Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Copper-Catalyzed Enantioselective C(sp^3)–SCF_3 Coupling of Carbon-Centered Benzyl Radicals with $(Me_4N)SCF_3$

*W. Zhang, Y. Tian, X.-D. Liu, C. Luan, J.-R. Liu, Q.-S. Gu, Z.-L. Li, X.-Y. Liu**

Supporting Information for

Copper-Catalyzed Enantioselective C(sp^3)–SCF_3 Coupling of Carbon-Centered Benzyl Radicals with $(Me_4N)SCF_3$

Wei Zhang,[a],+ Yu Tian,[a],+ Xiao-Dong Liu,[a] Cheng Luan,[a] Ji-Ren Liu,[a] Qiang-Shuai Gu,[c] Zhong-Liang Li,[b] and Xin-Yuan Liu*[a]

[a] Dr. W. Zhang, Dr. Y. Tian, Dr. X.-D. Liu, C. Luan, Dr. J.-R. Liu, Prof. Dr. X.-Y. Liu
Shenzhen Key Laboratory of Cross-Coupling Reactions, Southern University of Science and Technology, Shenzhen 518055 (China)
Shenzhen Grubbs Institute, Department of Chemistry, and Guangming Advanced Research Institute, Southern University of Science and Technology, Shenzhen 518055 (China)
E-mail: liuxy3@sustech.edu.cn

[b] Dr. Z.-L. Li
School of Physical Sciences, Great Bay University, Dongguan, 523000 (China)

[c] Dr. Q.-S. Gu
Academy for Advanced Interdisciplinary Studies and Department of Chemistry, Southern University of Science and Technology, Shenzhen 518055 (China)

[+] These authors contributed equally to this work.

Correspondence to: liuxy3@sustech.edu.cn

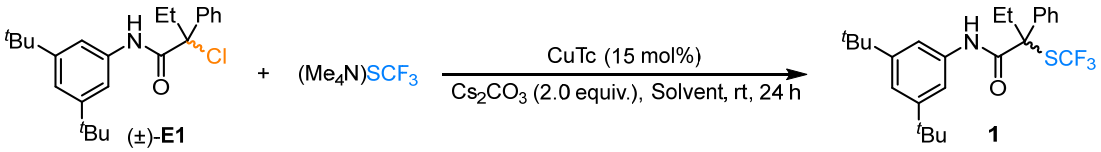
Table of Contents

1. General information

Reactions were carried out under argon atmosphere using Schlenk techniques. The substrates (including tertiary α-haloamides, secondary benzyl bromides, and α,β-unsaturated amides), chiral ligands and the nucleophilic trifluoromethylthiolation reagent (Me_4NSCF_3) were prepared according to the previously reported procedures. CuTc and Cs_2CO_3 were purchased from Bide Pharmatech Ltd. Anhydrous diethyl ether (Et_2O) was purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd, which was redistilled before using. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Visualization on TLC was achieved by use of UV light (254 nm), iodine or basic $KMnO_4$ indicator. Flash column chromatography was performed using Tsingtao silica gel (60, particle size 0.040–0.063 mm). NMR spectra were recorded on Bruker DRX-400 spectrometers at 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR, 162 MHz for ^{31}P NMR, and 376 MHz for ^{19}F NMR, respectively, in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. The chemical shifts were expressed in ppm and coupling constants were given in Hz. Data for NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hz), integration. Mass spectrometric data were obtained using Thermo Scientific Q Exactive (ESI), JEOL AccuTOFTM-GCV (FI), and Waters Premier GC-TOF MS (EI). Enantiomeric excess (e.e.) was determined using SHIMADZU LC-20AD with SPD-20AV detector or Agilent high-performance liquid chromatography (HPLC) with Hatachi detector (at appropriate wavelength). Column conditions were reported in the experimental section below. X-ray diffraction was measured on a 'Bruker APEX-II CCD' diffractometer with Cu–Kα radiation.

2. Supplementary tables for experiments

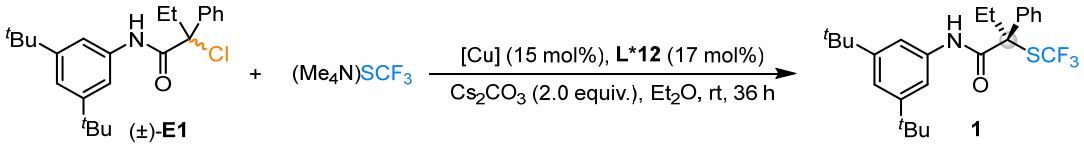
Table S1. Investigation of the nucleophilic substitution reaction[a]



Entry	Solvent	Yield of **1** [%][b]
1	DMF	84
2	MeCN	99
3	EA	99
4	DCE	93
5	THF	99
6	DME	99
7	Et_2O	14
8	MTBE	16
9	Toluene	14

[a] Reaction conditions: (±)-**E1** (0.05 mmol), $(Me_4N)SCF_3$ (0.075 mmol), CuTc (15 mol%), and Cs_2CO_3 (2.0 equiv.) in solvent (1.0 mL) at rt for 24 h under argon. [b] Yields were based on ^{19}F NMR analysis of the crude product using CF_3CH_2OH as an internal standard.

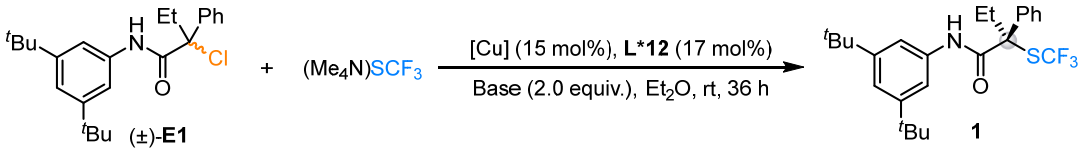
Table S2. Reaction condition optimization: screening of different copper salt[a]



Entry	[Cu]	Yield [%][b]	Ee [%][c]
1	CuTc	99	89
2	CuI	99	88
3	CuSCN	99	88
4	CuBr·Me_2S	99	88

[a] Reaction conditions: (±)-**E1** (0.05 mmol), $(Me_4N)SCF_3$ (0.075 mmol), [Cu] (15 mol%), **L*12** (17 mol%), and Cs_2CO_3 (2.0 equiv.) in Et_2O (1.0 mL) at rt for 36 h under argon. [b] Yields were based on ^{19}F NMR analysis of the crude product using CF_3CH_2OH as an internal standard. [c] Ee values were based on chiral HPLC analysis.

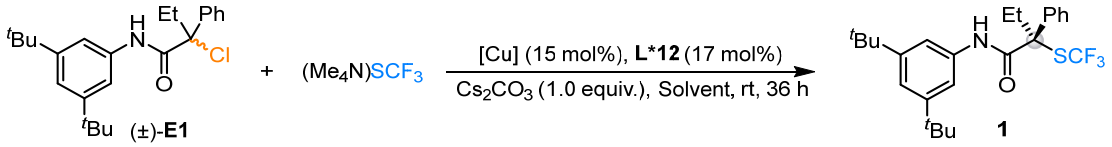
Table S3. Reaction condition optimization: screening of different base[a]



Entry	Base	Yield [%][b]	Ee [%][c]
1	Na_2CO_3	trace	--[d]
2	K_2CO_3	7	88
3	K_3PO_4	10	88
5	Cs_2CO_3 (4.0 equiv.)	99	88
6	Cs_2CO_3 (3.0 equiv.)	99	89
7	Cs_2CO_3 (1.0 equiv.)	99	89

[a] Reaction conditions: (±)-**E1** (0.05 mmol), $(Me_4N)SCF_3$ (0.075 mmol), CuTc (15 mol%), **L*12** (17 mol%), and base (2.0 equiv.) in Et_2O (1.0 mL) at rt for 36 h under argon. [b] Yields were based on ^{19}F NMR analysis of the crude product using CF_3CH_2OH as an internal standard. [c] Ee values were based on chiral HPLC analysis. [d] Not determined.

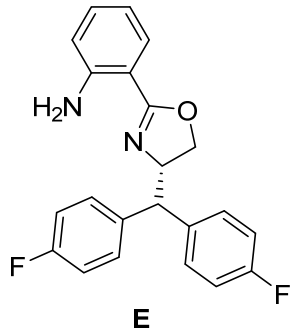
Table S4. Reaction condition optimization: screening of different solvent[a]



Entry	Solvent	Yield [%][b]	Ee [%][c]
1	1,4-Dioxane	27	65
2	MTBE	99	86
3	Toluene	99	83
4	Et_2O (0.5 mL)	99	88
5	Et_2O (2.0 mL)	99	89

[a] Reaction conditions: (±)-**E1** (0.05 mmol), $(Me_4N)SCF_3$ (0.075 mmol), CuTc (15 mol%), **L*12** (17 mol%), and base (1.0 equiv.) in solvent (1.0 mL) at rt for 36 h under argon. [b] Yields were based on ^{19}F NMR analysis of the crude product using CF_3CH_2OH as an internal standard. [c] Ee values were based on chiral HPLC analysis.

3. Supplementary figures and scheme for experiments



E

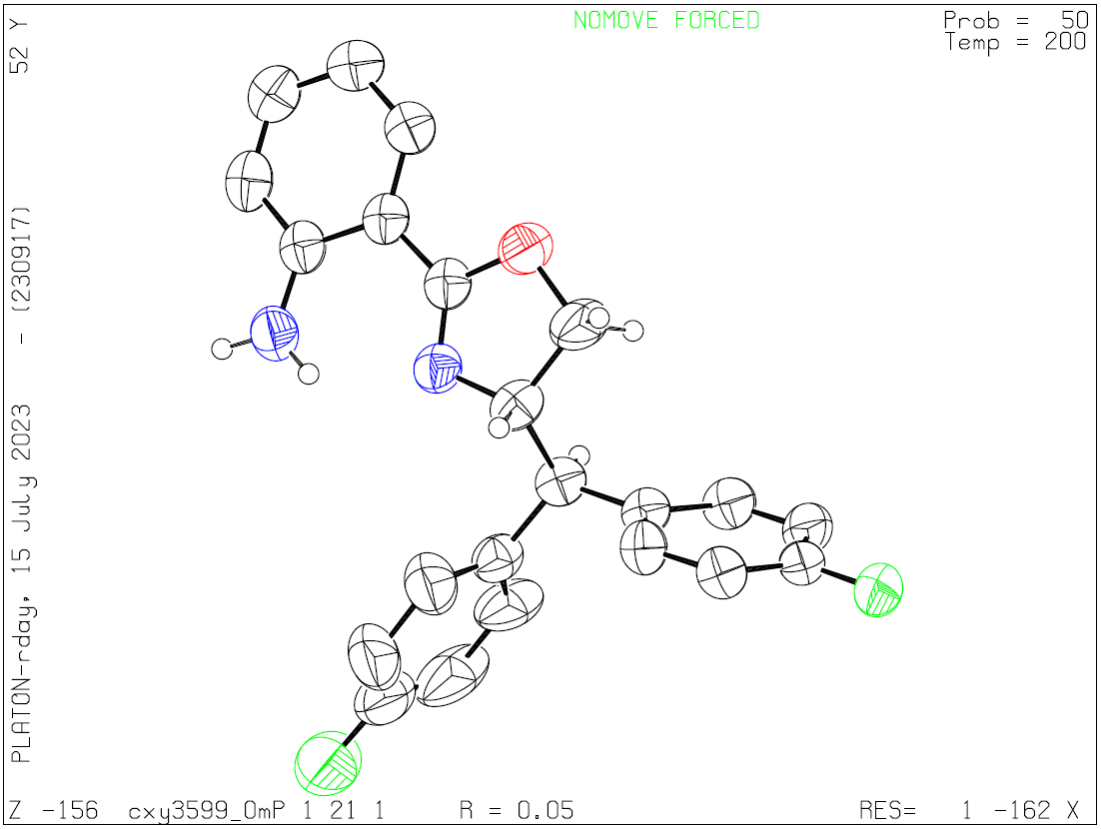
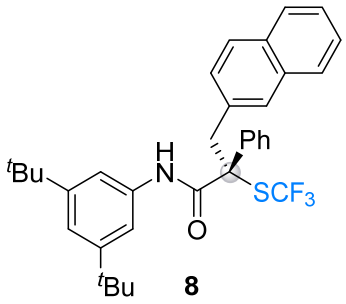


Figure S1. The X-ray structure of **E** (CCDC 2220220).



8

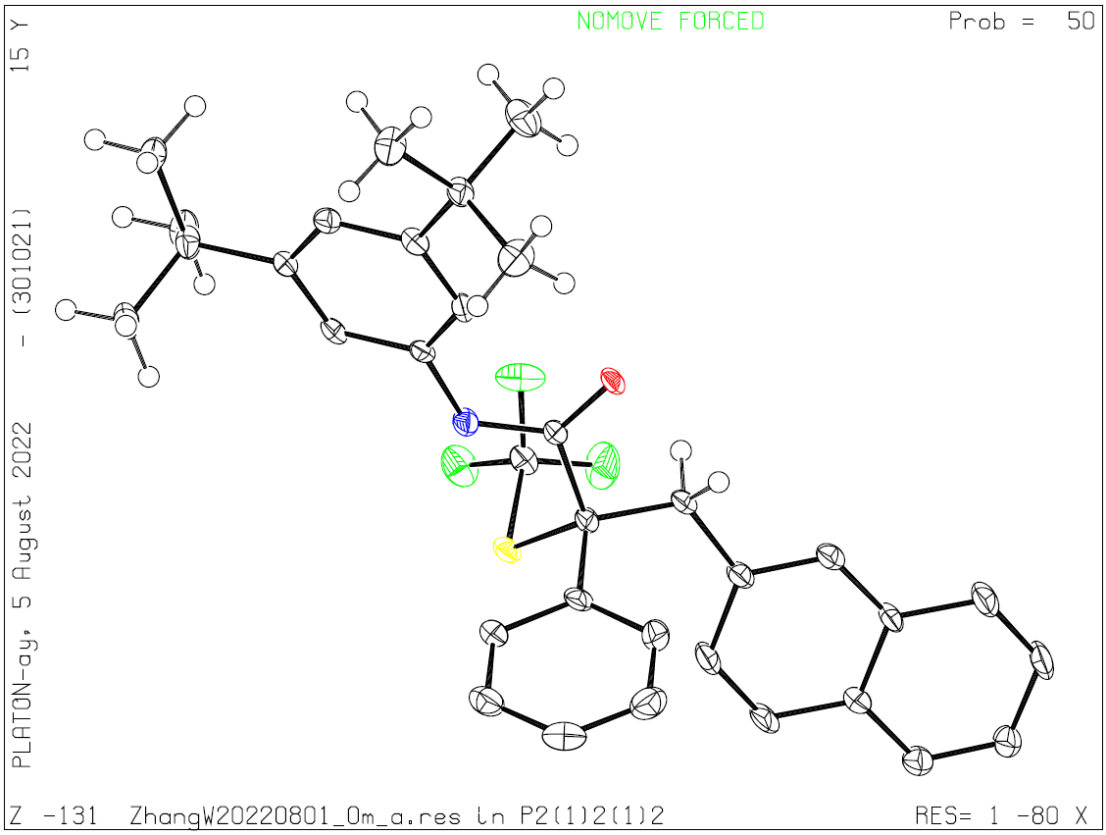
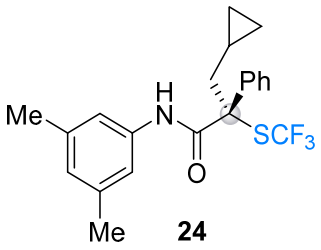


Figure S2. The X-ray structure of **8** (CCDC 2220219).



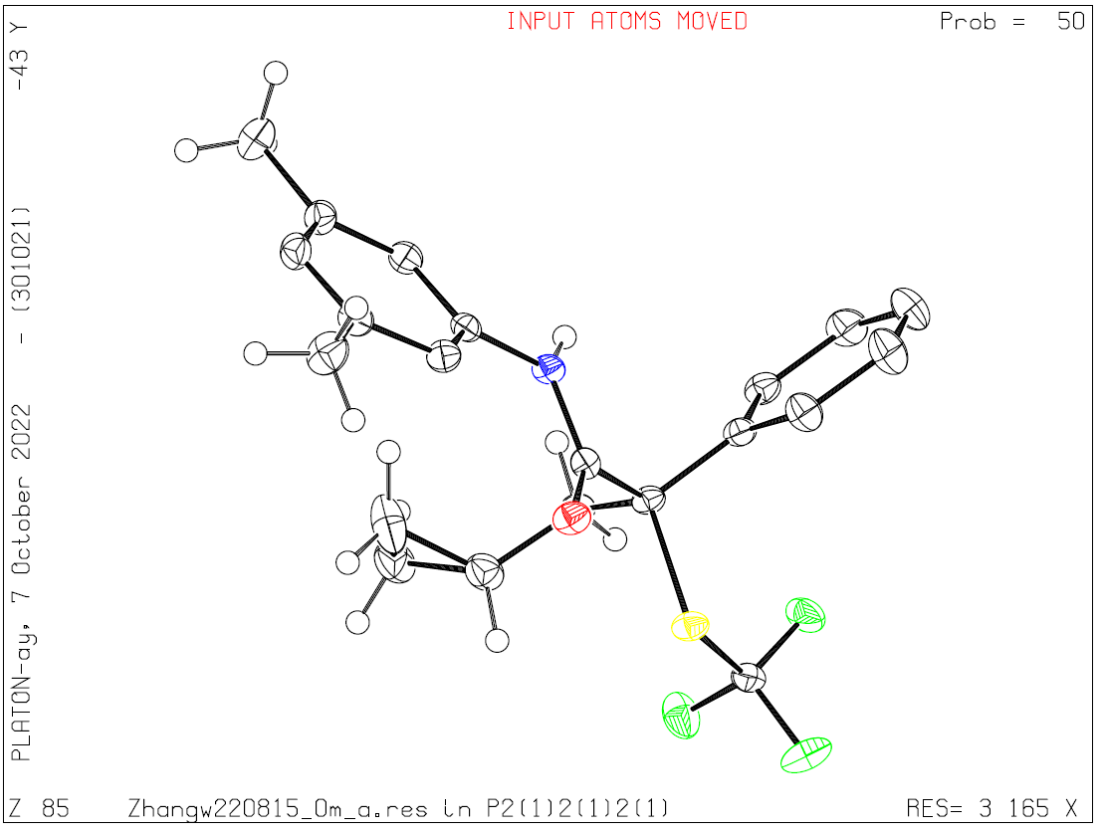
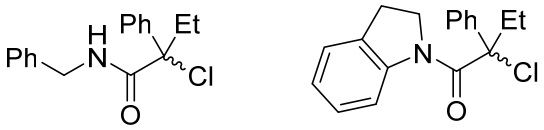
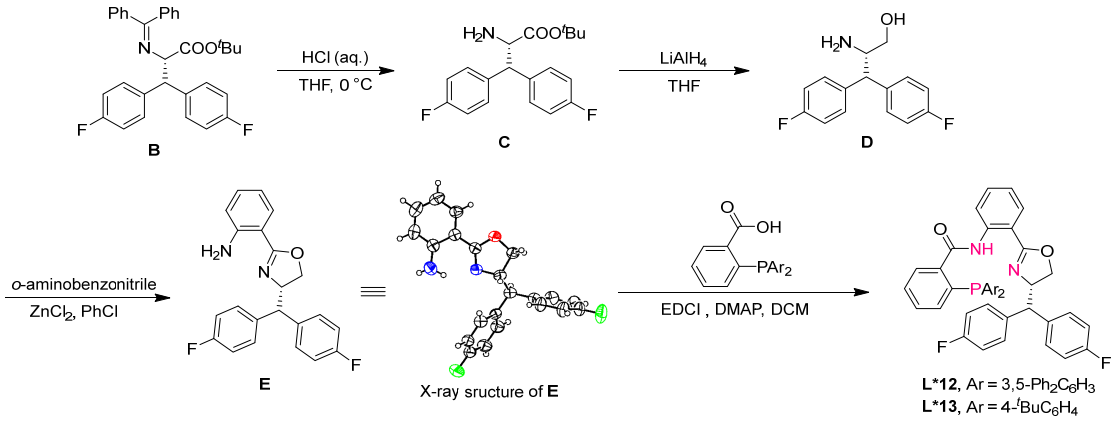


Figure S3. The X-ray structure of **24** (CCDC 2220238).

Scheme S1. Unsuccessful examples of tertiary α-chloroamides



4. The Synthesis of the Chiral Ligand L*12 and L*13



B (5.0 mmol), which was prepared according to the previously reported procedure,[1] was dissolved in THF (25.0 mL), followed by dropping aqueous HCl (1.0 M, 10.0 mL) in ice-water bath. After the reaction finished monitored by TLC, the THF was evaporated. The residue was washed twice with ether in a separating funnel, then the water phase was basified with saturated aqueous Na_2CO_3 till pH = 8~9, and **C** could be extracted with ethyl acetate (EA).

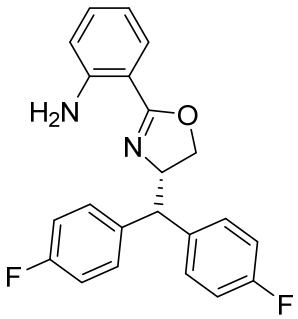
After the EA was evaporated, the crude product **C**, without further purification, was dissolved in THF (25.0 mL), then $LiAlH_4$ (11.0 mmol, 2.2 equiv.) was added into the mixture in portions in ice-water bath followed by being heated in 50 °C water bath for 2 h. The mixture was quenched by wet Na_2SO_4 in ice-water bath, then the mixture was filtered and the filtrate was concentrated under reduced pressure to give crude product **D** which was used in the next step without further purification.

$ZnCl_2$ (10.0 mmol, 2.0 equiv.) was added into the mixture of **D** and *o*-aminobenzonitrile (5.0 mmol, 1.0 equiv.) in chlorobenzene (25.0 mL), then the mixture was heated to reflux for overnight. After completion of the reaction, the reaction was added 5.0 mL TMEDA and quenched with 50.0 mL saturated aqueous NH_4Cl and the mixture was extracted with EA. The combined organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel using EA/PE = 1/15 as eluent to provide the

intermediate **E** as a white solid. *As shown above, the absolute configuration of **E** was confirmed by X-ray diffraction.*

2-(Di(aryl)phosphanyl)benzoic acid (1.2 equiv.) was added into the mixture containing **E** (1.0 mmol), EDCI (3.0 equiv.), DMAP (2.0 equiv.) and DCM (10.0 mL), then the reaction mixture was stirred at room temperature till the transformation completed monitored by TLC. The crude product was purified by flash chromatography on silica gel using EA/PE = 1/10 to 1/5 as eluent to provide the ligand **L*12** and **L*13** as a pale yellow solid respectively.

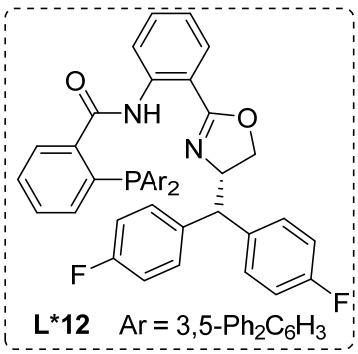
(*S*)-2-(4-(Bis(4-fluorophenyl)methyl)-4,5-dihydrooxazol-2-yl)aniline (E)



E

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.27 – 7.16 (m, 5H), 7.02 – 6.94 (m, 4H), 6.65 – 6.60 (m, 2H), 5.92 (s, 2H), 5.01 (q, *J* = 8.8 Hz, 1H), 4.30 (t, *J* = 8.8 Hz, 1H), 3.96 – 3.92 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –115.60 – –115.67 (m, 1F), –116.54 – –116.62 (m, 1F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 161.7 (d, *J* = 244.3 Hz), 161.5 (d, *J* = 243.3 Hz), 148.7, 138.1 (d, *J* = 3.4 Hz), 137.5 (d, *J* = 3.3 Hz), 132.2, 130.0 (d, *J* = 7.8 Hz), 129.8 (d, *J* = 7.8 Hz), 129.5, 115.9, 115.7, 115.6 (d, *J* = 21.1 Hz), 115.0 (d, *J* = 21.0 Hz), 108.6, 70.5, 69.7, 55.7. **HRMS** (ESI) *m/z* calcd. for $C_{22}H_{19}F_2N_2O^+$ $[M+H]^+$ 365.1460, found 365.1461.

(*S*)-*N*-(2-(4-(Bis(4-fluorophenyl)methyl)-4,5-dihydrooxazol-2-yl)phenyl)-2-(di([1,1':3',1''-terphenyl]-5'-yl)phosphanyl)benzamide (L*12)

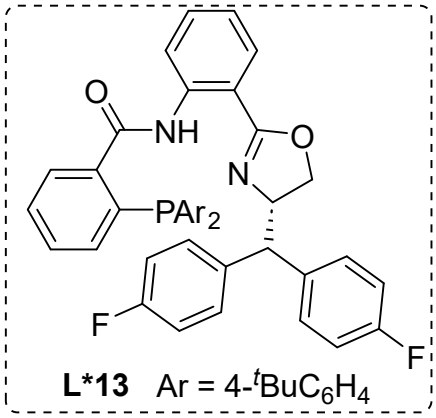


L*12 Ar = 3,5-$Ph_2C_6H_3$

^{1}H NMR (400 MHz, $CDCl_3$) 12.21 (s, 1H), 8.68 (d, *J* = 8.8 Hz, 1H), 7.79 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.75–7.69 (m, 4H), 7.64 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 2H), 7.57 – 7.50 (m, 8H), 7.41 – 7.28 (m, 16H), 7.07 – 6.95 (m, 4H), 6.89 – 6.84 (m, 4H), 6.55 (t, *J* = 8.8 Hz, 2H), 4.75 – 4.68 (m, 1H), 4.15 (t, *J* = 9.2 Hz, 1H), 3.85 (t, *J* = 8.4 Hz, 1H), 3.70 (d, *J* = 9.6 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –115.33 – –115.40 (m, 1F), –115.50 – –115.57 (m, 1F). **^{31}P NMR** (162 MHz, $CDCl_3$) –6.13. **^{13}C NMR**

(100 MHz, $CDCl_3$) 167.9, 164.3, 162.7, 162.3, 160.3, 159.9, 141.7, 141.64, 141.57, 141.49, 141.42, 141.2, 140.9, 140.8, 139.8, 139.1, 139.0, 138.9, 137.5, 137.41, 137.37, 137.26, 137.04, 137.00, 134.3, 132.8, 132.0, 131.8, 131.7, 131.5, 130.2, 129.5, 129.44, 129.39, 129.31, 129.0, 128.73, 128.71, 127.42, 127.39, 127.25, 127.19, 126.80, 126.76, 126.62, 126.58, 122.4, 120.1, 115.7, 115.5, 115.1, 114.9, 113.0, 69.9, 69.8, 55.0. **HRMS** (ESI) *m/z* calcd. for $C_{65}H_{48}F_2N_2O_2P^+$ $[M+H]^+$ 957.3416, found 957.3416.

(*S*)-2-(Bis(4-(*tert*-butyl)phenyl)phosphanyl)-*N*-(2-(4-(bis(4-fluorophenyl)methyl)-4,5-dihydrooxazol-2-yl)phenyl)benzamide (L*13)



L*13 Ar = 4-^{t}BuC$_6$H$_4$

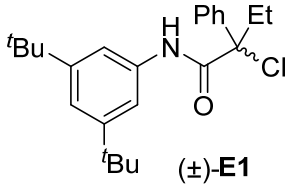
^{1}H NMR (400 MHz, $CDCl_3$) 12.15 (s, 1H), 8.58 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.42 – 7.27 (m, 7 H), 7.22 – 7.06 (m, 10 H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.92 (t, *J* = 8.8 Hz, 2H), 6.63 (t, J = 8.8 Hz, 2H), 5.08 – 5.01 (m, 1H), 4.31 (t, *J* = 9.2 Hz, 1H), 4.03 (t, *J* = 8.0 Hz, 1H), 3.92 (d, *J* = 9.2 Hz, 1H), 1.29 (s, 9H), 1.22 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –115.34 – –115.41 (m, 1F), –115.59 – –115.67 (m, 1F). **^{31}P NMR** (162 MHz, $CDCl_3$) –10.49. **^{13}C NMR** (100 MHz, $CDCl_3$) 168.0, 164.4, 162.8, 162.4, 160.34, 159.97, 151.4, 151.3, 141.4, 141.2, 139.9, 139.0, 138.8, 137.6, 137.5, 136.93, 136.90, 134.5, 134.4, 134.2, 134.1, 133.9, 133.74, 133.68, 133.5, 132.6, 130.01, 129.7, 129.63, 129.60, 129.55, 129.0, 128.1, 126.99, 126.95, 125.34, 125.26, 125.23, 125.16, 122.3, 120.2, 115.8, 115.6, 115.2, 115.0, 112.9, 69.9, 55.2, 34.6, 34.5, 31.2, 31.1. **HRMS** (ESI) *m/z* calcd. for $C_{49}H_{48}F_2N_2O_2P^+$ $[M+H]^+$ 765.3416, found 765.3415.

5. The preparation of the substrates

5.1 The synthesis of tertiary α-chloroamides

The tertiary α-chloroamides were prepared according to the previously reported procedure.[2]

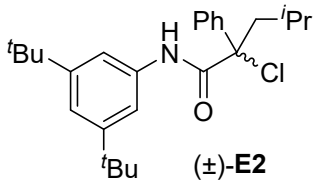
2-Chloro-*N*-(3,5-di-*tert*-butylphenyl)-2-phenylbutanamide ((±)-E1)



(±)-**E1**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.63 – 7.60 (m, 2H), 7.41 – 7.29 (m, 5H), 7.22 (t, *J* = 1.6 Hz, 1H), 2.73–2.64 (m, 1H), 2.47 – 2.38 (m, 1H), 1.32 (s, 18H), 1.09 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 151.8, 140.6, 136.7, 128.5, 128.4, 126.4, 119.1, 114.2, 79.5, 35.0, 34.8, 31.4, 9.6. **HRMS** (ESI) *m/z* calcd. for $C_{24}H_{33}ClNO^+$ $[M+H]^+$ 386.2245, found 386.2241.

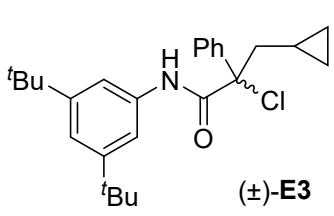
2-Chloro-*N*-(3,5-di-*tert*-butylphenyl)-4-methyl-2-phenylpentanamide ((±)-E2)



(±)-**E2**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.66 – 7.63 (m, 2H), 7.39 –7 .30 (m, 5H), 7.21 (t, *J* = 1.6 Hz, 1H), 2.66 – 2.61 (m, 1H), 2.38 – 2.33 (m, 1H), 2.02 – 1.92 (m, 1H), 1.31 (s, 18H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 151.8, 141.1, 136.8, 128.5, 128.3, 126.4, 119.1, 114.3, 78.5, 49.4, 34.9, 31.4, 25.7, 24.3, 23.3. **HRMS** (ESI) *m/z* calcd. for $C_{26}H_{37}ClNO^+$ $[M+H]^+$ 414.2558, found 414.2554.

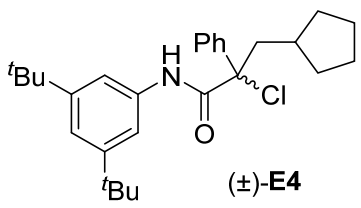
2-Chloro-3-cyclopropyl-*N*-(3,5-di-*tert*-butylphenyl)-2-phenylpropanamide ((±)-E3)



(±)-**E3**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.63 – 7.60 (m, 2H), 7.42 (d, *J* = 1.6 Hz, 2H), 7.38 – 7.28 (m, 3H), 7.22 (t, *J* = 1.6 Hz, 1H), 2.55 – 2.50 (m, 1H), 2.46 – 2.41 (m, 1H), 1.32 (s, 18H), 1.00 – 0.90 (m, 1H), 0.49 – 0.42 (m, 2H), 0.31 – 0.22 (m, 1H), 0.16 – 0.07 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 151.8, 140.9, 136.7, 128.42, 128.36, 126.5, 119.1, 114.4, 78.7, 46.0, 35.0, 31.4, 7.1, 4.6, 4.3. **HRMS** (ESI) *m/z* calcd. for $C_{26}H_{35}ClNO^+$ $[M+H]^+$ 412.2402, found 412.2404.

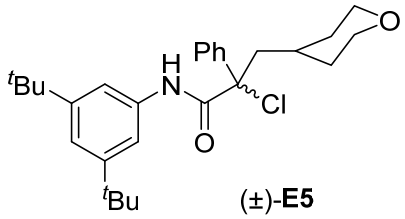
2-Chloro-3-cyclopentyl-*N*-(3,5-di-*tert*-butylphenyl)-2-phenylpropanamide ((±)-E4)



(±)-**E4**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.66 – 7.63 (m, 2H), 7.40 (d, *J* = 1.6 Hz, 2H), 7.38 – 7.26 (m, 3H), 7.21 (t, *J* = 1.6 Hz, 1H), 2.79 – 2.74 (m, 1H), 2.58 – 2.52 (m, 1H), 2.08 – 1.97 (m, 1H), 1.88 – 1.81 (m, 1H), 1.72 – 1.63 (m, 1H), 1.62 – 1.50 (m, 2H), 1.49 – 1.38 (m, 2H), 1.36 – 1.19 (s, 19H), 1.15 – 1.05 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 151.7, 141.0, 136.8, 128.4, 128.3, 126.4, 119.0, 114.3, 78.6, 47.1, 37.3, 34.9, 34.0, 33.4, 31.3, 24.8, 24.7. **HRMS** (ESI) *m/z* calcd. for $C_{28}H_{39}ClNO^+$ $[M+H]^+$ 440.2715, found 440.2711.

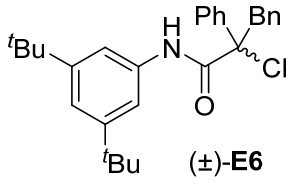
2-Chloro-*N*-(3,5-di-*tert*-butylphenyl)-2-phenyl-3-(tetrahydro-2H-pyran-4-yl)propanamide ((±)-E5)



(±)-**E5**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.66–7.63 (m, 2H), 7.39 – 7.30 (m, 5H), 7.22 (t, *J* = 1.6 Hz, 1H), 3.90 – 3.82 (m, 2H), 3.37 – 3.29 (m, 2H), 2.69 – 2.64 (m, 1H), 2.39 – 2.34 (m, 1H), 1,94 – 1.89 (m, 1H), 1.72 – 1.66 (m, 2H), 1.51 – 1.41 (m, 2H), 1.31 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 151.8, 140.7, 136.7, 128.6, 128.5, 126.2, 119.2, 114.3, 78.0, 67.9, 67.8, 48.0, 34.9, 34.3, 33.6, 32.5, 31.3. **HRMS** (ESI) *m/z* calcd. for $C_{28}H_{39}ClNO_2^+$ $[M+H]^+$ 456.2664, found 456.2658.

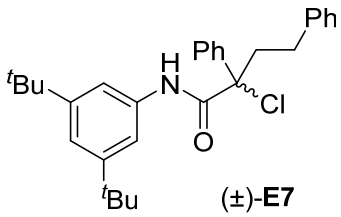
2-Chloro-*N*-(3,5-di-*tert*-butylphenyl)-2,3-diphenylpropanamide ((±)-E6)



(±)-**E6**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.63 – 7.58 (m, 2H), 7.38 – 7.30 (m, 3H), 7.28 – 7.26 (m, 2H), 7.23 – 7.15 (m, 6H), 4.02 (d, *J* = 13.6 Hz, 1H), 3.61 (d, *J* = 14.0 Hz, 1H), 1.31 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 151.6, 140.3, 136.4, 135.3, 131.2, 128.5, 128.4, 127.7, 127.1, 126.7, 119.2, 114.9, 77.8, 46.9, 34.9, 31.4. **HRMS** (ESI) *m/z* calcd. for $C_{29}H_{35}ClNO^+$ $[M+H]^+$ 448.2402, found 448.2398.

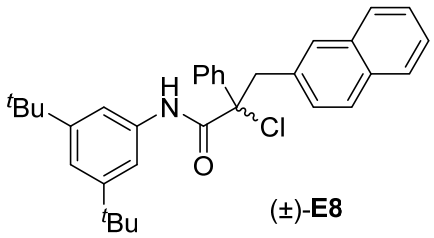
2-Chloro-*N*-(3,5-di-*tert*-butylphenyl)-2,4-diphenylbutanamide ((±)-E7)



(±)-**E7**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.67 – 7.64 (m, 2H), 7.42 – 7.31 (m, 5H), 7.29 – 7.16 (m, 6H), 3.01 – 2.92 (m, 1H), 2.89 – 2.77 (m, 2H), 2.70 – 2.61 (m, 1H), 1.33 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 151.9, 141.0, 140.4, 136.6, 128.6, 128.55, 128.52, 128.4, 126.3, 126.0, 119.2, 114.3, 78.2, 43.8, 35.0, 31.5, 31.4. **HRMS** (ESI) *m/z* calcd. for $C_{30}H_{37}ClNO^+$ $[M+H]^+$ 462.2558, found 462.2555.

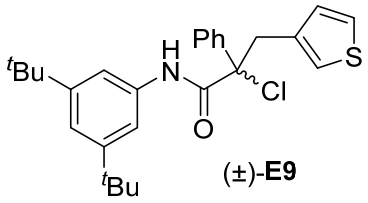
2-Chloro-N-(3,5-di-tert-butylphenyl)-3-(naphthalen-2-yl)-2-phenylpropanamide ((±)-E8)



(±)-**E8**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.76–7.70 (m, 2H), 7.67 – 7.62 (m, 4H), 7.41 – 7.31 (m, 5H), 7.27 – 7.18 (m, 4H), 4.19 (d, *J* = 14.0 Hz, 1H), 3.76 (d, *J* = 13.6 Hz, 1H), 1.29 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 151.6, 140.3, 136.4, 133.0, 132.8, 132.5, 132.0, 129.2, 128.6, 128.5, 127.8, 127.5, 127.1, 126.7, 125.8, 125.7, 119.2, 114.8, 78.0, 47.1, 34.9, 31.3. **HRMS** (ESI) *m/z* calcd. for $C_{33}H_{37}ClNO^+$ $[M+H]^+$ 498.2558, found 498.2554.

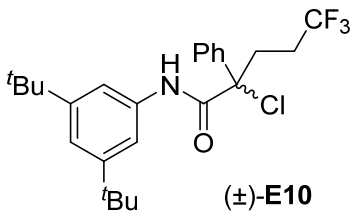
2-Chloro-*N*-(3,5-di-*tert*-butylphenyl)-2-phenyl-3-(thiophen-3-yl)propenamide ((±)-E9)



(±)-**E9**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.63 – 7.60 (m, 2H), 7.39 – 7.29 (m, 5H), 7.21 (t, *J* = 1.6 Hz, 1H), 7.14 – 7.12 (m, 1H), 7.04 – 7.03 (m, 1H), 6.88 (d, *J* = 4.8 Hz, 1H), 4.02 (d, *J* = 14.4Hz, 1H), 3.67 (d, *J* = 14.4Hz, 1H), 1.31 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 151.7, 140.1, 136.4, 135.5, 130.0, 128.6, 128.5, 126.6, 124.7, 124.3, 119.2, 114.7, 77.6, 41.9, 34.9, 31.3. **HRMS** (ESI) *m/z* calcd. for $C_{27}H_{33}ClNOS^+$ $[M+H]^+$ 454.1966, found 454.1959.

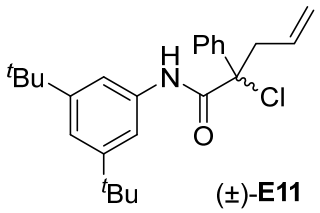
2-Chloro-*N*-(3,5-di-*tert*-butylphenyl)-5,5,5-trifluoro-2-phenylpentanamide ((±)-E10)



(±)-**E10**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.64 – 7.61 (m, 2H), 7.43 – 7.34 (m, 5H), 7.23 (t, *J* = 2.0 Hz, 1H), 2.89 – 2.82 (m, 1H), 2.67 – 2.60 (m, 1H), 2.47 – 2.32 (m, 1H), 2.31 – 2.17 (m, 1H), 1.32 (s, 18H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.0 (t, *J* = 10.5 Hz, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 152.0, 139.0, 136.4, 129.0, 128.9, 126.8 (q, *J* = 274.5 Hz), 126.1, 119.4, 114.2, 76.4, 35,0, 34.9 (q, *J* = 3.2 Hz), 31.4, 30.3 (q, *J* = 29.1 Hz). **HRMS** (ESI) *m/z* calcd. for $C_{25}H_{32}ClF_3NO^+$ $[M+H]^+$ 454.2119, found 454.2117.

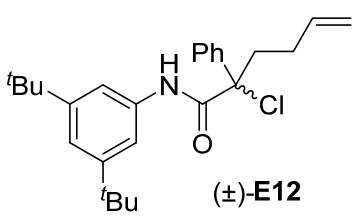
2-Chloro-*N*-(3,5-di-*tert*-butylphenyl)-2-phenylpent-4-enamide ((±)-E11)



(±)-**E11**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.64 – 7.61 (m, 2H), 7.39 – 7.29 (m, 5H), 7.22 (t, *J* = 1.6 Hz, 1H), 5.89 – 5.78 (m, 1H), 5.23 – 5.14 (m, 2H), 3.43 – 3.37 (m, 1H), 3.18 – 3.12 (m, 1H), 1.31 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.4, 151.8, 140.0, 136.6, 132.1, 128.54, 128.50, 126.4, 120.0, 119.1, 114.3, 77.0, 45.8, 34.9, 31.3. **HRMS** (ESI) *m/z* calcd. for $C_{25}H_{33}ClNO^+$ $[M+H]^+$ 398.2245, found 398.2247.

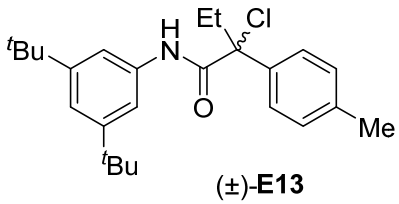
2-Chloro-*N*-(3,5-di-*tert*-butylphenyl)-2-phenylhex-5-enamide ((±)-E12)



(±)-**E12**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.39 – 7.30 (m, 5H), 7.22 (s, 1H), 5.89 – 5.79 (m, 1H), 5.09 – 4.97 (m, 2H), 2.77 – 2.70 (m, 1H), 2.51 – 2.44 (m, 1H), 2.34 – 2.20 (m, 2H), 1.32 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 151.8, 140.4, 137.1, 136.6, 128.6, 128.5, 126.3, 119.2, 115.3, 114.3, 78.2, 40.9, 35.0, 31.2, 29.3. **HRMS** (ESI) *m/z* calcd. for $C_{26}H_{35}ClNO^+$ $[M+H]^+$ 412.2402, found 412.2400.

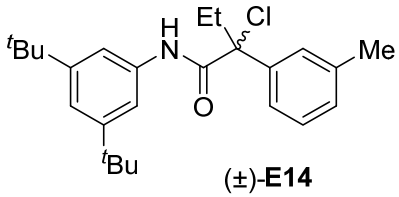
2-Chloro-*N*-(3,5-di-*tert*-butylphenyl)-2-(p-tolyl)butanamide ((±)-E13)



(±)-**E13**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 1.6 Hz, 2H), 7.21 (t, *J* = 1.6 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 2.71 – 2.62 (m, 1H), 2.46 – 2.37 (m, 1H), 2.34 (s, 3H), 1.32 (s, 18H), 1.09 (t, *J* = 7.2 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 151.8, 138.3, 137.8, 136.7, 129.2, 126.3, 119.1, 114.2, 79.5, 35.0, 34.7, 31.4, 21.0, 9.6. **HRMS** (ESI) *m/z* calcd. for $C_{25}H_{35}ClNO^+$ $[M+H]^+$ 400.2402, found 400.2399.

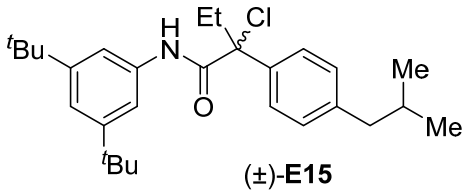
2-Chloro-*N*-(3,5-di-*tert*-butylphenyl)-2-(m-tolyl)butanamide ((±)-E14)



(±)-**E14**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.42 – 7.40 (m, 4H), 7.27 – 7.24 (m, 1H), 7.22 (t, *J* = 1.6 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 2.72 – 2.63 (m, 1H), 2.46 – 2.37 (m, 4H), 1.32 (s, 18H), 1.09 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 151.8, 140.5, 138.2, 136.7, 129.2, 128.4, 127.0, 123.5, 119.1, 114.3, 79.5, 35.0, 34.7, 31.3, 21.6, 9.6. **HRMS** (ESI) *m/z* calcd. for $C_{25}H_{35}ClNO^+$ $[M+H]^+$ 400.2402, found 400.2401.

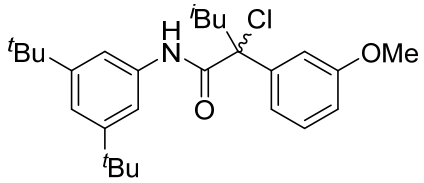
2-Chloro-*N*-(3,5-di-*tert*-butylphenyl)-2-(4-isobutylphenyl)butanamide ((±)-E15)



(±)-**E15**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 1.6 Hz, 2H), 7.22 (t, *J* = 1.6 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 2.72 – 2.63 (m, 1H), 2.47 – 2.37 (m, 3H), 1.91 – 1.80 (m, 1H), 1.32 (s, 18H), 1.09 (t, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 151.8, 142.1, 138.0, 136.8, 129.2, 126.2, 119.1, 114.2, 79.6, 44.9, 35.0, 34.8, 31.4, 30.1, 22.4, 9.6. **HRMS** (ESI) *m/z* calcd. for $C_{28}H_{41}ClNO^+$ $[M+H]^+$ 442.2871, found 442.2869.

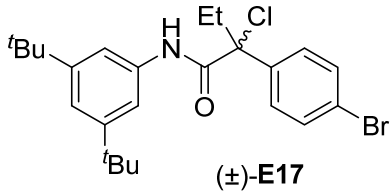
2-Chloro-*N*-(3,5-di-*tert*-butylphenyl)-2-(3-methoxyphenyl)-4-methylpentanamide ((±)-E16)



(±)-**E16**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.37 (d, *J* = 1.6 Hz, 2H), 7.28 – 7.20 (m, 4H), 6.86 – 6.83 (m, 1H), 3.81 (s, 3H), 2.64 – 2.59 (m, 1H), 2.37 – 2.32 (m, 1H), 2.00 – 1.01 (m, 1H), 1.31 (s, 18H), 1.00 (d, *J* = 6.4 Hz, 3H), 0.88 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 159.6, 151.7, 142.6, 136.8, 129.5, 119.0, 118.7, 114.3, 113.4, 112.8, 78.2, 55.3, 49.2, 34.9, 31.4, 25.7, 24.3, 23.4. **HRMS** (ESI) *m/z* calcd. for $C_{27}H_{39}ClNO_2^+$ $[M+H]^+$ 444.2664, found 444.2660.

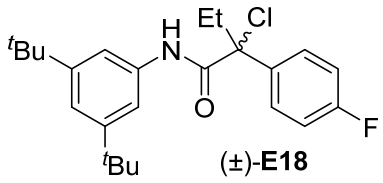
2-(4-Bromophenyl)-2-chloro-*N*-(3,5-di-*tert*-butylphenyl)butanamide ((±)-E17)



(±)-**E17**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.50 (s, 4H), 7.39 (s, 2H), 7.23 (s, 1H), 2.70 – 2.61 (m, 1H), 2.43 – 2.34 (m, 1H), 1.32 (s, 18H), 1.10 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 151.9, 139.7, 136.5, 131.6, 128.2, 122.6, 119.3, 114.3, 78.9, 35.0, 34.8, 31.4, 9.5. **HRMS** (ESI) *m/z* calcd. for $C_{24}H_{32}BrClNO^+$ $[M+H]^+$ 464.1350, found 464.1350.

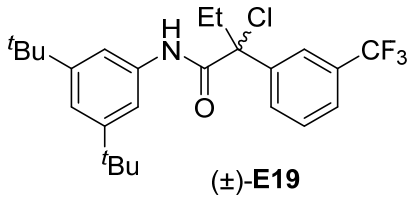
2-Chloro-*N*-(3,5-di-*tert*-butylphenyl)-2-(4-fluorophenyl)butanamide ((±)-E18)



(±)-**E18**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.63 – 7.58 (m, 2H), 7.41 (d, *J* = 1.6 Hz, 2H), 7.23 (t, *J* = 2.0 Hz, 1H), 7.05 (t, *J* = 8.8 Hz, 2H), 2.71 – 2.63 (m, 1H), 2.44 – 2.35 (m, 1H), 1.32 (s, 18H), 1.10 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –113.50 – –113.57 (m, 1F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 162.5 (d, *J* = 246.9 Hz), 151.9, 136.6 (d, *J* = 3.3 Hz), 136.5, 128.4 (d, *J* = 8.3 Hz), 119.3, 115.4 (d, *J* = 21.6 Hz), 114.3, 78.9, 35.02, 34.96, 31.4, 9.6. **HRMS** (ESI) *m/z* calcd. for $C_{24}H_{32}ClFNO^+$ $[M+H]^+$ 404.2151, found 404.2149.

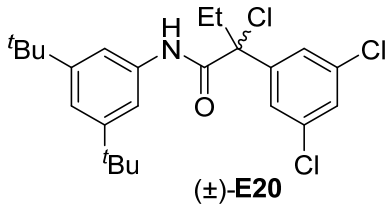
2-Chloro-*N*-(3,5-di-*tert*-butylphenyl)-2-(3-(trifluoromethyl)phenyl)butanamide((±)-E19)



(±)-**E19**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.93 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 1.6 Hz, 2H), 7.24 (t, *J* = 1.6 Hz, 1H), 2.76 – 2.67 (m, 1H), 2.48 – 2.39 (m, 1H), 1.32 (s, 18H), 1.12 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ – 62.5 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 151.9, 141.7, 136.4, 131.0 (q, *J* = 32.3 Hz), 130.0, 129.1, 125.3 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 270.5 Hz), 123.4 (q, *J* = 3.8 Hz), 119.4, 114.5, 78.7, 35.1, 35.0, 31.3, 9.5. **HRMS** (ESI) *m/z* calcd. for $C_{25}H_{32}ClF_3NO^+$ $[M+H]^+$ 454.2119, found 454.2119.

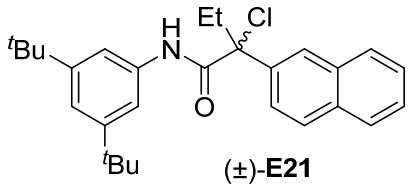
2-Chloro-N-(3,5-di-tert-butylphenyl)-2-(3,5-dichlorophenyl)butanamide ((±)-E20)



(±)-**E20**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.54 (s, 2H), 7.40 (s, 2H), 7.33 (s, 1H), 7.25 (s, 1H), 2.70 – 2.61 (m, 1H), 2.41 – 2.32 (m, 1H), 1.33 (s, 18H), 1.10 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 151.9, 143.8, 136.3, 135.1, 128.6, 125.3, 119.5, 114.4, 77.9, 35.0, 34.9, 31.3, 9.4. **HRMS** (ESI) *m/z* calcd. for $C_{24}H_{31}Cl_3NO^+$ $[M+H]^+$ 454.1466, found 454.1467.

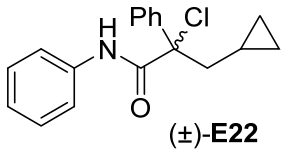
2-Chloro-*N*-(3,5-di-*tert*-butylphenyl)-2-(naphthalen-2-yl)butanamide ((±)-E21)



(±)-**E21**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.11 (d, *J* = 2.0 Hz, 1H), 7.84 – 7.76 (m, 3H), 7.67 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 7.47 – 7.42 (m, 4H), 7.23 (t, *J* = 1.6 Hz, 1H), 2.83 – 2.74 (m, 1H), 2.59 – 2.50 (m, 1H), 1.31 (s, 18H), 1.11 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 151.7, 137.7, 136.7, 132.9, 132.8, 128.4, 127.4, 126.7, 126.4, 125.5, 124.2, 119.1, 114.3, 79.6, 34.9, 34.6, 31.3, 9.5. **HRMS** (ESI) *m/z* calcd. for $C_{28}H_{35}ClNO^+$ $[M+H]^+$ 436.2402, found 436.2400.

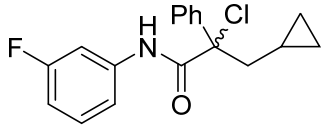
2-Chloro-3-cyclopropyl-*N*,2-diphenylpropanamide ((±)-E22)



(±)-**E22**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.61 – 7.58 (m, 2H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.38 – 7.29 (m, 5H), 7.14 (t, *J* = 7.6 Hz, 1H), 2.51 – 2.42 (m, 2H), 0.99 – 0.89 (m, 1H), 0.49 – 0.40 (m, 2H), 0.29 – 0.20 (m, 1H), 0.16 – 0.06 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 140.8, 137.2, 129.0, 128.5, 128.4, 126.4, 124.9, 120.0, 78.6, 45.9, 7.0, 4.5, 4.3. **HRMS** (ESI) *m/z* calcd. for $C_{18}H_{19}ClNO^+$ $[M+H]^+$ 300.1150, found 300.1151.

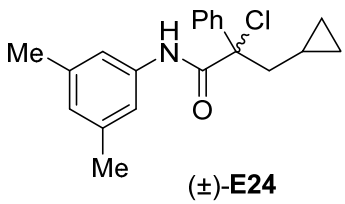
2-Chloro-3-cyclopropyl-*N*-(3-fluorophenyl)-2-phenylpropanamide ((±)-E23)



(±)-**E23**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.59 – 7.56 (m, 2H), 7.54 (dt, J_1 = 10.8 Hz, J_2 = 2.4 Hz, 1H), 7.39 – 7.24 (m, 4H), 7.17 – 7.15 (m, 1H), 6.86 – 6.81 (m, 1H), 2.45 (d, *J* = 6.8 Hz, 2H), 0.97 – 0.87 (m, 1H), 0.48 – 0.40 (m, 2H), 0.27 – 0.18 (m, 1H), 0.15 – 0.05 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –111.17 – –111.13 (m, 1F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.2, 163.0 (d, *J* = 243.8 Hz), 140.5, 138.7 (d, *J* = 10.7 Hz), 130.1 (d, *J* = 9.2 Hz), 128.53, 128.51, 126.3, 115.2 (d, *J* = 3.0 Hz), 111.6 (d, *J* = 21.2 Hz), 107.4 (d, *J* = 26.3 Hz), 78.6, 46.0, 7.0, 4.5, 4.3. **HRMS** (ESI) *m/z* calcd. for $C_{18}H_{18}ClFNO^+$ $[M+H]^+$ 318.1055, found 318.1056.

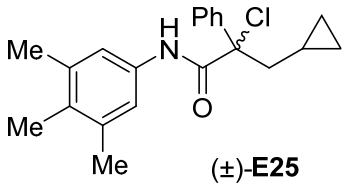
2-Chloro-3-cyclopropyl-*N*-(3,5-dimethylphenyl)-2-phenylpropanamide ((±)-E23)



(±)-**E24**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.60 – 7.56 (m, 2H), 7.36 – 7.26 (m, 3H), 7.19 (s, 2H), 6.77 (s, 1H), 2.51 – 2.46 (m, 1H), 2.44 – 2.39 (m, 1H), 2.28 (s, 6H), 0.97 – 0.88 (m, 1H), 0.48 – 0.39 (m, 2H), 0.28 – 0.19 (m, 1H), 0.15–0.06 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 140.8, 138.7, 137.0, 128.4, 128.3, 126.5, 126.3, 117.6, 78.6, 45.9, 21.2, 7.0, 4.5, 4.2. **HRMS** (ESI) *m/z* calcd. for $C_{20}H_{23}ClNO^+$ $[M+H]^+$ 328.1463, found 328.1464.

2-Chloro-3-cyclopropyl-2-phenyl-*N*-(3,4,5-trimethylphenyl)propenamide ((±)-E25)

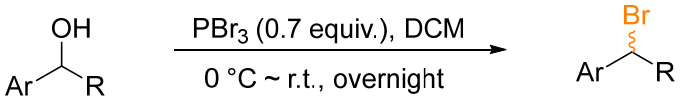


(±)-**E25**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.60 – 7.58 (m, 2H), 7.37 – 7.28 (m, 3H), 7.22 (s, 2H), 2.52 – 2.40 (m, 2H), 2.27 (s, 6H), 2.13 (s, 3H), 0.98 – 0.89 (m, 1H), 0.49 – 0.40 (m, 2H), 0.29 – 0.22 (m, 1H), 0.15 – 0.07 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 141.1, 137.2, 134.3, 131.8, 128.4, 128.3, 126.4, 119.1, 78.7, 45.9, 20.6, 14.9, 7.1, 4.5, 4.2. **HRMS** (ESI) *m/z* calcd. for $C_{21}H_{25}ClNO^+$ [M+H] 342.1619, found. 342.1621.

5.2 The synthesis of secondary benzyl bromides

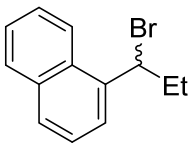
The secondary benzyl bromides ((±)-**E26-32**) were prepared according to the previously reported procedure.[3] Among them, (±)-**E32** is known compound.[4]



(±)-**E26–31**

The alcohol was resolved in CH_2Cl_2 (2.0 mL/mmol alcohol), then PBr_3 (0.7 equiv.) was added with vigorous stirring at 0 °C and the resulting reaction mixture was stirred at room temperature for overnight. After completion of reaction, the mixture was quenched by water in ice-water bath and extracted with CH_2Cl_2 three times. The combined organic phase was dried over $MgSO_4$, filtered through a Na_2SO_4 pad, and concentrated under reduced pressure to afford the corresponding crude benzyl bromide product, which was directly used in the next step without further purification or stored in a refrigerator. (The product usually readily decomposed in air and on silica gel.)

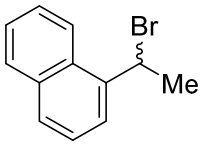
1-(1-Bromopropyl)naphthalene ((±)-E26)



(±)-**E26**

^{1}H NMR (400 MHz, $CDCl_3$) 8.18 (d, J = 8.8 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 7.2 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.51 – 7.43 (m, 2H), 5.68 (t, J = 8.4 Hz, 1H), 2.60 – 2.49 (m, 1H), 2.45 – 2.34 (m, 1H), 1.12 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.1, 133.9, 130.5, 129.1, 128.9, 126.3, 125.8, 125.4, 124.4 (brs), 123.0 (brs), 53.1, 31.9, 13.3.

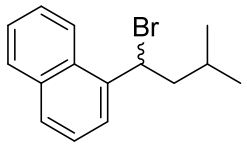
1-(1-Bromoethyl)naphthalene ((±)-E27)



(±)-**E27**

^{1}H NMR (400 MHz, $CDCl_3$) 8.20 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 7.2 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.51 – 7.47 (m, 1H), 7.44 (t, J = 7.6 Hz, 1H), 5.98 (q, J = 7.2 Hz, 1H), 2.24 (d, J = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.9, 133.9, 130.3, 129.3, 128.9, 126.4, 125.9, 125.3, 123.5, 123.1, 44.9, 25.4.

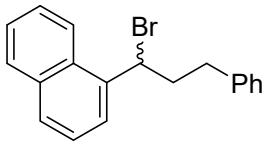
1-(1-Bromo-3-methylbutyl)naphthalene ((±)-E28)



(±)-**E28**

^{1}H NMR (400 MHz, $CDCl_3$) 8.19 (brs, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.71 (brs, 1H), 7.61 – 7.56 (m, 1H), 7.51 – 7.43 (m, 2H), 5.90 (brs, 1H), 2.50 – 2.43 (m, 1H), 2.22 – 1.95 (m, 1H), 1.90 (brs, 1H), 1.00 (d, J = 6.8 Hz, 3H), 0.96 (d, J = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.2, 133.9, 130.4, 129.1, 129.0, 126.4, 125.8, 125.4, 124.6, 122.7, 47.4, 26.7, 22.5, 21.8.

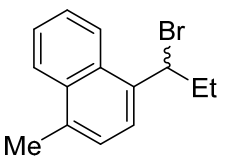
1-(1-Bromo-3-phenylpropyl)naphthalene ((±)-E29)



(±)-**E29**

^{1}H NMR (400 MHz, $CDCl_3$) 7.99 (brs, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.71 (brs, 1H), 7.53 – 7.40 (m, 3H), 7.30 – 7.26 (m, 2H), 7.22 – 7.15 (m, 3H), 5.70 (brs, 1H), 2.98 – 2.91 (m, 1H), 2.87 – 2.77 (m, 2H), 2.65 – 2.57 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.4, 137.0, 133.9, 130.3, 129.1, 128.9, 128.6, 128.5, 126.4, 126.2, 125.9, 125.4, 124.5 (brs), 122.8 (brs), 50.0 (brs), 40.1, 34.3.

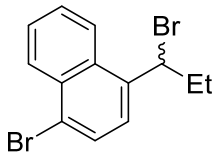
1-(1-Bromopropyl)-4-methylnaphthalene ((±)-E30)



(±)-**E30**

^{1}H NMR (400 MHz, $CDCl_3$) 8.21 (d, J = 8.0 Hz, 1H), 8.05 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.57 – 7.52 (m, 1H), 7.31 (d, J = 7.2 Hz, 1H), 5.70 (t, J = 6.0 Hz, 1H), 2.68 (s, 3H), 2.61 – 2.50 (m, 1H), 2.46 – 2.35 (m, 1H), 1.13 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.5, 135.3, 133.0, 130.5, 126.3, 126.0, 125.7, 125.0, 124.1, 123.5, 53.6 (brs), 31.8, 19.7, 13.3.

1-Bromo-4-(1-bromopropyl)naphthalene ((±)-E31)

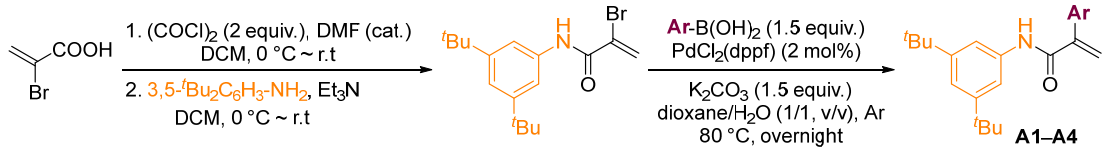


(±)-**E31**

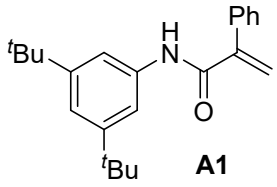
^{1}H NMR (400 MHz, $CDCl_3$) 8.33 – 8.29 (m, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.65 – 7.58 (m, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 5.62 (t, *J* = 7.2 Hz, 1H), 2.56 – 2.45 (m, 1H), 2.41 – 2.30 (m, 1H), 1.12 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.3, 132.2, 131.7, 129.6, 128.1, 127.3, 127.1, 124.8, 123.8, 123.4, 52.0 (brs), 31.8, 13.2.

5.3 The synthesis of the alkenes.

The α,β-unsaturated amide (**A1**-**A4**) were prepared according to the previously reported procedure.[5] And 1-vinylnaphthalene (**A5**) is commercially available.



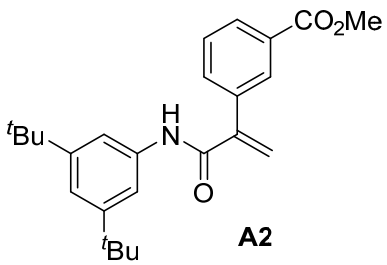
***N*-(3,5-Di-*tert*-butylphenyl)-2-phenylacrylamide (A1)**



A1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.46–7.35 (m, 7H), 7.20 (s, 1H), 6.22 (s, 1H), 5.69 (s, 1H), 1.30 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.3, 151.5, 145.4, 137.0, 136.7, 128.8, 128.6, 128.1, 122.5, 118.7, 114.5, 34.8, 31.3. **HRMS** (ESI) *m/z* calcd. for $C_{23}H_{30}NO^+$ $[M+H]^+$ 336.2322, found 336.2324.

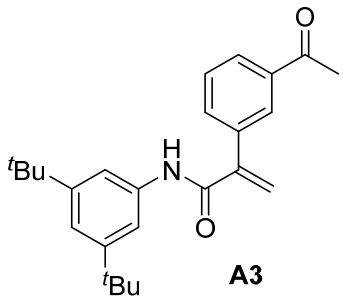
Methyl 3-(3-((3,5-di-*tert*-butylphenyl)amino)-3-oxoprop-1-en-2-yl)benzoate (A2)



A2

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.68 (d *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.38 (s, 2H), 7.32 (s, 1H), 7.21 (s, 1H), 6.24 (s, 1H), 5.81 (s, 1H), 3.94 (s, 3H), 1.32 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 165.2, 151.8, 144.9, 137.0, 136.9, 132.6, 130.9, 129.8, 129.2, 128.9, 122.8, 119.0, 114.7, 52.3, 34.9, 31.4. **HRMS** (ESI) *m/z* calcd. for $C_{25}H_{32}NO_3^+$ $[M+H]^+$ 394.2377, found 394.2379.

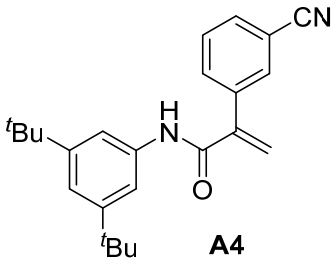
2-(Benzo[d][1,3]dioxol-5-yl)-*N*-(3,5-di-tert-butylphenyl)acrylamide (A3)



A3

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.39 (s, 3H), 7.22 (t, *J* = 1.6 Hz, 1H), 6.23 (s, 1H), 5.81 (s, 1H), 2.63 (s, 2H), 1.31 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.7, 165.2, 151.8, 145.1, 137.7, 137.2, 136.9, 132.7, 129.1, 128.6, 127.9, 122.7, 119.1, 114.7, 35.0, 31.4, 26.7. **HRMS** (ESI) *m/z* calcd. for $C_{25}H_{32}NO_2^+$ $[M+H]^+$ 378.2428, found 378.2425.

***N*-(3,5-Di-*tert*-butylphenyl)-2-(furan-3-yl)acrylamide (A4)**

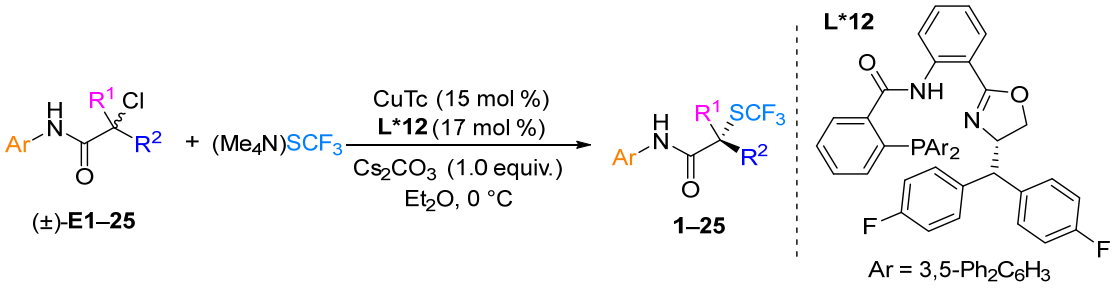


A4

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 6.8 Hz, 2H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.42 (s, 2H), 7.23 (s, 1H), 6.13 (s, 1H), 5.83 (s, 1H), 1.32 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.1, 151.8, 144.2, 137.7, 136.7, 132.2, 132.0, 131.4, 129.5, 122.2, 119.1, 118.3, 114.7, 112.9, 34.9, 31.3. **HRMS** (ESI) *m/z* calcd. for $C_{24}H_{29}N_2O^+$ $[M+H]^+$ 361.2274, found 361.2272.

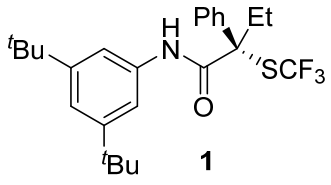
6. General procedure of enantioselective radical trifluoromethylthiolation

6.1 The procedure of enantioselective radical trifluoromethylthiolation of tertiary α-chloroamides



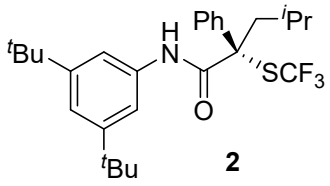
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with the substrates (±)-**E** (0.1 mmol), $(Me_4N)SCF_3$ (26.3 mg, 0.15 mmol, 1.5 equiv.), CuTc (2.86 mg, 0.015 mmol, 15 mol%), **L*12** (16.3 mg, 0.017 mmol, 17 mol%), Cs_2CO_3 (32.6 mg, 0.10 mmol, 1.0 equiv.), and Et_2O (2.0 mL) successively. Then the reaction mixture was stirred in 0 °C ethanol bath for 120 h. Upon completion, the precipitate was filtered off and washed by ethyl acetate. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product **1**–**25**.

(*R*)-*N*-(3,5-Di-*tert*-butylphenyl)-2-phenyl-2-((trifluoromethyl)thio)butanamide (1)



The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **1** (37.4 mg, 83% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.51 (m, 2H), 7.43 – 7.33 (m, 4H), 7.25 (d, J = 1.6 Hz, 2H), 7.21 (t, J = 1.6 Hz, 1H), 2.71 – 2.62 (m, 1H), 2.51 – 2.42 (m, 1H), 1.30 (s, 18H), 1.09 (t, J = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –37.2 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.1, 151.8, 138.4, 136.6, 129.7 (q, J = 307.3 Hz), 128.9, 128.7, 127.3, 119.2, 114.4, 67.8, 34.9, 31.3, 30.9, 9.3. **HRMS** (ESI) *m/z* calcd. for $C_{25}H_{33}F_3NOS^+$ $[M+H]^+$ 452.2229, found 452.2227. **HPLC** analysis: Chiralcel IG (hexane/*i*-PrOH = 99/1, flow rate 0.40 mL/min, λ = 254 nm), t_R (minor) = 10.00 min, t_R (major) = 10.66 min, 90% ee.

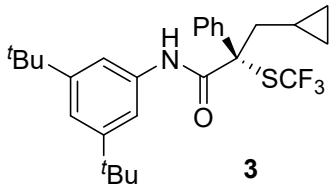
(*R*)-*N*-(3,5-Di-*tert*-butylphenyl)-4-methyl-2-phenyl-2-((trifluoromethyl)thio)pentanamide (2)



2

The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **2** (34.4 mg, 72% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.54 (m, 2H), 7.43 – 7.33 (m, 3H), 7.25 (s, 1H), 7.21 – 7.19 (m, 3H), 2.59 (dd, J_1 = 14.8 Hz, J_2 = 4.8 Hz, 1H), 2.33 (dd, J_1 = 14.8 Hz, J_2 = 5.6 Hz, 1H), 2.11 – 2.02 (m, 1H), 1.29 (s, 18H), 0.91 (d, J = 6.4 Hz, 3H), 0.84 (d, J = 6.4 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –36.9 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.5, 151.8, 139.1, 136.4, 129.8 (q, J = 307.3 Hz), 128.9, 128.7, 127.3, 119.2, 114.4, 66.8, 46.1, 34.9, 31.3, 24.9, 24.5, 23.8. **HRMS** (ESI) *m/z* calcd. for $C_{27}H_{37}F_3NOS^+$ $[M+H]^+$ 480.2542, found 480.2539. **HPLC** analysis: two connected Chiralcel IC (hexane/*i*-PrOH = 99/1, flow rate 0.40 mL/min, λ = 254 nm), t_R (minor) = 17.16 min, t_R (major) = 17.75 min, 94% ee.

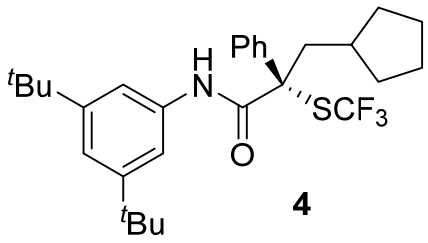
(*R*)-3-Cyclopropyl-*N*-(3,5-di-*tert*-butylphenyl)-2-phenyl-2-((trifluoromethyl)thio)propanamide (3)



3

The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **3** (40.6 mg, 85% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 2H), 7.47 – 7.38 (m, 4H), 7.29 (d, J = 1.6 Hz, 2H), 7.25 (t, J = 1.6 Hz, 1H), 2.62 (dd, J_1 = 14.8 Hz, J_2 = 6.4 Hz, 1H), 2.42 (dd, J_1 = 14.8 Hz, J_2 = 6.8 Hz, 1H), 1.34 (s, 18H), 1.09 – 0.99 (m, 1H), 0.54 – 0.44 (m, 2H), 0.17 – 0.09 (m, 1H), 0.09 – 0.01 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –36.9 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.2, 151.8, 138.5, 136.5, 129.8 (q, J = 307.4 Hz), 128.8, 128.7, 127.7, 119.2, 114.4, 67.4, 43.3, 34.9, 31.3, 6.9, 4.8, 4.7. **HRMS** (ESI) *m/z* calcd. for $C_{27}H_{35}F_3NOS^+$ $[M+H]^+$ 478.2386, found 478.2384. **HPLC** analysis: Chiralcel IG (hexane/*i*-PrOH = 99/1, flow rate 0.50 mL/min, λ = 254 nm), t_R (minor) = 8.14 min, t_R (major) = 8.57 min, 92% ee.

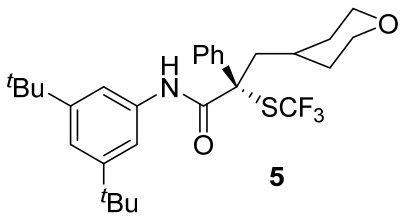
(*R*)-3-Cyclopentyl-*N*-(3,5-di-*tert*-butylphenyl)-2-phenyl-2-((trifluoromethyl)thio)propenamide (4)



4

The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **4** (41.9 mg, 83% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.2 Hz, 2H), 7.43 – 7.34 (m, 3H), 7.27 (s, 1H), 7.21 (s, 2H), 7.20 (s, 1H), 2.76 (dd, J_1 = 14.8 Hz, J_2 = 5.6 Hz, 1H), 2.51 (dd, J_1 = 15.2 Hz, J_2 = 6.0 Hz, 1H), 2,20 – 2.08 (m, 1H), 1.81 – 1.73 (m, 1H), 1.66 – 1.50 (m, 3H), 1.47 – 1.41(m, 2H), 1.29 (s, 18H), 1.14 – 0.95 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –36.9 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.5, 151.8, 139.1, 136.5, 129.8 (q, *J* = 307.3 Hz), 128.9, 128.7, 127.3, 119.1, 114.4, 67.1, 44.0, 36.7, 34.9, 34.1, 33.7, 31.3, 24.9, 24.7. **HRMS** (ESI) *m/z* calcd. for $C_{29}H_{39}F_3NOS^+$ $[M+H]^+$ 506.2699, found 506.2698. **HPLC** analysis: Chiralcel IG (hexane/*i*-PrOH = 99/1, flow rate 0.40 mL/min, λ = 254 nm), t_R (minor) = 9.31 min, t_R (major) = 9.76 min, 95% ee.

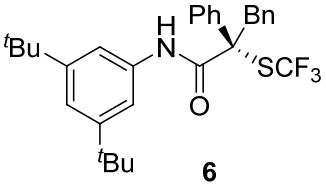
(*R*)-*N*-(3,5-Di-*tert*-butylphenyl)-2-phenyl-3-(tetrahydro-2H-pyran-4-yl)-2-((trifluoromethyl)thio)propenamide (5)



5

The residue was purified by column chromatography on silica gel with an eluent of EA and petroleum ether (1:12, v/v) to afford product **5** (32.8 mg, 63% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.53 (m, 2H), 7.44 – 7.35 (m, 3H), 7.28 (s, 1H), 7.20 (t, *J* = 1.6 Hz, 1H), 7.19 (d, *J* = 1.6 Hz, 2H), 3.84 – 3.79 (m, 2H), 3.36 – 3.28 (m, 2H), 2.62 (dd, J_1 = 15.2 Hz, J_2 = 4.8 Hz, 1H), 2.35 (dd, J_1 = 15.2 Hz, J_2 = 5.6 Hz, 1H), 2.05 – 1.94 (m, 1H), 1.50 – 1.44 (m, 1H), 1.37 – 1.26 (m, 21H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –36.8 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.3, 151.8, 138.7, 136.3, 129.7 (q, *J* = 307.4 Hz), 129.1, 128.9, 127.1, 119.3, 114.5, 67.9, 67.8, 66.2, 44.6, 34.9, 34.3, 34.0, 31.7, 31.3. **HRMS** (ESI) *m/z* calcd. for $C_{29}H_{39}F_3NO_2S^+$ $[M+H]^+$ 522.2648, found 522.2648. **HPLC** analysis: Chiralcel OD-H (hexane/*i*-PrOH = 95/5, flow rate 0.50 mL/min, λ = 254 nm), t_R (minor) = 9.01 min, t_R (major) = 12.35 min, 94% ee.

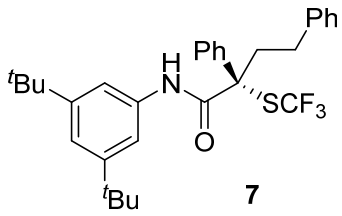
(*R*)-*N*-(3,5-Di-*tert*-butylphenyl)-2,3-diphenyl-2-((trifluoromethyl)thio)propenamide (6)



6

The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **6** (41.4 mg, 81% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.35 (s, 5H), 7.23 – 7.14 (m, 6H), 6.99 – 6.96 (m, 2H), 3.83 (d, *J* = 14.4 Hz, 1H), 3.76 (d, *J* = 14.0 Hz, 1H), 1.31 (s, 18H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –36.2 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.4, 151.7, 137.7, 136.4, 134.7, 131.1, 129.6 (q, *J* = 308.2 Hz), 128.8, 128.7, 127.8, 127.7, 127.2, 119.3, 114.7, 66.7, 44.5, 34.9, 31.4. **HRMS** (ESI) *m/z* calcd. for $C_{30}H_{35}F_3NOS^+$ $[M+H]^+$ 514.2386, found 514.2387. **HPLC** analysis: Chiralcel IE (hexane/*i*-PrOH = 99/1, flow rate 0.40 mL/min, λ = 254 nm), t_R (minor) = 16.04 min, t_R (major) = 18.04 min, 91% ee.

(*R*)-*N*-(3,5-Di-*tert*-butylphenyl)-2,4-diphenyl-2-((trifluoromethyl)thio)butanamide (7)

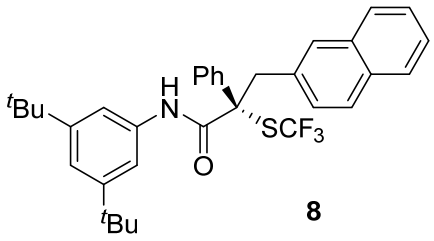


7

The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **7** (43.2 mg, 82% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 2H), 7.45 – 7.36 (m, 4H), 7.29 – 7.22 (m, 5H), 7.21 – 7.15 (m, 3H), 2.97 – 2.84 (m, 2H), 2.74 – 2.63 (m, 2H), 1.31 (s, 18H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –37.0 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.0, 151.9, 140.9, 138.3, 136.5, 129.7 (q, *J* = 307.5 Hz), 129.1, 128.9, 128.5, 128.4, 127.2, 126.1, 119.3, 114.5, 66.7, 39.9, 34.9, 31.3, 31.2. **HRMS** (ESI) *m/z* calcd. for $C_{31}H_{37}F_3NOS^+$ $[M+H]^+$ 528.2542, found 528.2549. **HPLC** analysis: two connected Chiralcel IC (hexane/*i*-PrOH = 99/1, flow rate 0.50 mL/min, λ = 254 nm), t_R (major) = 16.21 min, t_R (minor) = 18.43 min, 85% ee.

(*R*)-*N*-(3,5-Di-*tert*-butylphenyl)-3-(naphthalen-2-yl)-2-phenyl-2-((trifluoromethyl)thio)propenamide (8)

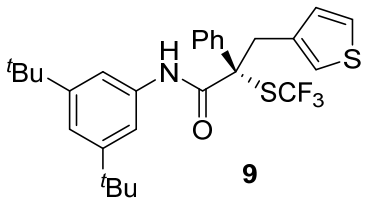
The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **8** (47.9 mg, 85% yield) as



8

a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 1H), 7.67 – 7.74 (m, 2H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.46 – 7.44 (m, 1H), 7.42 – 7.40 (m, 2H), 7.39 – 7.31 (m, 5H), 7.23 – 7.21 (m, 3H), 7.02 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 3.99 (d, *J* = 14.4 Hz, 1H), 3.92 (d, *J* = 14.0 Hz, 1H), 1.30 (s, 18H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –36.1 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.4, 151.8, 137.7, 136.4, 132.9, 132.4, 132.2, 130.3, 129.6 (q, *J* = 308.0 Hz), 129.0, 128.8, 128.7, 127.8, 127.7, 127.5, 127.1, 125.83, 125.80, 119.3, 114.7, 66.8, 44.7, 34.9, 31.3. **HRMS** (ESI) *m/z* calcd. for $C_{34}H_{37}F_3NOS^+$ $[M+H]^+$ 564.2542, found 564.2538. **HPLC** analysis: Chiralcel OD-H (hexane/*i*-PrOH = 95/5, flow rate 0.50 mL/min, λ = 254 nm), t_R (major) = 10.98 min, t_R (minor) = 14.78 min, 91% ee.

(*R*)-*N*-(3,5-Di-*tert*-butylphenyl)-2-phenyl-3-(thiophen-3-yl)-2-((trifluoromethyl)thio)propenamide (9)

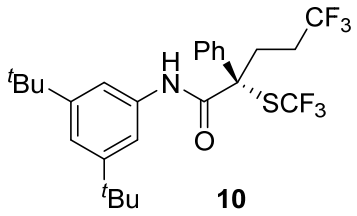


9

The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **9** (45.2 mg, 87% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.36 (s, 5H), 7.24 – 7.22 (m, 3H), 7.11 – 7.09 (m, 1H), 6.86 – 6.85 (m, 1H), 6.62 (dd, J_1 = 5.2 Hz, J_2 = 1.6 Hz, 1H), 3.89 (d, *J* = 14.8 Hz, 1H), 3.78 (d, *J* = 14.8 Hz, 1H), 1.31 (s, 18H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –36.3 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.5, 151.8, 137.6, 136.4, 134.9, 129.9, 129.6 (q, *J* = 308.0 Hz), 128.81, 128.78, 127.4, 124.9, 124.4, 119.3, 114.6, 66.2, 39.3, 34.9, 31.3. **HRMS** (ESI) *m/z* calcd. for $C_{28}H_{33}F_3NOS_2^+$ $[M+H]^+$ 520.1950, found 520.1952. **HPLC** analysis: Chiralcel OD-H (hexane/*i*-PrOH = 95/5, flow rate 0.50 mL/min, λ = 254 nm), t_R (major) = 8.19 min, t_R (minor) = 10.51 min, 89% ee.

(*R*)-*N*-(3,5-Di-*tert*-butylphenyl)-5,5,5-trifluoro-2-phenyl-2-((trifluoromethyl)thio)pentanamide (10)

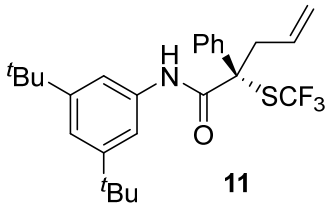
The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **10** (43.1 mg, 83% yield)



10

as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.50 – 7.39 (m, 5H), 7.26 – 7.23 (m, 3H), 2.91 (td, J_1 = 14.0 Hz, J_2 = 4.4 Hz, 1H), 2.64 (td, J_1 = 12.8 Hz, J_2 = 4.0 Hz, 1H), 2.40 – 2.24 (m, 1H), 2.24 – 2.09 (m, 1H), 1.31 (s, 18H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –37.0 (s, 3F), –66.1 (t, J = 10.5 Hz, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 152.0, 136.7, 136.3, 129.5, 129.4, 129.2 (q, J = 308.1 Hz), 126.8 (q, J = 274.7 Hz), 126.7, 119.5, 114.5, 64.6, 35,0, 31.3, 31.0, 30.2 (q, J = 29.0 Hz). **HRMS** (ESI) *m/z* calcd. for $C_{26}H_{32}F_6NOS^+$ $[M+H]^+$ 520.2103, found 520.2102. **HPLC** analysis: Chiralcel OD-H (hexane/*i*-PrOH = 97/3, flow rate 0.50 mL/min, λ = 254 nm), t_R (major) = 7.02 min, t_R (minor) = 7.92 min, 87% ee.

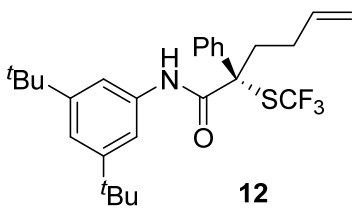
(*R*)-*N*-(3,5-Di-*tert*-butylphenyl)-2-phenyl-2-((trifluoromethyl)thio)pent-4-enamide (11)



11

The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **11** (39.4 mg, 85% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 3H), 7.43 – 7.35 (m, 3H), 7.25 (s, 2H), 7.22 (s, 1H), 5.89 – 5.79 (m, 1H), 5.15 – 5.08 (m, 2H), 3.37 (dd, J_1 = 14.8 Hz, J_2 = 6.8 Hz, 1H), 3.21 (dd, J_1 = 14.8 Hz, J_2 = 7.2 Hz, 1H), 1.30 (s, 18H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –36.8 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.7, 151.8, 137.6, 136.4, 131.9, 129.6 (q, J = 307.6 Hz), 129.0, 128.8, 127.3, 120.1, 119.3, 114.6, 65.8, 42.7, 34.9, 31.3. **HRMS** (ESI) *m/z* calcd. for $C_{26}H_{33}F_3NOS^+$ $[M+H]^+$ 464.2229, found 464.2229. **HPLC** analysis: Chiralcel IE (hexane/*i*-PrOH = 99/1, flow rate 0.40 mL/min, λ = 254 nm), t_R (minor) = 11.89 min, t_R (major) = 12.88 min, 84% ee.

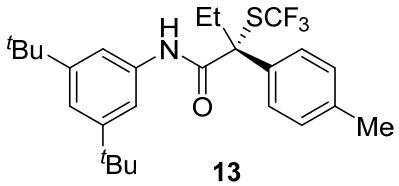
(*R*)-*N*-(3,5-Di-*tert*-butylphenyl)-2-phenyl-2-((trifluoromethyl)thio)hex-5-enamide (12)



12

The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **12** (42.9 mg, 90% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.51 (m, 2H), 7.44 – 7.35 (m, 4H), 7.25 (d, J = 1.6 Hz, 2H), 7.21 (t, J = 1.6 Hz, 1H), 5.87 – 5.77 (m, 1H), 5.06 (dq, J_1 = 16.8 Hz, J_2 = 1.6 Hz, 1H), 4.99 (dq, J_1 = 10.4 Hz, J_2 = 1.6 Hz, 1H), 2.75 – 2.67 (m, 1H), 2.51 – 2.44 (m, 1H), 2.33 – 2.24 (m, 1H), 2.22 – 2.12 (m, 1H), 1.30 (s, 18H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –37.1 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.0, 151.8, 138.2, 137.0, 136.5, 129.6 (q, J = 307.5 Hz), 129.1, 128.8, 127.1, 119.2, 115.4, 114.4, 66.5, 37.1, 34.9, 31.3, 29.1. **HRMS** (ESI) *m/z* calcd. for $C_{27}H_{35}F_3NOS^+$ $[M+H]^+$ 478.2386, found 478.2386. **HPLC** analysis: Chiralcel OD-H (hexane/*i*-PrOH = 99/1, flow rate 0.50 mL/min, λ = 254 nm), t_R (major) = 7.93 min, t_R (minor) = 8.74 min, 92% ee.

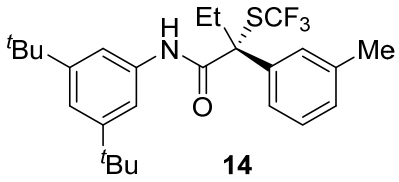
(*R*)-*N*-(3,5-Di-*tert*-butylphenyl)-2-(*p*-tolyl)-2-((trifluoromethyl)thio)butanamide (13)



13

The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **13** (40.9 mg, 88% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.0 Hz, 2H), 7.36 (s, 1H), 7.26 – 7.19 (m, 5H), 2.68 – 2.59 (m, 1H), 2.48 – 2.39 (m, 1H), 2.37 (s, 3H), 1.30 (s, 18H), 1.07 (t, J = 7.6 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –37.2 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.4, 151.8, 138.7, 136.6, 135.3, 129.7 (q, J = 307.3 Hz), 129.6, 127.2, 119.1, 114.4, 67.6, 34.9, 31.3, 30.9, 21.1, 9.3. **HRMS** (ESI) *m/z* calcd. for $C_{26}H_{35}F_3NOS^+$ $[M+H]^+$ 466.2386, found 466.2385. **HPLC** analysis: Chiralcel OD-H connecting OD-3 (hexane/*i*-PrOH = 99/1, flow rate 0.40 mL/min, λ = 254 nm), t_R (minor) = 18.95 min, t_R (major) = 20.67 min, 90% ee.

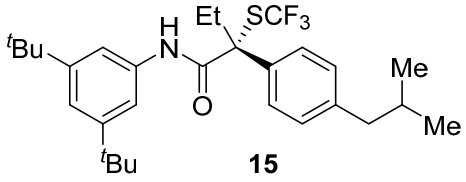
(*R*)-*N*-(3,5-Di-*tert*-butylphenyl)-2-(*m*-tolyl)-2-((trifluoromethyl)thio)butanamide (14)



14

The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **14** (32.1 mg, 69% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.32 – 7.29 (m, 3H), 7.24 (d, *J* = 1.6 Hz, 2H), 7.20 (t, *J* = 1.6 Hz, 1H), 7.18 – 7.16 (m, 1H), 2.69 – 2.60 (m, 1H), 2.49 – 2.39 (m, 1H), 2.37 (s, 3H), 1.30 (s, 18H), 1.06 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –37.2 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.3, 151.8, 138.8, 138.2, 136.6, 129.7 (q, *J* = 307.3 Hz), 129.5, 128.8, 127.8, 124.1, 119.1, 114.4, 67.6, 34.9, 31.3, 30.9, 21.6, 9.3. **HRMS** (ESI) *m/z* calcd. for $C_{26}H_{35}F_3NOS^+$ $[M+H]^+$ 466.2386, found 466.2385. **HPLC** analysis: two connected Chiralcel IC (hexane/*i*-PrOH = 99/1, flow rate 0.40 mL/min, λ = 254 nm), t_R (minor) = 18.04 min, t_R (major) = 19.07 min, 92% ee.

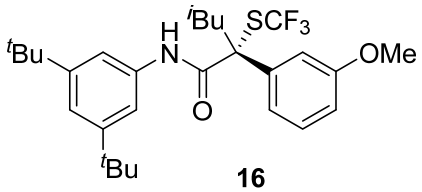
(*R*)-*N*-(3,5-Di-*tert*-butylphenyl)-2-(4-isobutylphenyl)-2-((trifluoromethyl)thio)butanamide (15)



15

The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **15** (43.6 mg, 86% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.35 (s, 1H), 7.23 (s, 2H), 7.20 – 7.17 (m, 3H), 2.69 – 2.60 (m, 1H), 2.49 (d, *J* = 7.2 Hz, 2H), 2.48 – 2.40 (m, 1H), 1.92 – 1.82 (m, 1H), 1.30 (s, 18H), 1.08 (t, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 6.4 Hz, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –37.2 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.4, 151.8, 142.5, 136.6, 135.6, 129.8 (q, *J* = 307.3 Hz), 129.6, 127.1, 119.1, 114.3, 67.7, 44.9, 34.9, 31.3, 30.9, 30.1, 22.28, 22.26, 9.4. **HRMS** (ESI) *m/z* calcd. for $C_{29}H_{41}F_3NOS^+$ $[M+H]^+$ 508.2855, found 508.2853. **HPLC** analysis: two connected Chiralcel IE (hexane/*i*-PrOH = 99/1, flow rate 0.40 mL/min, λ = 254 nm), t_R (major) = 22.97 min, t_R (minor) = 24.07 min, 85% ee.

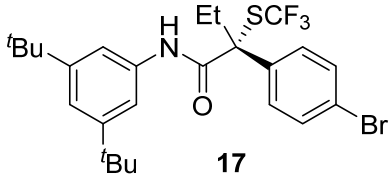
(*R*)-*N*-(3,5-Di-*tert*-butylphenyl)-2-(3-methoxyphenyl)-4-methyl-2-((trifluoromethyl)thio)pentanamide (16)



16

The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **16** (44.3 mg, 87% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 8.0 Hz, 1H), 7.22 (s, 1H), 7.19 (s, 3H), 7.15 – 7.12 (m, 1H), 7.10 (t, *J* = 2.0 Hz, 1H), 6.89 (dd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, 1H), 3.82 (s, 3H), 2.56 (dd, J_1 = 14.8 Hz, J_2 = 4.8 Hz, 1H), 2.32 (dd, J_1 = 14.8 Hz, J_2 = 5.6 Hz, 1H), 2.11 – 2.02 (m, 1H), 1.29 (s, 18H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –36.9 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.3, 159.8, 151.8, 140.7, 136.4, 129.9, 129.8 (q, *J* = 307.3 Hz), 119.5, 119.2, 114.5, 113.8, 113.5, 66.7, 55.4, 46.0, 34.9, 31.3, 24.9, 24.5, 23.8. **HRMS** (ESI) *m/z* calcd. for $C_{28}H_{39}F_3NO_2S^+$ $[M+H]^+$ 510.2648, found 510.2648. **HPLC** analysis: Chiralcel IC (hexane/*i*-PrOH = 99/1, flow rate 0.50 mL/min, λ = 254 nm), t_R (minor) = 14.08 min, t_R (major) = 14.70 min, 94% ee.

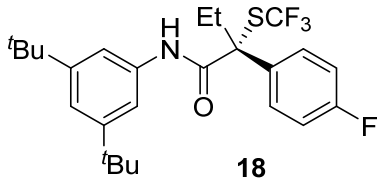
(*R*)-2-(4-Bromophenyl)-*N*-(3,5-di-*tert*-butylphenyl)-2-((trifluoromethyl)thio)butanamide (17)



17

The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **17** (43.5 mg, 82% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H), 7.43 – 7.39 (m, 2H), 7.35 (s, 1H), 7.25 (d, *J* = 1.6 Hz, 2H), 7.22 (d, *J* = 1.6 Hz, 1H), 2.67 – 2.58 (m, 1H), 2.48 – 2.39 (m, 1H), 1.30 (s, 18H), 1.10 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –37.1 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.5, 151.9, 137.6, 136.3, 132.1, 129.5 (q, *J* = 307.3 Hz), 129.0, 123.0, 119.4, 114.4, 67.4, 34.9, 31.3, 30.9, 9.3. **HRMS** (ESI) *m/z* calcd. for $C_{25}H_{32}BrF_3NOS^+$ $[M+H]^+$ 530.1335, found 530.1340. **HPLC** analysis: Chiralcel OD-H (hexane/*i*-PrOH = 99/1, flow rate 0.40 mL/min, λ = 254 nm), t_R (minor) = 14.79 min, t_R (major) = 20.70 min, 86% ee.

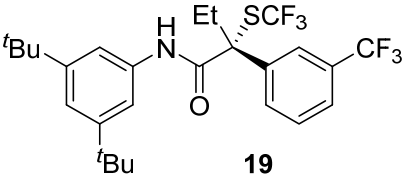
(*R*)-*N*-(3,5-Di-*tert*-butylphenyl)-2-(4-fluorophenyl)-2-((trifluoromethyl)thio)butan amide (18)



18

The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **18** (41.3 mg, 88% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H), 7.33 (s, 1H), 7.24 (s, 2H), 7.22 (m, 1H), 7.11 (t, *J* = 8.4 Hz, 2H), 2.68 – 2.59 (m, 1H), 2.49 – 2.40 (m, 1H), 1.30 (s, 18H), 1.11 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –37.2 (s, 3F), –112.26 – –112.33 (m, 1F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.8, 162.5 (d, *J* = 248.0 Hz), 151.9, 136.4, 134.4 (d, *J* = 3.4 Hz), 129.6 (q, *J* = 307.4 Hz), 129.4 (d, *J* = 8.4 Hz), 119.3, 116.0 (d, *J* = 21.5 Hz), 114.4, 67.4, 34.9, 31.3, 31.1, 9.3. **HRMS** (ESI) *m/z* calcd. for $C_{25}H_{32}F_4NOS^+$ $[M+H]^+$ 470.2135, found 470.2133. **HPLC** analysis: Chiralcel IG (hexane/*i*-PrOH = 99/1, flow rate 0.40 mL/min, λ = 254 nm), t_R (minor) = 9.89 min, t_R (major) = 10.58 min, 90% ee.

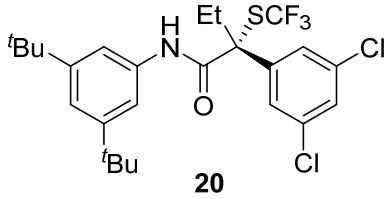
(*R*)-*N*-(3,5-Di-*tert*-butylphenyl)-2-(3-(trifluoromethyl)phenyl)-2-((trifluoromethy l)thio)butanamide (19)



19

The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **19** (46.7 mg, 90% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.41 (s, 1H), 7.24 (s, 3H), 2.73 – 2.64 (m, 1H), 2.54 – 2.45 (m, 1H), 1.31 (s, 18H), 1.13 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –37.1 (s, 3F), –62.6 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.2, 152.0, 139.9, 136.1, 131.3 (q, *J* = 32.4 Hz), 131.1, 129.6, 129.5 (q, *J* = 307.5 Hz), 125.6 (q, *J* = 3.7 Hz), 123.9 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 270.9 Hz), 119.6, 114.7, 67.3, 34.9, 31.3, 31.0, 9.3. **HRMS** (ESI) *m/z* calcd. for $C_{26}H_{32}F_6NOS^+$ $[M+H]^+$ 520.2103, found 520.2102. **HPLC** analysis: Chiralcel IG (hexane/*i*-PrOH = 99/1, flow rate 0.40 mL/min, λ = 254 nm), t_R (minor) = 8.81 min, t_R (major) = 9.25 min, 86% ee.

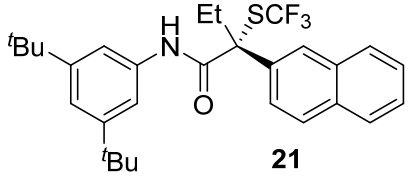
(*R*)-*N*-(3,5-Di-*tert*-butylphenyl)-2-(3,5-dichlorophenyl)-2-((trifluoromethyl)thio)butanamide (20)



20

The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **20** (40.1 mg, 77% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 2.0 Hz, 2H), 7.39 – 7.37 (m, 2H), 7.26 – 7.24 (m, 3H), 2.65 – 2.56 (m, 1H), 2.48 – 2.39 (m, 1H), 1.31 (s, 18H), 1.12 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –37.0 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 152.0, 142.2, 136.1, 135.6, 129.4 (q, *J* = 307.6 Hz), 129.0, 125.9, 119.7, 114.6, 67.0, 35.0, 31.3, 30.8, 9.2. **HRMS** (ESI) *m/z* calcd. for $C_{25}H_{31}Cl_2F_3NOS^+$ $[M+H]^+$ 520.1450, found 520.1449. **HPLC** analysis: Chiralcel OD-H (hexane/*i*-PrOH = 99/1, flow rate 0.40 mL/min, λ = 254 nm), t_R (minor) = 11.23 min, t_R (major) = 13.25 min, 84% ee.

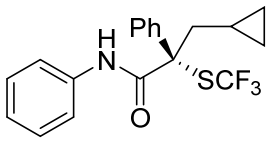
(*R*)-*N*-(3,5-Di-*tert*-butylphenyl)-2-(naphthalen-2-yl)-2-((trifluoromethyl)thio)butanamide (21)



21

The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **21** (41.1 mg, 82% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 2.0 Hz, 1H), 7.92 – 7.83 (m, 3H), 7.62 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.24 (s, 1H), 7.23 (d, *J* = 2.0 Hz, 2H), 7.19 (t, *J* = 1.6 Hz, 1H), 2.84 – 2.75 (m, 1H), 2.63 – 2.54 (m, 1H), 1.28 (s, 18H), 1.16 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –37.2 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.0, 151.8, 136.5, 135.9, 133.0, 132.8, 129.8 (q, *J* = 307.2 Hz), 129.1, 128.4, 127.7, 127.1, 126.8, 125.9, 125.5, 119.2, 114.4, 68.3, 34.9, 31.3, 30.6, 9.3. **HRMS** (ESI) *m/z* calcd. for $C_{29}H_{35}F_3NOS^+$ $[M+H]^+$ 502.2386, found 502.2384. **HPLC** analysis: Chiralcel OD-H (hexane/*i*-PrOH = 90/10, flow rate 0.50 mL/min, λ = 254 nm), t_R (minor) = 7.81 min, t_R (major) = 10.21 min, 91% ee.

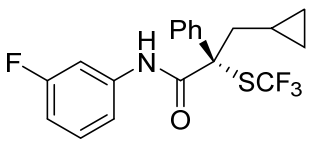
(*R*)-3-Cyclopropyl-*N*,2-diphenyl-2-((trifluoromethyl)thio)propenamide (22)



22

The residue was purified by column chromatography on silica gel with an eluent of ethyl acetate and petroleum ether (1:50~1:20, v/v) to afford product **22** (22.3 mg, 61% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 2H), 7.47 (s, 1H), 7.43 – 7.34 (m, 5H), 7.34 – 7.29 (m, 2H), 7.13 (tt, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 2.56 (dd, J_1 = 14.8 Hz, J_2 = 6.4 Hz, 1H), 2.36 (dd, J_1 = 14.8 Hz, J_2 = 6.8 Hz, 1H), 1.02 – 0.92 (m, 1H), 0.49 – 0.38 (m, 2H), 0.11 – 0.03 (m, 1H), 0.03 – –0.05 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –36.9 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.3, 138.3, 137.0, 129.7 (q, J = 307.3 Hz), 129.1, 128.82, 128.78, 127.6, 124.9, 120.0, 67.2, 43.3, 6.8, 4.8, 4.7. **HRMS** (ESI) *m/z* calcd. for $C_{19}H_{19}F_3NOS^+$ $[M+H]^+$ 366.1134, found 366.1131. **HPLC** analysis: Chiralcel OD-H (hexane/*i*-PrOH = 95/5, flow rate 0.50 mL/min, λ = 254 nm), t_R (minor) = 13.12 min, t_R (major) = 17.33 min, 87% ee.

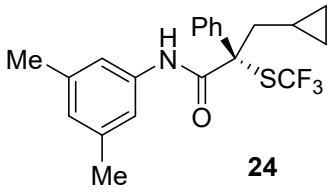
(*R*)-3-Cyclopropyl-*N*-(3-fluorophenyl)-2-phenyl-2-((trifluoromethyl)thio)propenamide (23)



23

The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **23** (33.0 mg, 86% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.51 – 7.48 (m, 2H), 7.43 – 7.35 (m, 4H), 7.27 – 7.22 (m, 1H), 7.02 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 6.83 (td, J_1 = 8.0 Hz, J_2 = 2.8 Hz, 1H), 2.54 (dd, J_1 = 14.8 Hz, J_2 = 6.4 Hz, 1H), 2.35 (dd, J_1 = 14.8 Hz, J_2 = 6.4 Hz, 1H), 0.99 – 0.86 (m, 1H), 0.48 – 0.37 (m, 2H), 0.09 – 0.03 (m, 1H), –0.02 – –0.08 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –36.9 (s, 3F), –111.07 – –111.14 (m, 1F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.4, 163.0 (d, J = 244.1 Hz), 138.5 (d, J = 10.8 Hz), 138.0, 130.1 (d, J = 9.2 Hz), 129.8 (q, J = 307.5 Hz), 128.9, 127.5, 115.2 (d, J = 3.1 Hz), 111.6 (d, J = 21.2 Hz), 107.5 (d, J = 26.1 Hz), 67.0, 43.3, 6.7, 4.7, 4.6. **HRMS** (ESI) *m/z* calcd. for $C_{19}H_{18}F_4NOS^+$ $[M+H]^+$ 384.1040, found 384.1048. **HPLC** analysis: Chiralcel OD-H (hexane/*i*-PrOH = 95/5, flow rate 0.50 mL/min, λ = 254 nm), t_R (minor) = 12.48 min, t_R (major) = 15.27 min, 84% ee.

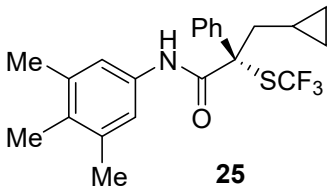
(*R*)-3-Cyclopropyl-*N*-(3,5-dimethylphenyl)-2-phenyl-2-((trifluoromethyl)thio)propenamide (24)



24

The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **24** (19.7 mg, 50% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.49 (m, 2H), 7.42 – 7.33 (m, 4H), 7.05 (s, 2H), 6.77 (s, 1H), 2.56 (dd, J_1 = 14.8 Hz, J_2 = 6.4 Hz, 1H), 2.34 (dd, J_1 = 14.8 Hz, J_2 = 6.8 Hz, 1H), 2.28 (s, 6H), 1.01 – 0.92 (m, 1H), 0.49 – 0.39 (m, 2H), 0.11 – 0.038 (m, 1H), 0.034 – –0.038 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –36.9 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.2, 138.9, 138.4, 136.9, 129.7 (q, J = 307.4 Hz), 128.8, 128.7, 127.6, 126.6, 117.6, 67.2, 43.3, 21.3, 6.8, 4.8, 4.7. **HRMS** (ESI) *m/z* calcd. for $C_{21}H_{23}F_3NOS^+$ $[M+H]^+$ 394.1447, found 394.1443. **HPLC** analysis: Chiralcel OD-H (hexane/*i*-PrOH = 99/1, flow rate 0.50 mL/min, λ = 254 nm), t_R (minor) = 6.34 min, t_R (major) = 6.90 min, 91% ee.

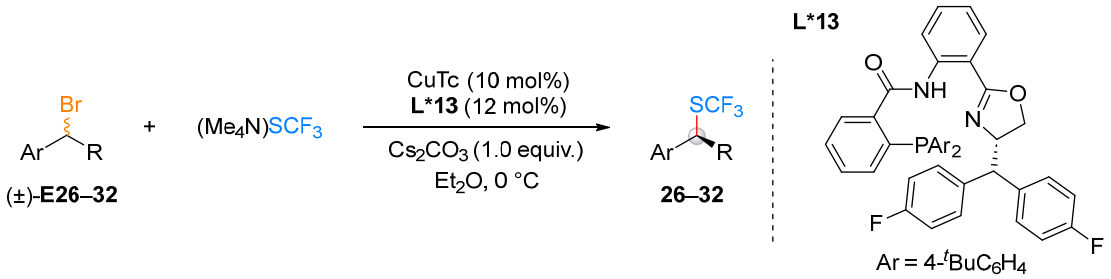
(*R*)-3-Cyclopropyl-2-phenyl-2-((trifluoromethyl)thio)-*N*-(3,4,5-trimethylphenyl)propenamide (25)



25

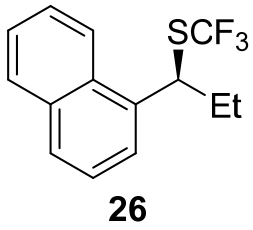
The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **25** (34.6 mg, 85% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) 7.53 – 7.50 (m, 2H), 7.42 – 7.33 (m, 4H), 7.08 (s, 2H), 2.56 (dd, J_1 = 14.8 Hz, J_2 = 6.4 Hz, 1H), 2.35 (dd, J_1 = 14.8 Hz, J_2 = 6.8 Hz, 1H), 2.25 (s, 6H), 2.12 (s, 3H), 1.03 – 0.93 (m, 1H), 0.49 – –0.40 (m, 2H), 0.12 – 0.050 (m, 1H), 0.04 – –0.02 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –36.9 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.1, 138.5, 137.2, 134.0, 131.9, 129.8 (q, J = 307.4 Hz), 128.75, 128.68, 127.6, 119.0, 67.3, 43.3, 20.6, 14.9, 6.8, 4.8, 4.7. **HRMS** (ESI) *m/z* calcd. for $C_{22}H_{25}F_3NOS^+$ $[M+H]^+$ 408.1603, found 408.1601. **HPLC** analysis: Chiralcel IC (hexane/*i*-PrOH = 95/5, flow rate 0.50 mL/min, λ = 254 nm), t_R (minor) = 10.44 min, t_R (major) = 12.50 min, 88% ee.

6.2 The procedure of enantioselective radical trifluoromethylthiolation of secondary benzyl bromide



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with the substrates (±)-**E26**–**32** (0.1 mmol), $(Me_4N)SCF_3$ (26.3 mg, 0.15 mmol, 1.5 equiv.), CuTc (1.91 mg, 0.01 mmol, 10 mol%), **L*13** (9.18 mg, 0.012 mmol, 12 mol%), Cs_2CO_3 (32.6 mg, 0.10 mmol, 1.0 equiv.), and Et_2O (2.0 mL) successively. Then the reaction mixture was stirred in 0 °C ethanol bath for 120 h. Upon completion, the precipitate was filtered off and washed by ethyl acetate. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the targeted molecule **26**–**32**.

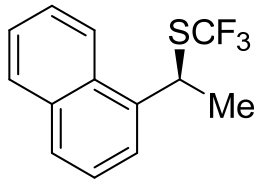
(*S*)-(1-(Naphthalen-1-yl)propyl)(trifluoromethyl)sulfane (26)



26

The residue was purified by column chromatography on silica ge l with an eluent of petroleum ether to afford product **26** (21.9 mg, 81% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) 8.08 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.58 – 7.44 (m, 4H), 5.06 (brs, 1H), 2.30 – 2.23 (m, 2H), 0. 93 (t, J = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –40.0 (brs, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.3, 134.0, 130.8, 130.7 (q, J = 305.5 Hz), 129.2, 128.6, 126.5, 125. 8, 125.34 (brs), 125.32, 122.5 (brs), 46.0 (brs), 30.1, 12.0. **HRMS** (FI) *m/z* calcd. for $C_{14}H_{13}F_3S$ [M] 270.0690, found 270.0685. **HPLC** analysis: Chiralcel OD-H (hexane, flo w rate 1.00 mL/min, λ = 214 nm), t_R (minor) = 19.18 min, t_R (major) = 24.30 min, 91% ee.

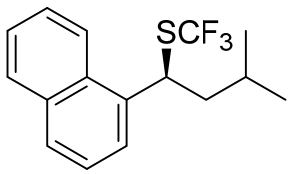
(*S*)-(1-(Naphthalen-1-yl)ethyl)(trifluoromethyl)sulfane (27)



27

The residue was purified by column chromatography on silica g el with an eluent of petroleum ether to afford product **27** (19.5 mg, 76% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) 8.14 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.55 – 7.51 (m, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 5.33 (q, *J* = 6.8 Hz, 1H), 1.96 (d, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MH z, $CDCl_3$) δ –40.3 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.9, 133.9, 130.7 (q, *J* = 3 05.8 Hz), 130.2, 129.2, 128.9, 126.7, 125.9, 125.3, 124.8, 122.5, 39.8, 23.1. **HRMS** (F I) *m/z* calcd. for $C_{13}H_{11}F_3S$ [M] 256.0534, found 256.0528. **HPLC** analysis: Chiralcel OD-H (hexane/*i*-PrOH = 99/1, flow rate 0.50 mL/min, λ = 225 nm), t_R (minor) = 8.85 min, t_R (major) = 9.44 min, 88% ee.

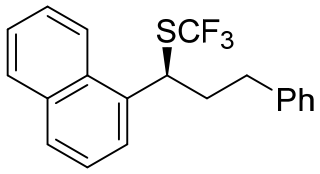
(*S*)-(3-Methyl-1-(naphthalen-1-yl)butyl)(trifluoromethyl)sulfane (28)



28

The residue was purified by column chromatography on silica gel with an eluent of petroleum ether to afford product **28** (2 0.6 mg, 69% yield) as a colorless oil. **^{1}H NMR** (400 MHz, C DCl_3) 8.11 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.68 – 7.55 (m, 2H), 7.53 – 7.43 (m, 2H), 5.32 (brs, 1H), 2.26 – 2.15 (m, 1H), 2.05 – 1.98 (m, 1H), 1.60 (brs, 1H), 0.95 (d, *J* = 3. 6 Hz, 3H), 0.90 (d, *J* = 6.4 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –39.9 (brs, 3F). **^{13} C NMR** (100 MHz, $CDCl_3$) δ 135.7 (brs), 134.0 (brs), 130.7 (q, *J* = 305.0 Hz), 130.6 (brs), 129.2, 128.5 (brs), 126.7 (brs), 125.8, 125.4, 125.2 (brs), 121.9 (brs), 45.9 (brs), 41.7 (brs), 25.9 (brs), 22.7, 21.9 (brs). **HRMS** (FI) *m/z* calcd. for $C_{16}H_{17}F_3S$ [M] 298.1 003, found 298.0998. **HPLC** analysis: Chiralcel OD-H (hexane, flow rate 1.00 mL/mi n, λ = 214 nm), t_R (major) = 10.51 min, t_R (major) = 12.01 min, 92% ee.

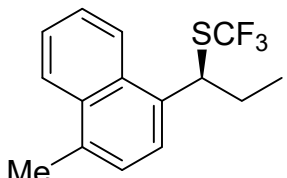
(*S*)-(1-(Naphthalen-1-yl)-3-phenylpropyl)(trifluoromethyl)sulfane (29)



29

The residue was purified by column chromatography on silica gel with an eluent of petroleum ether to afford product **29** (27.7mg, 80% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) 7.91 – 7.80 (m, 3H), 7.64 (brs, 1H), 7.52 – 7.46 (m, 3H), 7.29 – 7.18 (m, 3H), 7.09 (d, *J* = 6.8 Hz, 2H), 5.13 (brs, 1H), 2.65 (t, *J* = 6.8 Hz, 2H), 2.60 – 2.46 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –39.9 (brs, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.3, 135.3, 134.0, 130.6 (q, *J* = 305.5 Hz), 130.5, 129.2, 128.7, 128.5, 128.4, 126.5, 126.3, 125.9, 125.4, 125.2 (brs), 122.3 (brs), 43.0 (brs), 38.3, 33.3. **HRMS** (FI) *m/z* calcd. for $C_{20}H_{17}F_3S$ [M] 346.1003, found 346.0998. **HPLC** analysis: Chiralcel OD-H (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 214 nm), t_R (minor) = 6.29 min, t_R (major) = 7.54 min, 87% ee.

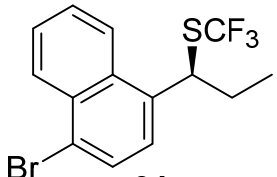
(*S*)-(1-(4-Methylnaphthalen-1-yl)propyl)(trifluoromethyl)sulfane (30)



30

The residue was purified by column chromatography on silica gel with an eluent of petroleum ether to afford product **30** (20. 5 mg, 72% yield) as a colorless oil. **^{1}H NMR** (400 MHz, CDC l_3) 8.12 – 8.09 (m, 1H), 8.07 – 8.05 (m, 1H), 7.60 – 7.53 (m, 2 H), 7.50 – 7.42 (m, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 5.06 (brs, 1 H), 2.69 (s, 3H), 2.27 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –40.0 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 134.8, 133.2, 133.1, 130.8, 130.7 (q, *J* = 305.5 Hz), 126.2, 126.1, 125.7, 125.2, 125.1 (brs), 123.0 (brs), 45.9 (brs), 30.1, 19. 7, 12.0. **HRMS** (FI) *m/z* calcd. for $C_{15}H_{15}F_3S$ [M] 284.0847, found 284.0841. **HPLC** a nalysis: Chiralcel OD-H (hexane, flow rate 1.00 mL/min, λ = 214 nm), t_R (minor) = 1 2.15 min, t_R (major) = 19.71 min, 87% ee.

(*S*)-(1-(4-Bromonaphthalen-1-yl)propyl)(trifluoromethyl)sulfane (31)

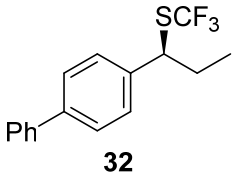


31

The residue was purified by column chromatography on silica gel with an eluent of petroleum ether to afford product **31** (23.4 mg, 67%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) 8.36 – 8.32 (m, 1H), 8.11 – 8.07 (m, 1H), 7.79 (d, *J* = 7.6 Hz, 1H),

7.65 – 7.61 (m, 2H), 7.44 (d, J = 7.6 Hz, 1H), 5.04 (brs, 1H), 2.27 – 2.22 (m, 2H), 0.94 (t, J = 7.6 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –40.0 (brs, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.7, 132.2, 132.0, 130.5 (q, J = 305.5 Hz), 129.5, 128.4, 127.3(4), 127.2(8), 125.8 (brs), 123.3, 122.9 (brs), 45.7 (brs), 30.0, 11.9. **HRMS** (FI) *m/z* calcd. for $C_{14}H_{12}BrF_3S$ [M] 347.9795, found 347.9790. **HPLC** analysis: Chiralcel OD-H (hexane, flow rate 1.00 mL/min, λ = 214 nm), t_R (minor) = 9.87 min, t_R (major) = 14.92 min, 88% ee.

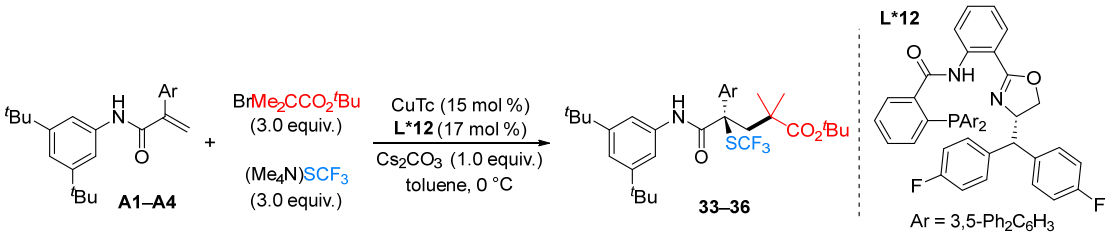
(*S*)-(1-([1,1'-biphenyl]-4-yl)propyl)(trifluoromethyl)sulfane (32)[15]



32

The residue was purified by column chromatography on silica gel with an eluent of petroleum ether to afford product **32** (23.1 mg, 78%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) 7.59 – 7.54 (m, 4H), 7.45 – 7.40 (m, 2H), 7.37 – 7.33 (m, 3H), 4.26 – 4.22 (m, 1H), 2.13 – 1.94 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –39.7 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.7, 140.5, 139.4, 130.6 (q, J = 305.2 Hz), 128.8, 127.9, 127.41, 127.37, 127.0, 51.0 (q, J = 6.0 Hz), 29.8, 11.9. **HPLC** analysis: Chiralcel OD-H (hexane, flow rate 1.00 mL/min, λ = 214 nm), t_R (minor) = 10.87 min, t_R (major) = 17.11 min, 73% ee.

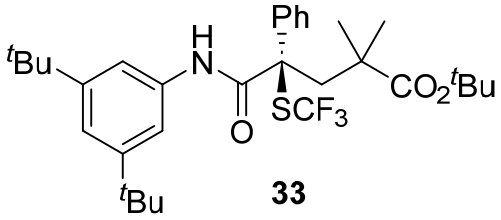
6.3 The procedure of enantioselective radical trifluoromethylthiolation of the alkenes



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with the substrates **A** (0.1 mmol), $(Me_4N)SCF_3$ (52.6 mg, 0.3 mmol, 3.0 equiv.), CuTc (2.86 mg, 0.015 mmol, 15 mol%), **L*12** (16.3 mg, 0.017 mmol, 17 mol%), Cs_2CO_3 (32.6 mg, 0.10 mmol, 1.0 equiv.), toluene (2.0 mL), and $BrMe_2CCO_2{}^tBu$ (66.9 mg, 0.30 mmol, 3.0 equiv.) successively. Then the reaction mixture was stirred in 0 °C ethanol bath for 120 h. Upon completion, the precipitate

was filtered off and washed by ethyl acetate. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product **33**–**36**.

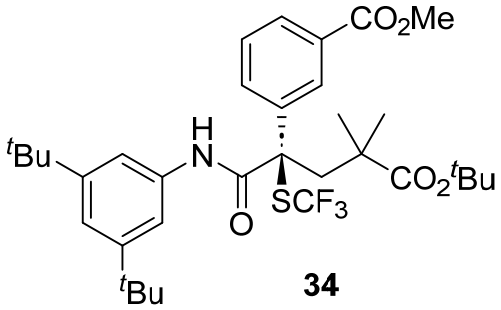
***Tert*-butyl (*R*)-5-((3,5-di-*tert*-butylphenyl)amino)-2,2-dimethyl-5-oxo-4-phenyl-4-((trifluoromethyl)thio)pentanoate (33)**



33

The residue was purified by column chromatography on silica gel with an eluent of ethyl acetate and petroleum ether (1:50~1:30, v/v) to afford product **33** (38.8 mg, 67% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.60 – 7.57 (m, 2H), 7.40 – 7.31 (m, 3H), 7.30 (d, *J* = 1.6 Hz, 2H), 7.21 (t, *J* = 2.0 Hz, 1H), 3.19 (d, *J* = 15.2 Hz, 1H), 2.86 (d, *J* = 15.2 Hz, 1H), 1.36 (s, 9H), 1.31 (s, 18H), 1.19 (s, 3H), 1.14 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –36.3 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.2, 168.2, 151.7, 138.5, 136.6, 129.2 (q, *J* = 308.4 Hz), 128.6, 128.0, 119.2, 114.6, 80.3, 65.3, 46.2, 43.0, 34.9, 31.3, 28.6, 27.8, 25.2. **HRMS** (ESI) *m/z* calcd. for $C_{32}H_{45}F_3NO_3S^+$ $[M+H]^+$ 580.3067, found 580.3063. **HPLC** analysis: Chiralcel IC (hexane/*i*-PrOH = 99/1, flow rate 0.40 mL/min, λ = 254 nm), t_R (minor) = 9.69 min, t_R (major) = 10.60 min, 88% ee.

Methyl (*R*)-3-(5-(*tert*-butoxy)-1-((3,5-di-*tert*-butylphenyl)amino)-4,4-dimethyl-1,5-dioxo-2-((trifluoromethyl)thio)pentan-2-yl)benzoate (34)

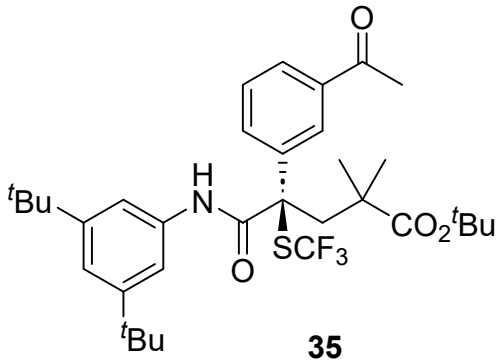


34

The residue was purified by column chromatography on silica gel with an eluent of ethyl acetate and petroleum ether (1:10~1:7.5, v/v) to afford product **34** (22.3 mg, 35% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (t, *J* = 2.0 Hz, 1H), 8.04 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 2.0 Hz, 2H), 7.23 (t, *J* = 2.0 Hz, 1H), 3.94 (s, 3H), 3.18 (d, *J* = 15.2 Hz, 1H), 2.91 (d, *J* = 15.2 Hz, 1H), 1.36 (s, 9H), 1.31 (s, 18H), 1.23 (s, 3H), 1.16 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ –36.1 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.1, 167.6, 166.5, 151.7, 139.5, 136.4, 132.9, 130.5, 129.8, 129.1 (q, J = 308.4 Hz), 128.81, 128.76, 119.4, 114.9, 80.6, 65.0, 52.3, 46.2, 43.1, 34.9, 31.3, 28.7, 27.7, 25.1. **HRMS** (ESI) *m/z* calcd. for $C_{34}H_{47}F_3NO_5S^+$ $[M+H]^+$ 638.3122, found 638.3118. **HPLC** analysis: Chiralcel OD-H (hexane/*i*-PrOH = 95/5, flow rate 0.50 mL/min, λ = 254 nm), t_R (minor) = 7.13 min, t_R (major) = 8.21 min, 86% ee.

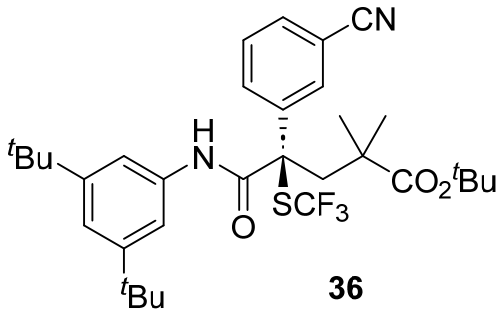
***Tert*-butyl (*R*)-4-(3-acetylphenyl)-5-((3,5-di-*tert*-butylphenyl)amino)-2,2-dimethyl-5-oxo-4-((trifluoromethyl)thio)pentanoate (35)**



35

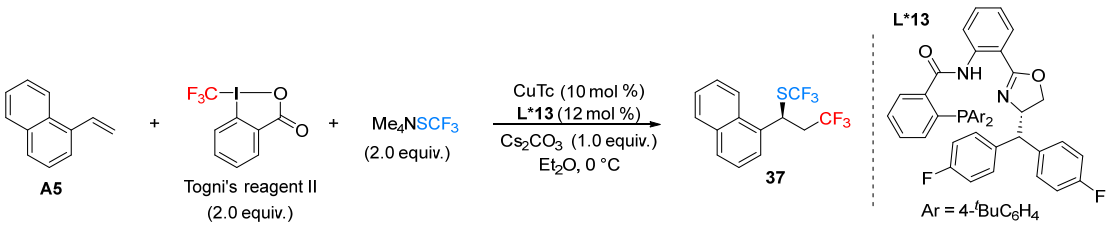
The residue was purified by column chromatography on silica gel with an eluent of ethyl acetate and petroleum ether (1:10~1:7.5, v/v) to afford product **35** (29.2 mg, 47% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (t, J = 2.0 Hz, 1H), 8.08 (s, 1H), 7.91 (dt, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.81 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.31 (d, J = 2.0 Hz, 2H), 7.23 (t, J = 1.6 Hz, 1H), 3.18 (d, J = 15.2 Hz, 1H), 2.92 (d, J = 14.8 Hz, 1H), 2.62 (s, 3H), 1.35 (s, 9H), 1.31 (s, 18H), 1.24 (s, 3H), 1.17 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –36.1 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.4, 176.1, 167.6, 151.8, 139.7, 137.2, 136.4, 133.0, 129.1 (q, J = 308.5 Hz), 128.9, 128.6, 127.5, 119.4, 114.8, 80.6, 65.0, 46.1, 43.1, 34.9, 31.3, 28.8, 27.7, 26.7, 25.1. **HRMS** (ESI) *m/z* calcd. for $C_{34}H_{47}F_3NO_4S^+$ $[M+H]^+$ 622.3172, found 622.3169. **HPLC** analysis: Chiralcel OD-H (hexane/*i*-PrOH = 95/5, flow rate 0.50 mL/min, λ = 254 nm), t_R (minor) = 7.19 min, t_R (major) = 8.29 min, 83% ee.

***Tert*-butyl (*R*)-4-(3-cyanophenyl)-5-((3,5-di-tert-butylphenyl)amino)-2,2-dimethyl-5-oxo-4-((trifluoromethyl)thio)pentanoate (36)**



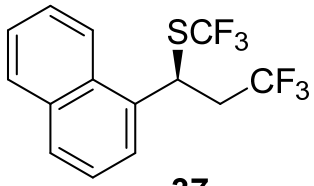
36

The residue was purified by column chromatography on silica gel with an eluent of ethyl acetate and petroleum ether (1:10~1:7.5, v/v) to afford product **36** (27.1 mg, 45% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.95 (t, *J* = 2.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.61 (dt, J_1 = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 1.6 Hz, 2H), 7.26 (t, *J* = 1.6 Hz, 1H), 3.08 (d, *J* = 15.2 Hz, 1H), 2.84 (d, *J* = 14.8 Hz, 1H), 1.34 (s, 9H), 1.33 (s, 18H), 1.24 (s, 3H), 1.15 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –36.0 (s, 3F). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.8, 166.6, 151.8, 140.8, 136.2, 133.0, 132.0, 131.7, 129.3, 128.8 (q, *J* = 308.8 Hz), 119.7, 118.3, 114.9, 112.7, 80.9, 64.3, 46.4, 43.1, 34.9, 31.3, 29.0, 27.7, 24.7. **HRMS** (ESI) *m/z* calcd. for $C_{33}H_{43}F_3N_2NaO_3S^+$ $[M+Na]^+$ 627.2839, found 627.2836. **HPLC** analysis: Chiralcel OD-H (hexane/*i*-PrOH = 95/5, flow rate 0.50 mL/min, λ = 254 nm), t_R (major) = 7.82 min, t_R (major) = 10.20 min, 87% ee.



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with 1-vinylnaphthalene (**A5**, 0.1 mmol), Togni's reagent II (63.2 mg, 0.2 mmol, 2.0 equiv.), $(Me_4N)SCF_3$ (35.0 mg, 0.2 mmol, 2.0 equiv.), CuTc (1.91 mg, 0.01 mmol, 10 mol%), **L*13** (9.18 mg, 0.012 mmol, 12 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 1.0 equiv.), and Et_2O (2.0 mL) successively. Then the reaction mixture was stirred in 0 °C ethanol bath for 120 h. Upon completion, the precipitate was filtered off and washed by ethyl acetate. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product **37**.

(*S*)-(3,3,3-Trifluoro-1-(naphthalen-1-yl)propyl)(trifluoromethyl)sulfane (37)

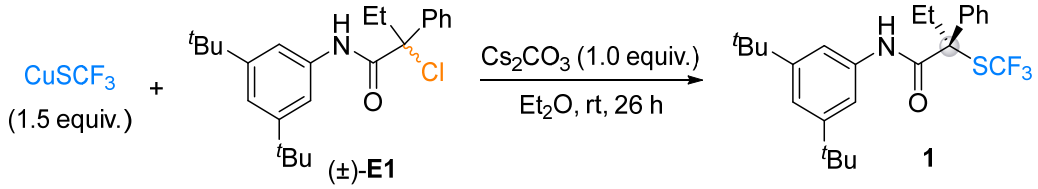


37

The residue was purified by column chromatography on silica gel with an eluent of petroleum ether to afford product **37** (15.0 mg, 46% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (brs, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.65–7.48 (m, 4H), 5.54 (brs, 1H), 3.21–3.05 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –40.7 (brs, 3F), –64.1 (brs, 3F). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 134.1 (brs), 132.8 (brs), 130.0 (q, *J* = 306.6 Hz), 129.8 (brs), 129.6 (brs), 129.4 (brs), 127.2 (brs), 126.3, 125.21, 125.15 (brs), 124.9 (q, *J* = 276.3 Hz), 121.6 (brs), 41.0 (q, *J* = 28.1 Hz), 36.9 (brs). **HRMS** (EI) *m/z* calcd. for $C_{14}H_{10}F_6S$ [M] 324.0407, found 324.0401. **HPLC** analysis: Chiralcel OD-H (hexane/*i*-PrOH = 99/1, flow rate 0.50 mL/min, λ = 225 nm), t_R (major) = 10.76 min, t_R (minor) = 12.67 min, 92% ee.

7. Mechanistic Investigations

7.1 The experiment with $CuSCF_3$

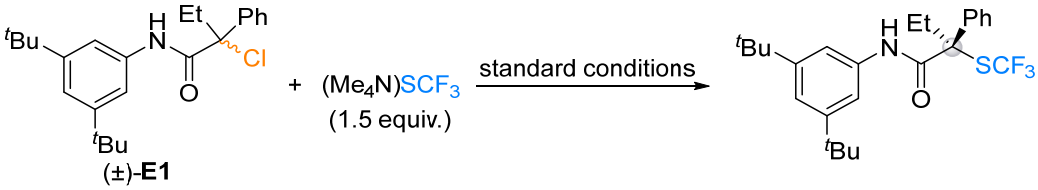


Entry	L*	Result	Ee
1	--	trace	--
2	**L*12** (12 mol%)	26%	65%
3[a]	**L*12** (1.7 equiv.)	92%	87%

[a] 3.0 equiv. Cs_2CO_3 was used.

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with the substrates (±)-**E1** (0.05 mmol), **L*12** (5.74 mg, 0.006 mmol, 0.12 equiv., or without this ligand), $CuSCF_3$ (12.3 mg, 0.75 mmol, 1.5 equiv.), Cs_2CO_3 (16.3 mg, 0.05 mmol, 1.0 equiv.), and Et_2O (1.0 mL) successively. Then the reaction mixture was stirred at room temperature for 26 h. Upon completion, the precipitate was filtered off and washed by ethyl acetate. The filtrate was evaporated and the residue was resolved with 1.0 mL $CDCl_3$, then 0.05 mmol CF_3OPh was added into the mixture. ^{19}F NMR test and HPLC analysis gave the results above.

7.2 Radical inhibition experiments of the tertiary electrophiles

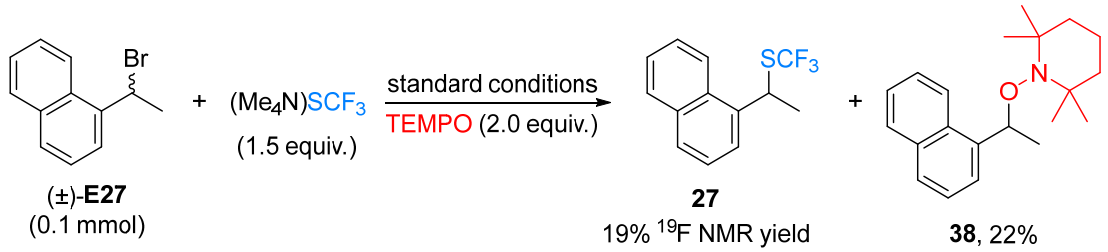


Entry	Additive (1.0 equiv)	Result	Ee
1	TEMPO	trace	--
2	BHT	trace	--

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with the substrates (±)-**E1** (0.05 mmol), $(Me_4N)SCF_3$ (13.13 mg, 0.075 mmol, 1.5 equiv.), CuTc (1.43 mg, 0.0075 mmol, 15 mol%), **L*12** (8.14 mg, 0.0085 mmol, 17 mol%), Cs_2CO_3 (16.3 mg, 0.05 mmol, 1.0 equiv.), Et_2O (1.0 mL), and TEMPO (7.82 mg, 0.05 mmol, 1.0 equiv.) or BHT (11.02 mg, 0.05 mmol, 1.0

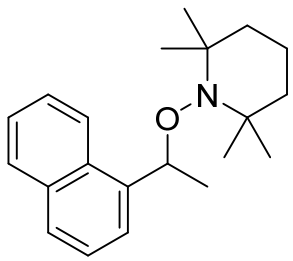
equiv.) successively. Then the reaction mixture was stirred in 0 ℃ ethanol bath for 120 h. Upon completion, the precipitate was filtered off and washed by ethyl acetate. The filtrate was evaporated and the residue was resolved with 1.0 mL $CDCl_3$, then 0.05 mmol CF_3OPh was added into the mixture. ^{19}F NMR test gave the results above, which revealed that both TEMPO and BHT could inhibit the reaction substantially.

7.3 Radical inhibition experiments of the secondary electrophiles



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with the substrates (±)-**E27** (0.1 mmol), $(Me_4N)SCF_3$ (26.3 mg, 0.15 mmol, 1.5 equiv.), CuTc (1.91 mg, 0.01 mmol, 10 mol%), **L*13** (9.18 mg, 0.012 mmol, 12 mol%), Cs_2CO_3 (32.6 mg, 0.10 mmol, 1.0 equiv.), Et_2O (2.0 mL), and TEMPO (31.2 mg, 2.0 equiv.) successively. Then the reaction mixture was stirred in 0 ℃ ethanol bath for 120 h. Upon completion, the precipitate was filtered off and washed by ethyl acetate. The filtrate was evaporated and the residue was resolved with 1.5 mL $CDCl_3$, then 0.1 mmol CF_3OPh was added into the mixture. ^{19}F NMR test indicated that the reaction gave the product **27** in 19% yield. Then the residue was purified by column chromatography on silica gel to afford the radical trapped product **38**.

2,2,6,6-Tetramethyl-1-(1-(naphthalen-1-yl)ethoxy)piperidine (38)

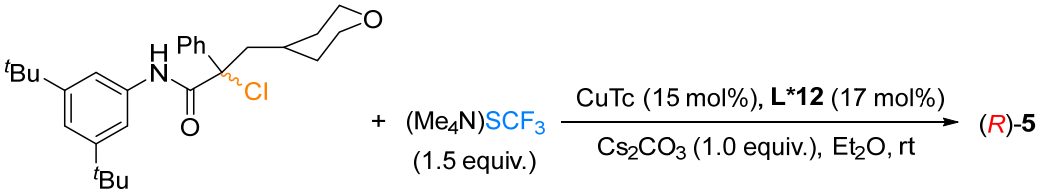


38

The residue was purified by column chromatography on silica gel with an eluent of petroleum ether to afford product **38** (7 mg, 22% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) 8.18 (d, J = 8.0 Hz, 1H), 7.86 – 7.83 (m, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 6.8 Hz, 1H),7.52 – 7.43 (m, 3H), 5.45 (q, J = 6.4 Hz, 1H), 1.65 (d, J = 6.8 Hz, 3H), 1.54 (s, 3H), 1.4

5 – 1.29 (m, 6H), 1.24 (s, 3H), 1.01 (s, 3H), 0.62 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.4, 133.8, 130.3, 128.7, 127.0, 125.5, 125.4, 125.2, 124.4, 123.8, 82.2, 59.8, 59.5, 40.3, 34.7, 33.6, 29.7, 23.8, 20.5, 20.2, 17.2. **HRMS** (ESI) *m/z* calcd. for $C_{21}H_{30}NO^+$ $[M+H]^+$ 312.2322, found 312.2322.

7.4 Control reactions with the enantiopure or racemic substrates



Entry	Sub.	Time	Recovered sub.	(*R*)-**5**
1	**E5** (>99% ee)	2.75 h	32% of **E5**	52%, 92% ee
2	**E5'** (>–99% ee)	2.75 h	55% of **E5'**	34%, 92% ee
3	(±)-**E5** (0% ee)	4 h	70%, –21% ee for **E5'**	24%, 92% ee
4	(±)-**E5** (0% ee)	6 h	33%, –61% ee for **E5'**	44%, 92% ee

(1) Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with the substrates **E5** or **E5′** (0.05 mmol, which was prepared with Semi-Prep.HPLC), $(Me_4N)SCF_3$ (13.13 mg, 0.075 mmol, 1.5 equiv.), CuTc (1.43 mg, 0.0075 mmol, 15 mol%), **L*12** (8.14 mg, 0.0085 mmol, 17 mol%), Cs_2CO_3 (16.3 mg, 0.05 mmol, 1.0 equiv.), and Et_2O (1.0 mL) successively. Then the reaction mixture was stirred at room temperature for 2.75 h. Upon completion, the precipitate was filtered off and washed by ethyl acetate. The filtrate was evaporated and the residue was resolved with 1.0 mL $CDCl_3$, then 0.05 mmol 1,3,5-$MeO_3C_6H_3$ was added into the mixture. ^{1}H NMR test and HPLC analysis gave the results of **entry 1, 2** in the above table.

(2) Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with the substrates (±)-**E5** (0.05 mmol), $(Me_4N)SCF_3$ (13.13 mg, 0.075 mmol, 1.5 equiv.), CuTc (1.43 mg, 0.0075 mmol, 15 mol%), **L*12** (8.14 mg, 0.0085 mmol, 17 mol%), Cs_2CO_3 (16.3 mg, 0.05 mmol, 1.0 equiv.), and Et_2O (1.0 mL) successively. Then the reaction mixture was stirred at room temperature for 4 h or 6 h respectively. Upon completion, the precipitate was filtered off and washed by ethyl acetate. The filtrate was evaporated and the residue was resolved with 1.0 mL

$CDCl_3$, then 0.05 mmol 1,3,5-$MeO_3C_6H_3$ was added into the mixture. ^1H NMR test and HPLC analysis gave the results of **entry 3, 4** in the above table.

8. Determination on Configuration of Product 27

8.1 Experimental Details on ECD (Electronic Circular Dichroism) Spectrum

Samples of **27** for ECD were dissolved in CH_2Cl_2, and spectra were acquired in a 1.0-mm pathlength cuvette, respectively. The UV and ECD spectra were recorded using a Chirascan Spectrophotometer with the following instrumental parameters: 210–290 nm with a 1 nm step and a 2 nm bandwidth with data averaging over 1.0 sec per point. Three spectral acquisitions were taken for each sample and were averaged and smoothed thereafter.

Wavelength (nm)	θ (mdeg)
290	-0.94649
289	-0.93623
288	-0.96825
287	-1.06092
286	-1.1228
285	-1.20936
284	-1.19546
283	-1.15225
282	-1.04039
281	-0.91237
280	-0.72784
279	-0.45829
278	-0.29542
277	-0.18861
276	-0.14267
275	-0.18329
274	-0.22054
273	-0.24809
272	-0.20525
271	-0.07778
270	-0.00015
269	0.113357
268	0.205386
267	0.255983
266	0.26612
265	0.206761
264	0.158093
263	0.053001
262	-0.04058

261	-0.08085
260	-0.14627
259	-0.19021
258	-0.28424
257	-0.40528
256	-0.54407
255	-0.77674
254	-0.97958
253	-1.19221
252	-1.48612
251	-1.74683
250	-2.07893
249	-2.54912
248	-3.14204
247	-3.85964
246	-4.56526
245	-5.19158
244	-5.73461
243	-6.09715
242	-6.28336
241	-6.32554
240	-6.26072
239	-5.86903
238	-5.31496
237	-3.70894
236	-2.13138
235	0.272447
234	2.79179
233	6.55886
232	9.74115
231	13.7558
230	16.5718
229	22.2327
228	22.1913
227	25.6629
226	25.4196
225	28.4053
224	37.996
223	56.016
222	65.0181
221	67.0062
220	70.7882
219	55.3
218	51.2891
217	65.966
216	60.4344
215	39.0506
214	23.0689

213	-7.36228
212	-19.9041
211	-39.6586
210	-65.1681

8.2 Computational Details on ECD Spectrum

All density functional theory (DFT) calculations were performed using Gaussian 16 program[6] with default parameters. (5d,7f) keyword in Gaussian 16 software is used.

Geometry optimizations were conducted with B3LYP functional,[7] employing the D3 version of Grimme's dispersion corrections[8] with Becke-Johnson damping[9]. 6-31G(d) basis set was used for all atoms. Single-point energies and solvent effects at DCM (dichloromethane) were evaluated with B3LYP functional and D3 version of Grimme's dispersion corrections with Becke-Johnson damping and 6-311+G(d,p) basis set was used for all atoms. The solvation energies were calculated with a self-consistent reaction field (SCRF) using the SMD implicit solvent model[10]. Frequency analysis was also performed at the same level of theory as geometry optimization to confirm whether optimized stationary points were either local minimum or not, as well as to evaluate zero-point vibrational energies and thermal corrections for enthalpies and free energies at 298.15 K.

Conformational search of (*S*)-**27** was executed using Conformer-Rotamer Ensemble Sampling Tool (abbreviated as CREST) (version 2.10.2)[11] in combination with the xTB package (version 6.1)[12] in implicit dichloromethane solvent phase. Atoms in the forming/cleaving bonds were constrained by applying a force constant of 1.0 Hartree/Bohr^2. An energy window of 6.0 kcal/mol and a RMSD threshold of 0.25 Å were used. MD Sampling length was set to 0.5 ps and Shake<1> model was also used. "--noreftopo" keyword was also used to avoid accidental optimization failure.

Once all the conformers were located, Boltzmann distribution analysis was performed to obtain contribution of each conformer on spectrum.

ECD of these corresponding conformers was computed using TD-DFT with nstate keyword set to 20. M06-2X functional[13] combined with 6-311++G(d,p) basis set for all atoms were used. Computational CD data was exported from GView program with UV-Vis peak at half-width and half height set to 0.25 eV.

8.3 Comparison of Experimental ECD and Computational ECD for (S)-configuration product 27

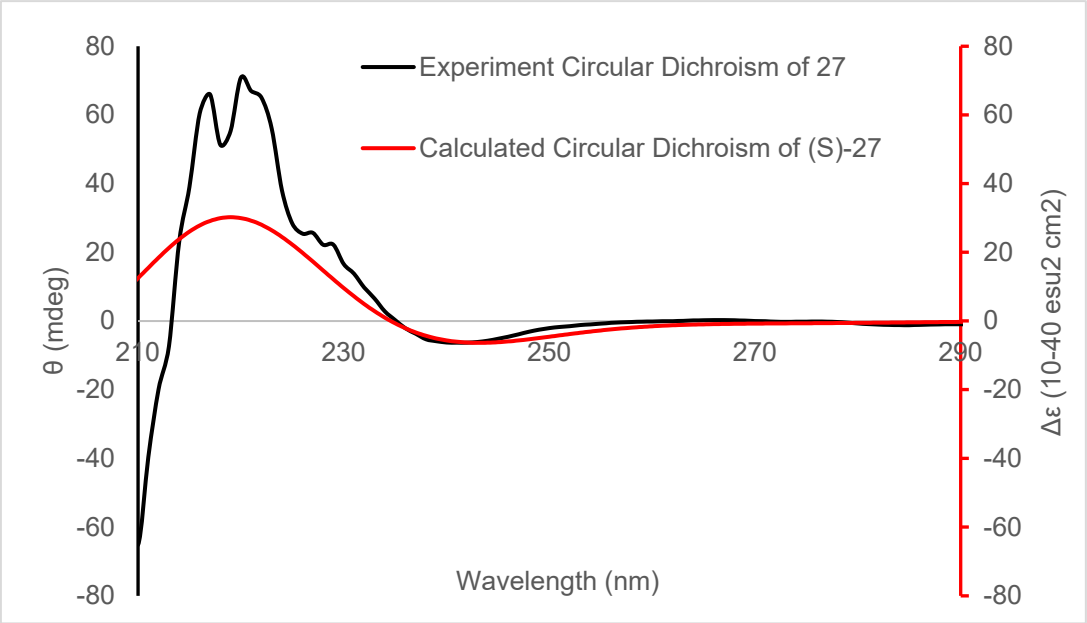


Figure S4. Comparison of Experimental ECD and Computational ECD for (*S*)-configuration product **27** with half-width and half height set to 0.25 eV.

The calculated spectrum for (*S*)-**27** was similar trend to the experimental one, and thus, the absolute configuration of compound **27** was assigned to *S* accordingly. The absolute configurations of other chiral products were assigned by analogue to that of **27**.

8.4 Tables of Free Energies and Boltzmann Distributions of Located Conformers of (S)-27

Table S5. Tables of Free Energies and Boltzmann Distribution Probabilities of Located Conformers of *(S)*-27. Free energies were compared to **(*S*)-27-C2**

Conformers	Free Energies (Hartree)	ΔΔG (kcal/mol)	Probability of conformers
(S)-**27-C1**	−1199.898082	1.1	0.063
(S)-**27-C2**	−1199.899896	0.0	0.434
(S)-**27-C3**	−1199.893297	4.1	0.000
(S)-**27-C4**	−1199.891069	5.5	0.000
(S)-**27-C5**	−1199.898652	0.8	0.116

(S)-**27-C6**	−1199.898334	1.0	0.083
(S)-**27-C7**	−1199.899558	0.2	0.303

Table S6. Energies in **Table S5**. Zero-point correction (ZPE), thermal correction to enthalpy (TCH), thermal correction to Gibbs free energy (TCG), energies (***E***), enthalpies (***H***), and Gibbs free energies (***G***) (in Hartree) of the structures calculated at B3LYP-D3(BJ)/6-31G(d)-LANL2DZ level of theory.

Structure	*ZPE*	*TCH*	*TCG*	*E*	*H*	*G*	Imaginary Frequency
(S)-**27-C1**	0.211322	0.226819	0.168967	−1200.067049	−1199.840230	−1199.898082	
(S)-**27-C2**	0.210954	0.226708	0.167380	−1200.067276	−1199.840568	−1199.899896	
(S)-**27-C3**	0.211463	0.226949	0.169200	−1200.062497	−1199.835548	−1199.893297	
(S)-**27-C4**	0.211247	0.226888	0.168651	−1200.059720	−1199.832832	−1199.891069	
(S)-**27-C5**	0.211126	0.226830	0.168143	−1200.066795	−1199.839965	−1199.898652	
(S)-**27-C6**	0.211200	0.226902	0.167818	−1200.066152	−1199.839250	−1199.898334	
(S)-**27-C7**	0.211479	0.227043	0.168623	−1200.068181	−1199.841138	−1199.899558	

8.5 Cartesian Coordinates of Computed Species

(*S*)-27-C1

Charge = 0, Multiplicity = 1

C	-3.79728200	-1.35512700	-0.37804000
C	-3.59642800	-0.02665000	-0.67223100
C	-2.39892900	0.63452800	-0.29308800
C	-1.38424900	-0.09273000	0.41312500
C	-1.62485900	-1.46511900	0.69290500
C	-2.79740700	-2.07883700	0.31024700
H	-2.96933700	2.54040900	-1.14282100
H	-4.71724700	-1.85024700	-0.67485000
H	-4.35456100	0.54206400	-1.20466300
C	-2.19251800	2.00408700	-0.60410700
C	-0.18370100	0.59280200	0.80002200
H	-0.86869000	-2.05355900	1.19802500
H	-2.95223500	-3.13020400	0.53495200

C	-0.03226100	1.92520900	0.47124400
C	-1.03238200	2.63541700	-0.23055100
H	0.87415100	2.44961300	0.74874800
H	-0.87291500	3.68258000	-0.46990300
C	0.90677700	-0.13391400	1.55715600
H	0.43884900	-0.83930200	2.25123700
C	1.86301400	0.74920300	2.36240700
H	1.29294400	1.40089300	3.03416000
H	2.52766200	0.12307700	2.96334300
H	2.48569300	1.36951400	1.71576700
S	1.87327400	-1.32893800	0.47823700
C	2.22931500	-0.31033600	-0.97975500
F	1.15788100	-0.08652400	-1.75683800
F	3.13792800	-0.97278500	-1.71770500
F	2.74738700	0.89897100	-0.67009800

(*S*)-27-C2
Charge = 0, Multiplicity = 1

C	-3.37803800	-1.88873200	0.38049400
C	-3.53868000	-0.72106000	-0.32601000
C	-2.50959500	0.25703300	-0.37157000
C	-1.28426000	0.02986900	0.34531100
C	-1.15127900	-1.19936400	1.05060100
C	-2.16555400	-2.12955400	1.06735600
H	-3.60602000	1.59979900	-1.66213000
H	-4.17155200	-2.62987100	0.40531300
H	-4.45924200	-0.52653100	-0.87047700
C	-2.67444000	1.44731900	-1.12342800
C	-0.26755900	1.03968300	0.30033500
H	-0.22559600	-1.43718600	1.55911900

H	-2.02976100	-3.06171100	1.60816400
C	-0.47251600	2.17360100	-0.46296700
C	-1.66946500	2.38372900	-1.17797600
H	0.31233500	2.92144200	-0.52565200
H	-1.79086300	3.28924300	-1.76506000
C	1.01684200	0.90815200	1.09372000
H	0.98935100	0.02846700	1.73337600
C	1.30135300	2.12390500	1.98640200
H	2.18963400	1.95435800	2.60221700
H	1.45710600	3.03467600	1.40064500
H	0.44256900	2.29228700	2.64360400
S	2.52571600	0.68558400	0.02093300
C	2.21070200	-0.98967000	-0.59259600
F	3.28230700	-1.38131800	-1.30136900
F	1.13089200	-1.07931300	-1.38634700
F	2.02852700	-1.87756500	0.41193200

(*S*)-27-C3

Charge = 0, Multiplicity = 1

C	-4.63971700	-0.83430100	0.01111800
C	-4.24001500	0.47933400	0.08764100
C	-2.86593100	0.83363800	0.04147000
C	-1.87455900	-0.19649200	-0.09287800
C	-2.32851300	-1.54359700	-0.16672500
C	-3.66970300	-1.85411800	-0.11762900
H	-3.22185800	2.95884900	0.22853700
H	-5.69432800	-1.09088700	0.04902900
H	-4.97447400	1.27454000	0.18752600
C	-2.45994400	2.19036300	0.12759200
C	-0.48870600	0.17828600	-0.14312900

H	-1.61336700	-2.35307100	-0.26055100
H	-3.98412700	-2.89211100	-0.17796200
C	-0.14775600	1.51134400	-0.05289100
C	-1.12801800	2.52032600	0.08366600
H	0.89503500	1.79827200	-0.09218000
H	-0.81539500	3.55830900	0.14916800
C	0.56170700	-0.91918200	-0.23646800
H	0.18400700	-1.70640900	-0.89504400
C	0.85608800	-1.54852800	1.13369100
H	-0.08331400	-1.91683100	1.55749100
H	1.55884600	-2.38103300	1.04997400
H	1.26432400	-0.80703700	1.82328700
S	2.08712400	-0.44440900	-1.18992100
C	3.28255700	0.05584600	0.07898300
F	4.33174300	0.59829600	-0.56130800
F	3.74520200	-0.96848100	0.82153700
F	2.80591200	0.97356700	0.95008200

(*S*)-27-C4

Charge = 0, Multiplicity = 1

C	2.96062200	-2.27467100	0.10450100
C	3.38984100	-1.05832400	-0.36880000
C	2.56175900	0.09348100	-0.29591400
C	1.25259400	-0.00559900	0.29347900
C	0.84132700	-1.28822900	0.75062300
C	1.66688600	-2.38593400	0.66179200
H	4.00995200	1.38133400	-1.25233500
H	3.60335900	-3.14793600	0.04235000
H	4.37583600	-0.95511500	-0.81469500
C	3.01929600	1.33376200	-0.80786400

C	0.44877200	1.18098600	0.37730500
H	-0.15165600	-1.42399900	1.14677800
H	1.31385400	-3.35005600	1.01636500
C	0.94962400	2.36303500	-0.14221200
C	2.22223600	2.44978000	-0.74230300
H	0.34034800	3.26165700	-0.08483800
H	2.56680900	3.40172200	-1.13503900
C	-0.91744400	1.28315500	1.04133200
H	-1.05523500	2.35251000	1.23282300
C	-1.13856200	0.58303200	2.39062700
H	-0.23677700	0.67848900	3.00498100
H	-1.97009400	1.06534500	2.91250700
H	-1.38442700	-0.47291300	2.29936100
S	-2.37307800	1.08529400	-0.12050800
C	-2.31909300	-0.64203700	-0.65907600
F	-1.22595000	-0.95424900	-1.37325000
F	-3.39485300	-0.84315100	-1.44001700
F	-2.38695900	-1.53041800	0.36203600

(*S*)-27-C5

Charge = 0, Multiplicity = 1

C	3.55842400	-1.38395400	-0.96641400
C	3.52579000	-0.01682700	-0.82294300
C	2.41261300	0.63197400	-0.22637400
C	1.30713400	-0.15227600	0.24806900
C	1.37023100	-1.56098600	0.06372800
C	2.46278900	-2.15920900	-0.52411400
H	3.22773500	2.62017400	-0.46974400
H	4.41511600	-1.86780800	-1.42642400
H	4.35429300	0.59504900	-1.17064900

C	2.38118500	2.04584100	-0.10254500
C	0.20116900	0.52478200	0.86312500
H	0.53144200	-2.17628000	0.35820500
H	2.47760700	-3.23726400	-0.65637400
C	0.21348400	1.90485700	0.93967200
C	1.29817300	2.67279500	0.46154000
H	-0.63640100	2.41584600	1.38361400
H	1.26751600	3.75493500	0.54656800
C	-0.98404900	-0.17829800	1.48964100
H	-1.66433200	0.59318600	1.85590000
C	-0.63538400	-1.08841200	2.67612500
H	-1.54396100	-1.49381000	3.13289700
H	0.01399200	-1.91890300	2.39304900
H	-0.10618500	-0.49269200	3.42663400
S	-2.02445500	-1.18220100	0.30877000
C	-2.40422100	0.10815600	-0.90793300
F	-3.40106200	-0.33844500	-1.69124200
F	-1.36674300	0.41874600	-1.70240700
F	-2.80881400	1.25660000	-0.32451200

(*S*)-27-C6
Charge = 0, Multiplicity = 1

C	3.83140100	-1.91002600	-0.26663300
C	4.04247200	-0.55846900	-0.40866200
C	2.98577200	0.37238300	-0.22852400
C	1.67579900	-0.10473700	0.11647300
C	1.49645400	-1.51016500	0.24864800
C	2.54208700	-2.38698200	0.06101300
H	4.20579100	2.10683000	-0.65243700
H	4.64851200	-2.61106600	-0.40936800

H	5.02730200	-0.17778400	-0.66715400
C	3.20755500	1.76467900	-0.39229700
C	0.62042600	0.85048900	0.29151500
H	0.51870400	-1.90891500	0.48991600
H	2.37249200	-3.45470500	0.16489200
C	0.88788100	2.19342700	0.10744800
C	2.17802100	2.65893100	-0.23124000
H	0.08400700	2.91428800	0.23149100
H	2.34568400	3.72377400	-0.36238600
C	-0.78197500	0.46731000	0.71759500
H	-1.39011800	1.37281800	0.66758700
C	-0.87365300	-0.10378100	2.13813900
H	-0.46826300	0.63327900	2.84108700
H	-1.91357100	-0.30508300	2.40322400
H	-0.29986000	-1.02550700	2.25055500
S	-1.55642500	-0.65340500	-0.56802800
C	-3.28180800	-0.14352600	-0.36180800
F	-4.01913800	-0.77870800	-1.28538500
F	-3.45766300	1.18537500	-0.52495200
F	-3.79102800	-0.44562900	0.85267600

(*S*)-27-C7

Charge = 0, Multiplicity = 1

C	-3.22393900	-2.43433000	0.12531400
C	-3.75101700	-1.19287900	-0.14432300
C	-2.93359200	-0.03242900	-0.12899500
C	-1.53897200	-0.15617600	0.18212200
C	-1.02657700	-1.45649100	0.44334200
C	-1.84690900	-2.56306100	0.41675600
H	-4.53479800	1.32314900	-0.65686600

H	-3.85892100	-3.31533200	0.10929400
H	-4.80665500	-1.07916500	-0.37754300
C	-3.47671500	1.24674300	-0.42017800
C	-0.72955100	1.03005800	0.21356700
H	0.02904500	-1.59422700	0.64107900
H	-1.42894400	-3.54563200	0.61589800
C	-1.30556400	2.24890500	-0.08538300
C	-2.67834700	2.36330200	-0.40497800
H	-0.70211200	3.14944800	-0.06980200
H	-3.09315000	3.34094700	-0.63175900
C	0.74078600	0.93988500	0.56862000
H	0.87950900	0.14326900	1.30237500
C	1.37169000	2.22113800	1.11350800
H	0.80694100	2.57314600	1.98442700
H	2.40176200	2.02738600	1.41849000
H	1.39148100	3.01690400	0.36426800
S	1.63718600	0.34943200	-0.96611400
C	3.00065900	-0.54620400	-0.18267300
F	3.72306300	-1.14517300	-1.14063300
F	2.56825400	-1.50296600	0.67456900
F	3.83192200	0.24352200	0.53026100

9. Reference

[1] D. E. Patterson, S. Xie, L. A. Jones, M. H. Osterhout, C. G. Henry, T. D. Roper, *Org. Process Res. Dev.* **2007**, *11*, 624−627.

[2] F.-L. Wang, C.-J. Yang, J.-R. Liu, N.-Y. Yang, X.-Y. Dong, R.-Q. Jiang, X.-Y. Chang, Z.-L. Li, G.-X. Xu, D.-L. Yuan, Y.-S. Zhang, Q.-S. Gu, X. Hong, X.-Y. Liu, *Nat. Chem.* **2022**, *14*, 949−957.

[3] X.-Y. Dong, Y.-F. Zhang, C.-L. Ma, Q.-S. Gu, F.-L. Wang, Z.-L. Li, S.-P. Jiang, X.-Y. Liu, *Nat. Chem.* **2019**, *11*, 1158−1166.

[4] Y. Tian, X.-T. Li, J.-R. Liu, J. Cheng, A. Gao, N.-Y. Yang, Z. Li, K.-X. Guo, W. Zhang, H.-T. Wen, Z.-L. Li, Q.-S. Gu, X. Hong, X.-Y. Liu, *Nat. Chem.* **2023**, DOI: 10.1038/s41557-023-01385-w.

[5] L. Wu, Z. Zhang, D. Wu, F. Wang, P. Chen, Z. Lin, G. Liu, *Angew. Chem. Int. Ed.* **2021**, *60*, 6997−7001.

[6] Gaussian 16, Revision A.03: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, K. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[7] (a) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37,* 785–789. (b) A. D. Becke, *J. Chem. Phys.* **1993**, *98,* 5648–5652.

[8] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132,* 154104.

[9] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comp. Chem.* **2011**, *32,* 1456–1465.

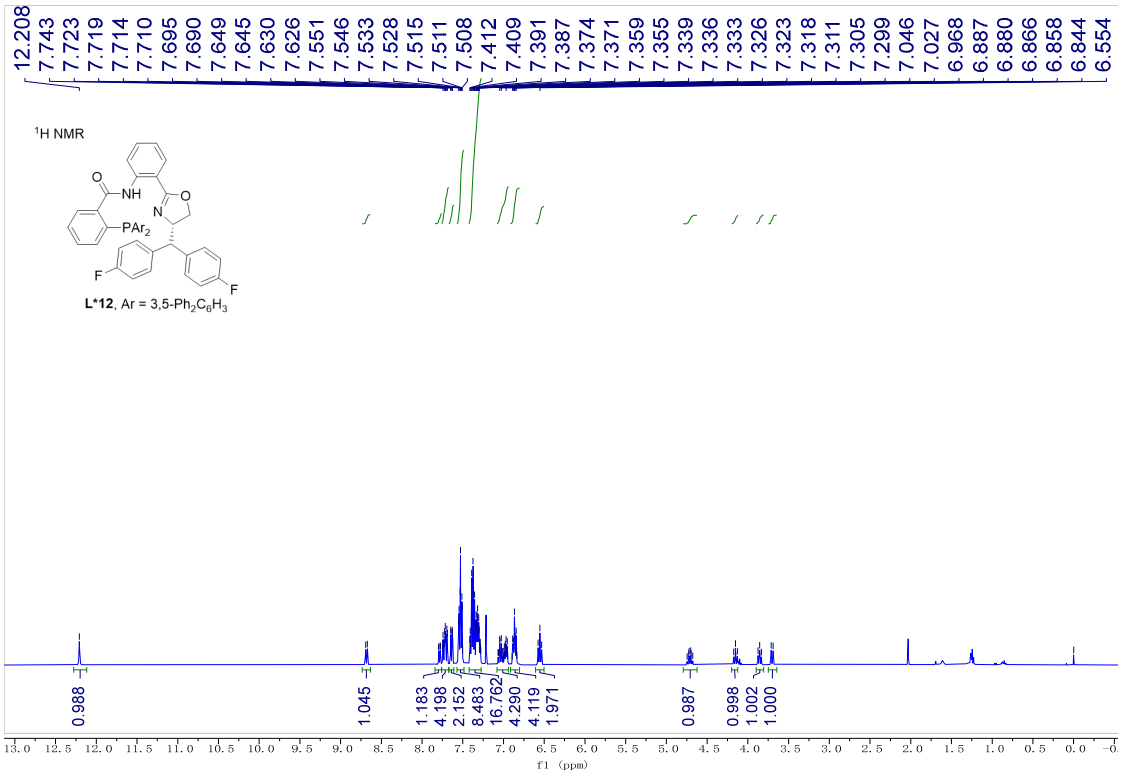
[10] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113,* 6378–6396.

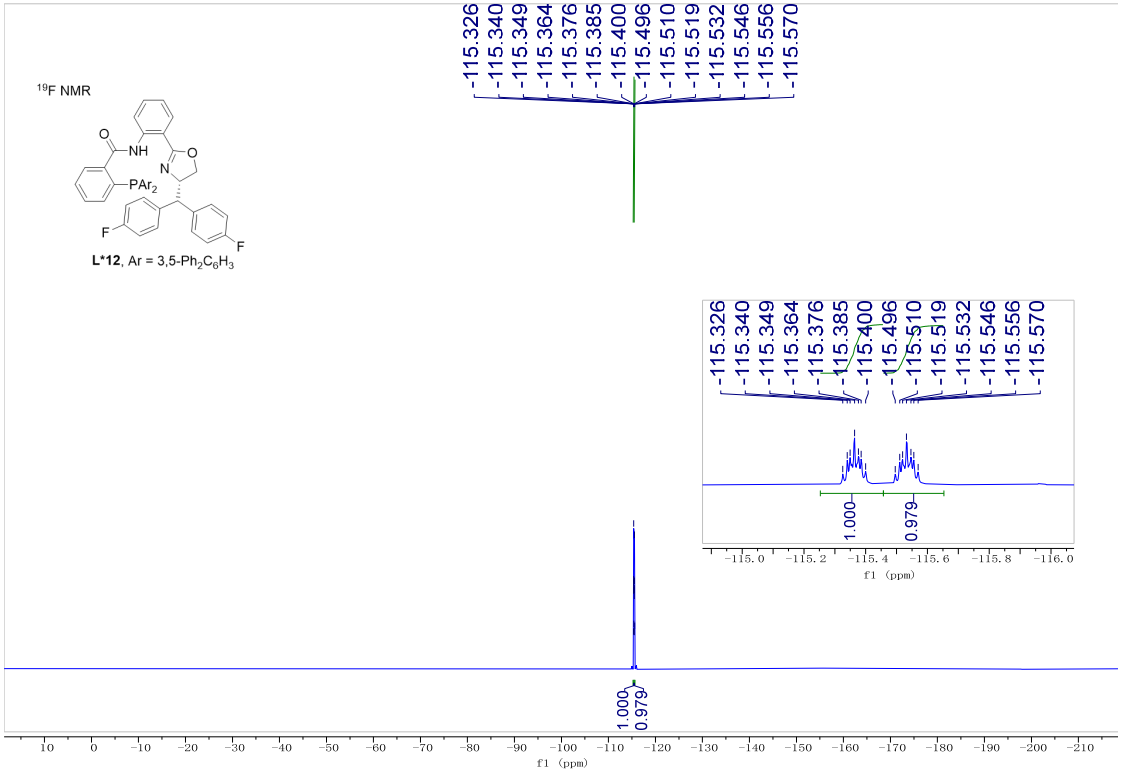
[11] P. Pracht, F. Bohle, S. Grimme, *Phys. Chem. Chem. Phys.* **2020**, *22,* 7169–7192.

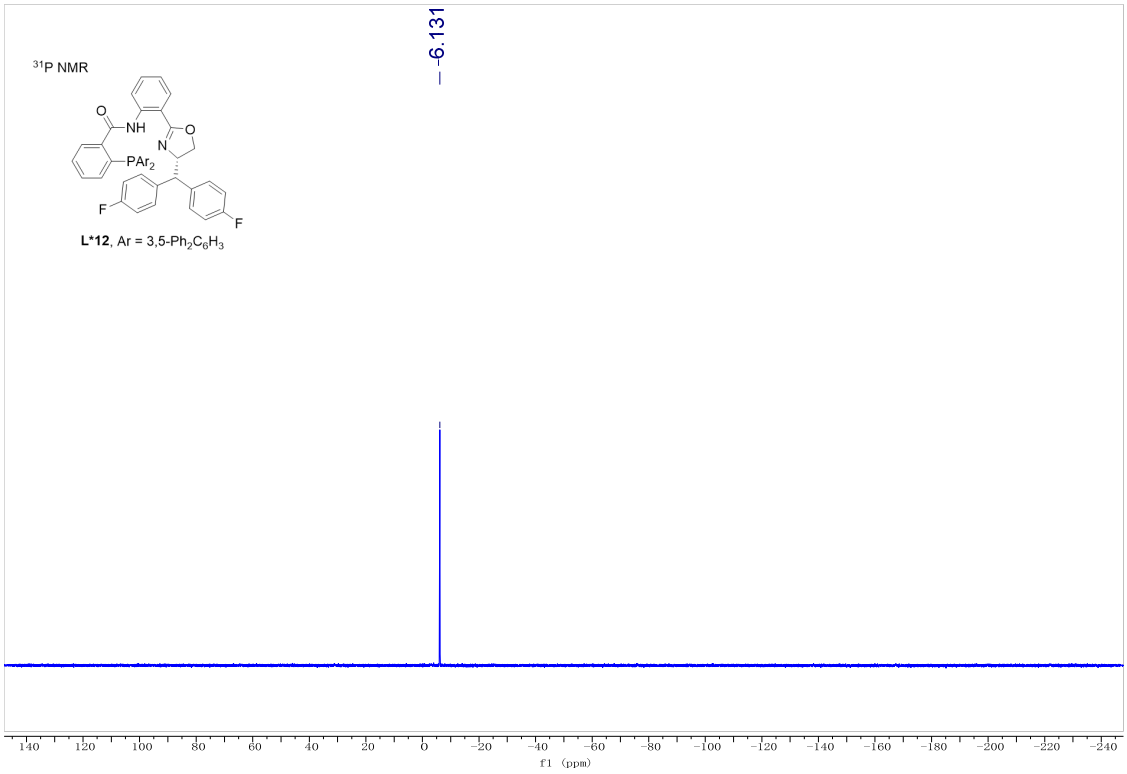
[12] S. Grimme, *J. Chem. Theory Comput.* **2019**, *15,* 2847–2862.

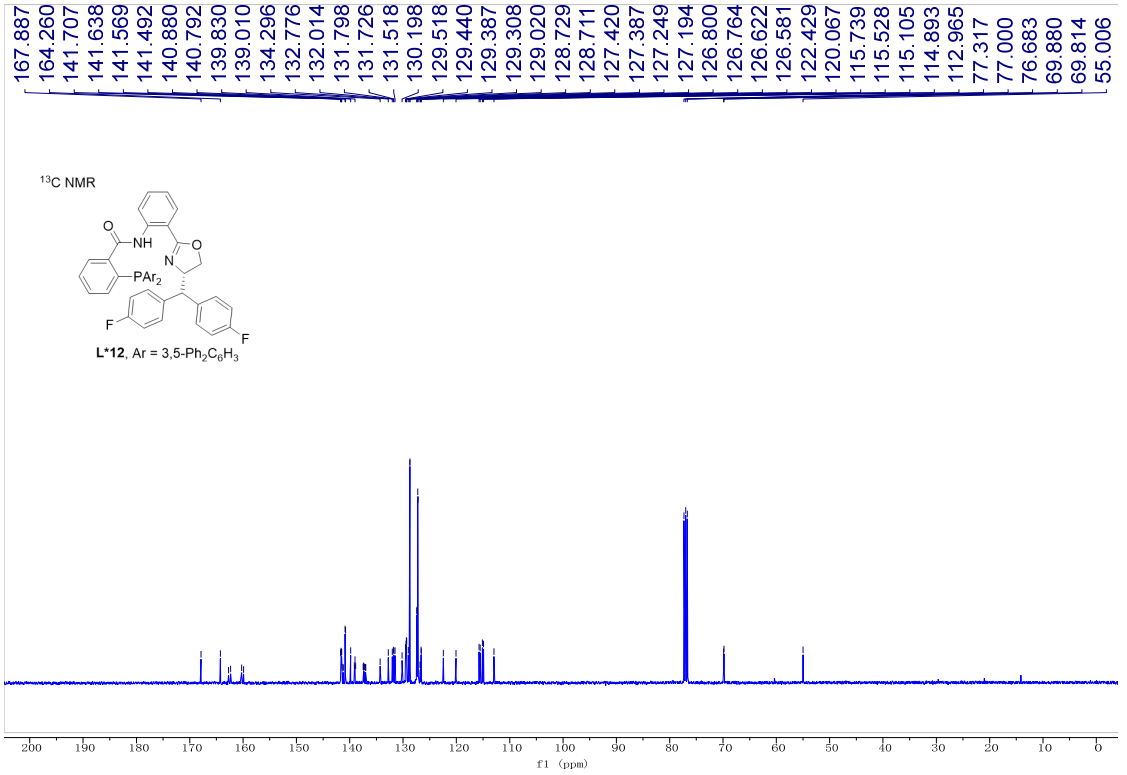
[13] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120,* 215–241.

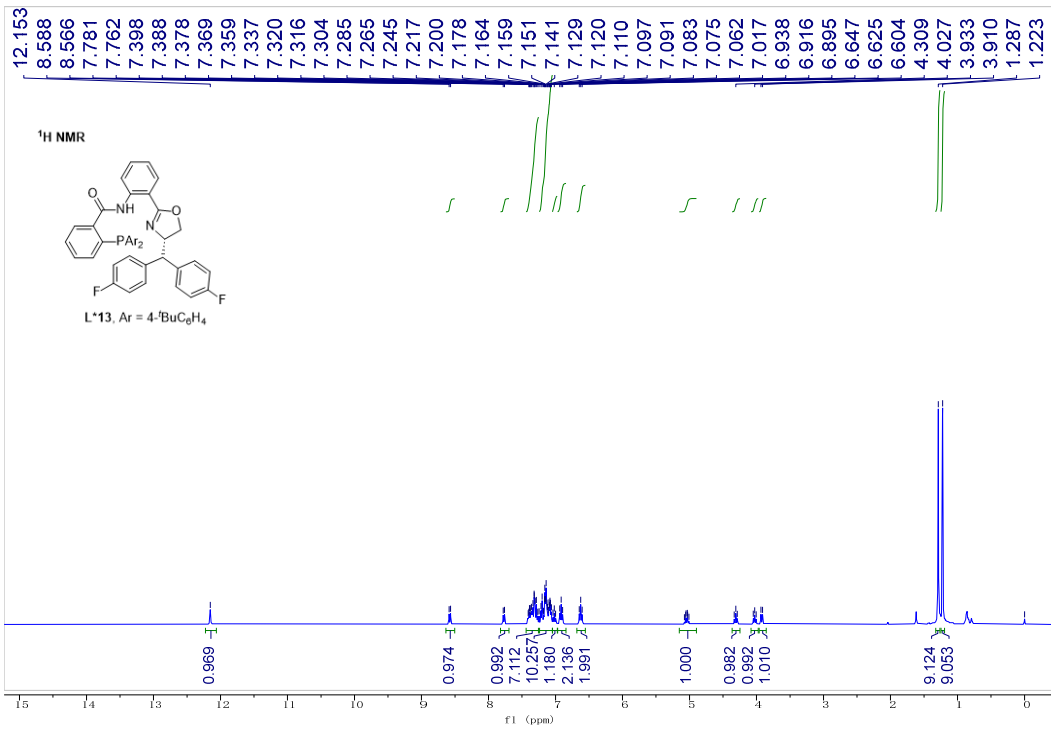
10. NMR spectra of the optimized ligands and the products

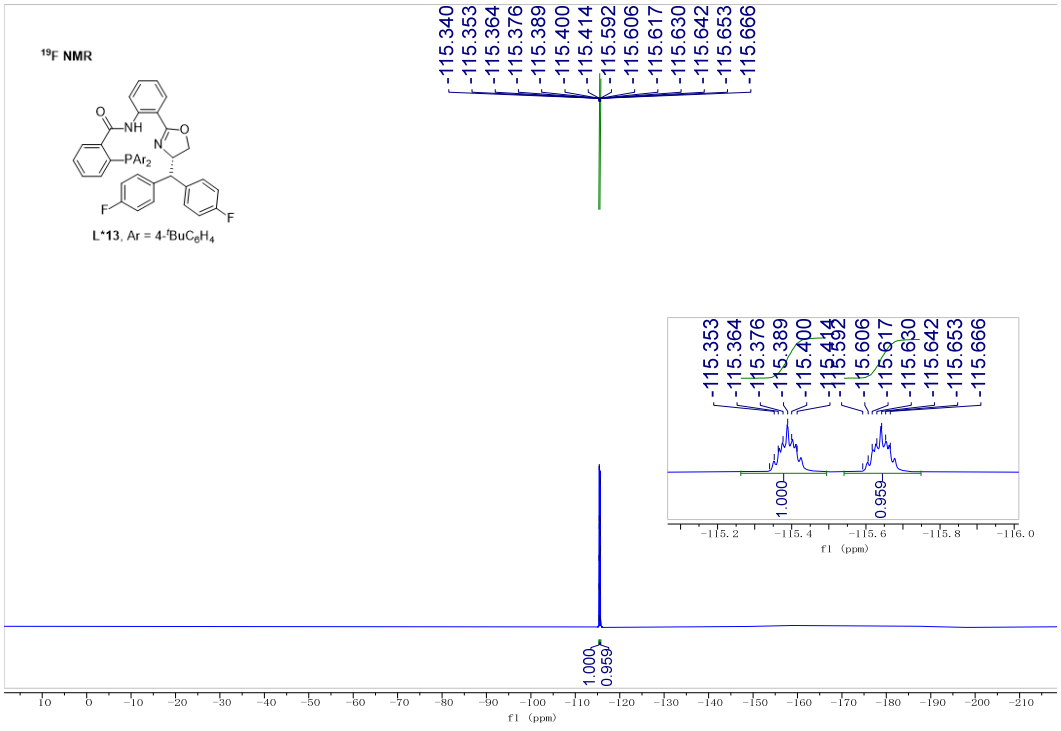


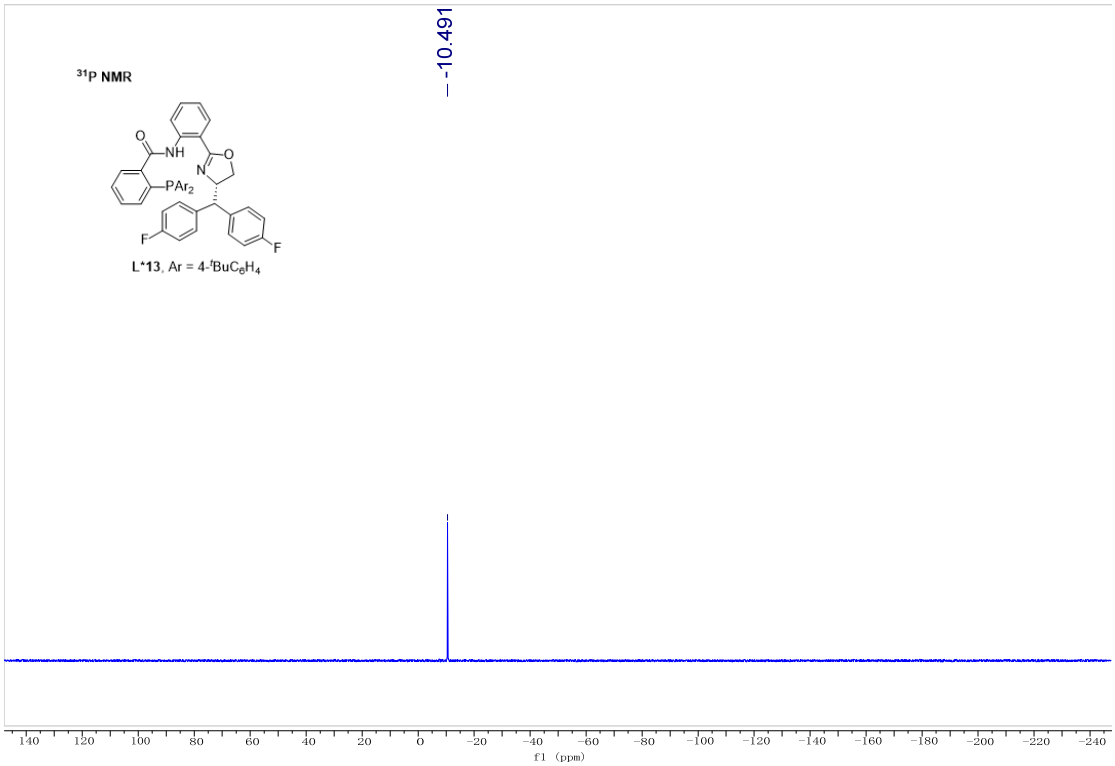


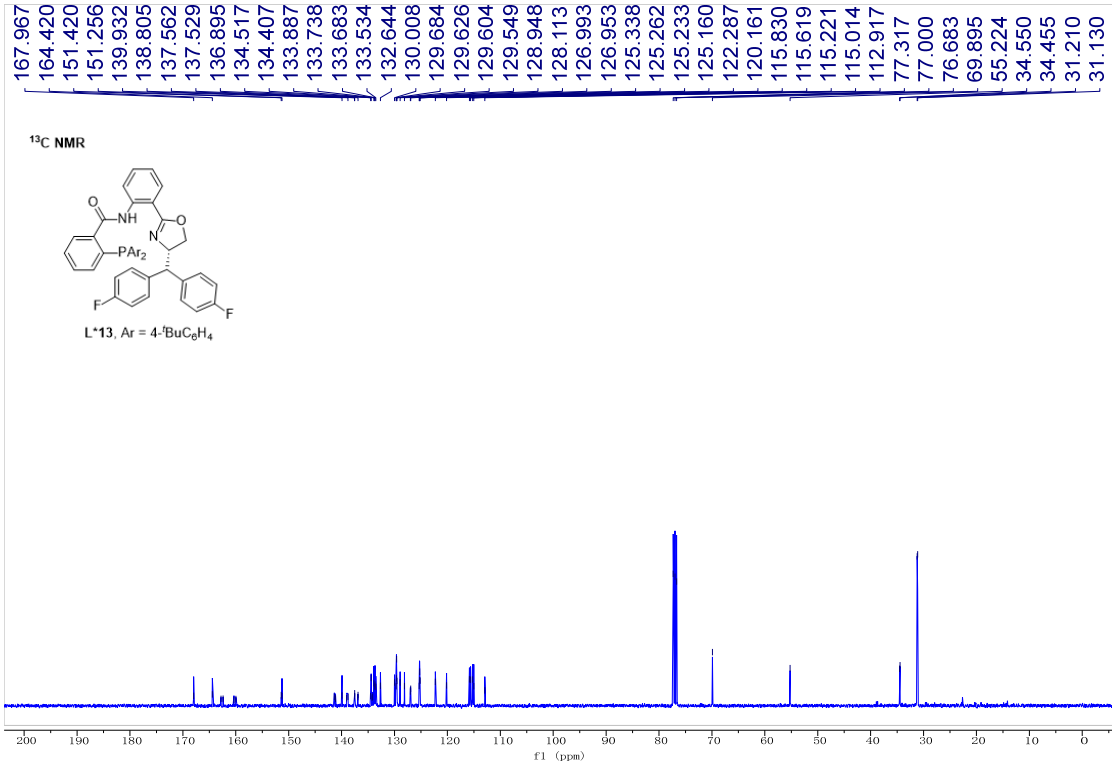

31P NMR
−6.131
L*12, Ar = 3,5-Ph2C6H3
f1 (ppm)

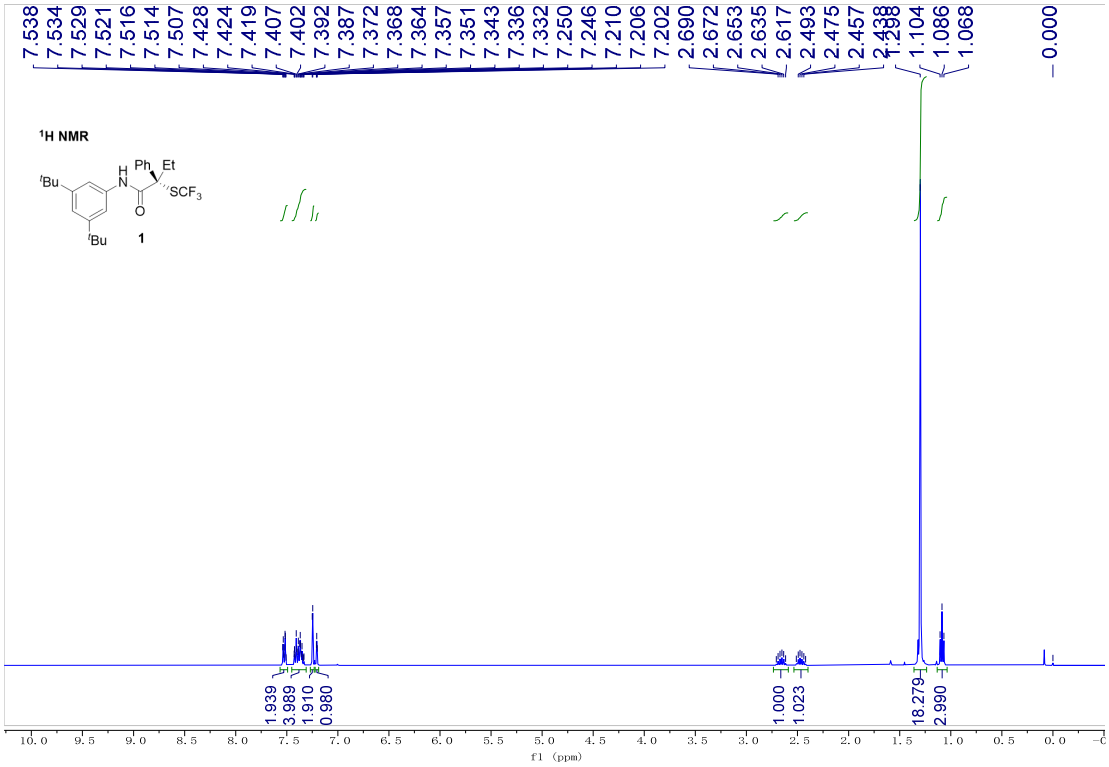

167.887
164.260
141.707
141.638
141.569
141.492
140.880
140.792
139.830
139.010
134.296
132.776
132.014
131.798
131.726
131.518
130.198
129.518
129.440
129.387
129.308
129.020
128.729
128.711
127.420
127.387
127.249
127.194
126.800
126.764
126.622
126.581
122.429
120.067
115.739
115.528
115.105
114.893
112.965
77.317
77.000
76.683
69.880
69.814
55.006
13C NMR
L*12, Ar = 3,5-Ph2C6H3
f1 (ppm)

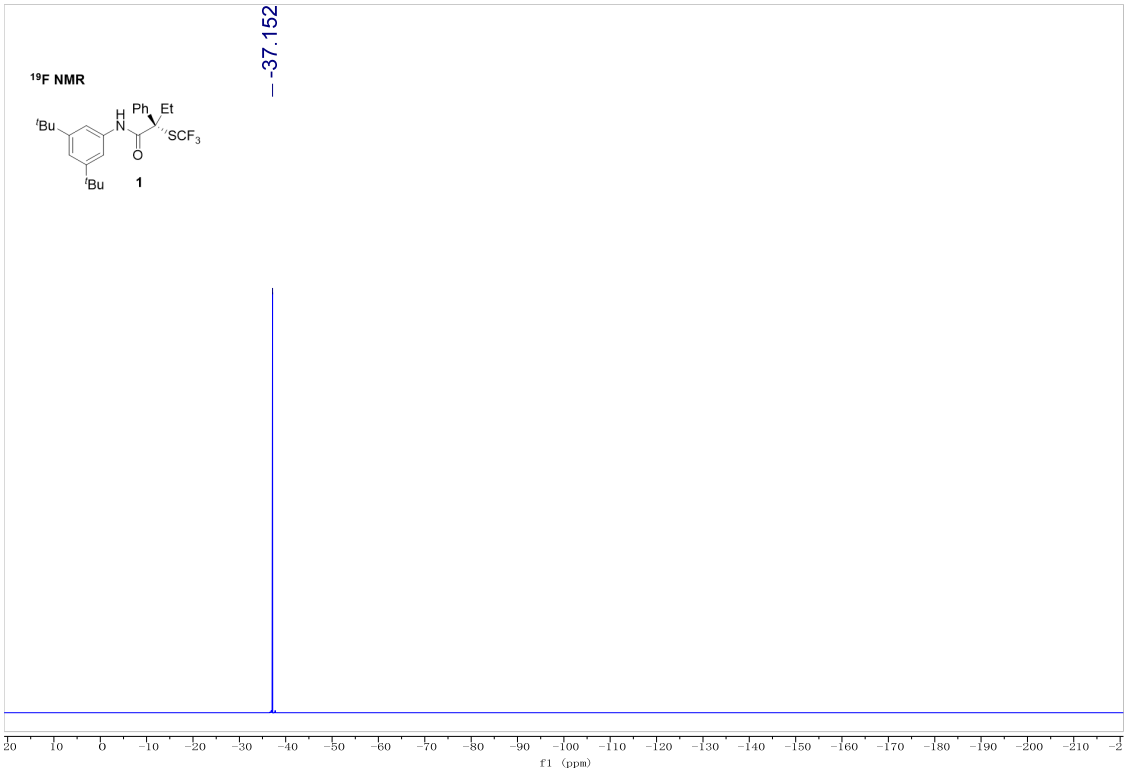

12.153
8.588
8.566
7.781
7.762
7.398
7.388
7.378
7.369
7.359
7.337
7.320
7.316
7.304
7.285
7.265
7.245
7.217
7.200
7.178
7.164
7.159
7.151
7.141
7.129
7.120
7.110
7.097
7.091
7.083
7.075
7.062
7.017
6.938
6.916
6.895
6.647
6.625
6.604
4.309
4.027
3.933
3.910
1.287
1.223
1H NMR
L*13, Ar = 4-tBuC6H4
0.969
0.974
0.992
7.112
10.257
1.180
2.136
1.991
1.000
0.982
0.992
1.010
9.124
9.053
f1 (ppm)

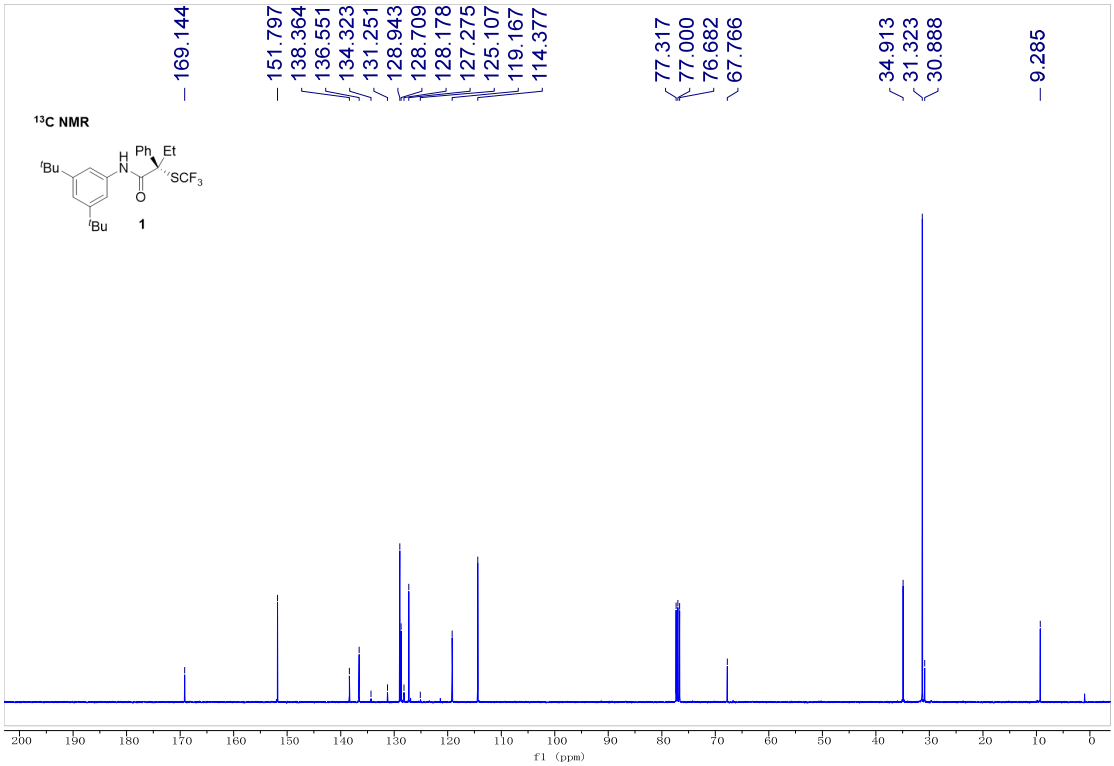

-115.340
-115.353
-115.364
-115.376
-115.389
-115.400
-115.414
-115.592
-115.606
-115.617
-115.630
-115.642
-115.653
-115.666
19F NMR
L*13, Ar = 4-tBuC6H4
1.000
0.959
f1 (ppm)

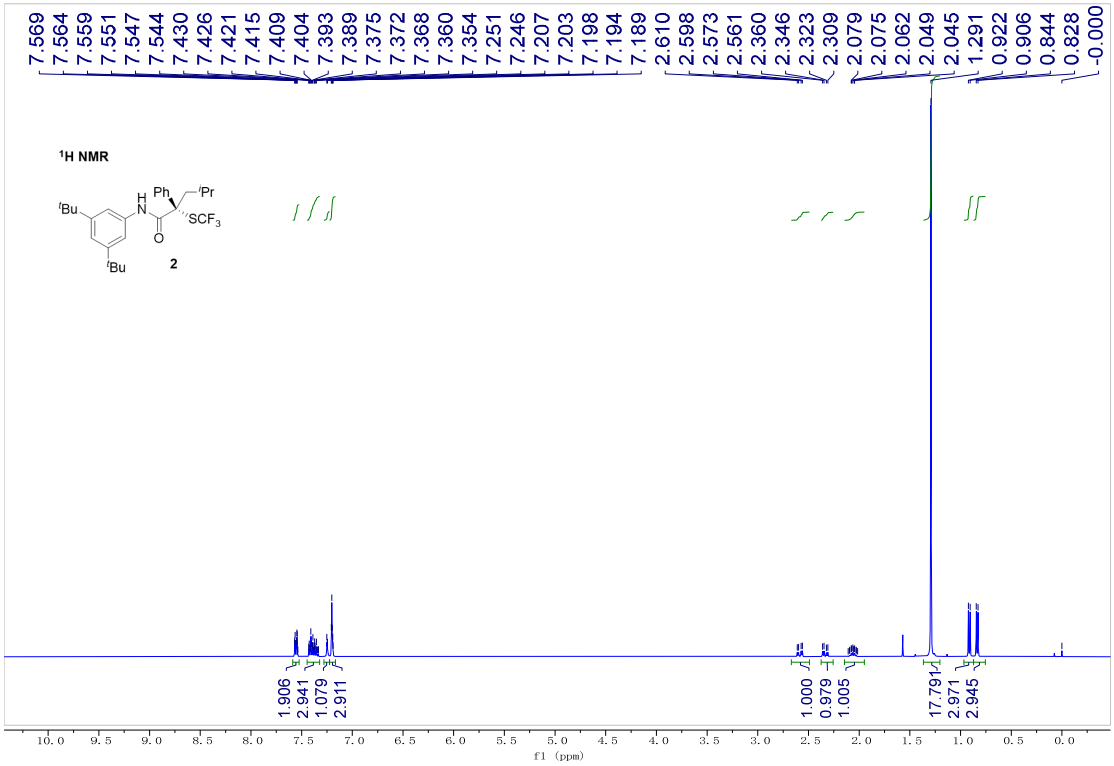

31P NMR
-10.491
L*13, Ar = 4-tBuC6H4
f1 (ppm)

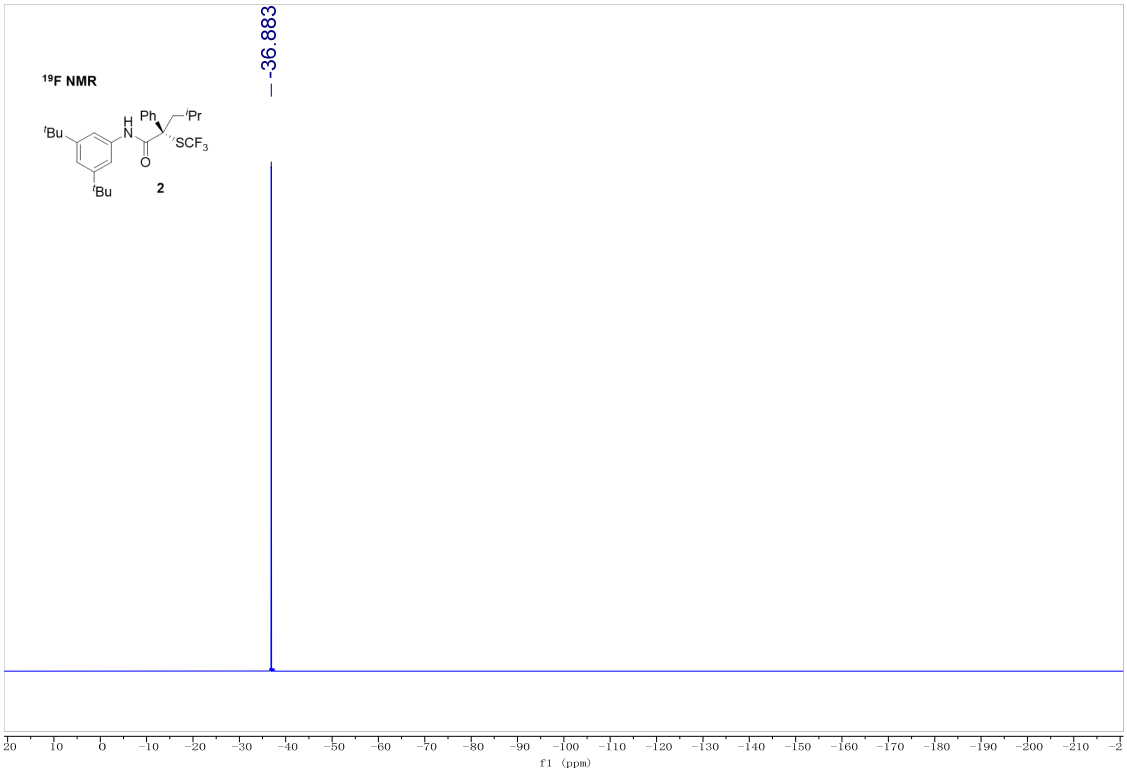

167.967
164.420
151.420
151.256
139.932
138.805
137.562
137.529
136.895
134.517
134.407
133.887
133.738
133.683
133.534
132.644
130.008
129.684
129.626
129.604
129.549
128.948
128.113
126.993
126.953
125.338
125.262
125.233
125.160
122.287
120.161
115.830
115.619
115.221
115.014
112.917
77.317
77.000
76.683
69.895
55.224
34.550
34.455
31.210
31.130
13C NMR
L*13, Ar = 4-tBuC6H4
f1 (ppm)

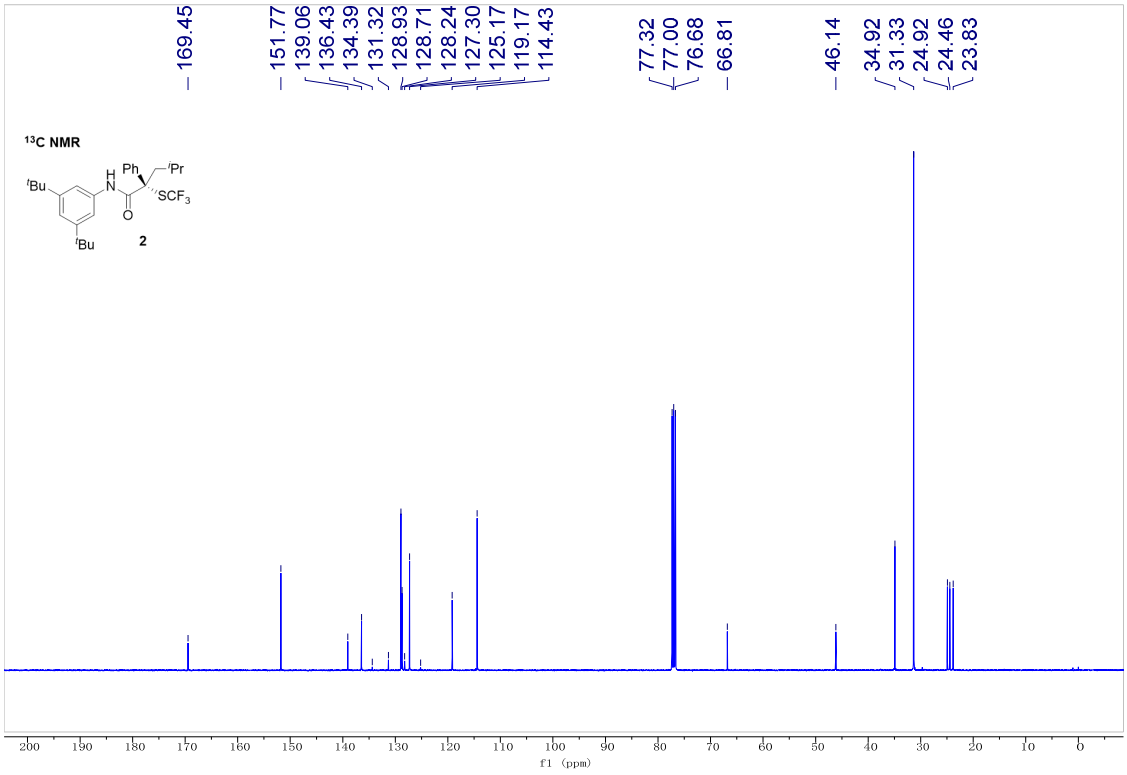

7.538
7.534
7.529
7.521
7.516
7.514
7.507
7.428
7.424
7.419
7.407
7.402
7.392
7.387
7.372
7.368
7.364
7.357
7.351
7.343
7.336
7.332
7.250
7.246
7.210
7.206
7.202
2.690
2.672
2.653
2.635
2.617
2.493
2.475
2.457
1.104
1.086
1.068
0.000
1H NMR
tBu
H
N
Ph
Et
SCF3
O
tBu
1
1.939
3.989
1.910
0.980
1.000
1.023
18.279
2.990
f1 (ppm)

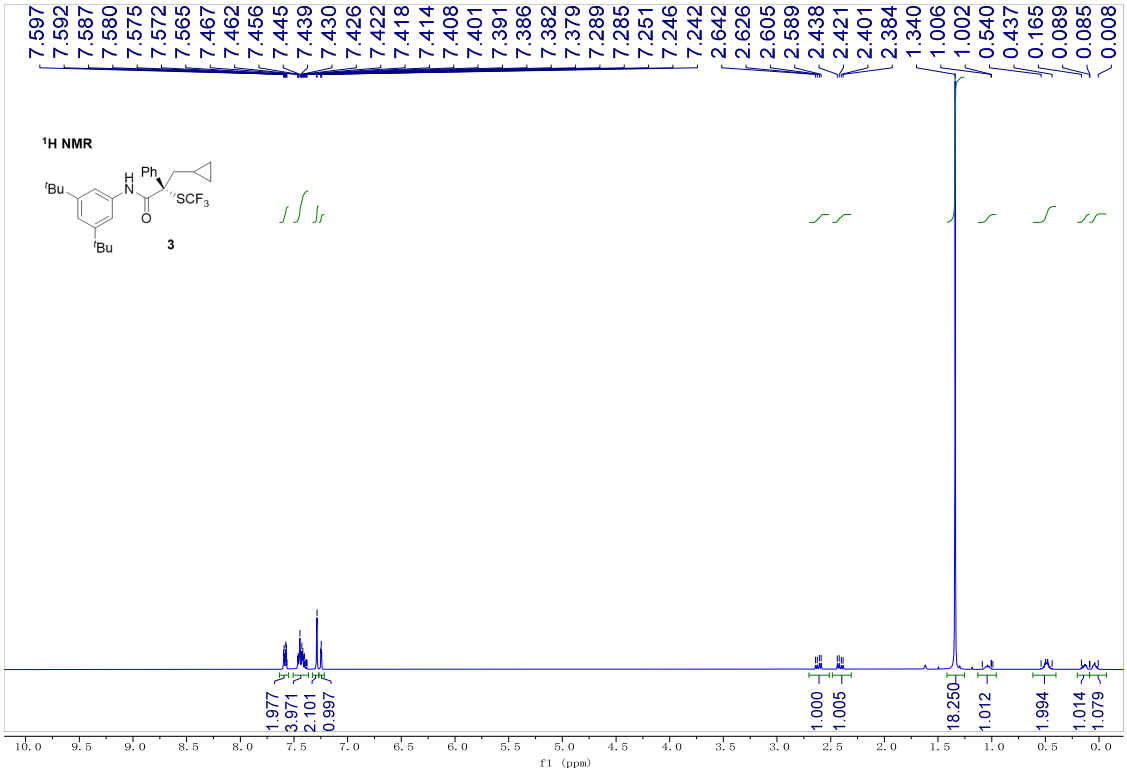

-37.152
19F NMR
tBu
H
N
Ph
Et
SCF3
O
tBu
1
f1 (ppm)

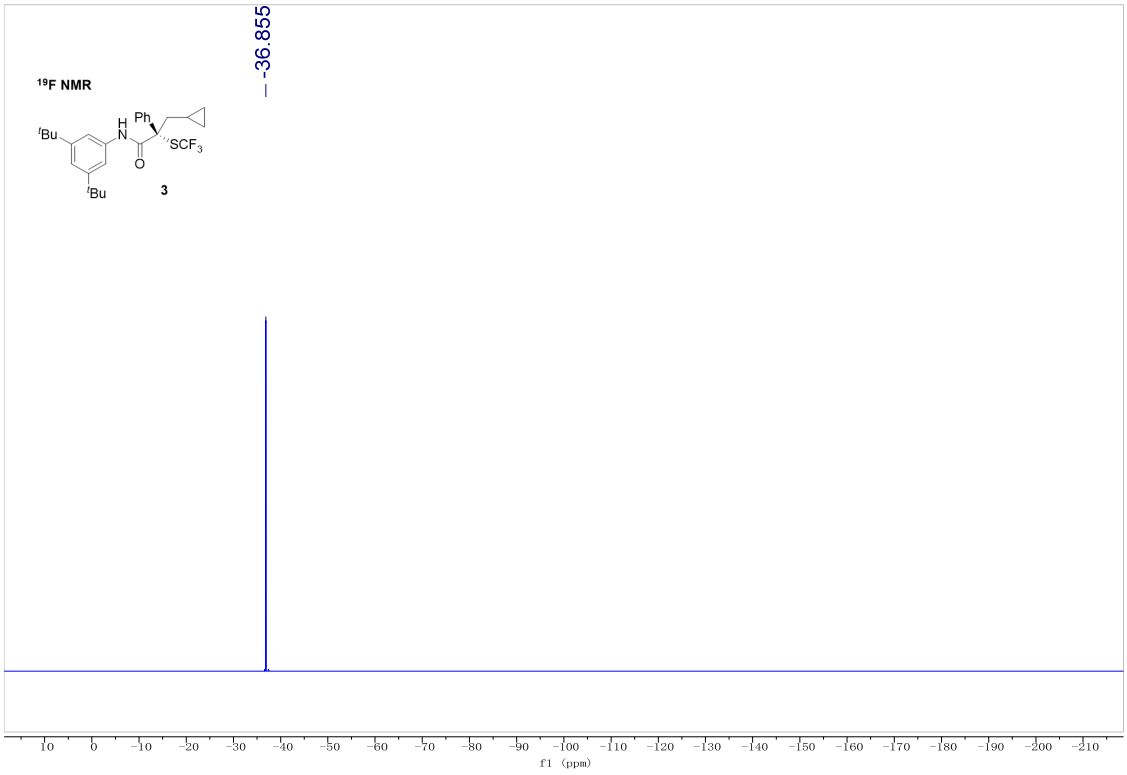

169.144
151.797
138.364
136.551
134.323
131.251
128.943
128.709
128.178
127.275
125.107
119.167
114.377
77.317
77.000
76.682
67.766
34.913
31.323
30.888
9.285
13C NMR
tBu
H
N
Ph
Et
SCF3
O
tBu
1
f1 (ppm)

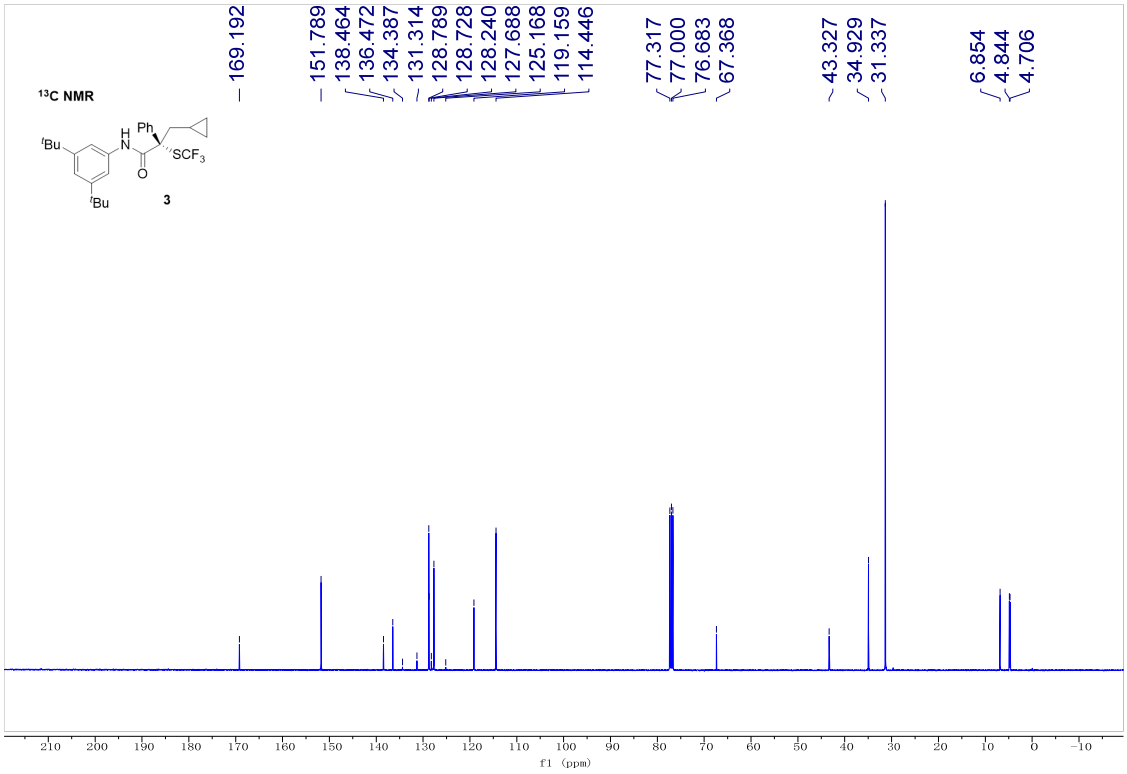

7.569
7.564
7.559
7.551
7.547
7.544
7.430
7.426
7.421
7.415
7.409
7.404
7.393
7.389
7.375
7.372
7.368
7.360
7.354
7.251
7.246
7.207
7.203
7.198
7.194
7.189
2.610
2.598
2.573
2.561
2.360
2.346
2.323
2.309
2.079
2.075
2.062
2.049
2.045
1.291
0.922
0.906
0.844
0.828
-0.000
1H NMR
tBu
H
N
Ph
iPr
SCF3
O
tBu
2
1.906
2.941
1.079
2.911
1.000
0.979
1.005
17.791
2.971
2.945
f1 (ppm)

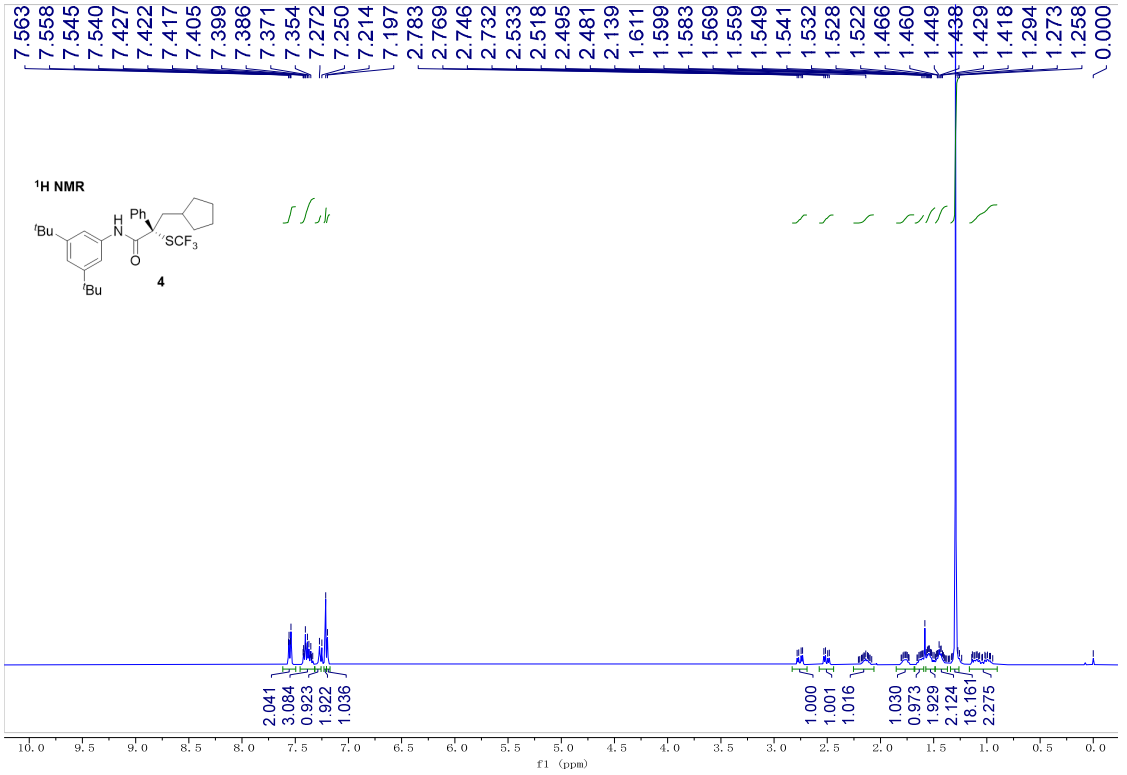

19F NMR
-36.883
tBu
H
N
Ph
iPr
SCF3
O
tBu
2
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

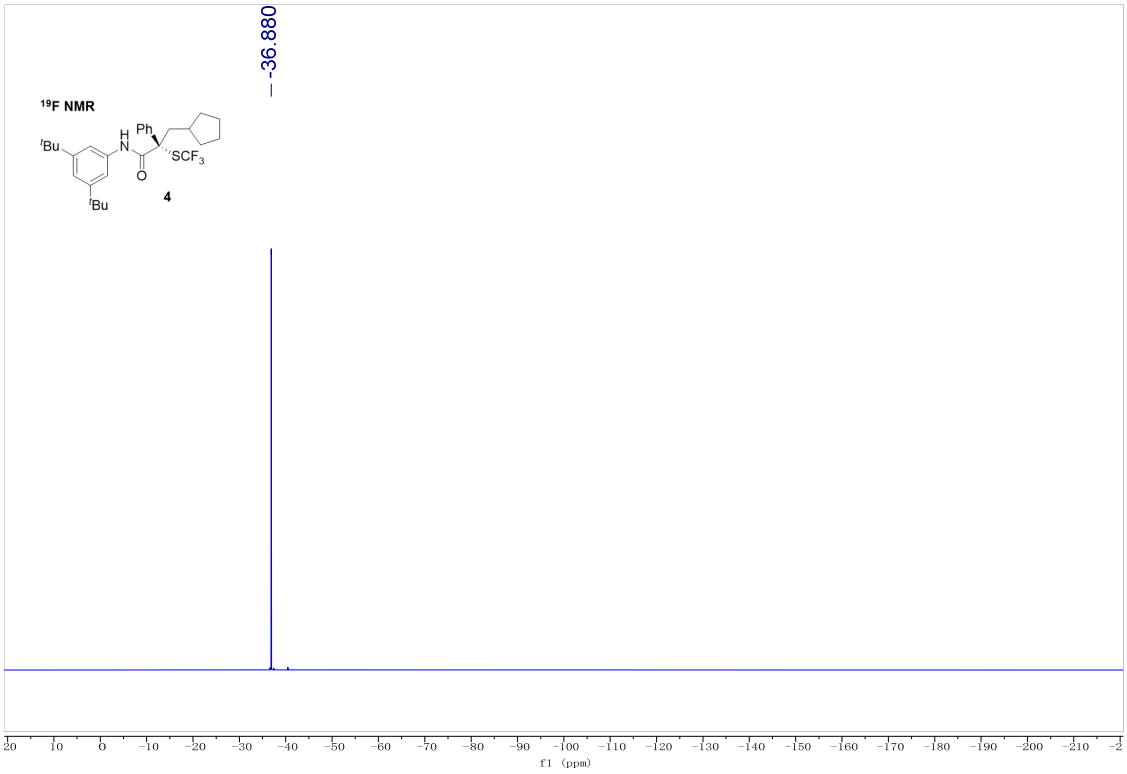

169.45
151.77
139.06
136.43
134.39
131.32
128.93
128.71
128.24
127.30
125.17
119.17
114.43
77.32
77.00
76.68
66.81
46.14
34.92
31.33
24.92
24.46
23.83
13C NMR
tBu
H
N
Ph
iPr
SCF3
O
tBu
2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

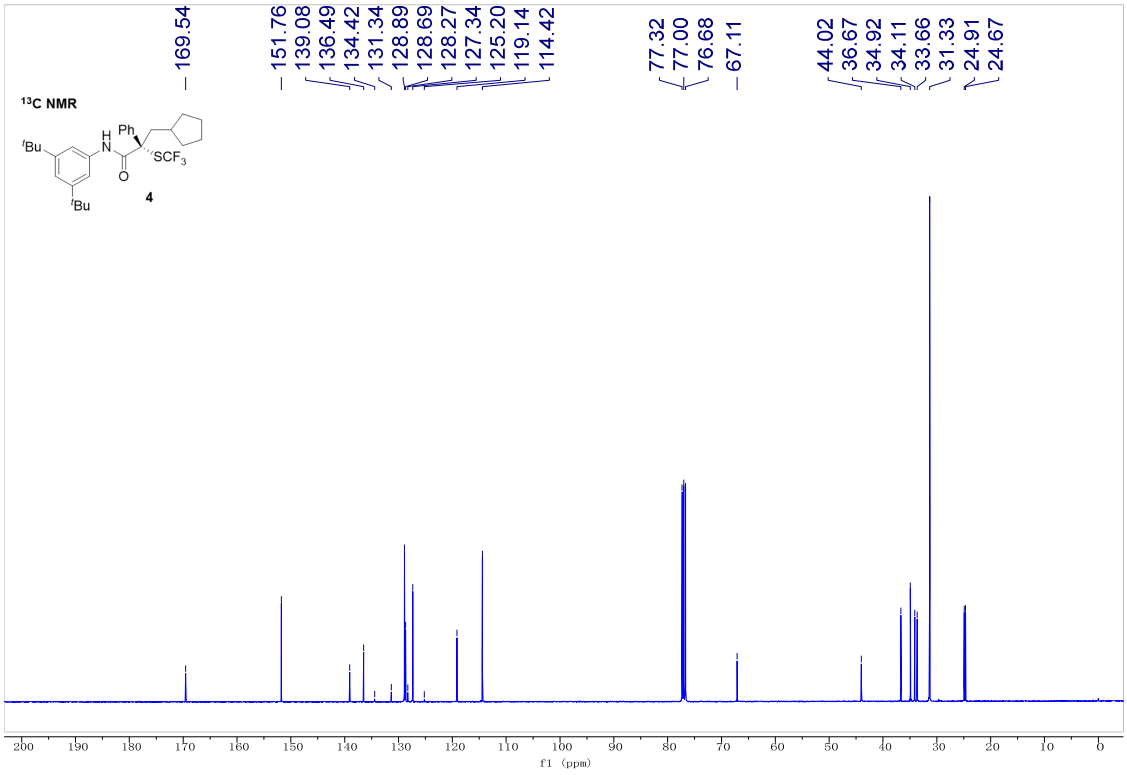

7.597
7.592
7.587
7.580
7.575
7.572
7.565
7.467
7.462
7.456
7.445
7.439
7.430
7.426
7.422
7.418
7.414
7.408
7.401
7.391
7.386
7.382
7.379
7.289
7.285
7.251
7.246
7.242
2.642
2.626
2.605
2.589
2.438
2.421
2.401
2.384
1.340
1.006
1.002
0.540
0.437
0.165
0.089
0.085
0.008
1H NMR
Ph
H
N
O
SCF3
tBu
tBu
3
1.977
3.971
2.101
0.997
1.000
1.005
18.250
1.012
1.994
1.014
1.079
f1 (ppm)

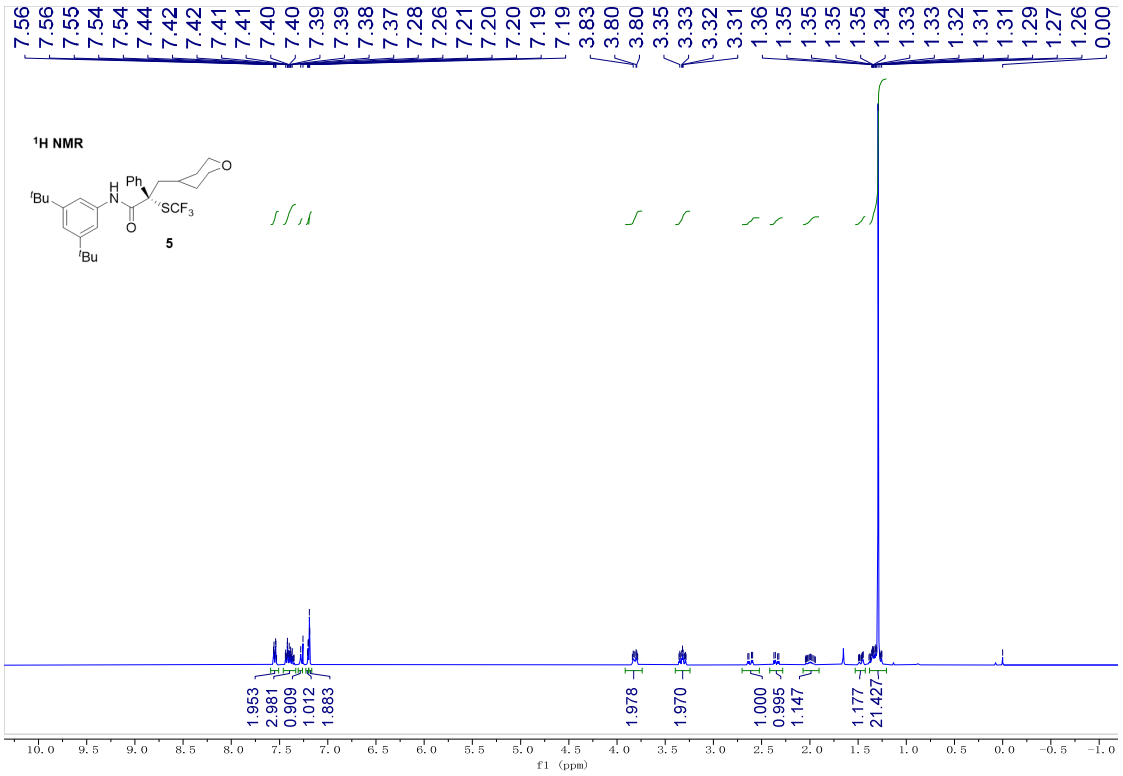

-36.855
19F NMR
Ph
H
N
O
SCF3
tBu
tBu
3
f1 (ppm)

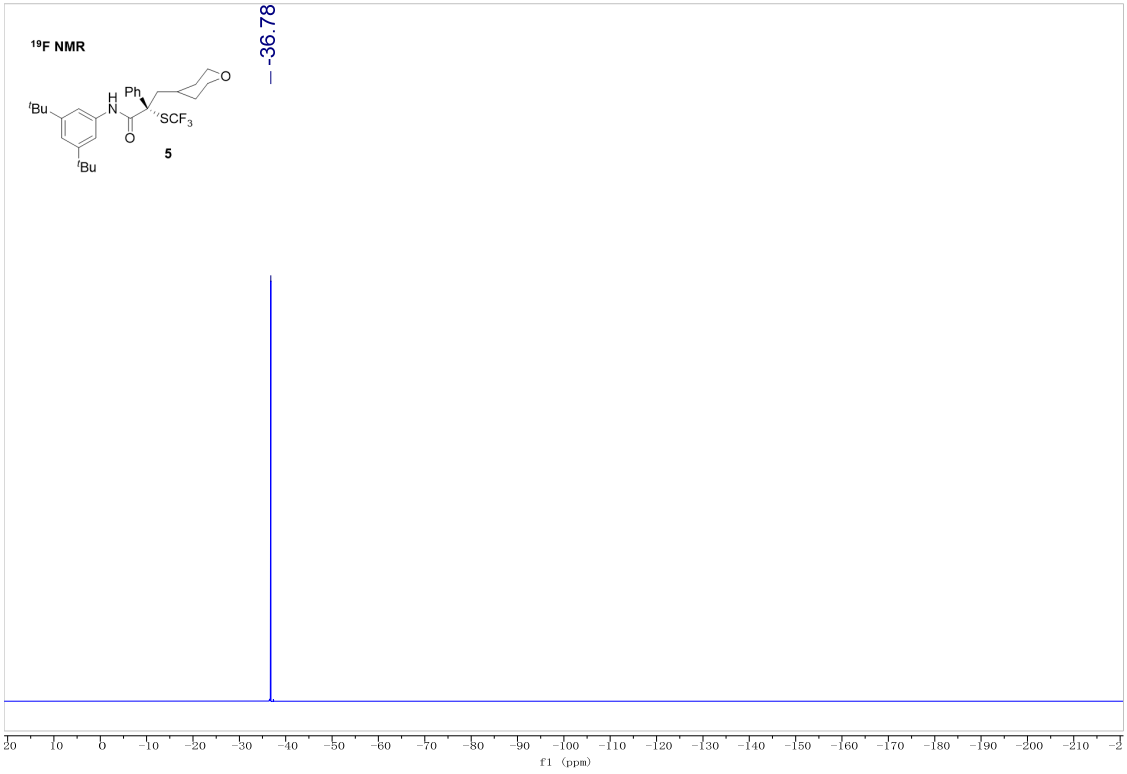

169.192
151.789
138.464
136.472
134.387
131.314
128.789
128.728
128.240
127.688
125.168
119.159
114.446
77.317
77.000
76.683
67.368
43.327
34.929
31.337
6.854
4.844
4.706
13C NMR
tBu
H
N
Ph
SCF3
O
tBu
3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

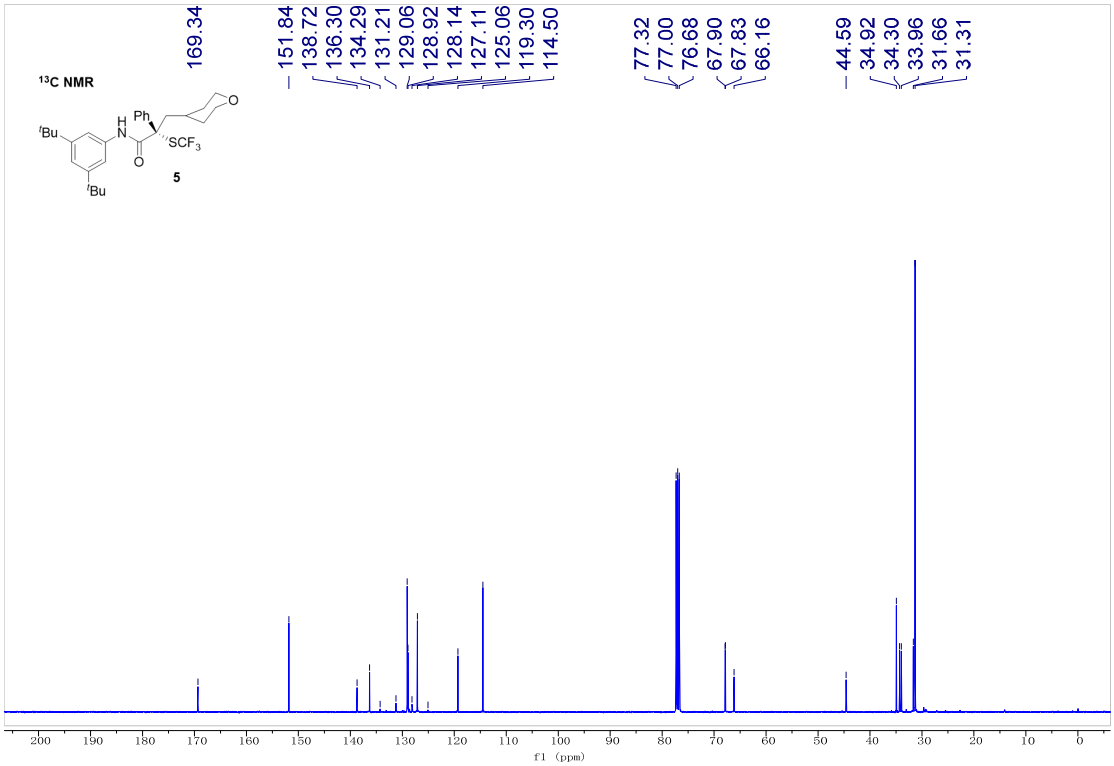

7.563
7.558
7.545
7.540
7.427
7.422
7.417
7.405
7.399
7.386
7.371
7.354
7.272
7.250
7.214
7.197
2.783
2.769
2.746
2.732
2.533
2.518
2.495
2.481
2.139
1.611
1.599
1.583
1.569
1.559
1.549
1.541
1.532
1.528
1.522
1.466
1.460
1.449
1.438
1.429
1.418
1.294
1.273
1.258
0.000
1H NMR
tBu
H
N
Ph
SCF3
O
tBu
4
2.041
3.084
0.923
1.922
1.036
1.000
1.001
1.016
1.030
0.973
1.929
2.124
18.161
2.275
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

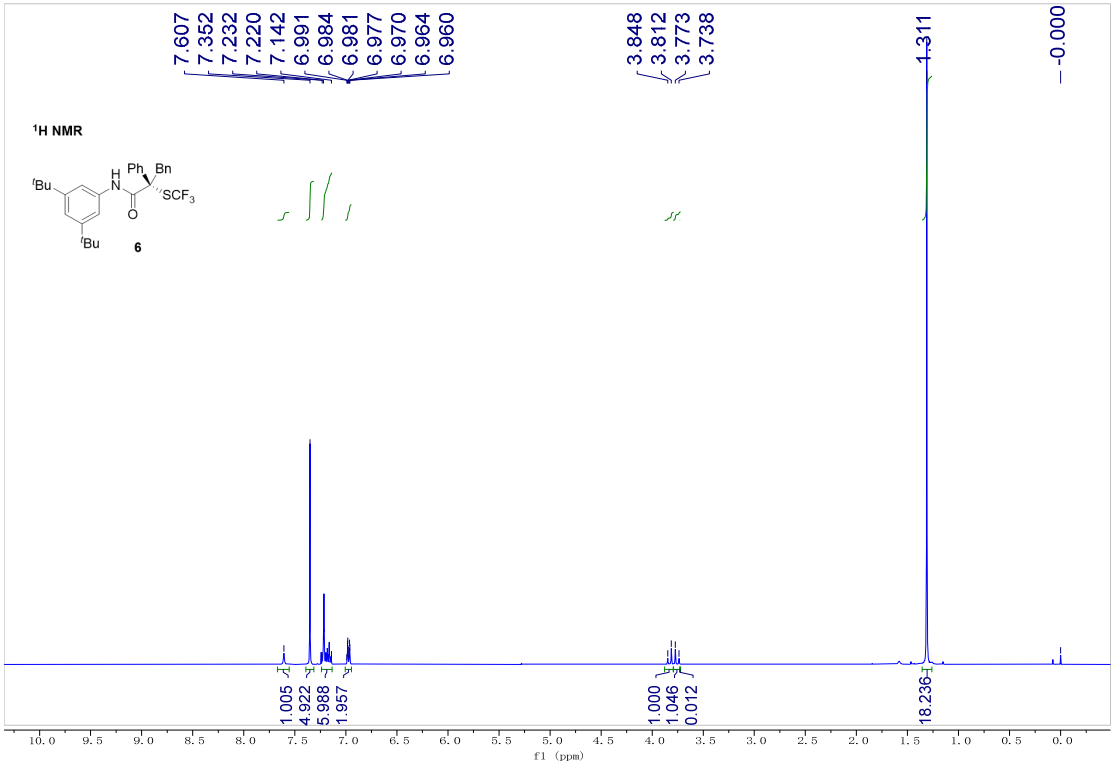

-36.880
19F NMR
tBu
H
N
Ph
SCF3
O
tBu
4
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

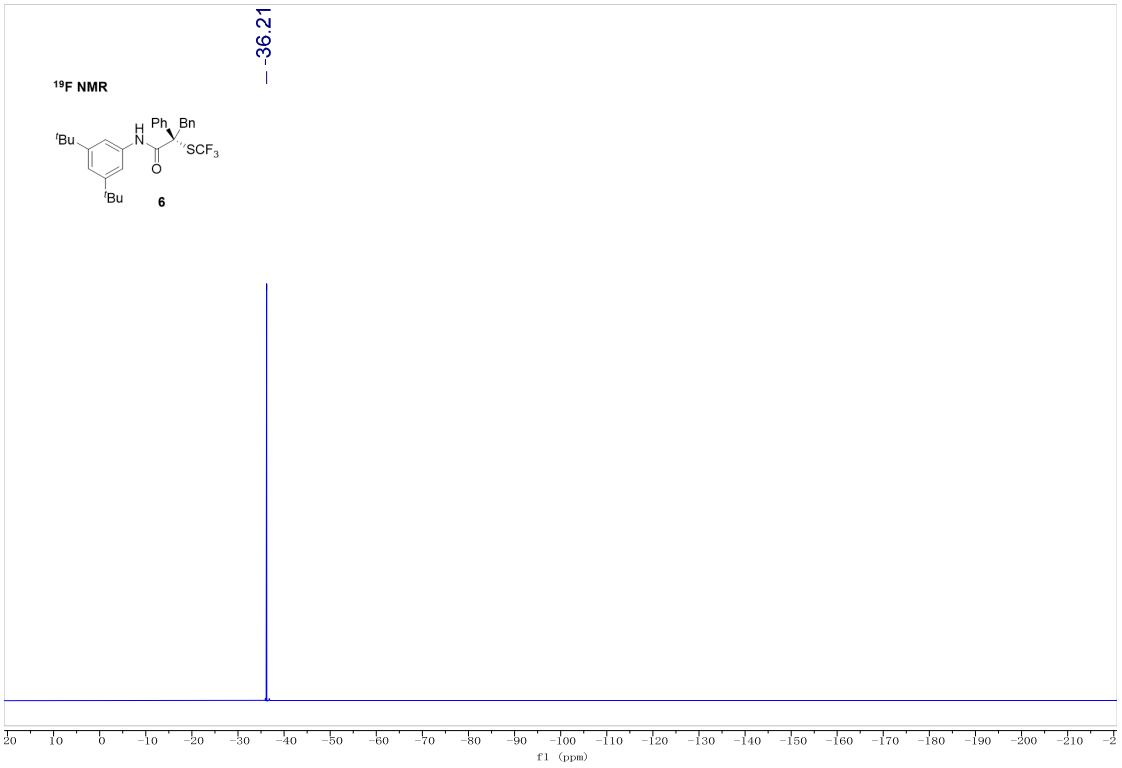

169.54
151.76
139.08
136.49
134.42
131.34
128.89
128.69
128.27
127.34
125.20
119.14
114.42
77.32
77.00
76.68
67.11
44.02
36.67
34.92
34.11
33.66
31.33
24.91
24.67
13C NMR
tBu
H
N
Ph
SCF3
O
tBu
4
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

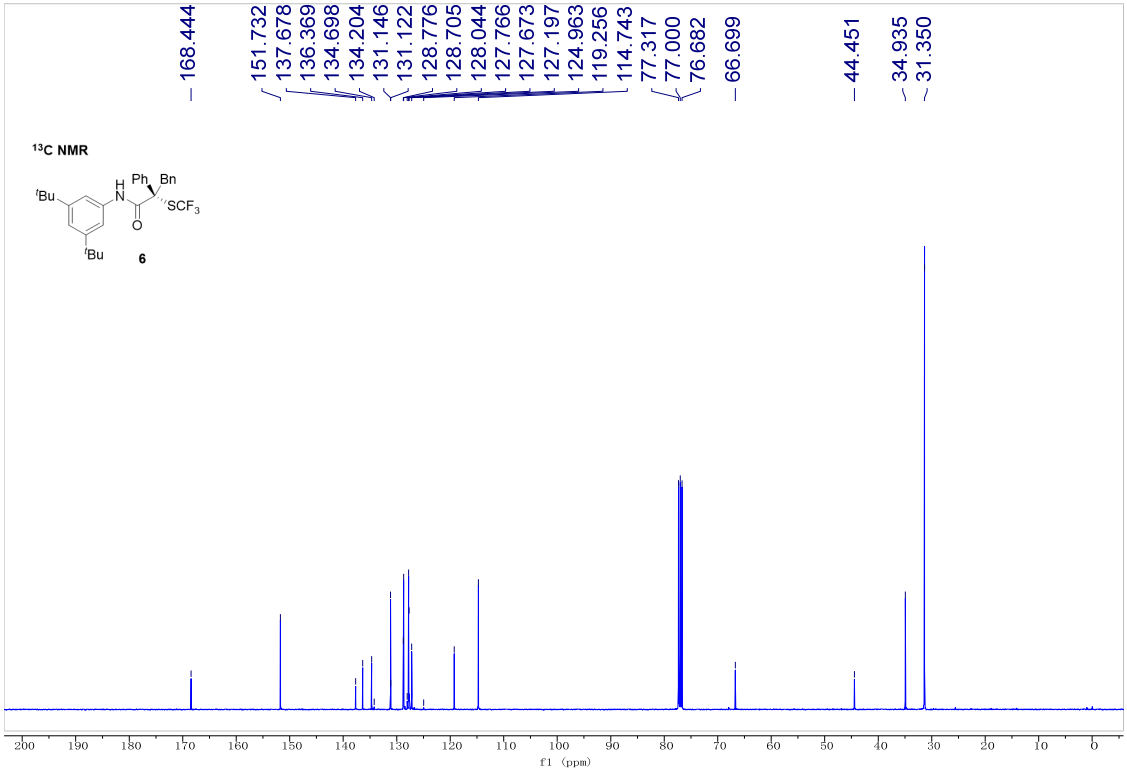

7.56 7.56 7.55 7.54 7.54 7.44 7.42 7.42 7.41 7.41 7.40 7.40 7.39 7.39 7.38 7.37 7.28 7.26 7.21 7.20 7.20 7.19 7.19
3.83 3.80 3.80 3.35 3.33 3.32 3.31
1.36 1.35 1.35 1.35 1.34 1.33 1.33 1.32 1.31 1.31 1.29 1.27 1.26 0.00
1H NMR
tBu
H
N
Ph
SCF3
O
O
tBu
5
1.953 2.981 0.909 1.012 1.883
1.978 1.970
1.000 0.995 1.147
1.177 21.427
f1 (ppm)

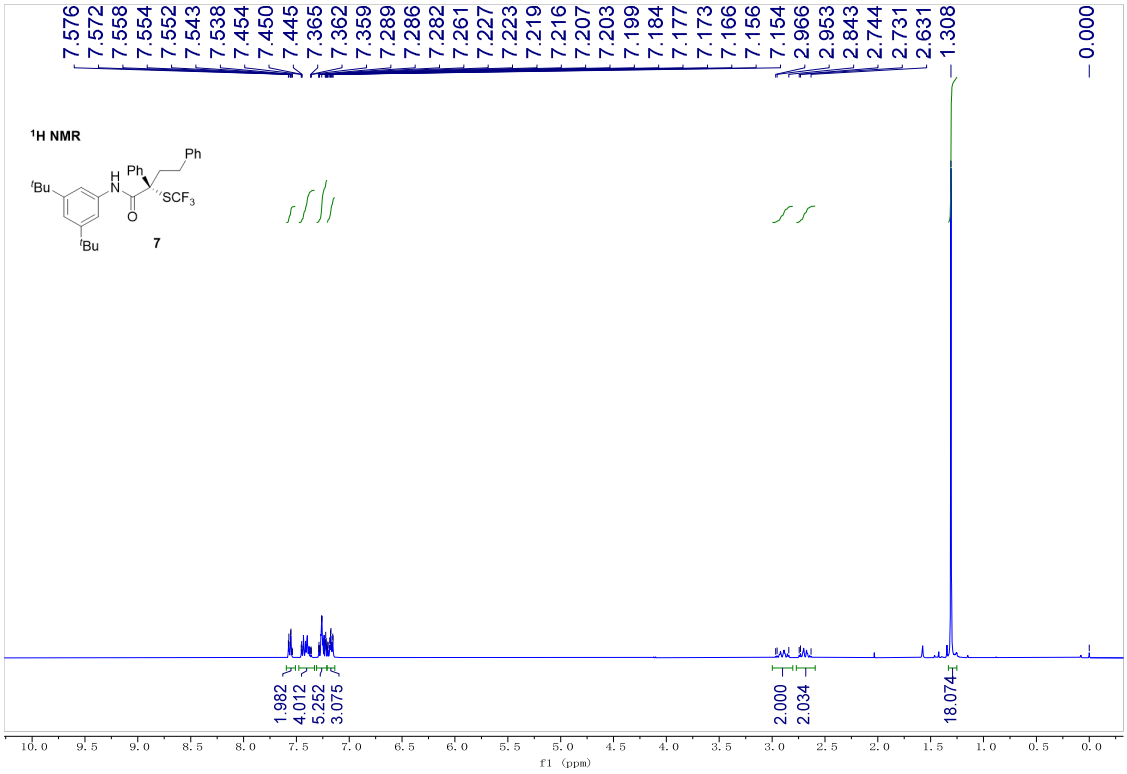

-36.78
19F NMR
tBu
H
N
Ph
SCF3
O
O
tBu
5
f1 (ppm)

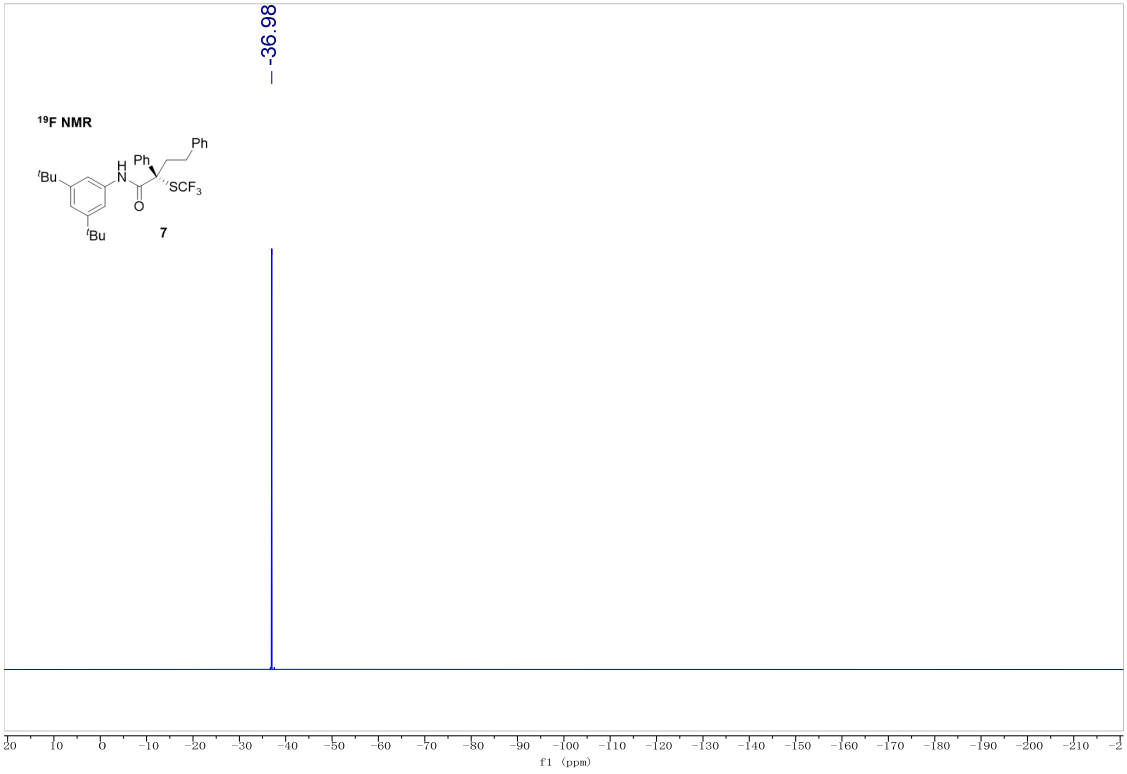

169.34
151.84
138.72
136.30
134.29
131.21
129.06
128.92
128.14
127.11
125.06
119.30
114.50
77.32
77.00
76.68
67.90
67.83
66.16
44.59
34.92
34.30
33.96
31.66
31.31
13C NMR
tBu
Ph
H
N
O
SCF3
O
tBu
5
f1 (ppm)

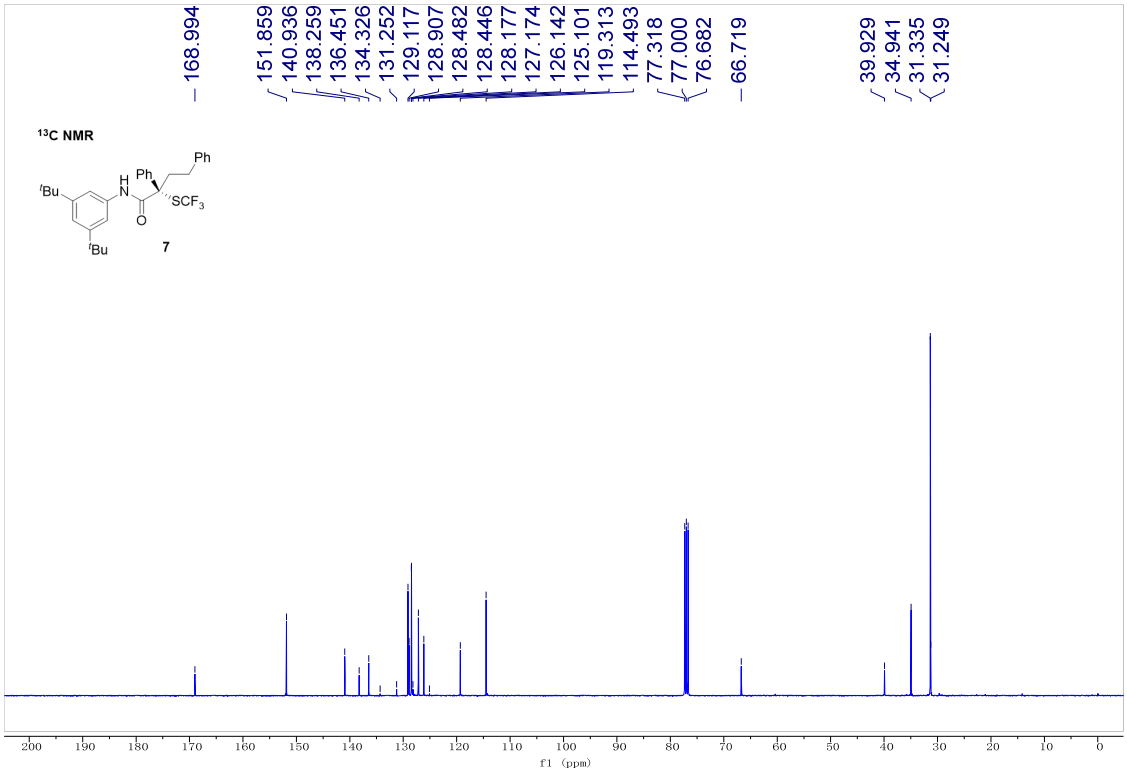

7.607
7.352
7.232
7.220
7.142
6.991
6.984
6.981
6.977
6.970
6.964
6.960
3.848
3.812
3.773
3.738
1.311
-0.000
1H NMR
tBu
Ph
Bn
H
N
O
SCF3
tBu
6
1.005
4.922
5.988
1.957
1.000
1.046
0.012
18.236
f1 (ppm)

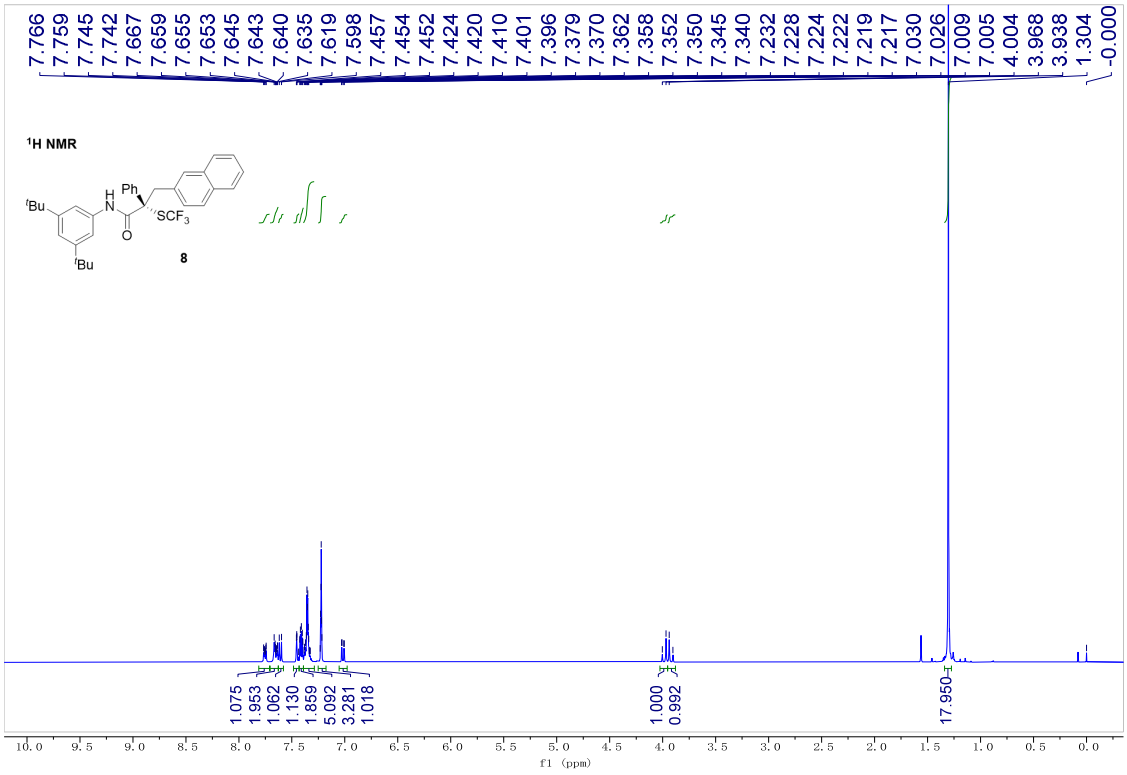

19F NMR
-36.21
tBu
Ph
Bn
SCF3
tBu
6
f1 (ppm)

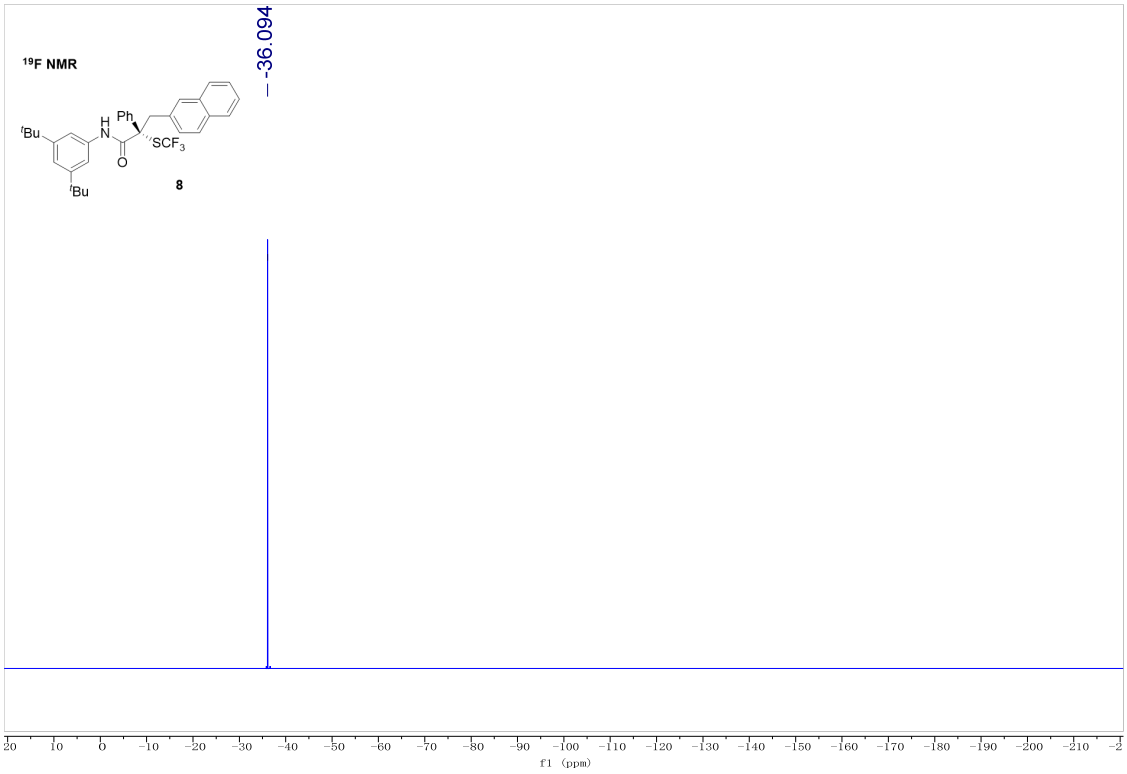

13C NMR
168.444
151.732
137.678
136.369
134.698
134.204
131.146
131.122
128.776
128.705
128.044
127.766
127.673
127.197
124.963
119.256
114.743
77.317
77.000
76.682
66.699
44.451
34.935
31.350
tBu
Ph
Bn
SCF3
tBu
6
f1 (ppm)

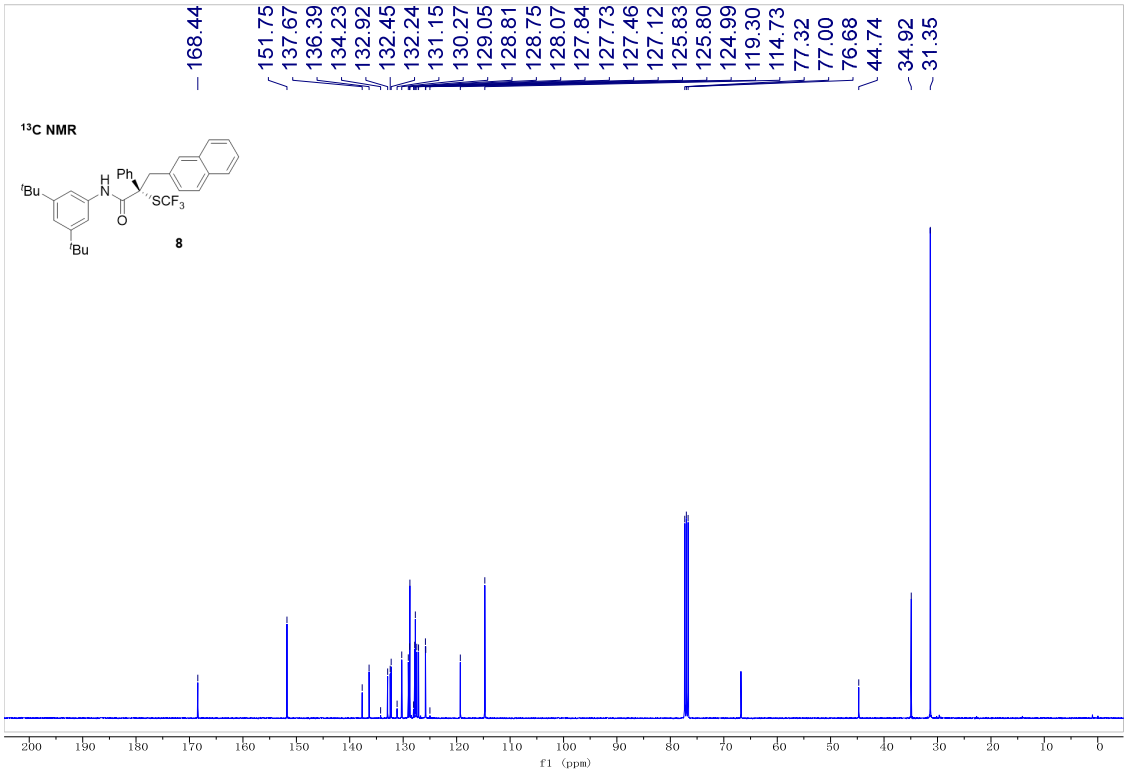

7.576
7.572
7.558
7.554
7.552
7.543
7.538
7.454
7.450
7.445
7.365
7.362
7.359
7.289
7.286
7.282
7.261
7.227
7.223
7.219
7.216
7.207
7.203
7.199
7.184
7.177
7.173
7.166
7.156
7.154
2.966
2.953
2.843
2.744
2.731
2.631
1.308
0.000
1H NMR
Ph
H
N
Ph
tBu
SCF3
O
tBu
7
1.982
4.012
5.252
3.075
2.000
2.034
18.074
f1 (ppm)

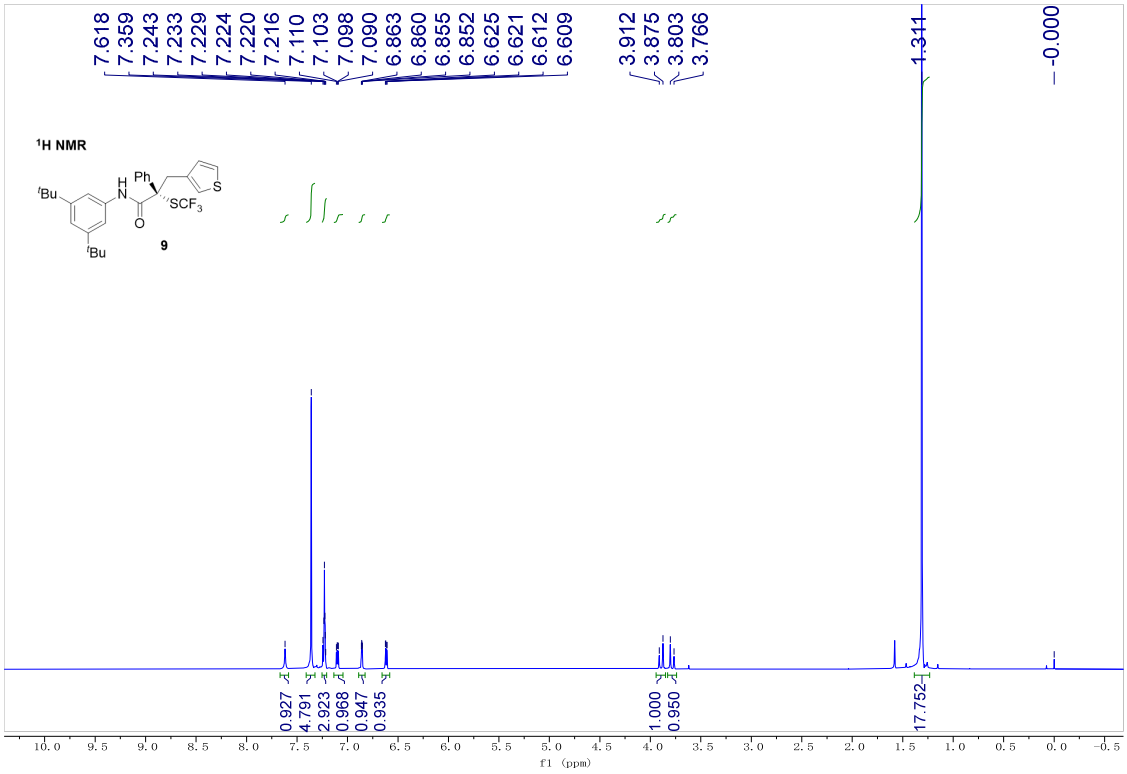

-36.98
19F NMR
Ph
H
N
Ph
tBu
SCF3
O
tBu
7
f1 (ppm)

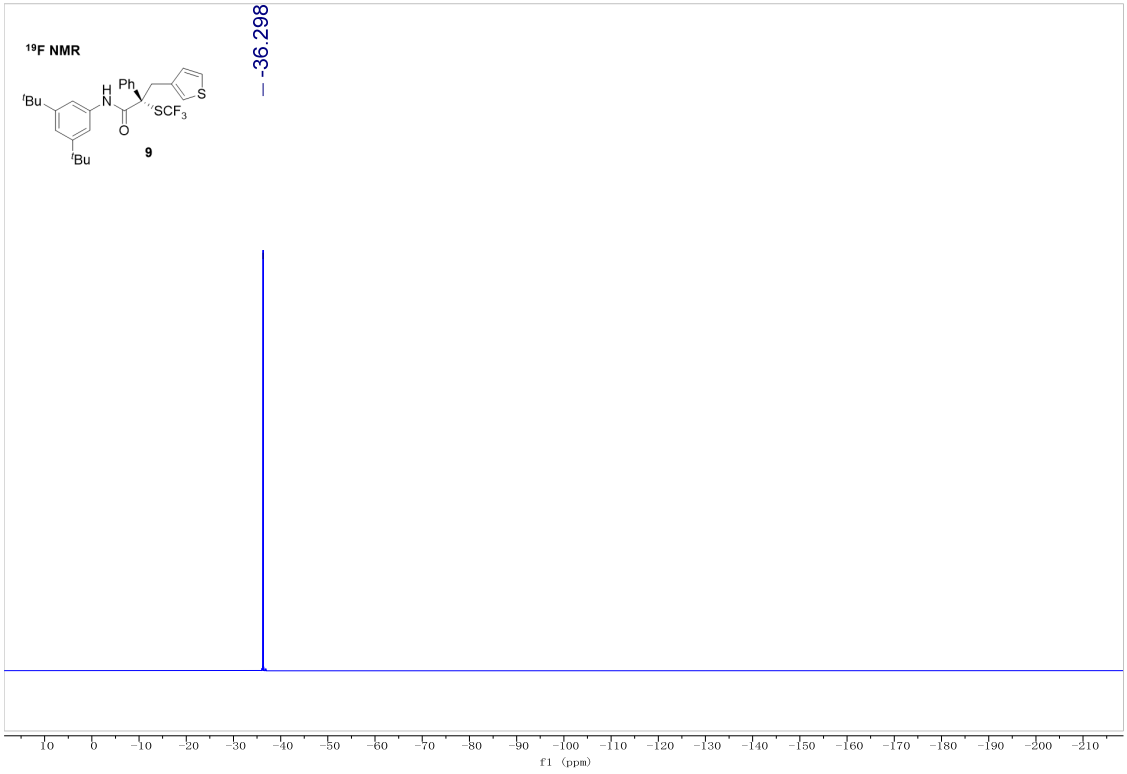

168.994
151.859
140.936
138.259
136.451
134.326
131.252
129.117
128.907
128.482
128.446
128.177
127.174
126.142
125.101
119.313
114.493
77.318
77.000
76.682
66.719
39.929
34.941
31.335
31.249
13C NMR
Ph
Ph
H
N
O
SCF3
tBu
tBu
7
f1 (ppm)

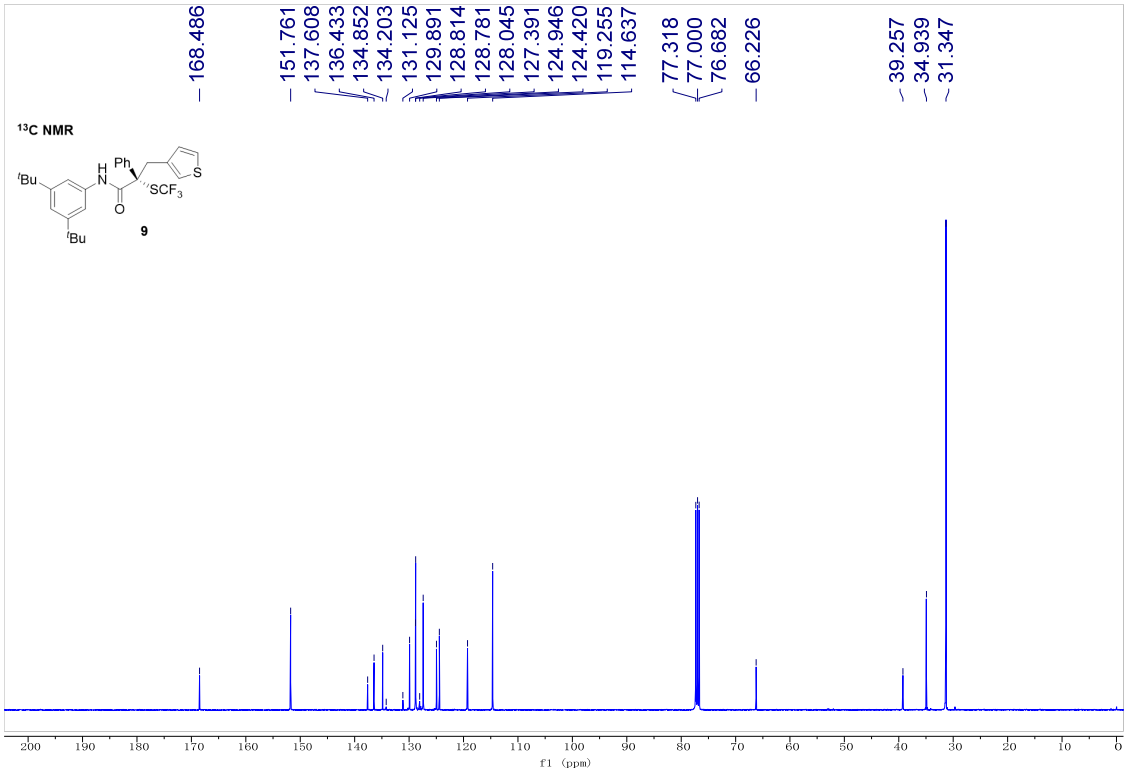

7.766
7.759
7.745
7.742
7.667
7.659
7.655
7.653
7.645
7.643
7.640
7.635
7.619
7.598
7.457
7.454
7.452
7.424
7.420
7.410
7.401
7.396
7.379
7.370
7.362
7.358
7.352
7.350
7.345
7.340
7.232
7.228
7.224
7.222
7.219
7.217
7.030
7.026
7.009
7.005
4.004
3.968
3.938
1.304
-0.000
1H NMR
Ph
H
N
O
SCF3
tBu
tBu
8
1.075
1.953
1.062
1.130
1.859
5.092
3.281
1.018
1.000
0.992
17.950
f1 (ppm)

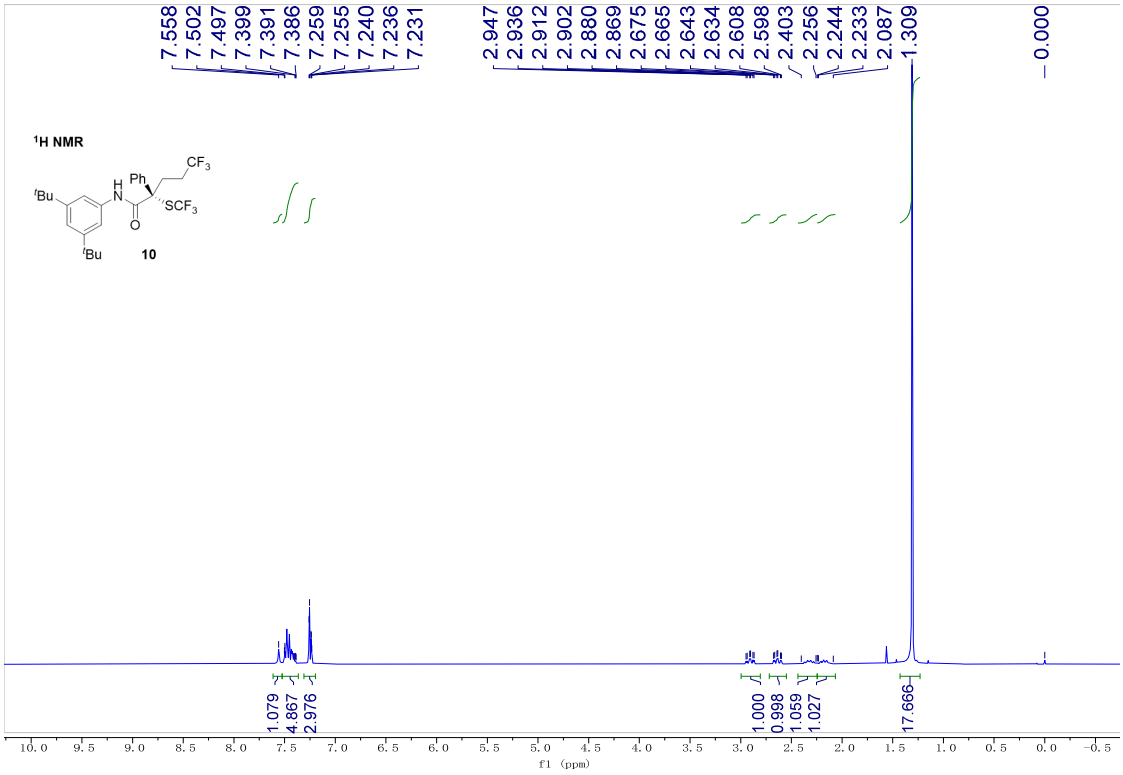

19F NMR
-36.094
tBu
H
N
Ph
SCF3
O
tBu
8
f1 (ppm)

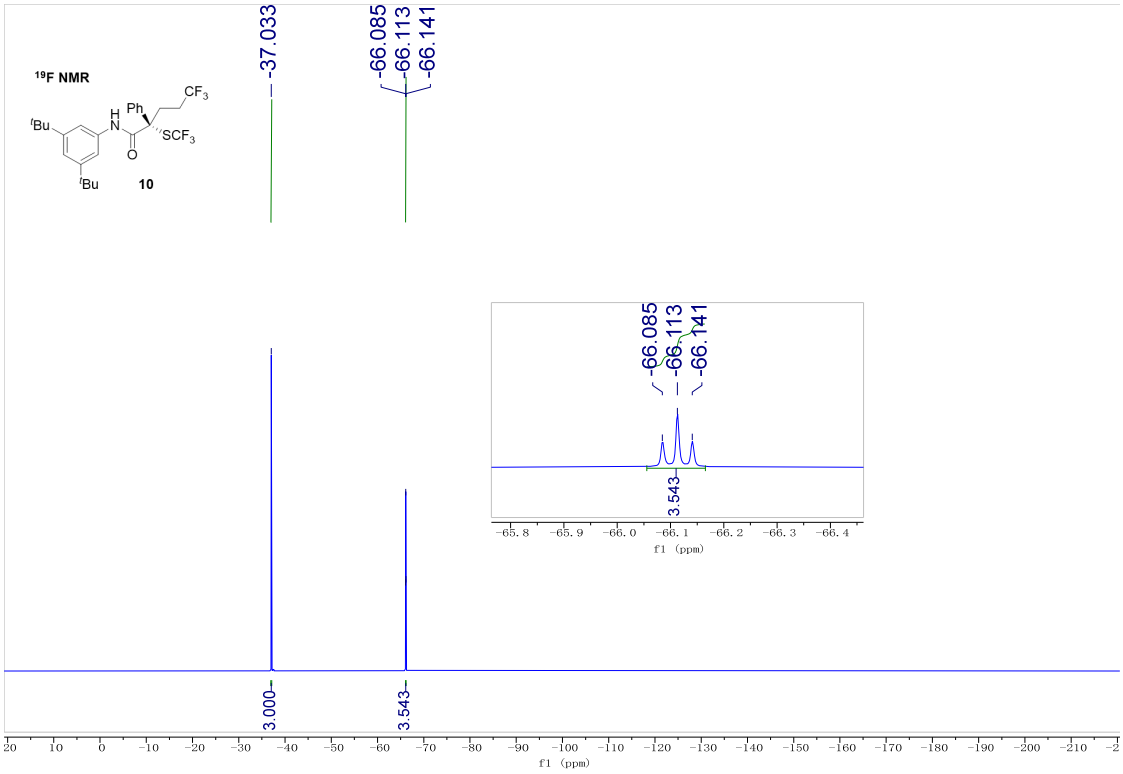

168.44
151.75
137.67
136.39
134.23
132.92
132.45
132.24
131.15
130.27
129.05
128.81
128.75
128.07
127.84
127.73
127.46
127.12
125.83
125.80
124.99
119.30
114.73
77.32
77.00
76.68
44.74
34.92
31.35
13C NMR
tBu
H
N
Ph
SCF3
O
tBu
8
f1 (ppm)

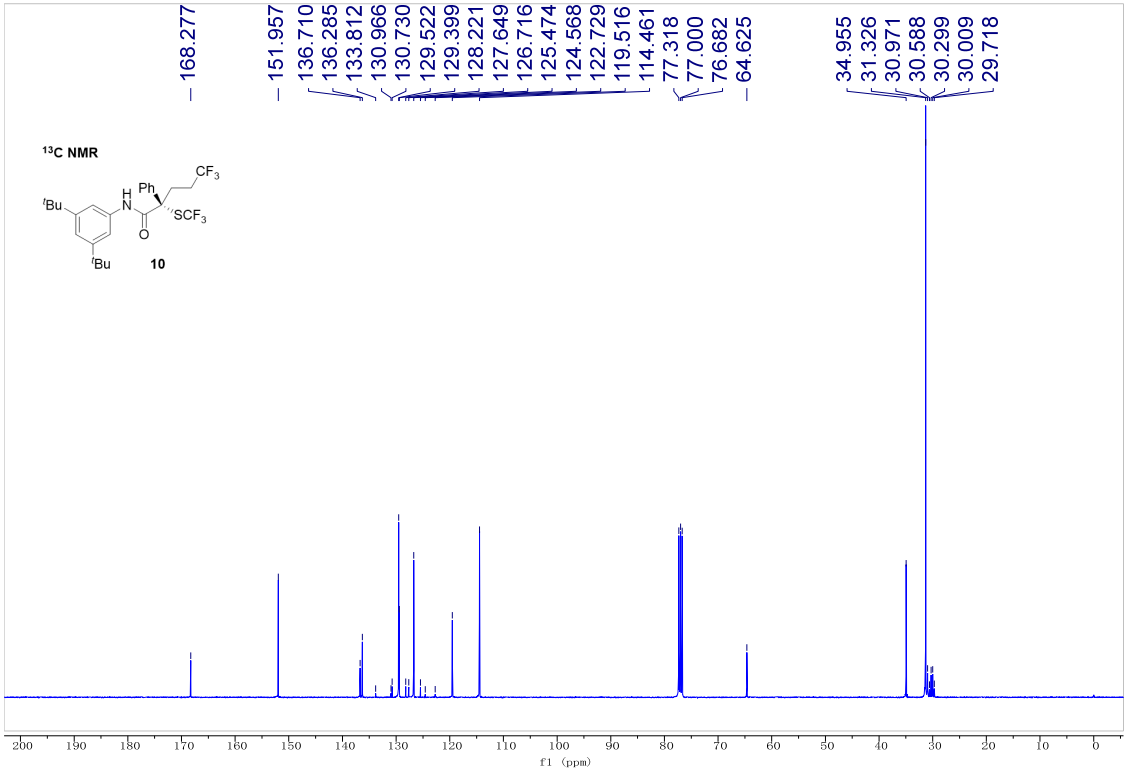

7.618
7.359
7.243
7.233
7.229
7.224
7.220
7.216
7.110
7.103
7.098
7.090
6.863
6.860
6.855
6.852
6.625
6.621
6.612
6.609
3.912
3.875
3.803
3.766
1.311
-0.000
¹H NMR
tBu
Ph
H
N
O
SCF3
S
tBu
9
0.927
4.791
2.923
0.968
0.947
0.935
1.000
0.950
17.752
f1 (ppm)

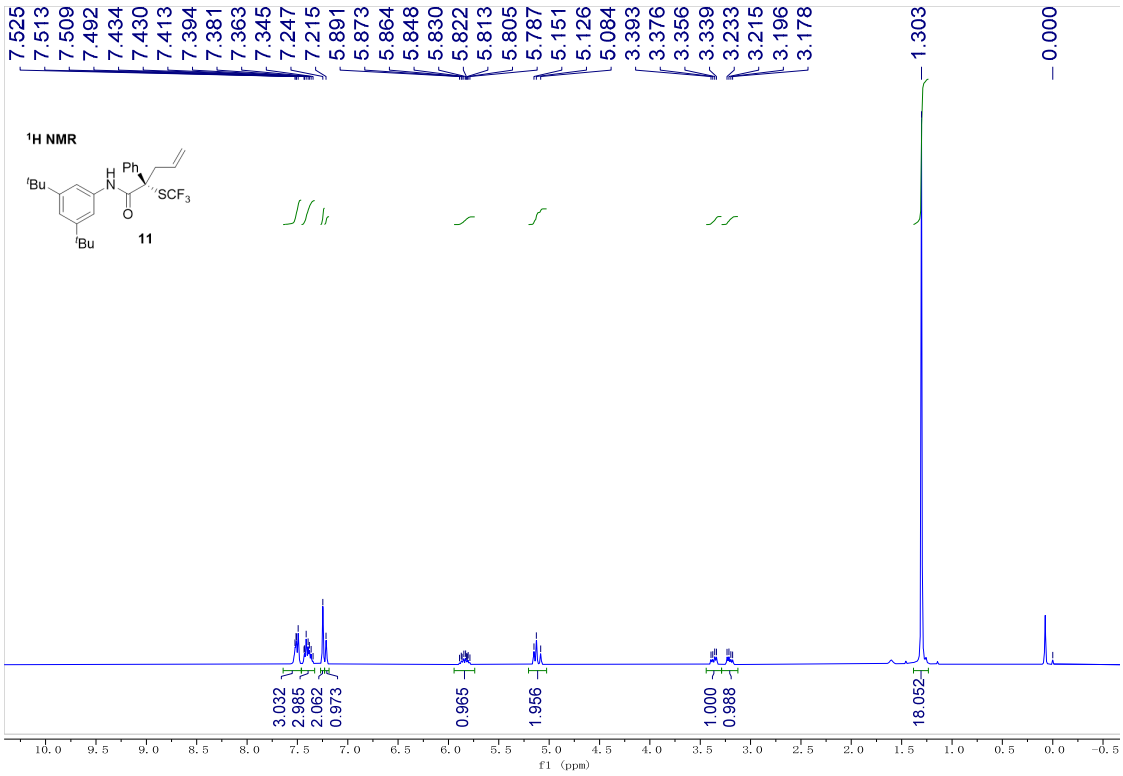

-36.298
¹⁹F NMR
tBu
Ph
H
N
O
SCF3
S
tBu
9
f1 (ppm)

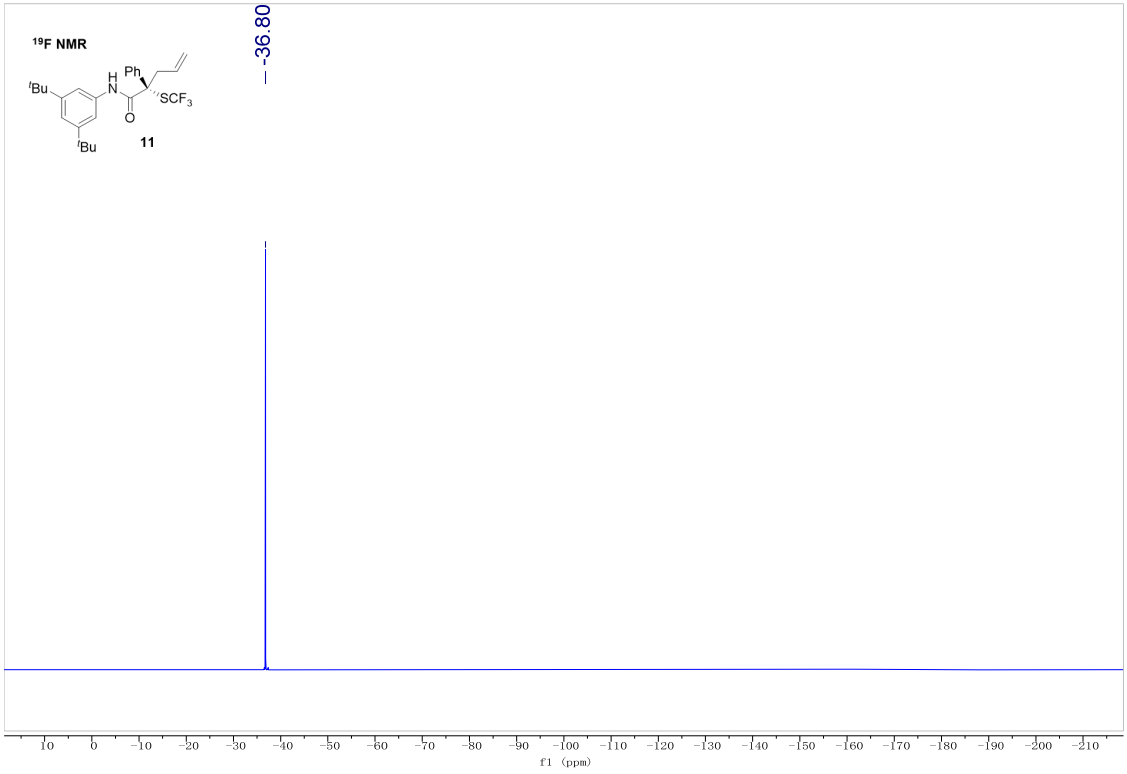

168.486
151.761
137.608
136.433
134.852
134.203
131.125
129.891
128.814
128.781
128.045
127.391
124.946
124.420
119.255
114.637
77.318
77.000
76.682
66.226
39.257
34.939
31.347
13C NMR
tBu
Ph
N
H
O
SCF3
S
tBu
9
f1 (ppm)

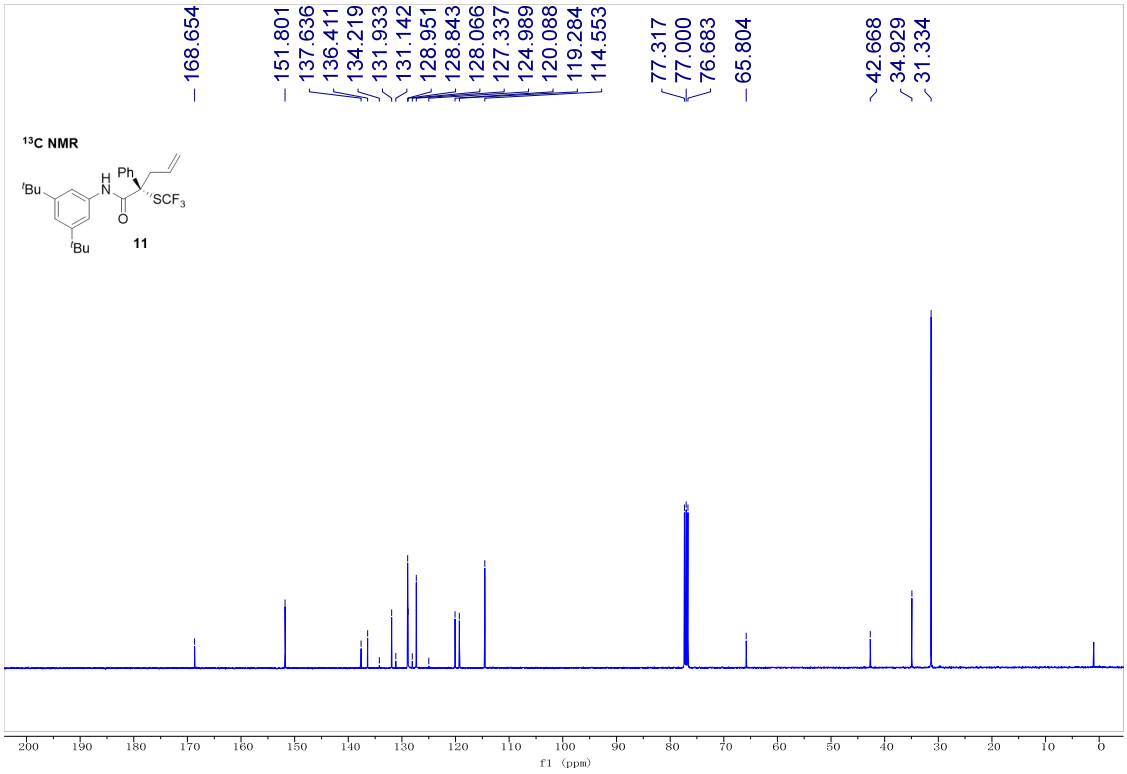

7.558
7.502
7.497
7.399
7.391
7.386
7.259
7.255
7.240
7.236
7.231
2.947
2.936
2.912
2.902
2.880
2.869
2.675
2.665
2.643
2.634
2.608
2.598
2.403
2.256
2.244
2.233
2.087
1.309
0.000
1H NMR
CF3
tBu
Ph
N
H
O
SCF3
tBu
10
1.079
4.867
2.976
1.000
0.998
1.059
1.027
17.666
f1 (ppm)

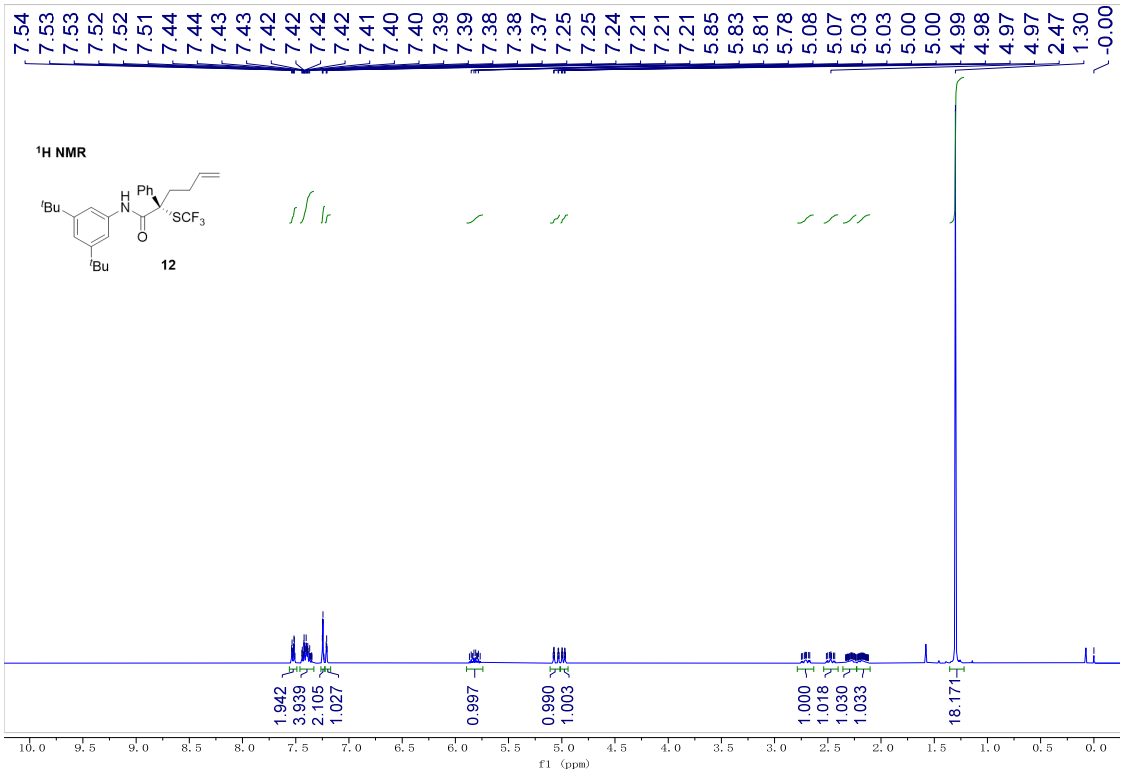

19F NMR
-37.033
-66.085
-66.113
-66.141
10
3.000
3.543
f1 (ppm)

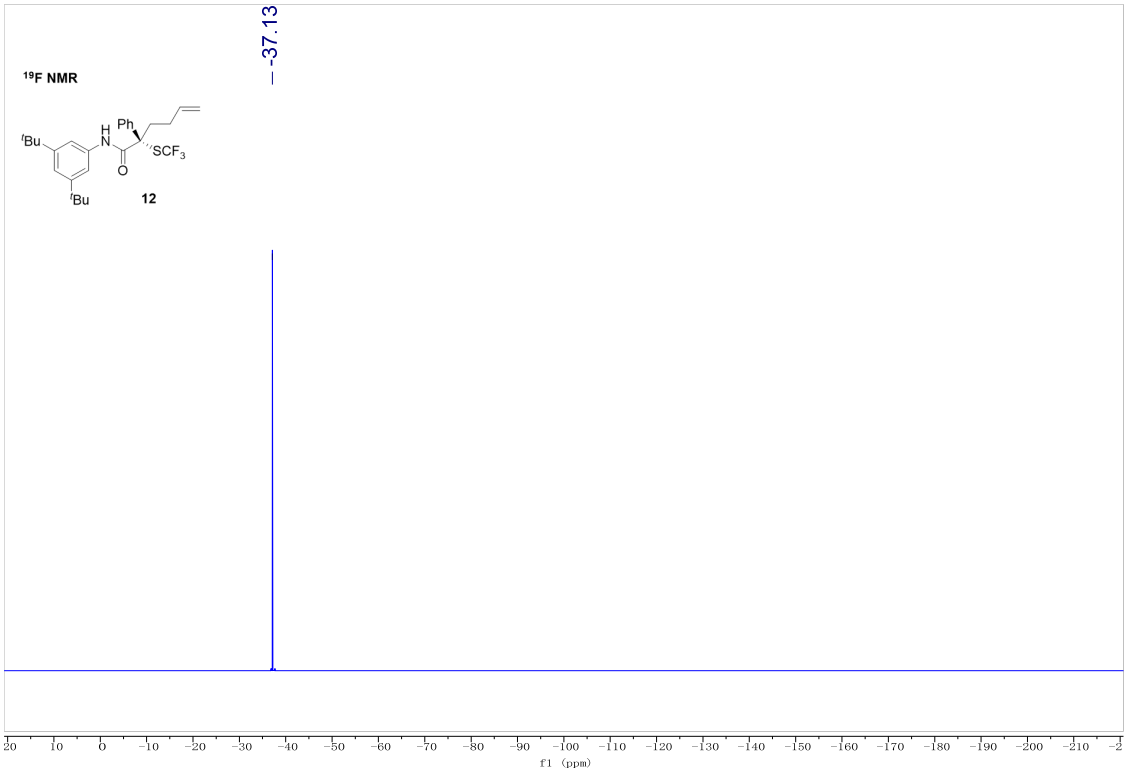

13C NMR
168.277
151.957
136.710
136.285
133.812
130.966
130.730
129.522
129.399
128.221
127.649
126.716
125.474
124.568
122.729
119.516
114.461
77.318
77.000
76.682
64.625
34.955
31.326
30.971
30.588
30.299
30.009
29.718
10
f1 (ppm)

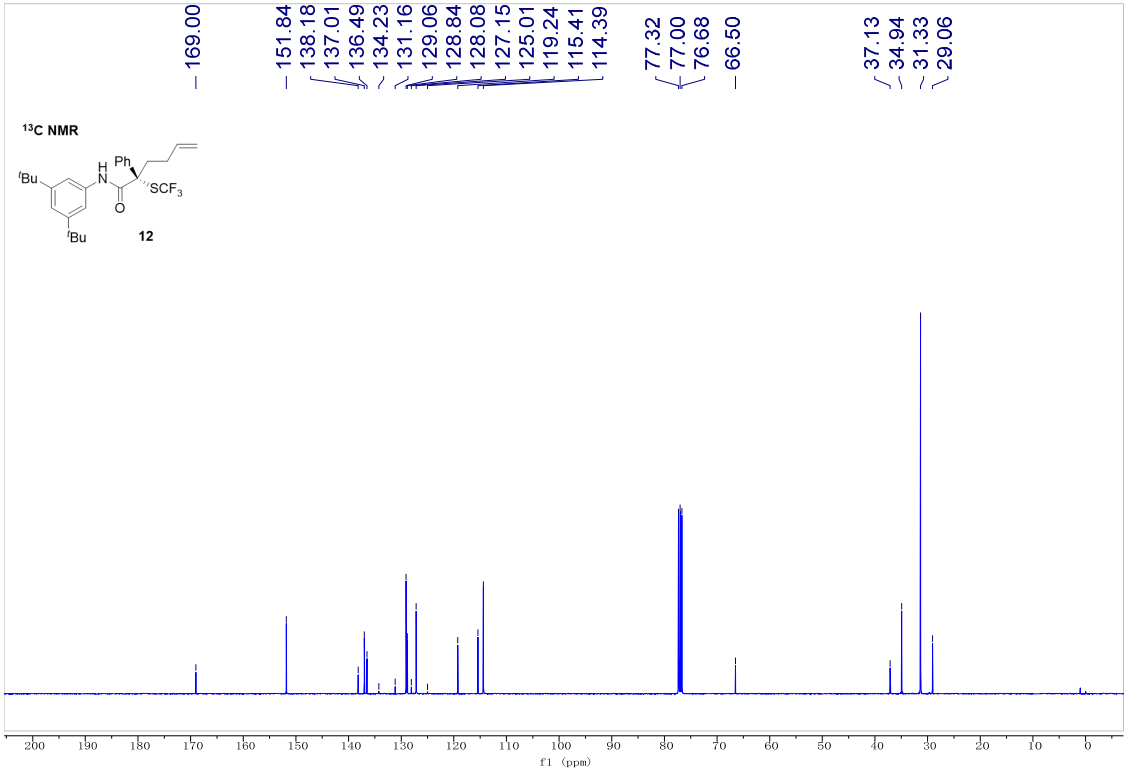

7.525
7.513
7.509
7.492
7.434
7.430
7.413
7.394
7.381
7.363
7.345
7.247
7.215
5.891
5.873
5.864
5.848
5.830
5.822
5.813
5.805
5.787
5.151
5.126
5.084
3.393
3.376
3.356
3.339
3.233
3.215
3.196
3.178
1.303
0.000
1H NMR
tBu
H
N
Ph
SCF3
O
tBu
11
3.032
2.985
2.062
0.973
0.965
1.956
1.000
0.988
18.052
f1 (ppm)

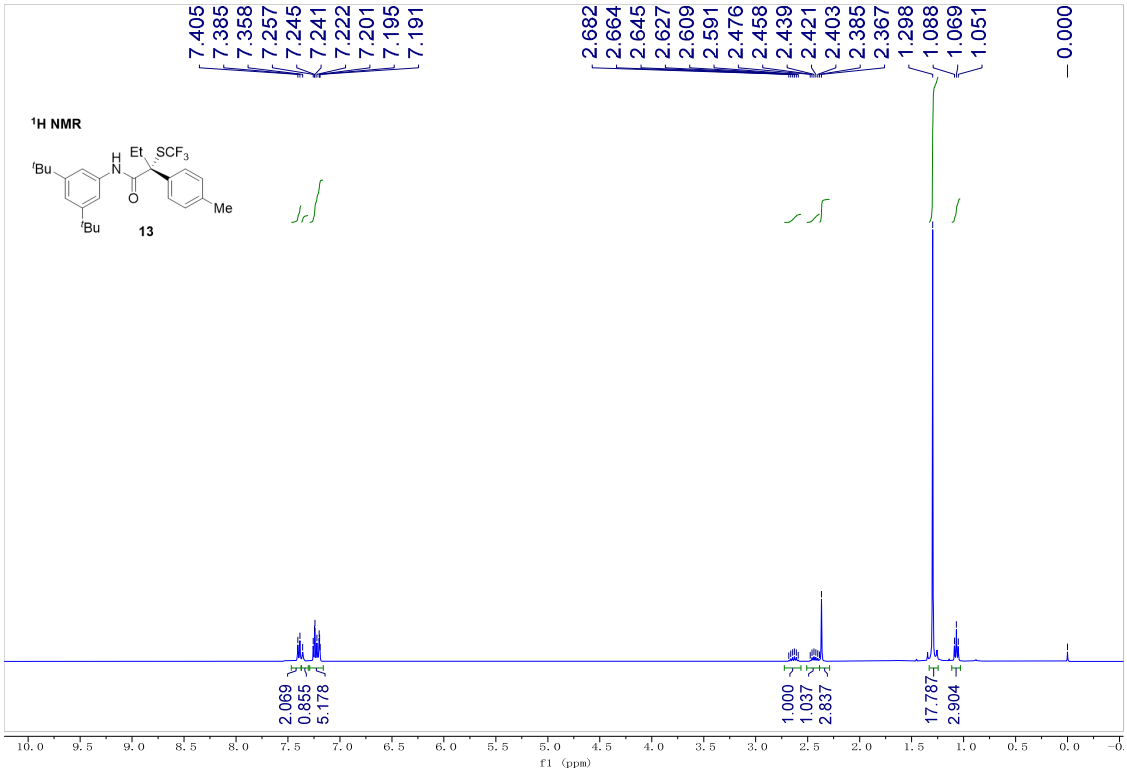

-36.80
19F NMR
tBu
H
N
Ph
SCF3
O
tBu
11
f1 (ppm)

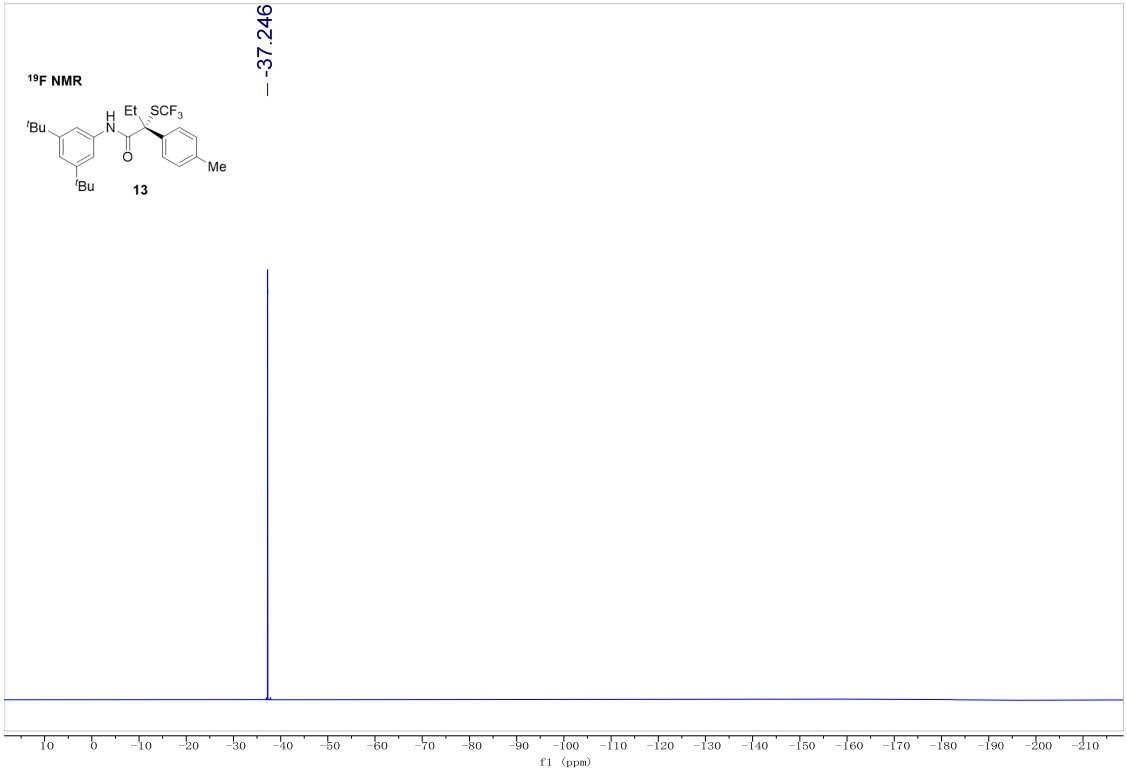

168.654
151.801
137.636
136.411
134.219
131.933
131.142
128.951
128.843
128.066
127.337
124.989
120.088
119.284
114.553
77.317
77.000
76.683
65.804
42.668
34.929
31.334
13C NMR
tBu
H
N
Ph
SCF3
O
tBu
11
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

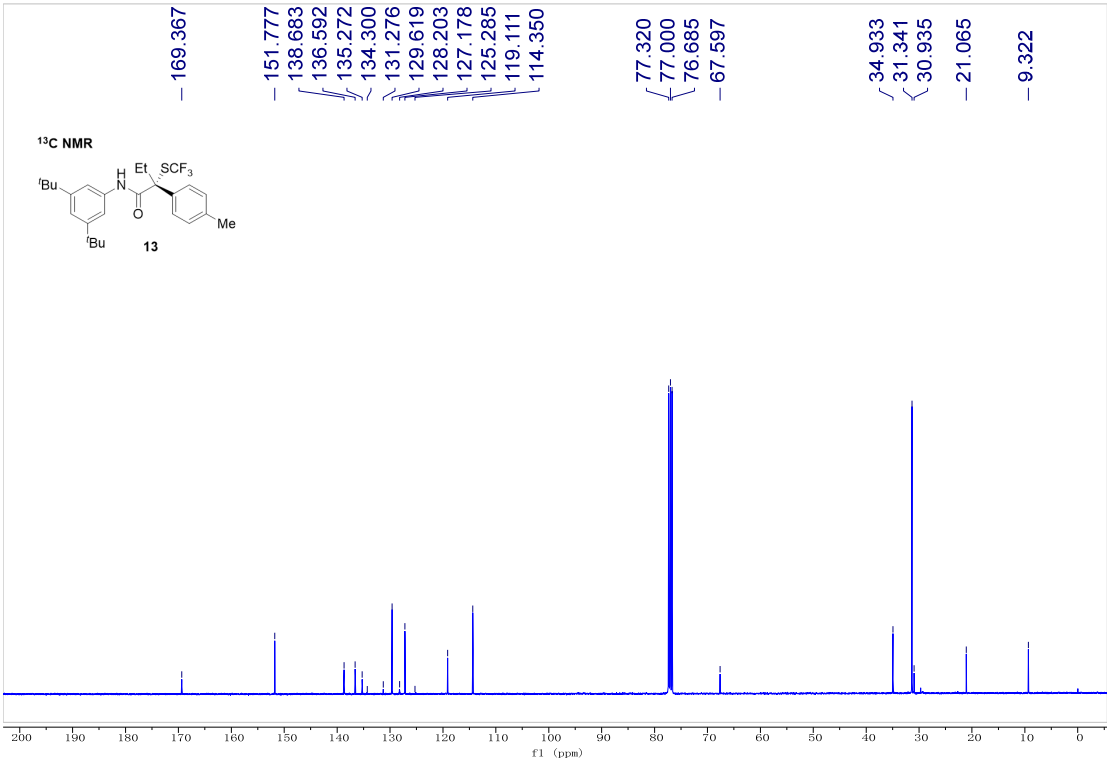

7.54
7.53
7.53
7.52
7.52
7.51
7.44
7.44
7.43
7.43
7.42
7.42
7.42
7.42
7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.25
7.25
7.24
7.21
7.21
7.21
5.85
5.83
5.81
5.78
5.08
5.07
5.03
5.03
5.00
5.00
4.99
4.98
4.97
2.47
1.30
-0.00
1H NMR
tBu
H
N
Ph
SCF3
O
tBu
12
1.942
3.939
2.105
1.027
0.997
0.990
1.003
1.000
1.018
1.030
1.033
18.171
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

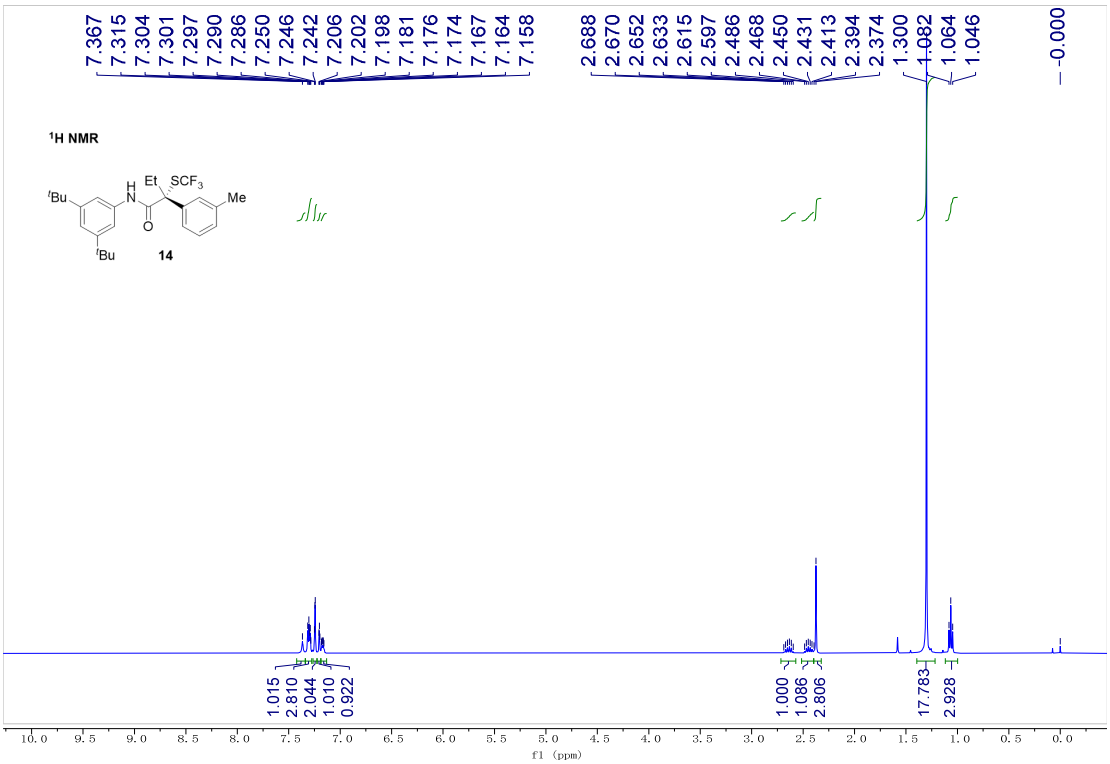

19F NMR
-37.13
tBu
Ph
H
N
O
SCF3
tBu
12
f1 (ppm)

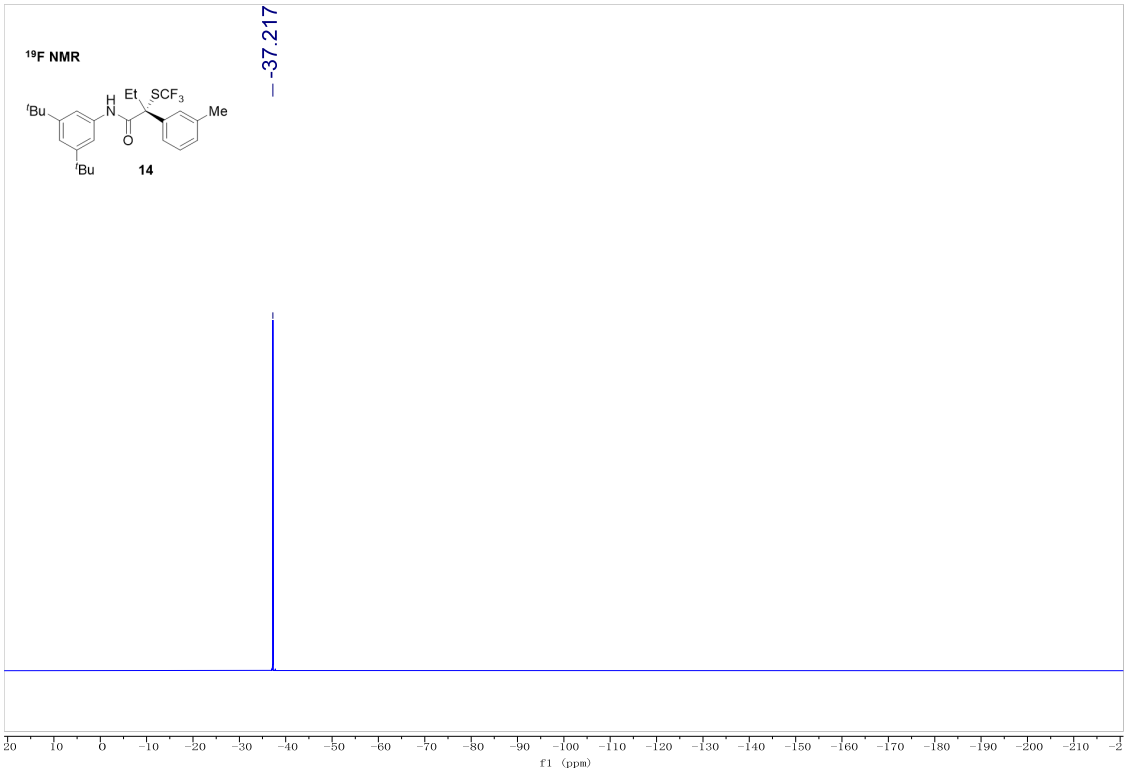

13C NMR
169.00
151.84
138.18
137.01
136.49
134.23
131.16
129.06
128.84
128.08
127.15
125.01
119.24
115.41
114.39
77.32
77.00
76.68
66.50
37.13
34.94
31.33
29.06
tBu
Ph
H
N
O
SCF3
tBu
12
f1 (ppm)

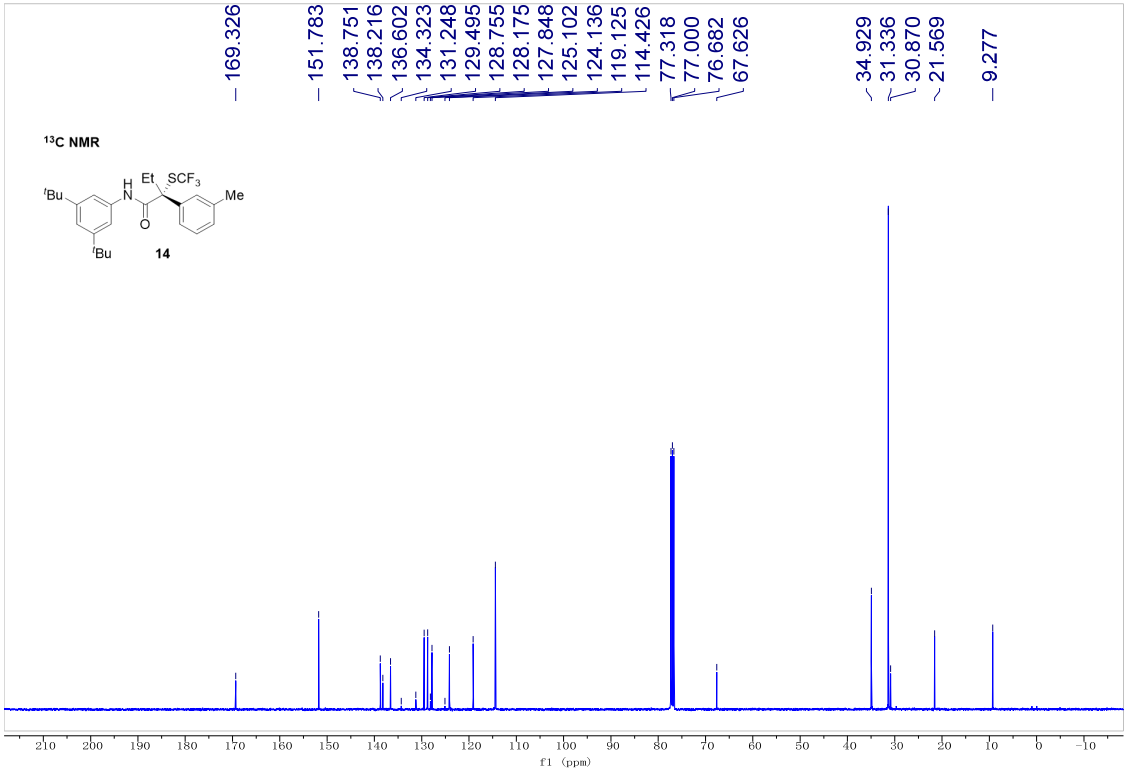

7.405
7.385
7.358
7.257
7.245
7.241
7.222
7.201
7.195
7.191
2.682
2.664
2.645
2.627
2.609
2.591
2.476
2.458
2.439
2.421
2.403
2.385
2.367
1.298
1.088
1.069
1.051
0.000
1H NMR
tBu
H
N
Et
SCF3
O
Me
tBu
13
2.069
0.855
5.178
1.000
1.037
2.837
17.787
2.904
f1 (ppm)

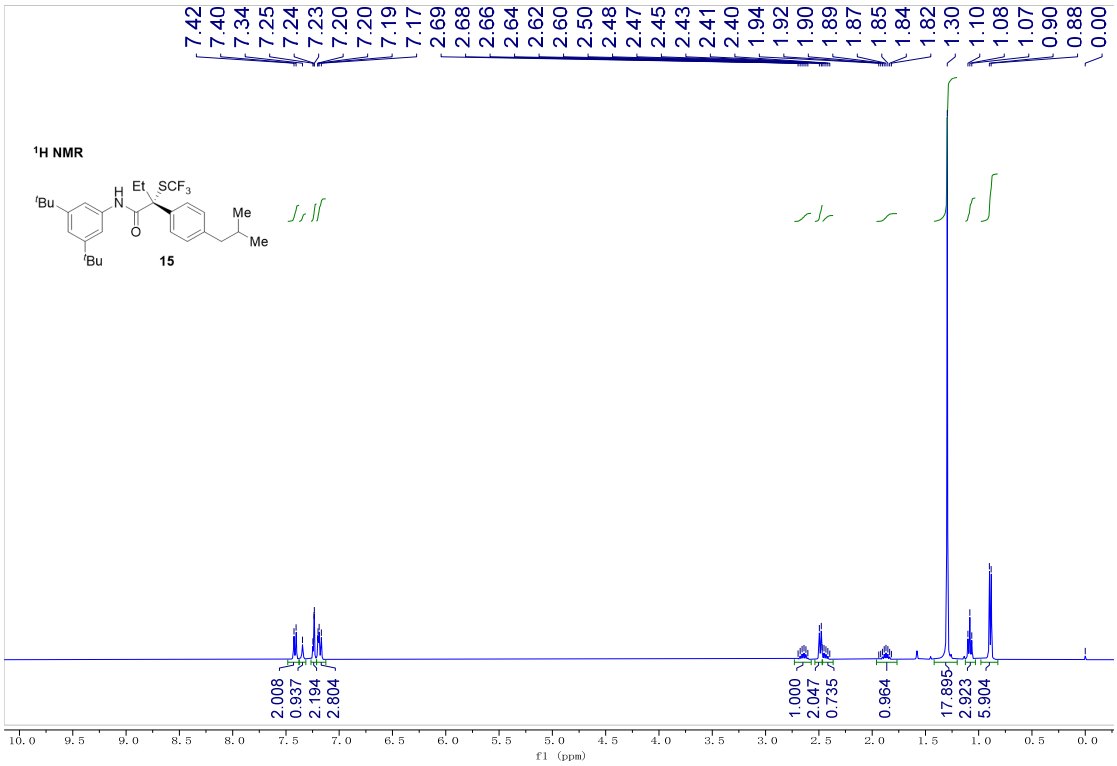

-37.246
19F NMR
tBu
H
N
Et
SCF3
O
Me
tBu
13
f1 (ppm)

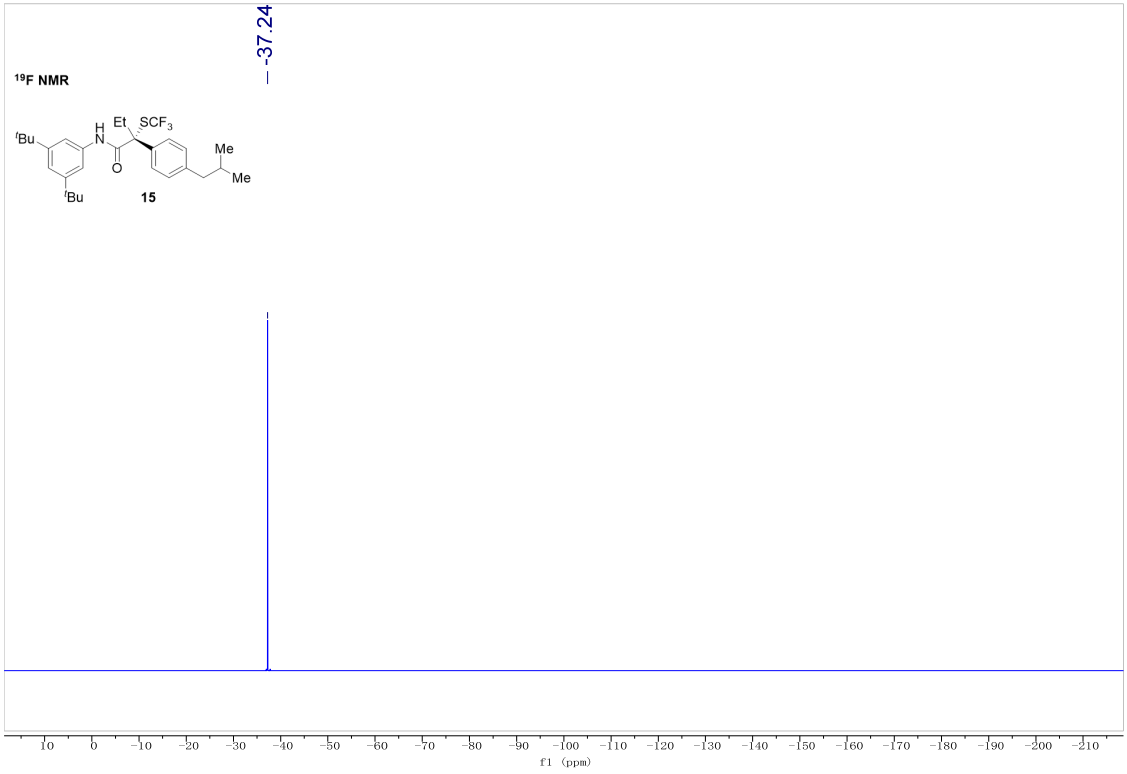

169.367
151.777
138.683
136.592
135.272
134.300
131.276
129.619
128.203
127.178
125.285
119.111
114.350
77.320
77.000
76.685
67.597
34.933
31.341
30.935
21.065
9.322
13C NMR
tBu
H
N
Et
SCF3
O
Me
tBu
13
f1 (ppm)

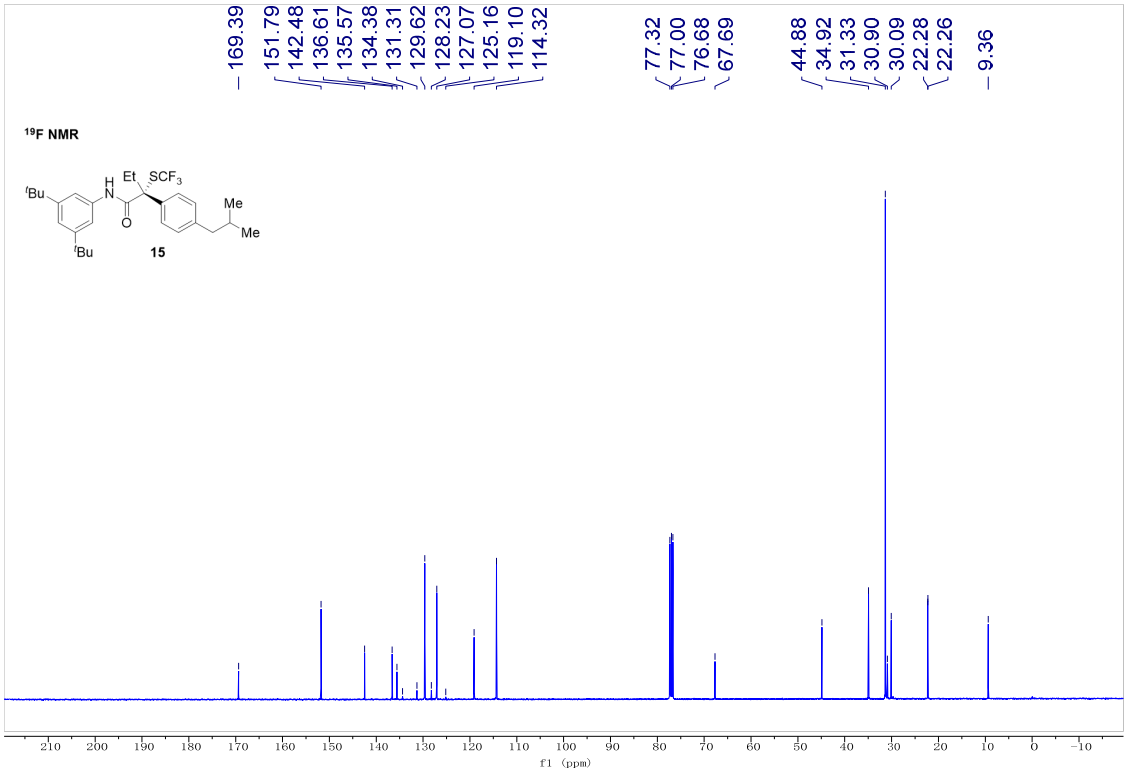

7.367
7.315
7.304
7.301
7.297
7.290
7.286
7.250
7.246
7.242
7.206
7.202
7.198
7.181
7.176
7.174
7.167
7.164
7.158
2.688
2.670
2.652
2.633
2.615
2.597
2.486
2.468
2.450
2.431
2.413
2.394
2.374
1.300
1.082
1.064
1.046
-0.000
1H NMR
tBu
H
N
Et
SCF3
Me
O
tBu
14
1.015
2.810
2.044
1.010
0.922
1.000
1.086
2.806
17.783
2.928
f1 (ppm)

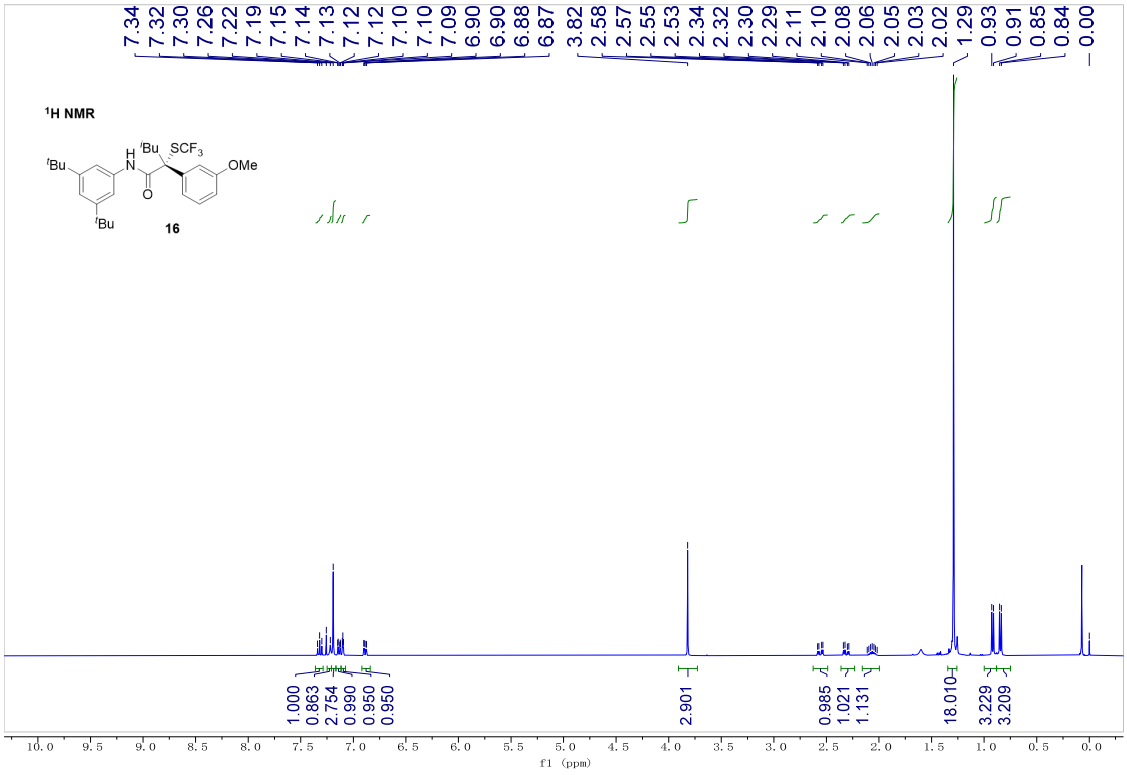

19F NMR
-37.217
tBu
H
N
Et
SCF3
Me
O
tBu
14
f1 (ppm)

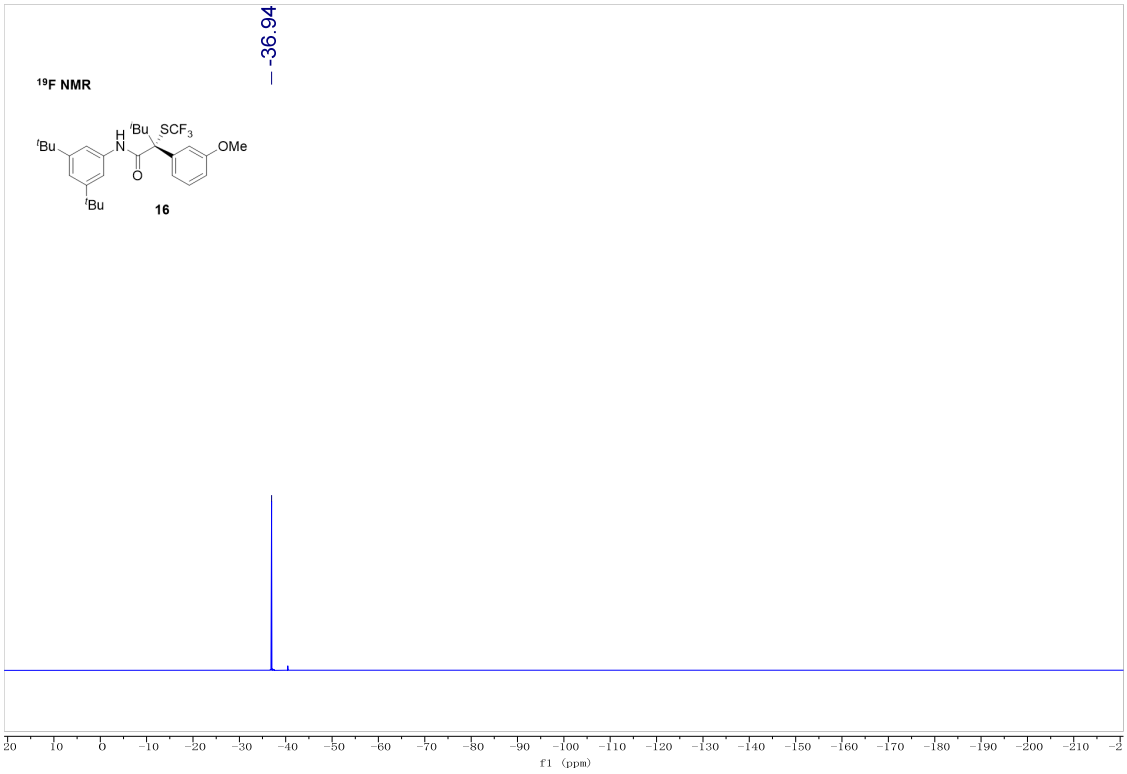

169.326
151.783
138.751
138.216
136.602
134.323
131.248
129.495
128.755
128.175
127.848
125.102
124.136
119.125
114.426
77.318
77.000
76.682
67.626
34.929
31.336
30.870
21.569
9.277
13C NMR
tBu
H
N
Et
SCF3
Me
O
tBu
14
f1 (ppm)

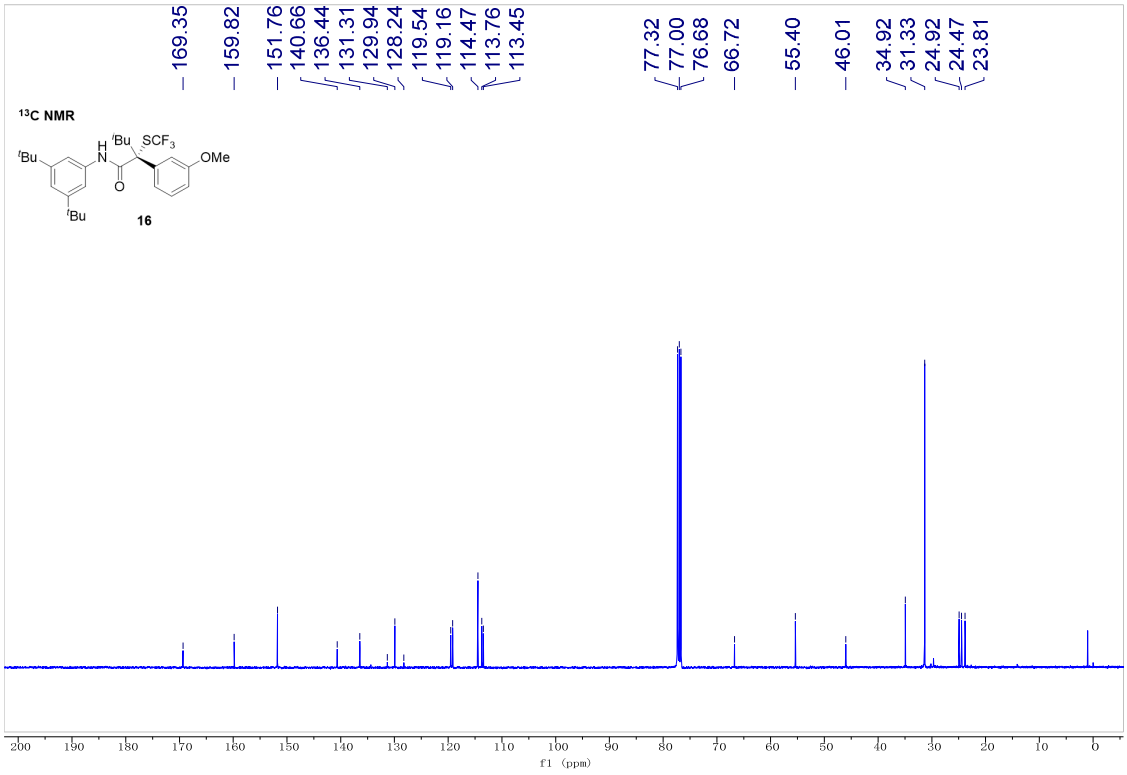

7.42
7.40
7.34
7.25
7.24
7.23
7.20
7.20
7.19
7.17
2.69
2.68
2.66
2.64
2.62
2.60
2.50
2.48
2.47
2.45
2.43
2.41
2.40
1.94
1.92
1.90
1.89
1.87
1.85
1.84
1.82
1.30
1.10
1.08
1.07
0.90
0.88
0.00
1H NMR
tBu
H
N
Et
SCF3
O
Me
Me
tBu
15
2.008
0.937
2.194
2.804
1.000
2.047
0.735
0.964
17.895
2.923
5.904
f1 (ppm)

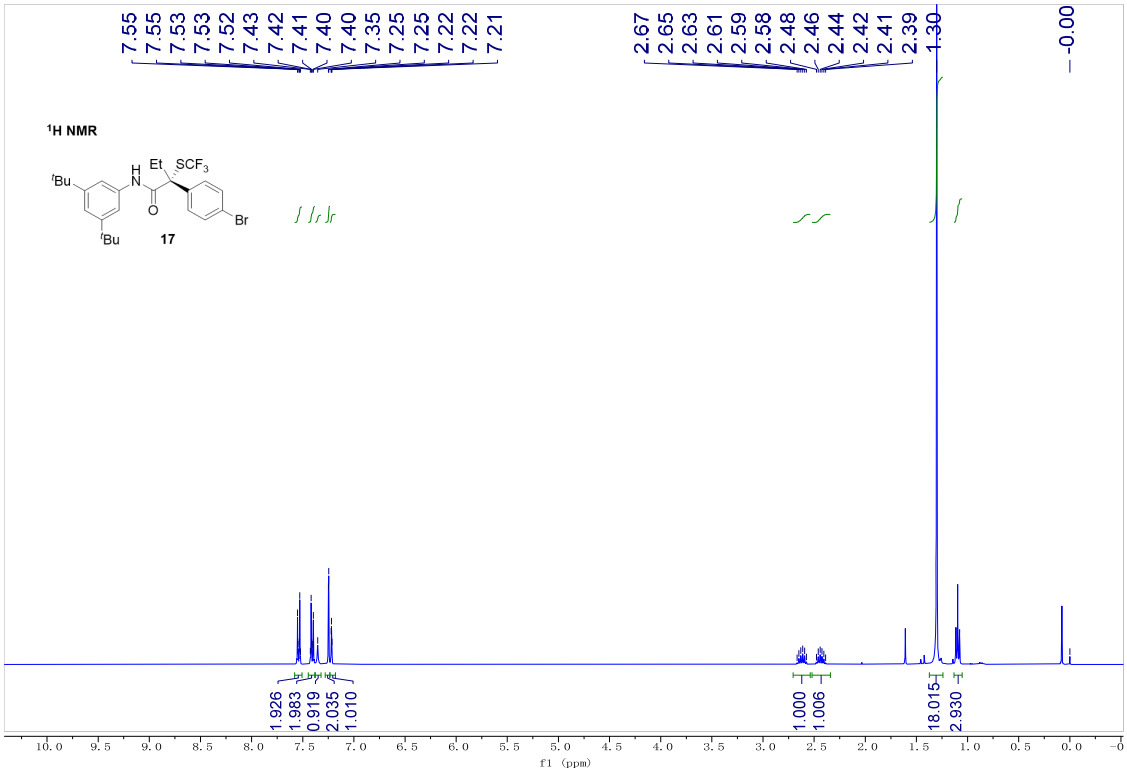

-37.24
19F NMR
tBu
H
N
Et
SCF3
O
Me
Me
tBu
15
f1 (ppm)

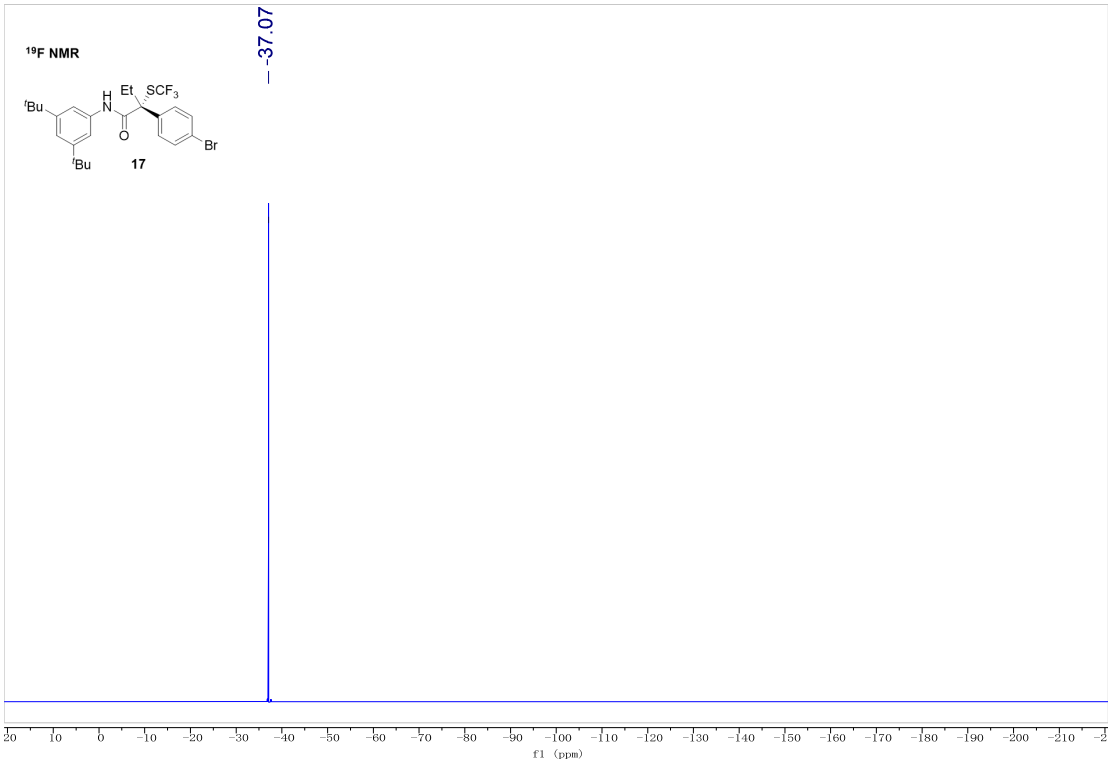

169.39
151.79
142.48
136.61
135.57
134.38
131.31
129.62
128.23
127.07
125.16
119.10
114.32
77.32
77.00
76.68
67.69
44.88
34.92
31.33
30.90
30.09
22.28
22.26
9.36
19F NMR
tBu
Et
SCF3
H
N
O
Me
Me
tBu
15
f1 (ppm)

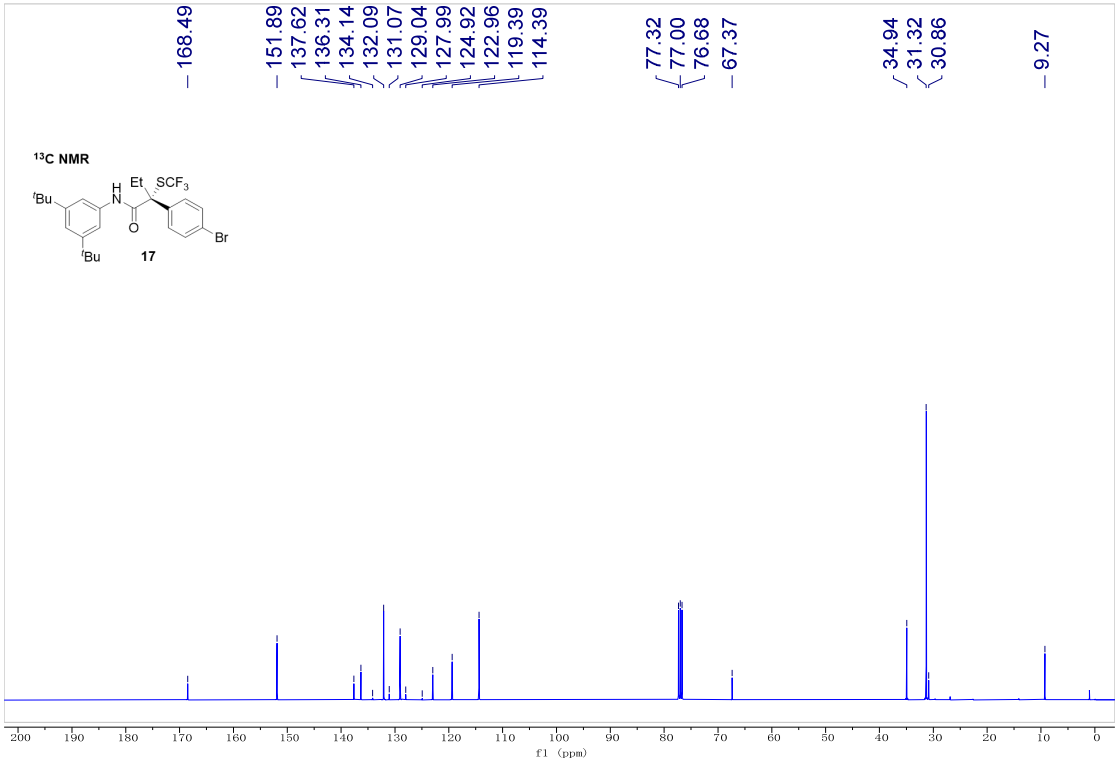

7.34
7.32
7.30
7.26
7.22
7.19
7.15
7.14
7.13
7.12
7.12
7.10
7.10
7.09
6.90
6.90
6.88
6.87
3.82
2.58
2.57
2.55
2.53
2.34
2.32
2.30
2.29
2.11
2.10
2.08
2.06
2.05
2.03
2.02
1.29
0.93
0.91
0.85
0.84
0.00
1H NMR
tBu
tBu
H
N
tBu
SCF3
O
OMe
tBu
16
1.000
0.863
2.754
0.990
0.950
0.950
2.901
0.985
1.021
1.131
18.010
3.229
3.209
f1 (ppm)

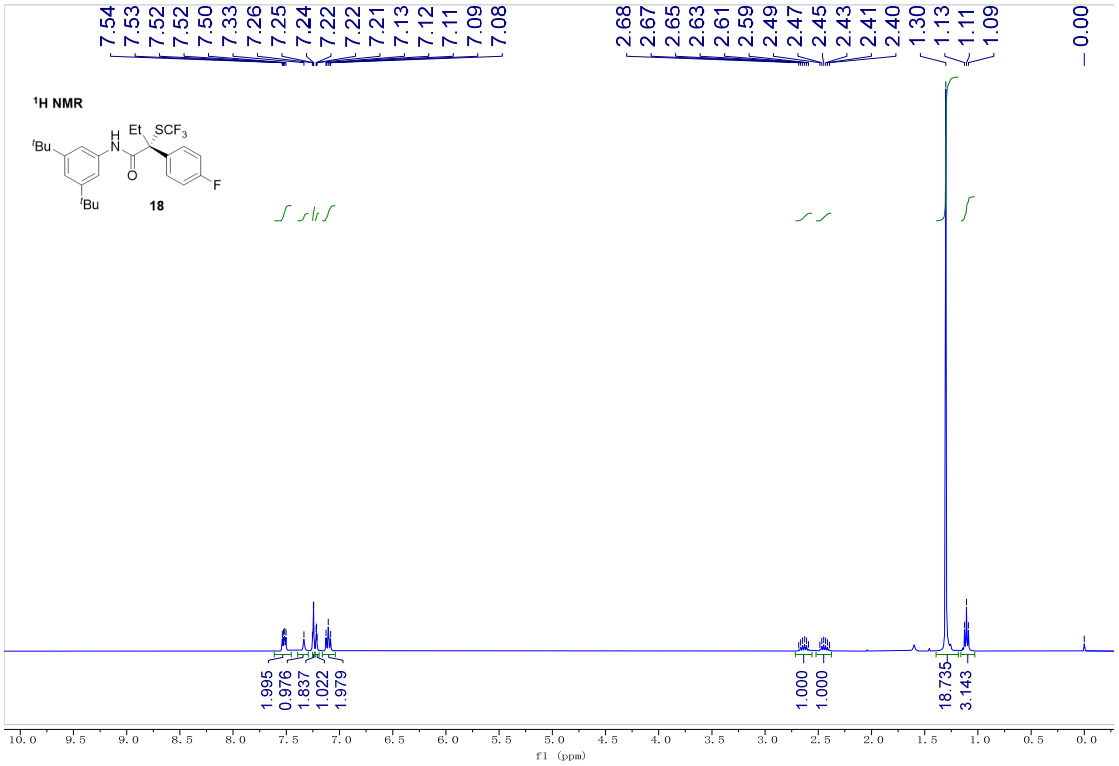

-36.94
19F NMR
tBu
tBu
H
N
O
tBu
SCF3
OMe
16
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

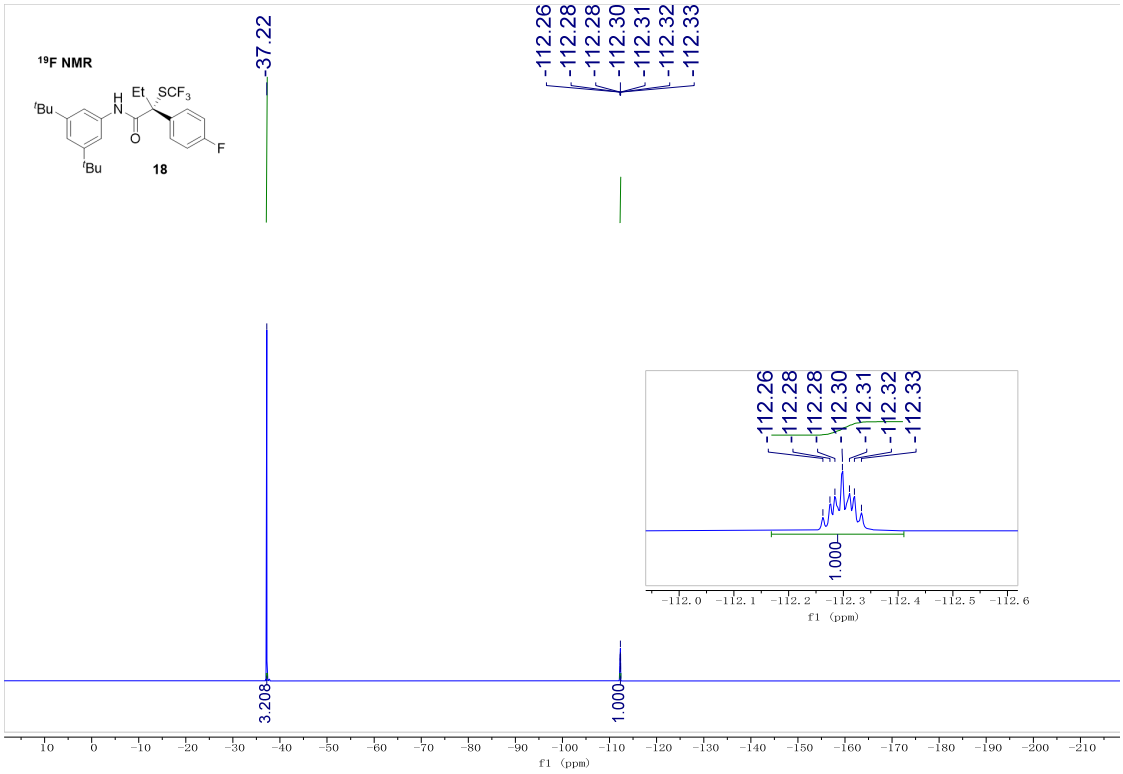

169.35
159.82
151.76
140.66
136.44
131.31
129.94
128.24
119.54
119.16
114.47
113.76
113.45
77.32
77.00
76.68
66.72
55.40
46.01
34.92
31.33
24.92
24.47
23.81
13C NMR
tBu
tBu
H
N
O
tBu
SCF3
OMe
16
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

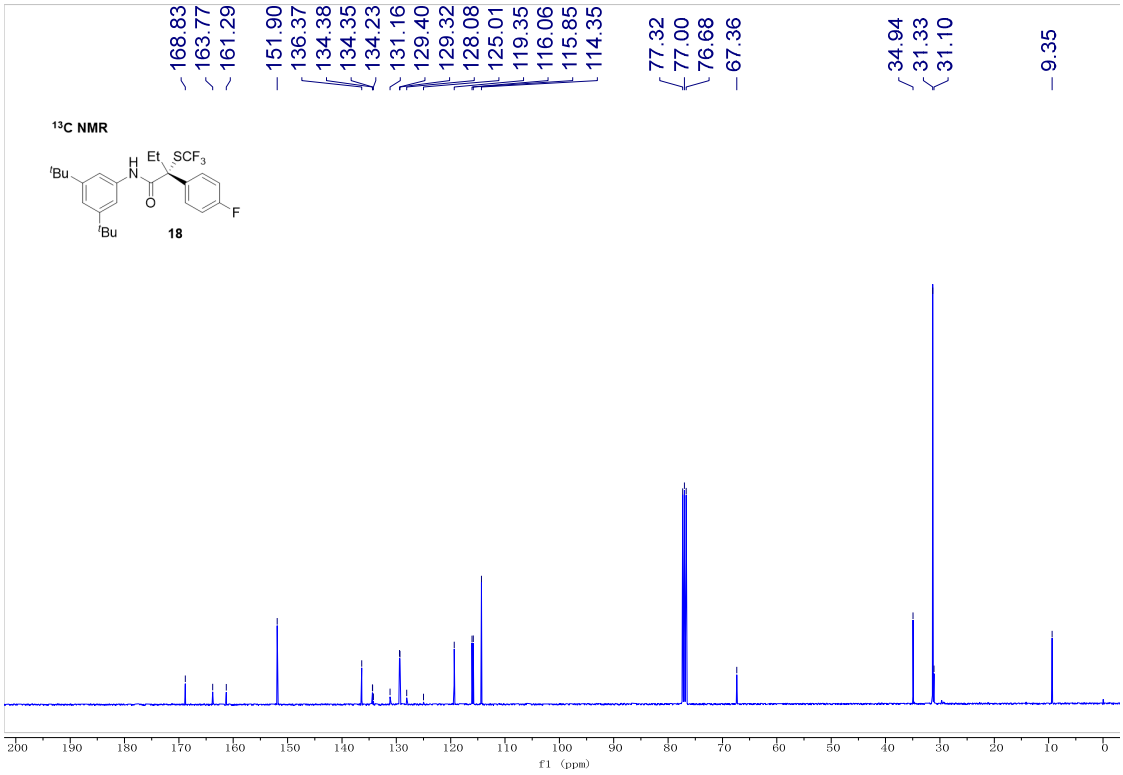

7.55
7.55
7.53
7.53
7.52
7.43
7.42
7.41
7.40
7.40
7.35
7.25
7.25
7.22
7.22
7.21
2.67
2.65
2.63
2.61
2.59
2.58
2.48
2.46
2.44
2.42
2.41
2.39
1.30
-0.00
1H NMR
tBu
Et
SCF3
H
N
O
Br
tBu
17
1.926
1.983
0.919
2.035
1.010
1.000
1.006
18.015
2.930
f1 (ppm)

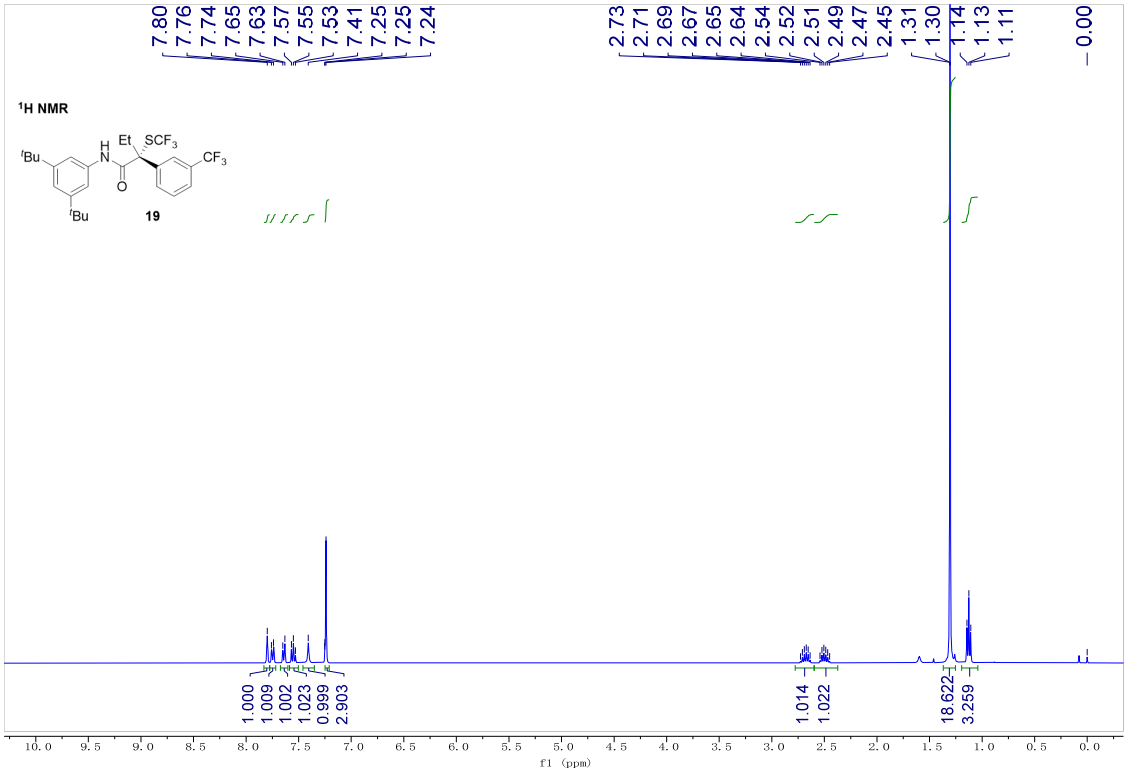

-37.07
19F NMR
tBu
Et
SCF3
H
N
O
Br
tBu
17
f1 (ppm)

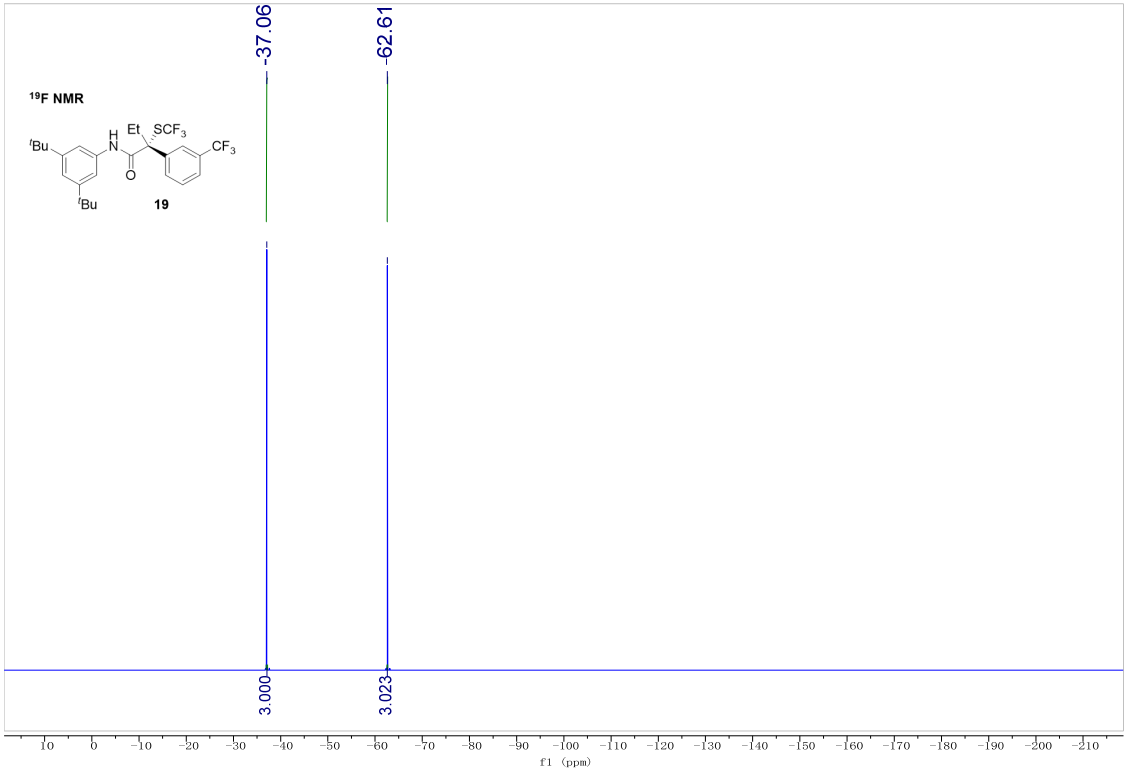

168.49
151.89
137.62
136.31
134.14
132.09
131.07
129.04
127.99
124.92
122.96
119.39
114.39
77.32
77.00
76.68
67.37
34.94
31.32
30.86
9.27
13C NMR
tBu
Et
SCF3
H
N
O
Br
tBu
17
f1 (ppm)

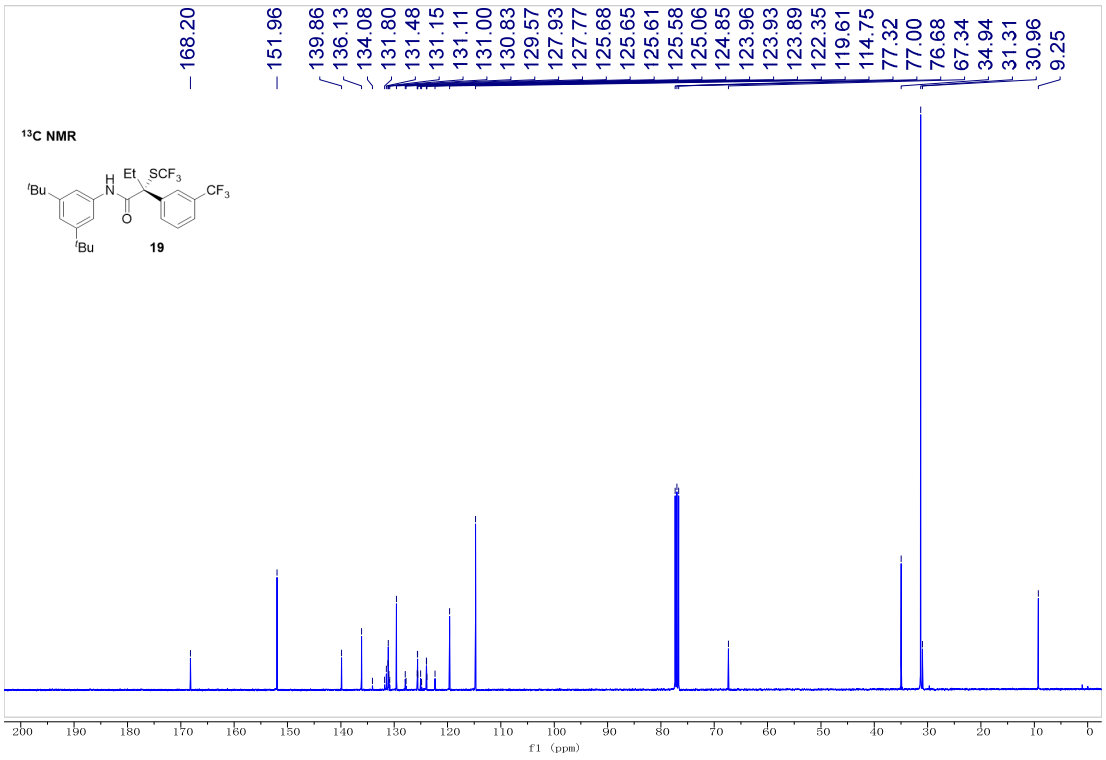

7.54
7.53
7.52
7.52
7.50
7.33
7.26
7.25
7.24
7.22
7.22
7.21
7.13
7.12
7.11
7.09
7.08
2.68
2.67
2.65
2.63
2.61
2.59
2.49
2.47
2.45
2.43
2.41
2.40
1.30
1.13
1.11
1.09
0.00
1H NMR
tBu
Et
SCF3
H
N
O
F
tBu
18
1.995
0.976
1.837
1.022
1.979
1.000
1.000
18.735
3.143
f1 (ppm)

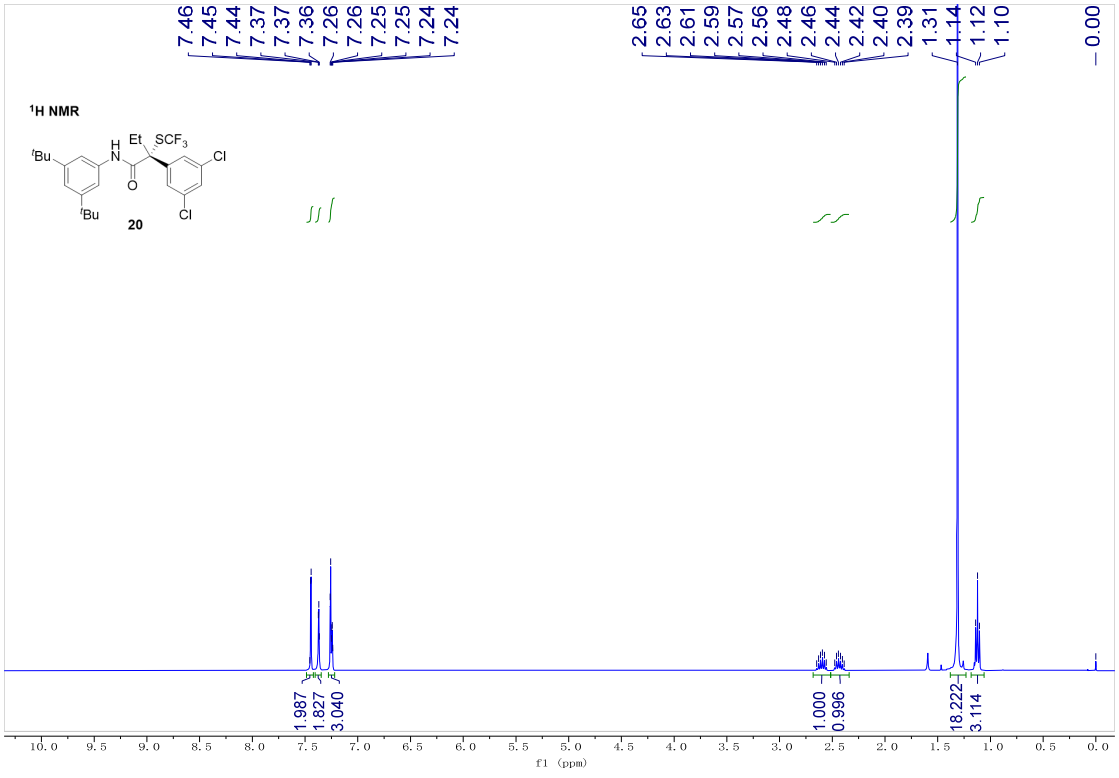

19F NMR
18
-37.22
-112.26
-112.28
-112.28
-112.30
-112.31
-112.32
-112.33
3.208
1.000
1.000
f1 (ppm)

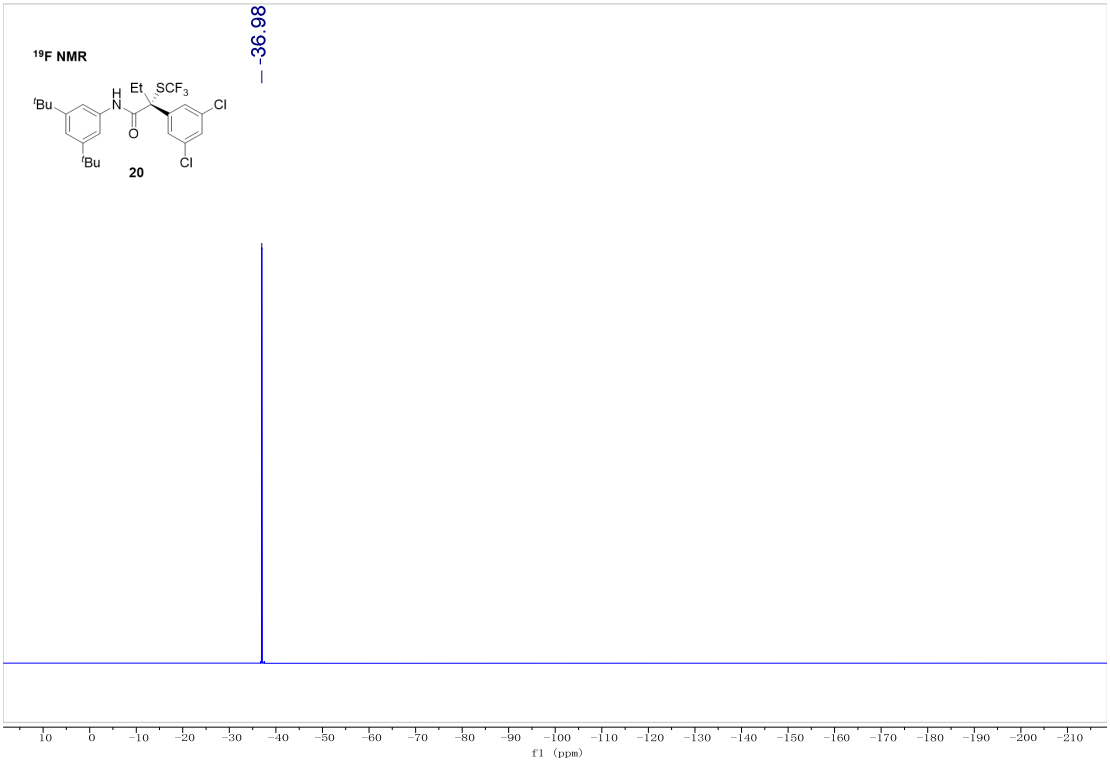

13C NMR
18
168.83
163.77
161.29
151.90
136.37
134.38
134.35
134.23
131.16
129.40
129.32
128.08
125.01
119.35
116.06
115.85
114.35
77.32
77.00
76.68
67.36
34.94
31.33
31.10
9.35
f1 (ppm)

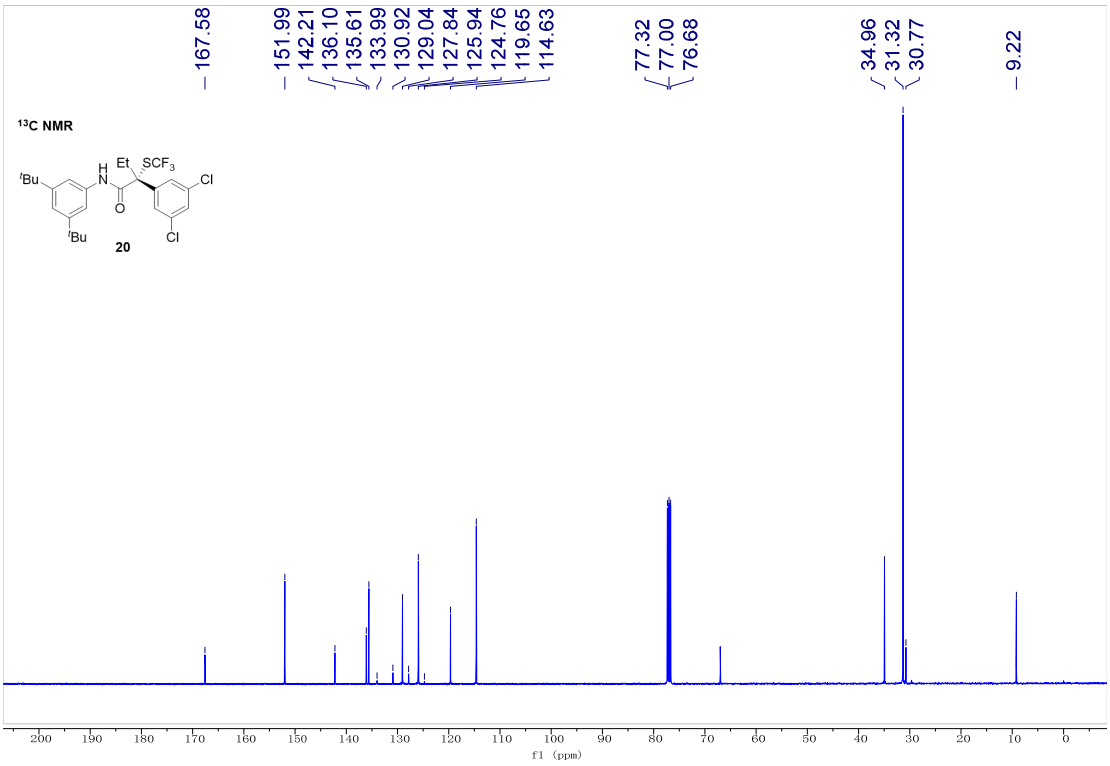

7.80
7.76
7.74
7.65
7.63
7.57
7.55
7.53
7.41
7.25
7.25
7.24
2.73
2.71
2.69
2.67
2.65
2.64
2.54
2.52
2.51
2.49
2.47
2.45
1.31
1.30
1.14
1.13
1.11
0.00
1H NMR
19
1.000
1.009
1.002
1.023
0.999
2.903
1.014
1.022
18.622
3.259
f1 (ppm)

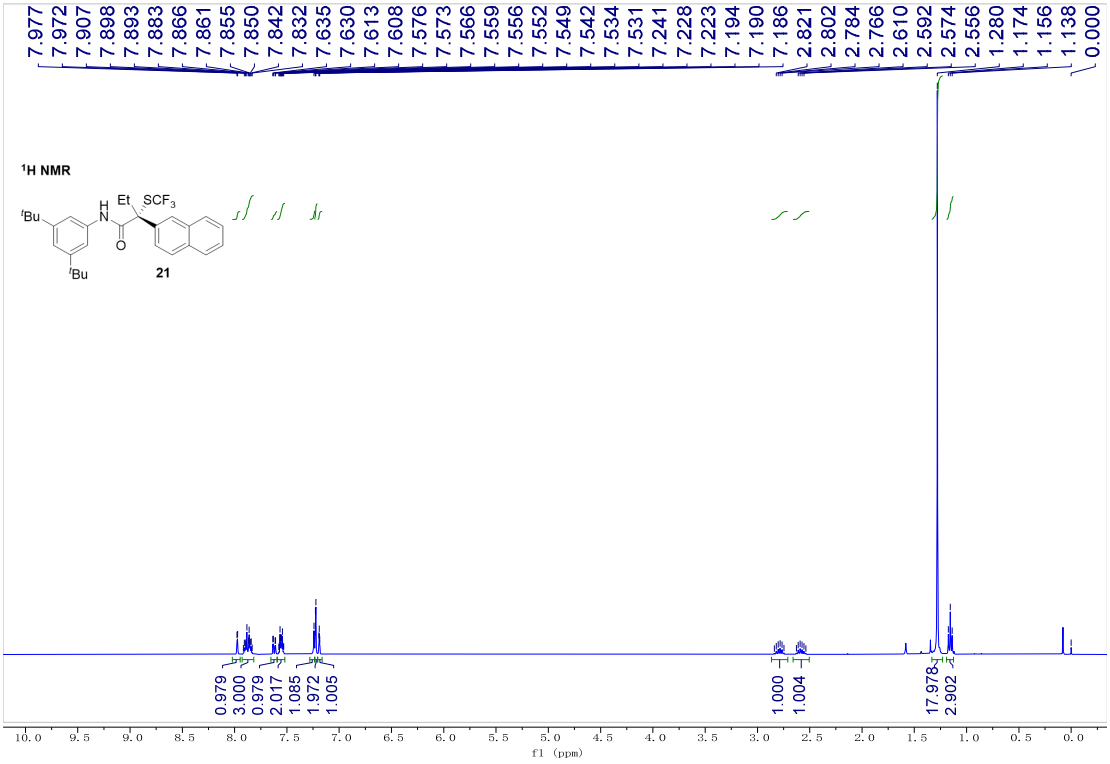

-37.06
-62.61
19F NMR
19
3.000
3.023
f1 (ppm)

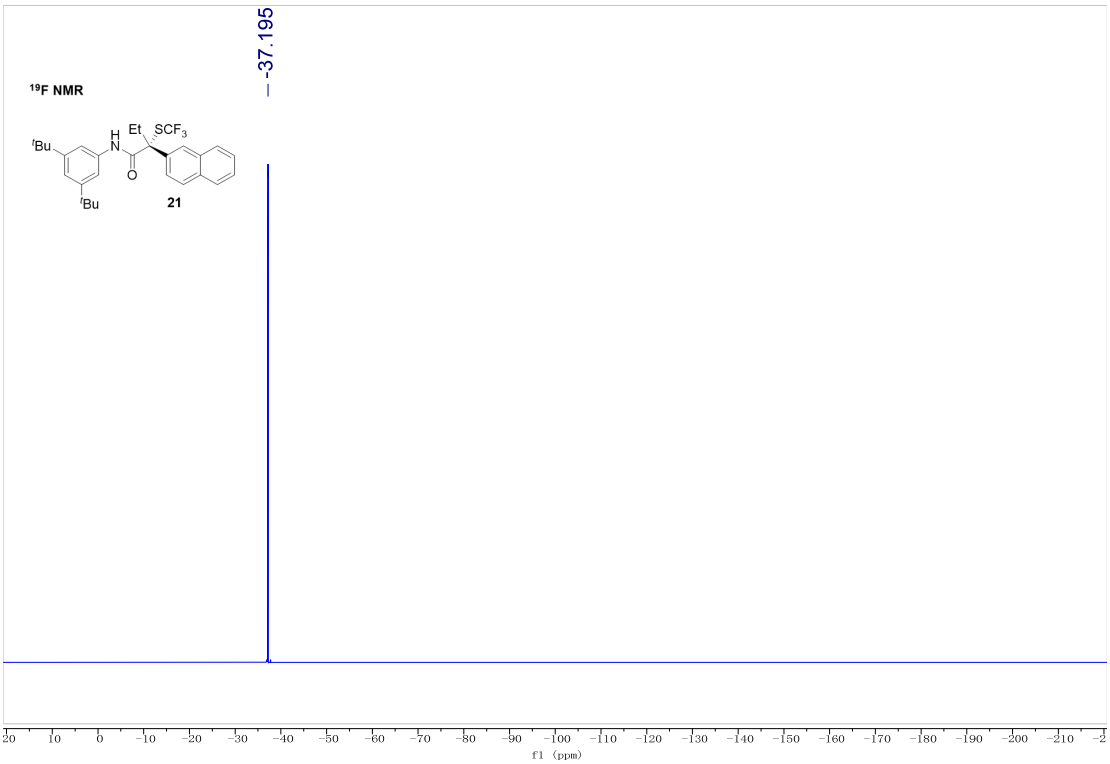

168.20
151.96
139.86
136.13
134.08
131.80
131.48
131.15
131.11
131.00
130.83
129.57
127.93
127.77
125.68
125.65
125.61
125.58
125.06
124.85
123.96
123.93
123.89
122.35
119.61
114.75
77.32
77.00
76.68
67.34
34.94
31.31
30.96
9.25
13C NMR
19
f1 (ppm)

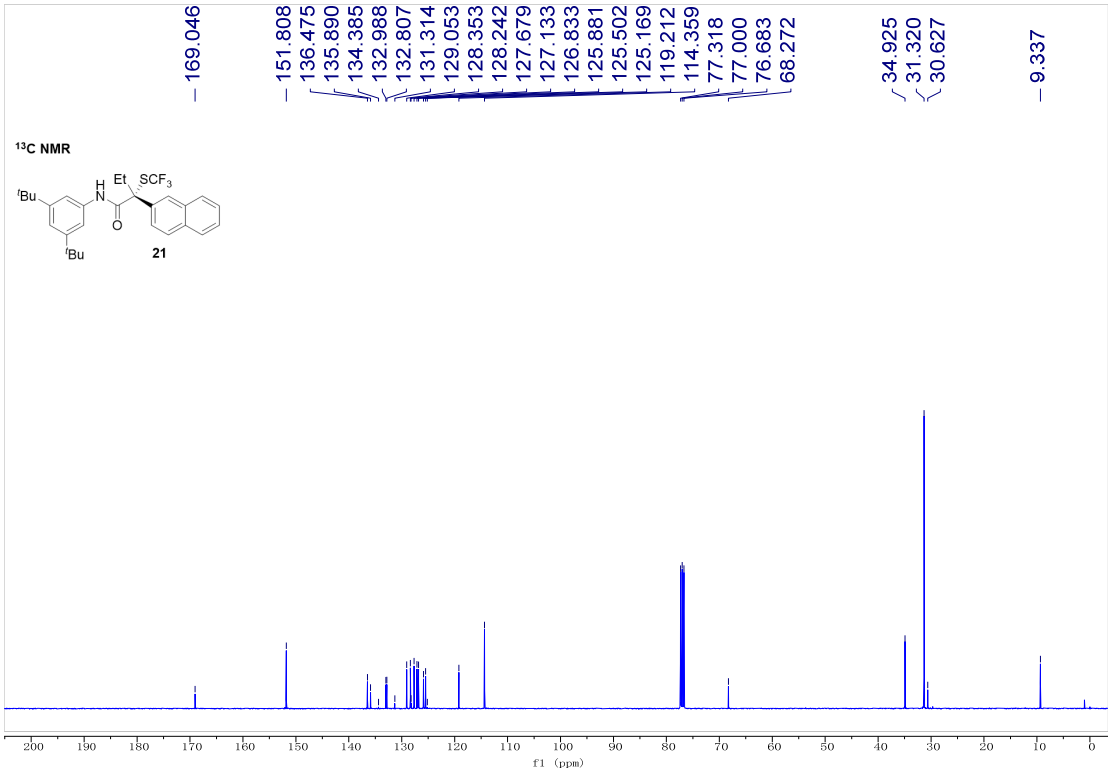

7.46
7.45
7.44
7.37
7.37
7.36
7.26
7.26
7.25
7.25
7.24
7.24
2.65
2.63
2.61
2.59
2.57
2.56
2.48
2.46
2.44
2.42
2.40
2.39
1.31
1.14
1.12
1.10
0.00
1H NMR
20
1.987
1.827
3.040
1.000
0.996
18.222
3.114
f1 (ppm)

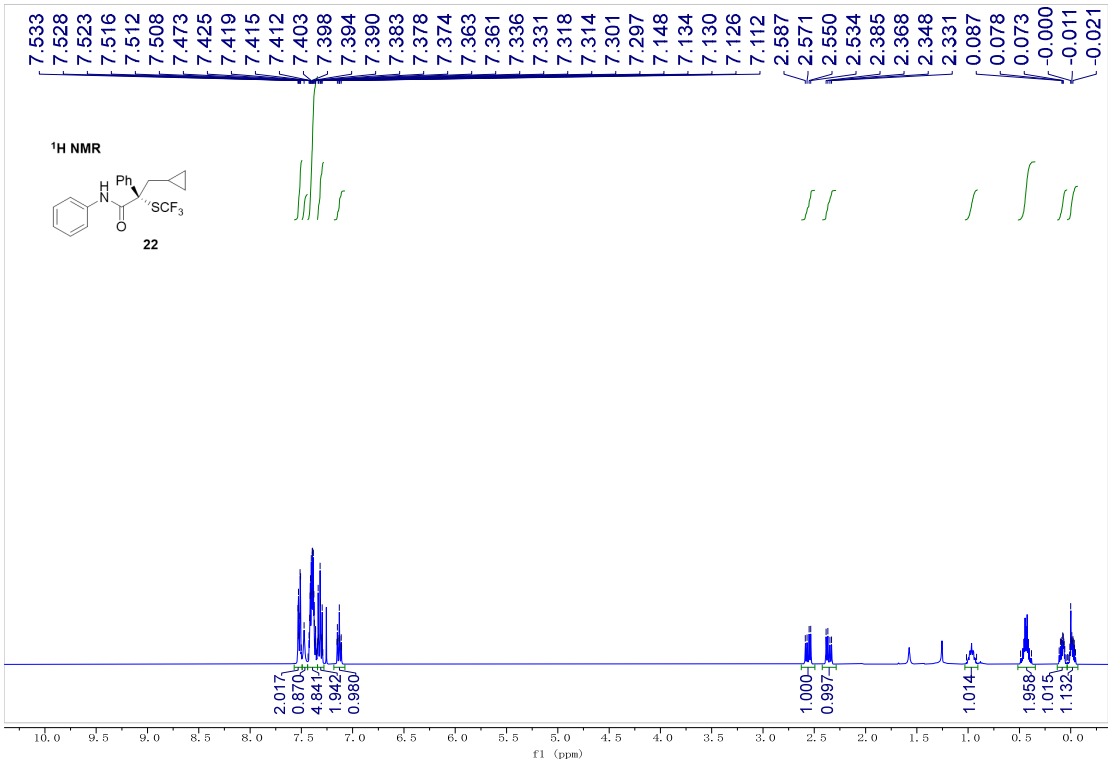

19F NMR
-36.98
tBu
Et
SCF3
Cl
tBu
Cl
20
f1 (ppm)

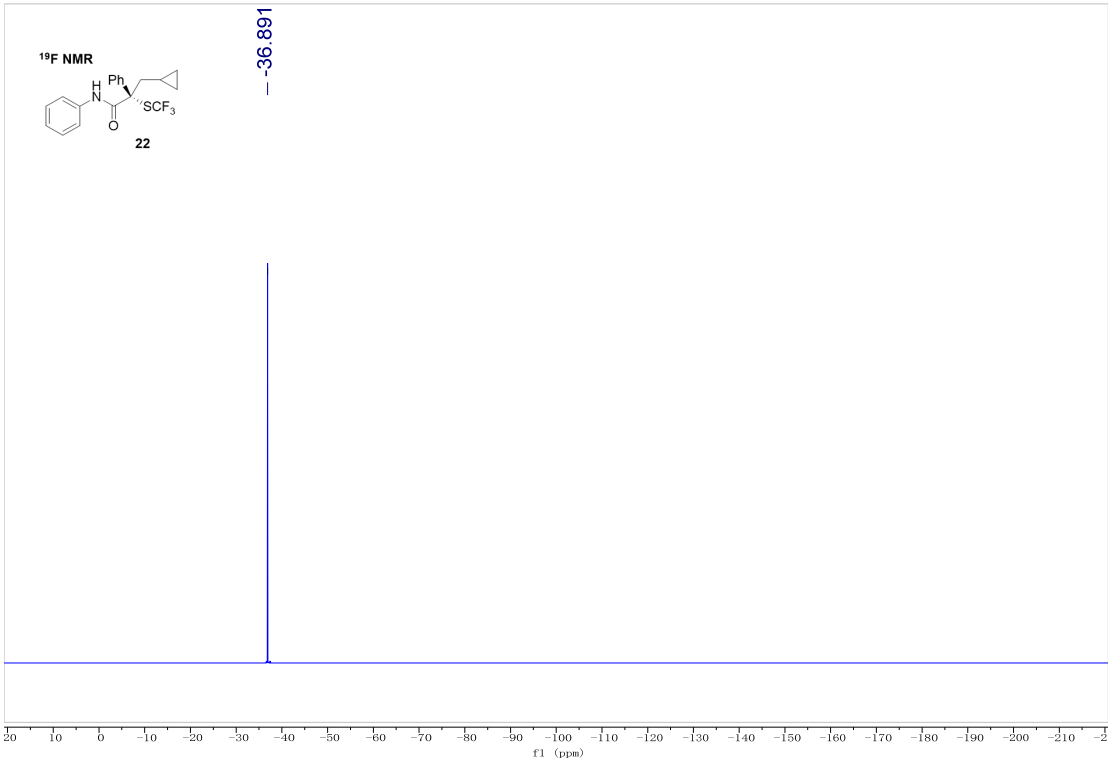

13C NMR
167.58
151.99
142.21
136.10
135.61
133.99
130.92
129.04
127.84
125.94
124.76
119.65
114.63
77.32
77.00
76.68
34.96
31.32
30.77
9.22
tBu
Et
SCF3
Cl
tBu
Cl
20
f1 (ppm)

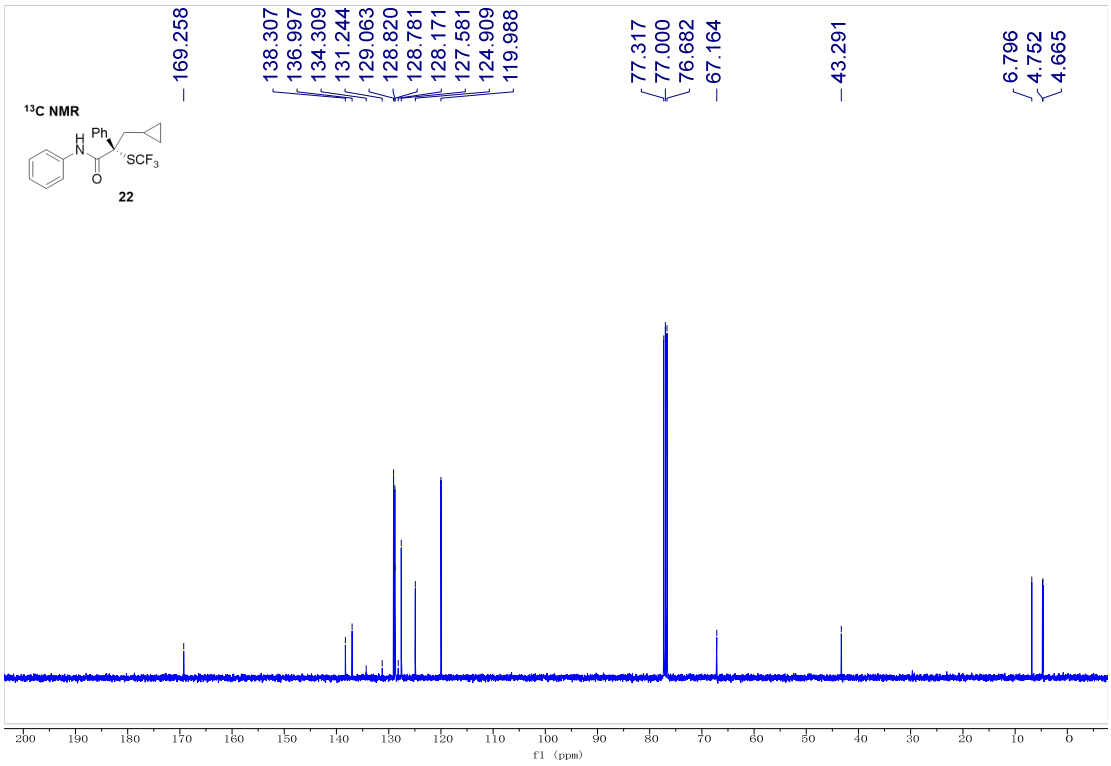

7.977
7.972
7.907
7.898
7.893
7.883
7.866
7.861
7.855
7.850
7.842
7.832
7.635
7.630
7.613
7.608
7.576
7.573
7.566
7.559
7.556
7.552
7.549
7.542
7.534
7.531
7.241
7.228
7.223
7.194
7.190
7.186
2.821
2.802
2.784
2.766
2.610
2.592
2.574
2.556
1.280
1.174
1.156
1.138
0.000
1H NMR
Et
SCF3
tBu
tBu
21
0.979
3.000
0.979
2.017
1.085
1.972
1.005
1.000
1.004
17.978
2.902
f1 (ppm)

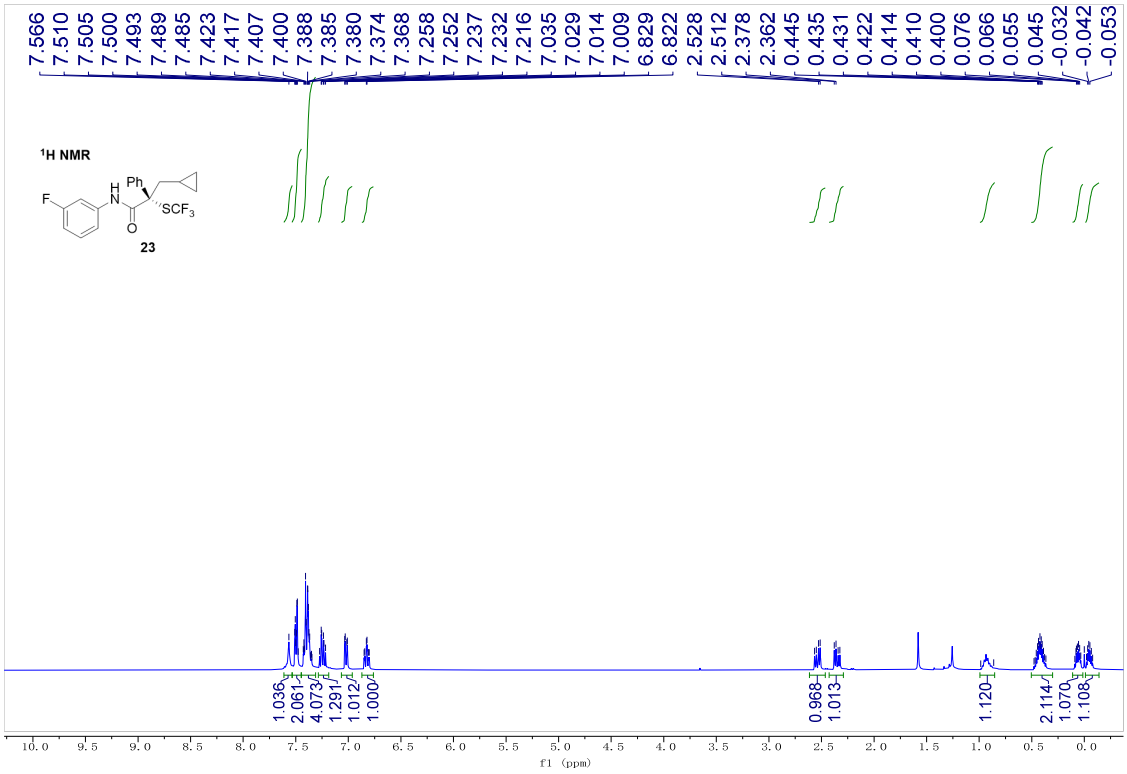

-37.195
19F NMR
Et
SCF3
tBu
tBu
21
f1 (ppm)

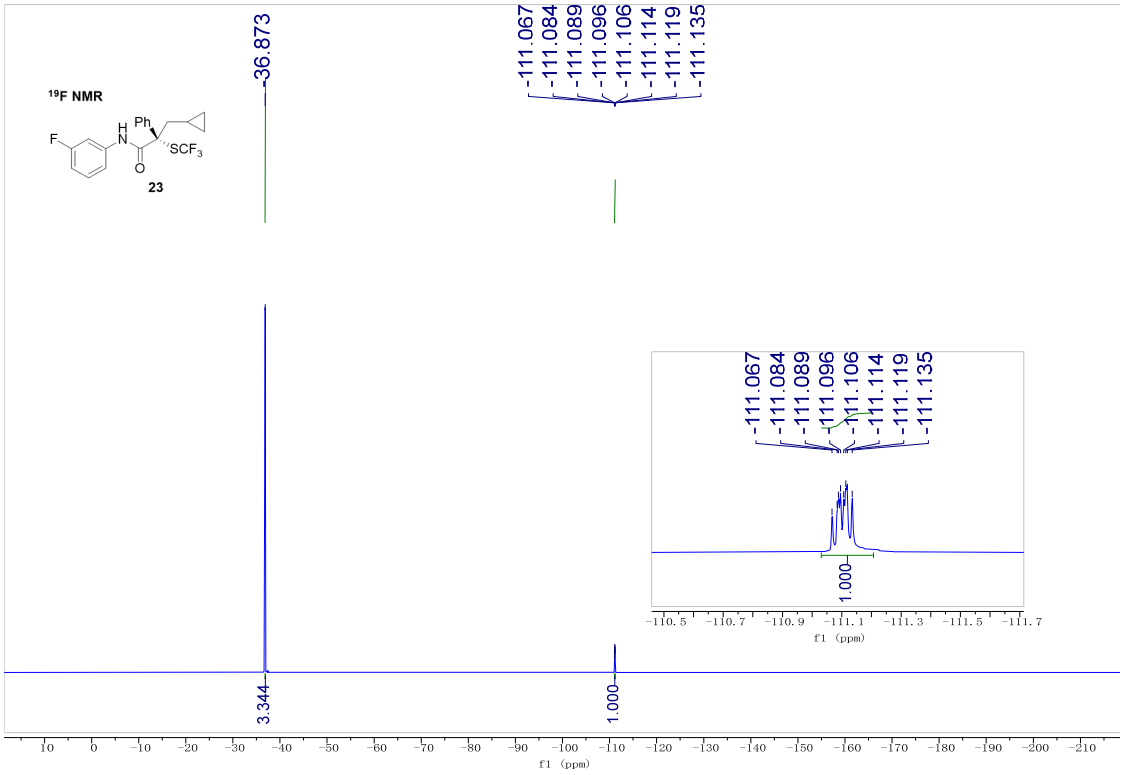

169.046
151.808
136.475
135.890
134.385
132.988
132.807
131.314
129.053
128.353
128.242
127.679
127.133
126.833
125.881
125.502
125.169
119.212
114.359
77.318
77.000
76.683
68.272
34.925
31.320
30.627
9.337
13C NMR
tBu
H
N
Et
SCF3
O
tBu
21
f1 (ppm)

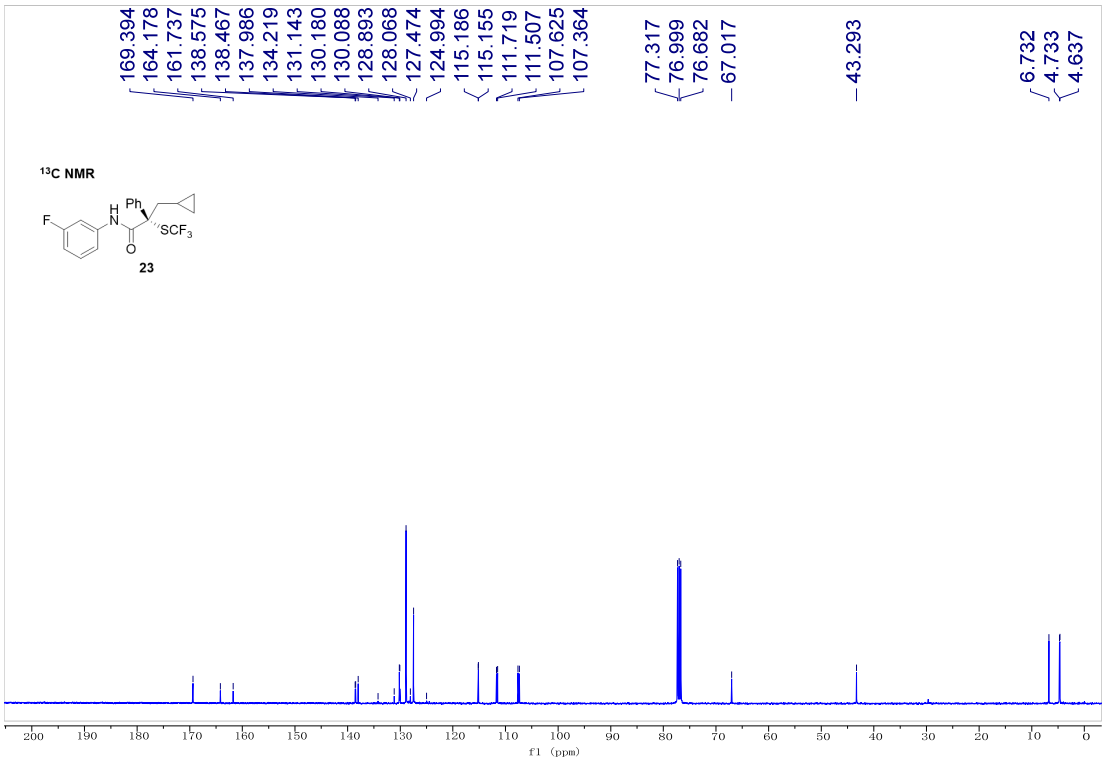

7.533
7.528
7.523
7.516
7.512
7.508
7.473
7.425
7.419
7.415
7.412
7.403
7.398
7.394
7.390
7.383
7.378
7.374
7.363
7.361
7.336
7.331
7.318
7.314
7.301
7.297
7.148
7.134
7.130
7.126
7.112
2.587
2.571
2.550
2.534
2.385
2.368
2.348
2.331
0.087
0.078
0.073
-0.000
-0.011
-0.021
1H NMR
H
N
Ph
SCF3
O
22
2.017
0.870
4.841
1.942
0.980
1.000
0.997
1.014
1.958
1.015
1.132
f1 (ppm)

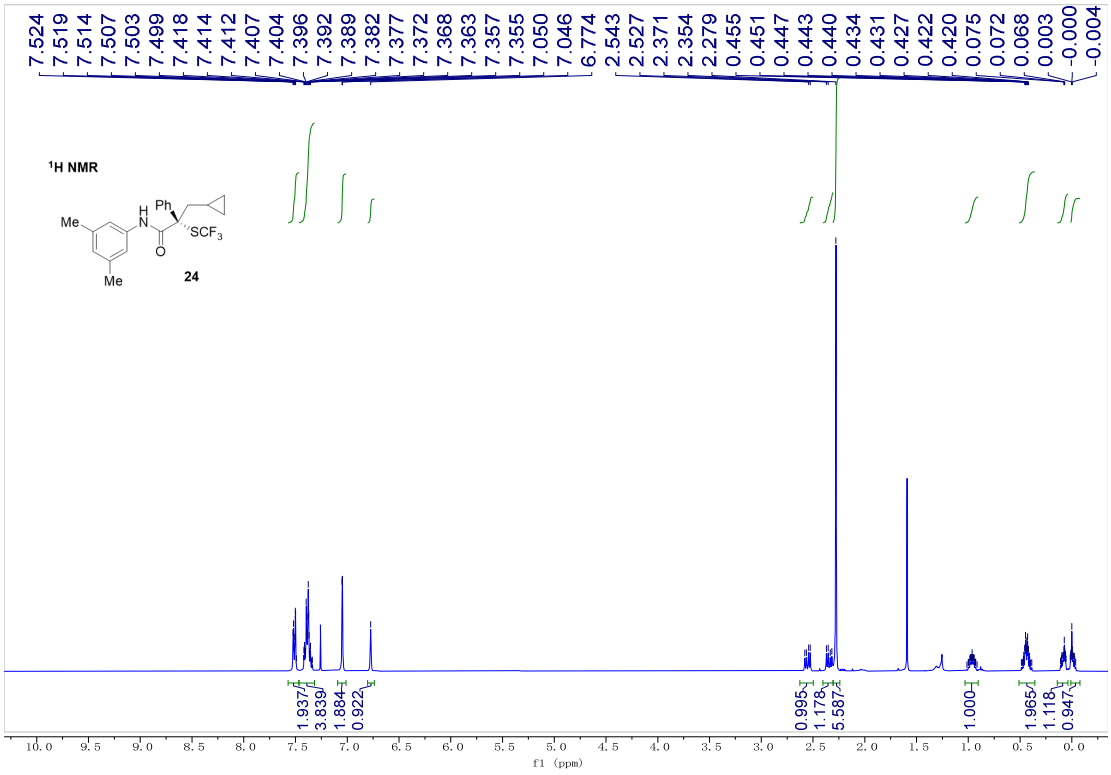

19F NMR
Ph
H
N
O
SCF3
22
-36.891
f1 (ppm)

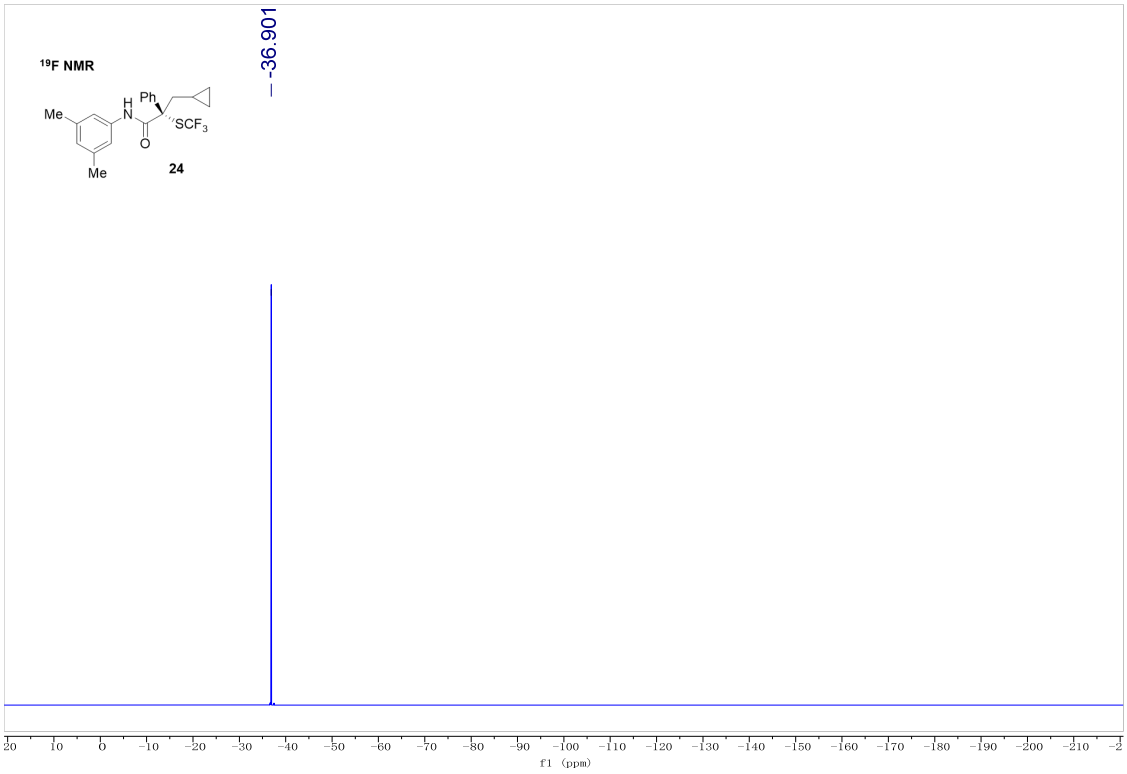

13C NMR
Ph
H
N
O
SCF3
22
169.258
138.307
136.997
134.309
131.244
129.063
128.820
128.781
128.171
127.581
124.909
119.988
77.317
77.000
76.682
67.164
43.291
6.796
4.752
4.665
f1 (ppm)

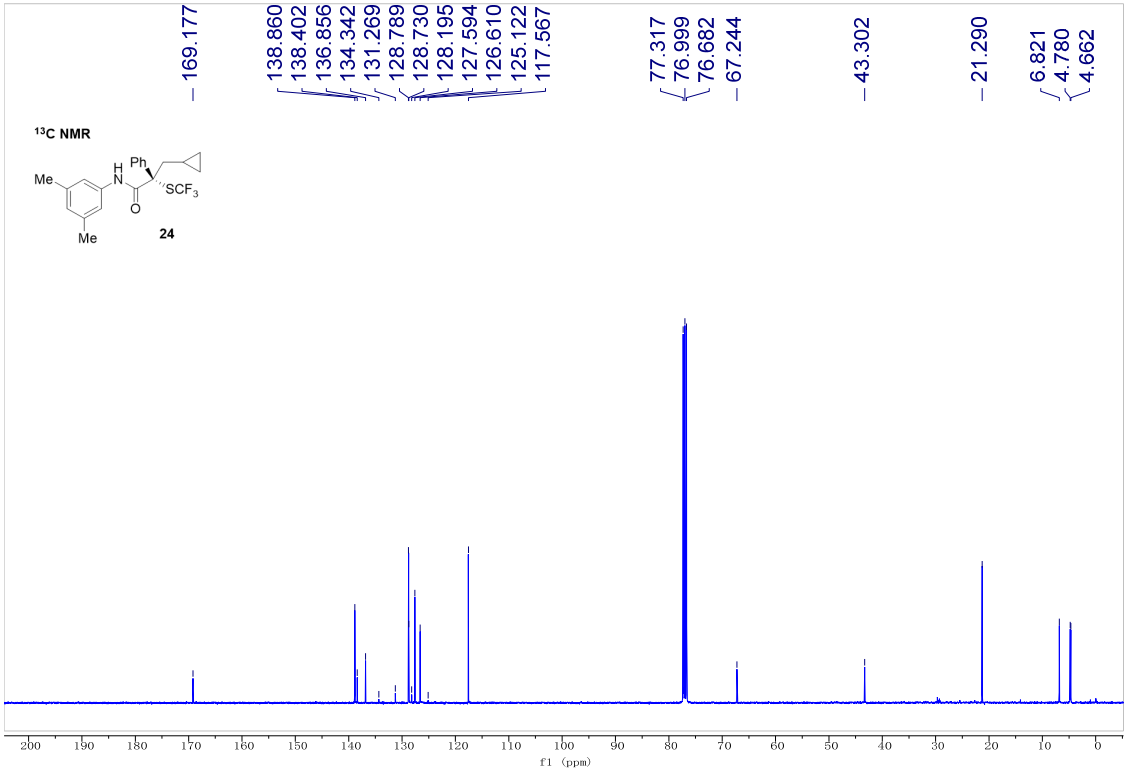

7.566
7.510
7.505
7.500
7.493
7.489
7.485
7.423
7.417
7.407
7.400
7.388
7.385
7.380
7.374
7.368
7.258
7.252
7.237
7.232
7.216
7.035
7.029
7.014
7.009
6.829
6.822
2.528
2.512
2.378
2.362
0.445
0.435
0.431
0.422
0.414
0.410
0.400
0.076
0.066
0.055
0.045
-0.032
-0.042
-0.053
1H NMR
23
1.036
2.061
4.073
1.291
1.012
1.000
0.968
1.013
1.120
2.114
1.070
1.108
f1 (ppm)

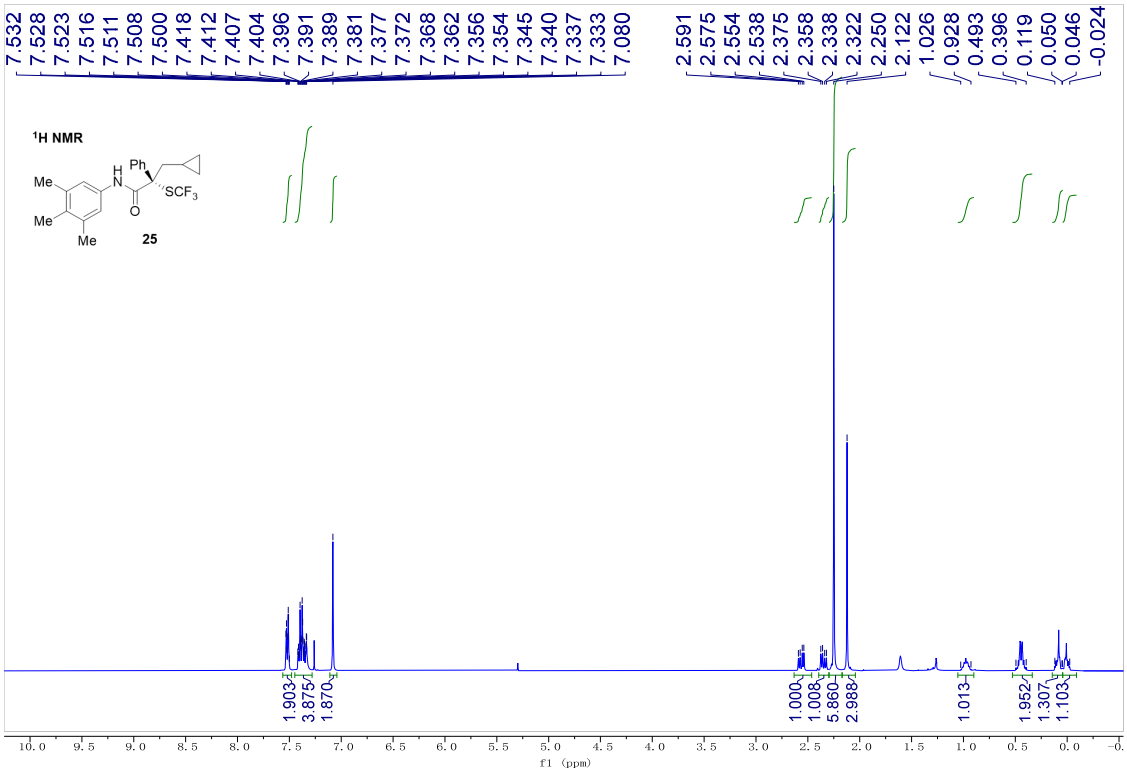

-36.873
-111.067
-111.084
-111.089
-111.096
-111.106
-111.114
-111.119
-111.135
19F NMR
23
3.344
1.000
1.000
f1 (ppm)

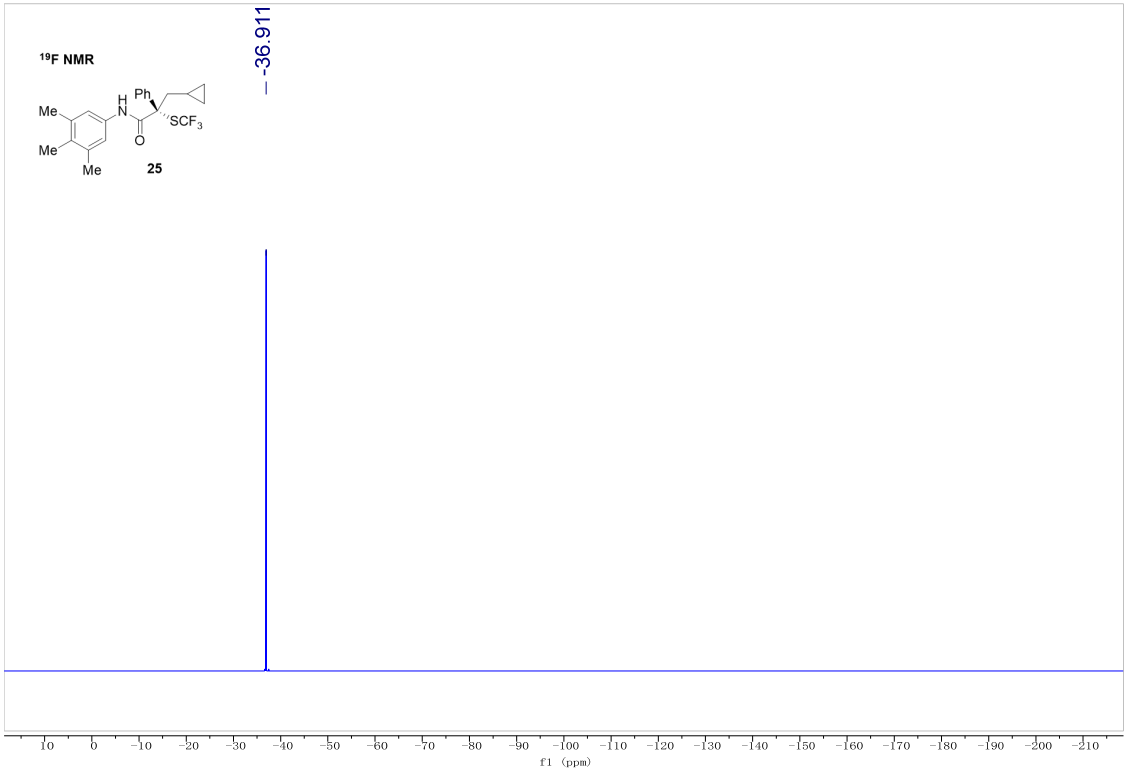

169.394
164.178
161.737
138.575
138.467
137.986
134.219
131.143
130.180
130.088
128.893
128.068
127.474
124.994
115.186
115.155
111.719
111.507
107.625
107.364
77.317
76.999
76.682
67.017
43.293
6.732
4.733
4.637
13C NMR
Ph
H
N
F
SCF3
O
23
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

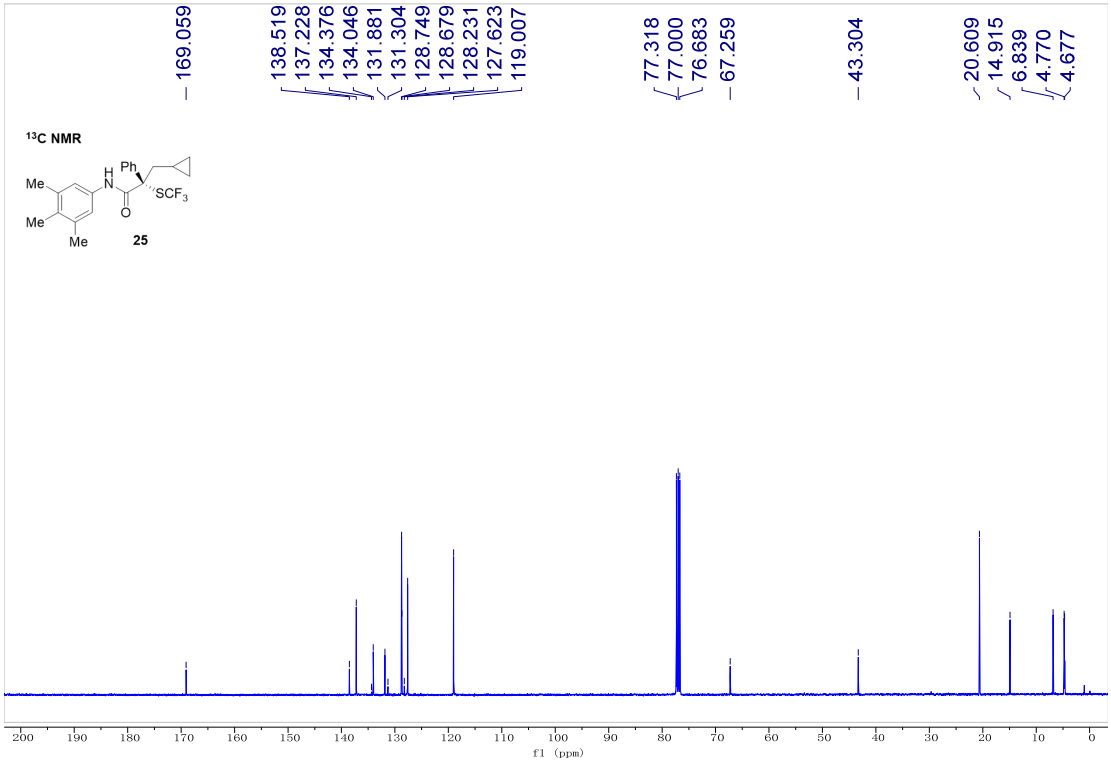

7.524
7.519
7.514
7.507
7.503
7.499
7.418
7.414
7.412
7.407
7.404
7.396
7.392
7.389
7.382
7.377
7.372
7.368
7.363
7.357
7.355
7.050
7.046
6.774
2.543
2.527
2.371
2.354
2.279
0.455
0.451
0.447
0.443
0.440
0.434
0.431
0.427
0.422
0.420
0.075
0.072
0.068
0.003
-0.000
-0.004
1H NMR
Ph
H
N
Me
SCF3
O
Me
24
1.937
3.839
1.884
0.922
0.995
1.178
5.587
1.000
1.965
1.118
0.947
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

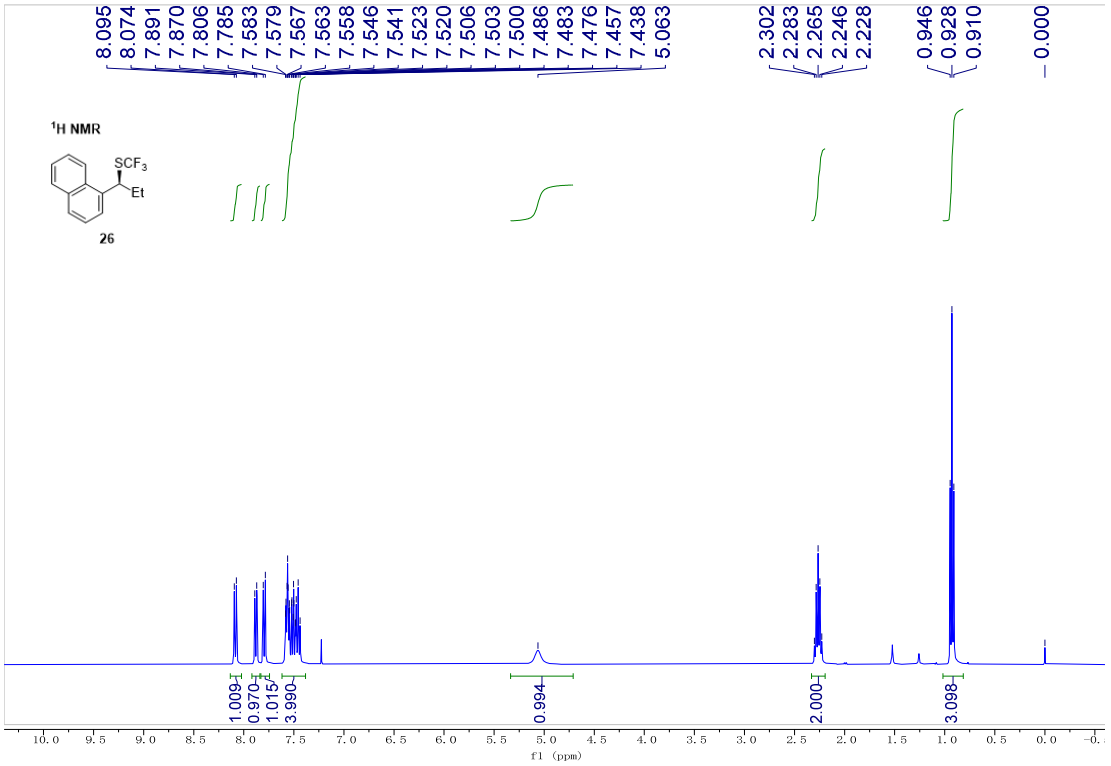

19F NMR
-36.901
Me
Ph
H
N
O
SCF3
Me
24
f1 (ppm)

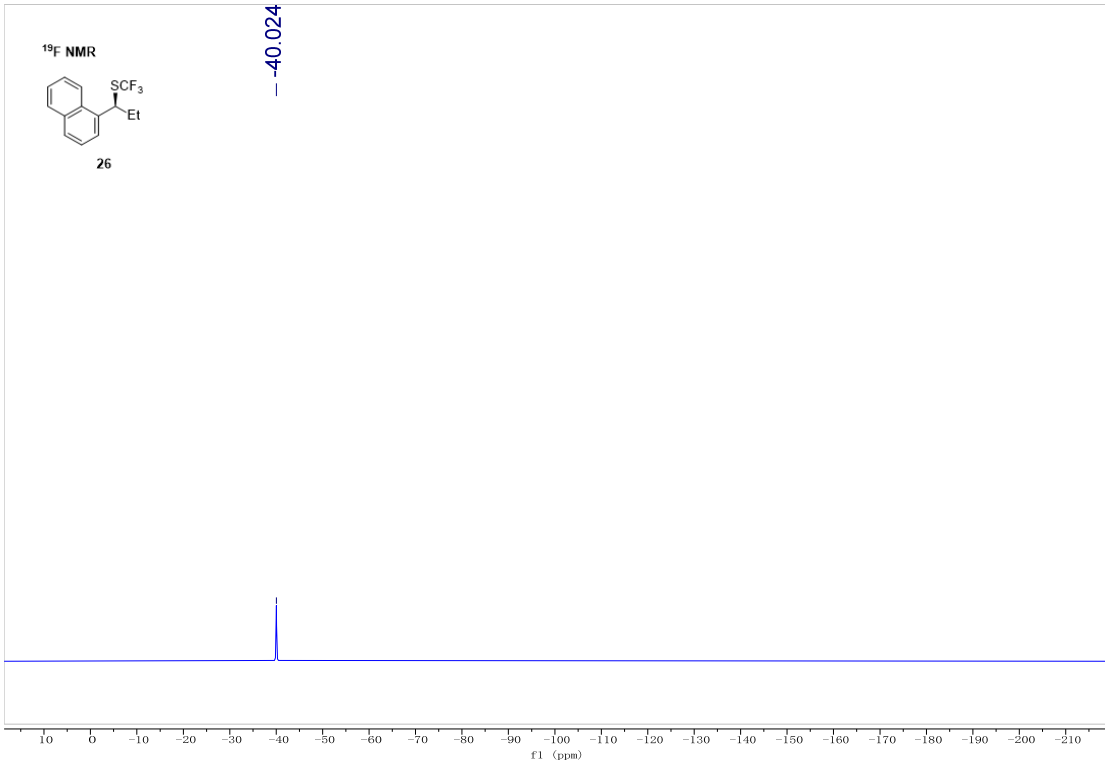

169.177
138.860
138.402
136.856
134.342
131.269
128.789
128.730
128.195
127.594
126.610
125.122
117.567
77.317
76.999
76.682
67.244
43.302
21.290
6.821
4.780
4.662
13C NMR
Me
Ph
H
N
O
SCF3
Me
24
f1 (ppm)

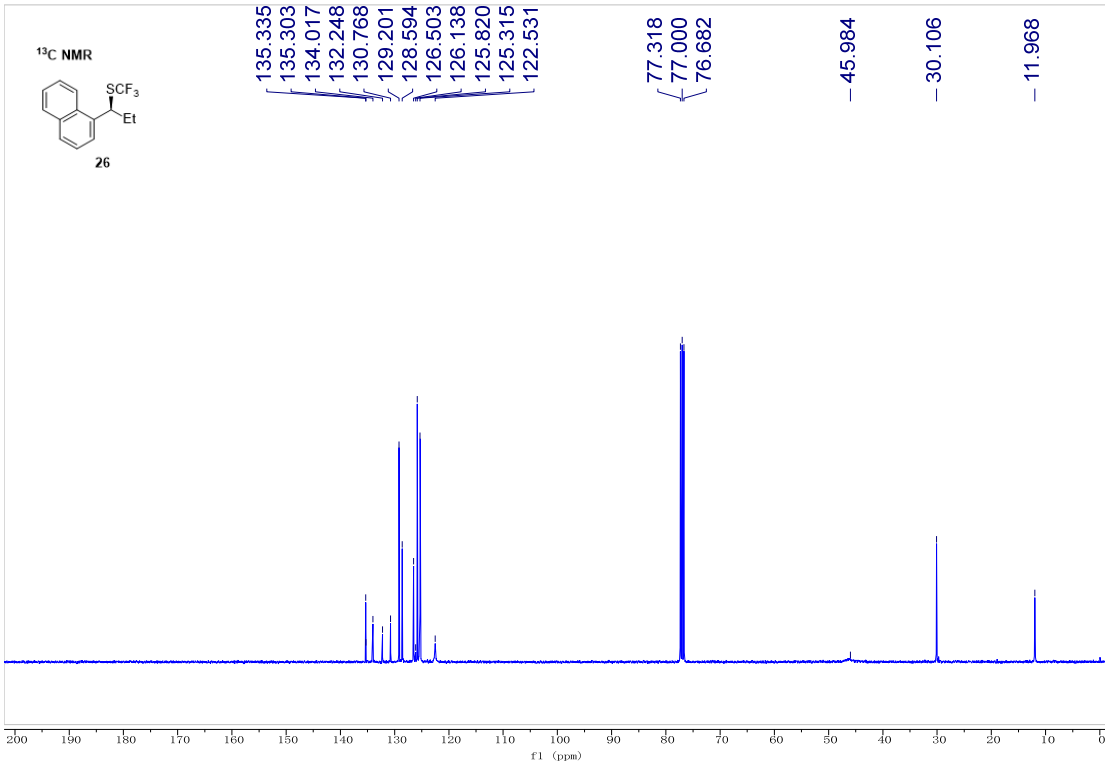

7.532
7.528
7.523
7.516
7.511
7.508
7.500
7.418
7.412
7.407
7.404
7.396
7.391
7.389
7.381
7.377
7.372
7.368
7.362
7.356
7.354
7.345
7.340
7.337
7.333
7.080
2.591
2.575
2.554
2.538
2.375
2.358
2.338
2.322
2.250
2.122
1.026
0.928
0.493
0.396
0.119
0.050
0.046
-0.024
1H NMR
Me
Me
Me
H
N
Ph
SCF3
O
25
1.903
3.875
1.870
1.000
1.008
5.860
2.988
1.013
1.952
1.307
1.103
f1 (ppm)

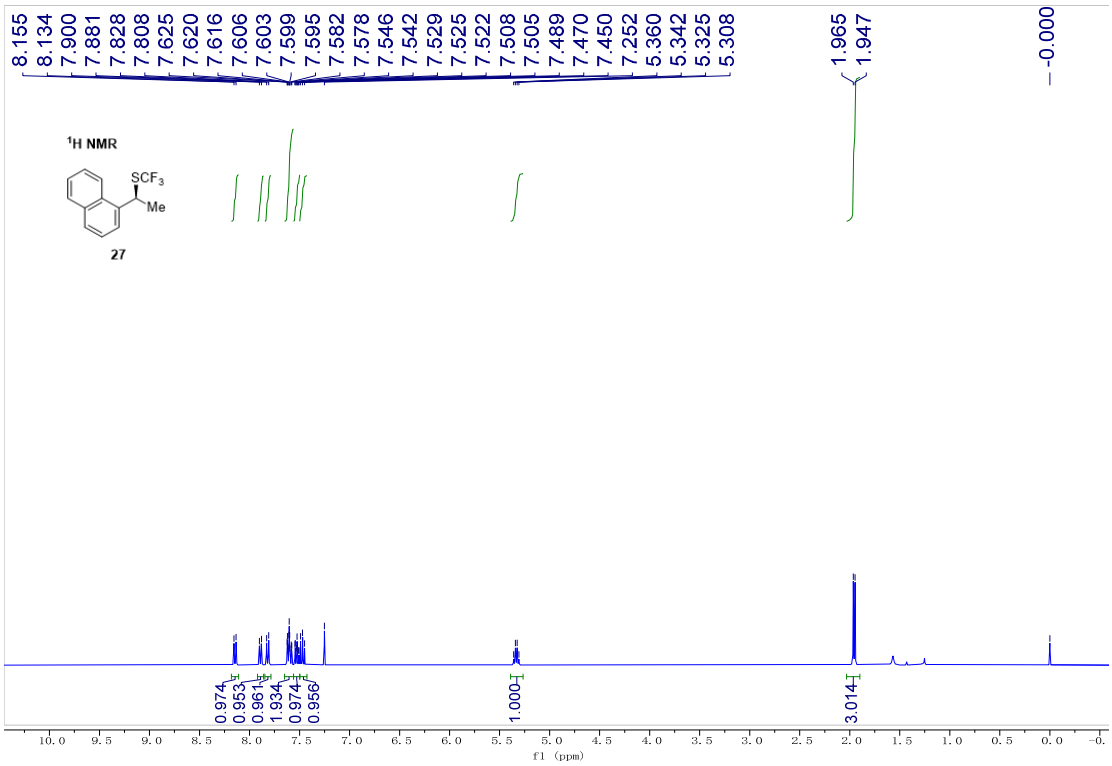

-36.911
19F NMR
Me
Me
Me
H
N
Ph
SCF3
O
25
f1 (ppm)

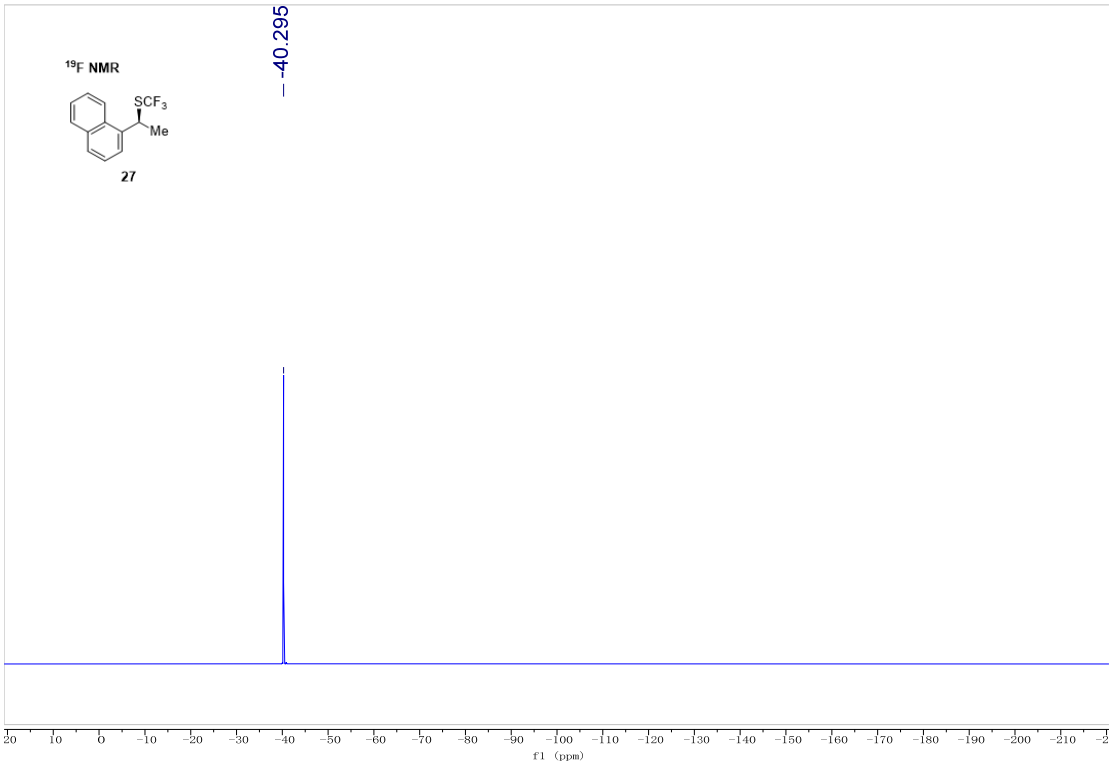

169.059
138.519
137.228
134.376
134.046
131.881
131.304
128.749
128.679
128.231
127.623
119.007
77.318
77.000
76.683
67.259
43.304
20.609
14.915
6.839
4.770
4.677
13C NMR
Me
Me
Me
H
N
O
Ph
SCF3
25
f1 (ppm)

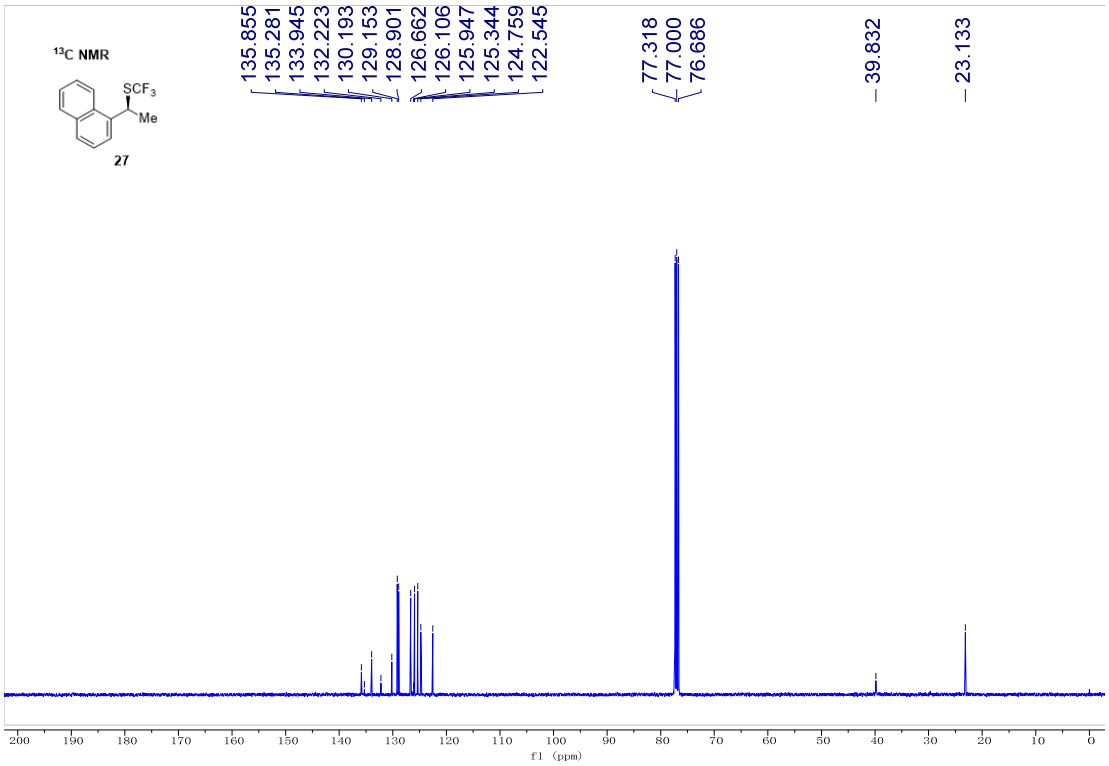

8.095
8.074
7.891
7.870
7.806
7.785
7.583
7.579
7.567
7.563
7.558
7.546
7.541
7.523
7.520
7.506
7.503
7.500
7.486
7.483
7.476
7.457
7.438
5.063
2.302
2.283
2.265
2.246
2.228
0.946
0.928
0.910
0.000
1H NMR
SCF3
Et
26
1.009
0.970
1.015
3.990
0.994
2.000
3.098
f1 (ppm)

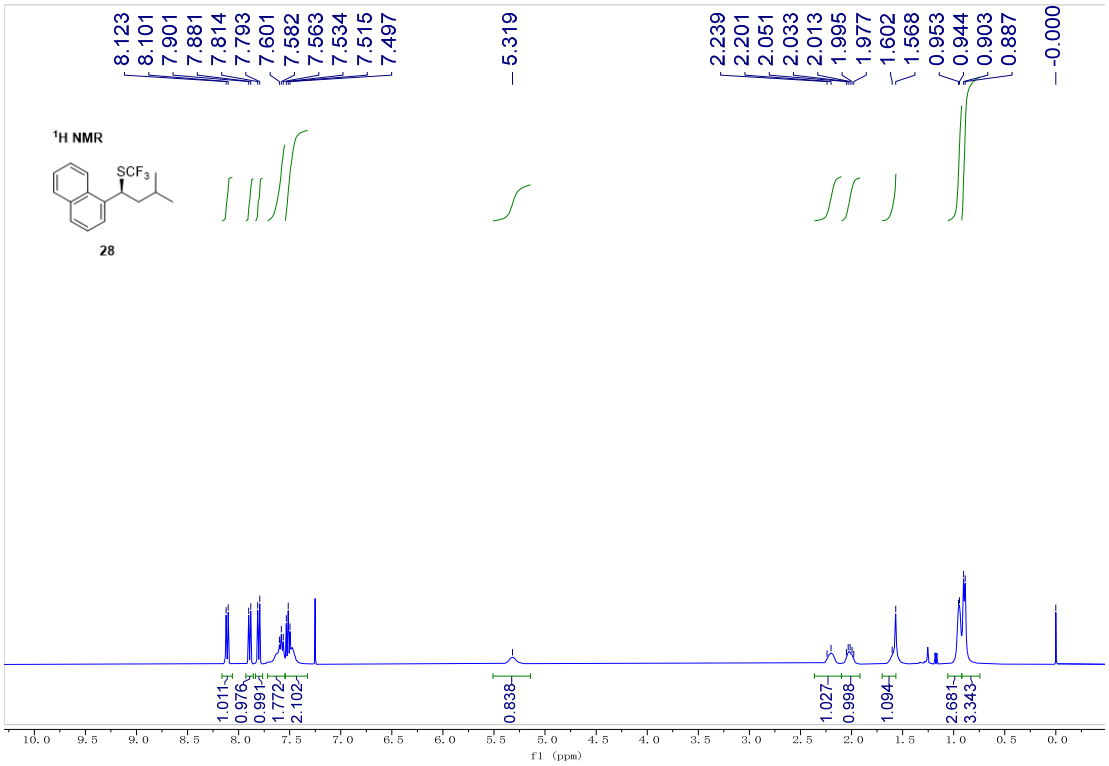

19F NMR
SCF3
Et
26
-40.024
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

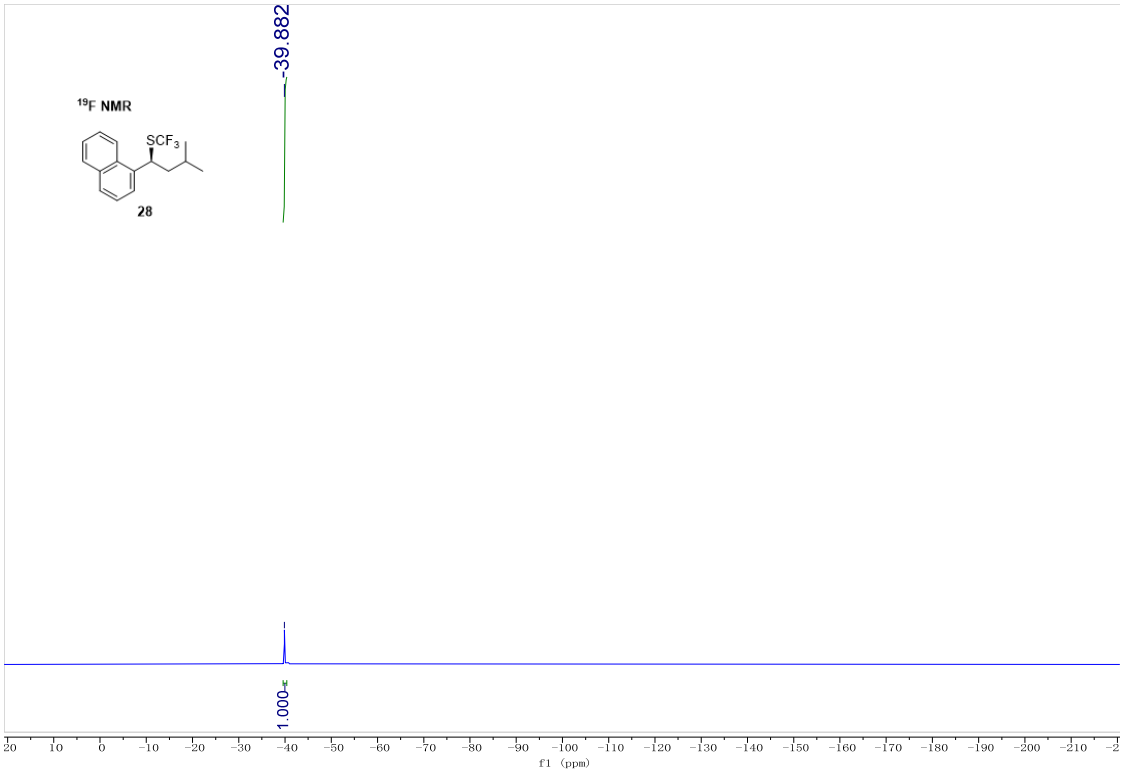

13C NMR
SCF3
Et
26
135.335
135.303
134.017
132.248
130.768
129.201
128.594
126.503
126.138
125.820
125.315
122.531
77.318
77.000
76.682
45.984
30.106
11.968
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

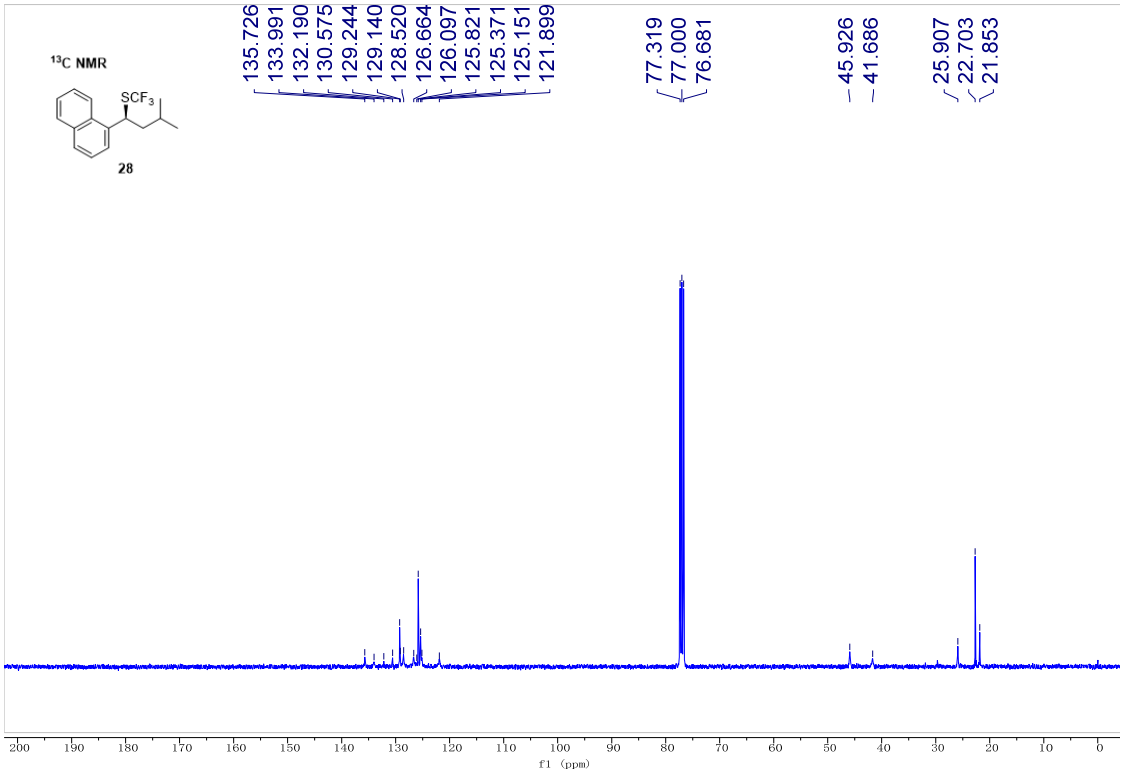

8.155
8.134
7.900
7.881
7.828
7.808
7.625
7.620
7.616
7.606
7.603
7.599
7.595
7.582
7.578
7.546
7.542
7.529
7.525
7.522
7.508
7.505
7.489
7.470
7.450
7.252
5.360
5.342
5.325
5.308
1.965
1.947
-0.000
1H NMR
SCF3
Me
27
0.974
0.953
0.961
1.934
0.974
0.956
1.000
3.014
f1 (ppm)

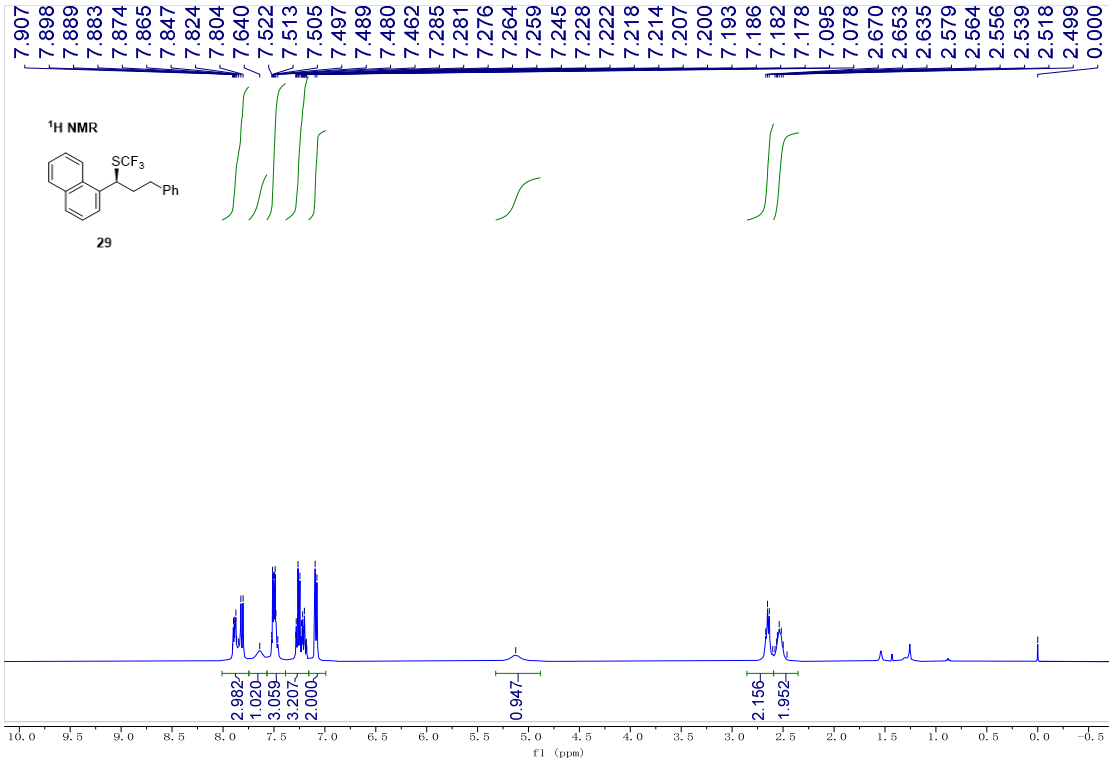

-40.295
19F NMR
SCF3
Me
27
f1 (ppm)

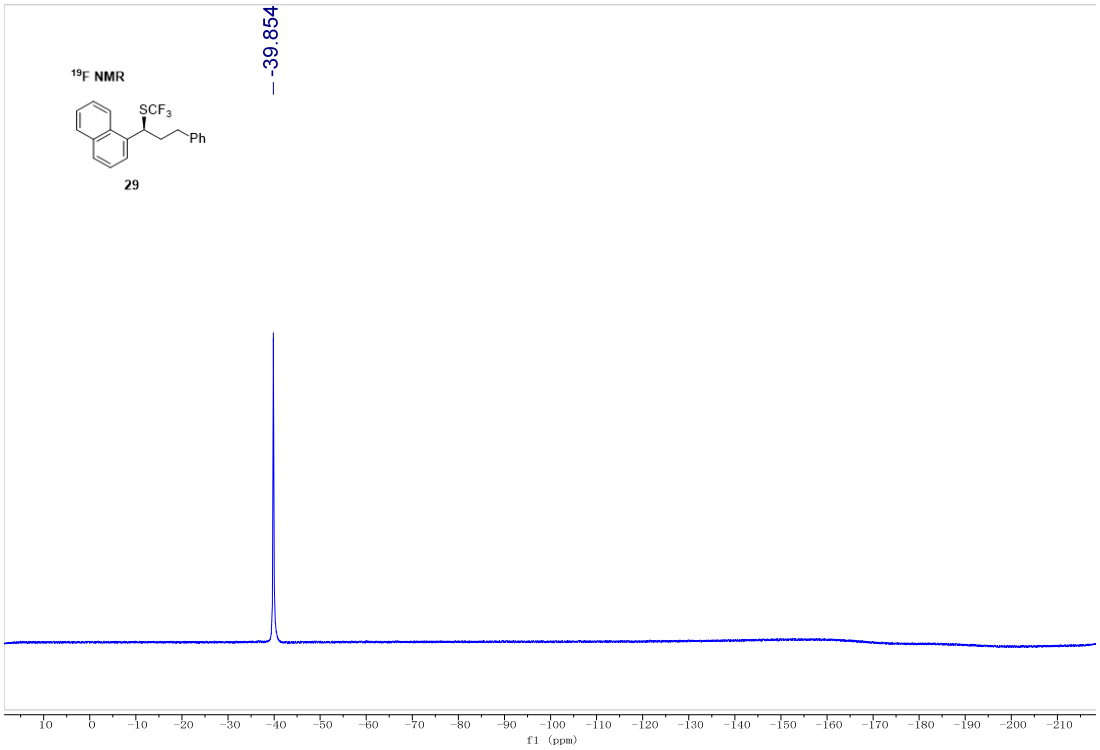

135.855
135.281
133.945
132.223
130.193
129.153
128.901
126.662
126.106
125.947
125.344
124.759
122.545
77.318
77.000
76.686
39.832
23.133
13C NMR
SCF3
Me
27
f1 (ppm)

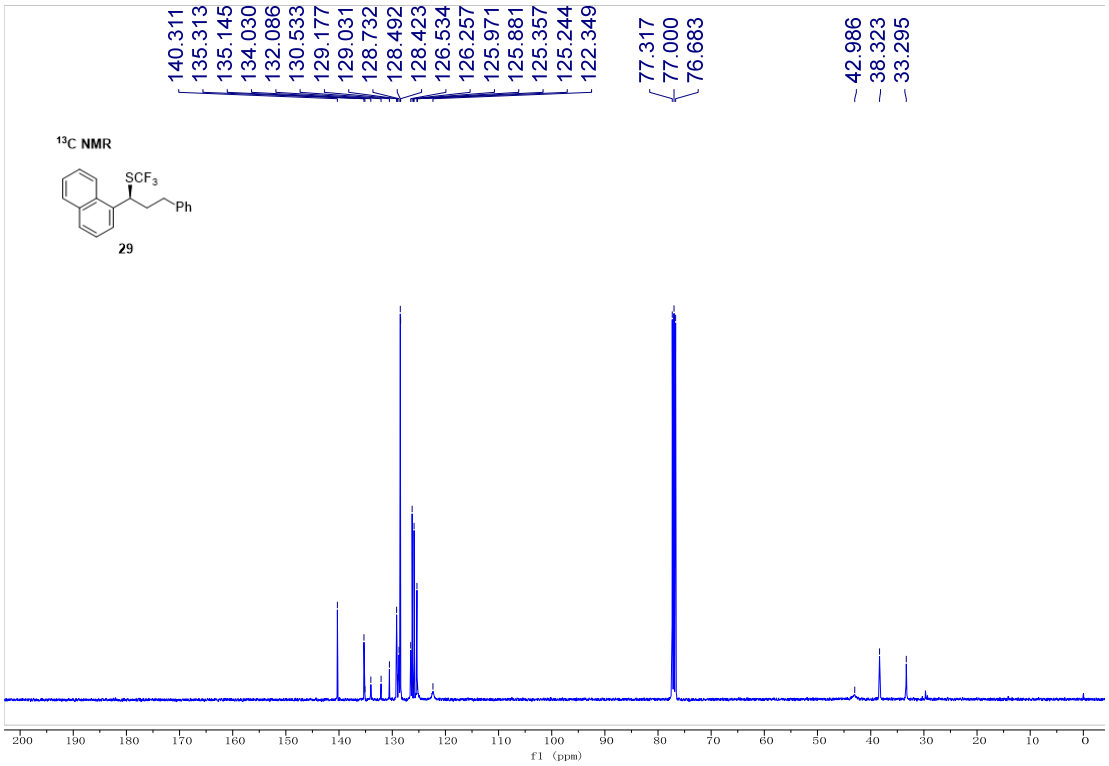

8.123
8.101
7.901
7.881
7.814
7.793
7.601
7.582
7.563
7.534
7.515
7.497
5.319
2.239
2.201
2.051
2.033
2.013
1.995
1.977
1.602
1.568
0.953
0.944
0.903
0.887
-0.000
1H NMR
SCF3
28
1.011
0.976
0.991
1.772
2.102
0.838
1.027
0.998
1.094
2.681
3.343
f1 (ppm)

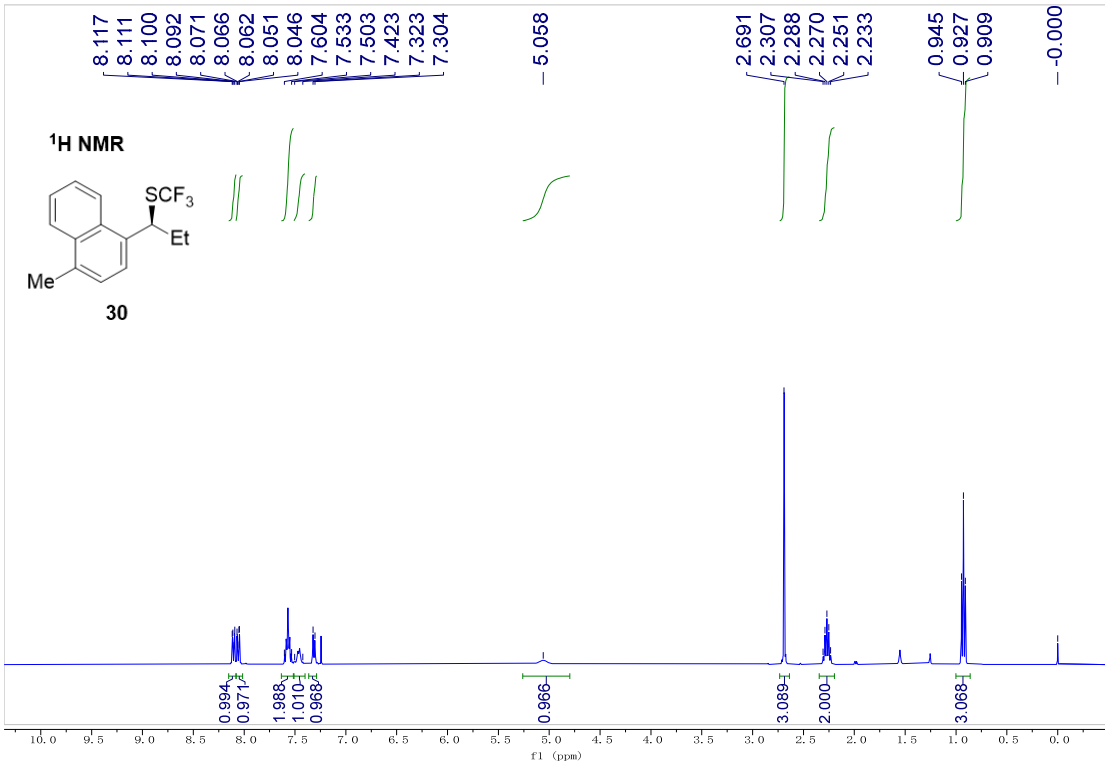

19F NMR
SCF3
28
-39.882
1.000
f1 (ppm)

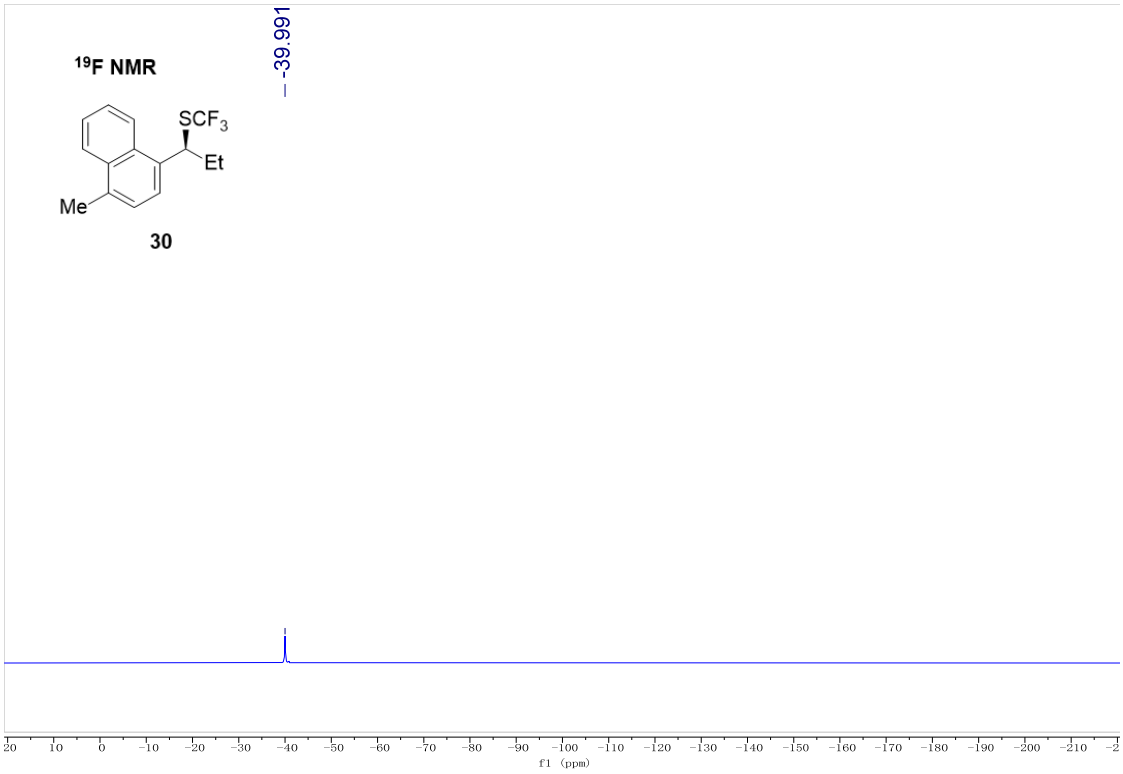

13C NMR
SCF3
28
135.726
133.991
132.190
130.575
129.244
129.140
128.520
126.664
126.097
125.821
125.371
125.151
121.899
77.319
77.000
76.681
45.926
41.686
25.907
22.703
21.853
f1 (ppm)

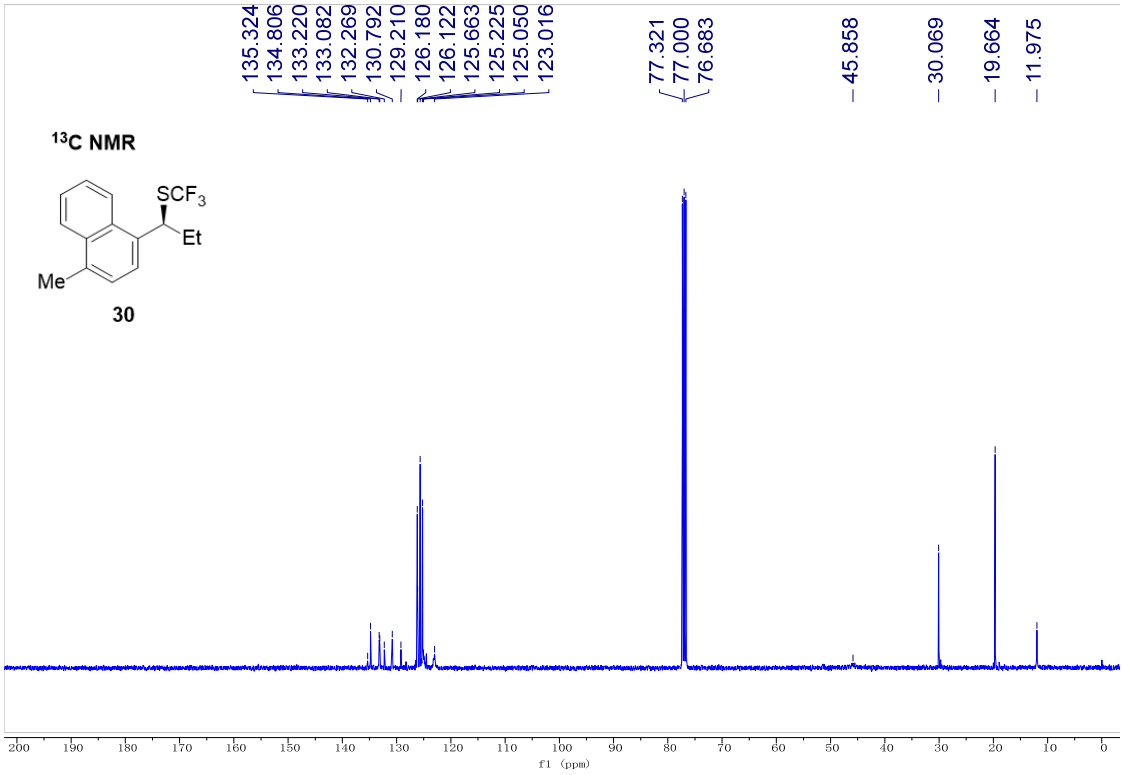

7.907
7.898
7.889
7.883
7.874
7.865
7.847
7.824
7.804
7.640
7.522
7.513
7.505
7.497
7.489
7.480
7.462
7.285
7.281
7.276
7.264
7.259
7.245
7.228
7.222
7.218
7.214
7.207
7.200
7.193
7.186
7.182
7.178
7.095
7.078
2.670
2.653
2.635
2.579
2.564
2.556
2.539
2.518
2.499
0.000
1H NMR
SCF3
Ph
29
2.982
1.020
3.059
3.207
2.000
0.947
2.156
1.952
f1 (ppm)

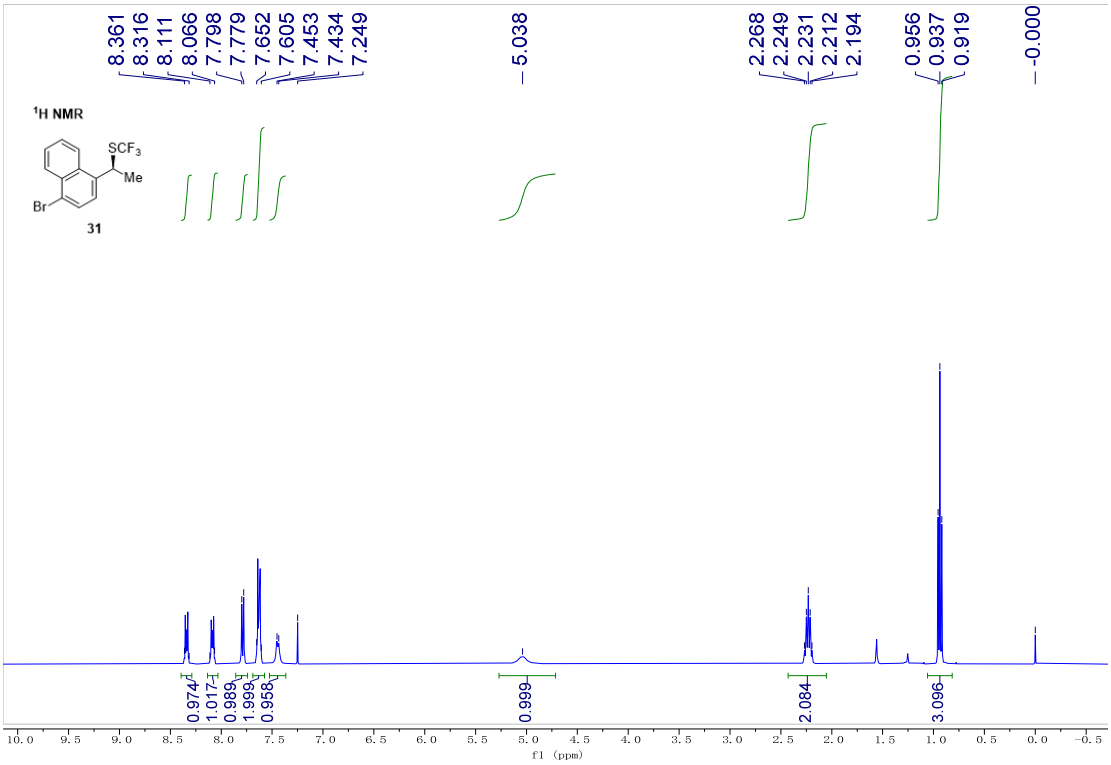

-39.854
19F NMR
SCF3
Ph
29
f1 (ppm)

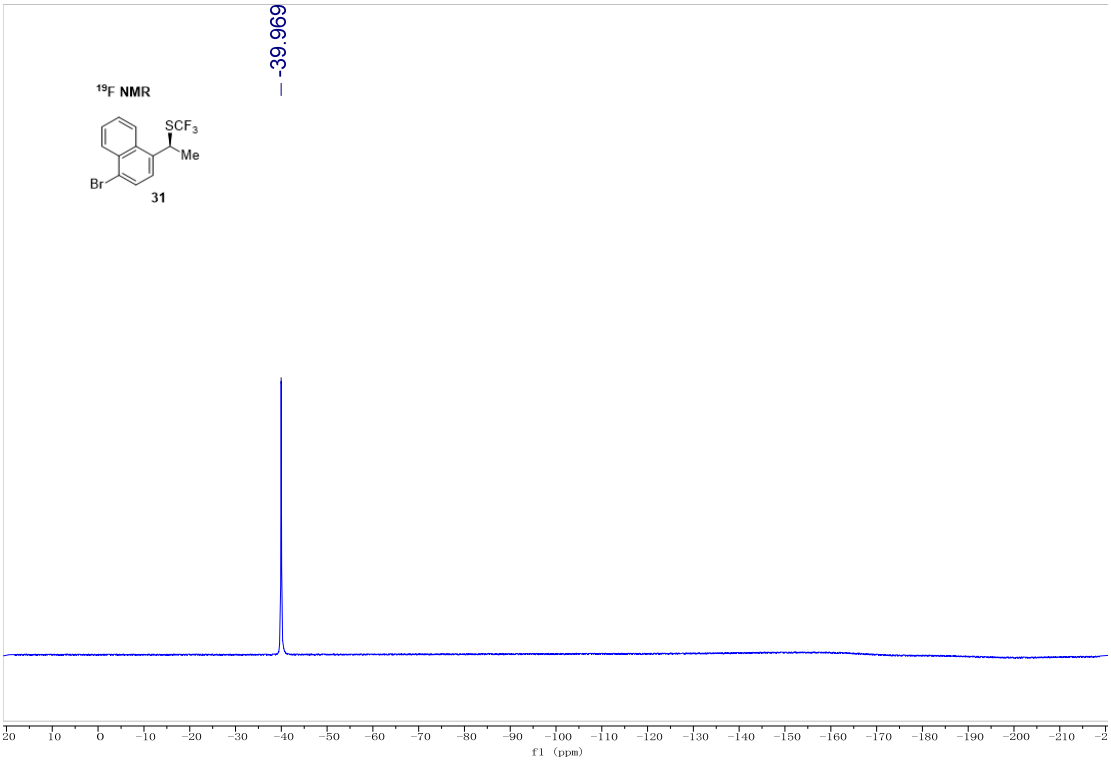

140.311
135.313
135.145
134.030
132.086
130.533
129.177
129.031
128.732
128.492
128.423
126.534
126.257
125.971
125.881
125.357
125.244
122.349
77.317
77.000
76.683
42.986
38.323
33.295
13C NMR
SCF3
Ph
29
f1 (ppm)

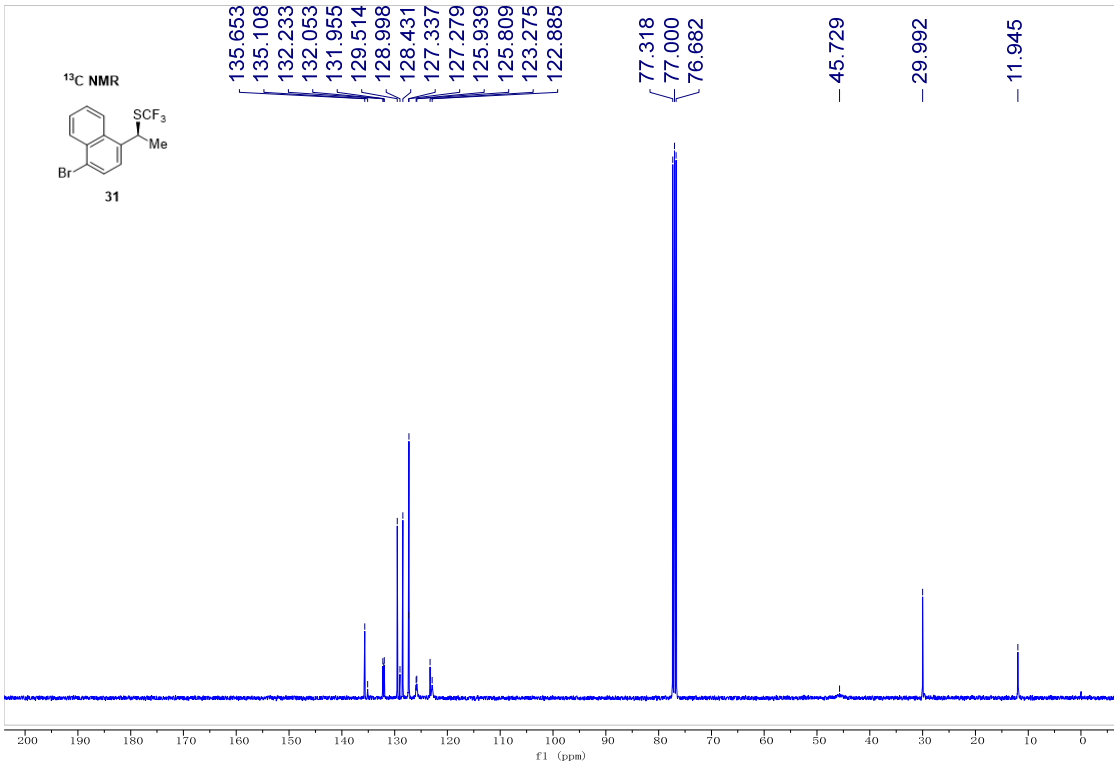

8.117
8.111
8.100
8.092
8.071
8.066
8.062
8.051
8.046
7.604
7.533
7.503
7.423
7.323
7.304
5.058
2.691
2.307
2.288
2.270
2.251
2.233
0.945
0.927
0.909
-0.000
1H NMR
SCF3
Et
Me
30
0.994
0.971
1.988
1.010
0.968
0.966
3.089
2.000
3.068
f1 (ppm)

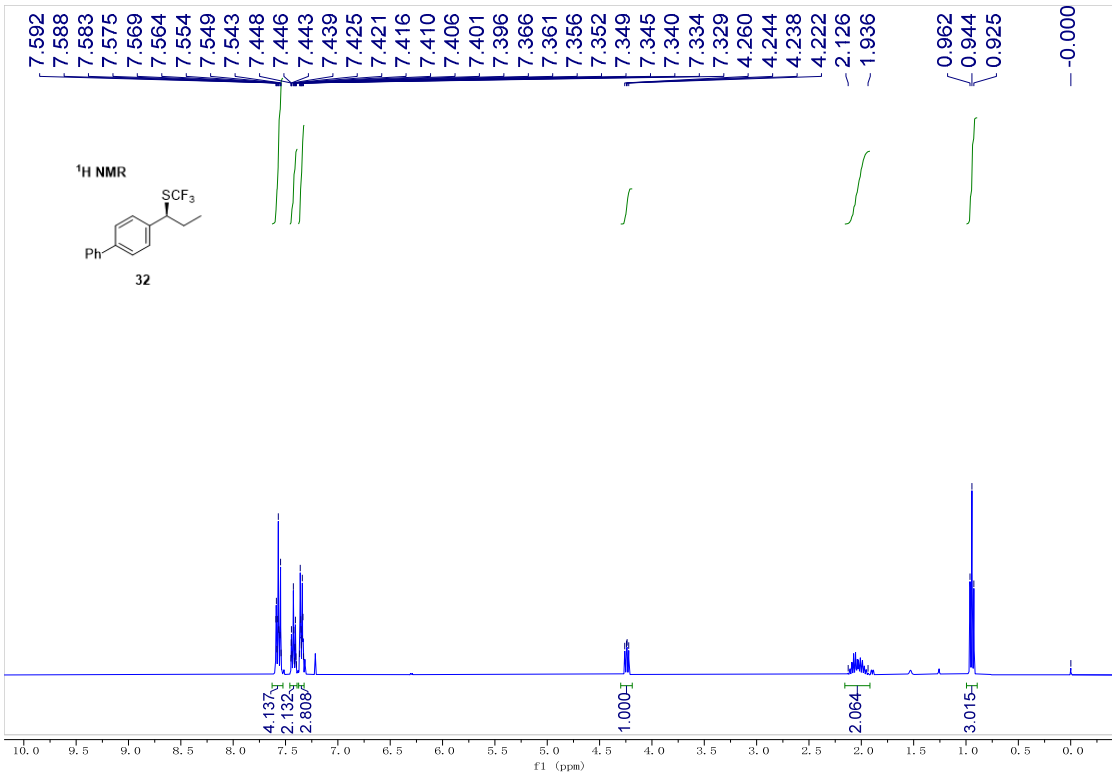

19F NMR
-39.991
SCF3
Et
Me
30
f1 (ppm)

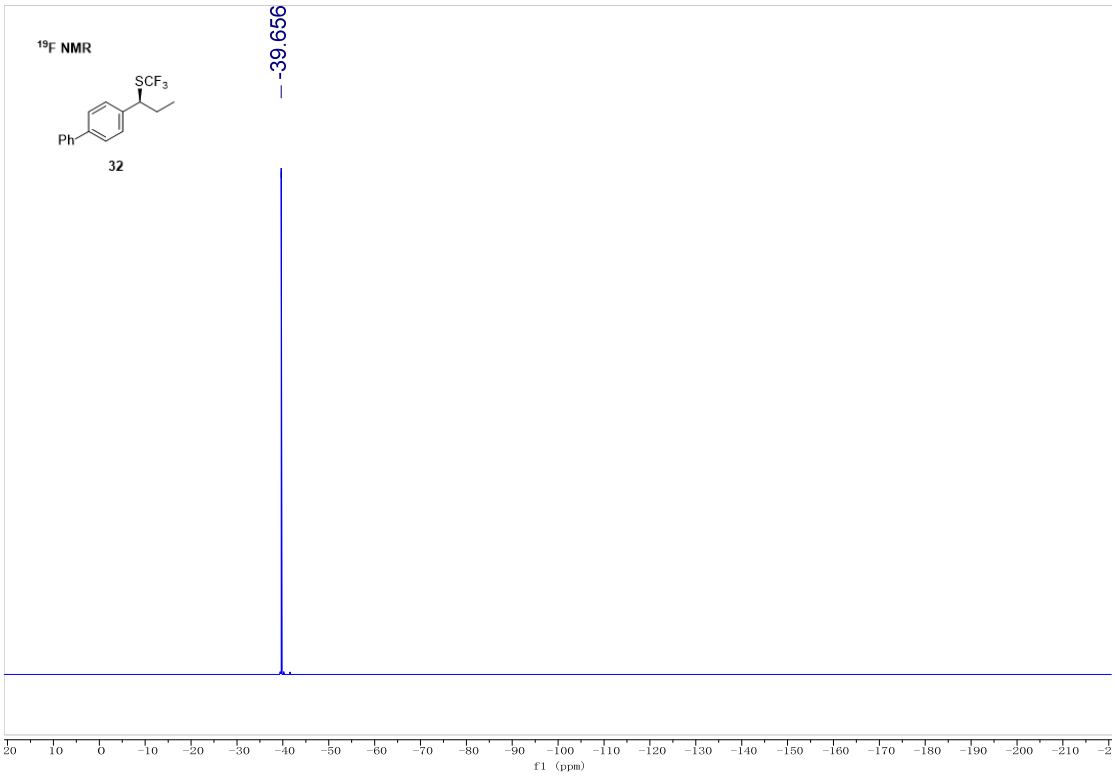

135.324
134.806
133.220
133.082
132.269
130.792
129.210
126.180
126.122
125.663
125.225
125.050
123.016
77.321
77.000
76.683
45.858
30.069
19.664
11.975
13C NMR
SCF3
Et
Me
30
f1 (ppm)

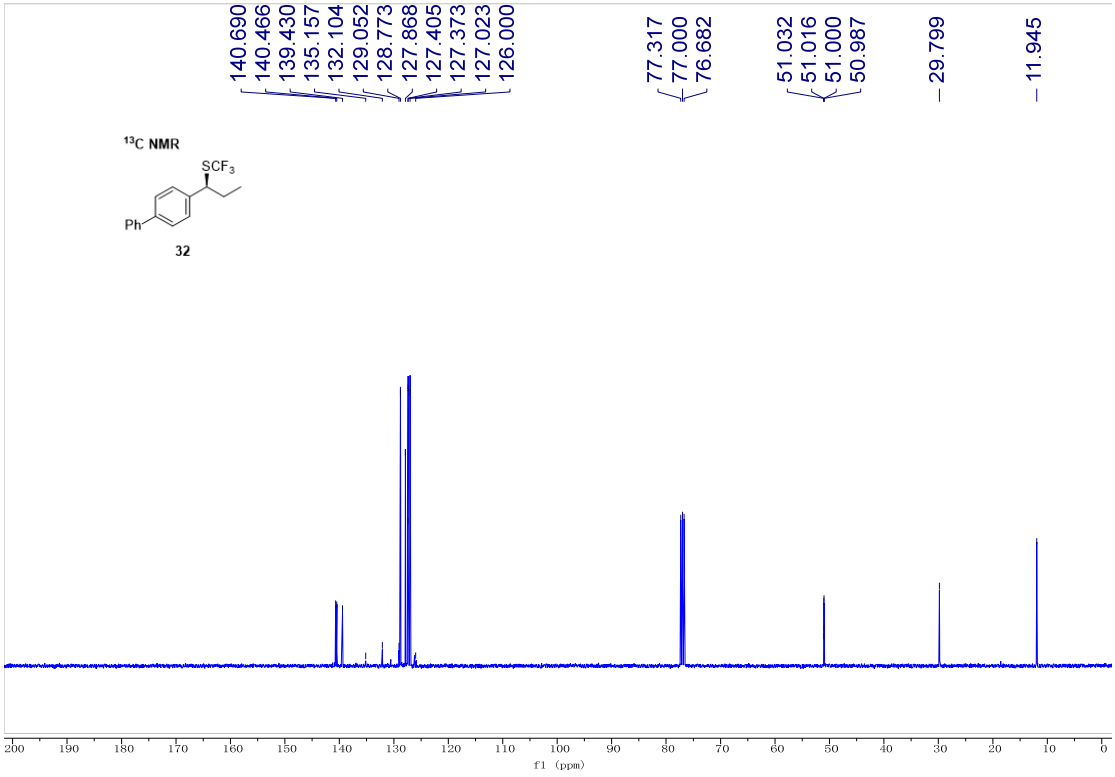

8.361
8.316
8.111
8.066
7.798
7.779
7.652
7.605
7.453
7.434
7.249
5.038
2.268
2.249
2.231
2.212
2.194
0.956
0.937
0.919
-0.000
1H NMR
SCF3
Me
Br
31
0.974
1.017
0.989
1.999
0.958
0.999
2.084
3.096
f1 (ppm)

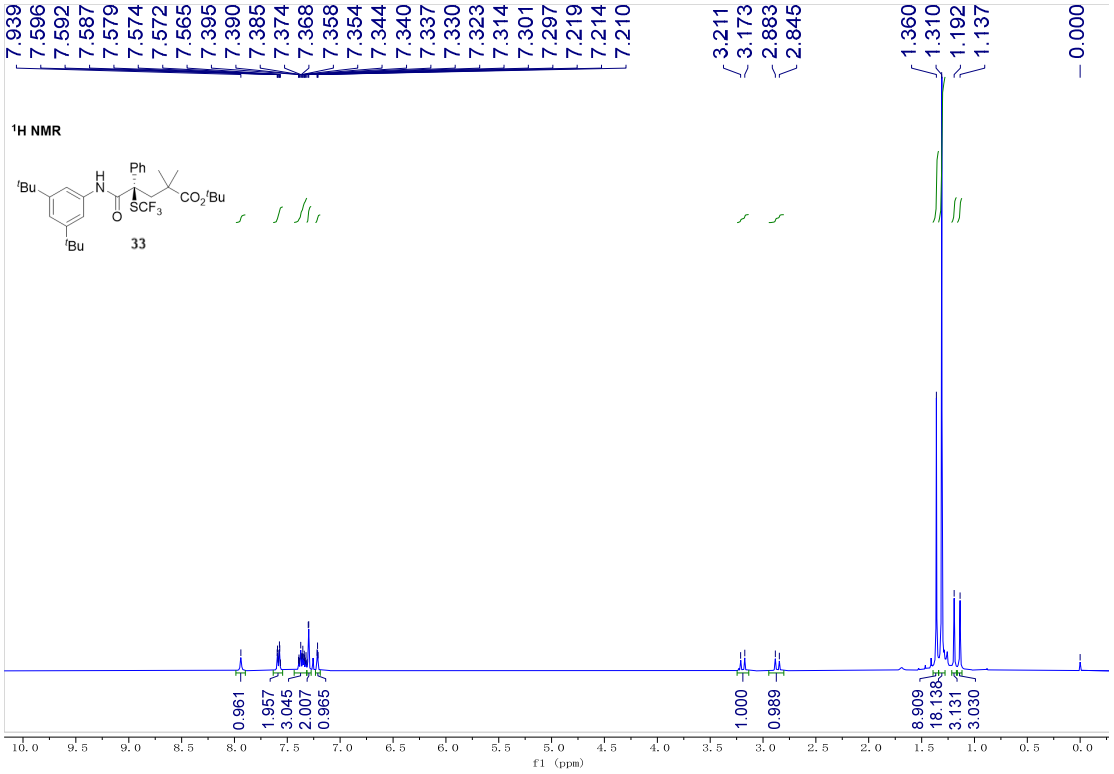

-39.969
19F NMR
SCF3
Me
Br
31
f1 (ppm)

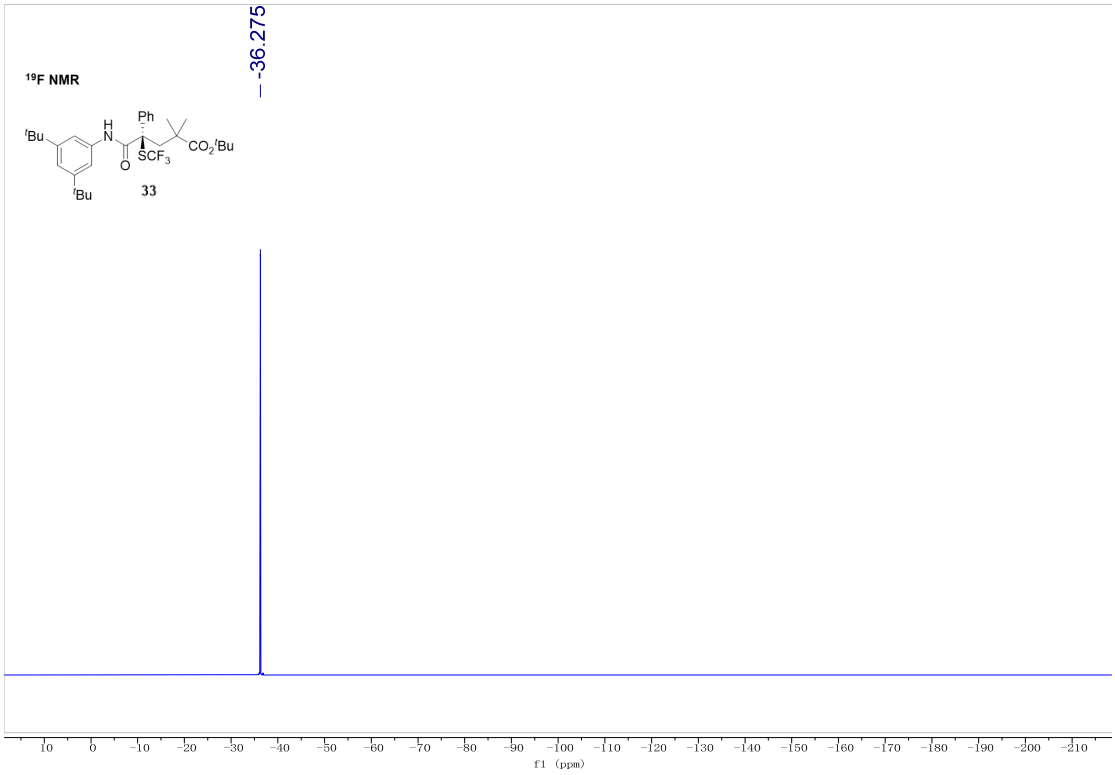

135.653
135.108
132.233
132.053
131.955
129.514
128.998
128.431
127.337
127.279
125.939
125.809
123.275
122.885
77.318
77.000
76.682
45.729
29.992
11.945
13C NMR
SCF3
Me
Br
31
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

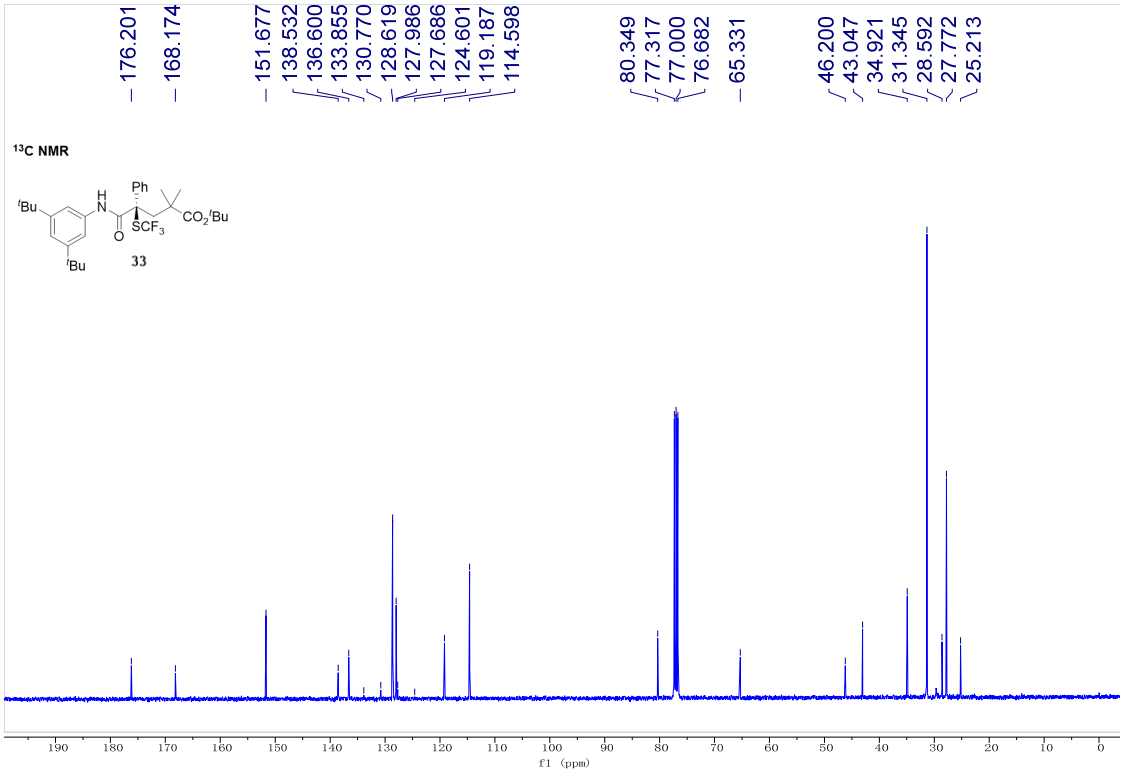

7.592
7.588
7.583
7.575
7.569
7.564
7.554
7.549
7.543
7.448
7.446
7.443
7.439
7.425
7.421
7.416
7.410
7.406
7.401
7.396
7.366
7.361
7.356
7.352
7.349
7.345
7.340
7.334
7.329
4.260
4.244
4.238
4.222
2.126
1.936
0.962
0.944
0.925
-0.000
1H NMR
SCF3
Ph
32
4.137
2.132
2.808
1.000
2.064
3.015
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

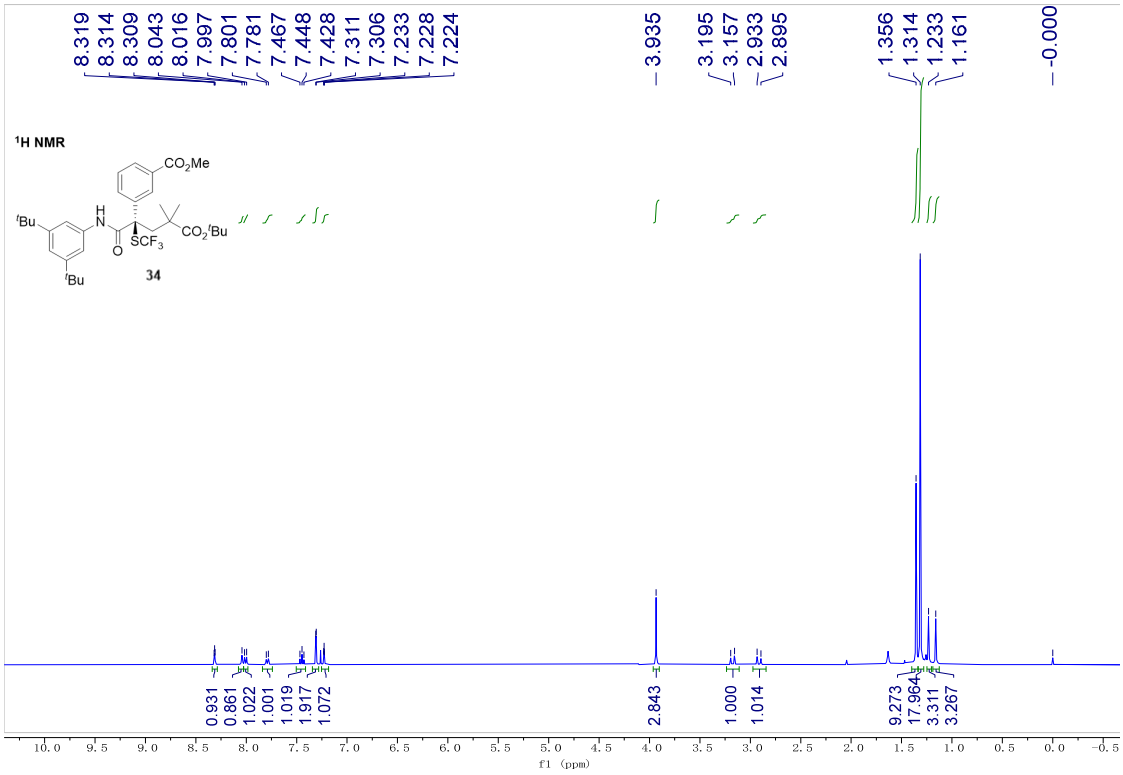

19F NMR
SCF3
Ph
32
-39.656
f1 (ppm)

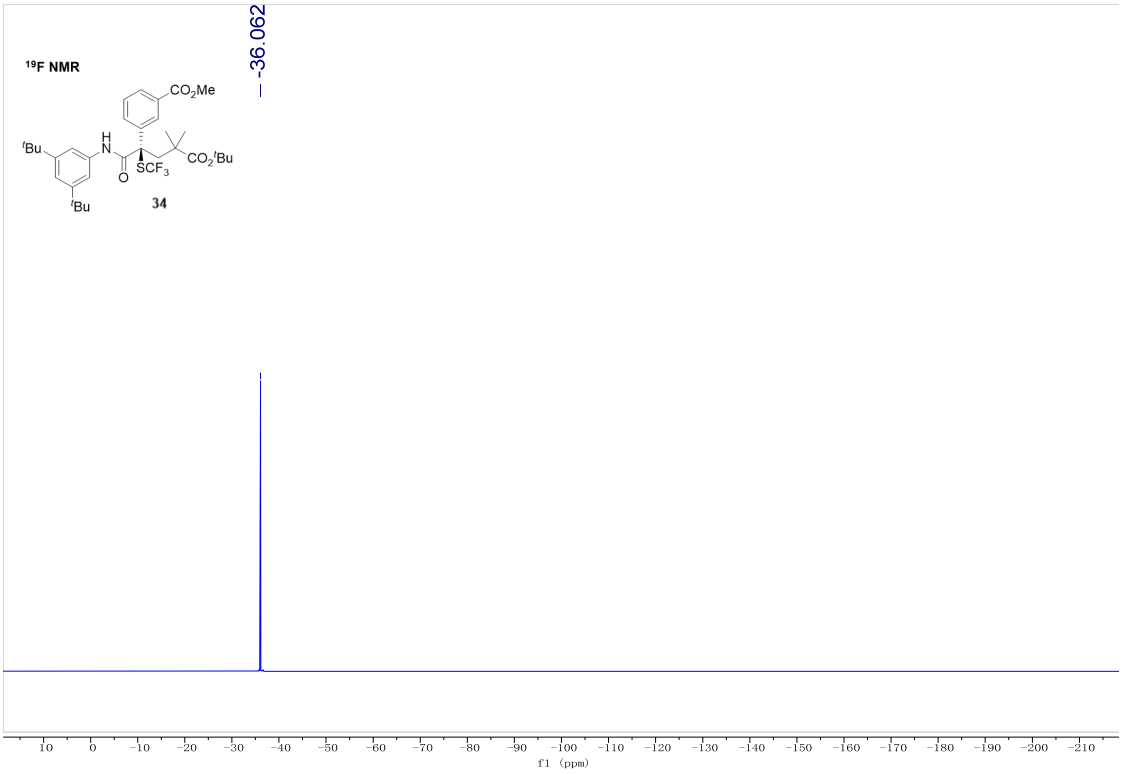

140.690
140.466
139.430
135.157
132.104
129.052
128.773
127.868
127.405
127.373
127.023
126.000
77.317
77.000
76.682
51.032
51.016
51.000
50.987
29.799
11.945
13C NMR
SCF3
Ph
32
f1 (ppm)

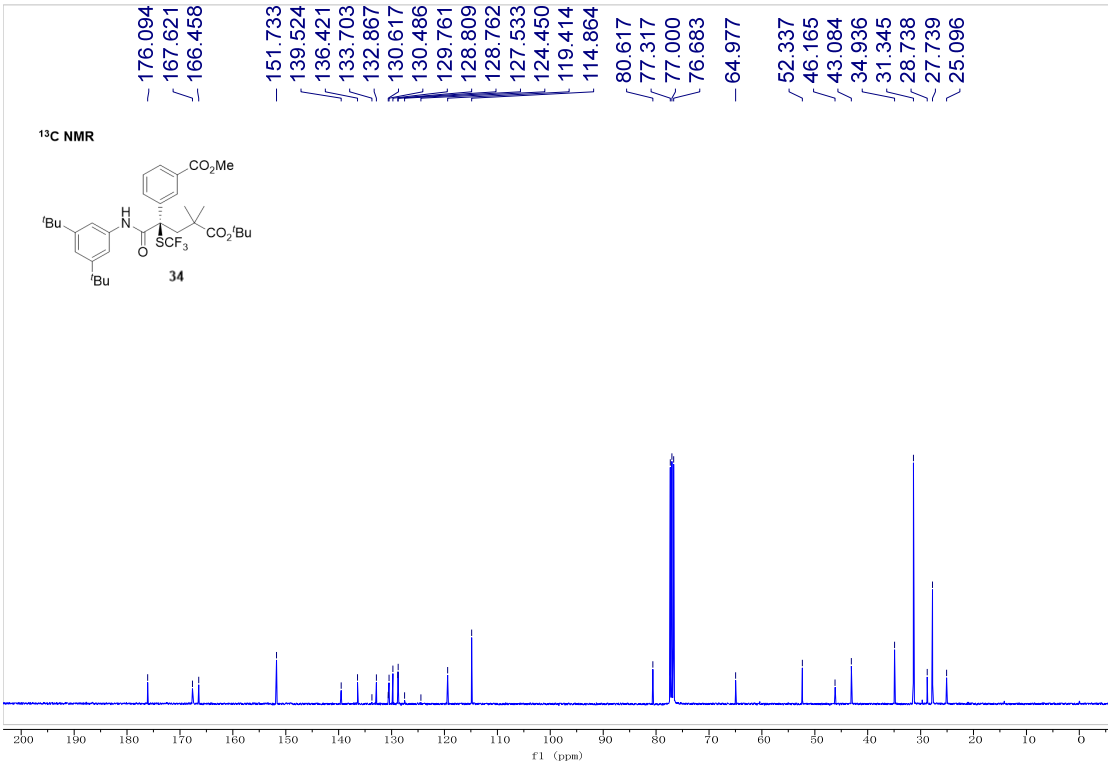

7.939
7.596
7.592
7.587
7.579
7.574
7.572
7.565
7.395
7.390
7.385
7.374
7.368
7.358
7.354
7.344
7.340
7.337
7.330
7.323
7.314
7.301
7.297
7.219
7.214
7.210
3.211
3.173
2.883
2.845
1.360
1.310
1.192
1.137
0.000
1H NMR
tBu
H
N
O
Ph
SCF3
CO2tBu
tBu
33
0.961
1.957
3.045
2.007
0.965
1.000
0.989
8.909
18.138
3.131
3.030
f1 (ppm)

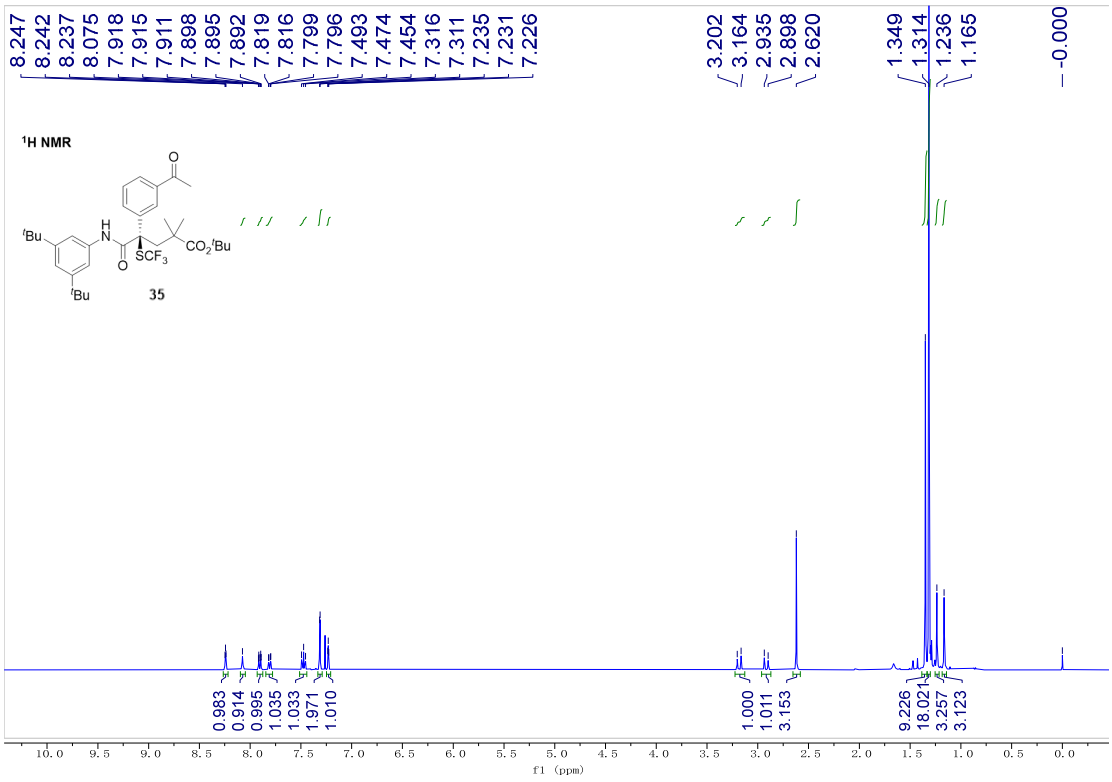

-36.275
19F NMR
tBu
H
N
O
Ph
SCF3
CO2tBu
tBu
33
f1 (ppm)

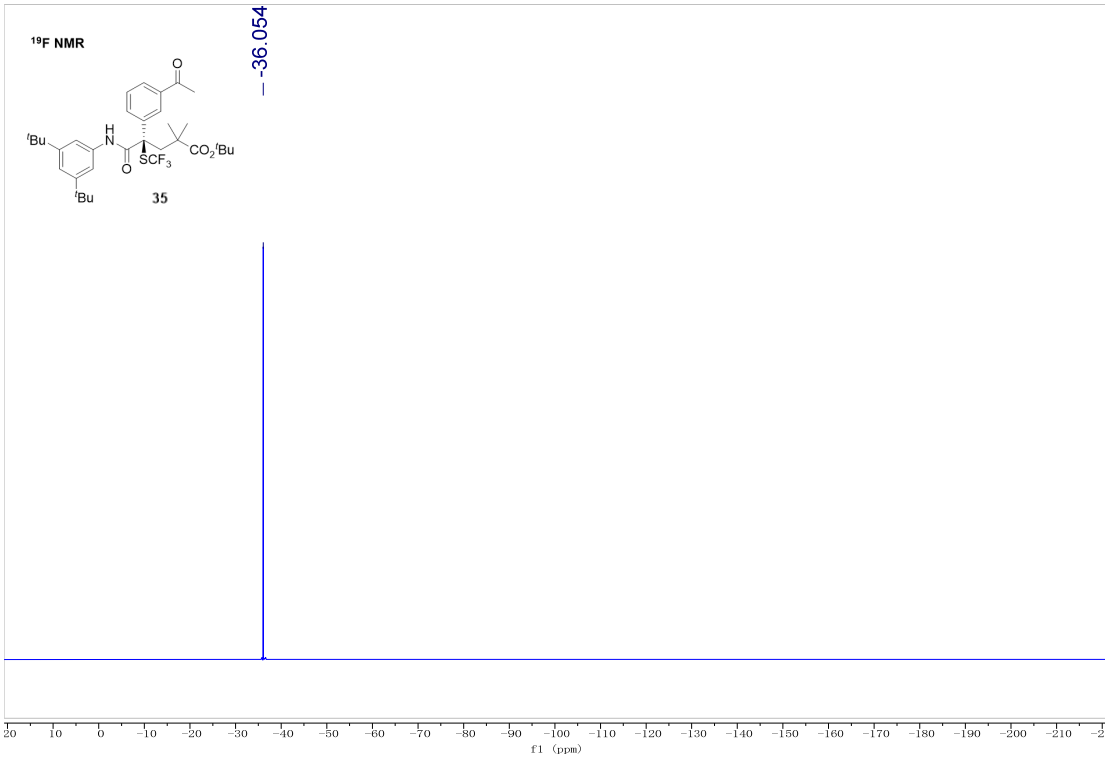

176.201
168.174
151.677
138.532
136.600
133.855
130.770
128.619
127.986
127.686
124.601
119.187
114.598
80.349
77.317
77.000
76.682
65.331
46.200
43.047
34.921
31.345
28.592
27.772
25.213
13C NMR
tBu
Ph
H
N
O
SCF3
CO2tBu
tBu
33
f1 (ppm)

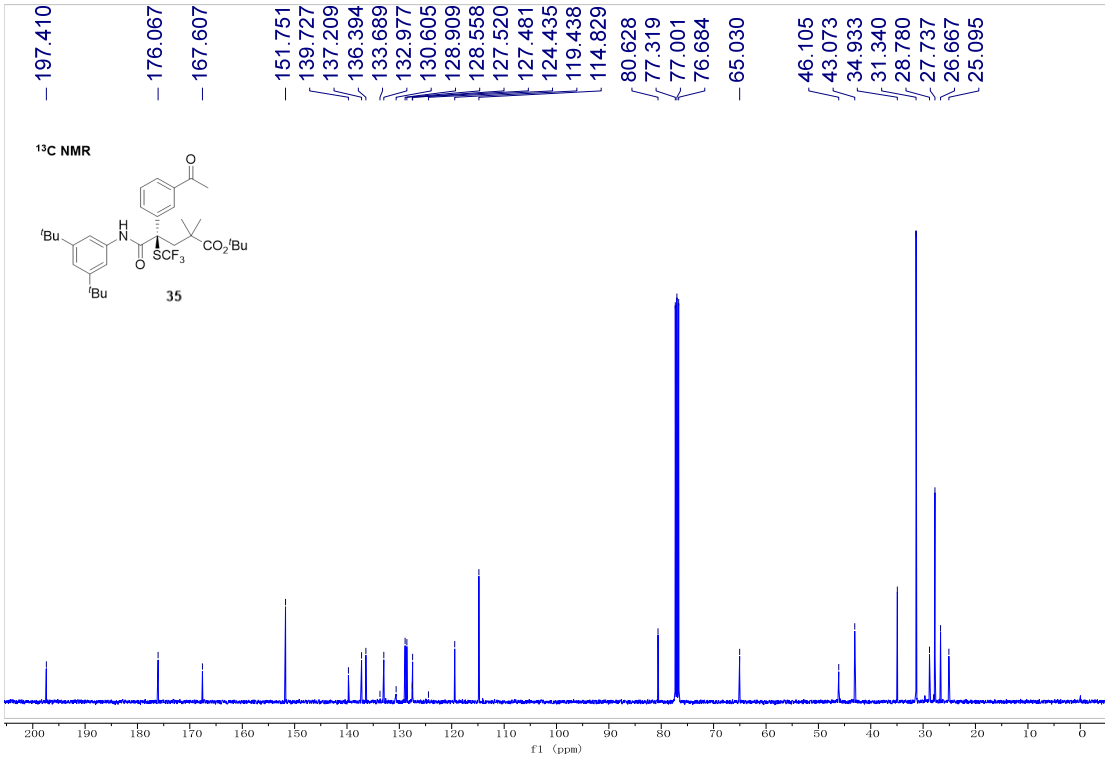

8.319
8.314
8.309
8.043
8.016
7.997
7.801
7.781
7.467
7.448
7.428
7.311
7.306
7.233
7.228
7.224
3.935
3.195
3.157
2.933
2.895
1.356
1.314
1.233
1.161
-0.000
1H NMR
CO2Me
tBu
H
N
O
SCF3
CO2tBu
tBu
34
0.931
0.861
1.022
1.001
1.019
1.917
1.072
2.843
1.000
1.014
9.273
17.964
3.311
3.267
f1 (ppm)

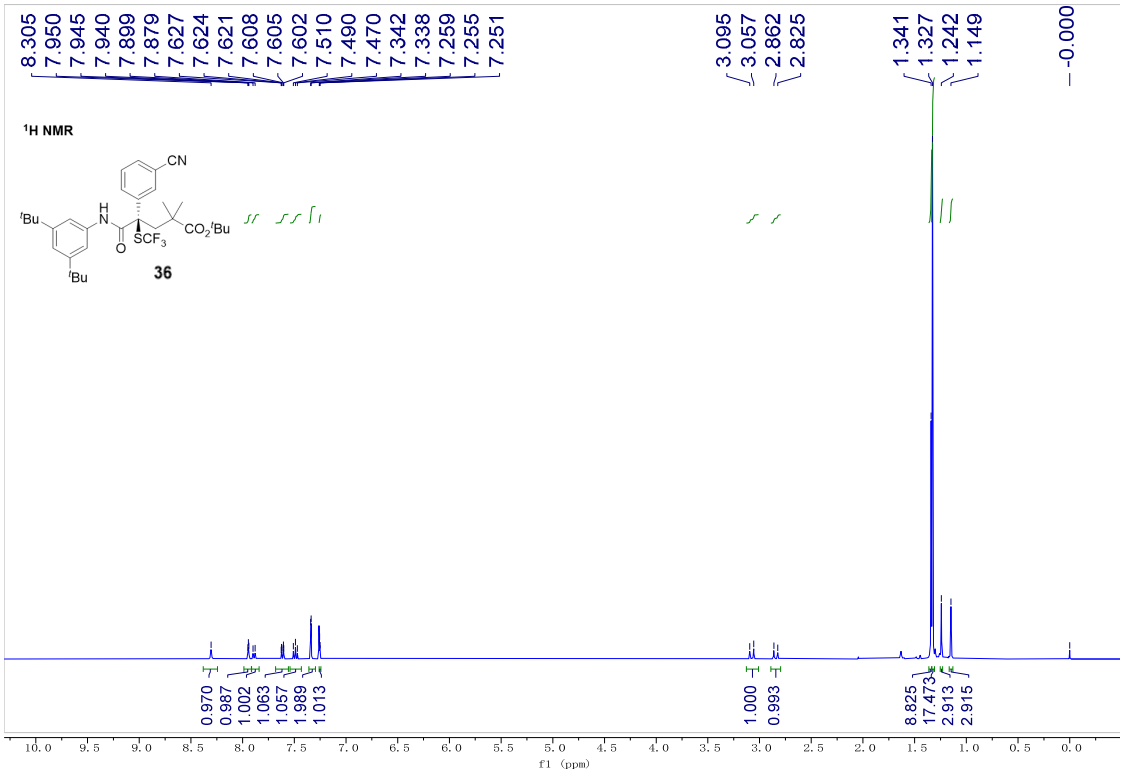

19F NMR
-36.062
CO2Me
tBu
N
H
O
SCF3
CO2tBu
tBu
34
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

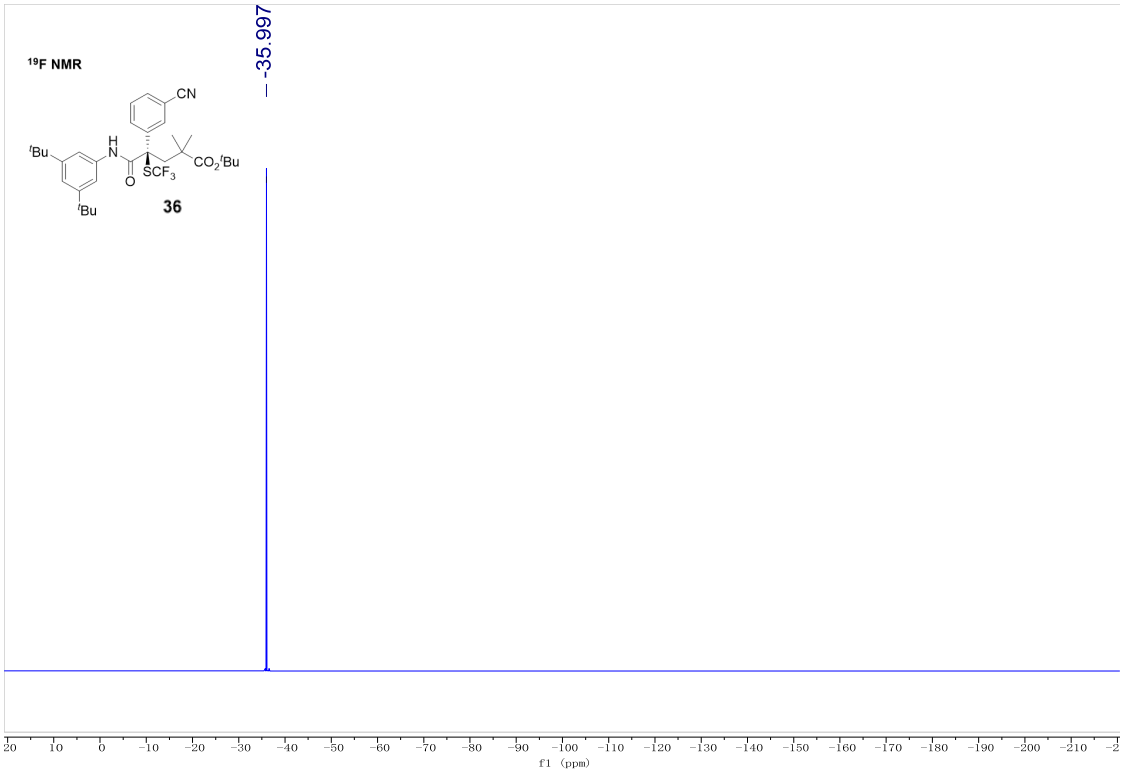

176.094
167.621
166.458
151.733
139.524
136.421
133.703
132.867
130.617
130.486
129.761
128.809
128.762
127.533
124.450
119.414
114.864
80.617
77.317
77.000
76.683
64.977
52.337
46.165
43.084
34.936
31.345
28.738
27.739
25.096
13C NMR
CO2Me
tBu
N
H
O
SCF3
CO2tBu
tBu
34
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

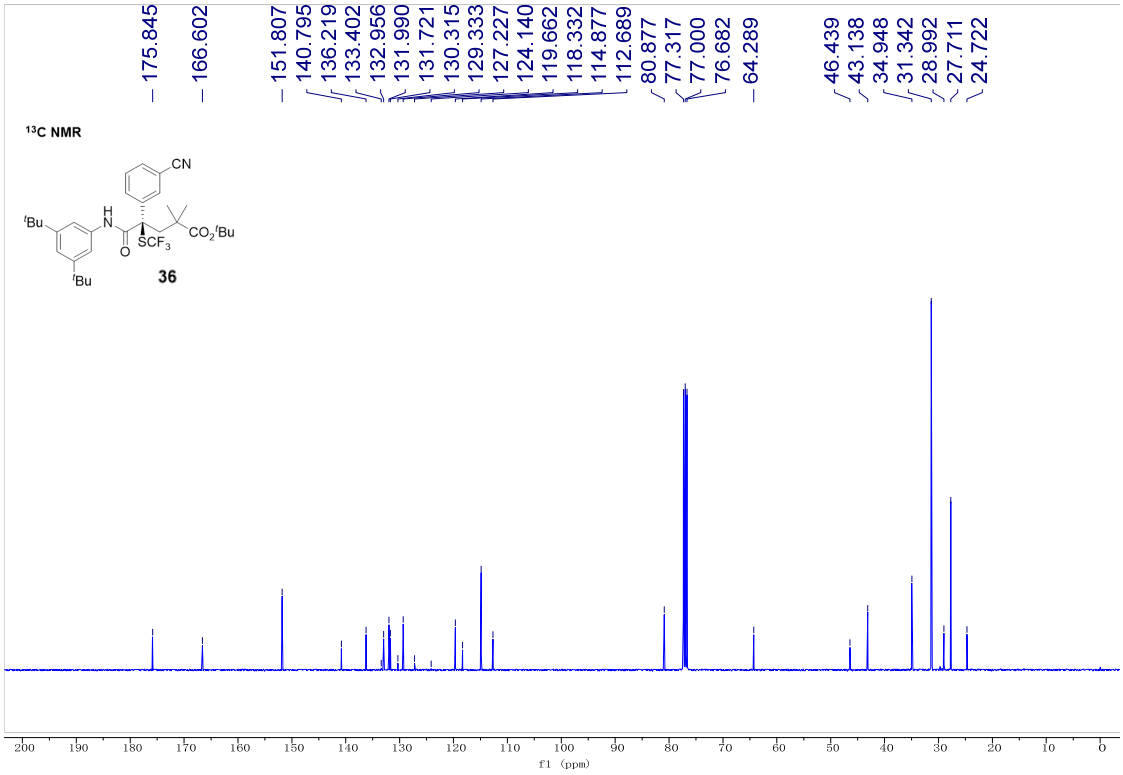

8.247
8.242
8.237
8.075
7.918
7.915
7.911
7.898
7.895
7.892
7.819
7.816
7.799
7.796
7.493
7.474
7.454
7.316
7.311
7.235
7.231
7.226
3.202
3.164
2.935
2.898
2.620
1.349
1.314
1.236
1.165
-0.000
1H NMR
tBu
tBu
SCF3
CO2tBu
35
0.983
0.914
0.995
1.035
1.033
1.971
1.010
1.000
1.011
3.153
9.226
18.021
3.257
3.123
f1 (ppm)

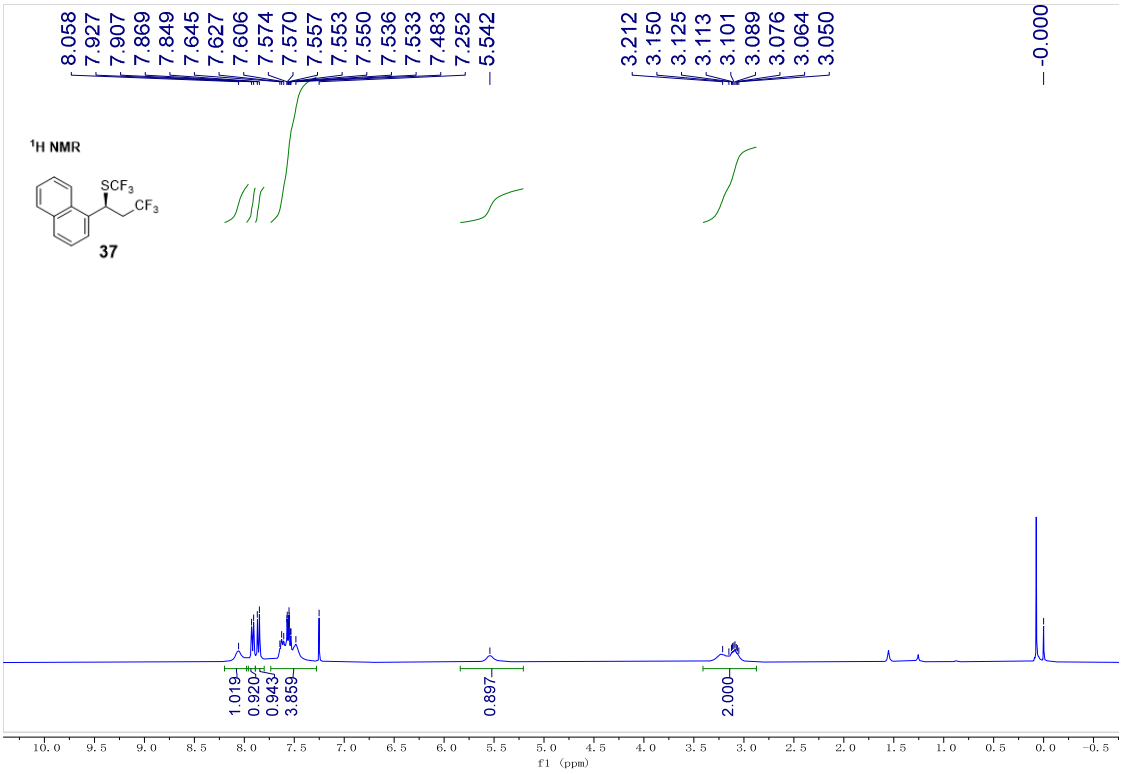

19F NMR
-36.054
tBu
tBu
SCF3
CO2tBu
35
f1 (ppm)

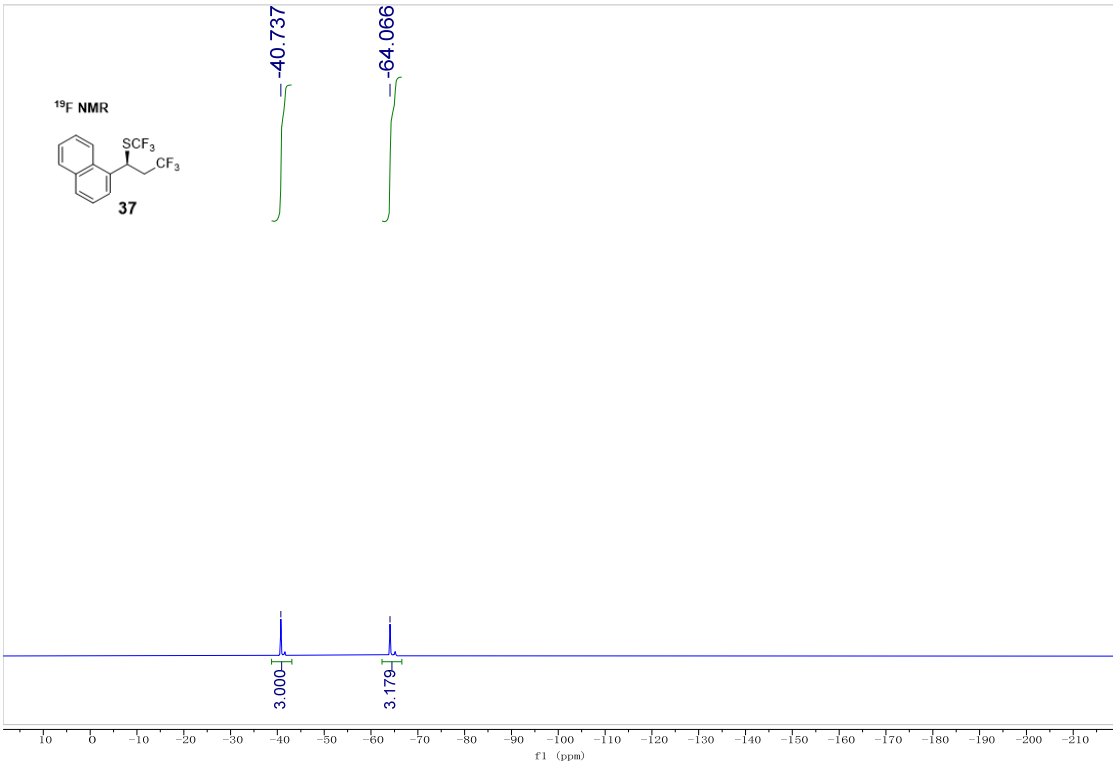

197.410
176.067
167.607
151.751
139.727
137.209
136.394
133.689
132.977
130.605
128.909
128.558
127.520
127.481
124.435
119.438
114.829
80.628
77.319
77.001
76.684
65.030
46.105
43.073
34.933
31.340
28.780
27.737
26.667
25.095
13C NMR
35
f1 (ppm)

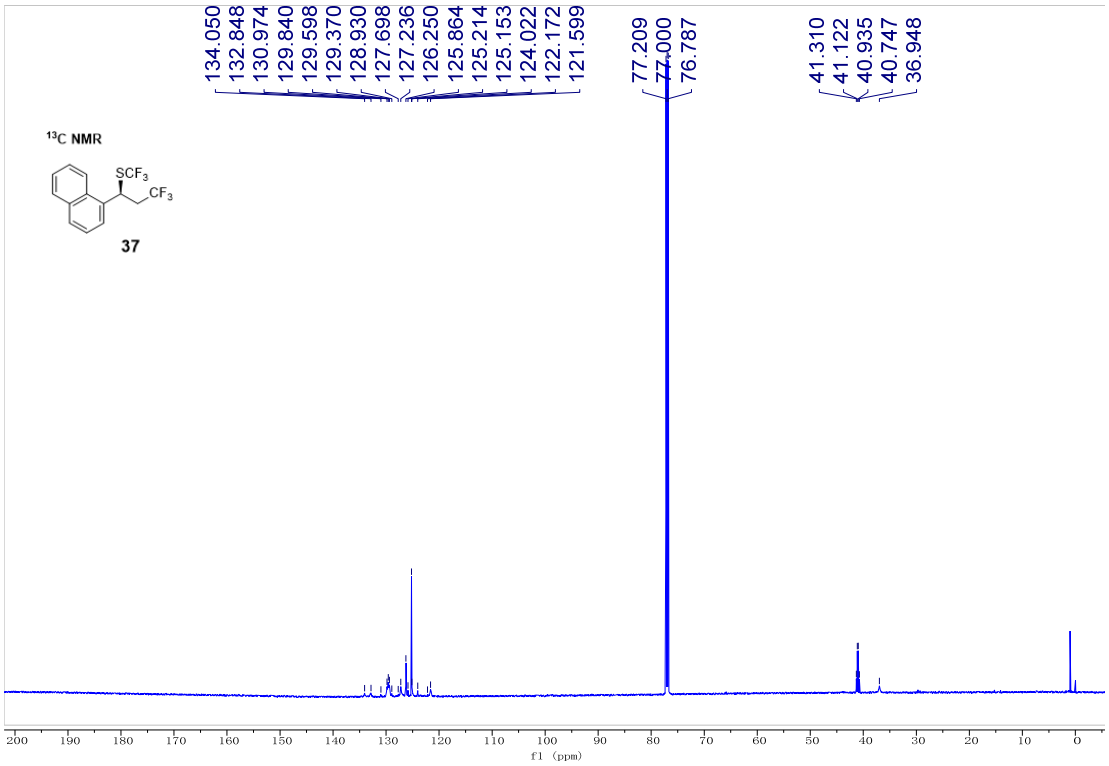

8.305
7.950
7.945
7.940
7.899
7.879
7.627
7.624
7.621
7.608
7.605
7.602
7.510
7.490
7.470
7.342
7.338
7.259
7.255
7.251
3.095
3.057
2.862
2.825
1.341
1.327
1.242
1.149
-0.000
1H NMR
36
0.970
0.987
1.002
1.063
1.057
1.989
1.013
1.000
0.993
8.825
17.473
2.913
2.915
f1 (ppm)

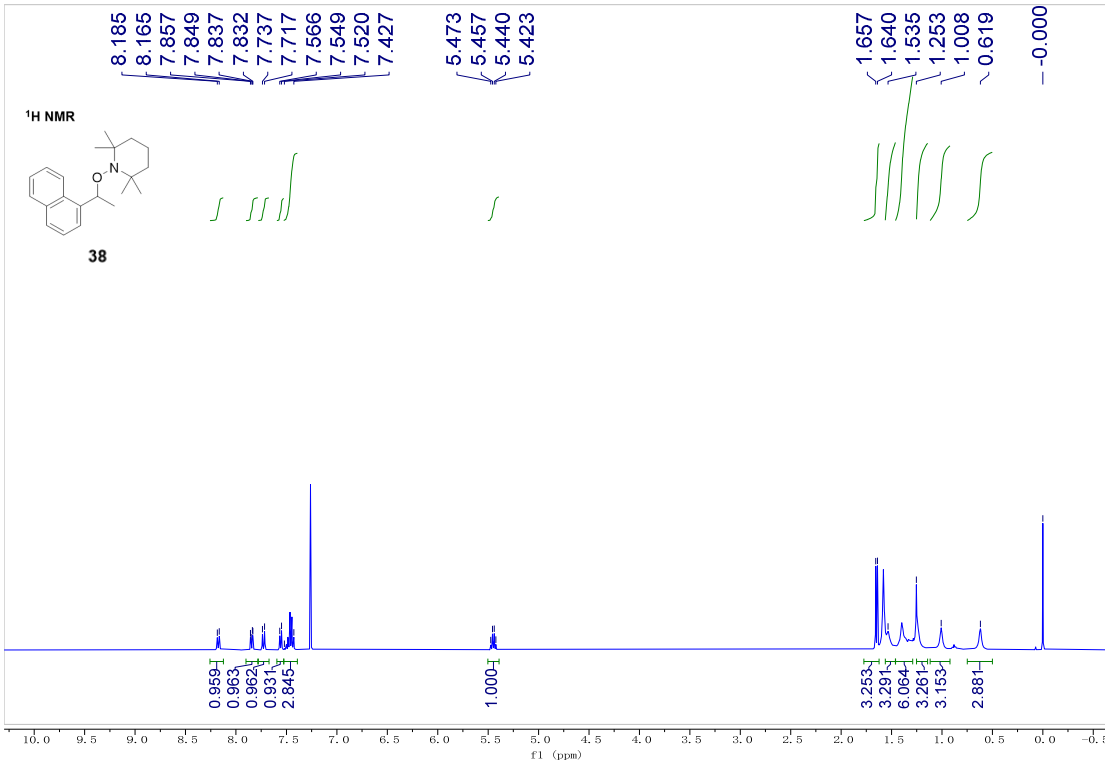

19F NMR
-35.997
CN
tBu
tBu
SCF3
CO2tBu
36
f1 (ppm)

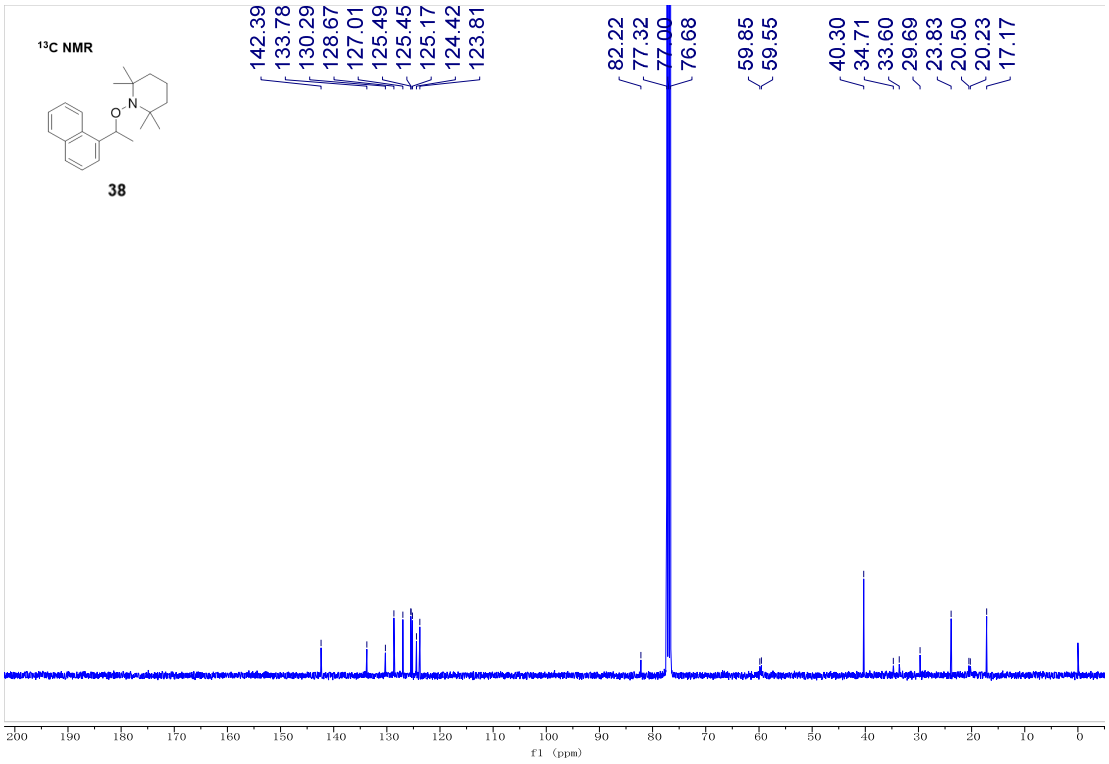

175.845
166.602
151.807
140.795
136.219
133.402
132.956
131.990
131.721
130.315
129.333
127.227
124.140
119.662
118.332
114.877
112.689
80.877
77.317
77.000
76.682
64.289
46.439
43.138
34.948
31.342
28.992
27.711
24.722
13C NMR
CN
tBu
tBu
SCF3
CO2tBu
36
f1 (ppm)


8.058
7.927
7.907
7.869
7.849
7.645
7.627
7.606
7.574
7.570
7.557
7.553
7.550
7.536
7.533
7.483
7.252
5.542
3.212
3.150
3.125
3.113
3.101
3.089
3.076
3.064
3.050
-0.000
1H NMR
SCF3
CF3
37
1.019
0.920
0.943
3.859
0.897
2.000
f1 (ppm)

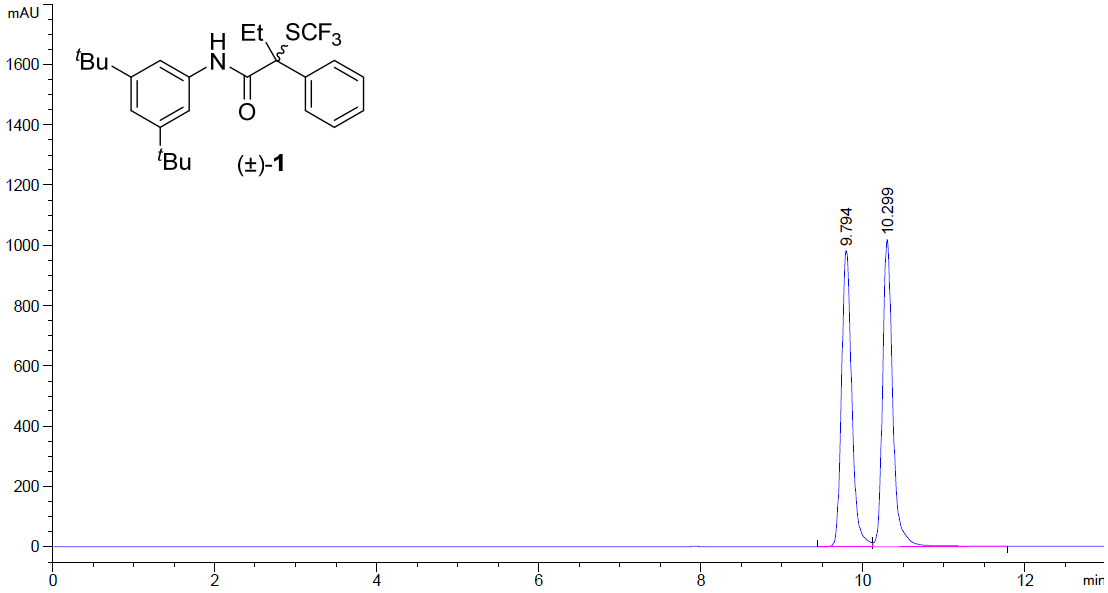

-40.737
-64.066
19F NMR
SCF3
CF3
37
3.000
3.179
f1 (ppm)


134.050
132.848
130.974
129.840
129.598
129.370
128.930
127.698
127.236
126.250
125.864
125.214
125.153
124.022
122.172
121.599
77.209
77.000
76.787
41.310
41.122
40.935
40.747
36.948
13C NMR
SCF3
CF3
37
f1 (ppm)


8.185
8.165
7.857
7.849
7.837
7.832
7.737
7.717
7.566
7.549
7.520
7.427
5.473
5.457
5.440
5.423
1.657
1.640
1.535
1.253
1.008
0.619
-0.000
1H NMR
N
O
38
0.959
0.963
0.962
0.931
2.845
1.000
3.253
3.291
6.064
3.261
3.153
2.881
f1 (ppm)

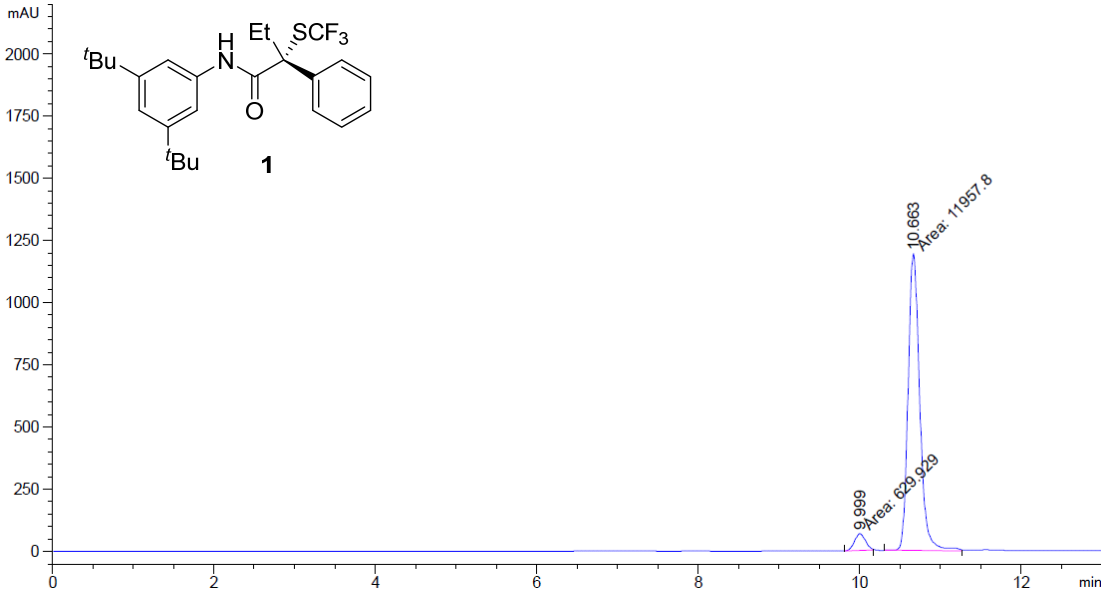

13C NMR
38
142.39
133.78
130.29
128.67
127.01
125.49
125.45
125.17
124.42
123.81
82.22
77.32
77.00
76.68
59.85
59.55
40.30
34.71
33.60
29.69
23.83
20.50
20.23
17.17
f1 (ppm)

11. HPLC spectra of the products



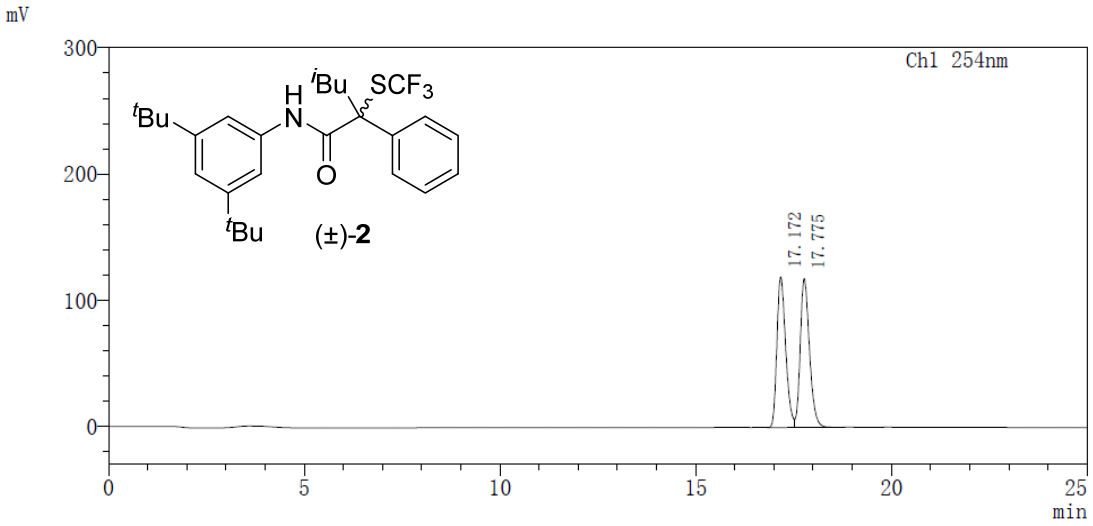
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.794	BV	0.1346	8640.30176	982.50580	49.3669
2	10.299	VB	0.1315	8861.91211	1018.89716	50.6331



Signal 1: DAD1 B, Sig=254,4 Ref=360,100

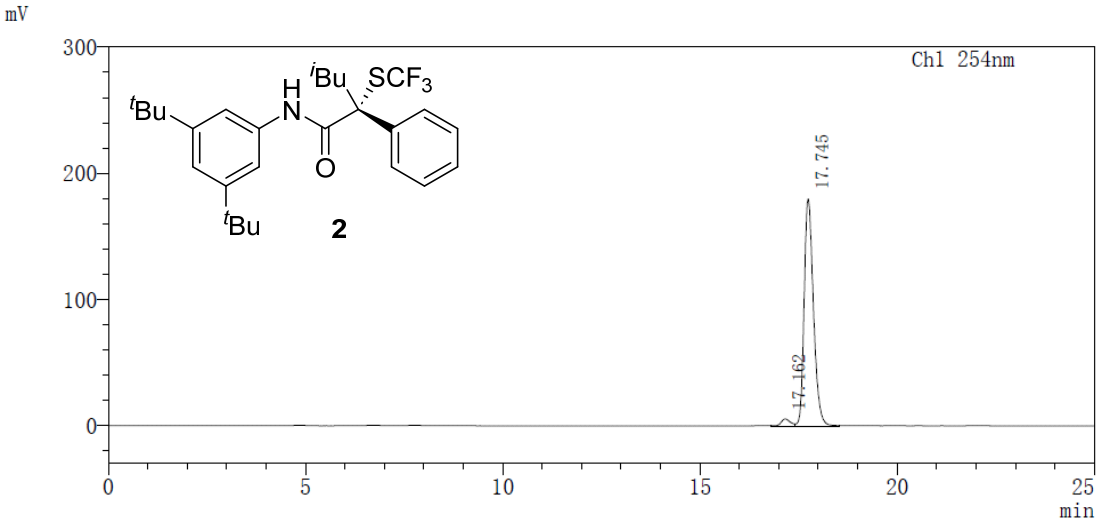
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.999	MM	0.1577	629.92908	66.58321	5.0043
2	10.663	MM	0.1672	1.19578e4	1191.62732	94.9957



Peak Table

Ch1 254nm

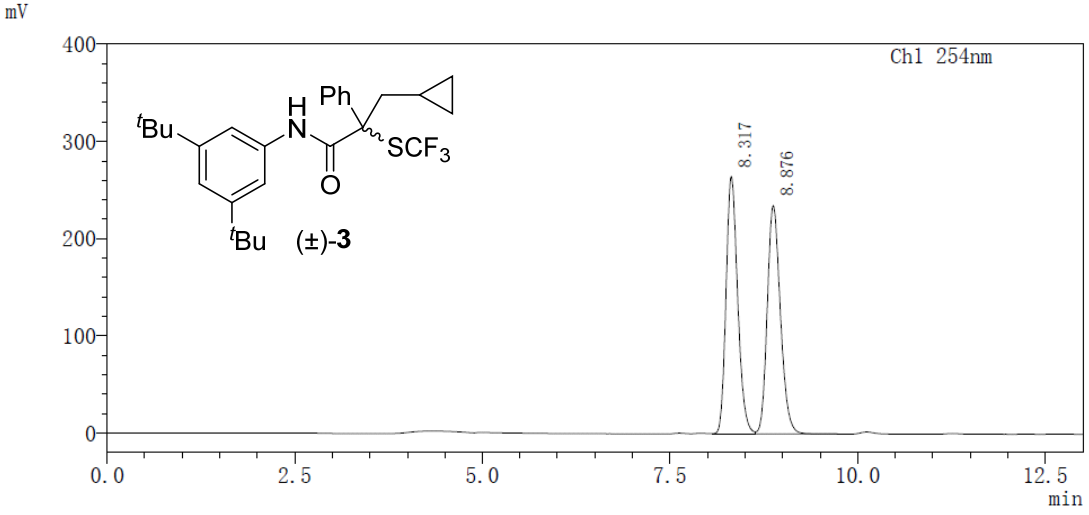
Peak#	Ret. Time	Area	Area%
1	17.172	1865258	49.052
2	17.775	1937337	50.948



Peak Table

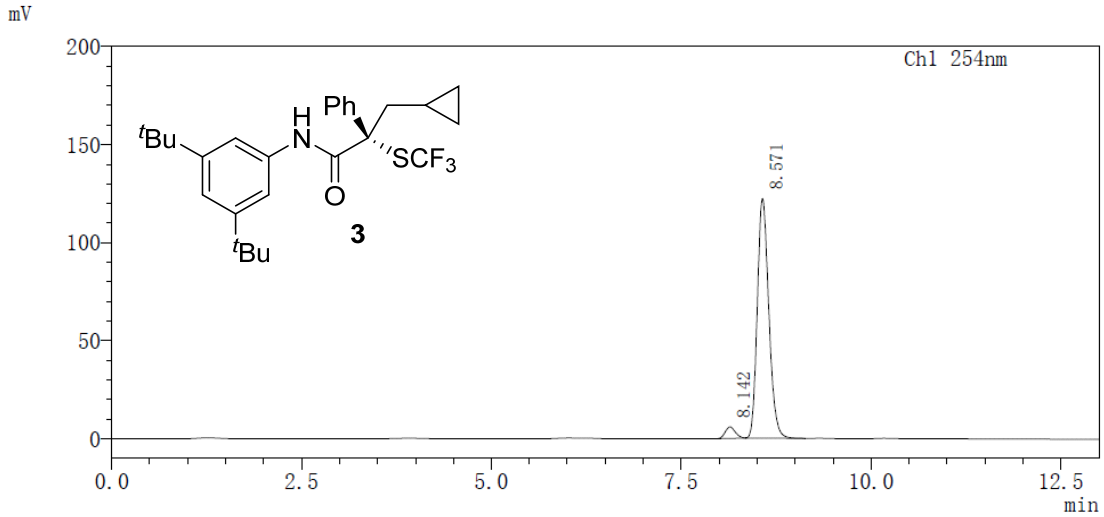
Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.162	89237	2.936
2	17.745	2950239	97.064



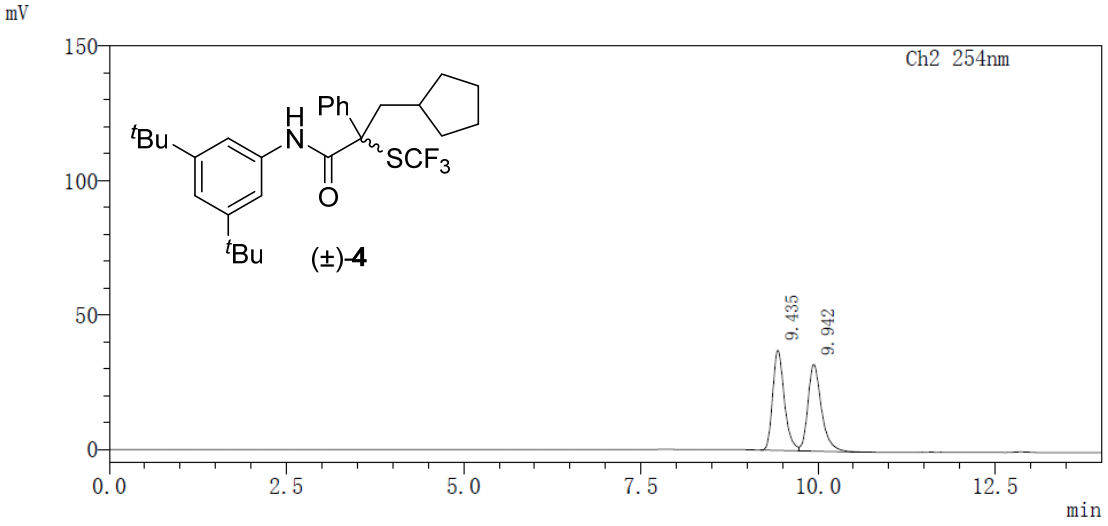
Ch1 254nm

T	Hight	Area	Area%
8.317	264949	2853743	49.889
8.876	235104	2866466	50.111



Ch1 254nm

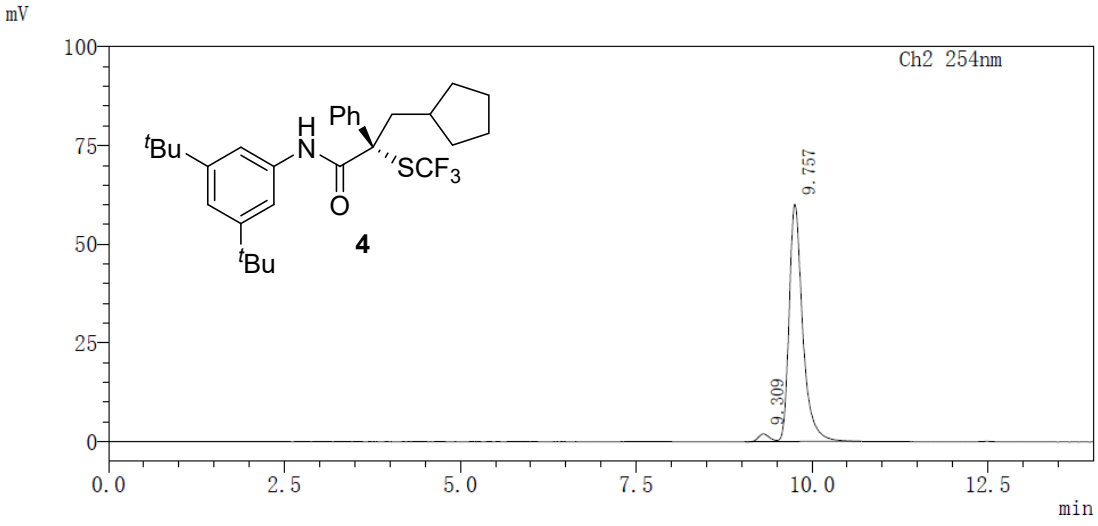
T	Hight	Area	Area%
8.142	5775	52845	3.945
8.571	122196	1286541	96.055



Peak Table

Ch2 254nm

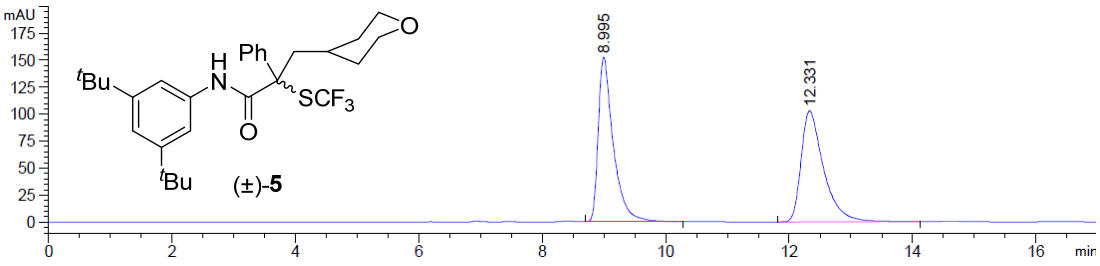
Peak#	Ret. Time	Area	Area%
1	9.435	427612	49.828
2	9.942	430557	50.172



Peak Table

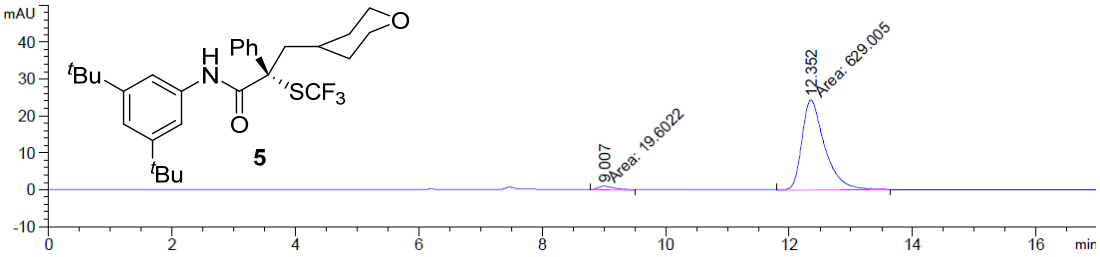
Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	9.309	21521	2.601
2	9.757	805925	97.399



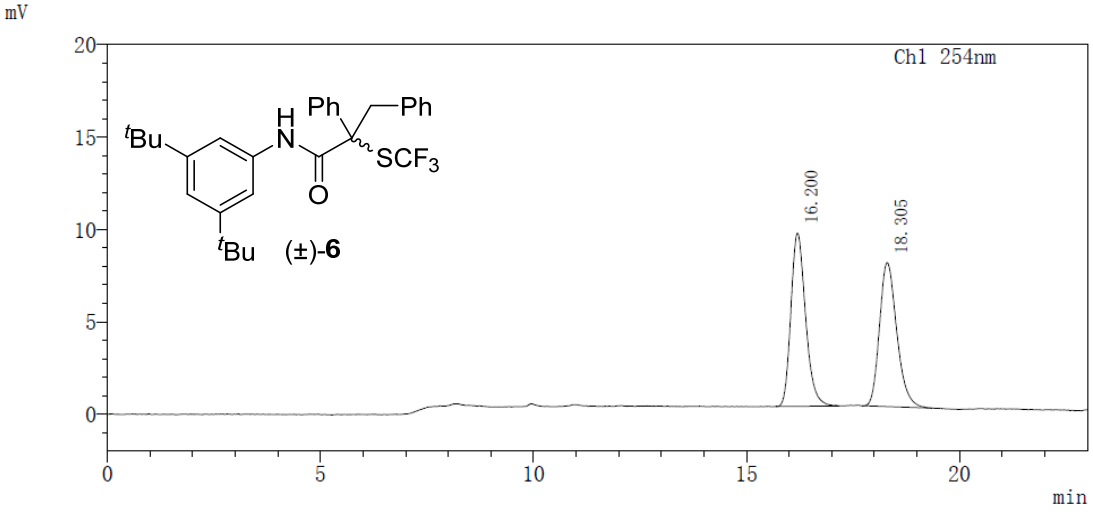
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.995	BB	0.2470	2578.02319	152.63982	49.8340
2	12.331	BB	0.3744	2595.20313	102.83403	50.1660
Totals :				5173.22632	255.47385	



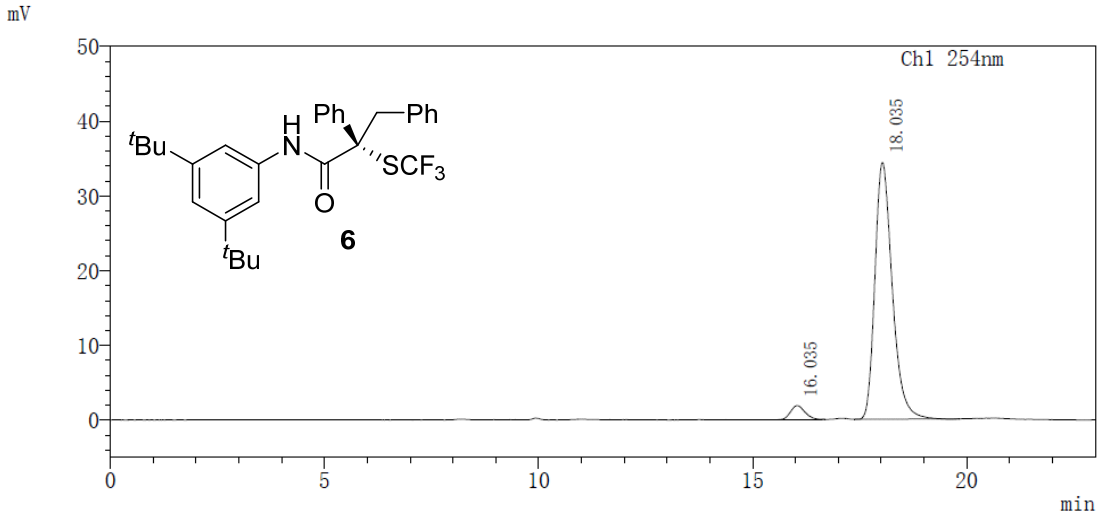
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.007	MM	0.3284	19.60225	9.94965e-1	3.0222
2	12.352	MM	0.4296	629.00525	24.40534	96.9778
Totals :				648.60750	25.40031	



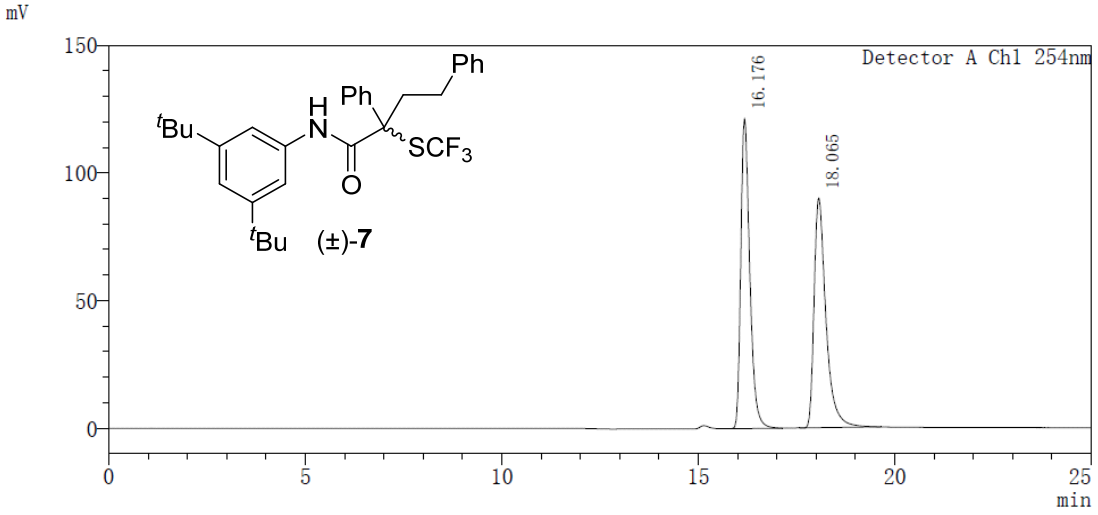
Ch1 254nm

T	Hight	Area	Area%
16.200	9378	224845	50.518
18.305	7803	220238	49.482



Ch1 254nm

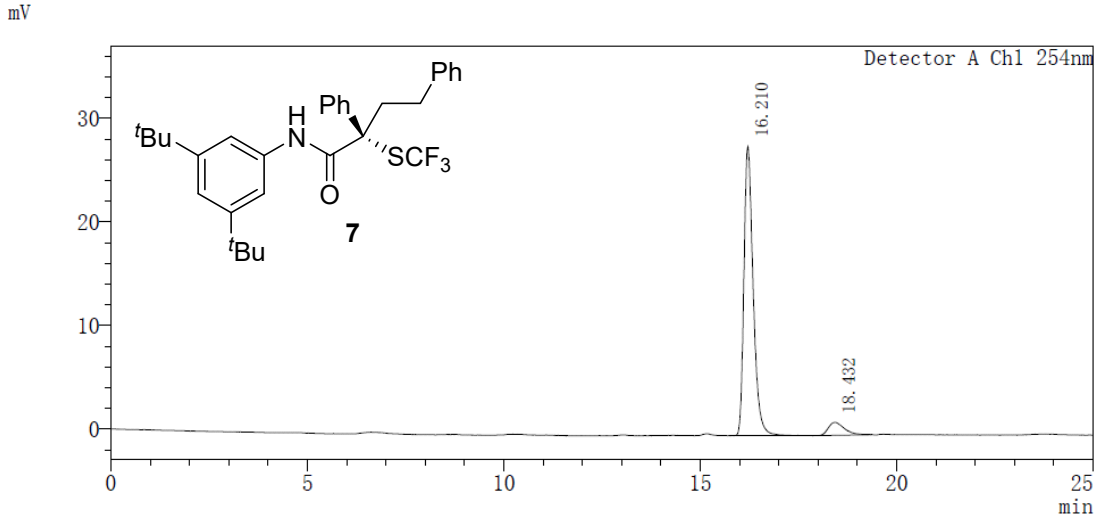
T	Hight	Area	Area%
16.035	1871	44317	4.368
18.035	34360	970164	95.632



Peak Table

Detector A Ch1 254nm

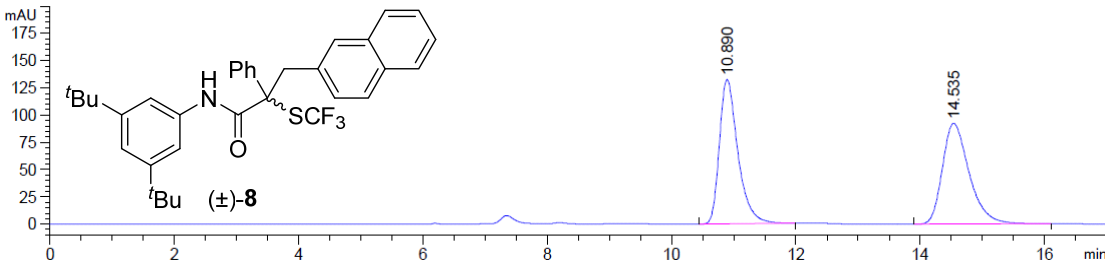
Peak#	Ret. Time	Area	Area%
1	16.176	1929548	50.610
2	18.065	1883020	49.390



Peak Table

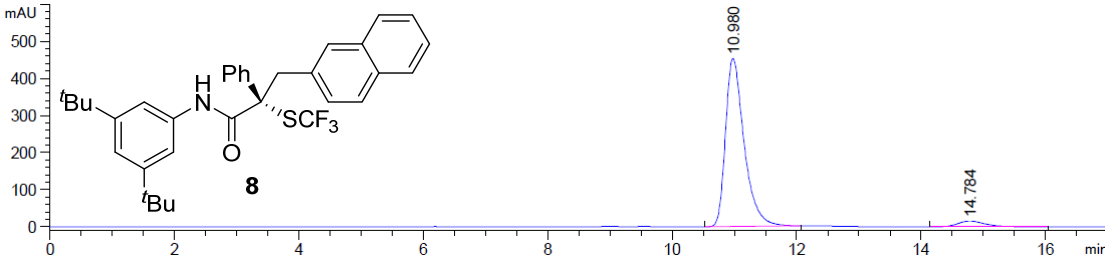
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.210	458293	92.726
2	18.432	35952	7.274



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

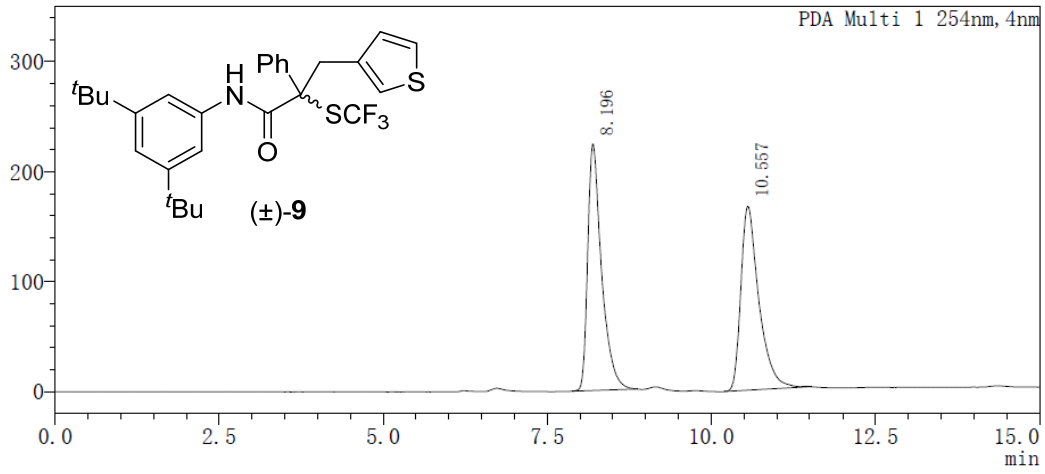
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.890	BB	0.3131	2737.50391	132.48270	49.7758
2	14.535	BB	0.4531	2762.16309	92.32162	50.2242
Totals :				5499.66699	224.80431	



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.980	BB	0.3139	9391.73145	452.91617	95.3427
2	14.784	BB	0.4641	458.77042	15.03215	4.6573
Totals :				9850.50186	467.94831	

mAU

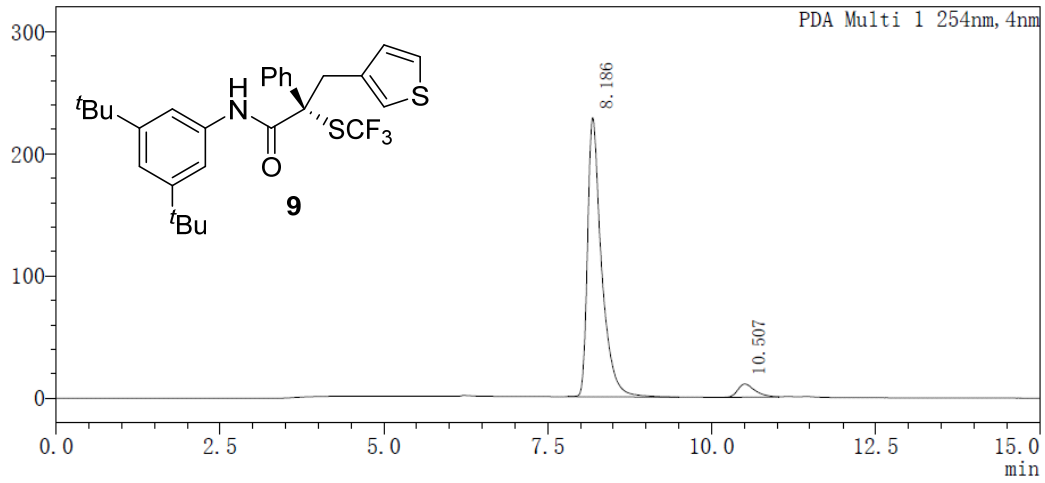


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.196	3291899	50.645
2	10.557	3208092	49.355

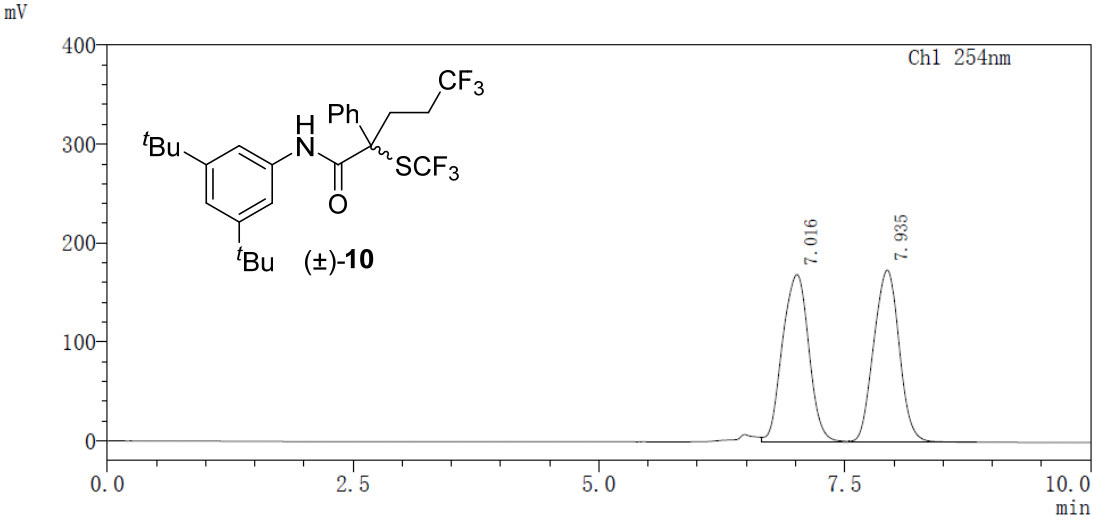
mAU



Peak Table

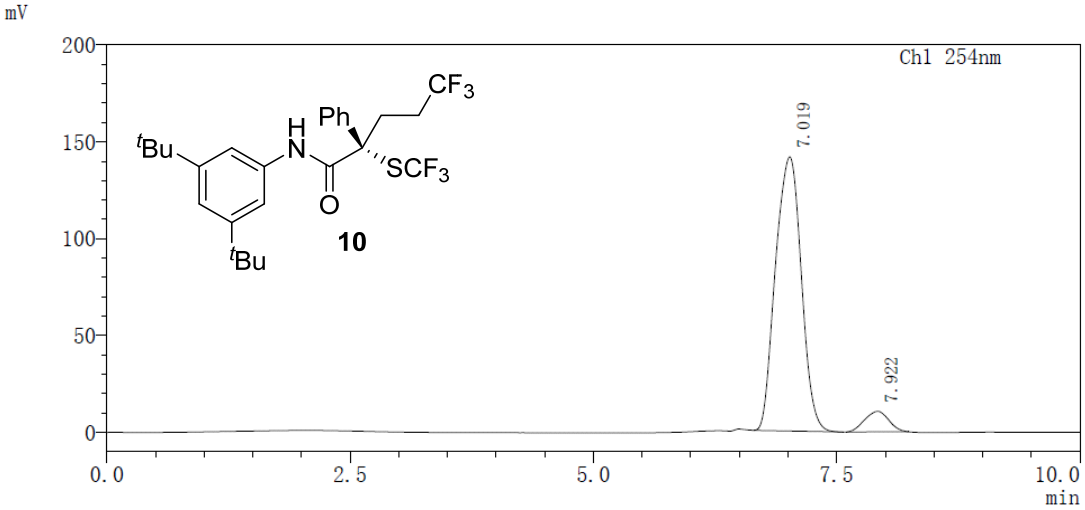
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.186	3388570	94.516
2	10.507	196611	5.484



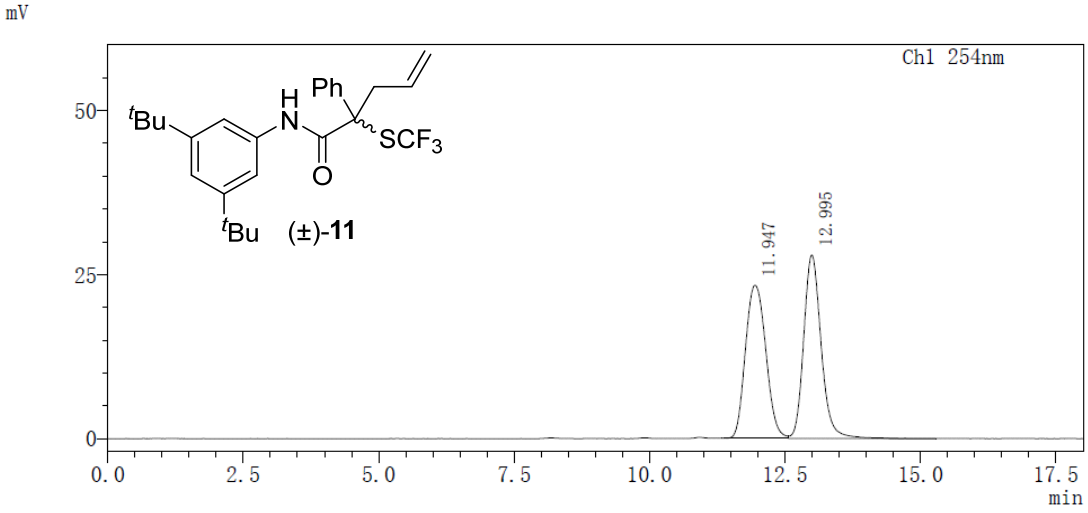
Ch1 254nm

T	Hight	Area	Area%
7.016	169228	3169084	50.413
7.935	173871	3117127	49.587



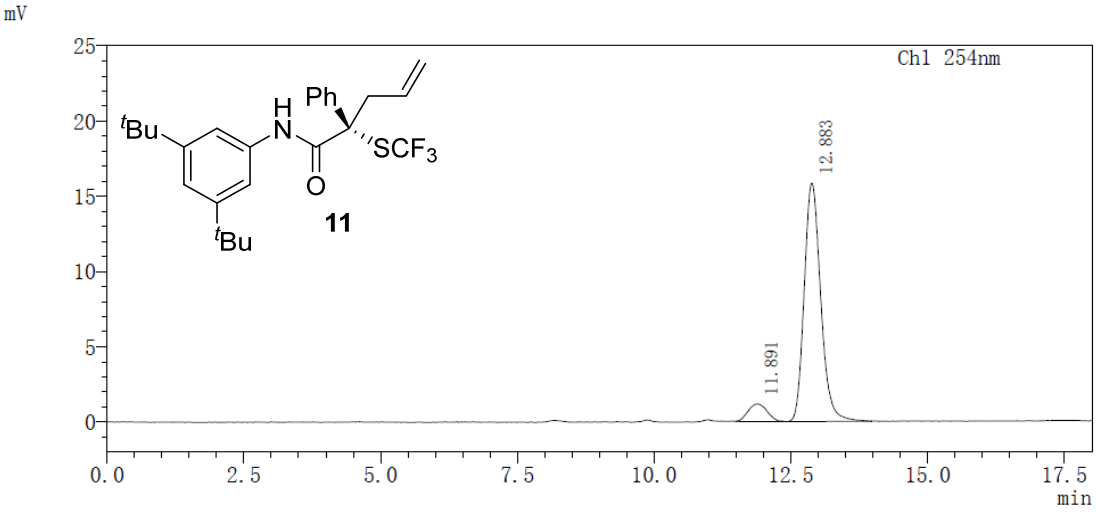
Ch1 254nm

T	Hight	Area	Area%
7.019	141573	2616275	93.513
7.922	10587	181479	6.487



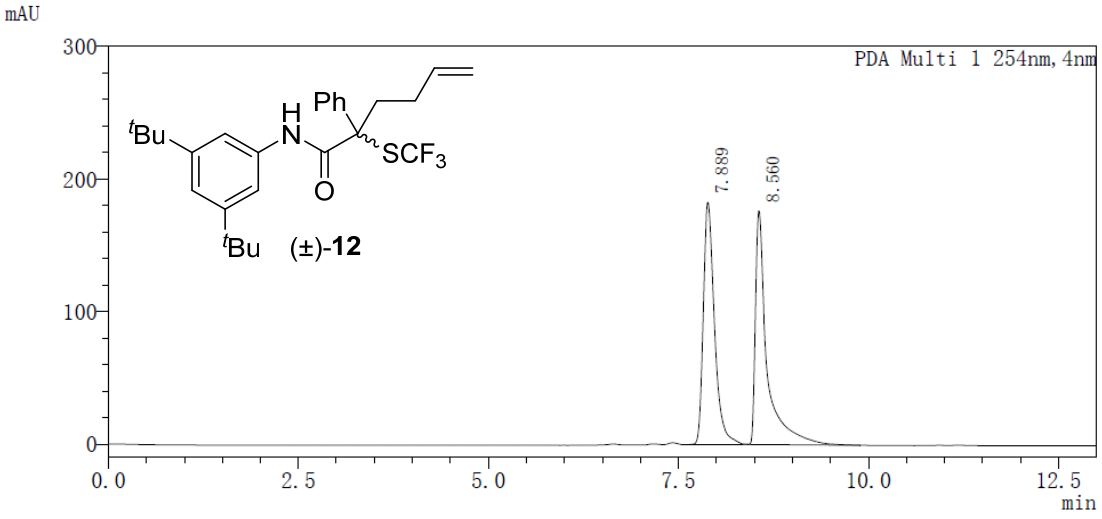
Ch1 254nm

T	Hight	Area	Area%
11.947	23391	613070	49.397
12.995	27981	628040	50.603



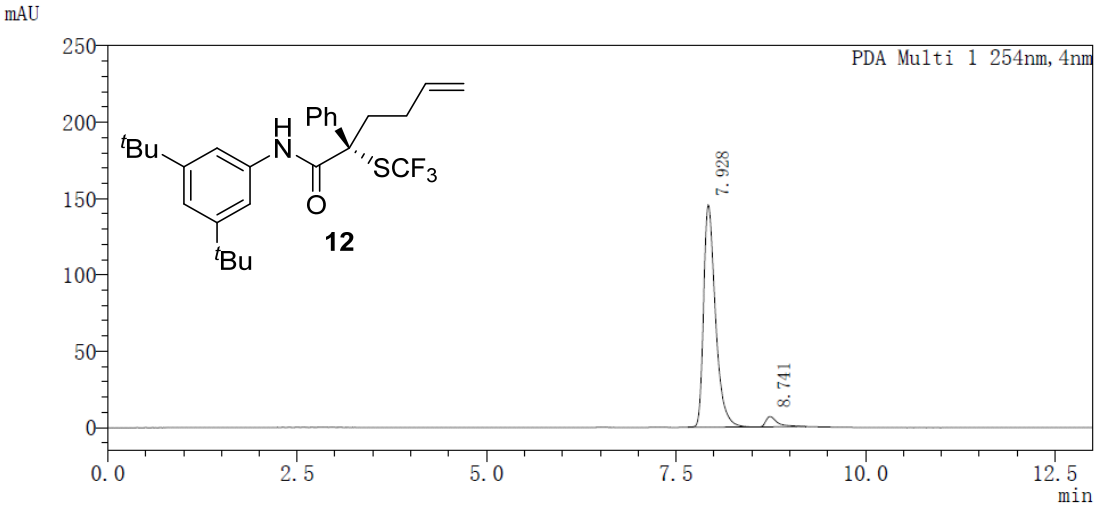
Ch1 254nm

T	Hight	Area	Area%
11.891	1164	28333	7.818
12.883	15858	334056	92.182



PDA Ch1 254nm

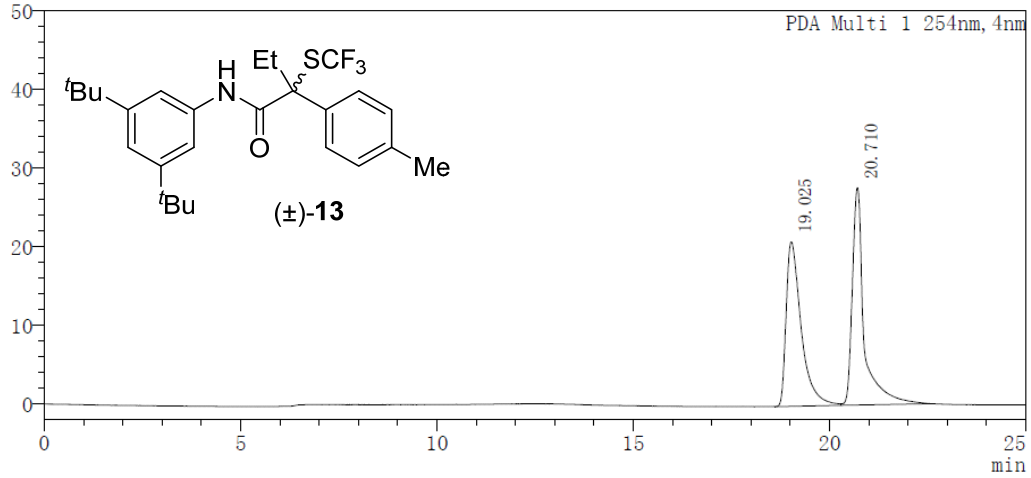
T	Hight	Area	Area%
7.889	182847	1887758	50.094
8.560	176277	1880694	49.906



PDA Ch1 254nm

T	Hight	Area	Area%
7.928	145541	1587526	95.764
8.741	6705	70226	4.236

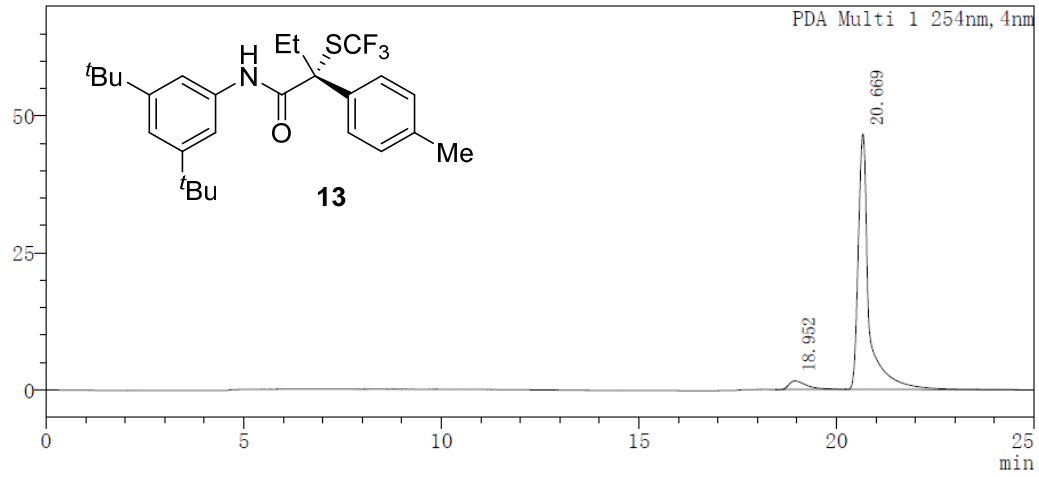
mAU



PDA Ch1 254nm

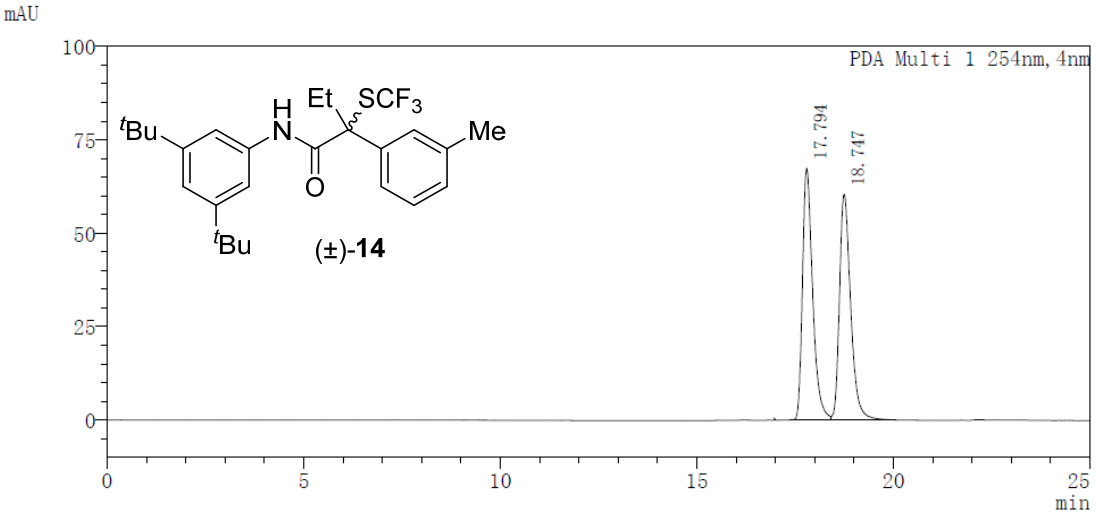
T	Hight	Area	Area%
19.025	20911	557963	49.078
20.710	27659	578936	50.922

mAU



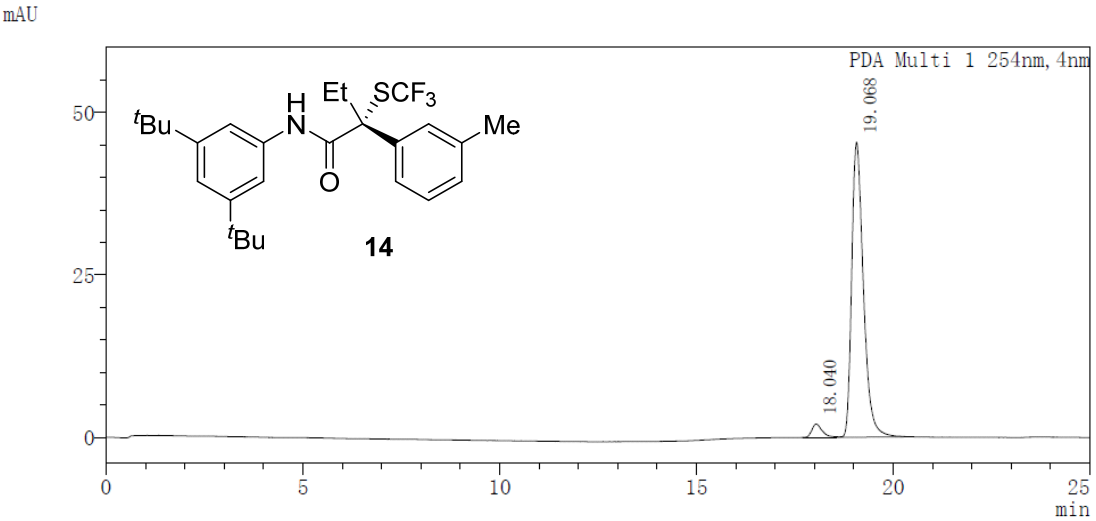
PDA Ch1 254nm

T	Hight	Area	Area%
18.952	1538	48640	5.213
20.669	46648	884493	94.787



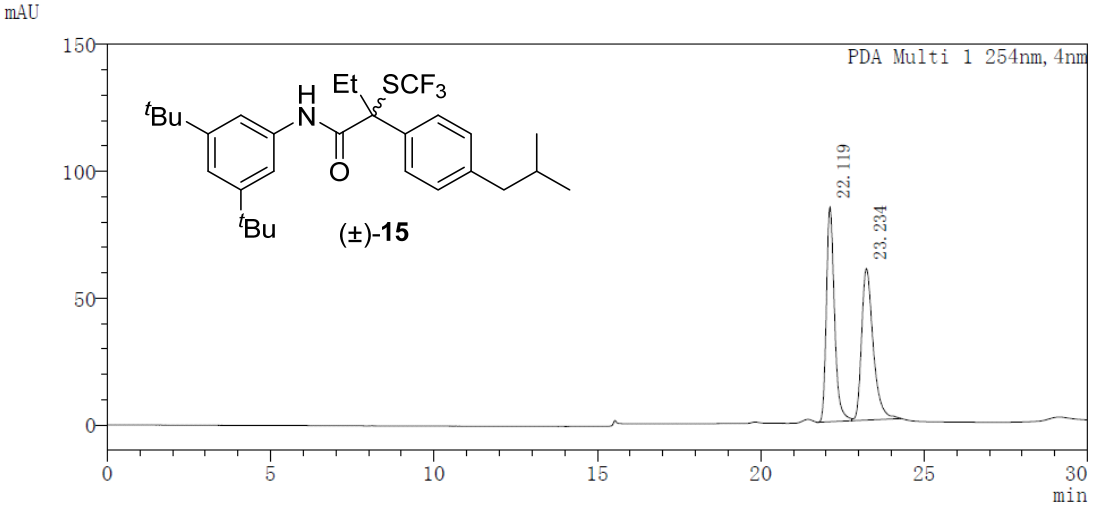
PDA Ch1 254nm

T	Hight	Area	Area%
17.794	67378	1209890	50.291
18.747	60358	1195892	49.709



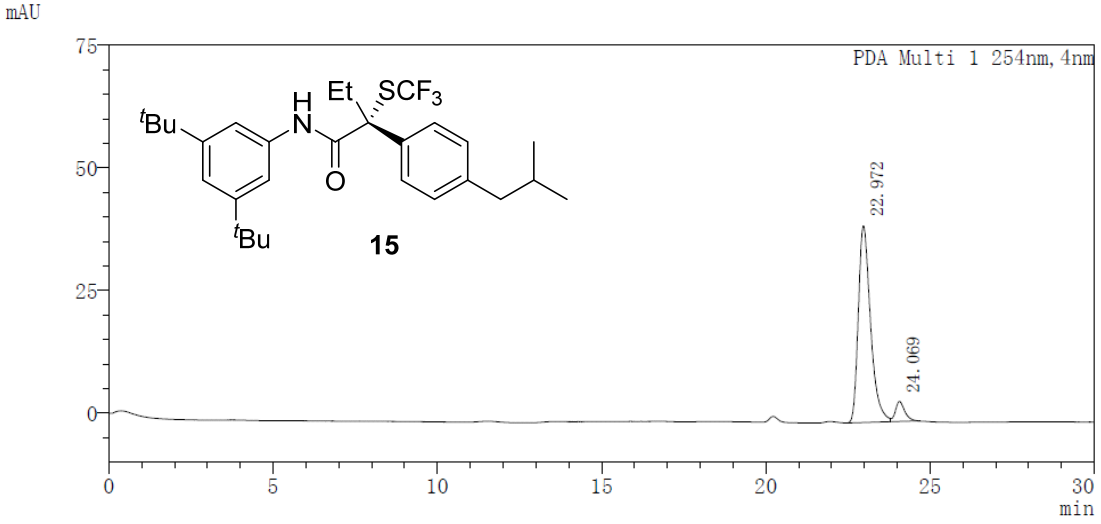
PDA Ch1 254nm

T	Hight	Area	Area%
18.040	2031	36997	3.793
19.068	45384	938421	96.207



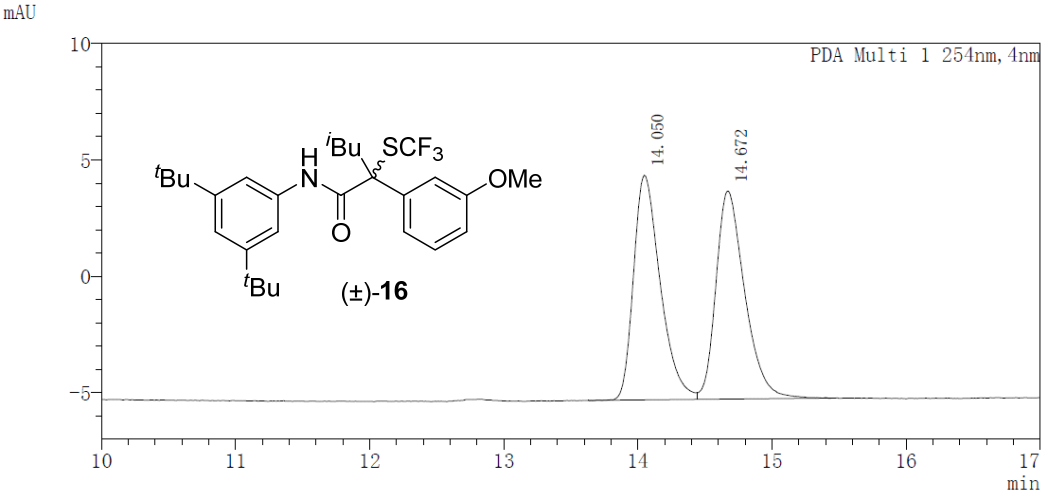
PDA Ch1 254nm

T	Hight	Area	Area%
22.119	84561	1461979	49.757
23.234	59743	1476254	50.243



PDA Ch1 254nm

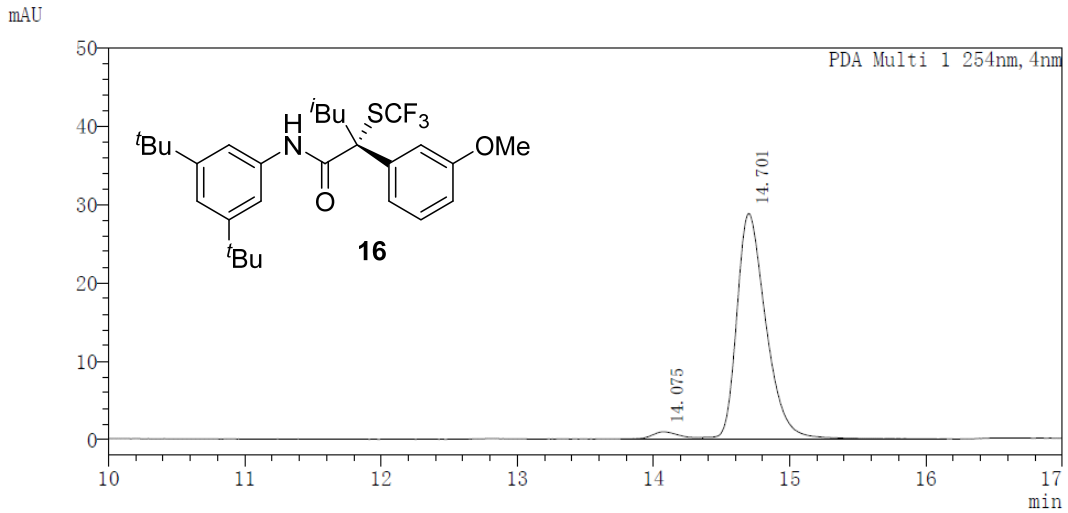
T	Hight	Area	Area%
22.972	40112	1037673	92.622
24.069	4081	82654	7.378



Peak Table

PDA Ch1 254nm

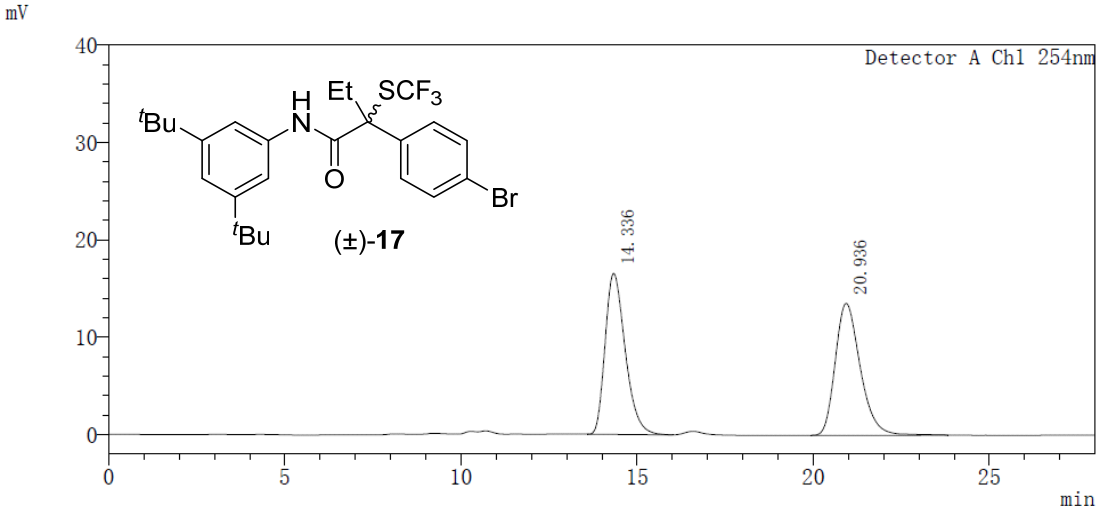
Peak#	Ret. Time	Area	Area%
1	14.050	133961	50.056
2	14.672	133663	49.944



Peak Table

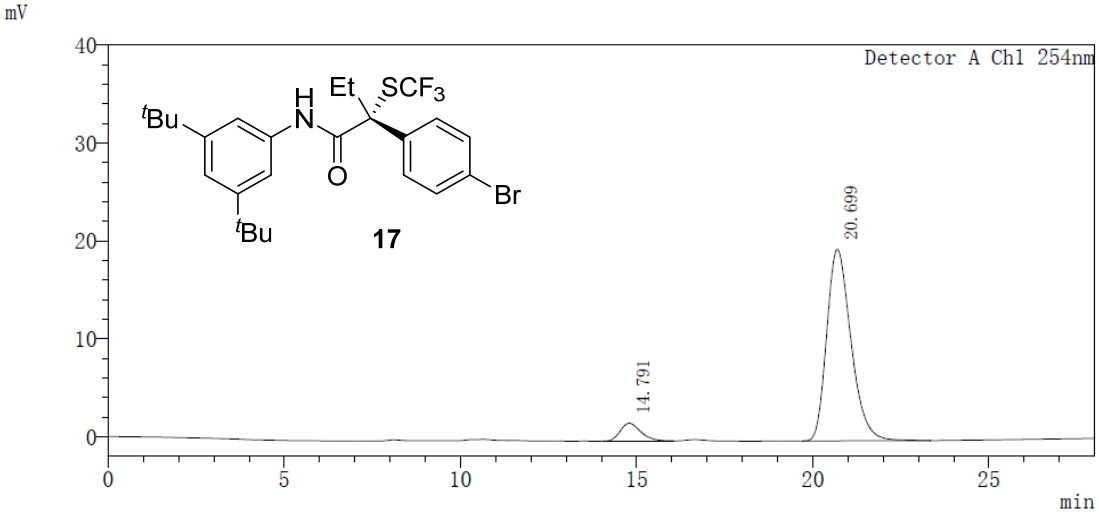
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.075	13080	2.972
2	14.701	426988	97.028



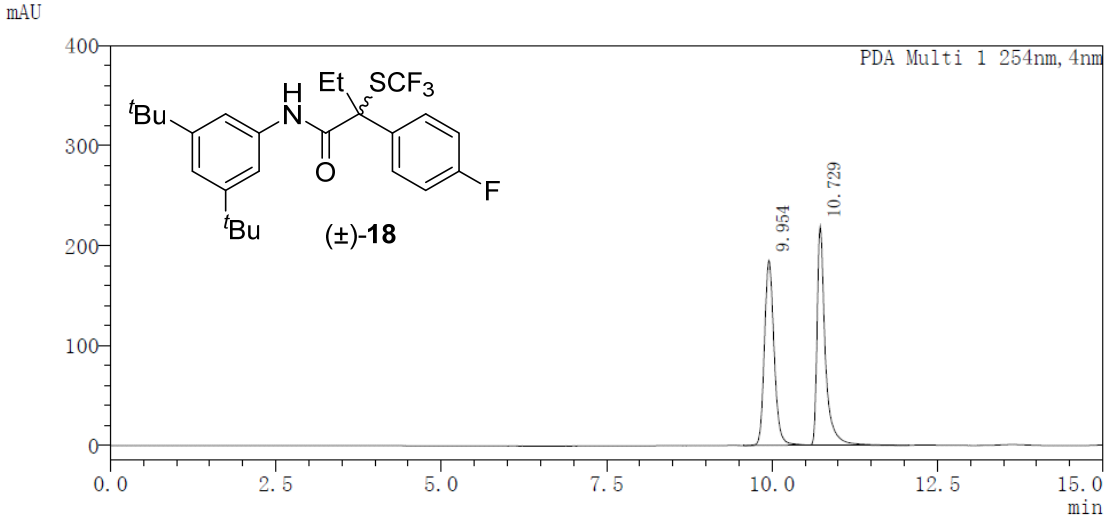
Detector A Ch1 254nm

T	Hight	Area	Area%
14.336	16541	658597	49.598
20.936	13557	669271	50.402



Detector A Ch1 254nm

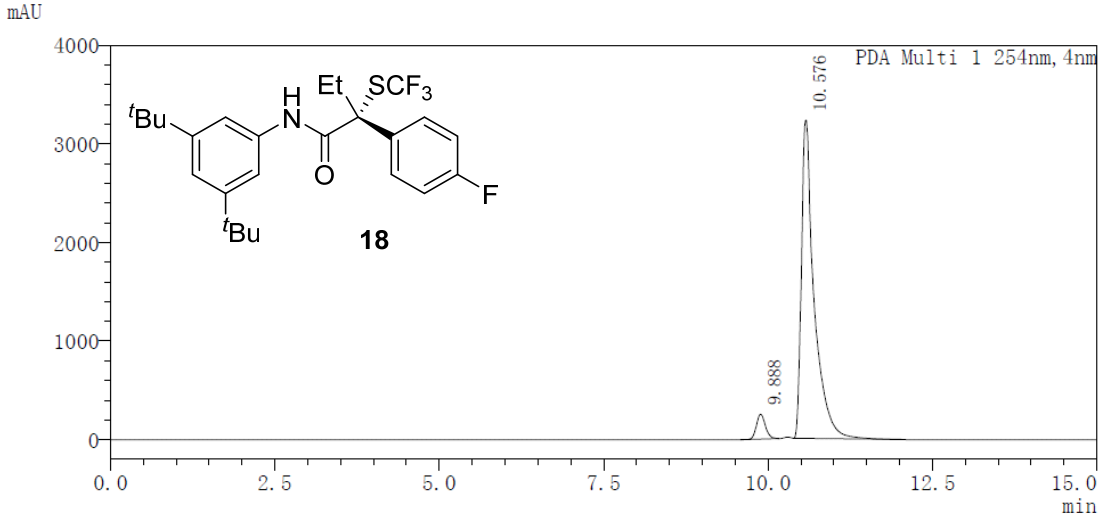
T	Hight	Area	Area%
14.791	1804	72742	7.197
20.699	19565	937976	92.803



Peak Table

PDA Ch1 254nm

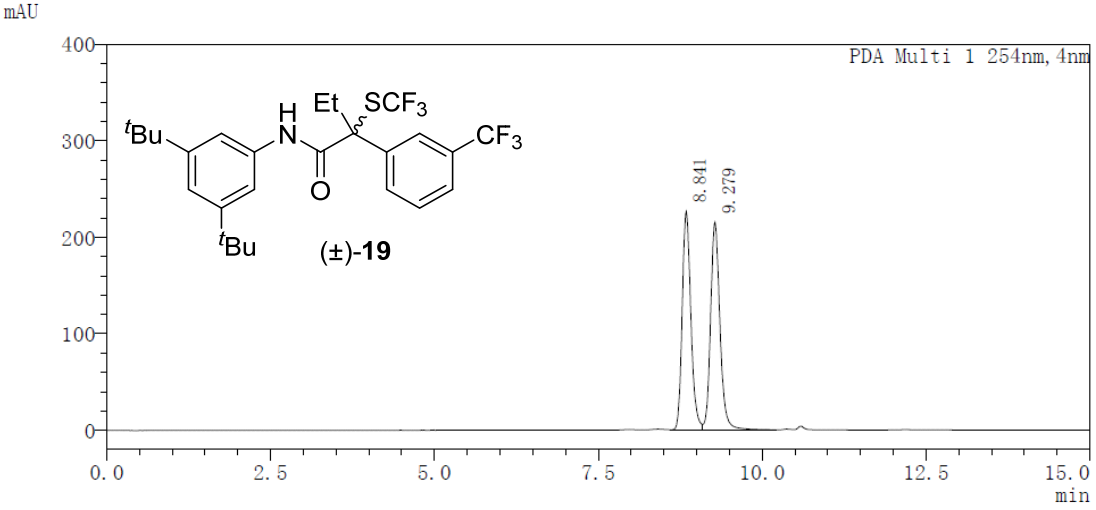
Peak#	Ret. Time	Area	Area%
1	9.954	1872336	50.040
2	10.729	1869338	49.960



Peak Table

PDA Ch1 254nm

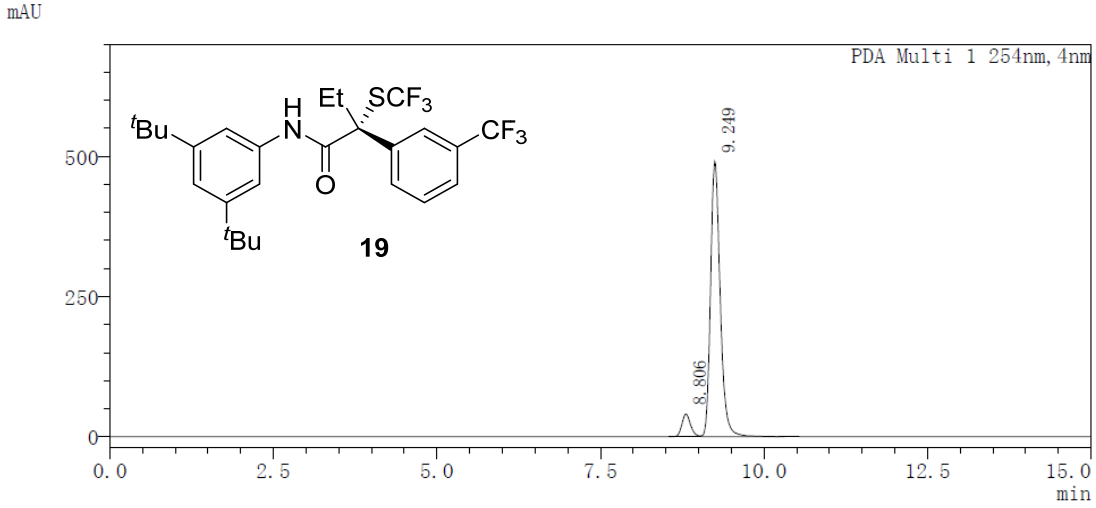
Peak#	Ret. Time	Area	Area%
1	9.888	2385470	5.213
2	10.576	43370374	94.787



Peak Table

PDA Ch1 254nm

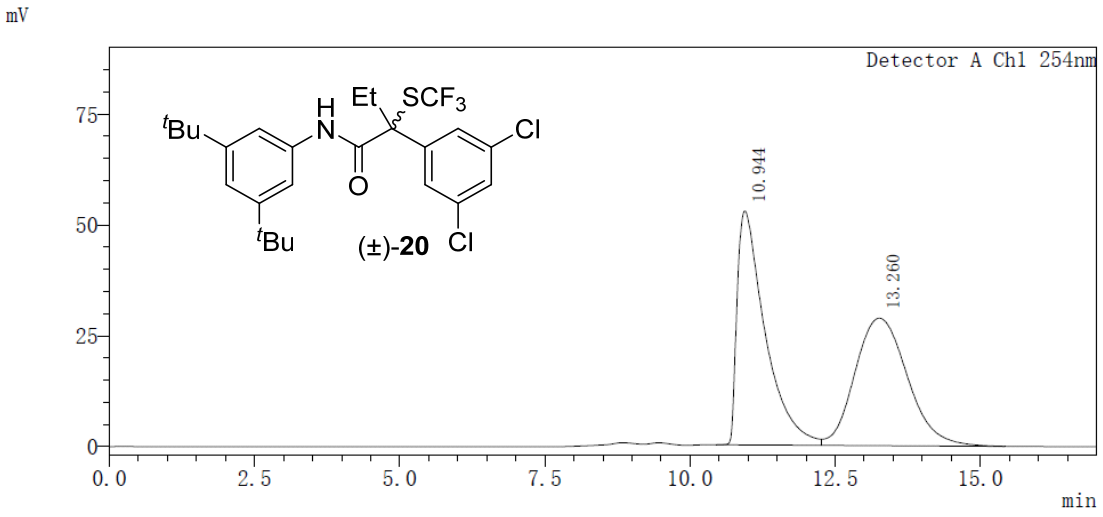
Peak#	Ret. Time	Area	Area%
1	8.841	2072170	49.168
2	9.279	2142285	50.832



Peak Table

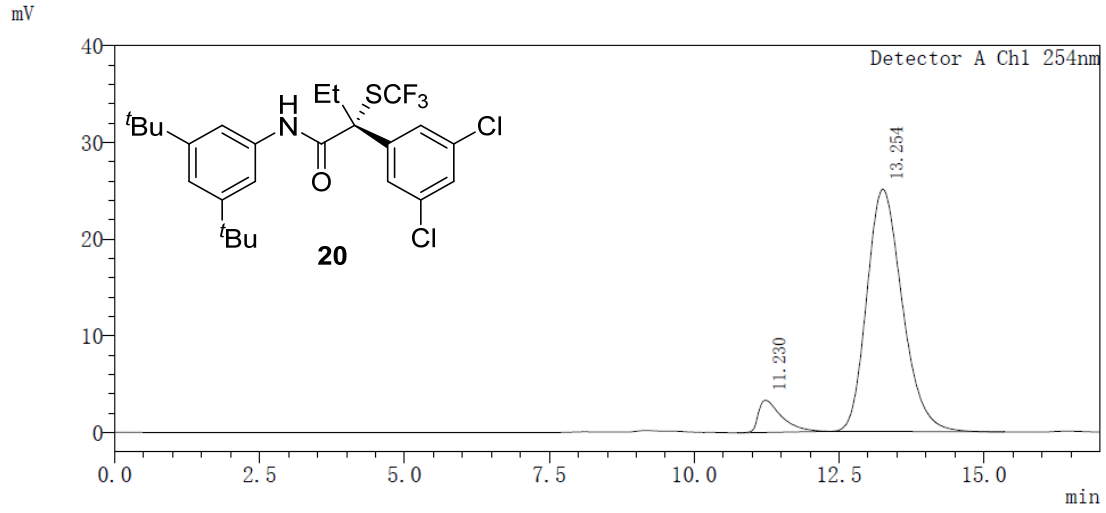
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	8.806	376889	6.973
2	9.249	5028479	93.027



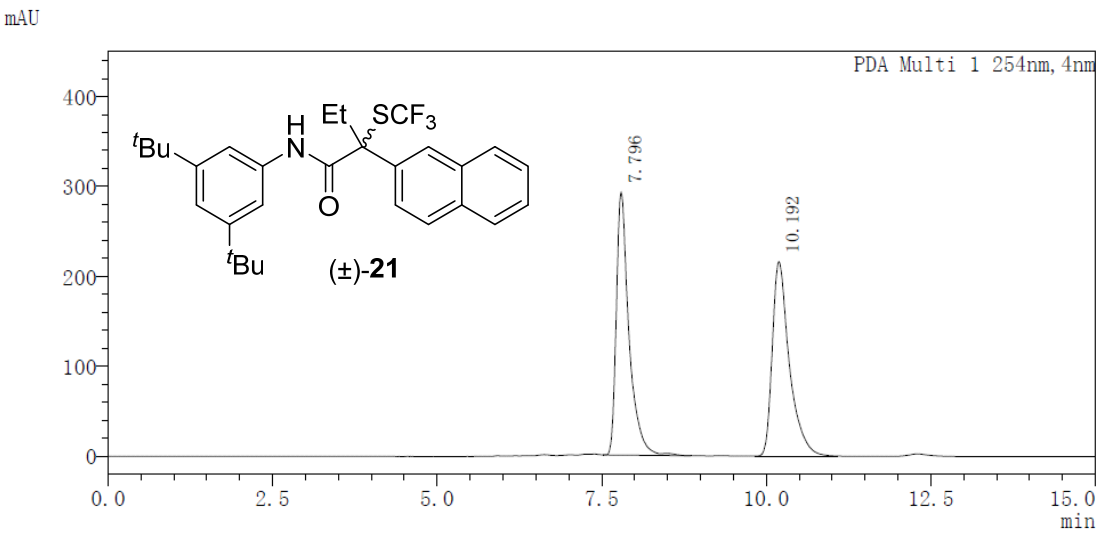
Detector A Ch1 254nm

T	Hight	Area	Area%
10.944	52763	1774846	49.521
13.260	28759	1809206	50.479



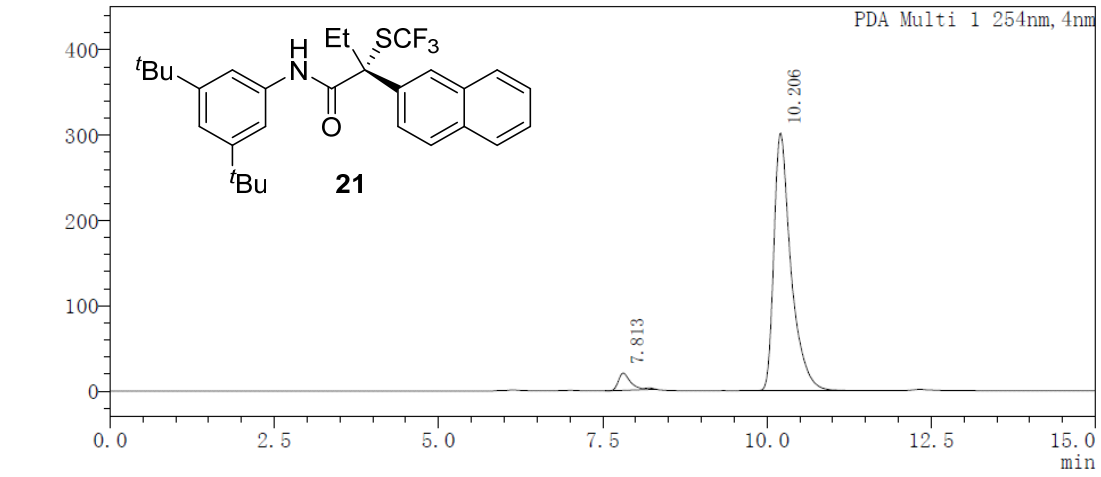
Detector A Ch1 254nm

T	Hight	Area	Area%
11.230	3343	93330	8.017
13.254	25052	1070820	91.983



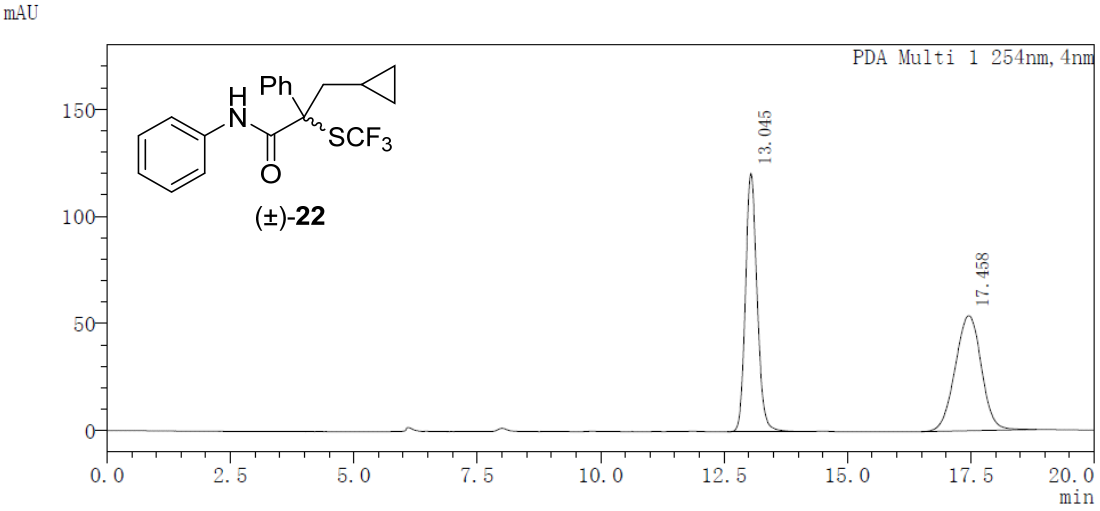
PDA Ch1 254nm

T	Hight	Area	Area%
7.796	292323	3930780	50.177
10.192	216174	3903071	49.823



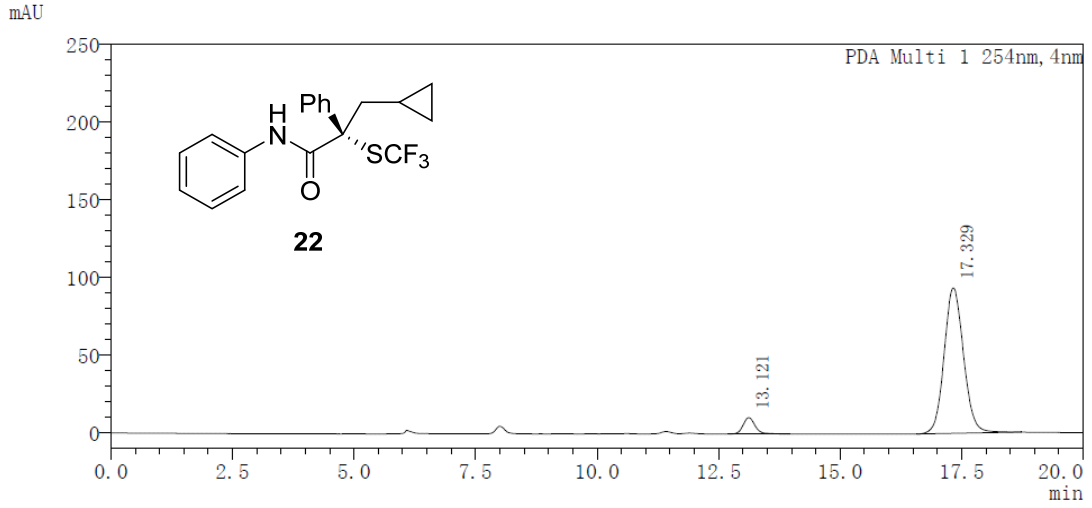
PDA Ch1 254nm

T	Hight	Area	Area%
7.813	20117	270085	4.705
10.206	301864	5470492	95.295



PDA Ch1 254nm

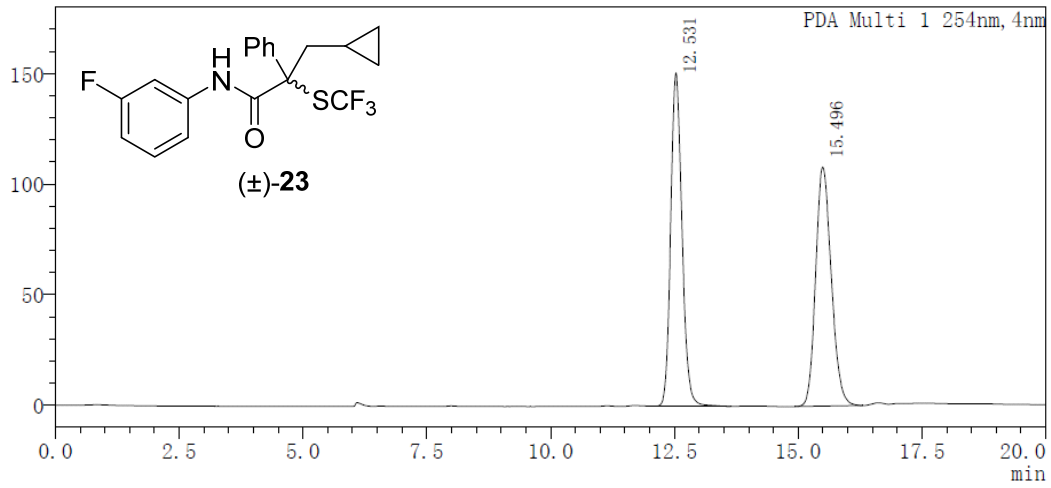
T	Hight	Area	Area%
13.045	120513	1984063	49.946
17.458	53706	1988325	50.054



PDA Ch1 254nm

T	Hight	Area	Area%
13.121	10571	182805	6.544
17.329	93632	2610675	93.456

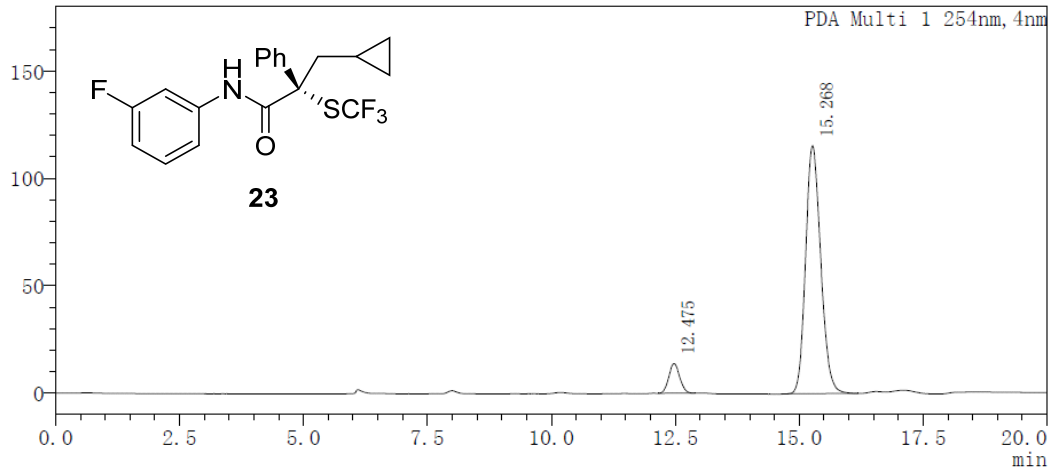
mAU



PDA Ch1 254nm

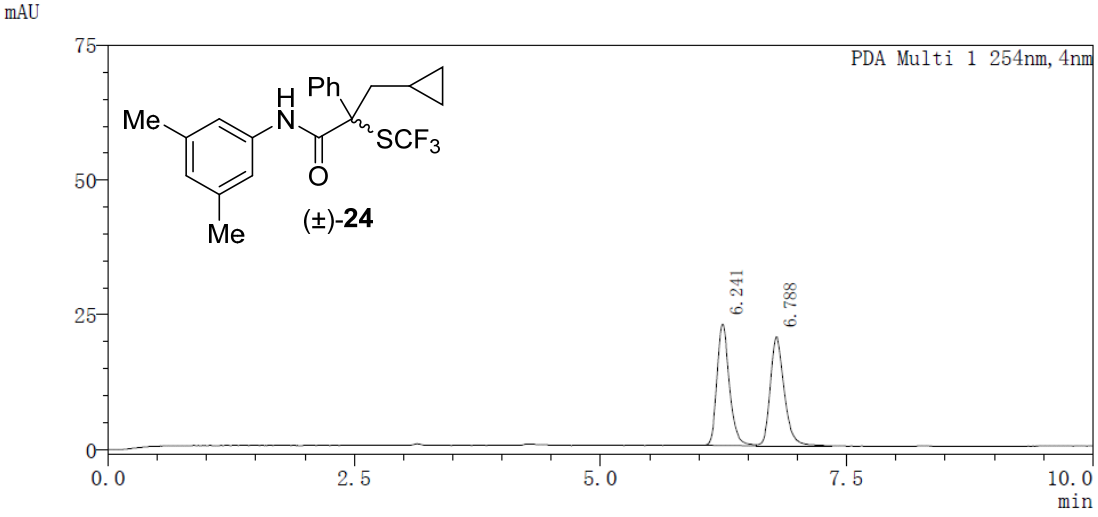
T	Hight	Area	Area%
12.531	150647	2390726	50.137
15.496	108119	2377684	49.863

mAU



PDA Ch1 254nm

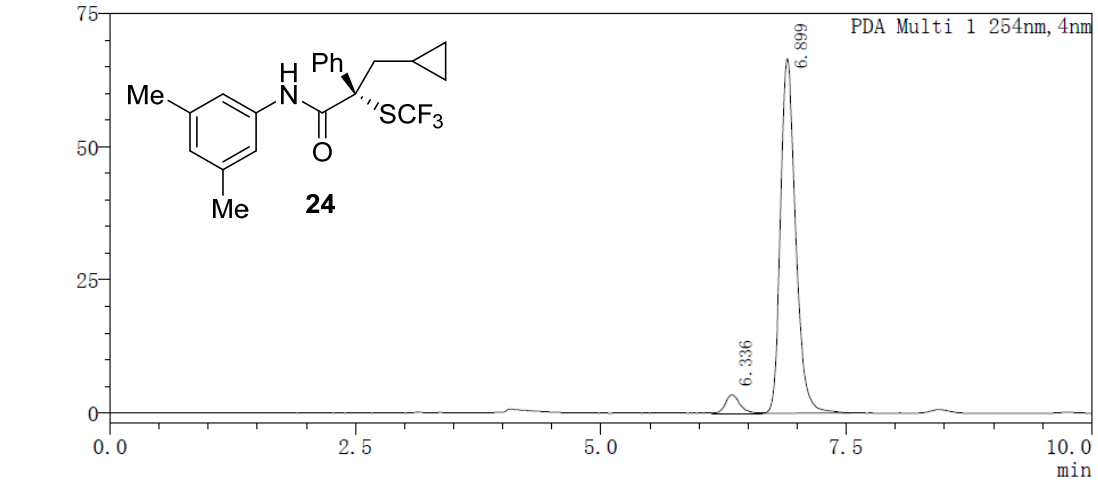
T	Hight	Area	Area%
12.475	13756	209263	7.829
15.268	115516	2463583	92.171



Peak Table

PDA Ch1 254nm

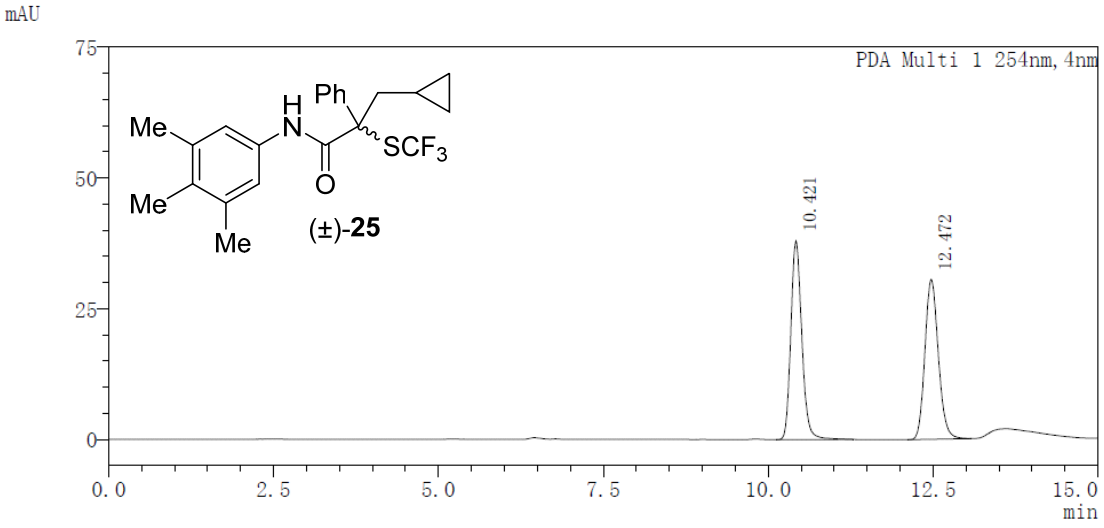
Peak#	Ret. Time	Area	Area%
1	6.241	198253	49.863
2	6.788	199345	50.137



Peak Table

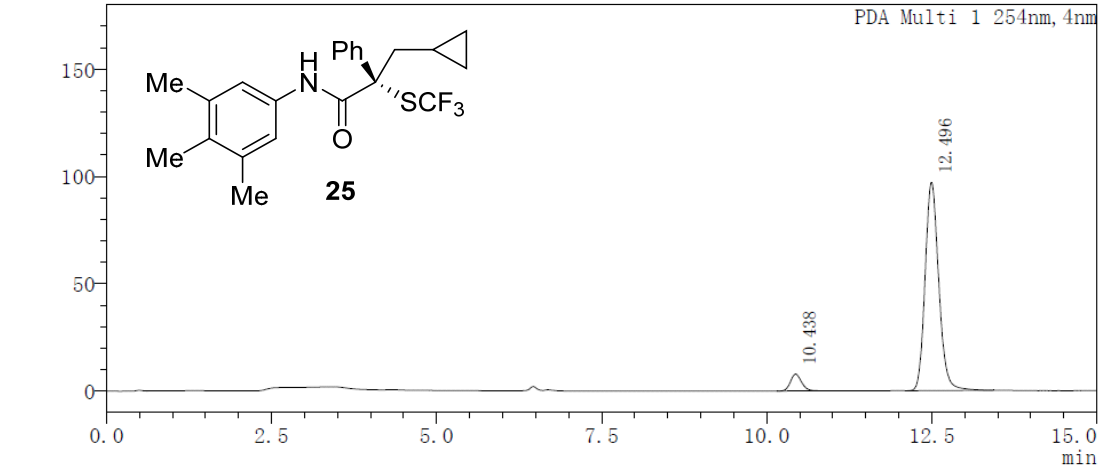
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.336	34366	4.572
2	6.899	717351	95.428



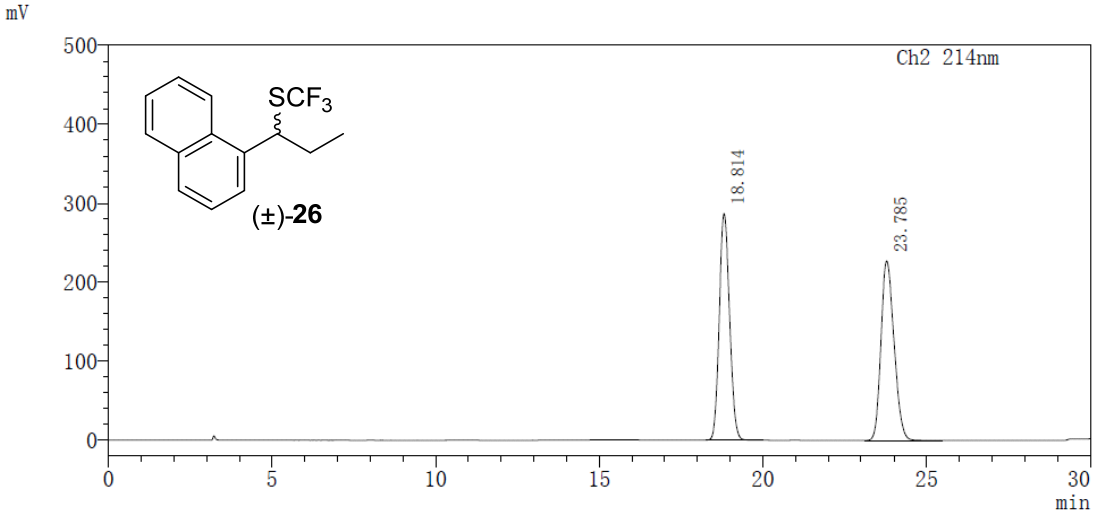
PDA Ch1 254nm

T	Hight	Area	Area%
10.421	37979	442318	50.422
12.472	30592	434921	49.578



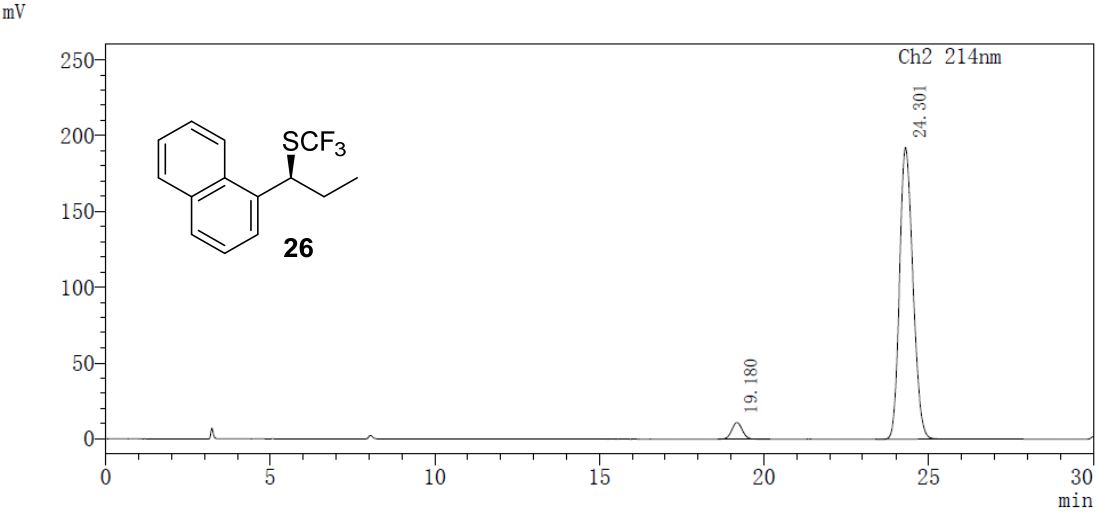
PDA Ch1 254nm

T	Hight	Area	Area%
10.438	7807	90846	6.097
12.496	97023	1399240	93.903



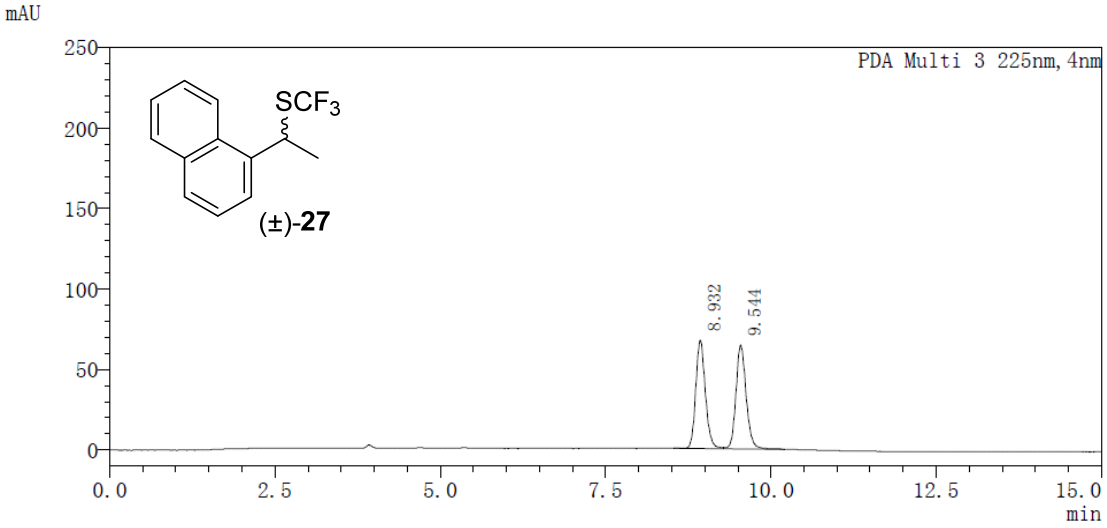
Ch2 214nm

Peak	RetTime	Area	Height	Area%
1	18.814	6296204	287013	49.938
2	23.785	6311899	227184	50.062



Ch2 214nm

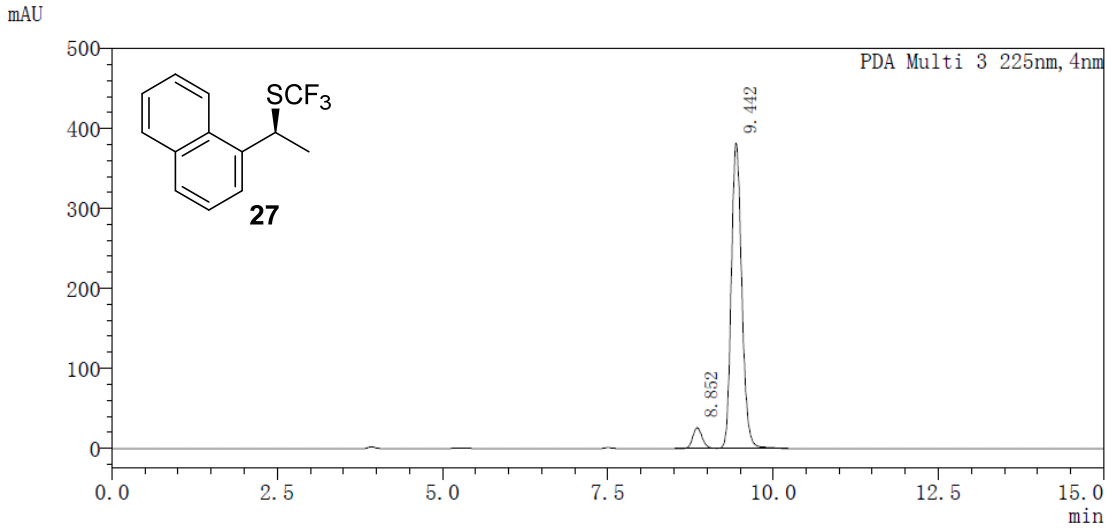
Peak	RetTime	Area	Height	Area%
1	19.180	245046	11019	4.312
2	24.301	5437660	192169	95.688



Peak Table

PDA Ch3 225nm

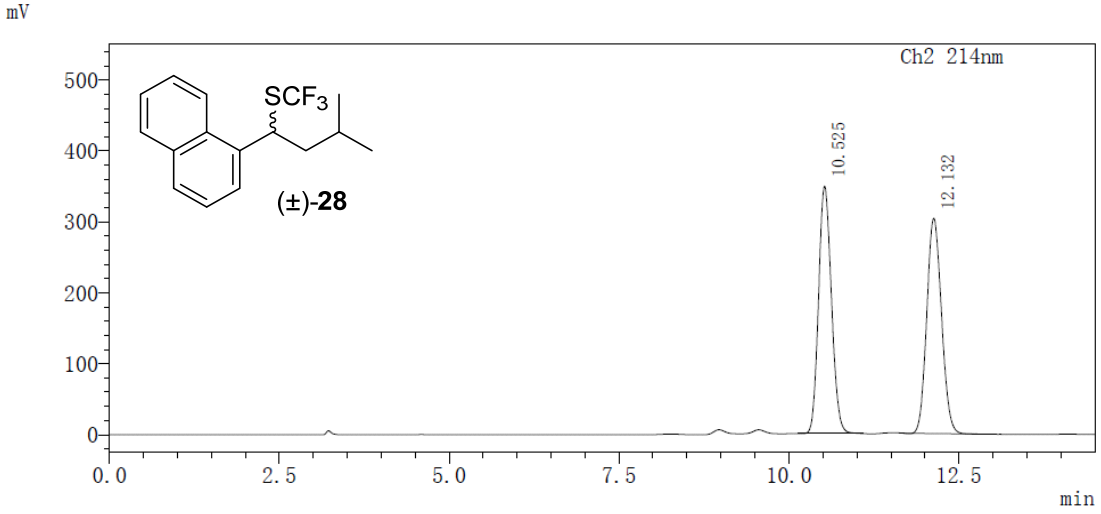
Peak#	Ret. Time	Area	Area%
1	8.932	683490	49.651
2	9.544	693109	50.349



Peak Table

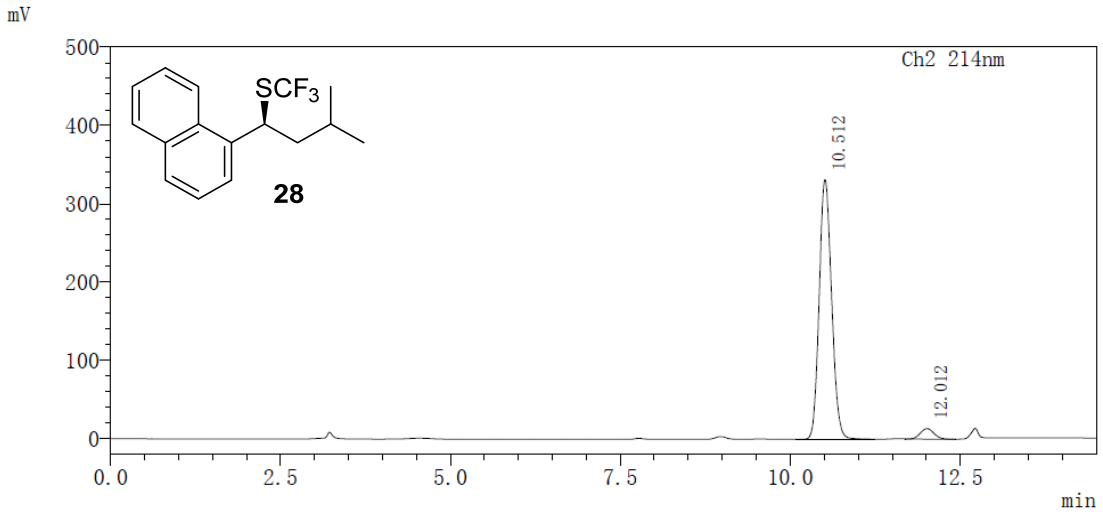
PDA Ch3 225nm

Peak#	Ret. Time	Area	Area%
1	8.852	259159	5.785
2	9.442	4220863	94.215



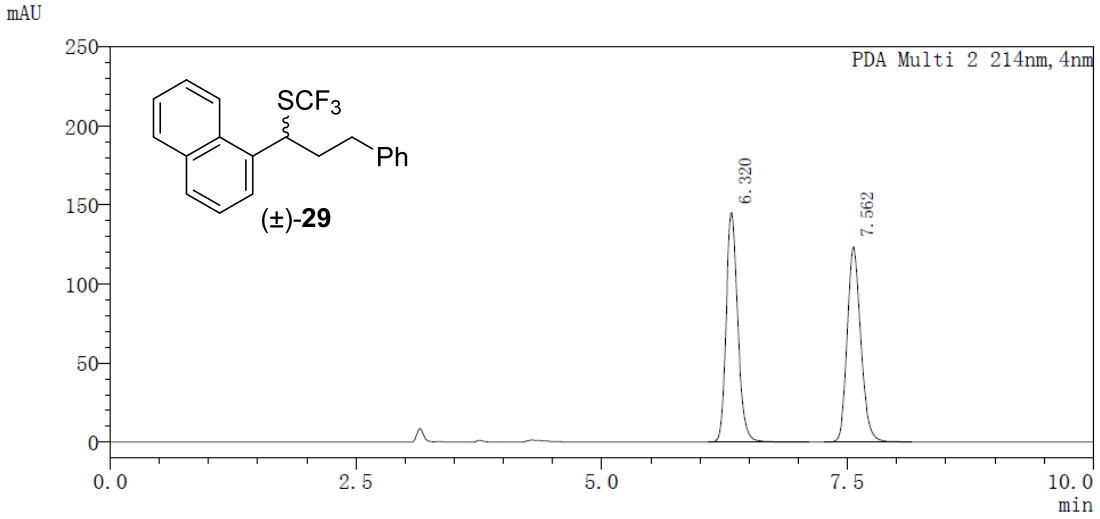
Ch2 214nm

Peak	RetTime	Area	Height	Area%
1	10.525	4592532	348168	50.063
2	12.132	4580888	303249	49.937



Ch2 214nm

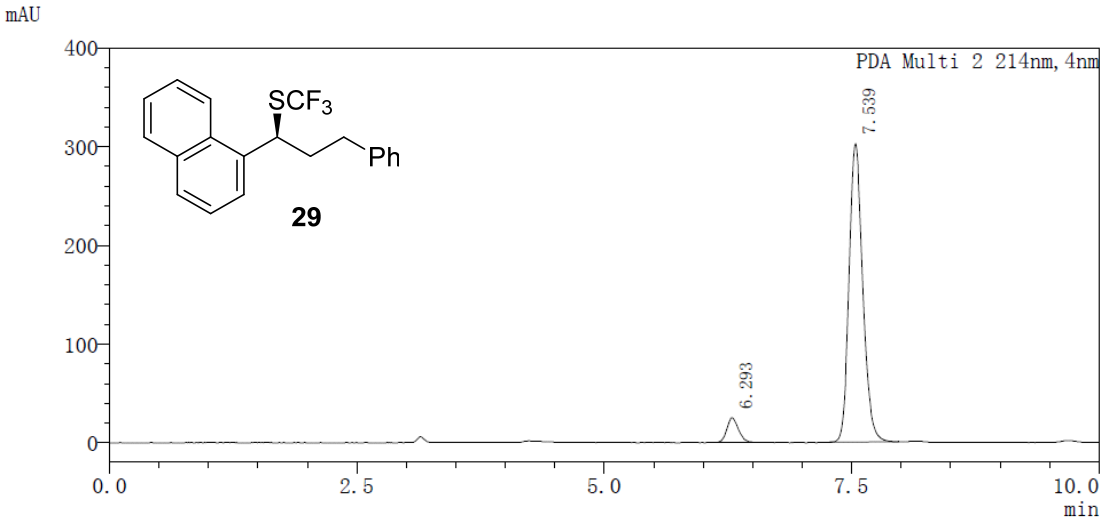
Peak	RetTime	Area	Height	Area%
1	10.512	4218017	331394	95.818
2	12.012	184081	13328	4.182



Peak Table

PDA Ch2 214nm

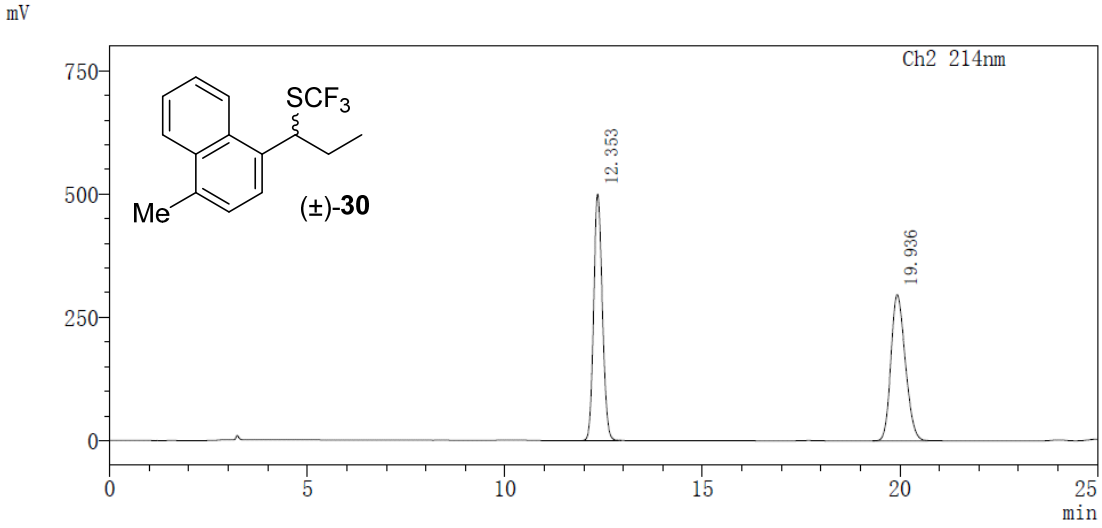
Peak#	Ret. Time	Area	Area%
1	6.320	1197305	50.043
2	7.562	1195240	49.957



Peak Table

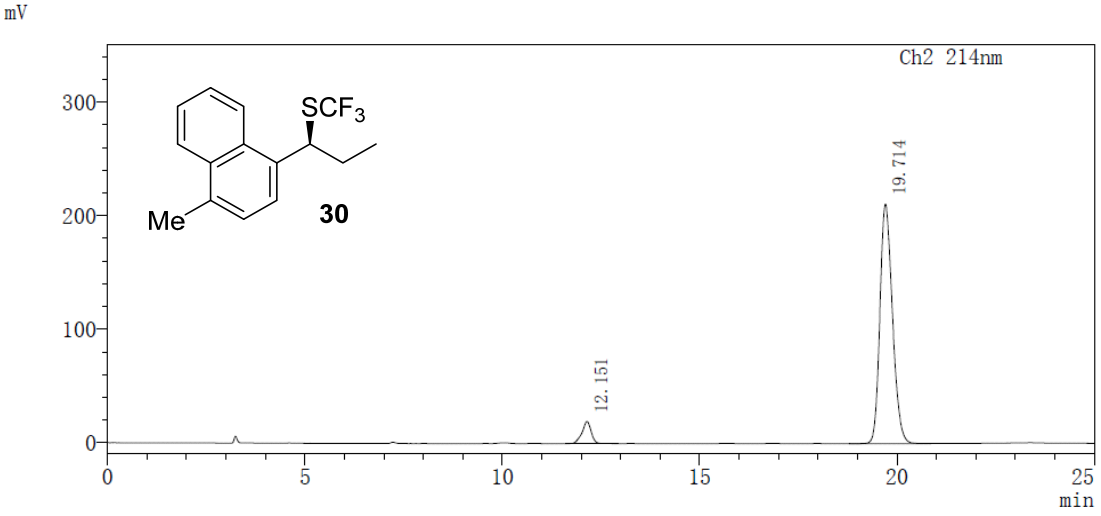
PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	6.293	204875	6.560
2	7.539	2918318	93.440



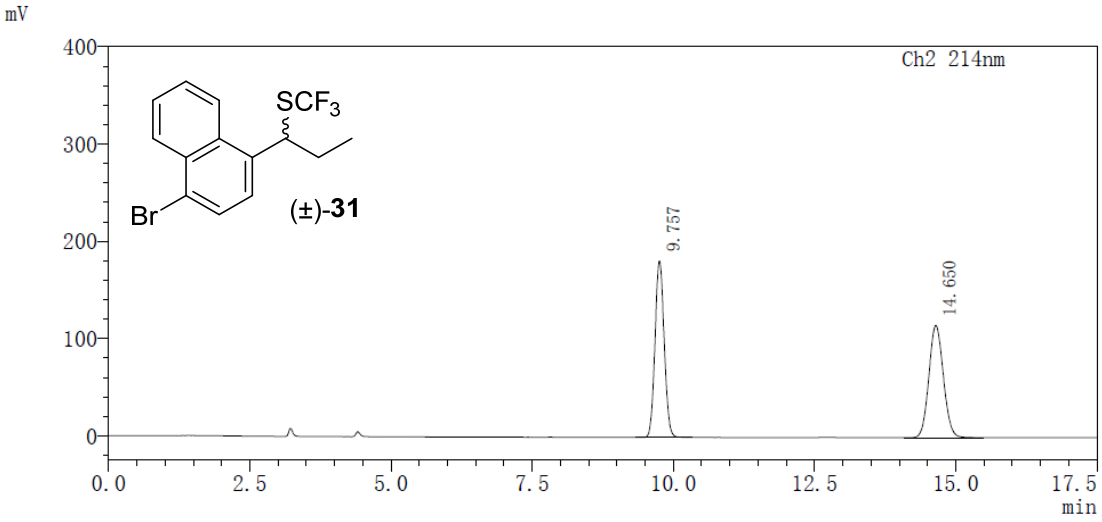
Ch2 214nm

Peak	RetTime	Area	Height	Area%
1	12.353	7644881	499955	50.365
2	19.936	7533936	296959	49.635



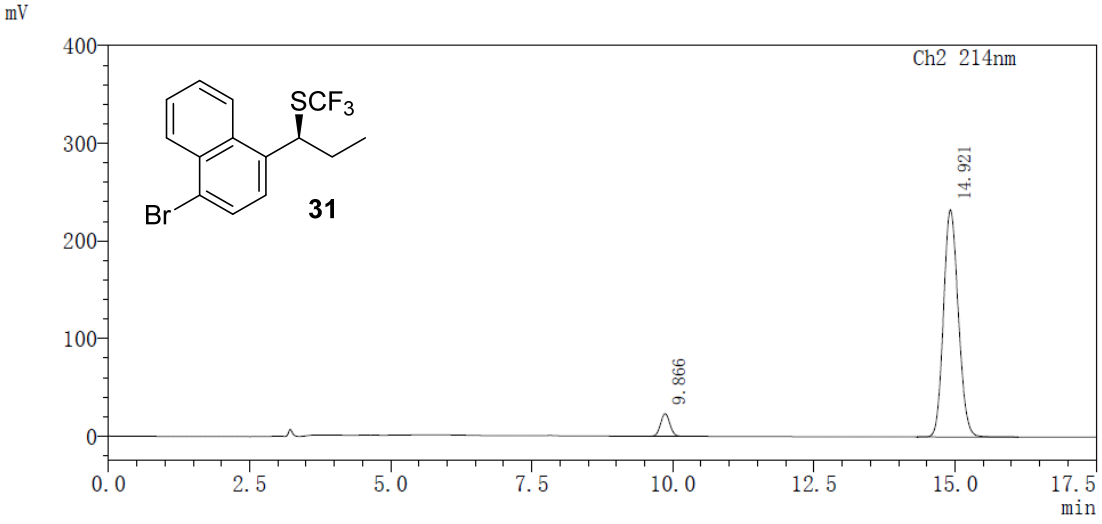
Ch2 214nm

Peak	RetTime	Area	Height	Area%
1	12.151	318830	19586	6.398
2	19.714	4664717	210913	93.602



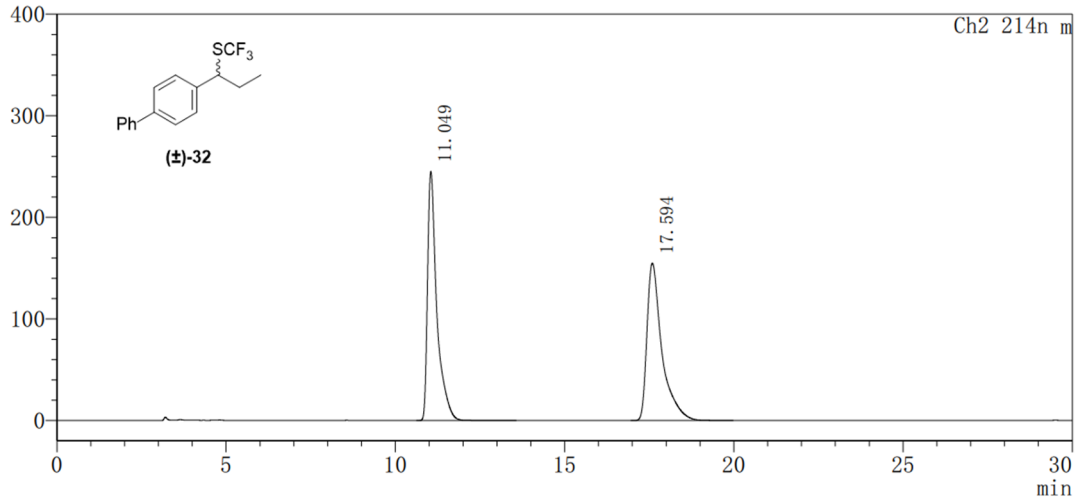
Ch2 214nm

Peak	RetTime	Area	Height	Area%
1	9.757	2059136	181400	49.975
2	14.650	2061231	115447	50.025



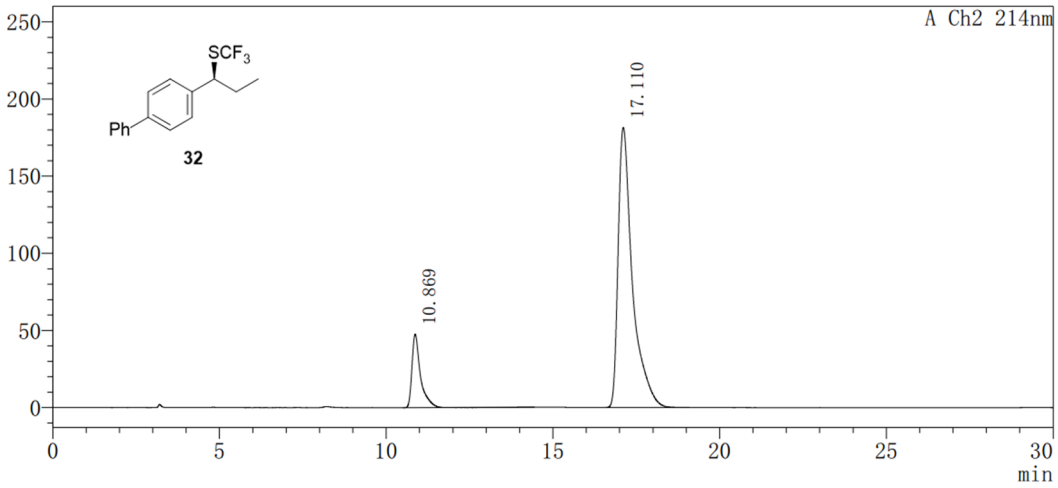
Ch2 214nm

Peak	RetTime	Area	Height	Area%
1	9.866	268858	23266	5.941
2	14.921	4256779	232944	94.059



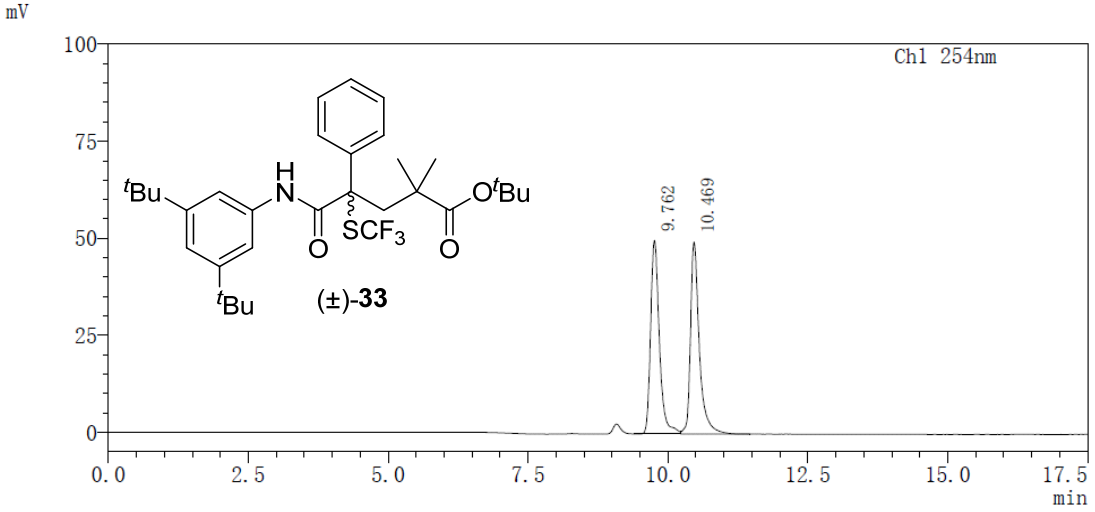
Ch2 214nm

T	Hight	Area	Area%
11.049	245127	4690932	49.636
17.594	154948	4759697	50.364



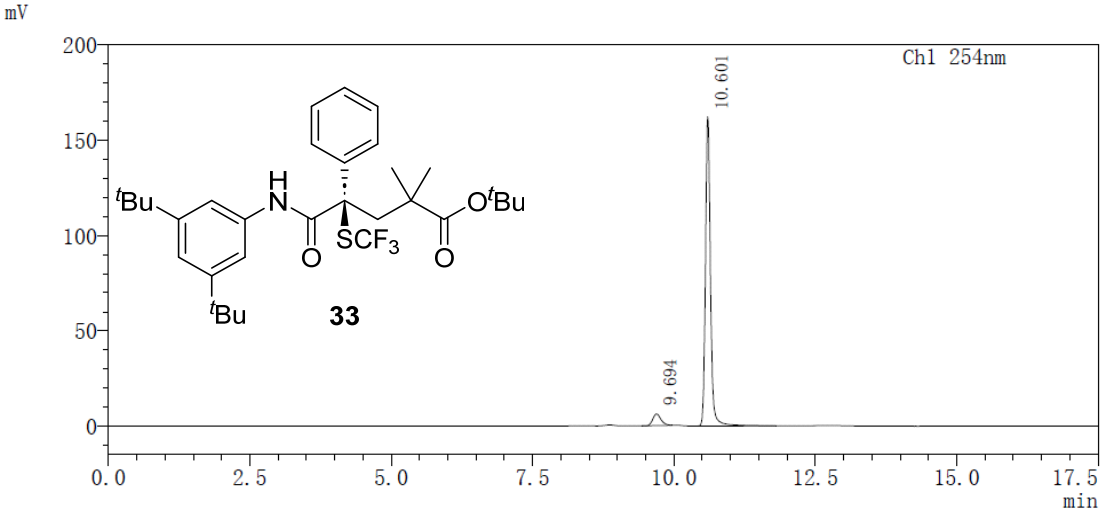
Ch2 214nm

T	Hight	Area	Area%
10.869	47596	833919	13.329
17.110	181556	5422589	86.671



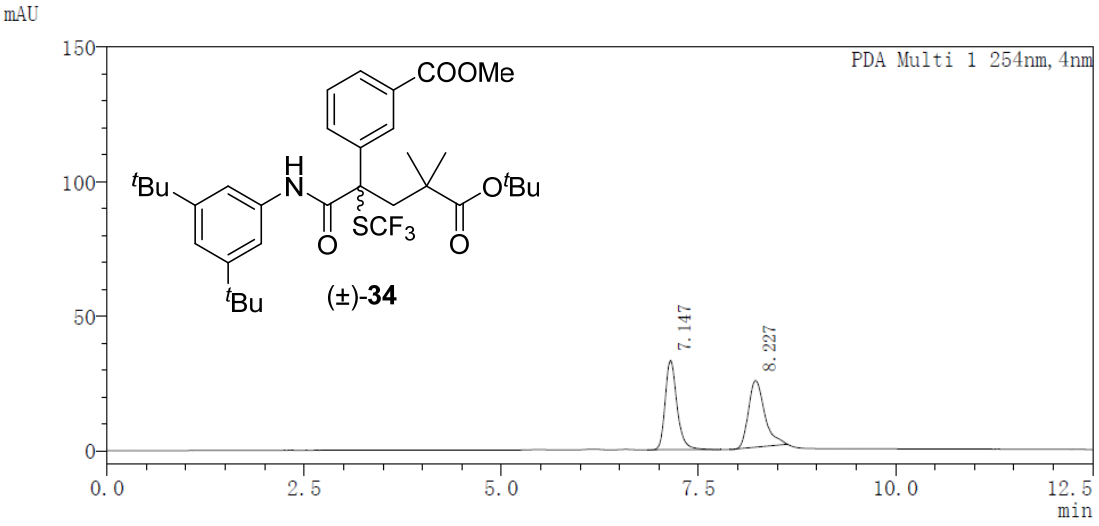
Ch1 254nm

Peak	RetTime	Area	Height	Area%
1	9.762	544229	49874	49.951
2	10.469	545290	49502	50.049



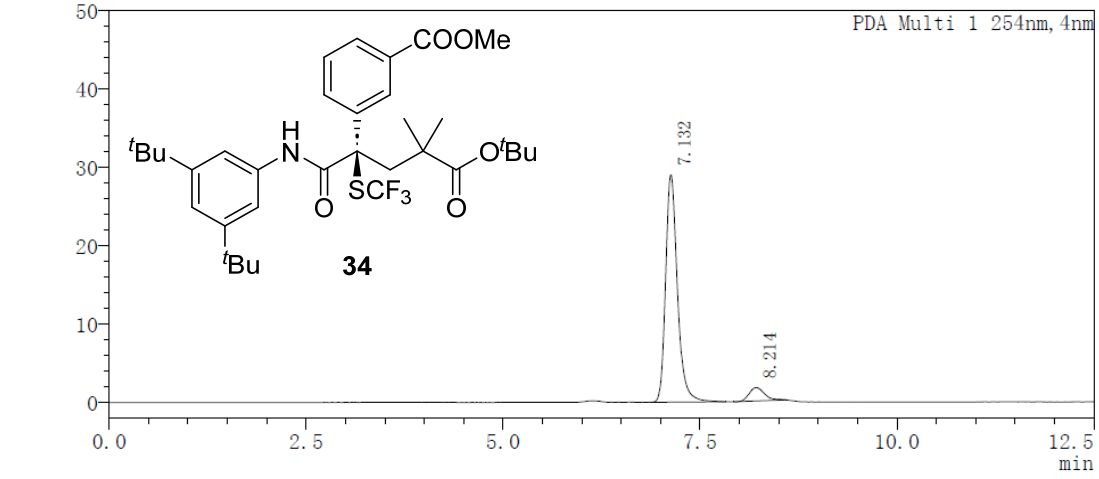
Ch1 254nm

Peak	RetTime	Area	Height	Area%
1	9.694	62308	6157	5.846
2	10.601	1003441	162441	94.154



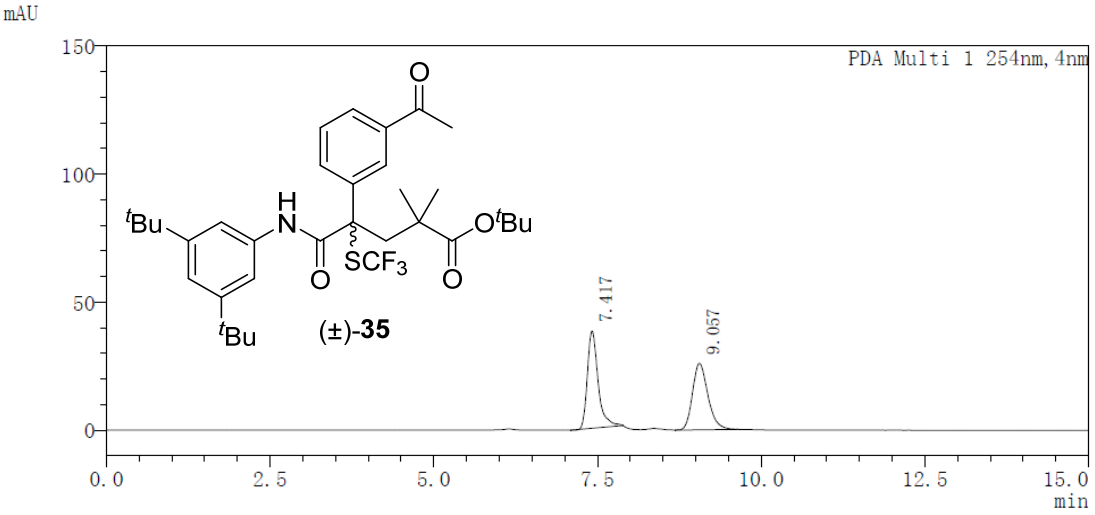
PDA Ch1 254nm

T	Hight	Area	Area%
7.147	33162	347375	49.463
8.227	24787	354915	50.537



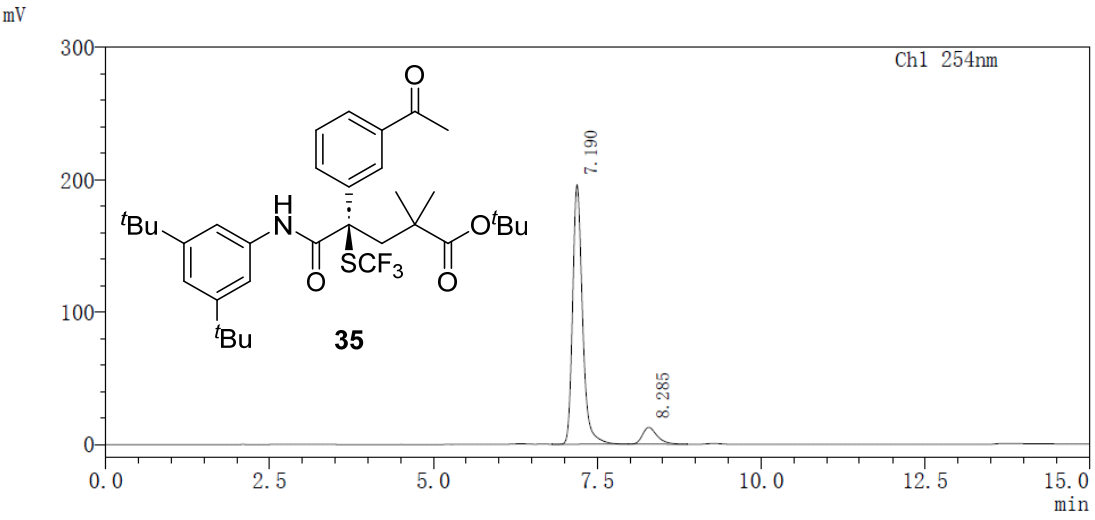
PDA Ch1 254nm

T	Hight	Area	Area%
7.132	28989	302009	92.856
8.214	1713	23234	7.144



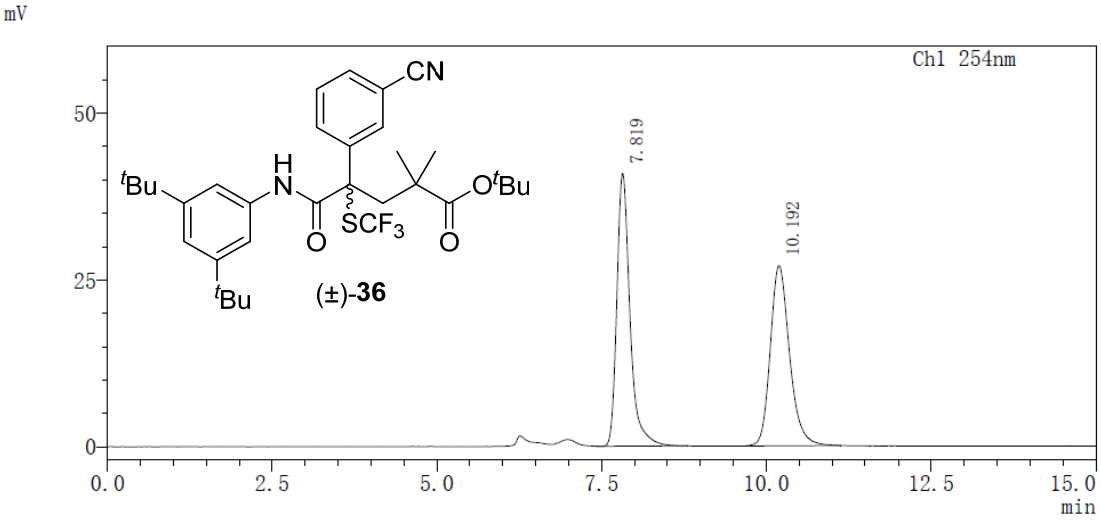
PDA Ch1 254nm

T	Hight	Area	Area%
7.417	38033	433201	50.339
9.057	25972	427361	49.661



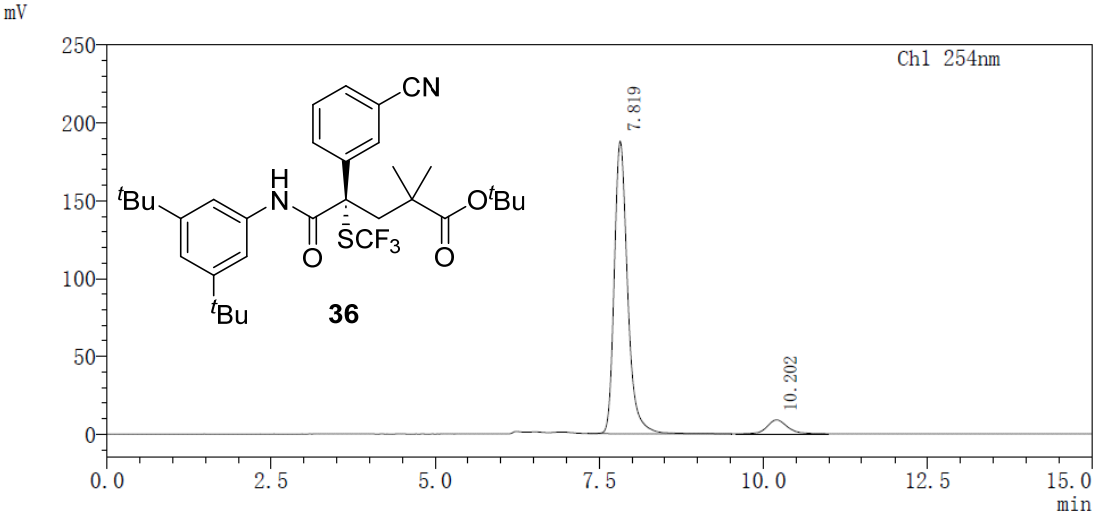
Ch1 254nm

Peak	RetTime	Area	Height	Area%
1	7.190	2065050	196180	91.334
2	8.285	195929	12636	8.666



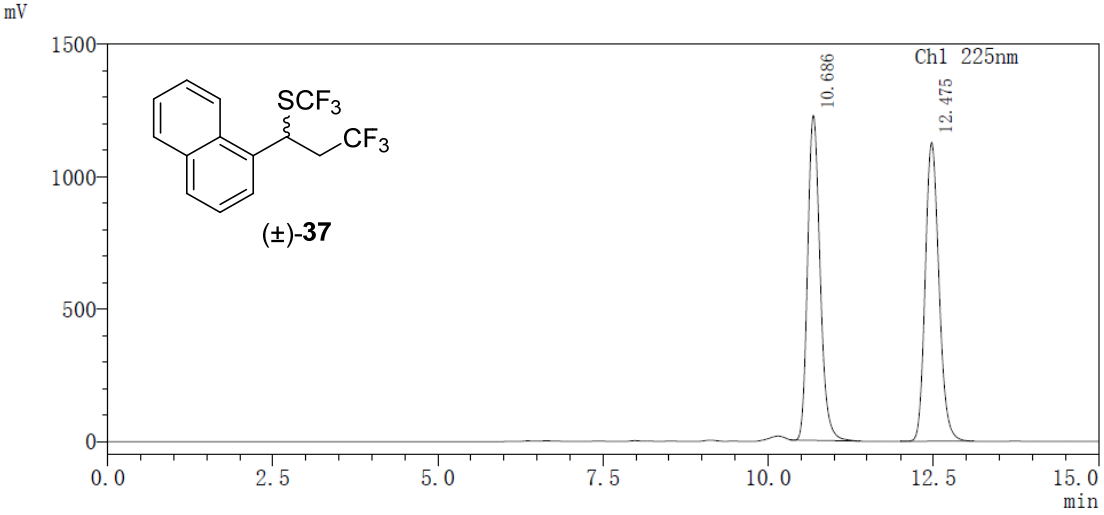
Ch1 254nm

Peak	RetTime	Area	Height	Area%
1	7.819	565933	40910	50.710
2	10.192	550082	27043	49.290



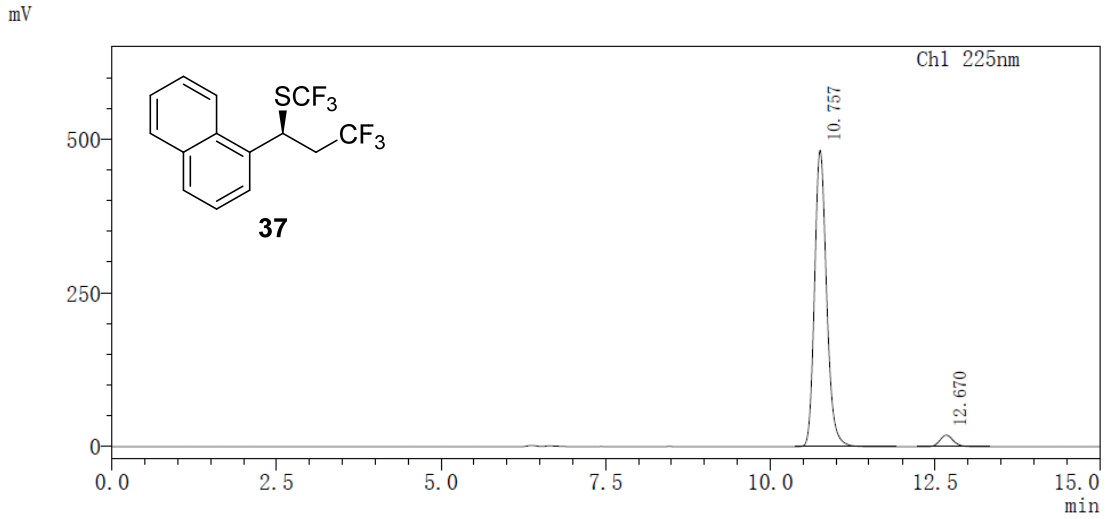
Ch1 254nm

Peak	RetTime	Area	Height	Area%
1	7.819	2663775	188087	93.278
2	10.202	191952	8948	6.722



Ch1 225nm

Peak	RetTime	Area	Height	Area%
1	10.686	16137849	1228013	49.578
2	12.475	16412883	1128831	50.422



Ch1 225nm

Peak	RetTime	Area	Height	Area%
1	10.757	6159518	482419	95.845
2	12.670	267044	18824	4.155