



Supporting Information

Copper-Catalyzed Enantioselective C(sp³)–SCF₃ Coupling of Carbon-Centered Benzyl Radicals with (Me₄N)SCF₃

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

Supporting Information for

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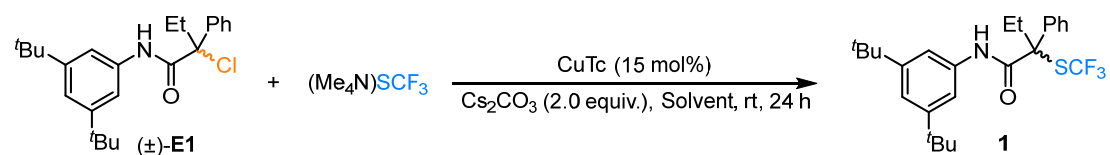
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1. General information

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 $\text{Cu-K}\alpha$ radiation.

2. Supplementary tables for experiments

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



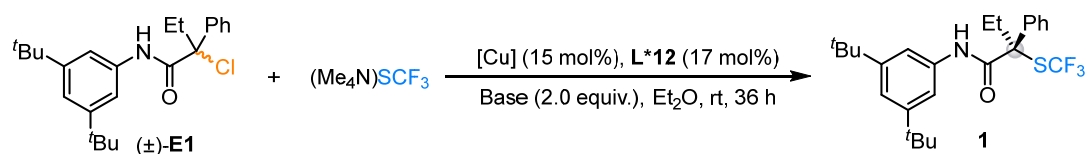
Entry	Solvent	Yield of 1 [%] ^[b]
1	DMF	84
2	MeCN	99
3	EA	99
4	DCE	93
5	THF	99
6	DME	99
7	Et ₂ O	14
8	MTBE	16
9	Toluene	14

[a] Reaction conditions: (±)-E1 (0.05 mmol), (Me₄N)SCF₃ (0.075 mmol), CuTc (15 mol%), and Cs₂CO₃ (2.0 equiv.) in solvent (1.0 mL) at rt for 24 h under argon. [b] Yields were based on ¹⁹F NMR analysis of the crude product using CF₃CH₂OH 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 ₂ S	99	88

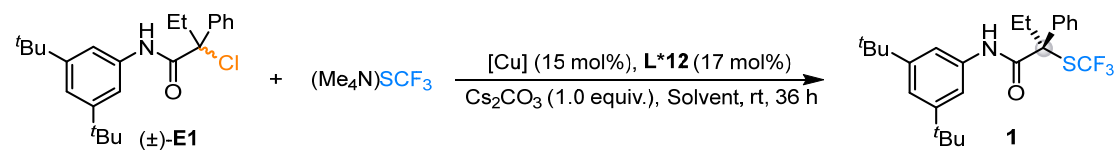
[a] Reaction conditions: (±)-**E1** (0.05 mmol), (Me₄N)SCF₃ (0.075 mmol), [Cu] (15 mol%), **L*12** (17 mol%), and Cs₂CO₃ (2.0 equiv.) in Et₂O (1.0 mL) at rt for 36 h under argon. [b] Yields were based on ¹⁹F NMR analysis of the crude product using CF₃CH₂OH as an internal standard. [c] Ee values were based on chiral HPLC analysis.

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

Entry	Base	Yield [%] ^[b]	Ee [%] ^[c]
1	Na ₂ CO ₃	trace	-- ^[d]
2	K ₂ CO ₃	7	88
3	K ₃ PO ₄	10	88
5	Cs ₂ CO ₃ (4.0 equiv.)	99	88
6	Cs ₂ CO ₃ (3.0 equiv.)	99	89
7	Cs ₂ CO ₃ (1.0 equiv.)	99	89

[a] Reaction conditions: (±)-E1 (0.05 mmol), (Me₄N)SCF₃ (0.075 mmol), CuTc (15 mol%), L*12 (17 mol%), and base (2.0 equiv.) in Et₂O (1.0 mL) at rt for 36 h under argon. [b] Yields were based on ¹⁹F NMR analysis of the crude product using CF₃CH₂OH 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 ₂ O (0.5 mL)	99	88
5	Et ₂ O (2.0 mL)	99	89

[a] Reaction conditions: (±)-E1 (0.05 mmol), (Me₄N)SCF₃ (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 ¹⁹F NMR analysis of the crude product using CF₃CH₂OH as an internal standard. [c] Ee values were based on chiral HPLC analysis.

3. Supplementary figures and scheme for experiments

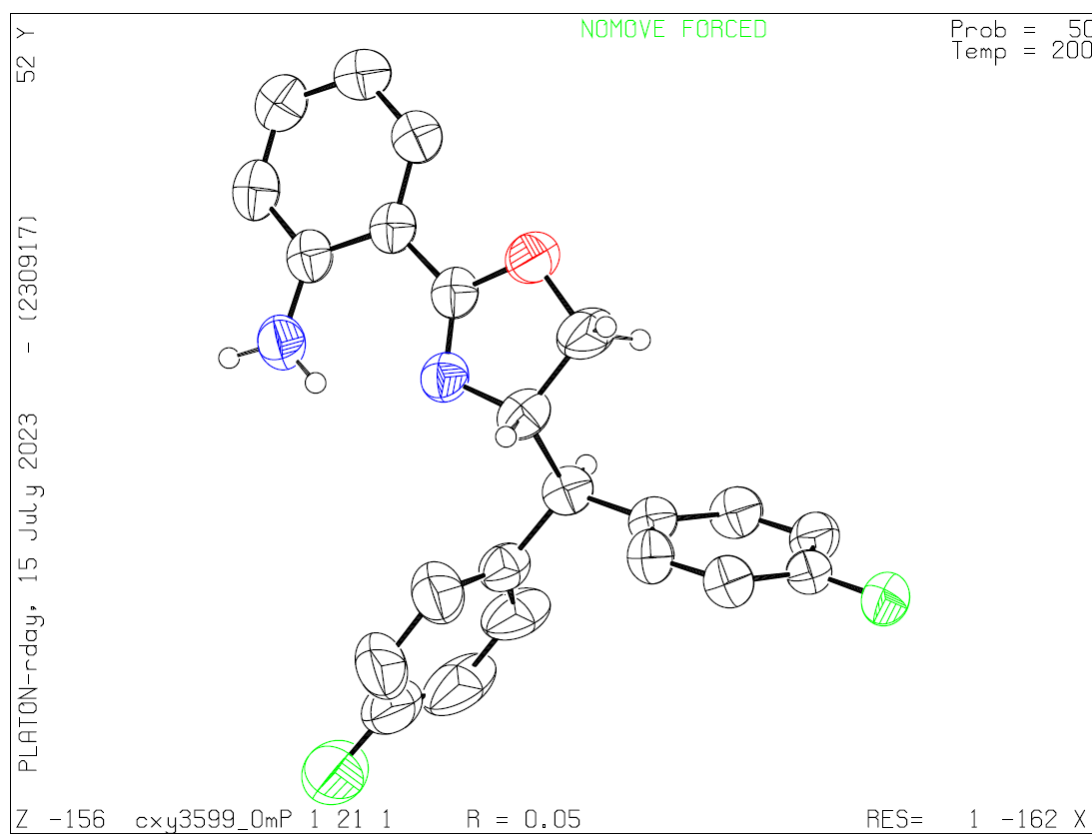
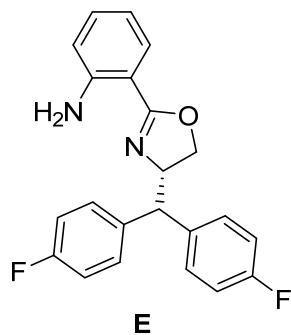


Figure S1. The X-ray structure of **E** (CCDC 2220220).

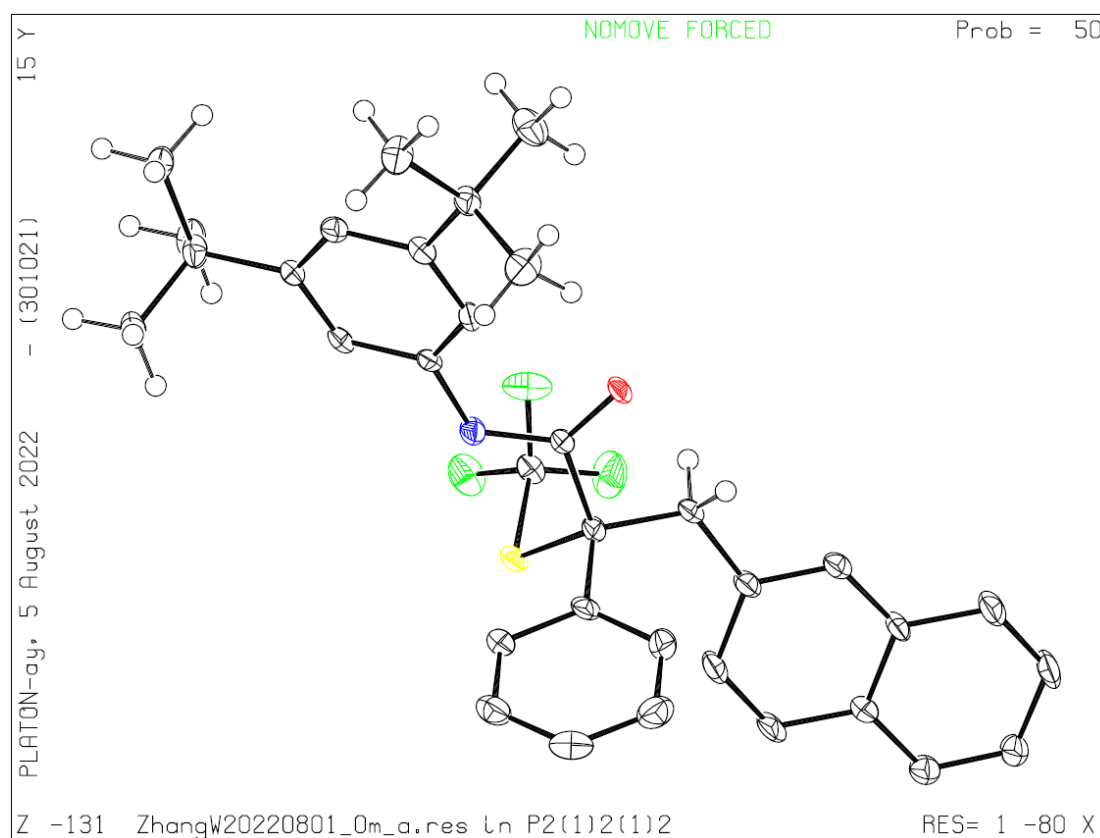
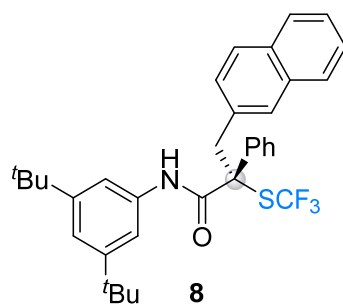


Figure S2. The X-ray structure of **8** (CCDC 2220219).

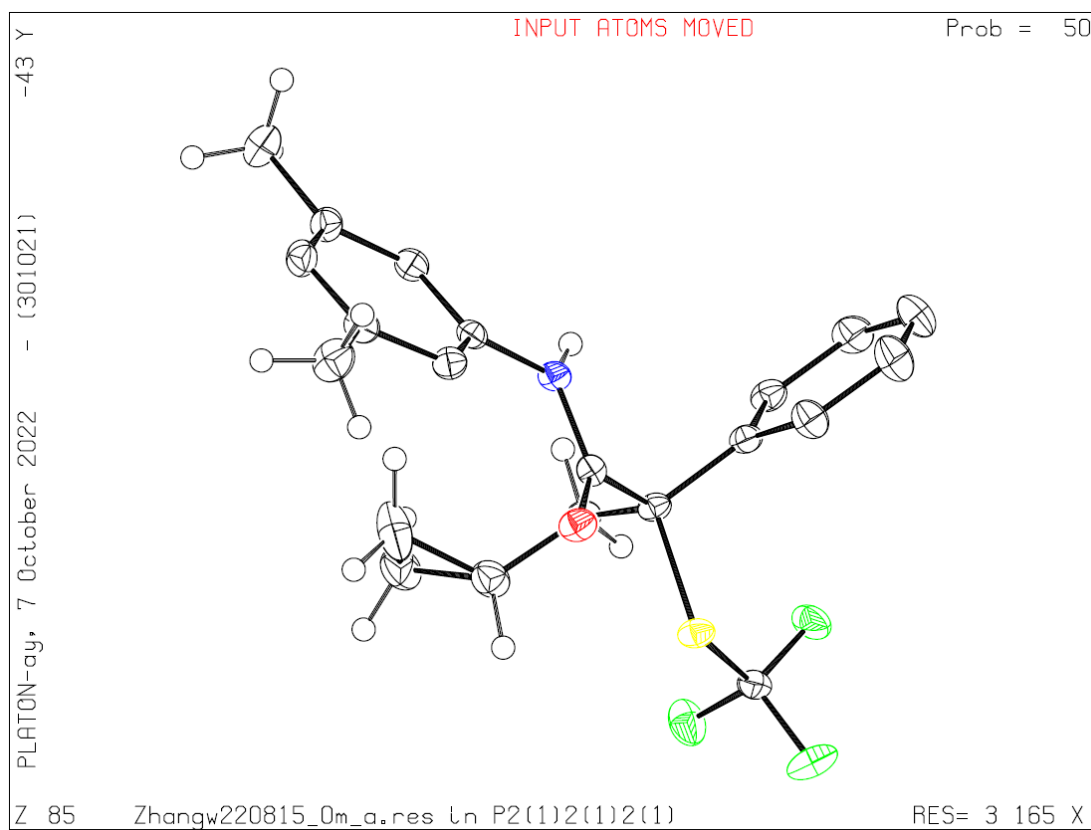
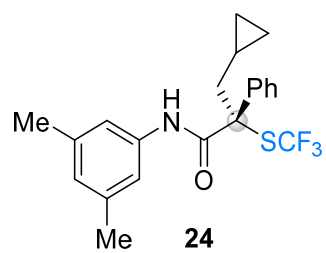
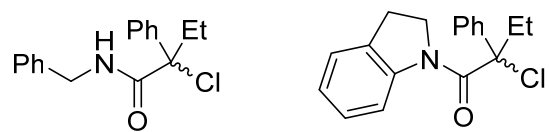
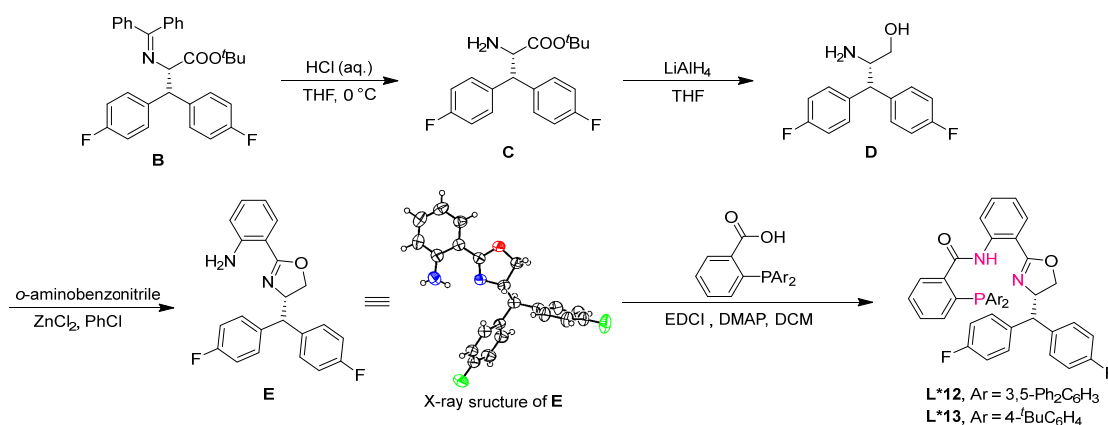


Figure S3. The X-ray structure of **24** (CCDC 2220238).

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 Na₂CO₃ till pH = 8~9, and **C** could be extracted with ethyl acetate (EA).

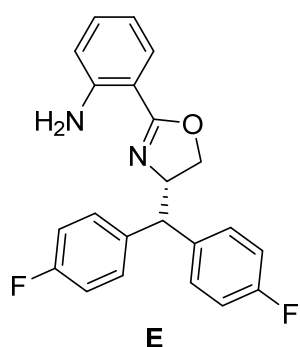
After the EA was evaporated, the crude product **C**, without further purification, was dissolved in THF (25.0 mL), then LiAlH₄ (11.0 mmol, 2.2 equiv.) was added into the mixture in portions in ice-water bath followed by being heated in 50 °C water bath for 2 h. The mixture was quenched by wet Na₂SO₄ 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.

ZnCl₂ (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 NH₄Cl and the mixture was extracted with EA. The combined organic phase was dried over Na₂SO₄, 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.

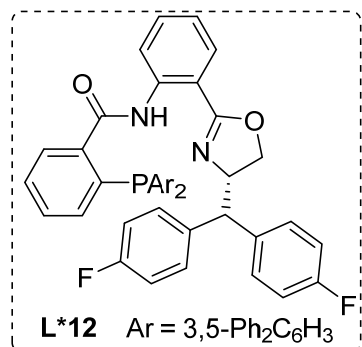
2-(Di(aryl)phosphanyl)benzoic acid (1.2 equiv.) was added into the mixture containing **E** (1.0 mmol), EDCI (3.0 equiv.), DMAP (2.0 equiv.) and DCM (10.0 mL), then the reaction mixture was stirred at room temperature till the transformation completed monitored by TLC. The crude product was purified 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**)**



¹H NMR (400 MHz, CDCl₃) 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). **¹⁹F NMR** (376 MHz, CDCl₃) δ –115.60 – –115.67 (m, 1F), –116.54 – –116.62 (m, 1F). **¹³C NMR** (100 MHz, CDCl₃) 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 C₂₂H₁₉F₂N₂O⁺ [*M*+*H*]⁺ 365.1460, found 365.1461.

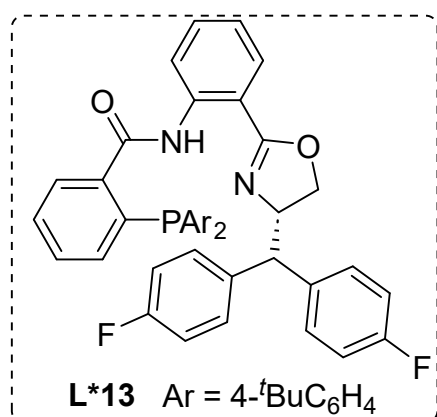
(S)-N-(2-(4-(Bis(4-fluorophenyl)methyl)-4,5-dihydrooxazol-2-yl)phenyl)-2-(di([1,1':3',1''-terphenyl]-5'-yl)phosphanyl)benzamide (L*12**)**



¹H NMR (400 MHz, CDCl₃) 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). **¹⁹F NMR** (376 MHz, CDCl₃) δ –115.33 – –115.40 (m, 1F), –115.50 – –115.57 (m, 1F). **³¹P NMR** (162 MHz, CDCl₃) –6.13. **¹³C NMR**

(100 MHz, CDCl₃) 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 C₆₅H₄₈F₂N₂O₂P⁺ [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)



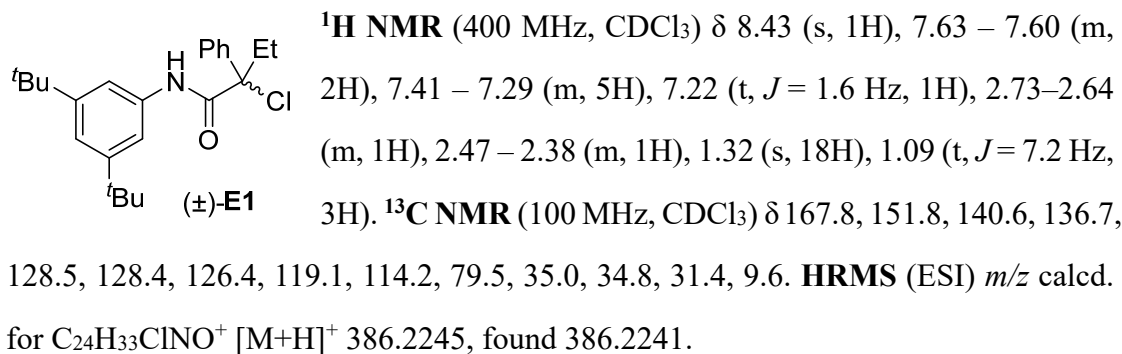
¹H NMR (400 MHz, CDCl₃) 12.15 (s, 1H), 8.58 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.42 – 7.27 (m, 7 H), 7.22 – 7.06 (m, 10 H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.92 (t, *J* = 8.8 Hz, 2H), 6.63 (t, *J* = 8.8 Hz, 2H), 5.08 – 5.01 (m, 1H), 4.31 (t, *J* = 9.2 Hz, 1H), 4.03 (t, *J* = 8.0 Hz, 1H), 3.92 (d, *J* = 9.2 Hz, 1H), 1.29 (s, 9H), 1.22 (s, 9H). **¹⁹F NMR** (376 MHz, CDCl₃) δ –115.34 – –115.41 (m, 1F), –115.59 – –115.67 (m, 1F). **³¹P NMR** (162 MHz, CDCl₃) –10.49. **¹³C NMR** (100 MHz, CDCl₃) 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 C₄₉H₄₈F₂N₂O₂P⁺ [M+H]⁺ 765.3416, found 765.3415.

5. The preparation of the substrates

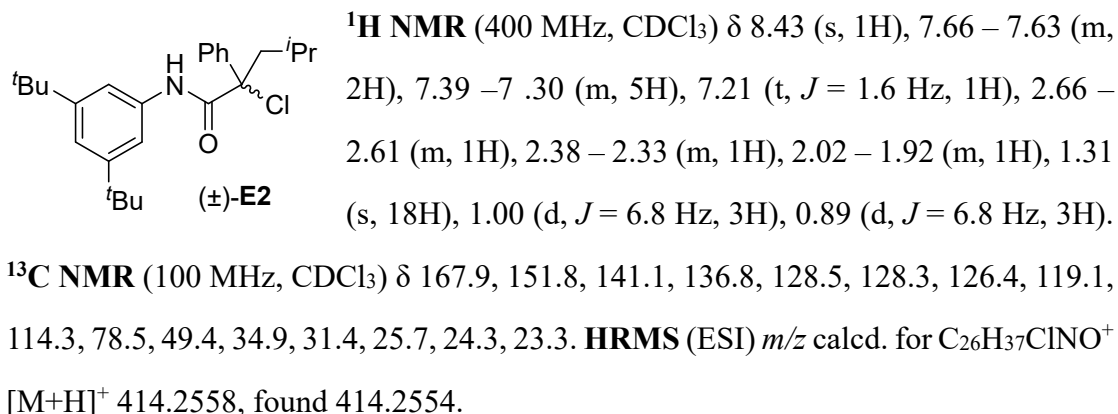
5.1 The synthesis of tertiary α -chloroamides

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

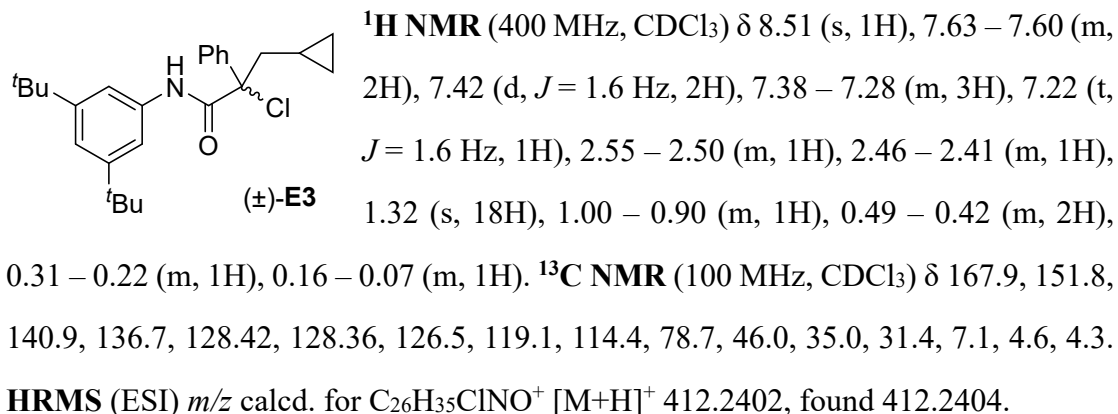
2-Chloro-*N*-(3,5-di-*tert*-butylphenyl)-2-phenylbutanamide (($\pm$)-E1)



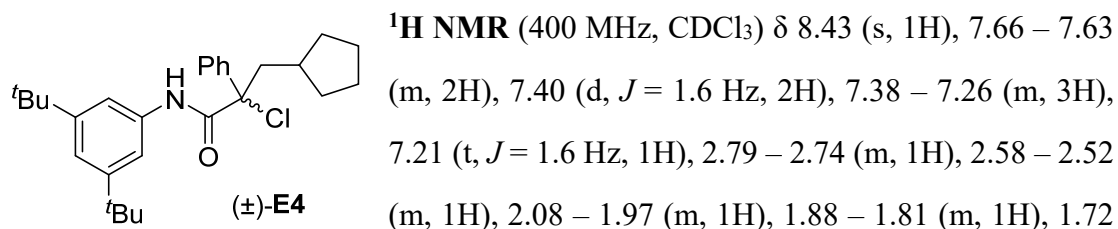
2-Chloro-*N*-(3,5-di-*tert*-butylphenyl)-4-methyl-2-phenylpentanamide (($\pm$)-E2)



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

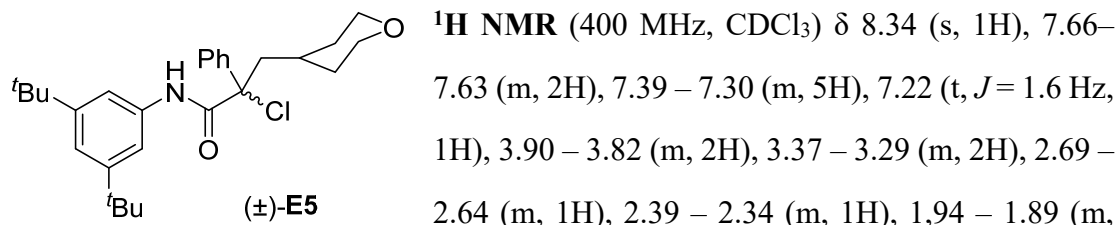


2-Chloro-3-cyclopentyl-*N*-(3,5-di-*tert*-butylphenyl)-2-phenylpropanamide ((±)-E4)



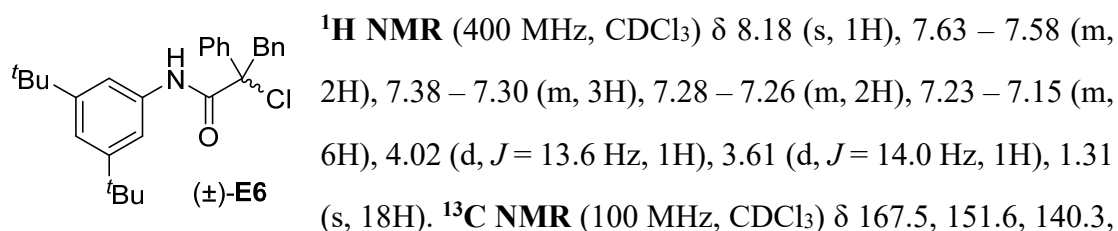
– 1.63 (m, 1H), 1.62 – 1.50 (m, 2H), 1.49 – 1.38 (m, 2H), 1.36 – 1.19 (s, 19H), 1.15 – 1.05 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 168.0, 151.7, 141.0, 136.8, 128.4, 128.3, 126.4, 119.0, 114.3, 78.6, 47.1, 37.3, 34.9, 34.0, 33.4, 31.3, 24.8, 24.7. HRMS (ESI) *m/z* calcd. for C₂₈H₃₉ClNO⁺ [M+H]⁺ 440.2715, found 440.2711.

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



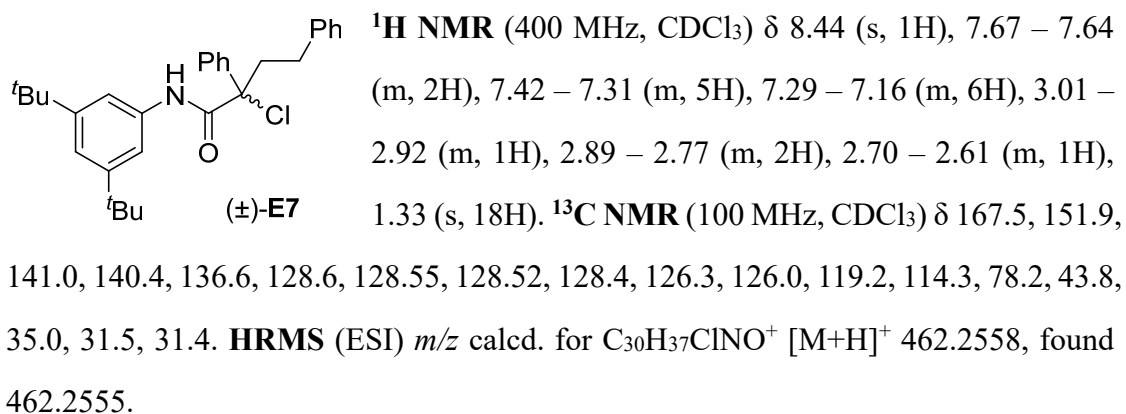
1H), 1.72 – 1.66 (m, 2H), 1.51 – 1.41 (m, 2H), 1.31 (s, 18H). ¹³C NMR (100 MHz, CDCl₃) δ 167.7, 151.8, 140.7, 136.7, 128.6, 128.5, 126.2, 119.2, 114.3, 78.0, 67.9, 67.8, 48.0, 34.9, 34.3, 33.6, 32.5, 31.3. HRMS (ESI) *m/z* calcd. for C₂₈H₃₉ClNO₂⁺ [M+H]⁺ 456.2664, found 456.2658.

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

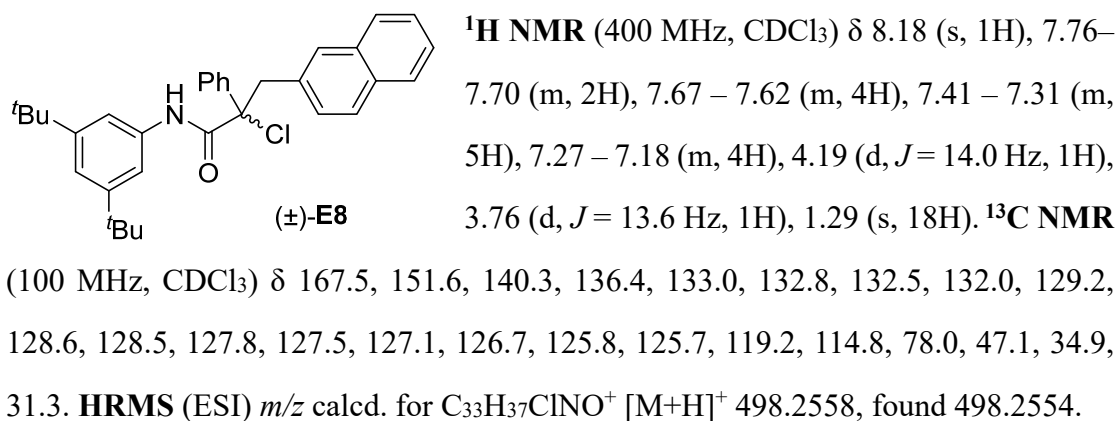


136.4, 135.3, 131.2, 128.5, 128.4, 127.7, 127.1, 126.7, 119.2, 114.9, 77.8, 46.9, 34.9, 31.4. HRMS (ESI) *m/z* calcd. for C₂₉H₃₅ClNO⁺ [M+H]⁺ 448.2402, found 448.2398.

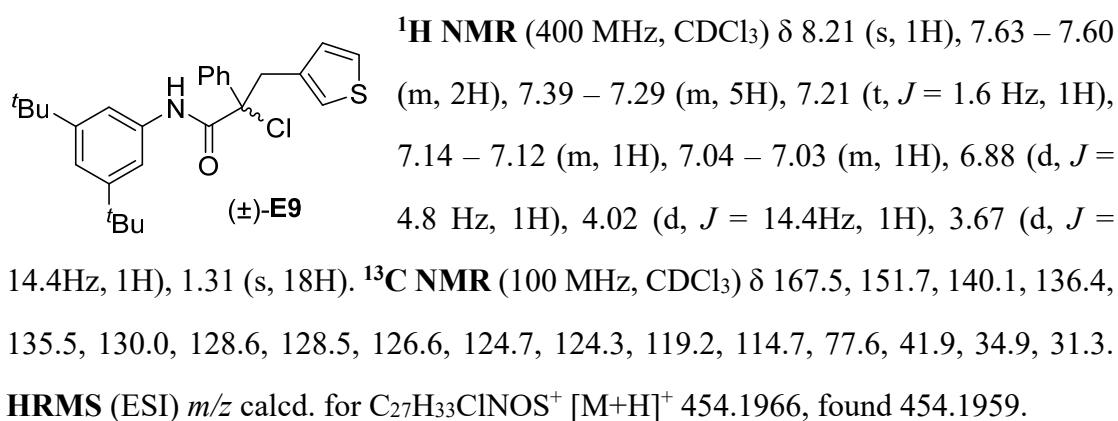
2-Chloro-*N*-(3,5-di-*tert*-butylphenyl)-2,4-diphenylbutanamide ((±)-E7)



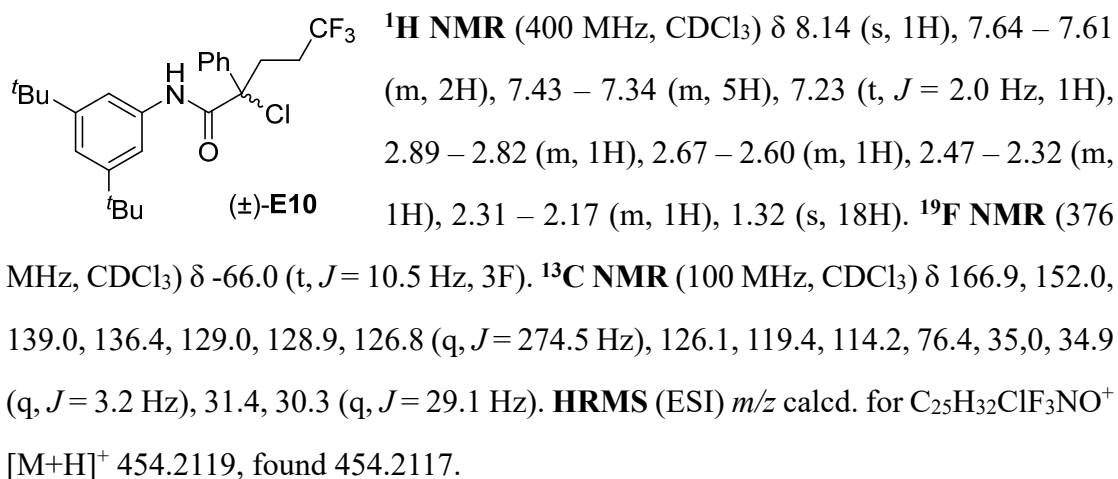
2-Chloro-N-(3,5-di-tert-butylphenyl)-3-(naphthalen-2-yl)-2-phenylpropanamide ((±)-E8)



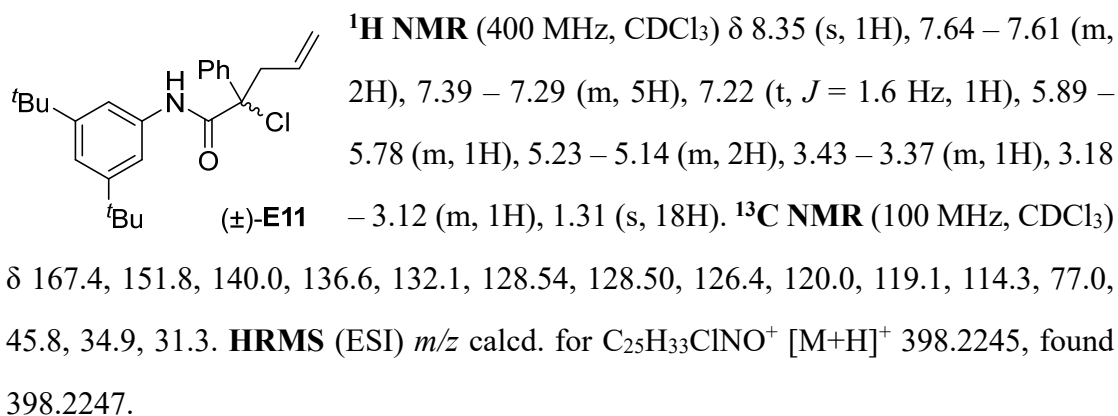
2-Chloro-N-(3,5-di-tert-butylphenyl)-2-phenyl-3-(thiophen-3-yl)propenamide ((±)-E9)



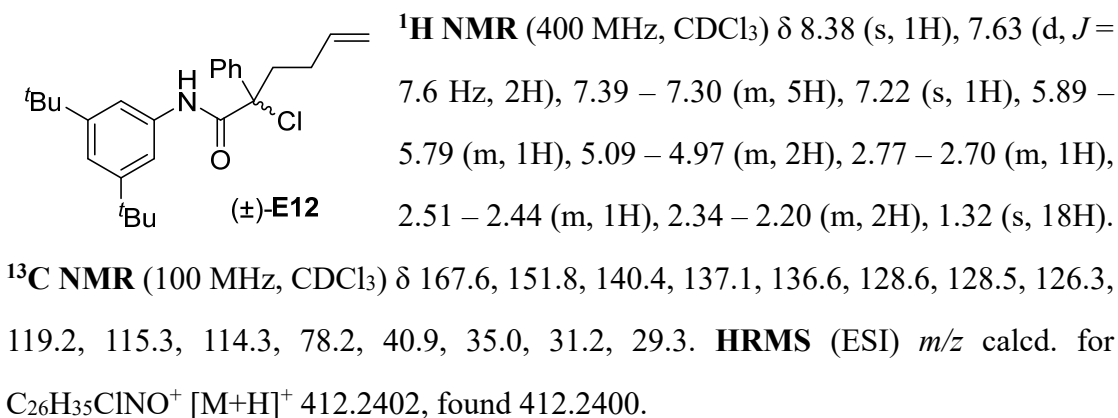
2-Chloro-N-(3,5-di-tert-butylphenyl)-5,5,5-trifluoro-2-phenylpentanamide ((±)-E10)



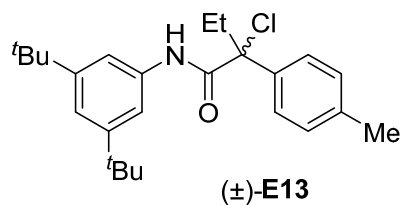
2-Chloro-*N*-(3,5-di-*tert*-butylphenyl)-2-phenylpent-4-enamide ((±)-E11)



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

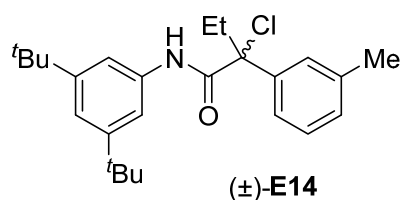


2-Chloro-*N*-(3,5-di-*tert*-butylphenyl)-2-(*p*-tolyl)butanamide ((±)-E13)



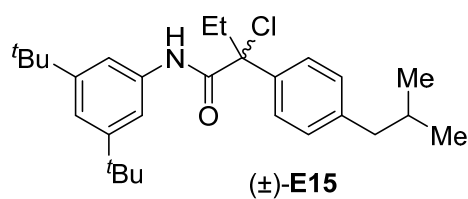
¹H NMR (400 MHz, CDCl₃) δ 8.43 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 1.6 Hz, 2H), 7.21 (t, *J* = 1.6 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 2.71 – 2.62 (m, 1H), 2.46 – 2.37 (m, 1H), 2.34 (s, 3H), 1.32 (s, 18H), 1.09 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 167.9, 151.8, 138.3, 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 C₂₅H₃₅ClNO⁺ [M+H]⁺ 400.2402, found 400.2399.

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



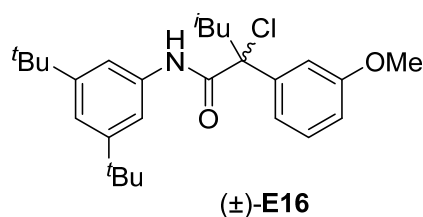
¹H NMR (400 MHz, CDCl₃) δ 8.40 (s, 1H), 7.42 – 7.40 (m, 4H), 7.27 – 7.24 (m, 1H), 7.22 (t, *J* = 1.6 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 2.72 – 2.63 (m, 1H), 2.46 – 2.37 (m, 4H), 1.32 (s, 18H), 1.09 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 167.9, 151.8, 140.5, 138.2, 136.7, 129.2, 128.4, 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 C₂₅H₃₅ClNO⁺ [M+H]⁺ 400.2402, found 400.2401.

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



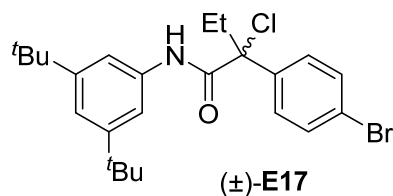
¹H NMR (400 MHz, CDCl₃) δ 8.43 (s, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 1.6 Hz, 2H), 7.22 (t, *J* = 1.6 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 2.72 – 2.63 (m, 1H), 2.47 – 2.37 (m, 3H), 1.91 – 1.80 (m, 1H), 1.32 (s, 18H), 1.09 (t, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 6H). **¹³C NMR** (100 MHz, CDCl₃) 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 C₂₈H₄₁ClNO⁺ [M+H]⁺ 442.2871, found 442.2869.

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



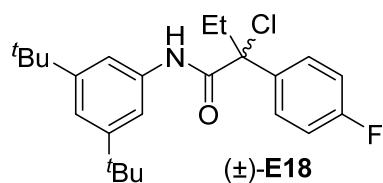
¹H NMR (400 MHz, CDCl₃) δ 8.35 (s, 1H), 7.37 (d, *J* = 1.6 Hz, 2H), 7.28 – 7.20 (m, 4H), 6.86 – 6.83 (m, 1H), 3.81 (s, 3H), 2.64 – 2.59 (m, 1H), 2.37 – 2.32 (m, 1H), 2.00 – 1.01 (m, 1H), 1.31 (s, 18H), 1.00 (d, *J* = 6.4 Hz, 3H), 0.88 (d, *J* = 6.4 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 167.9, 159.6, 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 C₂₇H₃₉ClNO₂⁺ [M+H]⁺ 444.2664, found 444.2660.

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



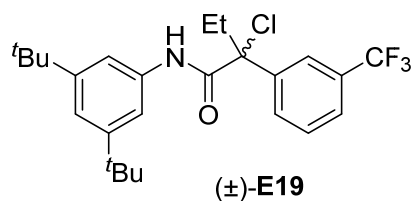
¹H NMR (400 MHz, CDCl₃) δ 8.48 (s, 1H), 7.50 (s, 4H), 7.39 (s, 2H), 7.23 (s, 1H), 2.70 – 2.61 (m, 1H), 2.43 – 2.34 (m, 1H), 1.32 (s, 18H), 1.10 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 167.3, 151.9, 139.7, 136.5, 131.6, 128.2, 122.6, 119.3, 114.3, 78.9, 35.0, 34.8, 31.4, 9.5. **HRMS** (ESI) *m/z* calcd. for C₂₄H₃₂BrClNO⁺ [M+H]⁺ 464.1350, found 464.1350.

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



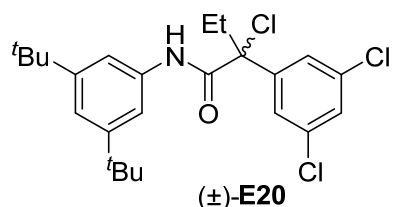
¹H NMR (400 MHz, CDCl₃) δ 8.51 (s, 1H), 7.63 – 7.58 (m, 2H), 7.41 (d, *J* = 1.6 Hz, 2H), 7.23 (t, *J* = 2.0 Hz, 1H), 7.05 (t, *J* = 8.8 Hz, 2H), 2.71 – 2.63 (m, 1H), 2.44 – 2.35 (m, 1H), 1.32 (s, 18H), 1.10 (t, *J* = 7.2 Hz, 3H). **¹⁹F NMR** (376 MHz, CDCl₃) δ –113.50 – –113.57 (m, 1F). **¹³C NMR** (100 MHz, CDCl₃) 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 C₂₄H₃₂ClFNO⁺ [M+H]⁺ 404.2151, found 404.2149.

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



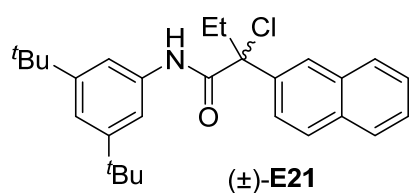
¹H NMR (400 MHz, CDCl₃) δ 8.55 (s, 1H), 7.93 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 1.6 Hz, 2H), 7.24 (t, *J* = 1.6 Hz, 1H), 2.76 – 2.67 (m, 1H), 2.48 – 2.39 (m, 1H), 1.32 (s, 18H), 1.12 (t, *J* = 7.2 Hz, 3H). **¹⁹F NMR** (376 MHz, CDCl₃) δ – 62.5 (s, 3F). **¹³C NMR** (100 MHz, CDCl₃) 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 C₂₅H₃₂ClF₃NO⁺ [M+H]⁺ 454.2119, found 454.2119.

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



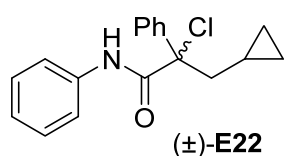
¹H NMR (400 MHz, CDCl₃) δ 8.50 (s, 1H), 7.54 (s, 2H), 7.40 (s, 2H), 7.33 (s, 1H), 7.25 (s, 1H), 2.70 – 2.61 (m, 1H), 2.41 – 2.32 (m, 1H), 1.33 (s, 18H), 1.10 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 166.5, 151.9, 143.8, 136.3, 135.1, 128.6, 125.3, 119.5, 114.4, 77.9, 35.0, 34.9, 31.3, 9.4. **HRMS** (ESI) *m/z* calcd. for C₂₄H₃₁Cl₃NO⁺ [M+H]⁺ 454.1466, found 454.1467.

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



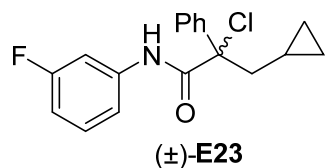
¹H NMR (400 MHz, CDCl₃) δ 8.47 (s, 1H), 8.11 (d, *J* = 2.0 Hz, 1H), 7.84 – 7.76 (m, 3H), 7.67 (dd, *J*₁ = 8.8 Hz, *J*₂ = 2.0 Hz, 1H), 7.47 – 7.42 (m, 4H), 7.23 (t, *J* = 1.6 Hz, 1H), 2.83 – 2.74 (m, 1H), 2.59 – 2.50 (m, 1H), 1.31 (s, 18H), 1.11 (t, *J* = 6.8 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 167.7, 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 C₂₈H₃₅ClNO⁺ [M+H]⁺ 436.2402, found 436.2400.

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



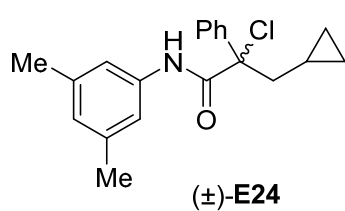
¹H NMR (400 MHz, CDCl₃) δ 8.54 (s, 1H), 7.61 – 7.58 (m, 2H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.38 – 7.29 (m, 5H), 7.14 (t, *J* = 7.6 Hz, 1H), 2.51 – 2.42 (m, 2H), 0.99 – 0.89 (m, 1H), 0.49 – 0.40 (m, 2H), 0.29 – 0.20 (m, 1H), 0.16 – 0.06 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ 168.1, 140.8, 137.2, 129.0, 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 C₁₈H₁₉ClNO⁺ [M+H]⁺ 300.1150, found 300.1151.

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



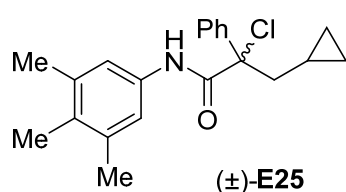
¹H NMR (400 MHz, CDCl₃) δ 8.55 (s, 1H), 7.59 – 7.56 (m, 2H), 7.54 (dt, *J*₁ = 10.8 Hz, *J*₂ = 2.4 Hz, 1H), 7.39 – 7.24 (m, 4H), 7.17 – 7.15 (m, 1H), 6.86 – 6.81 (m, 1H), 2.45 (d, *J* = 6.8 Hz, 2H), 0.97 – 0.87 (m, 1H), 0.48 – 0.40 (m, 2H), 0.27 – 0.18 (m, 1H), 0.15 – 0.05 (m, 1H). **¹⁹F NMR** (376 MHz, CDCl₃) δ –111.17 – –111.13 (m, 1F). **¹³C NMR** (100 MHz, CDCl₃) 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 C₁₈H₁₈ClFNO⁺ [M+H]⁺ 318.1055, found 318.1056.

2-Chloro-3-cyclopropyl-N-(3,5-dimethylphenyl)-2-phenylpropanamide ((±)-E24)



¹H NMR (400 MHz, CDCl₃) 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). **¹³C NMR** (100 MHz, CDCl₃) 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 C₂₀H₂₃ClNO⁺ [M+H]⁺ 328.1463, found 328.1464.

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

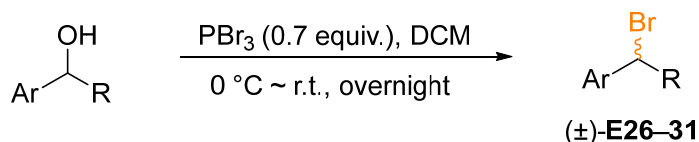


¹H NMR (400 MHz, CDCl₃) δ 8.42 (s, 1H), 7.60 – 7.58 (m, 2H), 7.37 – 7.28 (m, 3H), 7.22 (s, 2H), 2.52 – 2.40 (m, 2H), 2.27 (s, 6H), 2.13 (s, 3H), 0.98 – 0.89 (m, 1H), 0.49 – 0.40 (m, 2H), 0.29 – 0.22 (m, 1H), 0.15 – 0.07 (m, 1H).

¹³C NMR (100 MHz, CDCl₃) 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 C₂₁H₂₅ClNO⁺ [M+H] 342.1619, found. 342.1621.

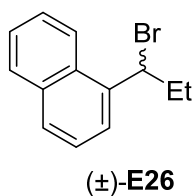
5.2 The synthesis of secondary benzyl bromides

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



The alcohol was resolved in CH₂Cl₂ (2.0 mL/mmol alcohol), then PBr₃ (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 CH₂Cl₂ three times. The combined organic phase was dried over MgSO₄, filtered through a Na₂SO₄ 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.)

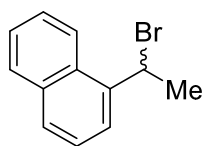
1-(1-Bromopropyl)naphthalene ((±)-**E26**)



¹H NMR (400 MHz, CDCl₃) 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). **¹³C NMR** (100 MHz,

CDCl₃) 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)

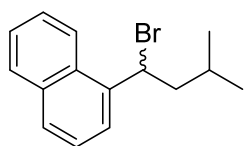


((±)-E27

¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (100 MHz, CDCl₃)

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)

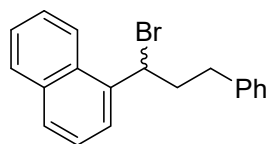


((±)-E28

¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (100 MHz, CDCl₃) 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)

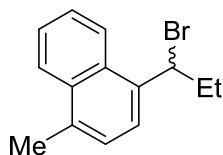


((±)-E29

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (100 MHz, CDCl₃) 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)

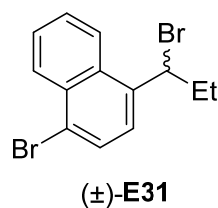


((±)-E30

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (100 MHz, CDCl₃) 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.

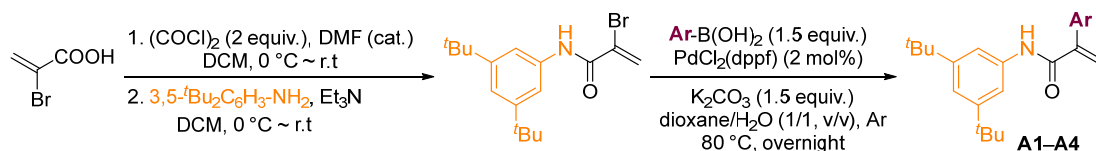
1-Bromo-4-(1-bromopropyl)naphthalene ((±)-E31)



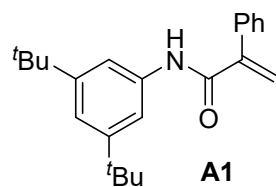
¹H NMR (400 MHz, CDCl₃) 8.33 – 8.29 (m, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.65 – 7.58 (m, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 5.62 (t, *J* = 7.2 Hz, 1H), 2.56 – 2.45 (m, 1H), 2.41 – 2.30 (m, 1H), 1.12 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 137.3, 132.2, 131.7, 129.6, 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.

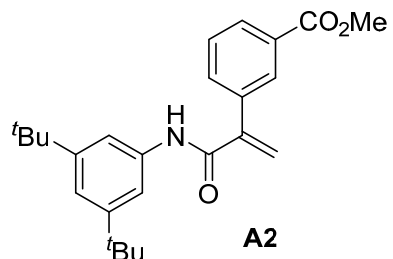


N-(3,5-Di-*tert*-butylphenyl)-2-phenylacrylamide (A1)



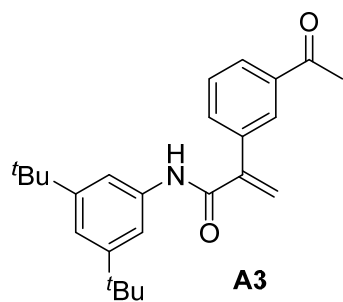
¹H NMR (400 MHz, CDCl₃) δ 7.53 (s, 1H), 7.46–7.35 (m, 7H), 7.20 (s, 1H), 6.22 (s, 1H), 5.69 (s, 1H), 1.30 (s, 18H). ¹³C NMR (100 MHz, CDCl₃) δ 165.3, 151.5, 145.4, 137.0, 136.7, 128.8, 128.6, 128.1, 122.5, 118.7, 114.5, 34.8, 31.3. HRMS (ESI) *m/z* calcd. for C₂₃H₃₀NO⁺ [M+H]⁺ 336.2322, found 336.2324.

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



¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (100 MHz, CDCl₃) 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 C₂₅H₃₂NO₃⁺ [M+H]⁺ 394.2377, found 394.2379.

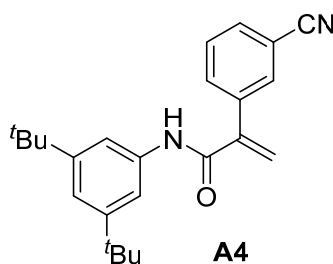
2-(Benzo[d][1,3]dioxol-5-yl)-N-(3,5-di-tert-butylphenyl)acrylamide (A3)



^1H 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 $\text{C}_{25}\text{H}_{32}\text{NO}_2^+$ $[\text{M}+\text{H}]^+$ 378.2428, found 378.2425.

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

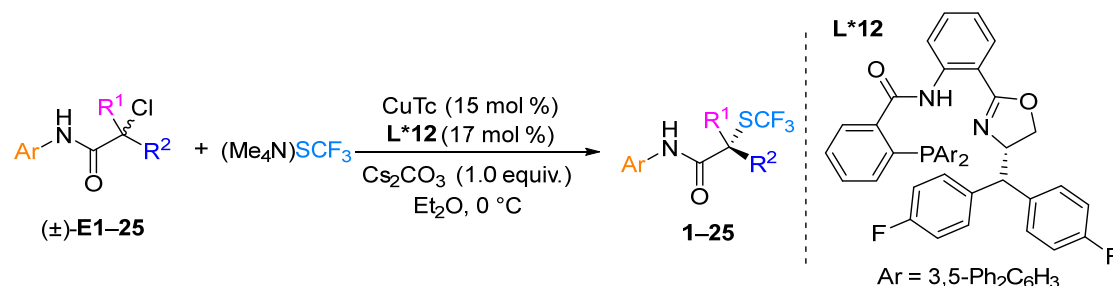


^1H NMR (400 MHz, CDCl_3) δ 7.79 (s, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 6.8 Hz, 2H), 7.50 (t, J = 8.0 Hz, 1H), 7.42 (s, 2H), 7.23 (s, 1H), 6.13 (s, 1H), 5.83 (s, 1H), 1.32 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.1, 151.8, 144.2, 137.7, 136.7, 132.2, 132.0, 131.4, 129.5, 122.2,

119.1, 118.3, 114.7, 112.9, 34.9, 31.3. **HRMS** (ESI) m/z calcd. for $\text{C}_{24}\text{H}_{29}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$ 361.2274, found 361.2272.

6. General procedure of enantioselective radical trifluoromethylthiolation

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

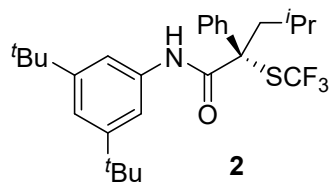


Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with the substrates ($\pm$)-**E** (0.1 mmol), (Me_4N) SCF_3 (26.3 mg, 0.15 mmol, 1.5 equiv.), CuTc (2.86 mg, 0.015 mmol, 15 mol%), **L*12** (16.3 mg, 0.017 mmol, 17 mol%), Cs_2CO_3 (32.6 mg, 0.10 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**)

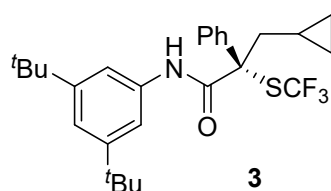
The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **1** (37.4 mg, 83% yield) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.54 – 7.51 (m, 2H), 7.43 – 7.33 (m, 4H), 7.25 (d, $J = 1.6$ Hz, 2H), 7.21 (t, $J = 1.6$ 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 $\text{C}_{25}\text{H}_{33}\text{F}_3\text{NOS}^+$ $[\text{M}+\text{H}]^+$ 452.2229, found 452.2227. HPLC analysis: Chiralcel IG (hexane/*i*-PrOH = 99/1, flow rate 0.40 mL/min, $\lambda = 254$ 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)pentamide (2)



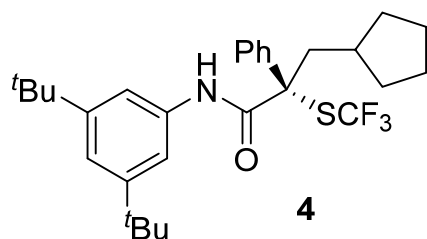
The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **2** (34.4 mg, 72% yield) as a white solid. **¹H NMR** (400 MHz, CDCl₃) δ 7.57 – 7.54 (m, 2H), 7.43 – 7.33 (m, 3H), 7.25 (s, 1H), 7.21 – 7.19 (m, 3H), 2.59 (dd, *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). **¹⁹F NMR** (376 MHz, CDCl₃) δ –36.9 (s, 3F). **¹³C NMR** (100 MHz, CDCl₃) 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 C₂₇H₃₇F₃NOS⁺ [*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)



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. **¹H NMR** (400 MHz, CDCl₃) 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). **¹⁹F NMR** (376 MHz, CDCl₃) δ –36.9 (s, 3F). **¹³C NMR** (100 MHz, CDCl₃) 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 C₂₇H₃₅F₃NOS⁺ [*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.

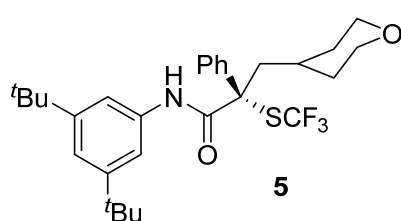
(*R*)-3-Cyclopentyl-*N*-(3,5-di-*tert*-butylphenyl)-2-phenyl-2-((trifluoromethyl)thio)propanamide (4)



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. **¹H NMR** (400 MHz, CDCl₃) 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). **¹⁹F NMR** (376 MHz, CDCl₃) δ –36.9 (s, 3F). **¹³C NMR** (100 MHz, CDCl₃) 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 C₂₉H₃₉F₃NOS⁺ [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.

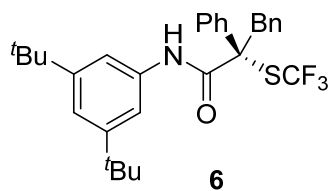
(*R*)-*N*-(3,5-Di-*tert*-butylphenyl)-2-phenyl-3-(tetrahydro-2H-pyran-4-yl)-2-((trifluoromethylthio)propenamide (5**)**



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. **¹H NMR** (400 MHz, CDCl₃) δ 7.56

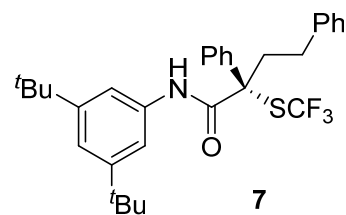
– 7.53 (m, 2H), 7.44 – 7.35 (m, 3H), 7.28 (s, 1H), 7.20 (t, *J* = 1.6 Hz, 1H), 7.19 (d, *J* = 1.6 Hz, 2H), 3.84 – 3.79 (m, 2H), 3.36 – 3.28 (m, 2H), 2.62 (dd, *J*₁ = 15.2 Hz, *J*₂ = 4.8 Hz, 1H), 2.35 (dd, *J*₁ = 15.2 Hz, *J*₂ = 5.6 Hz, 1H), 2.05 – 1.94 (m, 1H), 1.50 – 1.44 (m, 1H), 1.37 – 1.26 (m, 21H). **¹⁹F NMR** (376 MHz, CDCl₃) δ –36.8 (s, 3F). **¹³C NMR** (100 MHz, CDCl₃) 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 C₂₉H₃₉F₃NO₂S⁺ [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)



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. ¹H NMR (400 MHz, CDCl₃) 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). ¹⁹F NMR (376 MHz, CDCl₃) δ –36.2 (s, 3F). ¹³C NMR (100 MHz, CDCl₃) 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 C₃₀H₃₅F₃NOS⁺ [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.

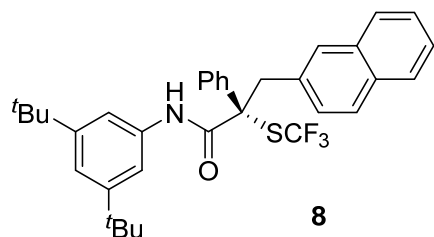
(*R*)-*N*-(3,5-Di-*tert*-butylphenyl)-2,4-diphenyl-2-((trifluoromethyl)thio)butanamide (7)



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. ¹H NMR (400 MHz, CDCl₃) 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). ¹⁹F NMR (376 MHz, CDCl₃) δ –37.0 (s, 3F). ¹³C NMR (100 MHz, CDCl₃) 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 C₃₁H₃₇F₃NOS⁺ [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)

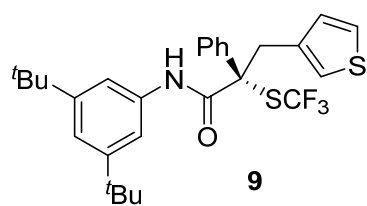
The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **8** (47.9 mg, 85% yield) as



8

a white solid. **¹H NMR** (400 MHz, CDCl₃) 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). **¹⁹F NMR** (376 MHz, CDCl₃) δ –36.1 (s, 3F). **¹³C NMR** (100 MHz, CDCl₃) 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 C₃₄H₃₇F₃NOS⁺ [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)propanamide (9**)**

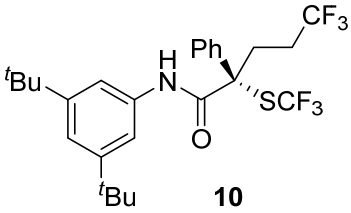


9

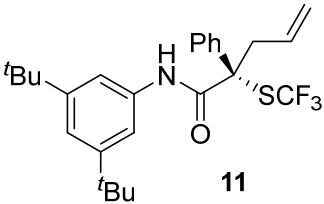
The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **9** (45.2 mg, 87% yield) as a white solid. **¹H NMR** (400 MHz, CDCl₃) δ 7.62 (s, 1H), 7.36 (s, 5H), 7.24 – 7.22 (m, 3H), 7.11 – 7.09 (m, 1H), 6.86 – 6.85 (m, 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). **¹⁹F NMR** (376 MHz, CDCl₃) δ –36.3 (s, 3F). **¹³C NMR** (100 MHz, CDCl₃) 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 C₂₈H₃₃F₃NOS₂⁺ [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**)**

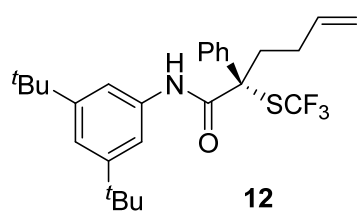
The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **10** (43.1 mg, 83% yield)


10 as a white solid. **¹H NMR** (400 MHz, CDCl₃) 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). **¹⁹F NMR** (376 MHz, CDCl₃) δ –37.0 (s, 3F), –66.1 (t, $J = 10.5$ Hz, 3F). **¹³C NMR** (100 MHz, CDCl₃) 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 C₂₆H₃₂F₆NOS⁺ [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. **¹H NMR** (400 MHz, CDCl₃) 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). **¹⁹F NMR** (376 MHz, CDCl₃) δ –36.8 (s, 3F). **¹³C NMR** (100 MHz, CDCl₃) 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 C₂₆H₃₃F₃NOS⁺ [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.

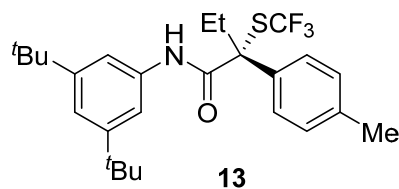
(*R*)-*N*-(3,5-Di-*tert*-butylphenyl)-2-phenyl-2-((trifluoromethyl)thio)hex-5-enamide (12)



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. ¹H NMR (400 MHz, CDCl₃) 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). ¹⁹F NMR (376 MHz, CDCl₃) δ –37.1 (s, 3F). ¹³C NMR (100 MHz, CDCl₃) 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 C₂₇H₃₅F₃NOS⁺ [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.

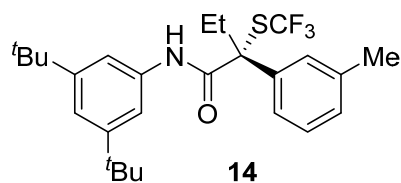
(*R*)-*N*-(3,5-Di-*tert*-butylphenyl)-2-(*p*-tolyl)-2-((trifluoromethyl)thio)butanamide (13)



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. ¹H NMR (400 MHz,

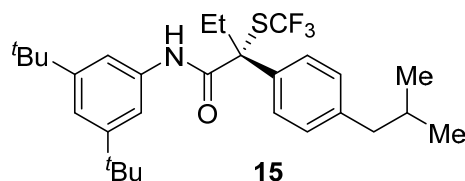
CDCl₃) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.36 (s, 1H), 7.26 – 7.19 (m, 5H), 2.68 – 2.59 (m, 1H), 2.48 – 2.39 (m, 1H), 2.37 (s, 3H), 1.30 (s, 18H), 1.07 (t, *J* = 7.6 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ –37.2 (s, 3F). ¹³C NMR (100 MHz, CDCl₃) δ 169.4, 151.8, 138.7, 136.6, 135.3, 129.7 (q, *J* = 307.3 Hz), 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 C₂₆H₃₅F₃NOS⁺ [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)



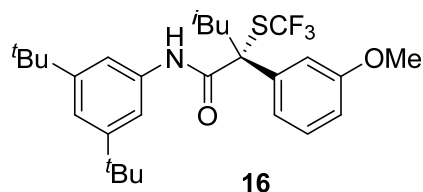
The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **14** (32.1 mg, 69% yield) as a white solid. **¹H NMR** (400 MHz, CDCl₃) δ 7.37 (s, 1H), 7.32 – 7.29 (m, 3H), 7.24 (d, *J* = 1.6 Hz, 2H), 7.20 (t, *J* = 1.6 Hz, 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). **¹⁹F NMR** (376 MHz, CDCl₃) δ –37.2 (s, 3F). **¹³C NMR** (100 MHz, CDCl₃) 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 C₂₆H₃₅F₃NOS⁺ [*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**)**



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. **¹H NMR** (400 MHz, CDCl₃) 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). **¹⁹F NMR** (376 MHz, CDCl₃) δ –37.2 (s, 3F). **¹³C NMR** (100 MHz, CDCl₃) 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 C₂₉H₄₁F₃NOS⁺ [*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.

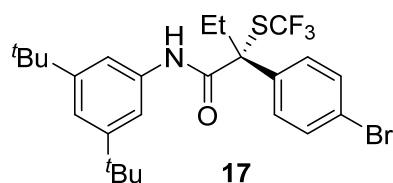
(*R*)-*N*-(3,5-Di-*tert*-butylphenyl)-2-(3-methoxyphenyl)-4-methyl-2-((trifluoromethyl)thio)pentanamide (16**)**



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. **¹H NMR** (400 MHz, CDCl₃) 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).

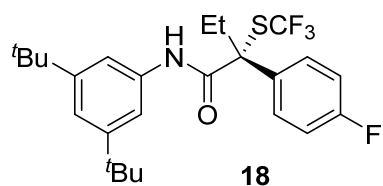
¹⁹F NMR (376 MHz, CDCl₃) δ –36.9 (s, 3F). **¹³C NMR** (100 MHz, CDCl₃) δ 169.3, 159.8, 151.8, 140.7, 136.4, 129.9, 129.8 (q, *J* = 307.3 Hz), 119.5, 119.2, 114.5, 113.8, 113.5, 66.7, 55.4, 46.0, 34.9, 31.3, 24.9, 24.5, 23.8. **HRMS** (ESI) *m/z* calcd. for C₂₈H₃₉F₃NO₂S⁺ [M+H]⁺ 510.2648, found 510.2648. **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**)**



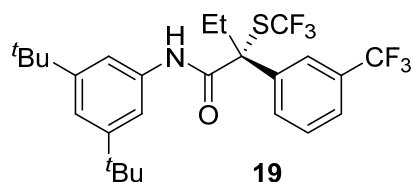
The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **17** (43.5 mg, 82% yield) as a white solid. **¹H NMR** (400 MHz, CDCl₃) δ 7.56 – 7.52 (m, 2H), 7.43 – 7.39 (m, 2H), 7.35 (s, 1H), 7.25 (d, *J* = 1.6 Hz, 2H), 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). **¹⁹F NMR** (376 MHz, CDCl₃) δ –37.1 (s, 3F). **¹³C NMR** (100 MHz, CDCl₃) 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 C₂₅H₃₂BrF₃NOS⁺ [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)butanamide (18**)**



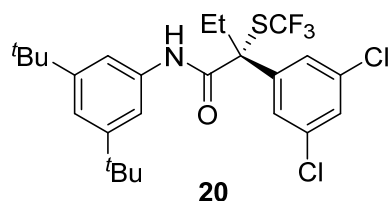
The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **18** (41.3 mg, 88% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.55 – 7.49 (m, 2H), 7.33 (s, 1H), 7.24 (s, 2H), 7.22 (m, 1H), 7.11 (t, *J* = 8.4 Hz, 2H), 2.68 – 2.59 (m, 1H), 2.49 – 2.40 (m, 1H), 1.30 (s, 18H), 1.11 (t, *J* = 7.2 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ –37.2 (s, 3F), –112.26 – –112.33 (m, 1F). ¹³C NMR (100 MHz, CDCl₃) 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 C₂₅H₃₂F₄NOS⁺ [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-((trifluoromethyl)thio)butanamide (19**)**



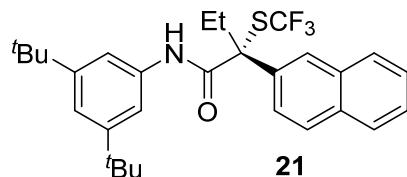
The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **19** (46.7 mg, 90% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.80 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 8.0 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). ¹⁹F NMR (376 MHz, CDCl₃) δ –37.1 (s, 3F), –62.6 (s, 3F). ¹³C NMR (100 MHz, CDCl₃) 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 C₂₆H₃₂F₆NOS⁺ [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**)**



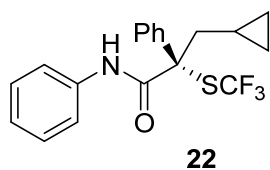
The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **20** (40.1 mg, 77% yield) as a white solid. **¹H NMR** (400 MHz, CDCl₃) δ 7.44 (d, *J* = 2.0 Hz, 2H), 7.39 – 7.37 (m, 2H), 7.26 – 7.24 (m, 3H), 2.65 – 2.56 (m, 1H), 2.48 – 2.39 (m, 1H), 1.31 (s, 18H), 1.12 (t, *J* = 7.2 Hz, 3H). **¹⁹F NMR** (376 MHz, CDCl₃) δ –37.0 (s, 3F). **¹³C NMR** (100 MHz, CDCl₃) 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 C₂₅H₃₁Cl₂F₃NOS⁺ [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**)**



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. **¹H NMR** (400 MHz, CDCl₃) 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). **¹⁹F NMR** (376 MHz, CDCl₃) δ –37.2 (s, 3F). **¹³C NMR** (100 MHz, CDCl₃) 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 C₂₉H₃₅F₃NOS⁺ [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**)**

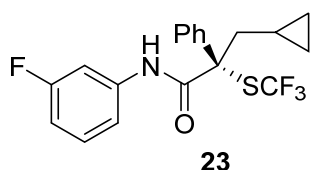


The residue was purified by column chromatography on silica gel with an eluent of ethyl acetate and petroleum ether (1:50~1:20, v/v) to afford product **22** (22.3 mg, 61% yield) as a

white solid. **¹H NMR** (400 MHz, CDCl₃) 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). **¹⁹F NMR** (376 MHz, CDCl₃) δ –36.9 (s, 3F). **¹³C NMR** (100 MHz, CDCl₃) 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 C₁₉H₁₉F₃NOS⁺ [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)propanamide (23**)**

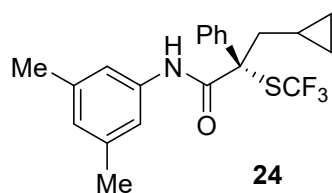


The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **23** (33.0 mg, 86% yield) as

a white solid. **¹H NMR** (400 MHz, CDCl₃) 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). **¹⁹F NMR** (376 MHz, CDCl₃) δ –36.9 (s, 3F), –111.07 – –111.14 (m, 1F). **¹³C NMR** (100 MHz, CDCl₃) 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 C₁₉H₁₈F₄NOS⁺ [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.

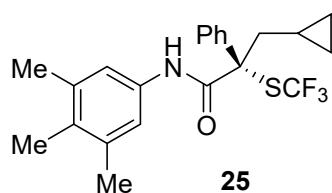
(*R*)-3-Cyclopropyl-*N*-(3,5-dimethylphenyl)-2-phenyl-2-((trifluoromethyl)thio)propenamide (24**)**



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. ¹H NMR (400 MHz, CDCl₃) 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). ¹⁹F NMR (376 MHz, CDCl₃) δ –36.9 (s, 3F). ¹³C NMR (100 MHz, CDCl₃) 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 C₂₁H₂₃F₃NOS⁺ [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.

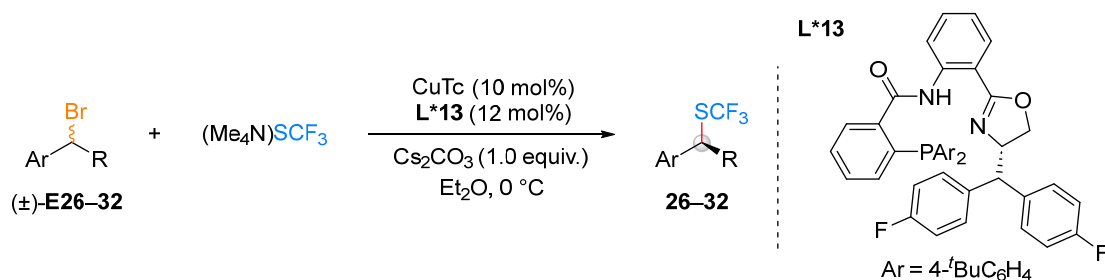
(*R*)-3-Cyclopropyl-2-phenyl-2-((trifluoromethyl)thio)-*N*-(3,4,5-trimethylphenyl)propenamide (25**)**



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. ¹H NMR (400 MHz, CDCl₃) 7.53 – 7.50 (m, 2

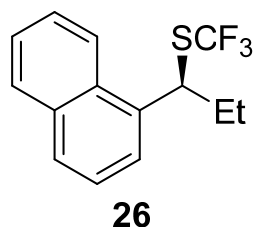
H), 7.42 – 7.33 (m, 4H), 7.08 (s, 2H), 2.56 (dd, *J*₁ = 14.8 Hz, *J*₂ = 6.4 Hz, 1H), 2.35 (dd, *J*₁ = 14.8 Hz, *J*₂ = 6.8 Hz, 1H), 2.25 (s, 6H), 2.12 (s, 3H), 1.03 – 0.93 (m, 1H), 0.49 – –0.40 (m, 2H), 0.12 – 0.050 (m, 1H), 0.04 – –0.02 (m, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ –36.9 (s, 3F). ¹³C NMR (100 MHz, CDCl₃) 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 C₂₂H₂₅F₃NOS⁺ [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



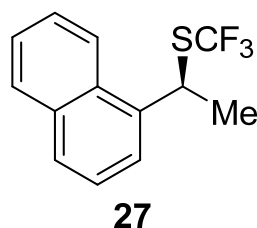
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with the substrates (±)-**E26-32** (0.1 mmol), (Me₄N)SCF₃ (26.3 mg, 0.15 mmol, 1.5 equiv.), CuTc (1.91 mg, 0.01 mmol, 10 mol%), **L*13** (9.18 mg, 0.012 mmol, 12 mol%), Cs₂CO₃ (32.6 mg, 0.10 mmol, 1.0 equiv.), and Et₂O (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**)



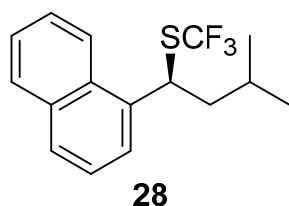
The residue was purified by column chromatography on silica gel with an eluent of petroleum ether to afford product **26** (21.9 mg, 81% yield) as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) 8.08 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.58 – 7.44 (m, 4H), 5.06 (brs, 1H), 2.30 – 2.23 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). **¹⁹F NMR** (376 MHz, CDCl₃) δ –40.0 (brs, 3F). **¹³C NMR** (100 MHz, CDCl₃) 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 C₁₄H₁₃F₃S [M] 270.0690, found 270.0685. **HPLC** analysis: Chiralcel OD-H (hexane, flow 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**)



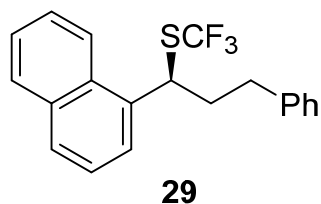
The residue was purified by column chromatography on silica gel with an eluent of petroleum ether to afford product **27** (19.5 mg, 76% yield) as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) 8.14 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.55 – 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). **¹⁹F NMR** (376 MHz, CDCl₃) δ –40.3 (s, 3F). **¹³C NMR** (100 MHz, CDCl₃) δ 135.9, 133.9, 130.7 (q, *J* = 305.8 Hz), 130.2, 129.2, 128.9, 126.7, 125.9, 125.3, 124.8, 122.5, 39.8, 23.1. **HRMS** (FI) *m/z* calcd. for C₁₃H₁₁F₃S [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)



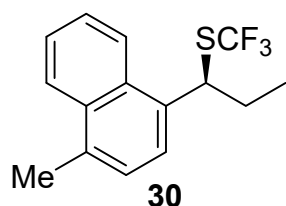
The residue was purified by column chromatography on silica gel with an eluent of petroleum ether to afford product **28** (2.6 mg, 69% yield) as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) 8.11 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.68 – 7.55 (m, 2H), 7.53 – 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). **¹⁹F NMR** (376 MHz, CDCl₃) δ –39.9 (brs, 3F). **¹³C NMR** (100 MHz, CDCl₃) 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 C₁₆H₁₇F₃S [M] 298.1003, found 298.0998. **HPLC** analysis: Chiralcel OD-H (hexane, flow rate 1.00 mL/min, 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)



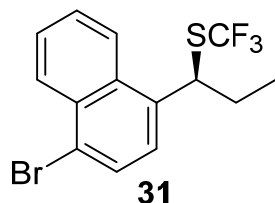
The residue was purified by column chromatography on silica gel with an eluent of petroleum ether to afford product **29** (27.7mg, 80% yield) as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) 7.91 – 7.80 (m, 3H), 7.64 (brs, 1H), 7.52 – 7.46 (m, 3H), 7.29 – 7.18 (m, 3H), 7.09 (d, *J* = 6.8 Hz, 2H), 5.13 (brs, 1H), 2.65 (t, *J* = 6.8 Hz, 2H), 2.60 – 2.46 (m, 2H). **¹⁹F NMR** (376 MHz, CDCl₃) δ –39.9 (brs, 3F). **¹³C NMR** (100 MHz, CDCl₃) 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 C₂₀H₁₇F₃S [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)



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. **¹H NMR** (400 MHz, CDCl₃) 8.12 – 8.09 (m, 1H), 8.07 – 8.05 (m, 1H), 7.60 – 7.53 (m, 2H), 7.50 – 7.42 (m, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 5.06 (brs, 1H), 2.69 (s, 3H), 2.27 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). **¹⁹F NMR** (376 MHz, CDCl₃) δ –40.0 (s, 3F). **¹³C NMR** (100 MHz, CDCl₃) 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 C₁₅H₁₅F₃S [M] 284.0847, found 284.0841. **HPLC** analysis: Chiralcel OD-H (hexane, flow rate 1.00 mL/min, λ = 214 nm), *t_R* (minor) = 12.15 min, *t_R* (major) = 19.71 min, 87% ee.

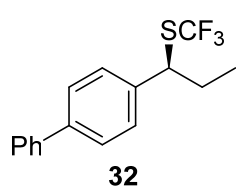
(S)-1-(4-Bromonaphthalen-1-yl)propyl(trifluoromethyl)sulfane (31)



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. **¹H NMR** (400 MHz, CDCl₃) 8.36 – 8.32 (m, 1H), 8.11 – 8.07 (m, 1H), 7.79 (d, *J* = 7.6 Hz, 1H),

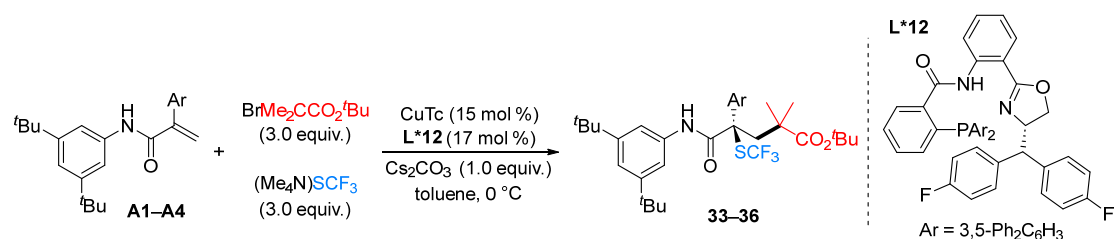
7.65 – 7.61 (m, 2H), 7.44 (d, $J = 7.6$ Hz, 1H), 5.04 (brs, 1H), 2.27 – 2.22 (m, 2H), 0.94 (t, $J = 7.6$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ –40.0 (brs, 3F). ^{13}C NMR (100 MHz, CDCl_3) δ 135.7, 132.2, 132.0, 130.5 (q, $J = 305.5$ Hz), 129.5, 128.4, 127.3(4), 127.2(8), 125.8 (brs), 123.3, 122.9 (brs), 45.7 (brs), 30.0, 11.9. HRMS (FI) m/z calcd. for $\text{C}_{14}\text{H}_{12}\text{BrF}_3\text{S}$ [M] 347.9795, found 347.9790. HPLC analysis: Chiralcel OD-H (hexane, flow rate 1.00 mL/min, $\lambda = 214$ nm), t_R (minor) = 9.87 min, t_R (major) = 14.92 min, 88% ee.

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



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. ^1H 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, $\lambda = 214$ nm), t_R (minor) = 10.87 min, t_R (major) = 17.11 min, 73% ee.

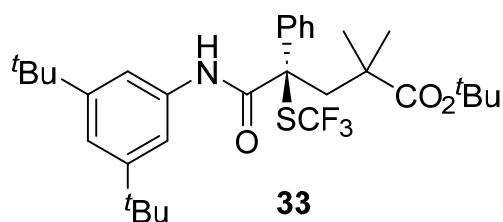
6.3 The procedure of enantioselective radical trifluoromethylthiolation of the alkenes



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with the substrates **A** (0.1 mmol), $(\text{Me}_4\text{N})\text{SCF}_3$ (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 $\text{BrMe}_2\text{CCO}_2^t\text{Bu}$ (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**.

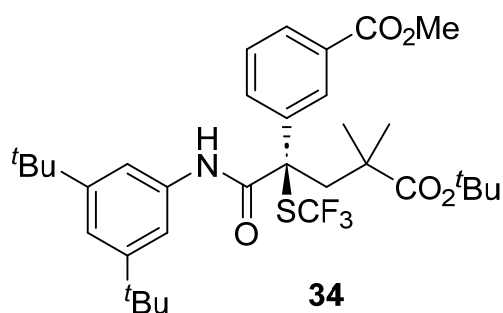
***Tert*-butyl (*R*)-5-((3,5-di-*tert*-butylphenyl)amino)-2,2-dimethyl-5-oxo-4-phenyl-4-((trifluoromethyl)thio)pentanoate (**33**)**



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. ¹H NMR

(400 MHz, CDCl₃) 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). ¹⁹F NMR (376 MHz, CDCl₃) δ –36.3 (s, 3F). ¹³C NMR (100 MHz, CDCl₃) 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 C₃₂H₄₅F₃NO₃S⁺ [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**)**

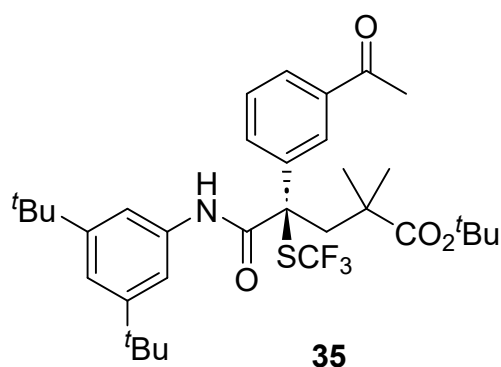


The residue was purified by column chromatography on silica gel with an eluent of ethyl acetate and petroleum ether (1:10~1:7.5, v/v) to afford product **34** (22.3 mg, 35% yield) as a white solid. ¹H NMR

(400 MHz, CDCl₃) 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).

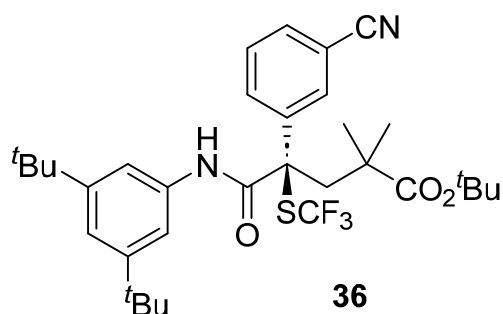
¹⁹F NMR (376 MHz, CDCl₃) δ -36.1 (s, 3F). **¹³C NMR** (100 MHz, CDCl₃) δ 176.1, 167.6, 166.5, 151.7, 139.5, 136.4, 132.9, 130.5, 129.8, 129.1 (q, *J* = 308.4 Hz), 128.81, 128.76, 119.4, 114.9, 80.6, 65.0, 52.3, 46.2, 43.1, 34.9, 31.3, 28.7, 27.7, 25.1. **HRMS** (ESI) *m/z* calcd. for C₃₄H₄₇F₃NO₅S⁺ [M+H]⁺ 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**)**



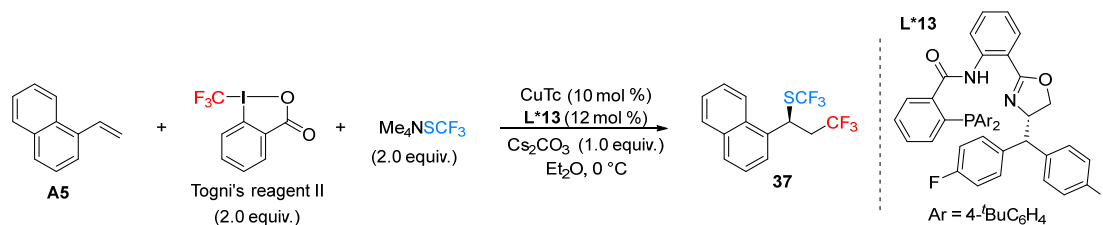
The residue was purified by column chromatography on silica gel with an eluent of ethyl acetate and petroleum ether (1:10~1:7.5, v/v) to afford product **35** (29.2 mg, 47% yield) as a white solid. **¹H NMR** (400 MHz, CDCl₃) δ 8.24 (t, *J* = 2.0 Hz, 1H), 8.08 (s, 1H), 7.91 (dt, *J_I* = 8.0 Hz, *J₂* = 1.2 Hz, 1H), 7.81 (dd, *J_I* = 8.0 Hz, *J₂* = 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). **¹⁹F NMR** (376 MHz, CDCl₃) δ -36.1 (s, 3F). **¹³C NMR** (100 MHz, CDCl₃) 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 C₃₄H₄₇F₃NO₄S⁺ [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**)**



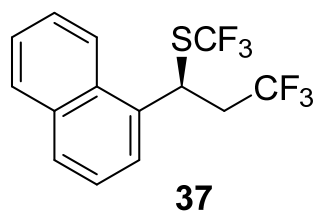
The residue was purified by column chromatography on silica gel with an eluent of ethyl acetate and petroleum ether (1:10~1:7.5, v/v) to afford product **36** (27.1 mg, 45% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.31 (s, 1H), 7.95 (t, *J* =

2.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.61 (dt, *J_I* = 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). ¹⁹F NMR (376 MHz, CDCl₃) δ -36.0 (s, 3F). ¹³C NMR (100 MHz, CDCl₃) 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 C₃₃H₄₃F₃N₂NaO₃S⁺ [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.), (Me₄N)SCF₃ (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%), Cs₂CO₃ (32.6 mg, 0.1 mmol, 1.0 equiv.), and Et₂O (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**.

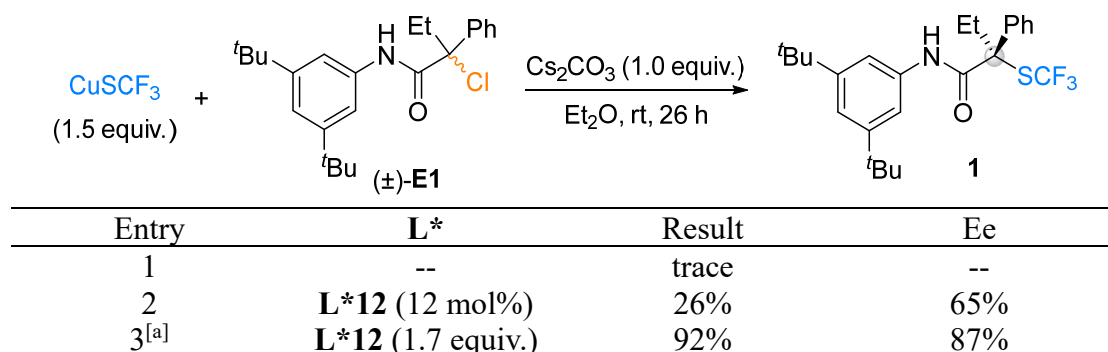
(S)-(3,3,3-Trifluoro-1-(naphthalen-1-yl)propyl)(trifluoromethyl)sulfane (37)



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. **¹H NMR** (400 MHz, CDCl₃) 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). **¹⁹F NMR** (376 MHz, CDCl₃) δ –40.7 (brs, 3F), –64.1 (brs, 3F). **¹³C NMR** (150 MHz, CDCl₃) 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 C₁₄H₁₀F₆S [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

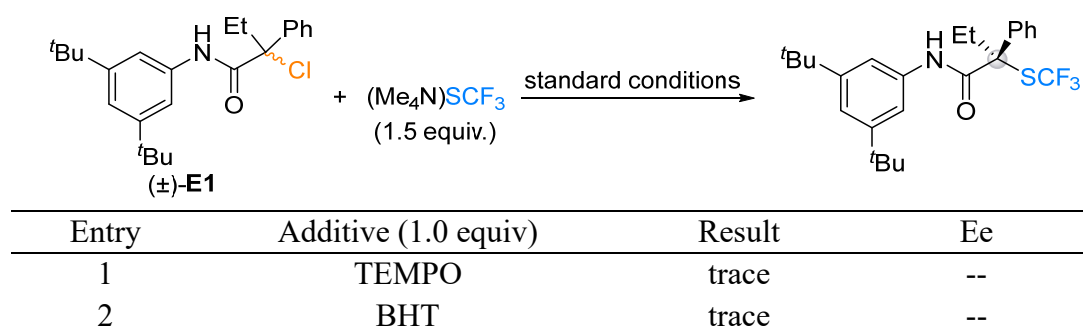
7.1 The experiment with CuSCF₃



[a] 3.0 equiv. Cs₂CO₃ 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), CuSCF₃ (12.3 mg, 0.75 mmol, 1.5 equiv.), Cs₂CO₃ (16.3 mg, 0.05 mmol, 1.0 equiv.), and Et₂O (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 CDCl₃, then 0.05 mmol CF₃OPh was added into the mixture. ¹⁹F NMR test and HPLC analysis gave the results above.

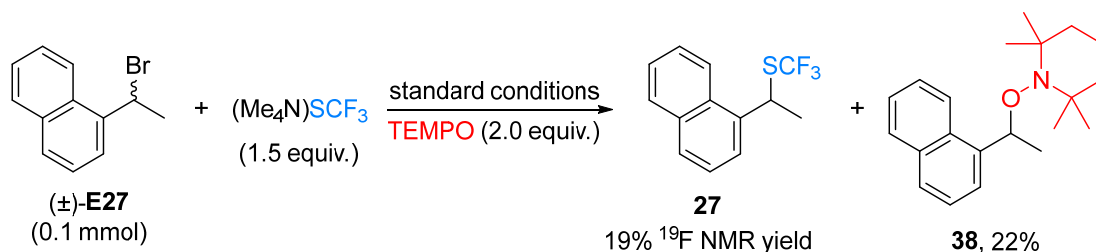
7.2 Radical inhibition experiments of the tertiary electrophiles



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with the substrates (±)-**E1** (0.05 mmol), (Me₄N)SCF₃ (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%), Cs₂CO₃ (16.3 mg, 0.05 mmol, 1.0 equiv.), Et₂O (1.0 mL), and TEMPO (7.82 mg, 0.05 mmol, 1.0 equiv.) or BHT (11.02 mg, 0.05 mmol, 1.0

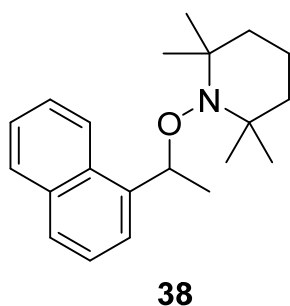
equiv.) successively. Then the reaction mixture was stirred in 0 °C ethanol bath for 120 h. Upon completion, the precipitate was filtered off and washed by ethyl acetate. The filtrate was evaporated and the residue was resolved with 1.0 mL CDCl₃, then 0.05 mmol CF₃OPh was added into the mixture. ¹⁹F 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), (Me₄N)SCF₃ (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%), Cs₂CO₃ (32.6 mg, 0.10 mmol, 1.0 equiv.), Et₂O (2.0 mL), and TEMPO (31.2 mg, 2.0 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 resolved with 1.5 mL CDCl₃, then 0.1 mmol CF₃OPh was added into the mixture. ¹⁹F 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**.

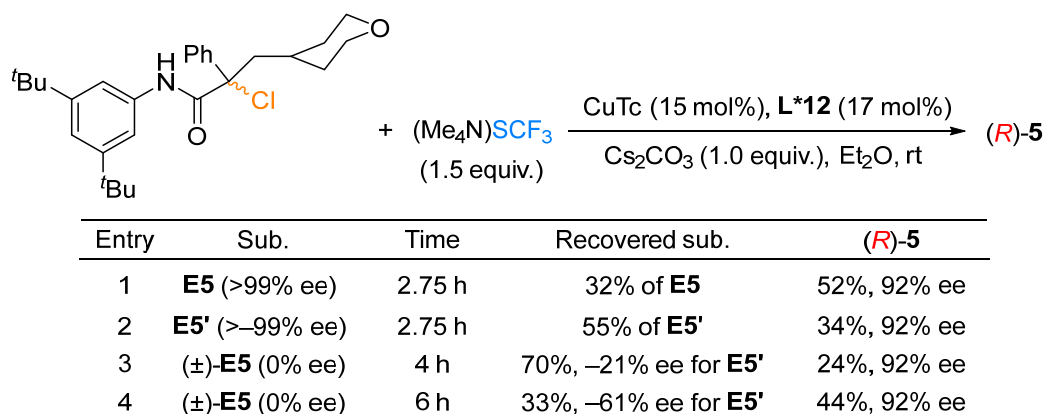
2,2,6,6-Tetramethyl-1-(1-(naphthalen-1-yl)ethoxy)piperidine (**38**)



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. ¹H NMR (400 MHz, CDCl₃) 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 $\text{C}_{21}\text{H}_{30}\text{NO}^+ [\text{M}+\text{H}]^+$ 312.2322, found 312.2322.

7.4 Control reactions with the enantiopure or racemic substrates



(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), $(\text{Me}_4\text{N})\text{SCF}_3$ (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- $\text{MeO}_3\text{C}_6\text{H}_3$ was added into the mixture. ^1H 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), $(\text{Me}_4\text{N})\text{SCF}_3$ (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

CDCl₃, then 0.05 mmol 1,3,5-MeO₃C₆H₃ 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 CH₂Cl₂, 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/Bohr². 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

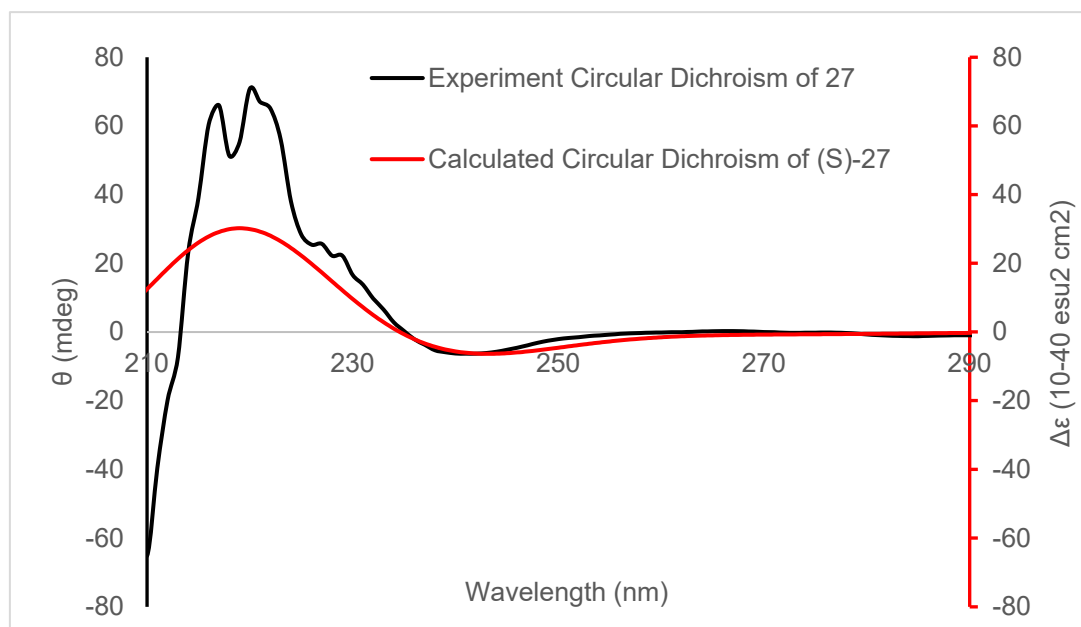


Figure S4. Comparison of Experimental ECD and Computational ECD for (S)-configuration product **27** with half-width and half height set to 0.25 eV.

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)	$\Delta\Delta G$ (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

<i>(S)</i> -27-C6	-1199.898334	1.0	0.083
<i>(S)</i> -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	<i>E</i>	<i>H</i>	<i>G</i>	Imaginary Frequency
<i>(S)</i> -27-C1	0.211322	0.226819	0.168967	-1200.067049	-1199.840230	-1199.898082	
<i>(S)</i> -27-C2	0.210954	0.226708	0.167380	-1200.067276	-1199.840568	-1199.899896	
<i>(S)</i> -27-C3	0.211463	0.226949	0.169200	-1200.062497	-1199.835548	-1199.893297	
<i>(S)</i> -27-C4	0.211247	0.226888	0.168651	-1200.059720	-1199.832832	-1199.891069	
<i>(S)</i> -27-C5	0.211126	0.226830	0.168143	-1200.066795	-1199.839965	-1199.898652	
<i>(S)</i> -27-C6	0.211200	0.226902	0.167818	-1200.066152	-1199.839250	-1199.898334	
<i>(S)</i> -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

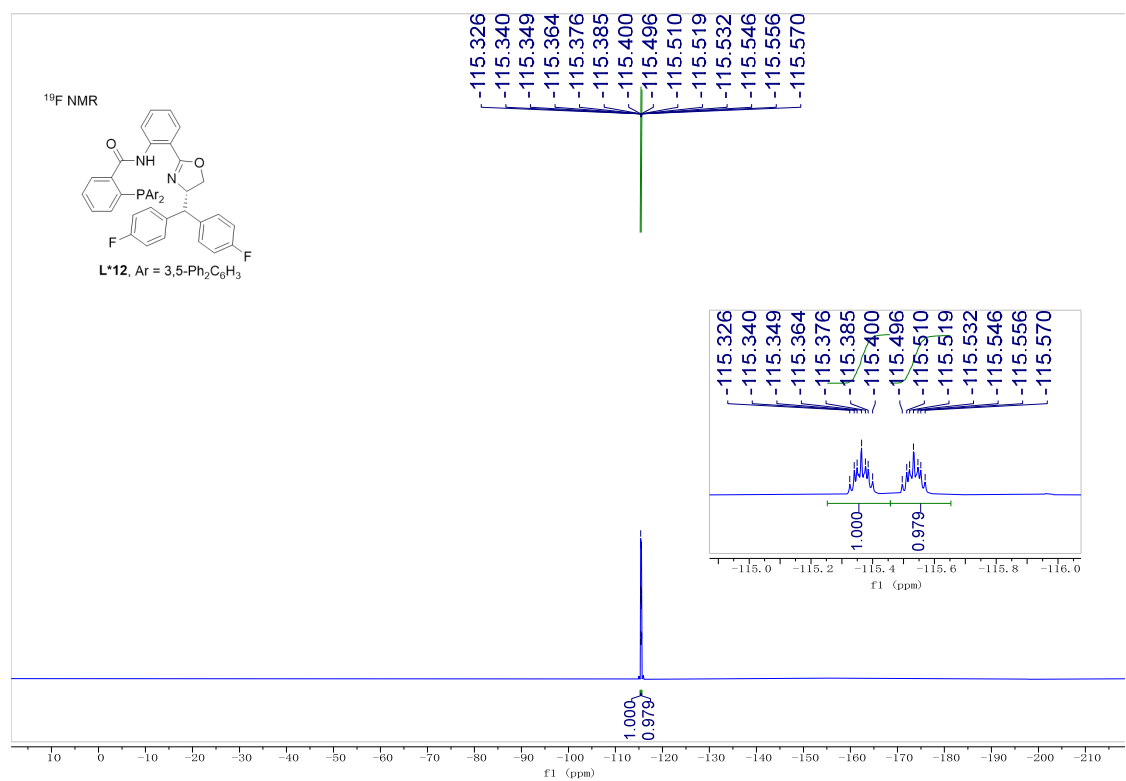
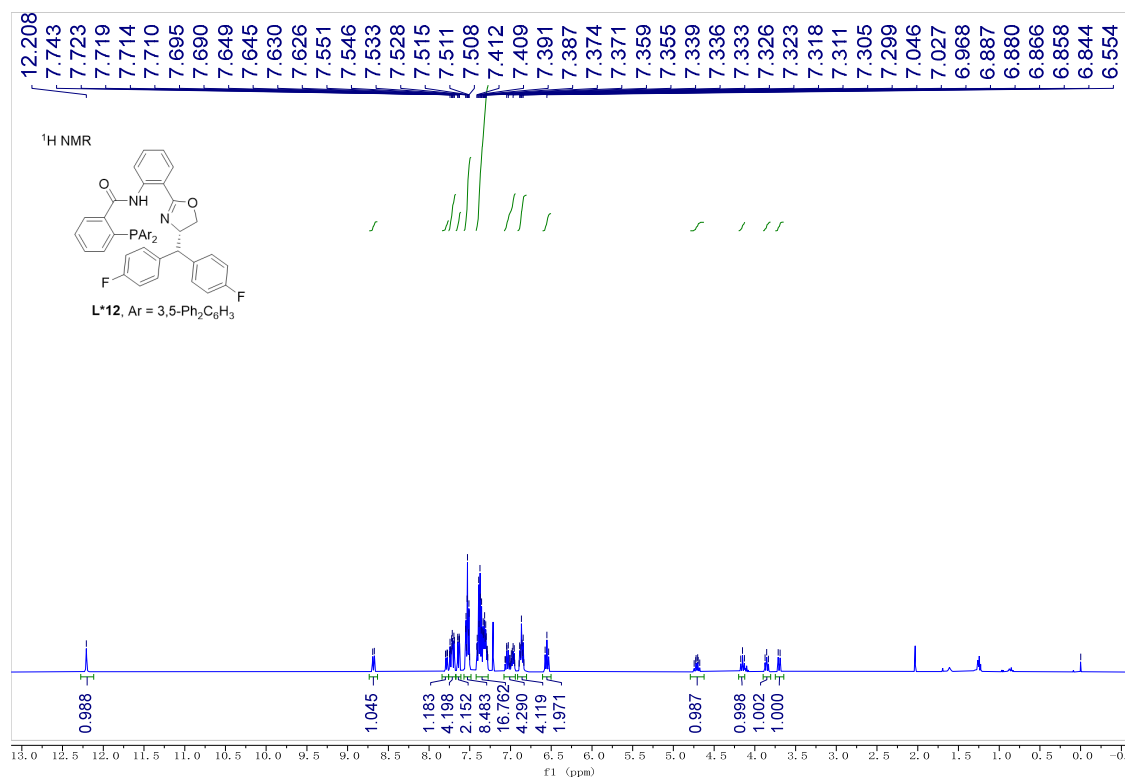
C	-3.22393900	-2.43433000	0.12531400
C	-3.75101700	-1.19287900	-0.14432300
C	-2.93359200	-0.03242900	-0.12899500
C	-1.53897200	-0.15617600	0.18212200
C	-1.02657700	-1.45649100	0.44334200
C	-1.84690900	-2.56306100	0.41675600
H	-4.53479800	1.32314900	-0.65686600

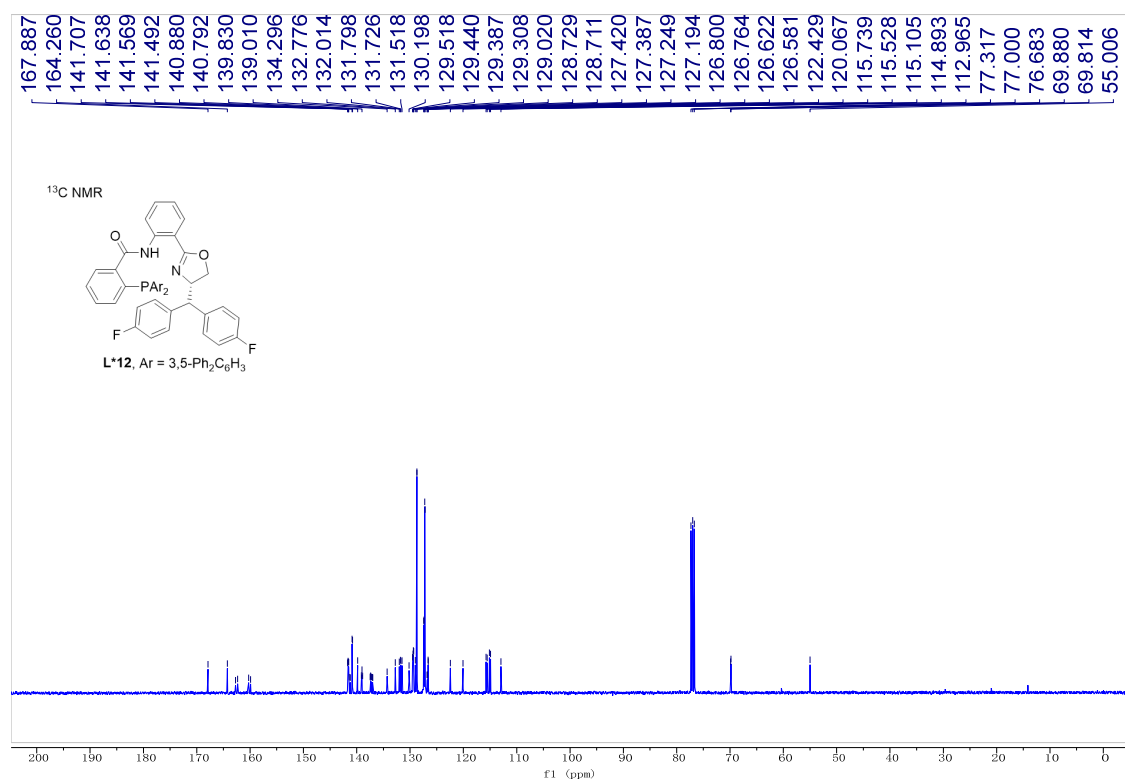
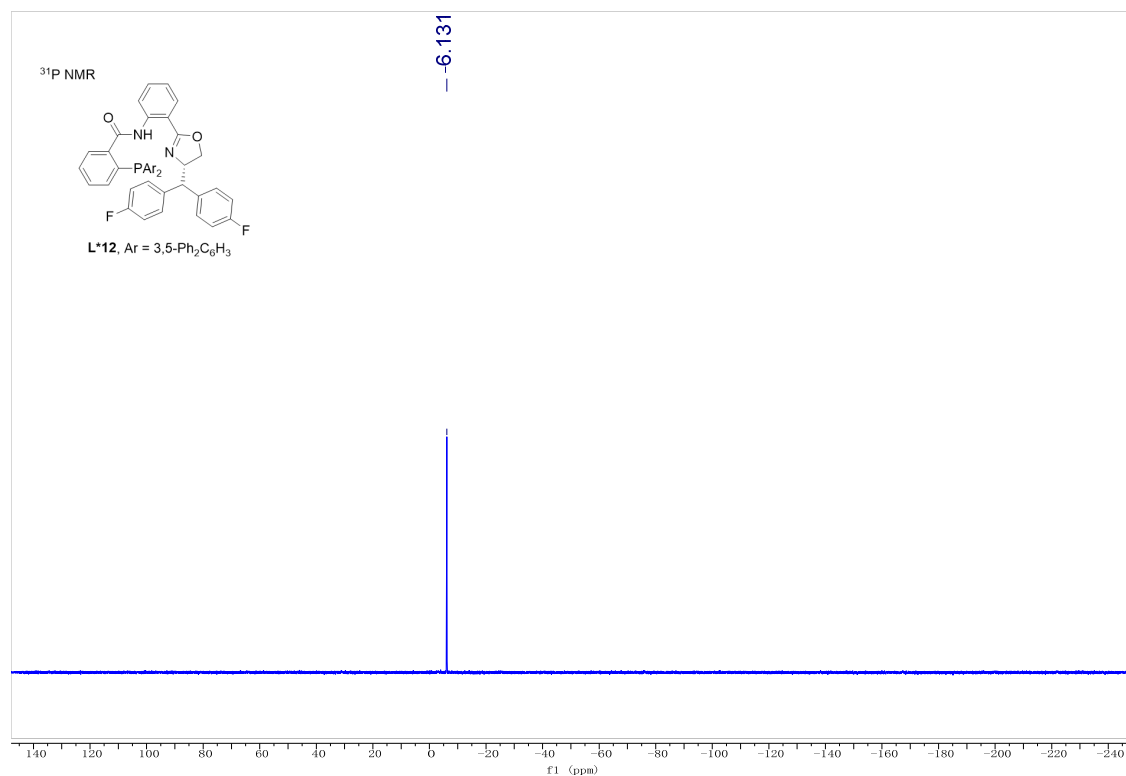
H	-3.85892100	-3.31533200	0.10929400
H	-4.80665500	-1.07916500	-0.37754300
C	-3.47671500	1.24674300	-0.42017800
C	-0.72955100	1.03005800	0.21356700
H	0.02904500	-1.59422700	0.64107900
H	-1.42894400	-3.54563200	0.61589800
C	-1.30556400	2.24890500	-0.08538300
C	-2.67834700	2.36330200	-0.40497800
H	-0.70211200	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

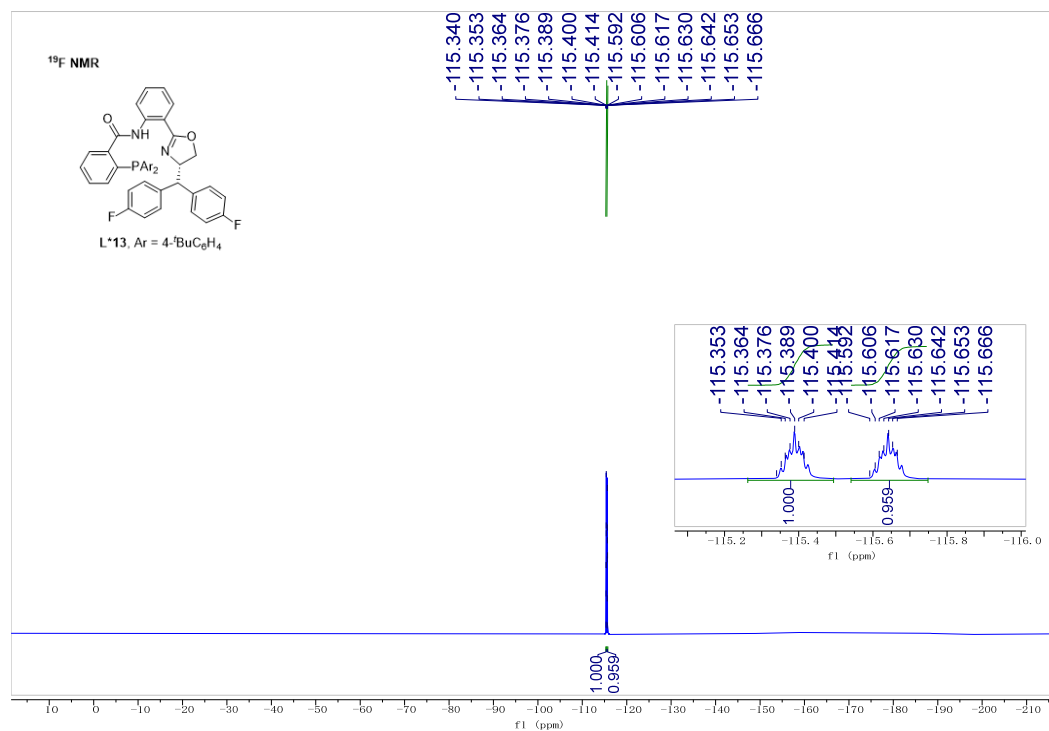
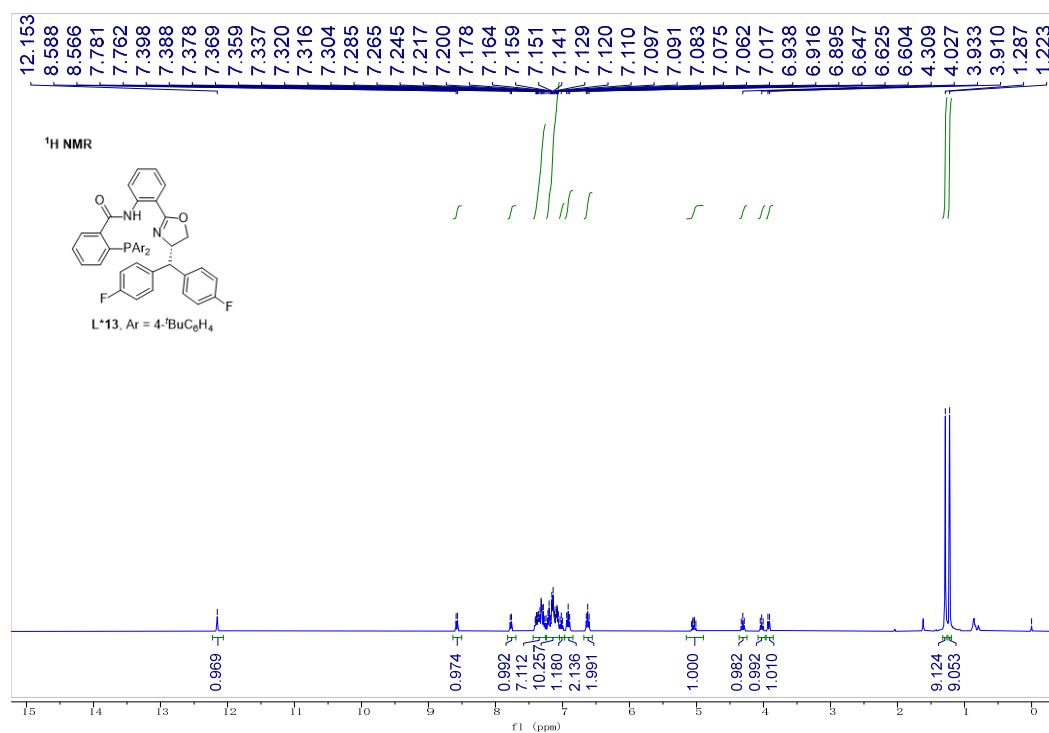
9. Reference

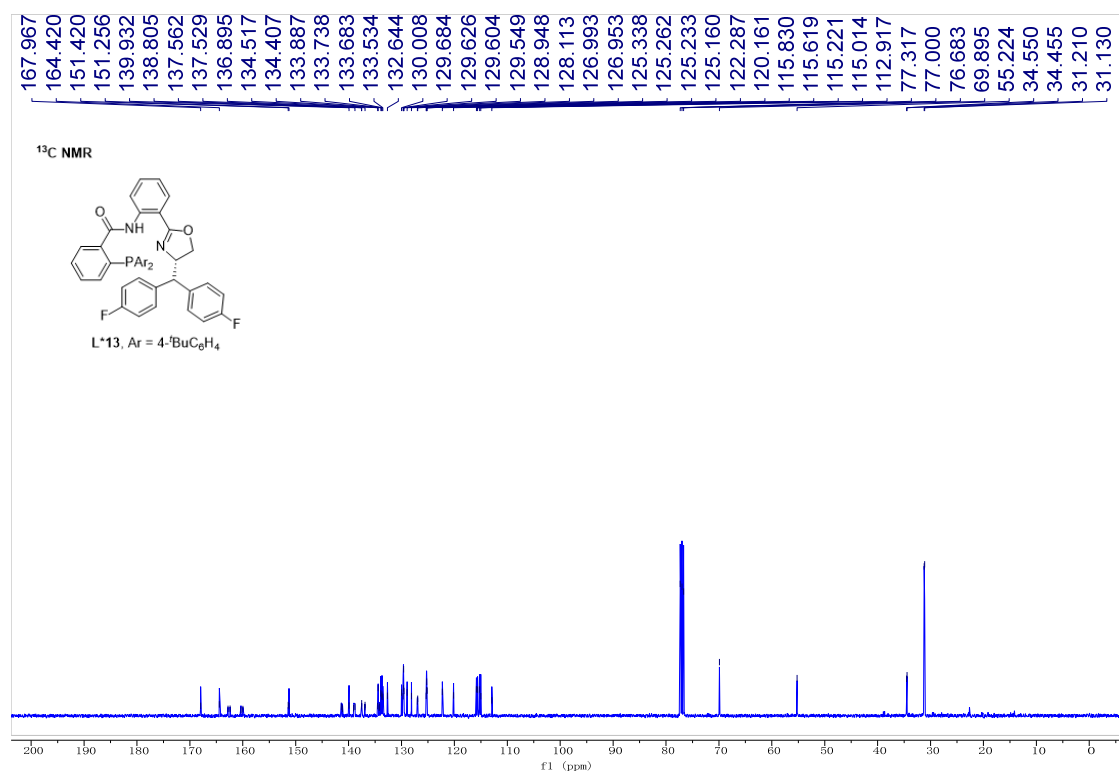
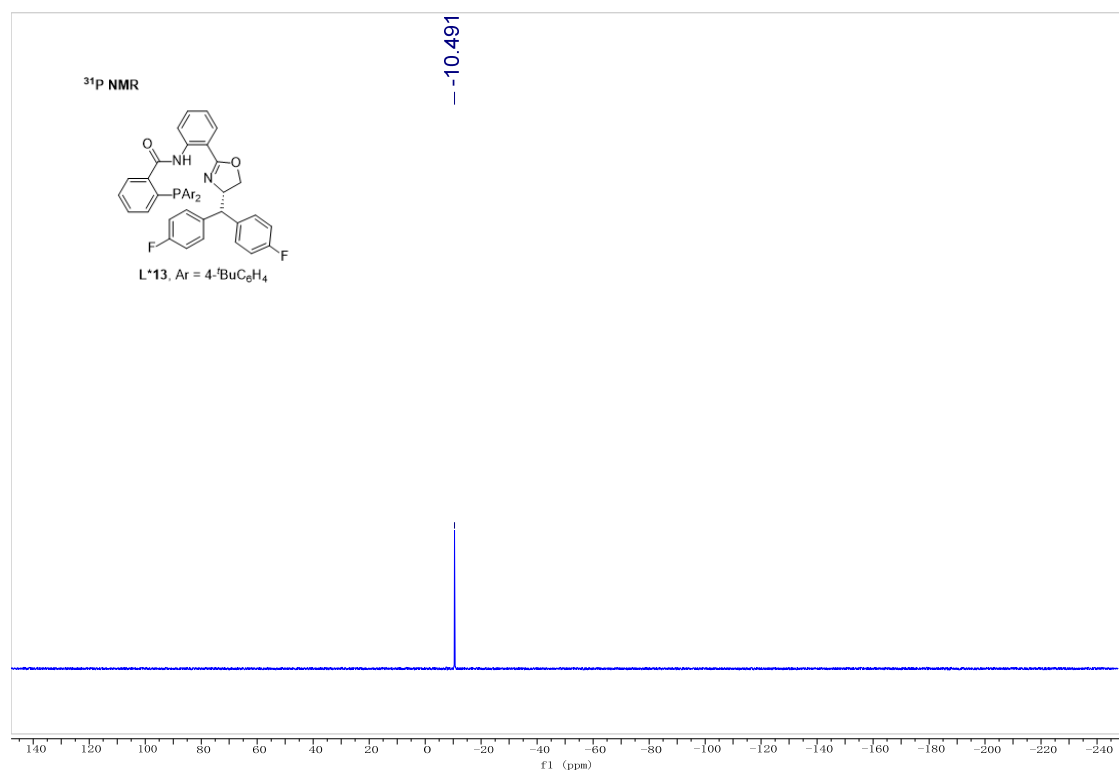
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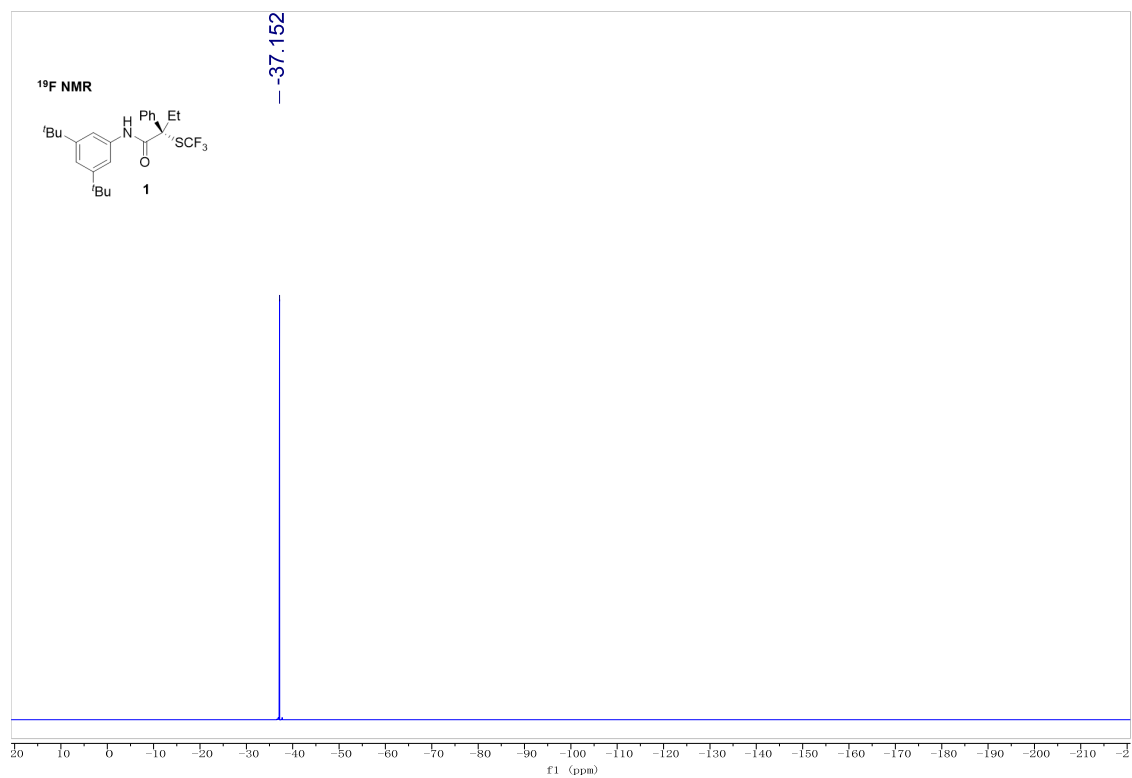
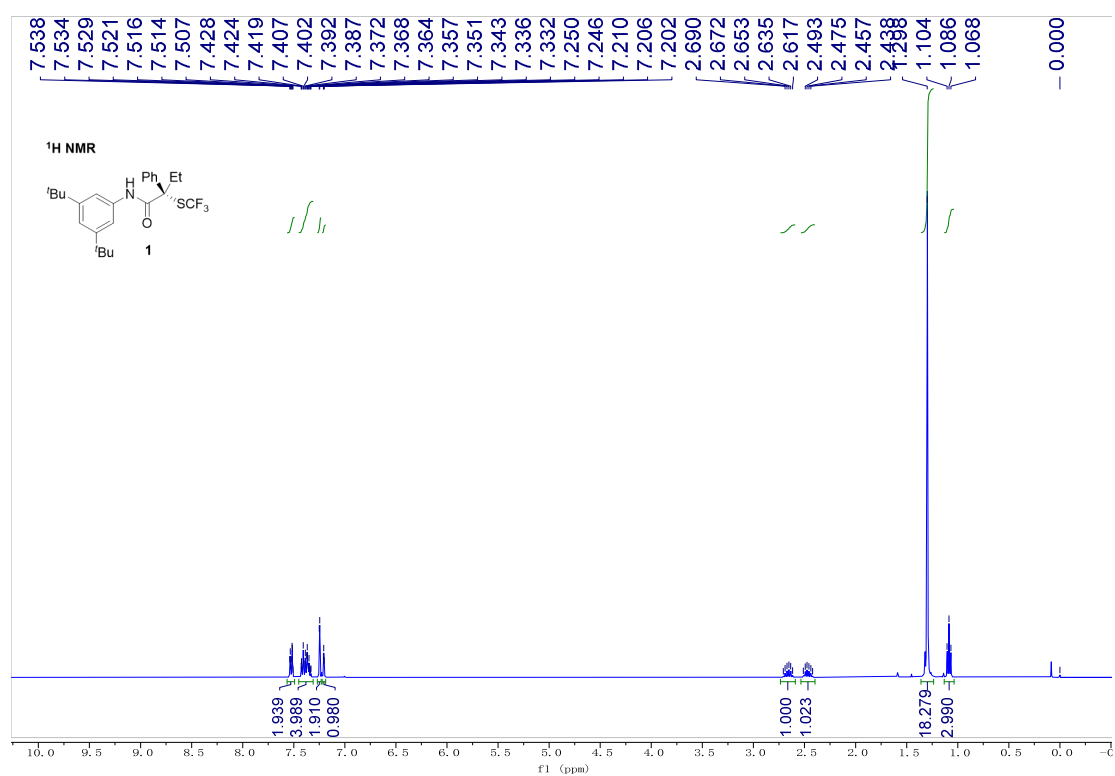
10. NMR spectra of the optimized ligands and the products

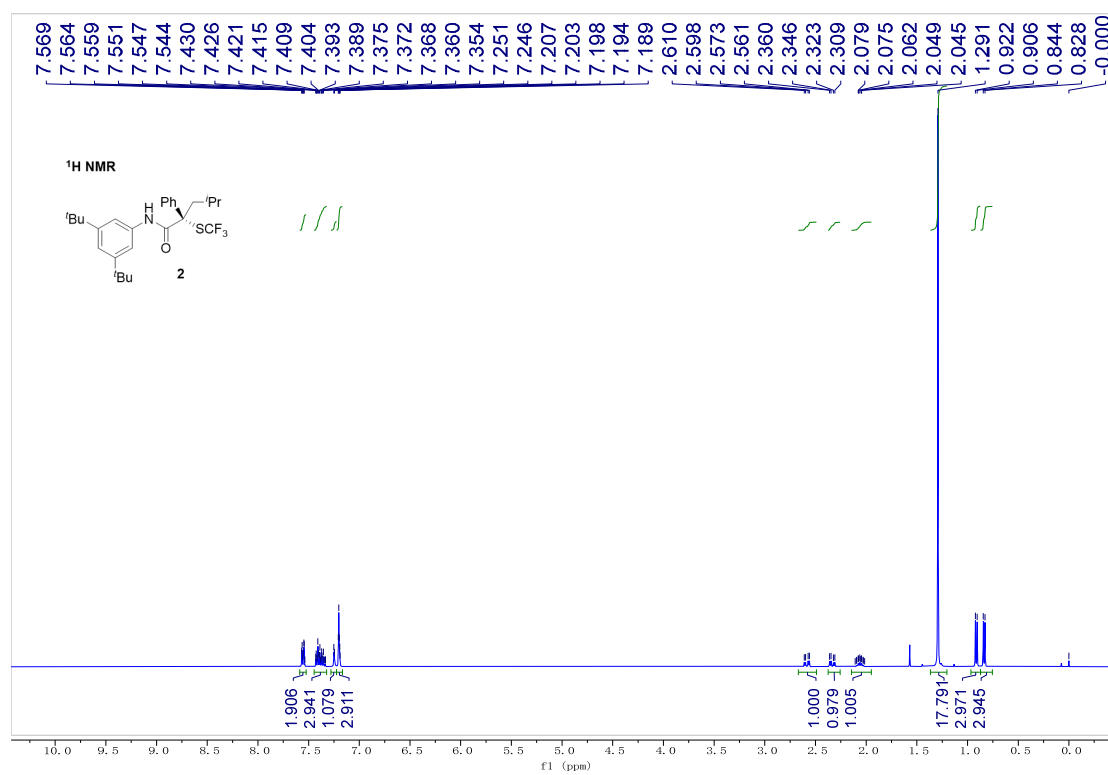
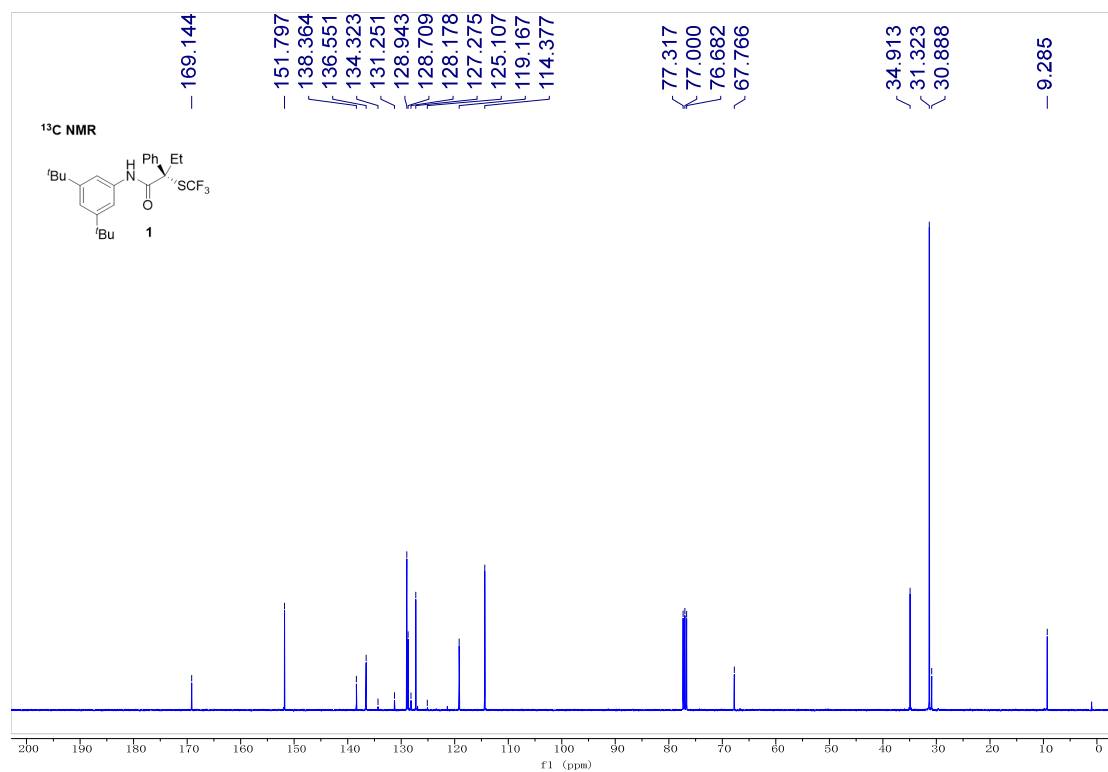


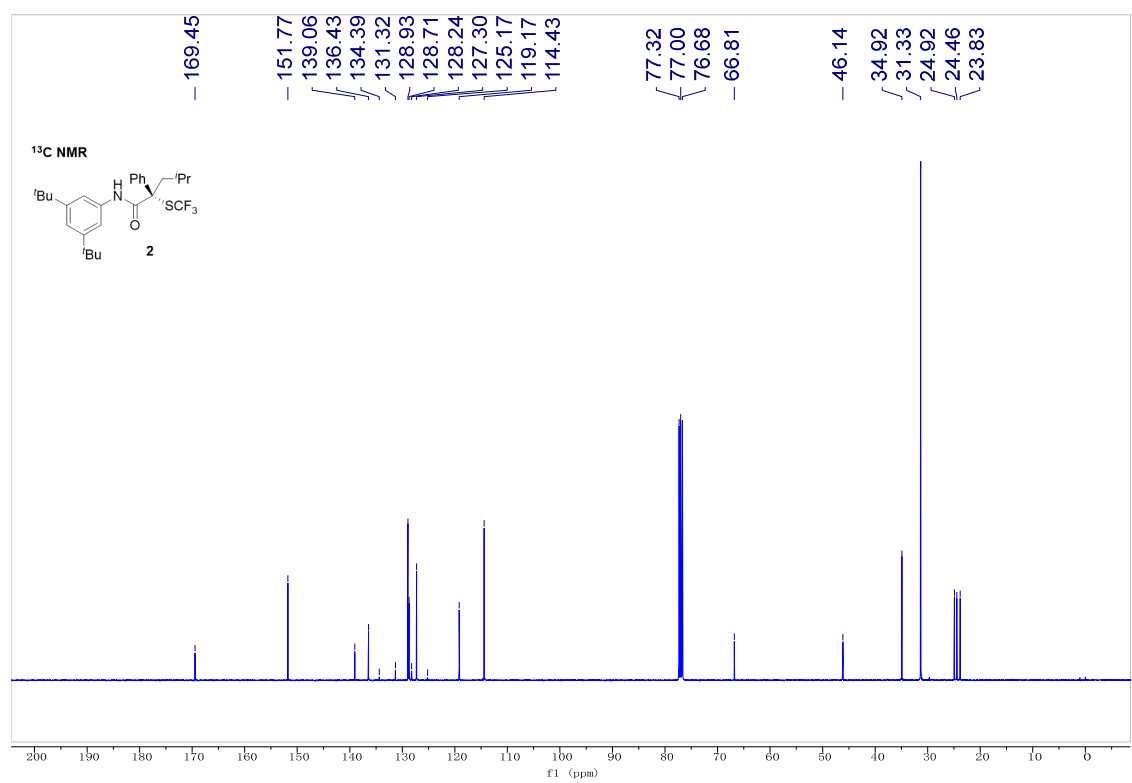
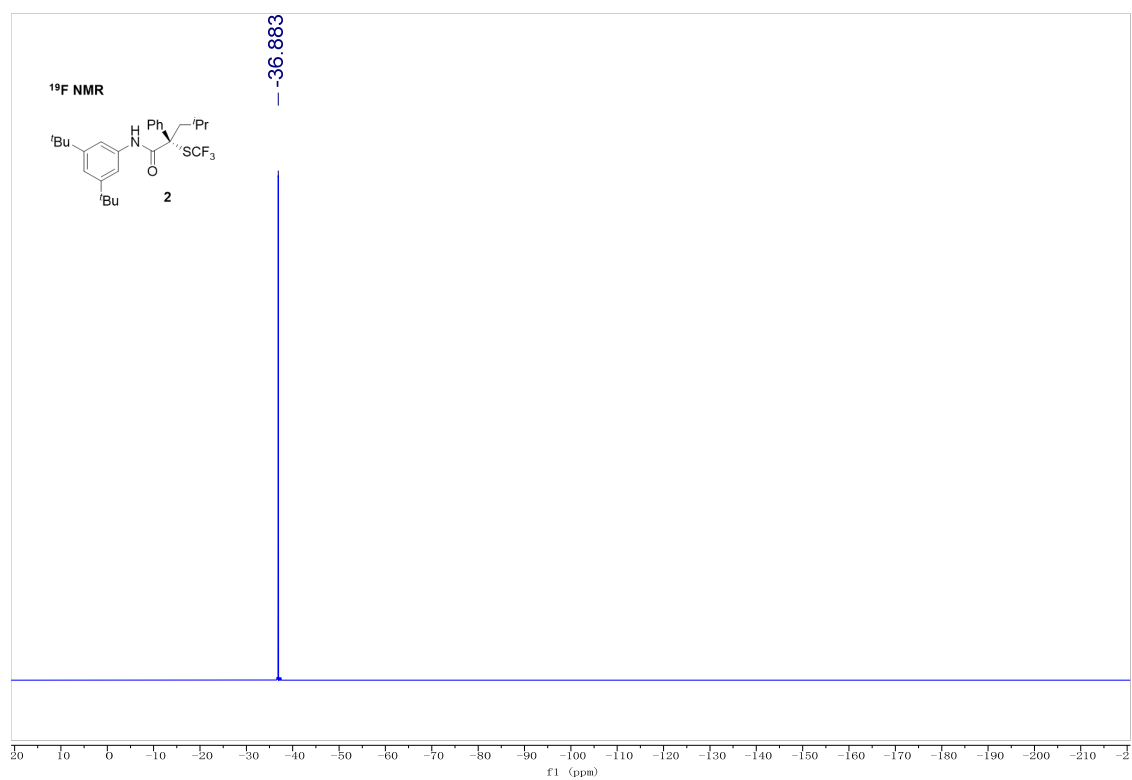


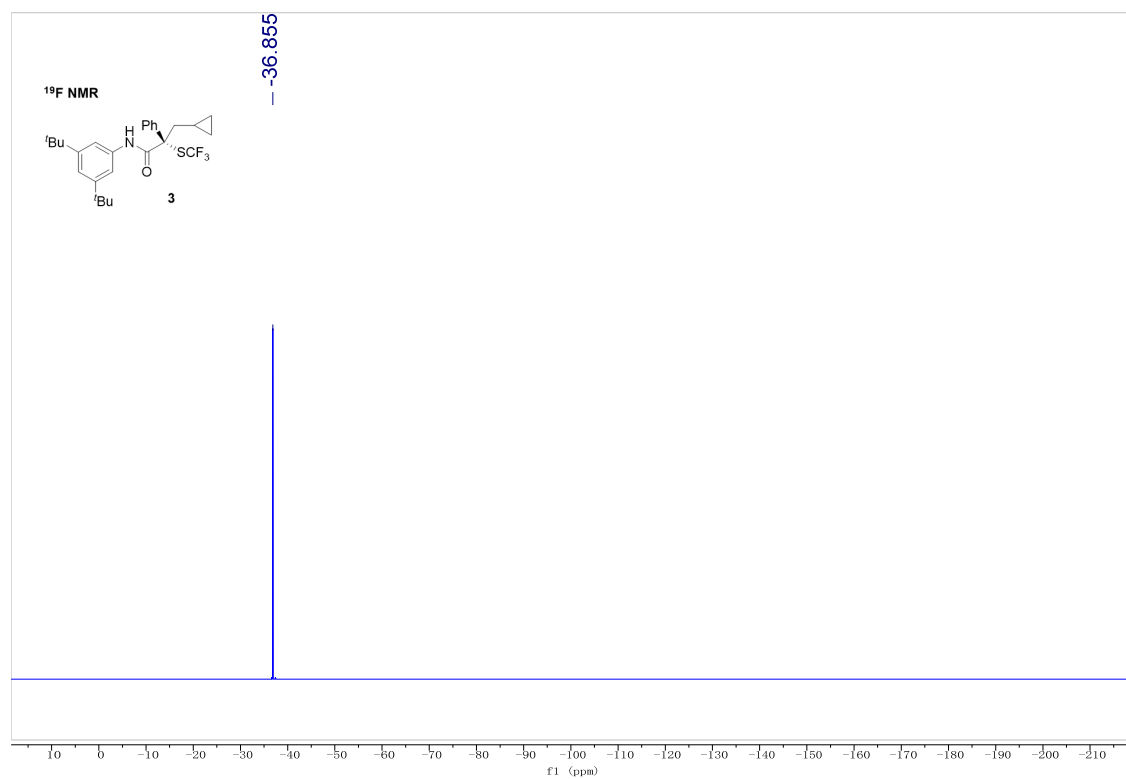
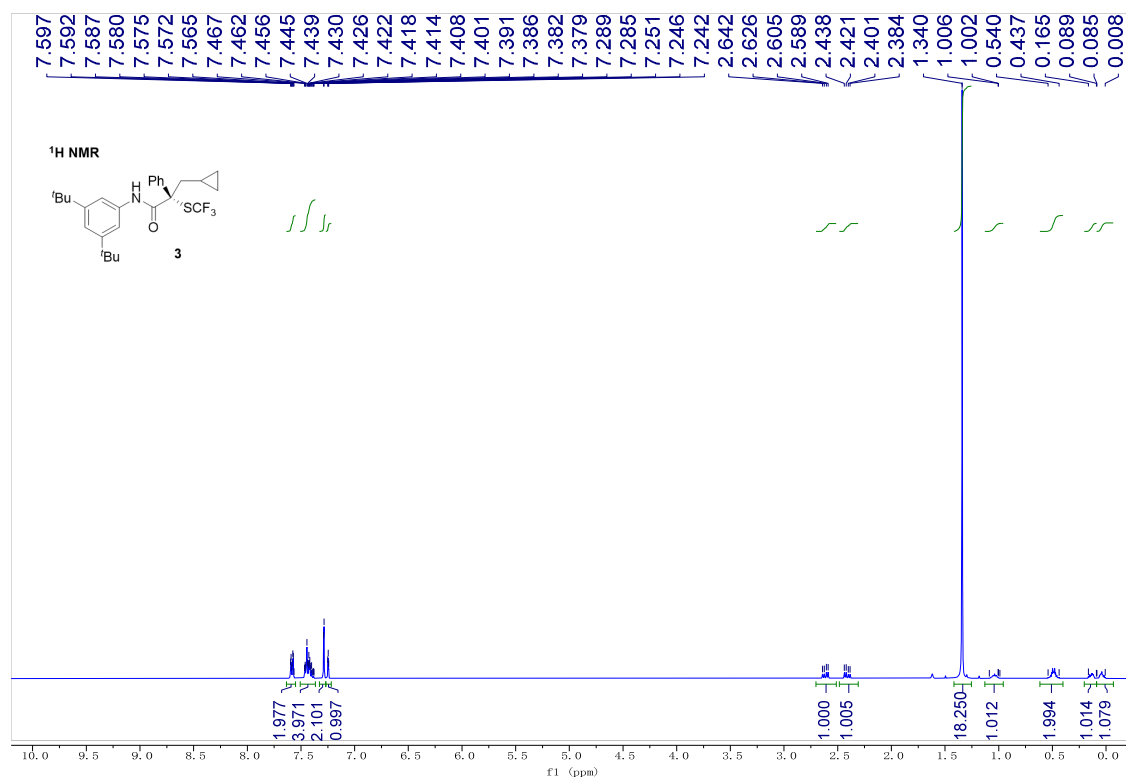


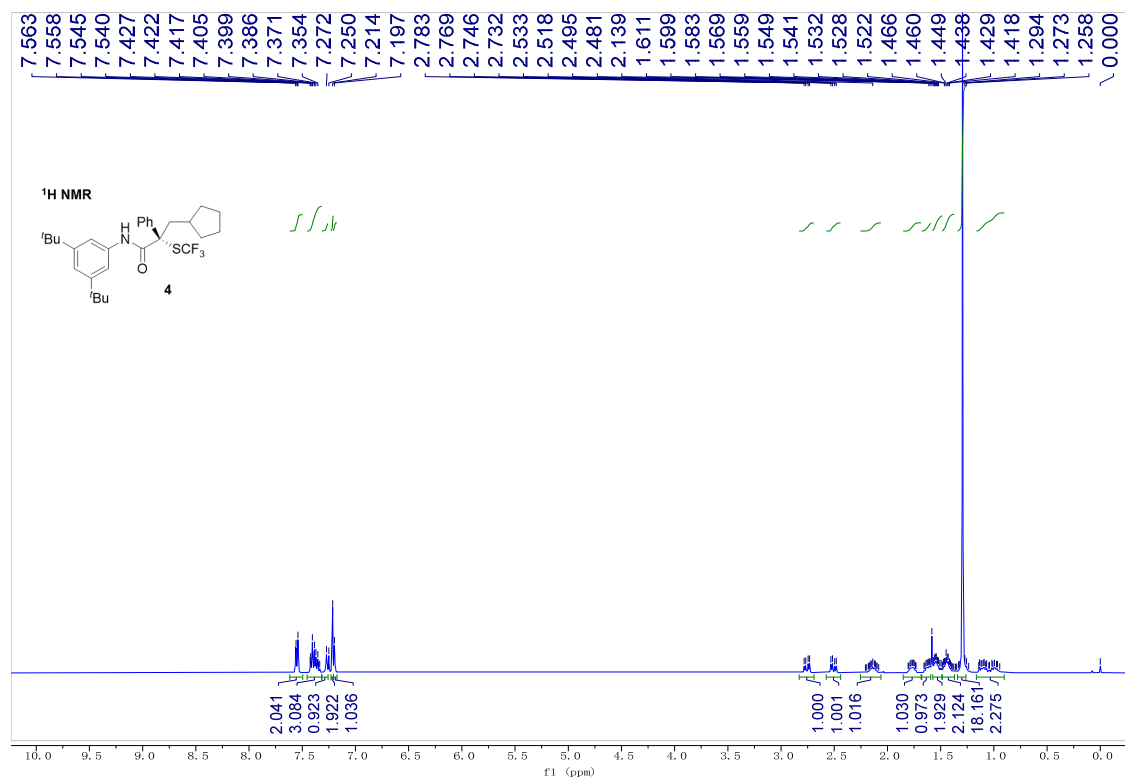
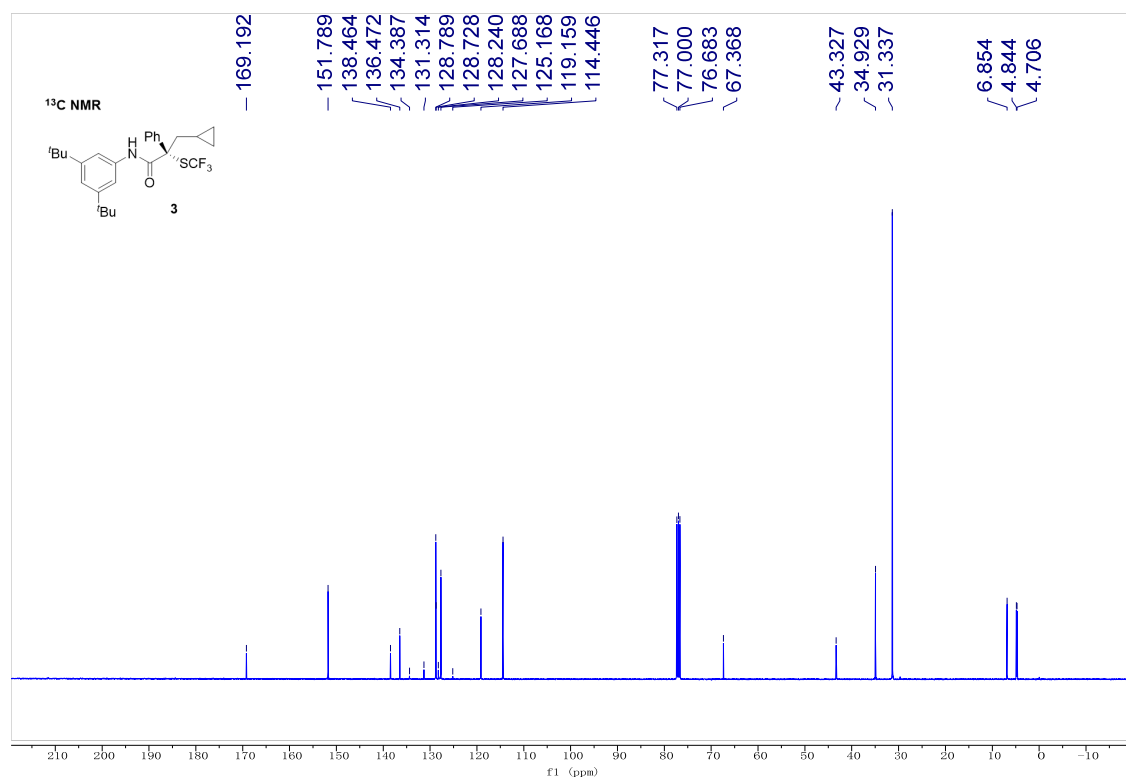


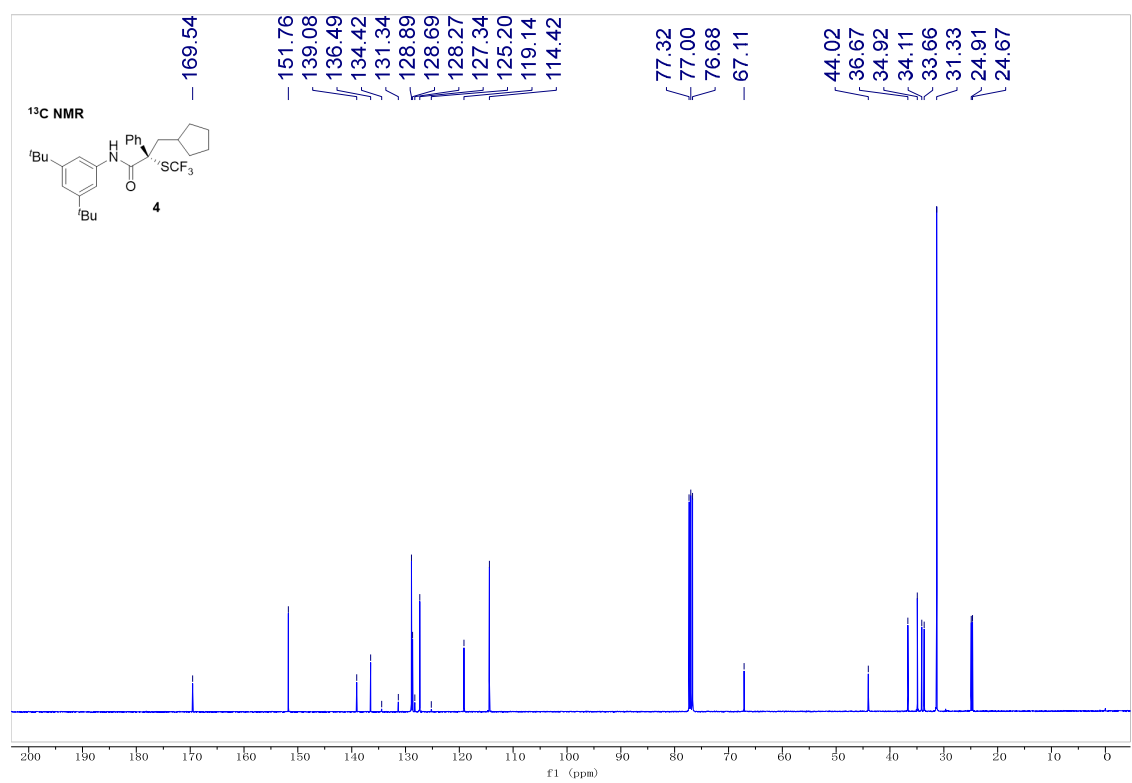
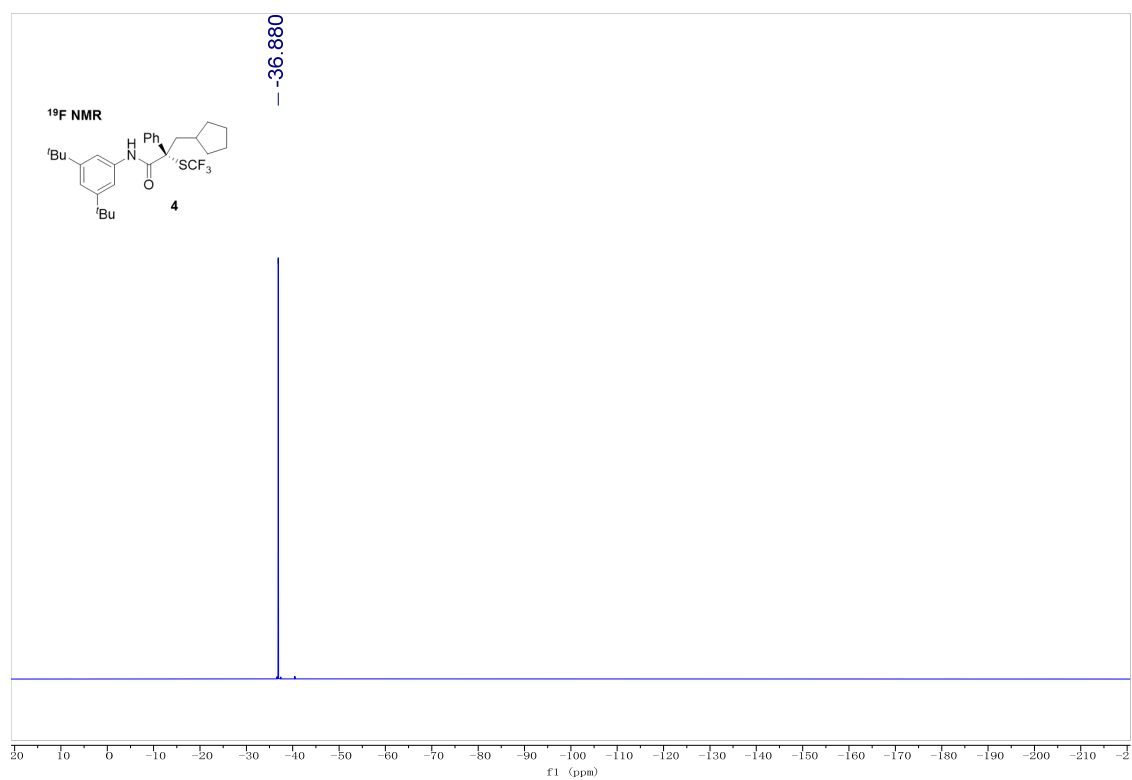


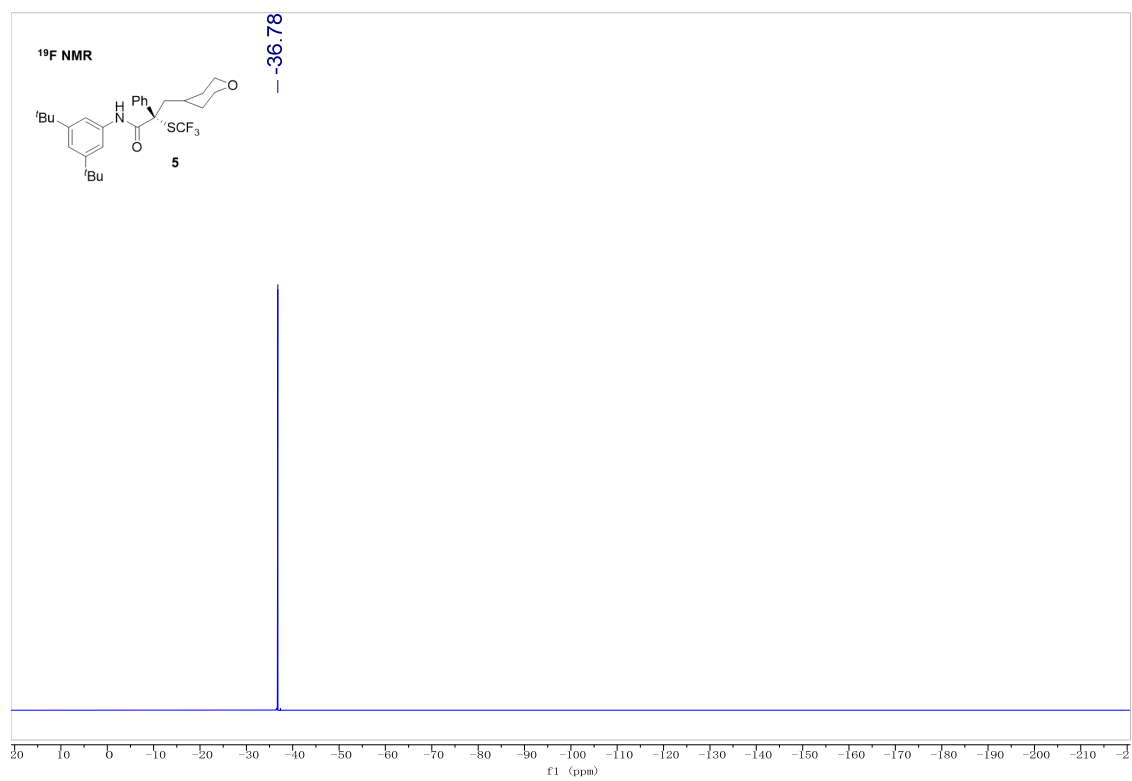
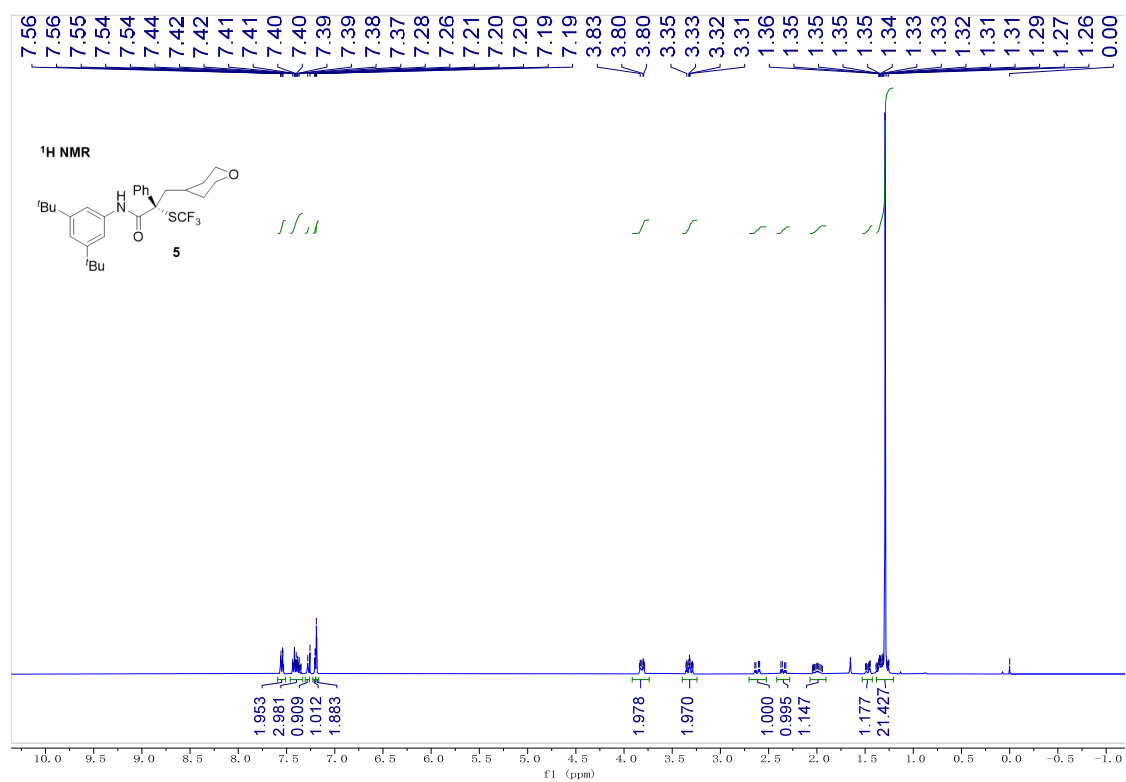


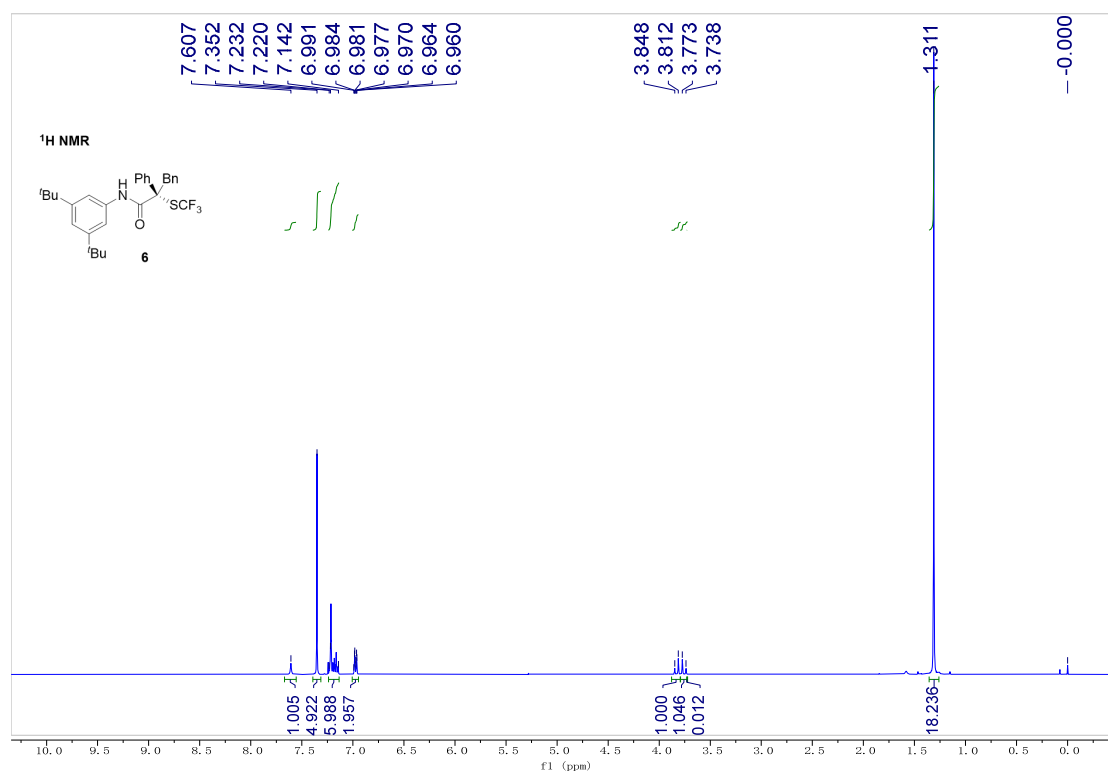
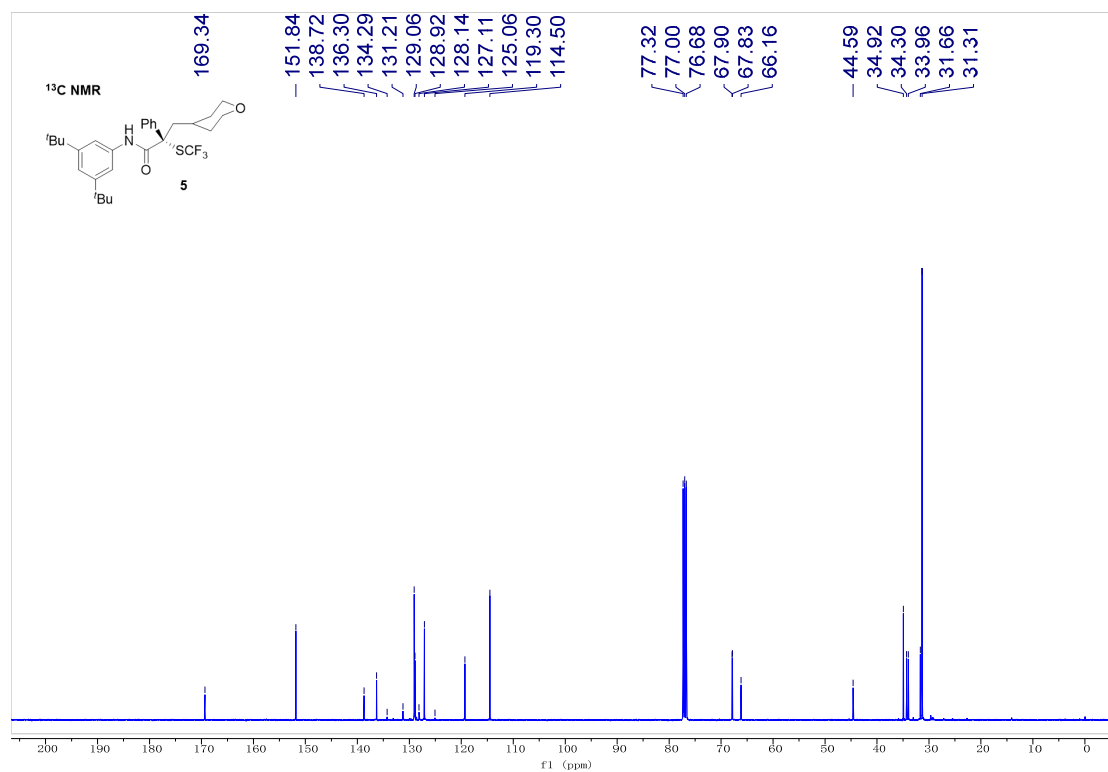


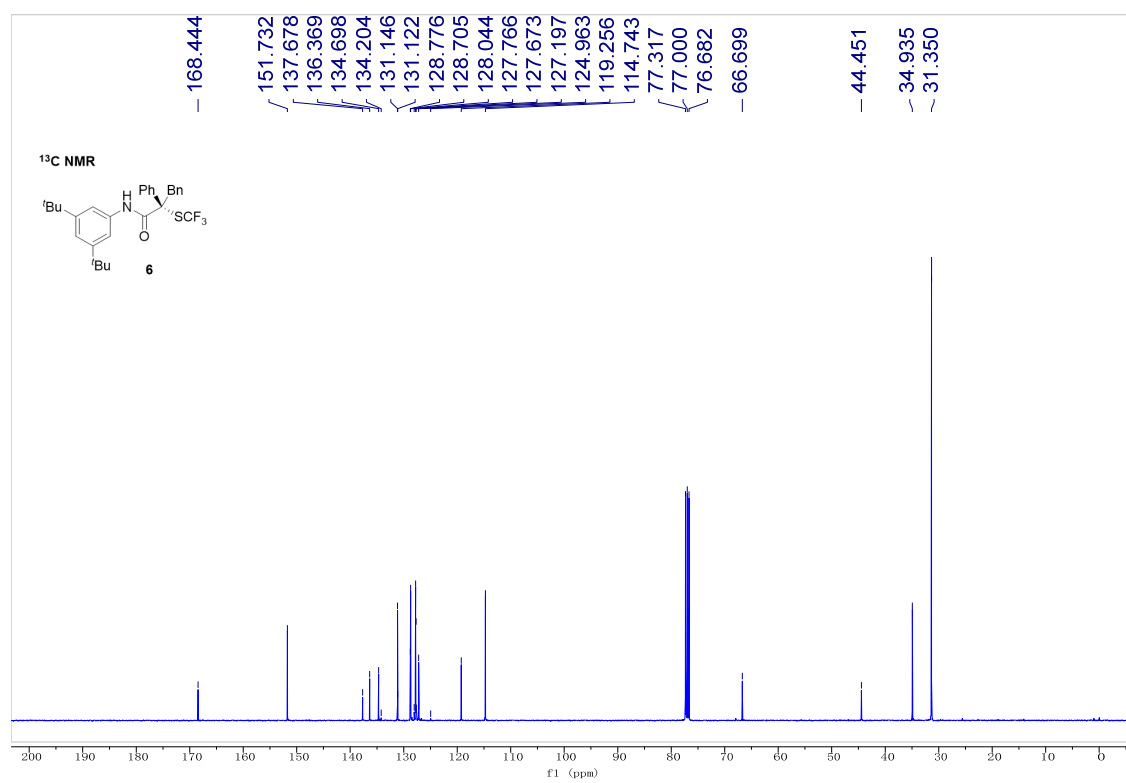
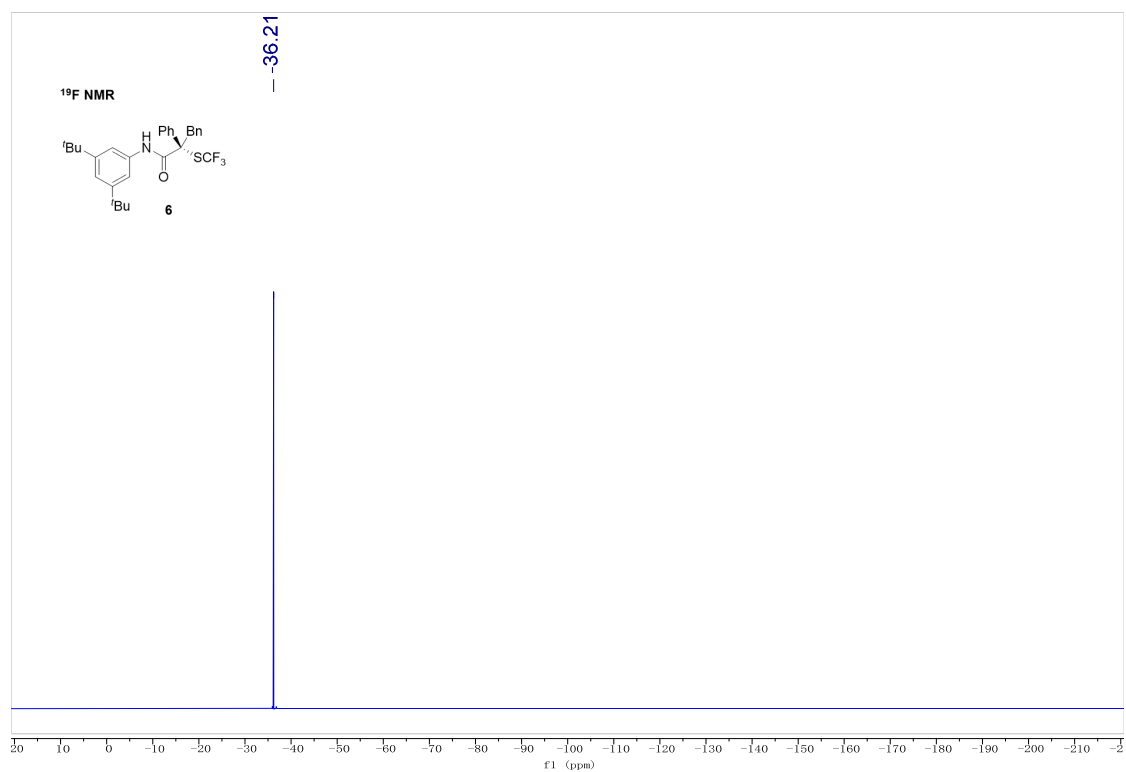


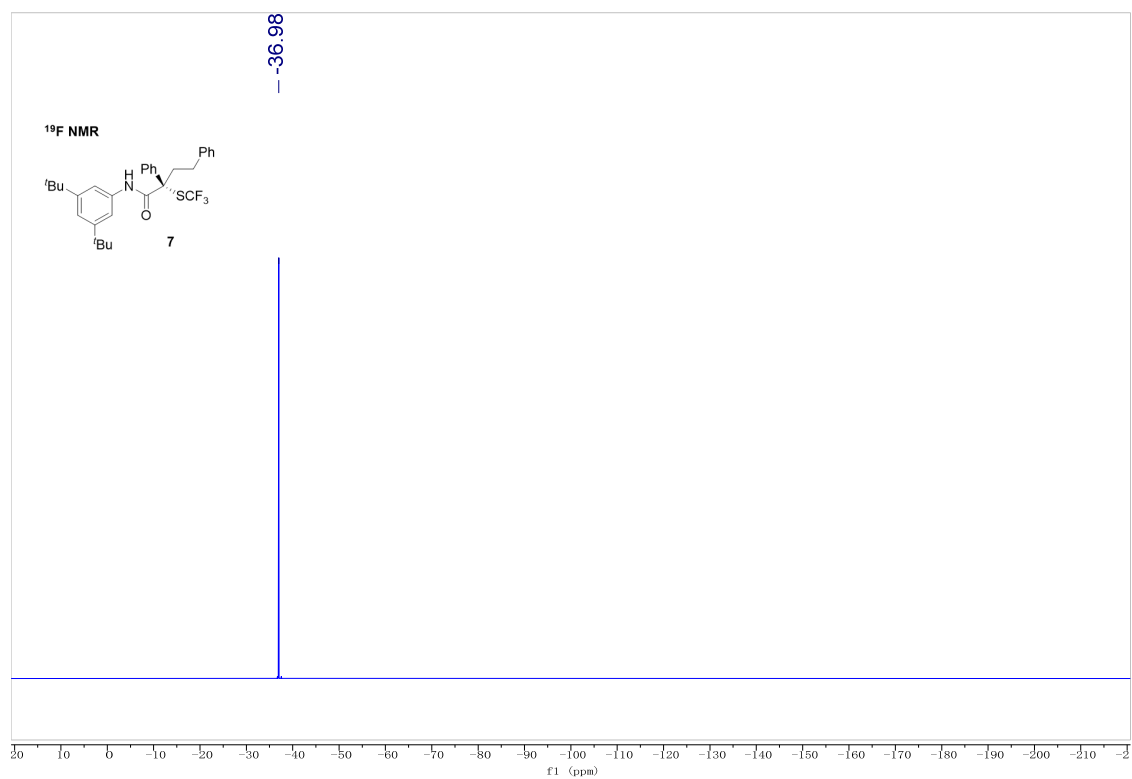
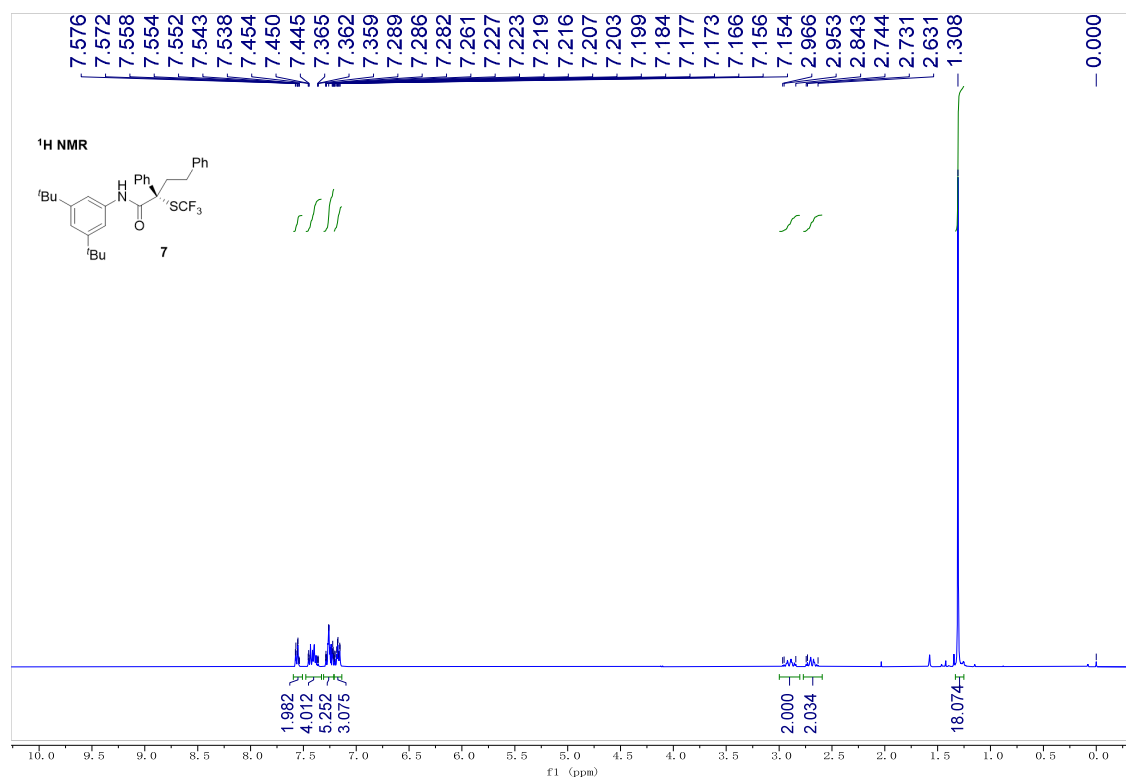


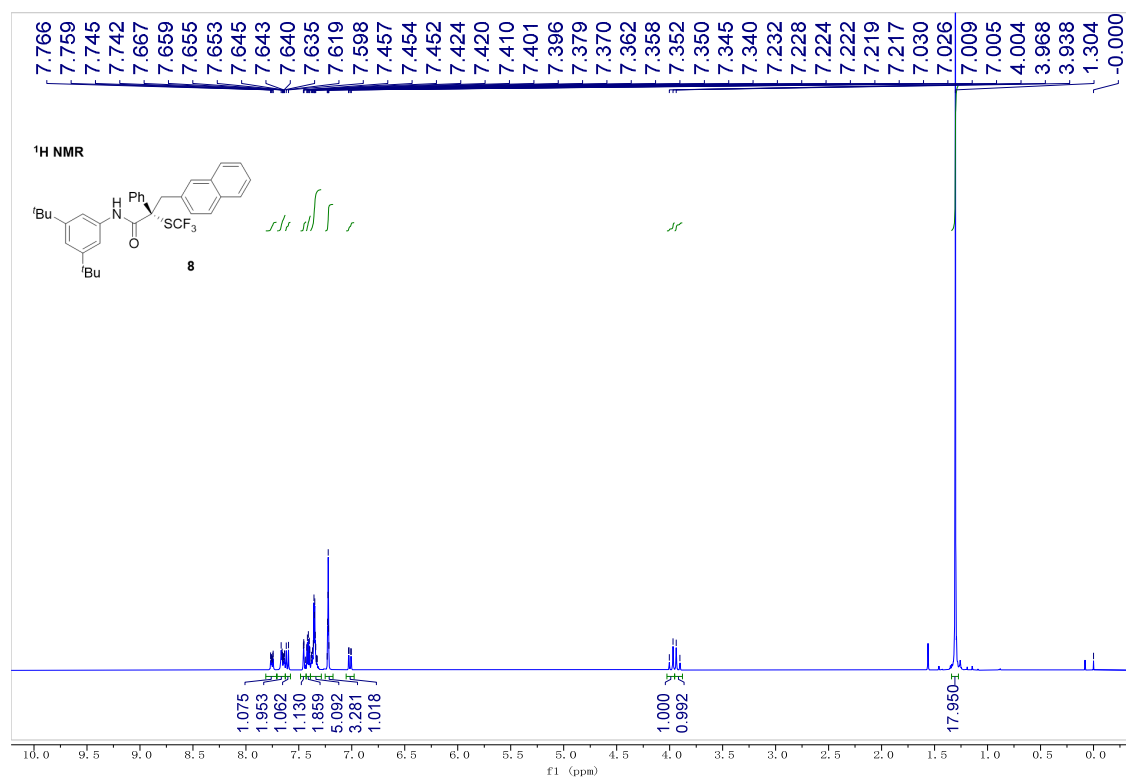
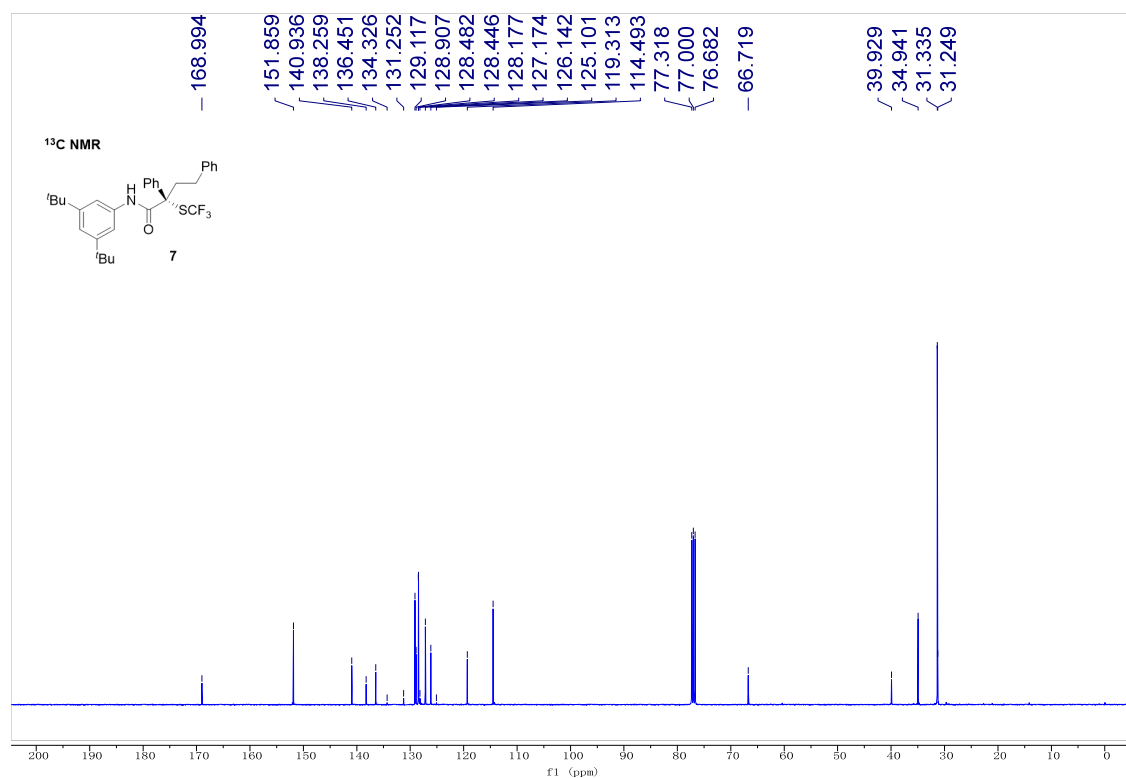


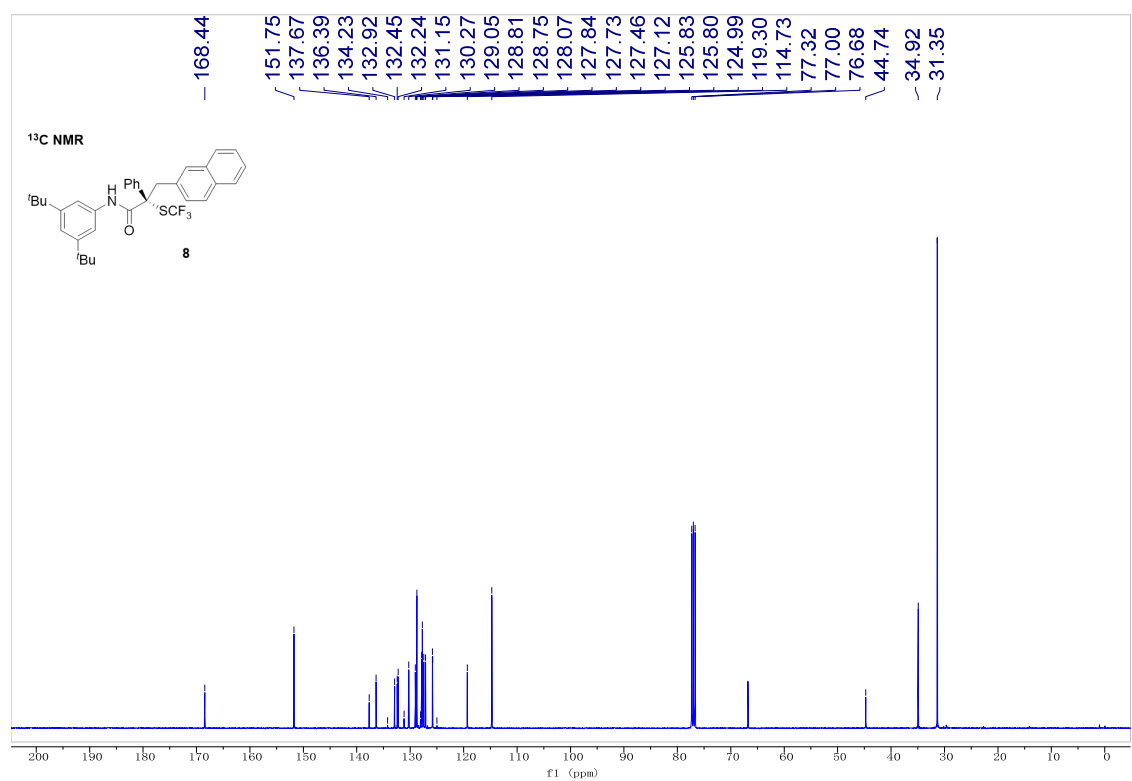
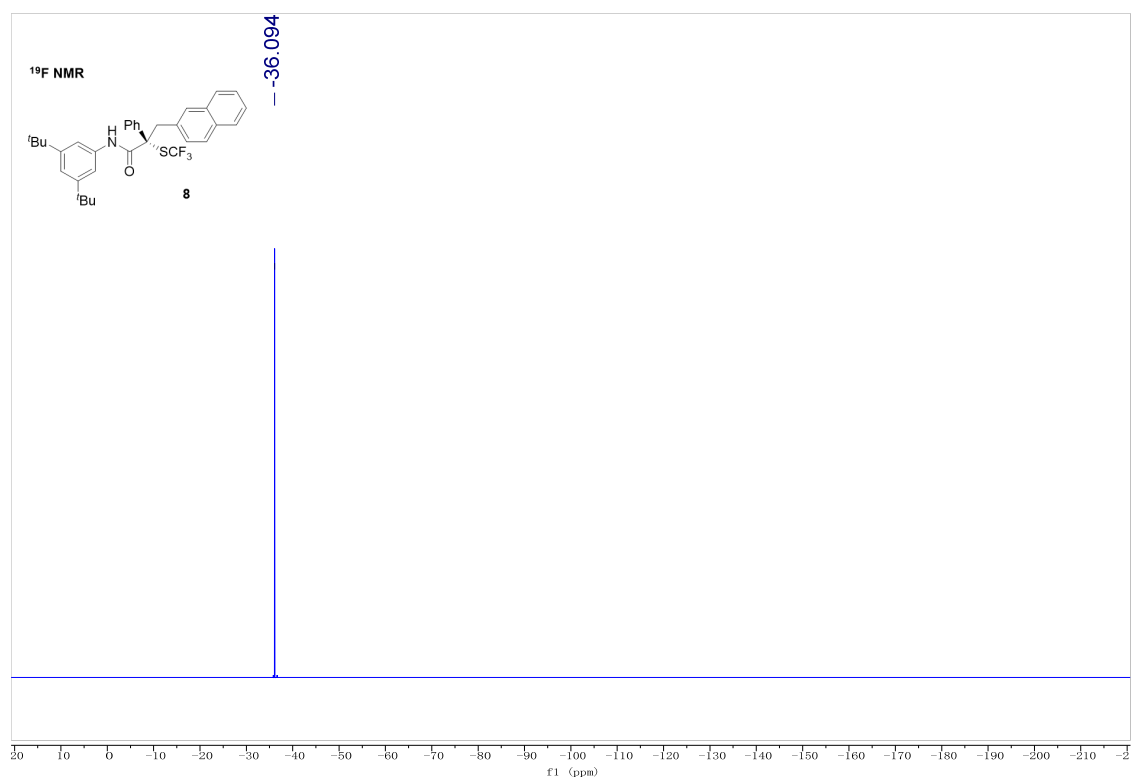


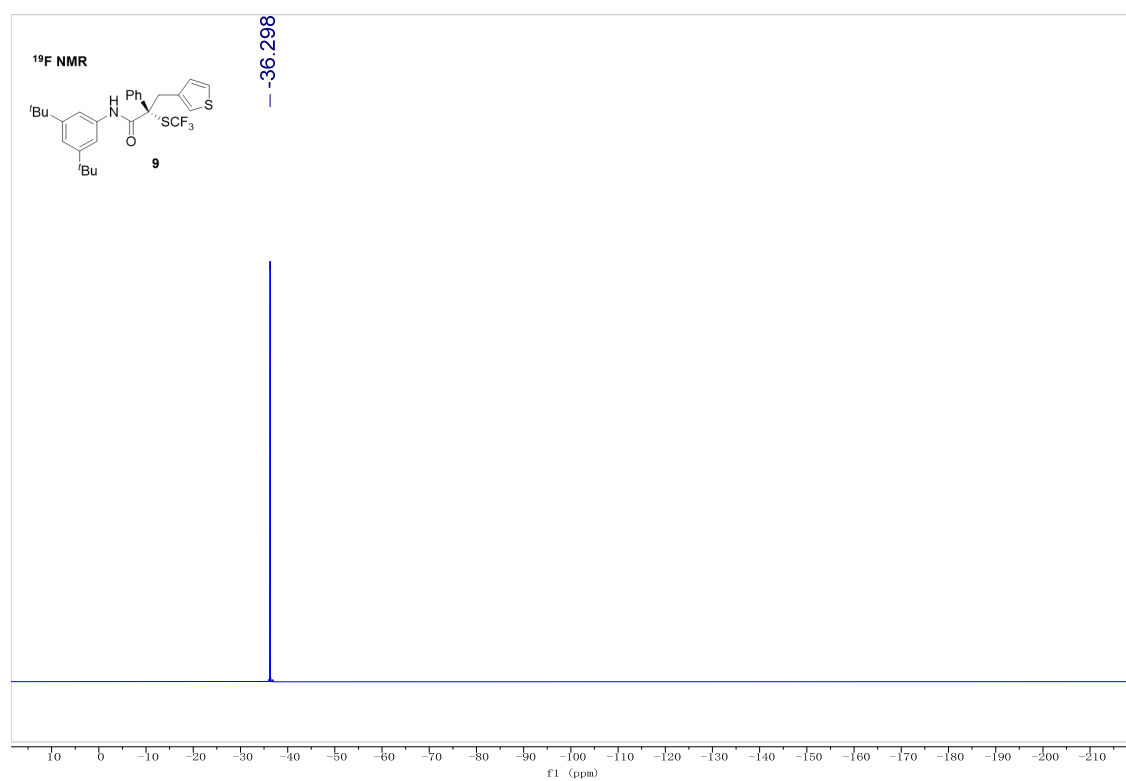
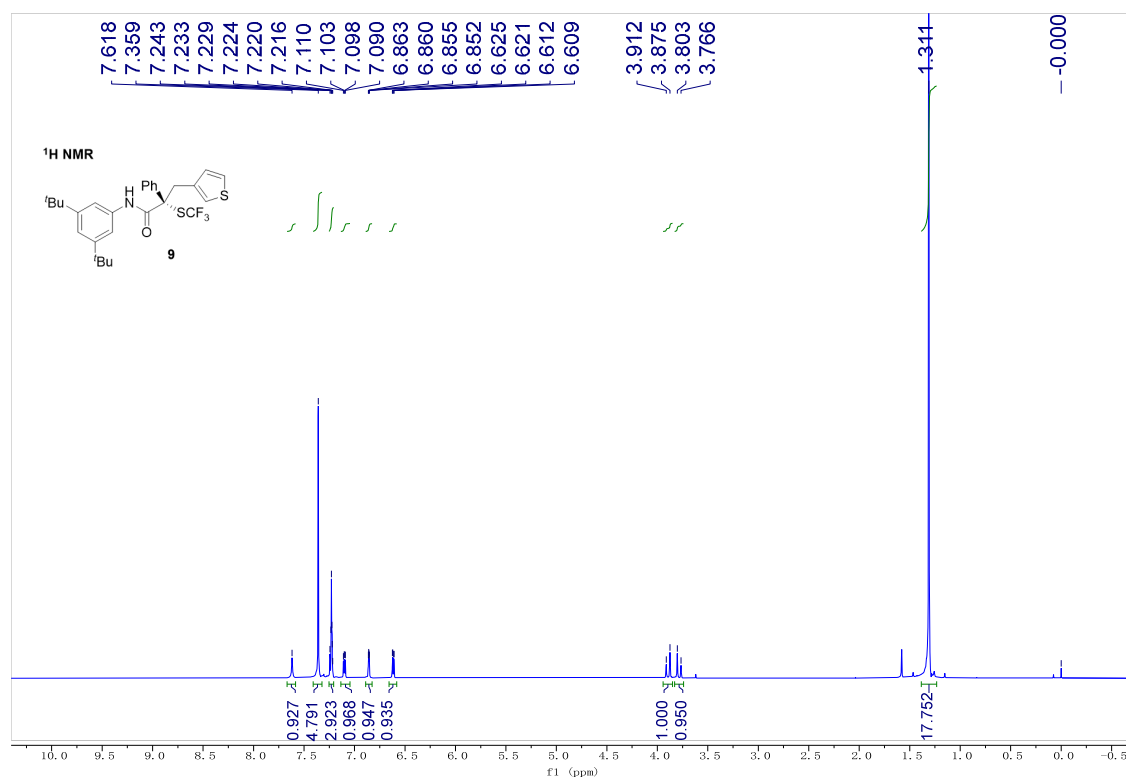


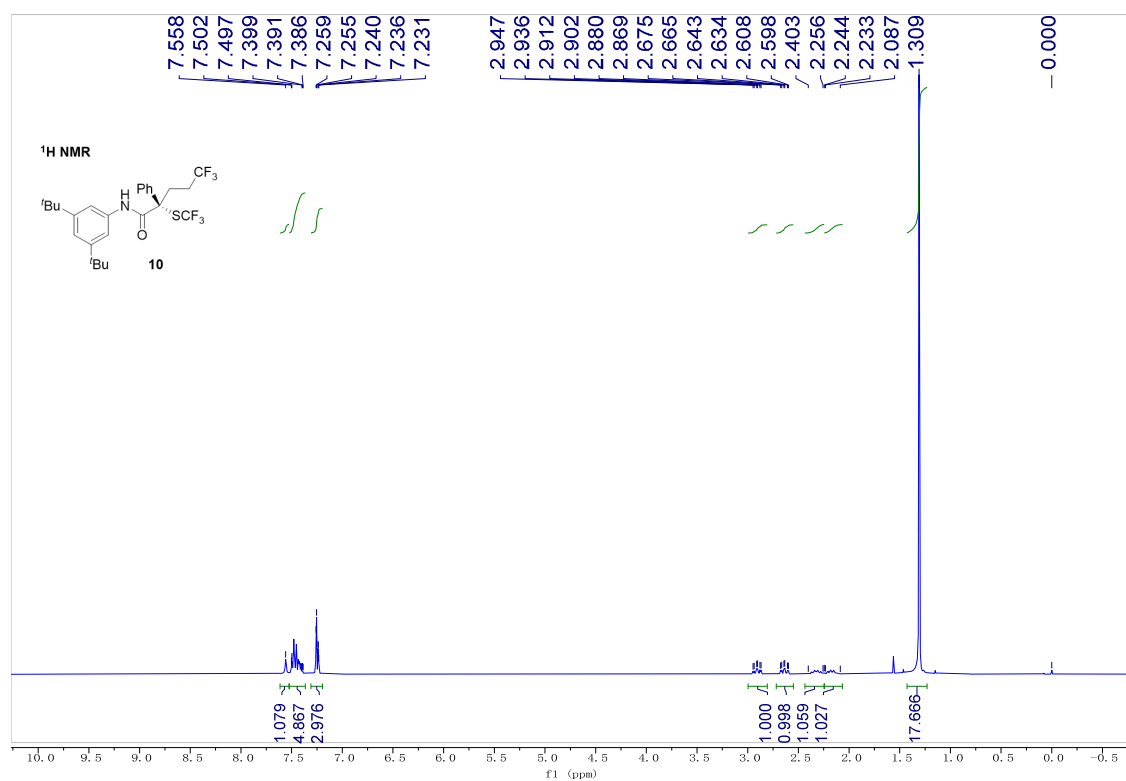
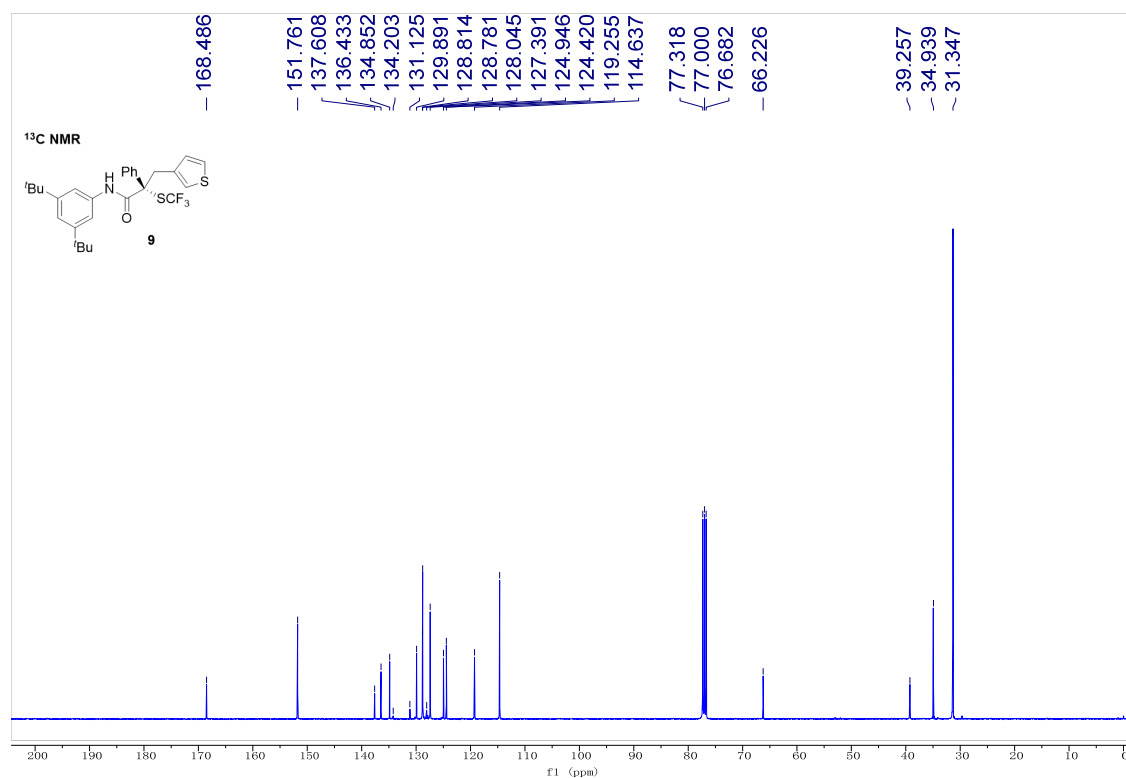


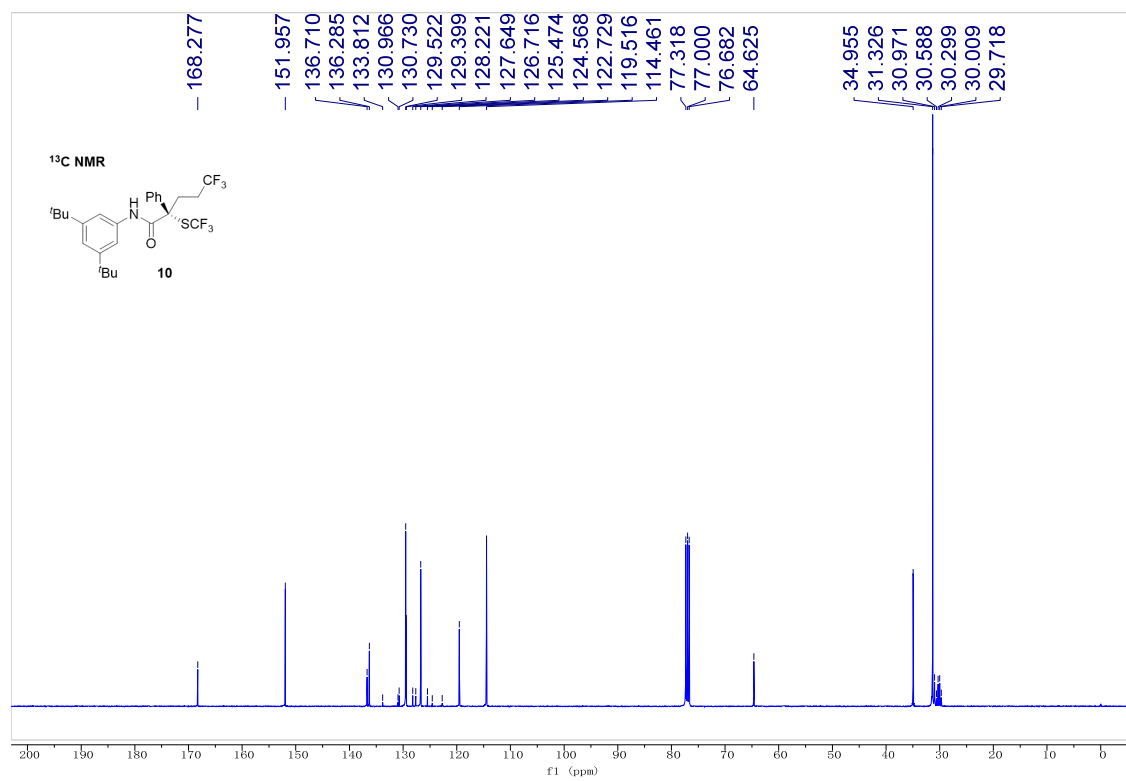
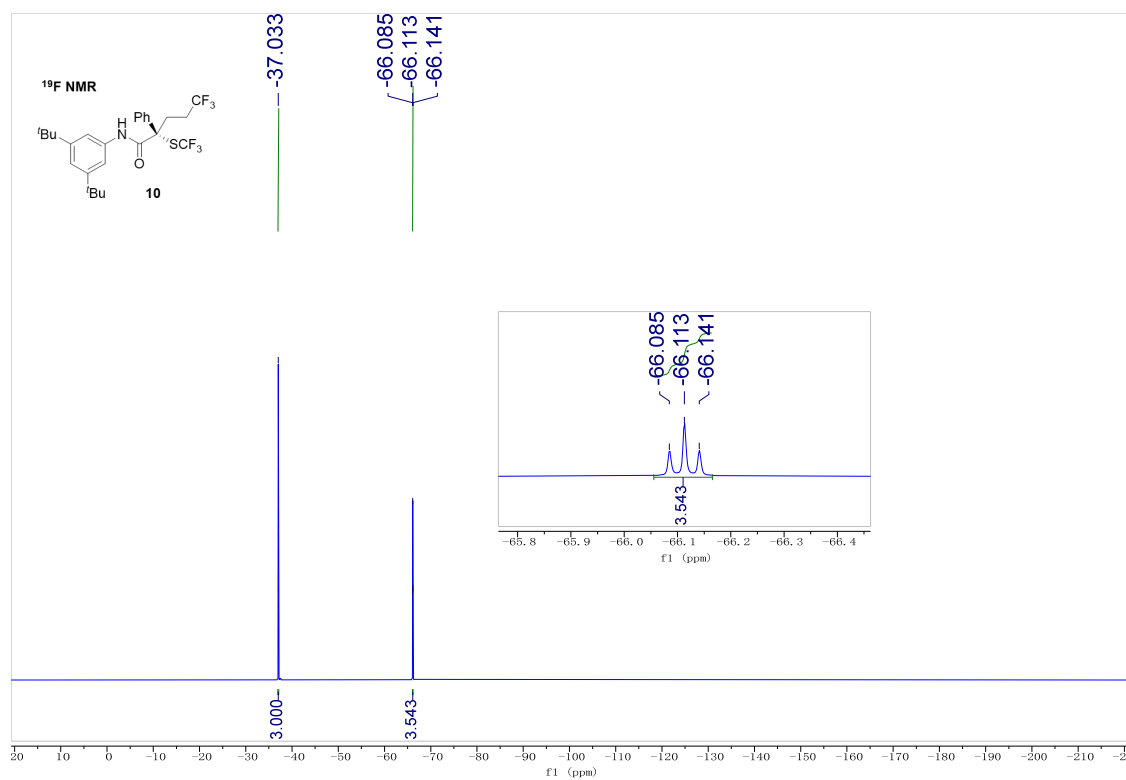


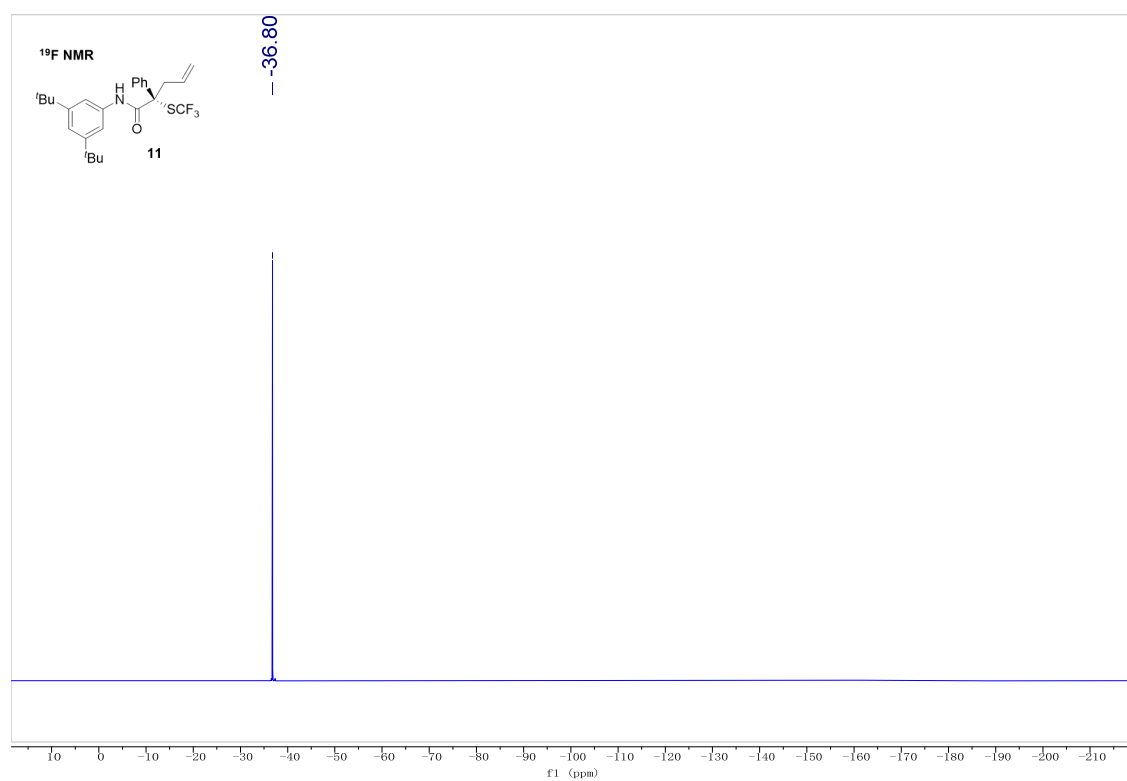
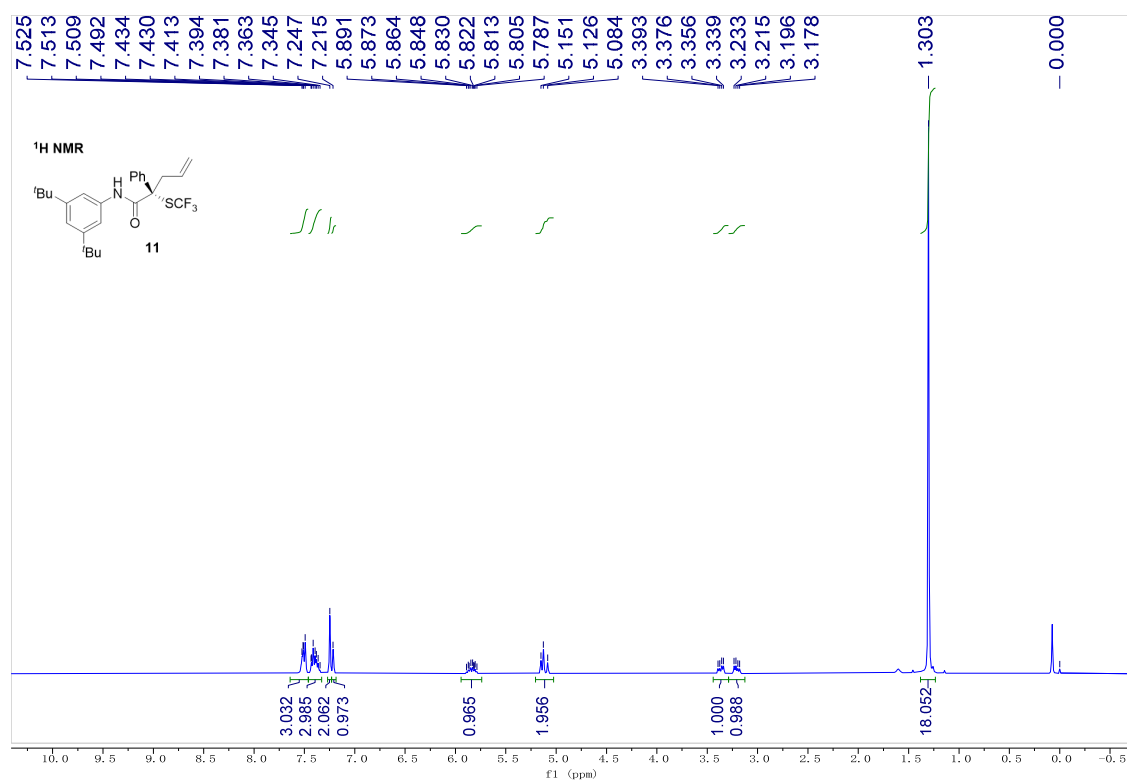


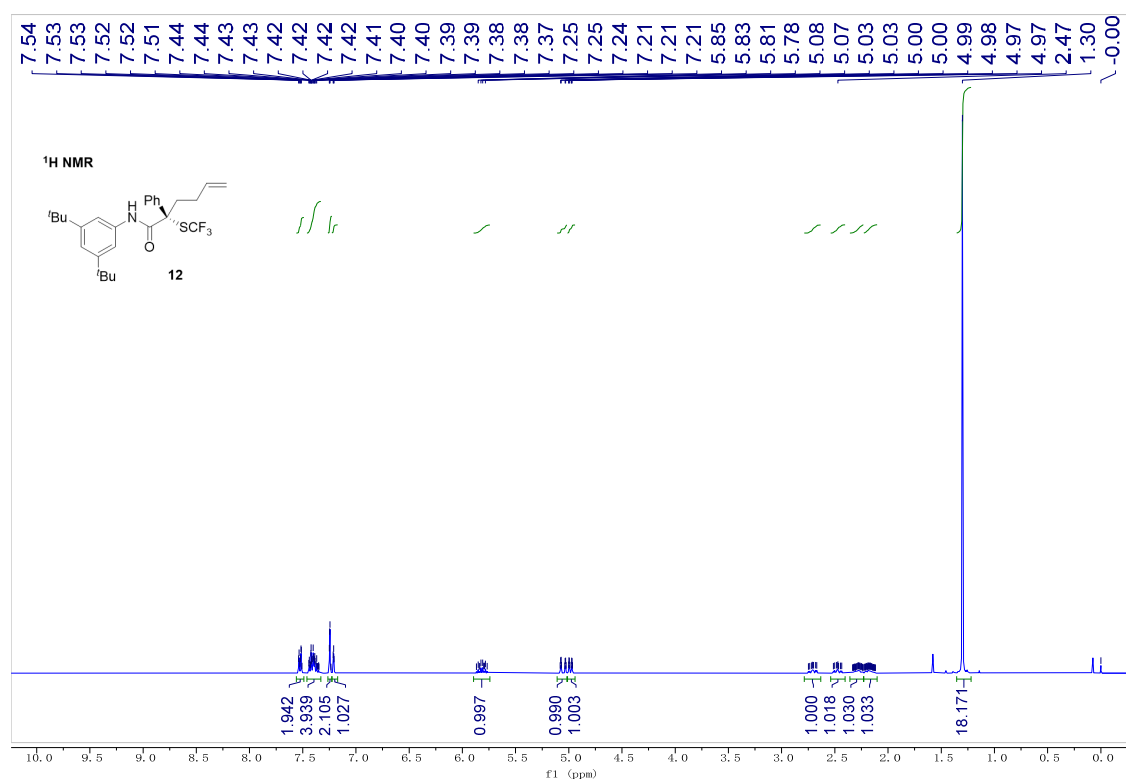
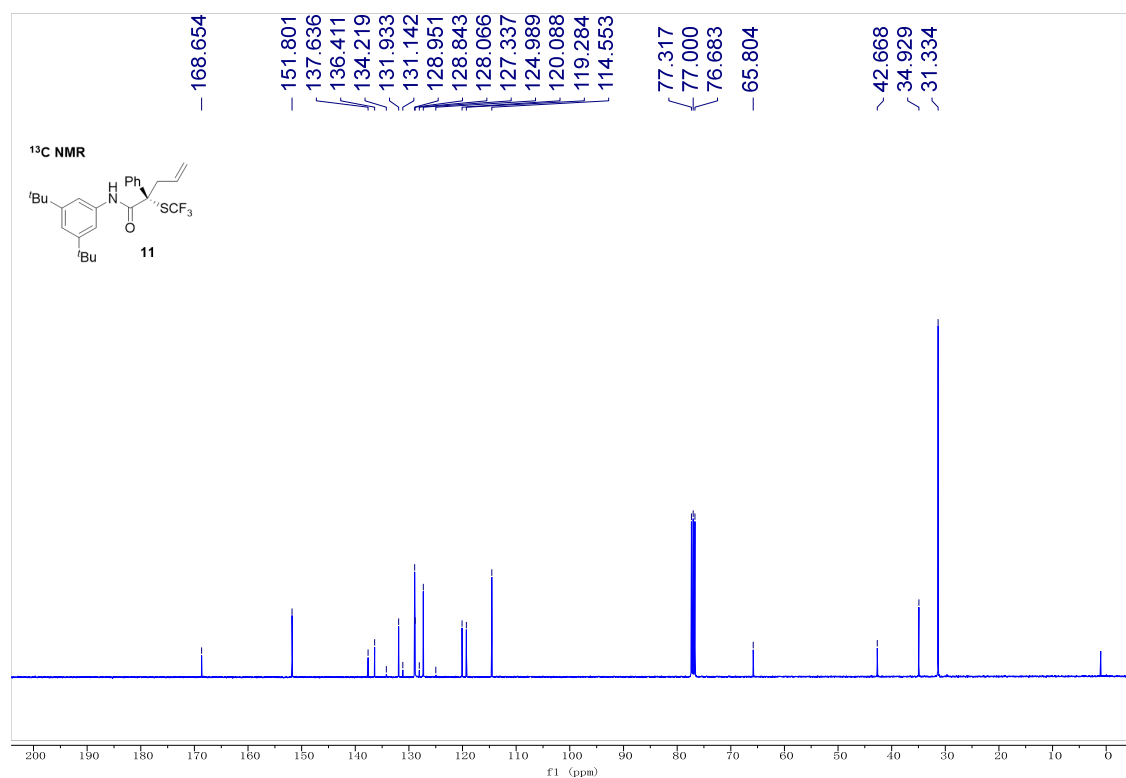


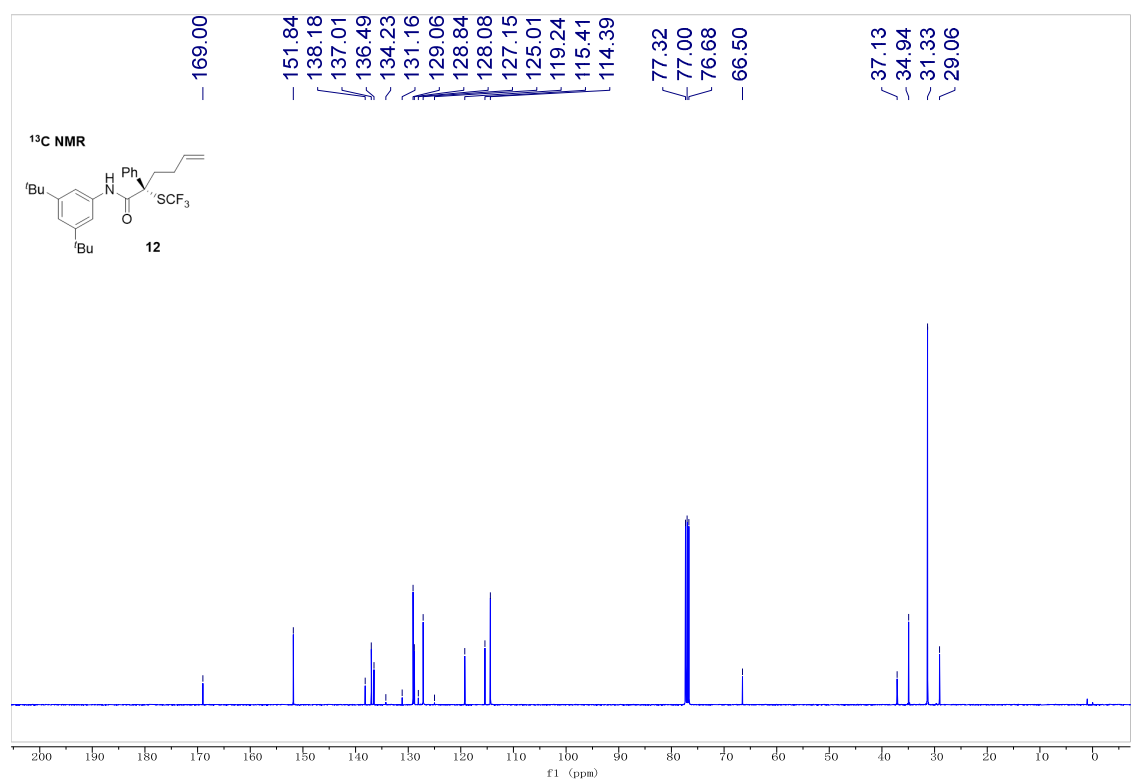
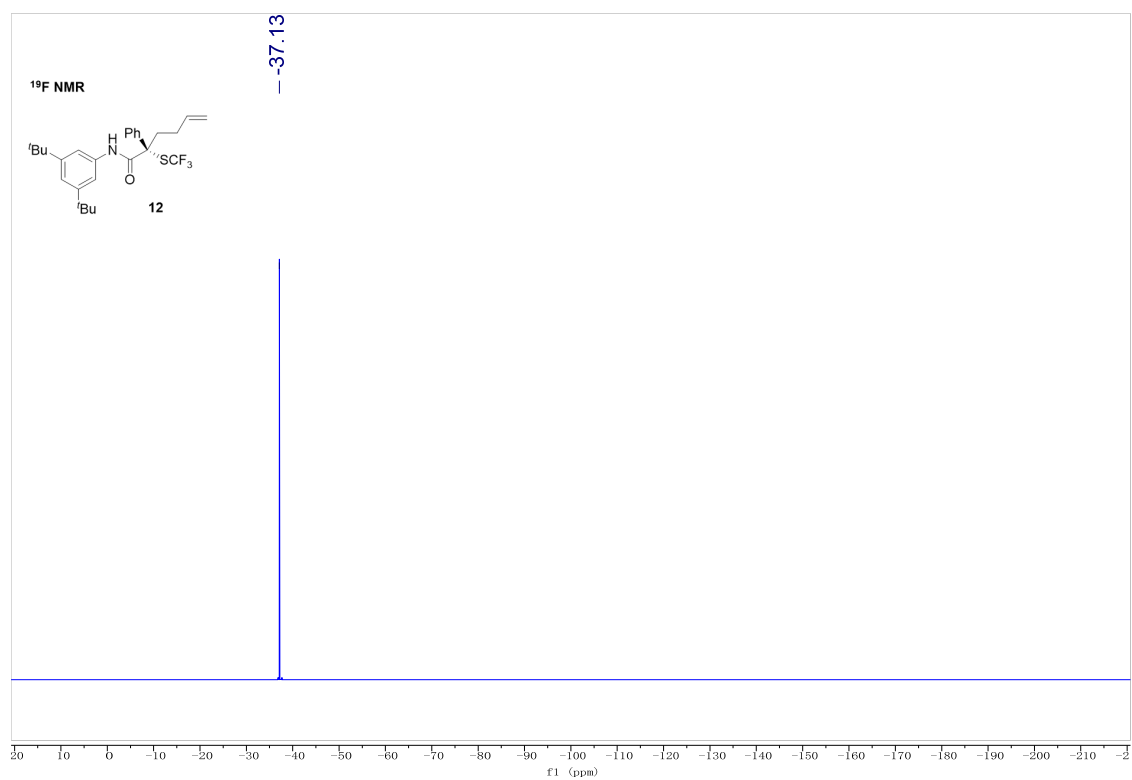


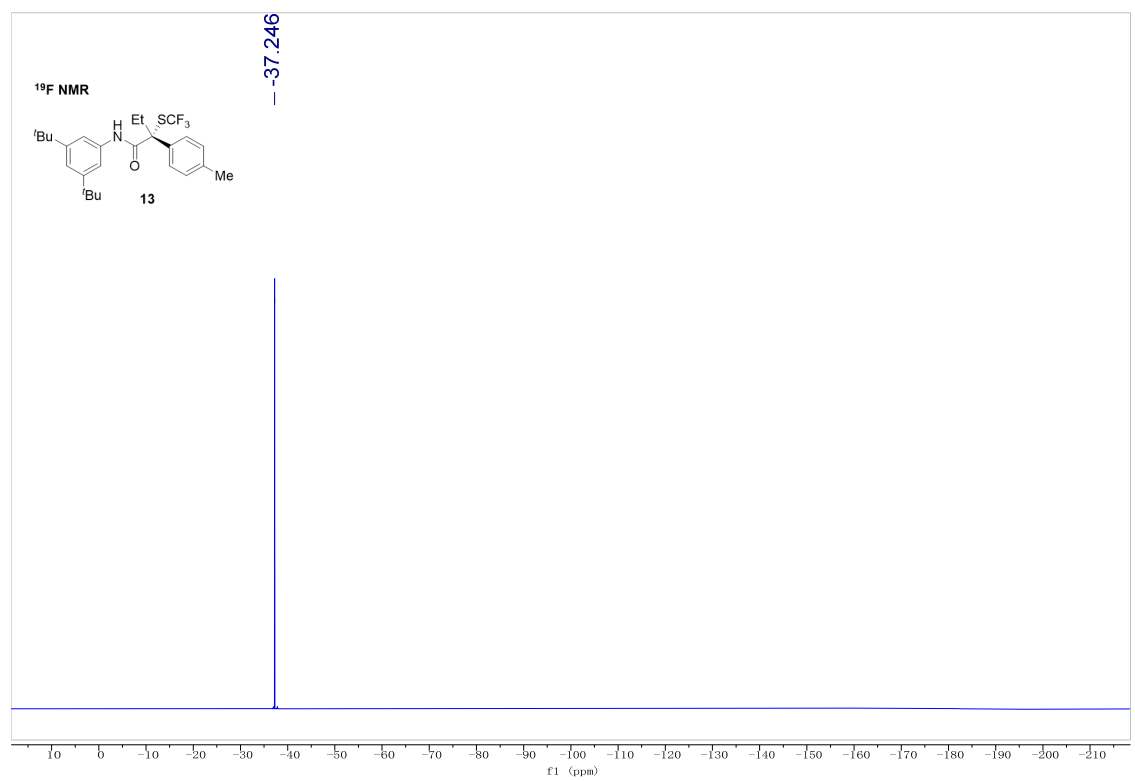
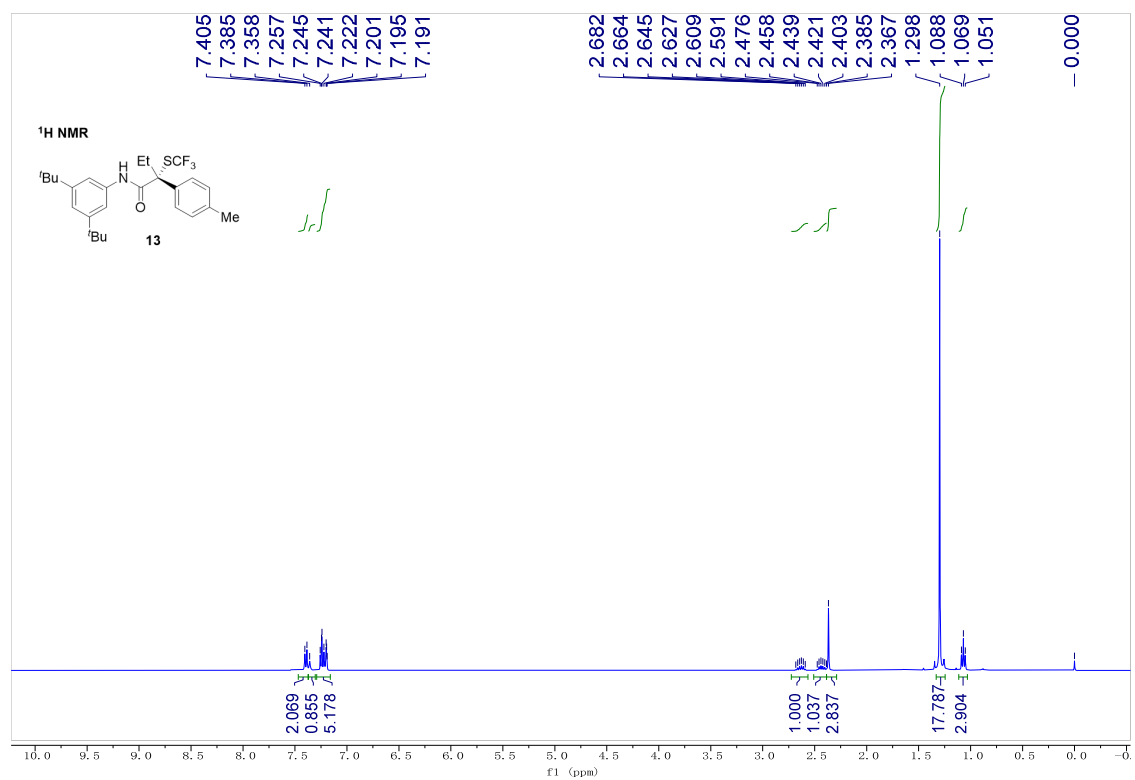


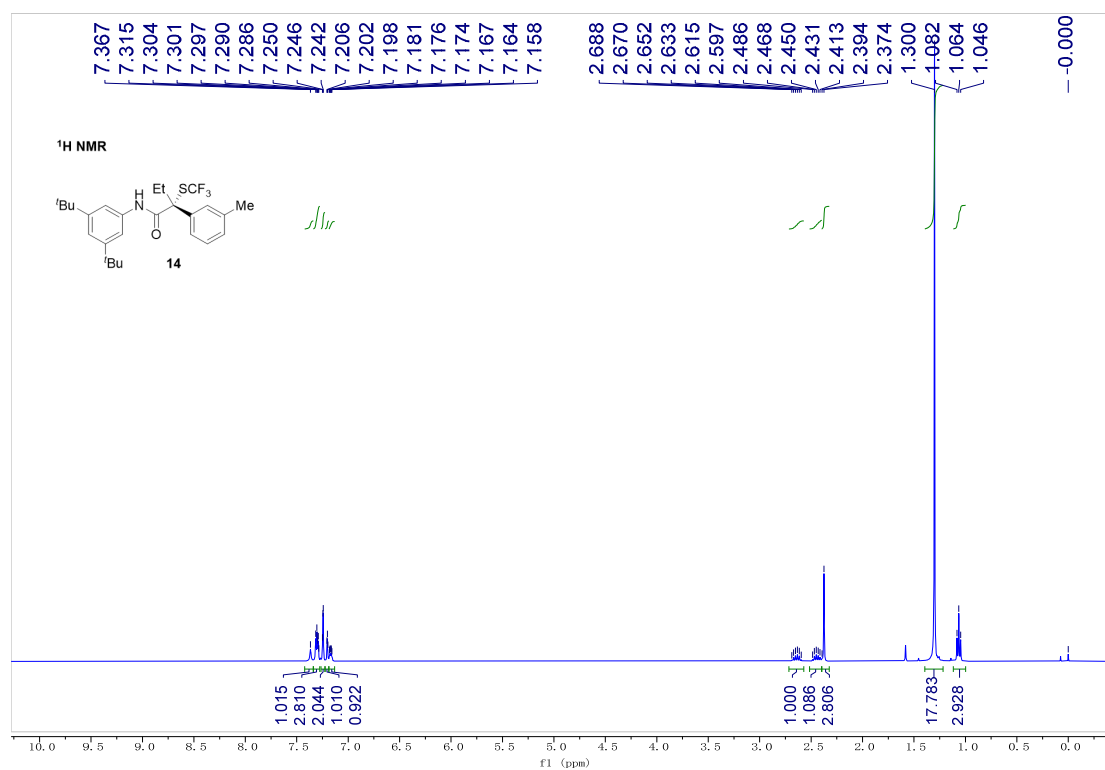
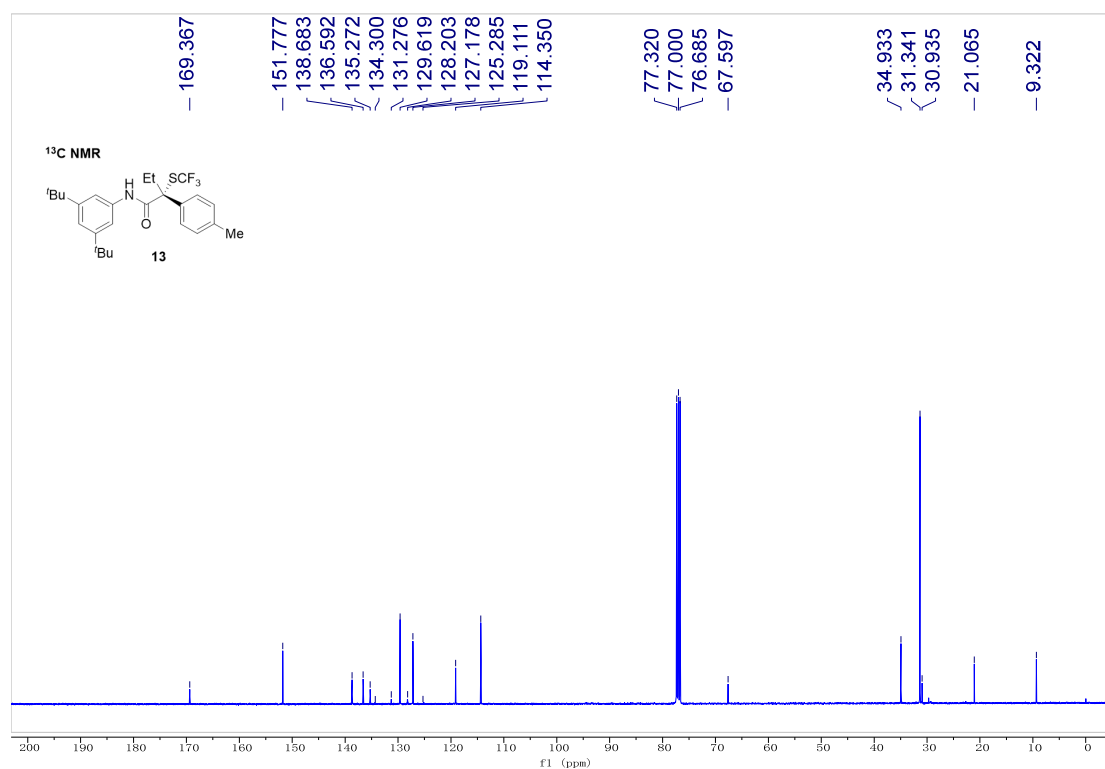


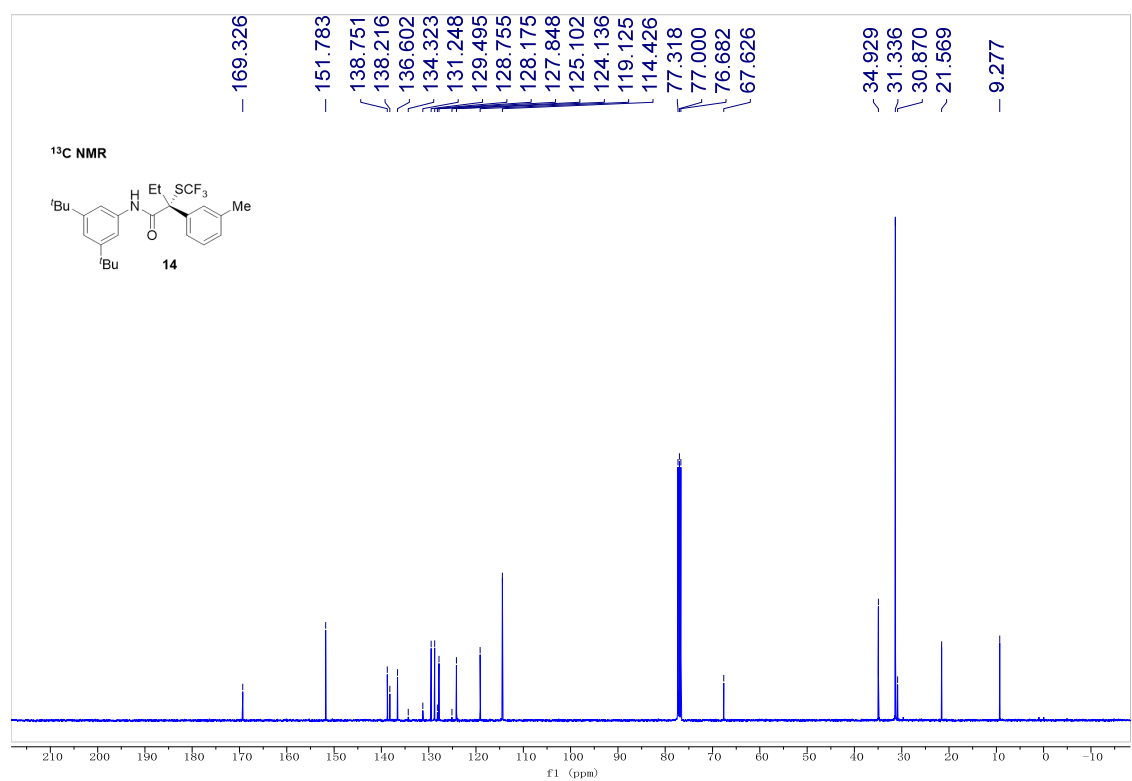


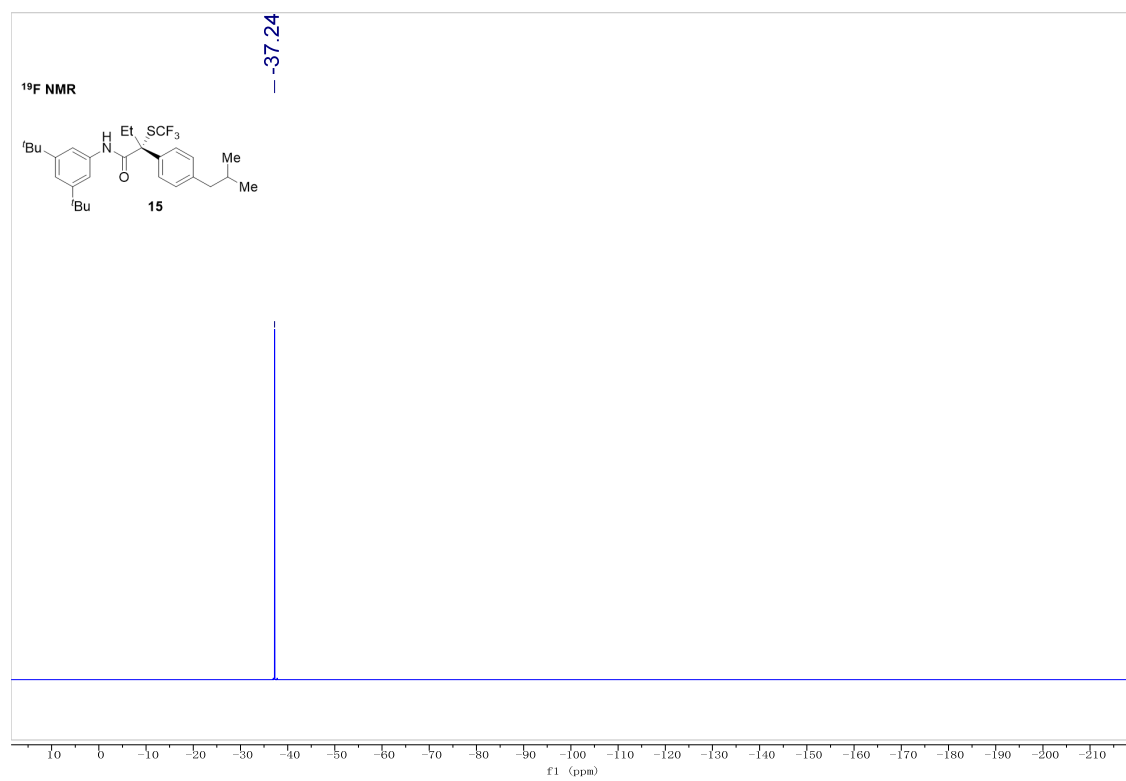
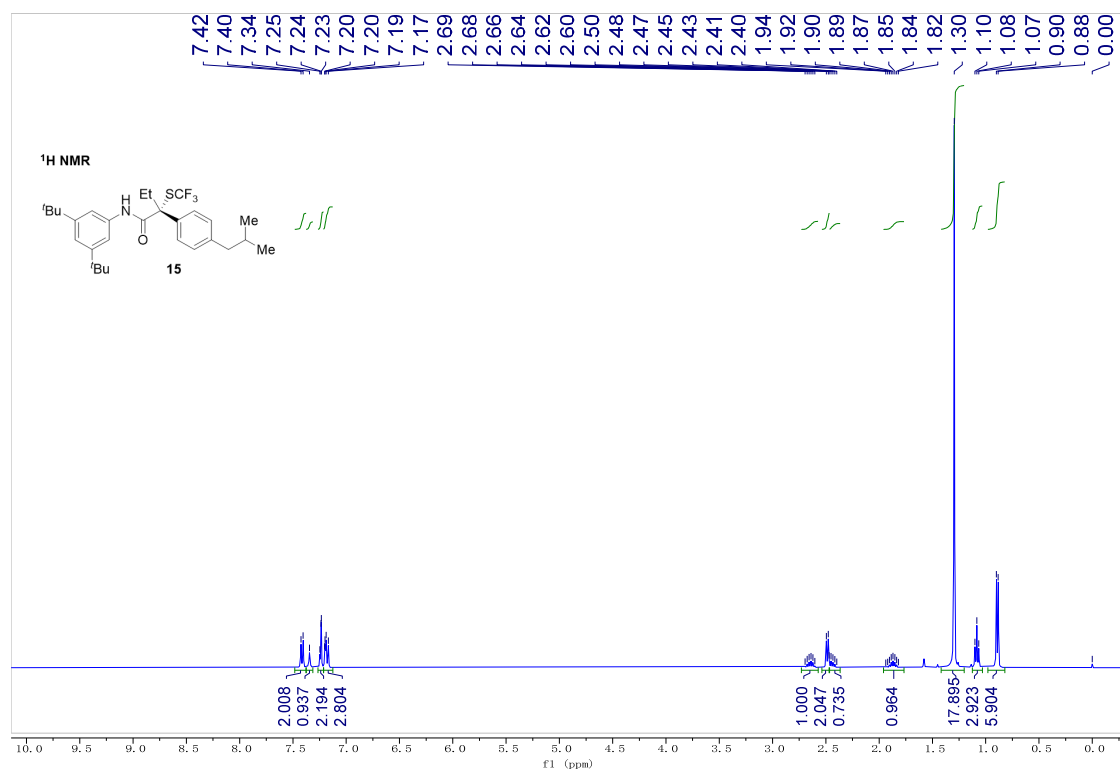


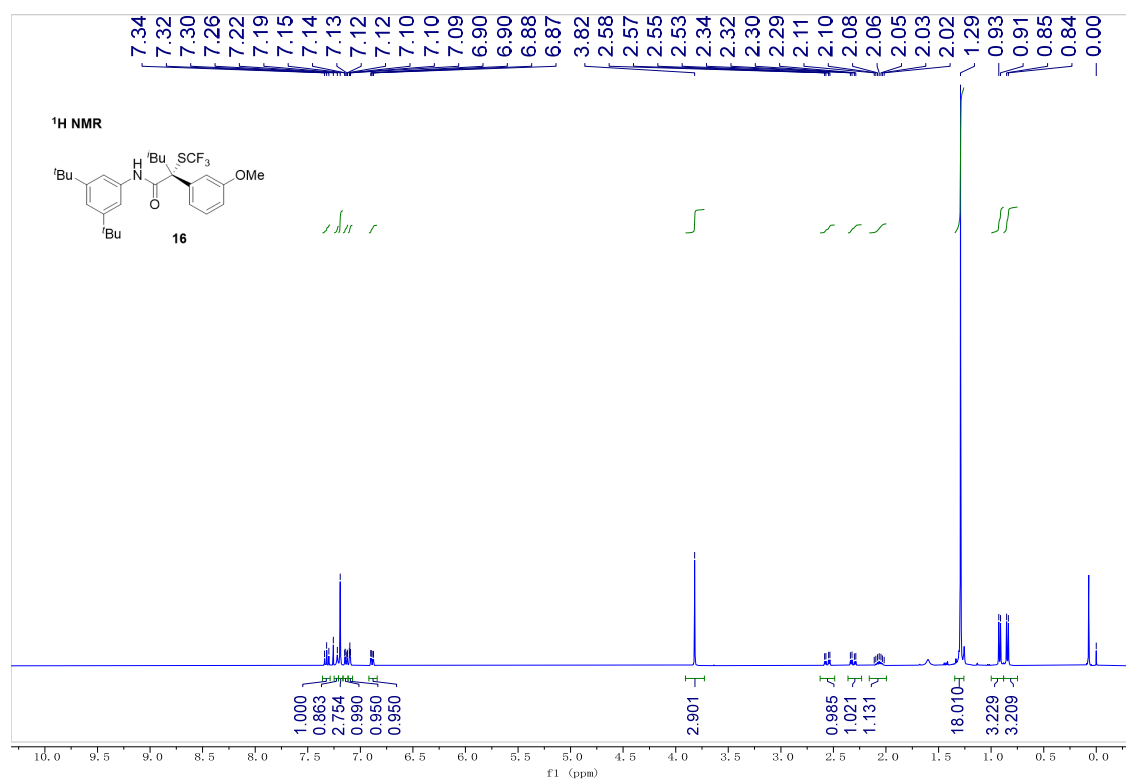
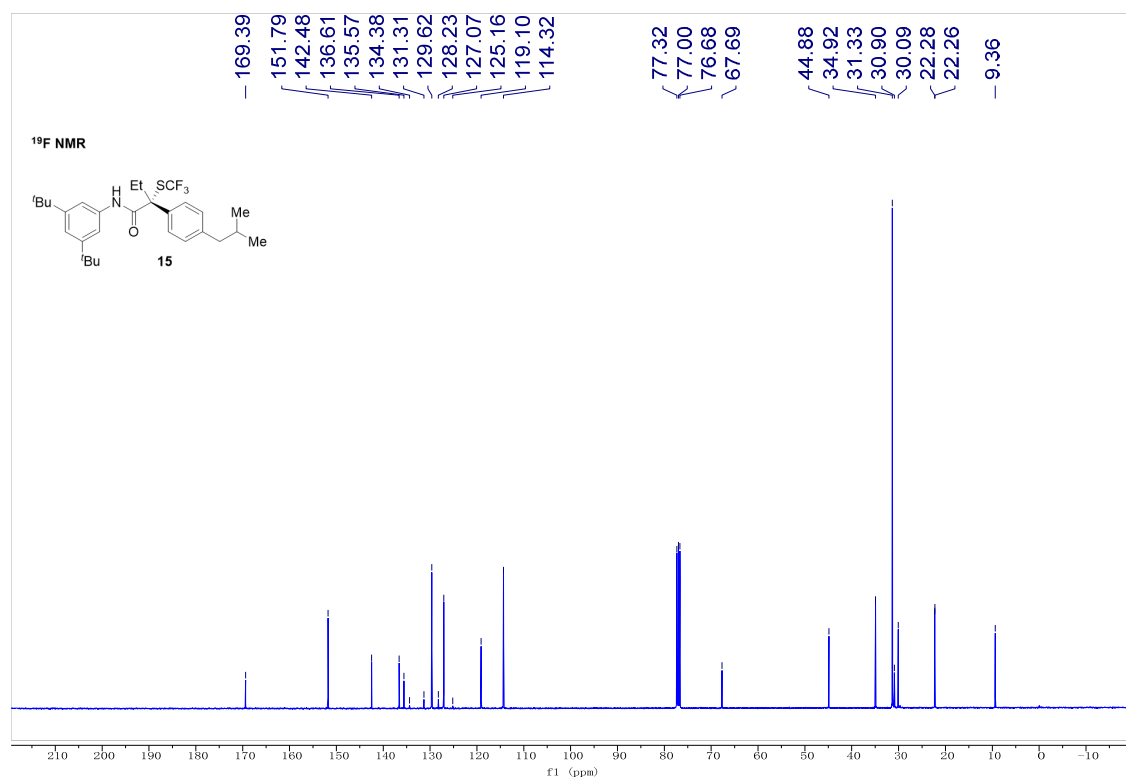


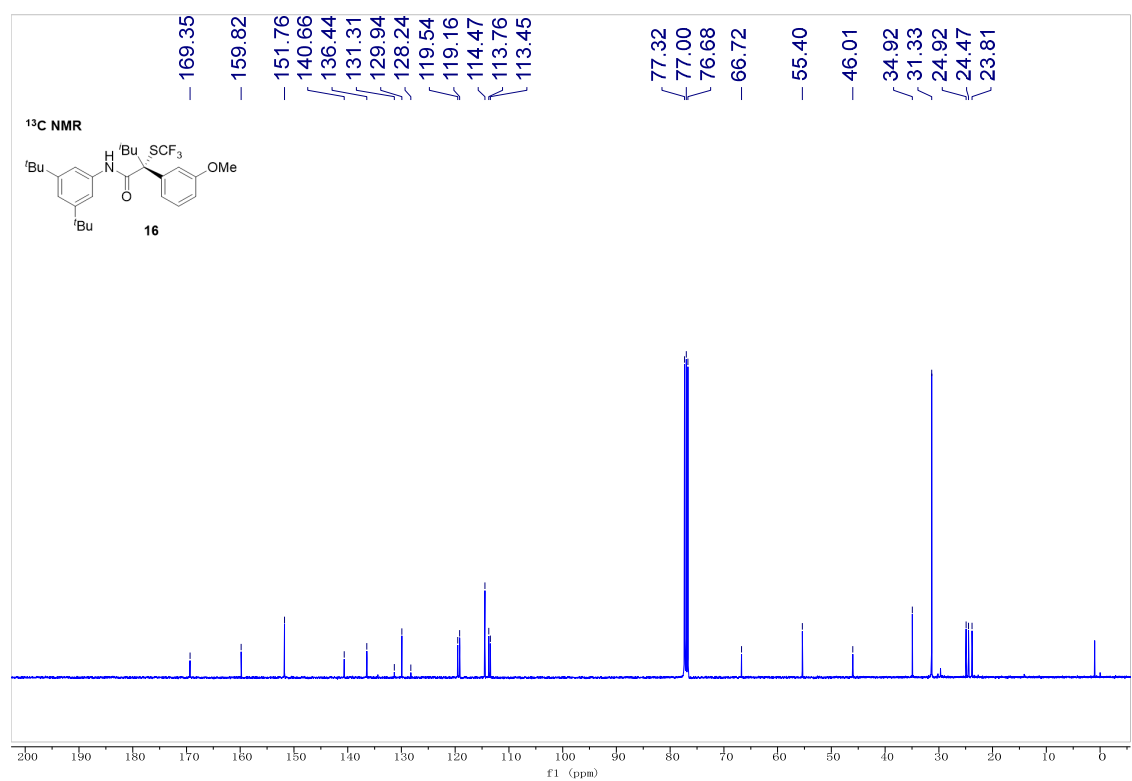
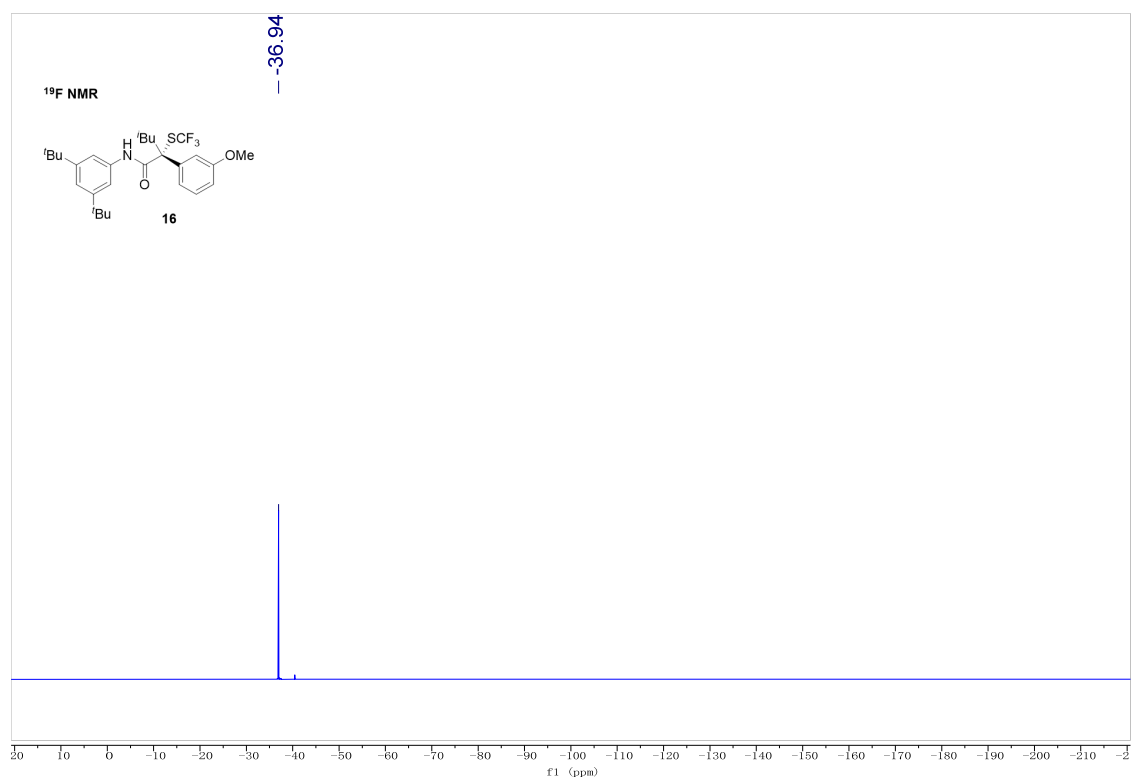


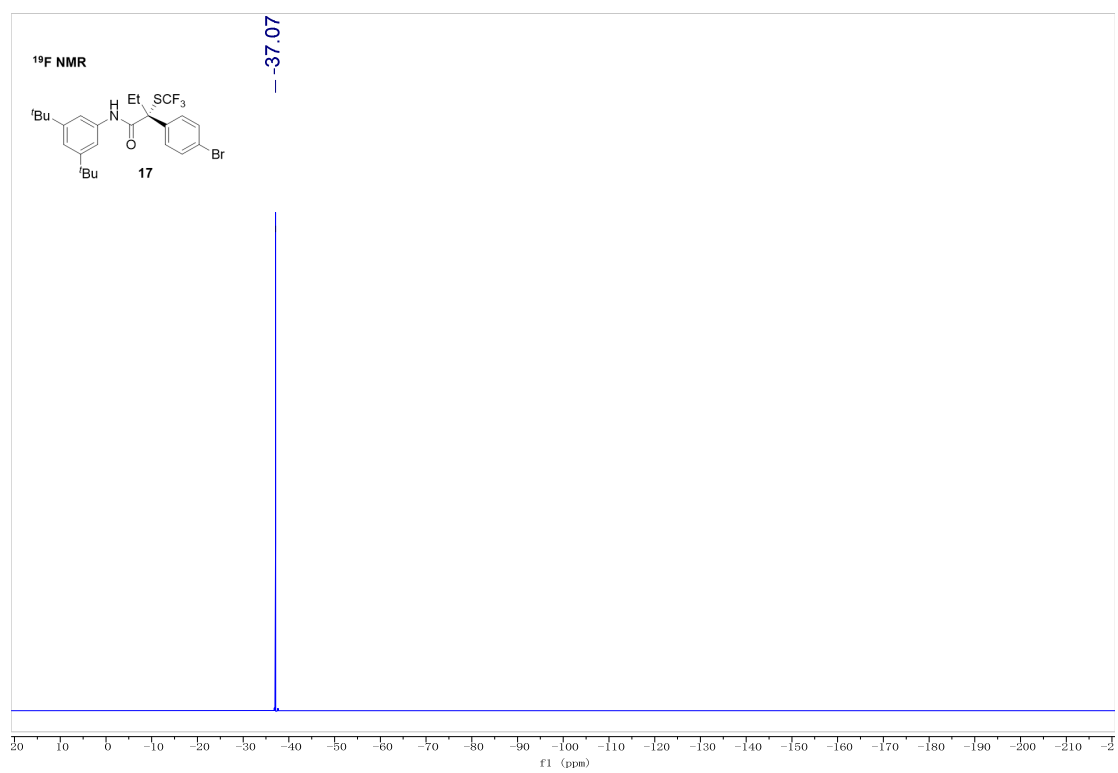
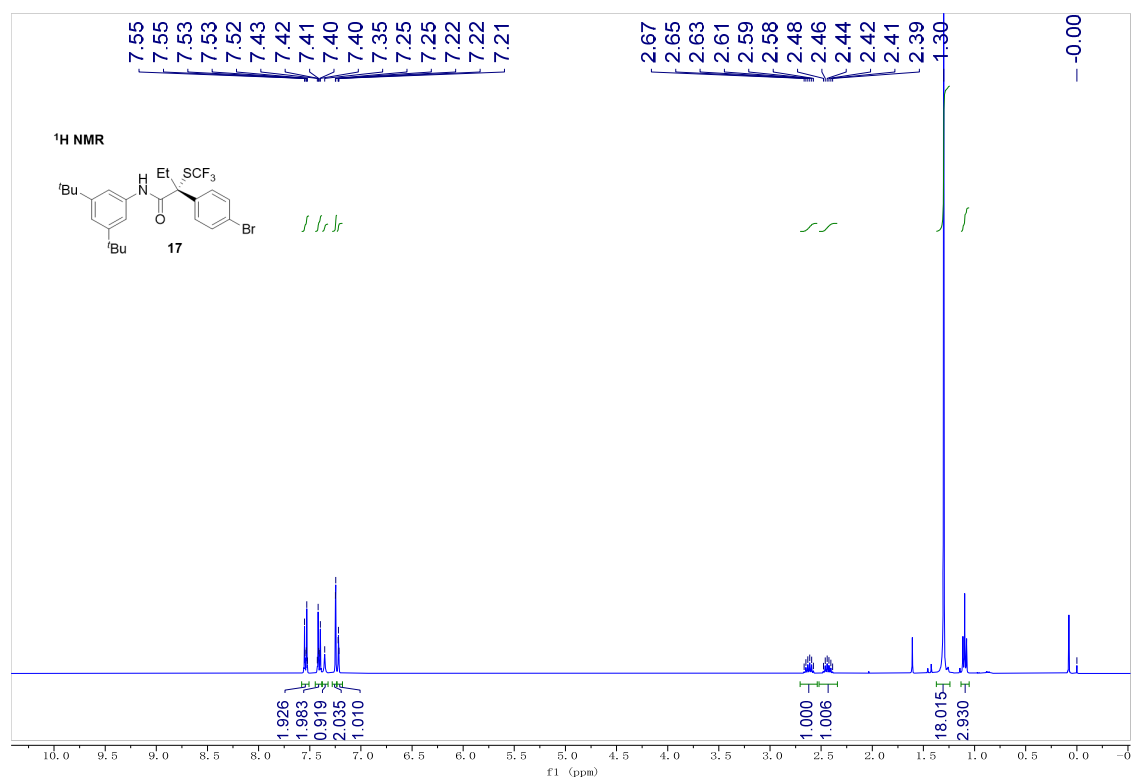


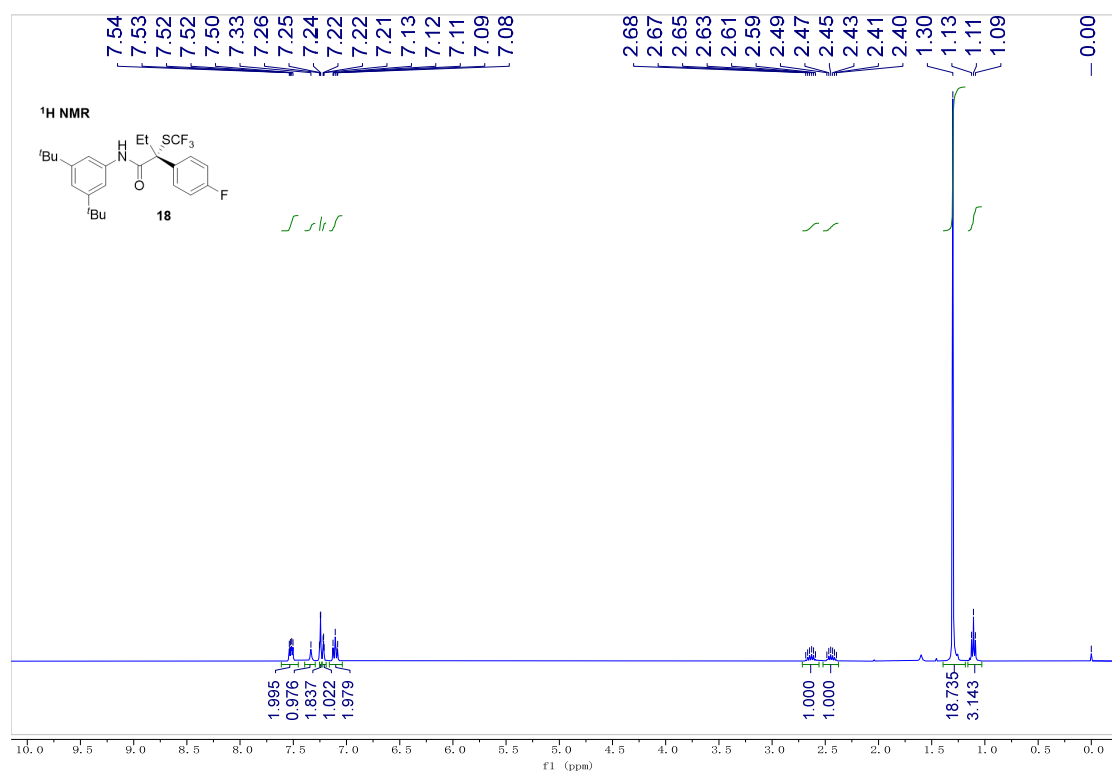
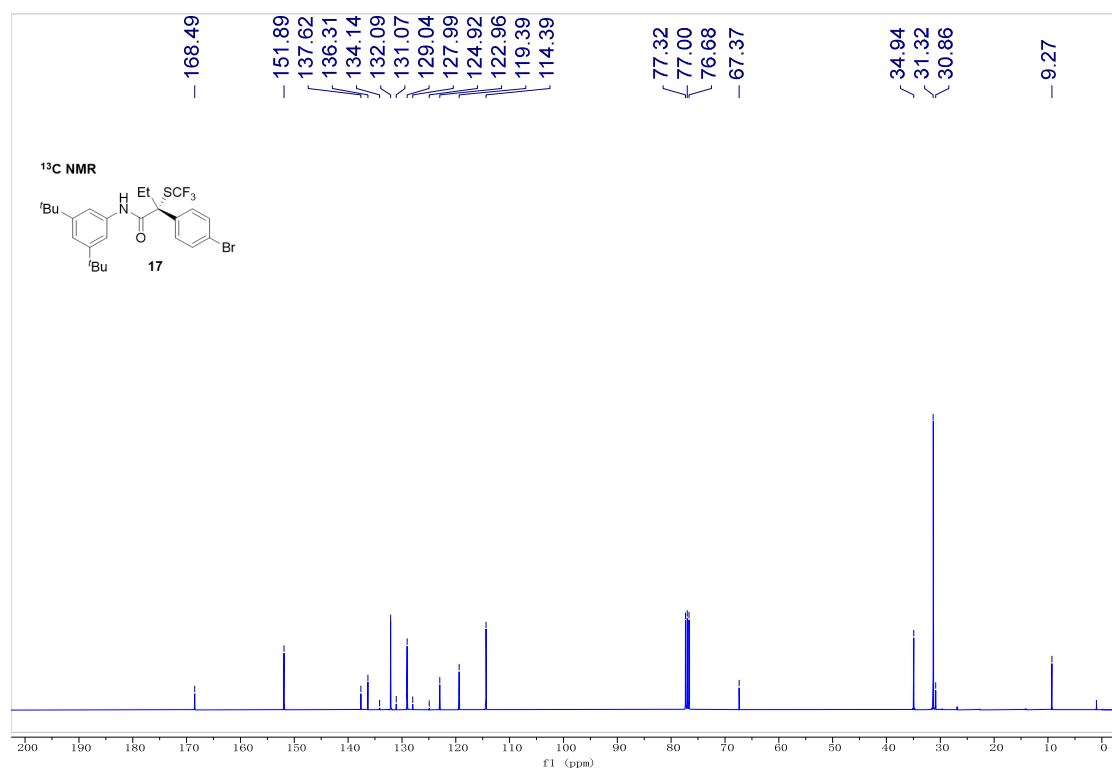


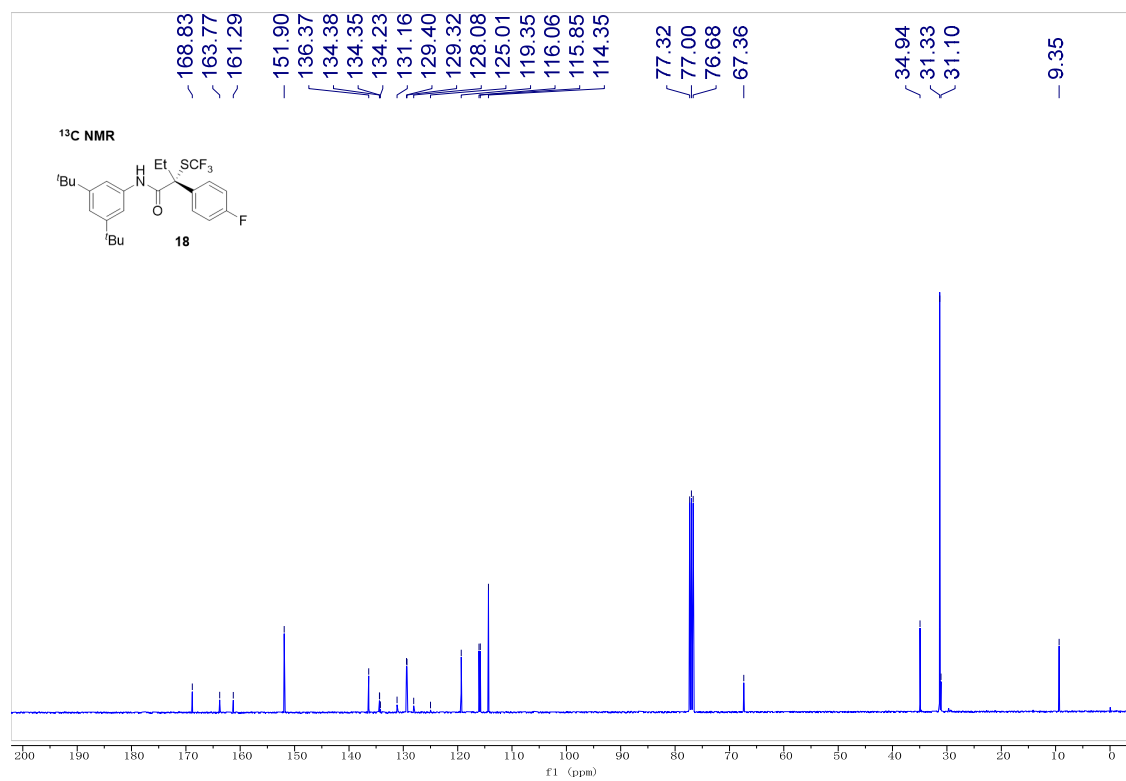
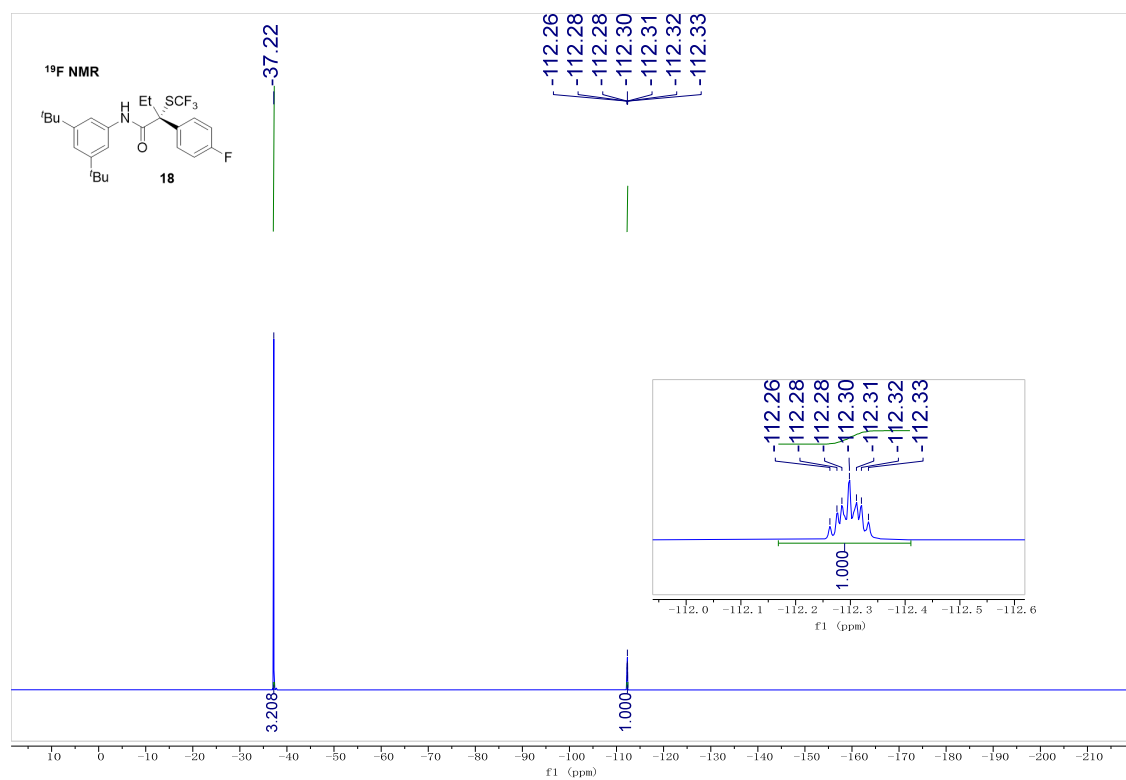


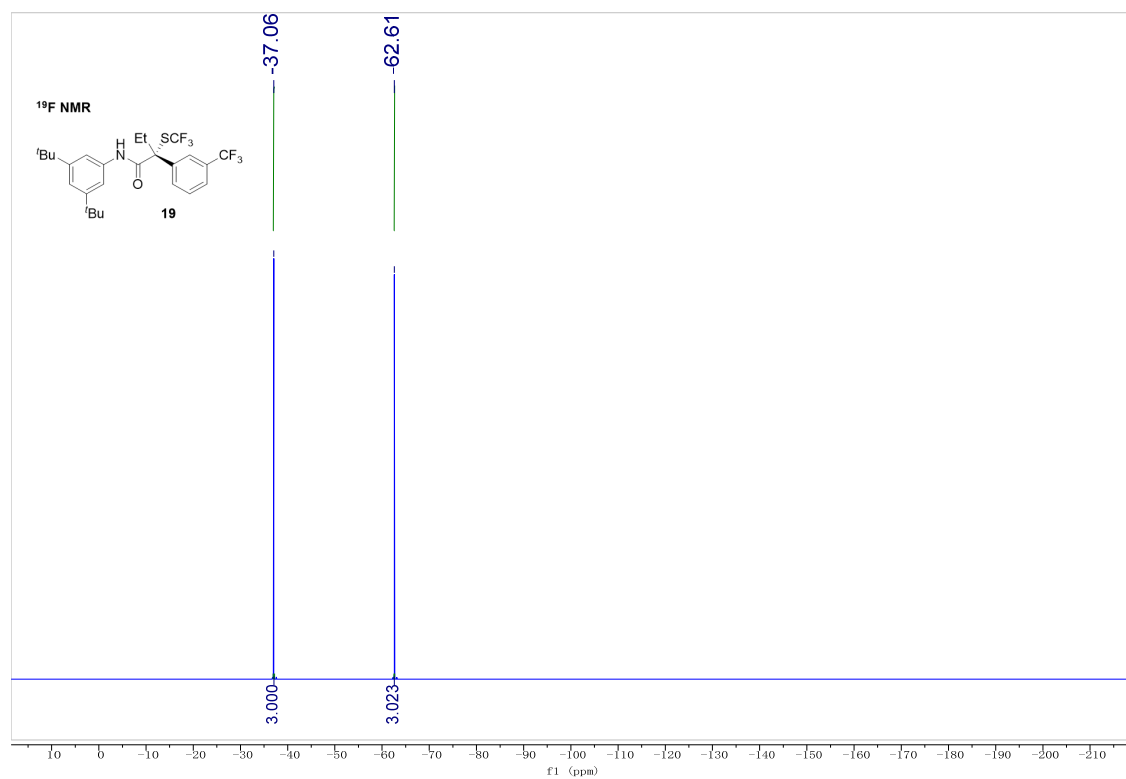
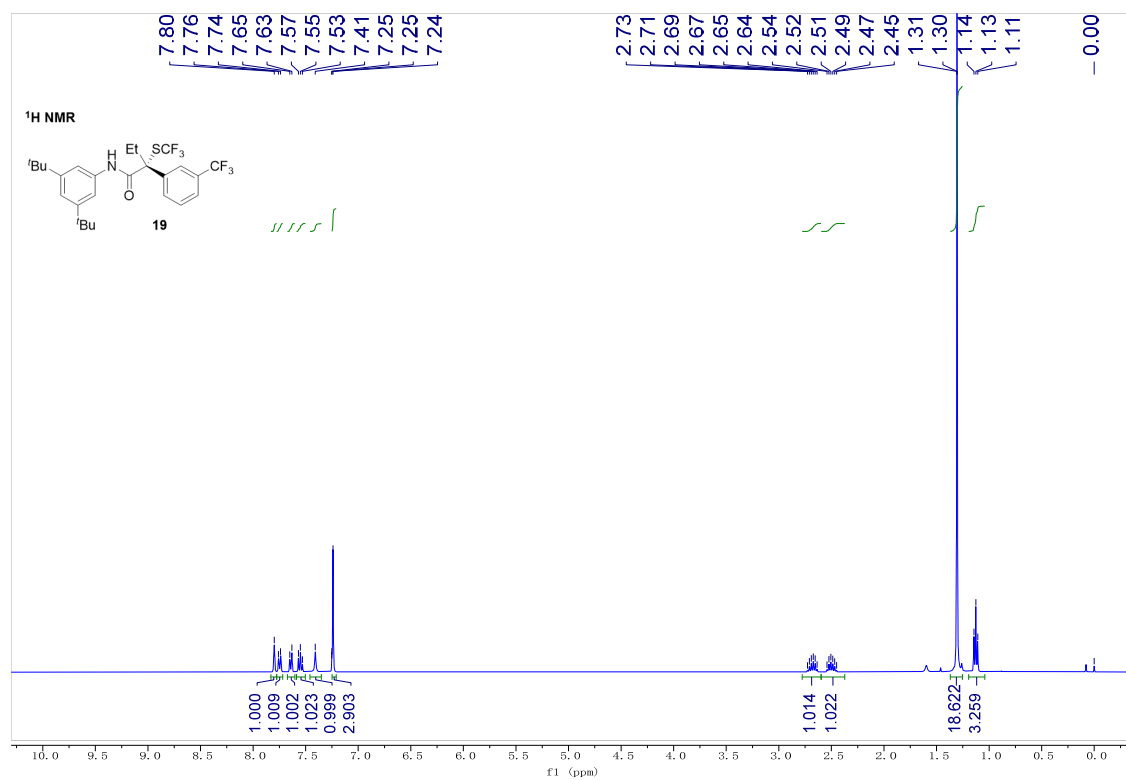


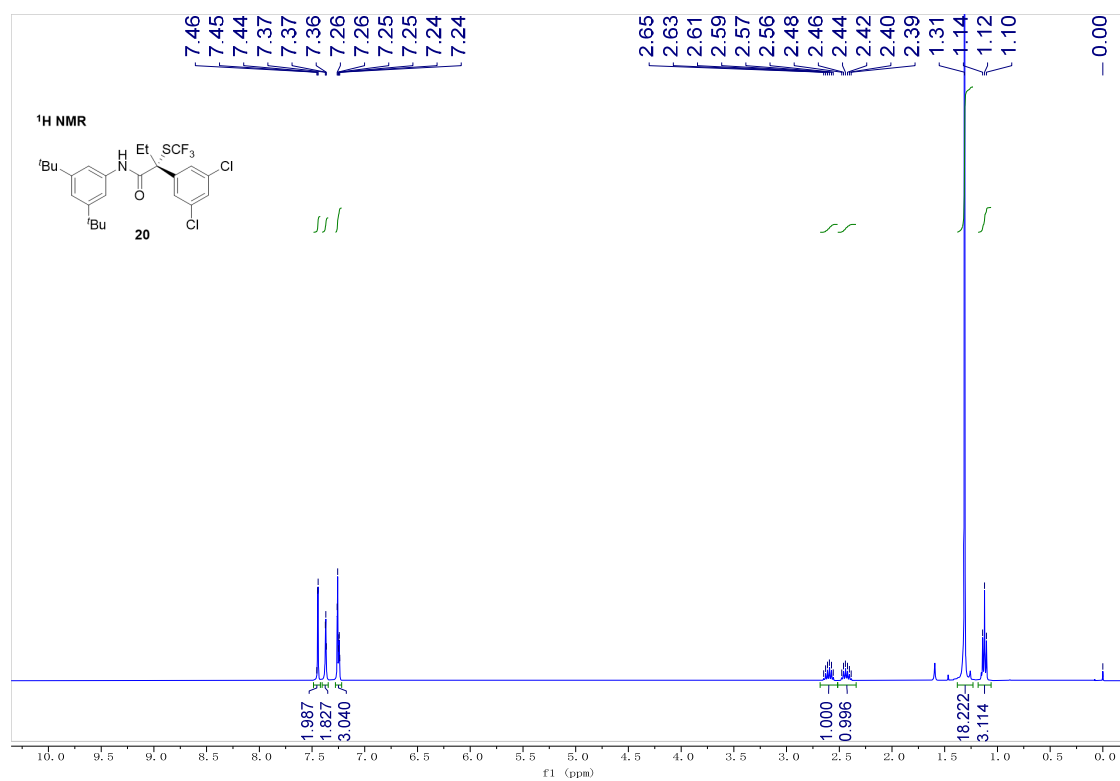
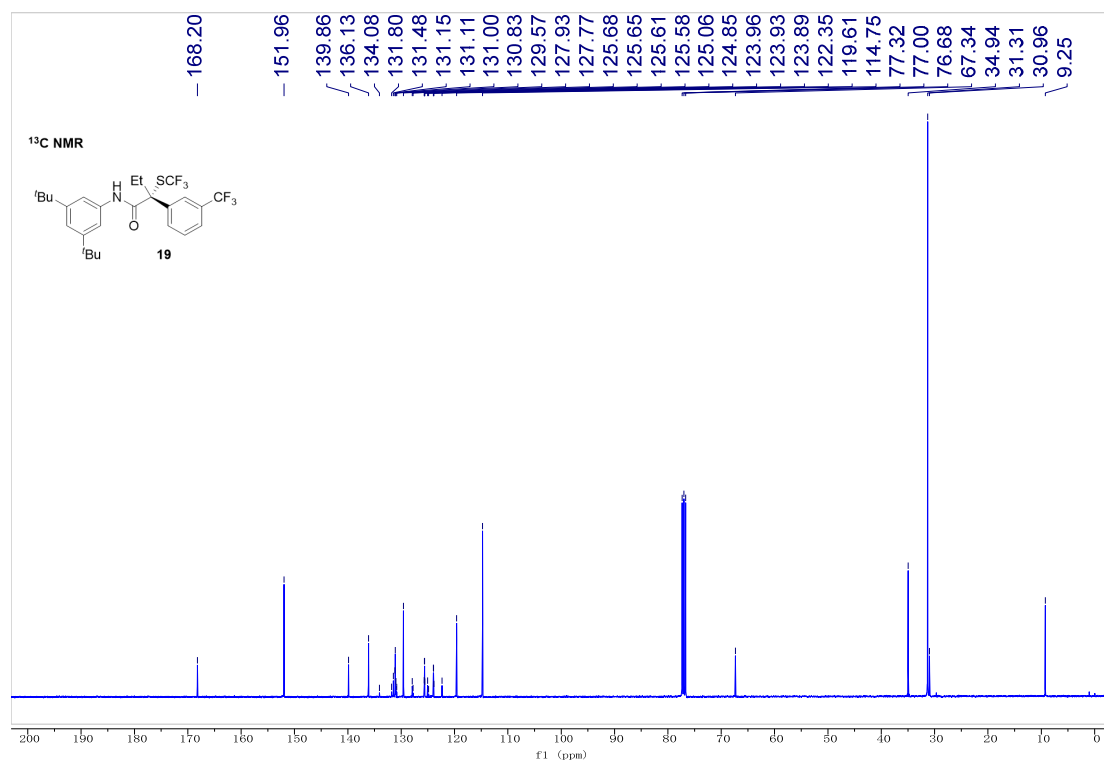


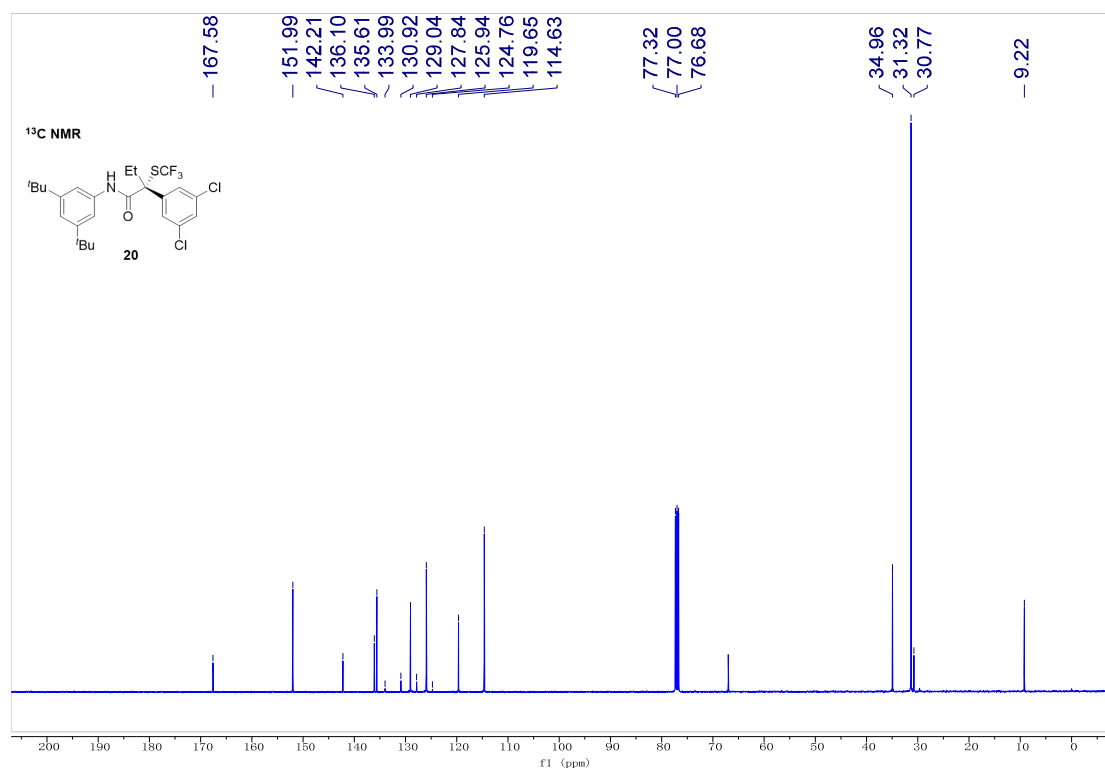
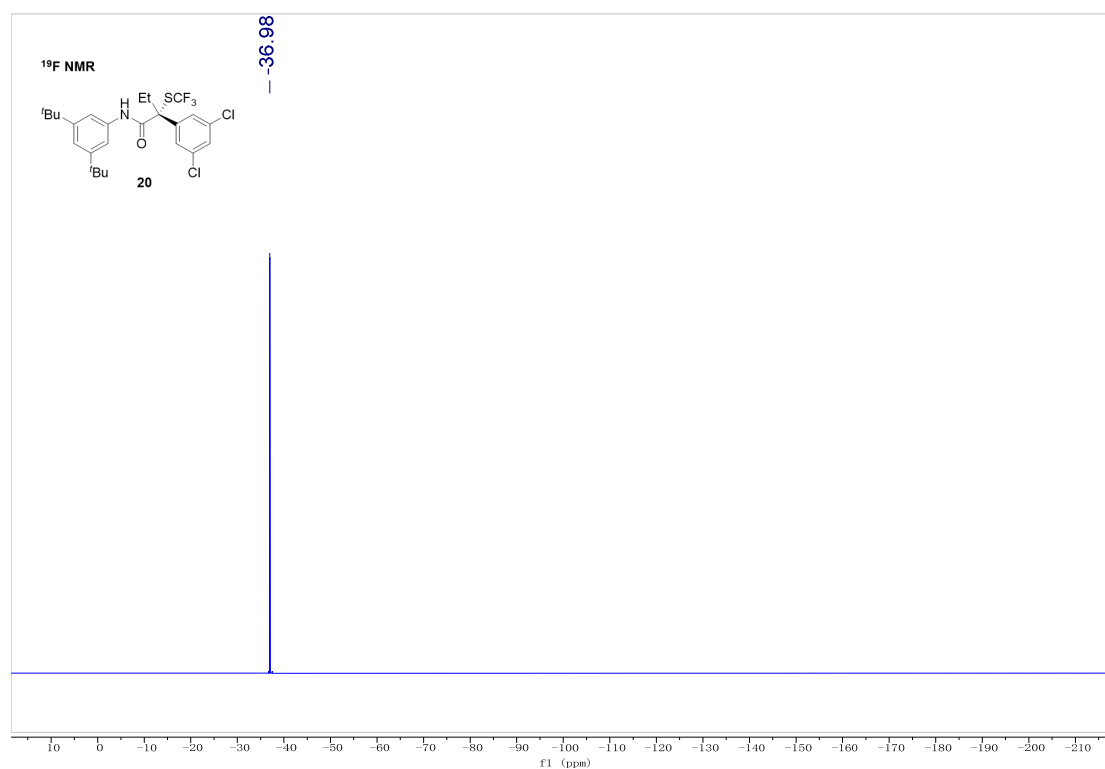


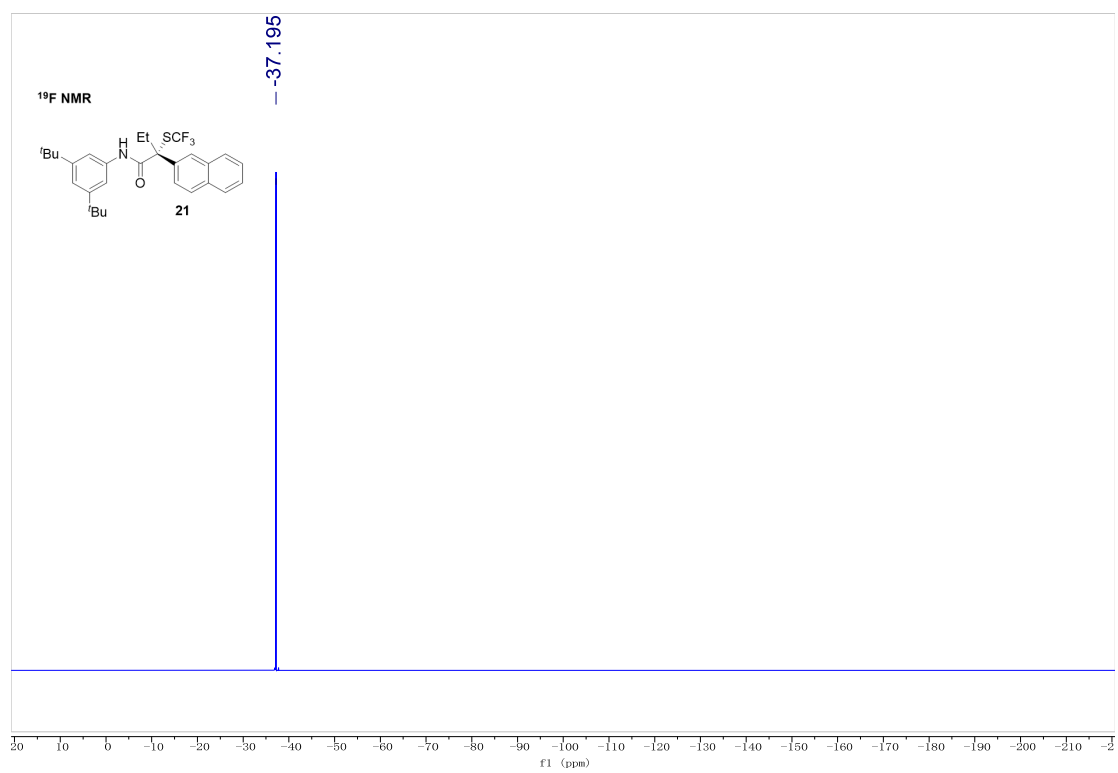
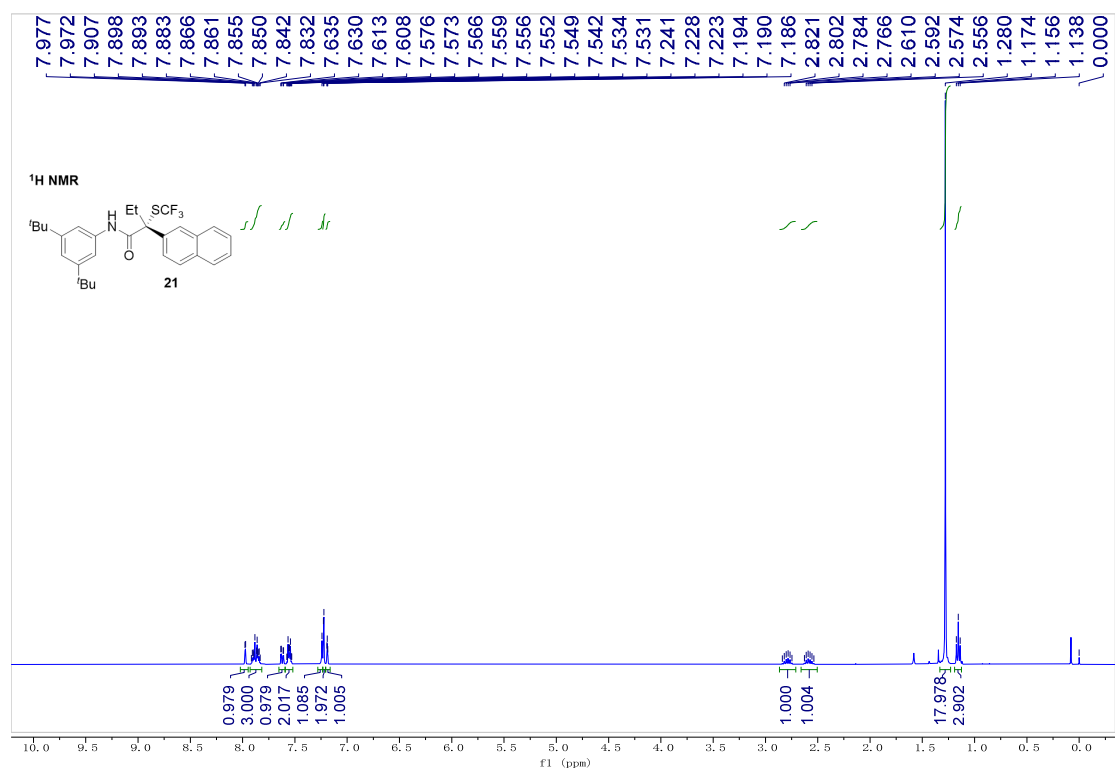


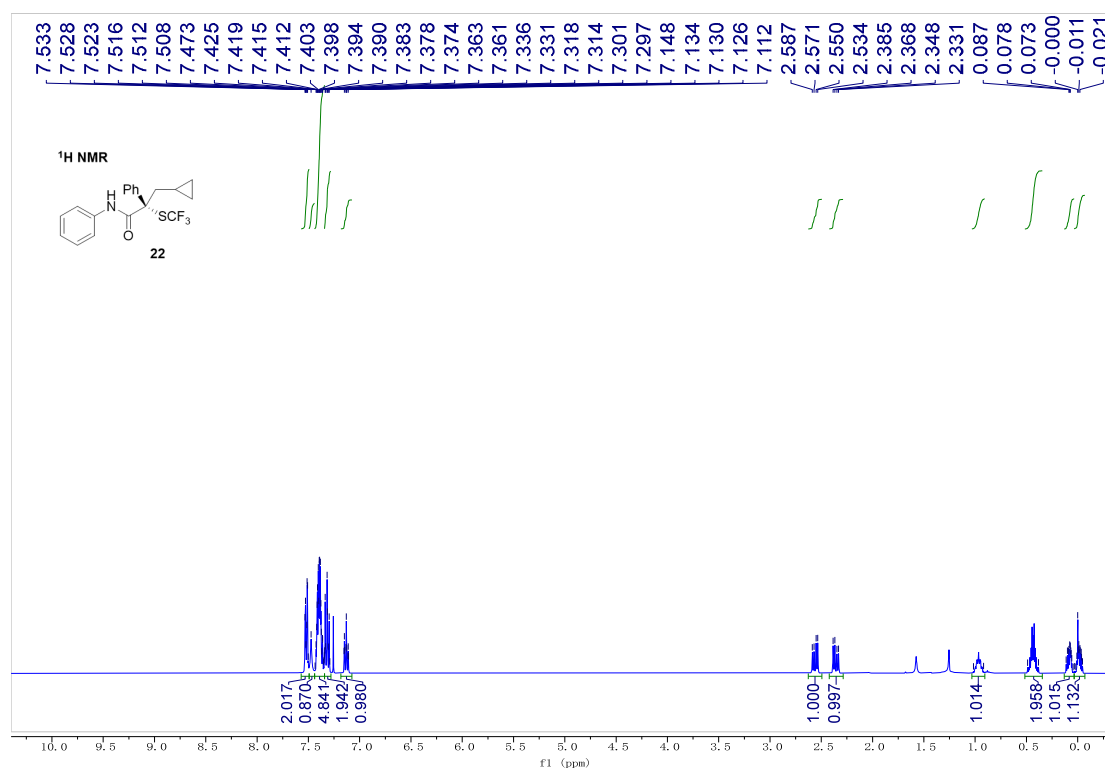
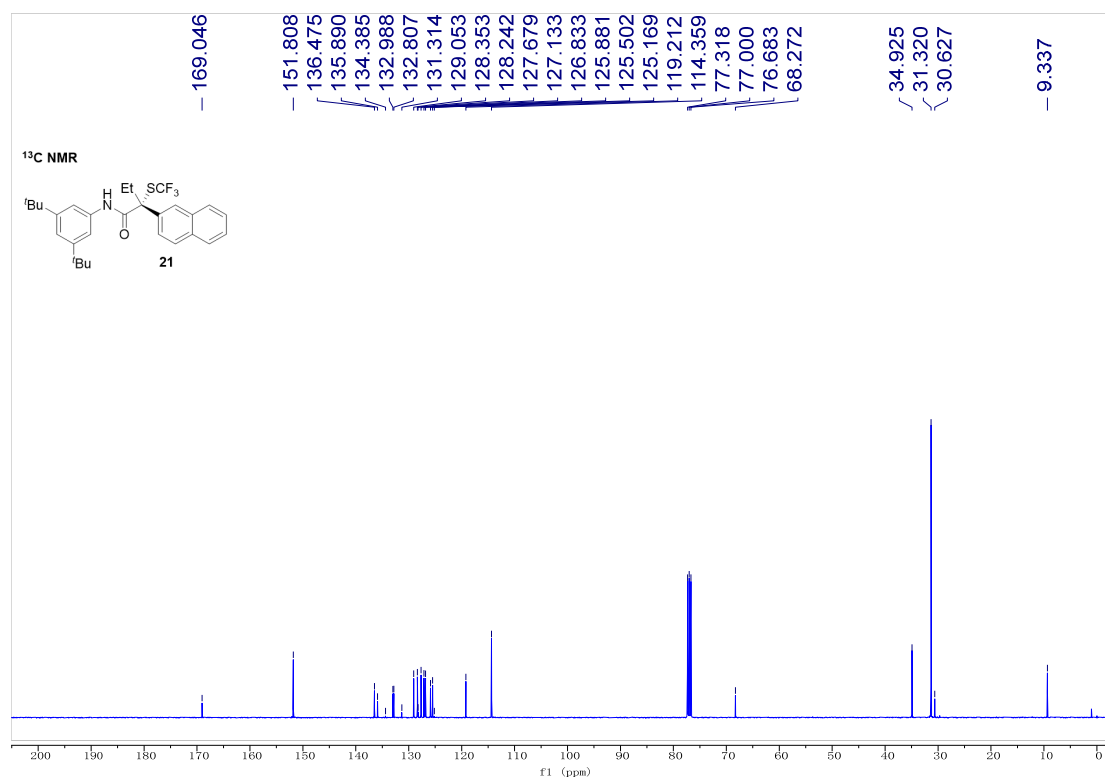


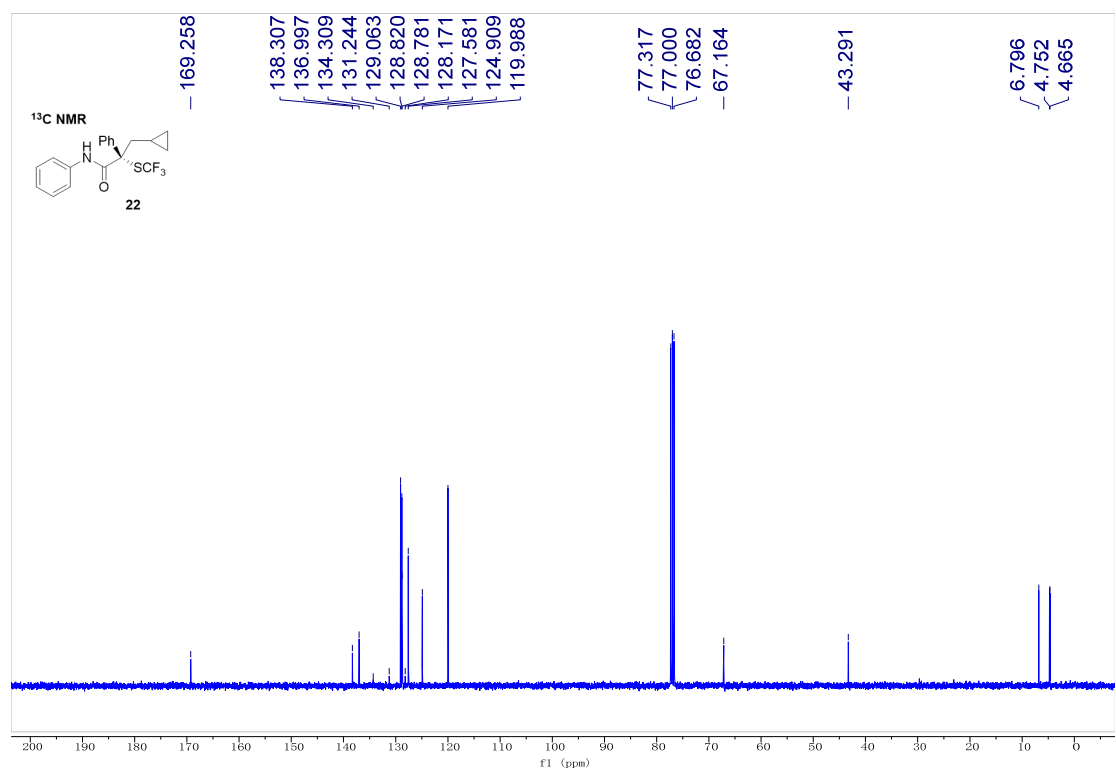
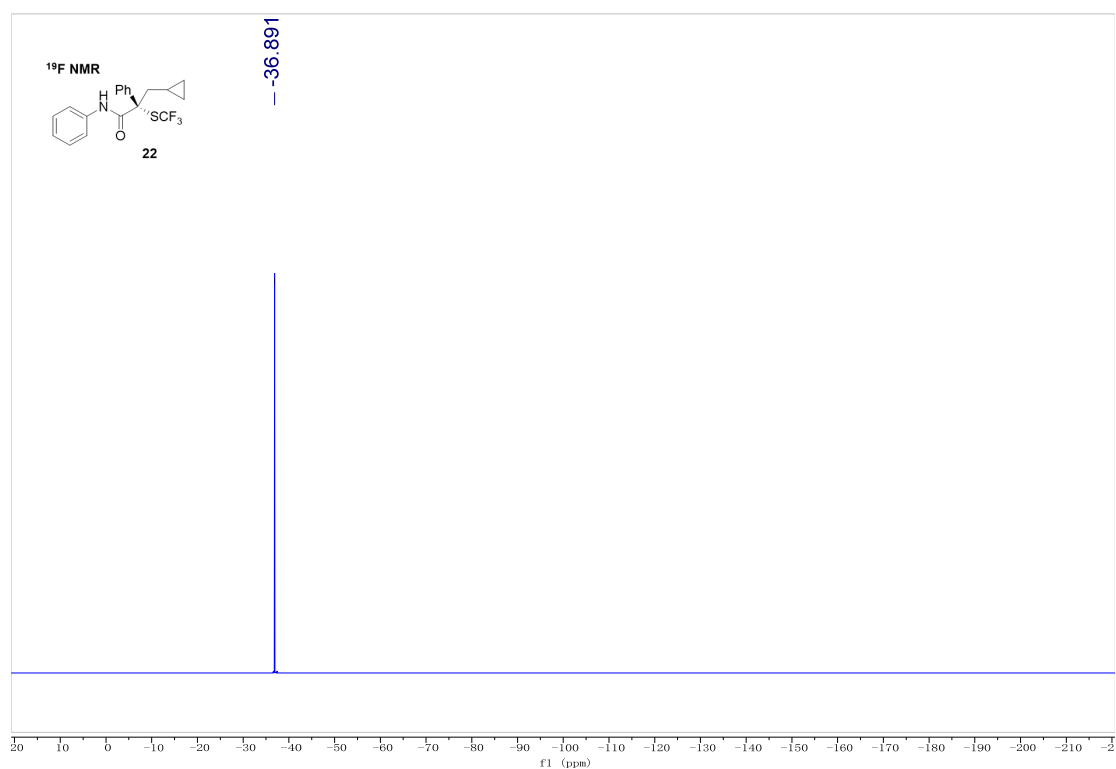


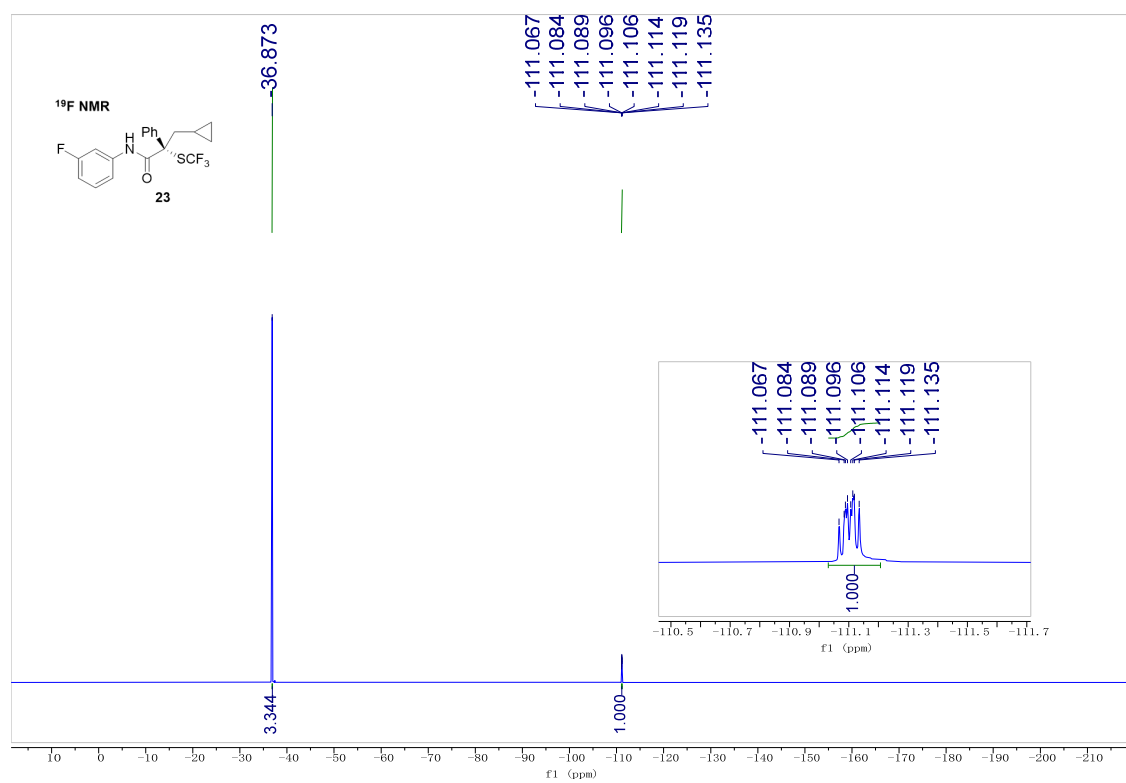
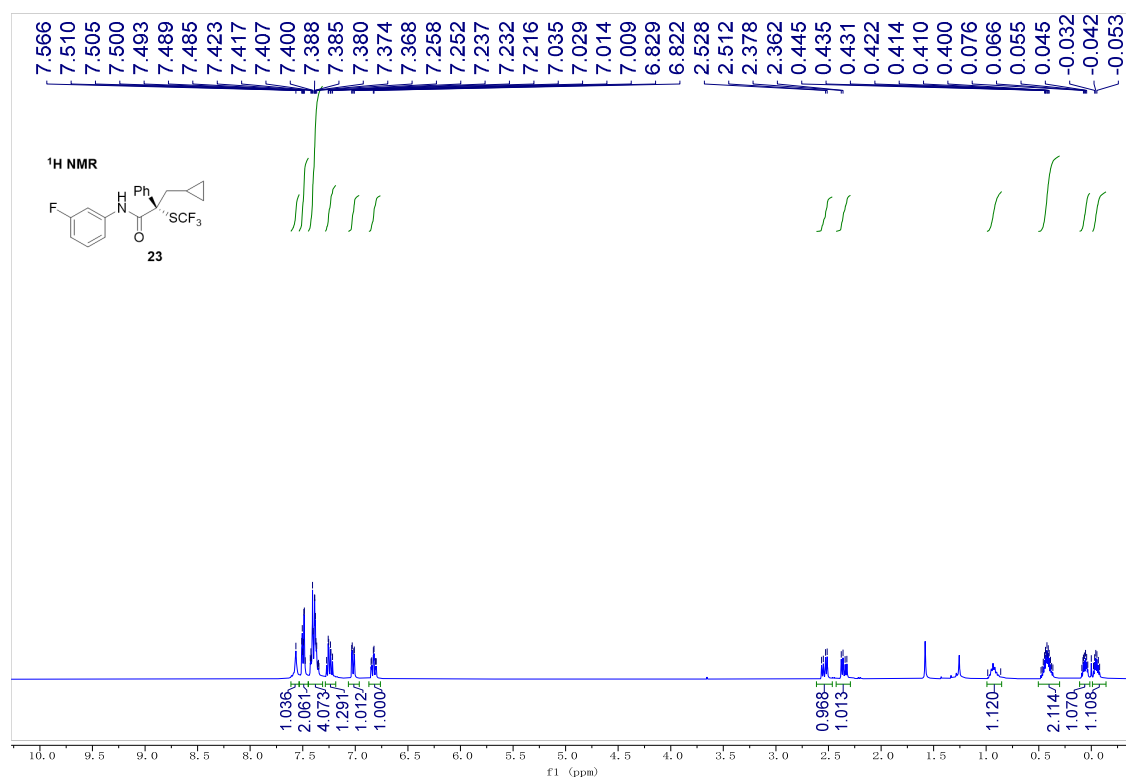


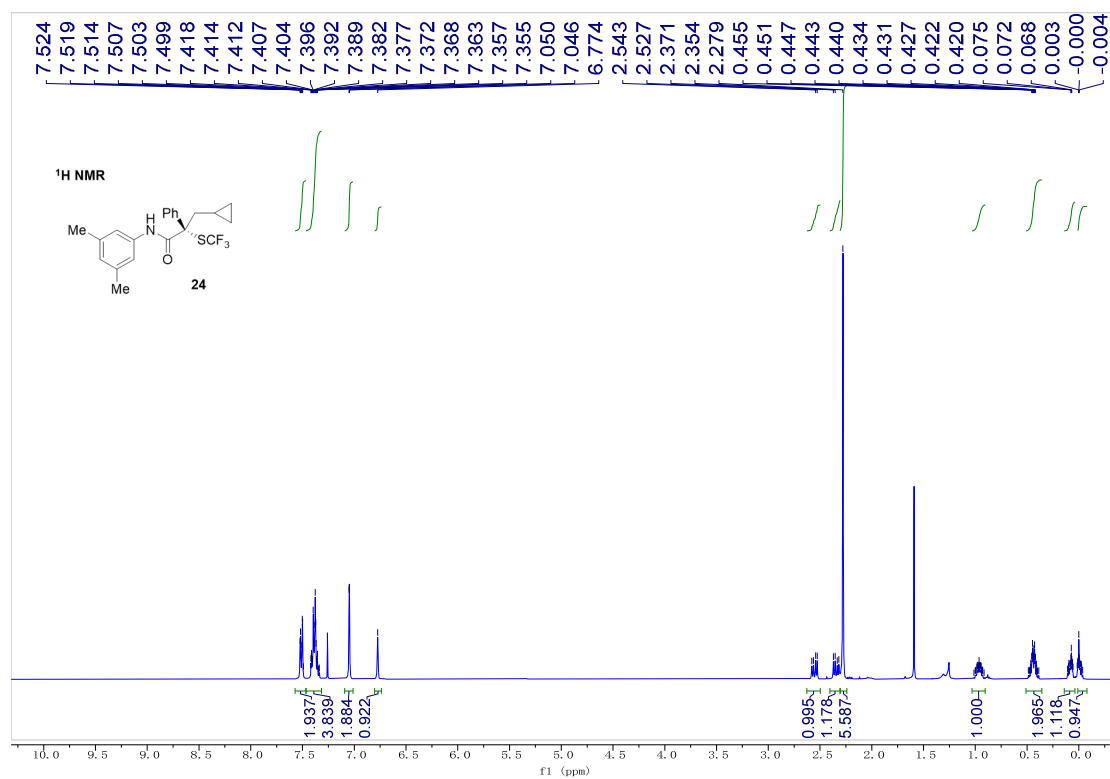
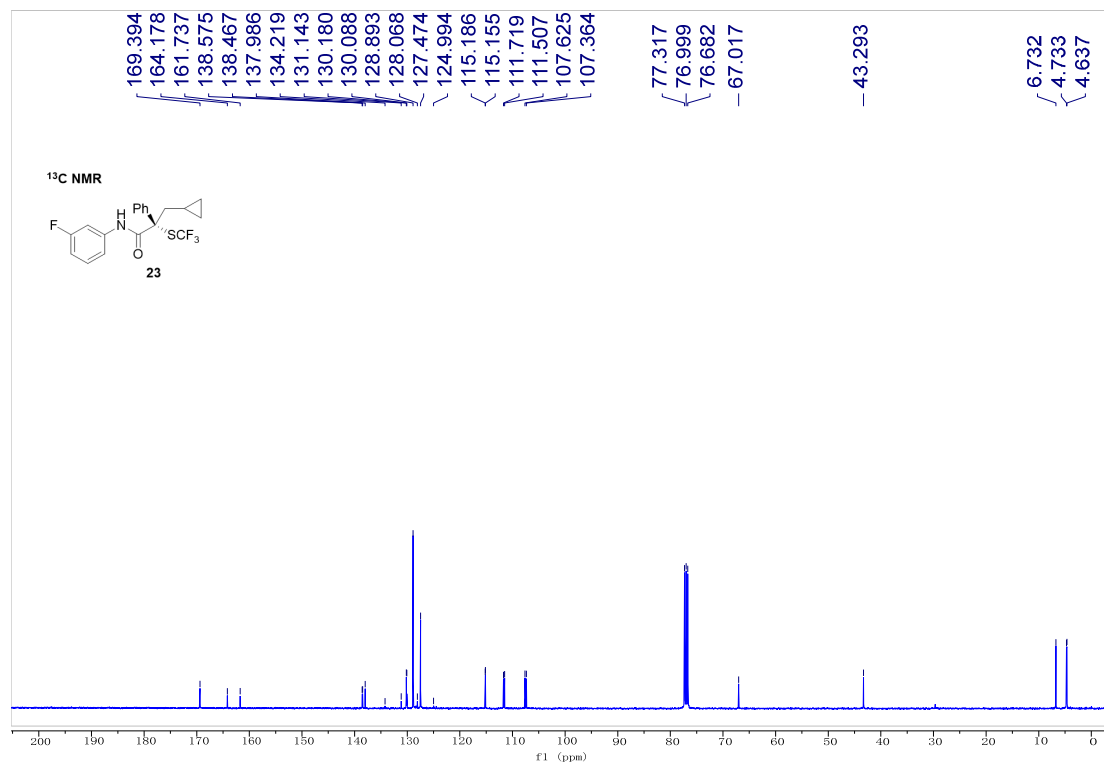


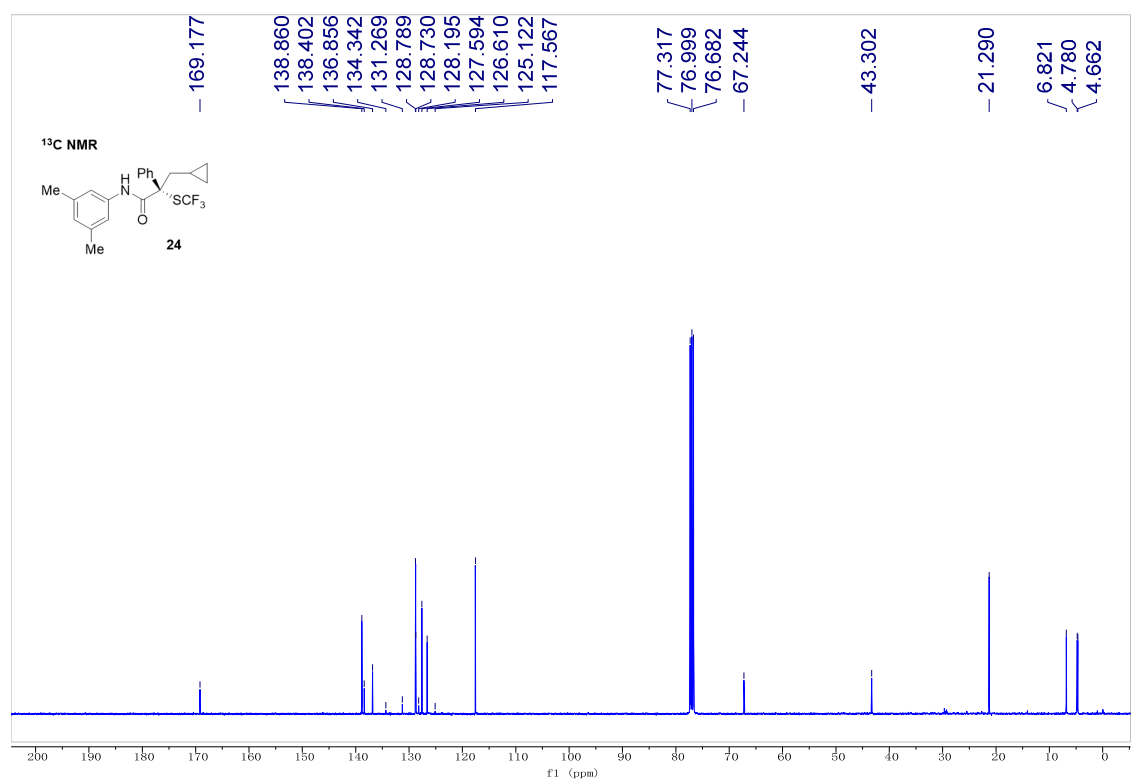
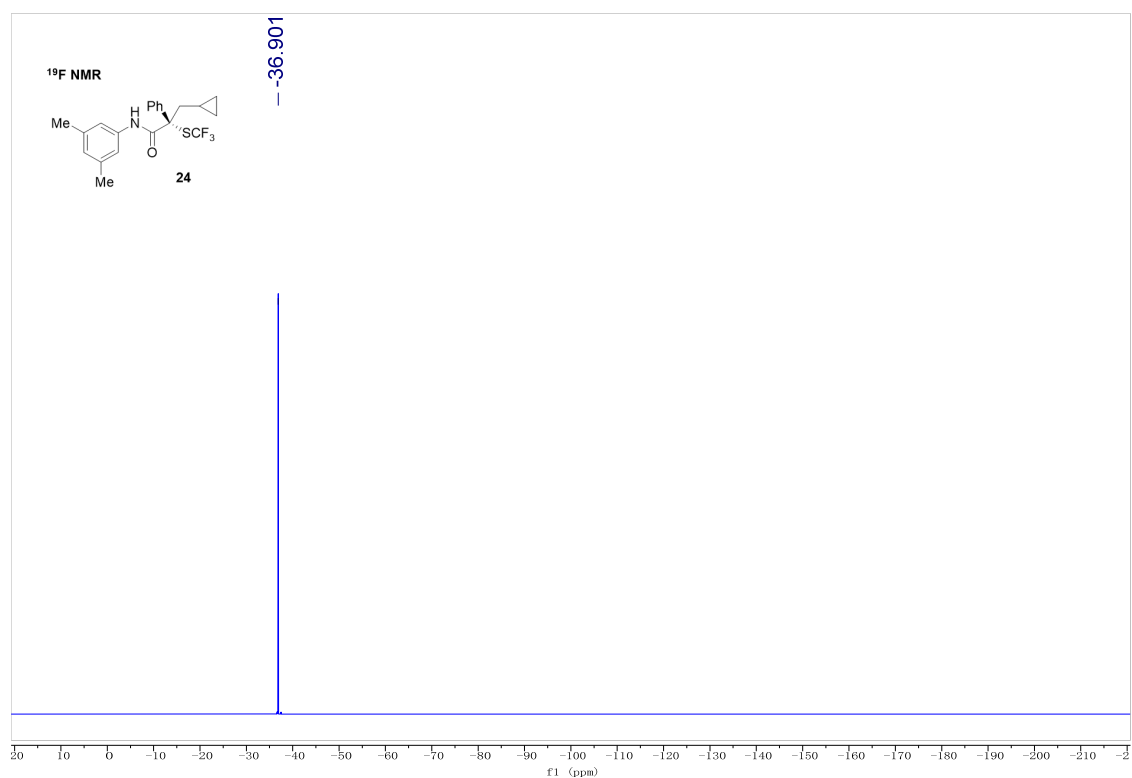


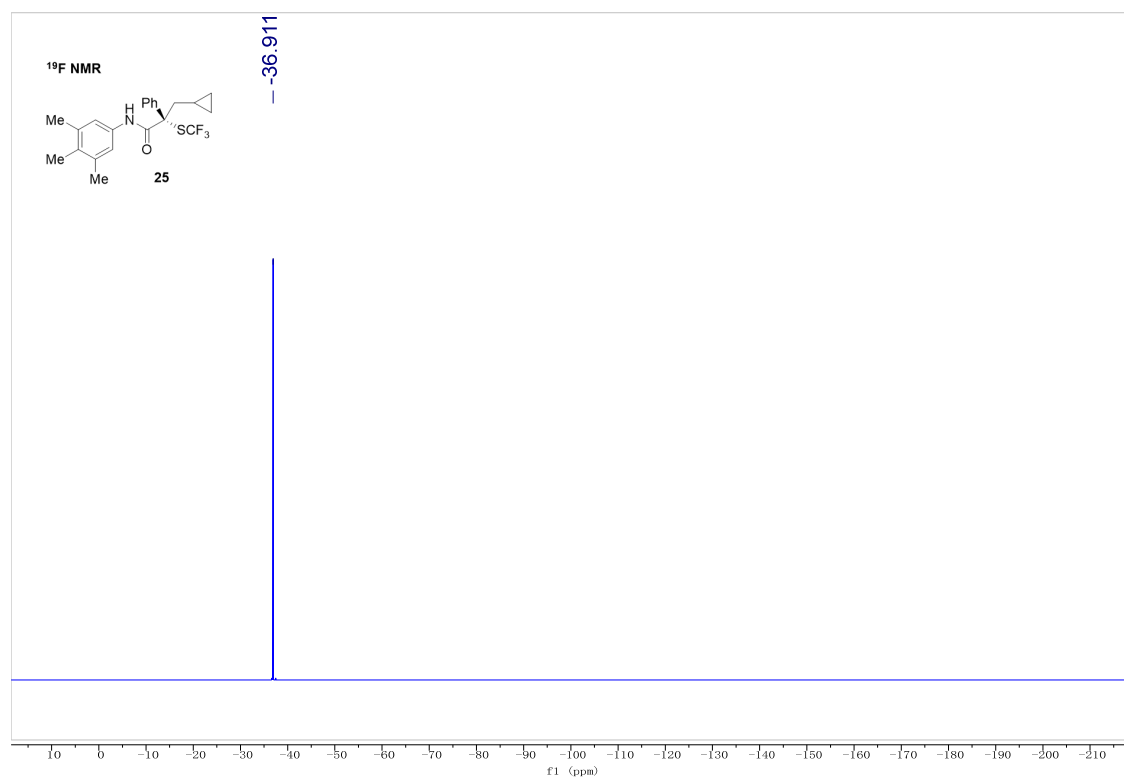
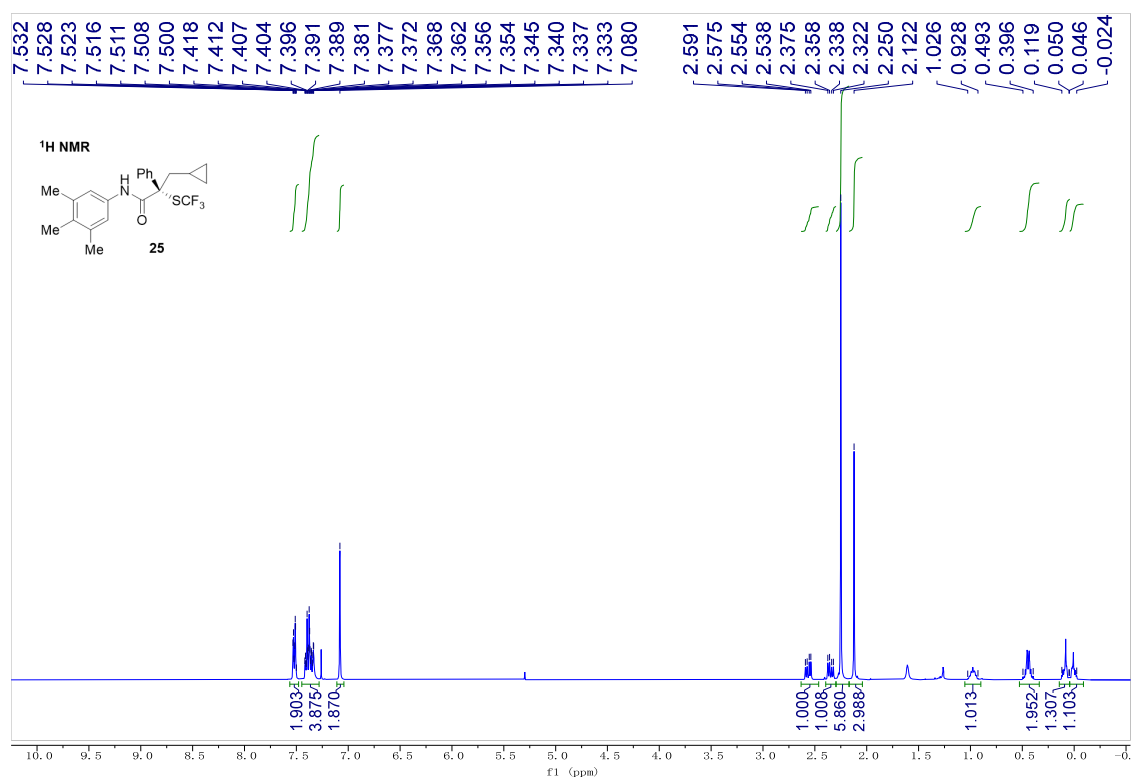


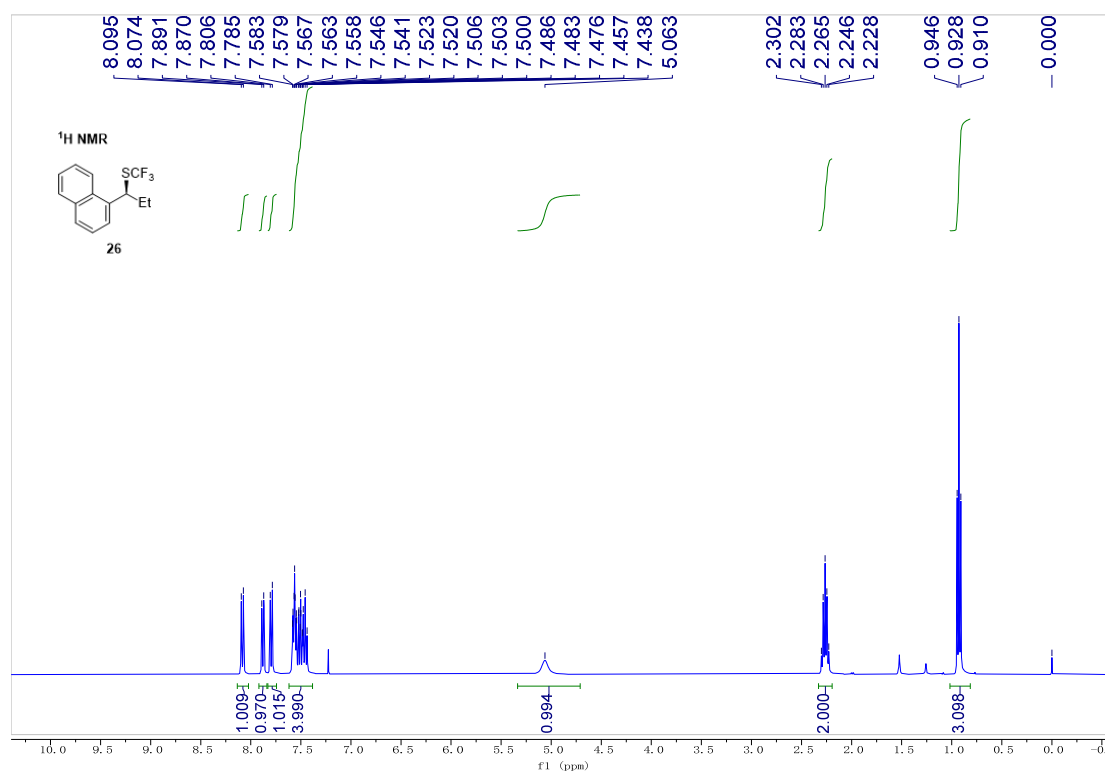
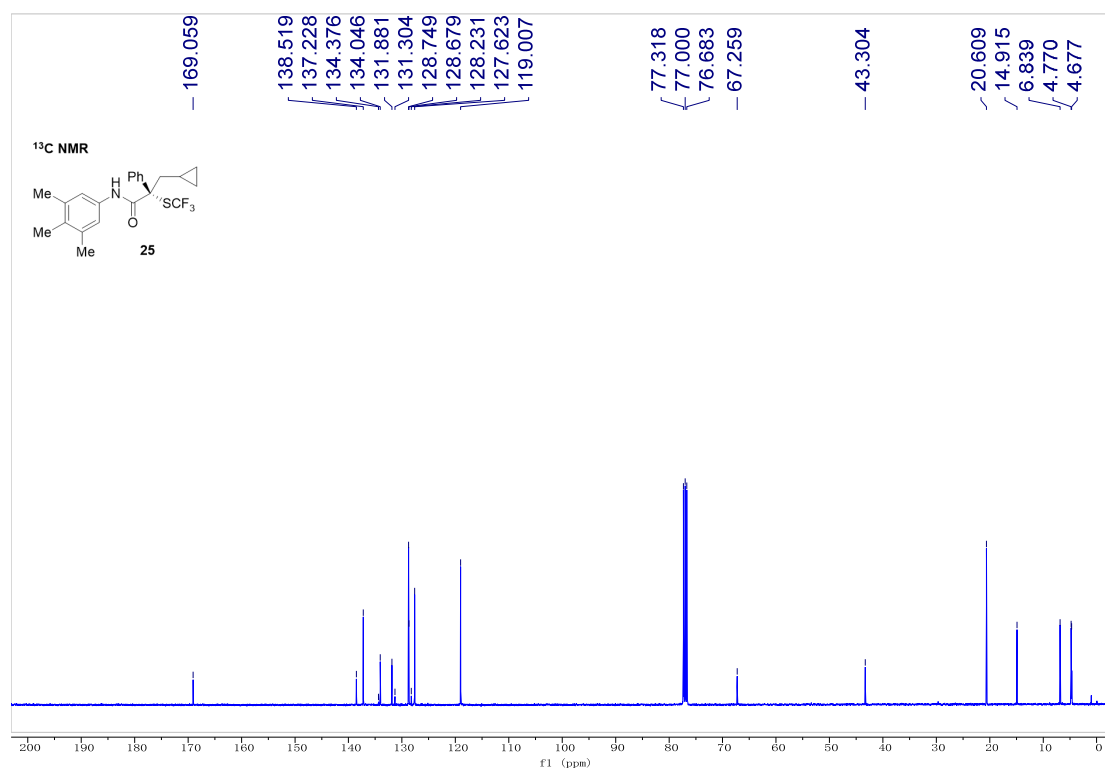


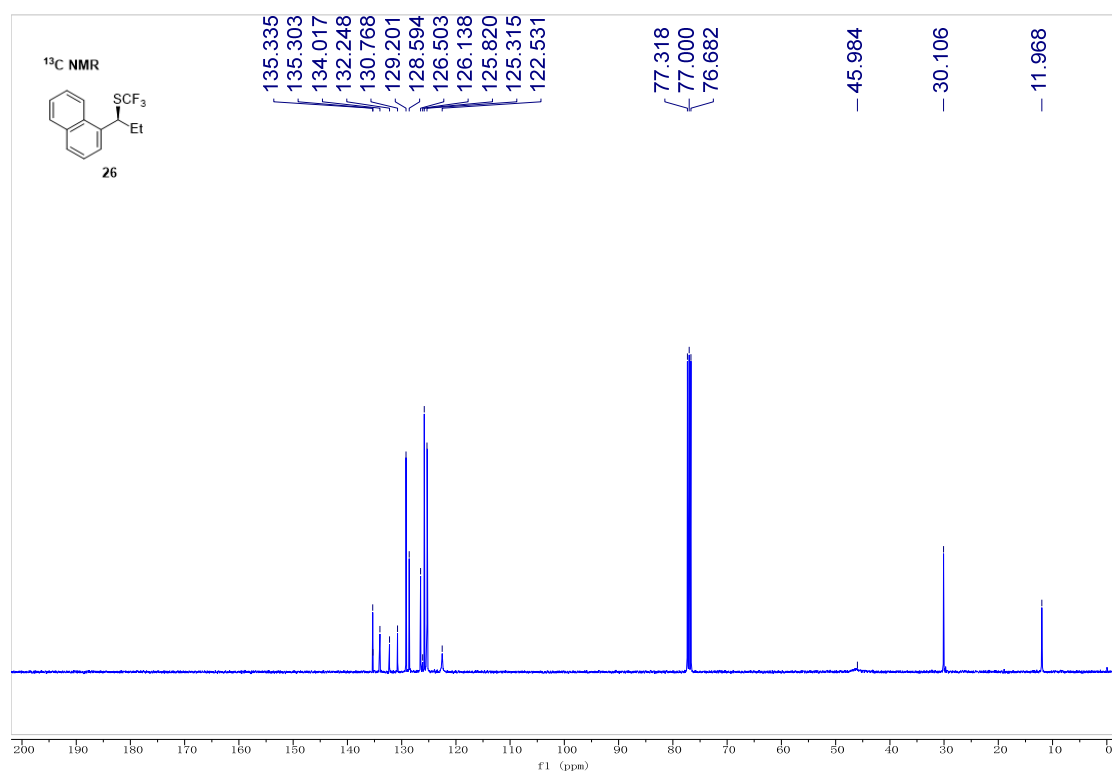
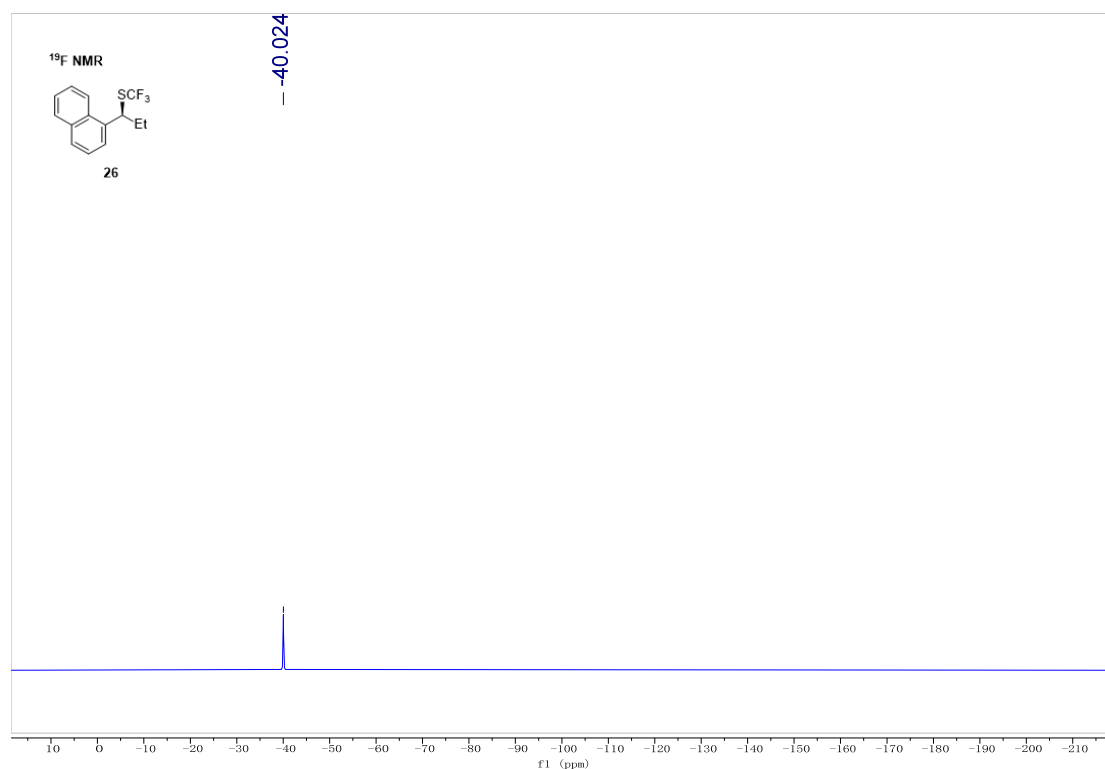


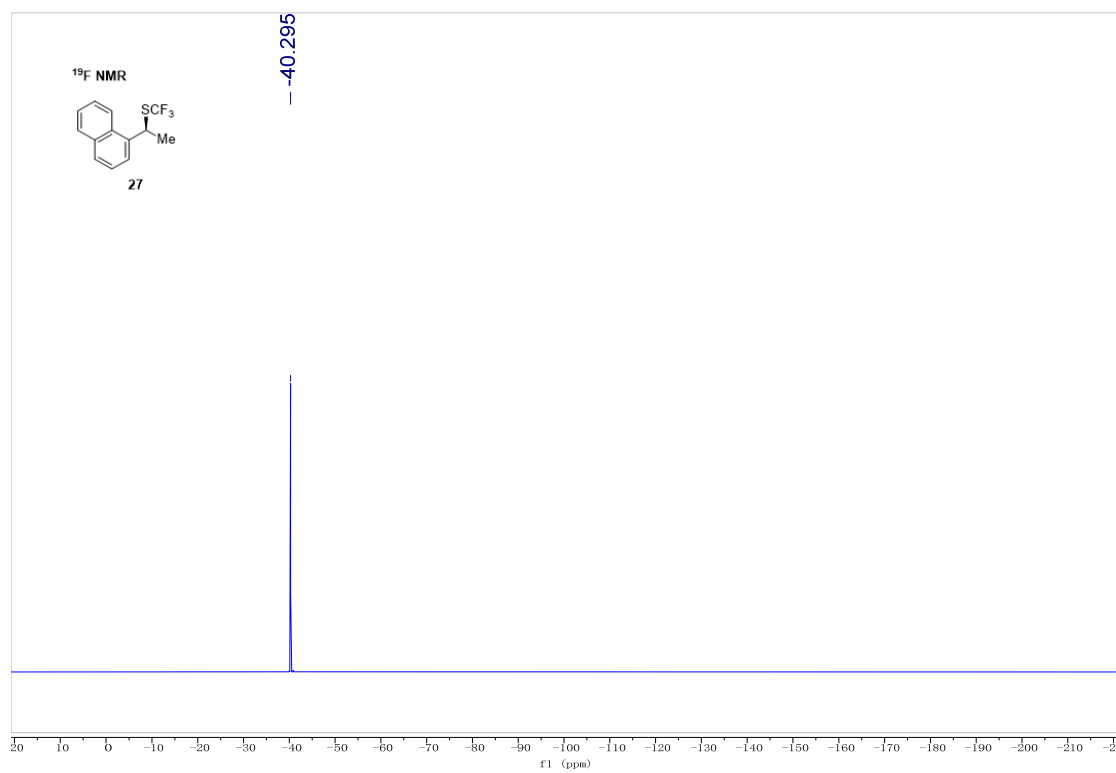
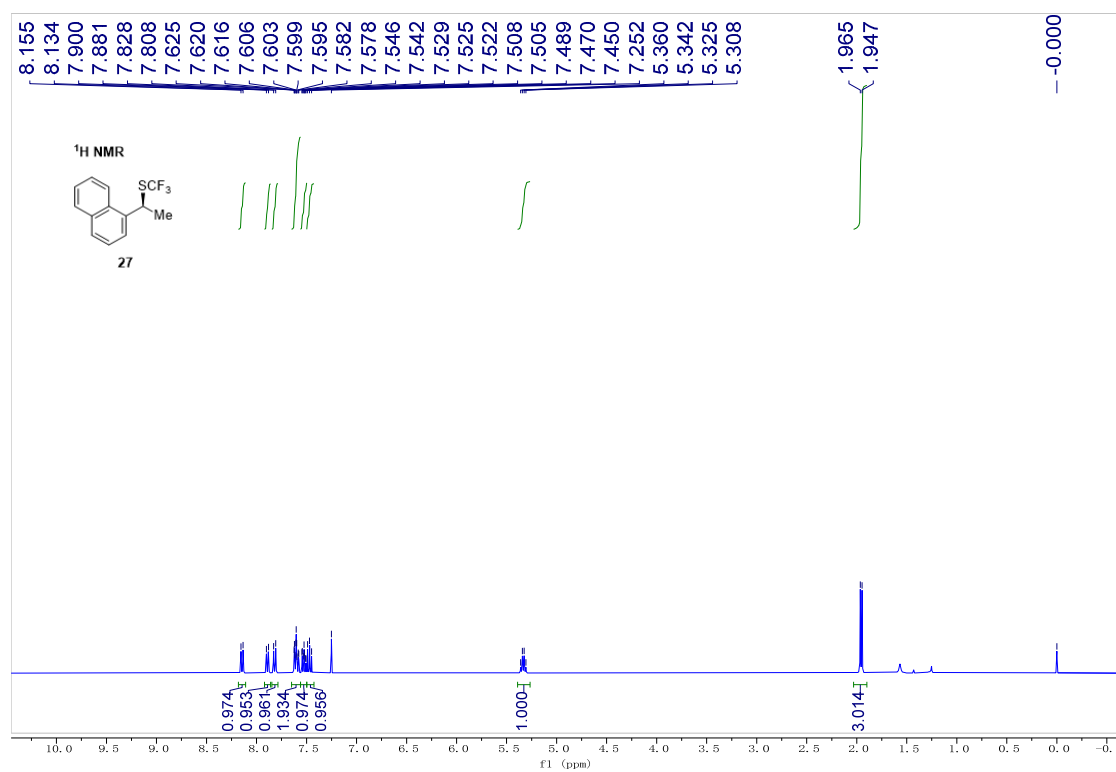


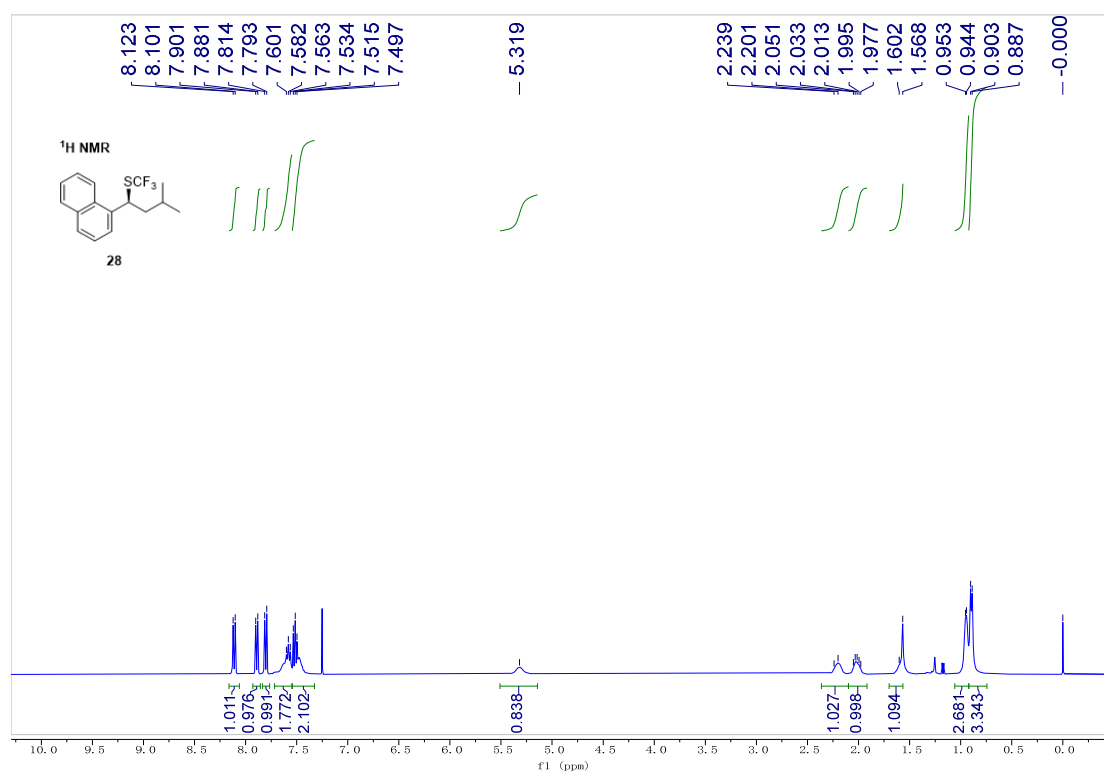
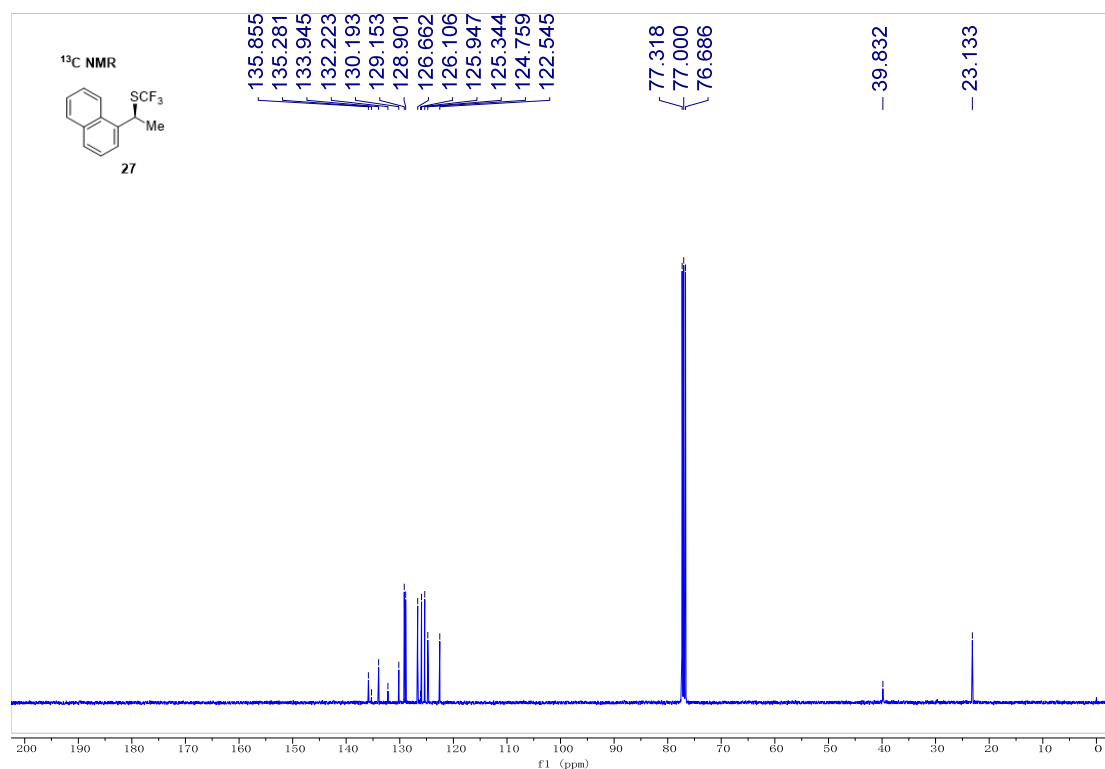


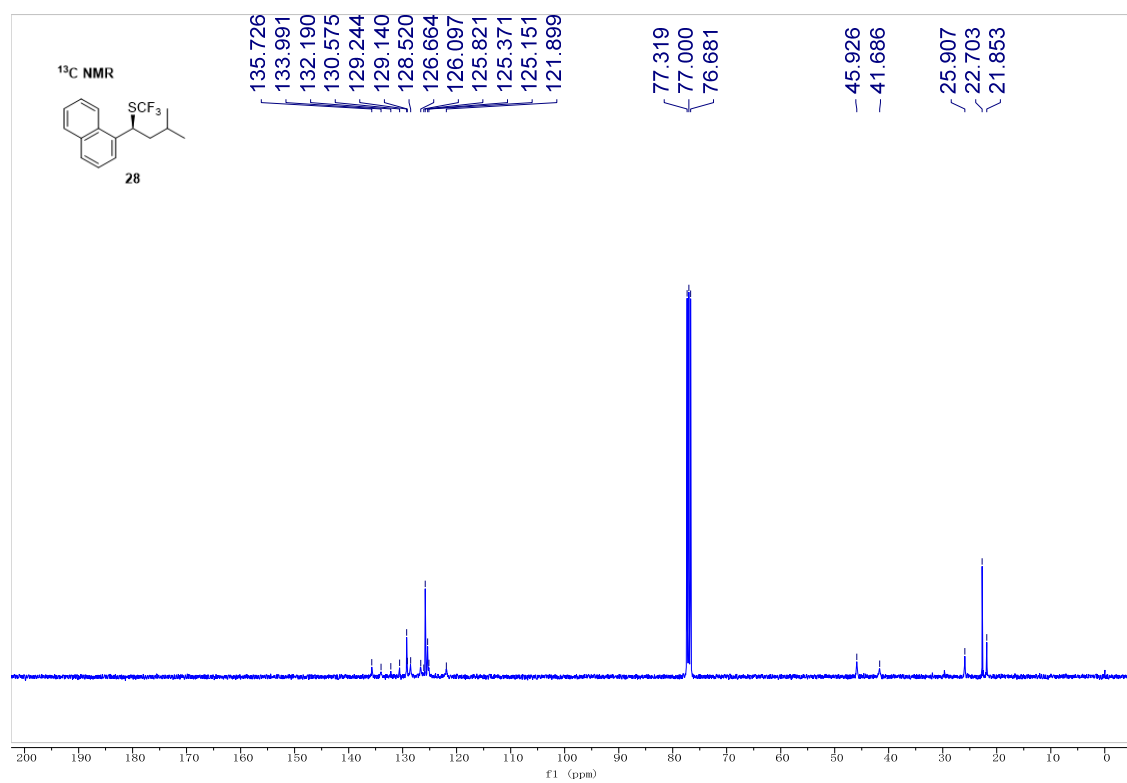
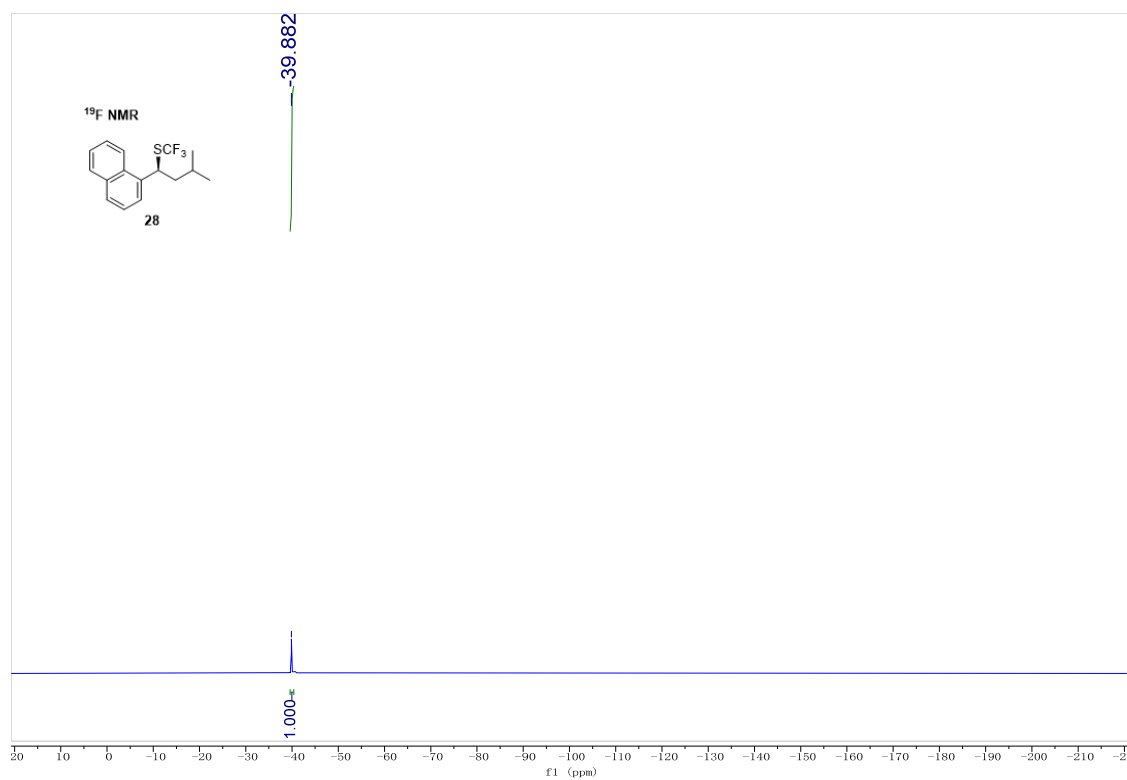


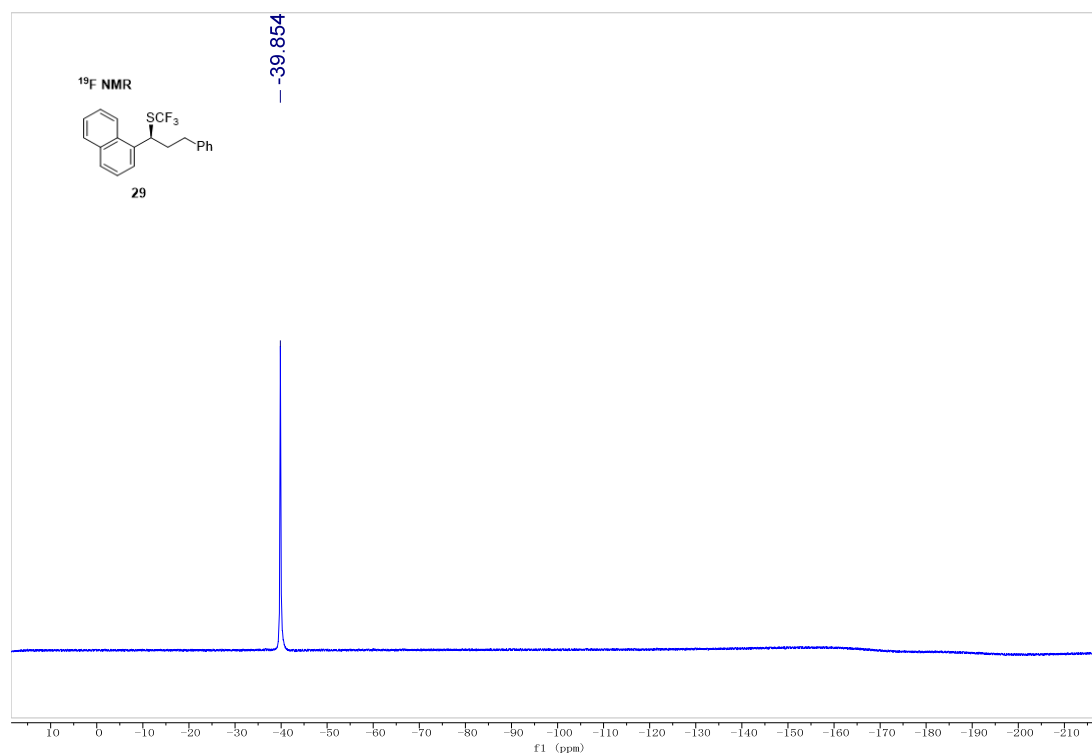
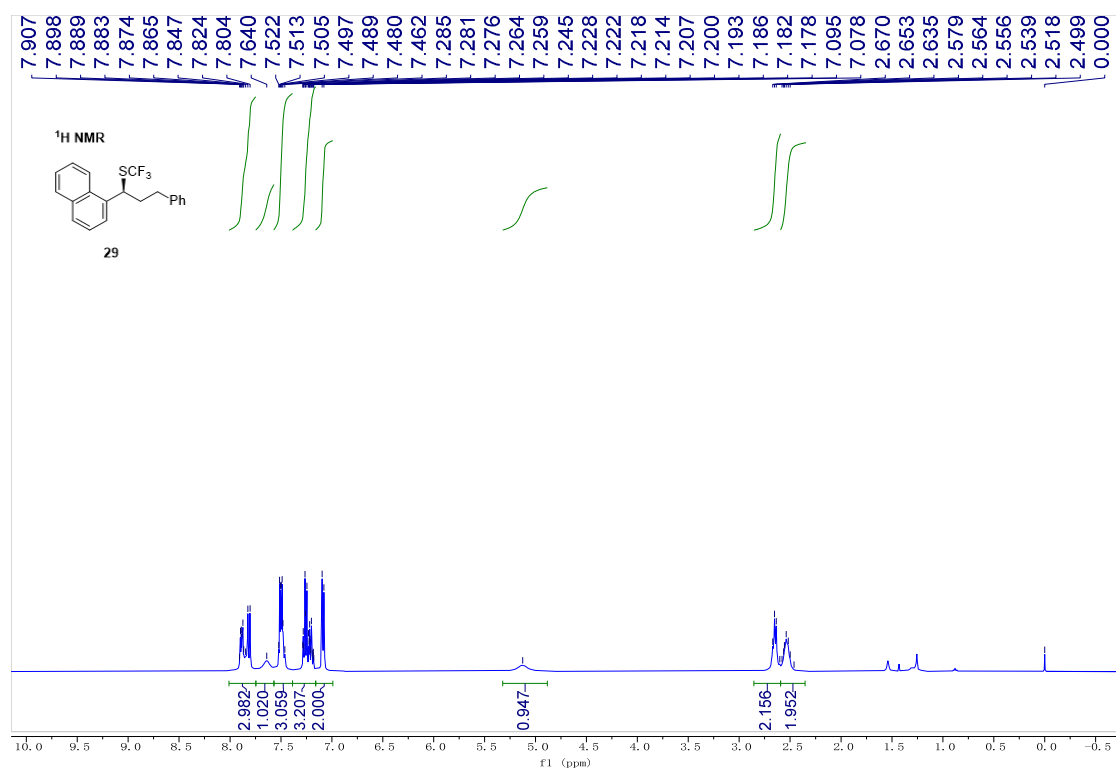


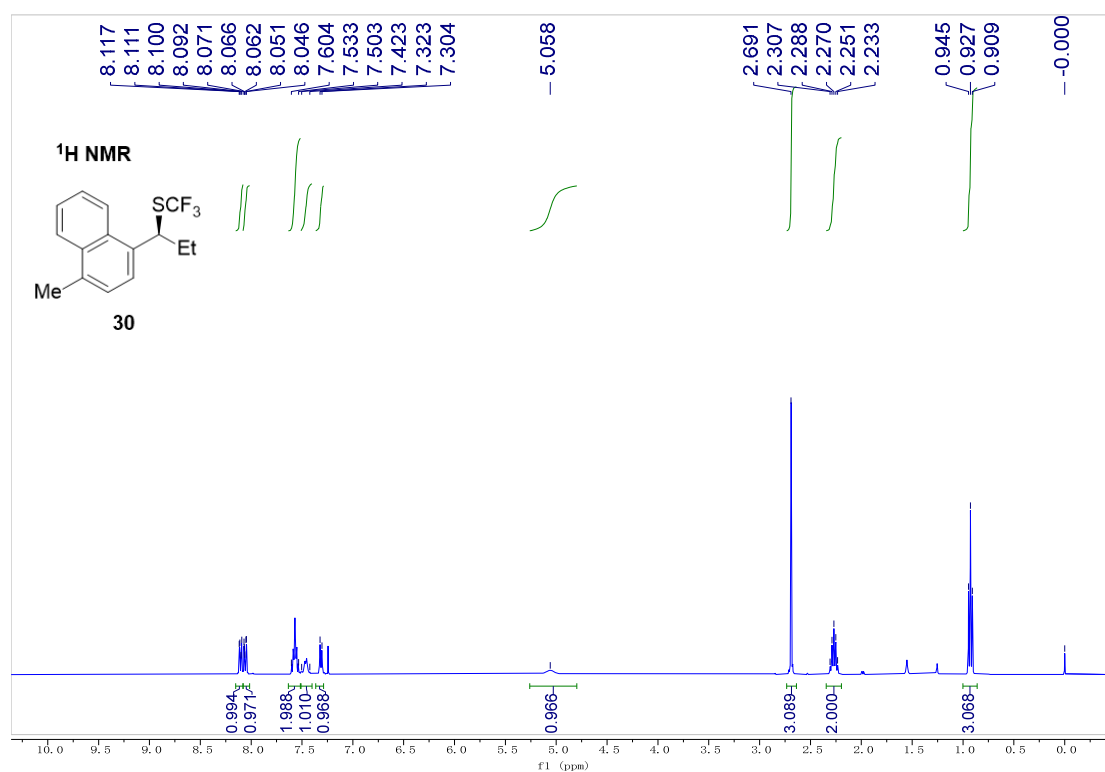
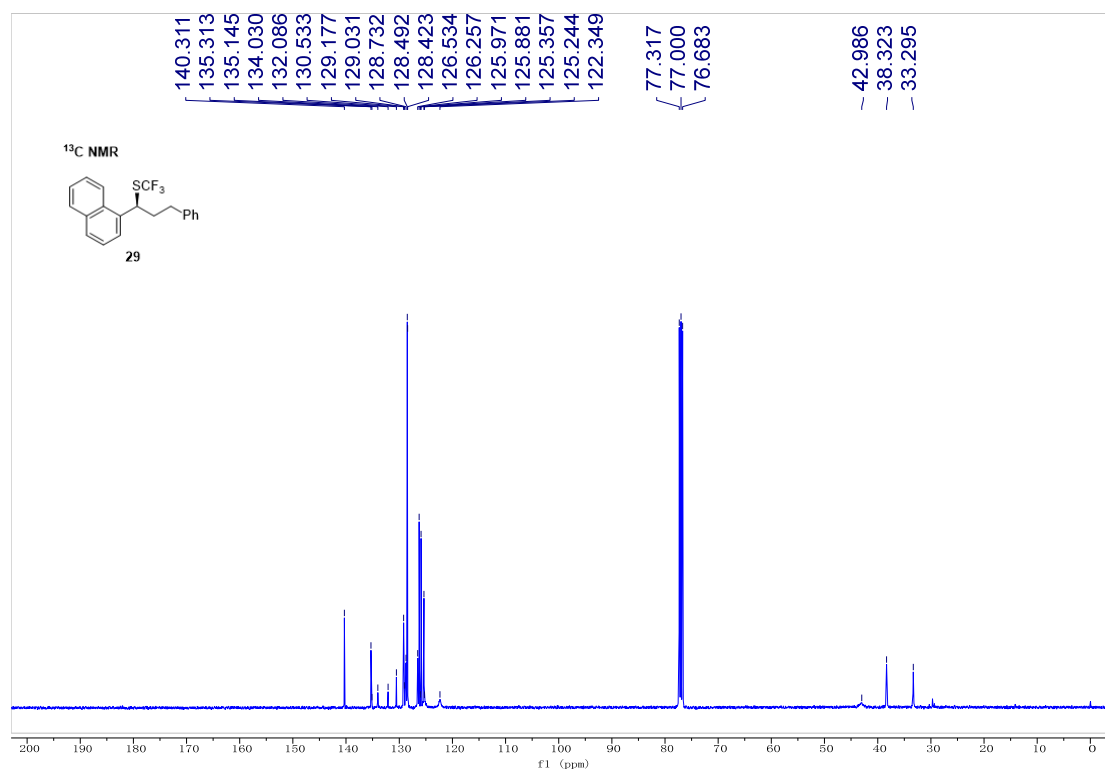


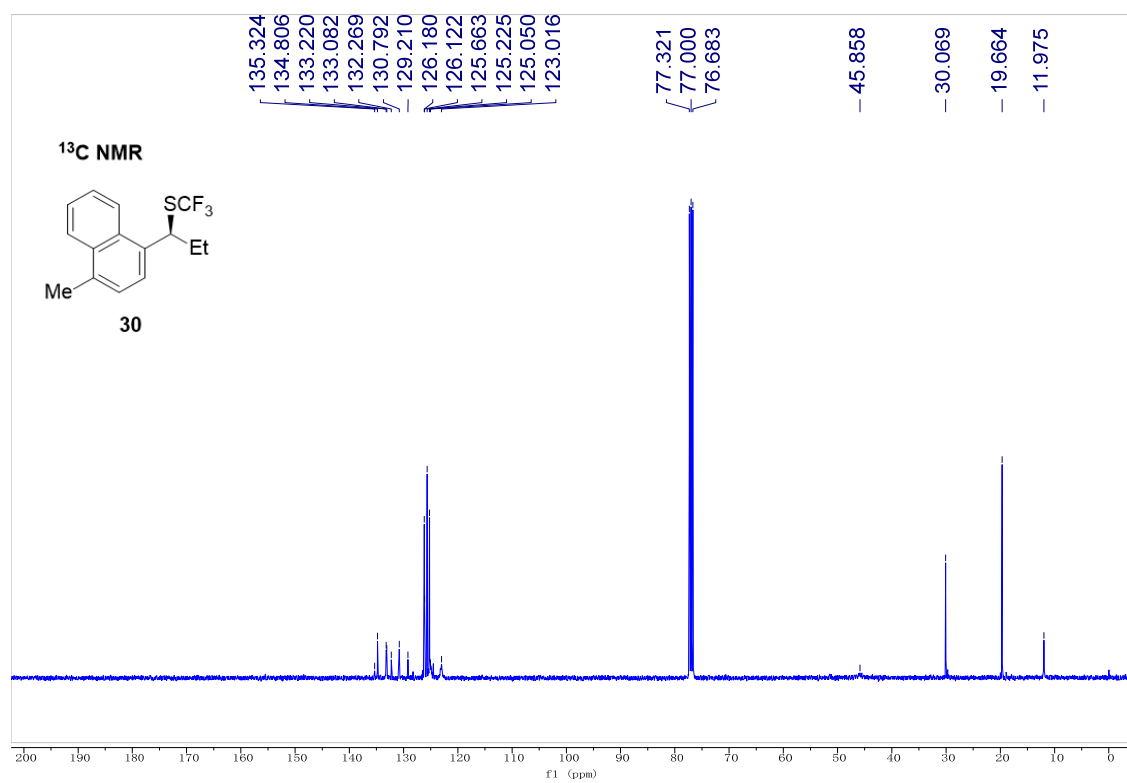
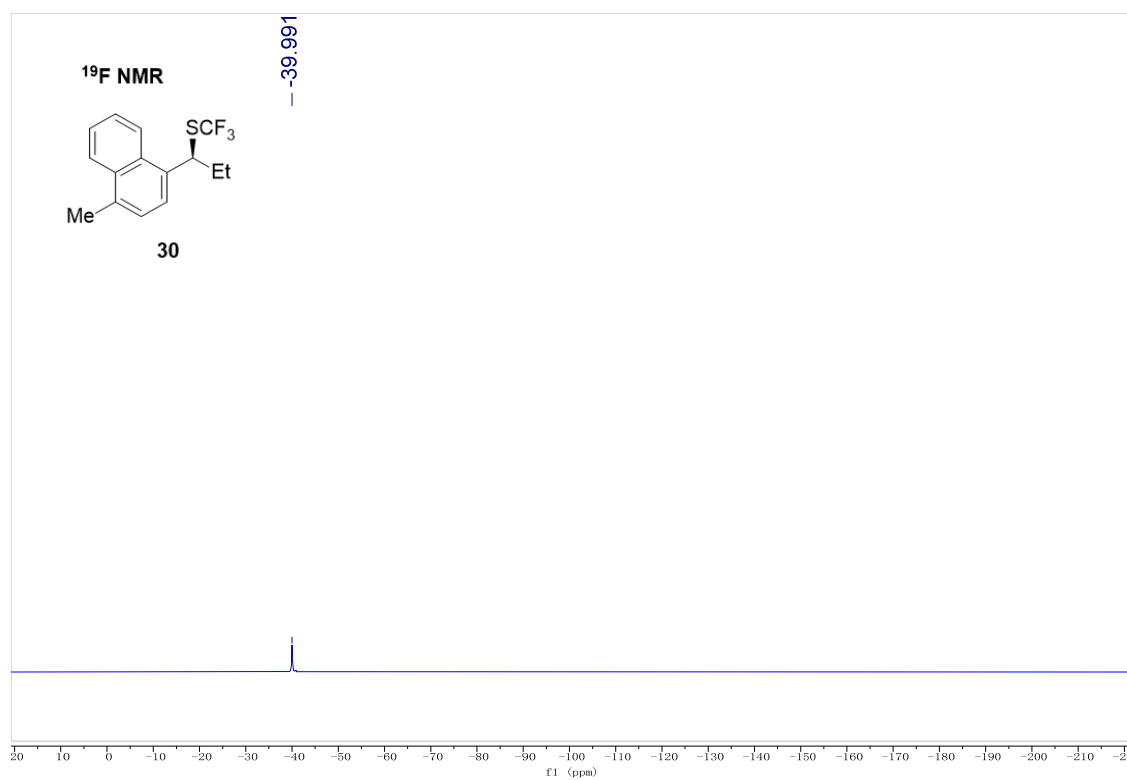


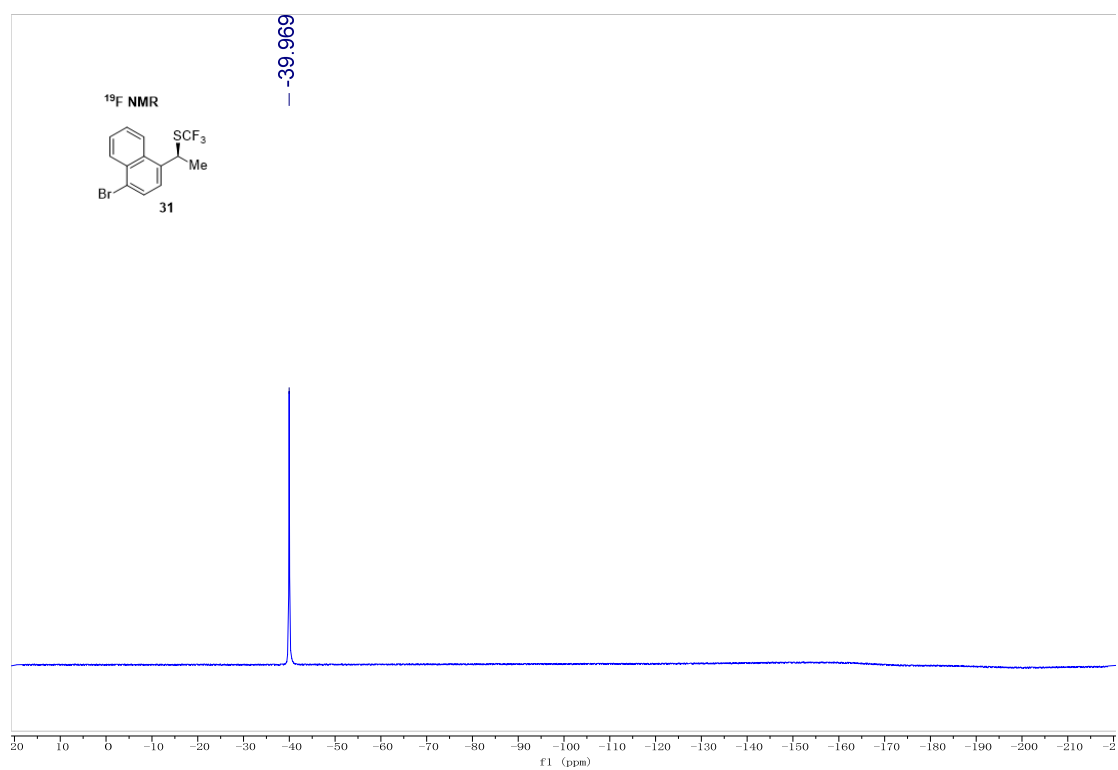
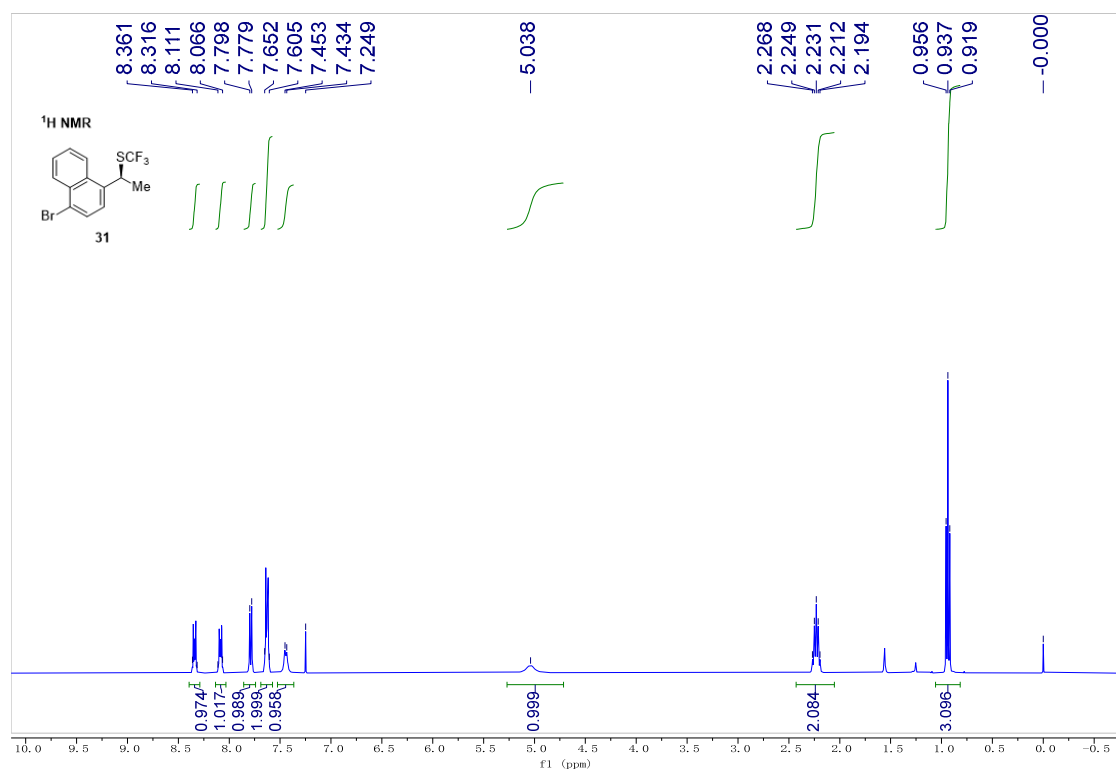


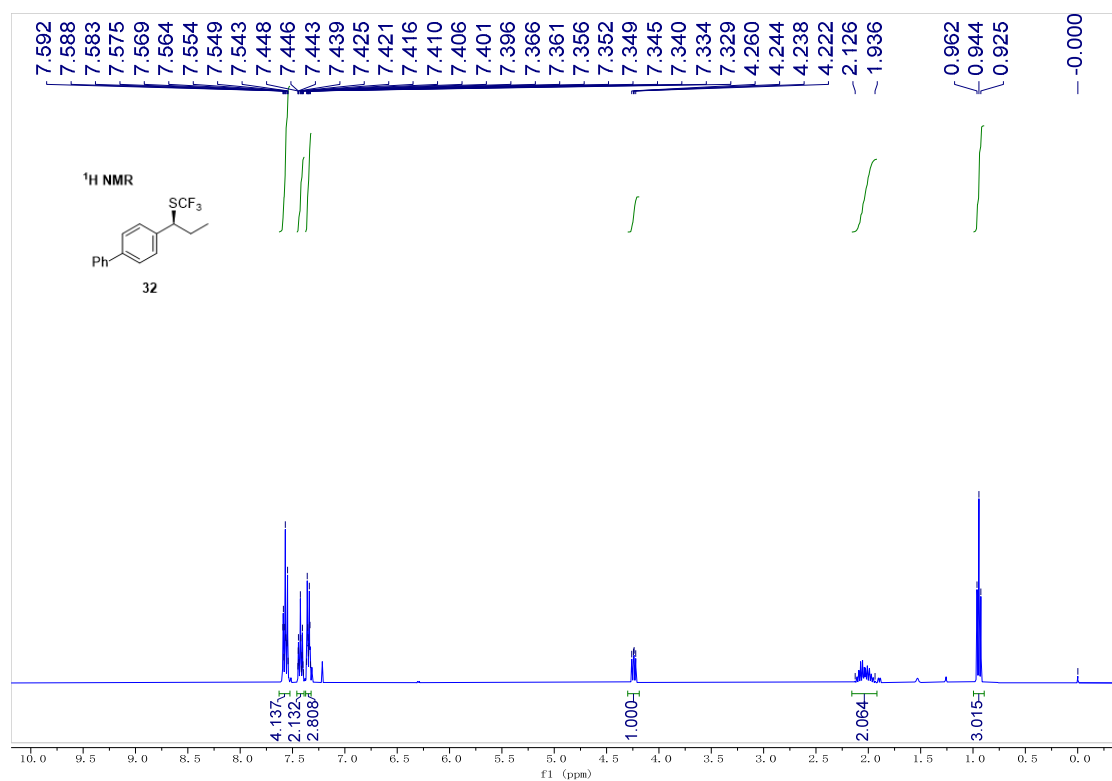
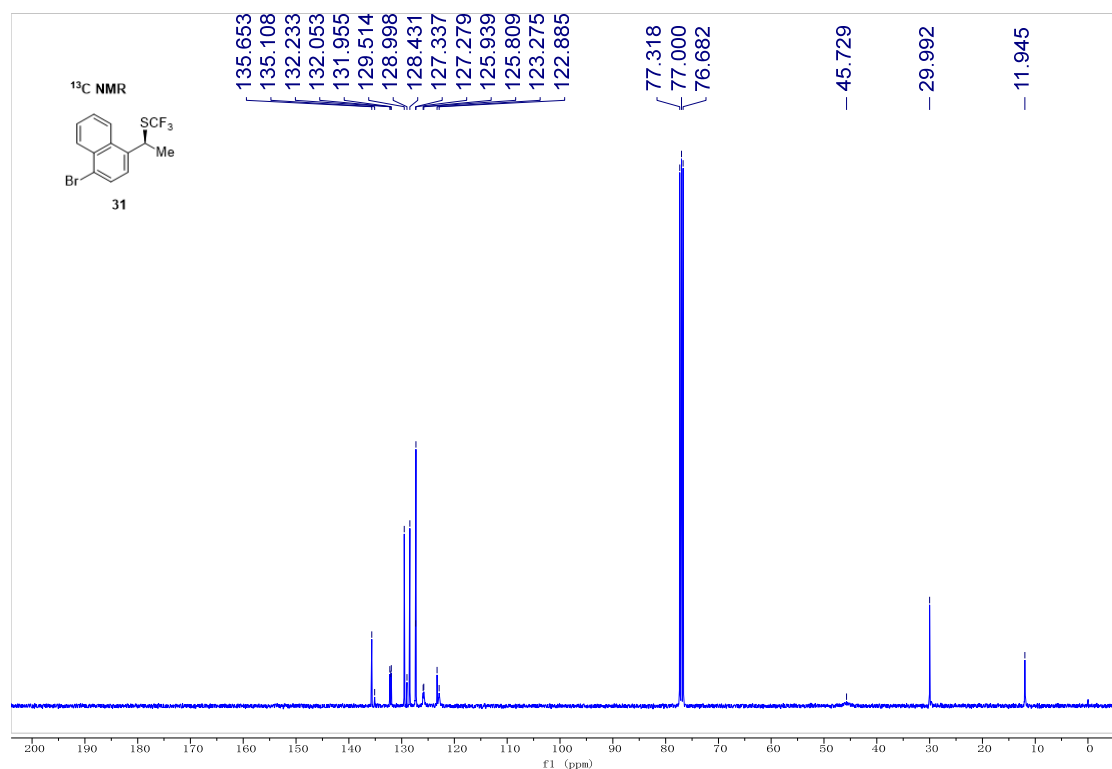


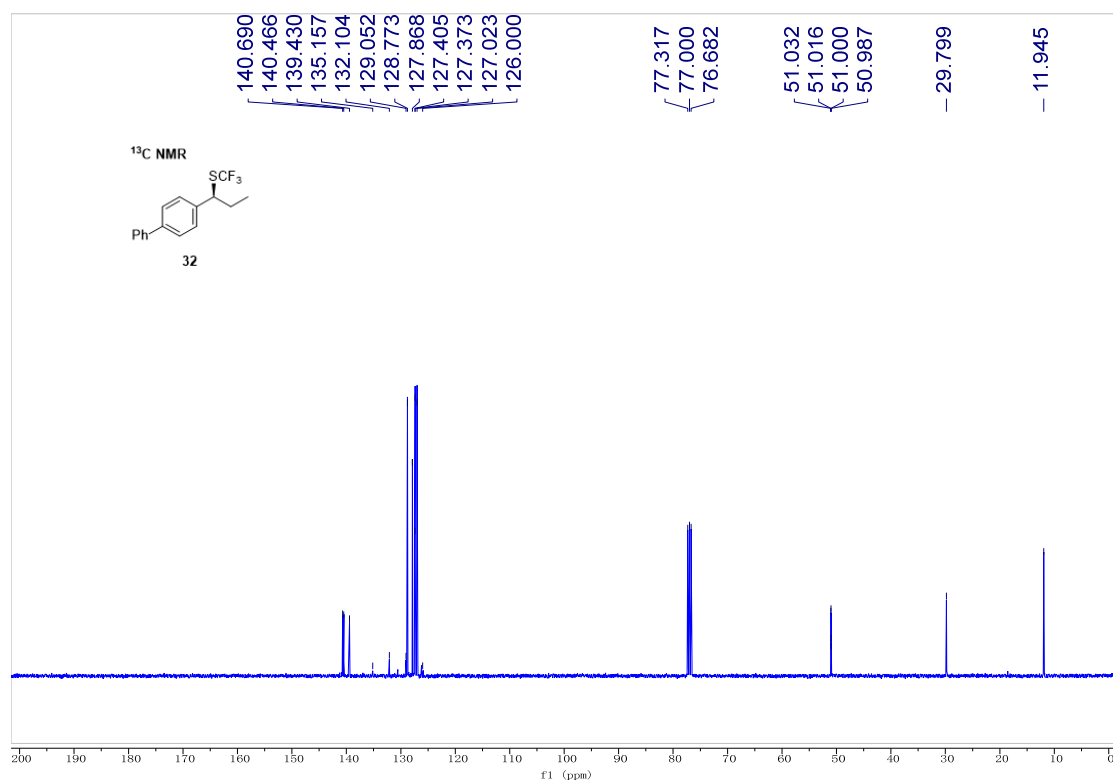
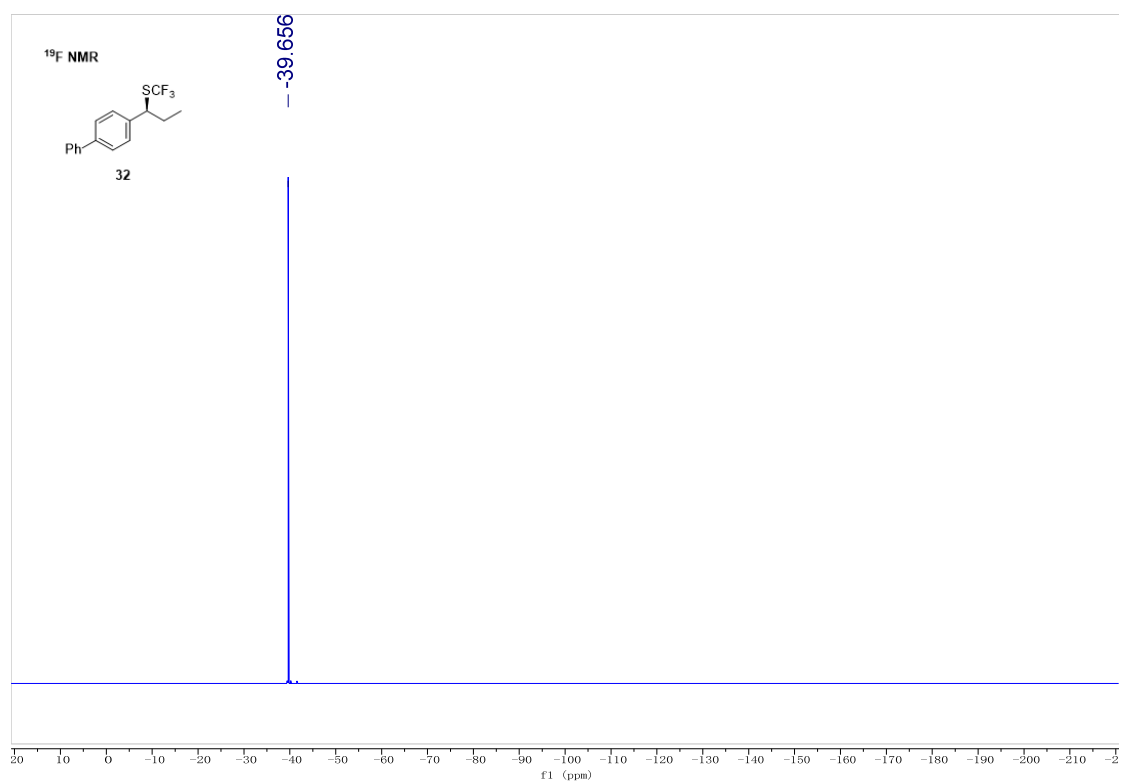


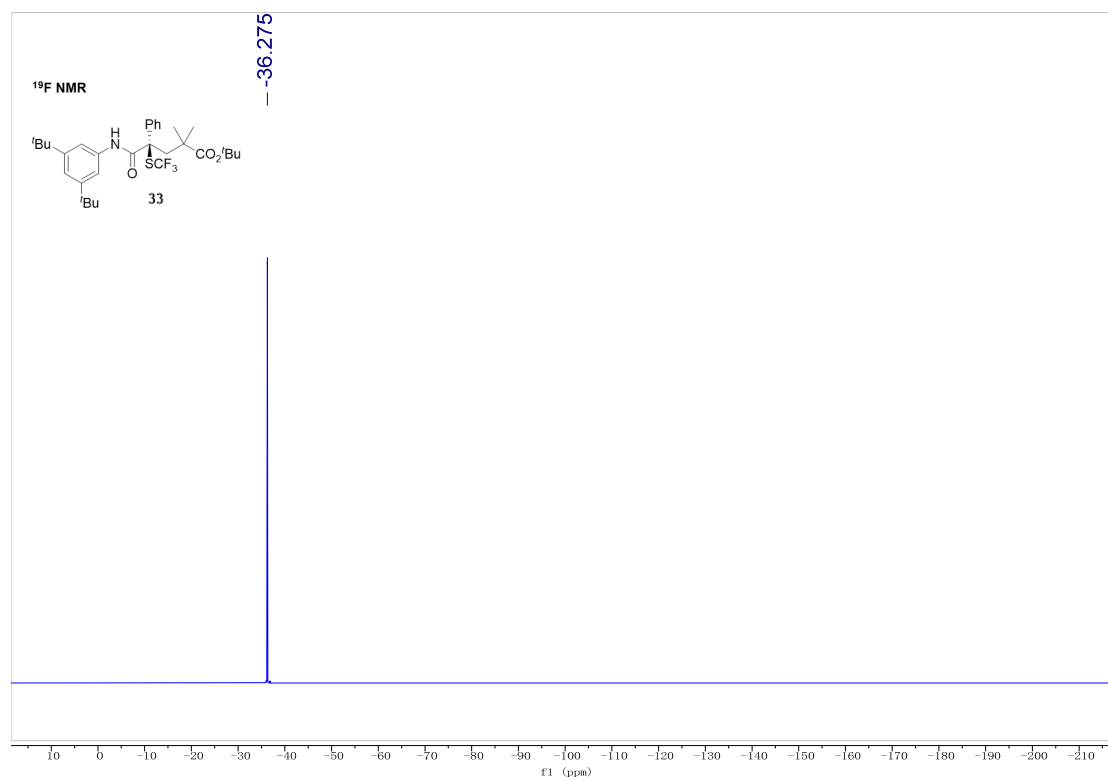
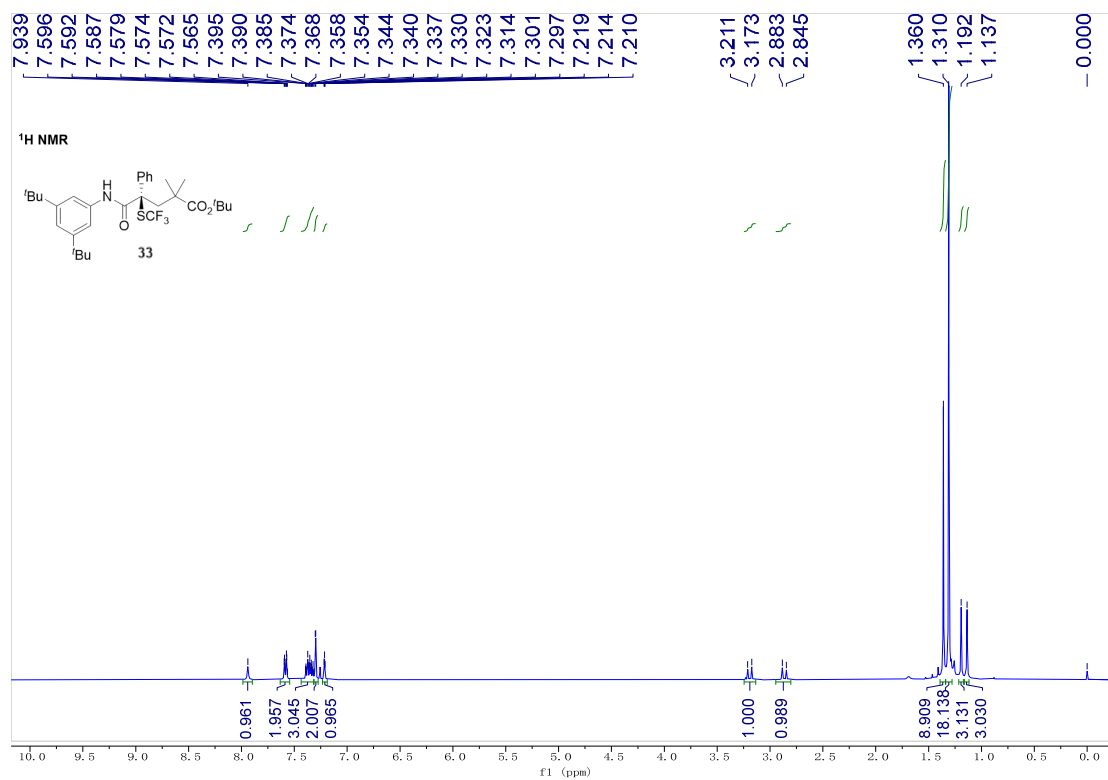


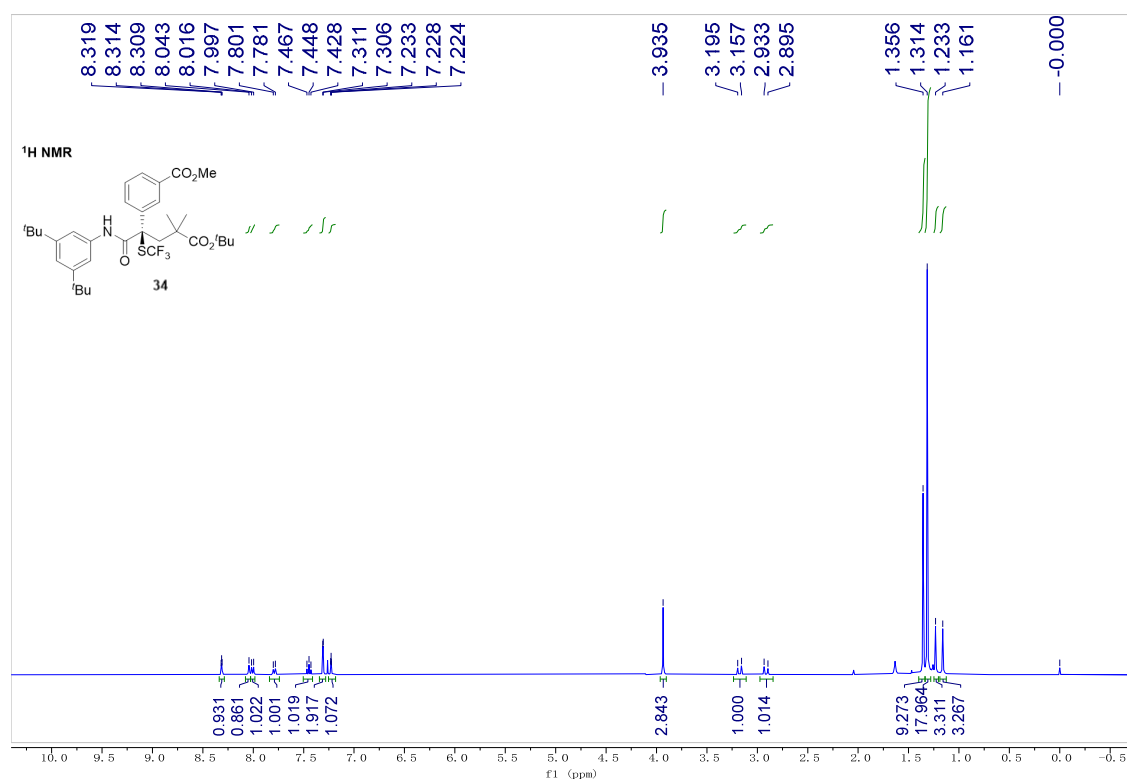
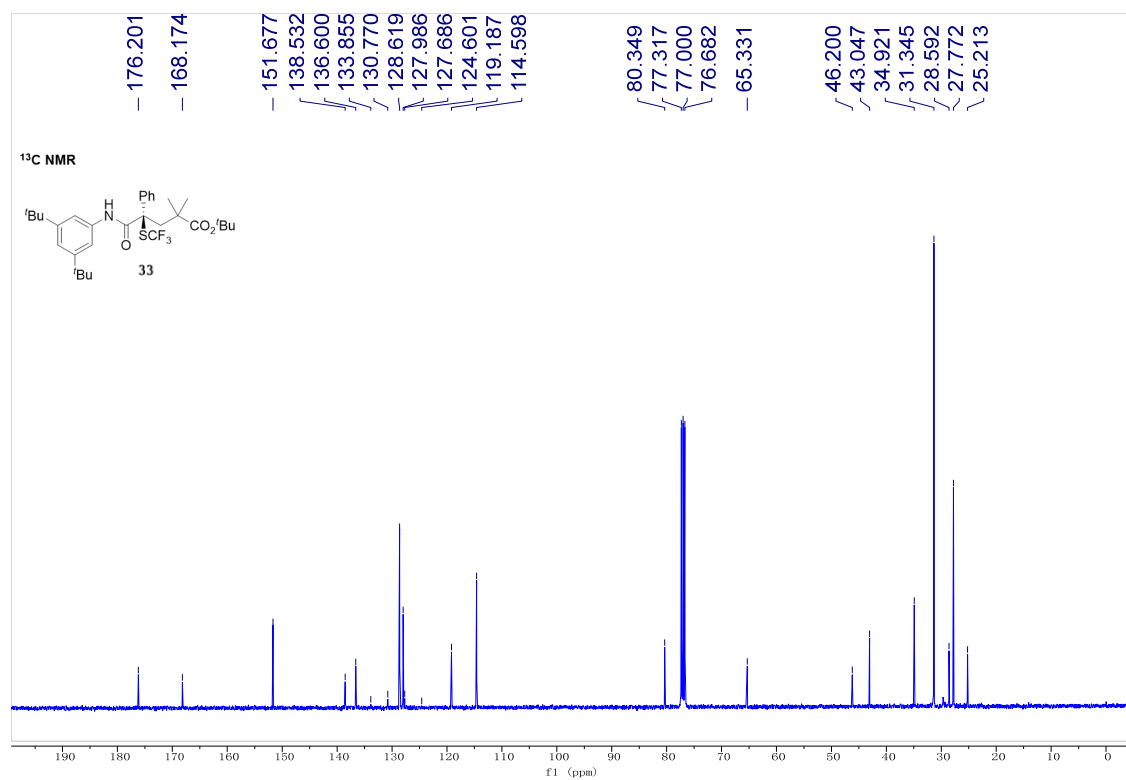


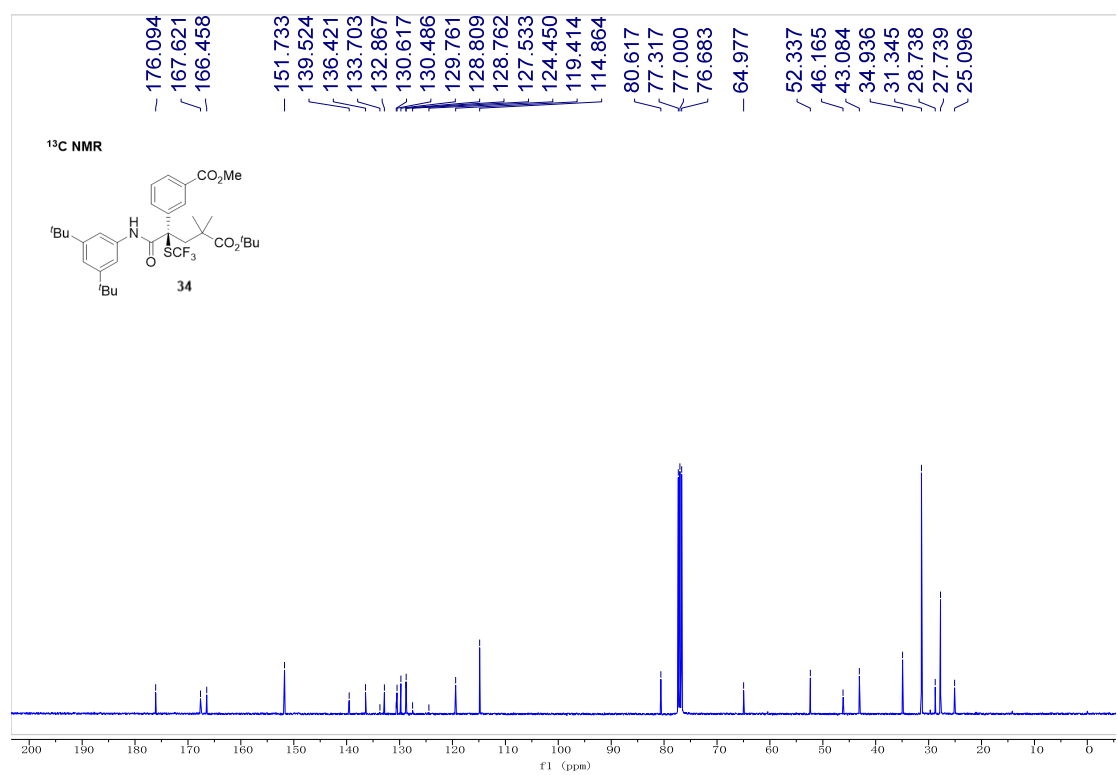
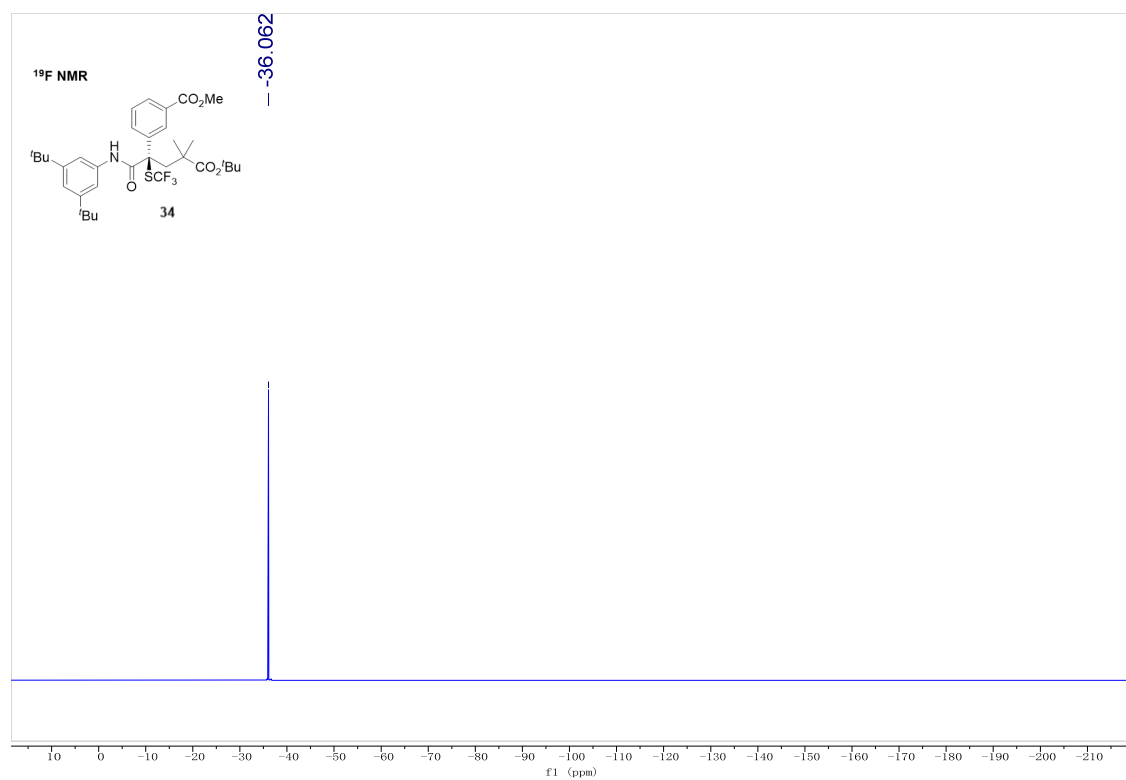


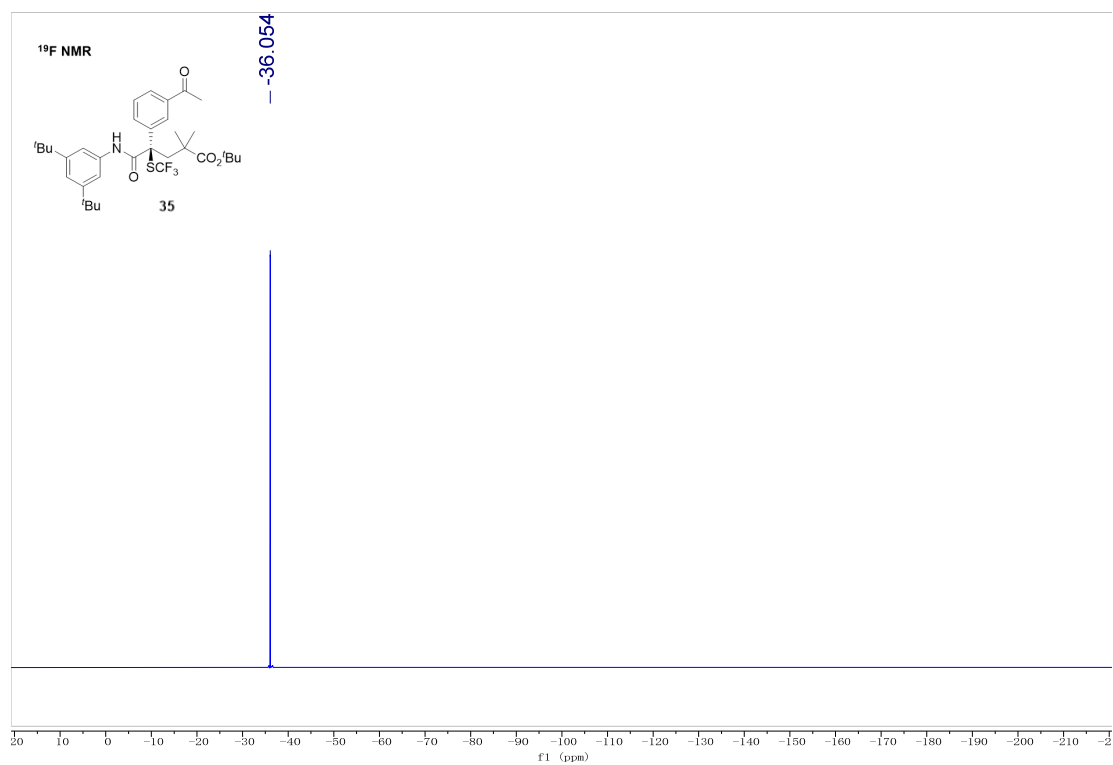
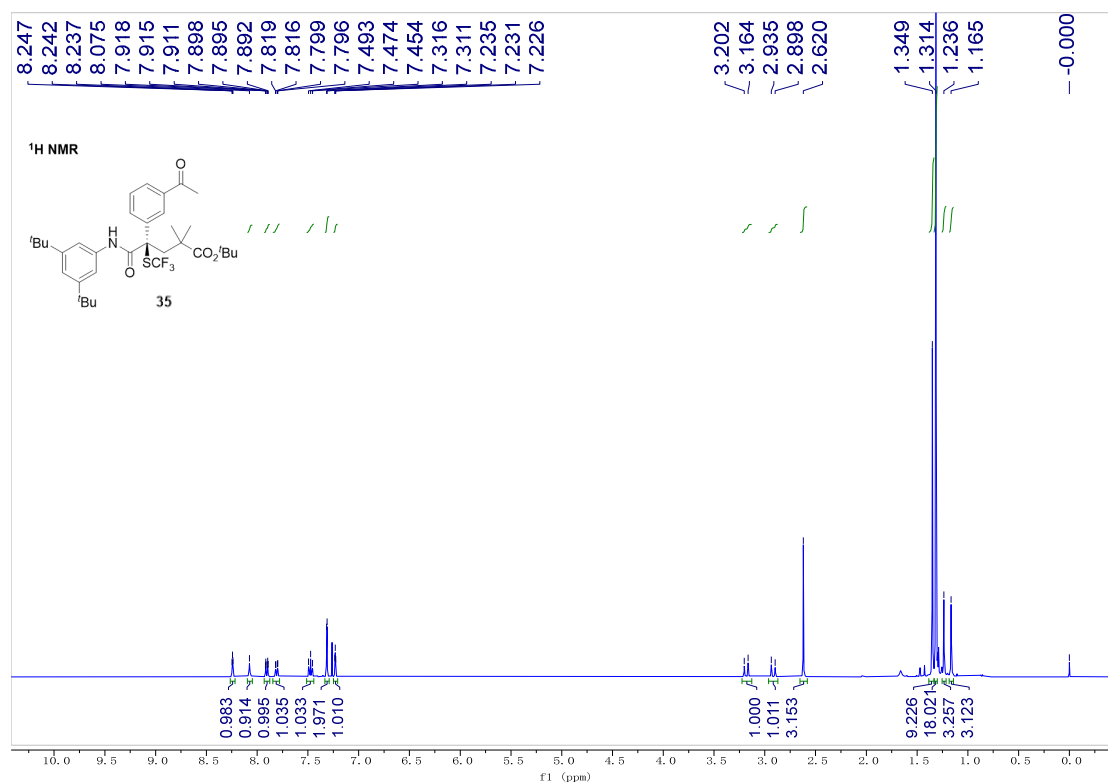


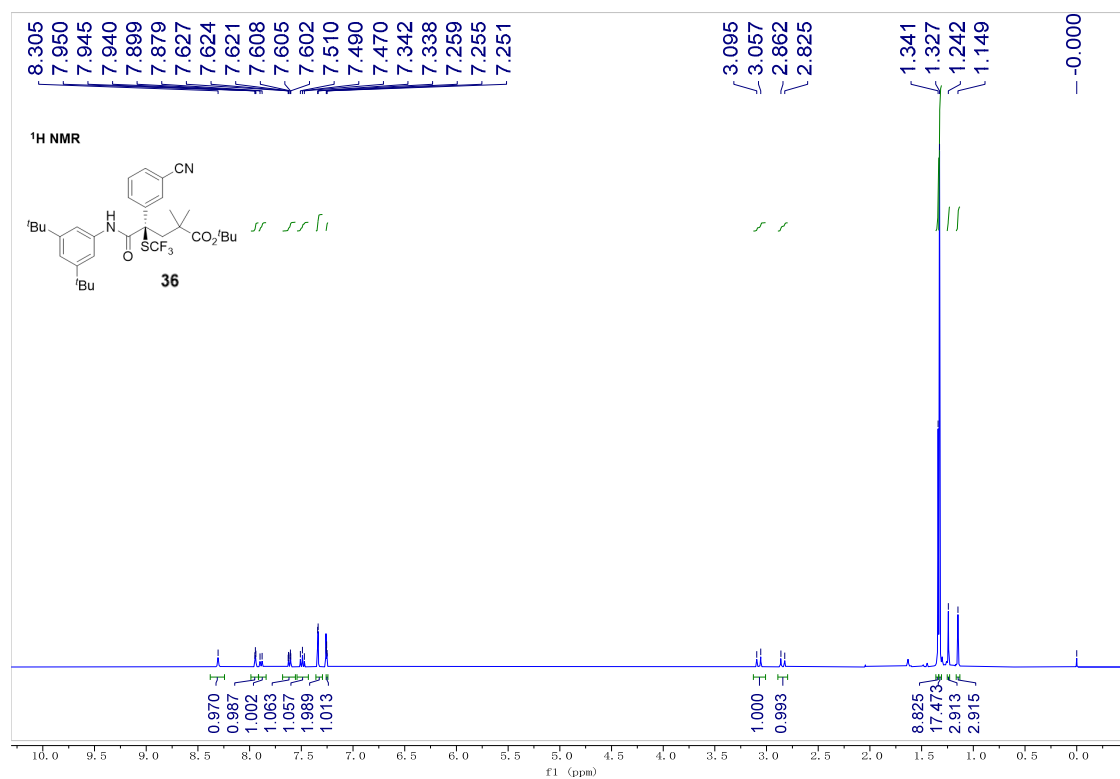
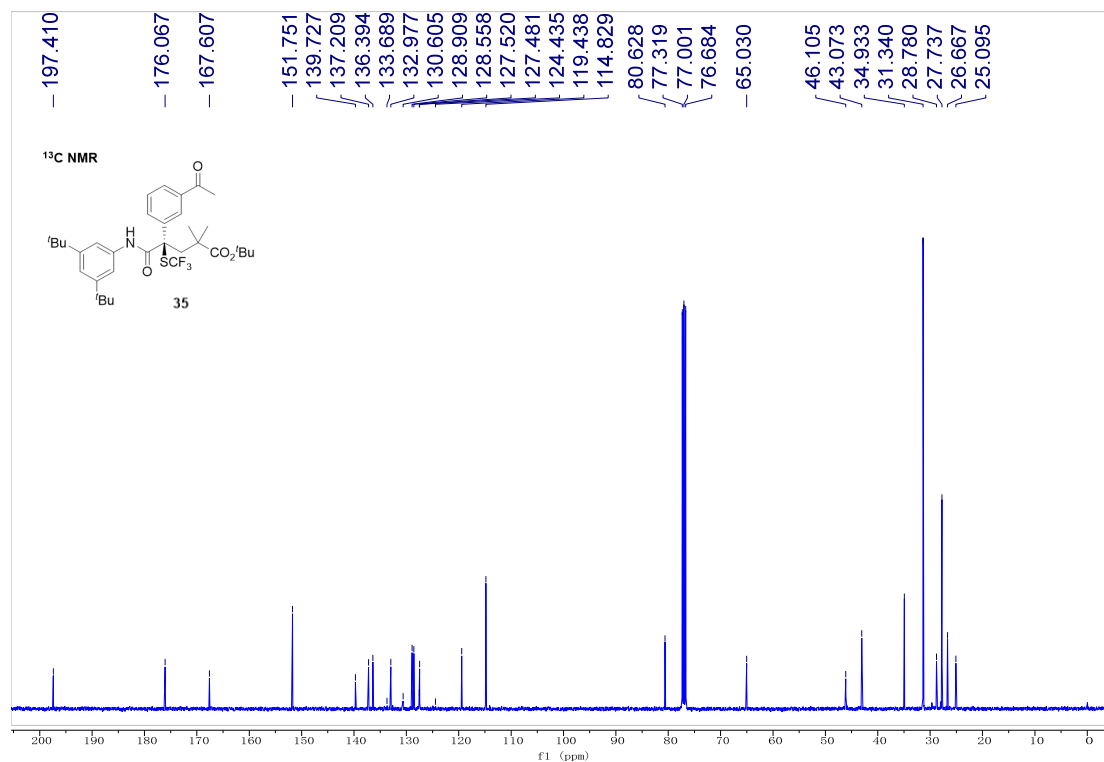


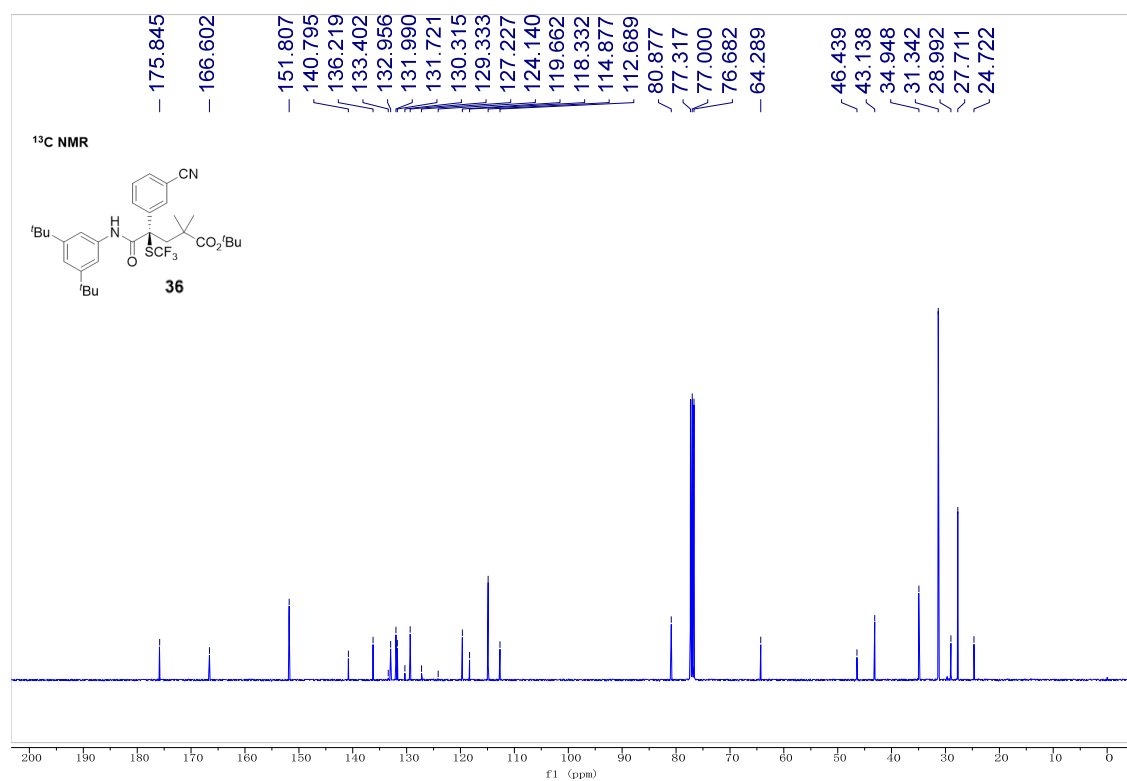
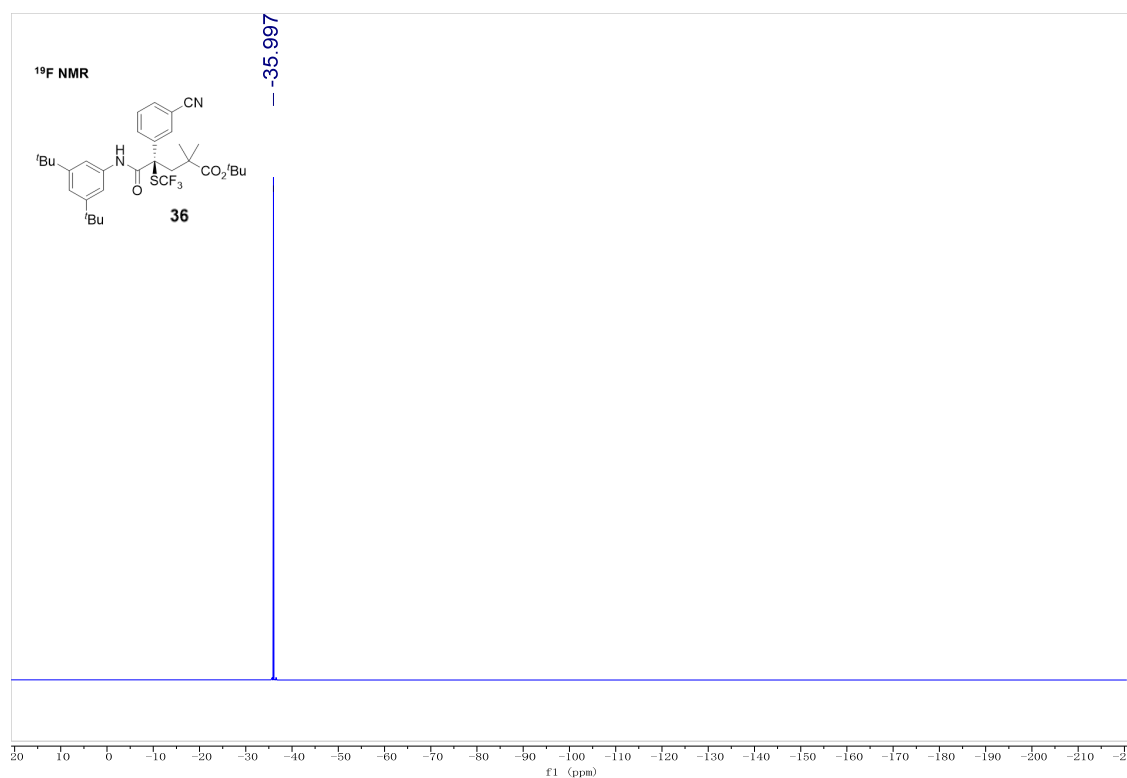


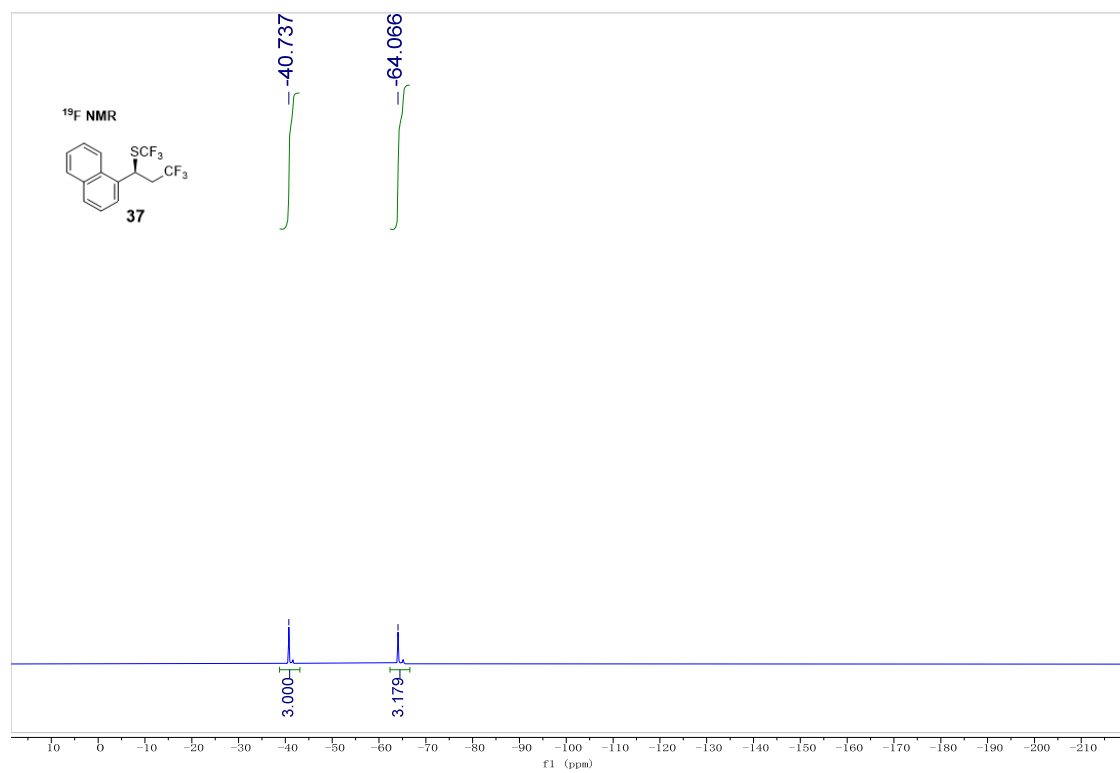
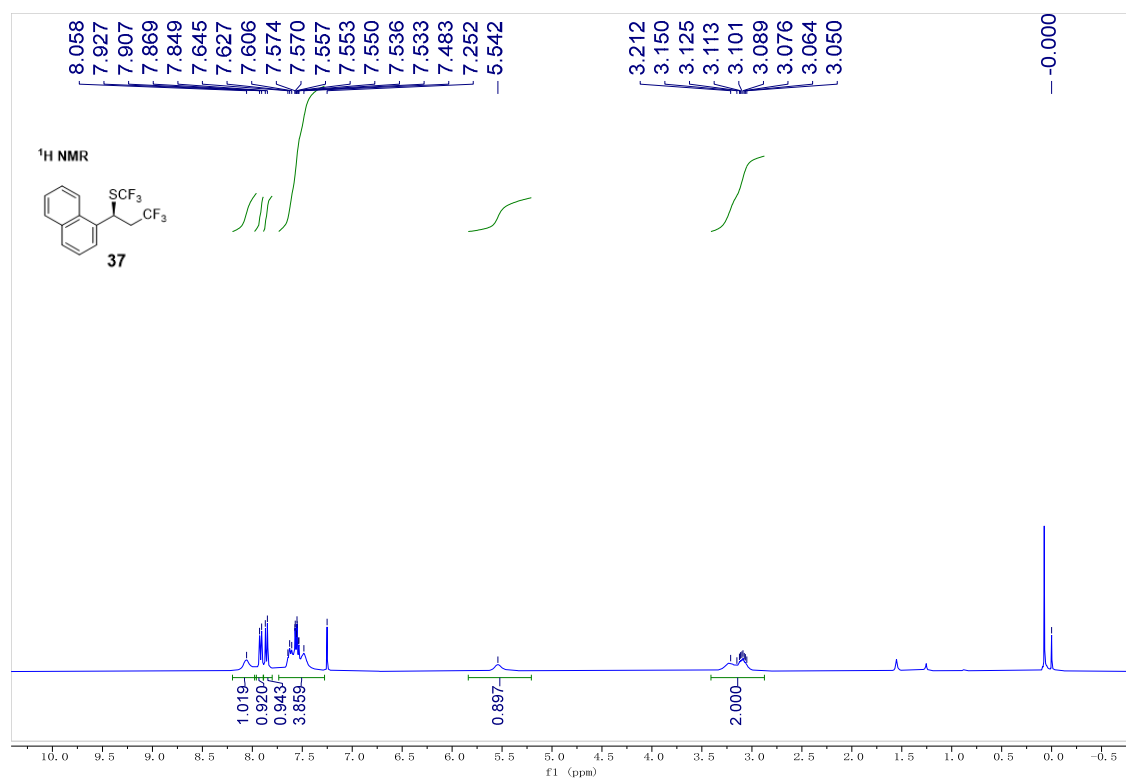


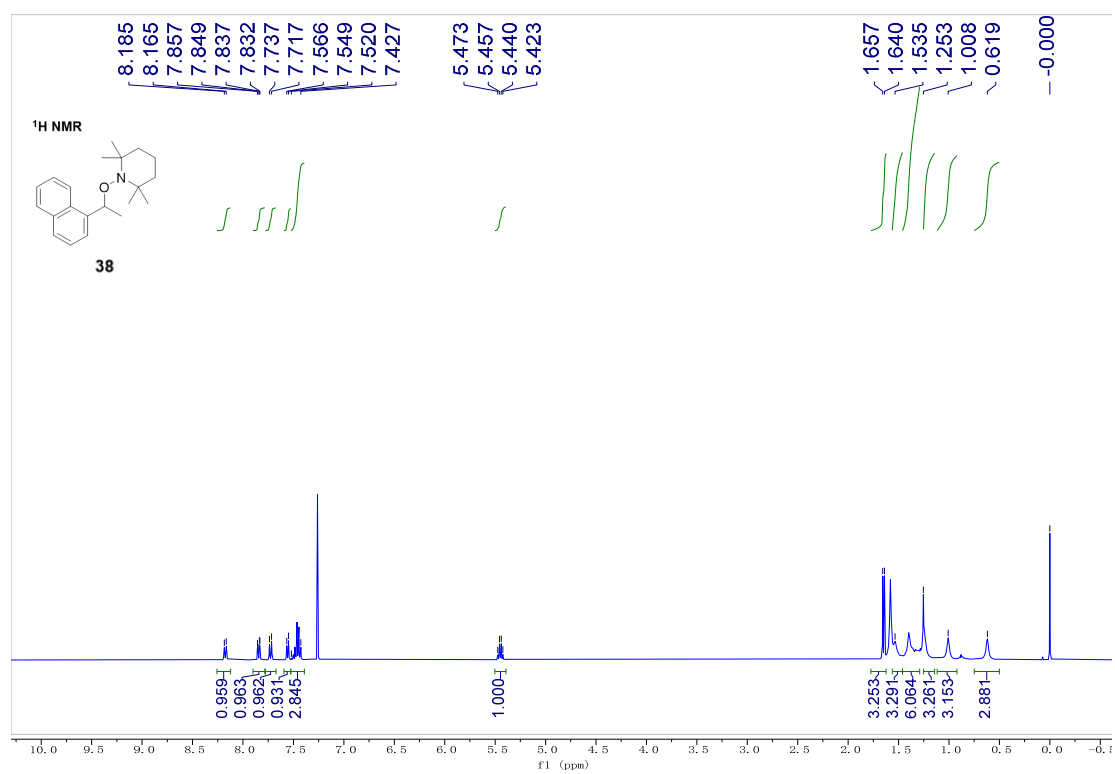
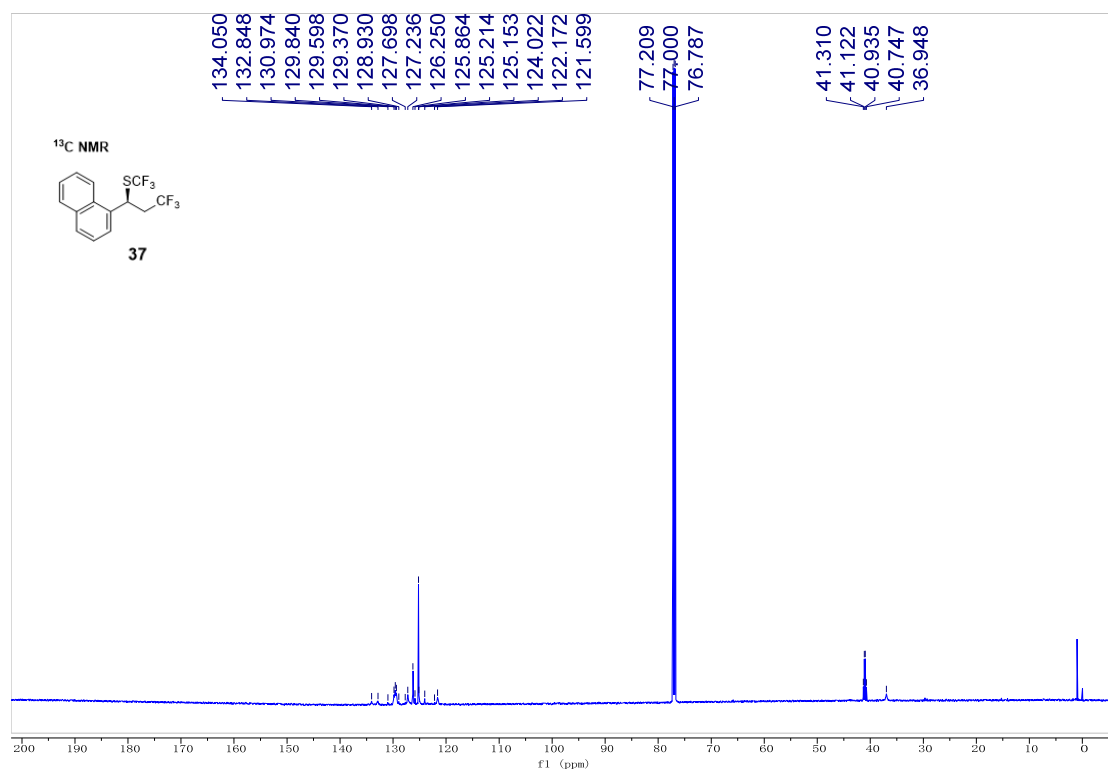


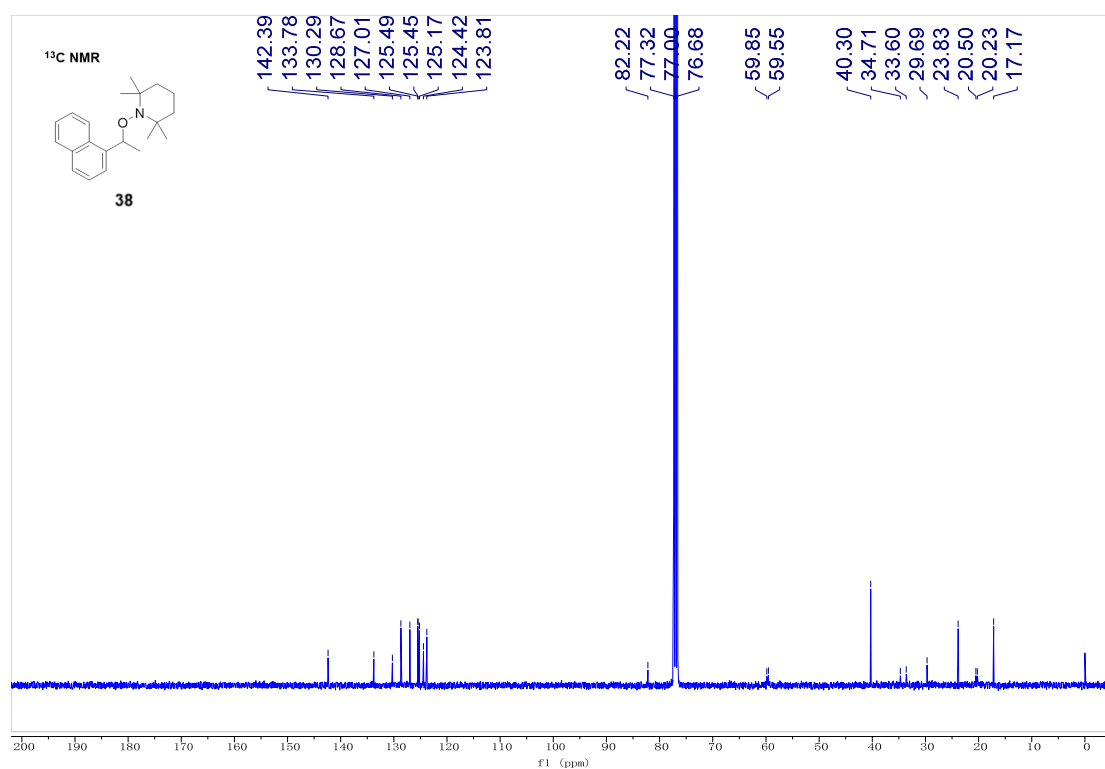




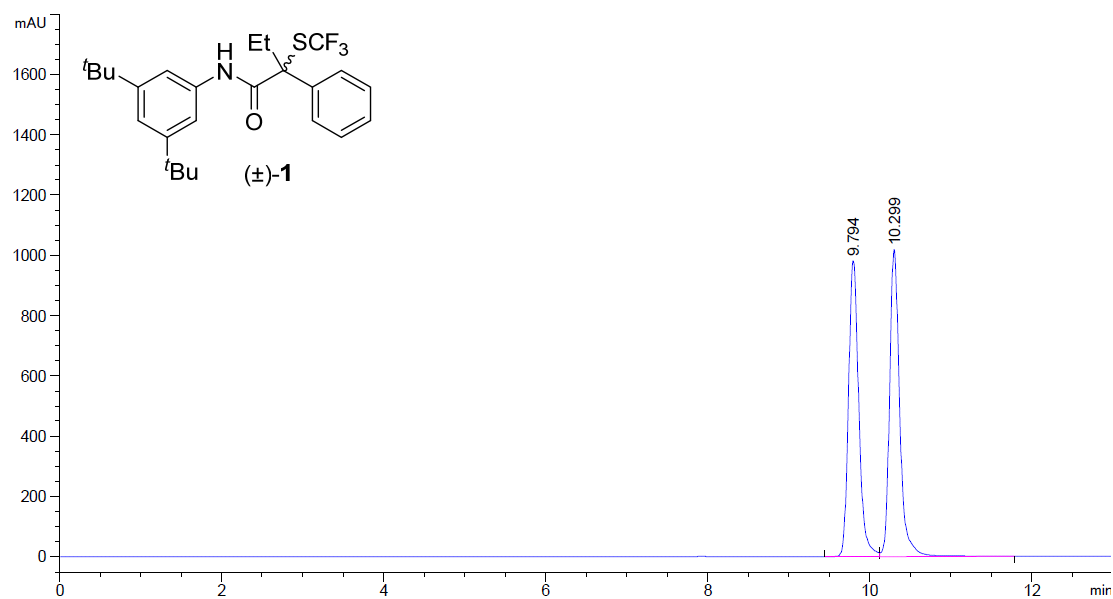






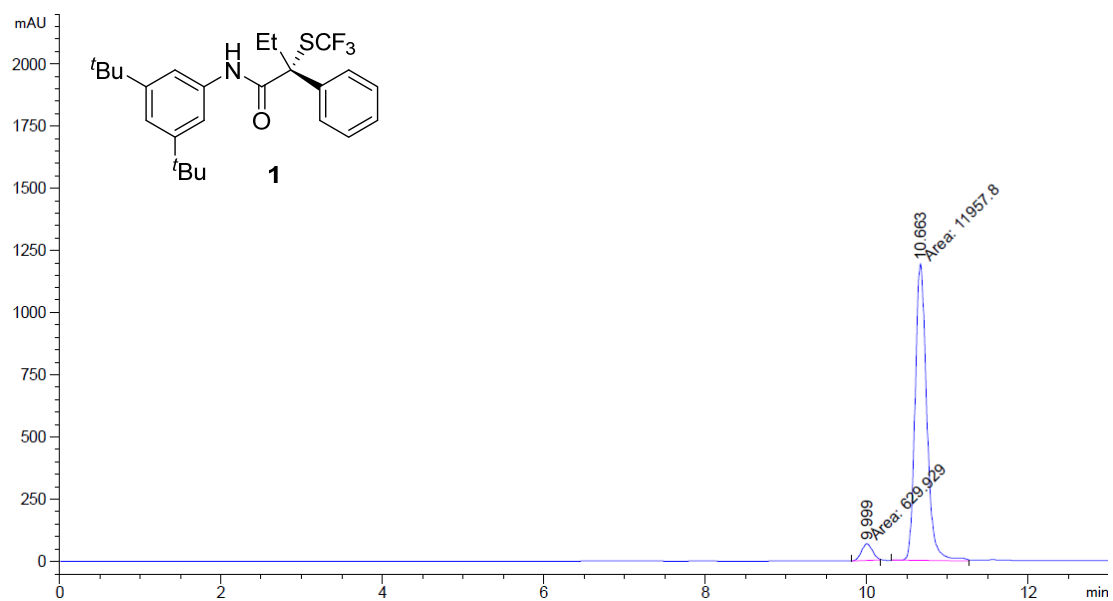


11. HPLC spectra of the products



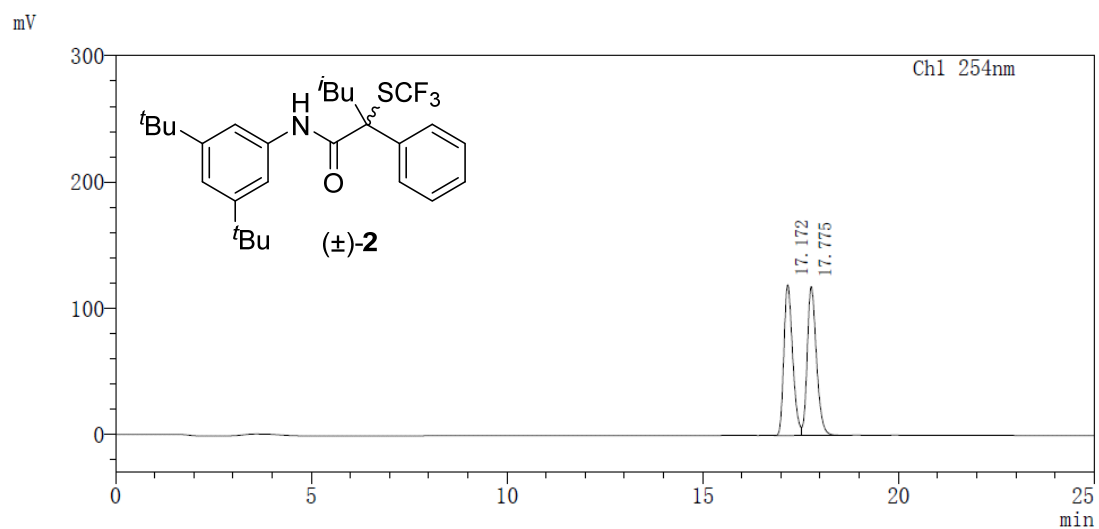
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

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

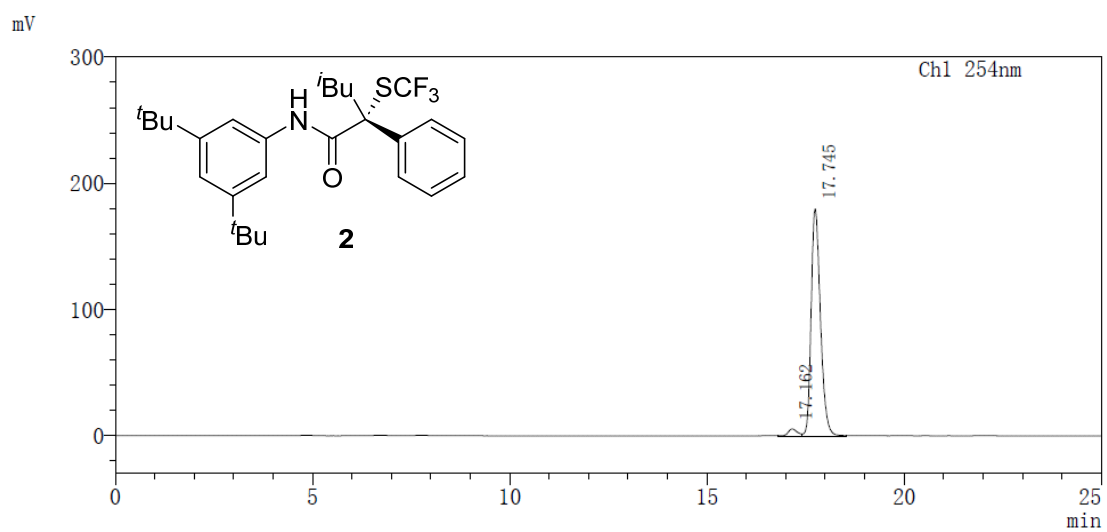
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.999	MM	0.1577	629.92908	66.58321	5.0043
2	10.663	MM	0.1672	1.19578e4	1191.62732	94.9957



Peak Table

Ch1 254nm

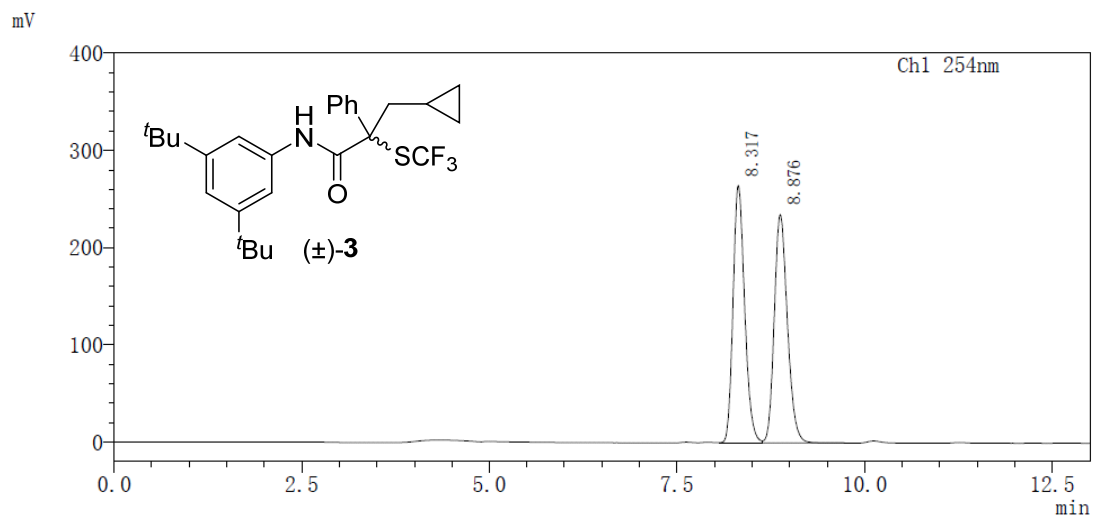
Peak#	Ret. Time	Area	Area%
1	17.172	1865258	49.052
2	17.775	1937337	50.948



Peak Table

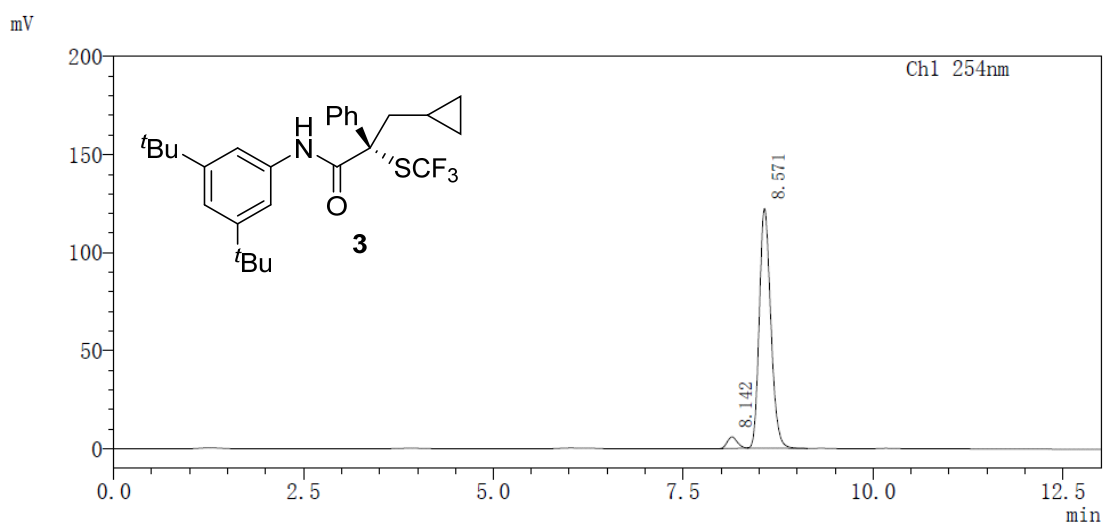
Ch1 254nm

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



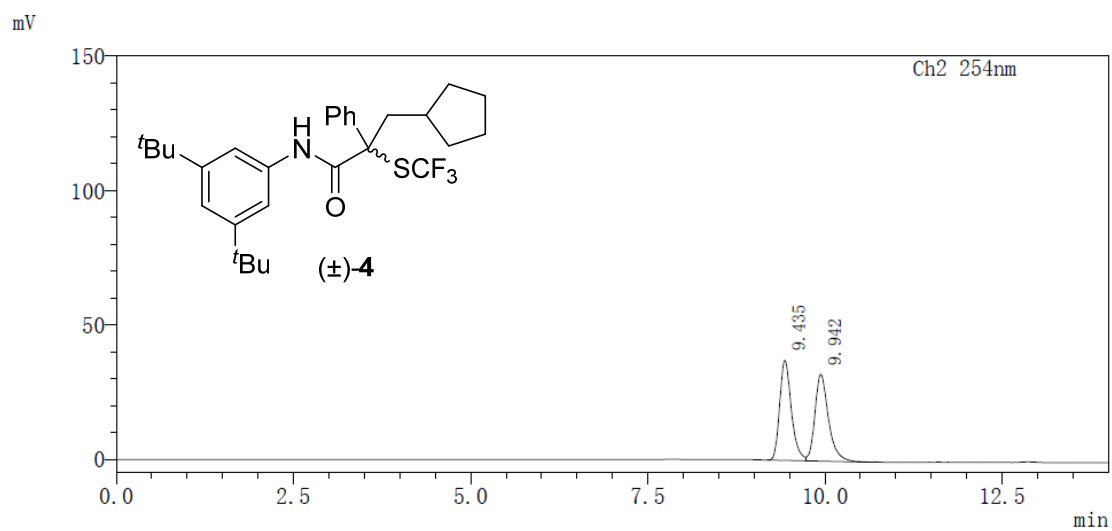
Ch1 254nm

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



Ch1 254nm

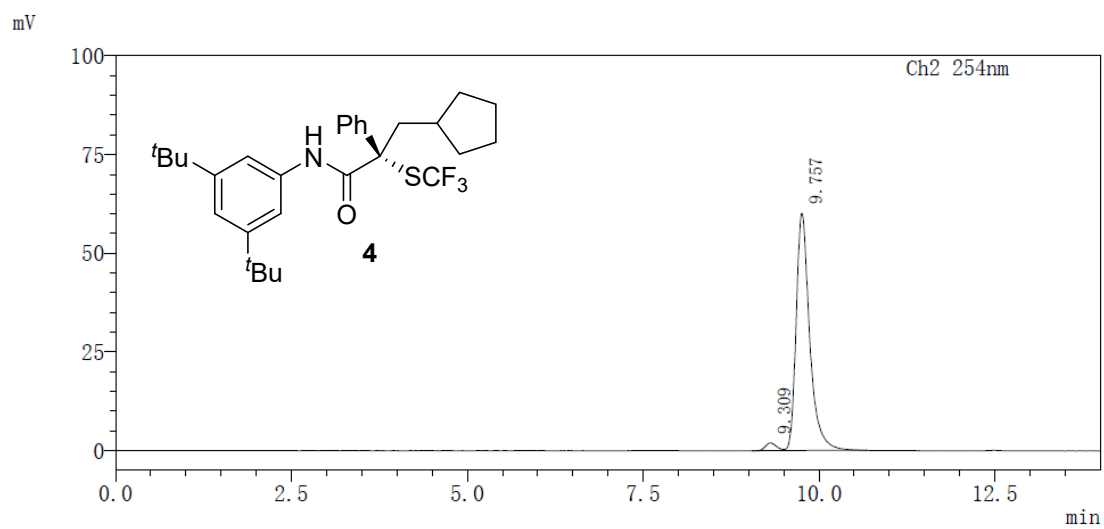
T	Hight	Area	Area%
8.142	5775	52845	3.945
8.571	122196	1286541	96.055



Peak Table

Ch2 254nm

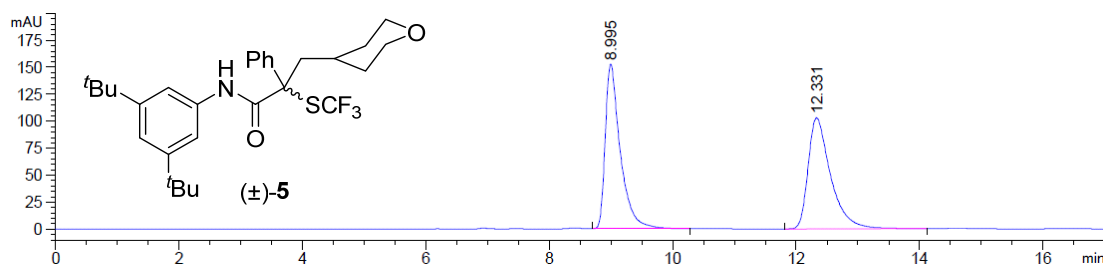
Peak#	Ret. Time	Area	Area%
1	9.435	427612	49.828
2	9.942	430557	50.172



Peak Table

Ch2 254nm

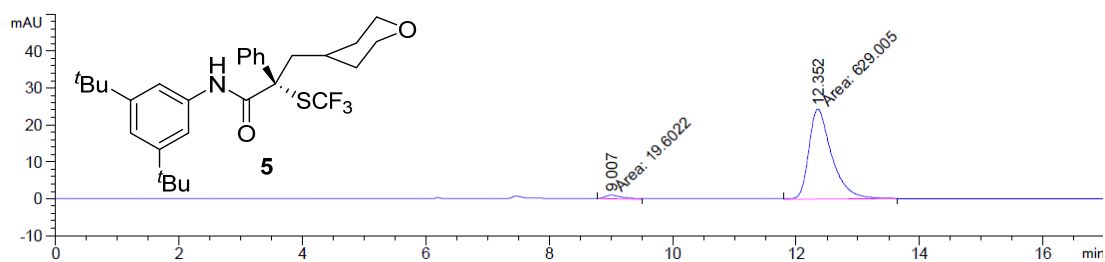
Peak#	Ret. Time	Area	Area%
1	9.309	21521	2.601
2	9.757	805925	97.399



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

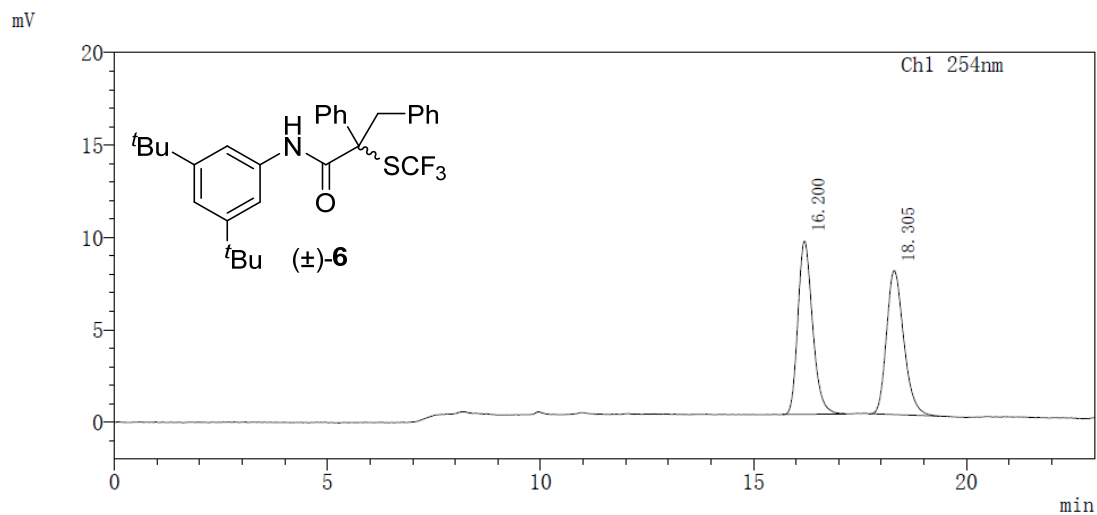
Totals : 5173.22632 255.47385



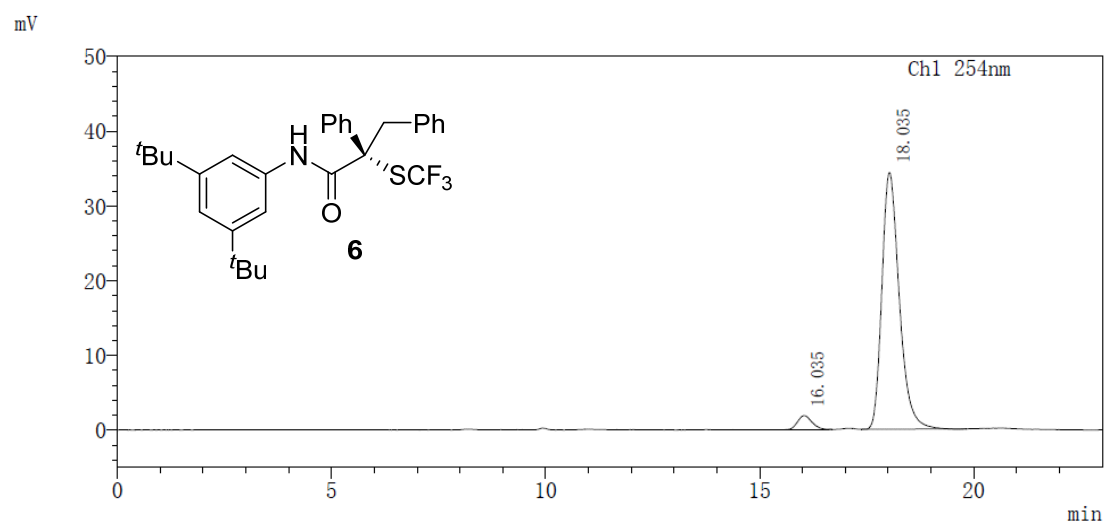
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

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

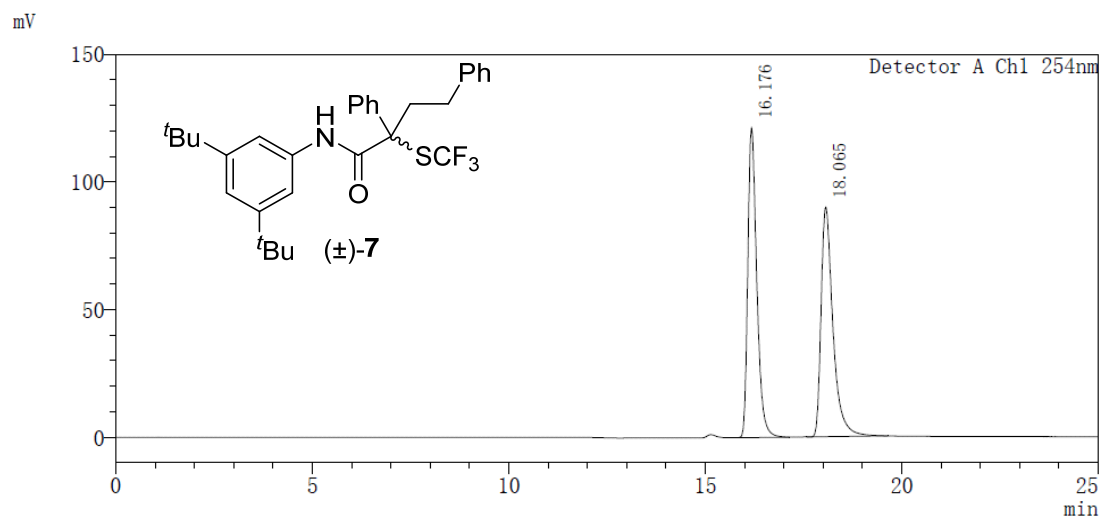
Totals : 648.60750 25.40031



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



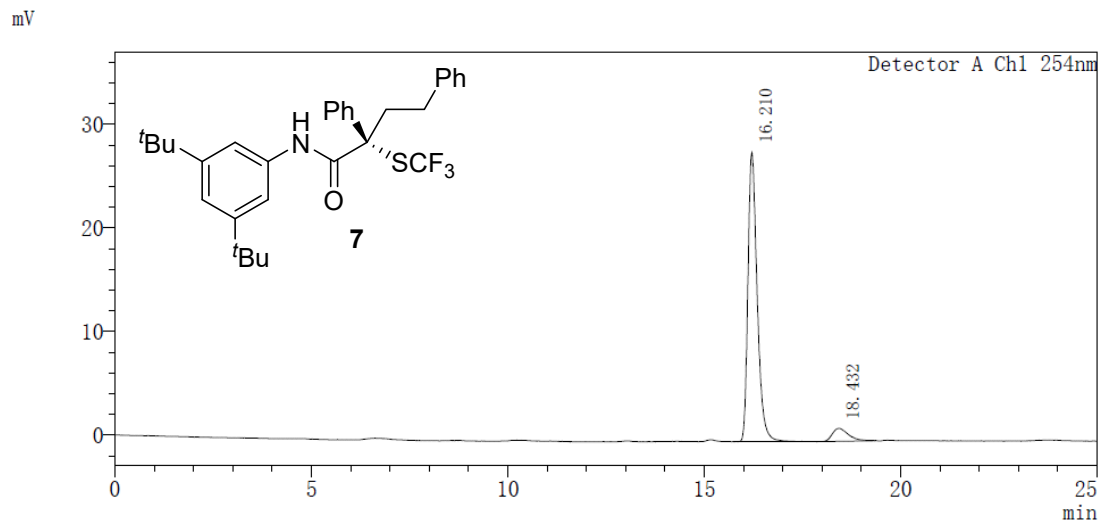
T	Hight	Area	Area%
16.035	1871	44317	4.368
18.035	34360	970164	95.632



Peak Table

Detector A Ch1 254nm

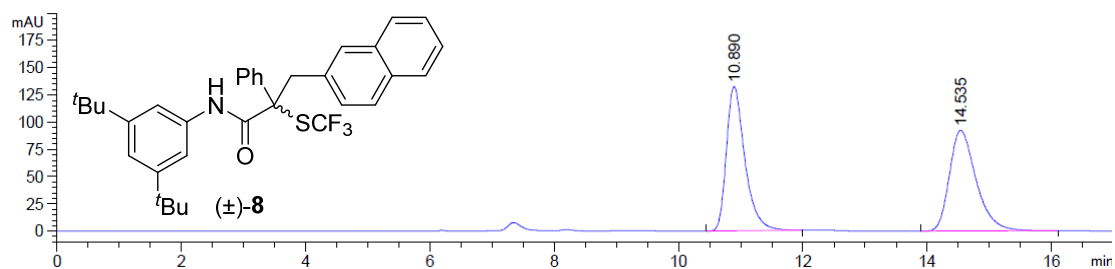
Peak#	Ret. Time	Area	Area%
1	16.176	1929548	50.610
2	18.065	1883020	49.390



Peak Table

Detector A Ch1 254nm

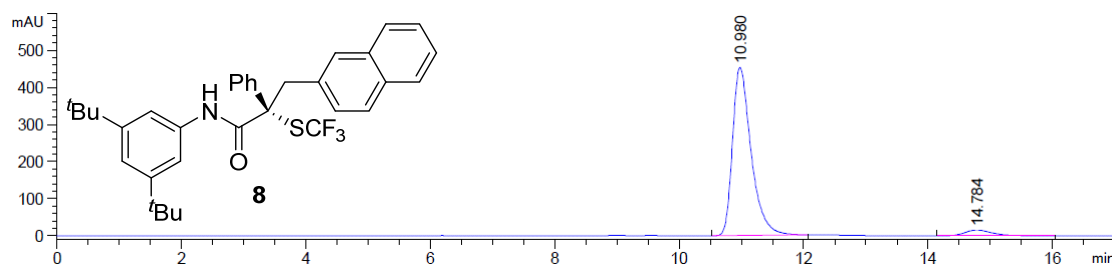
Peak#	Ret. Time	Area	Area%
1	16.210	458293	92.726
2	18.432	35952	7.274



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

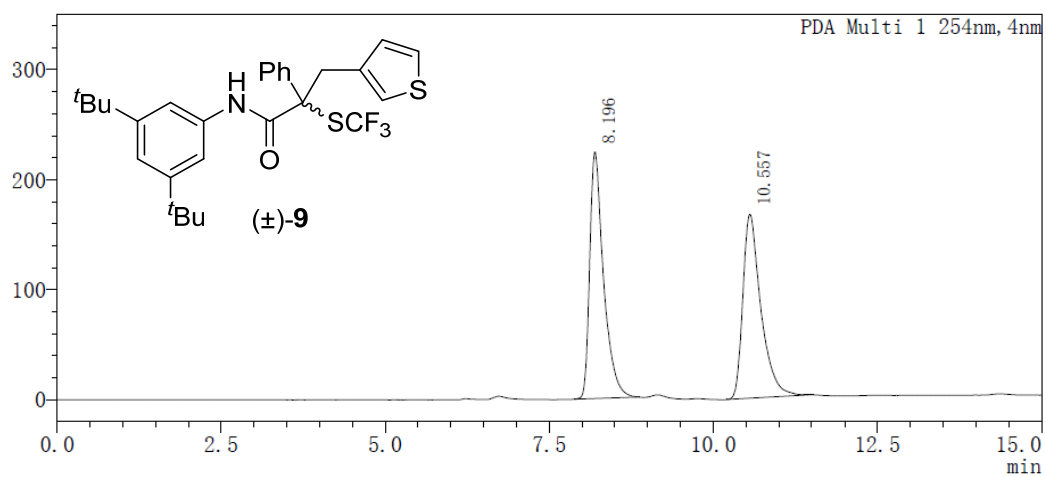


Signal 2: DAD1 B, Sig=254,4 Ref=360,100

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

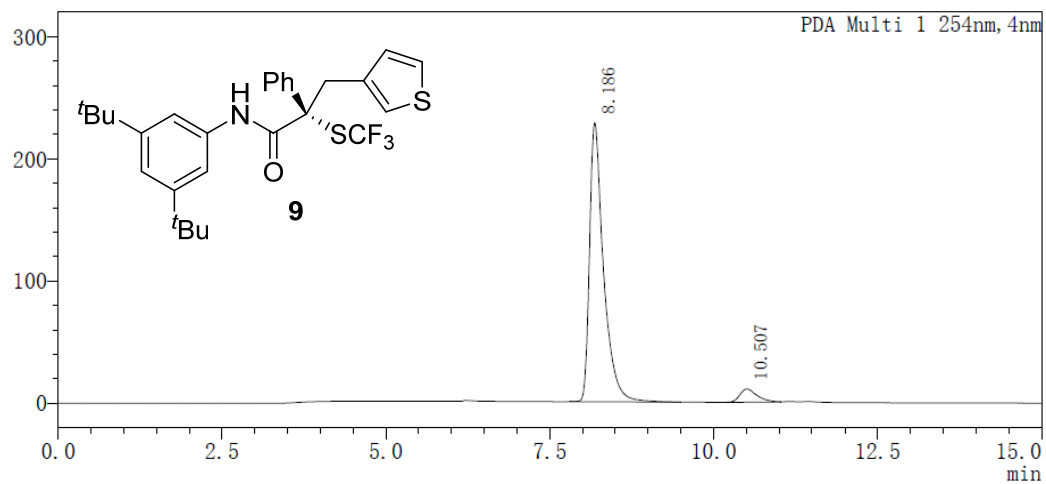


Peak Table

PDA Ch1 254nm

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

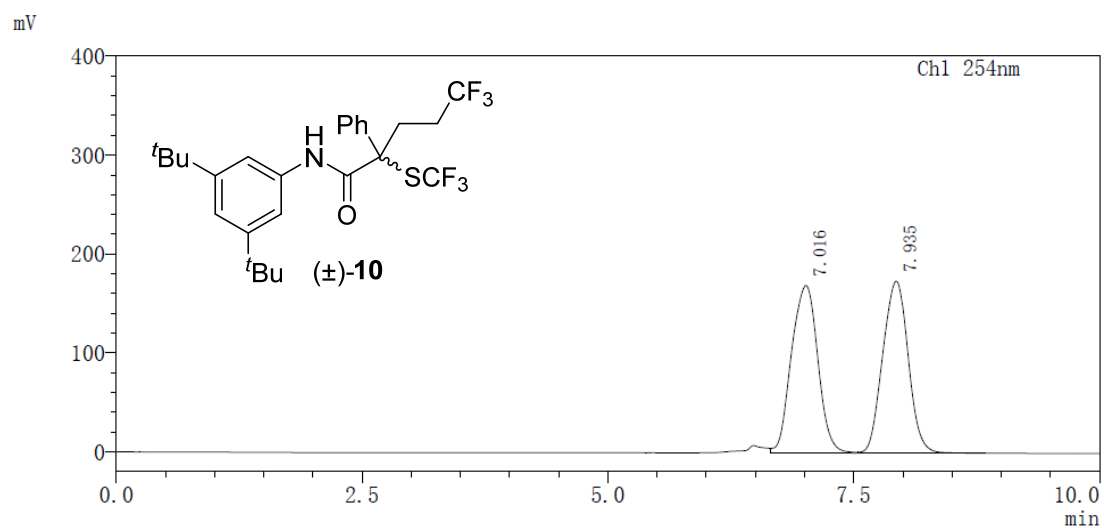
mAU



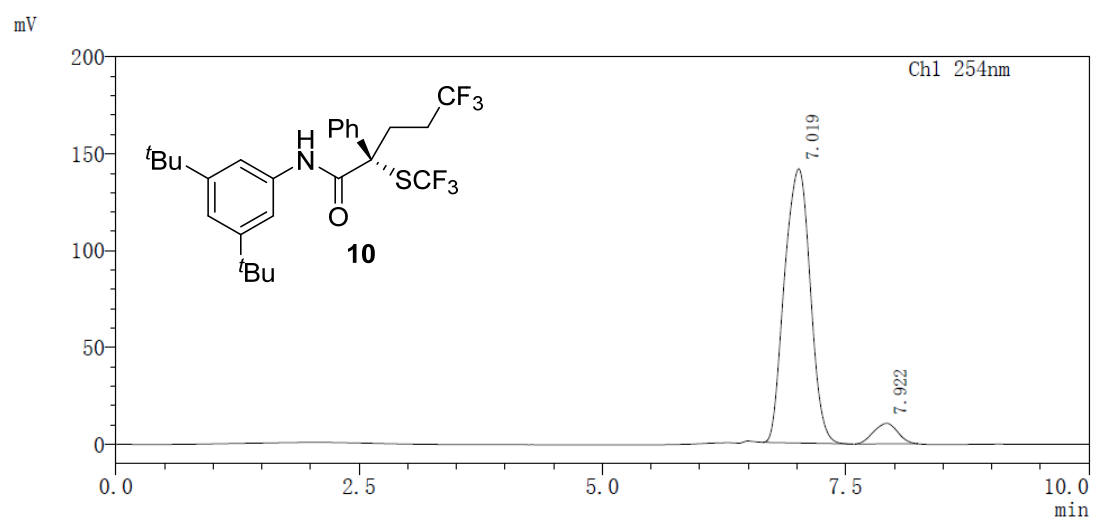
Peak Table

PDA Ch1 254nm

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

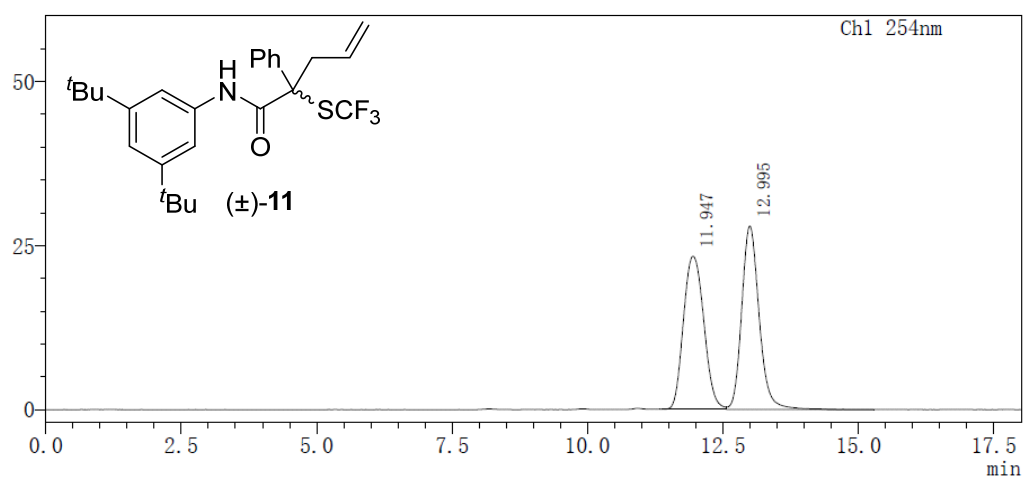


T	Hight	Area	Area%
7.016	169228	3169084	50.413
7.935	173871	3117127	49.587



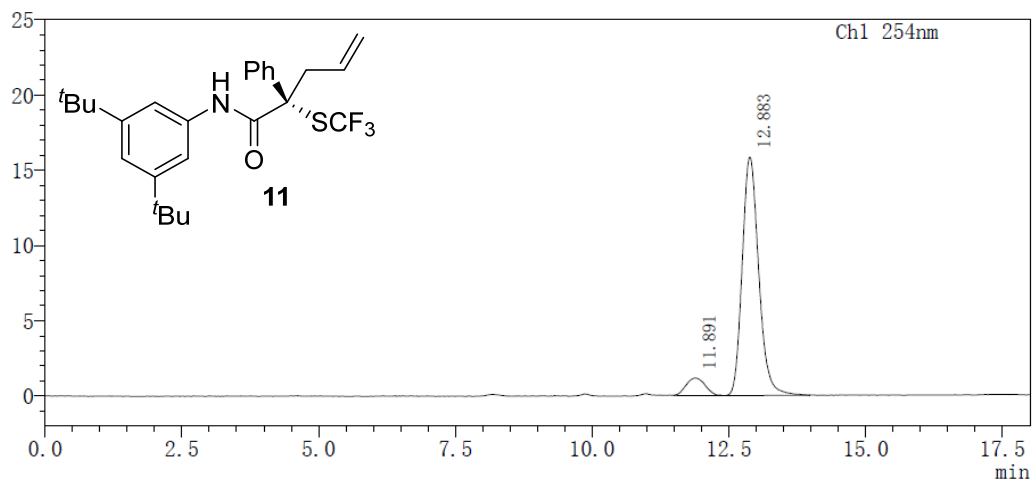
T	Hight	Area	Area%
7.019	141573	2616275	93.513
7.922	10587	181479	6.487

mV

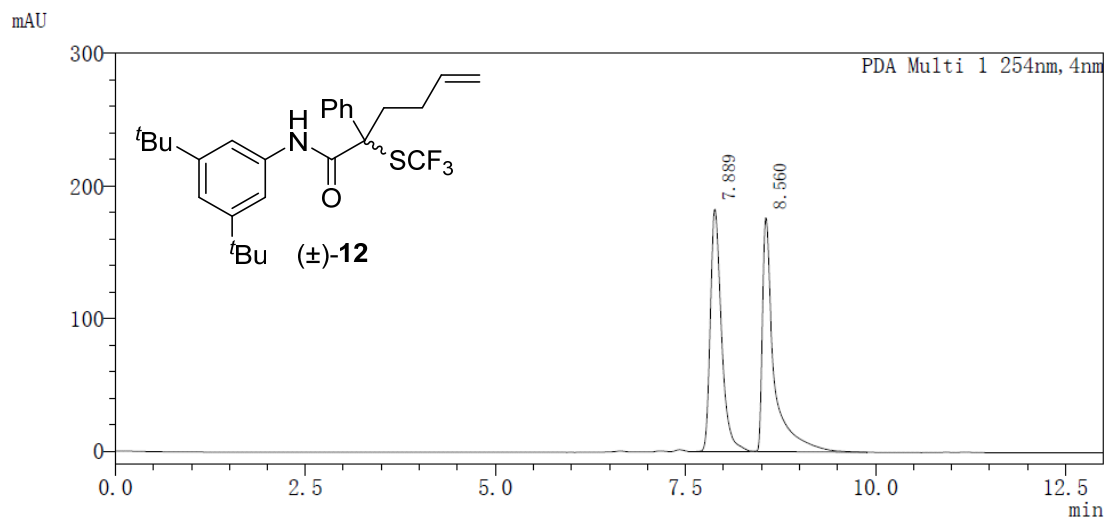


Ch1 254nm			
T	Hight	Area	Area%
11.947	23391	613070	49.397
12.995	27981	628040	50.603

mV

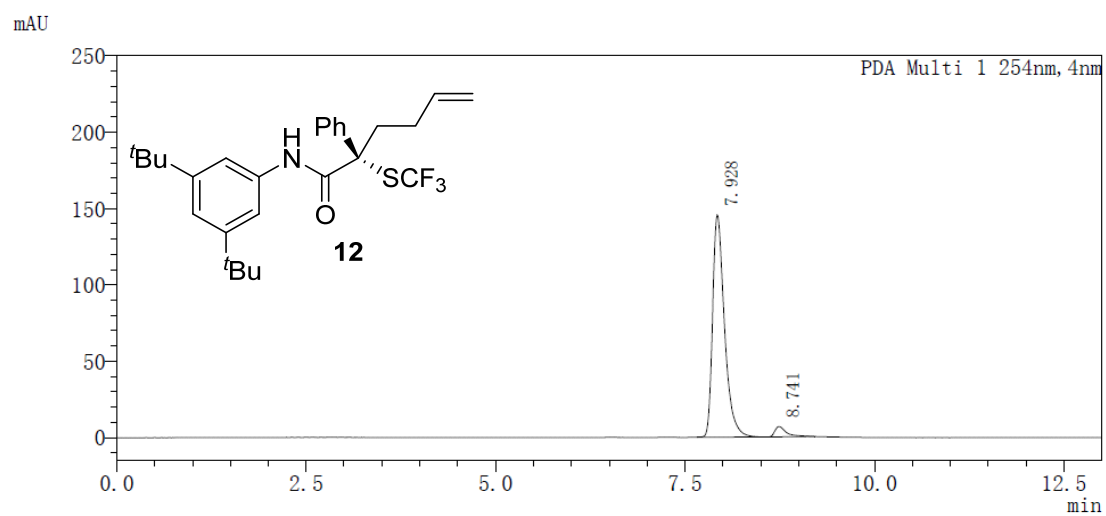


Ch1 254nm			
T	Hight	Area	Area%
11.891	1164	28333	7.818
12.883	15858	334056	92.182



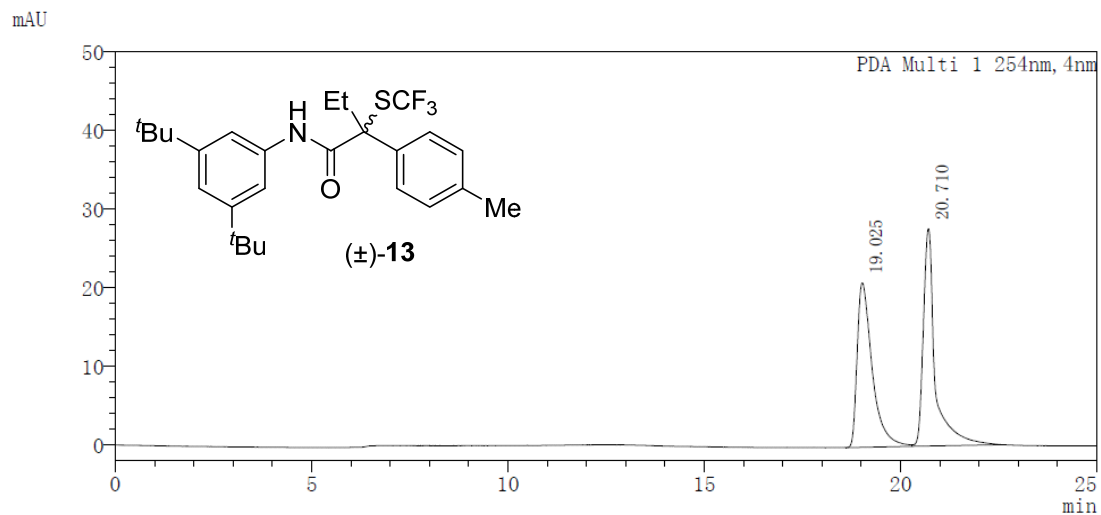
PDA Ch1 254nm

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



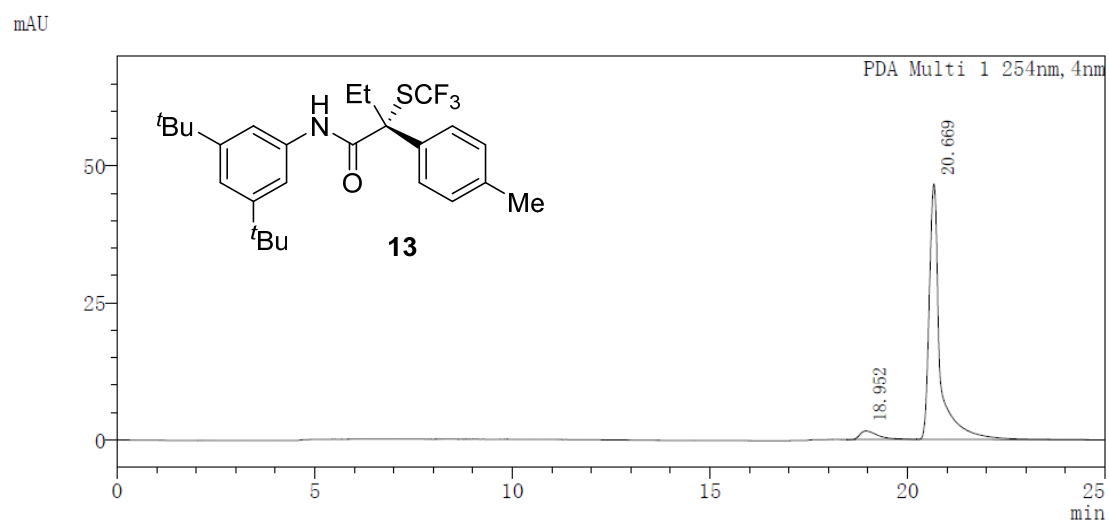
PDA Ch1 254nm

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



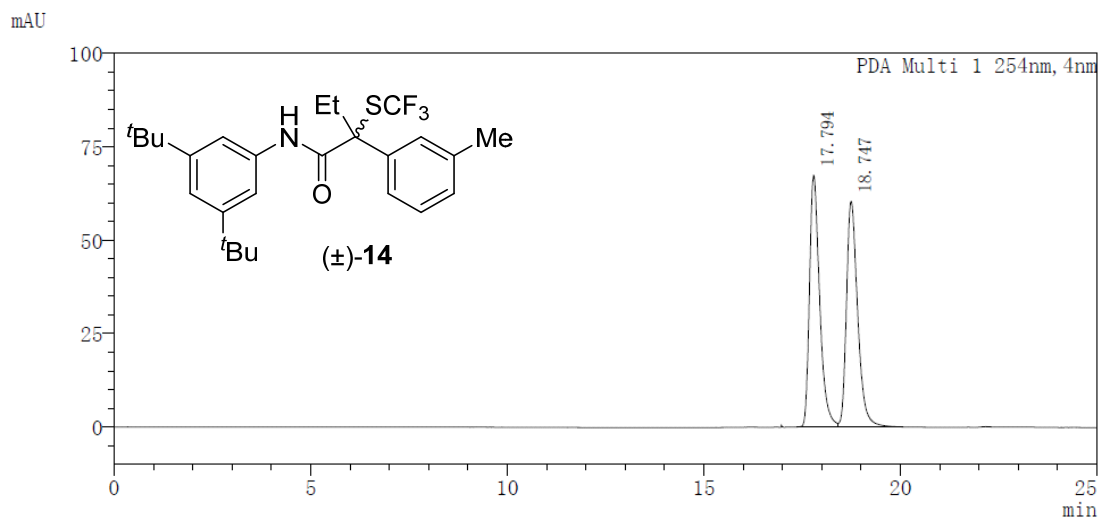
PDA Ch1 254nm

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



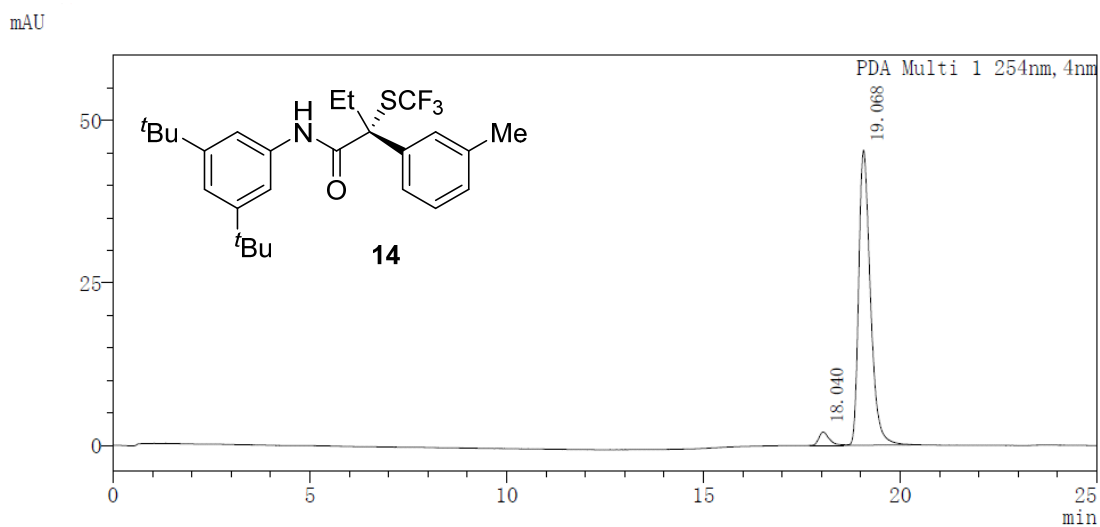
PDA Ch1 254nm

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



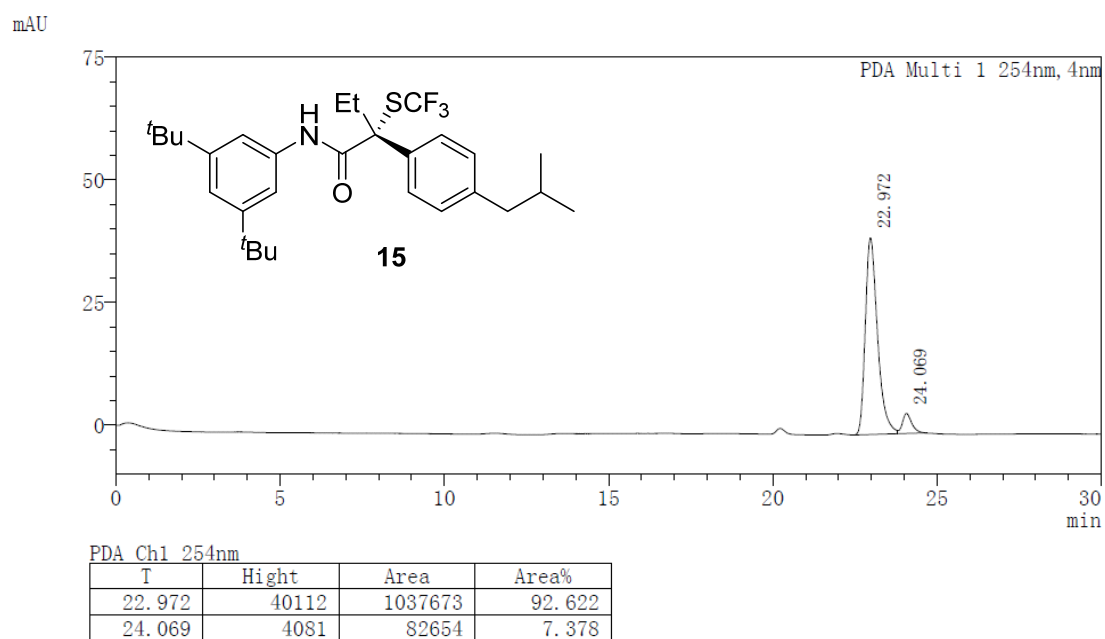
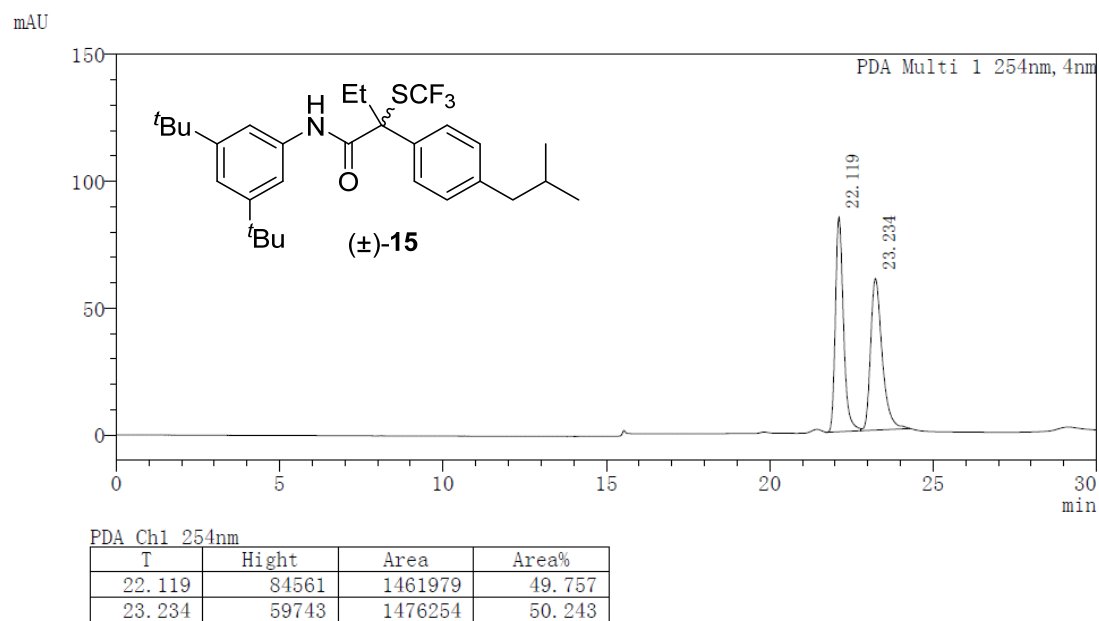
PDA Ch1 254nm

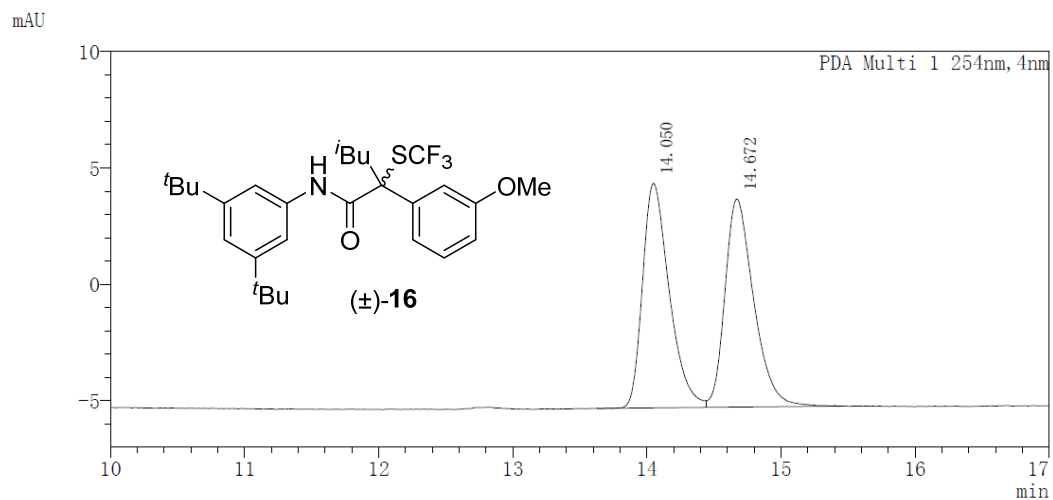
T	Hight	Area	Area%
17.794	67378	1209890	50.291
18.747	60358	1195892	49.709



PDA Ch1 254nm

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

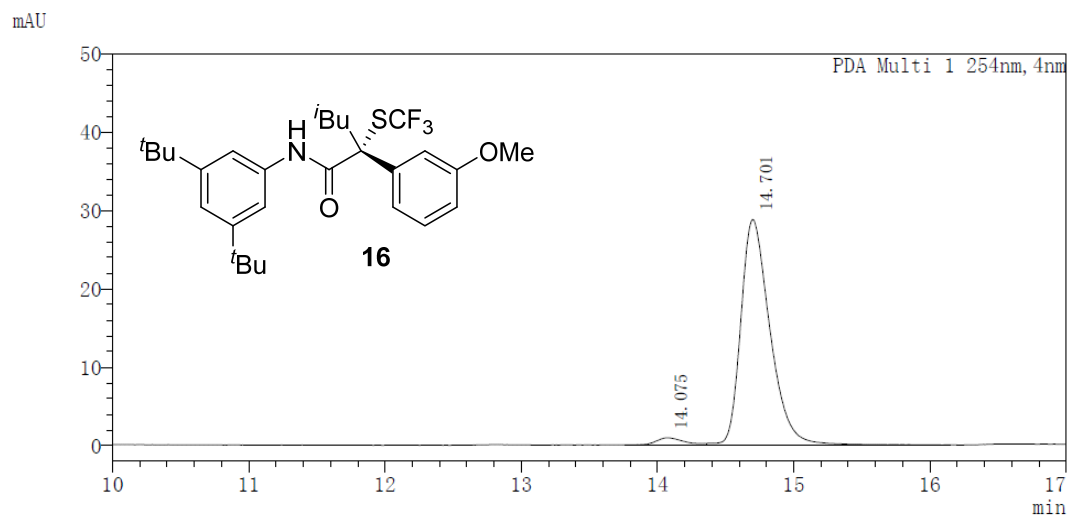




Peak Table

PDA Ch1 254nm

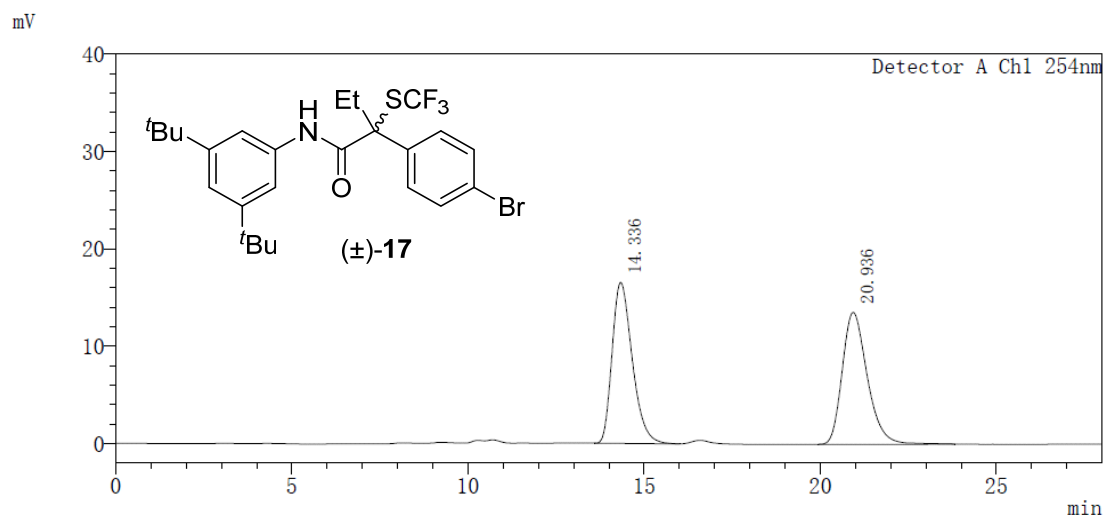
Peak#	Ret. Time	Area	Area%
1	14.050	133961	50.056
2	14.672	133663	49.944



Peak Table

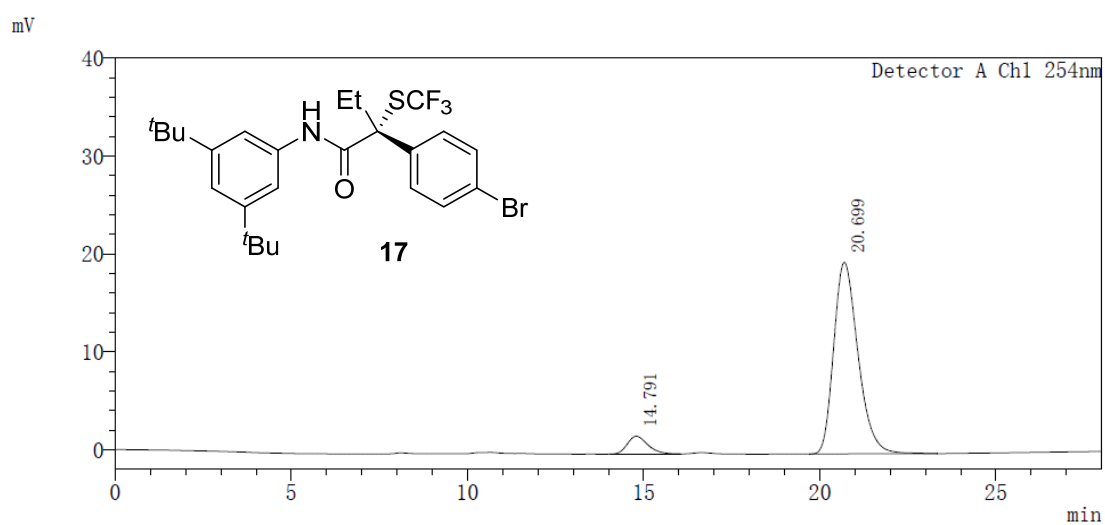
PDA Ch1 254nm

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



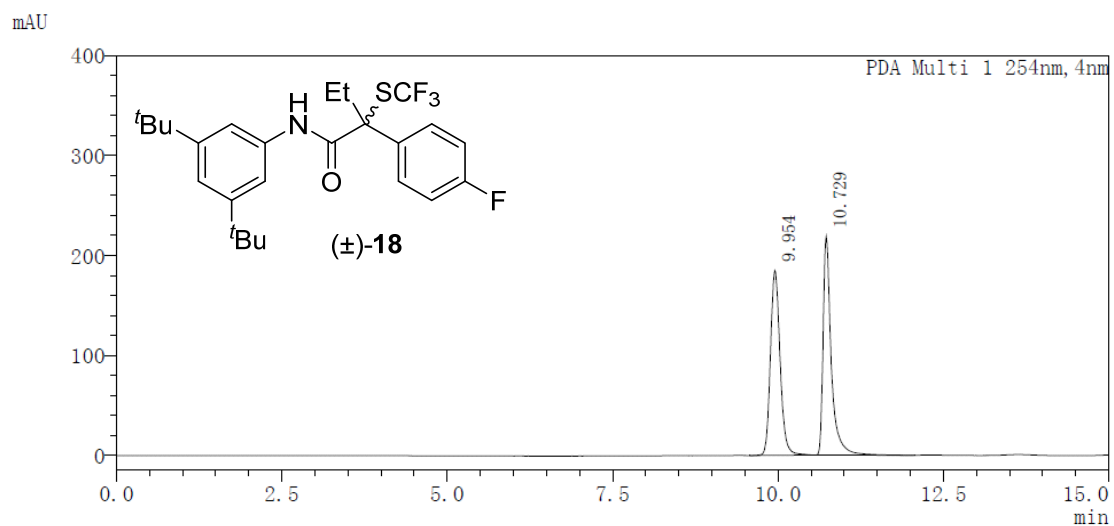
Detector A Ch1 254nm

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



Detector A Ch1 254nm

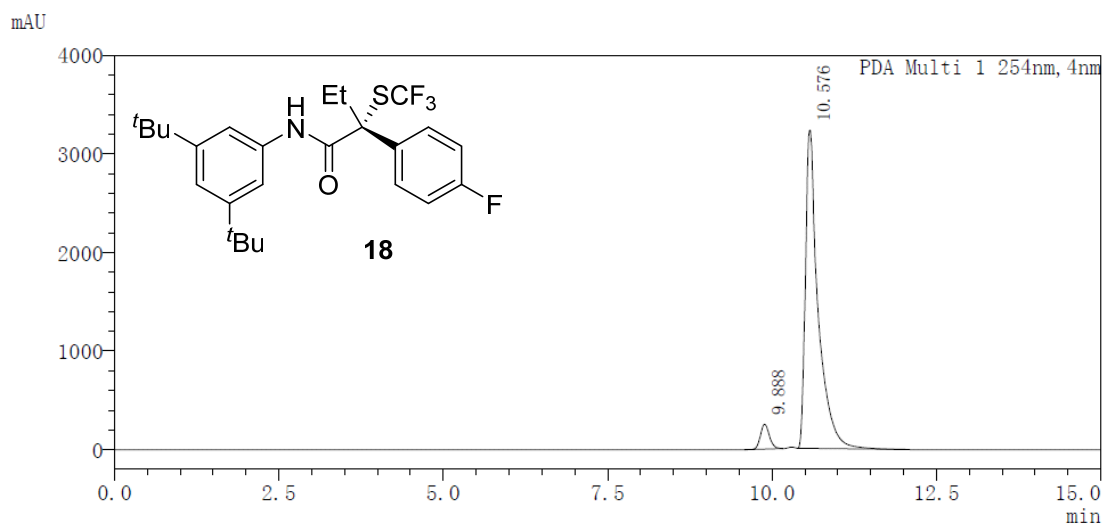
T	Hight	Area	Area%
14.791	1804	72742	7.197
20.699	19565	937976	92.803



Peak Table

PDA Ch1 254nm

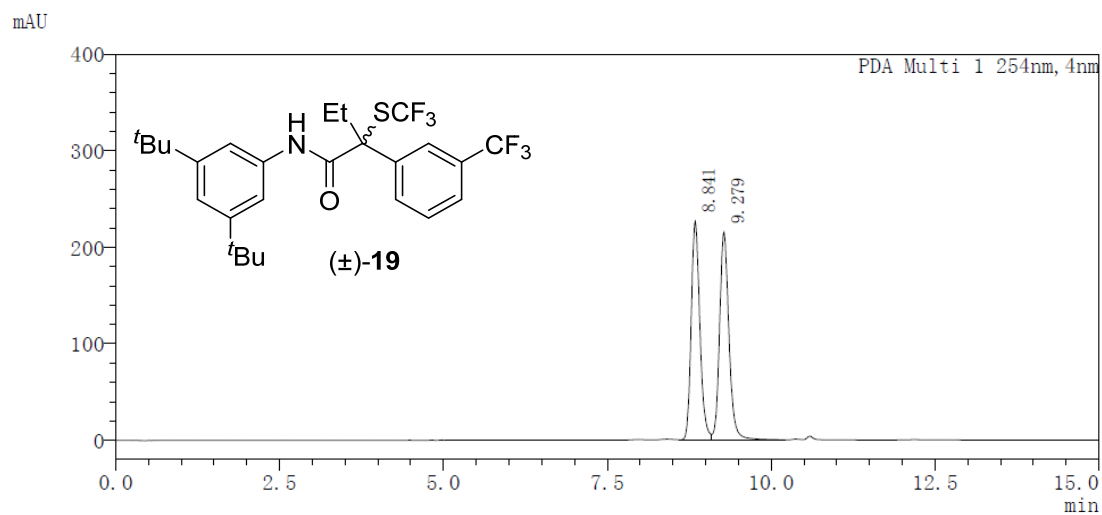
Peak#	Ret. Time	Area	Area%
1	9.954	1872336	50.040
2	10.729	1869338	49.960



Peak Table

PDA Ch1 254nm

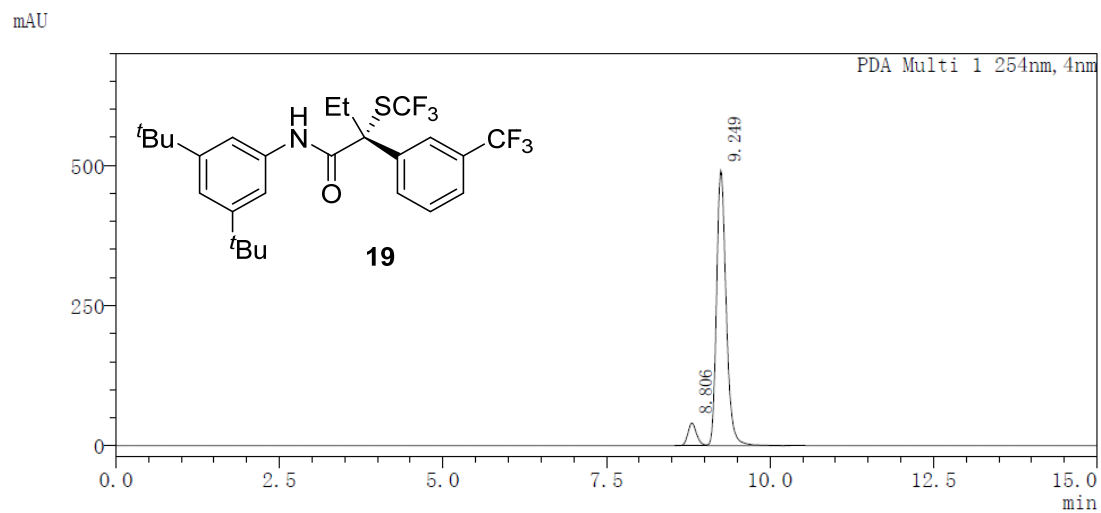
Peak#	Ret. Time	Area	Area%
1	9.888	2385470	5.213
2	10.576	43370374	94.787



Peak Table

PDA Ch1 254nm

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

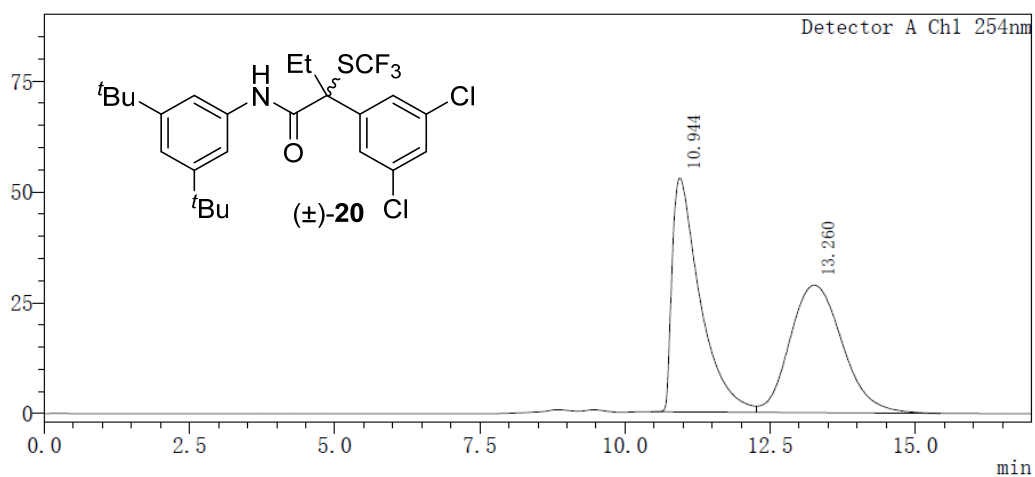


Peak Table

PDA Ch1 254nm

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

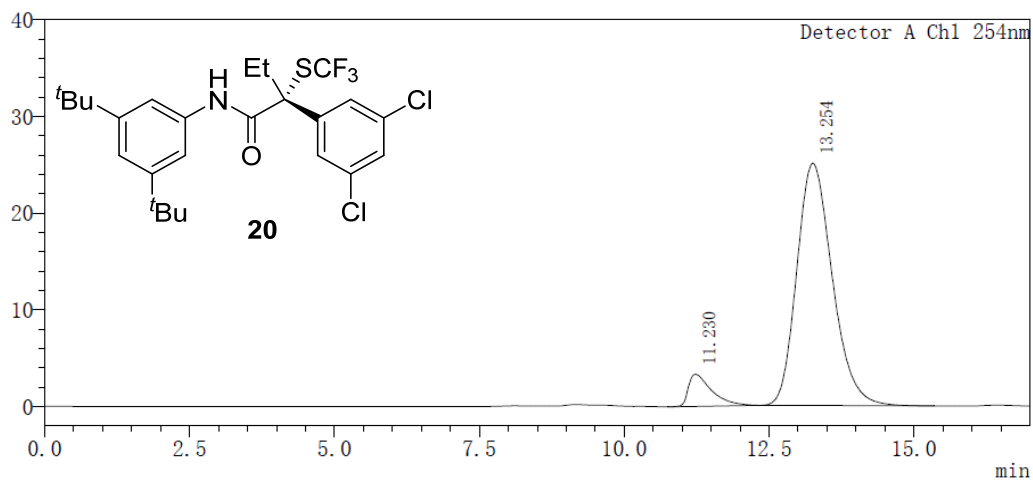
mV



Detector A Ch1 254nm

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

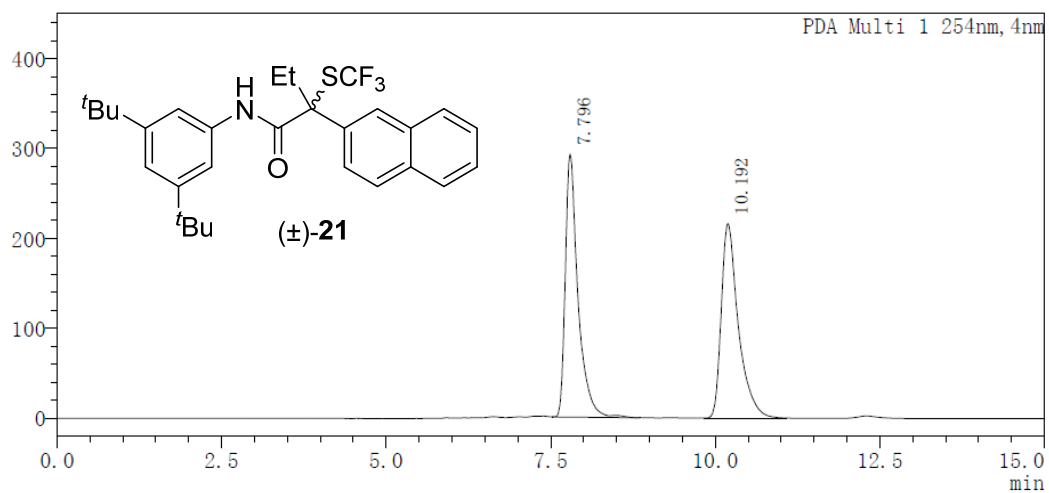
mV



Detector A Ch1 254nm

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

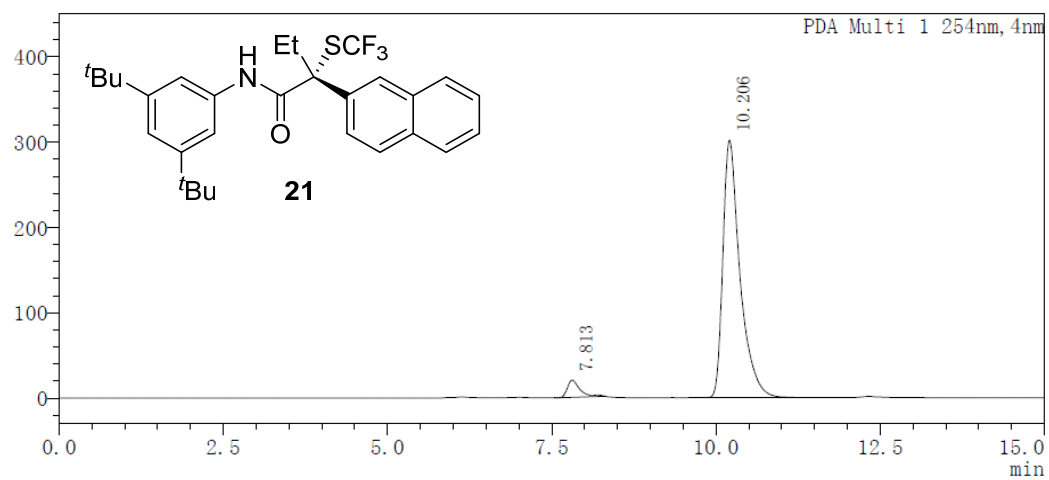
mAU



PDA Ch1 254nm

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

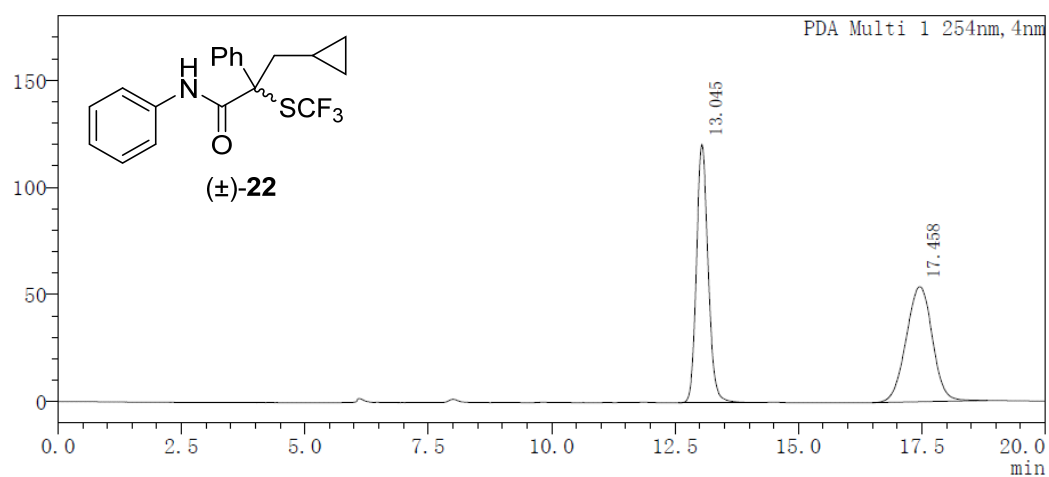
mAU



PDA Ch1 254nm

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

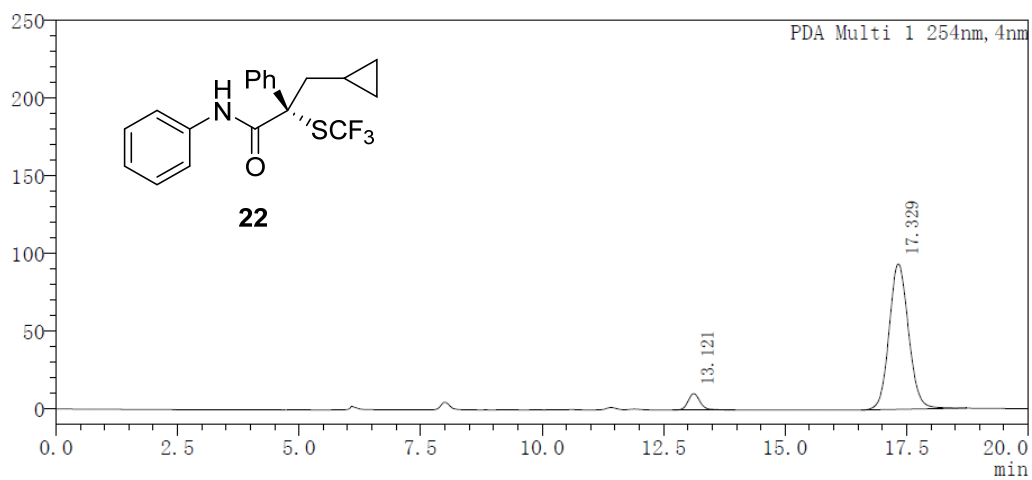
mAU



PDA Ch1 254nm

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

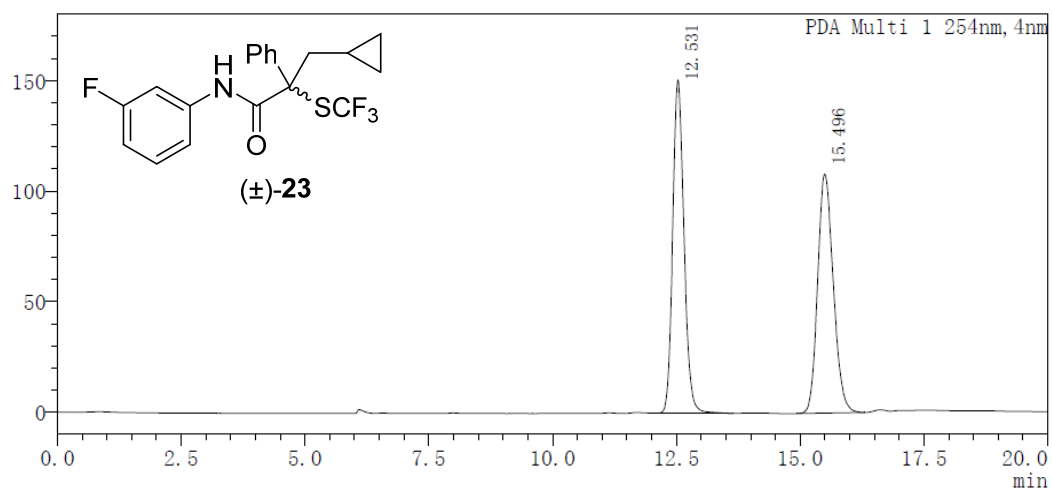
mAU



PDA Ch1 254nm

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

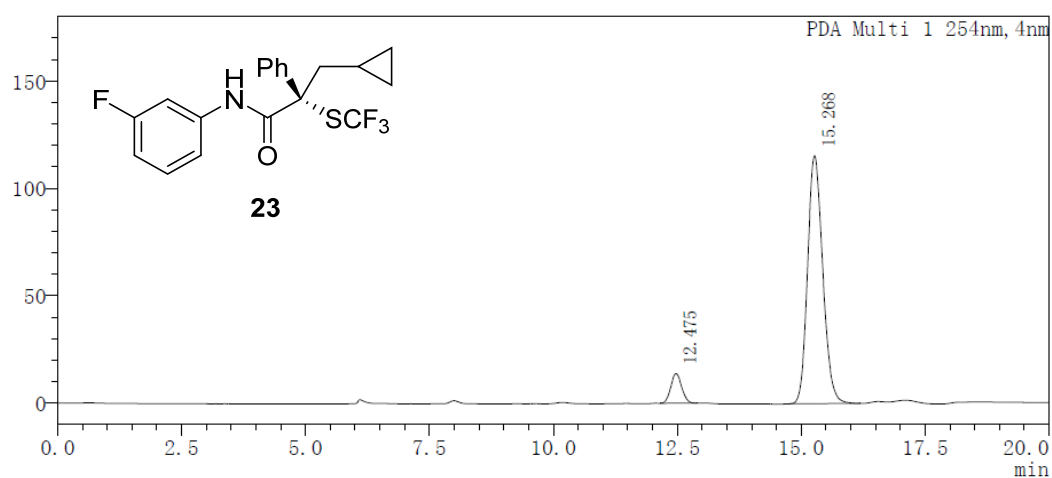
mAU



PDA Ch1 254nm

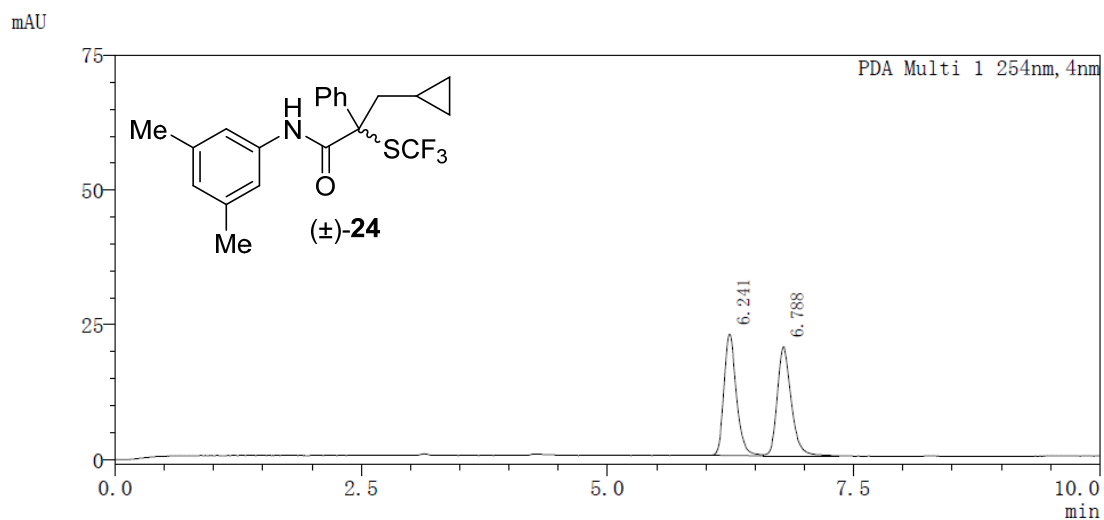
T	Hight	Area	Area%
12.531	150647	2390726	50.137
15.496	108119	2377684	49.863

mAU



PDA Ch1 254nm

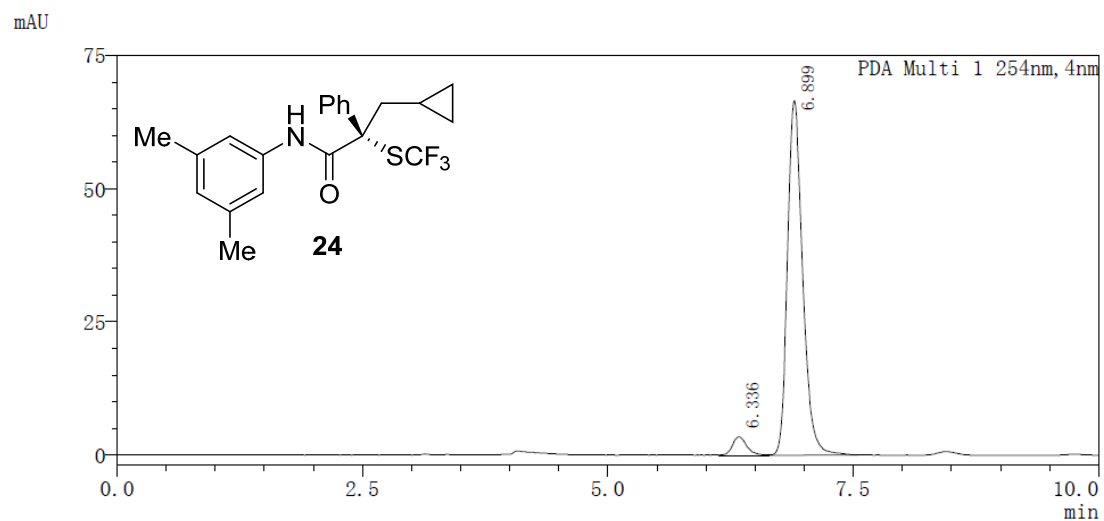
T	Hight	Area	Area%
12.475	13756	209263	7.829
15.268	115516	2463583	92.171



Peak Table

PDA Ch1 254nm

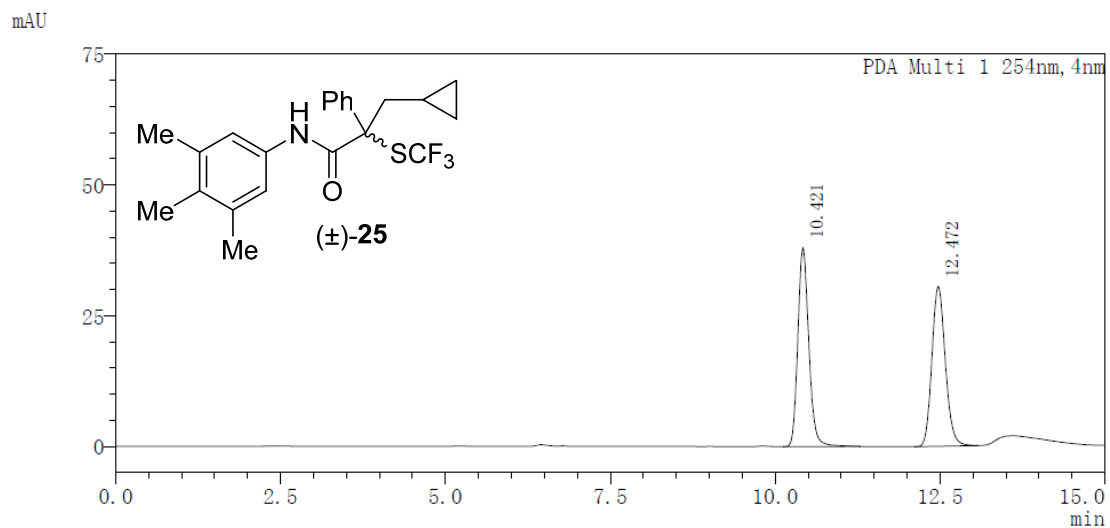
Peak#	Ret. Time	Area	Area%
1	6.241	198253	49.863
2	6.788	199345	50.137



Peak Table

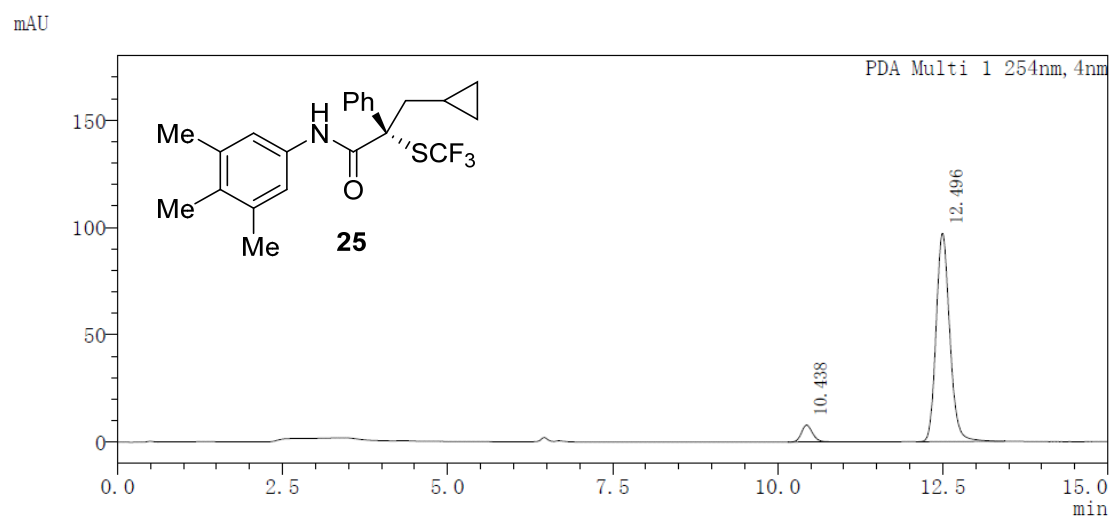
PDA Ch1 254nm

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



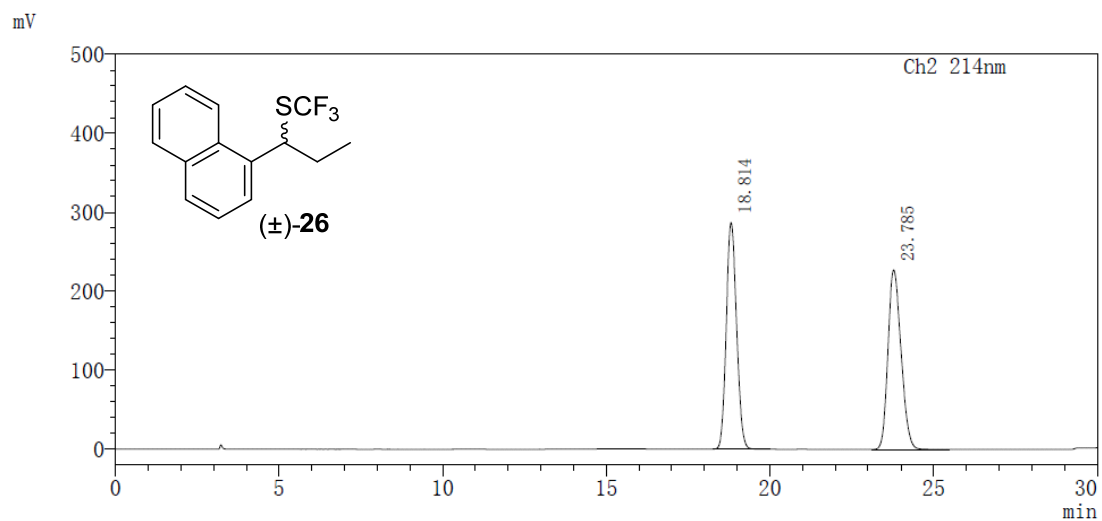
PDA Ch1 254nm

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



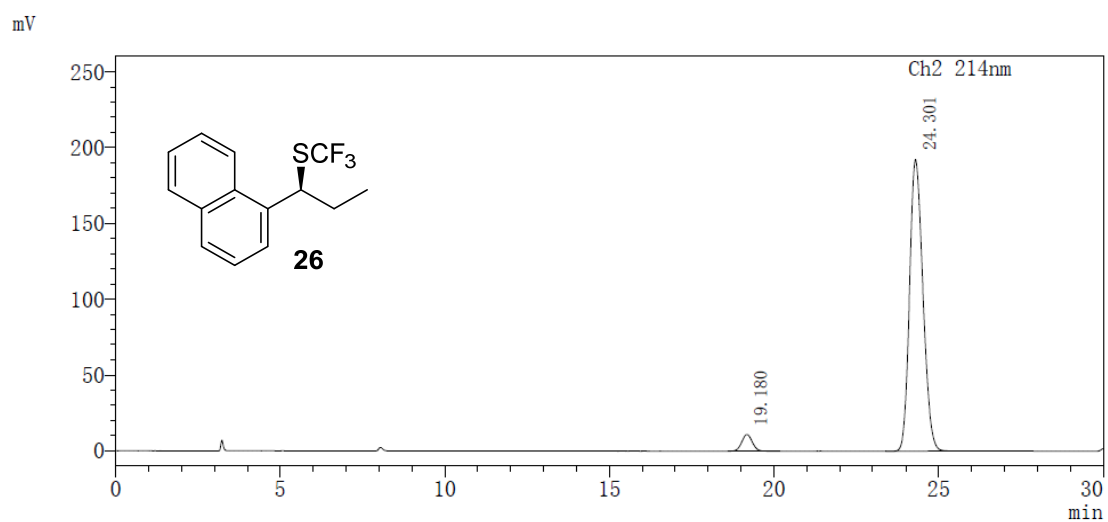
PDA Ch1 254nm

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



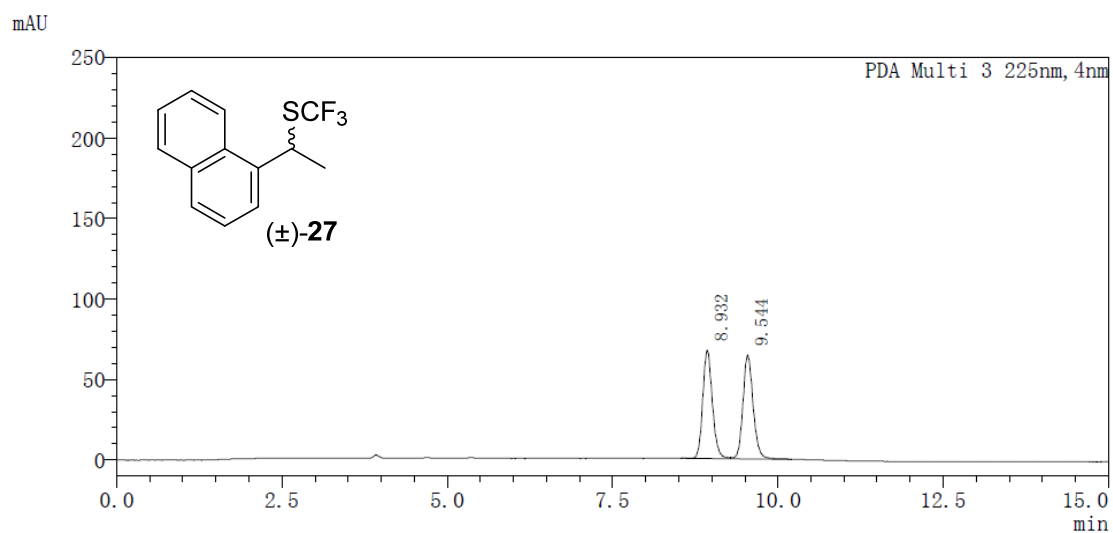
Ch2 214nm

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



Ch2 214nm

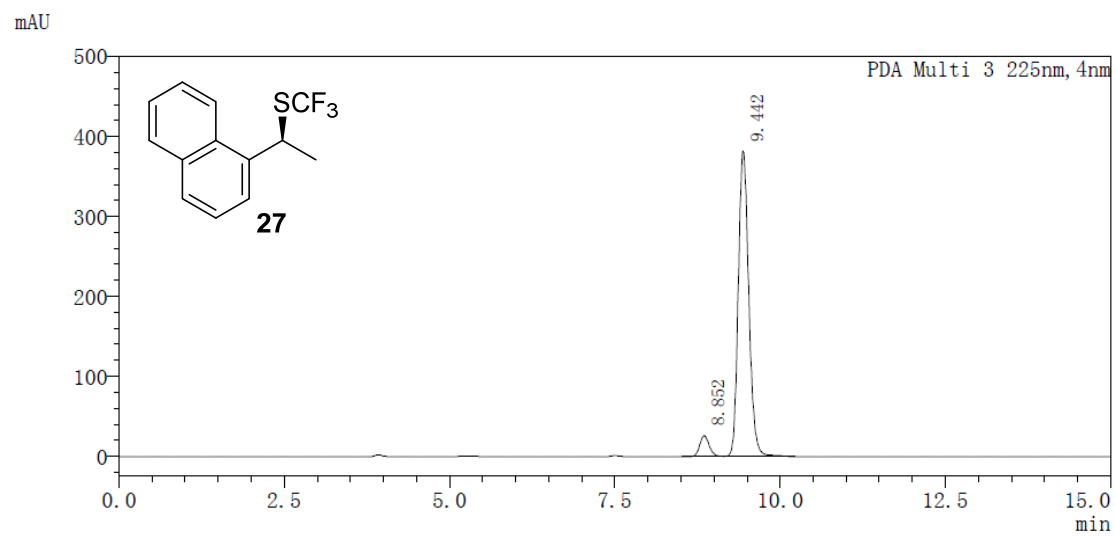
Peak	RetTime	Area	Height	Area%
1	19.180	245046	11019	4.312
2	24.301	5437660	192169	95.688



Peak Table

PDA Ch3 225nm

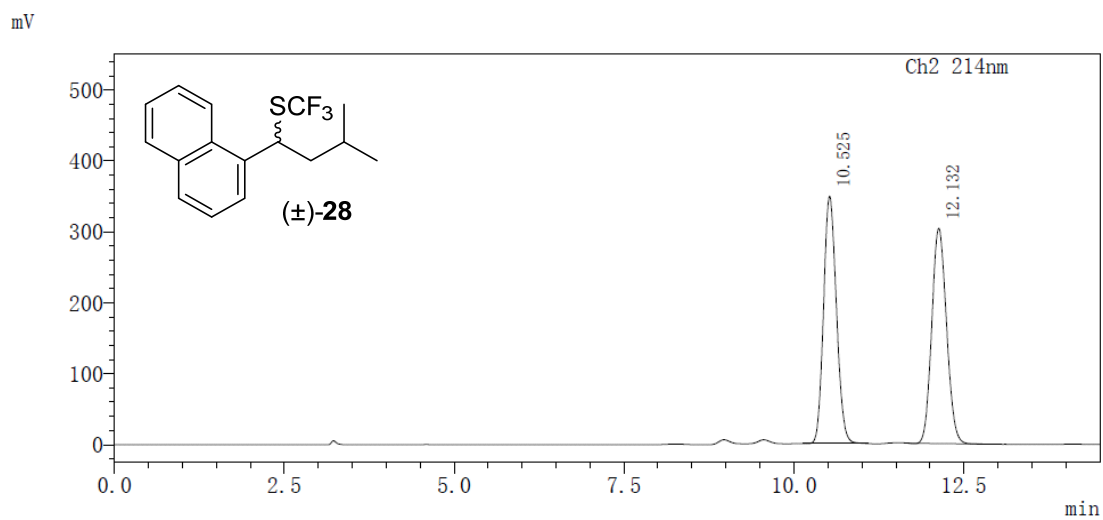
Peak#	Ret. Time	Area	Area%
1	8.932	683490	49.651
2	9.544	693109	50.349



Peak Table

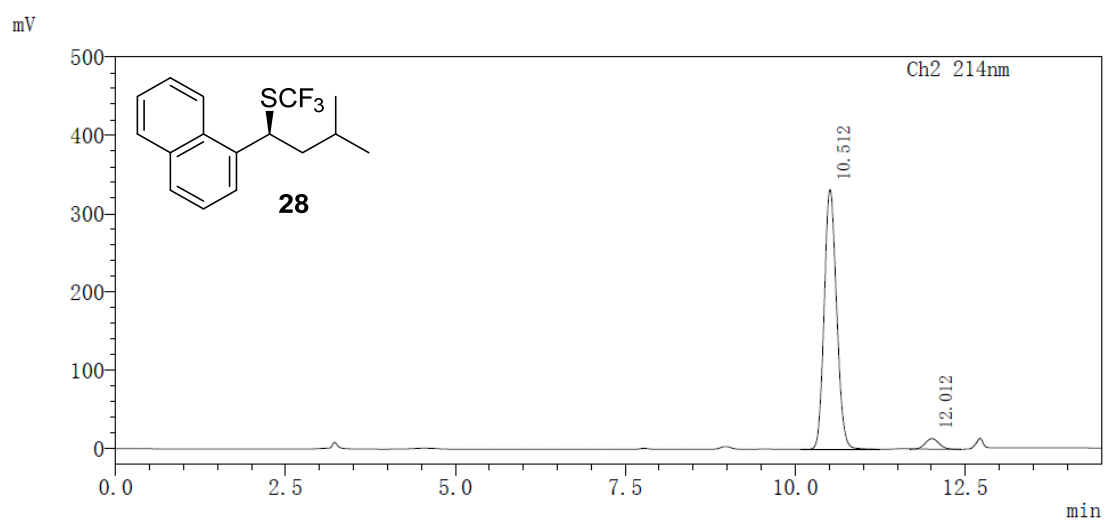
PDA Ch3 225nm

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



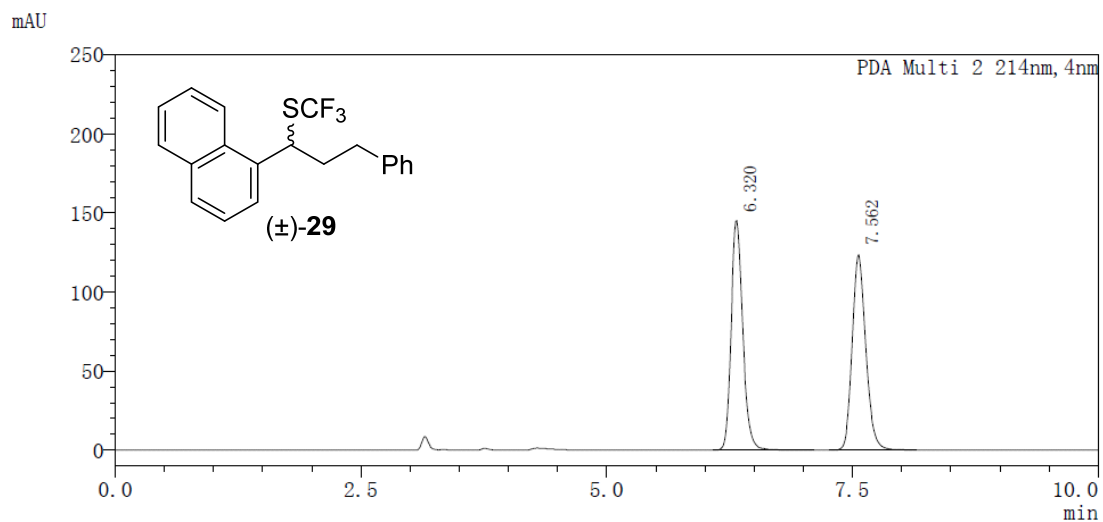
Ch2 214nm

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



Ch2 214nm

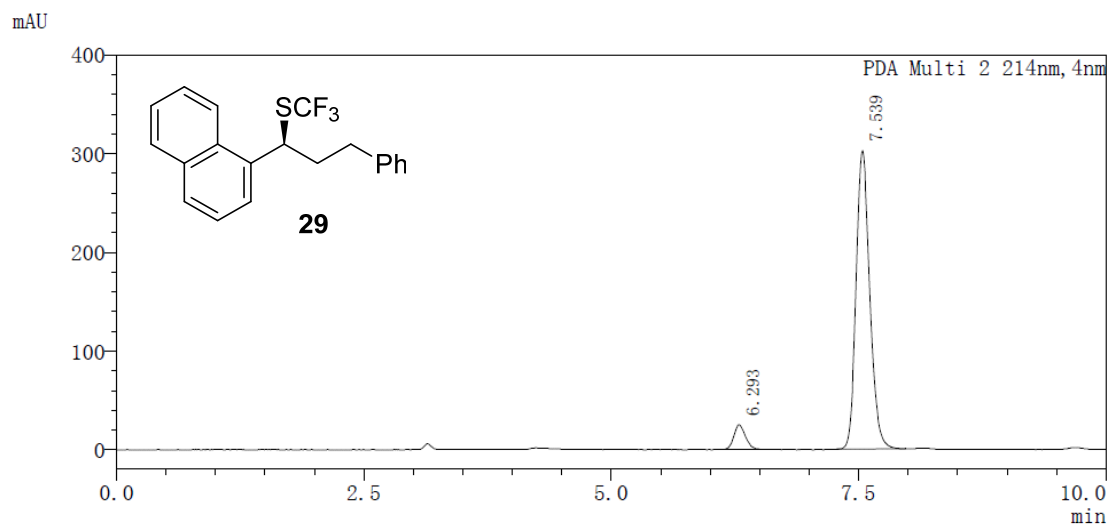
Peak	RetTime	Area	Height	Area%
1	10.512	4218017	331394	95.818
2	12.012	184081	13328	4.182



Peak Table

PDA Ch2 214nm

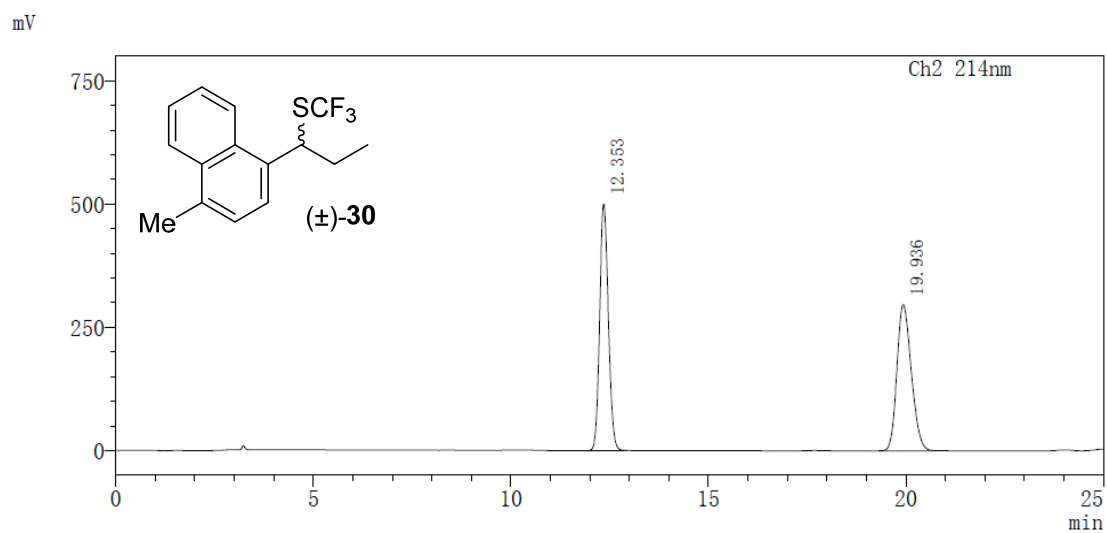
Peak#	Ret. Time	Area	Area%
1	6.320	1197305	50.043
2	7.562	1195240	49.957



Peak Table

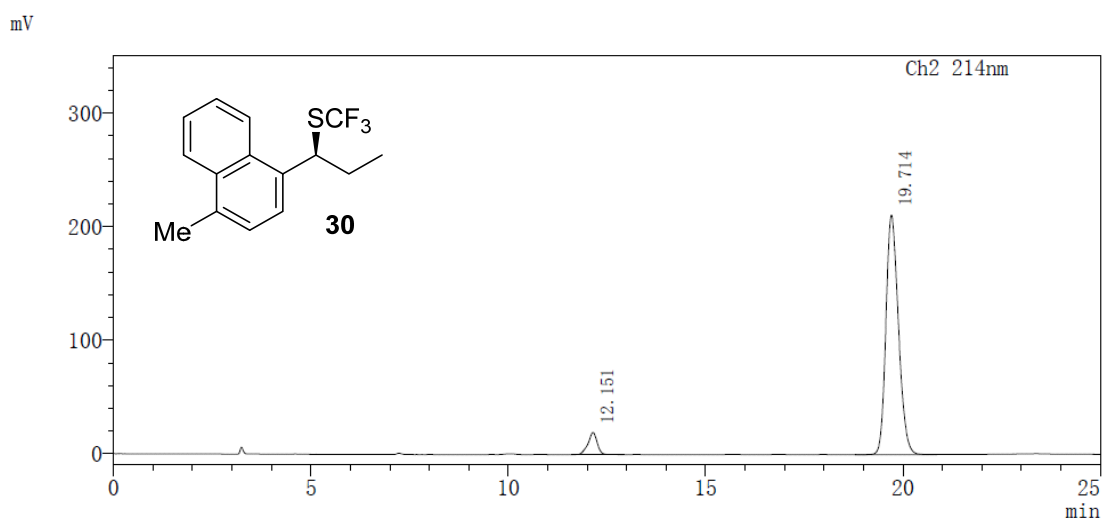
PDA Ch2 214nm

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



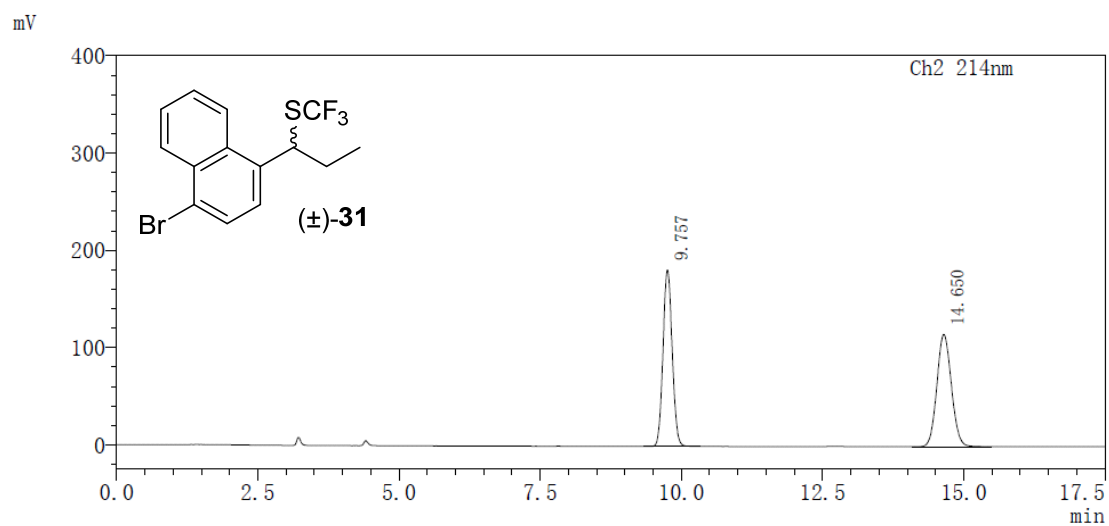
Ch2 214nm

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



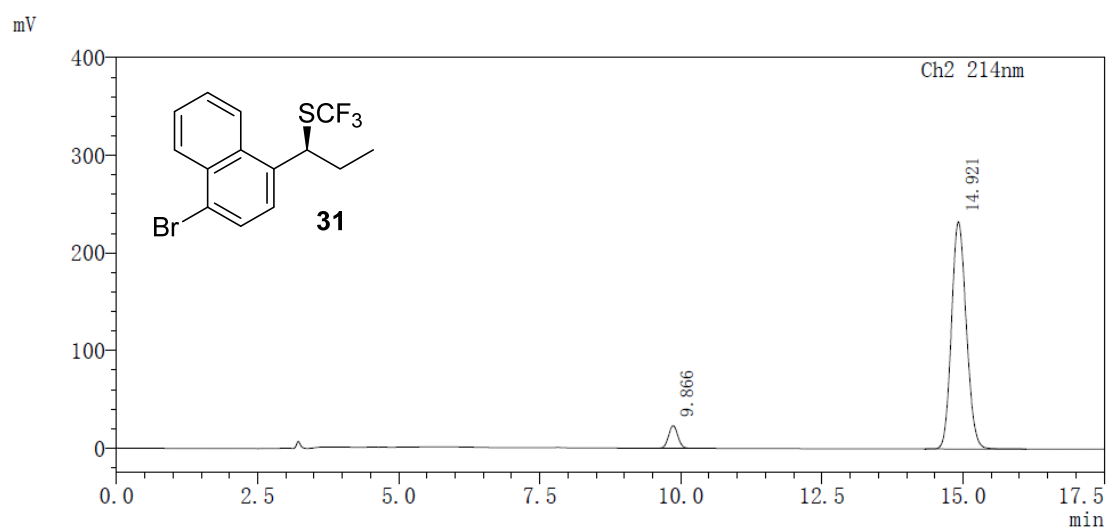
Ch2 214nm

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



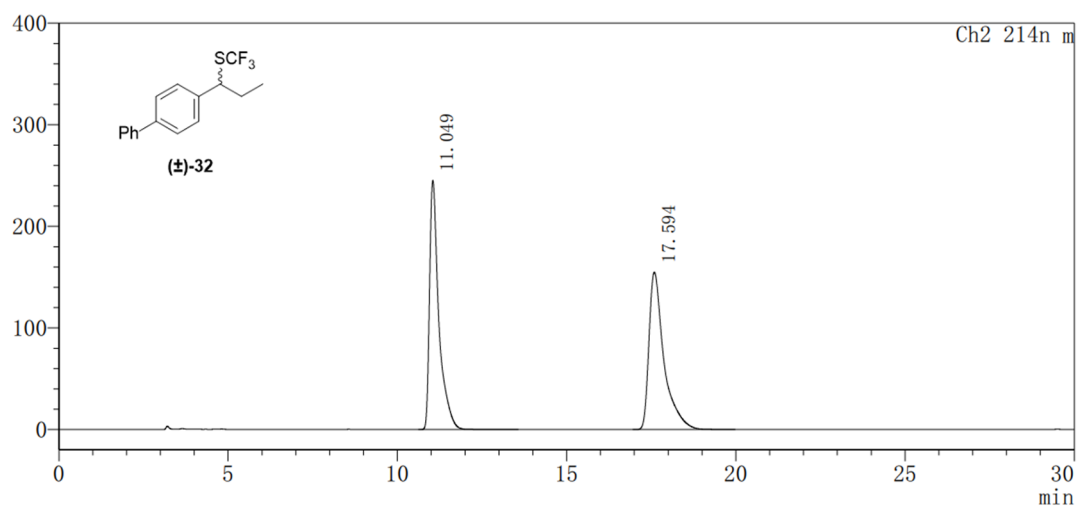
Ch2 214nm

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



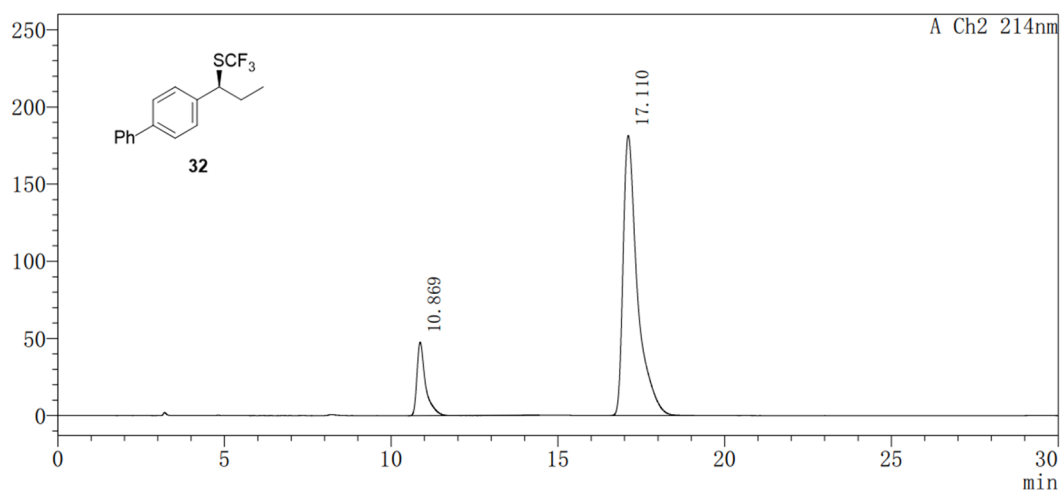
Ch2 214nm

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



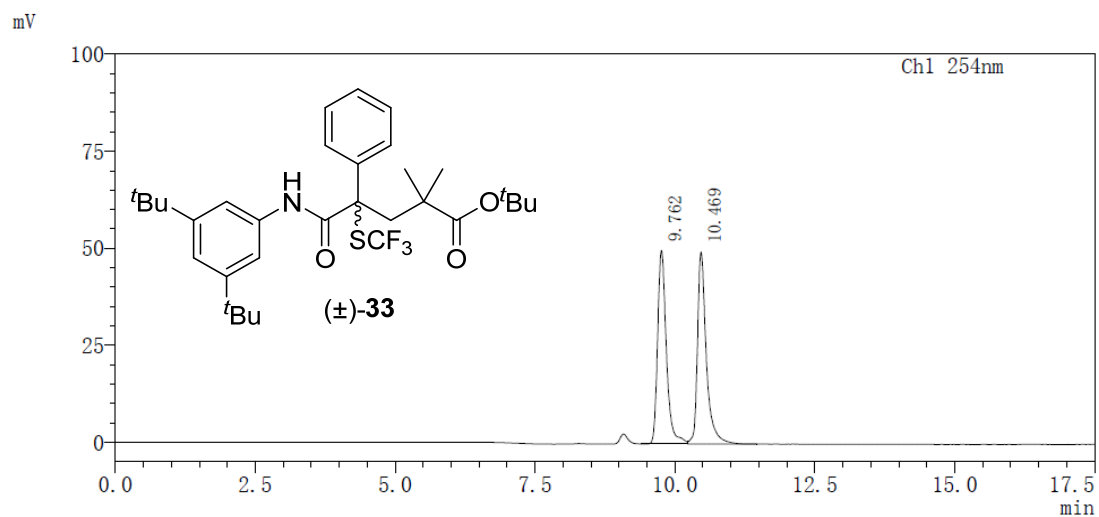
Ch2 214nm

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



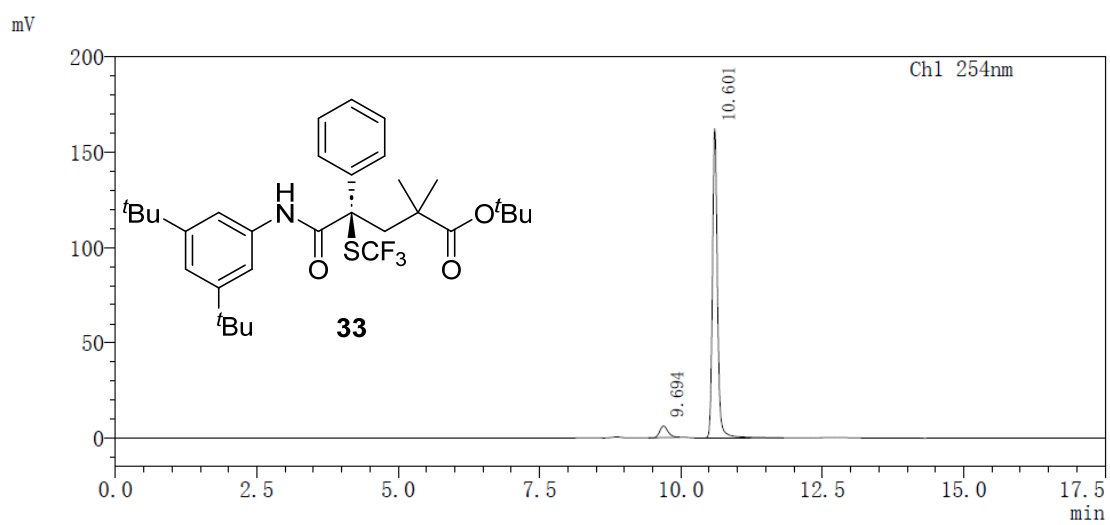
Ch2 214nm

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



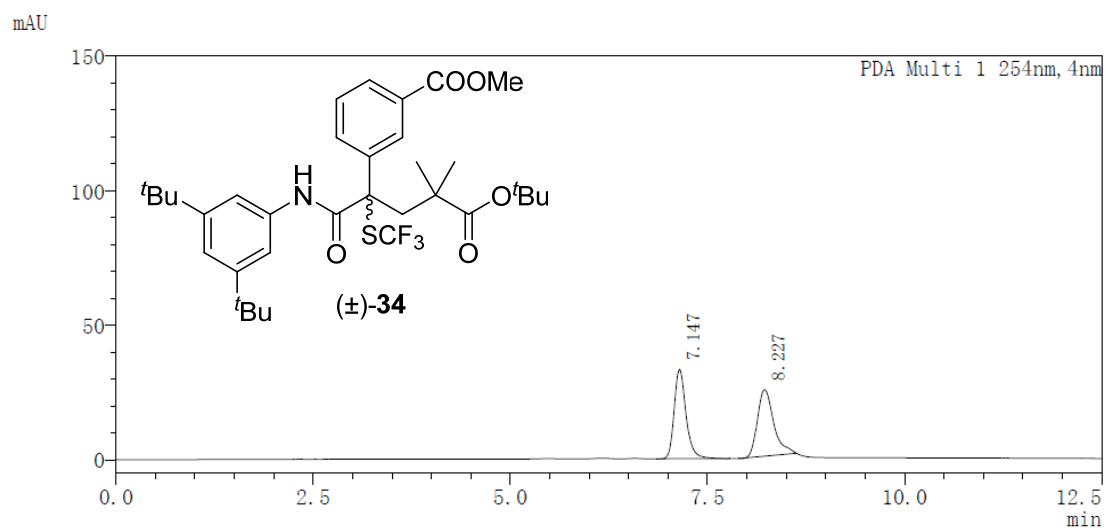
Ch1 254nm

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



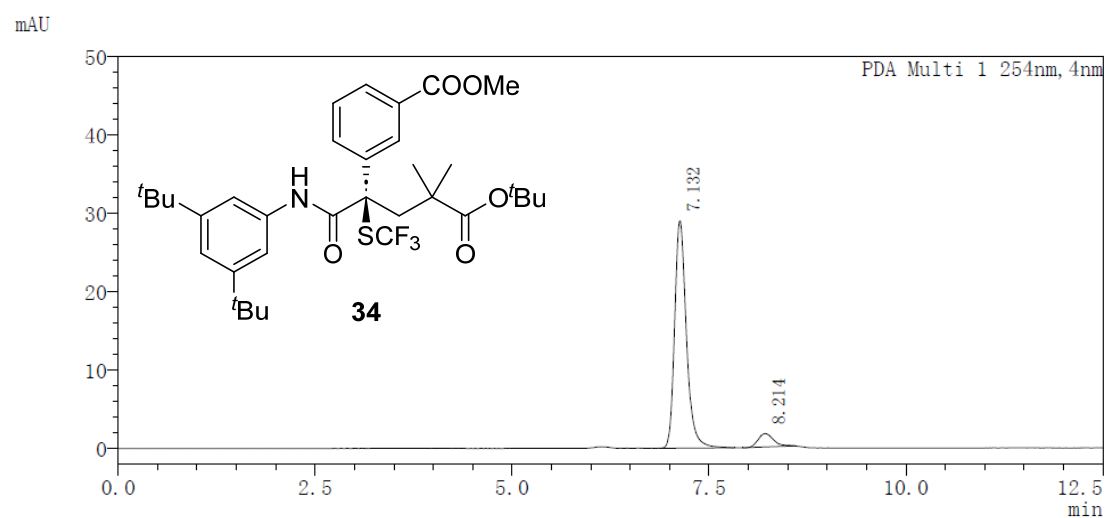
Ch1 254nm

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



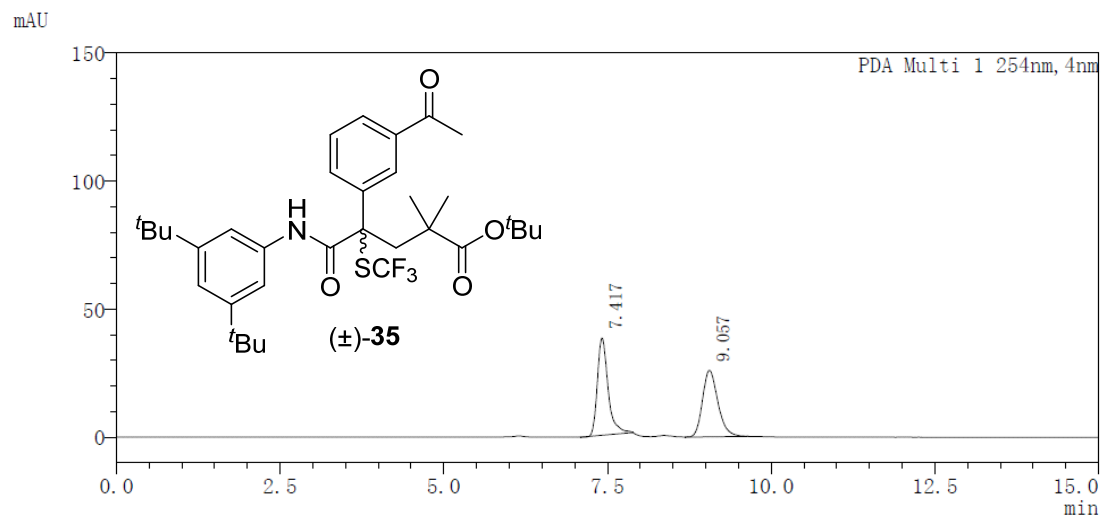
PDA Ch1 254nm

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



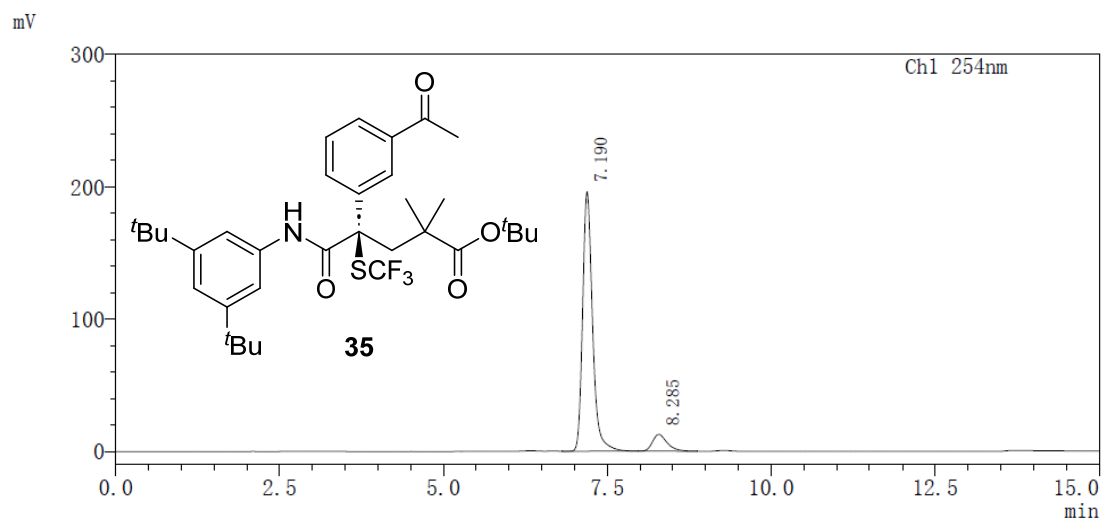
PDA Ch1 254nm

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



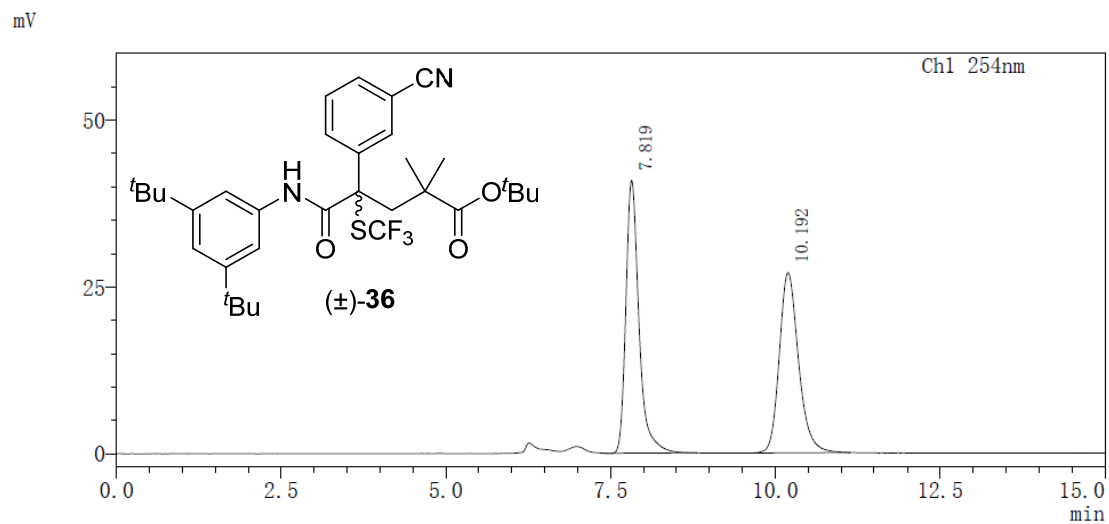
PDA Ch1 254nm

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



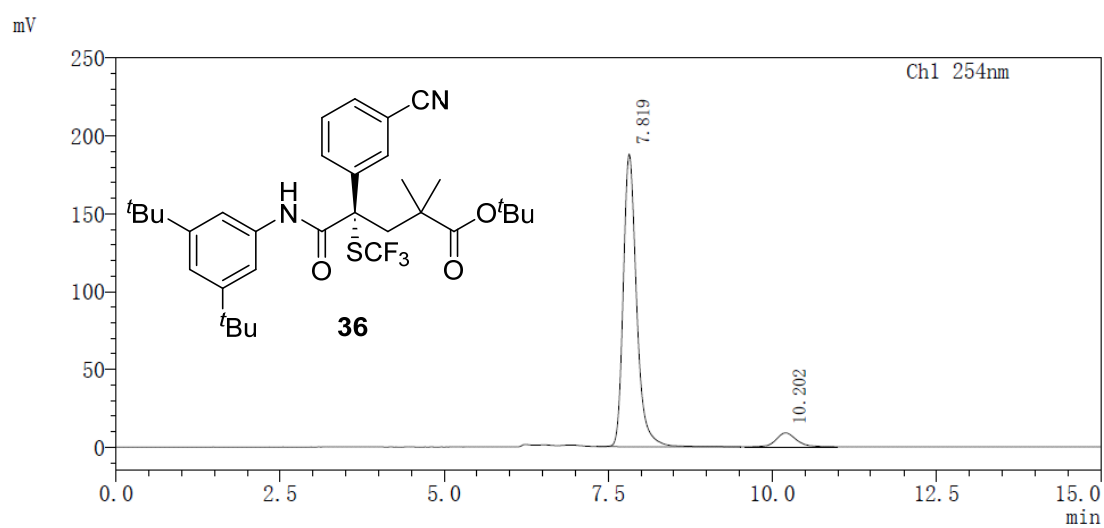
Ch1 254nm

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



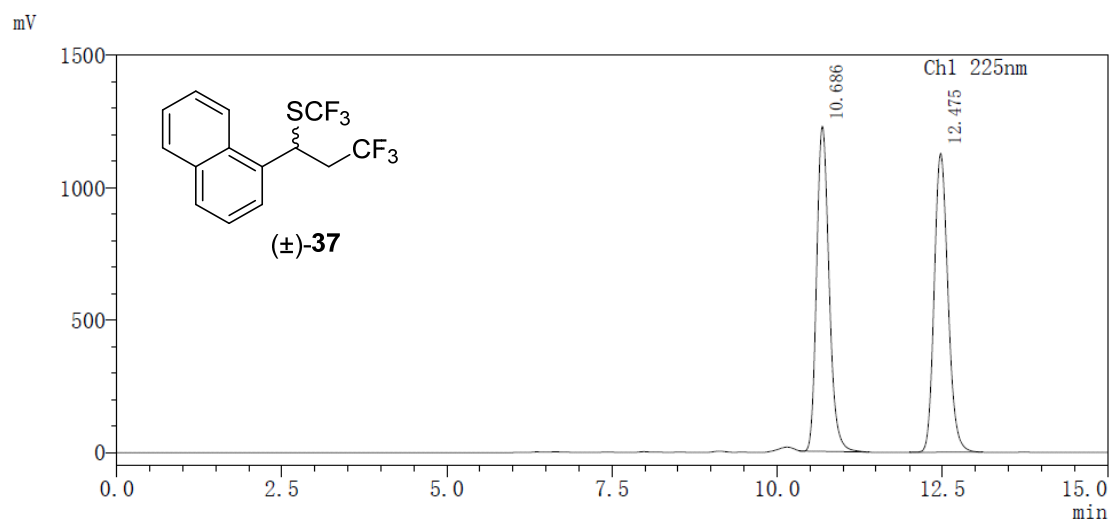
Ch1 254nm

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



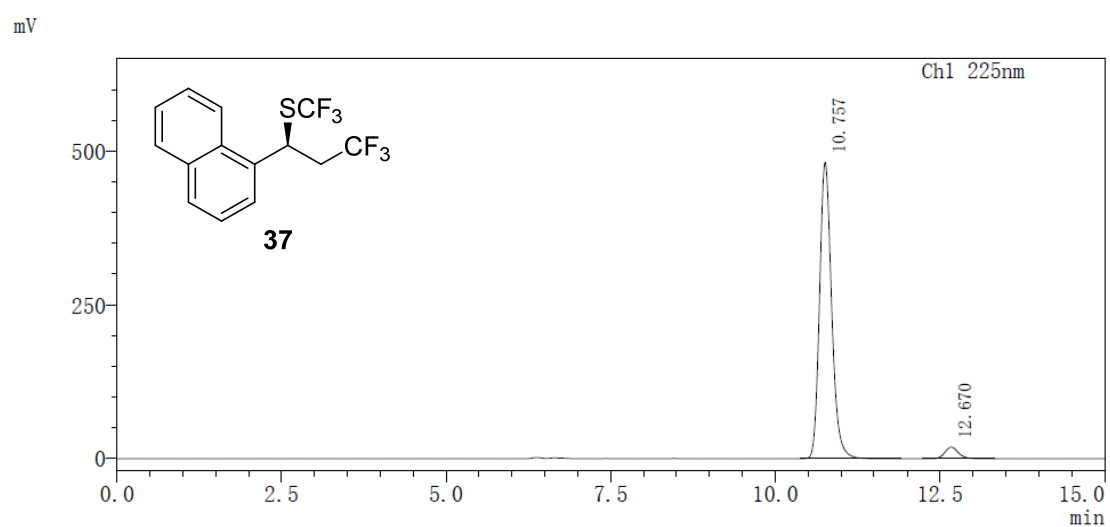
Ch1 254nm

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



Chl 225nm

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



Chl 225nm

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