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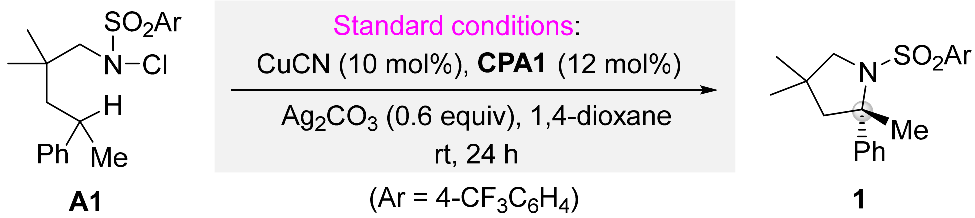
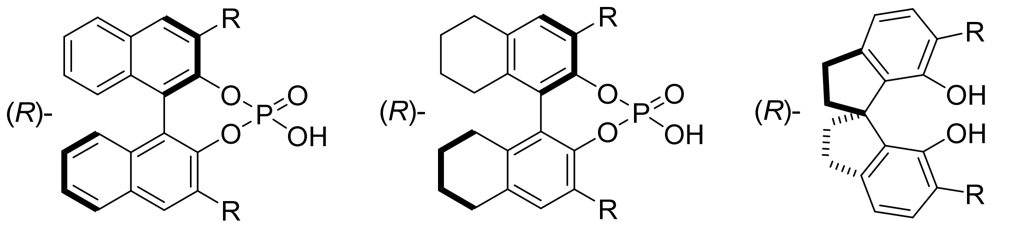
Table S1. Optimization of enantioselective tertiary C(sp^3)–H amination.





CPA1, R = 9-phenanthryl
CPA2, R = 9-anthranyl
CPA3, R = 2-naphthyl

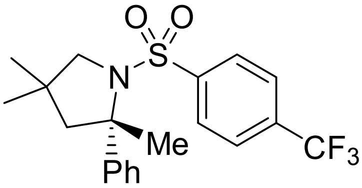
CPA4, R = 9-phenanthryl
CPA5, R = 9-anthranyl
CPA6, R = 2-naphthyl

CPA7, R = 9-phenanthryl
CPA8, R = 9-anthranyl
CPA9, R = 2-naphthyl

Entry	Variation from standard conditions[a]	Yield (%)[b]	Ee (%)[c]
1[d]	none	40 (33)	80
2[d]	**CPA2**, instead of **CPA1**	32	67
3[d]	**CPA3**, instead of **CPA1**	23	49
4	**CPA4**, instead of **CPA1**	16	32
5	**CPA5**, instead of **CPA1**	8	N.D.
6	**CPA6**, instead of **CPA1**	37	20
7	**CPA7**, instead of **CPA1**	42	27
8	**CPA8**, instead of **CPA1**	35	23
9	**CPA9**, instead of **CPA1**	30	11
10	CuBr, instead of CuCN	20	56
11	CuI, instead of CuCN	45	72
12	CuTc, instead of CuCN	50	33
13	$Cu(MeCN)_4PF_6$, instead of CuCN	<5	N.D.
14	CuOAc, instead of CuCN	<5	N.D.
15	Ag_3PO_4 (0.4 equiv), instead of Ag_2CO_3	85	<2
16[d]	Ag_2O (0.6 equiv), instead of Ag_2CO_3	11	49
17[d]	AgOAc (1.2 equiv), instead of Ag_2CO_3	22	60
18[d]	$AgNO_3$ (1.2 equiv), instead of Ag_2CO_3	20	11
19	AgOTf (1.2 equiv), instead of Ag_2CO_3	97	<2
20	THF, instead of 1,4-dioxane	21	43
21	CH_2Cl_2, instead of 1,4-dioxane	<5	N.D.
22	EtOAc, instead of 1,4-dioxane	<5	N.D.
23	PhCl, instead of 1,4-dioxane	0	–

[a] Standard conditions: **A1** (0.10 mmol), CuCN (10 mol%), **CPA1** (12 mol%), and Ag_2CO_3 (0.6 equiv) in 1,4-dioxane (2.0 mL) at rt for 24 h under argon. [b] Yields were based on ^{19}F NMR analysis

of the crude product using (trifluoromethyl)benzene as an internal standard. Isolated yield in parenthesis. [c] Ee values were determined by chiral HPLC analysis. [d] The olefinic by-product **BP2** was detected as the major product based on ^{19}F NMR analysis. N.D., not determined. Tc, 2-thiophenecarboxylato.



(*S*)-**1**

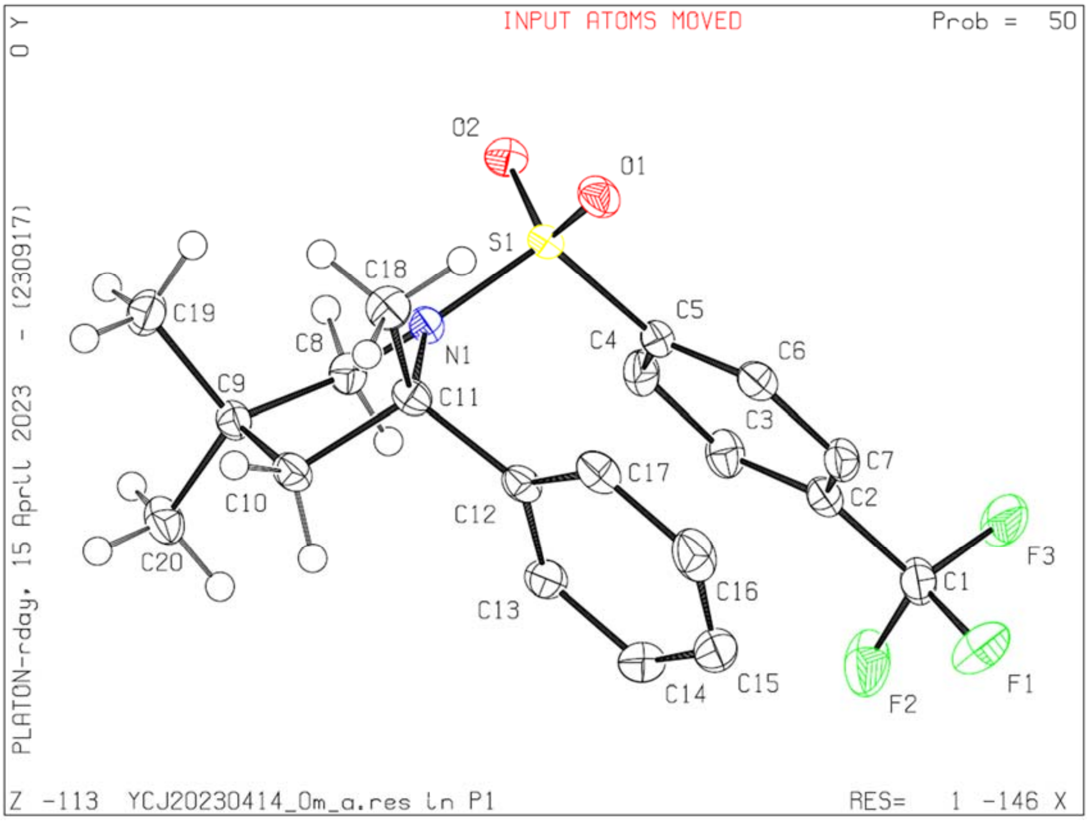


Figure S1. The X-ray structure of (*S*)-**1** (CCDC 2256562, 50% probability ellipsoids).

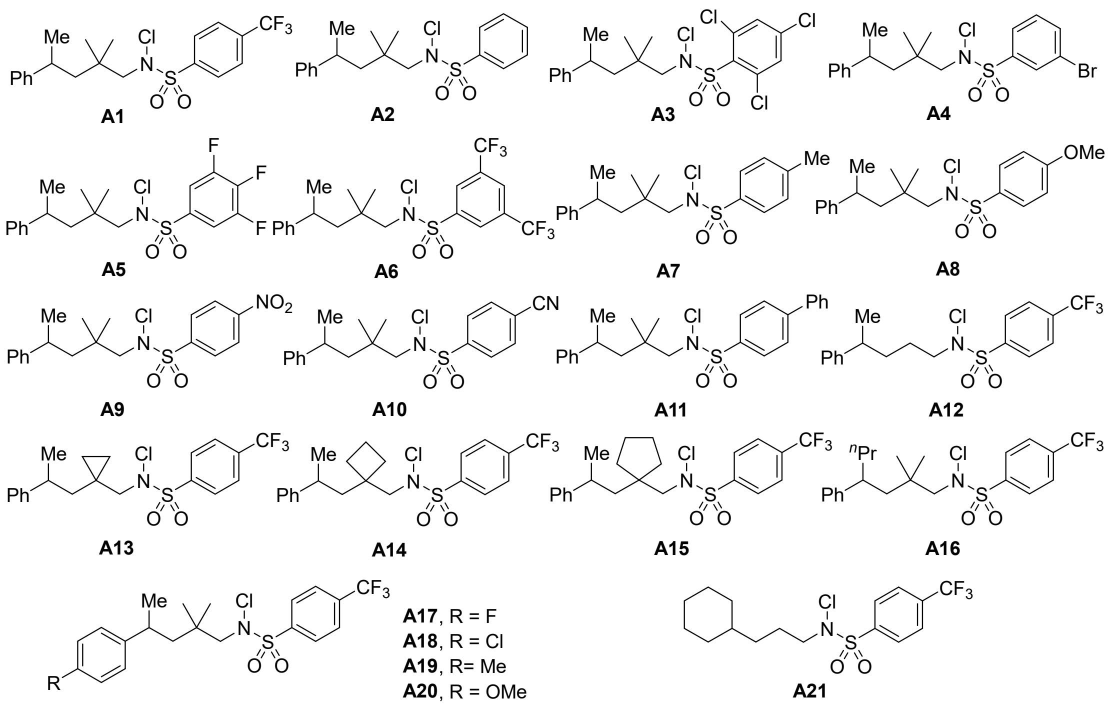
General information

Reactions were carried out under argon atmosphere using Schlenk techniques. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. CuTc (CAS No. 68986−76−5) and CuCN (CAS No. 544−92−3) were purchased from Alfa Aesar. AgOTf (CAS No. 2923−28−6), Ag_2CO_3 (CAS No. 534−16−7) and $(PhO)_2P(O)OH$ (CAS No. 838−85−7) were purchased from Bidepharm. Chiral phosphoric acid (**CPA**) was purchased from Daicel Chiral Technologies (China). Anhydrous 1,4-dioxane was purchased from Beijing J&K Scientific Co., Ltd.

Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm), iodine on silica gel or basic $KMnO_4$ indicator. NMR spectra were recorded on Bruker DRX-400 spectrometer at 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, and 376 MHz for ^{19}F NMR, respectively, in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; p, pentet, m, multiplet; br, broad), coupling constant (Hz), integration. Data for ^{13}C NMR were reported in terms of chemical shift (δ, ppm). Mass spectrometric data were obtained using Bruker Apex IV RTMS. Enantiomeric excess (ee) was determined using SHIMADZU LC-20AD with SPD-20AV detector (at appropriate wavelength). Column conditions were reported in the experimental section below.

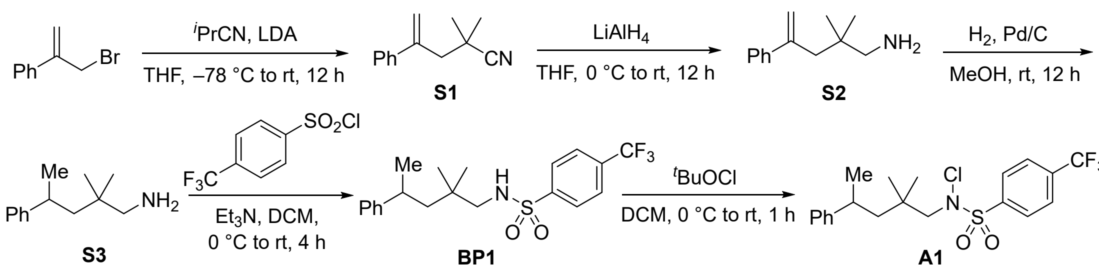
General procedure for the synthesis of substrates

The structures of substrates



General procedure

The synthesis of **A1** was described as the general procedure and **A2–A21** were prepared by analogy.



According to a modified literature procedure.[1] To a solution of the freshly prepared LDA (22 mmol, 1.1 equiv) in anhydrous THF (50 mL) was dropwise added isobutyronitrile (1.38 g, 20 mmol, 1.0 equiv) at −78 °C under argon atmosphere. The reaction mixture was stirred at −78 °C for 30 min. A solution of (3-bromoprop-1-en-2-yl)benzene (4.34 g, 22 mmol, 1.1 equiv) in anhydrous THF (10 mL) was then added into the mixture. The resulting mixture was warmed to room temperature and stirred for 12 h. Upon completion (monitored by TLC), the mixture was slowly quenched with saturated NH_4Cl (20 mL) under stirring. The mixture was concentrated under reduced pressure to remove the organic solvent. The remaining aqueous phase was diluted with DCM (50 mL), washed with saturated water (50 mL) and brine (50 mL × 2). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 80:1) to afford the pure product **S1** as a colorless oil (2.95 g, 80% yield).

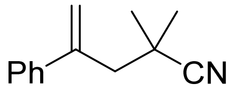
To a solution of **S1** (1.85 g, 10 mmol, 1.0 equiv) in anhydrous THF (20 mL) was added $LiAlH_4$ (0.76 g, 20 mmol, 2.0 equiv) in portions at 0 °C. The resulting mixture was warmed to room temperature and stirred for 12 h. Upon completion (monitored by TLC), the mixture was slowly quenched with saturated NH_4Cl (20 mL) under stirring. The mixture was concentrated under reduced pressure to remove the organic solvent. The remaining aqueous phase was diluted with DCM (20 mL), washed with saturated water (20 mL) and brine (20 mL × 2). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (DCM/MeOH 80:1) to afford the pure product **S2** as a colorless oil (1.53 g, 81% yield).

To a solution of **S2** (0.96 g, 5.0 mmol) in MeOH (10 mL) was added Pd/C (10% palladium on carbon, wet with ca. 50% water, 30 mg). The reaction flask was then evacuated and refilled with hydrogen through a balloon, and the mixture was stirred under a hydrogen atmosphere at room temperature for 12 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (10 mL). The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (DCM/MeOH 80:1) to give the product **S3** as a colorless oil (0.91 g, 95% yield).

To a solution of **S3** (0.57 g, 3.0 mmol, 1.0 equiv) in anhydrous DCM (10 mL) was added 4-(trifluoromethyl)benzenesulfonyl chloride (0.88 g, 3.6 mmol, 1.2 equiv) in portions at 0 °C. After being stirred at 0 °C for 10 min, Et_3N (0.61 g, 6.0 mmol, 2.0 equiv) was added slowly via a syringe. The resulting mixture was then warmed to room temperature and stirred for 4 h. Upon completion (monitored by TLC), the mixture was quenched with saturated NH_4Cl (10 mL) under stirring. The mixture was diluted with DCM (20 mL), washed with saturated water (20 mL) and brine (20 mL × 2). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 20:1) to afford the pure product **BP1** as a white solid (0.93 g, 78% yield).

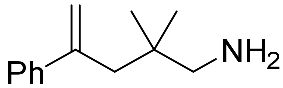
According to a modified literature procedure.[2] To a solution of **BP1** (0.40 g, 1.0 mmol, 1.0 equiv) in anhydrous DCM (5 mL) was dropwise added ^{t}BuOCl (0.11 g, 1.2 mmol, 1.2 equiv) at 0 °C under stirring. The resulting mixture was warmed to room temperature and stirred for 1 h. Upon completion (monitored by TLC), the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 100:1) to afford the pure product **A1** as a white solid (0.39 g, 91% yield).

2,2-dimethyl-4-phenylpent-4-enenitrile (S1)[3]



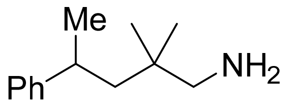
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.36 – 7.26 (m, 3H), 5.44 (d, *J* = 1.2 Hz, 1H), 5.28 (dd, *J* = 1.2, 0.9 Hz, 1H), 2.76 (d, *J* = 0.9 Hz, 2H), 1.25 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 141.6, 128.4, 127.7, 126.4, 124.6, 118.5, 45.4, 33.1, 27.0.

2,2-dimethyl-4-phenylpent-4-en-1-amine (S2)[1b]



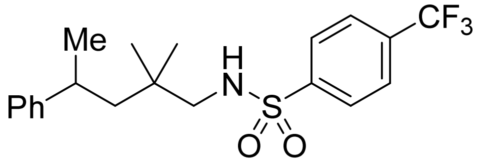
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.32 – 7.27 (m, 2H), 7.26 – 7.21 (m, 1H), 5.24 (d, *J* = 2.0 Hz, 1H), 5.04 (d, *J* = 2.0 Hz, 1H), 2.47 (s, 2H), 2.34 (s, 2H), 0.74 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 143.5, 128.1, 127.0, 126.4, 116.6, 53.4, 52.6, 44.4, 25.2.

2,2-dimethyl-4-phenylpentan-1-amine (S3)



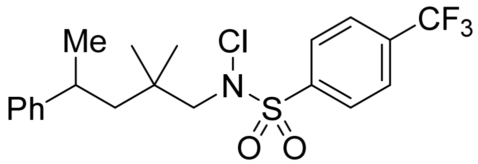
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.23 – 7.19 (m, 2H), 7.18 – 7.12 (m, 1H), 2.87 – 2.76 (m, 1H), 2.32 (s, 2H), 1.75 (dd, *J* = 14.2, 8.4 Hz, 1H), 1.47 (dd, *J* = 14.2, 4.1 Hz, 1H), 1.24 (d, *J* = 7.0 Hz, 3H), 0.80 (s, 3H), 0.73 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 128.4, 127.0, 125.7, 53.0, 47.3, 36.3, 35.4, 26.0, 25.5, 25.2.
HRMS (ESI) *m/z* calcd. for $C_{13}H_{22}N$ $[M + H]^+$ 192.1747, found 192.1748.

N-(2,2-dimethyl-4-phenylpentyl)-4-(trifluoromethyl)benzenesulfonamide (BP1)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 4H), 7.26 – 7.21 (m, 2H), 7.18 – 7.12 (m, 3H), 4.17 – 4.08 (m, 1H), 2.81 – 2.69 (m, 1H), 2.53 (dd, *J* = 12.6, 8.7 Hz, 1H), 2.36 (dd, *J* = 12.6, 5.6 Hz, 1H), 1.77 (dd, *J* = 14.5, 9.9 Hz, 1H), 1.45 (dd, *J* = 14.5, 3.0 Hz, 1H), 1.19 (d, *J* = 7.0 Hz, 3H), 0.86 (s, 3H), 0.82 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 143.4, 134.1 (q, *J* = 33.0 Hz), 128.7, 127.4, 126.9, 126.3, 126.1 (q, *J* = 3.7 Hz), 123.2 (q, *J* = 272.9 Hz), 52.6, 47.5, 36.3, 34.8, 26.7, 26.1, 25.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ −63.07.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{24}F_3NNaO_2S$ $[M + Na]^+$ 422.1372, found 422.1372.

***N*-chloro-*N*-(2,2-dimethyl-4-phenylpentyl)-4-(trifluoromethyl)benzene sulfonamide (A1)**



According to the general procedure, **A1** was prepared as a white solid (0.38 g, 88% yield in the final step).

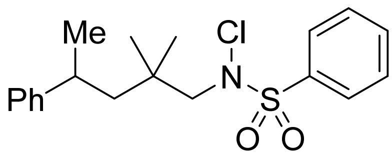
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.75 (m, 4H), 7.33 – 7.26 (m, 2H), 7.23 – 7.18 (m, 3H), 3.07 (d, *J* = 14.3 Hz, 1H), 2.93 – 2.84 (m, 1H), 2.80 (d, *J* = 14.3 Hz, 1H), 1.84 (dd, *J* = 14.4, 9.6 Hz, 1H), 1.64 (dd, *J* = 14.4, 3.4 Hz, 1H), 1.22 (d, *J* = 7.0 Hz, 3H), 1.00 (s, 3H), 0.97 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 137.2, 135.3 (q, *J* = 33.2 Hz), 129.7, 128.6, 127.1, 126.0 (q, *J* = 3.7 Hz), 125.9, 123.1 (q, *J* = 273.1 Hz), 68.1, 48.8, 36.6, 36.3, 26.7, 26.4, 25.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ −63.21.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{23}ClF_3NNaO_2S$ $[M + Na]^+$ 456.0982, found 456.0982.

***N*-chloro-*N*-(2,2-dimethyl-4-phenylpentyl)benzenesulfonamide (A2)**



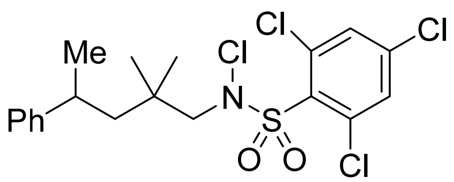
According to the general procedure, **A2** was prepared as a colorless oil (0.29 g, 79% yield in the final step).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 2H), 7.69 – 7.64 (m, 1H), 7.57 – 7.50 (m, 2H), 7.32 – 7.26 (m, 2H), 7.23 – 7.12 (m, 3H), 3.11 (d, *J* = 14.3 Hz, 1H), 2.93 – 2.81 (m, 2H), 1.83 (dd, *J* = 14.4, 9.3 Hz, 1H), 1.65 (dd, *J* = 14.4, 3.5 Hz, 1H), 1.23 (d, *J* = 7.0 Hz, 3H), 0.98 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 133.9, 133.8, 129.2, 128.9, 128.5, 127.1, 125.9, 68.1, 48.5, 36.5, 36.2, 26.5, 26.3, 25.4.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{25}ClNO_2S$ $[M + H]^+$ 366.1289, found 366.1286.

N,2,4,6-tetrachloro-*N*-(2,2-dimethyl-4-phenylpentyl)benzenesulfonamide (A3)

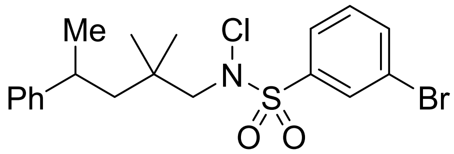


According to the general procedure, **A3** was prepared as a colorless oil (0.43 g, 92% yield in the final step).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 2H), 7.30 – 7.25 (m, 2H), 7.22 – 7.14 (m, 3H),

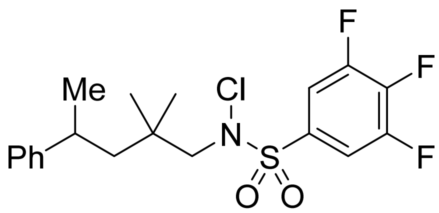
3.47 (d, *J* = 14.9 Hz, 1H), 3.37 (d, *J* = 14.9 Hz, 1H), 2.92 – 2.81 (m, 1H), 1.84 (dd, *J* = 14.3, 8.8 Hz, 1H), 1.66 (dd, *J* = 14.3, 4.0 Hz, 1H), 1.23 (d, *J* = 7.0 Hz, 3H), 0.96 (s, 3H), 0.89 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 139.7, 138.3, 131.5, 129.8, 128.5, 127.0, 125.9, 66.4, 48.3, 36.7, 36.2, 26.1, 26.0, 25.9.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{21}Cl_4NNaO_2S$ $[M + Na]^+$ 489.9939, found 489.9942.

3-bromo-*N*-chloro-*N*-(2,2-dimethyl-4-phenylpentyl)benzenesulfonamide (A4)



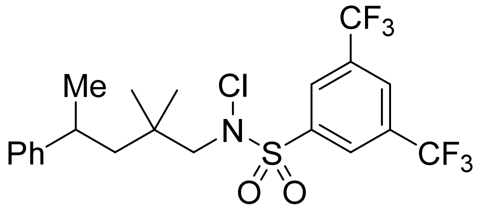
According to the general procedure, **A4** was prepared as a colorless oil (0.38 g, 85% yield in the final step).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (t, *J* = 1.9 Hz, 1H), 7.83 – 7.76 (m, 1H), 7.66 – 7.60 (m, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.24 – 7.16 (m, 3H), 3.09 (d, *J* = 14.3 Hz, 1H), 2.93 – 2.82 (m, 2H), 1.82 (dd, *J* = 14.4, 9.3 Hz, 1H), 1.65 (dd, *J* = 14.4, 3.6 Hz, 1H), 1.23 (d, *J* = 6.9 Hz, 3H), 0.98 (s, 3H), 0.93 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 137.0, 135.7, 131.9, 130.4, 128.6, 127.7, 127.0, 126.0, 123.0, 68.0, 48.5, 36.6, 36.2, 26.5, 26.2, 25.4.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{23}BrClNNaO_2S$ $[M + Na]^+$ 466.0214, found 466.0217.

***N*-chloro-*N*-(2,2-dimethyl-4-phenylpentyl)-3,4,5-trifluorobenzenesulfonamide (A5)**



According to the general procedure, **A5** was prepared as a white solid (0.39 g, 93% yield in the final step).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, *J* = 6.2 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.23 – 7.17 (m, 3H), 3.02 (d, *J* = 14.3 Hz, 1H), 2.93 – 2.82 (m, 1H), 2.74 (d, *J* = 14.3 Hz, 1H), 1.82 (dd, *J* = 14.4, 9.8 Hz, 1H), 1.63 (dd, *J* = 14.4, 3.3 Hz, 1H), 1.23 (d, *J* = 7.0 Hz, 3H), 1.00 (s, 3H), 0.98 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2 (dd, *J* = 10.5, 3.3 Hz), 149.6 (dd, *J* = 10.5, 3.3 Hz), 148.3, 144.9 (t, *J* = 15.0 Hz), 142.3 (t, *J* = 15.0 Hz), 129.9 – 129.5 (m), 128.6, 127.0, 126.2, 114.6 – 114.2 (m), 68.1, 49.0, 36.6, 36.3, 26.9, 26.2, 24.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ −129.23 (d, *J* = 19.8 Hz, 2F), −149.52 (t, *J* = 19.8 Hz, 1F).
HRMS (ESI) *m/z* calcd. for $C_{19}H_{21}ClF_3NNaO_2S$ $[M + Na]^+$ 442.0826, found 442.0829.

***N*-chloro-*N*-(2,2-dimethyl-4-phenylpentyl)-3,5-bis(trifluoromethyl)benzene sulfonamide (A6)**



According to the general procedure, **A6** was prepared as a white solid (0.45 g, 89% yield in the final step).

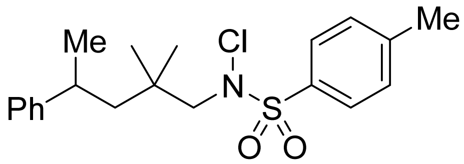
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 2H), 8.18 (s, 1H), 7.29 – 7.22 (m, 2H), 7.21 – 7.11 (m, 3H), 3.09 (d, *J* = 14.3 Hz, 1H), 2.98 (d, *J* = 14.3 Hz, 1H), 2.92 – 2.81 (m, 1H), 1.83 (dd, *J* = 14.4, 9.1 Hz, 1H), 1.66 (dd, *J* = 14.4, 3.8 Hz, 1H), 1.25 (d, *J* = 7.0 Hz, 3H), 1.00 (s, 3H), 0.92 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 137.0, 133.0 (q, *J* = 34.7 Hz), 129.2 (q, *J* = 3.3 Hz), 128.5, 127.5 (q, *J* = 3.6 Hz), 127.0, 126.0, 122.3 (q, *J* = 273.5 Hz), 67.8, 48.4, 36.7, 36.2, 26.2, 26.0, 25.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ −62.82.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{22}ClF_6NNaO_2S$ $[M + Na]^+$ 524.0856, found 524.0860.

***N*-chloro-*N*-(2,2-dimethyl-4-phenylpentyl)-4-methylbenzenesulfonamide (A7)**



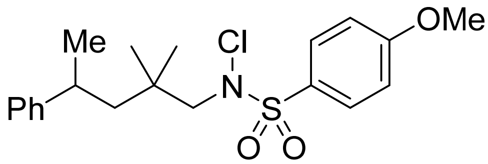
According to the general procedure, **A7** was prepared as a colorless oil (0.30 g, 79% yield in the final step).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.22 – 7.17 (m, 2H), 7.15 – 7.08 (m, 3H), 3.03 (d, *J* = 14.3 Hz, 1H), 2.86 – 2.73 (m, 2H), 2.39 (s, 3H), 1.75 (dd, *J* = 14.4, 9.2 Hz, 1H), 1.57 (dd, *J* = 14.4, 3.6 Hz, 1H), 1.15 (d, *J* = 6.9 Hz, 3H), 0.89 (s, 3H), 0.85 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 145.0, 130.8, 129.6, 129.3, 128.5, 127.1, 125.8, 68.1, 48.5, 36.5, 36.2, 26.4, 26.3, 25.5, 21.7.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{27}ClNO_2S$ $[M + H]^+$ 380.1446, found 380.1443.

***N*-chloro-*N*-(2,2-dimethyl-4-phenylpentyl)-4-methoxybenzenesulfonamide (A8)**

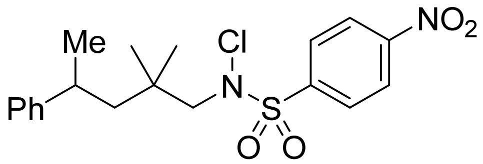


According to the general procedure, **A8** was prepared as a white solid (0.37 g, 93% yield in the final step).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.64 (m, 2H), 7.31 – 7.24 (m, 2H), 7.22 – 7.14 (m, 3H), 7.00 – 6.94 (m, 2H), 3.87 (s, 3H), 3.09 (d, *J* = 14.3 Hz, 1H), 2.91 – 2.80 (m,

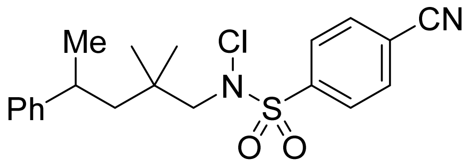
2H), 1.82 (dd, *J* = 14.4, 9.2 Hz, 1H), 1.64 (dd, *J* = 14.4, 3.6 Hz, 1H), 1.22 (d, *J* = 7.0 Hz, 3H), 0.96 (s, 3H), 0.92 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 148.6, 131.4, 128.4, 127.0, 125.7, 124.9, 114.1, 68.0, 55.6, 48.4, 36.3, 36.1, 26.3, 26.3, 25.4.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{27}ClNO_3S$ $[M + H]^+$ 396.1395, found 396.1395.

***N*-chloro-*N*-(2,2-dimethyl-4-phenylpentyl)-4-nitrobenzenesulfonamide (A9)**



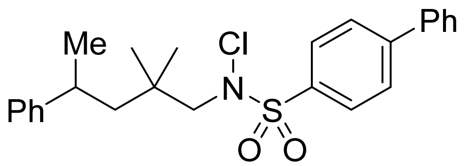
According to the general procedure, **A9** was prepared as a white solid (0.37 g, 90% yield in the final step).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 – 8.31 (m, 2H), 7.87 – 7.81 (m, 2H), 7.35 – 7.28 (m, 2H), 7.25 – 7.18 (m, 3H), 3.09 (d, *J* = 14.2 Hz, 1H), 2.93 – 2.83 (m, 1H), 2.75 (d, *J* = 14.2 Hz, 1H), 1.84 (dd, *J* = 14.5, 9.7 Hz, 1H), 1.63 (dd, *J* = 14.5, 3.3 Hz, 1H), 1.22 (d, *J* = 7.0 Hz, 3H), 1.01 (s, 3H), 0.99 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 148.5, 139.3, 130.4, 128.7, 127.1, 126.0, 124.0, 68.2, 48.9, 36.6, 36.3, 26.9, 26.4, 25.0.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{23}ClN_2NaO_4S$ $[M + Na]^+$ 433.0959, found 433.0962.

***N*-chloro-4-cyano-*N*-(2,2-dimethyl-4-phenylpentyl)benzenesulfonamide (A10)**



According to the general procedure, **A10** was prepared as a white solid (0.34 g, 88% yield in the final step).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.73 (m, 4H), 7.35 – 7.28 (m, 2H), 7.26 – 7.18 (m, 3H), 3.09 (d, *J* = 14.3 Hz, 1H), 2.94 – 2.83 (m, 1H), 2.75 (d, *J* = 14.3 Hz, 1H), 1.83 (dd, *J* = 14.4, 9.6 Hz, 1H), 1.63 (dd, *J* = 14.4, 3.3 Hz, 1H), 1.22 (d, *J* = 7.0 Hz, 3H), 1.00 (s, 3H), 0.98 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 137.9, 132.6, 129.7, 128.7, 127.1, 125.9, 117.5, 117.0, 68.1, 48.8, 36.6, 36.3, 26.9, 26.4, 25.0.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{23}ClN_2NaO_2S$ $[M + Na]^+$ 413.1061, found 413.1063.

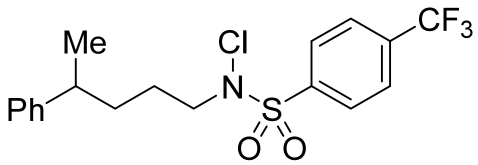
***N*-chloro-*N*-(2,2-dimethyl-4-phenylpentyl)-[1,1'-biphenyl]-4-sulfonamide (A11)**



According to the general procedure, **A11** was prepared as a white solid (0.34 g, 80% yield in the final step).

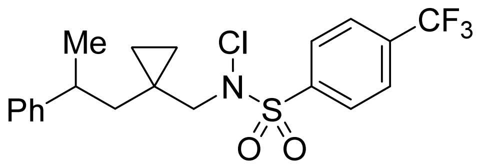
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.5 Hz, 2H), 7.72 (d, J = 8.5 Hz, 2H), 7.65 – 7.59 (m, 2H), 7.53 – 7.48 (m, 2H), 7.47 – 7.41 (m, 1H), 7.32 – 7.26 (m, 2H), 7.24 – 7.15 (m, 3H), 3.15 (d, J = 14.3 Hz, 1H), 2.95 – 2.82 (m, 2H), 1.84 (dd, J = 14.4, 9.3 Hz, 1H), 1.66 (dd, J = 14.4, 3.5 Hz, 1H), 1.23 (d, J = 6.9 Hz, 3H), 0.99 (s, 3H), 0.95 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 146.8, 139.0, 132.2, 129.8, 129.1, 128.7, 128.5, 127.5, 127.3, 127.1, 125.8, 68.1, 48.5, 36.5, 36.2, 26.5, 26.3, 25.4.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{28}ClNNaO_2S$ $[M + Na]^+$ 464.1421, found 464.1421.

***N*-chloro-*N*-(4-phenylpentyl)-4-(trifluoromethyl)benzenesulfonamide (A12)**



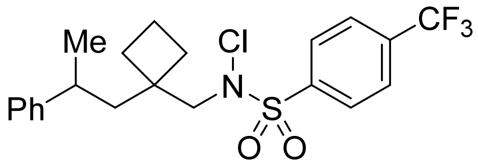
According to the general procedure, **A12** was prepared as a colorless oil (0.34 g, 84% yield in the final step).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.3 Hz, 2H), 7.32 – 7.26 (t, J = 7.5 Hz, 2H), 7.22 – 7.14 (m, 3H), 3.27 – 3.13 (m, 2H), 2.76 – 2.65 (m, 1H), 1.73 – 1.48 (m, 4H), 1.26 (d, J = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 136.5, 135.6 (q, J = 33.2 Hz), 129.9, 128.4, 126.9, 126.2 (q, J = 3.4 Hz), 126.1, 123.0 (q, J = 273.2 Hz), 56.6, 39.4, 34.3, 25.0, 22.5.
^{19}F NMR (376 MHz, $CDCl_3$) δ −63.22.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{19}ClF_3NNaO_2S$ $[M + Na]^+$ 428.0669, found 428.0669.

***N*-chloro-*N*-((1-(2-phenylpropyl)cyclopropyl)methyl)-4-(trifluoromethyl)benzene sulfonamide (A13)**



According to the general procedure, **A13** was prepared as a colorless oil (0.35 g, 80% yield in the final step).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.2 Hz, 2H), 7.86 (d, J = 8.2 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.257 – 7.16 (m, 3H), 3.28 (d, J = 13.1 Hz, 1H), 3.17 – 3.05 (m, 1H), 2.94 (d, J = 13.1 Hz, 1H), 1.75 – 1.64 (m, 2H), 1.30 (d, J = 6.9 Hz, 3H), 0.50 – 0.41 (m, 1H), 0.41 – 0.31 (m, 1H), 0.14 (t, J = 7.6 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 136.7, 135.7 (q, J = 33.2 Hz), 129.9, 128.4, 127.1, 126.2 (q, J = 3.7 Hz), 126.0, 123.0 (q, J = 273.3 Hz), 61.9, 42.4, 37.0, 22.4, 16.2, 11.0, 10.3.
^{19}F NMR (376 MHz, $CDCl_3$) δ −63.21.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{21}ClF_3NNaO_2S$ $[M + Na]^+$ 454.0826, found 454.0826.

***N*-chloro-*N*-((1-(2-phenylpropyl)cyclobutyl)methyl)-4-(trifluoromethyl) benzenesulfonamide (A14)**



According to the general procedure, **A14** was prepared as a white solid (0.37 g, 84% yield in the final step).

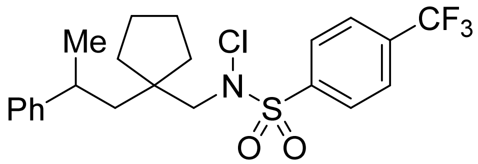
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.22 (m, 4H), 7.21 – 7.15 (m, 1H), 3.55 (d, *J* = 13.6 Hz, 1H), 3.08 (d, *J* = 13.6 Hz, 1H), 3.04 – 2.94 (m, 1H), 2.12 – 1.93 (m, 3H), 1.90 – 1.66 (m, 3H), 1.65 – 1.58 (m, 1H), 1.44 – 1.35 (m, 1H), 1.28 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 136.8, 135.6 (q, *J* = 33.3 Hz), 129.9, 128.5, 127.1, 126.2 (q, *J* = 3.7 Hz), 126.0, 123.1 (q, *J* = 272.9 Hz), 62.5, 44.9, 42.2, 36.2, 32.0, 30.3, 24.5, 16.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ −63.21.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{23}ClF_3NNaO_2S$ $[M + Na]^+$ 468.0982, found 468.0982.

***N*-chloro-*N*-((1-(2-phenylpropyl)cyclopentyl)methyl)-4-(trifluoromethyl)benzene sulfonamide (A15)**



According to the general procedure, **A15** was prepared as a white solid (0.33 g, 72% yield in the final step).

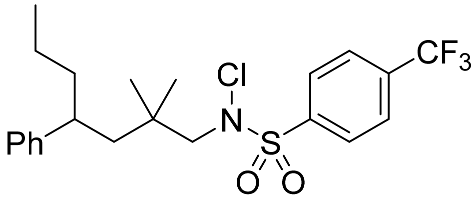
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.24 – 7.14 (m, 3H), 3.41 (d, *J* = 14.2 Hz, 1H), 2.99 – 2.87 (m, 2H), 1.92 – 1.78 (m, 2H), 1.74 – 1.46 (m, 6H), 1.40 – 1.31 (m, 1H), 1.24 (d, *J* = 7.0 Hz, 3H), 1.21 – 1.12 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 137.1, 135.5 (q, 33.2 Hz), 129.8, 128.5, 127.1, 126.1 (q, *J* = 3.7 Hz), 125.9, 123.1 (q, *J* = 273.2 Hz), 63.5, 47.7, 44.9, 36.6, 36.0, 35.5, 26.0, 23.8, 23.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ −63.22.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{25}ClF_3NNaO_2S$ $[M + Na]^+$ 482.1139, found 482.1138.

***N*-chloro-*N*-(2,2-dimethyl-4-phenylheptyl)-4-(trifluoromethyl)benzene sulfonamide (A16)**



According to the general procedure, **A16** was prepared as a colorless oil (0.44 g, 96% yield in the final step).

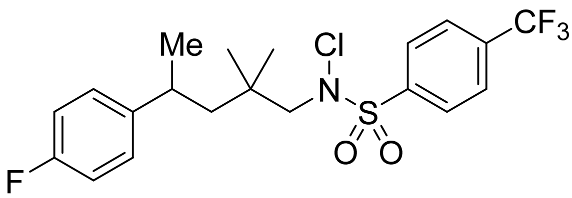
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.73 (m, 4H), 7.32 – 7.26 (m, 2H), 7.24 – 7.13 (m, 3H), 3.06 (d, *J* = 14.3 Hz, 1H), 2.73 (d, *J* = 14.3 Hz, 1H), 2.71 – 2.61 (m, 1H), 1.80 (dd, *J* = 14.4, 10.0 Hz, 1H), 1.66 (dd, *J* = 14.4, 2.7 Hz, 1H), 1.55 – 1.42 (m, 2H), 1.19 – 1.00 (m, 2H), 1.00 (s, 3H), 0.95 (s, 3H), 0.82 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 137.3, 135.4 (q, *J* = 33.3 Hz), 129.7, 128.5, 127.8, 126.0 (q, *J* = 3.7 Hz), 125.9, 123.1 (q, *J* = 273.2 Hz), 68.3, 47.8, 42.3, 41.6, 36.6, 26.9, 25.1, 20.5, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ −63.24.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{27}ClF_3NNaO_2S$ $[M + Na]^+$ 484.1295, found 484.1295.

***N*-chloro-*N*-(4-(4-fluorophenyl)-2,2-dimethylpentyl)-4-(trifluoromethyl)benzene sulfonamide (A17)**



According to the general procedure, **A17** was prepared as a white solid (0.45 g, 98% yield in the final step).

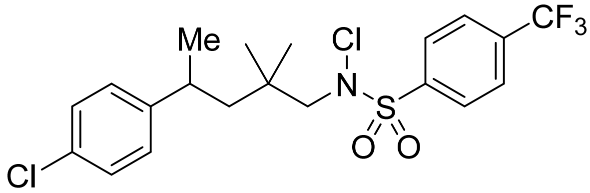
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.75 (m, 4H), 7.20 – 7.10 (m, 2H), 7.03 – 6.92 (m, 2H), 3.05 (d, *J* = 14.3 Hz, 1H), 2.94 – 2.83 (m, 1H), 2.82 (d, *J* = 14.3 Hz, 1H), 1.78 (dd, *J* = 14.4, 9.5 Hz, 1H), 1.65 (dd, *J* = 14.4, 3.5 Hz, 1H), 1.21 (d, *J* = 7.0 Hz, 3H), 0.99 (s, 3H), 0.94 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (d, *J* = 243.7 Hz), 144.2 (d, *J* = 3.2 Hz), 137.2, 135.6 (q, *J* = 33.2 Hz), 129.7, 128.4 (d, *J* = 7.7 Hz), 126.1 (q, *J* = 3.7 Hz), 123.0 (q, *J* = 273.1 Hz), 115.3 (d, *J* = 20.9 Hz), 68.1, 48.8, 36.5, 35.6, 26.6, 26.4, 25.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ −63.28, −117.14.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{23}ClF_4NO_2S$ $[M + H]^+$ 452.1069, found 452.1066.

***N*-chloro-*N*-(4-(4-chlorophenyl)-2,2-dimethylpentyl)-4-(trifluoromethyl)benzene sulfonamide (A18)**



According to the general procedure, **A18** was prepared as a white solid (0.28 g, 60% yield in the final step).

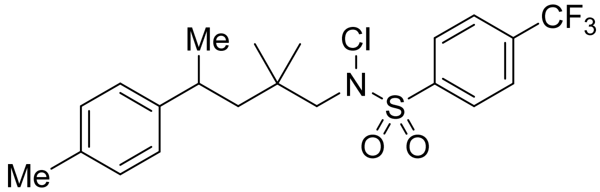
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.76 (m, 4H), 7.31 – 7.24 (m, 2H), 7.18 – 7.12 (m, 2H), 3.09 (d, *J* = 14.3 Hz, 1H), 2.93 – 2.84 (m, 1H), 2.80 (d, *J* = 14.3 Hz, 1H), 1.79 (dd, *J* = 14.5, 9.7 Hz, 1H), 1.65 (dd, *J* = 14.5, 3.4 Hz, 1H), 1.21 (d, *J* = 7.0 Hz, 3H), 0.99 (s, 3H), 0.96 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 137.2, 135.6 (q, *J* = 33.4 Hz), 131.5, 129.7, 128.7, 128.5, 126.1 (q, *J* = 3.7 Hz), 125.8 (q, *J* = 269.8 Hz), 68.1, 48.5, 36.6, 35.8, 26.7, 26.3, 25.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ −63.23.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{23}Cl_2F_3NO_2S$ $[M + H]^+$ 468.0773, found 468.0770.

***N*-chloro-*N*-(2,2-dimethyl-4-(*p*-tolyl)pentyl)-4-(trifluoromethyl)benzene sulfonamide (A19)**



According to the general procedure, **A19** was prepared as a white solid (0.30 g, 66% yield in the final step).

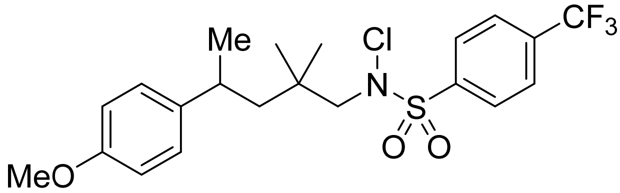
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.15 – 7.05 (m, 4H), 3.13 (d, *J* = 14.3 Hz, 1H), 2.89 – 2.77 (m, 2H), 2.34 (s, 3H), 1.82 (dd, *J* = 14.5, 9.5 Hz, 1H), 1.62 (dd, *J* = 14.5, 3.5 Hz, 1H), 1.20 (d, *J* = 7.0 Hz, 3H), 1.00 (s, 3H), 0.97 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 137.3, 135.4 (q, *J* = 33.1 Hz), 135.3, 129.7, 129.3, 126.9, 126.0 (q, *J* = 3.7 Hz), 123.1 (q, *J* = 273.2 Hz), 68.1, 48.7, 36.6, 35.8, 26.7, 26.5, 25.1, 21.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ −63.21.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{25}ClF_3NNaO_2S$ $[M + Na]^+$ 470.1139, found 470.1139.

_N_-chloro-_N_-(4-(4-methoxyphenyl)-2,2-dimethylpentyl)-4-(trifluoromethyl) benzenesulfonamide (A20)



According to the general procedure, **A20** was prepared as a white solid (0.32 g, 70% yield in the final step).

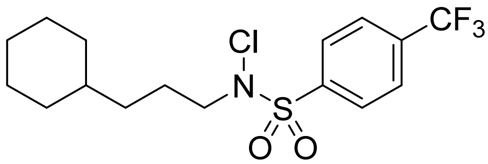
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.74 (m, 4H), 7.15 – 7.08 (m, 2H), 6.88 – 6.82 (m, 2H), 3.81 (s, 3H), 3.08 (d, J = 14.3 Hz, 1H), 2.91 – 2.79 (m, 1H), 2.71 (d, J = 14.3 Hz, 1H), 1.78 (dd, J = 14.4, 9.9 Hz, 1H), 1.62 (dd, J = 14.4, 3.2 Hz, 1H), 1.19 (d, J = 7.0 Hz, 3H), 1.01 (s, 3H), 1.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 140.5, 137.2, 135.4 (q, J = 33.2 Hz), 129.7, 127.9, 126.0 (q, J = 3.7 Hz), 123.1 (q, J = 273.1 Hz), 114.0, 68.3, 55.1, 49.2, 36.6, 35.4, 27.1, 26.6, 24.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ −63.23.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{25}ClF_3NNaO_3S$ $[M + Na]^+$ 486.1088, found 486.1085.

_N_-chloro-_N_-(3-cyclohexylpropyl)-4-(trifluoromethyl)benzenesulfonamide (A21)



According to the general procedure, **A21** was prepared as a white solid (0.36 g, 95% yield in the final step).

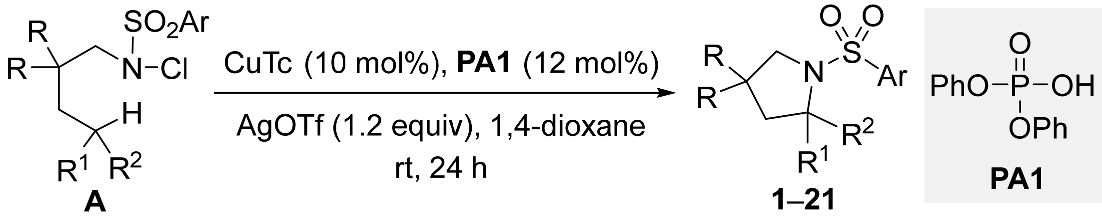
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.1 Hz, 2H), 7.87 (d, J = 8.1 Hz, 2H), 3.25 (t, J = 6.9 Hz, 2H), 1.75 – 1.61 (m, 7H), 1.29 – 1.12 (m, 6H), 0.96 – 0.81 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 135.7 (q, J = 33.3 Hz), 130.0, 126.2 (q, J = 3.7 Hz), 123.0 (q, J = 273.2 Hz), 57.0, 37.2, 33.6, 33.2, 26.5, 26.2, 24.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ −63.25.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{21}ClF_3NNaO_2S$ $[M + Na]^+$ 406.0826, found 406.0826.

General procedure for racemic tertiary C(sp^3)–H amination

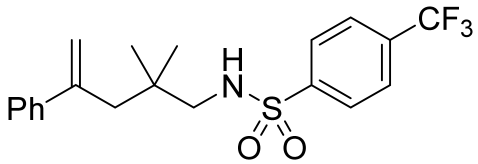


General procedure A

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **A** (0.10 mmol, 1.0 equiv), CuTc (1.9 mg, 0.01 mmol, 10 mol%), **PA1** (3.0 mg, 0.012 mmol, 12 mol%), AgOTf (30.8 mg, 0.12 mmol, 1.2 equiv) and anhydrous 1,4-dioxane (2.0 mL). The reaction mixture was stirred at room temperature for 24 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (5 mL). The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 20:1−10:1) to afford the desired product.

Analytical data for products

***N*-(2,2-dimethyl-4-phenylpent-4-en-1-yl)-4-(trifluoromethyl)benzenesulfonamide (BP2)**



The olefinic by-product **BP2** is a known compound,[4] and the analytical data were consistent with that reported in the literature.

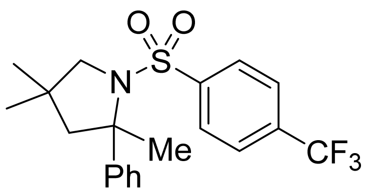
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 4H), 7.31 – 7.23 (m, 5H), 5.22 (d, *J* = 1.8 Hz, 1H), 5.05 – 5.00 (m, 1H), 4.54 (t, *J* = 7.0 Hz, 1H), 2.50 (d, *J* = 7.0 Hz, 2H), 2.46 (s, 2H), 0.83 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 143.3, 143.2, 134.1 (q, *J* = 32.9 Hz), 128.6, 127.5, 127.3, 126.3, 126.1 (q, *J* = 3.7 Hz), 123.2 (q, *J* = 272.9 Hz), 117.8, 52.8, 44.9, 35.2, 25.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ −63.08.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{23}F_3NO_2S$ $[M + H]^+$ 398.1396, found 398.1397.

2,4,4-trimethyl-2-phenyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)pyrrolidine (1)



According to the **general procedure A**, substrate **A1** (43.4 mg, 0.10 mmol, 1.0 equiv) was employed to yield product **1** as a white solid (36.6 mg, 92% yield).

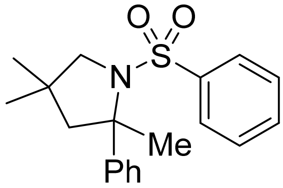
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 4H), 7.31 – 7.25 (m, 2H), 7.21 – 7.15 (m, 3H), 3.49 (d, *J* = 9.4 Hz, 1H), 3.39 (d, *J* = 9.4 Hz, 1H), 2.26 (d, *J* = 13.3 Hz, 1H), 2.02 (d, *J* = 13.3 Hz, 1H), 1.99 (s, 3H), 1.18 (s, 3H), 1.05 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 143.6, 133.3 (q, *J* = 32.9 Hz), 128.0, 127.5, 126.8, 126.0, 125.6 (q, *J* = 3.8 Hz), 123.3 (q, *J* = 272.9 Hz), 70.3, 63.1, 59.7, 36.7, 28.3, 28.1, 27.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ −63.01.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{23}F_3NO_2S$ $[M + H]^+$ 398.1396, found 398.1396.

2,4,4-trimethyl-2-phenyl-1-(phenylsulfonyl)pyrrolidine (2)



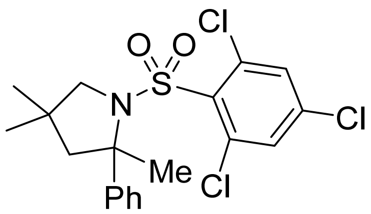
According to the **general procedure A**, substrate **A2** (36.6 mg, 0.10 mmol, 1.0 equiv) was employed to yield product **2** as a yellow oil (24.6 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.7 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.43 – 7.36 (m, 4H), 7.26 – 7.15 (m, 3H), 3.39 (s, 2H), 2.21 (d, *J* = 13.2 Hz, 1H), 1.98 (d, *J* = 13.2 Hz, 1H), 1.95 (s, 3H), 1.08 (s, 3H), 1.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 140.5, 131.9, 128.6, 128.0, 127.2, 126.5, 125.9, 70.5, 62.7, 59.8, 36.7, 28.2, 28.1, 27.4.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{24}NO_2S$ $[M + H]^+$ 330.1522, found 330.1521.

2,4,4-trimethyl-2-phenyl-1-((2,4,6-trichlorophenyl)sulfonyl)pyrrolidine (3)



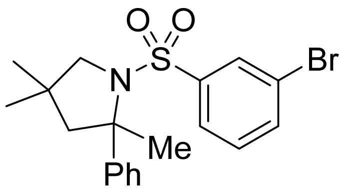
According to the **general procedure A**, substrate **A3** (46.9 mg, 0.10 mmol, 1.0 equiv) was employed to yield product **3** as a slightly yellow oil (30.0 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.19 (s, 2H), 7.11 – 7.01 (m, 3H), 3.92 – 3.82 (m, 2H), 2.30 (d, *J* = 13.4 Hz, 1H), 2.06 (d, *J* = 13.4 Hz, 1H), 2.00 (s, 3H), 1.29 (s, 3H), 1.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 137.0, 136.2, 135.5, 130.8, 127.6, 126.9, 126.6, 69.8, 63.8, 61.1, 35.6, 29.3, 29.1, 25.6.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{21}Cl_3NO_2S$ $[M + H]^+$ 432.0353, found 432.0353.

1-((3-bromophenyl)sulfonyl)-2,4,4-trimethyl-2-phenylpyrrolidine (4)

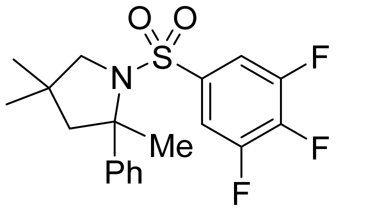


According to the **general procedure A**, substrate **A4** (44.5 mg, 0.10 mmol, 1.0 equiv) was employed to yield product **4** as yellow oil (26.5 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.9 Hz, 1H), 7.50 (s, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.26 – 7.17 (m, 4H), 3.47 (d, *J* = 9.4 Hz, 1H), 3.36 (d, *J* = 9.4 Hz, 1H), 2.26 (d, *J* = 13.3 Hz, 1H), 2.02 (d, *J* = 13.2 Hz, 1H), 1.98 (s, 3H), 1.18 (s, 3H), 1.05 (s, 3H).

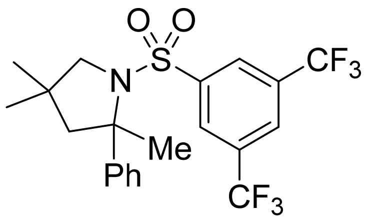
^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 142.0, 134.8, 130.0, 129.9, 127.9, 127.0, 126.0, 125.6, 122.5, 70.3, 62.9, 59.7, 36.7, 28.3, 28.2, 27.5.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{23}BrNO_2S$ $[M + H]^+$ 408.0627, found 408.0627.

2,4,4-trimethyl-2-phenyl-1-((3,4,5-trifluorophenyl)sulfonyl)pyrrolidine (5)



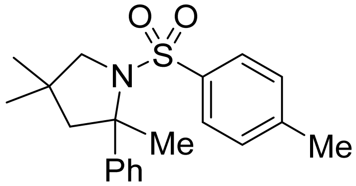
According to the **general procedure A**, substrate **A5** (42.0 mg, 0.10 mmol, 1.0 equiv) was employed to yield product **5** as a white solid (34.6 mg, 90% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.24 – 7.19 (m, 3H), 6.96 (t, *J* = 6.4 Hz, 2H), 3.51 (d, *J* = 9.3 Hz, 1H), 3.32 (d, *J* = 9.3 Hz, 1H), 2.31 (d, *J* = 13.4 Hz, 1H), 2.05 (d, *J* = 13.4 Hz, 1H), 2.01 (s, 3H), 1.25 (s, 3H), 1.10 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7 (dd, *J* = 10.5, 3.3 Hz), 149.2 (dd, *J* = 10.5, 3.3 Hz), 145.6, 143.3 (t, *J* = 15.0 Hz), 140.8 (t, *J* = 15.0 Hz), 136.0 – 135.8 (m), 127.9, 127.2, 126.3, 112.2 – 111.8 (m), 70.1, 63.1, 59.6, 36.7, 28.3, 28.2, 27.5.
^{19}F NMR (376 MHz, $CDCl_3$) δ −130.96 (d, *J* = 19.9 Hz, 2F), −153.75 (t, *J* = 19.9 Hz, 1F).
HRMS (ESI) *m/z* calcd. for $C_{19}H_{21}F_3NO_2S$ $[M + H]^+$ 384.1240, found 384.1238.

1-((3,5-bis(trifluoromethyl)phenyl)sulfonyl)-2,4,4-trimethyl-2-phenylpyrrolidine (6)



According to the **general procedure A**, substrate **A6** (50.2 mg, 0.10 mmol, 1.0 equiv) was employed to yield product **6** as a slightly yellow solid (37.8 mg, 81% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.77 (s, 2H), 7.23 – 7.16 (m, 2H), 7.16 – 7.09 (m, 3H), 3.63 (d, *J* = 9.4 Hz, 1H), 3.38 (d, *J* = 9.4 Hz, 1H), 2.31 (d, *J* = 13.5 Hz, 1H), 2.07 (d, *J* = 13.5 Hz, 1H), 2.04 (s, 3H), 1.28 (s, 3H), 1.13 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 142.9, 132.1 (q, *J* = 34.3 Hz), 128.0, 127.4, 127.1 (q, *J* = 3.3 Hz), 126.1, 125.3 (q, *J* = 3.6 Hz), 122.5 (q, *J* = 273.4 Hz), 70.1, 63.4, 59.8, 36.9, 28.3, 28.0, 27.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ −62.75.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{22}F_6NO_2S$ $[M + H]^+$ 466.1270, found 466.1270.

2,4,4-trimethyl-2-phenyl-1-tosylpyrrolidine (7)



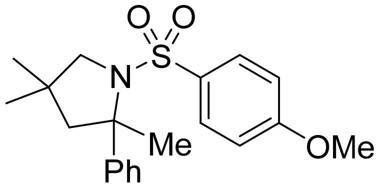
According to the **general procedure A**, substrate **A7** (38.0 mg, 0.10 mmol, 1.0 equiv) was employed to yield product **7** as a white solid (27.1 mg, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.38 (m, 2H), 7.29 – 7.23 (m, 2H), 7.22 – 7.16 (m, 3H), 3.40 – 3.32 (m, 2H), 2.40 (s, 3H), 2.20 (d, *J* = 13.1 Hz, 1H), 1.97 (d, *J* = 13.1 Hz, 1H), 1.93 (s, 3H), 1.07 (s, 3H), 0.98 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 142.5, 137.7, 129.1, 128.0, 127.3, 126.4, 125.9, 70.5, 62.6, 59.8, 36.7, 28.2, 28.1, 27.4, 21.5.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{25}NNaO_2S$ $[M + Na]^+$ 366.1498, found 366.1499.

1-((4-methoxyphenyl)sulfonyl)-2,4,4-trimethyl-2-phenylpyrrolidine (8)



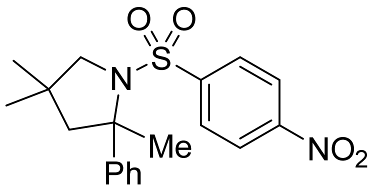
According to the **general procedure A**, substrate **A8** (39.6 mg, 0.10 mmol, 1.0 equiv) was employed to yield product **8** as a colorless semi-solid (14.8 mg, 41% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.9 Hz, 2H), 7.44 – 7.36 (m, 2H), 7.30 – 7.25 (m, 2H), 7.22 – 7.16 (m, 1H), 6.87 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H), 3.38 – 3.31 (m, 2H), 2.20 (d, *J* = 13.1 Hz, 1H), 1.98 (d, *J* = 13.1 Hz, 1H), 1.94 (s, 3H), 1.08 (s, 3H), 0.99 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 147.5, 132.5, 129.4, 128.0, 126.4, 125.9, 113.7, 70.4, 62.6, 59.8, 55.5, 36.7, 28.2, 28.1, 27.5.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{26}NO_3S$ $[M + H]^+$ 360.1628, found 360.1621.

2,4,4-trimethyl-1-((4-nitrophenyl)sulfonyl)-2-phenylpyrrolidine (9)



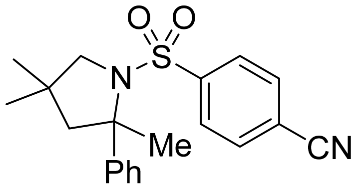
According to the **general procedure A**, substrate **A9** (41.1 mg, 0.10 mmol, 1.0 equiv) was employed to yield product **9** as a white solid (32.2 mg, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.29 – 7.25 (m, 2H), 7.21 – 7.14 (m, 3H), 3.53 (d, *J* = 9.4 Hz, 1H), 3.38 (d, *J* = 9.4 Hz, 1H), 2.29 (d, J = 13.4 Hz, 1H), 2.04 (d, J = 13.4 Hz, 1H), 2.01 (s, 3H), 1.21 (s, 3H), 1.08 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 145.8, 137.3, 128.2, 128.1, 127.0, 126.1, 123.7, 70.4, 63.2, 59.7, 36.9, 28.4, 28.2, 27.5.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{23}N_2O_4S$ $[M + H]^+$ 375.1373, found 375.1374.

4-((2,4,4-trimethyl-2-phenylpyrrolidin-1-yl)sulfonyl)benzonitrile (10)



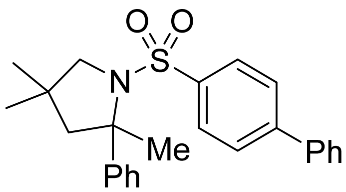
According to the **general procedure A**, substrate **A10** (39.1 mg, 0.10 mmol, 1.0 equiv) was employed to yield product **10** as a white solid (32.6 mg, 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.2 Hz, 2H), 7.52 (d, J = 8.2 Hz, 2H), 7.29 – 7.25 (m, 2H), 7.22 – 7.15 (m, 3H), 3.50 (d, J = 9.4 Hz, 1H), 3.36 (d, J = 9.4 Hz, 1H), 2.27 (d, J = 13.4 Hz, 1H), 2.03 (d, J = 13.4 Hz, 1H), 1.99 (s, 3H), 1.19 (s, 3H), 1.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 144.2, 132.3, 128.1, 127.6, 126.9, 126.1, 117.5, 115.3, 70.4, 63.1, 59.7, 36.8, 28.3, 28.2, 27.4.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{22}N_2NaO_2S$ $[M + H]^+$ 377.1294, found 377.1293.

1-([1,1'-biphenyl]-4-ylsulfonyl)-2,4,4-trimethyl-2-phenylpyrrolidine (11)



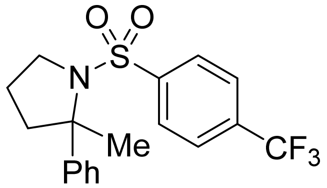
According to the **general procedure A**, substrate **A11** (44.2 mg, 0.10 mmol, 1.0 equiv) was employed to yield product **11** as a yellow oil (29.3 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.5 Hz, 2H), 7.62 – 7.55 (m, 4H), 7.51 – 7.45 (m, 2H), 7.43 – 7.36 (m, 3H), 7.25 – 7.16 (m, 3H), 3.48 – 3.39 (m, 2H), 2.23 (d, J = 13.2 Hz, 1H), 2.01 (d, J = 13.2 Hz, 1H), 1.98 (s, 3H), 1.12 (s, 3H), 1.02 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 144.6, 139.5, 139.0, 129.0, 128.3, 128.0, 127.7, 127.2, 127.1, 126.5, 126.0, 70.4, 62.8, 59.8, 36.7, 28.3, 28.2, 27.5.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{28}NO_2S$ $[M + H]^+$ 406.1835, found 406.1833.

2-methyl-2-phenyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)pyrrolidine (12)



According to the **general procedure A**, substrate **A12** (40.6 mg, 0.10 mmol, 1.0 equiv) was employed to yield product **12** as a white solid (25.0 mg, 68% yield).

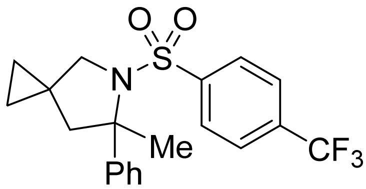
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.28 – 7.19 (m, 3H), 3.77 – 3.62 (m, 2H), 2.25 – 2.15 (m, 1H), 2.07 – 1.99 (m, 1H), 1.98 – 1.84 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 144.5, 133.5 (q, *J* = 32.9 Hz), 128.1, 127.3, 126.9, 126.0, 125.7 (q, *J* = 3.7 Hz), 123.3 (q, *J* = 272.8 Hz), 69.9, 50.2, 45.7, 26.6, 22.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ −62.99.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{18}F_3NNaO_2S$ $[M + Na]^+$ 392.0903, found 392.0901.

6-methyl-6-phenyl-5-((4-(trifluoromethyl)phenyl)sulfonyl)-5-azaspiro[2.4] heptane (13)



According to the **general procedure A**, substrate **A13** (43.2 mg, 0.10 mmol, 1.0 equiv) was employed to yield product **13** as a colorless oil (19.8 mg, 50% yield).

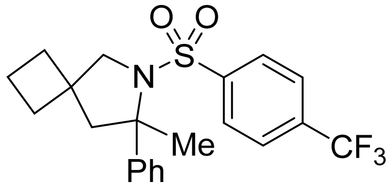
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.57 (s, 4H), 7.38 – 7.31 (m, 2H), 7.24 – 7.17 (m, 3H), 3.62 (s, 2H), 2.23 (d, *J* = 12.7 Hz, 1H), 2.02 (s, 3H), 1.99 (d, *J* = 12.7 Hz, 1H), 0.75 – 0.65 (m, 1H), 0.64 – 0.55 (m, 2H), 0.46 – 0.36 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 144.5, 133.4 (q, *J* = 32.9 Hz), 127.9, 127.3, 126.9, 126.2, 125.7 (q, *J* = 3.7 Hz), 123.3 (q, *J* = 272.8 Hz), 70.9, 57.5, 53.9, 26.6, 19.4, 11.1, 10.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ −63.01.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{21}F_3NO_2S$ $[M + H]^+$ 396.1240, found 396.1239.

7-methyl-7-phenyl-6-((4-(trifluoromethyl)phenyl)sulfonyl)-6-azaspiro[3.4]octane (14)



According to the **general procedure A**, substrate **A14** (44.6 mg, 0.10 mmol, 1.0 equiv) was employed to yield product **14** as a white solid (38.0 mg, 93% yield).

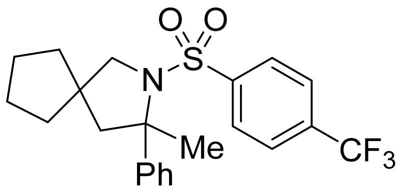
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 4H), 7.28 – 7.23 (m, 2H), 7.21 – 7.15 (m, 3H), 3.78 (d, *J* = 9.2 Hz, 1H), 3.65 (d, *J* = 9.2 Hz, 1H), 2.33 (d, *J* = 13.0 Hz, 1H), 2.12 (d, *J* = 13.0 Hz, 1H), 2.10 – 2.00 (m, 2H), 1.90 (s, 3H), 1.89 – 1.74 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 144.1, 133.4 (q, *J* = 32.9 Hz), 127.9, 127.4, 126.8, 126.1, 125.6 (q, *J* = 3.8 Hz), 123.3 (q, *J* = 272.8 Hz), 70.3, 61.5, 58.0, 43.2, 33.2, 31.6, 27.2, 16.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ −62.99.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{23}F_3NO_2S$ $[M + H]^+$ 410.1396, found 410.1386.

3-methyl-3-phenyl-2-((4-(trifluoromethyl)phenyl)sulfonyl)-2-azaspiro[4.4]nonane (15)



According to the **general procedure A**, substrate **A15** (46.0 mg, 0.10 mmol, 1.0 equiv) was employed to yield product **15** as a white solid (23.3 mg, 55% yield).

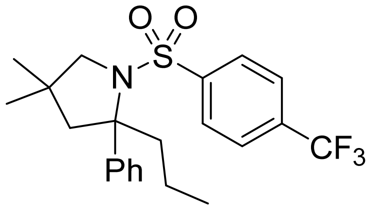
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.55 (m, 4H), 7.32 – 7.26 (m, 2H), 7.21 – 7.15 (m, 3H), 3.55 (d, *J* = 9.2 Hz, 1H), 3.42 (d, *J* = 9.2 Hz, 1H), 2.40 (d, *J* = 13.1 Hz, 1H), 2.10 (d, *J* = 13.1 Hz, 1H), 1.96 (s, 3H), 1.83 – 1.74 (m, 1H), 1.70 – 1.59 (m, 4H), 1.56 – 1.49 (m, 2H), 1.43 – 1.33 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 143.8, 133.3 (q, *J* = 32.9 Hz), 127.9, 127.4, 126.7, 126.1, 125.6 (q, *J* = 3.7 Hz), 123.3 (q, *J* = 272.8 Hz), 70.0, 61.8, 58.2, 47.7, 38.6, 37.5, 27.5, 24.7, 24.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ −63.00.

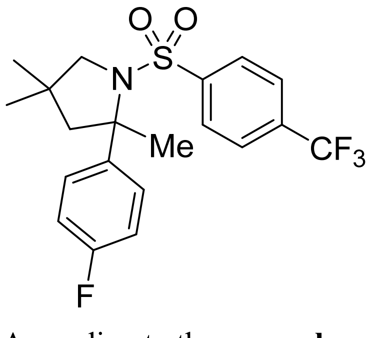
HRMS (ESI) *m/z* calcd. for $C_{22}H_{25}F_3NO_2S$ $[M + H]^+$ 424.1553, found 424.1551.

4,4-dimethyl-2-phenyl-2-propyl-1-((4-(trifluoromethyl)phenyl)sulfonyl) pyrrolidine (16)



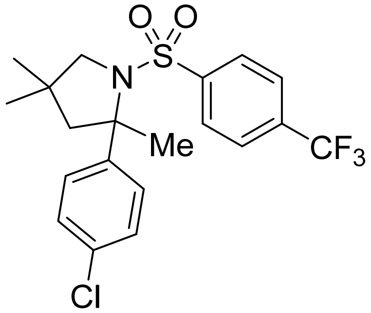
According to the **general procedure A**, substrate **A16** (46.2 mg, 0.10 mmol, 1.0 equiv) was employed to yield product **16** as a white solid (22.1 mg, 52% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.23 (m, 2H), 7.21 – 7.11 (m, 3H), 3.50 (d, *J* = 9.4 Hz, 1H), 3.21 (d, *J* = 9.4 Hz, 1H), 2.82 – 2.71 (m, 1H), 2.23 (s, 2H), 2.22 – 2.15 (m, 1H), 1.46 – 1.29 (m, 2H), 1.26 (s, 3H), 1.11 (s, 3H), 1.02 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 143.0, 133.0 (q, *J* = 32.8 Hz), 127.9, 127.5, 127.2, 127.0, 125.3 (q, *J* = 3.7 Hz), 123.3 (q, *J* = 272.8 Hz), 73.7, 62.9, 54.0, 41.9, 36.4, 29.0, 27.8, 19.5, 14.5.
^{19}F NMR (376 MHz, $CDCl_3$) δ −63.06.
HRMS (ESI) *m/z* calcd. for $C_{22}H_{27}F_3NO_2S$ $[M + H]^+$ 426.1709, found 426.1707.

2-(4-fluorophenyl)-2,4,4-trimethyl-1-((4-(trifluoromethyl)phenyl)sulfonyl) pyrrolidine (17)



According to the **general procedure A**, substrate **A17** (45.2 mg, 0.10 mmol, 1.0 equiv) was employed to yield product **17** as a white solid (35.7 mg, 86% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.58 (m, 4H), 7.32 – 7.24 (m, 2H), 6.93 – 6.83 (m, 2H), 3.49 – 3.35 (m, 2H), 2.20 (d, *J* = 13.3 Hz, 1H), 2.01 (d, *J* = 13.3 Hz, 1H), 1.95 (s, 3H), 1.15 (s, 3H), 1.04 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5 (d, *J* = 246.3 Hz), 143.7 (d, *J* = 1.1 Hz), 142.4 (d, *J* = 3.2 Hz), 133.6 (q, *J* = 33.0 Hz), 127.7 (d, *J* = 8.0 Hz), 127.5, 125.7 (q, *J* = 3.7 Hz), 123.3 (q, *J* = 272.8 Hz), 114.7 (d, *J* = 21.3 Hz), 70.0, 62.9, 59.7, 36.7, 28.2, 28.2, 27.5.
^{19}F NMR (376 MHz, $CDCl_3$) δ −63.03 (3F), −116.22 (1F).
HRMS (ESI) *m/z* calcd. for $C_{20}H_{22}F_4NO_2S$ $[M + H]^+$ 416.1302, found 416.1299.

2-(4-chlorophenyl)-2,4,4-trimethyl-1-((4-(trifluoromethyl)phenyl)sulfonyl) pyrrolidine (18)



According to the **general procedure A**, substrate **A18** (46.8 mg, 0.10 mmol, 1.0 equiv) was employed to yield product **18** as a white solid (40.6 mg, 94% yield).

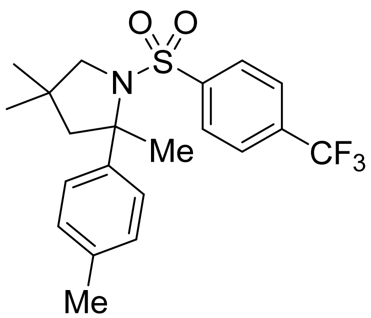
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.62 (m, 4H), 7.25 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 3.48 – 3.36 (m, 2H), 2.18 (d, *J* = 13.3 Hz, 1H), 2.01 (d, *J* = 13.3 Hz, 1H), 1.94 (s, 3H), 1.14 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 143.6, 133.7 (q, *J* = 33.0 Hz), 132.7, 128.1, 127.5, 127.4, 125.7 (q, *J* = 3.7 Hz), 123.3 (q, *J* = 272.8 Hz), 70.0, 63.0, 59.6, 36.8, 28.2, 28.0, 27.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ −63.00.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{22}ClF_3NO_2S$ $[M + H]^+$ 432.1006, found 432.0996.

2,4,4-trimethyl-2-(*p*-tolyl)-1-((4-(trifluoromethyl)phenyl)sulfonyl)pyrrolidine (19)



According to the **general procedure A**, substrate **A19** (44.8 mg, 0.10 mmol, 1.0 equiv) was employed to yield product **19** as a white solid (38.2 mg, 93% yield).

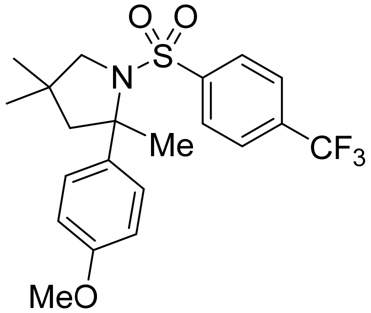
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.50 (m, 4H), 7.12 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 3.52 (d, *J* = 9.3 Hz, 1H), 3.39 (d, *J* = 9.3 Hz, 1H), 2.29 (s, 3H), 2.25 (d, *J* = 13.3 Hz, 1H), 2.01 (d, *J* = 13.3 Hz, 1H), 1.97 (s, 3H), 1.20 (s, 3H), 1.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 143.1, 136.5, 133.1 (q, *J* = 32.8 Hz), 128.5, 127.4, 126.0, 125.4 (q, *J* = 3.7 Hz), 123.4 (q, *J* = 272.8 Hz), 69.9, 63.2, 59.7, 36.7, 28.3, 28.1, 27.5, 20.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ −62.98.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{25}F_3NO_2S$ $[M + H]^+$ 412.1553, found 412.1552.

2-(4-methoxyphenyl)-2,4,4-trimethyl-1-((4-(trifluoromethyl)phenyl)sulfonyl) pyrrolidine (20)



According to the **general procedure A**, substrate **A20** (46.4 mg, 0.10 mmol, 1.0 equiv) was employed to yield product **20** as a white solid (38.5 mg, 90% yield).

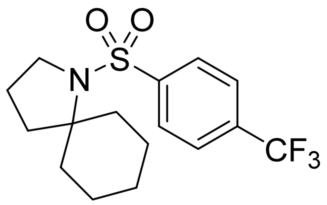
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.51 (m, 4H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.67 (d, *J* = 8.6 Hz, 2H), 3.77 (s, 3H), 3.51 (d, *J* = 9.3 Hz, 1H), 3.36 (d, *J* = 9.3 Hz, 1H), 2.24 (d, *J* = 13.3 Hz, 1H), 2.00 (d, *J* = 13.3 Hz, 1H), 1.97 (s, 3H), 1.21 (s, 3H), 1.08 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 143.6, 138.1, 133.2 (q, *J* = 32.9 Hz), 127.4, 127.3, 125.5 (q, *J* = 3.7 Hz), 123.3 (q, *J* = 272.7 Hz), 113.1, 69.7, 63.0, 59.7, 55.1, 36.6, 28.3, 28.3, 27.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ −62.97.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{25}F_3NO_3S$ $[M + H]^+$ 428.1502, found 428.1501.

1-((4-(trifluoromethyl)phenyl)sulfonyl)-1-azaspiro[4.5]decane (21)



According to the **general procedure A**, substrate **A21** (38.4 mg, 0.10 mmol, 1.0 equiv) was employed to yield product **21** as a colorless oil (32.0 mg, 92% yield).

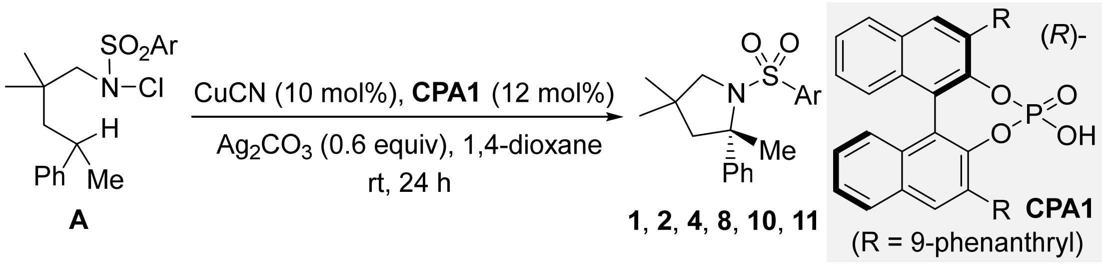
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 3.42 (t, *J* = 6.4 Hz, 2H), 2.38 – 2.24 (m, 2H), 1.92 – 1.76 (m, 4H), 1.76 – 1.68 (m, 2H), 1.65 – 1.60 (m, 1H), 1.55 – 1.46 (m, 2H), 1.32 – 1.19 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 133.5 (q, *J* = 33.0 Hz), 127.5, 125.9 (q, *J* = 3.7 Hz), 123.4 (q, *J* = 272.8 Hz), 70.3, 49.4, 36.5, 36.4, 24.9, 24.6, 22.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ −63.00.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{21}F_3NO_2S$ $[M + H]^+$ 348.1240, found 348.1231.

General procedure for enantioselective tertiary C(sp^3)–H amination

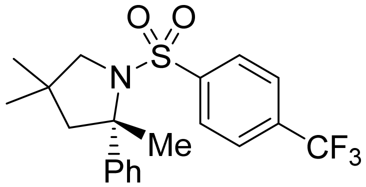


General procedure B

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **A** (0.10 mmol, 1.0 equiv), CuCN (0.9 mg, 0.01 mmol, 10 mol%), **CPA1** (8.4 mg, 0.012 mmol, 12 mol%), Ag_2CO_3 (16.5 mg, 0.06 mmol, 0.6 equiv), and anhydrous 1,4-dioxane (2.0 mL). The reaction mixture was stirred at room temperature for 24 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (5 mL). The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 20:1−10:1) to afford the desired product.

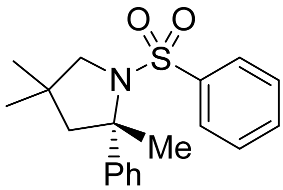
HPLC conditions for chiral products

(*S*)-2,4,4-trimethyl-2-phenyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)pyrrolidine ((*S*)-1)



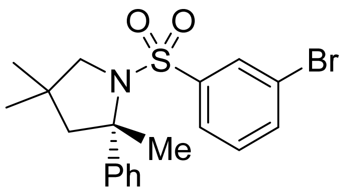
According to the **general procedure B**, substrate **A1** (43.4 mg, 0.10 mmol) was employed to yield product **1** as a white solid (13.0 mg, 33% yield, 80% ee).
HPLC analysis: Chiralcel AD-H (hexane/*i*-PrOH = 95/05, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 16.387 min, t_R (major) = 17.819 min.

(*S*)-2,4,4-trimethyl-2-phenyl-1-(phenylsulfonyl)pyrrolidine ((*S*)-2)



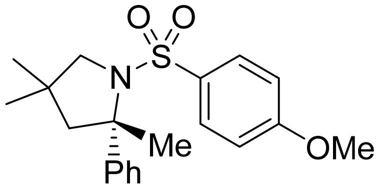
According to the **general procedure B**, substrate **A2** (41.1 mg, 0.10 mmol) was employed to yield product **2** as a yellow oil (7.5 mg, 23% yield, 63% ee).
HPLC analysis: Chiralcel AD-H (hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 10.613 min, t_R (major) = 13.156 min.

(*S*)-1-((3-bromophenyl)sulfonyl)-2,4,4-trimethyl-2-phenylpyrrolidine ((*S*)-4)



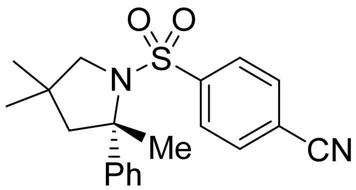
According to the **general procedure B**, substrate **A4** (44.5 mg, 0.10 mmol) was employed to yield product **4** as a yellow oil (10.1 mg, 25% yield, 72% ee).
HPLC analysis: Chiralcel AD-H (hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 7.919 min, t_R (major) = 9.096 min.

(*S*)-1-((4-methoxyphenyl)sulfonyl)-2,4,4-trimethyl-2-phenylpyrrolidine ((*S*)-8)



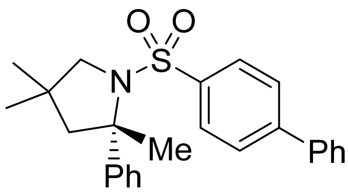
According to the **general procedure B**, substrate **A8** (39.6 mg, 0.10 mmol) was employed to yield product **8** as a colorless semi-solid (6.1 mg, 17% yield, 61% ee).
HPLC analysis: Chiralcel AD-H (hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 23.047 min, t_R (major) = 24.494 min.

(*S*)-4-((2,4,4-trimethyl-2-phenylpyrrolidin-1-yl)sulfonyl)benzonitrile ((*S*)-10)



According to the **general procedure B**, substrate **A10** (39.1 mg, 0.10 mmol) was employed to yield product **10** as a white solid (12.3 mg, 35% yield, 81% ee).
HPLC analysis: Chiralcel AD-H (hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 21.064 min, t_R (major) = 23.094 min.

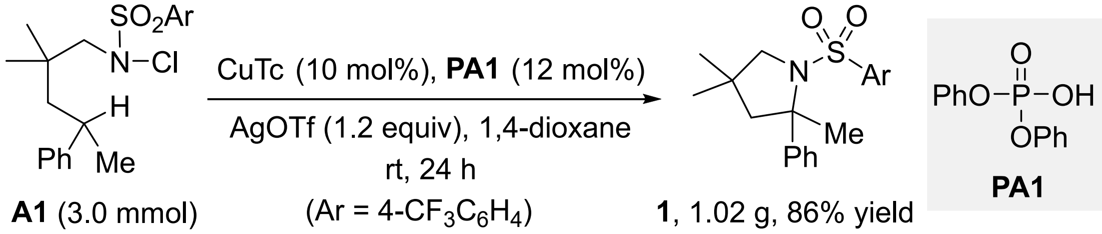
(*S*)-1-([1,1'-biphenyl]-4-ylsulfonyl)-2,4,4-trimethyl-2-phenylpyrrolidine ((*S*)-11)



According to the **general procedure B**, substrate **A11** (44.2 mg, 0.10 mmol) was employed to yield product **11** as a yellow oil (12.6 mg, 31% yield, 65% ee).
HPLC analysis: Chiralcel AD-H (hexane/*i*-PrOH = 95/05, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 21.143 min, t_R (major) = 24.593 min.

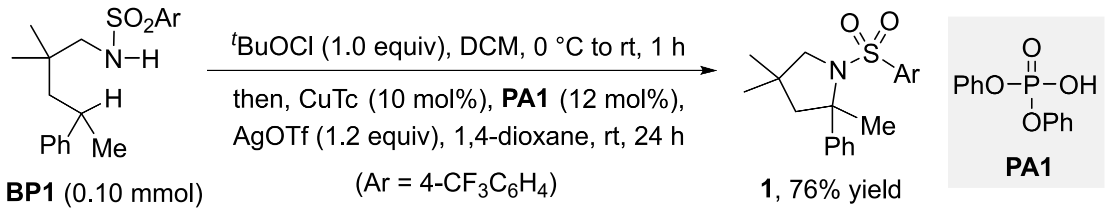
Scalability and synthetic utility

1. Gram-scale synthesis (Scheme 4a)



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **A1** (1.30 g, 3.0 mmol, 1.0 equiv), CuTc (57.2 mg, 0.3 mmol, 10 mol%), **PA1** (90.1 mg, 0.36 mmol, 12 mol%), AgOTf (925.0 mg, 3.6 mmol, 1.2 equiv) and anhydrous 1,4-dioxane (60 mL). The reaction mixture was stirred at room temperature for 24 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (100 mL). The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 20:1−10:1) to afford the product **1** as a white solid (1.02 g, 86% yield).

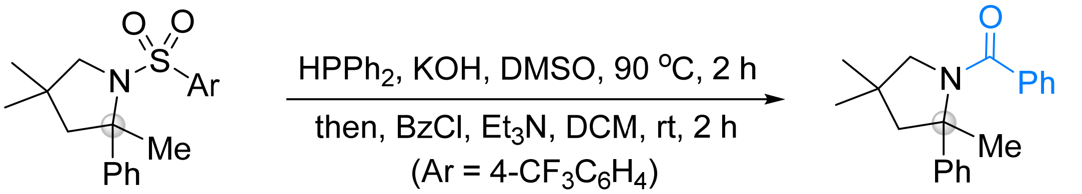
2. One-pot protocol (Scheme 4b)



To a solution of **BP1** (39.9 mg, 0.10 mmol, 1.0 equiv) in anhydrous DCM (2 mL) was dropwise added ^{t}BuOCl (10.9 mg, 0.10 mmol, 1.0 equiv) at 0 °C under stirring. The resulting mixture was warmed to room temperature and stirred for 1 h. Upon completion (monitored by TLC), the mixture was concentrated under reduced pressure. The residue was directly used in the next step without further purification.

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with the above-mentioned crude product, CuTc (1.9 mg, 0.01 mmol, 10 mol%), **PA1** (3.0 mg, 0.012 mmol, 12 mol%), AgOTf (30.8 mg, 0.12 mmol, 1.2 equiv) and anhydrous 1,4-dioxane (2.0 mL). The reaction mixture was stirred at room temperature for 24 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (5 mL). The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 20:1−10:1) to afford the product **1** as a white solid (30.0 mg, 76% yield).

3. Synthetic application (Scheme 4c)

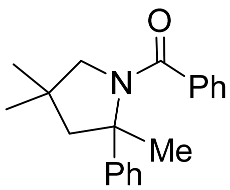


1 (0.25 mmol) **22**, 65% yield

According to the reported literature procedure.[5] To a stirred mixture of **1** (100 mg, 0.25 mmol, 1.0 equiv), KOH (35.3 mg, 0.63 mmol, 2.5 equiv) in anhydrous DMSO (3 mL) was dropwise added $HPPh_2$ (52.1 mg, 0.28 mmol, 1.1 equiv) under argon atmosphere at room temperature. The resulting mixture was then stirred at 90 °C for 2 h before being cooled to room temperature and diluted with DCM (2 mL). The reaction mixture was slowly quenched with water (5 mL) and extracted with DCM (5 mL × 2). The combined organic layers were washed with water (10 mL × 2) and brine (10 mL × 2). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was directly used in the next step without further purification.

To a solution of the above-mentioned crude product and Et_3N (208 μL, 1.50 mmol, 6.0 equiv) in anhydrous DCM (3 mL) was dropwise added benzoyl chloride (146 μL, 1.25 mmol, 5.0 equiv) at room temperature. The resulting mixture was then stirred at room temperature for 2 h before being diluted with DCM (5 mL). The reaction mixture was washed with HCl (1 M, 5 mL) and brine (10 mL × 2). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 10:1, then DCM/MeOH 100:1) to give the product **22** as a yellow oil (47.7 mg, 65% yield).

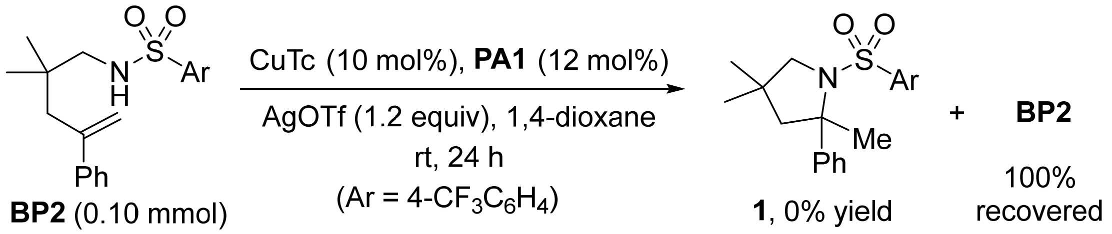
phenyl(2,4,4-trimethyl-2-phenylpyrrolidin-1-yl)methanone (22)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 2H), 7.44 – 7.37 (m, 3H), 7.36 – 7.29 (m, 4H), 7.23 – 7.17 (m, 1H), 3.43 (s, 2H), 2.23 – 2.05 (m, 5H), 1.17 (s, 3H), 0.94 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 147.5, 138.8, 129.1, 128.4, 128.3, 126.2, 126.0, 124.8, 68.0, 64.8, 58.9, 37.1, 28.0, 27.9, 27.3.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{24}NO$ $[M + H]^+$ 294.1852, found 294.1852.

Mechanistic studies

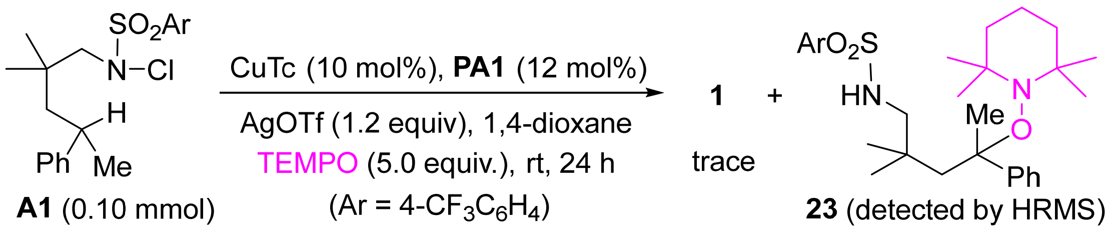
1. Control experiment (Scheme 5a)



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **BP2** (39.7 mg, 0.10 mmol, 1.0 equiv), CuTc (1.9 mg, 0.01 mmol, 10 mol%), **PA1** (3.0 mg, 0.012 mmol, 12 mol%), AgOTf (30.8 mg, 0.12 mmol, 1.2 equiv), and anhydrous 1,4-dioxane (2.0 mL). The reaction mixture was stirred at room temperature for 24 h before being filtered through a short pad of celite and rinsed with EtOAc (5 mL). The filtrate was concentrated under reduced pressure. The residue was analyzed by ^{19}F NMR analysis using (trifluoromethyl)benzene as an internal standard.

The desired product **1** was not detected and **BP2** was recovered in quantitative yield.

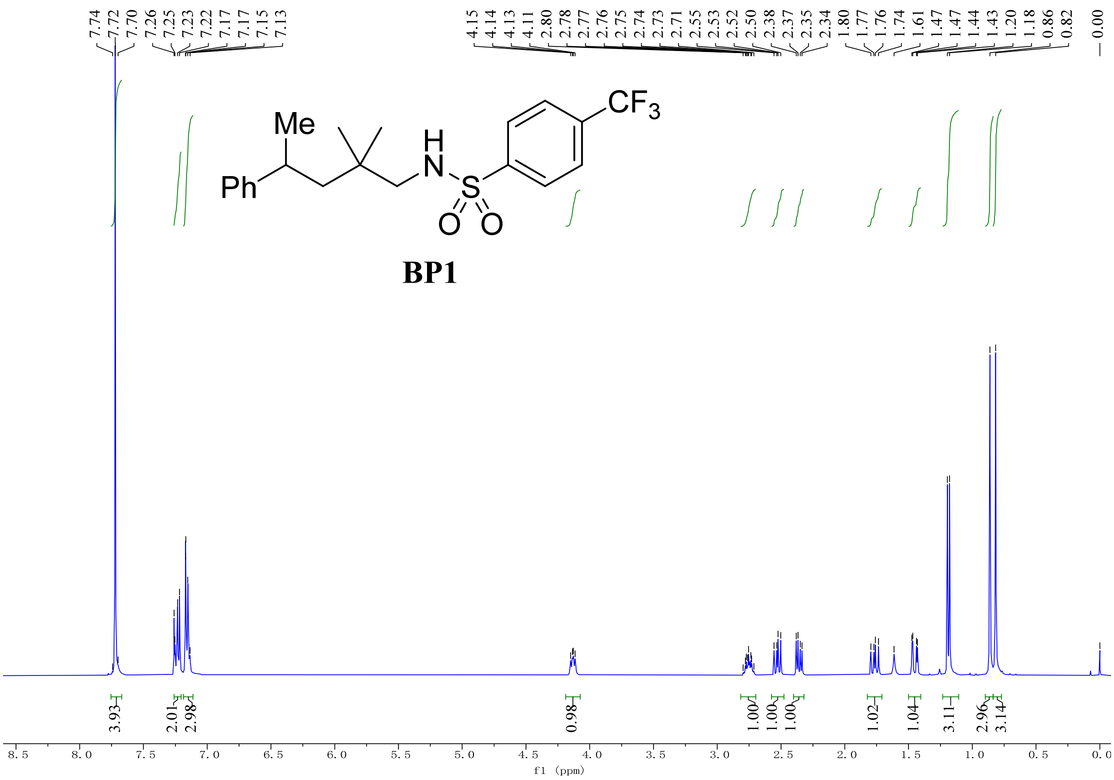
2. Radical inhibiting experiment (Scheme 5b)

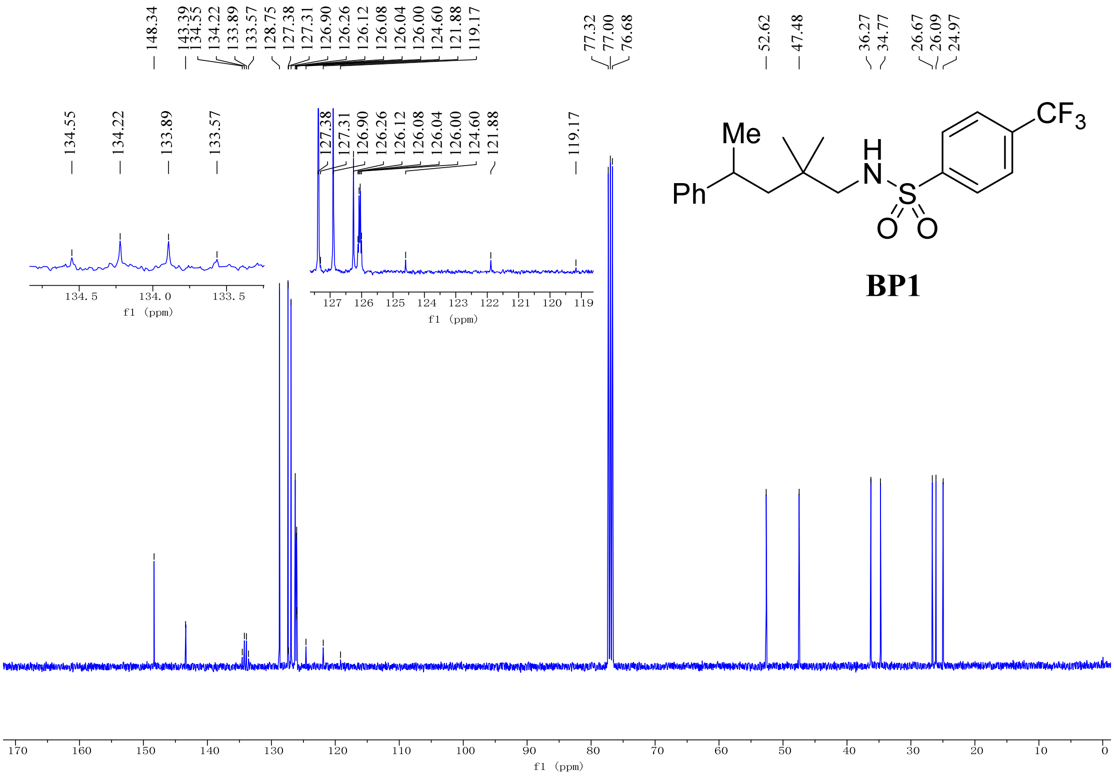


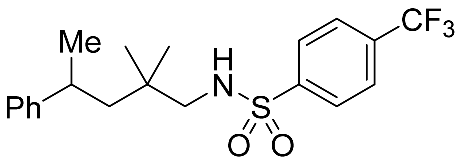
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **A1** (43.4 mg, 0.10 mmol, 1.0 equiv), CuTc (1.9 mg, 0.01 mmol, 10 mol%), **PA1** (3.0 mg, 0.012 mmol, 12 mol%), AgOTf (30.8 mg, 0.12 mmol, 1.2 equiv), and anhydrous 1,4-dioxane (2.0 mL). 2,2,6,6-Tetramethyl piperidinooxy (**TEMPO**, 78.1 mg, 0.50 mmol, 5.0 equiv) was then added into the mixture. The resulting mixture was stirred at room temperature for 24 h. The reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (5 mL). The filtrate was concentrated under reduced pressure. The residue was first analyzed by ^{19}F NMR analysis using (trifluoromethyl)benzene as an internal standard. The crude product was then analyzed by HRMS (ESI) analysis.

The desired reaction was inhibited and product **1** was not detected. The TEMPO-trapped product **23** was detected by HRMS (ESI) analysis. **HRMS** (ESI) *m/z* calcd. for $C_{29}H_{42}F_3N_2O_3S$ $[M + H]^+$ 555.2863, found 555.2852.

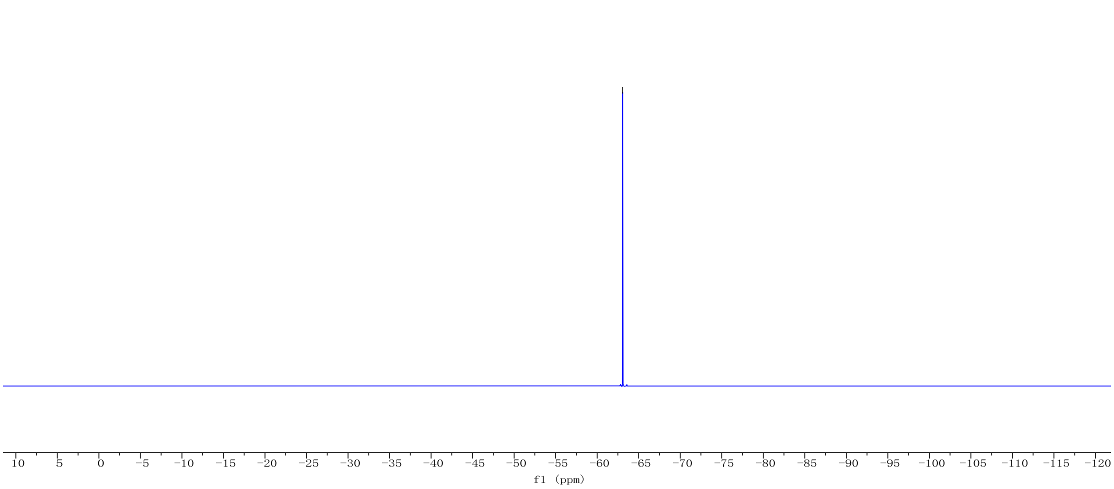
NMR spectra







BP1



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−5
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−15
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−30
−35
−40
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−55
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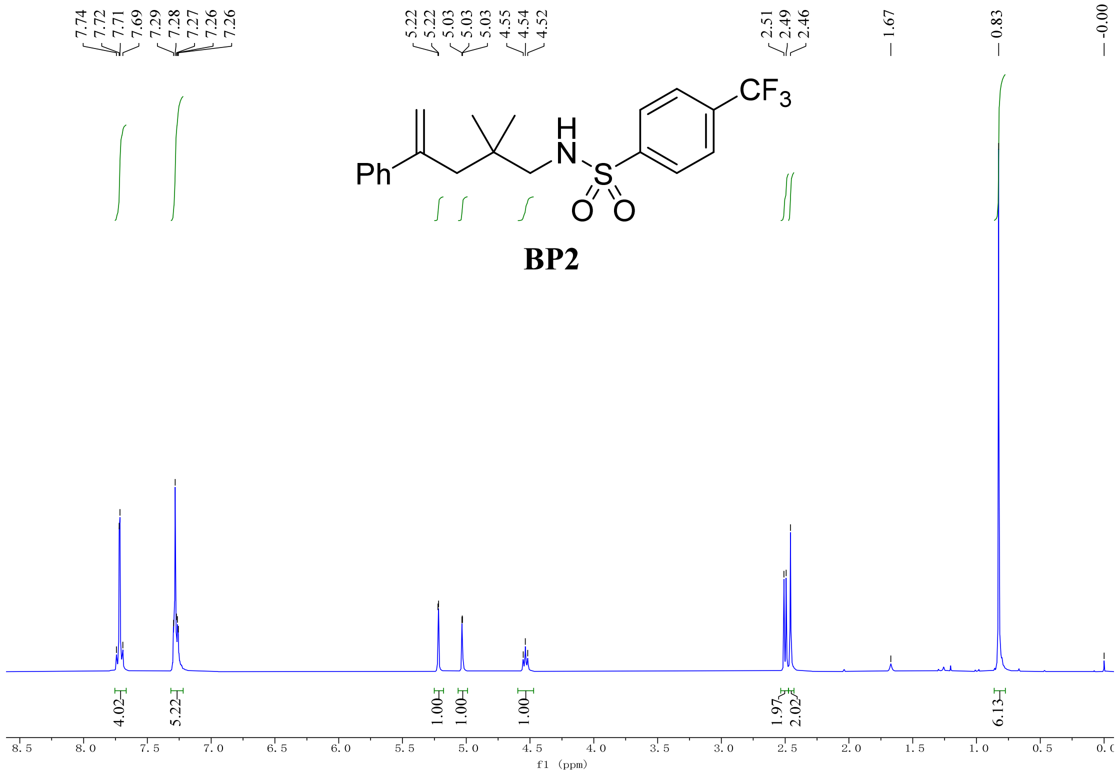
f1 (ppm)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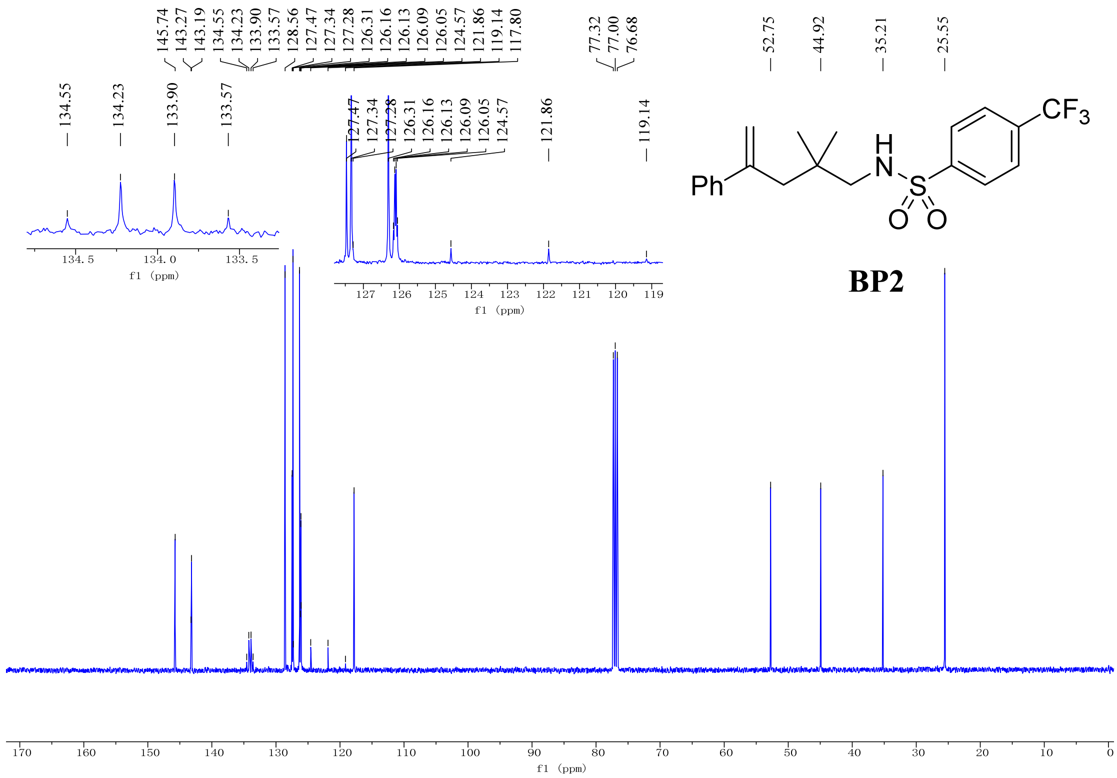
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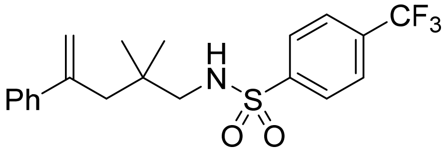
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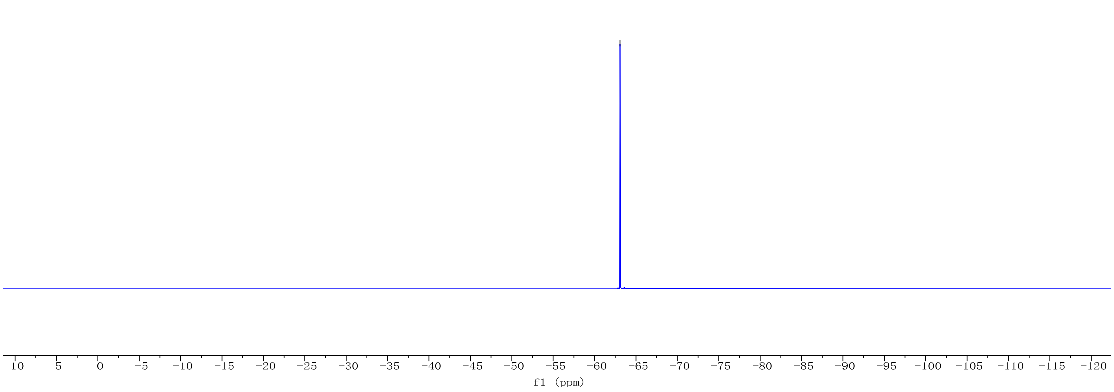
S
O
O
Ph

BP2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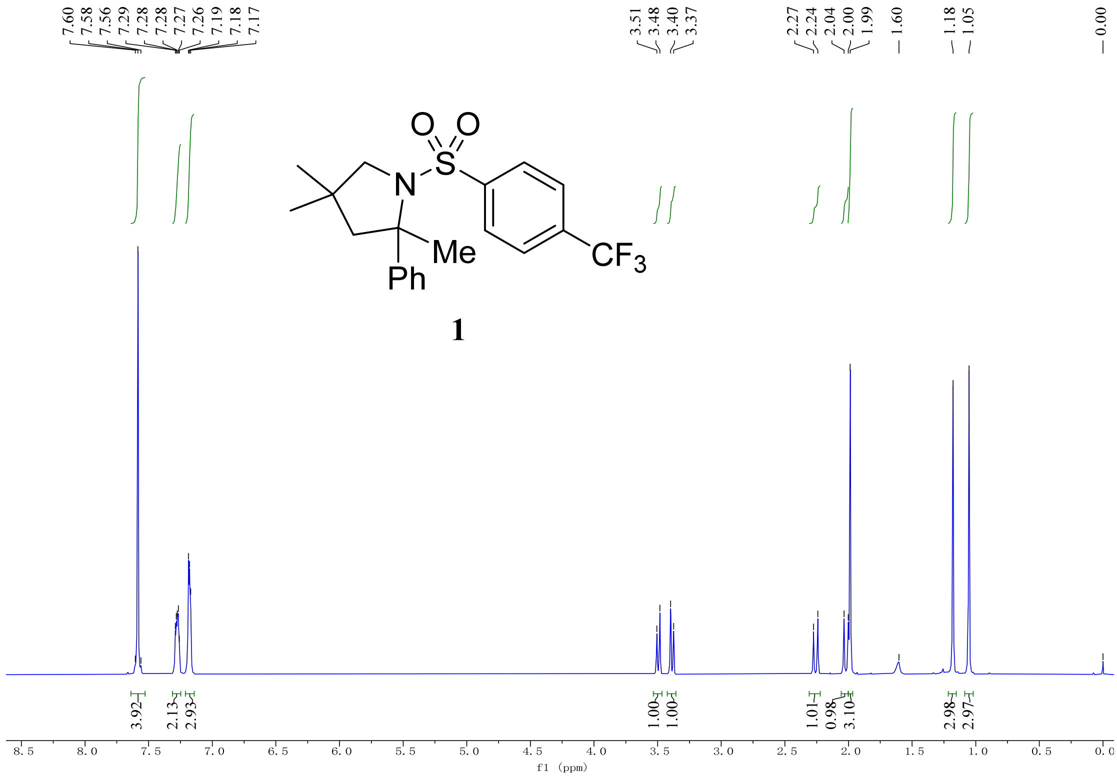
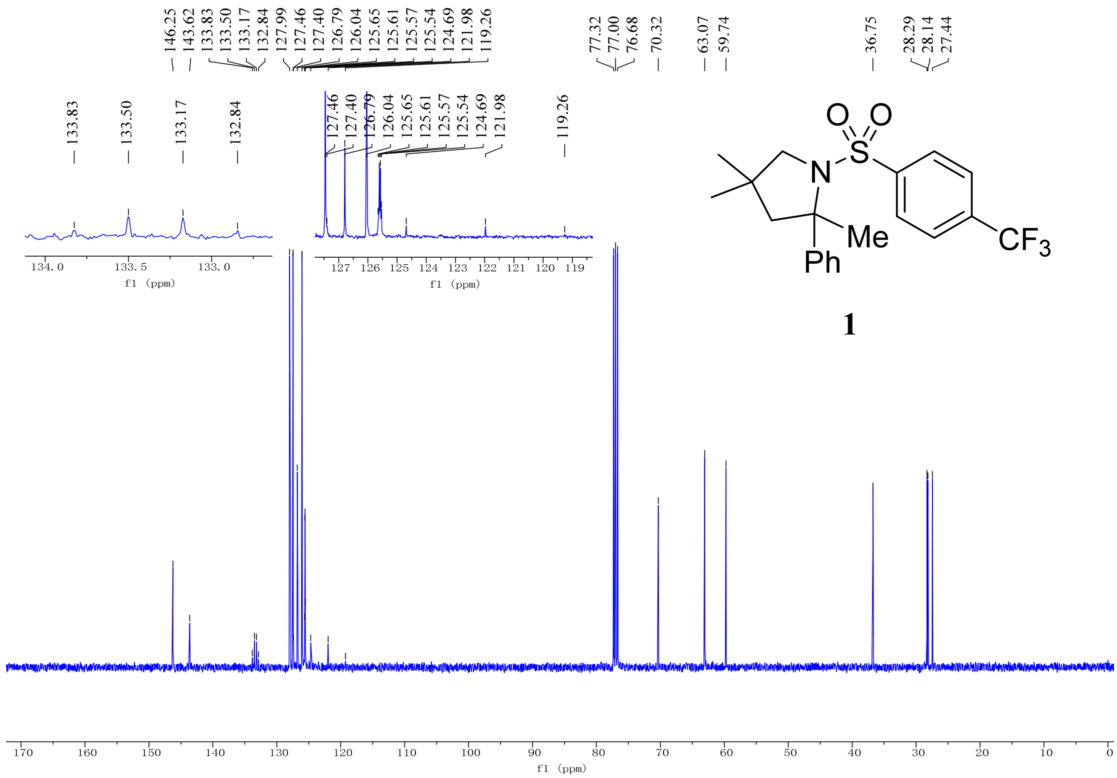
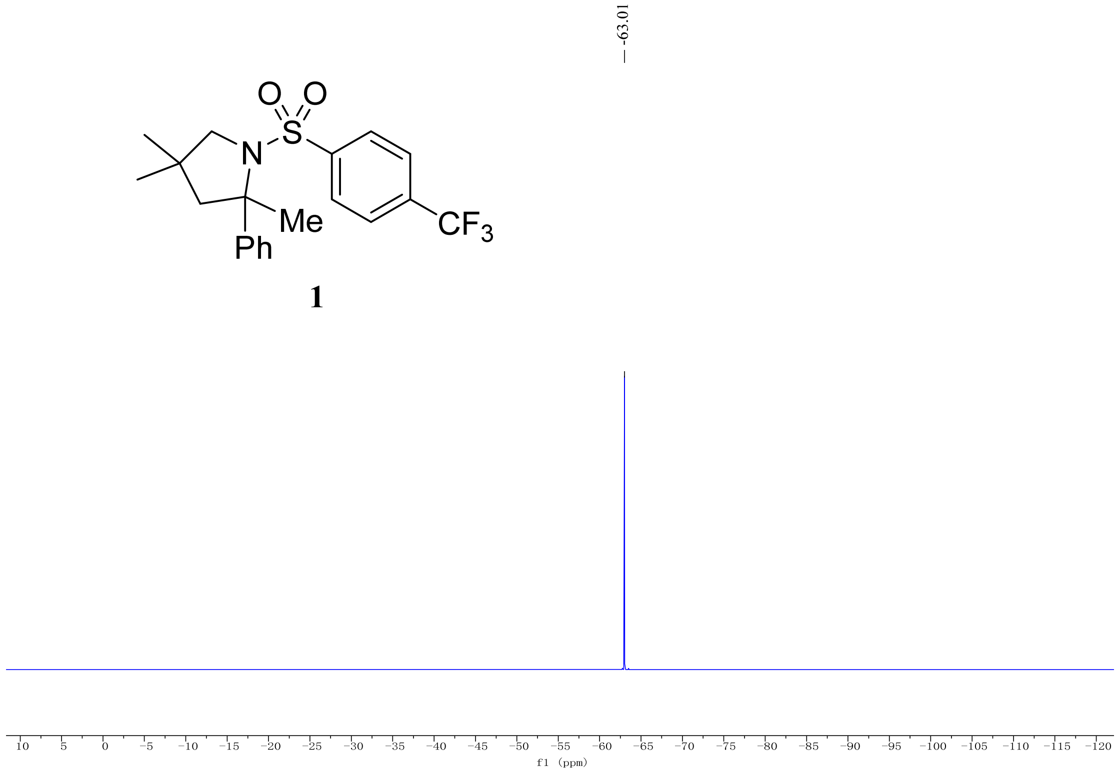
10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120
f1 (ppm)







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N
Me
Ph
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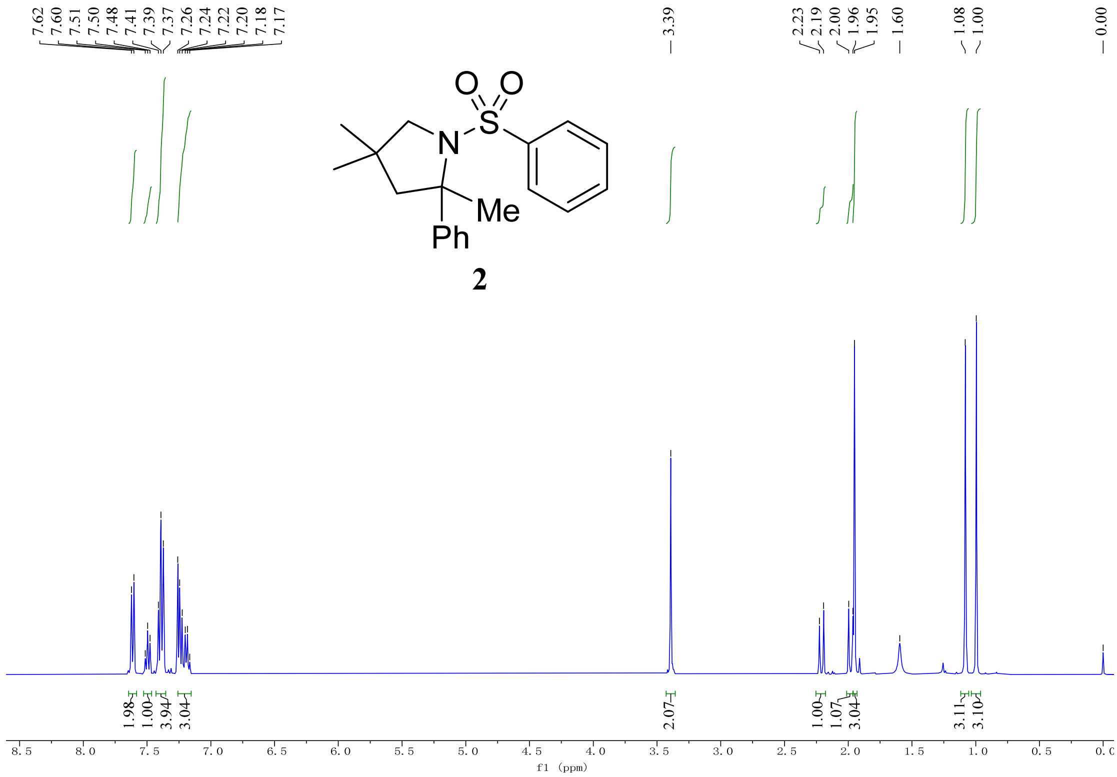
f1 (ppm)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3.39
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1.60
1.08 1.00
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O O S N Me Ph
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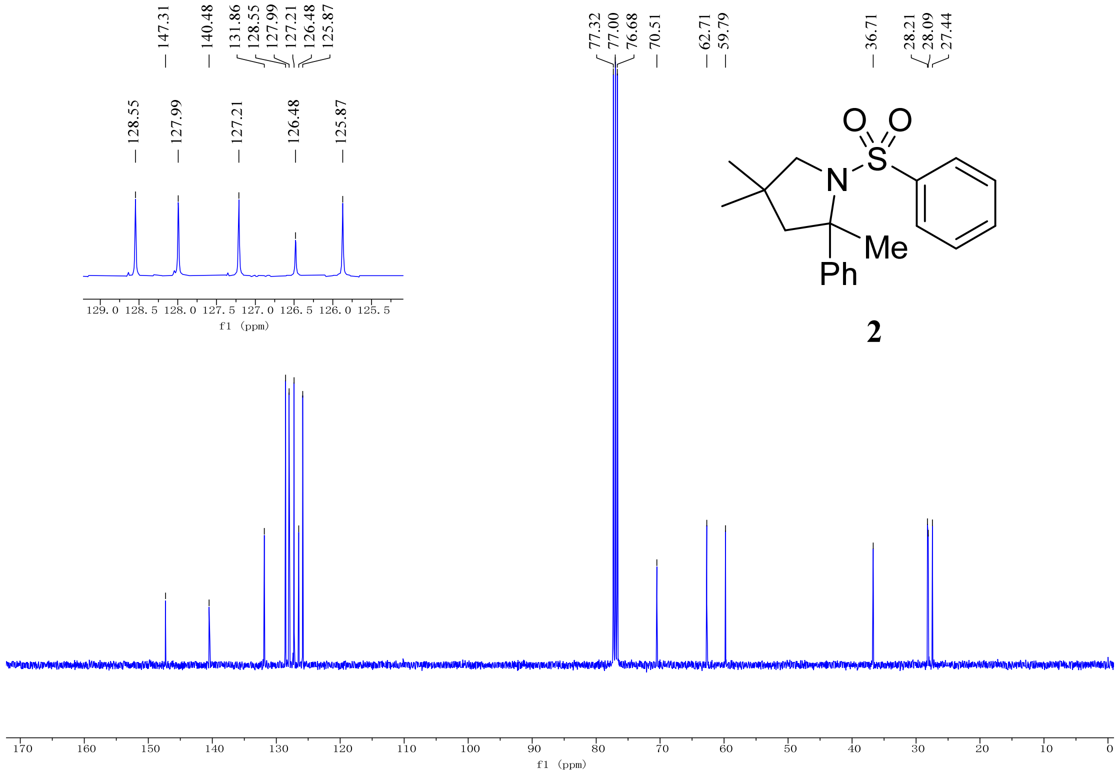
1.00 1.07 3.04
3.11 3.10
f1 (ppm)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77.32 77.00 76.68 70.51
62.71 59.79
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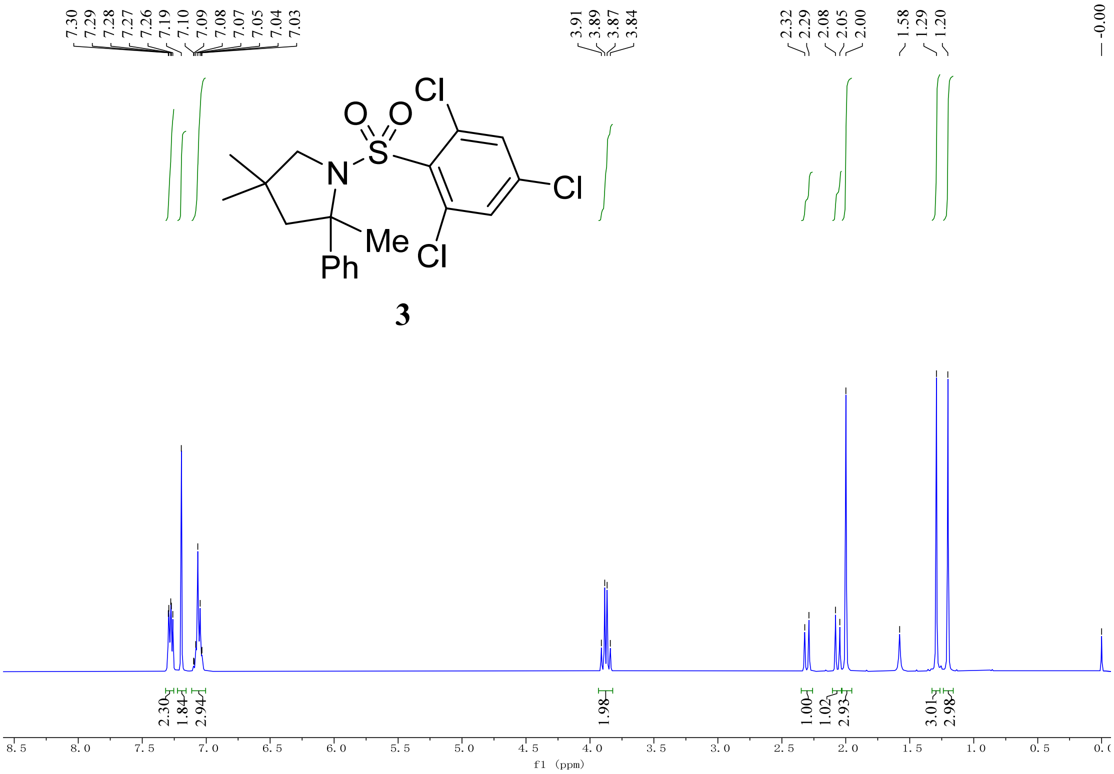
128.55 127.99 127.21 126.48 125.87
f1 (ppm)
O O S N Me Ph
2
f1 (ppm)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7.09
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7.07
7.05
7.04
7.03
3.91
3.89
3.87
3.84
2.32
2.29
2.08
2.05
2.00
1.58
1.29
1.20
-0.00
Cl
O
O
S
N
Cl
Me
Cl
Ph
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1.84
2.94
1.98
1.00
1.02
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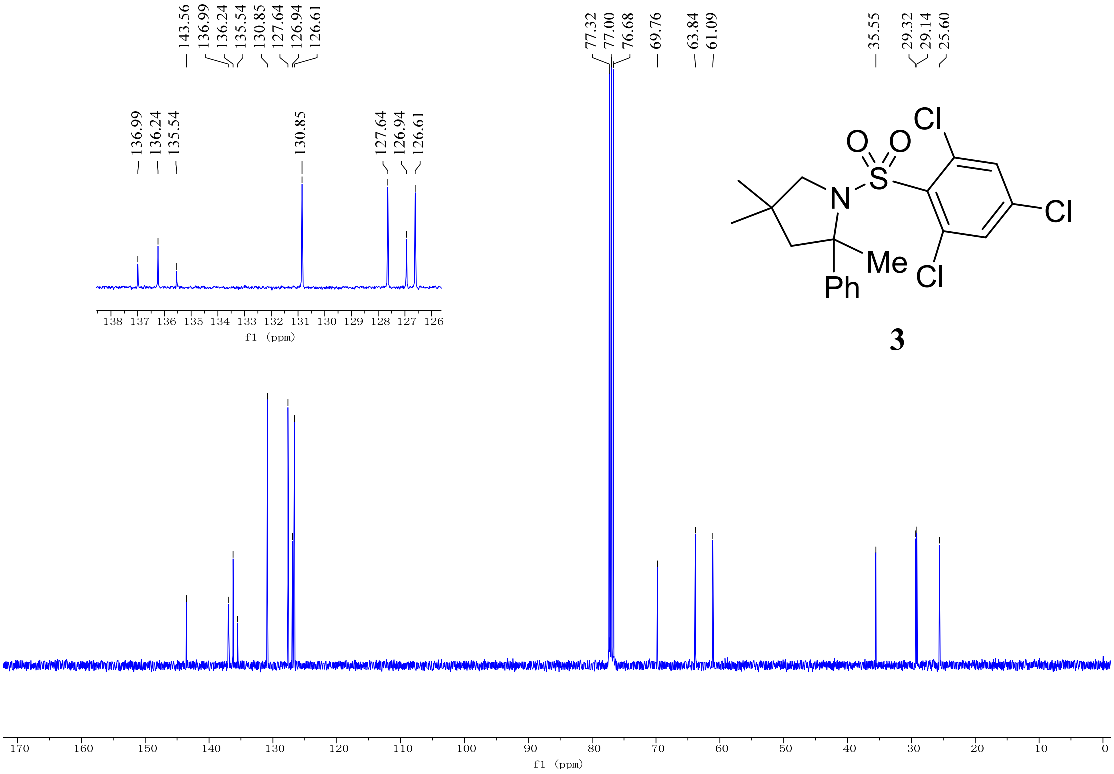
3.01
2.98
f1 (ppm)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61.09
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29.32
29.14
25.60
136.99
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135.54
130.85
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f1 (ppm)
Cl
O
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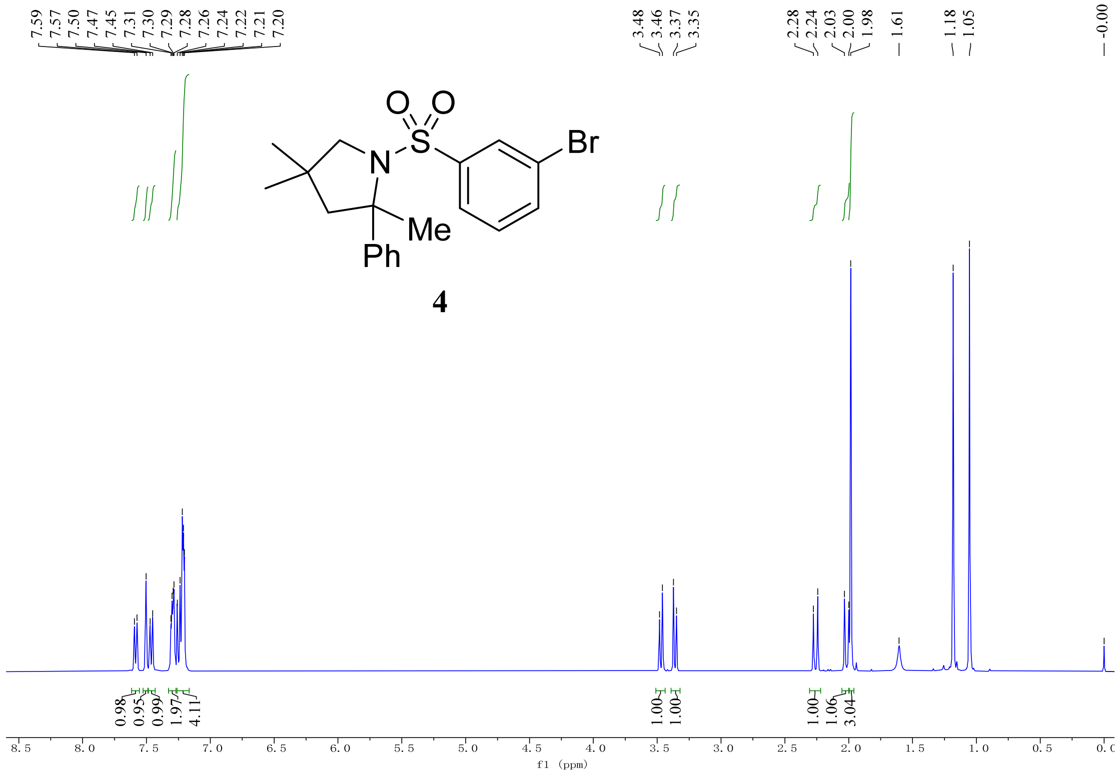
S
N
Cl
Me
Cl
Ph
3
f1 (ppm)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7.29
7.28
7.26
7.24
7.22
7.21
7.20
3.48
3.46
3.37
3.35
2.28
2.24
2.03
2.00
1.98
1.61
1.18
1.05
-0.00
Br
Me
Ph
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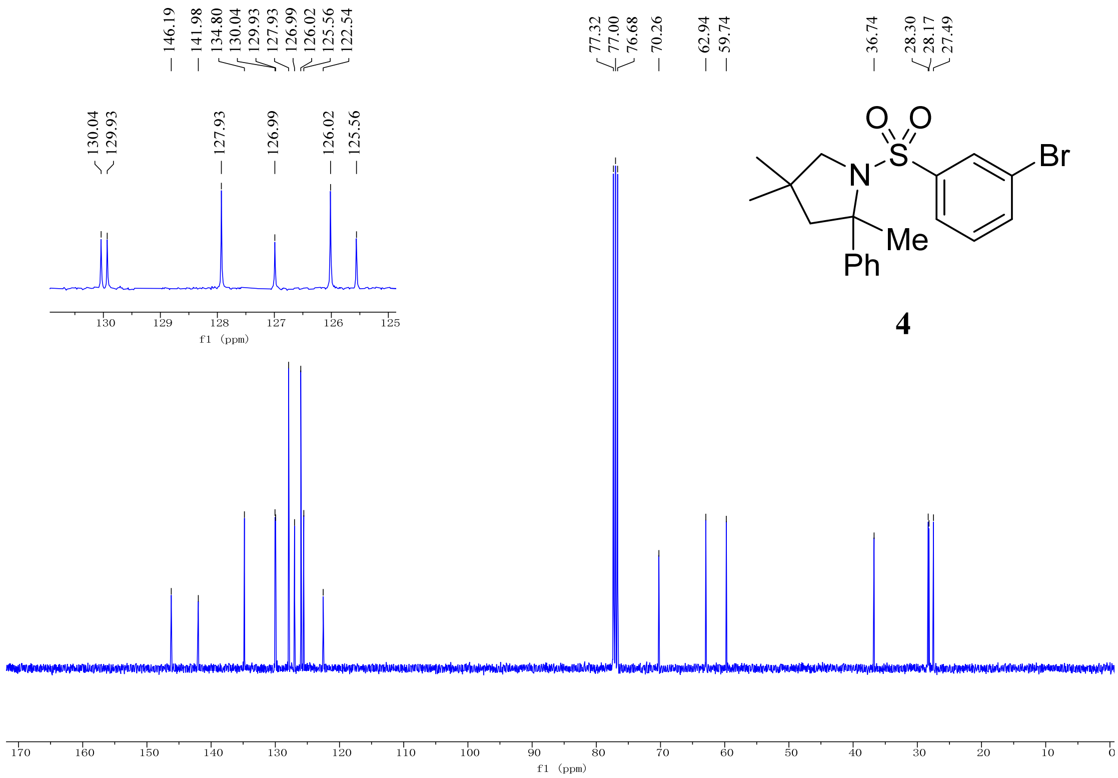
f1 (ppm)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Me
Ph
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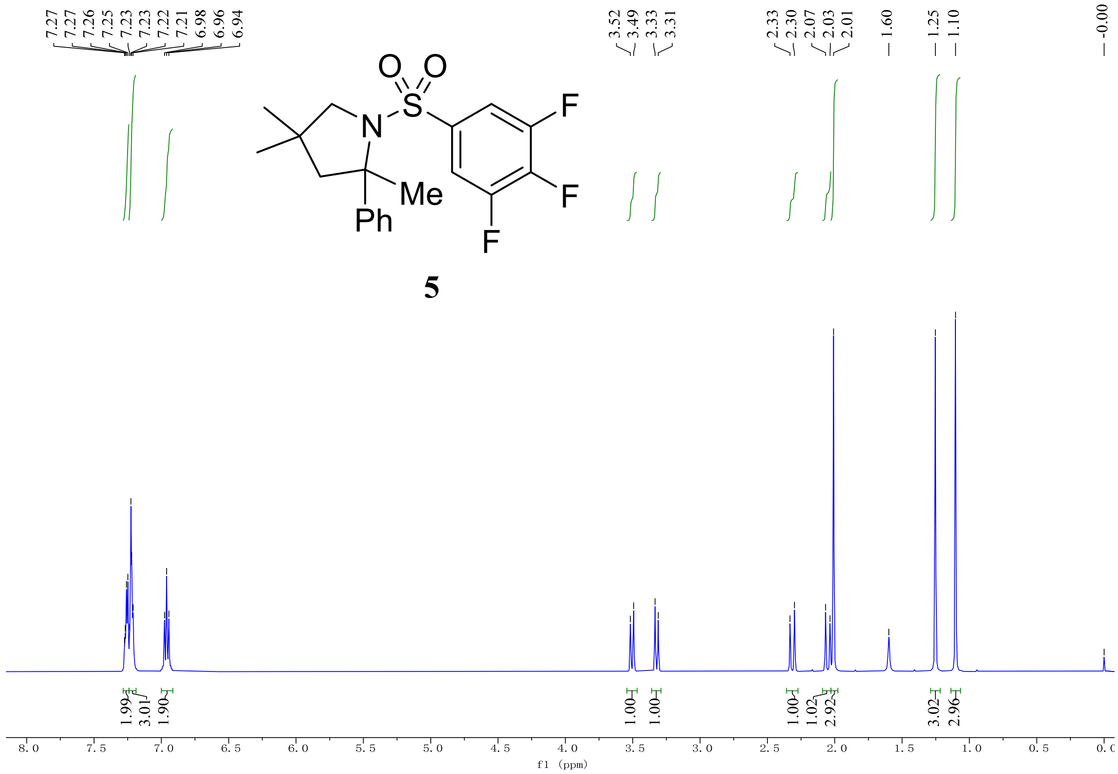
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2.33 2.30 2.07 2.03 2.01
1.60
1.25
1.10
-0.00
O O S N F F F Me Ph
5
1.99 3.01 1.90 1.00 1.00 1.00 1.02 2.92 3.02 2.96
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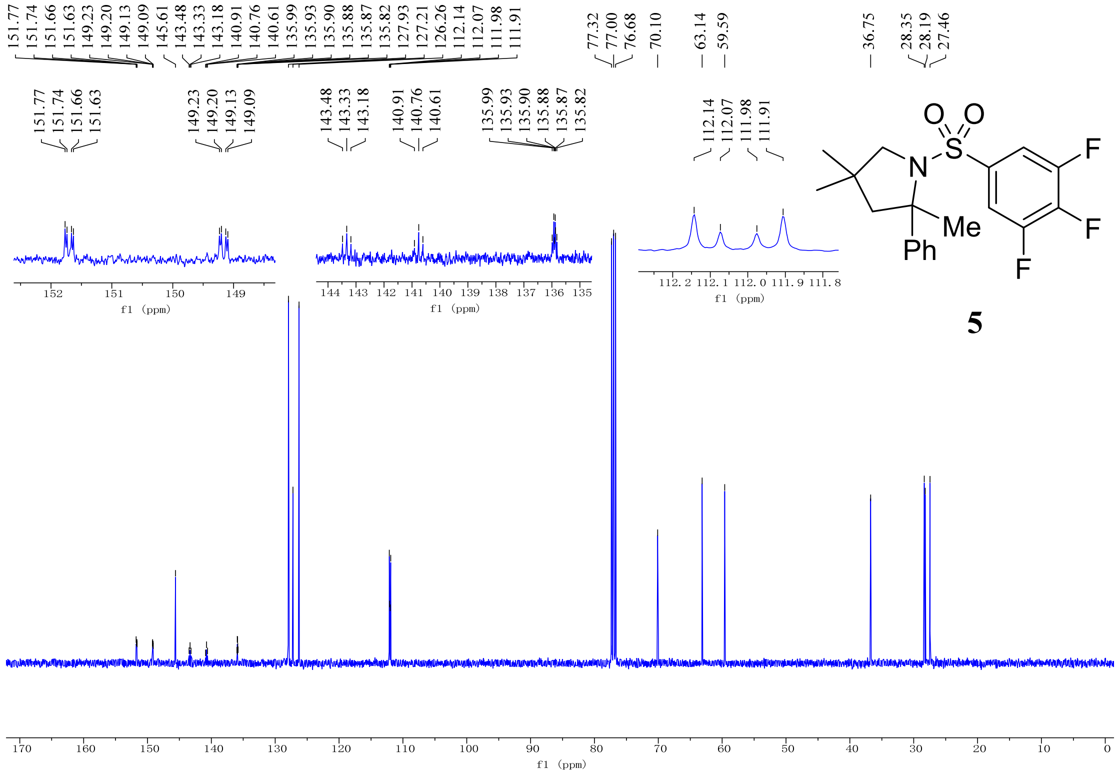
f1 (ppm)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77.32 77.00 76.68
70.10
63.14
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O O S N F F F Me Ph
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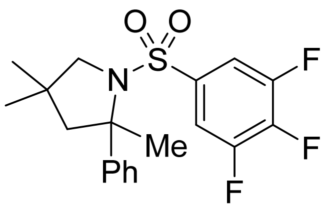
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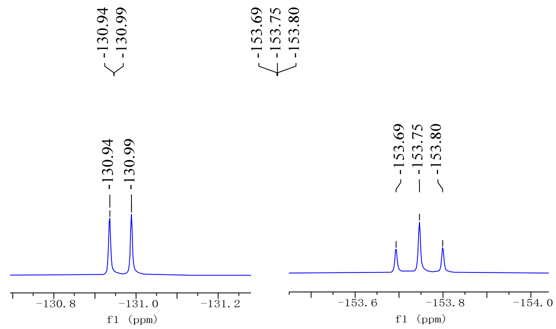
Me
Ph
F
F
F

5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-153.8
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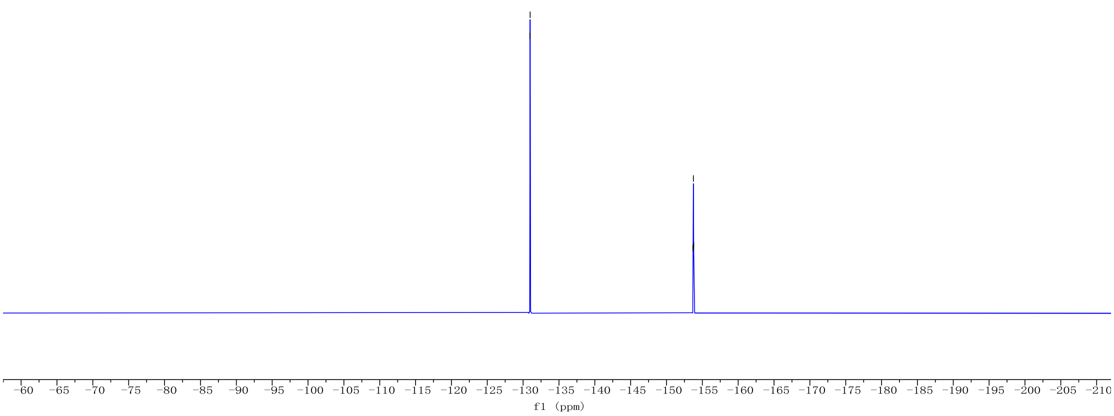
f1 (ppm)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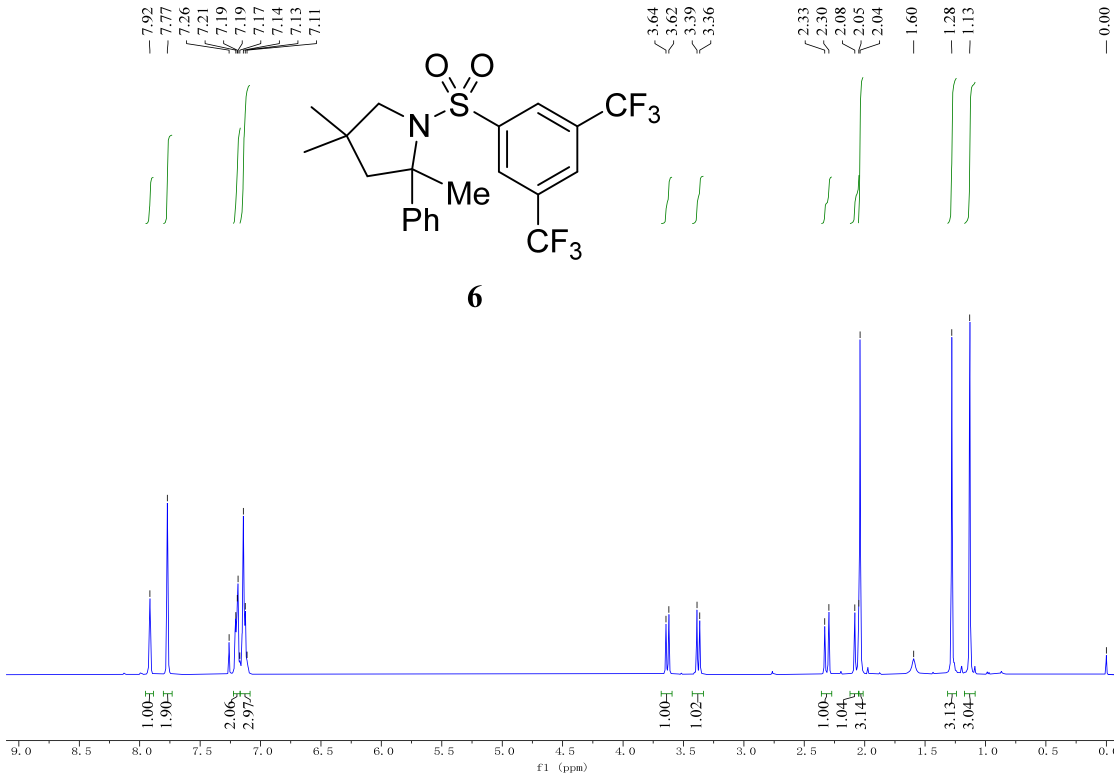
f1 (ppm)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7.11
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3.39
3.36
2.33
2.30
2.08
2.05
2.04
1.60
1.28
1.13
0.00
O O
S
N
Me
Ph
CF_3
CF_3
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1.02
1.00
1.04
3.14
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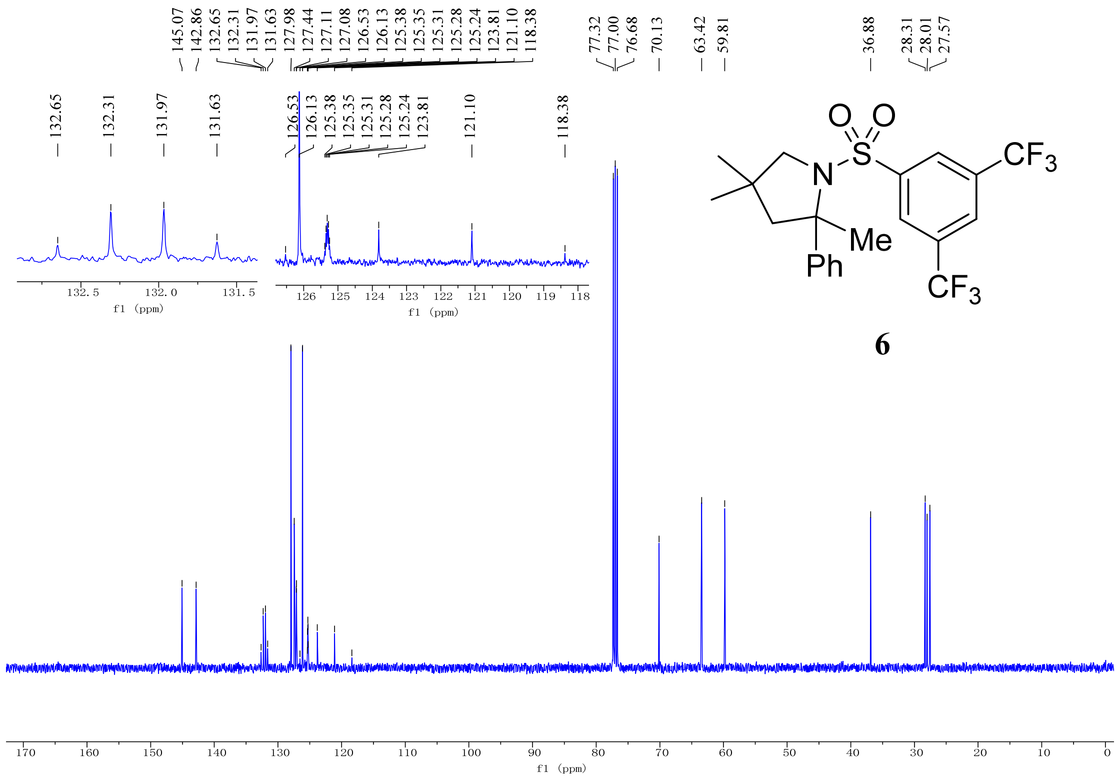
3.04
f1 (ppm)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125.31
125.28
125.24
123.81
121.10
118.38
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76.68
70.13
63.42
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28.01
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S
N
Me
Ph
CF_3
CF_3
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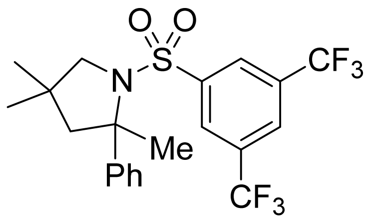
f1 (ppm)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S
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CF3
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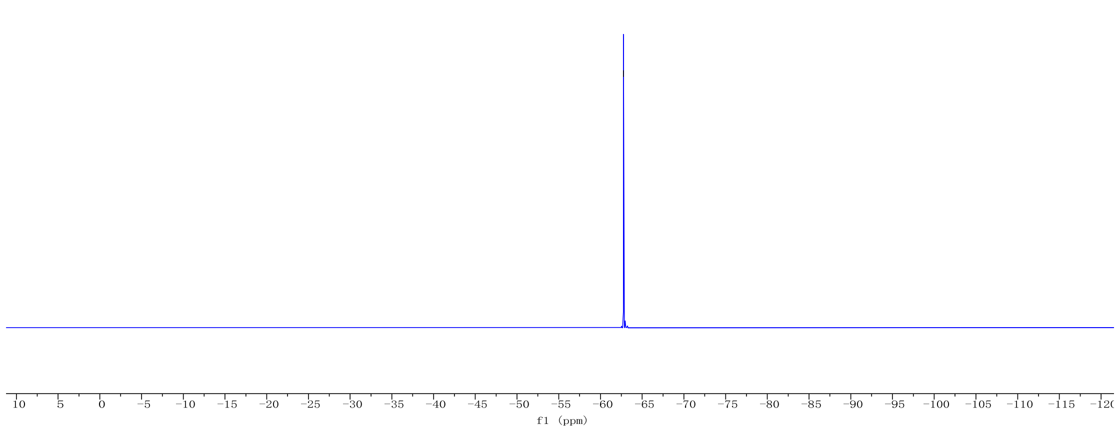
CF3

6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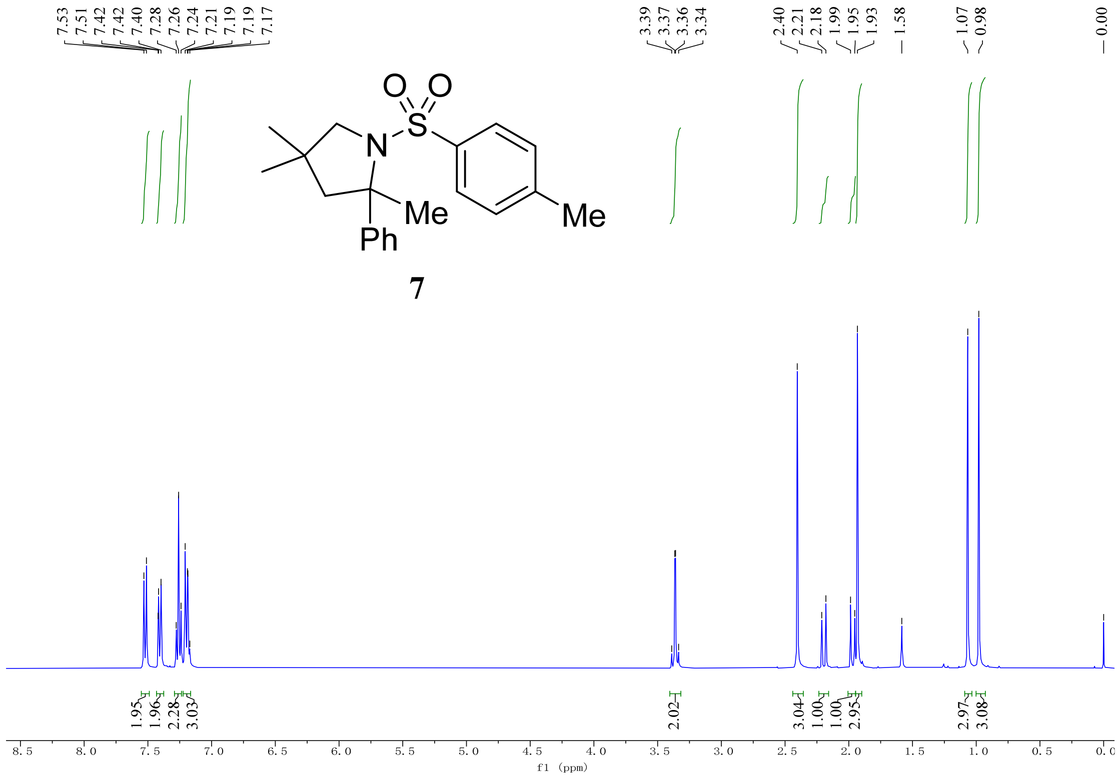
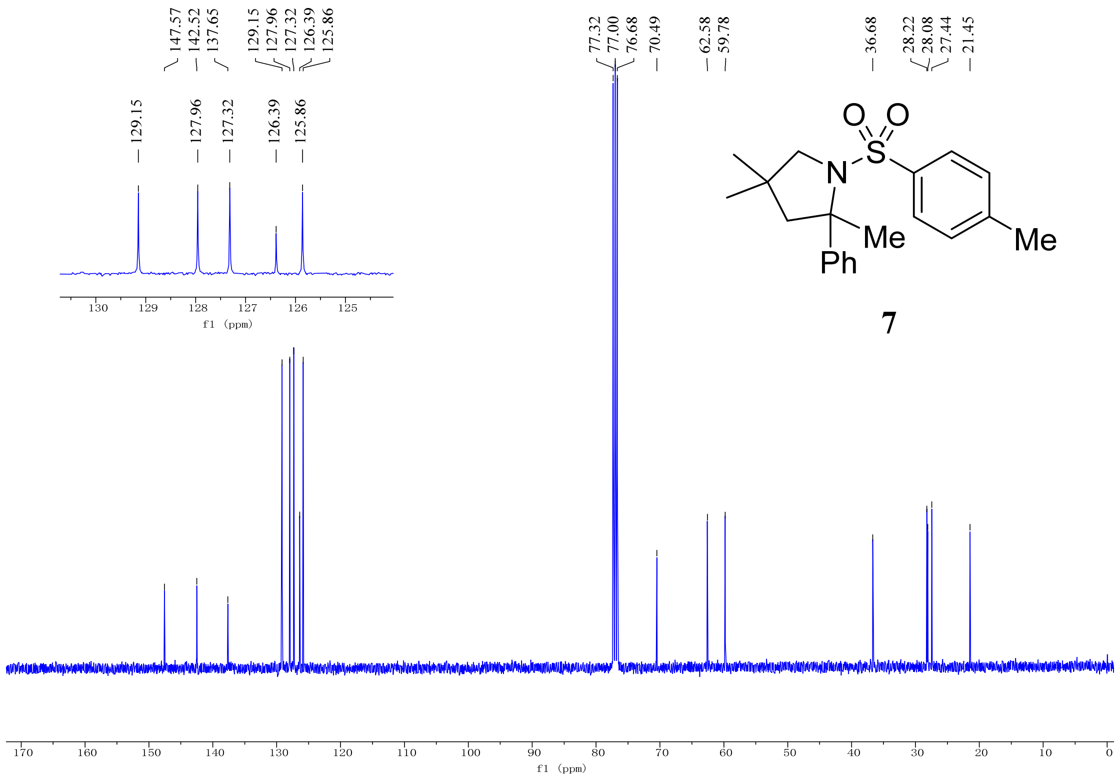
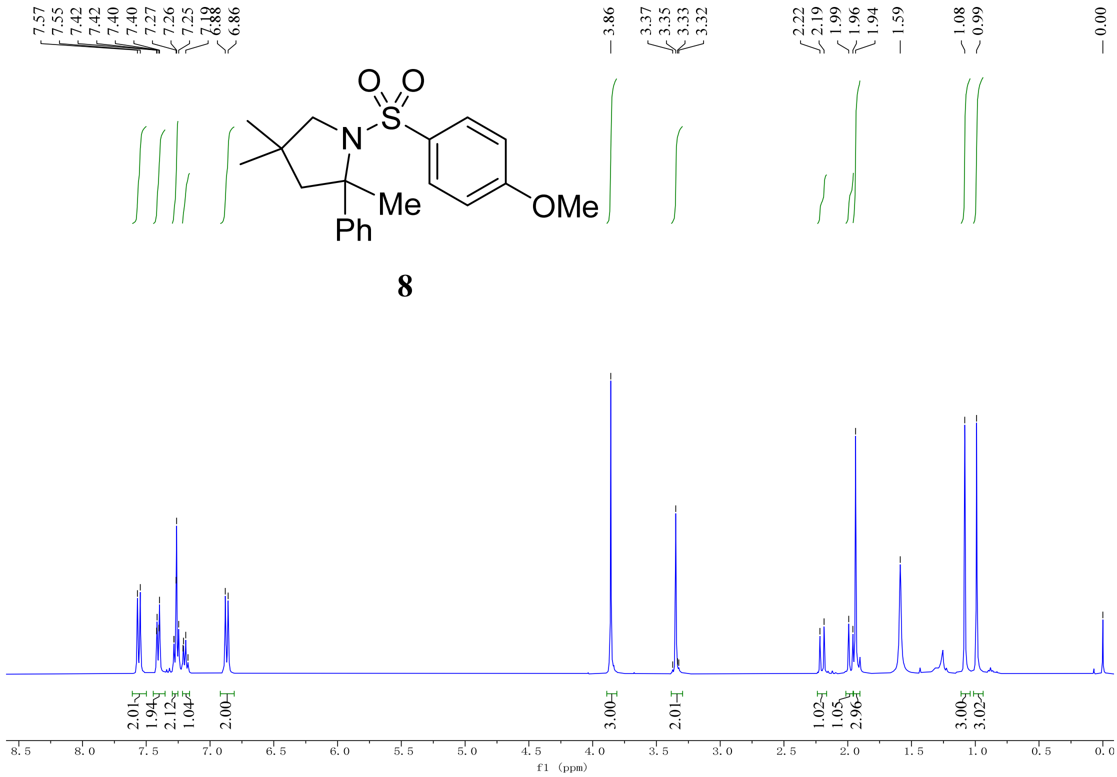
−110
−115
f1 (ppm)



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1.59
1.08 0.99
0.00
O O
S
N
Me
Ph
OMe
8
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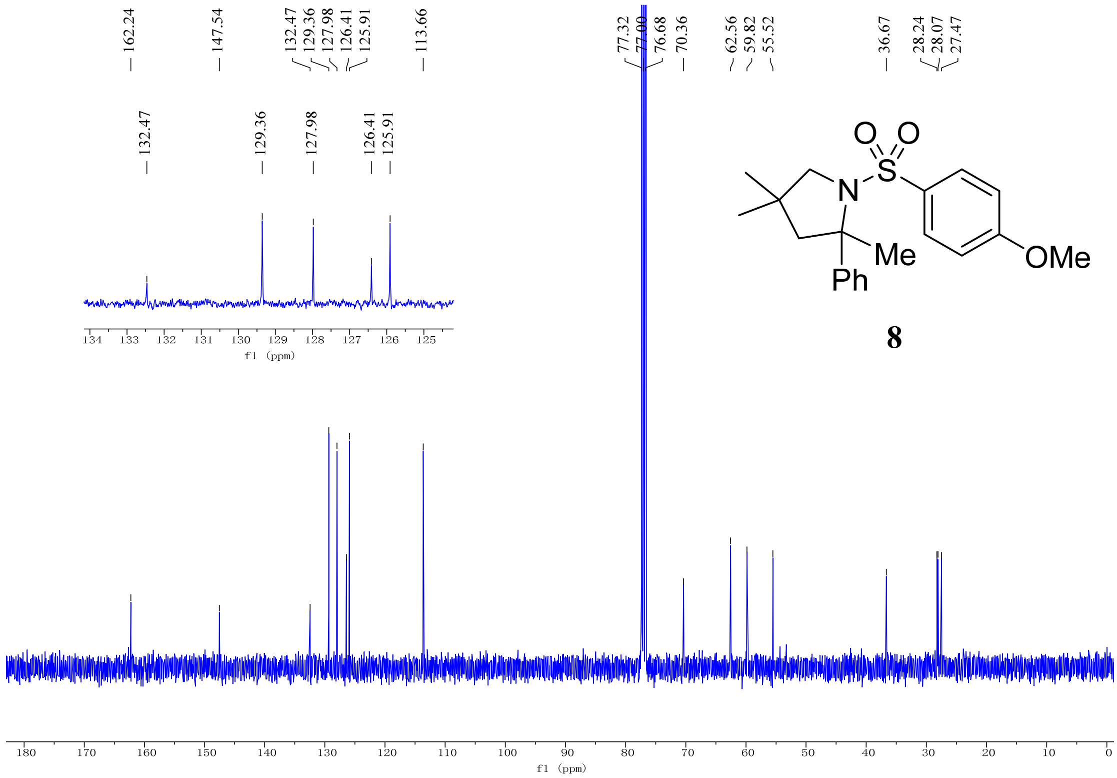
f1 (ppm)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36.67
28.24 28.07 27.47
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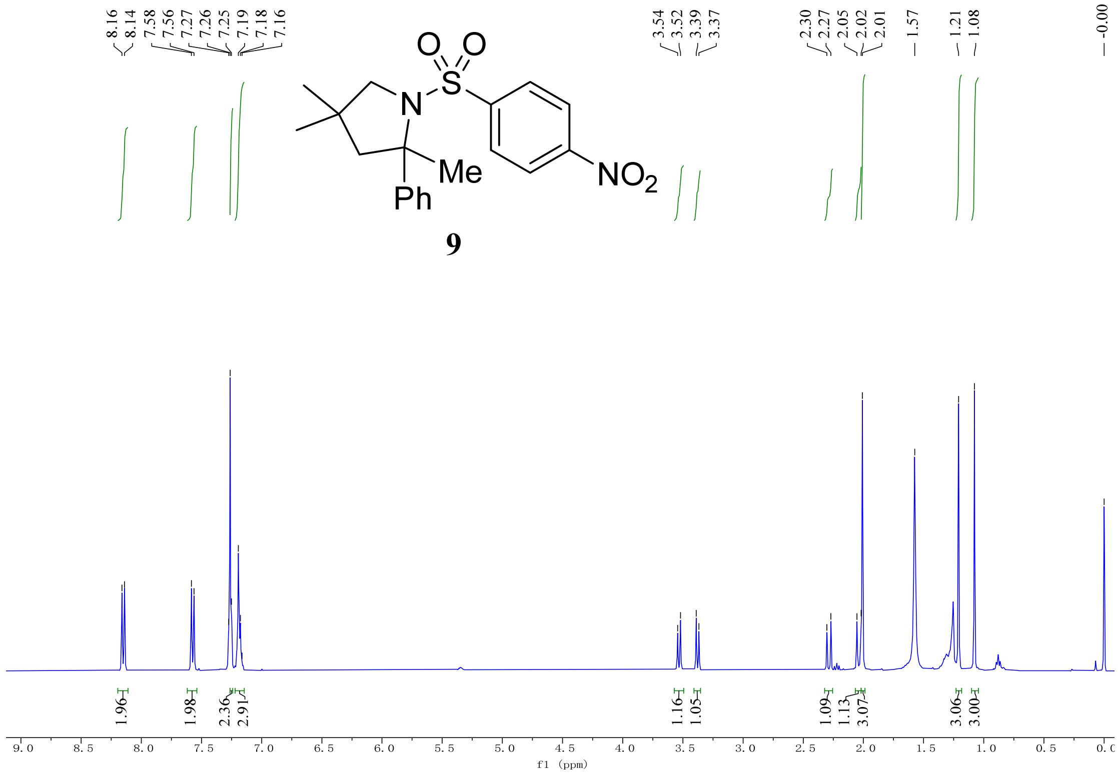
129.36
127.98
126.41 125.91
f1 (ppm)
O O
S
N
Me
Ph
OMe
8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3.37
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2.27
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2.02
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1.08
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Me
Ph
N
S
O
O
NO2
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1.13
3.07
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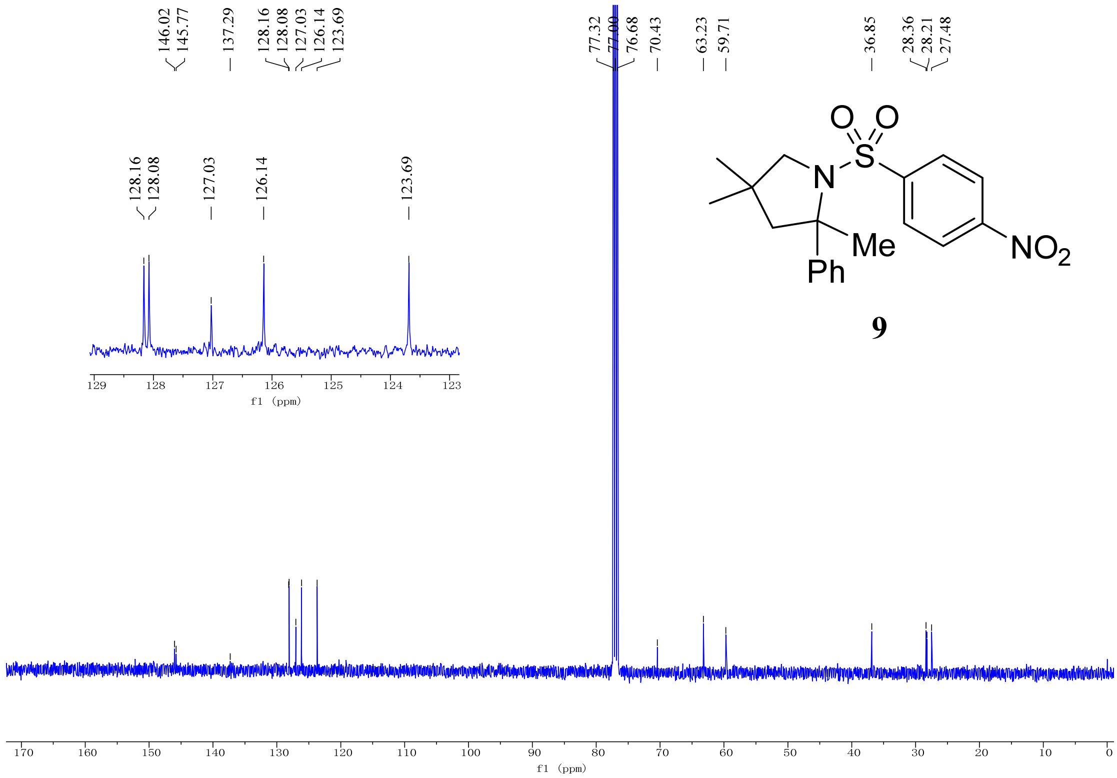
3.00
f1 (ppm)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Me
Ph
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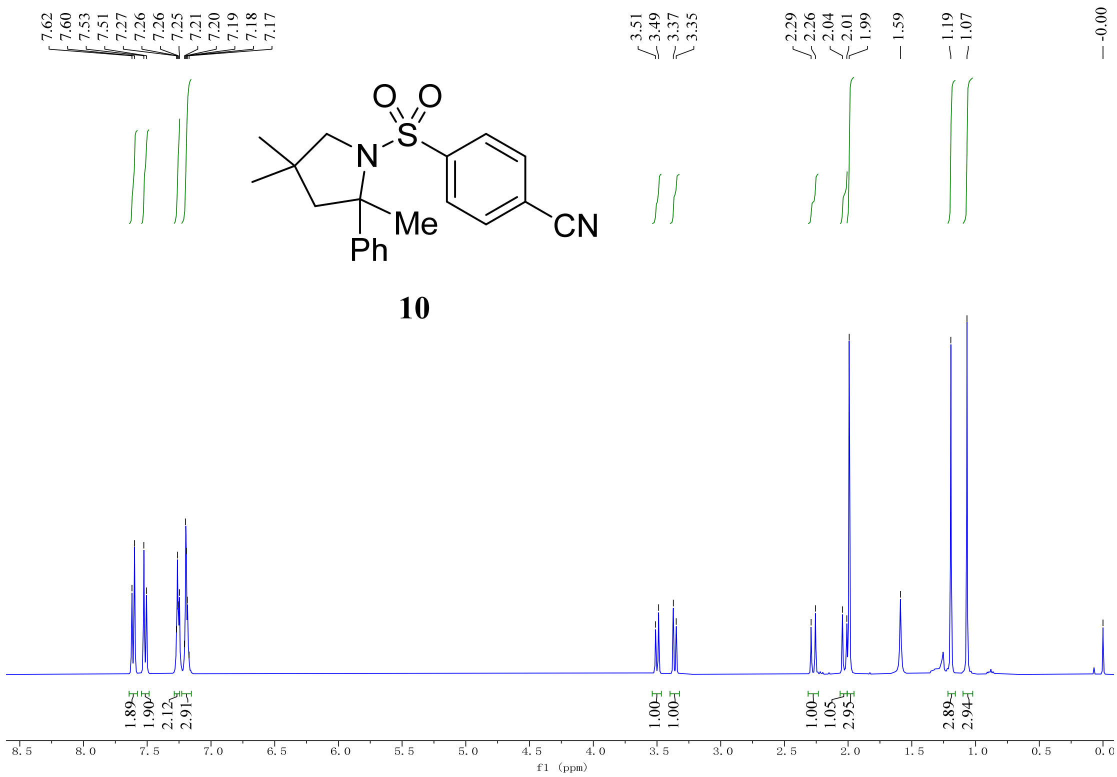
S
O
O
NO2
9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1.59
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f1 (ppm)

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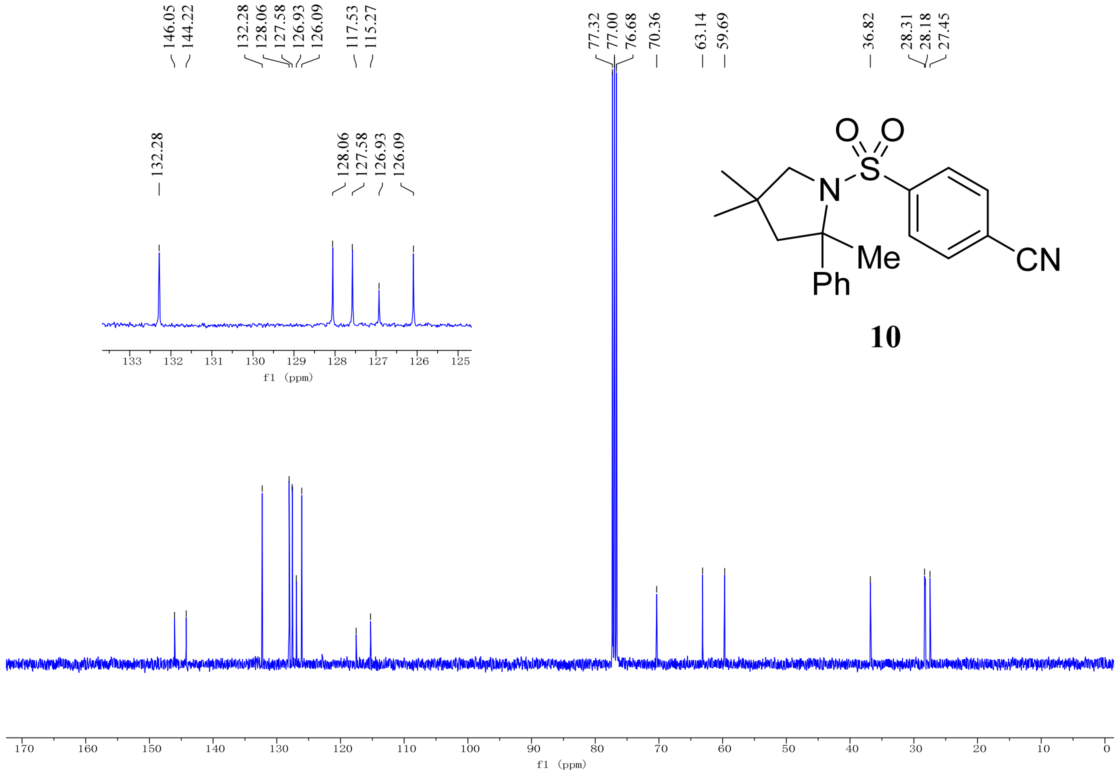
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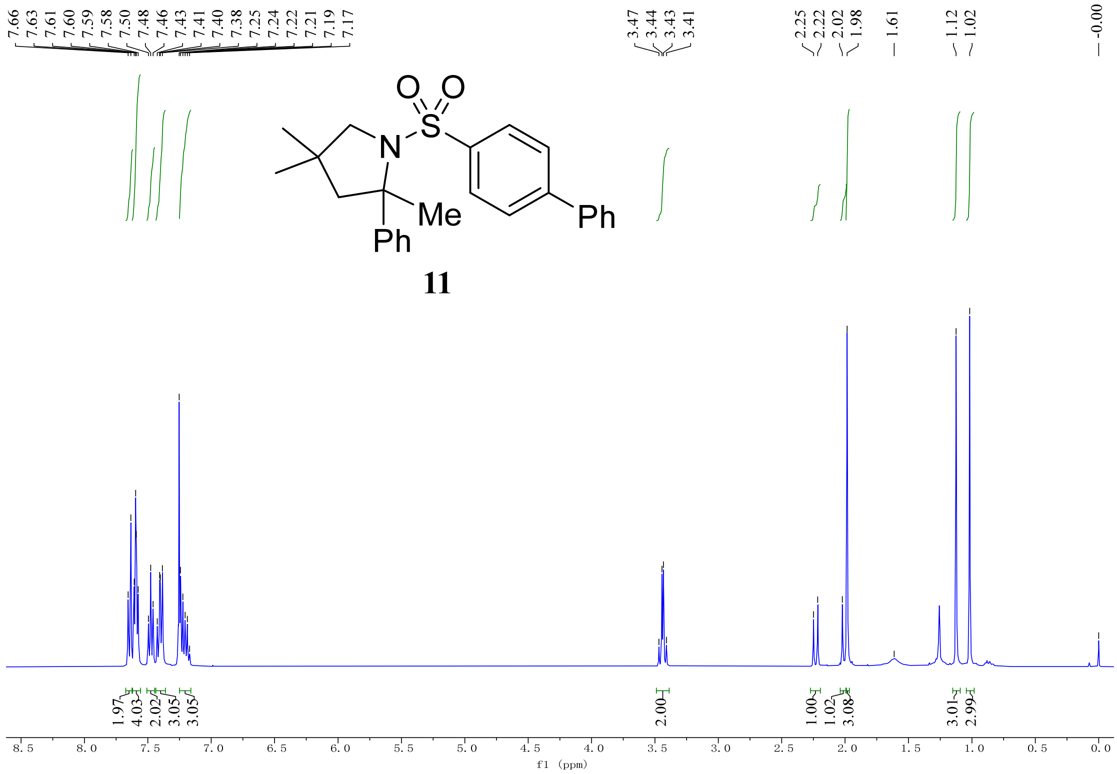
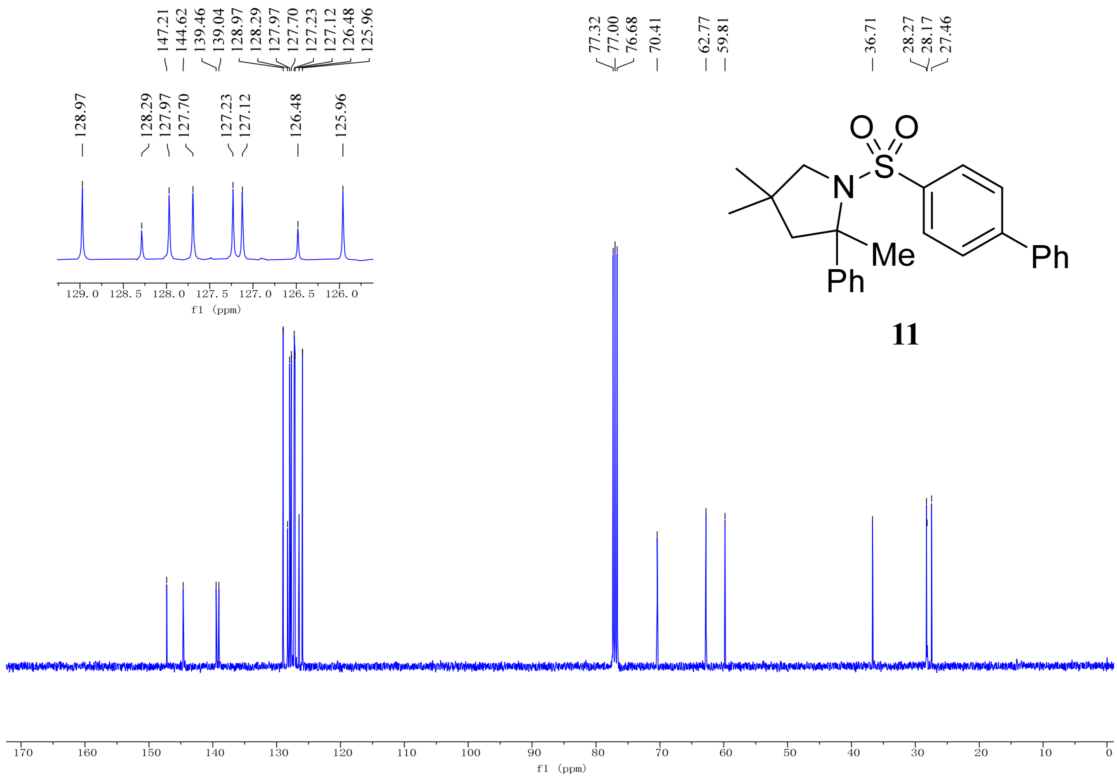
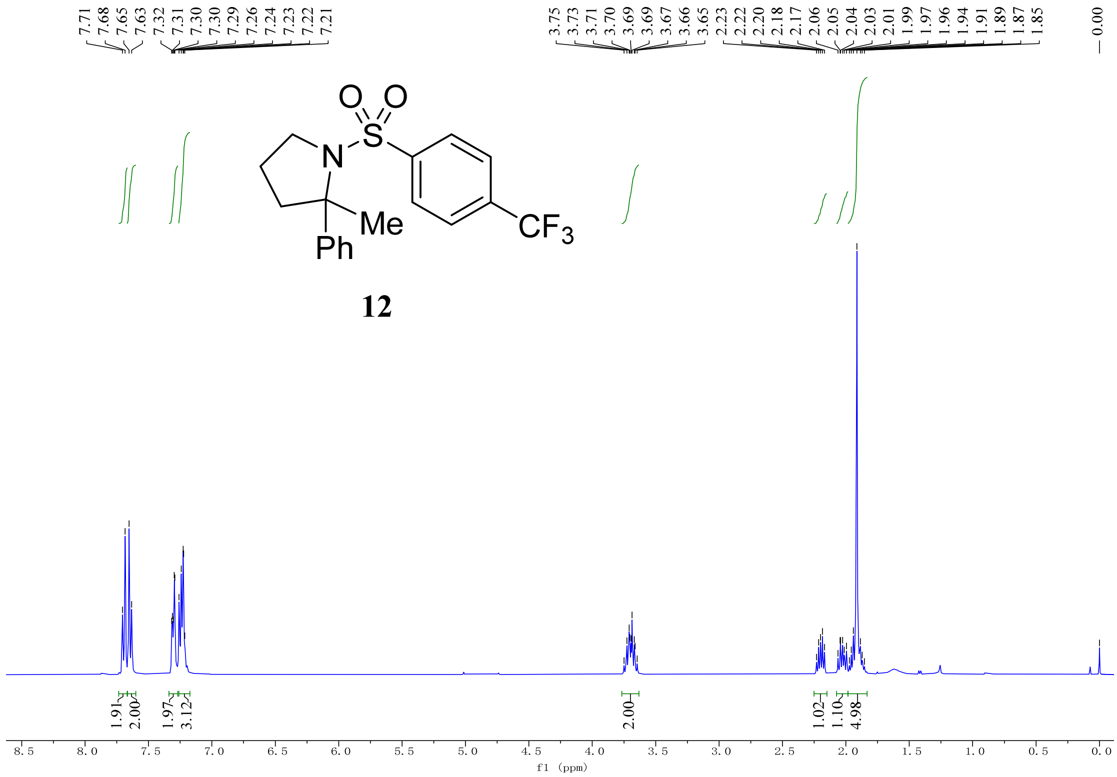
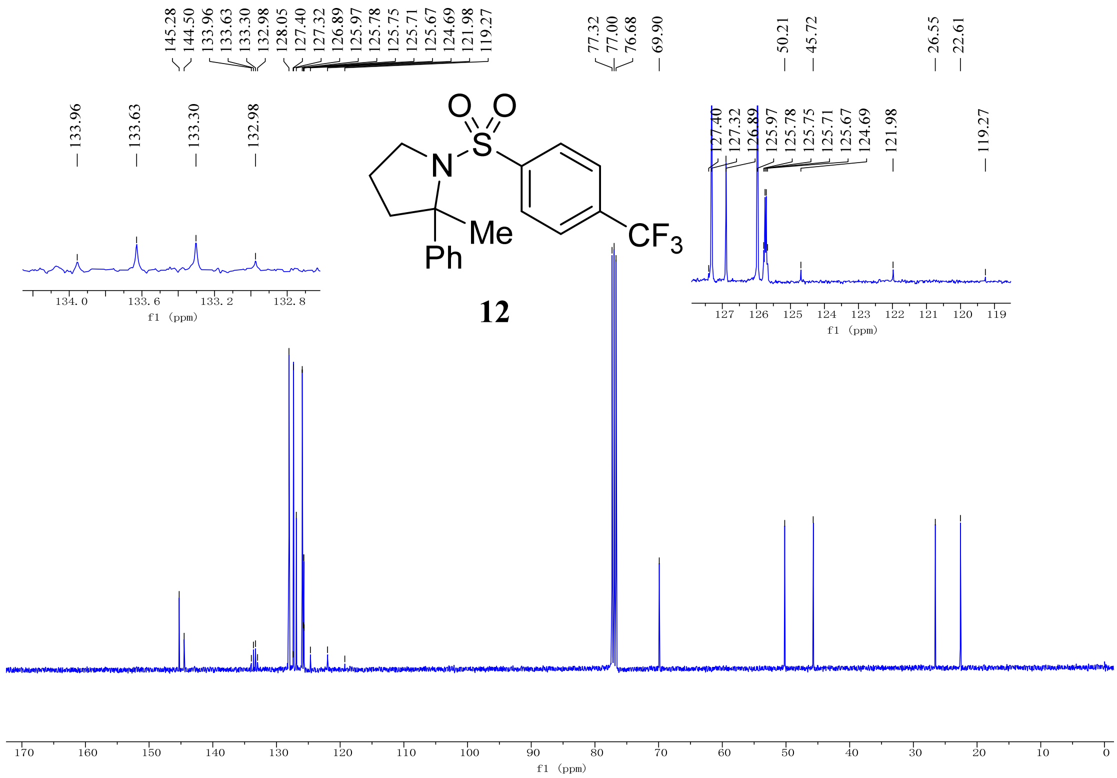
f1 (ppm)

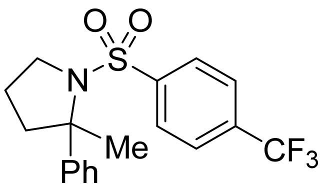
10










O
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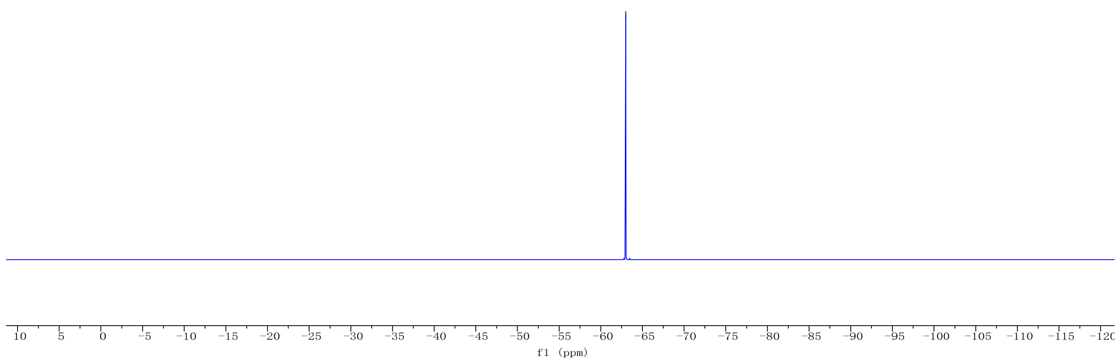
N
Me
Ph
CF3

12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-95
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-105
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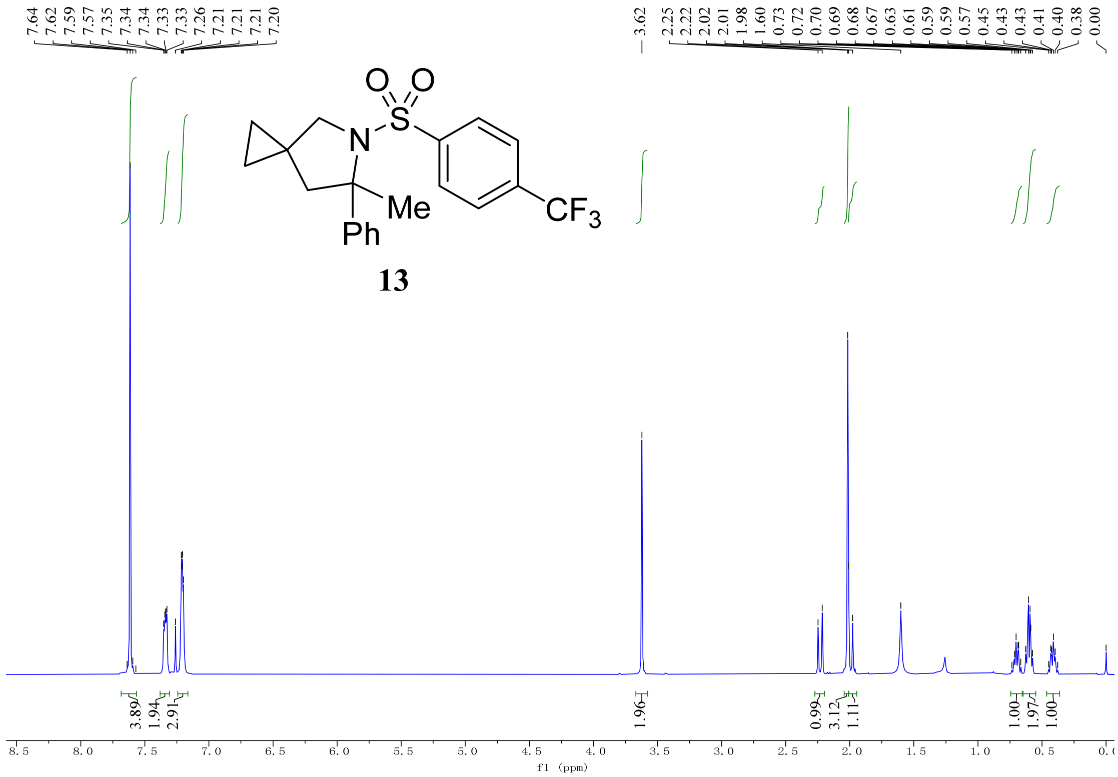
-120
f1 (ppm)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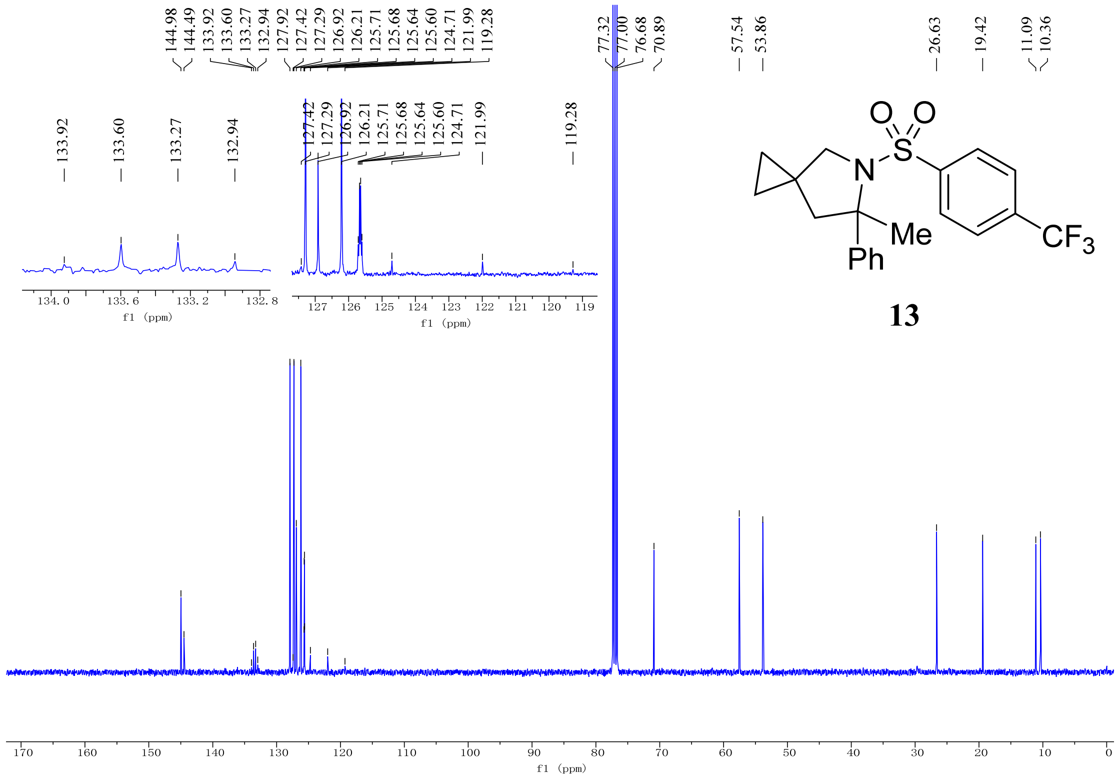
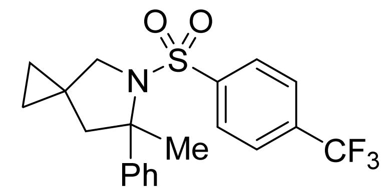
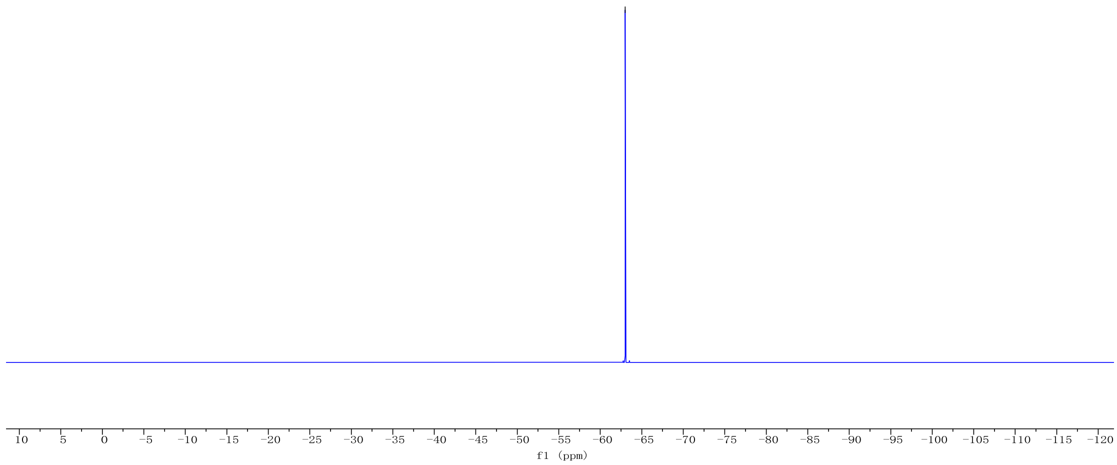
3.62
2.25 2.22 2.02 2.01 1.98 1.60 0.73 0.72 0.70 0.69 0.68 0.67 0.63 0.61 0.59 0.59 0.57 0.45 0.43 0.43 0.41 0.40 0.38 0.00
Me
Ph
CF_3
13
3.89 1.94 2.91 1.96 0.99 3.12 1.11 1.00 1.97 1.00
f1 (ppm)

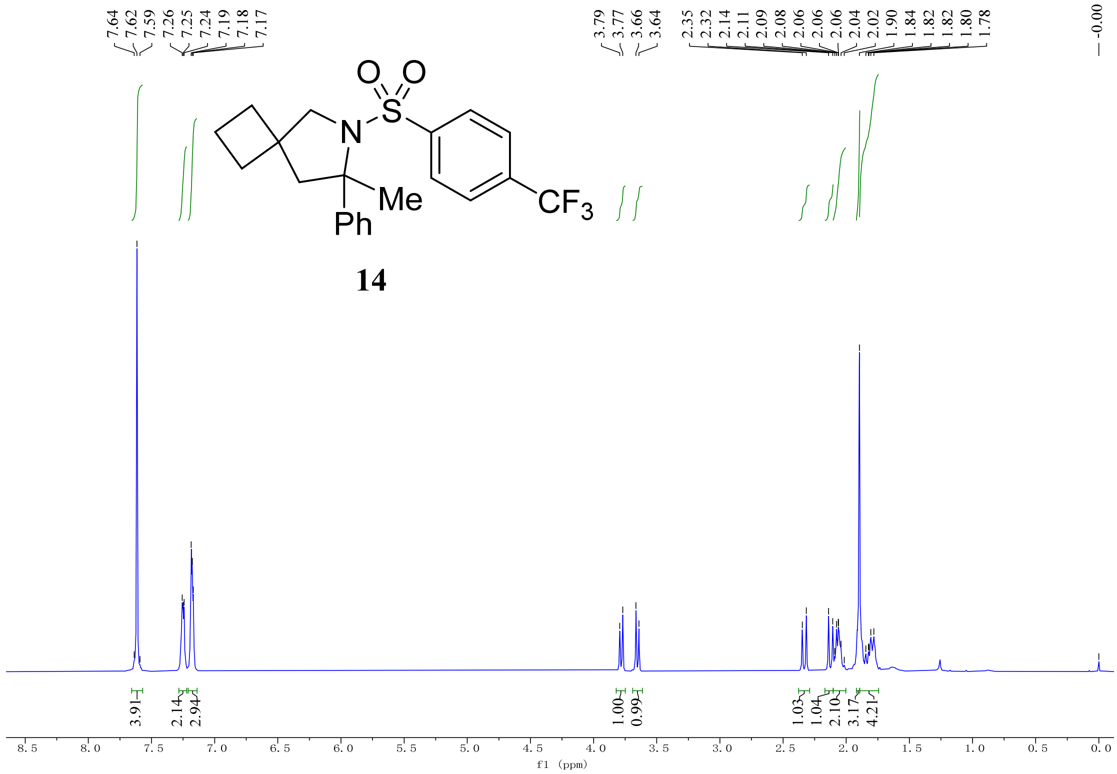

144.98 144.49 133.92 133.60 133.27 132.94 127.92 127.42 127.29 126.92 126.21 125.71 125.68 125.64 125.60 124.71 121.99 119.28
77.32 77.00 76.68 70.89
57.54 53.86
26.63 19.42 11.09 10.36
Me
Ph
CF_3
13
f1 (ppm)



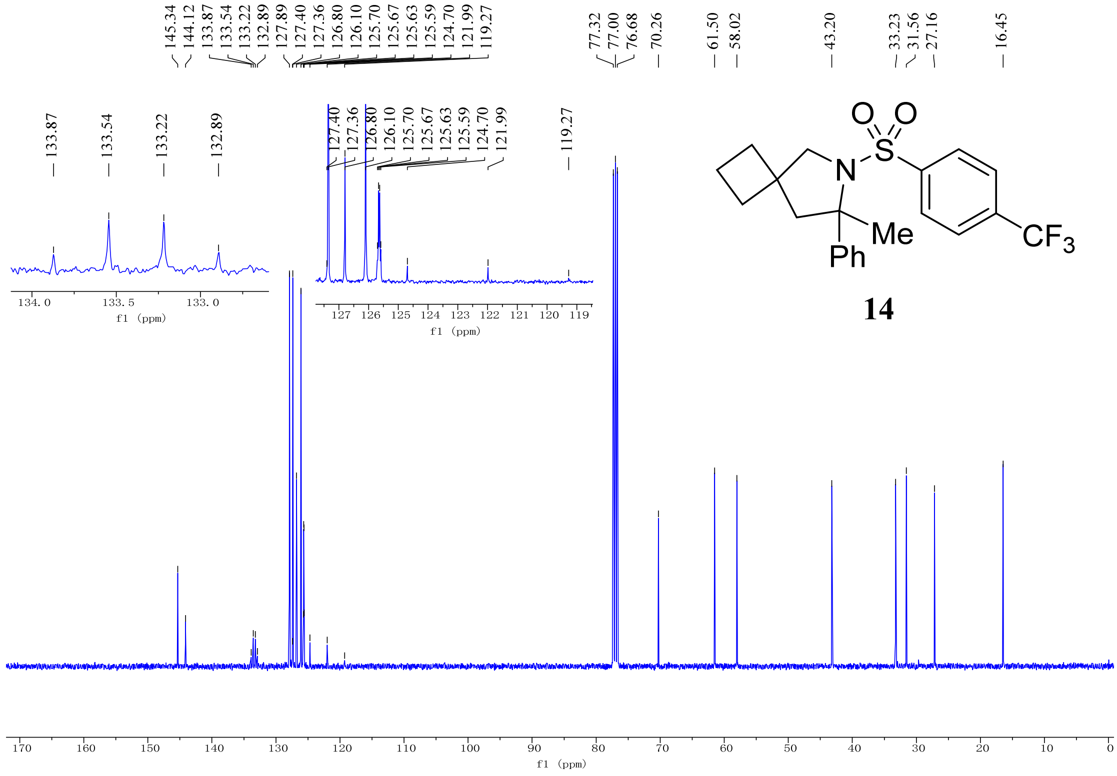
13



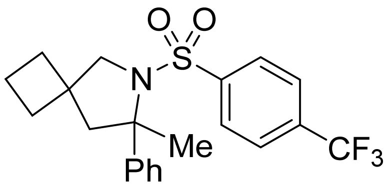
-63.01
10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120
f1 (ppm)



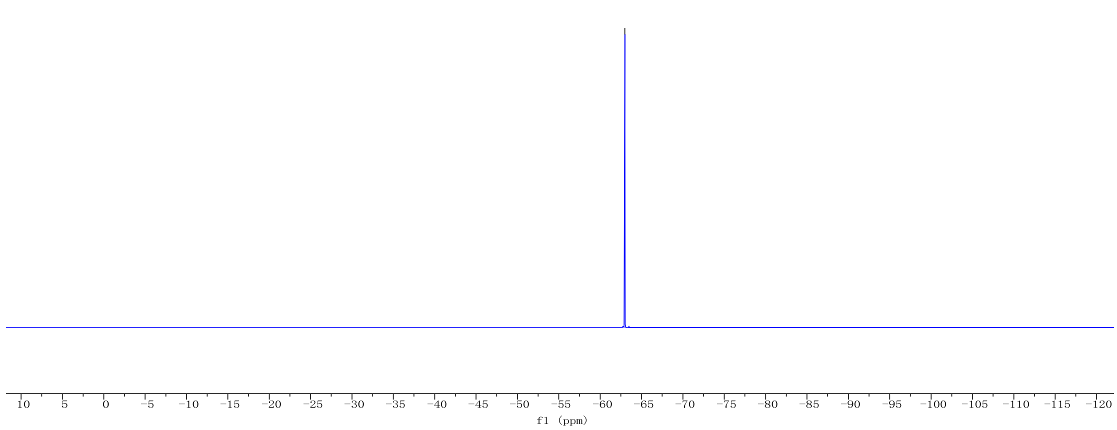
14



14


O
O
S
N
Me
Ph
CF3

14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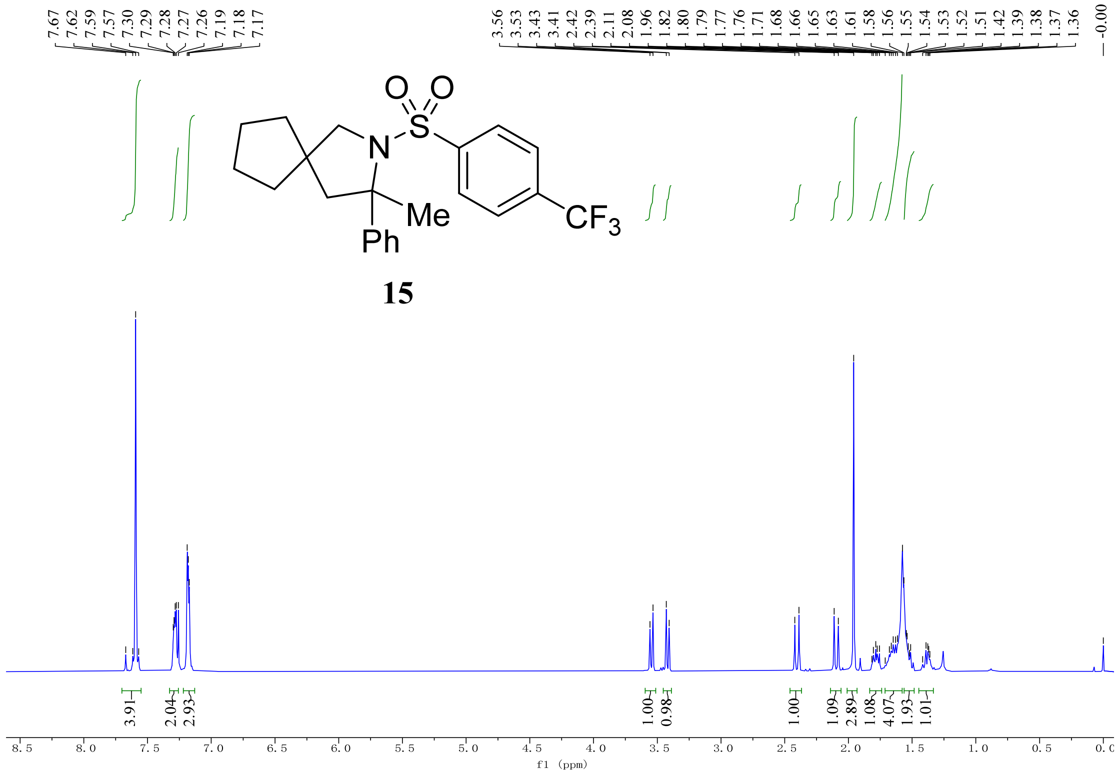
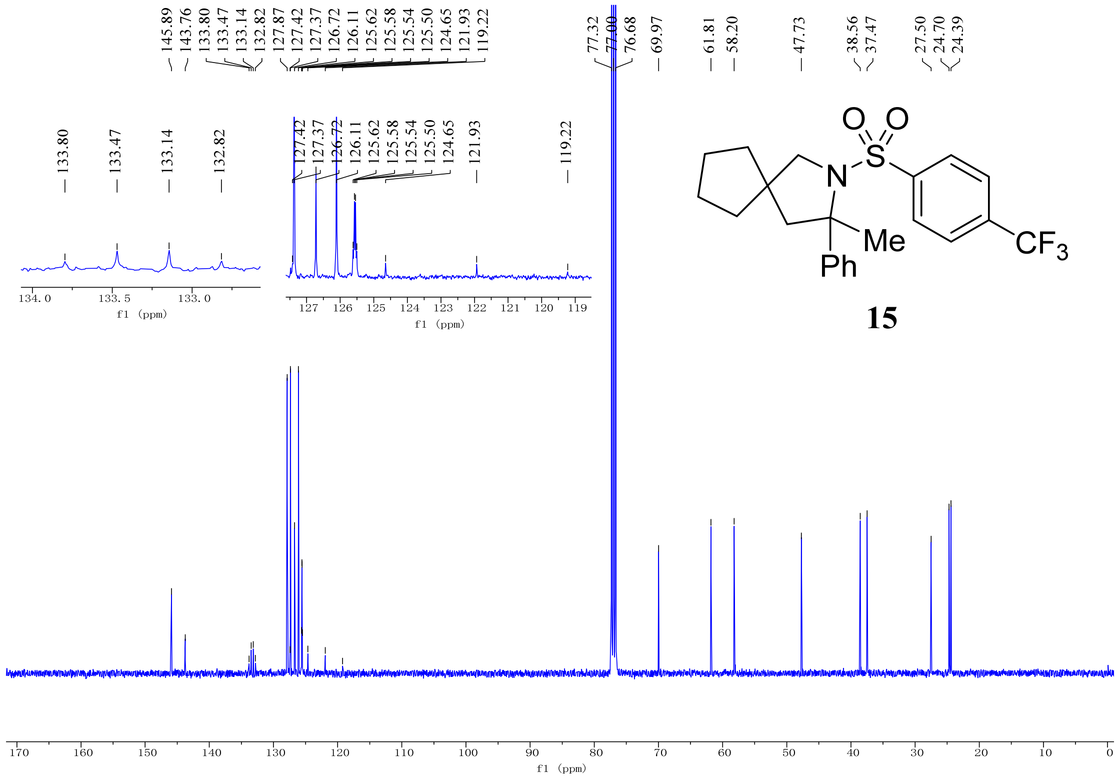
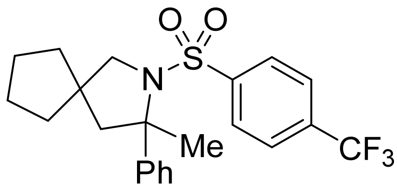
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−120
f1 (ppm)


7.67 7.62 7.59 7.57 7.30 7.29 7.28 7.27 7.26 7.19 7.18 7.17
3.56 3.53 3.43 3.41 2.42 2.39 2.11 2.08 1.96 1.82 1.80 1.79 1.77 1.76 1.71 1.68 1.66 1.65 1.63 1.61 1.58 1.56 1.55 1.54 1.53 1.52 1.51 1.42 1.39 1.38 1.37 1.36
-0.00
O O
S
N
Me
Ph
CF_3
15
3.91 2.04 2.93 1.00 0.98 1.00 1.09 2.89 1.08 4.07 1.93 1.01
f1 (ppm)


145.89 143.76 133.80 133.47 133.14 132.82 127.87 127.42 127.37 126.72 126.11 125.62 125.58 125.54 125.50 124.65 121.93 119.22
77.32 77.00 76.68 69.97 61.81 58.20 47.73 38.56 37.47 27.50 24.70 24.39
133.80 133.47 133.14 132.82
127.42 127.37 126.72 126.11 125.62 125.58 125.54 125.50 124.65 121.93 119.22
O O
S
N
Me
Ph
CF_3
15
f1 (ppm)



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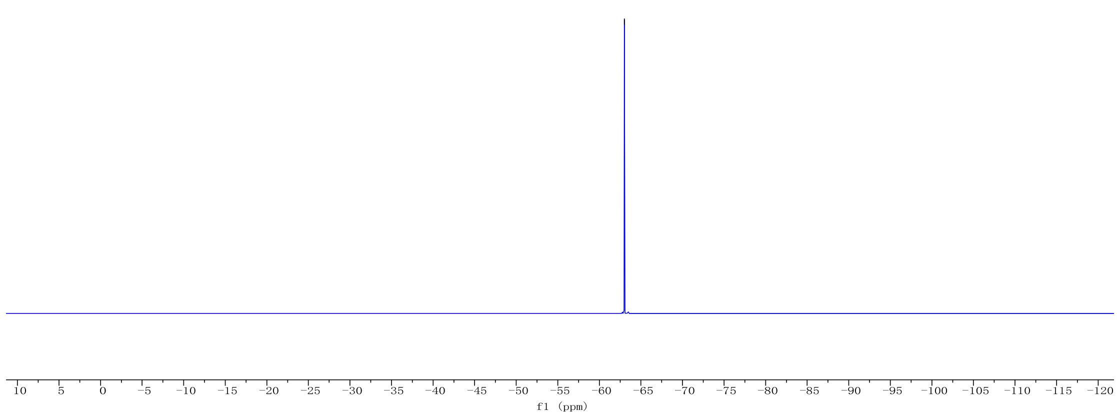
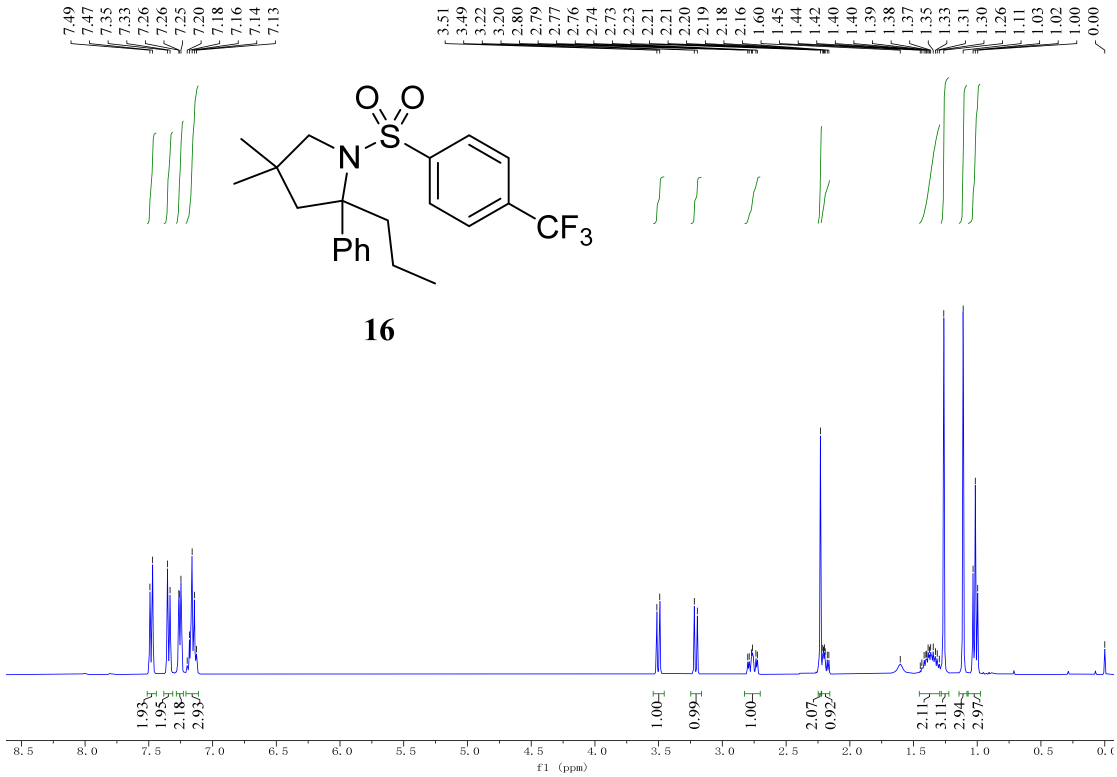
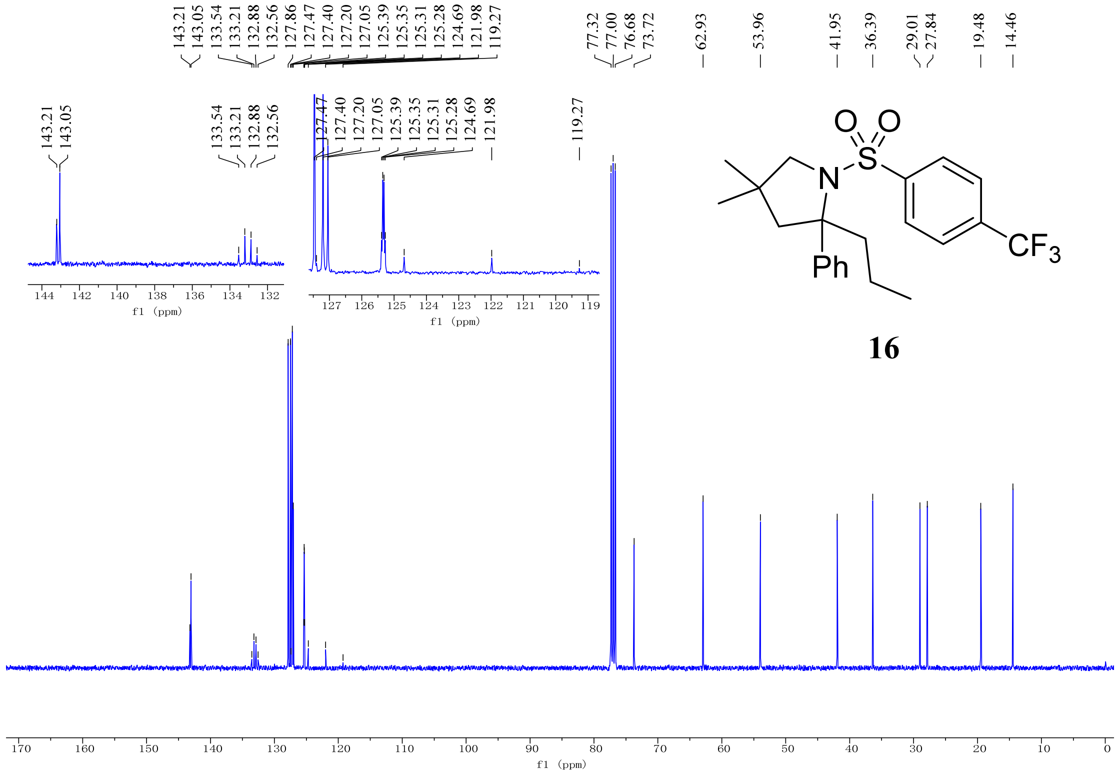
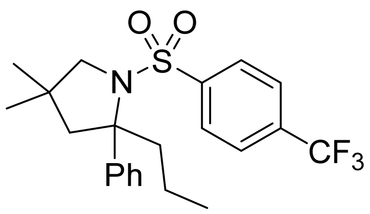
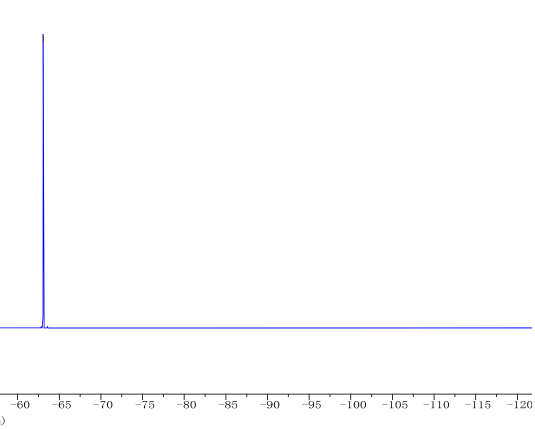

-63.00
10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120
f1 (ppm)


7.49
7.47
7.35
7.33
7.26
7.26
7.25
7.20
7.18
7.16
7.14
7.13
3.51
3.49
3.22
3.20
2.80
2.79
2.77
2.76
2.74
2.73
2.23
2.21
2.21
2.20
2.19
2.18
2.16
1.60
1.45
1.44
1.42
1.40
1.40
1.39
1.38
1.37
1.35
1.33
1.31
1.30
1.26
1.11
1.03
1.02
1.00
0.00
16
1.93
1.95
2.18
2.93
1.00
0.99
1.00
2.07
0.92
2.11
3.11
2.94
2.97
f1 (ppm)


143.21
143.05
133.54
133.21
132.88
132.56
127.86
127.47
127.40
127.20
127.05
125.39
125.35
125.31
125.28
124.69
121.98
119.27
77.32
77.00
76.68
73.72
62.93
53.96
41.95
36.39
29.01
27.84
19.48
14.46
16
f1 (ppm)



16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10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
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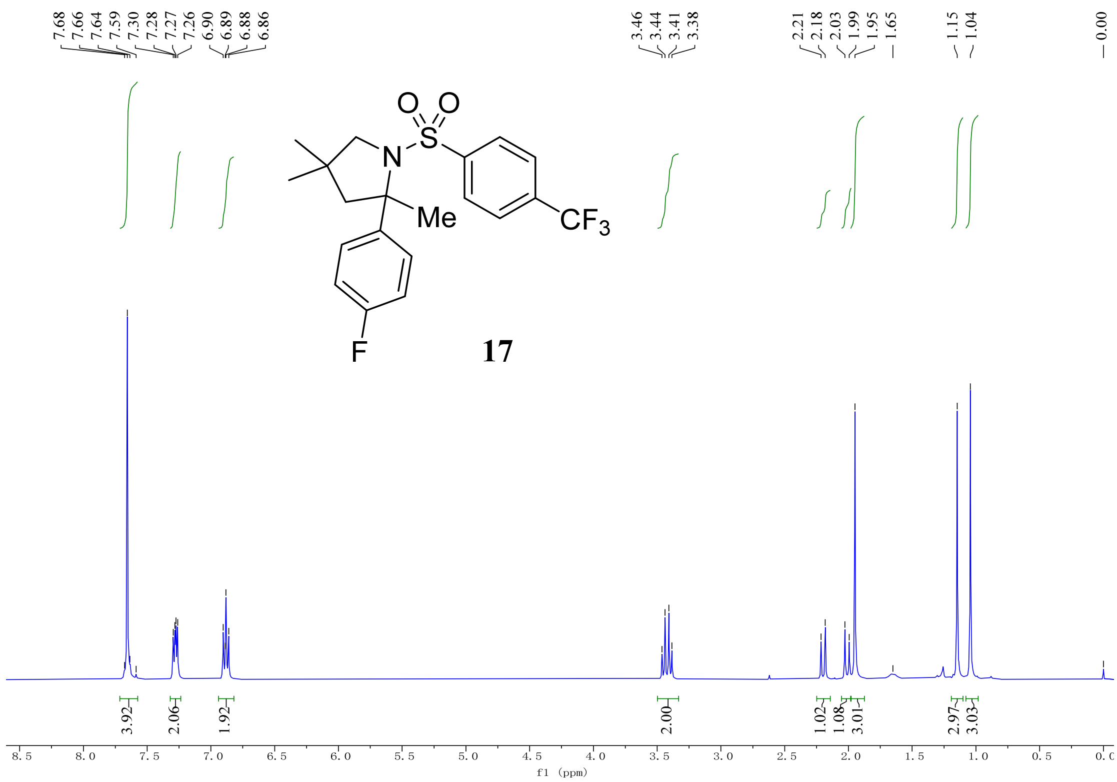
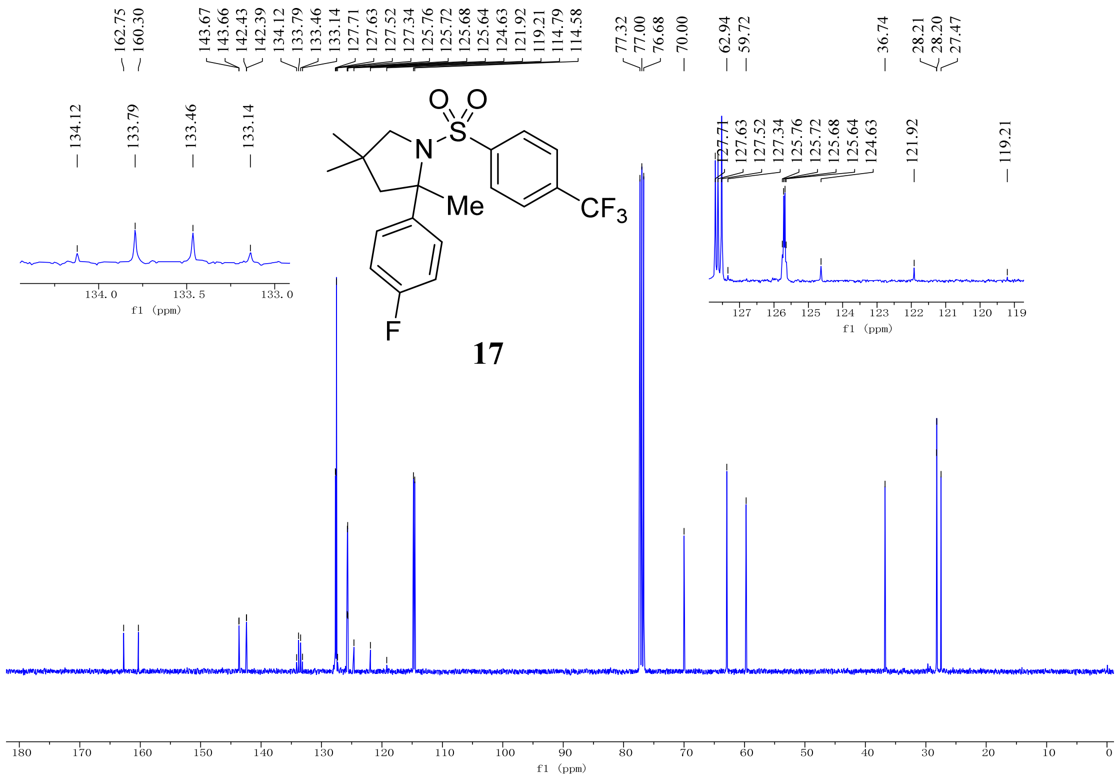
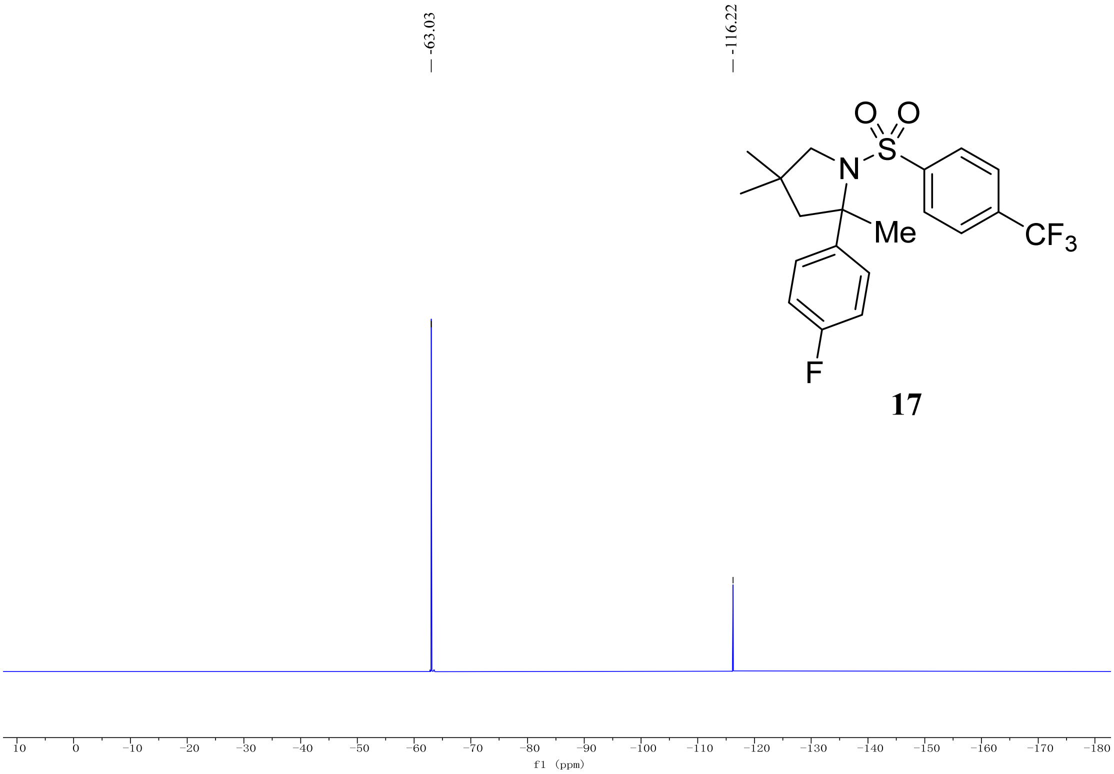
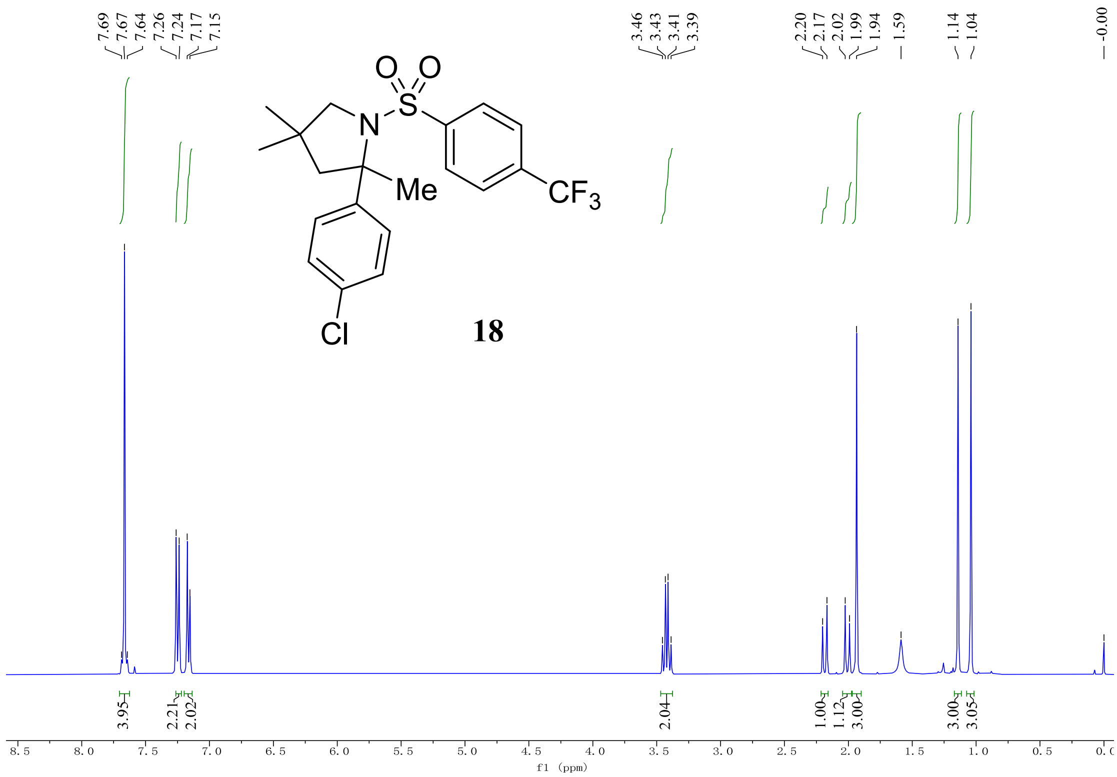
-115
-120
f1 (ppm)

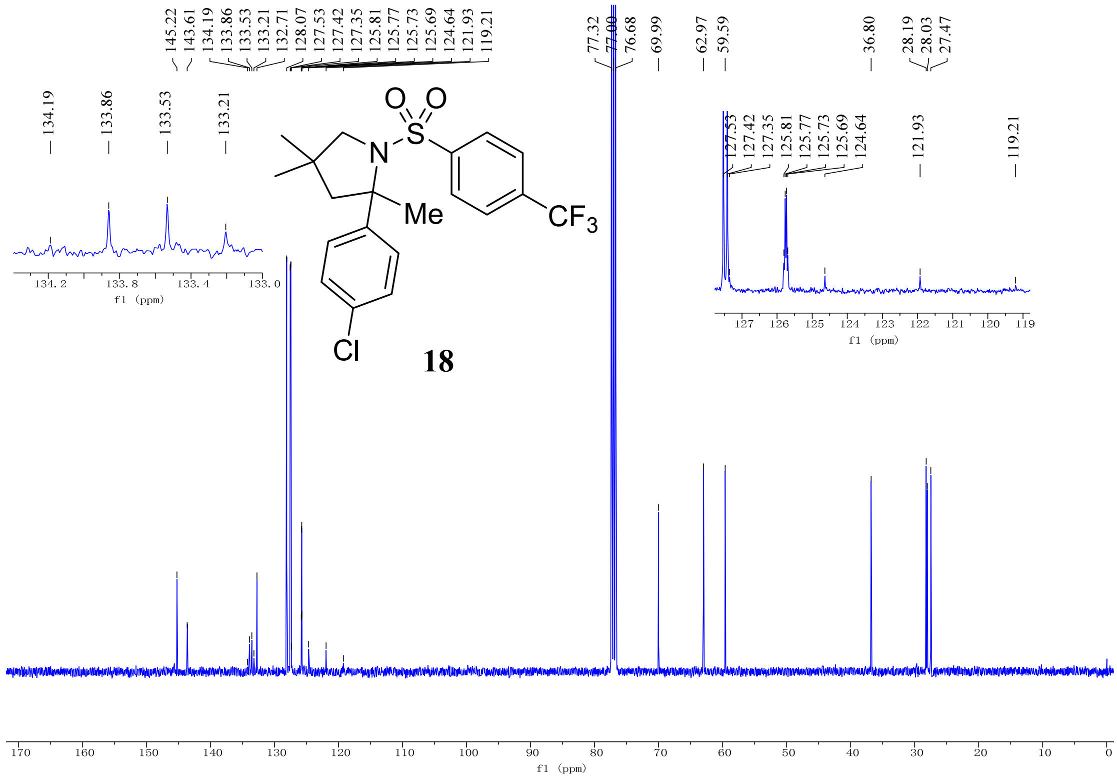

7.68
7.66
7.64
7.59
7.30
7.28
7.27
7.26
6.90
6.89
6.88
6.86
3.46
3.44
3.41
3.38
2.21
2.18
2.03
1.99
1.95
1.65
1.15
1.04
0.00
Me
CF3
F
17
3.92
2.06
1.92
2.00
1.02
1.08
3.01
2.97
3.03
f1 (ppm)

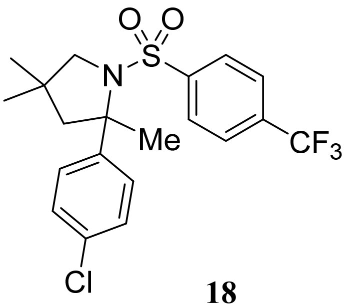

162.75
160.30
143.67
143.66
142.43
142.39
134.12
133.79
133.46
133.14
127.71
127.63
127.52
127.34
125.76
125.72
125.68
125.64
124.63
121.92
119.21
114.79
114.58
77.32
77.00
76.68
70.00
62.94
59.72
36.74
28.21
28.20
27.47
Me
CF3
F
17
f1 (ppm)


-63.03
-116.22
O
O
S
N
Me
CF3
F
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
f1 (ppm)

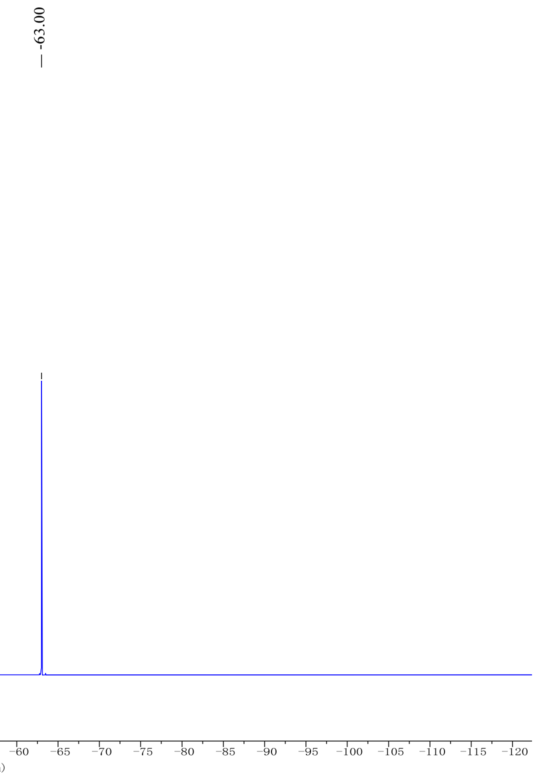
17


7.69
7.67
7.64
7.26
7.24
7.17
7.15
3.46
3.43
3.41
3.39
2.20
2.17
2.02
1.99
1.94
1.59
1.14
1.04
-0.00
O
S
O
N
Me
CF3
Cl
18
3.95
2.21
2.02
2.04
1.00
1.12
3.00
3.00
3.05
f1 (ppm)


145.22
143.61
134.19
133.86
133.53
133.21
132.71
128.07
127.53
127.42
127.35
125.81
125.77
125.73
125.69
124.64
121.93
119.21
77.32
77.00
76.68
69.99
62.97
59.59
36.80
28.19
28.03
27.47
O
S
O
N
Me
CF3
Cl
18
f1 (ppm)



18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10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
−55
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−95
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−105
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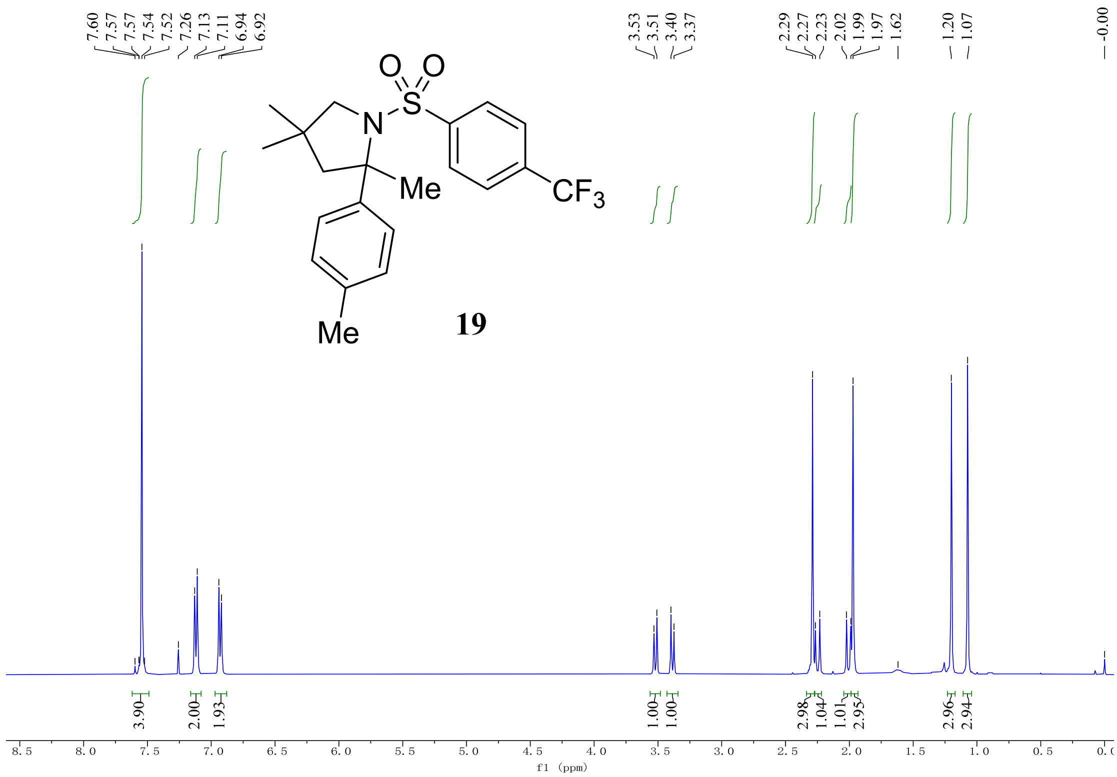
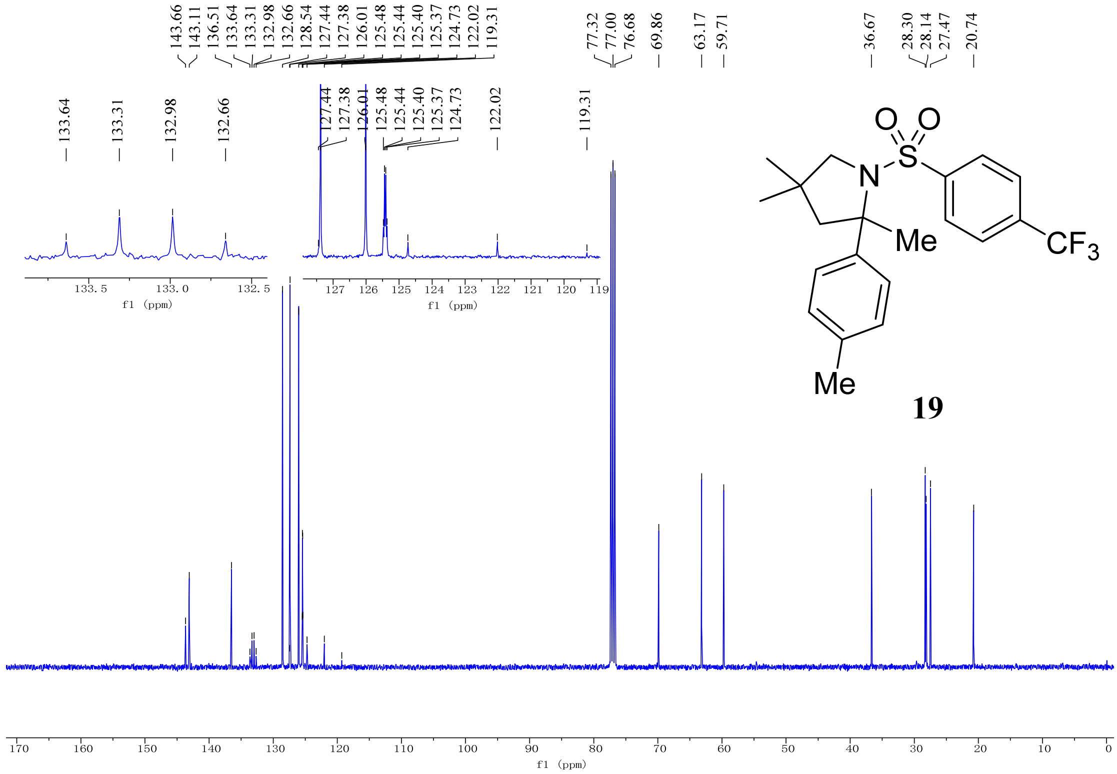
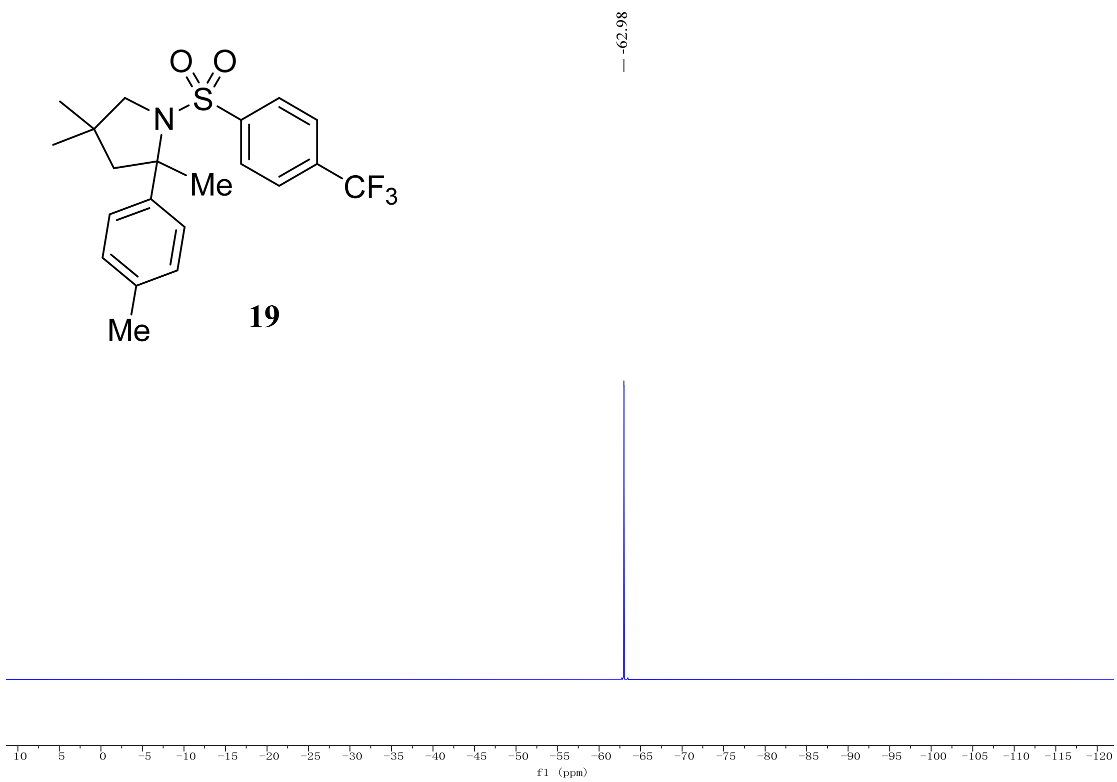
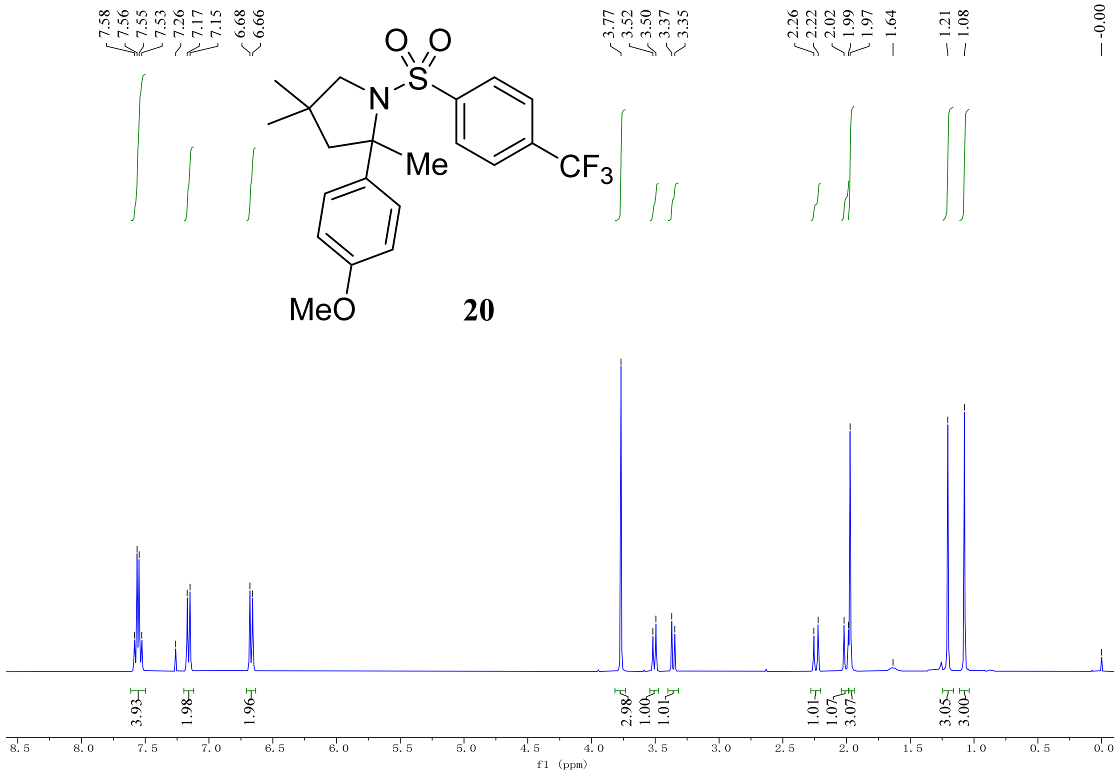
−115
−120
f1 (ppm)

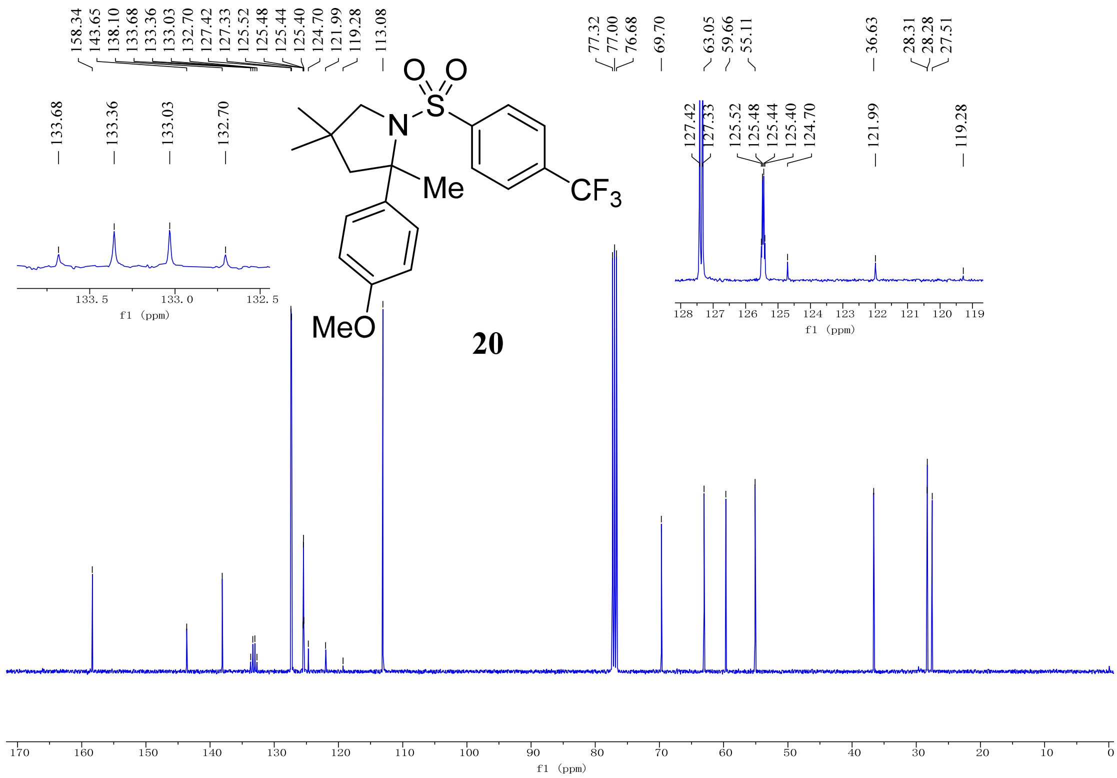


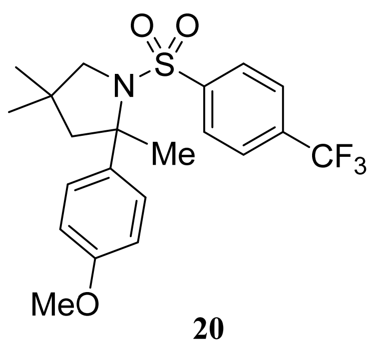




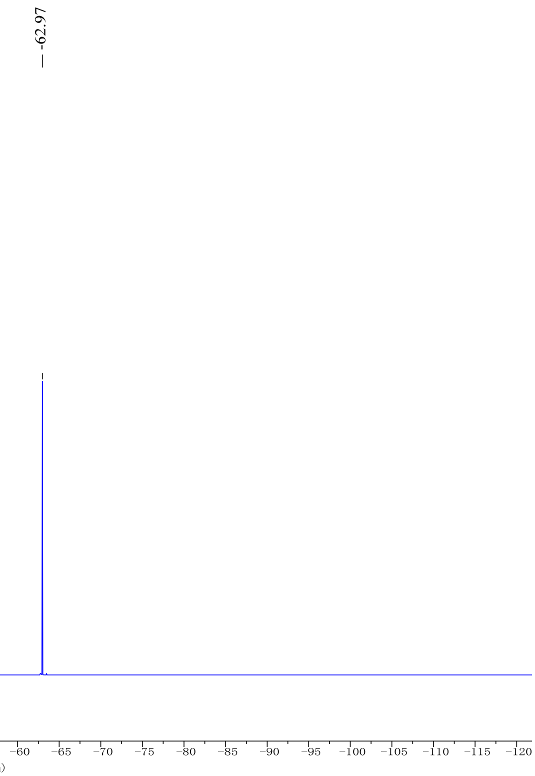
19







20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10
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0
−5
−10
−15
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−30
−35
−40
−45
−50
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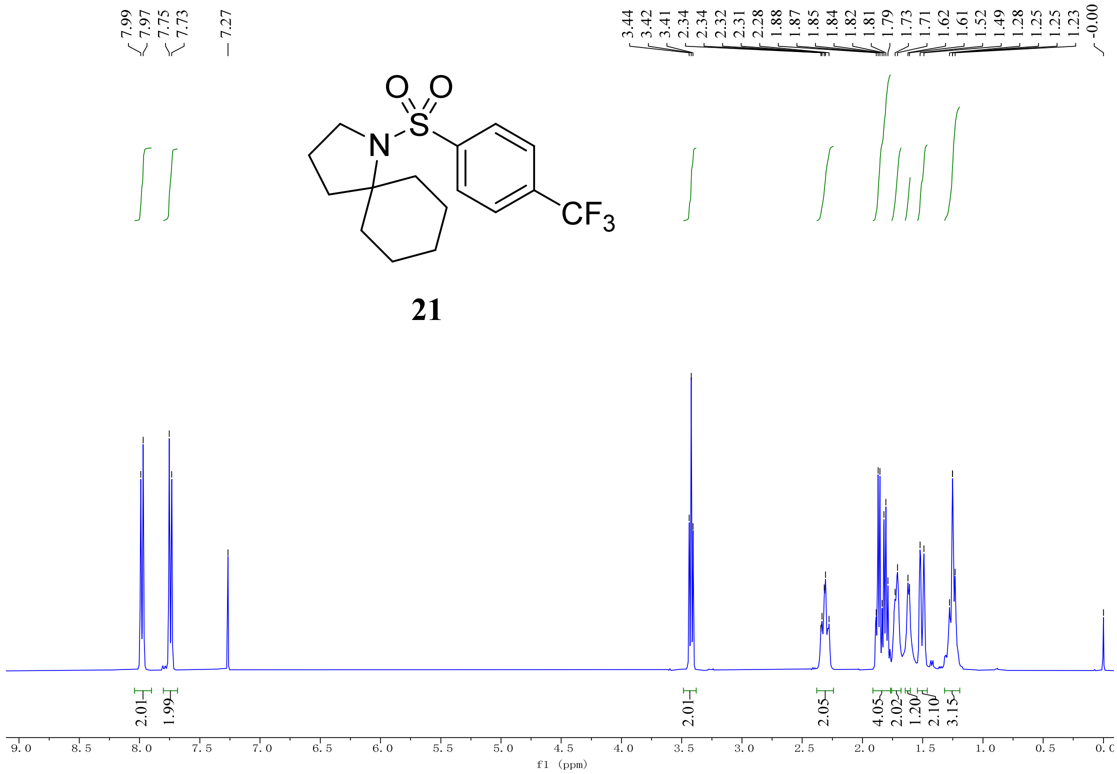
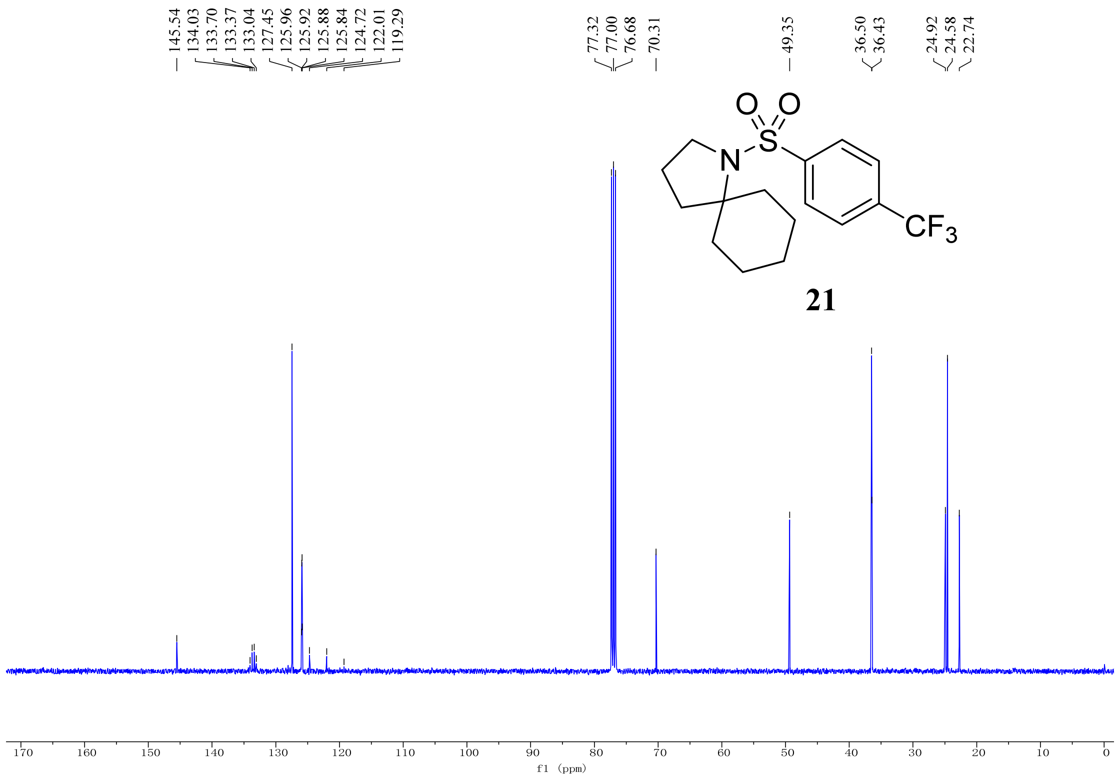
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−120
f1 (ppm)


7.99
7.97
7.75
7.73
7.27
3.44
3.42
3.41
2.34
2.34
2.32
2.31
2.28
1.88
1.87
1.85
1.84
1.82
1.81
1.79
1.73
1.71
1.62
1.61
1.52
1.49
1.28
1.25
1.25
1.23
-0.00
O
O
S
N
CF_3
21
2.01
1.99
2.01
2.05
4.05
2.02
1.20
2.10
3.15
f1 (ppm)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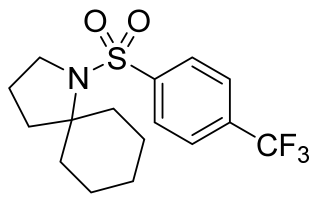
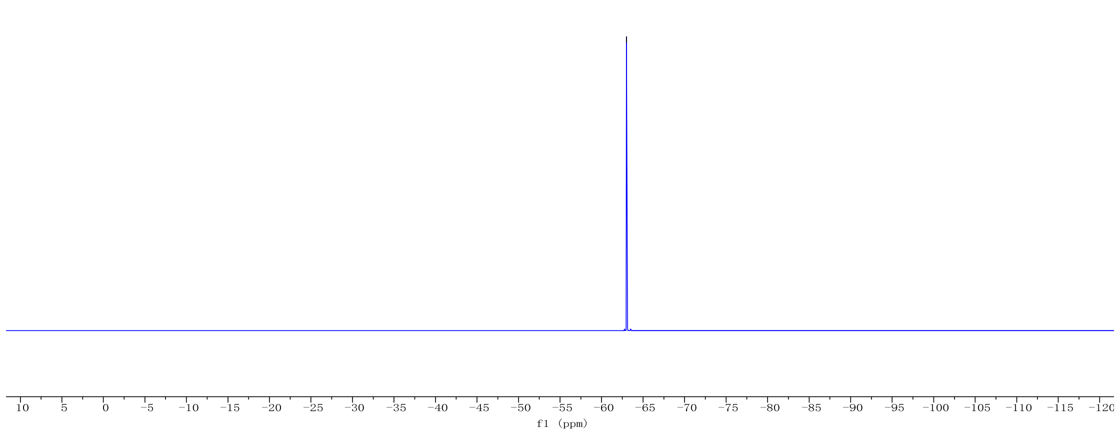
133.37
133.04
127.45
125.96
125.92
125.88
125.84
124.72
122.01
119.29
77.32
77.00
76.68
70.31
49.35
36.50
36.43
24.92
24.58
22.74
O
O
S
N
CF_3
21
f1 (ppm)


O
O
S
N
CF3

21


-63.00
10
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0
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-10
-15
-20
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-30
-35
-40
-45
-50
-55
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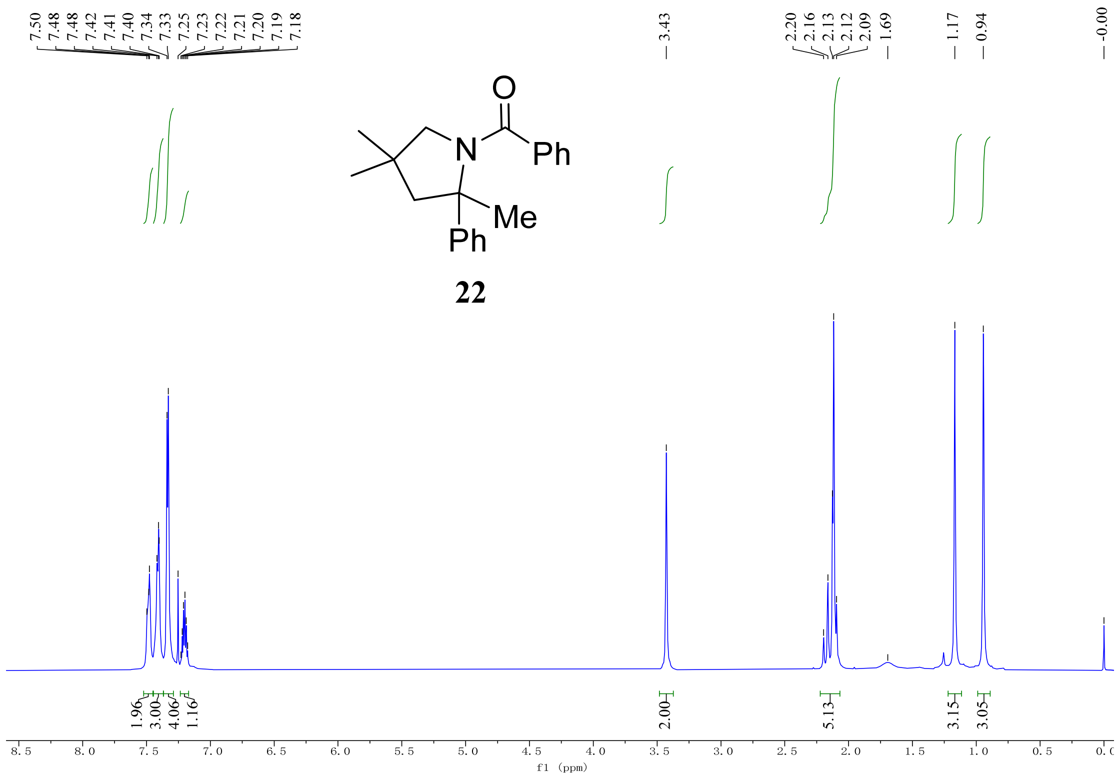
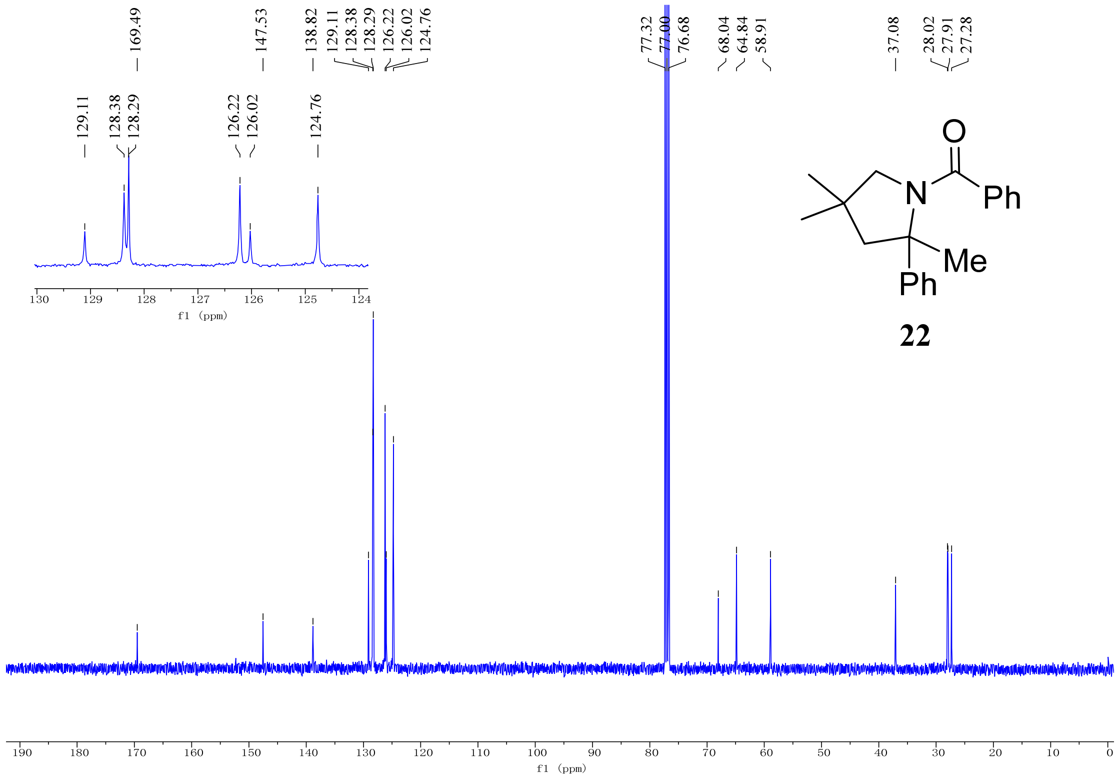
-115
-120
f1 (ppm)

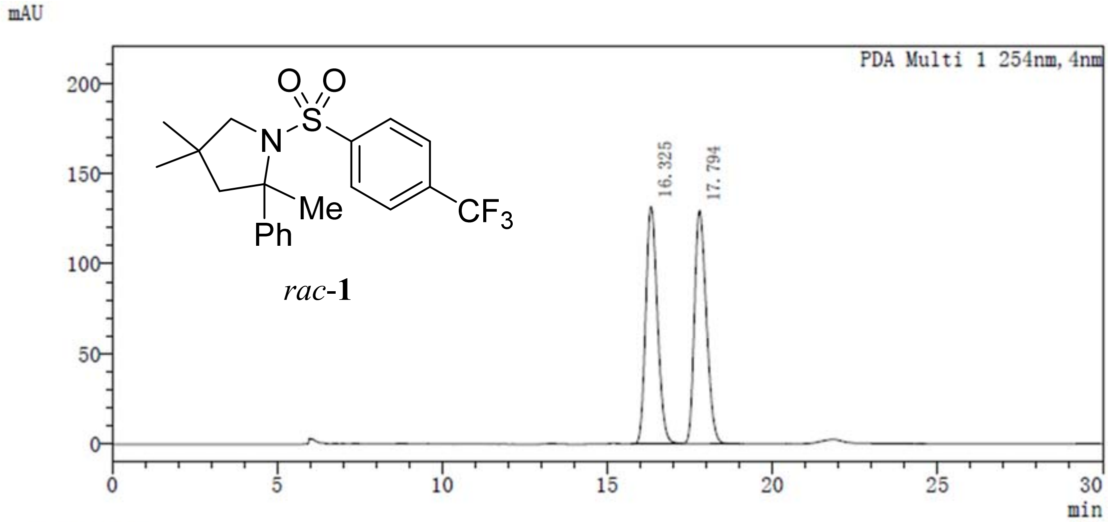


7.50 7.48 7.48 7.42 7.41 7.40 7.34 7.33 7.25 7.23 7.22 7.21 7.20 7.19 7.18
3.43
2.20 2.16 2.13 2.12 2.09
1.69
1.17
0.94
-0.00
O
N
Ph
Me
Ph
22
1.96 3.00 4.06 1.16
2.00
5.13
3.15
3.05
f1 (ppm)



169.49
147.53
138.82 129.11 128.38 128.29 126.22 126.02 124.76
77.32 77.00 76.68
68.04 64.84 58.91
37.08
28.02 27.91 27.28
129.11 128.38 128.29 126.22 126.02 124.76
f1 (ppm)
O
N
Ph
Me
Ph
22
f1 (ppm)

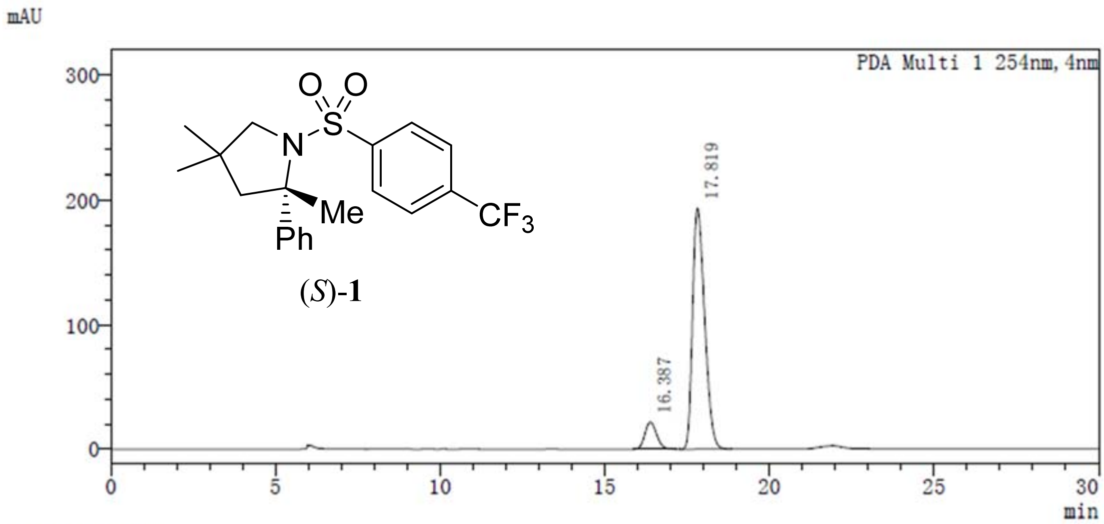
HPLC spectra



Peak Table

PDA Ch1 254nm

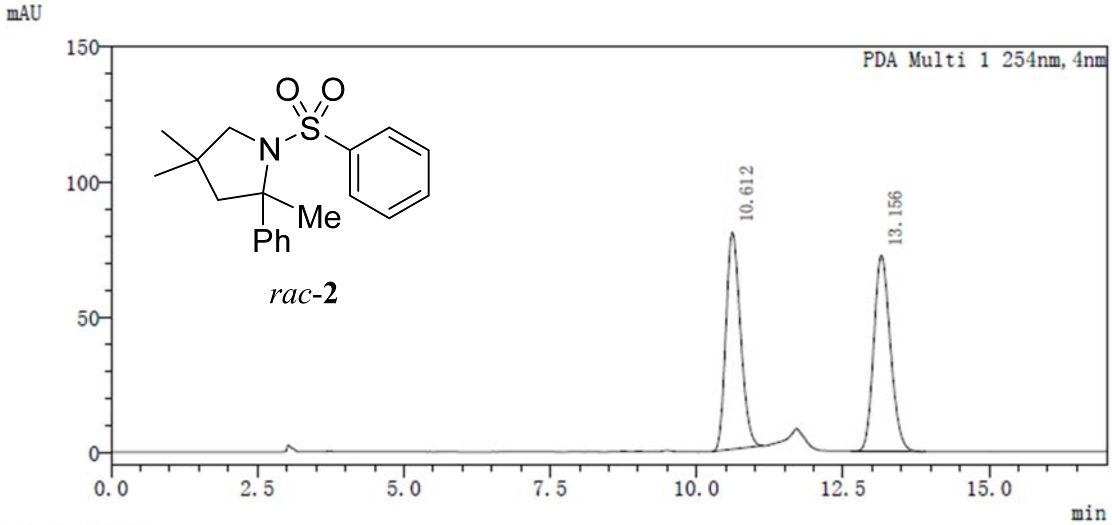
Peak#	Ret. Time	Area	Area%
1	16.325	3252383	50.031
2	17.794	3248294	49.969



Peak Table

PDA Ch1 254nm

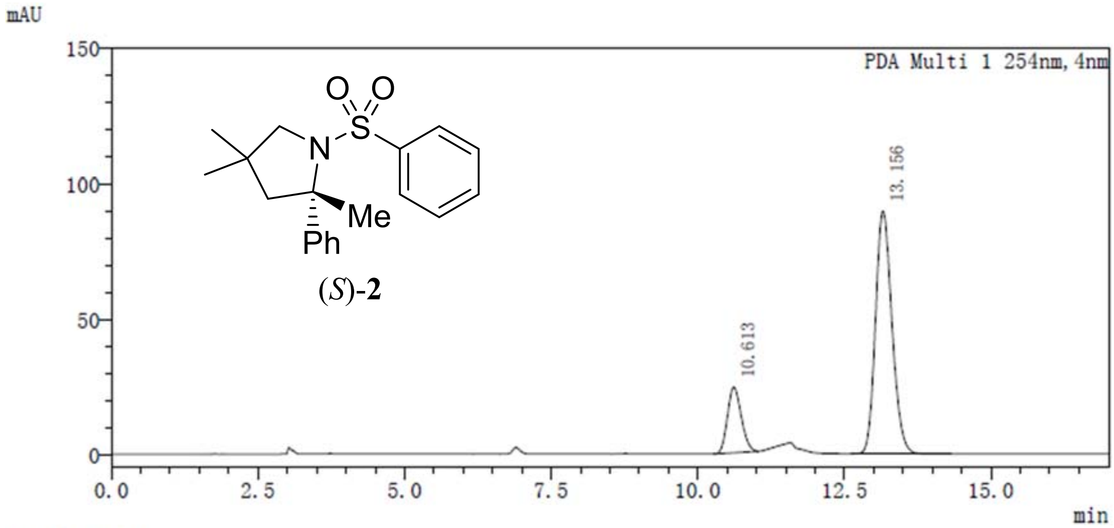
Peak#	Ret. Time	Area	Area%
1	16.387	536578	9.812
2	17.819	4931768	90.188



Peak Table

PDA Ch1 254nm

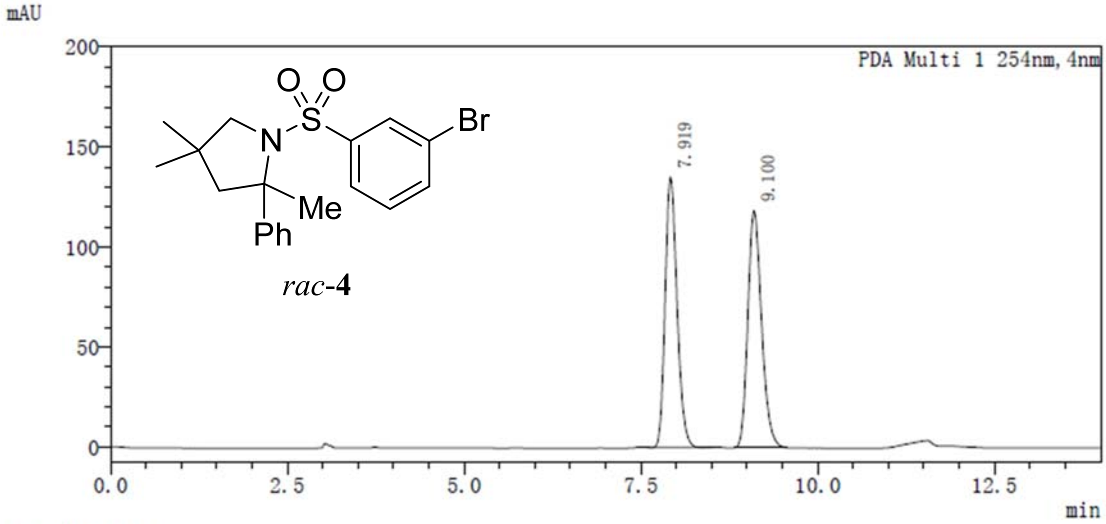
Peak#	Ret. Time	Area	Area%
1	10.612	1396205	49.260
2	13.156	1438130	50.740



Peak Table

PDA Ch1 254nm

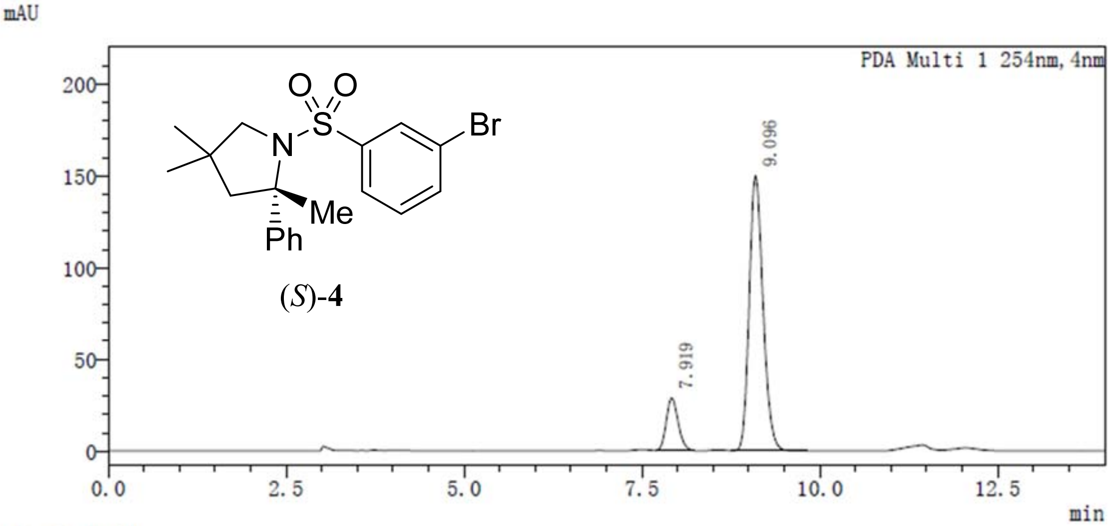
Peak#	Ret. Time	Area	Area%
1	10.613	398771	18.496
2	13.156	1757238	81.504



Peak Table

PDA Ch1 254nm

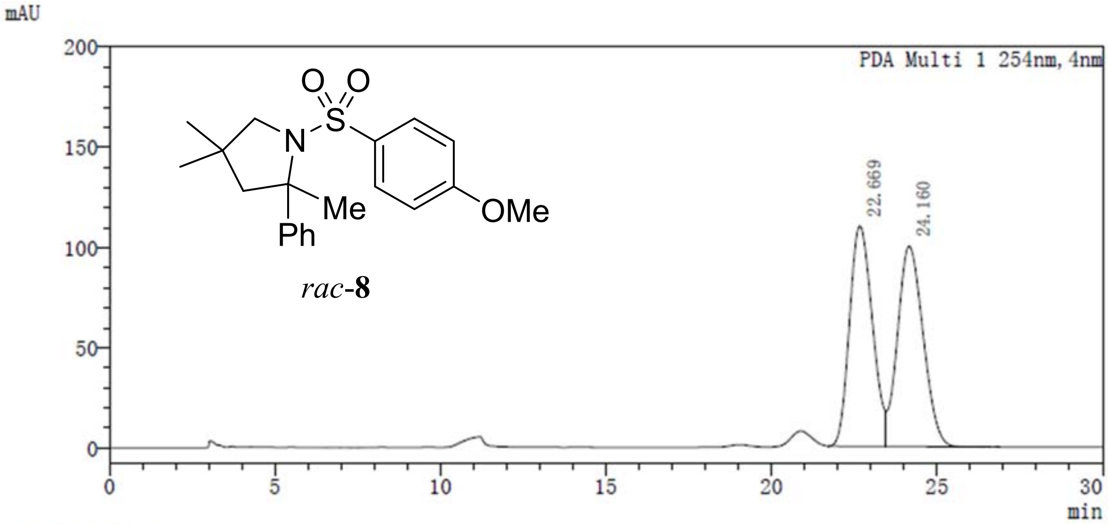
Peak#	Ret. Time	Area	Area%
1	7.919	1581918	49.597
2	9.100	1607614	50.403



Peak Table

PDA Ch1 254nm

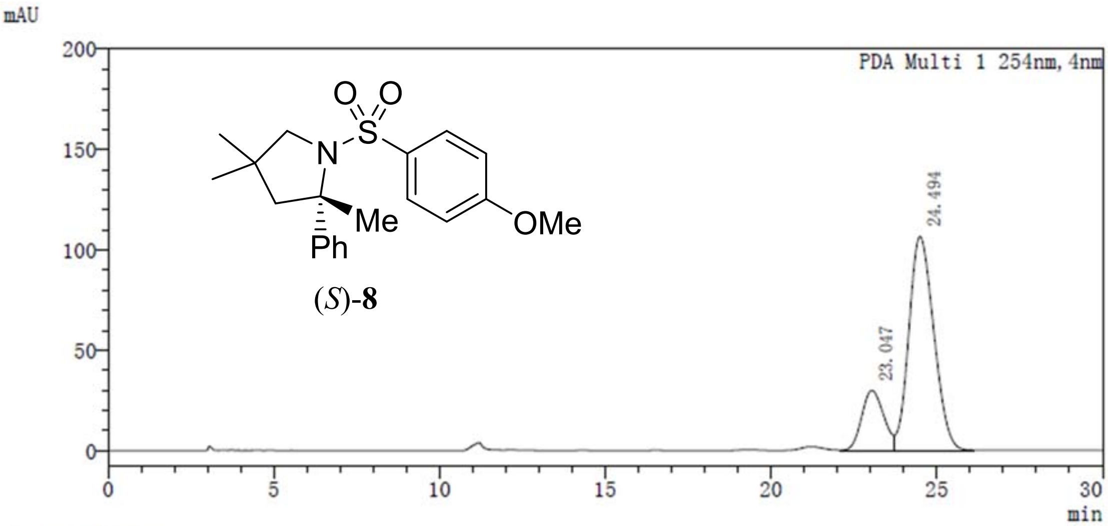
Peak#	Ret. Time	Area	Area%
1	7.919	330289	14.066
2	9.096	2017851	85.934



Peak Table

PDA Ch1 254nm

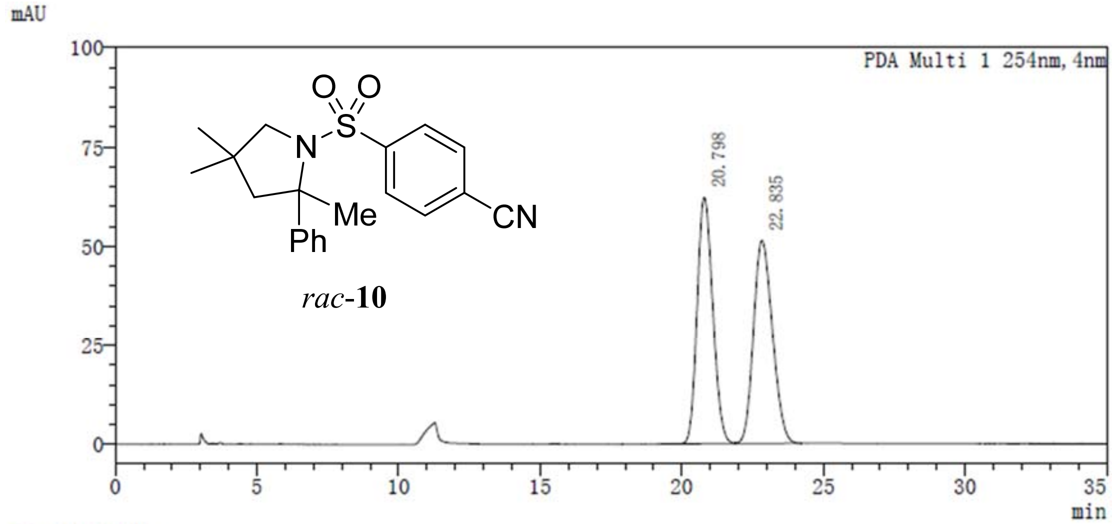
Peak#	Ret. Time	Area	Area%
1	22.669	5294007	49.586
2	24.160	5382382	50.414



Peak Table

PDA Ch1 254nm

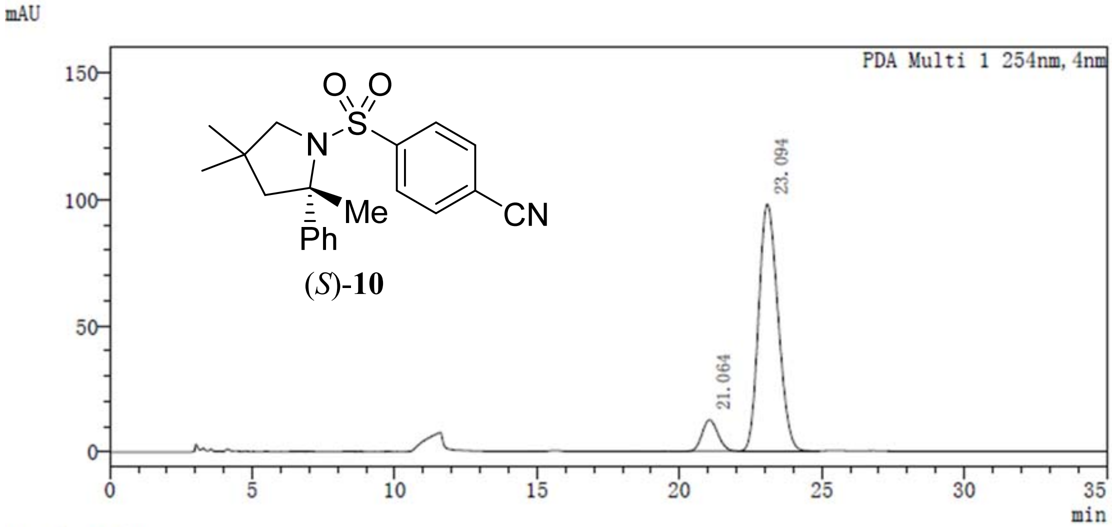
Peak#	Ret. Time	Area	Area%
1	23.047	1368286	19.722
2	24.494	5569719	80.278



Peak Table

PDA Ch1 254nm

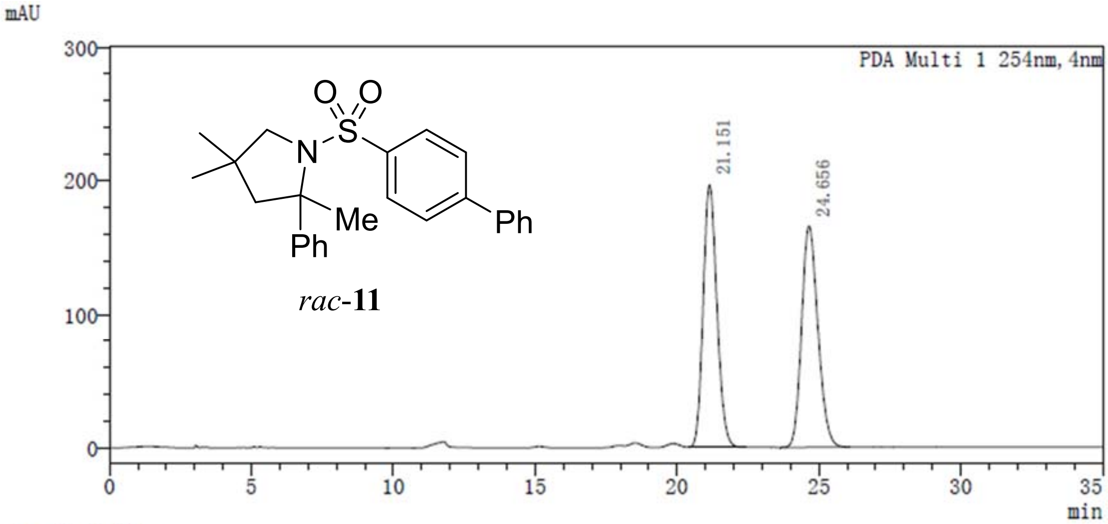
Peak#	Ret. Time	Area	Area%
1	20.798	2386907	49.979
2	22.835	2388928	50.021



Peak Table

PDA Ch1 254nm

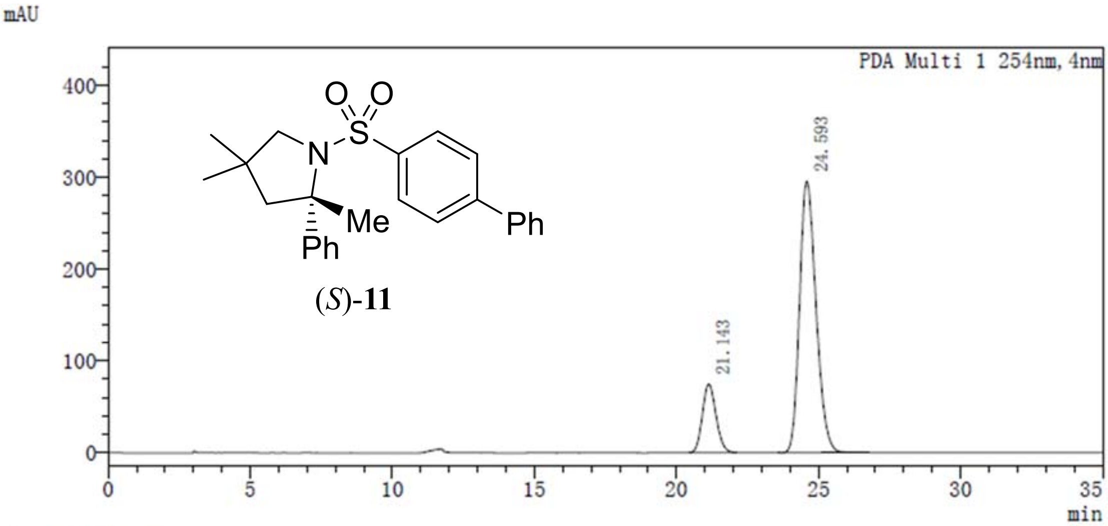
Peak#	Ret. Time	Area	Area%
1	21.064	476283	9.357
2	23.094	4614059	90.643



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	21.151	6609430	49.939
2	24.656	6625449	50.061



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	21.143	2488989	17.297
2	24.593	11900847	82.703

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