Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

An Unusual *trans*-hydrosilylation of prochiral 1,1-disubstituted cyclopropenes to realize different nature of asymmetric palladium and rhodium catalysis

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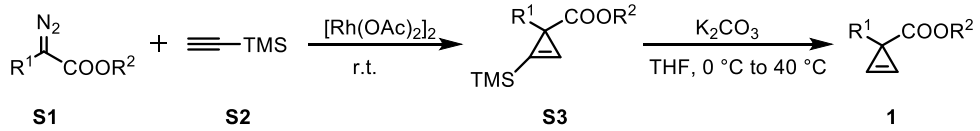
1. General Information

Unless specifically stated, all reagents were commercially obtained and where appropriate, purified prior to use. Dichloromethane (DCM), toluene, were freshly distilled from CaH_2, Ether (Et_2O), tetrahydrofuran (THF) and 1, 4-dioxane were dried and distilled from metal sodium and benzophenone. Alcohol solvents were dried and distilled from metal magnesium. Other commercially available reagents and solvents were used directly without purification. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica (200 - 300 mesh).

NMR spectra were recorded on a Bruker 400-, 500- (400 MHz for ^1H; 100 MHz for ^{13}C, 500 MHz for ^{19}F). The chemical shifts (δ) were quoted in parts per million (ppm) referenced to TMS (0.00 ppm for ^1H NMR) and $CDCl_3$ (77.16 ppm for ^{13}C NMR) The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, dd = doublets of doublet, t = triplet, q = quartet, m = multiplets. Coupling constants, *J*, were reported in Hertz unit (Hz). High resolution mass spectra (HRMS) of the products were obtained on a Bruker Daltonics micro TOF-spectrometer. HPLC analyses were carried out with an Agilent 1260 infinity, Waters AcQuity HPLC or Waters AcQuity UPLC using a chiralcel OD column, a chiralcel AD column, a chiralcel OX column, a Phenomenex chiral INA column, a chiralcel MD column and a chiralcel ND column.

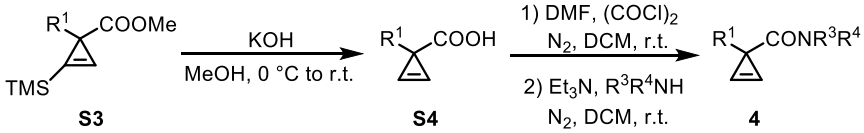
2. Experimental Section

2.1 Preparation of Substrates



S1 S2 S3 1

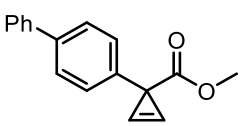
General procedure for the synthesis of cycloprop-2-ene-1-ester 1[1-5]: A solution of **S1** (15.0 mmol) in trimethylsilylacetylene **S2** (10.0 mL) was added via a syringe pump over 18 h to a stirred suspension of $[Rh(OAc)_2]_2$ (1.0 mol%) in **S2** (3.0 mL) under room temperature. After the reaction complete, the reaction was evaporated under reduced pressure to provide an oily residue, which was then purified by silica column chromatography to afford **S3**. To a solution of **S3** (5.0 mmol) and THF (10.0 mL) was added 2.0 M aq. K_2CO_3 (30.0 mL) dropwise at 0 °C. Then the reaction mixture was allowed to warm up to 40 °C and stirred for 20 h. The mixture was extracted three times with DCM. The combined organics were dried with Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography to afford **1**.



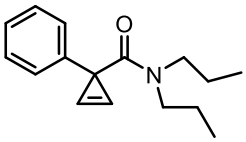
S3 S4 4

General procedure for the synthesis of cycloprop-2-ene-1-carboxamides 4 [1-5]: To a solution of **S3** (5.0 mmol) and methanol (20.0 mL) was added 1.5 M aq. KOH (30.0 mL) dropwise at 0 °C. Then the reaction mixture was allowed to warm up to room temperature and stirred overnight. 2.0 M aq. HCl was added to render the solution acidic (pH = 1-2), and the mixture was extracted three times with DCM. The combined organics were dried with Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography to afford **S4**. Flame-dried round bottom flask was charged with **S4** (2.0 mmol), DMF (2 drops) and freshly distilled anhydrous DCM (10.0 mL) under N_2 atmosphere. Oxalyl chloride (3.0 mmol) was then added dropwise and the mixture was stirred at room temperature for 2 h. The solution was concentrated under

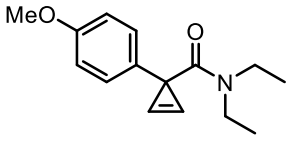
reduced pressure to provide a pale yellow solid or oil residue, which was dissolved in anhydrous DCM (4.0 mL) and added dropwise to a solution of R^3R^4NH (4.0 mmol) and Et_3N (4.0 mmol) in anhydrous DCM (4.0 mL). The reaction mixture was stirred for 18 hours at room temperature and then extracted three times with DCM. The combined organics were dried with Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography to afford **4**.



Methyl 1-([1,1'-biphenyl]-4-yl) cycloprop-2-ene-1-carboxylate (1h): Yellow solid, mp 91.4 - 94.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 - 7.42 (m, 4H), 7.38 - 7.31 (m, 2H), 7.29 - 7.21 (m, 3H), 7.16 (s, 2H), 3.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 141.0, 140.6, 139.6, 128.8, 128.7, 127.3, 127.2, 127.1, 107.7, 52.5, 30.5. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{17}H_{15}O_2$: 251.1067, found: 251.1087.

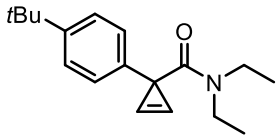


1-phenyl-*N*, *N*-dipropylcycloprop-2-ene-1-carboxamide (4b): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 - 7.19 (m, 2H), 7.19 (s, 2H), 7.13 (t, J = 7.2 Hz, 1H), 7.09 - 7.03 (m, 2H), 3.27 - 3.18 (m, 2H), 3.15 - 3.06 (m, 2H), 1.54 (dq, J = 14.8, 7.2 Hz, 2H), 1.26 (dq, J = 14.8, 7.2 Hz, 2H), 0.85 (t, J = 7.2 Hz, 3H), 0.61 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 143.7, 128.4, 126.4, 126.1, 110.0, 49.5, 46.4, 32.3, 21.7, 20.6, 11.7, 11.3. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{16}H_{22}NO$: 244.1696, found: 244.1791.

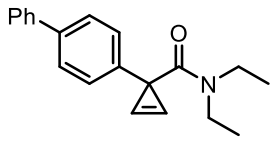


***N*, *N* - diethyl -1- (4-methoxyphenyl) cycloprop -2- ene -1-carboxamide (4f):** White solid, mp 86.4 - 90.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 2H), 7.01 - 6.90 (m, 2H), 6.80 - 6.71 (m, 2H), 3.71 (s, 3H), 3.29 (dq, J = 22.8, 7.2 Hz, 4H), 1.09 (t, J = 6.8 Hz, 3H), 0.84 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 158.3, 135.8, 127.2,

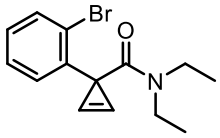
113.9, 110.3, 55.4, 42.0, 39.1, 31.6, 13.9, 12.7. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{15}H_{20}NO_2$: 246.1556, found: 246.1489.



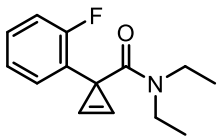
1-(4-(tert-butyl)phenyl)-*N*, *N*-diethylcycloprop-2-ene-1-carboxamide (4j): White solid, mp 94.0 - 95.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.30 (m, 2H), 7.26 (s, 2H), 7.09 - 7.04 (m, 2H), 3.42 (q, J = 7.2 Hz, 2H), 3.36 (q, J = 7.2 Hz, 2H), 1.31 (s, 9H), 1.20 (t, J = 7.2 Hz, 3H), 0.93 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 149.3, 140.6, 125.7, 125.3, 109.8, 42.0, 39.1, 34.5, 31.7, 31.5, 13.8, 12.8. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{18}H_{26}NO$: 272.3927, found: 272.3826.



1 - ([1,1'-biphenyl]-4-yl) -*N*, *N*- diethylcycloprop -2- ene -1-carboxamide (4k): White solid, mp 94.8 - 99.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 - 7.48 (m, 2H), 7.48 - 7.43 (m, 2H), 7.39 - 7.30 (m, 2H), 7.21 (s, 2H), 7.15 - 7.09 (m, 2H), 3.33 (dq, J = 22.4, 7.2 Hz, 4H), 1.12 (t, J = 7.2 Hz, 3H), 0.88 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 140.8, 139.2, 128.9, 127.3, 127.2, 127.1, 126.5, 109.7, 42.0, 39.1, 31.9, 13.9, 12.8. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{20}H_{22}NO$: 292.1696, found: 292.1750.

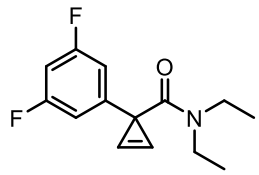


1-(2-bromophenyl)-*N*, *N*-diethylcycloprop-2-ene-carboxamide (4p): White solid, mp 33.0 - 34.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, J = 8.0, 1.2 Hz, 1H), 7.30 (s, 2H), 7.26 (dd, J = 8.0, 2.0 Hz, 1H), 7.22 - 7.16 (m, 1H), 7.01 (td, J = 7.6, 2.0 Hz, 1H), 3.25 (q, J = 6.8 Hz, 4H), 1.04 (t, J = 7.2 Hz, 3H), 0.56 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 142.7, 133.7, 131.2, 128.4, 127.7, 123.5, 110.0, 42.1, 40.5, 34.1, 25.7, 25.1, 13.0, 12.7. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{14}H_{17}BrNO$: 294.0564, found: 294.0488.



***N*, *N*-diethyl-1-(2-fluorophenyl)cycloprop-2-ene-1-carboxamide (4q):** White solid, mp 52.2 - 57.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$)

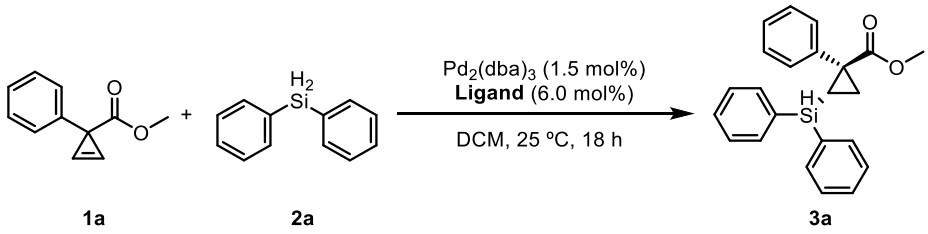
δ 7.36 (d, J = 1.2 Hz, 2H), 7.24 -7.14 (m, 2H), 7.11 - 7.05 (m, 1H), 7.03 - 6.95 (m, 1H), 3.35 (p, J = 6.8 Hz, 4H), 1.11 (t, J = 7.2 Hz, 3H), 0.75 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 161.5 (d, J = 245.7 Hz), 130.8 (d, J = 12.4 Hz), 129.7 (d, J = 3.8 Hz), 128.4 (d, J = 8.0 Hz), 124.3 (d, J = 3.6 Hz), 116.0 (d, J = 21.8 Hz), 110.3 (d, J = 1.9 Hz), 40.8 (d, J = 221.5 Hz), 34.1, 28.4, 25.4 (d, J = 66.2 Hz), 12.9 (d, J = 68.1 Hz). ^{19}F NMR (500 MHz, $CDCl_3$) δ -117.93 - -118.07 (m). HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{14}H_{17}FNO$: 234.1491, found: 234.1289.



1 - (3,5-difluorophenyl) -*N*, *N*- diethylcycloprop -2- ene -1- carboxamide (4r): Yellow solid, mp 53.4 - 58.9 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (s, 2H), 6.68 - 6.42 (m, 3H), 3.34 (q, J = 6.8 Hz, 2H), 3.26 (q, J = 7.2 Hz, 2H), 1.11 (t, J = 7.2 Hz, 3H), 0.93 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 164.5 (d, J = 12.6 Hz), 162.0 (d, J = 13.0 Hz), 148.3 (t, J = 8.2 Hz), 109.6 - 107.9 (m), 102.0 (t, J = 25.4 Hz), 49.1, 40.6 (d, J = 286.9 Hz), 33.0 (d, J = 222.0 Hz), 25.4 (d, J = 67.3 Hz), 13.3 (d, J = 130.2 Hz). ^{19}F NMR (500 MHz, $CDCl_3$) δ -109.61 (t, J = 8.4 Hz). HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{14}H_{16}F_2NO$: 252.1346, found: 252.1194.

2.2 Evaluation of Reaction Parameters

2.2.1 Hydrosilylation of Ester-substituted Cyclopropenes



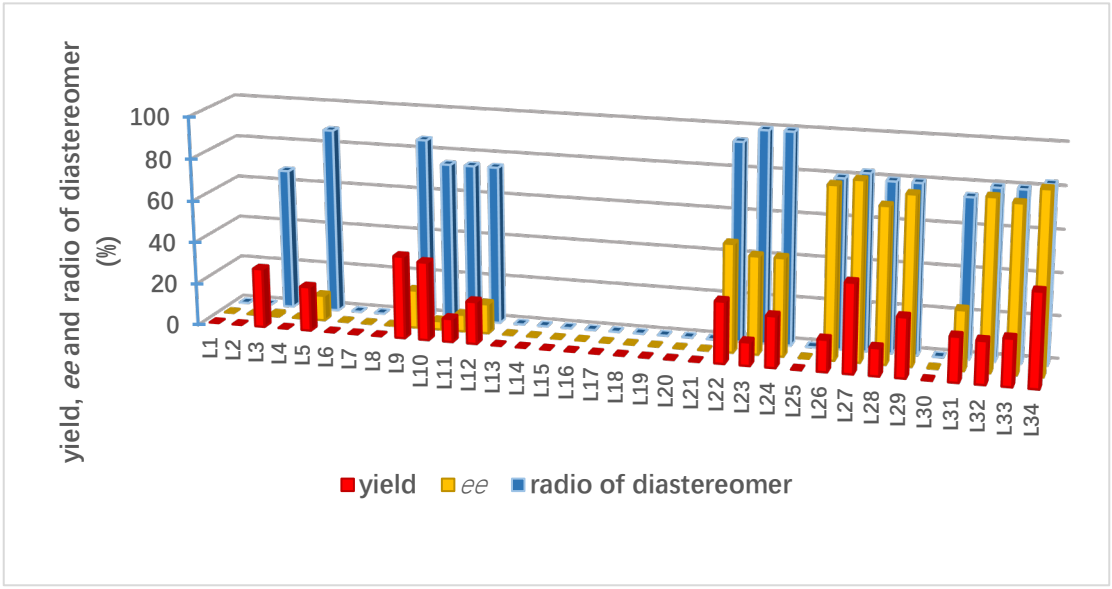
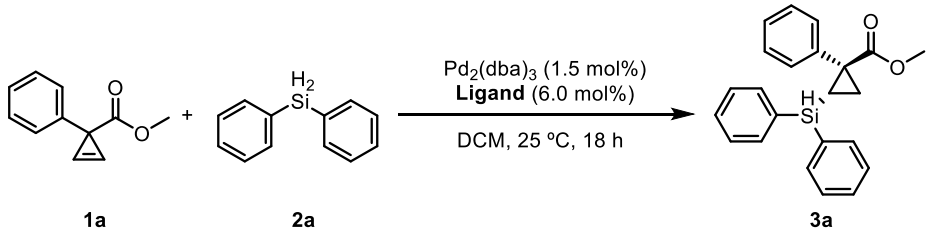


Figure S1. Results from evaluation of ligands for the asymmetric hydrosilylation of 1a (For the detailed reaction data, see Table S1).

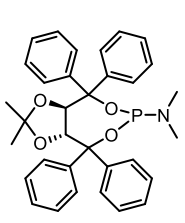
Table S1. Screening of the Chiral Phosphine Ligands[a]



Entry	Ligand	Yield of **3a** (%)[b]	*ee* of **3a** (%)[c]	*dr* of **3a**[d]
1	**L1**	trace	-	-
2	**L2**	nr	-	-
3	**L3**	28	1	2:1
4	**L4**	nr	-	-
5	**L5**	21	-12	7:1
6	**L6**	nr	-	-

7	**L7**	nr	-	-
8	**L8**	trace	-	-
9	**L9**	39	18	6:1
10	**L10**	37	4	3:1
11	**L11**	11	-8	3:1
12	**L12**	20	-14	3:1
13	**L13**	nr	-	-
14	**L14**	nr	-	-
15	**L15**	nr	-	-
16	**L16**	nr	-	-
17	**L17**	nr	-	-
18	**L18**	nr	-	-
19	**L19**	nr	-	-
20	**L20**	nr	-	-
21	**L21**	nr	-	-
22	**L22**	29	-51	16:1
23	**L23**	11	-46	>20:1
24	**L24**	24	-46	>20:1
25	**L25**	nr	-	-
26	**L26**	15	81	4:1
27	**L27**	42	84	5:1
28	**L28**	13	73	4:1
29	**L29**	28	79	4:1
30	**L30**	trace	-	-
31	**L31**	21	28	3:1
32	**L32**	20	80	4:1
33	**L33**	22	78	4:1
34	**L34**	44	85	5:1

[a]Unless otherwise noted, the reaction conditions were as follows: **1a** (0.2 mmol), **2a** (0.26 mmol), DCM (2 mL). [b]Isolated yield. [c]Determined by HPLC. [d]Determined by ^{1}H NMR.



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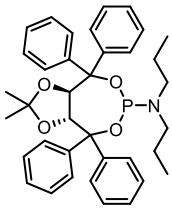
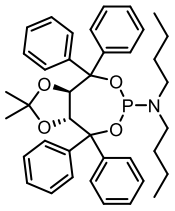
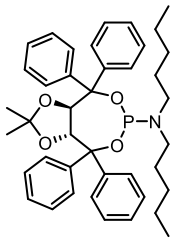


L26



L27



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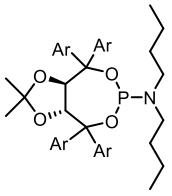
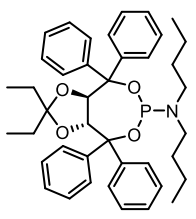


L29, Ar = 4-F-C_6H_4
L30, Ar = 4-OMe-C_6H_4
L31. Ar = 3,5-F-C_6H_3
L32, Ar = 4-TBS-C_6H_4
L33, Ar = 4-*t*-Bu-C_6H_4



L34

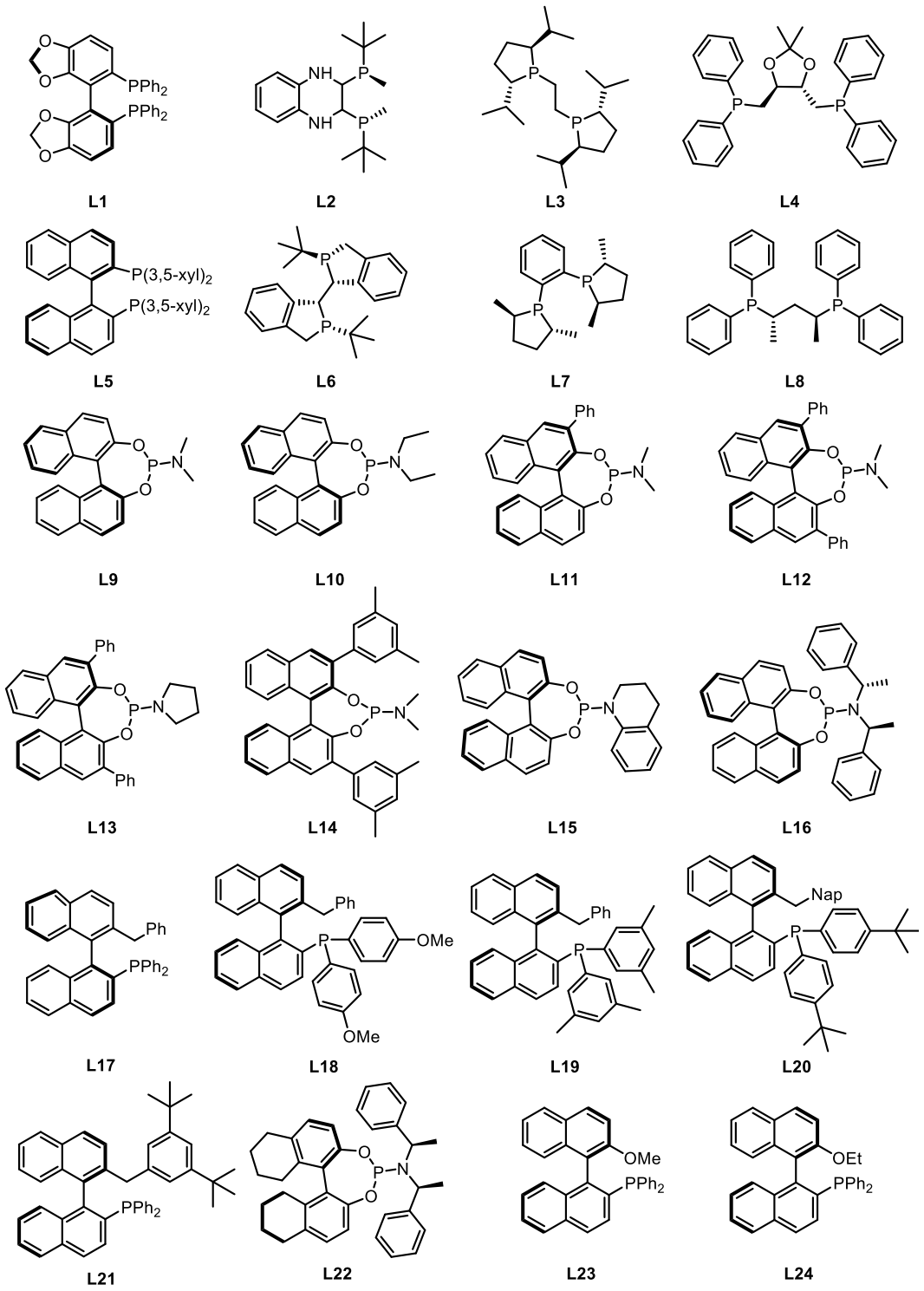
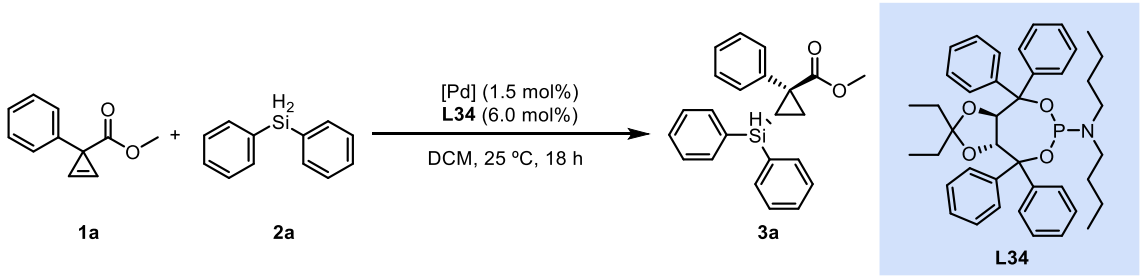


Figure S2. The structures for chiral ligands used in the asymmetric hydrosilylation of 1a (For the detailed reaction data, see Table S1).

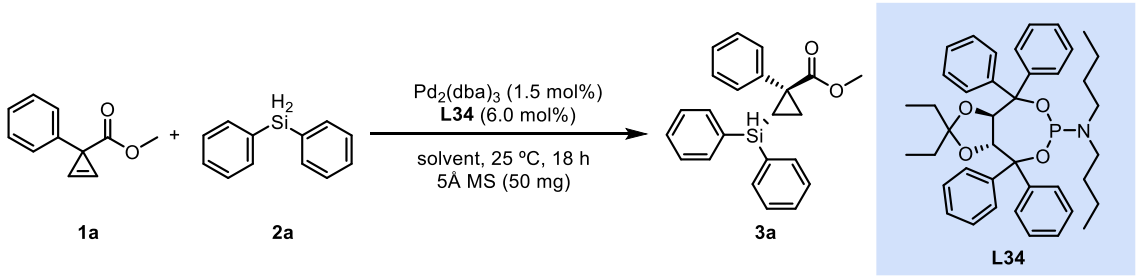
Table S2. Screening of the Palladium Catalysts[a]



Entry	[Pd] Cat.	Yield of **3a** (%)[b]	*ee* of **3a** (%)[c]	*dr* of **3a**[d]
1	$Pd_2(dba)_3$	44	85	5:1
2	$[PdCl(C_3H_5)]_2$	26	70	4:1
3	$Pd(OAc)_2$	20	90	3:1
4	$PdCl_2$	trace	-	-
5	$Pd(cod)Cl_2$	32	38	2:1
6	$Pd(TFA)_2$	36	71	13:1
7	$Pd(CH_3CN)_4(BF)_4$	21	25	2:1
8	$Pd(CH_3CN)_2Cl$	37	39	2:1
9	$Pd(nbd)Cl_2$	29	49	1:1
10	$[Pd(C_9H_9)Cl]_2$	59	76	3:1
11	$[PdCl(2\text{-}Me\text{-}C_3H_4)_2]_2$	20	51	1:1
12	$PdBr_2$	trace	-	-
13	$Pd(dba)_2$	23	80	3:1
14	$Pd(acac)_2$	trace	-	-
15	$Pd_2(dba)_3$[e]	49	88	5:1
16[f]	$[Rh(cod)_2]BF_4$	nr	-	-

[a]Unless otherwise noted, the reaction conditions were as follows: **1a** (0.2 mmol), **2a** (0.26 mmol), DCM (2 mL). [b]Isolated yield. [c]Determined by HPLC. [d]Determined by ^{1}H NMR. [e]5Å MS (50 mg). [f]$[Rh(cod)_2]BF_4$ (3.0 mol%), (*R*)-DTBM-SEGPHOS (3.6 mol%), $[B(2CF_3\text{-}C_6H_3)_4Na]$ (3.0 mol%), Hexane (2 mL), 30 °C.

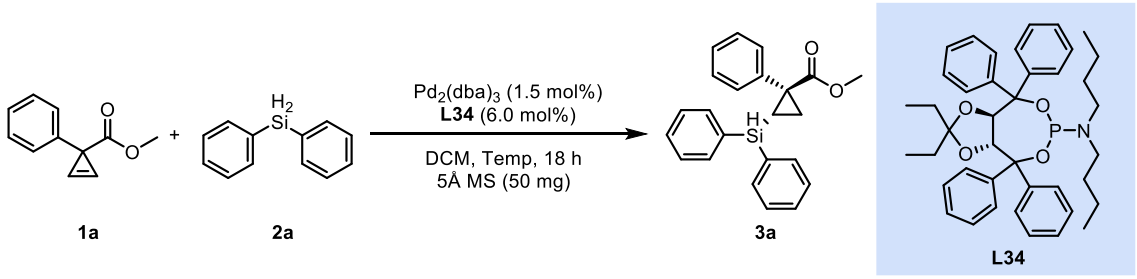
Table S3. Screening of the Solvents[a]



Entry	Solvent	Yield of 3a (%)[b]	*ee* of 3a (%)[c]	*dr* of 3a[d]
1	DCM	49	88	5:1
2	Et_2O	22	91	7:1
3	toluene	trace	-	-
4	CH_3CN	46	84	4:1
5	THF	nr	-	-
6	hexane	21	90	2:1
7	DMF	14	74	4:1
8	dioxane	48	86	3:1
9	DMSO	30	72	13:1
10	DCE	41	80	4:1

[a]Unless otherwise noted, the reaction conditions were as follows: **1a** (0.2 mmol), **2a** (0.26 mmol), solvent (2 mL). [b]Isolated yield. [c]Determined by HPLC. [d]Determined by ^{1}H NMR.

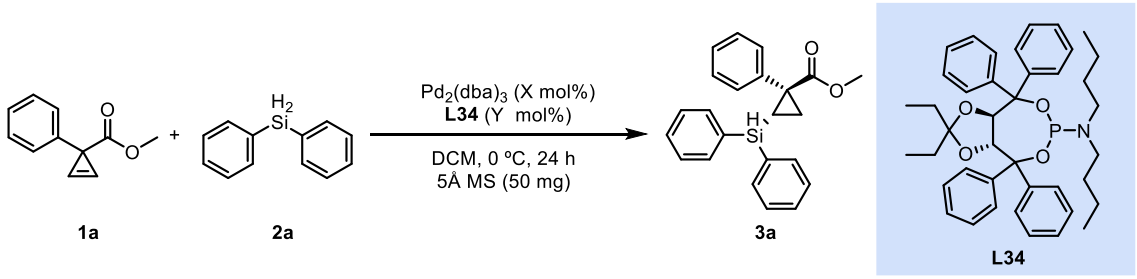
Table S4. Screening of the Temperature in this reaction[a]



Entry	Temp (°C)	Yield of **3a** (%)[b]	*ee* of **3a** (%)[c]	*dr* of **3a**[d]
1	-20[e]	trace	-	-
2	0[f]	49	90	10:1
3	25	49	88	5:1
4	40	43	80	3:1
5	70	38	76	3:1

[a]Unless otherwise noted, the reaction conditions were as follows: **1a** (0.2 mmol), **2a** (0.26 mmol), DCM (2 mL). [b]Isolated yield. [c]Determined by HPLC. [d]Determined by ^{1}H NMR. [e]2 d. [f]24 h

Table S5. Screening of the Loading of Palladium Catalyst with Ligand[a]



Entry	X (mol%)	Y (mol%)	Yield of **3a** (%)[b]	*ee* of **3a** (%)[c]	*dr* of **3a**[d]
1	1.5	6	49	90	10:1
2	3	12	38	89	10:1
3	1.5	3	40	85	5:1
4	0.75	3	32	90	10:1

[a]Unless otherwise noted, the reaction conditions were as follows: **1a** (0.2 mmol), **2a** (0.26 mmol), DCM (2 mL). [b]Isolated yield. [c]Determined by HPLC. [d]Determined by ^{1}H NMR.

2.2.2 Hydrosilylation of Amide-substituted Cyclopropenes

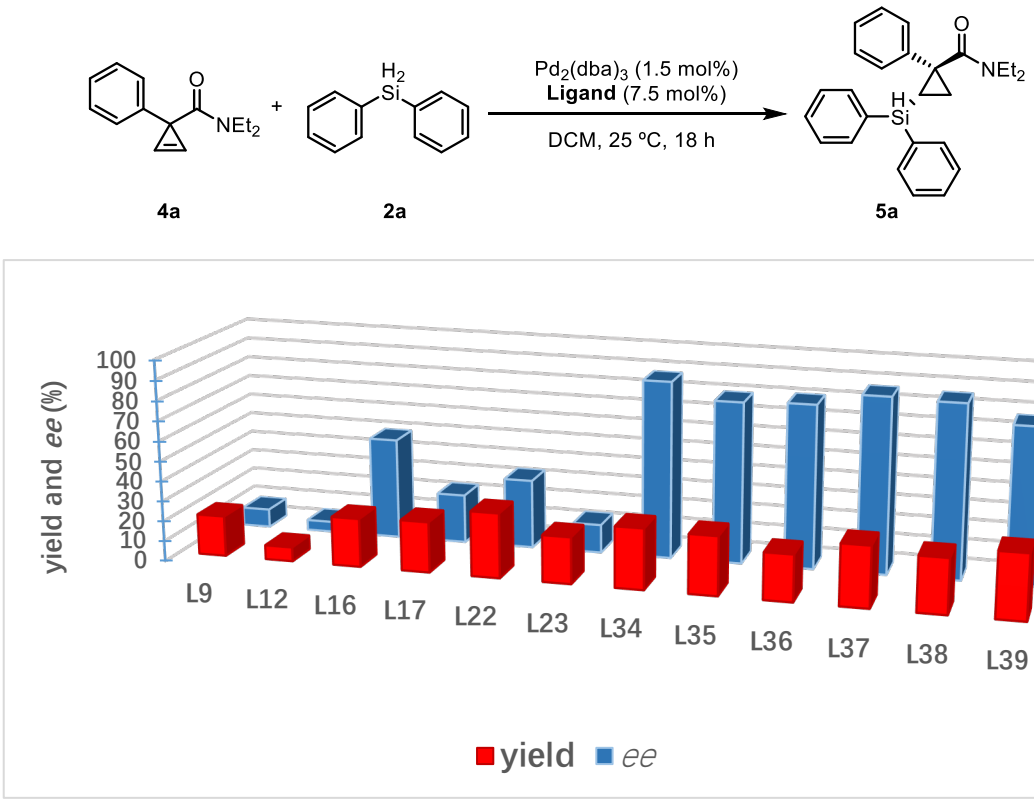
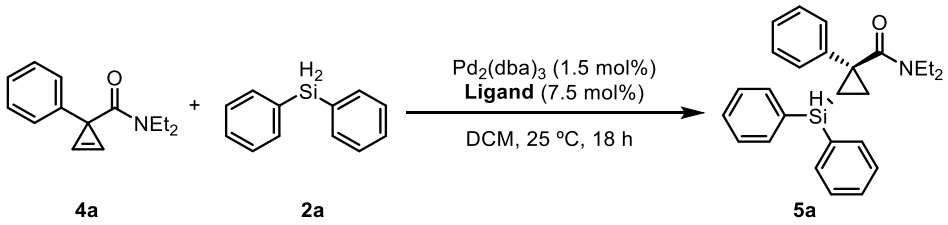


Figure S3. Results from evaluation of ligands for the asymmetric hydrosilylation of 4a (For detailed reaction data, see Table S6).

Table S6. Screening of the Chiral Phosphine Ligands[a]



Entry	Ligand	Yield of **5a** (%)[b]	*ee* of **5a** (%)[c]	*dr* of **5a**[d]
1	**L9**	20	9	>19:1
2	**L12**	7	5	>19:1
3	**L16**	24	50	>19:1
4	**L17**	25	24	>19:1
5	**L22**	32	34	>19:1
6	**L23**	23	14	>19:1
7	**L34**	30	88	>19:1
8	**L35**	29	80	>19:1

9	**L36**	23	81	>19:1
10	**L37**	30	87	>19:1
11	**L38**	27	86	>19:1
12	**L39**	32	77	>19:1

[a]Unless otherwise noted, the reaction conditions were as follows: **4a** (0.2 mmol), **2a** (0.3 mmol), DCM (2 mL). [b]Determined by 1H NMR using dibromomethane as an internal standard. [c]Determined by HPLC. [d]Determined by ^{1}H NMR.

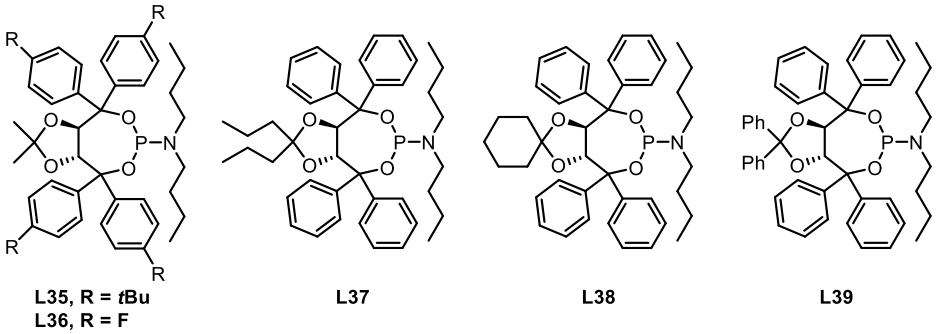
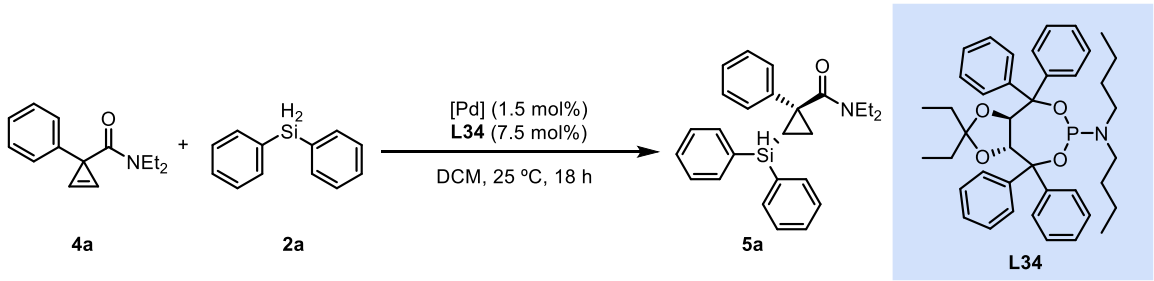


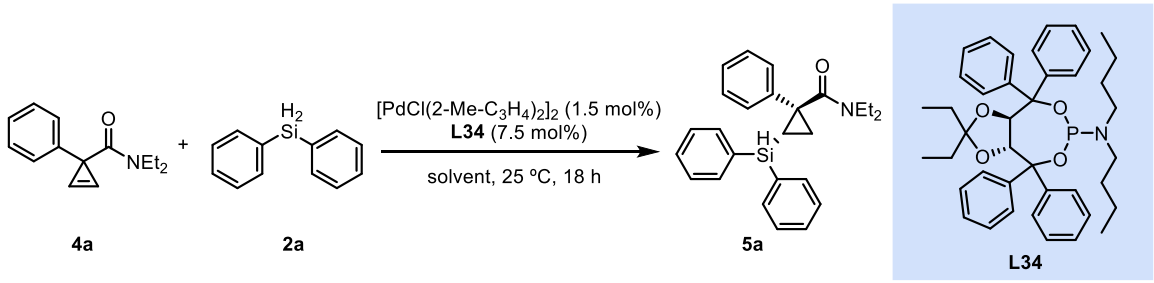
Table S7. Screening of the Palladium Catalysts[a]



Entry	[Pd] Cat.	Yield of **5a** (%)[b]	*ee* of **5a** (%)[c]	*dr* of **5a**[d]
1	$Pd_2(dba)_3$	30	88	>19:1
2	$Pd_2(dba)_3{\cdot}CH_3Cl$	37	91	>19:1
3	$Pd(dba)_2$	45	90	>19:1
4	$[PdCl(C_3H_5)]_2$	50	89	>19:1
5	$[PdCl(2\text{-}Me\text{-}C_3H_4)_2]_2$	50	90	>19:1
6	$Pd(OAc)_2$	trace	-	-
7	$PdCl_2$	nr	-	-
8	$PdBr_2$	nr	-	-
9	$Pd(TFA)_2$	42	89	>19:1
10	$[Pd(C_9H_9)Cl]_2$	trace	-	-

[a]Unless otherwise noted, the reaction conditions were as follows: **4a** (0.2 mmol), **2a** (0.3 mmol), DCM (2 mL). [b]Determined by 1H NMR using dibromomethane as an internal standard. [c]Determined by HPLC. [d]Determined by ^{1}H NMR.

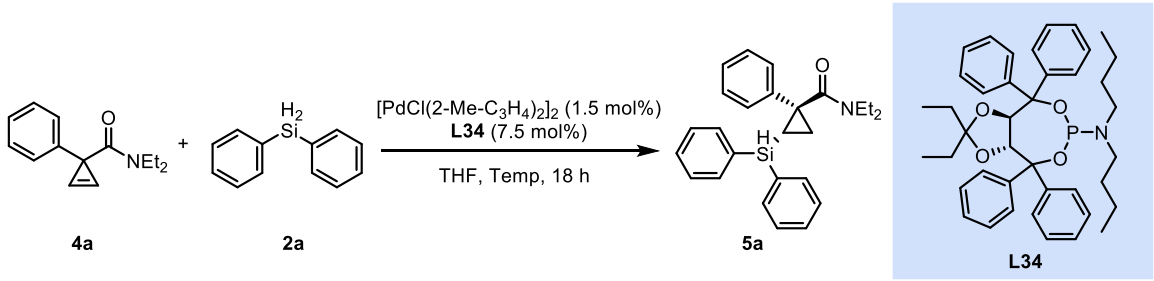
Table S8. Screening of the Solvent[a]



Entry	Solvent	Yield of **5a** (%)[b]	*ee* of **5a** (%)[c]	*dr* of **5a**[d]
1	DCM	50	90	>19:1
2	THF	52	90	>19:1
3	Et_2O	52	88	>19:1
4	Toluene	trace	-	-
5	DMF	nr	-	-
6	Hexane	nr	-	-
7	CH_3CN	46	87	-
8	DMSO	24	90	>19:1
9	1,4-Dioxane	49	90	>19:1
10	DCE	54	86	>19:1
11	2-Me-THF	20	86	>19:1

[a]Unless otherwise noted, the reaction conditions were as follows: **4a** (0.2 mmol), **2a** (0.3 mmol), solvent (2 mL). [b]Determined by 1H NMR using dibromomethane as an internal standard. [c]Determined by HPLC. [d]Determined by ^{1}H NMR.

Table S9. Screening of the Temperature in the reaction[a]

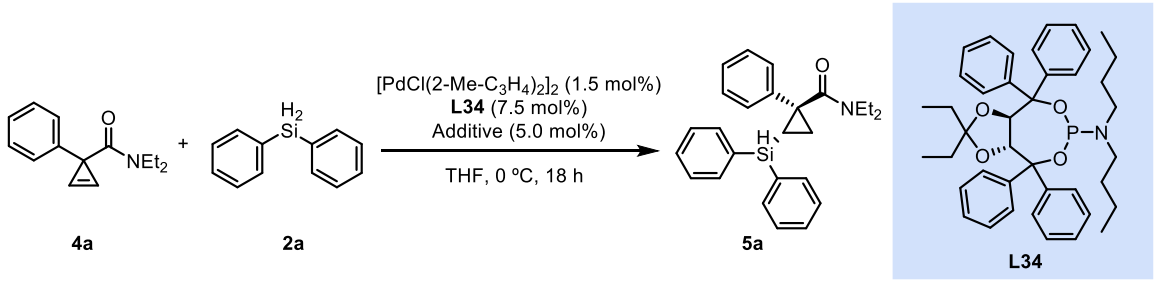


4a 2a 5a L34

Entry	Temp (°C)	Yield of **5a** (%)[b]	*ee* of **5a** (%)[c]	*dr* of **5a**[d]
1	50	26	90	>19:1
2	25	52	90	>19:1
3	0	52	92	>19:1
4	-20	48	92	>19:1
5	-40	52	92	>19:1

[a]Unless otherwise noted, the reaction conditions were as follows: **4a** (0.2 mmol), **2a** (0.3 mmol), THF (2 mL). [b]Determined by 1H NMR using dibromomethane as an internal standard. [c]Determined by HPLC. [d]Determined by ^{1}H NMR.

Table S10. Screening of the Additives[a]

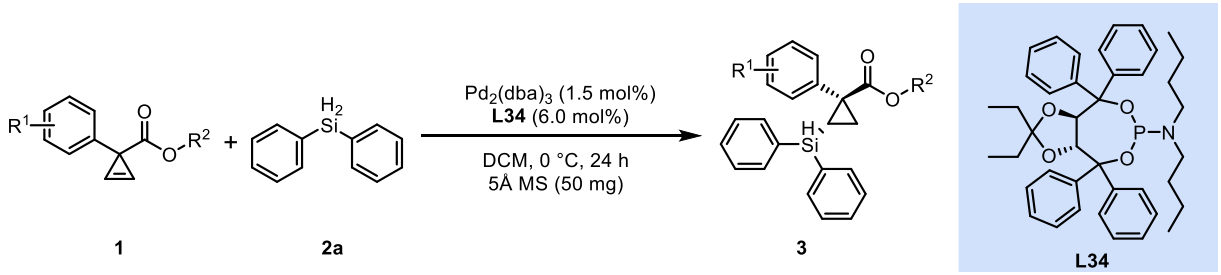


4a 2a 5a L34

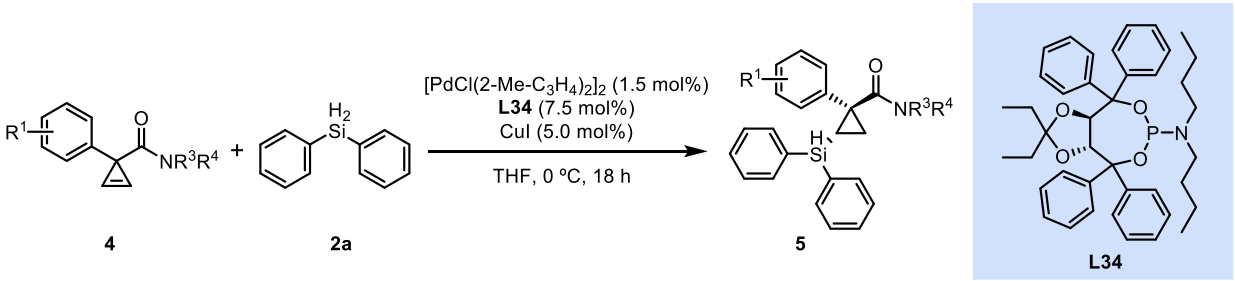
Entry	Additive	Yield of **5a** (%)[b]	*ee* of **5a** (%)[c]	*dr* of **5a**[d]
1	None	52	92	>19:1
2	$(C_6F_5)_3B$	32	92	>19:1
3	$NaBF_4$	52	87	>19:1
4	4(3,5-2(CF_3)Ph)BNa	24	90	>19:1
5	$NaBPh_4$	28	90	>19:1
6	$AgBF_4$	28	80	>19:1
7	$NaBEt_3H$	50	90	>19:1
8	$NaBH_4$	26	91	>19:1
9	$NaB(OCOCH_3)_3H$	40	91	>19:1
10	NEt_3	40	90	>19:1
11	K_2CO_3	46	91	>19:1
12	CuI	62	95	>19:1
13	CuBr	52	95	>19:1
14	CuCl	56	94	>19:1
15	$CuCl_2$	36	93	>19:1
16	$Cu(CH_3CN)_4PF_4$	trace	-	-
17	$Cu(OTf)_2$	16	92	>19:1
18	$Cu(CH_3CN)_4BF_4$	trace	-	-
19	NaI	trace	-	-
20	CuI[e]	60	95	>19:1
21	CuI[f]	nr	-	-
22	PdI_2[g]	trace	-	-

[a]Unless otherwise noted, the reaction conditions were as follows: **4a** (0.2 mmol), **2a** (0.3 mmol), THF (2 mL). [b]Determined by 1H NMR using dibromomethane as an internal standard. [c]Determined by HPLC. [d]Determined by ^{1}H NMR. [d]Determind by ^{1}H NMR. [e]CuI (3.0 mol%). [f]Without [PdCl(2-Me-C_3H_4)$_2$]$_2$. [g]Instead of [PdCl(2-Me-C_3H_4)$_2$]$_2$.

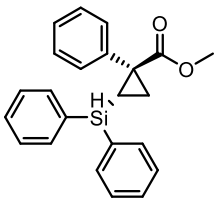
2.3 Asymmetric Synthesis of Silycyclopropanes



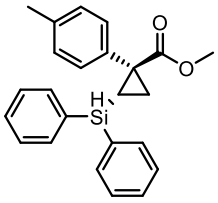
General procedure for asymmetric synthesis of silycyclopropanes 3: Under N_2 atmosphere, $Pd_2(dba)_3$ (2.7 mg, 1.5 mol%), **L34** (7.8 mg, 6.0 mol%) and 5Å MS (50 mg) were dissolved in 2 mL anhydrous DCM, and stirred at room temperature for 30 min. Cycloprop-2-ene-1-ester **1** (0.2 mmol) was added and stirred for 30 min, then the dihydrosilane **2a** (0.26 mmol) was added and stirred at 0 °C for 24 h. The mixture was filtered through celite and the filtrate was concentrated. A portion of the residue was analyzed with ^{1}H NMR to determine the diastereomeric ratio and recovered. The crude product was purified by column chromatography to give the products **3**.



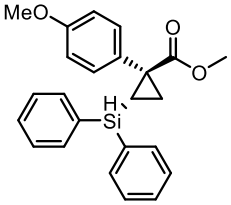
General procedure for asymmetric synthesis of silycyclopropanes 5: Under N_2 atmosphere, $[PdCl(2\text{-}Me\text{-}C_3H_4)_2]_2$ (1.5 mg, 1.5 mol%), **L34** (9.8 mg, 7.5 mol%) and CuI (1.9 mg, 5.0 mol%) were dissolved in 2 mL anhydrous THF, and stirred at room temperature for 20 min. Cycloprop-2-ene-1-carboxamide **4** (0.2 mmol) was added and stirred for 20 min, then the dihydrosilane **2a** (0.3 mmol) was added and stirred at 0 °C for 18 h. The mixture was filtered through celite and the filtrate was concentrated. A portion of the residue was analyzed with ^{1}H NMR to determine the diastereomeric ratio and recovered. The crude product was purified by column chromatography to give the products **5**.



Methyl (1*S*, 2*S*) - 2 - (diphenylsilyl) - 1 - phenylcyclopropane - 1 - carboxylate (3a): Yellow oil (39.4 mg, 55% yield), purified by column chromatography (Al_2O_3, PE/EA= 25:1). $[\alpha]_D^{25}$ = 18.7 (c = 0.75, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 - 7.41 (m, 2H), 7.34 - 7.20 (m, 4H), 7.18 - 7.07 (m, 7H), 7.06 - 7.00 (m, 2H), 4.11 (d, J = 4.4 Hz, 1H), 3.54 (s, 3H), 1.87 (dd, J = 10.8, 3.2 Hz, 1H), 1.54 (ddd, J = 10.8, 8.4, 4.4 Hz, 1H), 1.44 (dd, J = 8.4, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 137.0, 135.4, 135.3, 133.8, 133.3, 131.4, 129.9, 129.6, 128.1, 127.9, 127.9, 127.4, 52.8, 33.5, 19.6, 13.9. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{23}H_{22}NaO_2Si$: 381.5110, found: 381.5123. HPLC: Chiralpak OX-H and Phenomenex column (hexanes: isopropanol = 95.5:0.5, 0.6 mL/min, 211 nm, 90% *ee*, *dr* = 10:1). tR = 48.770 min (major), tR = 67.476 min (minor).

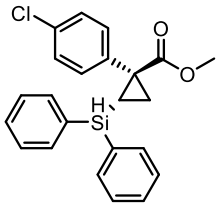


Methyl (1*S*, 2*S*) - 2 - (diphenylsilyl) - 1 - (*p* - tolyl) cyclopropane - 1 - carboxylate (3b): Yellow oil (25.3 mg, 34% yield), purified by column chromatography (Al_2O_3, PE/EA= 25:1). $[\alpha]_D^{25}$ = 16.2 (c = 0.63, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 - 7.41 (m, 1H), 7.36 - 7.10 (m, 8H), 6.96 - 6.83 (m, 4H), 4.13 (d, *J* = 4.4 Hz, 1H), 3.54 (s, 3H), 2.25 (s, 3H), 1.84 (dd, *J* = 10.8, 3.2 Hz, 1H), 1.57 - 1.46 (m, 1H), 1.41 (dd, *J* = 8.4, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 137.0, 135.4, 135.3, 134.0, 133.9, 133.4, 131.2, 129.8, 129.5, 128.7, 128.1, 127.8, 52.8, 33.1, 21.3, 19.6, 14.0. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{24}H_{24}NaO_2Si$: 395.1438, found: 395.1447. HPLC: Chiralpak OD-H column (hexanes: isopropanol = 99:1, 0.6 mL/min, 211 nm, 90% *ee*, *dr* = 13:1). tR = 14.519 min (major), tR = 21.737 min (minor).

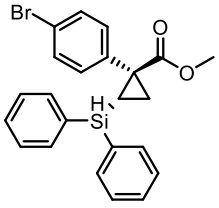


Methyl (1*S*, 2*S*) - 2 - (diphenylsilyl) - 1 - (4 - methoxyphenyl) cyclopropane - 1 - carboxylate (3c): Yellow oil (48.2 mg, 62% yield), purified by column chromatography (Al_2O_3, PE/EA= 15:1). $[\alpha]_D^{25}$ = 14.1 (c = 0.60, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.50

- 7.39 (m, 2H), 7.35 - 7.25 (m, 3H), 7.23 - 7.12 (m, 5H), 6.99 - 6.89 (m, 2H), 6.72 - 6.55 (m, 2H), 4.15 (d, J = 4.8 Hz, 1H), 3.71 (s, 3H), 3.54 (s, 3H), 1.85 (dd, J = 10.8, 3.2 Hz, 1H), 1.50 (ddd, J = 10.8, 8.4, 4.0 Hz, 1H), 1.41 (dd, J = 8.4, 3.2 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ 175.6, 158.8, 135.4, 135.2, 133.9, 133.4, 132.3, 129.9, 129.6, 129.2, 128.1, 127.8, 113.3, 55.3, 52.8, 32.7, 19.7, 14.1. HRMS (ESI) m/z: [M+Na]+ calculated for $C_{24}H_{24}NaO_3Si$: 411.1387, found: 411.1400. HPLC: Chiralpak OD-H column (hexanes: isopropanol = 99:1, 0.6 mL/min, 211 nm, 89% *ee*, *dr* = 9:1). tR = 25.447 min (major), tR = 40.328 min (minor).

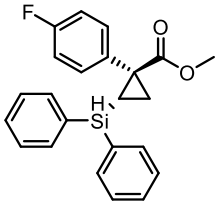


Methyl (1*S*, 2*S*) - 1 - (4 - chlorophenyl) - 2 - (diphenylsilyl) cyclopropane - 1 - carboxylate (3d): Yellow oil (36.9 mg, 47% yield), purified by column chromatography (Al_2O_3, PE/EA= 25:1). $[\alpha]_D^{25}$ = 75.1 (c = 0.38, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 - 7.40 (m, 2H), 7.35 - 7.21 (m, 4H), 7.19 - 7.14 (m, 4H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 4.18 (d, *J* = 4.4 Hz, 1H), 3.55 (s, 3H), 1.88 (dd, *J* = 10.7, 3.6 Hz, 1H), 1.57 - 1.51 (m, 1H), 1.41 (dd, *J* = 8.4, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 135.5, 135.4, 135.2, 133.4, 133.3, 132.8, 132.6, 130.0, 129.7, 128.2, 128.1, 127.9, 52.9, 32.8, 19.5, 14.0. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{23}H_{21}ClNaO_2Si$: 415.0892, found: 415.0901. HPLC: Chiralpak Phenomenex column (hexanes: isopropanol = 99:1, 0.6 mL/min, 211 nm, 94% *ee*, *dr* = 8:1). tR = 13.925 min (major), minor enantiomer tR = 20.578 min (minor).

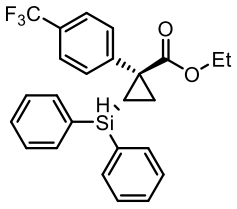


Methyl (1*S*, 2*S*) - 1 - (4 - bromophenyl) - 2 - (diphenylsilyl) cyclopropane - 1 - carboxylate (3e): Yellow oil (49.9 mg, 57% yield), purified by column chromatography (Al_2O_3, PE/EA= 25:1). $[\alpha]_D^{25}$ = 13.4 (c = 0.54, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 - 7.40 (m, 2H), 7.38 - 7.21 (m, 4H), 7.20 - 7.15 (m, 6H), 6.92 - 6.84 (m, 2H), 4.19 (d, *J* = 4.0 Hz, 1H), 3.55 (s, 3H), 1.88 (dd, *J* = 10.8, 3.6 Hz, 1H), 1.53 (ddd, *J* = 10.8, 8.4, 4.0 Hz, 1H), 1.41 (dd, *J* = 8.4, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 136.1,

135.4, 135.2, 133.4, 133.0, 132.8, 131.0, 130.0, 129.7, 128.2, 128.0, 121.5, 52.9, 32.9, 19.5, 14.0. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{23}H_{21}BrNaO_2Si$: 459.0386, found: 459.0395. HPLC: Chiralpak OD-H column (hexanes: isopropanol = 99:1, 0.6 mL/min, 211 nm, 92% *ee*, *dr* = 5:1). tR = 15.069 min (major), tR = 22.796 min (minor).

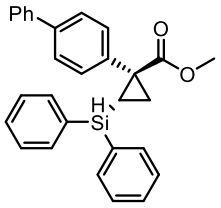


Methyl (1*S*, 2*S*) - 2 - (diphenylsilyl) - 1 - (4 - fluorophenyl) cyclopropane - 1 - carboxylate (3f): Yellow oil (36.1 mg, 48% yield), purified by column chromatography (Al_2O_3, PE/EA= 25:1). $[\alpha]_D^{25}$ = 12.7 (c = 0.61, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 - 7.41 (m, 2H), 7.36 - 7.26 (m, 3H), 7.24 - 7.10 (m, 5H), 7.02 - 6.94 (m, 2H), 6.83 - 6.70 (m, 2H), 4.16 (d, *J* = 4.4 Hz, 1H), 3.55 (s, 3H), 1.88 (dd, *J* = 10.8, 3.2 Hz, 1H), 1.57 - 1.46 (m, 1H), 1.41 (dd, *J* = 8.4, 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 162.1 (d, *J* = 244.5 Hz), 135.4, 135.12, 133.5, 133.0 (d, *J* = 5.8 Hz), 132.8 (d, *J* = 5.3 Hz),132.8, 130.0, 129.7, 128.2, 127.9, 114.8 (d, *J* = 21.5 Hz), 52.8, 32.7, 19.7, 14.0. ^{19}F NMR (500 MHz, $CDCl_3$) δ -108.2 - -129.0 (m). HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{23}H_{21}FNaO_2Si$: 399.1187, found: 399.1195. HPLC: Chiralpak OD-H column (hexanes: isopropanol = 99:1, 0.6 mL/min, 211 nm, 94% *ee*, *dr* = 3:1). tR = 15.418 min (major), tR = 21.965 min (minor).

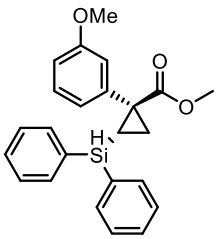


Ethyl (1*S*, 2*S*) - 2 - (diphenylsilyl) - 1 - (4 - (trifluoromethyl) phenyl) cyclopropane - 1 - carboxylate (3g): Yellow oil (22.0 mg, 25% yield), purified by column chromatography (Al_2O_3, PE/EA= 25:1). $[\alpha]_D^{25}$ = 19.1 (c = 0.79, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 - 7.38 (m, 2H), 7.35 - 7.25 (m, 5H), 7.24 - 7.19 (m, 1H), 7.13 - 7.05 (m, 6H), 4.23 (d, *J* = 3.6 Hz, 1H), 4.11 - 3.94 (m, 2H), 1.91 (dd, *J* = 10.8, 3.2 Hz, 1H), 1.55 (ddd, *J* = 10.8, 8.4, 3.6 Hz, 1H), 1.46 (dd, *J* = 8.4, 3.6 Hz, 1H), 1.08 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 141.0, 135.3, 135.2, 132.9 (d, *J* = 82.8 Hz), 131.6, 130.0, 129.7, 129.4 (d, *J* = 32.0 Hz), 128.2, 128.0, 124.7 (q, *J* = 3.7 Hz), 124.3 (d, *J* = 270.5 Hz), 61.7, 33.2, 19.1, 14.2, 13.7. ^{19}F NMR (500 MHz, $CDCl_3$) δ -62.4. HRMS

(ESI) m/z: $[M+Na]^+$ calculated for $C_{25}H_{23}F_3NaO_2Si$: 463.1312, found: 463.1325. HPLC: Chiralpak OD-H column (hexanes: isopropanol = 99:1, 0.6 mL/min, 211 nm, 92% *ee*, *dr* = 13:1). tR = 12.453 min (major), tR = 15.713 min (minor).

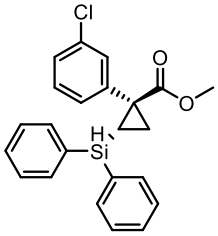


Methyl (1*S*, 2*S*) - 1 - ([1, 1'-biphenyl]-4-yl) - 2 - (diphenylsilyl) cyclopropane - 1 - carboxylate (3h): Yellow oil (55.6 mg, 64% yield), purified by column chromatography (Al_2O_3, PE/EA= 25:1). $[\alpha]_D^{25}$ = 8.4 (c = 0.42, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 - 7.48 (m, 2H), 7.47 - 7.41 (m, 2H), 7.41 - 7.24 (m, 9H), 7.18 - 7.03 (m, 6H), 4.26 (d, *J* = 4.0 Hz, 1H), 3.58 (s, 3H), 1.90 (dd, *J* = 10.4, 2.8 Hz, 1H), 1.56 (ddd, *J* = 10.8, 8.4, 4.0 Hz, 1H), 1.48 (dd, *J* = 8.4, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 141.0, 140.1, 136.0, 135.4, 135.3, 133.8, 133.0, 131.7, 129.9, 129.5, 128.9, 128.1, 127.9, 127.4, 127.2, 126.6, 52.9, 33.1, 19.5, 14.1. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{29}H_{26}NaO_2Si$: 457.1594, found: 457.1607. HPLC: Chiralpak OD-H column (hexanes: isopropanol = 99:1, 0.6 mL/min, 211 nm, 80% *ee*, *dr* = 10:1). tR = 23.796 min (major), tR = 34.269 min (minor).

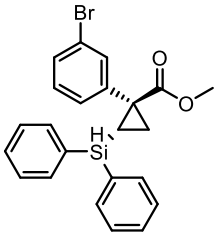


Methyl (1*S*, 2*S*) - 2 - (diphenylsilyl) - 1 - (3 - methoxyphenyl) cyclopropane - 1 - carboxylate (3i): Yellow oil (39.6 mg, 51% yield), purified by column chromatography (Al_2O_3, PE/EA= 15:1). $[\alpha]_D^{25}$ = 12.9 (c = 0.56, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 - 7.28 (m, 2H), 7.22 - 7.14 (m, 3H), 7.09 - 6.98 (m, 5H), 6.89 (t, *J* = 8.0 Hz, 1H), 6.61 - 6.51 (m, 2H), 6.39 (dd, *J* = 2.8, 1.6 Hz, 1H), 4.00 (d, *J* = 4.4 Hz, 1H), 3.43 (s, 3H), 3.31 (s, 3H), 1.71 (dd, *J* = 10.8, 3.2 Hz, 1H), 1.41 (ddd, *J* = 10.8, 8.4, 4.8 Hz, 1H), 1.31 (dd, *J* = 8.4, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 159.1, 138.5, 135.4, 135.2, 133.8, 133.4, 129.9, 129.6, 128.9, 128.1, 128.1, 127.9, 123.6, 116.4, 113.8, 55.0, 52.8, 33.6, 19.7, 13.7. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{24}H_{24}NaO_3Si$: 411.1387, found: 411.1412. HPLC: Chiralpak OD-H column (hexanes:

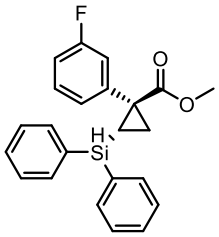
isopropanol = 99:1, 0.6 mL/min, 211 nm, 87% *ee*, *dr* = 3:1). tR = 25.447 min (major), tR = 40.328 min (minor).



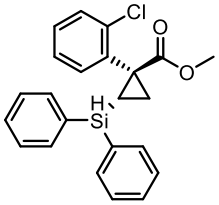
Methyl (1*S*, 2*S*) - 1 - (3 - chlorophenyl) - 2 - (diphenylsilyl) cyclopropane - 1 - carboxylate (3j): Yellow oil (11.8 mg, 15% yield), purified by column chromatography (Al_2O_3, PE/EA= 25:1). $[\alpha]_D^{25}$ = 12.8 (c = 0.16, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 - 7.40 (m, 2H), 7.37 - 7.27 (m, 3H), 7.22 - 7.11 (m, 6H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.99 - 6.91 (m, 2H), 4.16 (d, *J* = 4.4 Hz, 1H), 3.56 (s, 3H), 1.88 (dd, *J* = 10.7, 3.2 Hz, 1H), 1.56 - 1.50 (m, 1H), 1.43 (dd, *J* = 8.4, 3.2 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 139.0, 135.4, 135.2, 133.7, 133.3, 132.8, 131.6, 130.0, 129.8, 129.6, 129.1, 128.2, 128.0, 127.7, 52.9, 33.1, 19.6, 14.0. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{23}H_{21}ClNaO_2Si$: 415.0892, found: 415.0901. HPLC: Chiralpak Phenomenex column (hexanes: isopropanol = 99:1, 0.6 mL/min, 211 nm, 90% *ee*, *dr* = 5:1). tR = 13.857 min (major), tR = 21.098 min (minor).



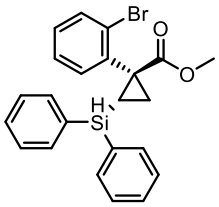
Methyl (1*S*, 2*S*) - 1 - (3 - bromophenyl) - 2 - (diphenylsilyl) cyclopropane - 1 - carboxylate (3k): Yellow oil (13.1 mg, 15% yield), purified by column chromatography (Al_2O_3, PE/EA= 25:1). $[\alpha]_D^{25}$ = 55.8 (c = 0.16, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 - 7.26 (m, 2H), 7.23 - 7.08 (m, 5H), 7.07 - 6.96 (m, 5H), 6.87 - 6.80 (m, 2H), 4.02 (d, *J* = 4.4 Hz, 1H), 3.41 (s, 3H), 1.73 (dd, *J* = 10.8, 3.2 Hz, 1H), 1.43 - 1.36 (m, 1H), 1.28 (dd, *J* = 8.8, 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 139.3, 135.4, 135.2, 134.4, 133.3, 132.8, 130.6, 130.1, 130.0, 129.8, 129.4, 128.3, 128.0, 122.0, 52.9, 33.1, 19.6, 14.0. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{23}H_{21}BrNaO_2Si$: 459.0386, found: 459.0401. HPLC: Chiralpak OD-H column (hexanes: isopropanol = 99:1, 0.6 mL/min, 211 nm, 91% *ee*, *dr* = 5:1). tR = 15.923 min (major), tR = 24.372 min (minor).



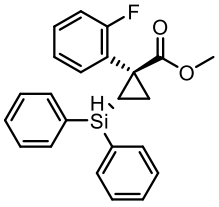
Methyl (1*S*, 2*S*) - 2 - (diphenylsilyl) - 1 - (3 - fluorophenyl) cyclopropane - 1 - carboxylate (3l): Yellow oil (34.6 mg, 46% yield), purified by column chromatography (Al_2O_3, PE/EA= 25:1). $[\alpha]_D^{25}$ = 23.2 (c = 0.52, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 - 7.40 (m, 2H), 7.36 - 7.26 (m, 3H), 7.23 - 7.14 (m, 4H), 7.05 (td, *J* = 8.0, 6.0 Hz, 1H), 6.88 - 6.79 (m, 2H), 6.69 (dt, *J* = 10.0, 1.6 Hz, 1H), 4.16 (d, *J* = 4.4 Hz, 1H), 3.55 (s, 3H), 1.87 (dd, *J* = 10.8, 3.2 Hz, 1H), 1.54 (ddd, *J* = 10.8, 8.4, 4.4 Hz, 1H), 1.43 (dd, *J* = 8.4, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 162.3 (d, *J* = 244.3 Hz), 139.4 (d, *J* = 7.4 Hz), 135.4, 135.2, 133.4, 132.9, 130.0, 129.7, 129.3 (d, *J* = 8.5 Hz), 128.2, 128.0, 127.0 (d, *J* = 2.5 Hz), 118.4 (d, *J* = 21.2 Hz), 114.4 (d, *J* = 20.9 Hz), 52.9, 33.2 (d, *J* = 2.1 Hz), 19.6, 14.0. ^{19}F NMR (500 MHz, $CDCl_3$) δ -98.5 - 121.9 (m). HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{23}H_{21}FNaO_2Si$: 399.1187, found: 399.1194. HPLC: Chiralpak OD-H column (hexanes: isopropanol = 99:1, 0.6 mL/min, 211 nm, 94% *ee*, *dr* = 7:1). tR = 16.081 min (major), tR = 23.926 min (minor).



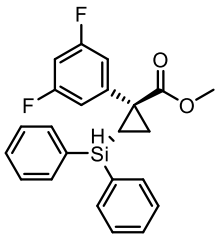
Methyl (1*S*, 2*S*) - 1 - (2 - chlorophenyl) - 2 - (diphenylsilyl) cyclopropane - 1 - carboxylate (3m): Yellow oil (11.8 mg, 15% yield), purified by column chromatography (Al_2O_3, PE/EA= 25:1). $[\alpha]_D^{25}$ = 15.6 (c = 0.40, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 6.4 Hz, 2H), 7.36 - 7.18 (m, 6H), 7.17 - 7.04 (m, 5H), 6.94 (td, *J* = 7.5, 1.2 Hz, 1H), 4.35 - 4.20 (m, 1H), 3.56 (s, 3H), 1.79 (s, 2H), 1.41 (d, *J* = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 135.6, 135.4, 135.3, 134.0, 133.2, 129.9, 129.6, 128.8, 128.1, 127.7, 126.5, 58.6, 52.9, 32.9, 18.6. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{23}H_{21}ClNaO_2Si$: 415.0892, found: 415.0910. HPLC: Chiralpak Phenomenex column (hexanes: isopropanol = 99:1, 0.6 mL/min, 211 nm, 85% *ee*, *dr* = 5:1). tR = 15.675 min (major), tR = 18.055 min (minor).



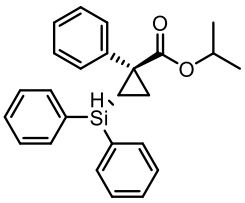
Methyl (1*S*, 2*S*) - 1 - (2 - bromophenyl) - 2 - (diphenylsilyl) cyclopropane - 1 - carboxylate (3n): Yellow oil (16.6 mg, 19% yield), purified by column chromatography (Al_2O_3, PE/EA= 25:1). $[\alpha]_D^{25}$ = 24.1 (c = 0.53, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 6.8 Hz, 2H), 7.47 (d, J = 8.0 Hz, 1H), 7.37 - 7.19 (m, 5H), 7.15 - 7.07 (m, 3H), 7.05 (td, J = 7.7, 2.0 Hz, 2H), 6.97 (t, J = 7.6 Hz, 1H), 4.33 (d, J = 3.2 Hz, 1H), 3.56 (s, 3H), 1.79 (d, J = 32.8 Hz, 2H), 1.40 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 137.3, 135.4, 135.4, 134.1, 133.2, 132.8, 129.9, 129.5, 129.0, 128.1, 127.9, 127.1, 58.6, 52.9, 35.0, 18.6. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{23}H_{21}BrNaO_2Si$: 459.0386, found: 459.0394. HPLC: Chiralpak OD-H column (hexanes: isopropanol = 99:1, 0.6 mL/min, 211 nm, 79% *ee*, *dr* = 5:1). tR = 21.213 min (major), tR = 23.164 min (minor).



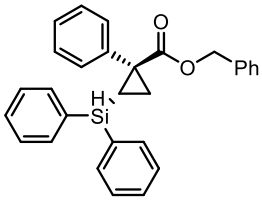
Methyl (1*S*, 2*S*) - 2 - (diphenylsilyl) - 1 - (2 - fluorophenyl) cyclopropane - 1 - carboxylate (3o): Yellow oil (35.3 mg, 47% yield), purified by column chromatography (Al_2O_3, PE/EA= 25:1). $[\alpha]_D^{25}$ = 1.6 (c = 1.45, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 - 7.38 (m, 2H), 7.34 - 7.19 (m, 4H), 7.18 - 7.10 (m, 5H), 6.92 - 6.80 (m, 3H), 4.20 (t, J = 3.2 Hz, 1H), 3.55 (s, 3H), 1.83 (dd, J = 10.8, 3.6 Hz, 1H), 1.64 (ddd, J = 10.8, 8.8, 4.0 Hz, 1H), 1.41 (dd, J = 8.8, 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 162.7 (d, J = 246.7 Hz), 135.3, 135.3, 133.5, 133.0, 131.5 (d, J = 4.1 Hz), 129.9, 129.6, 129.4 (d, J = 8.4 Hz), 128.0, 127.9, 124.9 (d, J = 14.4 Hz), 123.6 (d, J = 3.8 Hz), 115.3 (d, J = 21.5 Hz), 52.9, 28.7 (d, J = 1.9 Hz), 19.5, 13.5. ^{19}F NMR (500 MHz, $CDCl_3$) δ -112.19. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{23}H_{21}FNaO_2Si$: 399.1187, found: 399.1198. HPLC: Chiralpak OD-H column (hexanes: isopropanol = 99:1, 0.6 mL/min, 211 nm, 92% *ee*, *dr* = 4:1). tR = 17.463 min (major), tR = 21.545 min (minor).



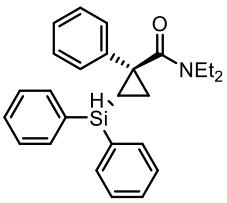
Methyl (1*S*, 2*S*) - 1 - (3, 5 - difluorophenyl) - 2 - (diphenylsilyl) cyclopropane - 1 - carboxylate (3p): Yellow oil (9.5 mg, 12% yield), purified by column chromatography (Al_2O_3, PE/EA= 25:1). $[\alpha]_D^{25}$ = 21.8 (c = 0.28, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 - 7.42 (m, 2H), 7.37 - 7.28 (m, 3H), 7.25 - 7.15 (m, 5H), 6.59 (tt, *J* = 9.2, 2.0 Hz, 1H), 6.55 - 6.49 (m, 2H), 4.21 (d, *J* = 4.4 Hz, 1H), 3.57 (s, 3H), 1.88 (dd, *J* = 10.8, 3.2 Hz, 1H), 1.54 (ddd, *J* = 10.8, 8.8, 4.4 Hz, 1H), 1.42 (dd, *J* = 8.4, 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 141.0, 135.3, 135.2, 132.9 (d, *J* = 83.4 Hz), 131.6, 130.0, 129.7, 129.4 (d, *J* = 32.0 Hz), 128.2, 128.0, 125.7, 124.7 (d, *J* = 3.7 Hz), 124.3 (d, *J* = 270.5 Hz), 123.0, 61.7, 33.2, 19.1, 14.0 (d, *J* = 51.6 Hz). ^{19}F NMR (500 MHz, $CDCl_3$) δ -110.6 - -110.8 (m). HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{23}H_{20}F_2NaO_2Si$: 417.1093, found: 417.1107. HPLC: Chiralpak OD-H column (hexanes: isopropanol = 99:1, 0.6 mL/min, 211 nm, 95% *ee*, *dr* = 4:1). tR = 15.721 min (major), tR = 24.285 min (minor).



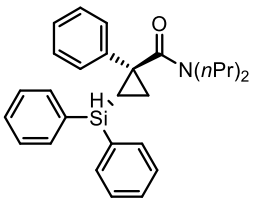
Isopropyl (1*S*, 2*S*) - 2 - (diphenylsilyl) - 1- phenylcyclopropane - 1 - carboxylate (3q): Yellow oil (18.6 mg, 24% yield), purified by column chromatography (Al_2O_3, PE/EA= 25:1). $[\alpha]_D^{25}$ = 27.0 (c = 0.48, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 - 7.41 (m, 2H), 7.37 - 7.21 (m, 4H), 7.19 - 7.10 (m, 5H), 7.10 - 6.98 (m, 4H), 4.94 - 4.83 (m, 1H), 4.11 (d, *J* = 4.4 Hz, 1H), 1.84 (dd, *J* = 10.0, 2.8 Hz, 1H), 1.49 (ddd, *J* = 10.4, 8.4, 4.4 Hz, 1H), 1.42 (dd, *J* = 8.0, 2.8 Hz, 1H), 1.06 (dd, *J* = 6.4, 4.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 137.2, 135.4, 135.3, 133.9, 133.5, 131.3, 129.8, 129.5, 128.1, 127.9, 127.8, 127.2, 68.7, 33.8, 21.8, 21.7, 18.8, 13.4. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{25}H_{26}NaO_2Si$: 409.1594, found: 409.1605. HPLC: Chiralpak AD-H column (hexanes: isopropanol = 99:1, 0.6 mL/min, 211 nm, 85% *ee*, *dr* = 18:1). tR = 20.603 min (major), tR = 25.370 min (minor).



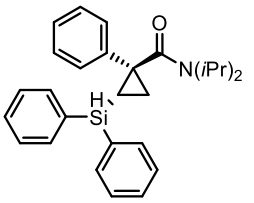
Benzyl (1*S*, 2*S*) - 2 - (diphenylsilyl) - 1 - phenylcyclopropane - 1 - carboxylate (3r): Yellow oil (45.2 mg, 52% yield), purified by column chromatography (Al_2O_3, PE/EA= 25:1). $[\alpha]_D^{25}$ = 12.3 (c = 0.92, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 - 7.38 (m, 2H), 7.32 - 7.23 (m, 3H), 7.21 - 7.16 (m, 4H), 7.16 - 7.10 (m, 5H), 7.10 - 7.03 (m, 6H), 5.07 (d, *J* = 12.8 Hz, 1H), 4.95 (d, *J* = 12.8 Hz, 1H), 4.13 (d, *J* = 4.8 Hz, 1H), 1.90 (dd, *J* = 10.4, 3.2 Hz, 1H), 1.54 (ddd, *J* = 10.8, 8.4, 4.4 Hz, 1H), 1.45 (dd, *J* = 8.8, 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 136.9, 136.3, 135.4, 135.3, 133.7, 133.3, 131.4, 129.9, 129.6, 128.5, 128.1, 128.0, 127.9, 127.9, 127.4, 127.4, 66.8, 33.7, 19.3, 13.8. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{29}H_{26}NaO_2Si$: 457.1594, found: 457.1607. HPLC: Chiralpak OD-H column (hexanes: isopropanol = 99:1, 0.6 mL/min, 211 nm, 83% *ee*, *dr* = 15:1). tR = 23.598 min (major), tR = 32.870 min (minor).



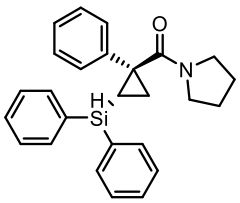
(1*S*, 2*S*) - 2 - (diphenylsilyl) - *N*, *N* - diethyl - 1 - phenylcyclopropane - 1 - carboxamide (5a): White solid (36.8 mg, 46% yield), mp 69.7 - 71.7 °C, purified by column chromatography (Al_2O_3, PE/EA= 15:1). $[\alpha]_D^{25}$ = 32.6 (c = 3.51, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (tt, *J* = 6.4, 1.6 Hz, 4H), 7.27 - 7.15 (m, 6H), 7.03 (s, 5H), 4.08 (d, *J* = 5.2 Hz, 1H), 3.39 (dq, *J* = 14.0, 7.2 Hz, 1H), 3.29 - 3.07 (m, 3H), 1.69 (dd, *J* = 8.4, 4.0 Hz, 1H), 1.61 (ddd, *J* = 10.4, 8.0, 4.8 Hz, 1H), 1.37 (dd, *J* = 10.4, 3.6 Hz, 1H), 0.98 (t, *J* = 6.8 Hz, 3H), 0.47 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 138.1, 135.4, 135.3, 134.4, 133.8, 129.5, 129.4, 128.5, 128.2, 127.9, 127.8, 127.8, 126.7, 41.5, 40.0, 35.6, 14.7, 12.7, 12.5, 10.0. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{26}H_{29}NNaOSi$: 422.1911, found: 422.1935. UPLC: Chiralpak ND column (hexanes: isopropanol = 95:5, 0.6 mL/min, 211 nm, 95% *ee*, *dr* > 19:1). tR = 9.169 min (major), tR = 7.403 min (minor).



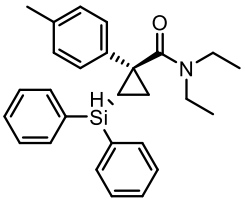
(1*S*, 2*S*) - 2 - (diphenylsilyl) - 1 - phenyl - *N*, *N* – dipropylcyclopropane - 1 - carboxamide (5b): Colorless oil (37.6 mg, 44% yield), purified by column chromatography (Al_2O_3, PE/EA= 15:1). $[\alpha]_D^{25}$ = 25.7 (c = 3.18, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 - 7.39 (m, 4H), 7.34 - 7.22 (m, 6H), 7.14 - 7.08 (m, 5H), 4.14 (d, J = 4.8 Hz, 1H), 3.32 (ddd, J = 15.2, 11.6, 4.0 Hz, 1H), 3.20 (t, J = 7.6 Hz, 2H), 3.07 (ddd, J = 14.4, 10.4, 5.6 Hz, 1H), 1.77 (dd, J = 8.4, 4.0 Hz, 1H), 1.69 (ddd, J = 10.4, 8.0, 4.8 Hz, 1H), 1.59 - 1.40 (m, 3H), 1.31 - 1.20 (m, 1H), 0.83 (t, J = 7.2 Hz, 3H), 0.56 (d, J = 5.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 138.2, 135.4, 135.3, 134.4, 133.8, 129.5, 129.4, 128.4, 128.1, 127.9, 127.8, 126.8, 49.1, 47.2, 35.7, 20.8, 20.4, 14.8, 11.5, 11.1, 10.1. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{28}H_{33}NNaOSi$: 450.2224, found: 450.2254. UPLC: Chiralpak ND column (hexanes: isopropanol = 95:5, 0.6 mL/min, 211 nm, 94% *ee*, *dr* > 19:1). tR = 7.964 min (major), tR = 5.670 min (minor).



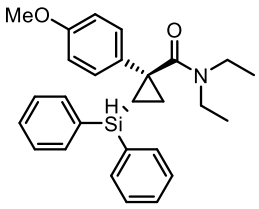
(1*S*, 2*S*) - 2 - (diphenylsilyl) - *N*, *N* - diisopropyl - 1 - phenylcyclopropane - 1 - carboxamide (5c): Colorless oil (48.8 mg, 59% yield), purified by column chromatography (Al_2O_3, PE/EA= 15:1). $[\alpha]_D^{25}$ = 32.2 (c = 4.78, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.29 (m, 4H), 7.26 - 7.12 (m, 6H), 7.02 (s, 5H), 4.37 (hept, J = 6.4 Hz, 1H), 4.11 (d, J = 4.8 Hz, 1H), 3.08 (hept, J = 6.8 Hz, 1H), 1.65 (dd, J = 8.0, 3.6 Hz, 1H), 1.59 (ddd, J = 10.0, 8.0, 4.8 Hz, 1H), 1.38 (dd, J = 10.0, 3.6 Hz, 1H), 1.32 (d, J = 6.8 Hz, 3H), 1.25 (d, J = 6.4 Hz, 3H), 0.97 (d, J = 6.8 Hz, 3H), 0.25 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 138.1, 135.4, 135.3, 134.5, 133.8, 129.5, 129.3, 128.2, 128.1, 127.9, 127.7, 126.6, 48.6, 45.8, 36.8, 21.0, 20.6, 19.4, 18.9, 14.2, 9.8. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{28}H_{33}NNaOSi$: 450.2224, found: 450.2248. UPLC: Chiralpak ND column (hexanes: isopropanol = 95:5, 0.6 mL/min, 211 nm, 97% *ee*, *dr* > 19:1). tR = 5.042 min (major), tR = 3.969 min (minor).



((1*S*, 2*S*) - 2 - (diphenylsilyl) - 1 - phenylcyclopropyl) (pyrrolidin - 1 - yl) methanone (5d): Colorless oil (11.9 mg, 15% yield), purified by column chromatography (Al_2O_3, PE/EA= 10:1). $[\alpha]_D^{25}$ = 15.8 (c = 1.88, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 - 7.38 (m, 4H), 7.35 - 7.24 (m, 6H), 7.16 - 7.03 (m, 5H), 4.14 (d, *J* = 5.2 Hz, 1H), 3.57 - 3.26 (m, 3H), 2.75 (dt, *J* = 10.8, 6.8 Hz, 1H), 1.90 - 1.56 (m, 6H), 1.45 (dd, *J* = 10.4, 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 137.5, 135.4, 135.4, 134.4, 133.8, 129.5, 129.5, 129.1, 128.1, 127.9, 127.8, 126.8, 46.8, 36.3, 26.2, 24.0, 14.8, 9.7. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{26}H_{27}NNaOSi$: 420.1754, found: 420.1765. UPLC: Chiralpak ND column (hexanes: isopropanol = 95:5, 0.6 mL/min, 211 nm, 93% *ee*, *dr* > 19:1). tR = 25.723 min (major), tR = 16.119 min (minor).

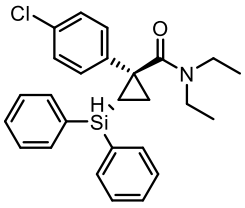


(1*S*, 2*S*) - 2 - (diphenylsilyl) - *N*, *N* - diethyl - 1 - (*p*- tolyl) cyclopropane - 1 - carboxamide (5e): White solid (33.1 mg, 40% yield), mp 91.4 - 94.9 °C, purified by column chromatography (Al_2O_3, PE/EA= 15:1). $[\alpha]_D^{25}$ = 33.1 (c = 2.75, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 - 7.40 (m, 4H), 7.34 - 7.21 (m, 6H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 7.6 Hz, 2H), 4.17 (d, *J* = 4.8 Hz, 1H), 3.44 (dq, *J* = 14.4, 7.2 Hz, 1H), 3.33 - 3.13 (m, 3H), 2.26 (s, 3H), 1.72 (dd, *J* = 8.4, 4.0 Hz, 1H), 1.64 (ddd, *J* = 10.8, 8.4, 5.2 Hz, 1H), 1.43 (dd, *J* = 10.4, 4.0 Hz, 1H), 1.05 (t, *J* = 6.8 Hz, 3H), 0.58 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 136.3, 135.4, 135.4, 135.0, 134.5, 133.9, 129.4, 129.4, 128.8, 128.3, 127.9, 127.7, 41.5, 39.9, 35.3, 21.2, 14.6, 12.8, 12.5, 9.9. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{27}H_{31}NNaOSi$: 436.2067, found: 436.2085. UPLC: Chiralpak ND column (hexanes: isopropanol = 95:5, 0.6 mL/min, 211 nm, 92% *ee*, *dr* > 19:1). tR = 7.001 min (major), tR = 5.838 min (minor).

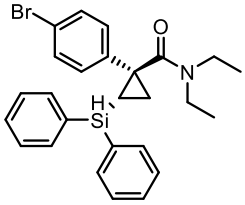


(1*S*, 2*S*) - 2 - (diphenylsilyl) - *N*, *N* - diethyl - 1 - (4 - methoxyphenyl)cyclopropane -1- carboxamide (5f): Colorless oil (38.7 mg, 45% yield), purified by column chromatography

(Al_2O_3, PE/EA= 15:1). $[\alpha]_D^{25}$ = 33.7 (c = 5.47, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.33 (m, 4H), 7.27 - 7.14 (m, 6H), 6.94 (d, J = 8.8 Hz, 2H), 6.54 (d, J = 8.8 Hz, 2H), 4.11 (d, J = 4.8 Hz, 1H), 3.66 (s, 3H), 3.46 - 3.33 (m, 1H), 3.29 - 3.06 (m, 3H), 1.63 (dd, J = 8.4, 4.0 Hz, 1H), 1.55 (ddd, J = 10.4, 8.0, 4.8 Hz, 1H), 1.36 (dd, J = 10.4, 3.6 Hz, 1H), 0.97 (t, J = 7.2 Hz, 3H), 0.51 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl3) δ 172.3, 158.4, 135.4, 135.3, 134.5, 133.9, 130.1, 129.6, 129.5, 129.4, 127.9, 127.8, 113.5, 55.3, 41.5, 40.0, 34.8, 14.8, 12.9, 12.5, 9.8. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{27}H_{32}NO_2Si$: 430.2197, found: 430.1917. UPLC: Chiralpak ND column (hexanes: isopropanol = 95:5, 0.6 mL/min, 211 nm, 92% *ee*, *dr* > 19:1). tR = 10.230 min (major), tR = 7.138 min (minor).

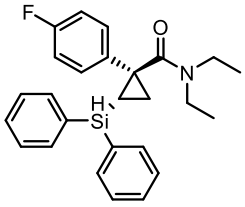


(1*S*, 2*S*) - 1 - (4 - chlorophenyl) - 2 - (diphenylsilyl) - *N*, *N* - diethylcyclopropane - 1 - carboxamide (5g): White Solid (35.6 mg, 41% yield), mp 139.2 - 145.5 °C, purified by column chromatography (Al_2O_3, PE/EA= 15:1). $[\alpha]_D^{25}$ = 16.0 (c = 4.46, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 - 7.30 (m, 4H), 7.27 - 7.15 (m, 6H), 6.98 - 6.90 (m, 4H), 4.15 (d, *J* = 4.4 Hz, 1H), 3.41 - 3.27 (m, 1H), 3.26 - 3.03 (m, 3H), 1.66 (dd, *J* = 8.0, 3.6 Hz, 1H), 1.60 (ddd, *J* = 10.0, 8.4, 4.4 Hz, 1H), 1.40 (dd, *J* = 10.0, 3.6 Hz, 1H), 0.97 (t, *J* = 7.2 Hz, 3H), 0.54 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 136.8, 135.4, 135.2, 133.9, 133.4, 132.6, 129.7, 129.6, 129.6, 128.3, 128.0, 127.9, 41.5, 40.0, 35.0, 14.9, 12.9, 12.5, 10.1. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{26}H_{28}ClNNaOSi$: 456.1521, found: 456.1559. UPLC: Chiralpak ND column (hexanes: isopropanol = 95:5, 0.6 mL/min, 211 nm, 95% *ee*, *dr* > 19:1). tR = 8.381 min (major), tR = 6.627 min (minor).

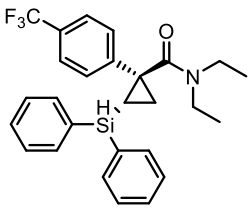


(1*S*, 2*S*) - 1 - (4 - bromophenyl) - 2 - (diphenylsilyl) - *N*, *N* - diethylcyclopropane - 1 - carboxamide (5h): Colorless oil (44.0 mg, 46% yield), purified by column chromatography (Al_2O_3, PE/EA= 15:1). $[\alpha]_D^{25}$ = 41.0 (c = 3.89, $CHCl_3$). ^1H NMR (400 MHz,

$CDCl_3$) δ 7.41 - 7.30 (m, 4H), 7.26 - 7.16 (m, 6H), 7.10 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 4.16 (d, J = 4.8 Hz, 1H), 3.42 - 3.26 (m, 1H), 3.23 - 3.06 (m, 3H), 1.65 (dd, J = 8.4, 4.0 Hz, 1H), 1.59 (ddd, J = 10.0, 8.0, 4.4 Hz, 1H), 1.40 (dd, J = 10.4, 4.0 Hz, 1H), 0.97 (t, J = 7.2 Hz, 3H), 0.54 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 137.3, 135.3, 135.2, 133.9, 133.4, 131.2, 130.0, 129.6, 129.5, 128.0, 127.9, 120.7, 41.5, 40.0, 35.1, 14.8, 12.9, 12.4, 10.1. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{26}H_{29}BrNOSi$: 478.1196, found: 478.1222. UPLC: Chiralpak ND column (hexanes: isopropanol = 95:5, 0.6 mL/min, 211 nm, 92% *ee*, *dr* > 19:1). tR = 6.923 min (major), tR = 5.877 min (minor).

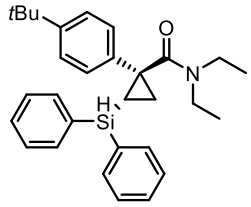


(1*S*, 2*S*) - 2 - (diphenylsilyl) - *N*, *N* - diethyl - 1 - (4-fluorophenyl) cyclopropane-1-carboxamide (5i): Colorless oil (30.1 mg, 36% yield), purified by column chromatography (Al_2O_3, PE/EA= 15:1). $[\alpha]_D^{25}$ = 31.4 (c = 2.32, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.33 (m, 4H), 7.29 - 7.18 (m, 6H), 7.05 - 6.89 (m, 2H), 6.75 - 6.56 (m, 2H), 4.12 (d, J = 4.8 Hz, 1H), 3.37 (dt, J = 14.8, 7.6 Hz, 1H), 3.28 - 3.07 (m, 3H), 1.66 (dd, J = 8.4, 4.0 Hz, 1H), 1.59 (ddd, J = 10.4, 8.0, 4.8 Hz, 1H), 1.40 (dd, J = 10.4, 3.6 Hz, 1H), 0.97 (t, J = 6.8 Hz, 3H), 0.51 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 161.7 (d, J = 244.3 Hz), 135.4, 135.3, 133.9 (d, J = 3.4 Hz), 133.8 (d, J = 50.9 Hz), 130.1, 130.0, 129.6, 129.5, 128.0, 127.9, 115.0 (d, J = 21.6 Hz), 41.5, 40.0, 34.9, 15.0, 12.9, 12.5, 9.9. ^{19}F NMR (500 MHz, $CDCl_3$) δ -115.7 - -115.8 (m). HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{26}H_{29}FNOSi$: 418.1997, found: 418.2181. UPLC: Chiralpak ND column (hexanes: isopropanol = 95:5, 0.6 mL/min, 211 nm, 95% *ee*, *dr* > 19:1). tR = 7.371 min (major), tR = 5.907 min (minor).

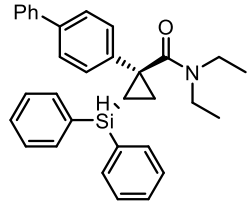


(1*S*, 2*S*) - 2 - (diphenylsilyl) - *N*, *N* - diethyl - 1 - (4 - (trifluoromethyl) phenyl) cyclopropane-1-carboxamide (5j): Colorless oil (42.1 mg, 45% yield), purified by column chromatography (Al_2O_3, PE/EA= 15:1). $[\alpha]_D^{25}$ = 64.6 (c = 1.40,

$CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 - 7.30 (m, 2H), 7.30 - 7.25 (m, 3H), 7.25 - 7.19 (m, 5H), 7.18 - 7.12 (m, 2H), 7.12 - 7.03 (m, 2H), 4.18 (d, J = 4.4 Hz, 1H), 3.38 - 3.22 (m, 2H), 3.21 - 3.08 (m, 2H), 1.75 (dd, J = 8.4, 4.4 Hz, 1H), 1.65 (ddd, J = 10.4, 8.0, 4.4 Hz, 1H), 1.46 (dd, J = 10.4, 4.0 Hz, 1H), 0.98 (t, J = 7.2 Hz, 3H), 0.51 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 124.99 (q, J = 3.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 142.2, 135.2, 135.0, 133.5, 133.1, 129.6, 129.5, 128.8 (d, J = 32.4 Hz), 128.5, 128.0, 127.8, 125.0 (q, J = 3.6 Hz), 124.11 (d, J = 270.5 Hz)41.4, 39.9, 35.3, 14.9, 12.8, 12.4, 10.2. ^{19}F NMR (500 MHz, $CDCl_3$) δ -62.5. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{27}H_{29}F_3NOSi$: 468.1965, found: 468.2119. UPLC: Chiralpak ND column (hexanes: isopropanol = 95:5, 0.6 mL/min, 211 nm, 96% *ee*, *dr* > 19:1). tR = 5.789 min (major), tR = 5.074 min (minor).

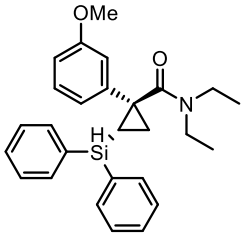


(1*S*, 2*S*) - 1 - (4 - (tert - butyl) phenyl) - 2 - (diphenylsilyl) - *N*, *N* - diethylcyclopropane - 1 - carboxamide (5k): Colorless oil (44.7 mg, 49% yield), purified by column chromatography (Al_2O_3, PE/EA= 15:1). $[\alpha]_D^{25}$ = 39.9 (c = 4.47, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.38 (m, 2H), 7.37 - 7.33 (m, 2H), 7.31 - 7.19 (m, 6H), 7.10 - 7.05 (m, 2H), 7.00 - 6.94 (m, 2H), 4.23 (d, J = 4.8 Hz, 1H), 3.50 - 3.38 (m, 1H), 3.37 - 3.14 (m, 3H), 1.74 (dd, J = 8.0, 3.6 Hz, 1H), 1.65 (ddd, J = 10.4, 8.0, 4.8 Hz, 1H), 1.43 (dd, J = 10.4, 4.0 Hz, 1H), 1.27 (s, 9H), 1.05 (t, J = 7.2 Hz, 3H), 0.53 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 149.6, 135.4, 135.3, 134.8, 134.4, 134.0, 129.4, 129.3, 128.1, 127.8, 127.7, 124.9, 41.6, 40.0, 35.0, 34.5, 31.5, 20.0, 14.8, 14.0, 12.6, 12.5, 9.8. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{30}H_{37}NNaOSi$: 478.2537, found: 478.2569. UPLC: Chiralpak ND column (hexanes: isopropanol = 95:5, 0.6 mL/min, 211 nm, 92% *ee*, *dr* > 19:1). tR = 7.276 min (major), tR = 4.618 min (minor).

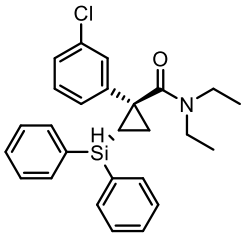


(1*S*, 2*S*) - 1 - ([1, 1'- biphenyl] - 4 - yl) - 2 - (diphenylsilyl) -*N*, *N*-diethylcyclopropane-1-carboxamide (5l): Colorless oil (33.3 mg, 35% yield), purified by column chromatography (Al_2O_3, PE/EA= 15:1). $[\alpha]_D^{25}$ = 34.3 (c = 4.36, $CHCl_3$). ^1H NMR (400 MHz,

$CDCl_3$) δ 7.52 - 7.41 (m, 2H), 7.39 - 7.32 (m, 6H), 7.26 - 7.13 (m, 9H), 7.10 - 7.04 (m, 2H), 4.21 (d, J = 4.4 Hz, 1H), 3.39 (dt, J = 14.4, 7.6 Hz, 1H), 3.29 - 3.10 (m, 3H), 1.73 (dd, J = 8.0, 4.0 Hz, 1H), 1.64 (ddd, J = 10.8, 8.4, 4.8 Hz, 1H), 1.42 (dd, J = 10.4, 4.0 Hz, 1H), 0.99 (t, J = 7.2 Hz, 3H), 0.53 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 140.7, 139.3, 137.2, 135.4, 135.3, 134.2, 133.8, 129.5, 129.4, 128.9, 128.8, 127.9, 127.8, 127.4, 127.0, 126.7, 41.60, 40.02, 35.24, 14.88, 12.85, 12.51, 10.15. HRMS (APCI) m/z: $[M+Na]^+$ calculated for $C_{32}H_{33}NNaOSi$: 498.2224, found: 498.2470. UPLC: Chiralpak ND column (hexanes: isopropanol = 95:5, 0.6 mL/min, 211 nm, 94% *ee*, *dr* > 19:1). tR = 6.617 min (major), tR = 5.825 min (minor).

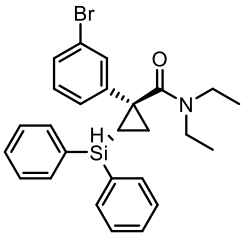


(1*S*, 2*S*) -2-(diphenylsilyl)-*N*,*N*-diethyl-1-(3-methoxyphenyl) cyclopropane-1-carboxamide (5m): Colorless oil (27.5 mg, 32% yield), purified by column chromatography (Al_2O_3, PE/EA= 15:1). $[\alpha]_D^{25}$ = 39.9 (c = 4.47, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.35 (m, 4H), 7.28 - 7.14 (m, 6H), 6.97 (t, J = 8.0 Hz, 1H), 6.66 (d, J = 7.6 Hz, 1H), 6.60 (dd, J = 8.0, 2.4 Hz, 1H), 6.52 (t, J = 2.0 Hz, 1H), 4.09 (d, J = 4.8 Hz, 1H), 3.45 - 3.31 (m, 4H), 3.25 - 3.15 (m, 3H), 1.68 (dd, J = 8.0, 3.6 Hz, 1H), 1.60 (ddd, J = 10.4, 8.0, 5.2 Hz, 1H), 1.37 (dd, J = 10.4, 4.0 Hz, 1H), 0.98 (t, J = 6.8 Hz, 3H), 0.54 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 159.4, 139.6, 135.4, 135.3, 134.5, 133.9, 129.5, 129.4, 129.1, 127.9, 127.8, 120.4, 113.6, 113.4, 55.0, 41.6, 40.1, 35.6, 14.8, 12.9, 12.5, 9.8. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{27}H_{32}NO_2Si$: 430.2197, found: 430.1917. UPLC: Chiralpak ND column (hexanes: isopropanol = 95:5, 0.6 mL/min, 211 nm, 94% *ee*, *dr* > 19:1). tR = 9.010 min (major), tR = 8.117 min (minor).

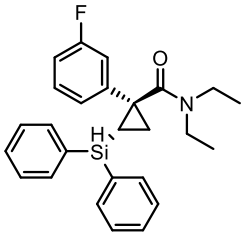


(1*S*, 2*S*) - 1 - (3 - chlorophenyl) - 2 - (diphenylsilyl) - *N*, *N* - diethylcyclopropane - 1 - carboxamide (5n): White Solid (35.6 mg, 41% yield), mp 137.8 - 141.1 °C, purified by column chromatography (Al_2O_3, PE/EA= 15:1). $[\alpha]_D^{25}$ = 35.3 (c = 2.56, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 - 7.38 (m, 4H), 7.36

- 7.22 (m, 6H), 7.14 - 7.07 (m, 1H), 7.05 - 6.92 (m, 3H), 4.23 (d, *J* = 4.8 Hz, 1H), 3.47 - 3.36 (m, 1H), 3.36 - 3.13 (m, 3H), 1.75 - 1.65 (m, 2H), 1.48 (dd, *J* = 9.6, 3.2 Hz, 1H), 1.05 (t, *J* = 7.2 Hz, 3H), 0.61 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 140.3, 135.4, 135.2, 134.1, 133.9, 133.3, 129.7, 129.6, 129.4, 128.5, 128.0, 127.9, 127.0, 126.8, 41.5, 40.0, 35.3, 15.0, 12.9, 12.4, 10.2. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{26}H_{28}ClNNaOSi$: 456.1521, found: 456.1546. UPLC: Chiralpak ND column (hexanes: isopropanol = 95:5, 0.6 mL/min, 211 nm, 96% *ee*, *dr* > 19:1). tR = 6.723 min (major), tR = 5.991 min (minor).

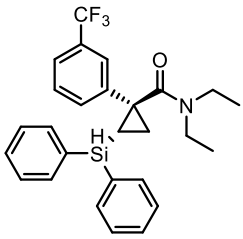


(1*S*, 2*S*) - 1 - (3 - bromophenyl) - 2 - (diphenylsilyl) - *N*, *N* -diethylcyclopropane-1-carboxamide (5o): Colorless oil (35.4 mg, 37% yield), purified by column chromatography (Al_2O_3, PE/EA= 15:1). $[\alpha]_D^{25}$ = 37.4 (c = 1.91, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 - 7.31 (m, 4H), 7.27 - 7.16 (m, 7H), 7.10 (t, *J* = 1.2 Hz, 1H), 7.01 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.90 (t, *J* = 8.0 Hz, 1H), 4.16 (d, *J* = 4.4 Hz, 1H), 3.33 (dt, *J* = 14.4, 7.2 Hz, 1H), 3.26 - 3.09 (m, 3H), 1.71 - 1.54 (m, 2H), 1.40 (dd, *J* = 9.6, 3.6 Hz, 1H), 0.98 (t, *J* = 6.8 Hz, 3H), 0.54 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 140.6, 135.4, 135.2, 133.8, 133.3, 131.4, 130.0, 129.7, 129.7, 129.7, 128.0, 127.9, 127.3, 122.4, 41.5, 40.0, 35.2, 15.0, 12.9, 12.4, 10.2. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{26}H_{29}BrNOSi$: 478.1196, found: 478.1203. UPLC: Chiralpak ND column (hexanes: isopropanol = 95:5, 0.6 mL/min, 211 nm, 95% *ee*, *dr* > 19:1). tR = 8.478 min (major), tR = 7.427 min (minor)

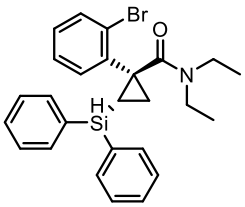


(1*S*, 2*S*) - 2 - (diphenylsilyl) - *N*, *N*- diethyl - 1 - (3-fluorophenyl) cyclopropane-1-carboxamide (5p): Colorless oil (25.1 mg, 30% yield), purified by column chromatography (Al_2O_3, PE/EA= 15:1). $[\alpha]_D^{25}$ = 5.0 (c = 1.24, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.30 (m, 4H), 7.26 - 7.15 (m, 6H), 6.99 (td, *J* = 8.0, 6.0 Hz, 1H), 6.84 (dt, *J* = 7.6, 1.6 Hz, 1H), 6.75 (td, *J* = 8.4, 2.8 Hz, 1H), 6.68 (dt, *J* = 10.0, 2.0 Hz,

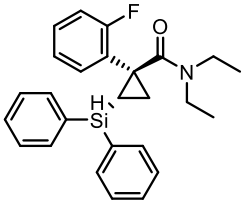
1H), 4.15 (d, *J* = 4.4 Hz, 1H), 3.36 (dq, *J* = 14.4, 7.2 Hz, 1H), 3.26 - 3.06 (m, 3H), 1.73 - 1.51 (m, 2H), 1.40 (dd, *J* = 9.6, 3.2 Hz, 1H), 0.98 (t, *J* = 6.8 Hz, 3H), 0.53 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 162.7 (d, *J* = 244.4 Hz), 140.8 (d, *J* = 7.6 Hz), 135.4, 135.3, 134.3 (d, *J* = 6.6 Hz), 134.0, 133.5, 129.7 (d, *J* = 8.7 Hz), 129.6 (d, *J* = 7.8 Hz), 128.0, 127.9, 124.2 (d, *J* = 2.7 Hz), 115.3 (d, *J* = 21.9 Hz), 113.8 (d, *J* = 21.0 Hz), 41.6, 40.0, 35.3 (d, *J* = 2.2 Hz), 15.1, 12.8, 12.5, 10.3. ^{19}F NMR (500 MHz, $CDCl_3$) δ -99.24 - -136.02 (m). HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{26}H_{29}FNOSi$: 418.1997, found: 418.2119. UPLC: Chiralpak ND column (hexanes: isopropanol = 95:5, 0.6 mL/min, 211 nm, 96% *ee*, *dr* > 19:1). tR = 7.701 min (major), tR = 6.795 min (minor).



(1*S*, 2*S*) - 2 - (diphenylsilyl) - *N*, *N* - diethyl - 1 - (3 - (trifluoromethyl) phenyl)cyclopropane-1-carboxamide (5q): Colorless oil (40.2 mg, 43% yield), purified by column chromatography (Al_2O_3, PE/EA= 15:1). $[\alpha]_D^{25}$ = 18.1 (c = 0.90, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 - 7.33 (m, 2H), 7.32 - 7.29 (m, 3H), 7.26 - 7.20 (m, 5H), 7.20 - 7.11 (m, 4H), 4.13 (d, *J* = 4.8 Hz, 1H), 3.35 (dq, *J* = 14.4, 6.8 Hz, 1H), 3.22 (q, *J* = 6.8 Hz, 2H), 3.11 (dq, *J* = 14.0, 6.8 Hz, 1H), 1.74 (dd, *J* = 8.4, 4.0 Hz, 1H), 1.66 (ddd, *J* = 10.0, 8.0, 4.8 Hz, 1H), 1.46 (dd, *J* = 10.4, 4.0 Hz, 1H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.48 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 139.3, 135.3, 135.1, 133.4 (d, *J* = 58.2 Hz), 131.9, 130.6 (d, *J* = 32.1 Hz), 129.7, 129.7, 128.7, 128.0, 127.9, 125.0 (d, *J* = 3.7 Hz), 124.0 (d, *J* = 270.6 Hz), 123.6 (d, *J* = 3.7 Hz), 41.5, 40.0, 35.3, 15.0, 12.8, 12.4, 10.2. ^{19}F NMR (500 MHz, $CDCl_3$) δ -62.59 (d, *J* = 70.0 Hz). HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{27}H_{29}F_3NOSi$: 468.1965, found: 468.1627. UPLC: Chiralpak ND column (hexanes: isopropanol = 95:5, 0.6 mL/min, 211 nm, 97% *ee*, *dr* > 19:1). tR = 6.589 min (major), tR = 6.019 min (minor).

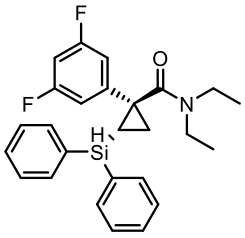


(1*S*, 2*S*) - 1 - (2 - bromophenyl) - 2 - (diphenylsilyl) - *N*, *N* -diethylcyclopropane-1-carboxamide (5r): Colorless oil (55.5 mg, 58% yield), purified by column chromatography (Al_2O_3, PE/EA= 15:1). $[\alpha]_D^{25}$ = 60.3 (c =5.17, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 - 7.36 (m, 3H), 7.27 - 7.23 (m, 1H), 7.22 - 7.19 (m, 2H), 7.18 - 7.10 (m, 5H), 6.97 (dtd, *J* = 14.0, 7.2, 2.0 Hz, 2H), 6.88 (dd, *J* = 7.6, 2.4 Hz, 1H), 4.11 (d, *J* = 3.6 Hz, 1H), 3.41 - 3.04 (m, 3H), 2.92 - 2.68 (m, 1H), 2.17 (ddd, *J* = 11.2, 8.0, 3.6 Hz, 1H), 1.59 (dd, *J* = 8.0, 4.0 Hz, 1H), 1.40 (dd, *J* = 10.8, 3.6 Hz, 1H), 1.02 (t, *J* = 7.2 Hz, 3H), 0.28 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 139.0, 135.4, 135.4, 134.2, 133.9, 133.5, 130.7, 130.0, 129.6, 129.4, 128.4, 128.1, 127.8, 127.1, 42.4, 41.8, 36.5, 17.6, 12.7, 12.4, 9.8. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{26}H_{29}BrNOSi$: 478.1196, found: 478.1292. UPLC: Chiralpak ND column (hexanes: isopropanol = 95:5, 0.6 mL/min, 211 nm, 81% *ee*, *dr* > 19:1). tR = 11.338 min (major), tR = 9.600 min (minor).

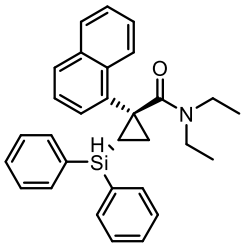


(1*S*, 2*S*) - 2 - (diphenylsilyl) - *N*, *N* - diethyl - 1 - (2 - fluorophenyl) cyclopropane-1-carboxamide (5s): Colorless oil (41.8 mg, 50% yield), purified by column chromatography (Al_2O_3, PE/EA= 15:1). $[\alpha]_D^{25}$ = 27.6 (c = 3.57, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 - 7.34 (m, 2H), 7.32 - 7.23 (m, 4H), 7.21 - 7.14 (m, 2H), 7.05 (tdd, *J* = 7.2, 4.8, 1.6 Hz, 1H), 6.99 (td, *J* = 8.0, 2.0 Hz, 1H), 6.81 (td, *J* = 7.6, 1.2 Hz, 4H), 6.75 - 6.68 (m, 1H), 4.12 (dd, *J* = 4.4, 1.2 Hz, 1H), 3.47 (s, 1H), 3.20 (s, 1H), 3.04 (s, 1H), 1.91 - 1.79 (m, 1H), 1.75 (dd, *J* = 8.0, 4.0 Hz, 2H), 1.38 (dd, *J* = 10.8, 4.0 Hz, 1H), 0.97 (s, 3H), 0.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 162.2 (d, *J* = 247.4 Hz), 135.4, 135.3, 134.3, 133.9, 133.5, 130.6 (d, *J* = 3.6 Hz), 129.5, 128.8 (d, *J* = 8.6 Hz), 127.9, 127.8, 126.0 (d, *J* = 12.4 Hz), 123.9 (d, *J* = 3.2 Hz), 115.9 (d, *J* = 22.3 Hz), 41.7, 40.6, 31.3, 18.5, 15.9, 15.9, 12.6, 9.2. ^{19}F NMR (500 MHz, $CDCl_3$) δ -101.10 - -154.70 (m). HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{26}H_{29}FNOSi$: 418.1997, found:

418.2395. UPLC: Chiralpak ND column (hexanes: isopropanol = 95:5, 0.6 mL/min, 211 nm, 93% *ee*, *dr* > 19:1). tR = 9.101 min (major), tR = 7.675 min (minor).

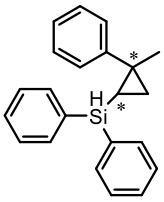


(1*S*, 2*S*) - 1 - (3, 5 - difluorophenyl) - 2 - (diphenylsilyl) - *N*, *N* - diethylcyclopropane-1-carboxamide (5t): Colorless oil (19.2 mg, 22% yield), purified by column chromatography (Al_2O_3, PE/EA= 15:1). $[\alpha]_D^{25}$ = 19.9 (c = 2.82, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (ddd, *J* = 9.2, 7.6, 1.6 Hz, 4H), 7.32 - 7.26 (m, 2H), 7.24 - 7.17 (m, 4H), 6.56 - 6.42 (m, 3H), 4.21 (d, *J* = 4.4 Hz, 1H), 3.46 - 2.99 (m, 4H), 1.68 - 1.54 (m, 1H), 1.48 - 1.36 (m, 1H), 1.17 (d, *J* = 6.8 Hz, 1H), 0.99 (t, *J* = 7.2 Hz, 3H), 0.60 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 162.9 (d, *J* = 247.3 Hz), 162.8 (d, *J* = 247.1 Hz), 142.3 (t, *J* = 9.4 Hz), 135.3, 135.2, 133.3 (d, *J* = 53.1 Hz), 129.8, 129.7, 128.1, 127.9, 111.3 (d, *J* = 25.4 Hz), 102.5 (d, *J* = 25.3 Hz), 41.5, 40.1, 35.3, 15.4, 12.9, 12.4, 10.7. ^{19}F NMR (500 MHz, $CDCl_3$) δ -109.76 (t, *J* = 8.5 Hz). HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{26}H_{28}F_2NOSi$: 436.1903, found: 436.2118. UPLC: Chiralpak ND column (hexanes: isopropanol = 95:5, 0.6 mL/min, 211 nm, 96% *ee*, *dr* > 19:1). tR = 6.925 min (major), tR = 6.244 min (minor).



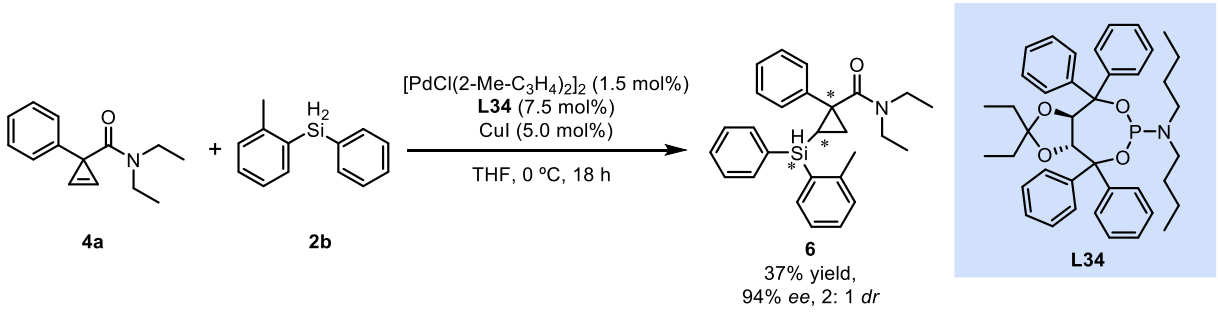
(1*S*, 2*S*)-2-(diphenylsilyl) - *N*, *N* - diethyl - 1 - (naphthalen-1-yl) cyclopropane-1-carboxamide (5u): Colorless oil (38.7 mg, 43% yield), purified by column chromatography (Al_2O_3, PE/EA= 15:1). $[\alpha]_D^{25}$ = 87.5 (c = 3.75, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.04 - 6.98 (m, 8H), 6.98 - 6.88 (m, 5H), 3.64 (d, *J* = 4.4 Hz, 1H), 3.56 - 3.34 (m, 1H), 3.08 - 2.93 (m, 2H), 2.92 - 2.79 (m, 1H), 2.02 (s, 1H), 1.71 - 1.60 (m, 1H), 1.46 - 1.35 (m, 1H), 0.76 (t, *J* = 7.6 Hz, 3H), 0.00 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 135.4, 135.3, 135.0, 134.3, 134.2, 134.1, 133.7, 129.3, 129.2, 127.9, 127.7, 127.6, 126.3, 126.1, 126.1, 125.9, 124.9, 42.3, 41.4, 34.8, 27.0, 16.3, 12.6, 9.7. HRMS (APCI) m/z: $[M+H]^+$ calculated for $C_{30}H_{32}NOSi$:

450.2248, found: 450.2457. UPLC: Chiralpak ND column (hexanes: isopropanol = 95:5, 0.6 mL/min, 211 nm, 78% *ee*, *dr* > 19:1). tR = 7.690 min (major), tR = 9.284 min (minor).

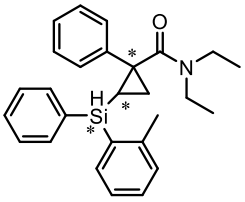


(2-methyl-2-phenylcyclopropyl)diphenylsilane (5v): Colorless oil (22.6 mg, 36% yield), purified by column chromatography (SiO_2, PE = 100%). $[\alpha]_D^{25}$ = 2.3 (c = 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 - 7.39 (m, 4H), 7.23 - 7.15 (m, 6H), 7.12 - 7.05 (m, 4H), 6.99 - 6.92 (m, 1H), 4.73 (d, *J* = 5.6 Hz, 1H), 1.29 (s, 3H), 1.28 - 1.19 (m, 1H), 0.80 (dd, *J* = 7.6, 4.0 Hz, 1H), 0.42 (ddd, *J* = 10.4, 7.6, 5.6 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 135.5, 135.3, 135.2, 134.8, 129.7, 129.7, 128.4, 128.2, 128.2, 126.9, 125.9, 25.7, 23.9, 20.2, 11.0. HRMS (APCI) m/z: $[M+Na]^+$ calculated for $C_{22}H_{22}NaSi$: 337.1383, found: 337.3466. After conversion to the corresponding silanol, the enantiomeric excess was determined by HPLC with a Chiralpak Phenomenex column (hexanes: isopropanol = 98:2, 0.6 mL/min, 211 nm, 27% *ee*, *dr* = 7:1). tR = 33.845 min (major), tR = 27.516 min (minor).

2.4 Asymmetric Synthesis of Silicon-Stereogenic Silycyclopropanes

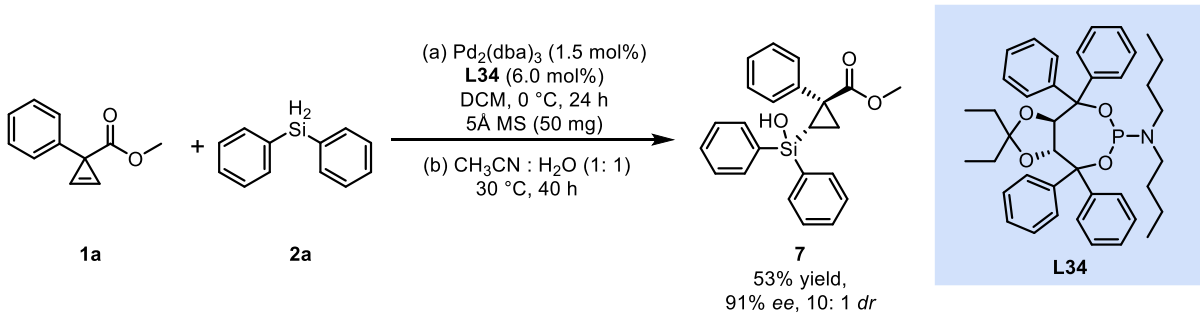


Under N_2 atmosphere, $[PdCl(2\text{-Me-}C_3H_4)_2]_2$ (1.5 mg, 1.5 mol%), **L34** (9.8 mg, 7.5 mol%) and CuI (1.9 mg, 5.0 mol%) were dissolved in 2 mL anhydrous THF, and stirred at room temperature for 20 min. Cycloprop-2-ene-1-carboxamide **4a** (0.2 mmol) was added and stirred for 20 min, then the dihydrosilane **2b** (0.3 mmol) was added and stirred at 0 °C for 18 h. The mixture was filtered through celite and the filtrate was concentrated. A portion of the residue was analyzed with ^{1}H NMR to determine the diastereomeric ratio and recovered. The crude product was purified by column chromatography to give the products **6** (30.6 mg, 37% yield, 94% *ee*, 2: 1 *dr*).

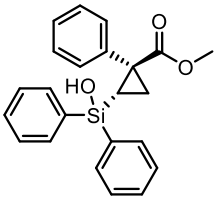


***N*, *N* - diethyl - 1 - phenyl - 2 - (phenyl (*o* - tolyl) silyl) cyclopropane - 1- carboxamide (6)**: Colorless oil (30.6 mg, 37% yield), purified by column chromatography (Al_2O_3, PE/EA= 15:1). $[\alpha]_D^{25}$ = 22.4 (c = 1.58, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, J = 7.6, 1.6 Hz, 1H), 7.32 - 7.28 (m, 2H), 7.20 - 7.12 (m, 6H), 7.05 (s, 5H), 4.09 (d, J = 4.8 Hz, 1H), 3.38 (dq, J = 14.4, 7.2 Hz, 1H), 3.29 - 3.19 (m, 2H), 3.17 - 3.07 (m, 1H), 2.15 (s, 3H), 1.66 - 1.57 (m, 1H), 1.45 - 1.33 (m, 2H), 0.99 (t, J = 7.1 Hz, 3H), 0.48 (t, J = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 144.5, 138.1, 136.9, 135.2, 134.0, 133.3, 130.0, 129.6, 129.2, 128.4, 128.2, 127.8, 126.7, 125.1, 41.6, 39.3, 36.1, 23.0, 14.9, 12.7, 12.5, 10.1. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{27}H_{31}NONaSi$: 436.2065, found: 436.2067. UPLC: Chiralpak MD column (hexanes: isopropanol = 95:5, 0.6 mL/min, 211 nm, 94% *ee*, *dr* = 2:1). tR = 5.137 min (major), tR = 4.473 min (minor).

2.5 Transformation of Chiral Silylcyclopropanes

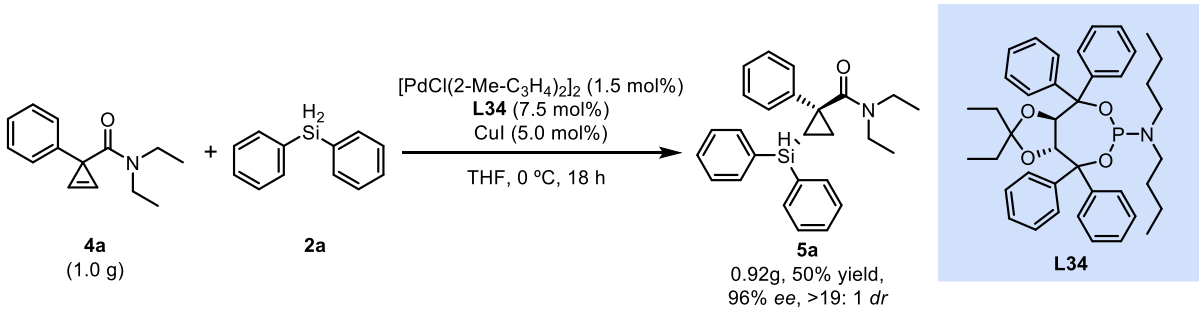


The procedure was followed the known literature [1]. Compound **3a** was obtained from **1a** (0.2 mmol) and **2a** (0.26 mmol) according to standard conditions. After the end of the reaction, DCM was directly removed without isolation. And then 1 mL of CH_3CN and 1 mL of H_2O were added and the mixture was stirred at 30 °C for 40 h. After reaction completed, the reaction was diluted with DCM and quenched with H_2O. The organic layer was separated and washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatography to afford **7** (41.1 mg, 53% yield, 91% *ee*, 10: 1 *dr*).



Methyl (1*S*, 2*S*) - 2 - (hydroxydiphenylsilyl) - 1 - phenylcyclopropane - 1 - carboxylate (7): Yellow oil (41.1 mg, 53% yield), purified by column chromatography (SiO_2, PE/EA= 20:1). $[\alpha]_D^{25}$ = 63.5 (c = 0.85, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 - 7.41 (m, 2H), 7.37 - 7.22 (m, 6H), 7.22 - 7.11 (m, 3H), 7.11 - 7.01 (m, 4H), 3.53 (s, 3H), 1.83 (dd, *J* = 10.8, 3.2 Hz, 1H), 1.65 (dd, *J* = 8.4, 3.2 Hz, 1H), 1.55 (dd, *J* = 10.8, 8.4 Hz, 1H), 0.85 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 137.3, 136.0, 135.4, 134.3, 131.2, 130.1, 130.0, 128.3, 128.1, 127.9, 127.8, 52.8, 33.4, 18.3, 15.5. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{23}H_{22}NaO_3Si$: 397.1230, found: 397.1235. UPLC: Chiralpak ND column (hexanes: isopropanol = 95:5, 0.6 mL/min, 211 nm, 91% *ee*, *dr* = 10:1). tR = 11.359 min (major), tR = 17.033 min (minor).

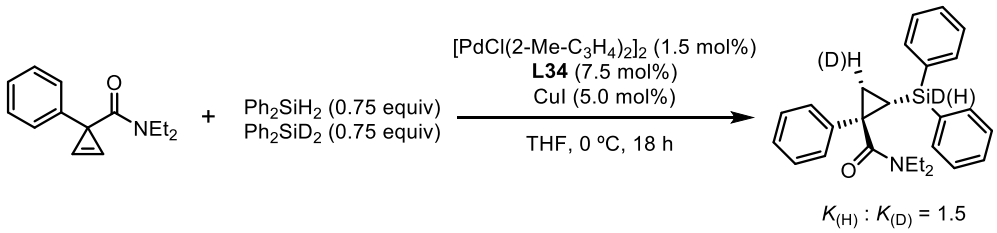
2.6 Gram Scale Reaction



Under N_2 atmosphere, $[PdCl(2\text{-}Me\text{-}C_3H_4)_2]_2$ (34.5 mg, 1.5 mol%), **L34** (225.4 mg, 7.5 mol%) and CuI (43.7 mg, 5.0 mol%) were dissolved in 2 mL anhydrous THF, and stirred at room temperature for 20 min. Cycloprop-2-ene-1-carboxamide **4a** (1g, 4.6 mmol) was added and stirred for 20 min, then the dihydrosilane **2a** (6.9 mmol) was added and stirred at 0 °C for 18 h. The mixture was filtered through celite and the filtrate was concentrated. A portion of the residue was analyzed with ^1H NMR to determine the diastereomeric ratio and recovered. The crude product was purified by column chromatography to give the products **5a** (0.92g, 50% yield, 96% *ee*, >19: 1 *dr*).4.6 mml

2.7 Experimental Mechanistic Study

2.7.1 Kinetic Study for the KIE



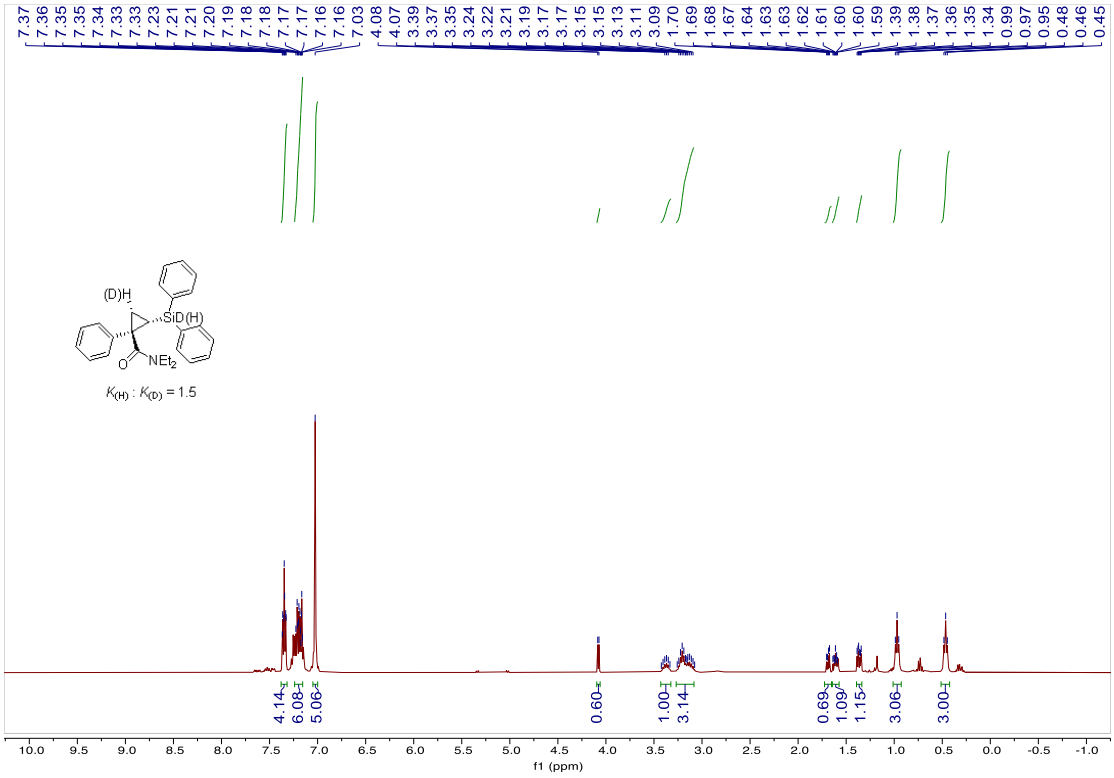
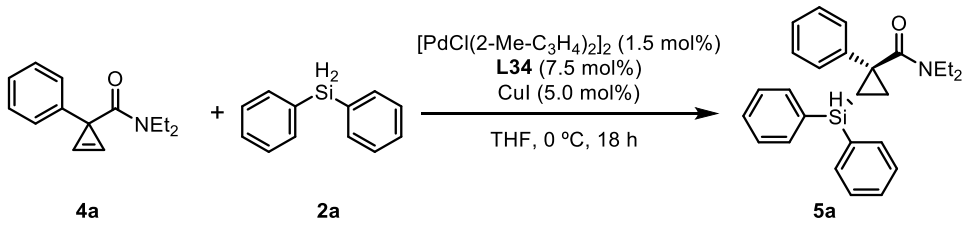


Figure S4. NMR analysis for Pd-catalyzed hydrosilylation of **2a** and **4a**.

2.7.2 The study of possible NLE in the Pd-catalyzed hydrosilylation of 4a



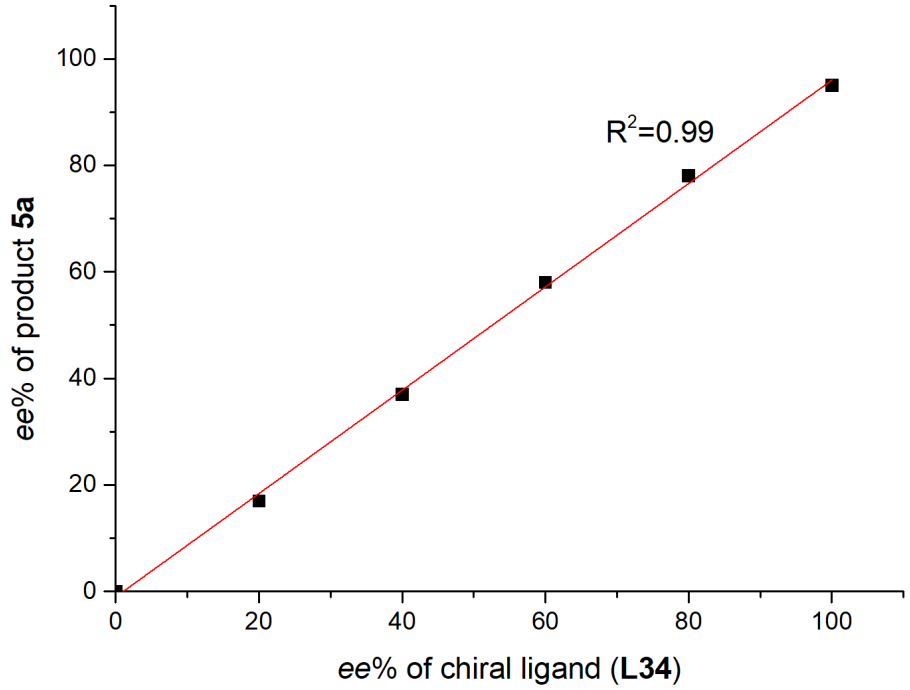
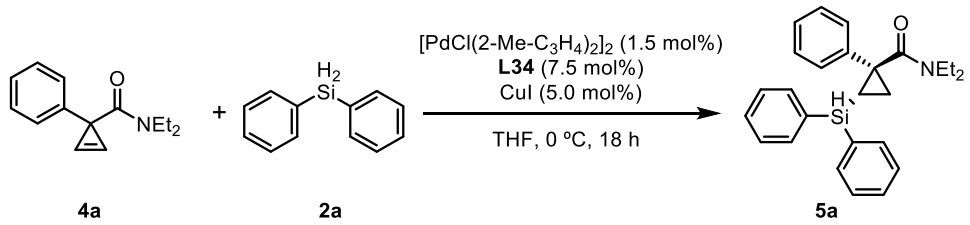


Figure S5. Non-linear effect for Pd-catalyzed hydrosilylation of **2a** and **4a**.

2.7.3 Comparison of ^{31}P NMR of ligand and Pd/L34 complex in the reaction with 4a and 2a.



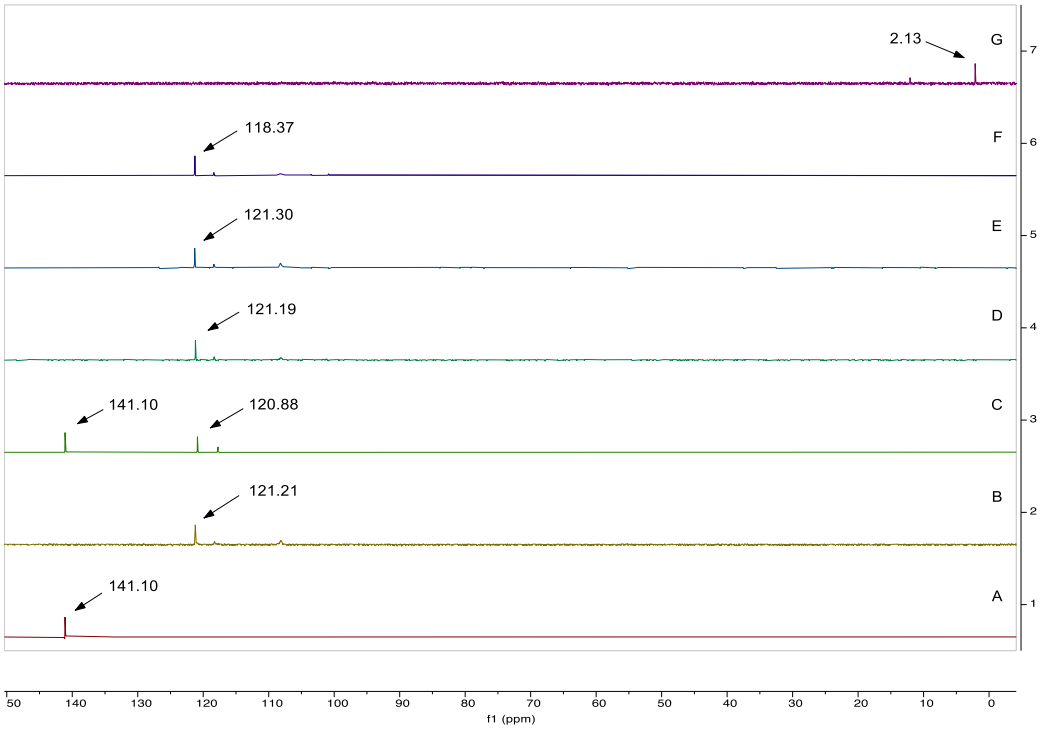


Figure S6. NMR analysis for Pd-catalyzed hydrosilylation of **2a** and **4a**. **A): L34** (0.015 mmol, 9.8 mg). **B): L34** (0.015 mmol, 9.8 mg) and $[PdCl(2\text{-}Me\text{-}C_3H_4)_2]_2$ (0.003 mmol, 1.5 mg) were stirred for 20 min. **C): L34** (0.015 mmol, 9.8 mg), $[PdCl(2\text{-}Me\text{-}C_3H_4)_2]_2$ (0.003 mmol, 1.5 mg) and CuI (0.01 mmol, 1.9 mg) were stirred for 20 min. **D) L34** (0.015 mmol, 9.8 mg), $[PdCl(2\text{-}Me\text{-}C_3H_4)_2]_2$ (0.003 mmol, 1.5 mg), CuI (0.01 mmol, 1.9 mg) were stirred for 20 min, then **4a** (0.2 mmol, 43.0 mg) was added and stirred for 20 min. **E) L34** (0.015 mmol, 9.8 mg), $[PdCl(2\text{-}Me\text{-}C_3H_4)_2]_2$ (0.003 mmol, 1.5 mg), CuI (0.01 mmol, 1.9 mg) were stirred for 20 min, then **2a** (0.3 mmol, 55.3 mg) was added and stirred for 20 min. **F) L34** (0.015 mmol, 9.8 mg), $[PdCl(2\text{-}Me\text{-}C_3H_4)_2]_2$ (0.003 mmol, 1.5 mg), CuI (0.01 mmol, 1.9 mg) were stirred for 20 min, then **4a** (0.2

mmol, 43.0 mg) was added and stirred for 20 min, then **2a** (0.3 mmol, 55.3 mg) was added and stirred for 20 min. **G) L34** (0.015 mmol, 9.8 mg), $[PdCl(2\text{-}Me\text{-}C_3H_4)_2]_2$ (0.003 mmol, 1.5 mg), CuI (0.01 mmol, 1.9 mg) were stirred for 20 min, then **4a** (0.2 mmol, 43.0 mg) was added and stirred for 20 min, then **2a** (0.3 mmol, 55.3 mg) was added and stirred for 12 h.

2.7.4 CD Spectra

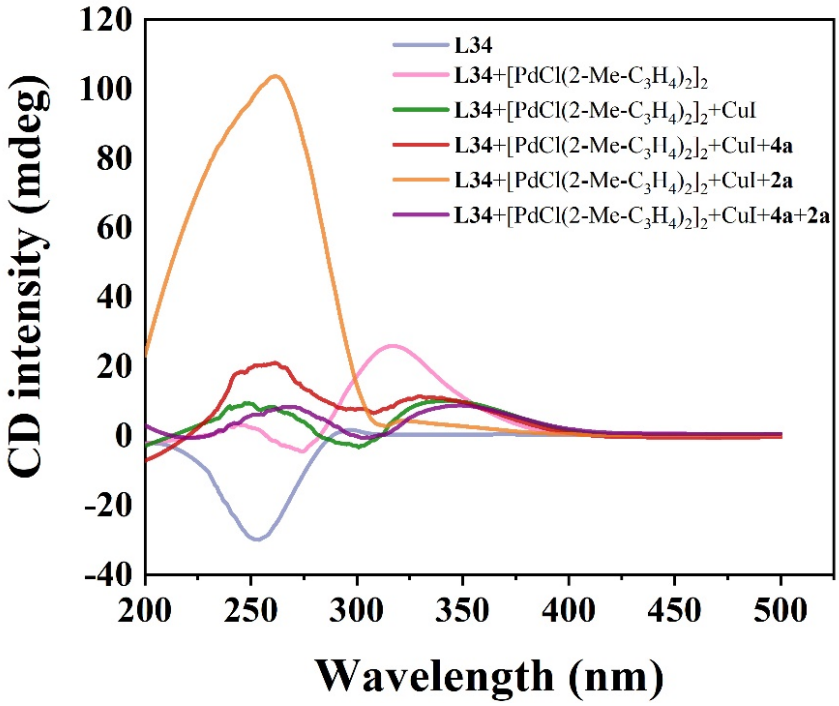


Figure S7. Circular dichroism spectroscopy analysis with 1.3×10^{-2} mol/L. CD spectra of the Pd-catalyzed hydrosilylation of amide **4a** with the aid of CuI, and the ratio is referred to **L34**/[Pd]/CuI/**1a**/**4a** = 1:0.2:0.7:1:1.5.

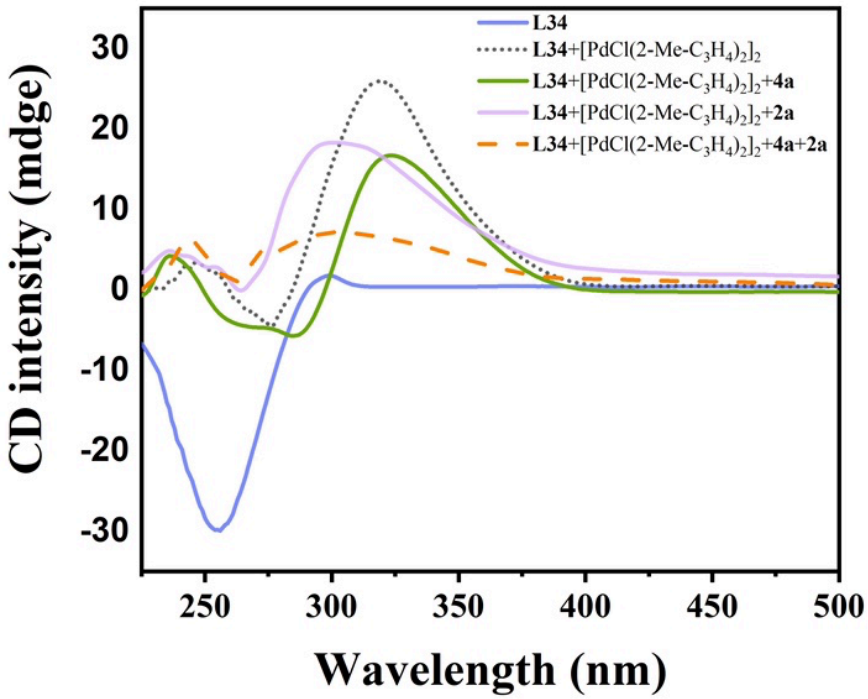


Figure S8. circular dichroism spectroscopy analysis with 2.4×10^{-5} mol/L. CD intensity spectra of the Pd-catalyzed hydrosilylation of amide **1a** without the aid of CuI.

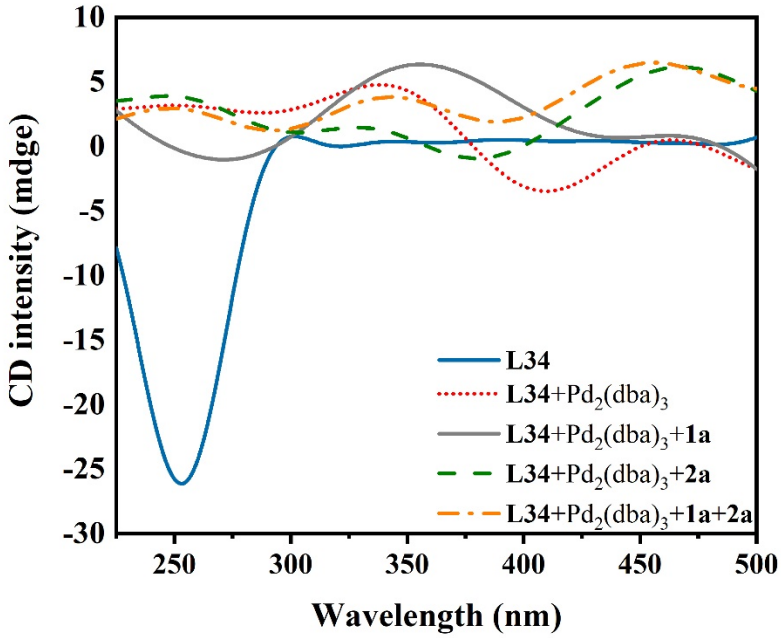
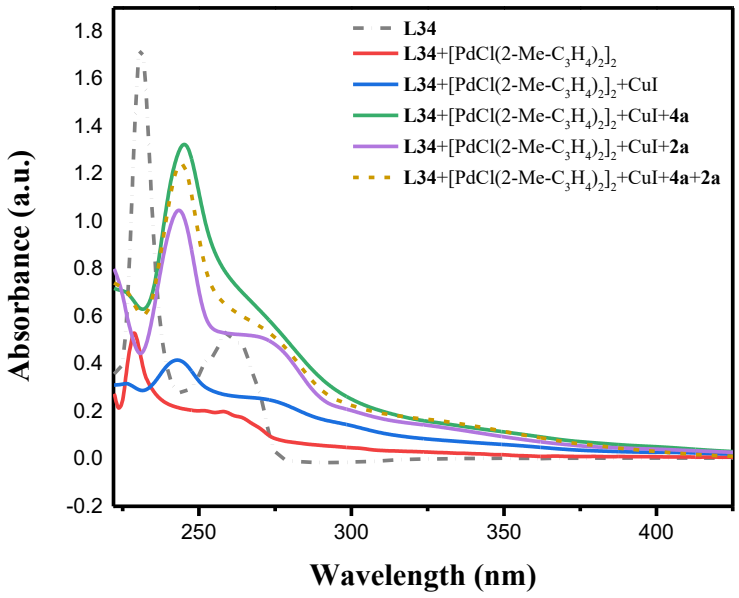
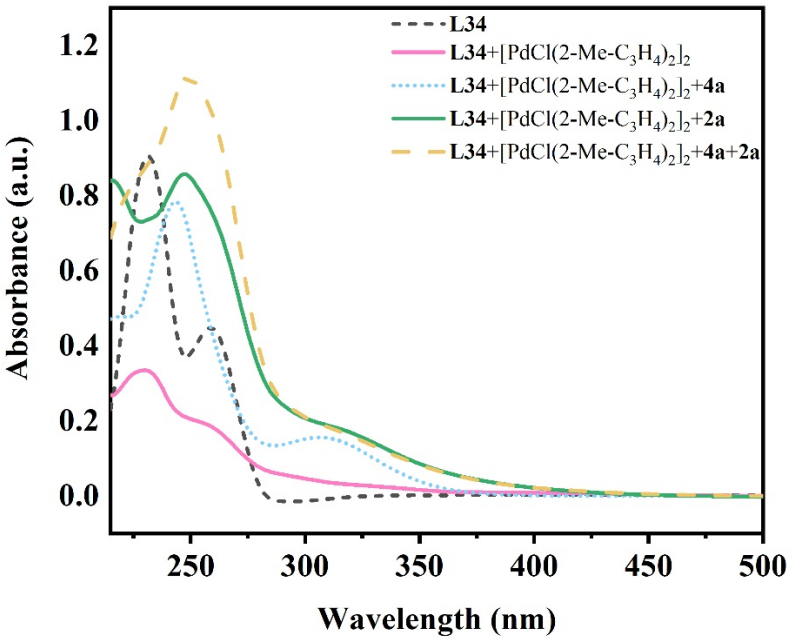


Figure S9. circular dichroism spectroscopy analysis with 2.4×10^{-5} mol/L. CD intensity spectra of the Pd-catalyzed hydrosilylation of ester **1a** without the aid of CuI.

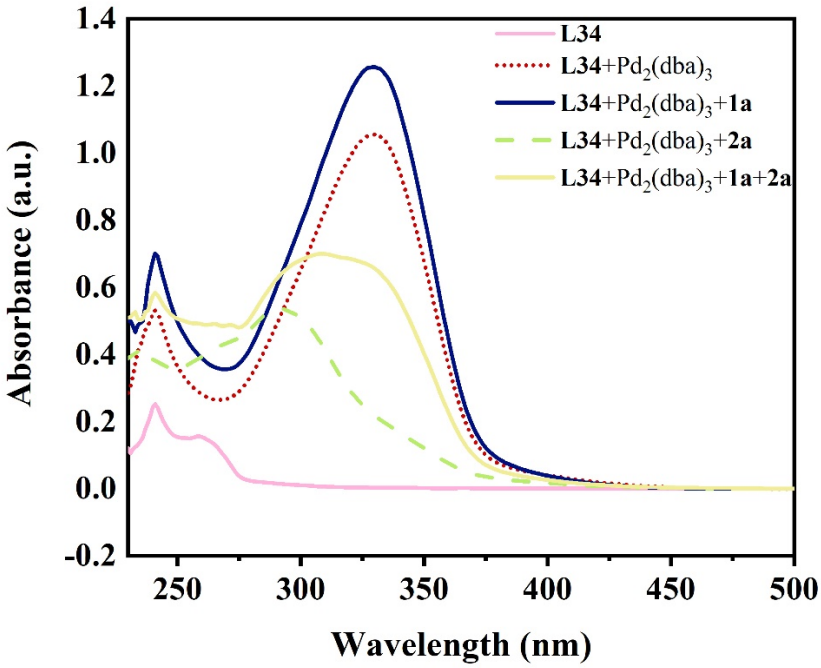
2.7.5 UV Spectra



(a)



(b)



(c)

Figure S10. UV-Vis spectroscopy analysis with 2.4×10^{-5} mol/L. (a) UV absorption spectra for the Pd-catalyzed hydrosilylation of amide **4a** with the aid of CuI. (b) UV absorption spectra of the Pd-catalyzed hydrosilylation of amide **4a** without CuI. (c) UV absorption spectra of the hydrosilylation of ester **1a**. The ratio of mixture is referred to **L34**/[Pd]/CuI/**1a**/**4a** = 1:0.2:0.7:1:1.5.

2.7.6 Control experiments

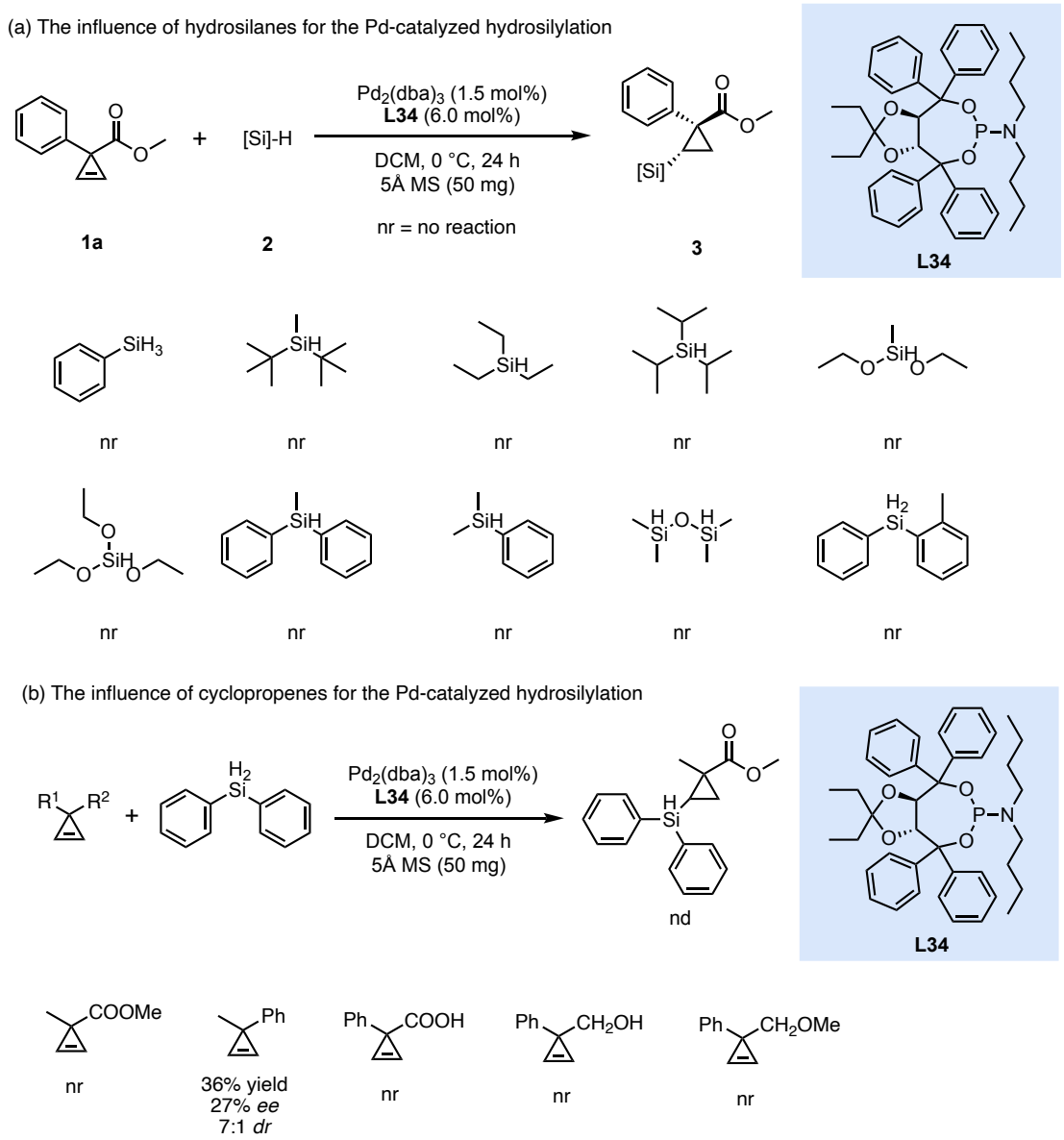
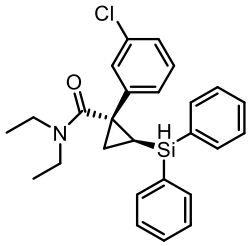


Figure S11. The influence of hydrosilanes or cyclopropenes for the Pd-catalyzed hydrosilylation: The direct evidence for the importance of aryl groups on carbonyl cyclopropenes and the different reactivity of hydrosilanes in this work.

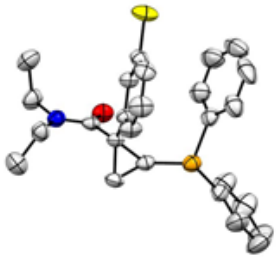
3. X-Ray Structure of 5n

Single crystals of **5n** were obtained by recrystallization from PE/DCM. The molecular structure and X-ray diffraction data/refinement of **5n** were shown below.



(1*S*, 2*S*)-**5n**

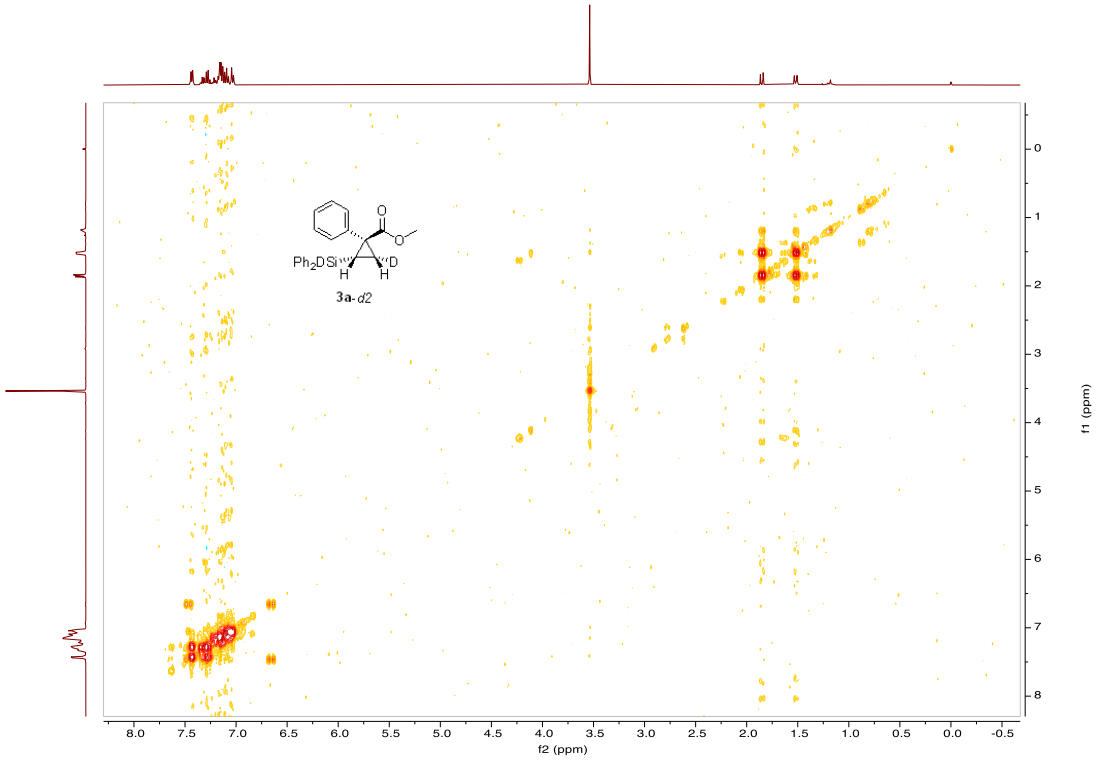
≡



(CCDC 2157919)

Empirical formula	$C_{26}H_{28}ClNOSi$
Formula weight	434.03
Temperature/K	296.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.7825(10)
b/Å	14.777(2)
c/Å	23.648(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2370.1(6)
Z	4
ρ_{calc}g/cm^3	1.216
μ/mm^{-1}	0.229
F(000)	920.0
Crystal size/mm^3	0.2 × 0.15 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.25 to 55.14
Index ranges	$-8 \le h \le 8$, $-18 \le k \le 19$, $-30 \le l \le 18$
Reflections collected	14333
Independent reflections	5375 [R_{int} = 0.0575, R_{sigma} = 0.0660]
Data/restraints/parameters	5375/0/273
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0602, wR_2 = 0.1540
Final R indexes [all data]	R_1 = 0.0990, wR_2 = 0.1835
Largest diff. peak/hole / e Å^{-3}	0.71/-0.25
Flack parameter	0.05(6)

4. NOESY spectrum of 3a-*d2*



5. References

[1] Zhao, Z. Y.; Nie, Y. X.; Tang, R. H.; Yin, G. W.; Cao, J.; Xu, Z.; Cui, Y. M.; Zheng, Z. J.; Xu, L. W. *ACS Catal*. **2019**, 9, 9110-9116.

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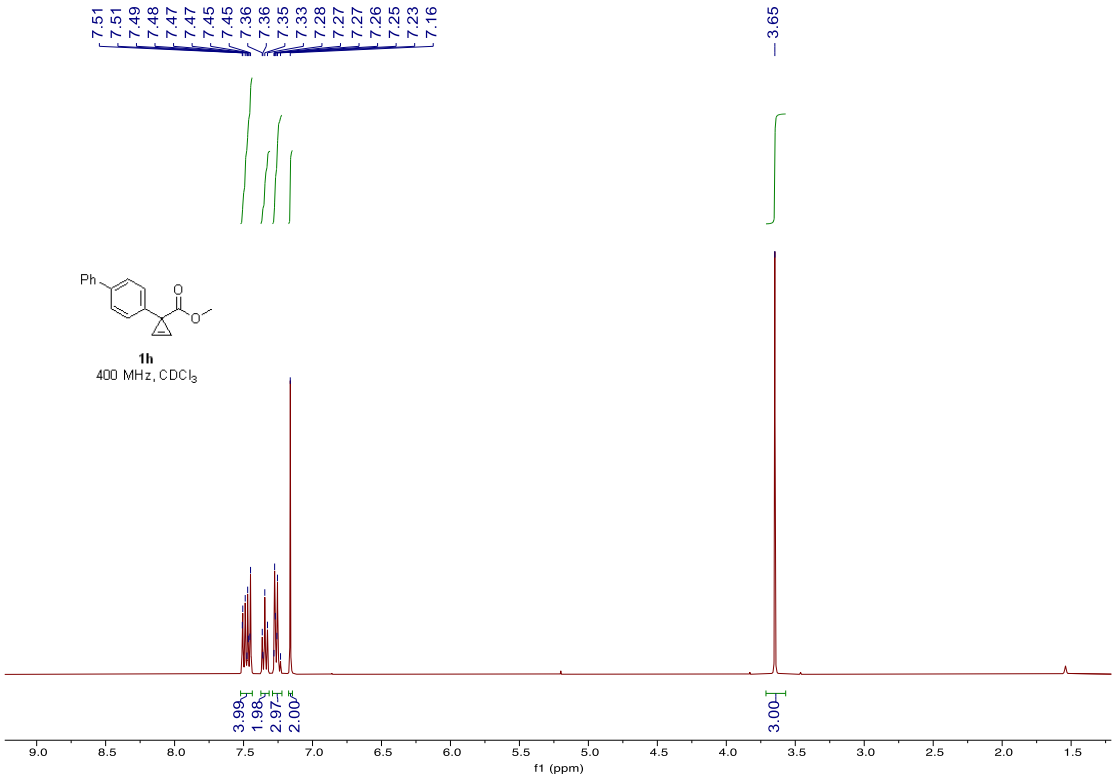
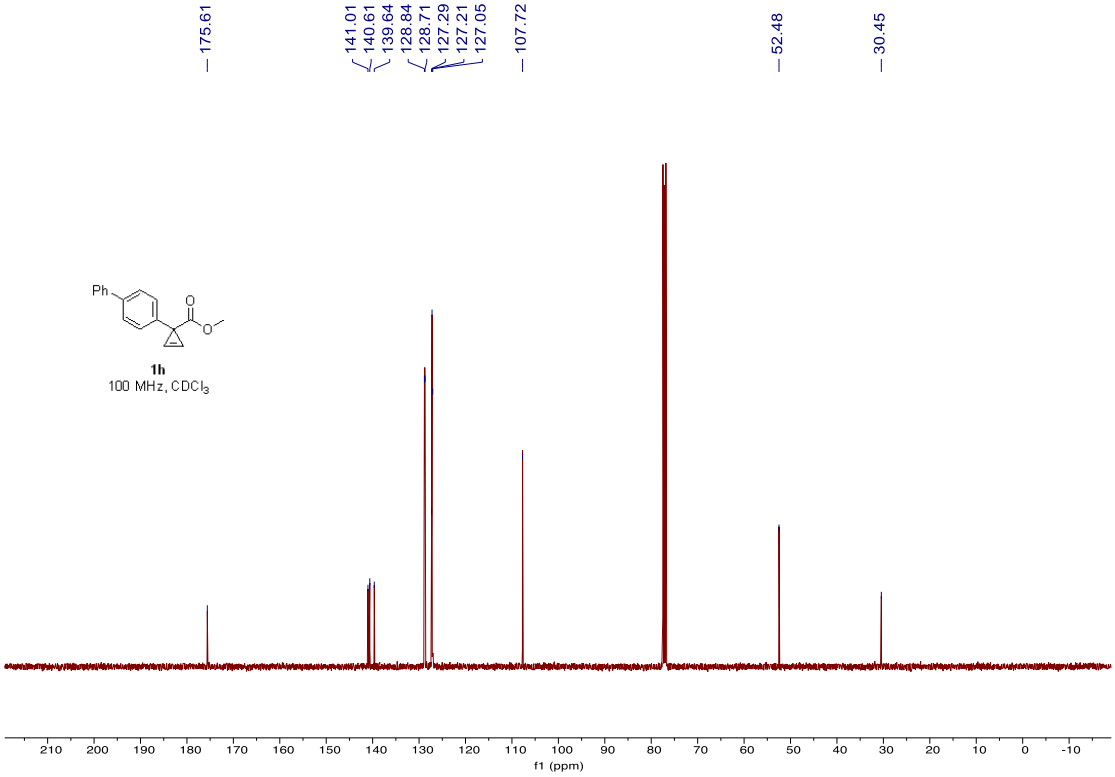
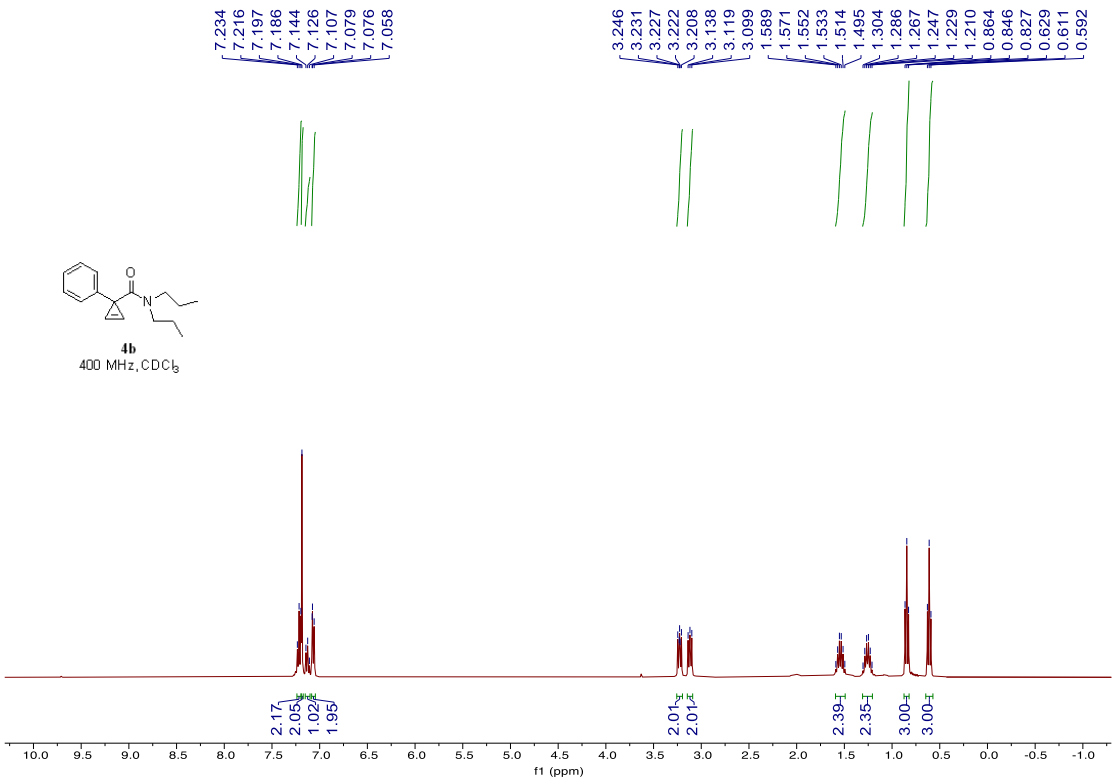
6. NMR Spectra



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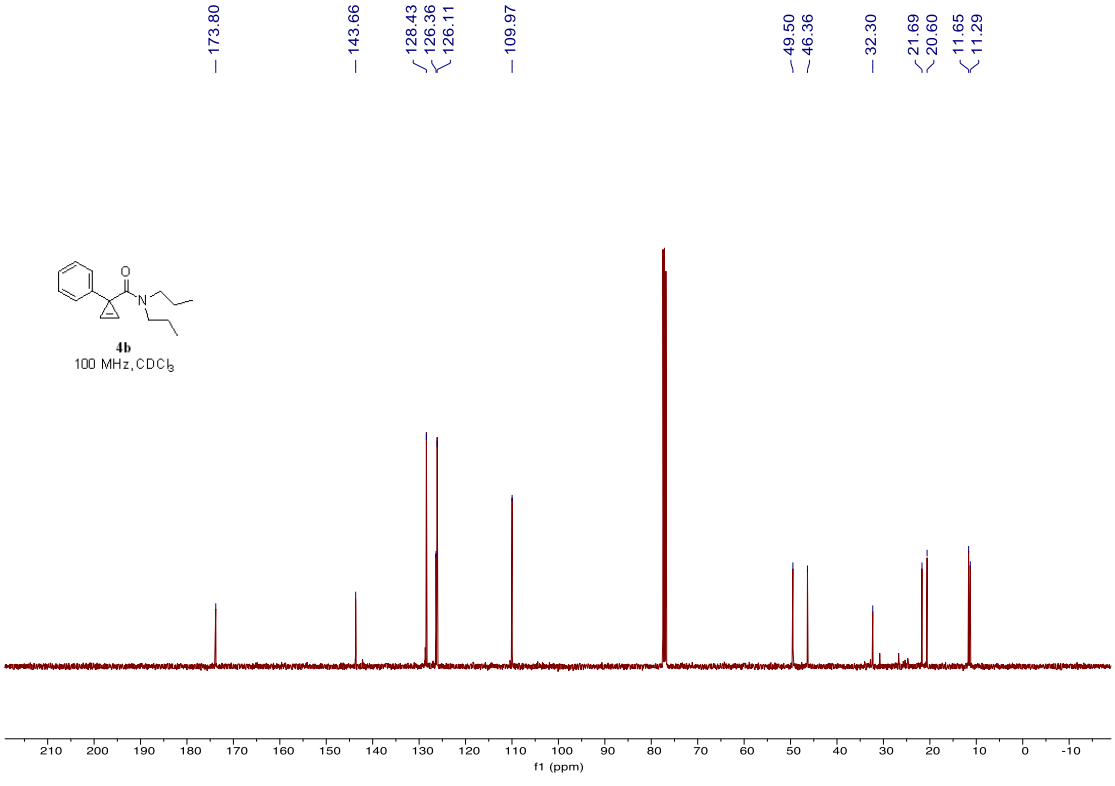
7.197
7.186
7.144
7.126
7.107
7.079
7.076
7.058
3.246
3.231
3.227
3.222
3.208
3.138
3.119
3.099
1.589
1.571
1.552
1.533
1.514
1.495
1.304
1.286
1.267
1.247
1.229
1.210
0.864
0.846
0.827
0.629
0.611
0.592
4b
400 MHz, CDCl3
2.17
2.05
1.02
1.95
2.01
2.01
2.39
2.35
3.00
3.00
f1 (ppm)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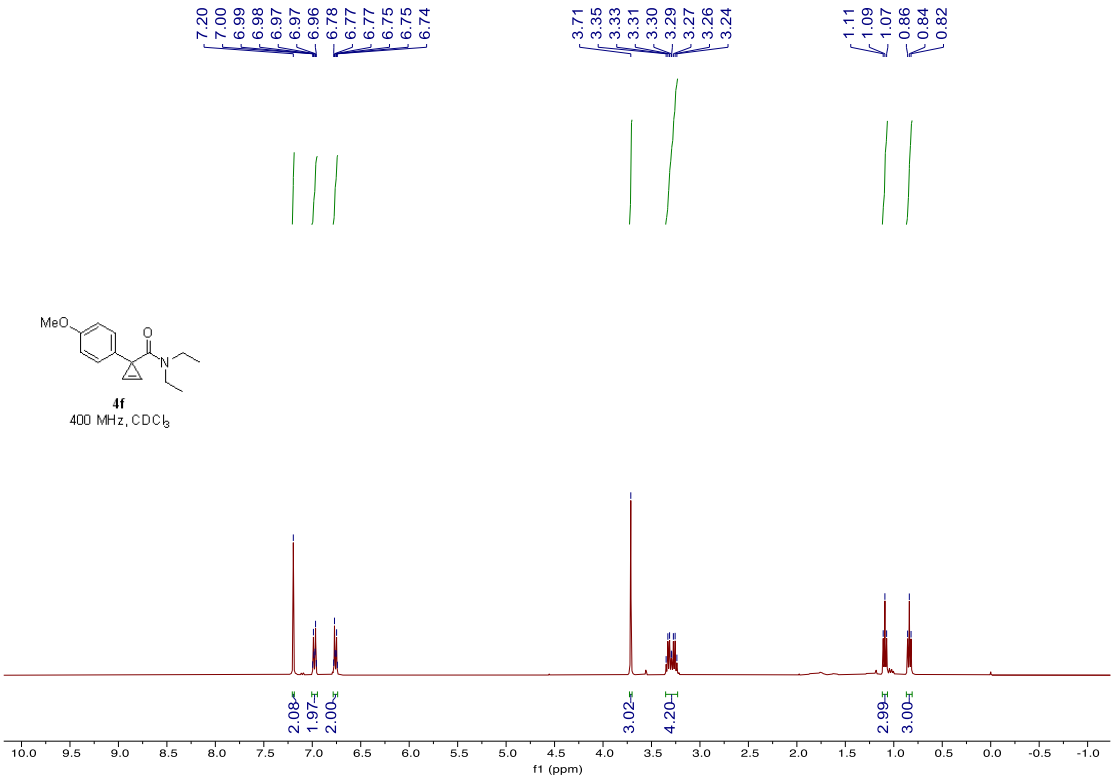
128.43
126.36
126.11
109.97
49.50
46.36
32.30
21.69
20.60
11.65
11.29
4b
100 MHz, CDCl3
f1 (ppm)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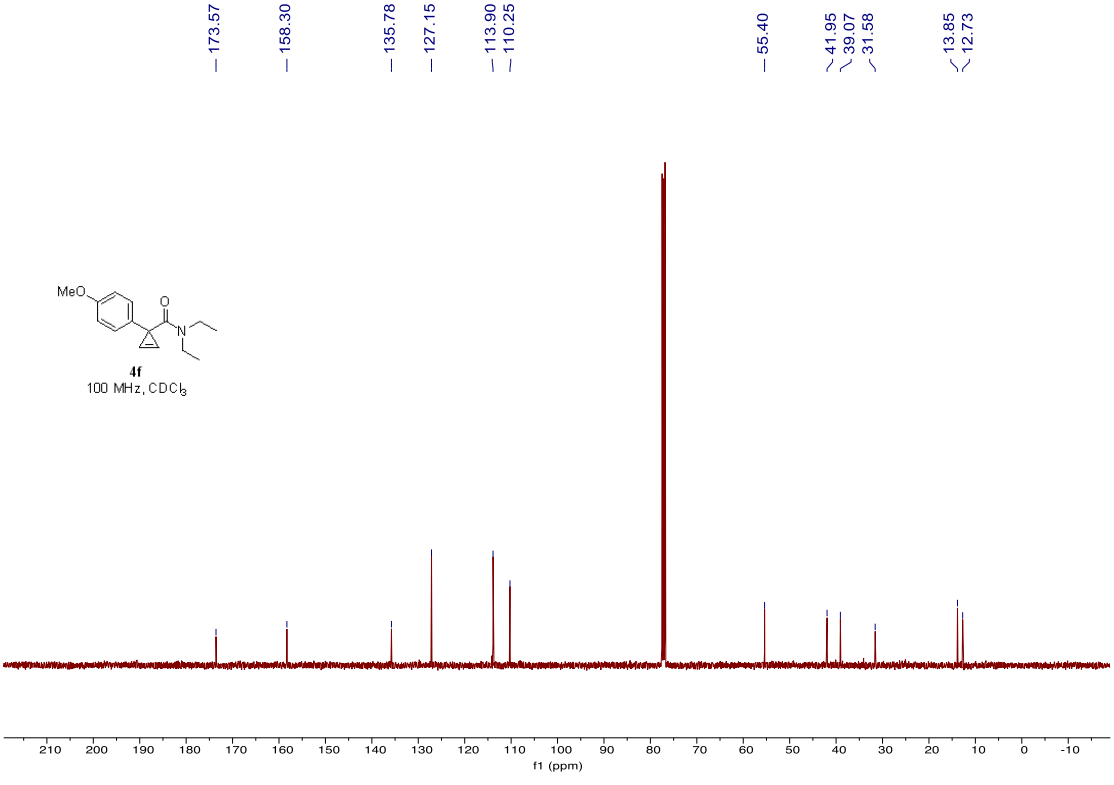
7.00
6.99
6.98
6.97
6.97
6.96
6.78
6.77
6.77
6.75
6.75
6.74
3.71
3.35
3.33
3.31
3.30
3.29
3.27
3.26
3.24
1.11
1.09
1.07
0.86
0.84
0.82
MeO
O
N
4f
400 MHz, CDCl3
2.08
1.97
2.00
3.02
4.20
2.99
3.00
f1 (ppm)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158.30
135.78
127.15
113.90
110.25
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31.58
13.85
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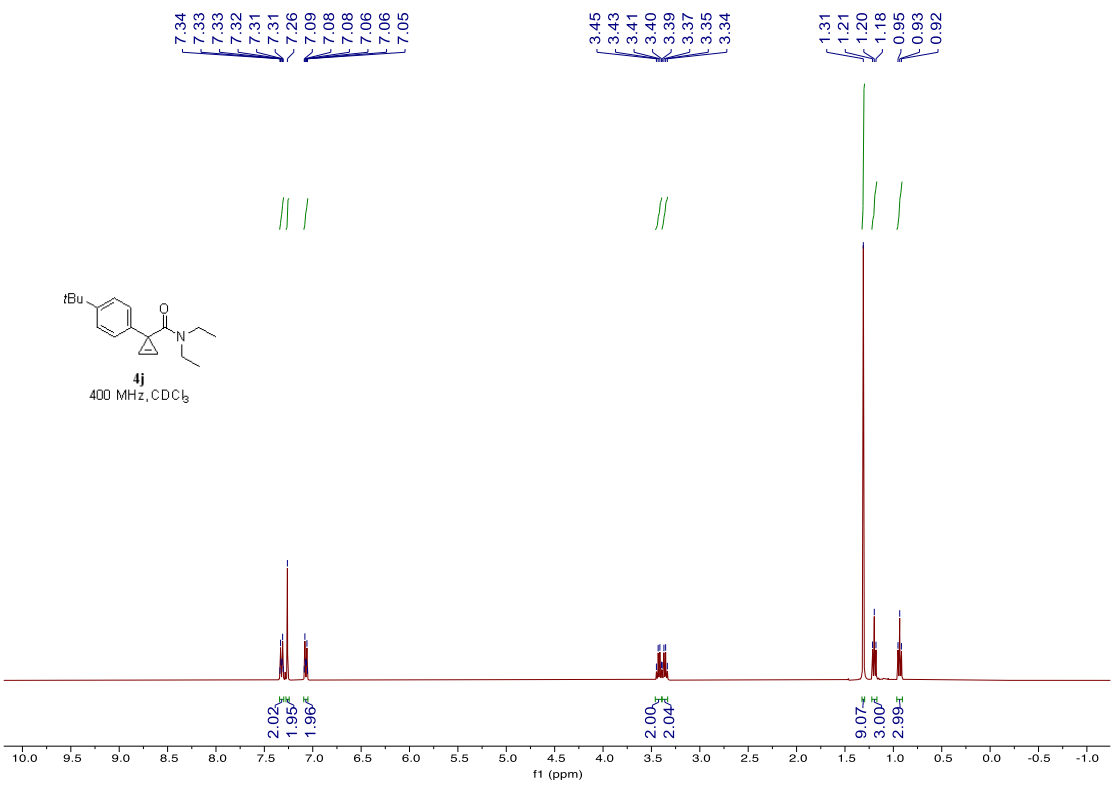
MeO
O
N
4f
100 MHz, CDCl3
f1 (ppm)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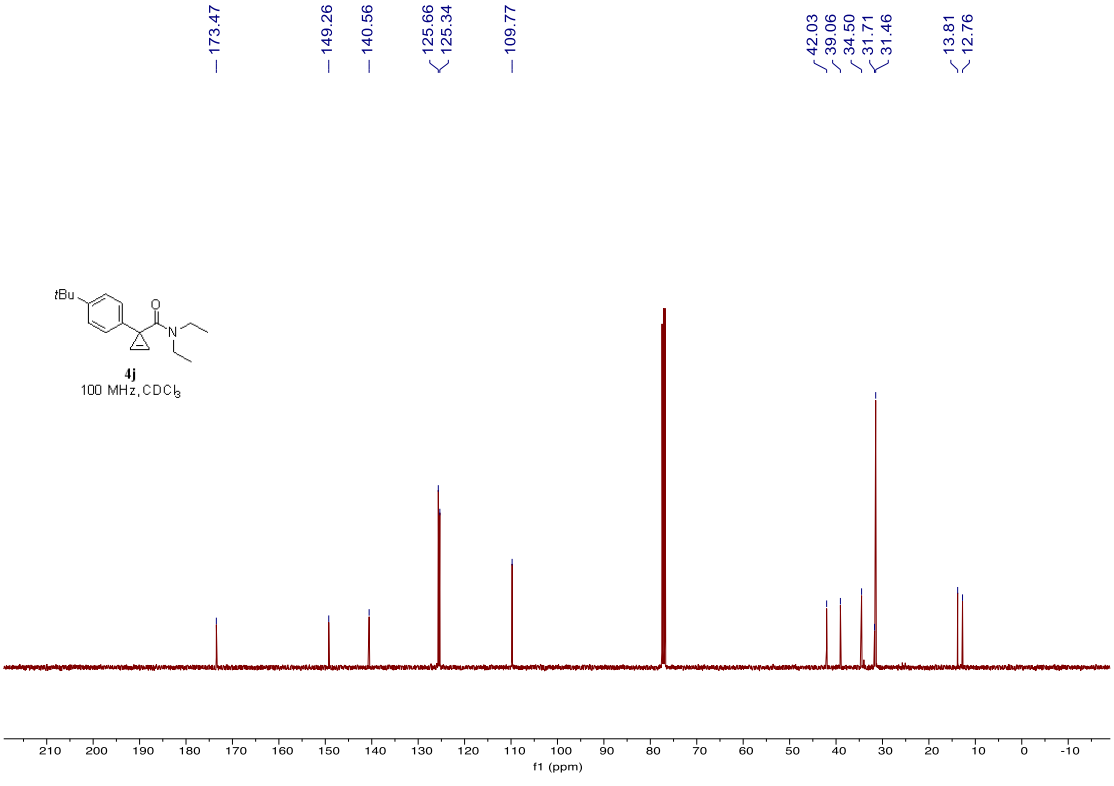
7.33
7.33
7.32
7.31
7.31
7.26
7.09
7.08
7.08
7.06
7.06
7.05
3.45
3.43
3.41
3.40
3.39
3.37
3.35
3.34
1.31
1.21
1.20
1.18
0.95
0.93
0.92
tBu
O
N
4j
400 MHz, CDCl3
2.02
1.95
1.96
2.00
2.04
9.07
3.00
2.99
f1 (ppm)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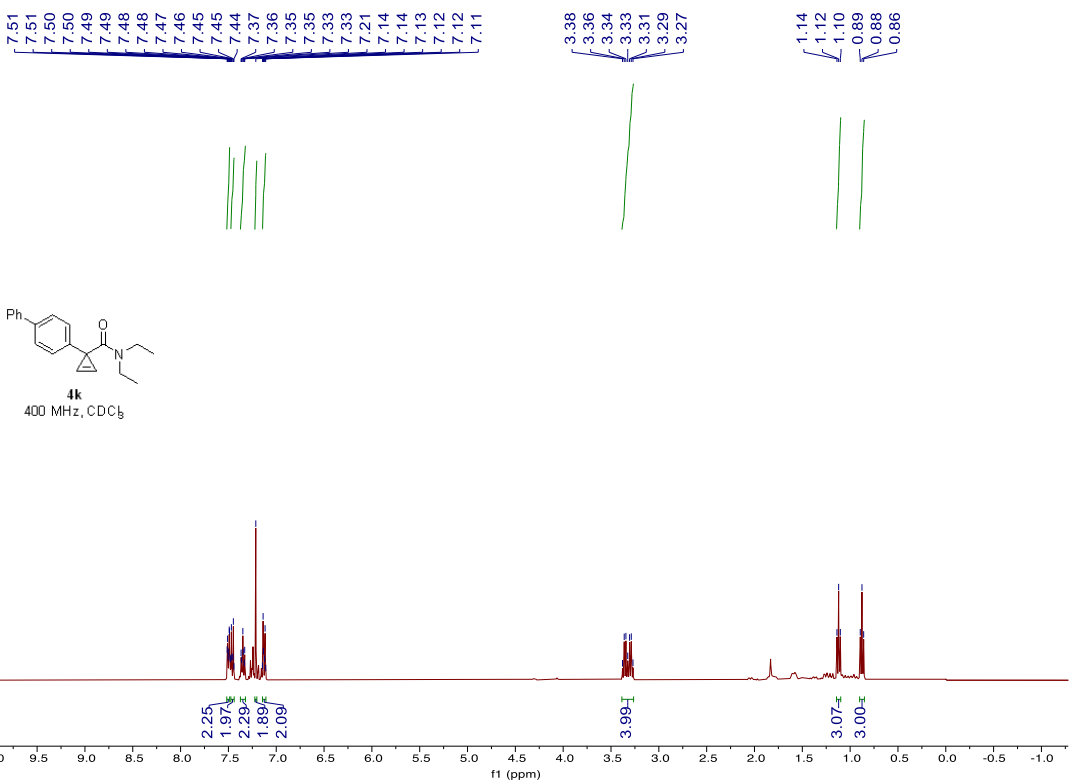
tBu
O
N
4j
100 MHz, CDCl3
f1 (ppm)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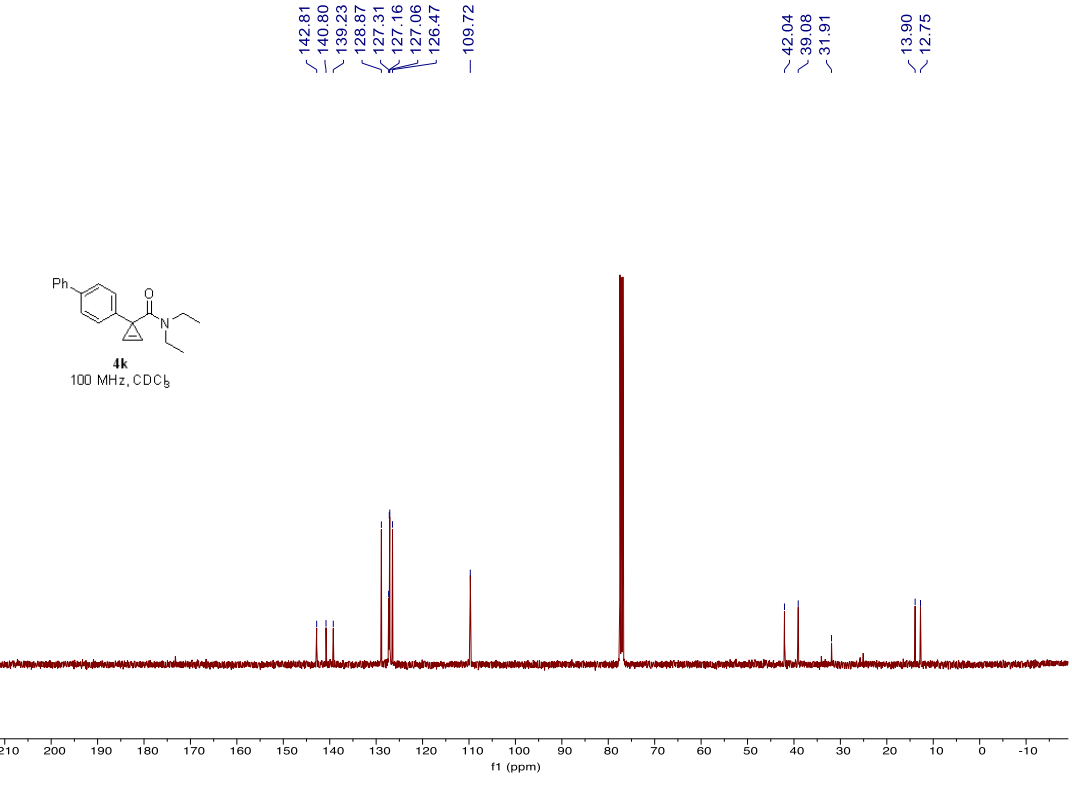
7.51
7.50
7.50
7.49
7.49
7.48
7.48
7.47
7.46
7.45
7.45
7.44
7.37
7.36
7.35
7.35
7.33
7.33
7.21
7.14
7.14
7.13
7.12
7.12
7.11
3.38
3.36
3.34
3.33
3.31
3.29
3.27
1.14
1.12
1.10
0.89
0.88
0.86
Ph
O
N
4k
400 MHz, CDCl3
2.25
1.97
2.29
1.89
2.09
3.99
3.07
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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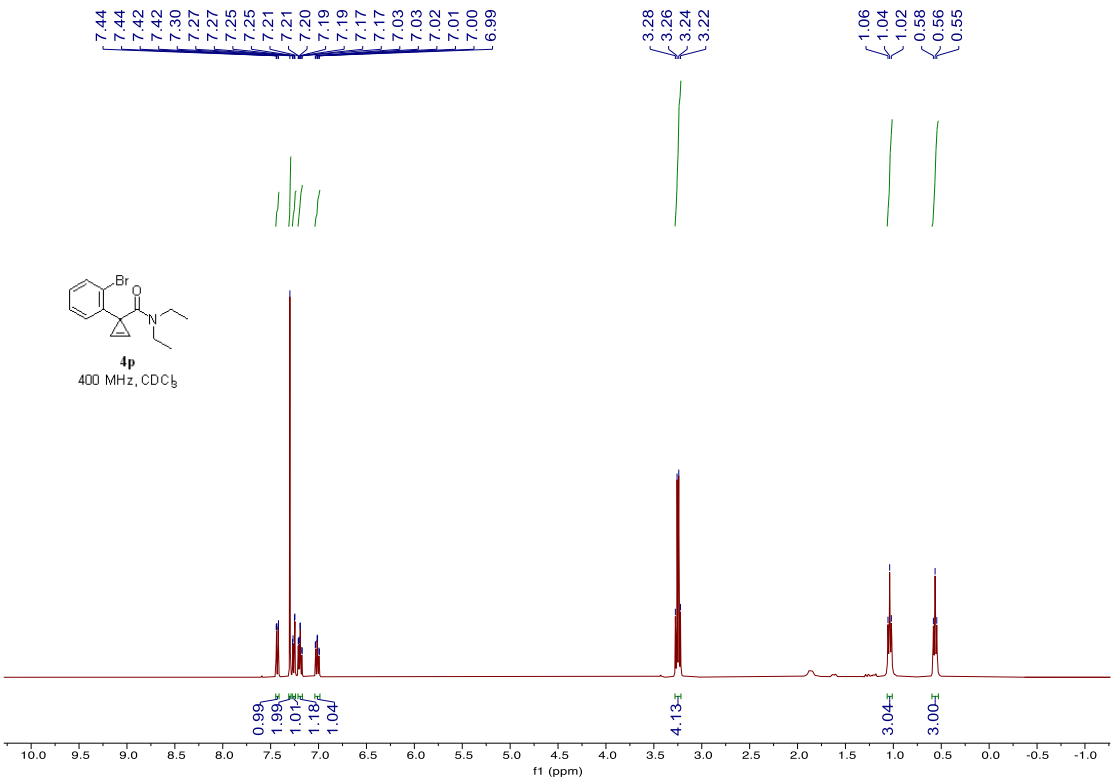
127.16
127.06
126.47
109.72
42.04
39.08
31.91
13.90
12.75
Ph
O
N
4k
100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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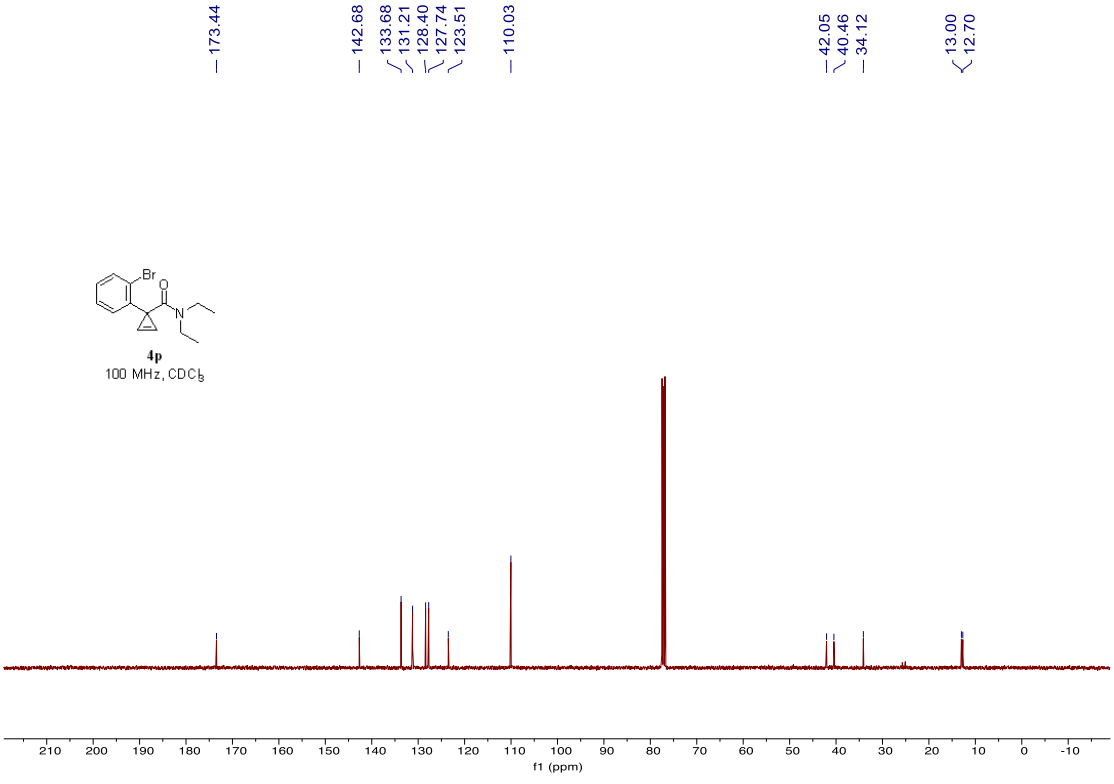
7.44
7.42
7.42
7.30
7.27
7.27
7.25
7.25
7.21
7.21
7.20
7.19
7.19
7.17
7.17
7.03
7.03
7.02
7.01
7.00
6.99
3.28
3.26
3.24
3.22
1.06
1.04
1.02
0.58
0.56
0.55
Br
O
N
4p
400 MHz, CDCl3
0.99
1.99
1.01
1.18
1.04
4.13
3.04
3.00
f1 (ppm)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133.68
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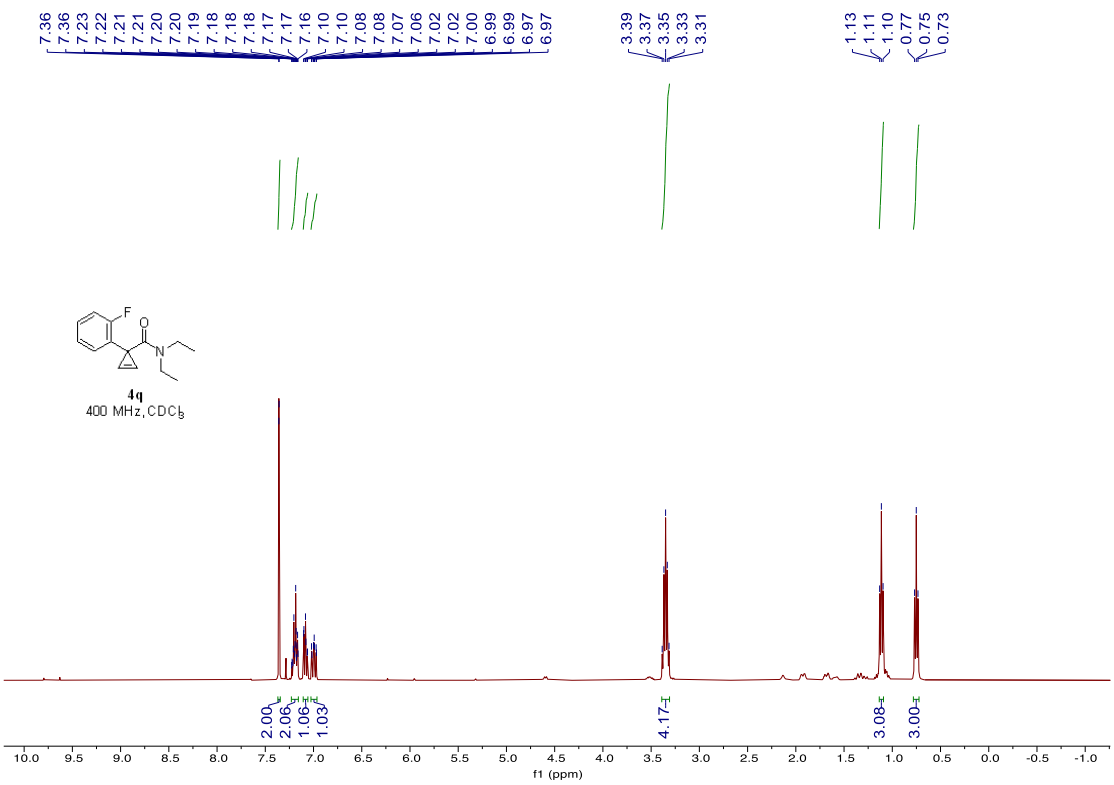
13.00
12.70
Br
O
N
4p
100 MHz, CDCl3
f1 (ppm)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7.36
7.23
7.22
7.21
7.21
7.20
7.20
7.19
7.18
7.18
7.18
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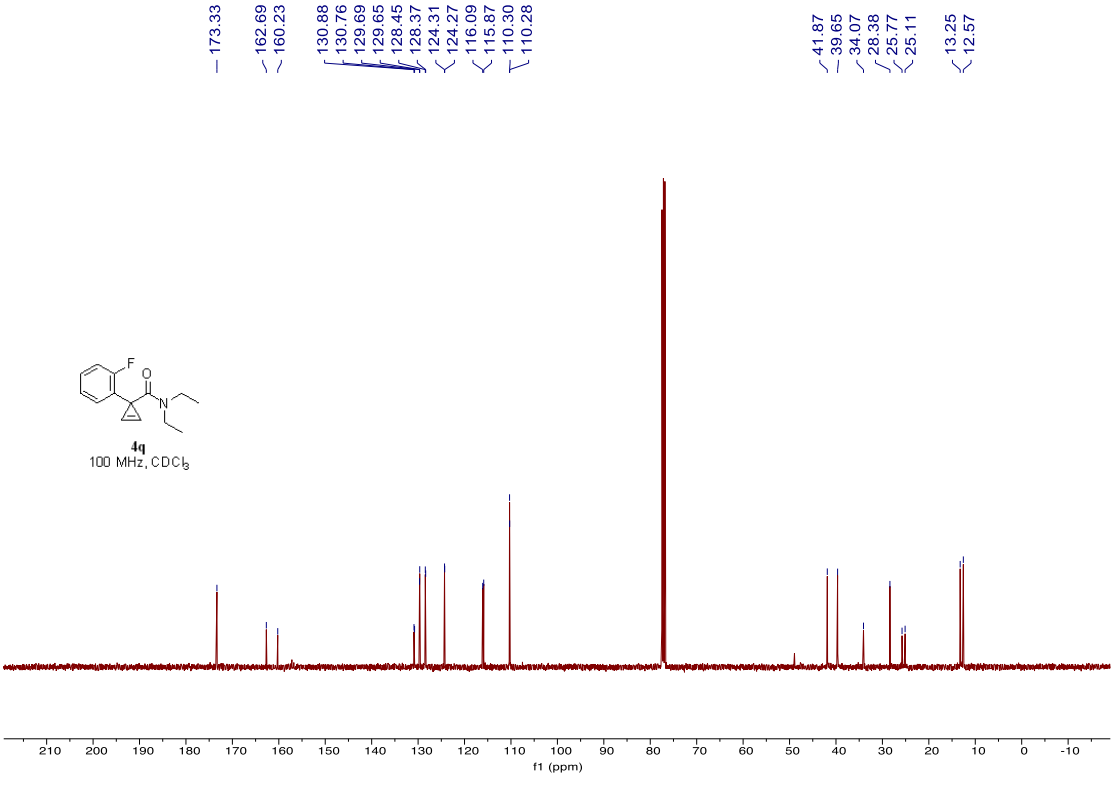
7.17
7.16
7.10
7.10
7.08
7.08
7.07
7.06
7.02
7.02
7.00
6.99
6.99
6.97
6.97
3.39
3.37
3.35
3.33
3.31
1.13
1.11
1.10
0.77
0.75
0.73
F
O
N
4q
400 MHz, CDCl3
2.00
2.06
1.06
1.03
4.17
3.08
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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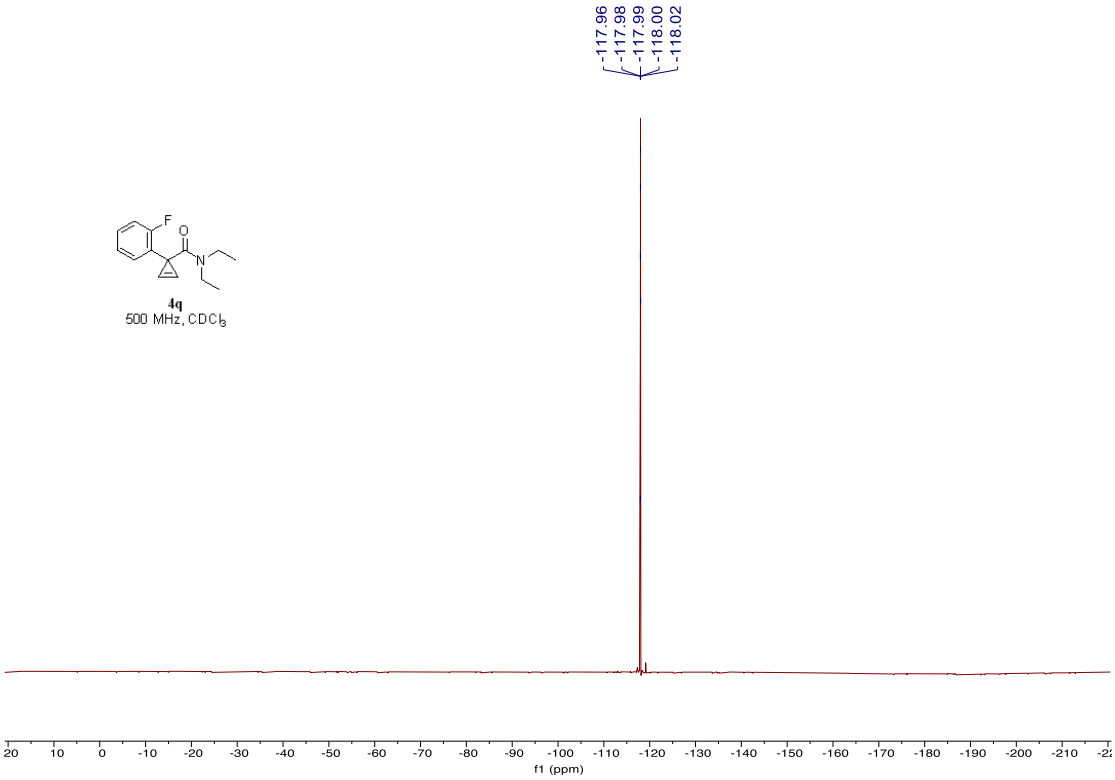
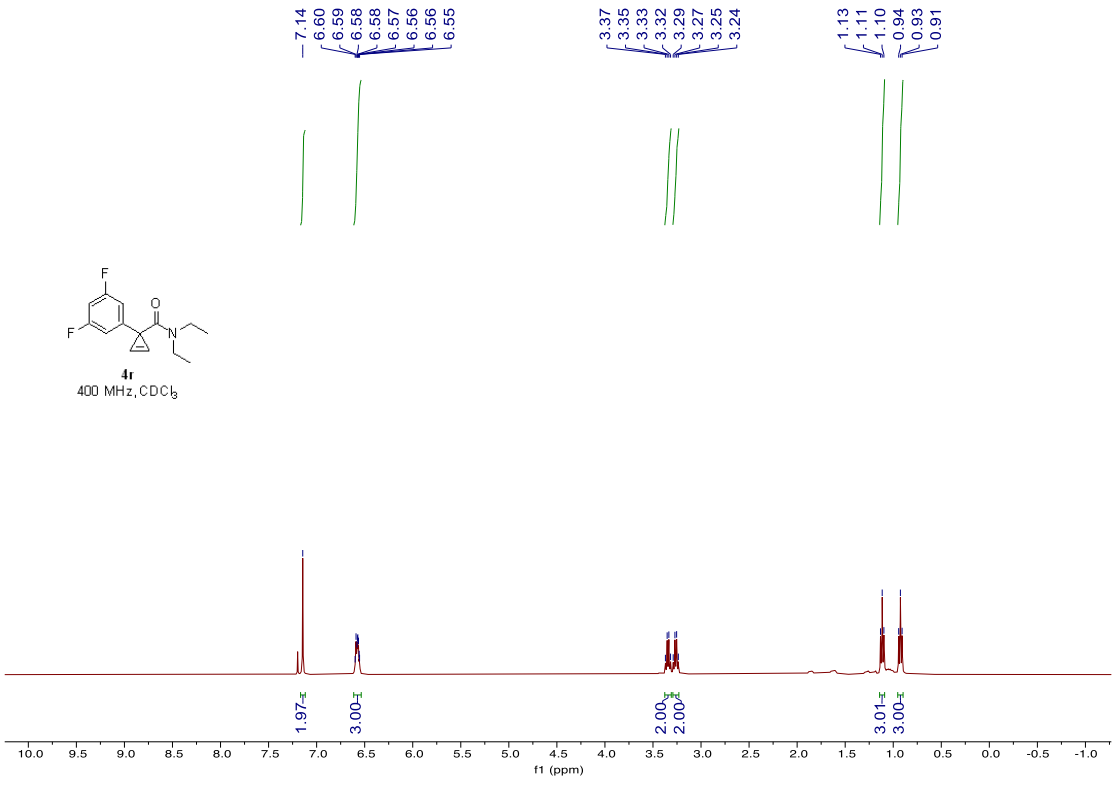
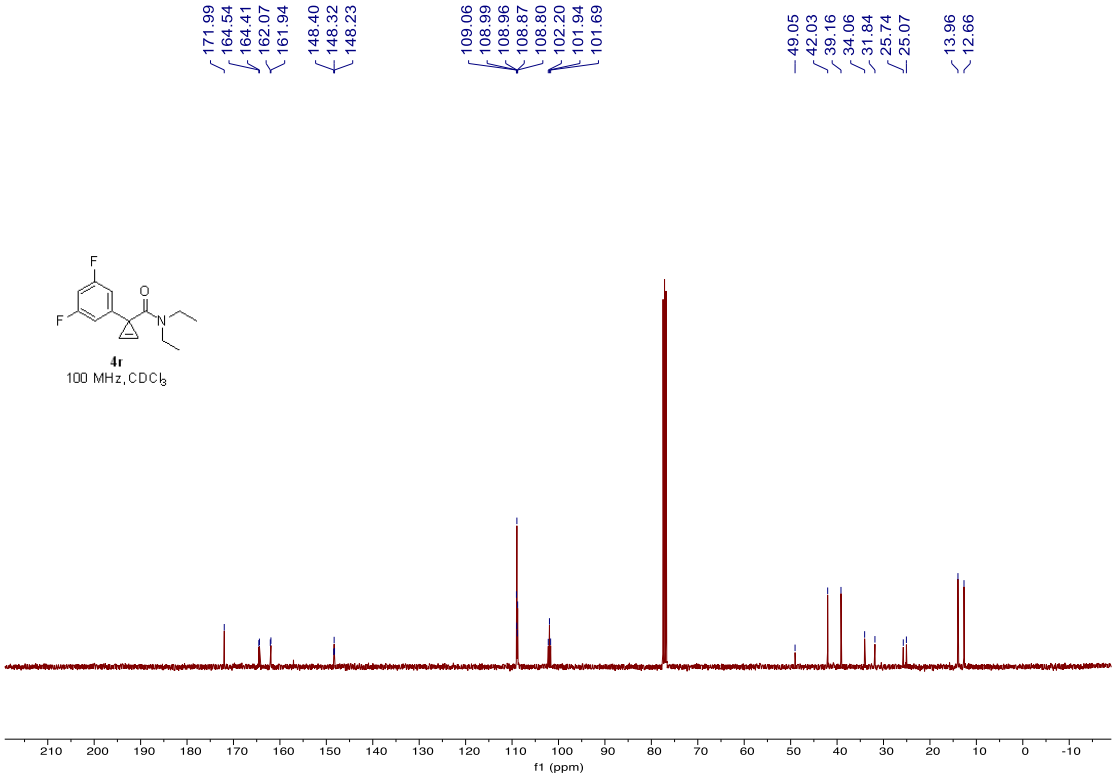
160.23
130.88
130.76
129.69
129.65
128.45
128.37
124.31
124.27
116.09
115.87
110.30
110.28
41.87
39.65
34.07
28.38
25.77
25.11
13.25
12.57
F
O
N
4q
100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



4q
500 MHz, $CDCl_3$



4r
400 MHz, $CDCl_3$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164.41
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161.94
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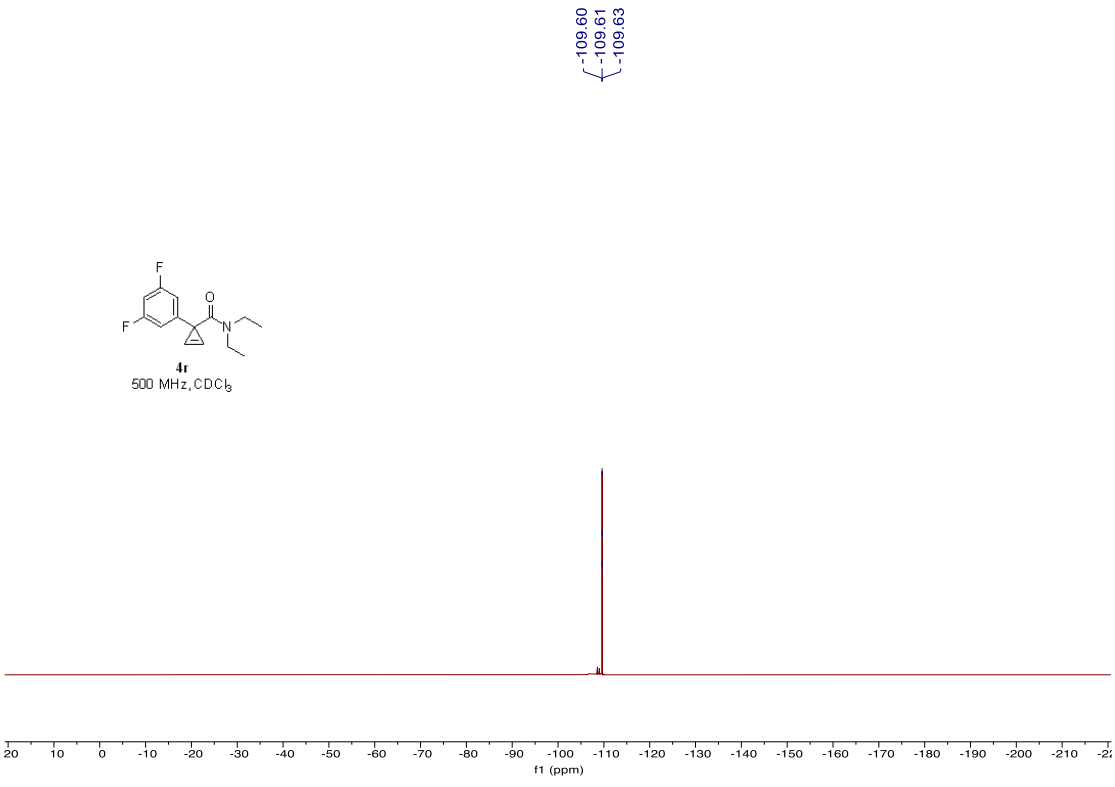
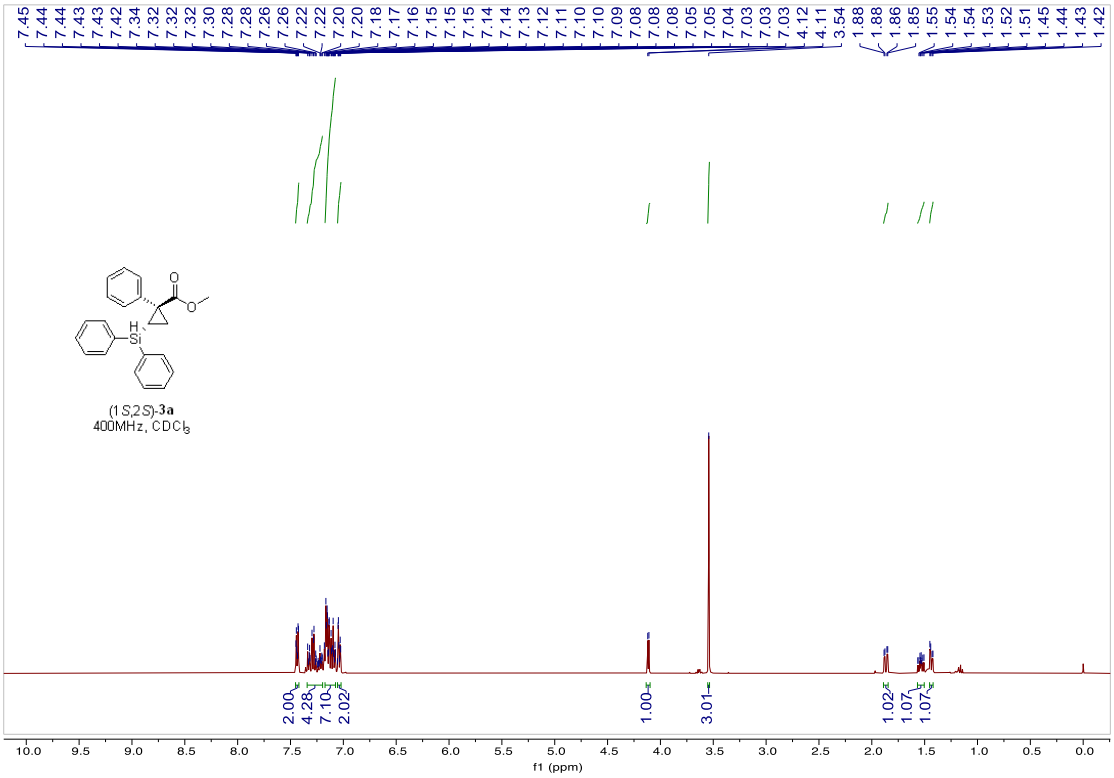
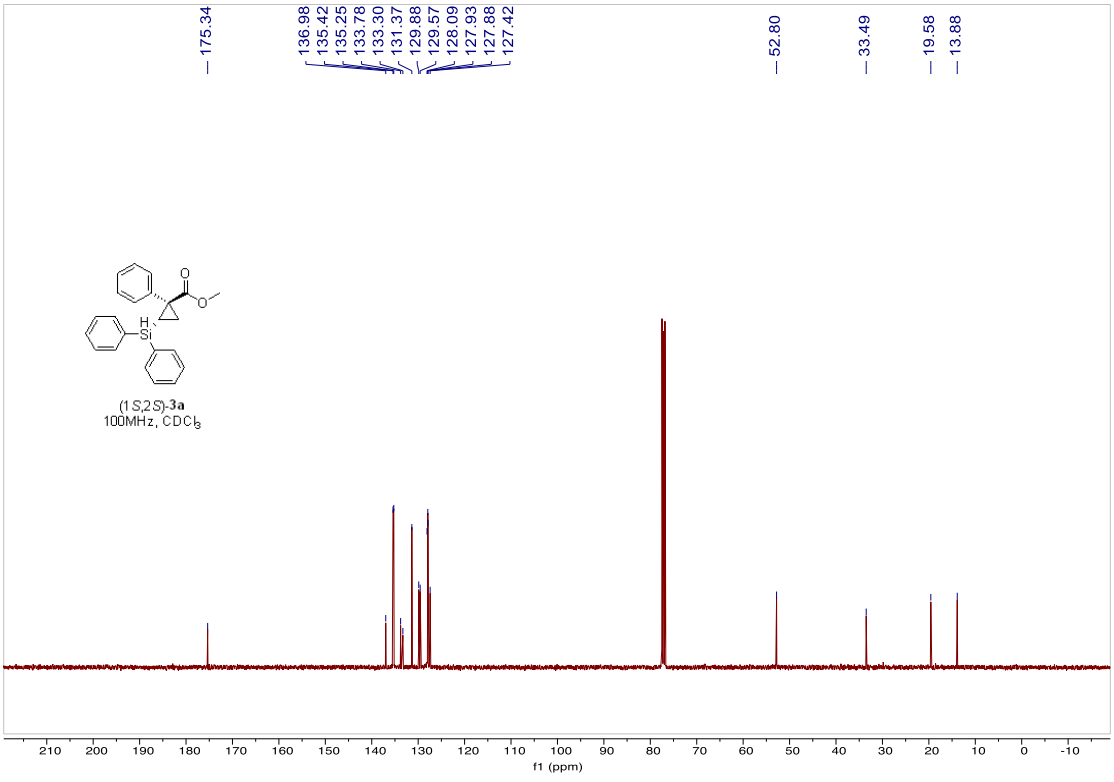
148.32
148.23
109.06
108.99
108.96
108.87
108.80
102.20
101.94
101.69
49.05
42.03
39.16
34.06
31.84
25.74
25.07
13.96
12.66
F
F
O
N
4r
100 MHz, CDCl3
f1 (ppm)


-109.60
-109.61
-109.63
F
F
O
N
4r
500 MHz, CDCl3
f1 (ppm)


(1S,2S)-3a
400MHz, CDCl3
f1 (ppm)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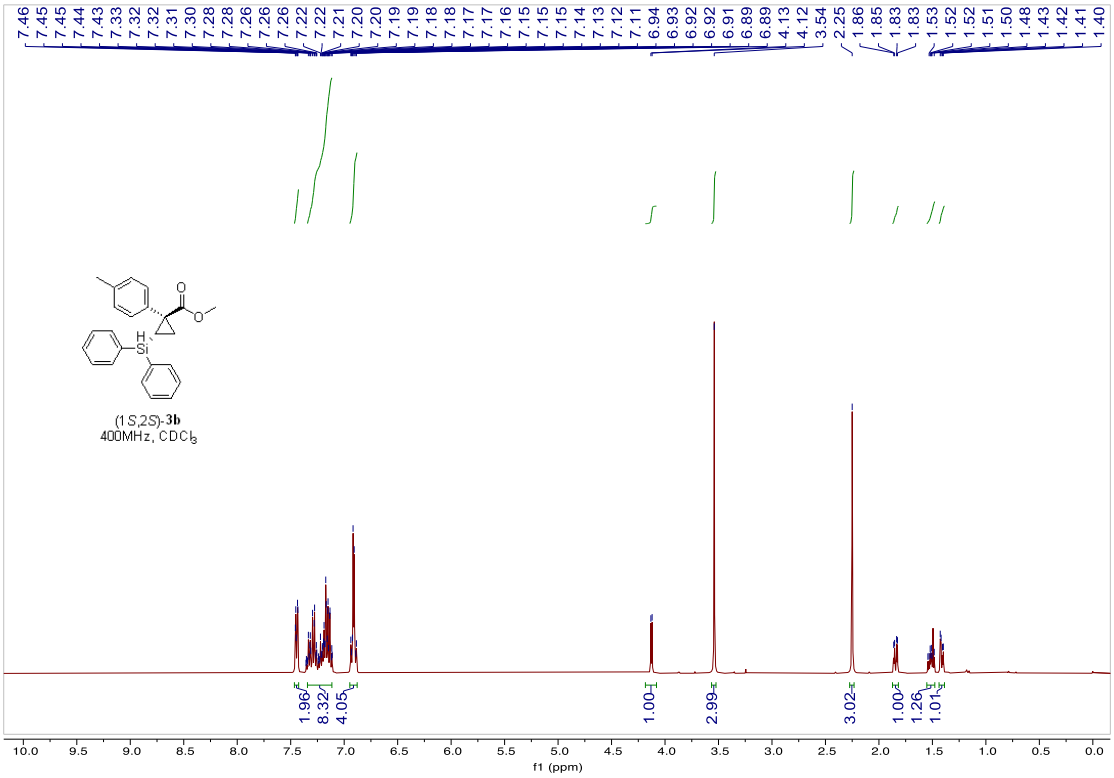
100MHz, CDCl3
f1 (ppm)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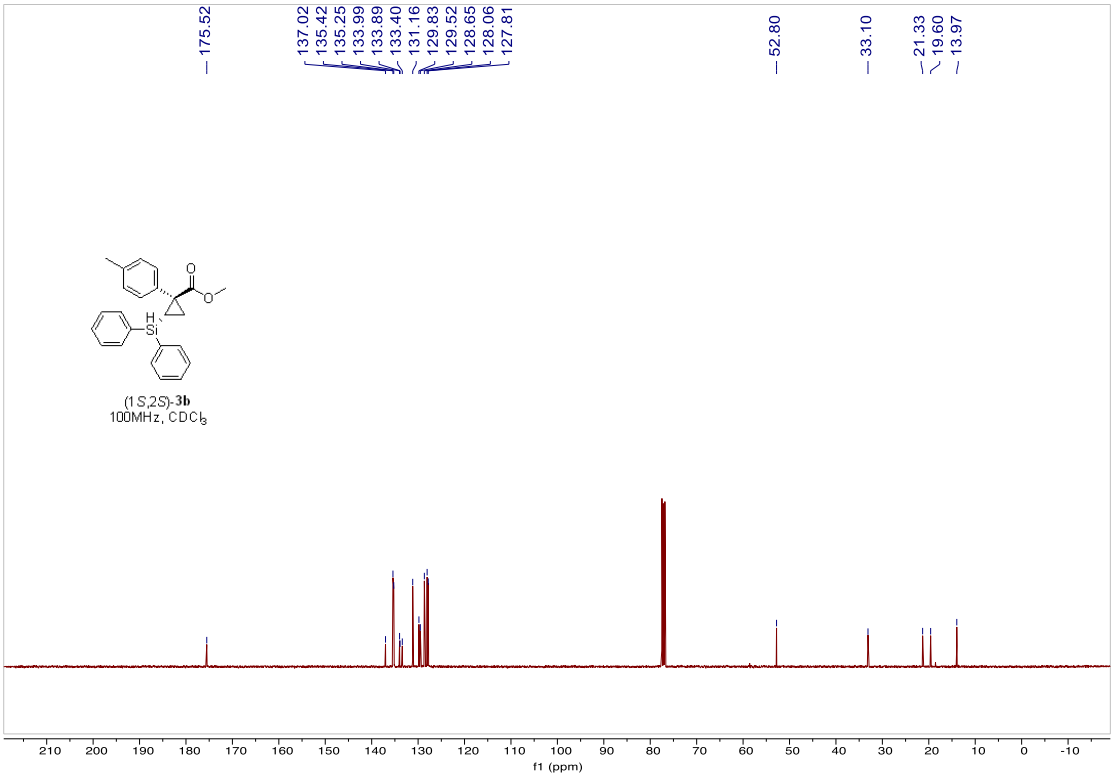
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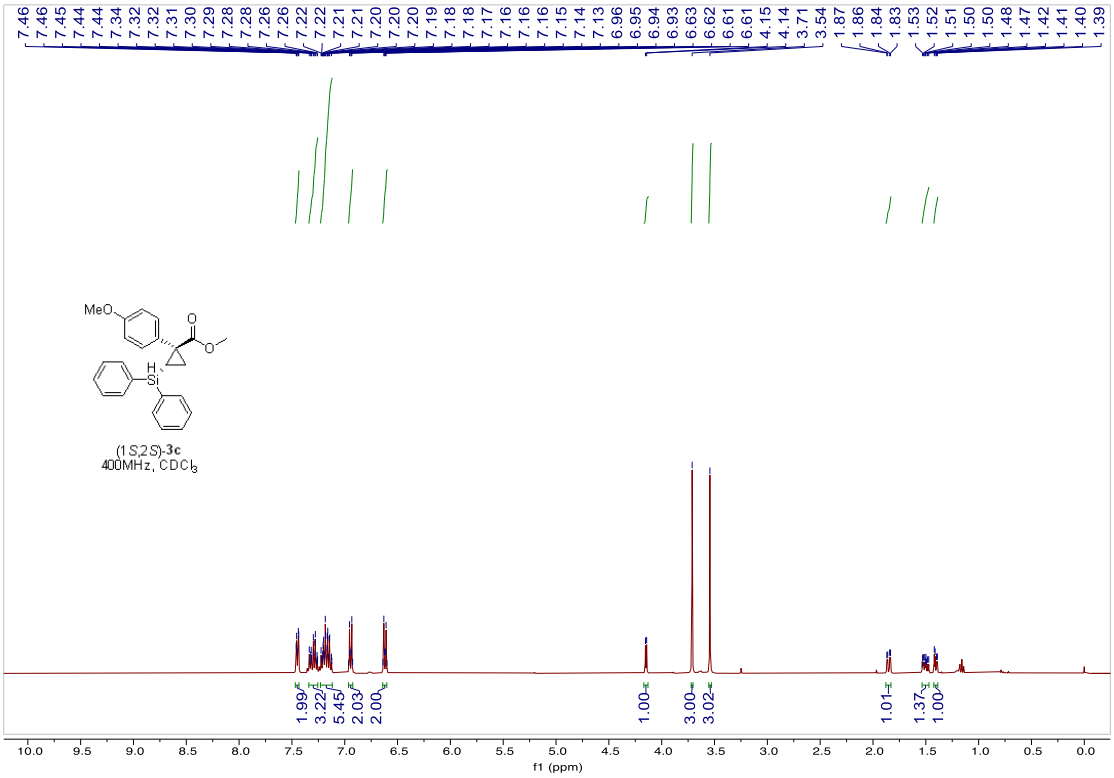
100MHz, CDCl3
f1 (ppm)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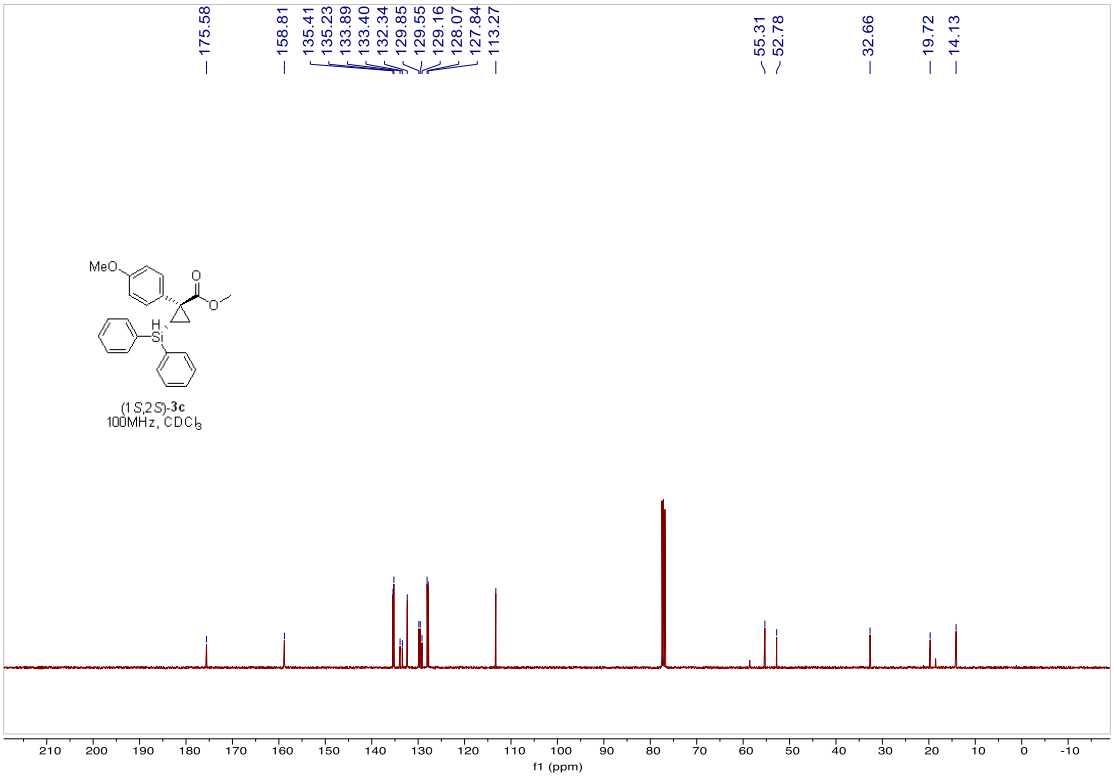
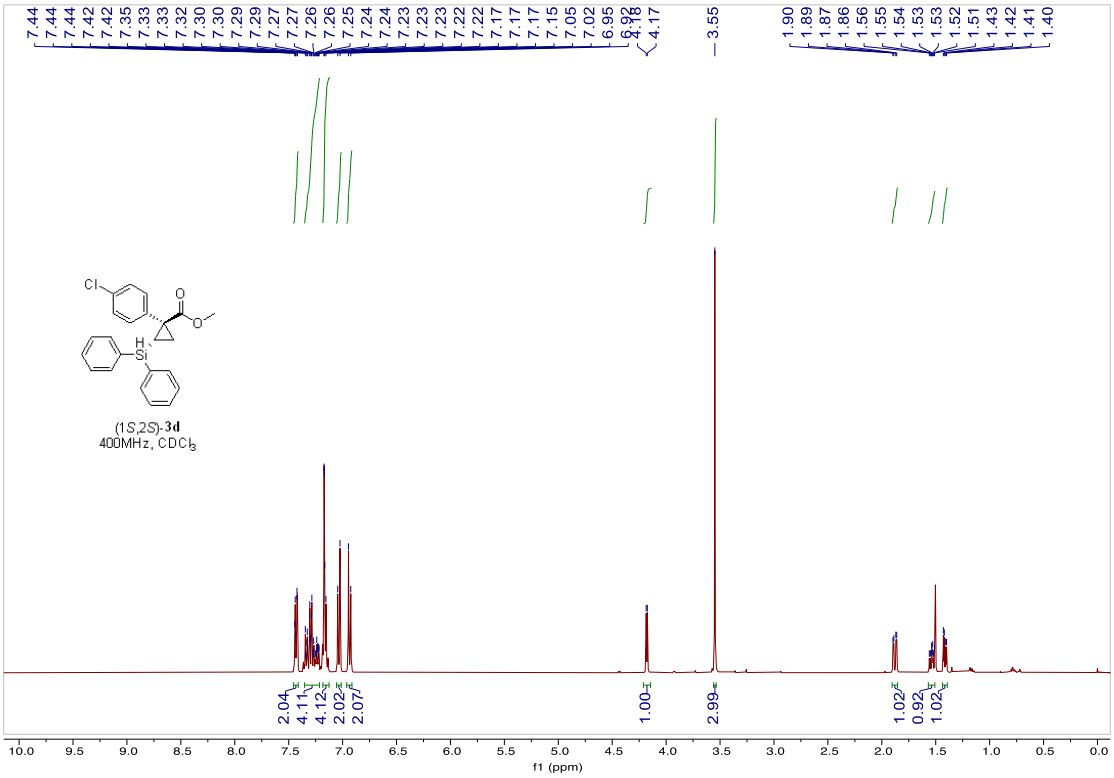
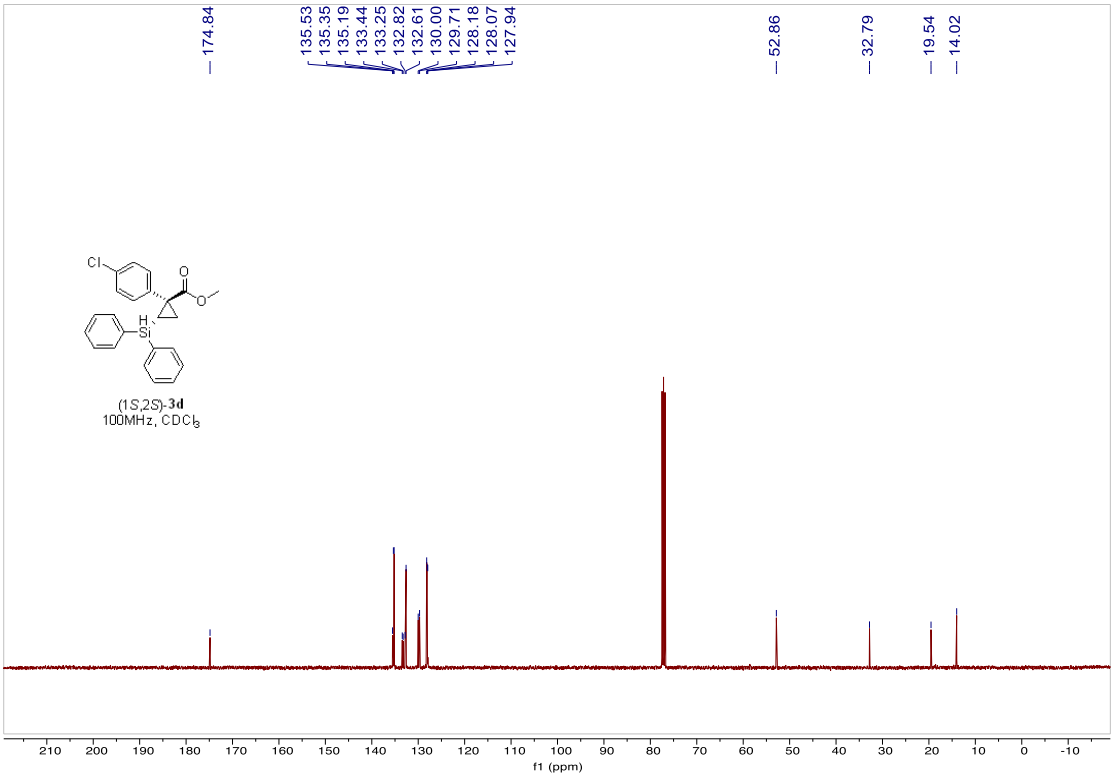
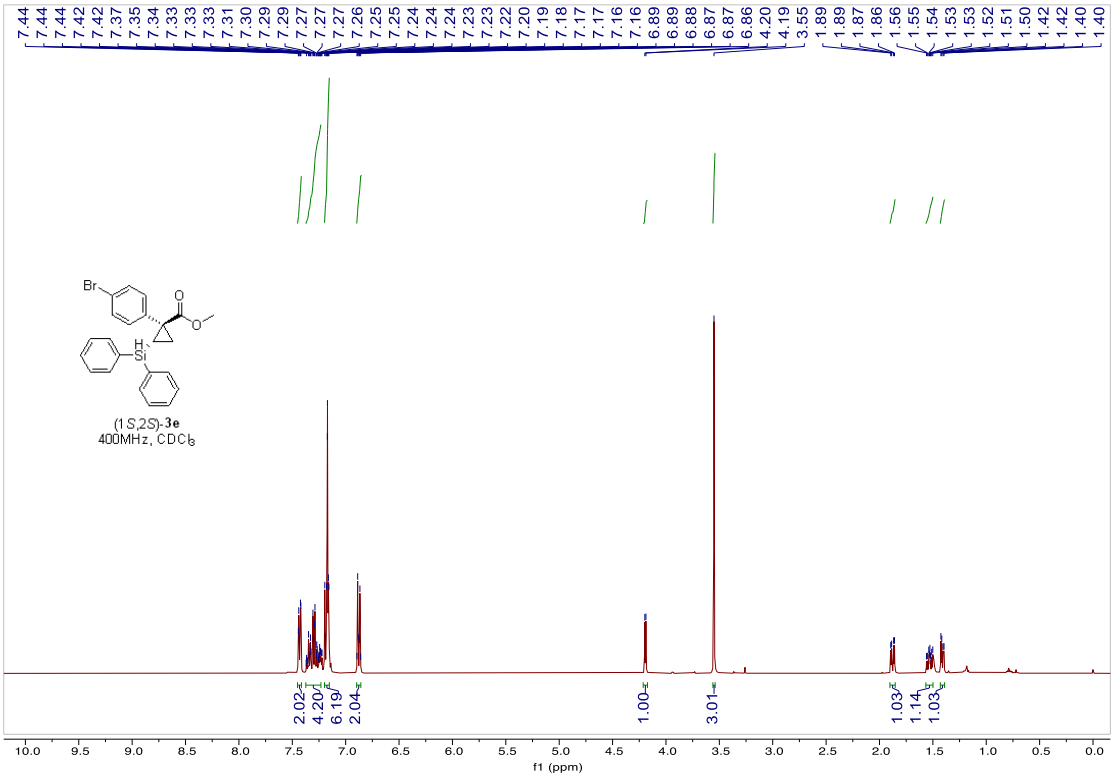
MeO
O
O
H
Si
(1S,2S)-3c
400MHz, CDCl3
1.99 3.22 5.45 2.03 2.00 1.00 3.00 3.02 1.01 1.37 1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


175.58 158.81 135.41 135.23 133.89 133.40 132.34 129.85 129.55 129.16 128.07 127.84 113.27 55.31 52.78 32.66 19.72 14.13
MeO
O
O
H
Si
(1S,2S)-3c
100MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.44 7.44 7.44 7.42 7.42 7.35 7.33 7.33 7.32 7.30 7.30 7.29 7.29 7.27 7.27 7.26 7.26 7.25 7.24 7.24 7.23 7.23 7.23 7.22 7.22 7.17 7.17 7.17 7.15 7.05 7.02 6.95 6.92 4.18 4.17
3.55
1.90 1.89 1.87 1.86 1.56 1.55 1.54 1.53 1.53 1.52 1.51 1.43 1.42 1.41 1.40
Cl
O
O
H
Si
(1S,2S)-3d
400MHz, CDCl3
2.04 4.11 4.12 2.02 2.07 1.00 2.99 1.02 0.92 1.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


174.84
135.53 135.35 135.19 133.44 133.25 132.82 132.61 130.00 129.71 128.18 128.07 127.94
52.86
32.79
19.54
14.02
Cl
O
O
H
Si
(1S,2S)-3d
100MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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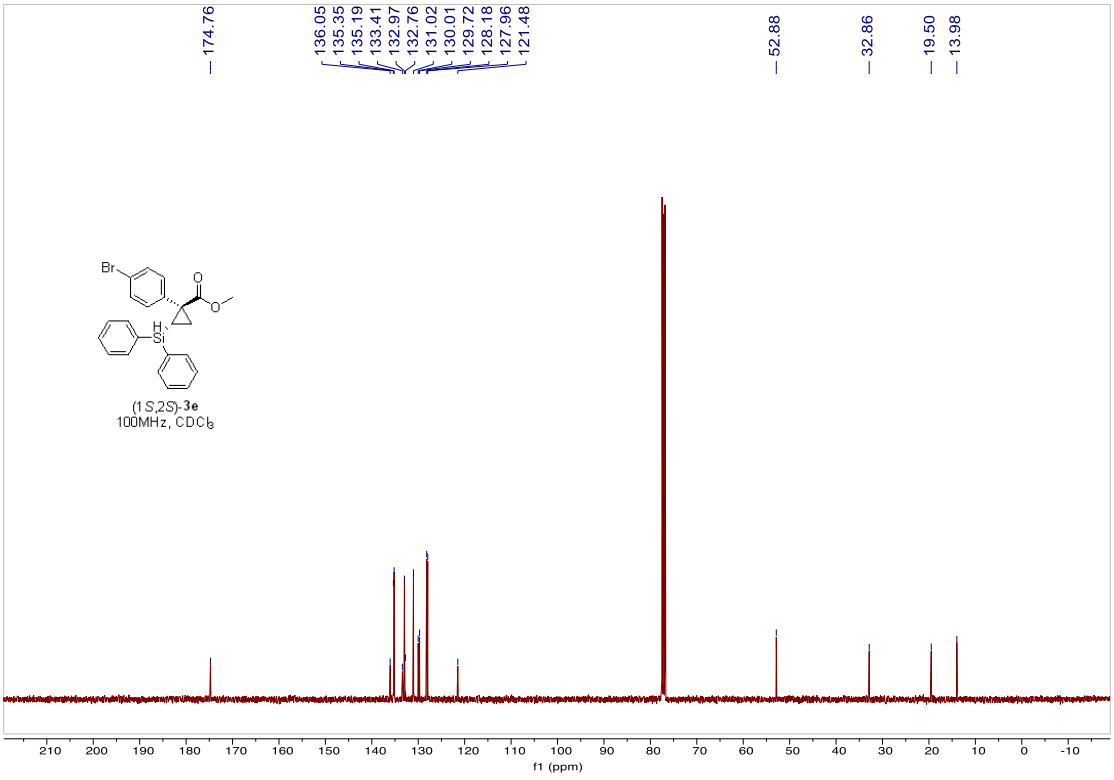
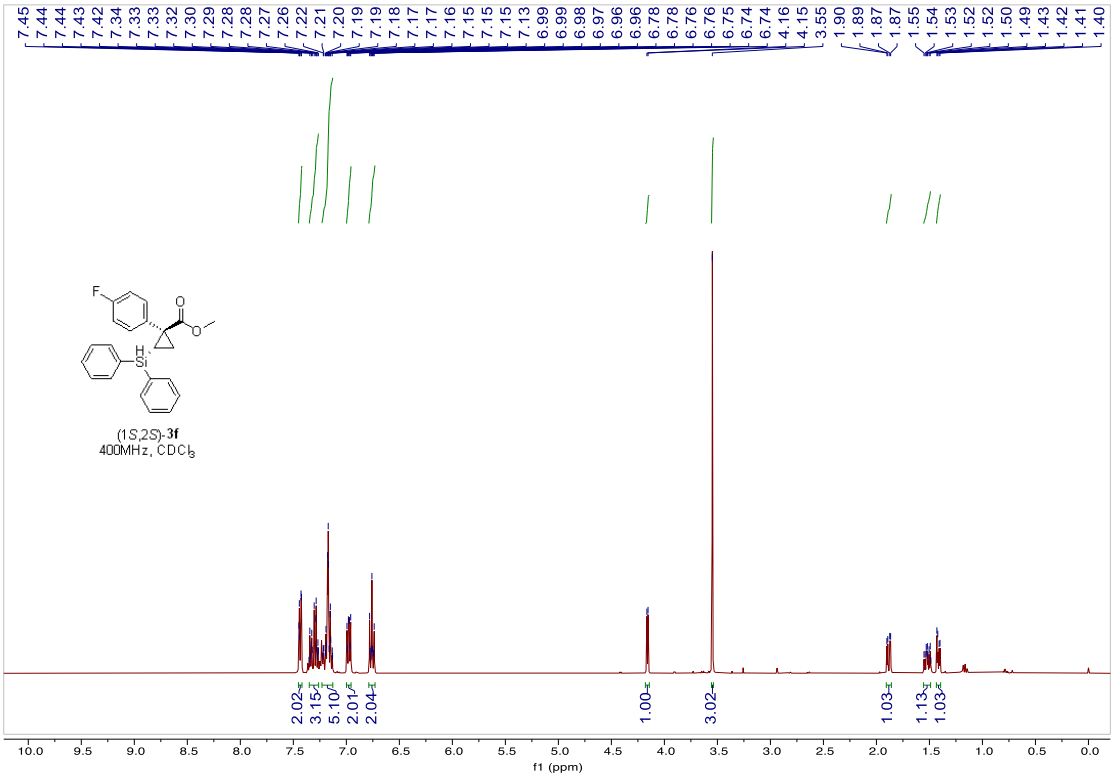
f1 (ppm)


(1S,2S)-3e
100MHz, CDCl3
f1 (ppm)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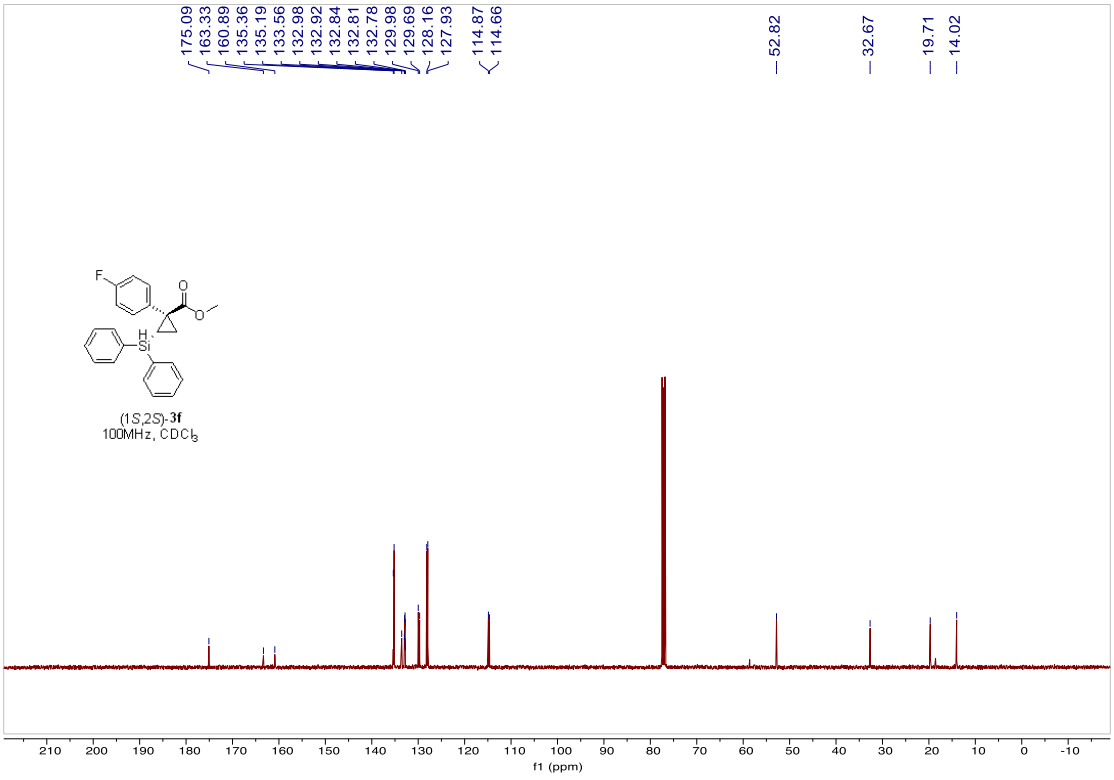
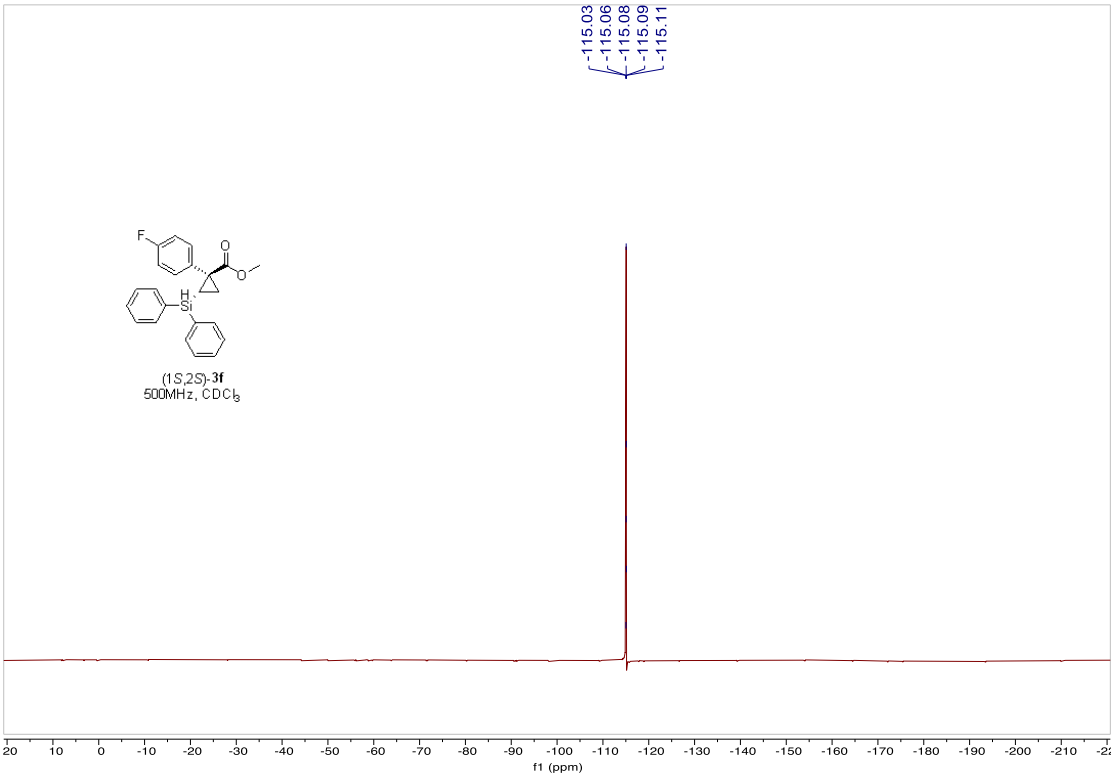
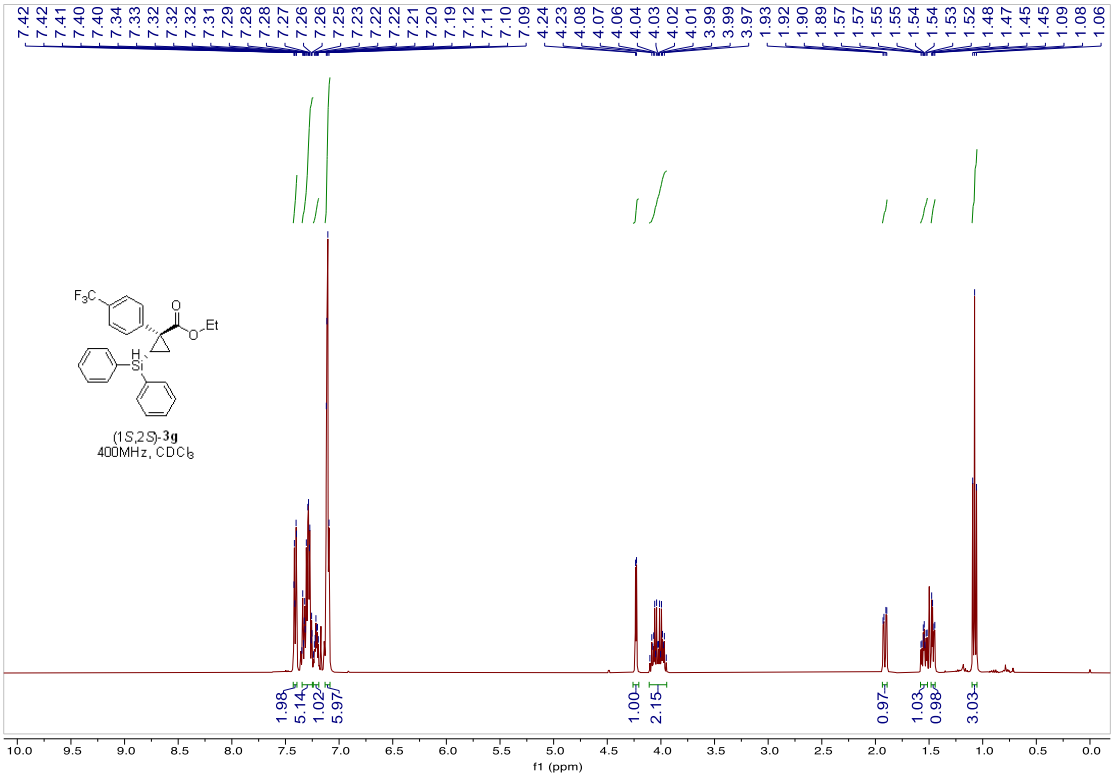
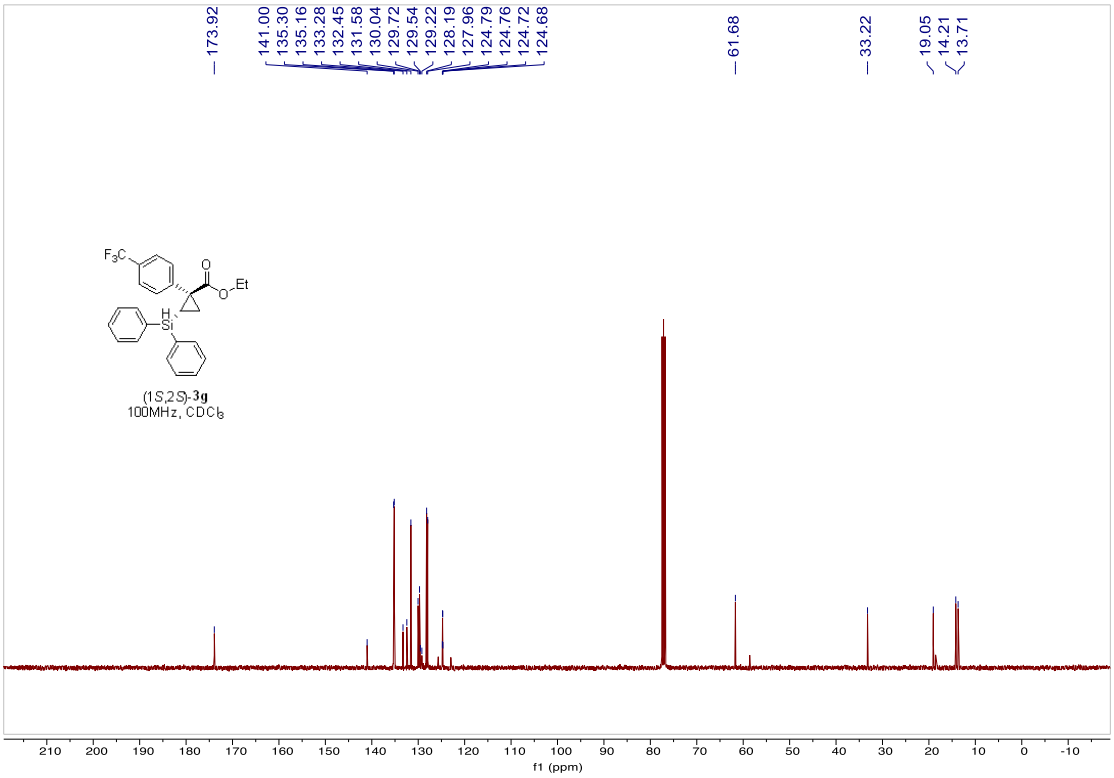
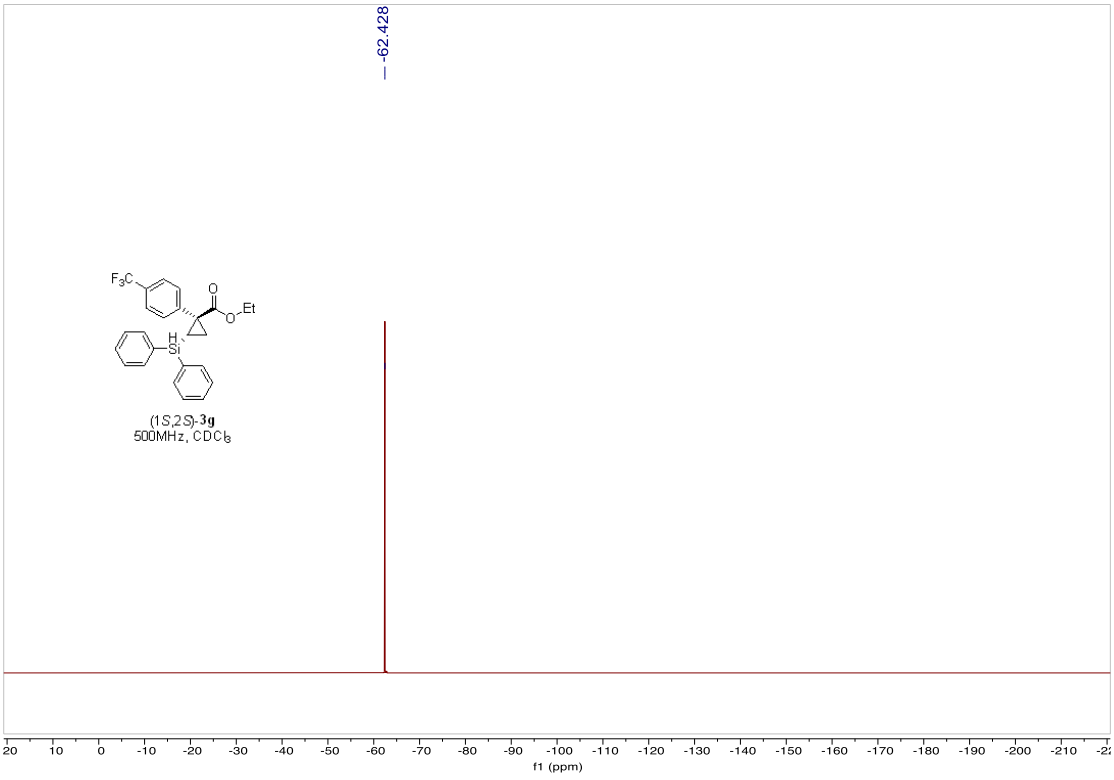
400MHz, CDCl3
f1 (ppm)

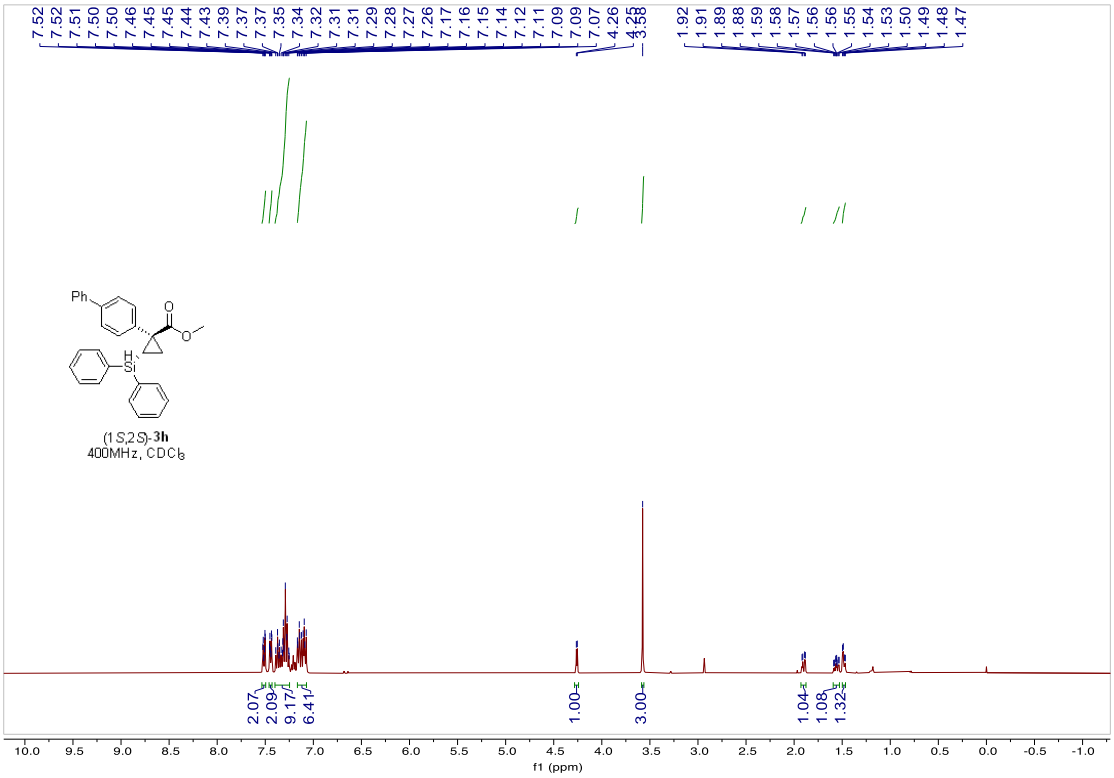

(1S,2S)-3f
100MHz, CDCl3
f1 (ppm)

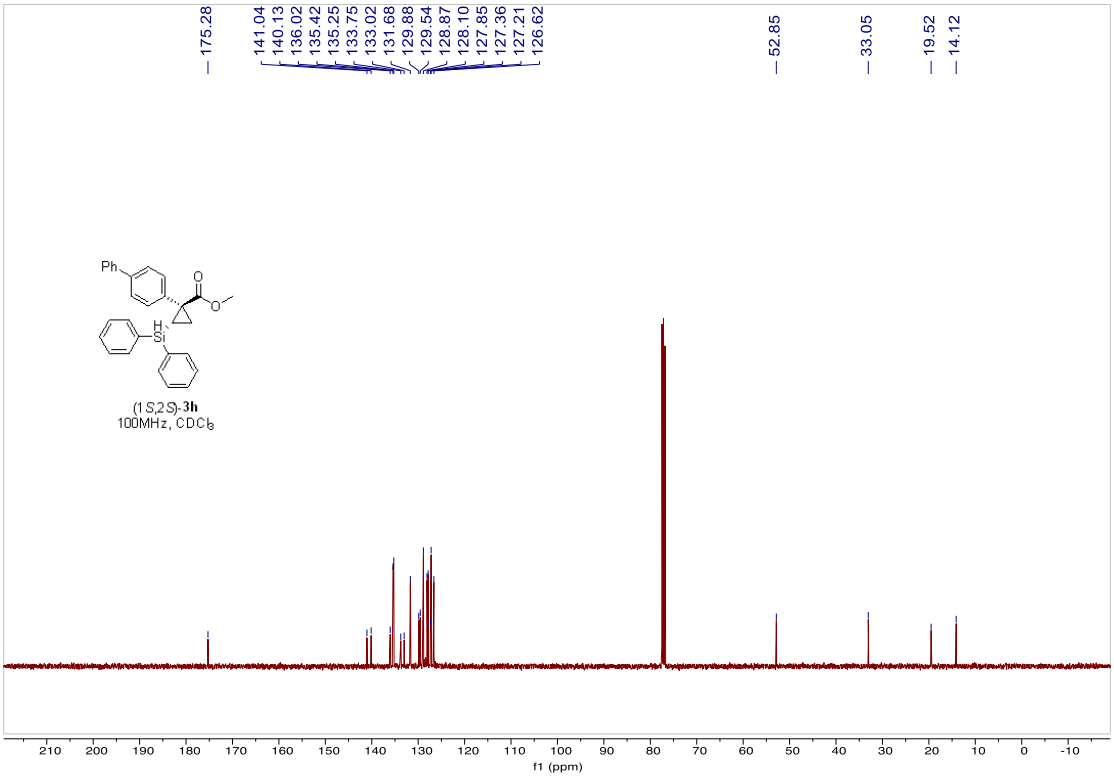

-115.03
-115.06
-115.08
-115.09
-115.11
F
O
O
H
Si
(1S,2S)-3f
500MHz, CDCl3
f1 (ppm)

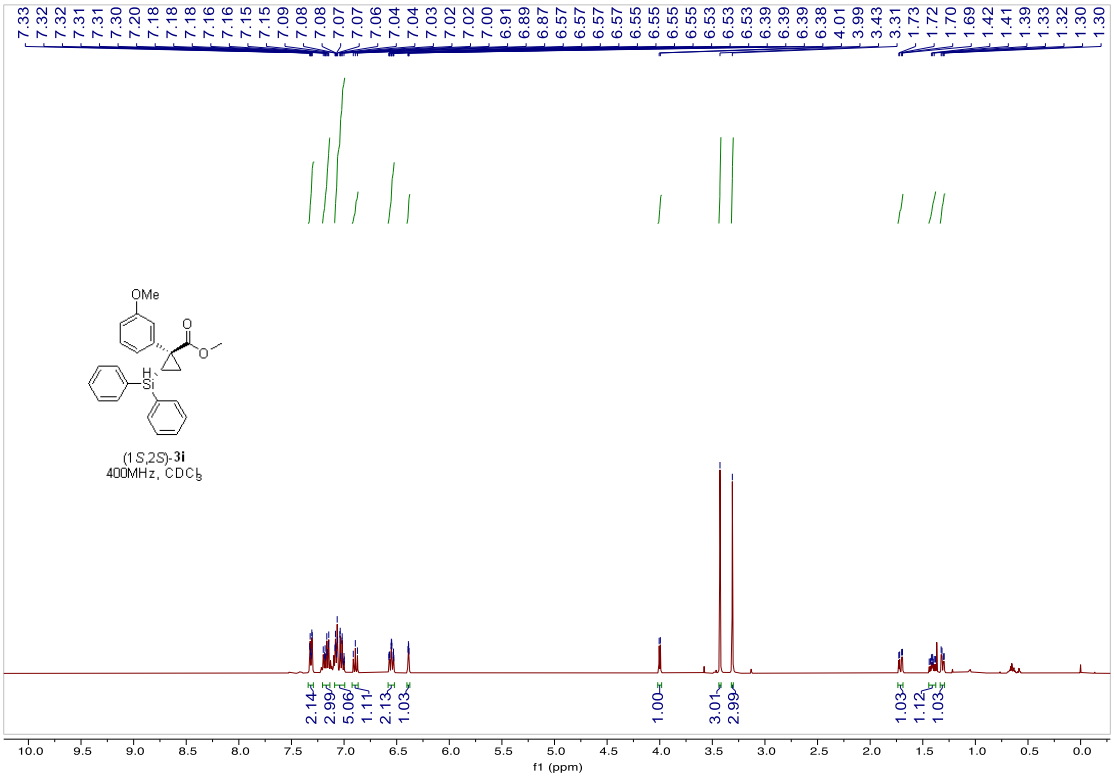

F3C
O
O
Et
H
Si
(1S,2S)-3g
400MHz, CDCl3
1.98
5.14
1.02
5.97
1.00
2.15
0.97
1.03
0.98
3.03
f1 (ppm)

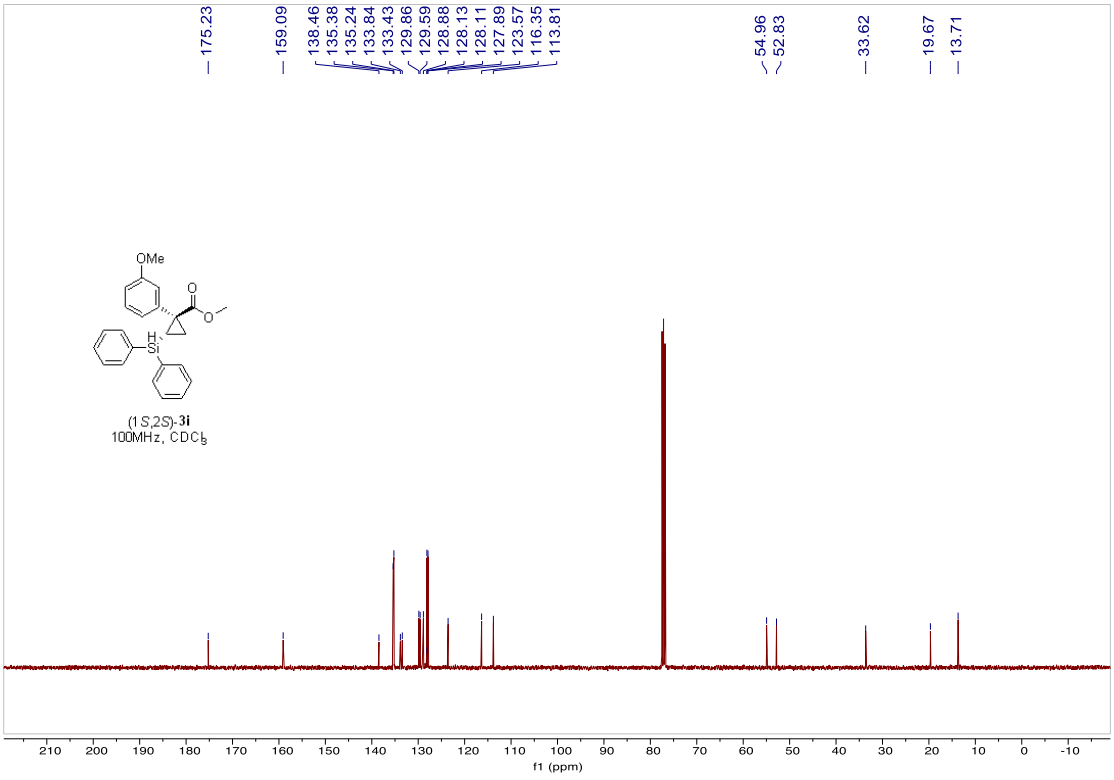

173.92
141.00
135.30
135.16
133.28
132.45
131.58
130.04
129.72
129.54
129.22
128.19
127.96
124.79
124.76
124.72
124.68
61.68
33.22
19.05
14.21
13.71
F3C
O
O
Et
H
Si
(1S,2S)-3g
100MHz, CDCl3
f1 (ppm)

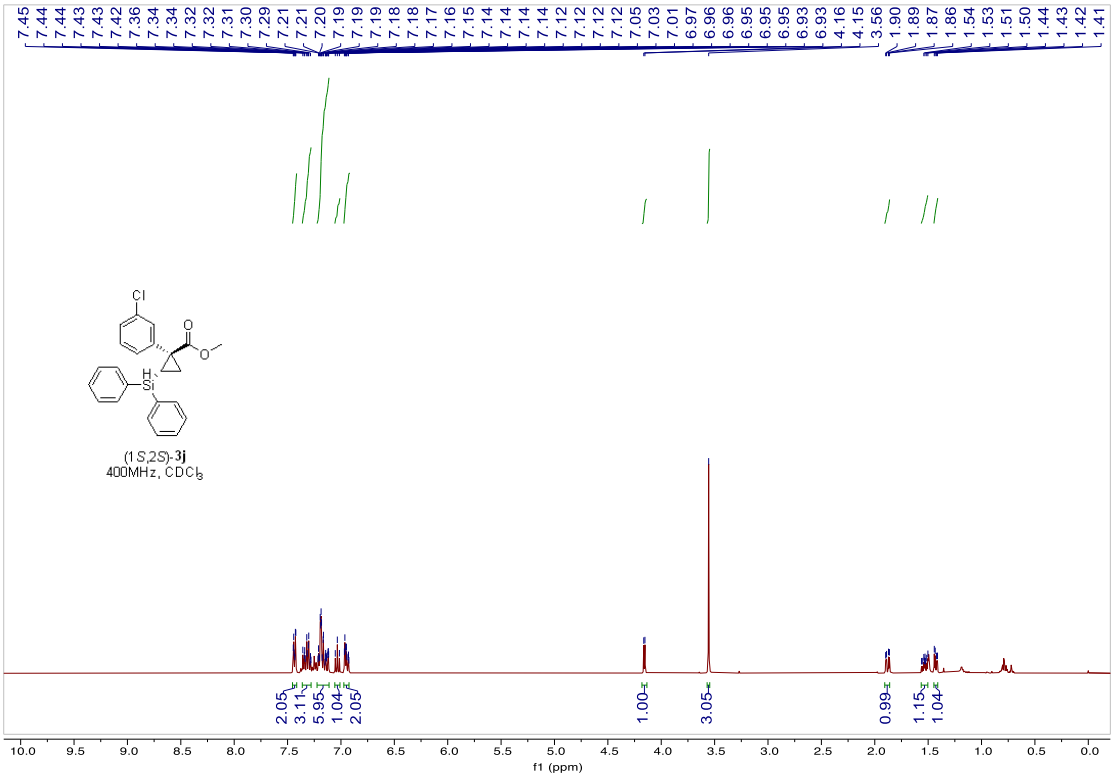

-62.428
F3C
O
O
Et
H
Si
(1S,2S)-3g
500MHz, CDCl3
f1 (ppm)

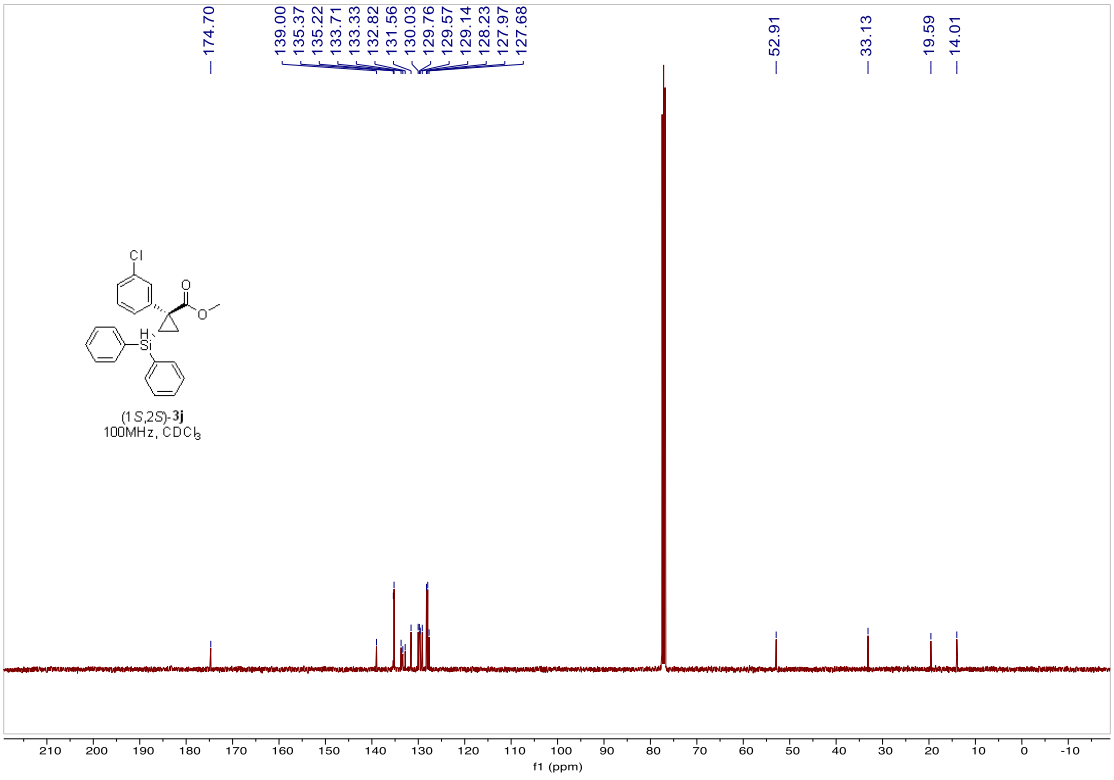

(1S,2S)-3h
400MHz, CDCl3
f1 (ppm)

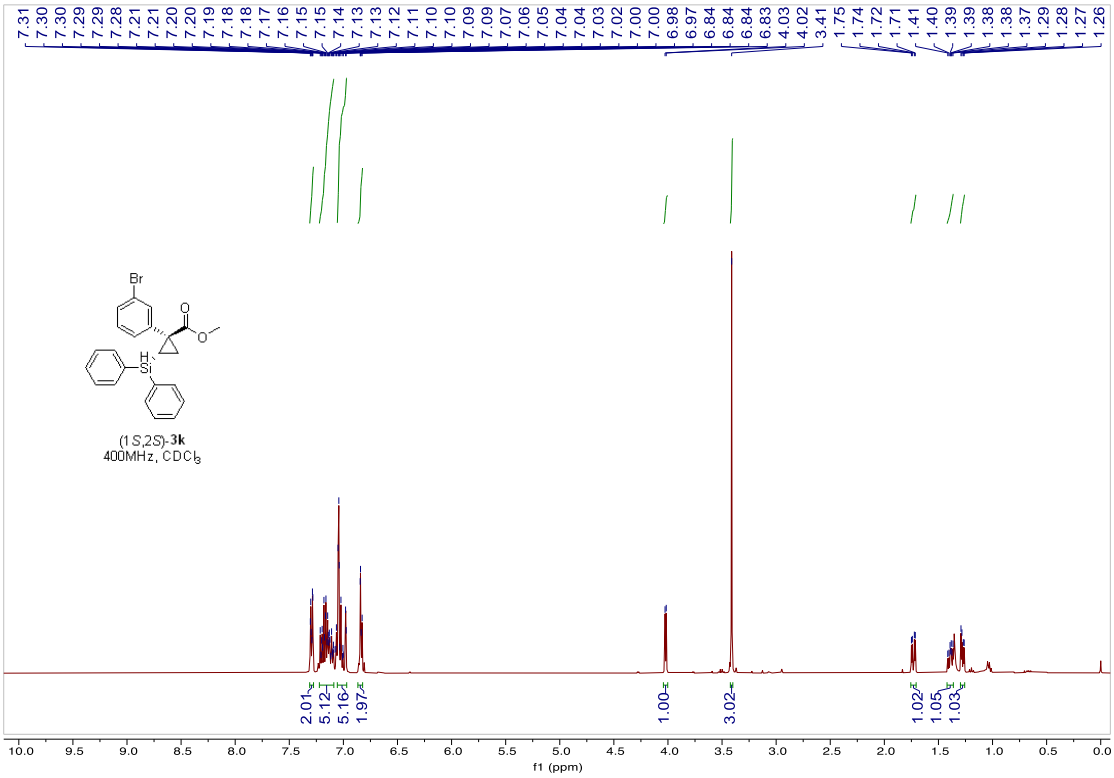

(1S,2S)-3h
100MHz, CDCl3
f1 (ppm)

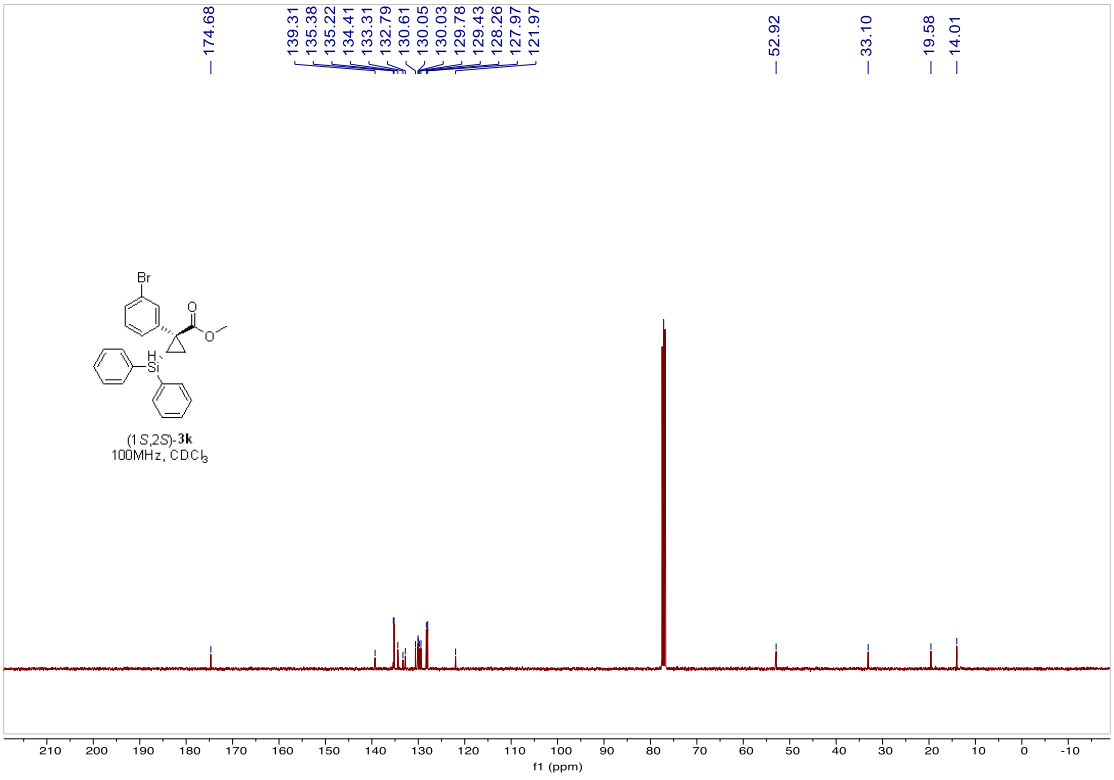

7.33 7.32 7.32 7.31 7.31 7.30 7.20 7.18 7.18 7.18 7.16 7.16 7.15 7.15 7.09 7.08 7.08 7.07 7.07 7.06 7.04 7.04 7.03 7.02 7.02 7.00 6.91 6.89 6.87 6.57 6.57 6.57 6.57 6.55 6.55 6.55 6.55 6.53 6.53 6.39 6.39 6.38 4.01 3.99 3.43 3.31 1.73 1.72 1.70 1.69 1.42 1.41 1.39 1.33 1.32 1.30 1.30
OMe
O
O
H
Si
(1S,2S)-3i
400MHz, CDCl3
2.14 2.99 5.06 1.11 2.13 1.03 1.00 3.01 2.99 1.03 1.12 1.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

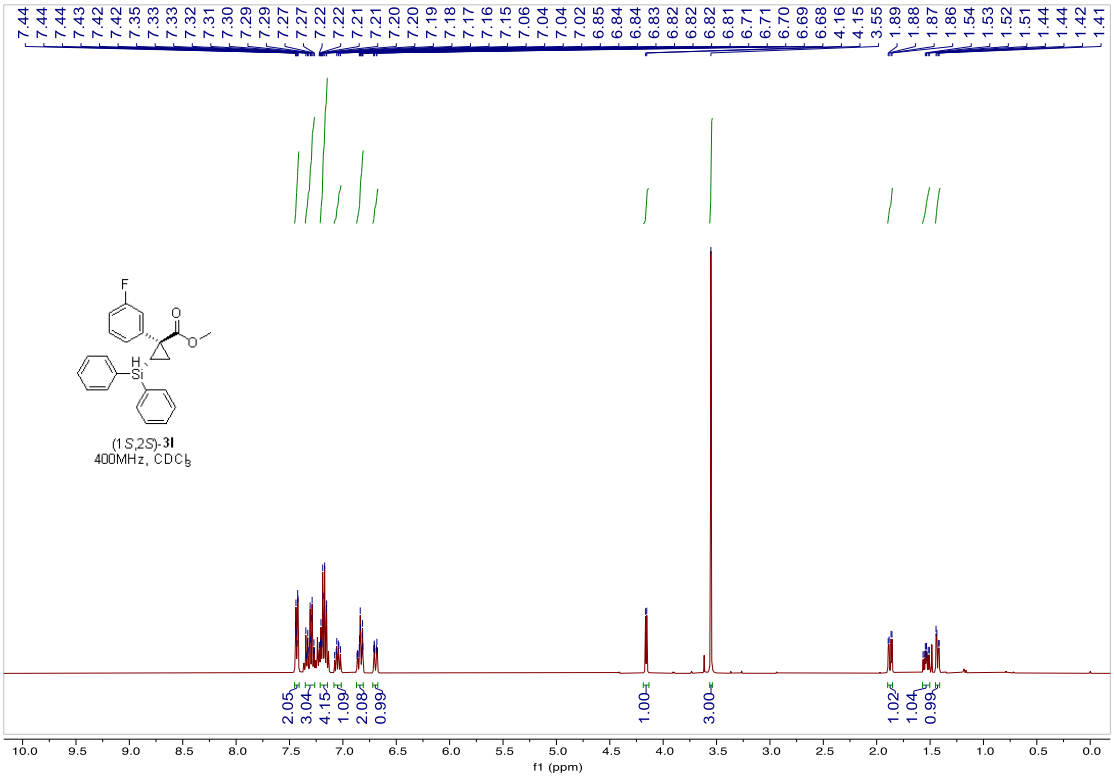

175.23 159.09 138.46 135.38 135.24 133.84 133.43 129.86 129.59 128.88 128.13 128.11 127.89 123.57 116.35 113.81 54.96 52.83 33.62 19.67 13.71
OMe
O
O
H
Si
(1S,2S)-3i
100MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

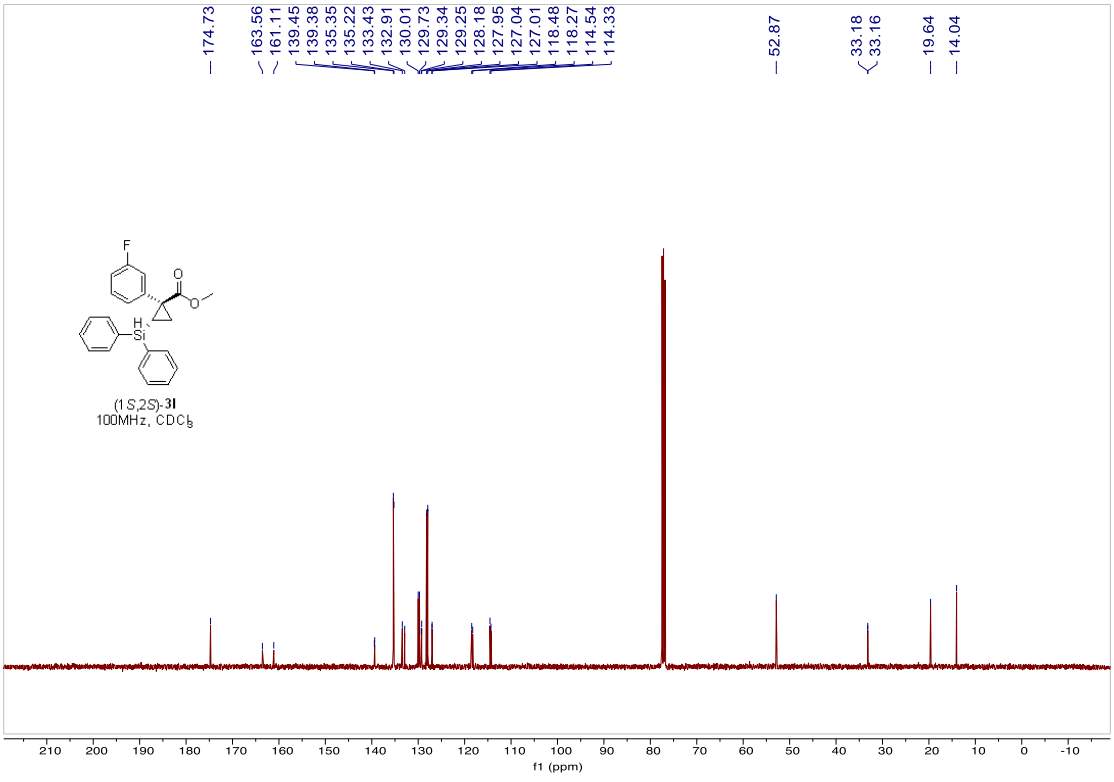

(1S,2S)-3j
400MHz, CDCl3
f1 (ppm)

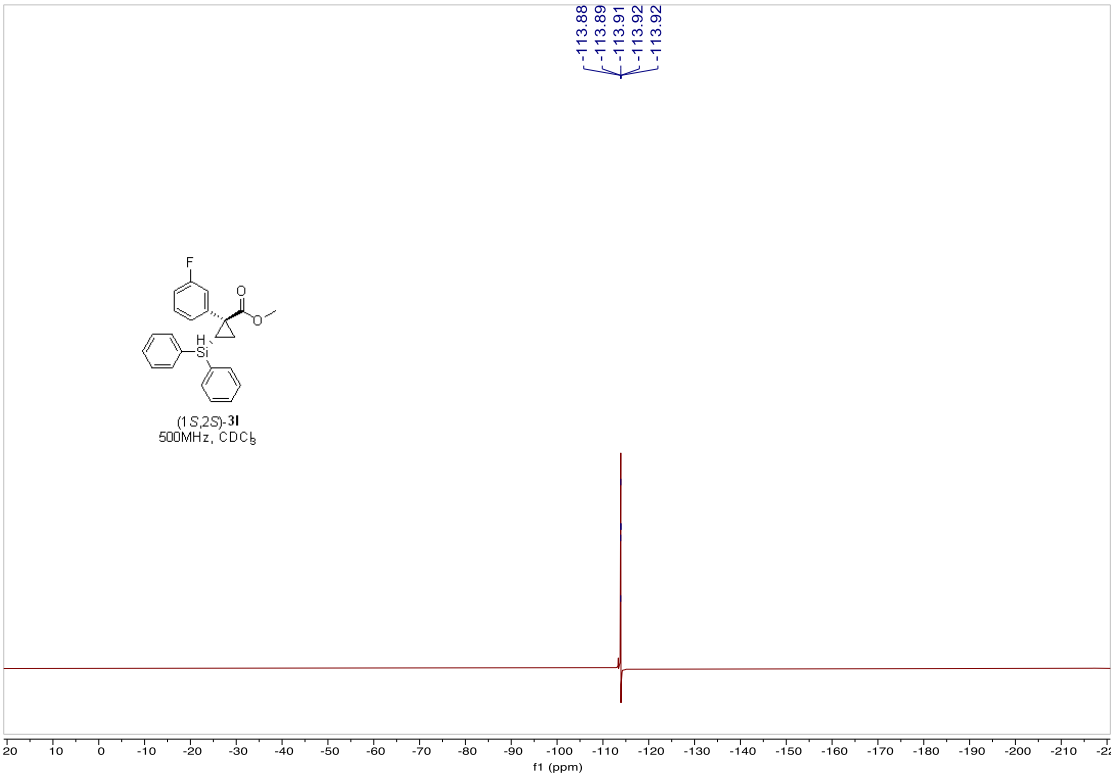

(1S,2S)-3j
100MHz, CDCl3
f1 (ppm)

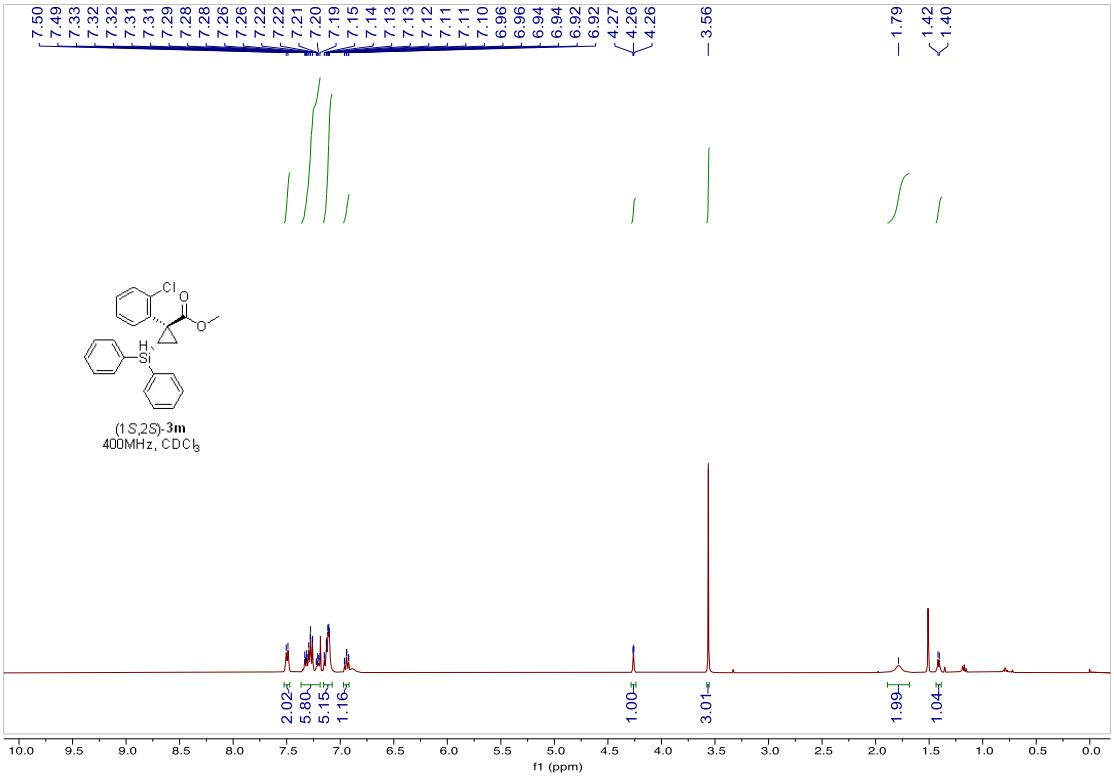

7.31 7.30 7.30 7.29 7.29 7.28 7.21 7.21 7.20 7.20 7.19 7.18 7.18 7.17 7.16 7.15 7.15 7.14 7.13 7.13 7.12 7.11 7.10 7.10 7.09 7.09 7.07 7.06 7.05 7.04 7.04 7.03 7.02 7.00 7.00 6.98 6.97 6.84 6.84 6.84 6.83 4.03 4.02 3.41 1.75 1.74 1.72 1.71 1.41 1.40 1.39 1.39 1.38 1.38 1.37 1.29 1.28 1.27 1.26
Br
O
O
H
Si
(1S,2S)-3k
400MHz, CDCl3
2.01 5.12 5.16 1.97 1.00 3.02 1.02 1.05 1.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

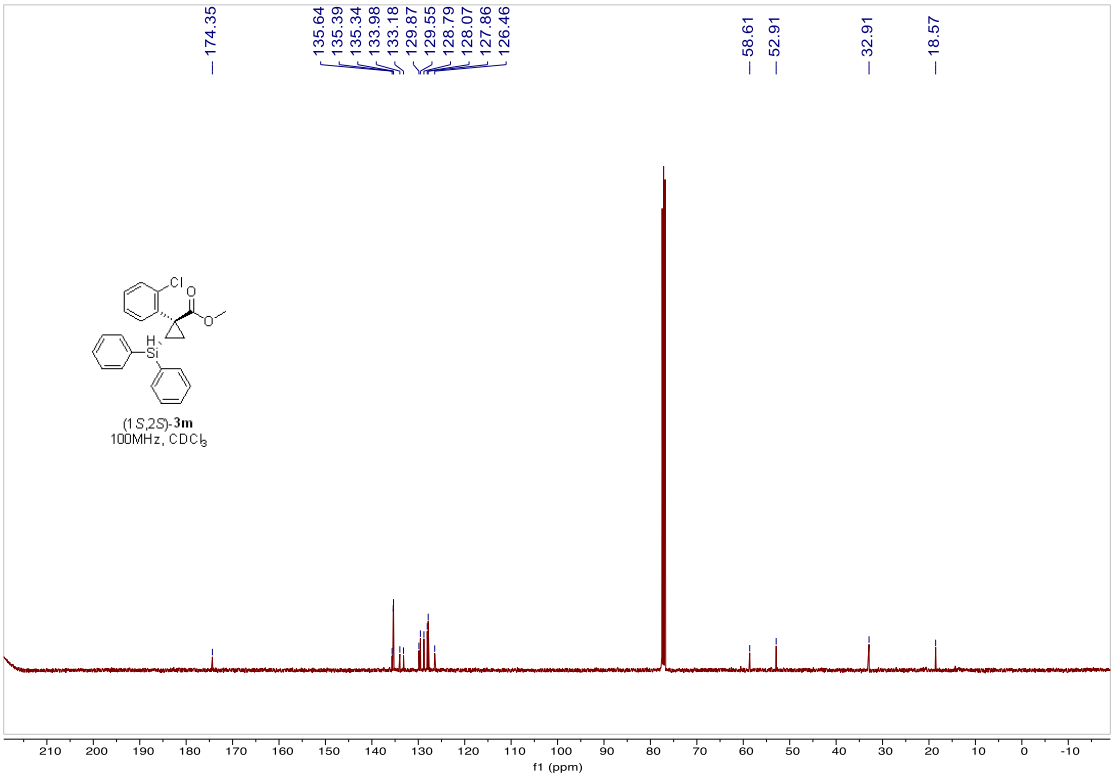

174.68
139.31 135.38 135.22 134.41 133.31 132.79 130.61 130.05 130.03 129.78 129.43 128.26 127.97 121.97
52.92
33.10
19.58
14.01
Br
O
O
H
Si
(1S,2S)-3k
100MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

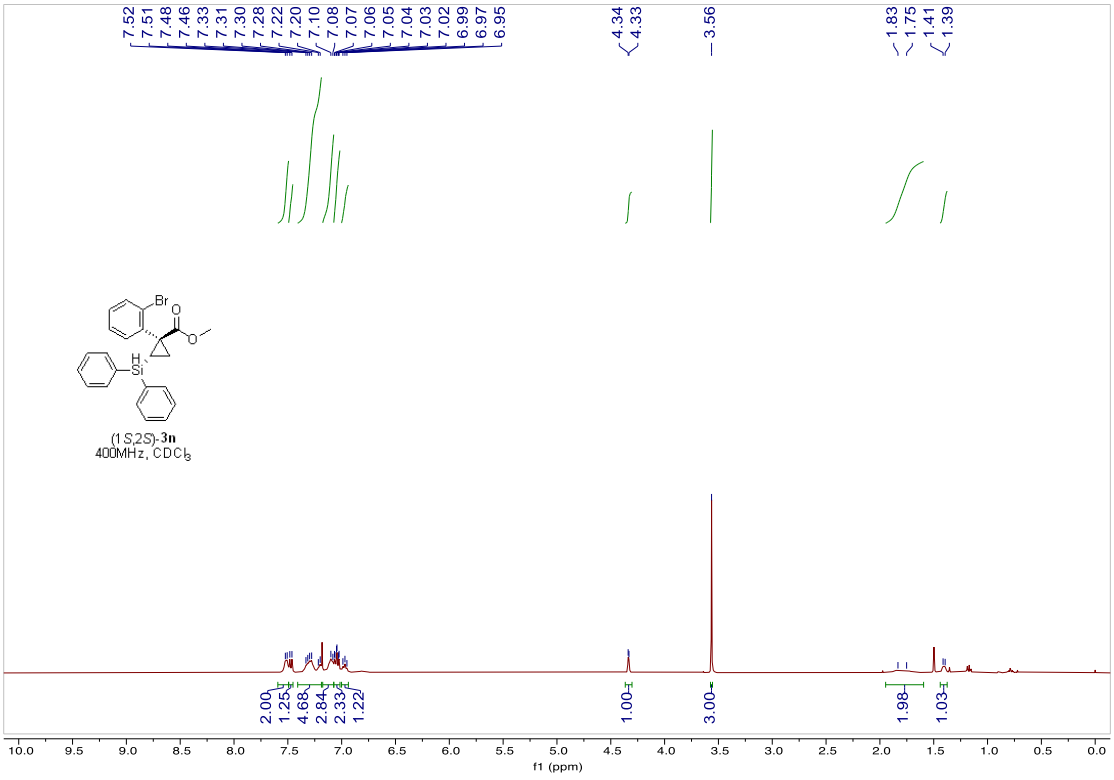

7.44 7.44 7.44 7.43 7.42 7.42 7.35 7.33 7.33 7.32 7.31 7.30 7.29 7.29 7.27 7.27 7.22 7.22 7.21 7.21 7.20 7.20 7.19 7.18 7.17 7.16 7.15 7.06 7.04 7.04 7.02 6.85 6.84 6.84 6.83 6.82 6.82 6.82 6.81 6.71 6.71 6.70 6.69 6.68 4.16 4.15 3.55 1.89 1.88 1.87 1.86 1.54 1.53 1.52 1.51 1.44 1.44 1.42 1.41
F
O
O
H
Si
(1S,2S)-3l
400MHz, CDCl3
2.05 3.04 4.15 1.09 2.08 0.99 1.00 3.00 1.02 1.04 0.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

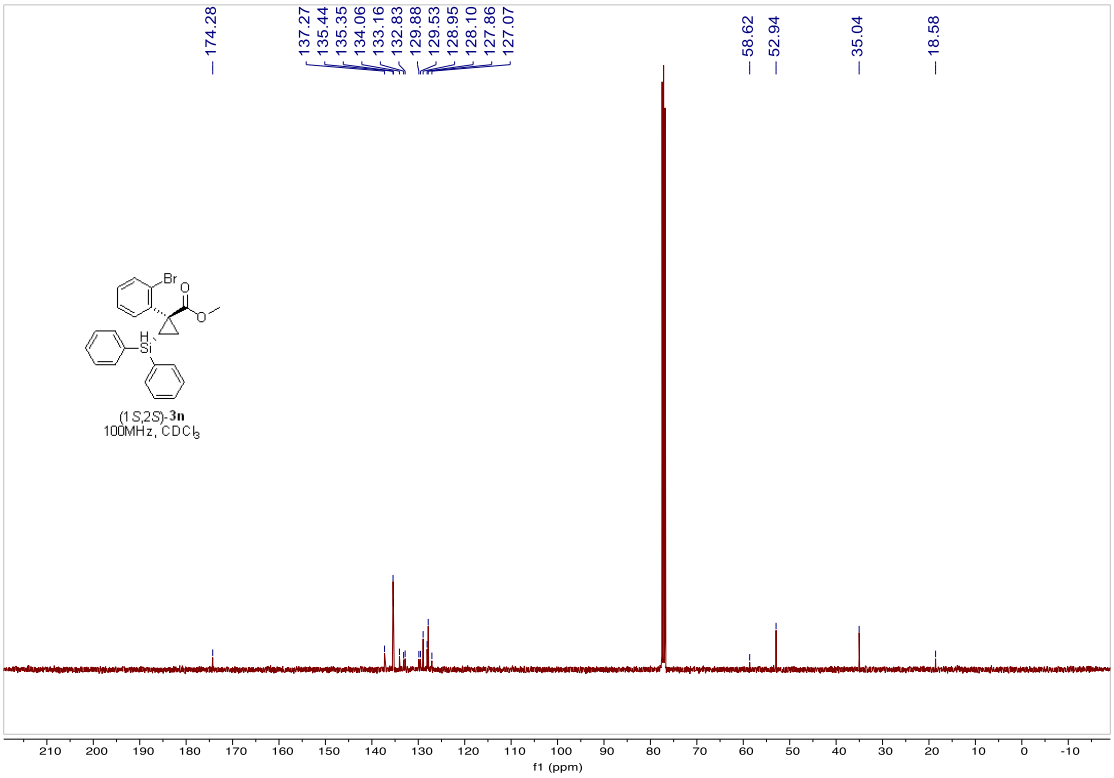

174.73 163.56 161.11 139.45 139.38 135.35 135.22 133.43 132.91 130.01 129.73 129.34 129.25 128.18 127.95 127.04 127.01 118.48 118.27 114.54 114.33 52.87 33.18 33.16 19.64 14.04
F
O
O
H
Si
(1S,2S)-3l
100MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-113.88
-113.89
-113.91
-113.92
-113.92
F
O
O
H
Si
(1S,2S)-3l
500MHz, CDCl3
f1 (ppm)

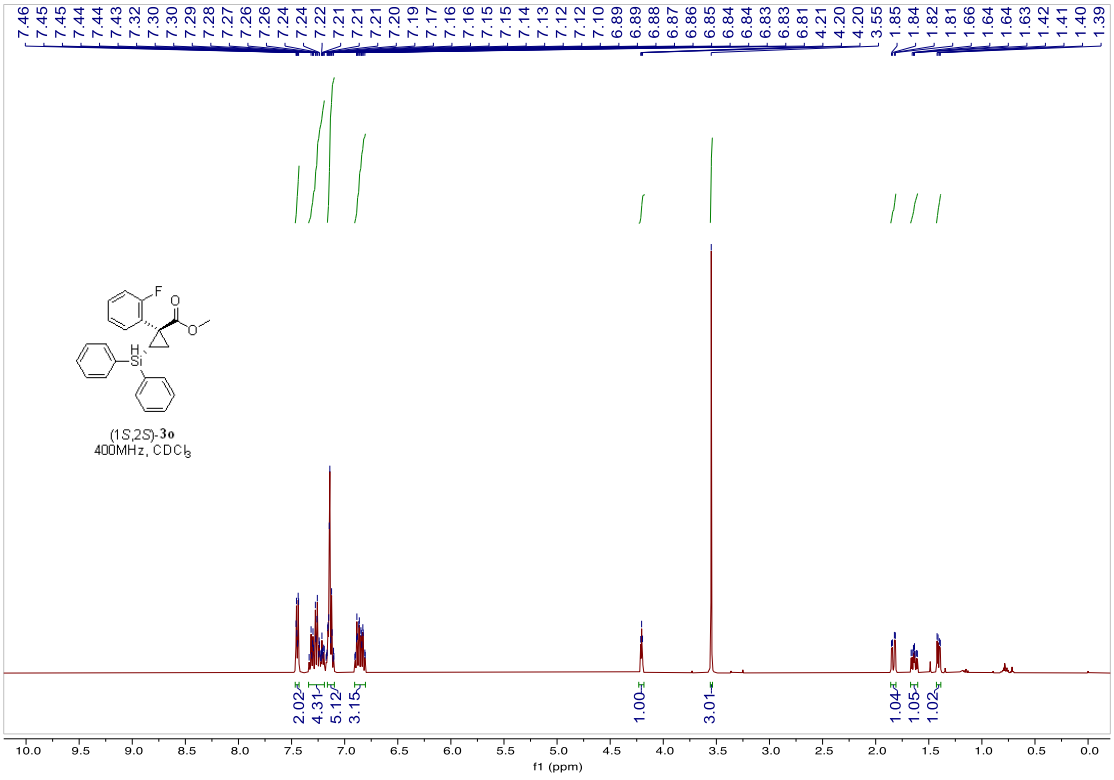

7.50
7.49
7.33
7.32
7.32
7.31
7.31
7.29
7.28
7.26
7.26
7.22
7.22
7.21
7.20
7.19
7.15
7.14
7.13
7.13
7.12
7.11
7.11
7.10
6.96
6.96
6.94
6.94
6.92
6.92
4.27
4.26
4.26
3.56
1.79
1.42
1.40
Cl
O
O
H
Si
(1S,2S)-3m
400MHz, CDCl3
2.02
5.80
5.15
1.16
1.00
3.01
1.99
1.04
f1 (ppm)


174.35
135.64
135.39
135.34
133.98
133.18
129.87
129.55
128.79
128.07
127.86
126.46
58.61
52.91
32.91
18.57
Cl
O
O
H
Si
(1S,2S)-3m
100MHz, CDCl3
f1 (ppm)

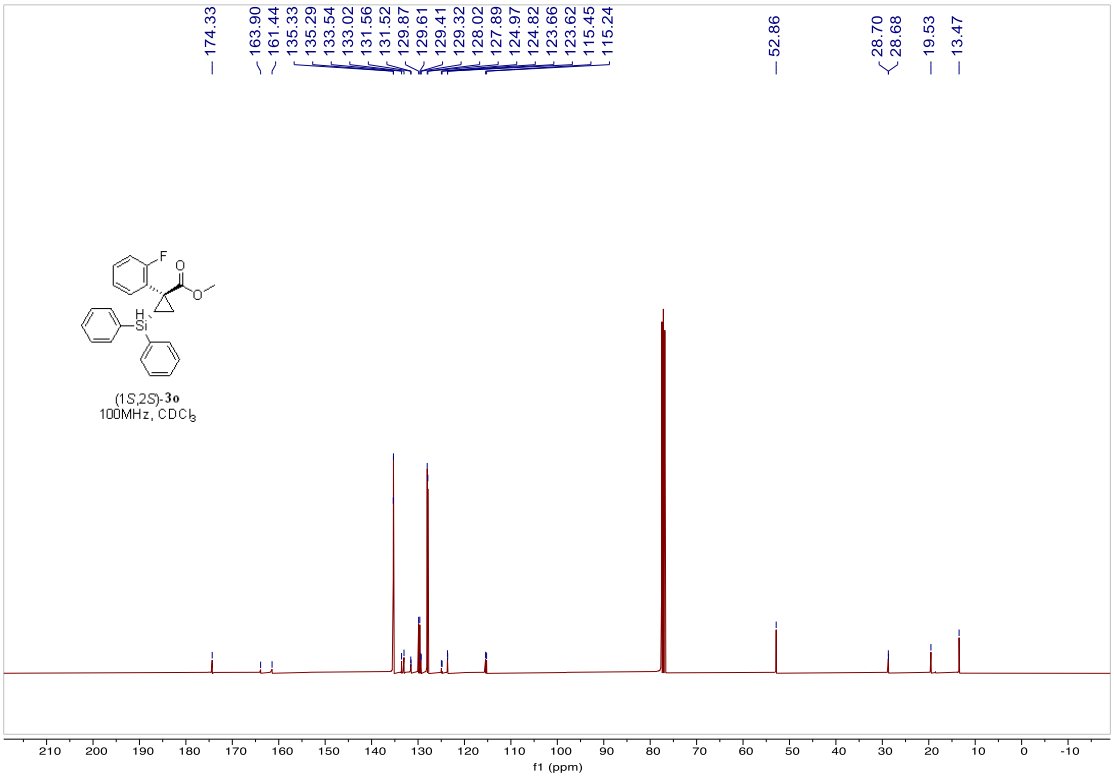

7.52
7.51
7.48
7.46
7.33
7.31
7.30
7.28
7.22
7.20
7.10
7.08
7.07
7.06
7.05
7.04
7.03
7.02
6.99
6.97
6.95
4.34
4.33
3.56
1.83
1.75
1.41
1.39
Br
O
O
H
Si
(1S,2S)-3n
400MHz, CDCl3
2.00
1.25
4.68
2.84
2.33
1.22
1.00
3.00
1.98
1.03
f1 (ppm)

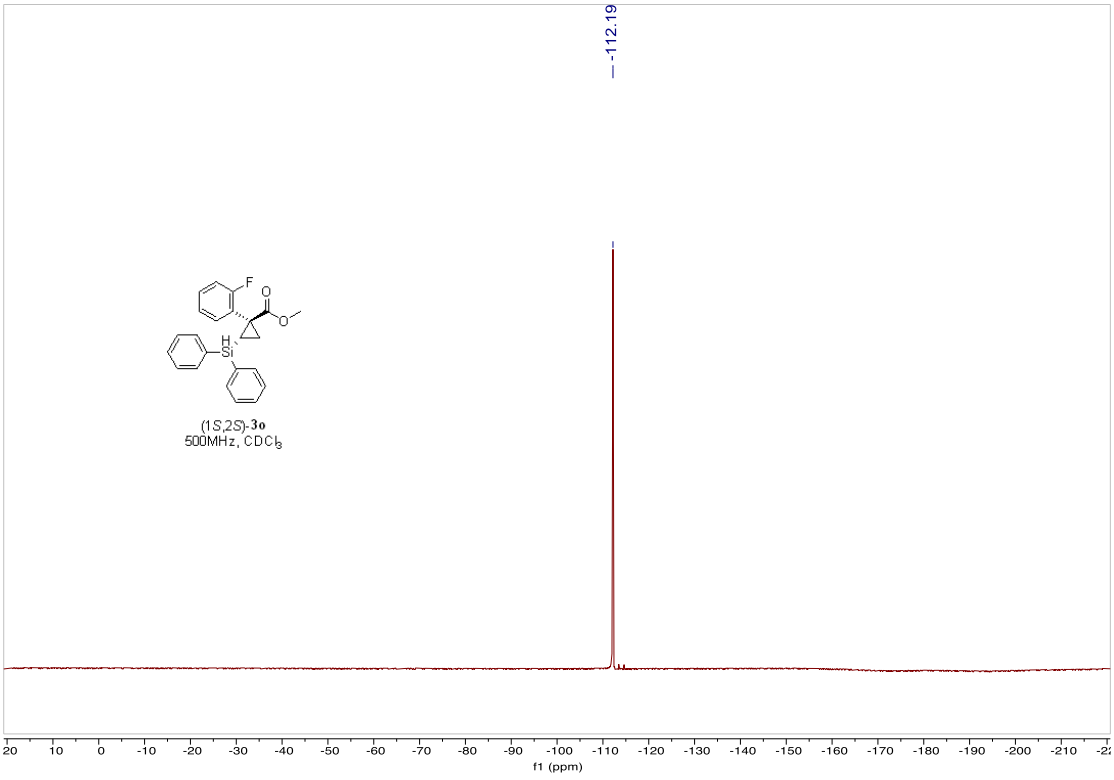


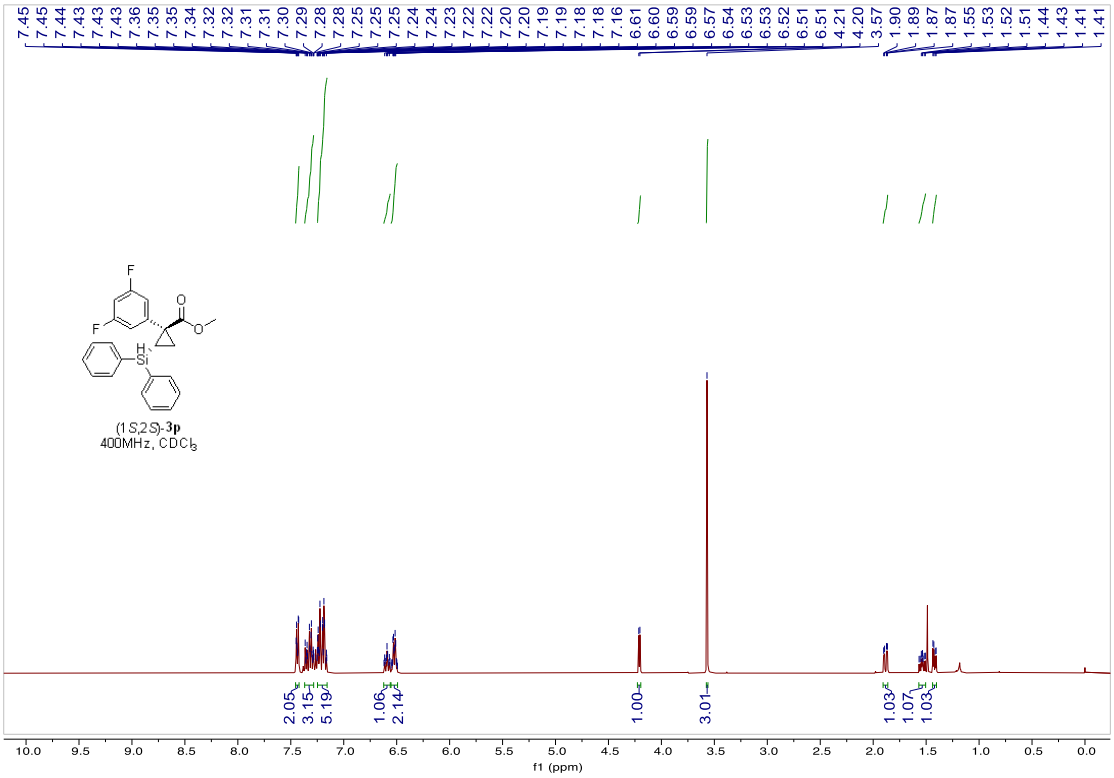
(1*S*,2*S*)-**3n**
100MHz, $CDCl_3$

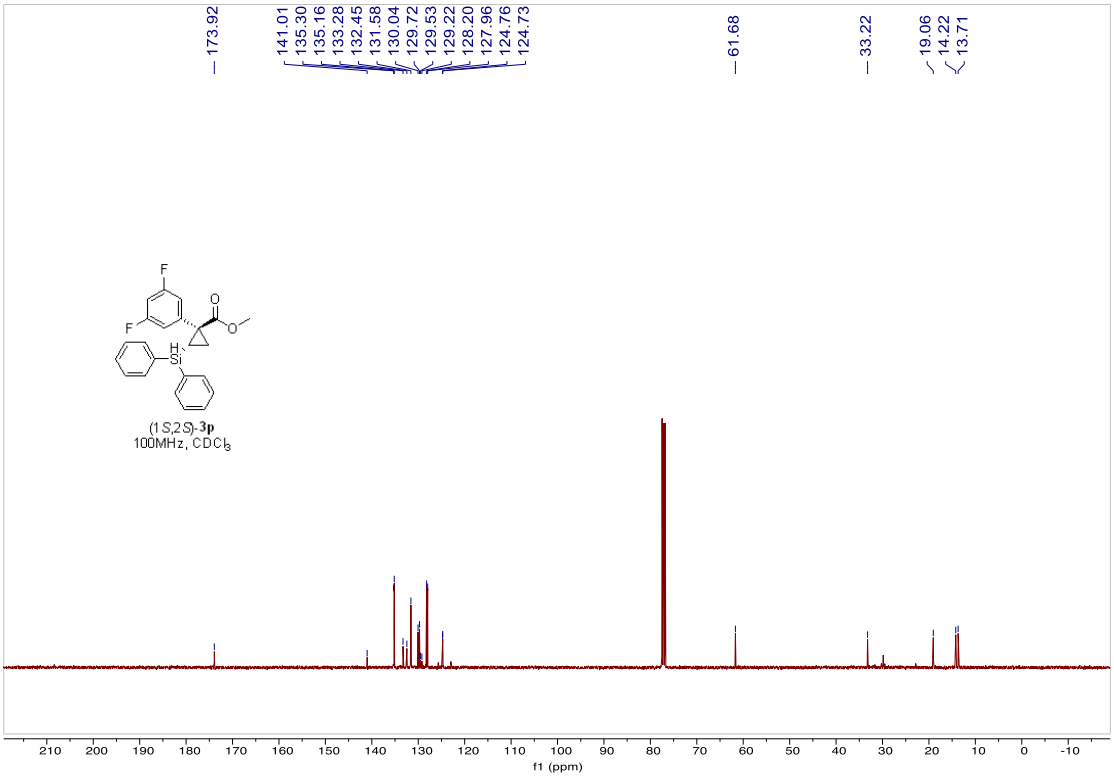


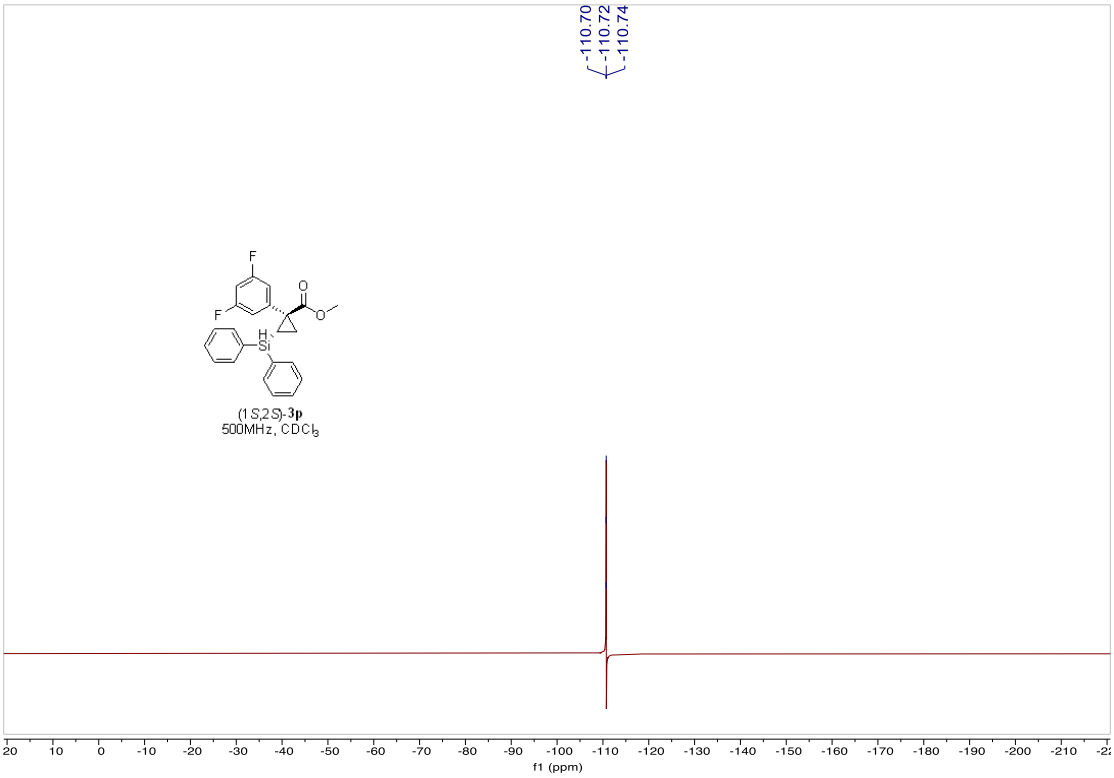
(1*S*,2*S*)-**3o**
400MHz, $CDCl_3$

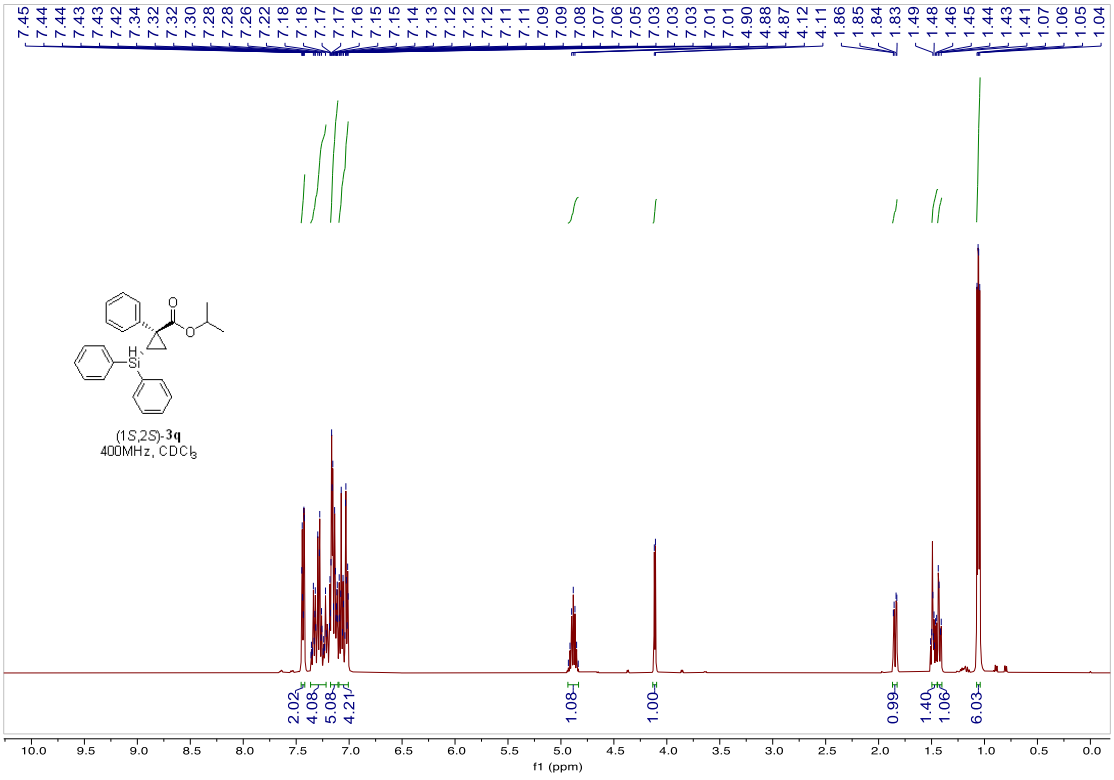

174.33
163.90
161.44
135.33
135.29
133.54
133.02
131.56
131.52
129.87
129.61
129.41
129.32
128.02
127.89
124.97
124.82
123.66
123.62
115.45
115.24
52.86
28.70
28.68
19.53
13.47
F
O
O
H
Si
(1S,2S)-3o
100MHz, CDCl3
f1 (ppm)

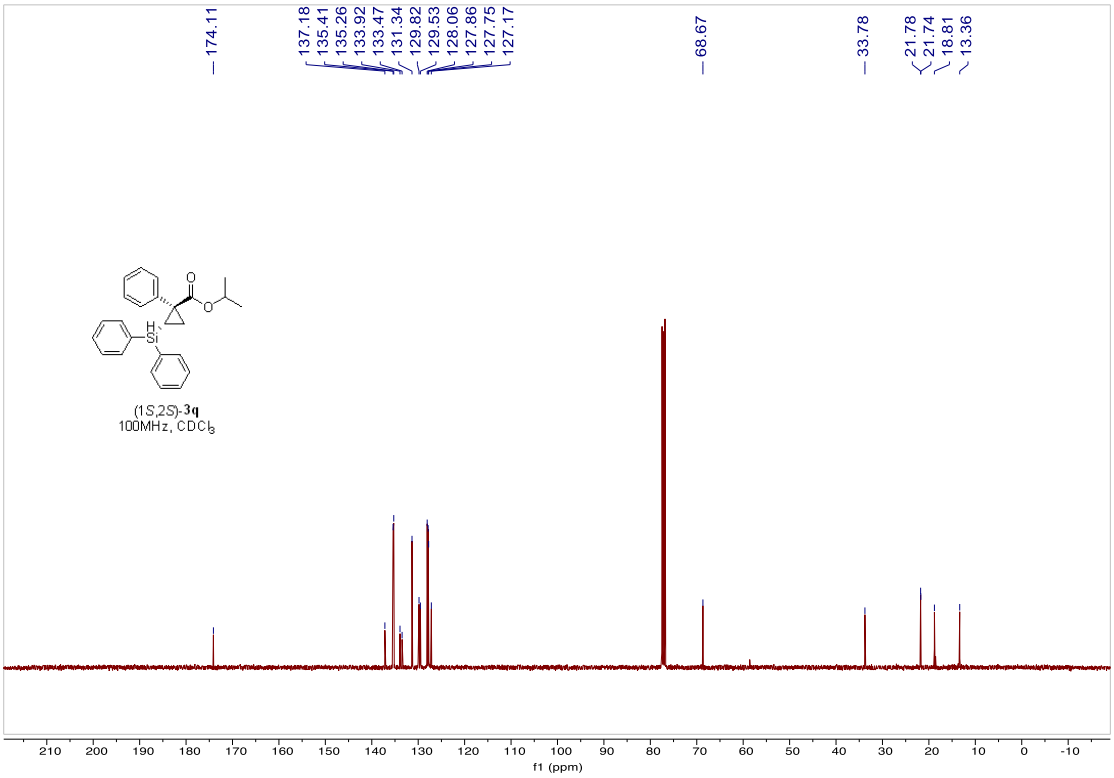

-112.19
F
O
O
H
Si
(1S,2S)-3o
500MHz, CDCl3
f1 (ppm)

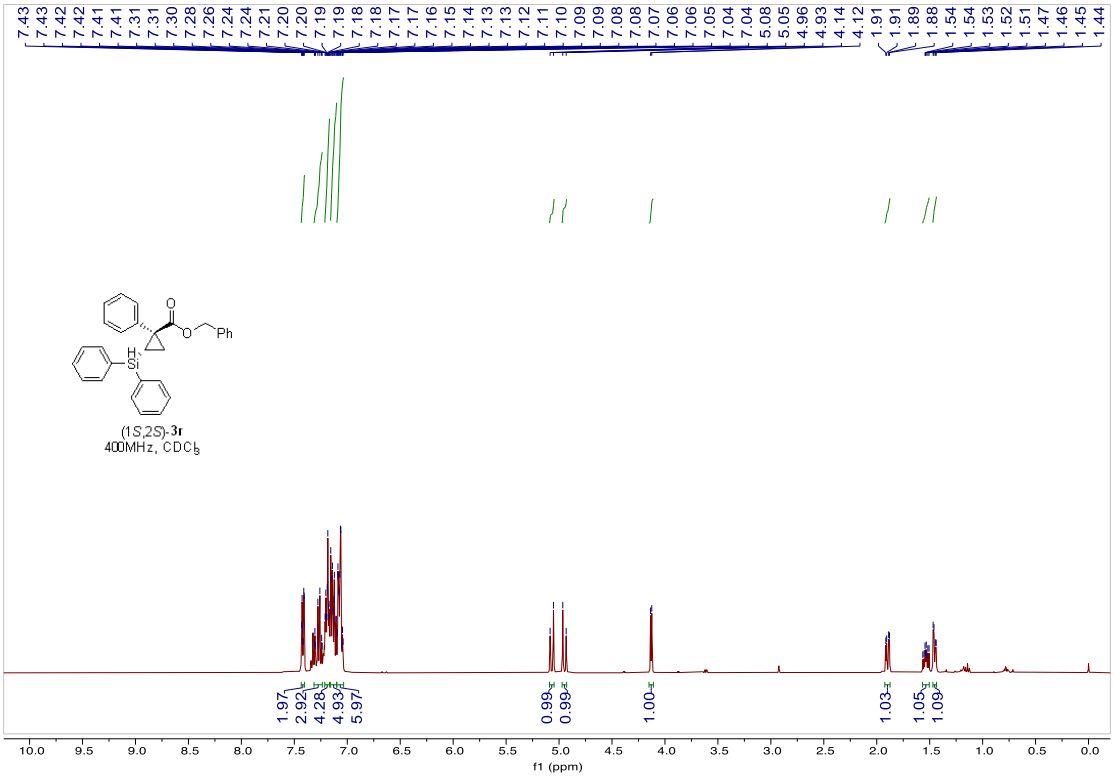

7.45 7.45 7.44 7.43 7.43 7.43 7.36 7.35 7.35 7.34 7.32 7.32 7.31 7.31 7.30 7.29 7.28 7.28 7.25 7.25 7.24 7.24 7.23 7.22 7.22 7.20 7.20 7.19 7.19 7.18 7.18 7.16 6.61 6.60 6.59 6.59 6.57 6.54 6.53 6.53 6.52 6.51 6.51 4.21 4.20 3.57 1.90 1.89 1.87 1.87 1.55 1.53 1.52 1.51 1.44 1.43 1.41 1.41
F
F
O
O
H
Si
(1S,2S)-3p
400MHz, CDCl3
2.05 3.15 5.19 1.06 2.14 1.00 3.01 1.03 1.07 1.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

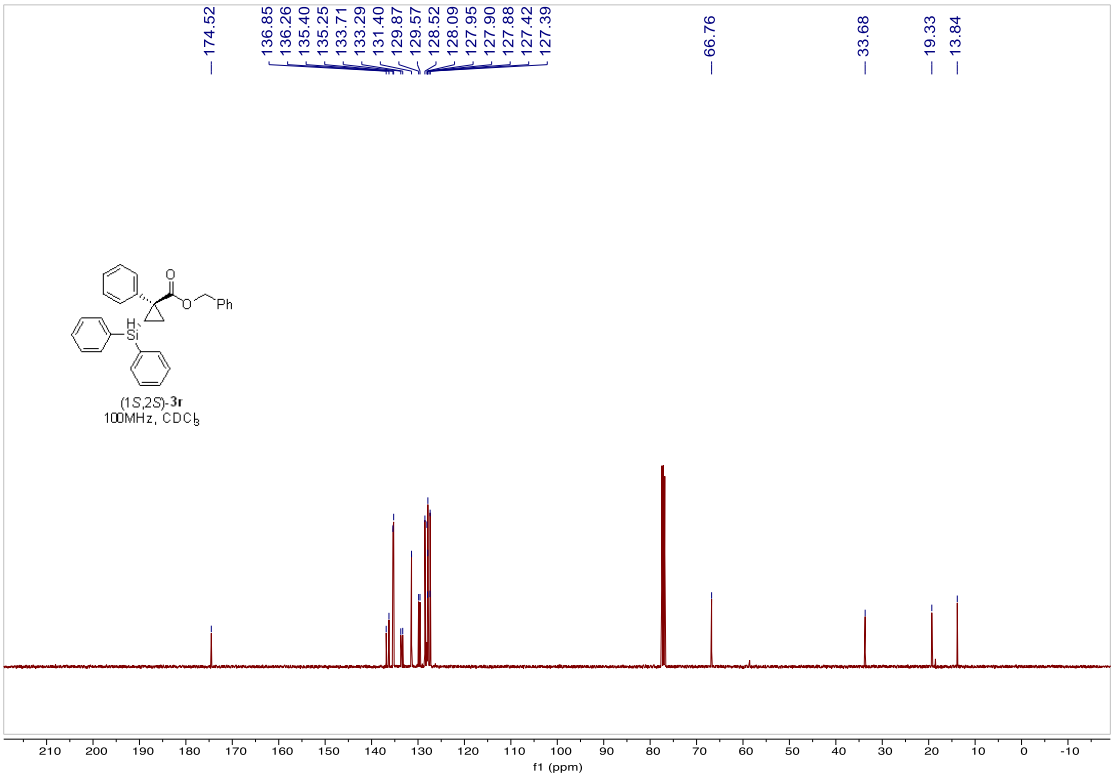

173.92
141.01 135.30 135.16 133.28 132.45 131.58 130.04 129.72 129.53 129.22 128.20 127.96 124.76 124.73
61.68
33.22
19.06 14.22 13.71
F
F
O
O
H
Si
(1S,2S)-3p
100MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

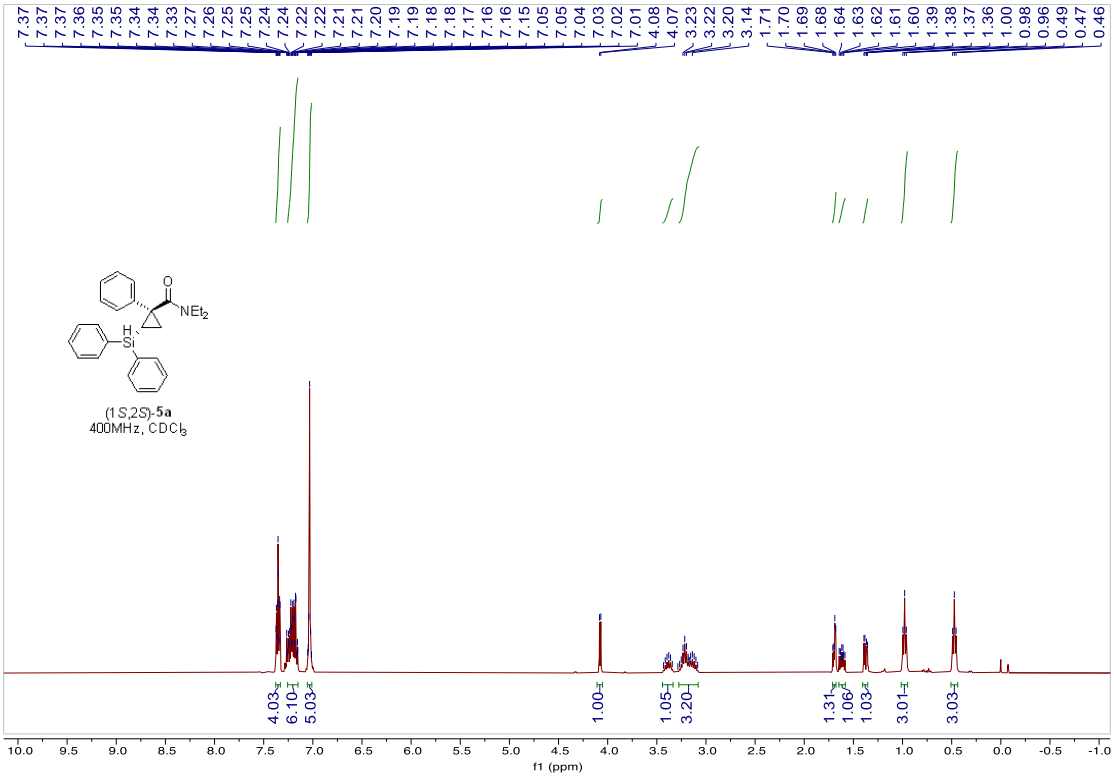

-110.70
-110.72
-110.74
F
F
O
O
H
Si
(1S,2S)-3p
500MHz, CDCl3
f1 (ppm)

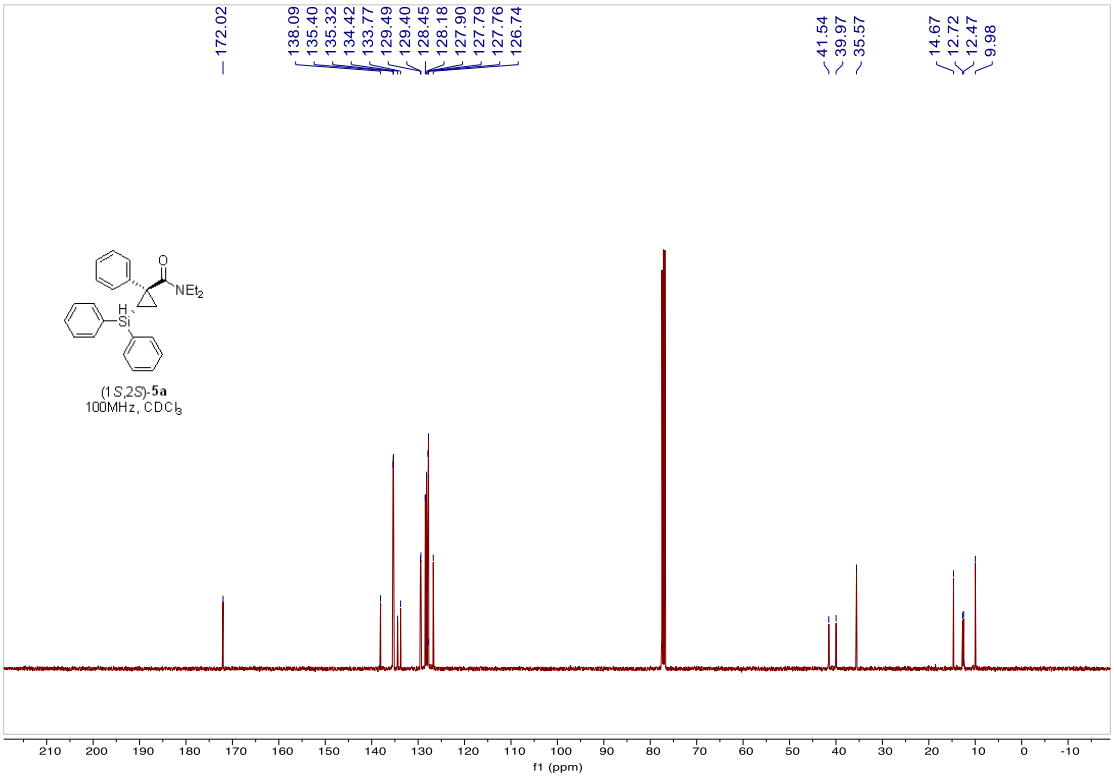

7.45 7.44 7.44 7.43 7.43 7.42 7.34 7.32 7.32 7.30 7.28 7.28 7.26 7.22 7.18 7.18 7.17 7.17 7.16 7.15 7.15 7.14 7.13 7.12 7.12 7.12 7.11 7.11 7.09 7.09 7.08 7.07 7.06 7.05 7.03 7.03 7.03 7.01 7.01 4.90 4.88 4.87 4.12 4.11 1.86 1.85 1.84 1.83 1.49 1.48 1.46 1.45 1.44 1.43 1.41 1.07 1.06 1.05 1.04
O
O
H
Si
(1S,2S)-3q
400MHz, CDCl3
2.02
4.08
5.08
4.21
1.08
1.00
0.99
1.40
1.06
6.03
f1 (ppm)

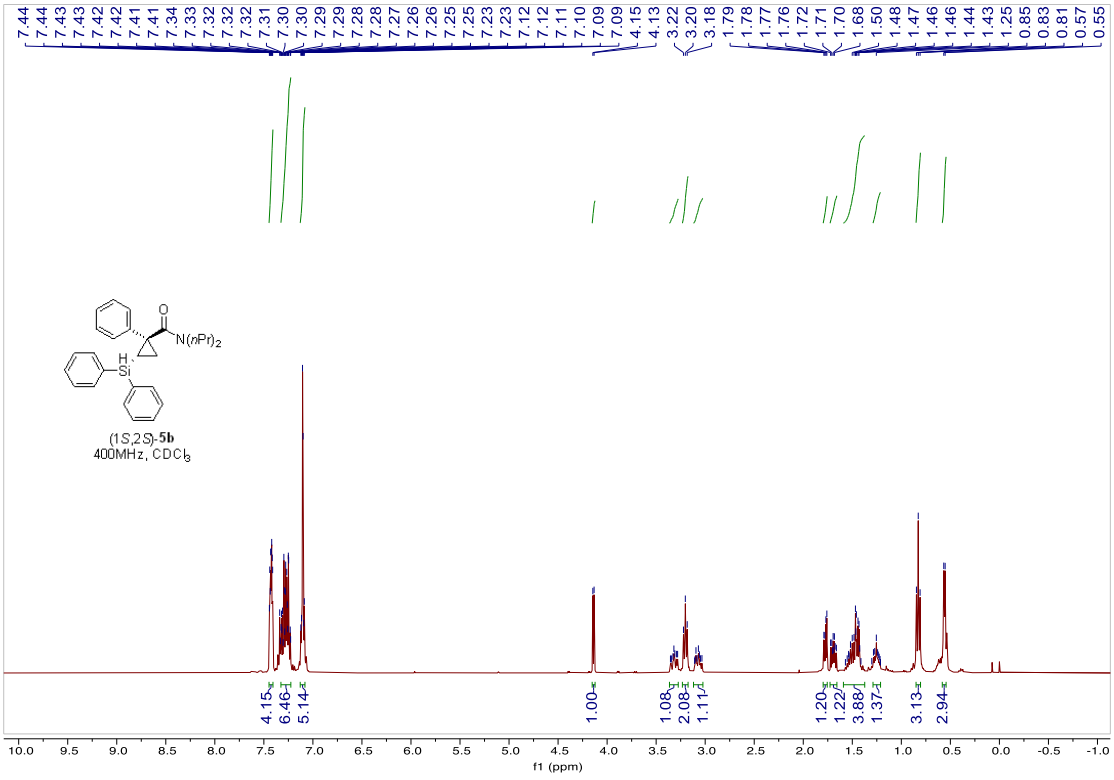

174.11
137.18
135.41
135.26
133.92
133.47
131.34
129.82
129.53
128.06
127.86
127.75
127.17
68.67
33.78
21.78
21.74
18.81
13.36
(1S,2S)-3q
100MHz, CDCl3
f1 (ppm)


(1S,2S)-3r
400MHz, CDCl3
1.97
2.92
4.28
4.93
5.97
0.99
0.99
1.00
1.03
1.05
1.09
f1 (ppm)


174.52
136.85
136.26
135.40
135.25
133.71
133.29
131.40
129.87
129.57
128.52
128.09
127.95
127.90
127.88
127.42
127.39
66.76
33.68
19.33
13.84
O
O
Ph
H
Si
(1S,2S)-3r
100MHz, CDCl3
f1 (ppm)


O
NEt2
H
Si
(1S,2S)-5a
400MHz, CDCl3
4.03
6.10
5.03
1.00
1.05
3.20
1.31
1.06
1.03
3.01
3.03
f1 (ppm)


172.02
138.09
135.40
135.32
134.42
133.77
129.49
129.40
128.45
128.18
127.90
127.79
127.76
126.74
41.54
39.97
35.57
14.67
12.72
12.47
9.98
NEt2
(1S,2S)-5a
100MHz, CDCl3
f1 (ppm)


7.44
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.34
7.33
7.32
7.32
7.32
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.26
7.26
7.25
7.25
7.23
7.23
7.12
7.12
7.11
7.10
7.09
7.09
4.15
4.13
3.22
3.20
3.18
1.79
1.78
1.77
1.76
1.72
1.71
1.70
1.68
1.50
1.48
1.47
1.46
1.46
1.44
1.43
1.25
0.85
0.83
0.81
0.57
0.55
N(nPr)2
(1S,2S)-5b
400MHz, CDCl3
4.15
6.46
5.14
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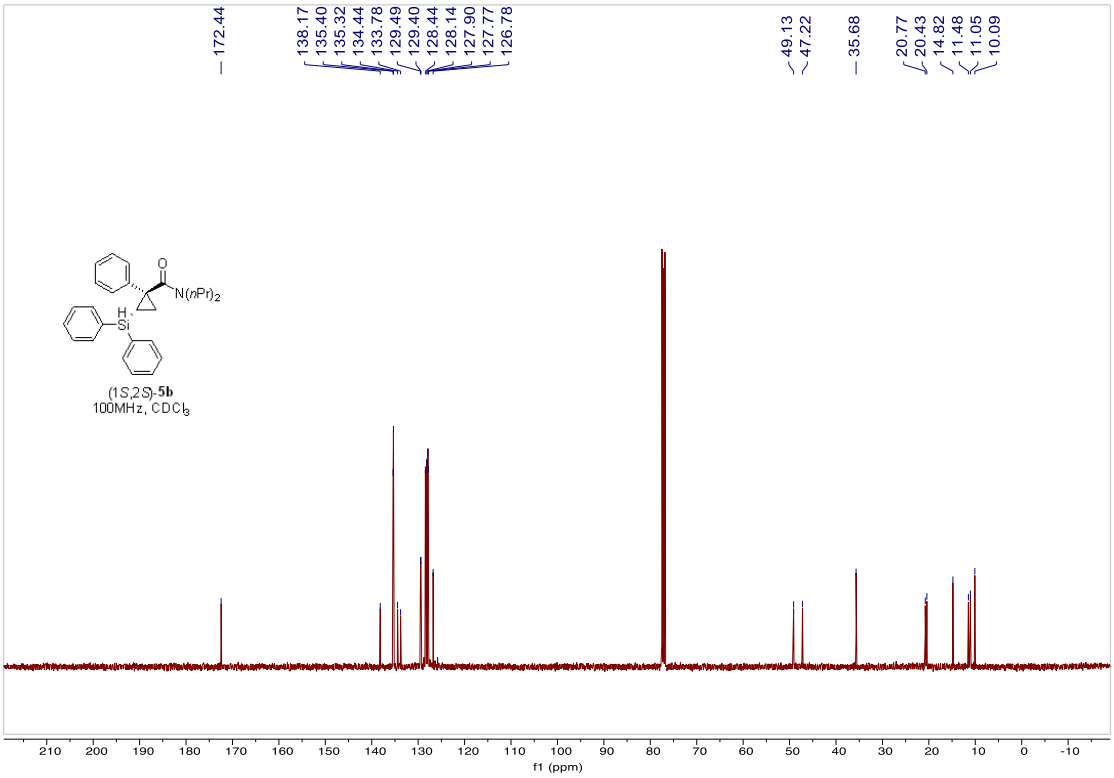
2.08
1.11
1.20
1.22
3.88
1.37
3.13
2.94
f1 (ppm)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126.78
49.13
47.22
35.68
20.77
20.43
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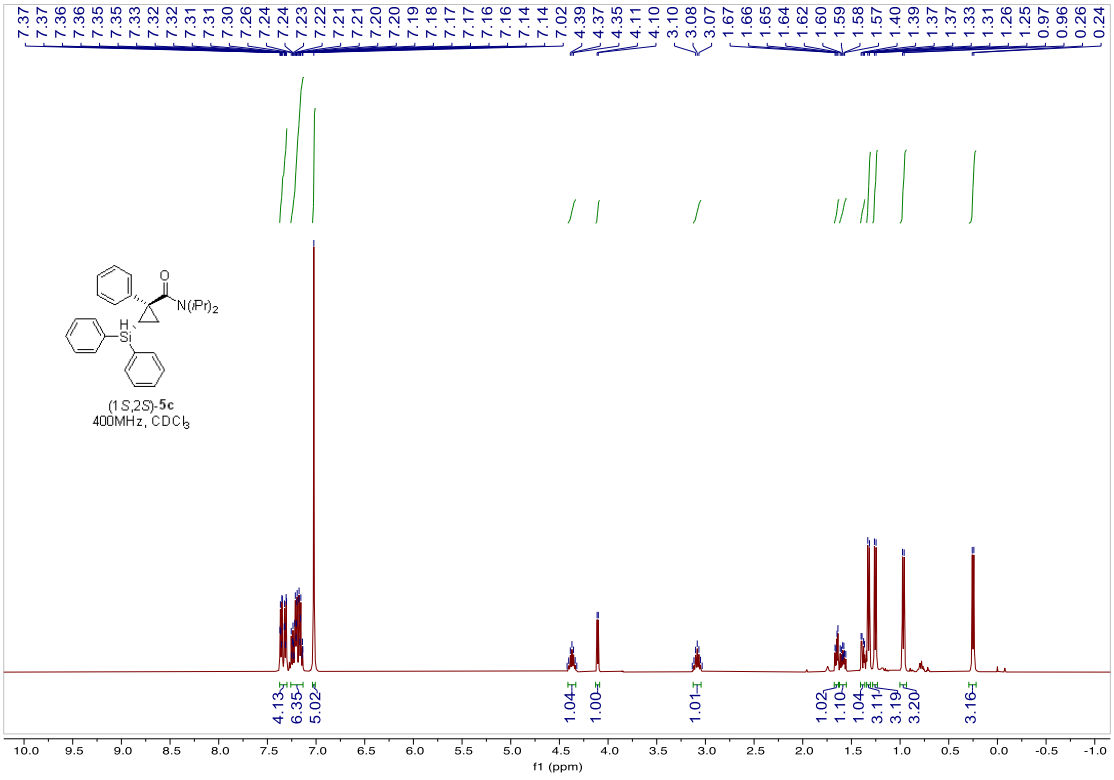
11.05
10.09
N(nPr)2
H
Si
(1S,2S)-5b
100MHz, CDCl3
f1 (ppm)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7.19
7.18
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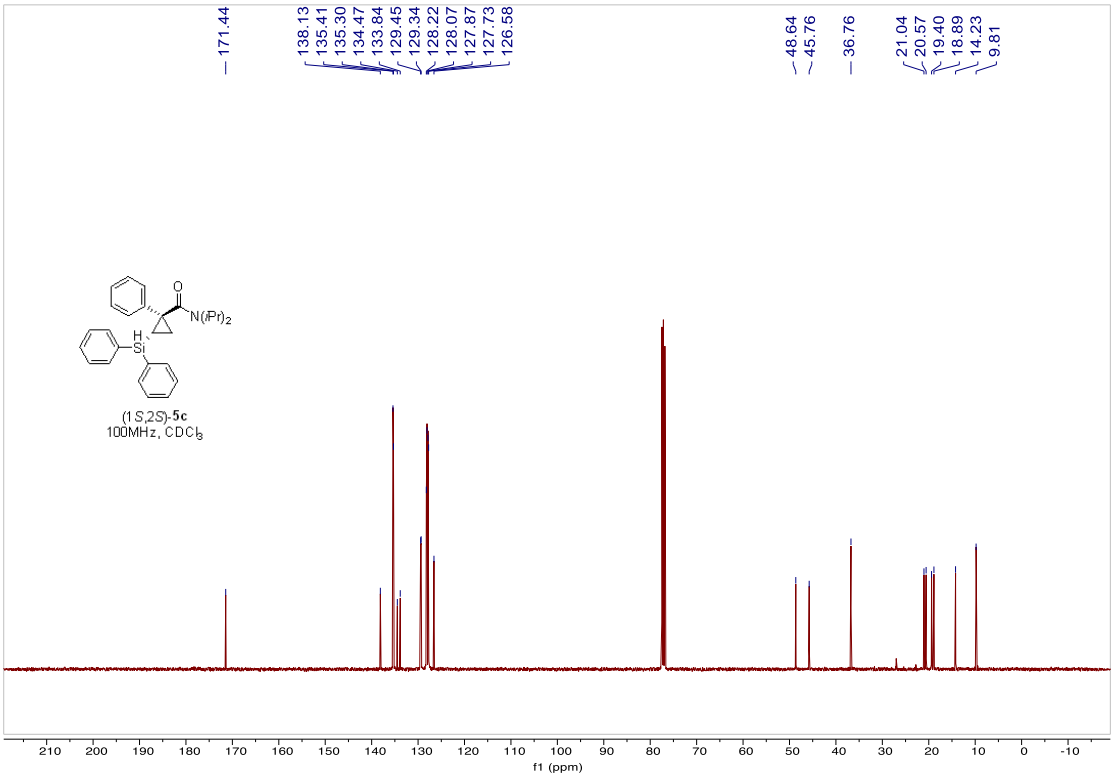
7.17
7.16
7.16
7.14
7.14
7.02
4.39
4.37
4.35
4.11
4.10
3.10
3.08
3.07
1.67
1.66
1.65
1.64
1.62
1.60
1.59
1.58
1.57
1.40
1.39
1.37
1.37
1.33
1.31
1.26
1.25
0.97
0.96
0.26
0.24
N(iPr)2
H
Si
(1S,2S)-5c
400MHz, CDCl3
4.13
6.35
5.02
1.04
1.00
1.01
1.02
1.10
1.04
3.11
3.19
3.20
3.16
f1 (ppm)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126.58
48.64
45.76
36.76
21.04
20.57
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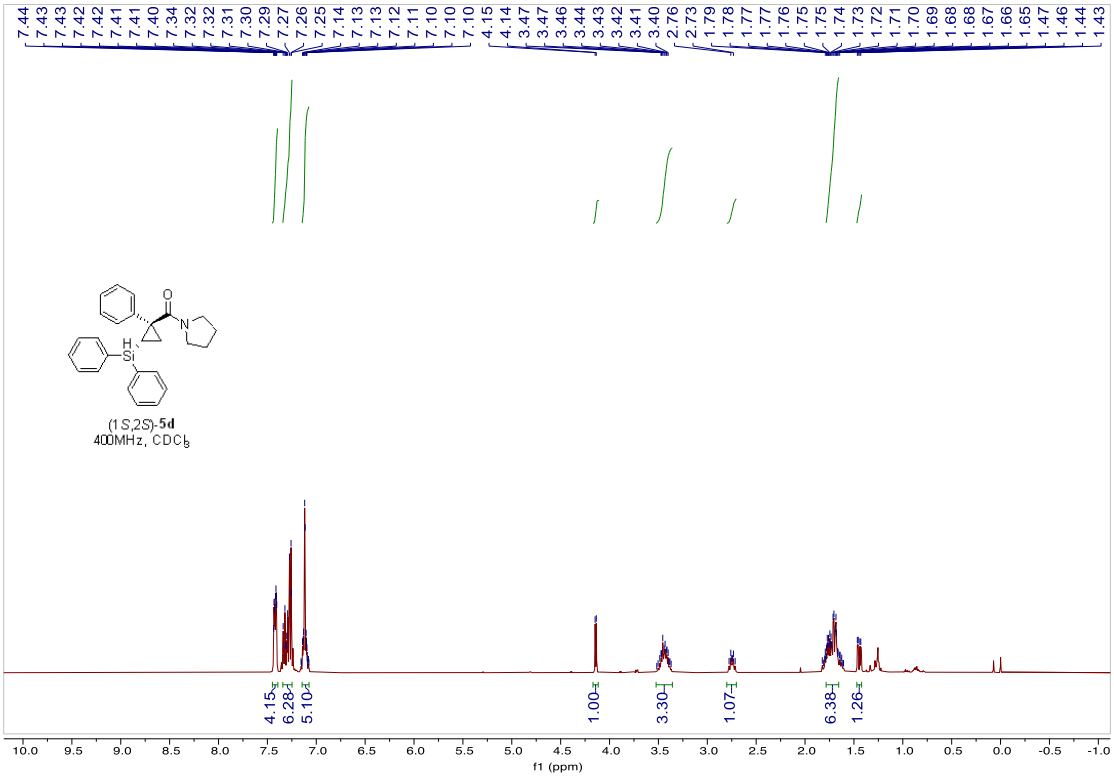
9.81
N(iPr)2
H
Si
(1S,2S)-5c
100MHz, CDCl3
f1 (ppm)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7.13
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7.11
7.10
7.10
7.10
4.15
4.14
3.47
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1.77
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1.76
1.75
1.75
1.74
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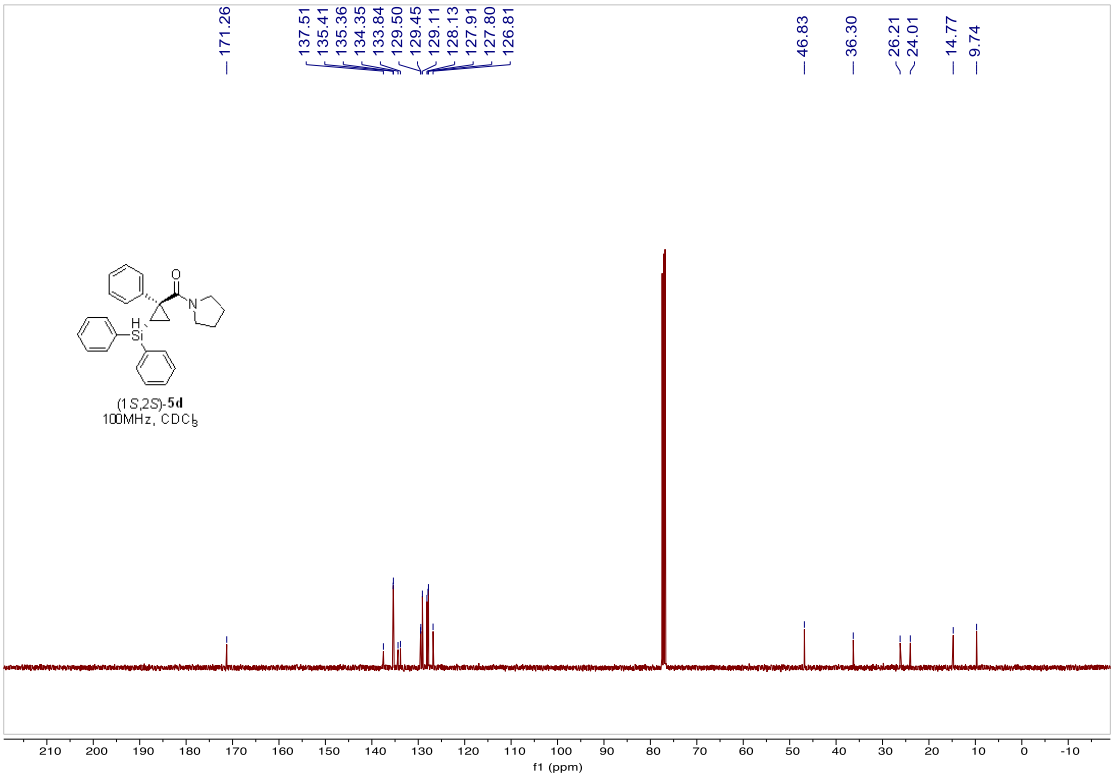
1.72
1.71
1.70
1.69
1.68
1.68
1.67
1.66
1.65
1.47
1.46
1.44
1.43
N
H
Si
(1S,2S)-5d
400MHz, CDCl3
4.15
6.28
5.10
1.00
3.30
1.07
6.38
1.26
f1 (ppm)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127.80
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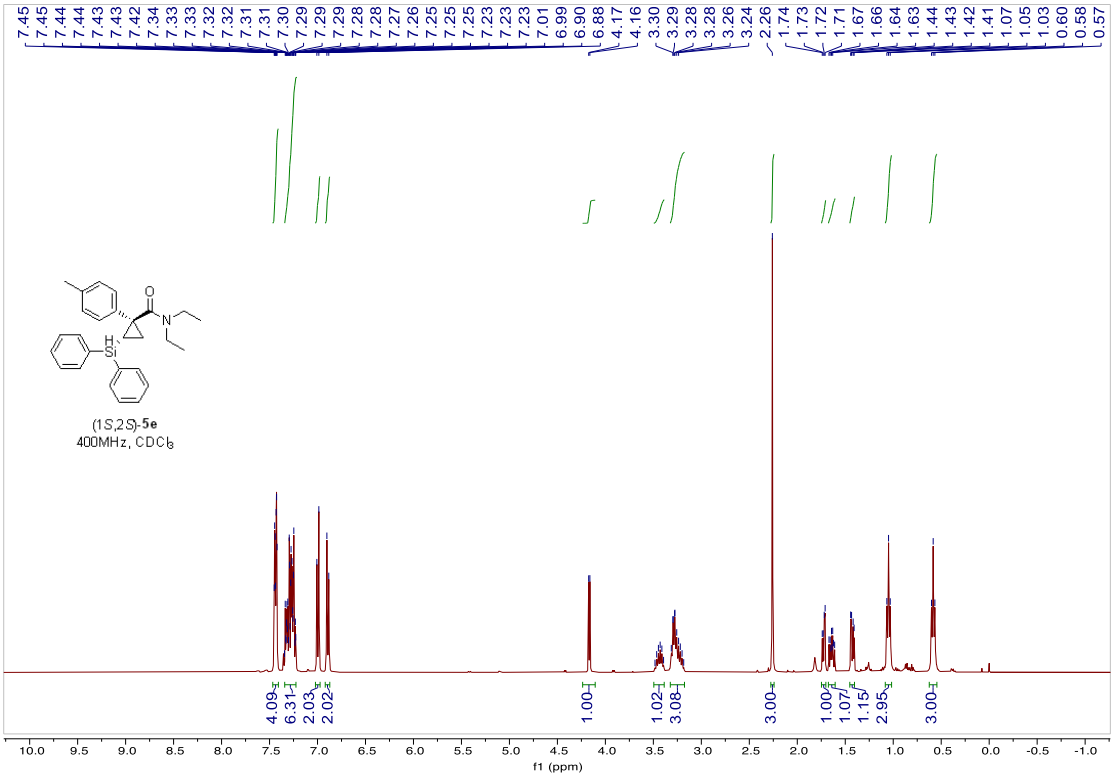
9.74
(1S,2S)-5d
100MHz, CDCl3
f1 (ppm)


(1S,2S)-5e
400MHz, CDCl3
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6.31
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1.02
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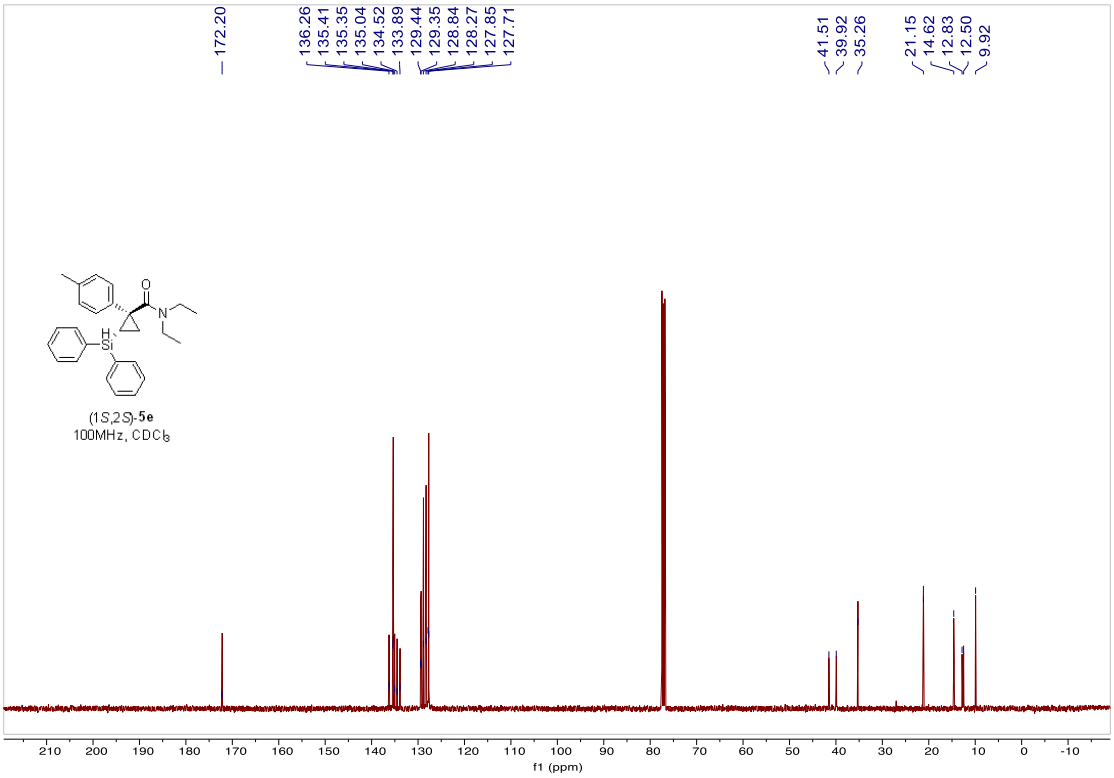
1.07
1.15
2.95
3.00
f1 (ppm)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128.27
127.85
127.71
41.51
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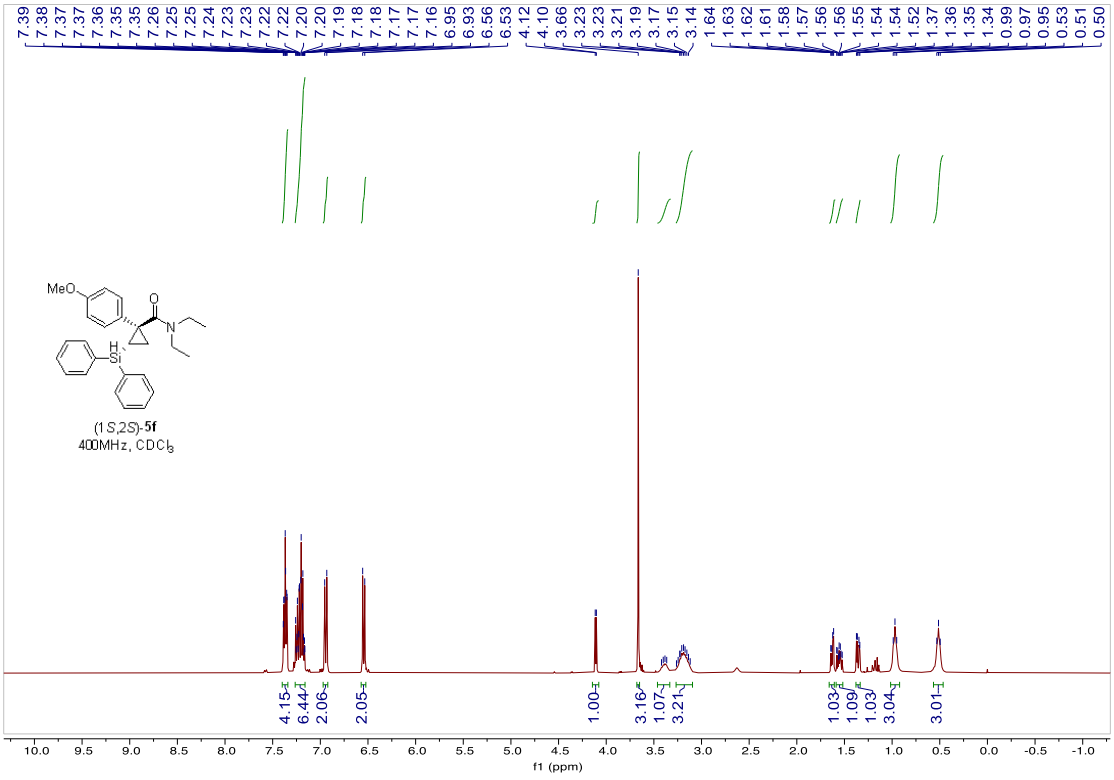
35.26
21.15
14.62
12.83
12.50
9.92
(1S,2S)-5e
100MHz, CDCl3
f1 (ppm)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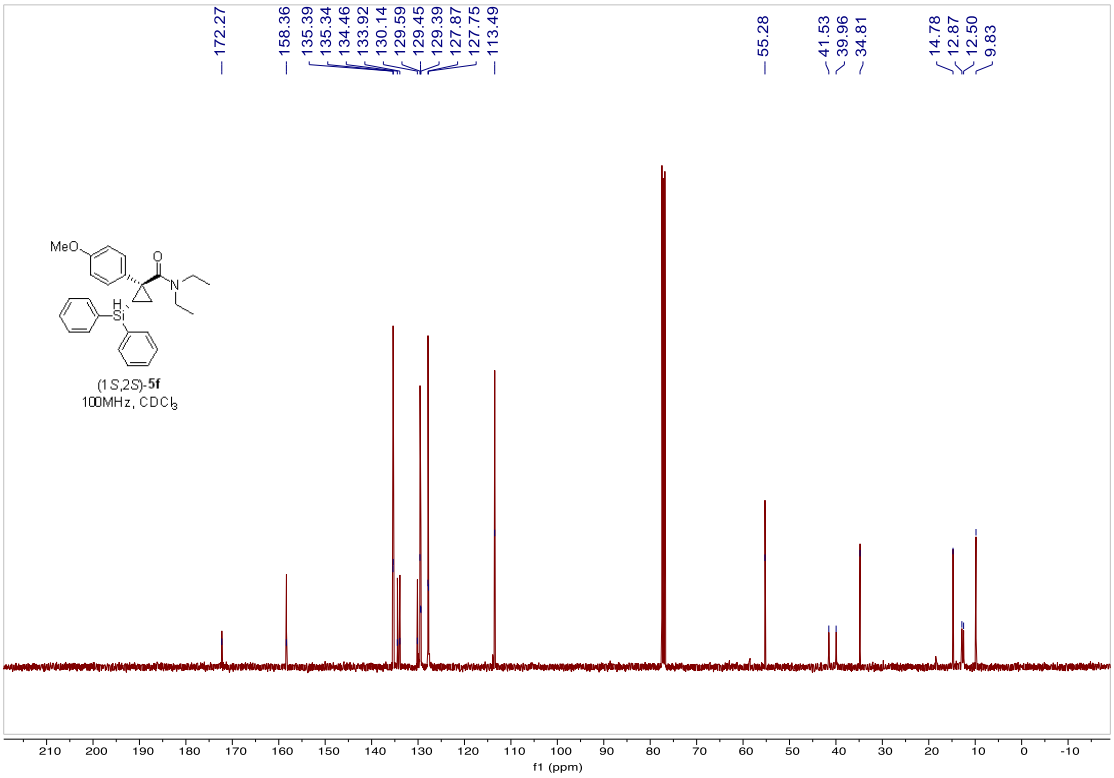
7.22
7.22
7.20
7.20
7.19
7.18
7.18
7.17
7.17
7.16
6.95
6.93
6.56
6.53
4.12
4.10
3.66
3.23
3.23
3.21
3.19
3.17
3.15
3.14
1.64
1.63
1.62
1.61
1.58
1.57
1.56
1.56
1.55
1.54
1.54
1.52
1.37
1.36
1.35
1.34
0.99
0.97
0.95
0.53
0.51
0.50
MeO
(1S,2S)-5f
400MHz, CDCl3
4.15
6.44
2.06
2.05
1.00
3.16
1.07
3.21
1.03
1.09
1.03
3.04
3.01
f1 (ppm)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127.87
127.75
113.49
55.28
41.53
39.96
34.81
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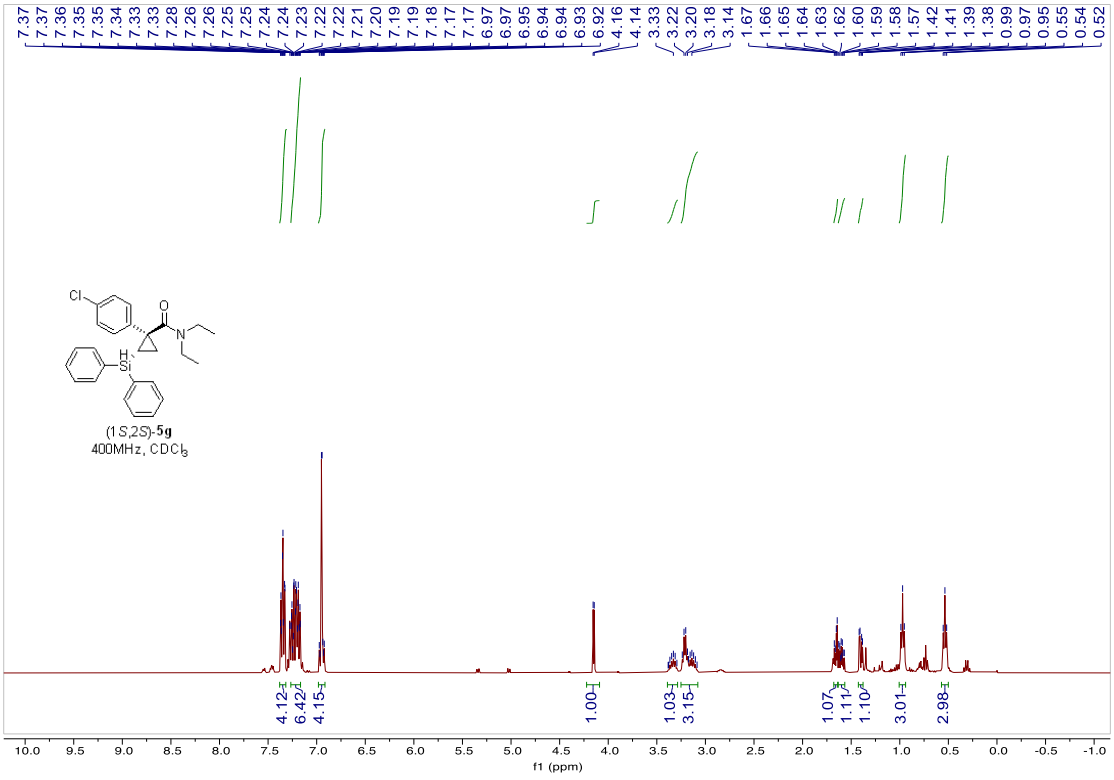
9.83
MeO
O
N
H
Si
(1S,2S)-5f
100MHz, CDCl3
f1 (ppm)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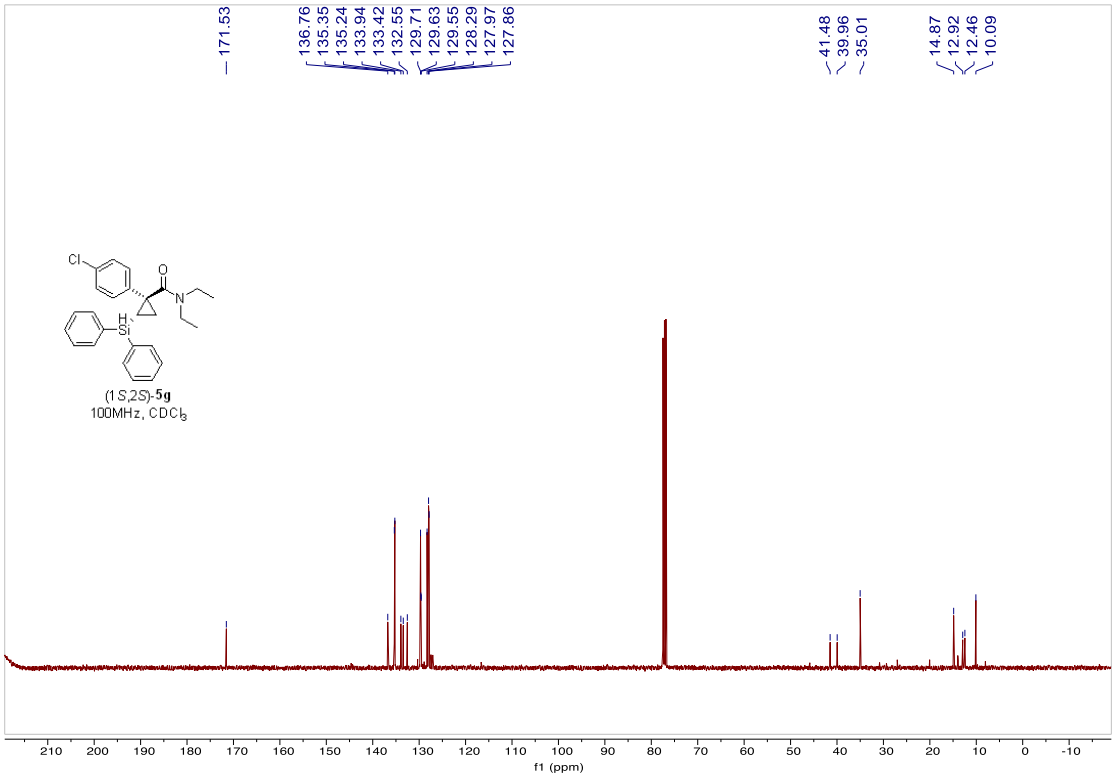
7.25
7.24
7.24
7.23
7.22
7.22
7.21
7.20
7.19
7.19
7.18
7.17
7.17
6.97
6.97
6.95
6.94
6.94
6.93
6.92
4.16
4.14
3.33
3.22
3.20
3.18
3.14
1.67
1.66
1.65
1.64
1.63
1.62
1.60
1.59
1.58
1.57
1.42
1.41
1.39
1.38
0.99
0.97
0.95
0.55
0.54
0.52
Cl
O
N
H
Si
(1S,2S)-5g
400MHz, CDCl3
4.12
6.42
4.15
1.00
1.03
3.15
1.07
1.11
1.10
3.01
2.98
f1 (ppm)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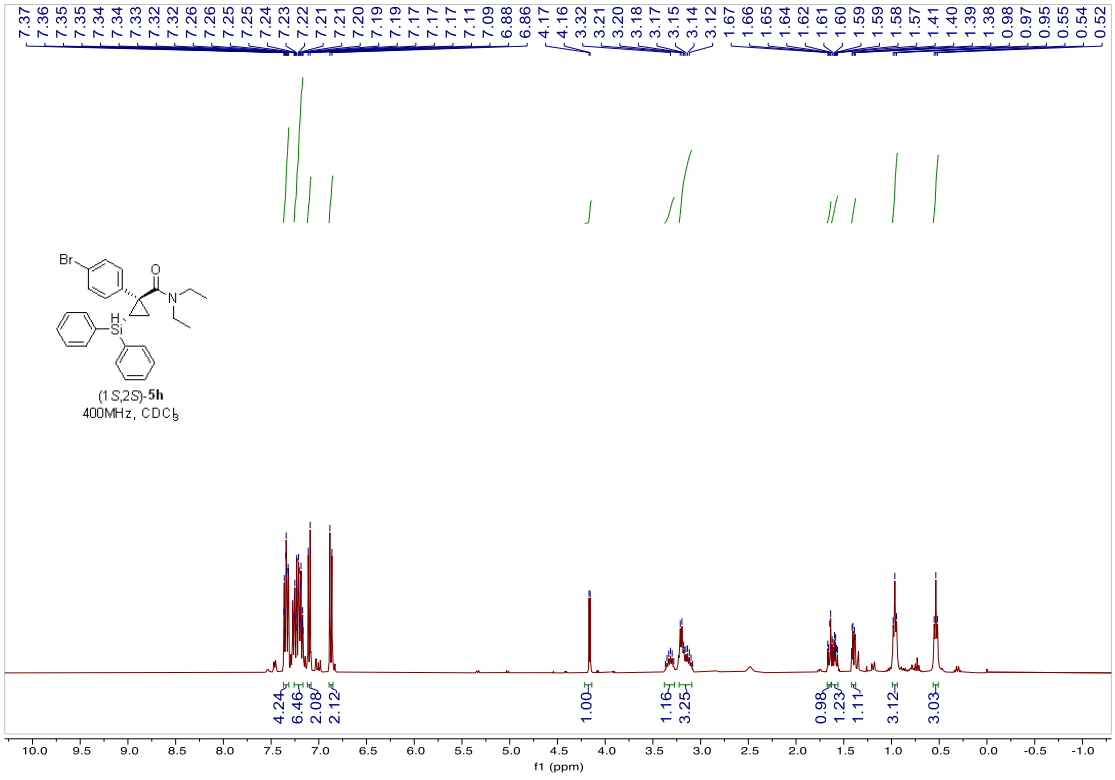
128.29
127.97
127.86
41.48
39.96
35.01
14.87
12.92
12.46
10.09
Cl
O
N
H
Si
(1S,2S)-5g
100MHz, CDCl3
f1 (ppm)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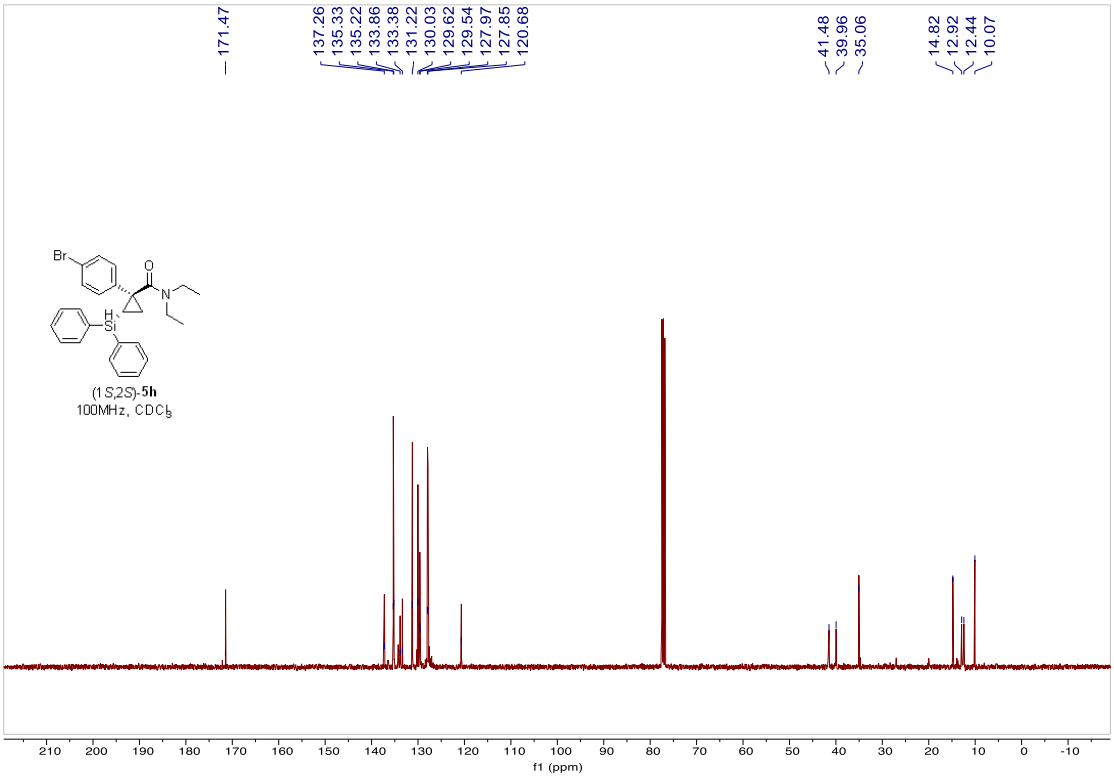
7.24
7.23
7.22
7.21
7.21
7.20
7.19
7.19
7.17
7.17
7.17
7.11
7.09
6.88
6.86
4.17
4.16
3.32
3.21
3.20
3.18
3.17
3.15
3.14
3.12
1.67
1.66
1.65
1.64
1.62
1.61
1.60
1.59
1.59
1.58
1.57
1.41
1.40
1.39
1.38
0.98
0.97
0.95
0.55
0.54
0.52
Br
O
N
H
Si
(1S,2S)-5h
400MHz, CDCl3
4.24
6.46
2.08
2.12
1.00
1.16
3.25
0.98
1.23
1.11
3.12
3.03
f1 (ppm)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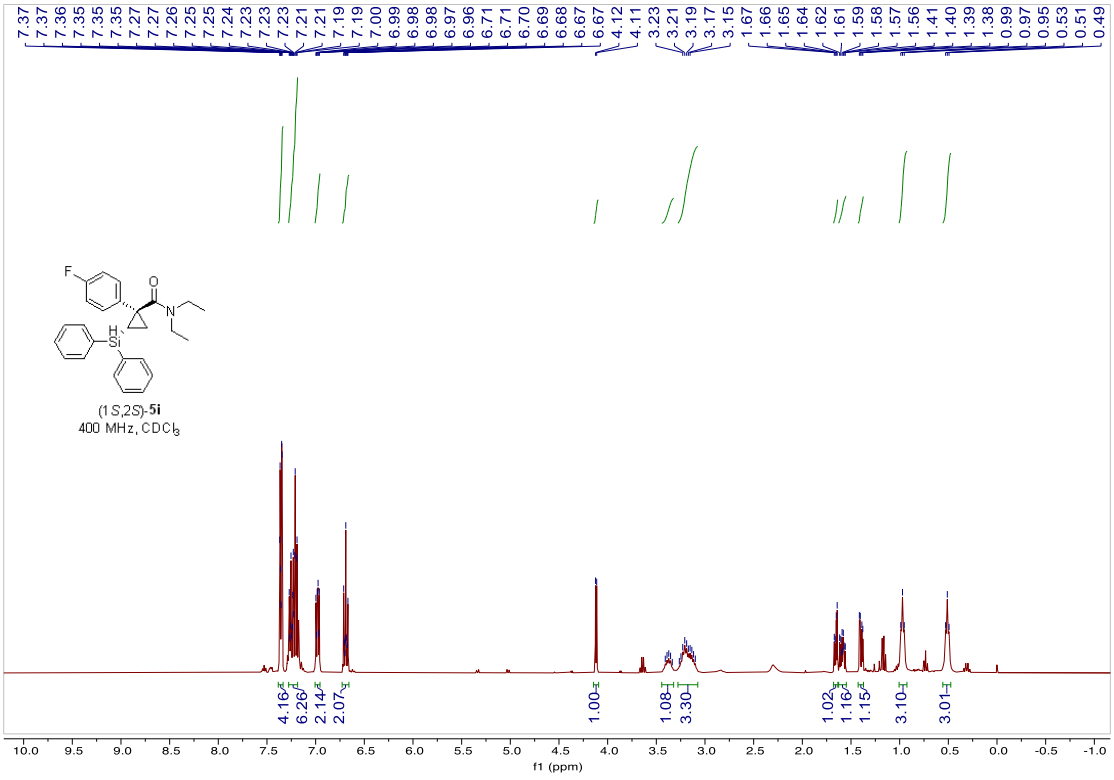
127.85
120.68
41.48
39.96
35.06
14.82
12.92
12.44
10.07
Br
O
N
H
Si
(1S,2S)-5h
100MHz, CDCl3
f1 (ppm)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7.23
7.23
7.21
7.21
7.19
7.19
7.00
6.99
6.98
6.98
6.97
6.96
6.71
6.71
6.70
6.69
6.68
6.67
6.67
4.12
4.11
3.23
3.21
3.19
3.17
3.15
1.67
1.66
1.65
1.64
1.62
1.61
1.59
1.58
1.57
1.56
1.41
1.40
1.39
1.38
0.99
0.97
0.95
0.53
0.51
0.49
F
O
N
H
Si
(1S,2S)-5i
400 MHz, CDCl3
4.16
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1.00
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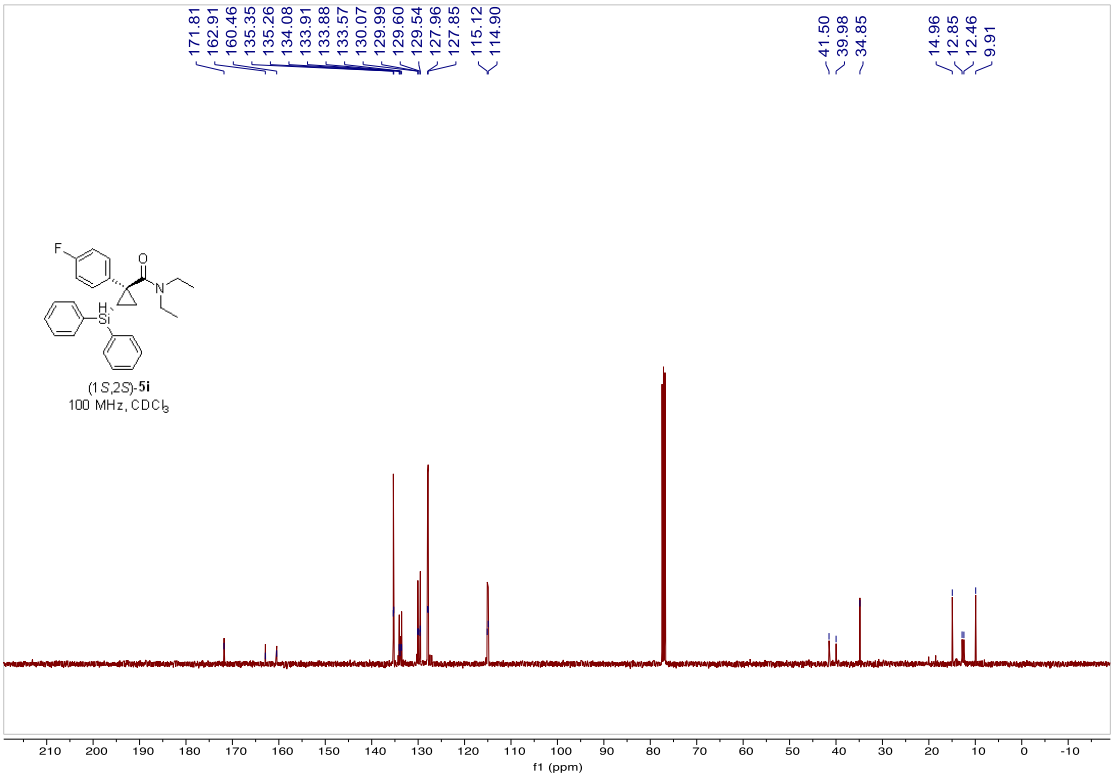
1.16
1.15
3.10
3.01
f1 (ppm)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127.96
127.85
115.12
114.90
41.50
39.98
34.85
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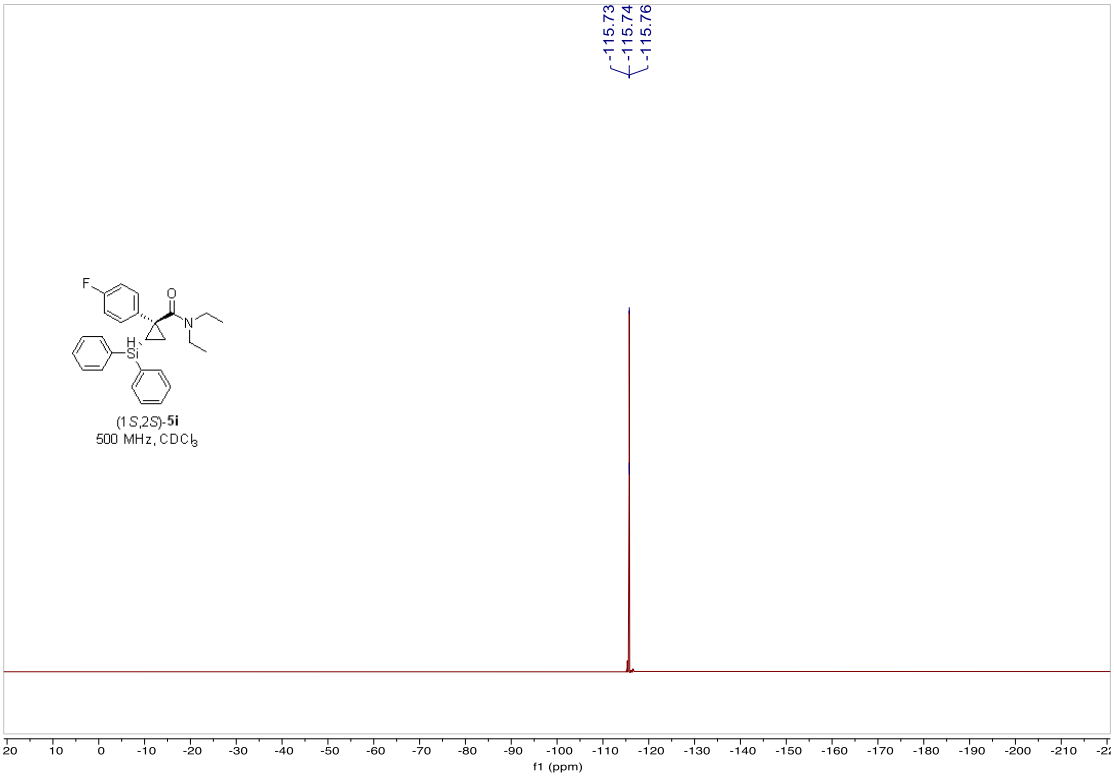
12.85
12.46
9.91
F
O
N
H
Si
(1S,2S)-5i
100 MHz, CDCl3
f1 (ppm)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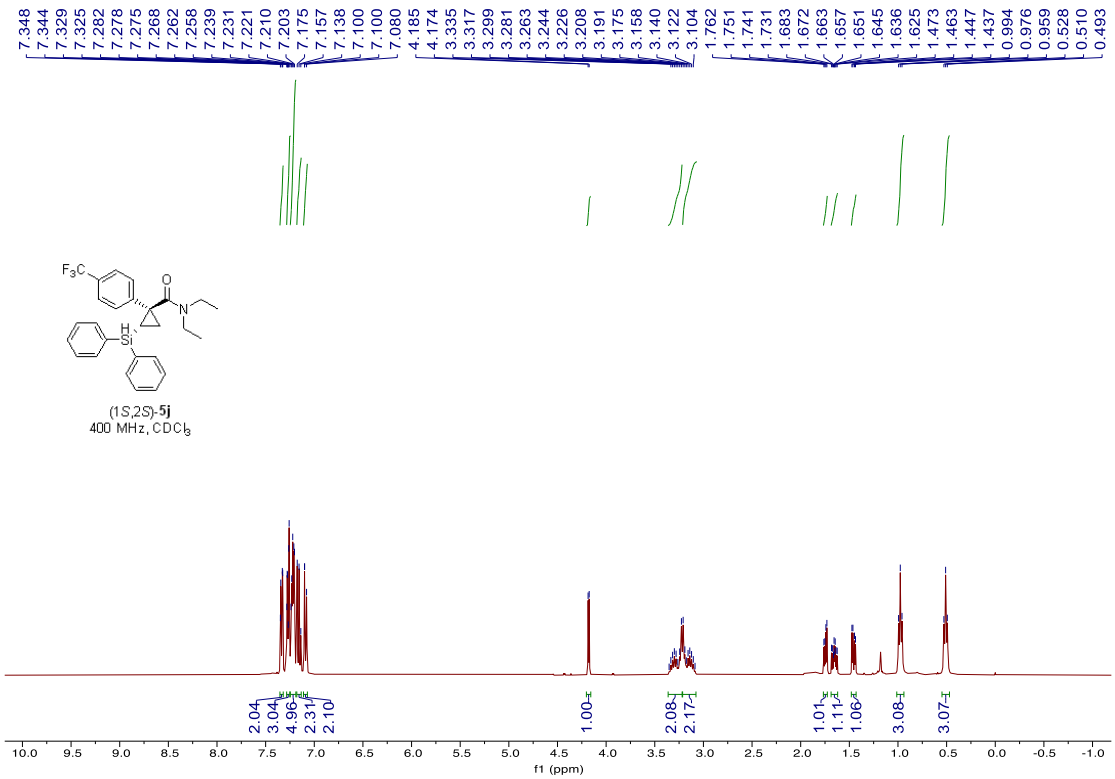
-115.74
-115.76
F
O
N
H
Si
(1S,2S)-5i
500 MHz, CDCl3
f1 (ppm)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7.210
7.203
7.175
7.157
7.138
7.100
7.100
7.080
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4.174
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3.317
3.299
3.281
3.263
3.244
3.226
3.208
3.191
3.175
3.158
3.140
3.122
3.104
1.762
1.751
1.741
1.731
1.683
1.672
1.663
1.657
1.651
1.645
1.636
1.625
1.473
1.463
1.447
1.437
0.994
0.976
0.959
0.528
0.510
0.493
F3C
O
N
H
Si
(1S,2S)-5j
400 MHz, CDCl3
2.04
3.04
4.96
2.31
2.10
1.00
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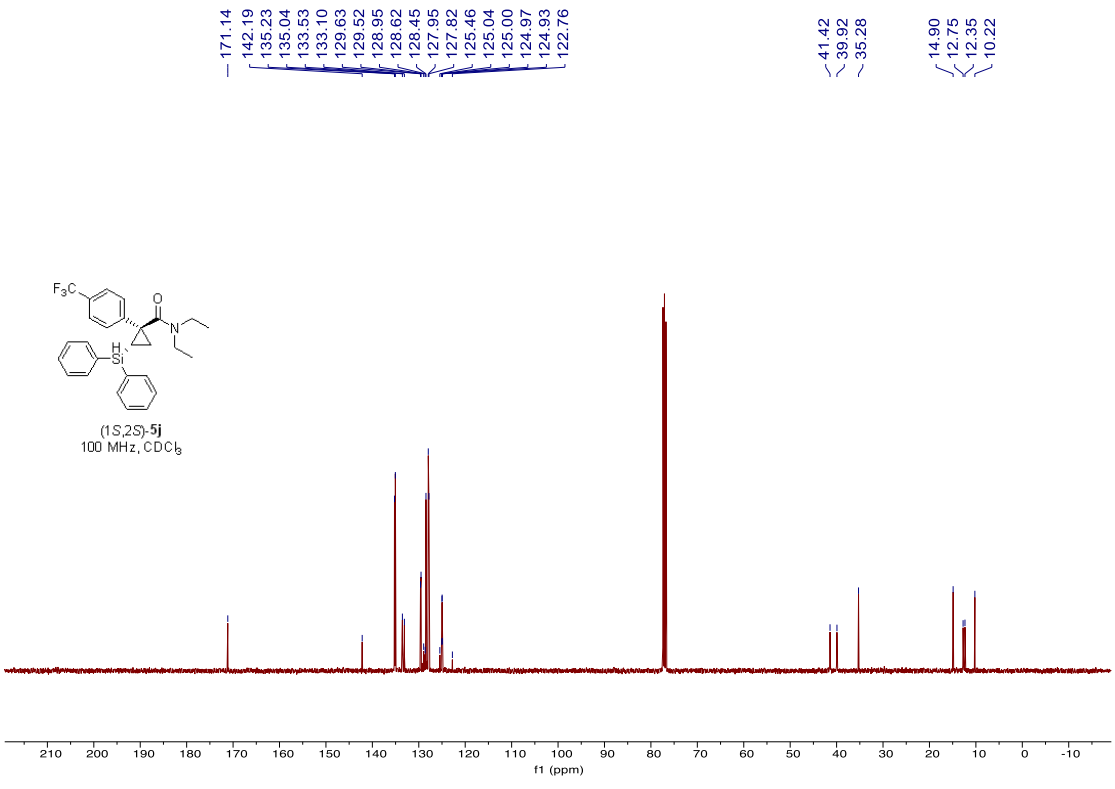
1.11
1.06
3.08
3.07
f1 (ppm)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129.52
128.95
128.62
128.45
127.95
127.82
125.46
125.04
125.00
124.97
124.93
122.76
41.42
39.92
35.28
14.90
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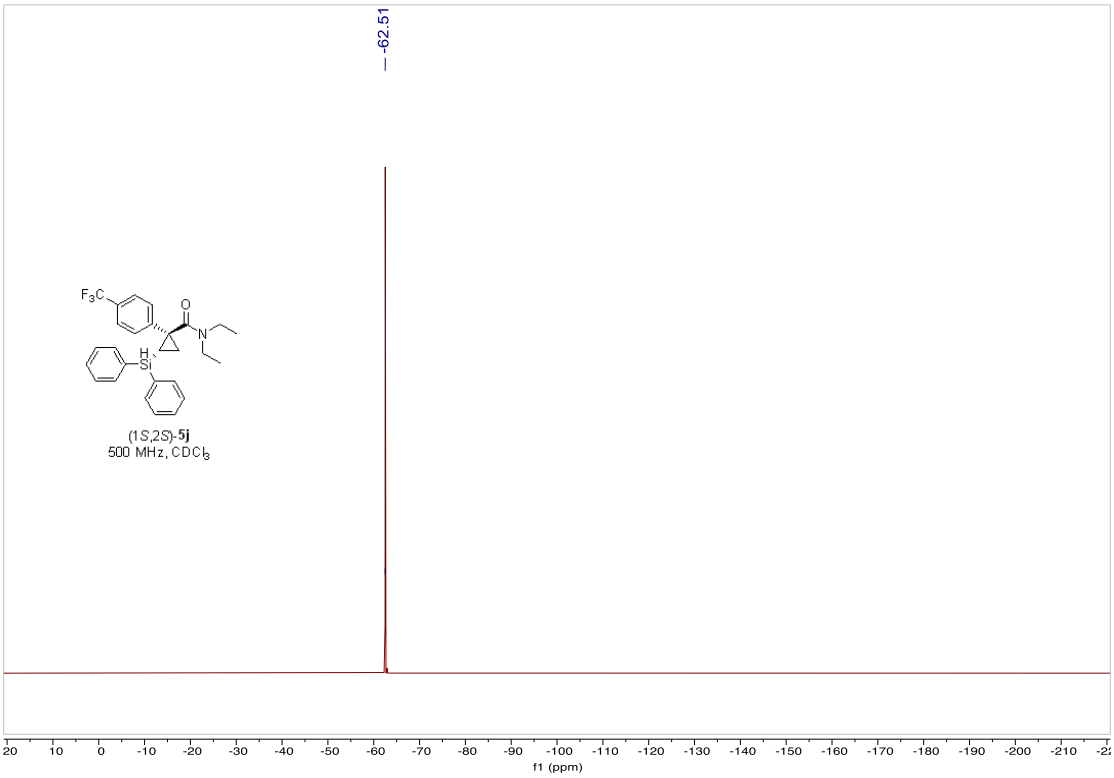
12.35
10.22
F3C
O
N
H
Si
(1S,2S)-5j
100 MHz, CDCl3
f1 (ppm)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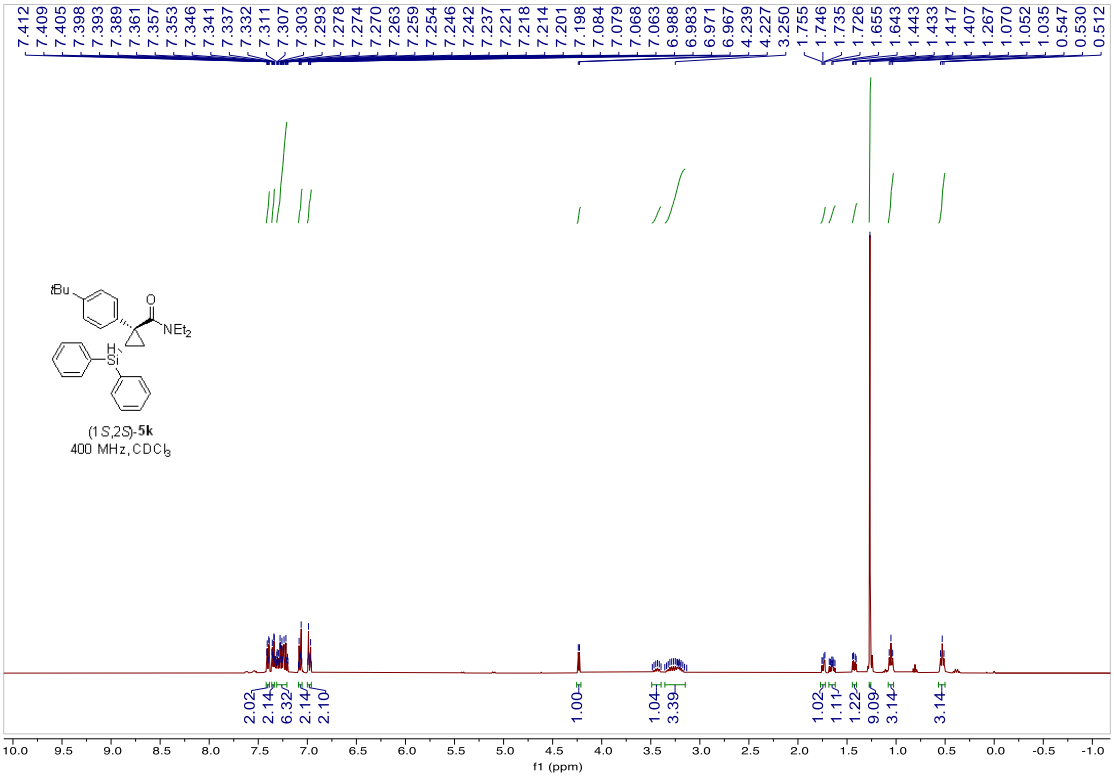
O
N
H
Si
(1S,2S)-5j
500 MHz, CDCl3
f1 (ppm)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7.242
7.237
7.221
7.218
7.214
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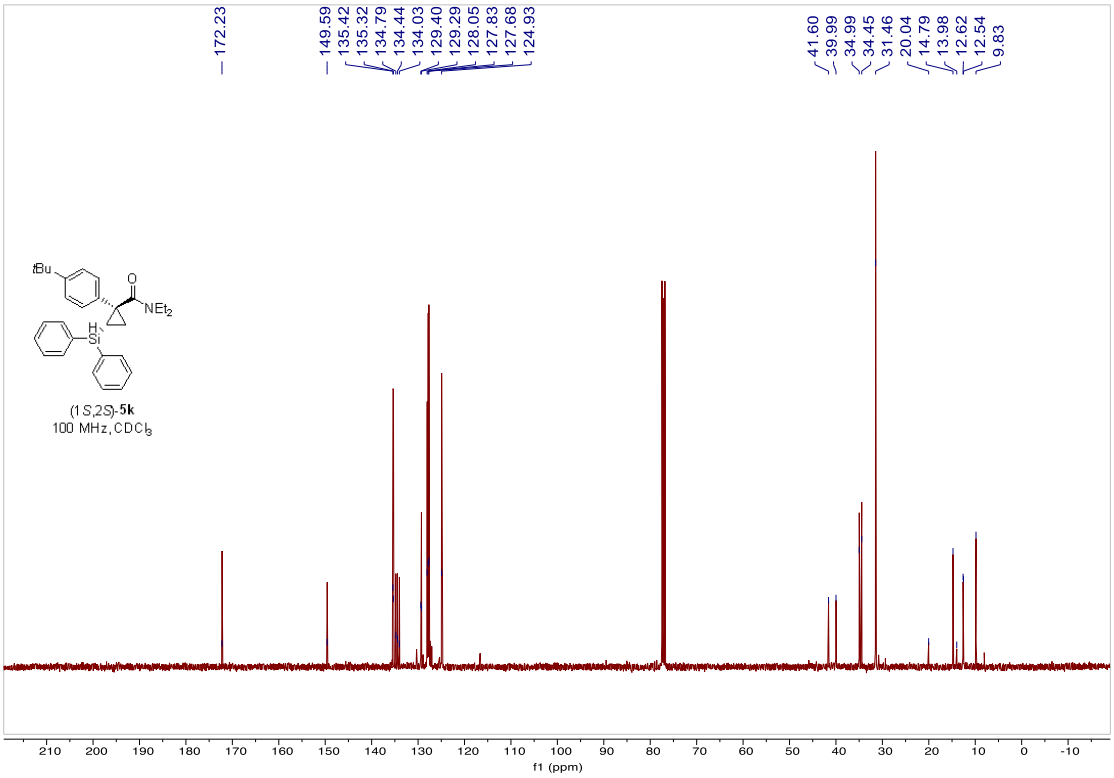
7.198
7.084
7.079
7.068
7.063
6.988
6.983
6.971
6.967
4.239
4.227
3.250
1.755
1.746
1.735
1.726
1.655
1.643
1.443
1.433
1.417
1.407
1.267
1.070
1.052
1.035
0.547
0.530
0.512
tBu
O
NEt2
H
Si
(1S,2S)-5k
400 MHz, CDCl3
2.02
2.14
6.32
2.14
2.10
1.00
1.04
3.39
1.02
1.11
1.22
9.09
3.14
3.14
f1 (ppm)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128.05
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127.68
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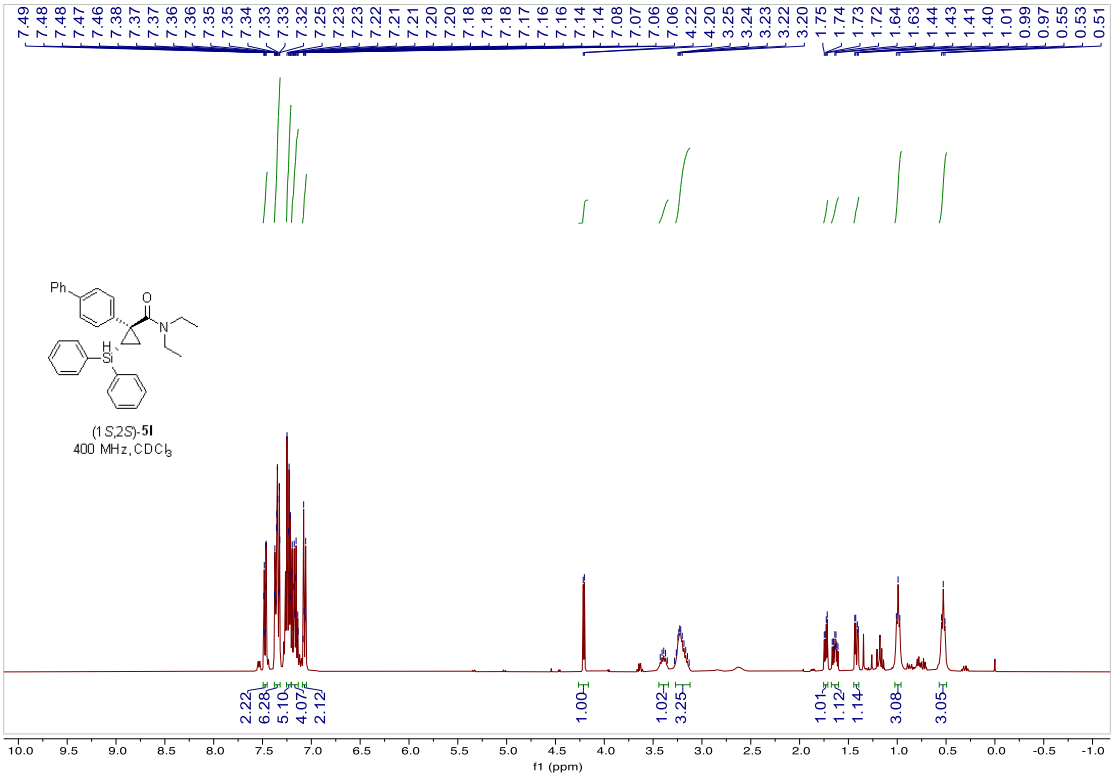
41.60
39.99
34.99
34.45
31.46
20.04
14.79
13.98
12.62
12.54
9.83
tBu
O
NEt2
H
Si
(1S,2S)-5k
100 MHz, CDCl3
f1 (ppm)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7.16
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7.14
7.08
7.07
7.06
7.06
4.22
4.20
3.25
3.24
3.23
3.22
3.20
1.75
1.74
1.73
1.72
1.64
1.63
1.44
1.43
1.41
1.40
1.01
0.99
0.97
0.55
0.53
0.51
Ph
O
N
H
Si
(1S,2S)-5l
400 MHz, CDCl3
2.22
6.28
5.10
4.07
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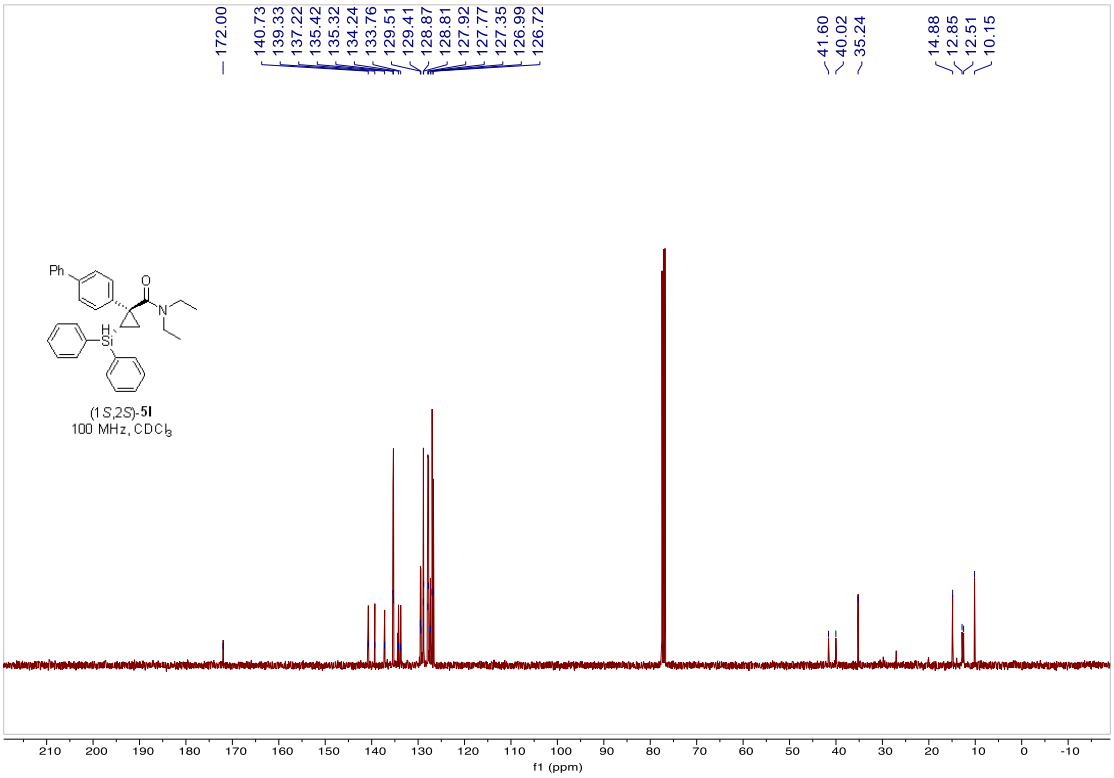
1.00
1.02
3.25
1.01
1.12
1.14
3.08
3.05
f1 (ppm)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127.77
127.35
126.99
126.72
41.60
40.02
35.24
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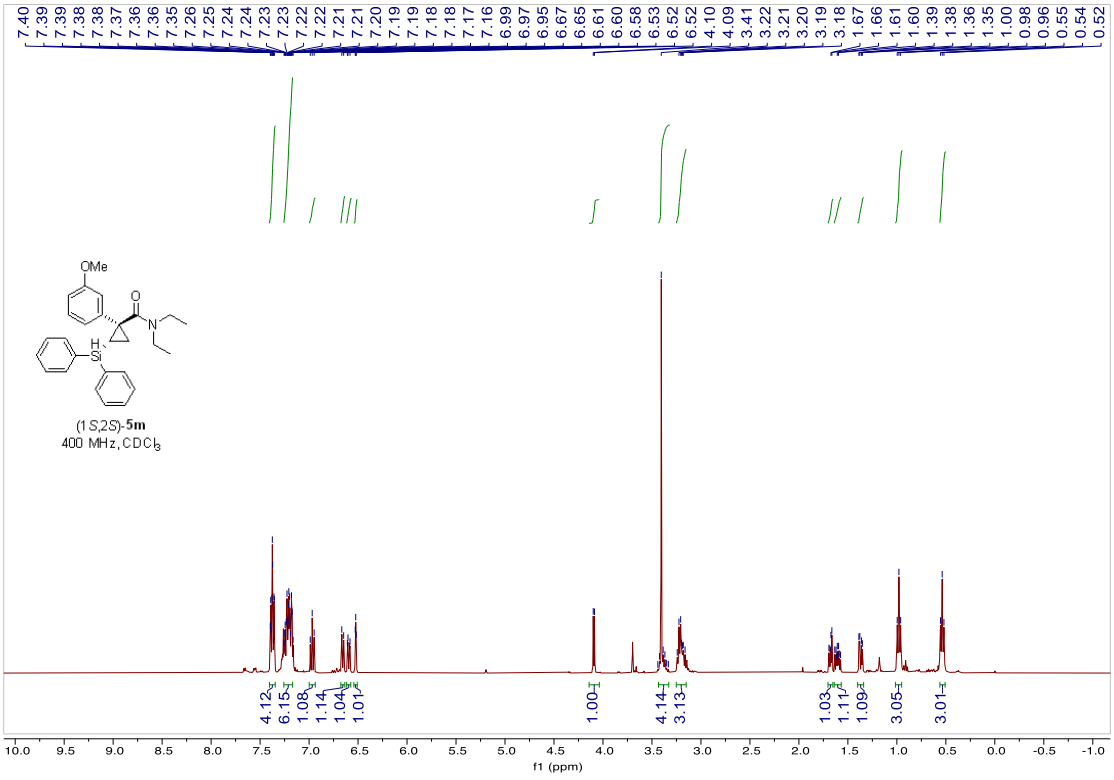
10.15
Ph
O
N
H
Si
(1S,2S)-5l
100 MHz, CDCl3
f1 (ppm)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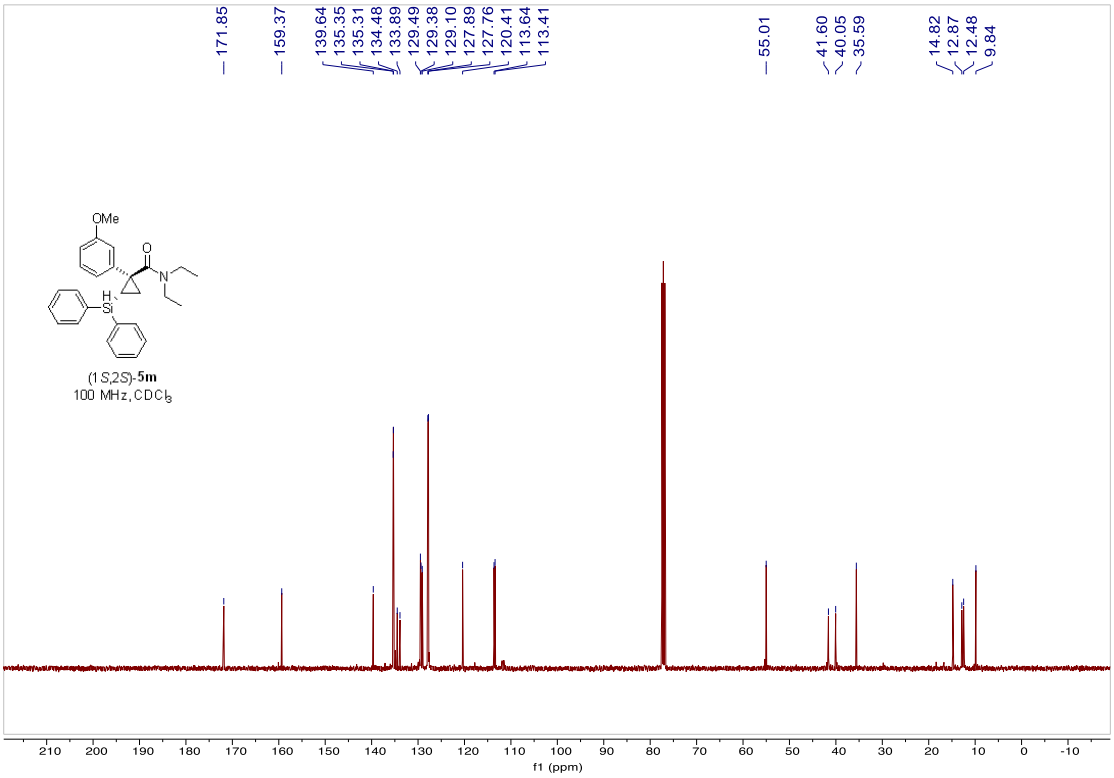
7.23
7.23
7.22
7.22
7.21
7.21
7.20
7.19
7.19
7.18
7.18
7.17
7.16
6.99
6.97
6.95
6.67
6.65
6.61
6.60
6.58
6.53
6.52
6.52
4.10
4.09
3.41
3.22
3.21
3.20
3.19
3.18
1.67
1.66
1.61
1.60
1.39
1.38
1.36
1.35
1.00
0.98
0.96
0.55
0.54
0.52
OMe
O
N
H
Si
(1S,2S)-5m
400 MHz, CDCl3
4.12
6.15
1.08
1.14
1.04
1.01
1.00
4.14
3.13
1.03
1.11
1.09
3.05
3.01
f1 (ppm)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129.49
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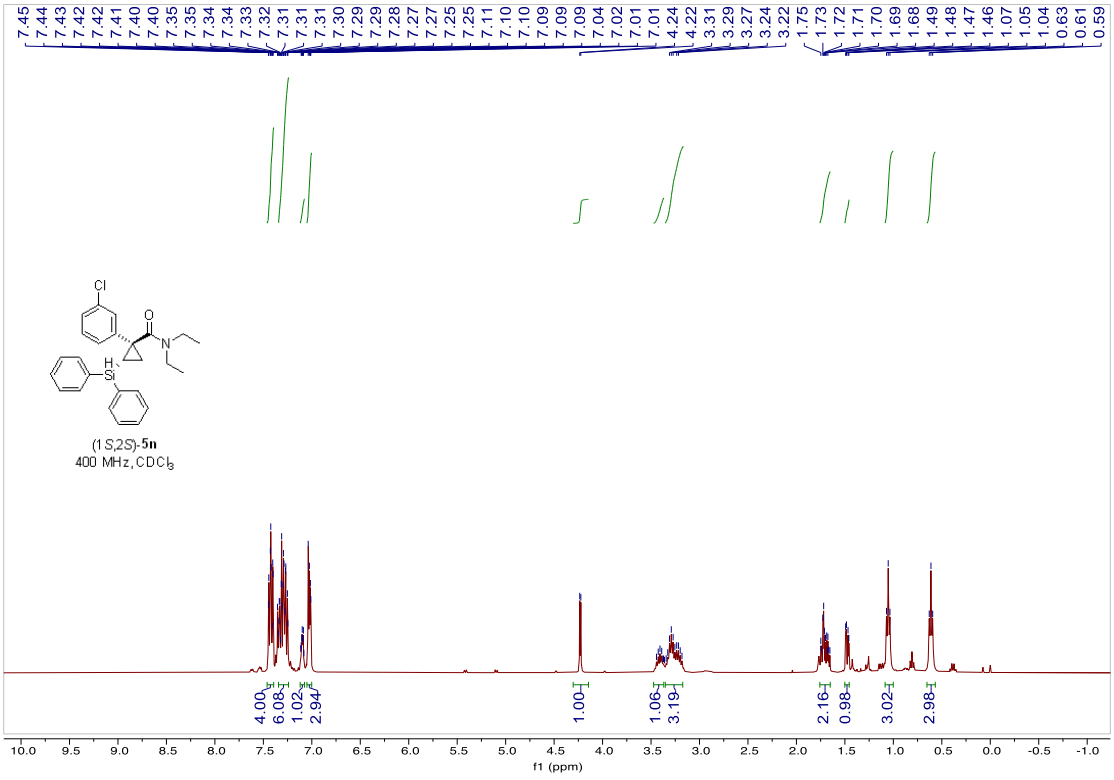
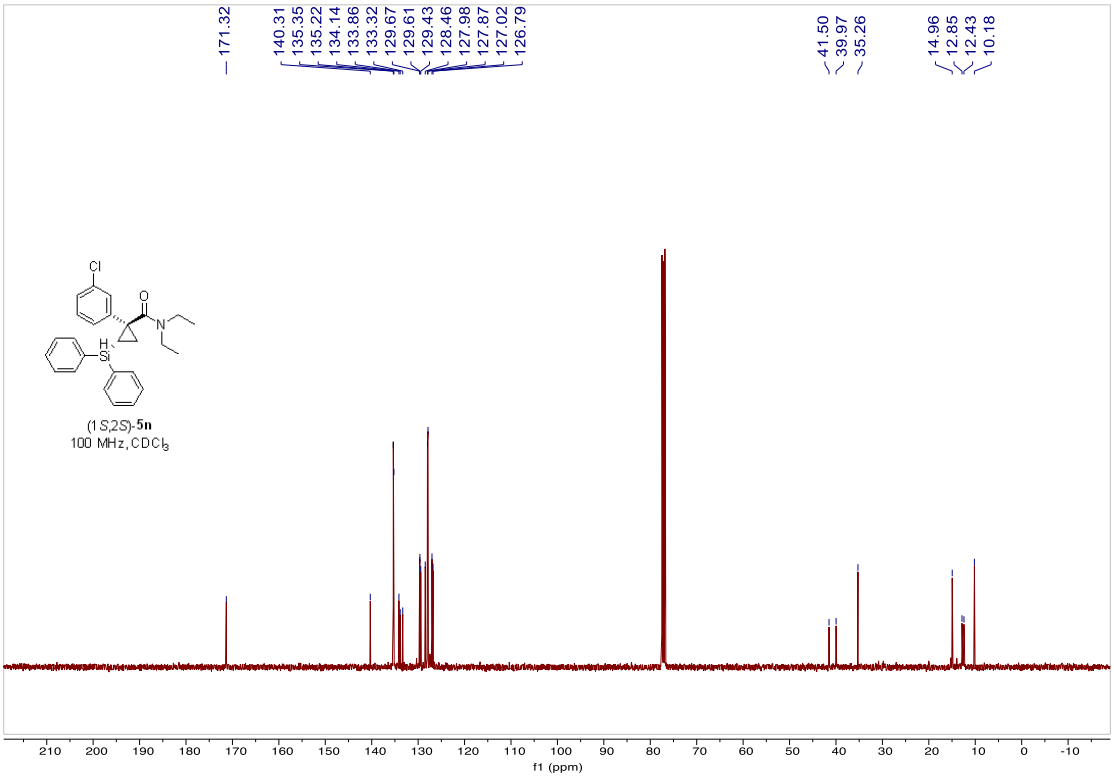
127.89
127.76
120.41
113.64
113.41
55.01
41.60
40.05
35.59
14.82
12.87
12.48
9.84
OMe
O
N
H
Si
(1S,2S)-5m
100 MHz, CDCl3
f1 (ppm)


Cl
O
N
H
Si
(1S,2S)-5n
400 MHz, CDCl3
4.00
6.08
1.02
2.94
1.00
1.06
3.19
2.16
0.98
3.02
2.98
f1 (ppm)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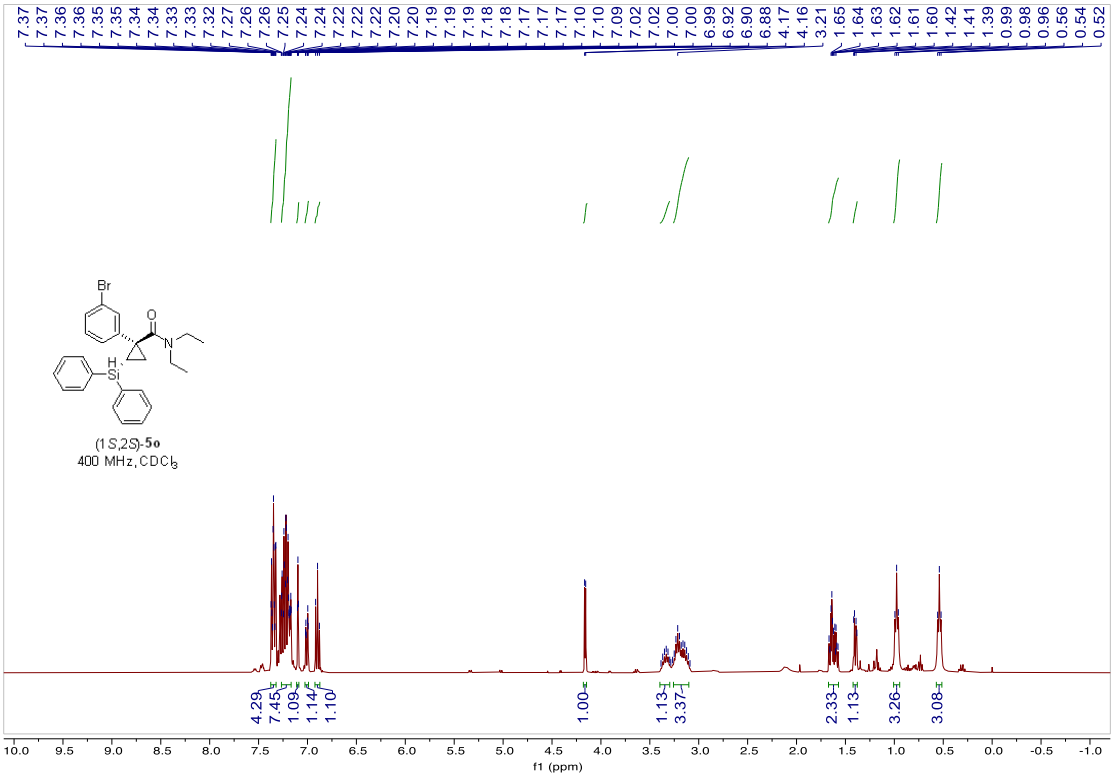
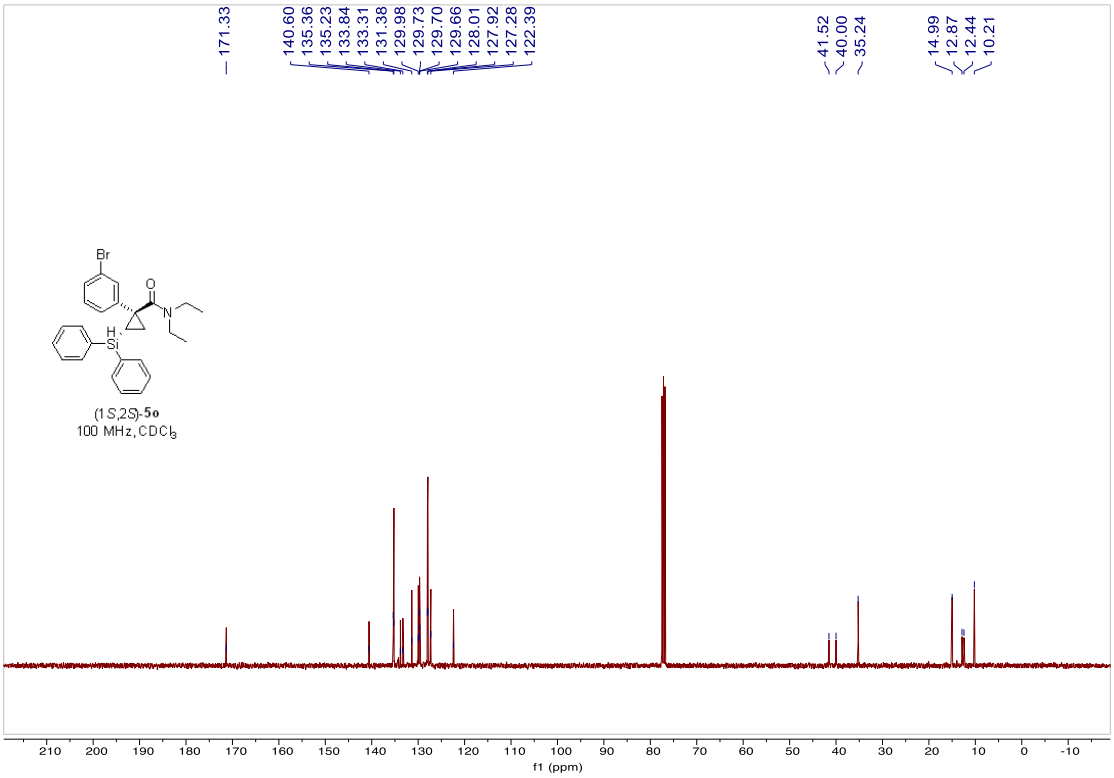
133.86
133.32
129.67
129.61
129.43
128.46
127.98
127.87
127.02
126.79
41.50
39.97
35.26
14.96
12.85
12.43
10.18
Cl
O
N
H
Si
(1S,2S)-5n
100 MHz, CDCl3
f1 (ppm)


Br
O
N
H
Si
(1S,2S)-5o
400 MHz, CDCl3
4.29
7.45
1.09
1.14
1.10
1.00
1.13
3.37
2.33
1.13
3.26
3.08
f1 (ppm)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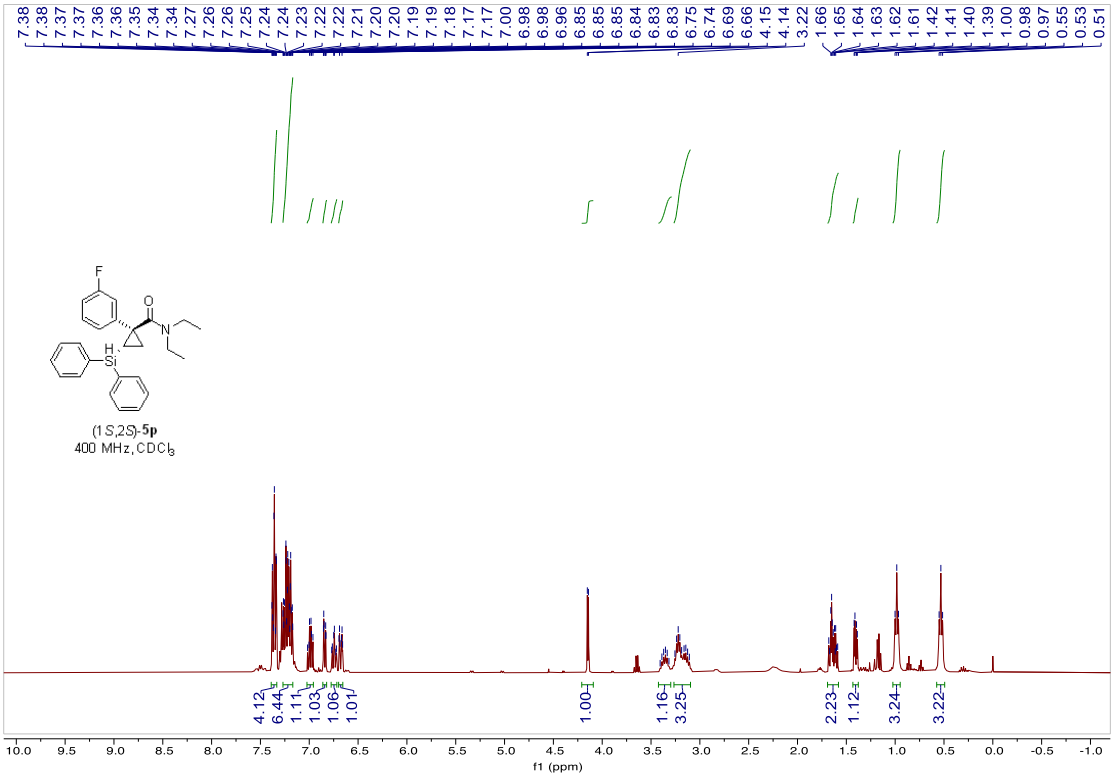
129.98
129.73
129.70
129.66
128.01
127.92
127.28
122.39
41.52
40.00
35.24
14.99
12.87
12.44
10.21
Br
O
N
H
Si
(1S,2S)-5o
100 MHz, CDCl3
f1 (ppm)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7.34
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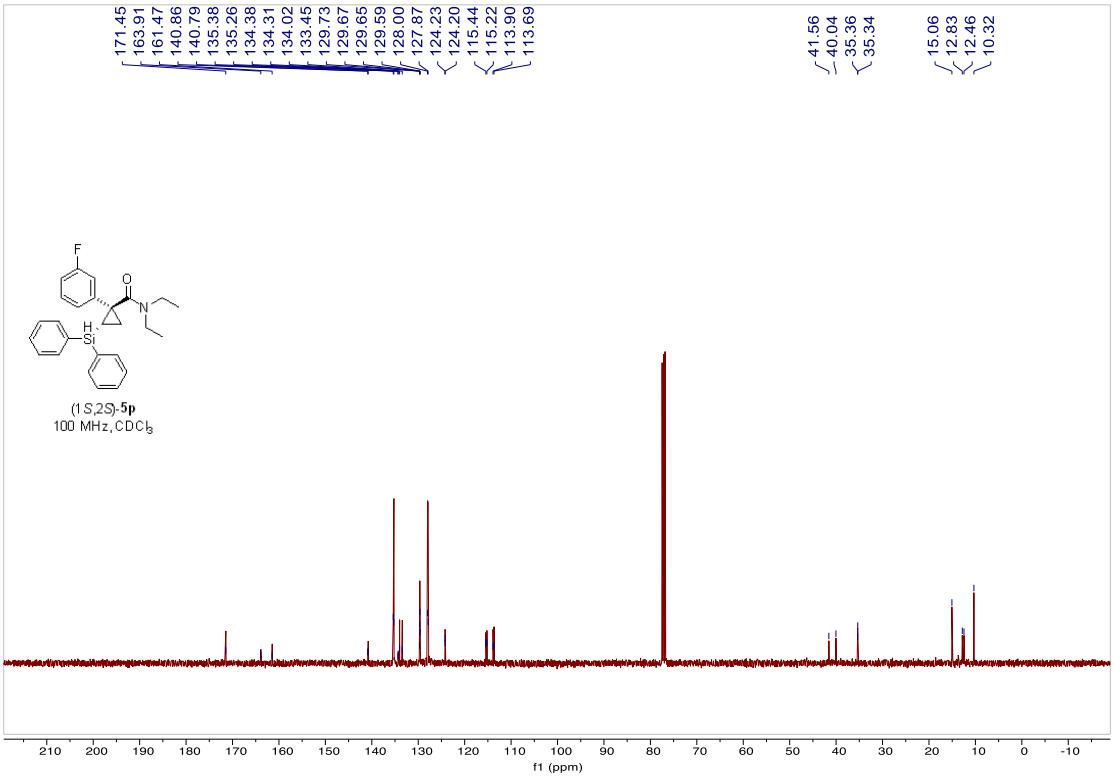
7.25
7.24
7.24
7.23
7.22
7.22
7.21
7.20
7.20
7.19
7.19
7.18
7.17
7.17
7.00
6.98
6.98
6.96
6.85
6.85
6.84
6.83
6.83
6.75
6.74
6.69
6.66
4.15
4.14
3.22
1.66
1.65
1.64
1.63
1.62
1.61
1.42
1.41
1.40
1.39
1.00
0.98
0.97
0.55
0.53
0.51
F
O
N
H
Si
(1S,2S)-5p
400 MHz, CDCl3
4.12
6.44
1.11
1.03
1.06
1.01
1.00
1.16
3.25
2.23
1.12
3.24
3.22
f1 (ppm)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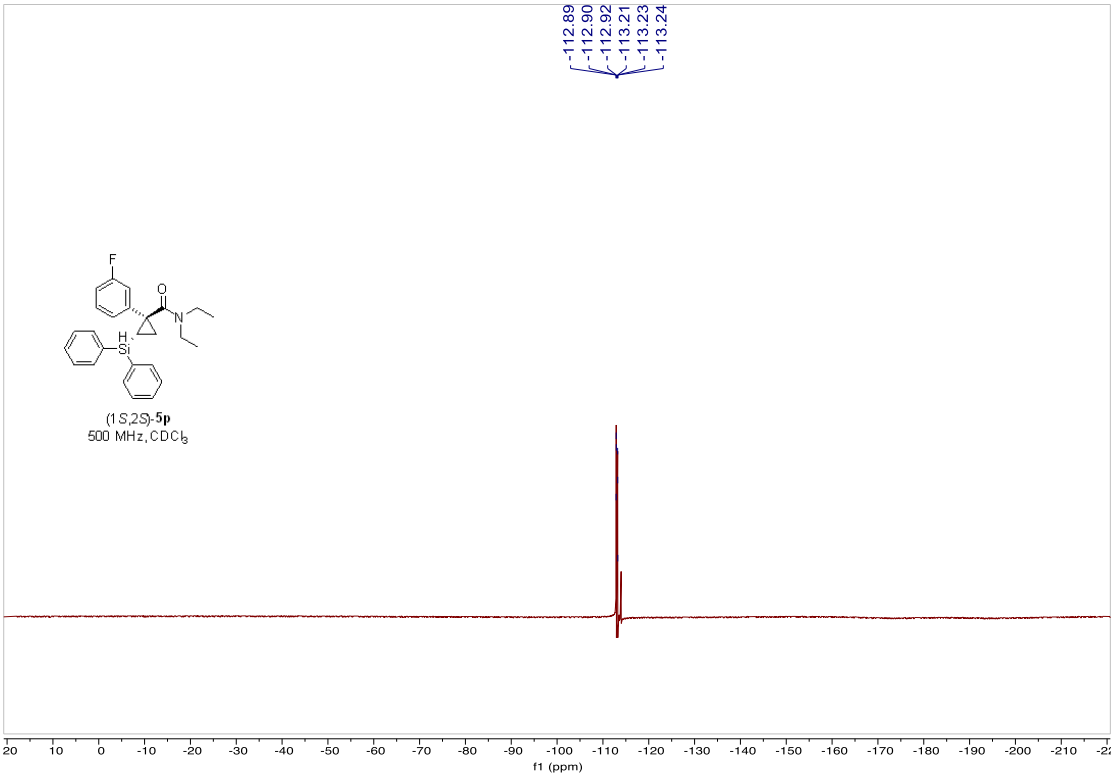
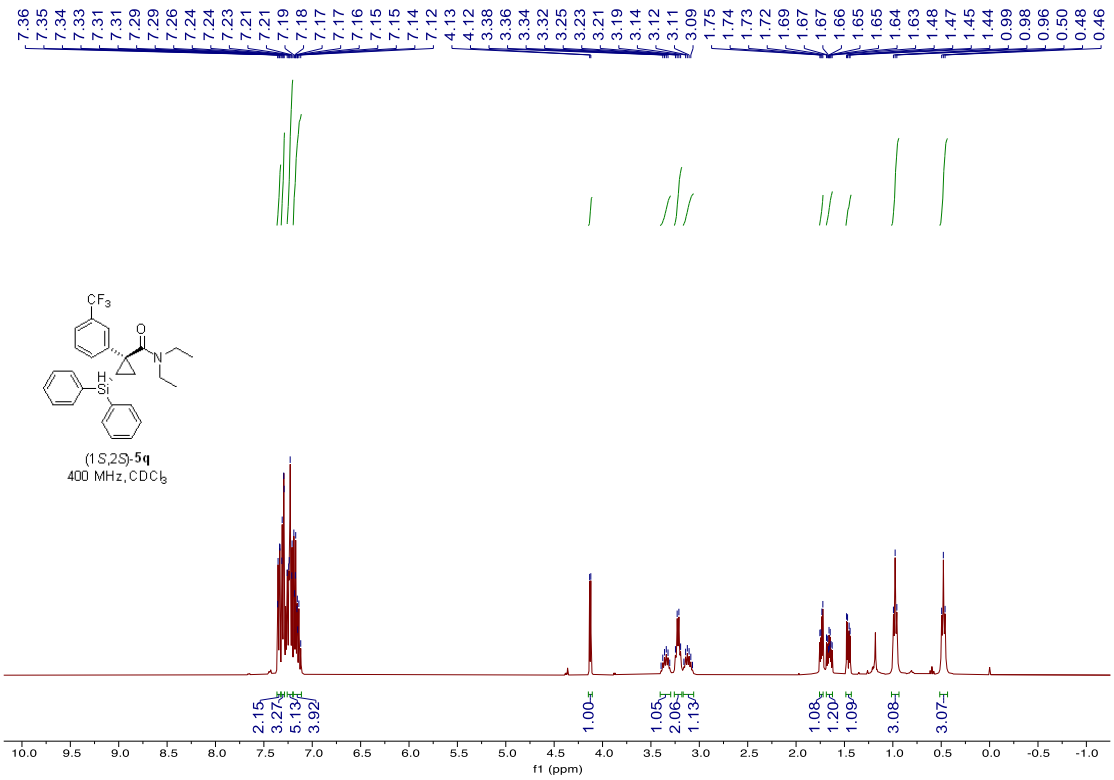
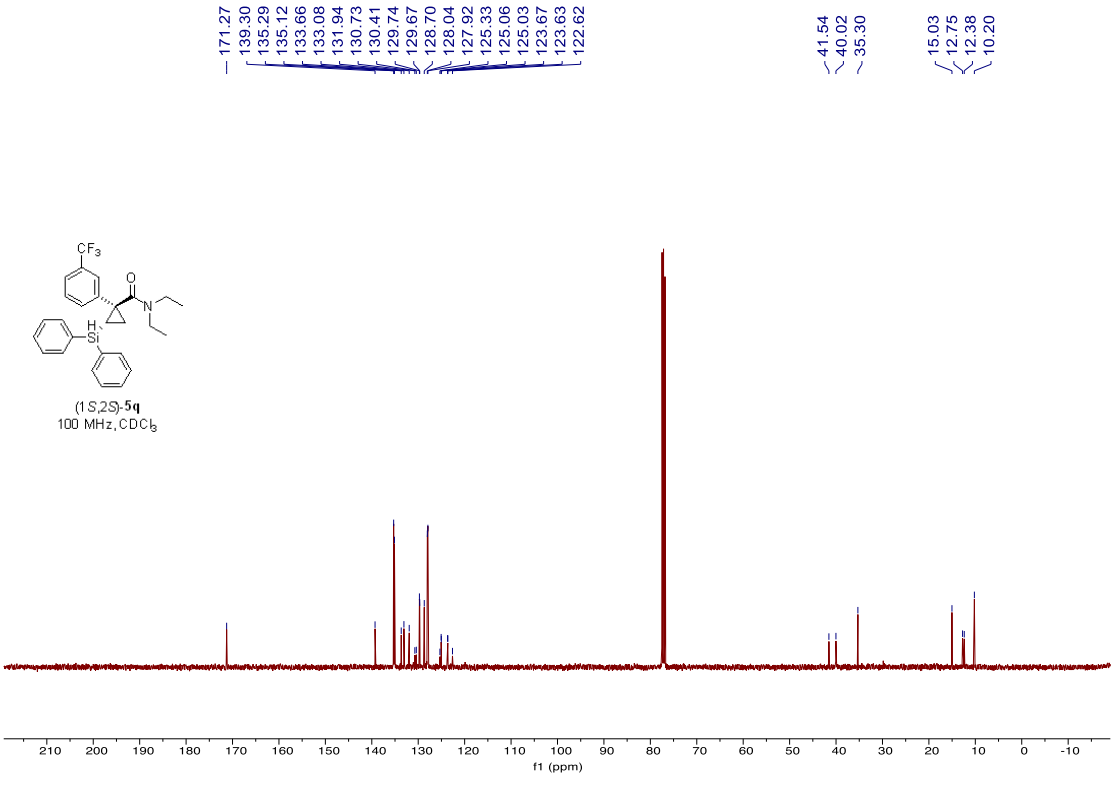
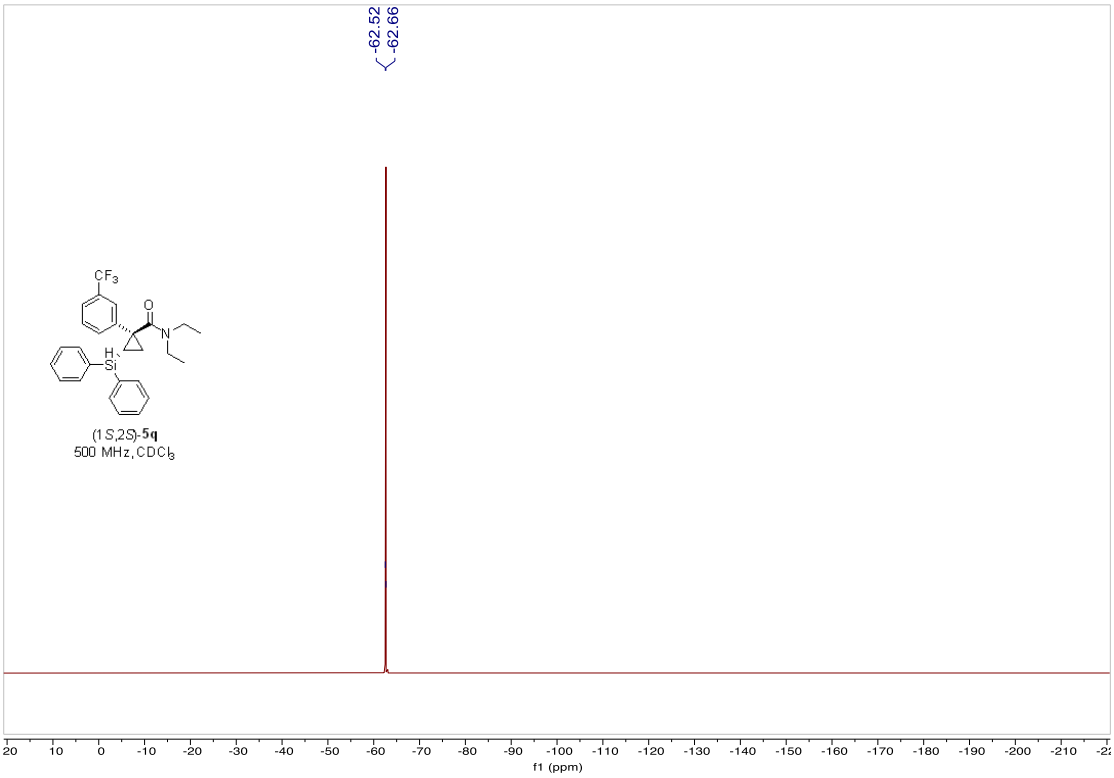
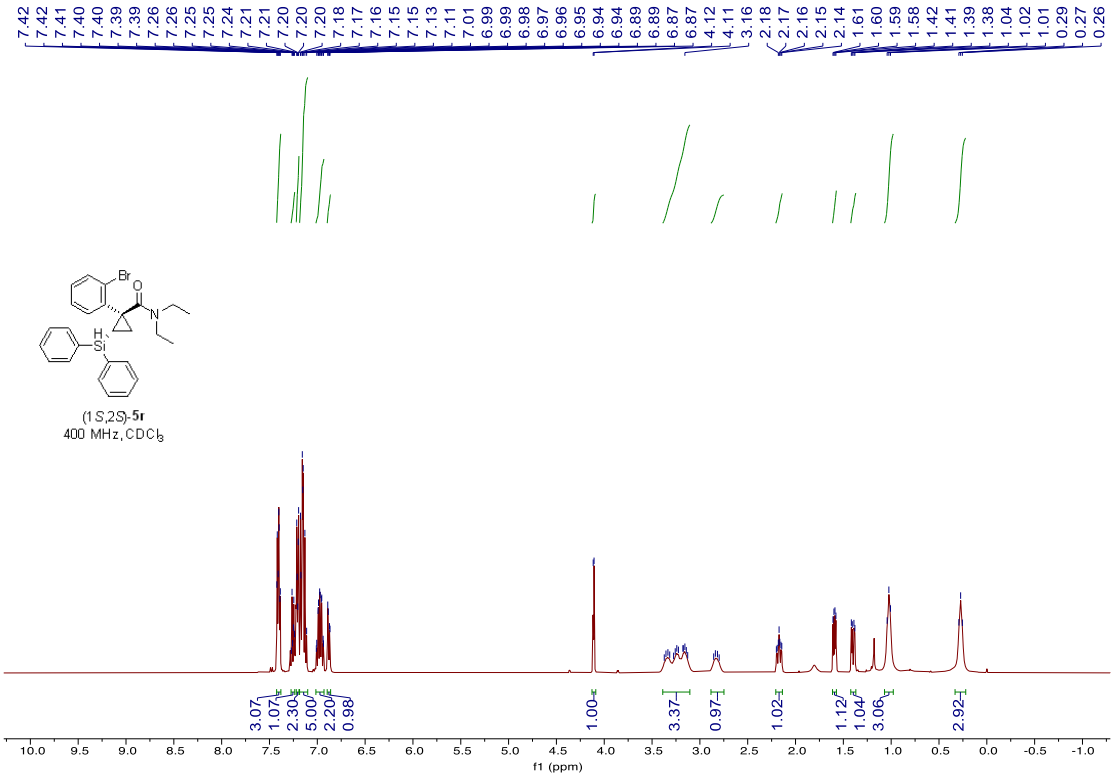
135.38
135.26
134.38
134.31
134.02
133.45
129.73
129.67
129.65
129.59
128.00
127.87
124.23
124.20
115.44
115.22
113.90
113.69
41.56
40.04
35.36
35.34
15.06
12.83
12.46
10.32
F
O
N
H
Si
(1S,2S)-5p
100 MHz, CDCl3
f1 (ppm)

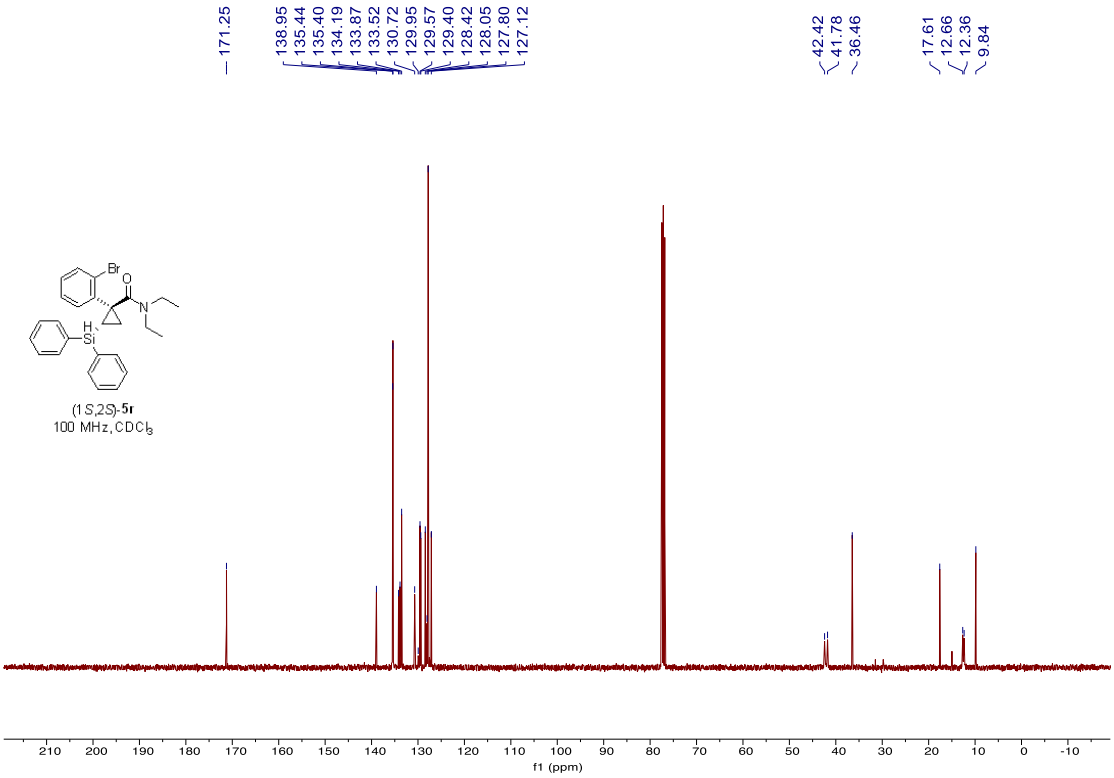

-112.89
-112.90
-112.92
-113.21
-113.23
-113.24
F
O
N
H
Si
(1S,2S)-5p
500 MHz, CDCl3
f1 (ppm)


7.36 7.35 7.34 7.33 7.31 7.31 7.29 7.29 7.26 7.24 7.24 7.23 7.21 7.21 7.19 7.18 7.17 7.17 7.16 7.15 7.15 7.14 7.12
4.13 4.12 3.38 3.36 3.34 3.32 3.25 3.23 3.21 3.19 3.14 3.12 3.11 3.09
1.75 1.74 1.73 1.72 1.69 1.67 1.67 1.66 1.65 1.65 1.64 1.63 1.48 1.47 1.45 1.44 0.99 0.98 0.96 0.50 0.48 0.46
CF3
O
N
H
Si
(1S,2S)-5q
400 MHz, CDCl3
2.15 3.27 5.13 3.92 1.00 1.05 2.06 1.13 1.08 1.20 1.09 3.08 3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


171.27 139.30 135.29 135.12 133.66 133.08 131.94 130.73 130.41 129.74 129.67 128.70 128.04 127.92 125.33 125.06 125.03 123.67 123.63 122.62
41.54 40.02 35.30
15.03 12.75 12.38 10.20
CF3
O
N
H
Si
(1S,2S)-5q
100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-62.52
-62.66
CF3
O
N
H
Si
(1S,2S)-5q
500 MHz, CDCl3
f1 (ppm)


7.42 7.42 7.41 7.40 7.40 7.39 7.39 7.26 7.26 7.25 7.25 7.24 7.21 7.21 7.20 7.20 7.20 7.18 7.17 7.16 7.15 7.15 7.13 7.11 7.01 6.99 6.99 6.98 6.97 6.96 6.95 6.94 6.94 6.89 6.89 6.87 6.87 4.12 4.11 3.16 2.18 2.17 2.16 2.15 2.14 1.61 1.60 1.59 1.58 1.42 1.41 1.39 1.38 1.04 1.02 1.01 0.29 0.27 0.26
Br
O
N
H
Si
(1S,2S)-5r
400 MHz, CDCl3
3.07 1.07 2.30 5.00 2.20 0.98 1.00 3.37 0.97 1.02 1.12 1.04 3.06 2.92
f1 (ppm)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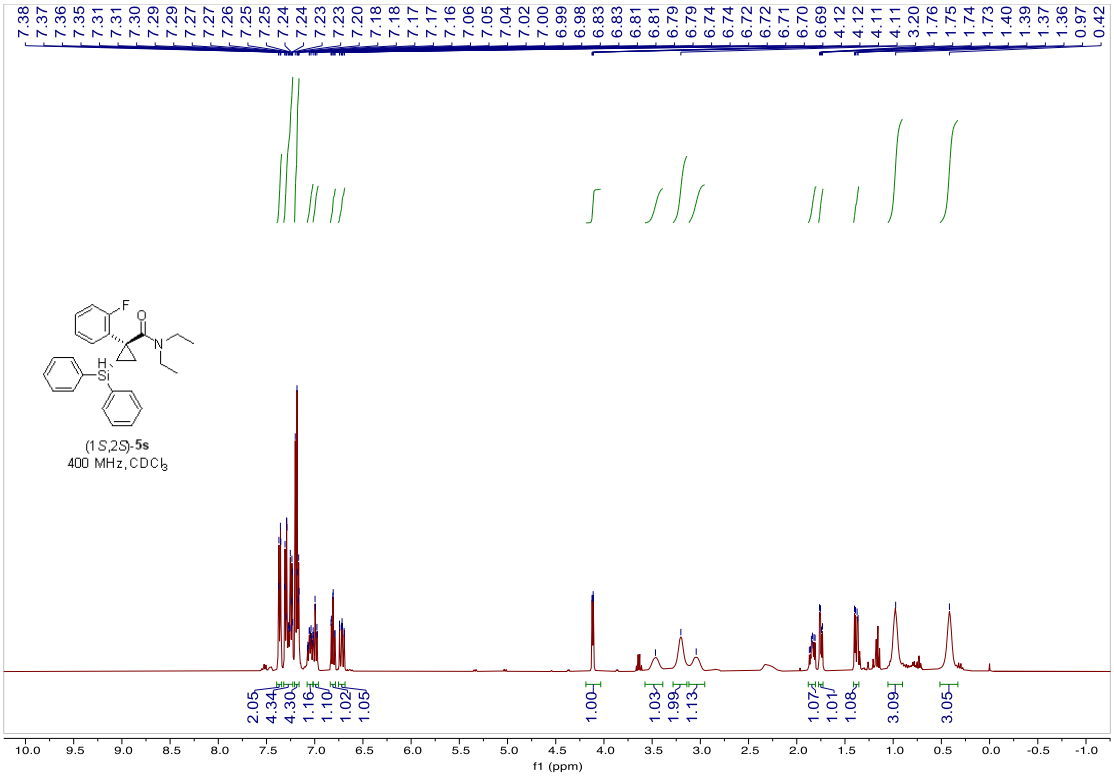
128.42
128.05
127.80
127.12
42.42
41.78
36.46
17.61
12.66
12.36
9.84
Br
O
N
H
Si
(1S,2S)-5r
100 MHz, CDCl3
f1 (ppm)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7.25
7.25
7.24
7.24
7.23
7.23
7.20
7.18
7.18
7.17
7.17
7.16
7.06
7.05
7.04
7.02
7.00
6.99
6.98
6.83
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6.81
6.81
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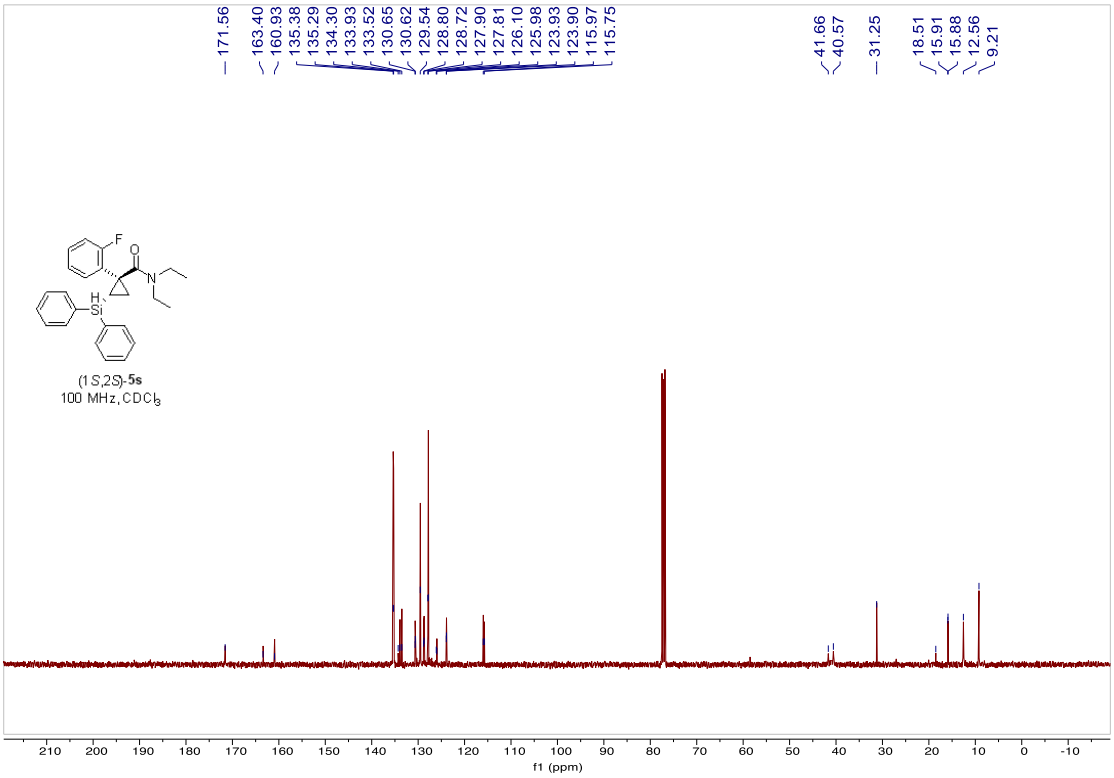
4.12
4.11
4.11
3.20
1.76
1.75
1.74
1.73
1.40
1.39
1.37
1.36
0.97
0.42
F
O
N
H
Si
(1S,2S)-5s
400 MHz, CDCl3
2.05
4.34
4.30
1.16
1.10
1.02
1.05
1.00
1.03
1.99
1.13
1.07
1.01
1.08
3.09
3.05
f1 (ppm)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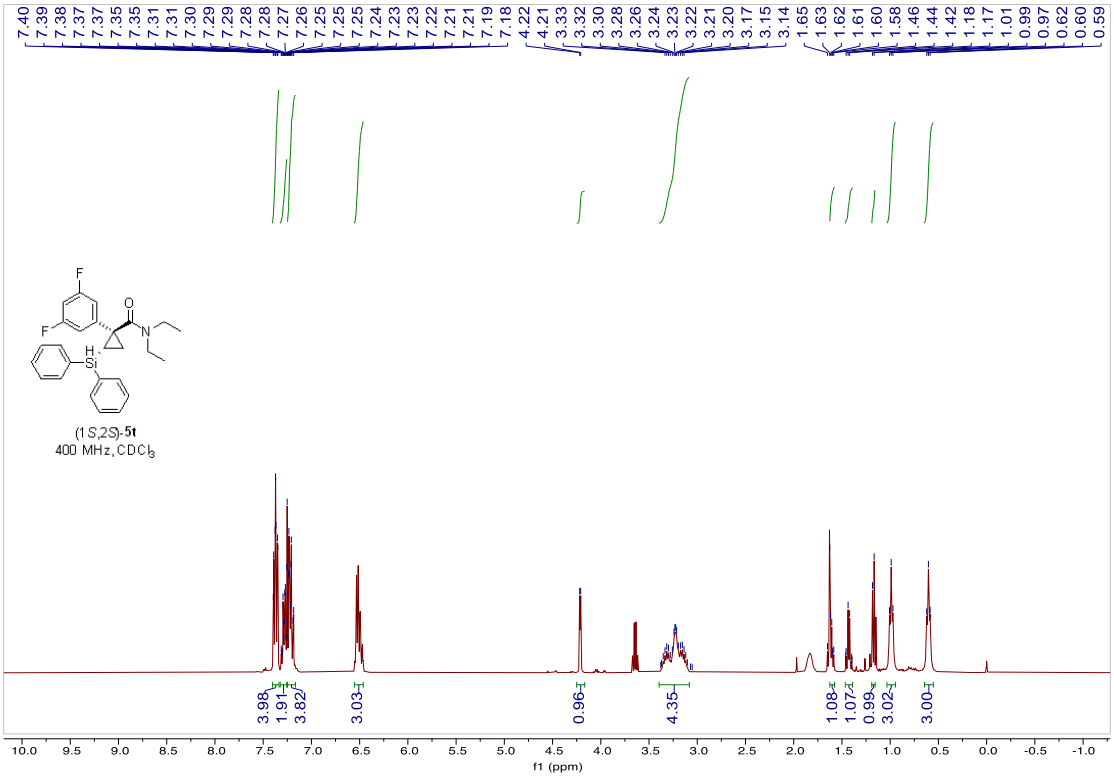
129.54
128.80
128.72
127.90
127.81
126.10
125.98
123.93
123.90
115.97
115.75
41.66
40.57
31.25
18.51
15.91
15.88
12.56
9.21
(1S,2S)-5s
100 MHz, CDCl3
f1 (ppm)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7.31
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7.30
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7.26
7.25
7.25
7.25
7.24
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7.19
7.18
4.22
4.21
3.33
3.32
3.30
3.28
3.26
3.24
3.23
3.22
3.21
3.20
3.17
3.15
3.14
1.65
1.63
1.62
1.61
1.60
1.58
1.46
1.44
1.42
1.18
1.17
1.01
0.99
0.97
0.62
0.60
0.59
3.98
1.91
3.82
3.03
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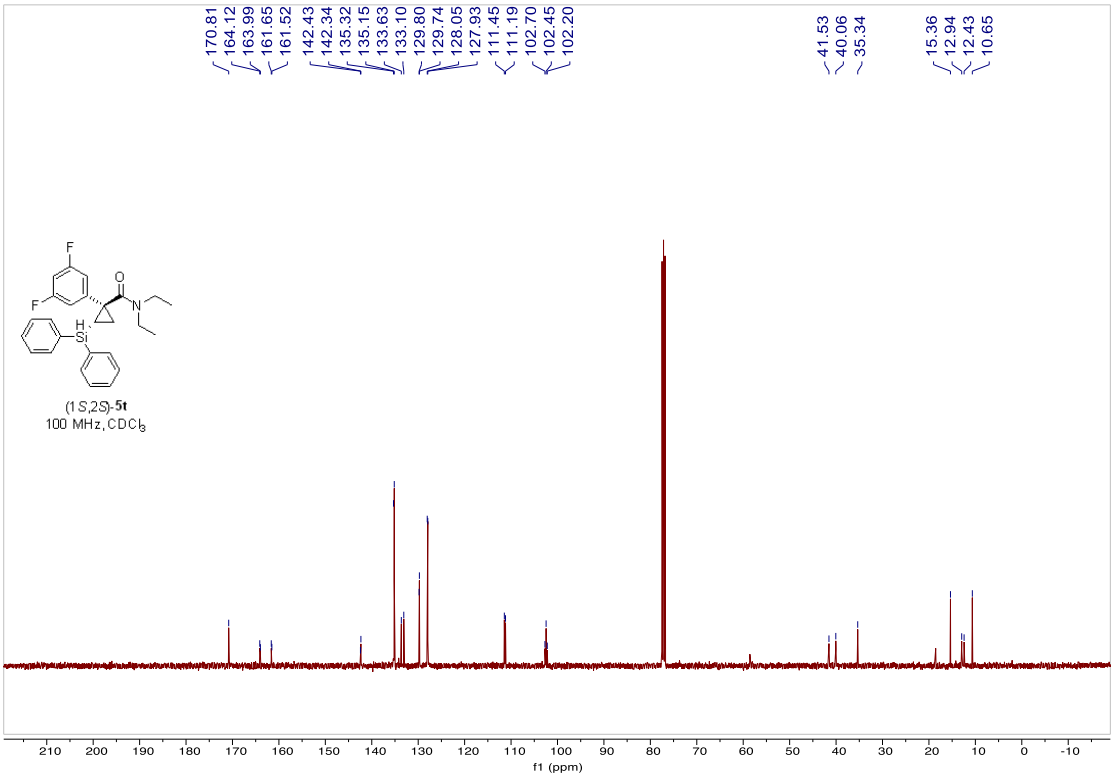
4.35
1.08
1.07
0.99
3.02
3.00
(1S,2S)-5t
400 MHz, CDCl3
f1 (ppm)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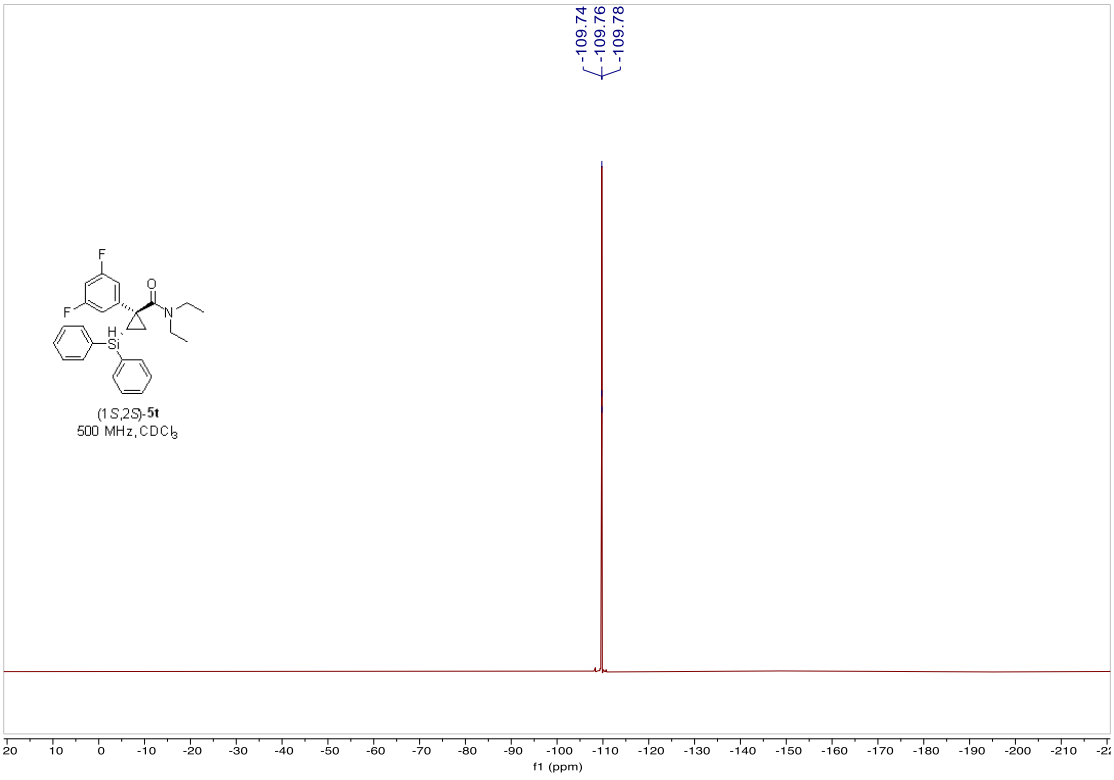
135.15
133.63
133.10
129.80
129.74
128.05
127.93
111.45
111.19
102.70
102.45
102.20
41.53
40.06
35.34
15.36
12.94
12.43
10.65
F
F
O
N
H
Si
(1S,2S)-5t
100 MHz, CDCl3
f1 (ppm)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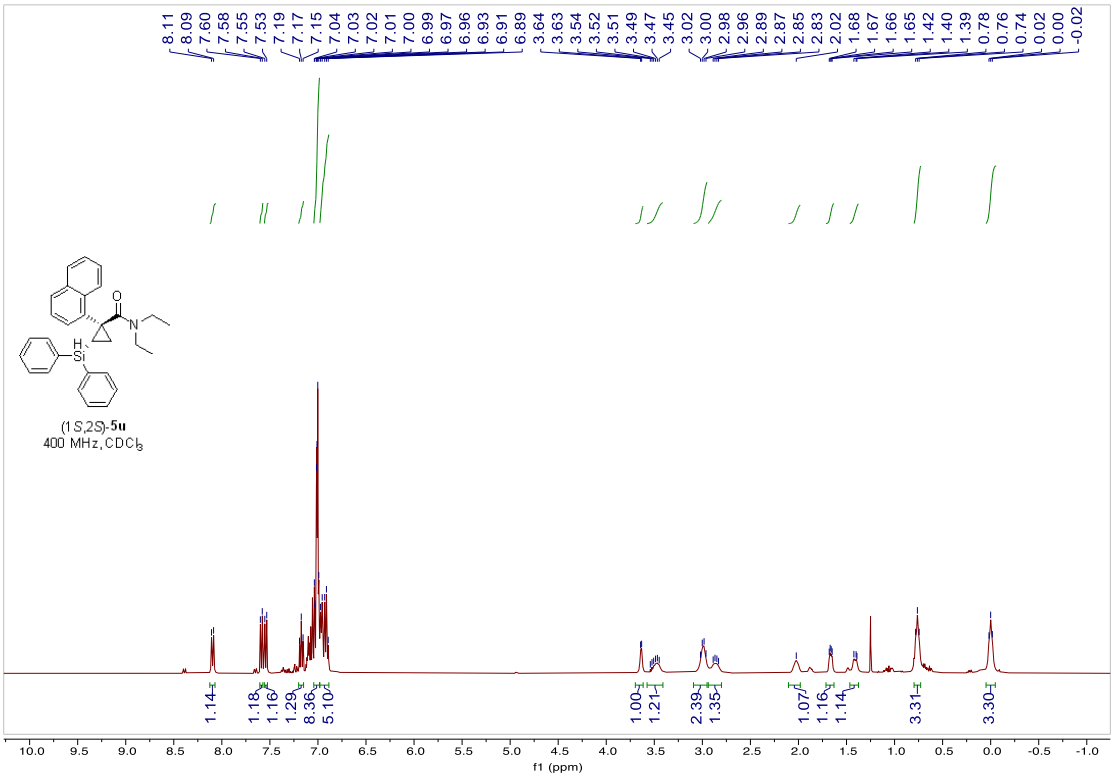
-109.76
-109.78
F
F
O
N
H
Si
(1S,2S)-5t
500 MHz, CDCl3
f1 (ppm)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7.58
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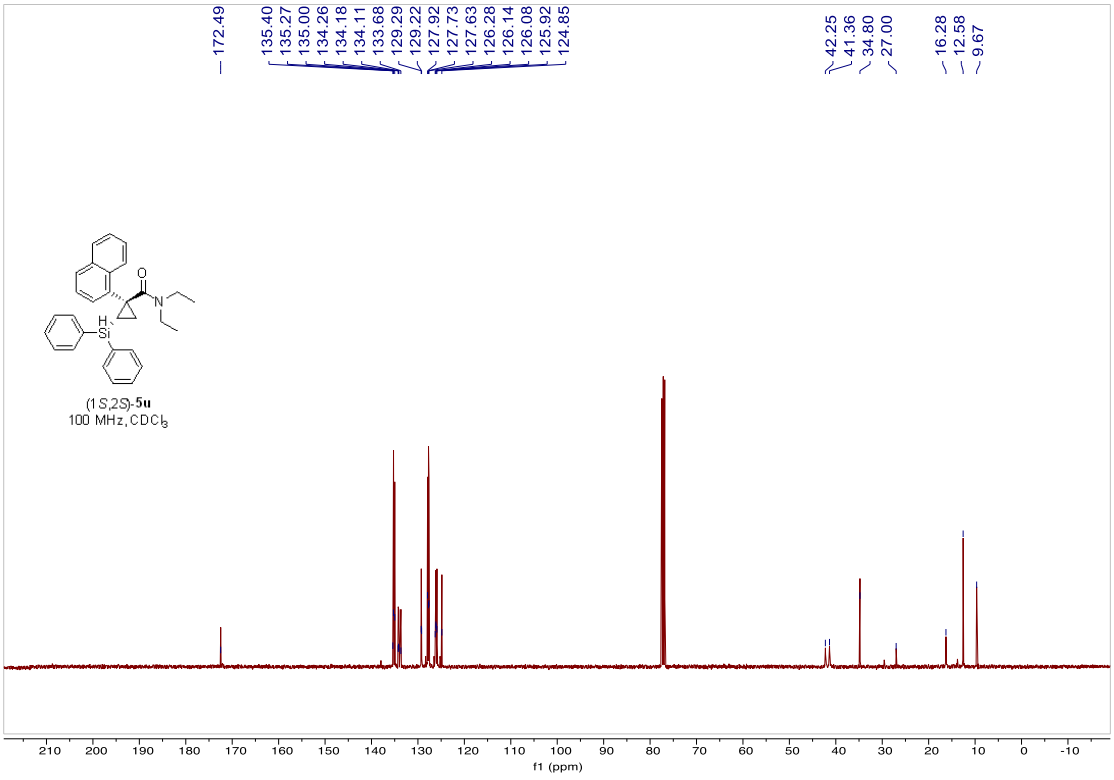
7.53
7.19
7.17
7.15
7.04
7.03
7.02
7.01
7.00
6.99
6.97
6.96
6.93
6.91
6.89
3.64
3.63
3.54
3.52
3.51
3.49
3.47
3.45
3.02
3.00
2.98
2.96
2.89
2.87
2.85
2.83
2.02
1.68
1.67
1.66
1.65
1.42
1.40
1.39
0.78
0.76
0.74
0.02
0.00
-0.02
(1S,2S)-5u
400 MHz, CDCl3
1.14
1.18
1.16
1.29
8.36
5.10
1.00
1.21
2.39
1.35
1.07
1.16
1.14
3.31
3.30
f1 (ppm)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134.11
133.68
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129.22
127.92
127.73
127.63
126.28
126.14
126.08
125.92
124.85
42.25
41.36
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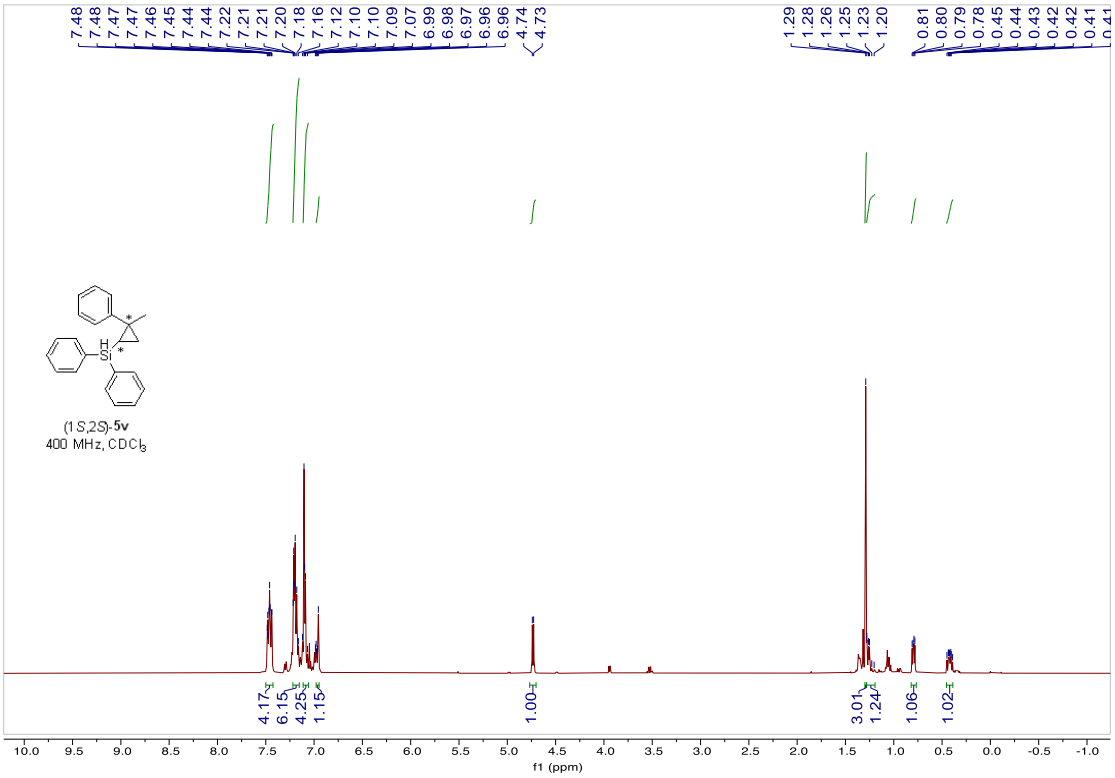
27.00
16.28
12.58
9.67
(1S,2S)-5u
100 MHz, CDCl3
f1 (ppm)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7.44
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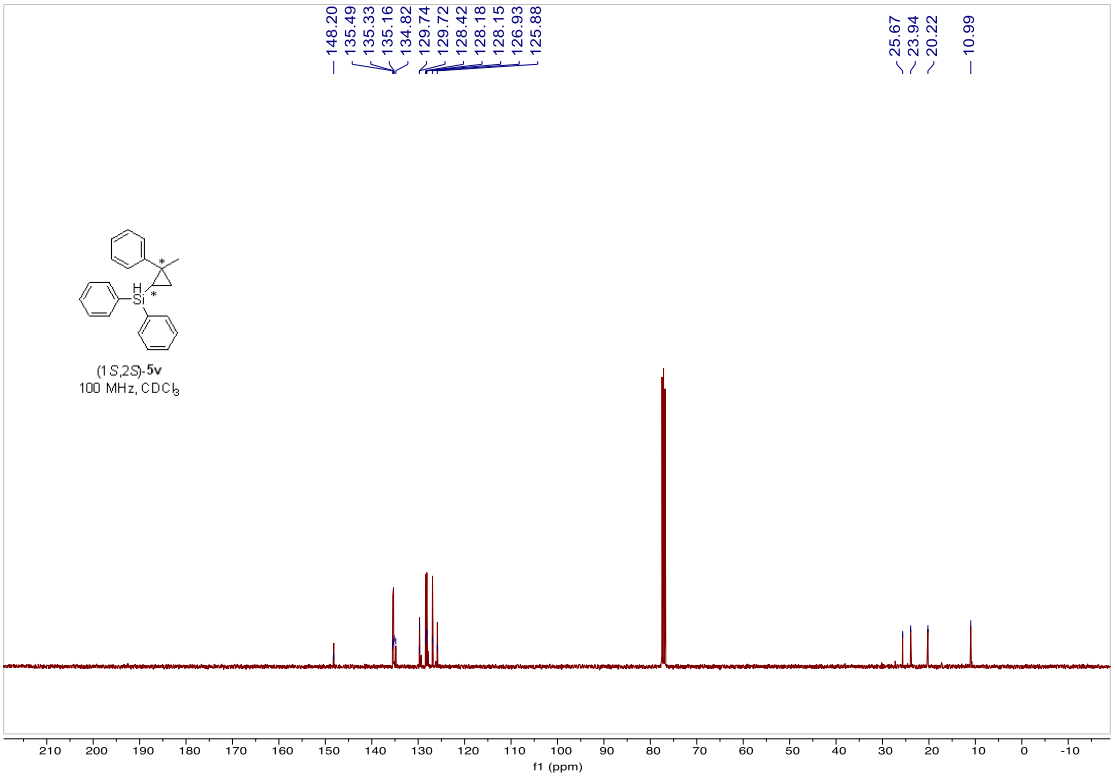
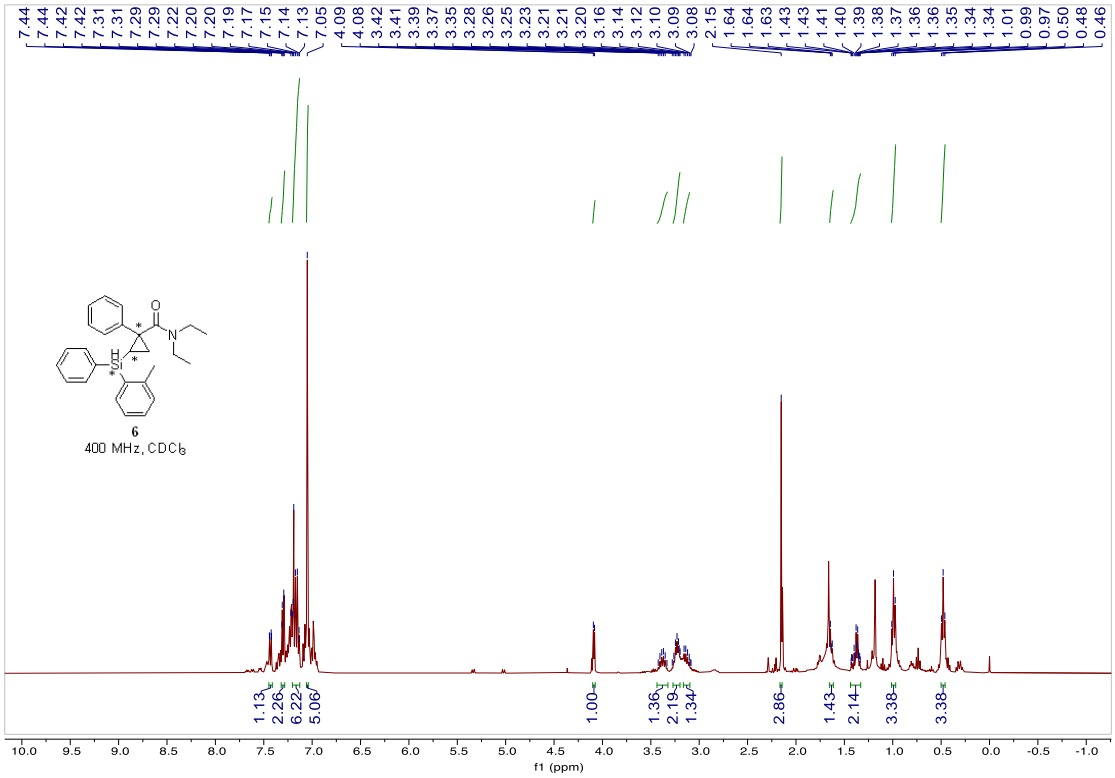
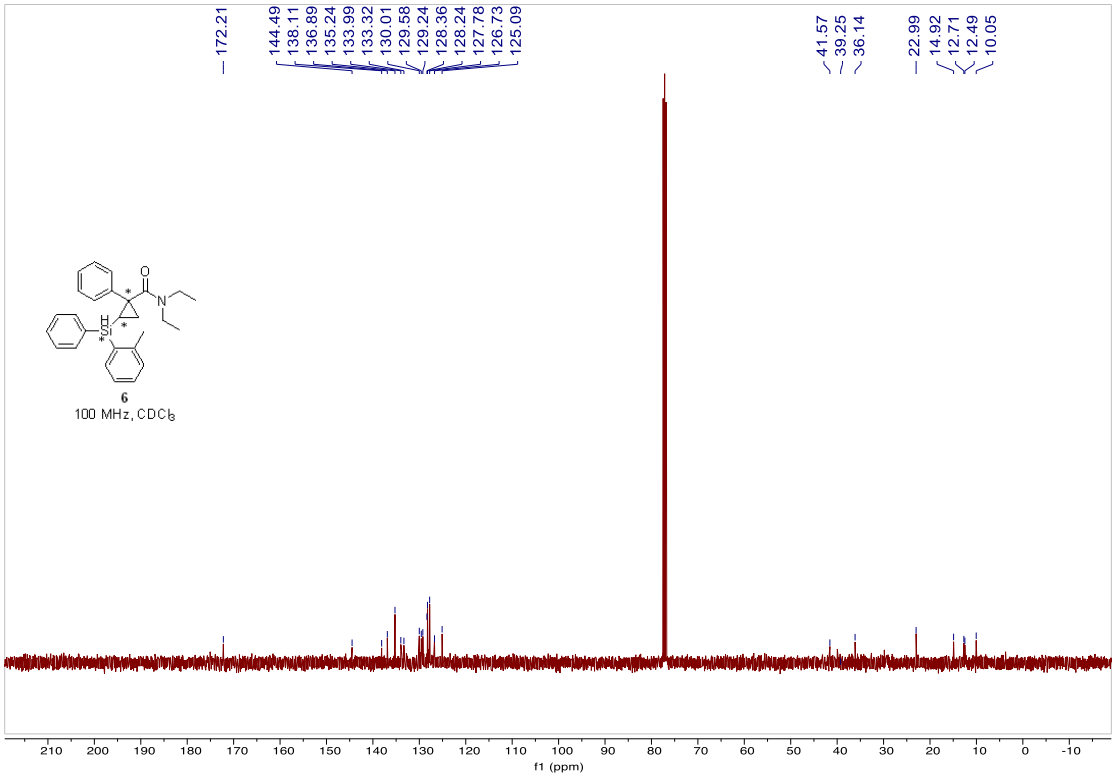
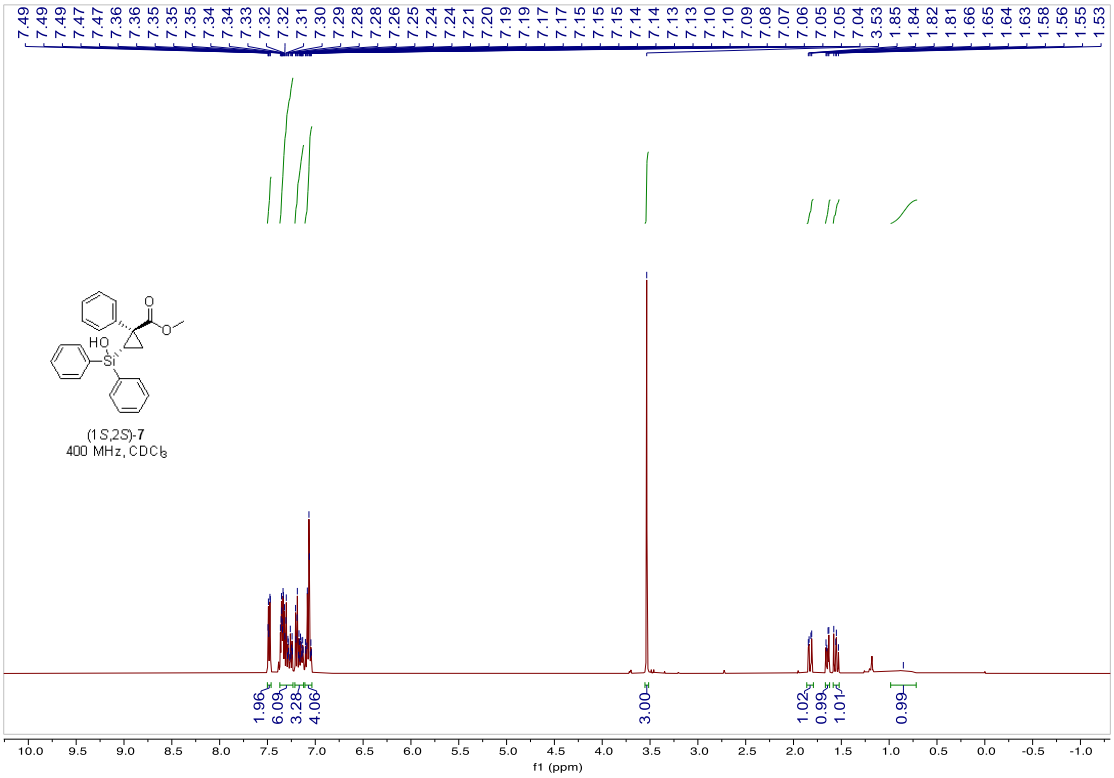
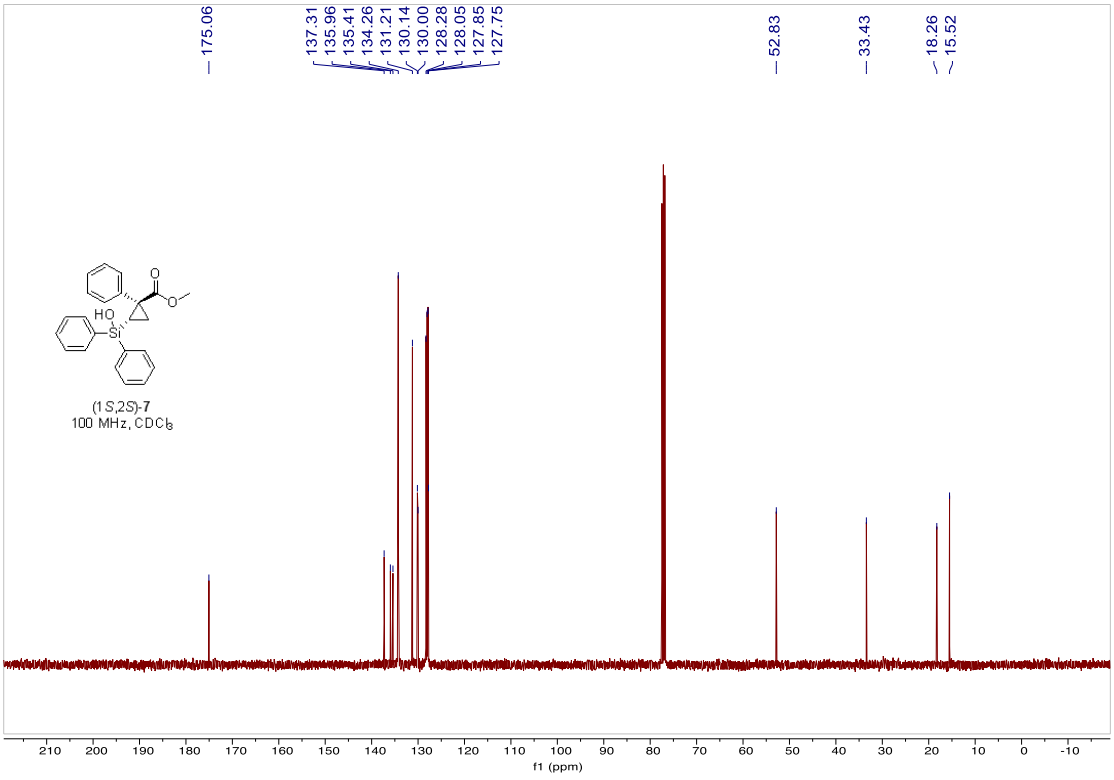
7.21
7.20
7.18
7.16
7.12
7.10
7.10
7.09
7.07
6.99
6.98
6.97
6.96
6.96
4.74
4.73
1.29
1.28
1.26
1.25
1.23
1.20
0.81
0.80
0.79
0.78
0.45
0.44
0.43
0.42
0.42
0.41
0.41
(1S,2S)-5v
400 MHz, CDCl3
4.17
6.15
4.25
1.15
1.00
3.01
1.24
1.06
1.02
f1 (ppm)


148.20
135.49
135.33
135.16
134.82
129.74
129.72
128.42
128.18
128.15
126.93
125.88
25.67
23.94
20.22
10.99
(1S,2S)-5v
100 MHz, CDCl3
f1 (ppm)

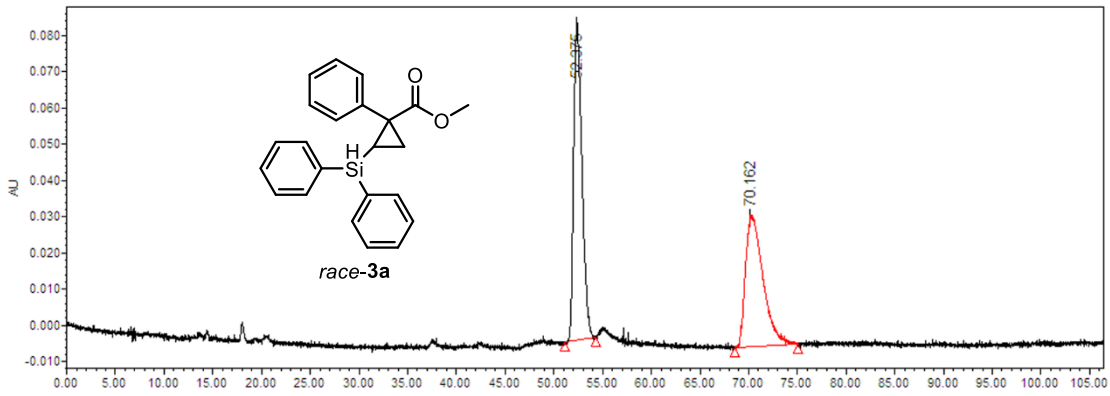

7.44
7.44
7.42
7.42
7.42
7.31
7.31
7.29
7.29
7.22
7.20
7.20
7.19
7.17
7.15
7.14
7.13
7.05
4.09
4.08
3.42
3.41
3.39
3.37
3.35
3.28
3.26
3.25
3.23
3.21
3.21
3.20
3.16
3.14
3.12
3.10
3.09
3.08
2.15
1.64
1.64
1.63
1.43
1.43
1.41
1.40
1.39
1.38
1.37
1.36
1.36
1.35
1.34
1.34
1.01
0.99
0.97
0.50
0.48
0.46
O
N
H
Si
6
400 MHz, CDCl3
1.13
2.26
6.22
5.06
1.00
1.36
2.19
1.34
2.86
1.43
2.14
3.38
3.38
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


172.21
144.49
138.11
136.89
135.24
133.99
133.32
130.01
129.58
129.24
128.36
128.24
127.78
126.73
125.09
41.57
39.25
36.14
22.99
14.92
12.71
12.49
10.05
O
N
H
Si
6
100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

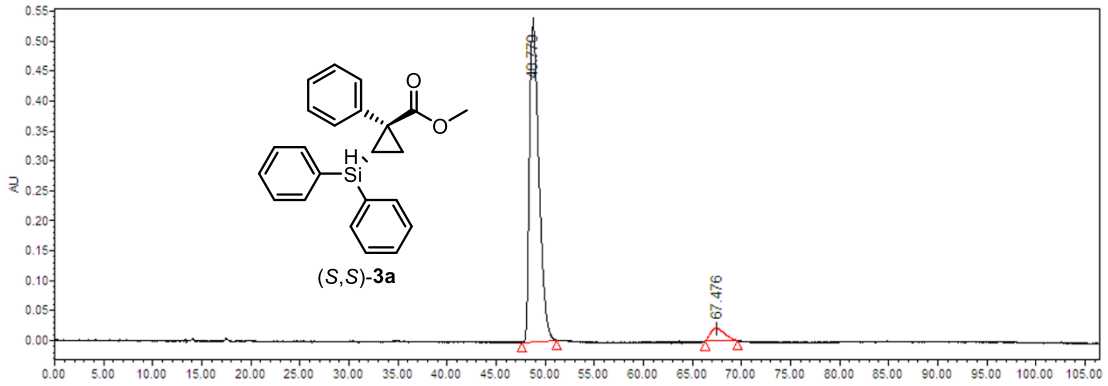

(1S,2S)-7
400 MHz, CDCl3
f1 (ppm)


(1S,2S)-7
100 MHz, CDCl3
f1 (ppm)

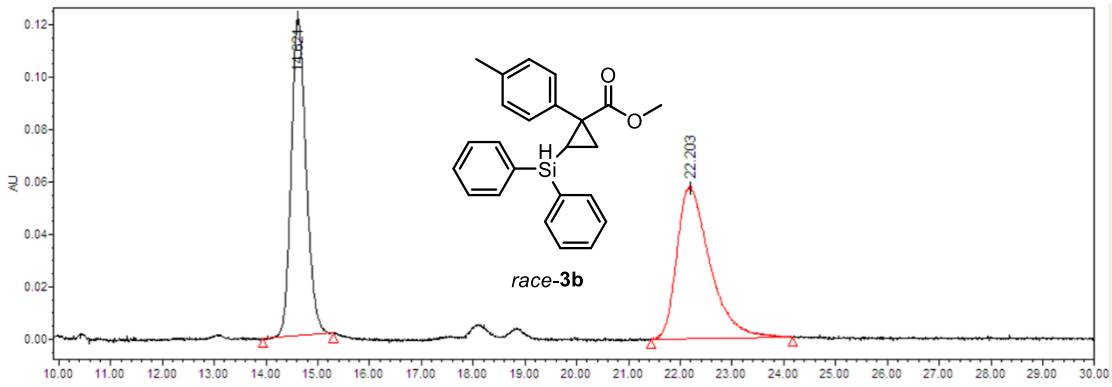
7. HPLC and UPLC Charts



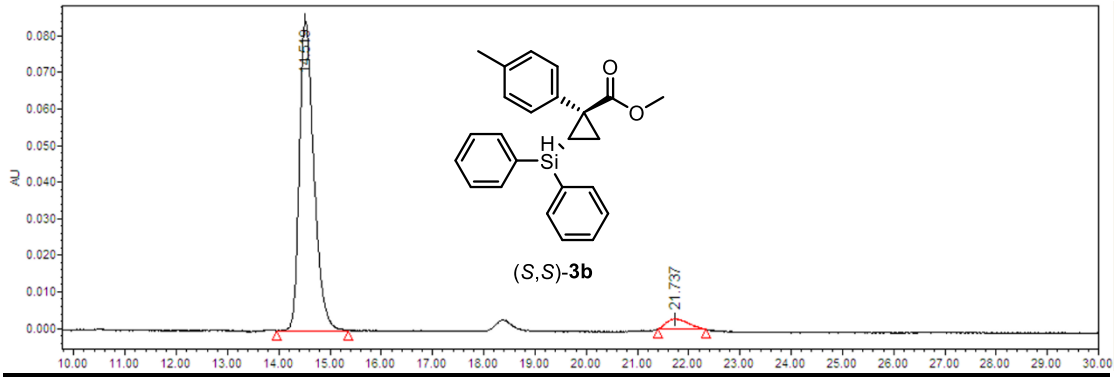
	Time/min	Area	Height	Area%
1	52.375	5185008	87108	53.11
2	70.162	4577828	36015	46.89



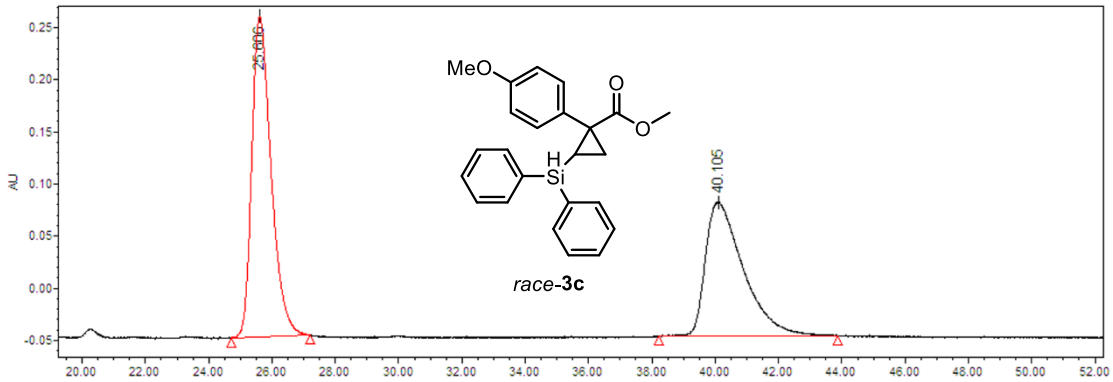
	Time/min	Area	Height	Area%
1	48.770	35847673	528231	94.44
2	67.476	2109211	21212	5.56



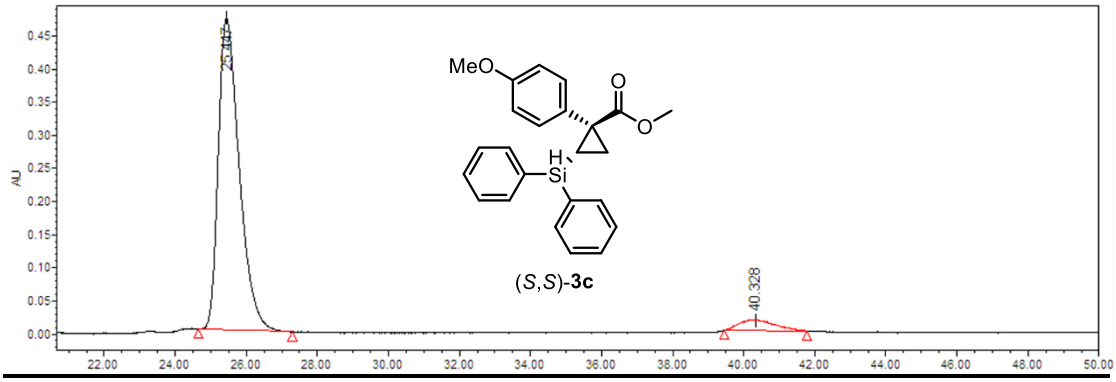
	Time/min	Area	Height	Area%
1	14.621	2428102	121122	48.43
2	22.203	2585210	57891	51.57



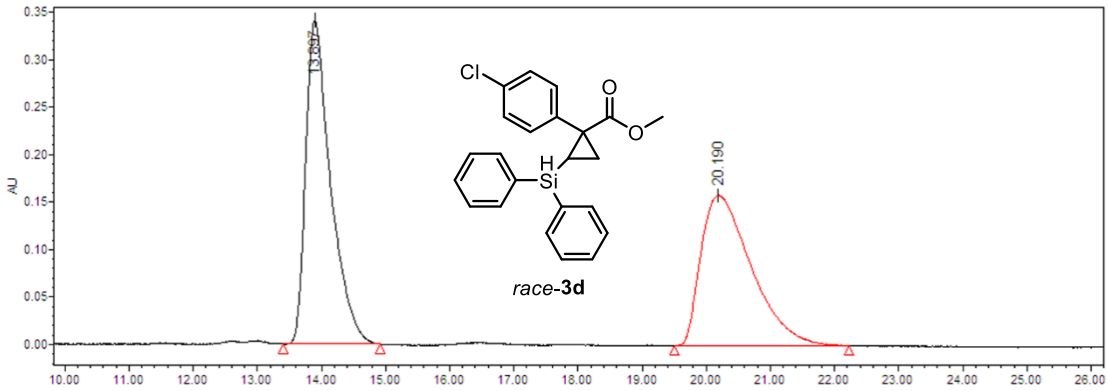
	Time/min	Area	Height	Area%
1	14.519	1668075	84837	95.21
2	21.737	83990	2861	4.79



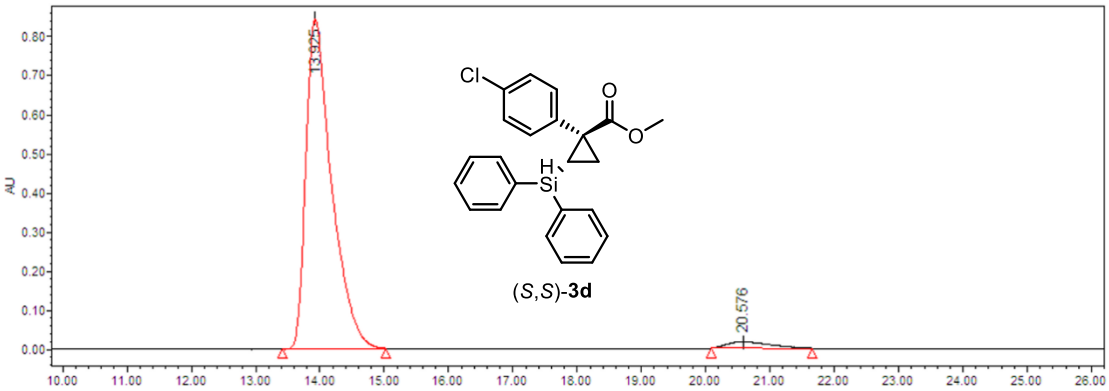
	Time/min	Area	Height	Area%
1	25.606	13007134	307353	55.11
2	40.105	10595566	128198	44.89



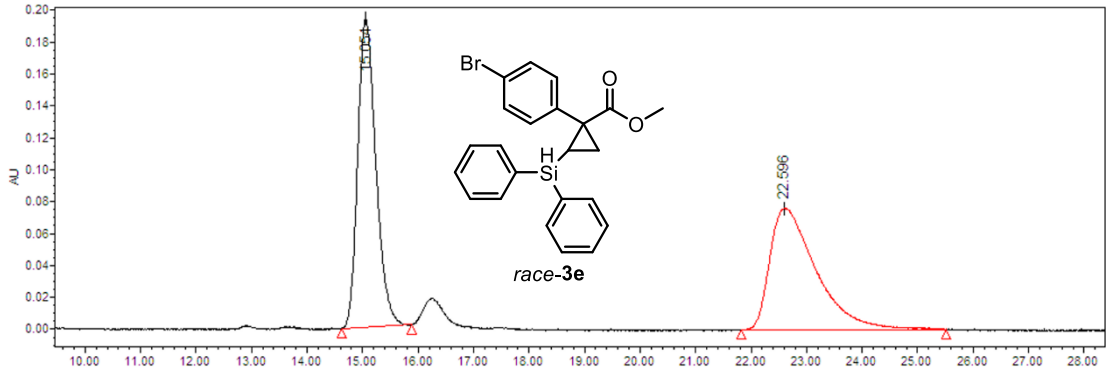
	Time/min	Area	Height	Area%
1	25.447	19275088	470031	94.65
2	40.328	1089874	15677	5.35



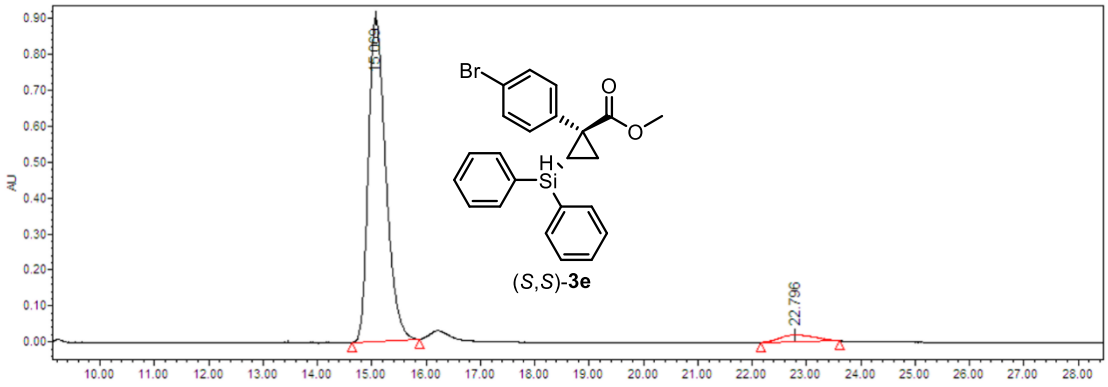
	Time/min	Area	Height	Area%
1	13.897	9153116	340313	51.32
2	20.190	8683331	158652	48.68



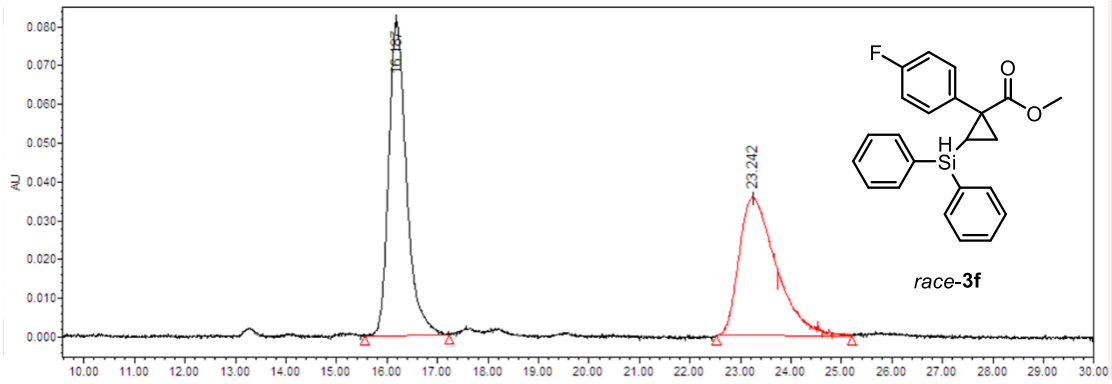
	Time/min	Area	Height	Area%
1	13.925	23379390	842596	96.91
2	20.576	744383	16190	3.09



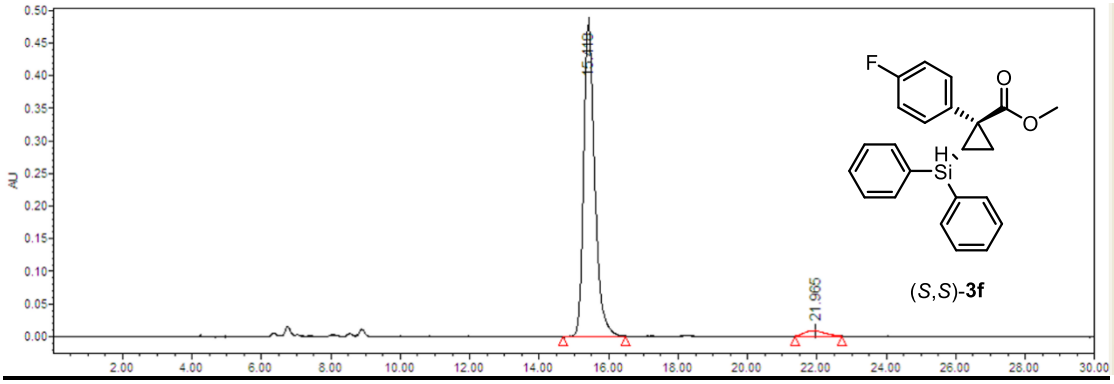
	Time/min	Area	Height	Area%
1	15.054	4382342	193347	49.97
2	22.596	4387169	76452	50.03



	Time/min	Area	Height	Area%
1	15.069	20100783	898846	96.05
2	22.796	825678	18651	3.95



	Time/min	Area	Height	Area%
1	16.187	1998165	81020	52.27
2	23.242	1824894	35547	47.73



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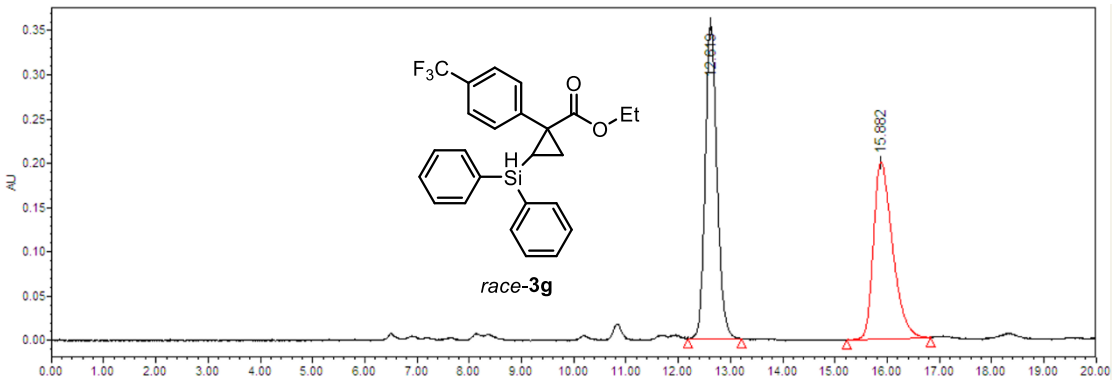
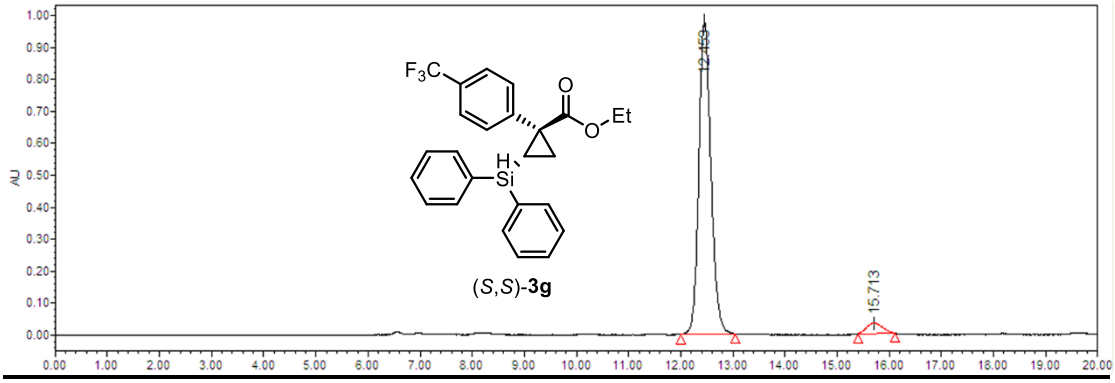
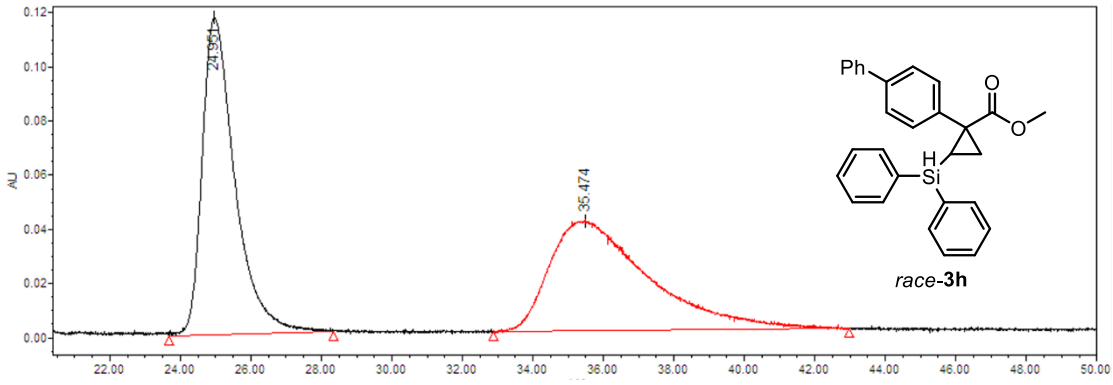
1	15.418	10690528	478785	96.94
2	21.965	337605	8394	3.06



	Time/min	Area	Height	Area%
1	12.619	5605040	355400	52.54
2	15.882	5063678	199582	47.46



	Time/min	Area	Height	Area%
1	12.453	15769027	980094	95.83
2	15.713	686977	32368	4.17



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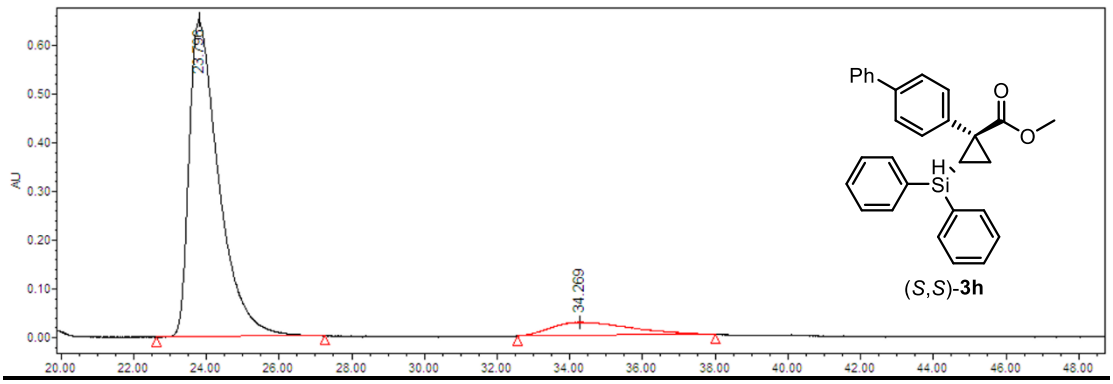
1	24.951	7535620	117053	49.00
2	35.474	7842137	40515	51.00



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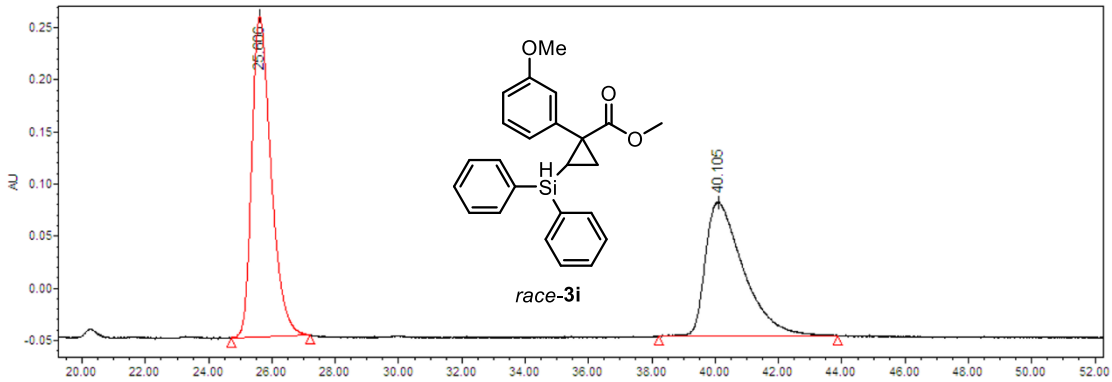
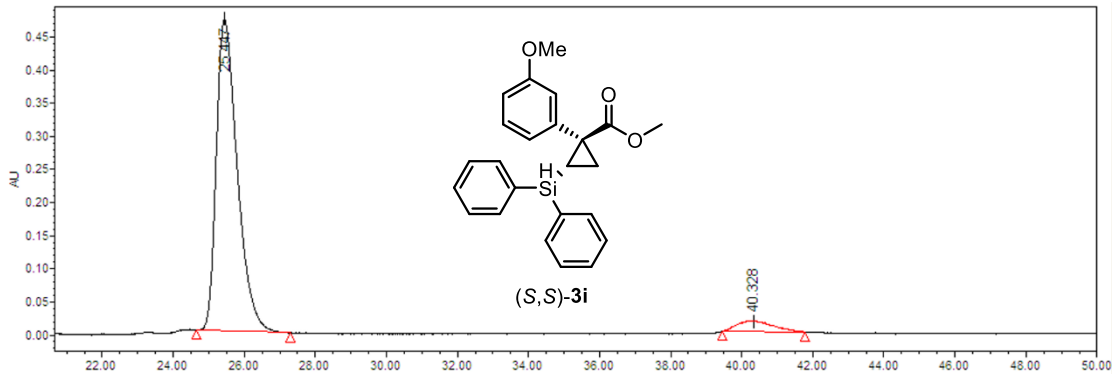
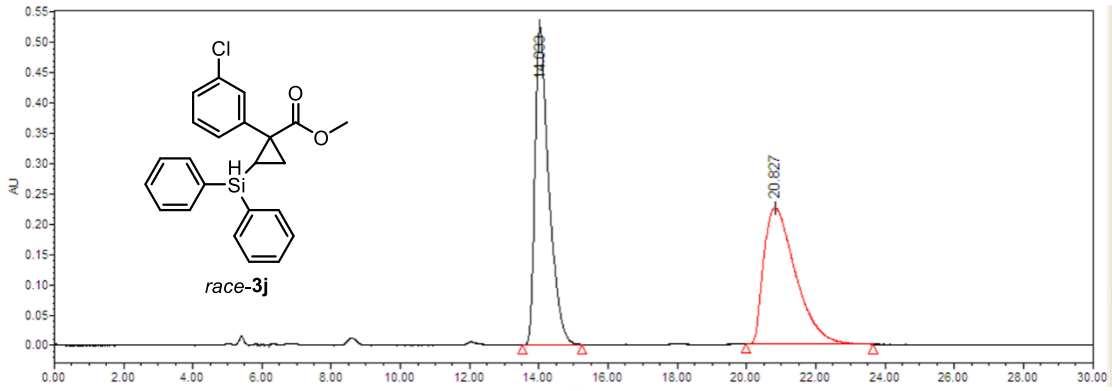
1	23.796	36995884	651360	89.96
2	34.269	41127671	27070	10.04



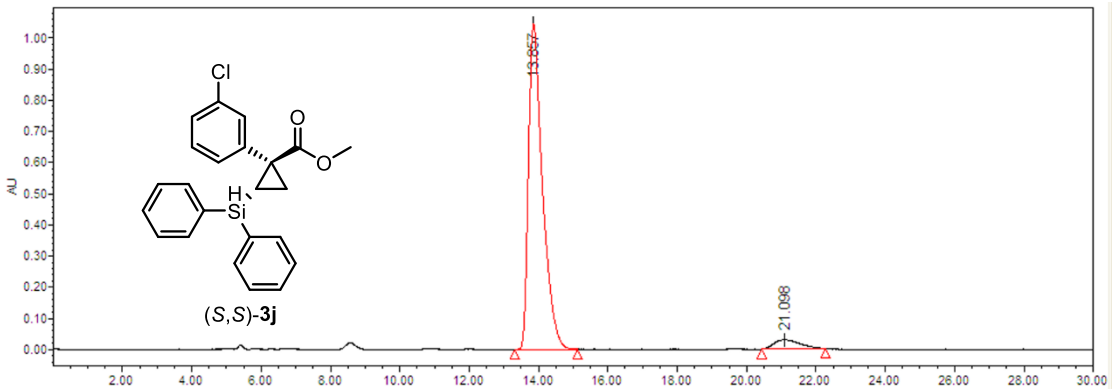
	Time/min	Area	Height	Area%
1	25.606	13007134	307353	55.11
2	40.105	10595566	128198	44.89



	Time/min	Area	Height	Area%
1	25.447	19275088	470031	94.65
2	40.328	1089874	15677	5.35



	Time/min	Area	Height	Area%
1	14.033	14567748	524975	50.39
2	20.827	14342463	2252260	49.61



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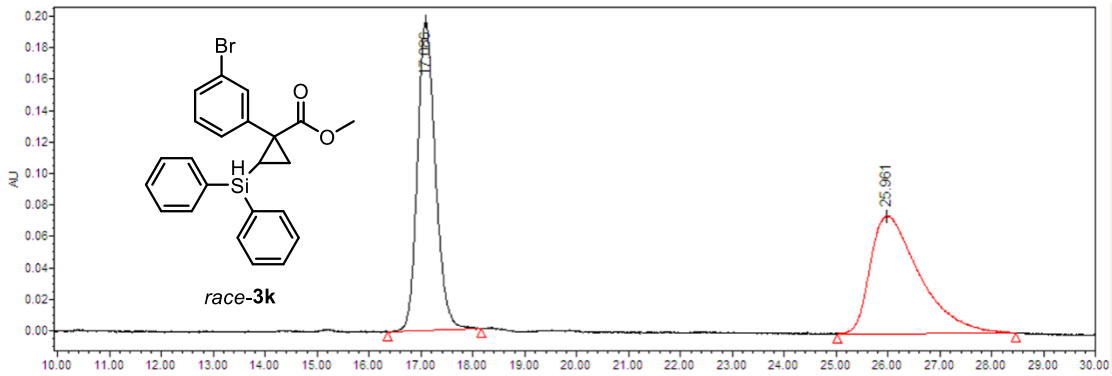
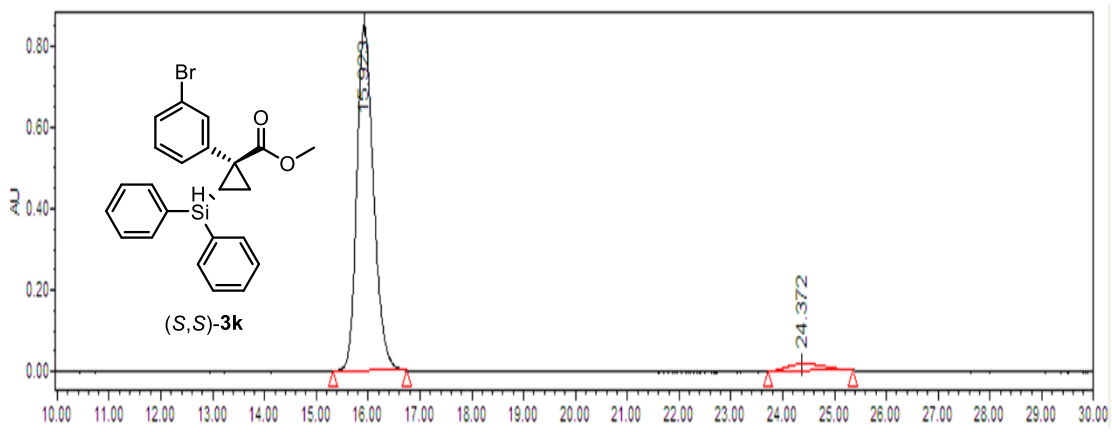
1	13.857	29143249	1044144	94.89
2	21.098	1569415	29786	5.11



	Time/min	Area	Height	Area%
1	17.086	4733893	196006	49.26
2	25.961	4876551	74654	50.74



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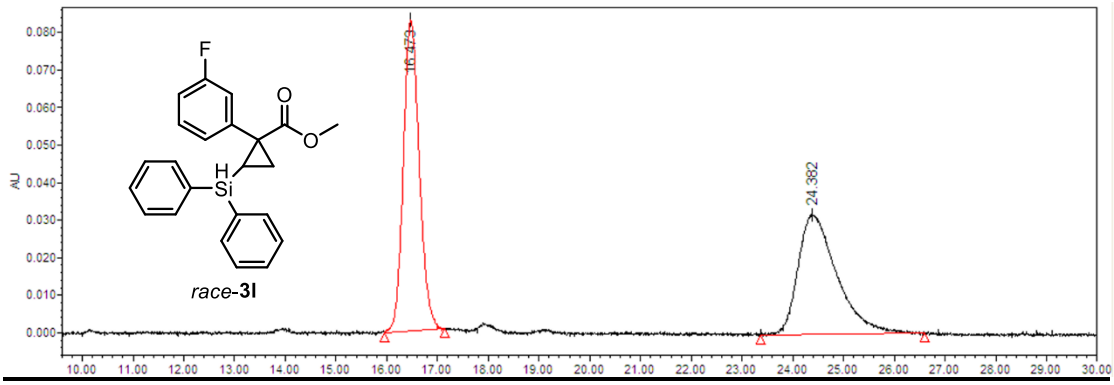
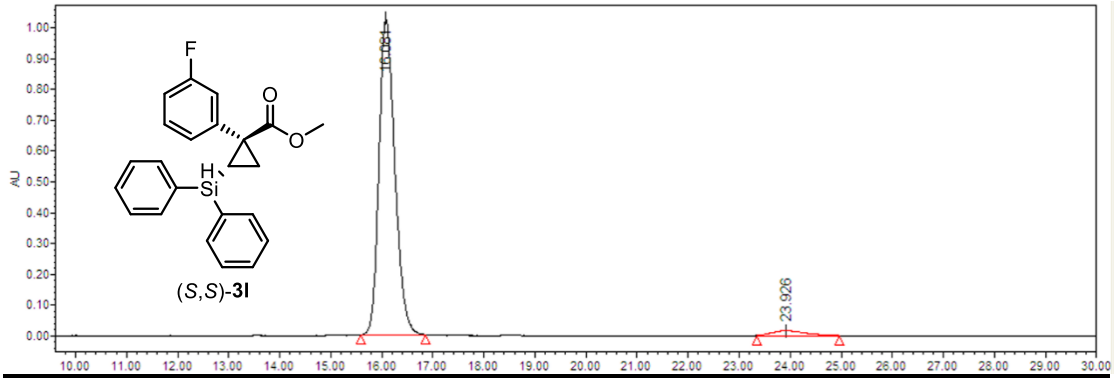
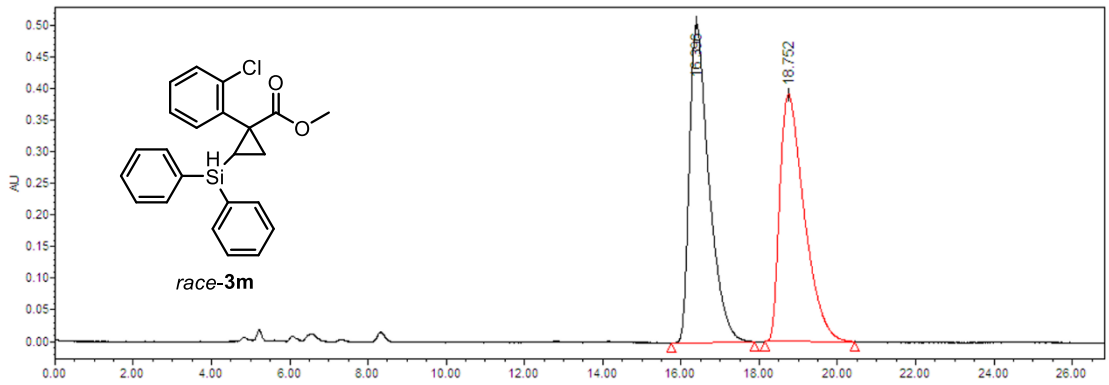
1	15.923	19072062	846727	95.41
2	24.372	916759	18117	4.59



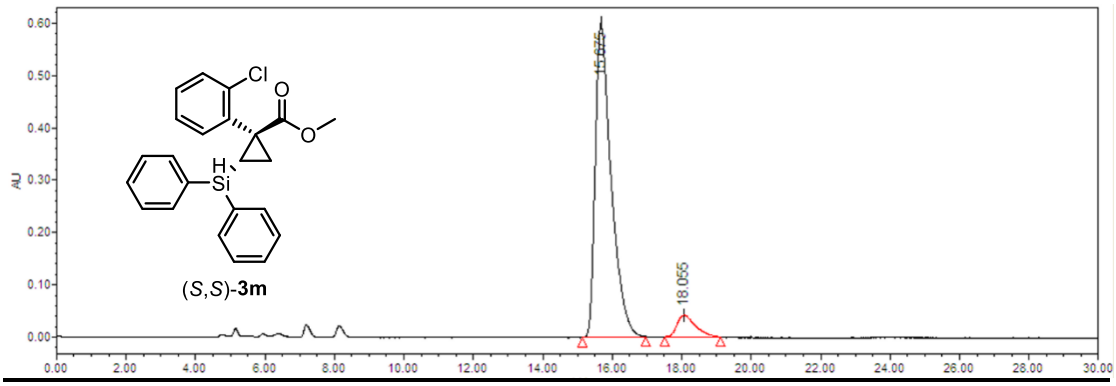
	Time/min	Area	Height	Area%
1	16.473	1811917	82895	51.56
2	24.382	1702226	31865	48.44



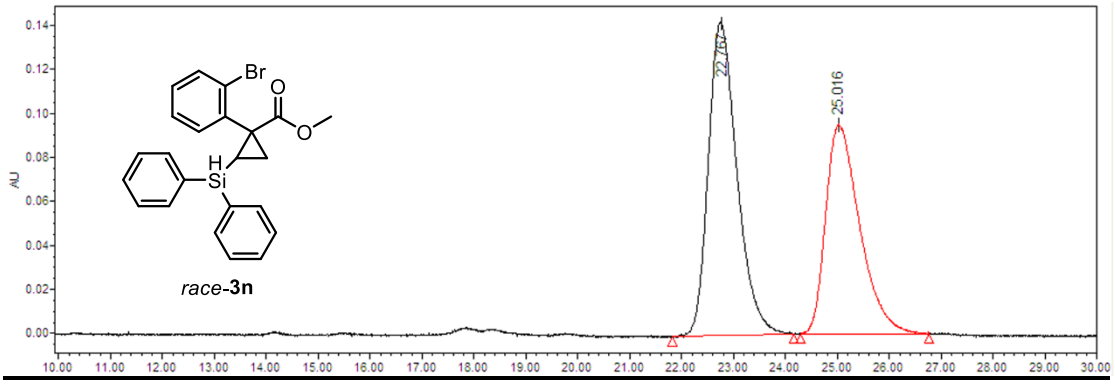
	Time/min	Area	Height	Area%
1	16.081	22174676	1024497	96.92
2	23.926	704670	15967	3.08



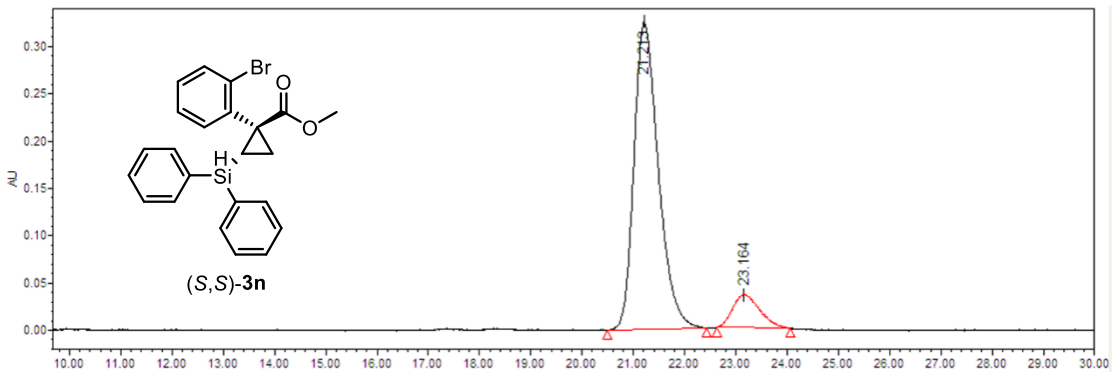
	Time/min	Area	Height	Area%
1	16.396	17481771	503819	50.74
2	18.752	16969330	390906	49.26



	Time/min	Area	Height	Area%
1	15.675	19099157	599769	92.65
2	18.055	1514815	41289	7.35



	Time/min	Area	Height	Area%
1	22.767	5464380	141955	55.89
2	25.016	4312016	94830	44.11



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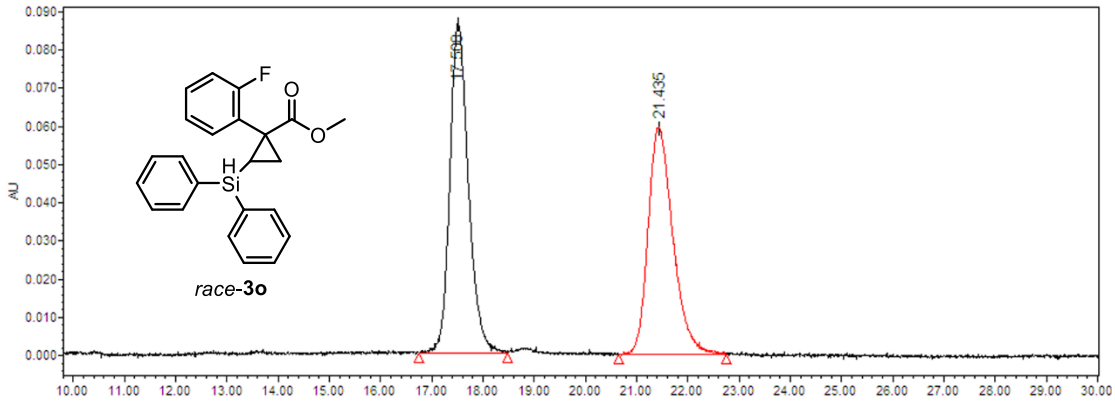
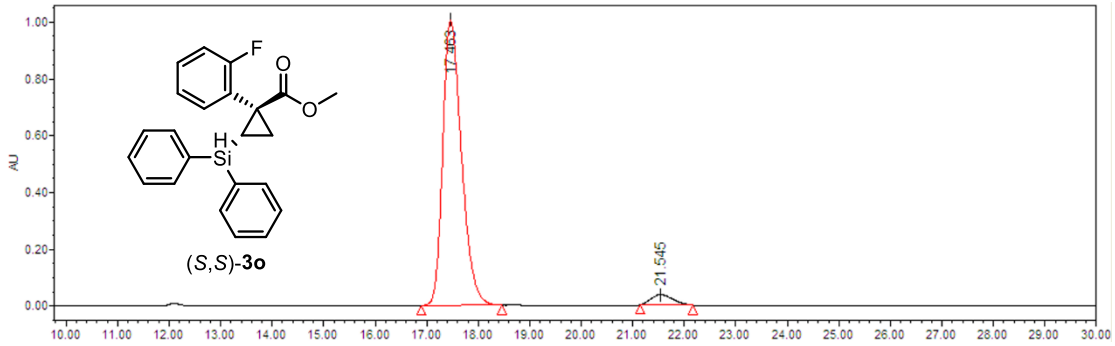
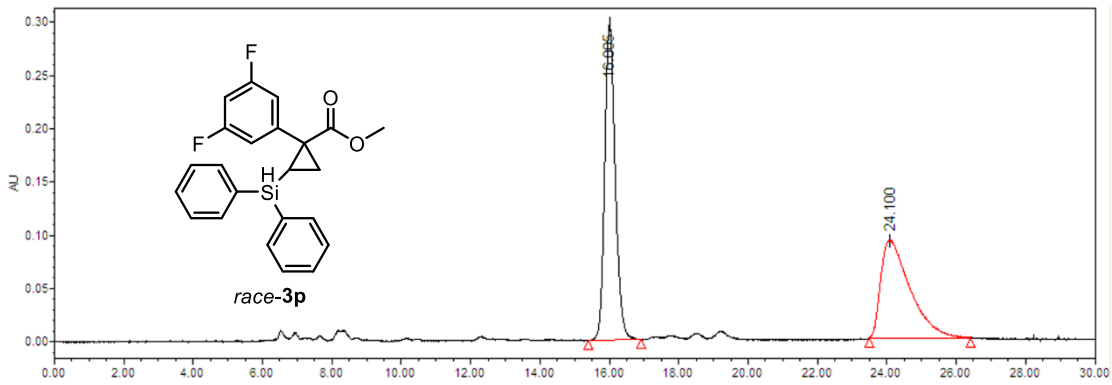
1	21.213	10721971	324627	89.29
2	23.164	1285555	35075	10.71



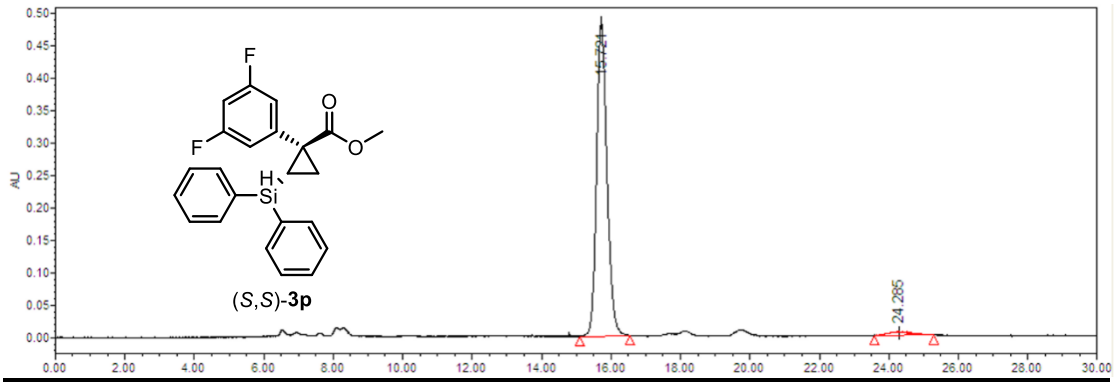
	Time/min	Area	Height	Area%
1	17.508	2177723	86039	52.04
2	21.435	2006996	59345	47.96



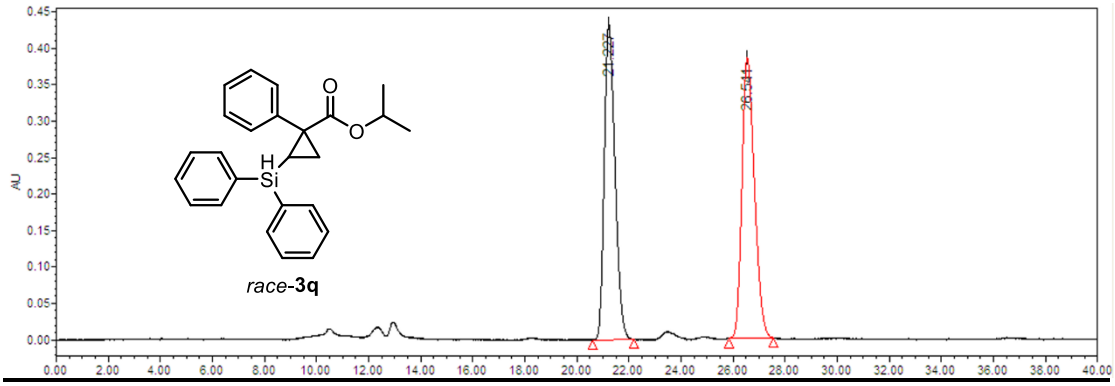
	Time/min	Area	Height	Area%
1	17.463	25379062	1003206	95.98
2	21.545	1062714	36074	4.02



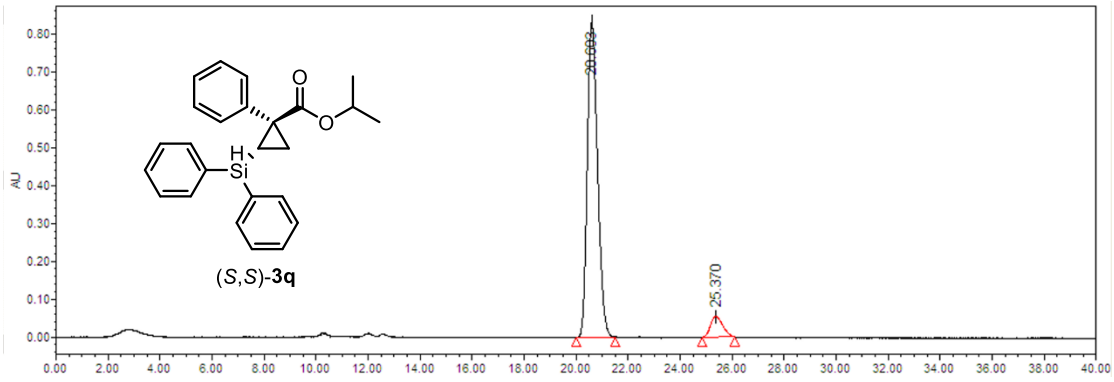
	Time/min	Area	Height	Area%
1	16.005	6251294	296275	53.92
2	24.100	5342385	91669	46.08



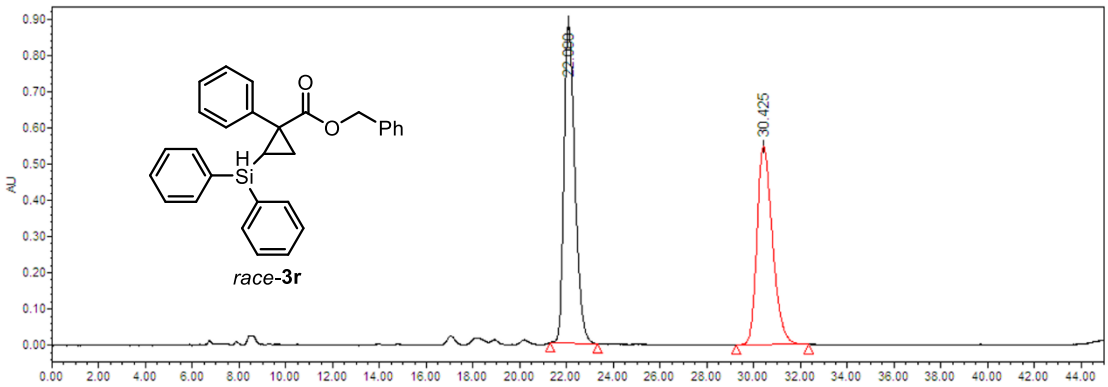
	Time/min	Area	Height	Area%
1	15.721	10077643	482577	97.43
2	24.285	266339	5303	2.57



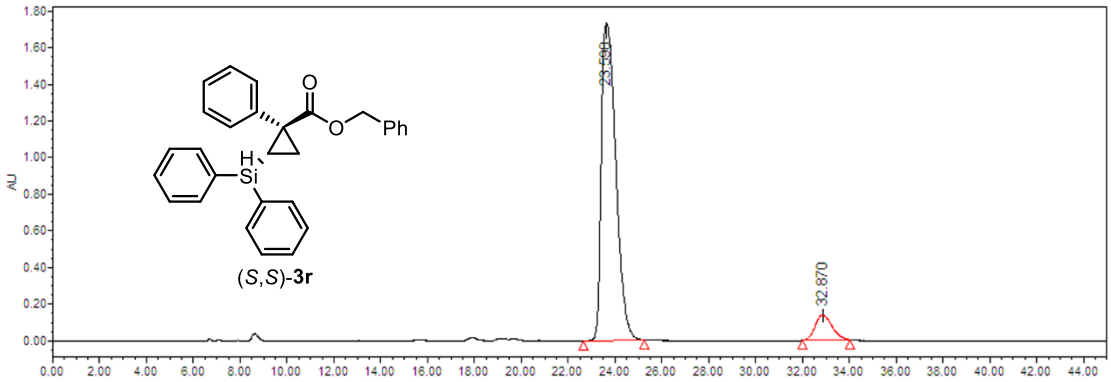
	Time/min	Area	Height	Area%
1	21.227	12321871	432492	49.00
2	26.541	12824185	384109	51.00



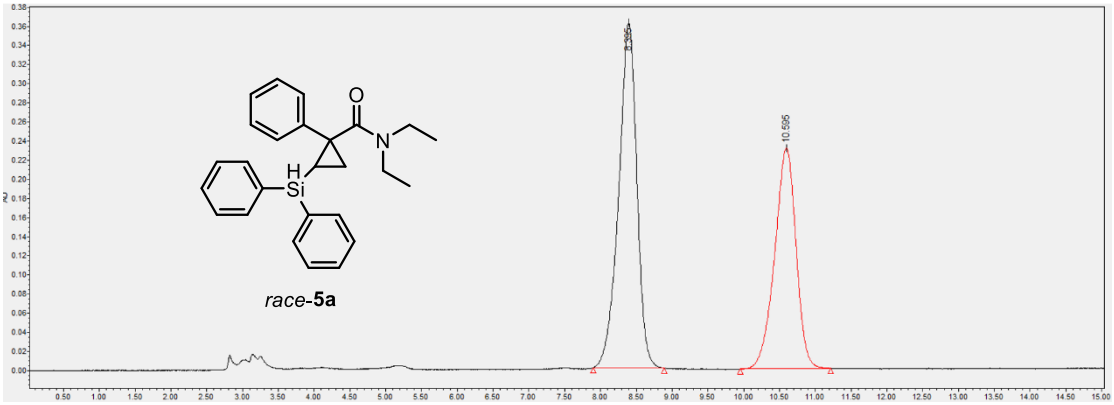
	Time/min	Area	Height	Area%
1	20.603	22816460	831593	92.69
2	25.370	1800394	55243	7.31



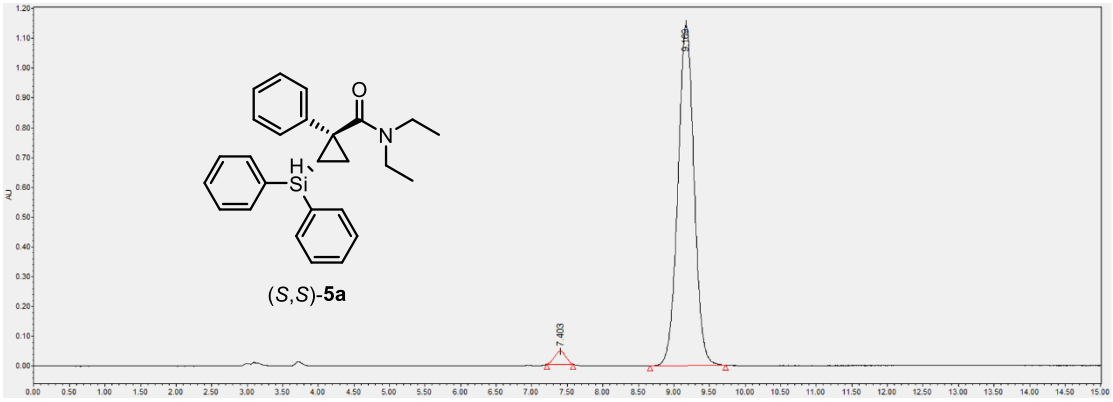
	Time/min	Area	Height	Area%
1	22.080	28703466	881365	53.22
2	30.425	25230852	547929	46.78



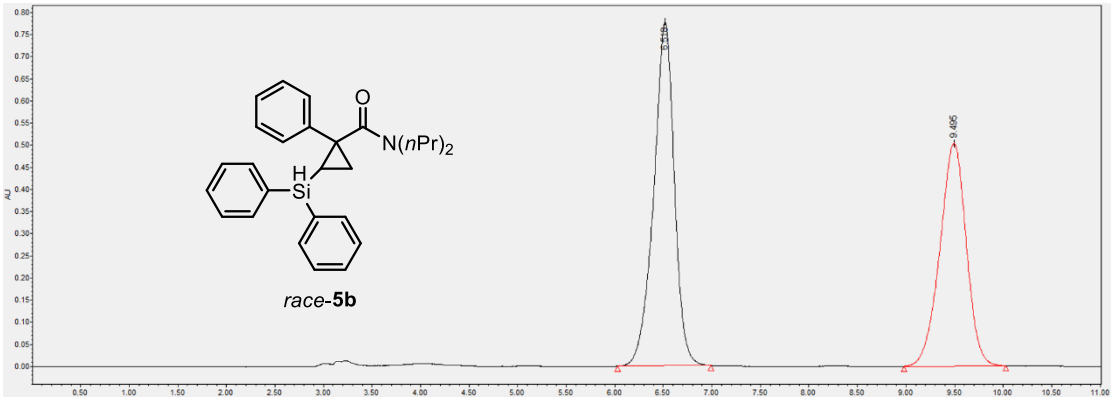
	Time/min	Area	Height	Area%
1	23.598	74362487	1701934	91.58
2	32.870	6833276	136282	8.42



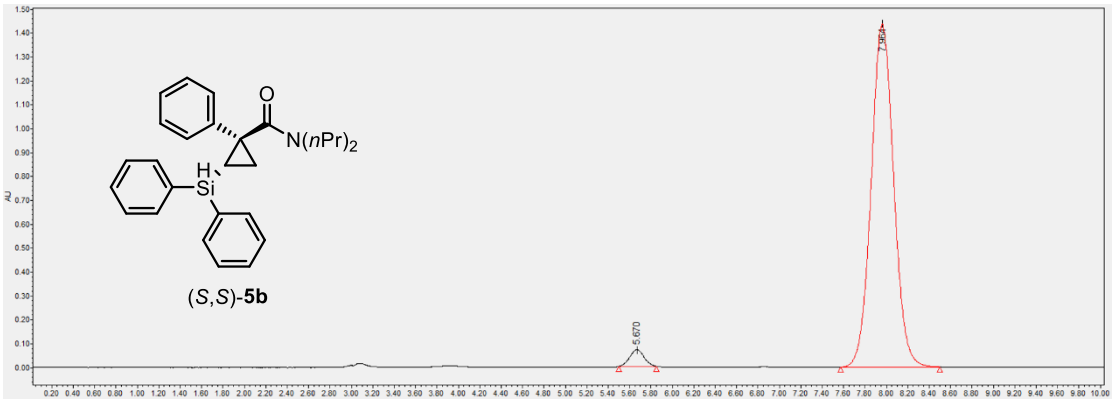
	Time/min	Area	Height	Area%
1	8.395	6351589	360830	57.04
2	10.595	4782853	230699	42.96



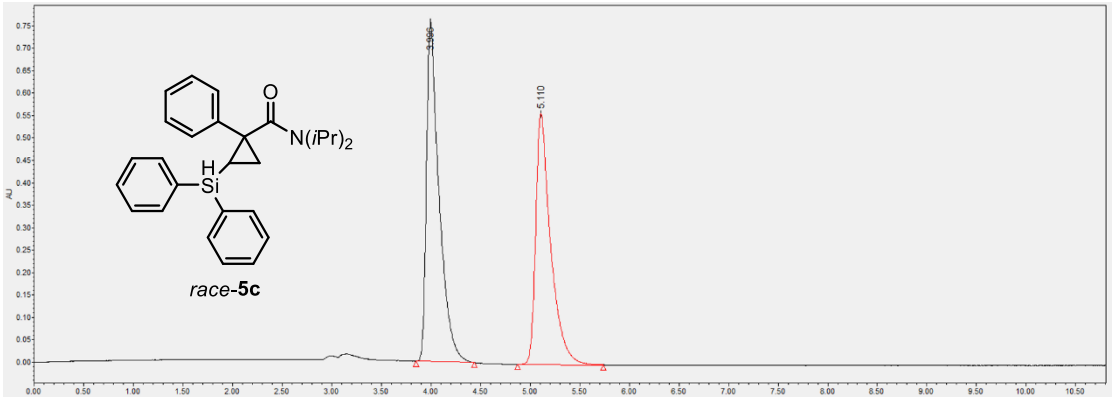
	Time/min	Area	Height	Area%
1	7.403	478960	44488	2.58
2	9.169	18097995	1145217	97.42



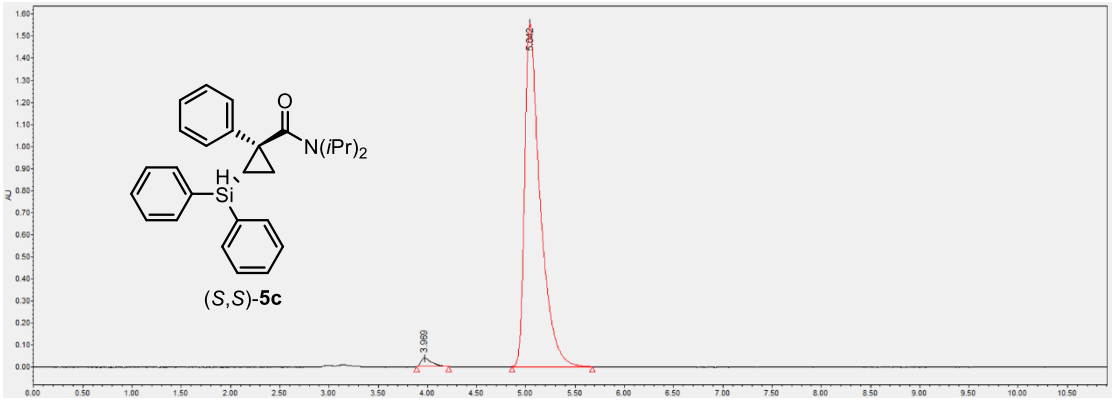
	Time/min	Area	Height	Area%
1	6.518	11497509	777016	54.70
2	9.495	9520003	504020	45.30



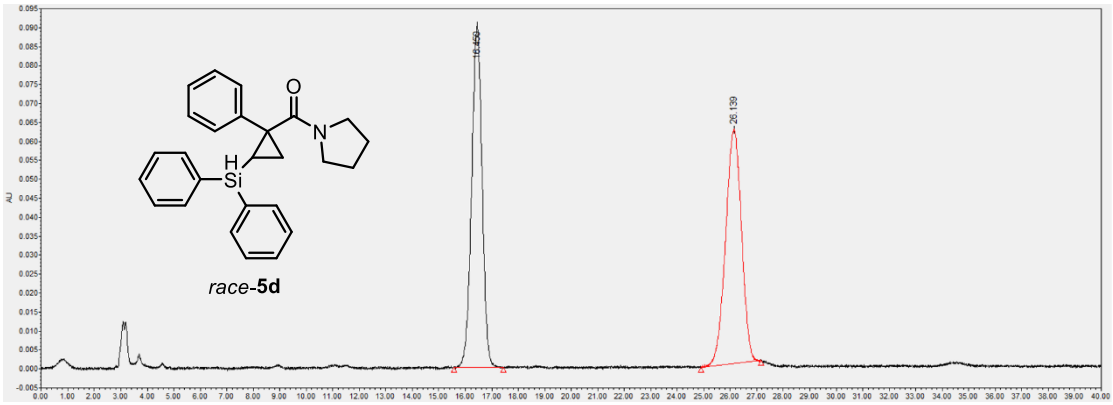
	Time/min	Area	Height	Area%
1	5.670	642781	69634	2.97
2	7.964	21034281	2.97	97.03



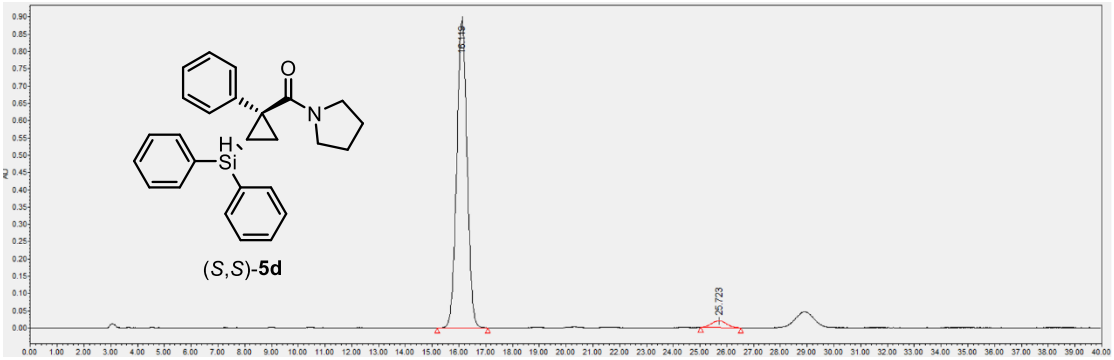
	Time/min	Area	Height	Area%
1	3.996	6670323	755791	53.33
2	5.110	5837586	559488	46.67



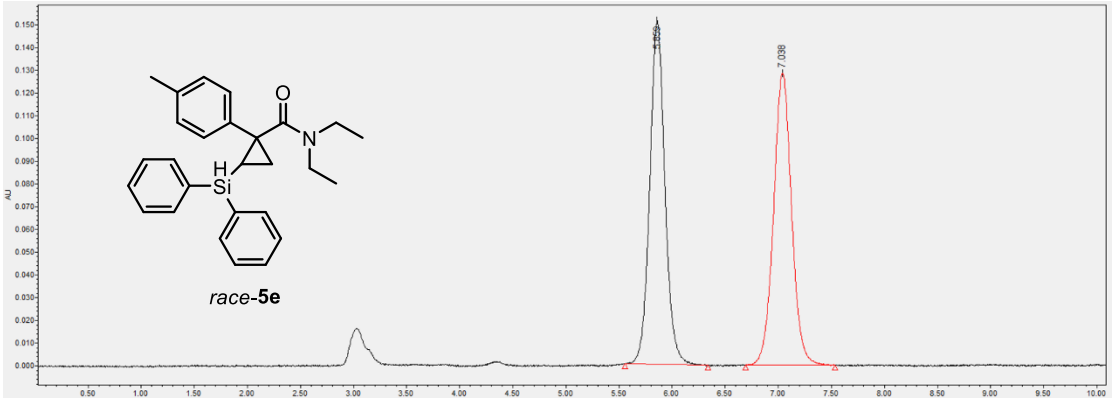
	Time/min	Area	Height	Area%
1	3.969	297112	38713	1.72
2	5.042	17024656	1555635	98.28



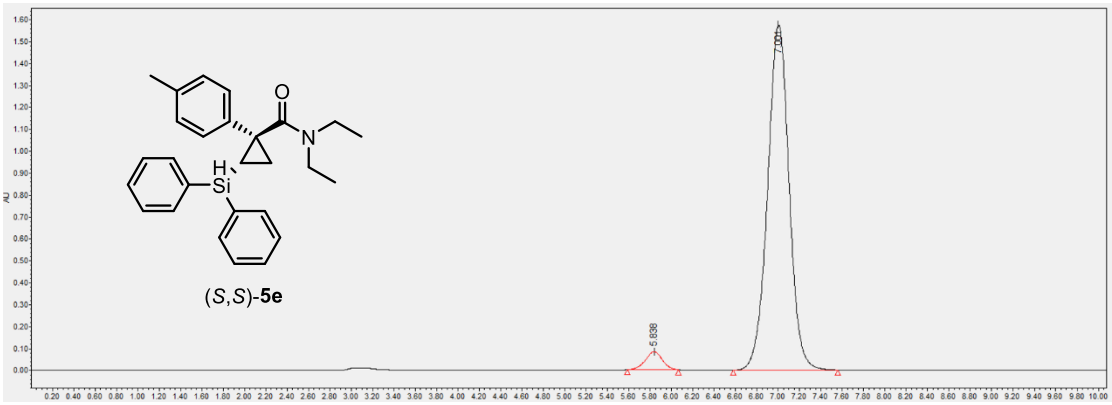
	Time/min	Area	Height	Area%
1	16.450	2487029	90121	49.26
2	26.139	2561552	61767	50.74



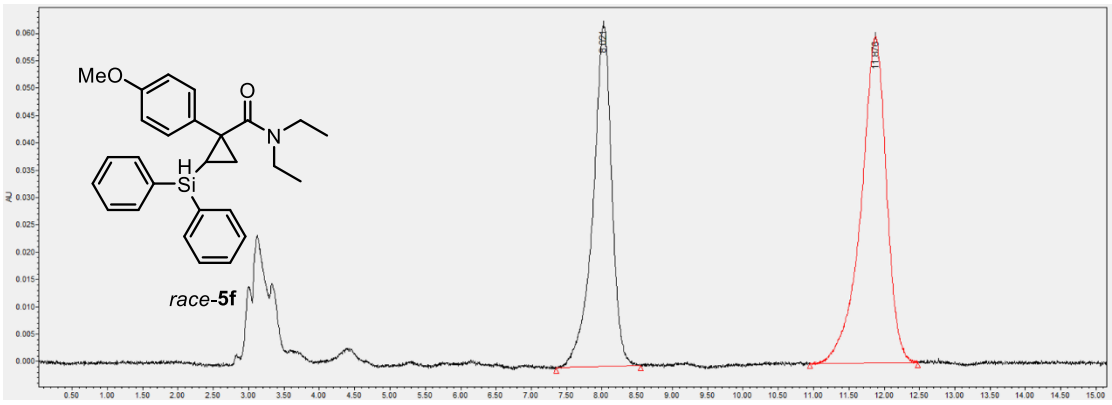
	Time/min	Area	Height	Area%
1	16.119	23944759	888832	96.84
2	25.723	781109	20434	3.16



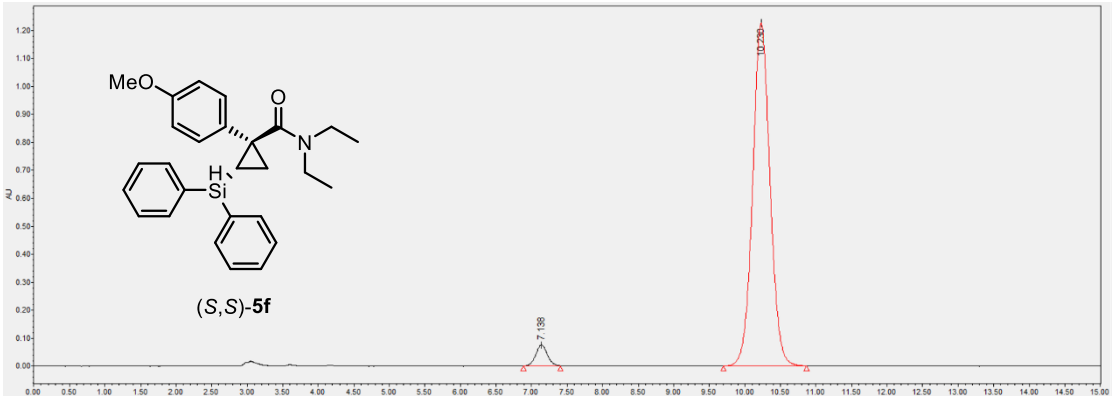
	Time/min	Area	Height	Area%
1	5.859	1502975	150895	49.78
2	7.038	1516417	128512	50.22



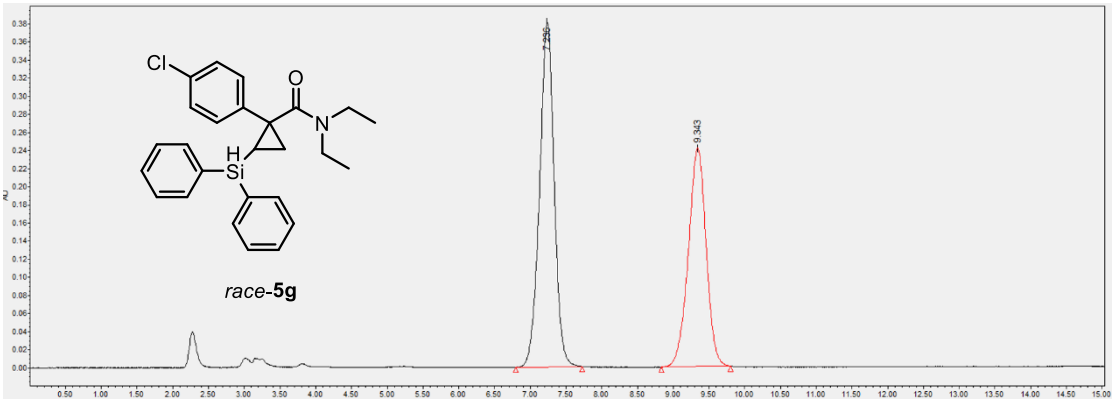
	Time/min	Area	Height	Area%
1	5.838	918022	83369	4.00
2	7.001	22041904	1575152	96.00



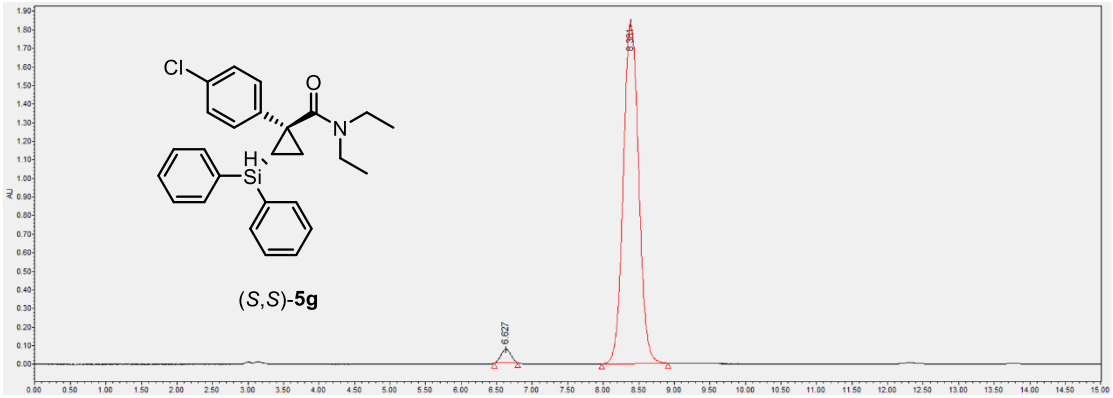
	Time/min	Area	Height	Area%
1	8.021	1159666	62545	43.63
2	11.876	1498076	59657	56.37



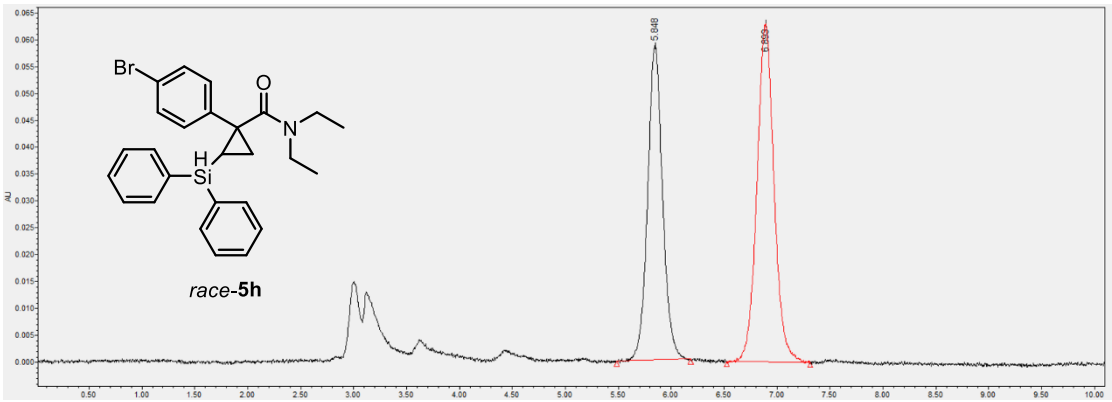
	Time/min	Area	Height	Area%
1	7.138	842907	75541	3.90
2	10.230	20794194	1225543	96.10



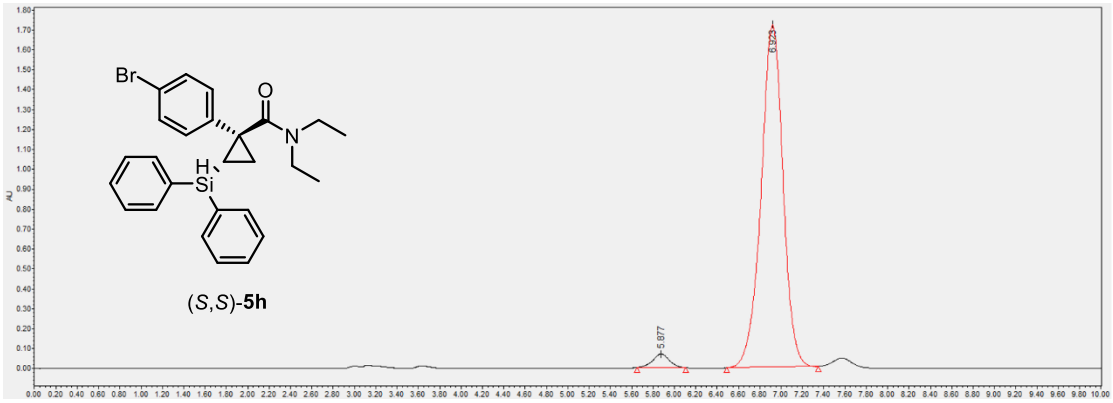
	Time/min	Area	Height	Area%
1	7.236	5393305	380793	56.32
2	9.343	4183457	241510	43.68



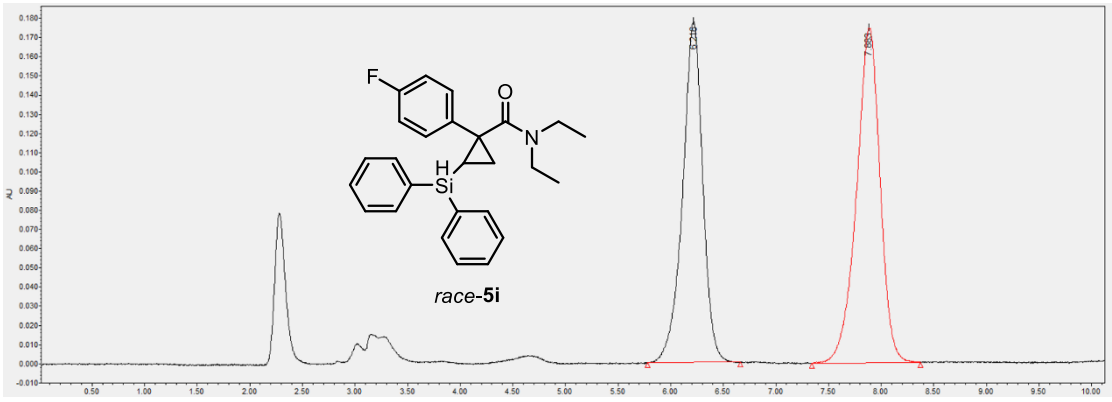
	Time/min	Area	Height	Area%
1	6.627	694828	73050	2.46
2	8.381	27607077	1831836	97.54



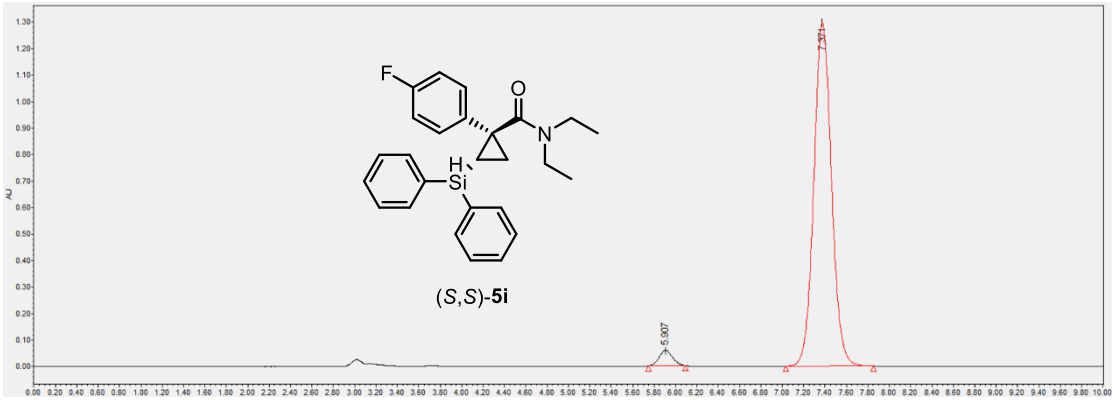
	Time/min	Area	Height	Area%
1	5.848	575215	58452	44.83
2	6.893	707974	62823	55.17



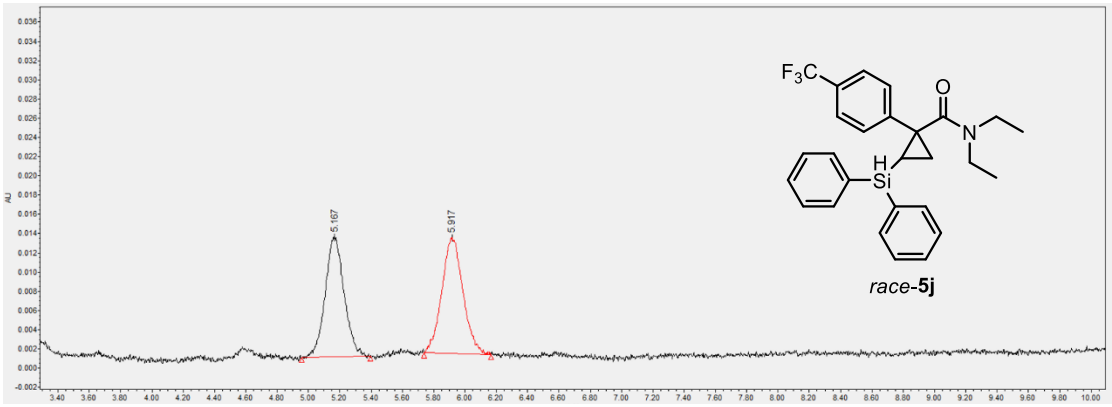
	Time/min	Area	Height	Area%
1	5.877	740487	69217	2.93
2	6.923	24536382	1718477	97.07



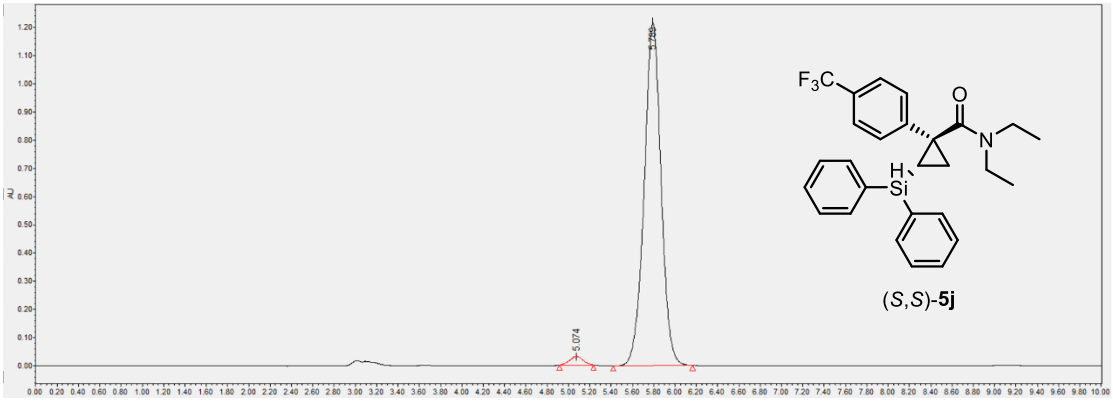
	Time/min	Area	Height	Area%
1	6.216	2365646	177689	46.49
2	7.883	2723087	174443	53.51



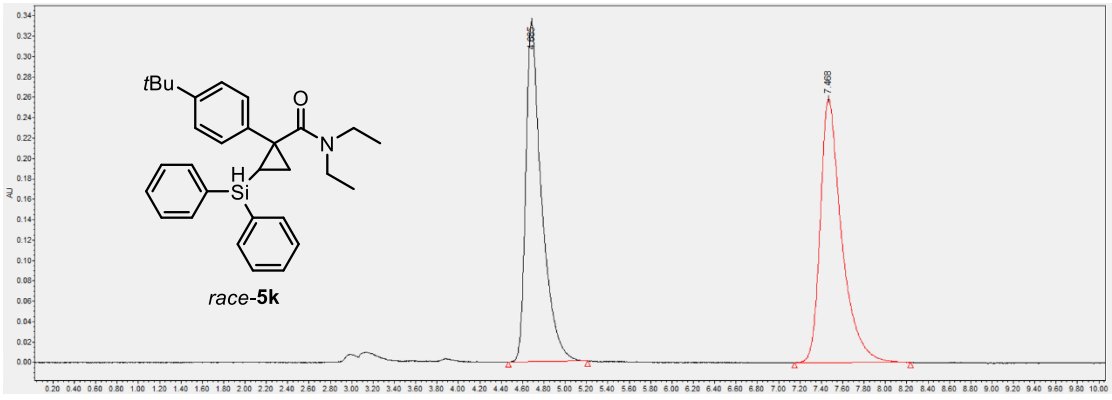
	Time/min	Area	Height	Area%
1	5.907	508323	58687	3.30
2	7.371	14889126	1295873	96.70



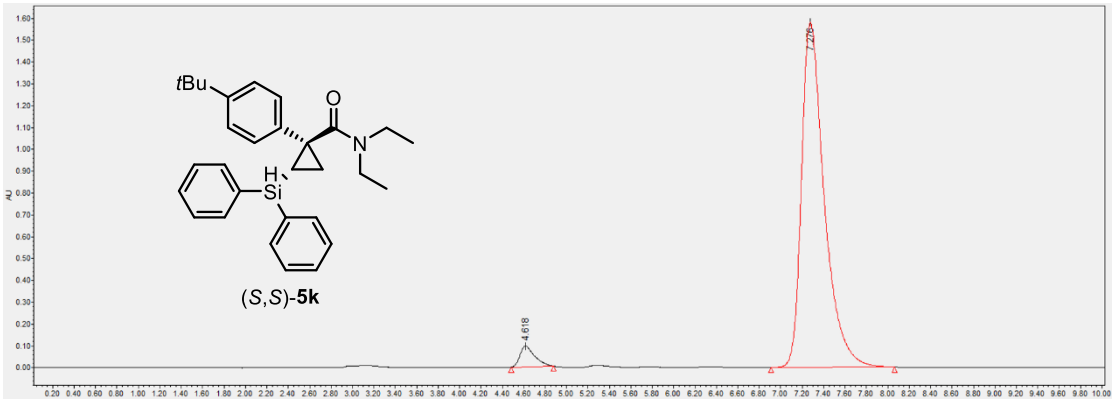
	Time/min	Area	Height	Area%
1	5.167	105041	12455	48.09
2	5.917	113390	12063	51.91



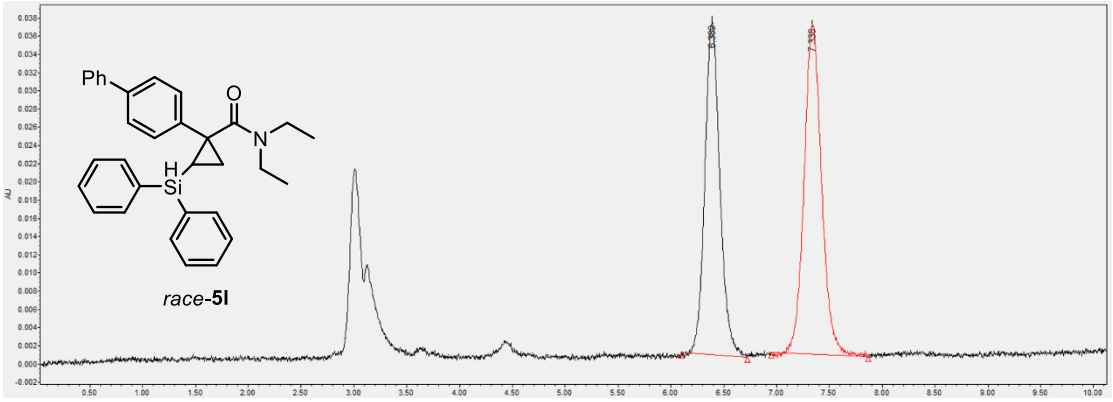
	Time/min	Area	Height	Area%
1	5.074	264550	30656	1.94
2	5.789	13395413	1216997	98.06



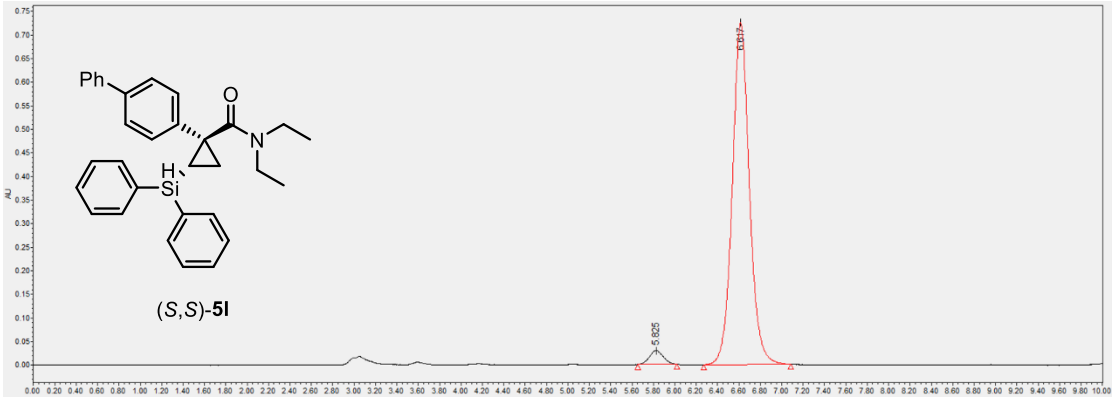
	Time/min	Area	Height	Area%
1	4.685	3443933	333297	48.84
2	7.468	3608184	258860	51.16



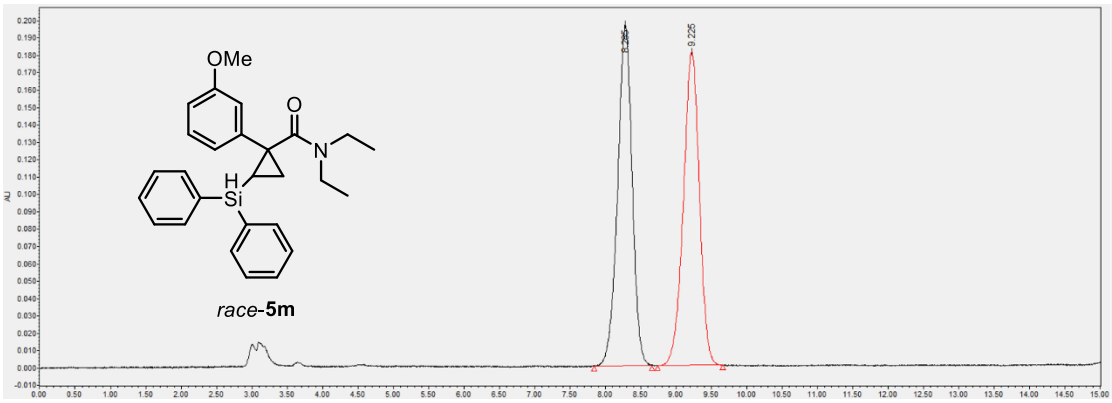
	Time/min	Area	Height	Area%
1	4.618	910830	96013	3.76
2	7.276	23323813	1579268	96.24



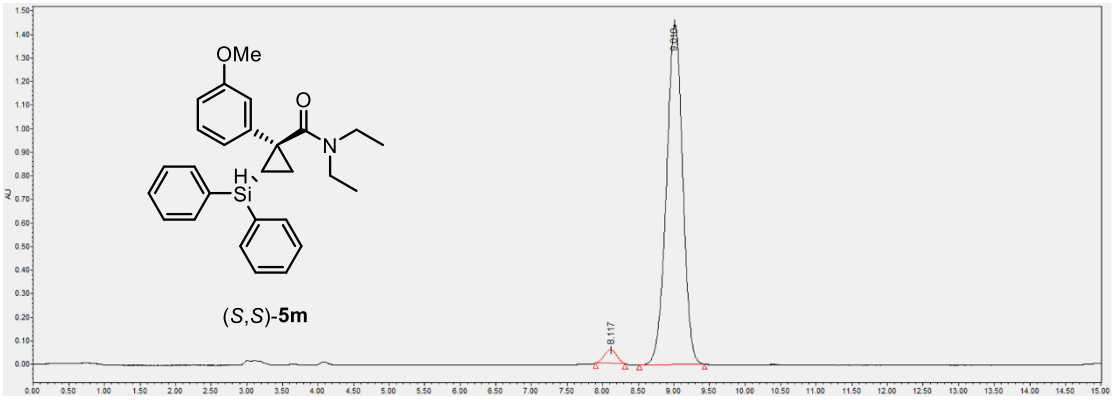
	Time/min	Area	Height	Area%
1	6.389	363147	36750	46.31
2	7.338	421023	36281	53.69



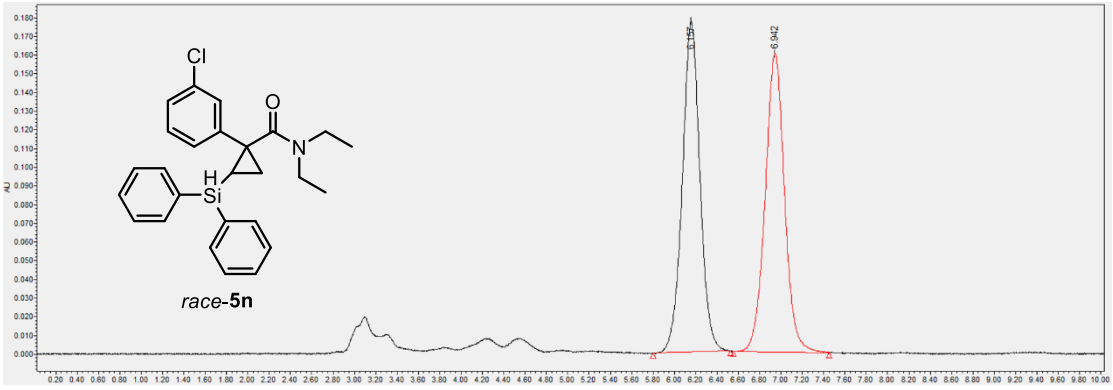
	Time/min	Area	Height	Area%
1	5.825	264274	29453	3.17
2	6.617	8066563	725140	96.83



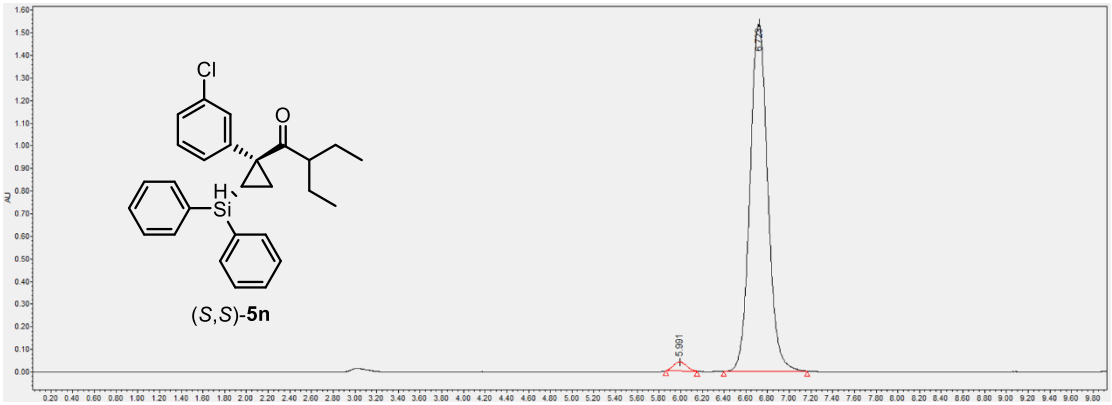
	Time/min	Area	Height	Area%
1	8.285	2802610	196161	49.71
2	9.225	2835590	180647	50.29



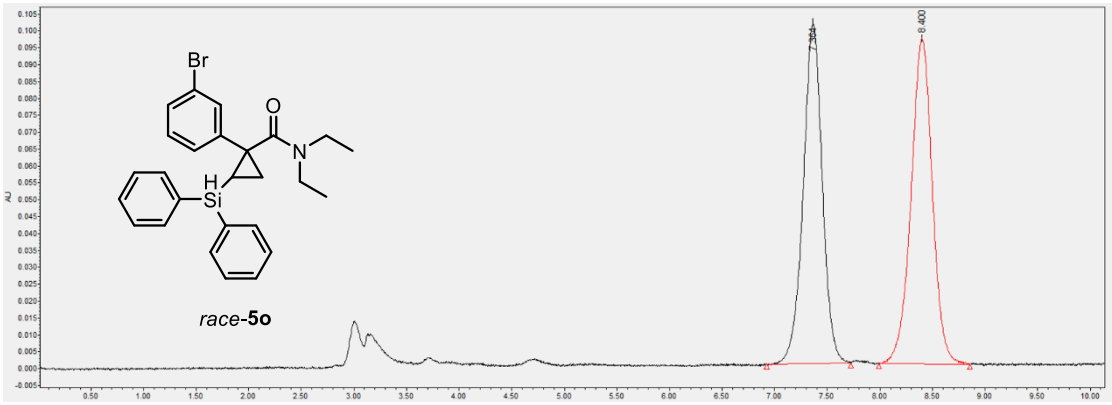
	Time/min	Area	Height	Area%
1	8.117	705222	58319	2.98
2	9.010	22993106	1447552	97.02



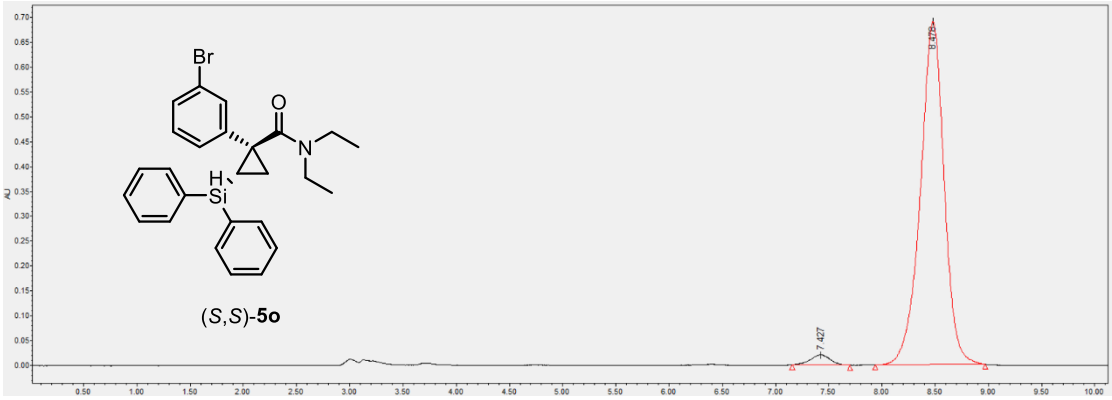
	Time/min	Area	Height	Area%
1	6.157	2034130	176974	50.21
2	6.942	2017210	159639	49.79



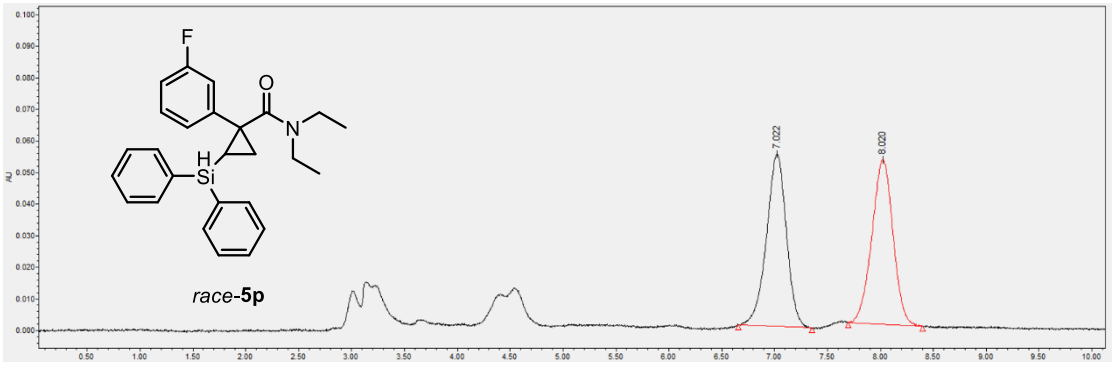
	Time/min	Area	Height	Area%
1	5.991	337561	40621	1.89
2	6.723	17478725	1537968	98.11



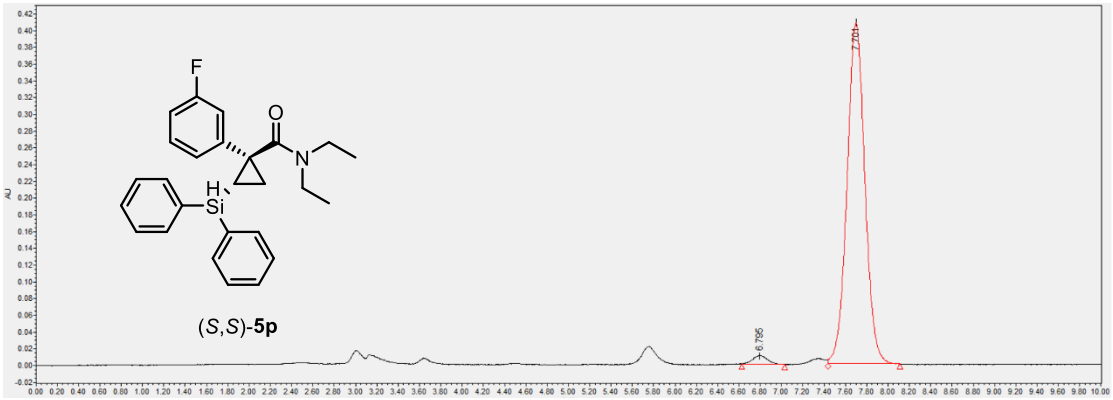
	Time/min	Area	Height	Area%
1	7.364	1266240	100920	48.30
2	8.400	1355189	96458	51.70



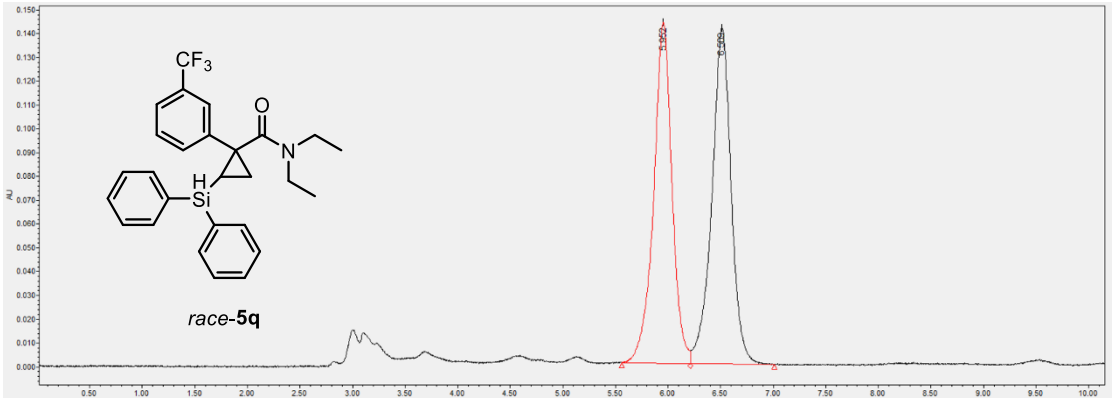
	Time/min	Area	Height	Area%
1	7.427	265760	20489	2.42
2	8.478	10697524	688638	97.58



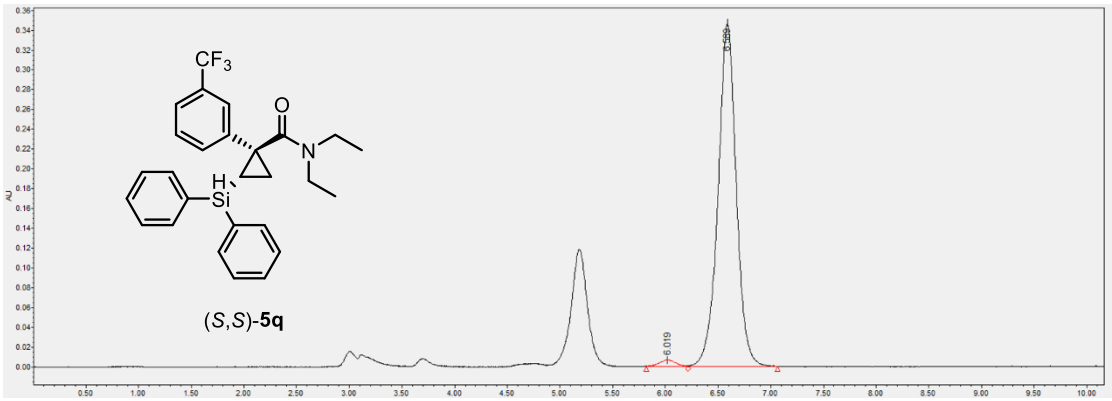
	Time/min	Area	Height	Area%
1	7.022	714220	54613	49.6
2	8.020	725794	52276	50.40



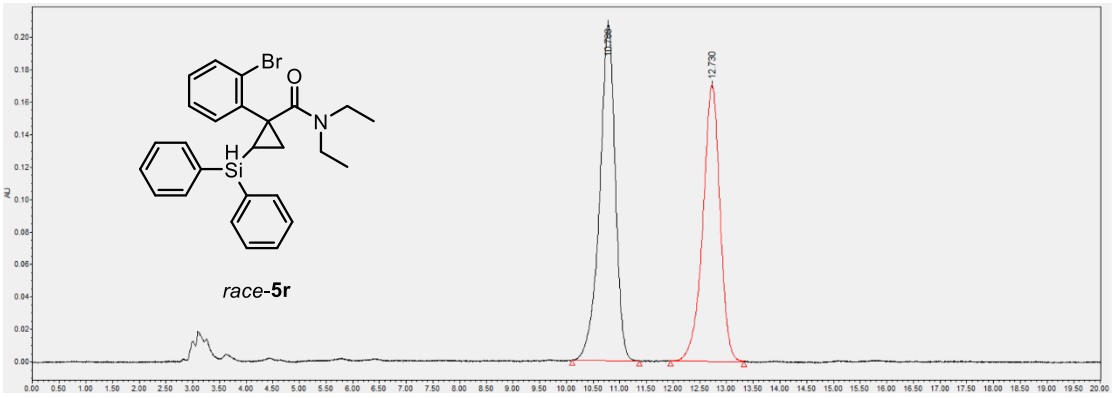
	Time/min	Area	Height	Area%
1	6.795	98019	10205	2.02
2	7.701	4743671	407415	97.98



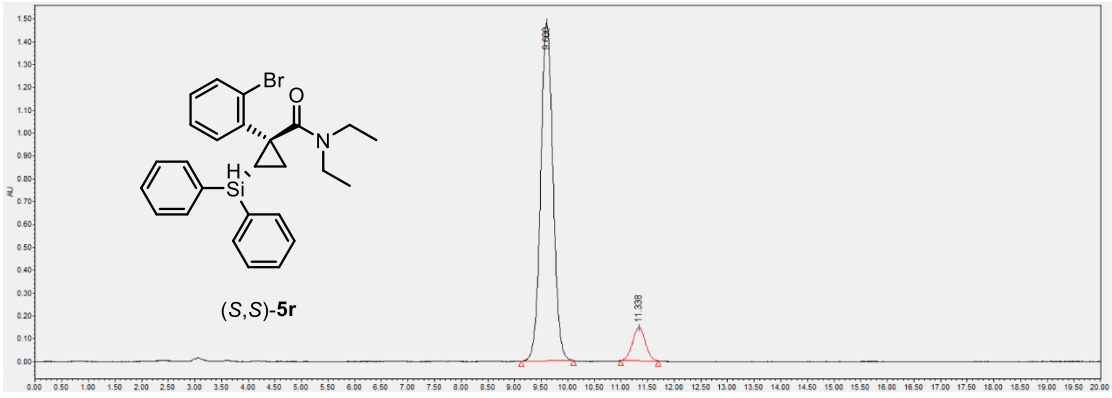
	Time/min	Area	Height	Area%
1	5.952	1738458	143186	49.05
2	6.509	1805939	141151	50.95



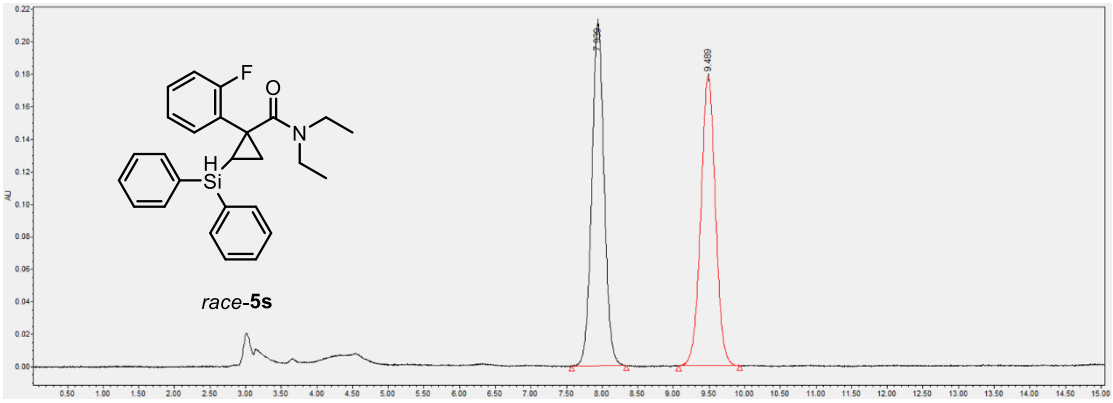
	Time/min	Area	Height	Area%
1	6.019	66940	6494	1.58
2	6.589	4166339	346568	98.42



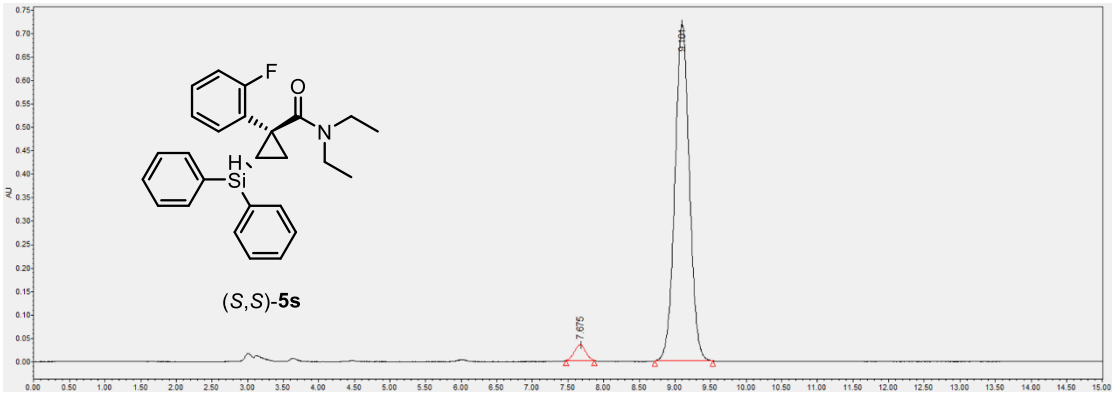
	Time/min	Area	Height	Area%
1	10.786	4192998	207163	52.42
2	12.730	3805638	170490	47.58



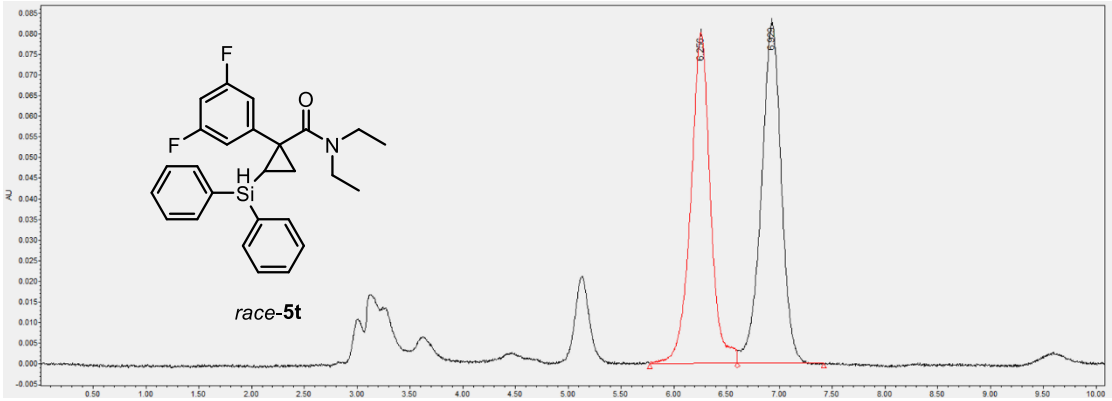
	Time/min	Area	Height	Area%
1	9.600	23701483	1481528	90.63
2	11.338	2450665	146637	9.37



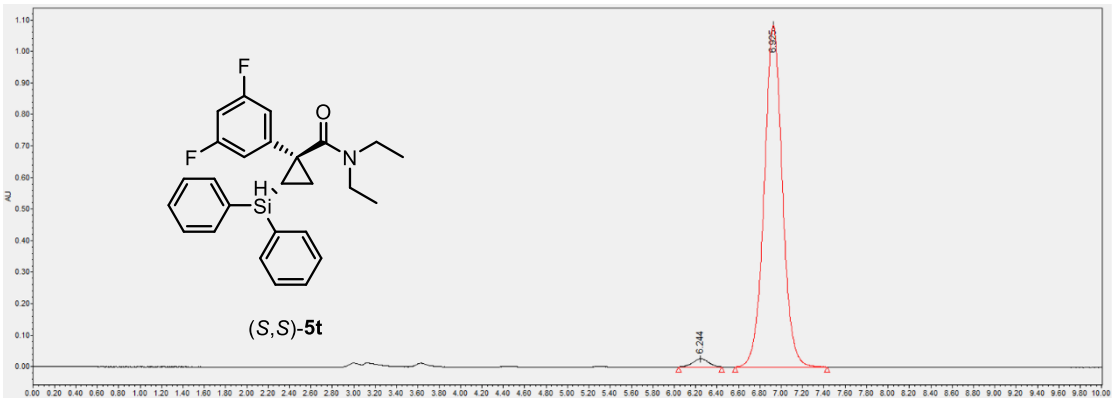
	Time/min	Area	Height	Area%
1	7.939	2537438	210983	49.98
2	9.489	2539915	177971	50.02



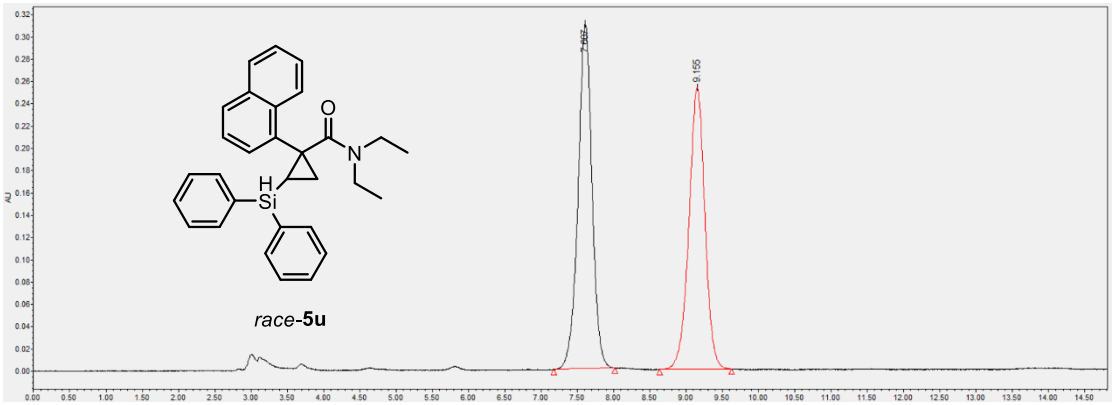
	Time/min	Area	Height	Area%
1	7.675	367183	33930	3.48
2	9.101	10174063	719013	96.52



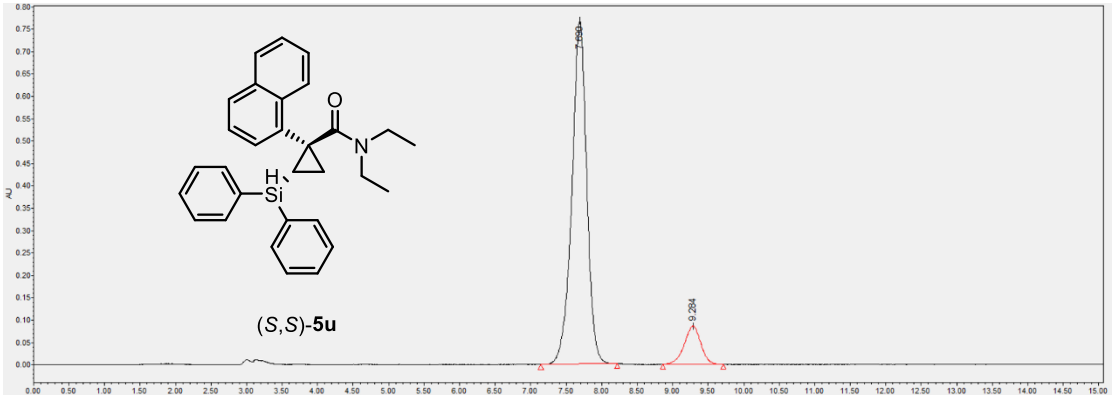
	Time/min	Area	Height	Area%
1	6.256	1035669	80074	48.79
2	6.929	1087143	82553	51.21



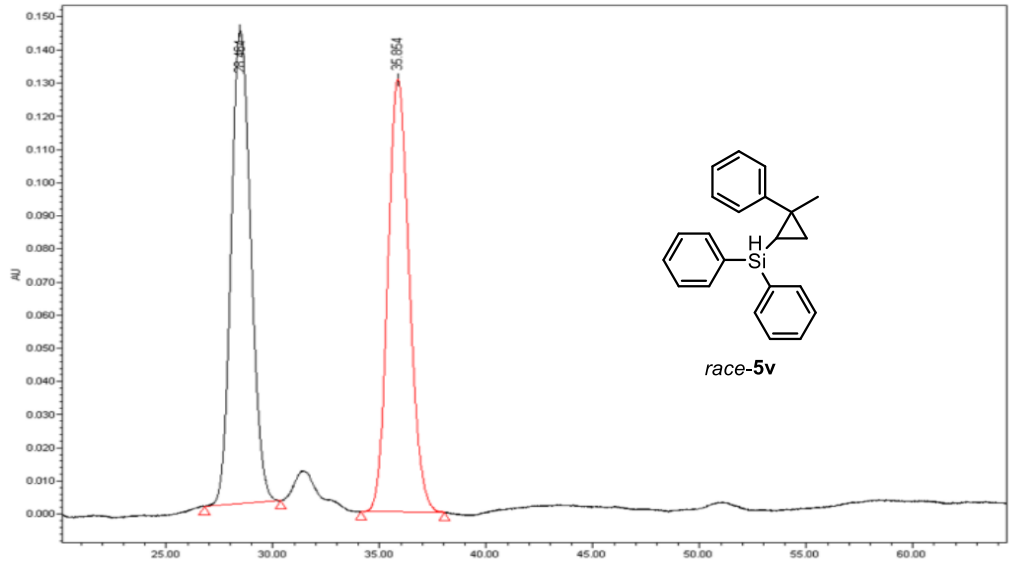
	Time/min	Area	Height	Area%
1	6.244	261164	26437	2.00
2	6.925	12805981	1083832	98.00



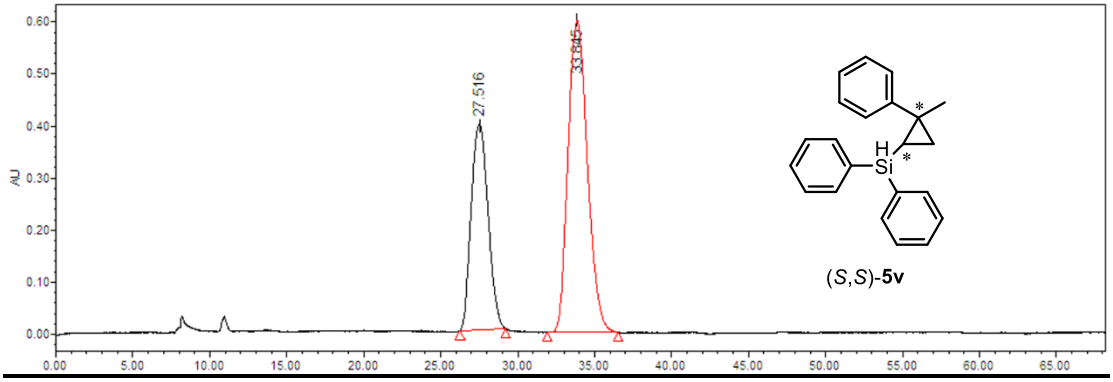
	Time/min	Area	Height	Area%
1	7.607	4136949	309303	51.56
2	9.155	3886507	253178	58.44



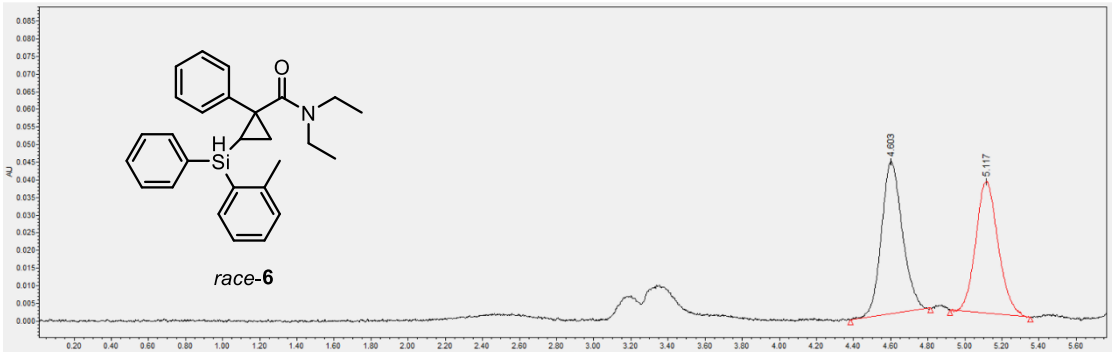
	Time/min	Area	Height	Area%
1	7.690	11164879	766531	88.99
2	9.284	1381604	85672	11.01



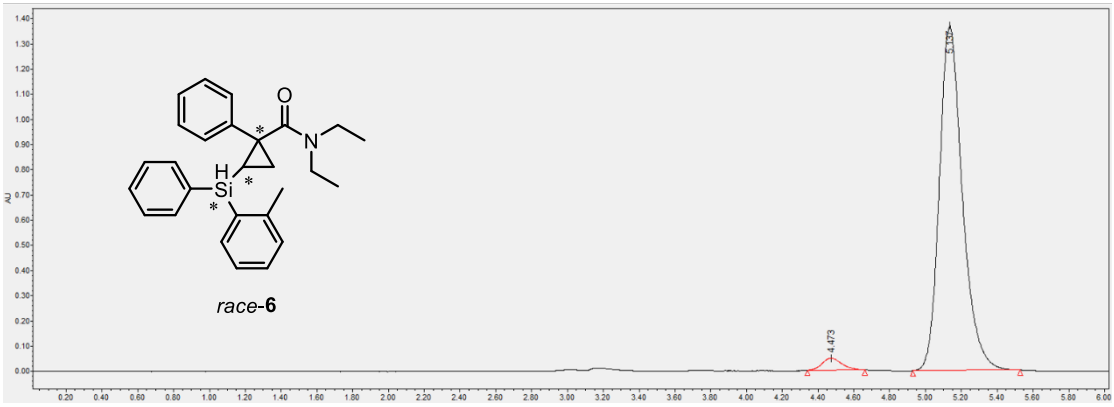
	Time/min	Area	Height	Area%
1	28.464	9094435	586631	49.94
2	35.854	9117072	426852	50.06



	Time/min	Area	Height	Area%
1	27.516	30073836	393915	36.44
2	33.845	52456555	598844	63.56

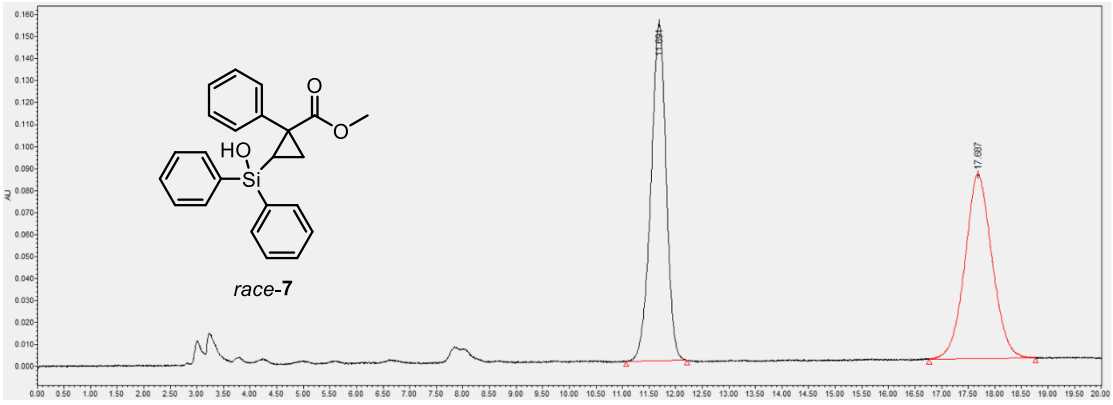


	Time/min	Area	Height	Area%
1	4.603	338618	43144	51.86
2	5.117	314293	37392	48.14



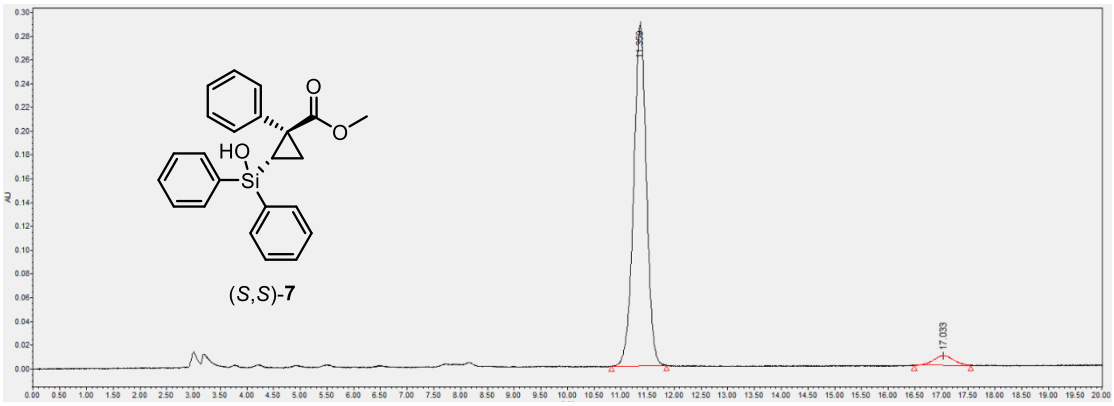
race-**6**

	Time/min	Area	Height	Area%
1	4.473	370653	48537	2.93
2	5.137	12266529	1368455	97.07



race-**7**

	Time/min	Area	Height	Area%
1	11.691	3050223	153456	50.61
2	17.687	2976185	83803	49.39



(*S*,*S*)-**7**

	Time/min	Area	Height	Area%
1	11.359	4778698	286438	95.71
2	17.033	214308	8386	4.29