Supporting Information for

Copper-Catalyzed Enantioselective C(sp³)–SCF₃ Coupling of

Carbon-Centered Benzyl Radicals with (Me₄N)SCF₃

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

Correspondence to: liuxy3@sustech.edu.cn

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

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

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

^{[&}lt;sup>+</sup>] These authors contributed equally to this work.

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 (Me₄NSCF₃) were prepared according to the previously reported procedures. CuTc and Cs₂CO₃ were purchased from Bide Pharmatech Ltd. Anhydrous diethyl ether (Et₂O) 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 KMnO₄ 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 ¹³C NMR, 162 MHz for ³¹P NMR, and 376 MHz for ¹⁹F NMR, respectively, in CDCl₃ with tetramethylsilane (TMS) as internal standard. The chemical shifts were expressed in ppm and coupling constants were given in Hz. Data for NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hz), integration. Mass spectrometric data were obtained using Thermo Scientific Q Exactive (ESI), JEOL AccuTOFTM-GCV (FI), and Waters Premier GC-TOF MS (EI). Enantiomeric excess (e.e.) was determined using SHIMADZU LC-20AD with SPD-20AV detector or Agilent high-performance liquid chromatography (HPLC) with Hatachi detector (at appropriate wavelength). Column conditions were reported in the experimental section below. X-ray diffraction was measured on a 'Bruker APEX-II CCD' diffractometer with Cu-Ka radiation.

2. Supplementary tables for experiments

^t Bu H H Cl O H Bu (±)- E1	$(\text{Me}_4\text{N})\text{SCF}_3 = \frac{\text{CuTc}}{\text{Cs}_2\text{CO}_3 (2.0 \text{ eq})}$	(15 mol%) uiv.), Solvent, rt, 24 h
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

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

[a] Reaction conditions: (\pm)-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.

^f Bu H Et F O ^f Bu (±)-E1	Ph Cl + (Me₄N)SCF₃ -	[Cu] (15 mol%), L*12 (17 mol%) Cs ₂ CO ₃ (2.0 equiv.), Et ₂ O, rt, 36 h	^{t}Bu H H SCF_{3} O O T H H SCF_{3} O O T H H H SCF_{3} O O H H H H H SCF_{3} O O H H H H H SCF_{3} O O O H H H H H H H SCF_{3} O O H
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

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

[a] Reaction conditions: (\pm)-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.

^t Bu H E ^t Bu C C	Et Ph CI + (Me ₄ N)SCF ₃ [Cu] (15 mo Base (2.0 e	bl%), L*12 (17 mol%) equiv.), Et₂O, rt, 36 h	H Et Ph SCF ₃
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

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

[a] Reaction conditions: (\pm)-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.

^{<i>i</i>} Bu H Et Ph O ^{<i>i</i>} Bu (±)- E1	+ (Me ₄ N)SCF ₃ ·	[Cu] (15 mol%), L*12 (17 mol%) Cs ₂ CO ₃ (1.0 equiv.), Solvent, rt, 36 h	^{t}Bu H Et Ph SCF_3 O ^{t}Bu 1
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

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

[a] Reaction conditions: (\pm)-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)



¹**H 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 = 7.8Hz), 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)



¹**H 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 = 9.2Hz, 1H), 4.03 (t, J = 8.0 Hz, 1H), 3.92 (d, J = 9.2**L*13** Ar = $4^{t}BuC_{6}H_{4}$ 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 ((±)-E1)



128.5, 128.4, 126.4, 119.1, 114.2, 79.5, 35.0, 34.8, 31.4, 9.6. **HRMS** (ESI) *m/z* calcd. for C₂₄H₃₃ClNO⁺ [M+H]⁺ 386.2245, found 386.2241.

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

¹³C NMR (100 MHz, CDCl₃) δ 167.9, 151.8, 141.1, 136.8, 128.5, 128.3, 126.4, 119.1, 114.3, 78.5, 49.4, 34.9, 31.4, 25.7, 24.3, 23.3. HRMS (ESI) *m/z* calcd. for C₂₆H₃₇ClNO⁺ [M+H]⁺ 414.2558, found 414.2554.

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



¹**H NMR** (400 MHz, CDCl₃) δ 8.51 (s, 1H), 7.63 – 7.60 (m, 2H), 7.42 (d, *J* = 1.6 Hz, 2H), 7.38 – 7.28 (m, 3H), 7.22 (t, *J* = 1.6 Hz, 1H), 2.55 – 2.50 (m, 1H), 2.46 – 2.41 (m, 1H), 1.32 (s, 18H), 1.00 – 0.90 (m, 1H), 0.49 – 0.42 (m, 2H),

0.31 – 0.22 (m, 1H), 0.16 – 0.07 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 167.9, 151.8, 140.9, 136.7, 128.42, 128.36, 126.5, 119.1, 114.4, 78.7, 46.0, 35.0, 31.4, 7.1, 4.6, 4.3. HRMS (ESI) *m/z* calcd. for C₂₆H₃₅ClNO⁺ [M+H]⁺ 412.2402, found 412.2404.

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)prop anamide ((±)-E5)



¹**H NMR** (400 MHz, CDCl₃) δ 8.34 (s, 1H), 7.66– 7.63 (m, 2H), 7.39 – 7.30 (m, 5H), 7.22 (t, *J* = 1.6 Hz, 1H), 3.90 – 3.82 (m, 2H), 3.37 – 3.29 (m, 2H), 2.69 – 2.64 (m, 1H), 2.39 – 2.34 (m, 1H), 1.94 – 1.89 (m,

1H), 1.72 - 1.66 (m, 2H), 1.51 - 1.41 (m, 2H), 1.31 (s, 18H). 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)



141.0, 140.4, 136.6, 128.6, 128.55, 128.52, 128.4, 126.3, 126.0, 119.2, 114.3, 78.2, 43.8, 35.0, 31.5, 31.4. **HRMS** (ESI) *m/z* calcd. for C₃₀H₃₇ClNO⁺ [M+H]⁺ 462.2558, found 462.2555.

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



¹H NMR (400 MHz, CDCl₃) δ 8.18 (s, 1H), 7.76– 7.70 (m, 2H), 7.67 – 7.62 (m, 4H), 7.41 – 7.31 (m, 5H), 7.27 – 7.18 (m, 4H), 4.19 (d, *J* = 14.0 Hz, 1H), 3.76 (d, *J* = 13.6 Hz, 1H), 1.29 (s, 18H). ¹³C NMR

(100 MHz, CDCl₃) δ 167.5, 151.6, 140.3, 136.4, 133.0, 132.8, 132.5, 132.0, 129.2, 128.6, 128.5, 127.8, 127.5, 127.1, 126.7, 125.8, 125.7, 119.2, 114.8, 78.0, 47.1, 34.9, 31.3. HRMS (ESI) *m/z* calcd. for C₃₃H₃₇ClNO⁺ [M+H]⁺ 498.2558, found 498.2554.

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

¹H NMR (400 MHz, CDCl₃) δ 8.21 (s, 1H), 7.63 – 7.60 ^tBu H NMR (400 MHz, CDCl₃) δ 8.21 (s, 1H), 7.63 – 7.60 (m, 2H), 7.39 – 7.29 (m, 5H), 7.21 (t, J = 1.6 Hz, 1H), 7.14 – 7.12 (m, 1H), 7.04 – 7.03 (m, 1H), 6.88 (d, J = 4.8 Hz, 1H), 4.02 (d, J = 14.4Hz, 1H), 3.67 (d, J = 4.8 Hz, 1H), 4.02 (d, J = 14.4Hz, 1H), 3.67 (d, J = 4.8 Hz, 1H), 4.02 (d, J = 14.4Hz, 1H), 3.67 (d, J = 4.8 Hz, 1H), 4.02 (d, J = 14.4Hz, 1H), 3.67 (d, J = 4.8 Hz, 1H), 4.02 (d, J = 14.4Hz, 1H), 3.67 (d, J = 4.8 Hz, 1H), 4.02 (d, J = 14.4Hz, 1H), 3.67 (d, J = 4.8 Hz, 1H), 4.02 (d, J = 14.4Hz, 1H), 3.67 (d, J = 4.8 Hz, 1H), 4.02 (d, J = 14.4Hz, 1H), 3.67 (d, J = 4.8 Hz, 1H), 4.02 (d, J = 14.4Hz, 1H), 3.67 (d, J = 4.8 Hz, 1H), 4.02 (d, J = 14.4Hz, 1H), 4.0

14.4Hz, 1H), 1.31 (s, 18H). ¹³C NMR (100 MHz, CDCl₃) δ 167.5, 151.7, 140.1, 136.4, 135.5, 130.0, 128.6, 128.5, 126.6, 124.7, 124.3, 119.2, 114.7, 77.6, 41.9, 34.9, 31.3. HRMS (ESI) *m/z* calcd. for C₂₇H₃₃ClNOS⁺ [M+H]⁺ 454.1966, found 454.1959.

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



MHz, CDCl₃) δ -66.0 (t, J = 10.5 Hz, 3F). ¹³C NMR (100 MHz, CDCl₃) δ 166.9, 152.0, 139.0, 136.4, 129.0, 128.9, 126.8 (q, J = 274.5 Hz), 126.1, 119.4, 114.2, 76.4, 35,0, 34.9 (q, J = 3.2 Hz), 31.4, 30.3 (q, J = 29.1 Hz). HRMS (ESI) m/z calcd. for C₂₅H₃₂ClF₃NO⁺ [M+H]⁺ 454.2119, found 454.2117.

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



45.8, 34.9, 31.3. **HRMS** (ESI) *m/z* calcd. for C₂₅H₃₃ClNO⁺ [M+H]⁺ 398.2245, found 398.2247.

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



119.2, 115.3, 114.3, 78.2, 40.9, 35.0, 31.2, 29.3. **HRMS** (ESI) m/z calcd. for C₂₆H₃₅ClNO⁺ [M+H]⁺ 412.2402, found 412.2400.

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



¹**H 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)



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)



¹**H** 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).

¹⁹**F NMR** (376 MHz, CDCl₃) δ –113.50 – –113.57 (m, 1F). ¹³**C 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)



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



¹**H** 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)



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)



-0.18 (m, 1H), 0.15 - 0.05 (m, 1H).¹⁹**F NMR** (376 MHz, CDCl₃) δ -111.17 - -111.13 (m, 1F). ¹³**C 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 ((±)-E23)



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)



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 ((\pm)-**E26-32**) were prepared according to the previously reported procedure.^[3] Among them, (\pm)-**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 ((\pm) -E27)



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

¹**H** 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 –

(±)-E28 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)



Br

¹**H 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)



¹**H** 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)



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)



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)



35.0, 31.4, 26.7. **HRMS** (ESI) m/z calcd. for C₂₅H₃₂NO₂⁺ [M+H]⁺ 378.2428, found 378.2425.

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



¹**H NMR** (400 MHz, CDCl₃) 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, CDCl₃) 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 C₂₄H₂₉N₂O⁺ [M+H]⁺ 361.2274, found 361.2272.

6. General procedure of enantioselective radical trifluoromethylthiolation

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



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with the substrates (\pm)-E (0.1 mmol), (Me4N)SCF₃ (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%), 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 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, CDCl₃) 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). ¹⁹F NMR (376 MHz, CDCl₃) δ –37.2 (s, 3F). ¹³C NMR (100 MHz, CDCl₃) 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 C₂₅H₃₃F₃NOS⁺ [M+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)penta namide (2)



The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **2** (34.4 mg, 72% yield) as a white solid. ¹**H NMR** (400 MHz, 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_I = 14.8 Hz, J_2 = 4.8 Hz, 1H), 2.33 (dd, J_I = 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. ¹**H 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, $J_I = 14.8$ Hz, $J_2 = 6.4$ Hz, 1H), 2.42 (dd, $J_I = 14.8$ 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, $\lambda = 254$ nm), t_R (minor) = 8.14 min, t_R (major) = 8.57 min, 92% ee.

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



The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **4** (41.9 mg, 83% yield) as a white solid. ¹**H NMR** (400 MHz, 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_l = 14.8 Hz, J_2 = 5.6 Hz, 1H), 2.51 (dd, J_l = 15.2 Hz, J_2 = 6.0 Hz, 1H), 2,20 – 2.08 (m, 1H), 1.81 – 1.73 (m, 1H), 1.66 – 1.50 (m, 3H), 1.47 – 1.41(m, 2H), 1.29 (s, 18H), 1.14 – 0.95 (m, 2H). ¹⁹**F** NMR (376 MHz, CDCl₃) δ –36.9 (s, 3F). ¹³**C** 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-((triflu oromethyl)thio)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. ¹**H 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, $\lambda = 254$ 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)propenami de (6)



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, $\lambda = 254$ 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)butanamid e (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



a white solid. ¹**H 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, $J_I = 8.4$ 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, $\lambda = 254$ 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)th io)propenamide (9)



The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **9** (45.2 mg, 87% yield) as a white solid. ¹**H NMR** (400 MHz, 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, $\lambda = 254$ 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 $(1:7.5\sim1:3, v/v)$ to afford product **10** (43.1 mg, 83% yield)



1.31 (s, 18H). ¹⁹**F NMR** (376 MHz, CDCl₃) δ –37.0 (s, 3F), –66.1 (t, J = 10.5 Hz, 3F). ¹³**C 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-enamid e (11)



(m, 3H), 7.43 – 7.35 (m, 3H), 7.25 (s, 2H), 7.22 (s, 1H), 5.89 – 5.79 (m, 1H), 5.15 – 5.08 (m, 2H), 3.37 (dd, J_1 = 14.8 Hz, J_2 = 6.8 Hz, 1H), 3.21 (dd, J_1 = 14.8 Hz, J_2 = 7.2 Hz, 1H), 1.30 (s, 18H). ¹⁹**F** NMR (376 MHz, CDCl₃) δ –36.8 (s, 3F). ¹³**C** 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. ¹**H 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, $J_l = 16.8$ Hz, $J_2 = 1.6$ Hz, 1H), 4.99 (dq, $J_l = 10.4$ 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, $\lambda = 254$ 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). ¹⁹**F NMR** (376 MHz, CDCl₃) δ –37.2 (s, 3F). ¹³**C 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, $\lambda = 254$ 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, $\lambda = 254$ 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)but anamide (15)



The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether $(1:7.5\sim1:3, v/v)$ to afford product **15** (43.6 mg, 86% yield) as a

white solid. ¹**H** 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). ¹⁹**F** NMR (376 MHz, CDCl₃) δ –37.2 (s, 3F). ¹³**C** 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-((trifluorometh yl)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, $J_I = 8.0$ Hz, $J_2 = 2.4$ Hz, 1H), 3.82 (s, 3H), 2.56 (dd, $J_I = 14.8$ Hz, $J_2 = 4.8$ Hz, 1H), 2.32 (dd, $J_I = 14.8$ 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, $\lambda = 254$ 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)buta namide (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, $\lambda = 254$ nm), t_R (minor) = 14.79 min, t_R (major) = 20.70 min, 86% ee.

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



The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **18** (41.3 mg, 88% yield) as a white solid. ¹**H NMR** (400 MHz, 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). ¹⁹**F NMR** (376 MHz, CDCl₃) δ –37.2 (s, 3F), –112.26 – –112.33 (m, 1F). ¹³**C 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, $\lambda = 254$ nm), t_R (minor) = 9.89 min, t_R (major) = 10.58 min, 90% ee.

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



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, $\lambda = 254$ 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)b utanamide (20)

The residue was purified by column chromatography Et SCF3 ^tBu on silica gel with an eluent of DCM and petroleum Ô ether (1:7.5~1:3, v/v) to afford product 20 (40.1 mg, ^tBu CI 77% yield) as a white solid. ¹H NMR (400 MHz, 20 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)buta namide (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, $J_I = 8.8$ 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, $\lambda = 254$ 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. ¹**H 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, $J_I = 7.2$ Hz, $J_2 = 1.6$ Hz, 1H), 2.56 (dd, $J_I = 14.8$ Hz, $J_2 = 6.4$ Hz, 1H), 2.36 (dd, $J_I = 14.8$ 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, $\lambda = 254$ 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)propena mide (23)



The residue was purified by column chromatography on silica gel with an eluent of DCM and petroleum ether (1:7.5~1:3, v/v) to afford product **23** (33.0 mg, 86% yield) as a white solid. ¹**H NMR** (400 MHz, 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, $\lambda = 254$ 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)pro penamide (24)



(m, 2H), 7.42 – 7.33 (m, 4H), 7.05 (s, 2H), 6.77 (s, 1H), 2.56 (dd, $J_I = 14.8$ Hz, $J_2 = 6.4$ Hz, 1H), 2.34 (dd, $J_I = 14.8$ 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, $\lambda = 254$ 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)p ropenamide (25)

The residue was purified by column chromatography on si lica gel with an eluent of DCM and petroleum ether (1:7.5 Me \sim 1:3, v/v) to afford product **25** (34.6 mg, 85% yield) as a w Me 25 Мe hite 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 (d d, $J_1 = 14.8$ 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, C DCl₃) 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 (\pm)-**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 ge 1 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 C ¹⁴H₁₃F₃S [M] 270.0690, found 270.0685. HPLC analysis: Chiralcel OD-H (hexane, flo w rate 1.00 mL/min, $\lambda = 214$ 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 g el 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 MH z, CDCl₃) δ –40.3 (s, 3F). ¹³C NMR (100 MHz, CDCl₃) δ 135.9, 133.9, 130.7 (q, J = 3 05.8 Hz), 130.2, 129.2, 128.9, 126.7, 125.9, 125.3, 124.8, 122.5, 39.8, 23.1. HRMS (F I) *m/z* calcd. for C₁₃H₁₁F₃S [M] 256.0534, found 256.0528. HPLC analysis: Chiralcel OD-H (hexane/*i*-PrOH = 99/1, flow rate 0.50 mL/min, $\lambda = 225$ 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 0.6 mg, 69% yield) as a colorless oil. ¹H NMR (400 MHz, C DCl₃) 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). ¹³ C 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] 298.1 003, found 298.0998. HPLC analysis: Chiralcel OD-H (hexane, flow rate 1.00 mL/mi n, $\lambda = 214$ 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

29 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, CDC l₃) 8.12 - 8.09 (m, 1H), 8.07 - 8.05 (m, 1H), 7.60 - 7.53 (m, 2 H), 7.50 - 7.42 (m, 1H), 7.31 (d, J = 7.6 Hz, 1H), 5.06 (brs, 1

H), 2.69 (s, 3H), 2.27 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H). 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 a nalysis: Chiralcel OD-H (hexane, flow rate 1.00 mL/min, λ = 214 nm), t_R (minor) = 1 2.15 min, t_R (major) = 19.71 min, 87% ee.

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



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). ¹⁹F NMR (376 MHz, CDCl₃) δ –40.0 (brs, 3F). ¹³C NMR (100 MHz, CDCl₃) 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 C₁₄H₁₂BrF₃S [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-([1,1'-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, CDCl₃) 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). ¹⁹F NMR (376 MHz, CDCl₃) δ – 39.7 (s, 3F). ¹³C NMR (100 MHz, CDCl₃) δ 140.7, 140.5, 139.4, 130.6 (q, J = 305.2Hz), 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), (Me4N)SCF₃ (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%), Cs₂CO₃ (32.6 mg, 0.10 mmol, 1.0 equiv.), toluene (2.0 mL), and BrMe₂CCO₂/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 $(1:50\sim1:30, v/v)$ 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, $\lambda = 254$ 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*₁ = 8.0 Hz, *J*₂ = 1.2 Hz,

1H), 7.81 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.31 (d, J = 2.0 Hz, 2H), 7.23 (t, J = 1.6 Hz, 1H), 3.18 (d, J = 15.2 Hz, 1H), 2.92 (d, J = 14.8 Hz, 1H), 2.62 (s, 3H), 1.35 (s, 9H), 1.31 (s, 18H), 1.24 (s, 3H), 1.17 (s, 3H). 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, $\lambda = 254$ 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, $\lambda = 254$ 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, $\lambda = 225$ nm), t_R (major) = 10.76 min, t_R (minor) = 12.67 min, 92% ee.

7. Mechanistic Investigations

CuSCF ₃ + (1.5 equiv.)	^t Bu H Et Ph O Cl ^t Bu (±)-E1	$\frac{\text{Cs}_2\text{CO}_3 (1.0 \text{ equiv.})}{\text{Et}_2\text{O}, \text{ rt}, 26 \text{ h}}$	^t Bu ^t Bu ^t Bu ^t Bu ^t Bu ^t Bu
Entry	L*	Result	Ee
1		trace	
2	L*12 (12 mol%)) 26%	65%
3 ^[a]	L*12 (1.7 equiv.) 92%	87%

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 (\pm)-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

^t Bu tBu (±)- E1	$ \begin{array}{c} Et Ph \\ \hline Cl \\ O + (Me_4N)SCF_3 \underline{standard} \\ (1.5 equiv.) \\ \hline $	d conditions	HEt, Ph SCF ₃
Entry	Additive (1.0 equiv)	Result	Ee
1	TEMPO	trace	
2	BHT	trace	

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with the substrates (\pm)-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 (\pm)-**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. ¹**H NMR** (400 MHz, CDCl 3) 8.18 (d, J = 8.0 Hz, 1H), 7.86 – 7.83 (m, 1H), 7.73 (d, J = 8. 0 Hz, 1H), 7.56 (d, J = 6.8 Hz, 1H), 7.52 – 7.43 (m, 3H), 5.45 (q, J = 6.4 Hz, 1H), 1.65 (d, J = 6.8 Hz, 3H), 1.54 (s, 3H), 1.4 5 – 1.29 (m, 6H), 1.24 (s, 3H), 1.01 (s, 3H), 0.62 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) 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 C₂₁H₃₀NO ⁺ [M+H]⁺ 312.2322, found 312.2322.

^t Bu	t _{Bu}	N CI	CO + (Me₄N)S (1.5 equ	CF ₃ CuTc (15 mol%), iv.) Cs ₂ CO ₃ (1.0 eq	L* 12 (17 mol%) wiv.), Et ₂ O, rt	(R)- 5
	Entry	Sub.	Time	Recovered sub.	(R)-5	_
	1	E5 (>99% ee)	2.75 h	32% of E5	52%, 92% ee	
	2	E5' (>–99% ee)	2.75 h	55% of E5'	34%, 92% ee	
	3	(±)- E5 (0% ee)	4 h	70%, –21% ee for E5'	24%, 92% ee	
	4	(±)- E5 (0% ee)	6 h	33%, –61% ee for E5'	44%, 92% ee	

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), (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.), and Et₂O (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 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 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 (\pm)-E5 (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.), and Et₂O (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

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 56.016 220 70.7882 219 55.3 218 51.2891 217 65.966 216 60.4344 215 39.0506 214 23.0689	261	-0.08085
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	260	-0.14627
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 56.016 220 70.7882 219 55.3 218 51.2891 217 65.966 216 60.4344 215 39.0506 214 23.0689	259	-0.19021
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	258	-0.28424
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	257	-0.40528
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 37.996 225 28.4053 224 37.996 225 28.4053 224 37.996 225 28.4053 214 51.2891 217 65.966 216 60.4344 215 39.0506 214 23.0689	256	-0.54407
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 56.016 220 70.7882 219 55.3 218 51.2891 217 65.966 216 60.4344 215 39.0506 214 23.0689	255	-0.77674
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 56.016 220 70.7882 219 55.3 218 51.2891 217 65.966 216 60.4344 215 39.0506 214 23.0689	254	-0.97958
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 56.016 220 70.7882 211 67.0062 220 70.7882 219 55.3 218 51.2891 217 65.966 216 60.4344 215 39.0506 214 23.0689	253	-1.19221
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 56.016 220 70.7882 211 67.0062 220 70.7882 219 55.3 218 51.2891 217 65.966 216 60.4344 215 39.0506 214 23.0689	252	-1.48612
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	251	-1.74683
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	250	-2.07893
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 56.016 220 70.7882 219 55.3 218 51.2891 217 65.966 216 60.4344 215 39.0506 214 23.0689	249	-2.54912
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 56.016 220 70.7882 219 55.3 218 51.2891 217 65.966 216 60.4344 215 39.0506 214 23.0689	248	-3.14204
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	247	-3.85964
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 37.996 225 28.4053 224 37.996 225 26.0181 221 67.0062 220 70.7882 219 55.3 218 51.2891 217 65.966 216 60.4344 215 39.0506 214 23.0689	246	-4.56526
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	245	-5.19158
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	244	-5.73461
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	243	-6.09715
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	242	-6.28336
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	241	-6.32554
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	240	-6.26072
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	239	-5.86903
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	238	-5.31496
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	237	-3.70894
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	236	-2.13138
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	235	0.272447
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	234	2.79179
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	233	6.55886
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	232	9.74115
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	231	13.7558
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	230	16.5718
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	229	22.2327
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	228	22.1913
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	227	25.6629
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	226	25.4196
22437.99622356.01622265.018122167.006222070.788221955.321851.289121765.96621660.434421539.050621423.0689	225	28.4053
22356.01622265.018122167.006222070.788221955.321851.289121765.96621660.434421539.050621423.0689	224	37.996
22265.018122167.006222070.788221955.321851.289121765.96621660.434421539.050621423.0689	223	56.016
22167.006222070.788221955.321851.289121765.96621660.434421539.050621423.0689	222	65.0181
22070.788221955.321851.289121765.96621660.434421539.050621423.0689	221	67.0062
21955.321851.289121765.96621660.434421539.050621423.0689	220	70.7882
21851.289121765.96621660.434421539.050621423.0689	219	55.3
21765.96621660.434421539.050621423.0689	218	51.2891
21660.434421539.050621423.0689	217	65.966
21539.050621423.0689	216	60.4344
214 23.0689	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.





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

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

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

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

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

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

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

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

8.5 Cartesian Coordinates of Computed Species

(S)-27-C1

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

С	-0.03226100	1.92520900	0.47124400
С	-1.03238200	2.63541700	-0.23055100
Н	0.87415100	2.44961300	0.74874800
Н	-0.87291500	3.68258000	-0.46990300
С	0.90677700	-0.13391400	1.55715600
Н	0.43884900	-0.83930200	2.25123700
С	1.86301400	0.74920300	2.36240700
Н	1.29294400	1.40089300	3.03416000
Н	2.52766200	0.12307700	2.96334300
Н	2.48569300	1.36951400	1.71576700
S	1.87327400	-1.32893800	0.47823700
С	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

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

Н	-2.02976100	-3.06171100	1.60816400
С	-0.47251600	2.17360100	-0.46296700
С	-1.66946500	2.38372900	-1.17797600
Н	0.31233500	2.92144200	-0.52565200
Н	-1.79086300	3.28924300	-1.76506000
С	1.01684200	0.90815200	1.09372000
Н	0.98935100	0.02846700	1.73337600
С	1.30135300	2.12390500	1.98640200
Н	2.18963400	1.95435800	2.60221700
Н	1.45710600	3.03467600	1.40064500
Н	0.44256900	2.29228700	2.64360400
S	2.52571600	0.68558400	0.02093300
С	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

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

Н	-1.61336700	-2.35307100	-0.26055100
Н	-3.98412700	-2.89211100	-0.17796200
С	-0.14775600	1.51134400	-0.05289100
С	-1.12801800	2.52032600	0.08366600
Н	0.89503500	1.79827200	-0.09218000
Н	-0.81539500	3.55830900	0.14916800
С	0.56170700	-0.91918200	-0.23646800
Н	0.18400700	-1.70640900	-0.89504400
С	0.85608800	-1.54852800	1.13369100
Н	-0.08331400	-1.91683100	1.55749100
Н	1.55884600	-2.38103300	1.04997400
Н	1.26432400	-0.80703700	1.82328700
S	2.08712400	-0.44440900	-1.18992100
С	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

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

С	0.44877200	1.18098600	0.37730500
Н	-0.15165600	-1.42399900	1.14677800
Н	1.31385400	-3.35005600	1.01636500
С	0.94962400	2.36303500	-0.14221200
С	2.2223600	2.44978000	-0.74230300
Н	0.34034800	3.26165700	-0.08483800
Н	2.56680900	3.40172200	-1.13503900
С	-0.91744400	1.28315500	1.04133200
Н	-1.05523500	2.35251000	1.23282300
С	-1.13856200	0.58303200	2.39062700
Н	-0.23677700	0.67848900	3.00498100
Н	-1.97009400	1.06534500	2.91250700
Н	-1.38442700	-0.47291300	2.29936100
S	-2.37307800	1.08529400	-0.12050800
С	-2.31909300	-0.64203700	-0.65907600
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F	-3.39485300	-0.84315100	-1.44001700
F	-2.38695900	-1.53041800	0.36203600

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

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

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

Н	5.02730200	-0.17778400	-0.66715400
С	3.20755500	1.76467900	-0.39229700
С	0.62042600	0.85048900	0.29151500
Н	0.51870400	-1.90891500	0.48991600
Н	2.37249200	-3.45470500	0.16489200
С	0.88788100	2.19342700	0.10744800
С	2.17802100	2.65893100	-0.23124000
Н	0.08400700	2.91428800	0.23149100
Н	2.34568400	3.72377400	-0.36238600
С	-0.78197500	0.46731000	0.71759500
Н	-1.39011800	1.37281800	0.66758700
С	-0.87365300	-0.10378100	2.13813900
Н	-0.46826300	0.63327900	2.84108700
Н	-1.91357100	-0.30508300	2.40322400
Н	-0.29986000	-1.02550700	2.25055500
S	-1.55642500	-0.65340500	-0.56802800
С	-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

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

Н	-3.85892100	-3.31533200	0.10929400
Н	-4.80665500	-1.07916500	-0.37754300
С	-3.47671500	1.24674300	-0.42017800
С	-0.72955100	1.03005800	0.21356700
Н	0.02904500	-1.59422700	0.64107900
Н	-1.42894400	-3.54563200	0.61589800
С	-1.30556400	2.24890500	-0.08538300
С	-2.67834700	2.36330200	-0.40497800
Н	-0.70211200	3.14944800	-0.06980200
Н	-3.09315000	3.34094700	-0.63175900
С	0.74078600	0.93988500	0.56862000
Н	0.87950900	0.14326900	1.30237500
С	1.37169000	2.22113800	1.11350800
Н	0.80694100	2.57314600	1.98442700
Н	2.40176200	2.02738600	1.41849000
Н	1.39148100	3.01690400	0.36426800
S	1.63718600	0.34943200	-0.96611400
С	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

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10. NMR spectra of the optimized ligands and the products





















































































S85

























20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2 f1 (ppm)





7.0 2.5 1.0 10.0 7.5 9.5 9.0 8.5 8.0 6.5 5.0 fl (ppm) 3.0 2.0 1.5 0.5 0.0 6.0 5.5 4.5 4.0 3.5


























































































































11. HPLC spectra of the products



Peak Table

1	Ch1 254nm							
	Peak#	Ret. Tim	le Area	Area%				
	1	17.172	1865258	49.052				
	2	17.775	1937337	50.948				



D 1		n :	1 1	
Poal	7	0	h l	\circ
i ea	n l	a	UI	L E

Ch1 254nm

Peak#	Ret.	Time	Area	Area%	
1	17.	162	89237	2.936	
2	17.	745	2950239	97.064	







Peak Table

Ch2 254nm							
Peak#	Ret. Time	Area	Area%				
1	9.435	427612	49.828				
2	9.942	430557	50.172				



Ch2 254nm

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





2	2 12	2.352	MM	0.4296	629.00525	24.40534	96.9778

Totals : 648.60750 25.40031



50-Ch1 254nm 18.035 H _b Рh 40-^tBu ′SCF₃ ∬ O 30-6 ^tBu 20-10-16.035 0-10 15 0 5 20 min Ch1 254nm T 16.035 18.035 Area% 4.368 95.632 Hight Area 1871 44317 34360 970164

mV





Detector A Ch1 254nm						
Peak#	Ret. Time	Area	Area%			
1	16.176	1929548	50.610			
2	18.065	1883020	49.390			

mV



Peak Table

Detector A Ch1 254nm							
Peak#	Ret. Time	Area	Area%				
1	16.210	458293	92.726				
2	18.432	35952	7.274				







Peak Table

PDA Ch1 254nm						
Peak#	Ret. Time	Area	Area%			
1	8.196	3291899	50.645			
2	10.557	3208092	49.355			





PI	PDA Ch1 254nm						
P	'eak#	Ret. Time	Area	Area%			
Γ	1	8.186	3388570	94. 516			
Γ	2	10.507	196611	5.484			







mV

























Peak Table

PDA Ch1 254nm					
	Peak#	Ret.	Time	Area	Area%
	1	14.	050	133961	50.056
	2	14.	672	133663	49.944



 PDA
 Ch1
 254nm

 Peak#
 Ret.
 Time
 Area
 Area%

 1
 14.075
 13080
 2.972

 2
 14.701
 426988
 97.028



mV





Peak Table

PDA Ch1 254nm						
Peak#	Ret. Time	Area	Area%			
1	9.954	1872336	50.040			
2	10.729	1869338	49.960			



 PDA Ch1 254nm

 Peak# Ret. Time
 Area
 Area%

 1
 9.888
 2385470
 5.213

 2
 10.576
 43370374
 94.787



PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	
1	8.841	2072170	49.168	
2	9.279	2142285	50 .832	

mAU



Peak Table

PDA Ch1 254nm

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








mAU





mAU



mAU







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 Ch	PDA Ch1 254nm					
Peak#	Ret. Time	Area	Area%			
1	6.336	34366	4.572			
2	6.899	717351	95.428			





mAU





Ch2 214nm					
Peak	RetTime	Area	Height	Area%	
1	18.814	6296204	287013	49.938	
2	23.785	6311899	227184	50.062	

mV



Ch2 21	4nm			
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 Ch	PDA Ch3 225nm					
Peak#	Ret. Time	Area	Area%			
1	8.852	259159	5.785			
2	9.442	4220863	94.215			



Ch2 21	4nm			
Peak	RetTime	Area	Height	Area%
1	10. 525	4592532	348168	50.063
2	12.132	4580888	303249	49.937



_Ch2_2	14nm			
Peak	RetTime	Area	Height	Area%
1	10.512	4218017	331394	95.818
2	12.012	184081	13328	4. 182



Peak Table

PDA Ch	PDA Ch2 214nm					
Peak#	Ret. Time	Area	Area%			
1	6. 320	1197305	50.043			
2	7.562	1195240	49.957			



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PDA Ch2 214nm						
Peak#	Ret. Time	Area	Area%			
1	6.293	204875	6.560			
2	7.539	2918318	93.440			



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

mV







 Ch2
 214nm

 Peak
 RetTime
 Area
 Height
 Area%

 1
 9.866
 268858
 23266
 5.941

 2
 14.921
 4256779
 232944
 94.059







Ch1 25	4nm			
Peak	RetTime	Area	Height	Area%
1	9.762	544229	49874	49.951
2	10.469	545290	49502	50.049



Ch1	25	4nm			
Pe	ak	RetTime	Area	Height	Area%
	1	9.694	62308	6157	5.846
	2	10.601	1003441	162441	94.154









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 25	4nm			
Peak	RetTime	Area	Height	Area%
1	7.819	2663775	188087	93.278
2	10.202	191952	8948	6.722



Ch1 225nm						
Peak	RetTime	Area	Height	Area%		
1	10.686	16137849	1228013	49.578		
2	12.475	16412883	1128831	50.422		

mV



Ch1 225nm						
Peak	RetTime	Area	Height	Area%		
1	10.757	6159518	482419	95.845		
2	12.670	267044	18824	4. 155		