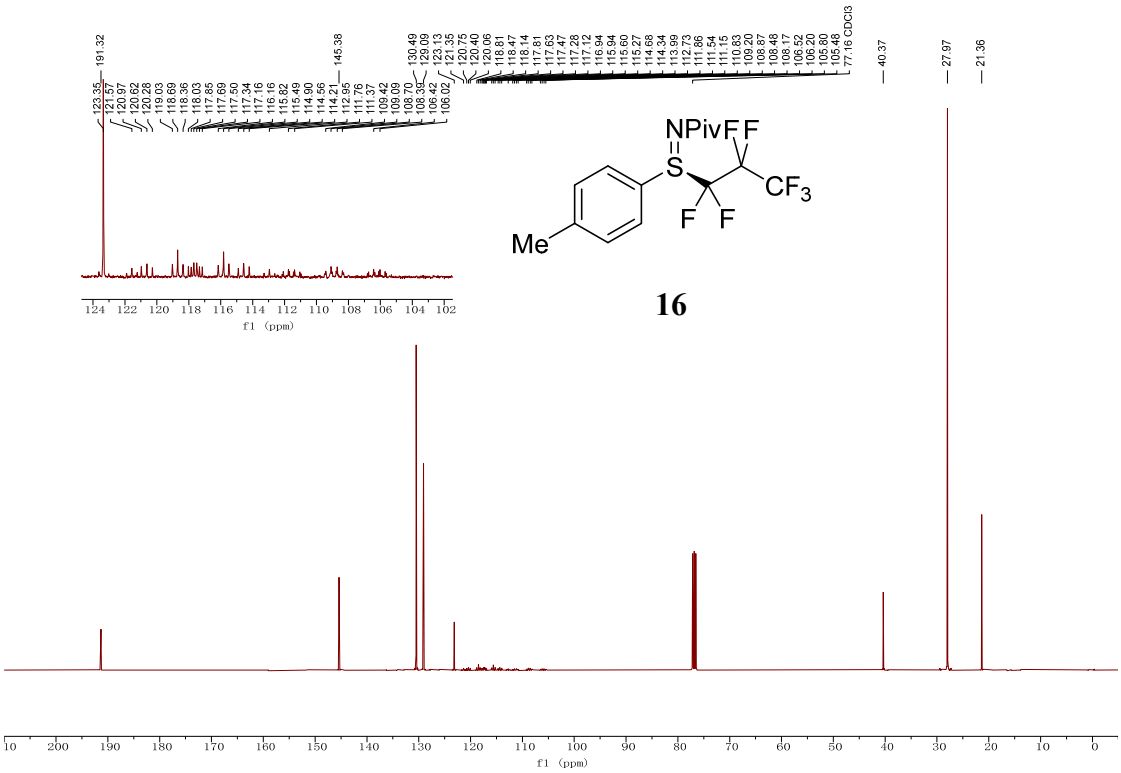


Figure S26. NMR spectra of compound **16**.

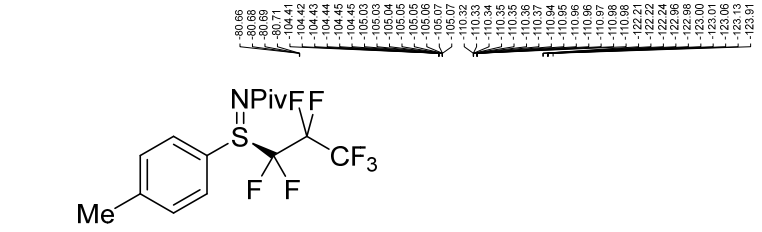
^{1}H NMR (400 MHz) spectrum of compound **16** ($CDCl_3$, 298.1 K)



^{13}C NMR (100 MHz) spectrum of compound **16** ($CDCl_3$, 298.2 K)



^{19}F NMR (376 MHz) spectrum of compound **16** ($CDCl_3$, 298.1 K)



16

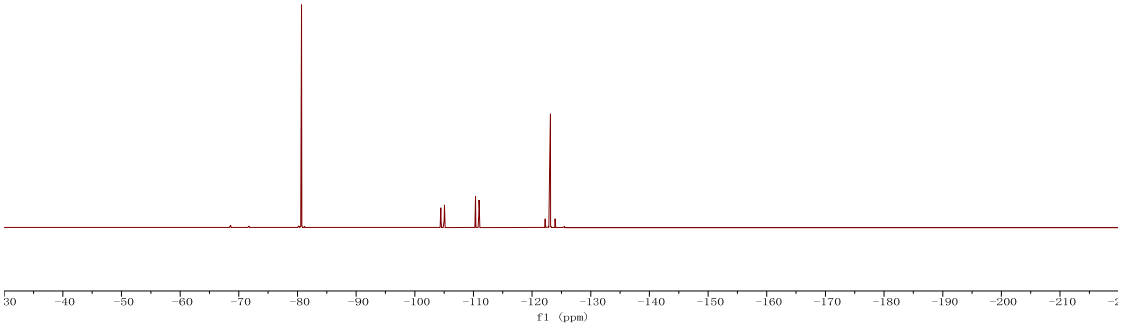
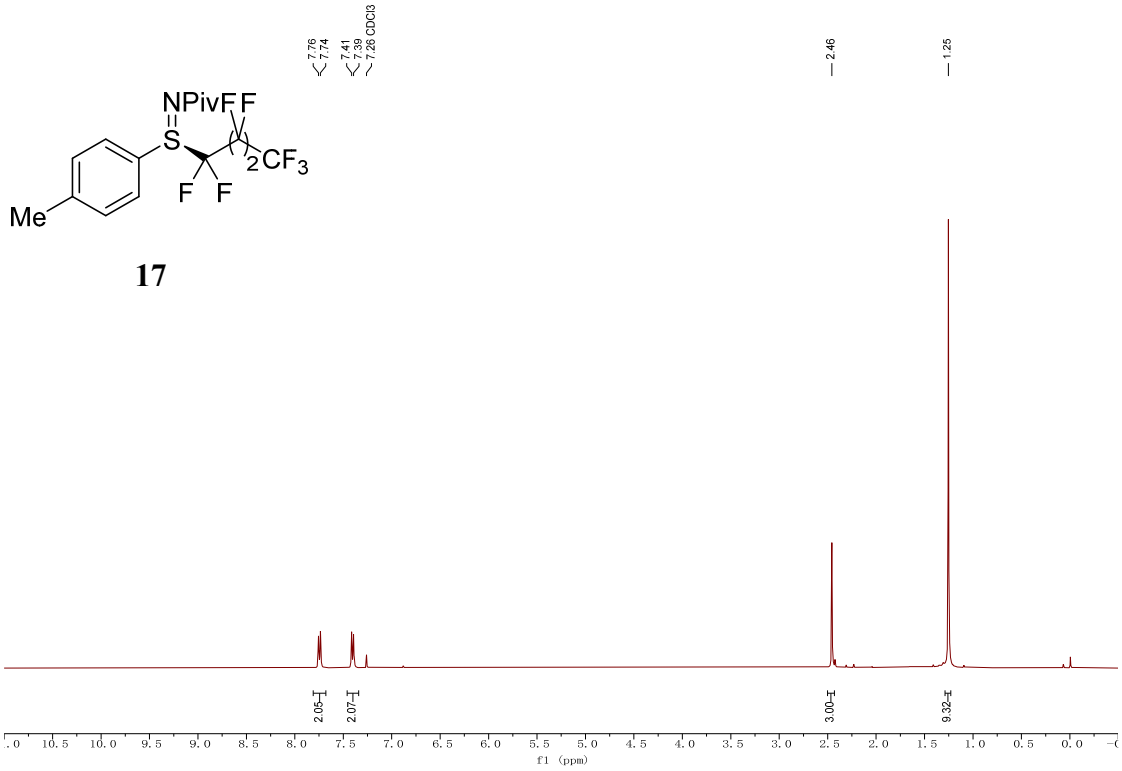


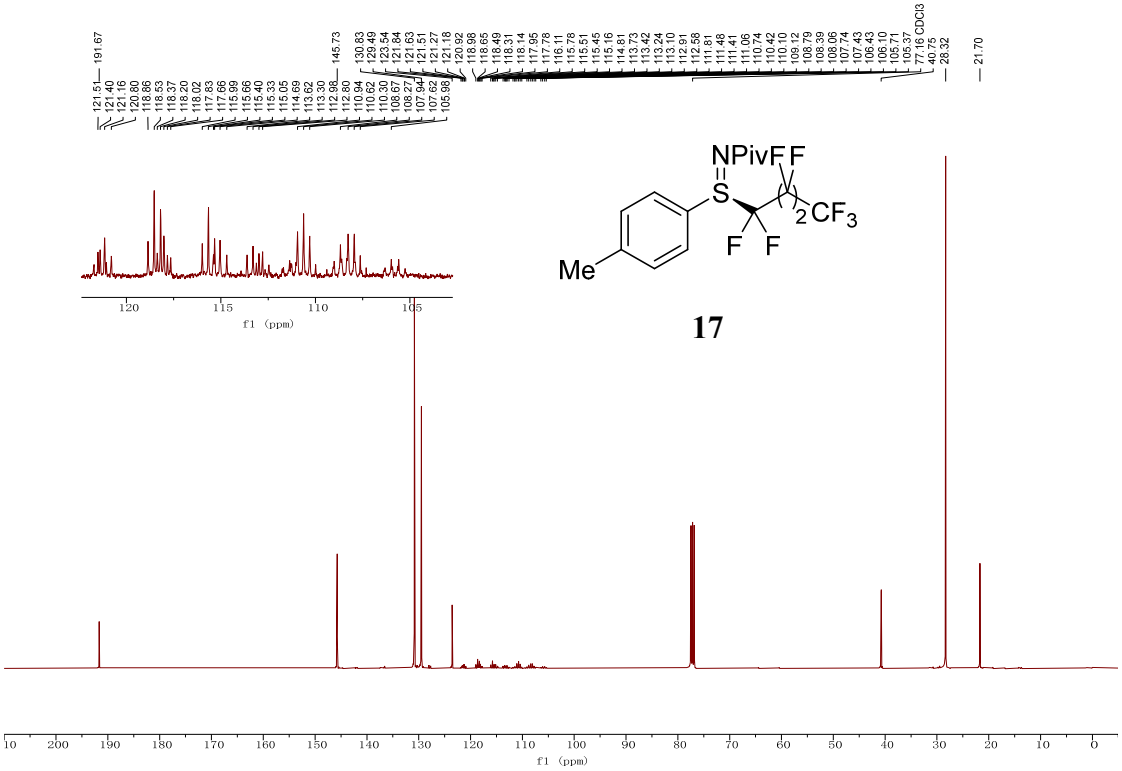
Figure S27. NMR spectra of compound **17**.

^{1}H NMR (400 MHz) spectrum of compound **17** ($CDCl_3$, 294.6 K)



17

^{13}C NMR (100 MHz) spectrum of compound **17** ($CDCl_3$, 294.8 K)



17

^{19}F NMR (376 MHz) spectrum of compound **17** ($CDCl_3$, 294.6 K)

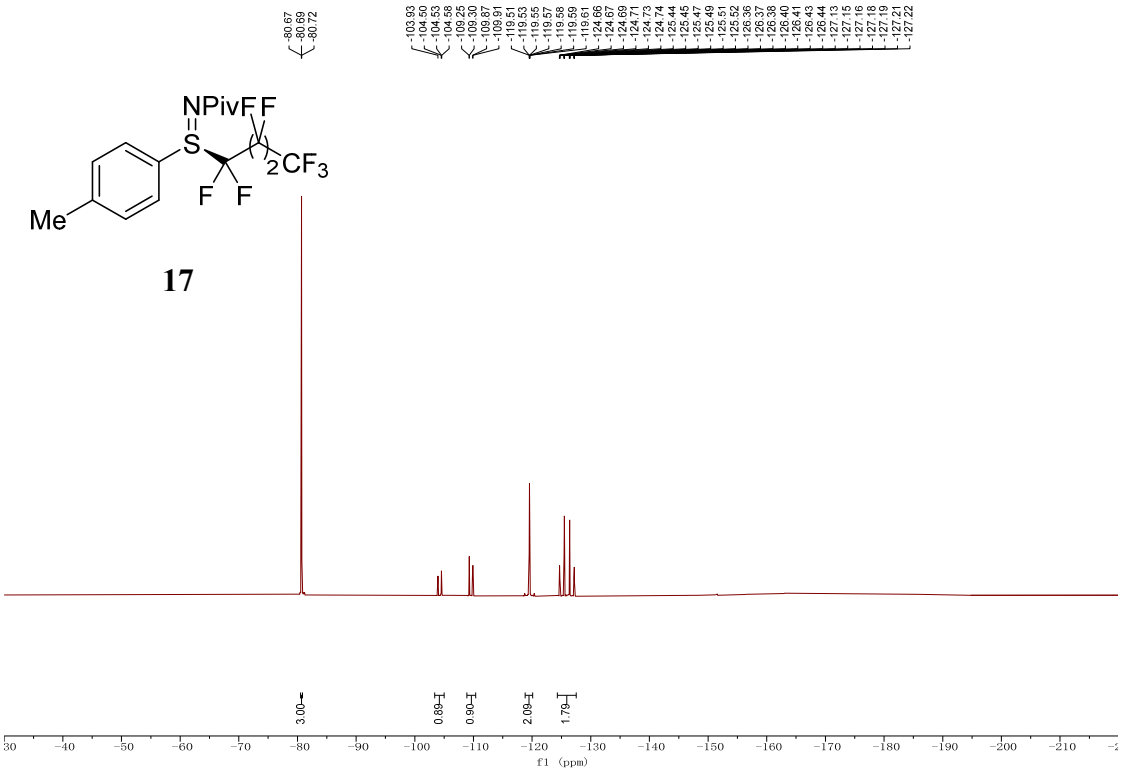
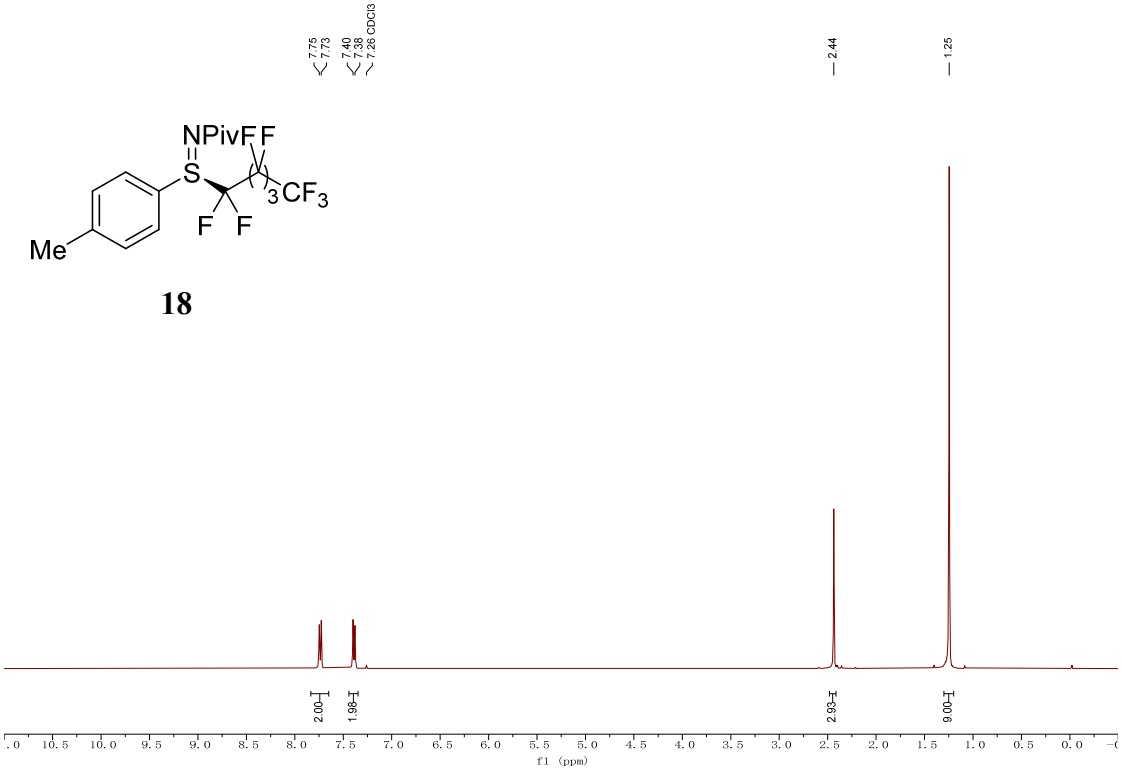
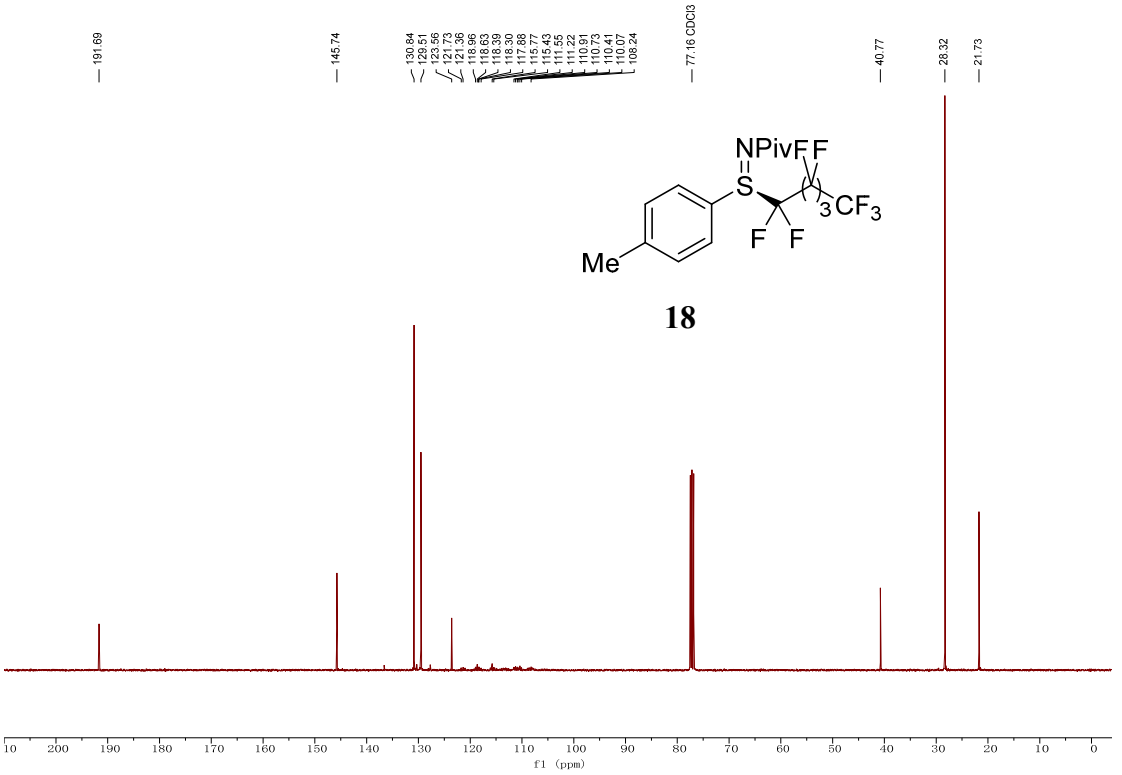


Figure S28. NMR spectra of compound **18**.

^{1}H NMR (400 MHz) spectrum of compound **18** ($CDCl_3$, 296.8 K)



^{13}C NMR (100 MHz) spectrum of compound **18** ($CDCl_3$, 297.1 K)



^{19}F NMR (376 MHz) spectrum of compound **18** ($CDCl_3$, 296.8 K)

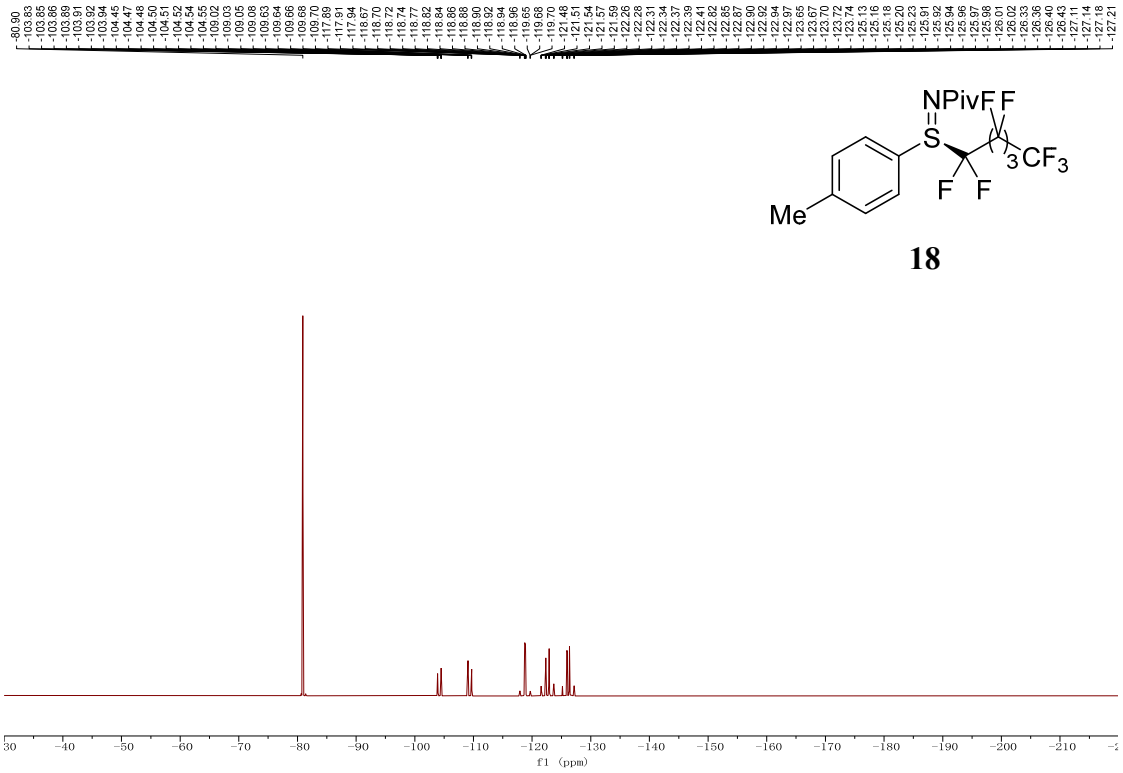
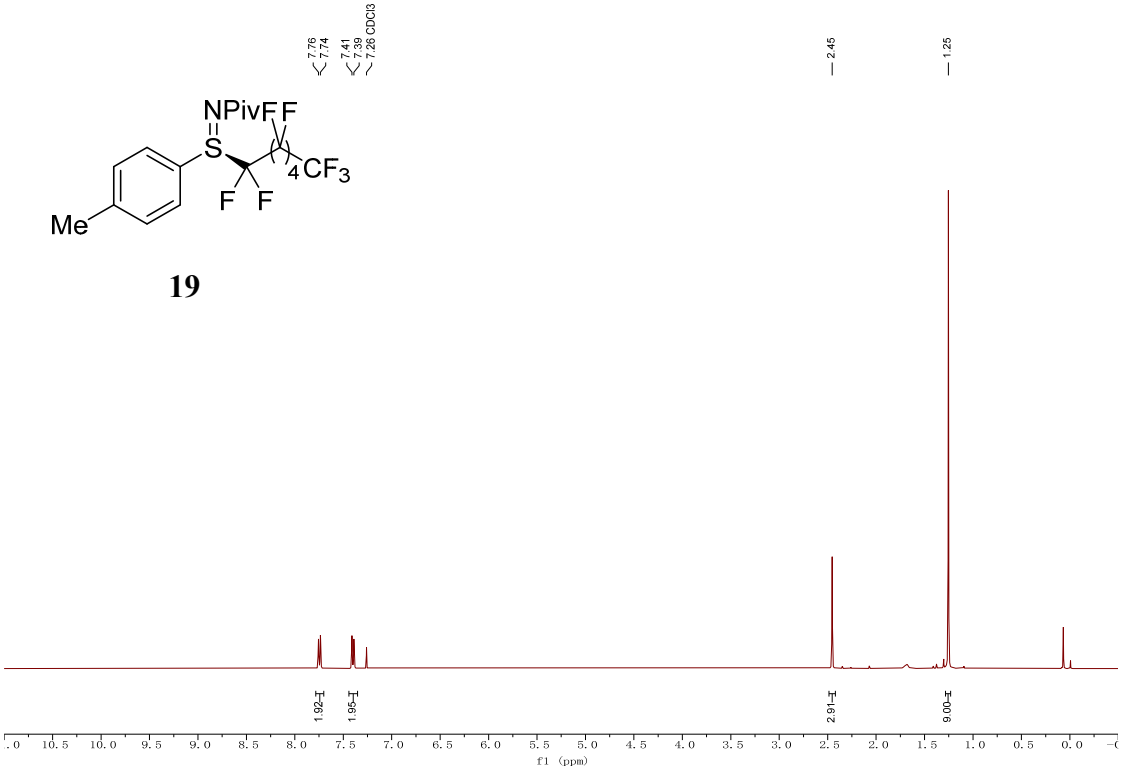
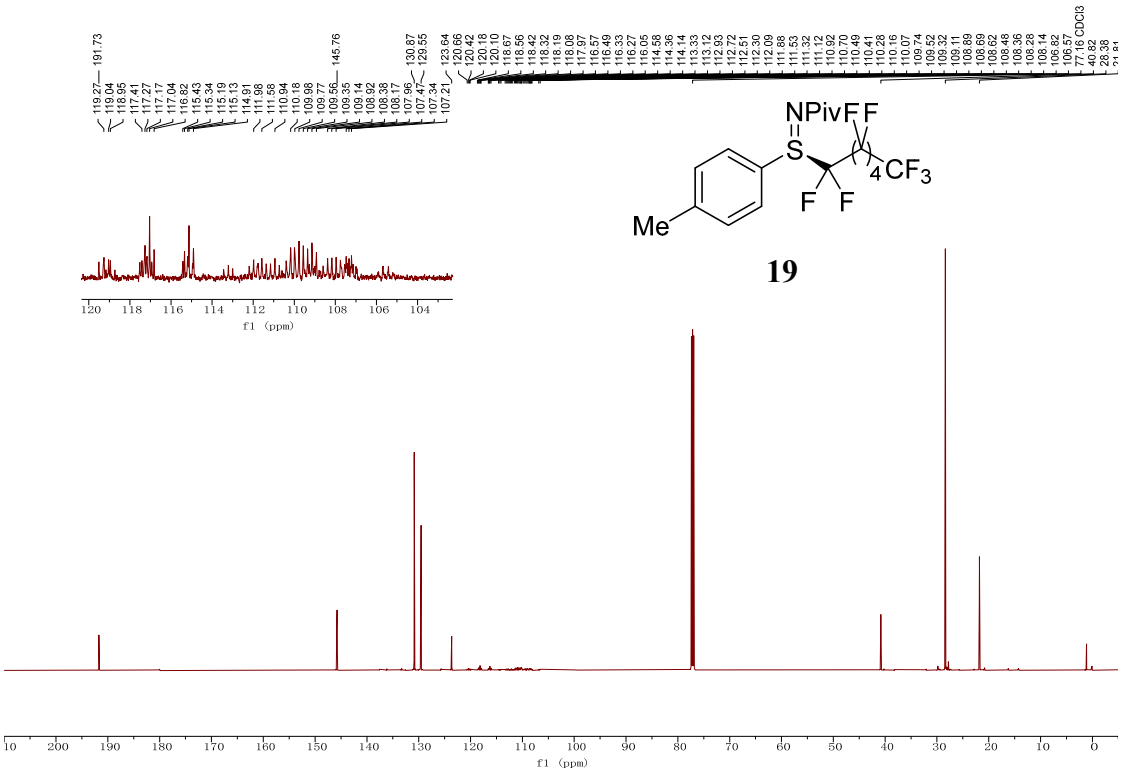


Figure S29. NMR spectra of compound **19**.

^{1}H NMR (400 MHz) spectrum of compound **19** ($CDCl_3$, 300.0 K)



^{13}C NMR (100 MHz) spectrum of compound **19** ($CDCl_3$, 299.8 K)



^{19}F NMR (376 MHz) spectrum of compound **19** ($CDCl_3$, 300.1 K)

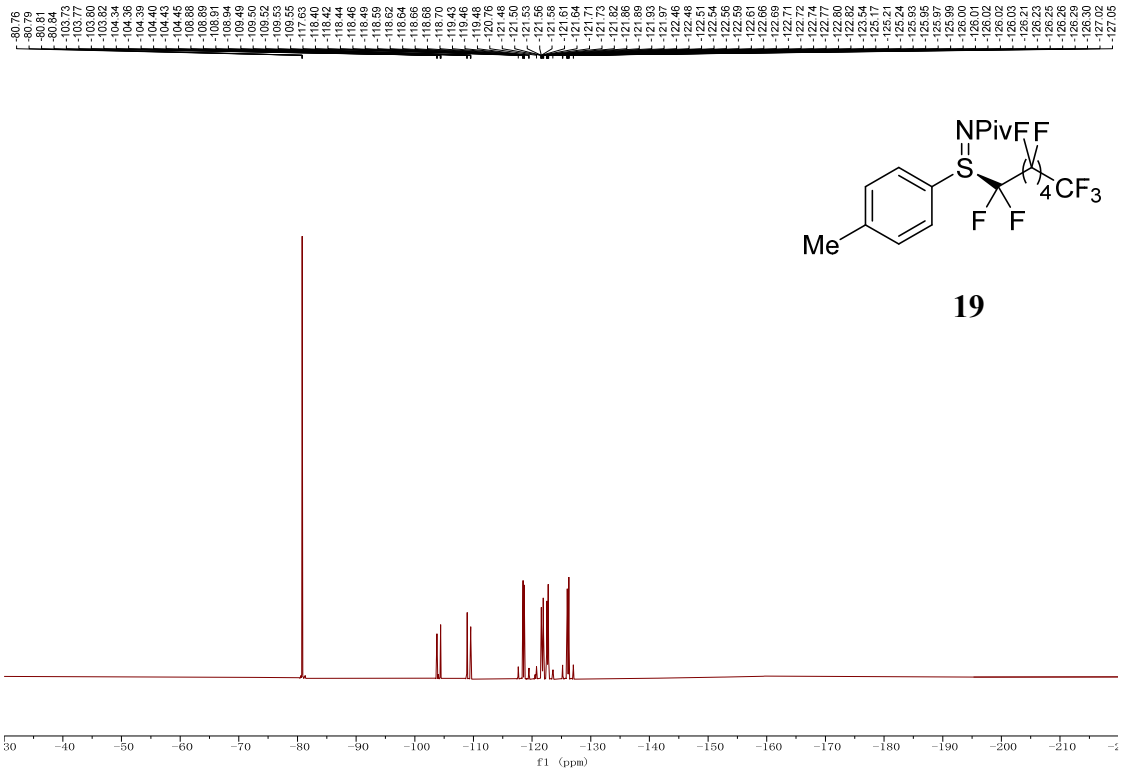
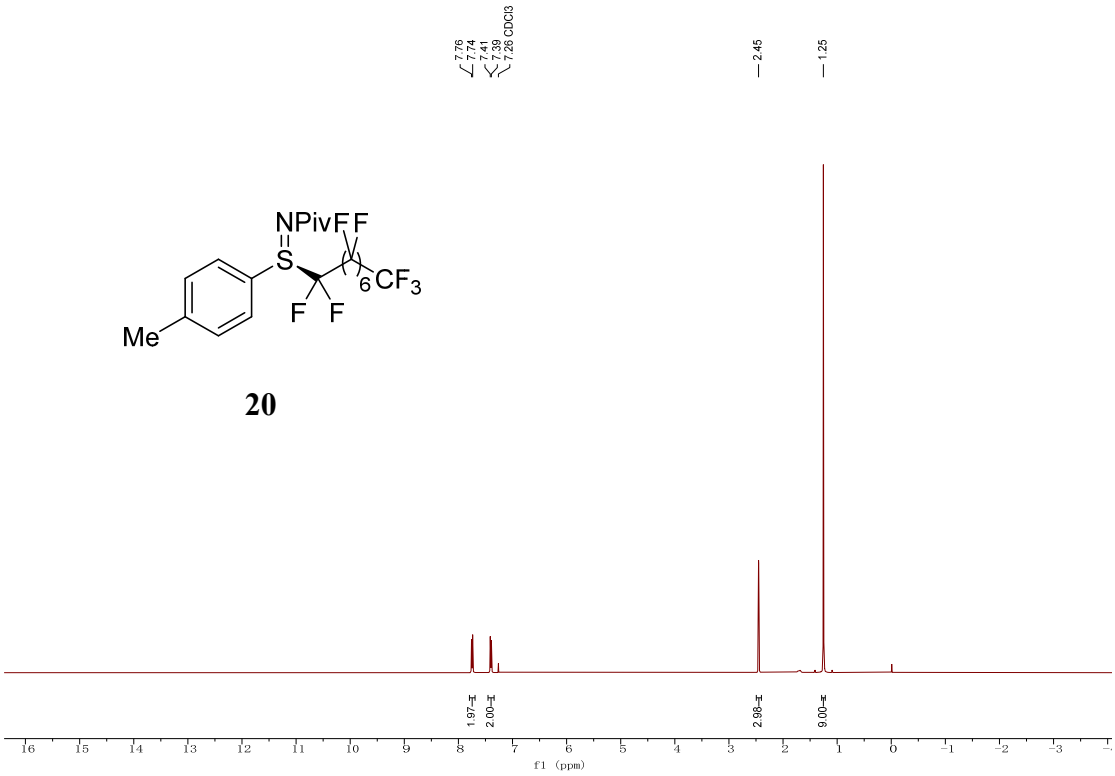
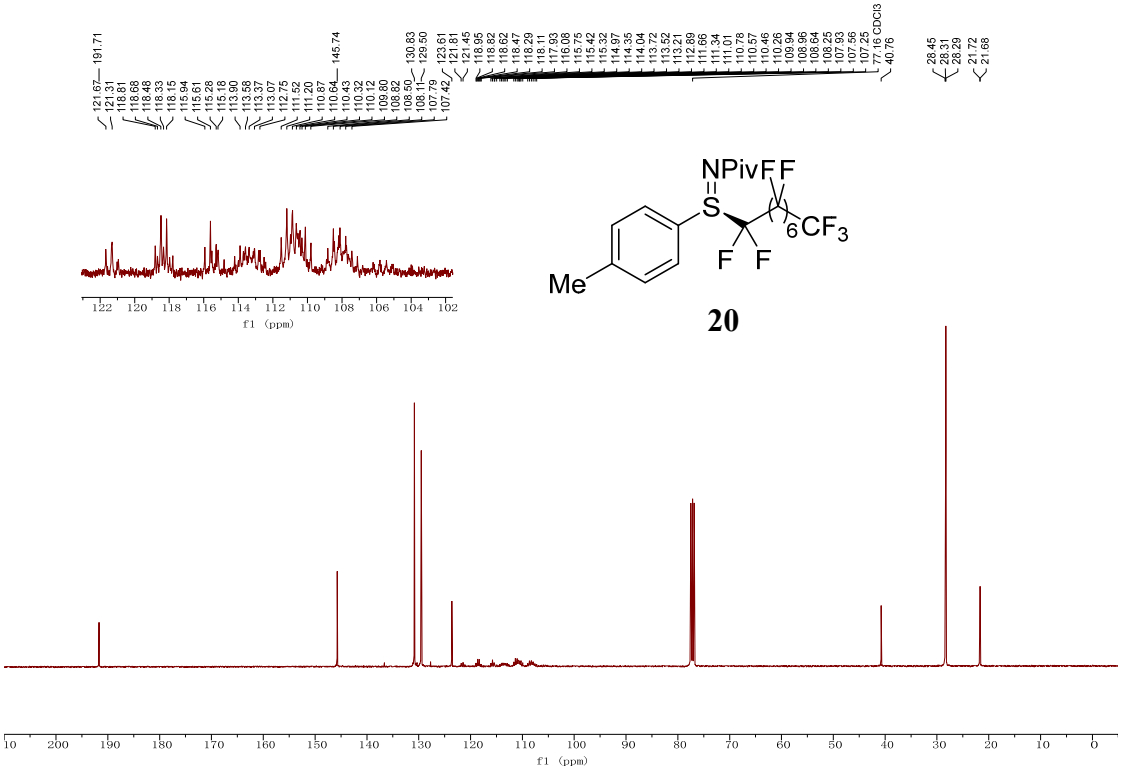


Figure S30. NMR spectra of compound **20**.

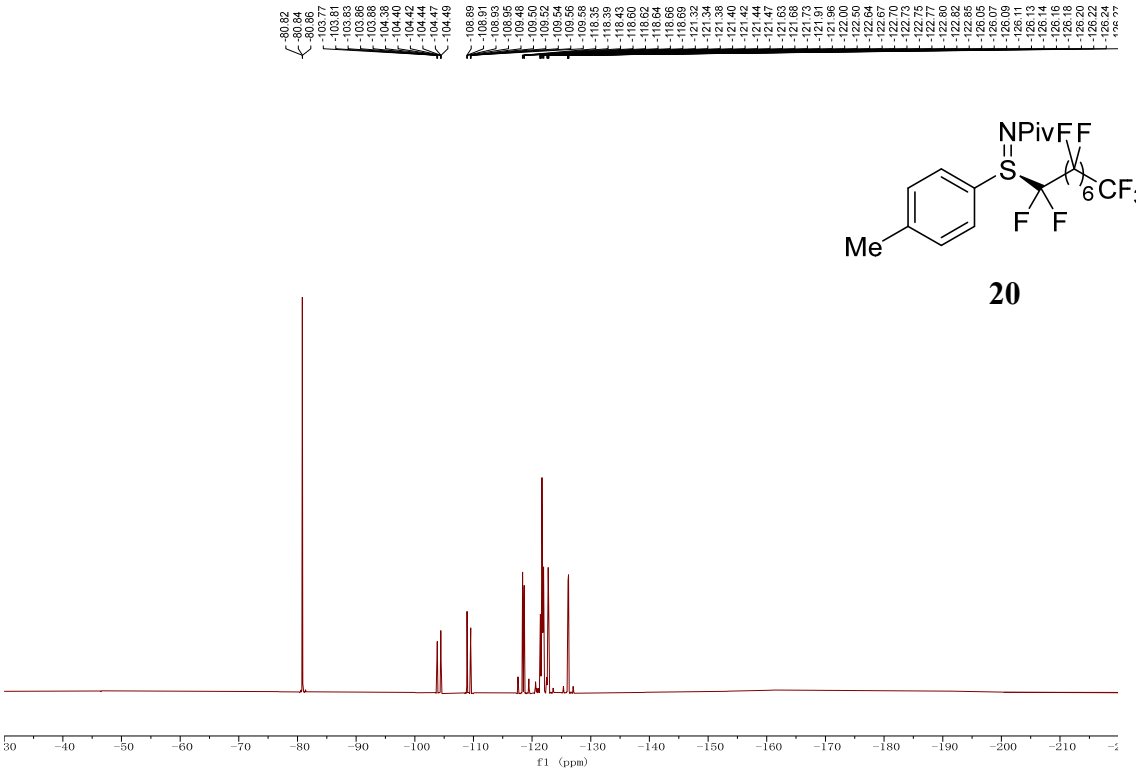
^{1}H NMR (400 MHz) spectrum of compound **20** ($CDCl_3$, 298.2 K)



^{13}C NMR (100 MHz) spectrum of compound **20** ($CDCl_3$, 298.2 K)



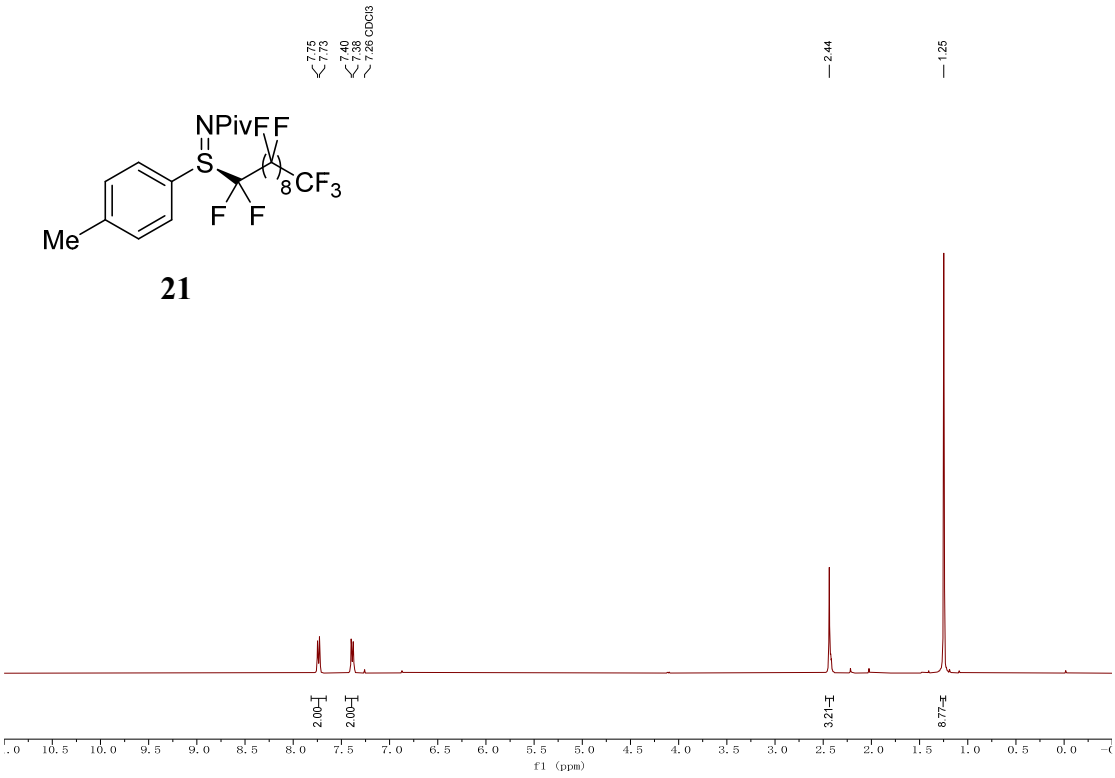
^{19}F NMR (376 MHz) spectrum of compound **20** ($CDCl_3$, 297.8 K)



20

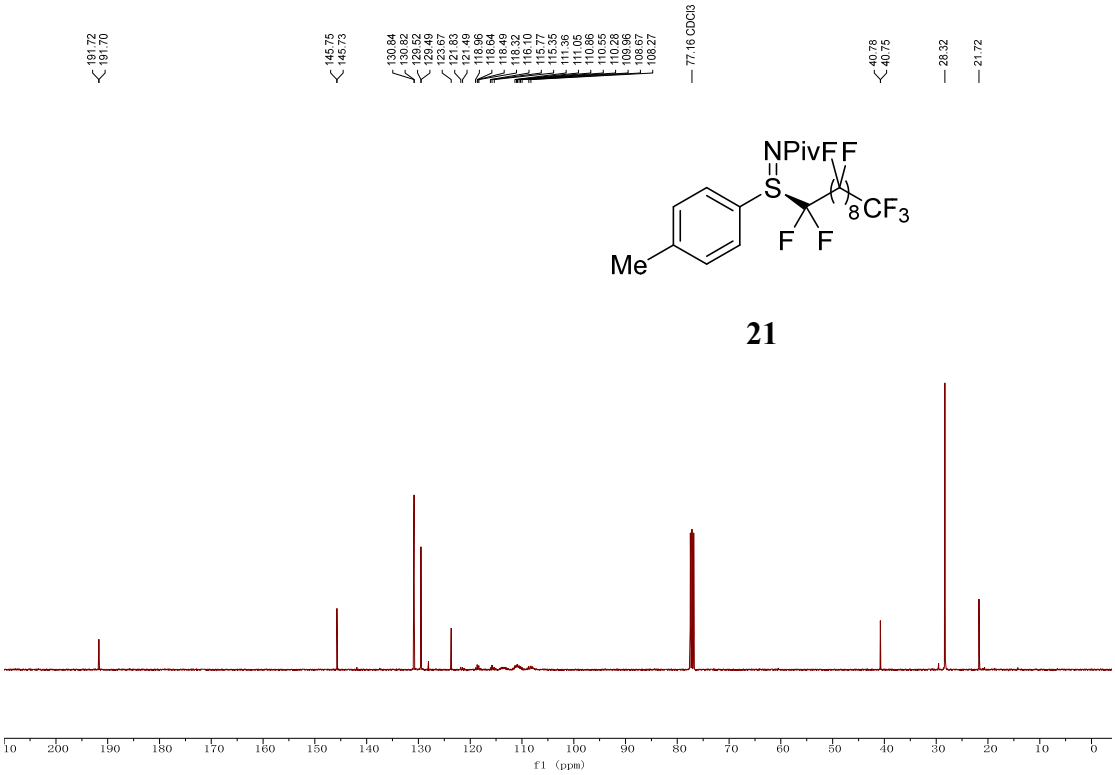
Figure S31. NMR spectra of compound **21**.

^{1}H NMR (400 MHz) spectrum of compound **21** ($CDCl_3$, 296.8 K)



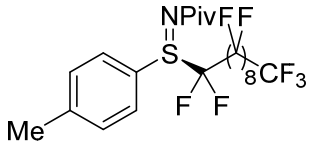
21

^{13}C NMR (100 MHz) spectrum of compound **21** ($CDCl_3$, 297.2 K)



21

^{19}F NMR (376 MHz) spectrum of compound **21** ($CDCl_3$, 296.9 K)



21

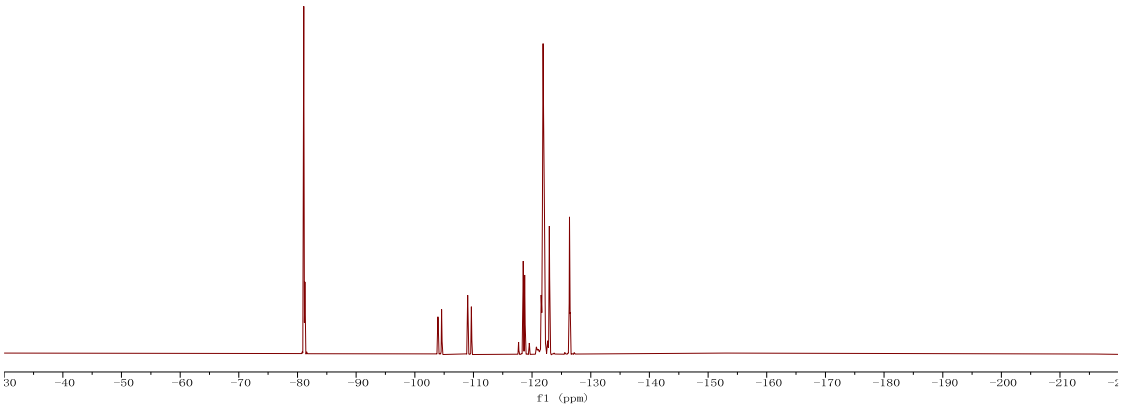
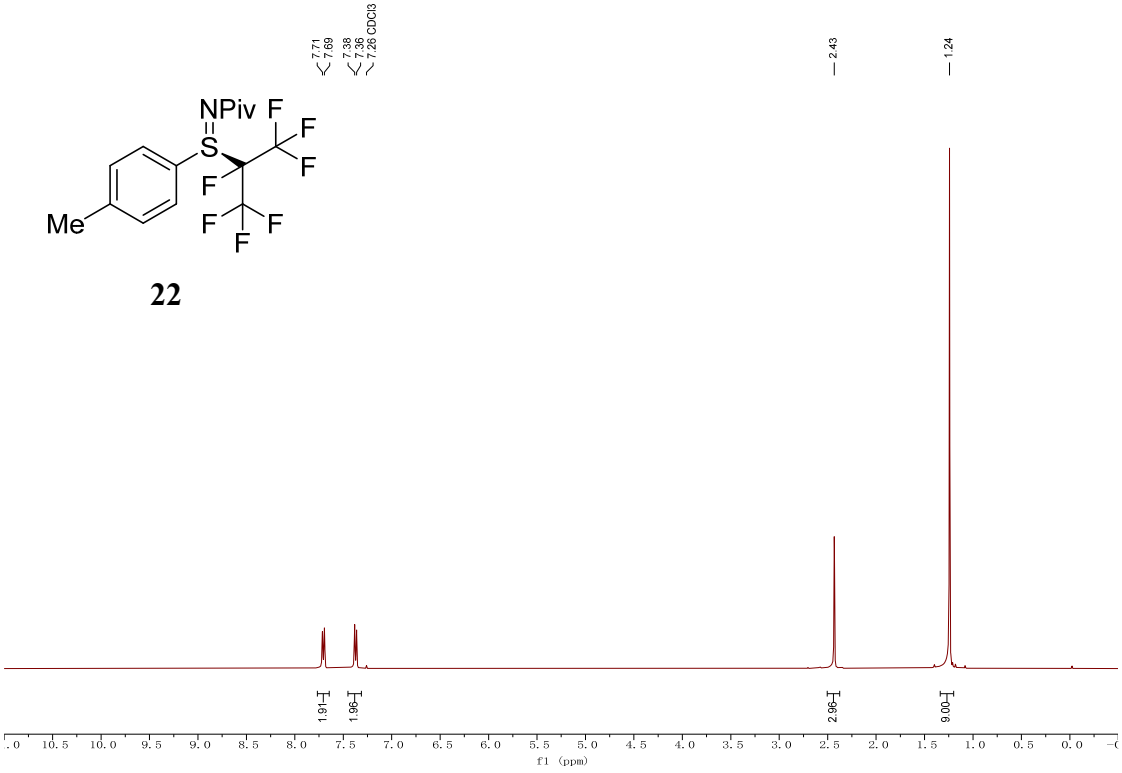
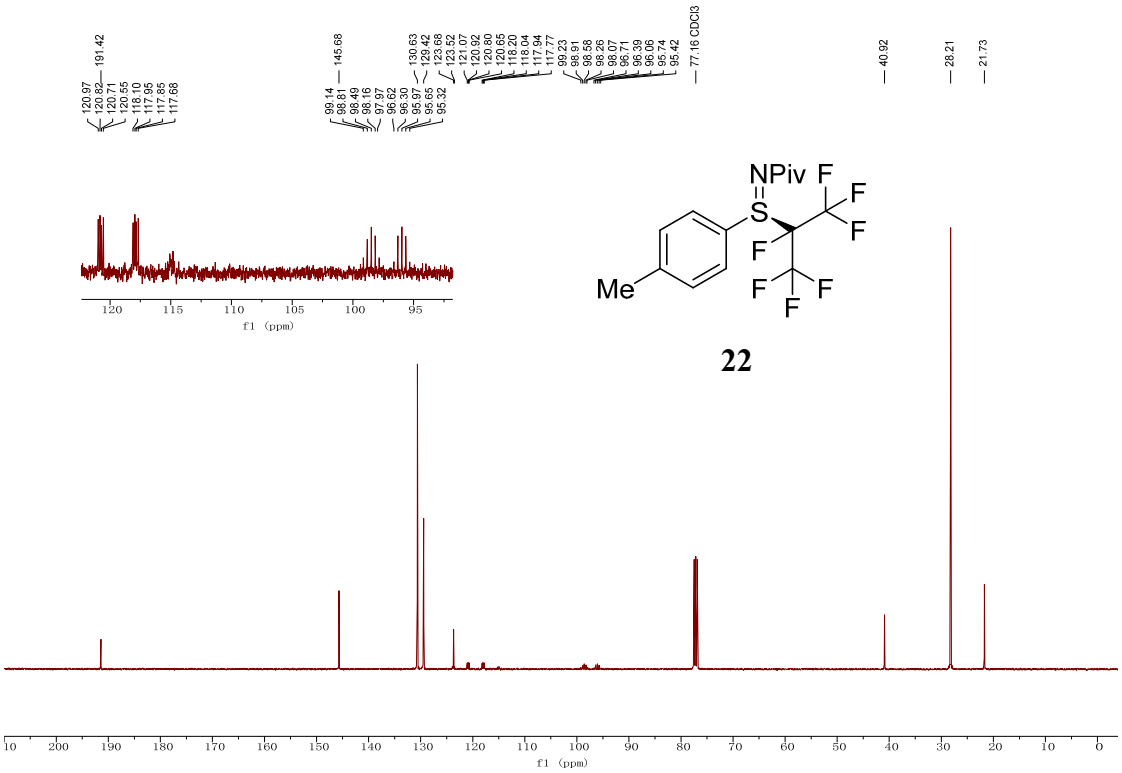


Figure S32. NMR spectra of compound **22**.

^{1}H NMR (400 MHz) spectrum of compound **22** ($CDCl_3$, 292.6 K)



^{13}C NMR (100 MHz) spectrum of compound **22** ($CDCl_3$, 293.2 K)



^{19}F NMR (376 MHz) spectrum of compound **22** ($CDCl_3$, 292.7 K)

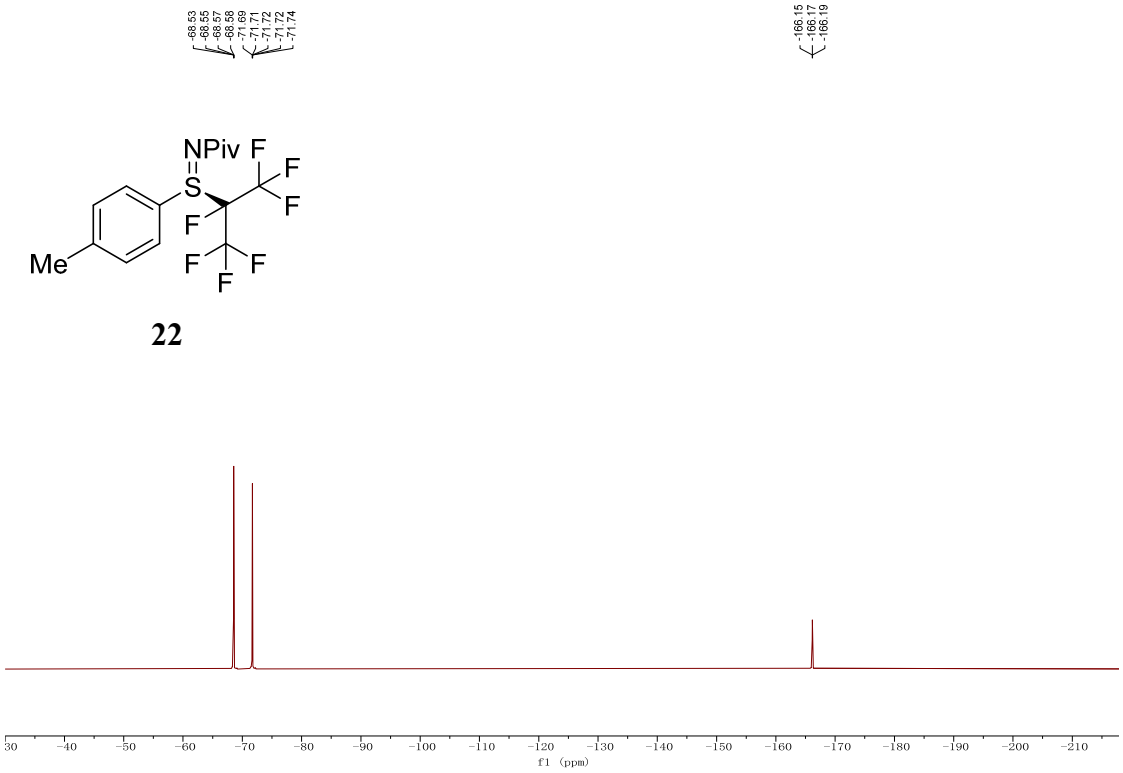
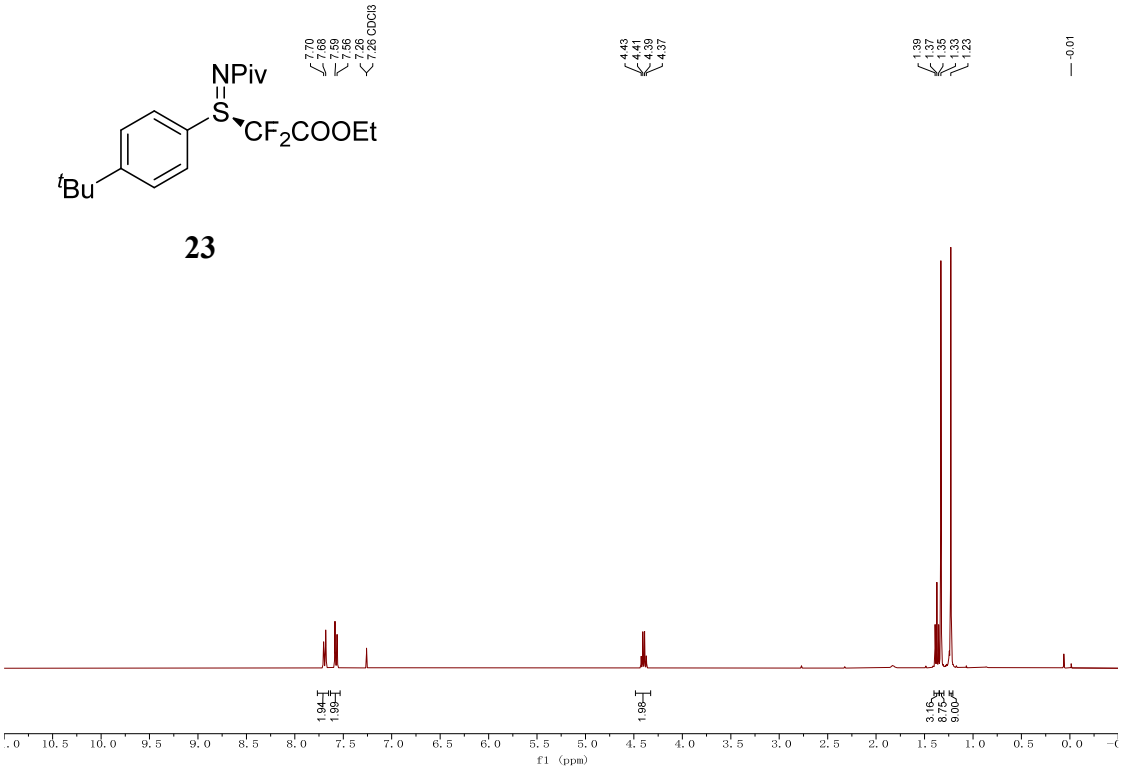
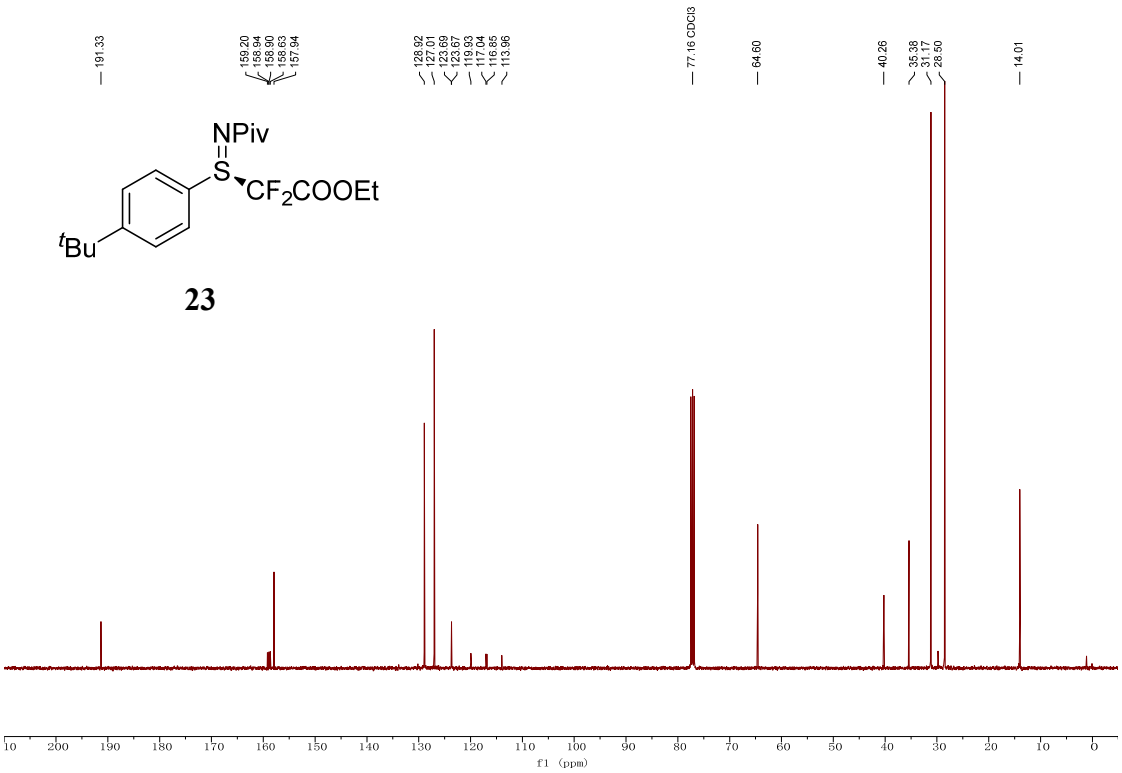


Figure S33. NMR spectra of compound **23**.

^{1}H NMR (400 MHz) spectrum of compound **23** ($CDCl_3$, 298.3 K)



^{13}C NMR (100 MHz) spectrum of compound **23** ($CDCl_3$, 298.8 K)



^{19}F NMR (376 MHz) spectrum of compound **23** ($CDCl_3$, 298.5 K)

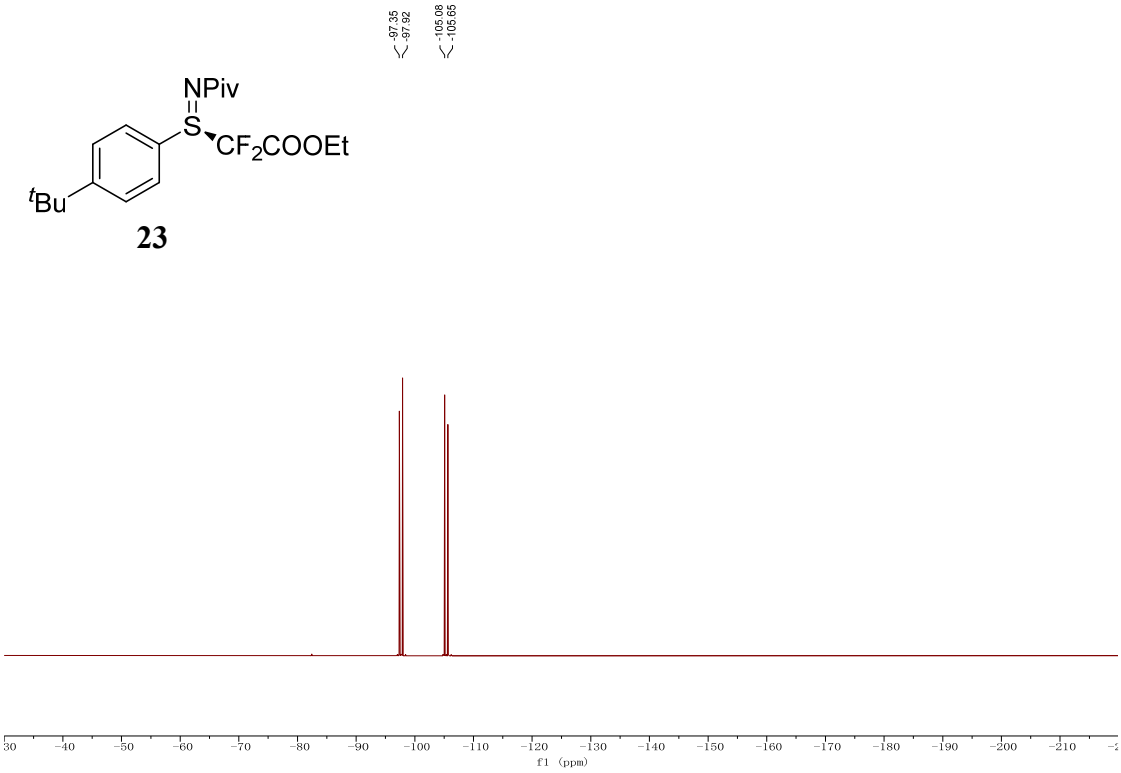
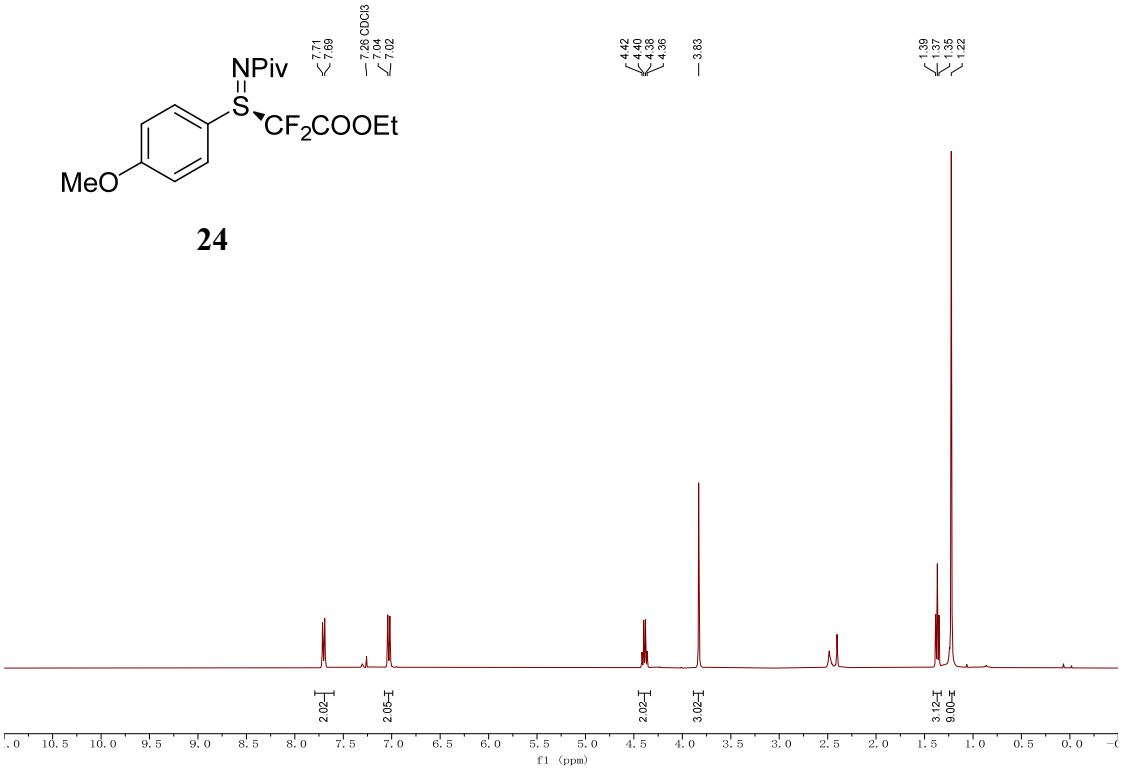


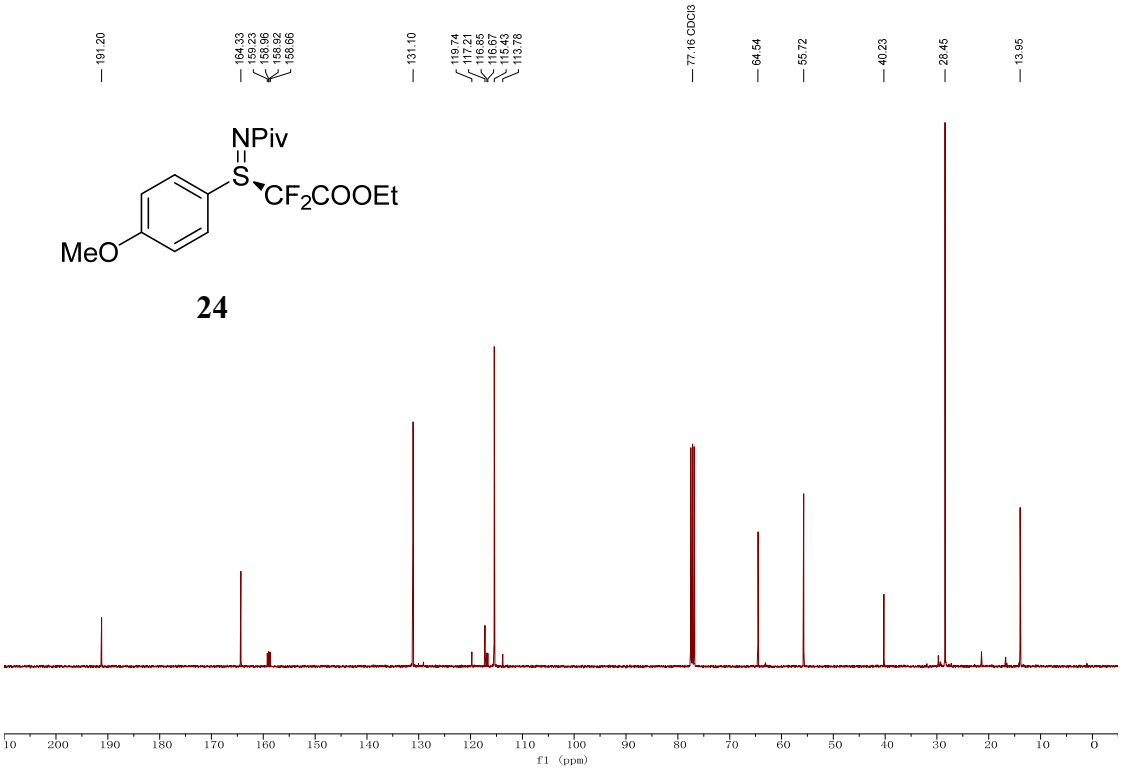
Figure S34. NMR spectra of compound **24**.

^{1}H NMR (400 MHz) spectrum of compound **24** ($CDCl_3$, 298.7 K)



24

^{13}C NMR (100 MHz) spectrum of compound **24** ($CDCl_3$, 300.2 K)



24

^{19}F NMR (376 MHz) spectrum of compound **24** ($CDCl_3$, 298.8 K)

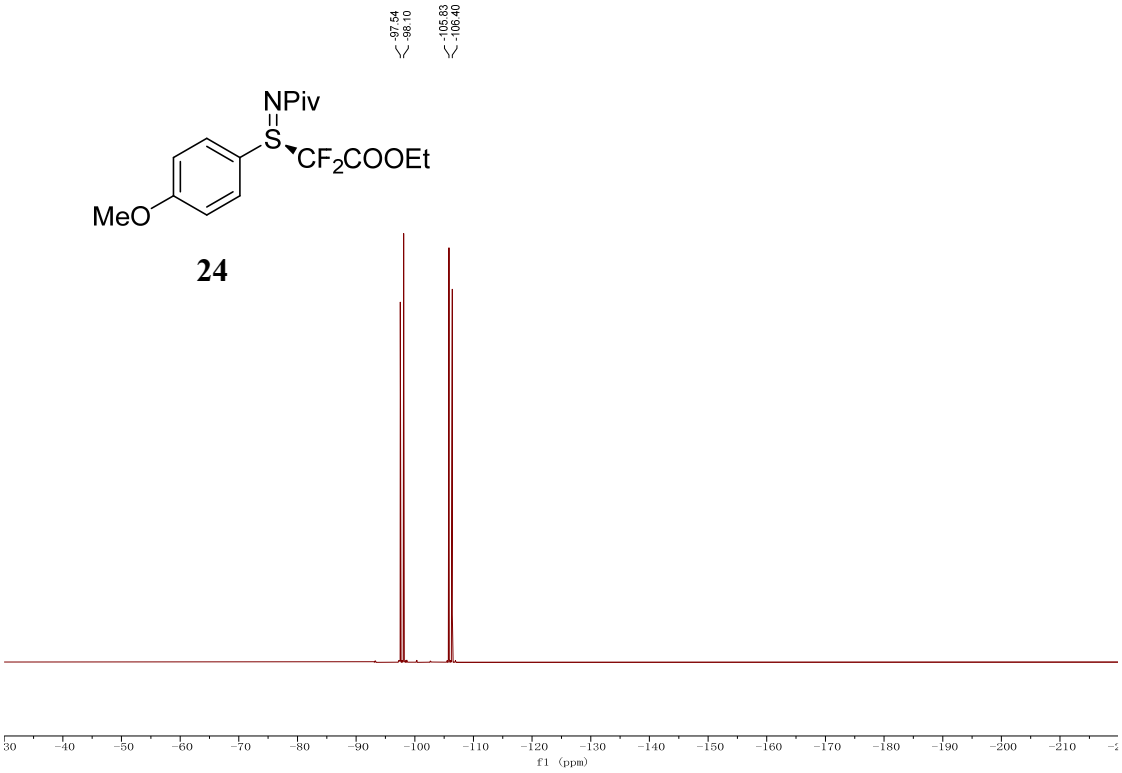
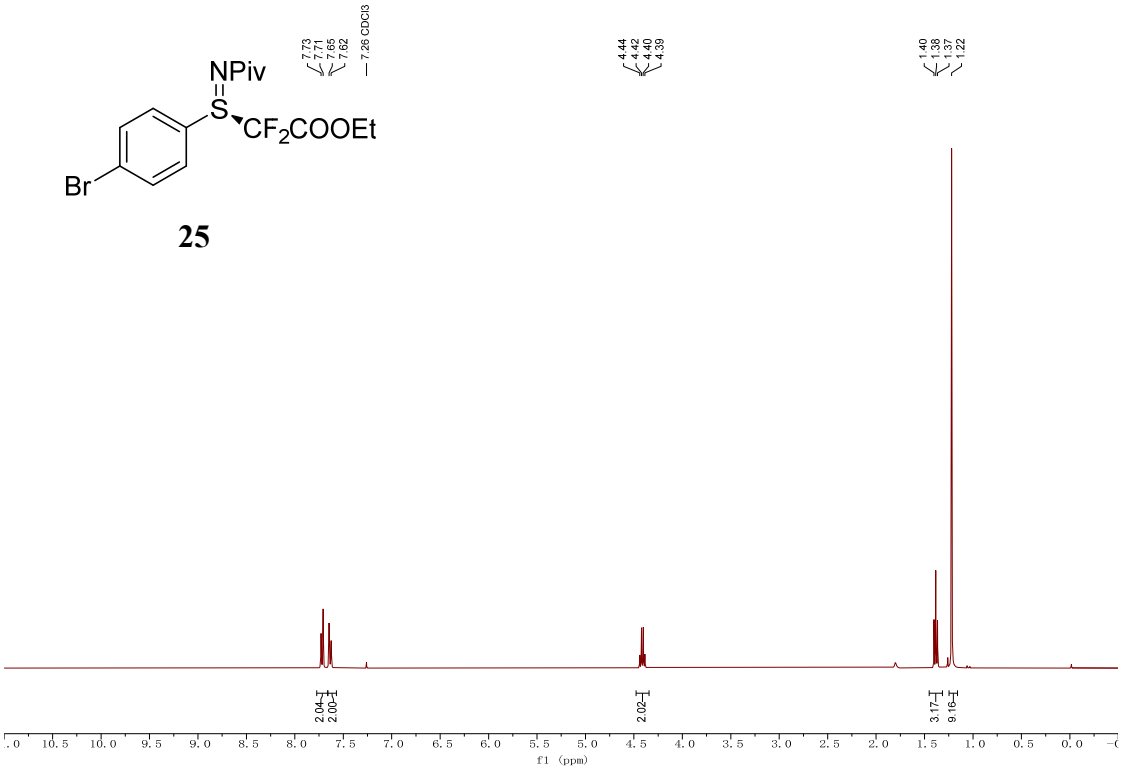


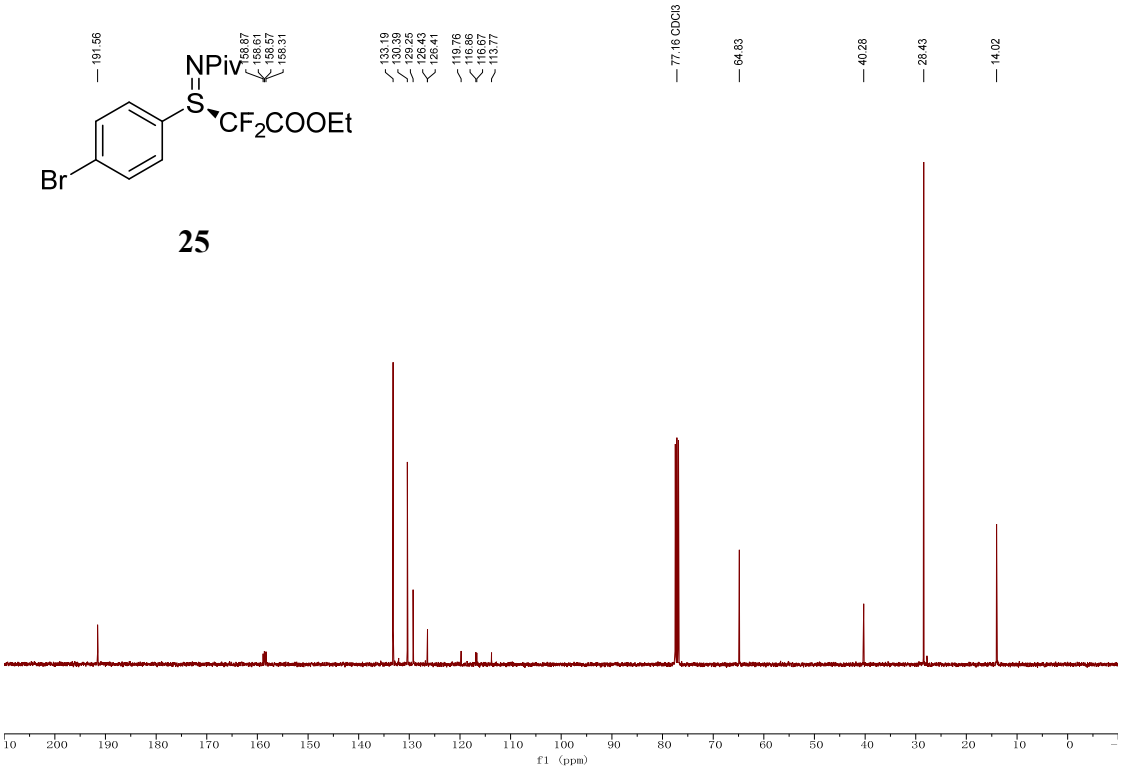
Figure S35. NMR spectra of compound **25**.

^{1}H NMR (400 MHz) spectrum of compound **25** ($CDCl_3$, 295.7 K)



25

^{13}C NMR (100 MHz) spectrum of compound **25** ($CDCl_3$, 296.4 K)



25

^{19}F NMR (376 MHz) spectrum of compound **25** ($CDCl_3$, 296.0 K)

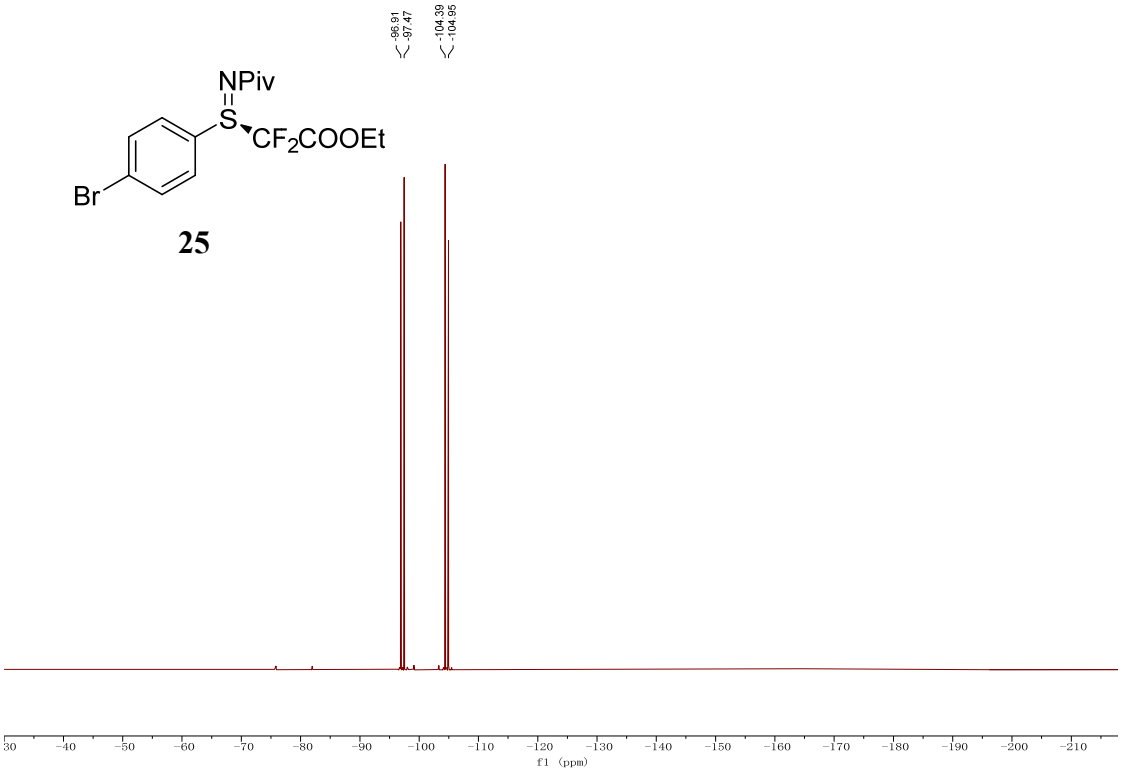
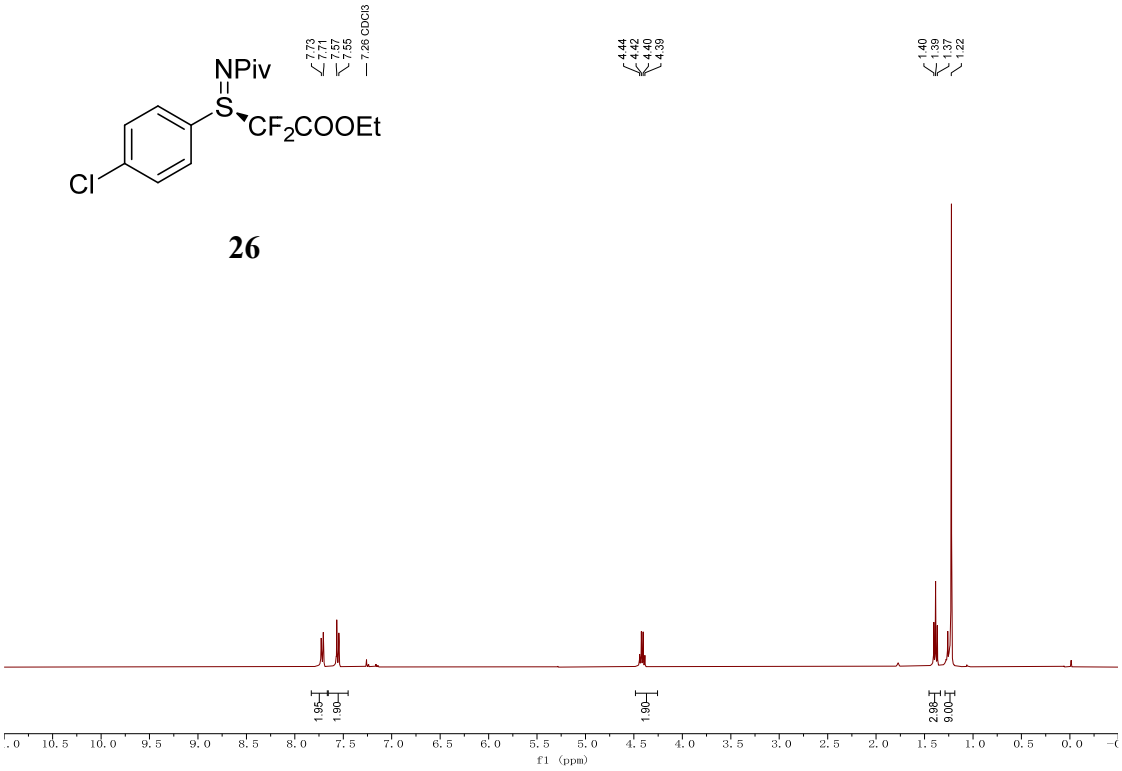


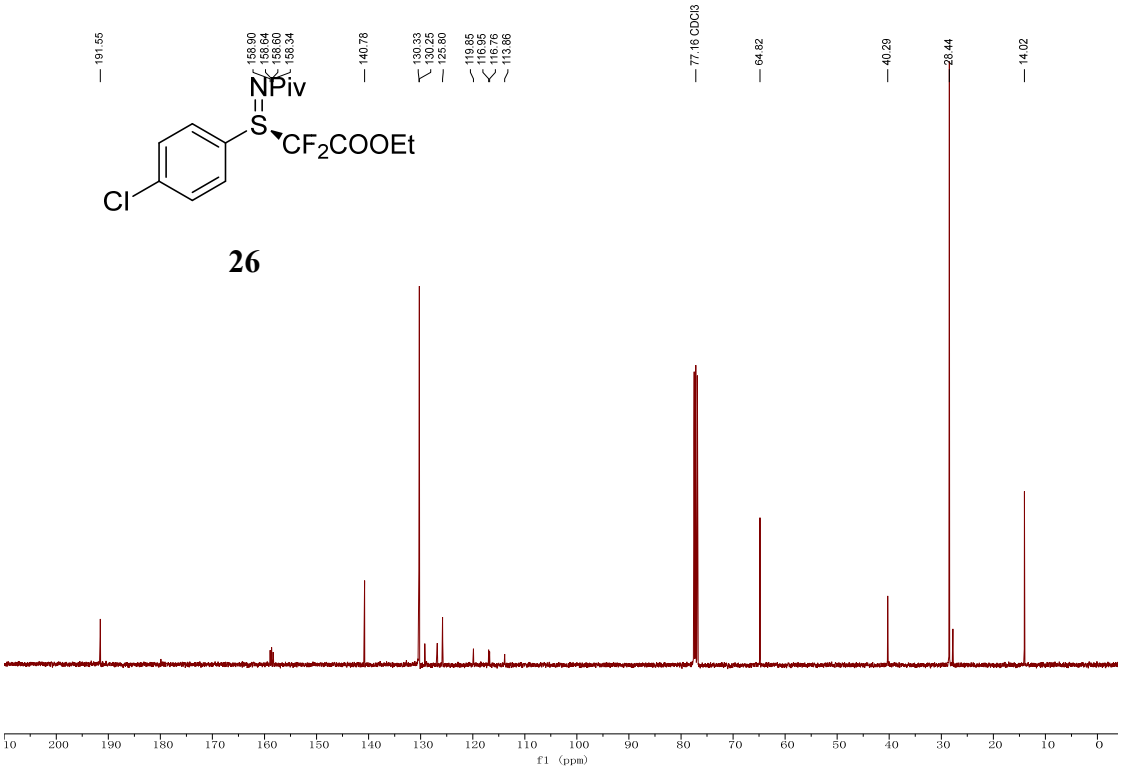
Figure S36. NMR spectra of compound **26**.

^{1}H NMR (400 MHz) spectrum of compound **26** ($CDCl_3$, 297.7 K)



26

^{13}C NMR (100 MHz) spectrum of compound **26** ($CDCl_3$, 298.2 K)



26

^{19}F NMR (376 MHz) spectrum of compound **26** ($CDCl_3$, 297.8 K)

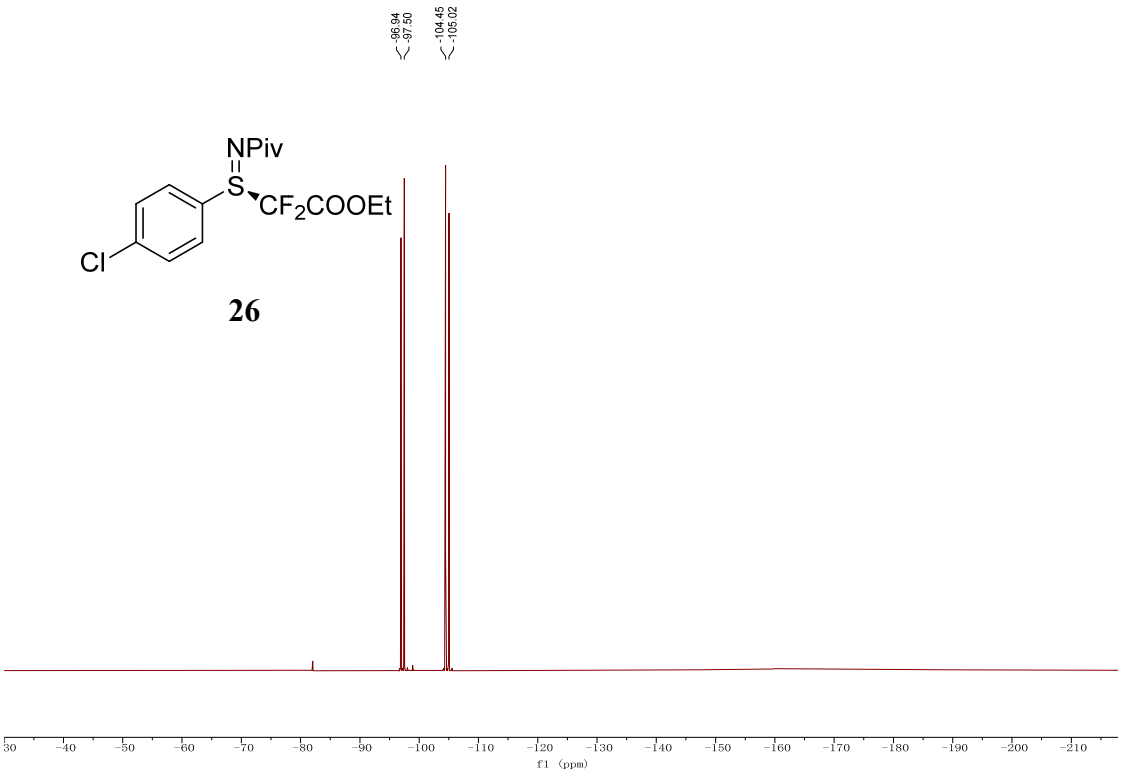
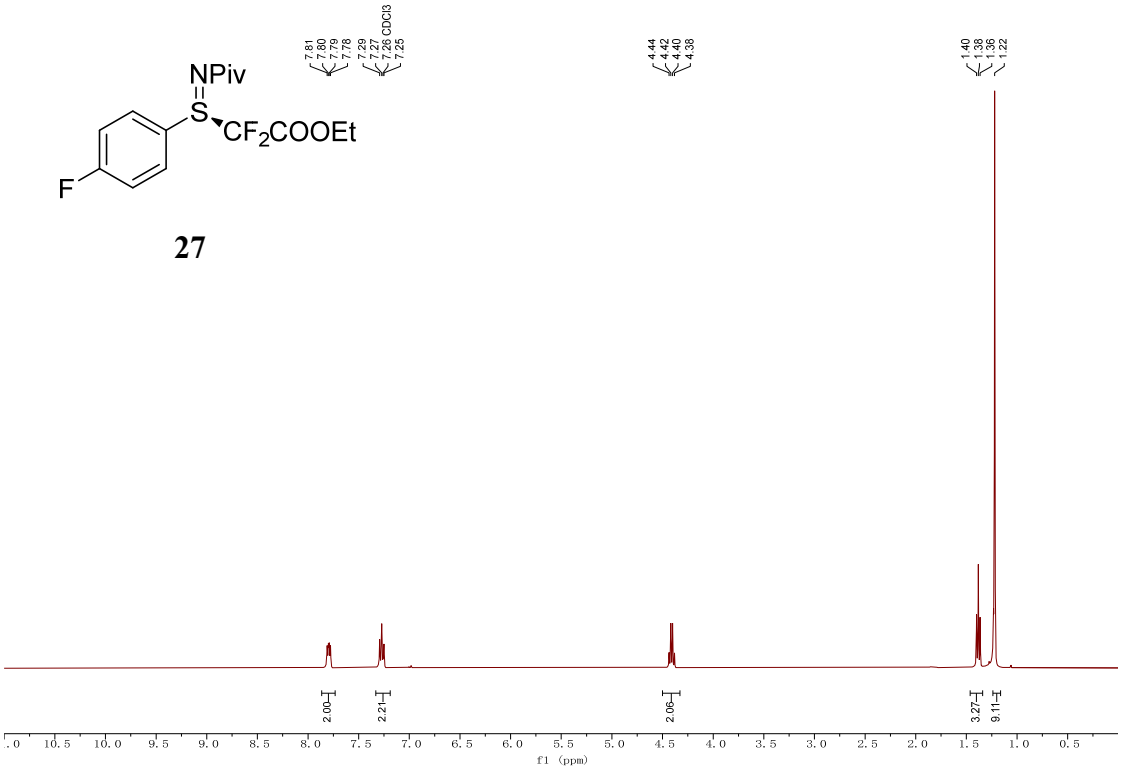


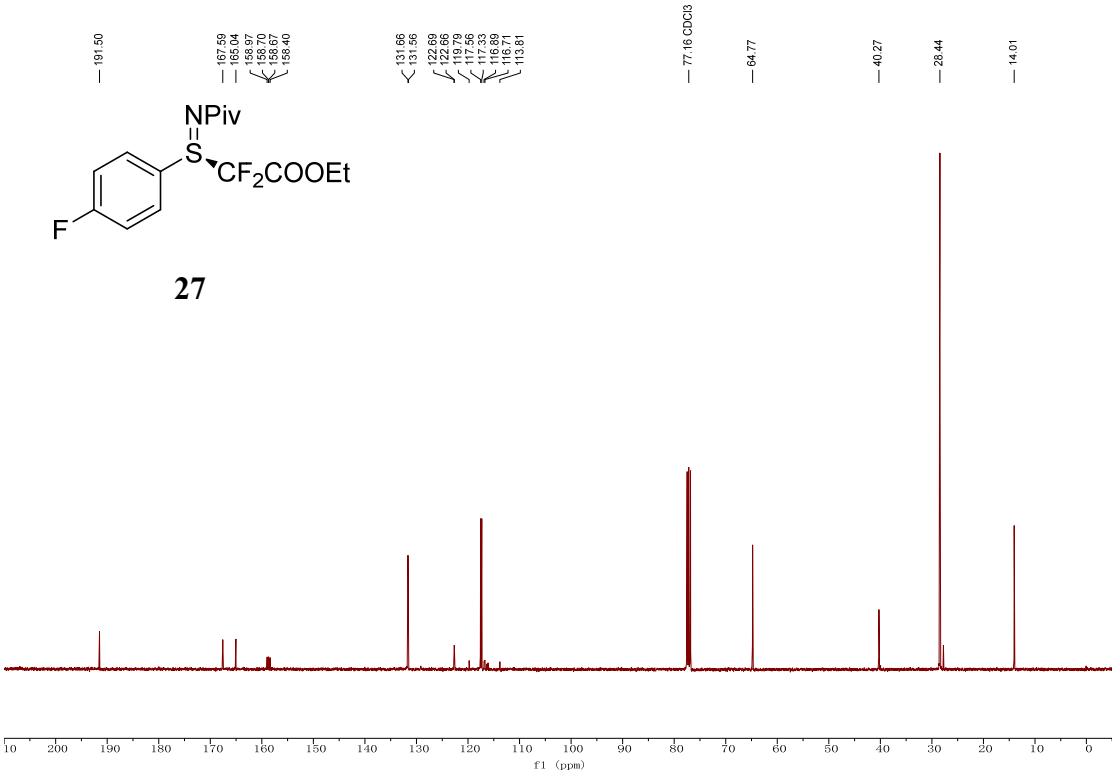
Figure S37. NMR spectra of compound **27**.

^{1}H NMR (400 MHz) spectrum of compound **27** ($CDCl_3$, 297.6 K)



27

^{13}C NMR (100 MHz) spectrum of compound **27** ($CDCl_3$, 297.8 K)

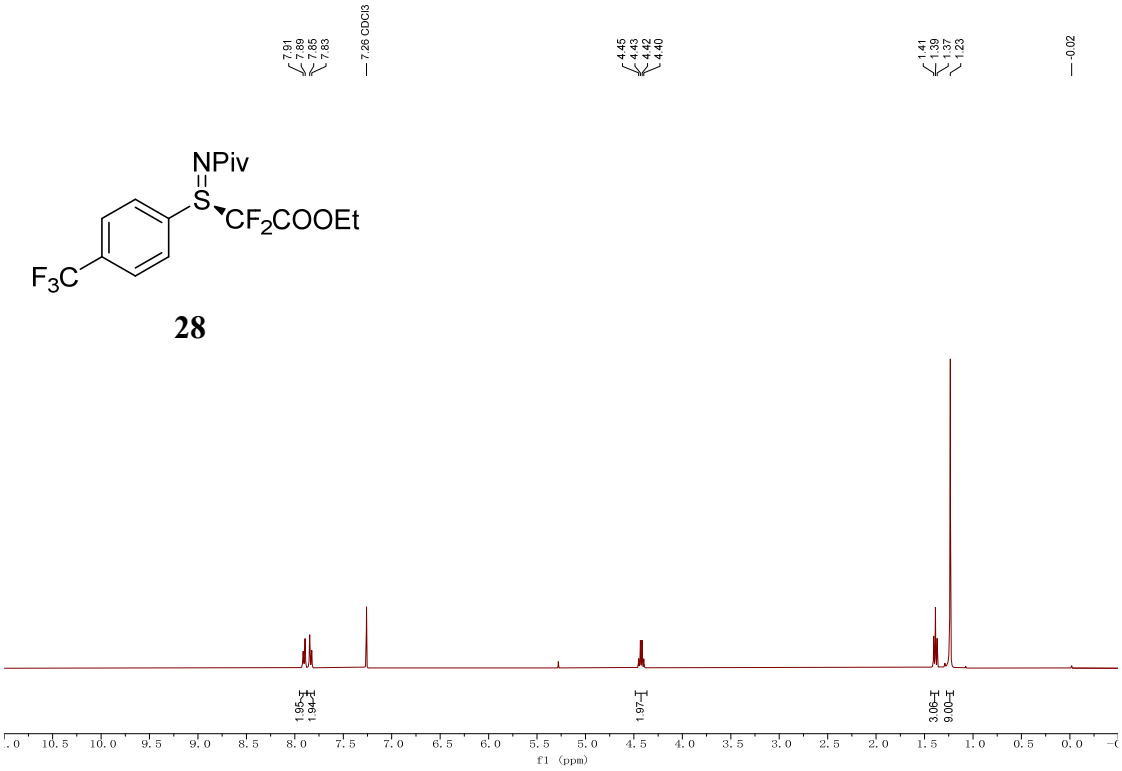


27

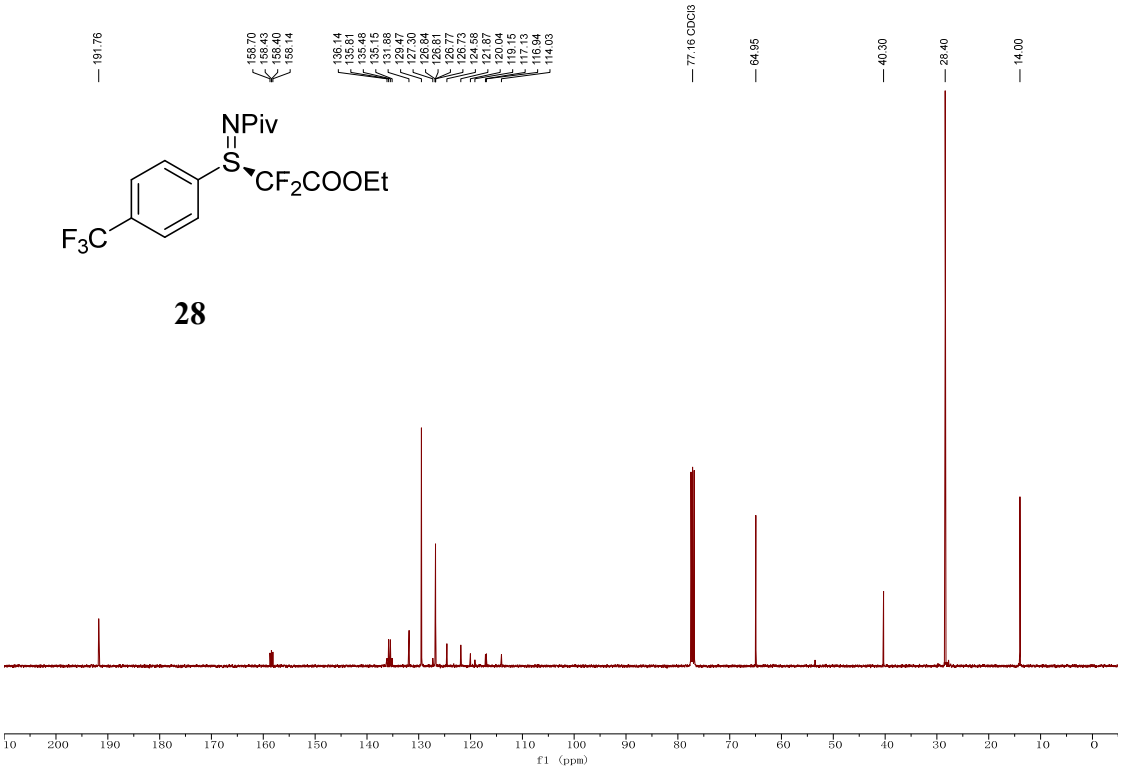
^{19}F NMR (376 MHz) spectrum of compound **27** ($CDCl_3$, 297.6)

Figure S38. NMR spectra of compound **28**.

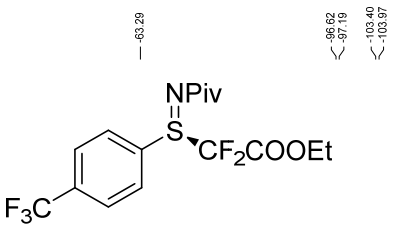
^{1}H NMR (400 MHz) spectrum of compound **28** ($CDCl_3$, 296.4 K)



^{13}C NMR (100 MHz) spectrum of compound **28** ($CDCl_3$, 296.9 K)



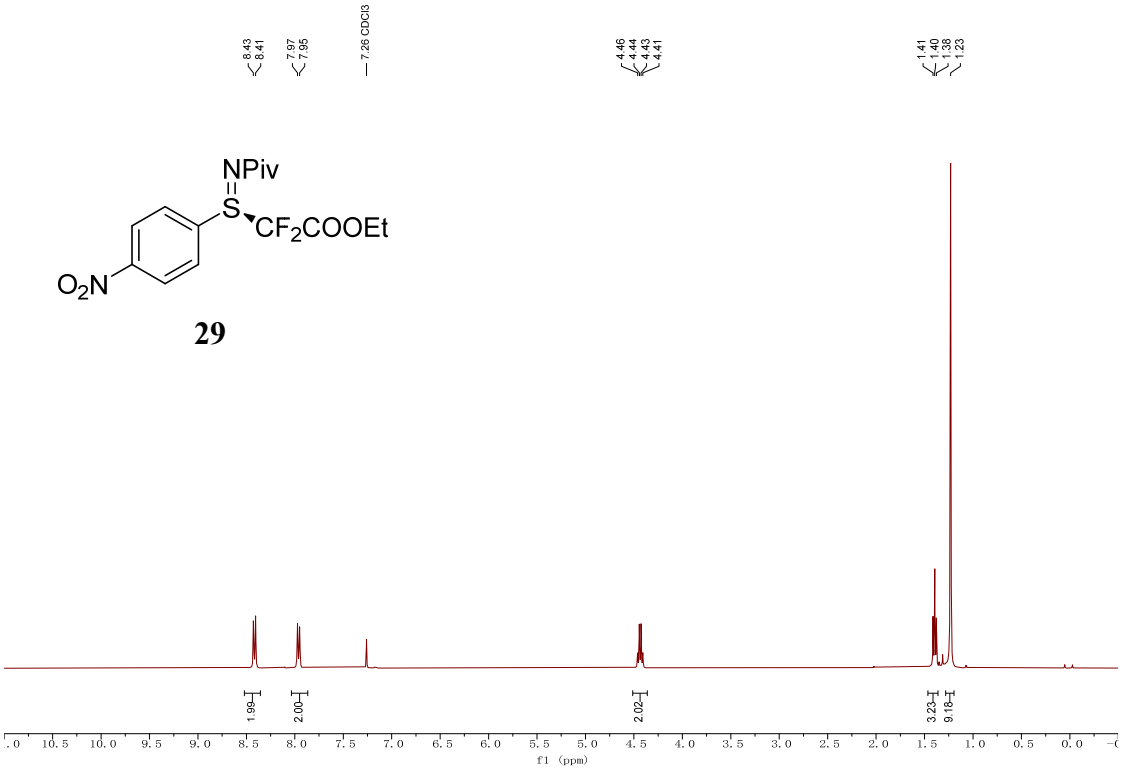
^{19}F NMR (376 MHz) spectrum of compound **28** ($CDCl_3$, 296.4 K)



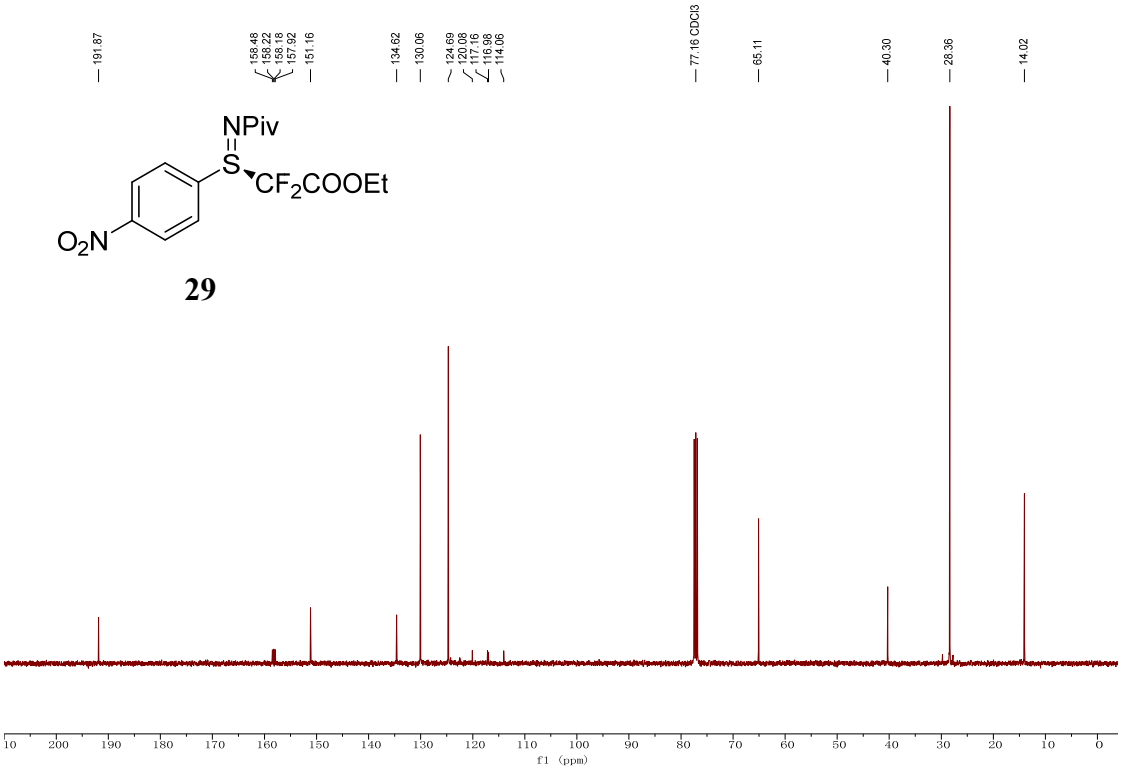
28

Figure S39. NMR spectra of compound **29**.

^{1}H NMR (400 MHz) spectrum of compound **29** ($CDCl_3$, 294.5 K)



^{13}C NMR (100 MHz) spectrum of compound **29** ($CDCl_3$, 294.8 K)



^{19}F NMR (376 MHz) spectrum of compound **29** ($CDCl_3$, 294.5 K)

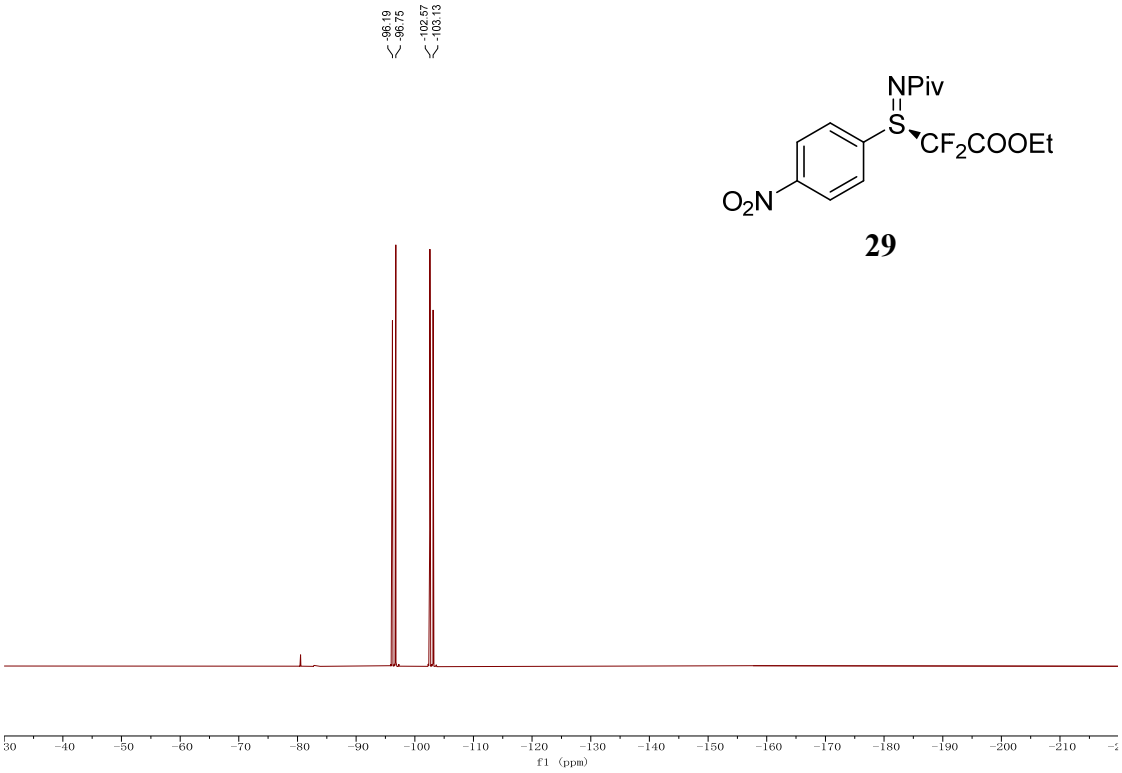
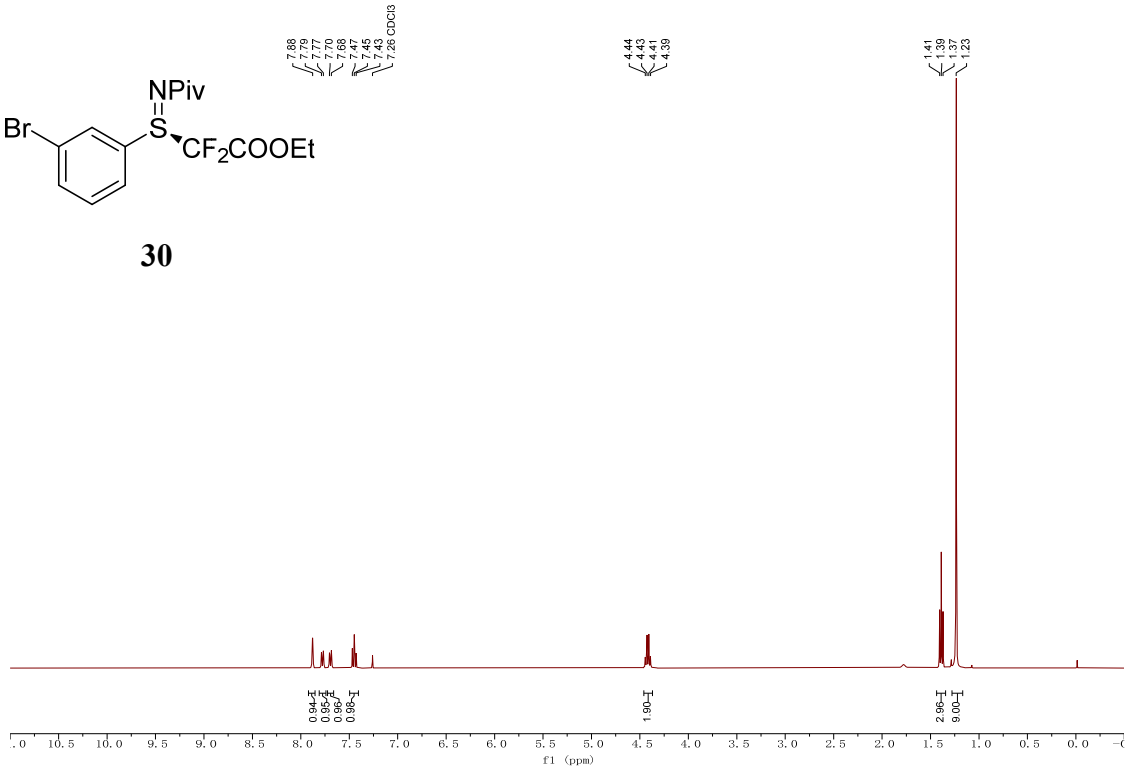
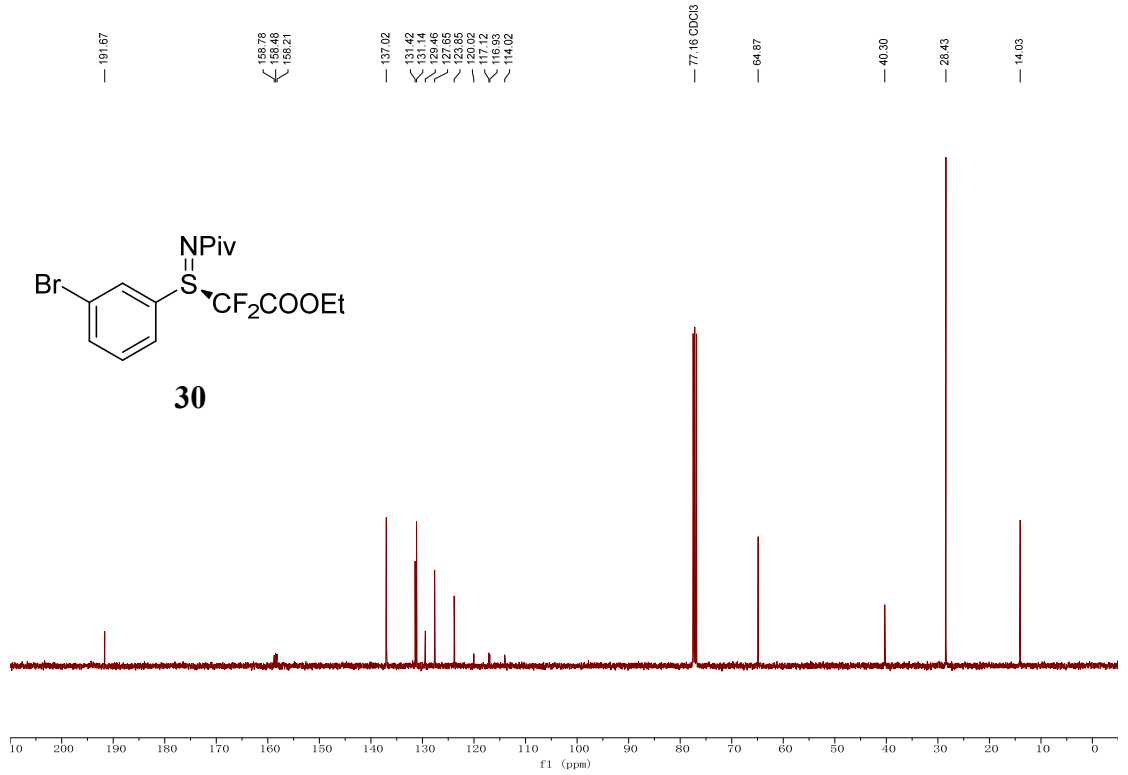


Figure S40. NMR spectra of compound **30**.

^{1}H NMR (400 MHz) spectrum of compound **30** ($CDCl_3$, 295.5 K)



^{13}C NMR (100 MHz) spectrum of compound **30** ($CDCl_3$, 295.9 K)



^{19}F NMR (376 MHz) spectrum of compound **30** ($CDCl_3$, 295.5 K)

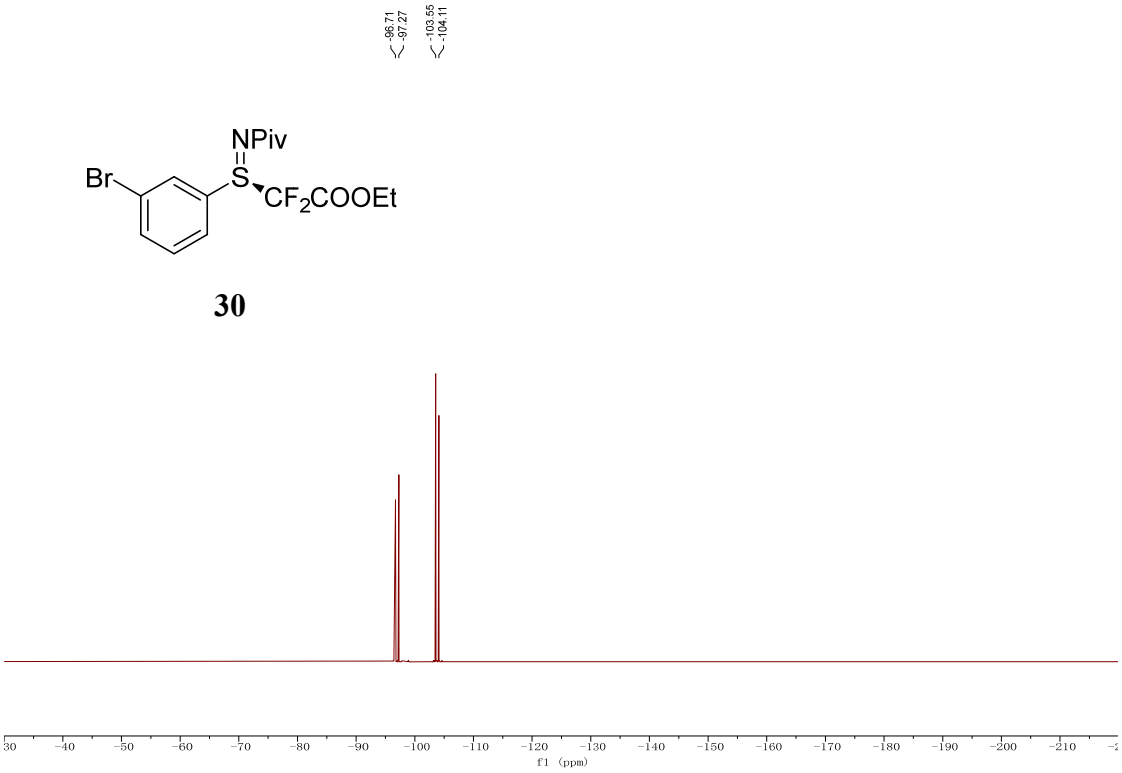
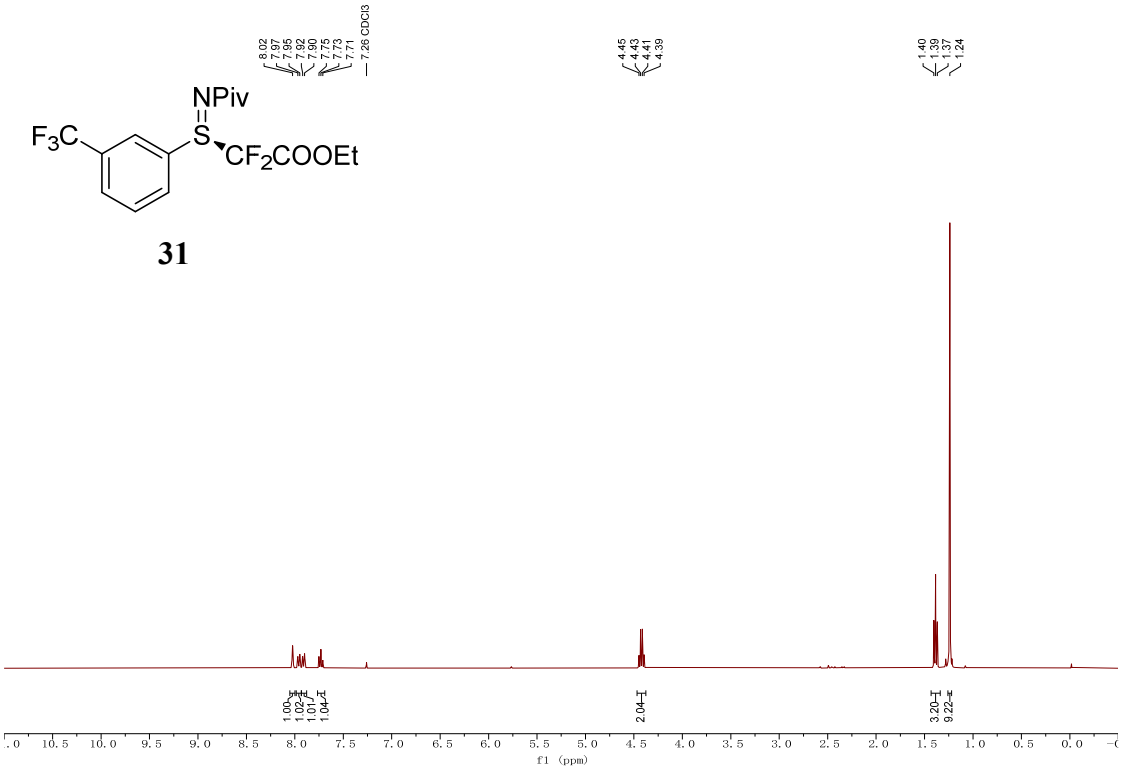
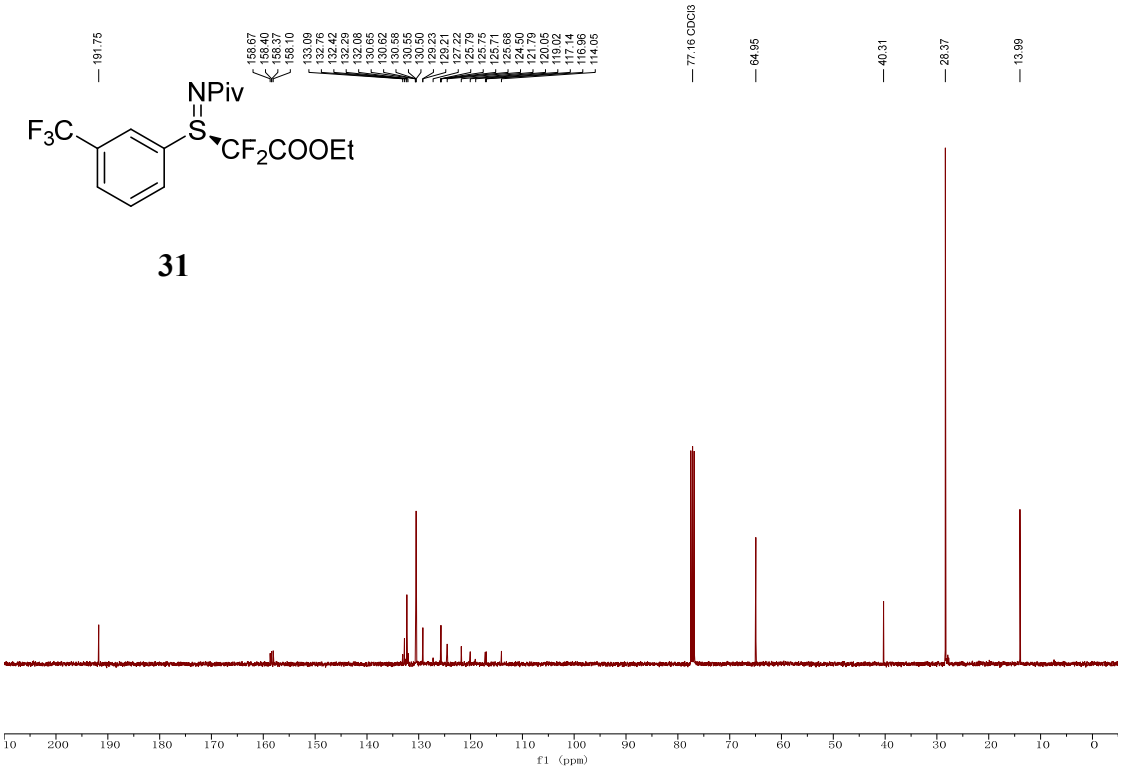


Figure S41. NMR spectra of compound **31**.

^{1}H NMR (400 MHz) spectrum of compound **31** ($CDCl_3$, 296.4 K)



^{13}C NMR (100 MHz) spectrum of compound **31** ($CDCl_3$, 296.5 K)



^{19}F NMR (376 MHz) spectrum of compound **31** ($CDCl_3$, 296.4 K)

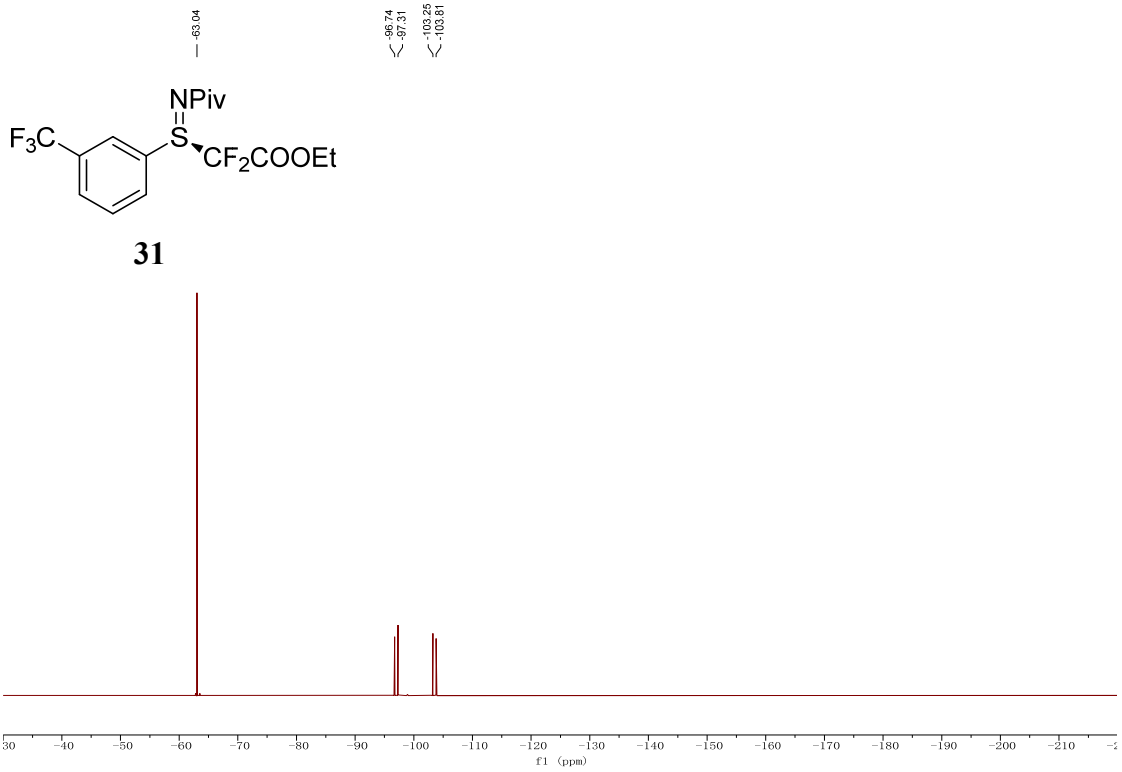
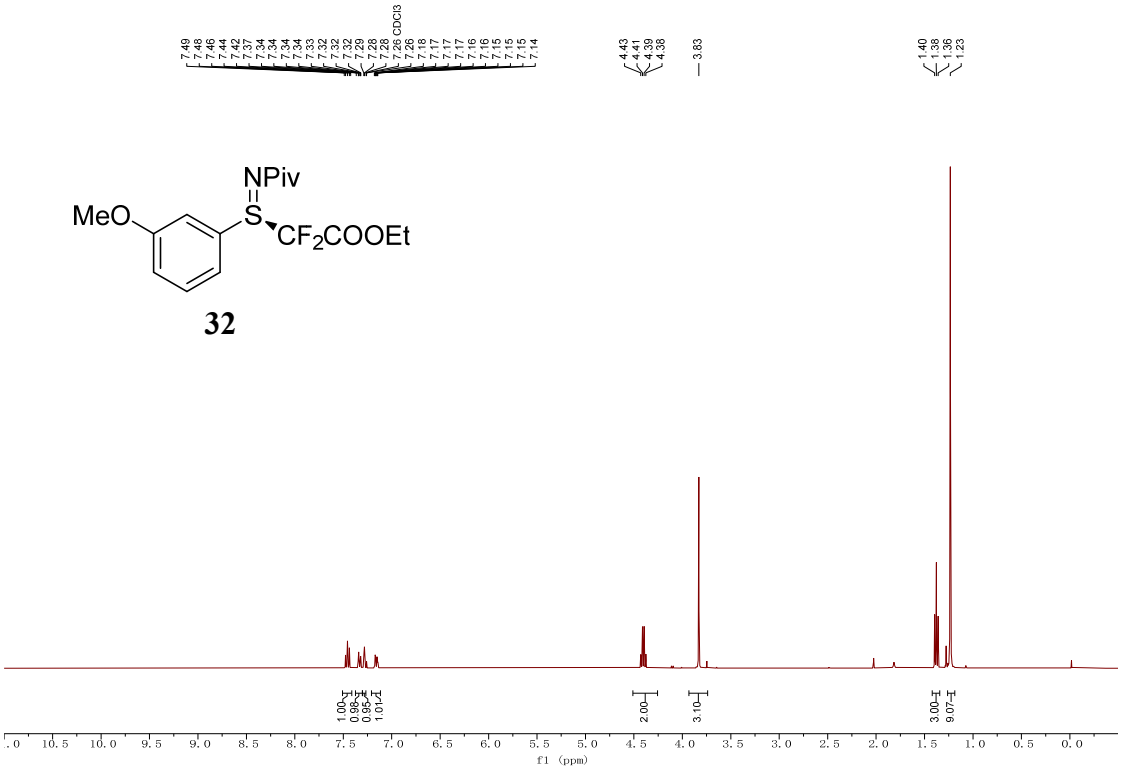
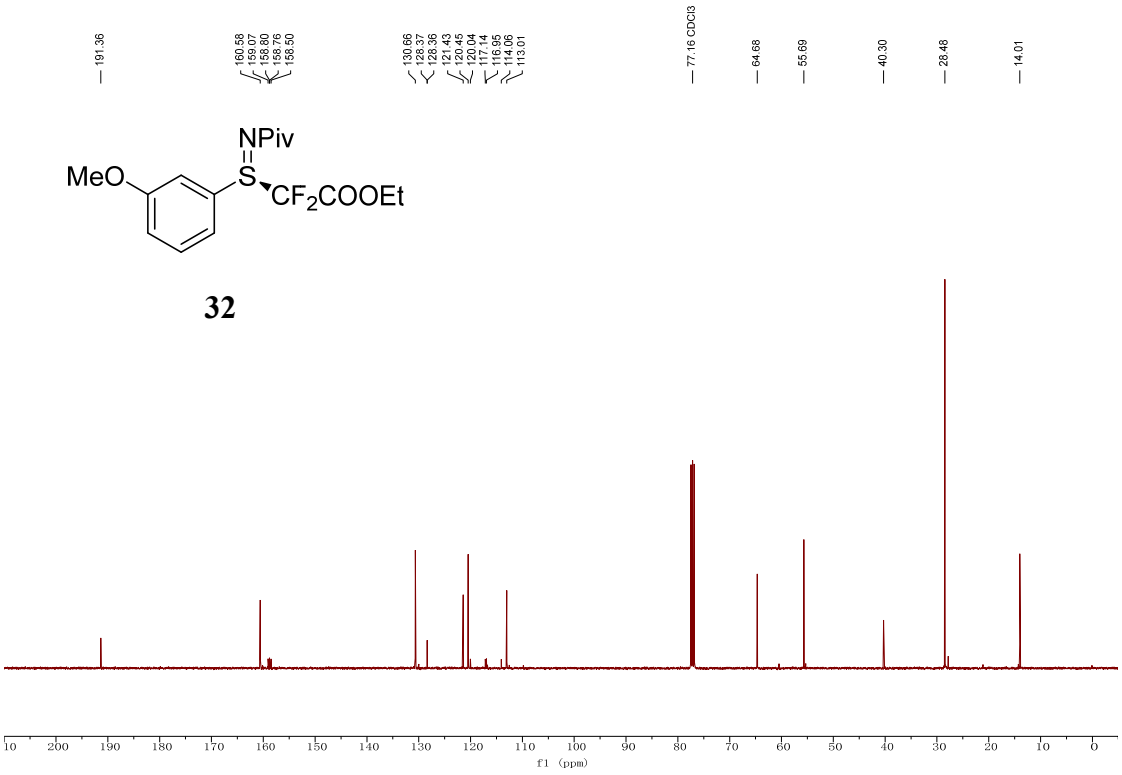


Figure S42. NMR spectra of compound **32**.

^{1}H NMR (400 MHz) spectrum of compound **32** ($CDCl_3$, 297.4 K)



^{13}C NMR (100 MHz) spectrum of compound **32** ($CDCl_3$, 297.9 K)



^{19}F NMR (376 MHz) spectrum of compound **32** ($CDCl_3$, 297.4 K)

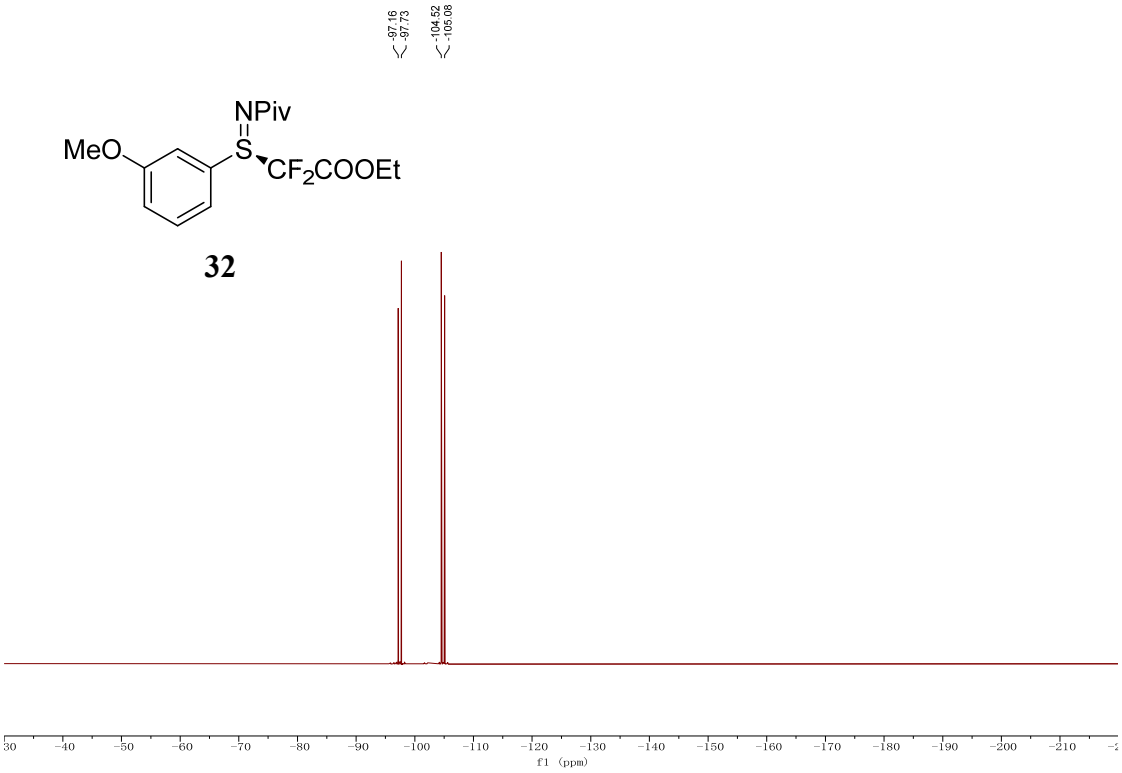
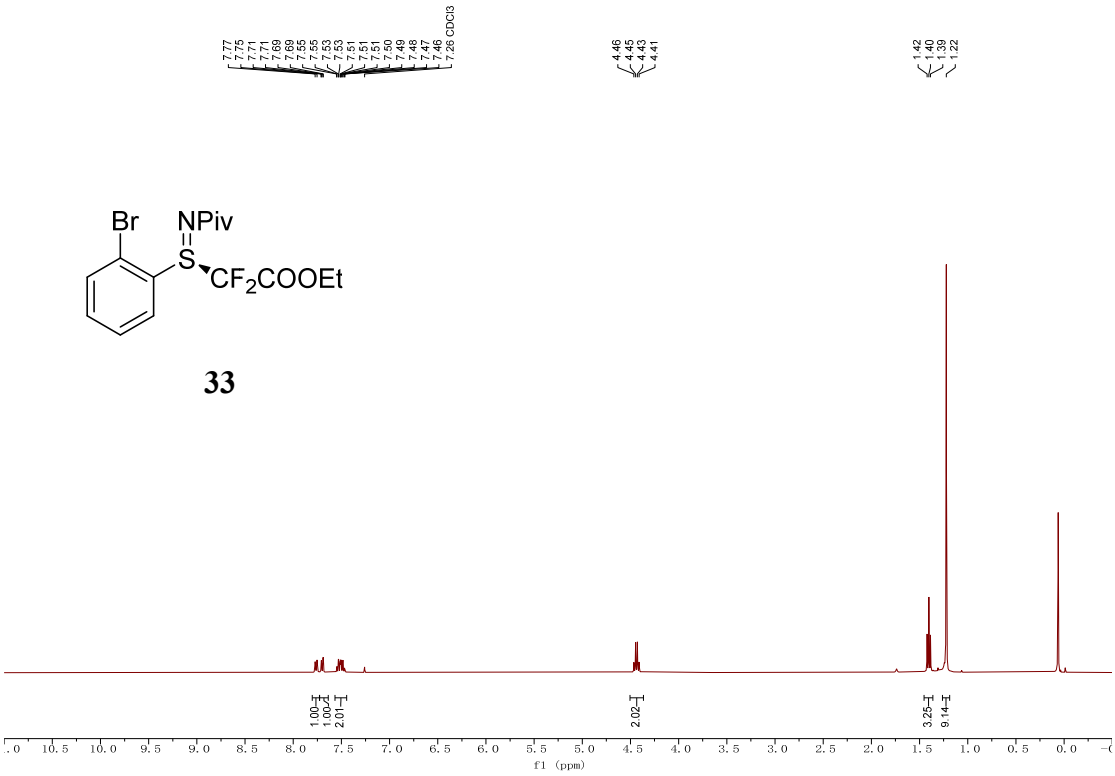
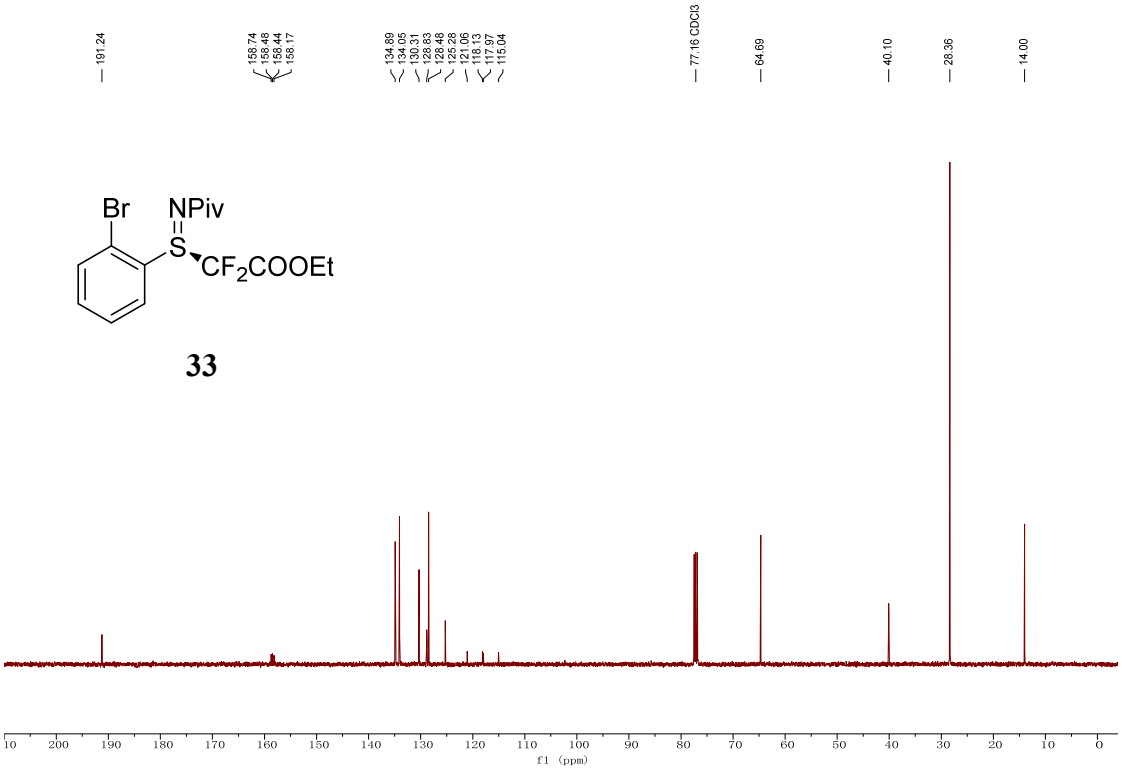


Figure S43. NMR spectra of compound **33**.

^{1}H NMR (400 MHz) spectrum of compound **33** ($CDCl_3$, 293.4 K)



^{13}C NMR (100 MHz) spectrum of compound **33** ($CDCl_3$, 293.6 K)



^{19}F NMR (376 MHz) spectrum of compound **33** ($CDCl_3$, 293.4 K)

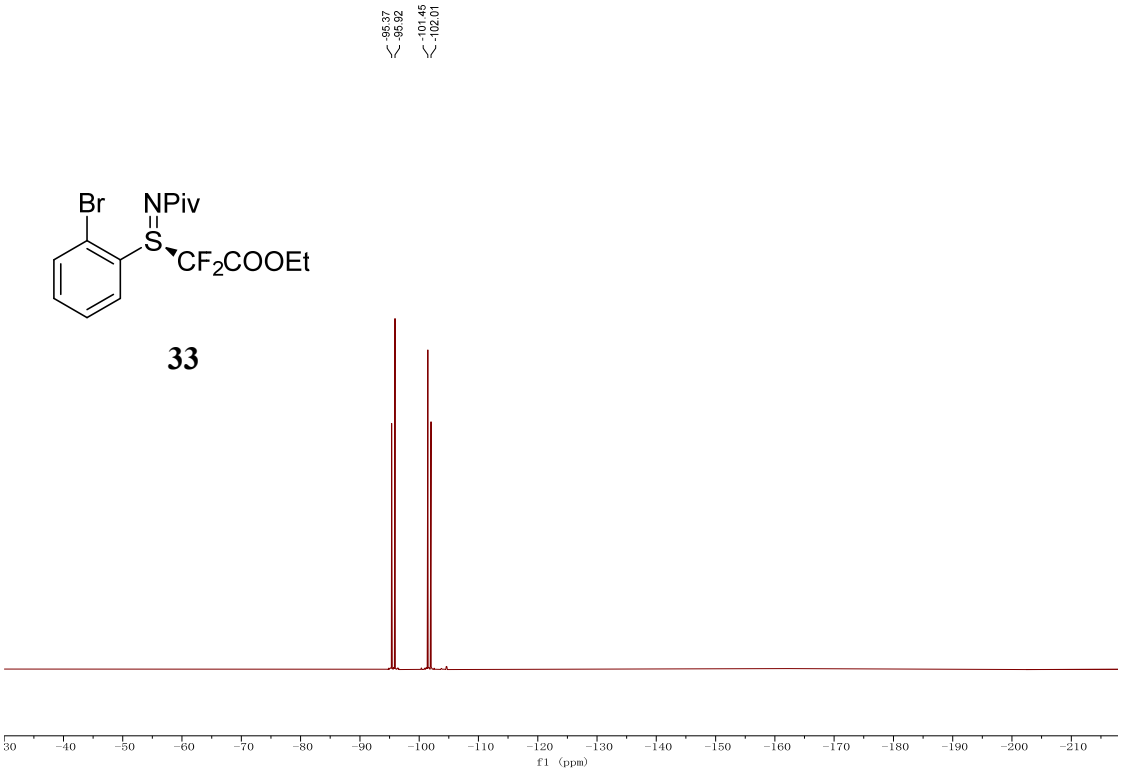
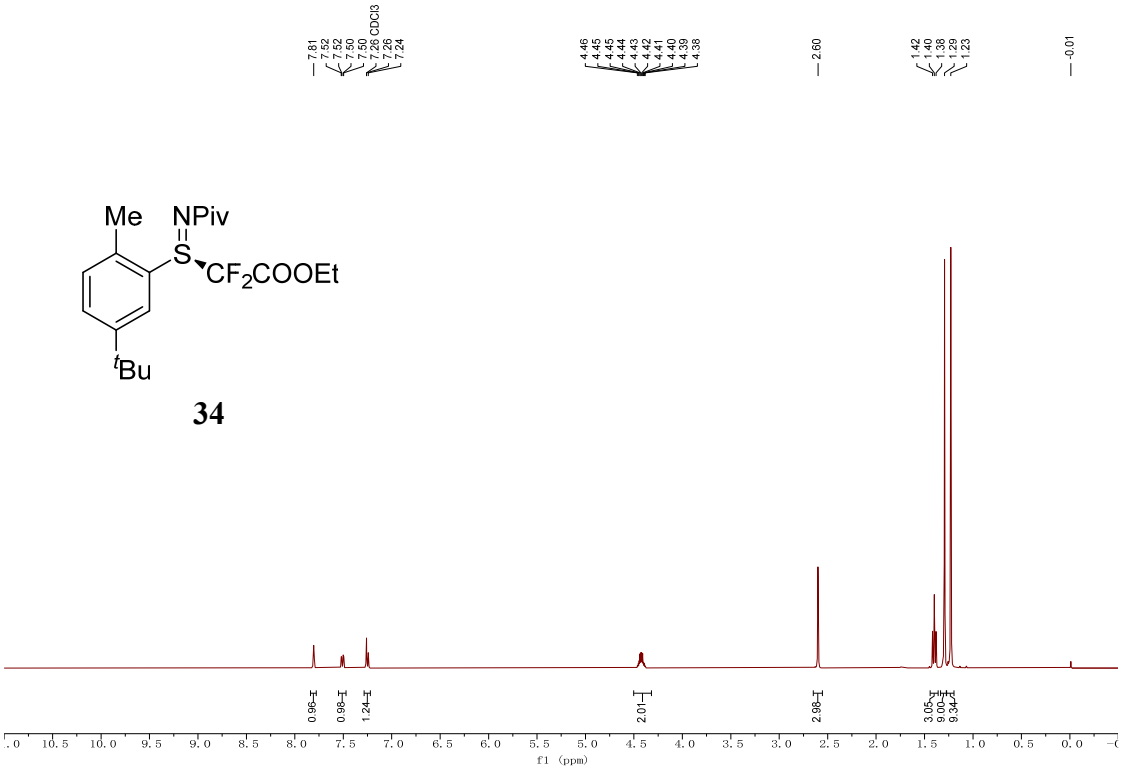
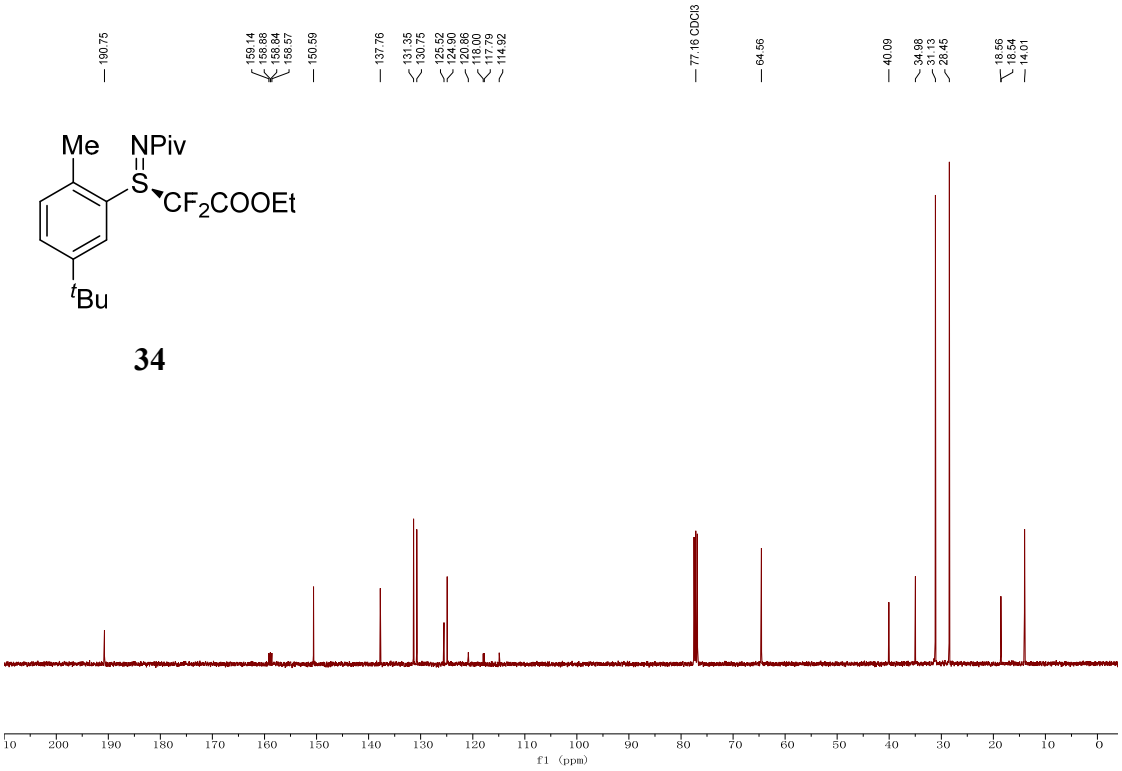


Figure S44. NMR spectra of compound **34**.

^{1}H NMR (400 MHz) spectrum of compound **34** ($CDCl_3$, 297.1 K)



^{13}C NMR (100 MHz) spectrum of compound **34** ($CDCl_3$, 296.9 K)



^{19}F NMR (376 MHz) spectrum of compound **34** ($CDCl_3$, 297.0 K)

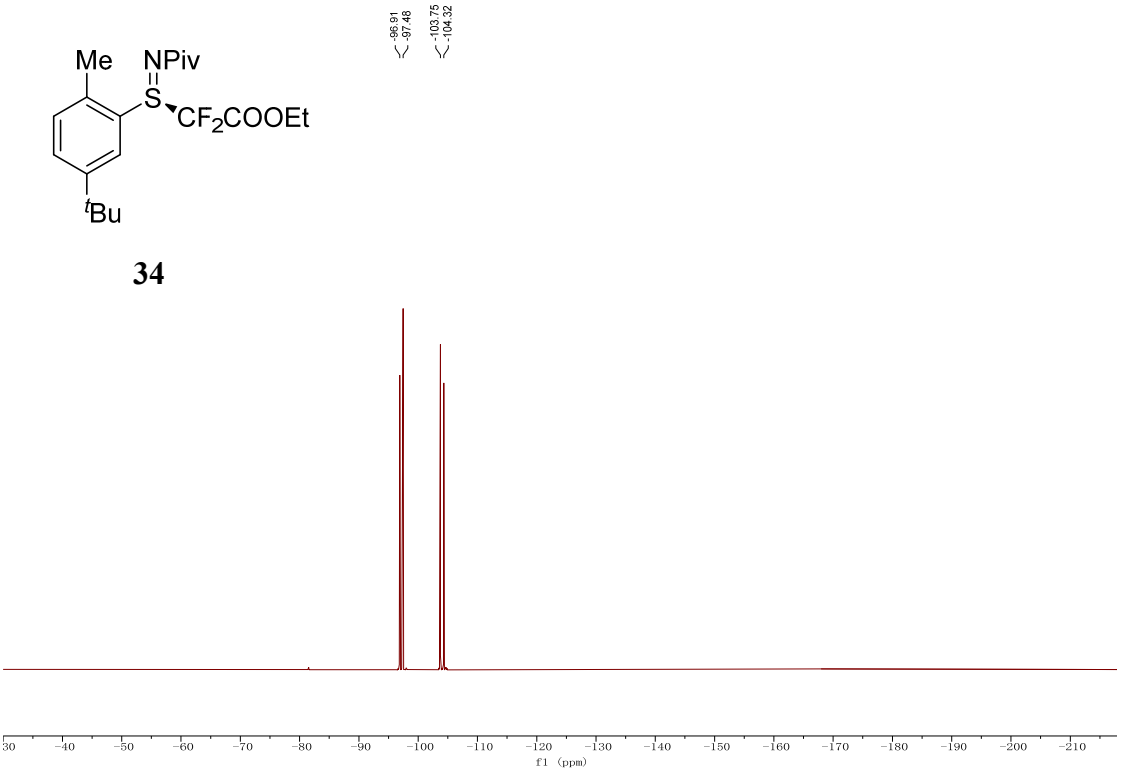
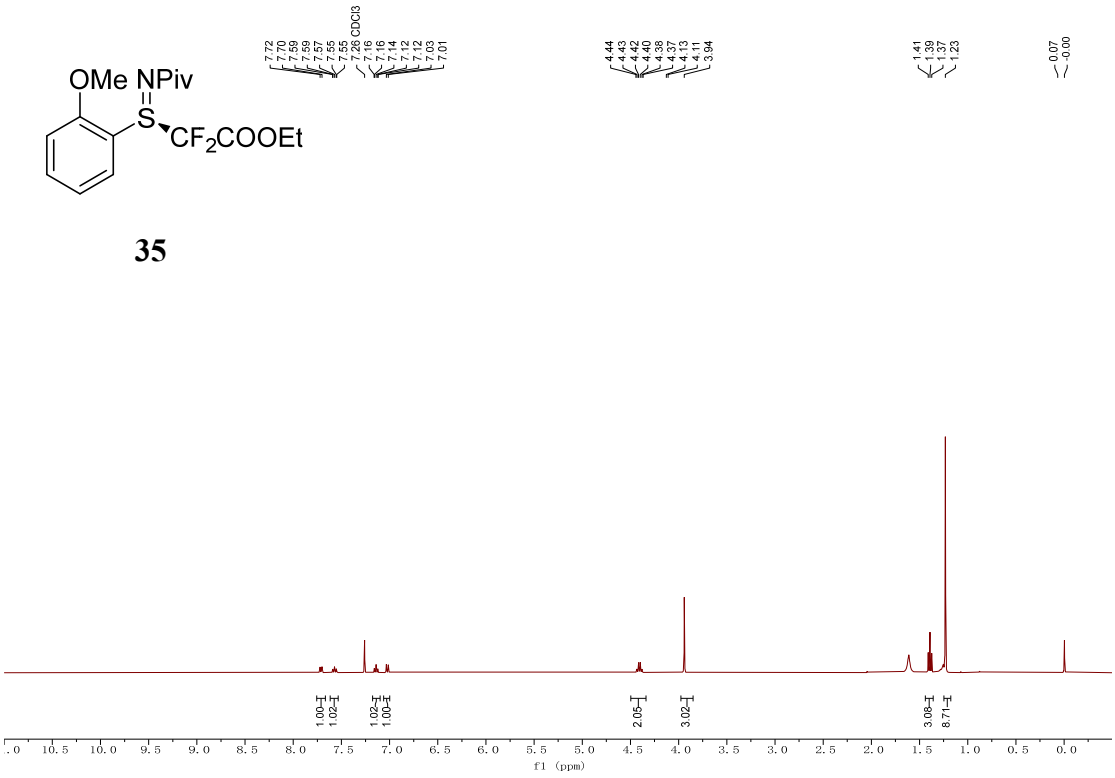


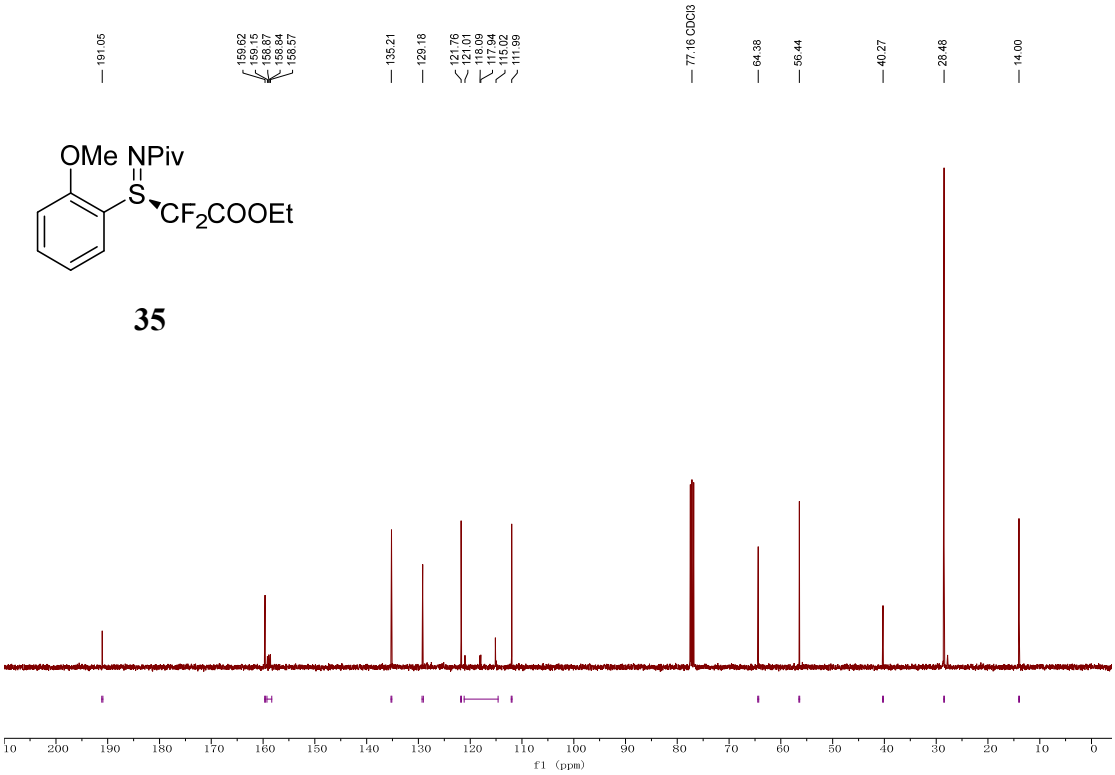
Figure S45. NMR spectra of compound **35**.

^{1}H NMR (400 MHz) spectrum of compound **35** ($CDCl_3$, 296.3 K)



35

^{13}C NMR (100 MHz) spectrum of compound **35** ($CDCl_3$, 296.7 K)



35

^{19}F NMR (376 MHz) spectrum of compound **35** ($CDCl_3$, 296.2 K)

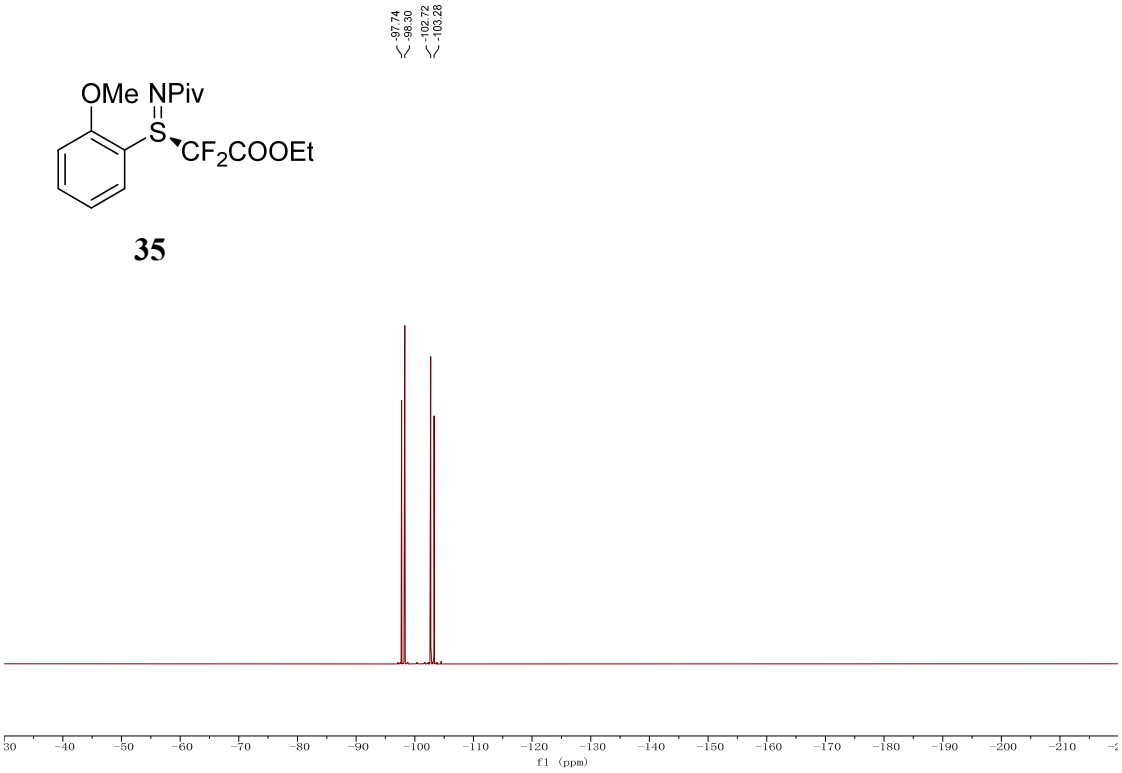
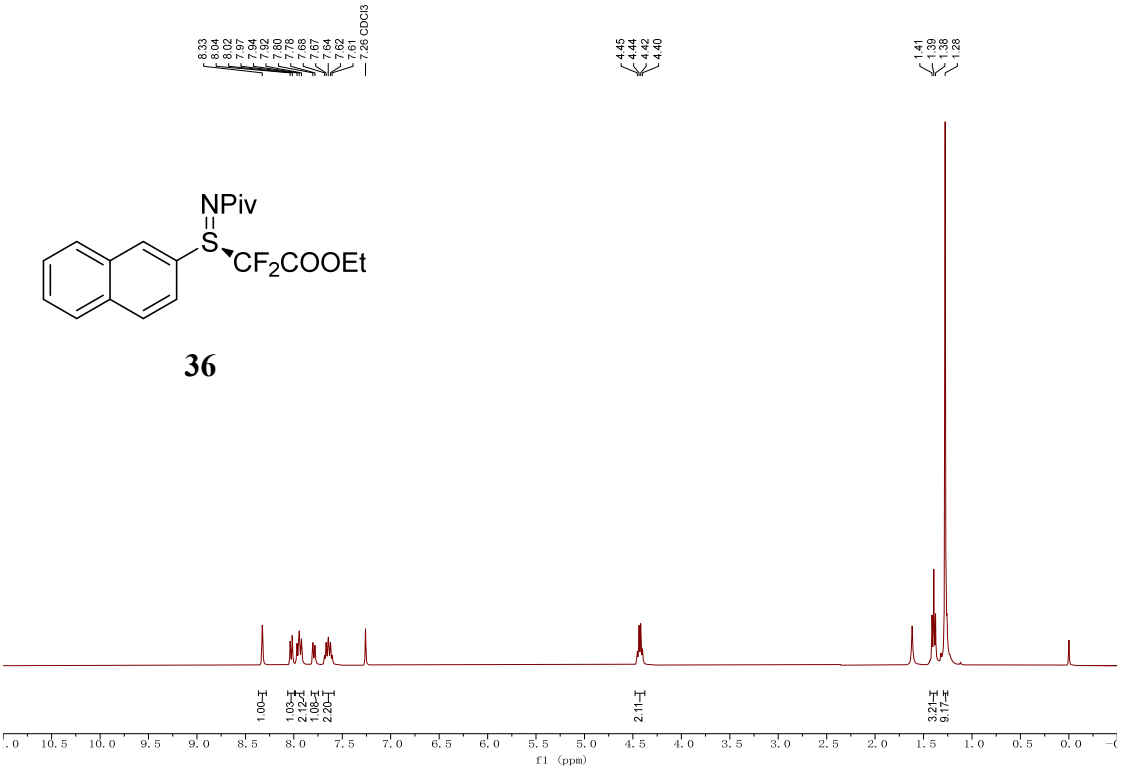
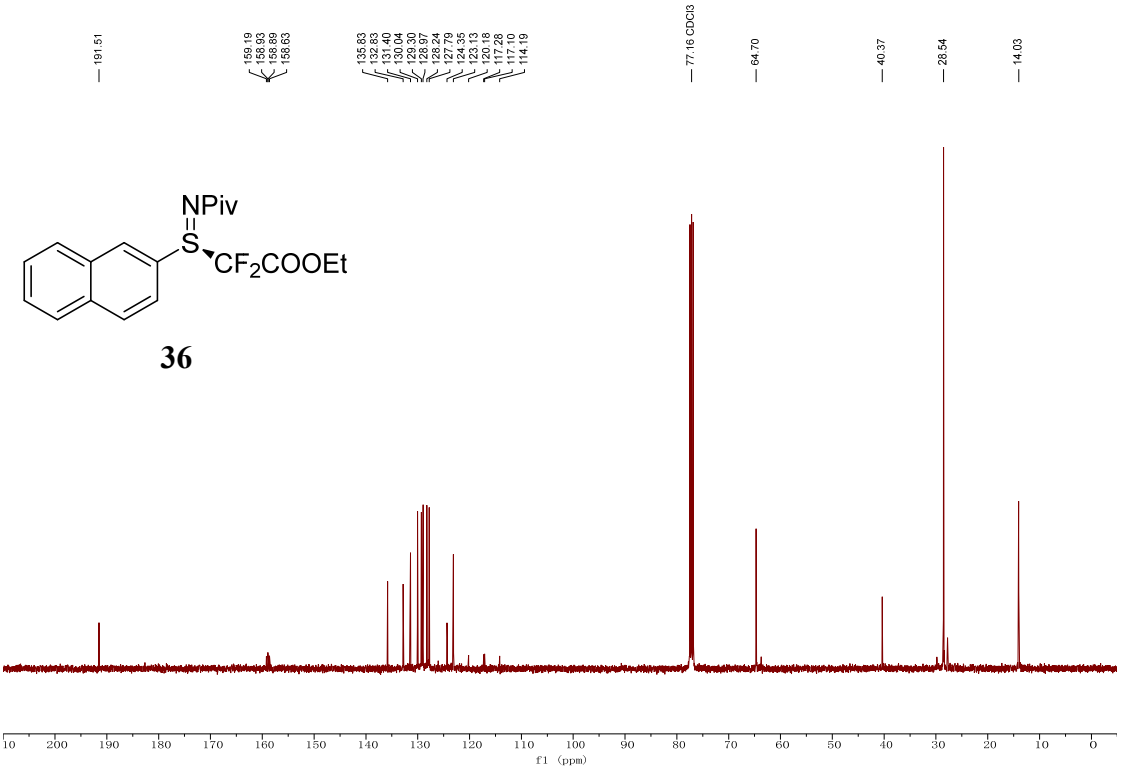


Figure S46. NMR spectra of compound **36**.

^{1}H NMR (400 MHz) spectrum of compound **36** ($CDCl_3$, 299.3 K)



^{13}C NMR (100 MHz) spectrum of compound **36** ($CDCl_3$, 299.6 K)



^{19}F NMR (376 MHz) spectrum of compound **36** ($CDCl_3$, 299.4 K)

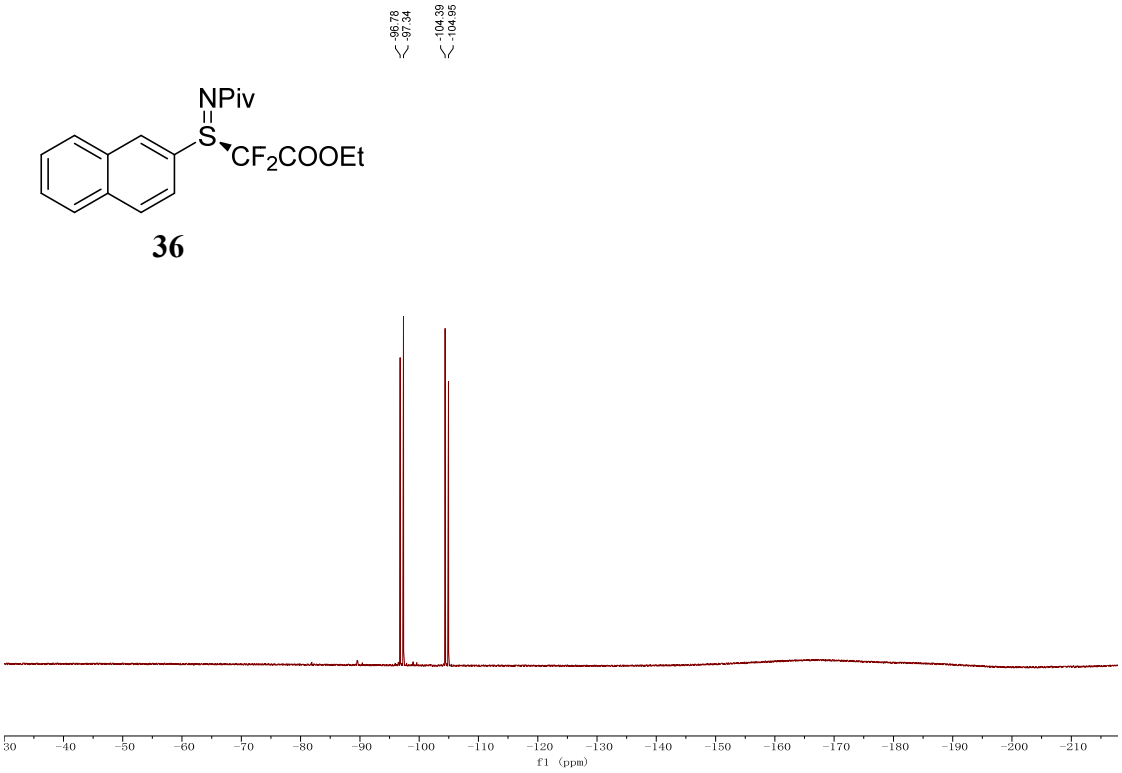
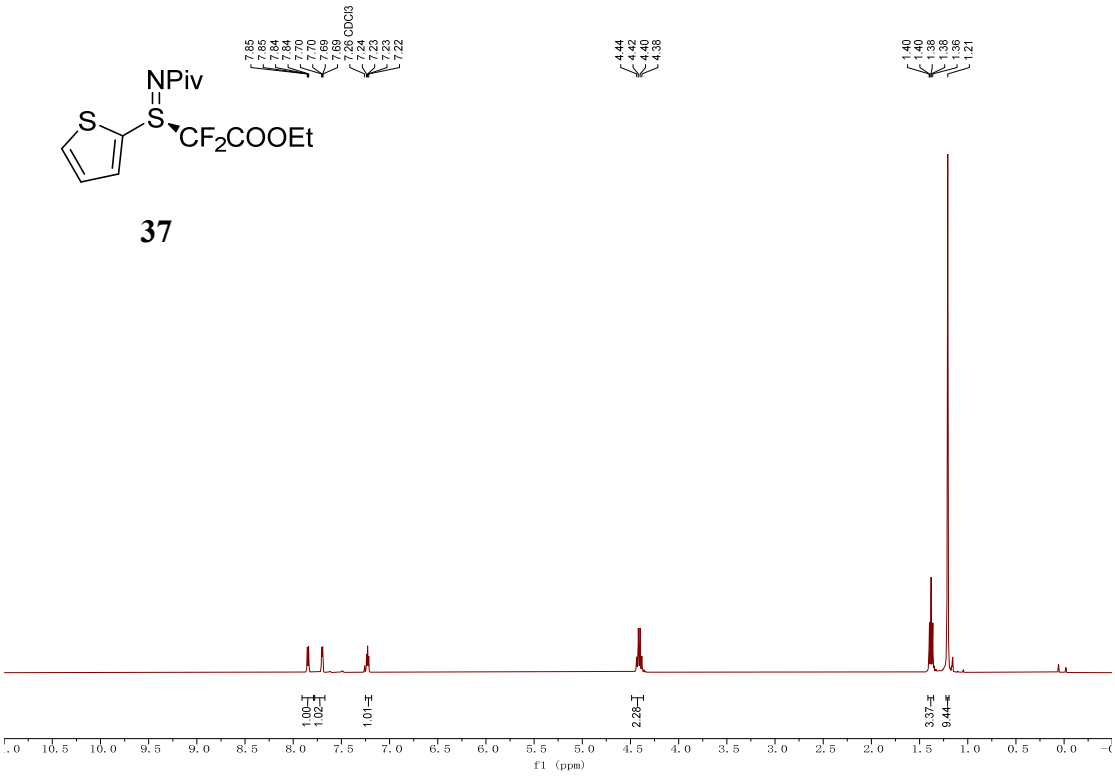
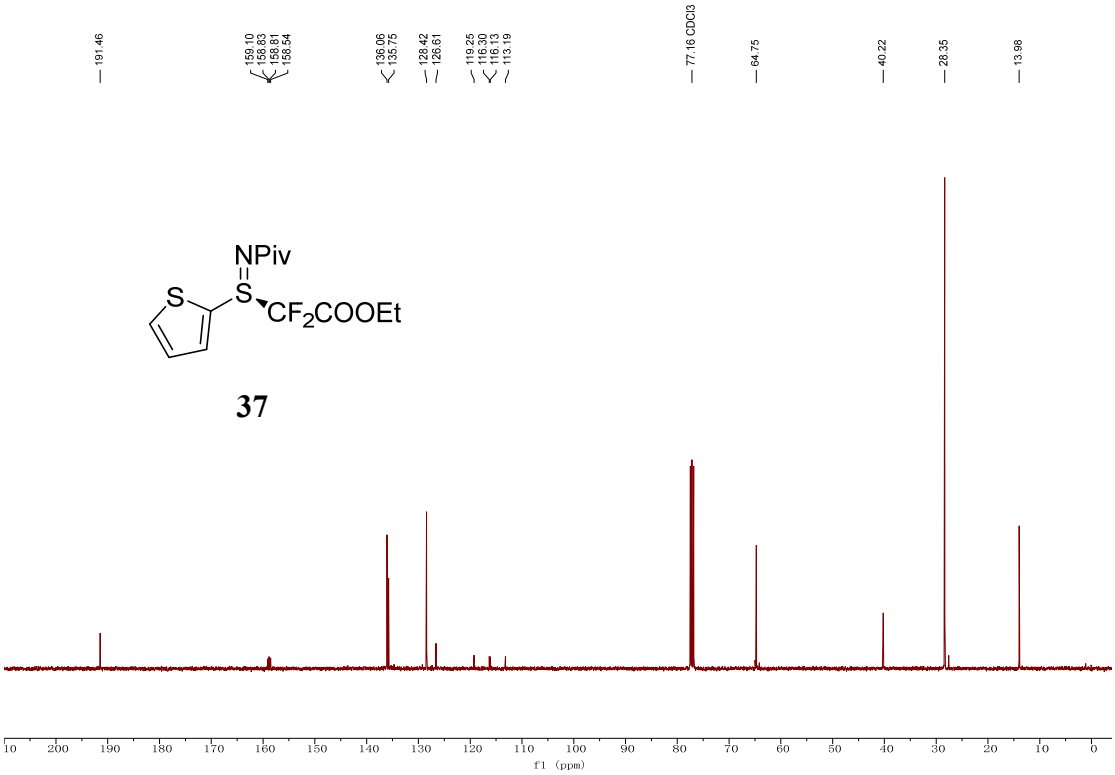


Figure S47. NMR spectra of compound **37**.

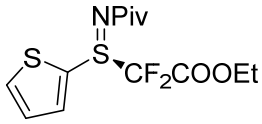
^{1}H NMR (400 MHz) spectrum of compound **37** ($CDCl_3$, 298.2 K)



^{13}C NMR (100 MHz) spectrum of compound **37** ($CDCl_3$, 298.1 K)



^{19}F NMR (376 MHz) spectrum of compound **37** ($CDCl_3$, 298.2 K)



37

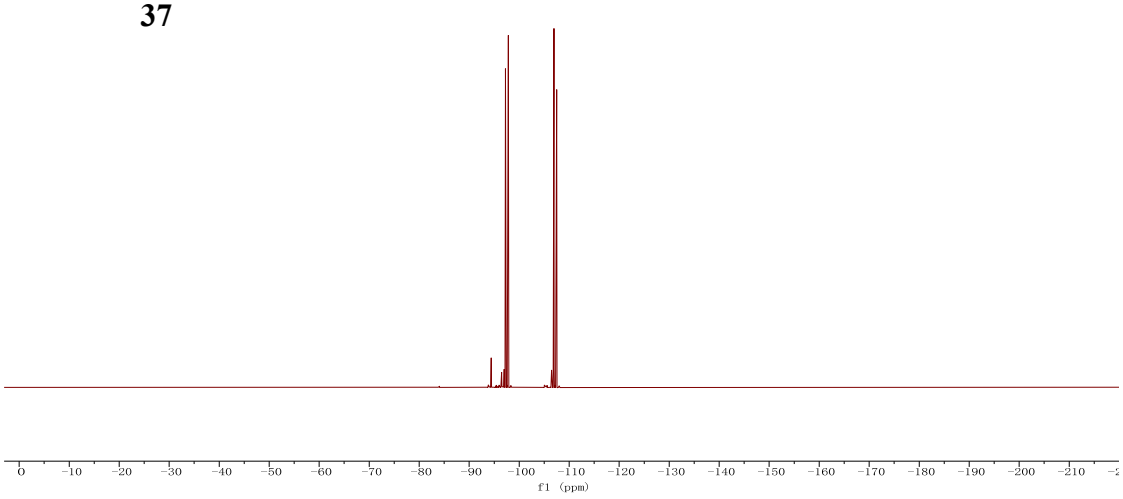
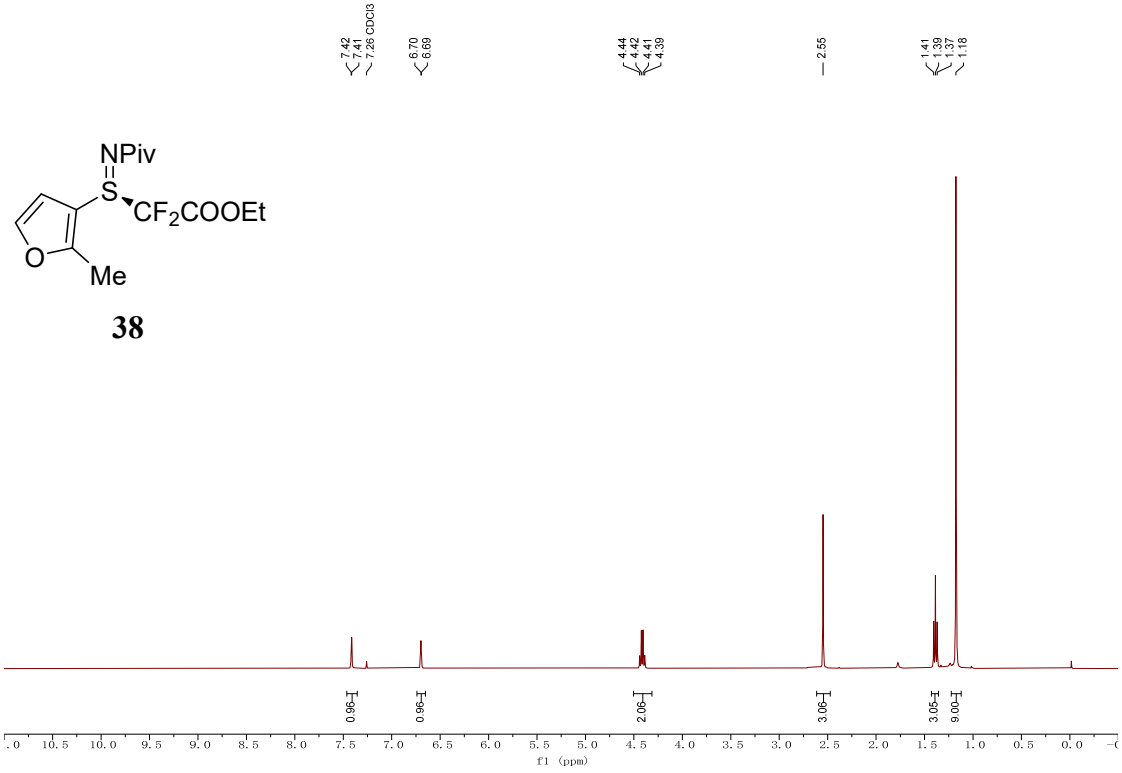
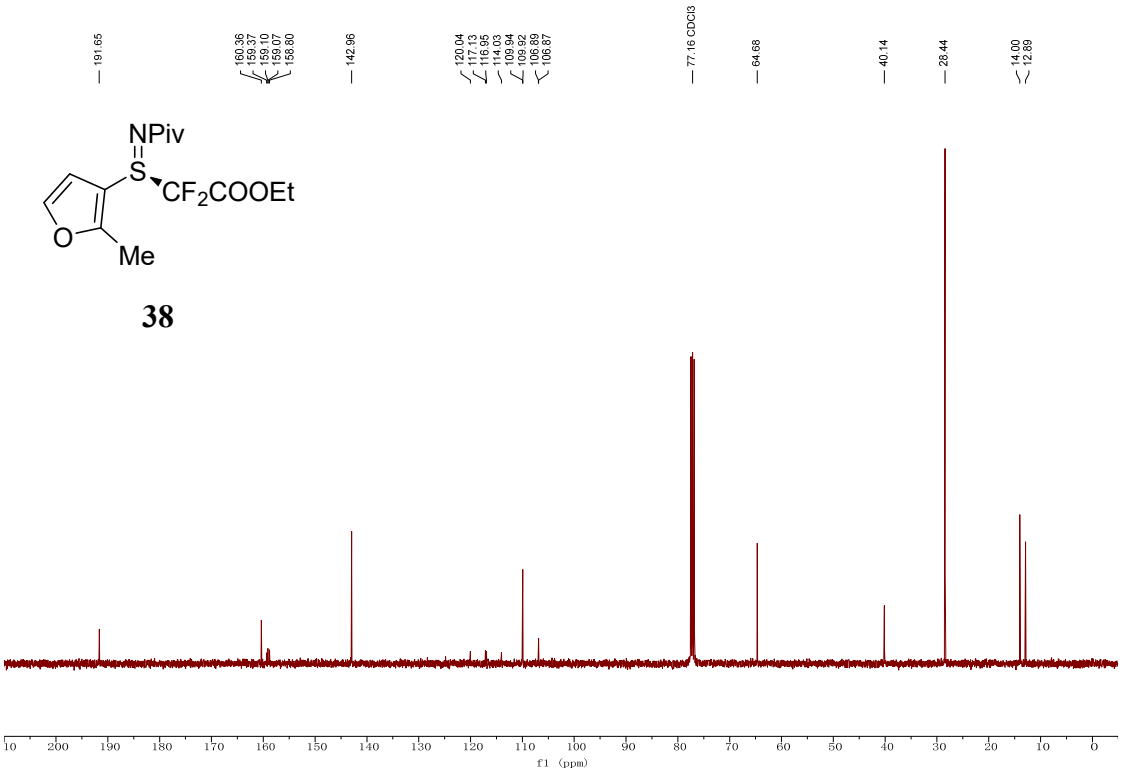


Figure S48. NMR spectra of compound **38**.

^{1}H NMR (400 MHz) spectrum of compound **38** ($CDCl_3$, 298.4 K)



^{13}C NMR (100 MHz) spectrum of compound **38** ($CDCl_3$, 298.8 K)



^{19}F NMR (376 MHz) spectrum of compound **38** ($CDCl_3$, 298.4 K)

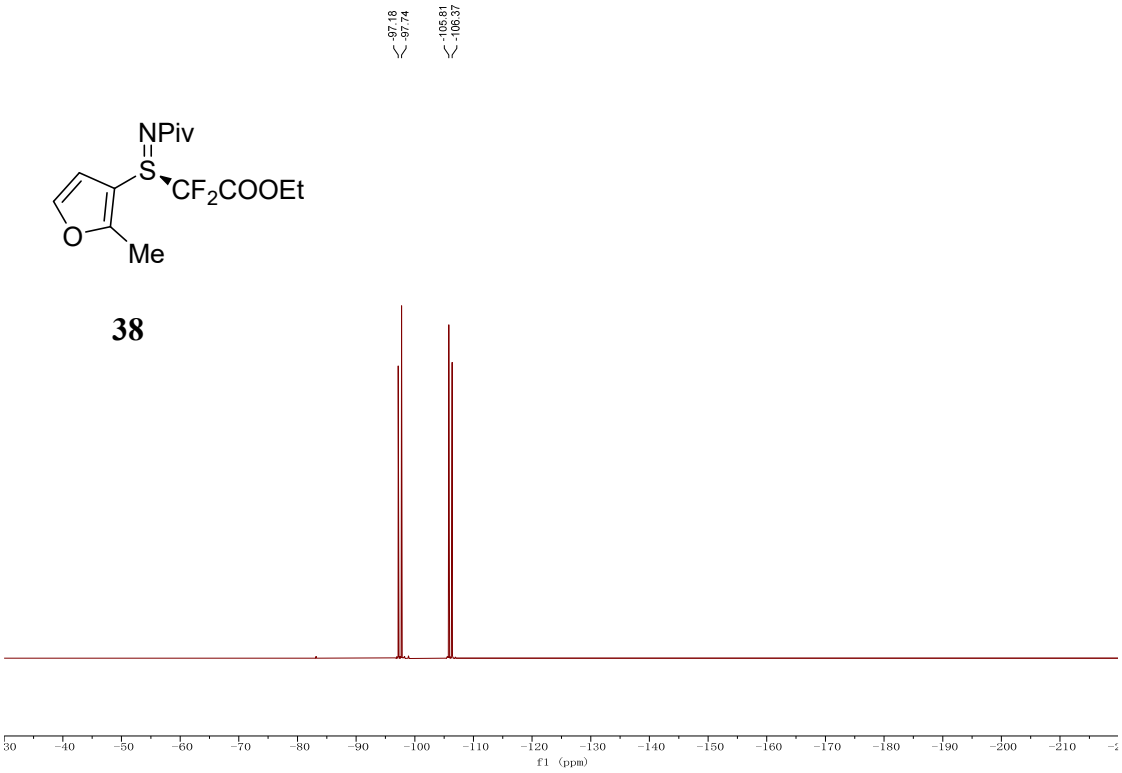
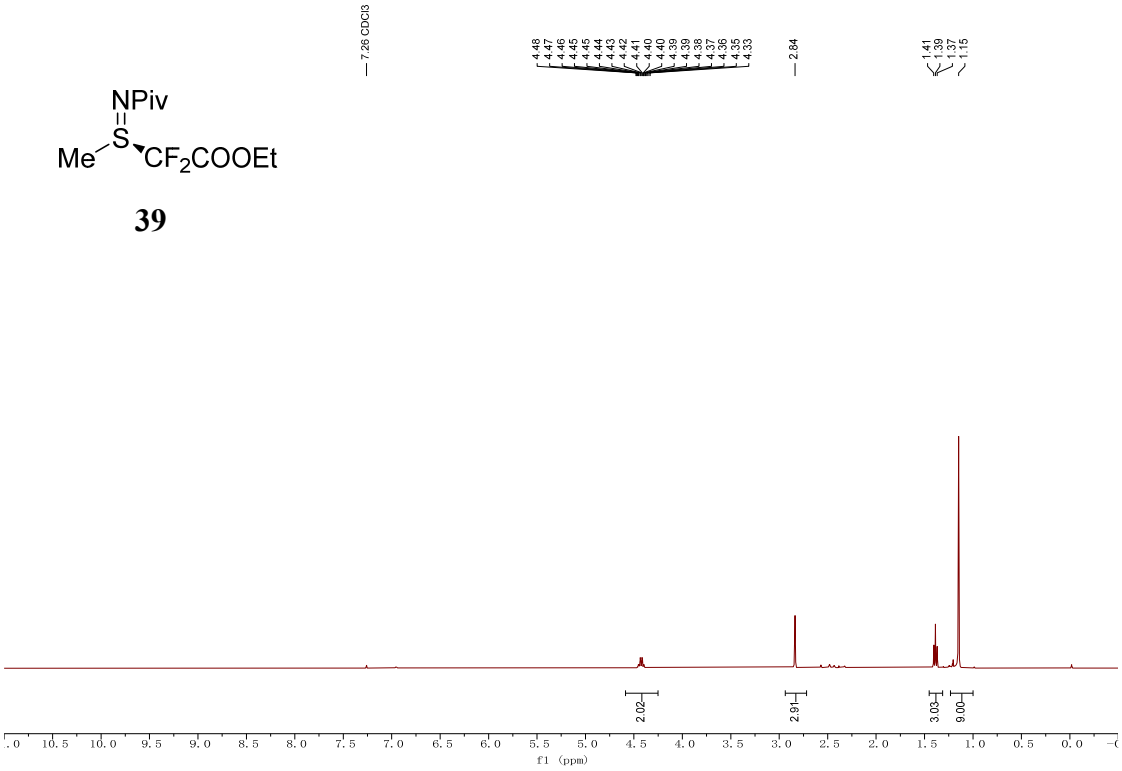
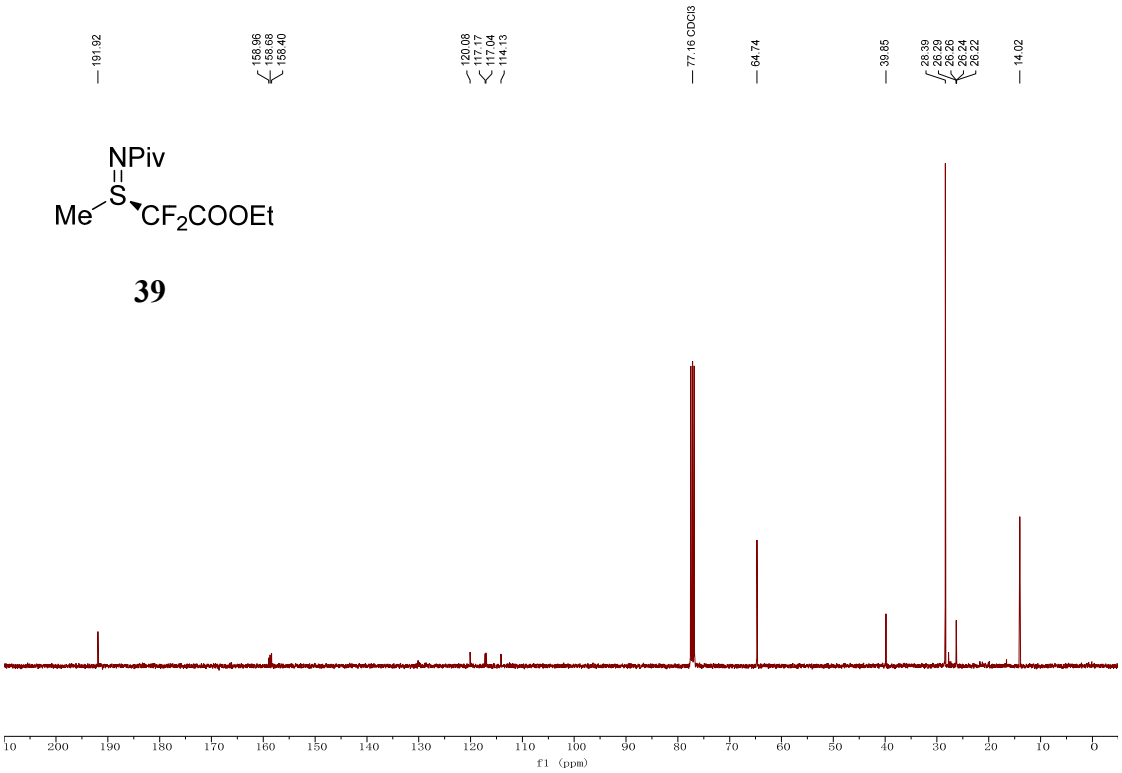


Figure S49. NMR spectra of compound **39**.

^{1}H NMR (400 MHz) spectrum of compound **39** ($CDCl_3$, 298.1 K)



^{13}C NMR (100 MHz) spectrum of compound **39** ($CDCl_3$, 298.1 K)



^{19}F NMR (376 MHz) spectrum of compound **39** ($CDCl_3$, 298.2 K)

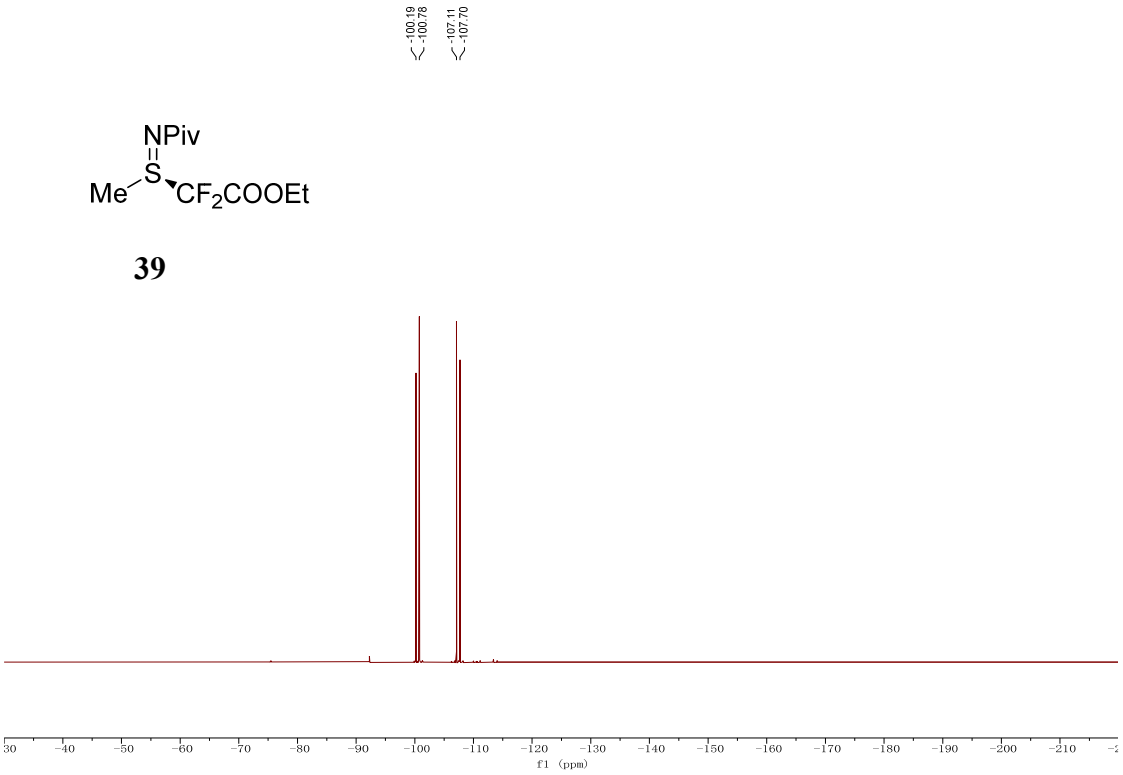
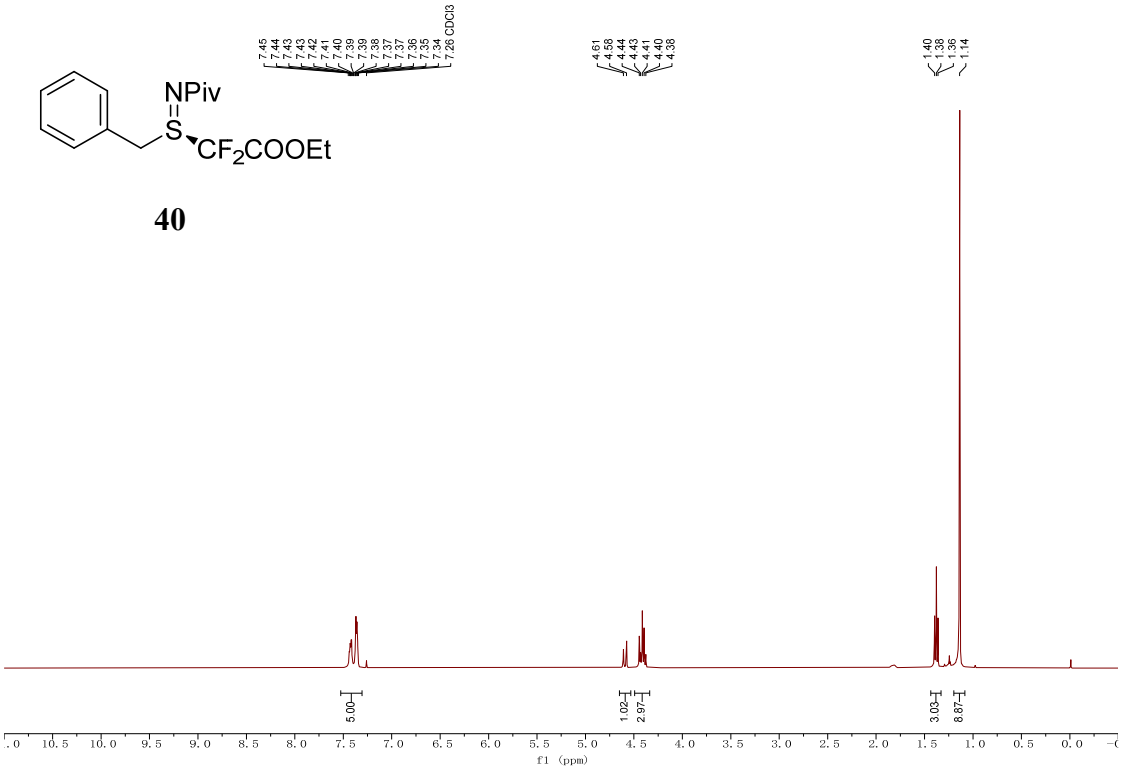
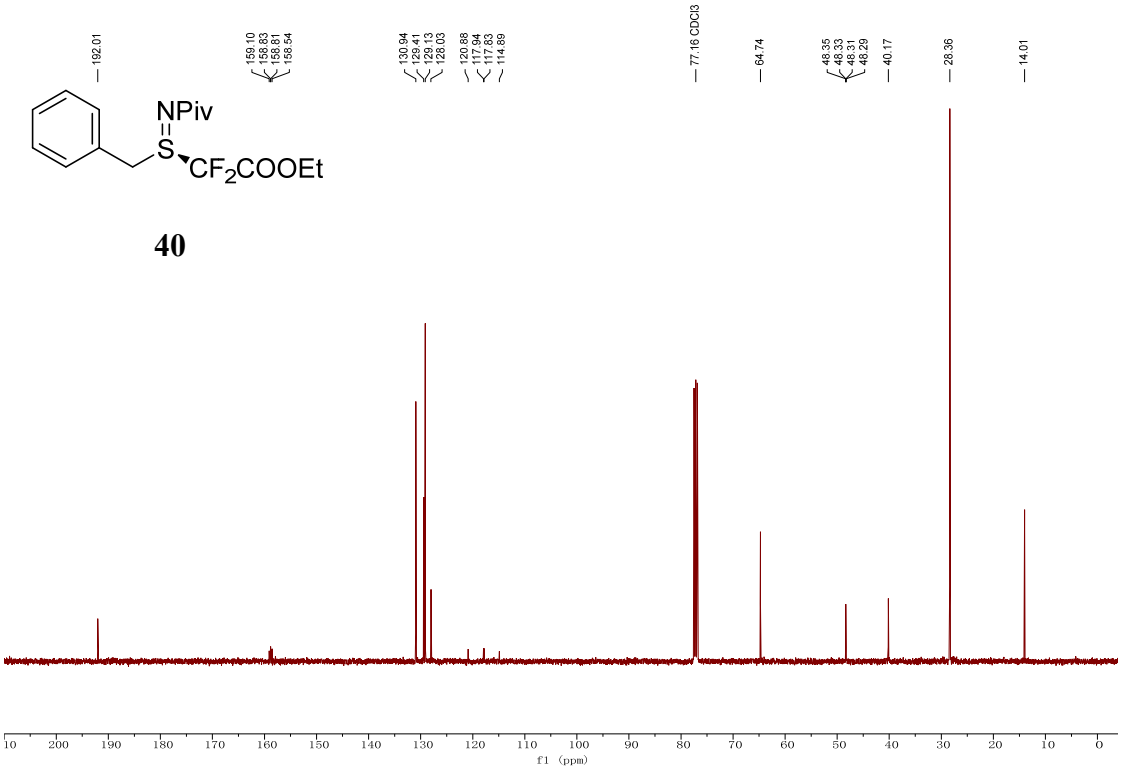


Figure S50. NMR spectra of compound **40**.

^{1}H NMR (400 MHz) spectrum of compound **40** ($CDCl_3$, 297.4 K)



^{13}C NMR (100 MHz) spectrum of compound **40** ($CDCl_3$, 297.2 K)



^{19}F NMR (376 MHz) spectrum of compound **40** ($CDCl_3$, 297.2 K)

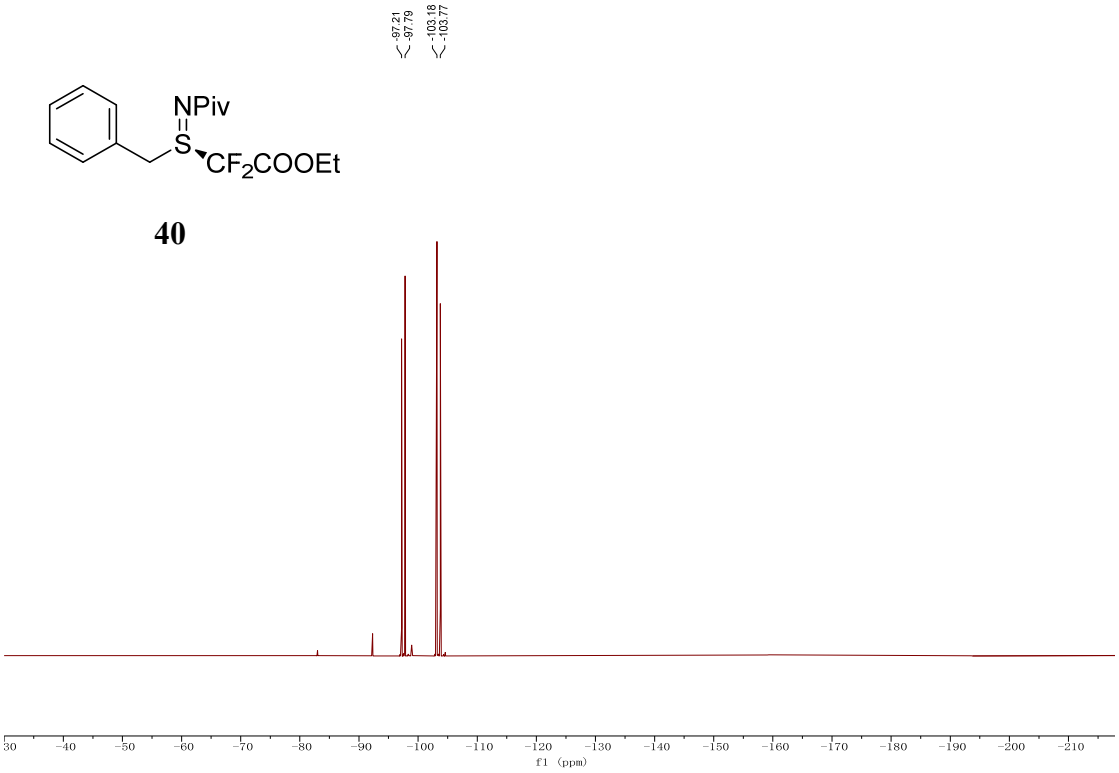
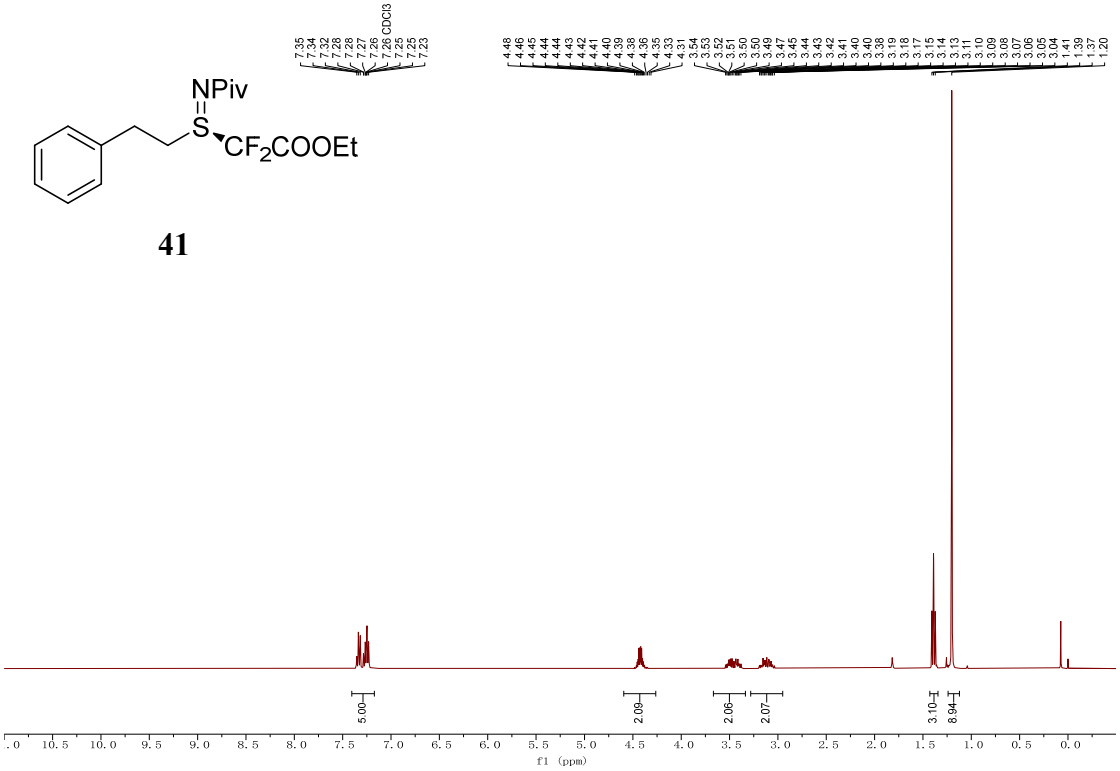
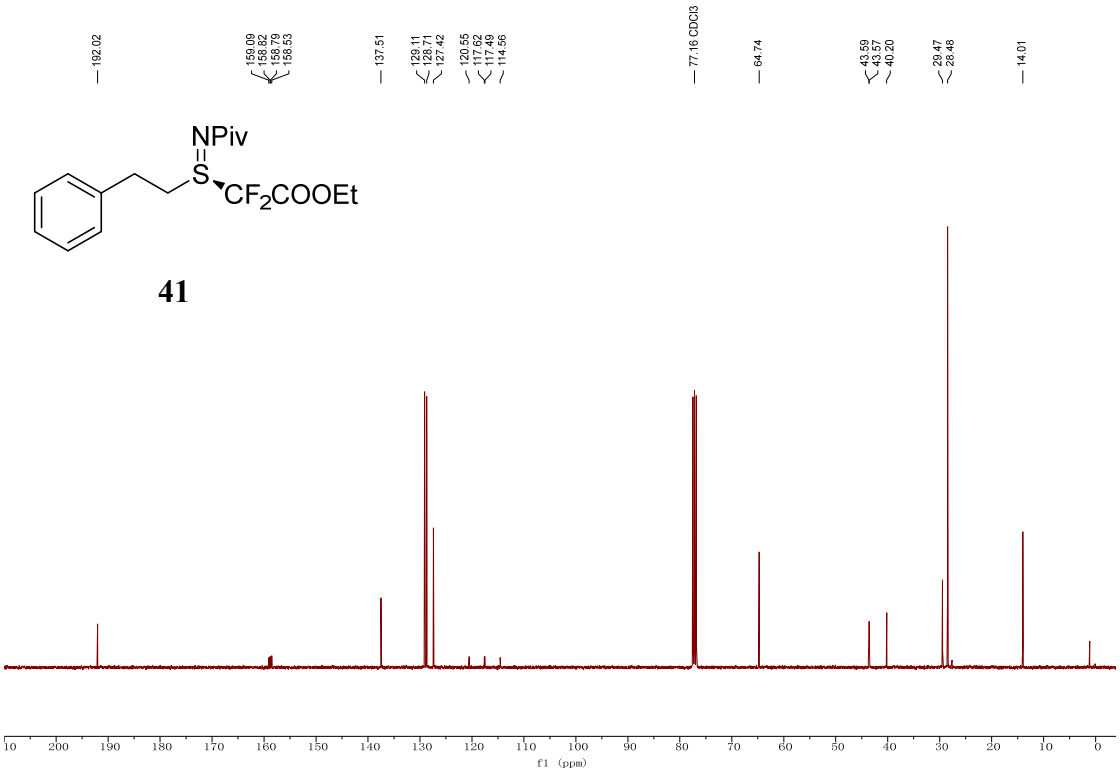


Figure S51. NMR spectra of compound **41**.

^{1}H NMR (400 MHz) spectrum of compound **41** ($CDCl_3$, 298.2 K)



^{13}C NMR (100 MHz) spectrum of compound **41** ($CDCl_3$, 298.2 K)



^{19}F NMR (376 MHz) spectrum of compound **41** ($CDCl_3$, 298.1 K)

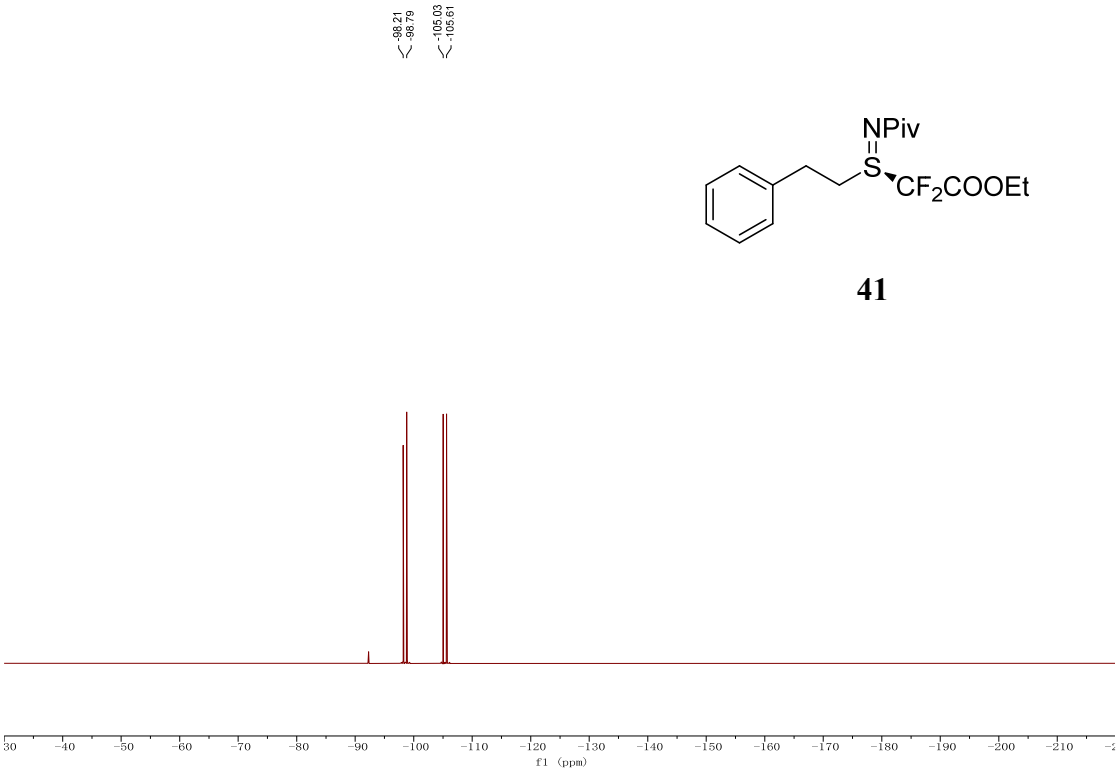
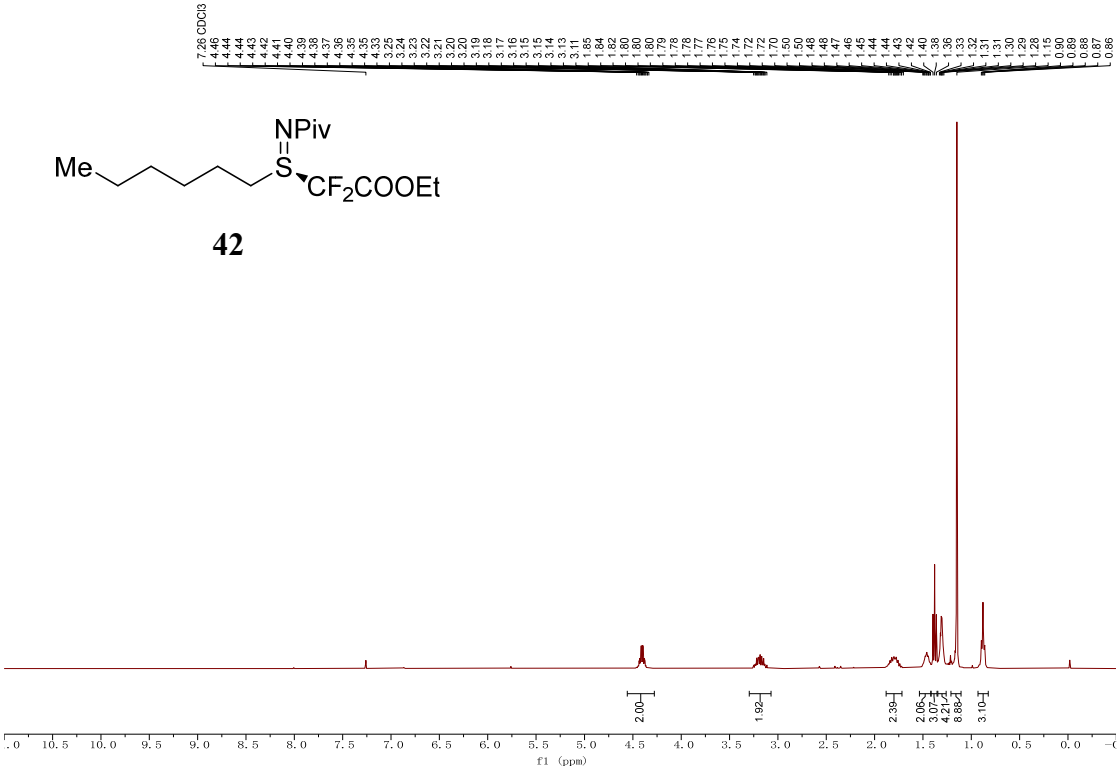
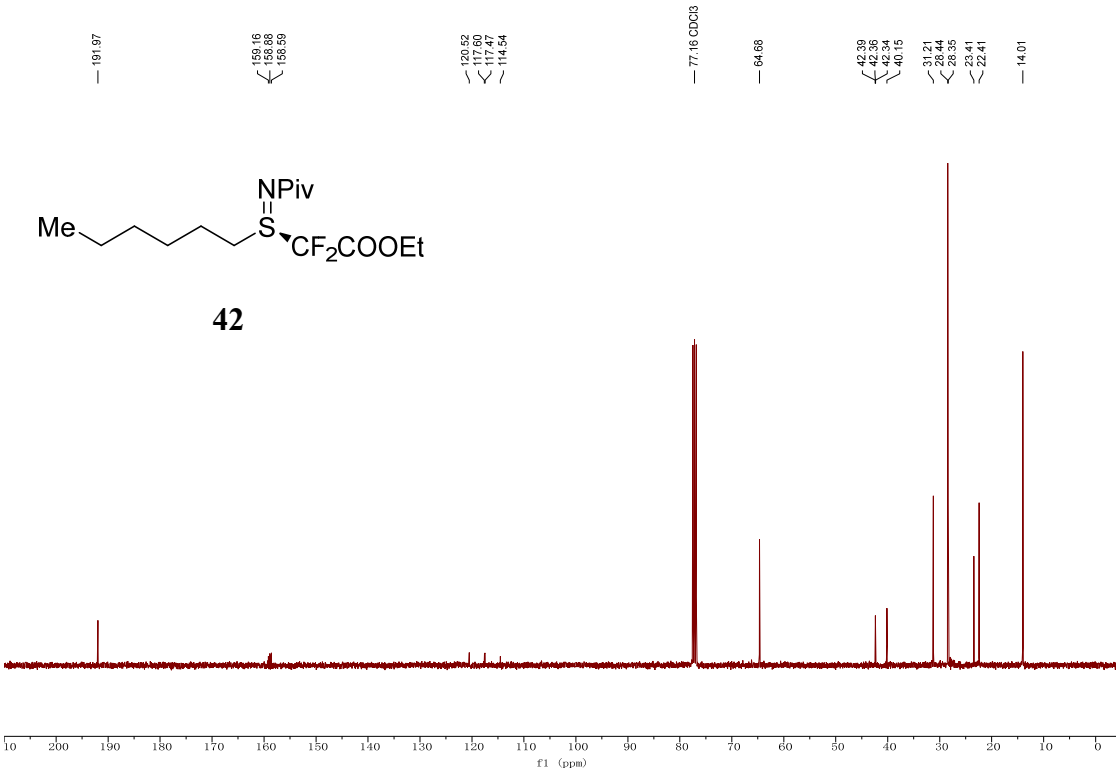


Figure S52. NMR spectra of compound **42**.

^{1}H NMR (400 MHz) spectrum of compound **42** ($CDCl_3$, 298.2 K)



^{13}C NMR (100 MHz) spectrum of compound **42** ($CDCl_3$, 298.1 K)



^{19}F NMR (376 MHz) spectrum of compound **42** ($CDCl_3$, 298.2 K)

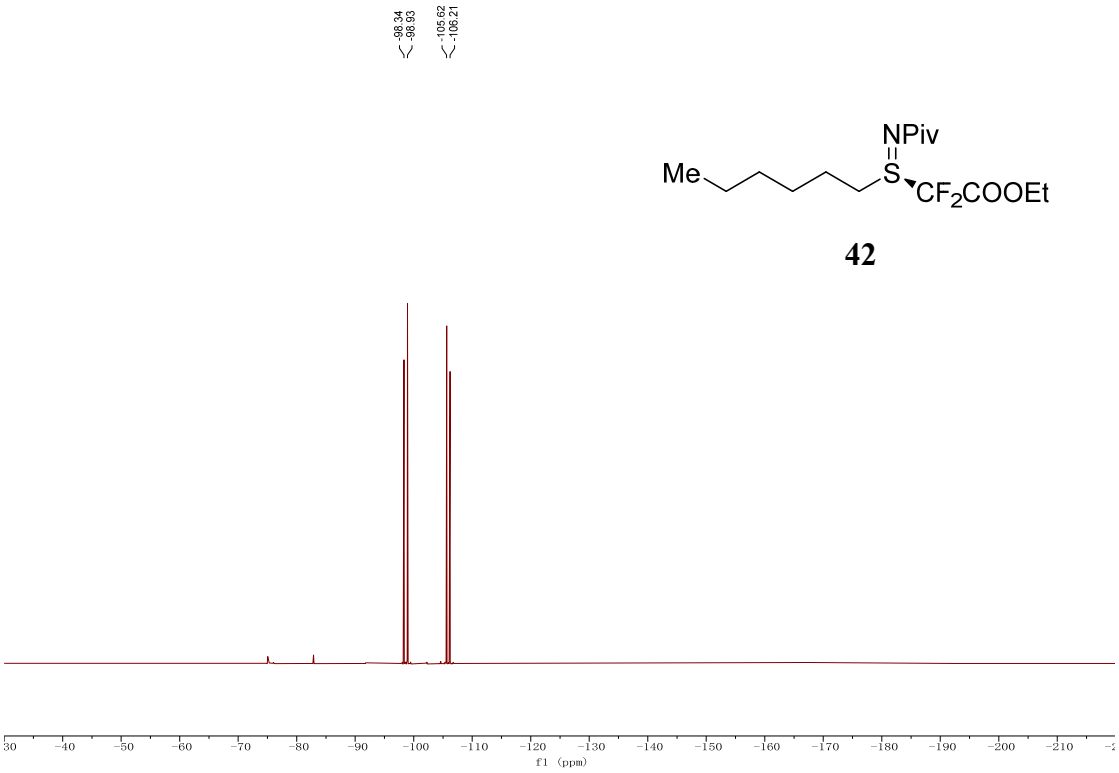
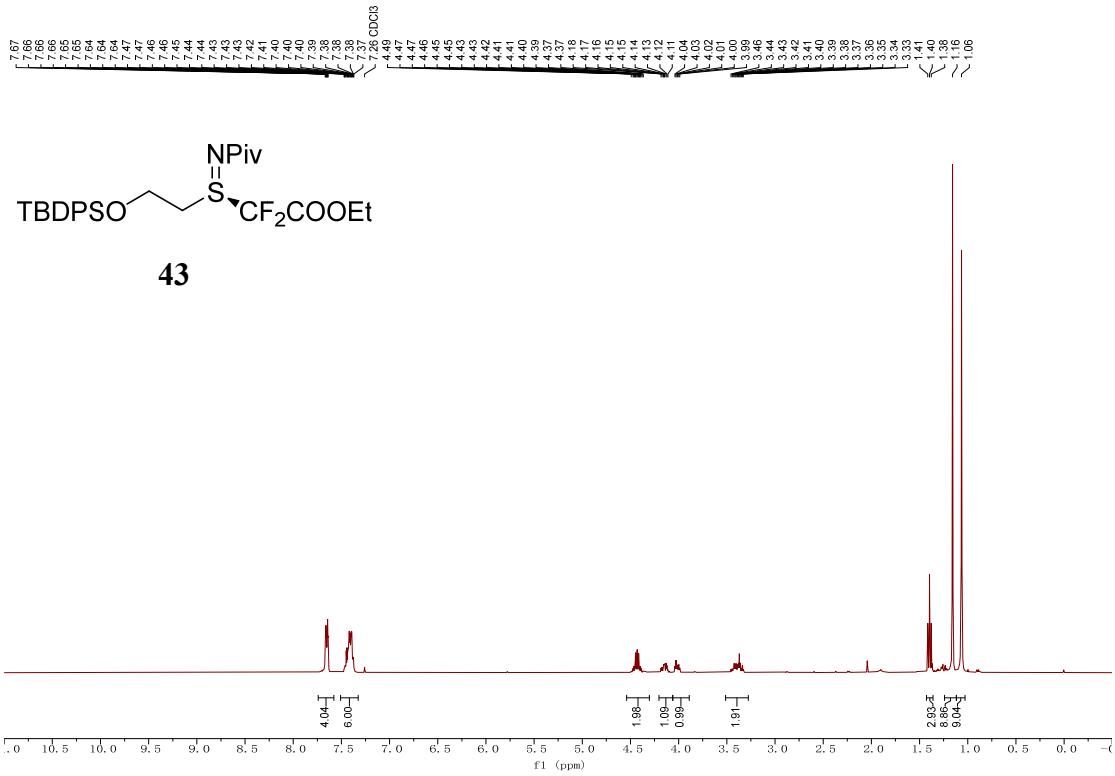
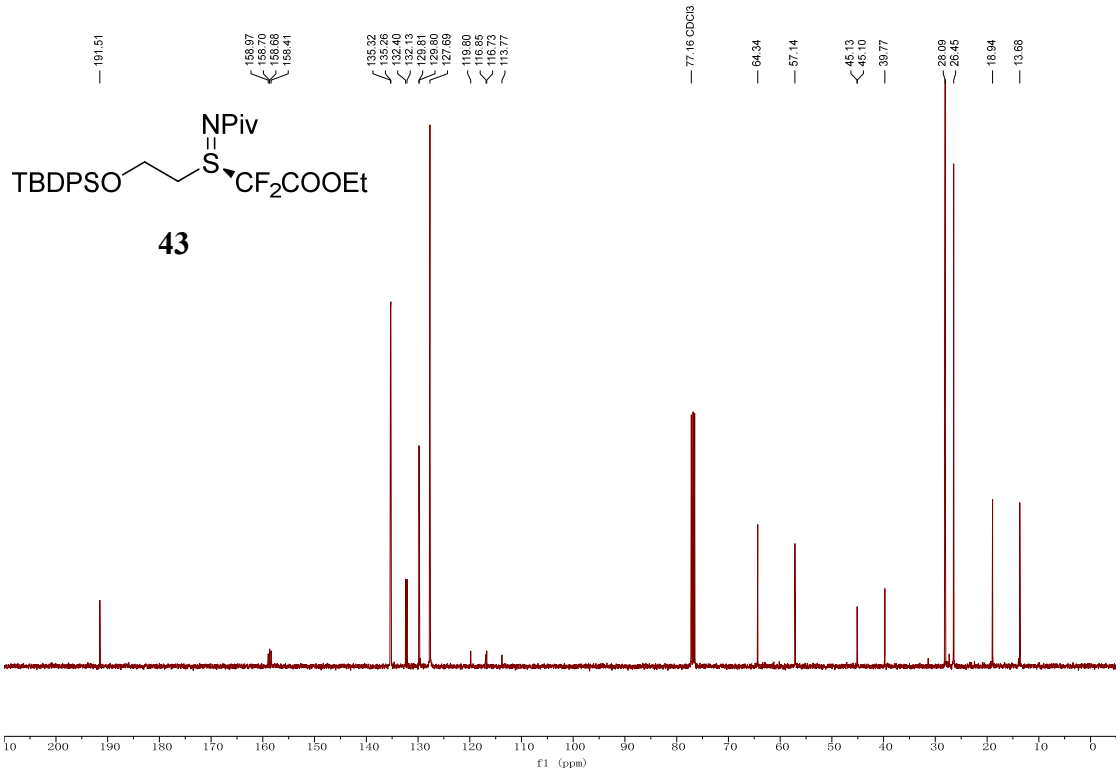


Figure S53. NMR spectra of compound **43**.

^{1}H NMR (400 MHz) spectrum of compound **43** ($CDCl_3$, 295.6 K)



^{13}C NMR (100 MHz) spectrum of compound **43** ($CDCl_3$, 295.7 K)



^{19}F NMR (376 MHz) spectrum of compound **43** ($CDCl_3$, 295.6 K)

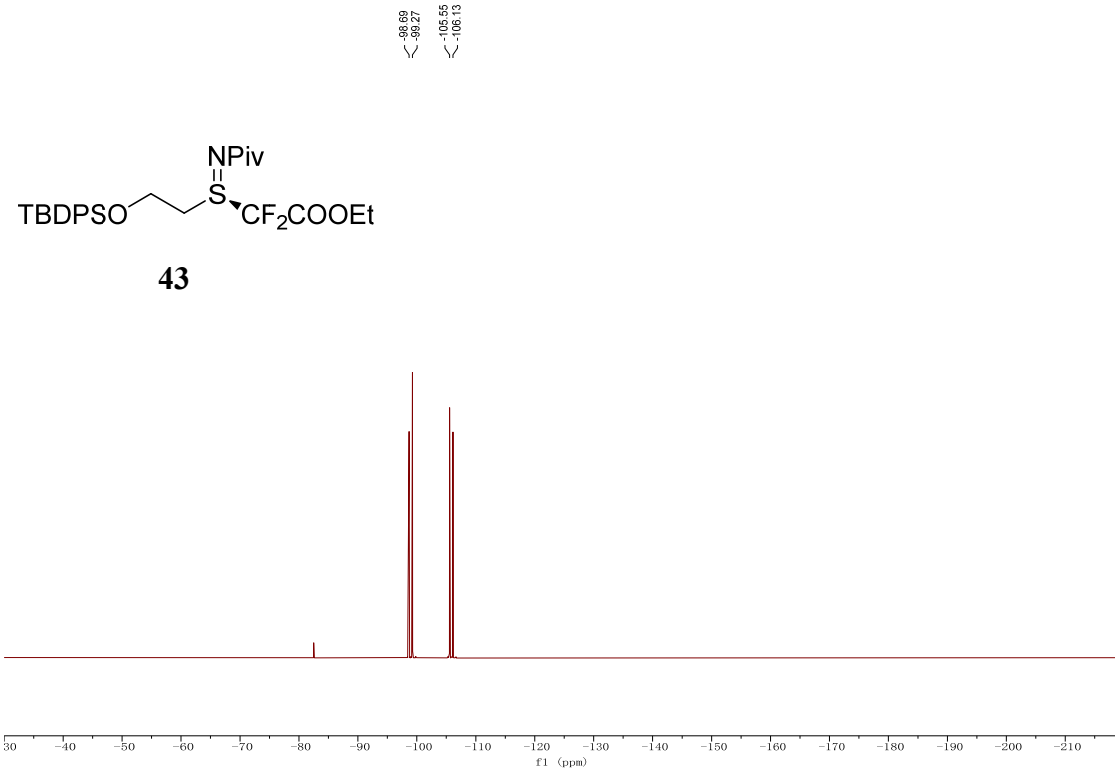
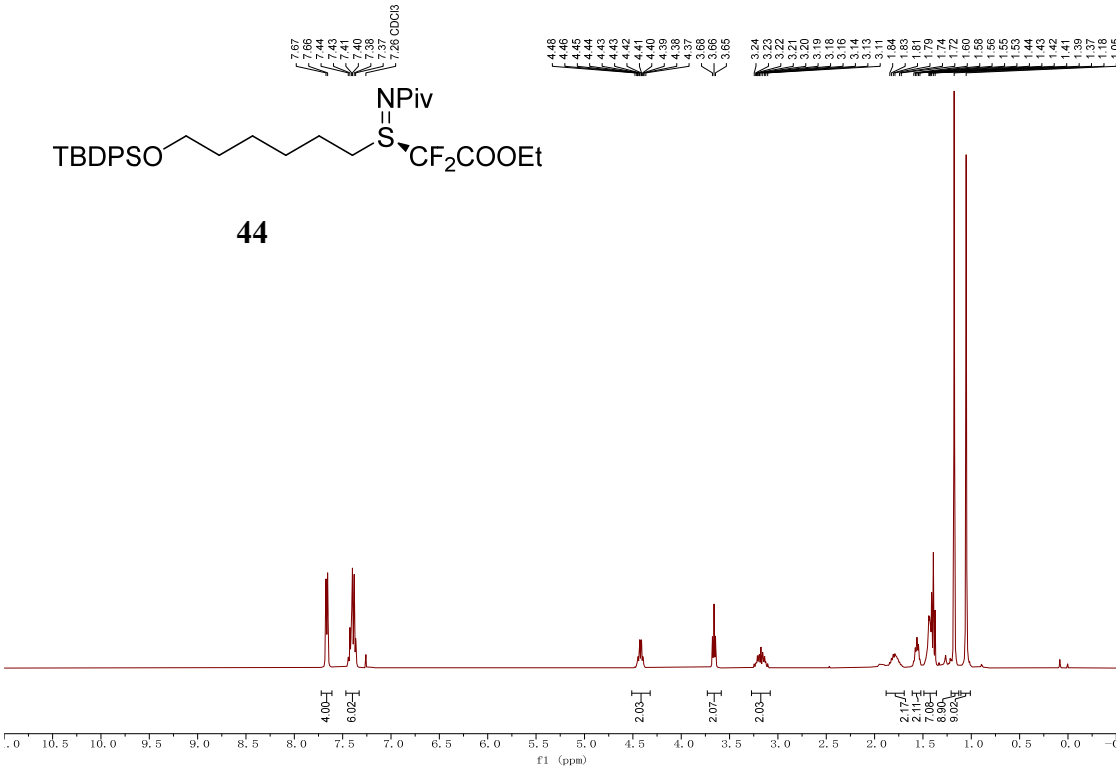
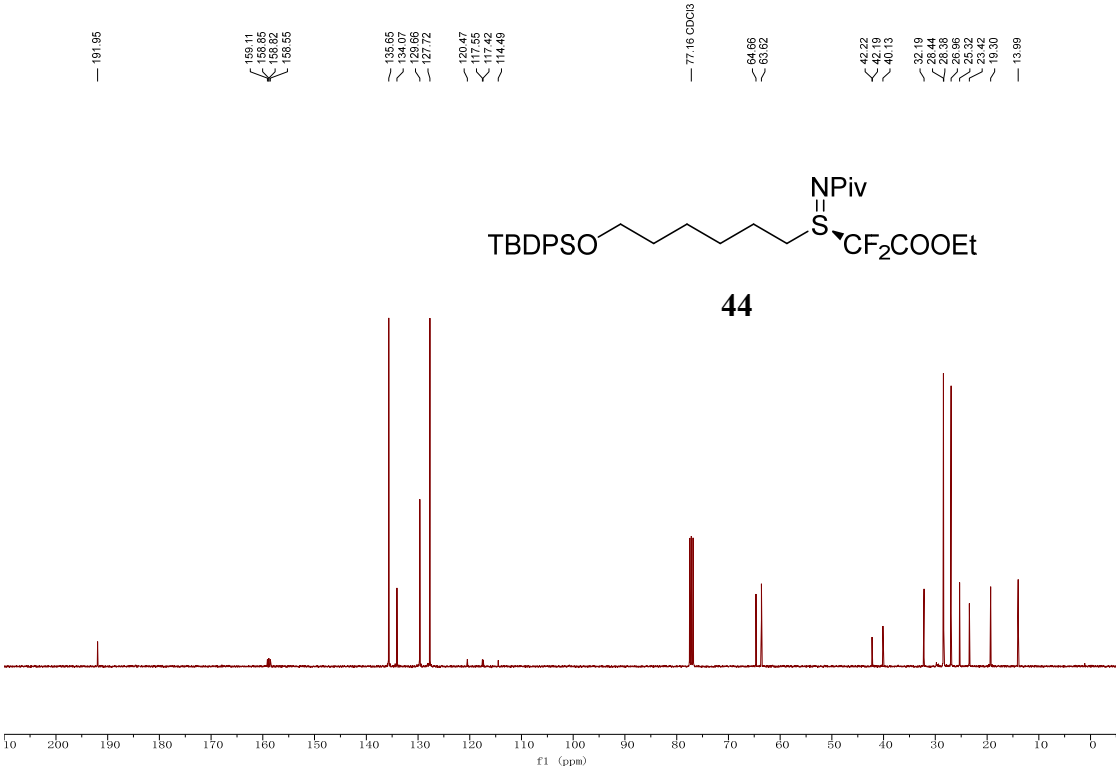


Figure S54. NMR spectra of compound **44**.

^{1}H NMR (400 MHz) spectrum of compound **44** ($CDCl_3$, 296.2 K)



^{13}C NMR (100 MHz) spectrum of compound **44** ($CDCl_3$, 296.3 K)



^{19}F NMR (376 MHz) spectrum of compound **44** ($CDCl_3$, 296.5 K)

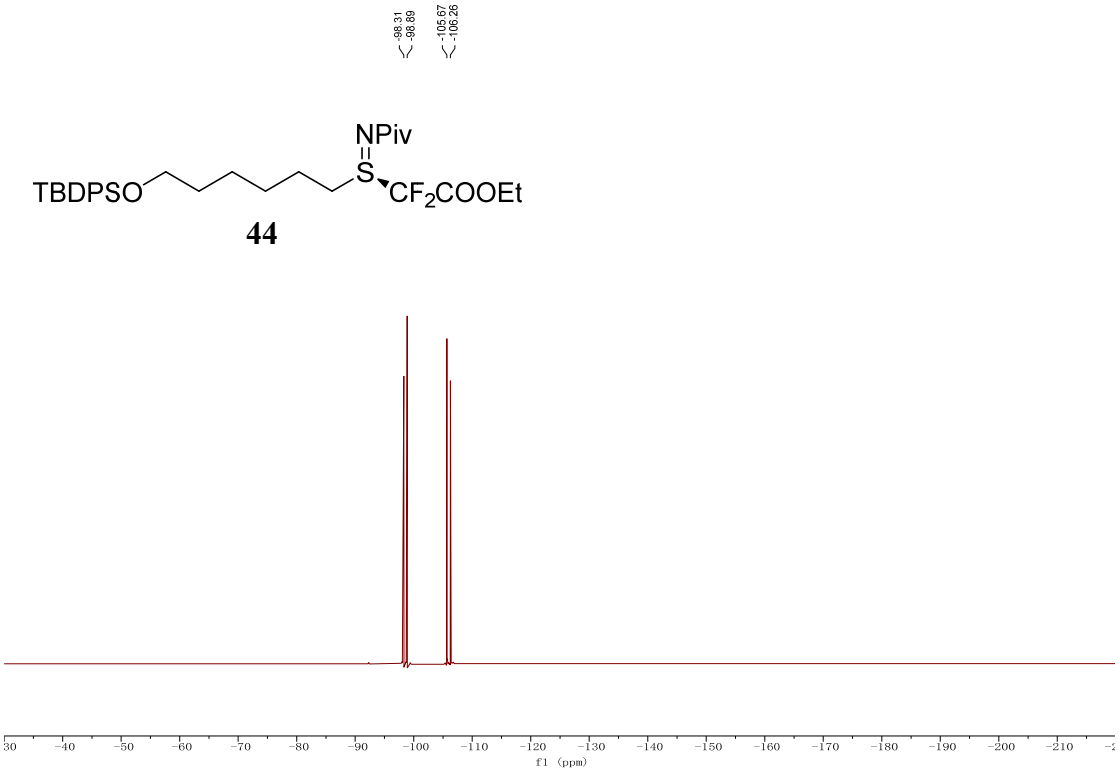
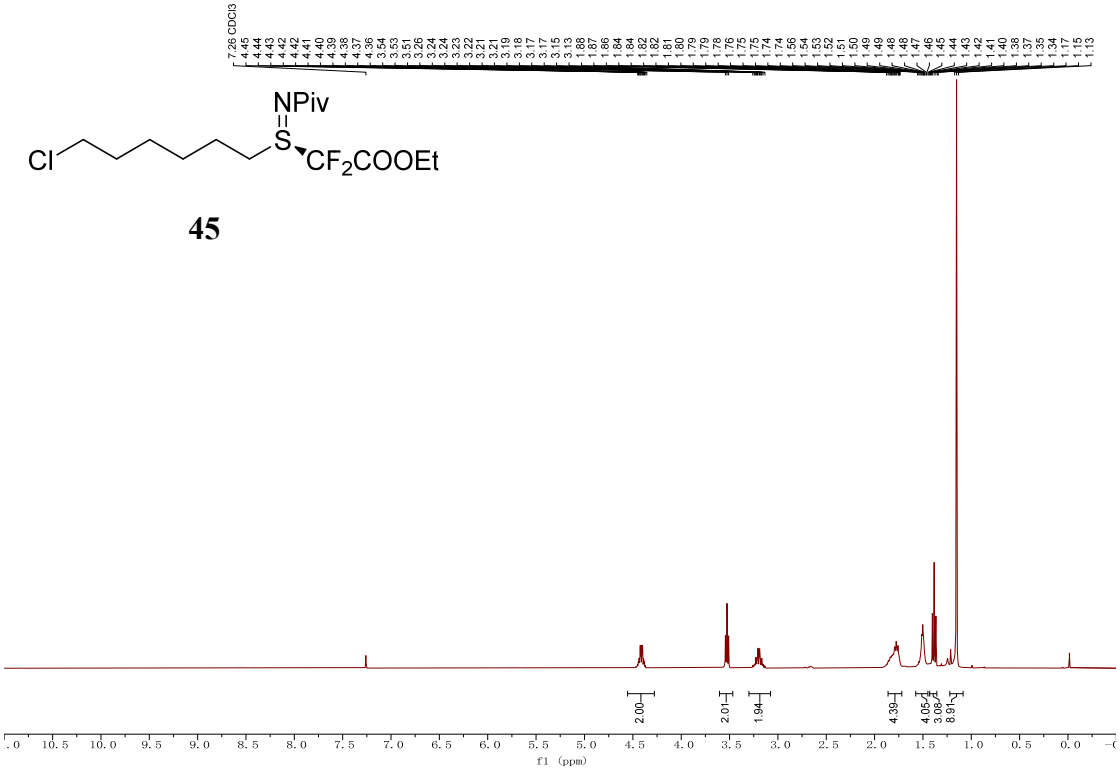
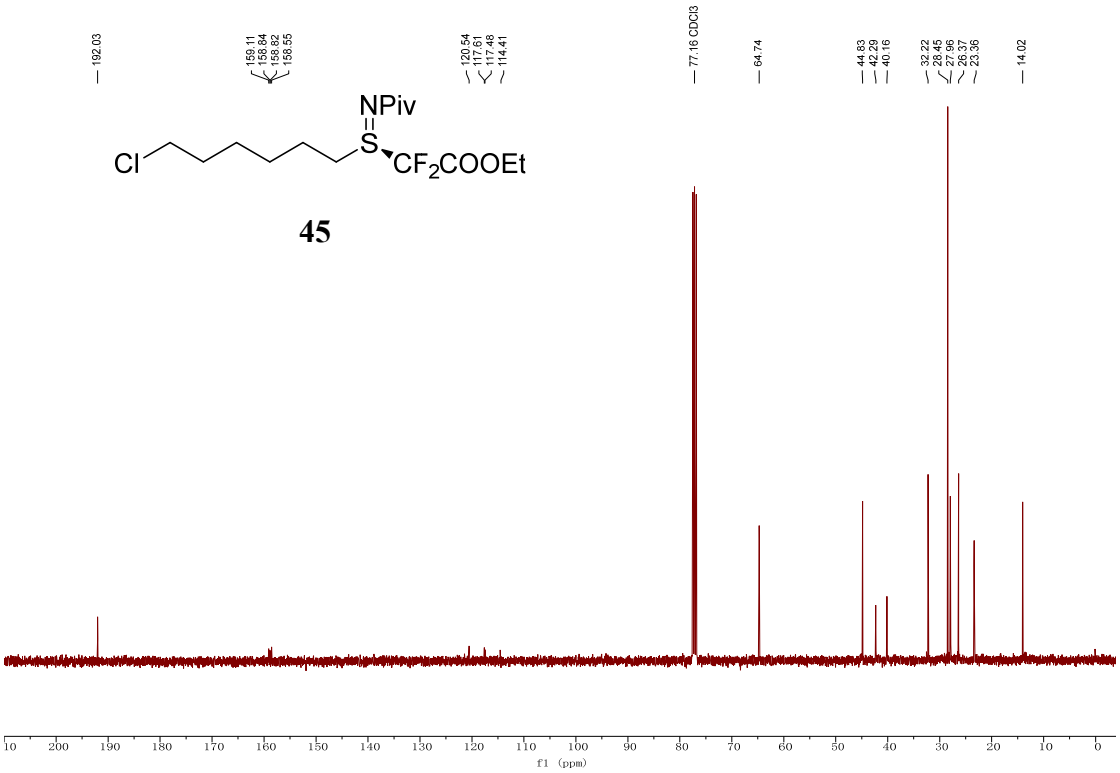


Figure S55. NMR spectra of compound **45**.

^{1}H NMR (400 MHz) spectrum of compound **45** ($CDCl_3$, 296.2 K)



^{13}C NMR (100 MHz) spectrum of compound **45** ($CDCl_3$, 296.4 K)



^{19}F NMR (376 MHz) spectrum of compound **45** ($CDCl_3$, 296.4 K)

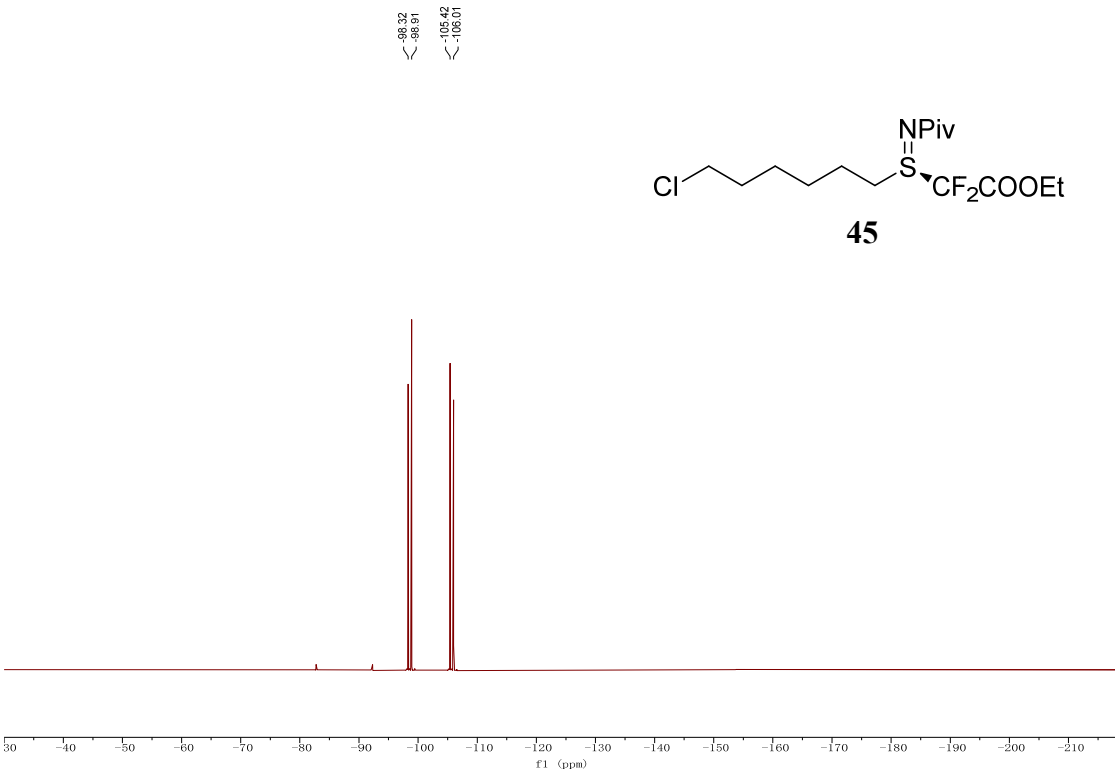
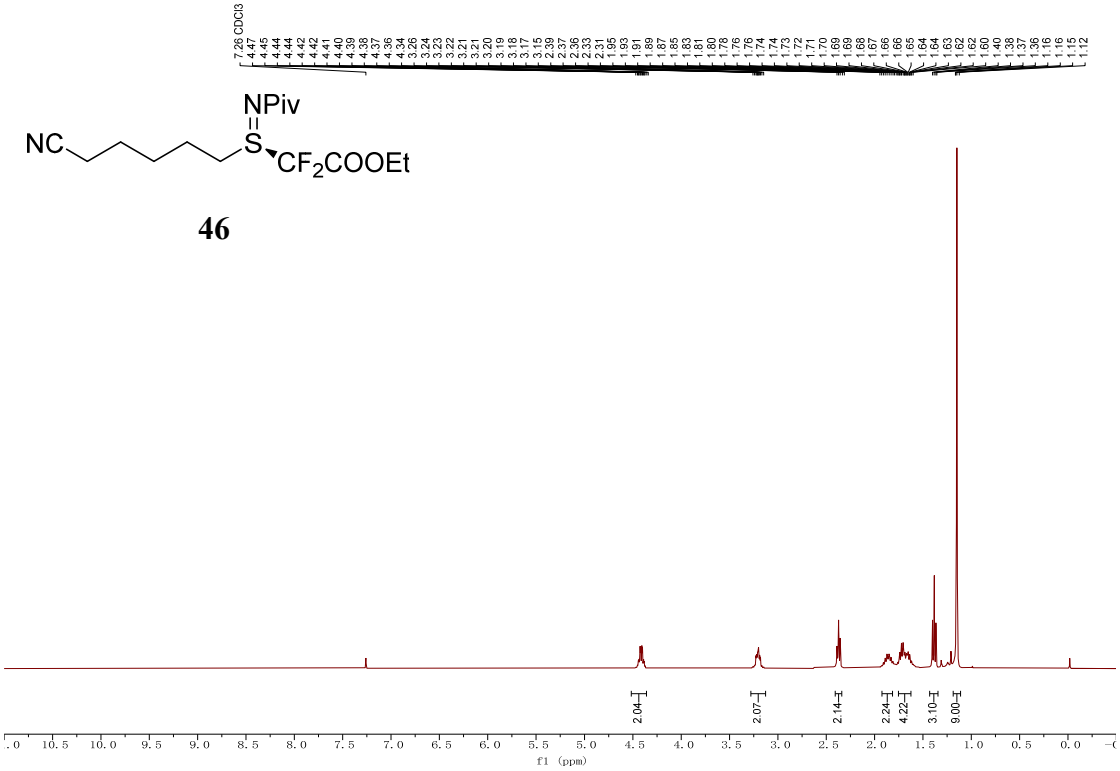
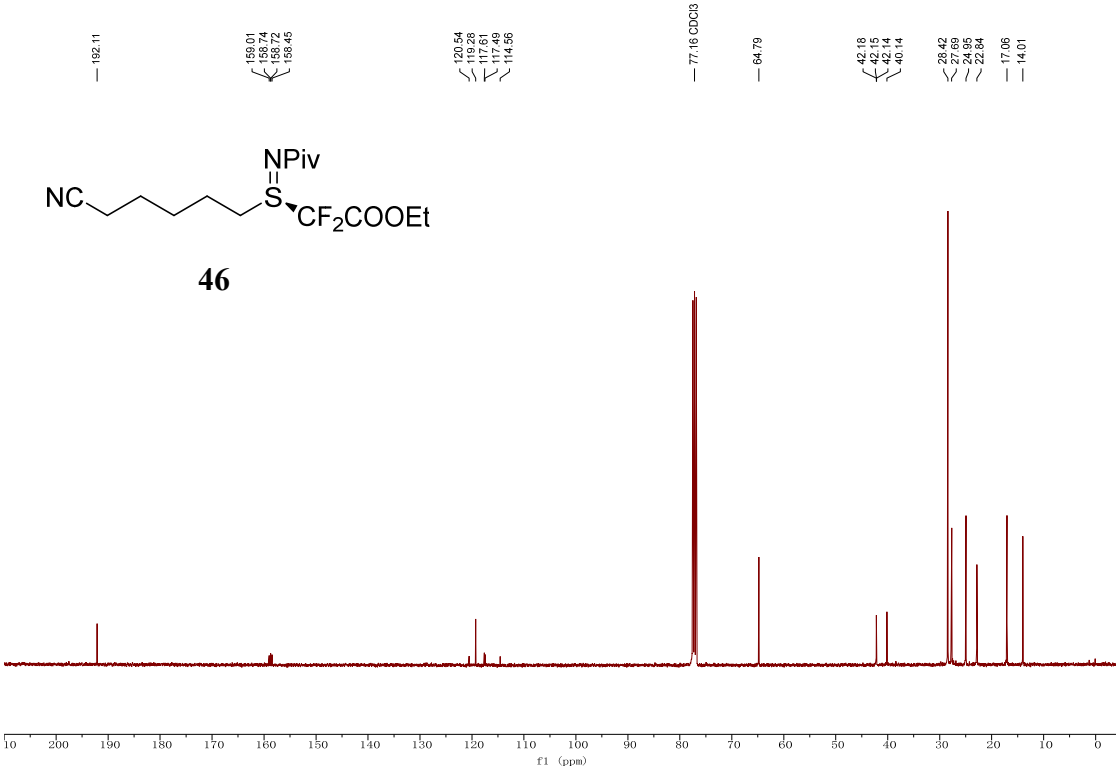


Figure S56. NMR spectra of compound **46**.

^{1}H NMR (400 MHz) spectrum of compound **46** ($CDCl_3$, 297.1 K)



^{13}C NMR (100 MHz) spectrum of compound **46** ($CDCl_3$, 297.2 K)



^{19}F NMR (376 MHz) spectrum of compound **46** ($CDCl_3$, 297.8 K)

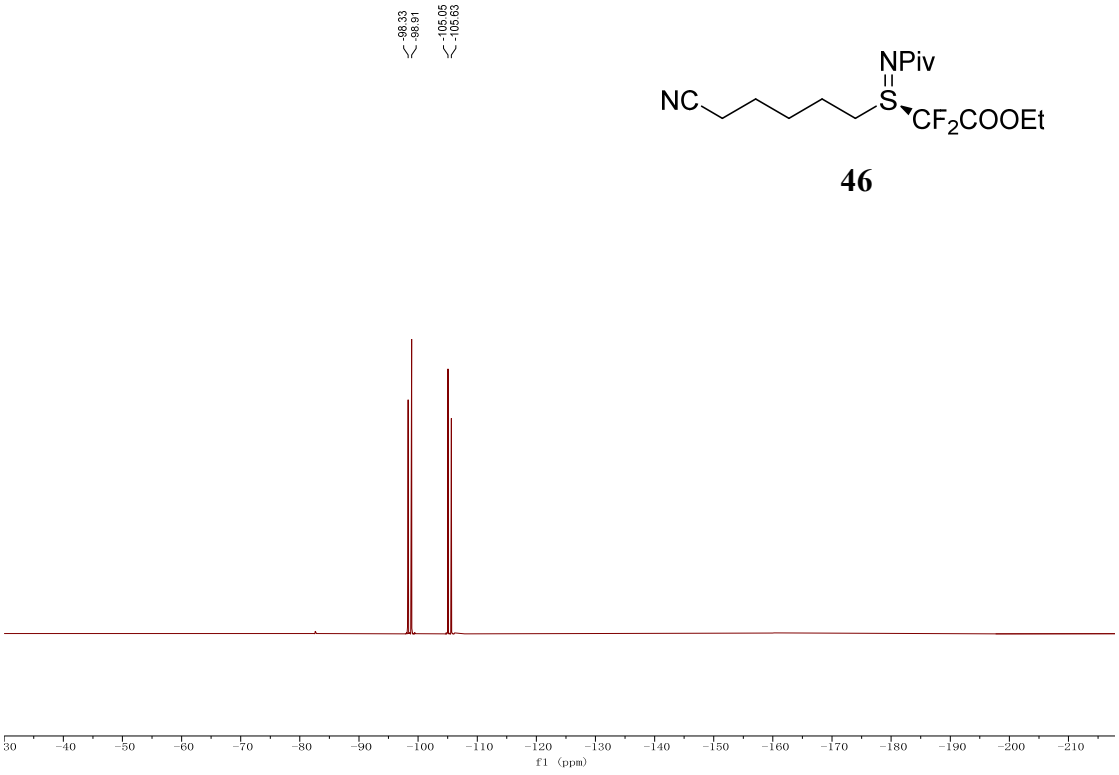
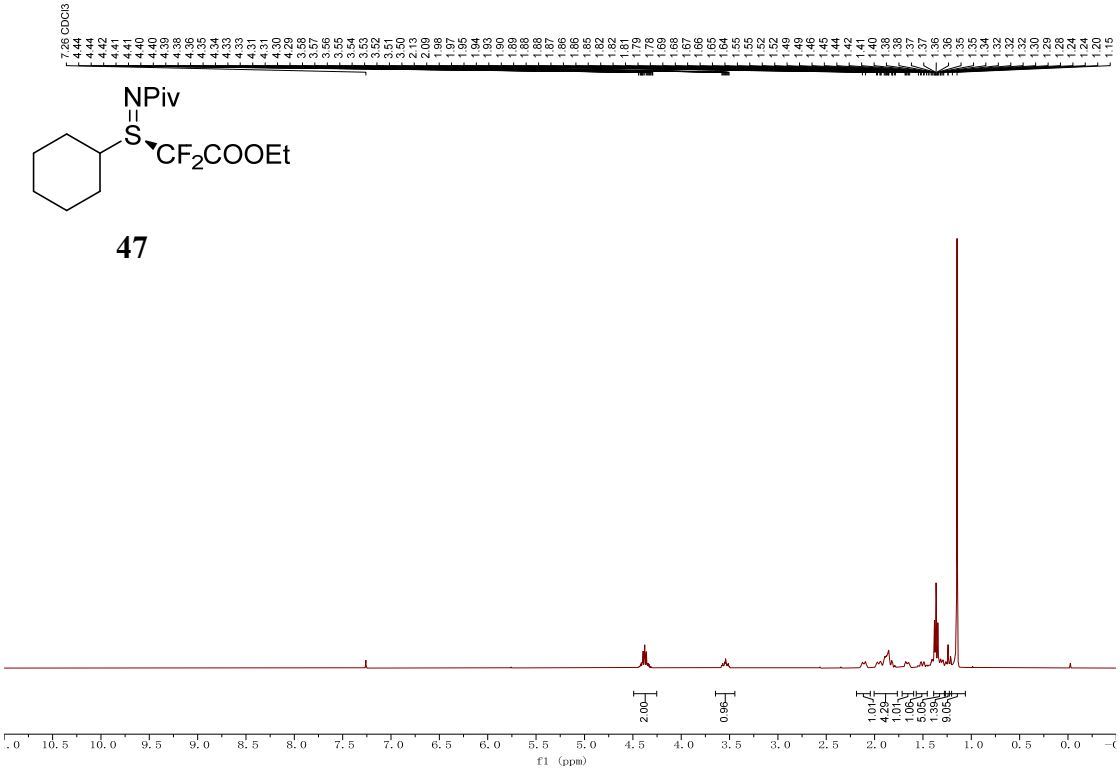
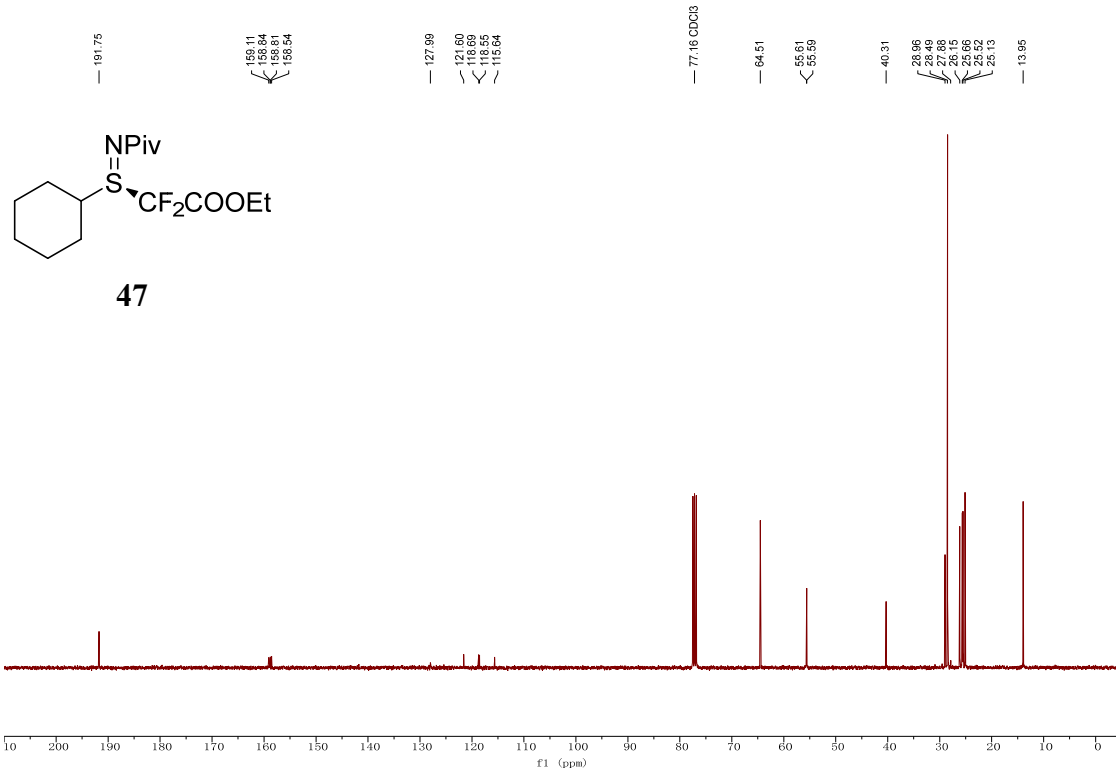


Figure S57. NMR spectra of compound **47**.

^{1}H NMR (400 MHz) spectrum of compound **47** ($CDCl_3$, 298.2 K)



^{13}C NMR (100 MHz) spectrum of compound **47** ($CDCl_3$, 298.2)



^{19}F NMR (376 MHz) spectrum of compound **47** ($CDCl_3$, 298.1)

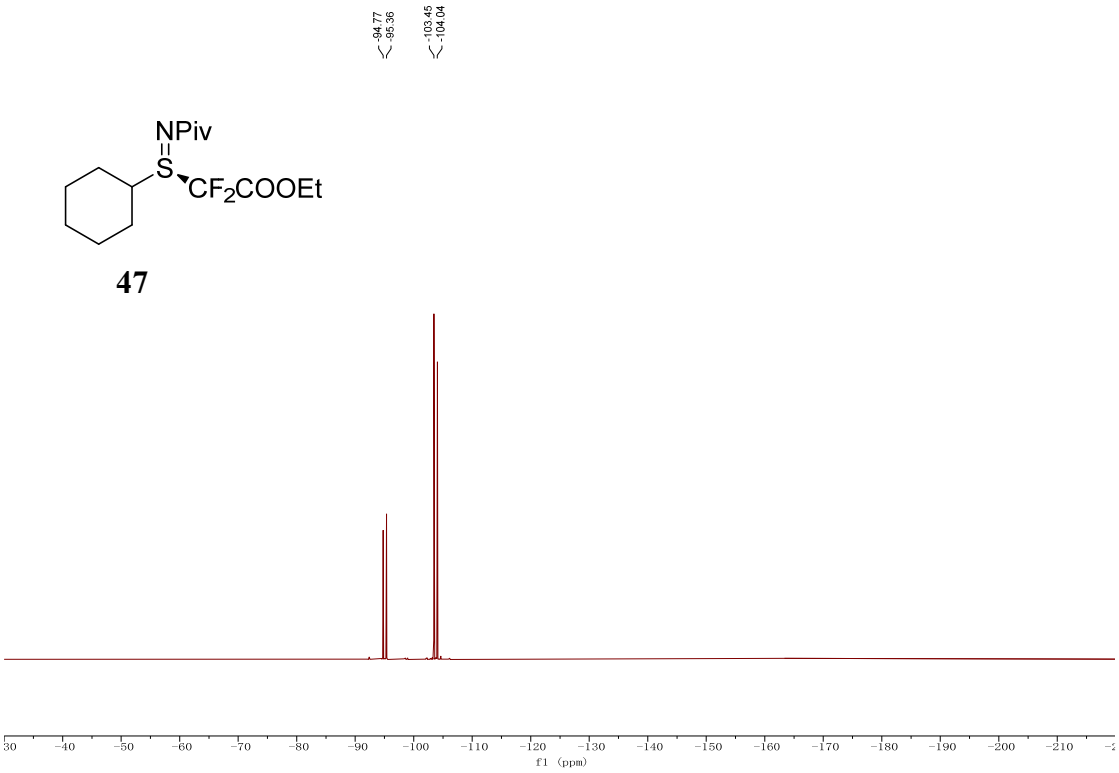
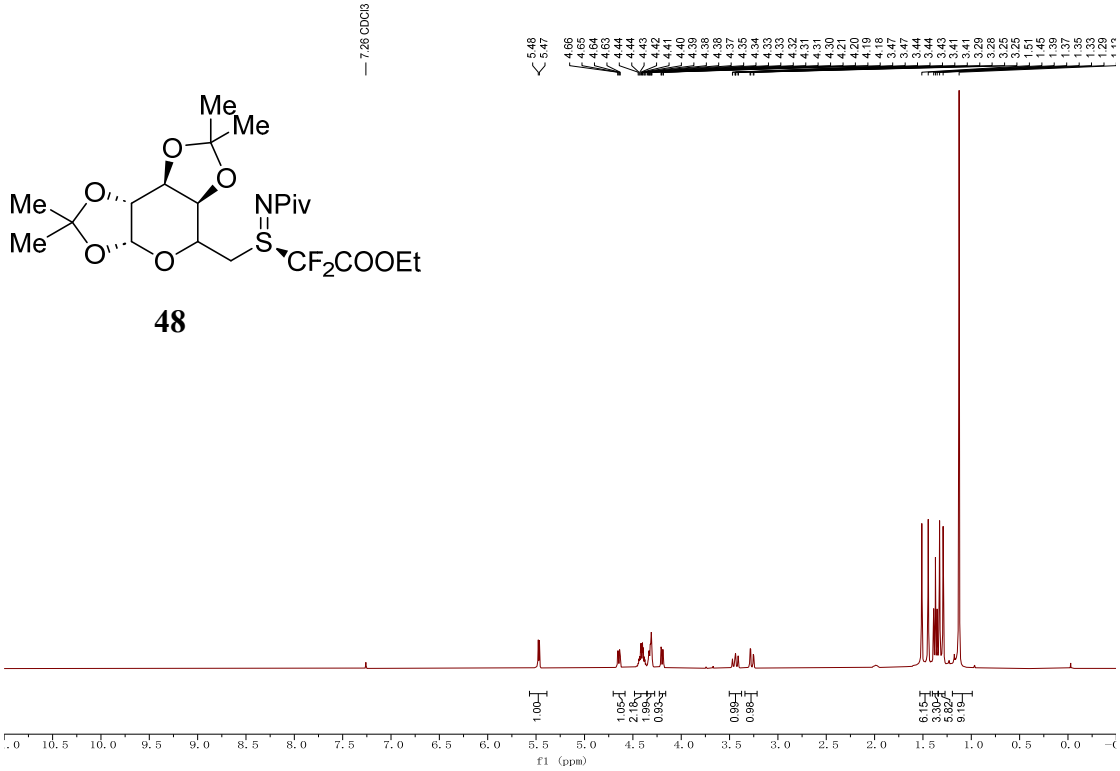
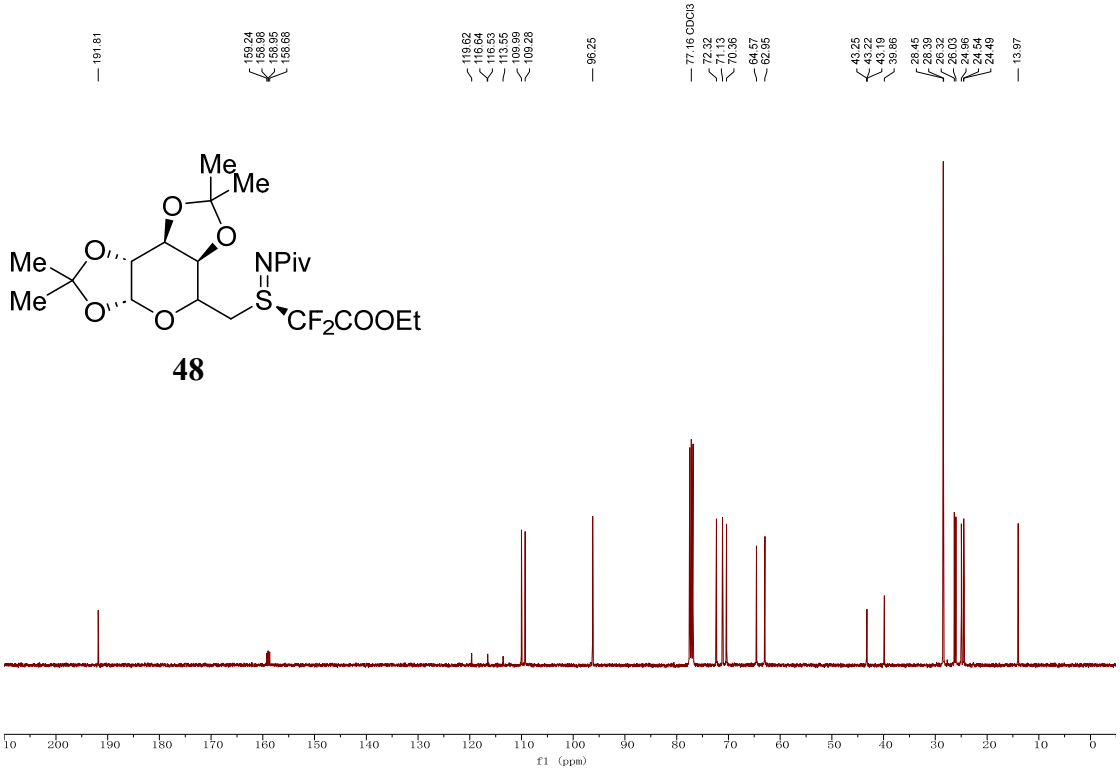


Figure S58. NMR spectra of compound **48**.

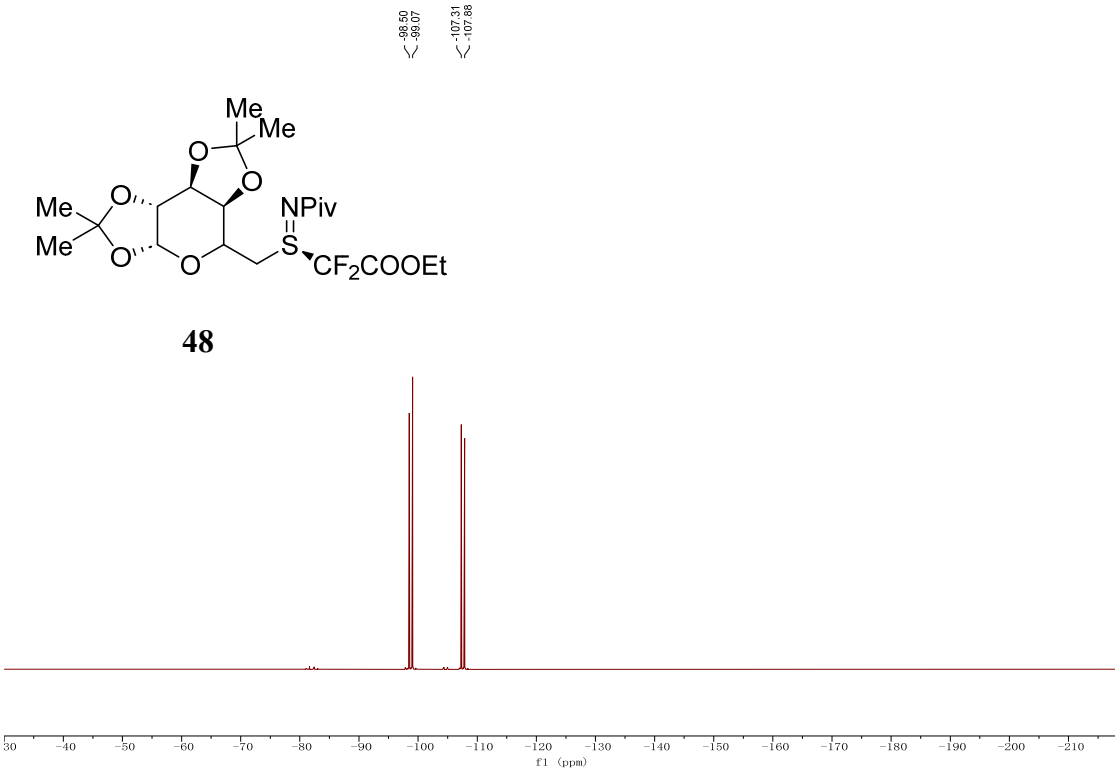
^{1}H NMR (400 MHz) spectrum of compound **48** ($CDCl_3$, 300.0 K)



^{13}C NMR (100 MHz) spectrum of compound **48** ($CDCl_3$, 300.1 K)



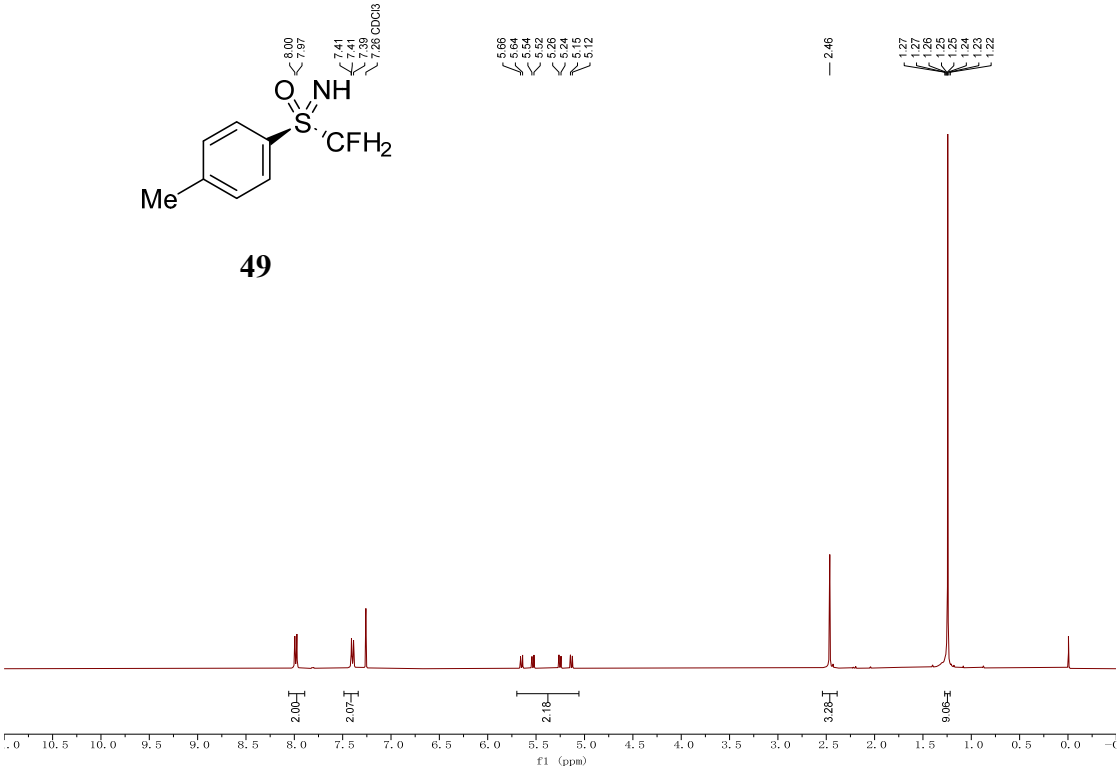
^{19}F NMR (376 MHz) spectrum of compound **48** ($CDCl_3$, 300.5 K)



48

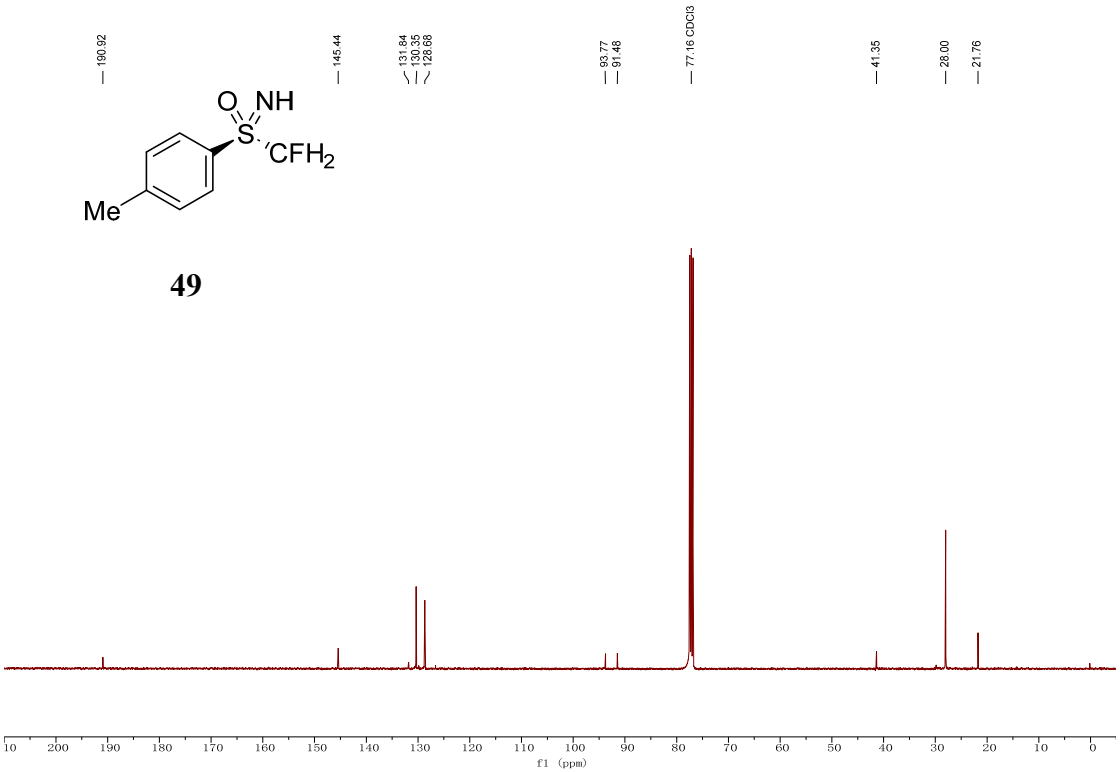
Figure S59. NMR spectra of compound **49**.

^{1}H NMR (400 MHz) spectrum of compound **49** ($CDCl_3$, 295.0 K)



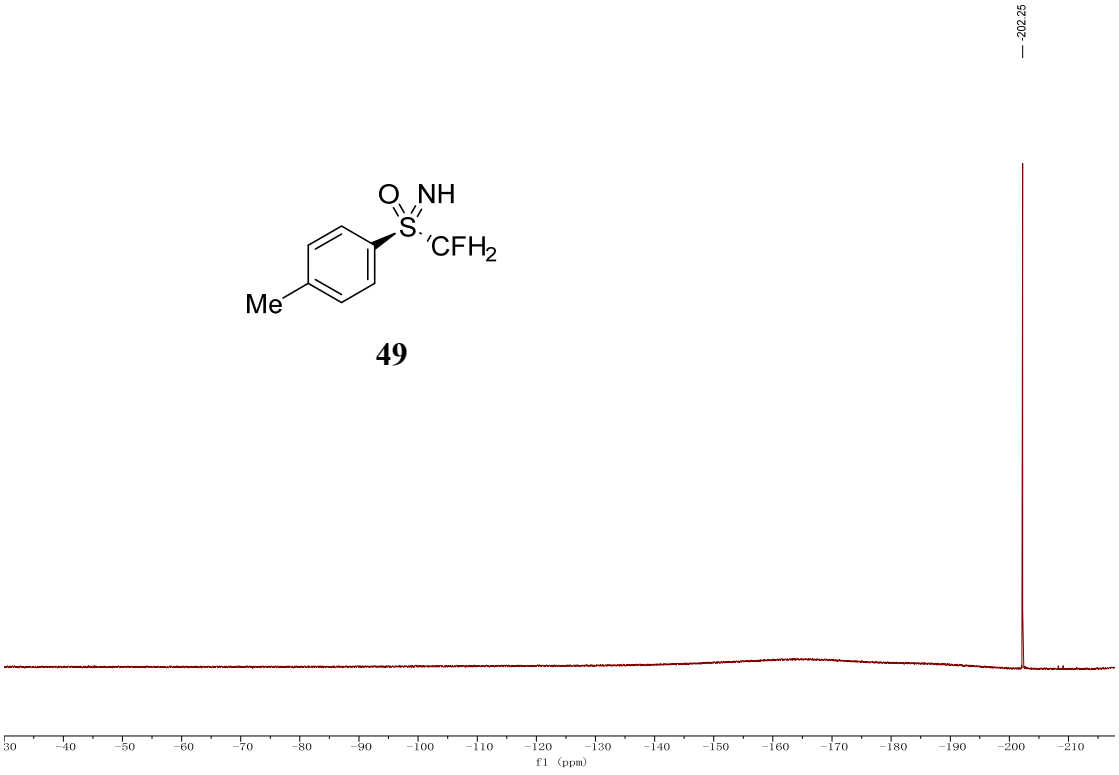
49

^{13}C NMR (100 MHz) spectrum of compound **49** ($CDCl_3$, 295.1 K)



49

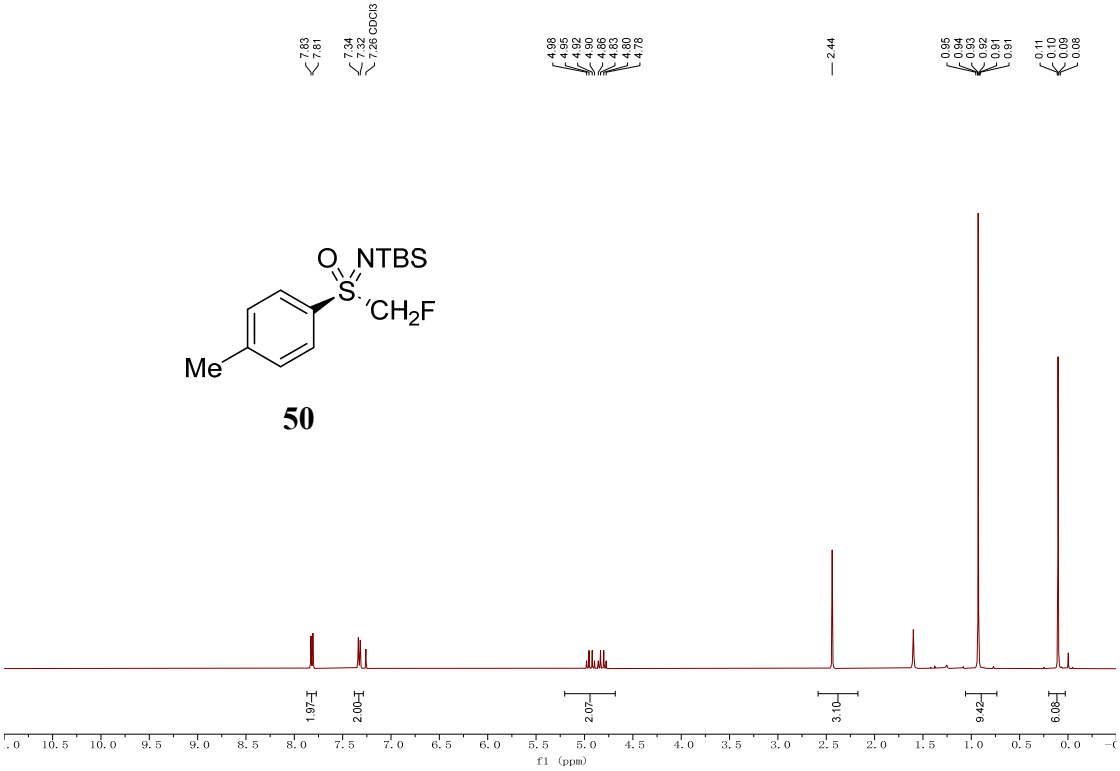
^{19}F NMR (376 MHz) spectrum of compound **49** ($CDCl_3$, 294.1 K)



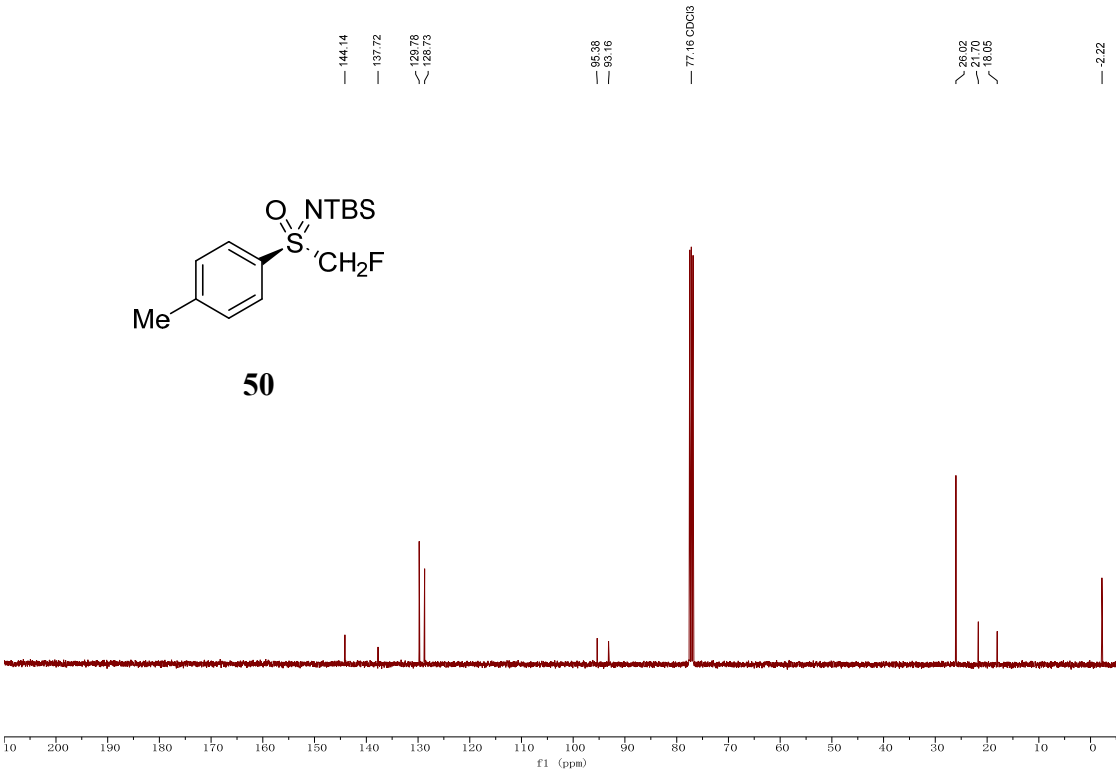
49

Figure S60. NMR spectra of compound **50**.

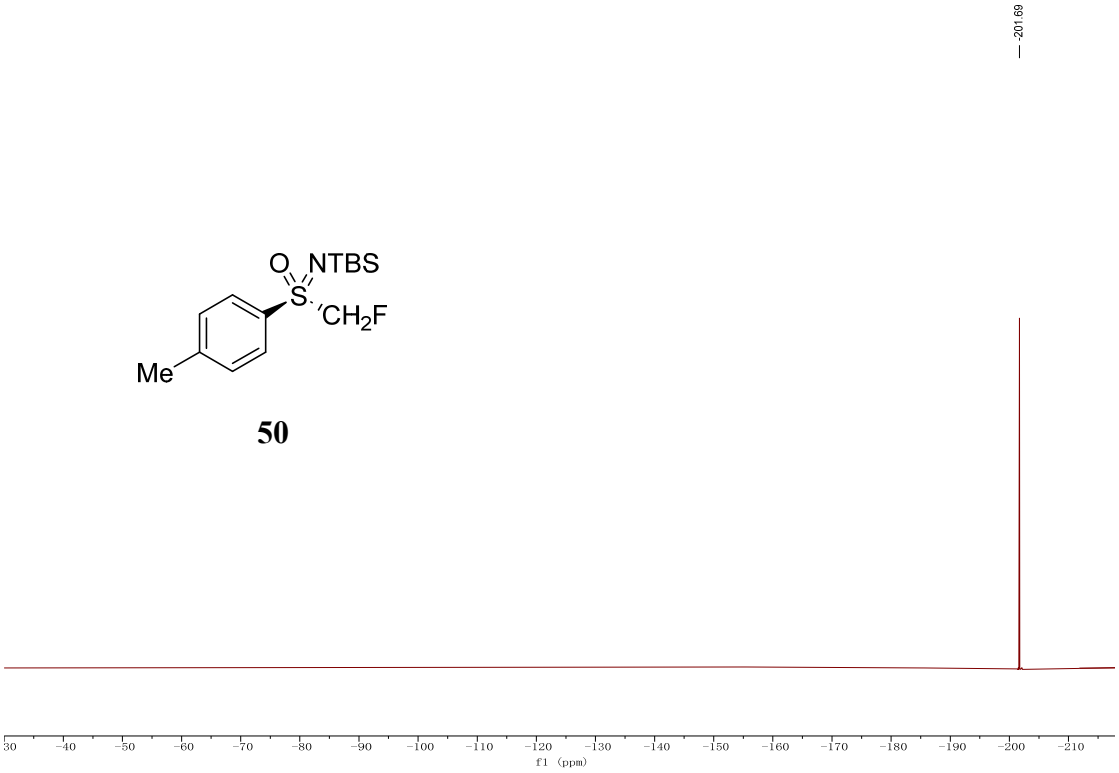
^{1}H NMR (400 MHz) spectrum of compound **50** ($CDCl_3$, 296.7 K)



^{13}C NMR (100 MHz) spectrum of compound **50** ($CDCl_3$, 296.8 K)



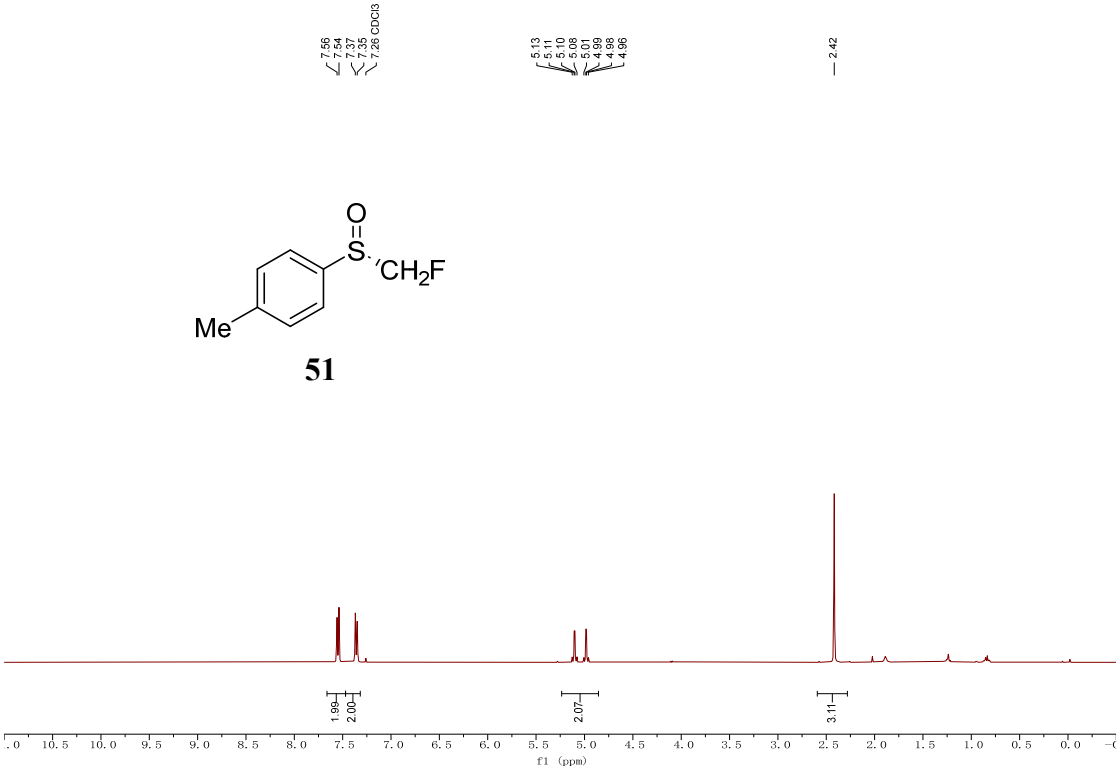
^{19}F NMR (376 MHz) spectrum of compound **50** ($CDCl_3$, 297.5 K)



50

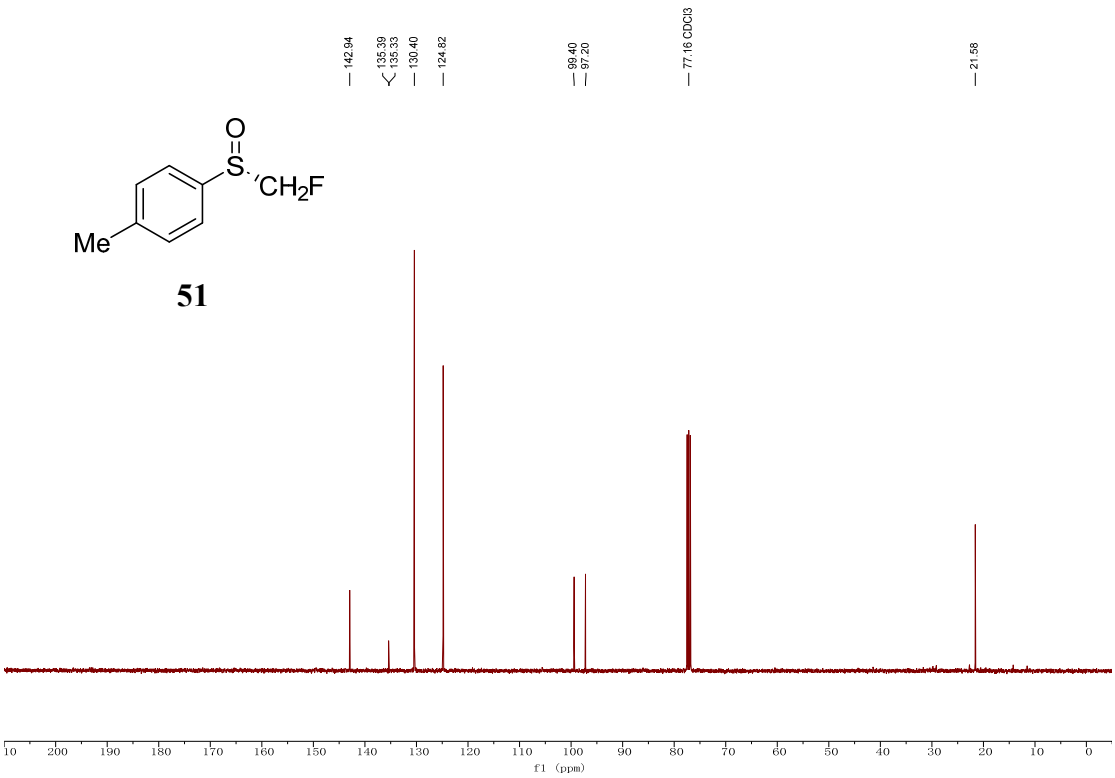
Figure S61. NMR spectra of compound **51**.

^{1}H NMR (400 MHz) spectrum of compound **51** ($CDCl_3$, 296.3 K)



51

^{13}C NMR (100 MHz) spectrum of compound **51** ($CDCl_3$, 296.5 K)



51

^{19}F NMR (376 MHz) spectrum of compound **51** ($CDCl_3$, 296.6 K)

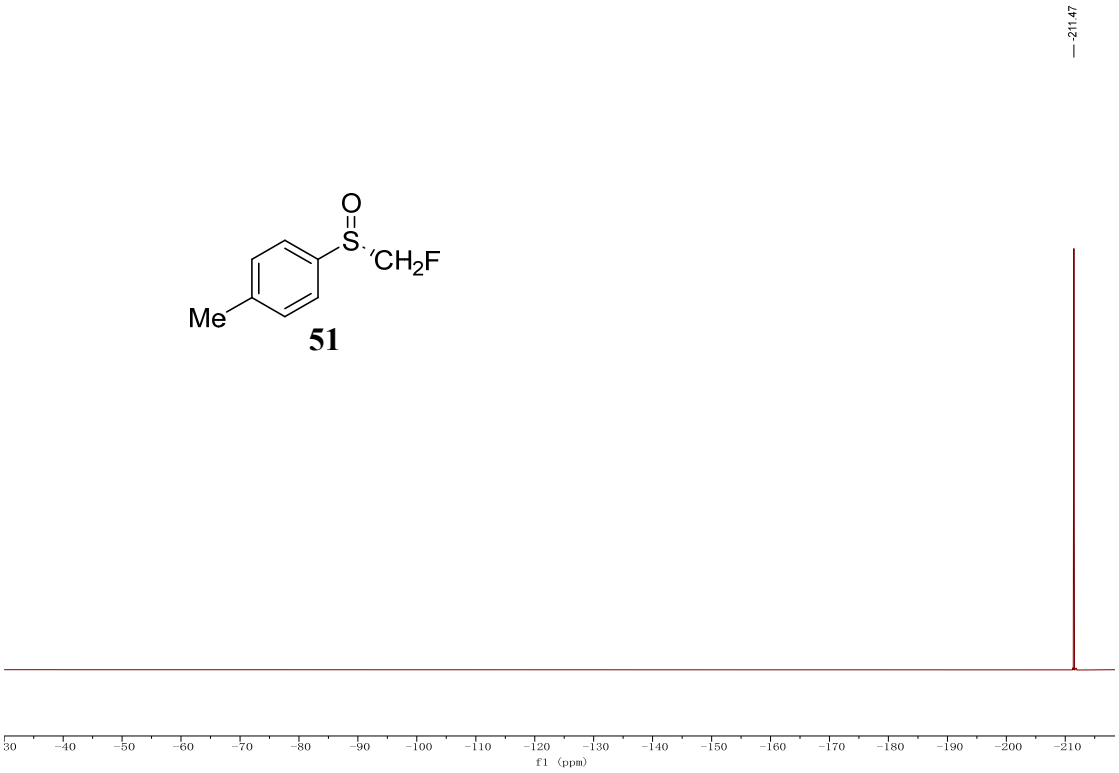
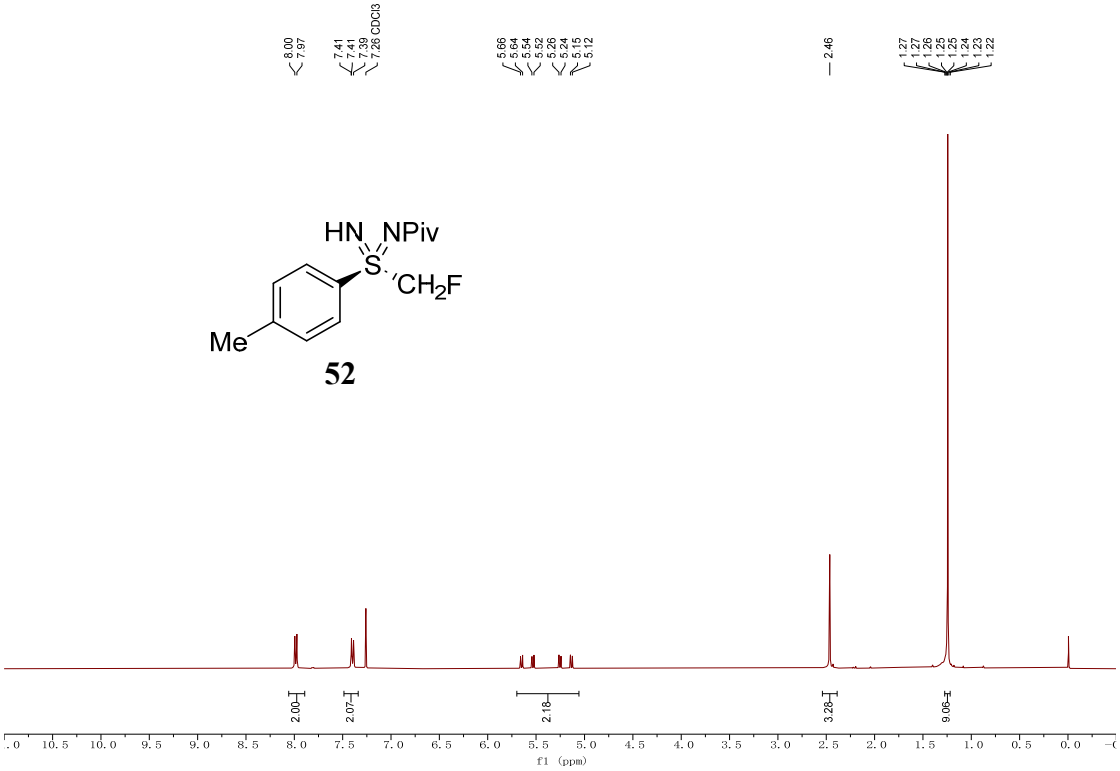
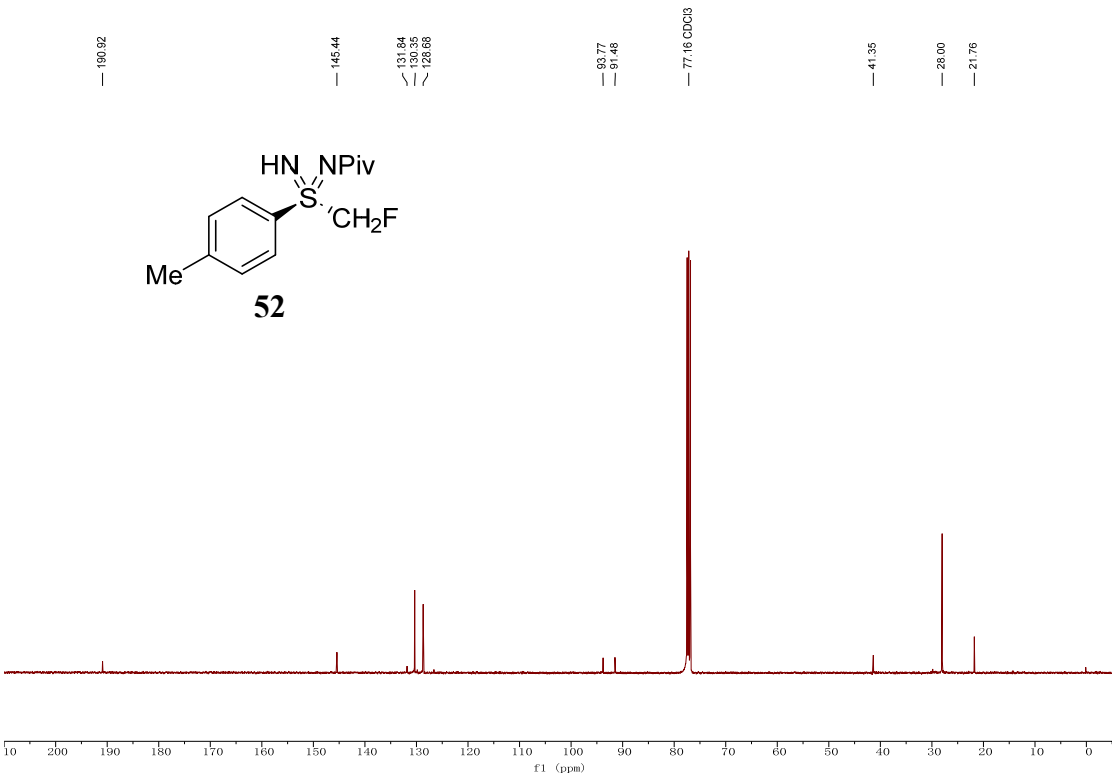


Figure S62. NMR spectra of compound **52**.

^{1}H NMR (400 MHz) spectrum of compound **52** ($CDCl_3$, 294.1 K)



^{13}C NMR (100 MHz) spectrum of compound **52** ($CDCl_3$, 294.1 K)



^{19}F NMR (376 MHz) spectrum of compound **52** ($CDCl_3$, 294.1 K)

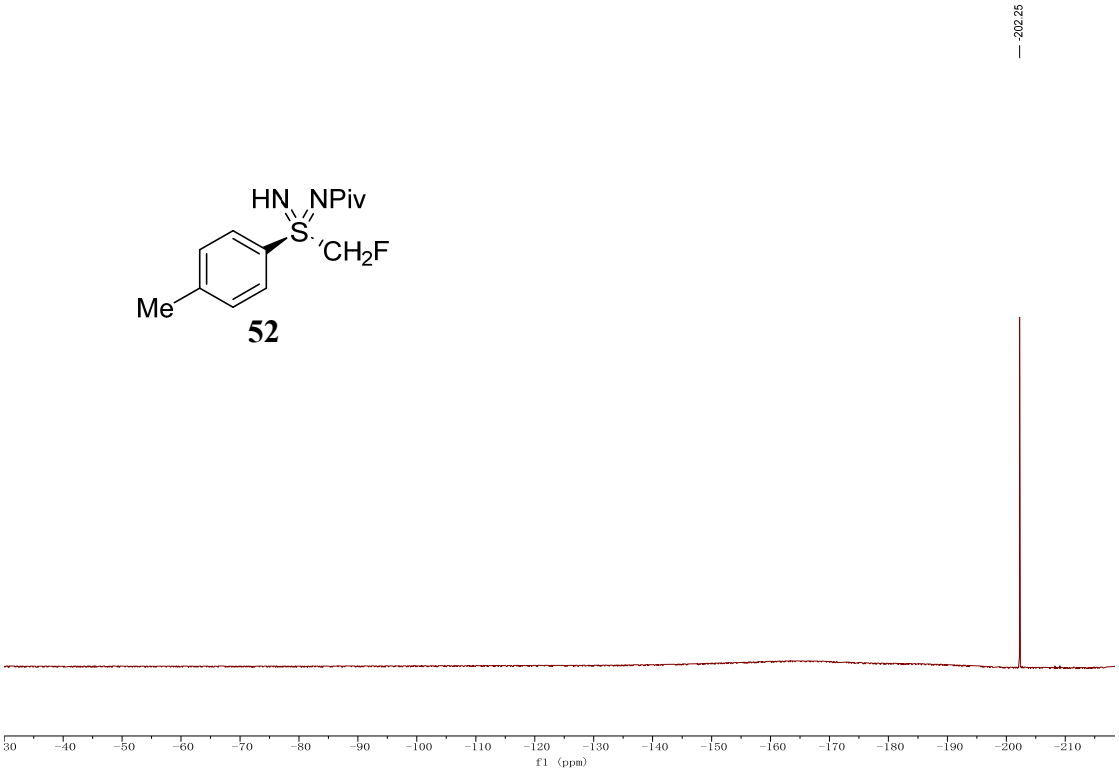
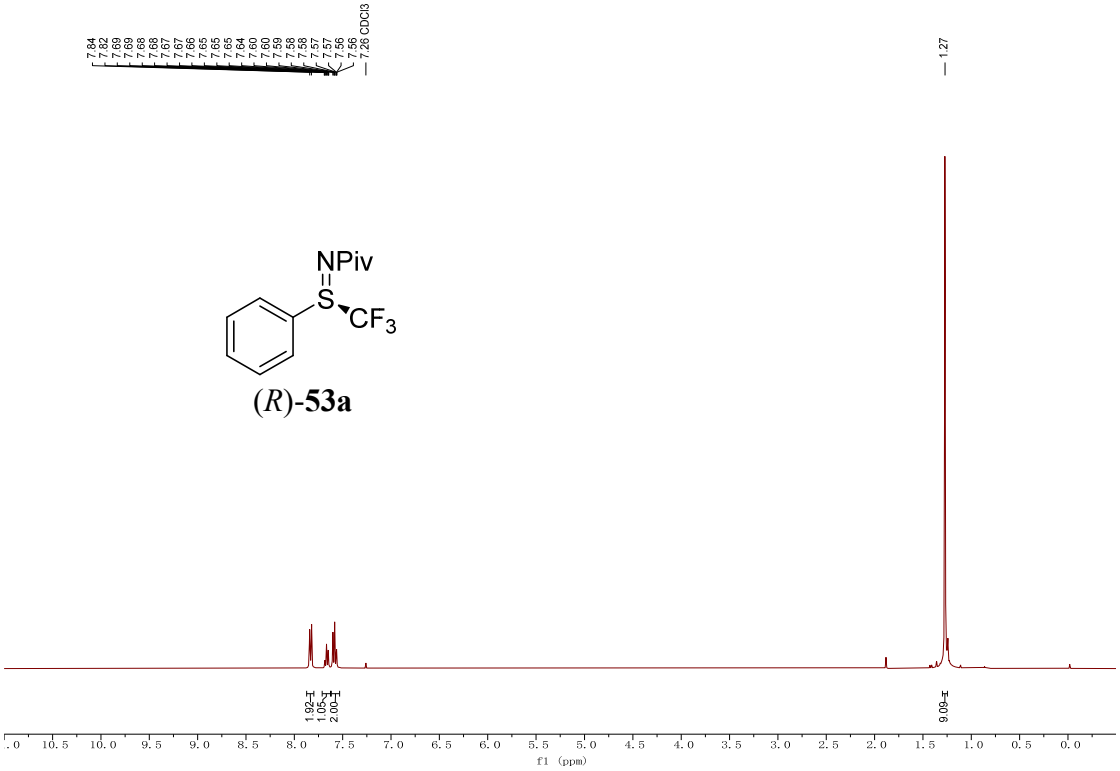
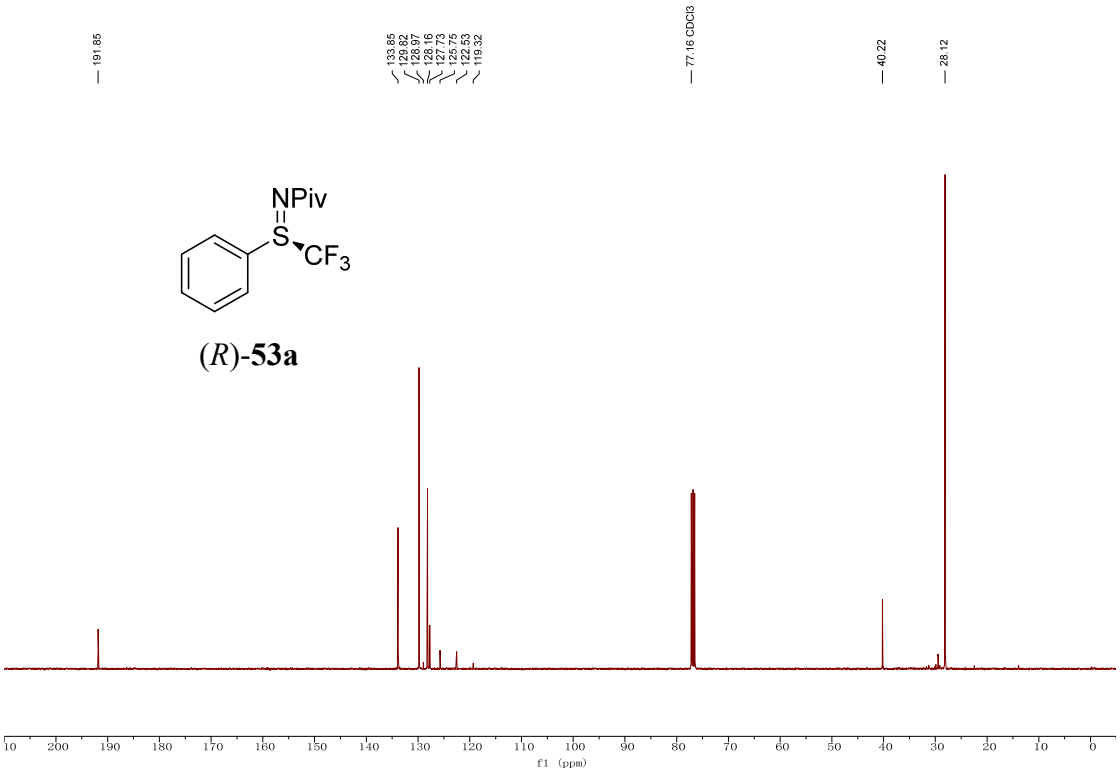


Figure S63. NMR spectra of compound (*R*)-**53a**.

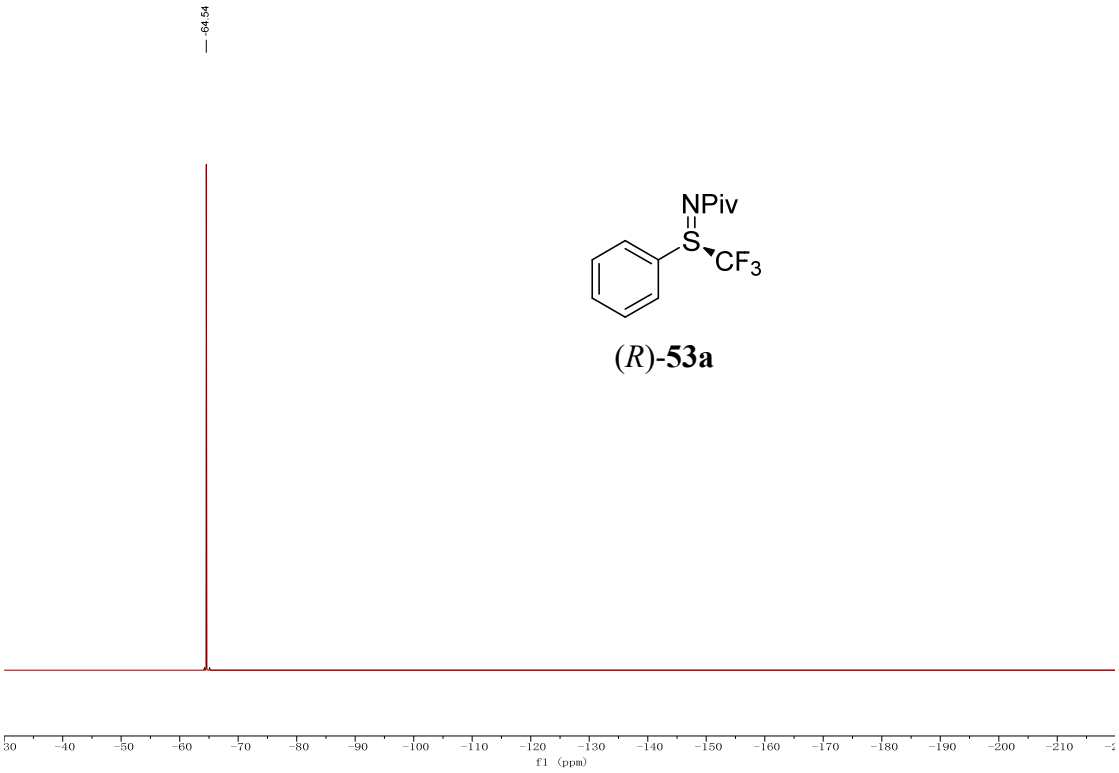
^{1}H NMR (400 MHz) spectrum of compound (*R*)-**53a** ($CDCl_3$, 295.7 K)



^{13}C NMR (100 MHz) spectrum of compound (*R*)-**53a** ($CDCl_3$, 295.7 K)



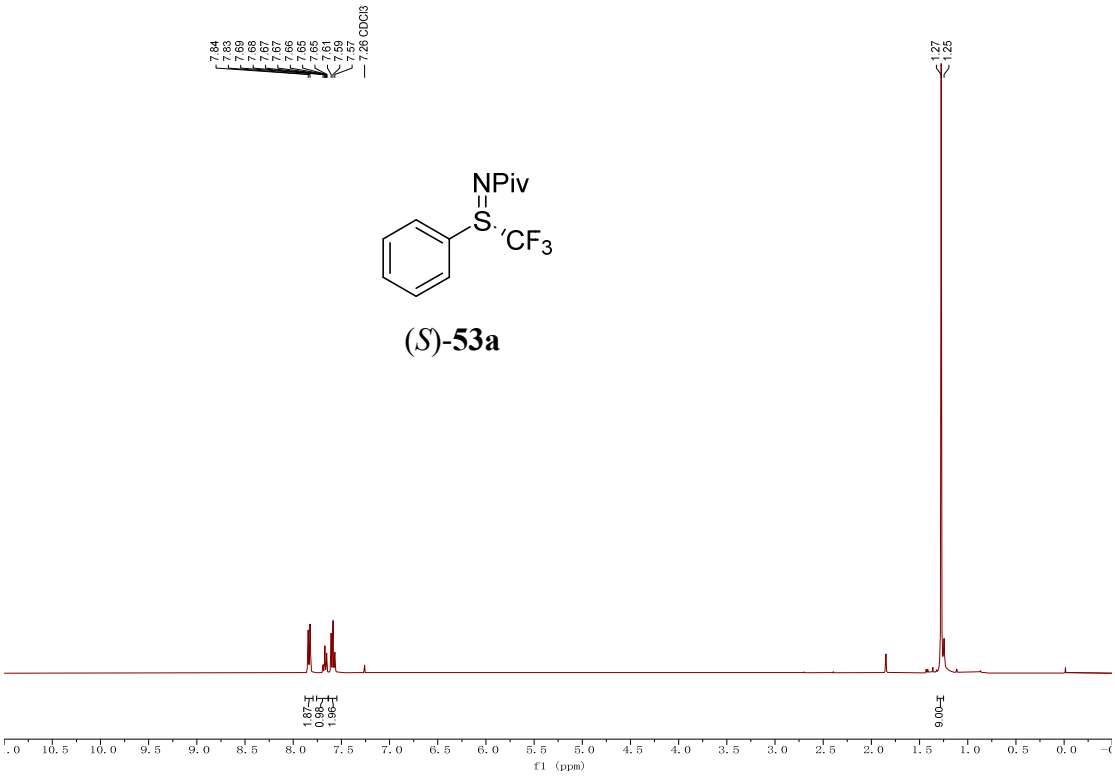
^{19}F NMR (376 MHz) spectrum of compound **(*R*)-53a** ($CDCl_3$, 296.0 K)



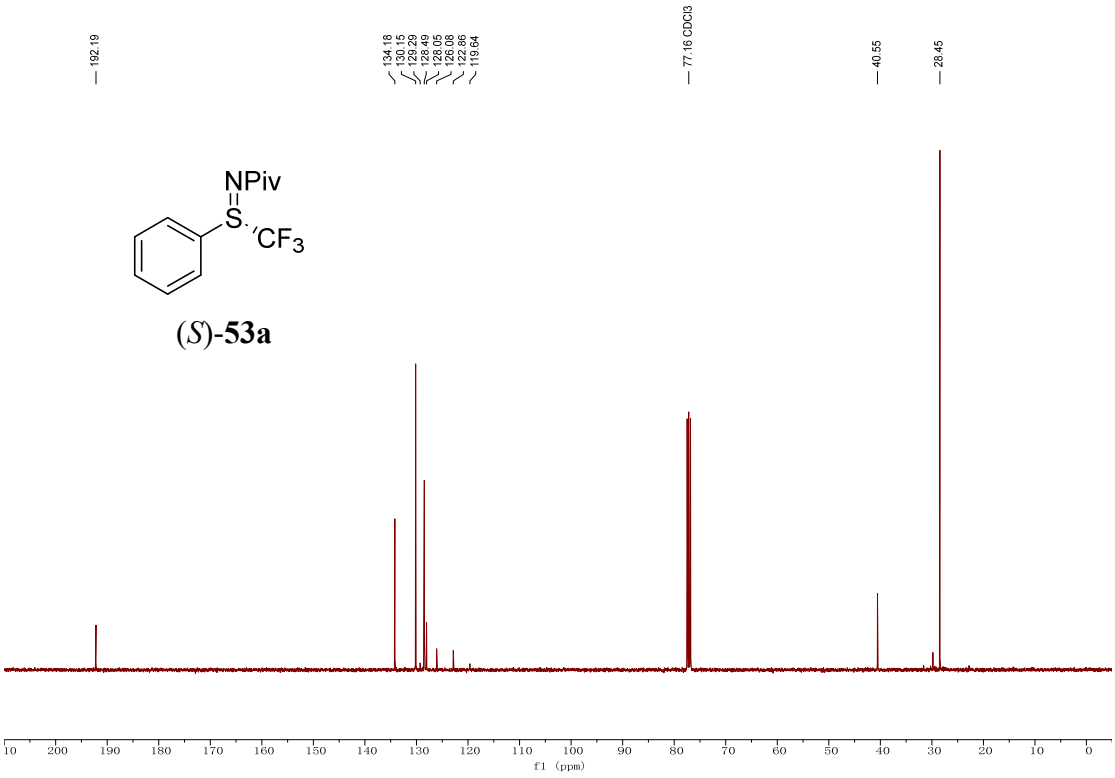
(*R*)-**53a**

Figure S64. NMR spectra of compound (*S*)-**53a**.

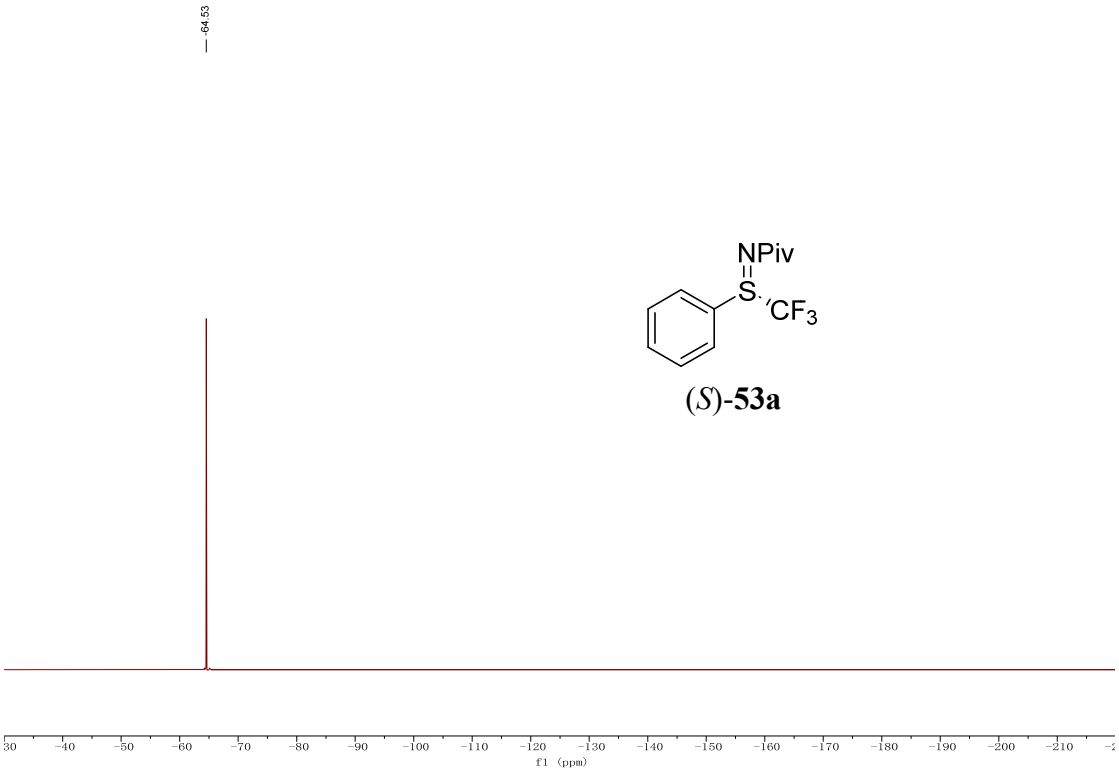
^{1}H NMR (400 MHz) spectrum of compound (*S*)-**53a** ($CDCl_3$, 295.6 K)



^{13}C NMR (100 MHz) spectrum of compound (*S*)-**53a** ($CDCl_3$, 295.6 K)



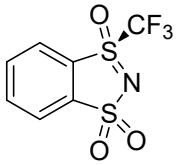
^{19}F NMR (376 MHz) spectrum of compound (*S*)-**53a** ($CDCl_3$, 296.0 K)



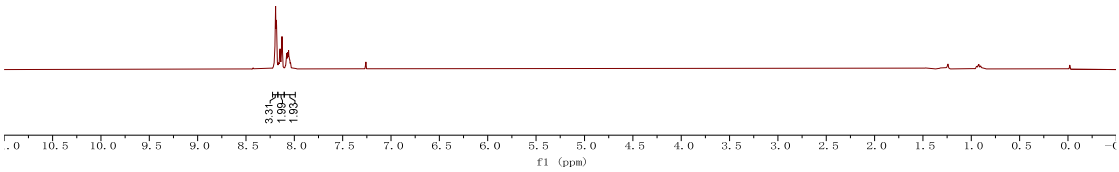
(*S*)-**53a**

Figure S65. NMR spectra of compound (*R*)-**53**.

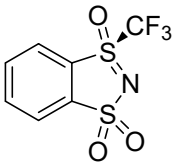
^{1}H NMR (400 MHz) spectrum of compound (*R*)-**53** ($CDCl_3$, 295.5 K)



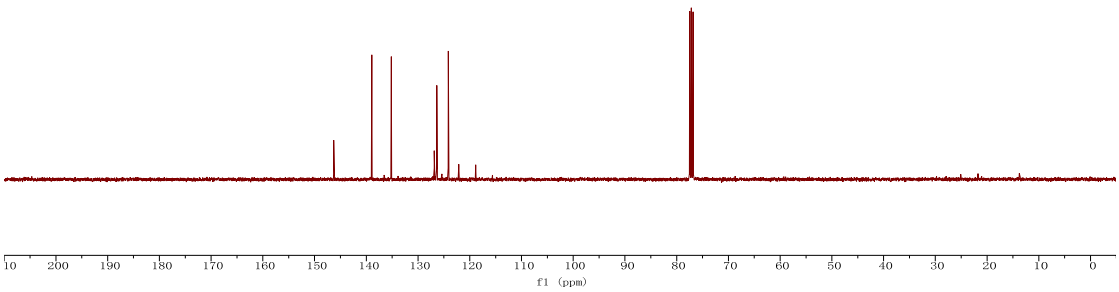
(*R*)-**53**



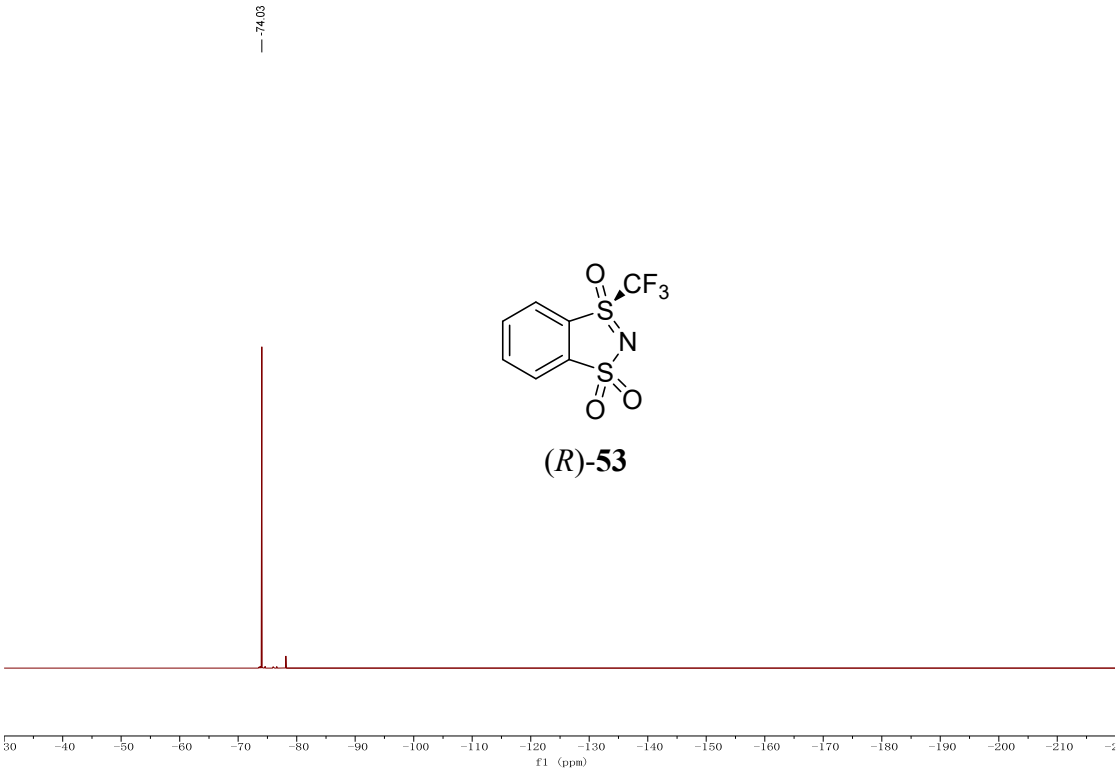
^{13}C NMR (100 MHz) spectrum of compound (*R*)-**53** ($CDCl_3$, 295.6 K)



(*R*)-**53**



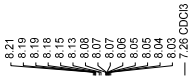
^{19}F NMR (376 MHz) spectrum of compound (*R*)-**53** ($CDCl_3$, 296.0 K)

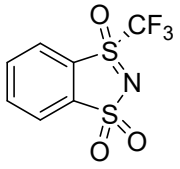


(*R*)-**53**

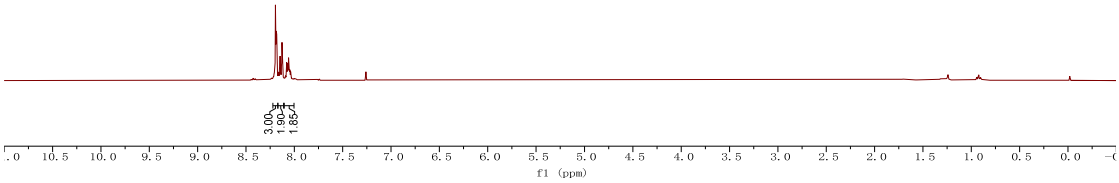
Figure S66. NMR spectra of compound (*S*)-**53a**.

^{1}H NMR (400 MHz) spectrum of compound **(*S*)-53** ($CDCl_3$, 295.6 K)

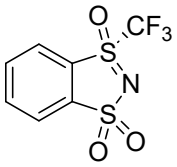




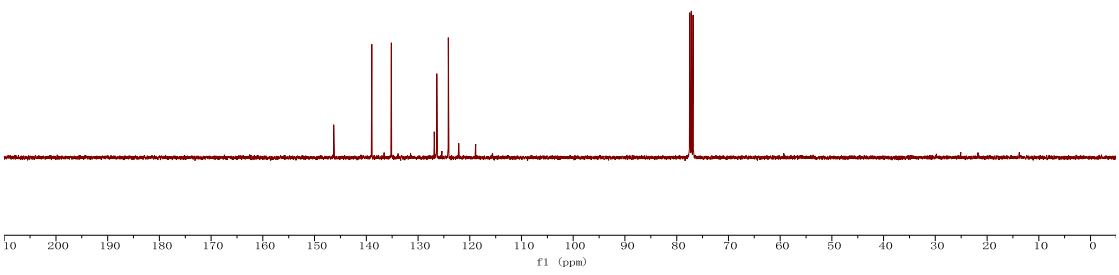
(*S*)-**53**



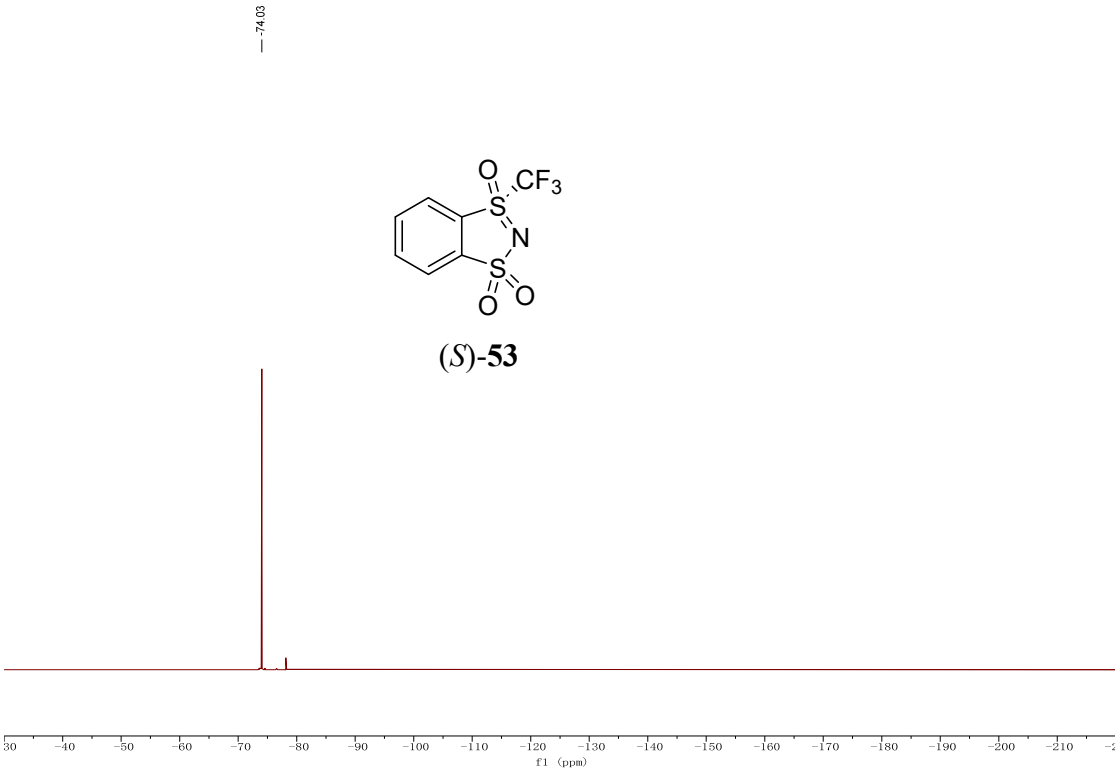
^{13}C NMR (100 MHz) spectrum of compound **53** ($CDCl_3$, 295.6 K)



(*S*)-**53**



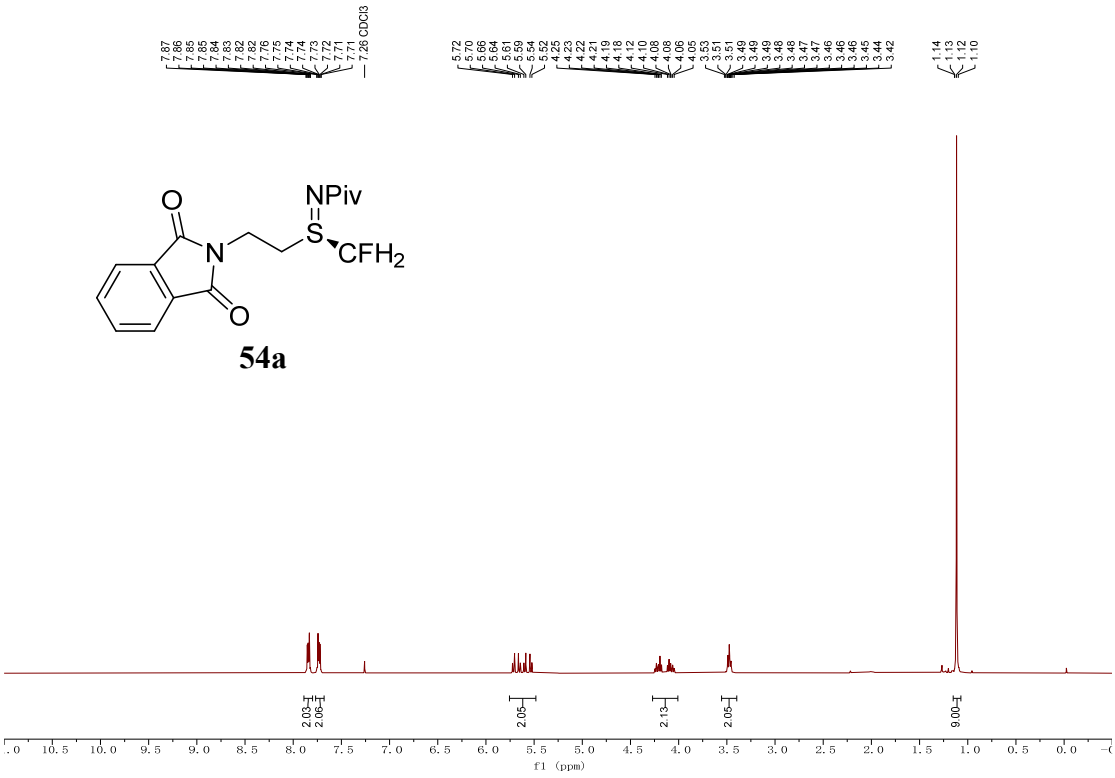
^{19}F NMR (376 MHz) spectrum of compound **53** ($CDCl_3$, 296.0 K)



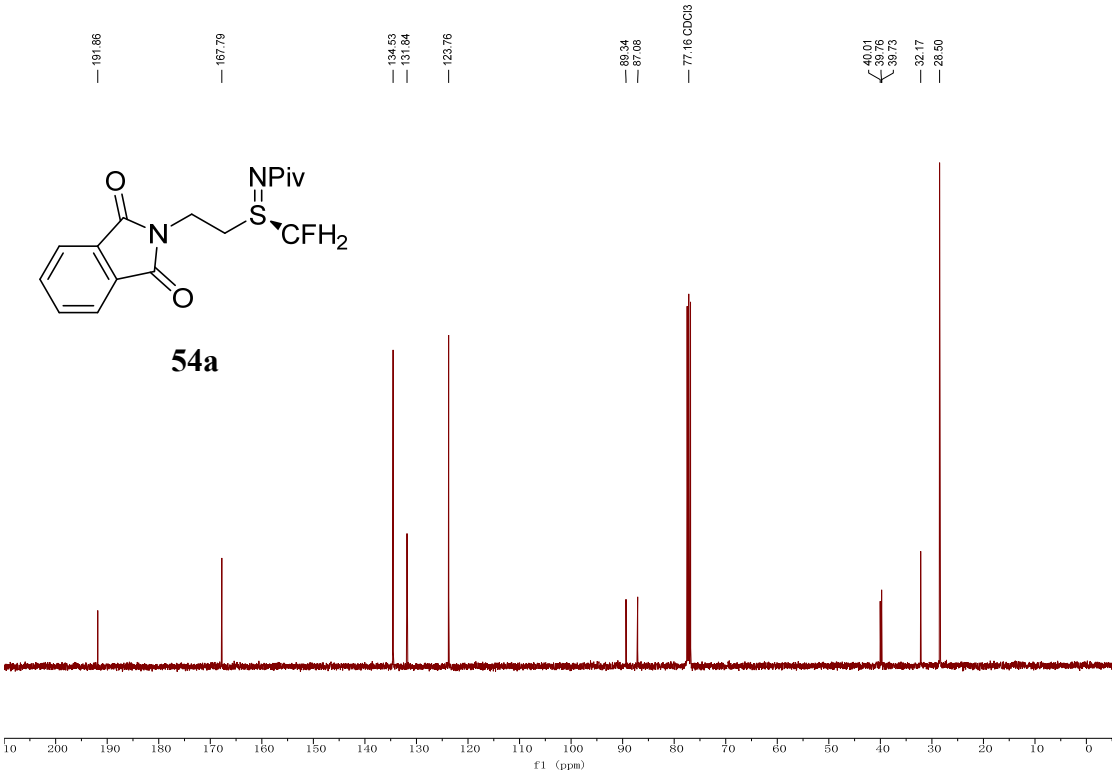
(*S*)-**53**

Figure S67. NMR spectra of compound **54a**.

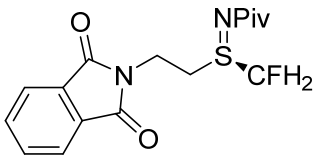
^{1}H NMR (400 MHz) spectrum of compound **54a** ($CDCl_3$, 294.4 K)



^{13}C NMR (100 MHz) spectrum of compound **54a** ($CDCl_3$, 294.5 K)



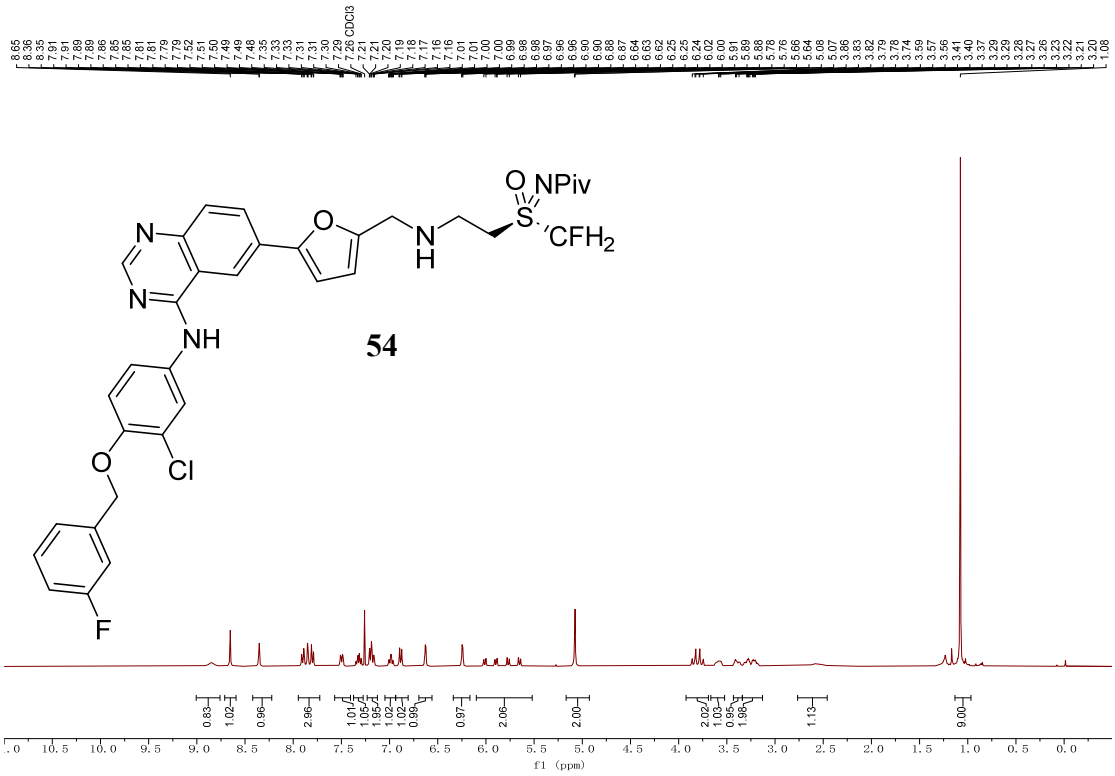
^{19}F NMR (376 MHz) spectrum of compound **54a** ($CDCl_3$, 294.6 K)



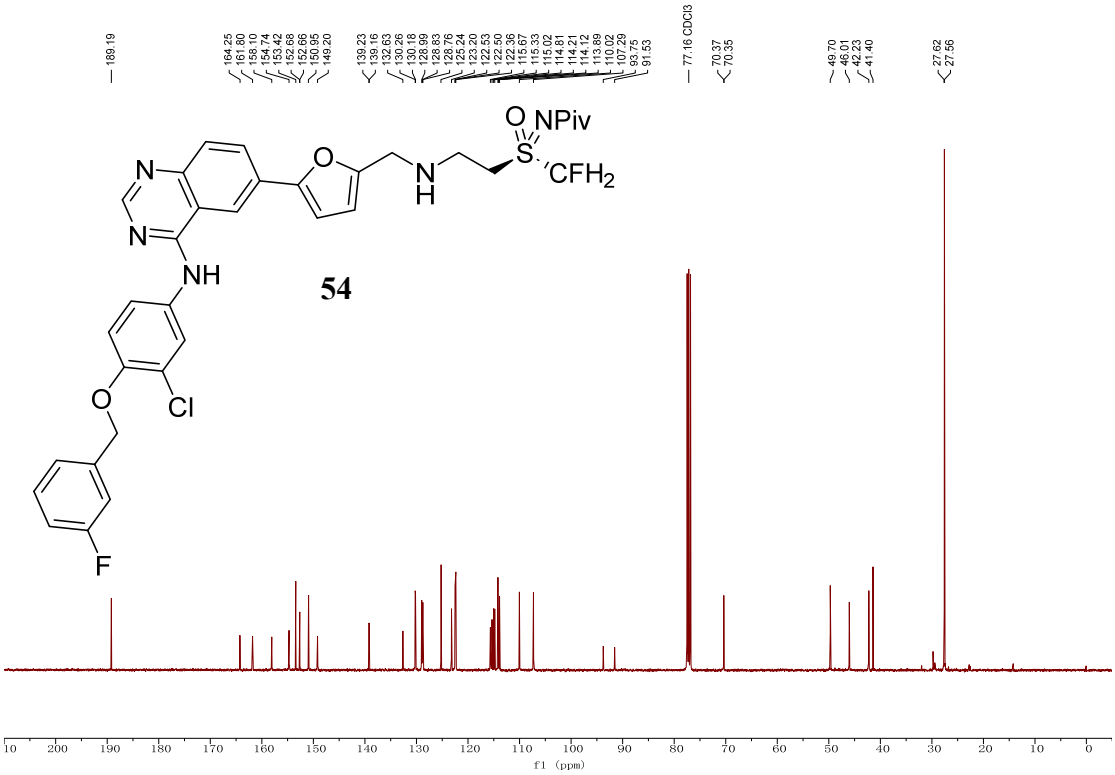
54a

Figure S68. NMR spectra of compound **54**.

^{1}H NMR (400 MHz) spectrum of compound **54** ($CDCl_3$, 294.3 K)



^{13}C NMR (100 MHz) spectrum of compound **54** ($CDCl_3$, 294.4 K)



^{19}F NMR (376 MHz) spectrum of compound **54** ($CDCl_3$, 294.8 K)

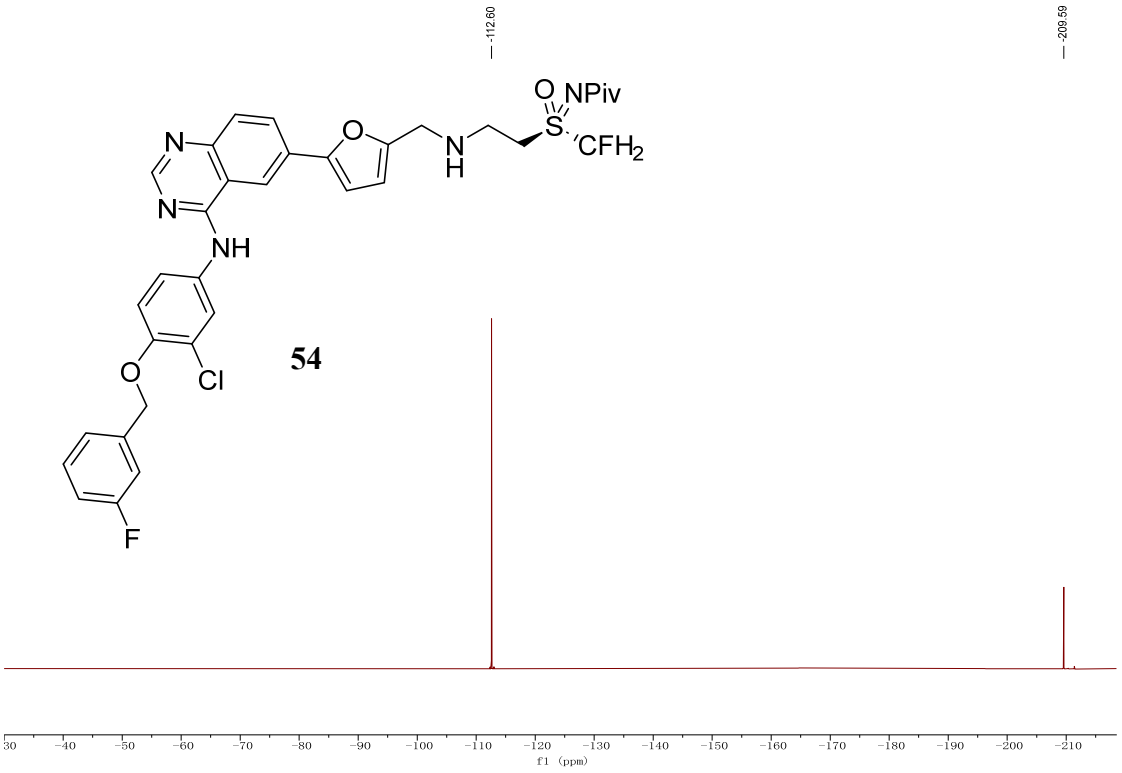
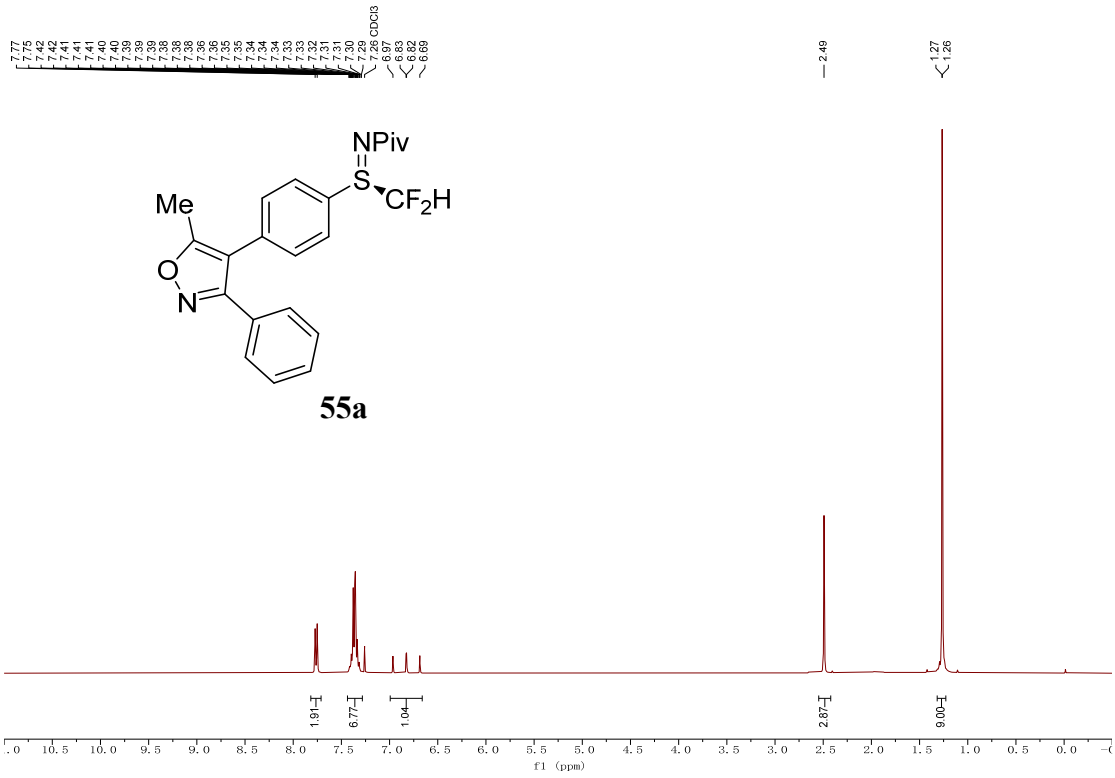
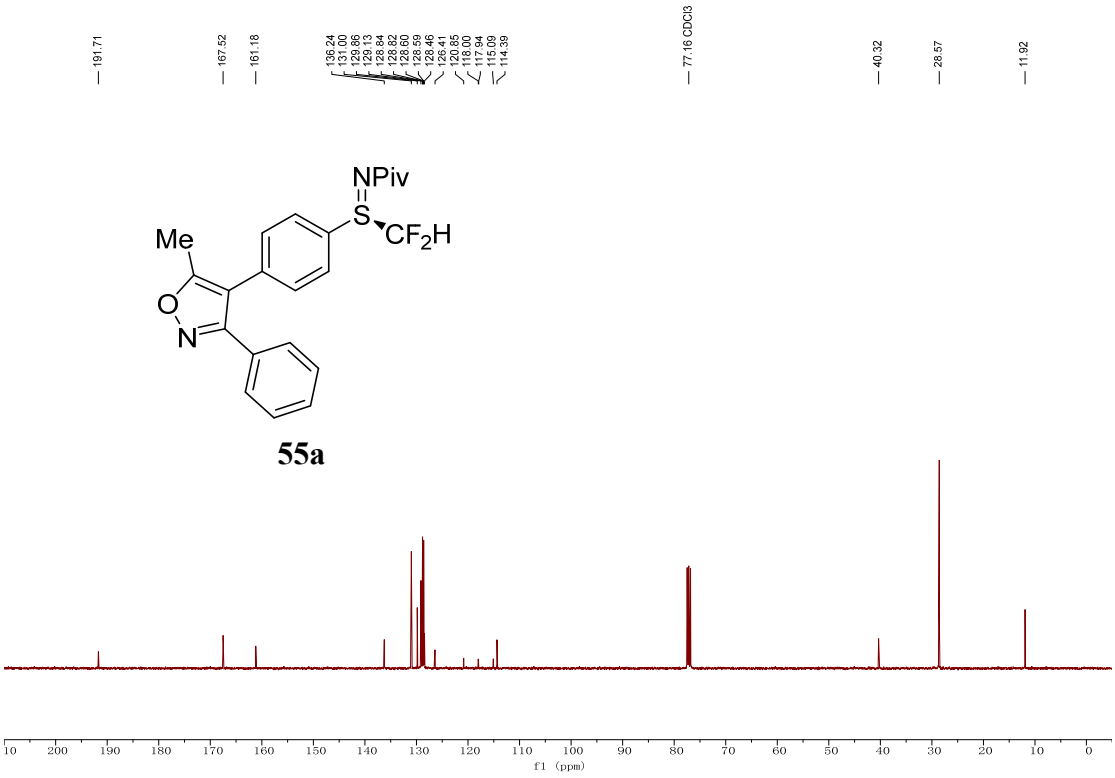


Figure S69. NMR spectra of compound **55a**.

^{1}H NMR (400 MHz) spectrum of compound **55a** ($CDCl_3$, 294.5 K)



^{13}C NMR (100 MHz) spectrum of compound **55a** ($CDCl_3$, 294.5 K)



^{19}F NMR (376 MHz) spectrum of compound **55a** ($CDCl_3$, 294.6 K)

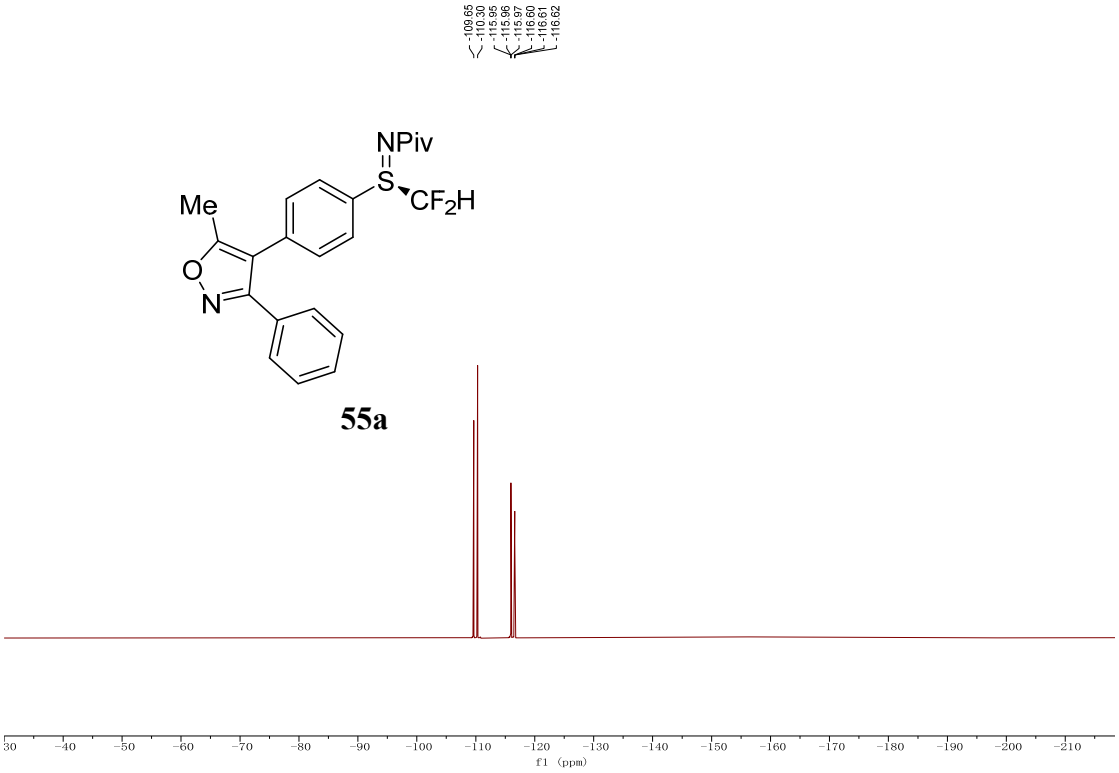
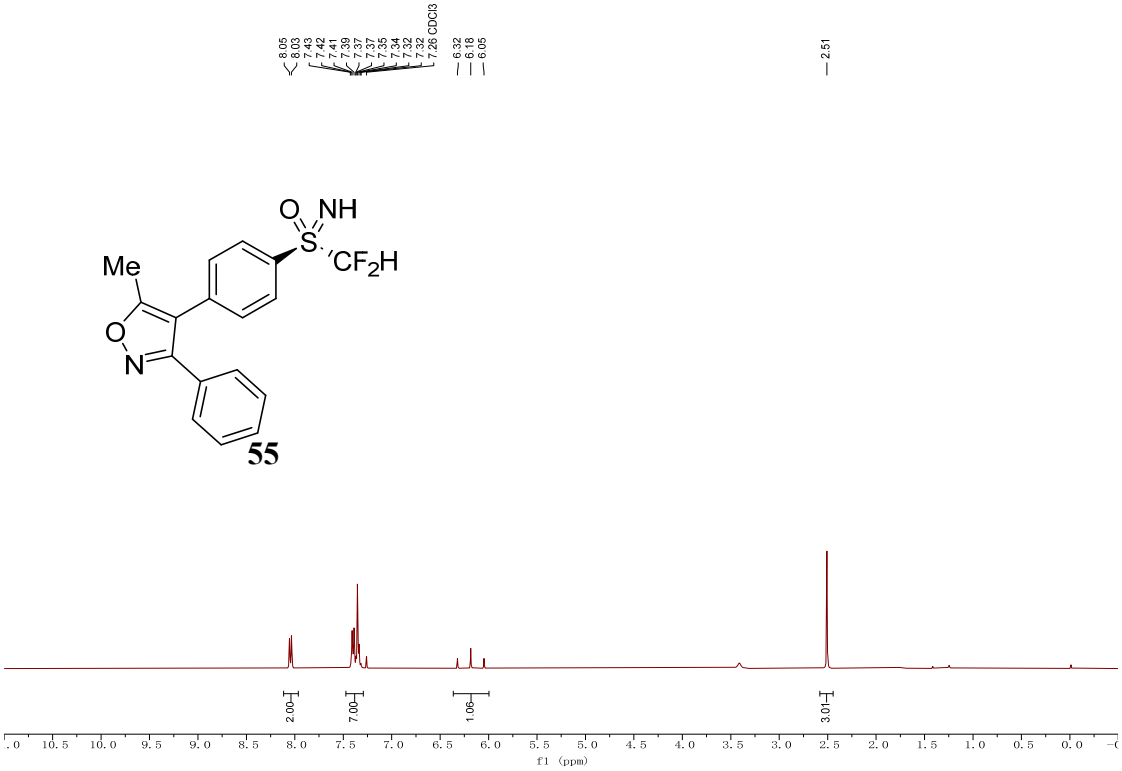
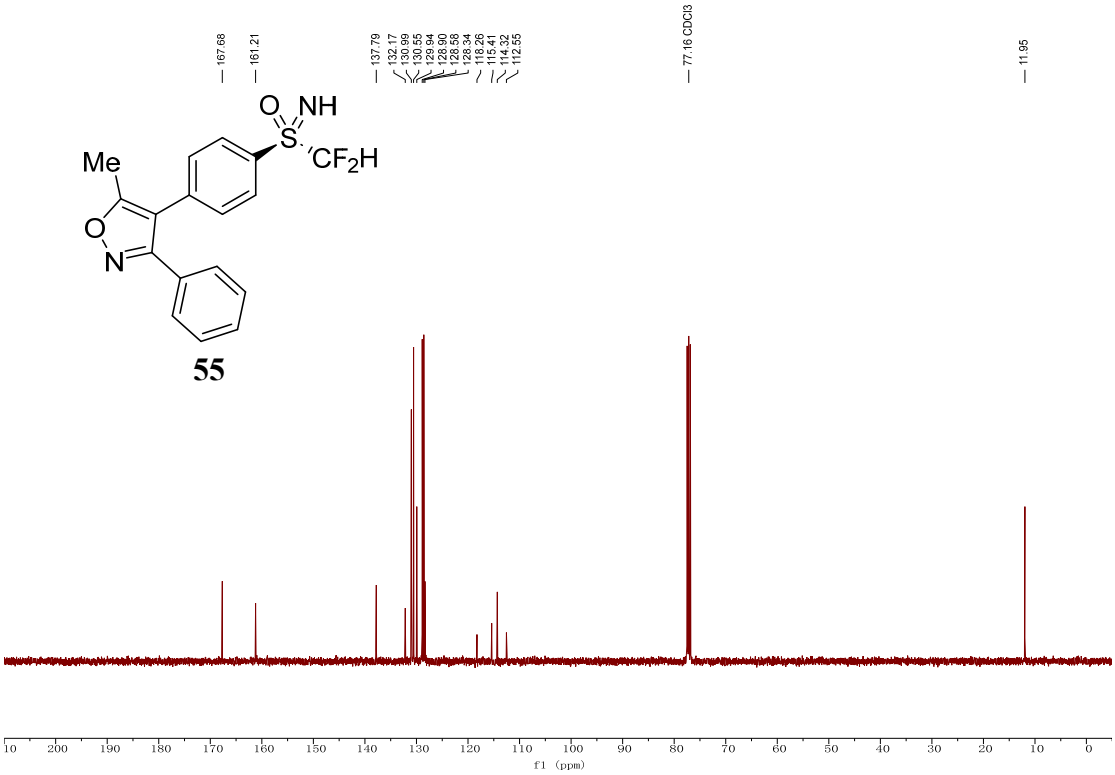


Figure S70. NMR spectra of compound **55**.

^{1}H NMR (400 MHz) spectrum of compound **55** ($CDCl_3$, 295.7 K)



^{13}C NMR (100 MHz) spectrum of compound **55** ($CDCl_3$, 295.7 K)



^{19}F NMR (376 MHz) spectrum of compound **55** ($CDCl_3$, 295.9 K)

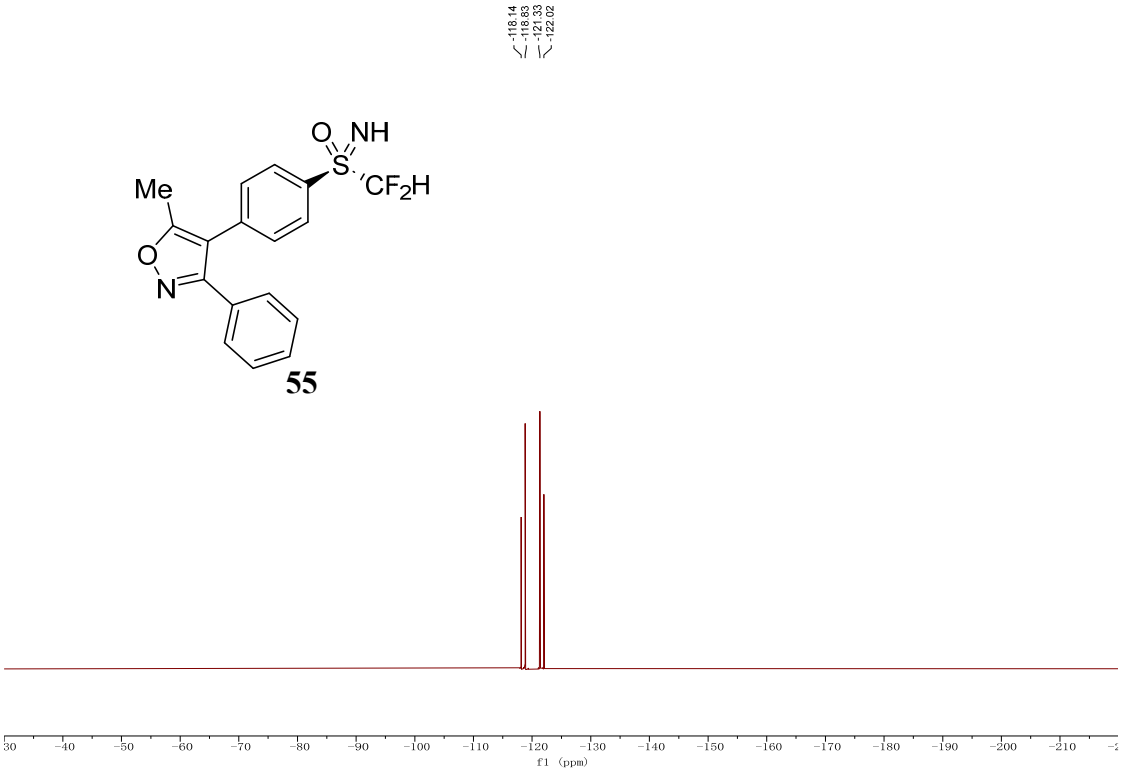


Figure S71. NMR spectra of compound **56**.

^{1}H NMR (400 MHz) spectrum of compound **56** ($CDCl_3$, 294.5 K)

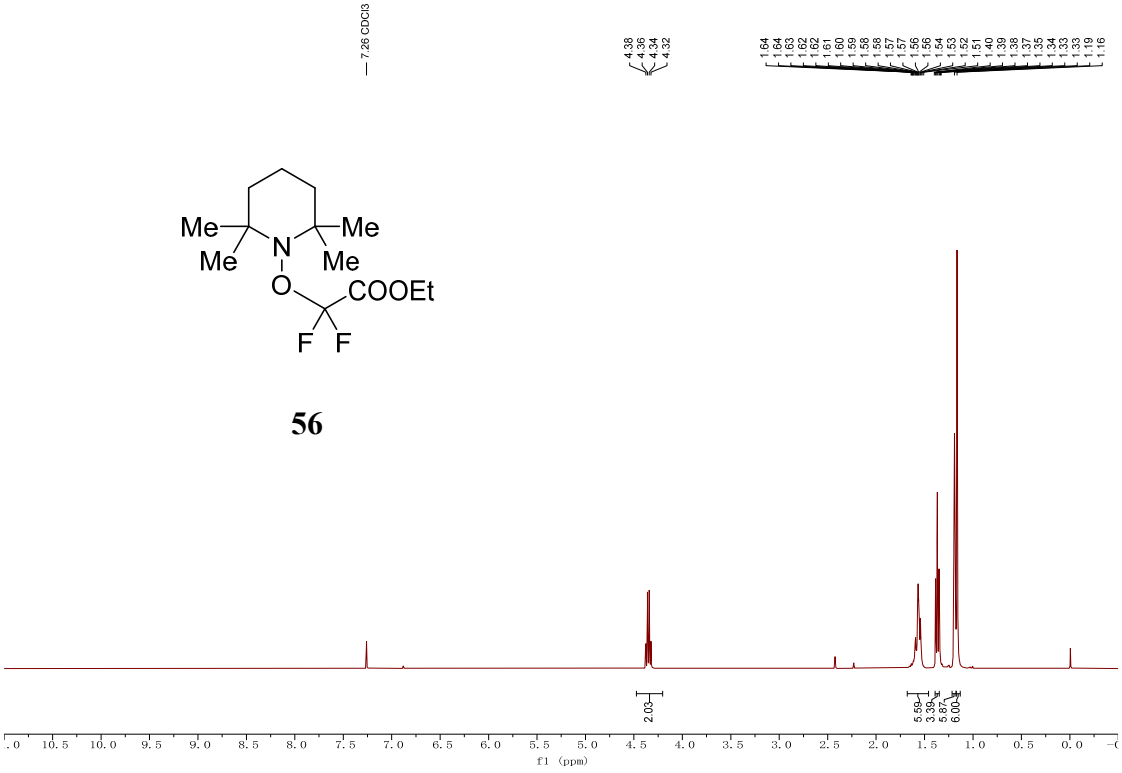
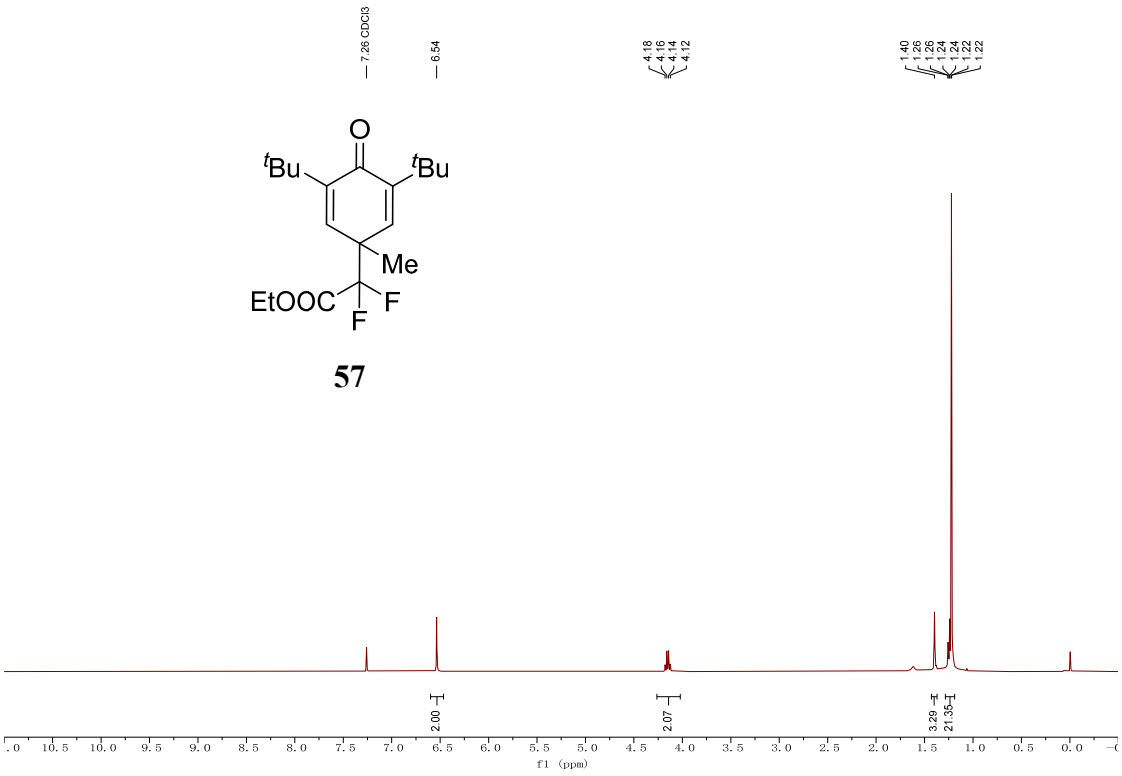


Figure S72. NMR spectra of compound **57**.

^{1}H NMR (400 MHz) spectrum of compound **57** ($CDCl_3$, 296.5 K)



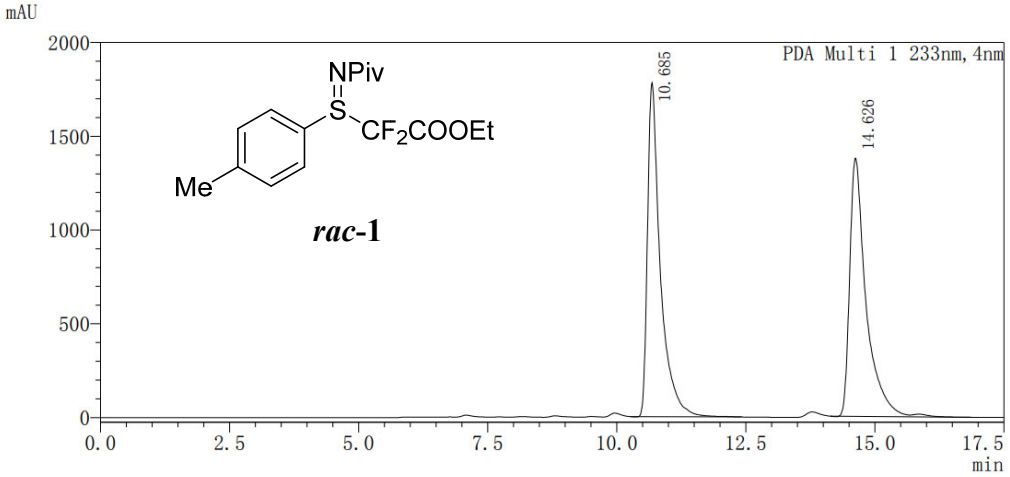
10. HPLC chromatograms

Figure S73. HPLC chromatograms of compound **1**.

HPLC spectra of **1**

HPLC analysis of **1**: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 233 nm), t_R (major) = 14.54 min, t_R (minor) = 10.65 min.

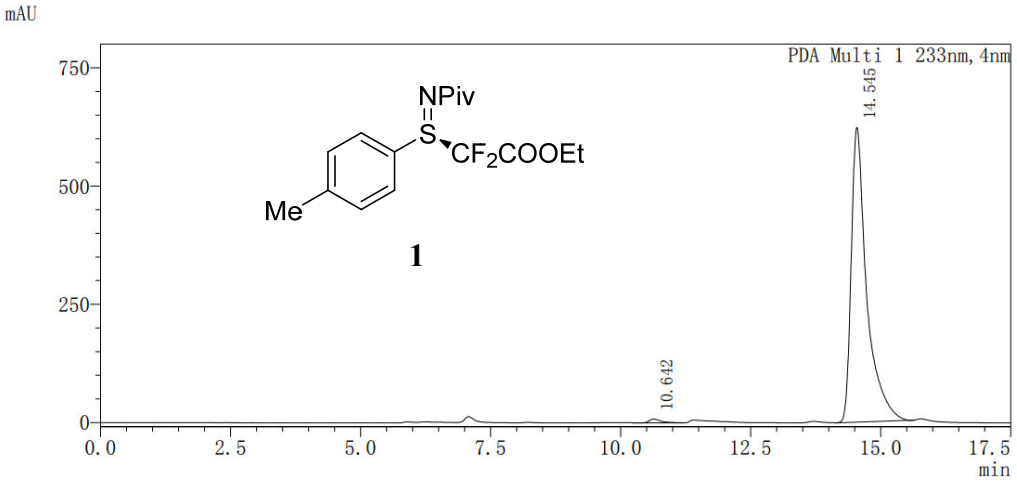
$[\alpha]_D^{27}$ = −58 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 233nm

Peak#	Ret. Time	Area	Area%
1	10.685	30861459	50.256
2	14.626	30547272	49.744



Peak Table

PDA Ch1 233nm

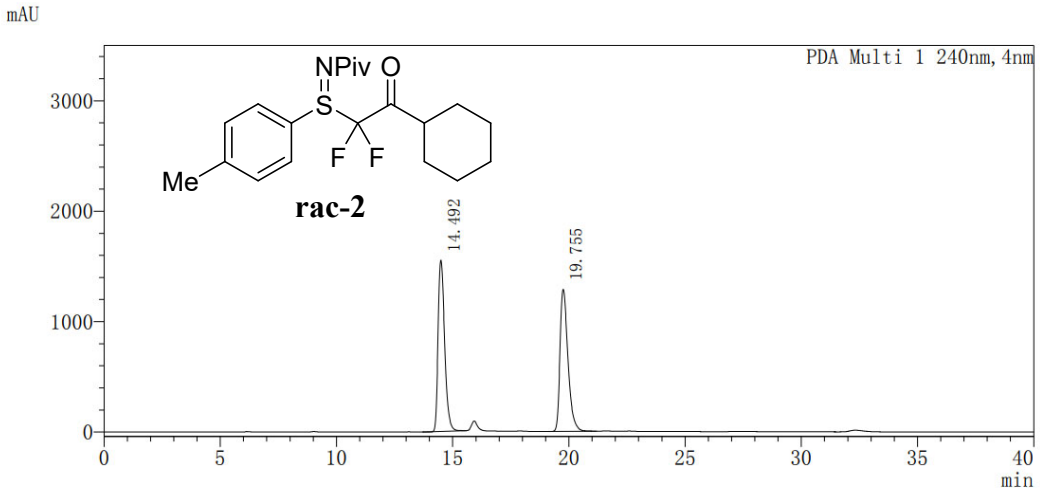
Peak#	Ret. Time	Area	Area%
1	10.642	122248	0.941
2	14.545	12871598	99.059

Figure S74. HPLC chromatograms of compound **2**.

HPLC spectra of **2**

HPLC analysis: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 240 nm), t_R (major) = 19.69 min, t_R (minor) = 14.55 min.

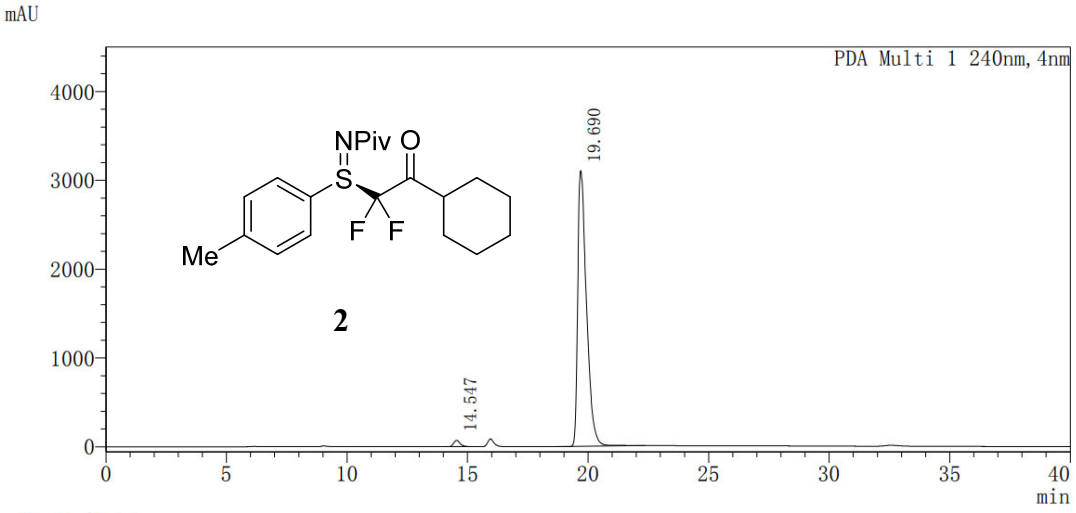
$[\alpha]_D^{27}$ = −33 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 240nm

Peak#	Ret. Time	Area	Area%
1	14.492	30348480	49.743
2	19.755	30662353	50.257



Peak Table

PDA Ch1 240nm

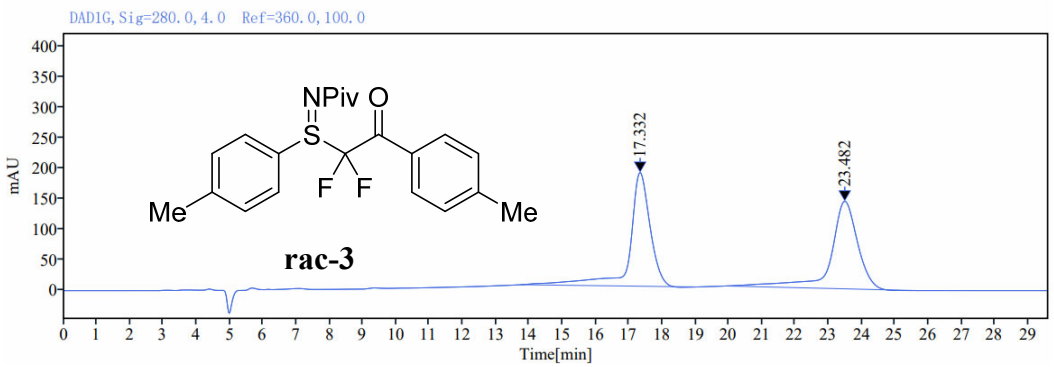
Peak#	Ret. Time	Area	Area%
1	14.547	1340983	1.676
2	19.690	78662412	98.324

Figure S75. HPLC chromatograms of compound **3**.

HPLC spectra of **3**

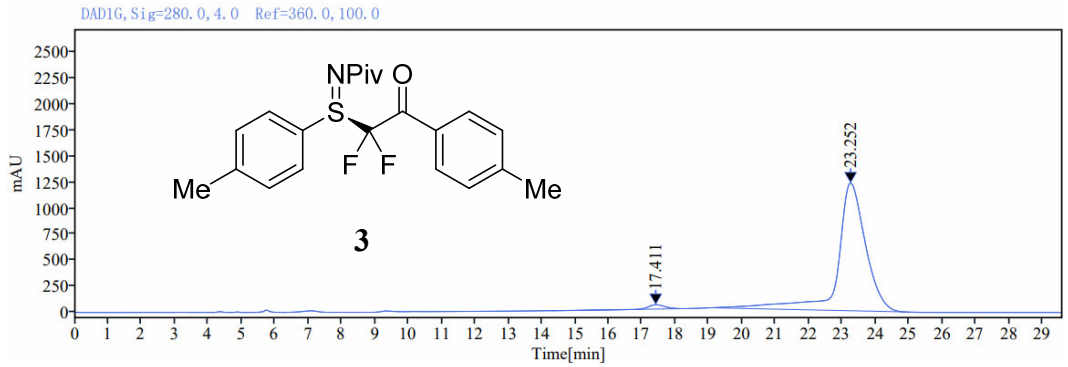
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 280 nm), t_R (major) = 23.25 min, t_R (minor) = 17.41 min.

$[\alpha]_D^{27} = -15$ (c 0.5, $CHCl_3$).



Signal 1: DAD1G,Sig=280.0,4.0 Ref=360.0,100.0

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area%
17.332	MM m	5.31	7973.24	185.91	49.91
23.482	MM m	5.80	8003.29	143.14	50.09
	Totals	11.11	15976.53		



Signal 1: DAD1G,Sig=280.0,4.0 Ref=360.0,100.0

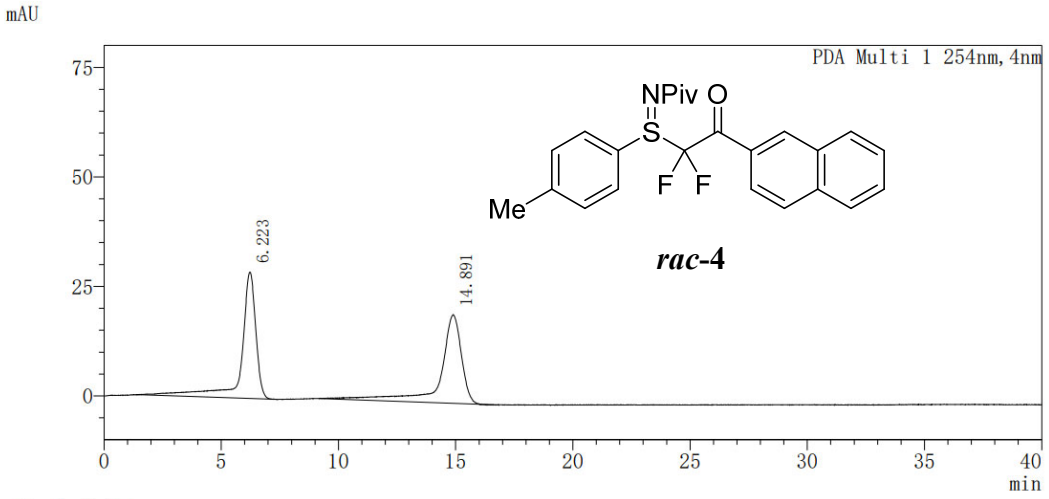
RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area%
17.411	MM m	4.02	1263.02	41.59	1.74
23.252	MM m	6.46	71403.53	1226.70	98.26
	Totals	10.48	72666.56		

Figure S76. HPLC chromatograms of compound **4**.

HPLC spectra of **4**

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 14.82 min, t_R (minor) = 6.20 min.

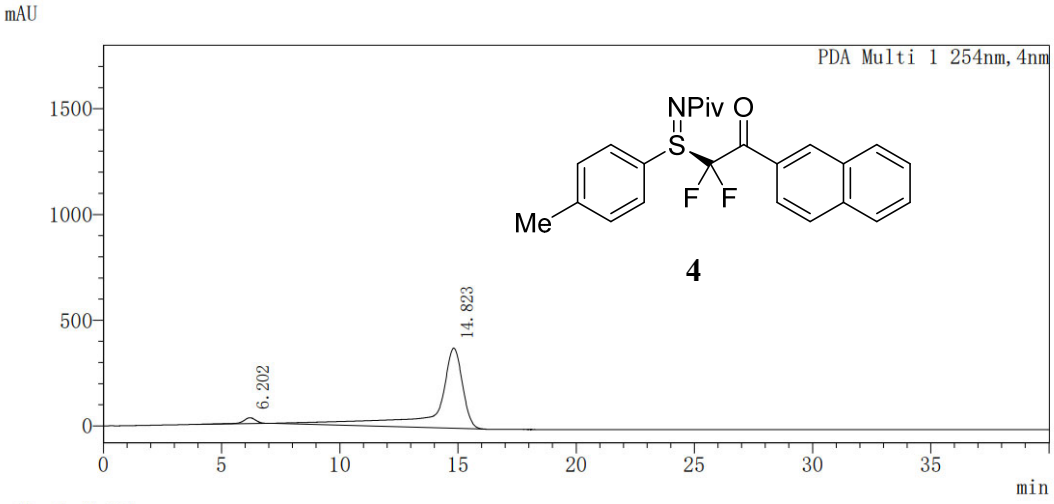
$[\alpha]_D^{27} = -10$ (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.223	1249164	49.500
2	14.891	1274395	50.500



Peak Table

PDA Ch1 254nm

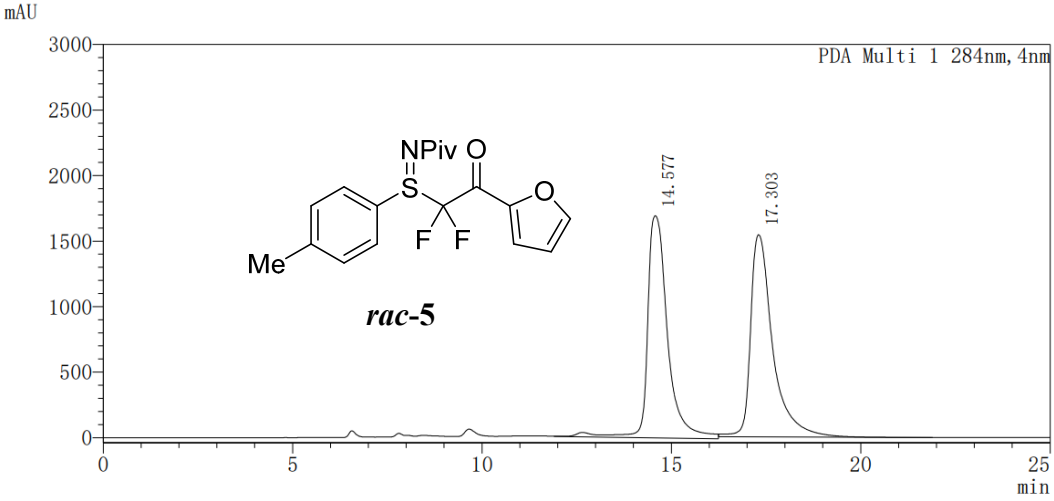
Peak#	Ret. Time	Area	Area%
1	6.202	1052156	3.537
2	14.823	28694775	96.463

Figure S77. HPLC chromatograms of compound **5**.

HPLC spectra of **5**

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.6 mL/min, λ = 284 nm), t_R (major) = 17.32 min, t_R (minor) = 14.67 min.

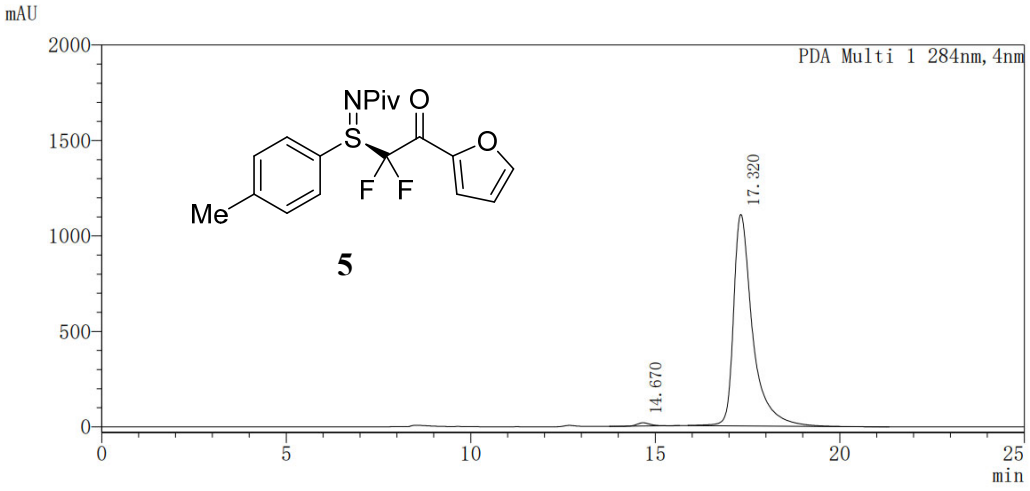
$[\alpha]_D^{27}$ = −66 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 284nm

Peak#	Ret. Time	Area	Area%
1	14.577	62741117	49.926
2	17.303	62928005	50.074



Peak Table

PDA Ch1 284nm

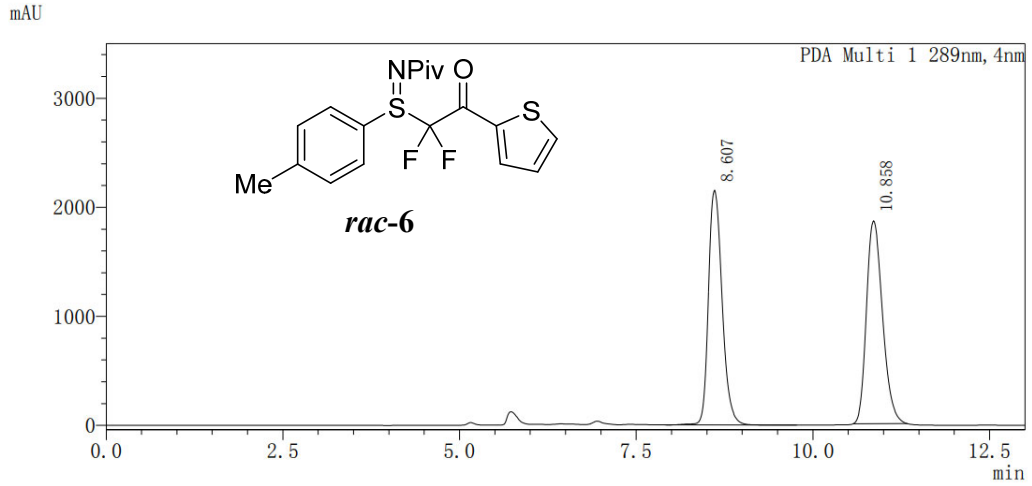
Peak#	Ret. Time	Area	Area%
1	14.670	426024	1.060
2	17.320	39771549	98.940

Figure S78. HPLC chromatograms of compound **6**.

HPLC spectra of **6**

HPLC analysis: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 289 nm), t_R (major) = 10.87 min, t_R (minor) = 8.63 min.

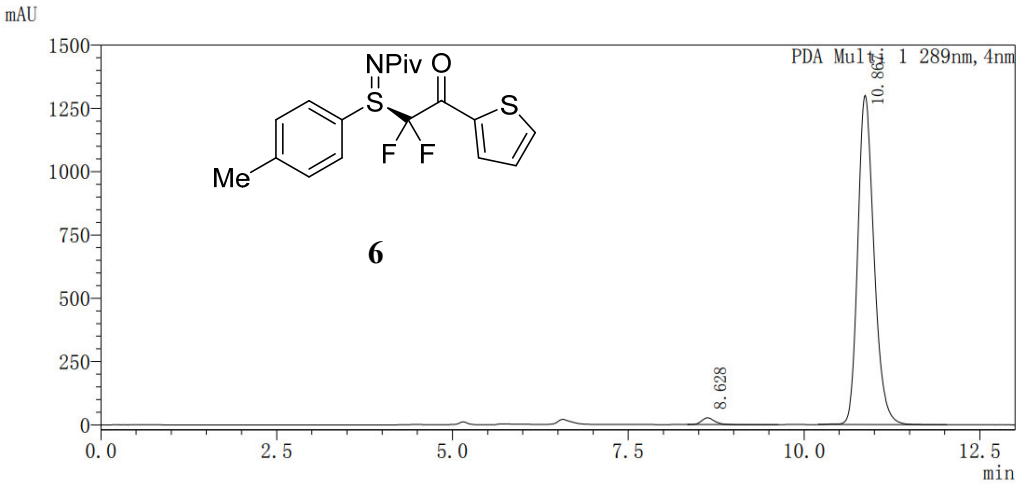
$[\alpha]_D^{27}$ = −76(c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 289nm

Peak#	Ret. Time	Area	Area%
1	8.607	28995944	49.623
2	10.858	29436232	50.377



Peak Table

PDA Ch1 289nm

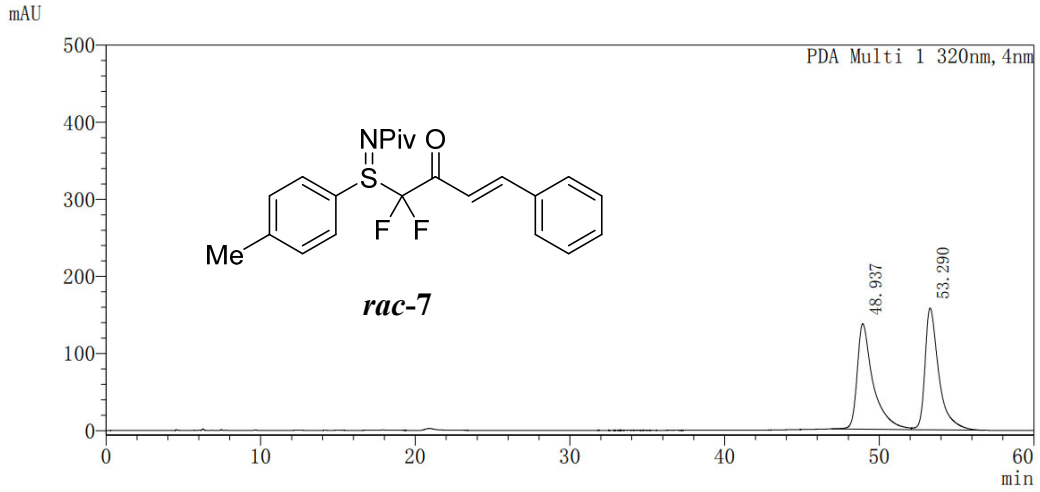
Peak#	Ret. Time	Area	Area%
1	8.628	339122	1.599
2	10.867	20870750	98.401

Figure S79. HPLC chromatograms of compound **7**.

HPLC spectra of **7**

HPLC analysis: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.7 mL/min, λ = 320 nm), t_R (major) = 48.87 min, t_R (minor) = 53.94 min.

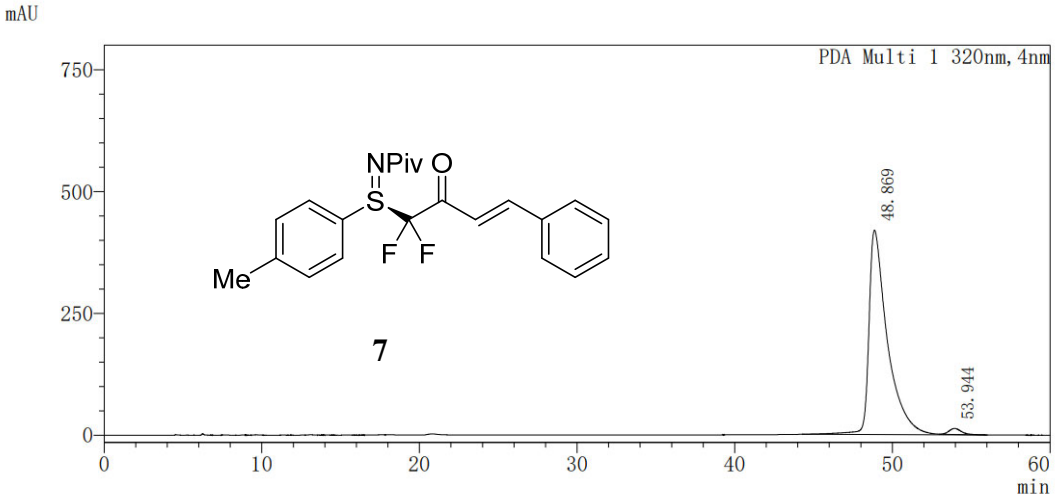
$[\alpha]_D^{27} = -5$ (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 320nm

Peak#	Ret. Time	Area	Area%
1	48.937	9850266	50.040
2	53.290	9834622	49.960



Peak Table

PDA Ch1 320nm

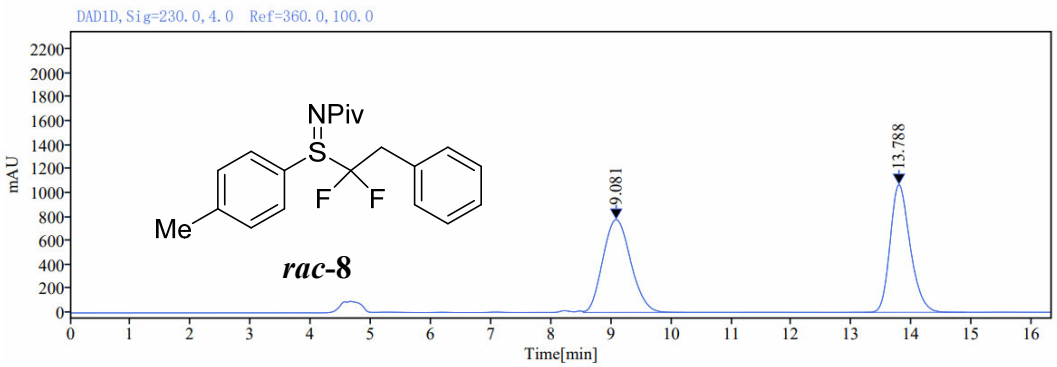
Peak#	Ret. Time	Area	Area%
1	48.869	34278912	98.119
2	53.944	657204	1.881

Figure S80. HPLC chromatograms of compound **8**.

HPLC spectra of **8**

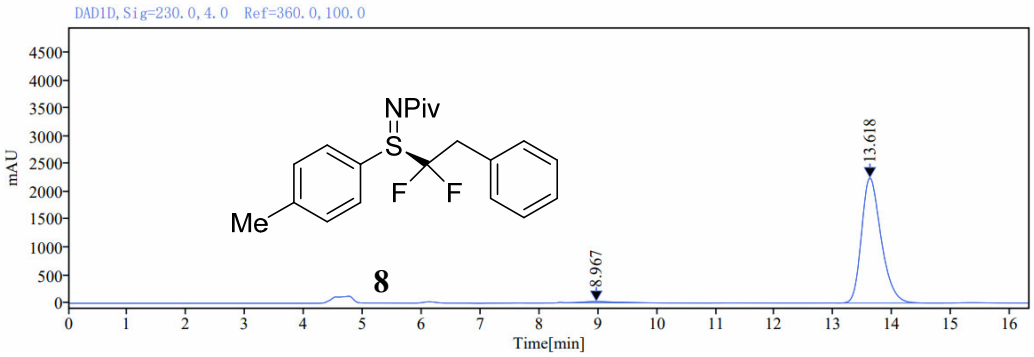
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 85/15, flow rate 0.7 mL/min, λ = 230 nm), t_R (major) = 13.62 min, t_R (minor) = 8.97 min.

$[\alpha]_D^{27}$ = −88 (c 0.5, $CHCl_3$).



Signal 1: DAD1D,Sig=230.0,4.0 Ref=360.0,100.0

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area%
9.081	VB	1.70	24930.80	773.86	50.27
13.788	VB	1.68	24666.33	1063.85	49.73
	Totals	3.38	49597.13		



Signal 1: DAD1D,Sig=230.0,4.0 Ref=360.0,100.0

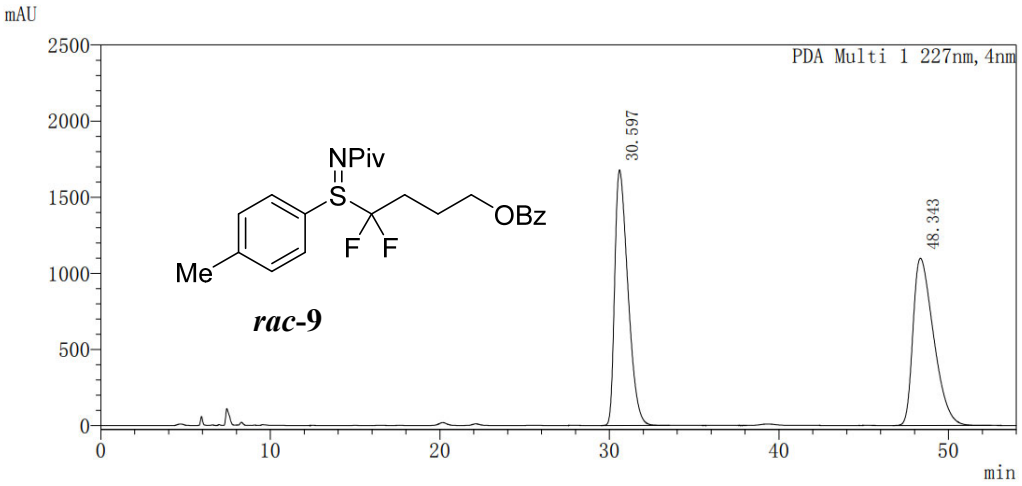
RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area%
8.967	MB m	2.47	881.04	23.26	1.66
13.618	VB	1.81	52102.13	2247.19	98.34
	Totals	4.28	52983.17		

Figure S81. HPLC chromatograms of compound **9**.

HPLC spectra of **9**

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 85/15, flow rate 0.7 mL/min, λ = 227 nm), t_R (major) = 48.61 min, t_R (minor) = 31.08 min.

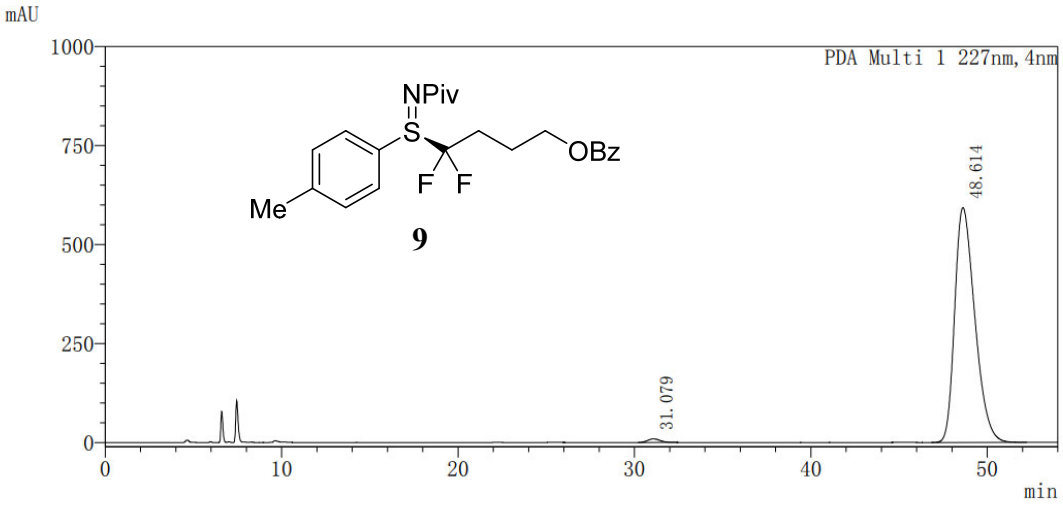
$[\alpha]_D^{27} = -140$ (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 227nm

Peak#	Ret. Time	Area	Area%
1	30.597	90778163	49.449
2	48.343	92799981	50.551



Peak Table

PDA Ch1 227nm

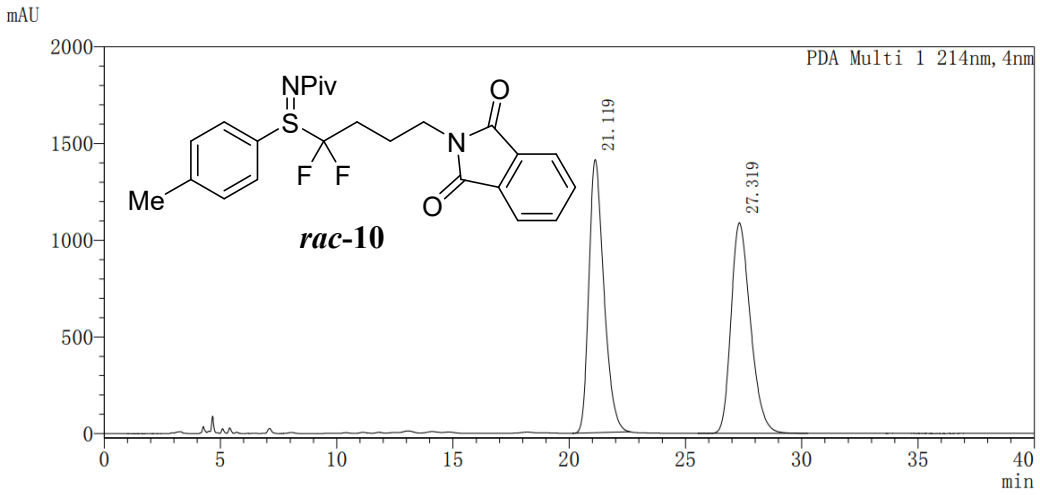
Peak#	Ret. Time	Area	Area%
1	31.079	452608	0.952
2	48.614	47085776	99.048

Figure S82. HPLC chromatograms of compound **10**.

HPLC spectra of **10**

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 27.64 min, t_R (minor) = 21.58 min.

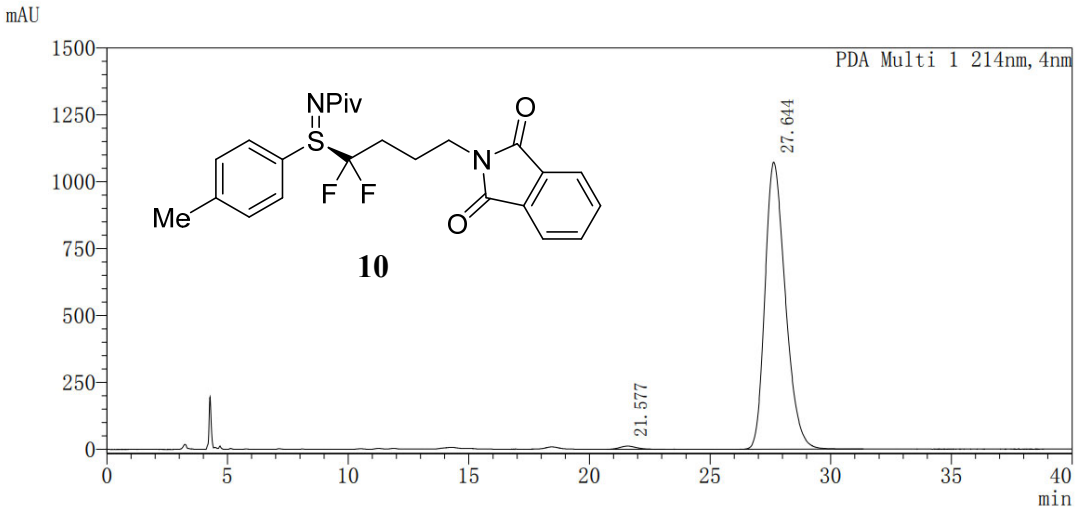
$[\alpha]_D^{27}$ = −133(c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 214nm

Peak#	Ret. Time	Area	Area%
1	21.119	63360673	50.056
2	27.319	63218946	49.944



Peak Table

PDA Ch1 214nm

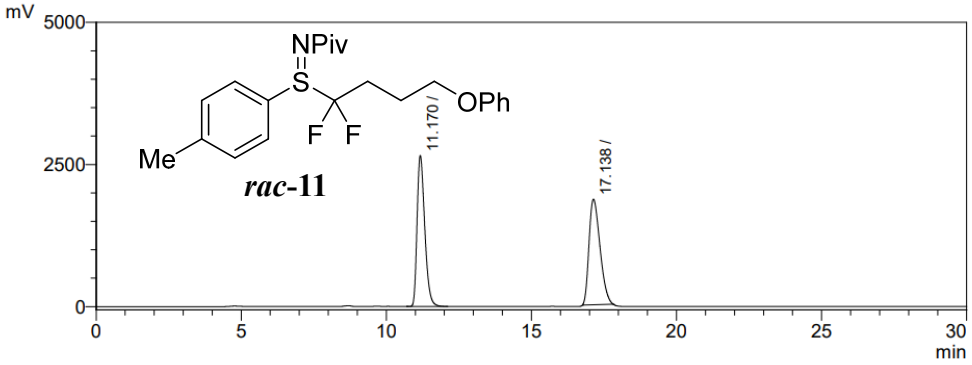
Peak#	Ret. Time	Area	Area%
1	21.577	565742	0.888
2	27.644	63177210	99.112

Figure S83. HPLC chromatograms of compound **11**.

HPLC spectra of **11**

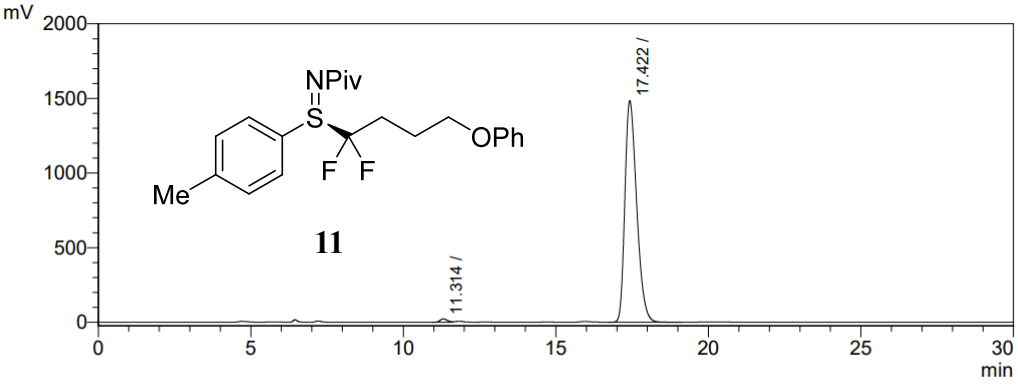
HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 85/15, flow rate 0.7 mL/min, λ = 240 nm), t_R (major) = 17.42 min, t_R (minor) = 11.31 min.

$[\alpha]_D^{27}$ = −56 (c 0.5, $CHCl_3$).



检测器A Ch2 240nm

Peak#	Ret. Time	Area	Area%
1	11.170	48826018	50.000
2	17.138	48825769	50.000



检测器A Ch2 240nm

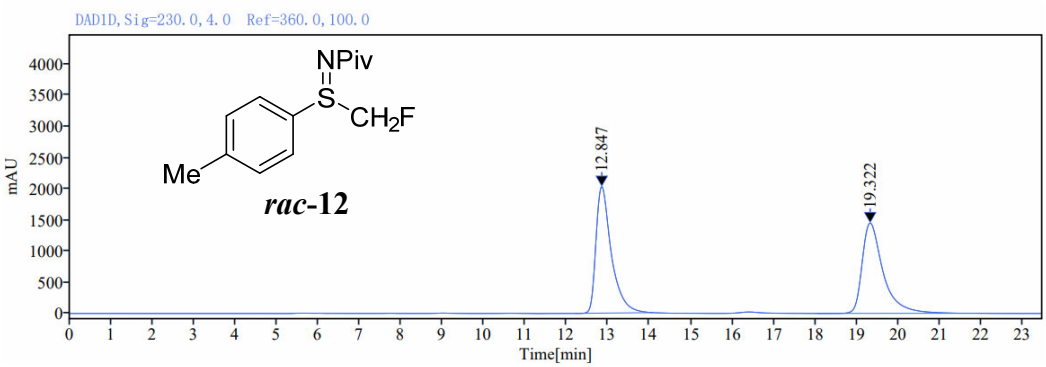
Peak#	Ret. Time	Area	Area%
1	11.314	371394	0.924
2	17.422	39811029	99.076

Figure S84. HPLC chromatograms of compound **12**.

HPLC spectra of **12**

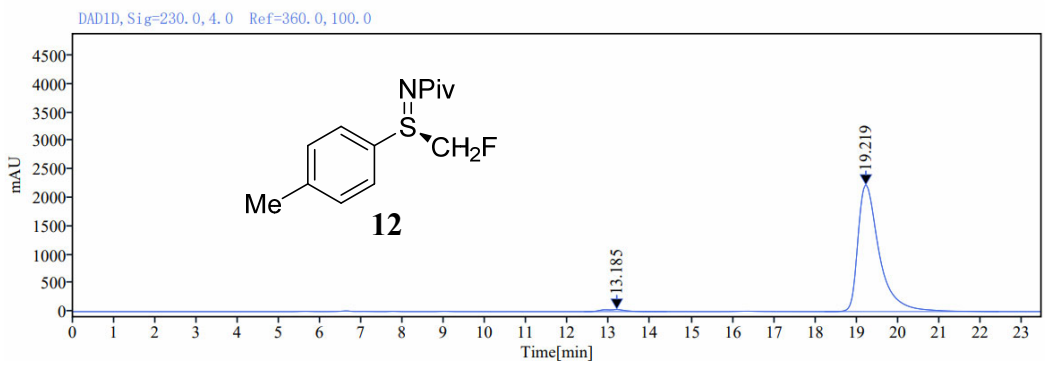
HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 19.22 min, t_R (minor) = 13.19 min.

$[\alpha]_D^{27} = -13$ (c 0.5, $CHCl_3$).



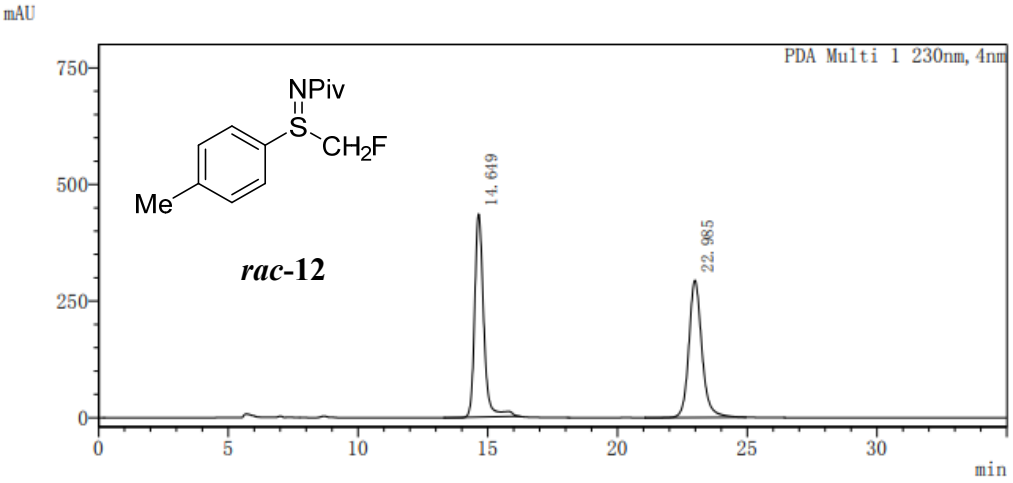
Signal 1: DAD1D,Sig=230.0,4.0 Ref=360.0,100.0

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area%
12.847	MM m	1.87	52338.66	2031.01	50.59
19.322	MM m	4.02	51122.48	1450.70	49.41
	Totals	5.89	103461.13		



Signal 1: DAD1D,Sig=230.0,4.0 Ref=360.0,100.0

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area%
13.185	MM m	2.00	1422.91	36.33	1.74
19.219	BM m	4.22	80342.00	2221.81	98.26
	Totals	6.21	81764.91		

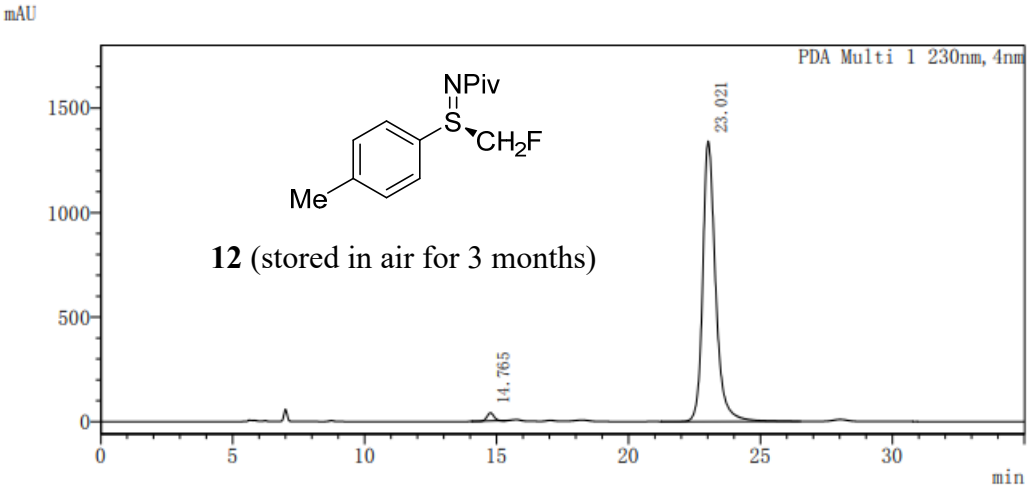


Peak Table

PDA Ch1 230nm

Peak#	Ret. Time	Area	Area%
1	14.649	10598073	50.725
2	22.985	10295281	49.275

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 23.02 min, t_R (minor) = 14.77 min.

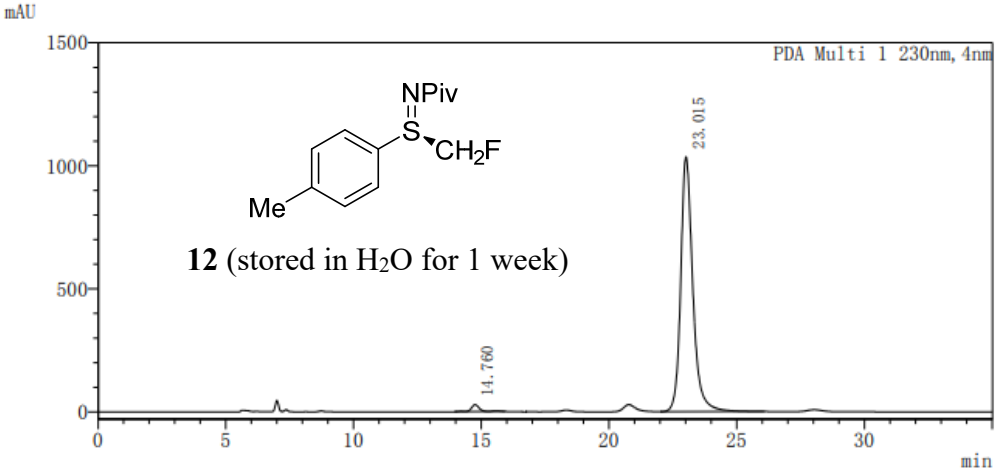


Peak Table

PDA Ch1 230nm

Peak#	Ret. Time	Area	Area%
1	14.765	660403	1.433
2	23.021	45428708	98.567

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 23.02 min, t_R (minor) = 14.76 min.



12 (stored in H_2O for 1 week)

Peak Table

PDA Ch1 230nm

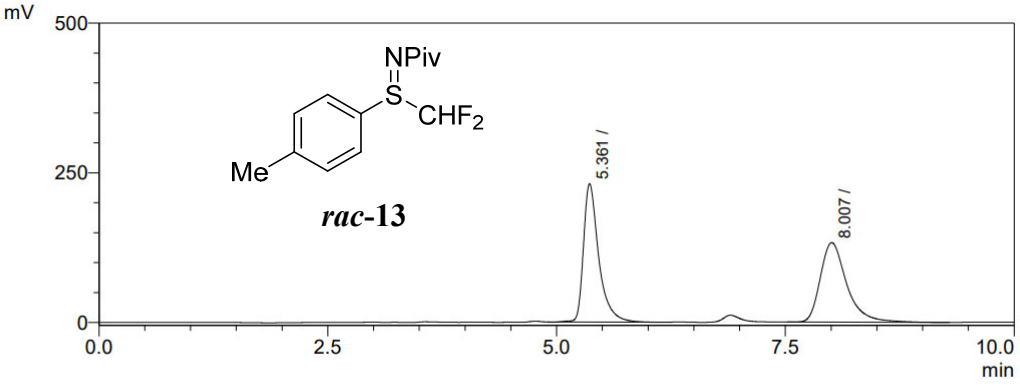
Peak#	Ret. Time	Area	Area%
1	14.760	656598	1.887
2	23.015	34146001	98.113

Figure S85. HPLC chromatograms of compound **13.**

HPLC spectra of **13**

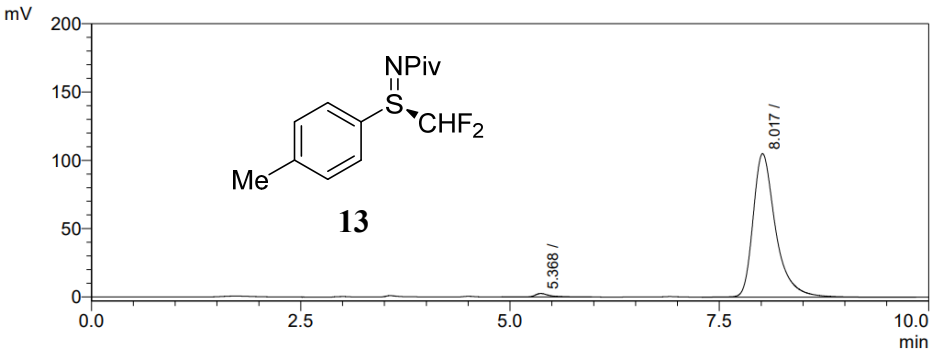
HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 8.02 min, t_R (minor) = 5.37 min.

$[\alpha]_D^{27}$ = −99 (c 0.5, $CHCl_3$).



检测器A 254nm

Peak#	Ret. Time	Area	Area%
1	5.361	2678453	50.156
2	8.007	2661799	49.844



检测器A 254nm

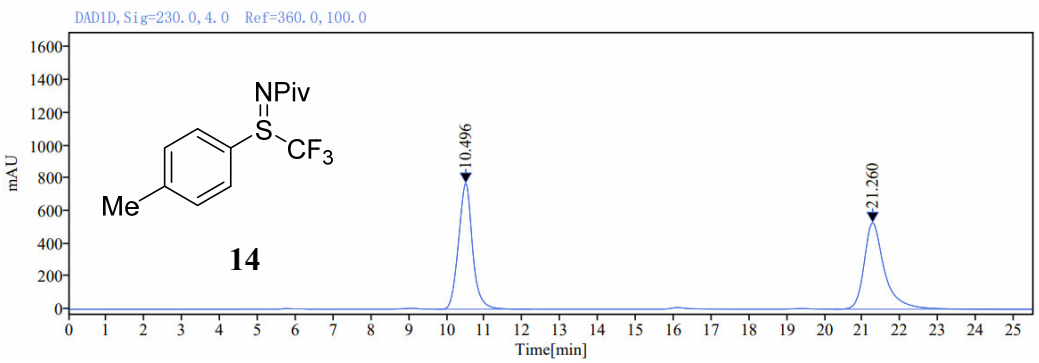
Peak#	Ret. Time	Area	Area%
1	5.368	30249	1.517
2	8.017	1963100	98.483

Figure S86. HPLC chromatograms of compound **14.**

HPLC spectra of **14**

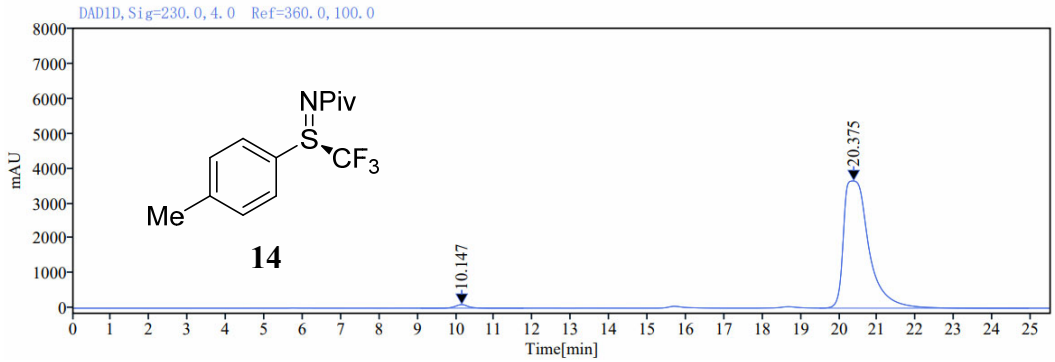
HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 20.38 min, t_R (minor) = 10.15 min.

$[\alpha]_D^{27}$ = −126(c 0.5, $CHCl_3$).



Signal 1: DAD1D,Sig=230.0,4.0 Ref=360.0,100.0

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area%
10.496	VB	2.46	19781.89	768.67	50.04
21.260	BB	5.27	19753.72	527.78	49.96
	Totals	7.73	39535.61		



Signal 1: DAD1D,Sig=230.0,4.0 Ref=360.0,100.0

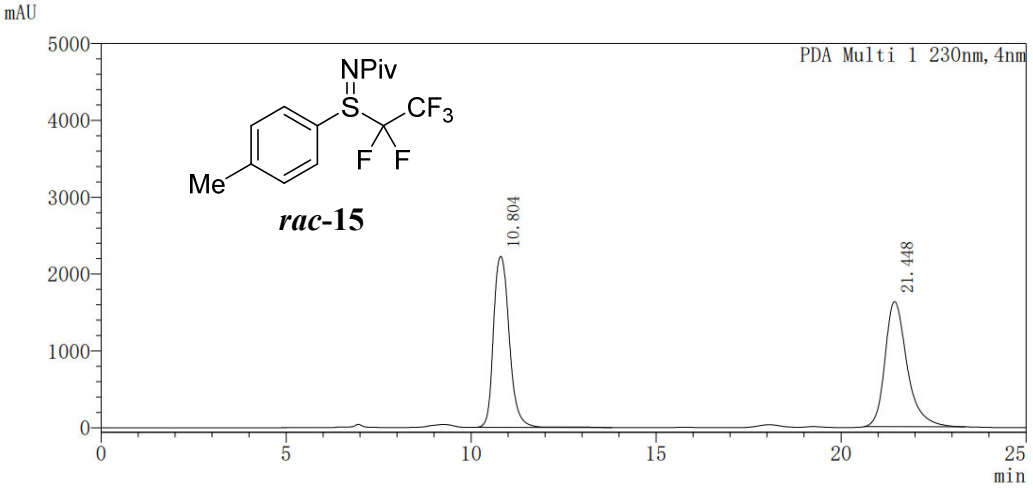
RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area%
10.147	BB	2.69	2425.36	102.37	1.42
20.375	VB	5.46	168038.79	3654.16	98.58
	Totals	8.15	170464.16		

Figure S87. HPLC chromatograms of compound **15.**

HPLC spectra of **15**

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 21.22 min, t_R (minor) = 10.72 min.

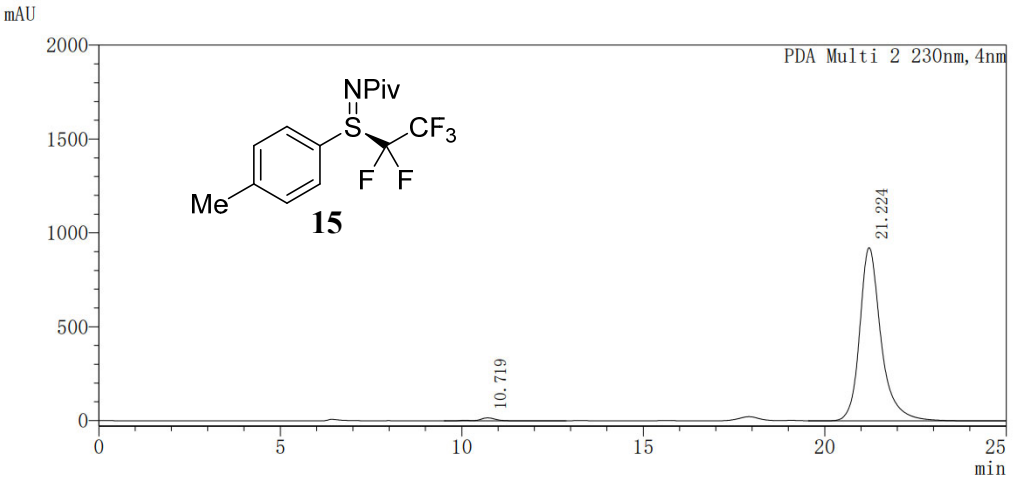
$[\alpha]_D^{27}$ = −133 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 230nm

Peak#	Ret. Time	Area	Area%
1	10.804	66119329	49.367
2	21.448	67813844	50.633



Peak Table

PDA Ch2 230nm

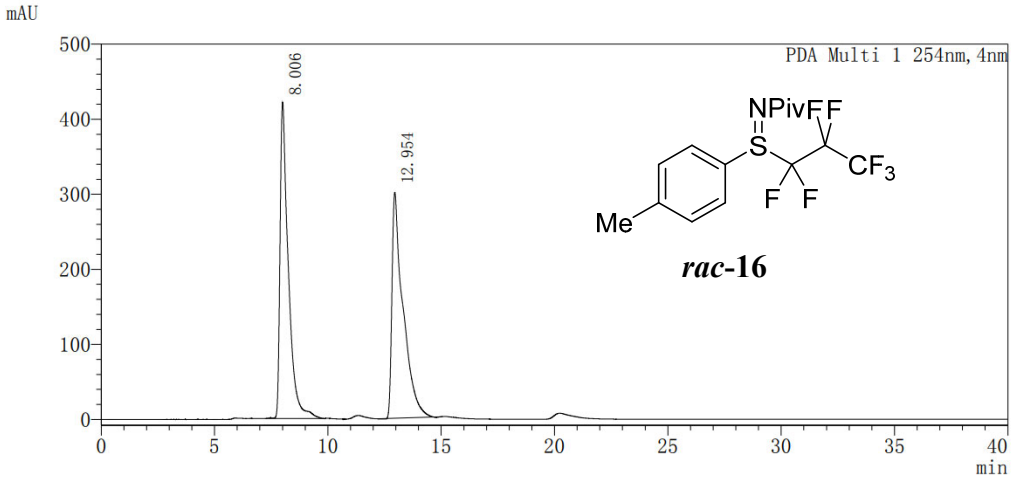
Peak#	Ret. Time	Area	Area%
1	10.719	497937	1.300
2	21.224	37799355	98.700

Figure S88. HPLC chromatograms of compound **16.**

HPLC spectra of **16**

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 12.95 min, t_R (minor) = 8.00 min.

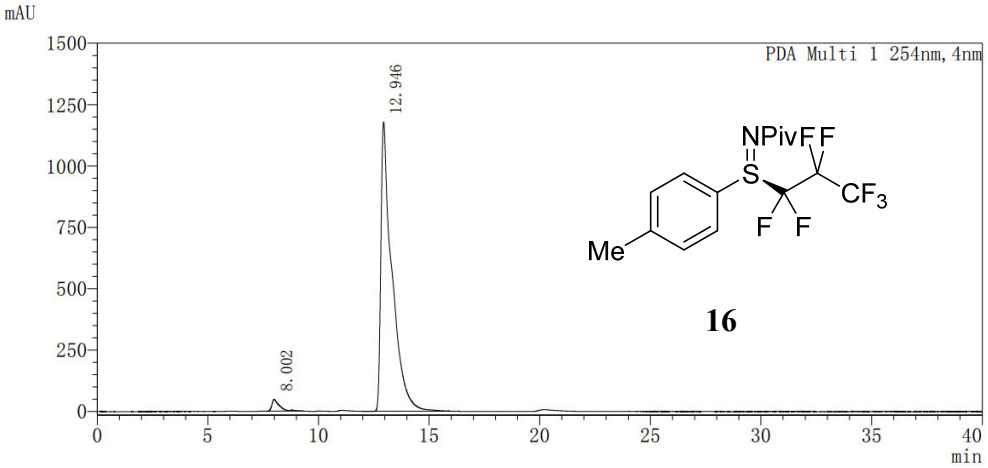
$[\alpha]_D^{27}$ = −154 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.006	10735799	51.116
2	12.954	10266943	48.884



Peak Table

PDA Ch1 254nm

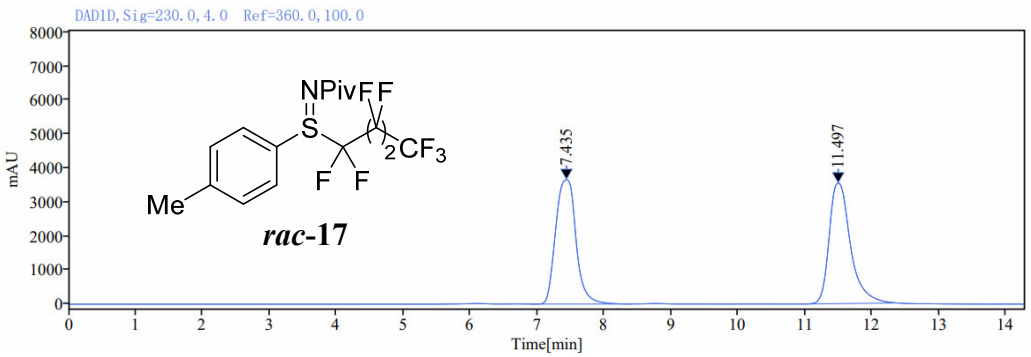
Peak#	Ret. Time	Area	Area%
1	8.002	1159654	2.738
2	12.946	41190435	97.262

Figure S89. HPLC chromatograms of compound **17.**

HPLC spectra of **17**

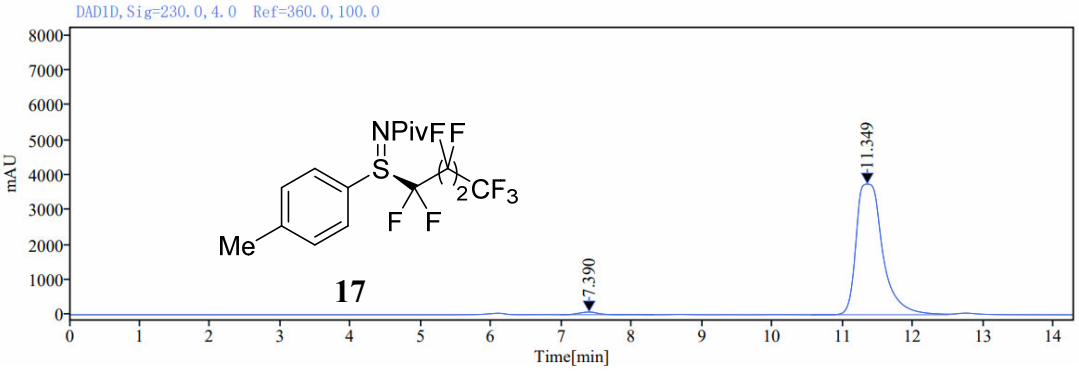
HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 11.35 min, t_R (minor) = 7.39 min.

$[\alpha]_D^{27}$ = −245 (c 0.5, $CHCl_3$).



Signal 1: DAD1D,Sig=230.0,4.0 Ref=360.0,100.0

RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area%
7.435	MV m	1.51	77335.53	3659.32	49.72
11.497	MM m	1.36	78196.23	3545.93	50.28
	Totals	2.87	155531.76		



Signal 1: DAD1D,Sig=230.0,4.0 Ref=360.0,100.0

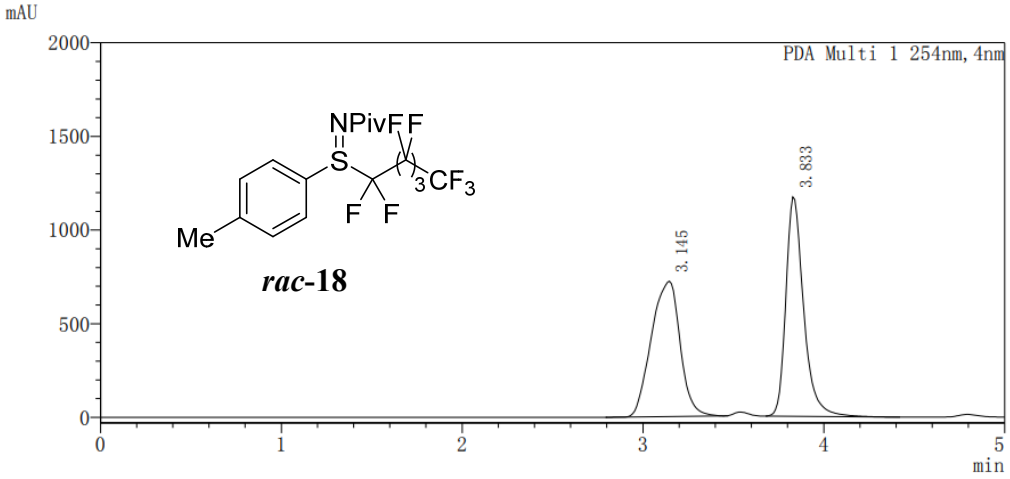
RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area%
7.390	MM m	1.33	1509.22	76.71	1.51
11.349	BV	1.95	98332.51	3741.45	98.49
	Totals	3.28	99841.73		

Figure S90. HPLC chromatograms of compound **18.**

HPLC spectra of **18**

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 3.82 min, t_R (minor) = 3.13 min.

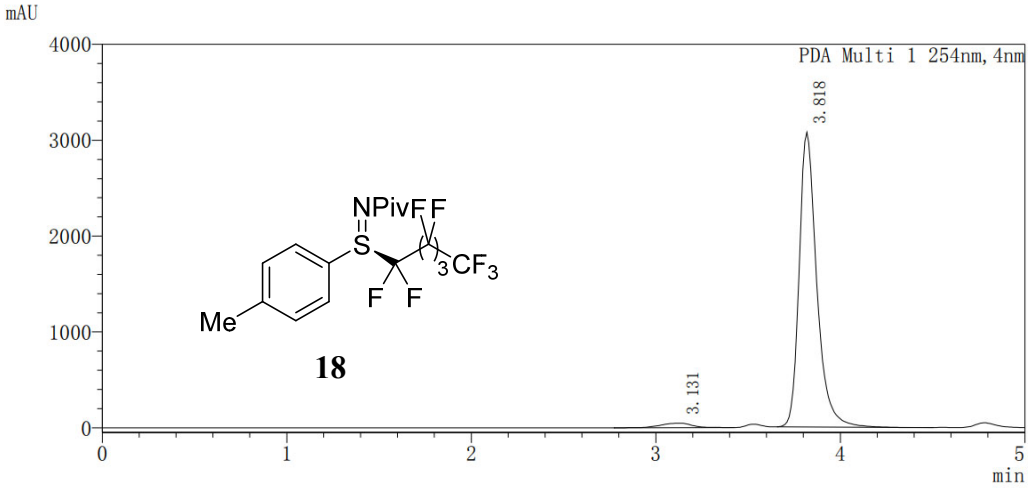
$[\alpha]_D^{27}$ = −230 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	3.145	7969224	49.877
2	3.833	8008596	50.123



Peak Table

PDA Ch1 254nm

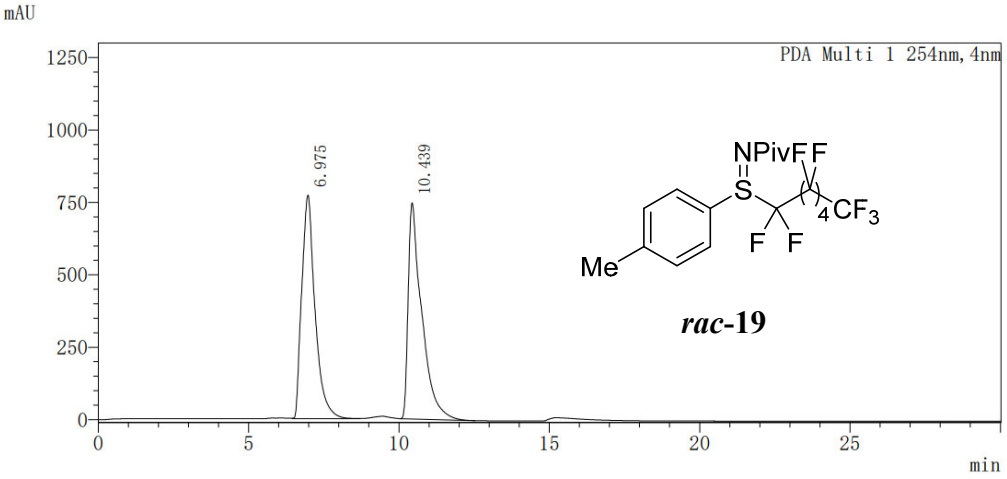
Peak#	Ret. Time	Area	Area%
1	3.131	554734	2.653
2	3.818	20358105	97.347

Figure S91. HPLC chromatograms of compound **19.**

HPLC spectra of **19**

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 10.44 min, t_R (minor) = 6.97 min.

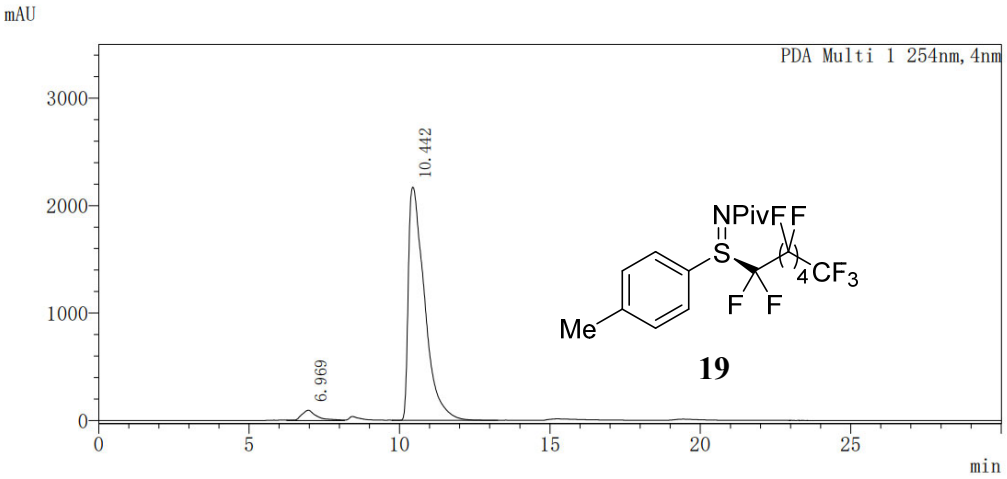
$[\alpha]_D^{27}$ = −309 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.975	23733678	50.230
2	10.439	23516629	49.770



Peak Table

PDA Ch1 254nm

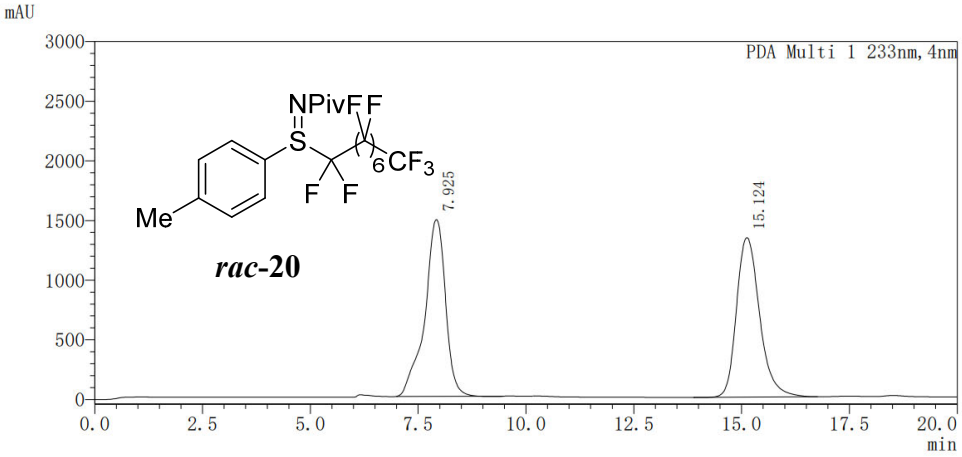
Peak#	Ret. Time	Area	Area%
1	6.969	3306041	3.901
2	10.442	81436062	96.099

Figure S92. HPLC chromatograms of compound **20.**

HPLC spectra of **20**

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 233 nm), t_R (major) =15.42 min, t_R (minor) = 8.31 min.

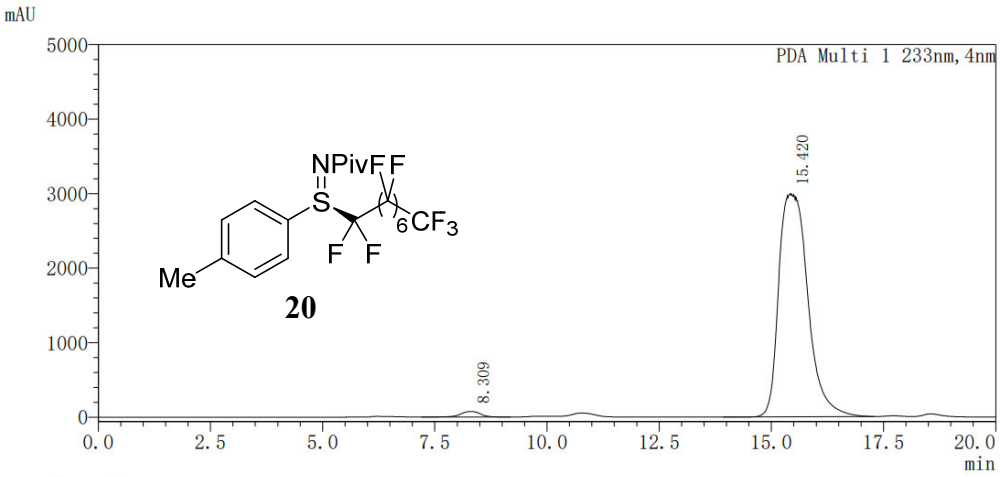
$[\alpha]_D^{27}$ = −150 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 233nm

Peak#	Ret. Time	Area	Area%
1	7.925	49740769	49.893
2	15.124	49954080	50.107



Peak Table

PDA Ch1 233nm

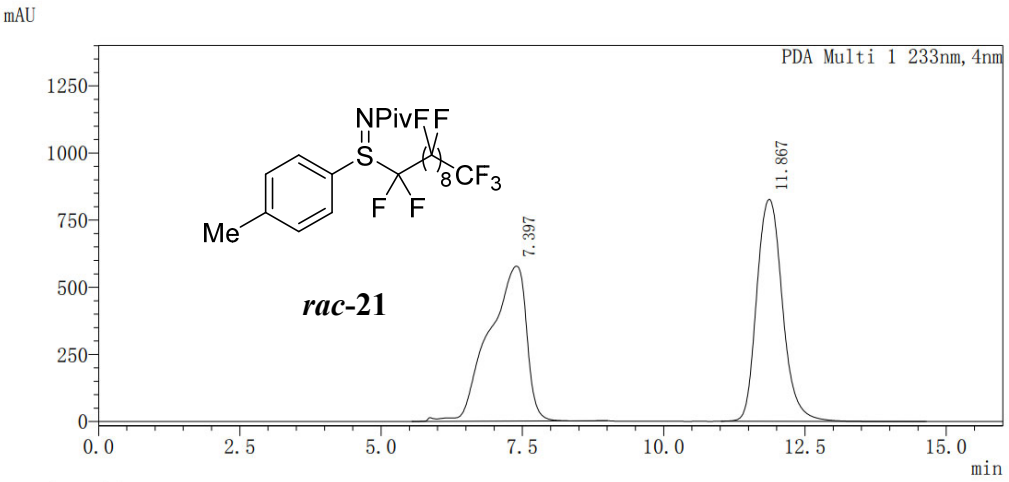
Peak#	Ret. Time	Area	Area%
1	8.309	2257670	1.640
2	15.420	135396499	98.360

Figure S93. HPLC chromatograms of compound **21.**

HPLC spectra of **21**

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 233 nm), t_R (major) = 12.08 min, t_R (minor) = 7.41 min.

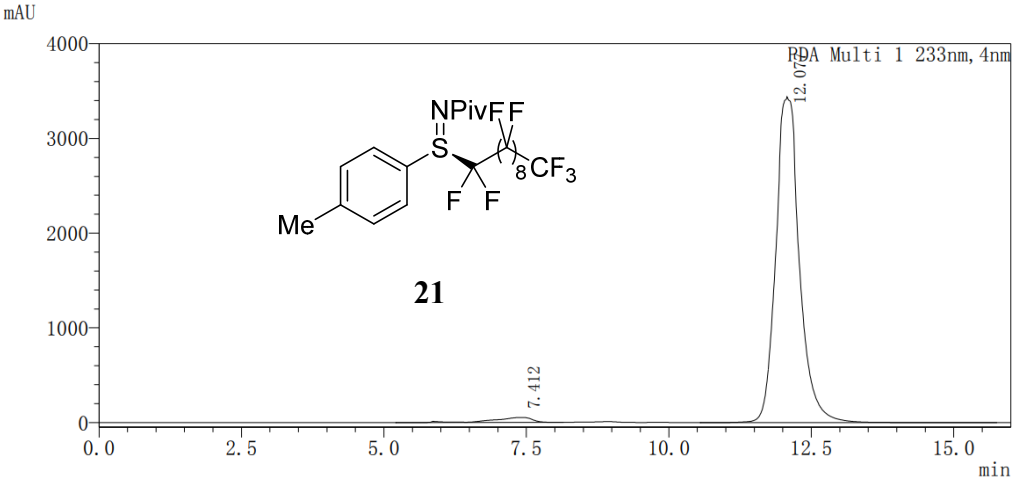
$[\alpha]_D^{27} = -144$ (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 233nm

Peak#	Ret. Time	Area	Area%
1	7.397	26681634	50.465
2	11.867	26189510	49.535



Peak Table

PDA Ch1 233nm

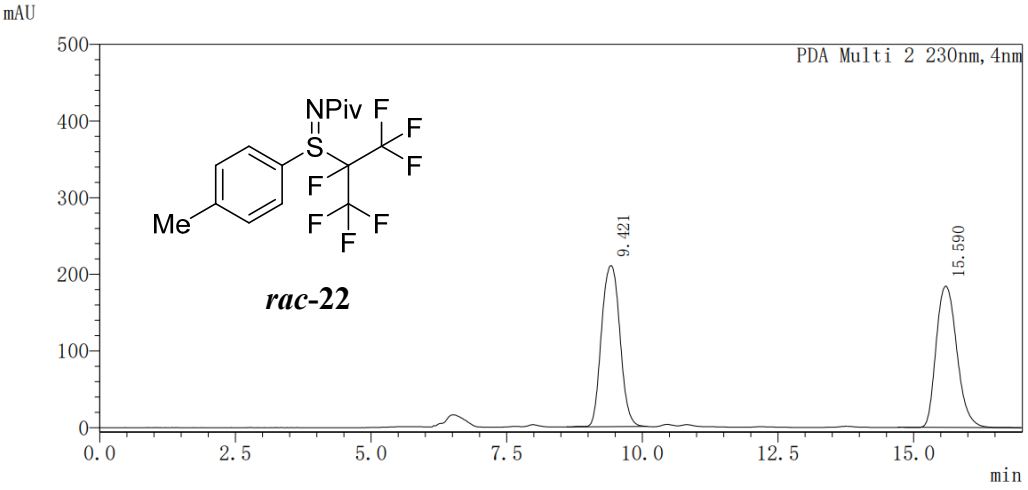
Peak#	Ret. Time	Area	Area%
1	7.412	2486322	2.443
2	12.077	99277674	97.557

Figure S94. HPLC chromatograms of compound **22.**

HPLC spectra of **22**

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 15.51 min, t_R (minor) = 9.41 min.

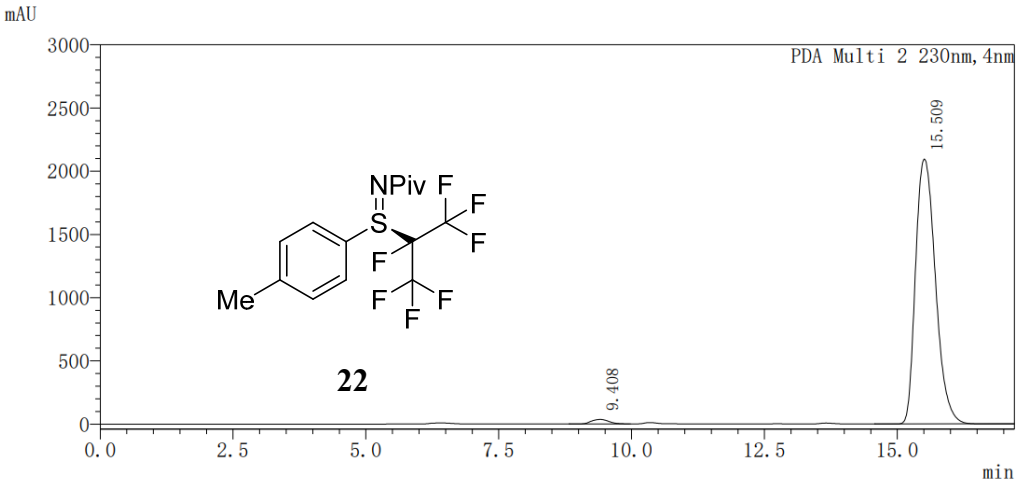
$[\alpha]_D^{27}$ = −160 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch2 230nm

Peak#	Ret. Time	Area	Area%
1	9.421	4970076	50.368
2	15.590	4897481	49.632



Peak Table

PDA Ch2 230nm

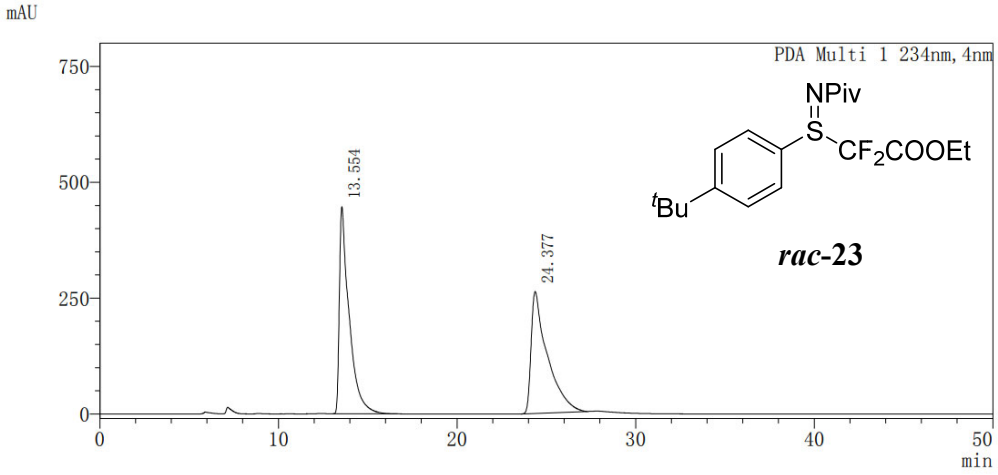
Peak#	Ret. Time	Area	Area%
1	9.408	812451	1.471
2	15.509	54432265	98.529

Figure S95. HPLC chromatograms of compound **23.**

HPLC spectra of **23**

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 234 nm), t_R (major) = 24.33 min, t_R (minor) = 13.60 min.

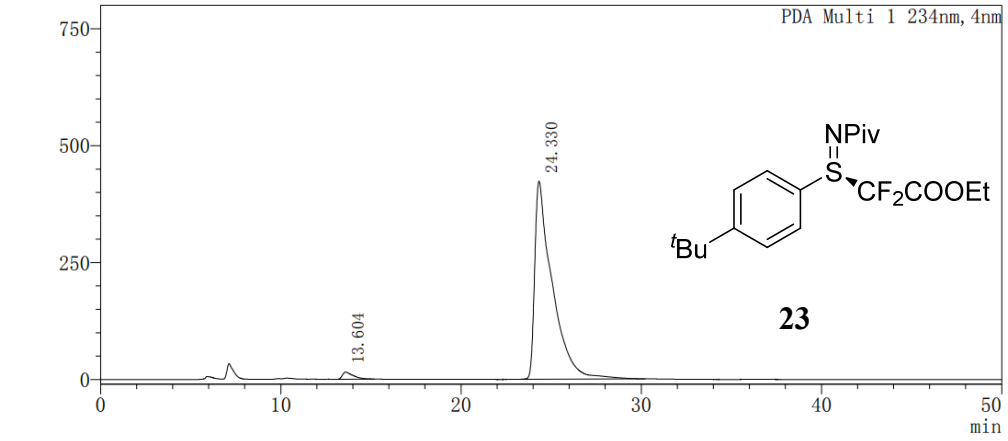
$[\alpha]_D^{27}$ = −25 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 234nm

Peak#	Ret. Time	Area	Area%
1	13.554	17021600	50.516
2	24.377	16673624	49.484



Peak Table

PDA Ch1 234nm

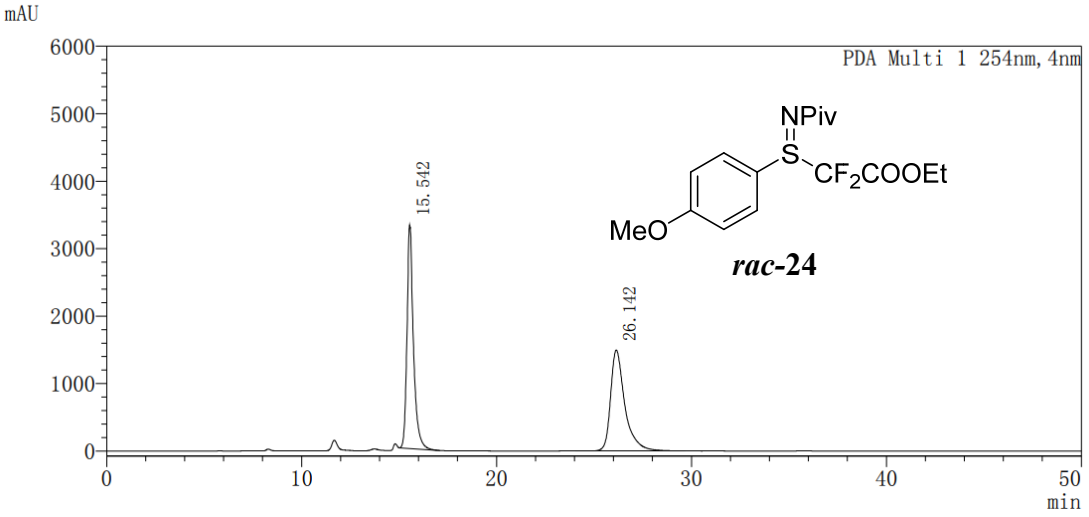
Peak#	Ret. Time	Area	Area%
1	13.604	628309	2.128
2	24.330	28904369	97.872

Figure S96. HPLC chromatograms of compound **24.**

HPLC spectra of **24**

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 25.94 min, t_R (minor) = 15.49 min.

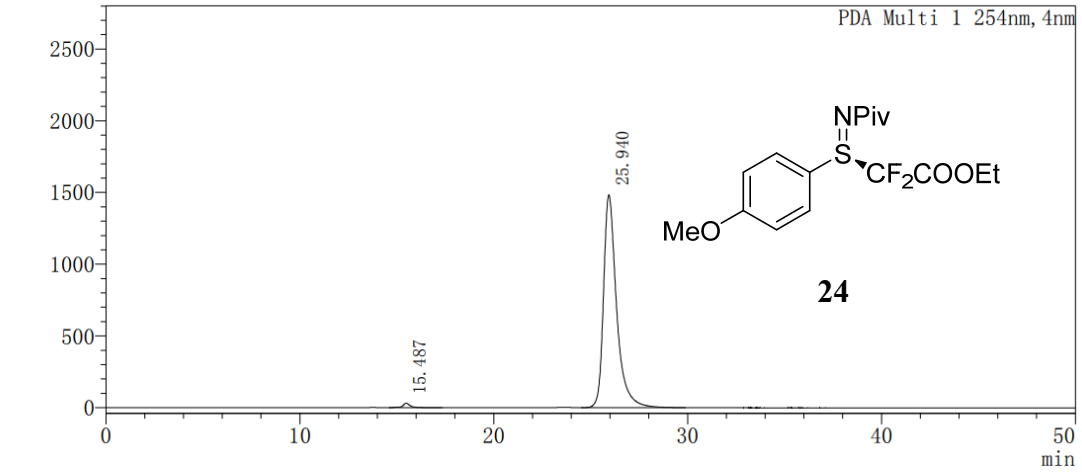
$[\alpha]_D^{27} = -5$ (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.542	76024380	50.066
2	26.142	75824622	49.934



Peak Table

PDA Ch1 254nm

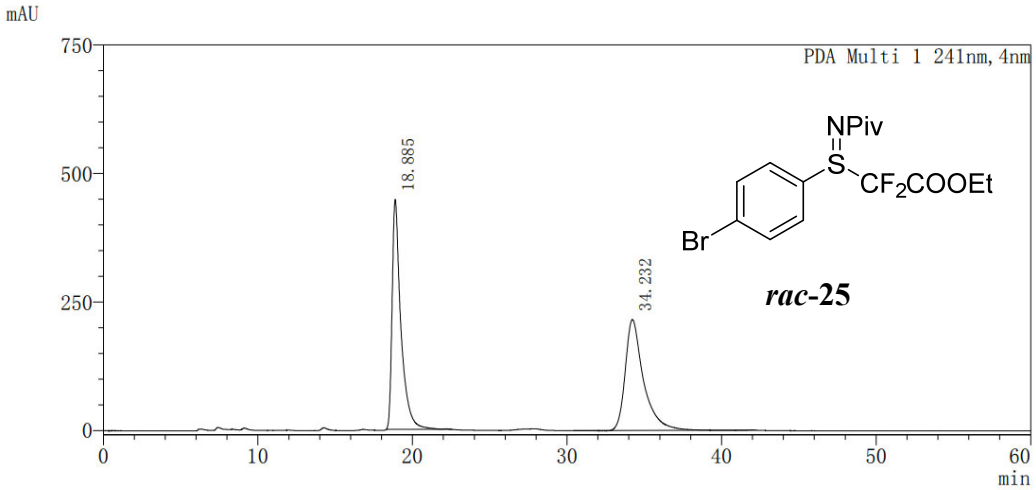
Peak#	Ret. Time	Area	Area%
1	15.487	888603	1.261
2	25.940	69574626	98.739

Figure S97. HPLC chromatograms of compound **25.**

HPLC spectra of **25**

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 241 nm), t_R (major) = 34.04 min, t_R (minor) = 18.87 min.

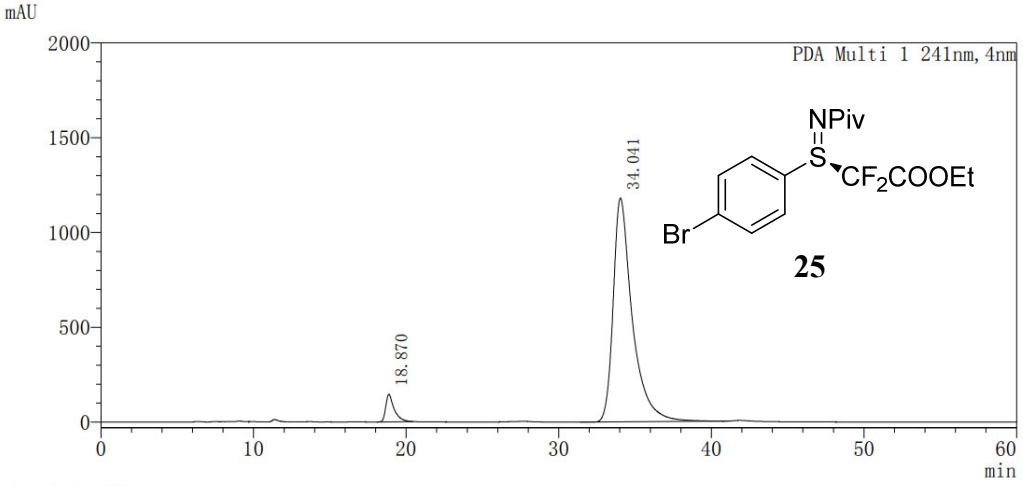
$[\alpha]_D^{27}$ = −22 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 241nm

Peak#	Ret. Time	Area	Area%
1	18.885	17629624	49.952
2	34.232	17663619	50.048



Peak Table

PDA Ch1 241nm

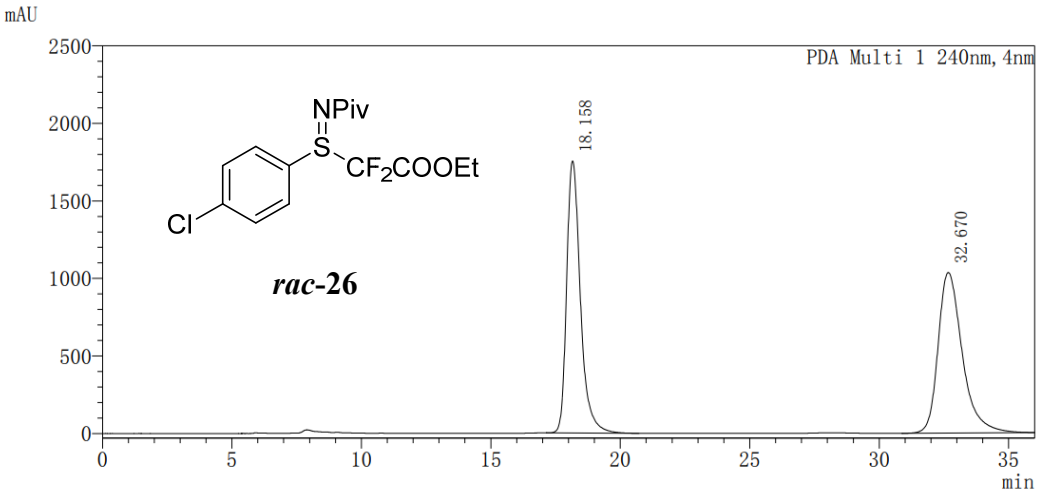
Peak#	Ret. Time	Area	Area%
1	18.870	5527422	5.096
2	34.041	102931589	94.904

Figure S98. HPLC chromatograms of compound **26.**

HPLC spectra of **26**

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 240 nm), t_R (major) = 32.00 min, t_R (minor) = 18.10 min.

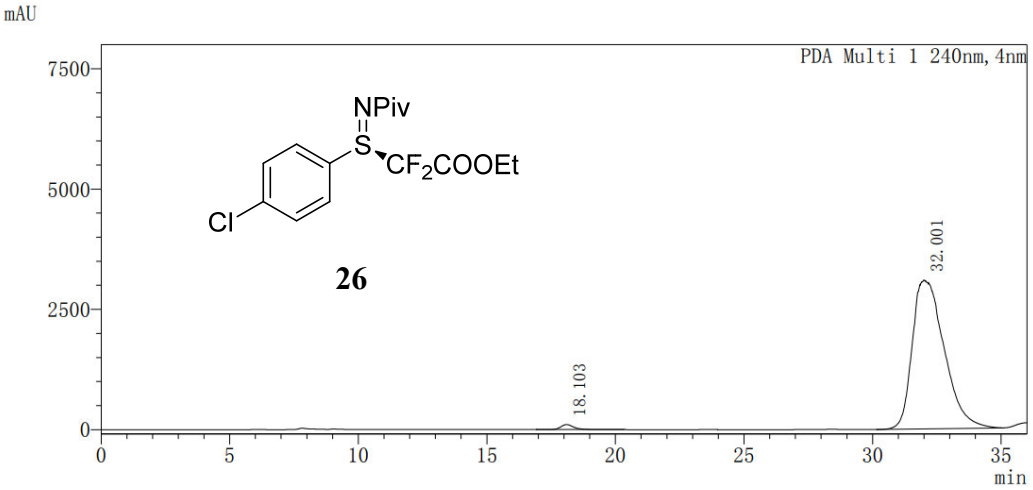
$[\alpha]_D^{27} = -15$ (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 240nm

Peak#	Ret. Time	Area	Area%
1	18.158	64845754	49.113
2	32.670	67188003	50.887



Peak Table

PDA Ch1 240nm

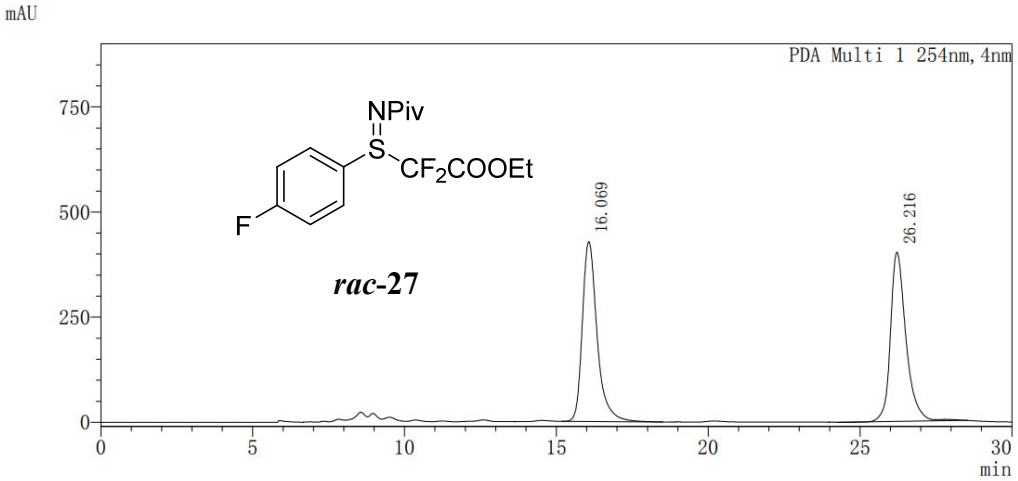
Peak#	Ret. Time	Area	Area%
1	18.103	3831025	1.413
2	32.001	267249185	98.587

Figure S99. HPLC chromatograms of compound **27.**

HPLC spectra of **27**

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 26.21 min, t_R (minor) = 16.11 min.

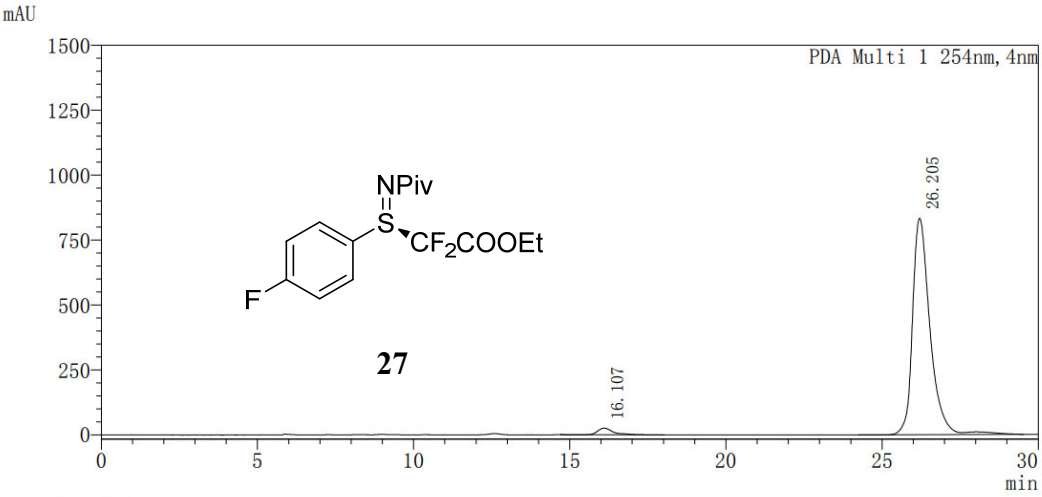
$[\alpha]_D^{27} = -14$ (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.069	14522841	50.364
2	26.216	14313183	49.636



Peak Table

PDA Ch1 254nm

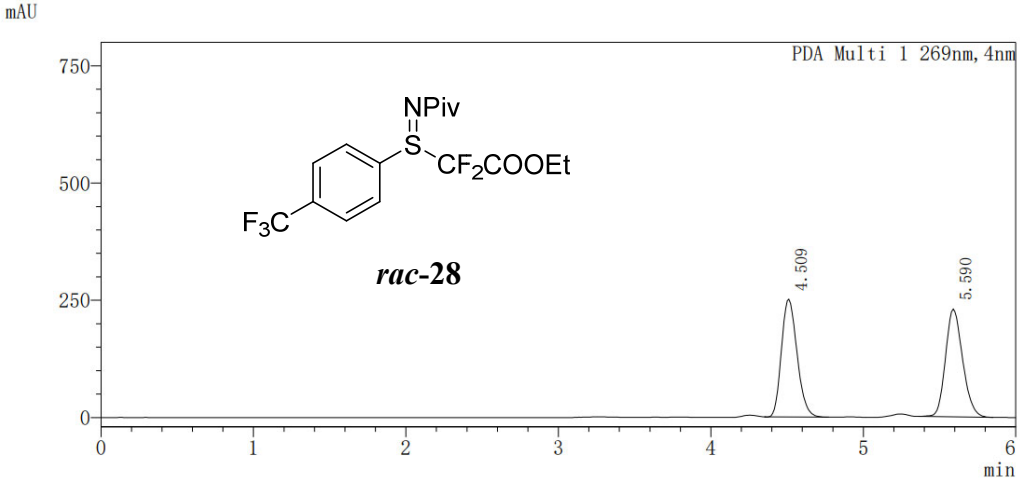
Peak#	Ret. Time	Area	Area%
1	16.107	884967	2.637
2	26.205	32678660	97.363

Figure S100. HPLC chromatograms of compound **28.**

HPLC spectra of **28**

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 269 nm), t_R (major) = 5.59 min, t_R (minor) = 4.52 min.

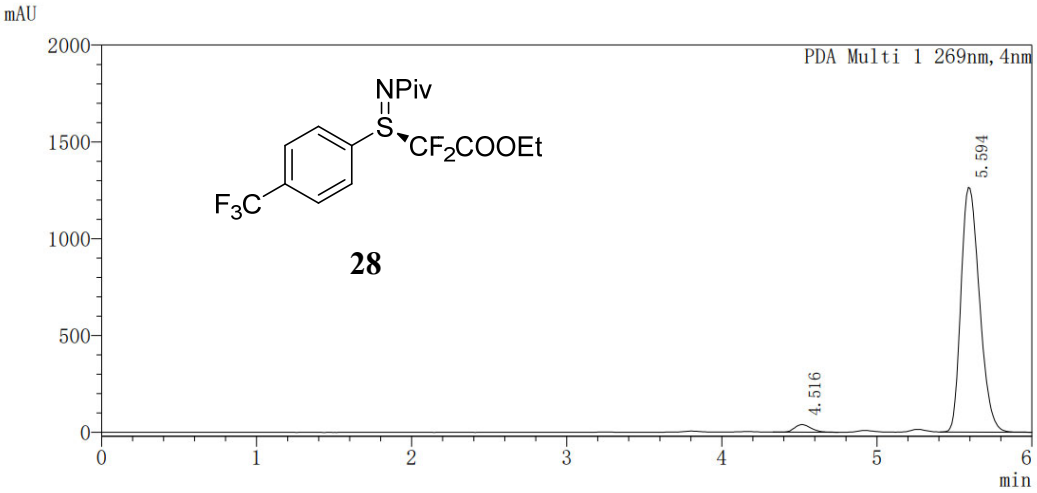
$[\alpha]_D^{27} = -14$ (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 269nm

Peak#	Ret. Time	Area	Area%
1	4.509	1790354	49.916
2	5.590	1796403	50.084



Peak Table

PDA Ch1 269nm

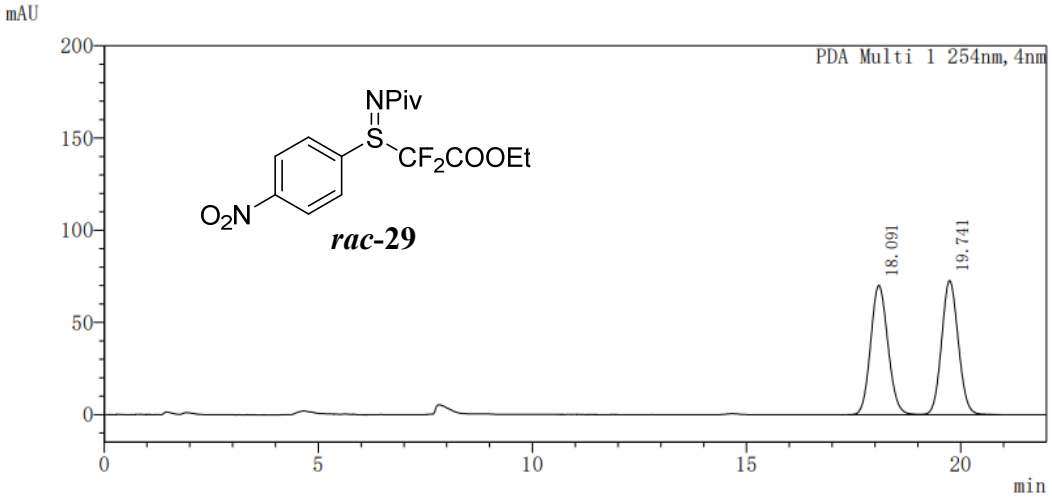
Peak#	Ret. Time	Area	Area%
1	4.516	282154	2.623
2	5.594	10475977	97.377

Figure S101. HPLC chromatograms of compound **29.**

HPLC spectra of **29**

HPLC analysis: Chiralcel ID (*n*-hexane/*i*-PrOH = 85/15, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 19.73 min, t_R (minor) = 18.12 min.

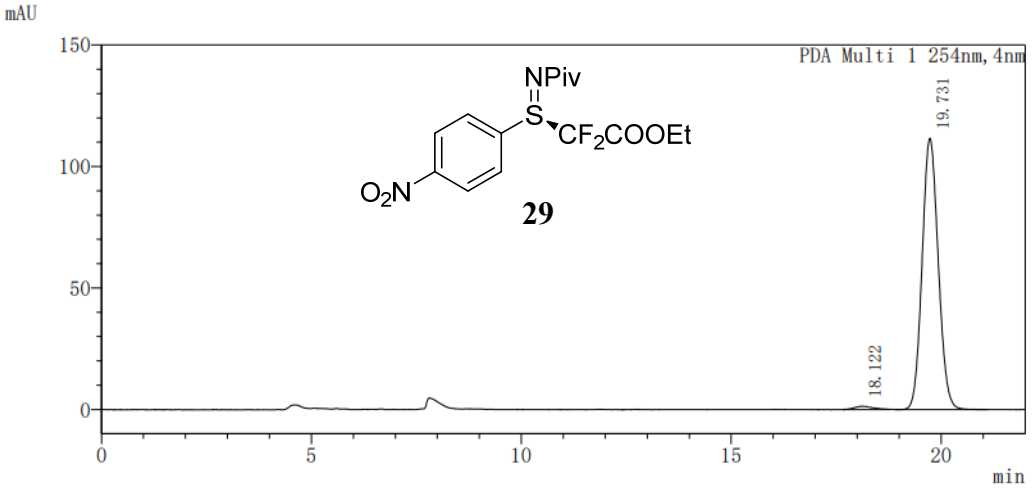
$[\alpha]_D^{27}$ = −8 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.091	1978136	50.089
2	19.741	1971077	49.911



Peak Table

PDA Ch1 254nm

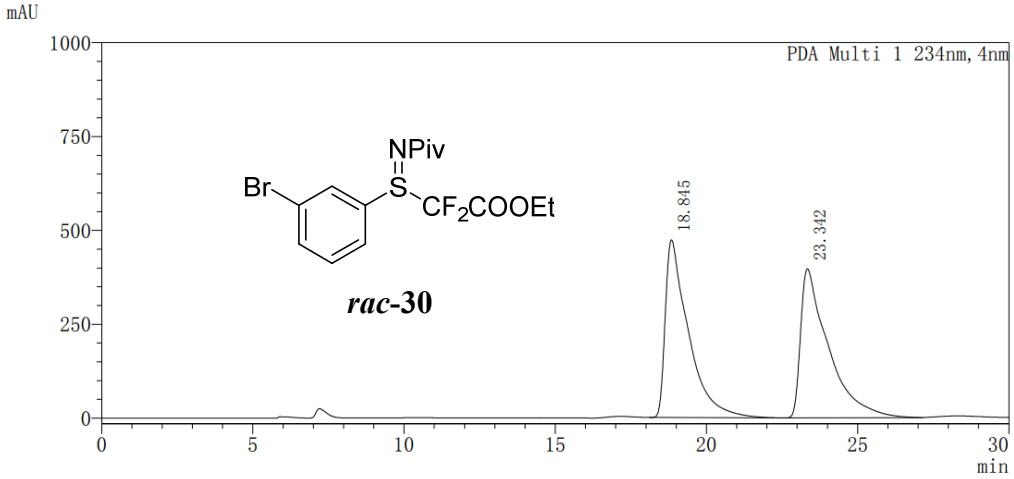
Peak#	Ret. Time	Area	Area%
1	18.122	45600	1.506
2	19.731	2982084	98.494

Figure S102. HPLC chromatograms of compound **30.**

HPLC spectra of **30**

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 224 nm), t_R (major) = 23.31 min, t_R (minor) = 18.85 min.

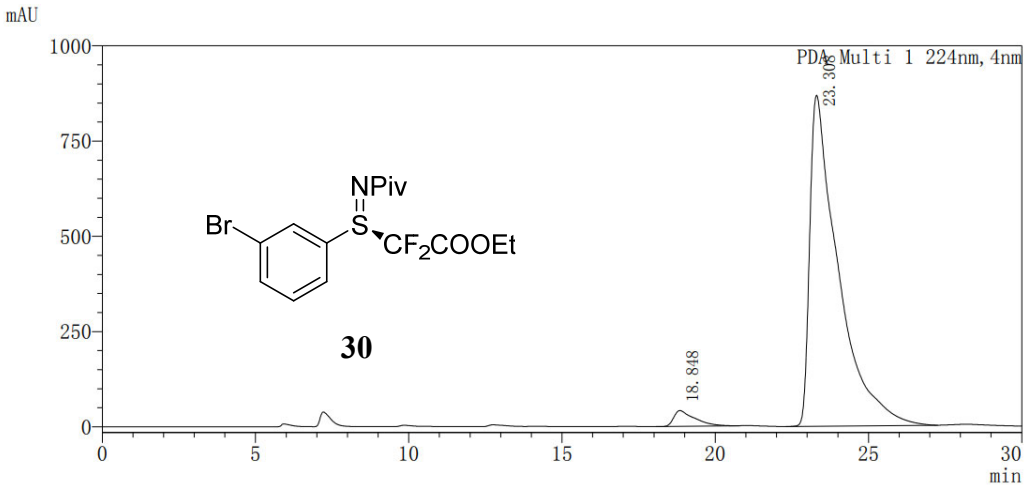
$[\alpha]_D^{27}$ = −5 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 234nm

Peak#	Ret. Time	Area	Area%
1	18.845	25280120	49.868
2	23.342	25413521	50.132



Peak Table

PDA Ch1 224nm

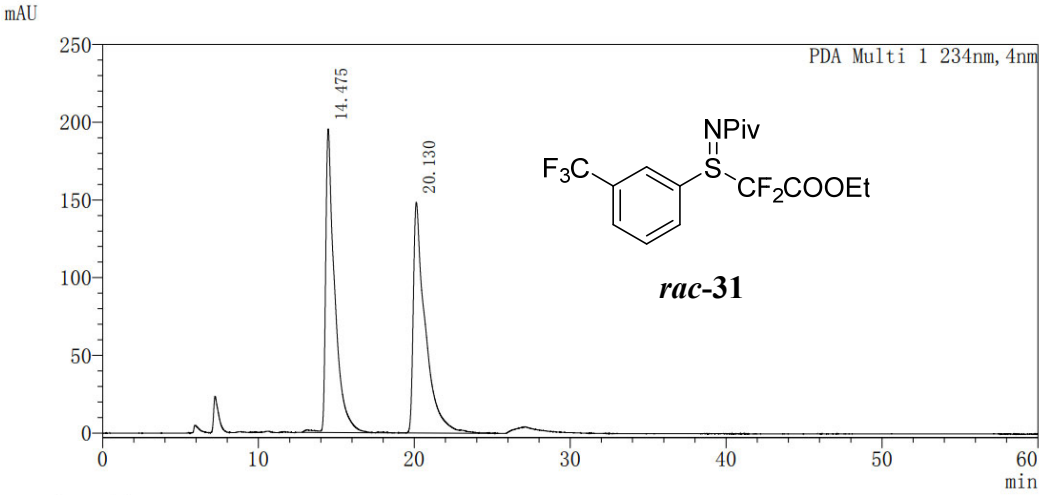
Peak#	Ret. Time	Area	Area%
1	18.848	1960632	3.375
2	23.308	56137166	96.625

Figure S103. HPLC chromatograms of compound **31.**

HPLC spectra of **31**

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 234 nm), t_R (major) = 20.05 min, t_R (minor) = 14.49 min.

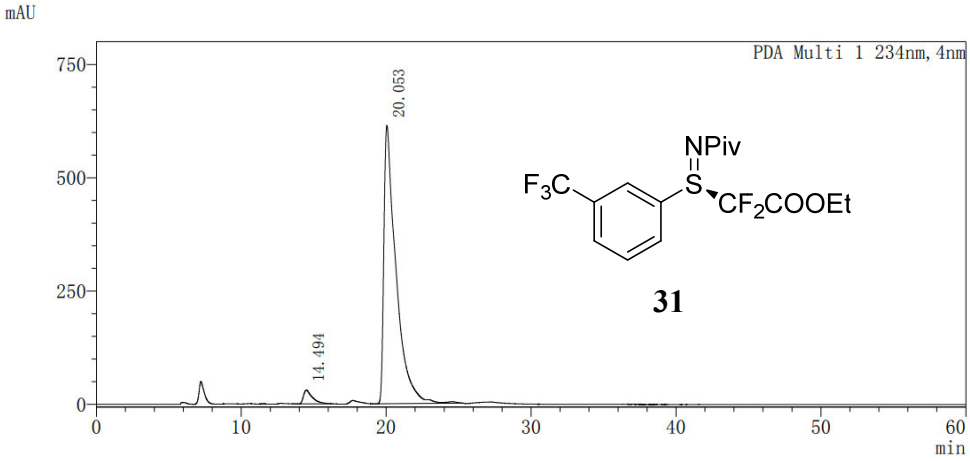
$[\alpha]_D^{27}$ = −5 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 234nm

Peak#	Ret. Time	Area	Area%
1	14.475	7932894	50.028
2	20.130	7924003	49.972



Peak Table

PDA Ch1 234nm

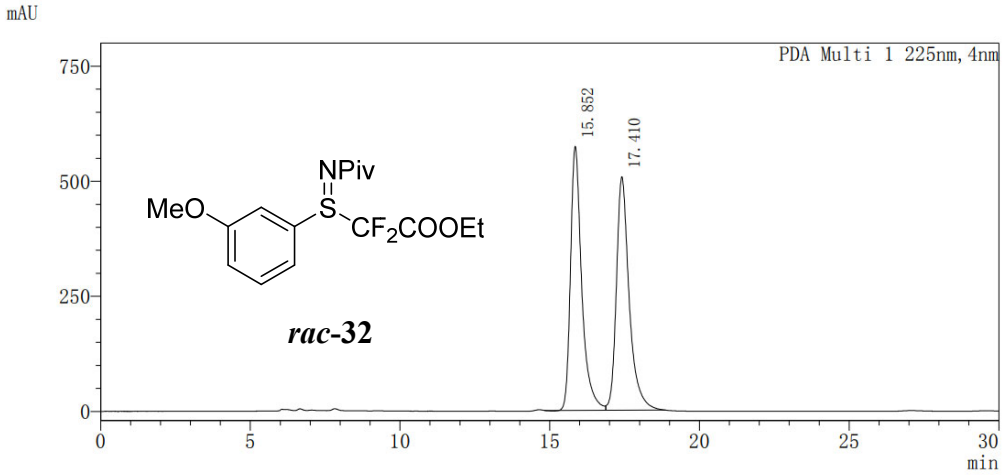
Peak#	Ret. Time	Area	Area%
1	14.494	1287060	3.470
2	20.053	35804902	96.530

Figure S104. HPLC chromatograms of compound **32.**

HPLC spectra of **32**

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 225 nm), t_R (major) = 17.33 min, t_R (minor) = 15.86 min.

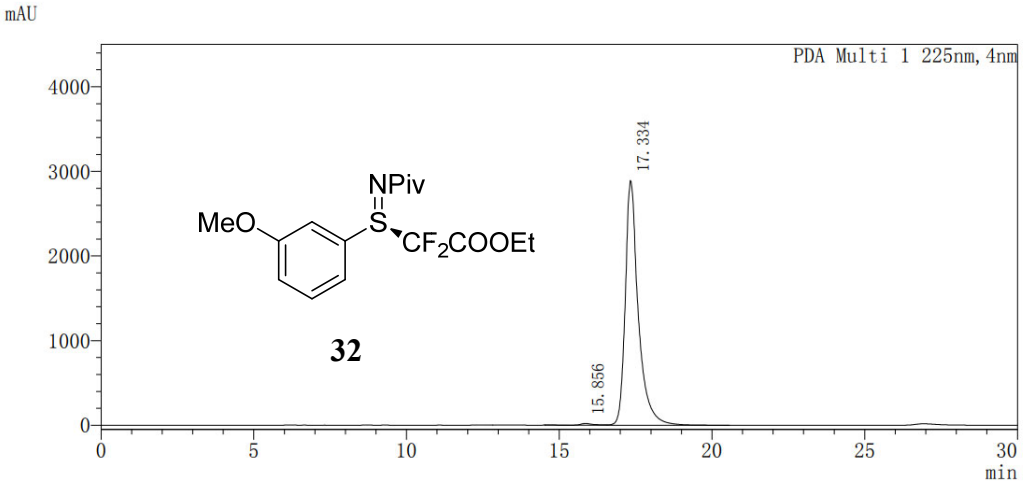
$[\alpha]_D^{27} = -10$ (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 225nm

Peak#	Ret. Time	Area	Area%
1	15.852	14928368	49.754
2	17.410	15075739	50.246



Peak Table

PDA Ch1 225nm

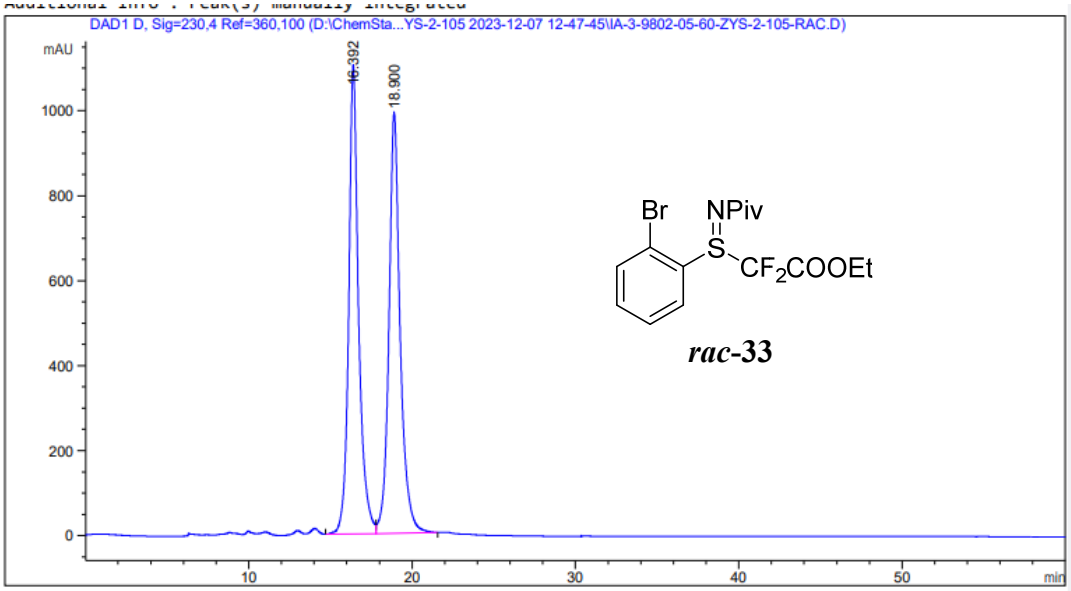
Peak#	Ret. Time	Area	Area%
1	15.856	555066	0.644
2	17.334	85618318	99.356

Figure S105. HPLC chromatograms of compound **33.**

HPLC spectra of **33**

HPLC analysis: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 18.82 min, t_R (minor) = 16.37 min.

$[\alpha]_D^{27} = -15$ (c 0.5, $CHCl_3$).

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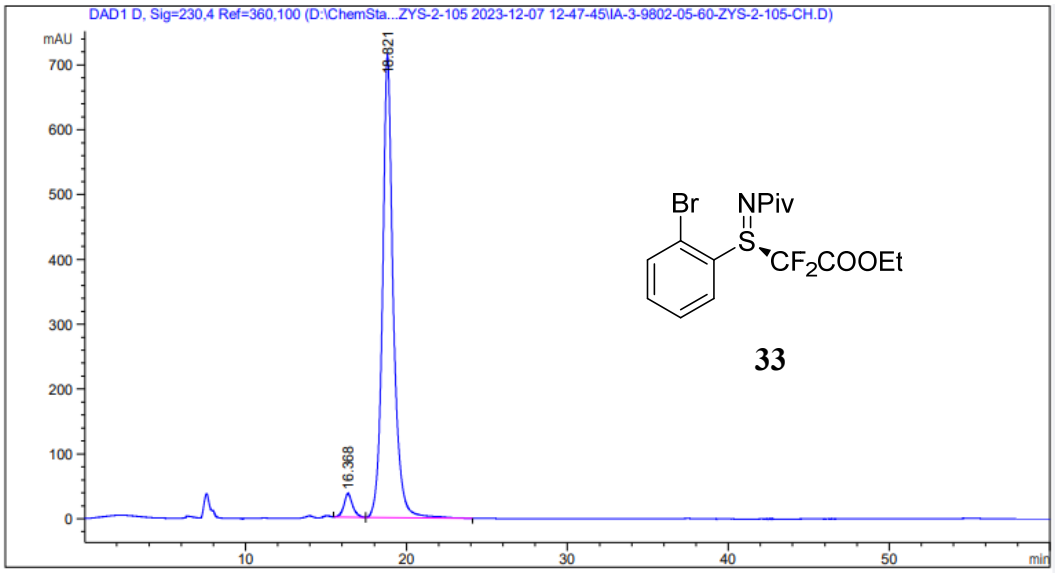
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.392 BV    0.6081 4.65915e4  1104.62183  49.5752
   2  18.900 VB    0.6862 4.73899e4   990.45978  50.4248
```



33

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=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.368 BB    0.5336 1366.90552   36.60883   3.9470
   2  18.821 BB    0.6687 3.32644e4   715.07251  96.0530
```
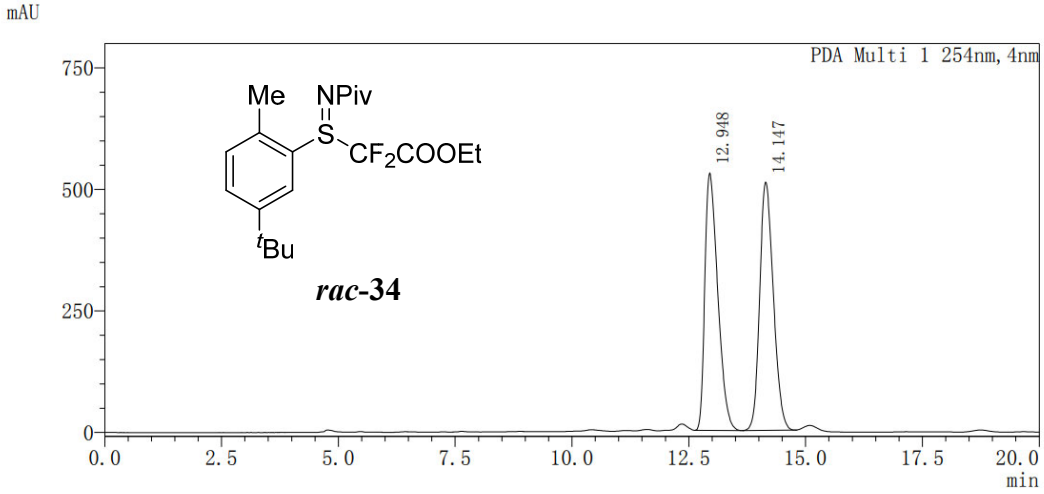

Figure S106. HPLC chromatograms of compound **34.**

HPLC spectra of **34**

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 14.08 min, t_R (minor) = 13.01 min.

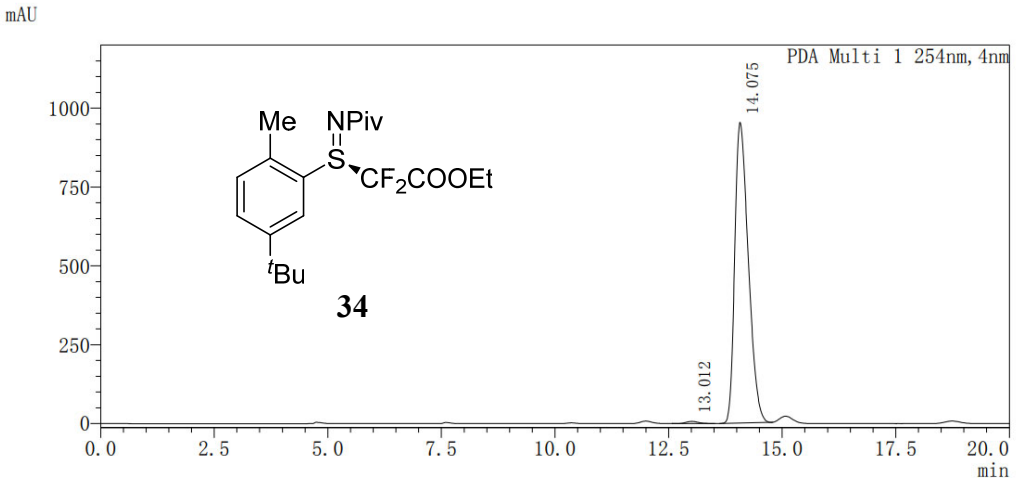
$[\alpha]_D^{27} = -14$ (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	12.948	10173738	49.466
2	14.147	10393339	50.534



Peak Table

PDA Ch1 254nm

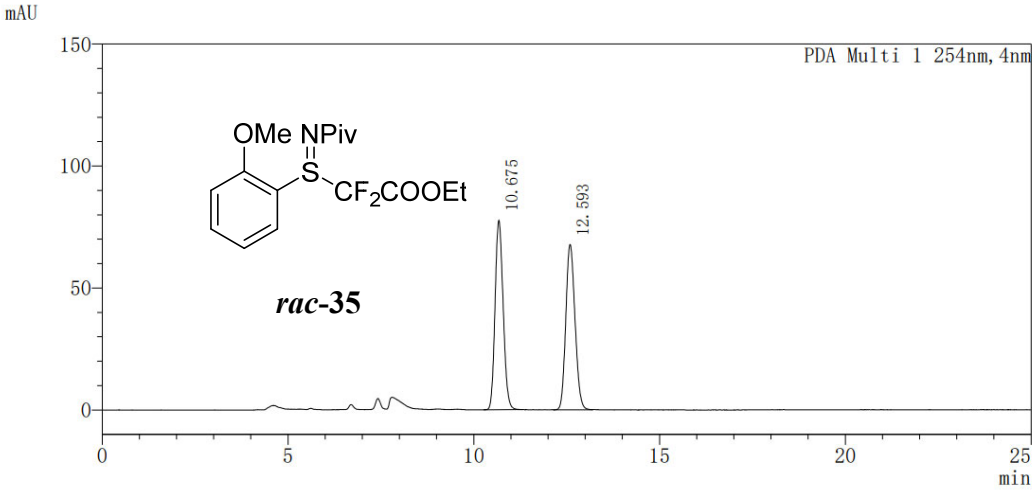
Peak#	Ret. Time	Area	Area%
1	13.012	127487	0.640
2	14.075	19803516	99.360

Figure S107. HPLC chromatograms of compound **35.**

HPLC spectra of **35**

HPLC analysis: Chiralcel ID (*n*-hexane/*i*-PrOH = 85/15, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 10.71 min, t_R (minor) = 12.67 min.

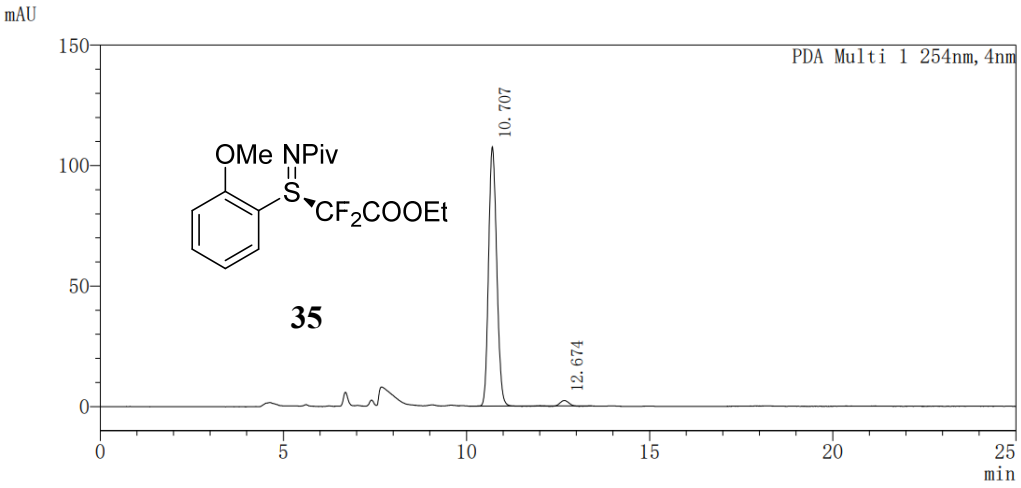
$[\alpha]_D^{27} = -13$ (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.675	1177088	50.130
2	12.593	1170994	49.870



Peak Table

PDA Ch1 254nm

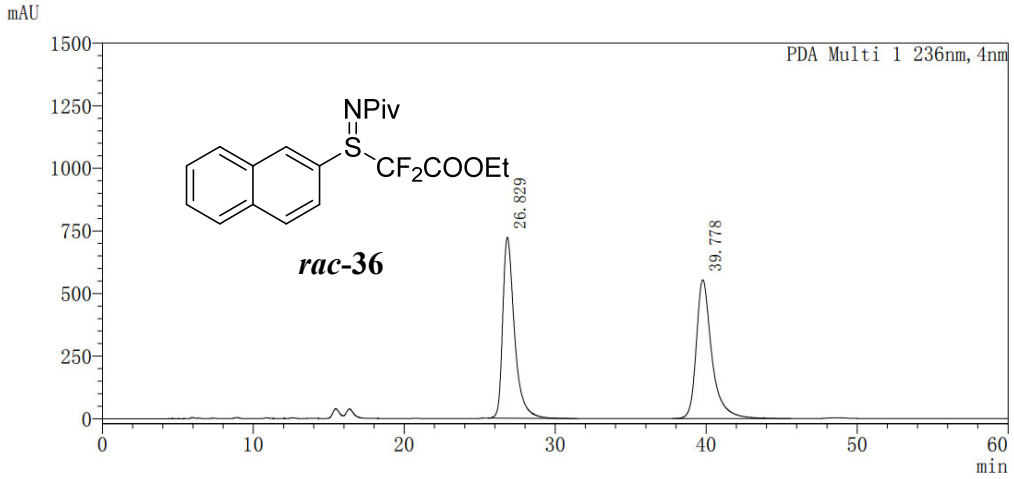
Peak#	Ret. Time	Area	Area%
1	10.707	1663677	98.123
2	12.674	31822	1.877

Figure S108. HPLC chromatograms of compound **36**.

HPLC spectra of **36**

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 236 nm), t_R (major) = 39.90 min, t_R (minor) = 27.10 min.

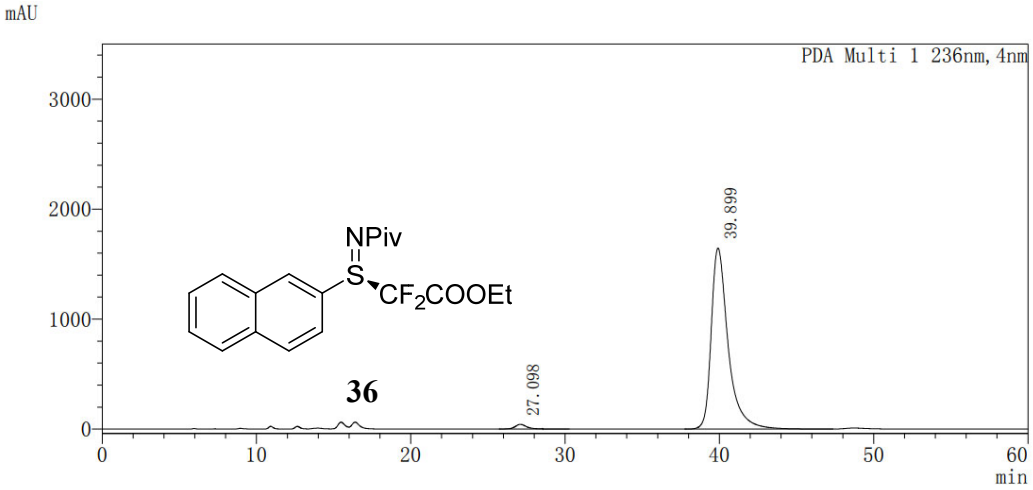
$[\alpha]_D^{27}$ = −22 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 236nm

Peak#	Ret. Time	Area	Area%
1	26.829	39120019	49.555
2	39.778	39823317	50.445



Peak Table

PDA Ch1 236nm

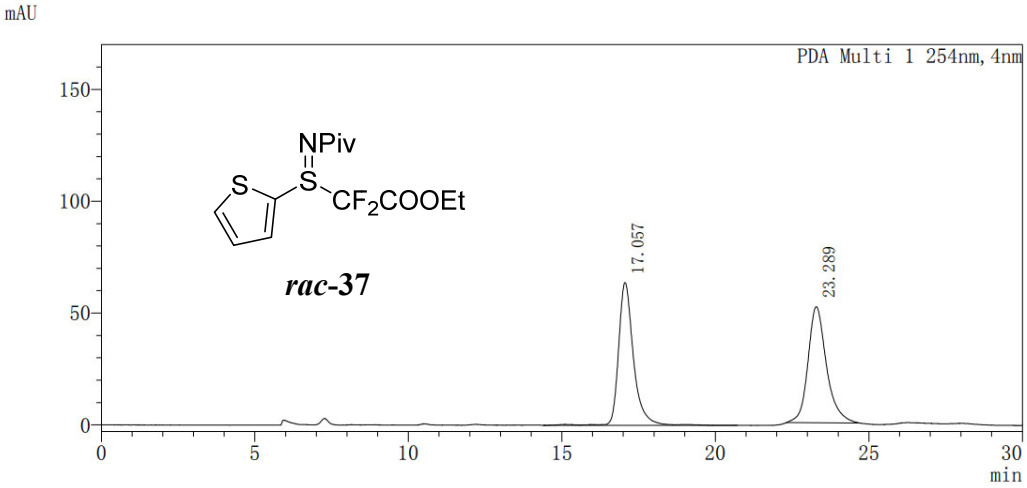
Peak#	Ret. Time	Area	Area%
1	27.098	2370191	1.852
2	39.899	125578878	98.148

Figure S109. HPLC chromatograms of compound **37**.

HPLC spectra of **37**

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 23.70 min, t_R (minor) = 17.33 min.

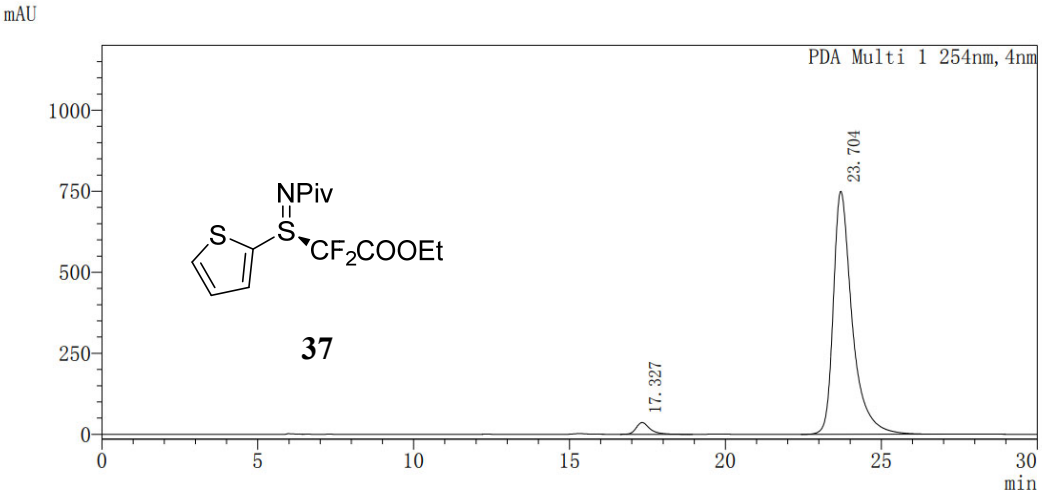
$[\alpha]_D^{27}$ = −25 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.057	2156219	49.728
2	23.289	2179802	50.272



Peak Table

PDA Ch1 254nm

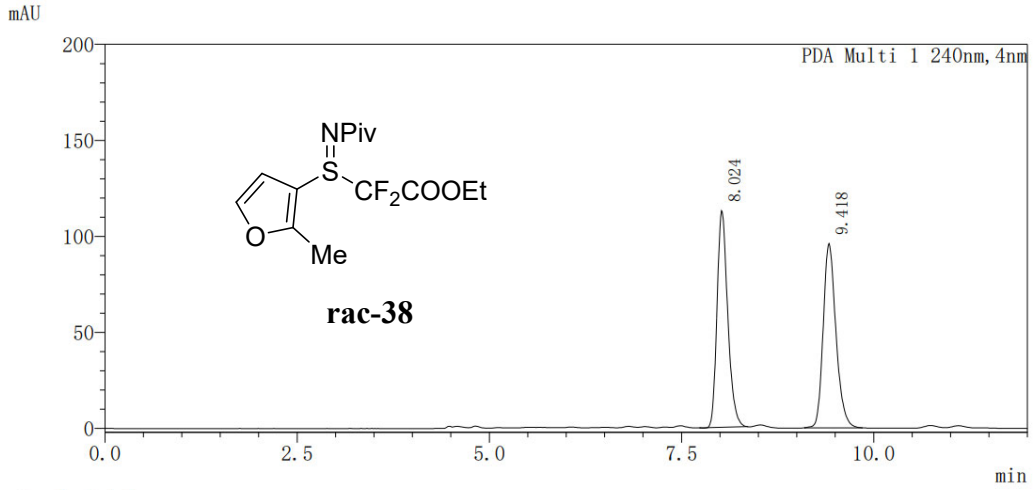
Peak#	Ret. Time	Area	Area%
1	17.327	1128871	3.442
2	23.704	31672368	96.558

Figure S110. HPLC chromatograms of compound **38**.

HPLC spectra of **38**

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min, λ = 240 nm), t_R (major) = 9.40 min, t_R (minor) = 8.01 min.

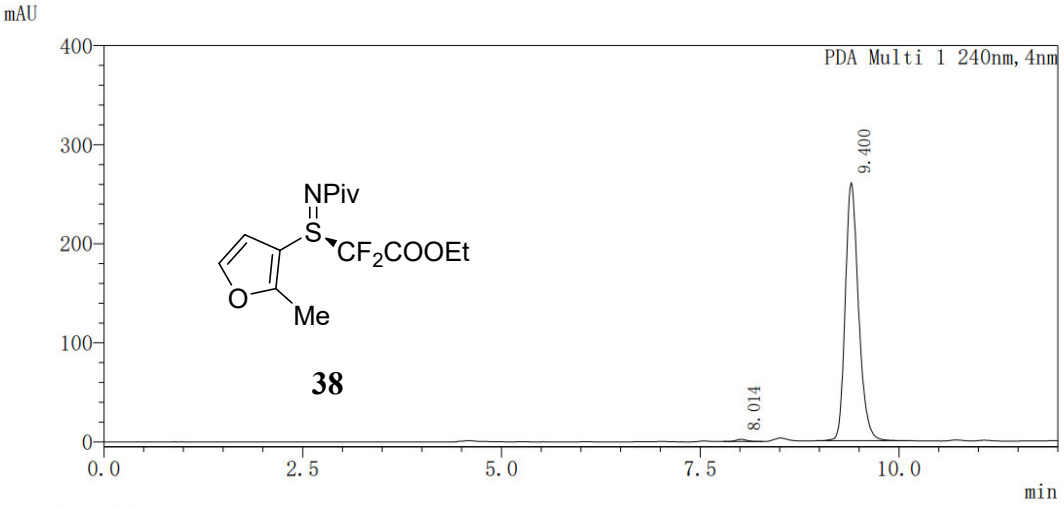
$[\alpha]_D^{27} = -11$ (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 240nm

Peak#	Ret. Time	Area	Area%
1	8.024	1093920	49.648
2	9.418	1109452	50.352



Peak Table

PDA Ch1 240nm

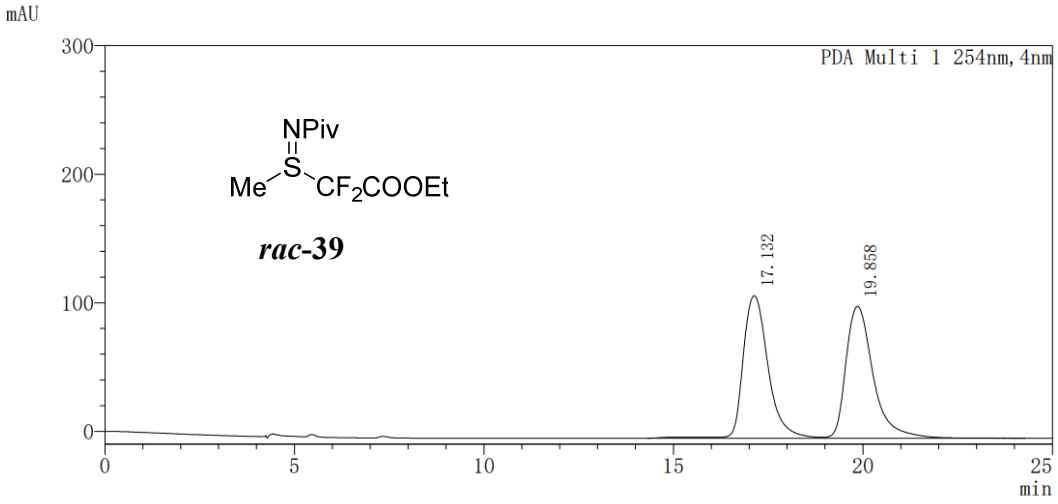
Peak#	Ret. Time	Area	Area%
1	8.014	20901	0.686
2	9.400	3027121	99.314

Figure S111. HPLC chromatograms of compound **39**.

HPLC spectra of **39**

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 19.74 min, t_R (minor) = 17.71 min.

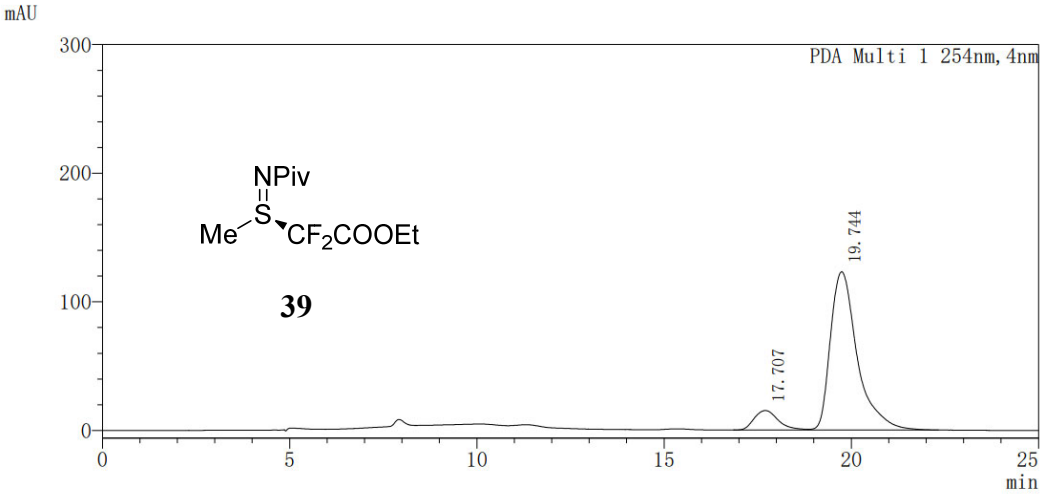
$[\alpha]_D^{27}$ = −8 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.132	5089045	49.857
2	19.858	5118323	50.143



Peak Table

PDA Ch1 254nm

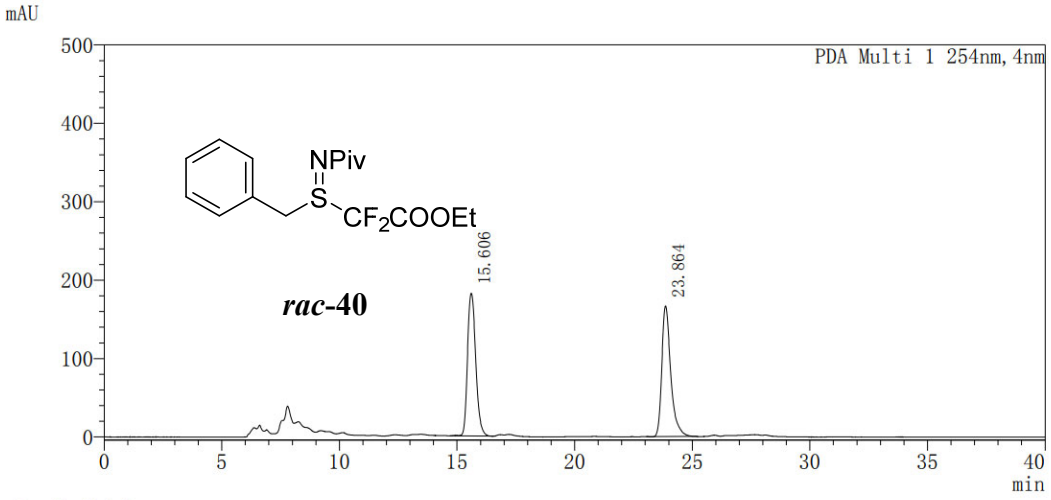
Peak#	Ret. Time	Area	Area%
1	17.707	682554	9.993
2	19.744	6147750	90.007

Figure S112. HPLC chromatograms of compound **40**.

HPLC spectra of **40**

HPLC analysis: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 23.54 min, t_R (minor) = 15.61 min.

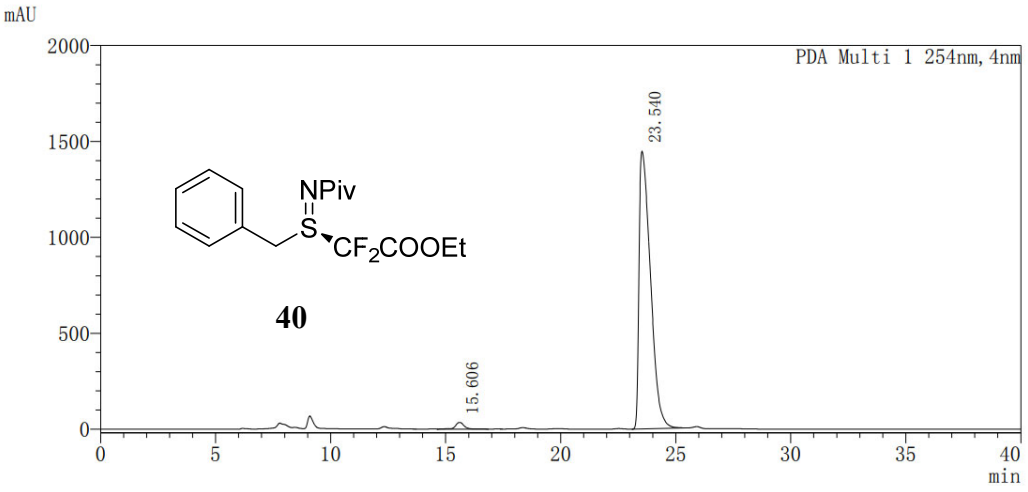
$[\alpha]_D^{27}$ = −33 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.606	4405873	50.013
2	23.864	4403498	49.987



Peak Table

PDA Ch1 254nm

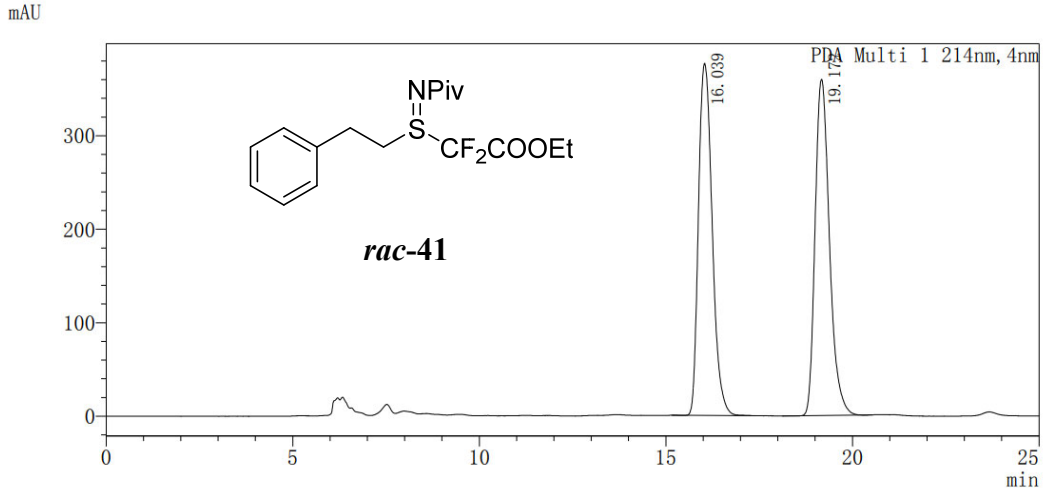
Peak#	Ret. Time	Area	Area%
1	15.606	913856	1.793
2	23.540	50043199	98.207

Figure S113. HPLC chromatograms of compound **41**.

HPLC spectra of **41**

HPLC analysis: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 214 nm), t_R (major) = 19.04 min, t_R (minor) = 16.03 min.

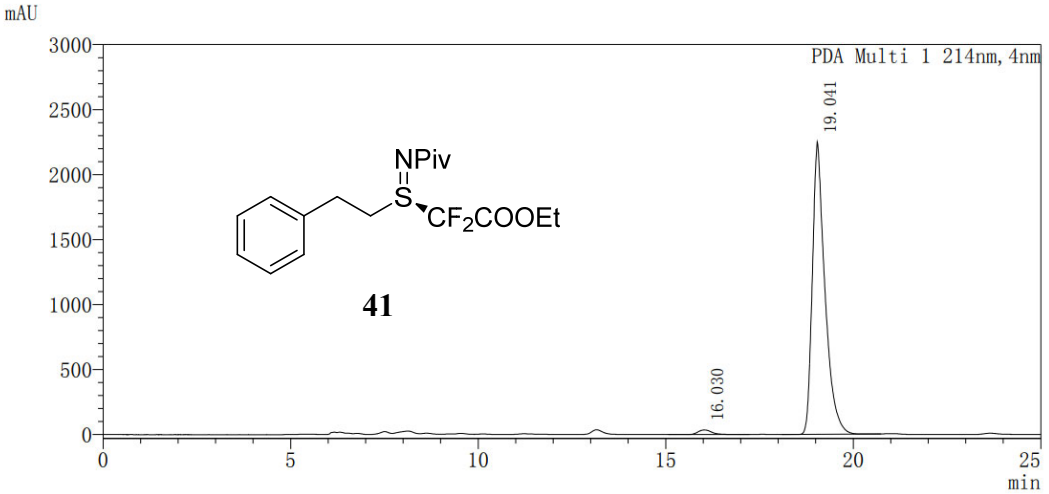
$[\alpha]_D^{27}$ = −88 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 214nm

Peak#	Ret. Time	Area	Area%
1	16.039	9613212	50.012
2	19.172	9608530	49.988



Peak Table

PDA Ch1 214nm

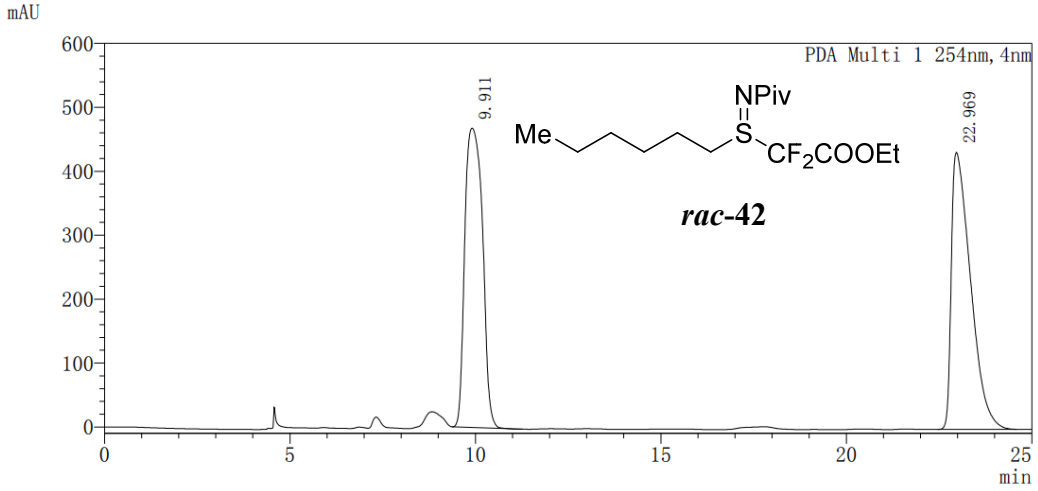
Peak#	Ret. Time	Area	Area%
1	16.030	890061	1.671
2	19.041	52375160	98.329

Figure S114. HPLC chromatograms of compound **42**.

HPLC spectra of **42**

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 22.14 min, t_R (minor) = 10.03 min.

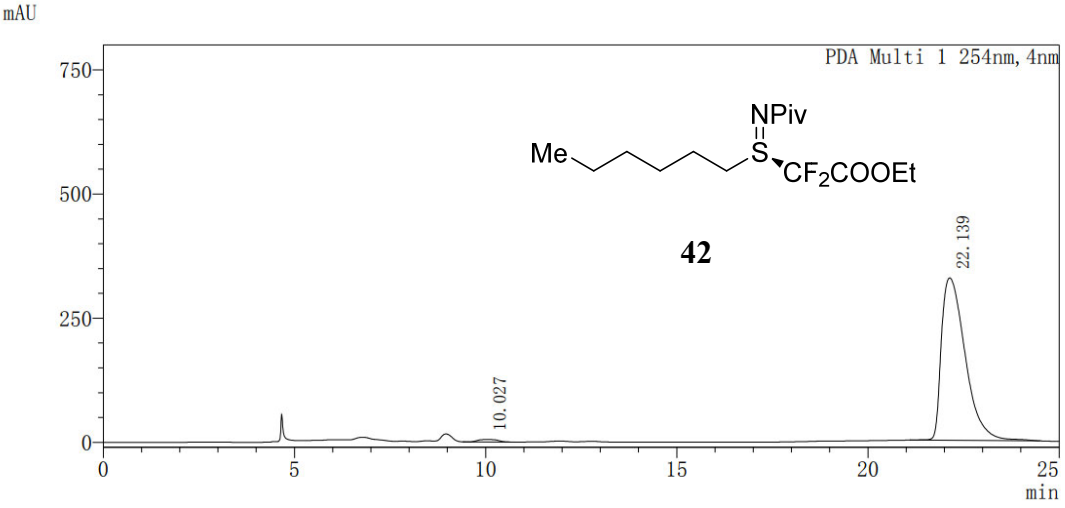
$[\alpha]_D^{27}$ = −56 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.911	15552806	49.937
2	22.969	15592270	50.063



Peak Table

PDA Ch1 254nm

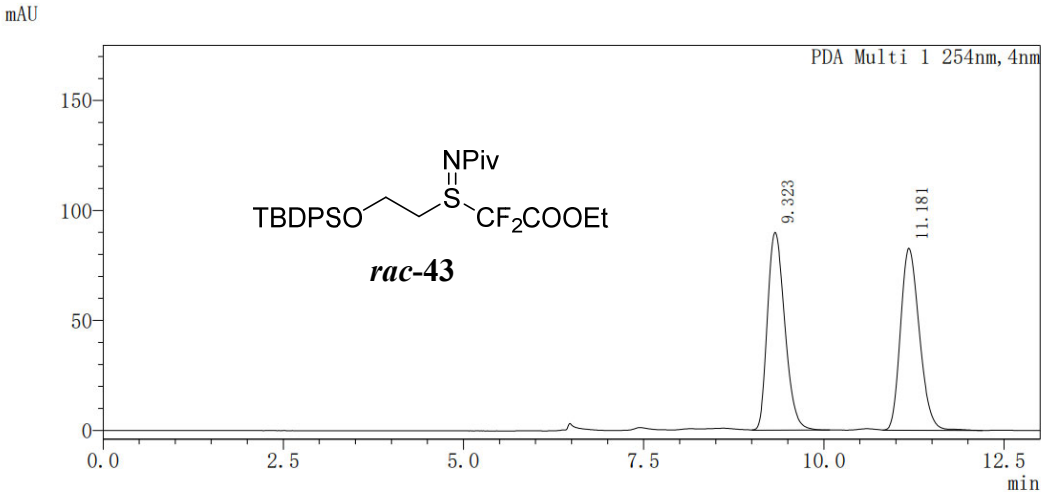
Peak#	Ret. Time	Area	Area%
1	10.027	173040	1.207
2	22.139	14168327	98.793

Figure S115. HPLC chromatograms of compound **43**.

HPLC spectra of **43**

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 11.25 min, t_R (minor) = 9.36 min.

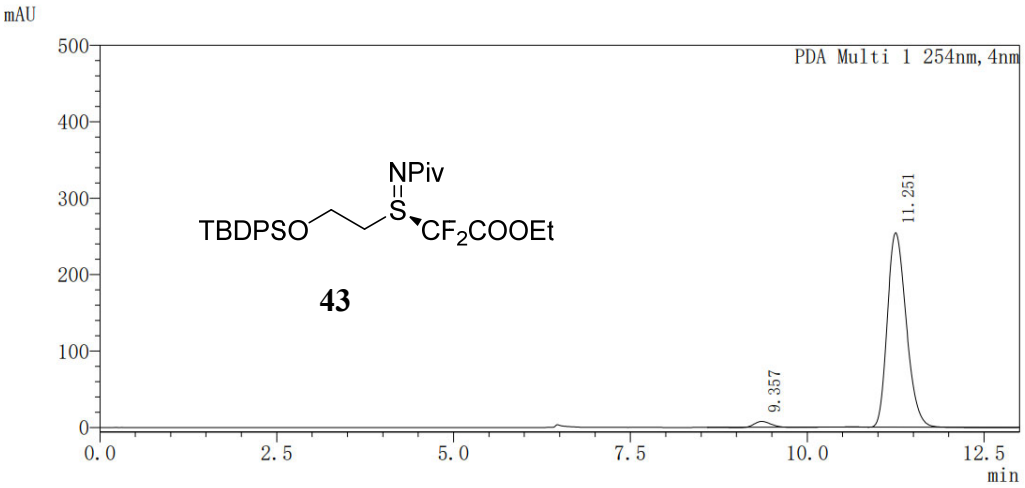
$[\alpha]_D^{27}$ = −44 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.323	1508478	49.969
2	11.181	1510334	50.031



Peak Table

PDA Ch1 254nm

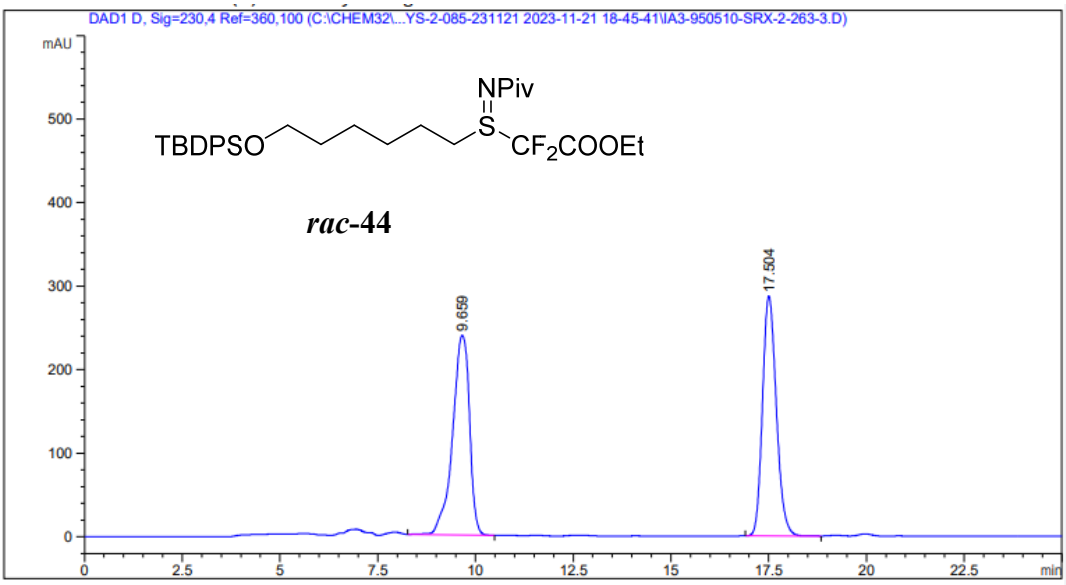
Peak#	Ret. Time	Area	Area%
1	9.357	110102	2.276
2	11.251	4727264	97.724

Figure S116. HPLC chromatograms of compound **44**.

HPLC spectra of **44**

HPLC analysis: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min, λ = 230 nm), t_R (major) = 17.56 min, t_R (minor) = 9.74 min.

$[\alpha]_D^{27} = -67$ (c 0.5, $CHCl_3$).

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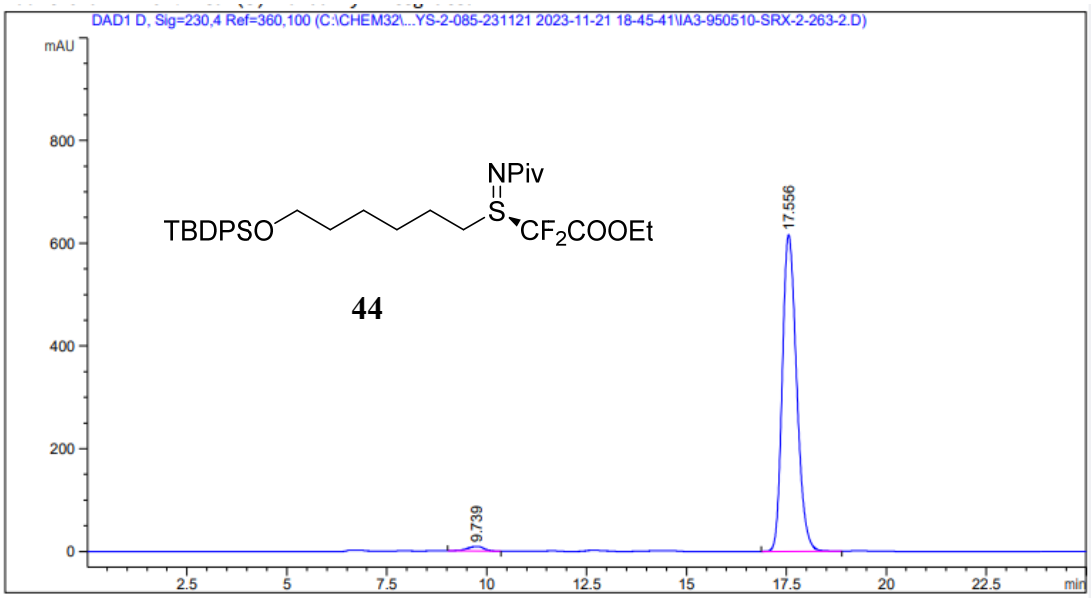
=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.659 BB    0.4527 7227.14844  239.08243  50.5231
   2  17.504 BB    0.3853 7077.48242  287.41425  49.4769
```

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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.739 BB    0.4356  256.03677    8.79686   1.6398
   2  17.556 BB    0.3887 1.53577e4   616.36432  98.3602
```
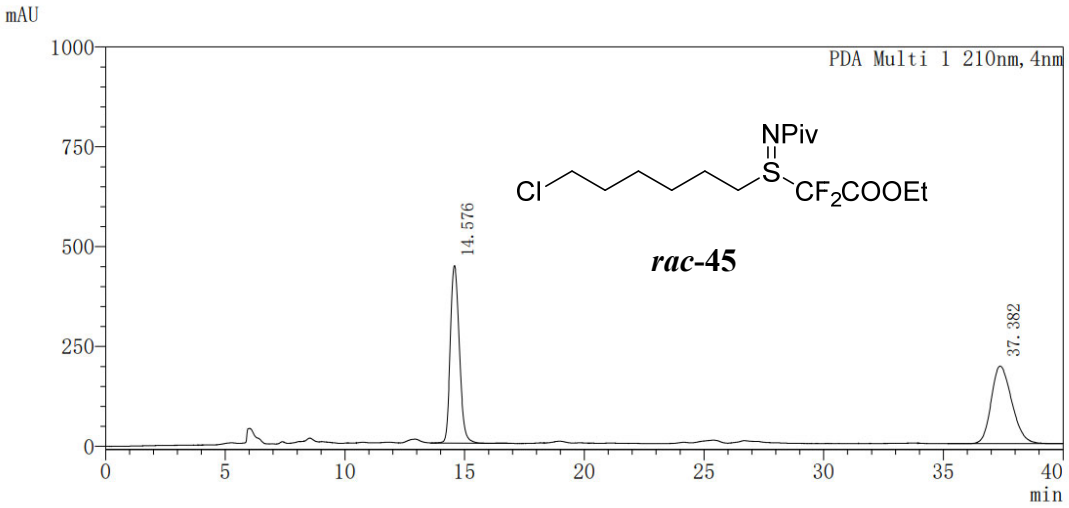

Figure S117. HPLC chromatograms of compound **45**.

HPLC spectra of **45**

HPLC analysis: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 210 nm), t_R (major) = 37.43 min, t_R (minor) = 14.60 min.

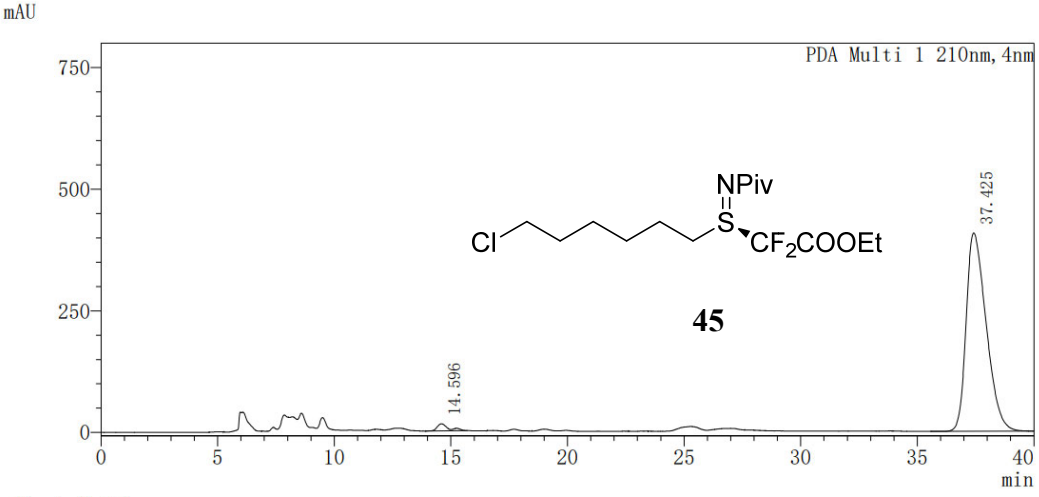
$[\alpha]_D^{27}$ = −50 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%
1	14.576	11715916	50.271
2	37.382	11589754	49.729



Peak Table

PDA Ch1 210nm

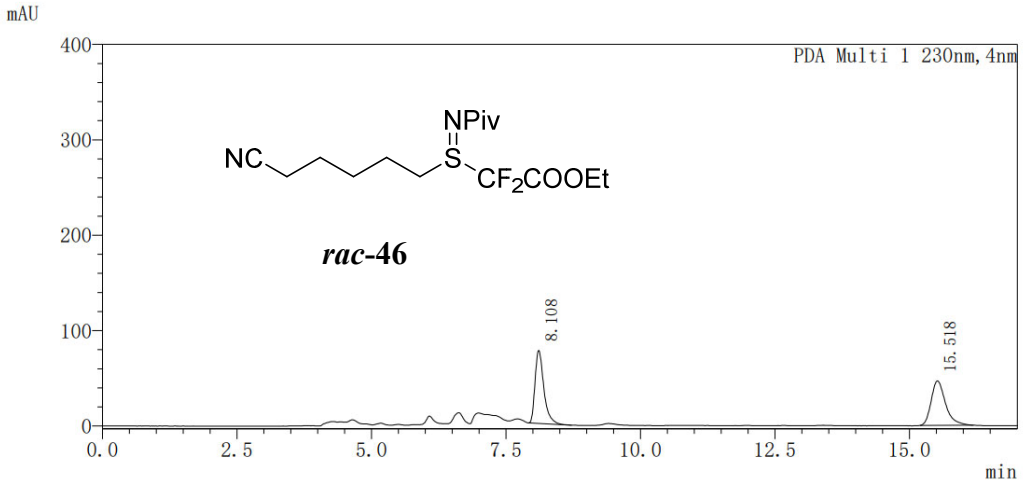
Peak#	Ret. Time	Area	Area%
1	14.596	498010	2.005
2	37.425	24336870	97.995

Figure S118. HPLC chromatograms of compound **46**.

HPLC spectra of **46**

HPLC analysis: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.7 mL/min, λ = 230 nm), t_R (major) = 15.42 min, t_R (minor) = 8.11 min.

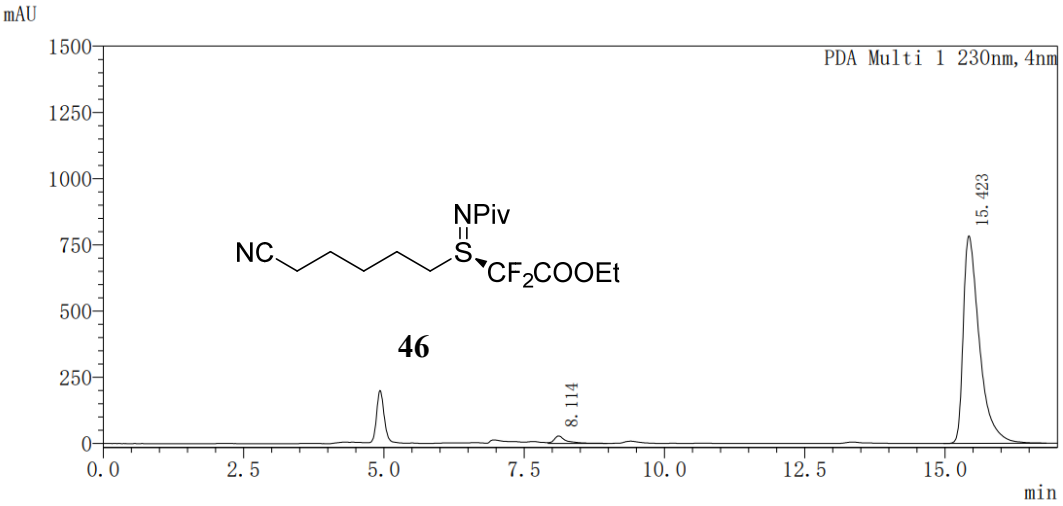
$[\alpha]_D^{27}$ = −40 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 230nm

Peak#	Ret. Time	Area	Area%
1	8.108	869602	50.344
2	15.518	857713	49.656



Peak Table

PDA Ch1 230nm

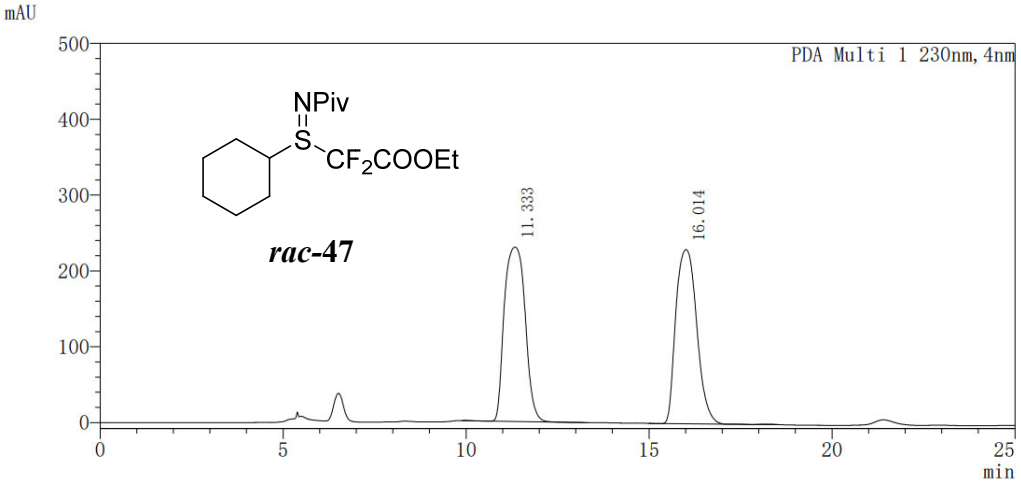
Peak#	Ret. Time	Area	Area%
1	8.114	455368	2.824
2	15.423	15667777	97.176

Figure S119. HPLC chromatograms of compound **47**.

HPLC spectra of **47**

HPLC analysis: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.7 mL/min, λ = 230 nm), t_R (major) = 16.06 min, t_R (minor) = 11.47 min.

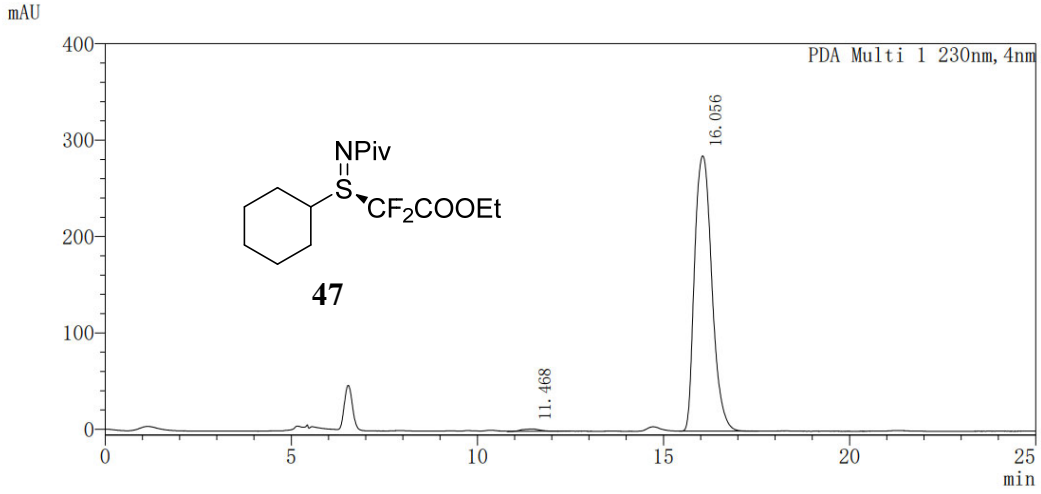
$[\alpha]_D^{27}$ = −35 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 230nm

Peak#	Ret. Time	Area	Area%
1	11.333	9095957	49.929
2	16.014	9121741	50.071



Peak Table

PDA Ch1 230nm

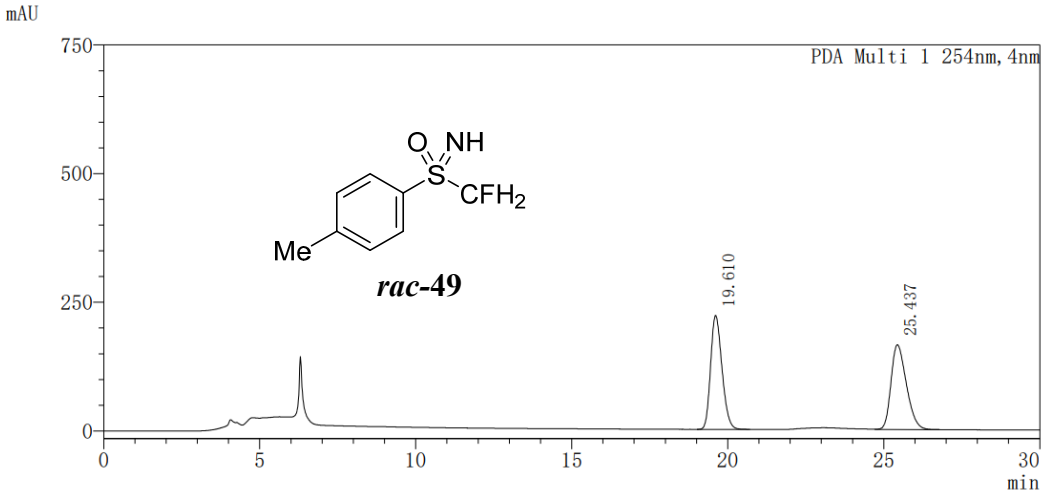
Peak#	Ret. Time	Area	Area%
1	11.468	74580	0.802
2	16.056	9229710	99.198

Figure S120. HPLC chromatograms of compound **49**.

HPLC spectra of **49**

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 24.82 min, t_R (minor) = 19.32 min.

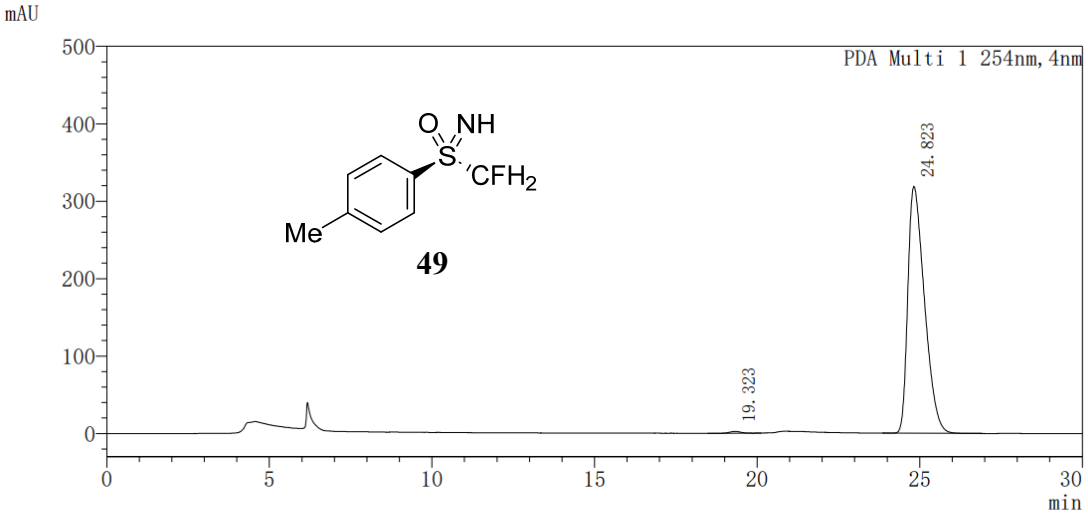
$[\alpha]_D^{27}$ = 4 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	19.610	5614433	49.867
2	25.437	5644492	50.133



Peak Table

PDA Ch1 254nm

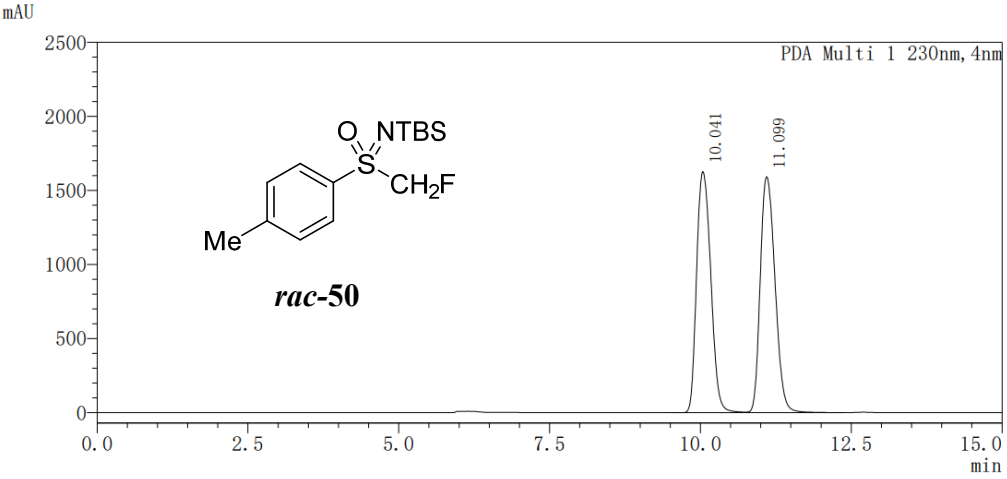
Peak#	Ret. Time	Area	Area%
1	19.323	49573	0.435
2	24.823	11343736	99.565

Figure S121. HPLC chromatograms of compound **50**.

HPLC spectra of **50**

HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 11.08 min, t_R (minor) = 10.04 min.

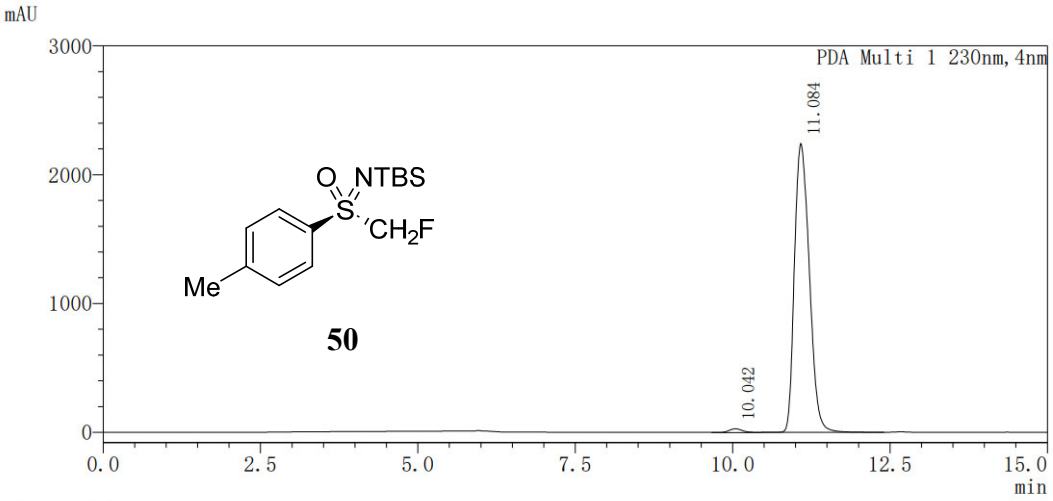
$[\alpha]_D^{27}$ = 5 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 230nm

Peak#	Ret. Time	Area	Area%
1	10.041	26662150	49.571
2	11.099	27123100	50.429



Peak Table

PDA Ch1 230nm

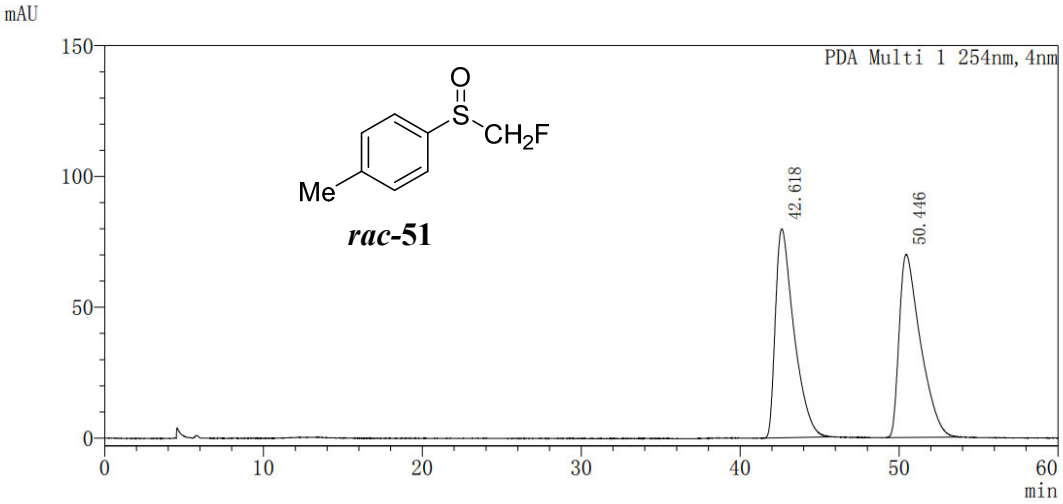
Peak#	Ret. Time	Area	Area%
1	10.042	442804	1.186
2	11.084	36881624	98.814

Figure S122. HPLC chromatograms of compound **51**.

HPLC spectra of **51**

HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 42.57 min, t_R (minor) = 51.60 min.

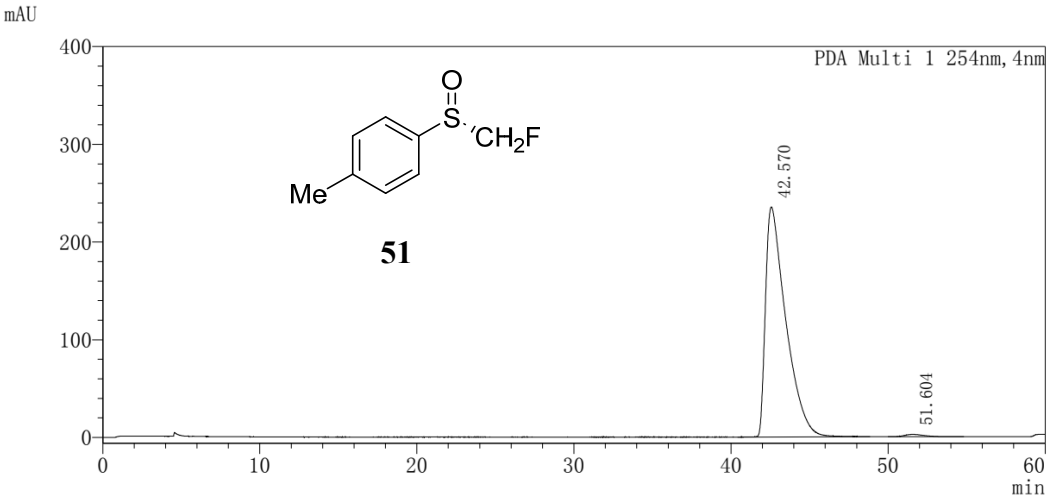
$[\alpha]_D^{27} = -5$ (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	42.618	6500142	49.906
2	50.446	6524636	50.094



Peak Table

PDA Ch1 254nm

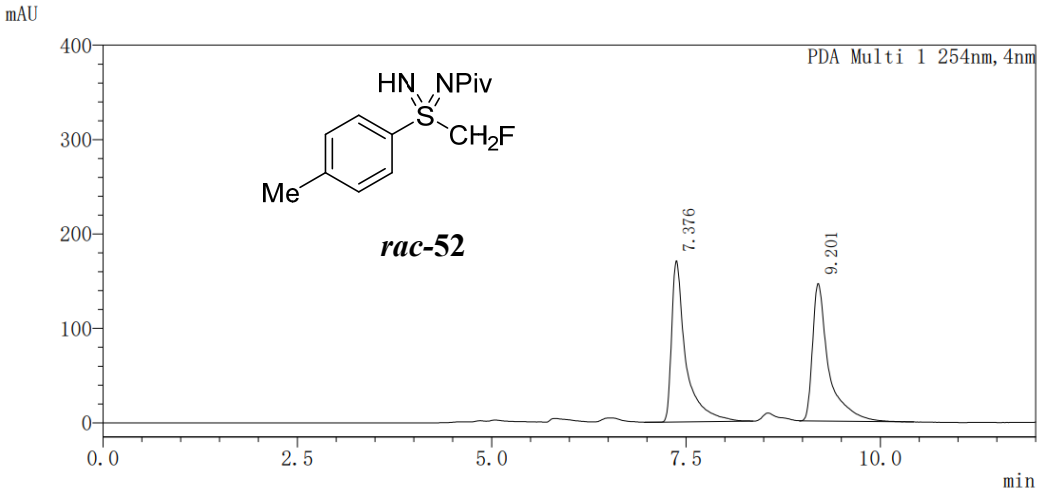
Peak#	Ret. Time	Area	Area%
1	42.570	21213635	99.041
2	51.604	205395	0.959

Figure S123. HPLC chromatograms of compound **52**.

HPLC spectra of **52**

HPLC analysis: Chiralcel IA-3 (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 9.18 min, t_R (minor) = 7.37 min.

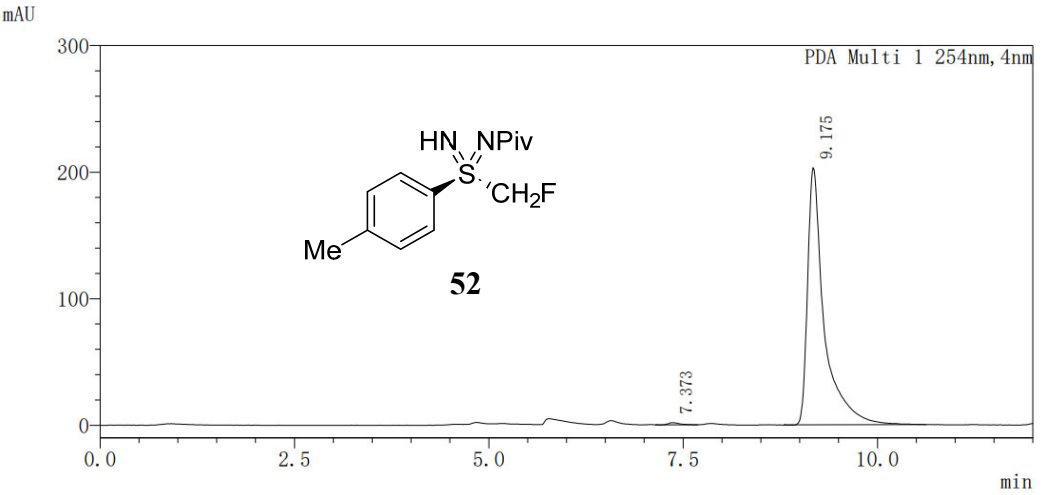
$[\alpha]_D^{27} = -18$ (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.376	2145950	50.597
2	9.201	2095296	49.403



Peak Table

PDA Ch1 254nm

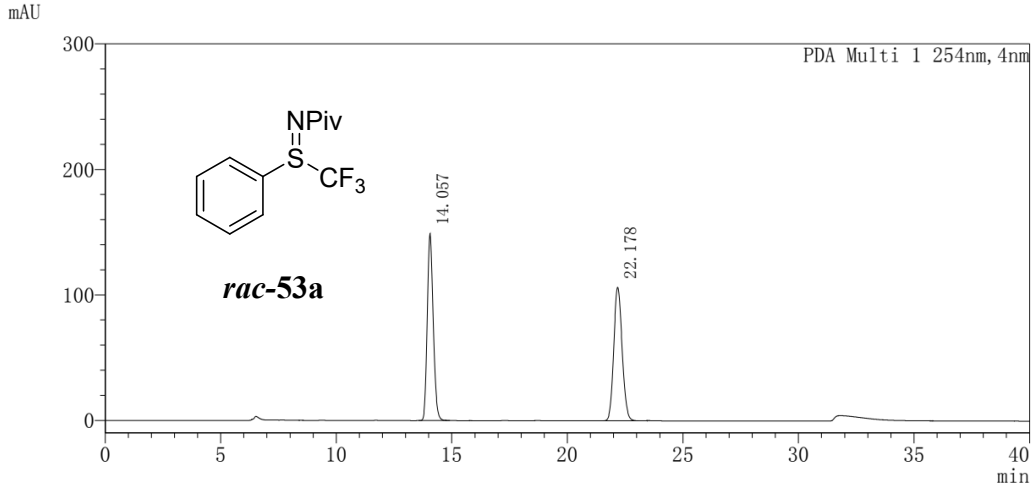
Peak#	Ret. Time	Area	Area%
1	7.373	15169	0.499
2	9.175	3025185	99.501

Figure S124. HPLC chromatograms of compound (*R*)-**53a**

HPLC spectra of (*R*)-**53a**

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 21.75 min, t_R (minor) = 13.94 min.

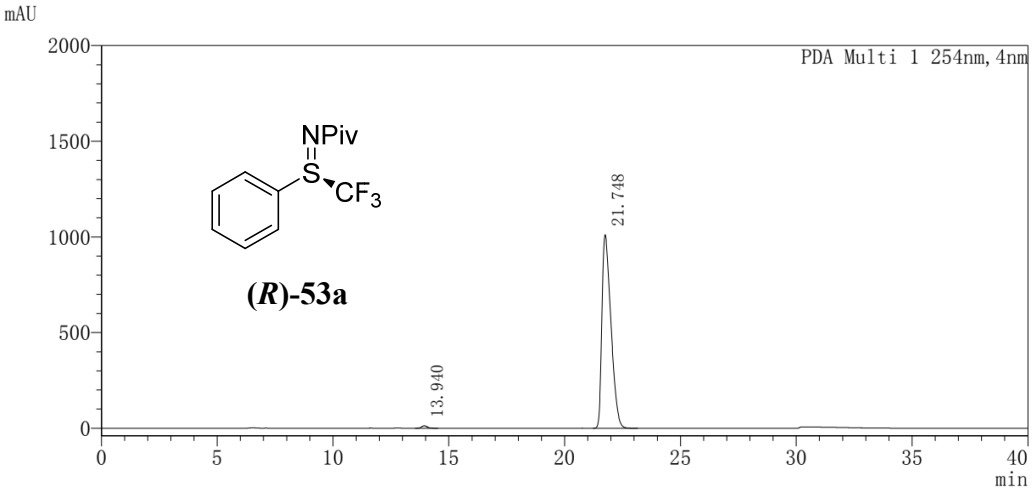
$[\alpha]_D^{27} = -140$ (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.057	2676832	49.924
2	22.178	2684987	50.076



Peak Table

PDA Ch1 254nm

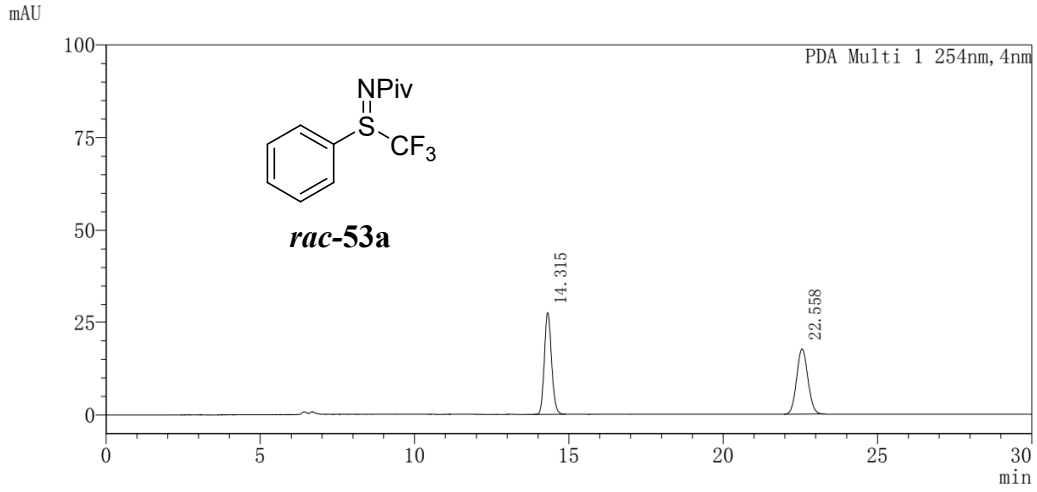
Peak#	Ret. Time	Area	Area%
1	13.940	221404	0.801
2	21.748	27418481	99.199

Figure S125. HPLC chromatograms of compound (*S*)-**53a**

HPLC spectra of (*S*)-**53a**

HPLC analysis: Chiralcel IC (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 14.37 min, t_R (minor) = 22.57 min.

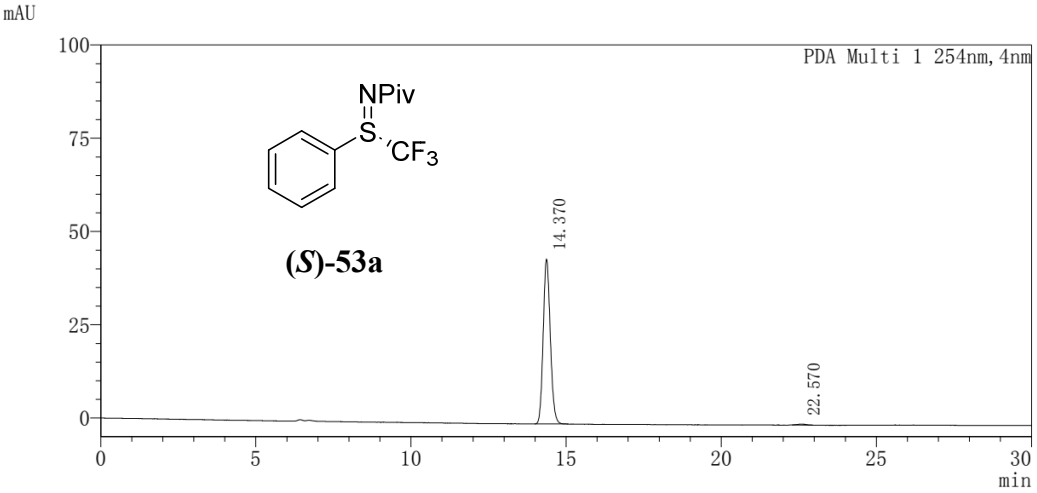
$[\alpha]_D^{27}$ = 96 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.315	445846	50.096
2	22.558	444130	49.904



Peak Table

PDA Ch1 254nm

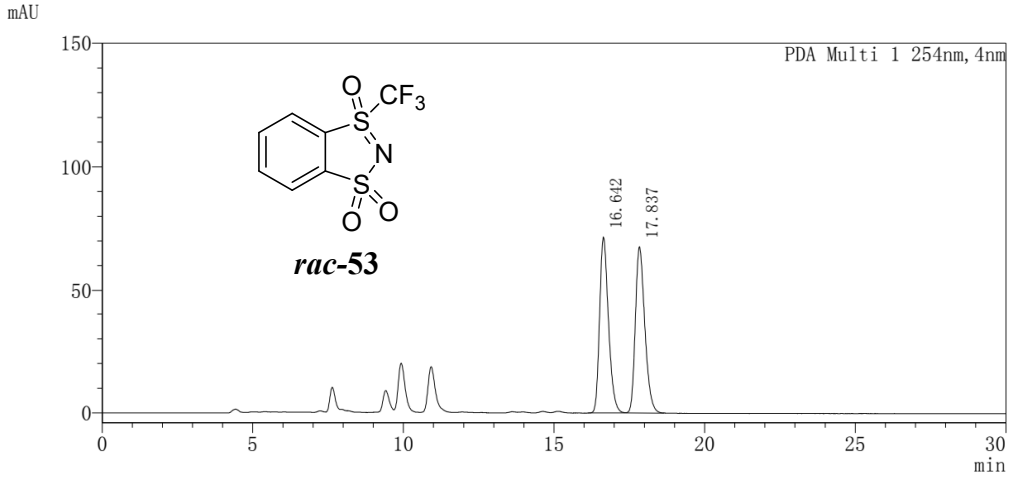
Peak#	Ret. Time	Area	Area%
1	14.370	704554	99.279
2	22.570	5116	0.721

Figure S126. HPLC chromatograms of compound (*R*)-**53**

HPLC spectra of (*R*)-**53**

HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 85/15, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 16.52 min, t_R (minor) = 17.78 min.

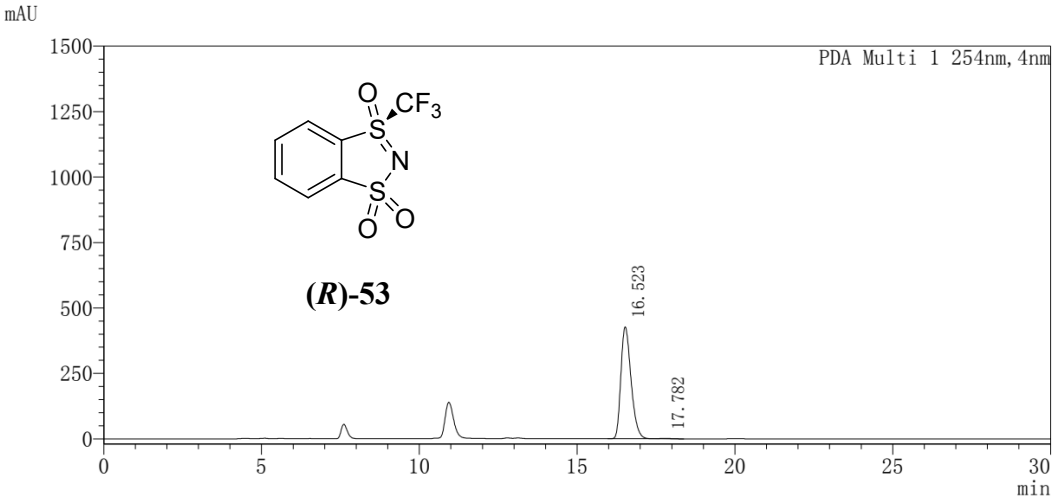
$[\alpha]_D^{27}$ = −15 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.642	1466339	49.784
2	17.837	1479074	50.216



Peak Table

PDA Ch1 254nm

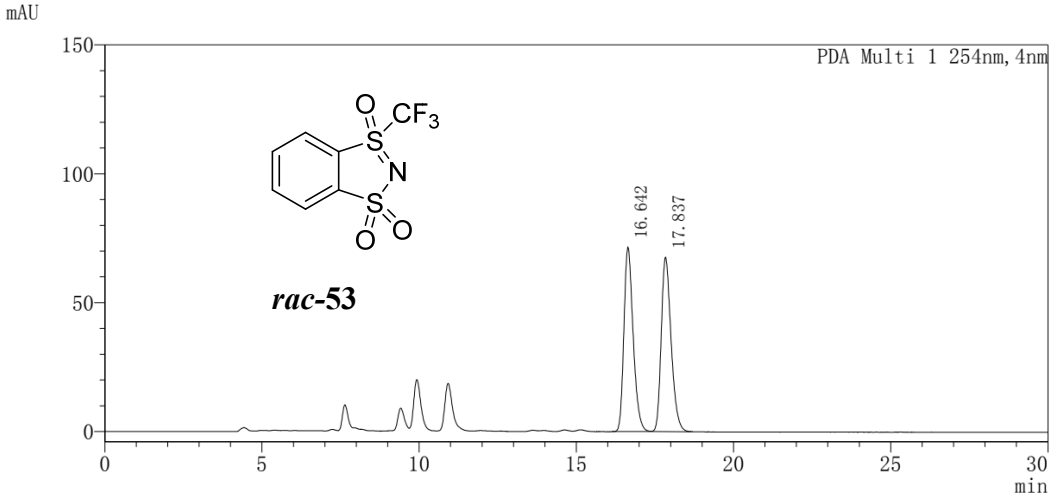
Peak#	Ret. Time	Area	Area%
1	16.523	9582455	99.591
2	17.782	39389	0.409

Figure S127. HPLC chromatograms of compound (*S*)-**53**

HPLC spectra of (*S*)-**53**

HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 85/15, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 17.68 min, t_R (minor) = 16.55 min.

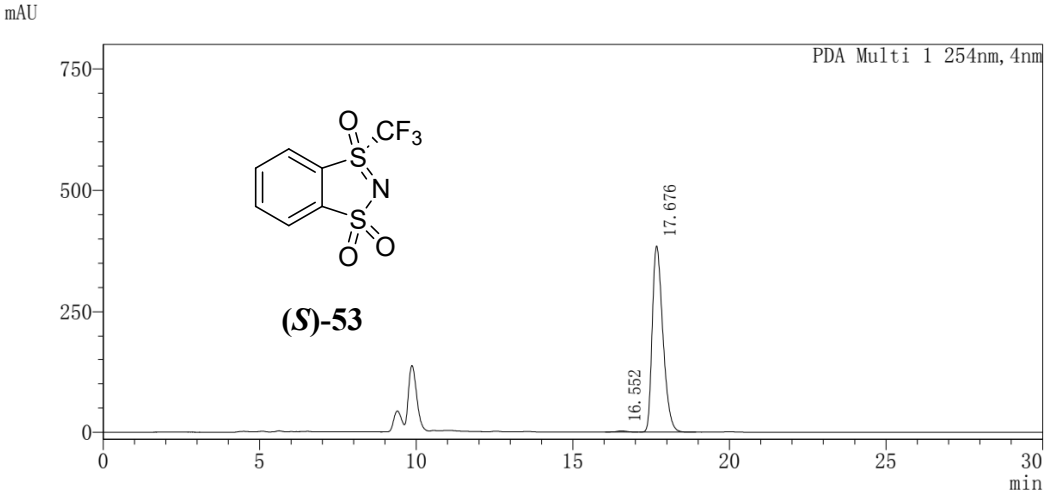
$[\alpha]_D^{27}$ = 8 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.642	1466339	49.784
2	17.837	1479074	50.216



Peak Table

PDA Ch1 254nm

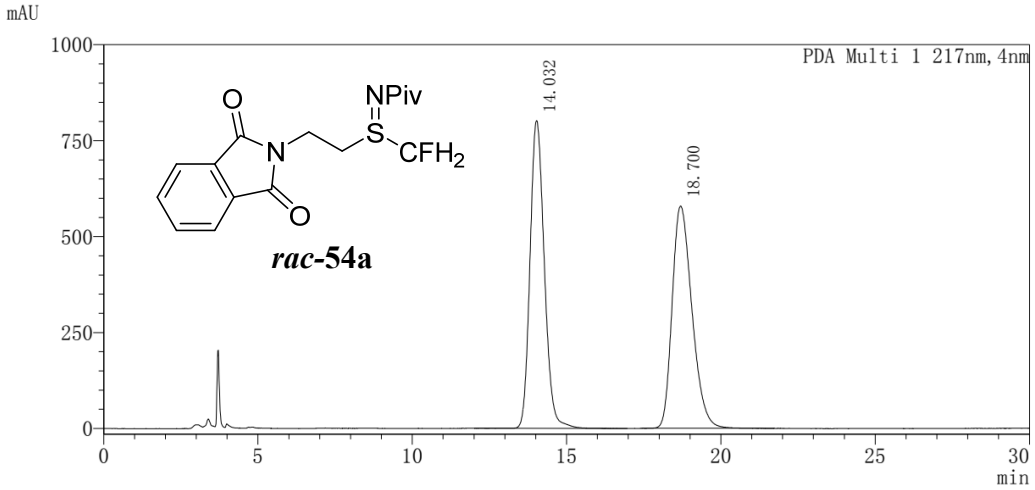
Peak#	Ret. Time	Area	Area%
1	16.552	50335	0.549
2	17.676	9123640	99.451

Figure S128. HPLC chromatograms of compound **54a**

HPLC spectra of **54a**

HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 217 nm), t_R (major) = 13.98 min, t_R (minor) = 18.99 min.

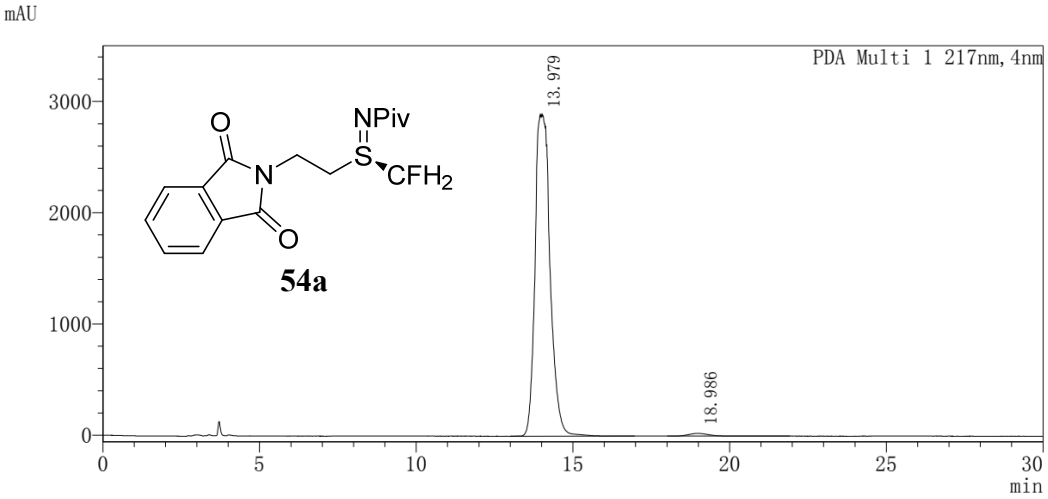
$[\alpha]_D^{27}$ = −55 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 217nm

Peak#	Ret. Time	Area	Area%
1	14.032	25861777	49.987
2	18.700	25875195	50.013



Peak Table

PDA Ch1 217nm

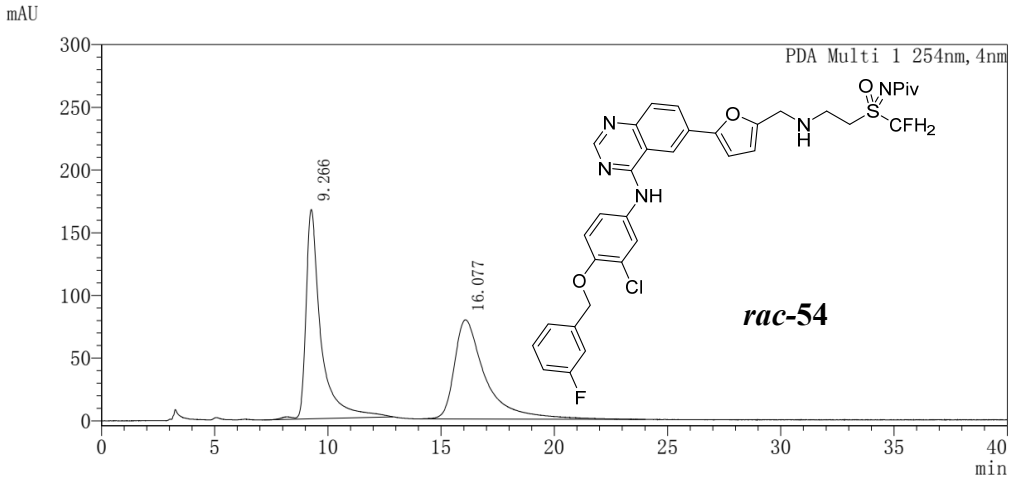
Peak#	Ret. Time	Area	Area%
1	13.979	97049915	98.840
2	18.986	1139021	1.160

Figure S129. HPLC chromatograms of compound **54**

HPLC spectra of **54**

HPLC analysis: Chiralcel ADH (*n*-hexane/*i*-PrOH = 50/50, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 15.99 min, t_R (minor) = 9.29 min.

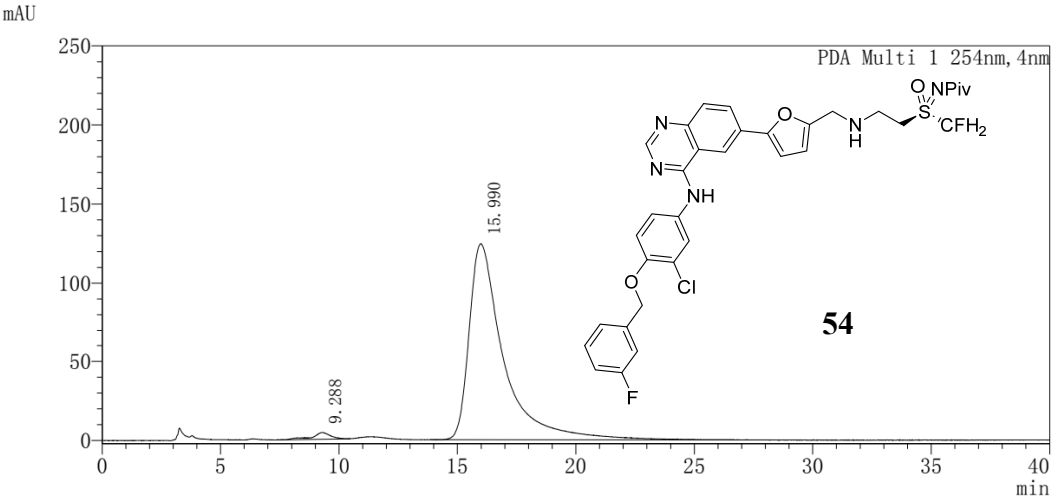
$[\alpha]_D^{27} = -7$ (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.266	7684215	50.429
2	16.077	7553394	49.571



Peak Table

PDA Ch1 254nm

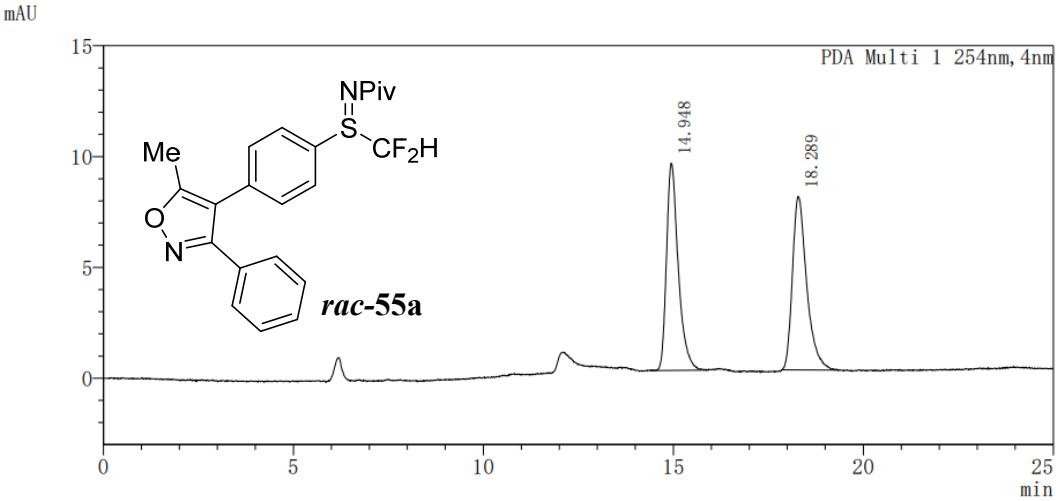
Peak#	Ret. Time	Area	Area%
1	9.288	224119	1.745
2	15.990	12622788	98.255

Figure S130. HPLC chromatograms of compound **55a**

HPLC spectra of **55a**

HPLC analysis: Chiralcel IF (*n*-hexane/*i*-PrOH = 85/15, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 18.10 min, t_R (minor) = 14.92 min.

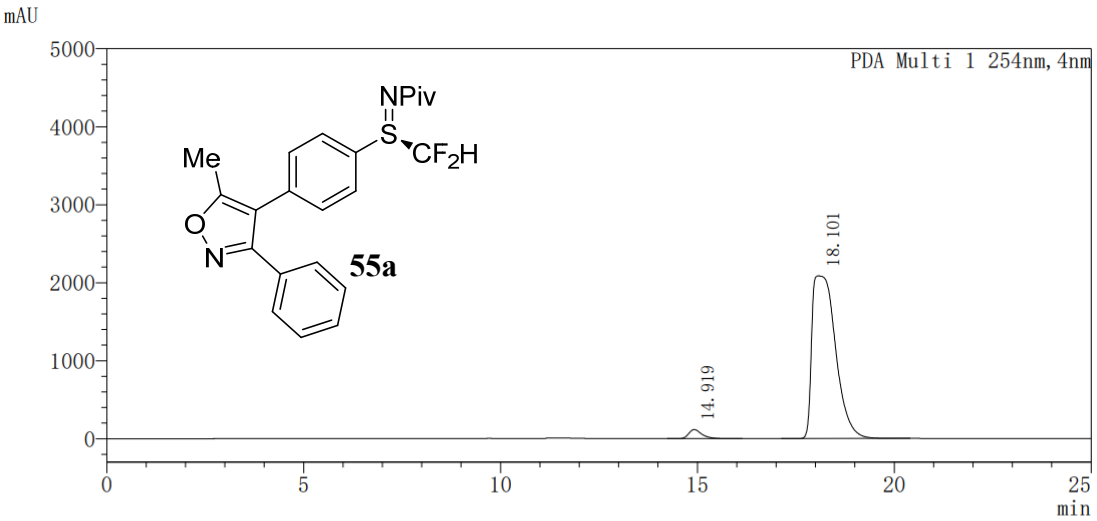
$[\alpha]_D^{27}$ = −60 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.948	201642	49.610
2	18.289	204810	50.390



Peak Table

PDA Ch1 254nm

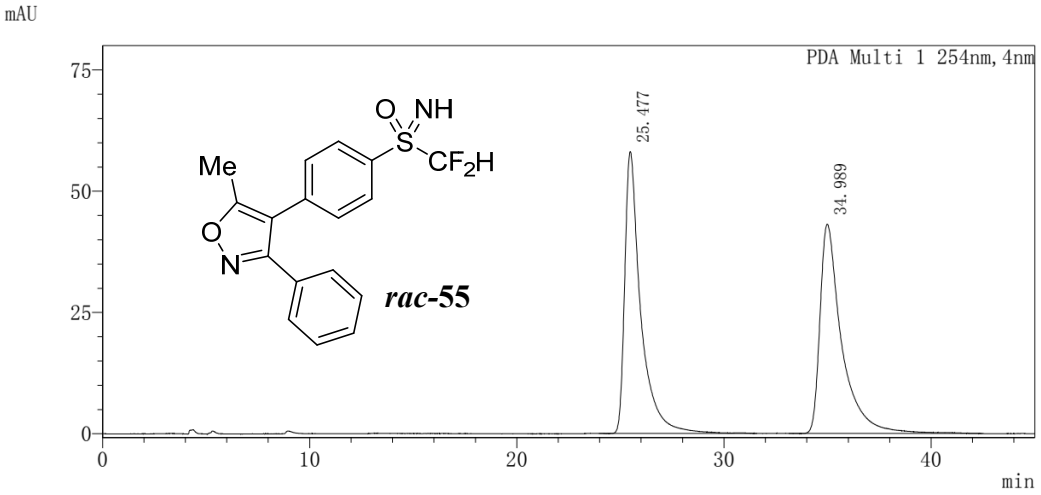
Peak#	Ret. Time	Area	Area%
1	14.919	2707687	3.014
2	18.101	87139031	96.986

Figure S131. HPLC chromatograms of compound **55**

HPLC spectra of **55**

HPLC analysis: Chiralcel IF (*n*-hexane/*i*-PrOH = 85/15, flow rate 0.7 mL/min, λ = 254 nm), t_R (major) = 33.83 min, t_R (minor) = 25.21 min.

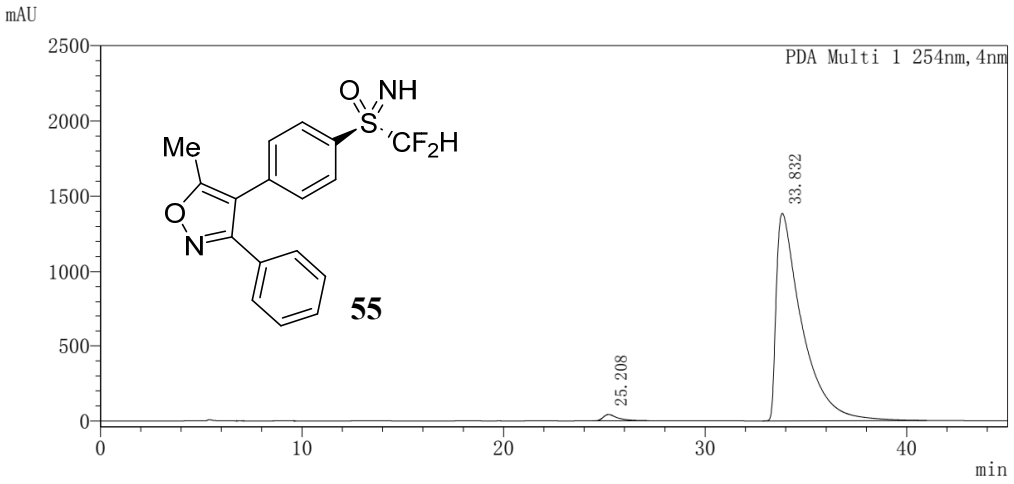
$[\alpha]_D^{27}$ = 25 (c 0.5, $CHCl_3$).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	25.477	3123544	49.808
2	34.989	3147687	50.192



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	25.208	2109900	1.690
2	33.832	122729113	98.310