Supplementary information

Organocatalytic Asymmetric Electrophilic Tandem Selenylation Semipinacol Rearrangement of 1-(1-Arylvinyl)cyclobutanols

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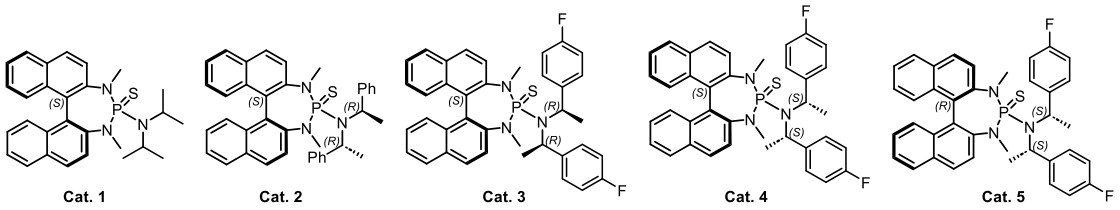
1. General Information

All reactions were performed using oven-dried (110 ℃) or flame-dried glassware equipped with a magnetic stir bar under an atmosphere of argon unless otherwise noted. All reagents were purchased from commercial suppliers (such as *TCI Company*, *Leyan* and *Energy Chemical*) and used without further purification. 5Å molecular sieve was purchased from commerical supplier Greagent (powder, ϕ 2-3mm). In addition to commercially available extra dry solvents, all solvents were purified by standard operating method. Dichloromethane (DCM) was distilled from calcium hydride, tetrahydrofuran (THF) and toluene were distilled from sodium. Thin-layer chromatography was performed with EMD silica gel 60 F254 plates eluting with solvents indicated, visualized by a 254 nm UV lamp and stained with phosphomolybdic acid (PMA).

^{1}H NMR, **^{13}C NMR**, **^{19}F NMR** and **^{77}Se NMR** spectra were obtained on Bruker AM-400. Chemical shifts (δ) were quoted in ppm relative to tetramethylsilane or residual protio solvent as internal standard ($CDCl_3$: 7.26 ppm for **^{1}H NMR**, 77.16 ppm for **^{13}C NMR**): s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectral analysis (HRMS) data were measured on a Buker impact II (Q-TOF) mass spectrum by means of the ESI technique. Crystallographic data was obtained from a XtaLAB Synergy R, HyPix diffractometer. Optical rotations were measured on a Anton Paar. The enantiomeric excesses (er) of the products were determined by high performance liquid chromatography (HPLC) analysis employing Daicel CHIRALPAK® AD-H or supercritical fluid chromatography (SFC, ACQUITY UPC^2 system of Waters) analysis employing Daicel Chiralcel OD-3, AD-3, IG-3 and IC-3.

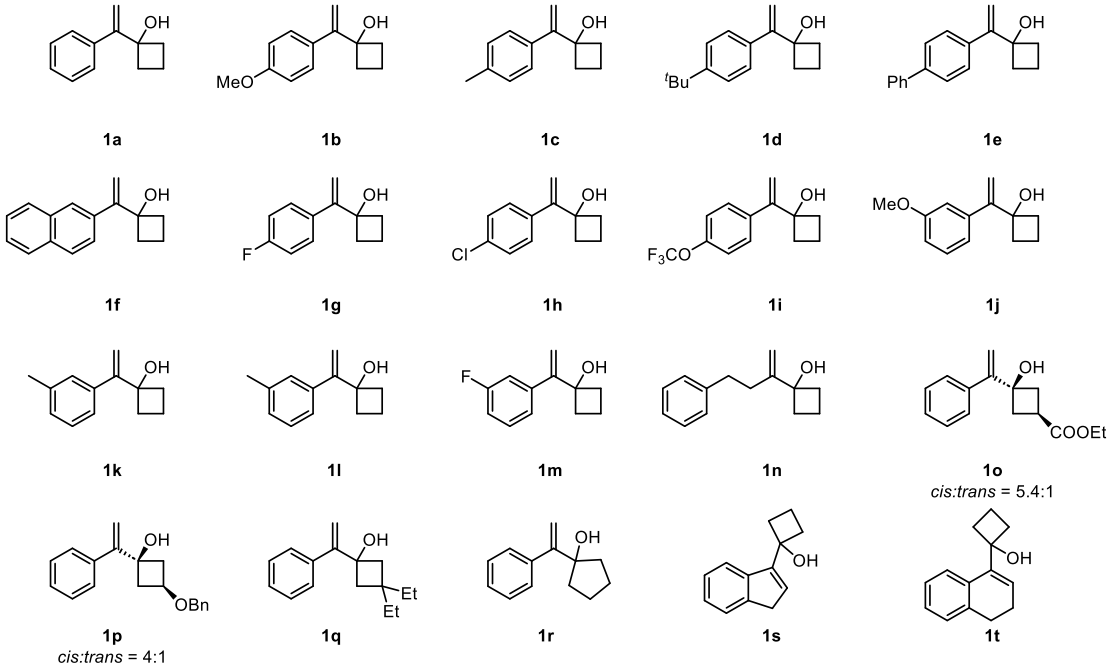
2. The preparation of catalysts



Cat. 1[1], **Cat. 2-Cat. 5**[2] are known compounds and the analytical data (**^{1}H NMR** and **^{13}C NMR**) match with the literature.

3 The preparation of substrates

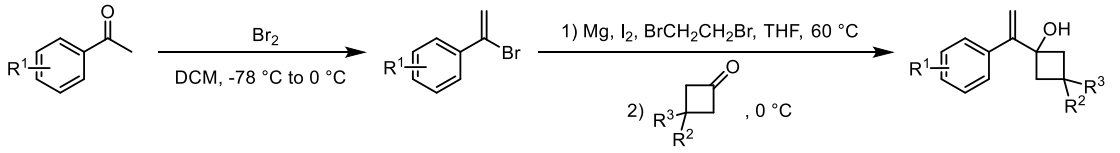
Substrates covered in this article:



1a-1h[3], **1j- 1n**[3], **1p**[4], **1r**[5], **1s**[6] and **1t**[7] and are known compounds and the analytical data (**^{1}H NMR** and **^{13}C NMR**) match with the literature.

1i, 1o and **1q** are synthesized according to procedure A.

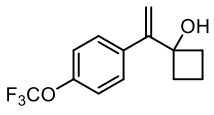
General procedure A



An oven-dried flask was equipped with a magnetic stirrer, $P(OPh)_3$ (1.1 equiv) was added and dissolved in dried DCM (0.6 M), and the solution was cooled to -78 ℃， Br_2 (1.2 equiv) was added slowly over 10 min, and the mixture was stirred for a further10 min at -78 ℃.Then, Et_3N (1.3 equiv) was added dropwise and stirred for additional 10 min at -78 ℃. A solution of acetophenone (1.0 equiv) in DCM (0.2 M) was then added dropwise and the mixture was stirred overnight at room temperature. The

reaction was quenched with saturated aqueous $Na_2S_2O_3$ (50 mL) and extracted twice with DCM (30 mL). The organic layer was extracted with brine (50 mL) and dried over Na_2SO_4, filtered and concentrated in *vacuo*. The crude product was purified by flash column chromatography on silica gel to give the corresponding pure product.

A crystal of iodine, 1,2-dibromoethane (0.4 equiv) was added to a suspension of Mg (3.0 equiv) in THF (0.1 M) under Ar in an oven-dried two-necked flask. A solution of (1-bromovinyl)arene (1.0 equiv) was then added dropwise and the mixture was stirred for 1 h at 60 ℃. The reaction mixture was then cooled to 0 ℃, a solution of the corresponding cyclobutanone (1.4 equiv) was added, and stirring was continued at room temperature for 1 h. After completion of the reaction (monitored by TLC), the mixture was subsequently quenched with saturated aqueous NH_4Cl (2 mL). The suspension was filtered through a Celite pad. The organic layer of the filtrate was separated and the aqueous layer was extracted twice with EA (30 mL), the combined organic layer was extracted with brine (20 mL) and dried over Na_2SO_4, filtered and concentrated in *vacuo*. The crude product was purified via column chromatography on silica gel.



1i

General procedure A, $P(OPh)_3$ (22.0 mmol, 1.1 equiv), Br_2 (24 mmol, 1.2 equiv), Et_3N (26.0 mmol, 1.3 equiv), 1-(4-(trifluoromethoxy)phenyl)ethan-1-one (20.0 mmol, 1.0 equiv) were added in sequence and the mixture was stirred overnight at room temperature. The crude product was purified by flash column chromatography on silica gel (petroleum ether) to afford 1-(1-bromovinyl)-4-(trifluoromethoxy)benzene as a yellow oil (4.02 g, 49% yield), R_f = 0.68 (petroleum ether).

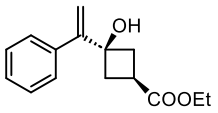
1-(1-bromovinyl)-4-(trifluoromethoxy)benzene is easily to degraded, proceed immediately to the next step. A crystal of iodine, Mg (15.0 mmol, 3.0 equiv), $BrCH_2CH_2Br$ (2.0 mmol, 0.4 equiv), 1-(1-bromovinyl)-4-(trifluoromethoxy)benzene (5.0 mmol, 1.0 equiv) was added in anhydrous THF (25 mL) and heated at 60 °C for1 h. The reaction mixture was then cooled to 0 ℃, a solution of the cyclobutanone (7.0 mmol, 1.4 equiv) was added, and stirring was continued at room temperature for 1 h. The crude product was purified by column chromatography on silica gel (petroleum ether : EtOAc = 30:1 to 10:1) to afford **1i** as a pale yellow oil (231 mg, 20% yield), R_f = 0.29 (petroleum ether : EtOAc = 8:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 5.38 (d, *J* = 12.4 Hz, 3H), 2.51 – 2.37 (m, 1H), 2.29 – 2.15 (m, 1H), 2.06 – 1.92 (m, 1H), 1.69 – 1.54 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.26, 148.75 (q, *J* = 1.9 Hz), 137.89, 129.14, 120.63, 120.61 (q, *J* = 257.0 Hz), 113.76, 78.12, 35.73, 13.44.

^{19}F NMR (377 MHz, $CDCl_3$) δ -57.81.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{13}F_3NaO_2$ 281.0765; found 281.0762;



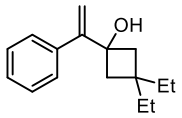
1o
cis:trans = 5.4:1

General procedure A, a crystal of iodine, Mg (17.4 mmol, 3.6 equiv), $BrCH_2CH_2Br$ (2.3 mmol, 0.4 equiv), 1-bromovinylbenzene (5.8 mmol, 1.0 equiv) was added in anhydrous THF (30 mL) and heated at 60 °C for1 h. The reaction mixture was then cooled to 0 ℃, a solution of the ethyl 3-oxocyclobutanecarboxylate (7.0 mmol, 1.2 equiv) was added, and stirring was continued at room temperature for 1 h. The crude product was purified by column chromatography on silica gel (petroleum ether : EtOAc = 20:1 to 8:1) to afford **1o** as a pale yellow oil (409 mg, 29% yield). A mixture of *cis* and *trans* diastereoisomers (*cis : trans* = 5.4:1) R_f = 0.27 (petroleum ether : EtOAc = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.2 Hz, 2H), 7.36 – 7.28 (m, 3H), 5.42 (d, *J* = 6.4 Hz, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.02 (s, 1H), 2.81 – 2.67 (m, 3H), 2.56 – 2.44 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). (*cis* diastereoisomer)

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.30, 151.28, 138.79, 128.34, 127.79, 127.71, 113.85, 74.62, 61.03, 39.59, 30.26, 14.32. (*cis* diastereoisomer)

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{18}O_3$ 269.1154; found 269.1151;



1q

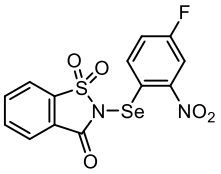
General procedure A, a crystal of iodine, Mg (7.5 mmol, 3.0 equiv), $BrCH_2CH_2Br$ (1.0 mmol, 0.4 equiv), 1-bromovinylbenzene (2.5 mmol, 1.0 equiv) was added in anhydrous THF (12 mL) and heated at 60 °C for1 h. The reaction mixture was then cooled to 0 ℃, a solution of the 3,3-diethylcyclobutanone (3.0 mmol, 1.2 equiv) was added, and stirring was continued at room temperature for 1 h. The crude product was purified by column chromatography on silica gel (petroleum ether : EtOAc = 30:1) to afford **1q** as a yellow oil (295 mg, 51% yield), R_f = 0.31 (petroleum ether : EtOAc = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 2H), 7.34 – 7.23 (m, 3H), 5.34 (d, *J* = 5.2 Hz, 2H), 2.27 – 2.18 (m, 2H), 2.06 – 1.95 (m, 2H), 1.89 (s, 1H), 1.64 (q, *J* = 7.6 Hz, 2H), 1.32 (q, *J* = 7.6 Hz, 2H), 0.78 (t, *J* = 7.6 Hz, 3H), 0.68 (t, *J* = 7.6 Hz, 3H)

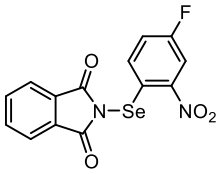
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.41, 139.20, 128.25, 127.65, 127.59, 113.16, 73.40, 44.86, 33.64, 30.70, 30.13, 8.23, 8.14.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{22}NaO$ 253.1568; found 253.1569;

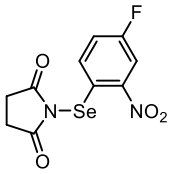
4. The preparation of selenylating reagents



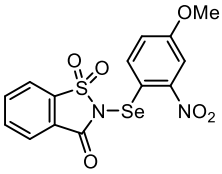
2a



2b



2c



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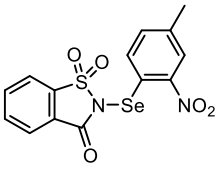
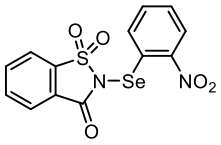
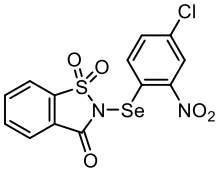


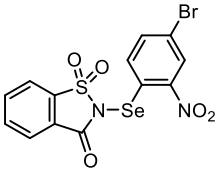
2e



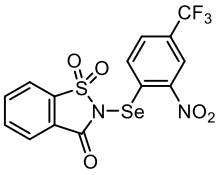
2f



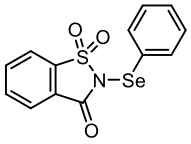
2g



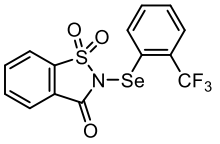
2h



2i



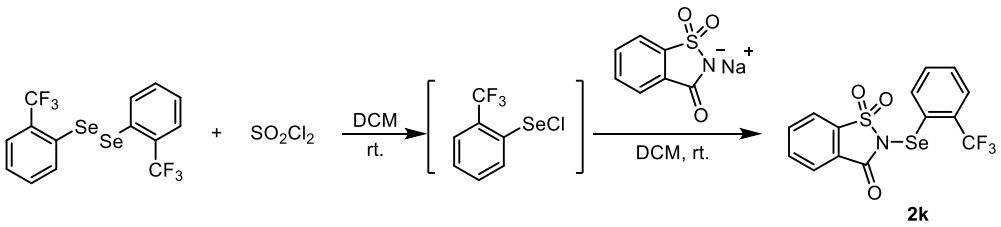
2j



2k

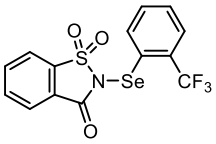
2a-2b[2]**, 2c**[8]**, 2d-2i**[2] **and 2g**[9] are known compounds and the analytical data (^{1}H NMR, ^{13}C NMR and ^{77}Se NMR) match with the literature.

The preparation of **2k**



2k

To an oven-dried 25 mL flask was added 1,2-bis(2-(trifluoromethyl)phenyl)diselane (1 mmol, 1.0 equiv). Under argon, dried DCM (6 mL) was added, and then, sulfuryl chloride (1.0 mmol, 1.0 equiv) was added slowly. After addition, the mixture was stirred at room temperature for 15 minutes. After the volatiles have been removed under reduced pressure, this mixture was dissolved in dried DCM (4 mL) and added to a suspension of sodium saccharin (2.5 mmol, 2.5 equiv.) in dried DCM (6 mL) under argon. While stirring for 3 h, the orange mixture gradually faded into pale yellow. After completion, the reaction mixture was filtered through celite and concentrated in *vacuo*. The crude product was recrystallized with petroleum ether and tetrahydrofuran to obtain the pure product (242 mg, 60% yield).



2k

^{1}H NMR (400 MHz, $CDCl_3$)δ 8.16 (d, *J* = 7.5 Hz, 1H), 8.01 (d, *J* = 7.4 Hz, 1H), 7.98 – 7.85 (m, 2H), 7.69 (d, *J* = 6.0 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.50 – 7.34 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.73, 139.09, 135.67, 134.67, 133.22, 130.81, 129.76, 128.37, 128.19, 127.43, 127.41 (q, *J* = 5.4 Hz), 126.25, 124.33 (q, *J* = 274.3 Hz), 121.89.

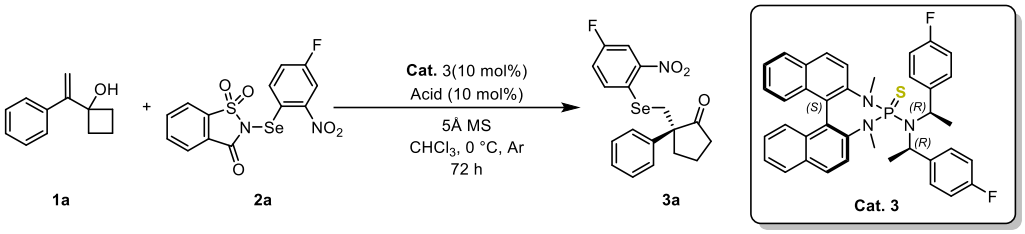
^{19}F NMR (377 MHz, $CDCl_3$) δ -59.03.

^{77}Se NMR (76 MHz, $CDCl_3$) δ 695.89.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{14}H_8F_3NNaO_3Se$ 429.9234; found 429.9235;

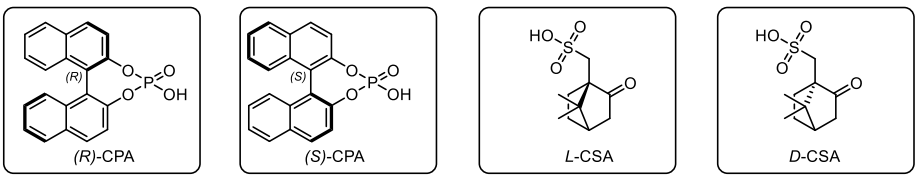
5. Screening of chiral acid catalysts and Lewis base catalysts

Table S1 Screening of chiral acid catalysts[a]



entry	acid	yield (%)	er
1	*(R)*-CPA	<10	54:46
2	*(S)*-CPA	<10	54:46
3	*L*-CSA	26	73:27
4	*D*-CSA	20	70:30

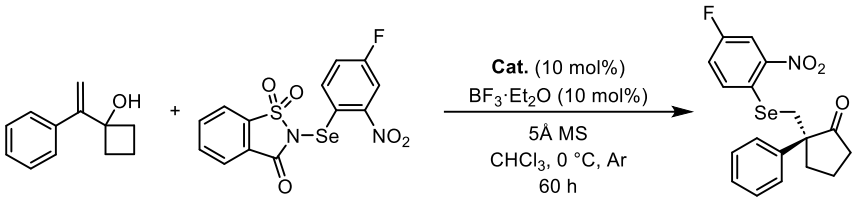
[a]Reactions conditions: unless stated otherwise, the reaction was performed with **1a** (0.05 mmol, 1.0 equiv), **2a** (0.55 mmol, 1.1 equiv), **Cat.3** (0.005 mmol, 0.1 equiv), acid (0.005 mmol, 0.1 equiv), and 5Å MS (15 mg) in CHCl3 (1.0 mL) at 0°C under Ar. Isolated yields are shown. The er values were determined by SFC.



We selected **1a** as the model substrate, **2a** was chosen as the selenylating reagent, **Cat. 3** as the catalyst, *(R)*-CPA (*(R)*-(-)-1,1'-Binaphthyl-2,2'-diyl hydrogenphosphate) as the acid, 5Å MS as an additive, and $CHCl_3$ as the solvent. The desired product **3a** was obtained at 0 °C under argon with a yield of less than 10% yield and 54:46 er (see Table S1, entry 1). The same result was obtained when *(S)*-CPA (*(S)*-(+)-1,1'-Binaphthyl-2,2'-diyl hydrogenphosphate) was used as the acid (see Table S1, entry 2). Switching to

camphorsulfonic acid *(L/D*-CSA) resulted in slight improvements in both yield and enantioselectivity. Interestingly, *L*-CSA afforded a marginally higher er value (73:27 er, see Table S1 entry 3) than *D*-CSA (70:30 er, see Table S1, entry 4), which demonstrates that the chirality of the acid catalysts can affect the enantioselectivity of the product. However, considering that the yield and enantioselectivity of the product are suboptimal relative to the current standard conditions, adopting it remains impractical at this stage.

Table S2 Screening of Lewis base catalysts[a]



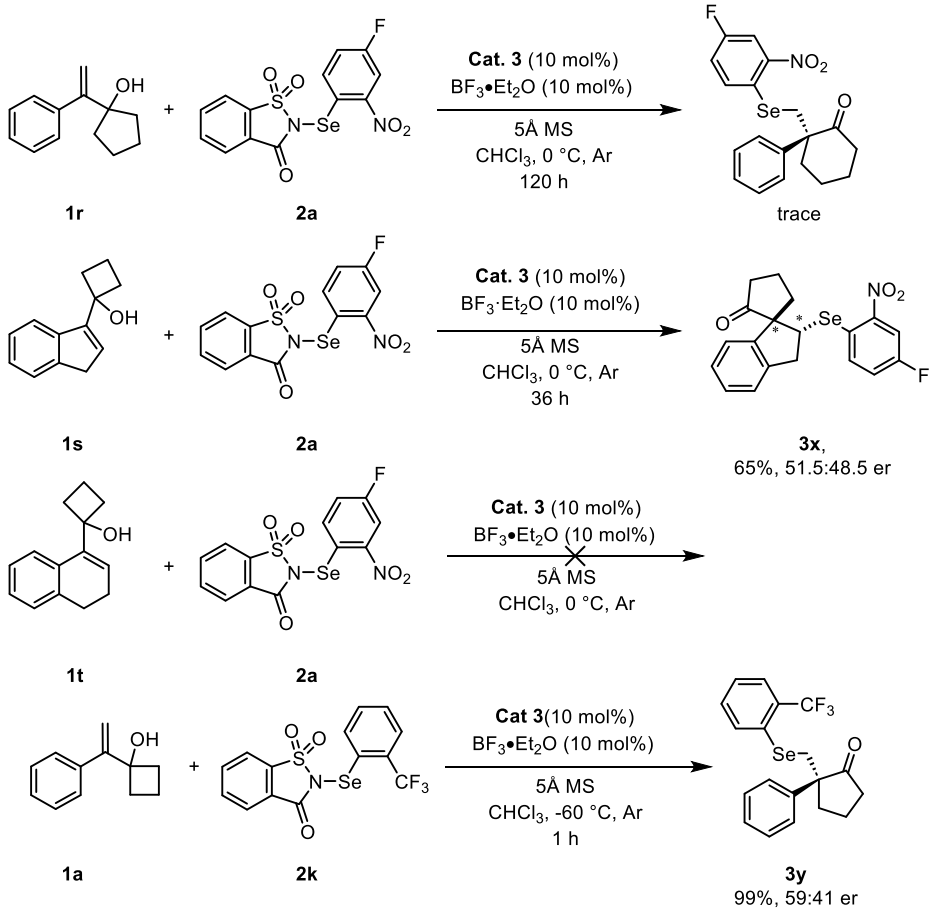
1a **2a** **3a**

entry	**Cat.**	yield (%)	er
1	**Cat. 3**	91	95:5
2	**Cat. 4**	71	93:7
3	**Cat. 5**	93	5:95

[a]Reactions conditions: unless stated otherwise, the reaction was performed with **1a** (0.05 mmol, 1.0 equiv), **2a** (0.55 mmol, 1.1 equiv), **Cat.** (0.005 mmol, 0.1 equiv), acid (0.005 mmol, 0.1 equiv), and 5Å MS (15 mg) in CHCl3 (1.0 mL) at 0°C under Ar. Isolated yields are shown. The er values were determined by SFC.

we performed the reaction with (*R,S,S*)-**Cat. 5** and observed the product in 93% yield with 5:95 er (see Table S2, entry 3). Regarding the diastereomeric catalysts (*S,R,R*)-**Cat.3** and (*S,S,S*)-**Cat.4**, we observed that **Cat.4** exhibits slightly lower enantioselectivity (93:7 er, see Table S2, entry 2)compared to **Cat.3** (95:5 er, see Table S2, entry 1), but does not affect the absolute configuration of the product **3a**. Meanwhile, **Cat.5** serves as the enantiomer of **Cat.3**, which delivers the enantiomer of the product **3a** but does not affect the enantioselectivity. These results suggest that the chirality of the amino moiety solely affects the enantioselectivity of the product and has no effect on the absolute configuration of the product, while the absolute configuration of the product is determined by the chirality of the BINAM framework.

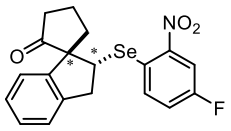
6. Some unsuccessful examples



We have tested **1s-1t** as the corresponding substrates, **2a** as the selenylating reagent, **Cat. 3** as the catalyst, $BF_3{\cdot}Et_2O$ as the acid, 5Å MS as an additive, and $CHCl_3$ as the solvent. The corresponding products were obtained at 0 °C under argon. Unfortunately, these substrates did not produce satisfactory results.

Compared to model substrate **1a**, the reactivity of compound **1r** is significantly lower, due to the limited driving force for cyclopentane ring expansion. The reaction proceeds for five days at 0°C, yielding only trace amounts of the desired rearrangement product. Using compound **1s** as the substrate, the desired product **3x** was obtained in 65% yield with only 51.5:48.5 er. However, no reaction occurred using compound **1t** as the substrate.

A new selenylating reagent containing an ortho-trifluoromethyl-substituted aryl group was also utilized in this reaction. However, our experimental results indicate that the selenylating reagent containing $-CF_3$ is excessively reactive. Even when the temperature was lowered to -60°C, the reaction remained rapid. The desired product **3y** was obtained in 99% yield with only 59:41 er. We guessed that the oxygen lone pairs from the nitro group play a crucial stabilizing role by interacting with the empty p-orbital of the selenium atom, which can effectively suppress the racemization process of enantioenriched seleniranium ion intermediate and achieves satisfactory enantiocontrol.



3x

(*R*)-2'-((4-fluoro-2-nitrophenyl)selanyl)-2',3'-dihydro-2'λ^3-spiro[cyclopentane-1,1'-inden]-2-one

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.66 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.33 – 7.15 (m, 2H), 3.87 (dd, *J* = 10.0, 8.0 Hz, 1H), 3.71 (dd, *J* = 16.4, 10.0 Hz, 1H), 3.49 (dd, *J* = 15.6, 8.0 Hz, 1H), 2.52 – 2.16 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 217.79, 160.47 (d, *J* = 250.4 Hz), 149.05 (d, *J* = 7.8 Hz), 145.10, 142.73, 132.38 (d, *J* = 7.4 Hz), 128.12, 127.46, 127.10 (d, *J* = 3.7 Hz), 124.88, 122.45, 121.53 (d, *J* = 21.5 Hz), 113.51 (d, *J* = 26.2 Hz), 64.92, 49.87, 40.42, 37.89, 35.52, 20.43.

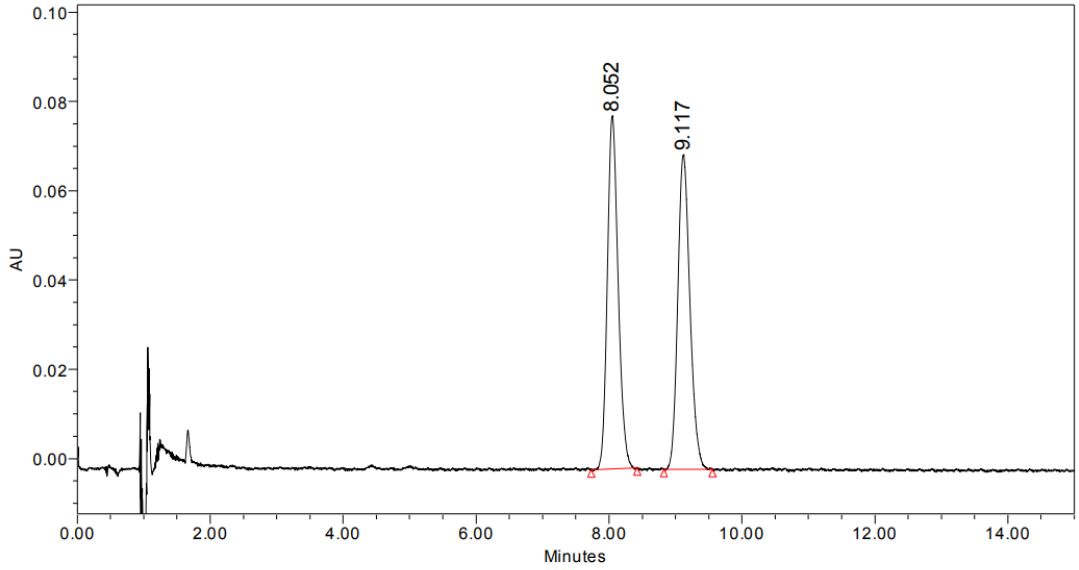
^{19}F NMR (377 MHz, $CDCl_3$) δ -113.83.

^{77}Se NMR (76 MHz, $CDCl_3$) δ 378.37.

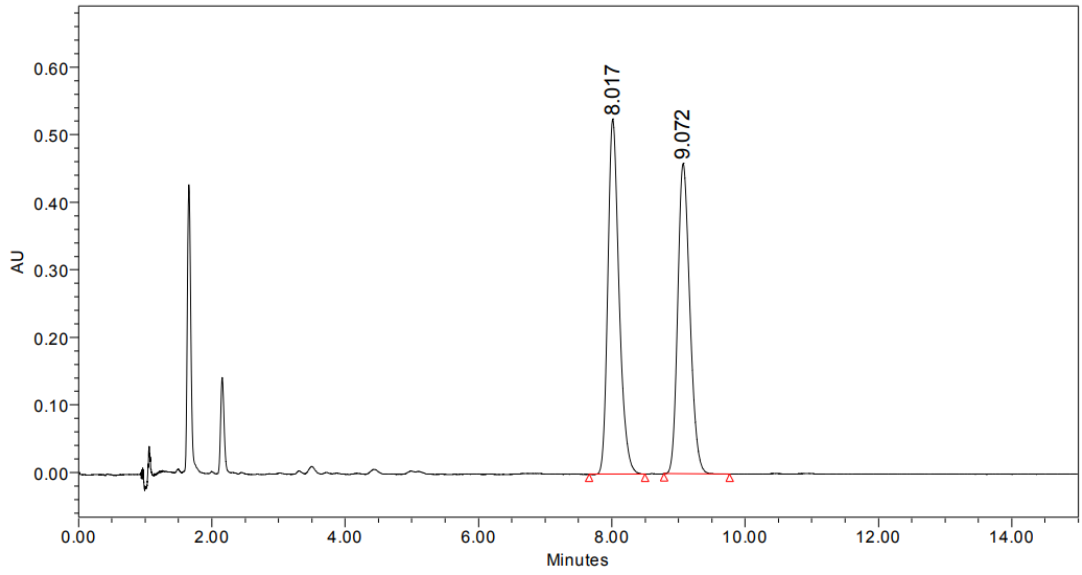
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{16}FNNaO_3Se$ 428.0172; found 428.0177;

SFC (Daicel Chiralpak® IC-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 8.02 min, t_R (minor) = 9.07 min, 51.5:48.5 er.

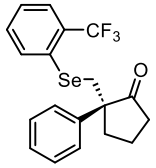
Specific Rotation: $[\alpha]_D^{20}$= -0.80 (c = 1.0, $CHCl_3$)



	RT (min)	Area	% Area	Height (μV)	Channel Name
1	8.052	889111	49.91	79113	254.0nm
2	9.117	892188	50.09	70420	254.0nm



	RT (min)	Area	% Area	Height (μV)	Channel Name
1	8.017	6142566	51.43	525736	254.0nm
2	9.072	5800510	48.57	459855	254.0nm



3y

(*R*)-2-phenyl-2-(((2-(trifluoromethyl)phenyl)selanyl)methyl)cyclopentan-1-one

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.44 – 7.40 (m, 2H), 7.37 – 7.22 (m, 5H), 3.49 (d, *J* = 12.0 Hz, 1H), 3.30 (d, *J* = 12.0 Hz, 1H), 2.76 – 2.67 (m, 1H), 2.44 – 2.14 (m, 3H), 2.03 – 1.91 (m, 1H), 1.85 – 1.71 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 217.85, 138.19, 134.86, 132.09, 131.53 (q, *J* = 30.3 Hz), 130.37 (q, *J* = 1.4 Hz), 128.97, 127.74, 126.88, 126.81, 126.73 (q, *J* = 10.3 Hz), 123.95 (q, *J* = 274.3 Hz), 57.74, 38.42, 37.45, 33.79, 18.60.

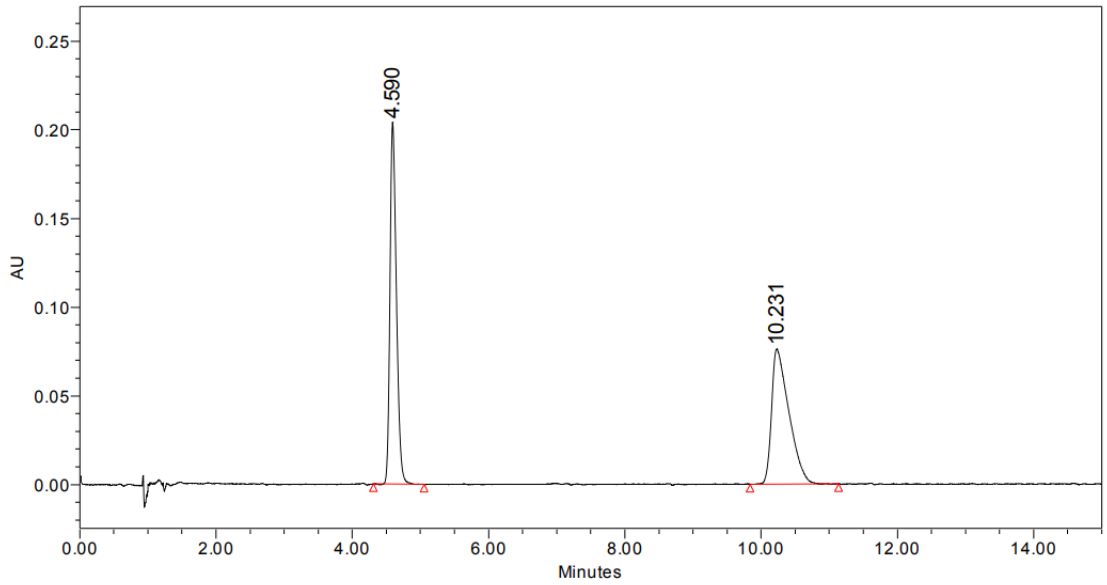
^{19}F NMR (377 MHz, $CDCl_3$) δ -60.68.

^{77}Se NMR (76 MHz, $CDCl_3$) δ 260.71.

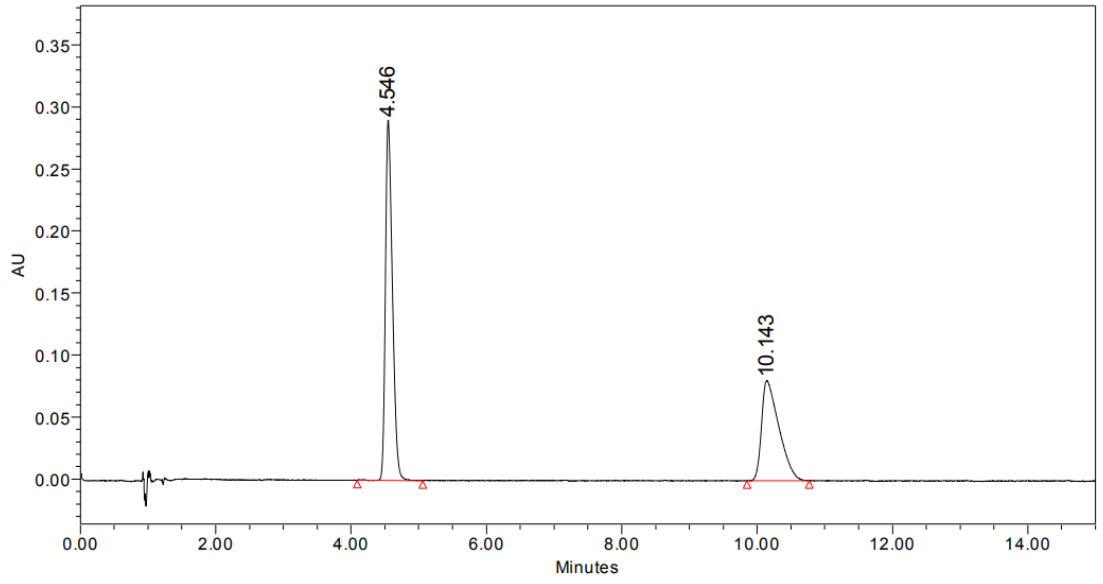
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{17}F_3NaOSe$ 421.0289; found 421.0290;

SFC (Daicel Chiralpak® IG-3, 10% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 4.55 min, t_R (minor) = 10.14 min, 59:41 er.

Specific Rotation: $[\alpha]_D^{20}$= -5.17 (c = 0.4, $CHCl_3$)

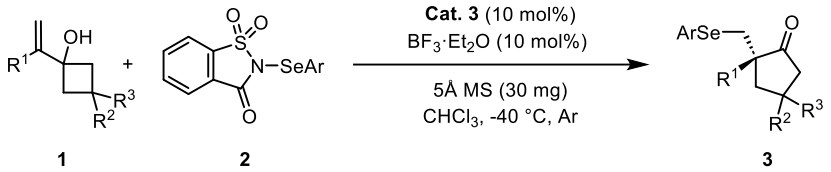


	RT (min)	Area	% Area	Height (μV)	Channel Name
1	4.590	1337686	49.91	203957	254.0nm
2	10.231	1342417	50.09	76028	254.0nm



	RT (min)	Area	% Area	Height (μV)	Channel Name
1	4.546	2079646	59.28	289966	254.0nm
2	10.143	1428589	40.72	80545	254.0nm

7. Enantioselective electrophilic selenylation/semipinacol rearrangement of 1-(1-arylvinyl)cyclobutanols



1 **2** **3**

General procedure B

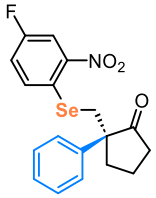
Activation of molecular sieves: 5Å MS (white powder, purchased from Energy Chemical®) was activated by placing the powder under vacuum and heating with a heat gun for 5 min. The activated 5Å MS was used immediately.

Purification and storage of chloroform: $CHCl_3$ is purified by a literature method[10] in order to remove EtOH and H_2O. The distilled $CHCl_3$ is stored in the dark with activated spherical 4Å MS under Ar, which is stable for several months without decomposition. Freshly distilled $CHCl_3$ has the same odor as DCM. If there is a foul odor, stop using it immediately!

Enantioselective electrophilic selenylation/semipinacol rearrangement of allyl alcohol: An oven-dried tube charged with **1** (0.1 mmol, 1.0 equiv), **2** (0.11 mmol, 1.1 equiv), **Cat. 3** (6.3 mg, 0.01 mmol, 0.1 equiv) and activated 5Å MS (30.0 mg) was evacuated and refilled three times with argon. Distilled $CHCl_3$ (2.0 mL) was added into the reaction system at the appropriate temperature. Subsequently, $BF_3 \cdot Et_2O$ (1.2 μL, 0.1 equiv) was added to the system using microliter syringe. The resulting mixture was then stirred for 2-4 days. After the reaction was completed, the crude product was immediately purified by column chromatography on silica gel to afford the corresponding product **3**. The er was determined by HPLC or SFC.

Synthesis of racemic samples: Racemic samples were afforded by using *(rac)*-**Cat. 1** as catalyst.

8. Product purification/characterization data



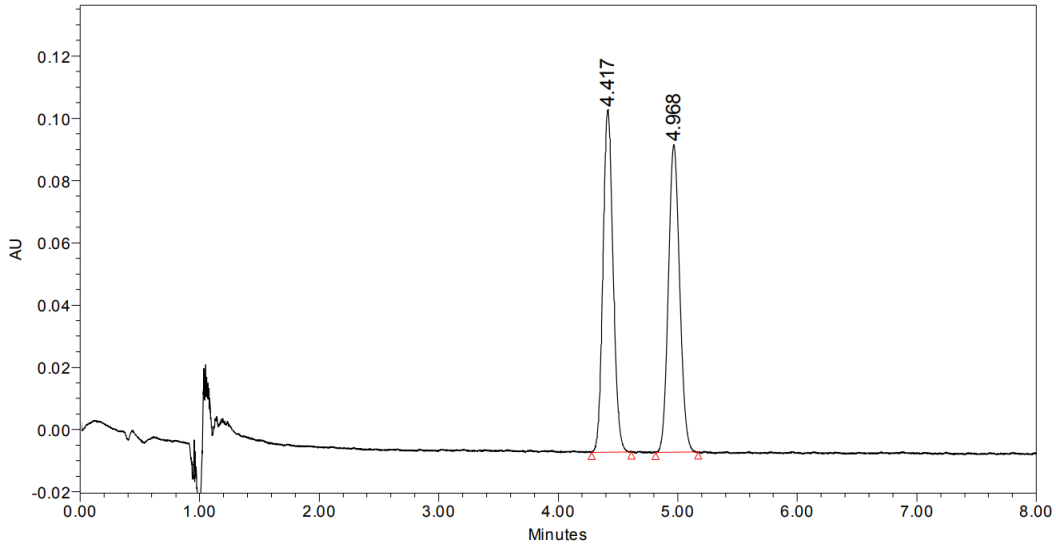
3a

***(R)*-2-(((4-fluoro-2-nitrophenyl)selanyl)methyl)-2-phenylcyclopentan-1-one (3a)**

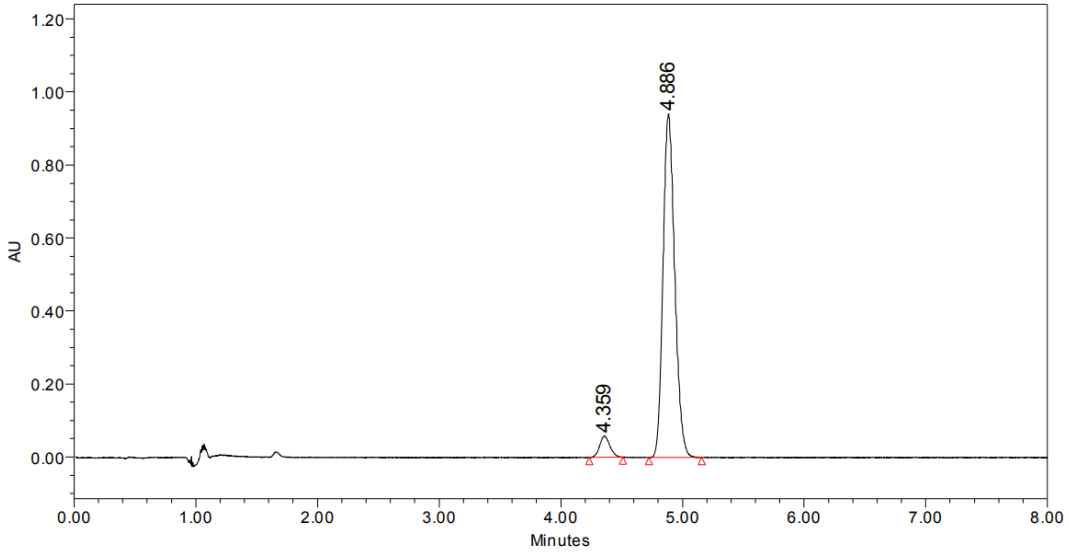
General procedure B, the reaction of **1a** (17.4 mg, 0.10 mmol, 1.0 equiv), **2a** (44.1 mg, 0.11 mmol, 1.1 equiv), **Cat. 3** (6.3 mg, 0.01 mmol, 0.1 equiv), $BF_3 \cdot Et_2O$ (1.2 μL, 0.01 mmol, 0.1 equiv) and activated 5Å MS (30.0 mg) in distilled $CHCl_3$ (2.0 mL) was stirred at -40 ℃ for 48 h. The mixture was purified by preparative thin layer chromatography (petroleum ether : DCM = 3:5) to afford **3a** as a yellow solid (35.3 mg, 91% yield, 95:5 er), R_f = 0.56 (petroleum ether : DCM = 3:5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J = 8.4, 2.8 Hz, 1H), 7.47 – 7.39 (m, 3H), 7.37 – 7.31 (m, 2H), 7.30 – 7.25 (m, 1H), 7.24 – 7.17 (m, 1H), 3.49 (d, J = 11.6 Hz, 1H), 3.18 (d, J = 11.6 Hz, 1H), 2.91 – 2.82 (m, 1H), 2.44 – 2.24 (m, 2H), 2.21 – 2.10 (m, 1H), 2.05 – 1.95 (m, 1H), 1.90 – 1.76 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 217.46, 160.04 (d, J = 249.0 Hz), 147.58 (d, J = 7.9 Hz), 137.29, 131.21 (d, J = 7.1 Hz), 129.12, 127.98, 127.76 (d, J = 3.6 Hz), 126.76, 121.50 (d, J = 21.3 Hz), 113.30 (d, J = 26.1 Hz), 56.66, 36.96, 36.37, 34.04, 18.54.
^{19}F NMR (377 MHz, $CDCl_3$) δ -115.05.
^{77}Se NMR (76 MHz, $CDCl_3$) δ 316.70.

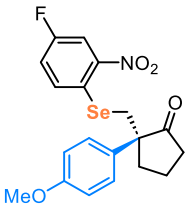
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{16}FNNaO_3Se$ 416.0177; found 416.0175;
SFC (Daicel Chiralpak® IC-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 4.89 min, t_R (minor) =4.36 min, 95:5 er.
Specific Rotation: $[\alpha]_D^{20}$= -74.60 (c = 1.0, $CHCl_3$)



	Retention Time (min)	Area	Height	% Area	Channel Name
1	4.417	647530	109920	50.01	254.0nm
2	4.968	647250	98744	49.99	254.0nm
Sum				100.0	



	Retention Time (min)	Area	Height	% Area	Channel Name
1	4.359	337935	58051	5.16	254.0nm
2	4.886	6215134	940478	94.84	254.0nm
Sum				100.0	



3b

***(R)*-2-(((4-fluoro-2-nitrophenyl)selanyl)methyl)-2-(4-methoxyphenyl)cyclopentan-1-one (3b)**

General procedure B, the reaction of **1b** (20.4 mg, 0.10 mmol, 1.0 equiv), **2a** (44.1 mg, 0.11 mmol, 1.1 equiv), **Cat. 3** (6.3 mg, 0.01 mmol, 0.1 equiv), $BF_3{\cdot}Et_2O$ (1.2 μL, 0.01 mmol, 0.1 equiv) and activated 5Å MS (30.0 mg) in distilled $CHCl_3$ (2.0 mL) was stirred at -40 ℃ for 48 h. The mixture was purified by preparative thin layer chromatography (petroleum ether : DCM = 3:5) to afford **3b** as a yellow oil (39.6 mg, 94% yield, 86:14 er), R_f = 0.44 (petroleum ether : DCM = 3:5).

^{1}H NMR (400 MHz, $CDCl_3$)δ 7.89 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.42 (dd, *J* = 9.2, 5.2 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.23 – 7.18 (m, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 3.48 (d, *J* = 11.2 Hz, 1H), 3.13 (d, *J* = 11.2 Hz, 1H), 2.86 – 2.79 (m, 1H), 2.41 – 2.22 (m, 1H), 2.14 – 2.05 (m, 1H), 2.03 – 1.94 (m, 1H), 1.88 – 1.75 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 217.48, 160.01 (d, *J* = 249.2 Hz), 159.24, 147.60 (d, *J* = 7.9 Hz), 131.30 (d, *J* = 7.2 Hz), 128.75, 128.01, 127.87 (d, *J* = 3.3 Hz), 121.47 (d, *J* = 21.4 Hz), 114.42, 113.26 (d, *J* = 26.2 Hz), 55.87, 55.35, 36.84, 36.68, 34.12, 18.48.

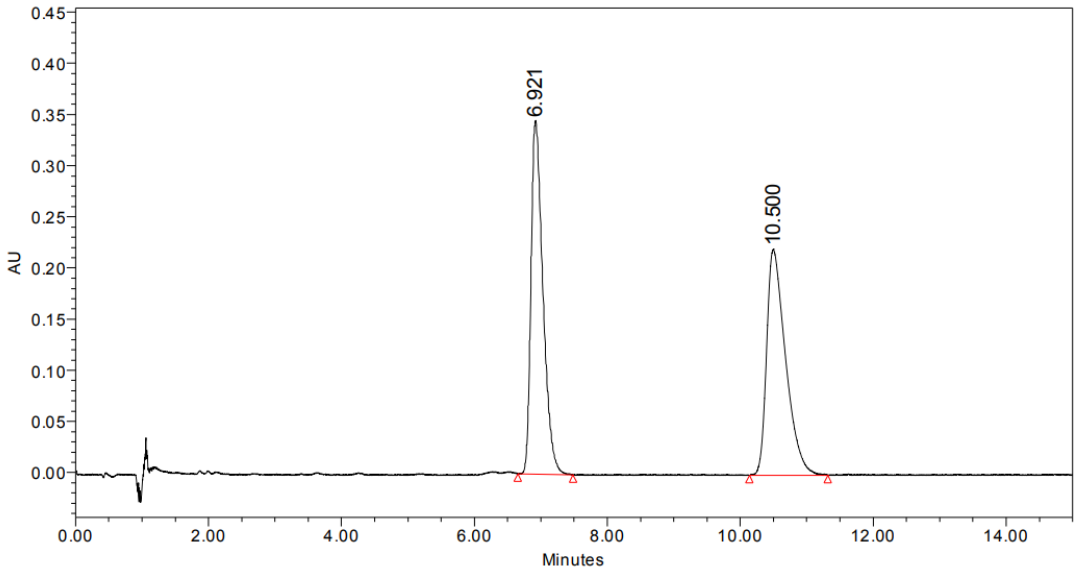
^{19}F NMR (377 MHz, $CDCl_3$) δ -115.15.

^{77}Se NMR (76 MHz, $CDCl_3$) δ 315.23.

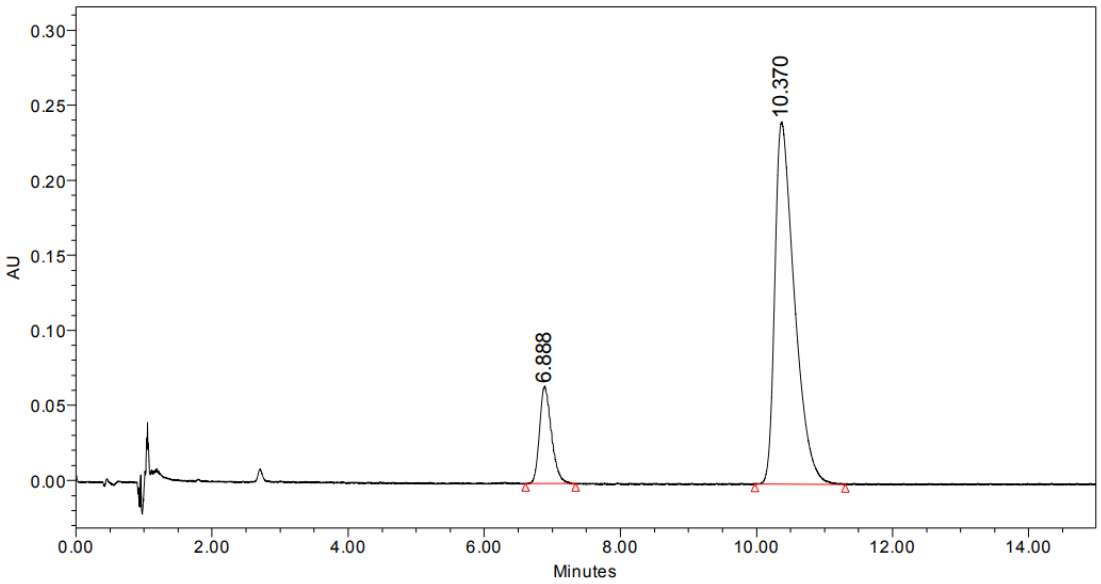
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{18}FNNaO_4Se$ 446.0283; found 446.0275;

SFC (Daicel Chiralpak® AD-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 ℃): t_R(major) = 10.37 min, t_R (minor) = 6.89 min, 86:14 er.

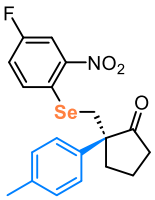
Specific Rotation: $[\alpha]_D^{20}$= -80.40 (c = 1.0, $CHCl_3$).



	Retention Time (min)	Area	Height	% Area	Channel Name
1	6.921	4348484	345290	49.89	254.0nm
2	10.500	4367424	220763	50.11	254.0nm
Sum				100.0	



	Retention Time (min)	Area	Height	% Area	Channel Name
1	6.888	796730	64788	14.17	254.0nm
2	10.370	4827793	241380	85.83	254.0nm
Sum				100.0	



3c

***(R)*-2-(((4-fluoro-2-nitrophenyl)selanyl)methyl)-2-(p-tolyl)cyclopentan-1-one (3c)**

General procedure B, the reaction of **1c** (20.4 mg, 0.10 mmol, 1.0 equiv), **2a** (44.1 mg, 0.11 mmol, 1.1 equiv), **Cat. 3** (6.3 mg, 0.01 mmol, 0.1 equiv), $BF_3{\cdot}Et_2O$ (1.2 μL, 0.01 mmol, 0.1 equiv) and activated 5Å MS (30.0 mg) in distilled $CHCl_3$ (2.0 mL) was stirred at -40 ℃ for 48 h. The mixture was purified by preparative thin layer chromatography (petroleum ether : DCM = 3:5) to afford **3c** as a yellow oil (36.5 mg, 90% yield, 94 : 6 er), R_f = 0.56 (petroleum ether : DCM = 3:5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.42 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.23 – 7.17 (m, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 3.48 (d, *J* = 11.6 Hz, 1H), 3.15 (d, *J* = 11.6 Hz, 1H), 2.90 – 2.81 (m, 1H), 2.43 – 2.22 (m, 5H), 2.17 – 2.06 (m, 1H), 2.03 – 1.92 (m, 1H), 1.87 – 1.73 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 217.52, 160.02 (d, *J* = 249.2 Hz), 147.56 (d, *J* = 7.9 Hz), 137.82, 134.06, 131.26 (d, *J* = 7.2 Hz), 129.82, 127.87 (d, *J* = 3.3 Hz), 126.65, 121.46 (d, *J* = 21.5 Hz), 113.24 (d, *J* = 26.3 Hz), 56.29, 36.87, 36.51, 34.01, 21.05, 18.51.

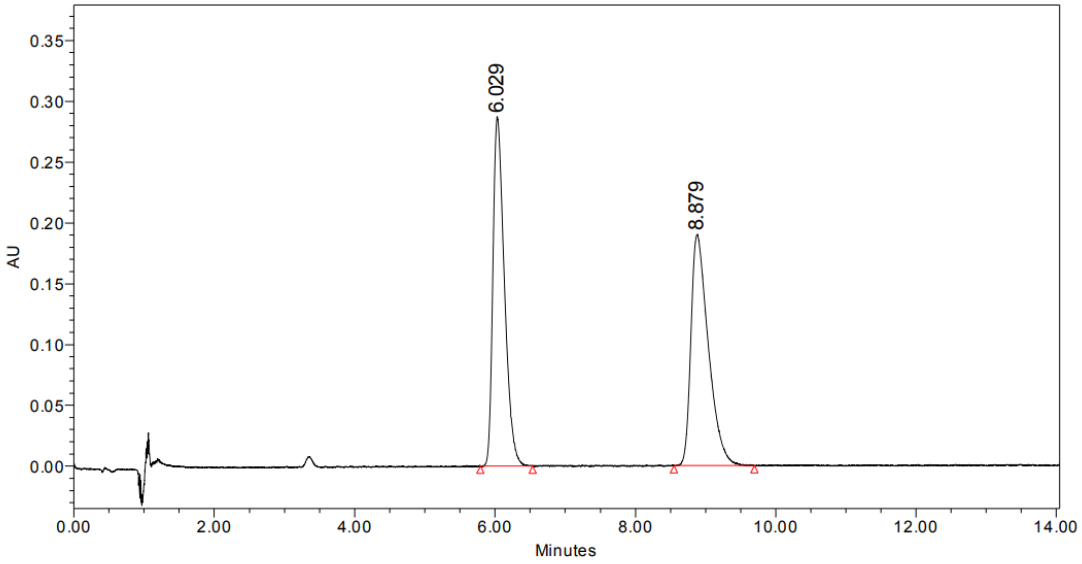
^{19}F NMR (377 MHz, $CDCl_3$) δ -115.17.

^{77}Se NMR (76 MHz, $CDCl_3$) δ 316.16.

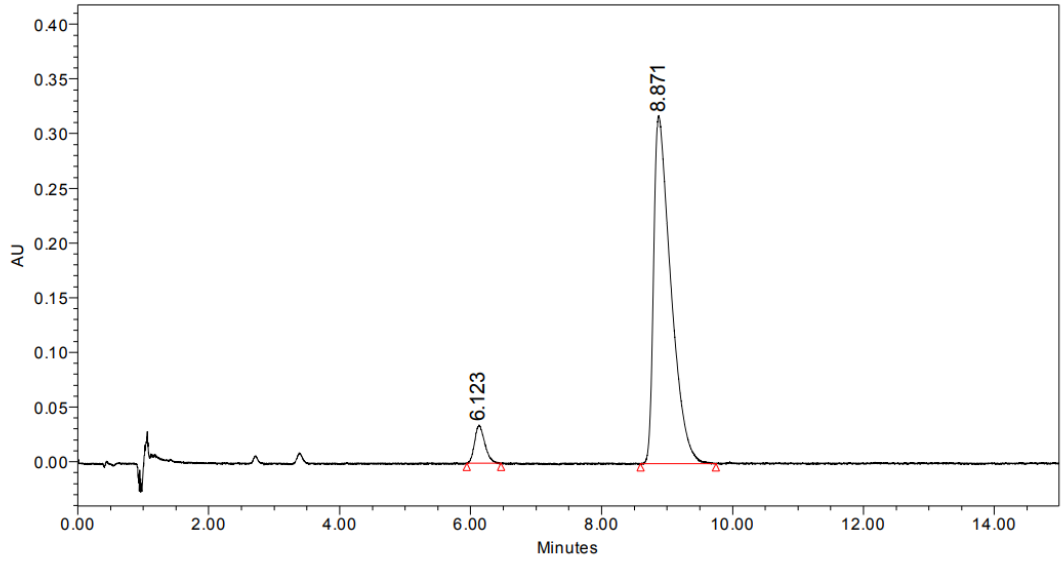
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{18}FNNaO_3Se$ 430.0334; found 430.0329;

SFC (Daicel Chiralpak® AD-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 ℃): t_R(major) = 8.87 min, t_R (minor) =6.12 min, 94:6 er.

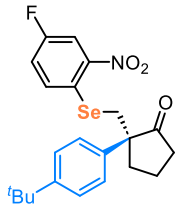
Specific Rotation: $[\alpha]_D^{20}$= -98.80 (c = 0.5, $CHCl_3$).



	Retention Time (min)	Area	Height	% Area	Channel Name
1	6.029	3258678	287147	49.93	254.0nm
2	8.879	3267950	189985	50.07	254.0nm
Sum				100.0	



	Retention Time (min)	Area	Height	% Area	Channel Name
1	6.123	378153	34884	6.12	254.0nm
2	8.871	5805599	318083	93.88	254.0nm
Sum				100.0	



3d

***(R)*-2-(4-(tert-butyl)phenyl)-2-(((4-fluoro-2-nitrophenyl)selanyl)methyl)cyclopentan-1-onee (3d)**

General procedure B, the reaction of **1d** (23.0 mg, 0.10 mmol, 1.0 equiv), **2a** (44.1 mg, 0.11 mmol, 1.1 equiv), **Cat. 3** (6.3 mg, 0.01 mmol, 0.1 equiv), $BF_3 \cdot Et_2O$ (1.2 μL, 0.01 mmol, 0.1 equiv) and activated 5Å MS (30.0 mg) in distilled $CHCl_3$ (2.0 mL) was stirred at -40 ℃ for 84 h. The mixture was purified by preparative thin layer chromatography (petroleum ether : DCM = 1:3) to afford **3d** as a yellow solid (97.0 mg, 97% yield, 92.5:7.5 er), R_f = 0.30 (petroleum ether : DCM = 1:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.44 – 7.29 (m, 5H), 7.21 – 7.12 (m, 1H), 3.48 (d, *J* = 11.6 Hz, 1H), 3.17 (d, *J* = 11.6 Hz, 1H), 2.92 – 2.78 (m, 1H), 2.44 – 2.21 (m, 2H), 2.20 – 2.03 (m, 1H), 2.05 – 1.89 (m, 1H), 1.92 – 1.72 (m, 1H), 1.28 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 217.67, 159.97 (d, *J* = 249.3 Hz), 150.86, 147.61 (d, *J* = 7.9 Hz), 134.03, 131.34 (d, *J* = 7.3 Hz), 127.81 (d, *J* = 3.5 Hz), 126.46, 126.00, 121.38 (d, *J* = 21.5 Hz), 113.24 (d, *J* = 26.2 Hz), 56.39, 37.03, 36.42, 34.55, 34.10, 31.35, 18.54.

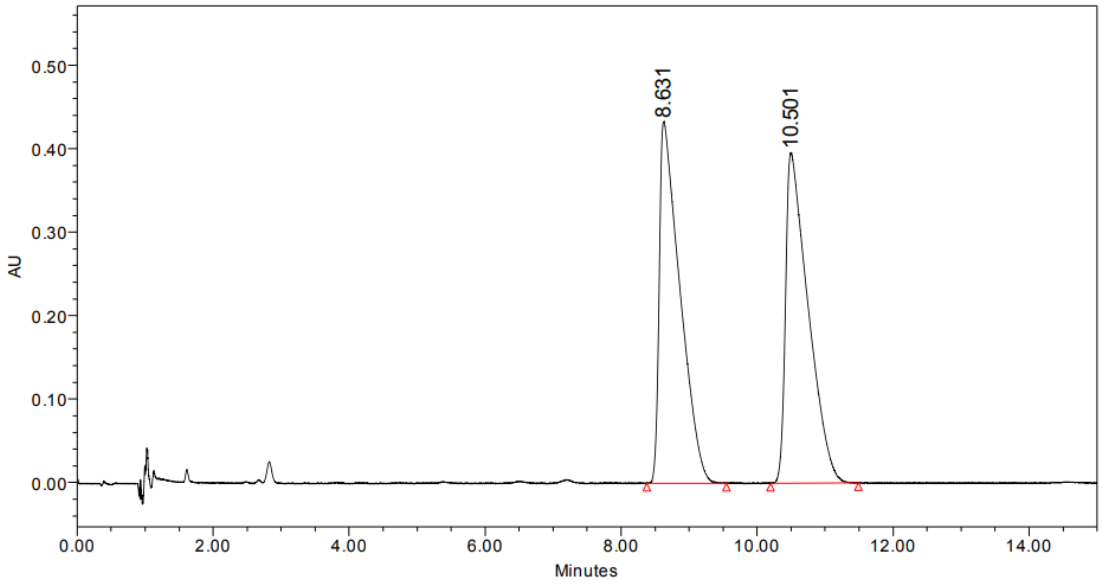
^{19}F NMR δ -115.14.

^{77}Se NMR (76 MHz, $CDCl_3$) δ 317.26.

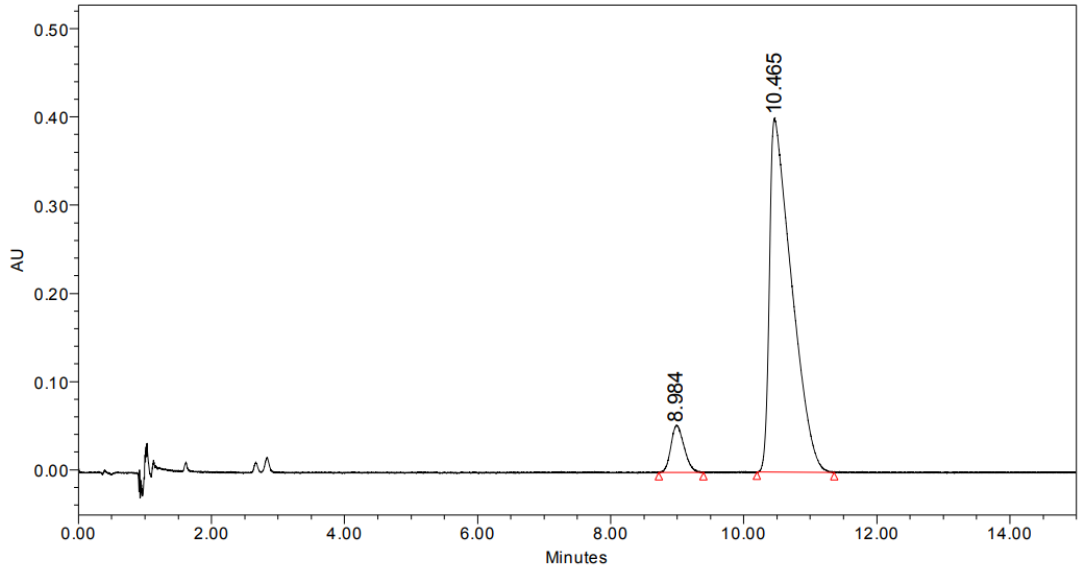
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{24}FNNaO_3Se$ 472.0803; found 428.0167;

SFC (Daicel Chiralpak® IG-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 ℃): t_R(major) = 10.46 min, t_R (minor) = 8.98 min, 92.5:7.5 er.

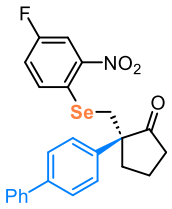
Specific Rotation: $[\alpha]_D^{20}$= -103.40 (c = 1.0, $CHCl_3$).



	Retention Time (min)	Area	Height	% Area	Channel Name
1	8.631	9120412	433219	50.03	254.0nm
2	10.501	9110162	395959	49.97	254.0nm
Sum				100.0	



	Retention Time (min)	Area	Height	% Area	Channel Name
1	8.984	739395	53373	7.40	254.0nm
2	10.465	9248776	401488	92.60	254.0nm
Sum				100.0	



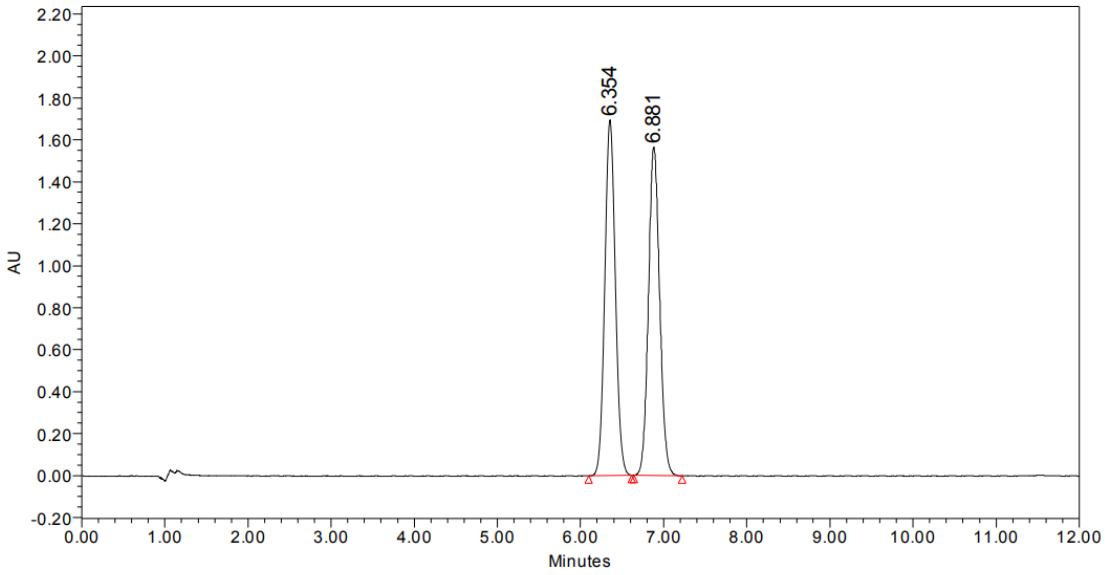
3e

***(R)*-2-([1,1'-biphenyl]-4-yl)-2-(((4-fluoro-2-nitrophenyl)selanyl)methyl)cyclopentan-1-one (3e)**

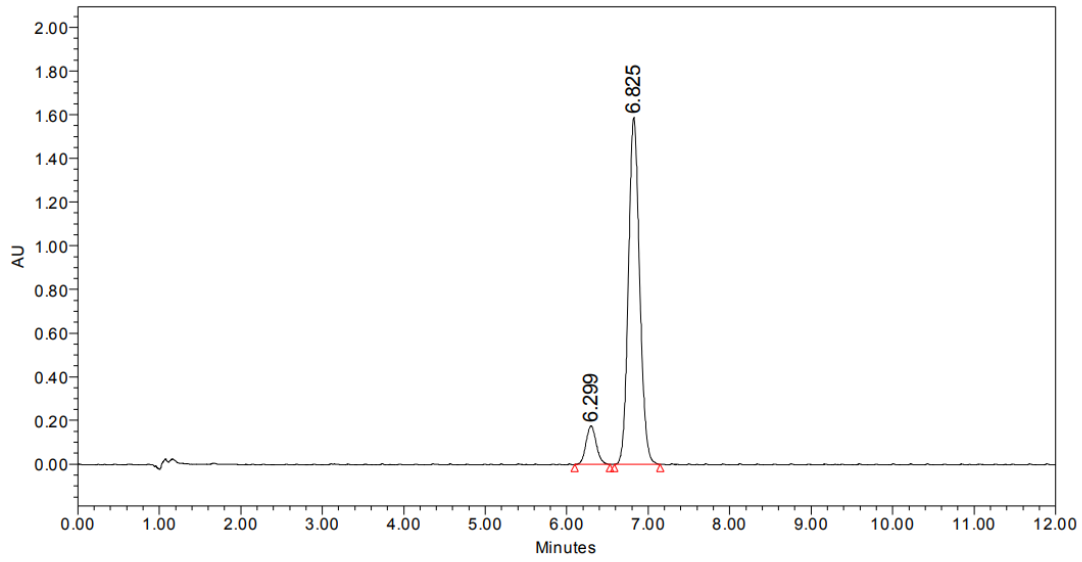
General procedure B, the reaction of **1e** (25.0 mg, 0.10 mmol, 1.0 equiv), **2a** (44.1 mg, 0.11 mmol, 1.1 equiv), **Cat. 3** (6.3 mg, 0.01 mmol, 0.1 equiv), $BF_3{\cdot}Et_2O$ (1.2 μL, 0.01 mmol, 0.1 equiv) and activated 5Å MS (30.0 mg) in distilled $CHCl_3$ (2.0 mL) was stirred at -40 ℃ for 72 h. The mixture was purified by preparative thin layer chromatography (petroleum ether : DCM = 3:5) to afford **3e** as a yellow solid (42.9 mg, 92% yield, 91:9 er), R_f = 0.43 (petroleum ether : DCM = 3:5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.59 – 7.49 (m, 6H), 7.47 – 7.41 (m, 3H), 7.38 – 7.33 (m, 1H), 7.23 – 7.16 (m, 1H), 3.54 (d, *J* = 11.6 Hz, 1H), 3.21 (d, *J* = 11.6 Hz, 1H), 2.94 – 2.87 (m, 1H), 2.47 – 2.27 (m, 2H), 2.23 – 2.13 (m, 1H), 2.07 – 1.95 (m, 1H), 1.94 – 1.81 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 217.42, 160.05 (d, *J* = 249.4 Hz), 147.69 (d, *J* = 7.9 Hz), 140.79, 140.24, 136.18, 131.38 (d, *J* = 7.4 Hz), 128.92, 127.69, 127.65, 127.57 (d, *J* = 3.5 Hz), 127.25, 127.10, 121.45 (d, *J* = 21.7 Hz), 113.26 (d, *J* = 26.3 Hz), 56.48, 37.02, 36.44, 34.06, 18.58.
^{19}F NMR (377 MHz, $CDCl_3$) δ -114.87.
^{77}Se NMR (76 MHz, $CDCl_3$) δ 315.66.

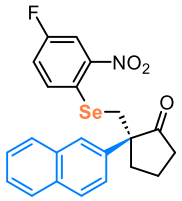
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{20}FNNaO_3Se$ 492.0490; found 429.0485;
SFC (Daicel Chiralpak® OD-3, 20% MeOH in CO2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 6.83 min, t_R (minor) = 6.30 min, 91:9 er.
Specific Rotation: $[\alpha]_D^{20}$= -113.60 (c = 1.0, $CHCl_3$)



	Retention Time (min)	Area	Height	% Area	Channel Name
1	6.354	14843349	1693532	49.95	254.0nm
2	6.881	14871733	1564160	50.05	254.0nm
Sum				100.0	



	Retention Time (min)	Area	Height	% Area	Channel Name
1	6.299	1542768	176685	9.22	254.0nm
2	6.825	15189453	1587175	90.78	254.0nm
Sum				100.0	



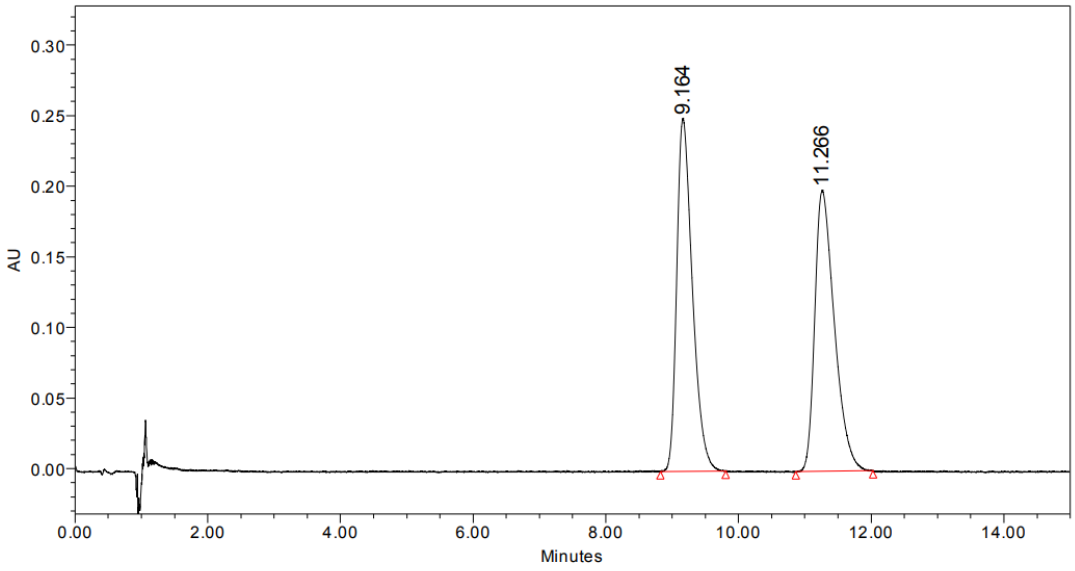
3f

***(R)*-2-(((4-fluoro-2-nitrophenyl)selanyl)methyl)-2-(naphthalen-2-yl)cyclopentan-1-one (3f)**

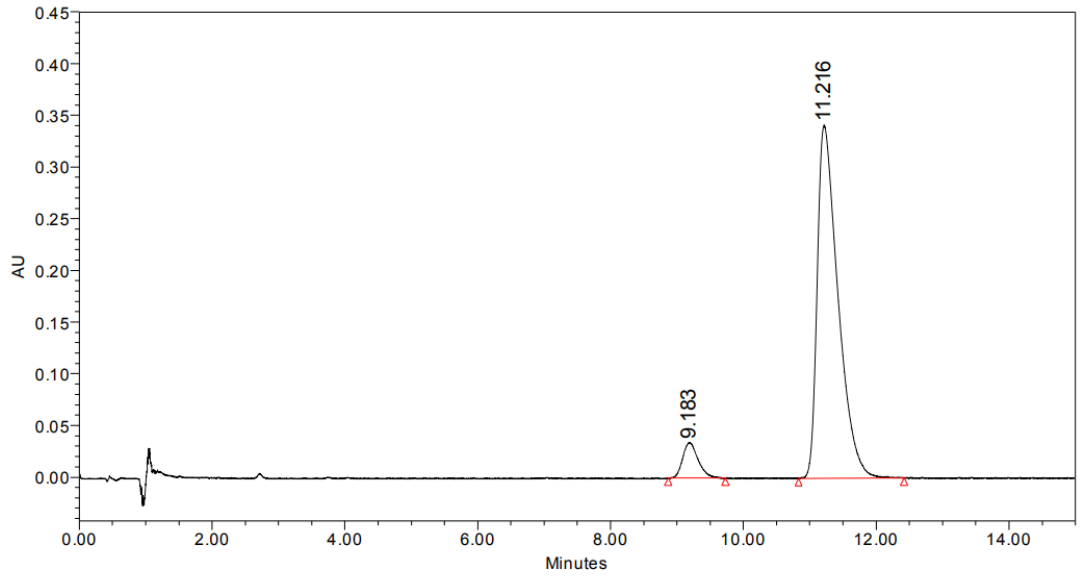
General procedure B, the reaction of **1f** (23.2 mg, 0.10 mmol, 1.0 equiv), **2a** (44.1 mg, 0.11 mmol, 1.1 equiv), **Cat. 3** (6.3 mg, 0.01 mmol, 0.1 equiv), $BF_3{\cdot}Et_2O$ (1.2 μL, 0.01 mmol, 0.1 equiv) and activated 5Å MS (30.0 mg) in distilled $CHCl_3$ (2.0 mL) was stirred at -40 ℃ for 72 h. The mixture was purified by preparative thin layer chromatography (petroleum ether : DCM = 3:5) to afford **3f** as a yellow solid (39.0 mg, 88% yield, 93:7 er), R_f = 0.44 (petroleum ether : DCM = 3:5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.77 (m, 5H), 7.59 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.41 (dd, *J* = 8.8, 5.3 Hz, 1H), 7.14 – 7.08 (m, 1H), 3.60 (d, *J* = 11.6 Hz, 1H), 3.24 (d, *J* = 11.6 Hz, 1H), 3.03 – 2.96 (m, 1H), 2.46 – 2.30 (m, 2H), 2.29 – 2.18 (m, 1H), 2.08 – 2.00 (m, 1H), 1.93 – 1.80 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 217.42, 159.96 (d, *J* = 249.5 Hz), 147.65 (d, *J* = 8.1 Hz), 134.48, 133.23, 132.71, 131.30 (d, *J* = 7.1 Hz), 129.04, 128.23, 127.57, 127.44 (d, *J* = 3.3 Hz), 126.65, 126.60, 126.12, 124.26, 121.33 (d, *J* = 21.6 Hz), 113.14 (d, *J* = 26.4 Hz), 56.89, 37.04, 36.34, 34.15, 18.59.
^{19}F NMR (377 MHz, $CDCl_3$) δ -114.94.
^{77}Se NMR (76 MHz, $CDCl_3$) δ 315.77.

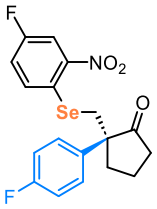
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{18}FNNaO_3Se$ 466.0334; found 466.0329;
SFC (Daicel Chiralpak® AD-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 11.22 min, t_R (minor) = 9.18 min, 93:7 er.
Specific Rotation: $[\alpha]_D^{20}$= -144.80 (c = 1.0, $CHCl_3$)



	Retention Time (min)	Area	Height	% Area	Channel Name
1	9.164	4099562	250071	50.09	254.0nm
2	11.266	4084950	199359	49.91	254.0nm
Sum				100.0	



	Retention Time (min)	Area	Height	% Area	Channel Name
1	9.183	550827	34405	6.92	254.0nm
2	11.216	7405920	341588	93.08	254.0nm
Sum				100.0	



3g

***(R)*-2-(((4-fluoro-2-nitrophenyl)selanyl)methyl)-2-(4-fluorophenyl)cyclopentan-1-one (3g)**

General procedure B, the reaction of **1g** (19.2 mg, 0.10 mmol, 1.0 equiv), **2a** (44.1 mg, 0.11 mmol, 1.1 equiv), **Cat. 3** (6.3 mg, 0.01 mmol, 0.1 equiv), $BF_3{\cdot}Et_2O$ (1.2 μL, 0.01 mmol, 0.1 equiv) and activated 5Å MS (30.0 mg) in distilled $CHCl_3$ (2.0 mL) was stirred at -40 ℃ for 84 h. The mixture was purified by preparative thin layer chromatography (petroleum ether : DCM = 3:5) to afford **3g** as a yellow oil (31.7 mg, 77% yield, 92.5:7.5 er), R_f = 0.54 (petroleum ether : DCM = 3:5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.46 – 7.37 (m, 3H), 7.25 – 7.17 (m, 1H), 7.05 – 6.97 (m, 2H), 3.45 (d, *J* = 11.6 Hz, 1H), 3.14 (d, *J* = 11.6 Hz, 1H), 2.85 – 2.76 (m, 1H), 2.45 – 2.24 (m, 2H), 2.22 – 2.11 (m, 1H), 2.05 – 1.95 (m, 1H), 1.90 – 1.75 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 217.25, 162.36 (d, *J* = 247.8 Hz), 160.13 (d, *J* = 249.6 Hz), 147.70 (d, *J* = 7.8 Hz), 132.97 (d, *J* = 3.3 Hz), 131.24 (d, *J* = 7.1 Hz), 128.63 (d, *J* = 7.9 Hz), 127.44 (d, *J* = 3.6 Hz), 121.55 (d, *J* = 21.3 Hz), 115.98 (d, *J* = 21.3 Hz), 113.37 (d, *J* = 26.5 Hz), 55.97, 36.97, 36.47, 34.23, 18.54.

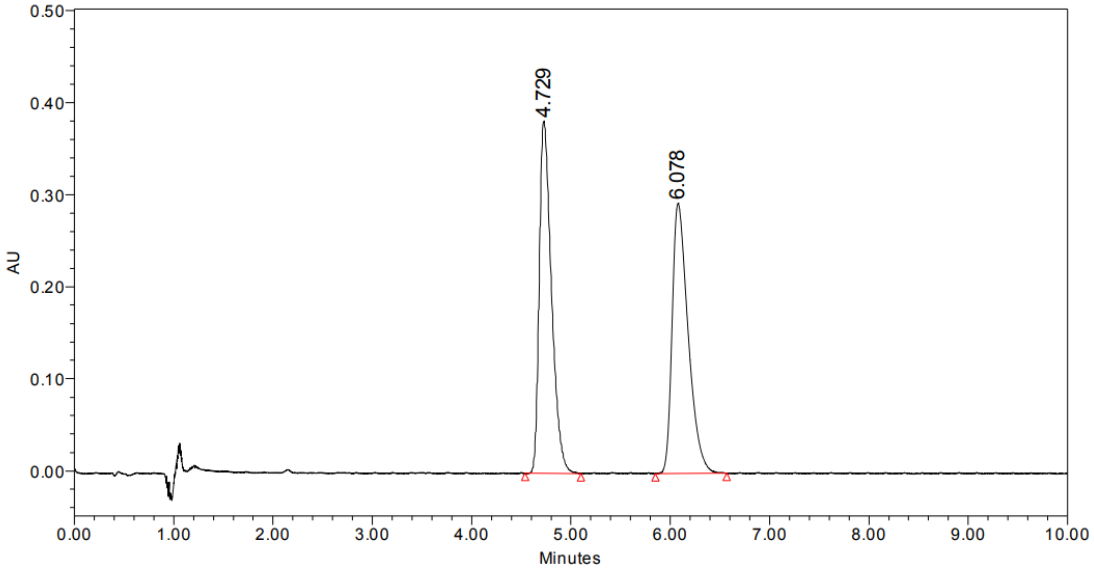
^{19}F NMR (377 MHz, $CDCl_3$) δ -114.18, -114.77.

^{77}Se NMR (76 MHz, $CDCl_3$) δ 313.74.

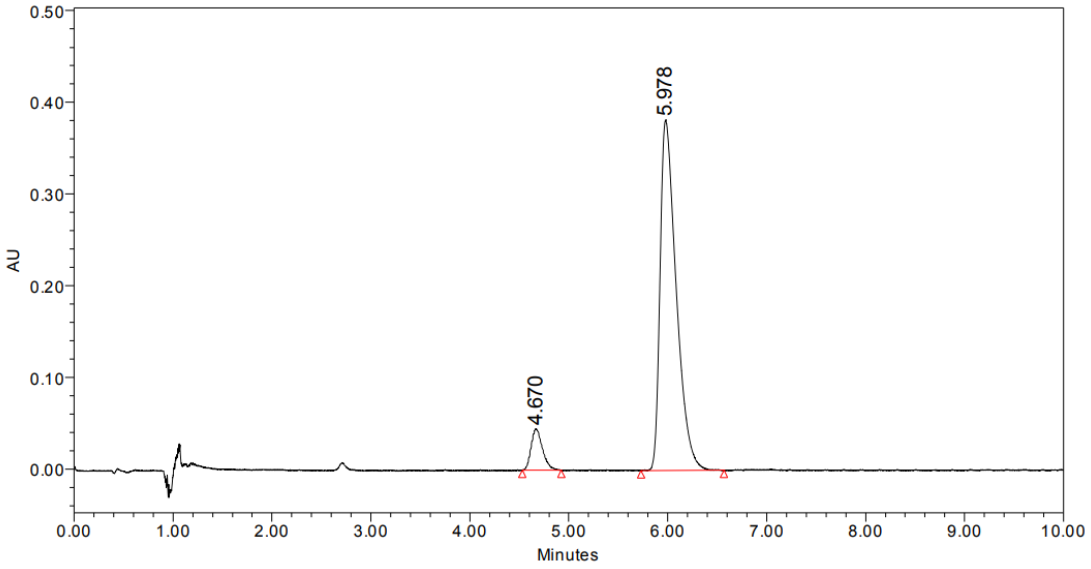
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{15}F_2NNaO_3Se$ 434.0083; found 434.0078;

SFC (Daicel Chiralpak® AD-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 5.98 min, t_R (minor) = 4.67 min, 92.5:7.5 er.

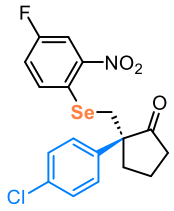
Specific Rotation: $[\alpha]_D^{20}$= -56.20 (c = 1.0, $CHCl_3$)



	Retention Time (min)	Area	Height	% Area	Channel Name
1	4.729	3266086	382484	49.96	254.0nm
2	6.078	3271347	293495	50.04	254.0nm
Sum				100.0	



	Retention Time (min)	Area	Height	% Area	Channel Name
1	4.670	359645	44911	7.69	254.0nm
2	5.978	4314842	382329	92.31	254.0nm
Sum				100.0	



3h

***(R)*-2-(4-chlorophenyl)-2-(((4-fluoro-2-nitrophenyl)selanyl)methyl)cyclopentan-1-one (3h)**

General procedure B, the reaction of **1h** (20.8 mg, 0.10 mmol, 1.0 equiv), **2a** (44.1 mg, 0.11 mmol, 1.1 equiv), **Cat. 3** (6.3 mg, 0.01 mmol, 0.1 equiv), $BF_3 \cdot Et_2O$ (1.2 μL, 0.01 mmol, 0.1 equiv) and activated 5Å MS (30.0 mg) in distilled $CHCl_3$ (2.0 mL) was stirred at -40 ℃ for 84 h. The mixture was purified by preparative thin layer chromatography (petroleum ether : DCM = 3:5) to afford **3h** as a yellow oil (22.5 mg, 53% yield, 91.5:8.5 er), R_f = 0.54 (petroleum ether : DCM = 3:5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.45 – 7.34 (m, 3H), 7.29 (d, *J* = 8.8 Hz, 2H), 7.25 – 7.19 (m, 1H), 3.44 (d, *J* = 11.6 Hz, 1H), 3.14 (d, *J* = 11.6 Hz, 1H), 2.84 – 2.76 (m, 1H), 2.40 – 2.23 (m, 2H), 2.22 – 2.09 (m, 1H), 2.06 – 1.95 (m, 1H), 1.88 – 1.73 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 217.09, 160.19 (d, *J* = 249.8 Hz), 147.78 (d, *J* = 8.3 Hz), 135.81, 134.11, 131.30 (d, *J* = 7.5 Hz), 129.24, 128.28, 127.26 (d, *J* = 3.6 Hz), 121.55 (d, *J* = 21.3 Hz), 113.39 (d, *J* = 26.5 Hz), 56.12, 37.03, 36.34, 34.07, 18.58.

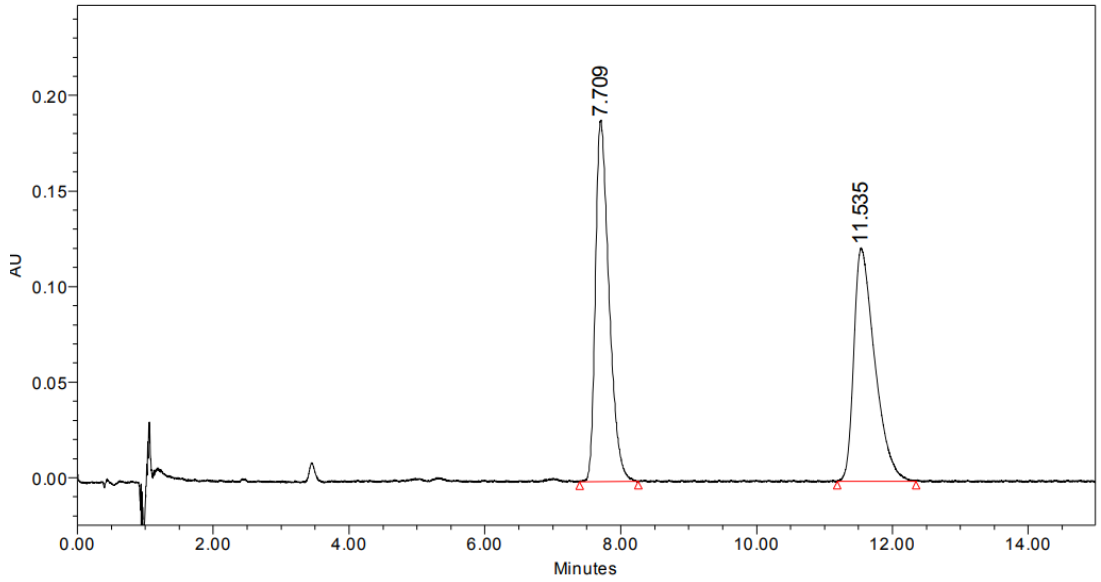
^{19}F NMR (377 MHz, $CDCl_3$) δ -114.63.

^{77}Se NMR (76 MHz, $CDCl_3$) δ 313.49.

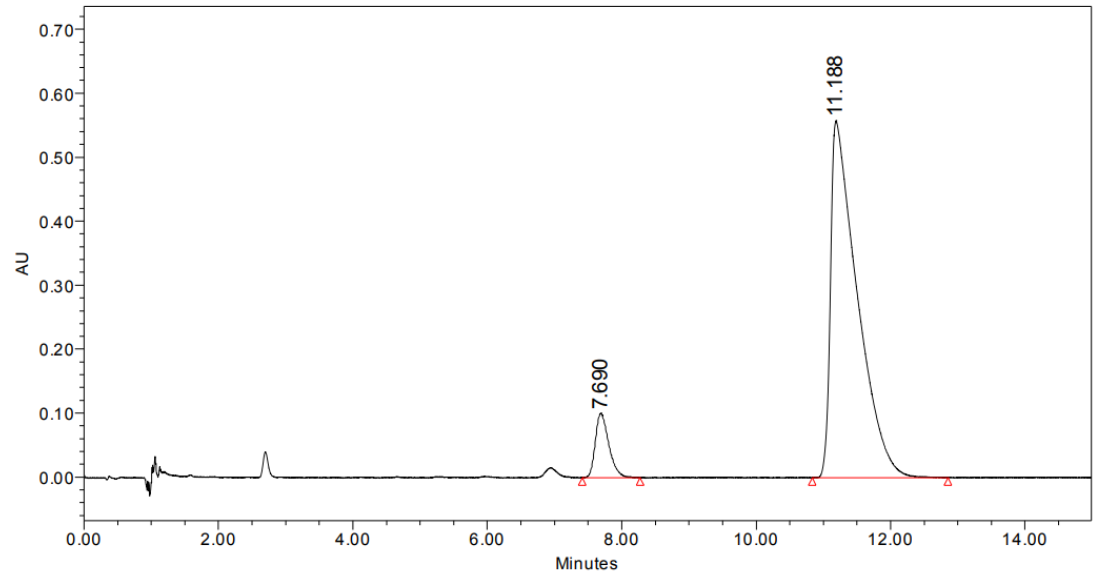
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{15}ClFNNaO_3Se$ 449.9787; found 449.9783;

SFC (Daicel Chiralpak® AD-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 11.19 min, t_R (minor) = 7.69 min, 91.5:8.5 er.

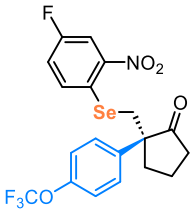
Specific Rotation: $[\alpha]_D^{20}$= -75.33 (c = 0.3, $CHCl_3$)



	Retention Time (min)	Area	Height	% Area	Channel Name
1	7.709	2621481	189140	50.05	254.0nm
2	11.535	2615983	122157	49.95	254.0nm
Sum				100.0	



	Retention Time (min)	Area	Height	% Area	Channel Name
1	7.690	1389940	100401	8.30	254.0nm
2	11.188	15358535	558144	91.70	254.0nm
Sum				100.0	



3i

***(R)*-2-(((4-fluoro-2-nitrophenyl)selanyl)methyl)-2-(4-(trifluoromethoxy)phenyl)cyclopentan-1-one (3i)**

General procedure B, the reaction of **1i** (25.8 mg, 0.10 mmol, 1.0 equiv), **2a** (44.1 mg, 0.11 mmol, 1.1 equiv), **Cat. 3** (6.3 mg, 0.01 mmol, 0.1 equiv), $BF_3{\cdot}Et_2O$ (1.2 μL, 0.01 mmol, 0.1 equiv) and activated 5Å MS (30.0 mg) in distilled $CHCl_3$ (2.0 mL) was stirred at -10 ℃ for 60 h. The mixture was purified by preparative thin layer chromatography (petroleum ether : DCM = 3:5) to afford **3i** as a yellow oil (40.2 mg, 84% yield, 88.5:11.5 er), R_f = 0.54 (petroleum ether : DCM = 3:5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.38 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.23 – 7.10 (m, 3H), 3.45 (d, *J* = 11.6 Hz, 1H), 3.16 (d, *J* = 11.6 Hz, 1H), 2.87 – 2.76 (m, 1H), 2.46 – 2.26 (m, 2H), 2.25 – 2.11 (m, 1H), 2.09 – 1.95 (m, 1H), 1.90 – 1.73 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 217.11, 160.19 (d, *J* = 249.8 Hz), 148.84 (d, *J* = 1.8 Hz), 147.77 (d, *J* = 7.8 Hz), 135.98, 131.25 (d, *J* = 7.4 Hz), 128.45, 127.11 (d, *J* = 3.6 Hz), 121.52 (d, *J* = 21.6 Hz), 121.31, 120.47 (q, *J* = 257.6 Hz), 113.38 (d, *J* = 26.3 Hz), 56.15, 37.12, 36.30, 34.20, 18.59.

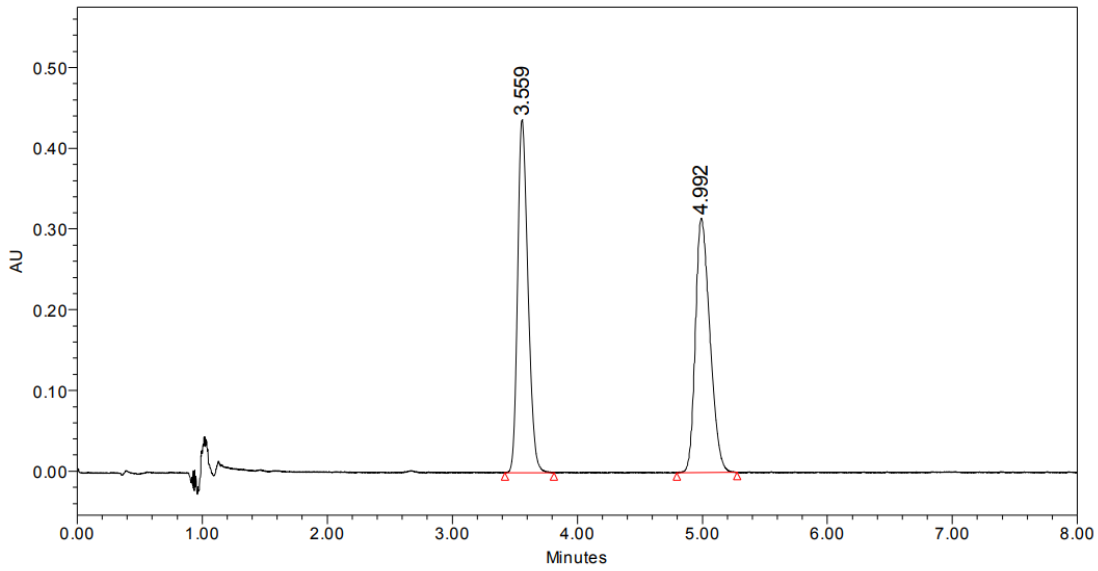
^{19}F NMR (377 MHz, $CDCl_3$) δ -57.83, -114.59.

^{77}Se NMR (76 MHz, $CDCl_3$) δ 313.37.

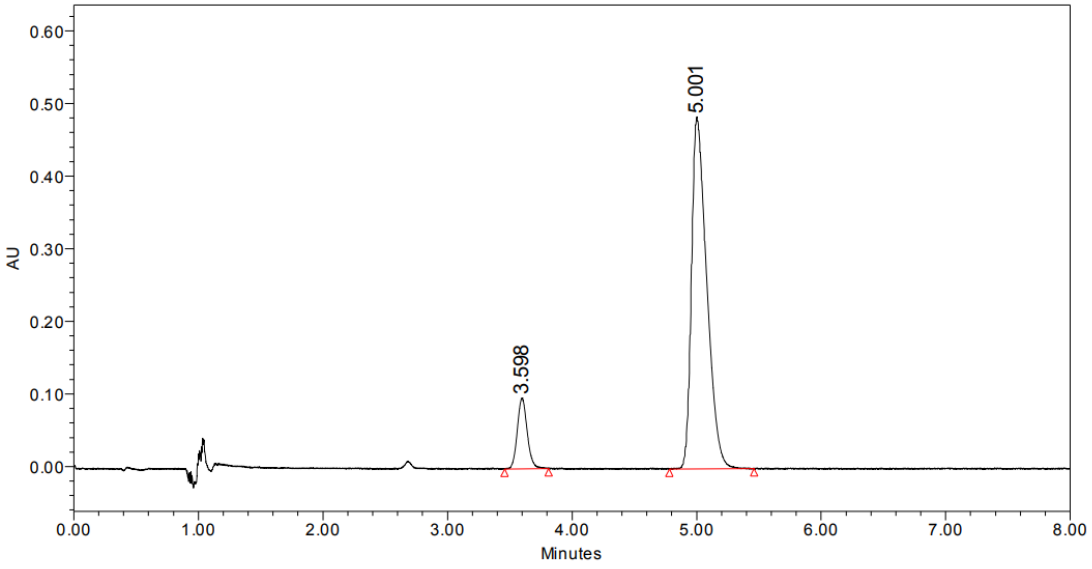
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{15}F_4NNaO_4Se$ 500.0000; found 499.9998;

SFC (Daicel Chiralpak® AD-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 5.00 min, t_R (minor) = 3.60 min, 88.5:11.5 er.

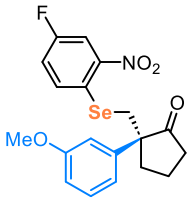
Specific Rotation: $[\alpha]_D^{20}$= -57.60 (c = 1.0, $CHCl_3$)



	Retention Time (min)	Area	Height	% Area	Channel Name
1	3.559	2518317	436901	50.00	254.0nm
2	4.992	2518033	315137	50.00	254.0nm
Sum				100.0	



	Retention Time (min)	Area	Height	% Area	Channel Name
1	3.598	537107	97393	11.61	254.0nm
2	5.001	4089886	484222	88.39	254.0nm
Sum				100.0	



3j

***(R)*-2-(((4-fluoro-2-nitrophenyl)selanyl)methyl)-2-(3-methoxyphenyl)cyclopentan-1-one (3j)**

General procedure B, the reaction of **1j** (17.4 mg, 0.10 mmol, 1.0 equiv), **2a** (44.1 mg, 0.11 mmol, 1.1 equiv), **Cat. 3** (6.3 mg, 0.01 mmol, 0.1 equiv), $BF_3{\cdot}Et_2O$ (1.2 μL, 0.01 mmol, 0.1 equiv) and activated 5Å MS (30.0 mg) in distilled $CHCl_3$ (2.0 mL) was stirred at -40 ℃ for 84 h. The mixture was purified by preparative thin layer chromatography (petroleum ether : DCM = 1:3) to afford **3j** as a yellow oil (37.3 mg, 88% yield, 95.5:4.5 er), R_f = 0.22 (petroleum ether : DCM = 1:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.43 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.30 – 7.17 (m, 2H), 7.05 – 6.96 (m, 2H), 6.80 (dd, *J* = 8.4, 2.8 Hz, 1H), 3.79 (s, 3H), 3.48 (d, *J* = 11.6 Hz, 1H), 3.16 (d, *J* = 11.6 Hz, 1H), 2.88 – 2.78 (m, 1H), 2.45 – 2.22 (m, 2H), 2.18 – 2.07 (m, 1H), 2.06 – 1.93 (m, 1H), 1.90 – 1.75 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 217.33, 160.12, 160.05 (d, *J* = 249.3 Hz), 147.61 (d, *J* = 7.8 Hz), 138.89, 131.26 (d, *J* = 7.3 Hz), 130.10, 127.82 (d, *J* = 3.5 Hz), 121.49 (d, *J* = 21.5 Hz), 118.99, 113.31 (d, *J* = 26.2 Hz), 113.22, 112.76, 56.68, 55.37, 36.96, 36.29, 34.15, 18.57.

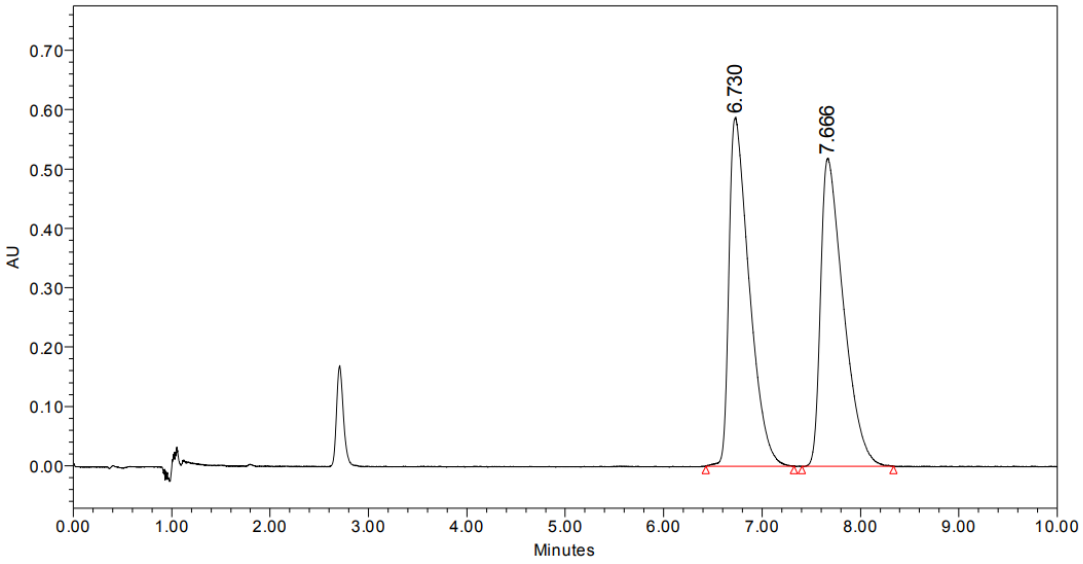
^{19}F NMR (377 MHz, $CDCl_3$) δ -115.08.

^{77}Se NMR (76 MHz, $CDCl_3$) δ 317.56.

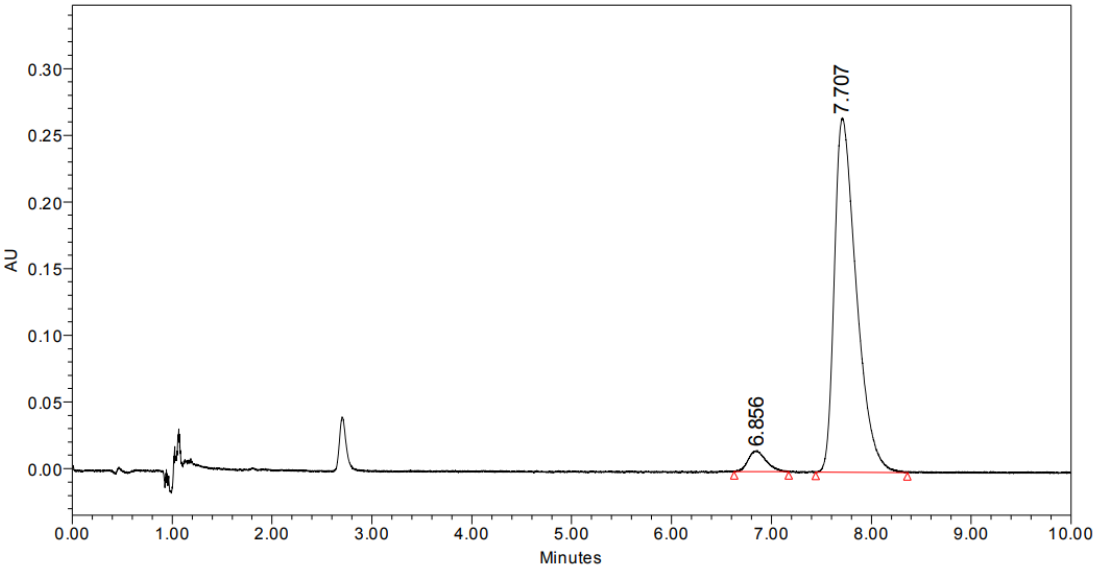
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{18}FNNaO_4Se$ 446.0283; found 446.0278;

SFC (Daicel Chiralpak® IG-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 7.70 min, t_R (minor) = 6.86 min, 95.5:4.5 er.

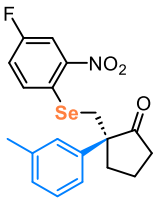
Specific Rotation: $[\alpha]_D^{20}$= -94.60 (c = 1.0, $CHCl_3$)



	Retention Time (min)	Area	Height	% Area	Channel Name
1	6.730	8402541	588006	50.09	254.0nm
2	7.666	8373739	519522	49.91	254.0nm
Sum				100.0	



	Retention Time (min)	Area	Height	% Area	Channel Name
1	6.856	190267	15695	4.48	254.0nm
2	7.707	4054483	265590	95.52	254.0nm
Sum				100.0	



3k

***(R)*-2-(((4-fluoro-2-nitrophenyl)selanyl)methyl)-2-(3-methoxyphenyl)cyclopentan-1-one (3k)**

General procedure B, the reaction of **1k** (18.8 mg, 0.10 mmol, 1.0 equiv), **2a** (44.1 mg, 0.11 mmol, 1.1 equiv), **Cat. 3** (6.3 mg, 0.01 mmol, 0.1 equiv), $BF_3{\cdot}Et_2O$ (1.2 μL, 0.01 mmol, 0.1 equiv) and activated 5Å MS (30.0 mg) in distilled $CHCl_3$ (2.0 mL) was stirred at -40 ℃ for 60 h. The mixture was purified by preparative thin layer chromatography (petroleum ether : DCM = 3:5) to afford **3k** as a yellow oil (42.6 mg, >99% yield, 95:5 er), R_f = 0.37 (petroleum ether : DCM = 3:5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.43 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.25 – 7.17 (m, 4H), 7.11 – 7.05 (m, 1H), 3.48 (d, *J* = 11.6 Hz, 1H), 3.17 (d, *J* = 11.6 Hz, 1H), 2.90 – 2.80 (m,1H), 2.43 – 2.22 (m, 5H), 2.18 – 2.07 (m, 1H), 2.04 – 1.93 (m, 1H), 1.88 – 1.74 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 217.56, 160.02 (d, *J* = 249.2 Hz), 147.60 (d, *J* = 7.9 Hz), 138.81, 137.13, 131.28 (d, *J* = 7.1 Hz), 128.98, 128.75, 127.85 (d, *J* = 3.5 Hz), 127.44, 121.45 (d, *J* = 21.7 Hz), 113.27 (d, *J* = 26.3 Hz), 56.65, 36.94, 36.38, 34.03, 21.73, 18.53.

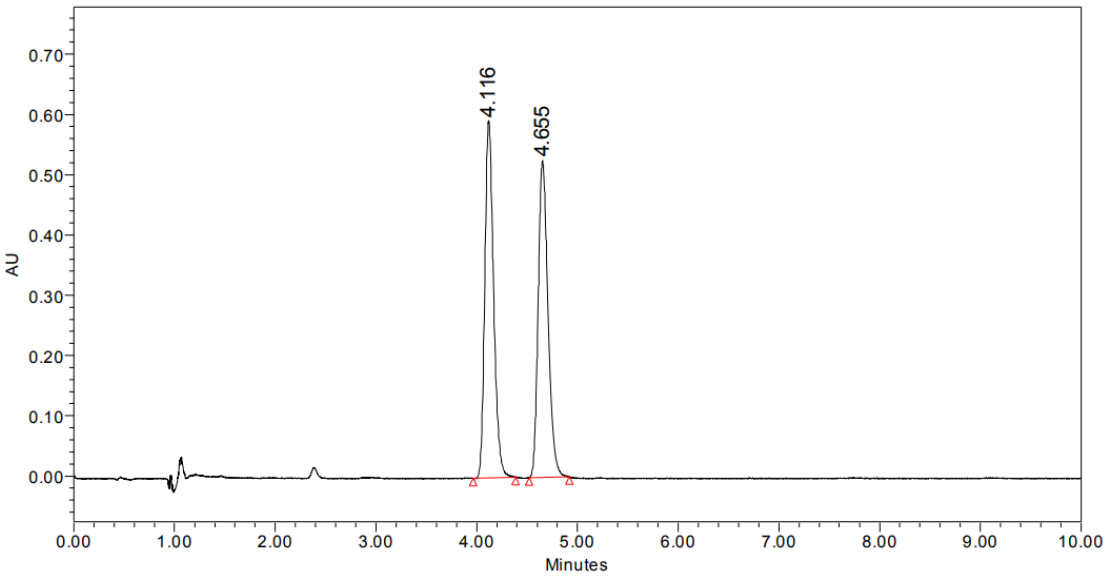
^{19}F NMR (377 MHz, $CDCl_3$) δ -115.12.

^{77}Se NMR (76 MHz, $CDCl_3$) δ 316.88.

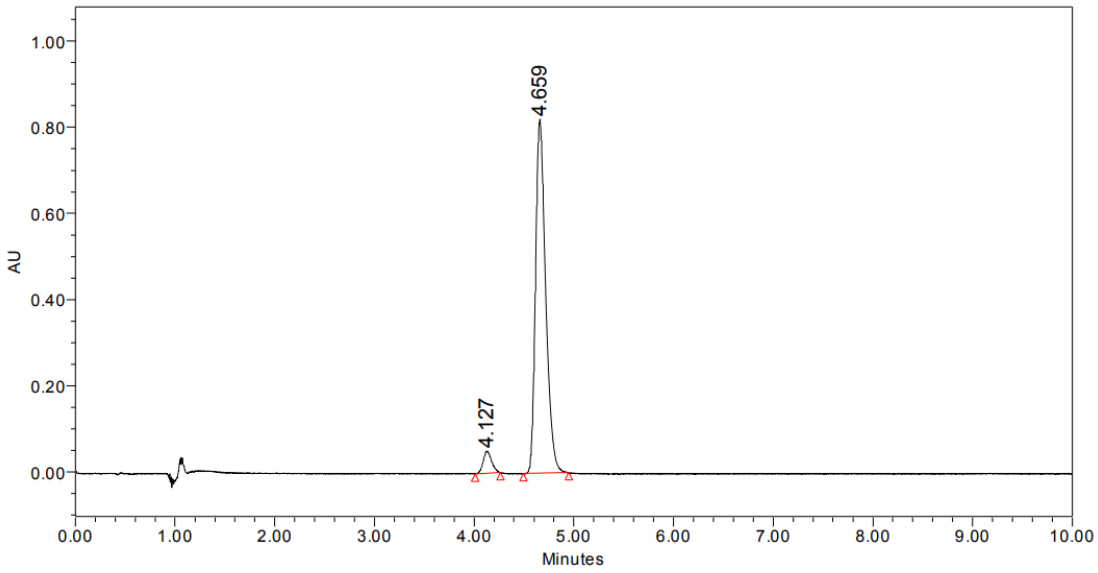
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{18}FNNaO_3Se$ 430.0328; found 430.0327;

SFC (Daicel Chiralpak® OD-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 4.66 min, t_R (minor) = 4.13 min, 95:5 er.

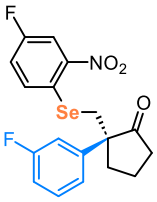
Specific Rotation: $[\alpha]_D^{20}$= -95.33 (c = 0.6, $CHCl_3$)



	RT (min)	Area	% Area	Height (μV)	Channel Name
1	4.116	3575907	50.06	592382	254.0nm
2	4.655	3568029	49.94	525739	254.0nm



	RT (min)	Area	% Area	Height (μV)	Channel Name
1	4.127	302997	4.96	51269	254.0nm
2	4.659	5806988	95.04	820632	254.0nm



3l

***(R)*-2-(((4-fluoro-2-nitrophenyl)selanyl)methyl)-2-(3-fluorophenyl)cyclopentan-1-one (3l)**

General procedure B, the reaction of **1l** (19.2 mg, 0.10 mmol, 1.0 equiv), **2a** (44.1 mg, 0.11 mmol, 1.1 equiv), **Cat. 3** (6.3 mg, 0.01 mmol, 0.1 equiv), $BF_3{\cdot}Et_2O$ (1.2 μL, 0.01 mmol, 0.1 equiv) and activated 5Å MS (30.0 mg) in distilled $CHCl_3$ (2.0 mL) was stirred at -10 ℃ for 60 h. The mixture was purified by preparative thin layer chromatography (petroleum ether : DCM = 6:1) to afford **3l** as a yellow oil (27.7 mg, 68% yield, 88.5:11.5 er), R_f = 0.31 (petroleum ether : DCM = 3:5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.42 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.34 – 7.14 (m, 4H), 6.96 (td, *J* = 8.1, 2.8 Hz, 1H), 3.46 (d, *J* = 11.6 Hz, 1H), 3.16 (d, *J* = 11.6 Hz, 1H), 2.85 – 2.74 (m, 1H), 2.46 – 2.25 (m, 2H), 2.23 – 2.12 (m, 1H), 2.08 – 1.96 (m, 1H), 1.90 – 1.74 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 216.94, 163.22 (d, *J* = 247.0 Hz), 160.15 (d, *J* = 249.6 Hz), 147.69 (d, *J* = 8.1 Hz), 140.07 (d, *J* = 7.0 Hz), 131.21 (d, *J* = 7.2 Hz), 130.59 (d, *J* = 8.3 Hz), 127.39 (d, *J* = 3.4 Hz), 122.48 (d, *J* = 2.8 Hz), 121.58 (d, *J* = 21.7 Hz), 115.01 (d, *J* = 21.0 Hz), 114.14 (d, *J* = 22.6 Hz), 113.41 (d, *J* = 26.4 Hz), 56.44 (d, *J* = 1.6 Hz), 37.07, 36.14, 34.14, 18.63.

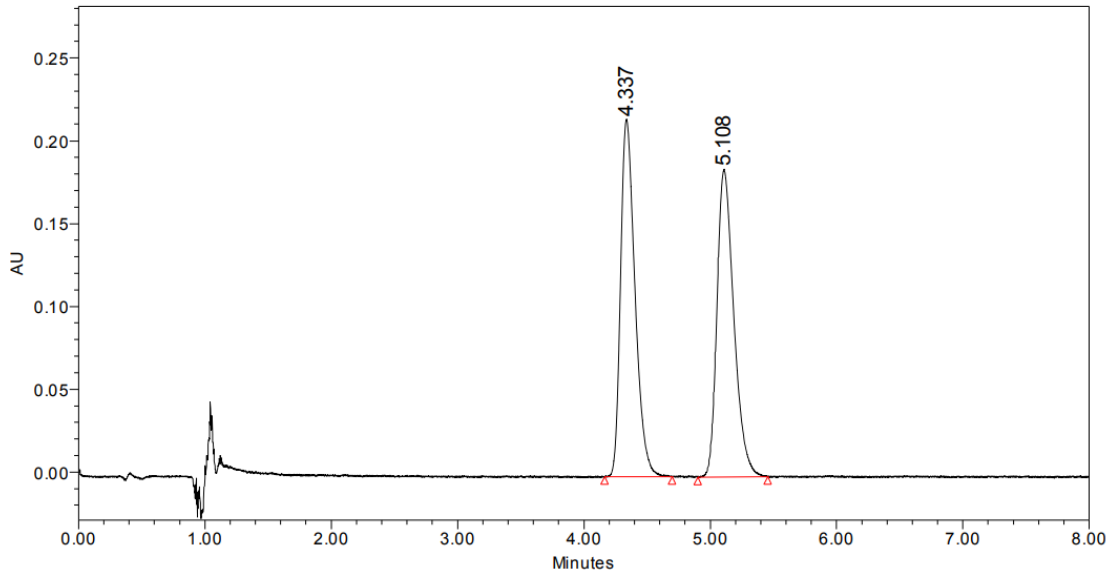
^{19}F NMR (377 MHz, $CDCl_3$) δ -111.31, -114.73.

^{77}Se NMR (76 MHz, $CDCl_3$) δ 315.40.

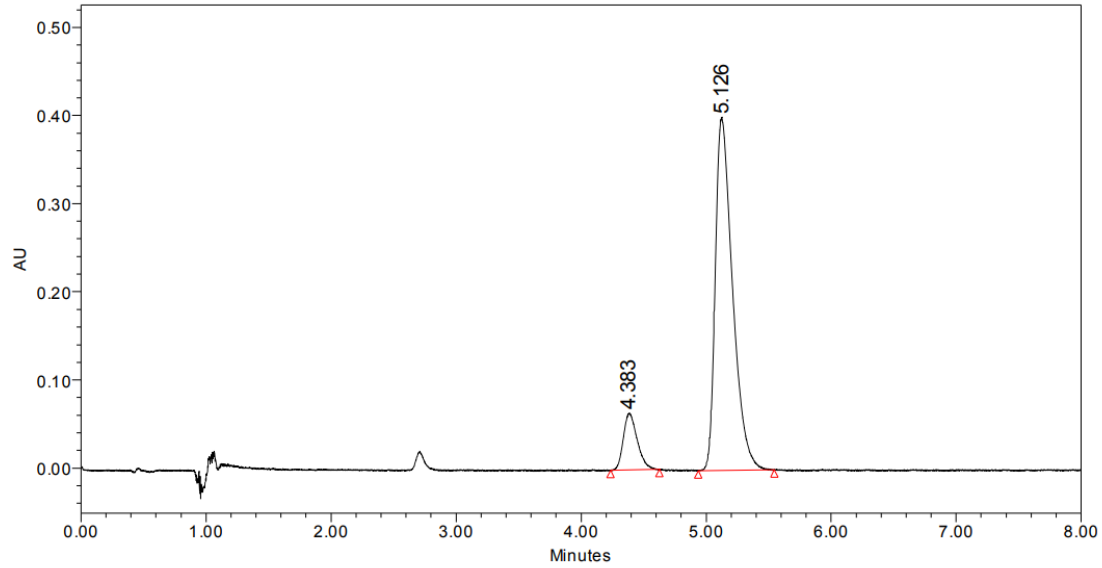
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{15}F_2NNaO_3Se$ 434.0083; found 434.0080;

SFC (Daicel Chiralpak® AD-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 5.13 min, t_R (minor) = 4.38 min, 88.5:11.5 er.

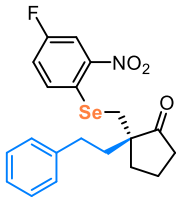
Specific Rotation: $[\alpha]_D^{20}$= -52.20 (c = 1.0, $CHCl_3$)



	Retention Time (min)	Area	Height	% Area	Channel Name
1	4.337	1713493	215554	49.99	254.0nm
2	5.108	1714514	185649	50.01	254.0nm
Sum				100.0	



	Retention Time (min)	Area	Height	% Area	Channel Name
1	4.383	499232	64357	11.50	254.0nm
2	5.126	3840504	400403	88.50	254.0nm
Sum				100.0	



3m

***(R)*-2-(((4-fluoro-2-nitrophenyl)selanyl)methyl)-2-phenethylcyclopentan-1-one (3m)**

General procedure B, the reaction of **1m** (20.2 mg, 0.10 mmol, 1.0 equiv), **2a** (44.1 mg, 0.11 mmol, 1.1 equiv), **Cat. 3** (6.3 mg, 0.01 mmol, 0.1 equiv), $BF_3{\cdot}Et_2O$ (1.2 μL, 0.01 mmol, 0.1 equiv) and activated 5Å MS (30.0 mg) in distilled $CHCl_3$ (2.0 mL) was stirred at -30 ℃ for 70 h. The mixture was purified by preparative thin layer chromatography (petroleum ether : DCM = 8:1) to afford **3m** as a yellow oil (39.3 mg, 91% yield, 74.5:8.5 er), R_f = 0.19 (petroleum ether : DCM = 8:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.52 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.34 – 7.24 (m, 3H), 7.21 – 7.13 (m, 3H), 3.17 (d, *J* = 11.2 Hz, 1H), 3.01 (d, *J* = 11.2 Hz, 1H), 2.72 – 2.53 (m, 2H), 2.46 – 2.24 (m, 2H), 2.18 – 1.83 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 220.23, 160.19 (d, *J* = 249.5 Hz), 147.69 (d, *J* = 8.1 Hz), 141.31, 131.12 (d, *J* = 7.3 Hz), 128.63, 128.41, 127.64 (d, *J* = 3.5 Hz), 126.26, 121.75 (d, *J* = 21.5 Hz), 113.54 (d, *J* = 26.1 Hz), 51.95, 37.81, 37.56, 34.53, 32.43, 30.55, 18.83.

^{19}F NMR (377 MHz, $CDCl_3$) δ -114.80.

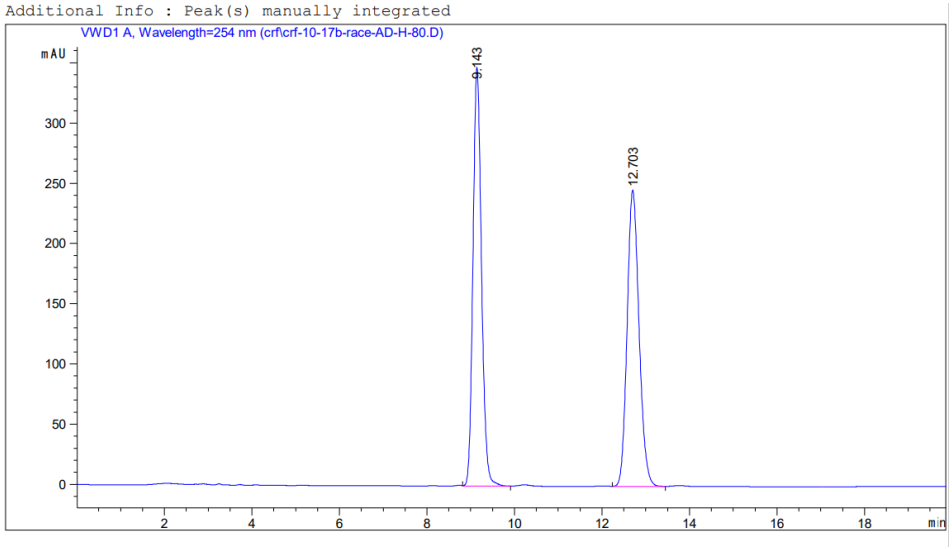
^{77}Se NMR (76 MHz, $CDCl_3$) δ 304.35.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{20}H_{20}FNNaO_3Se$ 444.0490; found 444.0491;

HPLC (Daicel Chiralpak® AD-H, *n*-hexane/*i*-PrOH = 80/20, 1 mL/min, 254 nm, 35 °C): t_R(major) = 9.10 min, t_R (minor) = 12.64 min, 74.5:8.5 er.

Specific Rotation: $[\alpha]_D^{20}$= +9.00 (c = 1.0, $CHCl_3$)

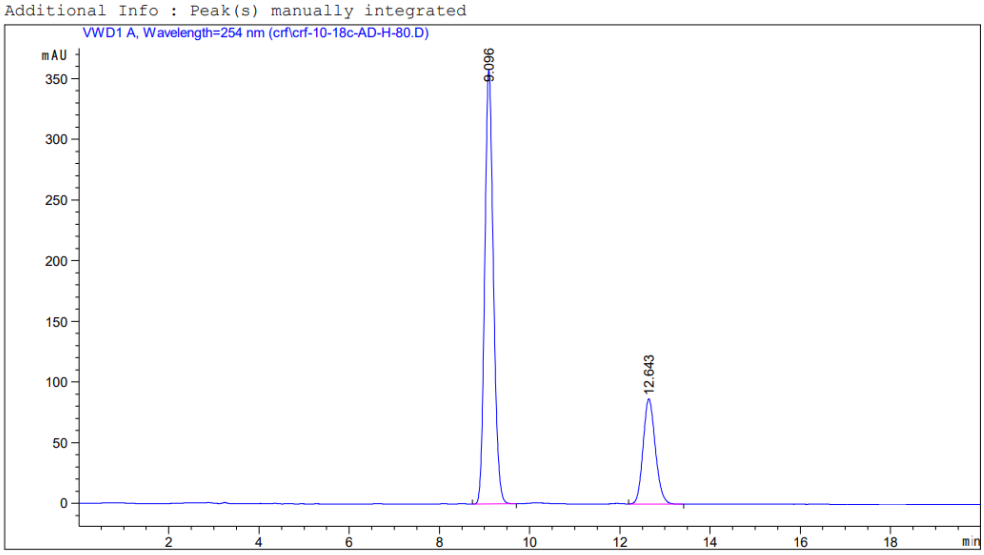
Additional Info : Peak(s) manually integrated



Signal 1: VWD1 A, Wavelength=254 nm

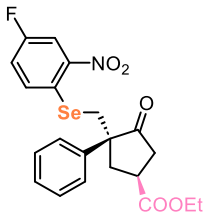
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.143	FM R	0.2249	4687.48730	347.36951	50.2083
2	12.703	FM R	0.3150	4648.59082	245.91960	49.7917
Totals :				9336.07813	593.28911	

Additional Info : Peak(s) manually integrated



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.096	BB	0.2056	4774.32715	357.96274	74.4725
2	12.643	FM R	0.3145	1636.53577	86.73178	25.5275
Totals :				6410.86292	444.69452	



3n

ethyl *(1S,3R)*-3-(((4-fluoro-2-nitrophenyl)selanyl)methyl)-4-oxo-3-phenylcyclopentane-1-carboxylate (3n)

General procedure B, the reaction of **1n** (24.6 mg, 0.10 mmol, 1.0 equiv), **2a** (44.1 mg, 0.11 mmol, 1.1 equiv), **Cat. 3** (6.3 mg, 0.01 mmol, 0.1 equiv), $BF_3 \cdot Et_2O$ (1.2 μL, 0.01 mmol, 0.1 equiv) and activated 5Å MS (30.0 mg) in distilled $CHCl_3$ (2.0 mL) was stirred at 0 ℃ for 72 h. The mixture was purified by preparative thin layer chromatography (DCM) to afford **3n** as a yellow oil (27.3 mg, 92% yield, 87.5:12.5 er). A mixture of *cis* and *trans* diastereoisomers (*cis : trans* = 6:1), R_f = 0.40 (DCM).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.47 – 7.39 (m, 2H), 7.40 – 7.32 (m, 3H), 7.31 – 7.25 (m, 1H), 7.23 – 7.16 (m, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.54 (d, *J* = 11.6 Hz, 1H), 3.23 – 3.13 (m, 2H), 3.08 – 2.94 (m, 1H), 2.70 – 2.56 (m, 2H), 2.23 (dd, *J* = 13.2, 12.0 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H). (*cis* diastereoisomer)

^{13}C NMR (101 MHz, $CDCl_3$) δ 213.78, 173.68, 160.10 (d, *J* = 249.6 Hz), 147.64 (d, *J* = 7.8 Hz), 135.91, 131.19 (d, *J* = 7.3 Hz), 129.41, 128.42, 127.33 (d, *J* = 3.4 Hz), 126.59, 121.53 (d, *J* = 21.7 Hz), 113.35 (d, *J* = 26.1 Hz), 61.37, 58.03, 39.70, 37.44, 37.12, 36.16, 14.31. (*cis* diastereoisomer)

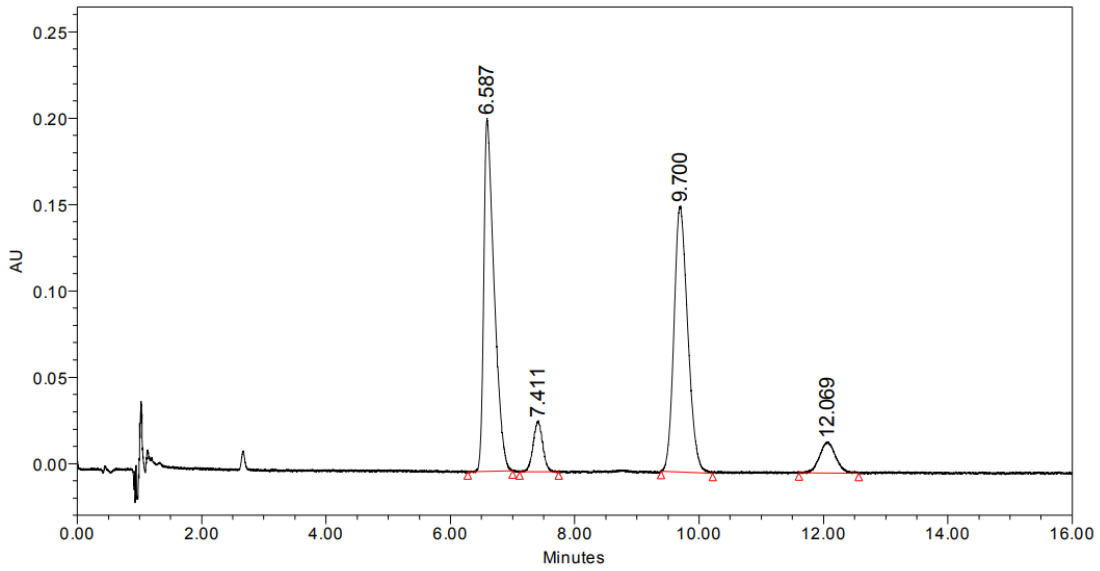
^{19}F NMR (377 MHz, $CDCl_3$) δ -114.82. (*cis* diastereoisomer)

^{77}Se NMR (76 MHz, $CDCl_3$) δ 314.28. (*cis* diastereoisomer)

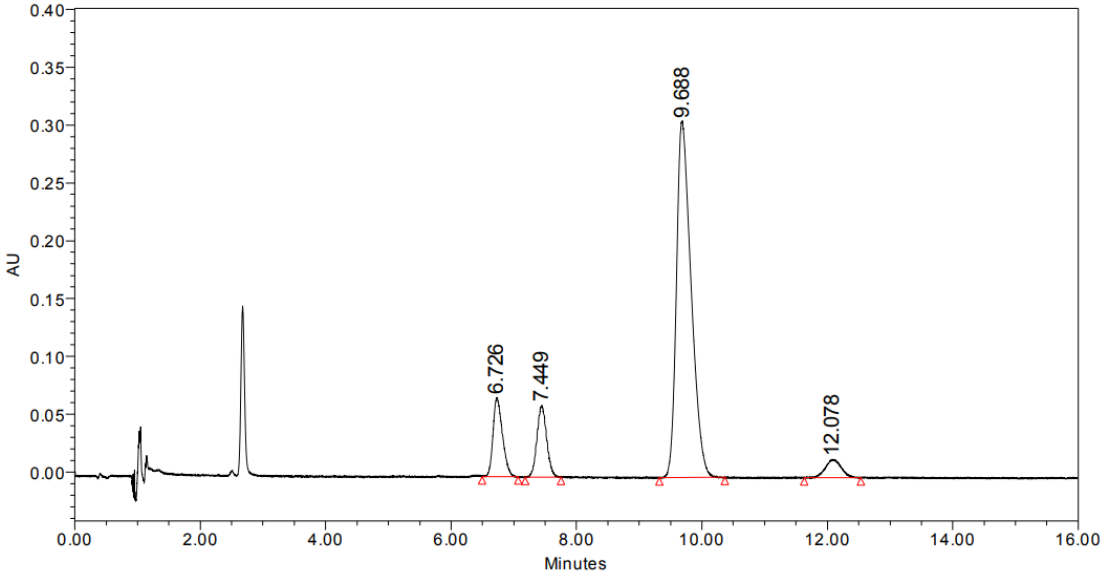
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{20}FNNaO_5Se$ 488.0383; found 488.0385;

SFC (Daicel Chiralpak® IG-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 9.69 min, t_R (minor) = 6.73 min, 87.5:12.5 er.

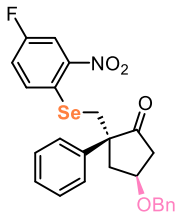
Specific Rotation: $[\alpha]_D^{20}$= -18.60 (c = 0.5, $CHCl_3$)



	Retention Time (min)	Area	Height	% Area	Channel Name
1	6.587	2359848	204276	44.01	254.0nm
2	7.411	315271	29413	5.88	254.0nm
3	9.700	2367855	153864	44.16	254.0nm
4	12.069	319159	17983	5.95	254.0nm
Sum				100.0	



	Retention Time (min)	Area	Height	% Area	Channel Name
1	6.726	713165	68179	10.71	254.0nm
2	7.449	668498	61912	10.04	254.0nm
3	9.688	4999112	307841	75.07	254.0nm
4	12.078	278270	15698	4.18	254.0nm
Sum				100.0	



3o

***(2R,4S)*-4-butyl-2-(((4-fluoro-2-nitrophenyl)selanyl)methyl)-2-phenylcyclopentan-1-one (4o)**

General procedure B, the reaction of **1o** (28.0 mg, 0.10 mmol, 1.0 equiv), **2a** (44.1 mg, 0.11 mmol, 1.1 equiv), **Cat. 3** (6.3 mg, 0.01 mmol, 0.1 equiv), $BF_3{\cdot}Et_2O$ (1.2 μL, 0.01 mmol, 0.1 equiv) and activated 5Å MS (30.0 mg) in distilled $CHCl_3$ (2.0 mL) was stirred at 0 ℃ for 72 h. The mixture was purified by preparative thin layer chromatography (DCM) to afford **3o** as a yellow oil (27.3 mg, 61% yield, 88.5:11.5 er), A mixture of *cis* and *trans* diastereoisomers (*cis : trans* = 8:1), R_f = 0.35 (DCM).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.49 – 7.40 (m, 2H), 7.36 – 7.22 (m, 9H), 7.08 – 7.02 (m, 1H), 4.53 (s, 2H), 4.31 – 4.22 (m, 1H), 3.54 (d, *J* = 11.6 Hz, 1H), 3.37 (d, *J* = 11.6 Hz, 1H), 3.08 – 2.98 (m, 1H), 2.76 – 2.66 (m, 1H), 2.60 – 2.48 (m, 2H). (*cis* diastereoisomer)

^{13}C NMR (101 MHz, $CDCl_3$) δ 214.06, 160.04 (d, *J* = 249.3 Hz), 147.64 (d, *J* = 7.9 Hz), 137.92, 137.73, 131.28 (d, *J* = 7.4 Hz), 129.09, 128.65, 128.08, 128.04, 127.81, 127.54 (d, *J* = 3.3 Hz), 126.61, 121.47 (d, *J* = 21.6 Hz), 113.30 (d, *J* = 26.2 Hz), 73.12, 71.51, 56.59, 44.66, 39.83, 37.31. (*cis* diastereoisomer)

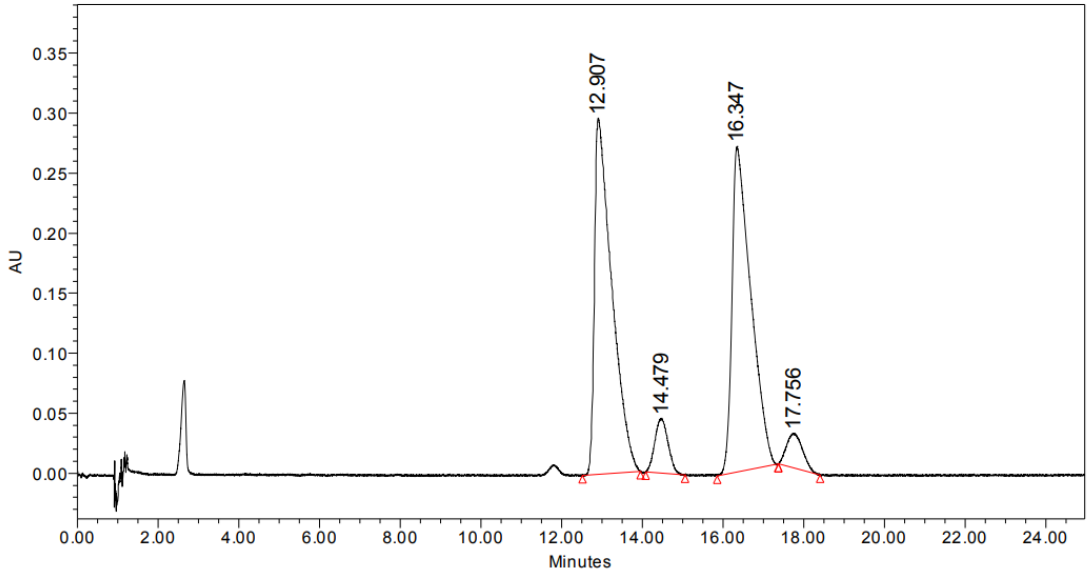
^{19}F NMR (377 MHz, $CDCl_3$) δ -115.05. (*cis* diastereoisomer)

^{77}Se NMR (76 MHz, $CDCl_3$) δ 314.69. (*cis* diastereoisomer)

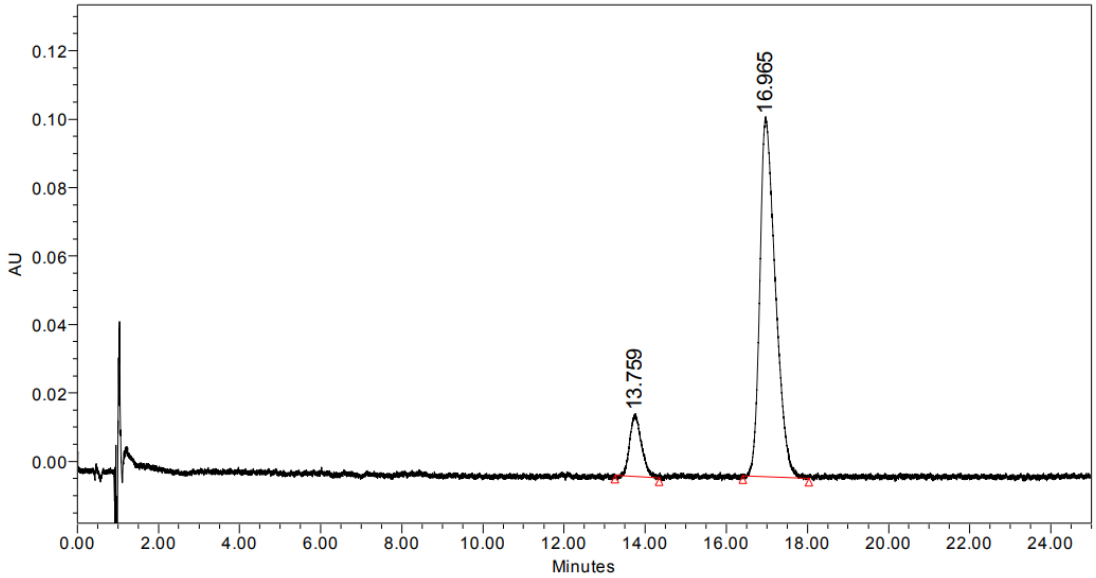
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{22}FNNaO_4Se$ 522.0591; found 522.0589;

SFC (Daicel Chiralpak® IG-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 16.97 min, t_R (minor) = 13.76 min, 88.5:11.5 er.

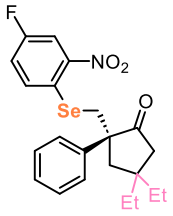
Specific Rotation: $[\alpha]_D^{20}$= -8.08 (c = 0.30, $CHCl_3$)



	Retention Time (min)	Area	Height	% Area	Channel Name
1	12.907	8872477	296482	45.55	254.0nm
2	14.479	1033111	45524	5.30	254.0nm
3	16.347	8769992	271170	45.02	254.0nm
4	17.756	802612	28937	4.12	254.0nm
Sum				100.0	



	RT (min)	Area	% Area	Height (μV)	Channel Name
1	13.759	363674	11.50	18245	254.0nm
2	16.965	2798919	88.50	105066	254.0nm



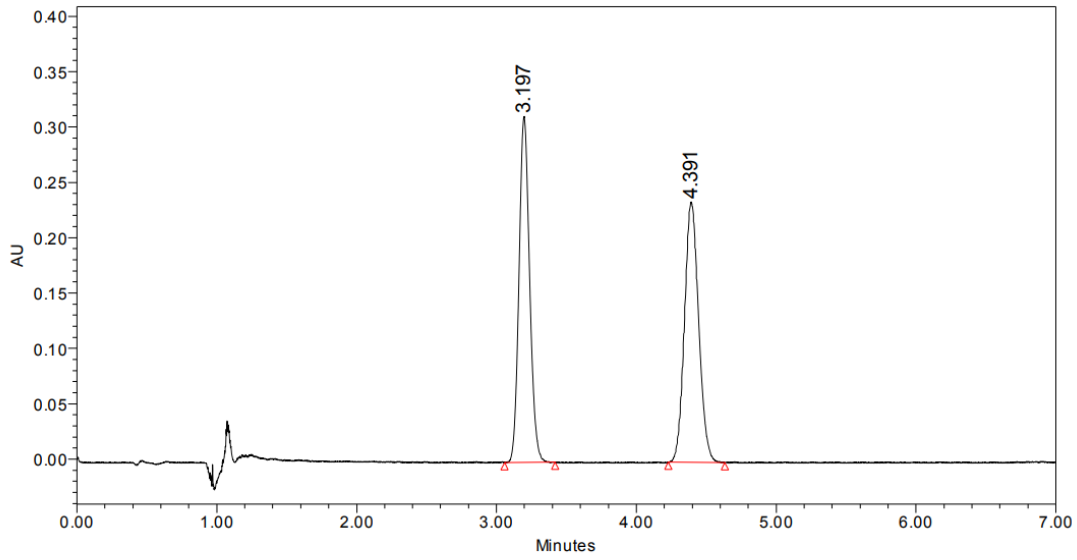
3p

***(R)*-4,4-diethyl-2-(((4-fluoro-2-nitrophenyl)selanyl)methyl)-2-phenylcyclopentan-1-one (3p)**

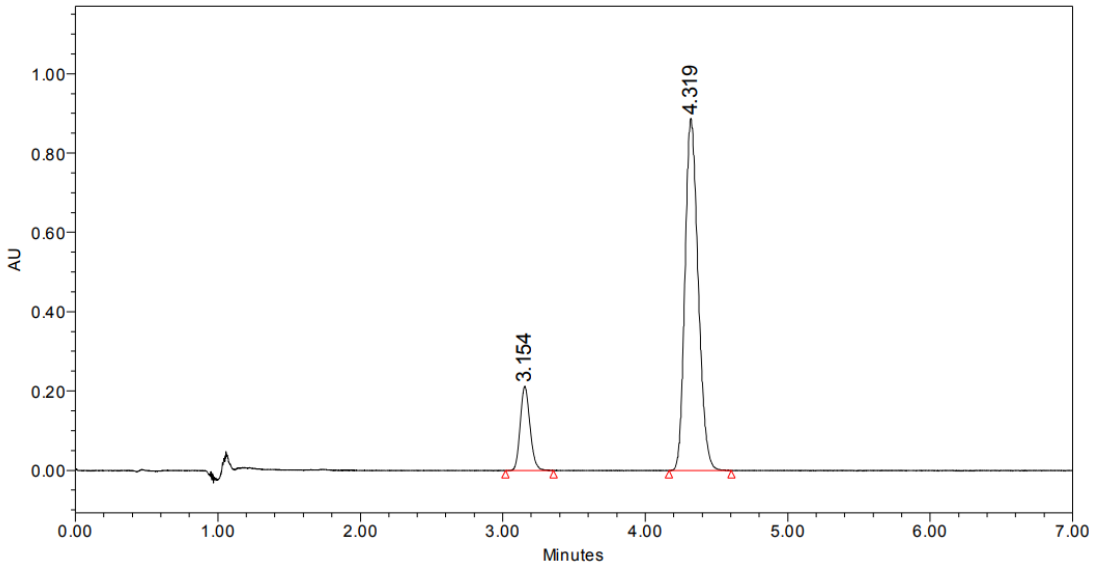
General procedure B, the reaction of **1p** (23.0 mg, 0.10 mmol, 1.0 equiv), **2a** (44.1 mg, 0.11 mmol, 1.1 equiv), **Cat. 3** (6.3 mg, 0.01 mmol, 0.1 equiv), $BF_3{\cdot}Et_2O$ (1.2 μL, 0.01 mmol, 0.1 equiv) and activated 5Å MS (30.0 mg) in distilled $CHCl_3$ (2.0 mL) was stirred at -20 ℃ for 70 h. The mixture was purified by preparative thin layer chromatography (petroleum ether : DCM = 3:5) to afford **3p** as a yellow oil (40.9 mg, 91% yield, 85:15 er), R_f = 0.54 (petroleum ether : DCM = 3:5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.6, 2.8 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.37 – 7.27 (m, 3H), 7.26 – 7.20 (m, 1H), 7.19 – 7.12 (m, 1H), 3.42 (d, *J* = 11.6 Hz, 1H), 3.13 (d, *J* = 11.6 Hz, 1H), 2.82 (d, *J* = 15.6 Hz, 1H), 2.33 (d, *J* = 18.4 Hz, 1H), 2.22 (d, *J* = 18.4 Hz, 1H), 2.08 (d, *J* = 14.0 Hz, 1H), 1.52 – 1.39 (m, 2H), 1.25 – 1.13 (m, 2H), 0.84 (t, *J* = 7.6 Hz, 3H), 0.69 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 218.01, 160.04 (d, *J* = 249.2 Hz), 147.68 (d, *J* = 7.9 Hz), 140.59, 131.28 (d, *J* = 7.4 Hz), 128.91, 127.62, 127.60 (d, *J* = 2.4 Hz), 126.36, 121.45 (d, *J* = 21.6 Hz), 113.25 (d, *J* = 26.3 Hz), 56.67, 50.16, 43.98, 39.61, 39.30, 31.38, 29.96, 8.53, 8.37.
^{19}F NMR (377 MHz, $CDCl_3$) δ -115.00.
^{77}Se NMR (76 MHz, $CDCl_3$) δ 315.77.

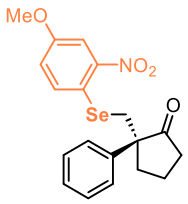
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{24}FNNaO_3Se$ 472.0803; found 472.0799;
SFC (Daicel Chiralpak® IC-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 4.32 min, t_R (minor) = 3.16 min, 85:15 er.
Specific Rotation: $[\alpha]_D^{20}$= -51.20 (c = 1.0, $CHCl_3$)



	Retention Time (min)	Area	Height	% Area	Channel Name
1	3.197	1647838	312131	49.94	254.0nm
2	4.391	1652023	235156	50.06	254.0nm
Sum				100.0	



	Retention Time (min)	Area	Height	% Area	Channel Name
1	3.154	1011329	211778	15.12	254.0nm
2	4.319	5676293	887287	84.88	254.0nm
Sum				100.0	



3q

***(R)*-2-(((4-methoxy-2-nitrophenyl)selanyl)methyl)-2-phenylcyclopentan-1-one (3q)**

General procedure B, the reaction of **1a** (17.4 mg, 0.10 mmol, 1.0 equiv), **2e** (45.5 mg, 0.11 mmol, 1.1equiv), **Cat. 3** (6.3 mg, 0.01 mmol, 0.1 equiv), $BF_3{\cdot}Et_2O$ (1.2 μL, 0.01 mmol, 0.1 equiv) and activated 5Å MS (30.0 mg) in distilled $CHCl_3$ (2.0 mL) was stirred at -50 ℃ for 72 h. The mixture was purified by preparative thin layer chromatography (petroleum ether : DCM = 3:5) to afford **3q** as a yellow solid (38.0 mg, 94% yield, 90.5:9.5 er), R_f = 0.32 (petroleum ether : DCM = 3:5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 2.8 Hz, 1H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.36 – 7.31 (m, 3H), 7.29 – 7.24 (m, 1H), 7.05 (dd, *J* = 8.8, 2.8 Hz, 1H), 3.84 (s, 3H), 3.46 (d, *J* = 11.6 Hz, 1H), 3.18 (d, *J* = 11.6 Hz, 1H), 2.88 – 2.79 (m, 1H), 2.43 – 2.25 (m, 2H), 2.26 – 2.12 (m, 1H), 2.03 – 1.94 (m, 1H), 1.88 – 1.74 (m, 1H).

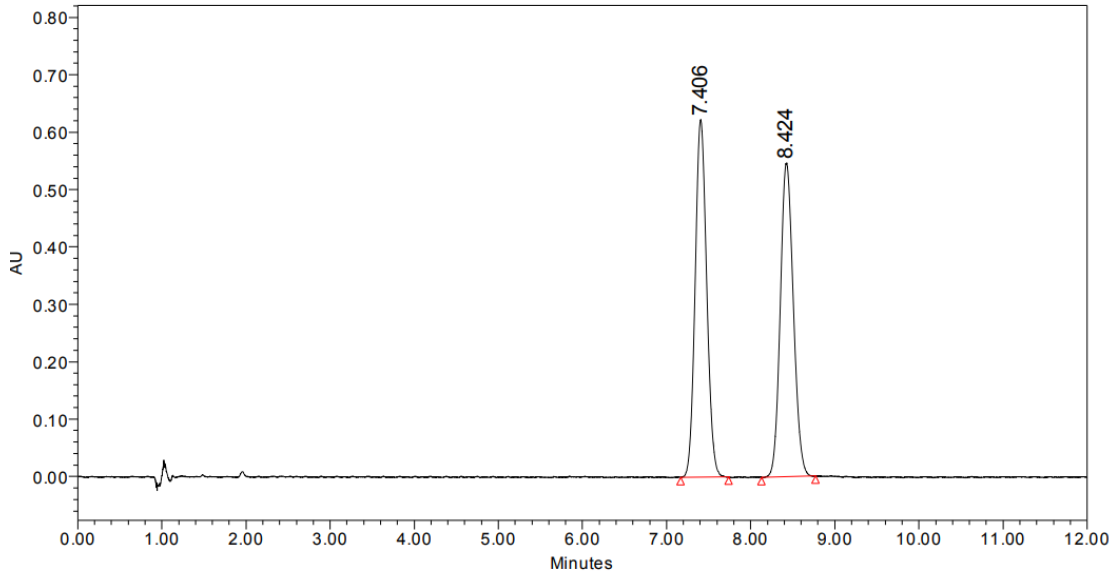
^{13}C NMR (101 MHz, $CDCl_3$) δ 217.65, 157.82, 148.06, 137.61, 130.81, 129.07, 127.86, 126.78, 122.89, 121.82, 109.71, 56.77, 55.97, 37.06, 36.17, 33.97, 18.58.

^{77}Se NMR (76 MHz, $CDCl_3$) δ 302.64.

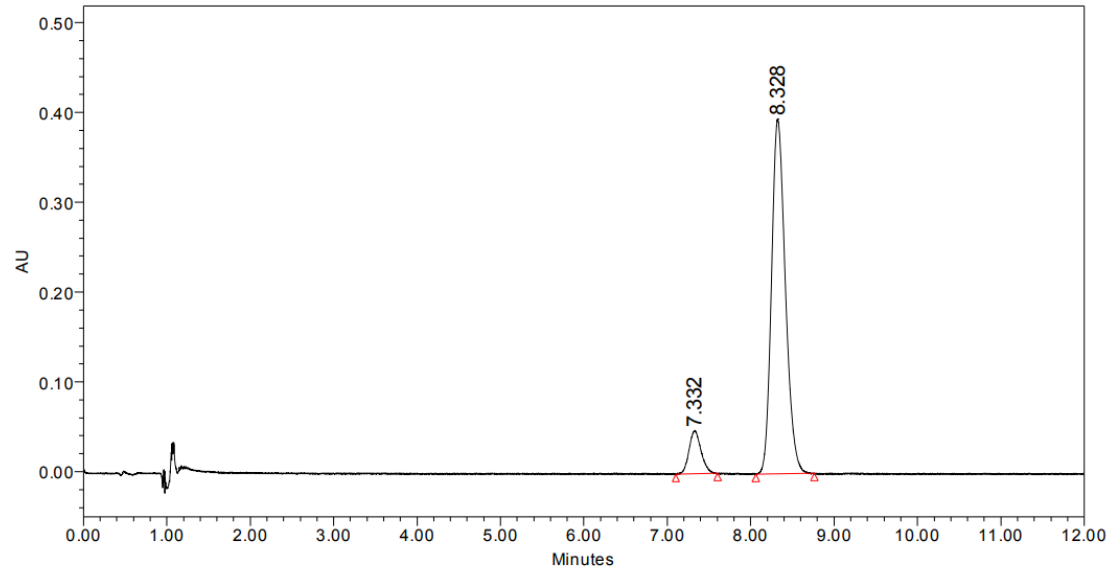
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{19}NNaO_4Se$ 428.0377; found 428.0375;

SFC (Daicel Chiralpak® IC-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 8.33 min, t_R (minor) = 7.33 min, 90.5:9.5 er.

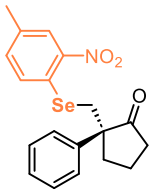
Specific Rotation: $[\alpha]_D^{20}$= -54.60 (c = 1.0, $CHCl_3$)



	Retention Time (min)	Area	Height	% Area	Channel Name
1	7.406	5904134	622804	50.03	254.0nm
2	8.424	5897267	546513	49.97	254.0nm
Sum				100.0	



	Retention Time (min)	Area	Height	% Area	Channel Name
1	7.332	471939	47640	9.36	254.0nm
2	8.328	4569334	395153	90.64	254.0nm
Sum				100.0	



3r

***(R)*-2-(((4-methyl-2-nitrophenyl)selanyl)methyl)-2-phenylcyclopentan-1-one (3r)**

General procedure B, the reaction of **1a** (17.4 mg, 0.10 mmol, 1.0 equiv), **2e** (43.7 mg, 0.11 mmol, 1.1 equiv), **Cat. 3** (6.3 mg, 0.01 mmol, 0.1 equiv), $BF_3{\cdot}Et_2O$ (1.2 μL, 0.01 mmol, 0.1 equiv) and activated 5Å MS (30.0 mg) in distilled $CHCl_3$ (2.0 mL) was stirred at -40 ℃ for 80 h. The mixture was purified by column chromatography on silica gel (petroleum ether : EtOAc = 8:1) to afford **3r** as a yellow solid (37.1 mg, 96% yield, 92.5:7.5 er), R_f = 0.23 (petroleum ether : EtOAc= 6:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.49 – 7.44 (m, 2H), 7.38 – 7.30 (m, 3H), 7.30 – 7.23 (m, 2H), 3.46 (d, *J* = 11.4 Hz, 1H), 3.19 (d, *J* = 11.4 Hz, 1H), 2.90 – 2.79 (m, 1H), 2.43 – 2.23 (m, 5H), 2.22 – 2.11 (m, 1H), 2.05 – 1.93 (m, 1H), 1.89 – 1.74 (m, 1H).

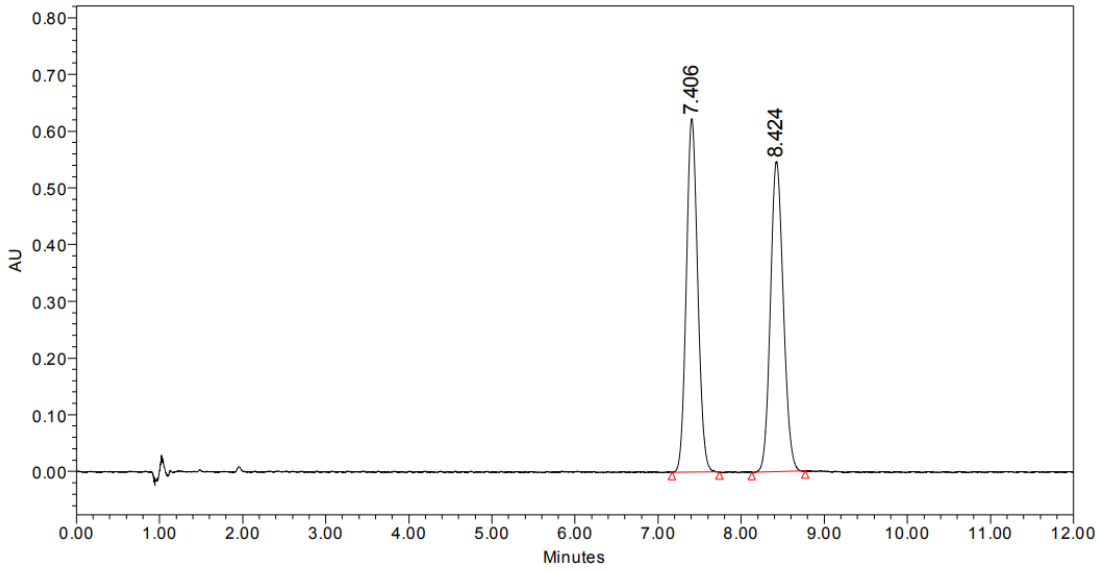
^{13}C NMR (101 MHz, $CDCl_3$) δ 217.63, 147.09, 137.60, 136.13, 134.76, 129.43, 129.29, 129.07, 127.84, 126.77, 126.40, 56.66, 37.00, 35.86, 33.95, 20.58, 18.58.

^{77}Se NMR (76 MHz, $CDCl_3$) δ 309.13.

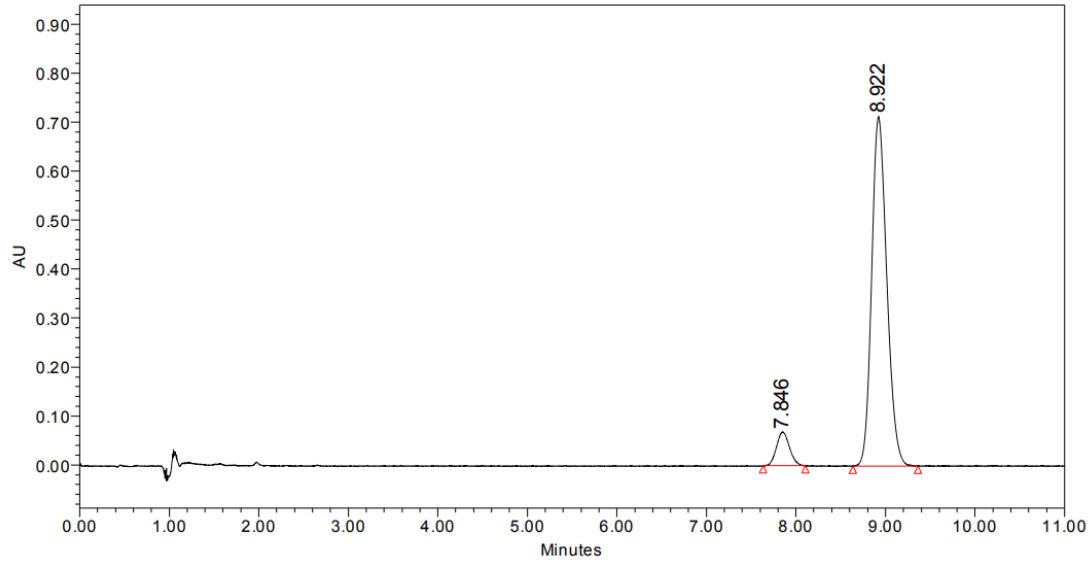
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{19}NNaO_3Se$ 412.0428; found 412.0423;

SFC (Daicel Chiralpak® IC-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 8.92 min, t_R (minor) = 7.85 min, 92.5:7.5 er.

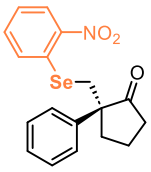
Specific Rotation: $[\alpha]_D^{20}$= -40.00 (c = 1.0, $CHCl_3$)



	Retention Time (min)	Area	Height	% Area	Channel Name
1	7.406	5904134	622804	50.03	254.0nm
2	8.424	5897267	546513	49.97	254.0nm
Sum				100.0	



	Retention Time (min)	Area	Height	% Area	Channel Name
1	7.846	692501	68575	7.63	254.0nm
2	8.922	8377677	713466	92.37	254.0nm
Sum				100.0	



3s

***(R)*-2-(((2-nitrophenyl)selanyl)methyl)-2-phenylcyclopentan-1-one (3s)**

General procedure B, the reaction of **1a** (17.4 mg, 0.10 mmol, 1.0 equiv), **2f** (42.2 mg, 0.11 mmol, 1.1 equiv), **Cat. 3** (6.3 mg, 0.01 mmol, 0.1 equiv), $BF_3{\cdot}Et_2O$ (1.2 μL, 0.01 mmol, 0.1 equiv) and activated 5Å MS (30.0 mg) in distilled $CHCl_3$ (2.0 mL) was stirred at -40 ℃ for 80 h. The mixture was purified by column chromatography on silica gel (petroleum ether : EtOAc = 8:1) to afford **3s** as a yellow oil (33.5 mg, 90% yield, 92:8 er), R_f = 0.27 (petroleum ether : EtOAc= 6:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.40 (m, 4H), 7.38 – 7.32 (m, 2H), 7.30 – 7.23 (m, 2H), 3.49 (d, *J* = 11.6 Hz, 1H), 3.20 (d, *J* = 11.6 Hz, 1H), 2.91 – 2.82 (m, 1H), 2.44 – 2.24 (m, 2H), 2.23 – 2.13 (m, 1H), 2.05 – 1.94 (m, 1H), 1.91 – 1.76 (m, 1H).

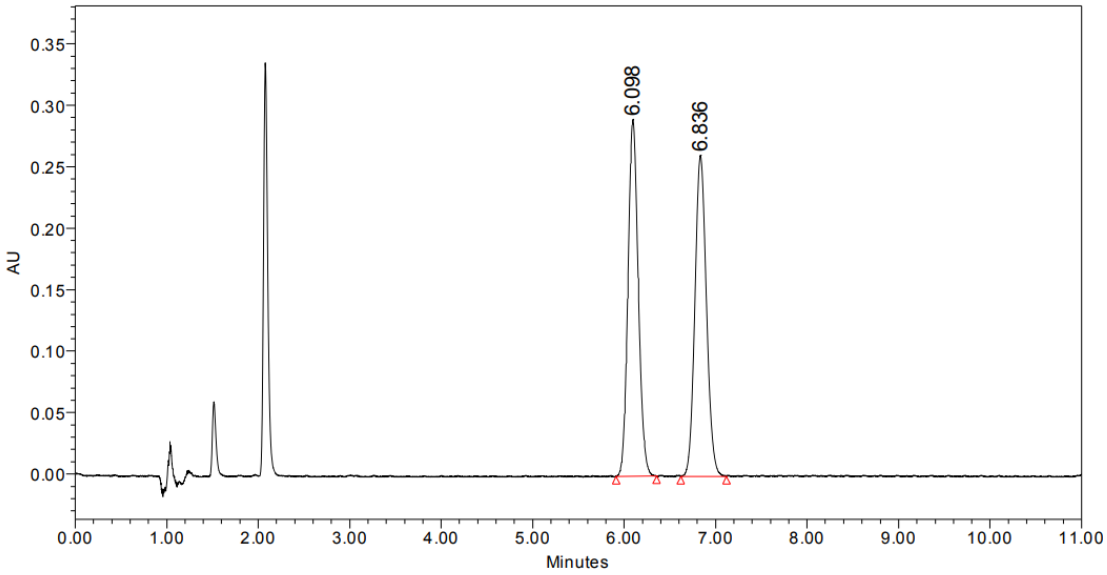
^{13}C NMR (101 MHz, $CDCl_3$) δ 217.56, 147.10, 137.47, 133.61, 133.21, 129.52, 129.10, 127.91, 126.77, 126.28, 125.60, 56.59, 36.96, 35.96, 33.99, 18.57.

^{77}Se NMR (76 MHz, $CDCl_3$) δ 317.78.

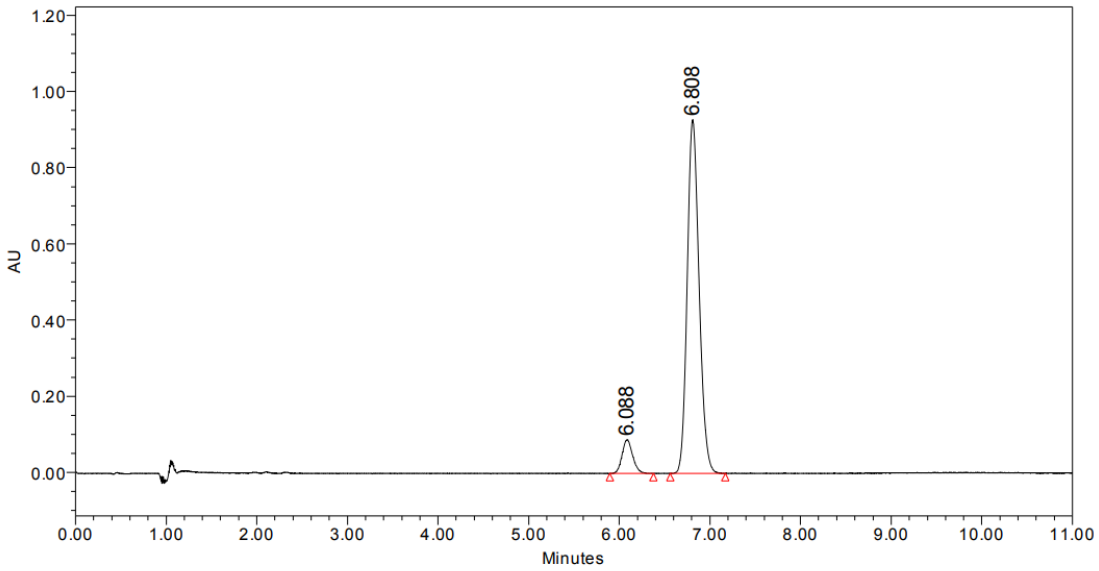
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{17}NNaO_3Se$398.0271; found 398.0265;

SFC (Daicel Chiralpak® IC-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 6.81 min, t_R (minor) = 6.09 min, 92:8 er.

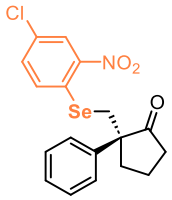
Specific Rotation: $[\alpha]_D^{20}$= -44.80 (c = 1.0, $CHCl_3$)



	Retention Time (min)	Area	Height	% Area	Channel Name
1	6.098	2268270	290176	49.87	254.0nm
2	6.836	2280193	261174	50.13	254.0nm
Sum				100.0	



	Retention Time (min)	Area	Height	% Area	Channel Name
1	6.088	715731	88323	7.83	254.0nm
2	6.808	8421253	927758	92.17	254.0nm
Sum				100.0	



3t

***(R)*-2-(((4-chloro-2-nitrophenyl)selanyl)methyl)-2-phenylcyclopentan-1-one (3t)**

General procedure B, the reaction of **1a** (17.4 mg, 0.10 mmol, 1.0 equiv), **2g** (45.9 mg, 0.11 mmol, 1.1 equiv), **Cat. 3** (6.3 mg, 0.01 mmol, 0.1 equiv), $BF_3{\cdot}Et_2O$ (1.2 μL, 0.01 mmol, 0.1 equiv) and activated 5Å MS (30.0 mg) in distilled $CHCl_3$ (2.0 mL) was stirred at -40 ℃ for 80 h. The mixture was purified by preparative thin layer chromatography (petroleum ether : DCM = 3:5) to afford **3t** as a yellow oil (35.7 mg, 87% yield, 94:6 er), R_f = 0.24 (petroleum ether : DCM = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 2.1 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.41 – 7.31 (m, 3H), 7.31 – 7.25 (m, 3H), 3.48 (d, *J* = 11.4 Hz, 1H), 3.18 (d, *J* = 11.5 Hz, 1H), 2.91 – 2.82 (m, 1H), 2.42 – 2.24 (m, 2H), 2.20 – 2.10 (m, 1H), 2.05 – 1.93 (m, 1H), 1.91 – 1.77 (m, 1H).

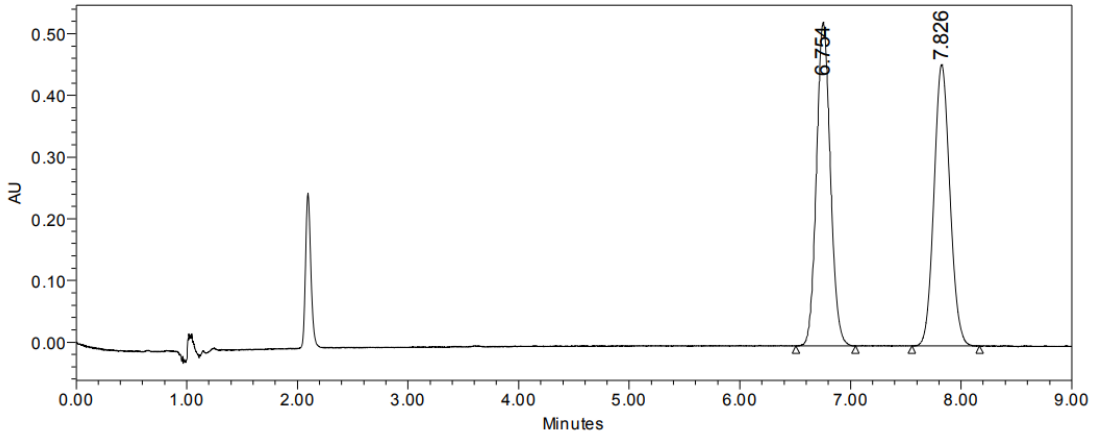
^{13}C NMR (101 MHz, $CDCl_3$) δ 217.40, 147.42, 137.22, 133.57, 131.54, 130.69, 129.16, 128.01, 126.75, 126.03, 56.59, 36.92, 36.23, 34.03, 18.53.

^{77}Se NMR (76 MHz, $CDCl_3$) δ 322.47.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{16}ClNNaO_3Se$ 431.9882; found 431.9871;

SFC (Daicel Chiralpak® IC-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 7.83 min, t_R (minor) = 6.77 min, 94:6 er.

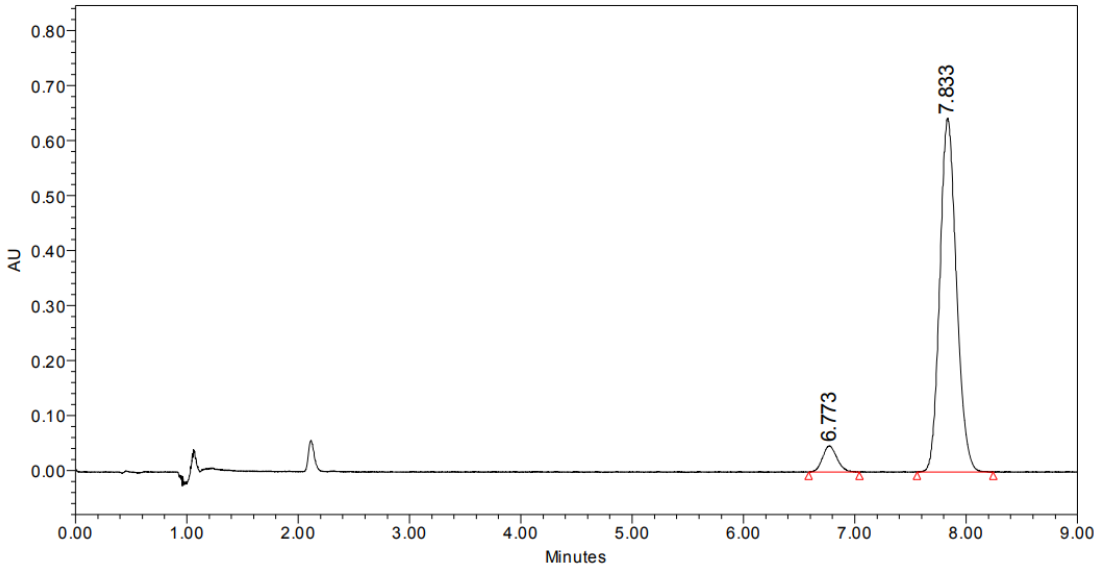
Specific Rotation: $[\alpha]_D^{20}$= -44.40 (c = 1.0, $CHCl_3$)



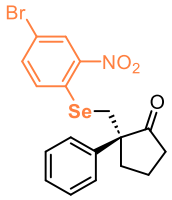
Channel: PDA Spectrum; Processed Channel: PDA Spectrum PDA 254.0 nm (PDA Spectrum (210-400)nm); Result Id: 16358; Processing Method: 1

Processed Channel Descr.: PDA Spectrum PDA 254.0 nm (PDA Spectrum (210-400)nm)

	Processed Channel Descr.	RT	Area	% Area
1	PDA Spectrum PDA 254.0 nm (PDA Spectrum (210-400)nm)	6.754	4589938	50.14
2	PDA Spectrum PDA 254.0 nm (PDA Spectrum (210-400)nm)	7.826	4564438	49.86



	Retention Time (min)	Area	Height	% Area	Channel Name
1	6.773	419519	47146	5.97	254.0nm
2	7.833	6607681	642847	94.03	254.0nm
Sum				100.0	



3u

***(R)*-2-(((4-bromo-2-nitrophenyl)selanyl)methyl)-2-phenylcyclopentan-1-one (3u)**

General procedure B, the reaction of **1a** (17.4 mg, 0.10 mmol, 1.0 equiv), **2h** (50.8 mg, 0.11 mmol, 1.1 equiv), **Cat. 3** (6.3 mg, 0.01 mmol, 0.1 equiv), $BF_3{\cdot}Et_2O$ (1.2 μL, 0.01 mmol, 0.1 equiv) and activated 5Å MS (30.0 mg) in distilled $CHCl_3$ (2.0 mL) was stirred at -40 ℃ for 80 h. The mixture was purified by preparative thin layer chromatography (petroleum ether : DCM = 3:5) to afford **3u** as a yellow oil (36.0 mg, 80% yield, 93.5:6.5 er), R_f = 0.27 (petroleum ether : DCM = 3:5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 2.1 Hz, 1H), 7.51 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.39 – 7.24 (m, 4H), 3.48 (d, *J* = 11.4 Hz, 1H), 3.17 (d, *J* = 11.4 Hz, 1H), 2.94 – 2.80 (m, 1H), 2.46 – 2.23 (m, 2H), 2.22 – 2.08 (m, 1H), 2.06 – 1.92 (m, 1H), 1.91 – 1.75 (m, 1H).

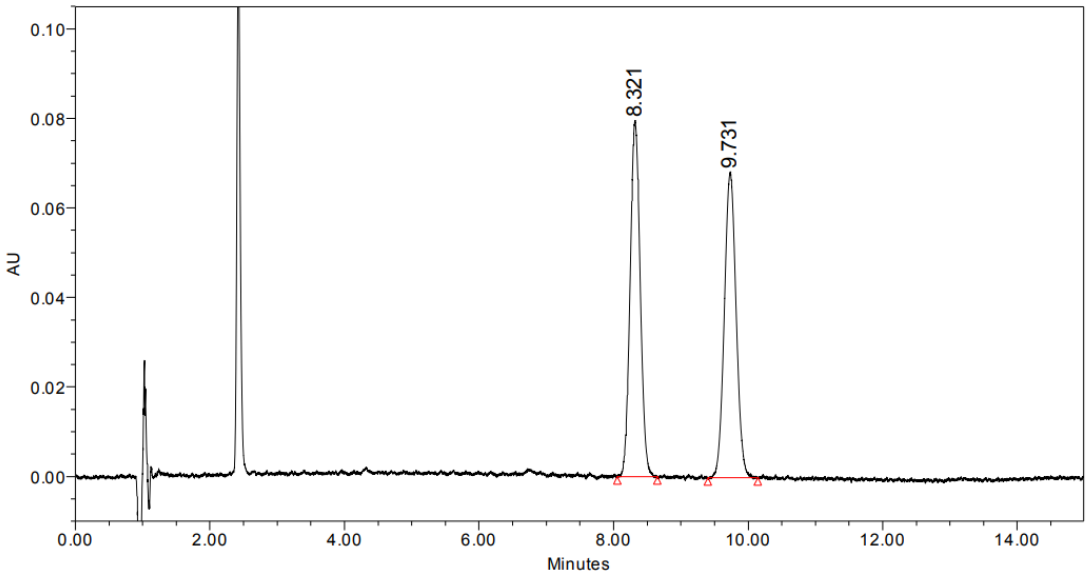
^{13}C NMR (101 MHz, $CDCl_3$) δ 217.39, 147.55, 137.20, 136.37, 132.26, 130.90, 129.16, 128.93, 128.01, 126.75, 118.63, 56.57, 36.91, 36.21, 34.03, 18.53.

^{77}Se NMR (76 MHz, $CDCl_3$) δ 322.94.

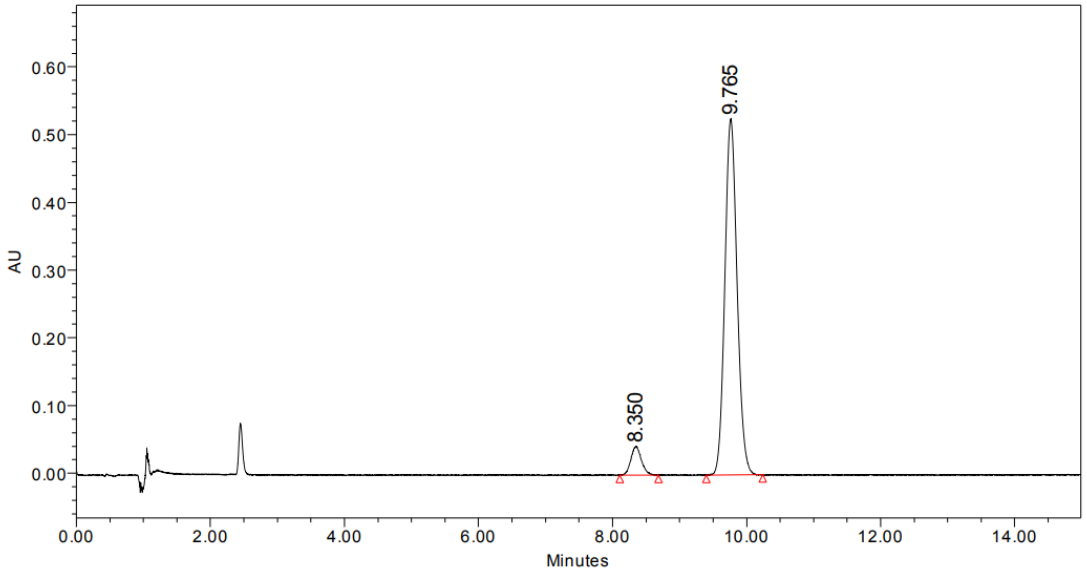
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{16}BrNNaO_3Se$ 475.9376; found 475.9374;

SFC (Daicel Chiralpak® IC-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 9.77 min, t_R (minor) = 8.35 min, 93.5:6.5 er.

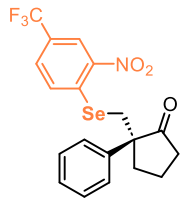
Specific Rotation: $[\alpha]_D^{20}$= -36.40 (c = 1.0, $CHCl_3$)



	Retention Time (min)	Area	Height	% Area	Channel Name
1	8.321	829299	79518	49.99	254.0nm
2	9.731	829469	68272	50.01	254.0nm
Sum				100.0	



	Retention Time (min)	Area	Height	% Area	Channel Name
1	8.350	457914	42142	6.41	254.0nm
2	9.765	6682256	525764	93.59	254.0nm
Sum				100.0	



3v

***(R)*-2-(((2-nitro-4-(trifluoromethyl)phenyl)selanyl)methyl)-2-phenylcyclopentan-1-one (3v)**

General procedure B, the reaction of **1a** (17.4 mg, 0.10 mmol, 1.0 equiv), **2i** (49.6 mg, 0.11 mmol, 1.1 equiv), **Cat. 3** (6.3 mg, 0.01 mmol, 0.1 equiv), $BF_3{\cdot}Et_2O$ (1.2 μL, 0.01 mmol, 0.1 equiv) and activated 5Å MS (30.0 mg) in distilled $CHCl_3$ (2.0 mL) was stirred at -20 ℃ for 108 h. The mixture was purified by preparative thin layer chromatography (petroleum ether : DCM = 3:5) to afford **3v** as a yellow solid (37.3 mg, 84% yield, 90:10 er), R_f = 0.51 (petroleum ether : DCM = 3:5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.65 – 7.54 (m, 2H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.31 – 7.25 (m, 1H), 3.54 (d, *J* = 11.6 Hz, 1H), 3.22 (d, *J* = 11.6 Hz, 1H), 2.94 – 2.87 (m, 1H), 2.45 – 2.25 (m, 2H), 2.22 – 2.10 (m, 1H), 2.08 – 1.97 (m, 1H), 1.92 – 1.79 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 217.29, 146.70, 138.74, 137.01, 130.34, 129.41 (q, *J* = 3.4 Hz), 129.23, 128.14 (q, *J* = 34.4 Hz), 128.14, 126.77, 123.45 (q, *J* = 4.0 Hz), 123.05 (q, *J* = 272.0 Hz), 56.54, 36.86, 36.43, 34.09, 18.53.

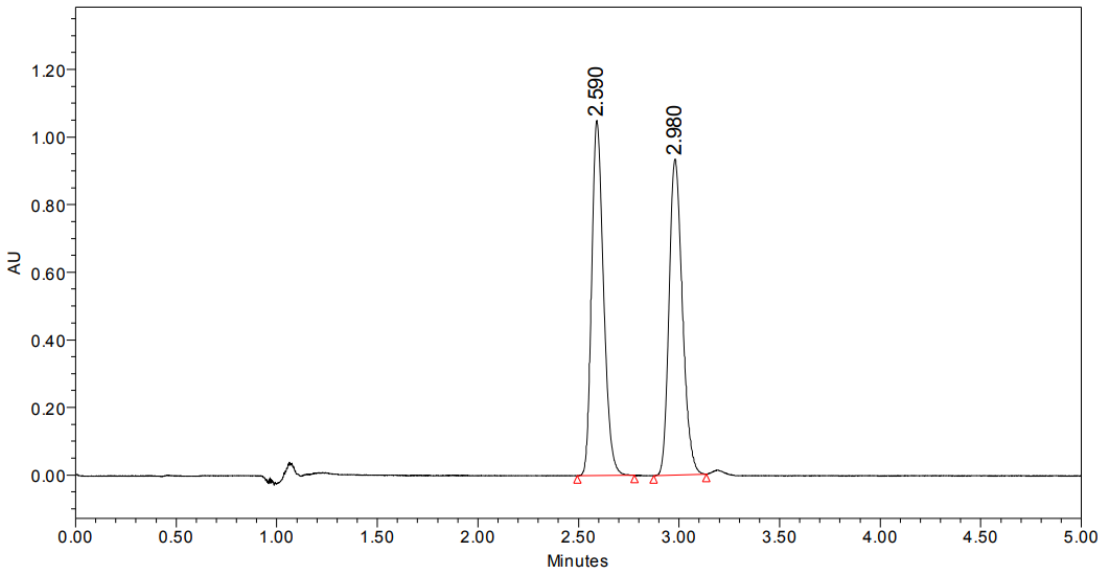
^{19}F NMR (377 MHz, $CDCl_3$) δ -62.78.

^{77}Se NMR (76 MHz, $CDCl_3$) δ 340.51.

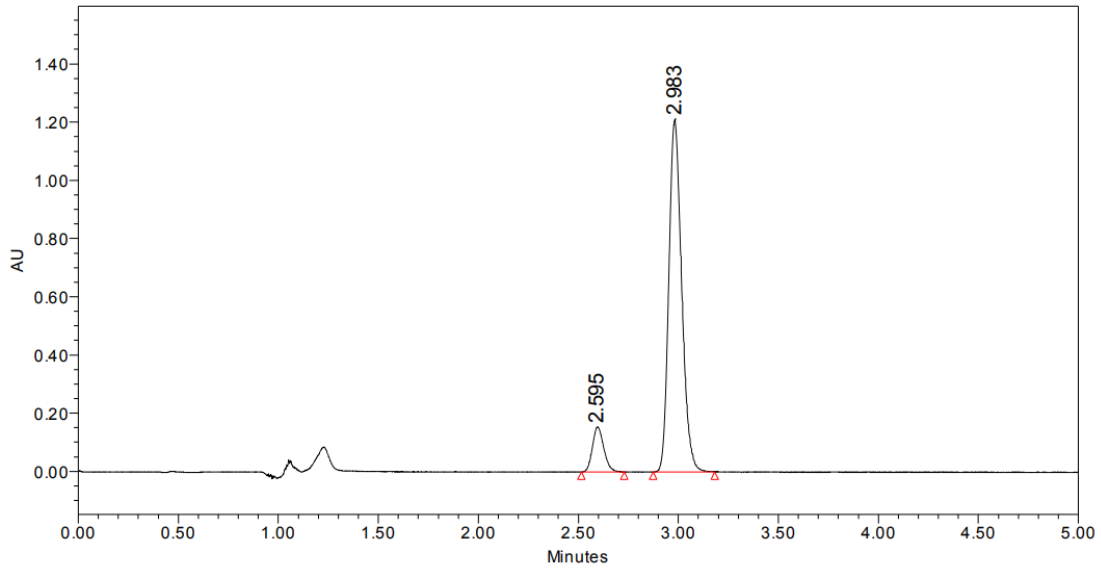
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{16}F_3NNaO_3Se$ 466.0145; found 466.0142;

SFC (Daicel Chiralpak® IC-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 2.98 min, t_R (minor) = 2.60 min, 90:10 er.

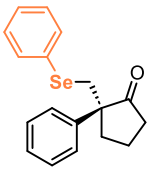
Specific Rotation: $[\alpha]_D^{20}$= -41.00 (c = 1.0, $CHCl_3$)



	Retention Time (min)	Area	Height	% Area	Channel Name
1	2.590	4330325	1050176	50.20	254.0nm
2	2.980	4295837	934534	49.80	254.0nm
Sum				100.0	



	Retention Time (min)	Area	Height	% Area	Channel Name
1	2.595	609661	154684	10.17	254.0nm
2	2.983	5383742	1212536	89.83	254.0nm
Sum				100.0	



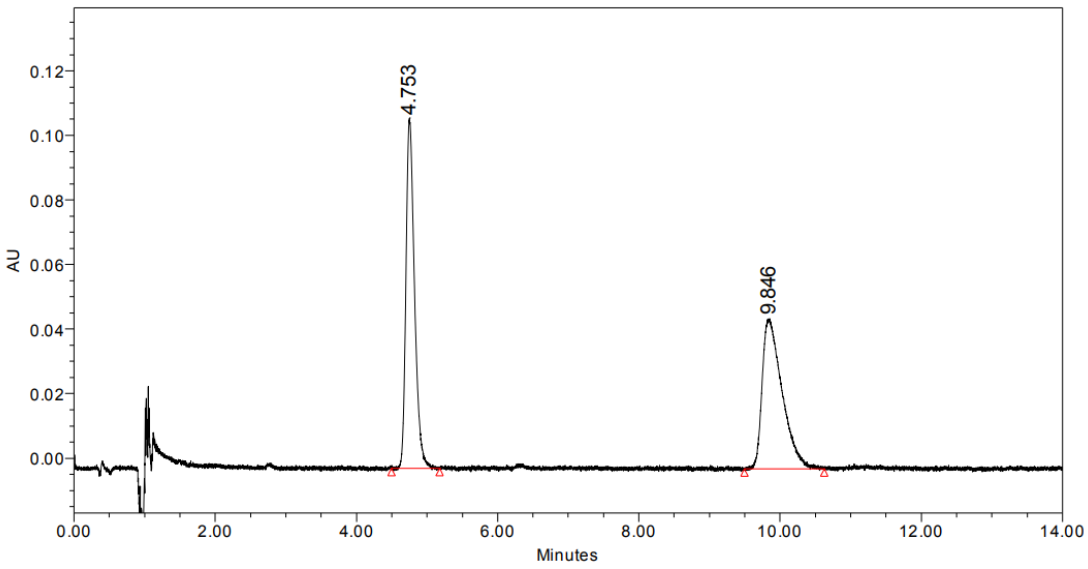
3w

***(R)*-2-phenyl-2-((phenylselanyl)methyl)cyclopentan-1-one (3w)**

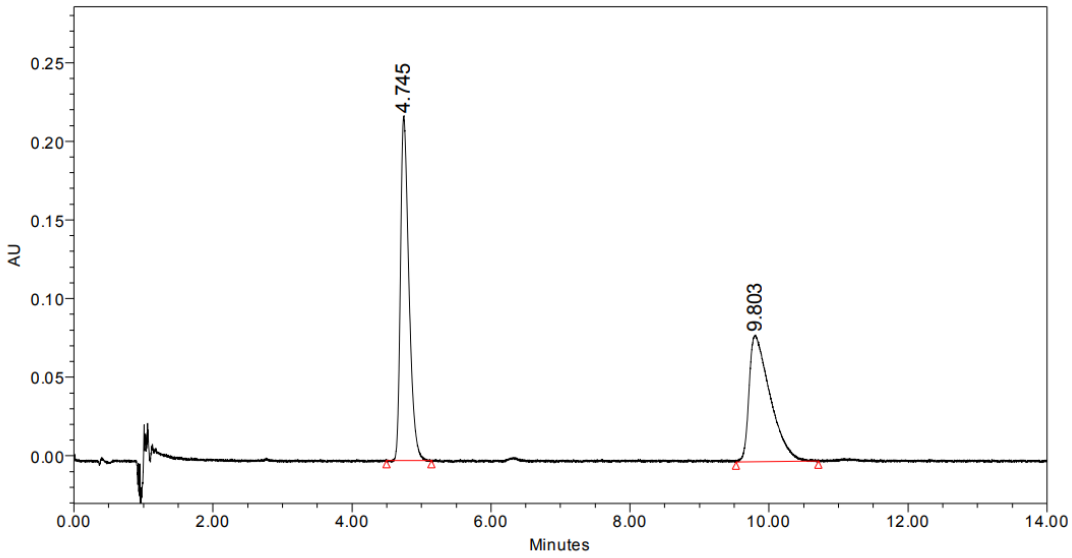
General procedure B, the reaction of **1a** (17.4 mg, 0.10 mmol, 1.0 equiv), **2g** (37.2 mg, 0.11 mmol, 1.1 equiv), **Cat. 3** (6.3 mg, 0.01 mmol, 0.1 equiv), $BF_3{\cdot}Et_2O$ (1.2 μL, 0.01 mmol, 0.1 equiv) and activated 5Å MS (30.0 mg) in distilled $CHCl_3$ (2.0 mL) was stirred at -40 ℃ for 48 h. The mixture was purified by preparative thin layer chromatography (petroleum ether : EtOAc= 16:1) to afford **3w** as a yellow oil (30.4 mg, 92% yield, 52.5:47.5 er), R_f = 0.33 (petroleum ether : EtOAc= 16:1).

3w[11] are known compounds and the analytical data (**^{1}H NMR** and **^{13}C NMR**) match with the literature.

SFC (Daicel Chiralpak® AD-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 9.80 min, t_R (minor) = 4.75 min, 52.5:47.5 er.

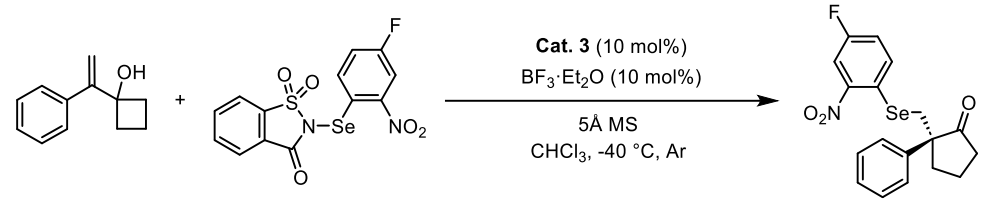


	Retention Time (min)	Area	Height	% Area	Channel Name
1	4.753	910542	108472	49.92	254.0nm
2	9.846	913310	46523	50.08	254.0nm
Sum				100.0	



	Retention Time (min)	Area	Height	% Area	Channel Name
1	4.745	1851984	219019	52.42	254.0nm
2	9.803	1681232	80369	47.58	254.0nm
Sum				100.0	

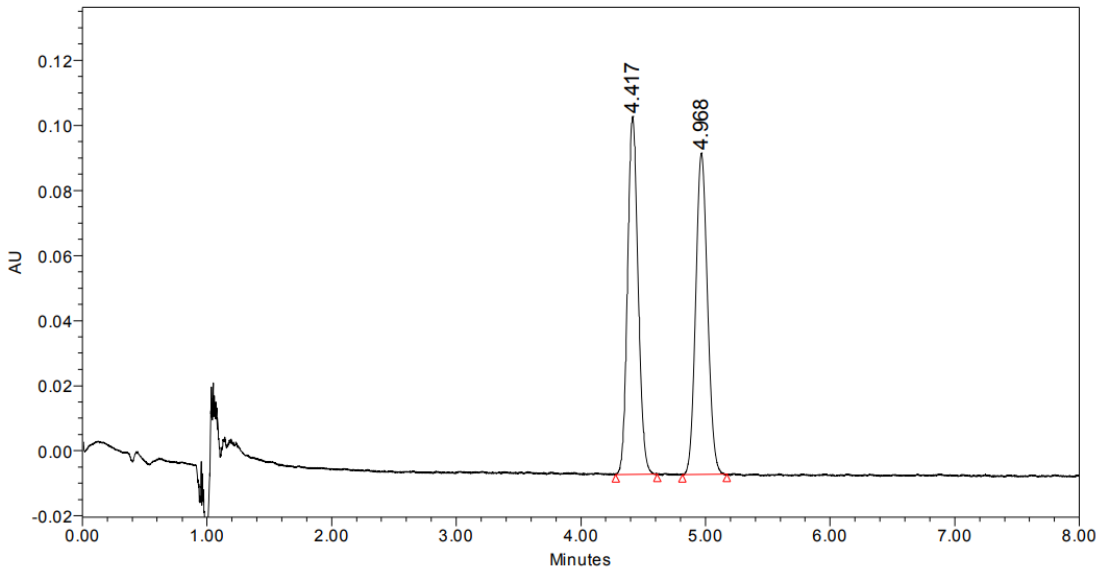
9. One–mmol-scale reaction and synthetic applications



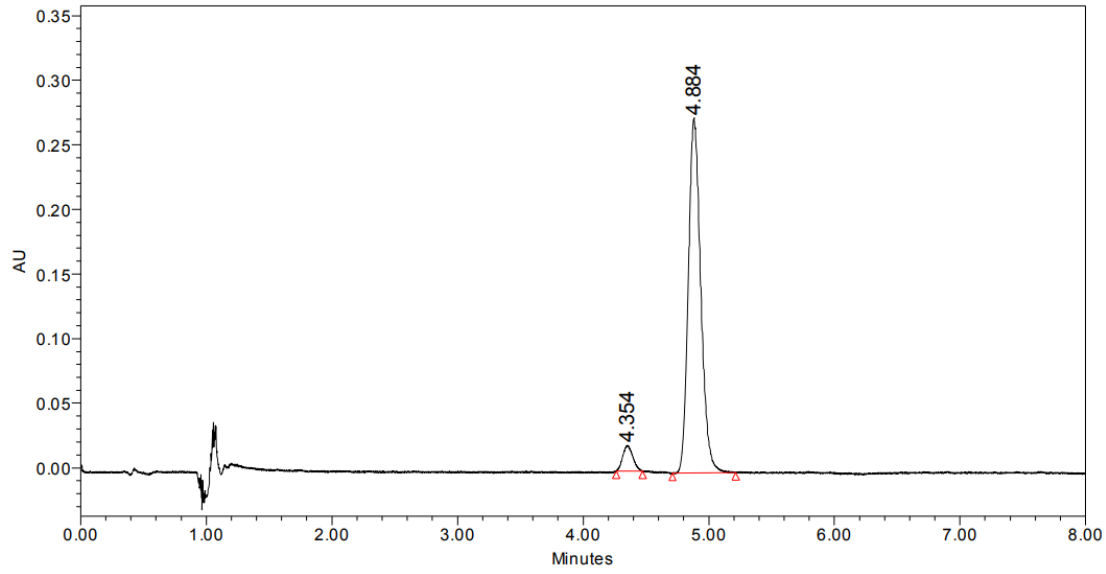
1a, 174 mg, 1.0 mmol **2a**, 441 mg, 1.1 mmol **3a**, 377 mg
96%, 94.5:5.5 er

Activation of molecular sieves: 5Å MS (white powder, purchased from Energy Chemical®) was activated by placing the powder under vacuum and heating with a heat gun for 5 min. The activated 5Å MS was used immediately.

An oven-dried flask charged with **1a** (1 mmol, 1.0 equiv), **2a** (1.1 mmol, 1.1 equiv), **Cat. 3** (63 mg, 0.1 mmol, 0.1 equiv) and activated 5Å MS (195 mg) was evacuated and refilled three times with argon. Distilled $CHCl_3$ (13 mL) was then added to the reaction system at -40 ℃. Subsequently, $BF_3 \cdot Et_2O$ (12.0 μL, 0.1 equiv) was added to the system using microliter syringe. The resulting mixture continued to stir for 80 h. At the end of the reaction, the mixture was filtered through Celite and washed with DCM, and quenched with saturated aqueous $NaHCO_3$ (10 mL). The organic layer of the filtrate was separated and the aqueous layer was extracted twice with DCM (20 mL), the combined organic layer was extracted with brine (20 mL) and dried over Na_2SO_4, filtered and concentrated in *vacuo*. The crude product was purified via column chromatography on silica gel (first: petroleum ether : DCM = 5:1, second: petroleum ether : EtOAc = 10:1) to afford **3a** (377 mg, 96% yield, 94.5:5.5 er) as a yellow solid. **SFC** (Daicel Chiralpak® IC-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 ℃): t_R(major) = 4.89 min, t_R (minor) =4.36 min, 94.5:5.5 er.

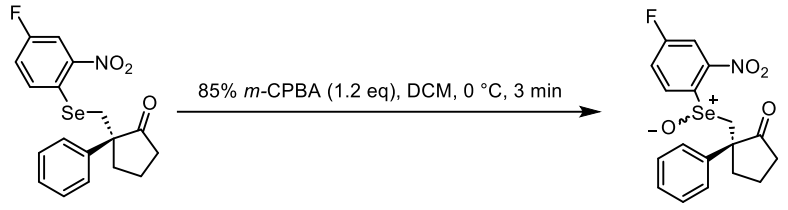


	Retention Time (min)	Area	Height	% Area	Channel Name
1	4.417	647530	109920	50.01	254.0nm
2	4.968	647250	98744	49.99	254.0nm
Sum				100.0	



	Retention Time (min)	Area	Height	% Area	Channel Name
1	4.354	110117	19722	5.57	254.0nm
2	4.884	1865605	274620	94.43	254.0nm
Sum				100.0	

Synthetic applications



3a **4a**

A oven-deied tube was charged with **3a** (39.2 mg, 0.1 mmol, 1.0 equiv) in DCM (1 mL), then m-CPBA (85%) (24.4 mg, 0.12 mmol, 1.2 equiv) was added at once at 0 ℃. The solution turned from yellow to light yellow in 3 min, indicating the end of reaction. The mixture was quenched with saturated aqueous $NaHCO_3$ (1 mL) and extracted with DCM twice, the combined organic layers were washed with brine (3 mL), dried over Na_2SO_4, filtered and concentrated in *vacuo*. The crude product was purified via column chromatography on silica gel (DCM : MeOH = 10 : 1) to afford **4a** as a pale yellow solid (42.2 mg, > 99% yield, 94.5:5.5 er), a mixture of *cis* and *trans* diastereoisomers (*cis:trans* = 1.6:1), R_f = 0.72 (DCM : MeOH = 10 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 8.8, 5.4 Hz, 1H), 8.02 (dd, *J* = 8.0, 2.8 Hz, 1H), 7.71 – 7.60 (m, 1H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.41 – 7.24 (m, 1H), 3.90 (d, *J* = 11.6 Hz, 1H), 3.31 – 3.25 (m, 1H), 2.78 (d, *J* = 11.6 Hz, 1H), 2.42 – 2.22 (m, 4H), 2.14 – 2.01 (m, 1H), 1.94 – 1.74 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 216.40, 164.24 (d, *J* = 256.2 Hz), 146.43 (d, *J* = 8.7 Hz), 135.69, 133.94 (d, *J* = 3.4 Hz), 130.30 (d, *J* = 8.5 Hz), 129.52, 128.58, 127.17, 123.02 (d, *J* = 21.6 Hz), 112.88 (d, *J* = 27.2 Hz), 64.61, 55.35, 35.82, 33.83, 18.67.

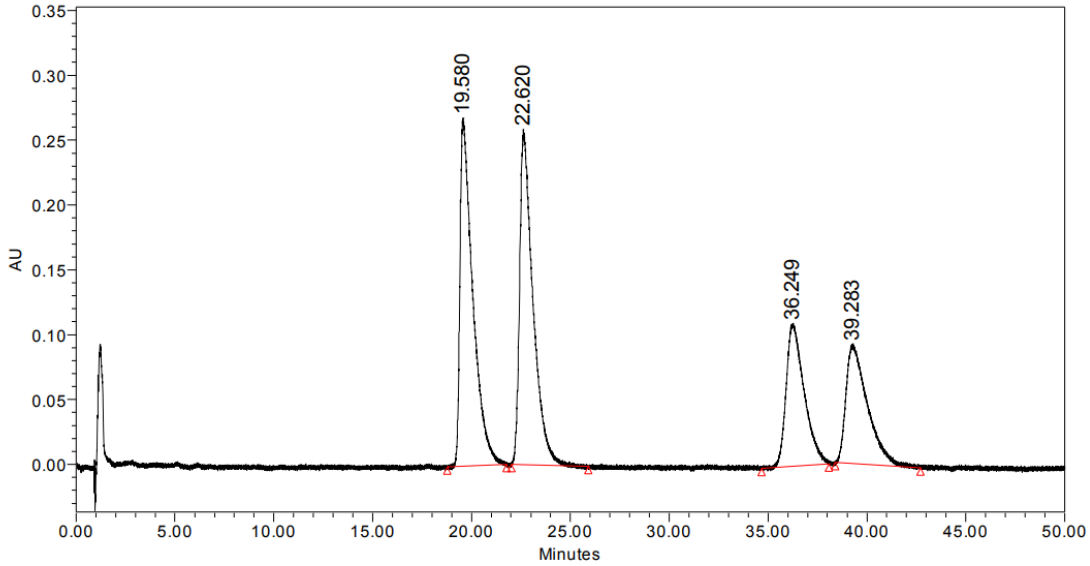
^{19}F NMR (377 MHz, $CDCl_3$) δ -105.76.

^{77}Se NMR (76 MHz, $CDCl_3$) δ 897.29.

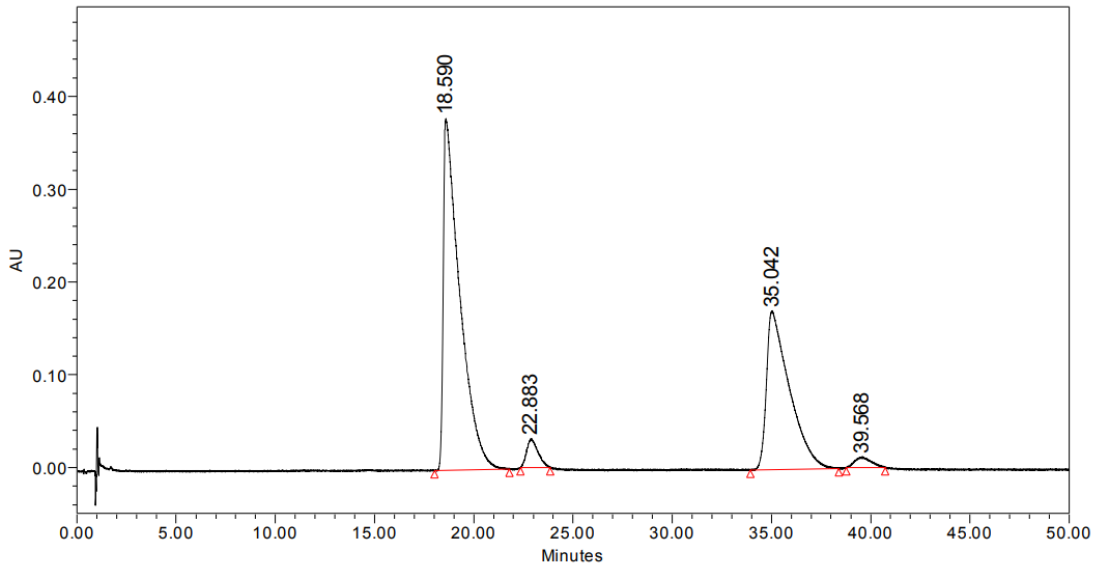
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{16}FNNaO_4Se$ 432.0121; found 432.0120;

SFC (Daicel Chiralpak® IG-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 18.59 min, t_R (minor) = 22.88 min, 94.5:5.5 er.

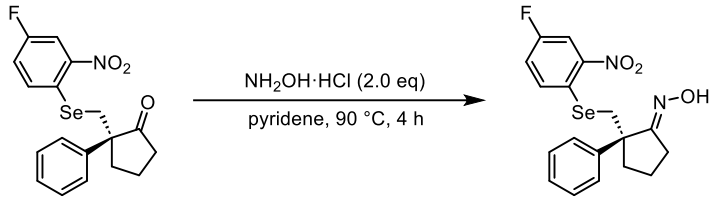
Specific Rotation: $[\alpha]_D^{20}$= -62.11 (c = 0.5, $CHCl_3$)



	RT (min)	Area	% Area	Height (μV)	Channel Name
1	19.580	12140359	31.89	268440	211.0nm
2	22.620	12174470	31.98	257995	211.0nm
3	36.249	6906155	18.14	110013	211.0nm
4	39.283	6847094	17.99	91983	211.0nm



	RT (min)	Area	% Area	Height (μV)	Channel Name
1	18.590	21990531	58.65	378961	254.0nm
2	22.883	1231077	3.28	30913	254.0nm
3	35.042	13639215	36.38	171048	254.0nm
4	39.568	635113	1.69	11364	254.0nm



3a **5a**

A oven-dried tube was charged with **3a** (39.2 mg, 0.1 mmol, 1.0 equiv) and NH_2OH • HCl (13.9 mg, 0.2 mmol, 2.0 equiv) in pyridine (1 mL), filled with Ar and heated at 90 ℃ for 4 h. At the end of the reaction, the solvent was removed in *vacuo*. The crude product was purified by preparative thin layer chromatography (petroleum ether : EtOAc = 3:1) to afford **5a** as a yellow solid (39.7 mg, 98% yield, 94.5:5.5 er), R_f = 0.36 (petroleum ether : EtOAc= 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.89 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.40 – 7.29 (m, 3H), 7.28 – 7.21 (m, 1H), 7.20 – 7.10 (m, 1H), 3.48 (d, *J* = 11.6 Hz, 1H), 3.40 (d, *J* = 11.6 Hz, 1H), 2.69 – 2.56 (m, 2H), 2.55 – 2.43 (m, 1H), 2.12 – 2.00 (m, 1H), 1.88 – 1.77 (m, 1H), 1.62 – 1.46 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.54, 159.94 (d, *J* = 249.0 Hz), 147.69 (d, *J* = 8.0 Hz), 140.91, 131.32 (d, *J* = 7.2 Hz), 128.87, 128.45 (d, *J* = 3.4 Hz), 127.56, 126.85, 121.38 (d, *J* = 21.5 Hz), 113.23 (d, *J* = 26.1 Hz), 54.10, 37.97, 37.29, 26.79, 20.45.

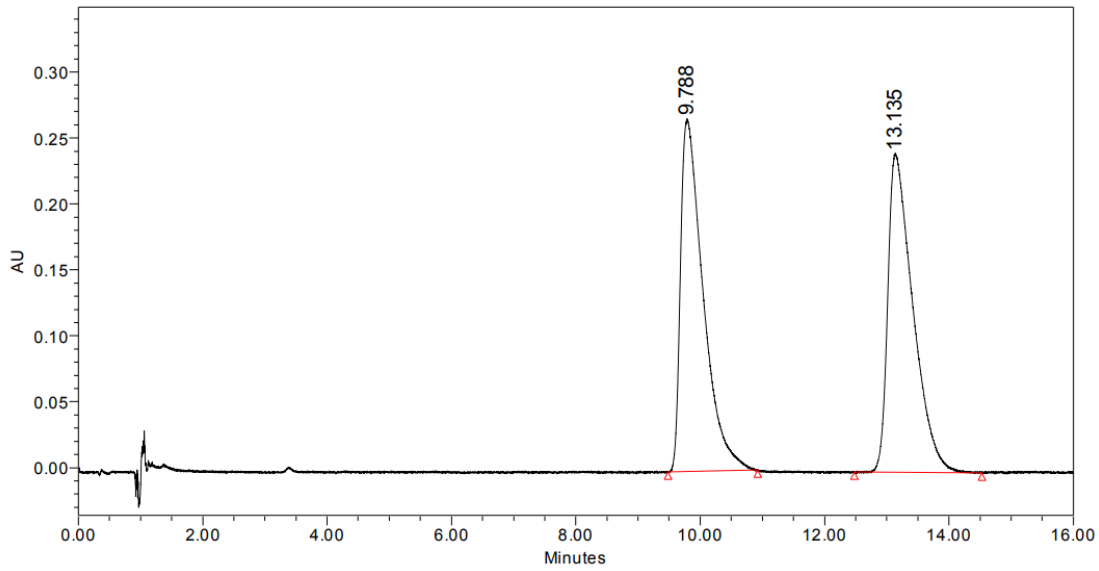
^{19}F NMR (377 MHz, $CDCl_3$) δ -115.37.

^{77}Se NMR (76 MHz, $CDCl_3$) δ 319.14.

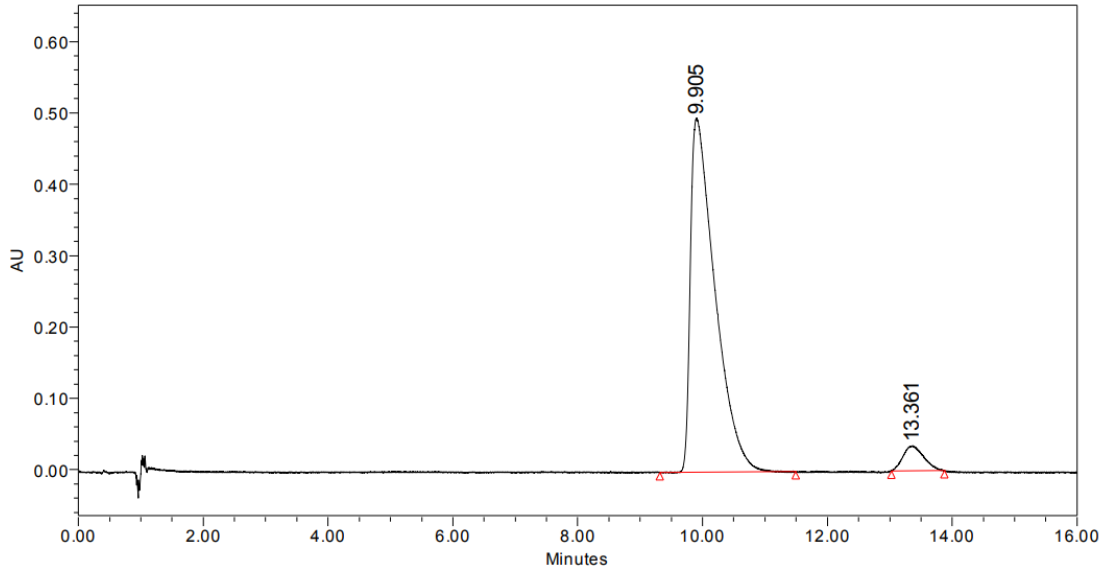
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{17}FN_2NaO_3Se$ 431.0281; found 431.0283;

SFC (Daicel Chiralpak® AD-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 9.91 min, t_R (minor) = 13.36 min, 94.5:5.5 er.

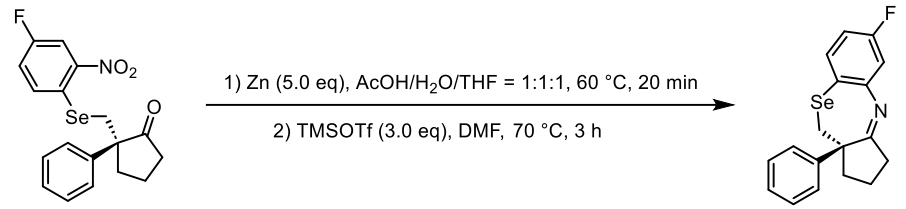
Specific Rotation: $[\alpha]_D^{20}$= -99.89 (c = 0.5, $CHCl_3$)



	RT (min)	Area	% Area	Height (μV)	Channel Name
1	9.788	6745260	49.95	267185	254.0nm
2	13.135	6758186	50.05	241808	254.0nm



	RT	Area	% Area	Height	Channel Name
1	9.905	13516246	94.47	496155	254.0nm
2	13.361	791952	5.53	34572	254.0nm



3a **6a**

A sealed tube charged with **3a** (39.2 mg, 0.1 mmol, 1.0 equiv) and Zn (32.7 mg, 0.5 mmol, 5.0 equiv) in AcOH/THF/H_2O = 0.5/0.5/0.5 mL and stirred at 60 ℃ for 20 min. The solution turns from yellow to colourless indicating the end of reaction. After completion of the reaction, the mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL) and extracted twice with Et_2O, the combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, filtered and concentrated in *vacuo*. The crude product is unstable and proceed immediately to the next step.

The crude product from the previous step was transferred to a oven-dried tube in an argon atmosphere in DMF (1 mL). TMSOTf (54 μL, 0.3 mmol, 3.0 equiv) was added and stirred at 70 ℃ for 3 h. After completion of the reaction, the mixture was quenched with H_2O (5 mL) and extracted twice with EtOAc, the combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, filtered and concentrated in *vacuo*. The crude product was purified by preparative thin layer chromatography (petroleum ether : EtOAc = 4:1) to afford **6a** as a yellow oil (23.8 mg, 69% yield, 94.5:5.5 er), R_f = 0.58 (petroleum ether : EtOAc= 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 1H), 7.13 – 6.98 (m, 5H), 6.46 (dd, *J* = 10.0, 2.8 Hz, 1H), 6.39 – 6.30 (m, 1H), 3.96 (d, *J* = 12.4 Hz, 1H), 3.61 (d, *J* = 12.4 Hz, 1H), 3.08 – 2.98 (m, 1H), 2.93 – 2.81 (m, 1H), 2.24 – 2.08 (m, 2H), 2.08 – 1.91 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.98, 163.18 (d, *J* = 246.5 Hz), 152.21 (d, *J* = 10.5 Hz), 141.85, 135.77 (d, *J* = 9.0 Hz), 128.28, 126.58, 126.49, 116.51 (d, *J* = 3.3 Hz), 111.30 (d, *J* = 23.3 Hz), 110.80 (d, *J* = 21.7 Hz), 57.67, 45.76, 39.01, 38.12, 20.81.

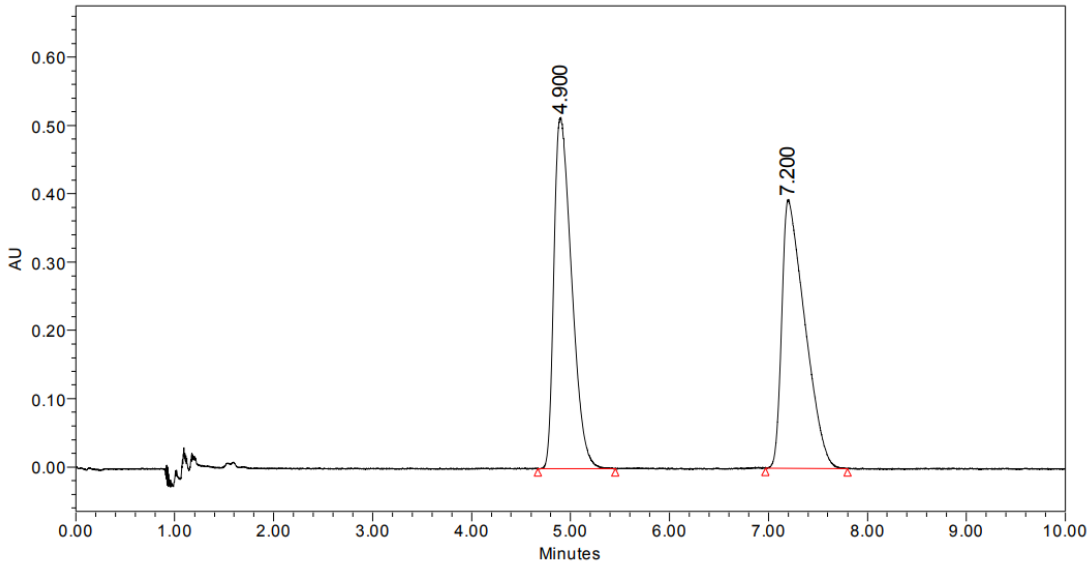
^{19}F NMR (377 MHz, $CDCl_3$) δ -113.90.

^{77}Se NMR (76 MHz, $CDCl_3$) δ 218.99.

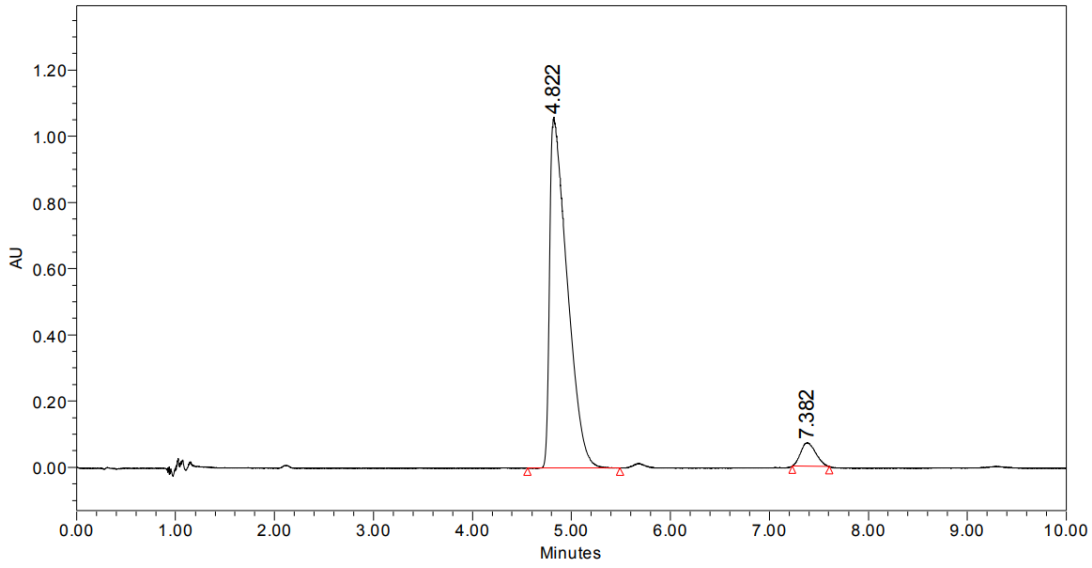
HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{17}FNSe$ 346.0505; found 346.0506;

SFC (Daicel Chiralpak® IG-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 4.82 min, t_R (minor) = 7.38 min, 94.5:5.5 er.

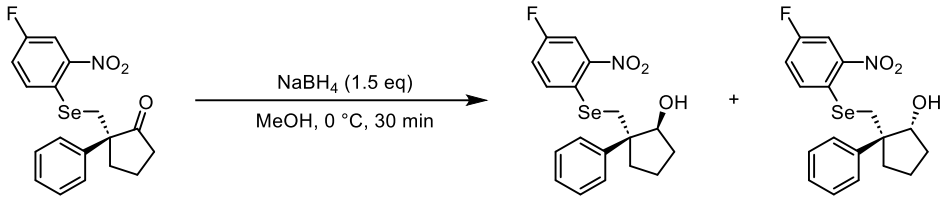
Specific Rotation: $[\alpha]_D^{20}$= +195.87 (c = 0.5, $CHCl_3$)



	RT (min)	Area	% Area	Height (μV)	Channel Name
1	4.900	6368391	50.09	513442	254.0nm
2	7.200	6345774	49.91	393279	254.0nm

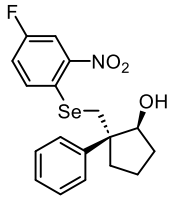


	RT (min)	Area	% Area	Height (μV)	Channel Name
1	4.822	12976607	94.52	1058722	254.0nm
2	7.382	753044	5.48	70898	254.0nm



3a **7a** **7b**

A oven-deied tube was charged with **3a** (39.2 mg, 0.1 mmol, 1.0 equiv) in dried MeOH (1 mL), then $NaBH_4$ (5.7 mg, 0.15 mmol, 1.5 equiv) was added at once at 0 ℃ for 30 min. At the end of reaction, the mixture was quenched with saturated aqueous H_2O (1 mL) and extracted twice with DCM, the combined organic layers were washed with brine (3 mL), dried over Na_2SO_4, filtered and concentrated in *vacuo*. The crude product was purified by preparative thin layer chromatography (petroleum ether : EtOAc = 3:1) to afford **7** as a yellow solid (35.7 mg, 90% yield, 94.5:5.5 er), a mixture of diastereoisomers (**7a:7b** = 6.5:1), R_f = 0.19 (petroleum ether : EtOAc= 3:1).



7a
major diastereoisomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.35 (d, *J* = 4.4 Hz, 4H), 7.31 – 7.23 (m, 2H), 7.20 – 7.10 (m, 1H), 4.43 – 4.39 (m, 1H), 3.25 (d, *J* = 10.8 Hz, 1H), 2.97 (d, *J* = 10.8 Hz, 1H), 2.40 – 2.29 (m, 1H), 2.27 – 2.11 (m, 2H), 2.10 – 1.95 (m, 1H), 1.89 – 1.74 (m, 2H), 1.40 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.92 (d, *J* = 249.0 Hz), 147.72 (d, *J* = 7.8 Hz), 141.34, 131.18 (d, *J* = 7.3 Hz), 129.16, 128.11 (d, *J* = 3.4 Hz), 127.87, 127.52, 121.34 (d, *J* = 21.5 Hz), 113.28 (d, *J* = 26.2 Hz), 79.76, 56.31, 37.06, 31.63, 31.29, 20.37.

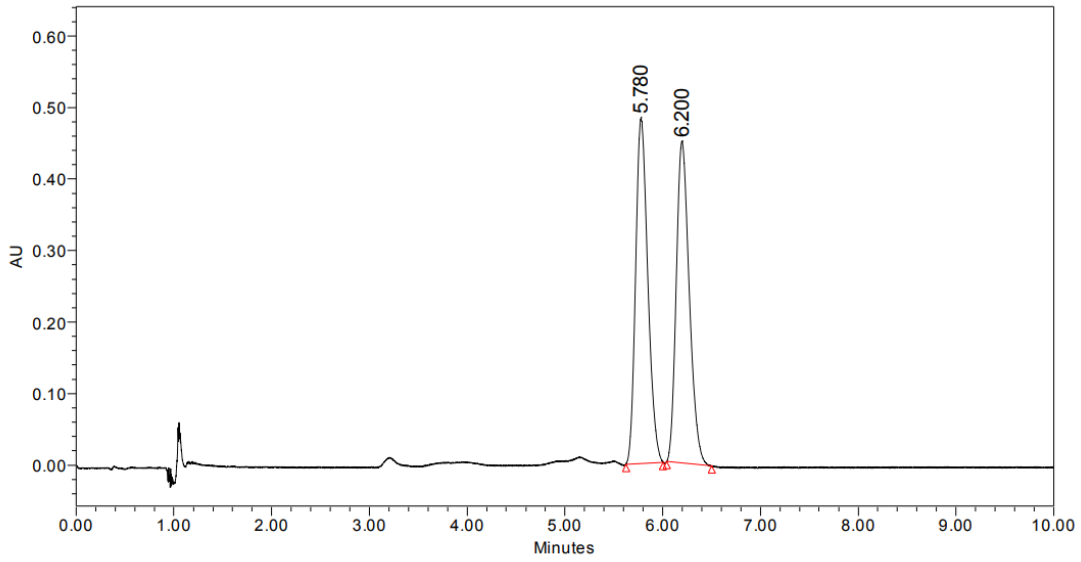
^{19}F NMR (377 MHz, $CDCl_3$) δ -115.25.

^{77}Se NMR (76 MHz, $CDCl_3$) δ 304.34.

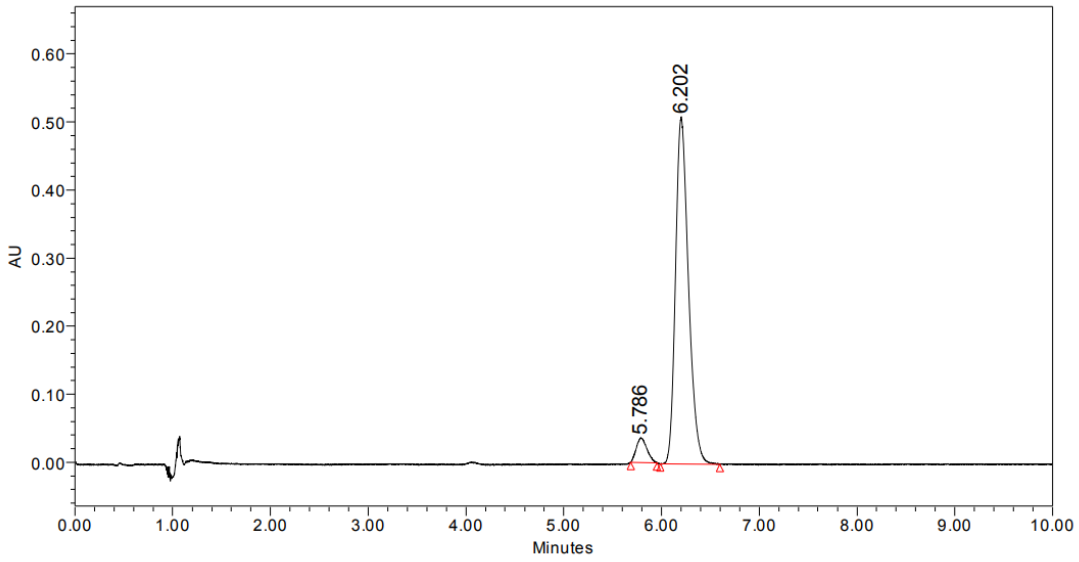
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{18}FNNaO_3Se$ 418.0328; found 418.0332;

SFC (Daicel Chiralpak® IC-3, 20% MeOH in CO_2, 2000 psi, 0.8 mL/min, 254 nm, 35 °C): t_R(major) = 6.20 min, t_R (minor) = 5.79 min, 94.5:5.5 er.

Specific Rotation: $[\alpha]_D^{20}$= +33.67 (c = 0.4, $CHCl_3$)



	RT (min)	Area	% Area	Height (μV)	Channel Name
1	5.780	4161200	50.03	483620	254.0nm
2	6.200	4156255	49.97	449814	254.0nm

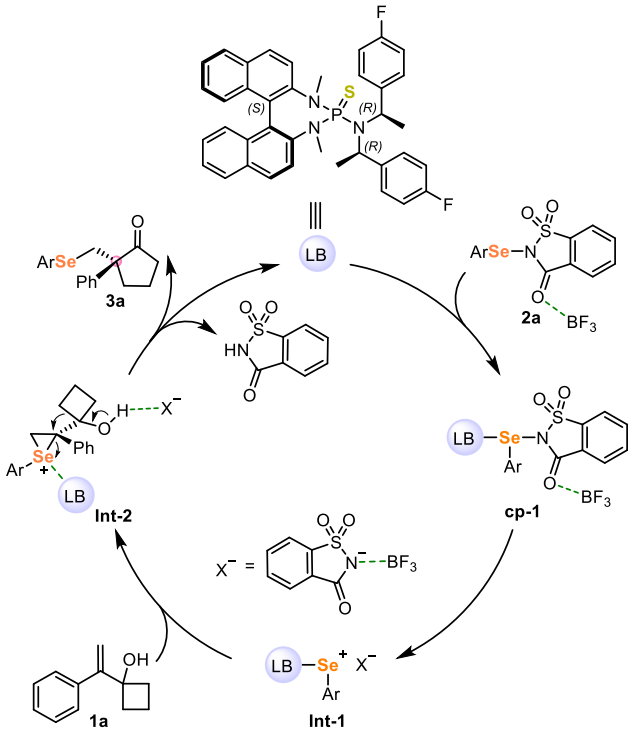


	RT (min)	Area	% Area	Height (μV)	Channel Name
1	5.786	271465	5.49	35849	254.0nm
2	6.202	4670208	94.51	509556	254.0nm

10. Proposed mechanism

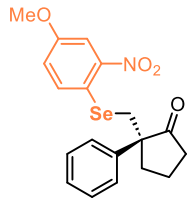
According to our experimental results and previous work, a plausible catalytic mechanism is proposed. The reaction begins with the formation of a complex, **cp-1**, through the interaction between the chiral Lewis base catalyst **Cat. 3** and the achiral Lewis acid boron trifluoride-activated selenylating reagent. This interaction is mediated by a chalcogen bond formed between the sulfur atom of the catalyst **Cat. 3** and the selenium atom of compound **2a**. Subsequently, the activated reagent facilitates the transfer of the 2-nitrophenylselenyl group to the Lewis base catalyst, thereby generating the catalytically active intermediate **Int-1**. Following this, an electrophilic addition reaction occurs with allylic alcohol **1a**, leading to the formation of intermediate **Int-2**. This transformation exhibits high *Si*-face selectivity. The final step involves a facile ring expansion via a 1,2-shift, accompanied by the nucleophilic ring opening of the seleniranium ion **Int-2**, ultimately yielding the desired product **3a**.

Scheme S1. Proposed mechanism.



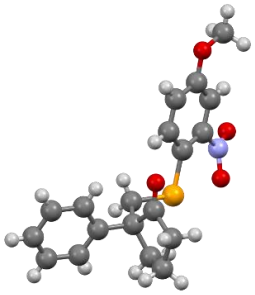
11. X-Ray crystallographic data

Crystal data of **3q**



3q

CCDC: 2430771



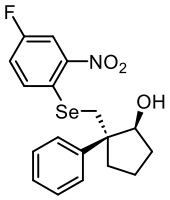
X-ray single crystal structures of 4j with thermal ellipsoids drawn at the 50% probability level.

Procedure for the recrystallization of **3q**: To a 2 mL vial containing **3q** (10 mg), was added hexane/isopropanol (0.5/0.5 mL) to form a clear solution. The solution was kept aside 10 days at room temperature to obtain crystals by slow evaporation. The crystal data was shown below:

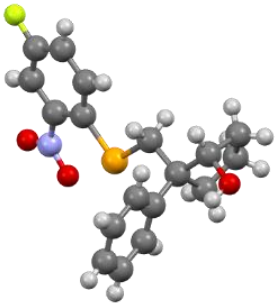
Crystal data and structure refinement for 3q

Identification code	**3q**
Empirical formula	$C_{19}H_{19}NO_4Se$
Formula weight	404.31
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12$
a/Å	25.6226(2)
b/Å	19.4121(2)
c/Å	7.06020(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3511.66(7)
Z	8
ρ_{calc}g/cm^3	1.529
μ/mm^{-1}	3.100
F(000)	1648.0
Crystal size/mm^3	0.1 × 0.05 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.712 to 154.016
Index ranges	-32 ⩽ h ⩽ 29, -24 ⩽ k ⩽ 24, -8 ⩽ l ⩽ 8
Reflections collected	45936
Independent reflections	7259 [R_{int} = 0.0488, R_{sigma} = 0.0267]
Data/restraints/parameters	7259/0/438
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0442, wR_2 = 0.1232
Final R indexes [all data]	R_1 = 0.0471, wR_2 = 0.1262
Largest diff. peak/hole / e Å^{-3}	0.92/-0.94
Flack parameter	0.010(11)

Crystal data of **7a**



7a
CCDC:2440328



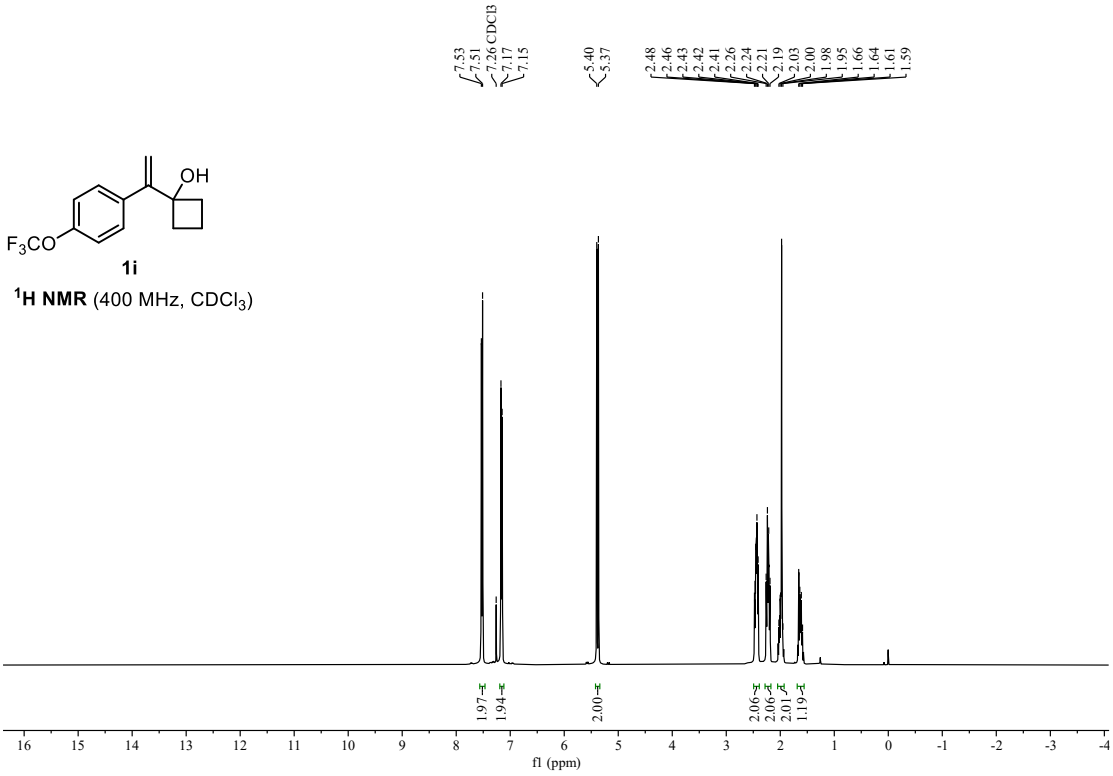
X-ray single crystal structures of 4j with thermal ellipsoids drawn at the 50% probability level.

Procedure for the recrystallization of **7a**: To a 2 mL vial containing **7a** (10 mg), was added hexane/DCM (0.9/0.1 mL) to form a clear solution. The solution was kept aside 2 days at room temperature to obtain crystals by slow evaporation. The crystal data was shown below:

Crystal data and structure refinement for **7a**

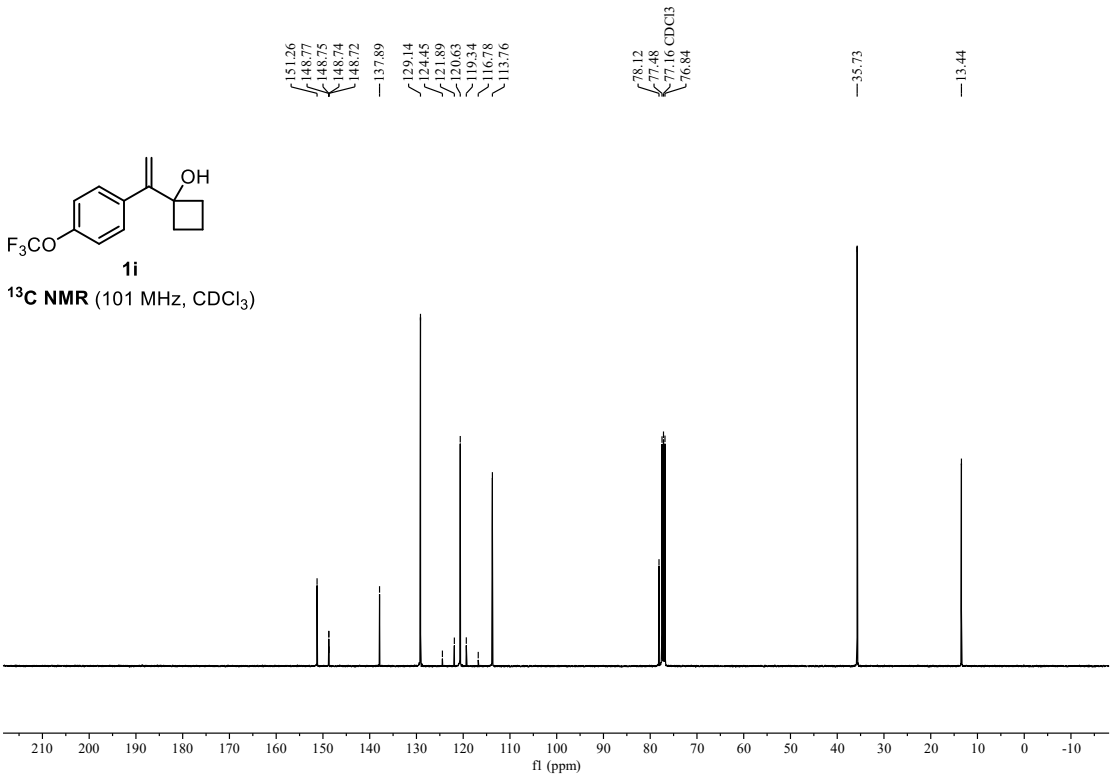
Identification code	**7a**
Empirical formula	$C_{18}H_{18}FNO_3Se$
Formula weight	394.29
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.23267(6)
b/Å	28.5347(2)
c/Å	8.41764(8)
α/°	90
β/°	103.3528(9)
γ/°	90
Volume/Å^3	1690.29(3)
Z	4
ρ_{calc}g/cm^3	1.549
μ/mm^{-1}	3.245
F(000)	800.0
Crystal size/mm^3	0.12 × 0.06 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.194 to 153.896
Index ranges	-9 ≤ h ≤ 8, -35 ≤ k ≤ 35, -10 ≤ l ≤ 10
Reflections collected	34526
Independent reflections	6810 [R_{int} = 0.0234, R_{sigma} = 0.0148]
Data/restraints/parameters	6810/3/415
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0327, wR_2 = 0.0856
Final R indexes [all data]	R_1 = 0.0345, wR_2 = 0.0867
Largest diff. peak/hole / e Å^{-3}	0.57/-0.65
Flack parameter	-0.028(5)

12. Copies of NMR spectra



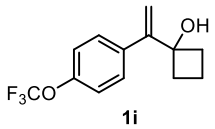
1i

^{1}H NMR (400 MHz, $CDCl_3$)



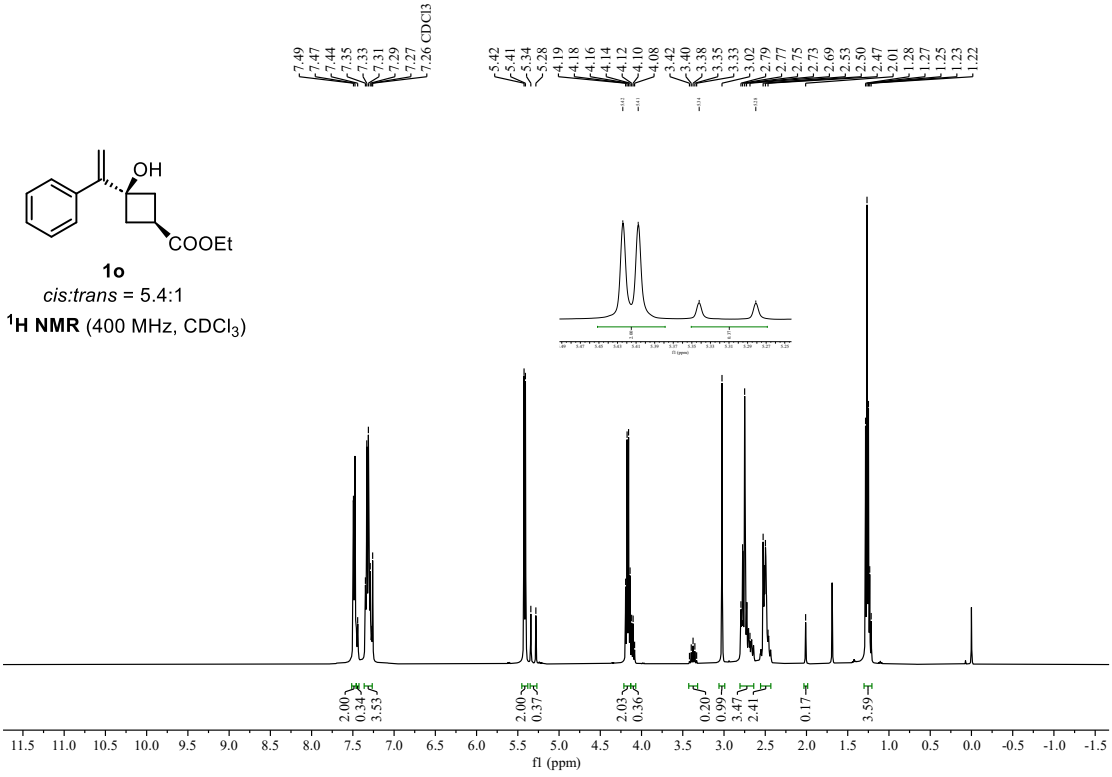
1i

^{13}C NMR (101 MHz, $CDCl_3$)



1i

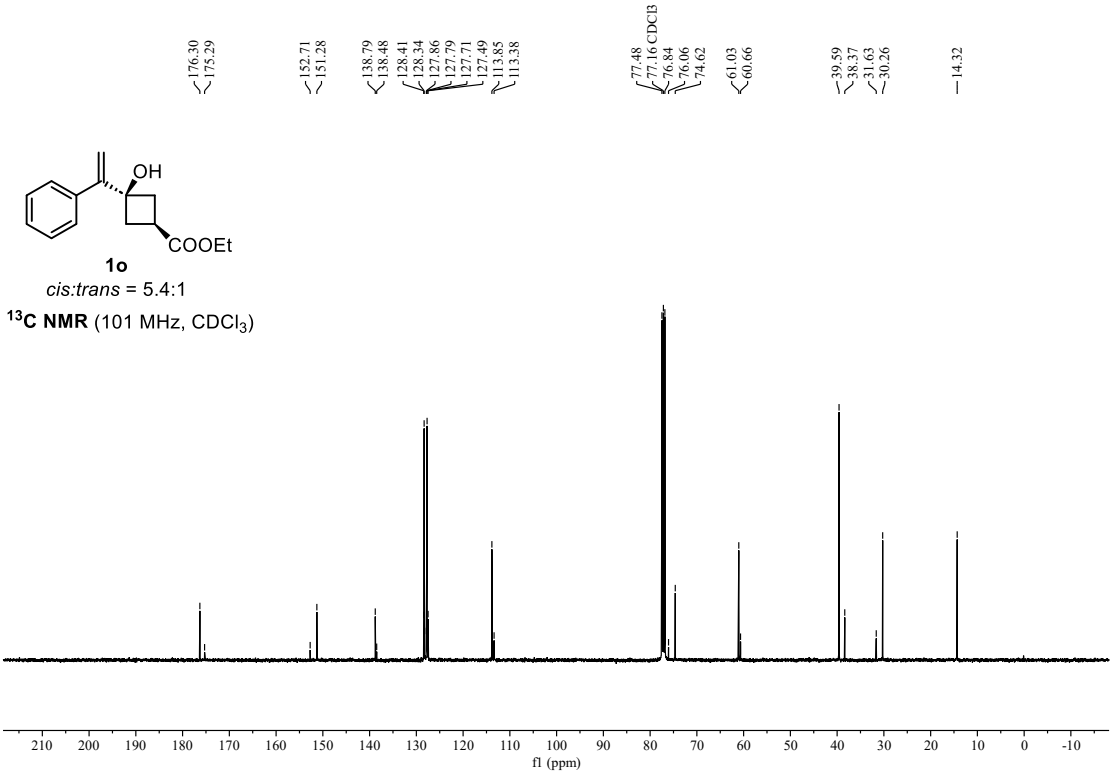
^{19}F NMR (377 MHz, $CDCl_3$)



1o

cis:trans = 5.4:1

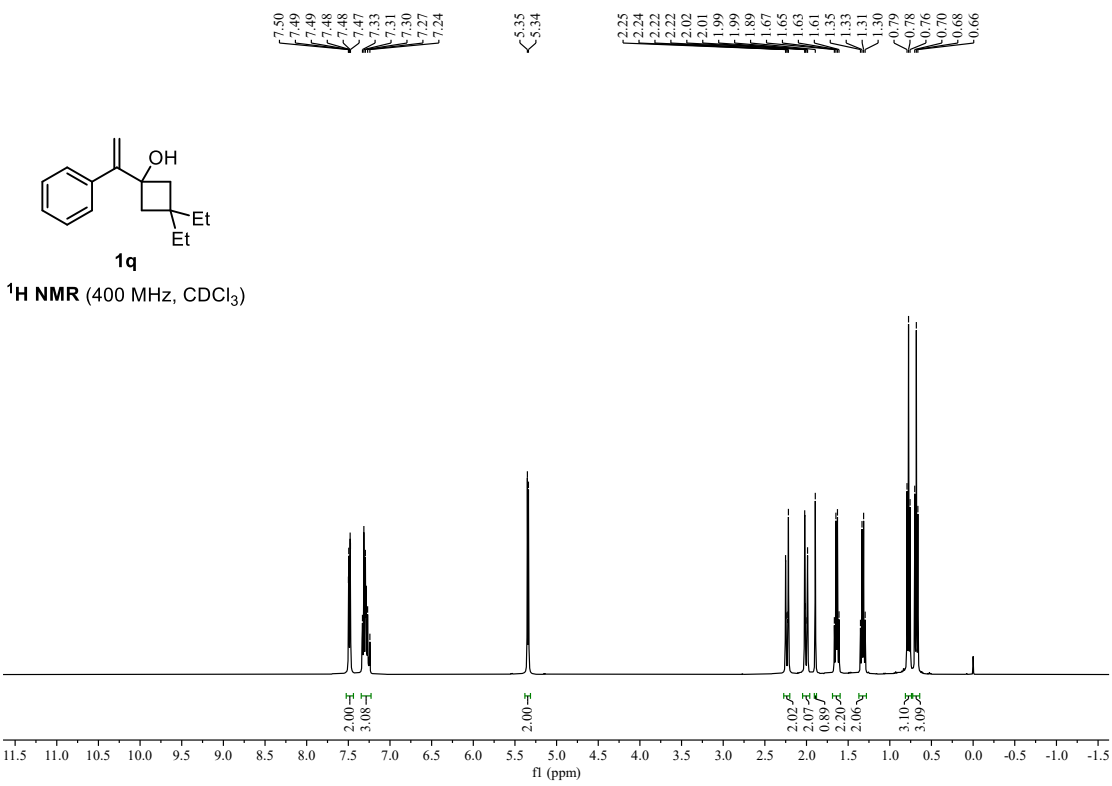
^{1}H NMR (400 MHz, $CDCl_3$)



1o

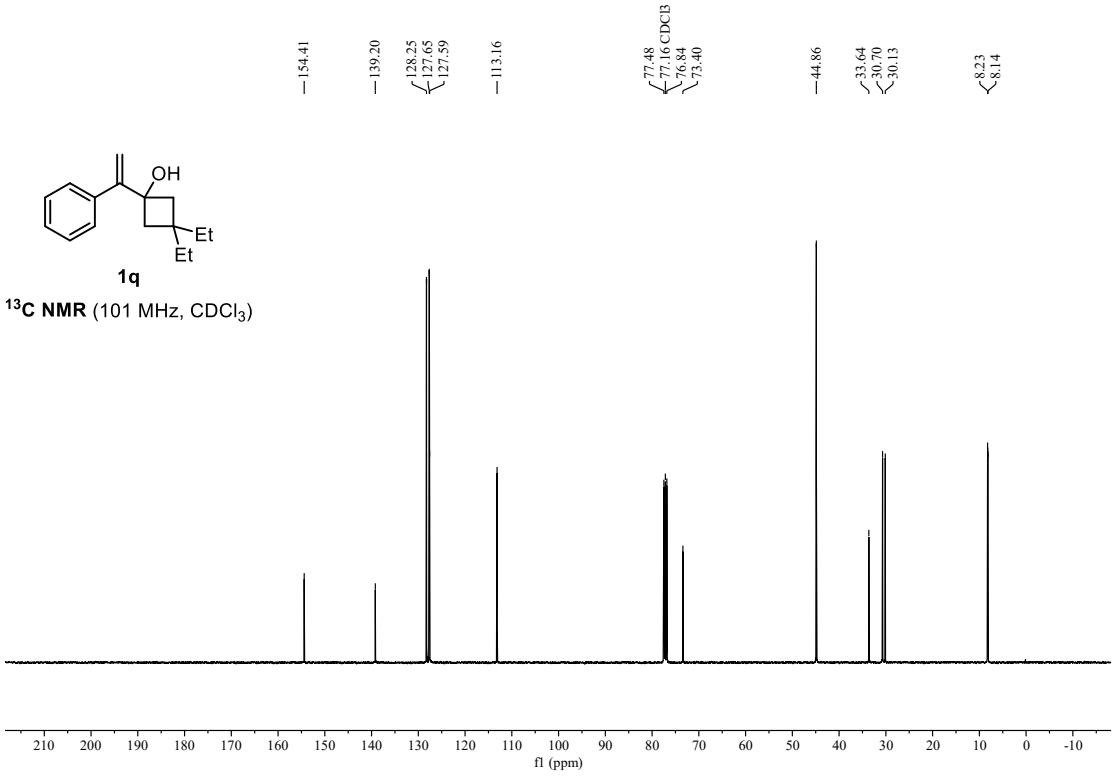
cis:trans = 5.4:1

^{13}C NMR (101 MHz, $CDCl_3$)



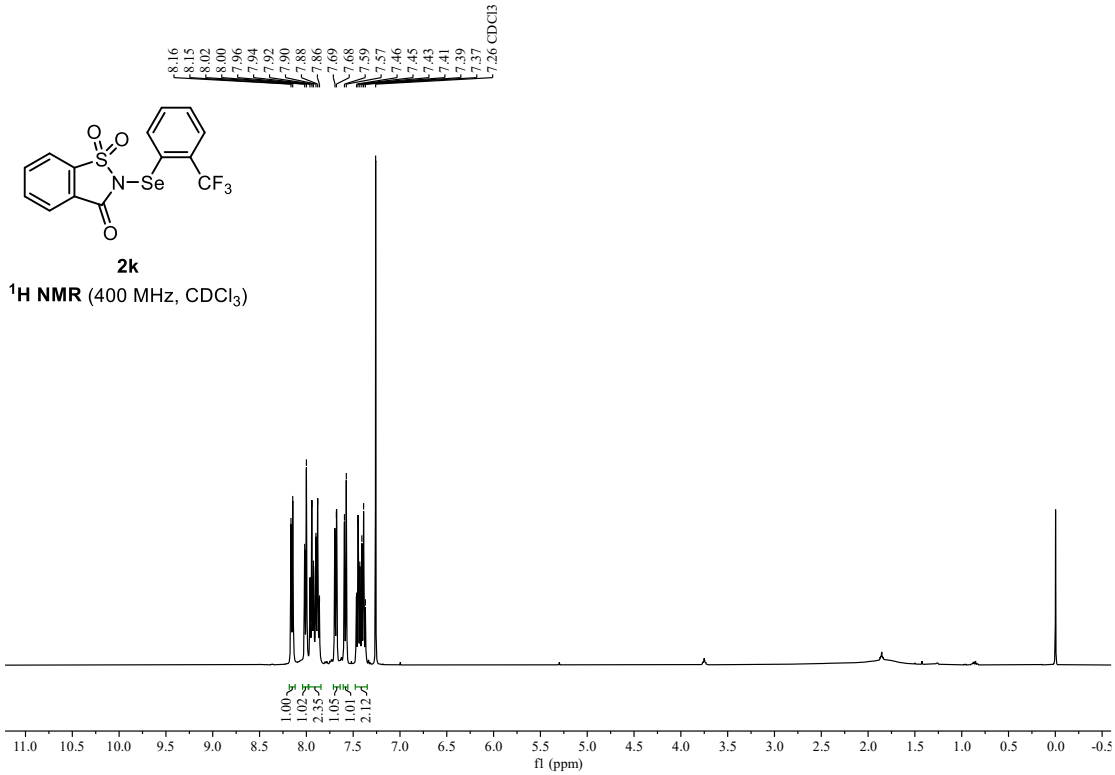
1q

^{1}H NMR (400 MHz, $CDCl_3$)



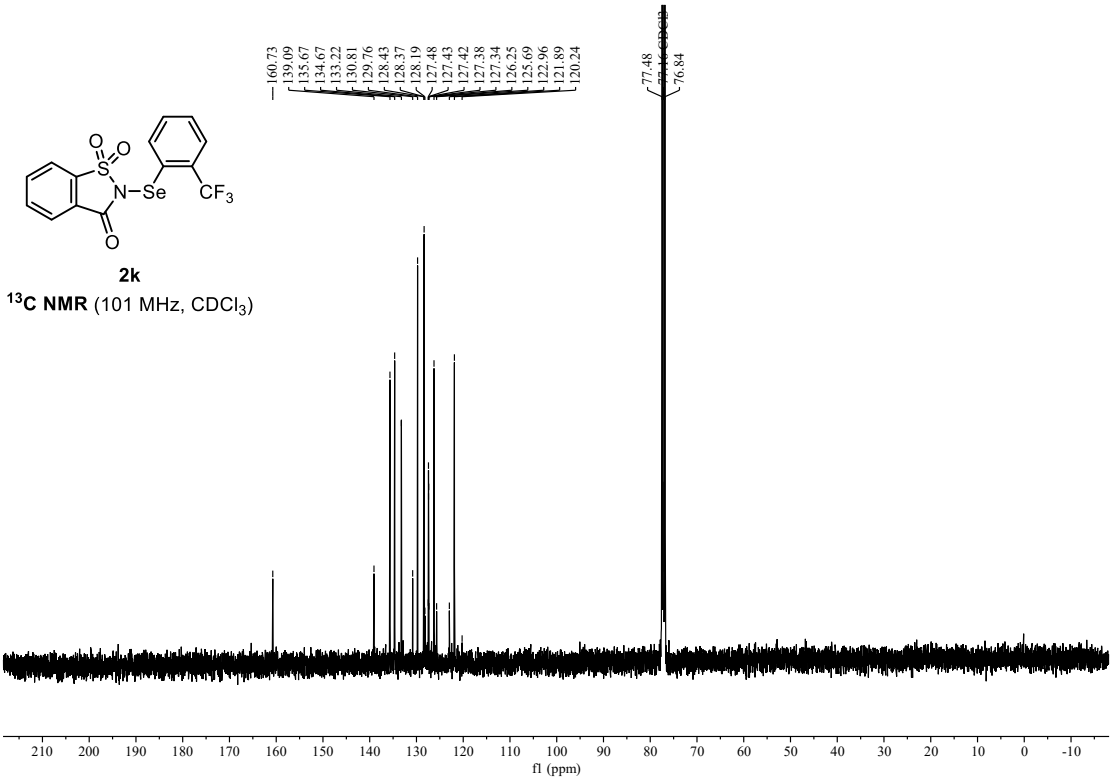
1q

^{13}C NMR (101 MHz, $CDCl_3$)



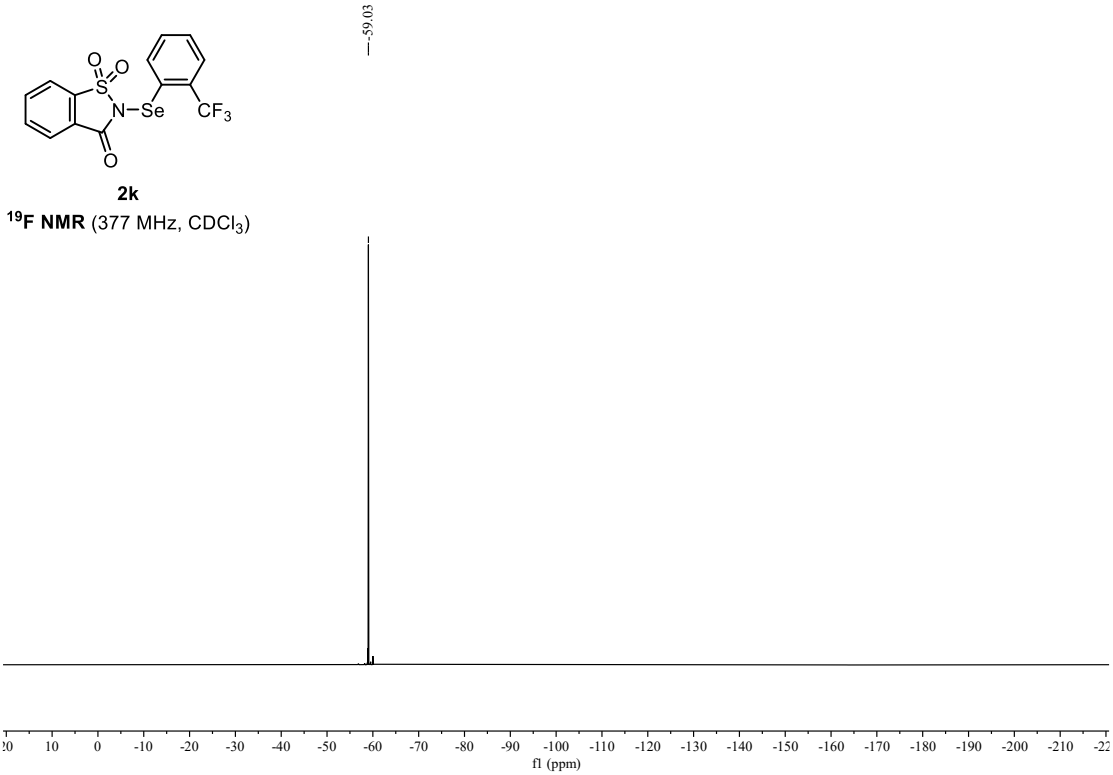
2k

^{1}H NMR (400 MHz, $CDCl_3$)



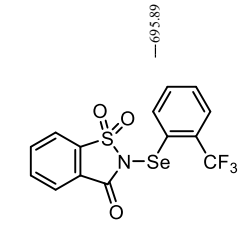
2k

^{13}C NMR (101 MHz, $CDCl_3$)



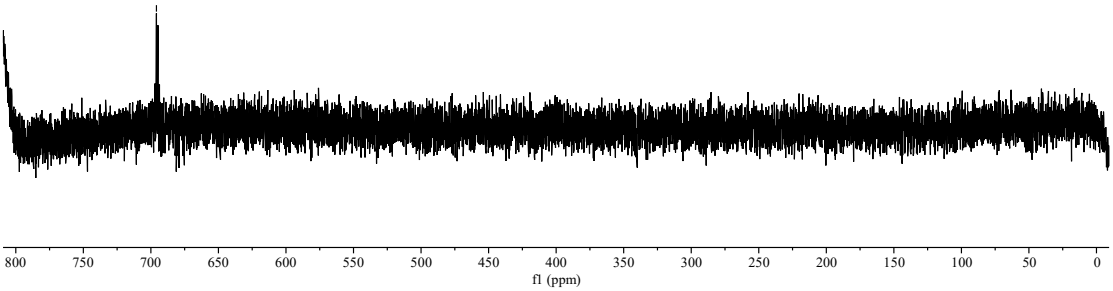
2k

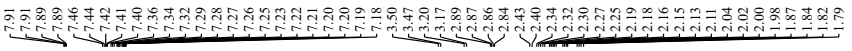
^{19}F NMR (377 MHz, $CDCl_3$)

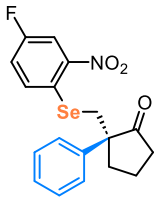


2k

^{77}Se NMR (400 MHz, $CDCl_3$)

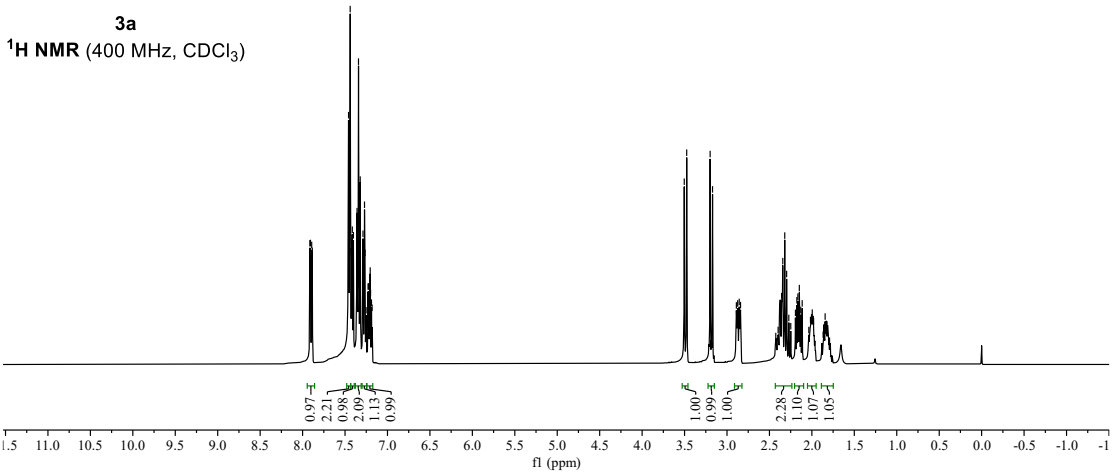


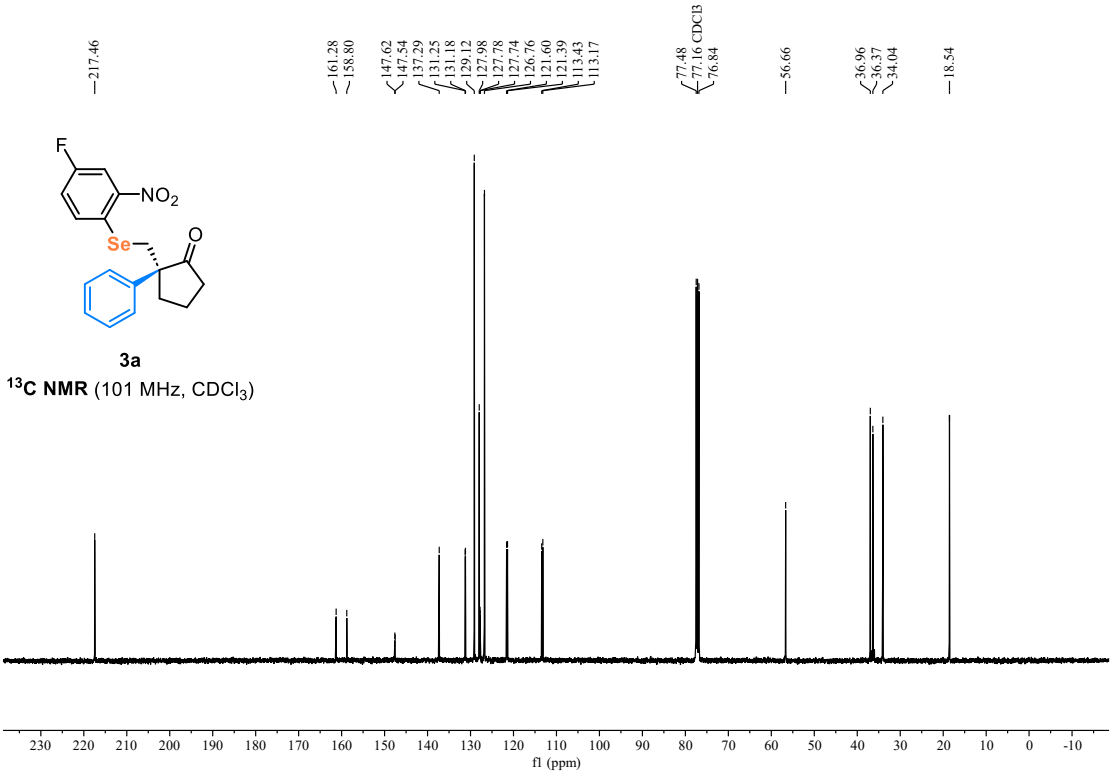




3a

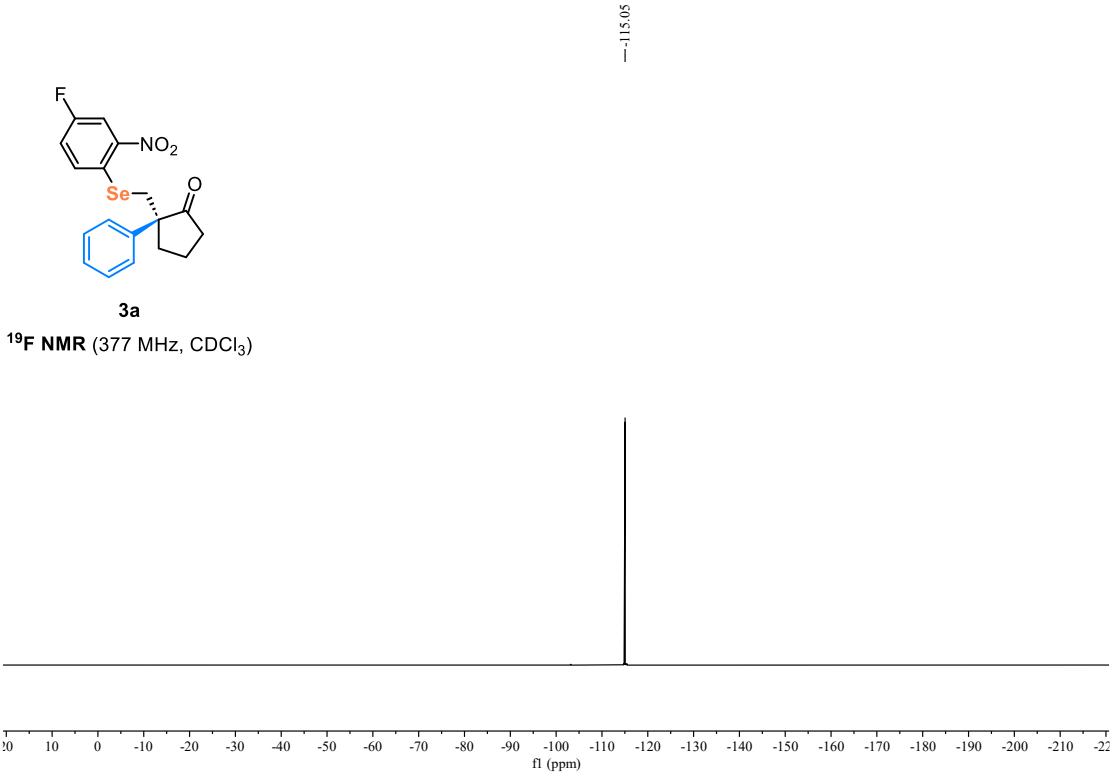
^{1}H NMR (400 MHz, $CDCl_3$)





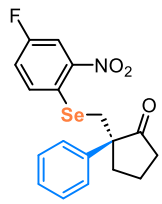
3a

^{13}C NMR (101 MHz, $CDCl_3$)



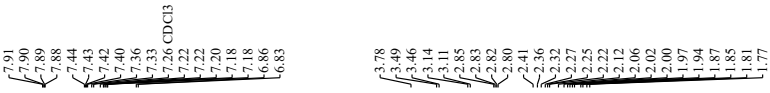
3a

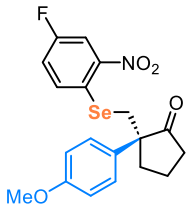
^{19}F NMR (377 MHz, $CDCl_3$)



3a

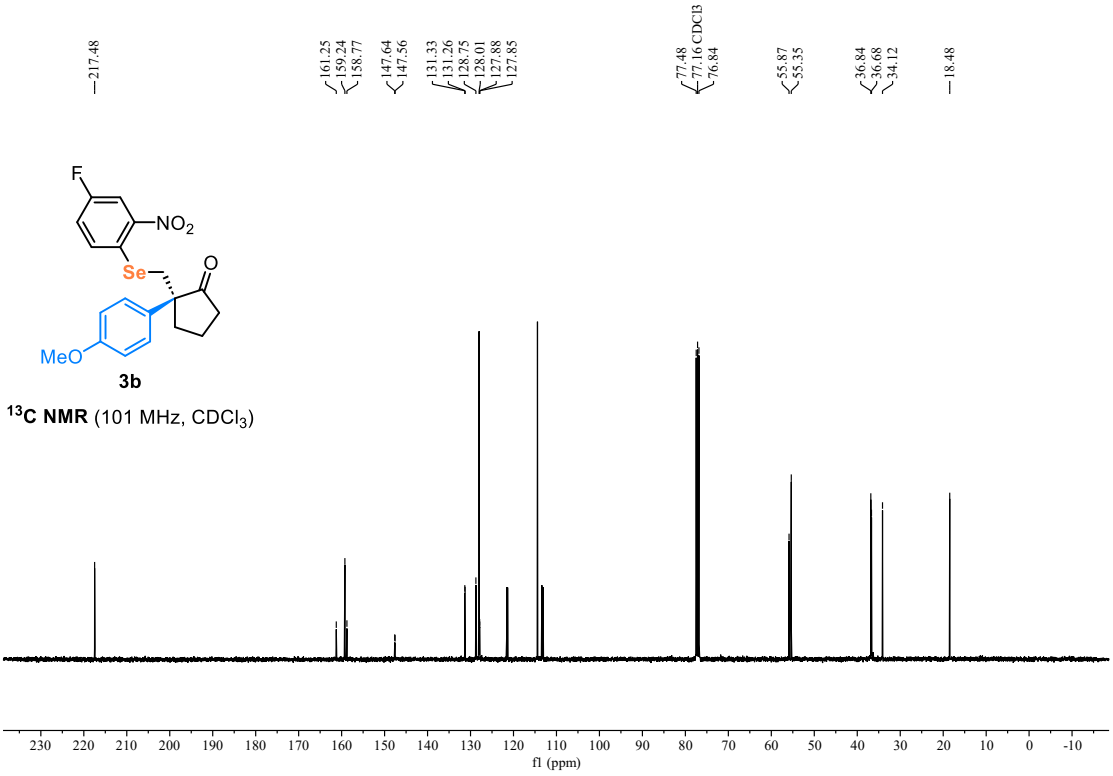
^{77}Se NMR (76 MHz, $CDCl_3$)



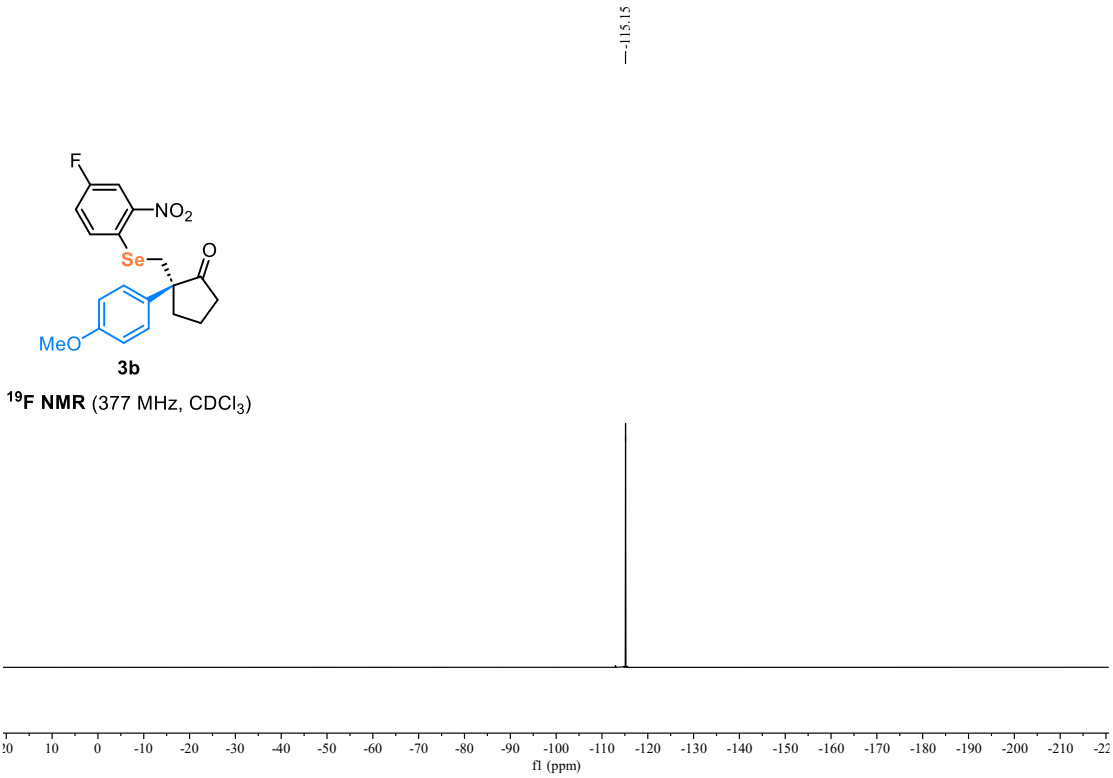


3b

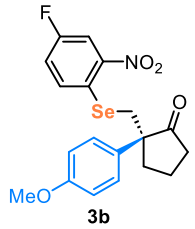
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

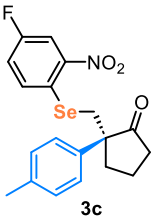


^{19}F NMR (377 MHz, $CDCl_3$)



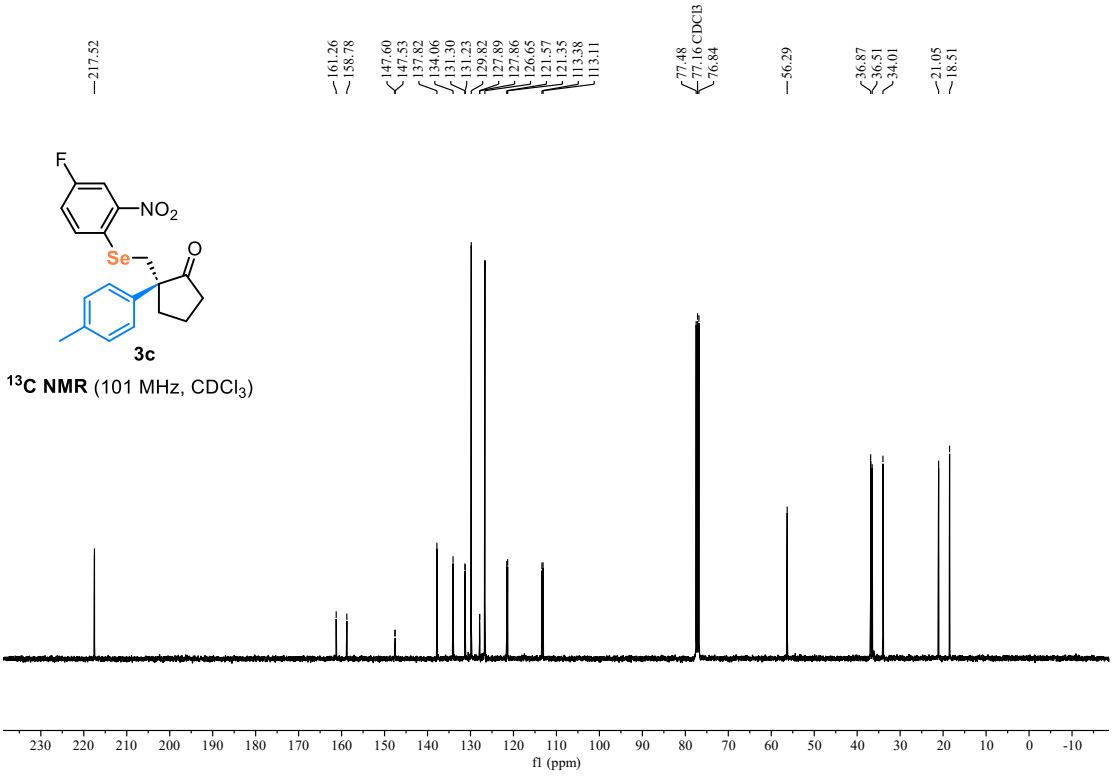
3b

^{77}Se NMR (76 MHz, $CDCl_3$)

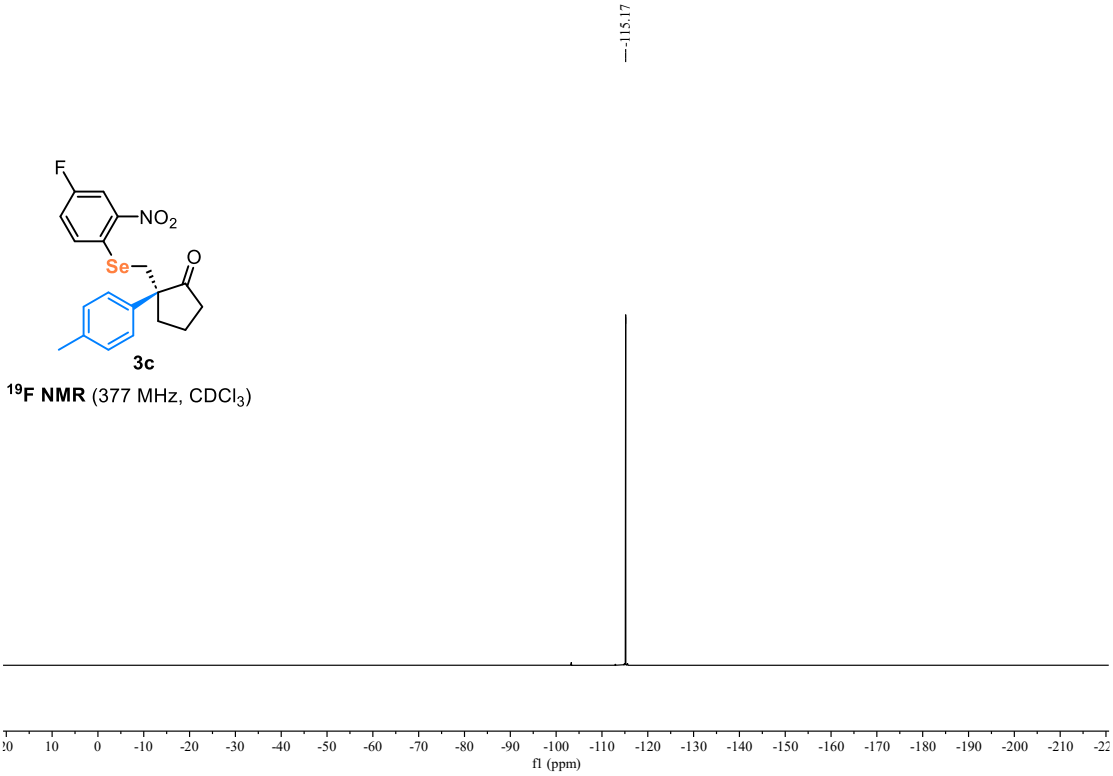


3c

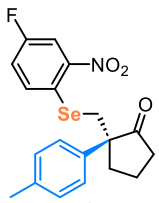
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

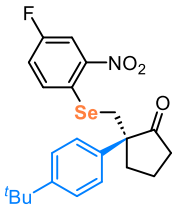


^{19}F NMR (377 MHz, $CDCl_3$)



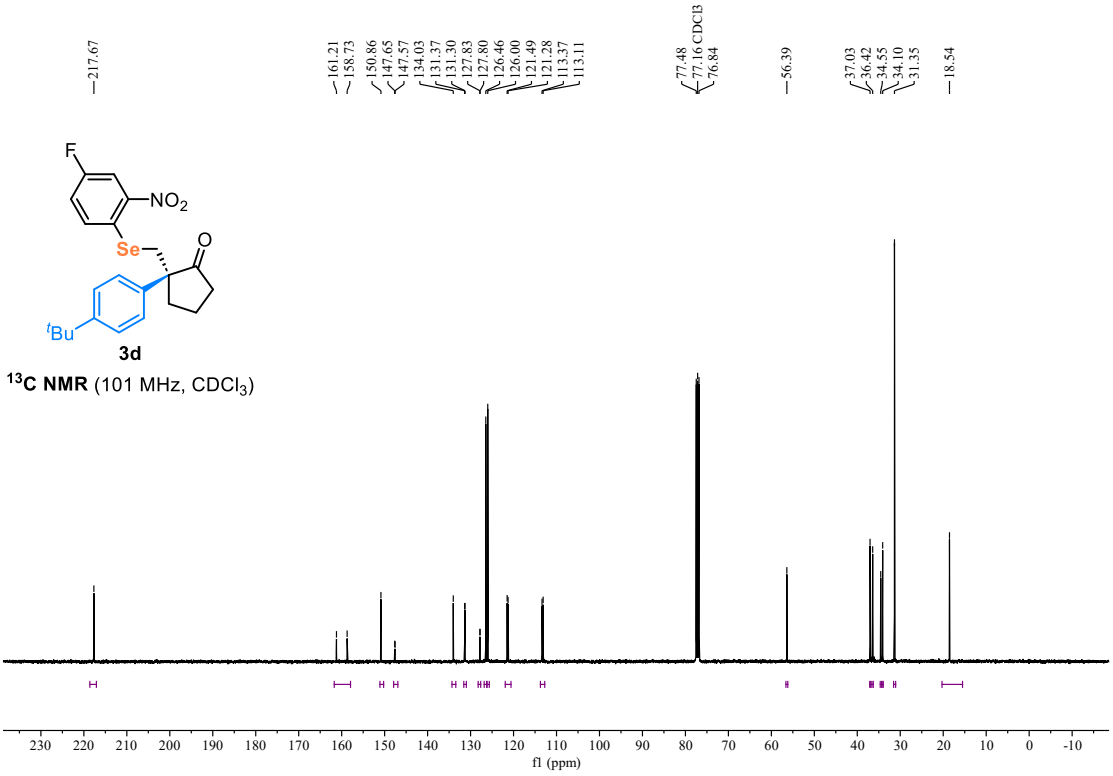
3c

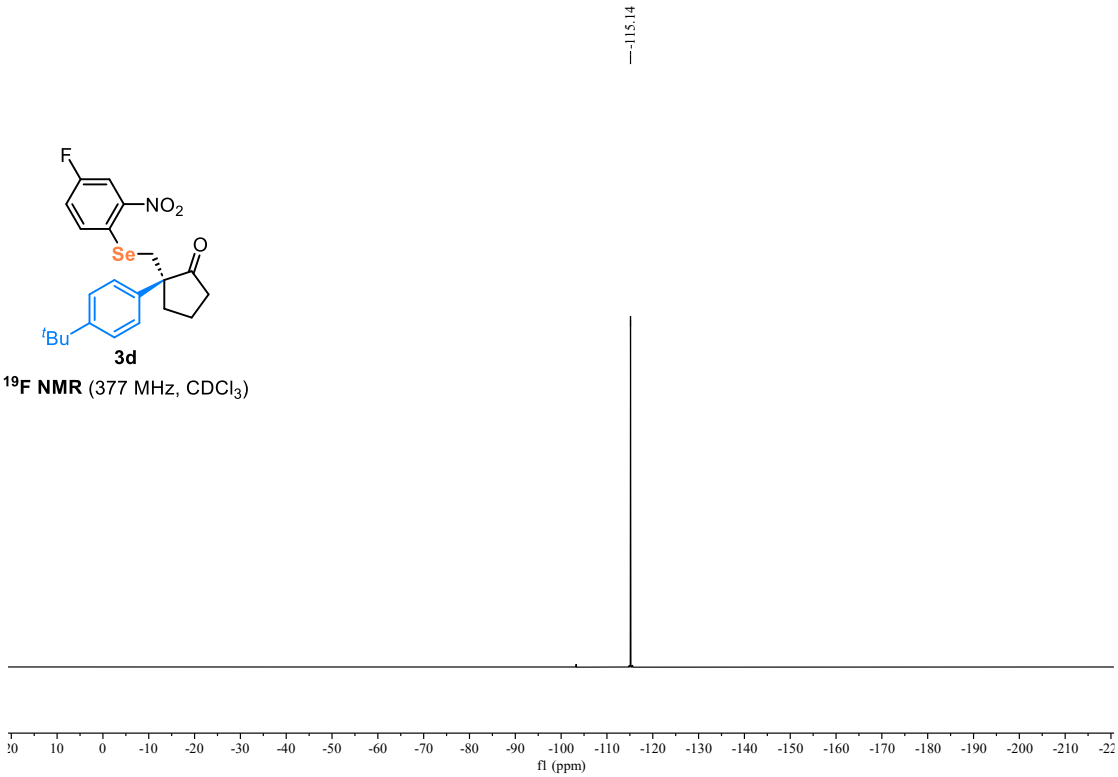
^{77}Se NMR (76 MHz, $CDCl_3$)

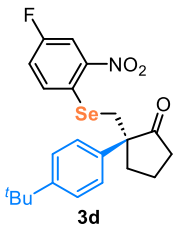


3d

^{1}H NMR (400 MHz, $CDCl_3$)

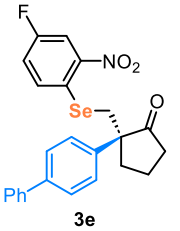

217.67
161.21
158.73
150.86
147.65
147.57
134.03
131.37
131.30
127.83
127.80
126.46
126.00
121.49
121.28
113.37
113.11
77.48
77.16 CDCl3
76.84
56.39
37.03
36.42
34.55
34.10
31.35
18.54
F
NO2
Se
O
tBu
3d
13C NMR (101 MHz, CDCl3)
f1 (ppm)


-115.14
F
NO2
Se
O
tBu
3d
19F NMR (377 MHz, CDCl3)
f1 (ppm)



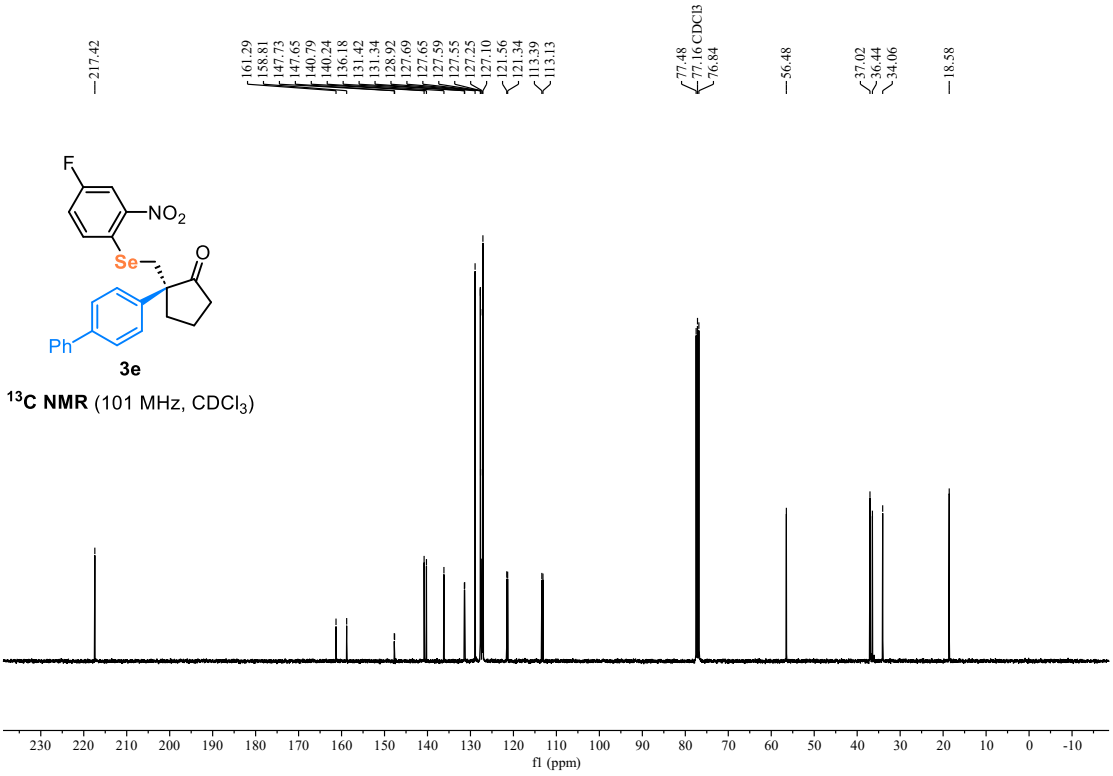
3d

^{77}Se NMR (76 MHz, $CDCl_3$)



3e

^{1}H NMR (400 MHz, $CDCl_3$)


217.42
161.29
158.81
147.73
147.65
140.79
140.24
136.18
131.42
131.34
128.92
127.69
127.65
127.59
127.55
127.25
127.10
121.56
121.34
113.39
113.13
77.48
77.16 CDCl3
76.84
56.48
37.02
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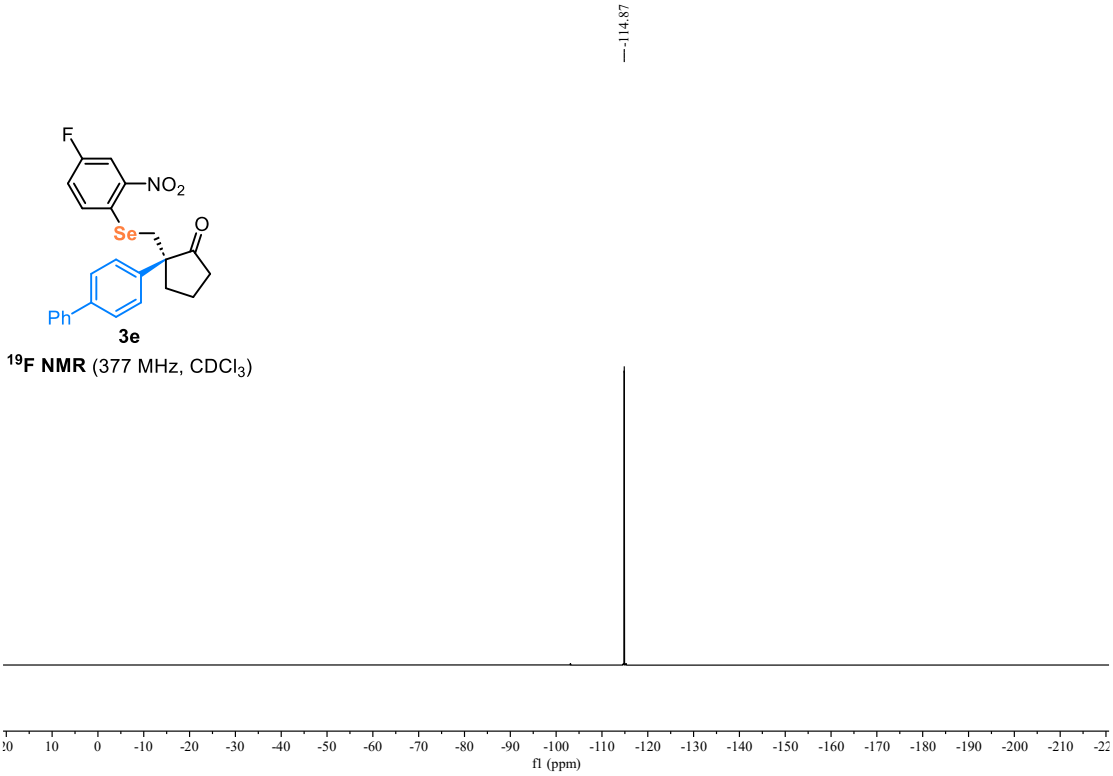
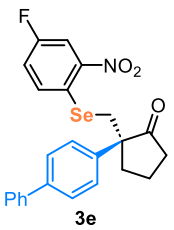
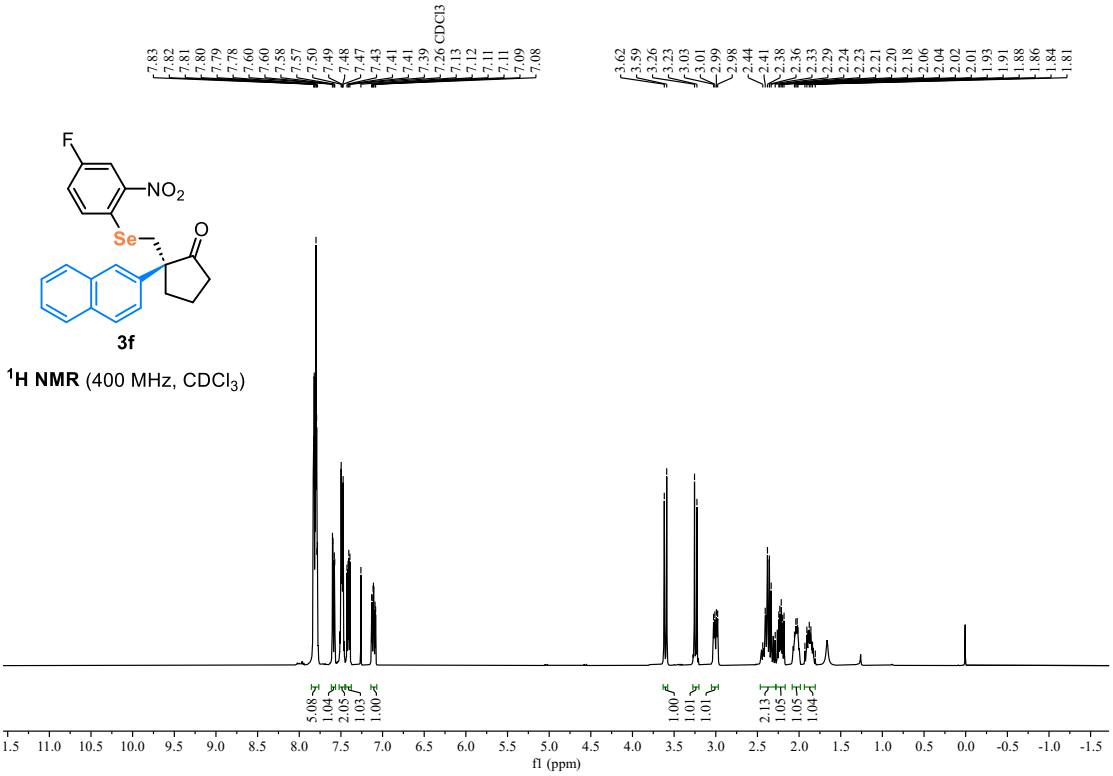
34.06
18.58
F
NO2
Se
O
Ph
3e
13C NMR (101 MHz, CDCl3)
fl (ppm)


-114.87
F
NO2
Se
O
Ph
3e
19F NMR (377 MHz, CDCl3)
fl (ppm)



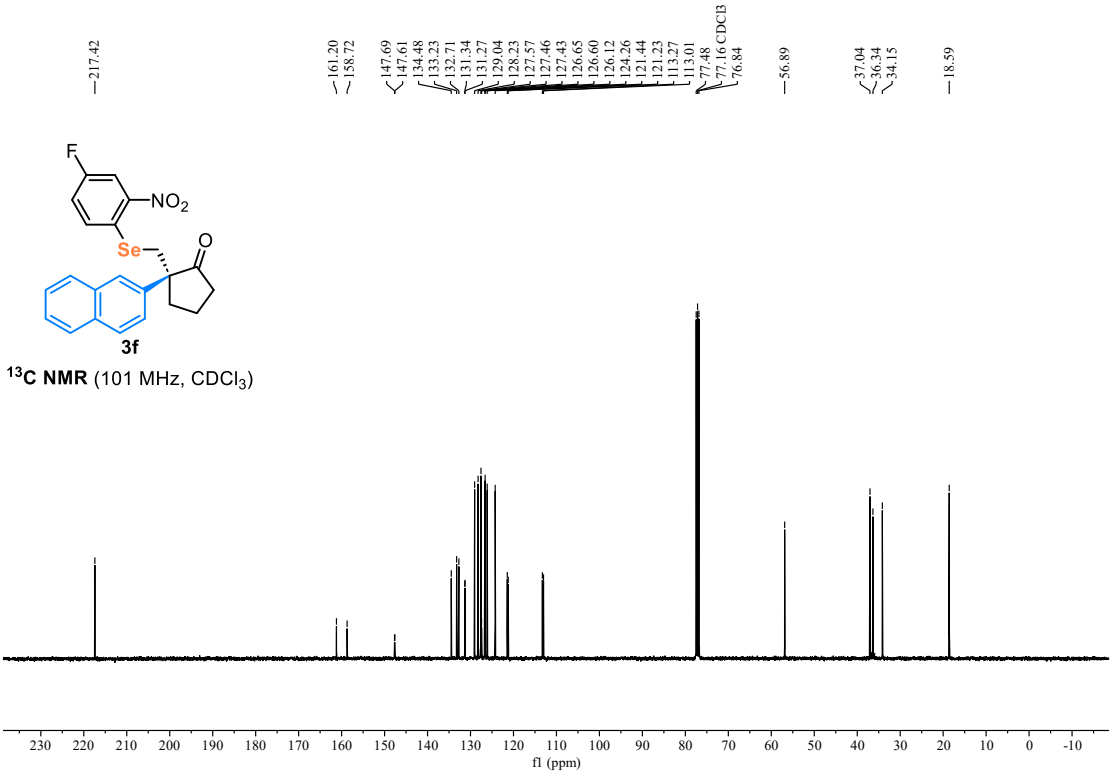
3e

^{77}Se NMR (76 MHz, $CDCl_3$)

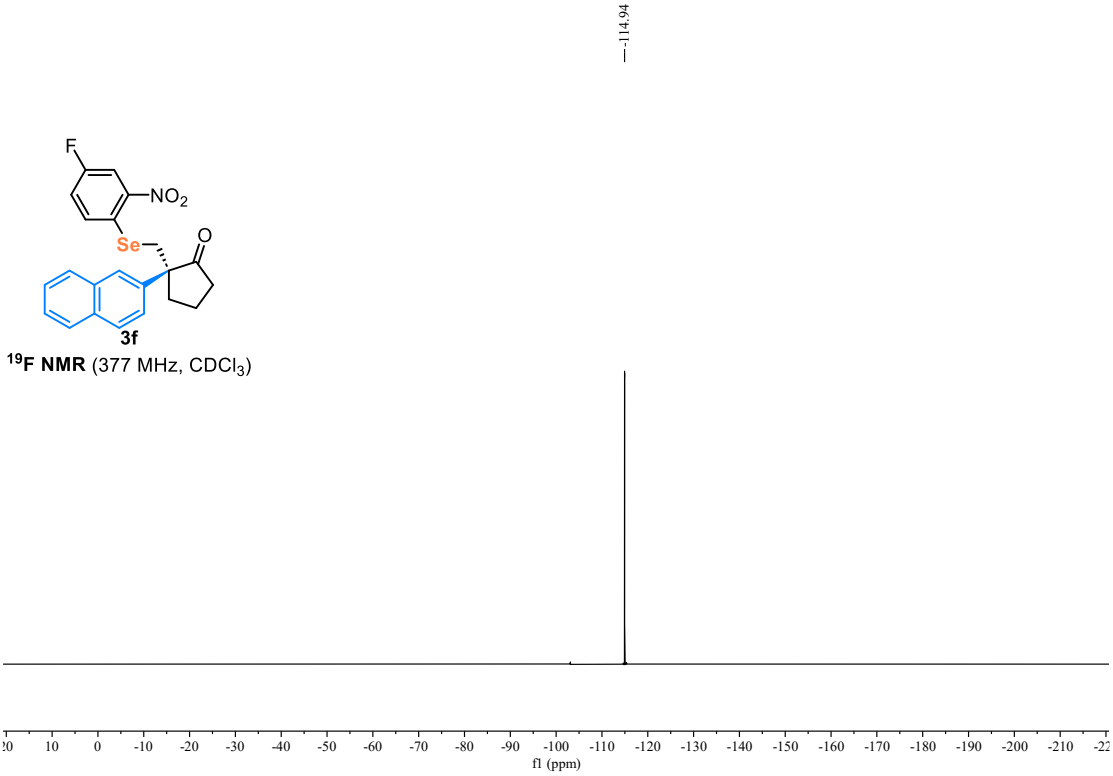


3f

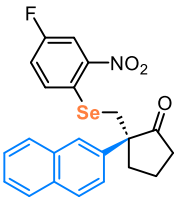
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

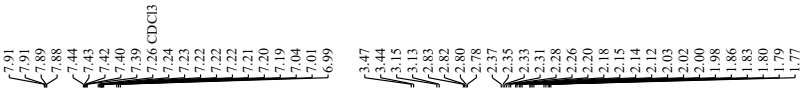


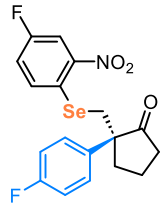
^{19}F NMR (377 MHz, $CDCl_3$)



3f

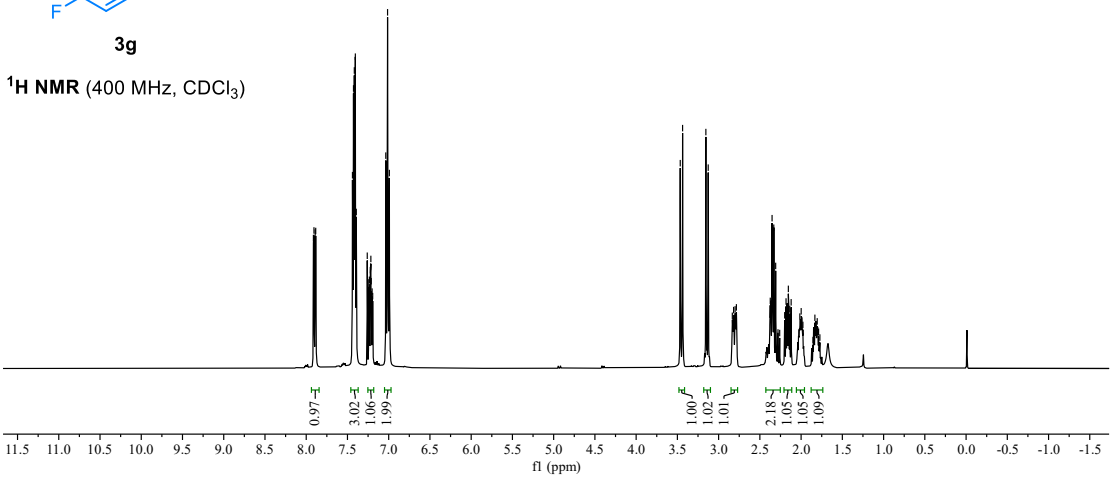
^{77}Se NMR (76 MHz, $CDCl_3$)

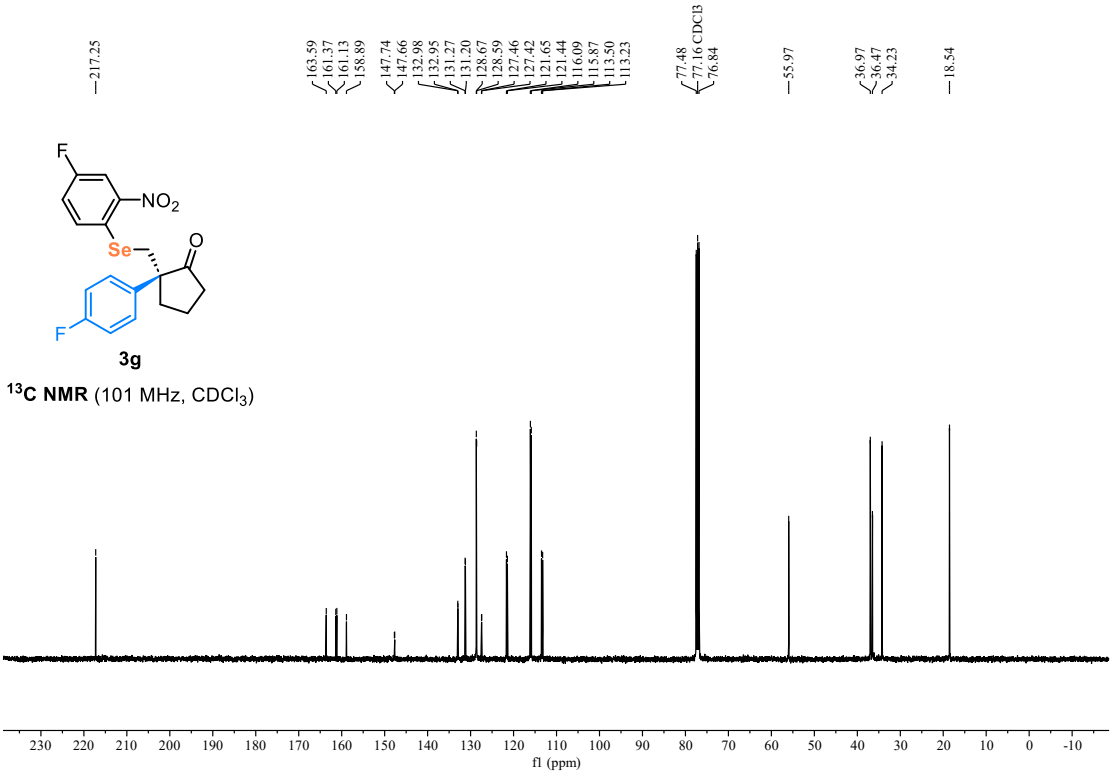


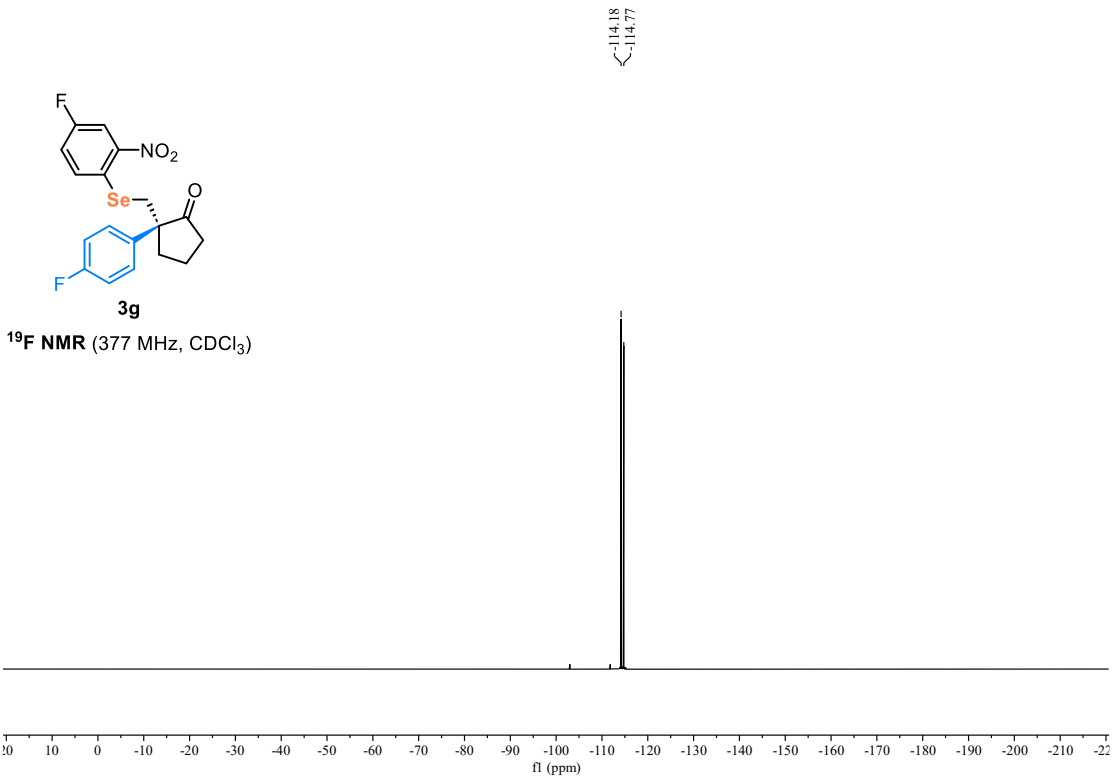


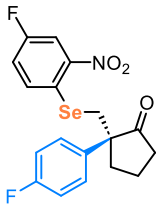
3g

^{1}H NMR (400 MHz, $CDCl_3$)




217.25
163.59
161.37
161.13
158.89
147.74
147.66
132.98
132.95
131.27
131.20
128.67
128.59
127.46
127.42
121.65
121.44
116.09
115.87
113.50
113.23
77.48
77.16 CDCl3
76.84
55.97
36.97
36.47
34.23
18.54
F
NO2
Se
O
F
3g
13C NMR (101 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-114.18
-114.77
F
NO2
Se
O
F
3g
19F NMR (377 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

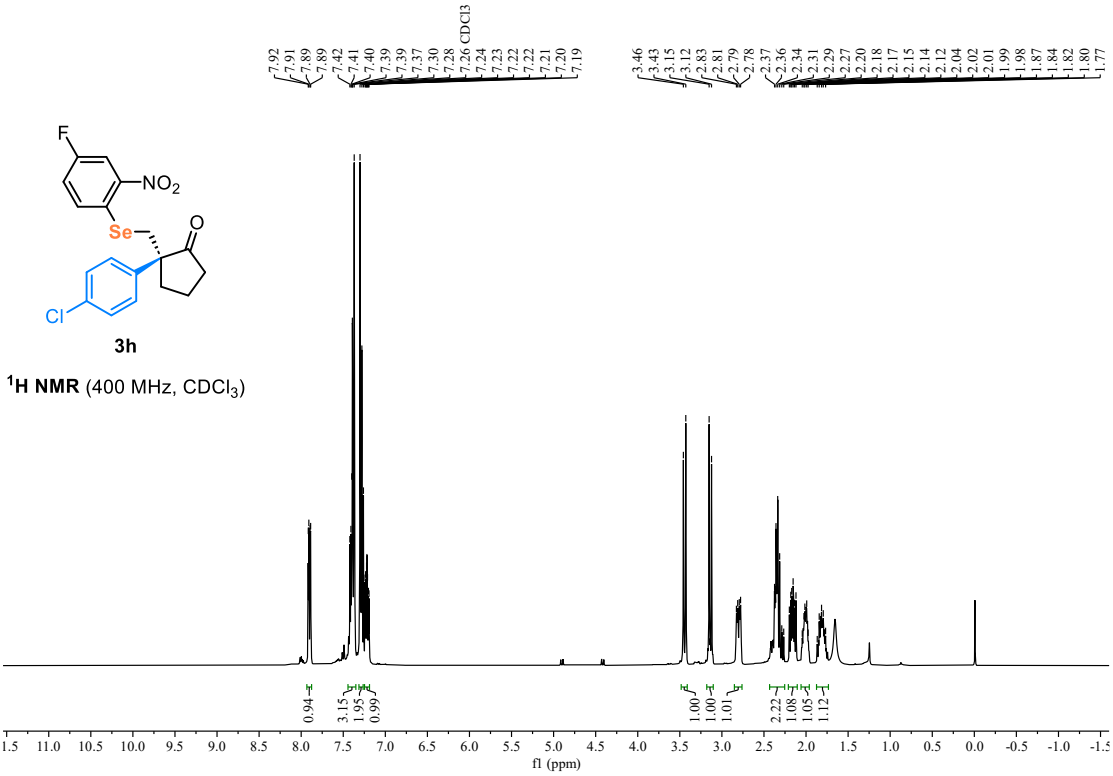


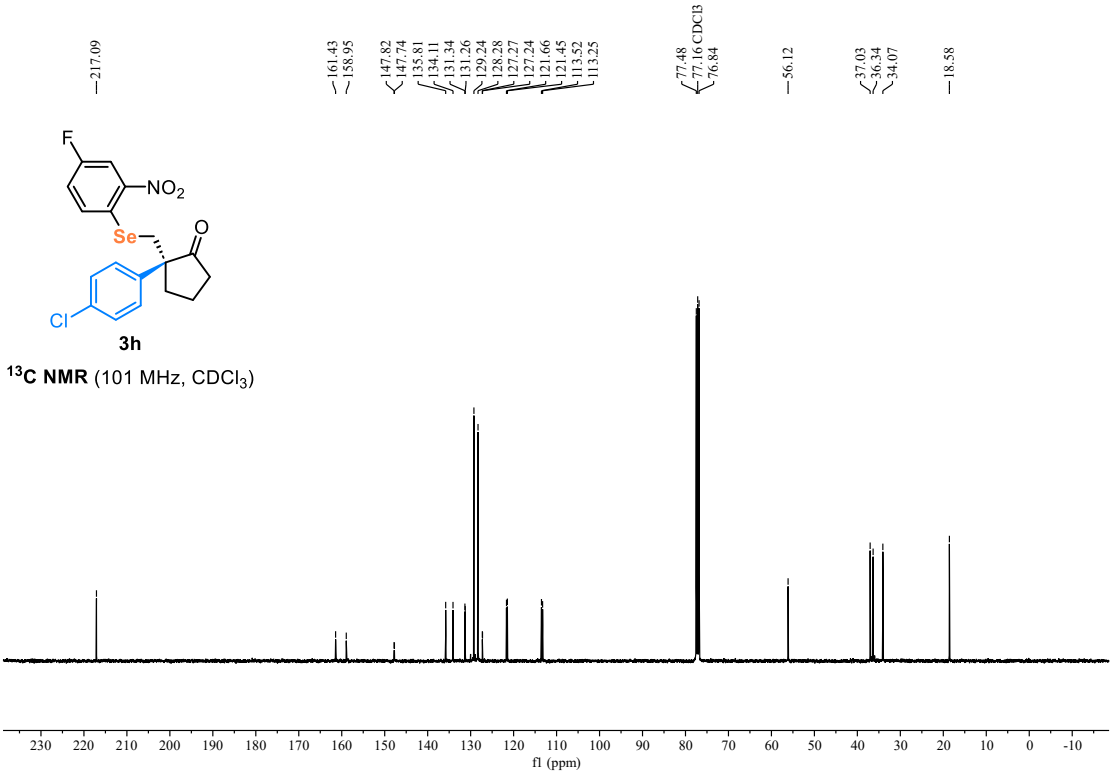
3g

^{77}Se NMR (76 MHz, $CDCl_3$)

3h

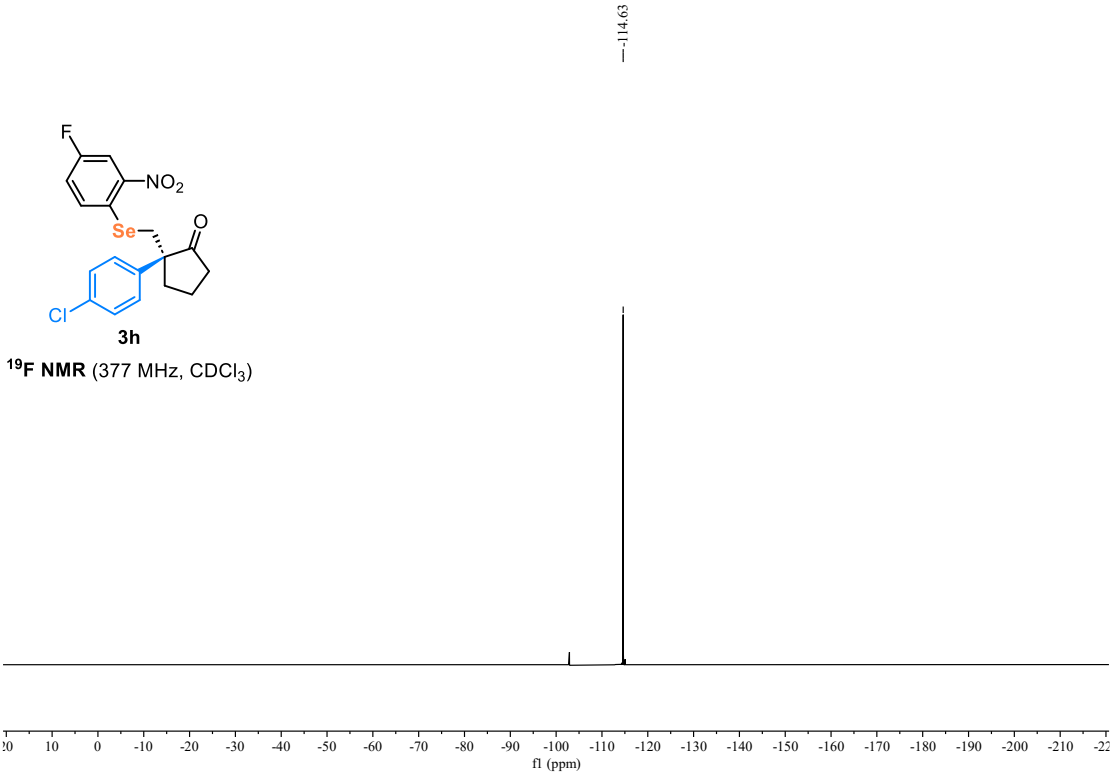
^{1}H NMR (400 MHz, $CDCl_3$)





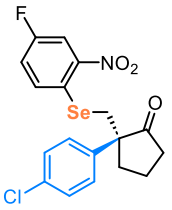
3h

^{13}C NMR (101 MHz, $CDCl_3$)



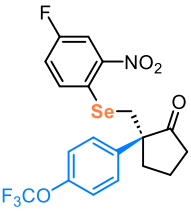
3h

^{19}F NMR (377 MHz, $CDCl_3$)



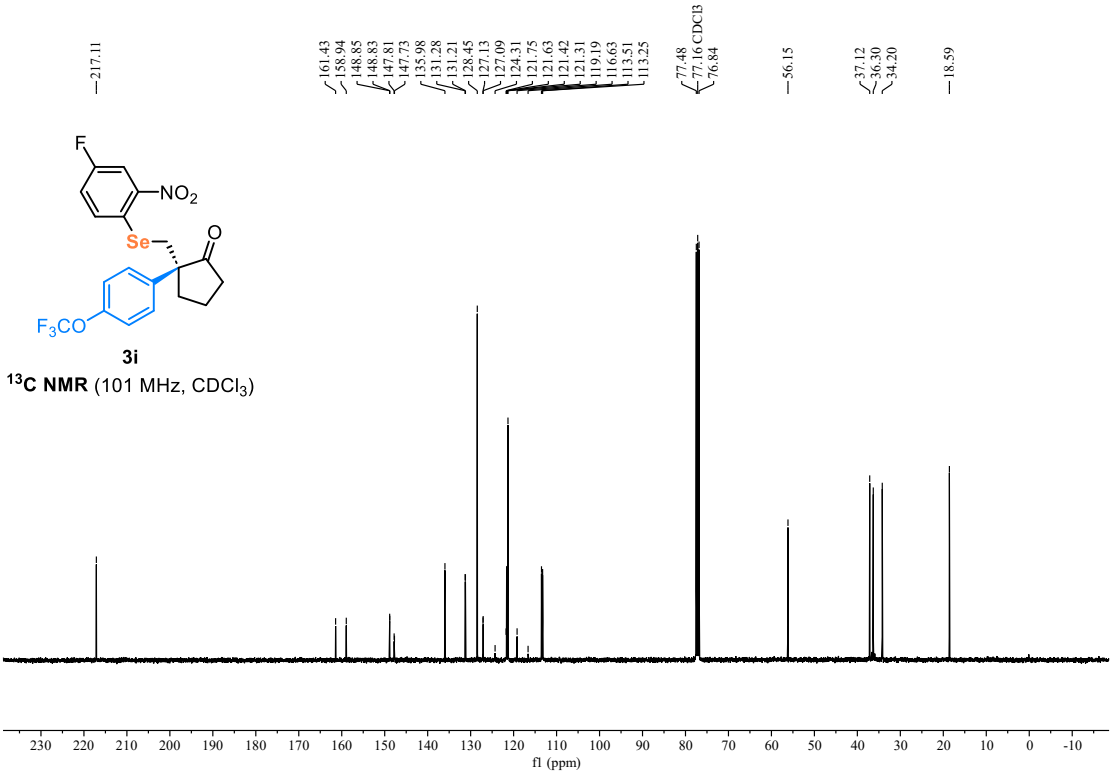
3h

^{77}Se NMR (76 MHz, $CDCl_3$)



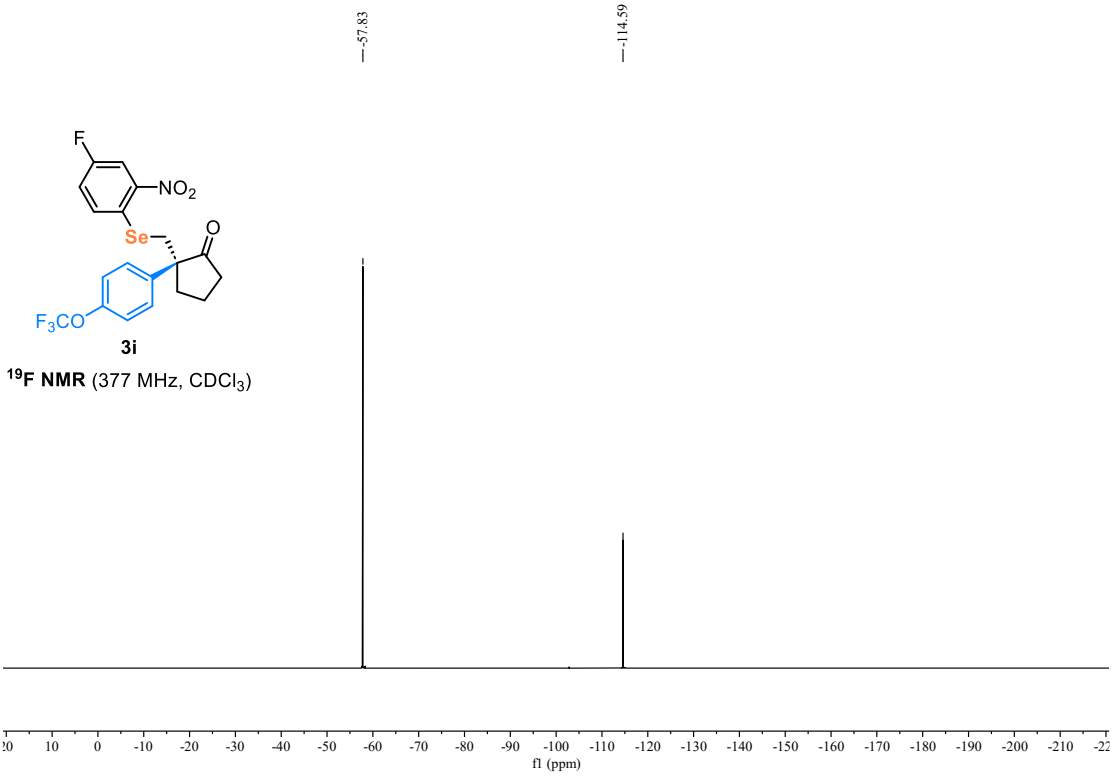
3i

^{1}H NMR (400 MHz, $CDCl_3$)



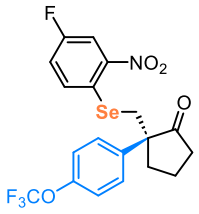
3i

^{13}C NMR (101 MHz, $CDCl_3$)



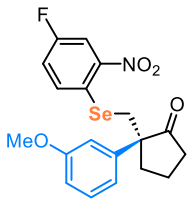
3i

^{19}F NMR (377 MHz, $CDCl_3$)



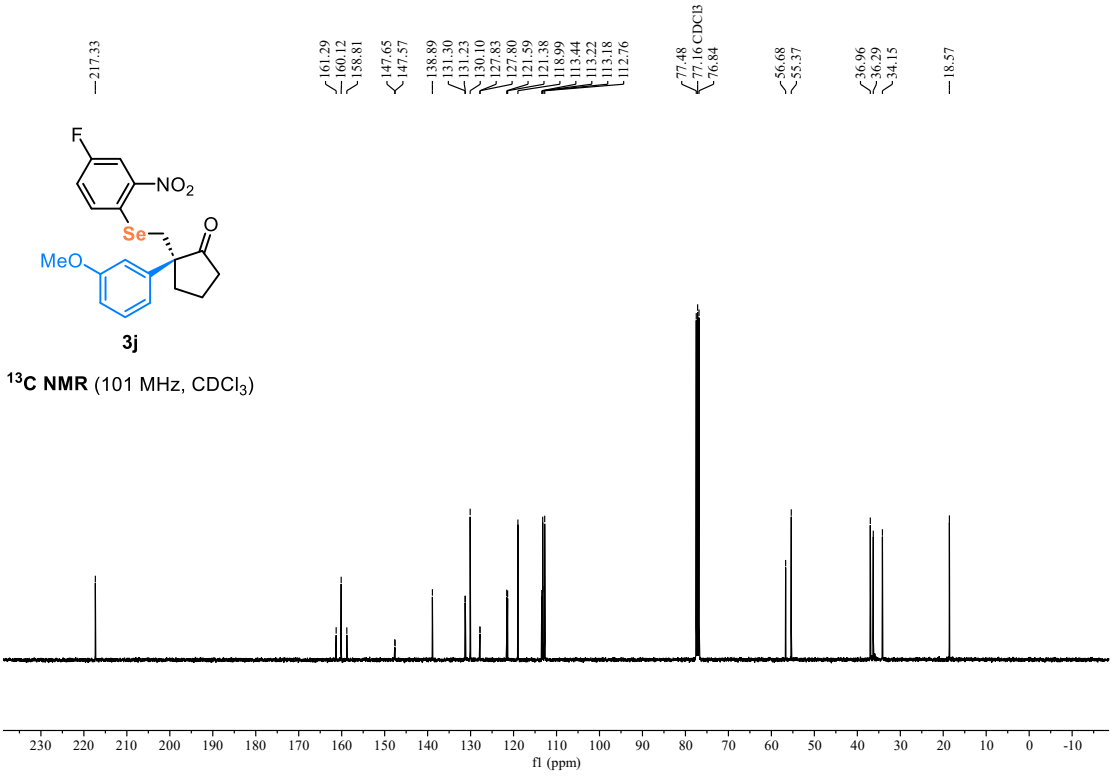
3i

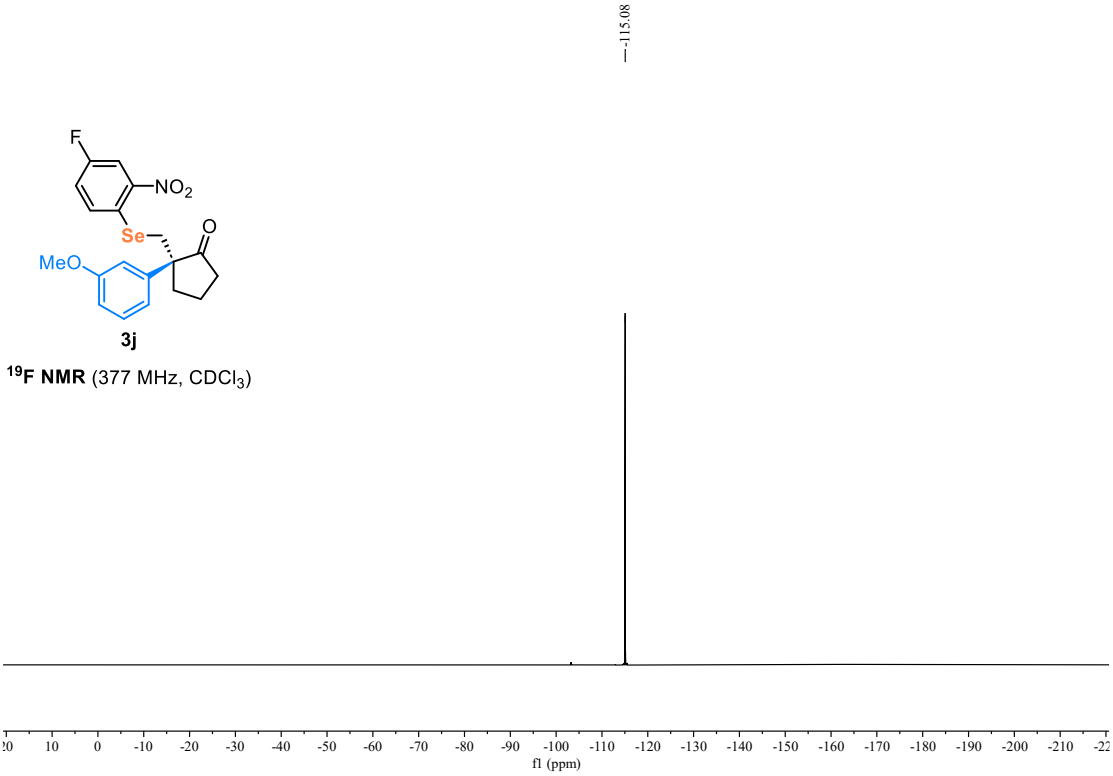
^{77}Se NMR (76 MHz, $CDCl_3$)

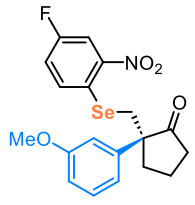


3j

^{1}H NMR (400 MHz, $CDCl_3$)

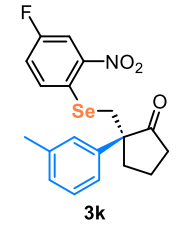

217.33
161.29
160.12
158.81
147.65
147.57
138.89
131.30
131.23
130.10
127.83
127.80
121.59
121.38
118.99
113.44
113.22
113.18
112.76
77.48
77.16 CDCl3
76.84
56.68
55.37
36.96
36.29
34.15
18.57
F
NO2
Se
O
MeO
3j
13C NMR (101 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-115.08
F
NO2
Se
O
MeO
3j
19F NMR (377 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



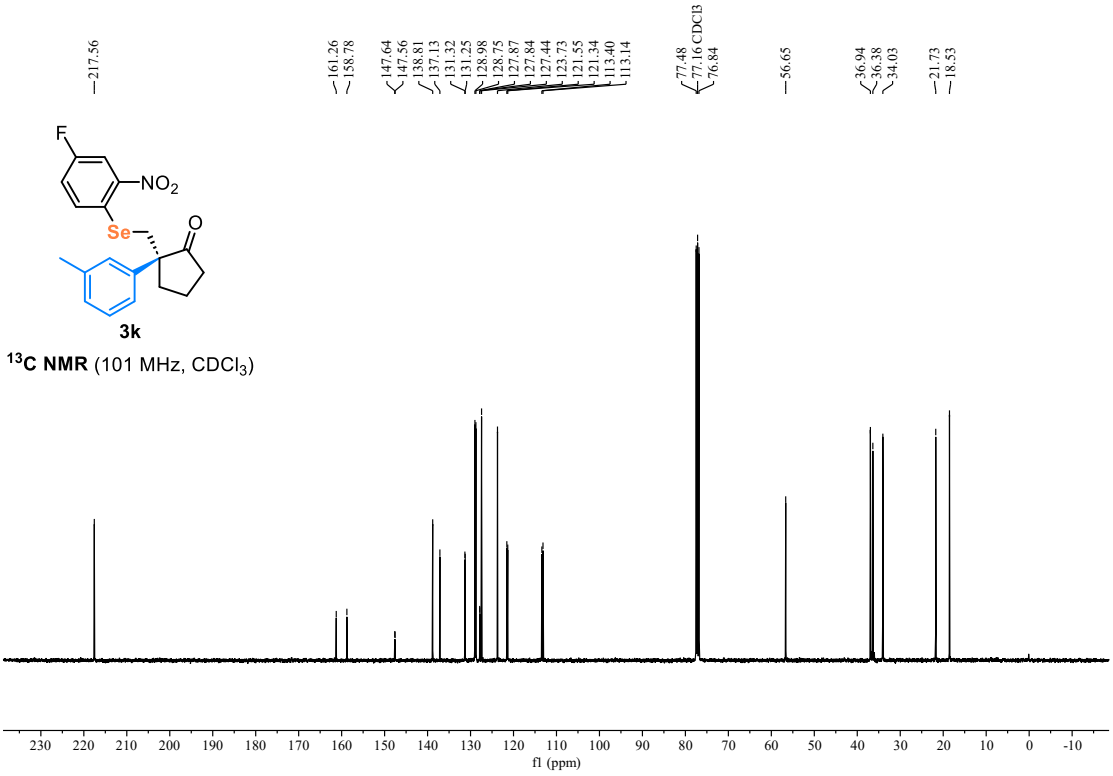
3j

^{77}Se NMR (76 MHz, $CDCl_3$)

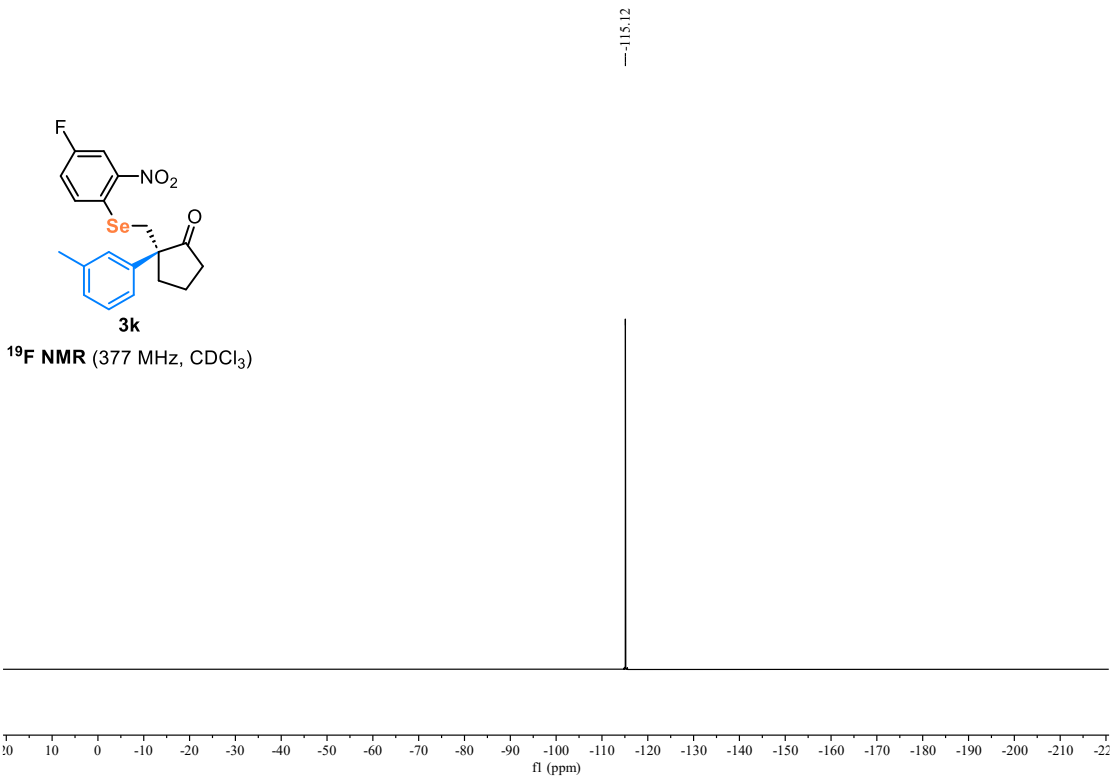


3k

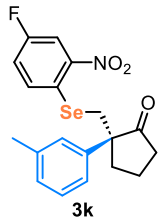
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

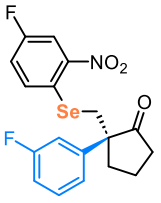


^{19}F NMR (377 MHz, $CDCl_3$)



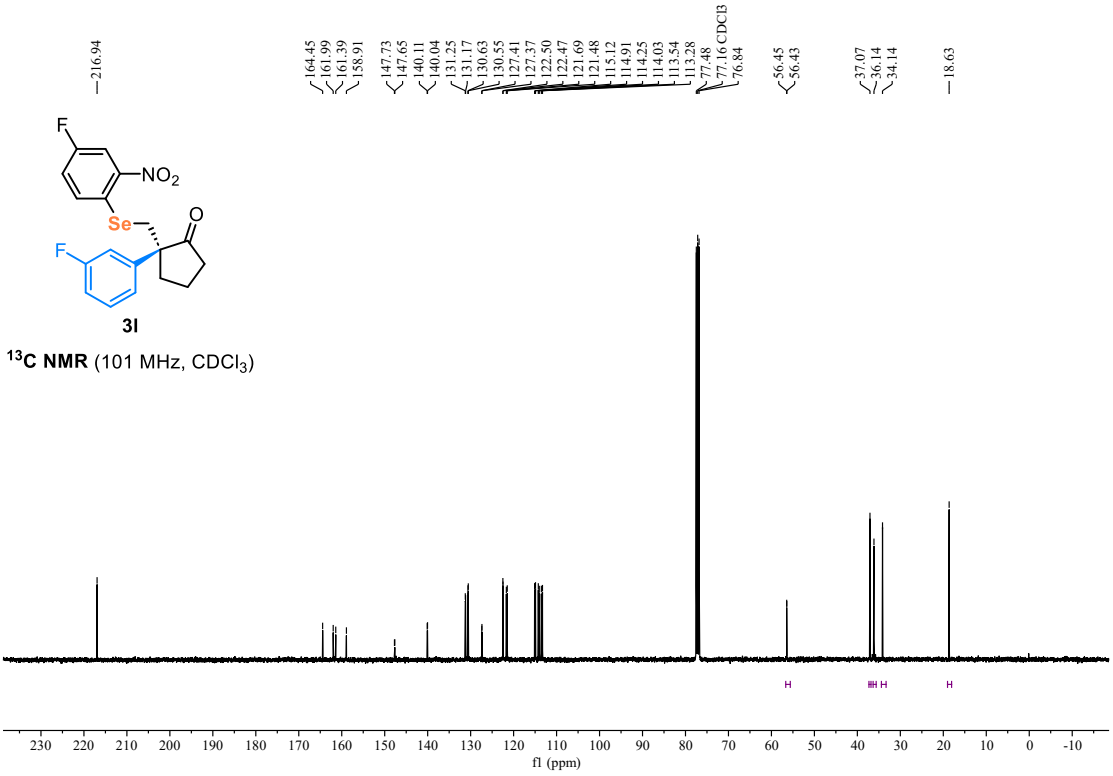
3k

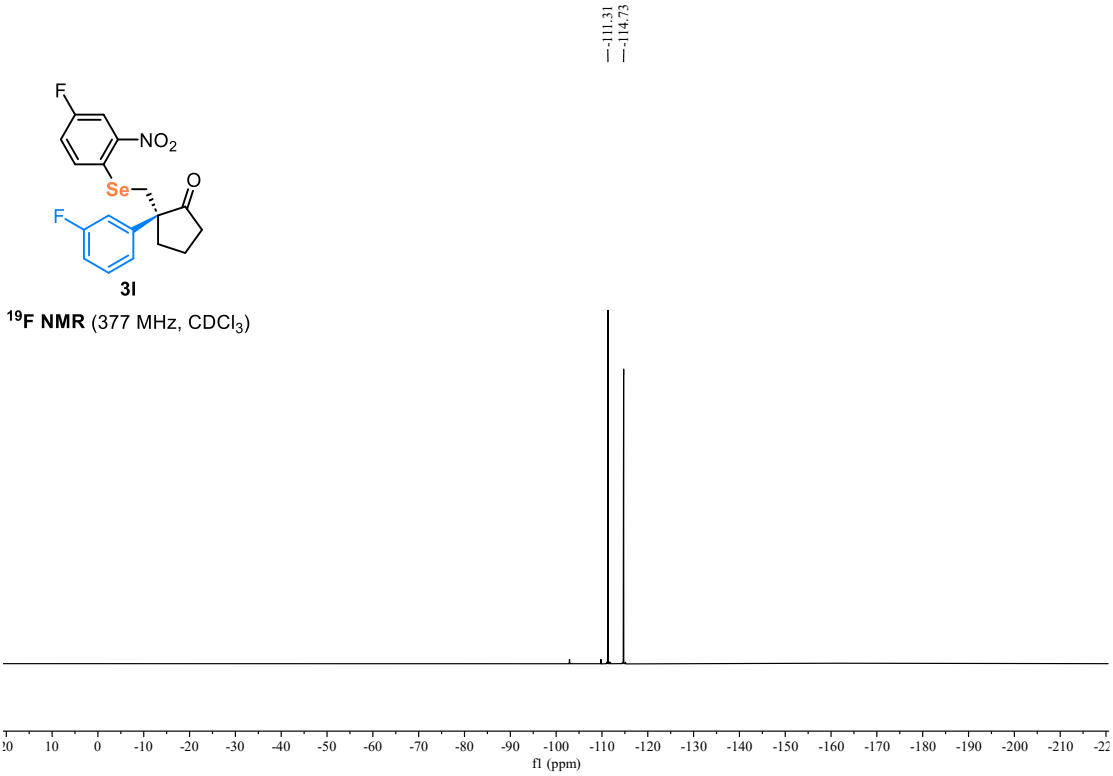
^{77}Se NMR (76 MHz, $CDCl_3$)

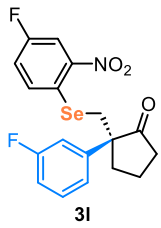


3l

^{1}H NMR (400 MHz, $CDCl_3$)

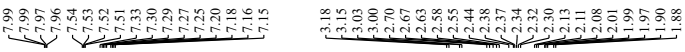

216.94
164.45
161.99
161.39
158.91
147.73
147.65
140.11
140.04
131.25
131.17
130.63
130.55
127.41
127.37
122.50
122.47
121.69
121.48
115.12
114.91
114.25
114.03
113.54
113.28
77.48
77.16 CDCl3
76.84
56.45
56.43
37.07
36.14
34.14
18.63
F
NO2
Se
O
F
3l
13C NMR (101 MHz, CDCl3)
f1 (ppm)

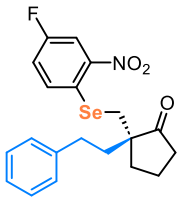

-111.31
-114.73
F
NO2
Se
O
F
3l
19F NMR (377 MHz, CDCl3)
f1 (ppm)



3l

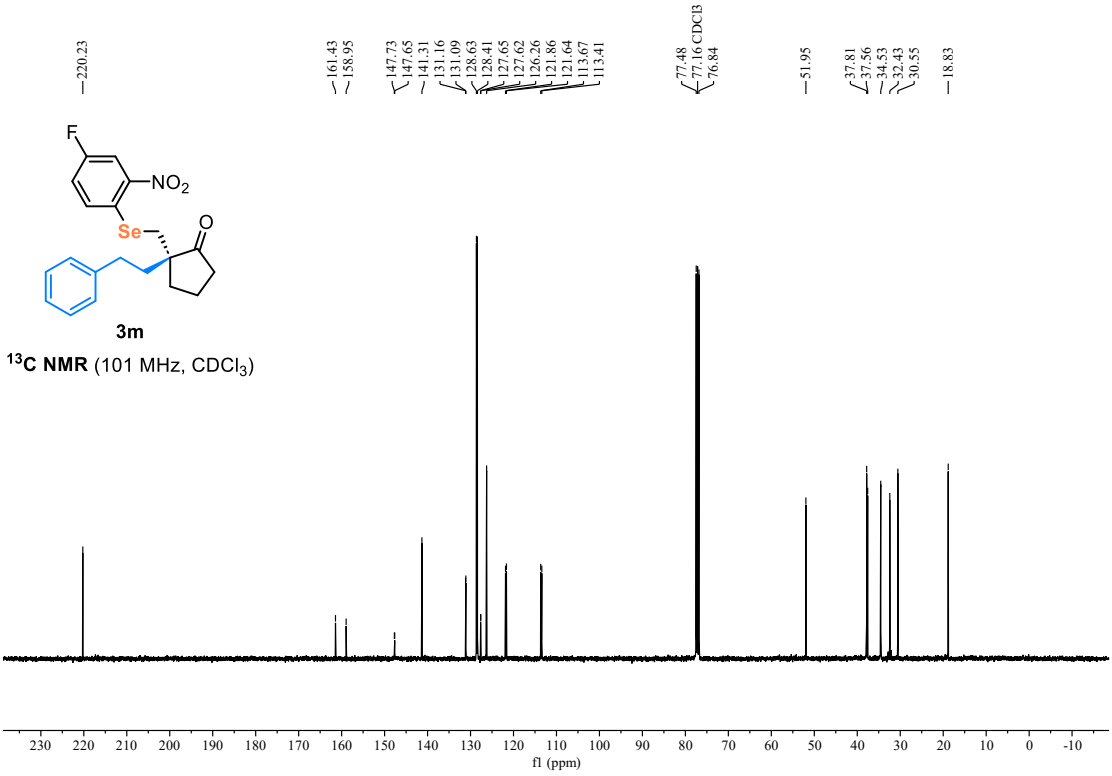
^{77}Se NMR (76 MHz, $CDCl_3$)

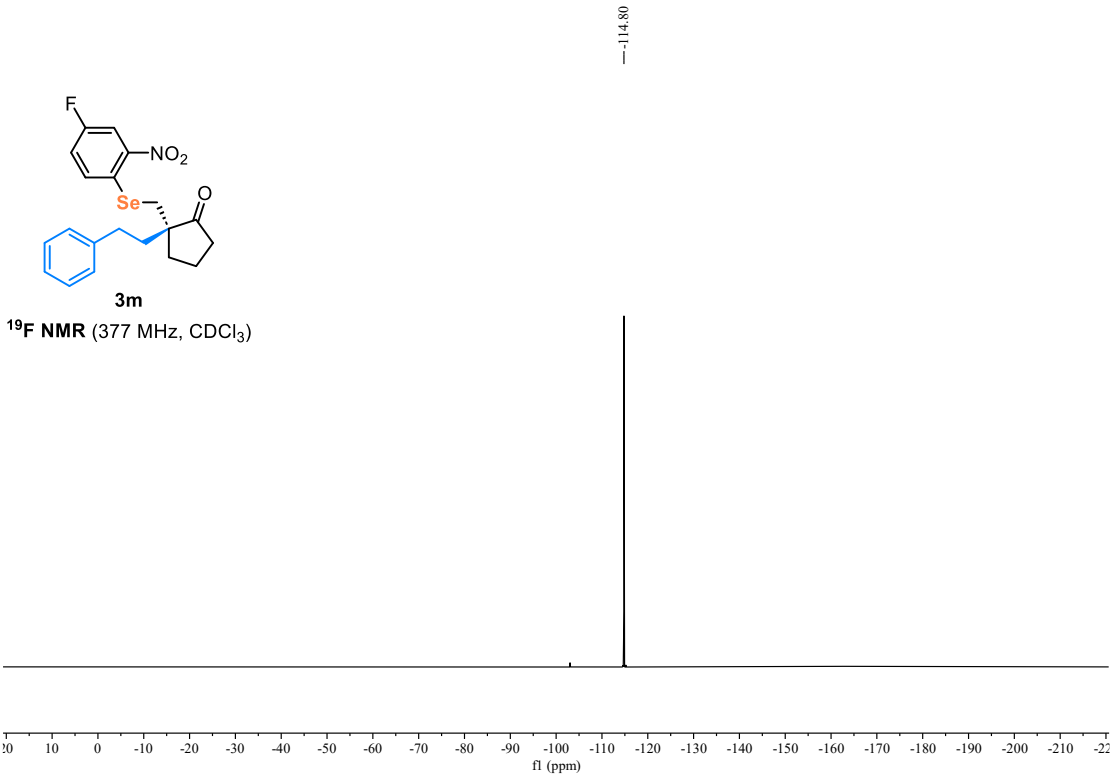


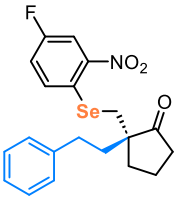


3m

^{1}H NMR (400 MHz, $CDCl_3$)

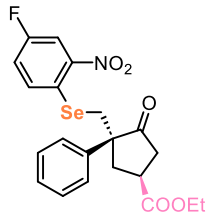

220.23
161.43
158.95
147.73
147.65
141.31
131.16
131.09
128.63
128.41
127.65
127.62
126.26
121.86
121.64
113.67
113.41
77.48
77.16 CDCl3
76.84
51.95
37.81
37.56
34.53
32.43
30.55
18.83
F
NO2
Se
O
3m
13C NMR (101 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-114.80
F
NO2
Se
O
3m
19F NMR (377 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



3m

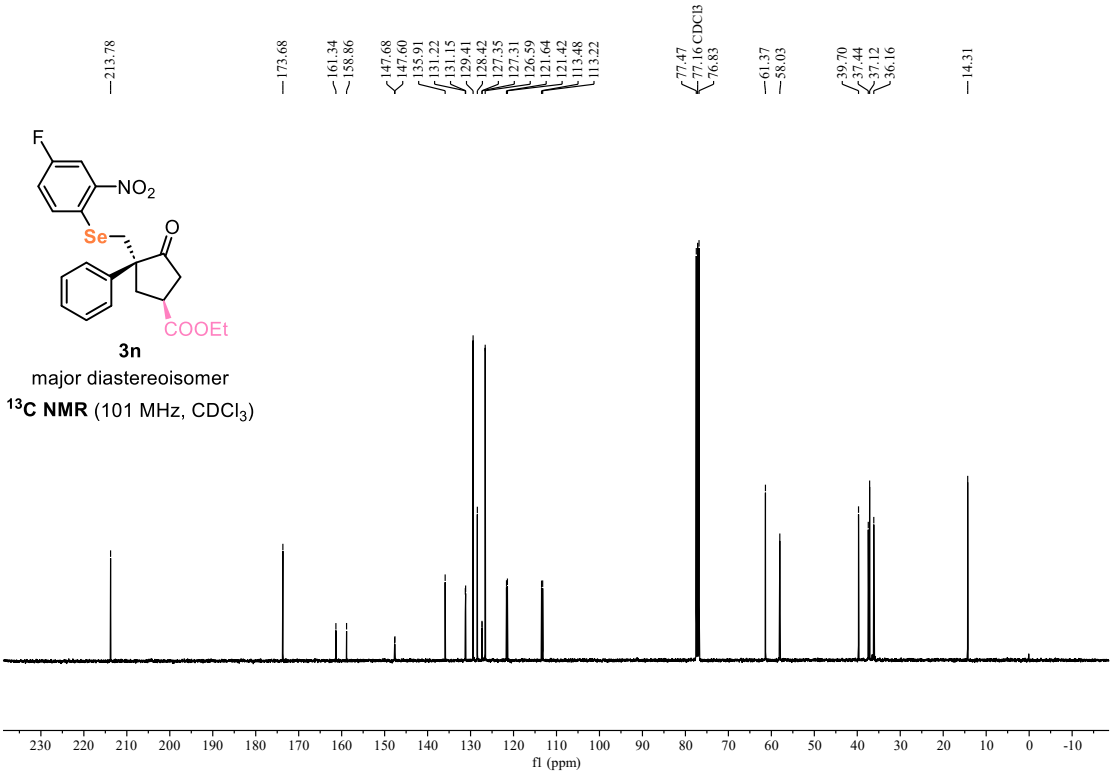
^{77}Se NMR (76 MHz, $CDCl_3$)



3n

major diastereoisomer

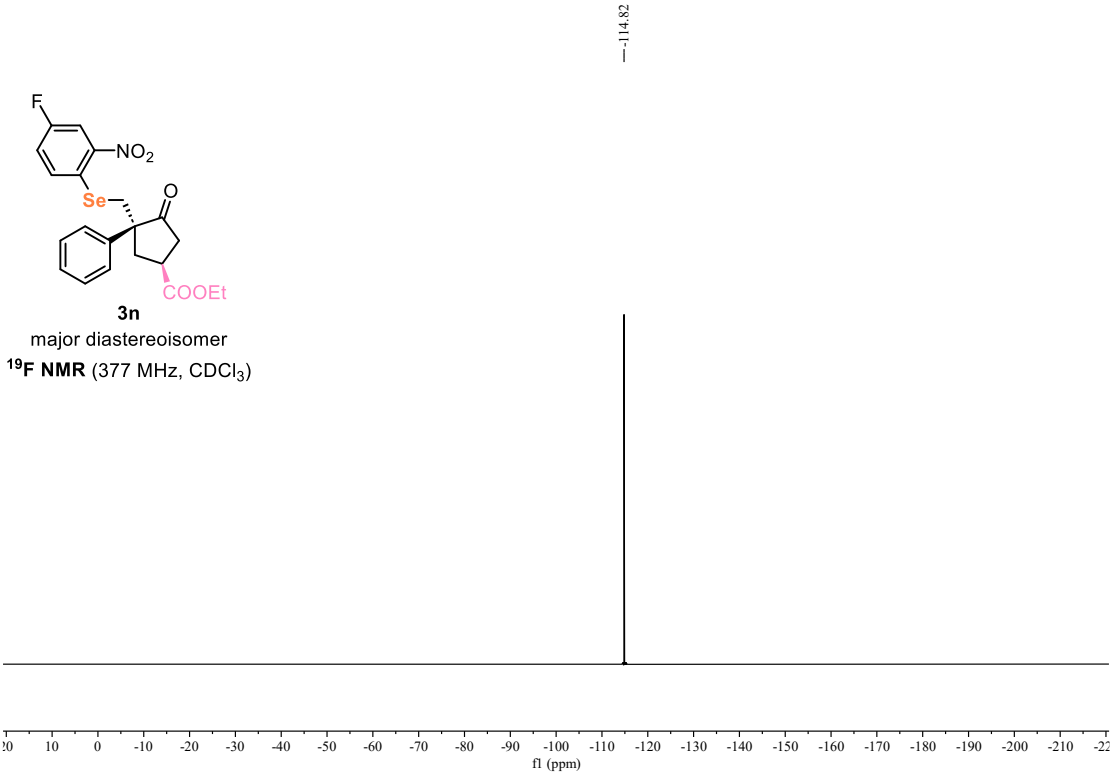
^{1}H NMR (400 MHz, $CDCl_3$)



3n

major diastereoisomer

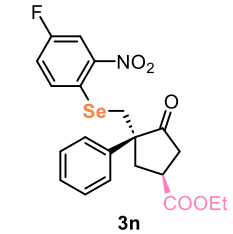
^{13}C NMR (101 MHz, $CDCl_3$)



3n

major diastereoisomer

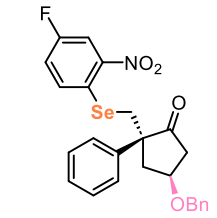
^{19}F NMR (377 MHz, $CDCl_3$)



3n

major diastereoisomer

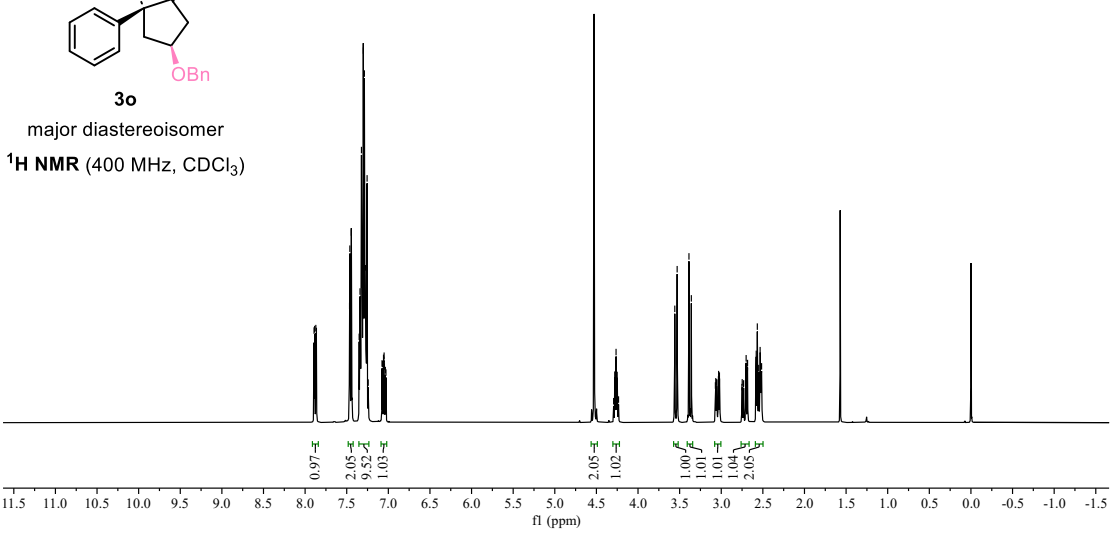
^{77}Se NMR (76 MHz, $CDCl_3$)

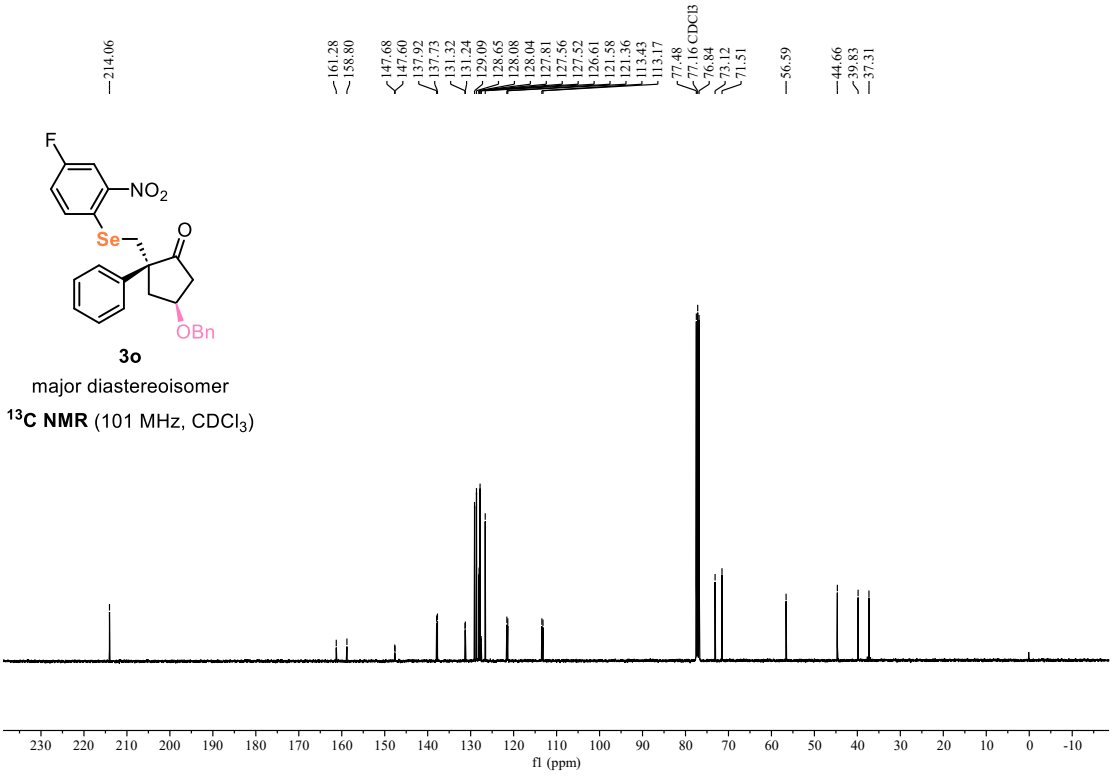


3o

major diastereoisomer

^{1}H NMR (400 MHz, $CDCl_3$)

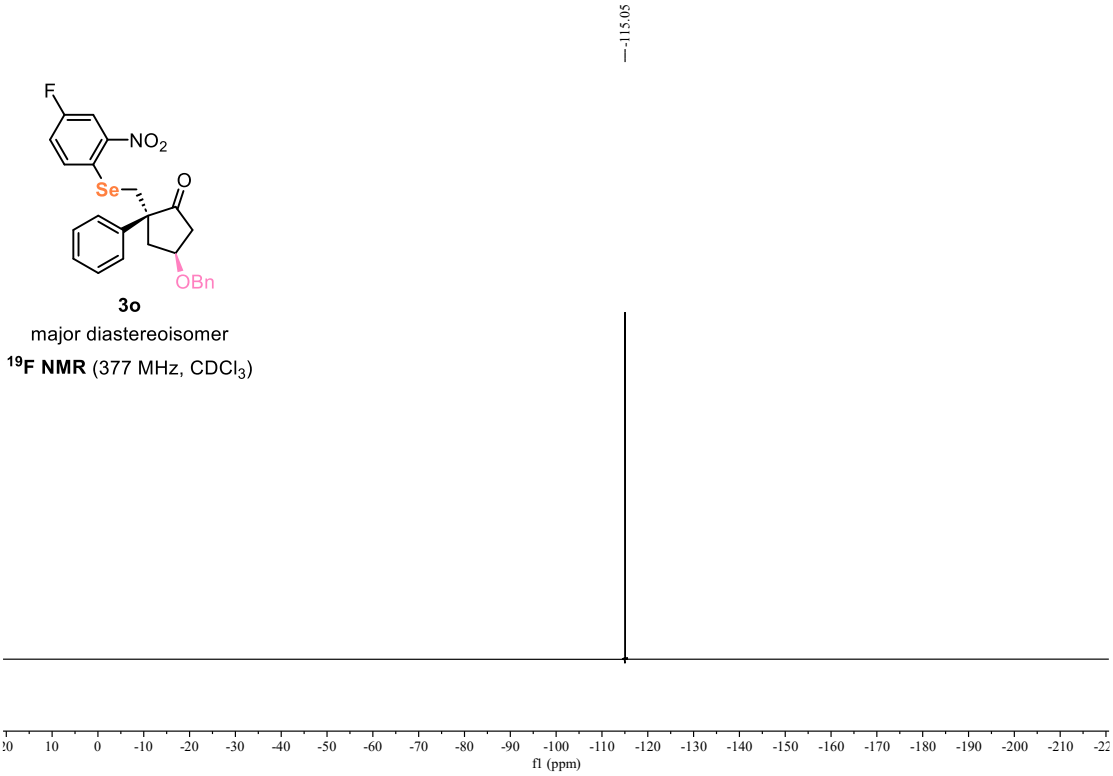




3o

major diastereoisomer

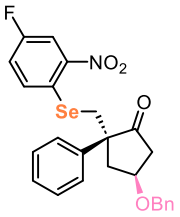
^{13}C NMR (101 MHz, $CDCl_3$)



3o

major diastereoisomer

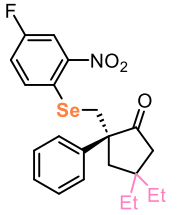
^{19}F NMR (377 MHz, $CDCl_3$)



3o

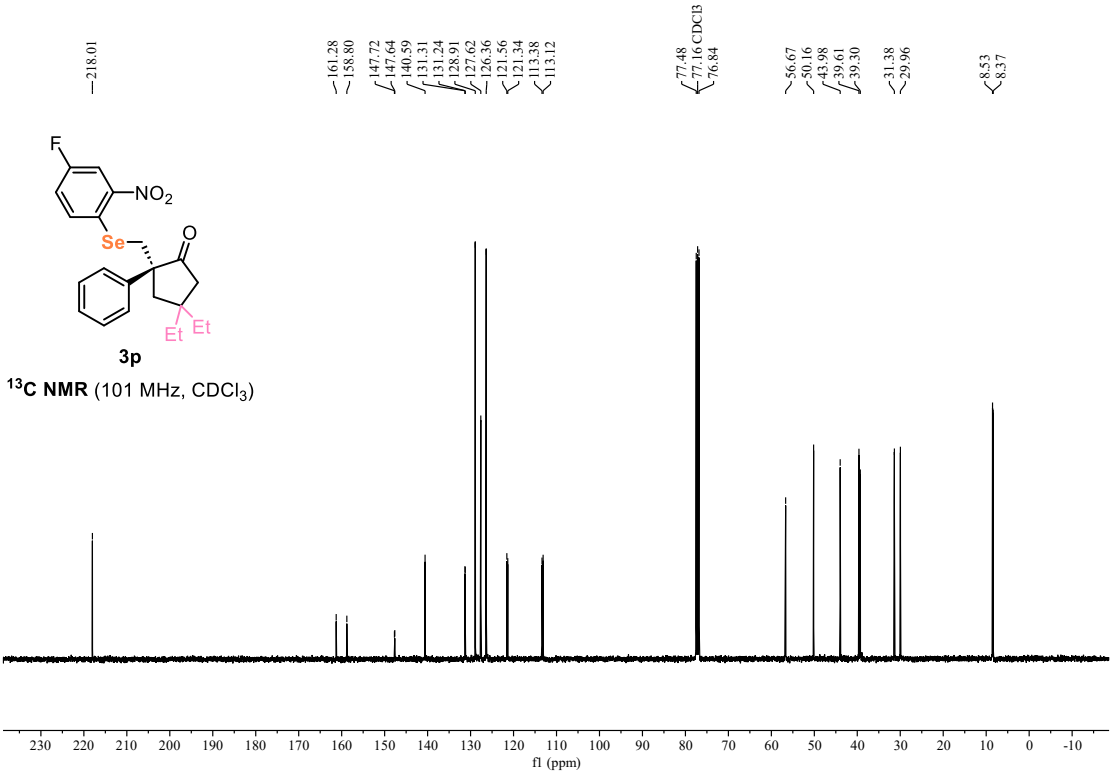
major diastereoisomer

^{77}Se NMR (76 MHz, $CDCl_3$)



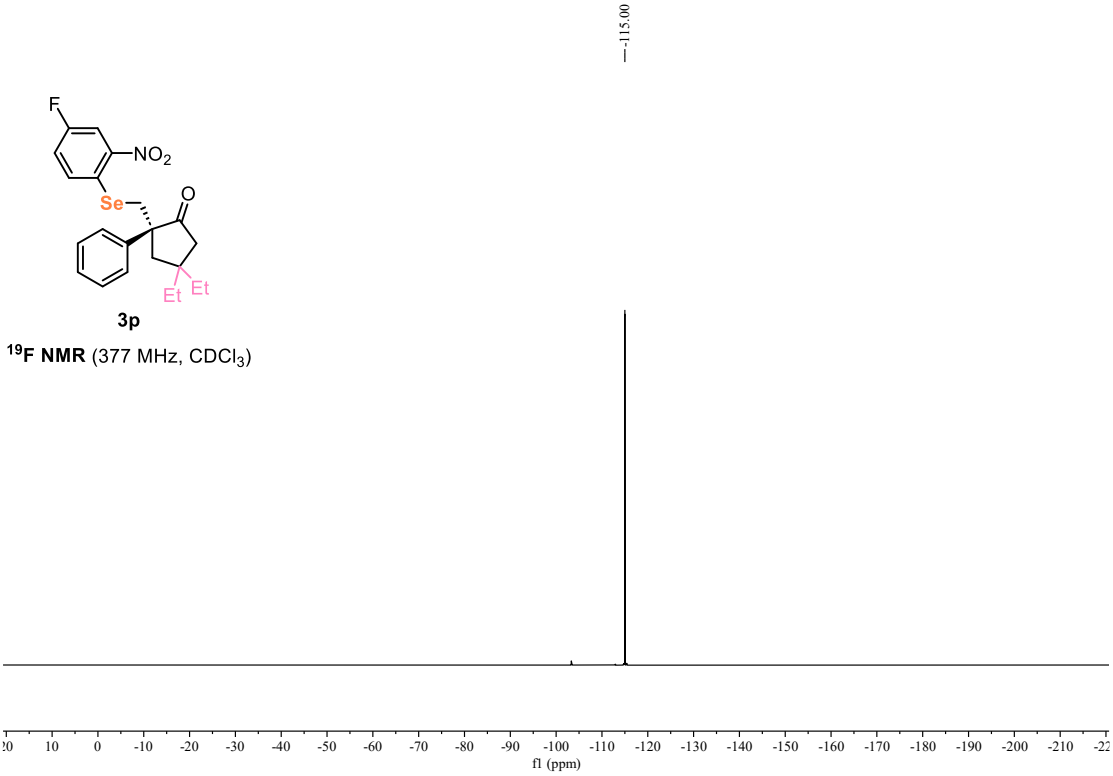
3p

^{1}H NMR (400 MHz, $CDCl_3$)



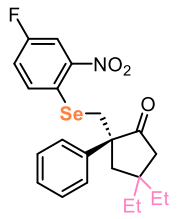
3p

^{13}C NMR (101 MHz, $CDCl_3$)



3p

^{19}F NMR (377 MHz, $CDCl_3$)

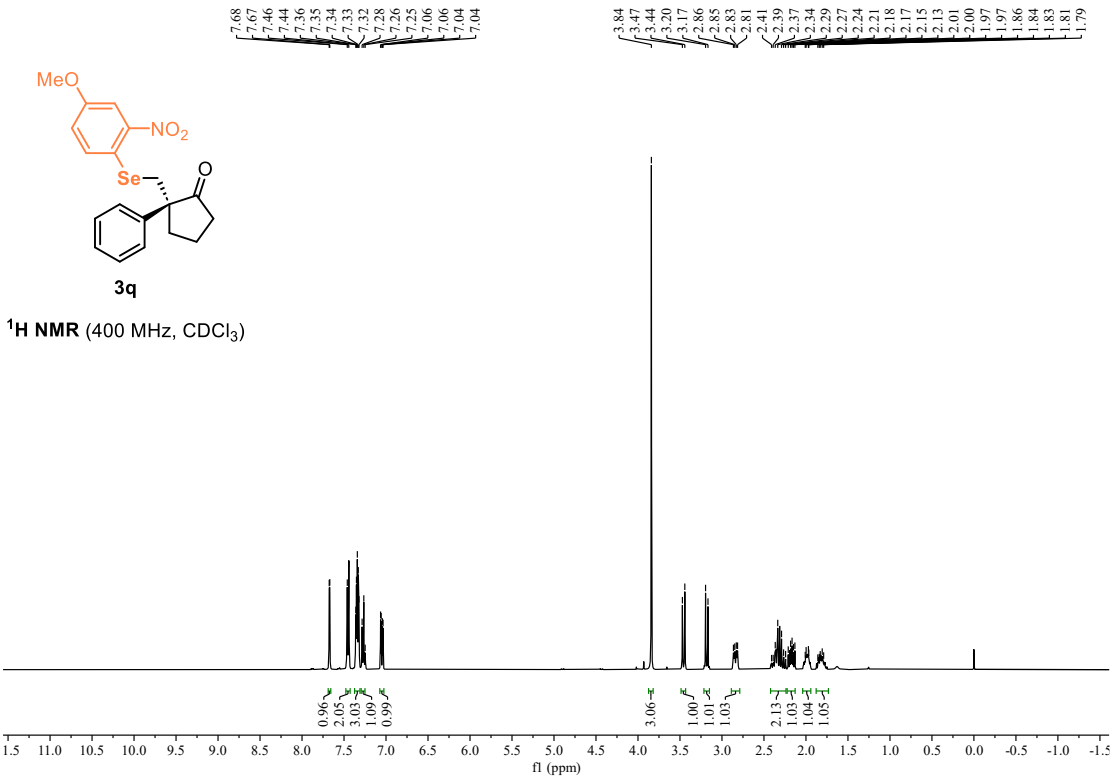


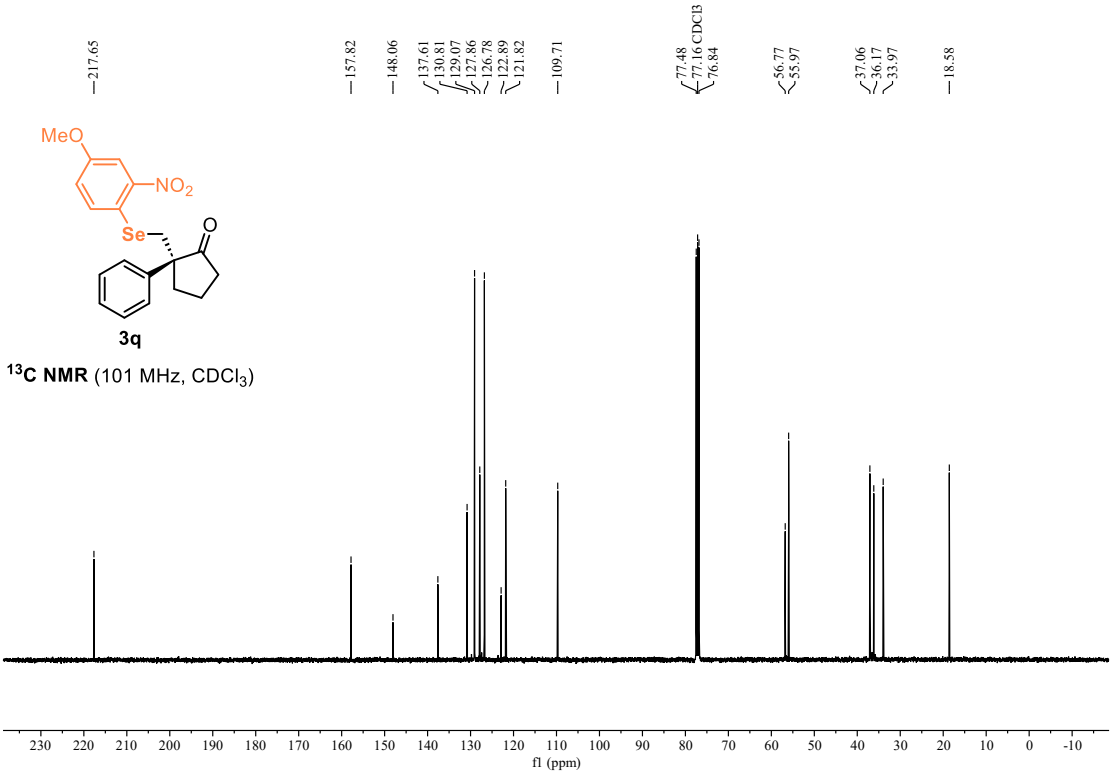
3p

^{77}Se NMR (76 MHz, $CDCl_3$)

3q

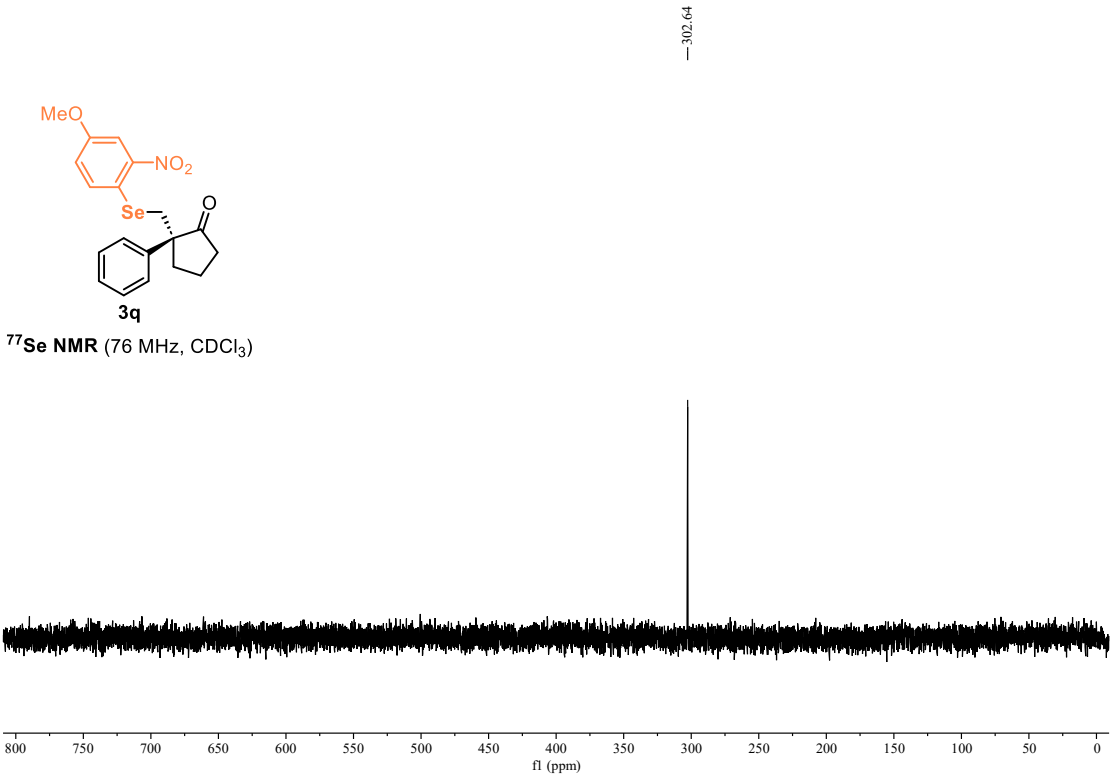
^{1}H NMR (400 MHz, $CDCl_3$)





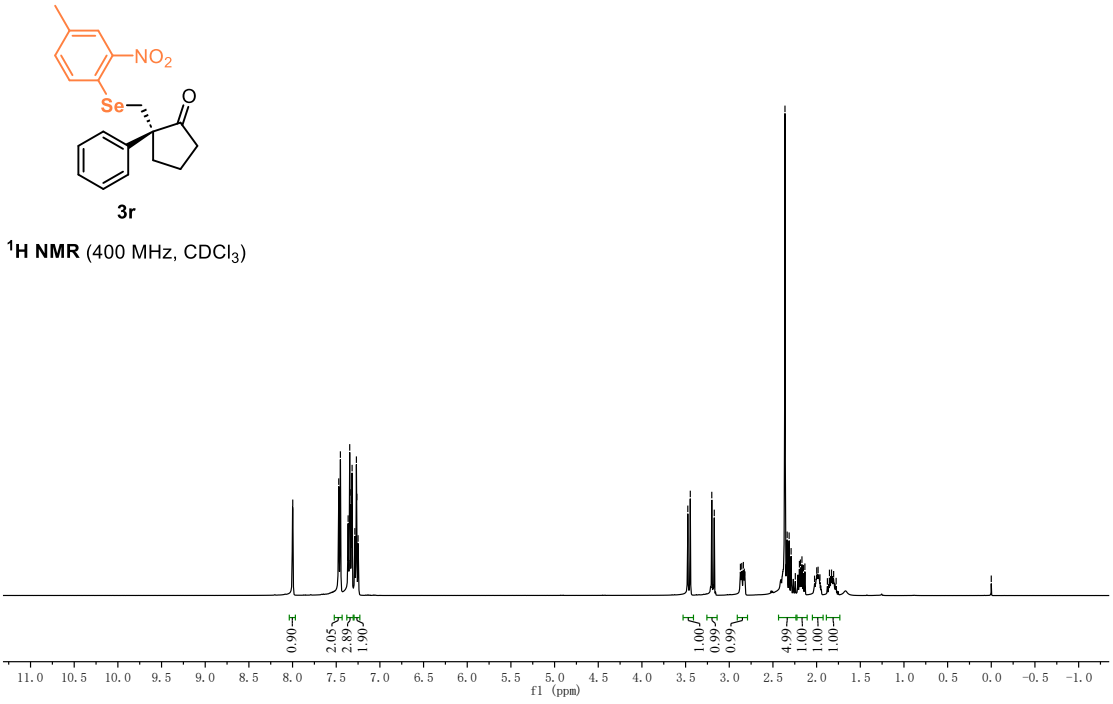
3q

^{13}C NMR (101 MHz, $CDCl_3$)



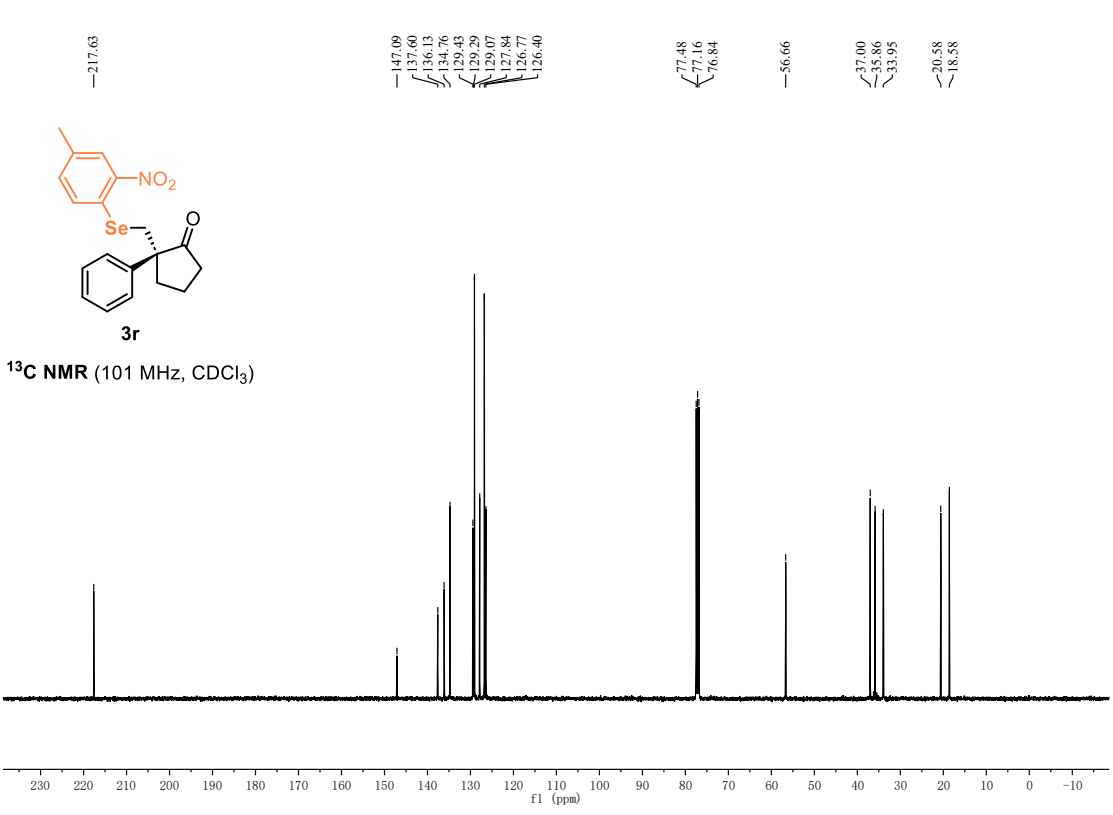
3q

^{77}Se NMR (76 MHz, $CDCl_3$)



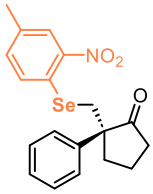
3r

^{1}H NMR (400 MHz, $CDCl_3$)



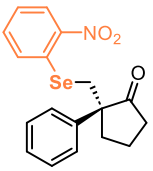
3r

^{13}C NMR (101 MHz, $CDCl_3$)



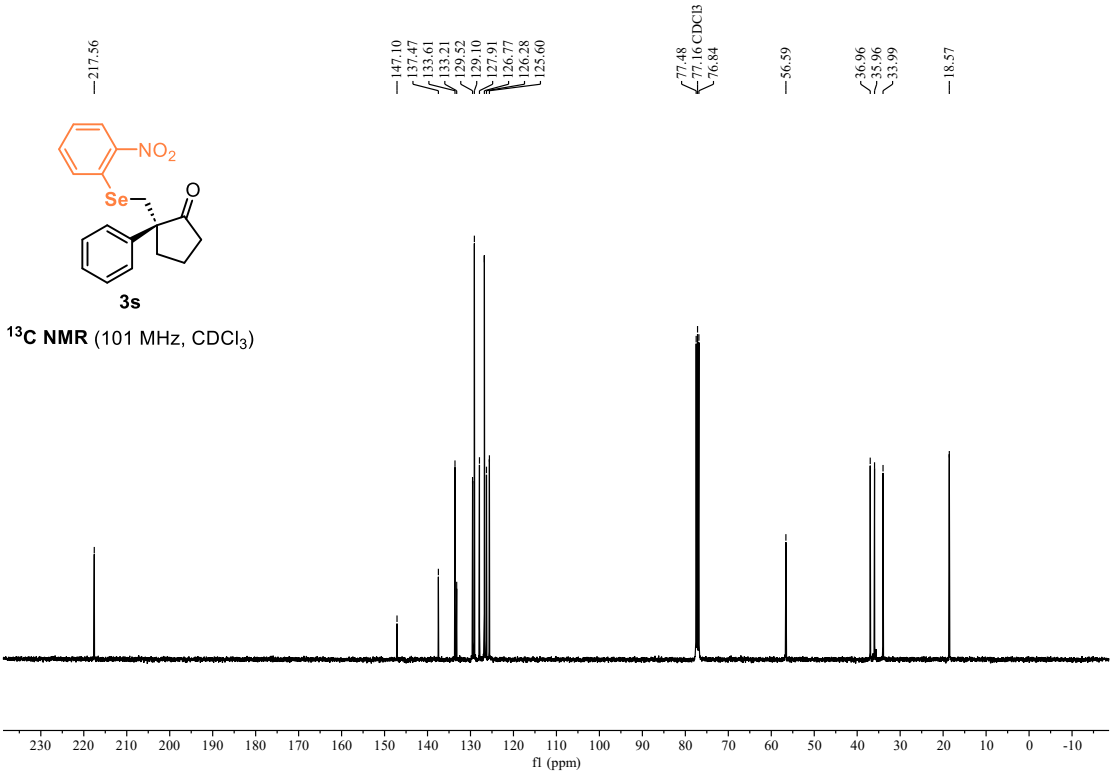
3r

^{77}Se NMR (76 MHz, $CDCl_3$)



3s

^{1}H NMR (400 MHz, $CDCl_3$)



3s

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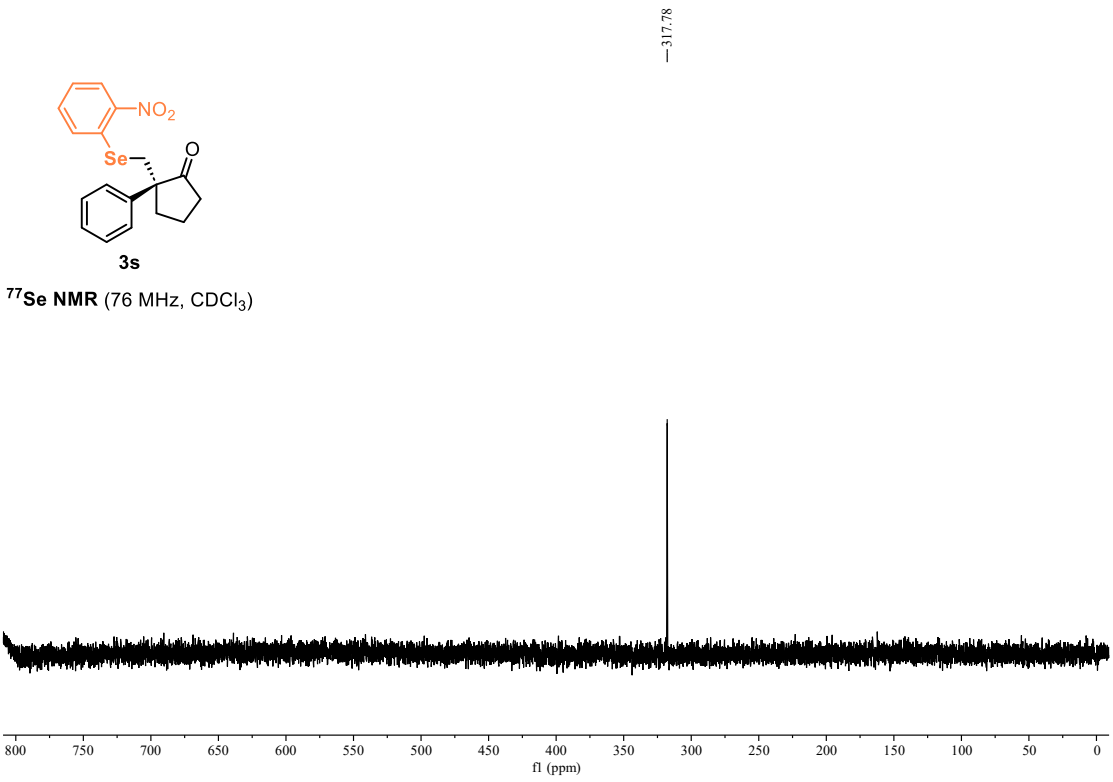
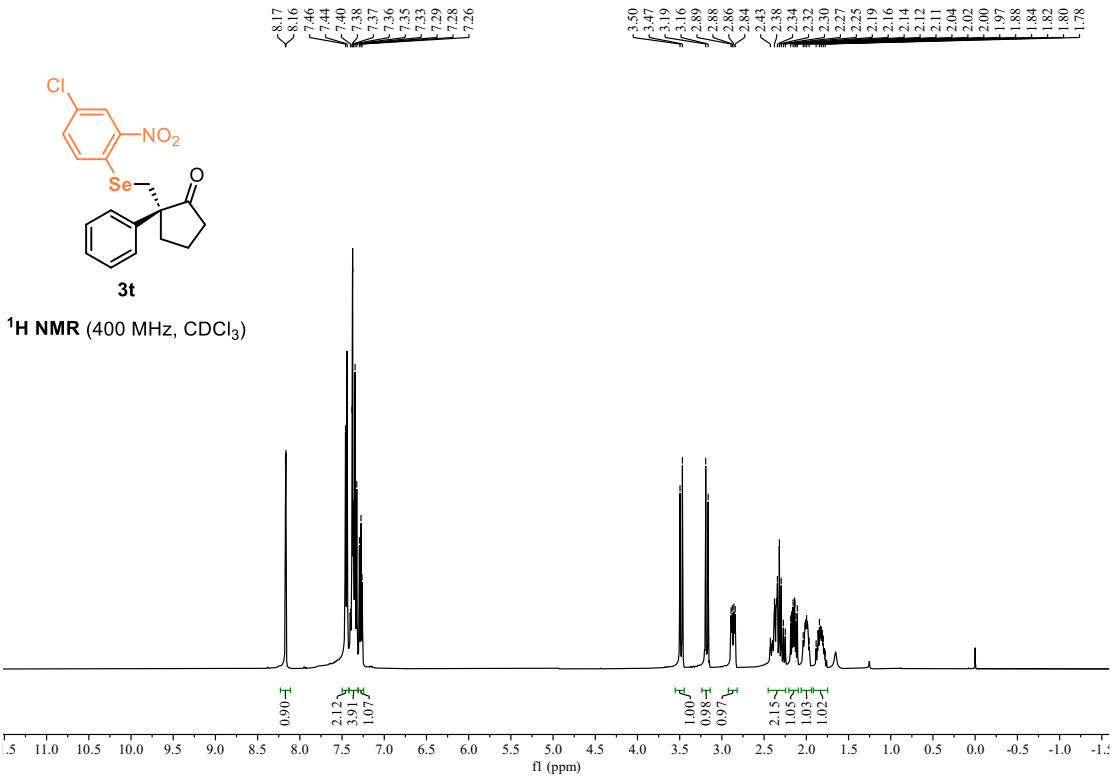
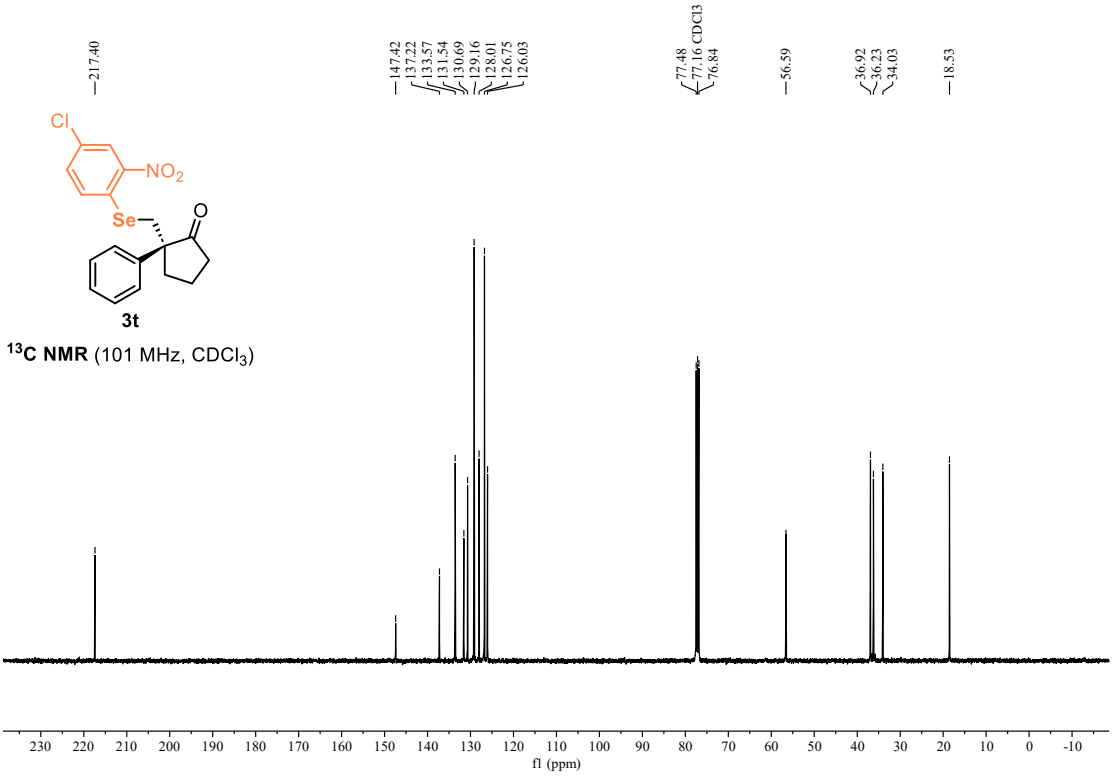
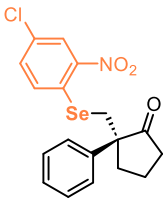


3s

^{77}Se NMR (76 MHz, $CDCl_3$)


Cl
NO2
Se
O
3t
1H NMR (400 MHz, CDCl3)
fl (ppm)


Cl
NO2
Se
O
3t
13C NMR (101 MHz, CDCl3)
fl (ppm)



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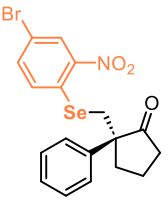

3u

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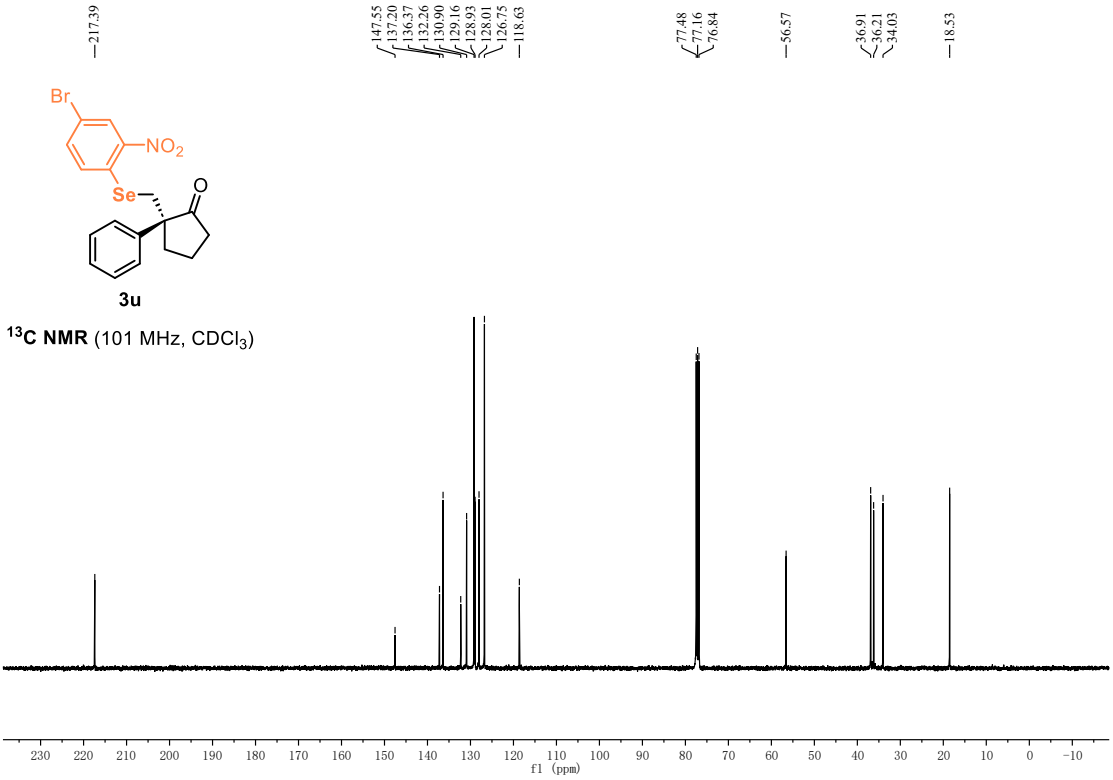

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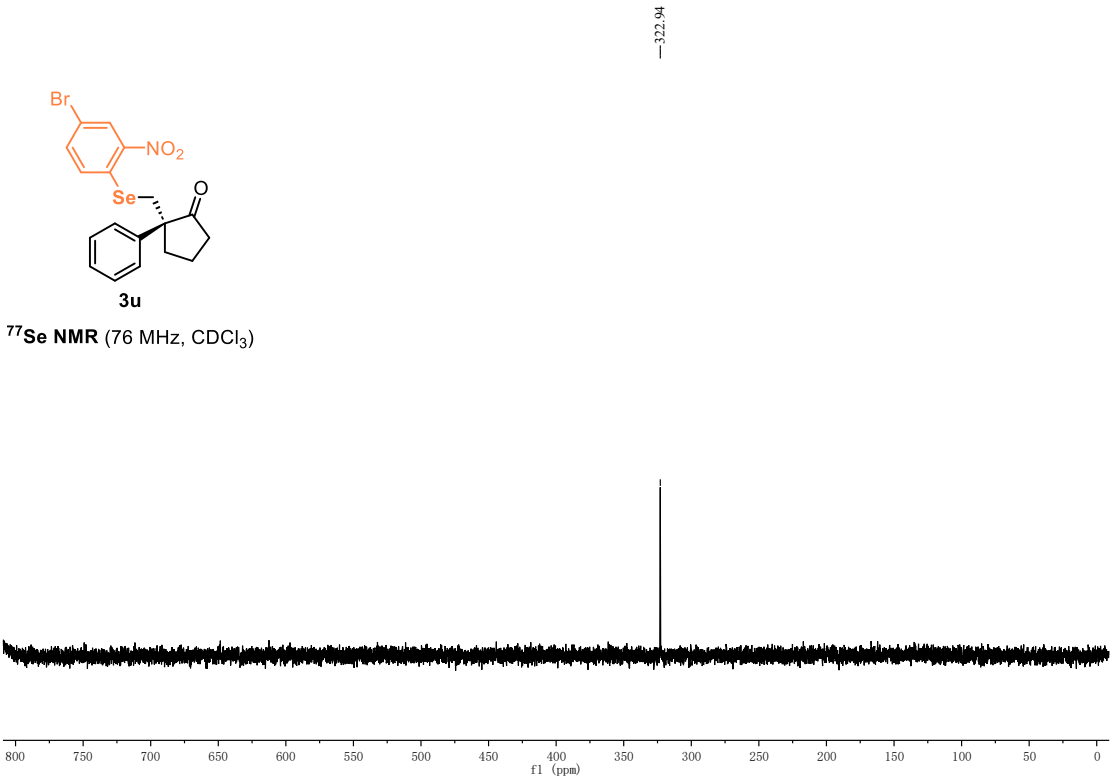
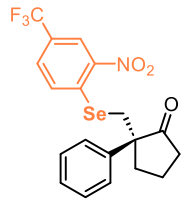


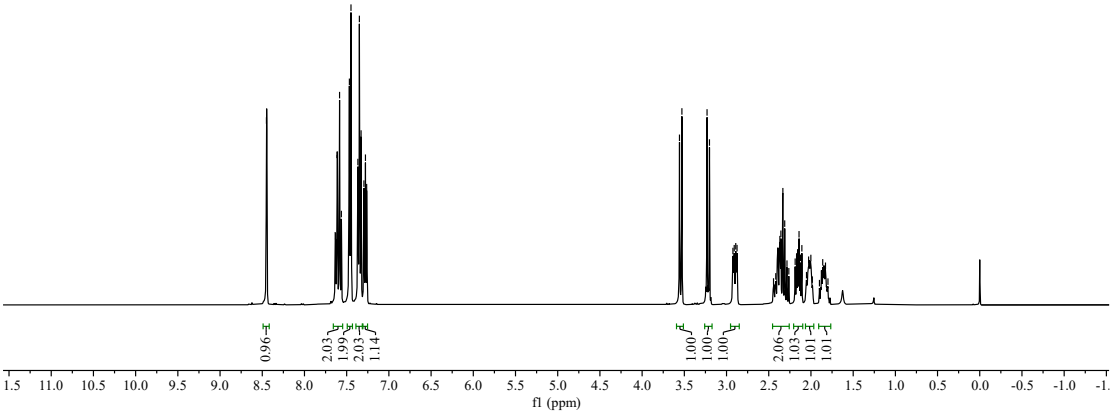
3u

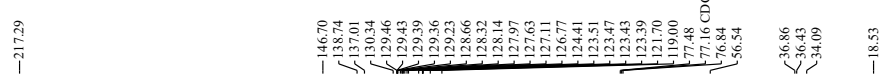
^{77}Se NMR (76 MHz, $CDCl_3$)

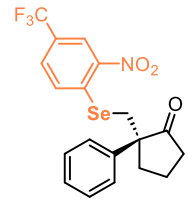


3v

^{1}H NMR (400 MHz, $CDCl_3$)

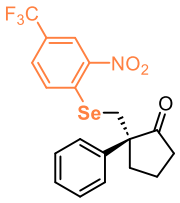






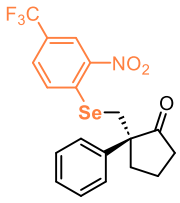
3v

^{13}C NMR (101 MHz, $CDCl_3$)



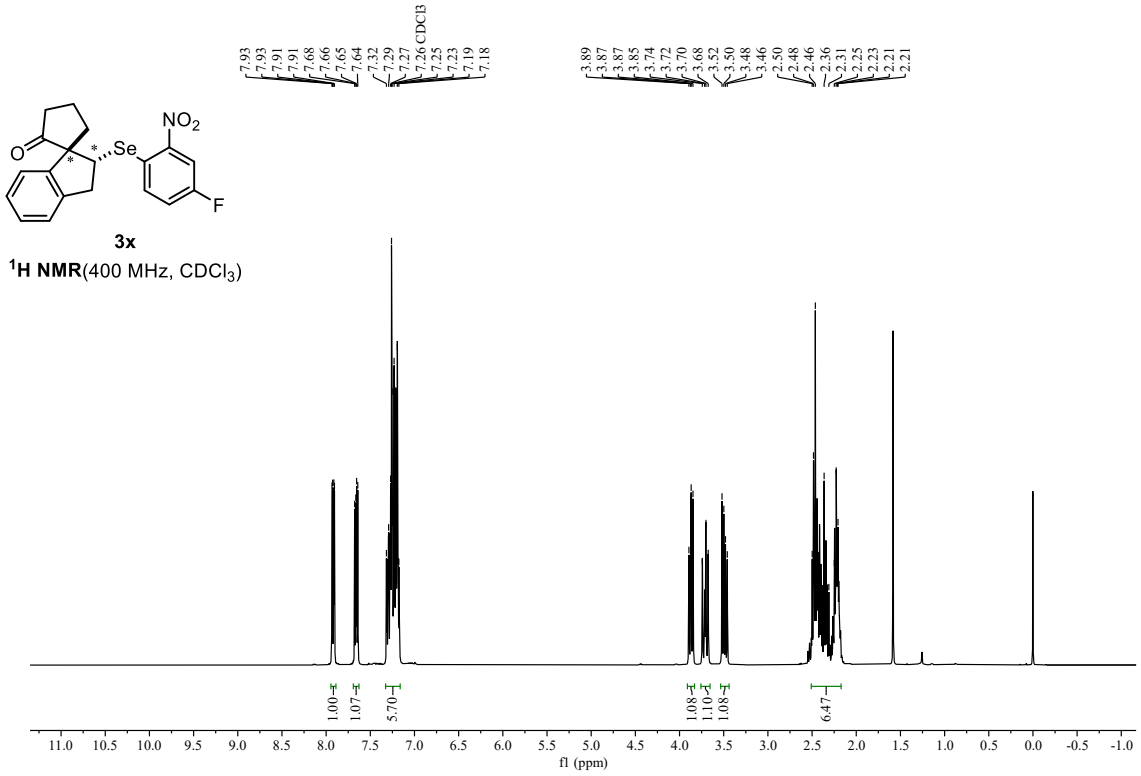
3v

^{19}F NMR (377 MHz, $CDCl_3$)



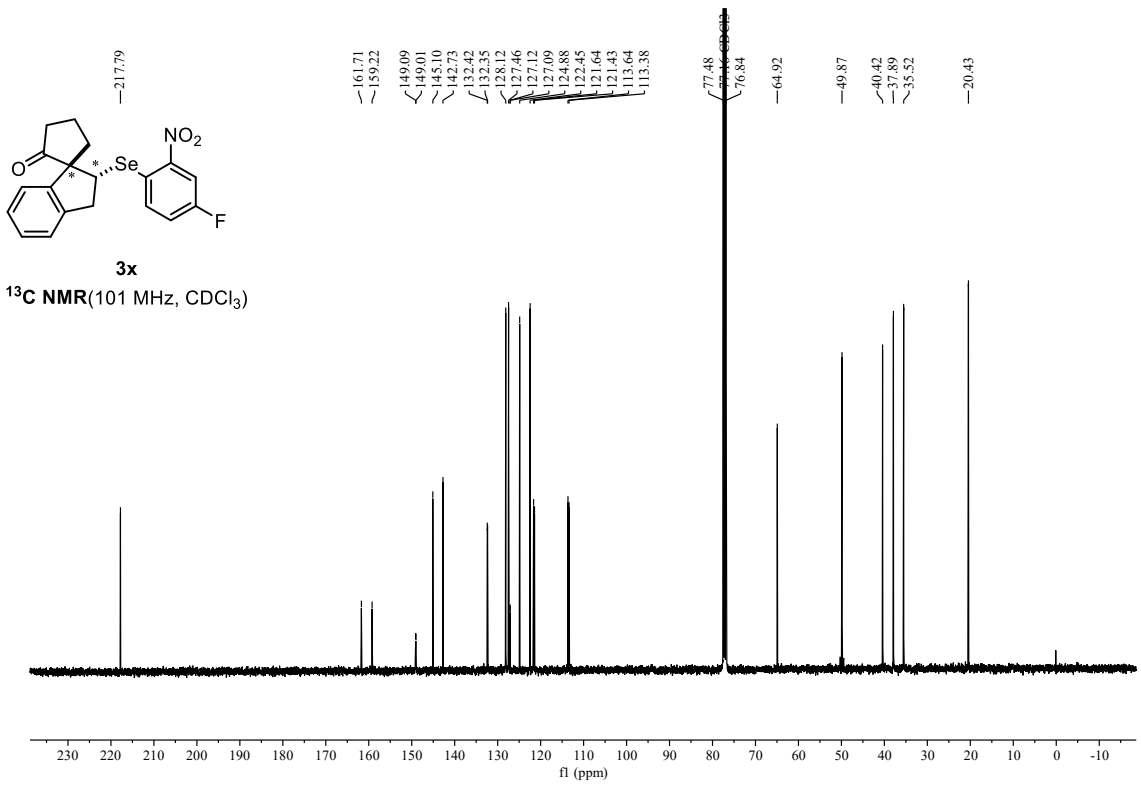
3v

^{77}Se NMR (76 MHz, $CDCl_3$)



3x

^{1}H NMR(400 MHz, $CDCl_3$)



3x

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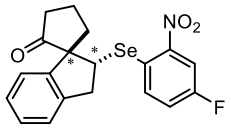
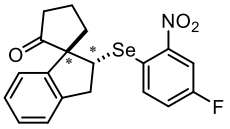


3x

^{19}F NMR(377 MHz, $CDCl_3$)



3x

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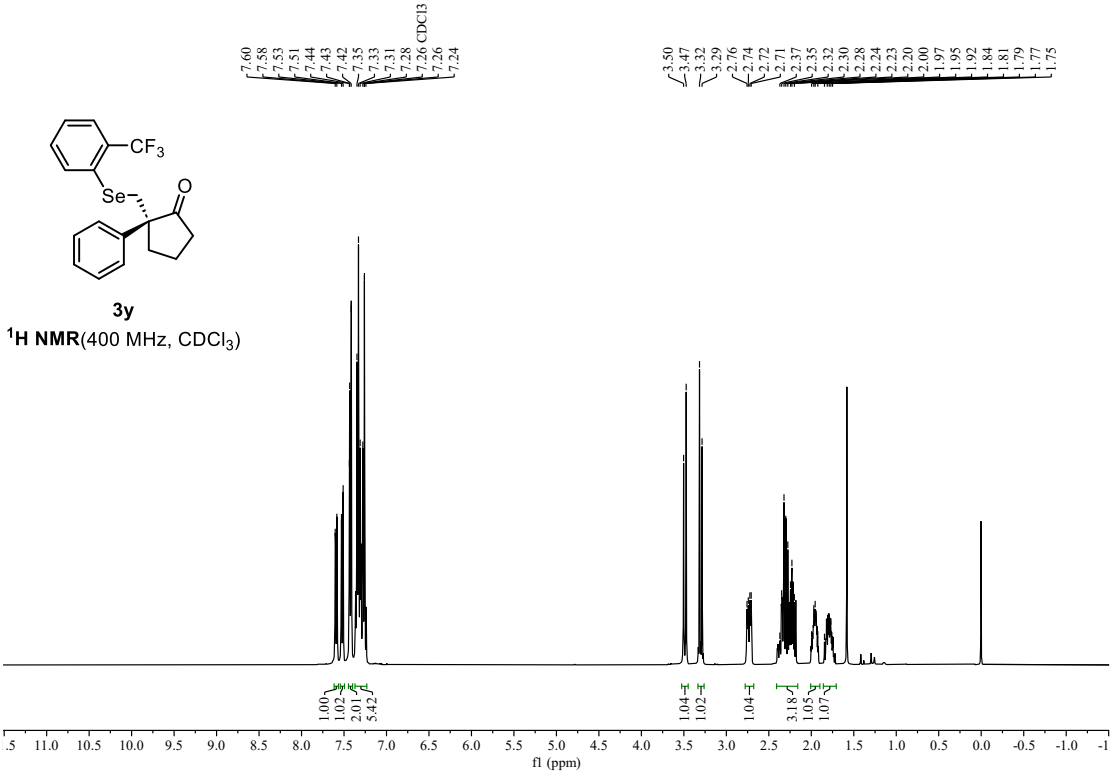
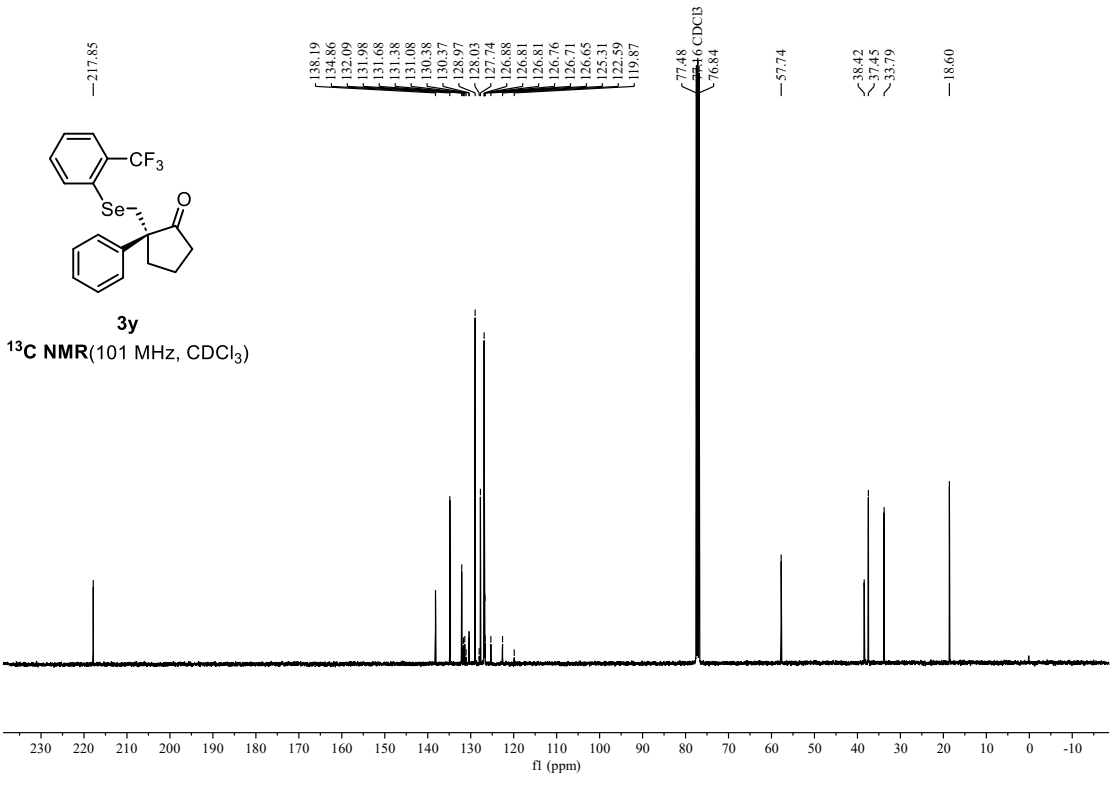


3y

^{1}H NMR(400 MHz, $CDCl_3$)



3y

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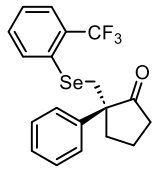

3y

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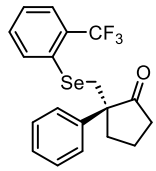

3y

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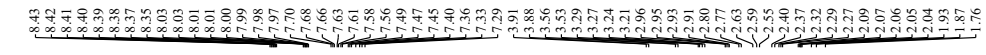
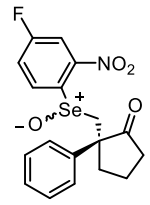
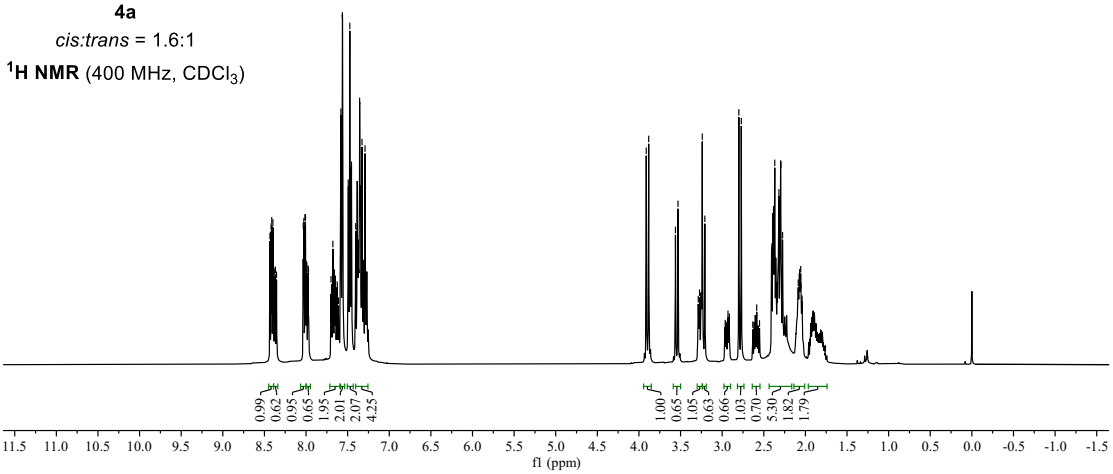


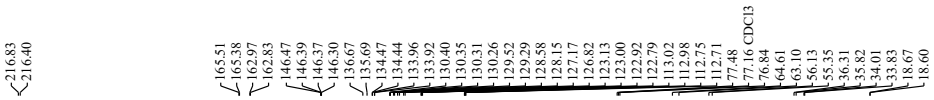


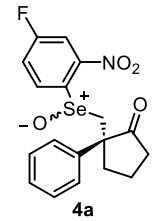
4a

cis:trans = 1.6:1

^{1}H NMR (400 MHz, $CDCl_3$)



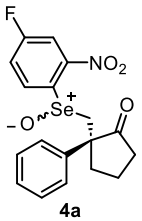




4a

cis:trans = 1.6:1

^{13}C NMR (101 MHz, $CDCl_3$)



4a

cis:trans = 1.6:1

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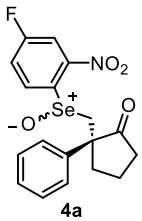
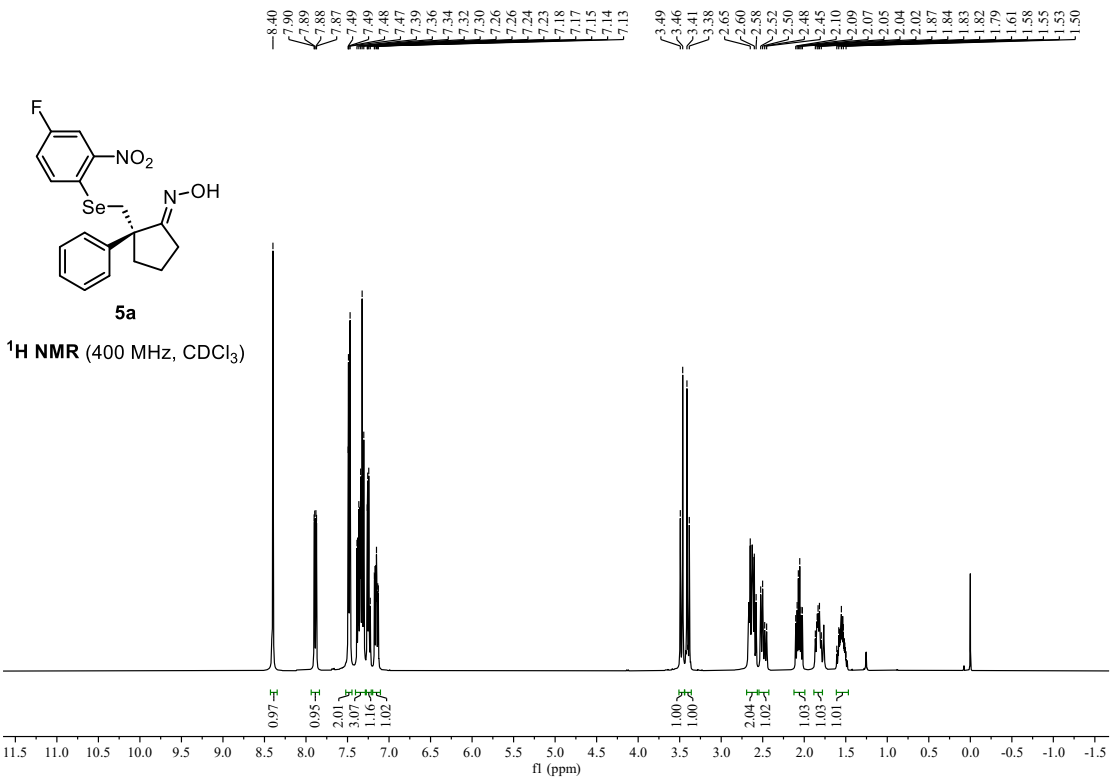


4a

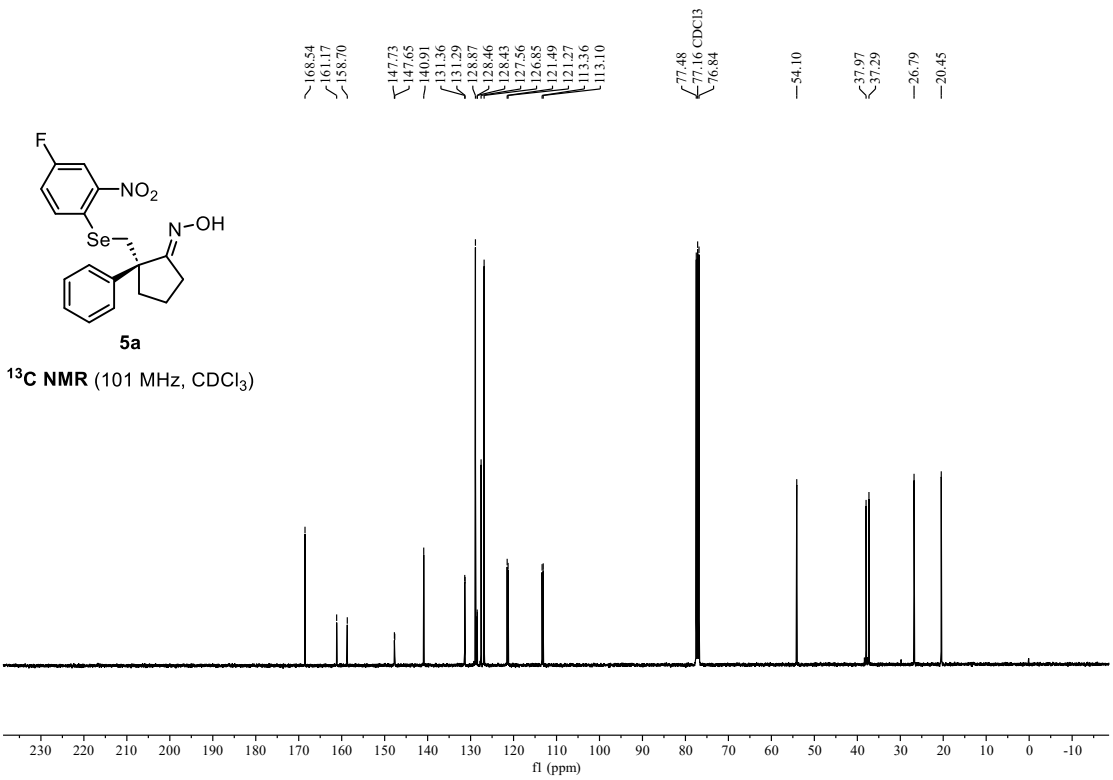
cis:trans = 1.6:1

^{77}Se NMR (76 MHz, $CDCl_3$)



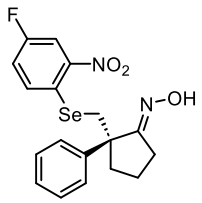
5a

^{1}H NMR (400 MHz, $CDCl_3$)



5a

^{13}C NMR (101 MHz, $CDCl_3$)



5a

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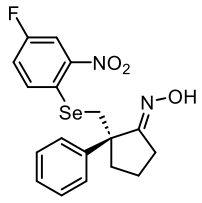
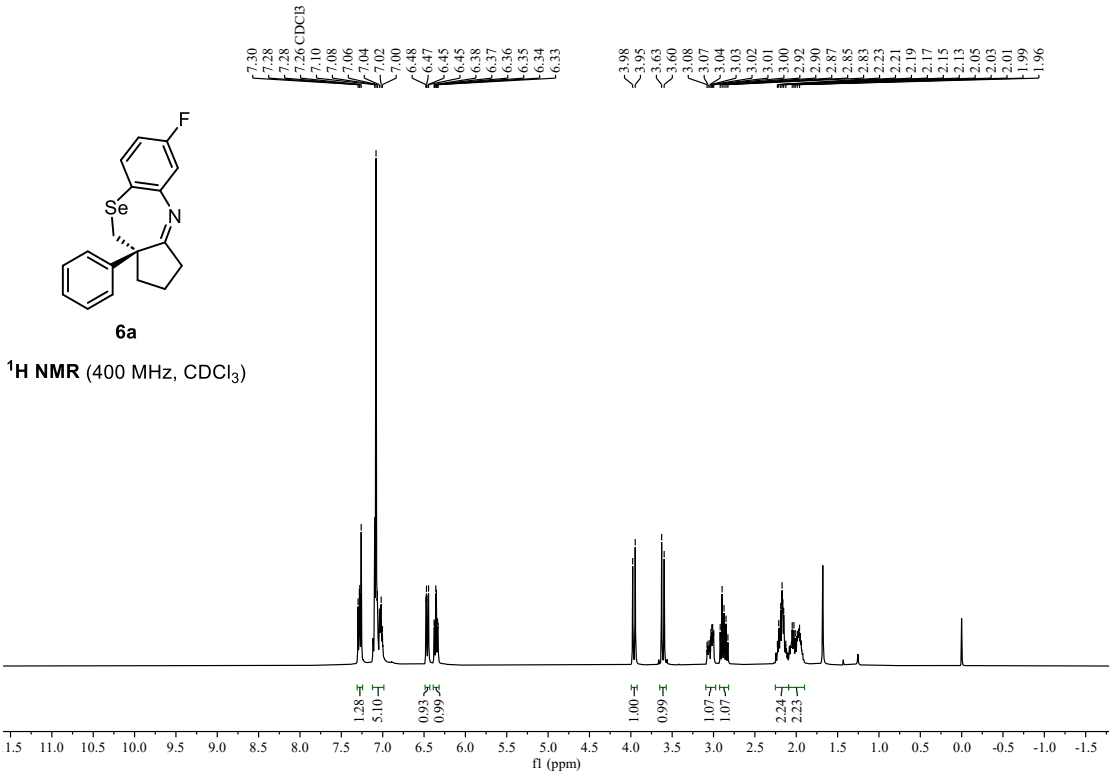


5a

^{77}Se NMR (76 MHz, $CDCl_3$)



6a

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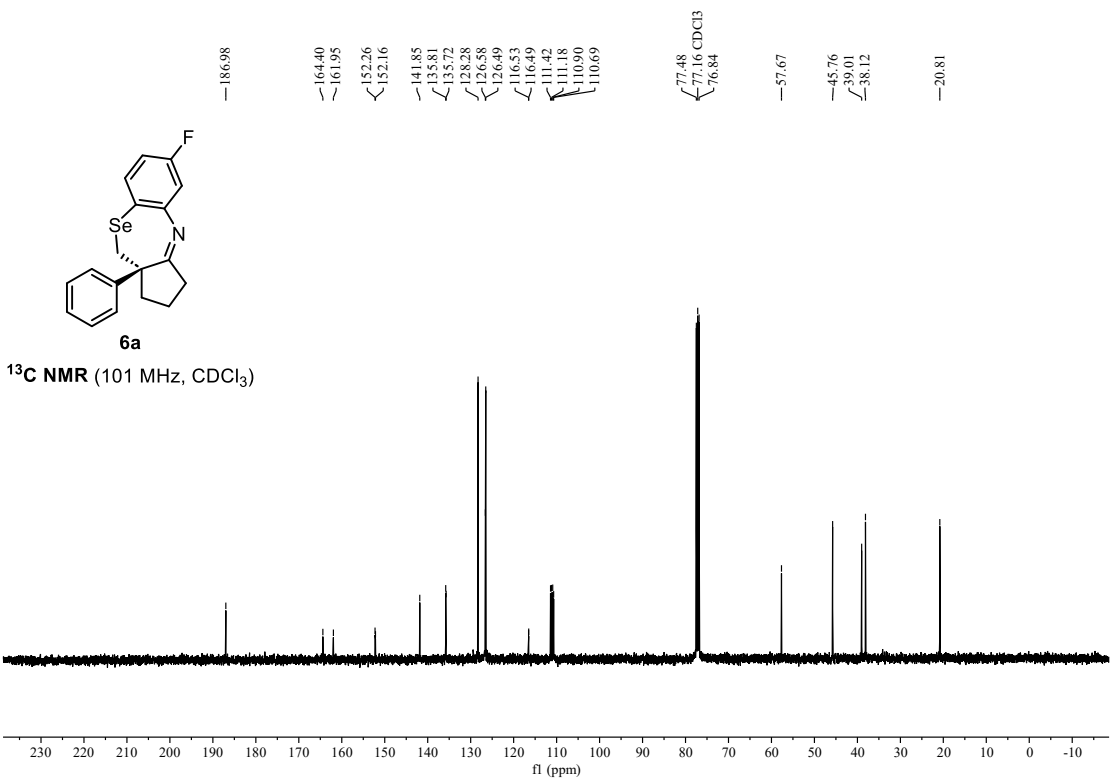
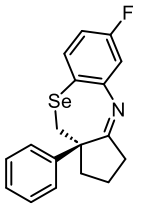


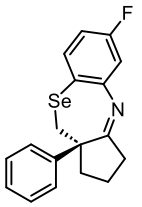
6a

^{13}C NMR (101 MHz, $CDCl_3$)



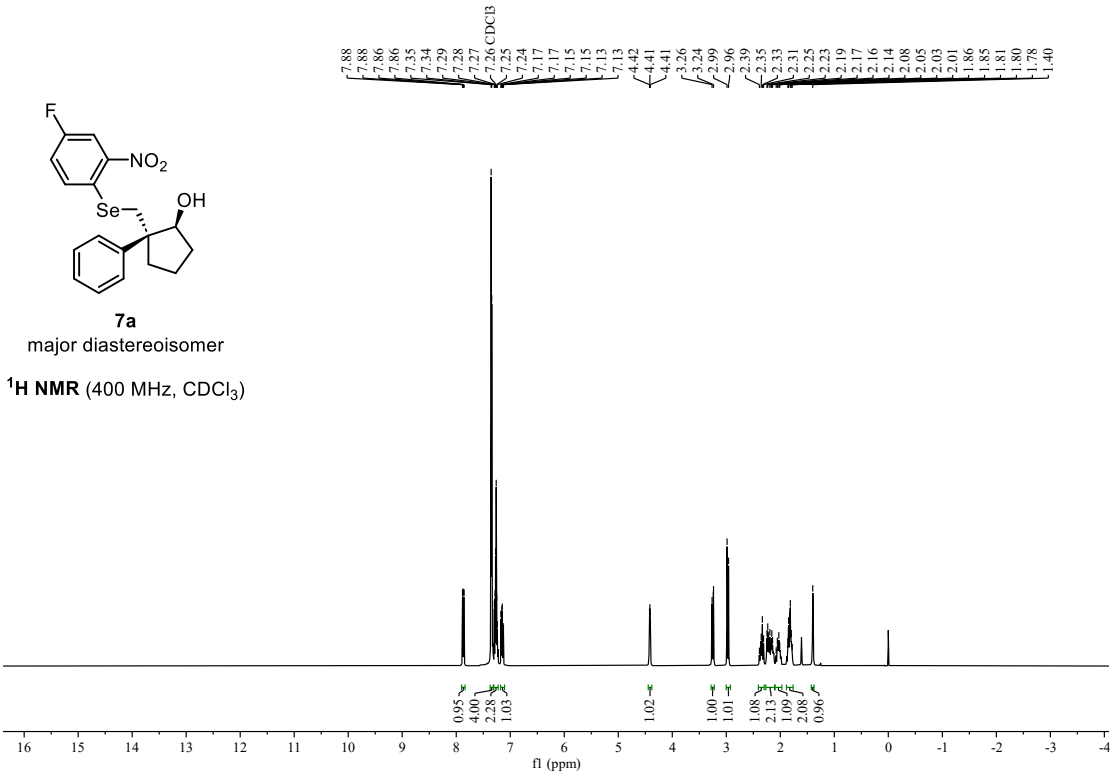
6a

^{19}F NMR (377 MHz, $CDCl_3$)



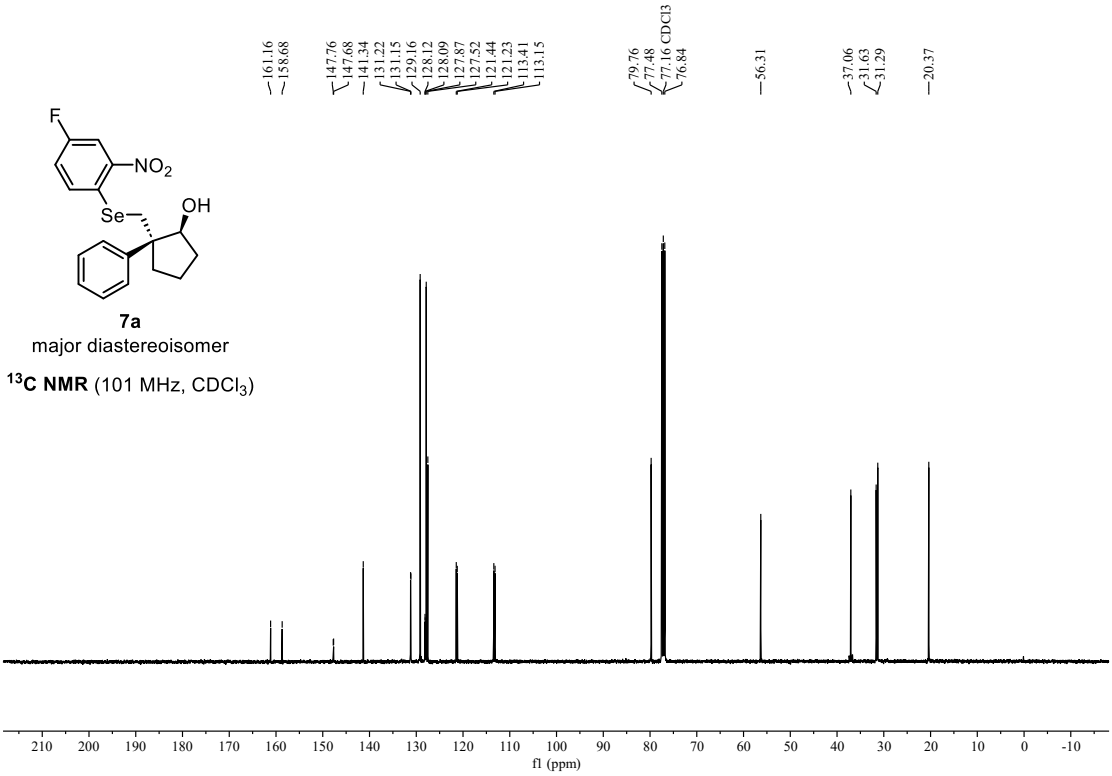
6a

^{77}Se NMR (76 MHz, $CDCl_3$)



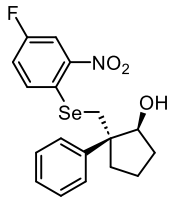
7a
major diastereoisomer

^{1}H NMR (400 MHz, $CDCl_3$)



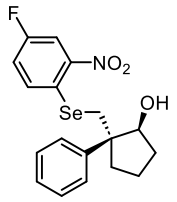
7a
major diastereoisomer

^{13}C NMR (101 MHz, $CDCl_3$)



7a
major diastereoisomer

^{19}F NMR (377 MHz, $CDCl_3$)



7a
major diastereoisomer

^{77}Se NMR (76 MHz, $CDCl_3$)

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