Supporting Information

Highly Enantioselective Synthesis of Trifluoromethyl Cyclopropanes by Using Ru(II)–Pheox Catalyst

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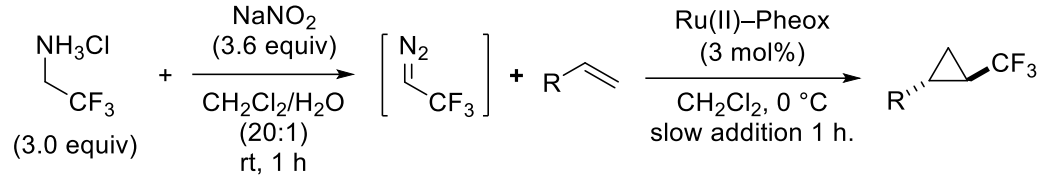
CONTENTS:

General methods: All reactions were carried out in glassware and stirred via magnetic stir-plates. Thin-layer chromatography analyses were performed using Merck pre-coated silica gel plates with 254 indicator. Visualization was accomplished by UV light (254 nm), potassium permanganate, phosphomolybdic acid, or anisaldehyde. Flash column chromatography was performed using silica gel 60 (mesh 40-100) supplied by Kanto Chemical Co., Inc. ^{1}H and ^{13}CNMR spectra were recorded on a JEOL JNM-ECS400 (400 MHz ^{1}H, 100 MHz ^{13}C, 376 MHz ^{19}F) or a JEOL JNM-ECX500 (500 MHz ^{1}H, 126 MHz ^{13}C, 470 MHz ^{19}F). Chemical shift values (δ) are reported in ppm (tetramethylsilane δ 0.00 ppm for ^{1}H; residual chloroform δ 77.0 ppm for ^{13}C, hexafluorobenzene δ −162.2 ppm). Optical rotations were measured on a JASCO P-1030 digital polarimeter. DART mass (positive mode) analyses were performed using a JEOL the Accu TOF TLC JMS-T100TD. Analytical HPLC was performed on a JASCO PU1586 with a UV-1575 UV/Vis detector using a chiral column.

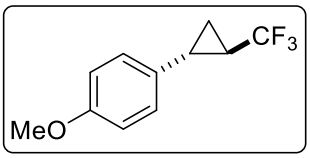
1. General procedure for catalytic asymmetric cyclopropanation of olefins with trifluorodiazoethane.



$NaNO_2$ (49.7 mg, 0.72 mmol) was added to solution of $CF_3CH_2NH_2$·HCl (81.3 mg, 0.6 mmol) in CH_2Cl_2 (2 mL) and H_2O (0.1 mL). The mixture was stirred under air condition at rt for 1 h. The solution of trifluorodiazoethane in CH_2Cl_2 (2.0 mL) was slowly added using a syringe pump over 1 h to a mixture of Ru(II)–Pheox catalyst (3.8 mg, 0.006 mmol) and olefins (0.2 mmol) in CH_2C1_2 (1.0 mL) at 0 ℃. After the addition completed, the reaction mixture was thenstirred under air condition at 0 ℃. The progress of the reaction was monitored by TLC. Upon completion, solvent was removed and the residue was purified by column chromatography to give desired product. The *trans*/*cis* ratio was determined from the crude ^{19}F NMR spectra, and the ee value was determined by chiral HPLC analysis.

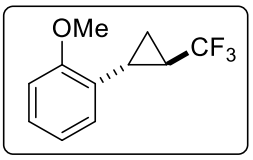
2. Analytical data of asymmetric cyclopropanation reaction products.

1-methoxy-4-((1R,2R)-2-(trifluoromethyl)cyclopropyl)benzene (6a)



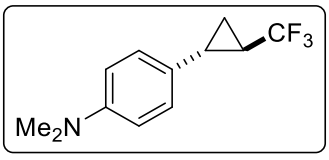
This compound was prepared according to the general procedure for asymmetric cyclopropanation between *p*-OMe-styrene (26.8 mg, 0.2 mmol) and in situ generated CF_3CHN_2. The resulting mixture was purified by silica gel column chromatography with Hexane as an eluent to give1-methoxy-4-((1R,2R)-2-(trifluoromethyl)cyclopropyl)benzene **6a** (96% yield, 41.5 mg, 0.19 mmol), 96% *trans* ee, 88% *cis* ee. ^{1}H NMR (500 MHz, $CDCl_3$) (*trans* isomer): δ 7.07-7.02 (m, 2H), 6.86-6.80 (m, 2H), 3.79 (s, 3H), 2.32 (ddd, *J* = 5.07, 5.07, 9.75 Hz, 1H), 1.77-1.67 (m, 1H), 1.32 (ddd, *J* = 5.54, 5.54, 9.56 Hz, 1H), 1.14-1.07 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) (*trans* isomer): δ 158.5, 130.9, 127.7, 126.0 (q, *J* = 270.87 Hz), 114.0, 55.3, 22.6 (q, *J* = 36.49 Hz), 18.9, 10.4; ^{19}F NMR (470 MHz, $CDCl_3$) (*trans* isomer): δ –67.1, ^{19}F NMR (470 MHz, $CDCl_3$) (*cis* isomer): δ –61.5 (d, *J* = 7.95 Hz); $[\alpha]^{24}_D$ = –45.1 (c = 1.0); For $C_{11}H_{11}F_3O$ [M] Calcd: 216.07620, Found: 216.07626; The enantiomeric ratio of **6a** (*trans* isomer) was determined by HPLC (Hexane 100%, 1.0 mL/min) using a CHIRALCEL OD column (0.46 cm x 25 cm): major isomer 16.4 min and minor isomer 13.0 min. The enantiomeric ratio of **6a** (*cis* isomer) was determined by HPLC (Hexane = 100%, 1.0 mL/min) using a CHIRALCEL OD column (0.46 cm x 25 cm): major isomer 24.7 min and minor isomer 38.8 min.

1-methoxy-2-((1R,2R)-2-(trifluoromethyl)cyclopropyl)benzene (6b)



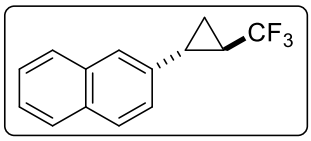
This compound was prepared according to the general procedure for asymmetric cyclopropanation between *o*-OMe-styrene (26.8 mg, 0.2 mmol) and in situ generated CF_3CHN_2. The resulting mixture was purified by silica gel column chromatography with Hexane as an eluent to give1-methoxy-2-((1R,2R)-2-(trifluoromethyl)cyclopropyl)benzene **6b** (99% yield, 42.7 mg, 0.20 mmol), 96% *trans* ee, 91% *cis* ee. ^{1}H NMR (400 MHz, $CDCl_3$) (*trans* isomer): δ 7.21 (ddd, *J* = 1.62, 7.78, 7.78 Hz, 1H), 6.95-6.83 (m, 3H), 3.85 (s, 3H), 2.51 (ddd, *J* = 5.42, 5.42, 9.46 Hz, 1H), 1.82-1.72 (m, 1H), 1.31 (ddd, *J* = 5.04, 5.04, 9.77 Hz, 1H), 1.13 (ddd, *J* = 6.18, 6.18, 8.54 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (*trans* isomer): δ 158.4, 127.8, 127.2, 126.4, 126.2 (q, *J* = 270.20 Hz), 120.4, 110.4, 55.4, 21.5 (q, *J* = 36.74 Hz) 14.8, 9.6; ^{19}F NMR (376 MHz, $CDCl_3$) (*trans* isomer): δ –67.2, (d, *J* = 7.27 Hz), ^{19}F NMR (376 MHz, $CDCl_3$) (*cis* isomer): δ –62.4, (d, *J* = 7.27 Hz); $[\alpha]^{27}_D$ = –23.4 (c = 1.0); For $C_{11}H_{11}F_3O$ [M] Calcd: 216.07620, Found: 216.07621; The enantiomeric ratio of **6b** (*trans* isomer) was determined by HPLC (Hexane : EA = 50 : 1, 1.0 mL/min) using a CHIRALPAK IB column (0.46 cm x 25 cm): major isomer 5.1 min and minor isomer 4.9 min. The enantiomeric ratio of **6b** (*cis* isomer) was determined by HPLC (Hexane : EA = 50 : 1, 1.0 mL/min) using a CHIRALPAK IB column (0.46 cm x 25 cm): major isomer 6.3 min and minor isomer 7.0 min.

N,N-dimethyl-4-((1R,2R)-2-(trifluoromethyl)cyclopropyl)aniline (6c)



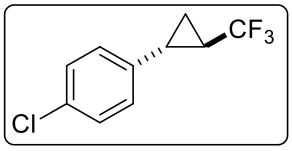
This compound was prepared according to the general procedure for asymmetric cyclopropanation between *p*-NMe_2-styrene (29.4 mg, 0.2 mmol) and in situ generated CF_3CHN_2. The resulting mixture was purified by silica gel column chromatography with Hexane/Et_2O as an eluent to give N,N-dimethyl-4-((1R,2R)-2-(trifluoromethyl)cyclopropyl)aniline **6c** (56% yield, 25.7 mg, 0.11 mmol), 96% *trans* ee, 91% *cis* ee. ^{1}H NMR (500 MHz, $CDCl_3$) (*trans* isomer): δ 7.05-6.97 (m, 2H), 6.71-6.64 (m, 2H), 2.91 (s, 6H), 2.28 (ddd, *J* = 5.07, 5.07, 9.65 Hz, 1H), 1.74-1.64 (m, 1H), 1.27 (ddd, *J* = 5.35, 5.35, 9.56 Hz, 1H), 1.12-1.04 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (*trans* and *cis* isomer): δ 149.6, 130.0, 127.4, 126.7, 126.2 (q, *J* = 270.61 Hz), 112.8, 112.2, 40.8, 40.5, 22.4 (q, *J* = 36.4 Hz), 18.8, 10.2; ^{19}F NMR (376 MHz, $CDCl_3$) (*trans* isomer): δ –67.0 (d, *J* = 6.32 Hz), ^{19}F NMR (376 MHz, $CDCl_3$) (*cis* isomer): δ –61.3 (d, *J* = 9.48 Hz); $[\alpha]^{24}_D$ = –45.8 (c = 1.0); For $C_{12}H_{14}F_3N$ $[M+H]^+$ Calcd: 230.11566, Found: 230.11567; The enantiomeric ratio of **6c** (*trans* isomer) was determined by HPLC (Hexane : IPA = 200 : 1, 1.0 mL/min) using a CHIRALCEL OJ-H column (0.46 cm x 25 cm): major isomer 21.3 min and minor isomer 23.3 min. The enantiomeric ratio of **6c** (*cis* isomer) was determined by HPLC (Hexane : IPA = 200 : 1, 1.0 mL/min) using a CHIRALCEL OJ-H column (0.46 cm x 25 cm): major isomer 46.4 min and minor isomer 33.1 min.

2-((1R,2R)-2-(trifluoromethyl)cyclopropyl)naphthalene (6d)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between 2-vinylnaphthalene (29.4 mg, 0.2 mmol) and in situ generated CF_3CHN_2. The resulting mixture was purified by silica gel column chromatography with Hexane/Et_2O as an eluent to give 2-((1R,2R)-2-(trifluoromethyl)cyclopropyl)naphthalene **6d** (80% yield, 37.7 mg, 0.16 mmol), 97% *trans* ee, 6% *cis* ee. ^{1}H NMR (500 MHz, $CDCl_3$) (*trans* isomer): δ 7.82-7.73 (m, 3H), 7.56 (s, 1H), 7.49-7.40 (m, 2H), 7.21 (dd, *J* = 1.72, 8.60 Hz, 1H), 2.52 (ddd, *J* = 5.06, 5.07, 9.46 Hz, 1H), 1.95-1.84 (m, 1H), 1.43 (ddd, *J* = 5.59, 5.59, 9.56 Hz, 1H), 1.31-1.23 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) (*trans* isomer): δ 136.4, 133.3, 132.4, 128.3, 127.6, 127.4, 126.4, 125.9 (q, *J* = 270.71 Hz) 125.7, 125.1, 124.8, 22.9 (q, *J* = 36.79 Hz), 19.8, 10.8; ^{19}F NMR (470 MHz, $CDCl_3$) (*trans* isomer): δ –67.1, ^{19}F NMR (470 MHz, $CDCl_3$) (*cis* isomer): δ –61.4 (d, *J* = 7.95 Hz); $[\alpha]^{25}_D$ = –53.0 (c = 1.0); For $C_{14}H_{11}F_3$ [M] Calcd: 236.08128, Found: 236.08127; The enantiomeric ratio of **6d** (*trans* isomer) was determined by HPLC (Hexane : IPA = 200 : 1, 1.0 mL/min) using a CHIRALCEL OD column (0.46 cm x 25 cm): major isomer 10.9 min and minor isomer 11.9 min. The enantiomeric ratio of **6d** (*cis* isomer) was determined by HPLC (Hexane : IPA = 200 : 1, 1.0 mL/min) using a CHIRALCEL OD column (0.46 cm x 25 cm): major isomer 16.8 min and minor isomer 17.8 min.

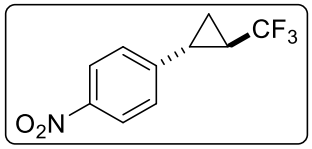
1-chloro-4-((1R,2R)-2-(trifluoromethyl)cyclopropyl)benzene (6e)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between *p*-Cl-styrene (27.7 mg, 0.2 mmol) and in situ generated CF_3CHN_2. The resulting mixture was purified by silica gel column chromatography with Hexane as an eluent to give 1-chloro-4-((1R,2R)-2-(trifluoromethyl)cyclopropyl)benzene **6e** (77% yield, 33.8 mg, 0.15 mmol), 96% *trans* ee, 38% *cis* ee. ^{1}H NMR (400 MHz, $CDCl_3$) (*trans* isomer): δ 7.30-7.22 (m, 2H), 7.09-7.02 (m, 2H), 2.33 (ddd, *J* =5.04, 5.04, 9.69 Hz, 1H), 1.83-1.70 (m, 1H), 1.38 (ddd, *J* = 5.57, 5.57, 9.46 Hz, 1H), 1.19-1.09 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (*trans* isomer): δ 137.5, 132.5, 128.7, 127.9, 125.7 (q, *J* = 270.93 Hz), 23.0 (q, *J* = 37.06 Hz), 19.0 (d, *J* = 1.92 Hz), 10.8 (d, *J* = 1.92 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) (*trans* isomer): δ –67.3, ^{19}F NMR (376 MHz, $CDCl_3$) (*cis* isomer): δ –61.6 (d, *J* = 7.27 Hz); $[\alpha]^{26}_D$ = –45.0 (c = 1.0); For $C_{10}H_8ClF_3$ [M] Calcd: 220.02666, Found: 220.02670; The enantiomeric ratio of **6e** (*trans* isomer) was determined by HPLC (Hexane 100%, 1.0 mL/min) using a CHIRALCEL OD column (0.46 cm x 25 cm): major isomer 7.54 min and minor isomer 6.80 min.

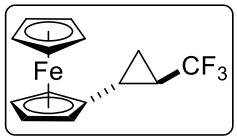
The enantiomeric ratio of **6e** (*cis* isomer) was determined by HPLC (Hexane 100%, 1.0 mL/min) using a CHIRALCEL OD column (0.46 cm x 25 cm): major isomer 21.7 min and minor isomer 24.1 min.

1-nitro-4-((1R,2R)-2-(trifluoromethyl)cyclopropyl)benzene (6f)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between *p*-NO_2-styrene (29.8 mg, 0.2 mmol) and in situ generated CF_3CHN_2. The resulting mixture was purified by silica gel column chromatography with Hexane/Et_2O as an eluent to give 1-nitro-4-((1R,2R)-2-(trifluoromethyl)cyclopropyl)benzene **6f** (48% yield, 22.3 mg, 0.10 mmol), 97% *trans* ee. ^{1}H NMR (500 MHz, $CDCl_3$) (*trans* isomer): δ 8.18-8.14 (m, 2H), 7.30-7.23 (m, 2H), 2.46 (ddd, *J* = 4.97, 4.97, 9.17 Hz, 1H), 1.97-1.87 (m, 1H), 1.53 (ddd, *J* = 5.92, 5.92, 9.17 Hz, 1H), 1.32-1.23 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) (*trans* isomer): δ 146.8, 146.7, 127.1, 125.3 (q, *J* = 270.71 Hz), 123.9, 23.9 (q, *J* = 37.19 Hz), 19.5 (d, *J* = 3.60 Hz), 11.8; ^{19}F NMR (470 MHz, $CDCl_3$) (*trans* isomer): δ –67.5; $[\alpha]^{27}_D$ = –50.0 (c = 1.0); For $C_{10}H_9F_3NO_2$ $[M+H]^+$ Calcd: 232.05854, Found: 232.05854; The enantiomeric ratio of **6f** (*trans* isomer) was determined by HPLC (Hexane : IPA = 50 : 1, 1.0 mL/min) using a CHIRALPAK AD-H column (0.46 cm x 25 cm): major isomer 6.86 min and minor isomer 7.33 min.

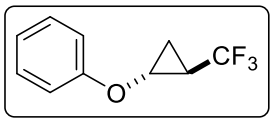
((1R,2R)-2-(Trifluoromethyl)cyclopropyl)ferrocene (6g)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between vinylferrocene (42.4 mg, 0.2 mmol) and in situ generated CF_3CHN_2. The resulting mixture was purified by silica gel column chromatography with Hexane as an eluent to give ((1R,2R)-2-(Trifluoromethyl)cyclopropyl)ferrocene **6g** (85% yield, 50.0 mg, 0.17 mmol), 92% *trans* ee, 75% *cis* ee. ^{1}H NMR (500 MHz, $CDCl_3$) (*trans* isomer): δ 4.16 (s, 5H), 4.09-4.04 (m, 3H), 3.98 (d, *J* = 1.53 Hz, 1H), 2.00 (ddd, *J* = 4.97, 4.97, 9.36 Hz, 1H), 1.73-1.62 (m, 1H), 1.24 (ddd, *J* = 5.26, 5.26, 9.56 Hz, 1H), 0.95-0.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (*trans* isomer): δ 126.0 (q, *J* = 270.29 Hz), 87.4, 68.6, 67.4, 67.4, 67.1, 66.0, 22.8 (q, *J* = 36.42 Hz), 15.0 (d, *J* = 2.88 Hz), 12.2 (d, *J* = 1.92 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) (*trans* isomer): δ –67.0, ^{19}F NMR (376 MHz, $CDCl_3$) (*cis* isomer): δ –61.1 (d, *J* = 6.32 Hz); $[\alpha]^{29}_D$ = +51.9 (c = 1.0); For $C_{14}H_{13}F_3Fe$ [M] Calcd: 294.03188, Found: 294.03186; The enantiomeric ratio of **6g** (*trans* isomer) was determined by HPLC (Hexane : EA = 20 : 1, 1.0 mL/min) using a CHIRALPAK IF-3 column (0.46 cm x 25 cm): major isomer 8.6 min and minor isomer 8.2 min. The enantiomeric ratio of **6g** (*cis* isomer) was determined by HPLC (Hexane : EA =

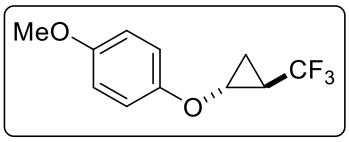
20 : 1, 1.0 mL/min) using a CHIRALPAK IF-3 column (0.46 cm x 25 cm): major isomer 9.1 min and minor isomer 10.0 min.

((1R,2R)-2-(trifluoromethyl)cyclopropoxy)benzene (6h)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between phenyl vinyl ether (48.1 mg, 0.4 mmol) and in situ generated CF_3CHN_2. The resulting mixture was purified by silica gel column chromatography with Hexane/Et_2O as an eluent to give ((1R,2R)-2-(trifluoromethyl)cyclopropoxy)benzene **6h** (76% yield, 61.4 mg, 0.30 mmol), 93% *trans* ee, 74% *cis* ee. ^{1}H NMR (500 MHz, $CDCl_3$) (*trans* isomer): δ 7.35-7.28 (m, 2H), 7.05-6.98 (m, 3H), 3.99 (ddd, *J* = 2.48, 4.01, 6.69 Hz, 1H), 1.93-1.83 (m, 1H), 1.37-1.25 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) (*trans* isomer): δ 157.7, 129.6, 125.1 (q, *J* = 271.71 Hz), 121.9, 114.7, 51.7 (d, *J* = 3.60 Hz), 21.1 (q, *J* = 36.79 Hz), 10.2; ^{19}F NMR (470 MHz, $CDCl_3$) (*trans* isomer): δ –65.9, ^{19}F NMR (470 MHz, $CDCl_3$) (*cis* isomer): δ –61.0; (*trans* isomer) $[\alpha]^{27}_D$ = +27.3 (c = 1.0); For $C_{10}H_9F_3O$ [M] Calcd: 202.06055, Found: 202.06055; The enantiomeric ratio of **6h** (*trans* isomer) was determined by HPLC (Hexane 100%, 1.0 mL/min) using a CHIRALCEL OJ-H column (0.46 cm x 25 cm): major isomer 6.7 min and minor isomer 8.2 min. The enantiomeric ratio of **6h** (*cis* isomer) was determined by HPLC (Hexane100%, 1.0 mL/min) using a CHIRALCEL OJ-H column (0.46 cm x 25 cm): major isomer 23.0 min and minor isomer 35.0 min.

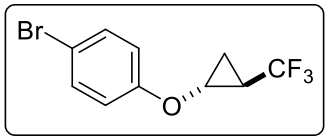
1-methoxy-4-((1R,2R)-2-(trifluoromethyl)cyclopropoxy)benzene (6i)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between *p*-methoxyphenyl vinyl ether (30.0 mg, 0.2 mmol) and in situ generated CF_3CHN_2. The resulting mixture was purified by silica gel column chromatography with Hexane/Et_2O as an eluent to give 1-methoxy-4-((1R,2R)-2-(trifluoromethyl)cyclopropoxy)benzene **6i** (88% yield, 40.7 mg, 0.18 mmol), 92% *trans* ee, 69% *cis* ee. ^{1}H NMR (400 MHz, $CDCl_3$) (*trans* isomer): δ 6.98-6.89 (m, 2H), 6.88-6.81 (m, 2H), 3.93 (ddd, *J* = 2.75, 3.81, 6.71 Hz, 1H), 3.77 (s, 3H), 1.92-1.77 (m, 1H), 1.35-1.20 (m, 2H), ^{1}H NMR (400 MHz, $CDCl_3$) (*cis* isomer): δ 7.00-6.93 (m, 2H), 6.88-6.81 (m, 2H), 3.95-3.87 (m, 1H), 3.78 (s, 3H), 1.82-1.68 (m, 1H), 1.34 (ddd, *J* = 4.27, 4.27, 7.02 Hz, 1H), 1.30-1.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (*trans* isomer): δ 154.6, 151.7, 125,1 (q, *J* = 270.61 Hz), 115.6, 114.7, 55.7, 52.2 (d, *J* = 3.83 Hz), 21.1 (q, *J* = 36.74 Hz), 10.2 (d, *J* = 1.92 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) (*trans* isomer): δ –65.8 (d, *J* = 6.32 Hz), ^{19}F NMR (376 MHz, $CDCl_3$) (*cis* isomer): δ –61.0 (d, *J* = 6.32 Hz); (*trans* isomer) $[\alpha]^{28}_D$ = +25.0 (c = 1.0); (*trans* isomer) For $C_{11}H_{11}F_3O_2$ [M] Calcd: 232.07111, Found:

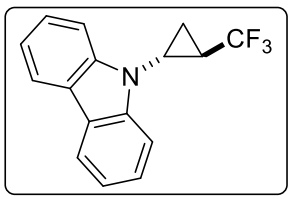
232.07115, (*cis* isomer) For $C_{11}H_{11}F_3O_2$ $[M+H]^+$ Calcd: 233.07894, Found: 233.07896; The enantiomeric ratio of **6i** (*trans* isomer) was determined by HPLC (Hexane : IPA = 200 : 1, 1.0 mL/min) using a CHIRALPAK IB column (0.46 cm x 25 cm): major isomer 4.1 min and minor isomer 4.4 min. The enantiomeric ratio of **6i** (*cis* isomer) was determined by HPLC (Hexane : IPA = 30 : 1, 1.0 mL/min) using a CHIRALCEL OD column (0.46 cm x 25 cm): major isomer 8.1 min and minor isomer 8.9 min.

1-bromo-4-((1R,2R)-2-(trifluoromethyl)cyclopropoxy)benzene (6j)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between *p*-bromophenyl vinyl ether (36.6 mg, 0.2 mmol) and in situ generated CF_3CHN_2. The resulting mixture was purified by silica gel column chromatography with Hexane/Et_2O as an eluent to give 1-bromo-4-((1R,2R)-2-(trifluoromethyl)cyclopropoxy)benzene **6j** (81% yield, 45.8 mg, 0.16 mmol), 92% *trans* ee, 69% *cis* ee. ^{1}H NMR (400 MHz, $CDCl_3$) (*trans* isomer): δ 7.44-7.36 (m, 2H), 6.93-6.85 (m, 2H), 3.95 (ddd, *J* = 2.52, 8.09, 6.64 Hz, 1H), 1.93-1.80 (m, 1H), 1.38-1.23 (m, 2H), ^{1}H NMR (400 MHz, $CDCl_3$) (*cis* isomer): δ 7.44-7.36 (m, 2H), 6.95-6.88 (m, 2H), 3.97-3.89 (m, 1H), 1.86-1.72 (m, 1H), 1.40-1.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (*trans* isomer): δ 156.8, 132.5, 124.9 (q, 270.29 Hz), 116.6, 114.3, 52.0 (d, *J* = 3.83 Hz), 21.1 (q, *J* = 37.06 Hz), 10.2 (d, *J* = 1.92 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) (*trans* isomer): δ –65.9 (d, *J* = 6.32 Hz), ^{19}F NMR (376 MHz, $CDCl_3$) (*cis* isomer): δ –61.1 (d, *J* = 9.48 Hz); (*trans* isomer) $[\alpha]^{27}_D$ = +18.9 (c = 1.0); (*trans* isomer) For $C_{10}H_8BrF_3O$ [M] Calcd: 279.97106, Found: 279.97106, (*cis* isomer) For $C_{10}H_8BrF_3O$ [M] Calcd: 279.97106, Found: 279.97113; The enantiomeric ratio of **6j** (*trans* isomer) was determined by HPLC (Hexane : IPA = 30 : 1, 1.0 mL/min) using a CHIRALCEL OD column (0.46 cm x 25 cm): major isomer 4.2 min and minor isomer 4.6 min. The enantiomeric ratio of **6j** (*cis* isomer) was determined by HPLC (Hexane : IPA = 30 : 1, 1.0 mL/min) using a CHIRALCEL OD column (0.46 cm x 25 cm): major isomer 7.0 min and minor isomer 8.0 min.

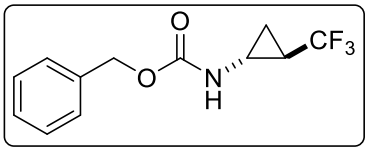
9-((1R,2R)-2-(trifluoromethyl)cyclopropyl)-9H-carbazole (6k)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between 9-vinylcarbazole (38.7 mg, 0.2 mmol) and in situ generated CF_3CHN_2. The resulting mixture was purified by silica gel column chromatography with Hexane/EA as an eluent to give 9-((1R,2R)-2-(trifluoromethyl)cyclopropyl)-9H-carbazole 6k (97% yield, 52.8 mg, 0.19 mmol), 97% *trans* ee, 83% *cis* ee. ^{1}H NMR (500 MHz, $CDCl_3$) (*trans* isomer): δ 8.04 (d, *J* = 7.64 Hz, 2H), 7.56 (d, *J* = 8.41 Hz, 2H), 7.46 (ddd, *J* = 1.15, 7.64, 7.64 Hz, 2H), 7.25 (ddd, *J*

= 0.76, 7.45, 7.45 Hz, 2H), 3.61 (ddd, *J* = 3.25, 4.40, 7.64 Hz, 1H), 2.25-2.15 (m, 1H), 1.74 (*J* = 6.63, 6.79, 6.79, 1H), 1.59 (ddd, *J* = 5.16, 5.16, 9.75 Hz, 1H), ^{1}H NMR (400 MHz, $CDCl_3$) (*cis* isomer): δ 8.06 (d, *J* = 7.63 Hz, 2H), 7.60 (d, *J* = 8.24 Hz, 2H), 7.46 (dd, *J* = 7.48, 7.48 Hz, 2H), 7.26 (dd, *J* = 7.32, 7.32 Hz 2H), 3.72-3.63 (m, 1H), 2.23-2.10 (m, 1H), 2.06 (ddd, *J* = 6.31, 6.31, 6.41 Hz, 1H), 1.89 (ddd, *J* = 7.32, 8.17, 8.17 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) (*trans* isomer): δ 140.6, 126.0, 125.3 (q, *J* = 271.11 Hz), 123.2, 120.4, 119.9, 109.5, 27.2 (d, *J* = 3.60 Hz), 21.9 (q, *J* = 36.39 Hz), 11.0; ^{19}F NMR (470 MHz, $CDCl_3$) (*trans* isomer): δ –66.2 (d, *J* = 7.95 Hz), ^{19}F NMR (376 MHz, $CDCl_3$) (*cis* isomer): δ –62.2 (d, *J* = 6.32 Hz); (*trans* isomer) $[\alpha]^{28}_D$ = –45.5 (c = 1.0), (*cis* isomer) $[\alpha]^{28}_D$ = –8.65 (c = 0.1); (*trans* isomer) For $C_{16}H_{12}F_3N$ $[M+H]^+$ Calcd: 276.10001, Found: 276.10001, (*cis* isomer) For $C_{16}H_{12}F_3N$ $[M+NH_4]^+$ Calcd: 293.12656, Found: 293.12660; The enantiomeric ratio of **6k** (*trans* isomer) was determined by HPLC (Hexane : IPA = 50 : 1, 1.0 mL/min) using a CHIRALPAK IB column (0.46 cm x 25 cm): major isomer 6.2 min and minor isomer 7.8 min. The enantiomeric ratio of **6k** (*cis* isomer) was determined by HPLC (Hexane : IPA = 50 : 1, 1.0 mL/min) using a CHIRALPAK IB column (0.46 cm x 25 cm): major isomer 10.8 min and minor isomer 13.5 min.

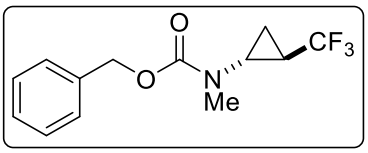
benzyl ((1R,2R)-2-(trifluoromethyl)cyclopropyl)carbamate (6l)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between benzyl N-vinylcarbamate (35.4 mg, 0.2 mmol) and in situ generated CF_3CHN_2. The resulting mixture was purified by silica gel column chromatography with Hexane/EA as an eluent to give 9-benzyl ((1R,2R)-2-(trifluoromethyl)cyclopropyl)carbamate **6l** (93% yield, 48.3 mg, 0.19 mmol), 92% *trans* ee, 55% *cis* ee. ^{1}H NMR (400 MHz, $CDCl_3$) (*trans* isomer): δ 7.40-7.27 (m, 5H), 5.21-5.0 (m, 3H), 3.0-2.86 (m, 1H), 1.69 (brs, 1H), 1.21 (ddd, *J* = 5.95, 5.95, 12.66 Hz, 1H), 1.12-0.97 (m, 1H), ^{1}H NMR (500 MHz, $CDCl_3$) (*cis* isomer): δ 7.41-7.29 (m, 5H), 5.13 (sbr, 2H), 4.97 (brs, 1H), 3.15-3.02 (m, 1H), 1.70 (ddd, *J* = 7.45, 7.45, 14.52 Hz, 1H), 1.28 (ddd, *J* = 7.64, 8.03, 8.03 Hz, 1H), 1.16 (ddd, *J* = 5.86, 5.86, 5.86 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (*trans* isomer): δ 156.4, 136.0, 128.5, 128.3, 128.2, 125.1 (q, *J* = 270.93 Hz), 67.1, 26.4, 21.8 (q, *J* = 37.38 Hz), 10.4, ^{13}C NMR (100 MHz, $CDCl_3$) (*cis* isomer): δ 156.6, 136.1, 128.5, 128.2, 128.1, 125.7 (q, *J* = 271.9 Hz), 67.1, 27.0, 19.0 (q, *J* = 35.46 Hz), 9.4; ^{19}F NMR (376 MHz, $CDCl_3$) (*trans* isomer): δ –66.8, ^{19}F NMR (376 MHz, $CDCl_3$) (*cis* isomer): δ –61.2 (d, *J* = 9.48 Hz); (*trans* isomer) $[\alpha]^{27}_D$ = –7.94 (c = 1.0), (*cis* isomer) $[\alpha]^{28}_D$ = –2.19 (c = 0.5); (*trans* isomer) For $C_{12}H_2F_3NO_2$ $[M+NH_4]^+$ Calcd: 277.11639, Found: 277.11648, (*cis* isomer) For $C_{12}H_{12}F_3NO_2$ $[M+H]^+$ Calcd: 260.08984, Found: 260.08985; The enantiomeric ratio of **6l** (*trans* isomer) was determined by HPLC (Hexane : IPA = 10 : 1, 1.0 mL/min) using a CHIRALPAK ID column (0.46 cm x 25 cm): major isomer 5.7 min and minor isomer 6.1 min. The enantiomeric ratio

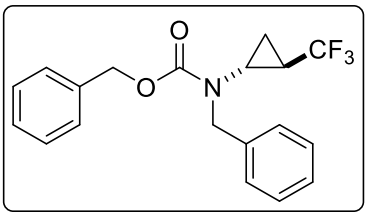
of **6l** (*cis* isomer) was determined by HPLC (Hexane : IPA = 10 : 1, 1.0 mL/min) using a CHIRALPAK ID column (0.46 cm x 25 cm): major isomer 8.7 min and minor isomer 8.0 min.

benzyl methyl((1R,2R)-2-(trifluoromethyl)cyclopropyl)carbamate (6m)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between benzylmethyl(vinyl)carbamate (38.2 mg, 0.2 mmol) and in situ generated CF_3CHN_2. The resulting mixture was purified by silica gel column chromatography with Hexane/EA as an eluent to give benzyl methyl((1R,2R)-2-(trifluoromethyl)cyclopropyl)carbamate **6m** (94% yield, 51.4 mg, 0.19 mmol), 97% *trans* ee, 75% *cis* ee. ^{1}H NMR (500 MHz, $CDCl_3$) (*trans* isomer): δ 7.41-7.27 (m, 5H), 5.15 (s, 2H), 2.93 (dd, *J* = 3.44, 4.59 Hz, 1H), 2.91 (s, 3H), 1.82-1.70 (m, 1H), 1.25 (*J* = 6.88, 6.88, 7.26 Hz, 1H), 1.17 (ddd, *J* = 4.97, 4.97, 9.17 Hz, 1H), ^{1}H NMR (400 MHz, $CDCl_3$) (*cis* isomer): δ 7.43-7.28 (m, 5H), 5.31-4.99 (m, 2H), 3.07-2.99 (m, 1H), 2.94 (s, 3H), 1.79-1.61 (m, 1H), 1.42-1.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (*trans* isomer): δ 156.8, 136.3, 128.4, 128.1, 128.1, 125.1 (q, *J* = 270.93 Hz), 67.4, 34.7, 33.2, 22.7 (q, *J* = 38.02 Hz), 11.5; ^{19}F NMR (470 MHz, $CDCl_3$) (*trans* isomer): δ –66.9, ^{19}F NMR (470 MHz, $CDCl_3$) (*cis* isomer): δ –62.4; (*trans* isomer) $[\alpha]^{27}_D$ = –15.5 (c = 1.0), (*cis* isomer) $[\alpha]^{28}_D$ = –16.6 (c = 0.5); (*trans* isomer) For $C_{13}H_{14}F_3NO$ $[M+H]^+$ Calcd: 274.10549, Found: 274.10541, (*cis* isomer) For $C_{13}H_{14}F_3NO$ $[M+H]^+$ Calcd: 274.10549, Found: 274.10542; The enantiomeric ratio of **6m** (*trans* isomer) was determined by HPLC (Hexane : IPA = 10 : 1, 1.0 mL/min) using a CHIRALPAK IE column (0.46 cm x 25 cm): major isomer 6.5 min and minor isomer 7.1 min. The enantiomeric ratio of **6m** (*cis* isomer) was determined by HPLC (Hexane : IPA = 15 : 1, 1.0 mL/min) using a CHIRALPAK IA column (0.46 cm x 25 cm): major isomer 8.9 min and minor isomer 8.3 min.

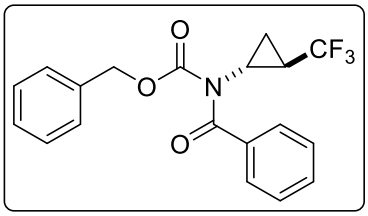
benzyl benzyl((1R,2R)-2-(trifluoromethyl)cyclopropyl)carbamate (6n)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between benzyl benzyl(vinyl)carbamate (53.5 mg, 0.2 mmol) and in situ generated CF_3CHN_2. The resulting mixture was purified by silica gel column chromatography with Hexane/EA as an eluent to give benzyl benzyl((1R,2R)-2-(trifluoromethyl)cyclopropyl)carbamate **6n** (92% yield, 64.2 mg, 0.18 mmol), 95% *trans* ee, 76% *cis* ee. ^{1}H NMR (400 MHz, $CDCl_3$) (*trans* isomer): δ 7.42-7.16 (m, 10H), 5.20 (s, 2H), 4.55 (d, *J* = 15.56 Hz, 1H), 4.41 (d, *J* = 15.26 Hz, 1H), 2.86 (ddd, *J* = 4.73, 4.73, 5.80 Hz, 1H), 1.86-1.69 (m, 1H), 1.24-1.12 (m, 1H), ^{1}H NMR (500 MHz, $CDCl_3$) (*cis* isomer): δ 7.44-7.12 (m. 10H), 5.27 (d, *J* = 9.17 Hz, 1H), 5.13 (d, *J* = 11.85 Hz, 1H), 4.83 (brs, 1H), 4.26 (brs, 1H), 2.89 (d, *J* = 4.59 Hz,

1H), 1.79-1.64 (m, 1H), 1.41-1.28 (m, 1H), 1.24-1.11 (m, 1H); ^{13}C NMR (100 MHz, DMSO) (*trans* isomer): δ 156.2, 137.6, 136.5, 128.5, 128.3, 127.9, 127.7, 127.2, 127.1, 125.5 (q, *J* = 270.93 Hz), 66.8, 50.4, 31.8, 21.8 (q, *J* = 36.74 Hz), 10.7; ^{19}F NMR (376 MHz, $CDCl_3$) (*trans* isomer): δ –66.7 (d, *J* = 6.32 Hz), ^{19}F NMR (376 MHz, $CDCl_3$) (*cis* isomer): δ –62.1; (*trans* isomer) $[\alpha]^{27}_D$ = –3.00 (c = 1.0); For $C_{19}H_{18}F_3NO_2$ $[M+H]^+$ Calcd: 350.13679, Found: 350.13681, (*cis* isomer) For $C_{19}H_{18}F_3NO_2$ $[M+NH_4]^+$ Calcd: 367.16334, Found: 367.16334; The enantiomeric ratio of **6n** (*trans* isomer) was determined by HPLC (Hexane : IPA = 30 : 1, 1.0 mL/min) using a CHIRALCEL OJ-H column (0.46 cm x 25 cm): major isomer 18.3 min and minor isomer 15.7 min. The enantiomeric ratio of **6n** (*cis* isomer) was determined by HPLC (Hexane : IPA = 20 : 1, 1.0 mL/min) using a CHIRALPAK IA column (0.46 cm x 25 cm): major isomer 22.4 min and minor isomer 14.0 min.

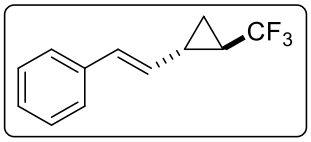
benzyl benzoyl((1R,2R)-2-(trifluoromethyl)cyclopropyl)carbamate (6o)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between benzyl benzoyl(vinyl)carbamate (56.2 mg, 0.2 mmol) and in situ generated CF_3CHN_2. The resulting mixture was purified by silica gel column chromatography with Hexane/EA as an eluent to give benzyl benzoyl((1R,2R)-2-(trifluoromethyl)cyclopropyl)carbamate **6o** (90% yield, 65.2 mg, 0.18 mmol), 91% *trans* ee, 70% *cis* ee. ^{1}H NMR (400 MHz, $CDCl_3$) (*trans* isomer): δ 7.53 (d, *J* = 7.02 Hz, 2H), 7.50 (t, *J* = 7.32 Hz, 1H), 7.36 (t, *J* = 7.78 Hz, 2H), 7.32-7.21 (m, 3H), 7.03 (dd, *J* = 1.23, 7.63 Hz, 2H), 5.06 (d, *J* = 2.14 Hz, 2H), 3.25 (ddd, *J* = 3.51, 4.43, 7.93 Hz, 1H), 2.05-1.92 (m, 1H) 1.48 (ddd, *J* =7.17, 7.17, 7.17 Hz, 1H), 1.19 (ddd, *J* = 4.58, 6.56, 10.07 Hz, 1H), ^{1}H NMR (400 MHz, $CDCl_3$) (*cis* isomer): δ 7.61 (dd, *J* = 0.92, 8.24 Hz, 2H), 7.52-7.45 (m, 1H), 7.36 (t, *J* = 7.63 Hz, 2H), 7.32-7.21 (m, 3H), 7.02 (dd, *J* = 1.53, 7.32 Hz, 2H), 5.10 (d, *J* = 12.21 Hz, 1H), 5.00 (d, *J* = 12.21 Hz, 1H), 3.28-3.19 (m, 1H), 2.01-1.87 (m, 1H), 1.63-1.54 (m,1H), 1.41 (ddd, *J* = 6.81, 6.81, 6.81 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (*trans* isomer): δ 173.1, 154.3, 135.7, 134.3, 132.4, 128.5, 128.4, 128.3, 128.3, 128.2, 125.0 (q, *J* = 271.57 Hz), 68.8, 31.0 (d, *J* = 3.83 Hz), 23.4 (q, *J* = 37.06 Hz), 11.8 (d, *J* = 1.92 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) (*trans* isomer): δ –67.1 (*J* = 6.32 Hz), ^{19}F NMR (376 MHz, $CDCl_3$) (*cis* isomer): δ –61.7 (d, *J* = 9.48 Hz); (*trans* isomer) $[\alpha]^{27}_D$ = –25.5 (c = 1.0); (*trans* isomer), (*cis* isomer) $[\alpha]^{28}_D$ = +30.7 (c = 0.1); For $C_{19}H_{16}F_3NO_3$ $[M+H]^+$ Calcd: 364.11605, Found: 364.11613, (*cis* isomer) For $C_{19}H_{16}F_3NO_3$ $[M+NH_4]^+$ Calcd: 381.14260, Found: 381.14255; The enantiomeric ratio of **6o** (*trans* isomer) was determined by HPLC (Hexane : IPA = 10 : 1, 1.0 mL/min) using a CHIRALPAK IE column (0.46 cm x 25 cm): major isomer 8.3 min and minor isomer 9.2 min. The enantiomeric ratio of **6o** (*cis* isomer) was determined by HPLC (Hexane : IPA = 20 : 1, 1.0 mL/min) using a CHIRALPAK IE column (0.46 cm x 25 cm): major isomer 19.1 min and minor isomer 14.6

min.

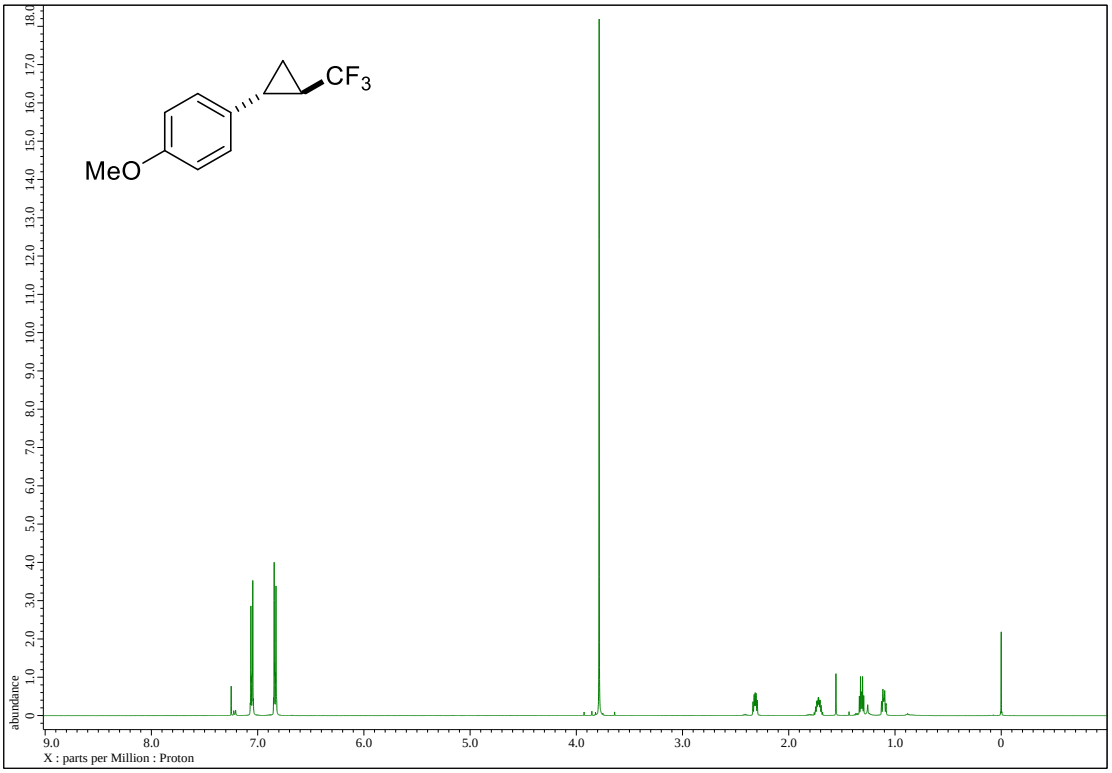
((E)-2-((1S,2R)-2-(trifluoromethyl)cyclopropyl)vinyl)benzene (6p)



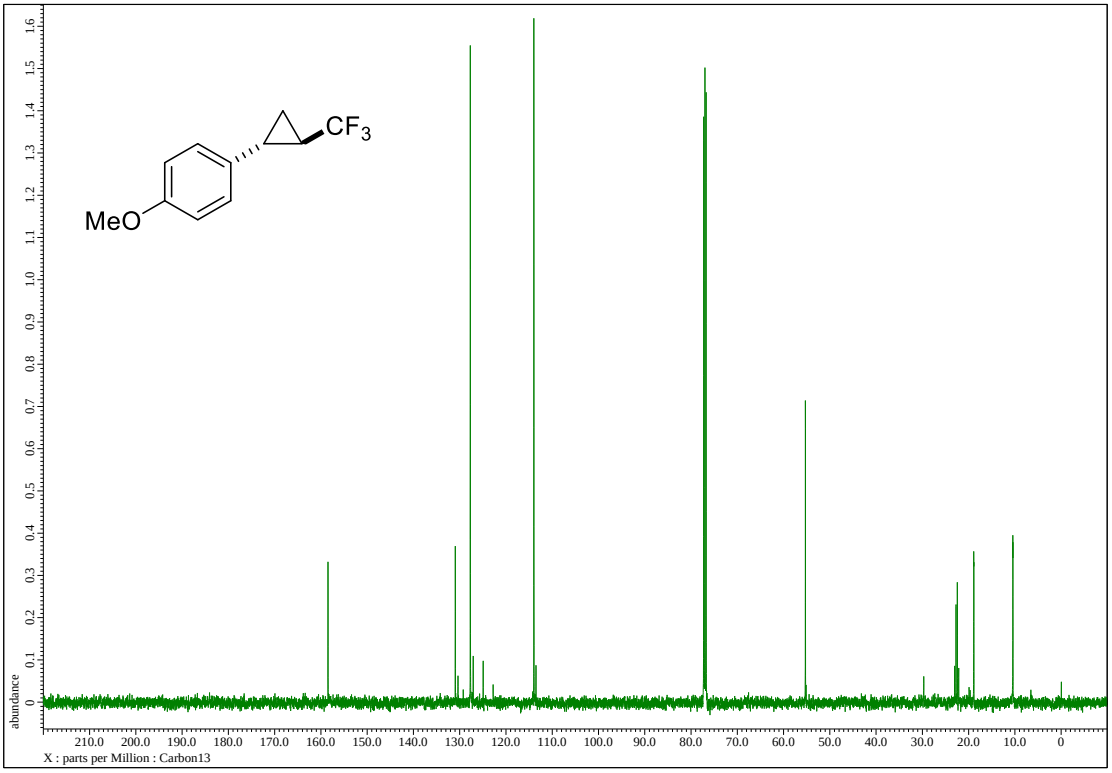
This compound was prepared according to the general procedure for asymmetric cyclopropanation between phenylbutadiene (26.0 mg, 0.2 mmol) and in situ generated CF_3CHN_2. The resulting mixture was purified by silica gel column chromatography with Hexane as an eluent to give ((E)-2-((1S,2R)-2-(trifluoromethyl)cyclopropyl)vinyl)benzene **6p** (89% yield, 37.8 mg, 0.18 mmol), 96% *trans* ee, 91% *cis* ee. ^{1}H NMR (400 MHz, $CDCl_3$) (*trans* isomer): δ 7.35-7.16 (m, 5H), 6.53 (d, *J* = 15.87 Hz, 1H), 5.75 (dd, *J* = 8.24, 15.87 Hz, 1H), 1.99 (dddd, *J* = 4.62, 4.62, 8.93, 9.46, 1H), 1.70-1.58 (m, 1H), 1.23 (ddd, *J* = 5.83, 5.83, 9.16 Hz, 1H), 1.00-0.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (*trans* and *cis* isomer): δ 136.7, 132.5, 130.7, 128.7, 128.6, 127.4, 126.0, 125.9; 125.9 (q, 271.25 Hz), 21.6, (q, *J* = 36.74 Hz), 18.4 (d, *J* = 2.88 Hz), 9.9; ^{19}F NMR (376 MHz, $CDCl_3$) (*trans* isomer): δ –67.1 (d, *J* = 7.27 Hz), ^{19}F NMR (376 MHz, $CDCl_3$) (*cis* isomer): δ –61.1 (d, *J* = 7.27 Hz); $[\alpha]^{29}_D$ = –48.1 (c = 1.0); For $C_{12}H_{11}F_3$ [M] Calcd: 212.08128, Found: 212.8122; The enantiomeric ratio of **6p** (*trans* isomer) was determined by HPLC (Hexane : IPA = 50 : 1, 1.0 mL/min) using a CHIRALPAK IB-3 column (0.46 cm x 25 cm): major isomer 6.3 min and minor isomer 7.4 min. The enantiomeric ratio of **6p** (*cis* isomer) was determined by HPLC (Hexane : EA = 50 : 1, 1.0 mL/min) using a CHIRALPAK IB-3 column (0.46 cm x 25 cm): major isomer 7.1 min and minor isomer 8.2 min.

4. NMR and HPLC spectral data.

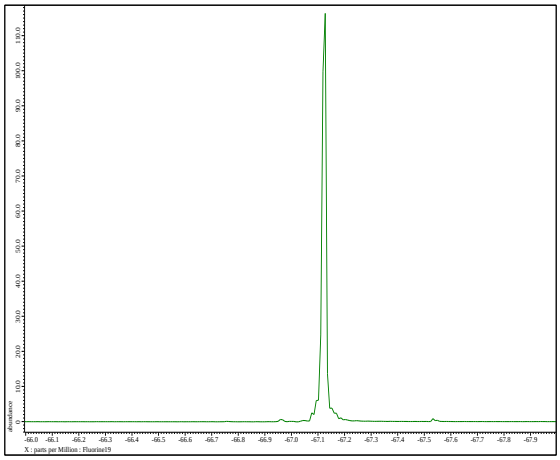
^{1}H NMR (**6a**)



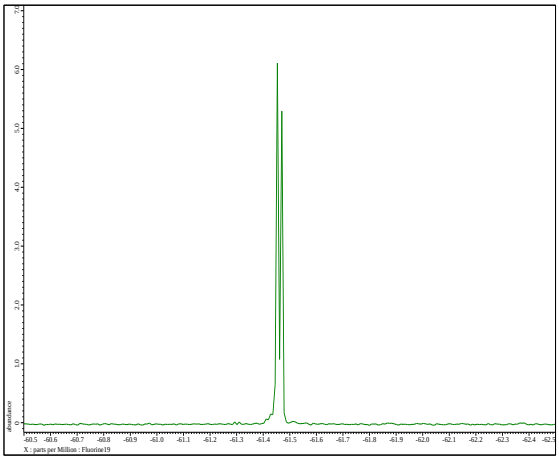
^{13}C NMR (**6a**)



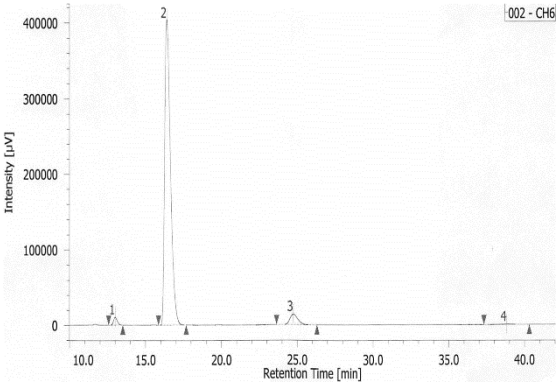
^{19}F NMR (*trans* isomer) (**6a**)



^{19}F NMR (*cis* isomer) (**6a**)

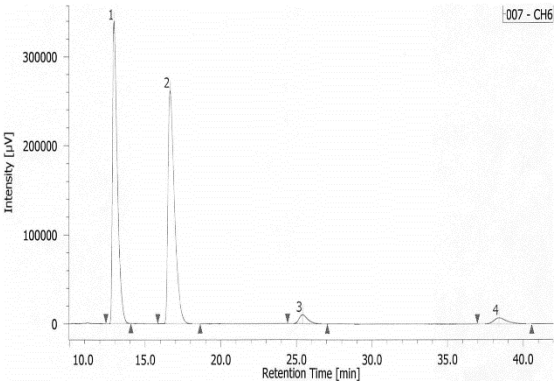


HPLC optically active (**6a**)



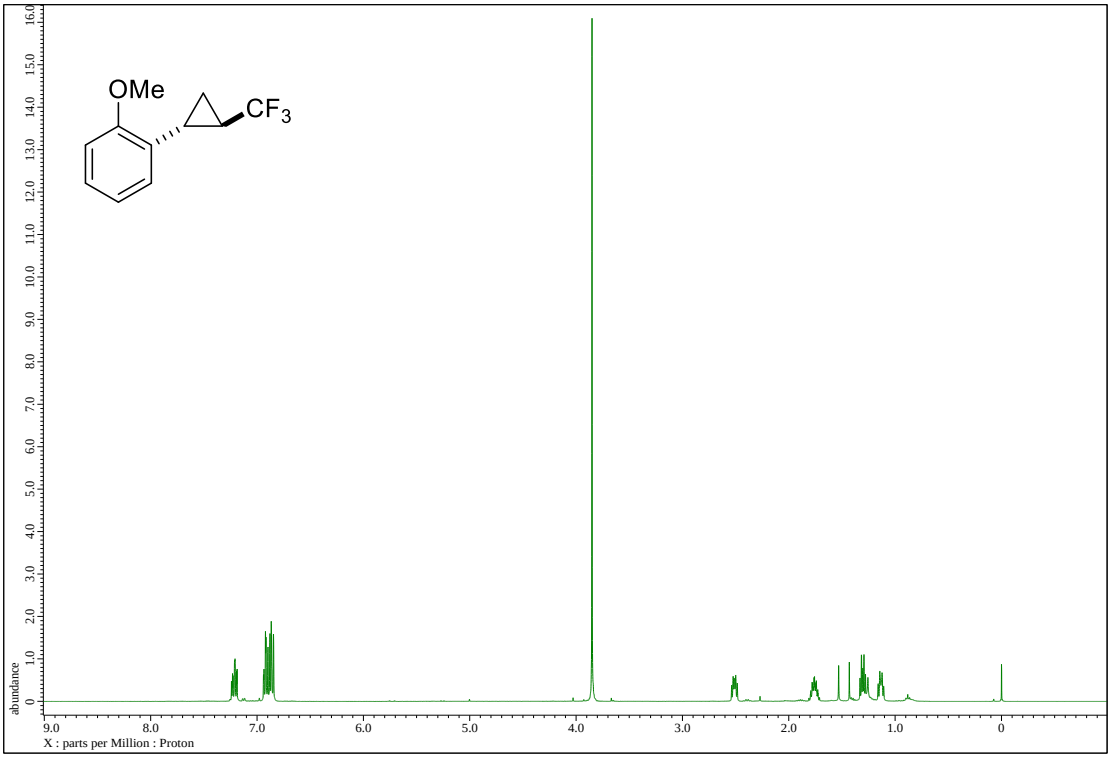
No.	tR [min]	Area	Area%
1	12.998	191484	1.677
2	16.390	10677527	93.536
3	24.732	513592	4.499
4	38.810	32757	0.287

HPLC racemic (**6a**)

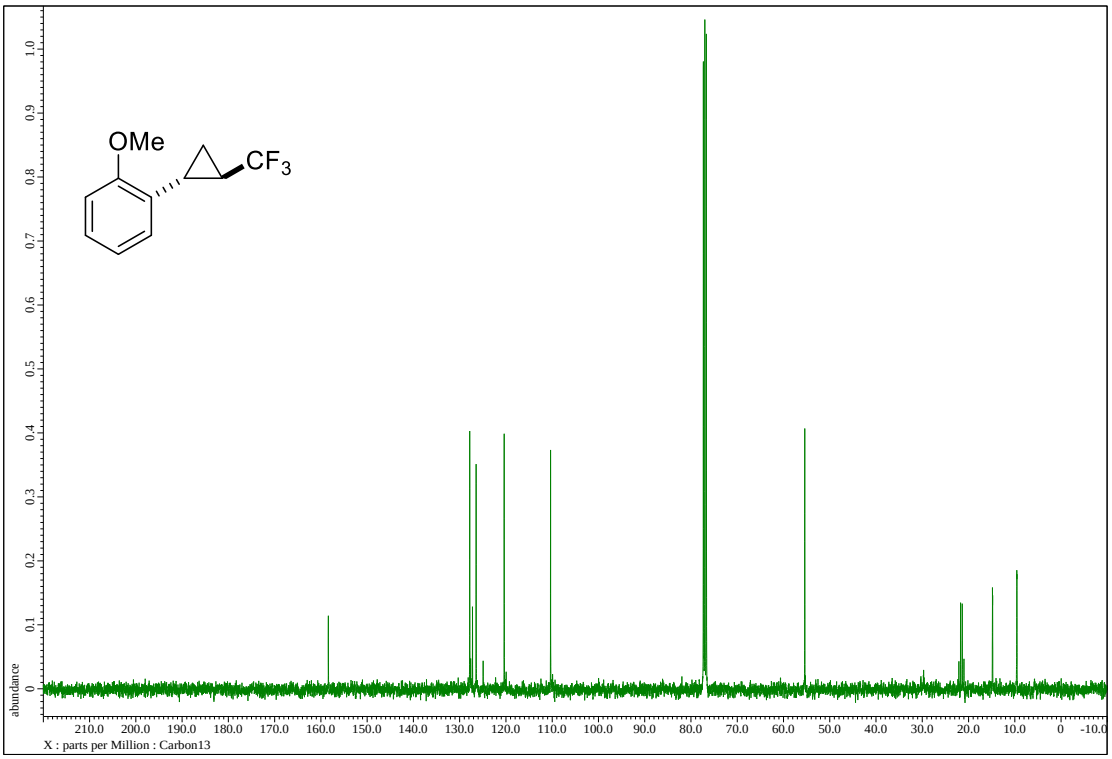


No.	tR [min]	Area	Area%
1	12.947	7756099	47.284
2	16.635	7814351	47.639
3	25.392	417500	2.545
4	38.380	415422	2.533

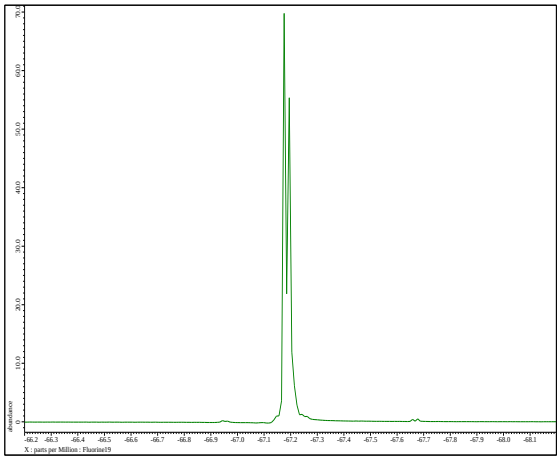
^{1}H NMR (**6b**)



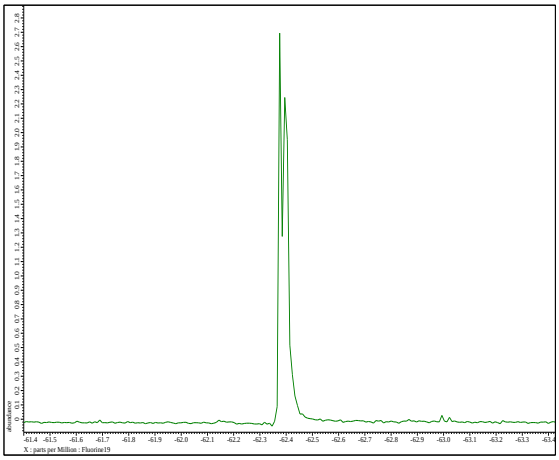
^{13}C NMR (**6b**)



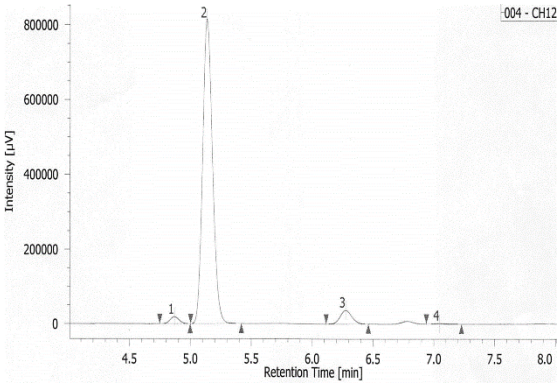
^{19}F NMR (*trans* isomer) (**6b**)



^{19}F NMR (*cis* isomer) (**6b**)

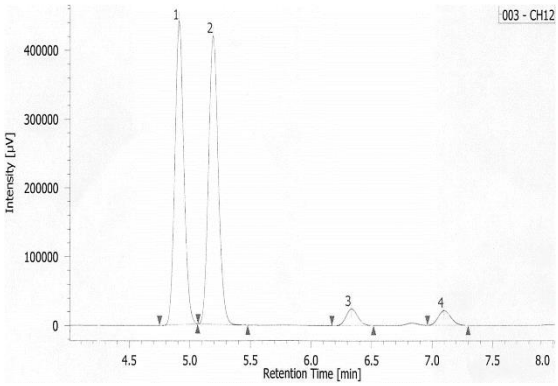


HPLC optically active (**6b**)



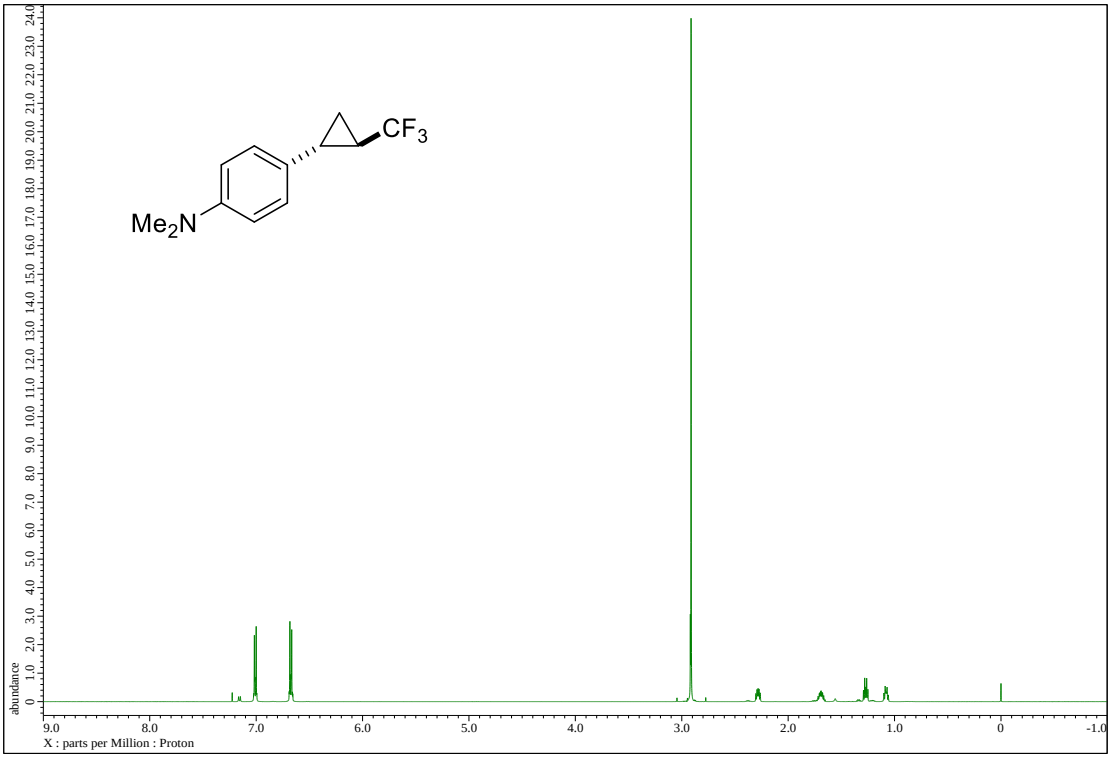
No.	tR [min]	Area	Area%
1	4.867	98376	1.999
2	5.133	4569862	92.841
3	6.275	242943	4.936
4	7.045	11059	0.225

HPLC racemic (**6b**)

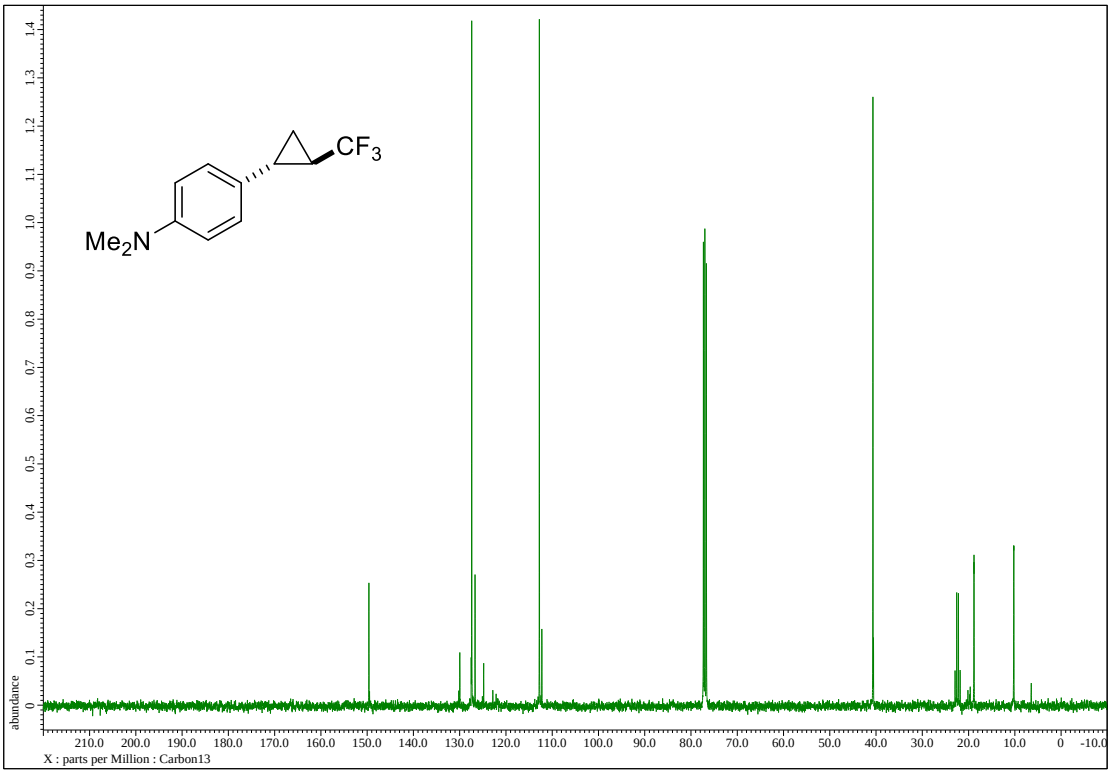


No.	tR [min]	Area	Area%
1	4.907	2329982	46.665
2	5.188	2341318	46.892
3	6.333	162369	3.252
4	7.098	159371	3.192

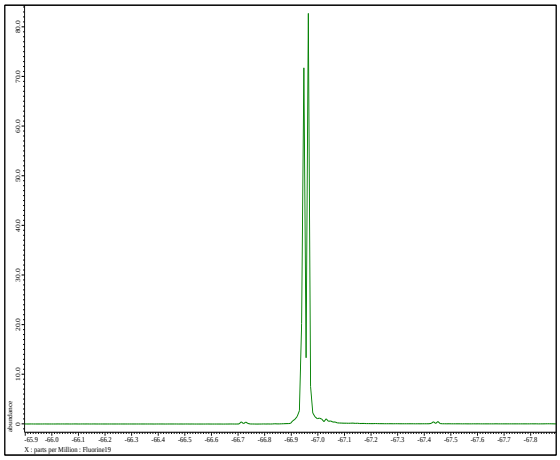
^{1}H NMR (**6c**)



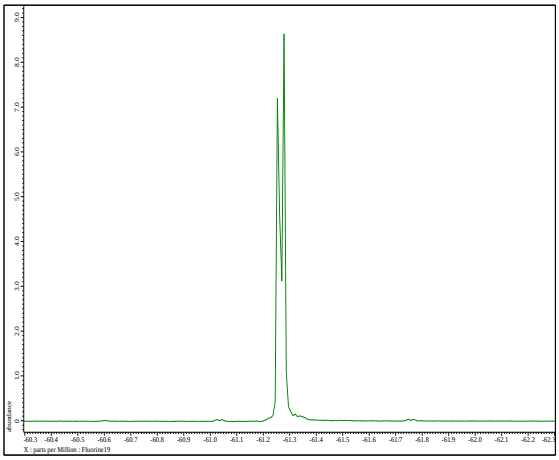
^{13}C NMR (**6c**)



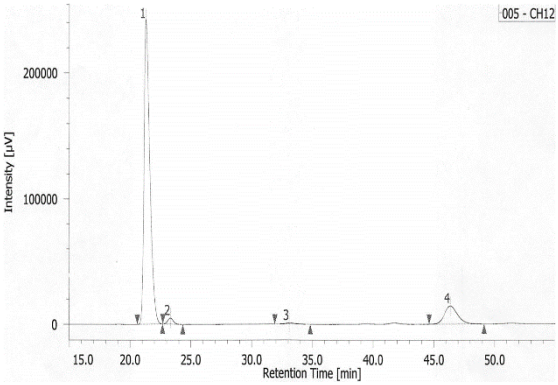
^{19}F NMR (*trans* isomer) (**6c**)



^{19}F NMR (*cis* isomer) (**6c**)

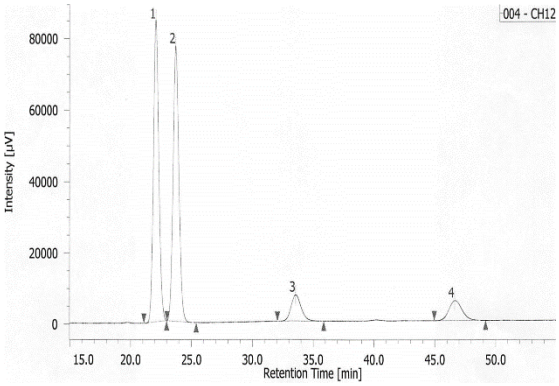


HPLC optically active (**6c**)



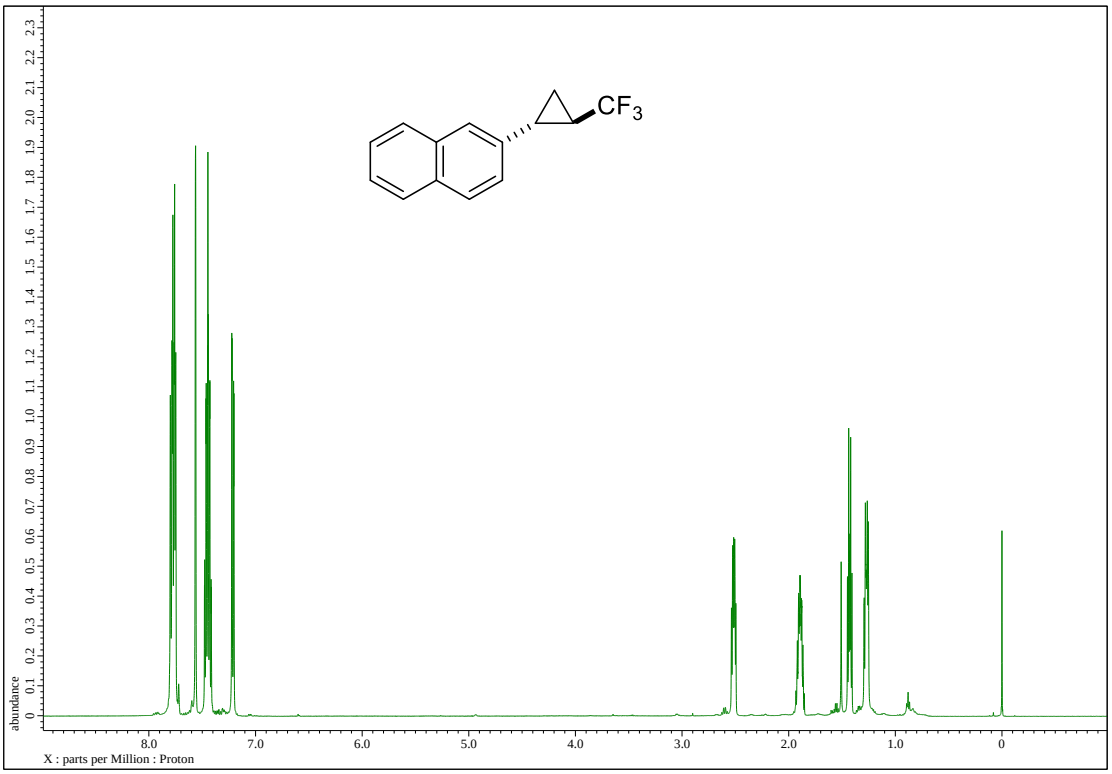
No.	tR [min]	Area	Area%
1	21.288	8030672	86.122
2	23.302	156627	1.680
3	33.082	51779	0.555
4	46.353	1085710	11.643

HPLC racemic (**6c**)

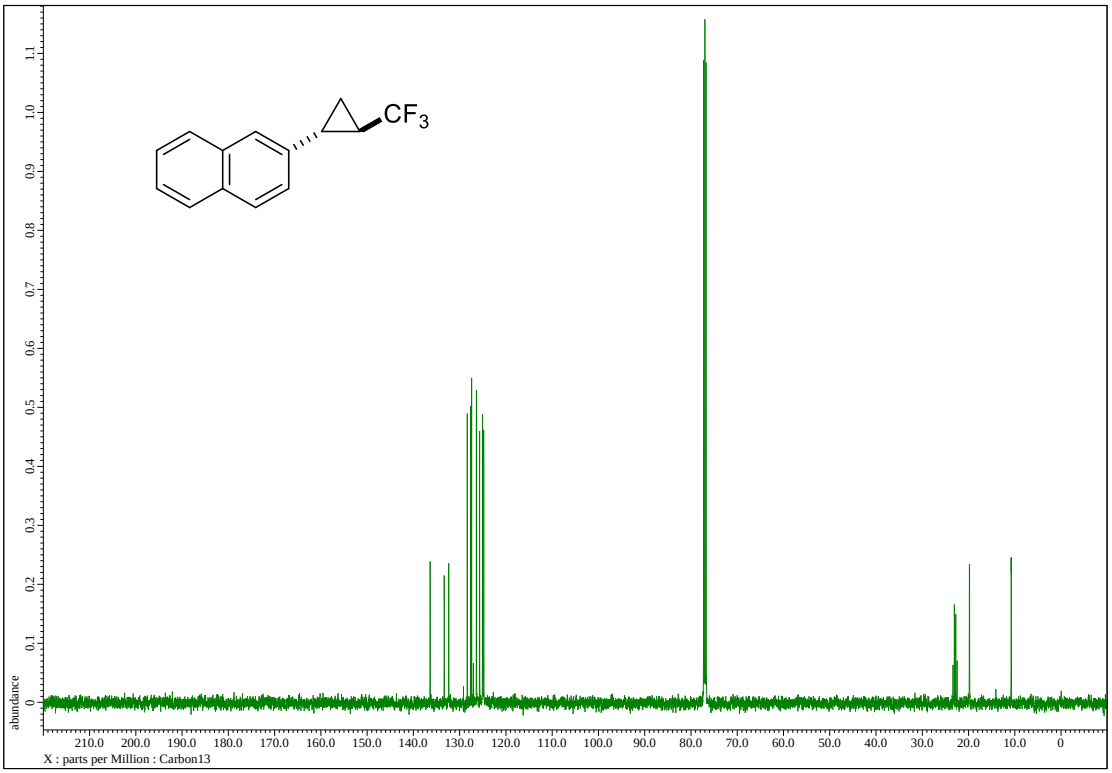


No.	tR [min]	Area	Area%
1	22.063	2564083	43.065
2	23.682	2547055	42.779
3	33.545	423623	7.115
4	46.632	419232	7.041

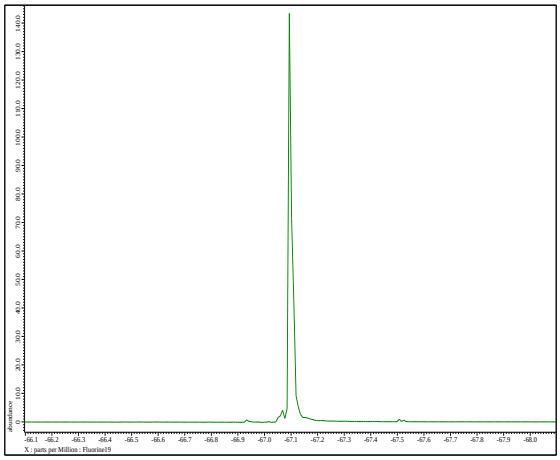
^{1}H NMR (**6d**)



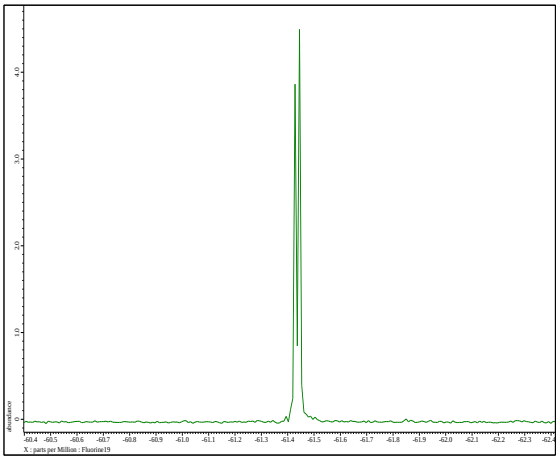
^{13}C NMR (**6d**)



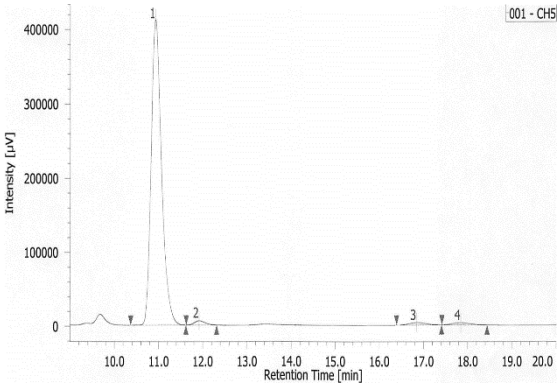
^{19}F NMR (*trans* isomer) (**6d**)



^{19}F NMR (*cis* isomer) (**6d**)

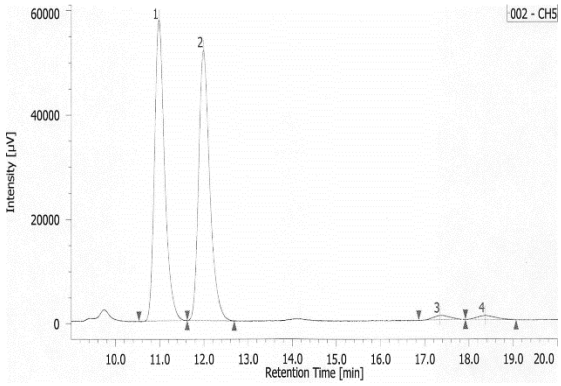


HPLC optically active (**6d**)



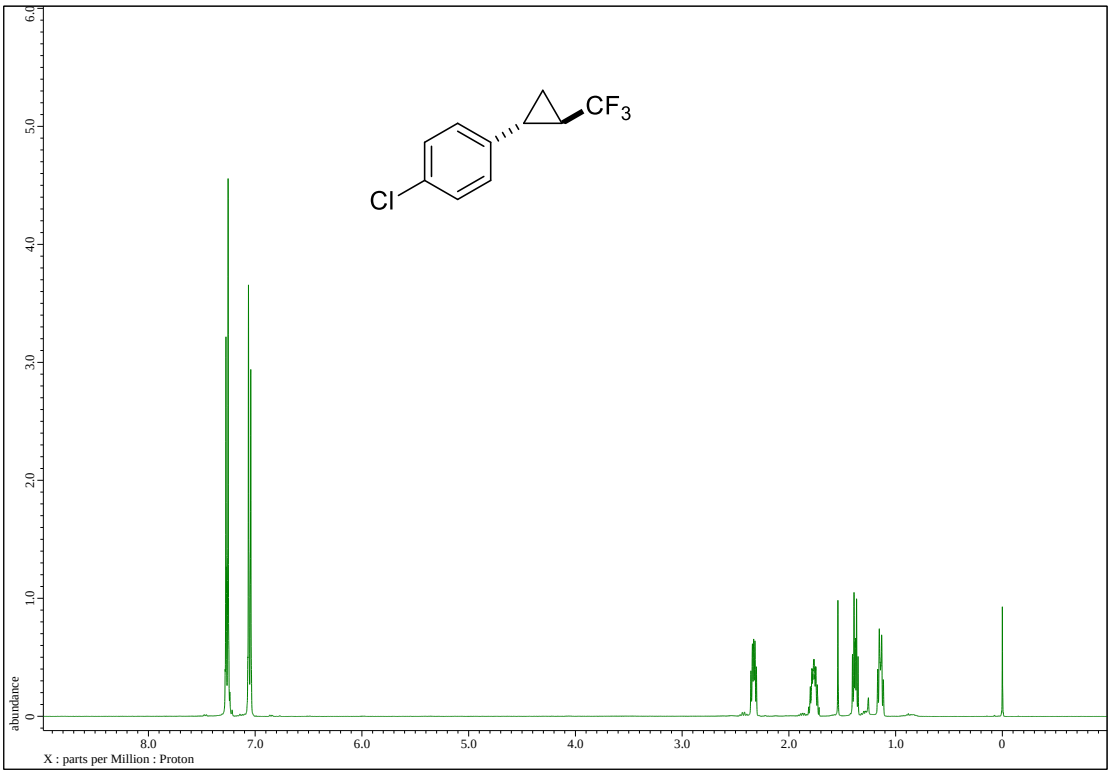
No.	tR [min]	Area	Area%
1	10.930	6687661	96.303
2	11.917	95325	1.373
3	16.840	85285	1.228
4	17.842	76135	1.096

HPLC racemic (**6d**)

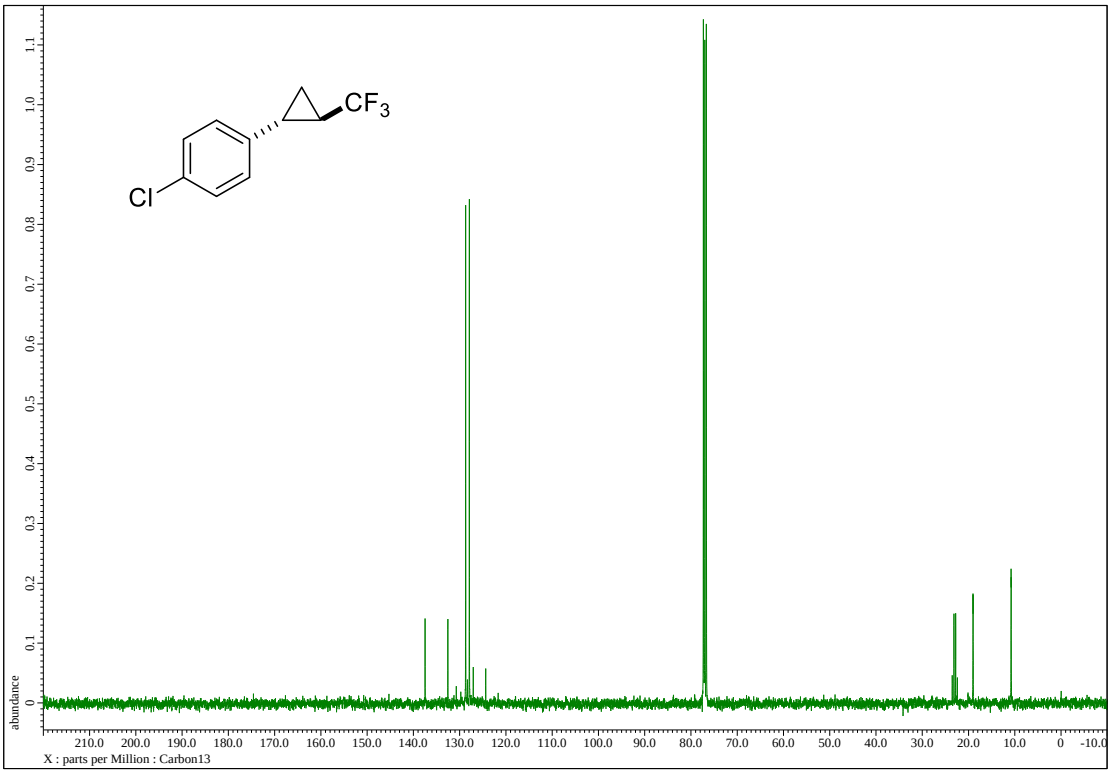


No.	tR [min]	Area	Area%
1	10.978	911530	49.027
2	11.988	902772	48.556
3	17.342	22285	1.199
4	18.362	22666	1.219

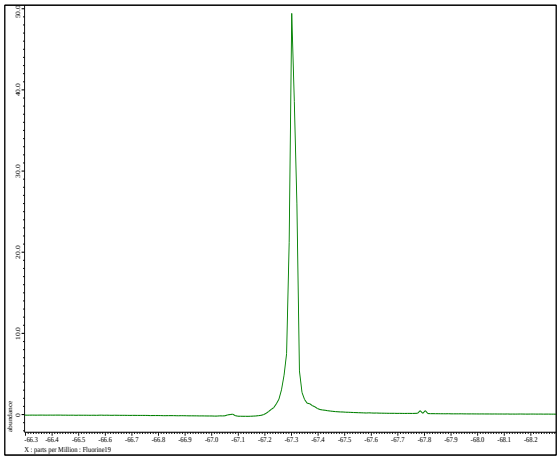
^{1}H NMR (**6e**)



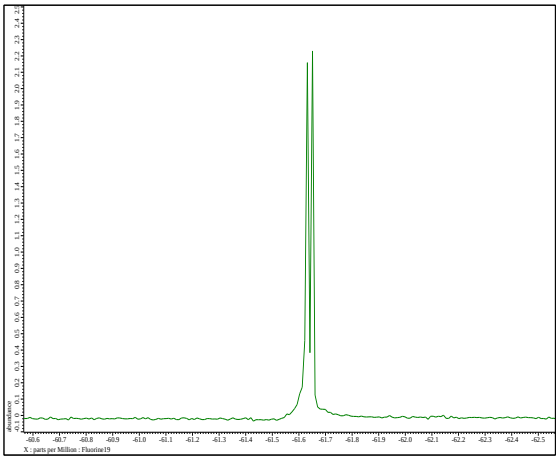
^{13}C NMR (**6e**)



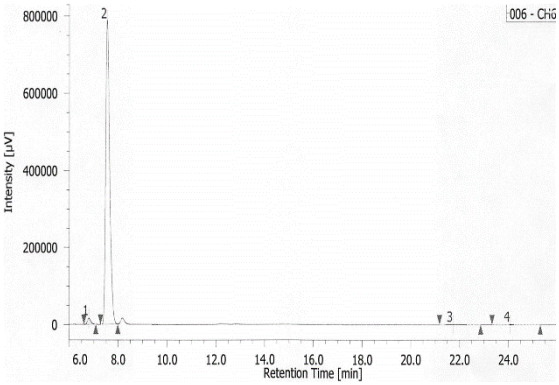
^{19}F NMR (*trans* isomer) (**6e**)



^{19}F NMR (*cis* isomer) (**6e**)

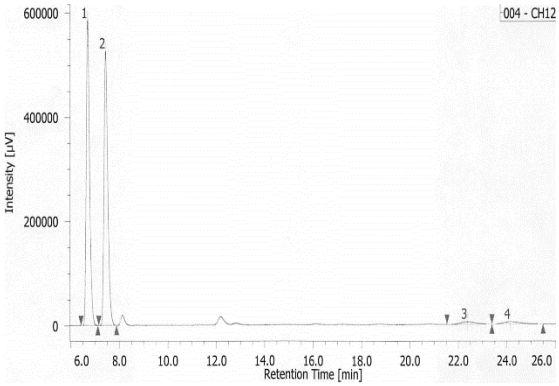


HPLC optically active (**6e**)



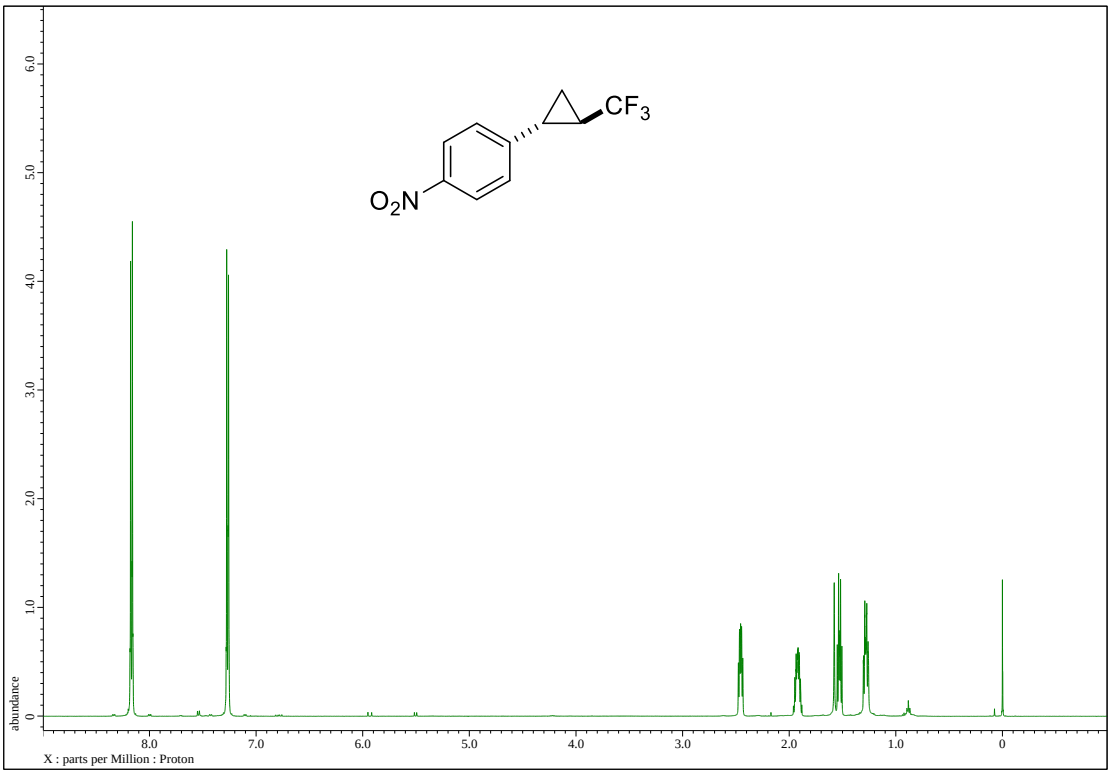
No.	tR [min]	Area	Area%
1	6.795	151478	1.616
2	7.535	9194447	98.106
3	21.728	17983	0.192
4	24.060	8025	0.086

HPLC racemic (**6e**)

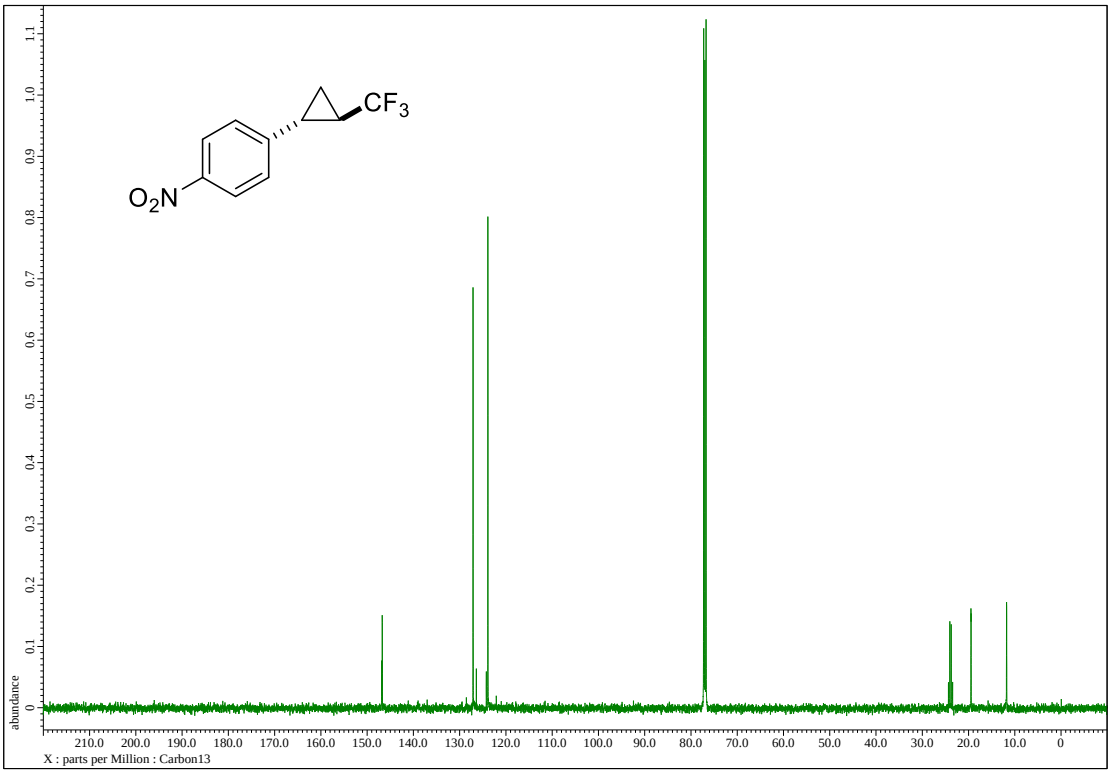


No.	tR [min]	Area	Area%
1	6.685	5575894	47.832
2	7.417	5653057	48.494
3	22.372	213367	1.830
4	24.140	214986	1.844

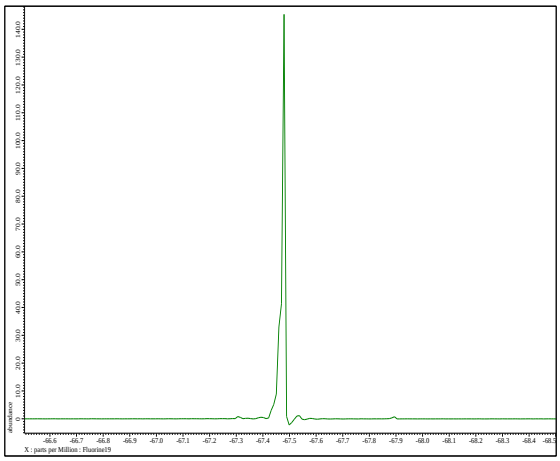
^{1}H NMR (**6f**)



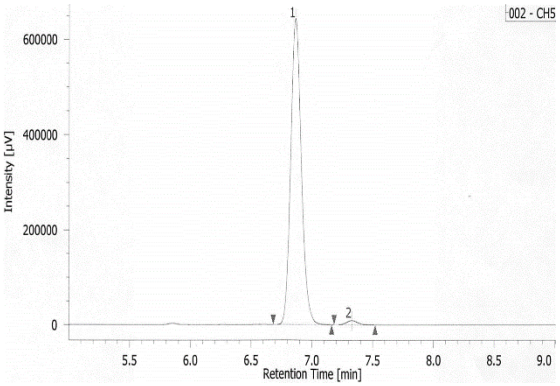
^{13}C NMR (**6f**)



^{19}F NMR (*trans* isomer) (**6f**)

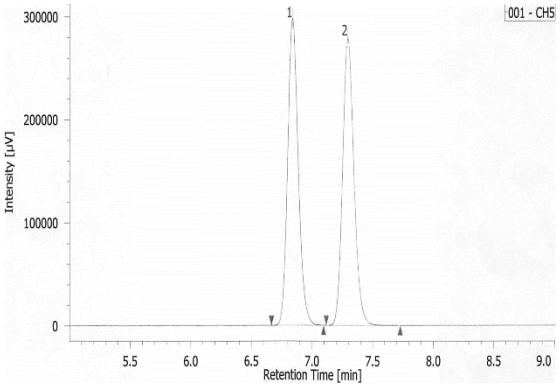


HPLC optically active (**6f**)



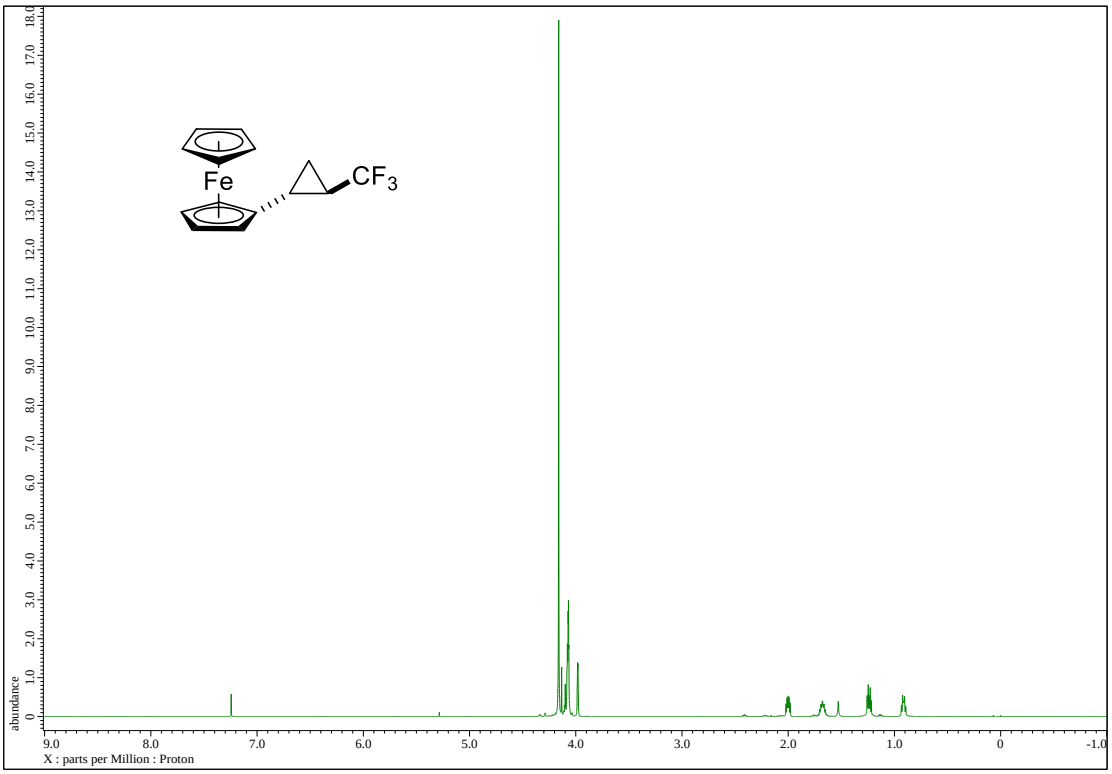
No.	tR [min]	Area	Area%
1	6.863	3906521	98.566
2	7.328	56815	1.434

HPLC racemic (**6f**)

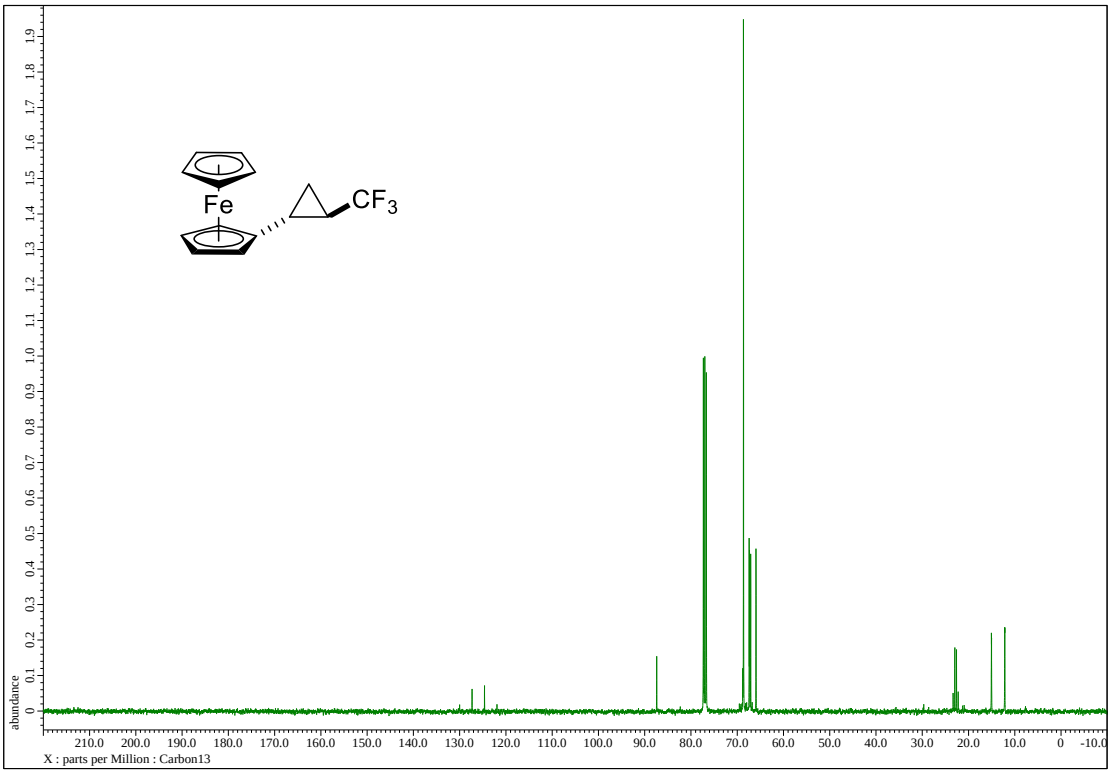


No.	tR [min]	Area	Area%
1	6.838	1805830	49.995
2	7.295	1806158	50.005

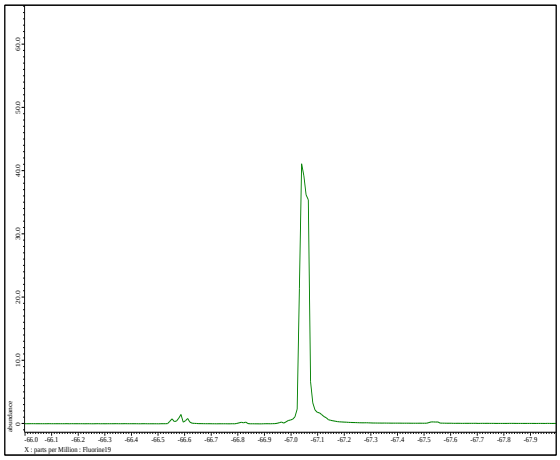
^{1}H NMR (**6g**)



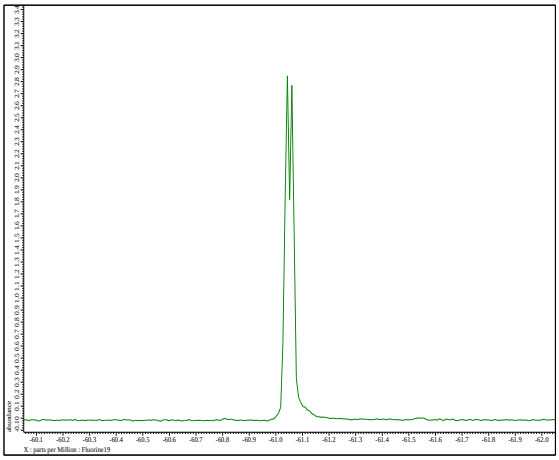
^{13}C NMR (**6g**)



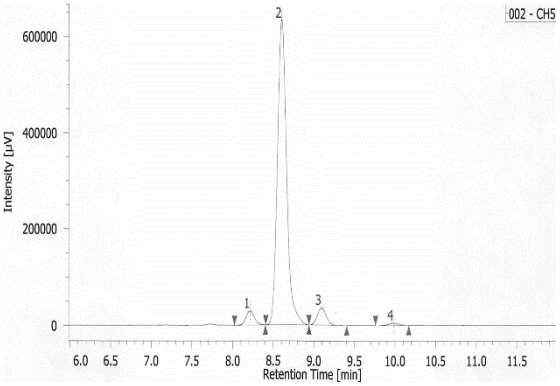
^{19}F NMR (*trans* isomer) (**6g**)



^{19}F NMR (*cis* isomer) (**6g**)

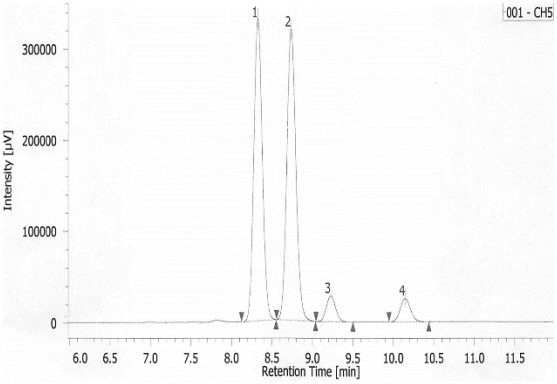


HPLC optically active (**6g**)



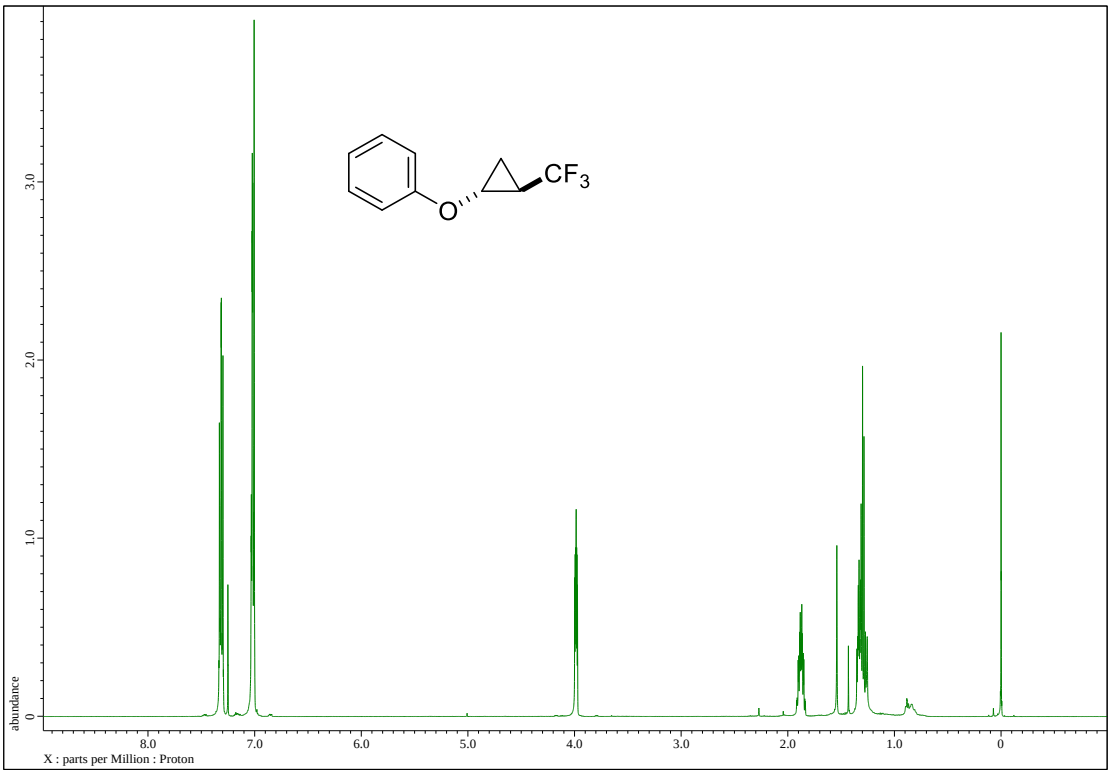
No.	tR [min]	Area	Area%
1	8.215	219182	4.002
2	8.600	4945123	90.288
3	9.095	273235	4.989
4	9.982	39528	0.722

HPLC racemic (**6g**)

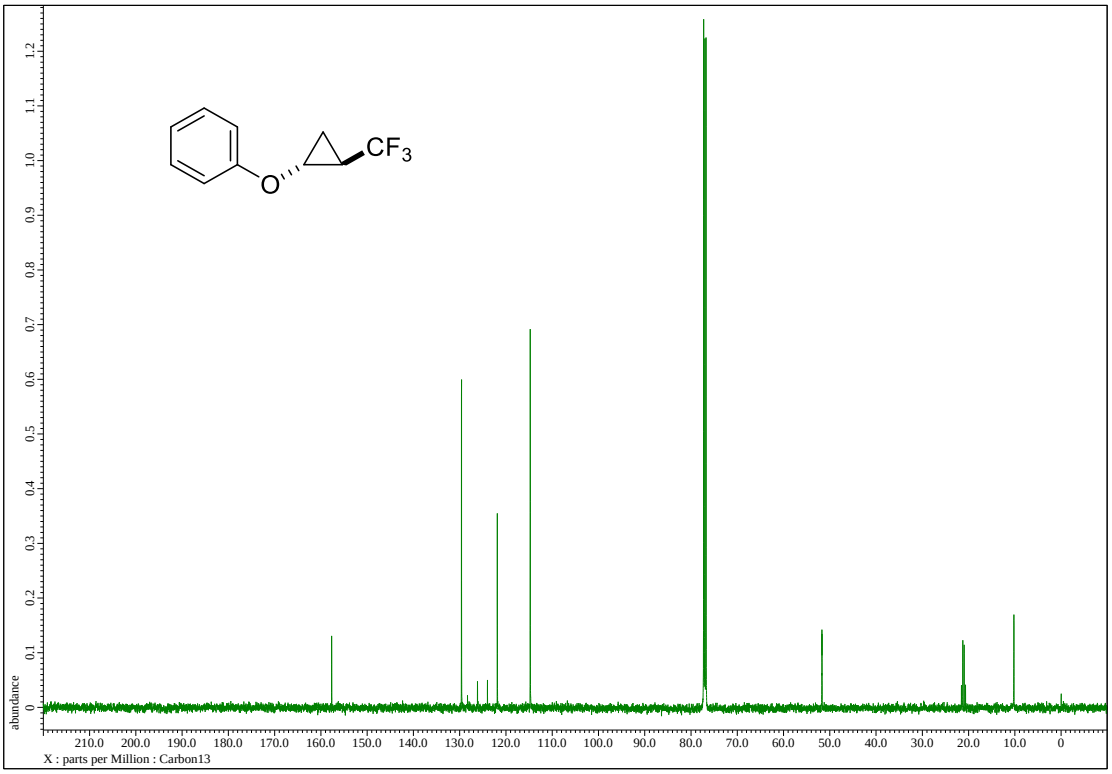


No.	tR [min]	Area	Area%
1	8.327	2406149	45.185
2	8.735	2472022	46.422
3	9.227	223325	4.194
4	10.145	223566	4.198

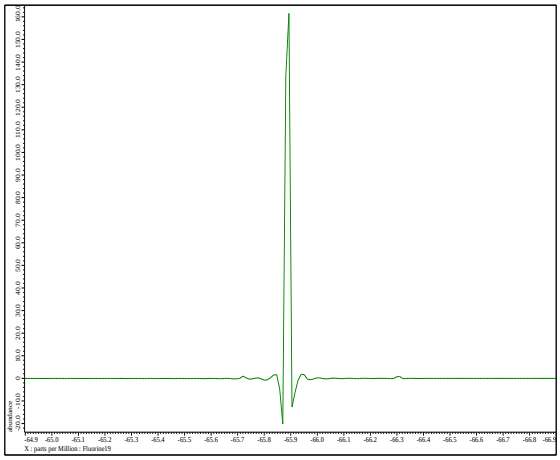
^{1}H NMR (**6h**)



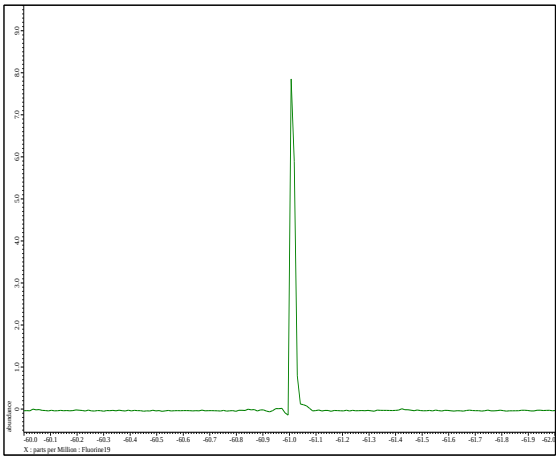
^{13}C NMR (**6h**)



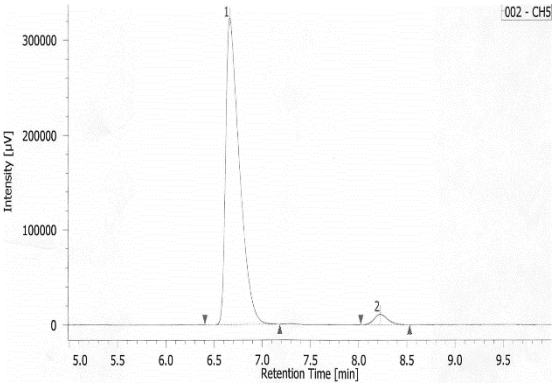
^{19}F NMR (*trans* isomer) (**6h**)



^{19}F NMR (*cis* isomer) (**6h**)

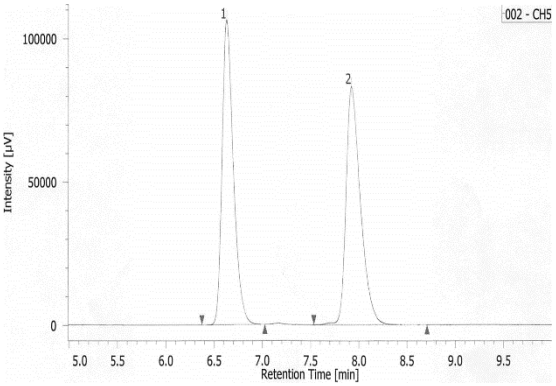


HPLC optically active (*trans* isomer) (**6h**)



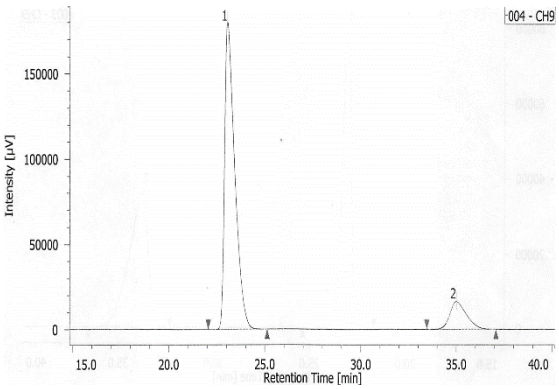
No.	tR [min]	Area	Area%
1	6.660	3192625	96.700
2	8.223	108937	3.300

HPLC racemic (*trans* isomer) (**6h**)



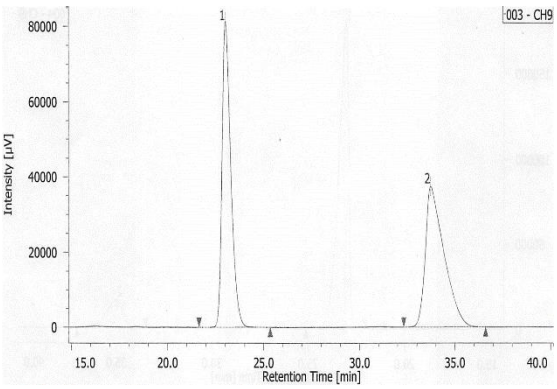
No.	tR [min]	Area	Area%
1	6.627	860793	49.943
2	7.920	862773	50.057

HPLC optically active (*cis* isomer) (**6h**)



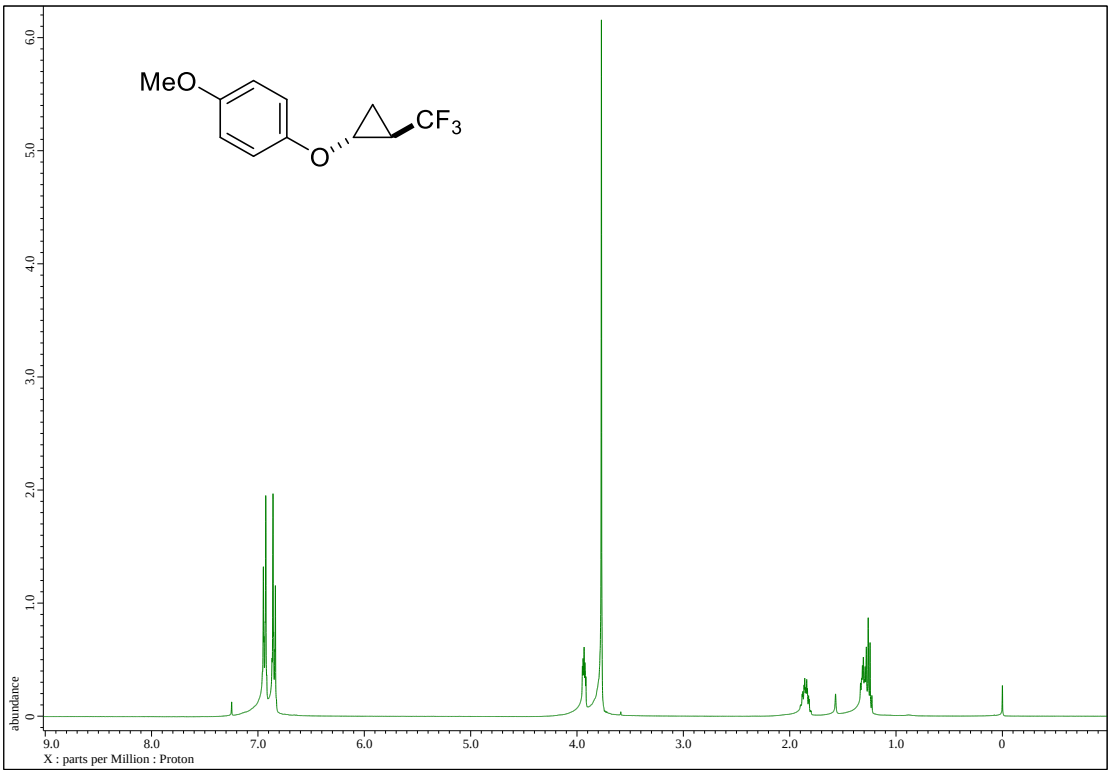
No.	tR [min]	Area	Area%
1	23.035	6545804	86.848
2	34.998	991311	13.152

HPLC racemic (*cis* isomer) (**6h**)

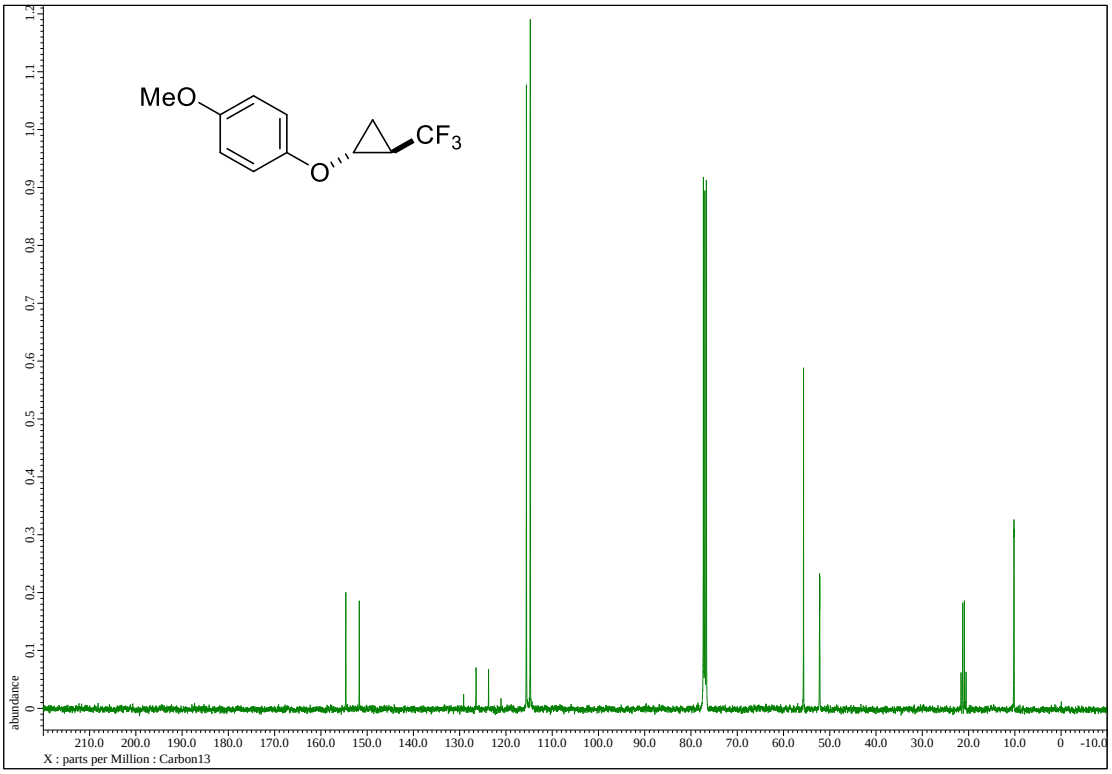


No.	tR [min]	Area	Area%
1	23.007	2549562	50.005
2	33.717	2549043	49.995

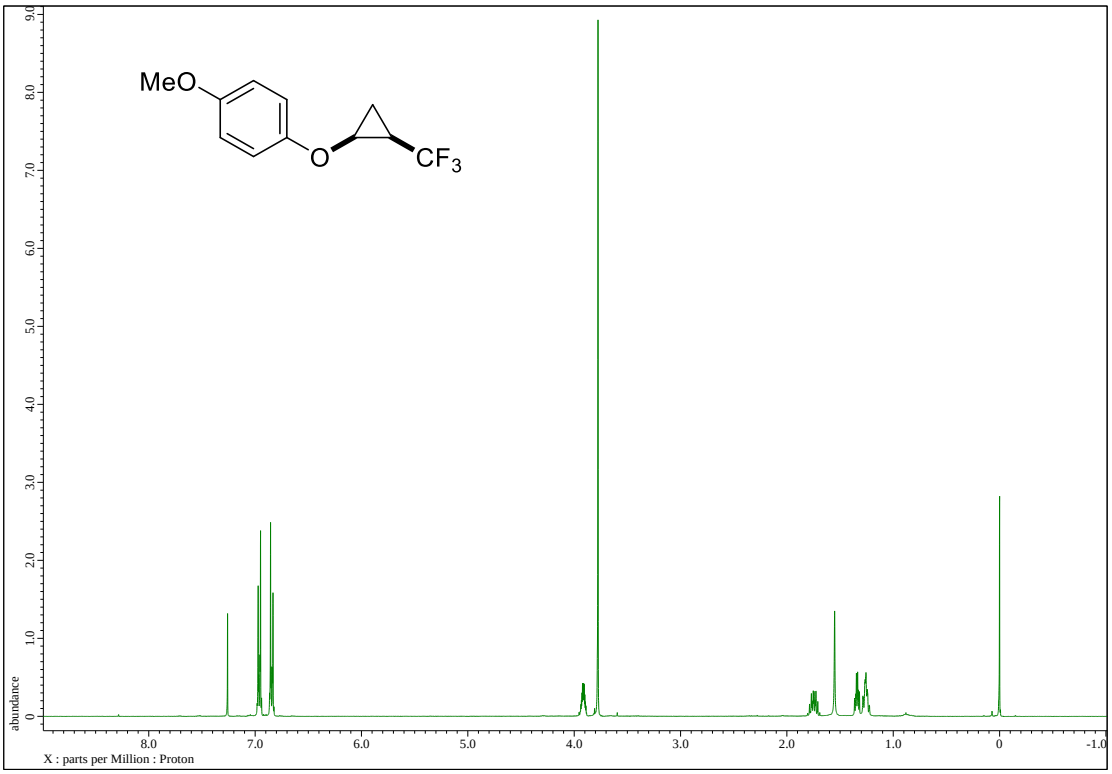
^{1}H NMR (**6i**)



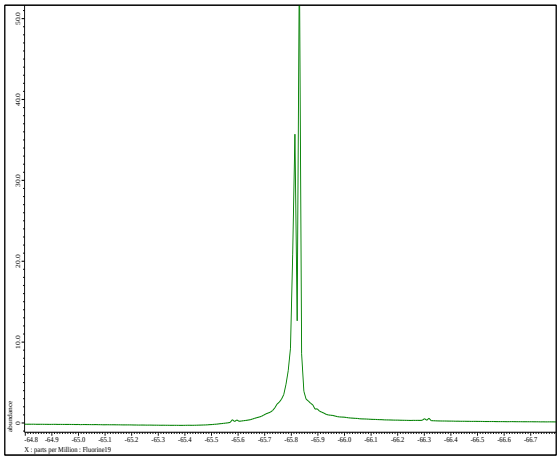
^{13}C NMR (**6i**)



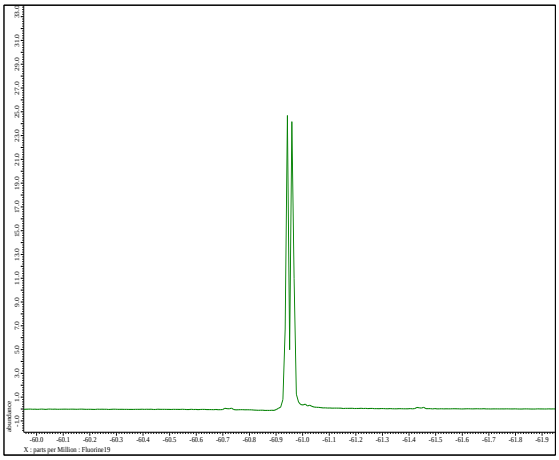
^{1}H NMR (**6i**)



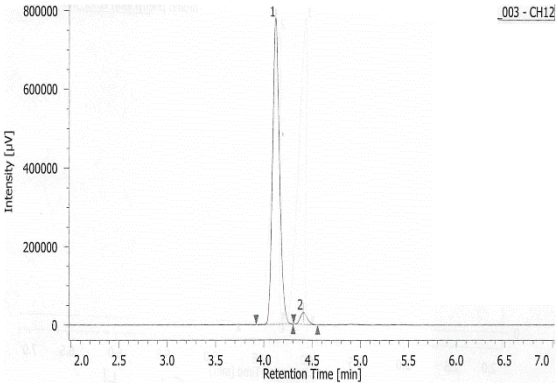
^{19}F NMR (*trans* isomer) (**6i**)



^{19}F NMR (*cis* isomer) (**6i**)

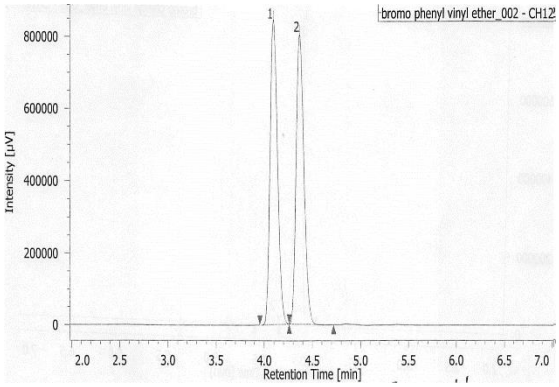


HPLC optically active (*trans* isomer) (**6i**)



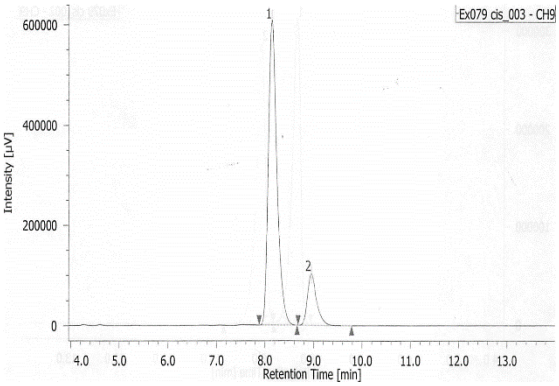
No.	tR [min]	Area	Area%
1	4.118	3867899	96.144
2	4.407	155111	3.856

HPLC racemic (*trans* isomer) (**6i**)



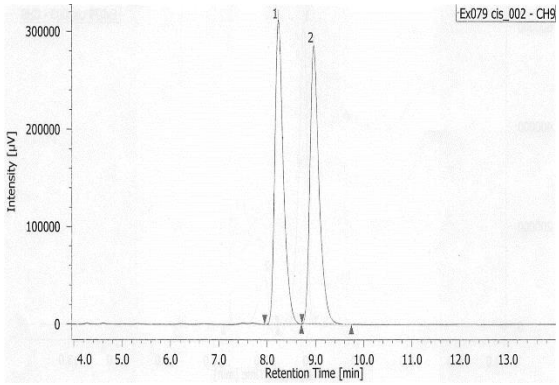
No.	tR [min]	Area	Area%
1	4.095	4504841	49.988
2	4.367	4507076	50.012

HPLC optically active (*cis* isomer) (**6i**)



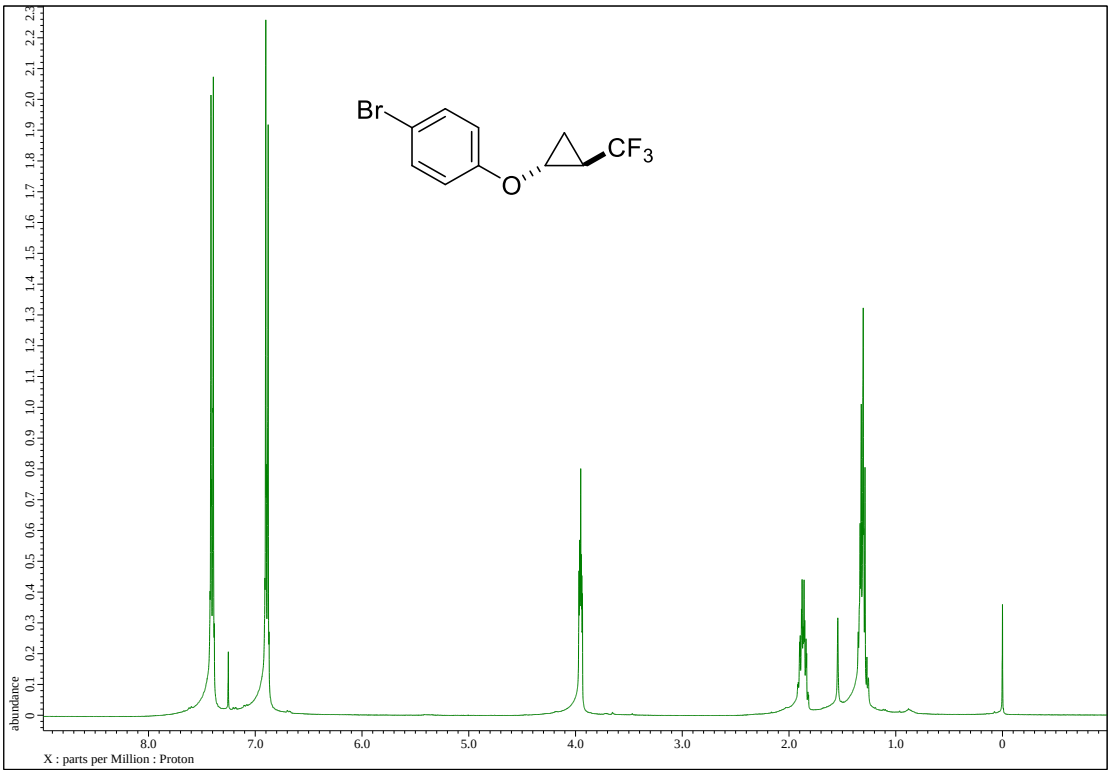
No.	tR [min]	Area	Area%
1	8.132	7461527	84.543
2	8.948	1364141	15.457

HPLC racemic (*cis* isomer) (**6i**)

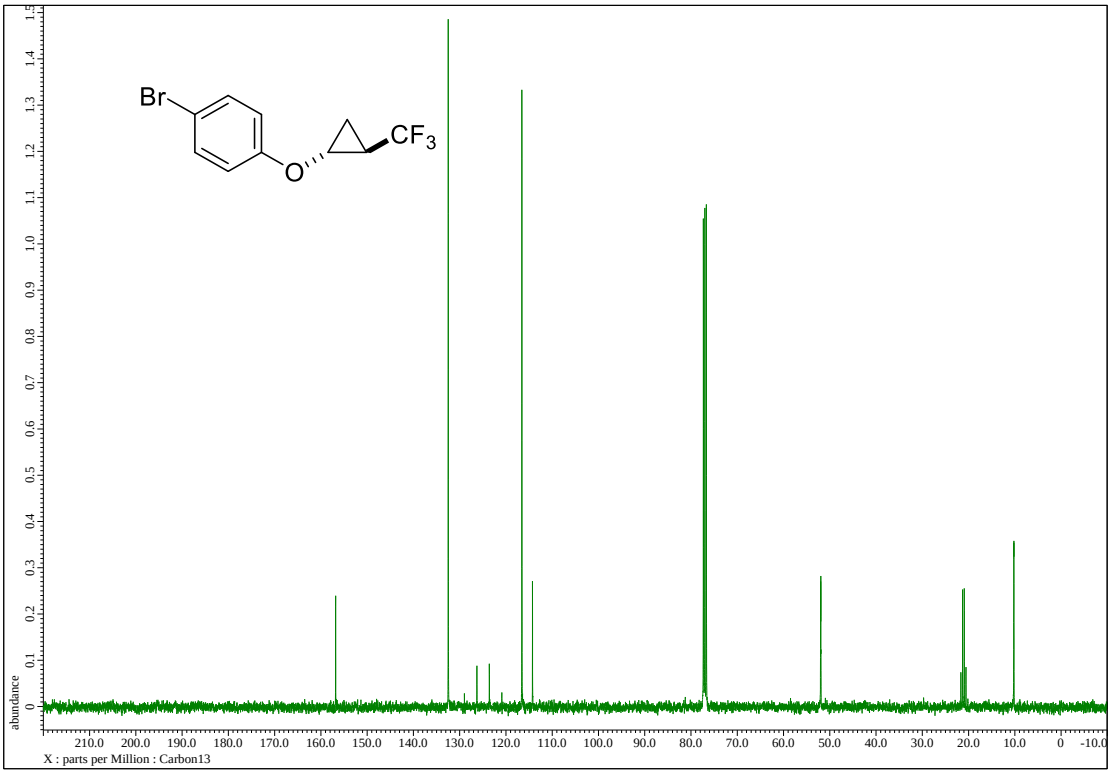


No.	tR [min]	Area	Area%
1	8.228	3818240	49.980
2	8.958	3821353	50.020

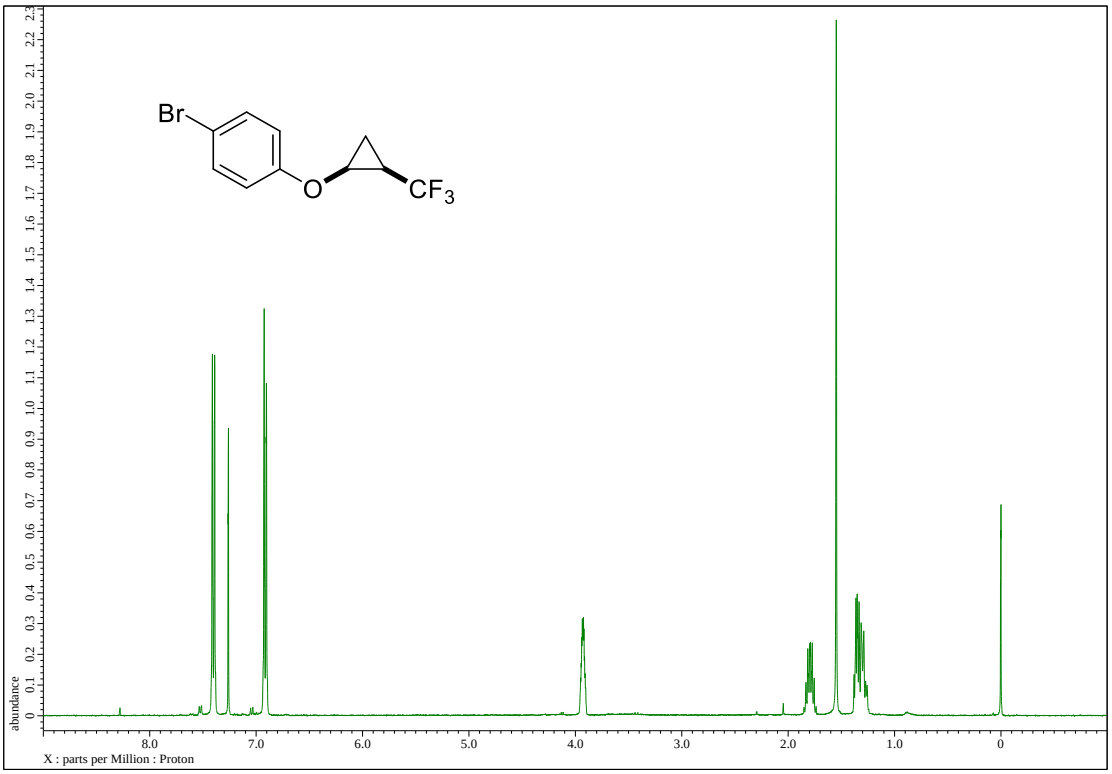
^{1}H NMR (**6j**)



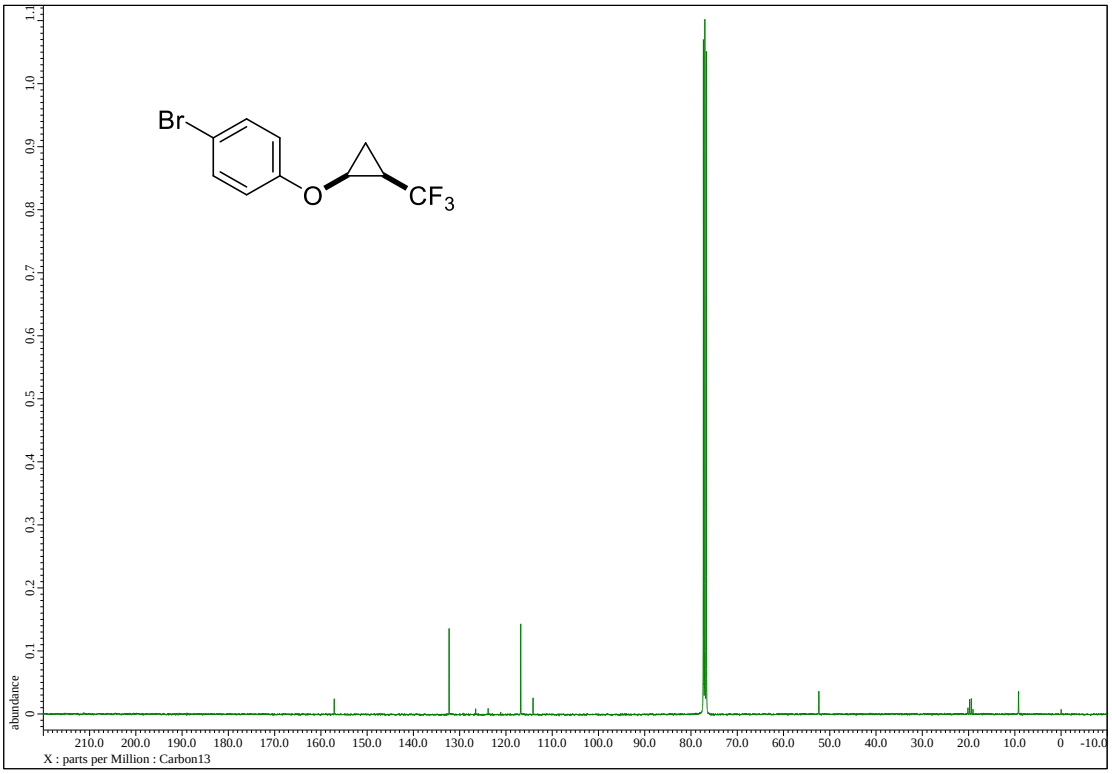
^{13}C NMR (**6j**)



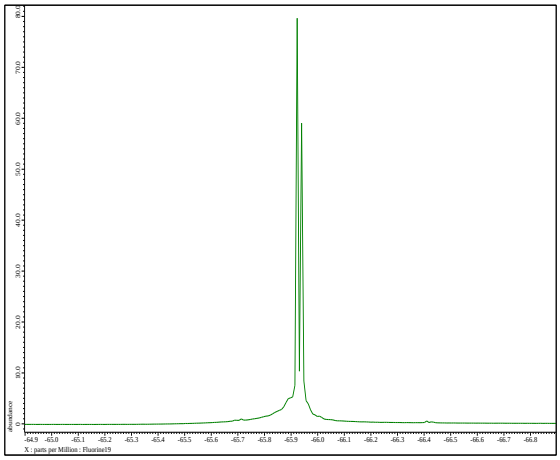
^{1}H NMR (**6j**)



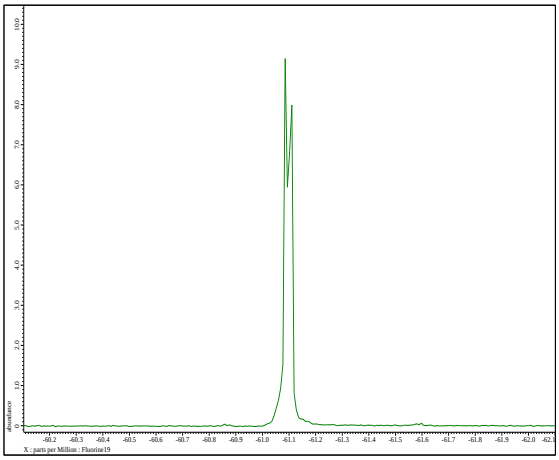
^{13}C NMR (**6j**)



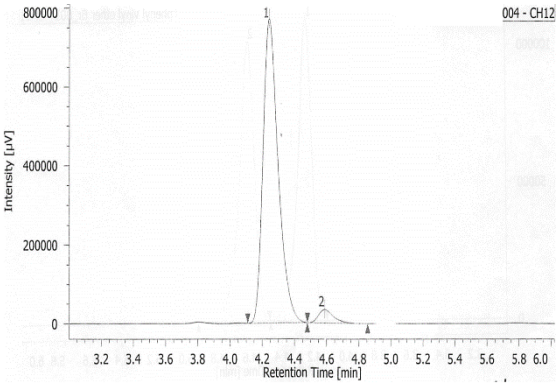
^{19}F NMR (*trans* isomer) (**6j**)



^{19}F NMR (*cis* isomer) (**6j**)

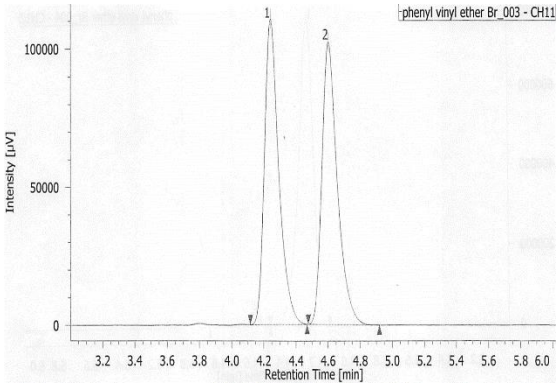


HPLC optically active (*trans* isomer) (**6j**)



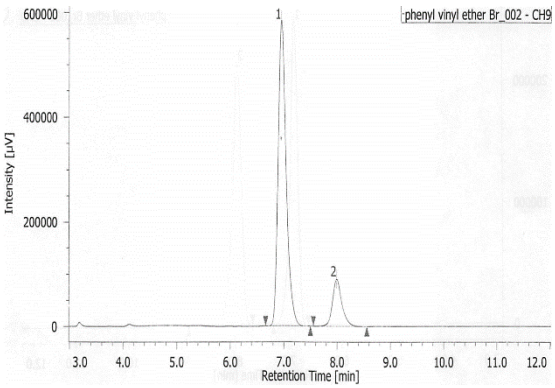
No.	tR [min]	Area	Area%
1	4.242	5012944	95.783
2	4.587	220711	4.217

HPLC racemic (*trans* isomer) (**6j**)



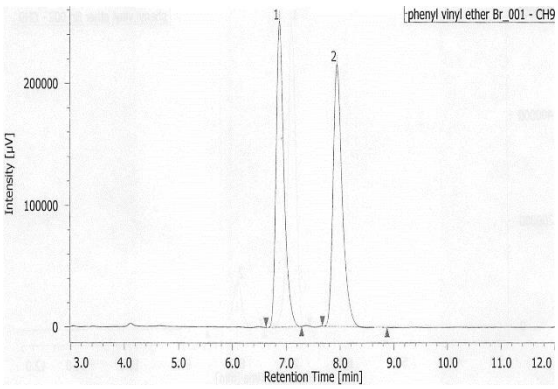
No.	tR [min]	Area	Area%
1	4.242	678190	49.858
2	4.602	682044	50.142

HPLC optically active (*cis* isomer) (**6j**)



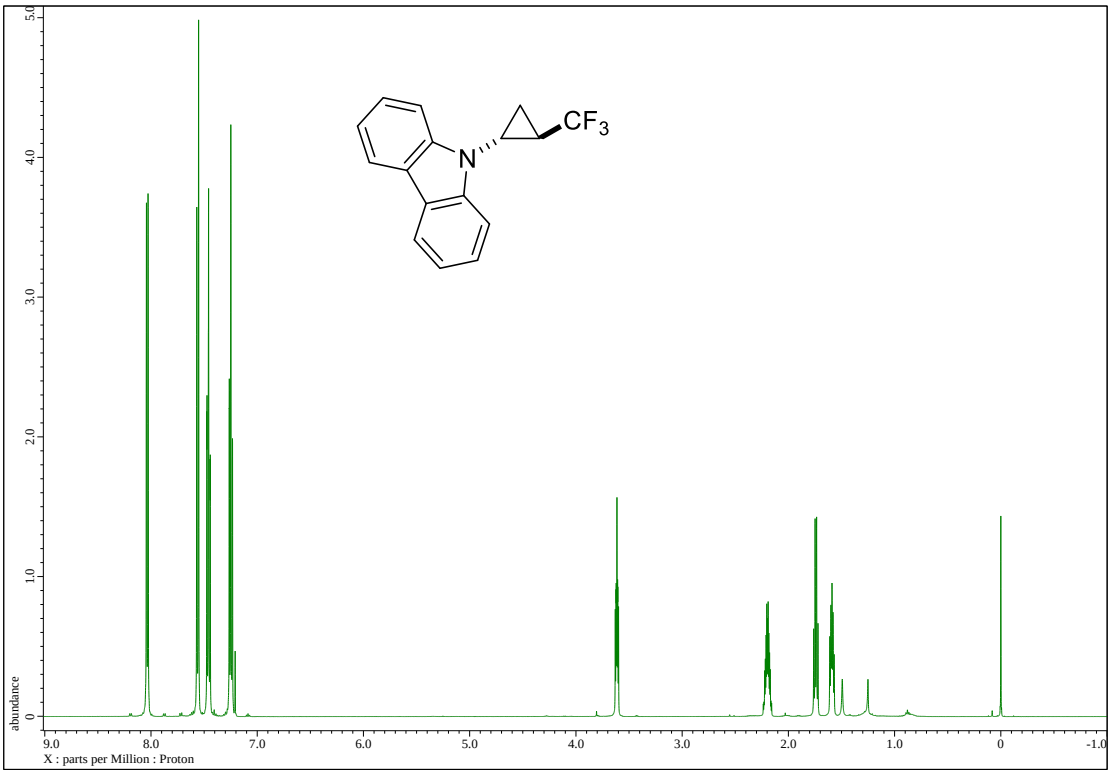
No.	tR [min]	Area	Area%
1	6.950	6057119	86.639
2	7.990	1092838	13.361

HPLC racemic (*cis* isomer) (**6j**)

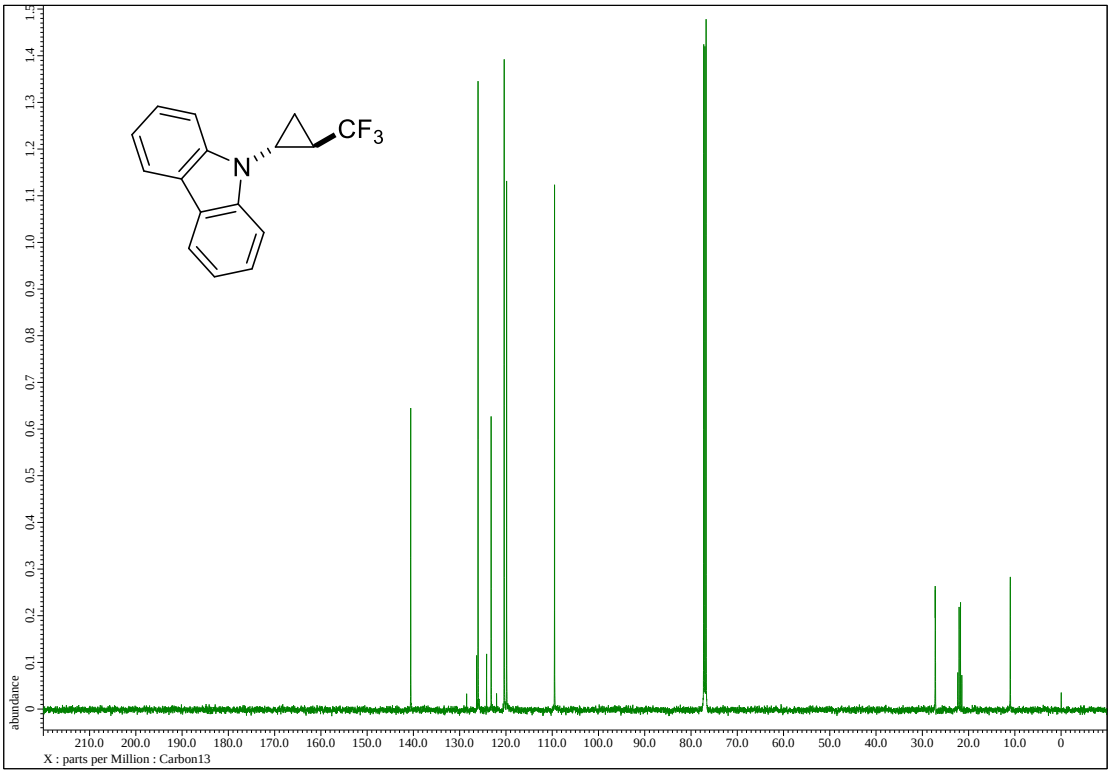


No.	tR [min]	Area	Area%
1	6.872	2541642	50.104
2	7.940	2531046	49.896

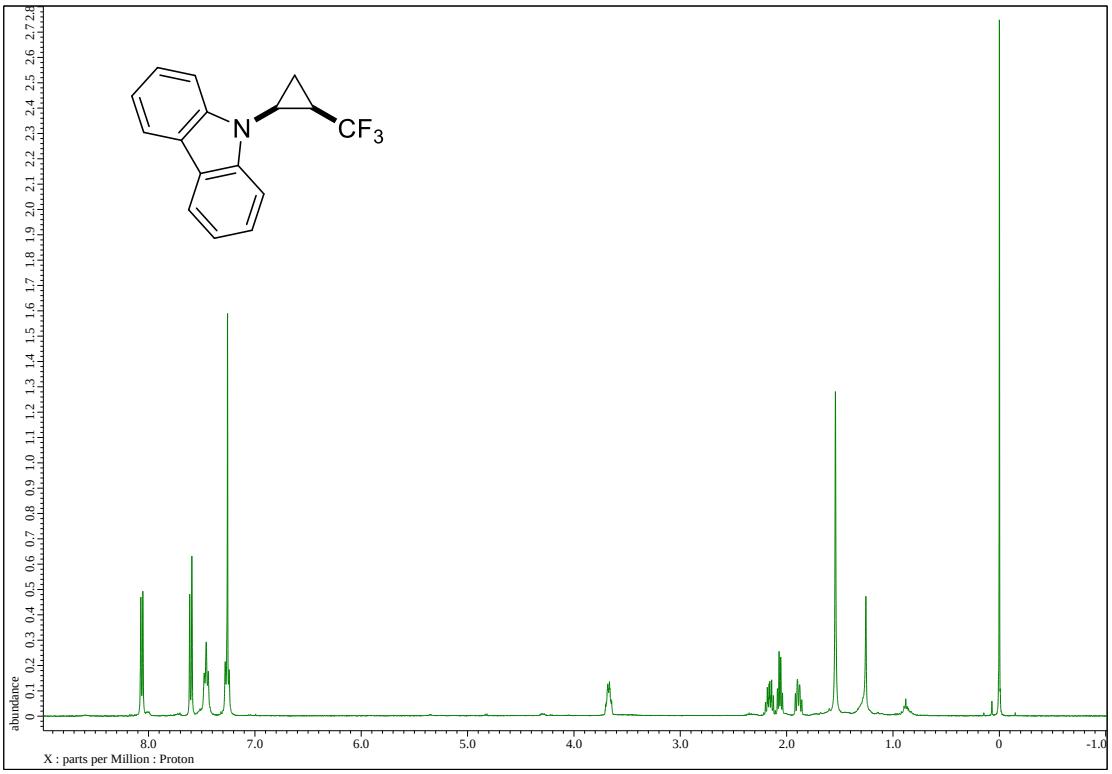
^{1}H NMR (**6k**)



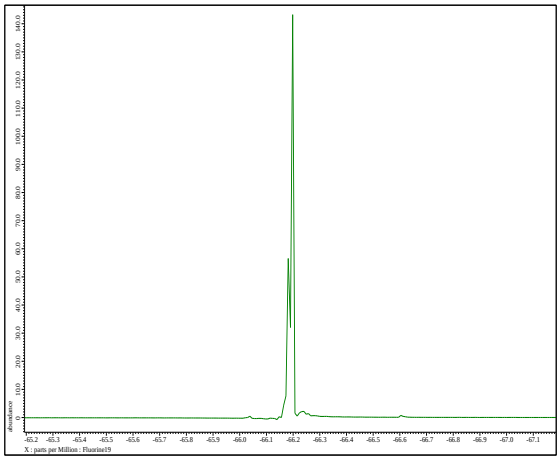
^{13}C NMR (**6k**)



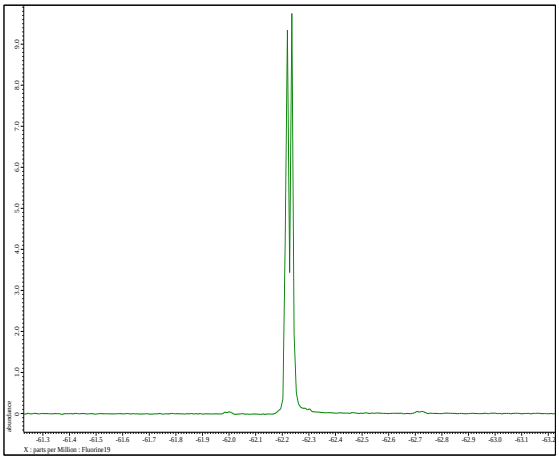
^{1}H NMR (**6k**)


N
CF3
abundance
X : parts per Million : Proton
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0

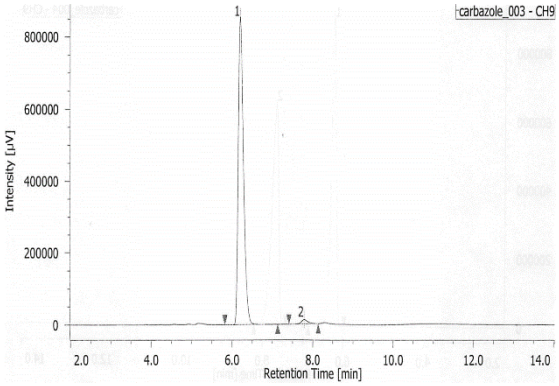
^{19}F NMR (*trans* isomer) (**6k**)



^{19}F NMR (*cis* isomer) (**6k**)

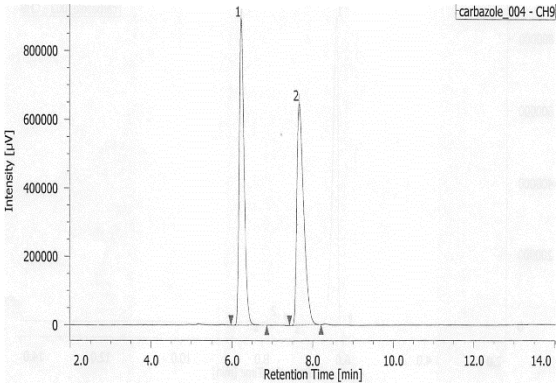


HPLC optically active (*trans* isomer) (**6k**)



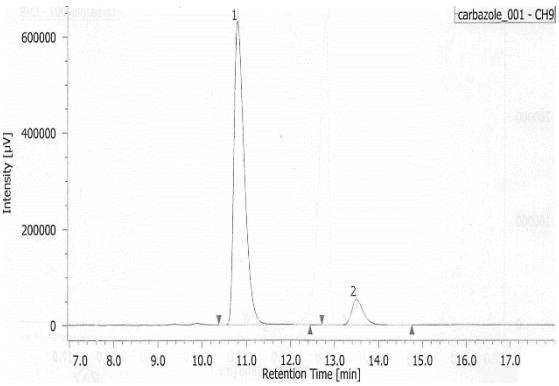
No.	tR [min]	Area	Area%
1	6.193	7632199	98.296
2	7.785	132329	1.704

HPLC racemic (*trans* isomer) (**6k**)



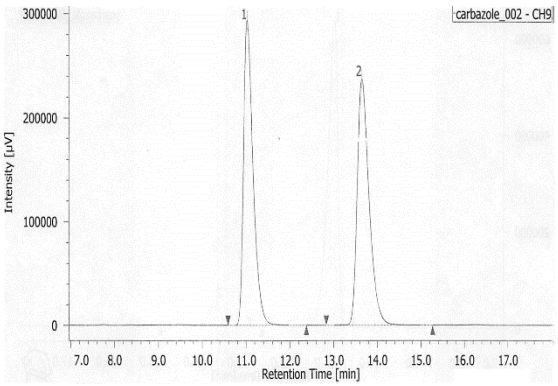
No.	tR [min]	Area	Area%
1	6.223	7570506	49.913
2	7.662	7597042	50.087

HPLC optically active (*cis* isomer) (**6k**)



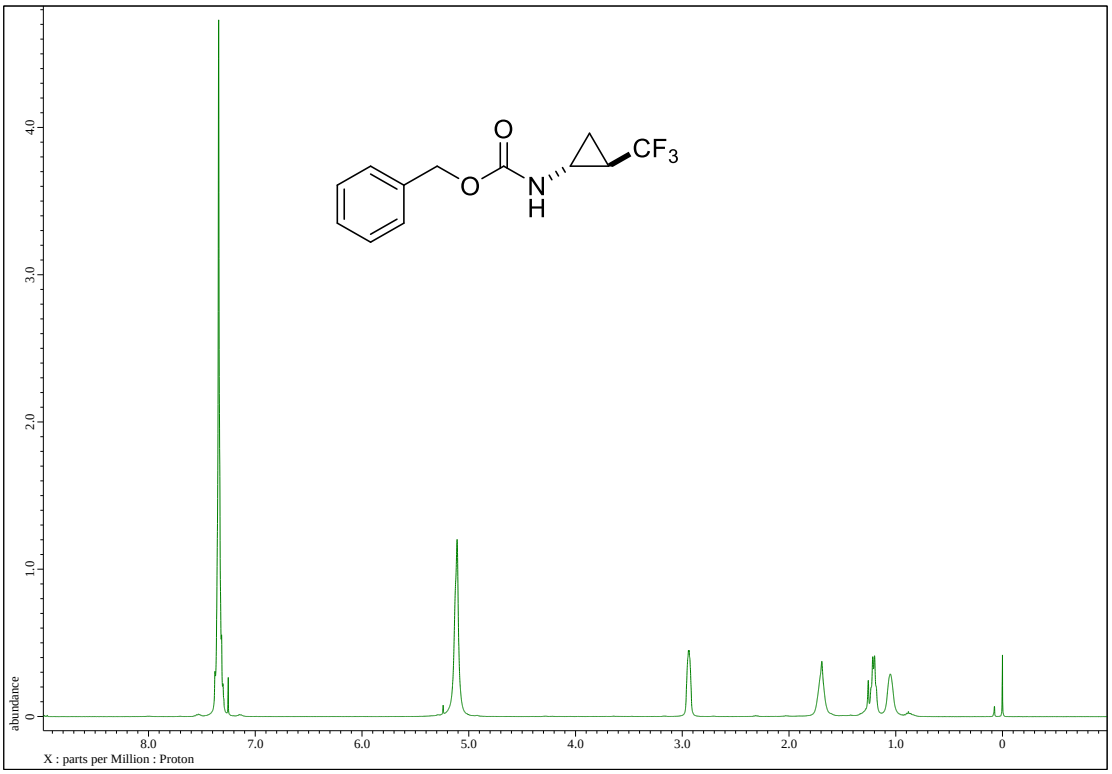
No.	tR [min]	Area	Area%
1	10.798	10280285	91.283
2	13.497	981749	8.717

HPLC racemic (*cis* isomer) (**6k**)

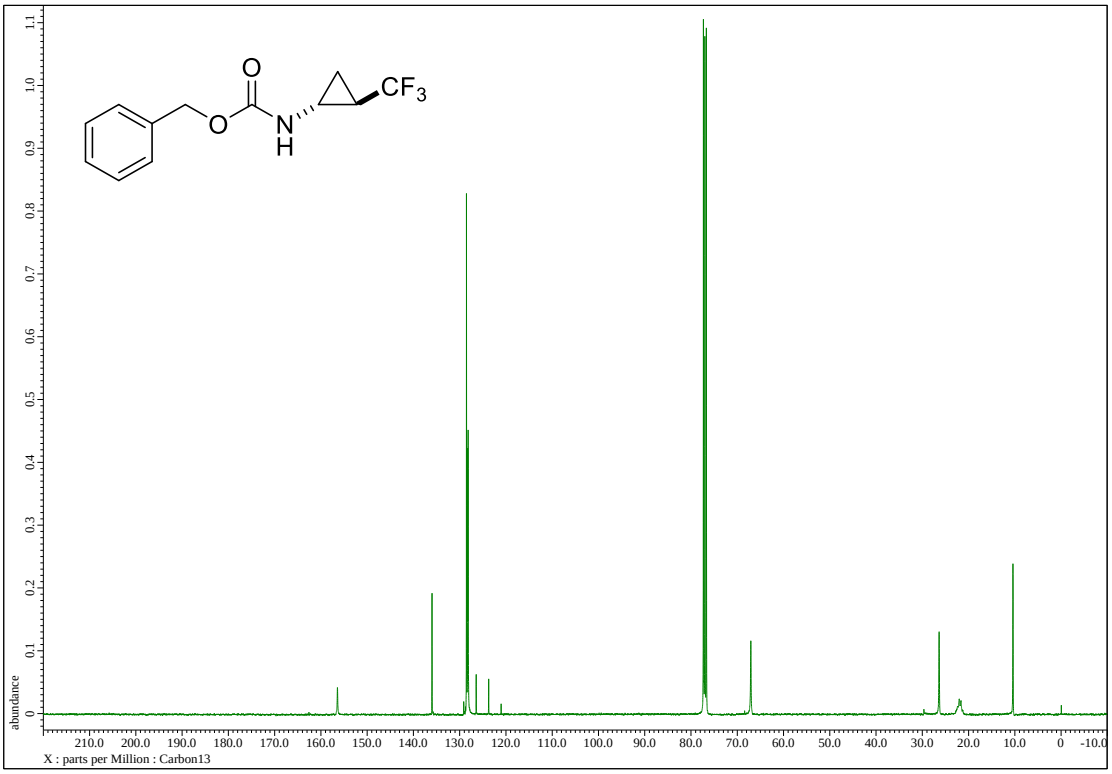


No.	tR [min]	Area	Area%
1	11.025	4521761	50.116
2	13.643	4500808	49.884

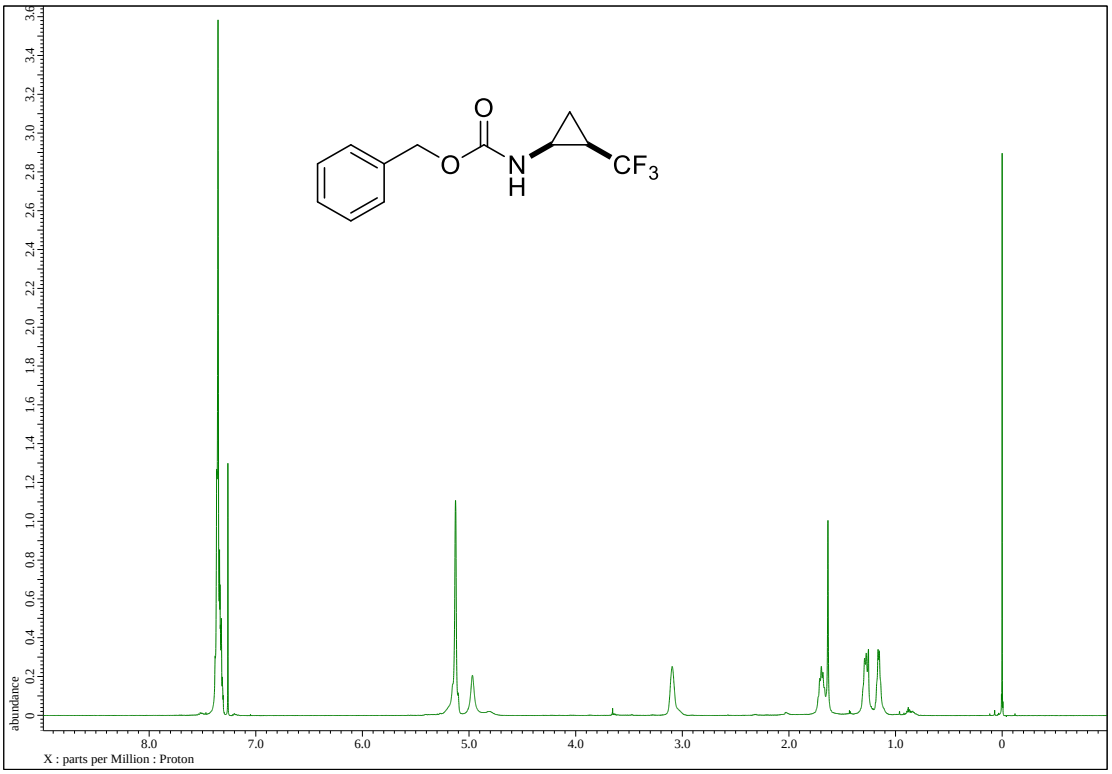
^{1}H NMR (**6l**)



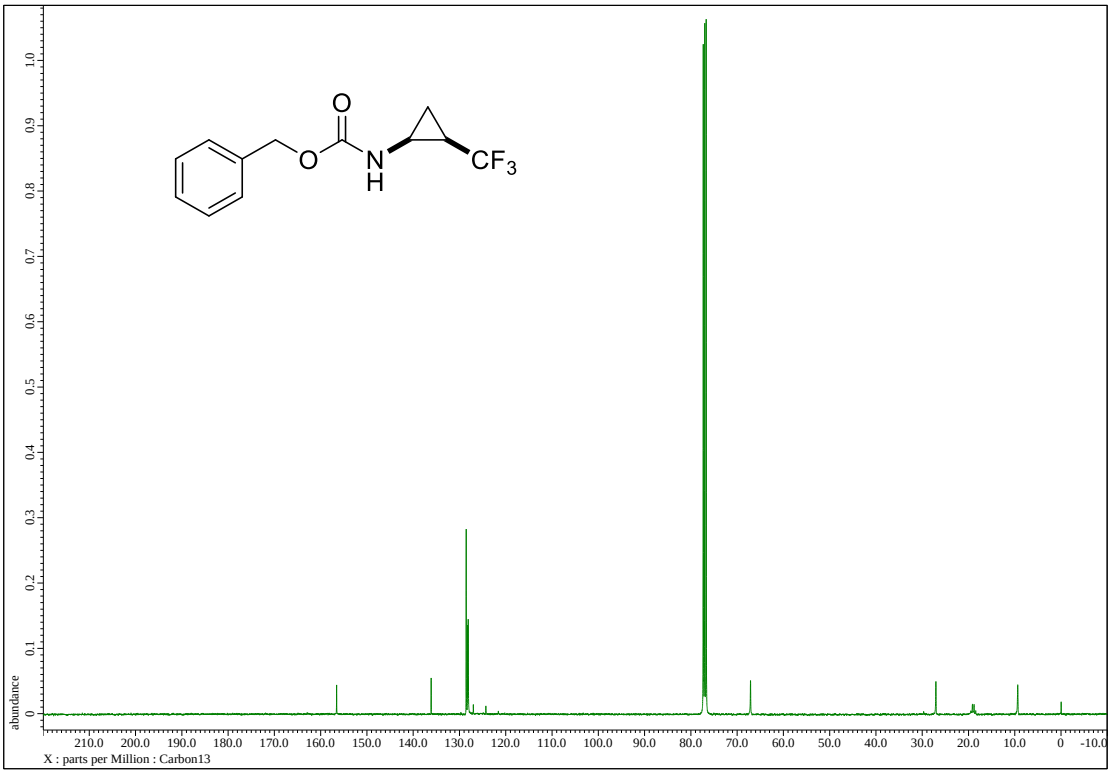
^{13}C NMR (**6l**)



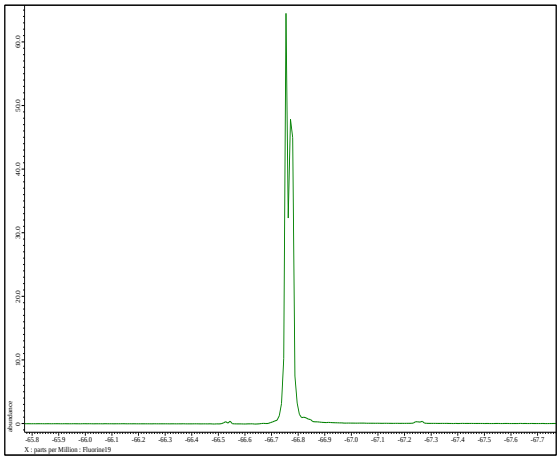
^{1}H NMR (**6l**)



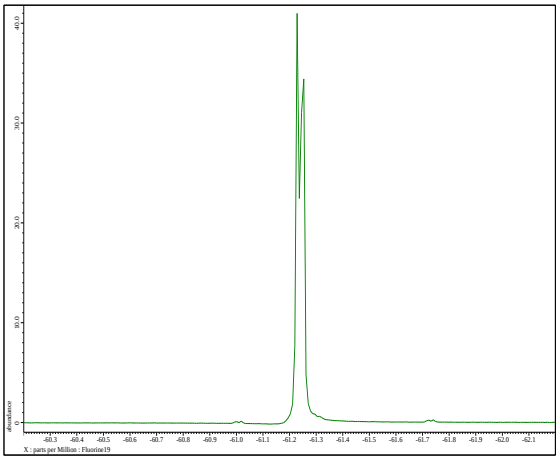
^{13}C NMR (**6l**)



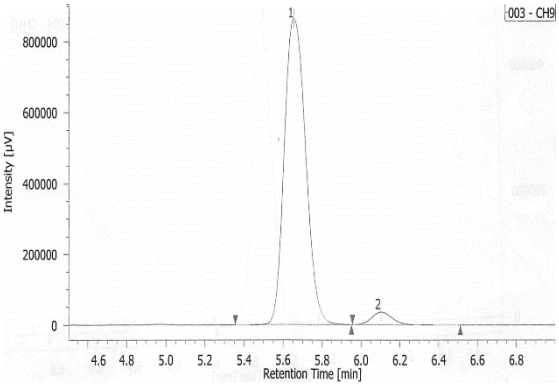
^{19}F NMR (*trans* isomer) (**6l**)



^{19}F NMR (*cis* isomer) (**6l**)

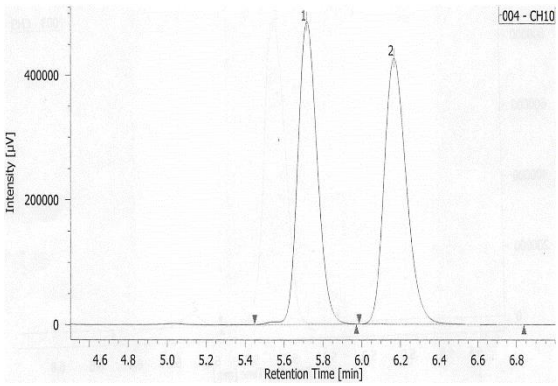


HPLC optically active (*trans* isomer) (**6l**)



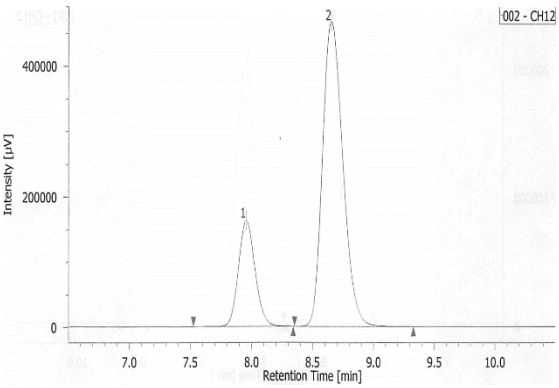
No.	tR [min]	Area	Area%
1	5.653	6572156	96.256
2	6.103	255622	3.744

HPLC racemic (*trans* isomer) (**6l**)



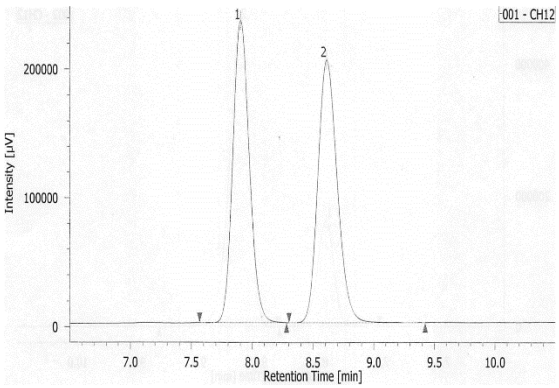
No.	tR [min]	Area	Area%
1	5.717	3381484	49.932
2	6.167	3390639	50.068

HPLC optically active (*cis* isomer) (**6l**)



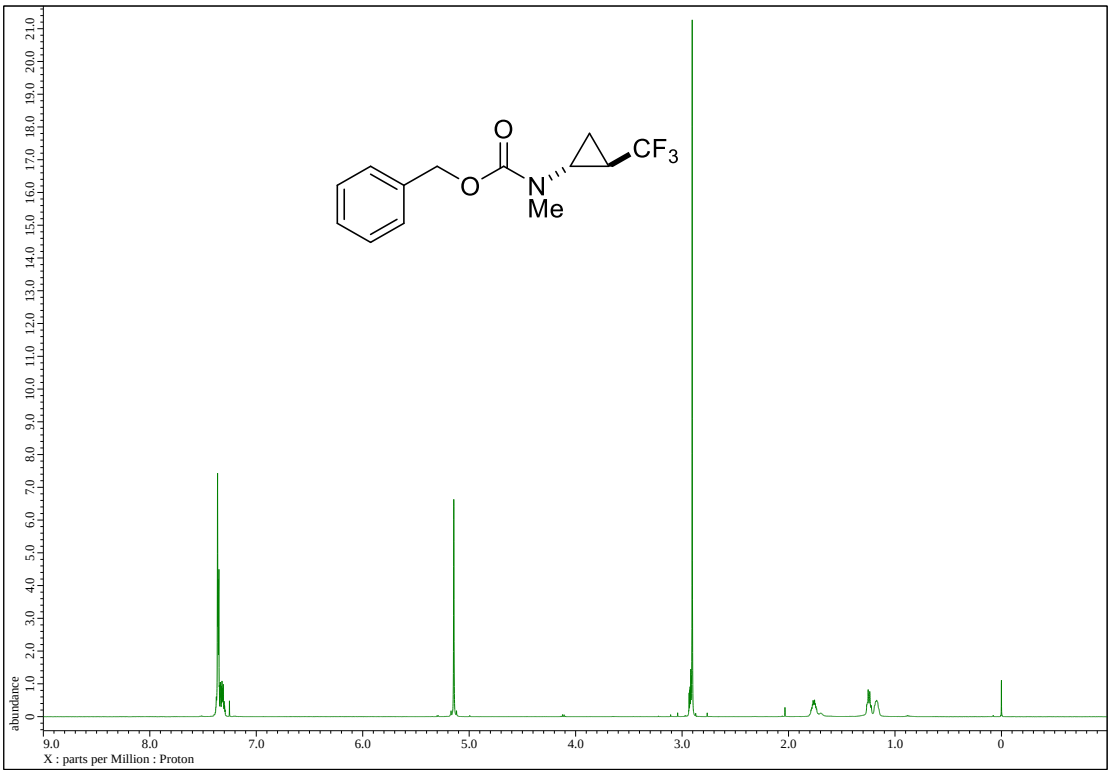
No.	tR [min]	Area	Area%
1	7.955	1554560	22.328
2	8.652	5407764	77.672

HPLC racemic (*cis* isomer) (**6l**)

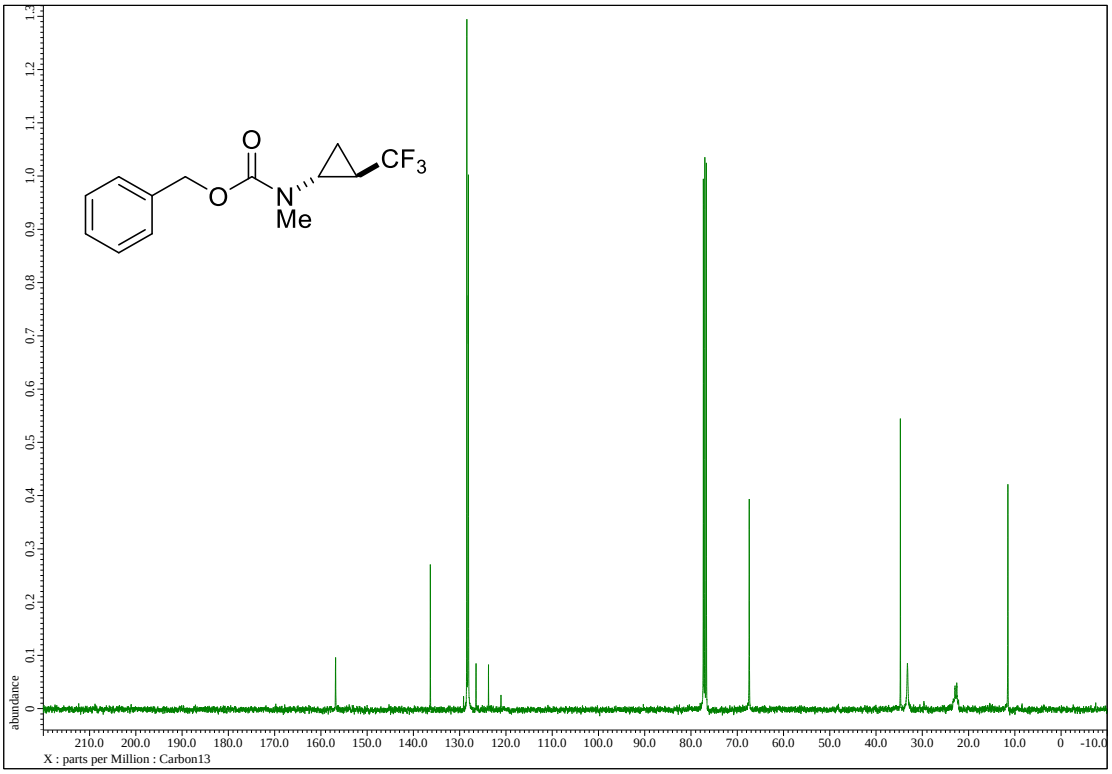


No.	tR [min]	Area	Area%
1	7.902	2230402	49.747
2	8.612	2253048	50.253

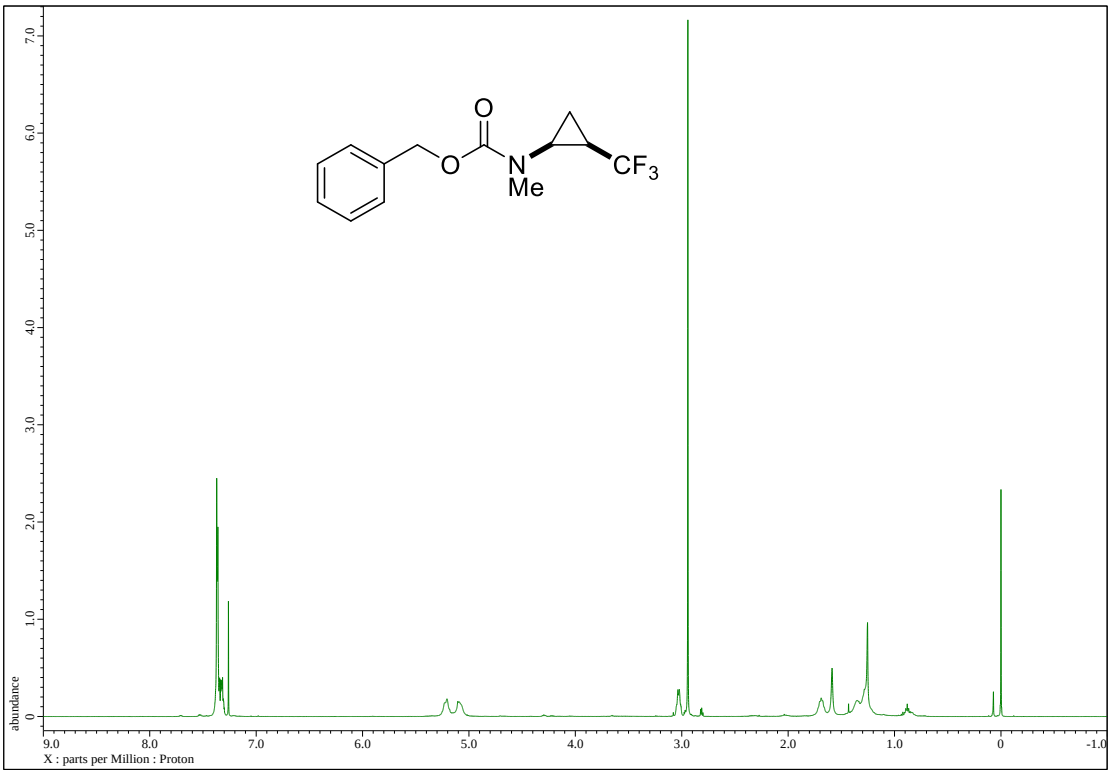
^{1}H NMR (**6m**)



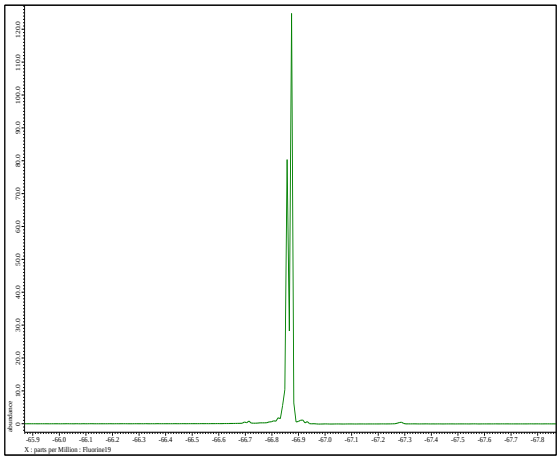
^{13}C NMR (**6m**)



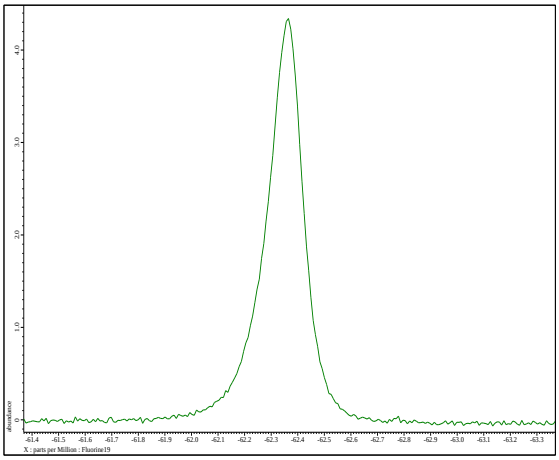
^{1}H NMR (**6m**)



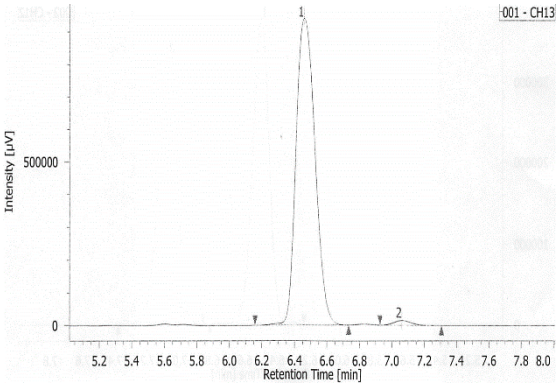
^{19}F NMR (*trans* isomer) (**6m**)



^{19}F NMR (*cis* isomer) (**6m**)

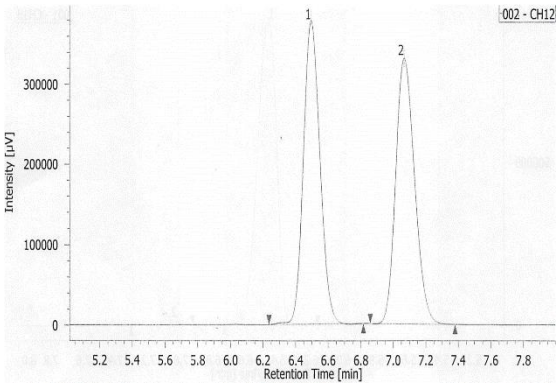


HPLC optically active (*trans* isomer) (**6m**)



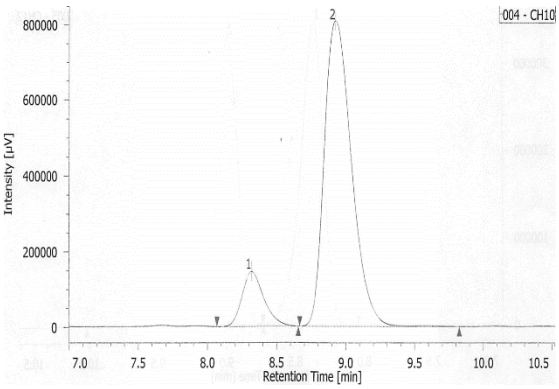
No.	tR [min]	Area	Area%
1	6.457	7662102	98.569
2	7.062	111234	1.431

HPLC racemic (*trans* isomer) (**6m**)



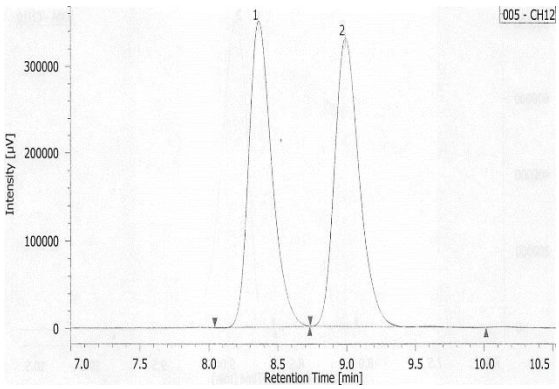
No.	tR [min]	Area	Area%
1	6.495	2683291	50.242
2	7.067	2657488	49.758

HPLC optically active (*cis* isomer) (**6m**)



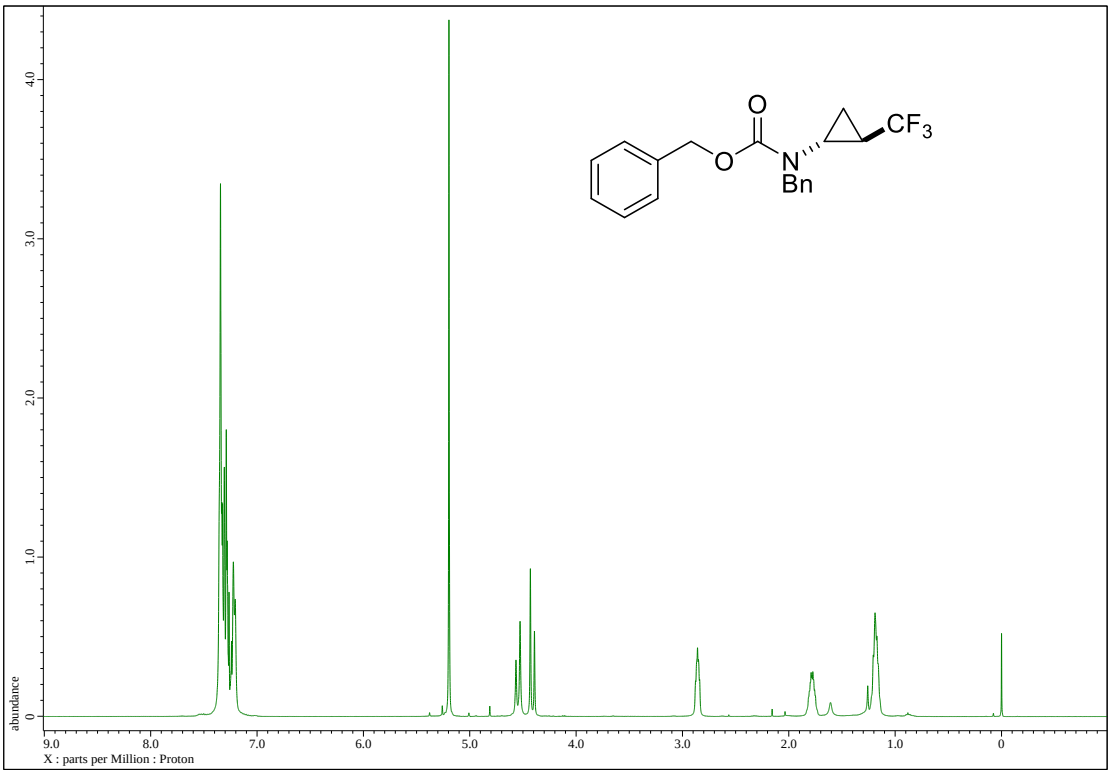
No.	tR [min]	Area	Area%
1	8.318	1600874	12.644
2	8.923	11060758	87.356

HPLC racemic (*cis* isomer) (**6m**)

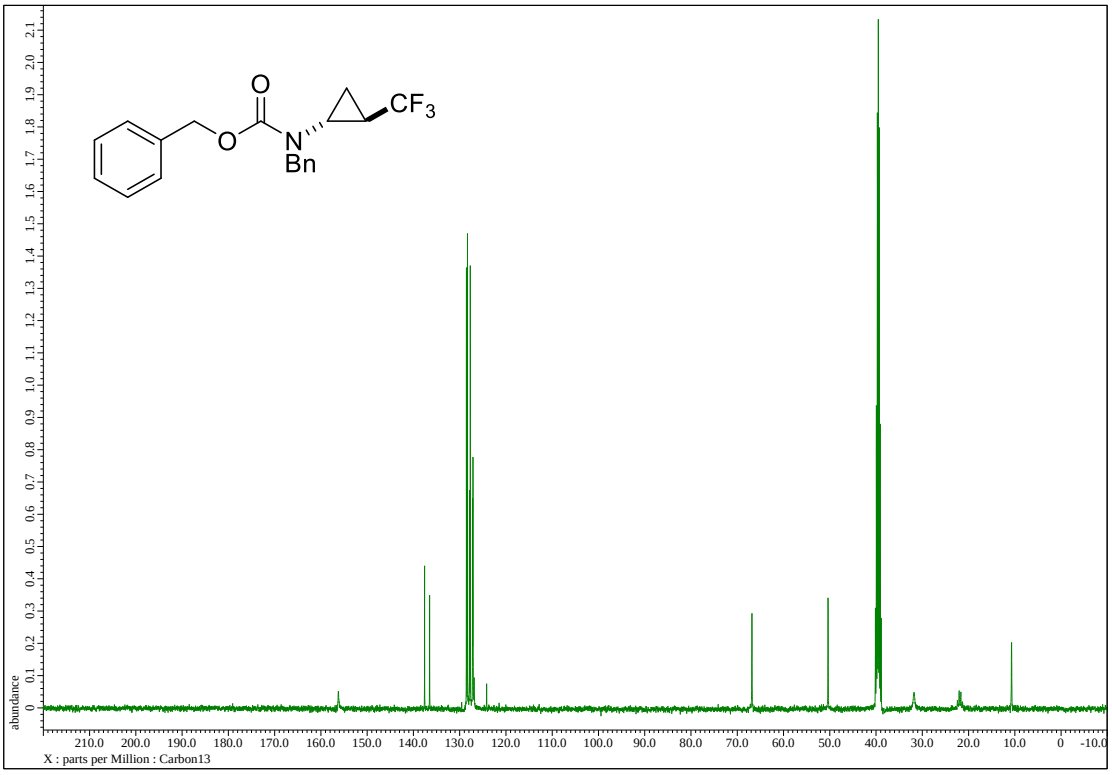


No.	tR [min]	Area	Area%
1	8.362	4056594	49.831
2	8.990	4084052	50.169

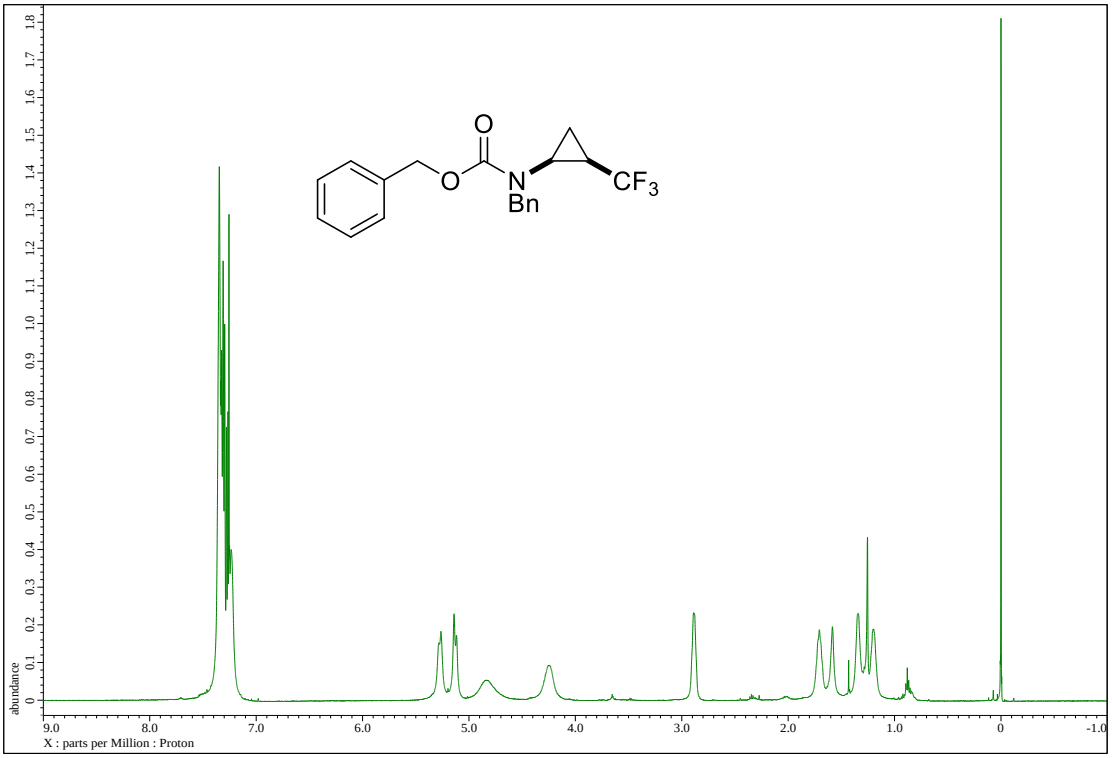
^{1}H NMR (**6n**)



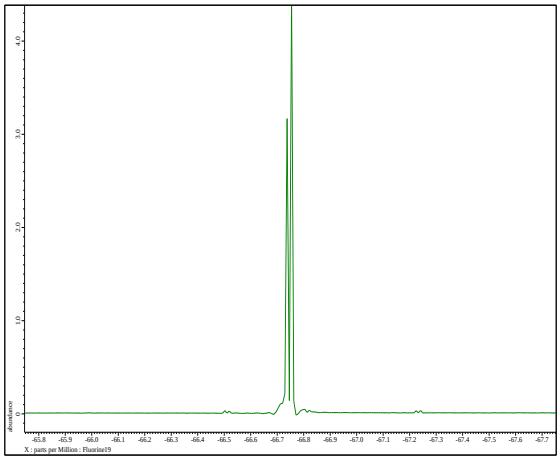
^{13}C NMR (**6n**)



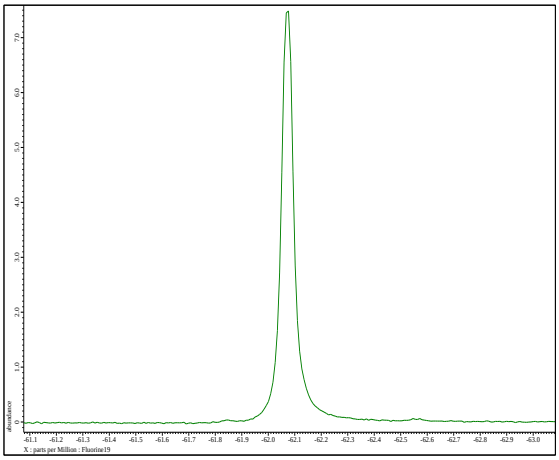
^{1}H NMR (**6n**)



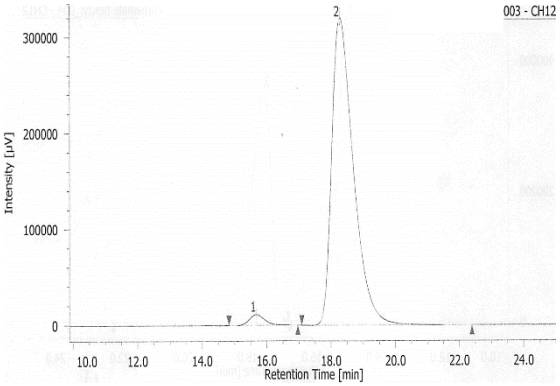
^{19}F NMR (*trans* isomer) (**6n**)



^{19}F NMR (*cis* isomer) (**6n**)

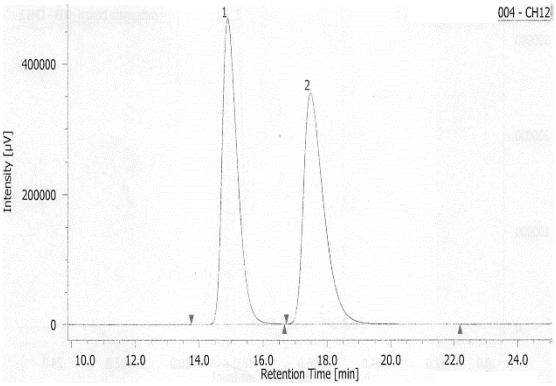


HPLC optically active (*trans* isomer) (**6n**)



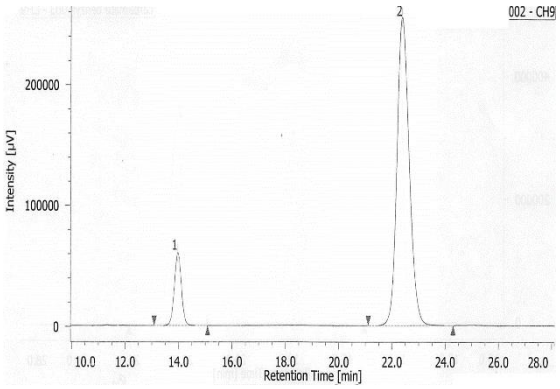
No.	tR [min]	Area	Area%
1	15.678	374430	2.453
2	18.268	14887302	97.547

HPLC racemic (*trans* isomer) (**6n**)



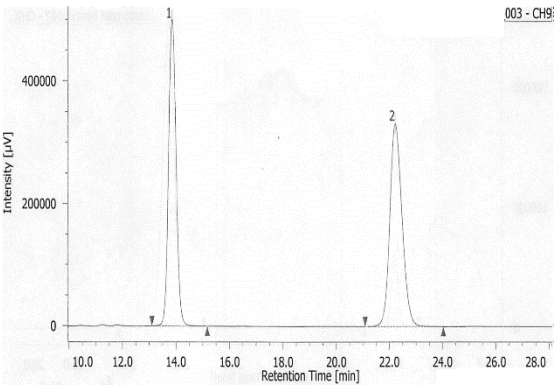
No.	tR [min]	Area	Area%
1	14.849	15471862	49.411
2	17.480	15840597	50,.589

HPLC optically active (*cis* isomer) (**6n**)



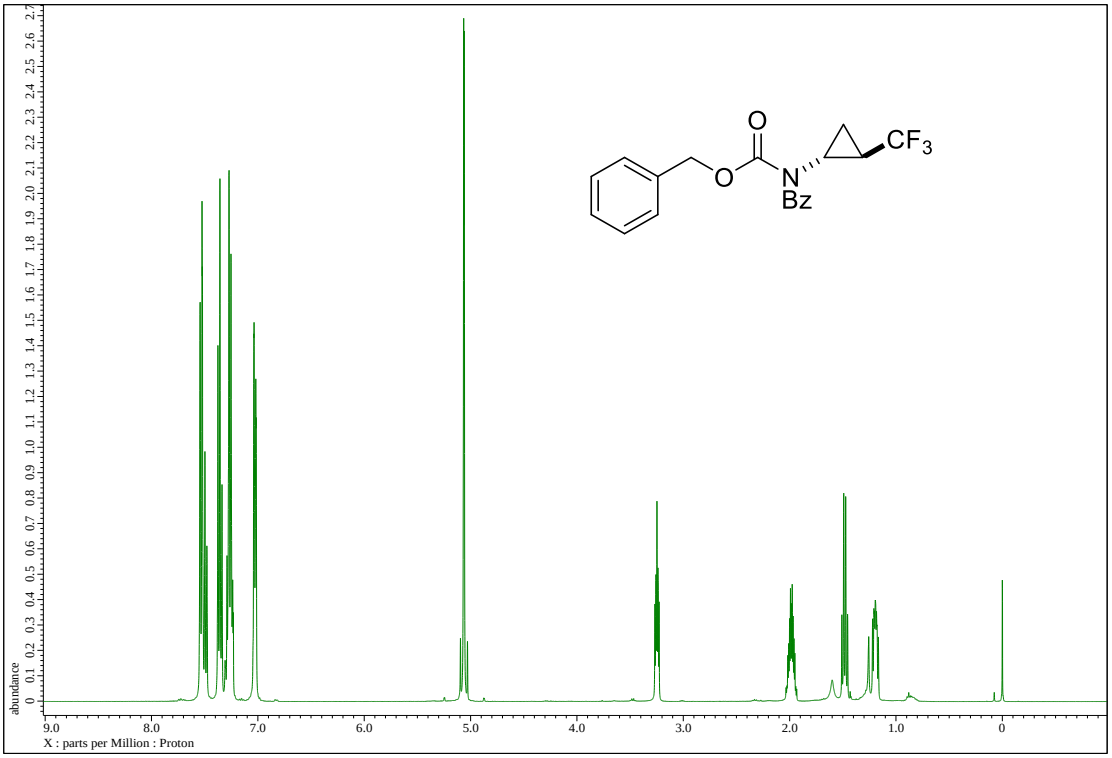
No.	tR [min]	Area	Area%
1	13.962	1110830	11.996
2	22.365	8149243	88.004

HPLC racemic (*cis* isomer) (**6n**)

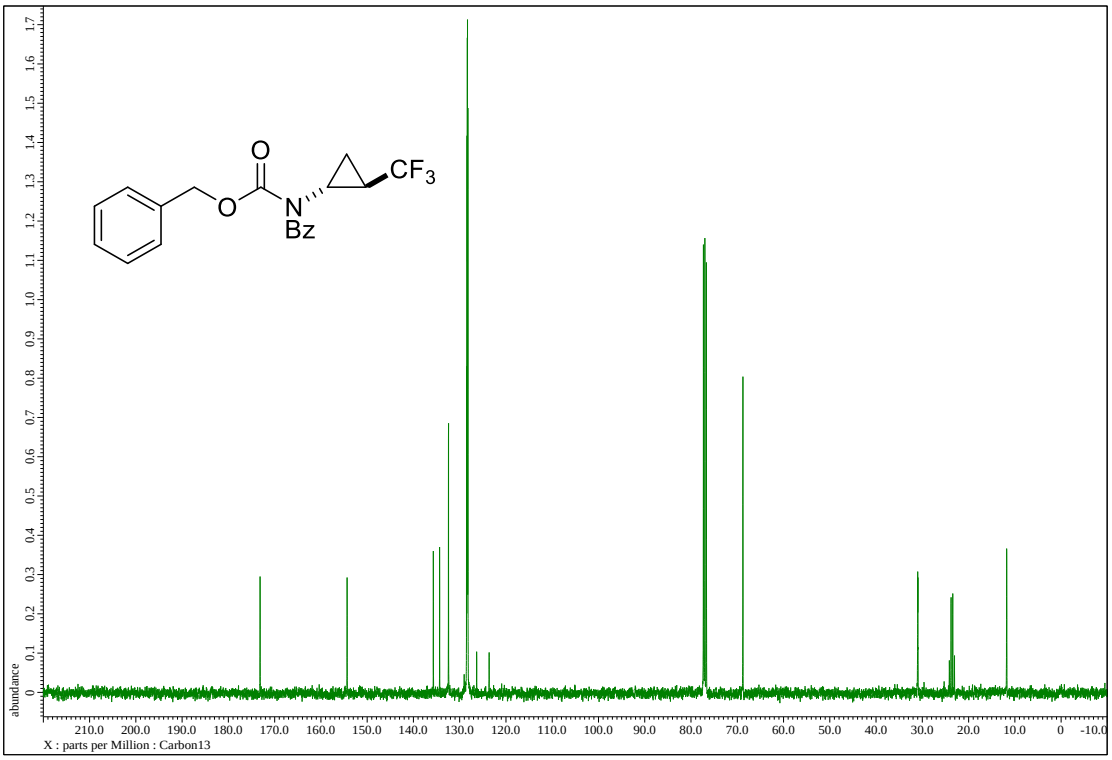


No.	tR [min]	Area	Area%
1	13.847	9903412	48.325
2	22.215	10590055	51.675

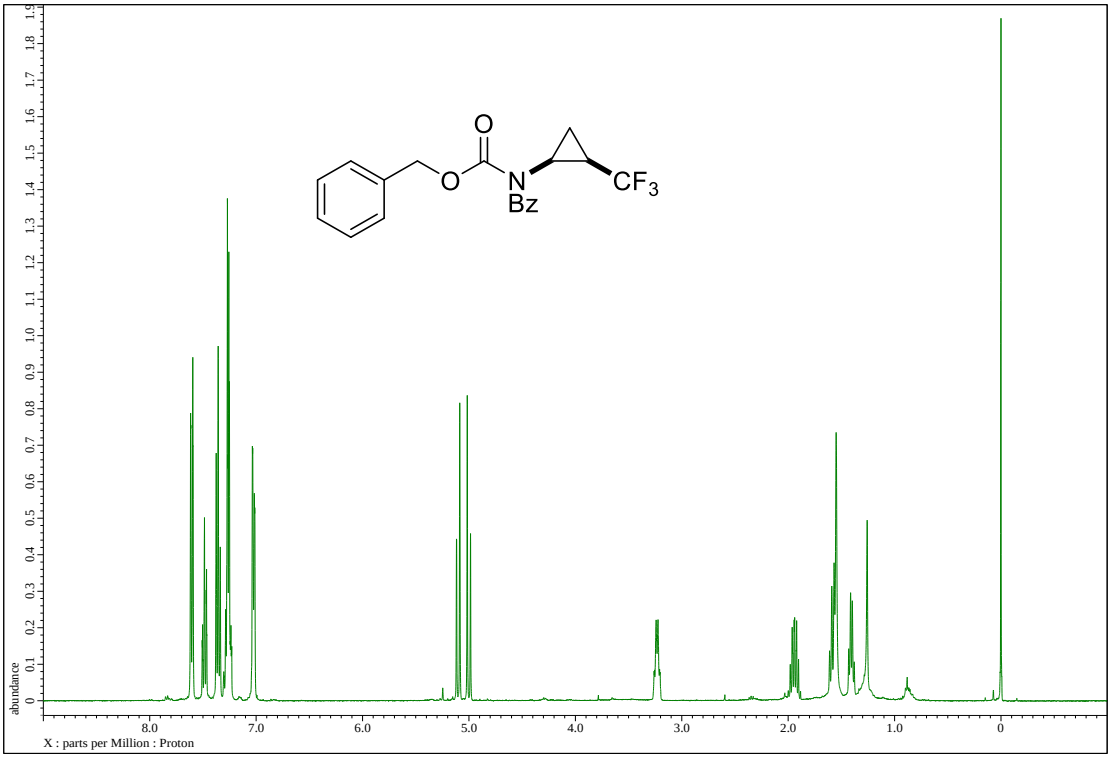
^{1}H NMR (**6o**)



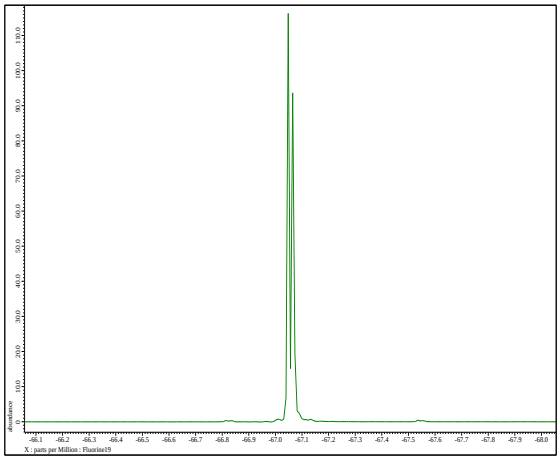
^{13}C NMR (**6o**)



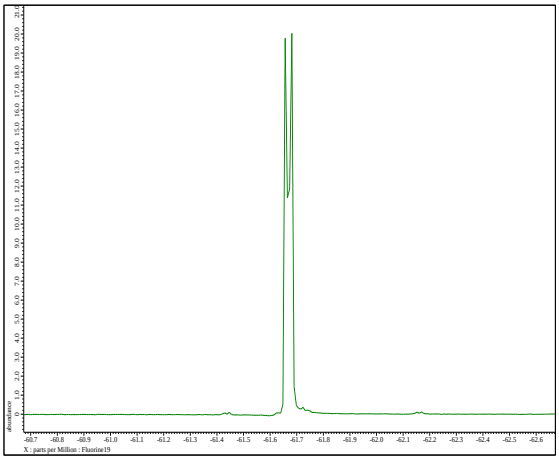
^{1}H NMR (**6o**)


O
O
N
Bz
CF3
abundance
X : parts per Million : Proton
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

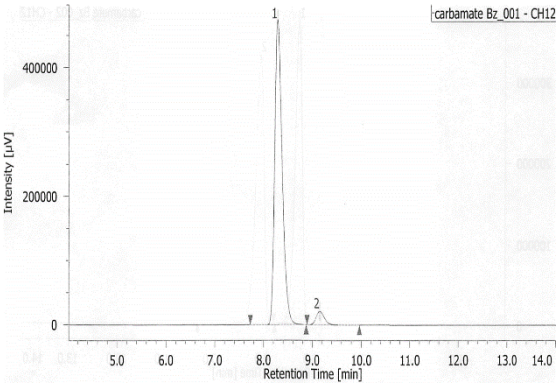
^{19}F NMR (*trans* isomer) (**6o**)



^{19}F NMR (*cis* isomer) (**6o**)

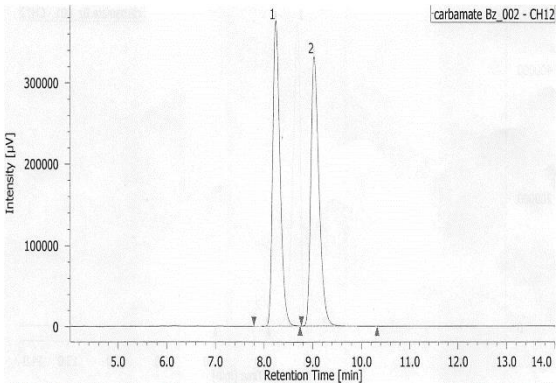


HPLC optically active (*trans* isomer) (**6o**)



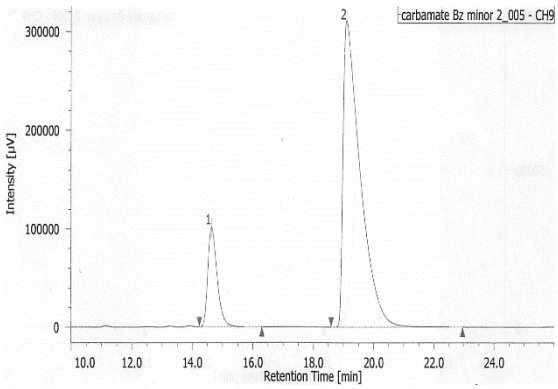
No.	tR [min]	Area	Area%
1	8.285	5021519	95.314
2	9.152	246878	4.686

HPLC racemic (*trans* isomer) (**6o**)



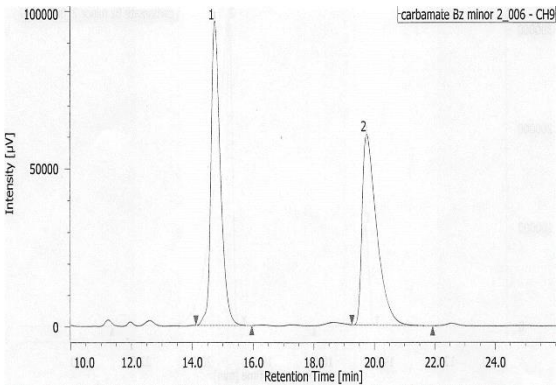
No.	tR [min]	Area	Area%
1	8.238	3929356	49.843
2	9.027	3954182	50.157

HPLC optically active (*cis* isomer) (**6o**)



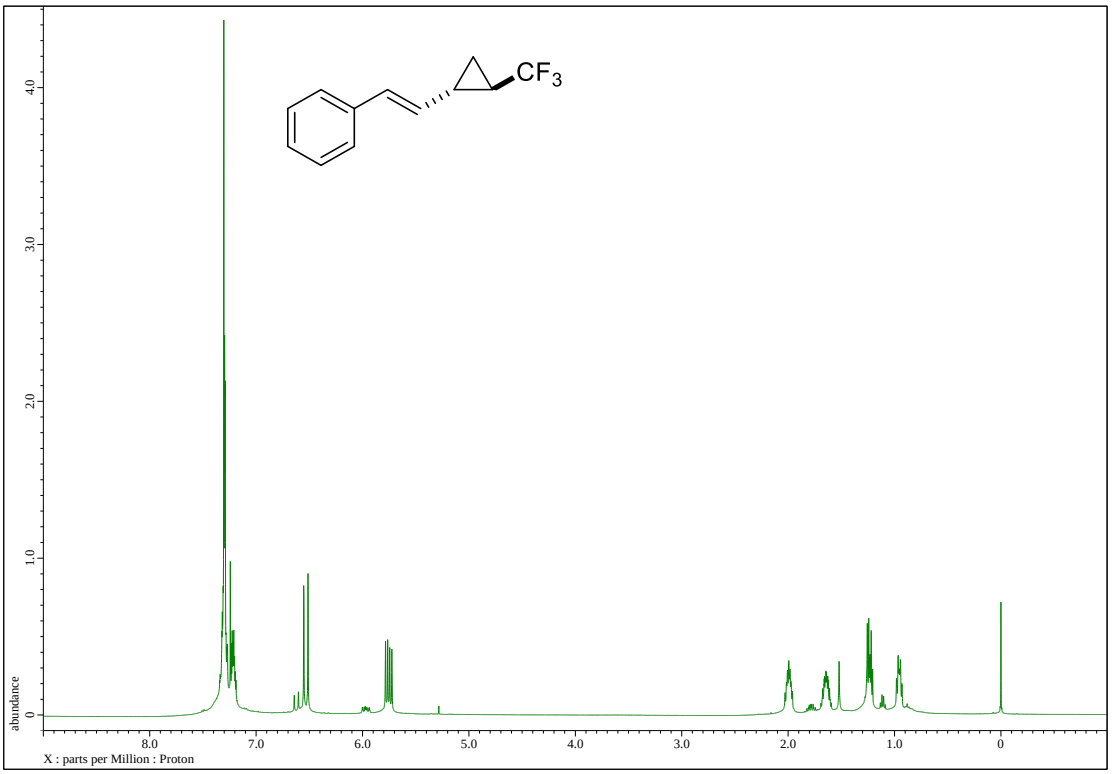
No.	tR [min]	Area	Area%
1	14.630	2149066	14.917
2	19.092	12257452	85.083

HPLC racemic (*cis* isomer) (**6o**)

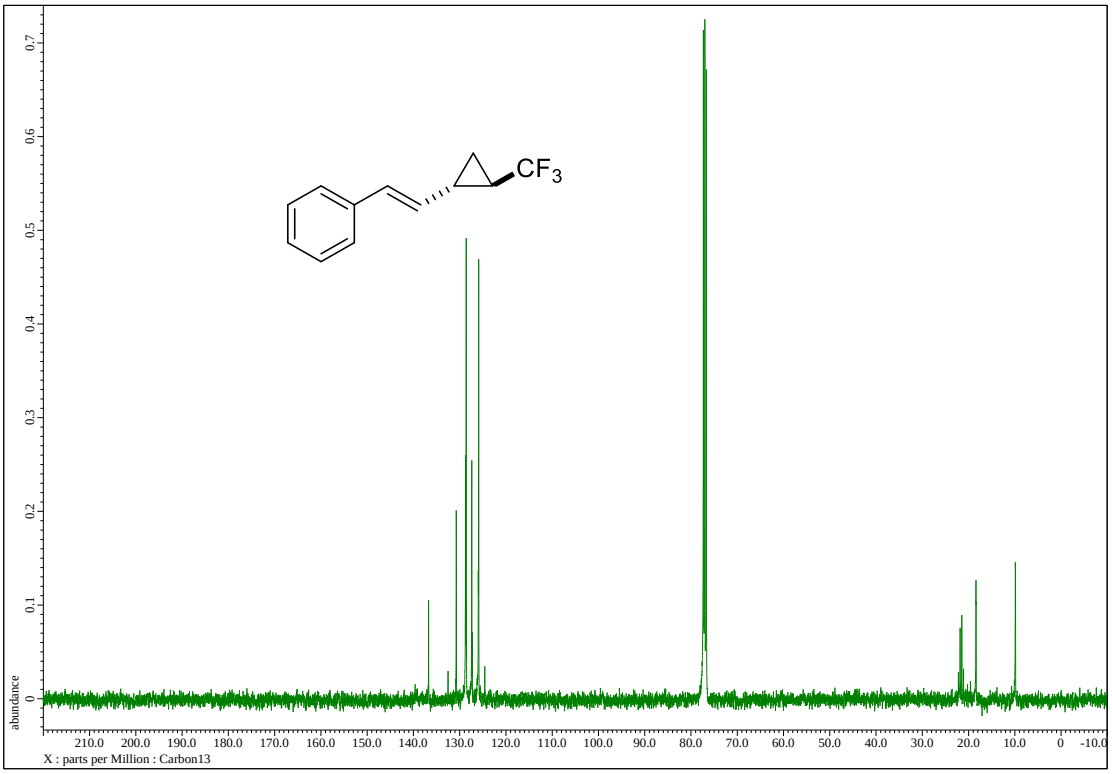


No.	tR [min]	Area	Area%
1	14.737	2094653	50.881
2	19.743	2022101	49.119

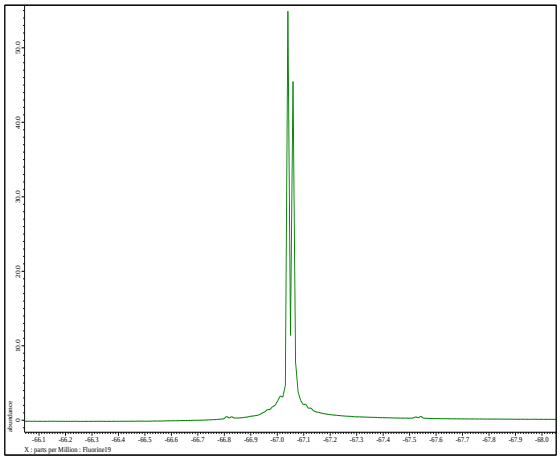
^{1}H NMR (**6p**)



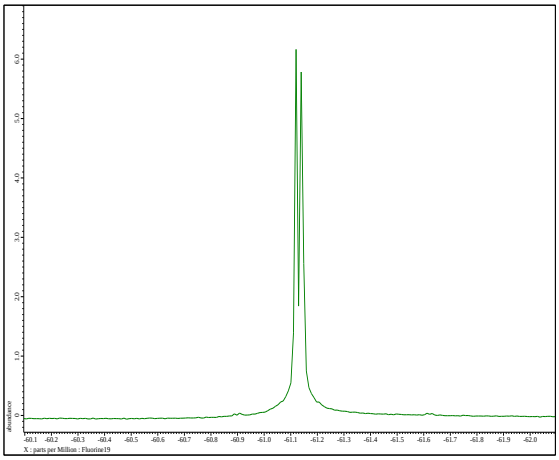
^{13}C NMR (**6p**)



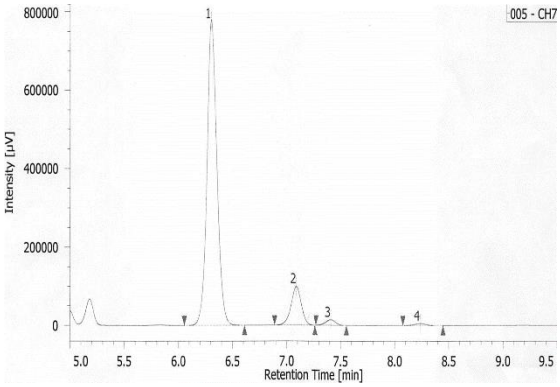
^{19}F NMR (*trans* isomer) (**6p**)



^{19}F NMR (*cis* isomer) (**6p**)

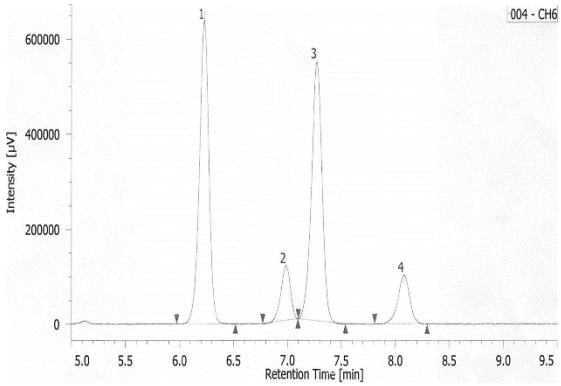


HPLC optically active (**6p**)



No.	tR [min]	Area	Area%
1	6.302	4928182	86.804
2	7.088	648658	11.044
3	7.408	92619	1.588
4	8.235	37876	0.564

HPLC racemic (**6p**)



No.	tR [min]	Area	Area%
1	6.230	3891910	42.619
2	6.987	701429	7.681
3	7.272	3756089	38.864
4	8.080	782521	7.385