An electrocatalytic mono-functionalization of alkenes towards alkenyl selenium sulfonates

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Supporting Information

List of Contents

1. Materials and equipment

Unless otherwise special indicated, all the reagents were purchased from commercial supplies unless otherwise stated. And all the solvents were used as received without further purification. The instrument for electrolysis was dual display potentiostat (HY3005B) (made in China, HYELEC, **Figure S1**), the Carbon rod anode (Ø = 8 mm) and Carbon rod cathode (Ø = 8 mm) were purchased from Shanghai Fanyue Electronic Technology Co., LTD. Thin layer chromatography (TLC) employed glass 0.20-0.25 mm silica gel plates (GF254). Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C). Gradient flash chromatography was conducted eluting with PE (petroleum)/EA (ethyl acetate), they are listed as volume/volume ratios. Melting points were measured on a capillary melting point apparatus and were uncorrected. NMR spectra were recorded on a Bruker Avance III spectrometer operating at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR) and 376.8 MHz (^{19}F NMR). Chemical shifts were reported in ppm downfield. Coupling constants were quoted in Hz (*J*). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). High resolution mass spectra (HRMS) were measured using Thermo Scientific Q Exactive. Mass spectra (MS) were measured using electron ionization (EI) method by GC-MS.

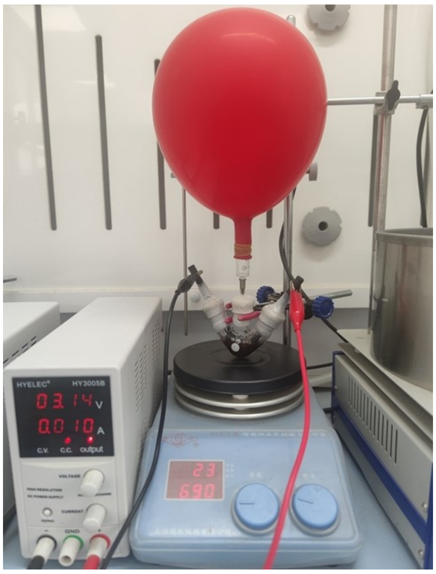
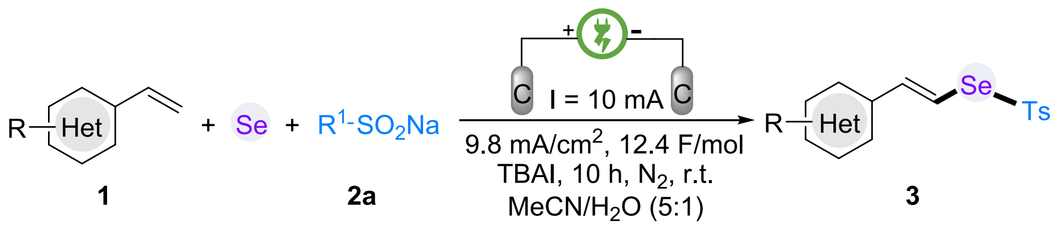


Figure S1. Assembling of setup for the reaction

2. Experimental procedure

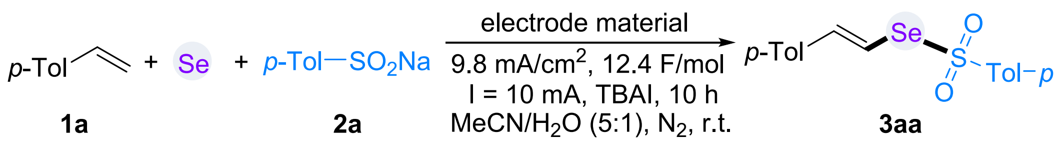
2.1 General procedure for the synthesis of 3



A 10-mL undivided three-necked bottle was equipped with a carbon rod anode (Ø = 8 mm) and carbon rod cathode (Ø = 8 mm) which was connected to a DC regulated power supply. Under N_2 atmosphere, **1** (0.3 mmol), Se (0.4 mmol), **2** (0.6 mmol) and TBAI (0.4 mmol) were dissolved in 5 mL MeCN and 1 mL H_2O, and the cell was electrolyzed at a constant current of 10 mA (~9.8 mA/cm^2), and the mixture was stirred for 10 h at environment temperature. The electrolysis was terminated when the starting materials were consumed as determined by TLC. Then the reaction mixture was diluted with 50 mL ethyl acetate, washed with a saturated solution of brine (2 × 15 mL), dried (Na_2SO_4), and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (eluent: PE/EA) to afford the desired products.

2.2 Optimization of reaction conditions

Table S1. Screening of electrode materials [a]

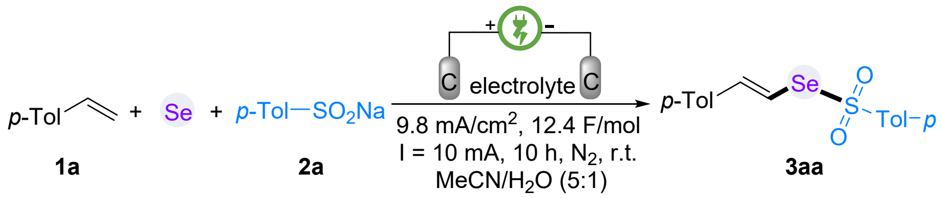


Entry	Variation from the standard conditions	Yield [b] (%)
1	None	80
2	C (+) I Mg (-)	36
3	C (+) I Zn (-)	32
4	C(+) I Ni-foam (-)	61
5	C (+) I Pt (-)	66
6	GF (+) I Mg (-)	30
7	GF (+) I GF (-)	59
8	GF (+) I Pt (-)	57
9	Ni-foam (+) I Mg (-)	trace
10	Ni-foam (+) I Pt (-)	trace
11	Ni-foam (+) I C (-)	trace
12	Pt (+) I Mg (-)	26
13	Pt (+) I C (-)	70
14	Pt (+) I Ni-foam (-)	46

15	Pt (+) ǀ Pt (-)	57

[a] Reaction conditions: Carbon rod anode (Ø = 8 mm), Carbon rod cathode (Ø = 8 mm), constant current = 10 mA, undivided cell, **1a** (0.3 mmol), **2a** (0.6 mmol), Se (0.4 mmol), TBAI (0.4 mmol), MeCN (5 mL), H_2O (1 mL), Room temperature, N_2, 10 h. [b] Isolated yield.

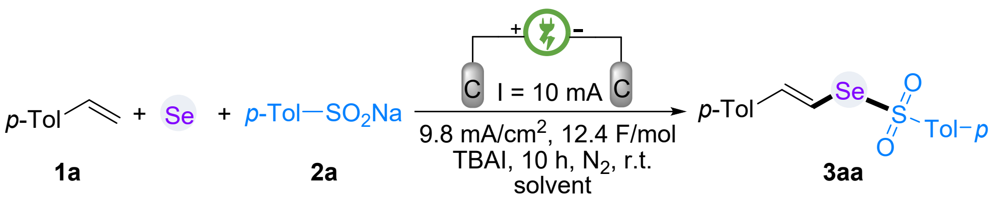
Table S2. Screening of electrolytes [a]



Entry	Variation from the standard conditions	Yield [b] (%)
1	None	80
2	NaI instead of TBAI	63
3	KI instead of TBAI	66
4	I_2 instead of TBAI	trace
5	*n*-Bu_4NBr instead of TBAI	37
6	NaBr instead of TBAI	45
7	NH_4I instead of TBAI	57
8	NH_4Br instead of TBAI	42
9	LiBr instead of TBAI	33
10	$LiClO_4$ instead of TBAI	trace
11	*n*-Bu_4NBF_4 instead of TBAI	trace

[a] Reaction conditions: Carbon rod anode (Ø = 8 mm), Carbon rod cathode (Ø = 8 mm), constant current = 10 mA, undivided cell, **1a** (0.3 mmol), **2a** (0.6 mmol), Se (0.4 mmol), TBAI (0.4 mmol), MeCN (5 mL), H_2O (1 mL), Room temperature, N_2, 10 h. [b] Isolated yield.

Table S3. Screening of solvents [a]

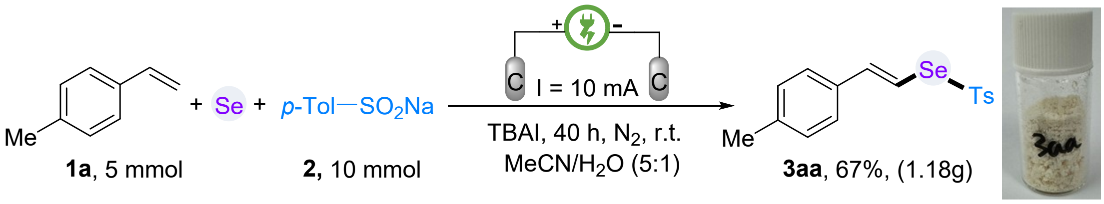


Entry	Variation from the standard conditions	Yield [b] (%)
1	None	80
2	CH_2Cl_2/H_2O (5:1, 6 mL)	37
3	DMSO/H_2O (5:1, 6 mL)	62
4	DMF/H_2O (5:1, 6 mL)	35
5	THF/H_2O (5:1, 6 mL)	43
6	EtOH/H_2O (5:1, 6 mL)	trace
7	MeCN /H_2O (3:1, 8 mL)	73
8	MeCN /H_2O (1:1, 6 mL)	71
9	MeCN (6 mL)	63

[a] Reaction conditions: Carbon rod anode (Ø = 8 mm), Carbon rod cathode (Ø = 8 mm), constant current = 10 mA, undivided cell, **1a** (0.3 mmol), **2a** (0.6 mmol), Se (0.4 mmol),

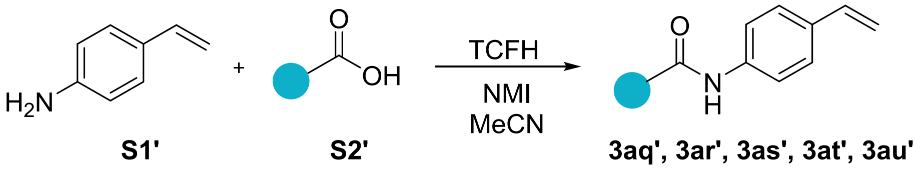
TBAI (0.4 mmol), MeCN (5 mL), H_2O (1 mL), Room temperature, N_2, 10 h. [b] Isolated yield.

2.3 Scale-up reaction procedure



A 250-mL undivided three-necked bottle was equipped with a carbon rod anode (Ø = 8 mm) and carbon rod cathode (Ø = 8 mm) which was connected to a DC regulated power supply. Under N_2 atmosphere, 4-methylstyrene **1a** (5 mmol), Se (6 mmol), sodium *p*-tolylsulfinate **2a** (10 mmol) and TBAI (6 mmol) were dissolved in 50 mL MeCN and 10 mL H_2O, the cell was electrolyzed at a constant current of 10 mA (~9.8 mA/cm^2), and the mixture was stirred for 40 h at environment temperature. The electrolysis and irradiation were terminated when the starting materials were consumed as determined by TLC. Then the reaction mixture was diluted with 150 mL ethyl acetate, washed with a saturated solution of brine (2 × 30 mL), dried (Na_2SO_4), and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (eluent: PE/EA = 5:1) to afford the desired product **3aa** (1.18 g, yield 67%).

2.4 General procedure for the synthesis of intermediate



An oven dried 100 mL round-bottomed flask was charged with acid **S2'** (5 mmol, 1.0 equiv), 4-vinylaniline **S1'** (6.5 mmol, 1.3 equiv), N-methylimidazole (17.5 mmol, 3.5 equiv), and TCFH (6.0 mmol, 1.2 equiv) in MeCN (40 mL). Then the reaction mixture was stirred at room temperature for 22 h. The reaction was terminated when the starting materials were consumed as determined by TLC. The reaction mixture was diluted in 50 mL ethyl acetate, washed with saturated solution of brine (20.0 mL), saturated solution of $NaHCO_3$ (20.0 mL), brine (20.0 mL). dried (Na_2SO_4), and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (PE/EA) to afford the desired product **3aq'**, **3ar'**,

3as', **3at'** and **3au'**.

3. Cyclic voltammetry experiments

Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line at room temperature. The working electrode was a steady glassy carbon disk electrode, the counter electrode a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. 5 mL of MeCN and 1 mL of H_2O containing 0.1 M $LiClO_4$ were poured into the electrochemical cell in all experiments. The scan rate is 0.01 V/s, ranging from 0.0 V to 2.0 V.

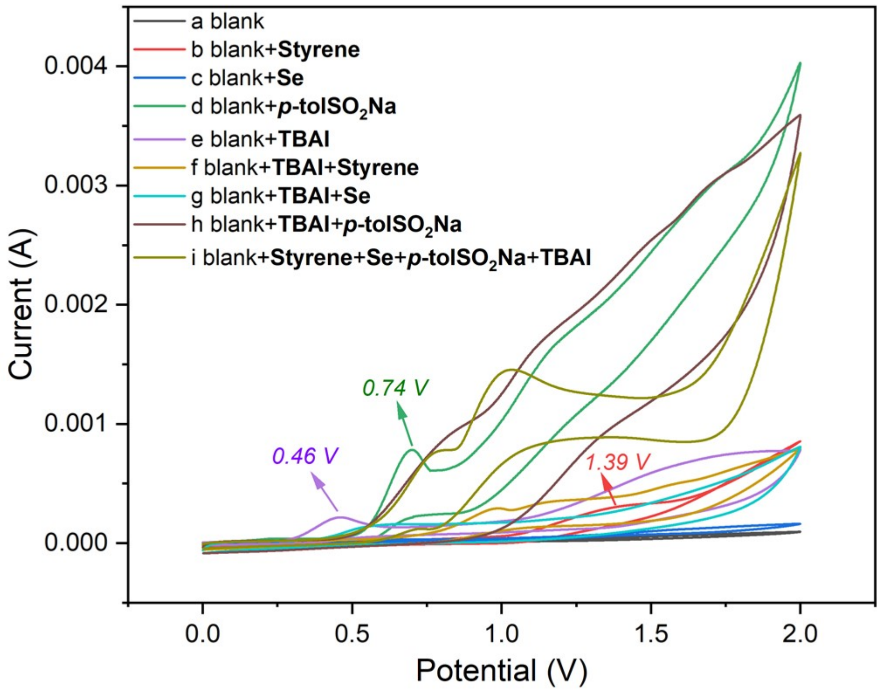
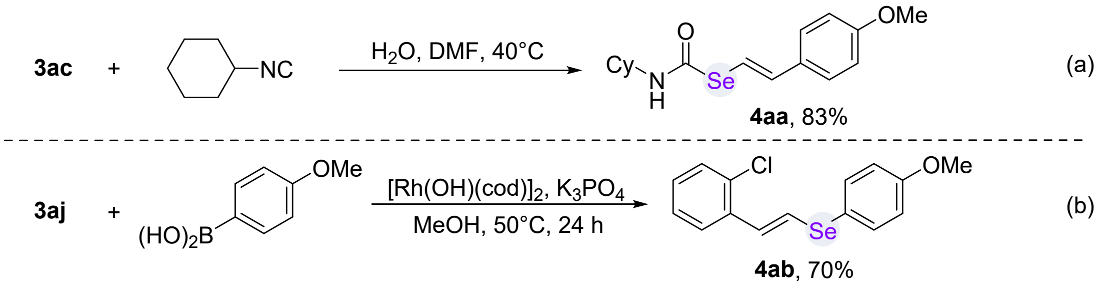


Figure S2. CV plotting convention (IUPAC)

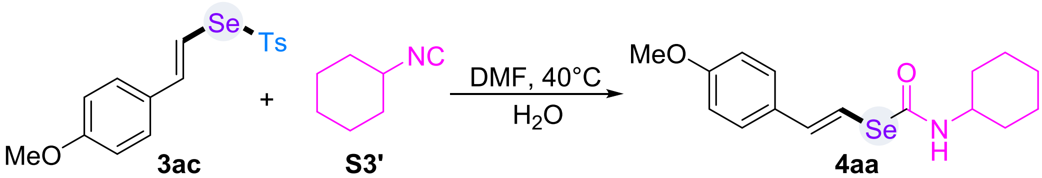
In **Figure S2**, Cyclic voltammograms of 0.1 mol L^{-1} of $LiClO_4$ in 5 mL of MeCN and 1 mL of H_2O solution containing different compounds: (a) blank experiment; (b) Styrene (0.3 mmol); (c) Selenium (0.4 mmol); (d) Sodium *p*-tolylsulfinate (0.6 mmol); (e) TBAI (0.4 mmol); (f) TBAI (0.4 mmol), Styrene (0.3 mmol); (g) TBAI (0.4 mmol), Selenium (0.4 mmol); (h) TBAI (0.4 mmol), Sodium *p*-tolylsulfinate (0.6 mmol); (i) Styrene (0.3 mmol), Selenium (0.4 mmol), Sodium *p*-tolylsulfinate (0.6 mmol), TBAI (0.4 mmol); with a GC disk working electrode, Pt counter electrode, and Ag/AgCl reference electrode at 0.01 V/s scan rate.

4. Derivatization reactions of products



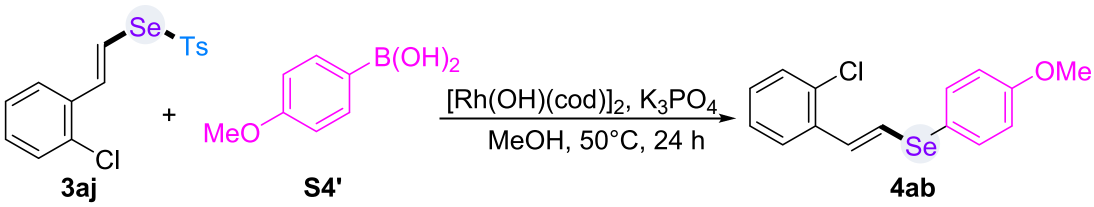
Scheme S1. Derivatization reactions of products.

4.1 Synthesis of selenocarbamates 4aa



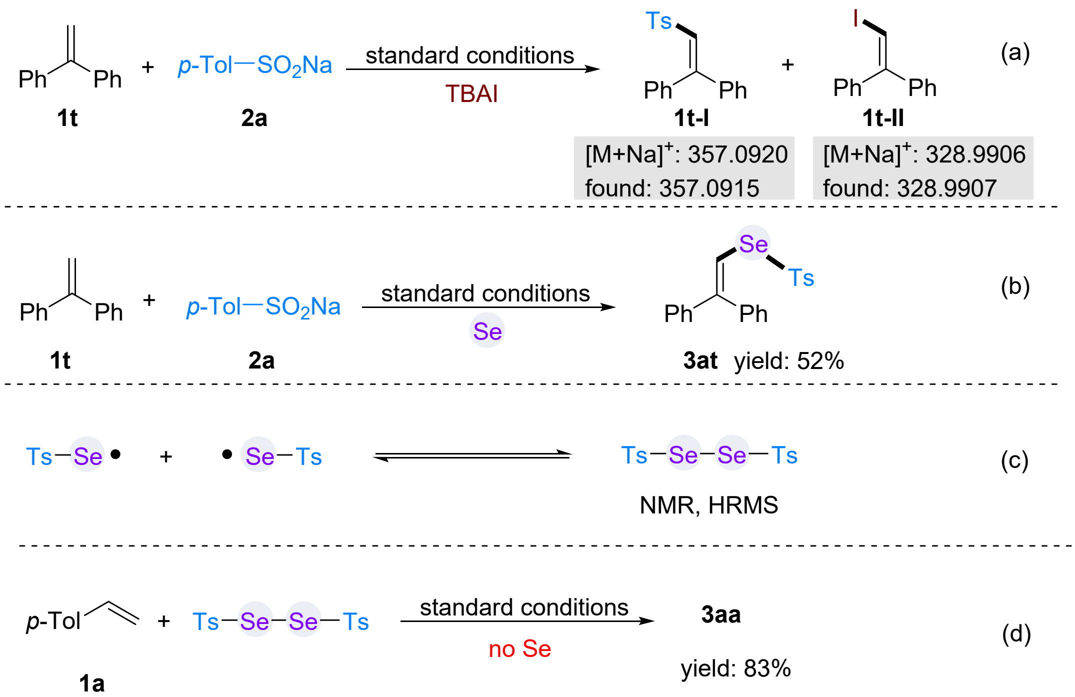
In an oven dried 10 mL schlenk tube with a magnetic stir bar, (*E*)-*Se*-(4-methoxystyryl) 4-methylbenzenesulfonoselenoate **3ac** (0.3 mmol, 1.0 equiv) was dissolved in DMF (2 mL). Isocyanocyclohexane **S3'** (0.6 mmol, 2.0 equiv) and H_2O (3.0 mmol, 10 equiv) were added subsequently. The system was stirred at 40 °C under air. After 12 h, the crude reaction mixture was cooled to room temperature and diluted with ethyl acetate (50 mL). The organic phase was washed with water (20 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (eluent: PE/EA) to obtain the desired product **4aa**.

4.2 Synthesis of 4ab



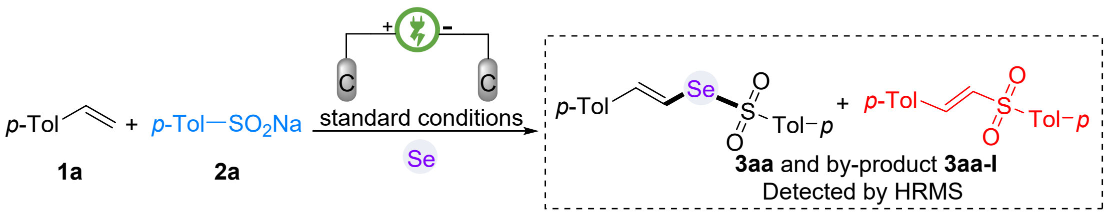
In an oven dried 10 mL schlenk tube with a magnetic stir bar, a mixture of (*E*)-*Se*-(2-chlorostyryl) 4-methylbenzenesulfonoselenoate **3aj** (0.25 mmol, 1.0 equiv), (4-methoxyphenyl)boronic acid **S4'** (0.5 mmol, 2.0 equiv), $[Rh(OH)(cod)]_2$ (2.9 mg, 6.3 μmol, 2.5 mol %), and tripotassium phosphate (0.5 mmol, 2.0 equiv) suspended in MeOH (2.5 mL) was stirred for 24 h at 50 ºC. After cooling to room temperature, the mixture was filtered, and then the filtrate was concentrated under reduced pressure. To the residue was added ethyl acetate (20 mL) and the mixture was washed with aqueous saturated solution of sodium bicarbonate (20 mL × 2) and brine (20 mL), and then dried (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (eluent: PE/EA) to obtain the desired product **4ab**.

5. Mechanism Studies



Scheme S2. Mechanism Studies.

5.1 Detection of by-product by high-resolution mass spectra



Reaction conditions: Carbon rod anode (Ø = 8 mm), Carbon rod cathode (Ø = 8 mm), constant current = 10 mA, undivided cell, **1a** (0.3 mmol), **2a** (0.6 mmol), Se (0.4 mmol), TBAI (0.4 mmol), MeCN (5 mL), H_2O (1 mL), Room temperature, N_2, 10 h. The corresponding reaction mixture was detected by HRMS. We detected the **3aa** and by-product **3aa-I** by HRMS analysis (**Figures S3**).

HRMS (ESI) calcd for $C_{16}H_{17}O_2SSe$ $[M+H]^+$: 353.0036, found: 353.0038.

HRMS (ESI) calcd for $C_{16}H_{17}O_2S$ $[M+H]^+$: 273.0871, found: 273.0874.

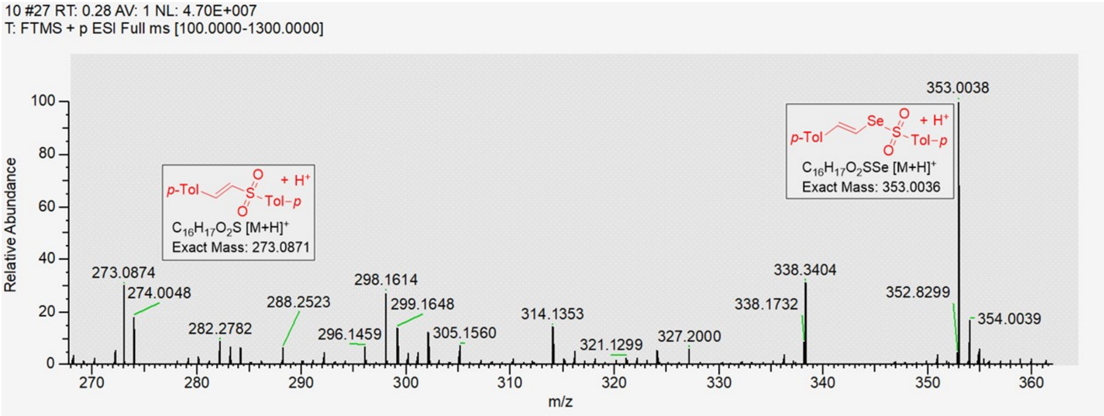
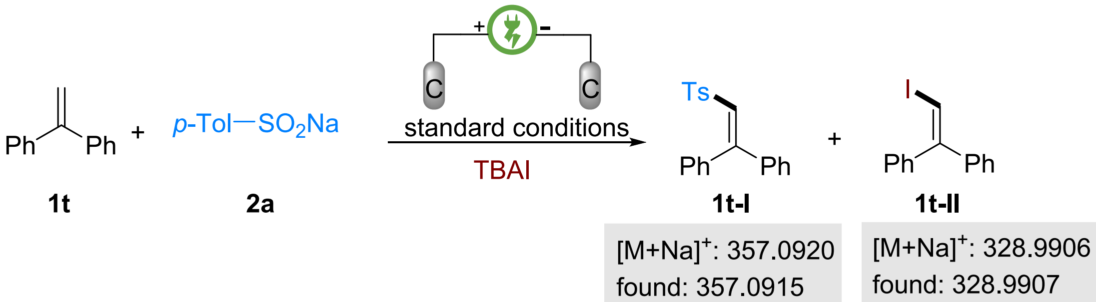


Figure S3. High-resolution mass spectra of reaction by-product.

5.2 Radical trapping experiment with 1,1-diphenylethylene



Reaction conditions: Carbon rod anode (Ø = 8 mm), Carbon rod cathode (Ø = 8 mm), constant current = 10 mA, undivided cell, **1t** (1.2 mmol), **2a** (0.6 mmol), TBAI (0.4 mmol), MeCN (5 mL), H_2O (1 mL), Room temperature, N_2, 10 h. The corresponding reaction mixture was detected by HRMS. We successfully detected the desired **1t-I** and **1t-II** by HRMS analysis (**Figures S4**).

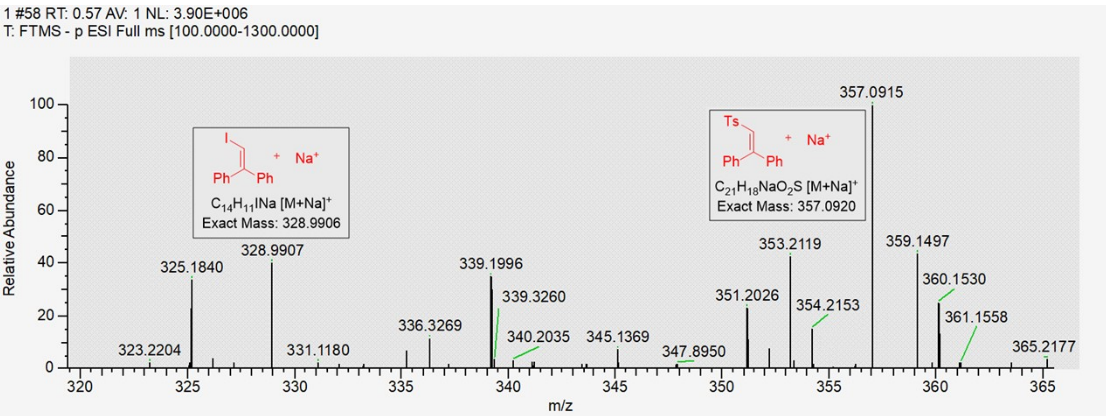
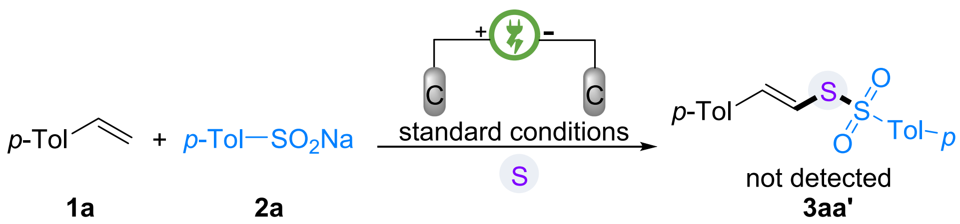


Figure S4. High-resolution mass spectra of 1,1-diphenylethylene adducts to reaction radicals.

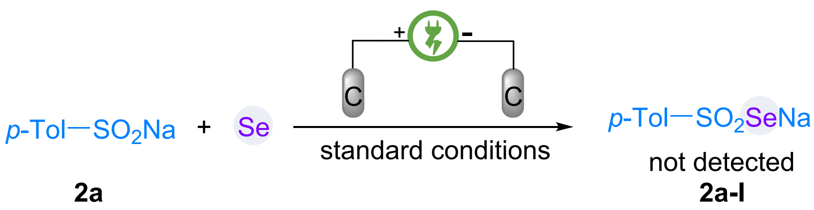
5.3 Control experiment

(1) Sulfur powder instead of Se powder



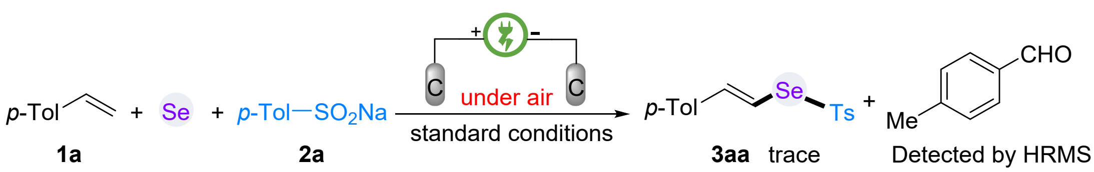
Reaction conditions: Carbon rod anode (Ø = 8 mm), Carbon rod cathode (Ø = 8 mm), constant current = 10 mA, undivided cell, **1a** (0.3 mmol), **2a** (0.6 mmol), S (0.4 mmol), TBAI (0.4 mmol), MeCN (5 mL), H_2O (1 mL), Room temperature, N_2, 10 h. No desired product **3aa'** was detected.

(2) The reaction of 2a with Se powder



Reaction conditions: Carbon rod anode (Ø = 8 mm), Carbon rod cathode (Ø = 8 mm), constant current = 10 mA, undivided cell, **2a** (0.6 mmol), Se (0.4 mmol), TBAI (0.4 mmol), MeCN (5 mL), H_2O (1 mL), Room temperature, N_2, 10 h. No desired product **2a-I** was detected.

(3) Performing the reaction under air



Reaction conditions: Carbon rod anode (Ø = 8 mm), Carbon rod cathode (Ø = 8 mm), constant current = 10 mA, undivided cell, **1a** (0.3 mmol), **2a** (0.6 mmol), Se (0.4 mmol), TBAI (0.4 mmol), MeCN (5 mL), H_2O (1 mL), Room temperature, Under air, 10 h. No desired product **3aa** was detected by HRMS analysis (**Figures S5**). 4-Methylbenzaldehyde was observed by high resolution mass spectra.

HRMS (ESI) calcd for C_8H_9O $[M+H]^+$: 121.0289, found: 121.0294.

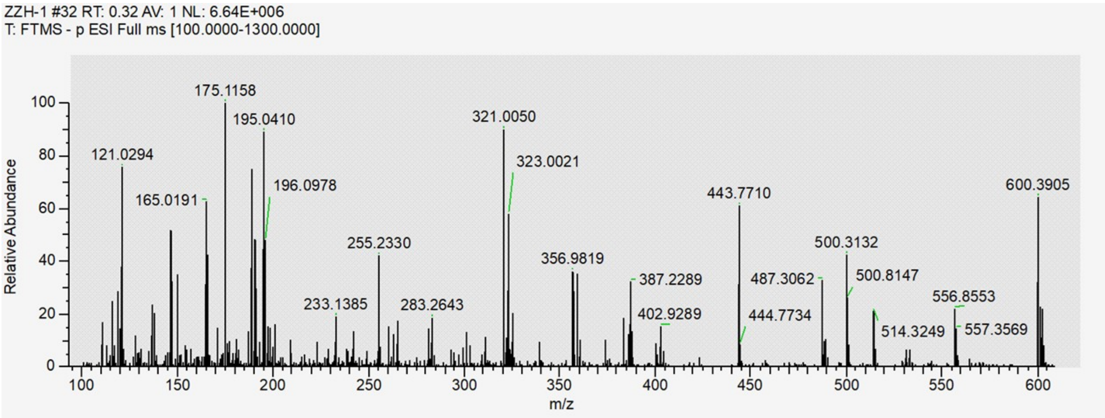
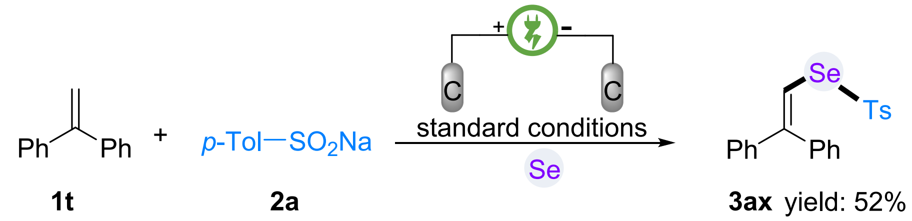


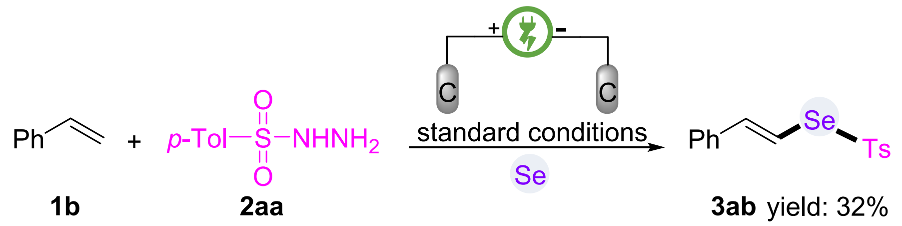
Figure S5. High-resolution mass spectra of reaction under air.

(4) Diphenylethylene as a free radical scavenger



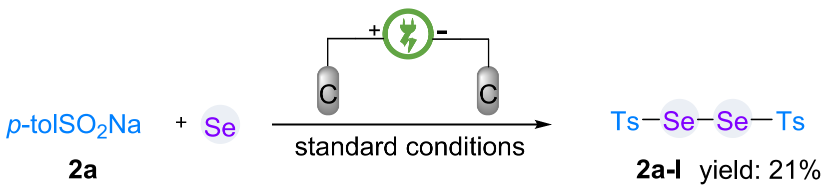
Reaction conditions: Carbon rod anode (Ø = 8 mm), Carbon rod cathode (Ø = 8 mm), constant current = 10 mA, undivided cell, **1t** (0.3 mmol), **2a** (0.6 mmol), Se (0.4 mmol), TBAI (0.4 mmol), MeCN (5 mL), H_2O (1 mL), Room temperature, N_2, 10 h.

(5) Performing the reaction with TsNHNH$_2$



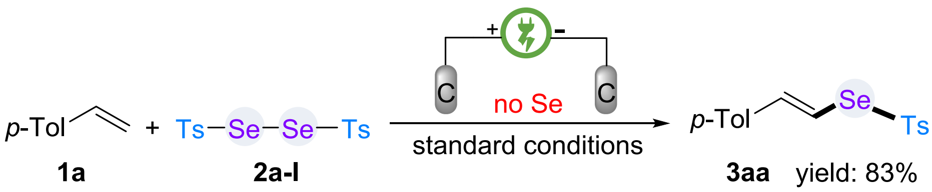
Reaction conditions: Carbon rod anode (Ø = 8 mm), Carbon rod cathode (Ø = 8 mm), constant current = 10 mA, undivided cell, **1b** (0.3 mmol), **2aa** (0.6 mmol), Se (0.4 mmol), TBAI (0.4 mmol), MeCN (5 mL), H_2O (1 mL), Room temperature, N_2, 10 h. The final product **3ab** was isolated in only 32% yield.

5.4 Synthesis of diselenide 2a-I



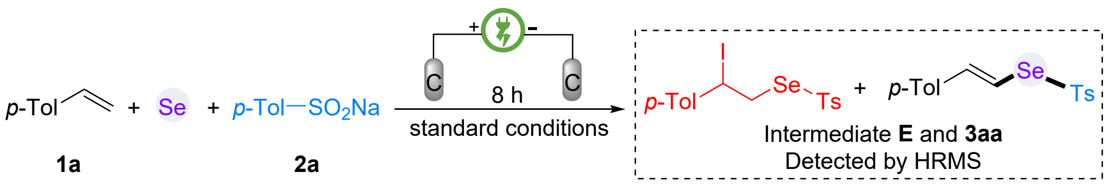
Reaction conditions: Carbon rod anode (Ø = 8 mm), Carbon rod cathode (Ø = 8 mm), constant current = 10 mA, undivided cell, **2a** (0.6 mmol), Se (0.4 mmol), TBAI (0.4 mmol), MeCN (5 mL), H_2O (1 mL), Room temperature, N_2, 10 h. Overall Yield: 21% (39.5 mg). Nature: pale yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 12:1). **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 7.82 (d, J = 8.0 Hz, 4H), 7.40 (d, J = 8.0 Hz, 4H), 2.33 (s, 6H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 144.1, 137.2, 130.3, 128.4, 21.7. **HRMS** (ESI) m/z: [M+H]$^+$ Calcd for: $C_{14}H_{15}O_4S_2Se_2^+$ 470.8664; Found: 470.8661.

5.5 Diselenide 2a-I used as the Se-source



Reaction conditions: Carbon rod anode (Ø = 8 mm), Carbon rod cathode (Ø = 8 mm), constant current = 10 mA, undivided cell, **1a** (0.3 mmol), **2a-I** (0.4 mmol), TBAI (0.4 mmol), MeCN (5 mL), H_2O (1 mL), Room temperature, N_2, 10 h. The desired product **3aa** (83%) was produced. The diselenide was the real selenium source in the reaction.

5.6 High-resolution mass spectra of reaction intermediates



Reaction conditions: Carbon rod anode (Ø = 8 mm), Carbon rod cathode (Ø = 8 mm), constant current = 10 mA, undivided cell, **1a** (0.3 mmol), **2a** (0.6 mmol), Se (0.4 mmol), TBAI (0.4 mmol), MeCN (5 mL), H_2O (1 mL), Room temperature, N_2, 8 h. The corresponding reaction mixture was detected by HRMS. We successfully detected the desired intermediate **E** and **3aa** by HRMS analysis (**Figures S6**).

HRMS (ESI) calcd for $C_{16}H_{17}O_2SSe$ [M+H]$^+$: 353.0036, found: 353.0038.

HRMS (ESI) calcd for $C_{16}H_{18}IO_2SSe$ [M+H]$^+$: 480.9159, found: 480.9157.

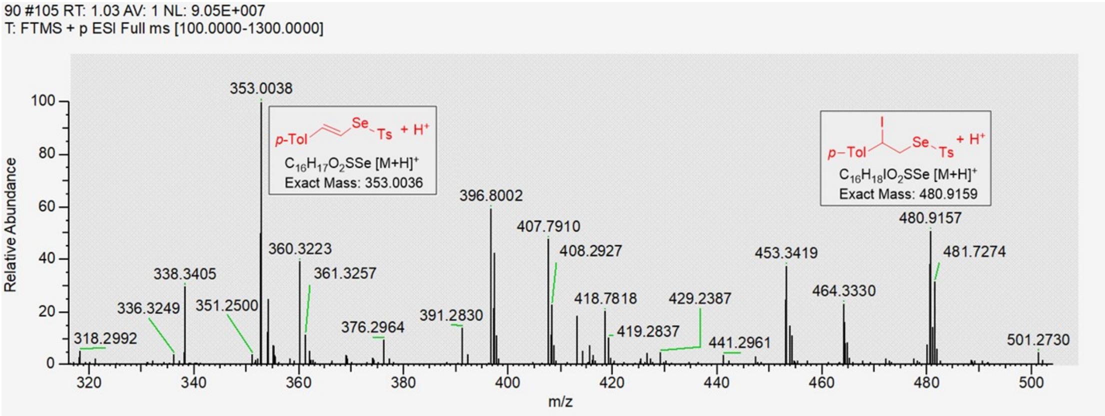


Figure S6. High-resolution mass spectra of reaction intermediates.

6. Density functional theory (DFT) calculations

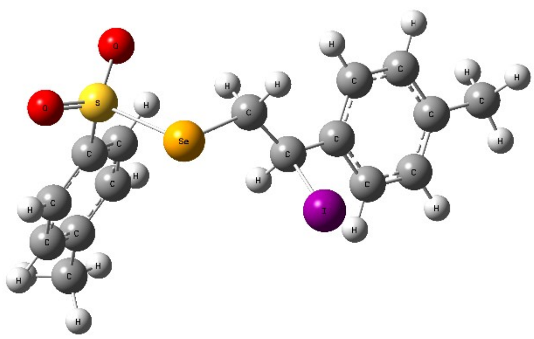
6.1.1 DFT modelling calculations for elimination reaction

All structures were optimized at the level of M06-2X/def2-SVP [1] with solvent acetonitrile in the PCM solvent model. Vibrational analyses were performed on all optimized geometries, to ensure that the optimized structures corresponded to local minima [2]. Unless otherwise specified, the solution-phase Gibbs free energy was used in the discussion. The Gaussian 16 suite of programs [3] was used throughout.

Table S4. Calculation results

A	B	C	D	E
	G	Corrected value	Calculated value (A.U.)	kcal/mol
Product **3aa**	-788.732474	0.220539	-788.511935	
Intermediate **E**	-800.728631	0.228618	-800.500013	
HI	-11.990771	-0.015223	-12.005994	
ΔG			-0.017916	-11.24229

6.1.2 Cartesian coordinates of stationary points



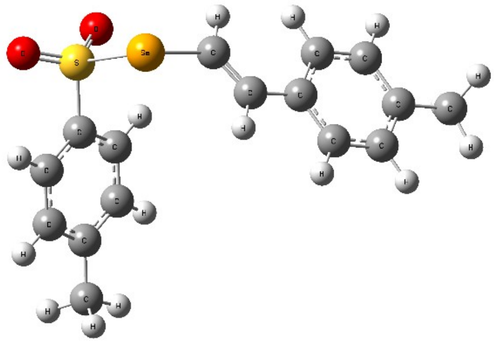
Intermediate **E**

Zero-point correction= 0.291027 (Hartree/Particle)
Thermal correction to Energy= 0.314367
Thermal correction to Enthalpy= 0.315311
Thermal correction to Gibbs Free Energy= 0.228618

Sum of electronic and zero-point Energies= -800.666222
Sum of electronic and thermal Energies= -800.642882
Sum of electronic and thermal Enthalpies= -800.641938
Sum of electronic and thermal Free Energies= -800.728631

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.083032	2.520517	-0.250542
2	6	0	4.177257	2.496231	-1.318055
3	6	0	3.087364	1.622326	-1.319309
4	6	0	2.865646	0.745067	-0.248421
5	6	0	3.778075	0.761002	0.821346
6	6	0	4.862175	1.633698	0.817954
7	1	0	4.322808	3.167703	-2.161309
8	1	0	2.401077	1.624022	-2.163319
9	1	0	3.652358	0.074461	1.654221
10	1	0	5.554603	1.624971	1.657292
11	6	0	6.259138	3.468925	-0.235520
12	1	0	6.345037	4.015345	-1.180418
13	1	0	6.161512	4.208494	0.569971
14	1	0	7.201946	2.933249	-0.069144
15	6	0	1.663317	-0.145847	-0.267792
16	6	0	0.823675	-0.102568	0.998079
17	1	0	0.456376	0.923392	1.152530
18	16	0	-2.329652	0.743532	1.544802
19	8	0	-2.958030	0.482925	2.942586
20	8	0	-1.454468	2.011326	1.279393
21	6	0	-3.716251	0.741871	0.304012
22	6	0	-3.516641	1.364613	-0.919626
23	6	0	-4.907192	0.115129	0.650652
24	6	0	-4.570378	1.358421	-1.836940
25	1	0	-2.574819	1.855145	-1.142955
26	6	0	-5.943528	0.119429	-0.283978
27	1	0	-5.022000	-0.345587	1.626547
28	6	0	-5.792694	0.737551	-1.536899
29	1	0	-4.438124	1.847614	-2.798778
30	1	0	-6.886048	-0.361030	-0.031467
31	6	0	-6.930599	0.736449	-2.530937
32	1	0	-7.278807	-0.283482	-2.734336
33	1	0	-7.789683	1.301290	-2.147164
34	1	0	-6.632722	1.186922	-3.482858
35	34	0	-0.825776	-1.233067	0.868909
36	1	0	1.374523	-0.423159	1.882507

37	1	0	1.046231	0.053880	-1.143388
38	53	0	2.253248	-2.308799	-0.652597



Product **3aa**

Zero-point correction= 0.277695 (Hartree/Particle)
Thermal correction to Energy= 0.299087
Thermal correction to Enthalpy= 0.300032
Thermal correction to Gibbs Free Energy= 0.220539
Sum of electronic and zero-point Energies= -788.675318
Sum of electronic and thermal Energies= -788.653926
Sum of electronic and thermal Enthalpies= -788.652981
Sum of electronic and thermal Free Energies= -788.732474

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.414740	0.979505	0.274503
2	6	0	4.718161	1.454255	-0.844754
3	6	0	3.477739	0.922476	-1.197182
4	6	0	2.885711	-0.109340	-0.444413
5	6	0	3.586935	-0.583245	0.685932
6	6	0	4.821376	-0.048637	1.032097
7	1	0	5.150473	2.249147	-1.448267
8	1	0	2.957869	1.308014	-2.071604
9	1	0	3.159341	-1.369195	1.301200
10	1	0	5.338890	-0.430582	1.909735
11	6	0	6.758542	1.545642	0.666317
12	1	0	7.070299	2.345835	-0.012598
13	1	0	6.735276	1.956989	1.683540
14	1	0	7.535449	0.770417	0.650999
15	6	0	1.583825	-0.626858	-0.862235
16	1	0	1.125722	-0.108390	-1.704191
17	6	0	0.917477	-1.679030	-0.329164
18	1	0	1.306063	-2.249280	0.508025
19	16	0	-2.180499	-1.325463	0.929402

20	8	0	-3.521509	-2.118136	0.955105
21	8	0	-1.226148	-1.270109	2.162076
22	6	0	-2.583093	0.436580	0.480541
23	6	0	-1.724416	1.442381	0.902184
24	6	0	-3.730543	0.686071	-0.264200
25	6	0	-2.037480	2.760582	0.556374
26	1	0	-0.849854	1.202756	1.498084
27	6	0	-4.022349	2.008923	-0.595590
28	1	0	-4.383074	-0.129863	-0.558410
29	6	0	-3.183525	3.063392	-0.193291
30	1	0	-1.381459	3.563788	0.883347
31	1	0	-4.920227	2.226037	-1.169979
32	6	0	-3.524916	4.490546	-0.554069
33	1	0	-3.690438	4.599898	-1.632748
34	1	0	-4.445254	4.814602	-0.051326
35	1	0	-2.726040	5.180129	-0.263540
36	34	0	-0.743027	-2.296364	-1.035543

HI

Zero-point correction= 0.004936 (Hartree/Particle)
Thermal correction to Energy= 0.007297
Thermal correction to Enthalpy= 0.008241
Thermal correction to Gibbs Free Energy= -0.015223
Sum of electronic and zero-point Energies= -11.970612
Sum of electronic and thermal Energies= -11.968251
Sum of electronic and thermal Enthalpies= -11.967307
Sum of electronic and thermal Free Energies= -11.990771

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	53	0	0.000000	0.000000	0.030311
2	1	0	0.000000	0.000000	-1.606460

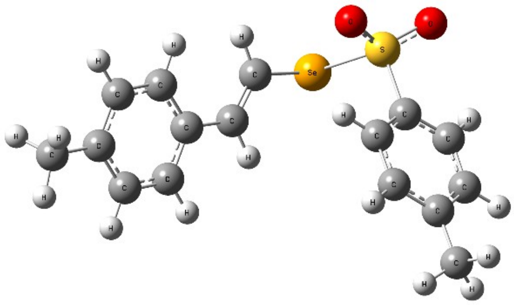
The calculations revealed that intermediate **E** undergoes elimination reaction smoothly to deliver the desired product **3aa**, in a highly exergonic transformation (ΔG = 11.24 kcal/mol from intermediate **E**)

6.2.1 DFT modelling calculations for the configuration of product 3aa

Density functional theoretical modelling calculations were performed to shine light on the configuration of product **3aa**. The calculations revealed that product (*E*)-**3aa** is more stable than (*Z*)-**3aa** (~22 kJ mol^{-1}). G_E = -788.472044 A.U., G_Z = -788.463512

A.U., ΔG = 0.008532 A.U.

6.2.2 Cartesian coordinates of stationary points

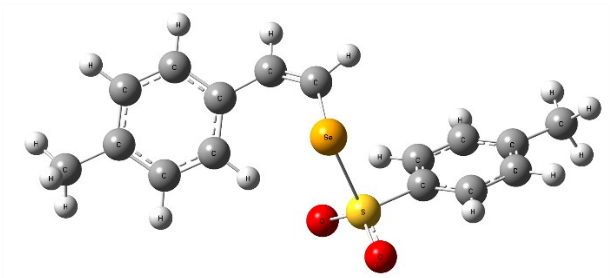


(*E*)-**3aa**

Thermal correction to Gibbs Free Energy= 0.220658
Sum of electronic and zero-point Energies= -788.635090
Sum of electronic and thermal Energies= -788.613690
Sum of electronic and thermal Enthalpies= -788.612746
Sum of electronic and thermal Free Energies= -788.692702

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.383551	0.943503	0.279883
2	6	0	4.660340	1.466222	-0.798579
3	6	0	3.423413	0.935366	-1.156696
4	6	0	2.860069	-0.141838	-0.449108
5	6	0	3.590999	-0.667536	0.637136
6	6	0	4.821613	-0.132921	0.990013
7	1	0	5.070690	2.298753	-1.364914
8	1	0	2.880494	1.358721	-1.998579
9	1	0	3.189645	-1.497834	1.209935
10	1	0	5.363374	-0.555194	1.833349
11	6	0	6.727761	1.506054	0.673325
12	1	0	6.992757	2.375680	0.064234
13	1	0	6.737924	1.815569	1.725677
14	1	0	7.522109	0.758450	0.552391
15	6	0	1.554774	-0.649570	-0.865996
16	1	0	1.105097	-0.131034	-1.711653
17	6	0	0.872971	-1.685080	-0.325779
18	1	0	1.240739	-2.250133	0.523278
19	34	0	-0.795247	-2.288294	-1.053138
20	16	0	-2.191175	-1.314905	0.939308
21	8	0	-3.545791	-2.066594	0.985179
22	8	0	-1.213753	-1.277647	2.144993
23	6	0	-2.553096	0.454542	0.491731

24	6	0	-1.638543	1.431212	0.860543
25	6	0	-3.720245	0.736334	-0.205158
26	6	0	-1.915406	2.752652	0.508211
27	1	0	-0.745992	1.162126	1.414648
28	6	0	-3.975687	2.063939	-0.544513
29	1	0	-4.410474	-0.060719	-0.461152
30	6	0	-3.081689	3.088231	-0.194693
31	1	0	-1.215313	3.535462	0.789272
32	1	0	-4.886175	2.308830	-1.085842
33	6	0	-3.386693	4.525690	-0.544133
34	1	0	-3.902155	4.603558	-1.507231
35	1	0	-4.039377	4.982679	0.211437
36	1	0	-2.474597	5.128681	-0.595585



(*Z*)-**3aa**

Thermal correction to Gibbs Free Energy= 0.222726
Sum of electronic and zero-point Energies= -788.630418
Sum of electronic and thermal Energies= -788.609317
Sum of electronic and thermal Enthalpies= -788.608372
Sum of electronic and thermal Free Energies= -788.686238

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.184901	0.354474	-0.823103
2	6	0	-5.153794	1.405721	0.104452
3	6	0	-3.965598	1.771688	0.726659
4	6	0	-2.765246	1.078459	0.470383
5	6	0	-2.788756	0.043571	-0.485977
6	6	0	-3.979861	-0.303770	-1.113661
7	1	0	-6.068571	1.947816	0.332174
8	1	0	-3.964222	2.593164	1.439600
9	1	0	-1.868061	-0.445404	-0.780758
10	1	0	-3.969880	-1.093914	-1.860673
11	6	0	-6.473710	-0.058253	-1.491570
12	1	0	-7.215381	0.746874	-1.468742
13	1	0	-6.309795	-0.342562	-2.536774

14	1	0	-6.917230	-0.927363	-0.987022
15	6	0	-1.567448	1.509139	1.185826
16	1	0	-1.584546	2.563958	1.471889
17	6	0	-0.463631	0.843878	1.609330
18	34	0	-0.154904	-1.051037	1.598304
19	16	0	1.077606	-1.330864	-0.690086
20	8	0	1.518897	-2.816466	-0.749101
21	8	0	0.192636	-0.691728	-1.799085
22	6	0	2.613930	-0.288092	-0.574227
23	6	0	2.557237	1.027352	-1.012404
24	6	0	3.761395	-0.859927	-0.041437
25	6	0	3.713703	1.801442	-0.907392
26	1	0	1.639470	1.424251	-1.432497
27	6	0	4.904114	-0.067409	0.051286
28	1	0	3.757652	-1.896239	0.279857
29	6	0	4.898394	1.269312	-0.378288
30	1	0	3.695042	2.833859	-1.247349
31	1	0	5.815974	-0.494813	0.460879
32	6	0	6.152858	2.106512	-0.296529
33	1	0	5.921283	3.176056	-0.275320
34	1	0	6.737631	1.866013	0.597657
35	1	0	6.800079	1.928162	-1.165407
36	1	0	0.311208	1.410203	2.116925

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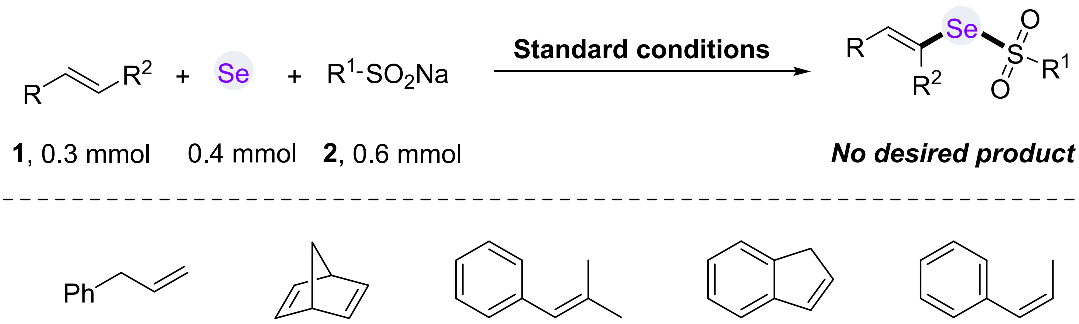
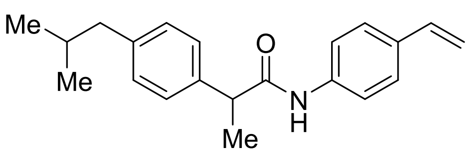
7. Unsuccessful substrates

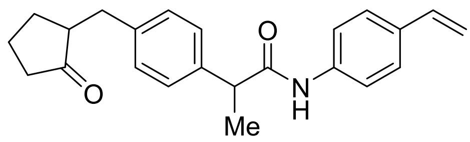


8. Characterization data of products



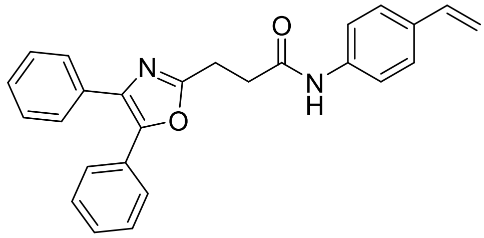
2-(4-isobutylphenyl)-*N*-(4-vinylphenyl)propenamide (3aq')

Overall Yield: 88% (1351.7 mg). Nature: white solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 6:1). **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 10.15 (s, 1H), 7.66 (d, J = 8.8 Hz, 2H), 7.39 (d, J = 8.8 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.64 (dd, J = 18.0 Hz, 11.2 Hz, 1H), 5.71 (d, J = 17.6 Hz, 1H), 5.14 (d, J = 11.6 Hz, 1H), 3.84 (q, J = 7.2 Hz, 1H), 2.37 (d, J = 7.2 Hz, 2H), 1.82-1.72 (m, 1H), 1.43 (d, J = 7.2 Hz, 3H), 0.82 (d, J = 6.8 Hz, 6H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 172.5, 139.6, 139.2, 139.1, 136.2, 132.2, 129.0, 127.1, 126.6, 119.2, 112.6, 45.7, 44.3, 29.7, 22.2, 18.8.



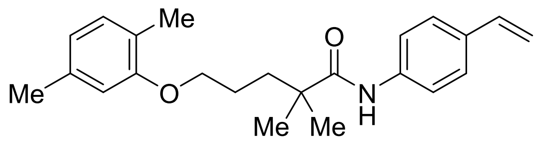
2-(4-((2-oxocyclopentyl)methyl)phenyl)-*N*-(4-vinylphenyl)propanamide (3ar')

Overall Yield: 85% (1475.6 mg). Nature: pale yellow solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 4:1). **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 10.15 (s, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.8 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 6.64 (dd, J = 17.6 Hz, 10.8 Hz, 1H), 5.70 (dd, J = 17.6 Hz, 0.8 Hz, 1H), 5.14 (d, J = 11.6 Hz, 1H), 3.83 (q, J = 6.8 Hz, 1H), 2.95 (dd, J = 13.6 Hz, 4.0 Hz, 1H), 2.43-2.37 (m, 1H), 2.35-2.27 (m, 1H), 2.23-2.16 (m, 1H), 2.06-1.99 (m, 1H), 1.91-1.76 (m, 2H), 1.66-1.57 (m, 1H), 1.47-1.37 (m, 4H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 219.3, 172.4, 139.5, 139.1, 138.6, 136.2, 132.2, 128.8, 127.3, 126.6, 119.2, 112.6, 50.1, 45.8, 37.6, 34.7, 28.8, 20.1, 18.7.



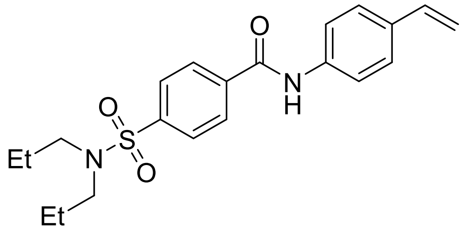
3-(4,5-diphenyloxazol-2-yl)-*N*-(4-vinylphenyl)propenamide (3as')

Overall Yield: 87% (1714.6 mg). Nature: white solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 3:1). **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 10.24 (s, 1H), 7.66 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 7.2 Hz, 2H), 7.50 (d, J = 6.8 Hz, 2H), 7.41-7.29 (m, 8H), 6.64 (dd, J = 17.6 Hz, 10.8 Hz, 1H), 5.70 (d, J = 17.6 Hz, 1H), 5.13 (d, J = 11.2 Hz, 1H), 3.18 (t, J = 7.2 Hz, 2H), 2.94 (t, J = 7.2 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 169.7, 162.7, 144.7, 139.1, 136.2, 134.5, 132.2, 132.2, 128.9, 128.8, 128.7, 128.6, 128.2, 127.5, 126.7, 126.3, 119.2, 112.7, 32.8, 23.2.



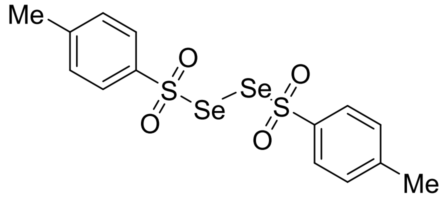
5-(2,5-dimethylphenoxy)-2,2-dimethyl-*N*-(4-vinylphenyl)pentanamide (3at')

Overall Yield: 88% (1545.3 mg). Nature: white solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 4:1). **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 9.26 (s, 1H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.70-6.59 (m, 3H), 5.72 (dd, *J* = 17.6 Hz, 0.8 Hz, 1H), 5.16 (d, *J* = 11.2 Hz, 1H), 3.89 (t, *J* = 6.4 Hz, 2H), 2.21 (s, 3H), 2.07 (s, 3H), 1.77-1.74 (m, 2H), 1.69-1.62 (m, 2H), 1.23 (s, 6H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 175.7, 156.5, 139.1, 136.3, 136.1, 132.2, 130.1, 126.3, 122.5, 120.5, 120.3, 112.7, 112.0, 67.6, 42.4, 36.7, 25.1, 24.7, 21.0, 15.6.



4-(*N*,*N*-dipropylsulfamoyl)-*N*-(4-vinylphenyl)benzamide (3au')

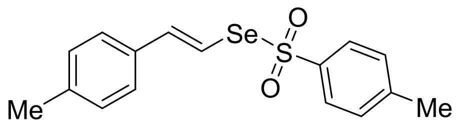
Overall Yield: 88% (1699.1 mg). Nature: white solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 4:1). **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 10.63 (s, 1H), 8.11 (d, *J* = 8.8 Hz, 2H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 6.69-6.62 (m, 1H), 5.72 (d, *J* = 17.6 Hz, 1H), 5.14 (d, *J* = 11.6 Hz, 1H), 3.03 (t, *J* = 7.2 Hz, 4H), 1.50-1.41 (m, 4H), 0.79 (t, *J* = 7.2 Hz, 6H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 166.3, 143.2, 138.4, 136.5, 134.3, 132.8, 130.3, 127.1, 126.3, 119.2, 112.6, 49.6, 21.6, 11.0.



4-methylbenzenesulfonic diselenoperoxyanhydride (2a-I)

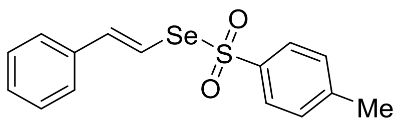
Overall Yield: 21% (39.5 mg). Nature: pale yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 12:1). **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 7.82 (d, *J* = 8.0 Hz, 4H), 7.40 (d, *J* = 8.0 Hz, 4H), 2.33

(s, 6H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 144.1, 137.2, 130.3, 128.4, 21.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{14}H_{15}O_4S_2Se_2^+$ 470.8664; Found: 470.8661.



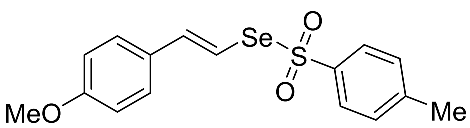
(*E*)-*Se*-(4-methylstyryl) 4-methylbenzenesulfonoselenoate (3aa)

Overall Yield: 80% (84.5 mg). Nature: white solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 7:1). **Mp**: 135 – 137 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 7.79 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 15.6 Hz, 1H), 7.50 (d, *J* = 15.6 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H), 2.32 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 144.1, 141.5, 141.3, 138.0, 130.1, 129.8, 129.7, 129.0, 127.3, 127.2, 21.2, 21.1; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{16}H_{17}O_2SSe^+$ 353.0036; Found: 353.0038.



(*E*)-*Se*-styryl 4-methylbenzenesulfonoselenoate (3ab)

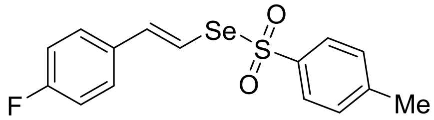
Overall Yield: 67% (67.9 mg). Nature: white solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 6:1). **Mp**: 112 – 114 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 7.83 (d, *J* = 8.4 Hz, 2H), 7.73 (dd, *J* = 6.8 Hz, 2.0 Hz, 2H), 7.66 (d, *J* = 15.2 Hz, 1H), 7.59 (d, *J* = 15.2 Hz, 1H), 7.43-7.37 (m, 5H), 2.35 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 144.1, 141.5, 137.9, 132.4, 131.1, 130.0, 129.0, 128.9, 128.4, 127.2, 21.0. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{15}H_{15}O_2SSe^+$ 338.9880; Found: 338.9886.



(*E*)-*Se*-(4-methoxystyryl) 4-methylbenzenesulfonoselenoate (3ac)

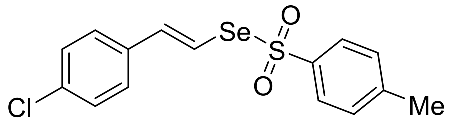
Overall Yield: 78% (86.1 mg). Nature: pale yellow solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 6:1). **Mp**: 97 – 99 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 7.78 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* =

15.6 Hz, 1H), 7.49 (d, J = 15.6 Hz, 1H), 7.39 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 3.71 (s, 3H), 2.38 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 159.1, 143.8, 140.6, 137.8, 131.2, 129.4, 128.1, 127.9, 124.7, 113.9, 55.0, 21.0; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{16}H_{17}O_3SSe^+$ 368.9985; Found: 368.9983.



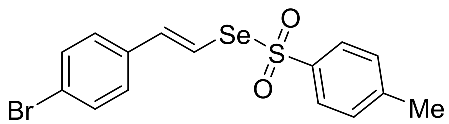
(*E*)-*Se*-(4-fluorostyryl) 4-methylbenzenesulfonoselenoate (3ad)

Overall Yield: 73% (78.0 mg). Nature: yellow solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 7:1). **Mp**: 149 – 151 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 7.79-7.75 (m, 4H), 7.60 (d, J = 15.6 Hz, 1H), 7.47 (d, J = 15.6 Hz, 1H), 7.41 (d, J = 8.0 Hz, 2H), 7.25-7.19 (m, 2H), 2.35 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 163.9 (d, J_{C-F} = 248.3 Hz), 144.6, 140.7, 137.9, 131.7 (d, J_{C-F} = 8.7 Hz), 130.4, 129.2 (d, J_{C-F} = 3.2 Hz), 128.3 (d, J_{C-F} = 2.1 Hz), 127.5, 116.3 (d, J_{C-F} = 21.9 Hz), 21.0; **^{19}F{^{1}H} NMR** (376.8 MHz, DMSO-d_6) δ = -108.6 ppm; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{15}H_{14}FO_2SSe^+$ 356.9786; Found: 356.97864.



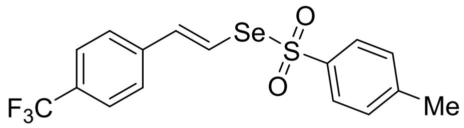
(*E*)-*Se*-(4-chlorostyryl) 4-methylbenzenesulfonoselenoate (3ae)

Overall Yield: 77% (85.9 mg). Nature: pale yellow solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 6:1). **Mp**: 150 – 152 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 7.80 (d, J = 8.4 Hz, 2H), 7.76 (dd, J = 6.8 Hz, 1.6 Hz, 2H), 7.63 (s, 2H), 7.46 (dd, J = 6.8 Hz, 2.0 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 2.37 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 144.3, 140.1, 137.7, 135.7, 131.4, 130.7, 130.1, 129.2, 129.1, 127.3, 21.1; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{15}H_{14}ClO_2SSe^+$ 372.9490; Found: 372.9490.



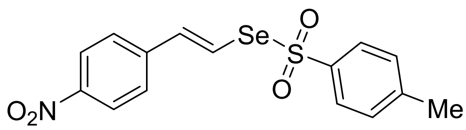
(*E*)-*Se*-(4-bromostyryl) 4-methylbenzenesulfonoselenoate (3af)

Overall Yield: 65% (81.1 mg). Nature: yellow solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 7:1). **Mp**: 143 – 145 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 7.79 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.62-7.58 (m, 4H), 7.42 (d, J = 8.4 Hz, 2H), 2.36 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 144.3, 140.3, 137.7, 132.0, 131.8, 130.9, 130.1, 129.2, 127.3, 124.7, 21.1; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{15}H_{14}BrO_2SSe^+$ 416.8985; Found: 416.8988.



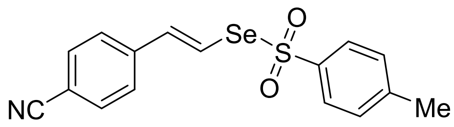
(*E*)-*Se*-(4-(trifluoromethyl)styryl) 4-methylbenzenesulfonoselenoate (3ag)

Overall Yield: 79% (96.2 mg). Nature: white solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 7:1). **Mp**: 124 – 126 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 7.94 (d, J = 8.4 Hz, 2H), 7.84-7.70 (m, 6H), 7.43 (d, J = 8.4 Hz, 2H), 2.36 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 163.9 (d, $J_{C\text{-}F}$ = 248.3 Hz), 144.5, 139.7, 137.4, 136.5, 131.3, 130.6 (d, $J_{C\text{-}F}$ = 31.8 Hz), 130.1, 129.6, 127.4, 125.7 (d, $J_{C\text{-}F}$ = 3.8 Hz), 123.9 (d, $J_{C\text{-}F}$ = 279.7 Hz), 21.1; **^{19}F{^{1}H} NMR** (376.8 MHz, DMSO-d_6) δ = -61.6 ppm; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{16}H_{14}F_3O_2SSe^+$ 406.9754; Found: 406.9756.



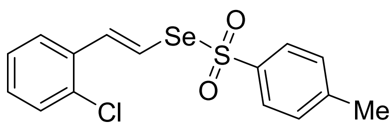
(*E*)-*Se*-(4-nitrostyryl) 4-methylbenzenesulfonoselenoate (3ah)

Overall Yield: 63% (72.4 mg). Nature: white solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 5:1). **Mp**: 167 – 169 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 8.26 (d, J = 8.8 Hz, 2H), 8.03 (d, J = 8.8 Hz, 2H), 7.88 (d, J = 15.6 Hz, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 15.2 Hz, 1H), 7.49 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 148.4, 144.6, 138.9, 138.9, 137.1, 132.5, 130.2, 130.1, 127.5, 124.0, 21.1; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{15}H_{14}NO_4SSe^+$ 383.9731; Found: 383.9735.



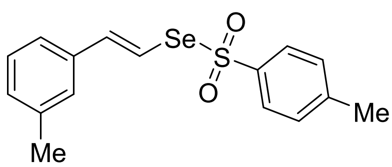
(*E*)-*Se*-(4-cyanostyryl) 4-methylbenzenesulfonoselenoate (3ai)

Overall Yield: 72% (78.4 mg). Nature: white solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 7:1). **Mp**: 121 – 123 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 7.93 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.83-7.79 (m, 3H), 7.70 (d, *J* = 15.2 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 144.6, 139.5, 137.2, 137.0, 132.8, 131.8, 130.2, 129.6, 127.4, 118.5, 113.0, 21.1; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{16}H_{14}NO_2SSe^+$ 363.9832; Found: 363.9834.



(*E*)-*Se*-(2-chlorostyryl) 4-methylbenzenesulfonoselenoate (3aj)

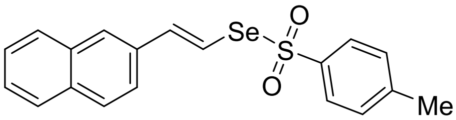
Overall Yield: 62% (69.2 mg). Nature: pale yellow solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 7:1). **Mp**: 146 – 148 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 7.91-7.85 (m, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 15.6 Hz, 1H), 7.54 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.47-7.42 (m, 3H), 7.37 (t, *J* = 7.2 Hz, 1H), 2.39 (s, 3H);**^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 144.5, 137.1, 136.1, 134.1, 132.6, 131.3, 130.2, 130.1, 130.0, 128.9, 127.8, 127.4, 21.1; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{15}H_{14}ClO_2SSe^+$ 372.9490; Found: 372.9492.



(*E*)-*Se*-(3-methylstyryl) 4-methylbenzenesulfonoselenoate (3ak)

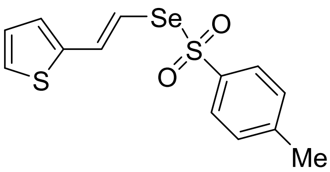
Overall Yield: 60% (63.4 mg). Nature: white solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 7:1). **Mp**: 128 – 130 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 7.79 (dd, *J* = 6.8 Hz, 2.0 Hz, 2H), 7.55 (d, *J* = 2.4 Hz, 3H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 2.39 (s, 3H), 2.29 (s, 3H); **^{13}C{^{1}H} NMR** (100

MHz, DMSO-d_6) δ (ppm) 144.2, 141.6, 138.3, 137.9, 132.4, 131.8, 130.1, 129.3, 128.9, 128.2, 127.2, 126.3, 21.1, 20.8; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{16}H_{17}O_2SSe^+$ 353.0036; Found: 353.0033.



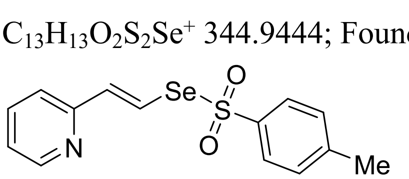
(*E*)-*Se*-(2-(naphthalen-2-yl)vinyl) 4-methylbenzenesulfonoselenoate (3al)

Overall Yield: 69% (80.3 mg). Nature: yellow solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 6:1). **Mp**: 118 – 120 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 8.25 (s, 1H), 7.93-7.85 (m, 6H), 7.80 (d, J = 15.2 Hz, 1H), 7.71 (d, J = 15.2 Hz, 1H), 7.58-7.52 (m, 2H), 7.44 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 144.2, 141.5, 137.9, 134.0, 132.7, 131.0, 130.1, 128.7, 128.7, 128.6, 127.7, 127.3, 126.9, 124.1, 21.1; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{19}H_{17}O_2SSe^+$ 389.0036; Found: 389.0032.



(*E*)-*Se*-(2-(thiophen-2-yl)vinyl) 4-methylbenzenesulfonoselenoate (3am)

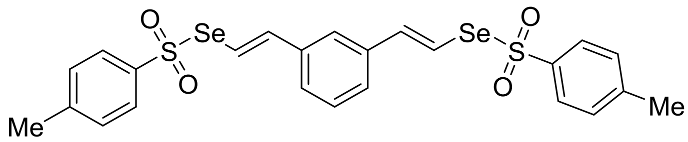
Overall Yield: 69% (71.2 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 6:1). **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 7.81-7.77 (m, 4H), 7.63 (d, J = 3.6 Hz, 1H), 7.45 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 15.2 Hz, 1H), 7.15 (dd, J = 5.2 Hz, 3.6 Hz, 1H), 2.39 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 144.1, 138.0, 136.6, 134.5, 133.3, 131.4, 130.1, 128.6, 127.2, 126.0, 21.1; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{13}H_{13}O_2S_2Se^+$ 344.9444; Found: 344.9448.



(*E*)-*Se*-(2-(pyridin-2-yl)vinyl) 4-methylbenzenesulfonoselenoate (3an)

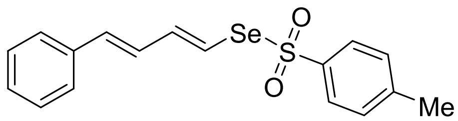
Overall Yield: 62% (63.1 mg). Nature: pale yellow solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 6:1). **Mp**: 93 –

95 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 8.60 (dd, J = 4.8 Hz, 0.8 Hz, 1H), 7.86-7.81 (m, 3H), 7.77 (d, J = 7.6 Hz, 1H), 7.67 (s, 2H), 7.41-7.37 (m, 3H), 2.33 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 150.7, 150.1, 144.5, 140.6, 137.4, 137.2, 131.8, 130.1, 127.5, 125.5, 125.3, 21.1; **HRMS** (ESI) m/z: [M+H]$^+$ Calcd for: $C_{14}H_{14}NO_2SSe^+$ 339.9832; Found: 339.9836.



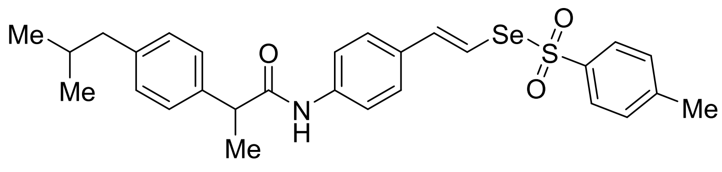
***Se*, *Se*'-((1*E*, 1'*E*)-1, 3-phenylenebis(ethene-2, 1-diyl)) bis(4-methylbenzenesulfonoselenoate) (3ao)**

Overall Yield: 75% (134.5 mg). Nature: white solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 10:1). **Mp**: 102 – 104 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 8.20 (s, 1H), 7.80-7.77 (m, 6H), 7.65 (d, J = 15.6 Hz, 2H), 7.61 (d, J = 15.6 Hz, 2H), 7.50-7.43 (m, 5H), 2.37 (s, 6H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 144.4, 140.6, 137.6, 133.2, 131.8, 130.2, 129.8, 129.5, 128.0, 127.3, 21.1; **HRMS** (ESI) m/z: [M+H]$^+$ Calcd for: $C_{24}H_{23}O_4S_2Se_2^+$ 598.9290; Found: 598.9290.



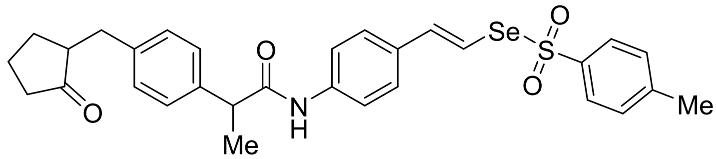
***Se*-((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl) 4-methylbenzenesulfonoselenoate (3ap)**

Overall Yield: 49% (53.5 mg). Nature: white solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 8:1). **Mp**: 127 – 129 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 7.76 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.41-7.30 (m, 6H), 7.22 (d, J = 15.6 Hz, 1H), 7.04 (dd, J = 15.6 Hz, 10.8 Hz, 1H), 6.90 (d, J = 14.4 Hz, 1H), 2.39 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 144.2, 142.5, 141.9, 138.0, 135.5, 132.3, 130.1, 129.5, 129.0, 127.4, 127.2, 124.3, 21.1; **HRMS** (ESI) m/z: [M+H]$^+$ Calcd for: $C_{17}H_{17}O_2SSe^+$ 365.0036; Found: 365.0038.



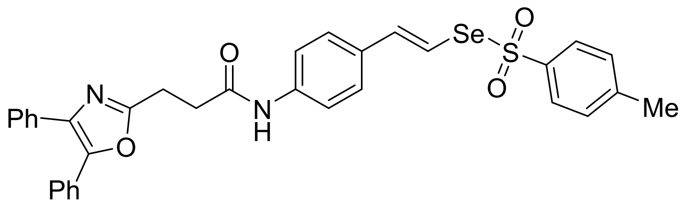
(*E*)-*Se*-(4-(2-(4-isobutylphenyl)propanamido)styryl) 4-methylbenzenesulfonoselenoate (3aq)

Overall Yield: 61% (99.0 mg). Nature: pale yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 3:1). **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 10.11 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 15.2 Hz, 1H), 7.59 (d, *J* = 15.6 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.39-7.32 (m, 4H), 7.20 (d, *J* = 8.8 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 4.01 (q, *J* = 7.2 Hz, 1H), 2.36 (d, *J* = 7.2 Hz, 2H), 2.34 (s, 3H), 1.80-1.71 (m, 1H), 1.42 (d, *J* = 6.8 Hz, 3H), 0.80 (d, *J* = 6.8 Hz, 6H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 172.5, 143.8, 139.5, 139.3, 139.2, 138.3, 137.8, 133.9, 129.4, 128.9, 127.9, 127.2, 127.0, 126.4, 119.2, 45.7, 44.3, 29.7, 22.1, 21.0, 18.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{28}H_{32}NO_3SSe^+$ 542.1190; Found: 542.1192.



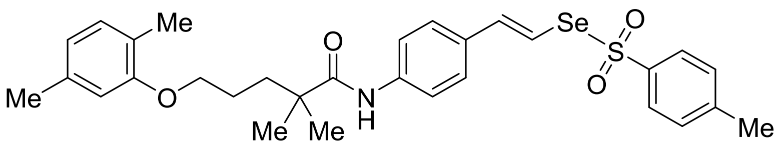
(*E*)-*Se*-(4-(2-(4-((2-oxocyclopentyl)methyl)phenyl)propanamido)styryl) 4-methylbenzenesulfonoselenoate (3ar)

Overall Yield: 70% (122.0 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 2:1). **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 10.09 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 14.0 Hz, 1H), 7.58-7.53 (m, 3H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.01 (q, *J* = 7.2 Hz, 1H), 2.93 (dd, *J* = 13.2 Hz, 3.6 Hz, 1H), 2.42-2.27 (m, 5H), 2.23-2.16 (m, 1H), 2.06-1.99 (m, 1H), 1.90-1.76 (m, 2H), 1.68-1.56 (m, 1H), 1.47-1.38 (m, 4H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 219.2, 172.4, 143.9, 139.5, 139.2, 138.6, 138.2, 137.8, 133.9, 129.4, 128.9, 128.8, 127.9, 127.3, 127.2, 119.2, 50.1, 45.7, 37.6, 34.6, 28.8, 21.1, 20.1, 18.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{30}H_{32}NO_4SSe^+$ 582.1139; Found: 582.1136.



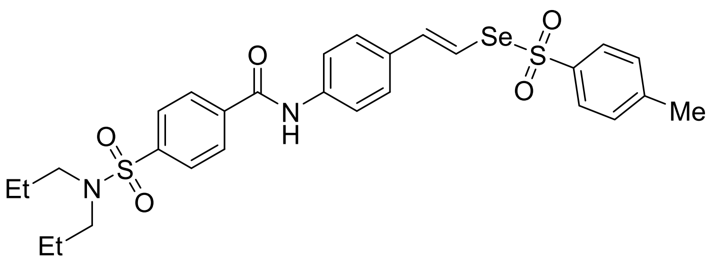
(*E*)-*Se*-(4-(3-(4,5-diphenyloxazol-2-yl)propanamido)styryl) 4-methylbenzenesulfonoselenoate (3as)

Overall Yield: 59% (111.2 mg). Nature: pale yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 1:1). **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 10.16 (s, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 15.2 Hz, 1H), 7.57-7.49 (m, 5H), 7.44-7.31 (m, 10H), 7.20 (d, J = 8.4 Hz, 2H), 3.15 (t, J = 7.2 Hz, 2H), 2.90 (t, J = 7.2 Hz, 2H), 2.37 (m, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 169.7, 162.7, 144.7, 143.9, 139.1, 138.2, 137.8, 134.4, 133.9, 132.1, 130.1, 129.4, 129.0, 128.8, 128.7, 128.5, 128.2, 127.9, 127.4, 127.3, 126.3, 119.1, 32.7, 23.2, 21.1. **HRMS** (ESI) m/z: [M+H]$^+$ Calcd for: $C_{33}H_{29}N_2O_4SSe^+$ 629.0935; Found: 629.0932.



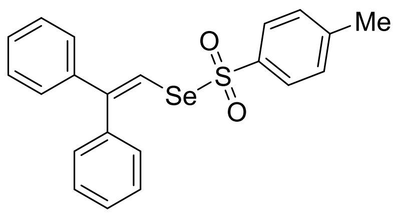
(*E*)-*Se*-(4-(5-(2,5-dimethylphenoxy)-2,2-dimethylpentanamido)styryl) 4-methylbenzenesulfonoselenoate (3at)

Overall Yield: 60% (114.3 mg). Nature: white solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 4:1). **Mp**: 142 – 144 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 9.58 (s, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 15.2 Hz, 1H), 7.65 (d, J = 14.4 Hz, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 7.6 Hz, 1H), 6.65 (s, 1H), 6.57 (d, J = 7.2 Hz, 1H), 3.88 (t, J = 6.4 Hz, 2H), 2.32 (s, 3H), 2.20 (s, 3H), 2.06 (s, 3H), 1.77-1.71 (m, 2H), 1.68-1.61 (m, 2H), 1.22 (s, 6H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 177.7, 156.3, 144.0, 139.3, 138.4, 137.6, 136.7, 135.8, 132.6, 130.5, 129.9, 129.4, 127.9, 125.7, 122.3, 120.9, 113.4, 67.4, 42.0, 36.7, 25.1, 24.6, 21.5, 20.8, 15.4; **HRMS** (ESI) m/z: [M+H]$^+$ Calcd for: $C_{30}H_{36}NO_4SSe^+$ 586.1452; Found: 586.1455.



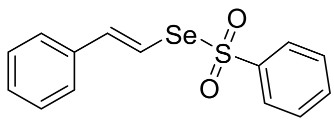
(*E*)-*Se*-(4-(4-(*N*,*N*-dipropylsulfamoyl)benzamido)styryl) 4-methylbenzenesulfonoselenoate (3au)

Overall Yield: 65% (120.9 mg). Nature: pale yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 4:1). **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 10.22 (s, 1H), 8.11 (d, *J* = 8.4 Hz, 2H), 7.91-7.86 (m, 4H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 14.4 Hz, 1H), 7.51 (d, *J* = 15.2 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 3.03 (t, *J* = 7.2 Hz, 4H), 2.31 (s, 3H), 1.49-1.40 (m, 4H), 0.78 (t, *J* = 7.2 Hz, 6H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 167.4, 143.3, 139.9, 139.8, 136.5, 135.4, 134.8, 132.5, 129.2, 129.2, 128.1, 127.3, 127.2, 120.4, 111.9, 49.3, 21.3, 20.6, 10.8; **HRMS** (ESI) m/z: [M+H]$^+$ Calcd for: $C_{28}H_{33}N_2O_5S_2Se^+$ 621.0918; Found: 621.0916.



***Se*-(2,2-diphenylvinyl) 4-methylbenzenesulfonoselenoate (3ax)**

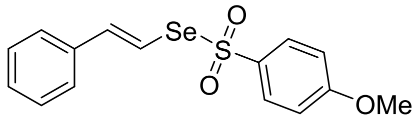
Overall Yield: 52% (64.6 mg). Nature: white solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 10:1). **Mp**: 107 – 109 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 7.93 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.36-7.30 (m, 6H), 7.29-7.21 (m, 4H), 7.03 (s, 1H), 2.24 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 154.3, 144.1, 139.0, 138.9, 136.9, 130.0, 129.7, 129.2, 128.5, 127.9, 127.9, 127.7, 127.6, 127.0, 21.0; **HRMS** (ESI) m/z: [M+H]$^+$ Calcd for: $C_{21}H_{19}O_2SSe^+$ 415.0193; Found: 415.0190.



(*E*)-*Se*-styryl benzenesulfonoselenoate (3ba)

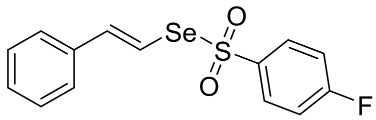
Overall Yield: 73% (70.9 mg). Nature: yellow oil. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 7:1). **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 7.93 (d, *J* = 8.8 Hz, 2H), 7.80-7.60 (m, 7H), 7.45-7.41 (m, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 142.1, 139.4, 133.7, 132.4, 131.3, 129.7, 129.1, 129.0, 128.1, 127.2; **HRMS** (ESI) m/z: [M+H]$^+$ Calcd for:

$C_{14}H_{13}O_2SSe^+$ 324.9723; Found: 324.9726.



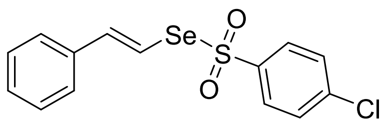
(*E*)-*Se*-styryl 4-methoxybenzenesulfonoselenoate (3ca)

Overall Yield: 82% (87.1 mg). Nature: white solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 7:1). **Mp**: 84 – 86 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 7.89-7.85 (m, 2H), 7.73-7.70 (m, 2H), 7.62 (d, J = 15.6 Hz, 1H), 7.55 (d, J = 15.2 Hz, 1H), 7.42-7.37 (m, 3H), 7.15 (dt, J = 3.2 Hz, 8.8 Hz, 2H), 3.82 (m, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 163.2, 140.9, 132.5, 132.2, 131.1, 129.6, 129.0, 128.9, 128.8, 114.9, 55.8; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{15}H_{15}O_3SSe^+$ 354.9829; Found: 354.9826.



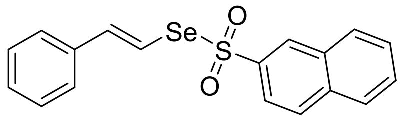
(*E*)-*Se*-styryl 4-fluorobenzenesulfonoselenoate (3da)

Overall Yield: 75% (76.9 mg). Nature: yellow solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 6:1). **Mp**: 89 – 91 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 8.03-7.98 (m, 2H), 7.74 (dd, J = 7.2 Hz, 1.6 Hz, 2H), 7.67 (d, J = 15.6 Hz, 1H), 7.63 (d, J = 15.6 Hz, 1H), 7.54-7.48 (m, 2H), 7.46-7.41 (m, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 164.9 (d, $J_{C\text{-}F}$ = 251.0 Hz), 142.2, 137.1 (d, $J_{C\text{-}F}$ = 2.9 Hz), 132.4, 131.3, 130.4 (d, $J_{C\text{-}F}$ = 9.7 Hz), 129.1, 129.1, 128.0, 116.9 (d, $J_{C\text{-}F}$ = 22.7 Hz); **^{19}F{^{1}H} NMR** (376.8 MHz, DMSO-d_6) δ = -105.0 ppm; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{14}H_{12}FO_2SSe^+$ 342.9629; Found: 342.9627.



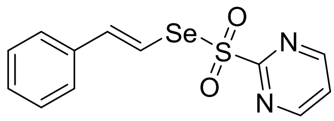
(*E*)-*Se*-styryl 4-chlorobenzenesulfonoselenoate (3ea)

Overall Yield: 79% (84.8 mg). Nature: pale yellow solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 6:1). **Mp**: 93 – 95 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 7.94 (dd, J = 6.4 Hz, 1.6 Hz, 2H), 7.76-7.72 (m, 4H), 7.69 (d, J = 14.4 Hz, 1H), 7.64 (d, J = 15.6 Hz, 1H), 7.46-7.41 (m, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 142.7, 139.6, 138.7, 132.4, 131.4, 129.9, 129.2, 129.2, 129.1, 127.7; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{14}H_{12}ClO_2SSe^+$ 358.9334; Found: 358.9334.



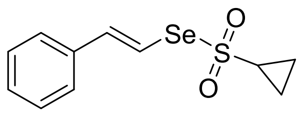
(*E*)-*Se*-styryl naphthalene-2-sulfonoselenoate (3fa)

Overall Yield: 69% (77.4 mg). Nature: brown solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 8:1). **Mp**: 105 – 107 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 8.15 (s, 1H), 8.13 (d, *J* = 9.2 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.99-7.95 (m, 3H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 14.4 Hz, 1H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.67-7.61 (m, 3H), 7.57-7.51 (m, 2H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 139.1, 137.4, 134.9, 133.7, 131.3, 130.0, 129.7, 129.4, 129.0, 128.6, 128.1, 127.8, 127.3, 124.4; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{18}H_{15}O_2SSe^+$ 374.9880; Found: 374.9882.



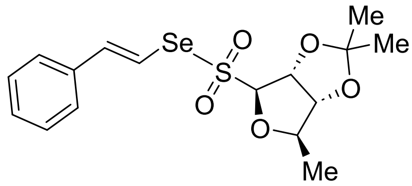
(*E*)-*Se*-styryl pyrimidine-2-sulfonoselenoate (3ga)

Overall Yield: 71% (69.4 mg). Nature: brown solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 7:1). **Mp**: 116 – 118 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 9.08 (d, *J* = 4.8 Hz, 2H), 7.85-7.83 (m, 3H), 7.76 (s, 2H), 7.52-7.44 (m, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 166.0, 159.3, 145.4, 132.3, 131.6, 129.3, 129.1, 124.9, 124.7; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{12}H_{11}N_2O_2SSe^+$ 326.9628; Found: 326.9624.



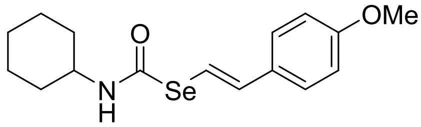
(*E*)-*Se*-styryl cyclopropanesulfonoselenoate (3ha)

Overall Yield: 58% (50.1 mg). Nature: pale yellow solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 8:1). **Mp**: 89 – 91 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 7.77-7.74 (m, 2H), 7.52 (d, *J* = 15.6 Hz, 1H), 7.48-7.44 (m, 4H), 2.74-2.67 (m, 1H), 1.06 (s, 2H), 1.05 (s, 2H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 141.6, 132.6, 131.0, 129.1, 128.8, 127.2, 30.8, 4.9; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{11}H_{13}O_2SSe^+$ 288.9723; Found: 288.9723.



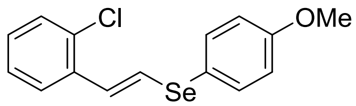
***Se*-((*E*)-styryl) (3a*R*,4*S*,6*R*,6a*R*)-2,2,6-trimethyltetrahydrofuro[3,4-*d*][1,3]dioxole-4-sulfonoselenoate (3ia)**

Overall Yield: 51% (61.8 mg). Nature: white solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 8:1). **Mp**: 92 – 94 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 7.66 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 15.2 Hz, 1H), 7.52 (d, J = 14.4 Hz, 1H), 7.44-7.40 (m, 3H), 5.12 (dd, J = 6.4 Hz, 2.0 Hz, 1H), 4.68 (dd, J = 6.0 Hz, 1.6 Hz, 1H), 4.33 (qd, J = 8.4 Hz, 1.6 Hz, 1H), 3.93 (d, J = 2.0 Hz, 1H), 1.30 (s, 6H), 1.11 (d, J = 6.4 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 141.3, 132.3, 130.7, 129.1, 128.7, 127.8, 121.3, 105.7, 90.4, 82.2, 72.5, 25.8, 25.6, 17.6; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{16}H_{21}O_5SSe^+$ 405.0197; Found: 405.0194.



(*E*)-*Se*-(4-methoxystyryl) cyclohexylcarbamoselenoate (4aa)

Overall Yield: 83% (84.4 mg). Nature: white solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 35:1). **Mp**: 95 – 97 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 8.43 (s, 1H), 7.59 (d, J = 15.6 Hz, 1H), 7.51-7.47 (m, 3H), 7.00 (d, J = 8.4 Hz, 2H), 3.82 (s, 3H), 3.23-3.16 (m, 1H), 1.97 (d, J = 12.8 Hz, 2H), 1.74 (d, J = 12.4 Hz, 2H), 1.56 (d, J = 13.2 Hz, 1H), 1.38-1.18 (m, 4H), 1.18-1.03 (m, 1H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 161.2, 159.1, 136.8, 129.3, 127.2, 124.2, 114.1, 55.2, 52.4, 33.1, 25.1, 24.3; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{16}H_{22}NO_2Se^+$ 340.0738; Found: 340.0739.



(*E*)-(2-chlorostyryl)(4-methoxyphenyl)selane (4ab)

Overall Yield: 70% (56.7 mg). Nature: pale yellow solid. Purification of the product was performed by silica gel column chromatography (eluent: PE/EA = 10:1). **Mp**: 81

– 83 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 7.87-7.81 (m, 2H), 7.69 (d, J = 15.2 Hz, 1H), 7.49 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.41 (d, J = 8.4 Hz, 2H), 7.36 (t, J = 7.2 Hz, 1H), 7.27 (t, J = 7.2 Hz, 1H), 7.04 (d, J = 8.4 Hz, 2H), 2.34 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6) δ (ppm) 159.2, 136.2, 134.7, 132.2, 130.1, 129.1, 128.6, 128.2, 127.7, 127.1, 126.8, 115.4, 55.2; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for: $C_{15}H_{14}ClOSe^+$ 324.9820; Found: 324.9823.

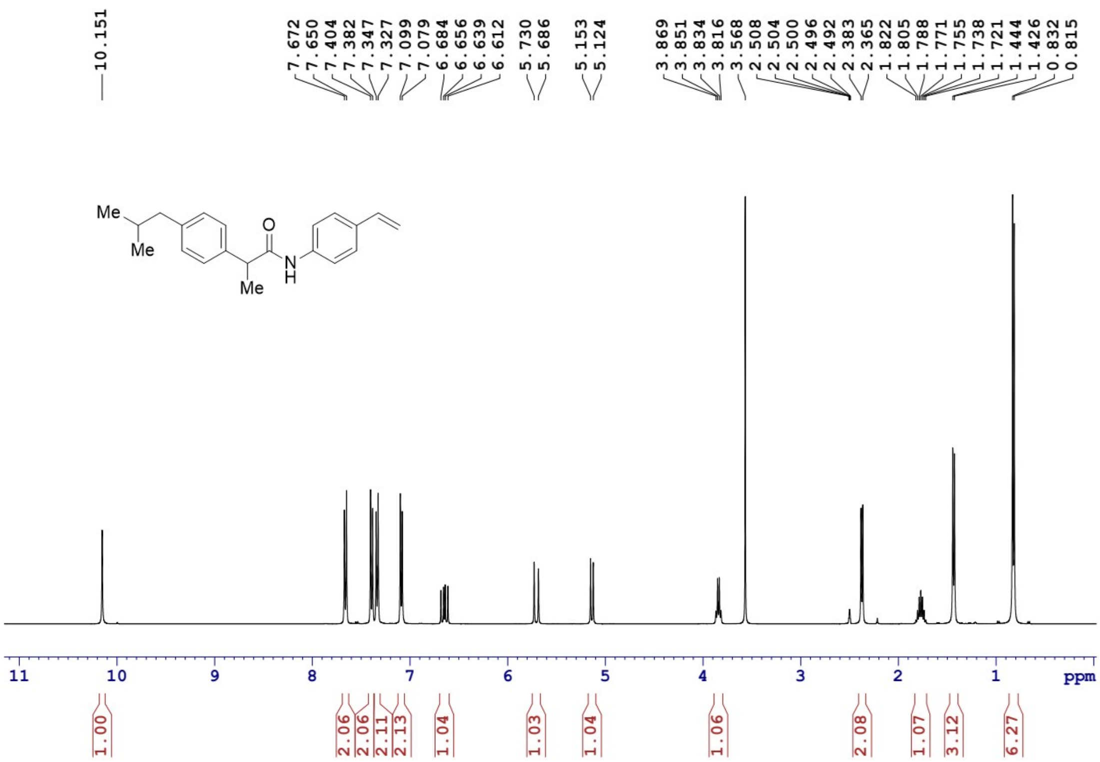
9. Reference

[1] Zhao, Y.; Truhlar, D. G.*Theor. Chem. Acc.* **2008**, *120*, 215−241.

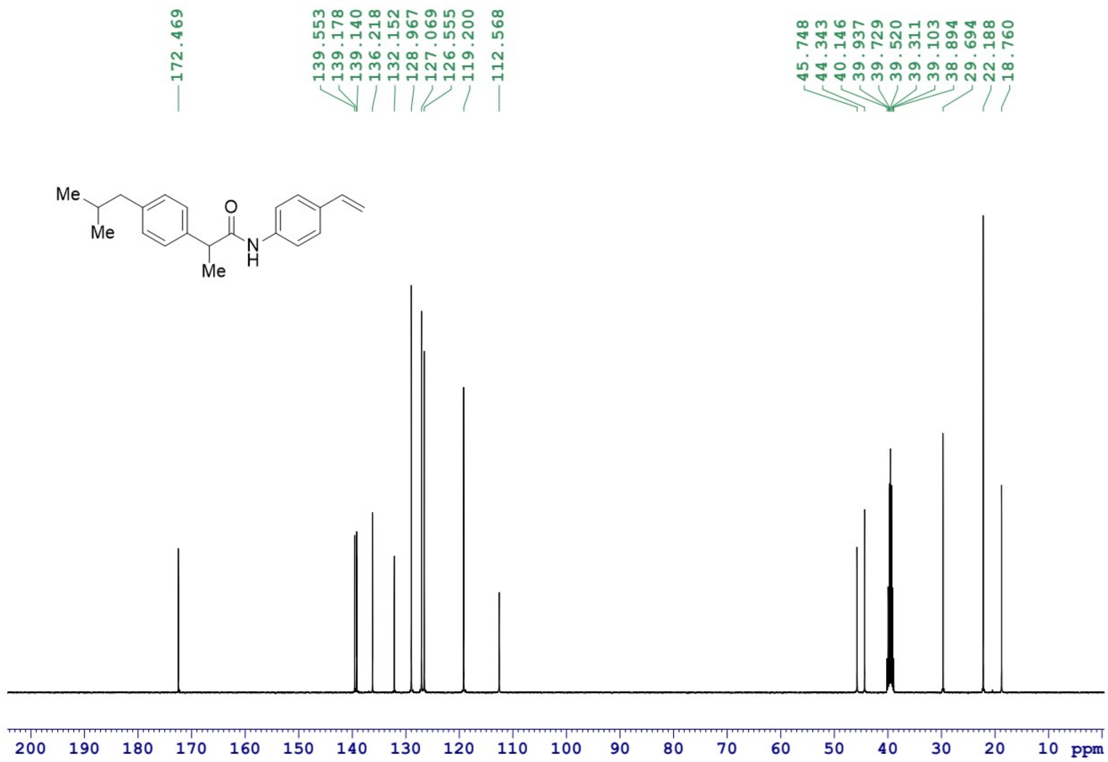
[2] Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta.***1973**, *28*, 213-222.

[3] Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, . Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

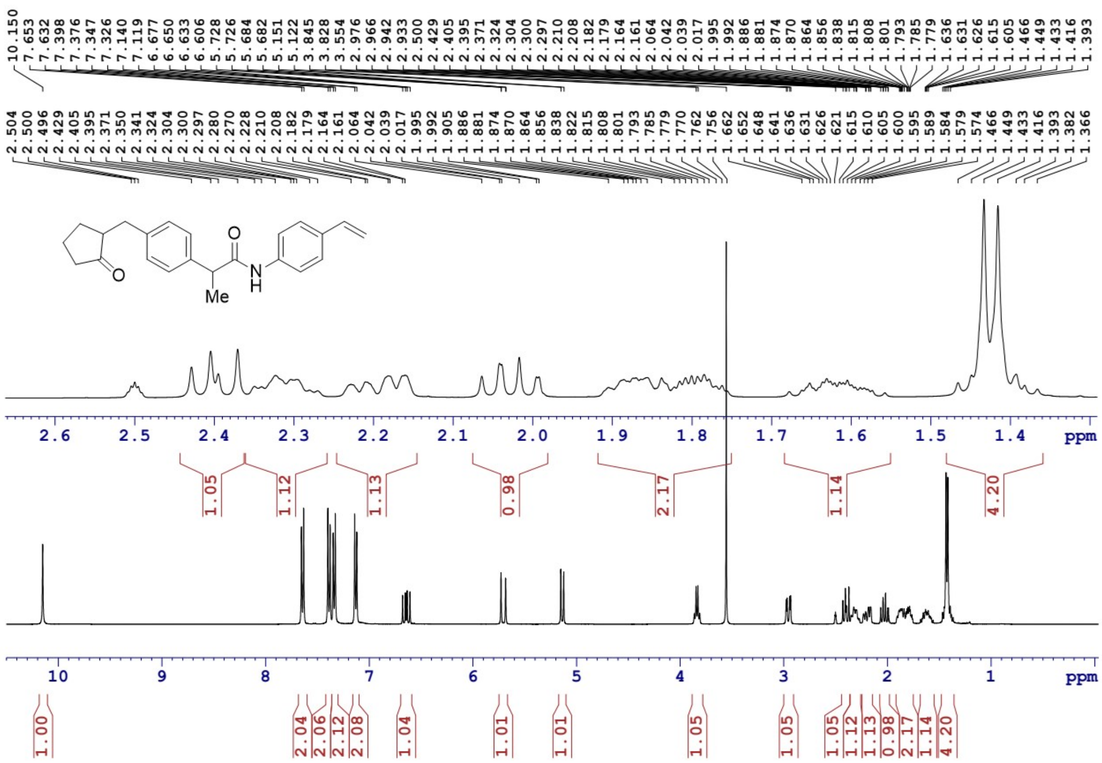
10. Copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HRMS spectra



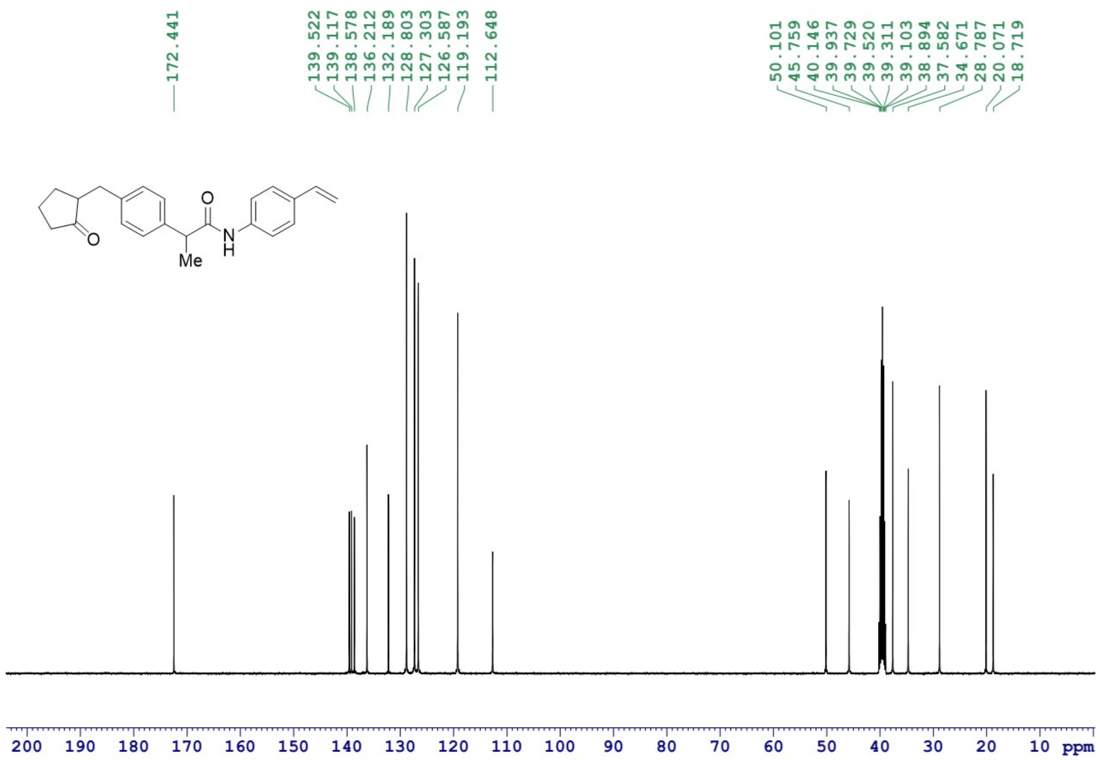
3aq'-[1]H NMR (400 MHz, DMSO-d_6)



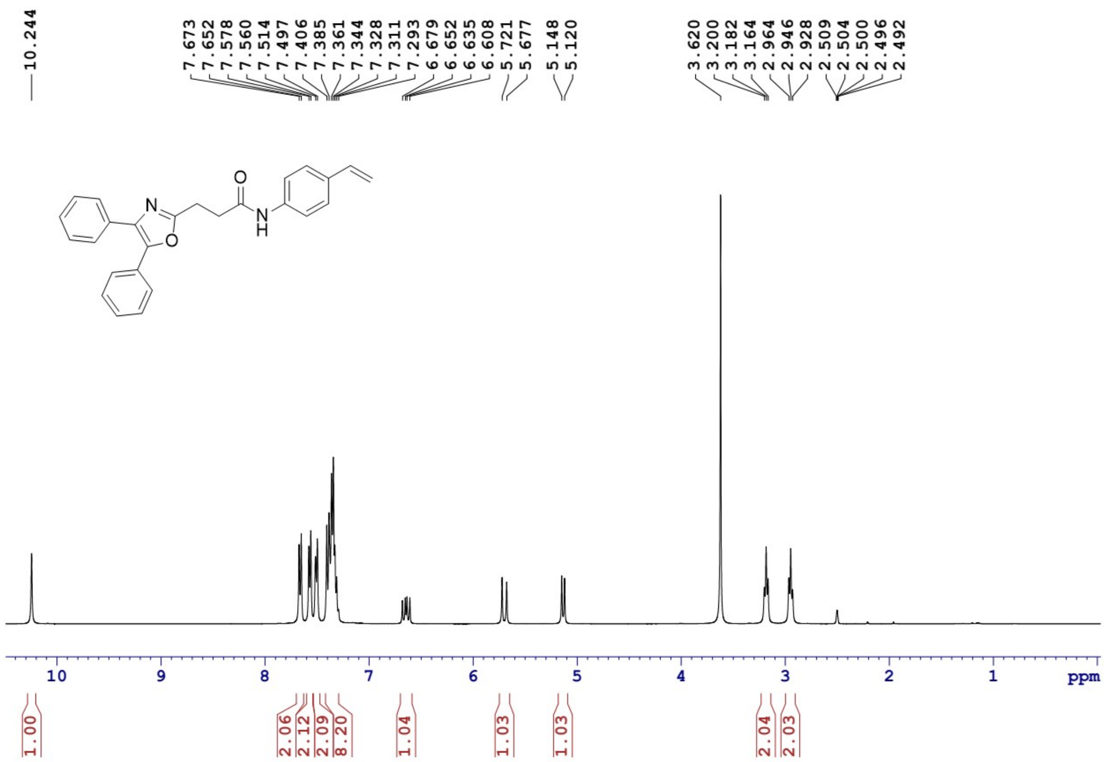
3aq'-[13]C NMR (100 MHz, DMSO-d_6)



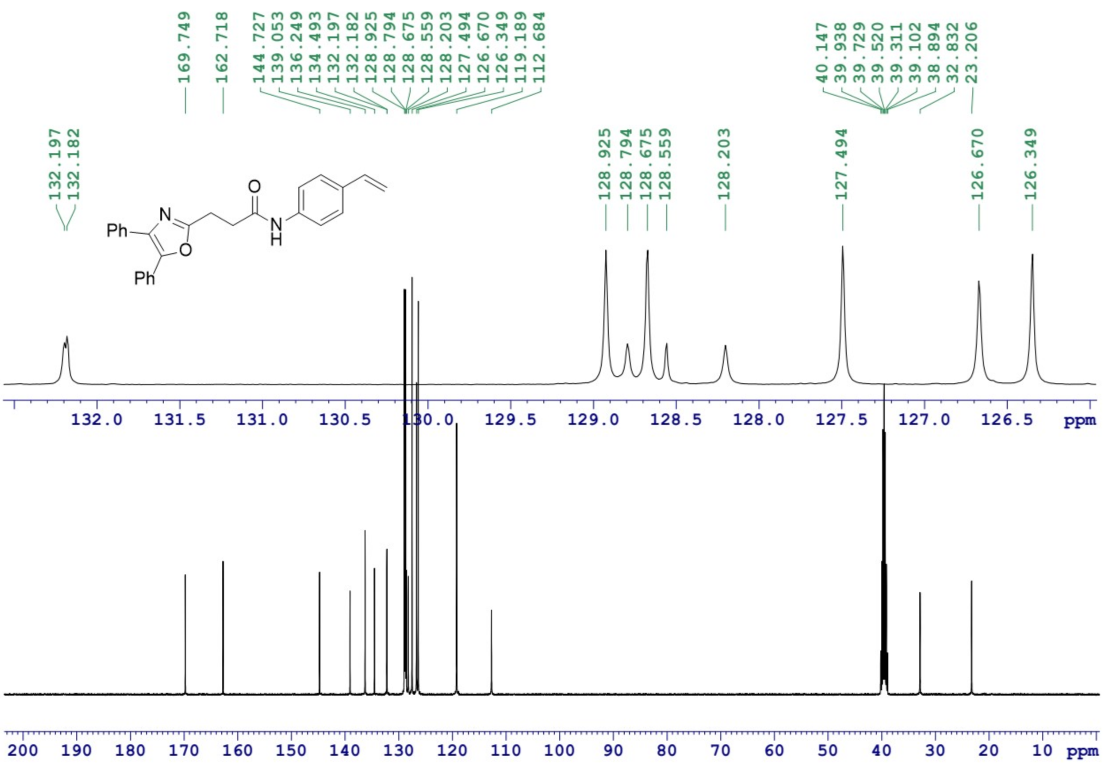
3ar'-[1]H NMR (400 MHz, DMSO-d_6)



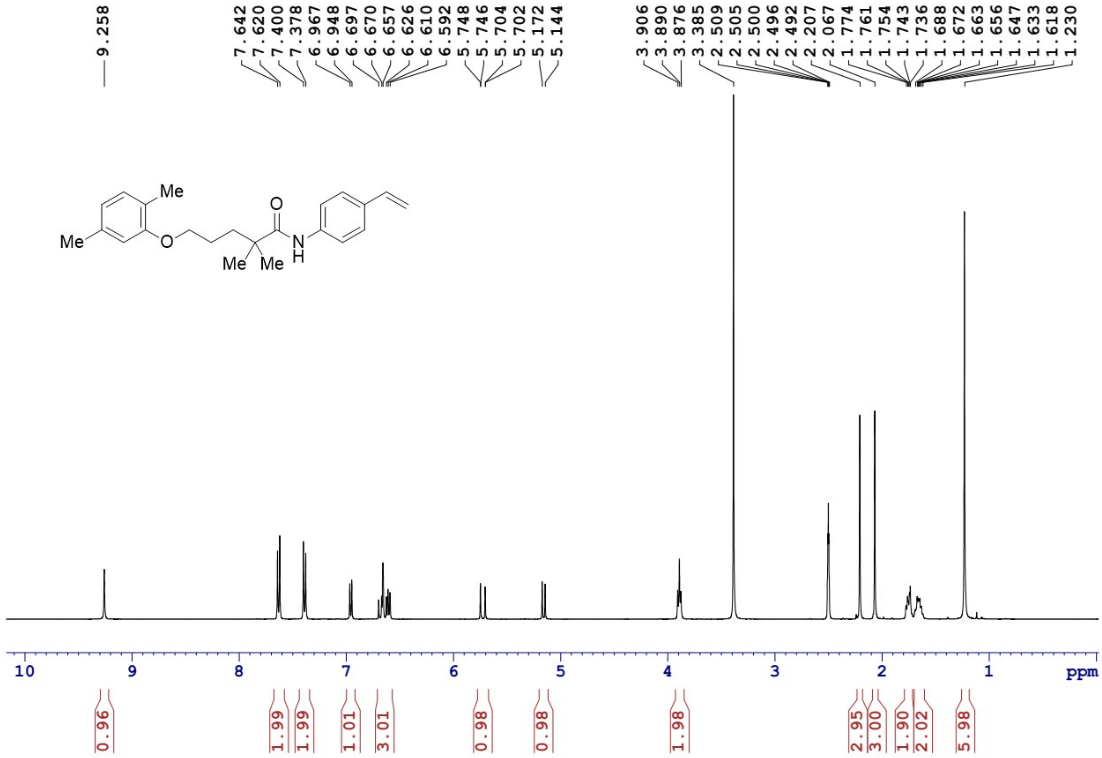
3ar'-[13]C NMR (100 MHz, DMSO-d_6)



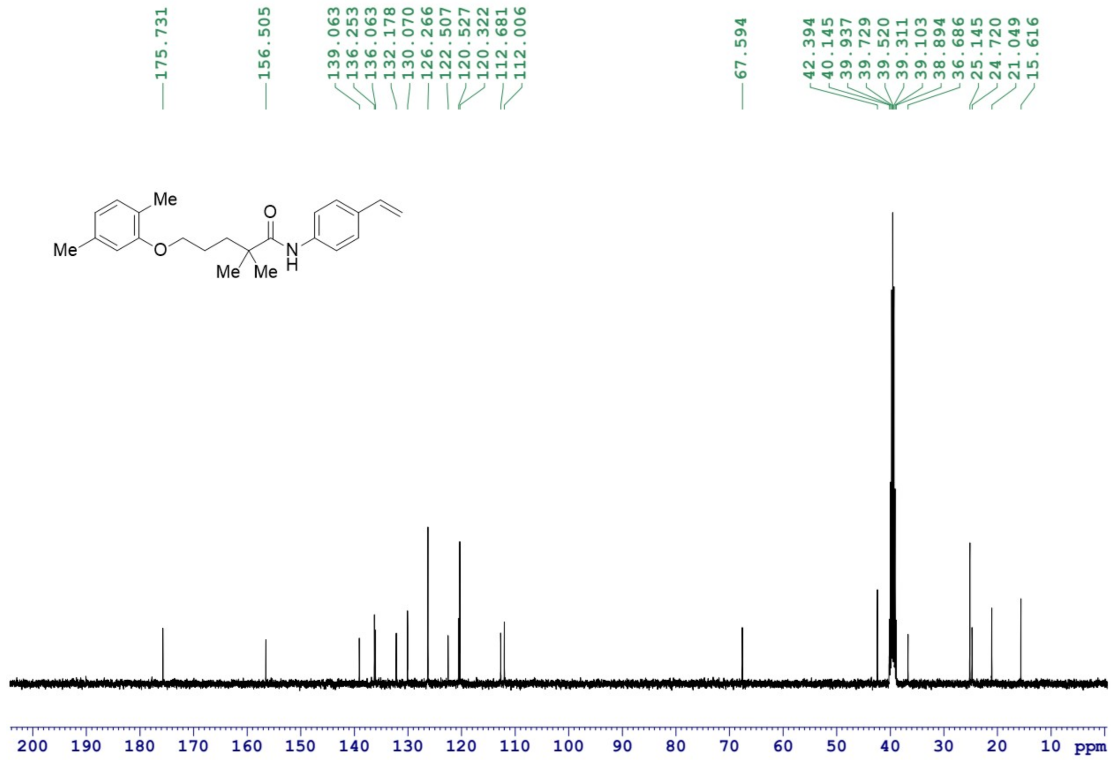
3as'-[1]H NMR (400 MHz, DMSO-d_6)



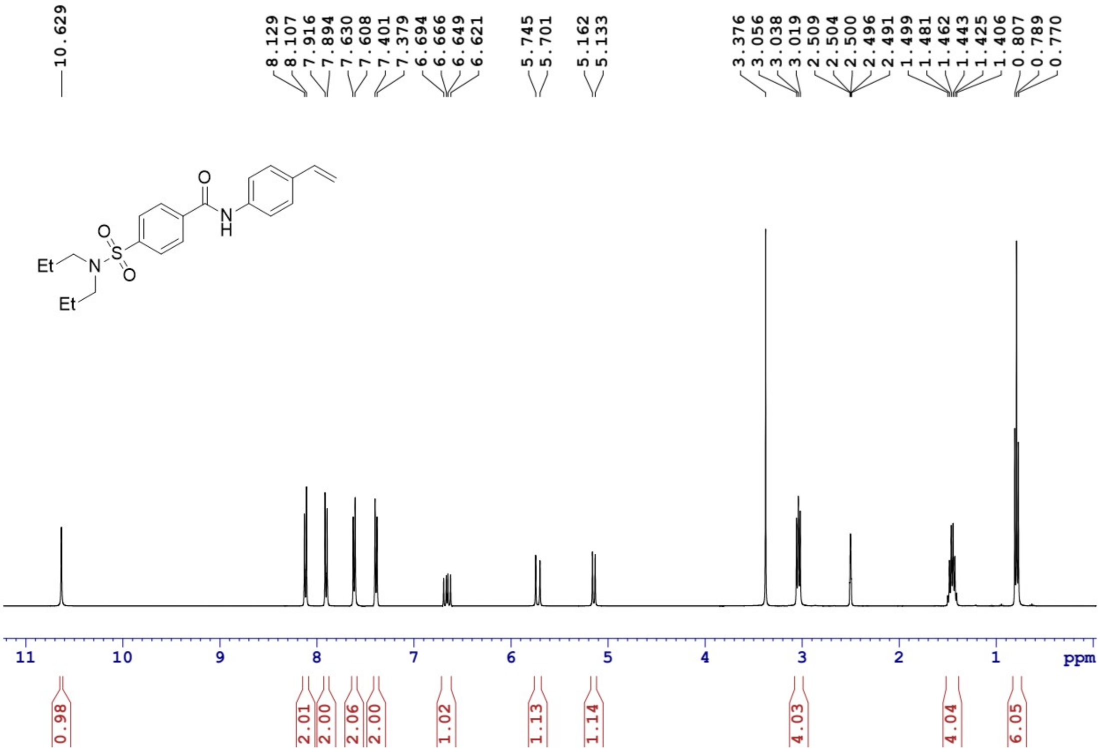
3as'-[13]C NMR (100 MHz, DMSO-d_6)



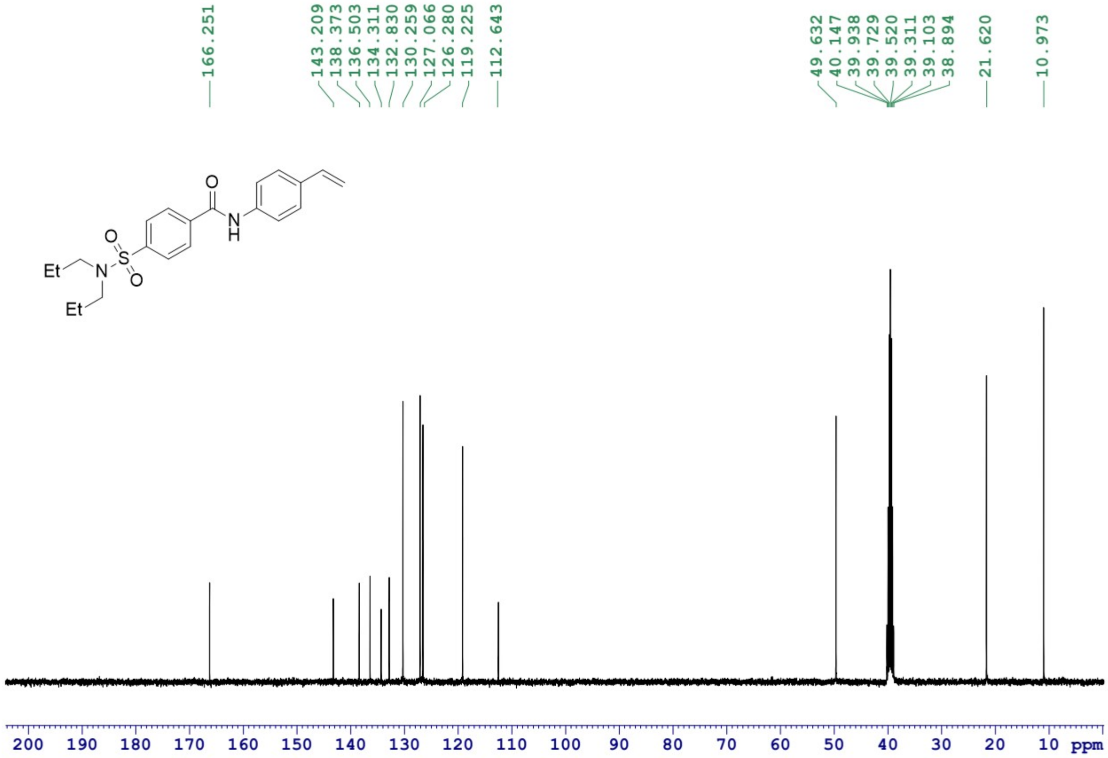
3at'-^{1}H NMR (400 MHz, DMSO-d_6)



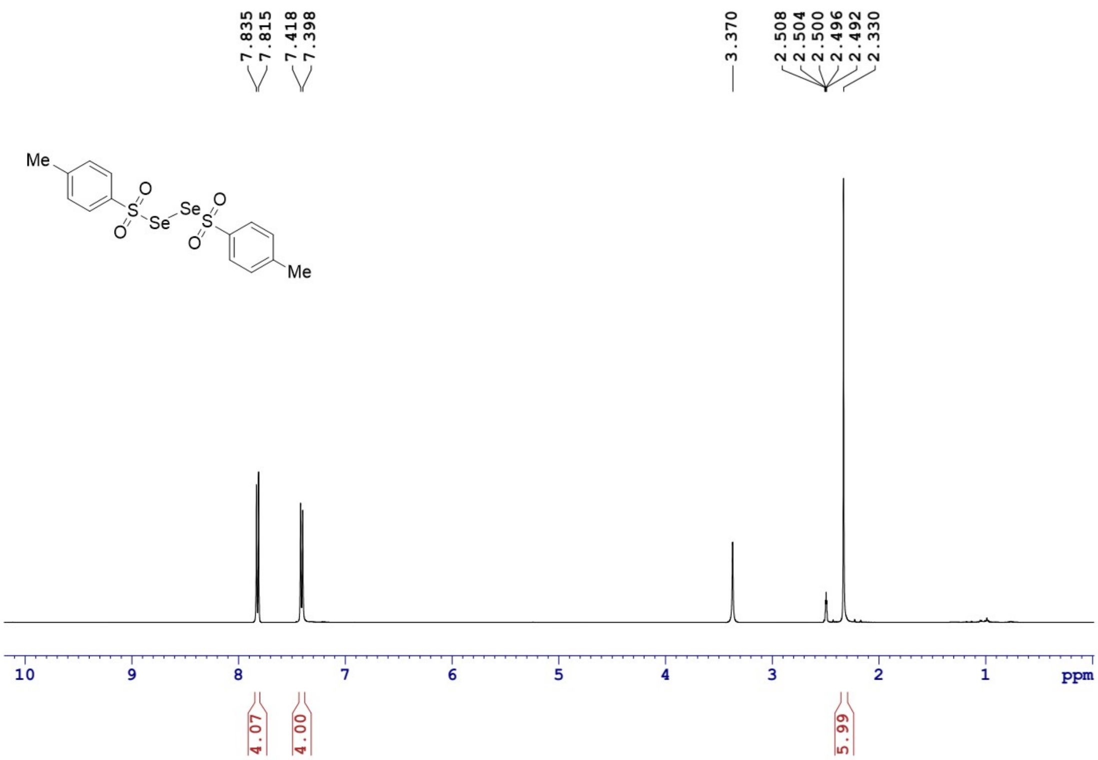
3at'-^{13}C NMR (100 MHz, DMSO-d_6)



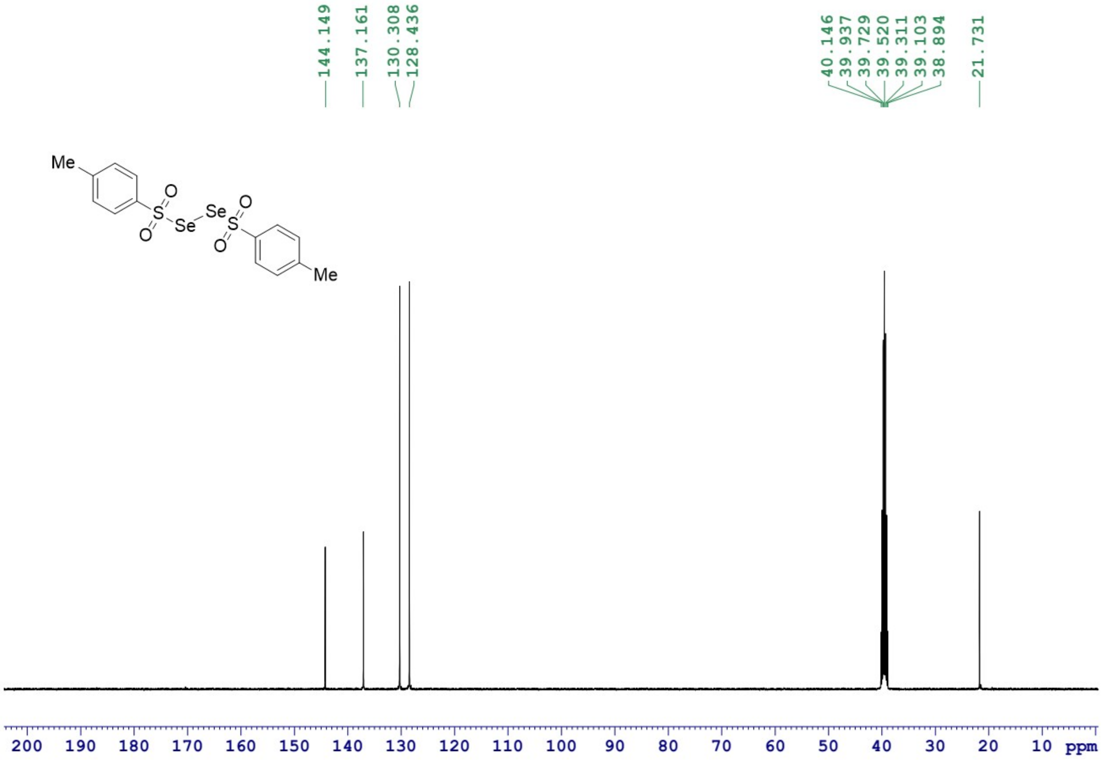
3au'-^{1}H NMR (400 MHz, DMSO-d_6)



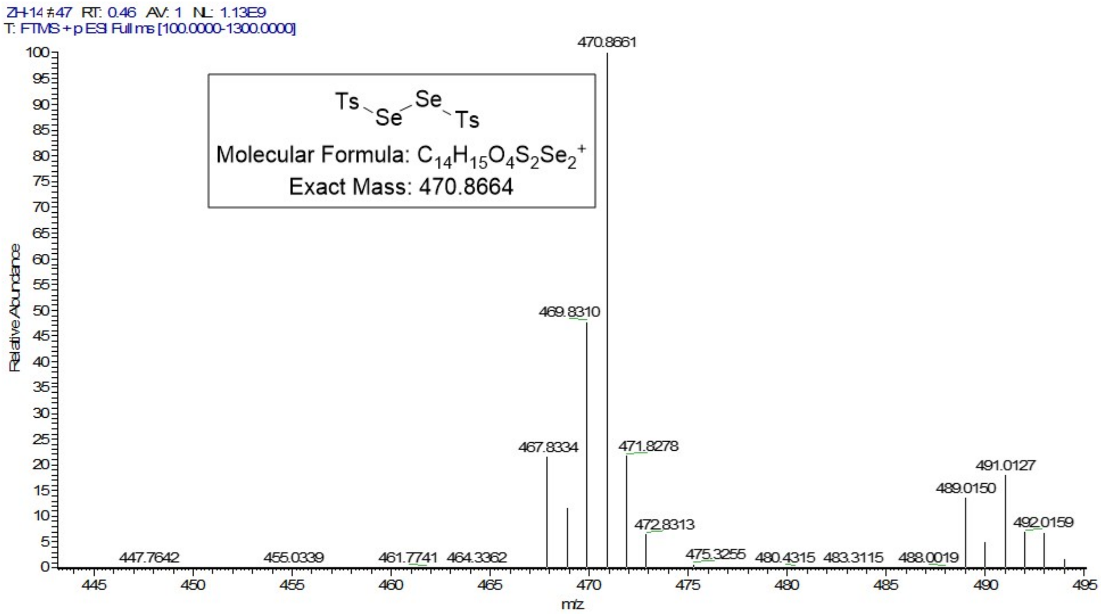
3au'-^{13}C NMR (100 MHz, DMSO-d_6)



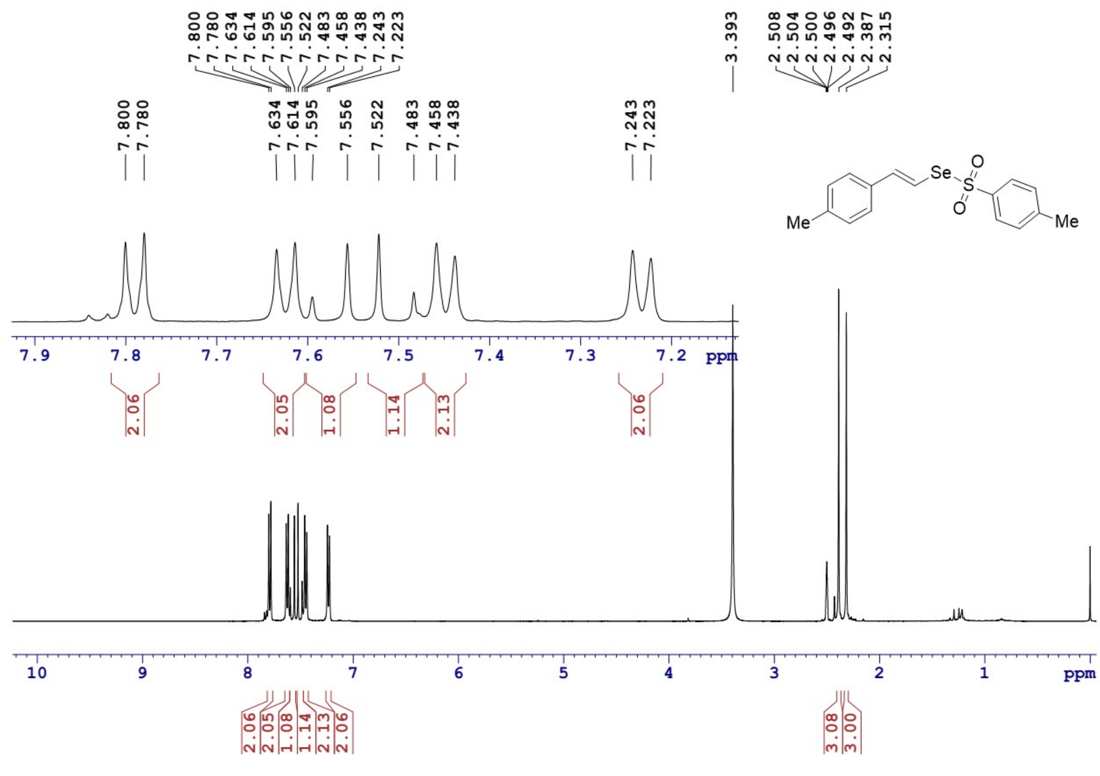
2a-I-^{1}H NMR (400 MHz, DMSO-d_6)



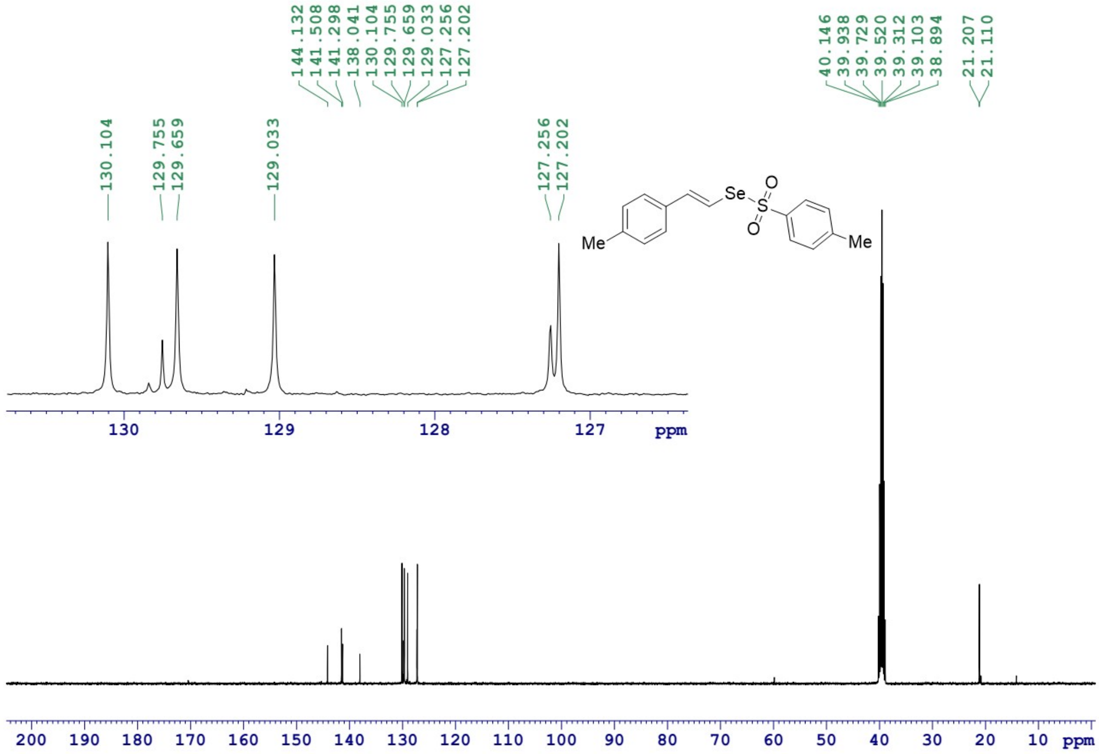
2a-I-^{13}C NMR (100 MHz, DMSO-d_6)



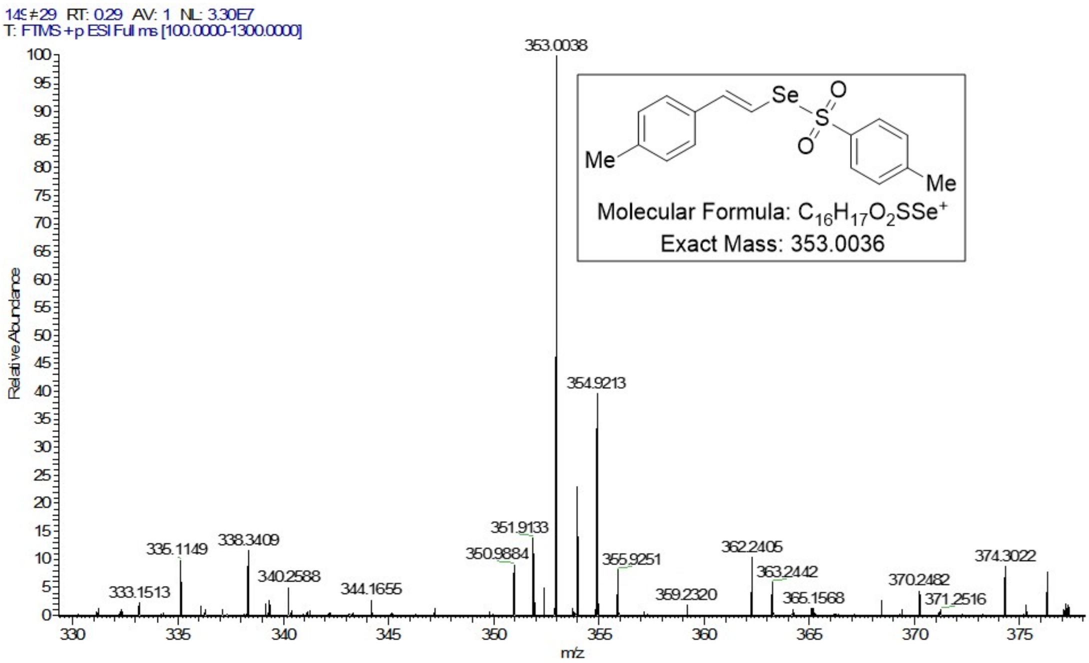
2a-I-HRMS



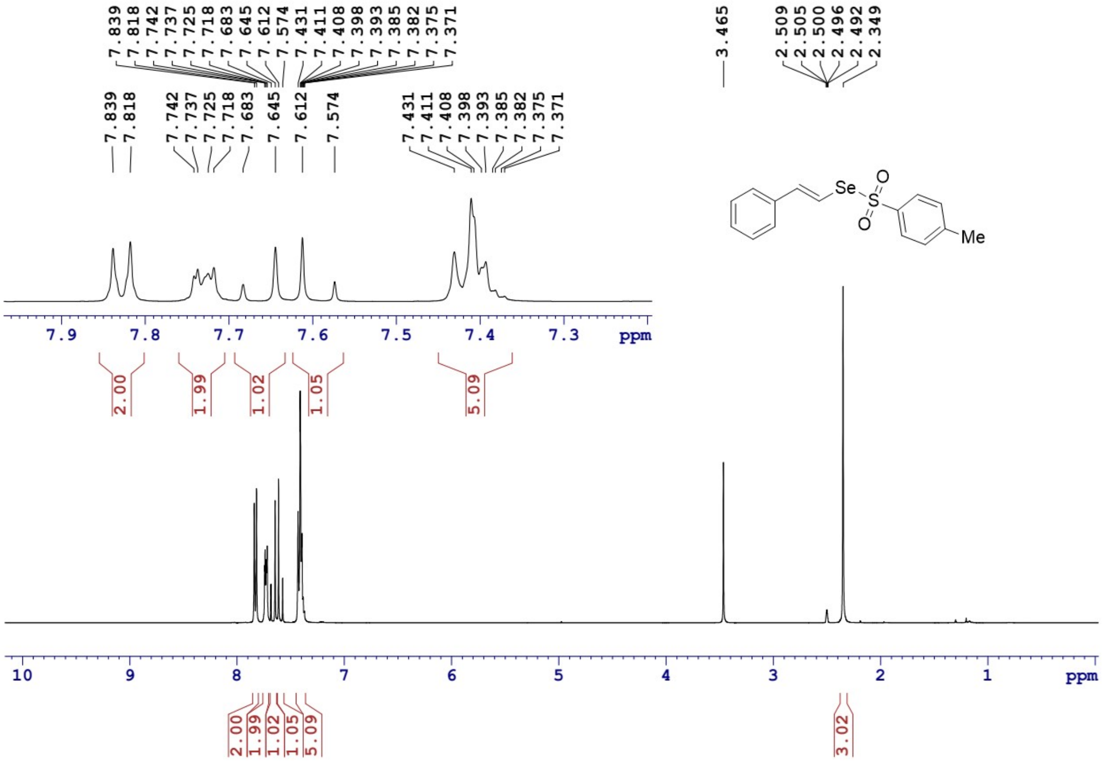
3aa-^{1}H NMR (400 MHz, DMSO-d_6)



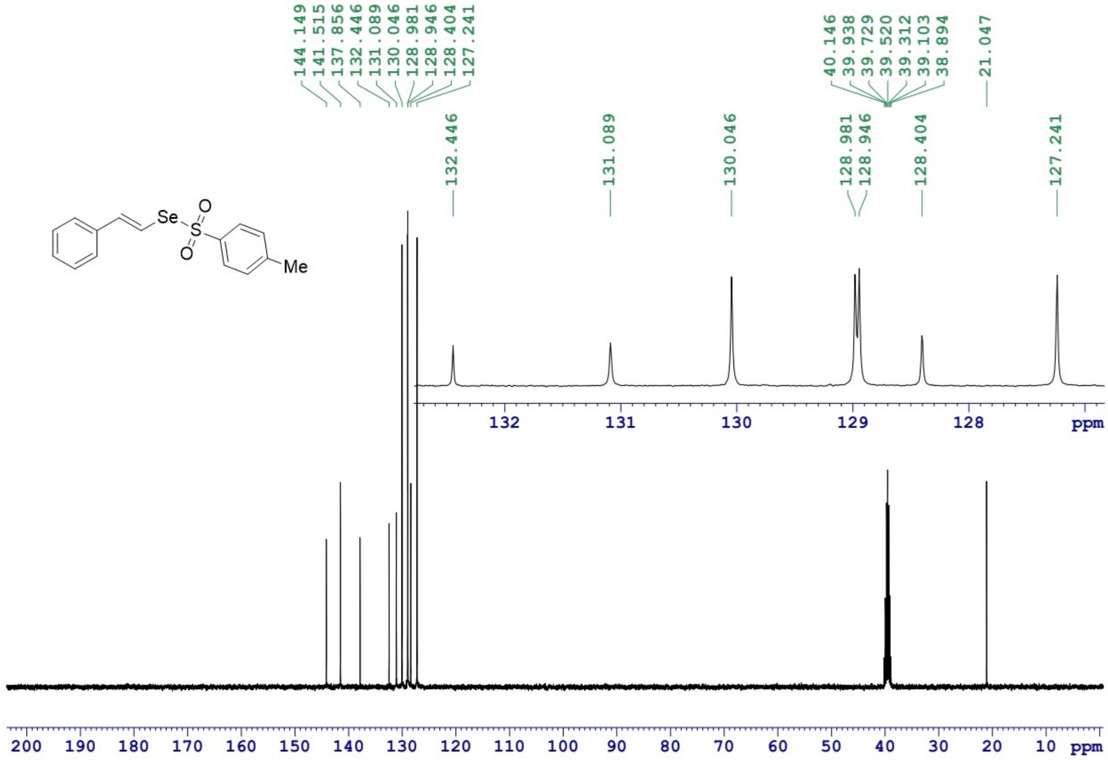
3aa-^{13}C NMR (100 MHz, DMSO-d_6)



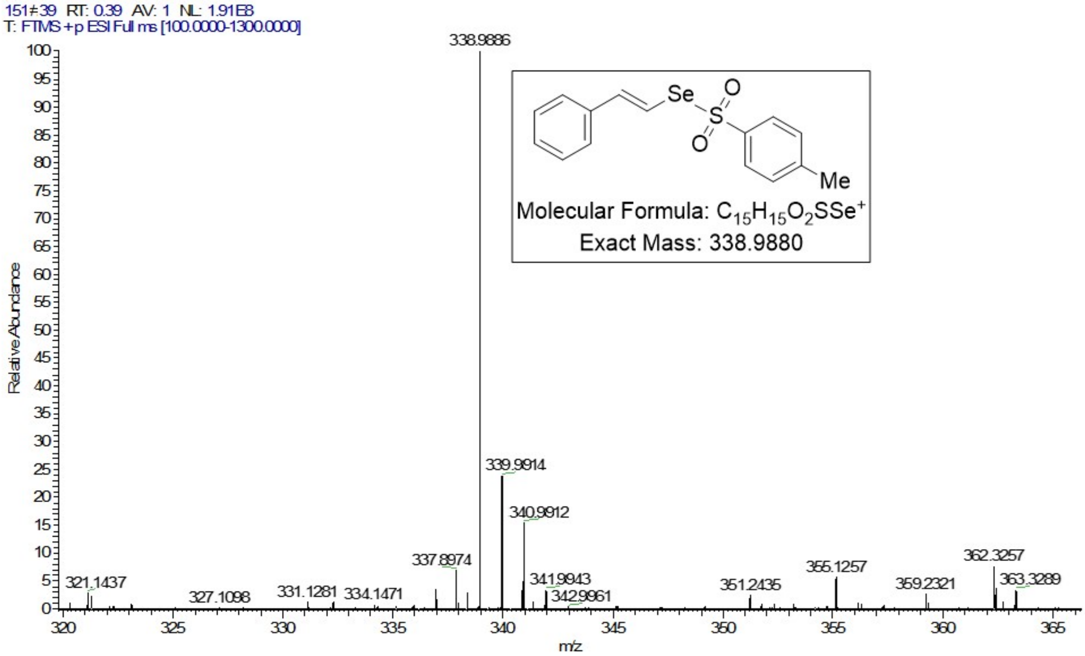
3aa-HRMS



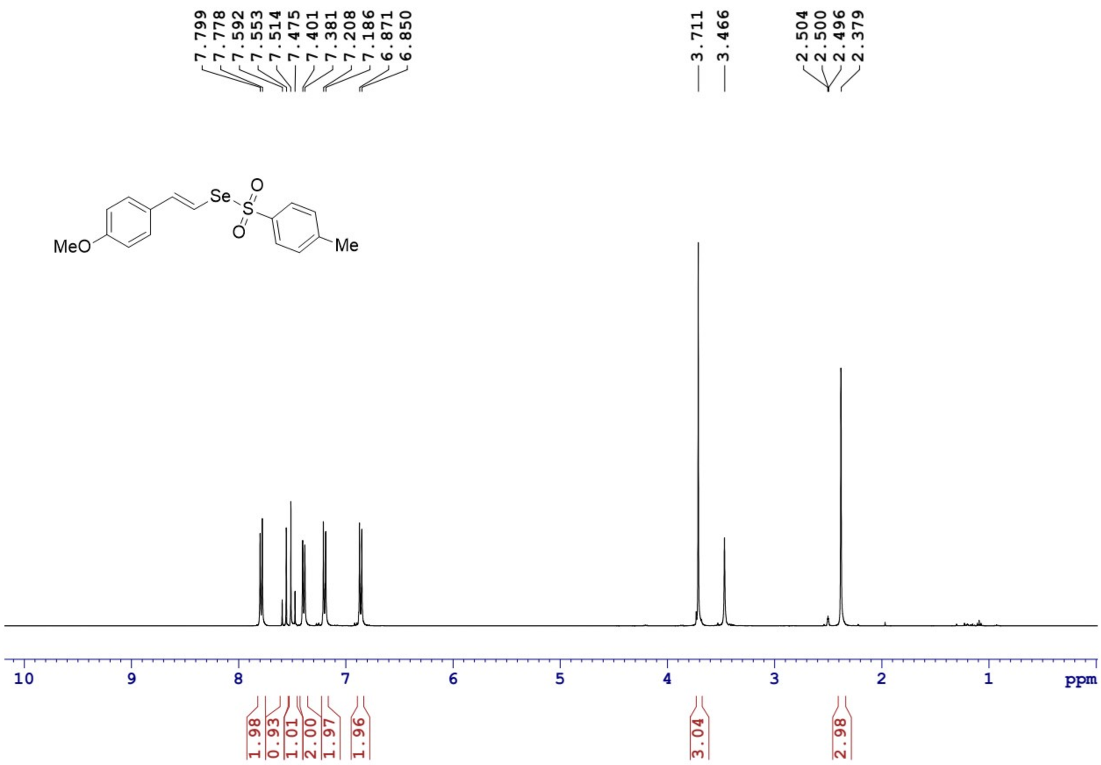
3ab-[1]H NMR (400 MHz, DMSO-d_6)



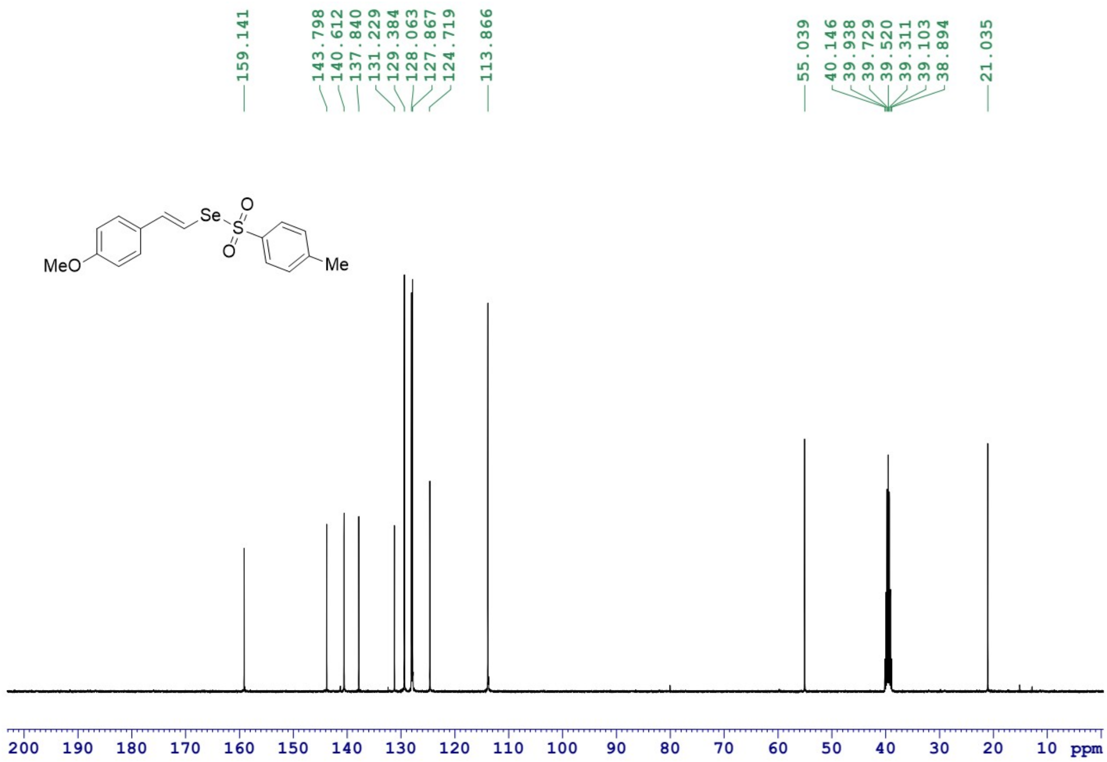
3ab-[13]C NMR (100 MHz, DMSO-d_6)



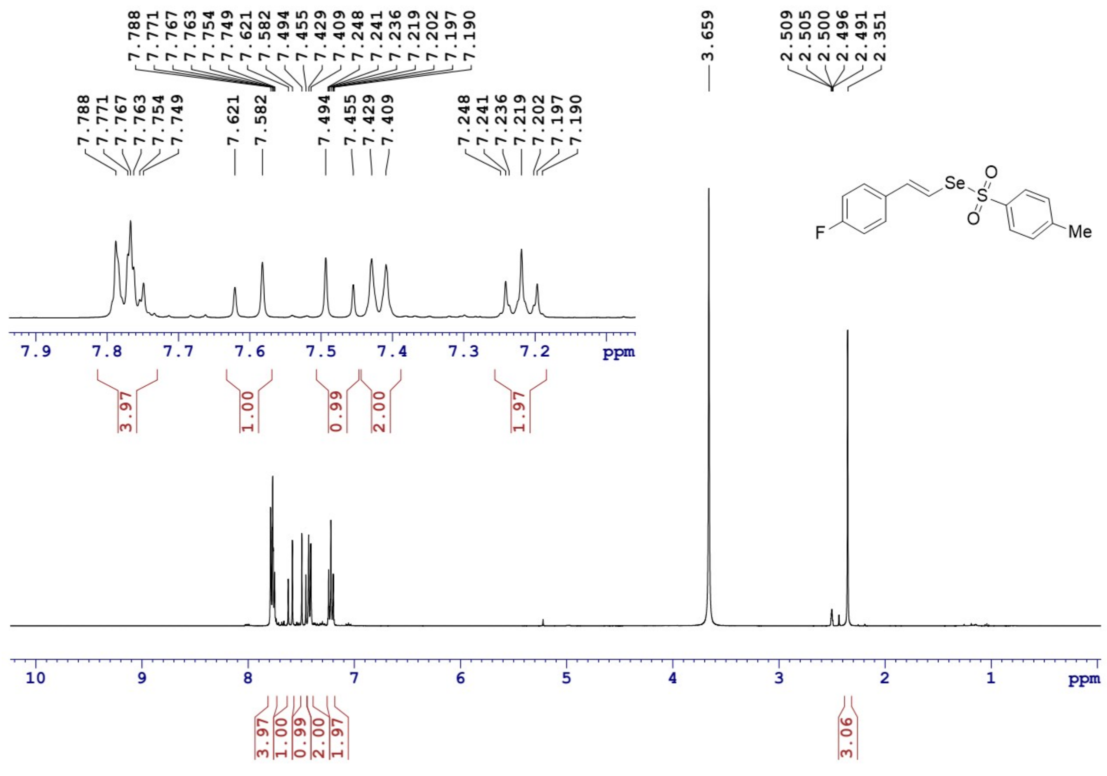
3ab-HRMS



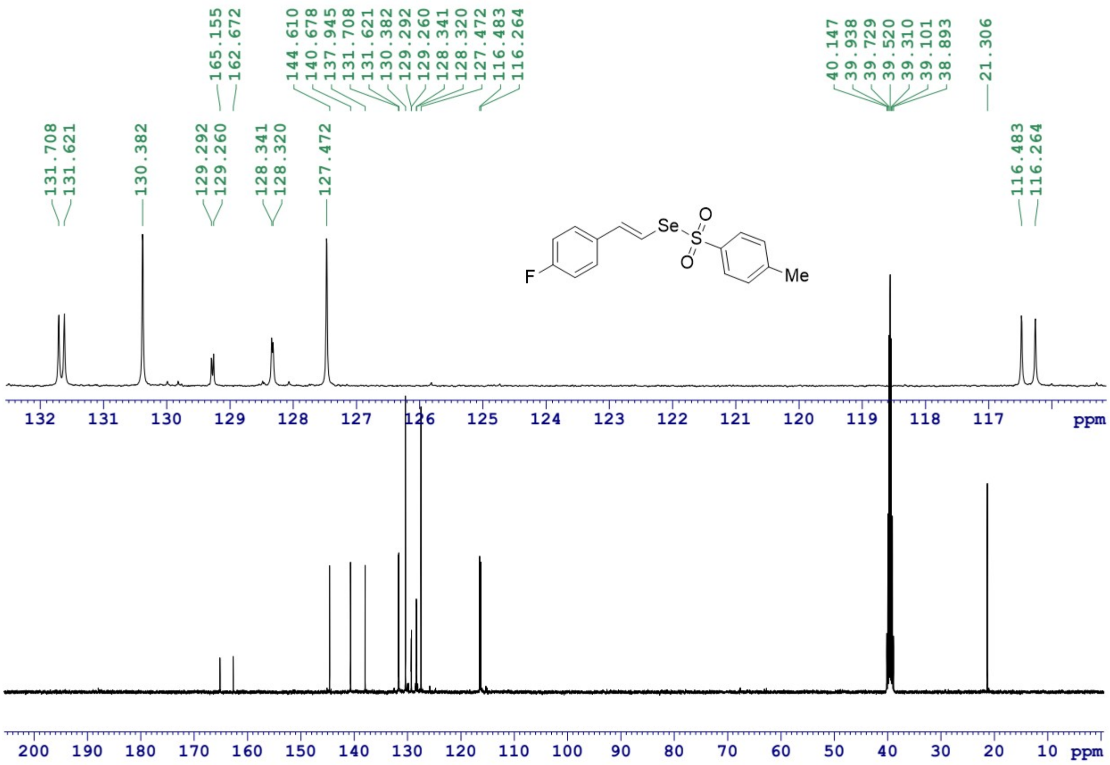
3ac-^{1}H NMR (400 MHz, DMSO-d_6)



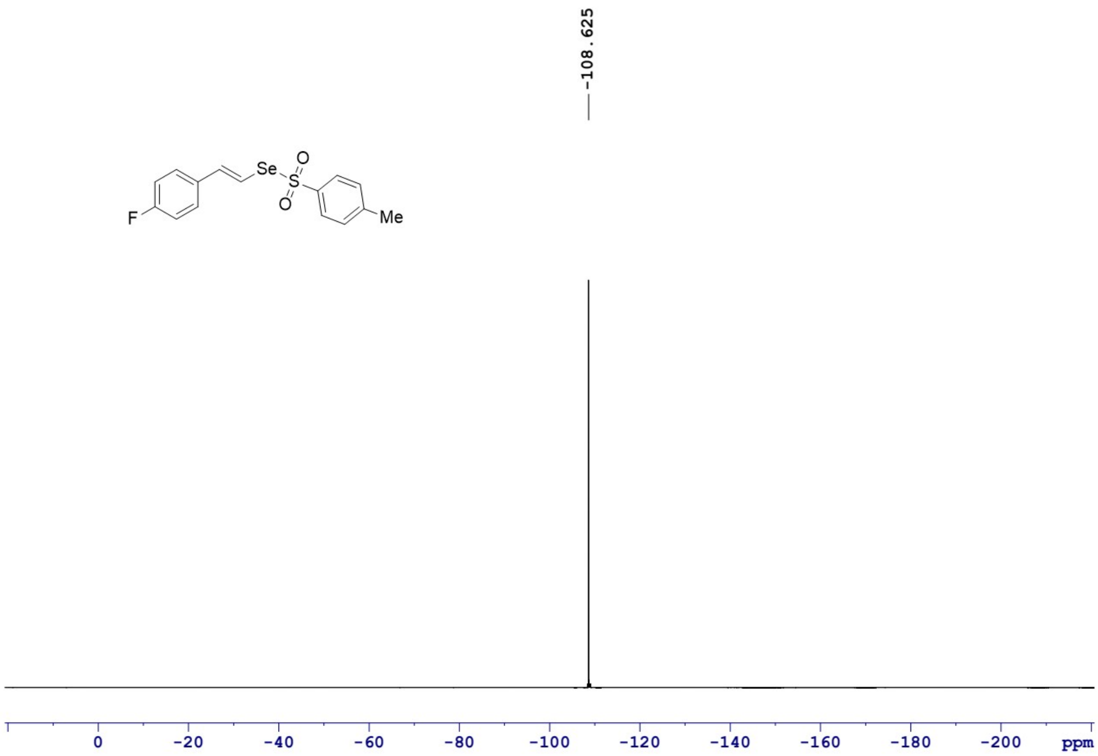
3ac-^{13}C NMR (100 MHz, DMSO-d_6)



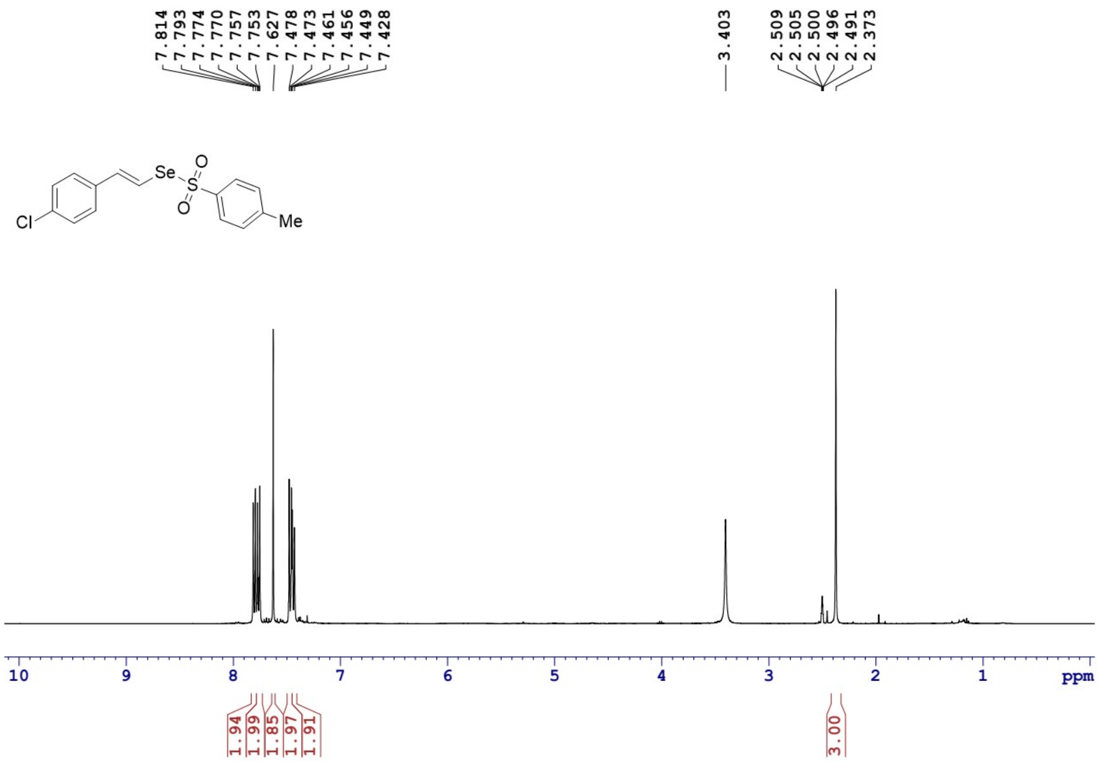
3ad-^{1}H NMR (400 MHz, DMSO-d_6)



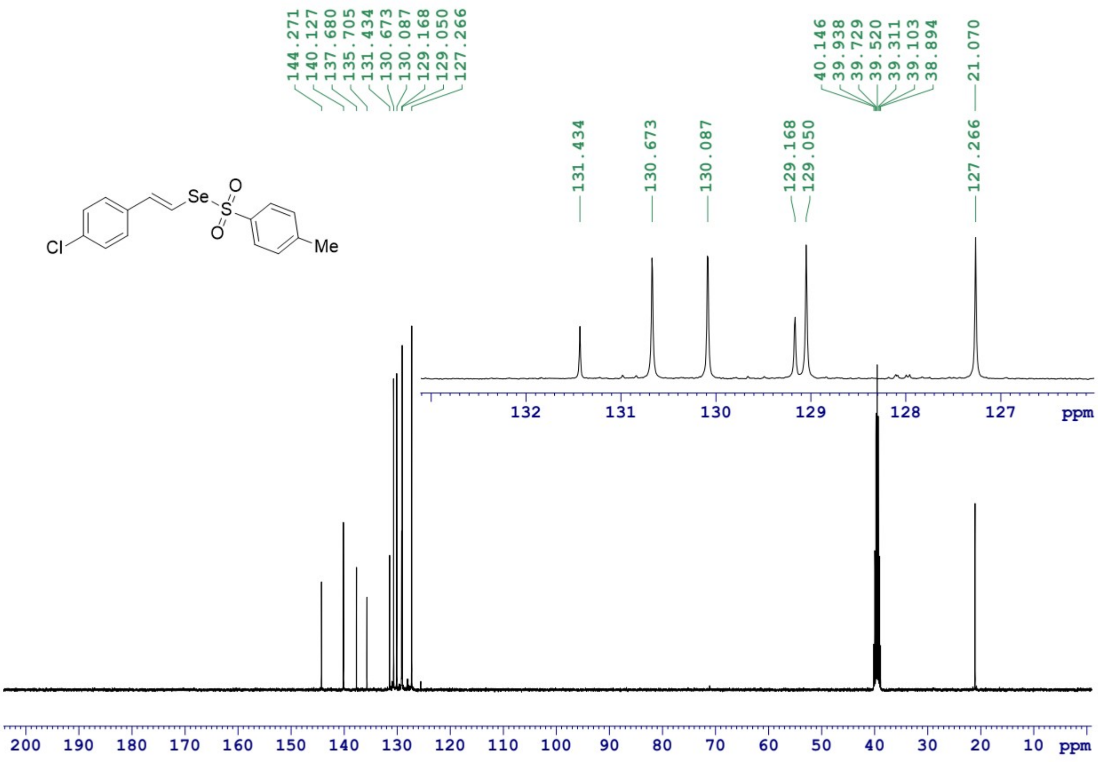
3ad-^{13}C NMR (100 MHz, DMSO-d_6)



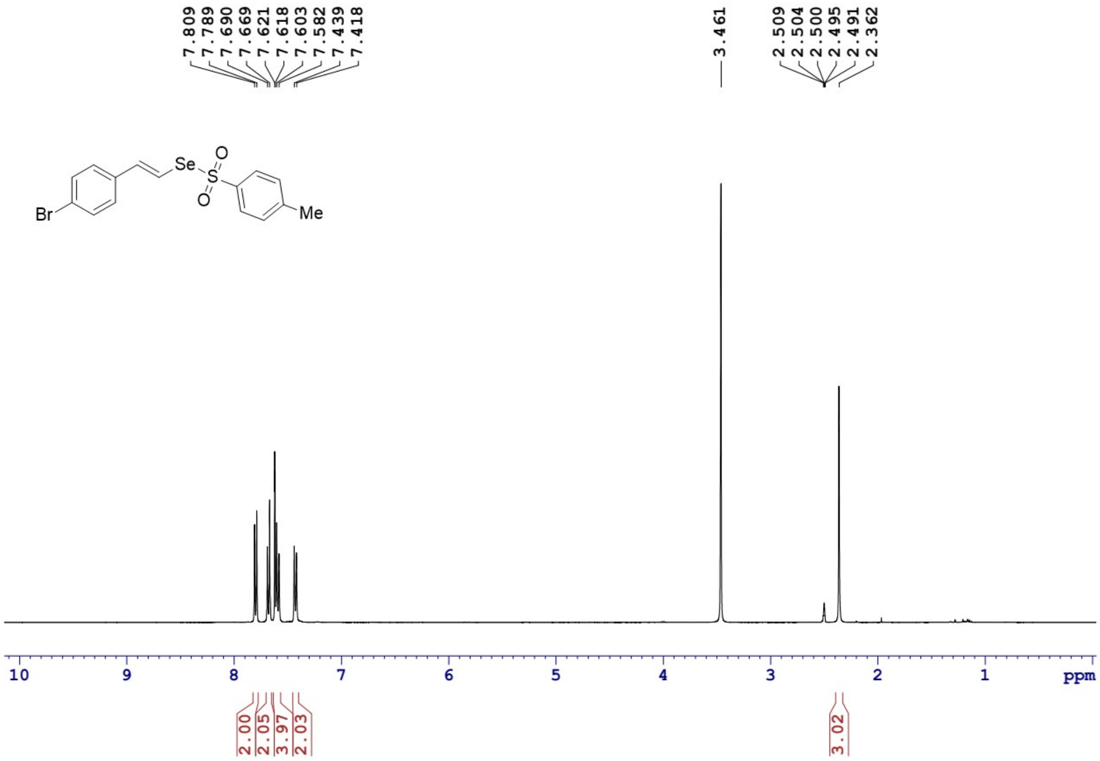
3ad-^{19}F NMR (376.8 MHz, DMSO-d_6)



3ae-^{1}H NMR (400 MHz, DMSO-d_6)



3ae-^{13}C NMR (100 MHz, DMSO-d_6)



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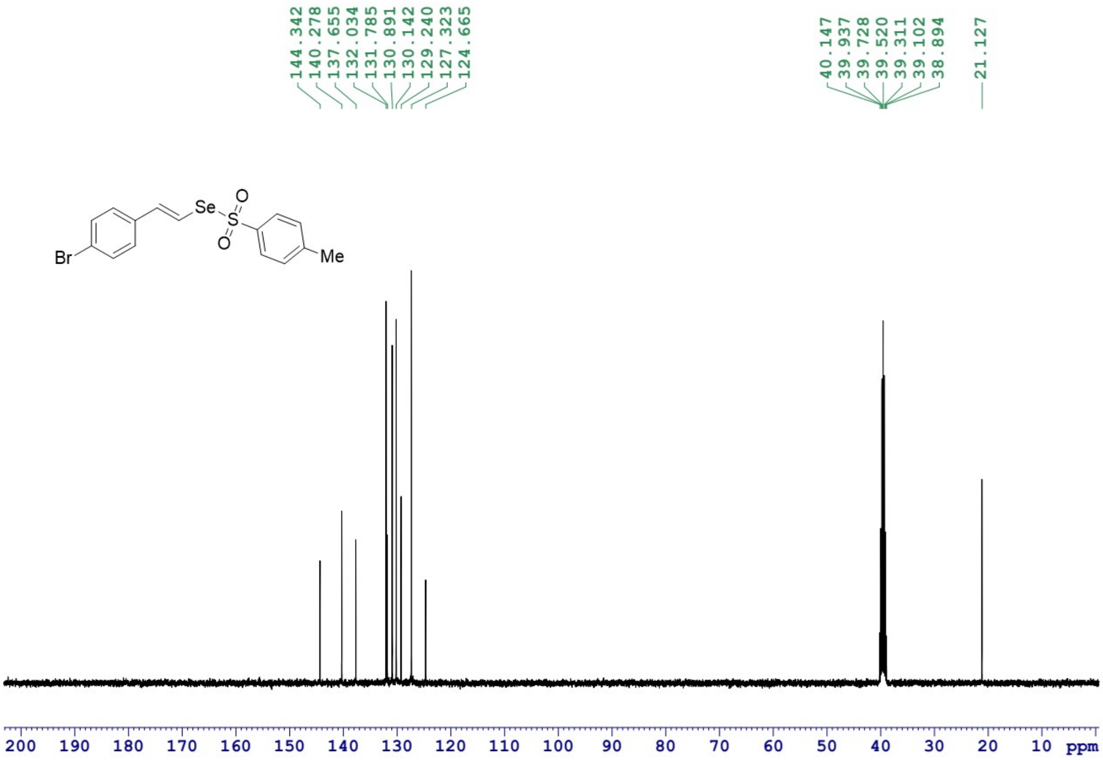

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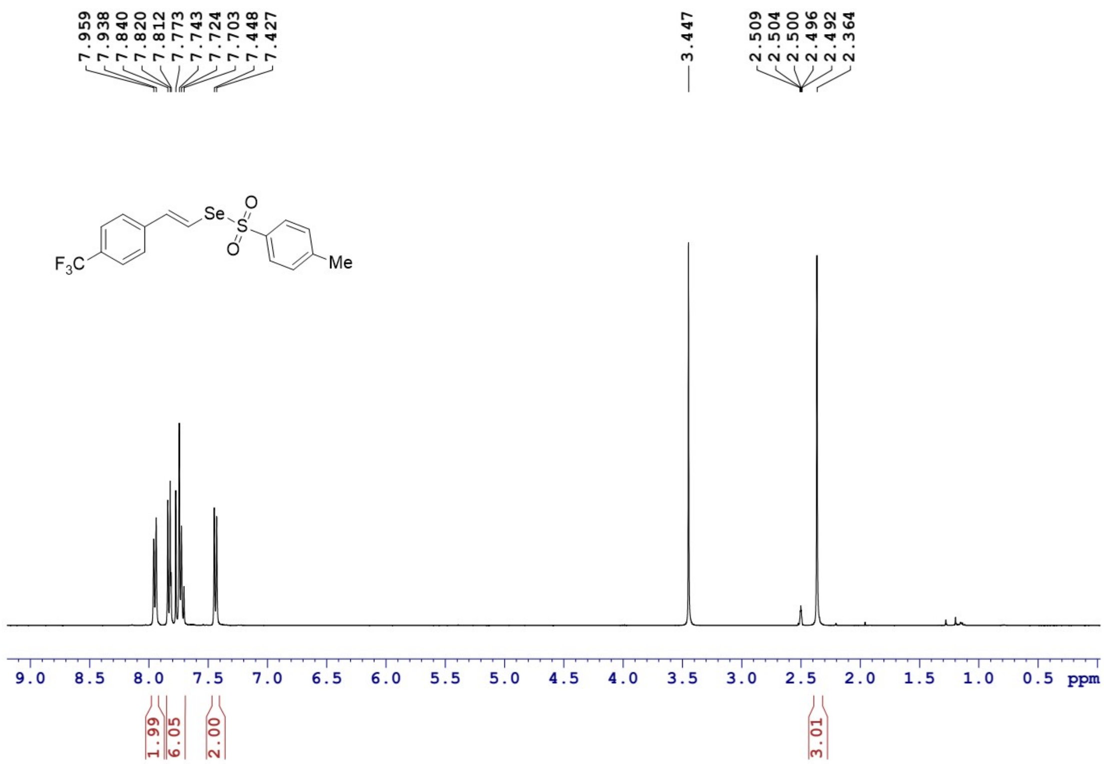
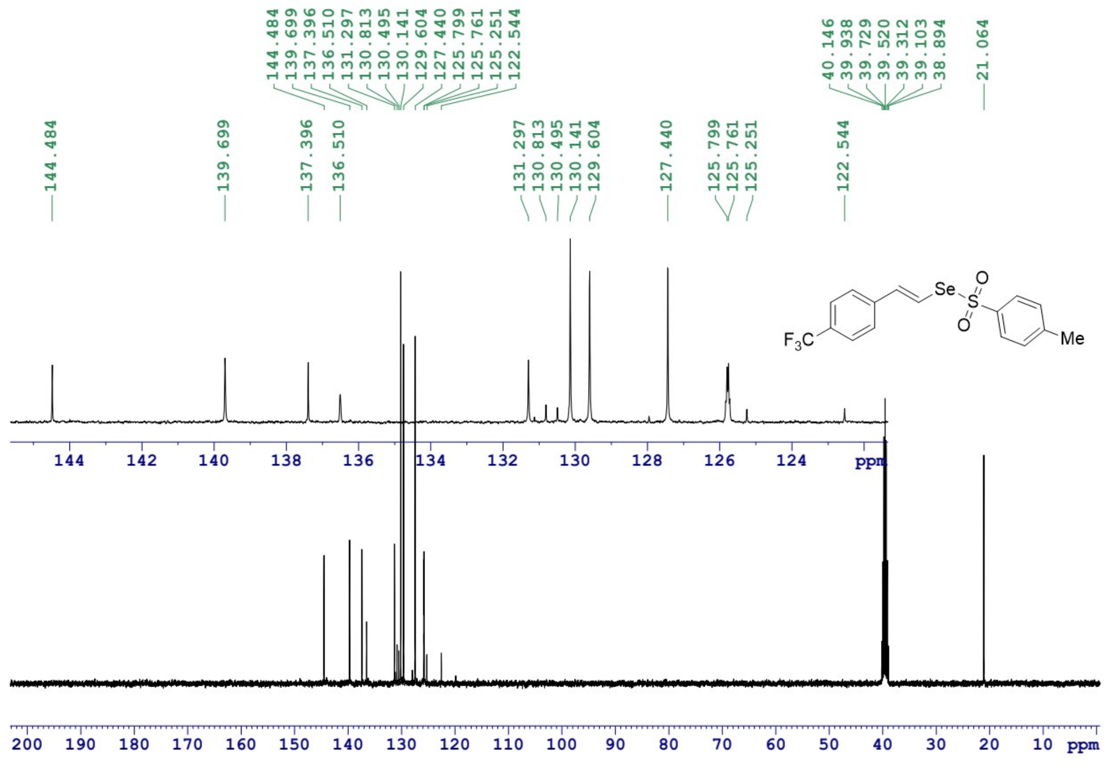


3ag-^{1}H NMR (400 MHz, DMSO-d_6)



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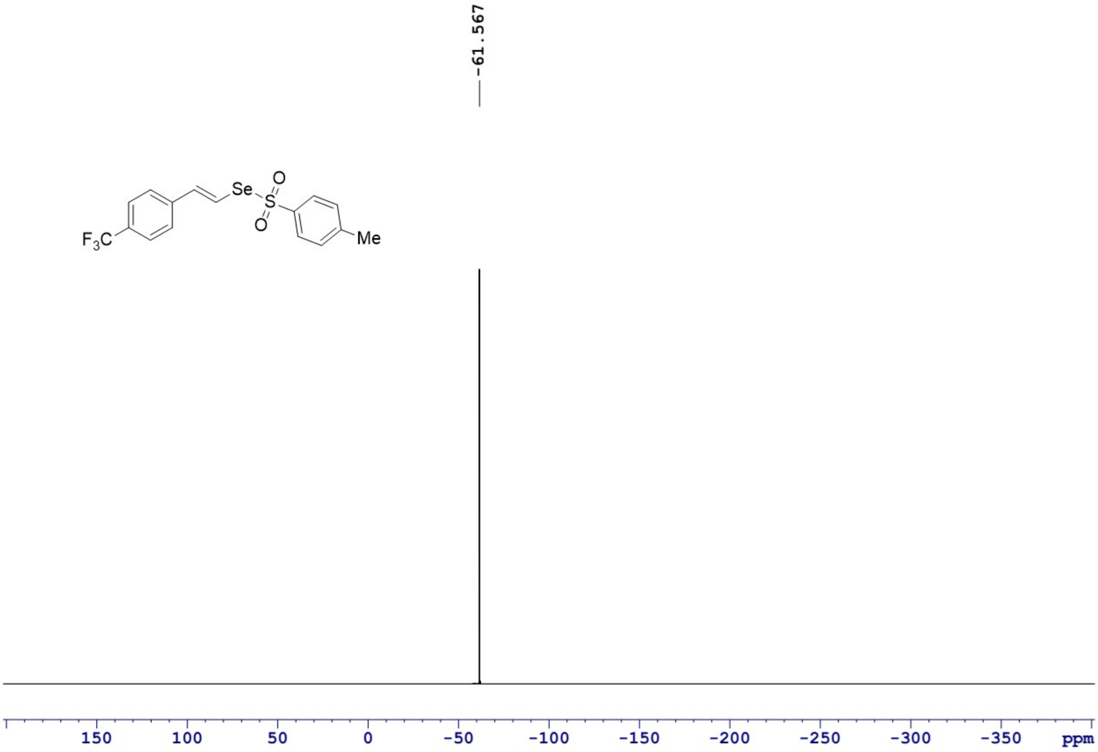
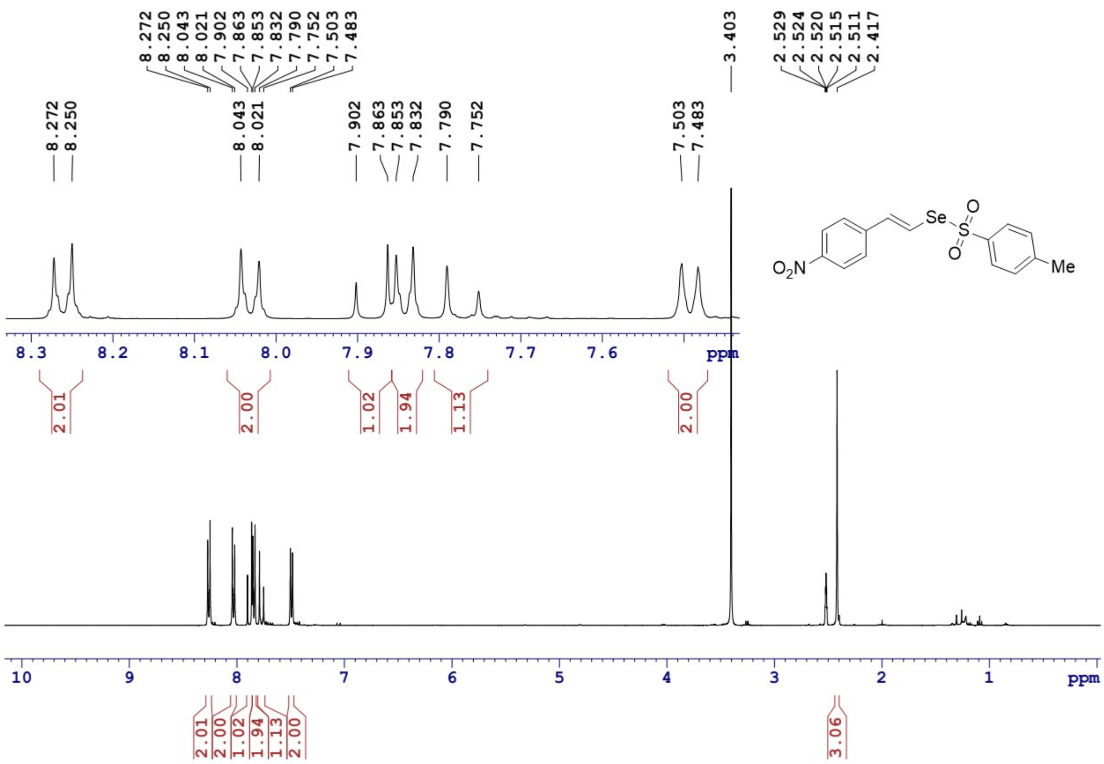
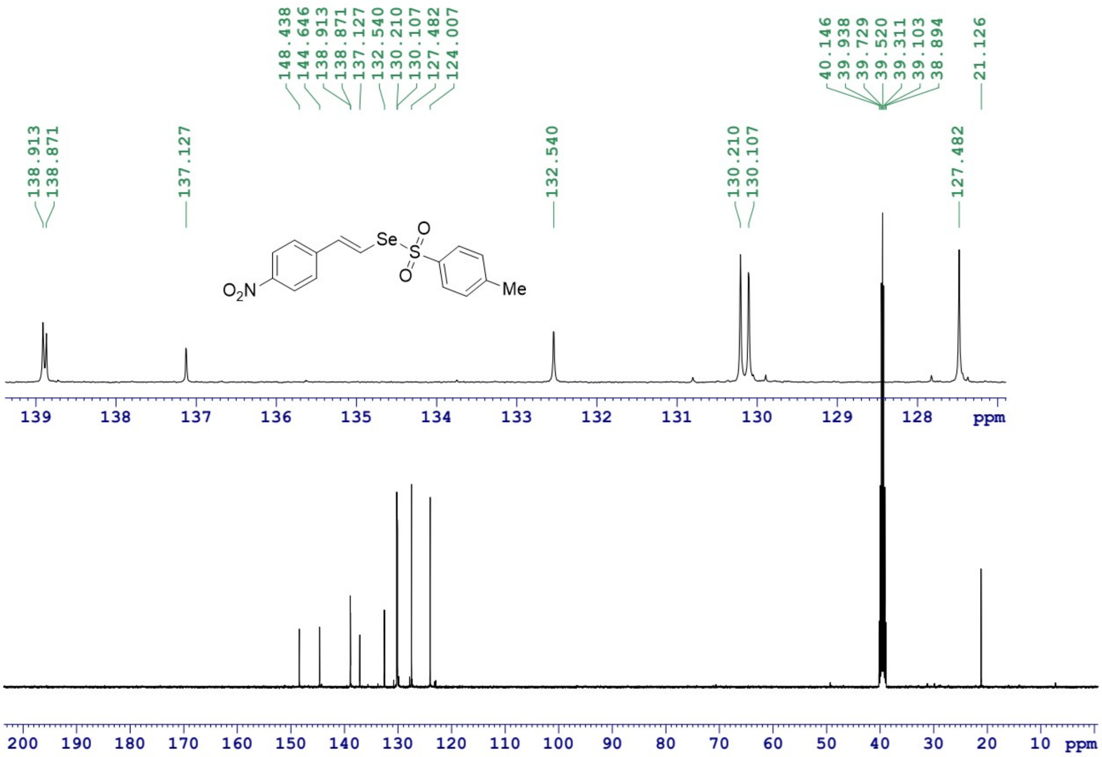


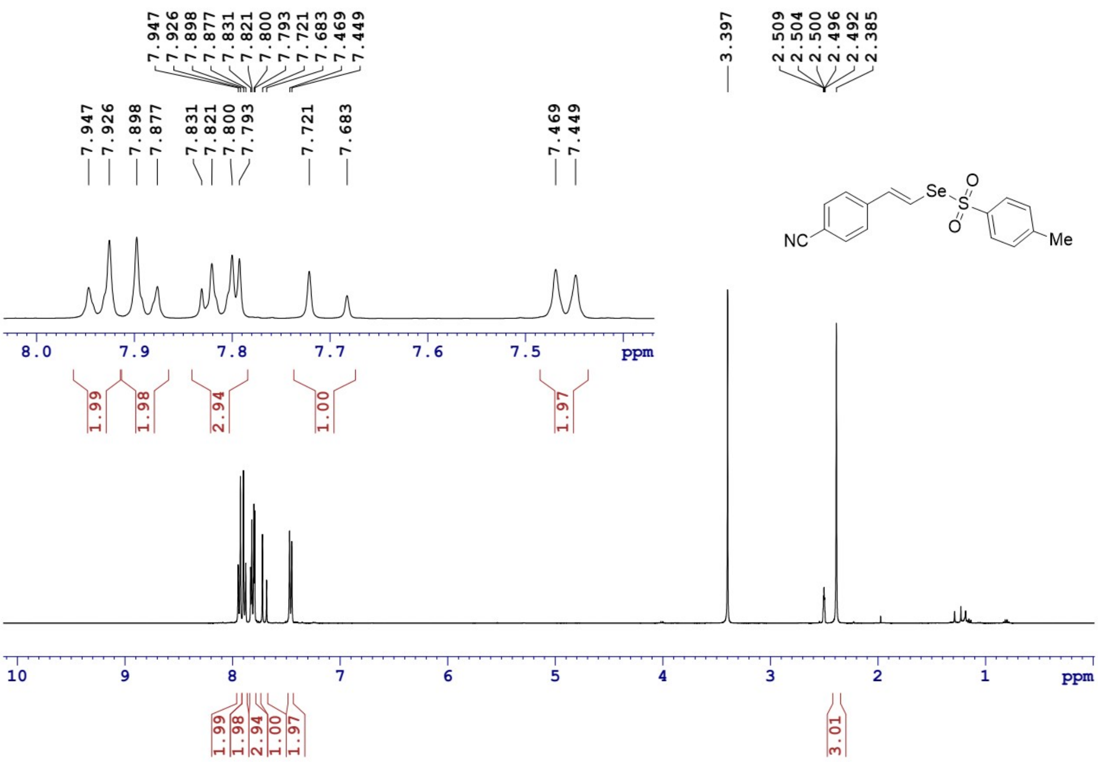
3ag-^{19}F NMR (376.8 MHz, DMSO-d_6)



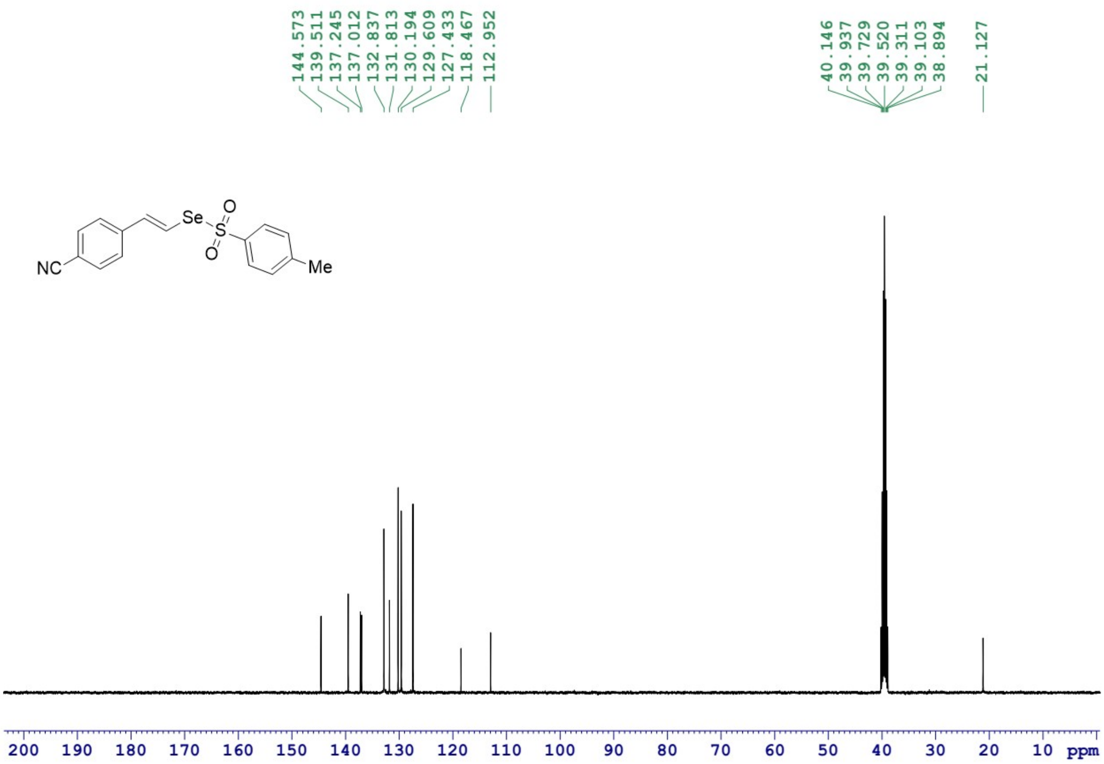
3ah-^{1}H NMR (400 MHz, DMSO-d_6)



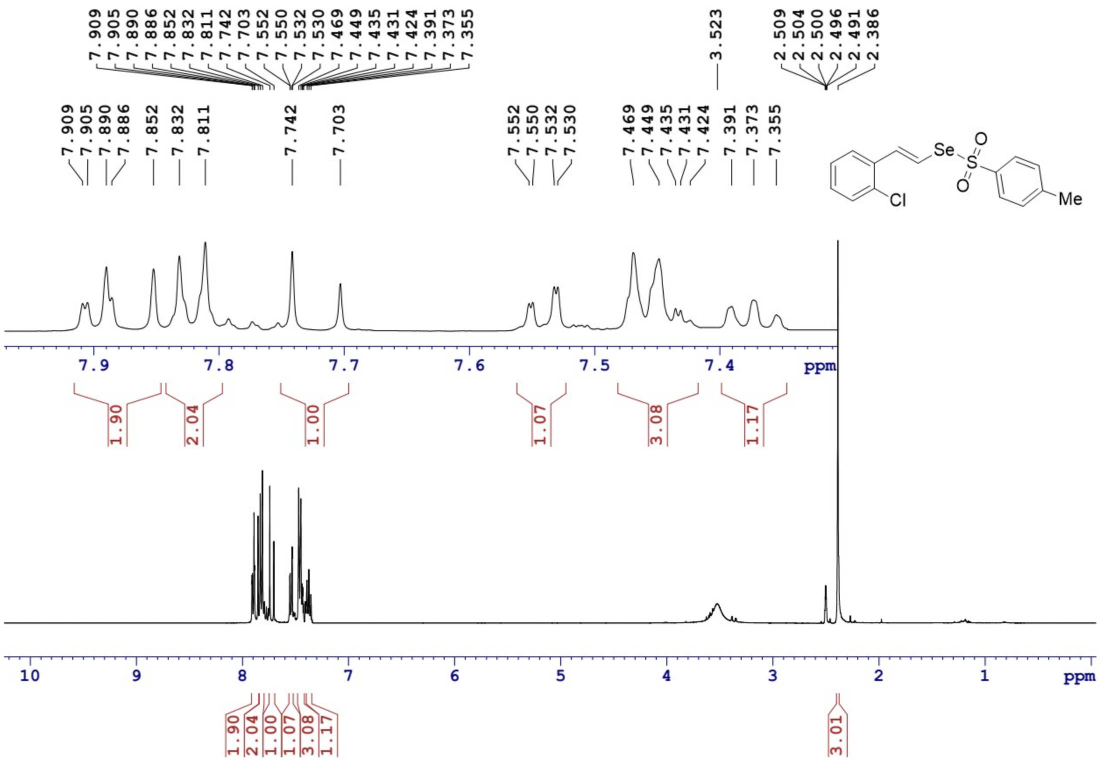
3ah-^{13}C NMR (100 MHz, DMSO-d_6)



3ai-^{1}H NMR (400 MHz, DMSO-d_6)



3ai-[13]C NMR (100 MHz, DMSO-d_6)



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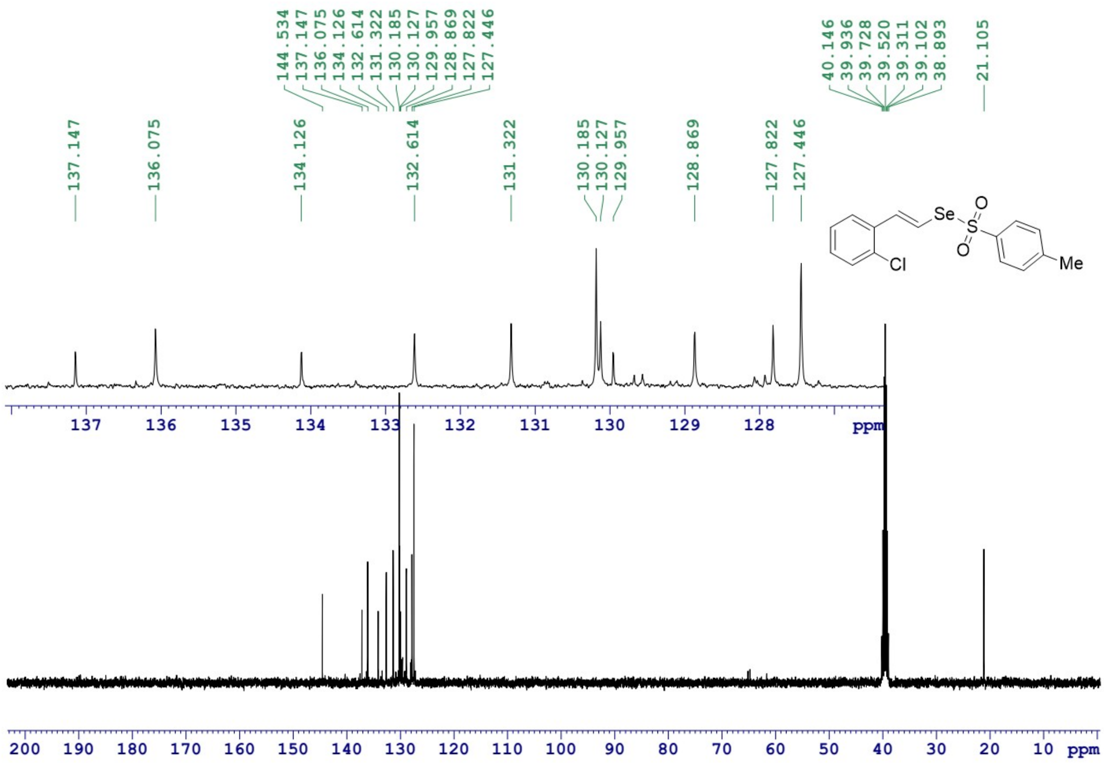

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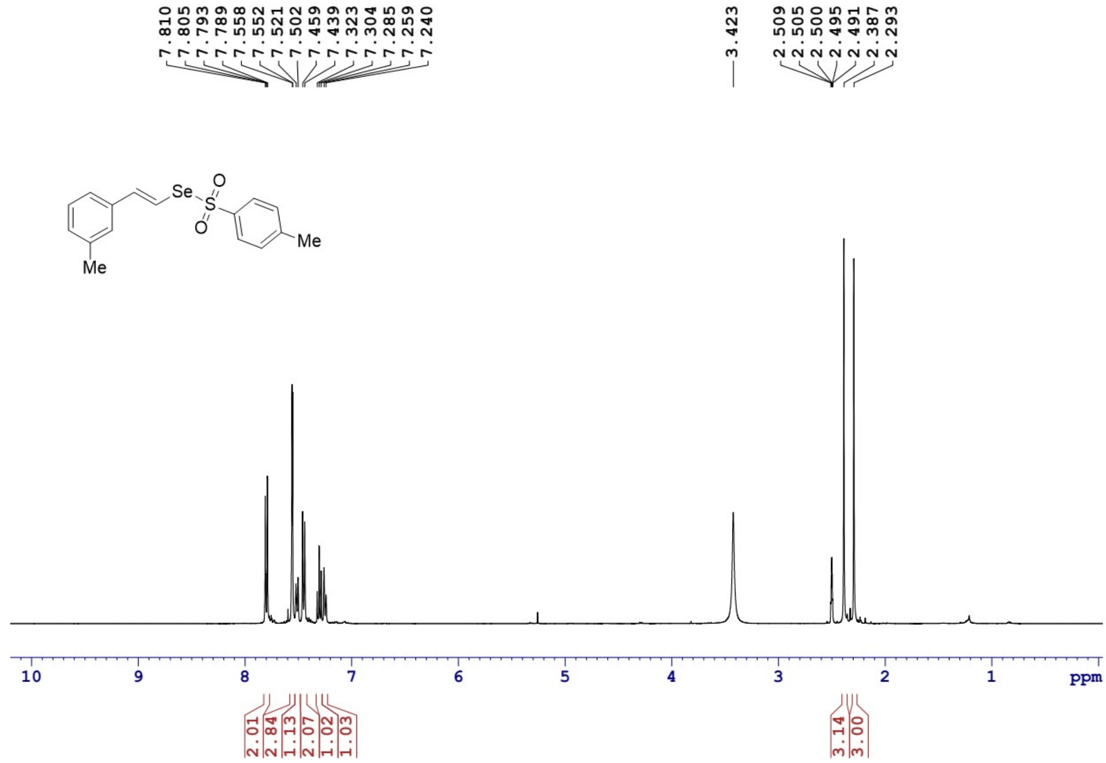

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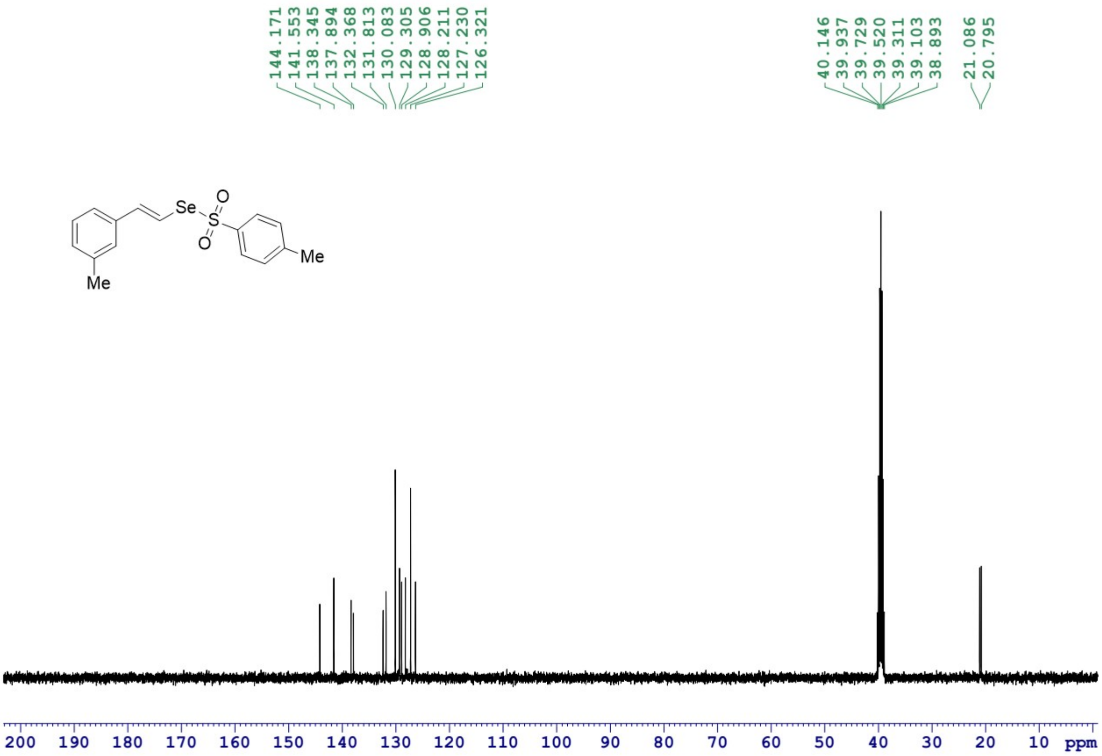
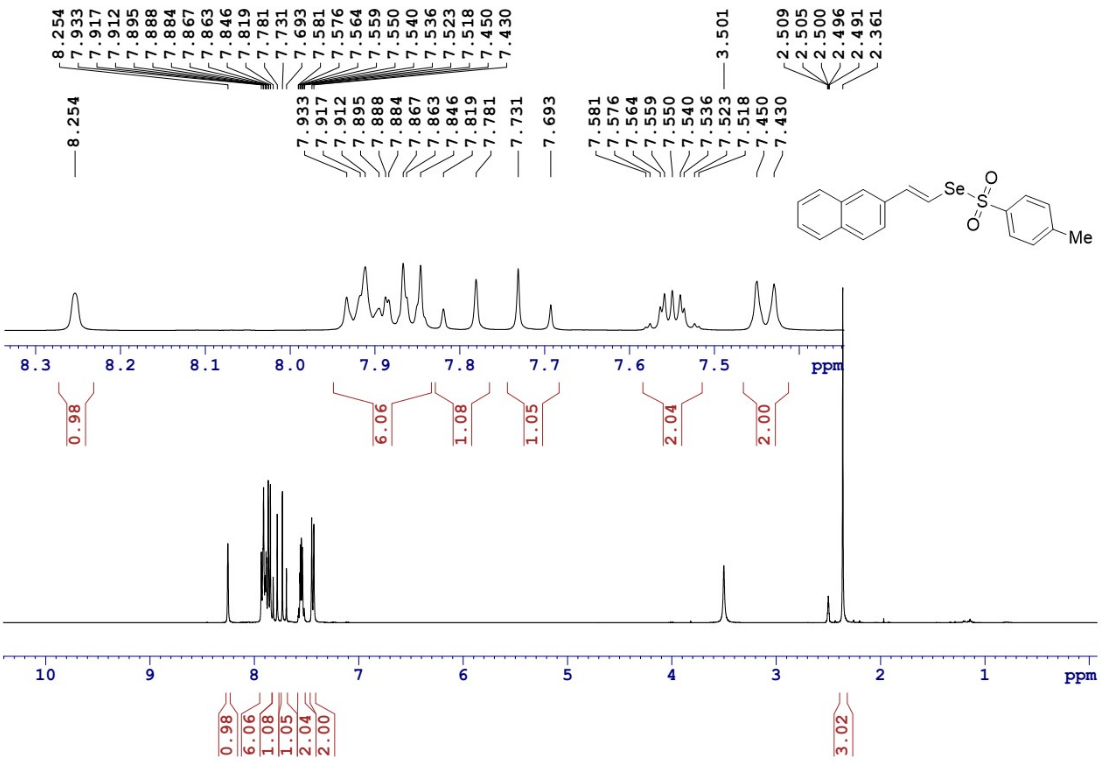
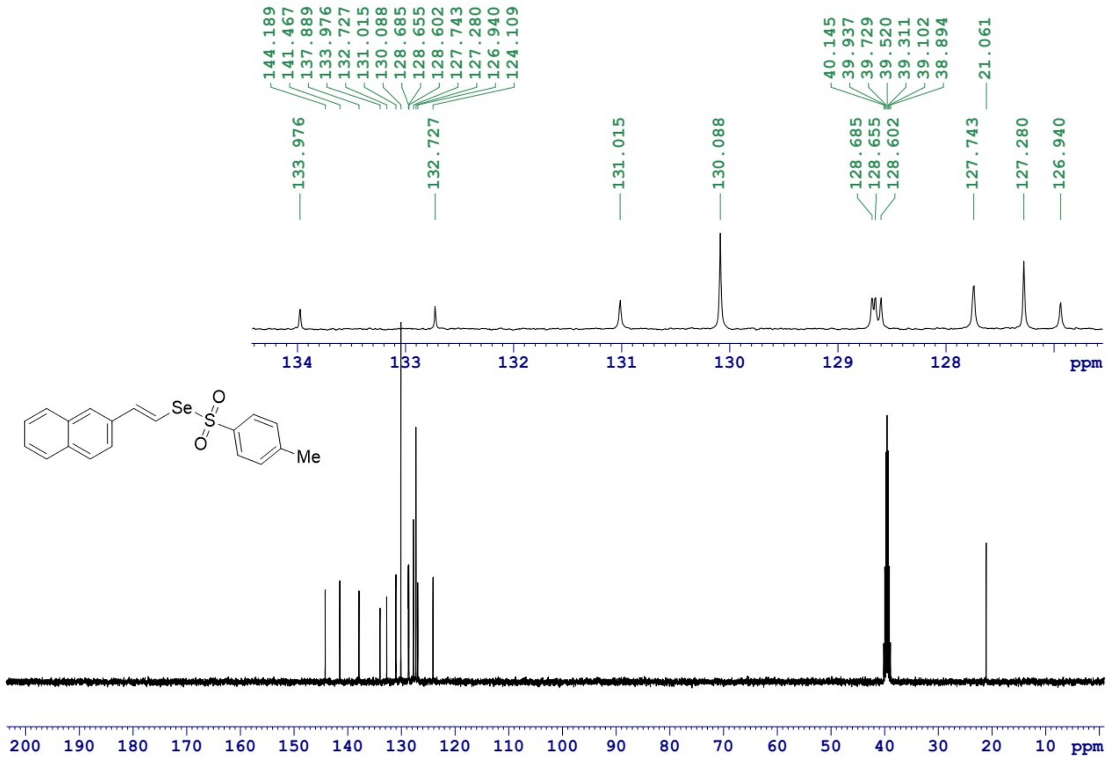


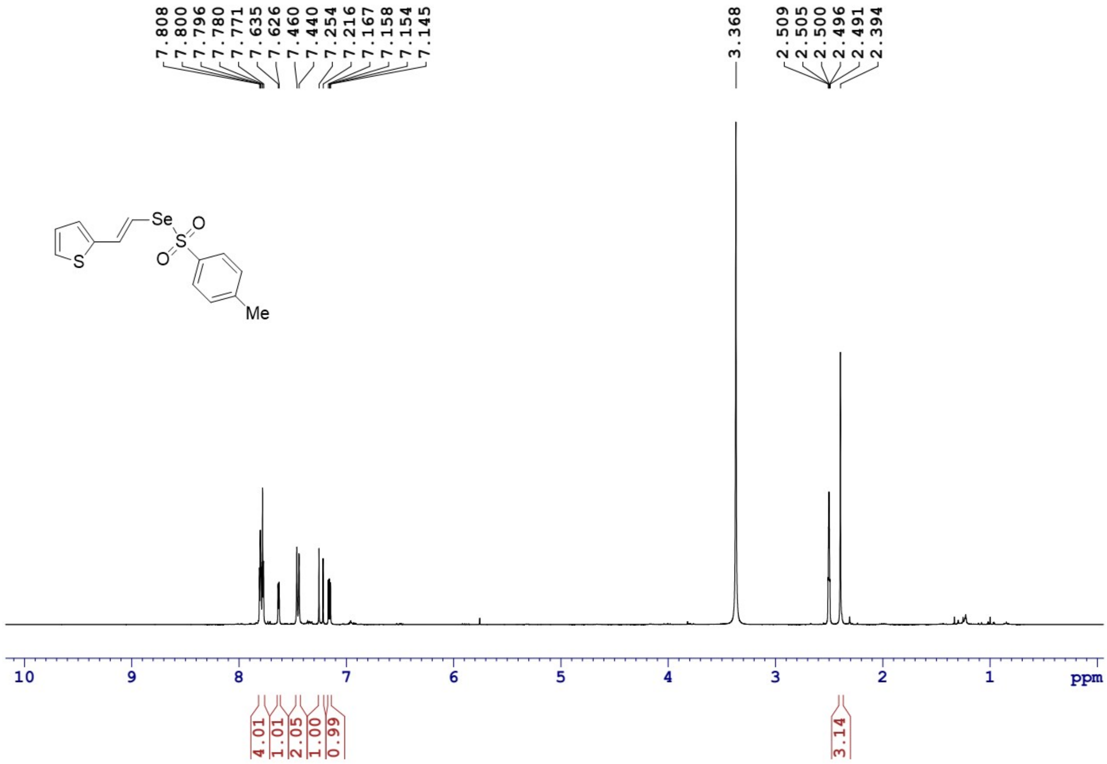
3ak-[13]C NMR (100 MHz, DMSO-d_6)



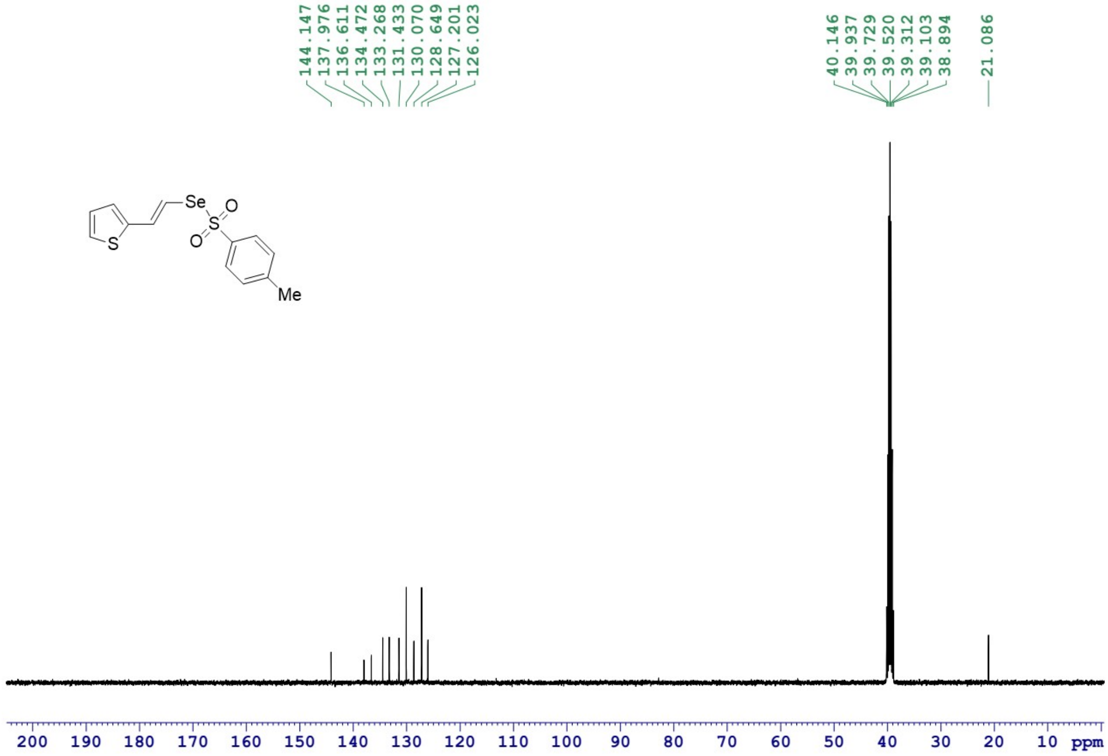
3al-[1]H NMR (400 MHz, DMSO-d_6)



3al-^{13}C NMR (100 MHz, DMSO-d_6)



3am-^{13}C NMR (100 MHz, DMSO-d_6)



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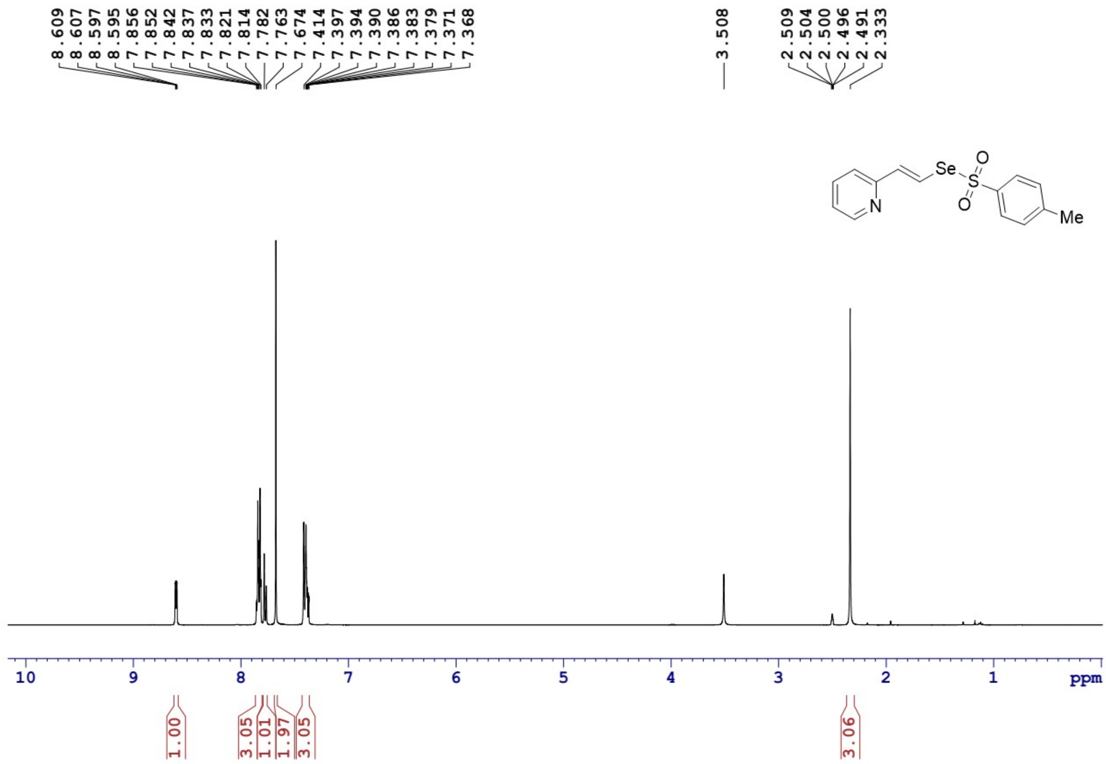

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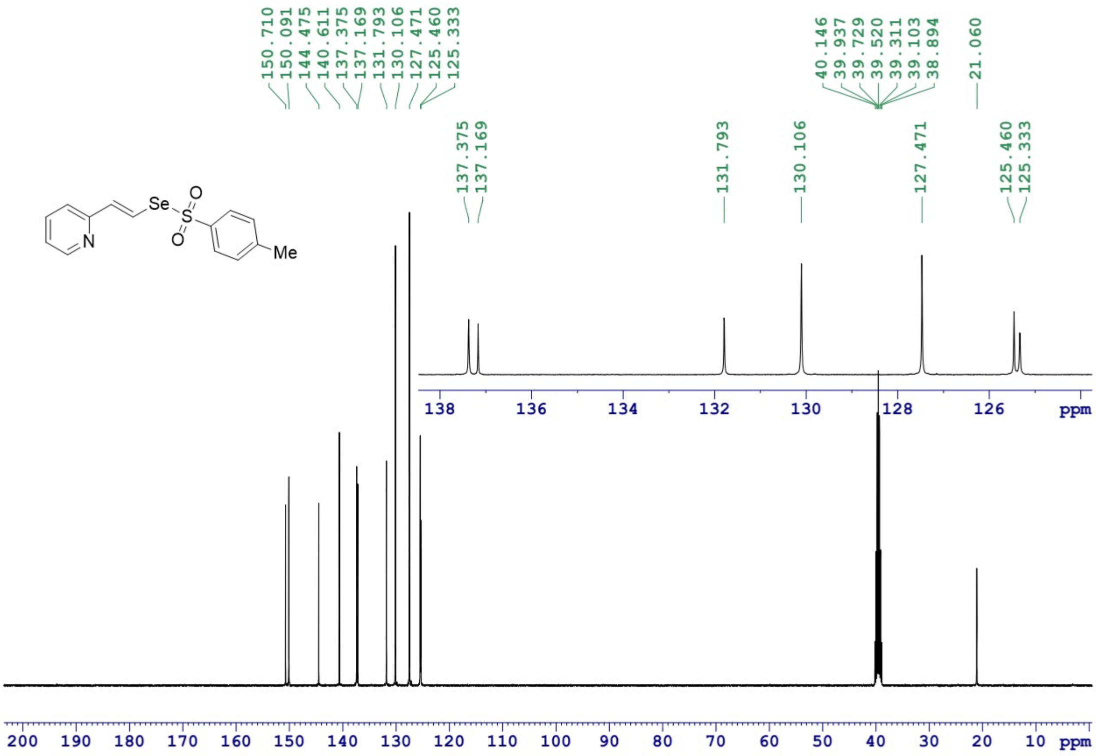

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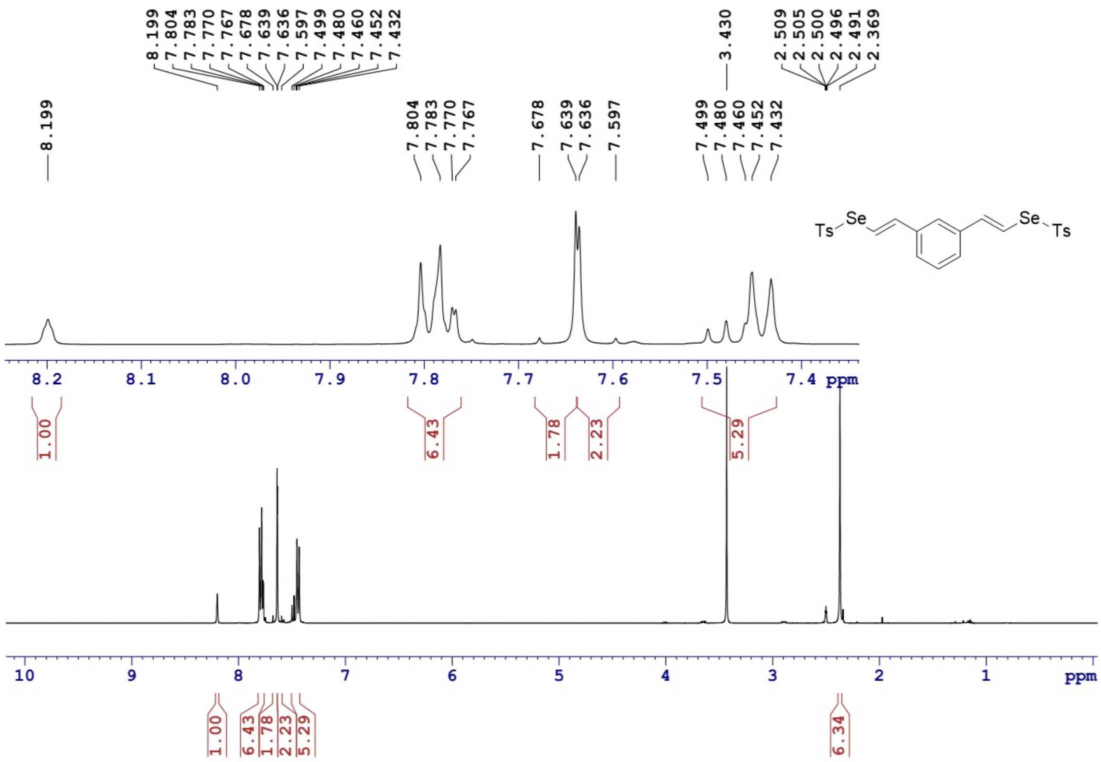

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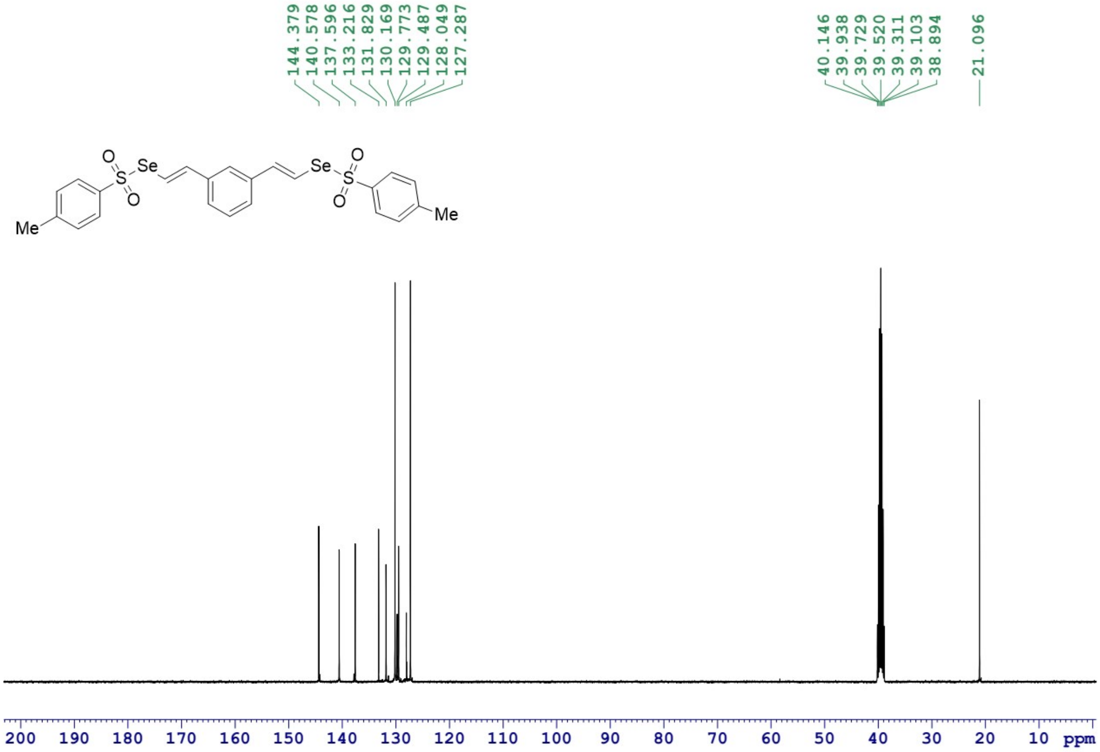
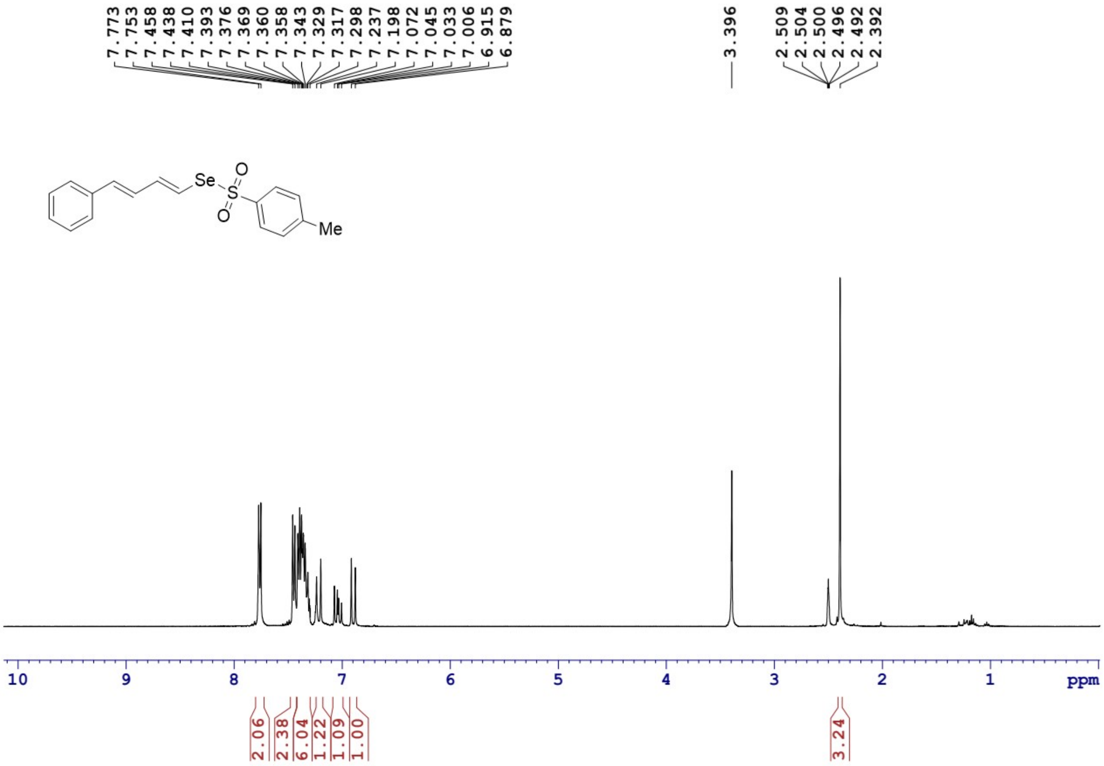
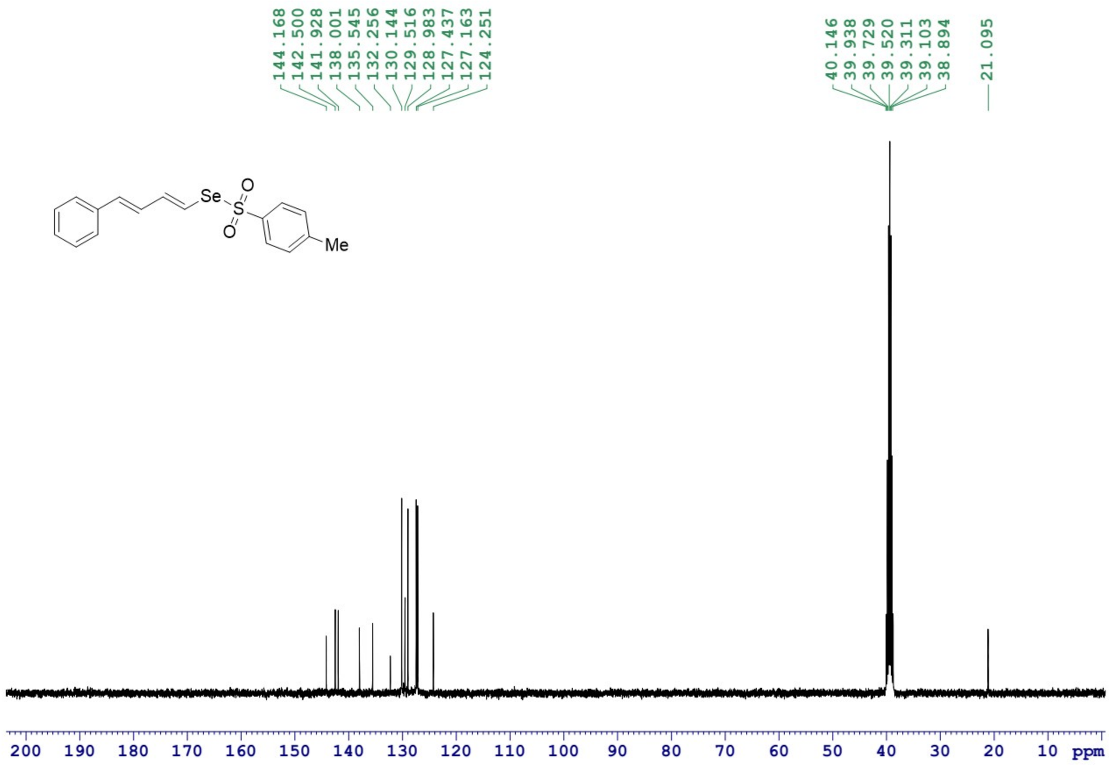


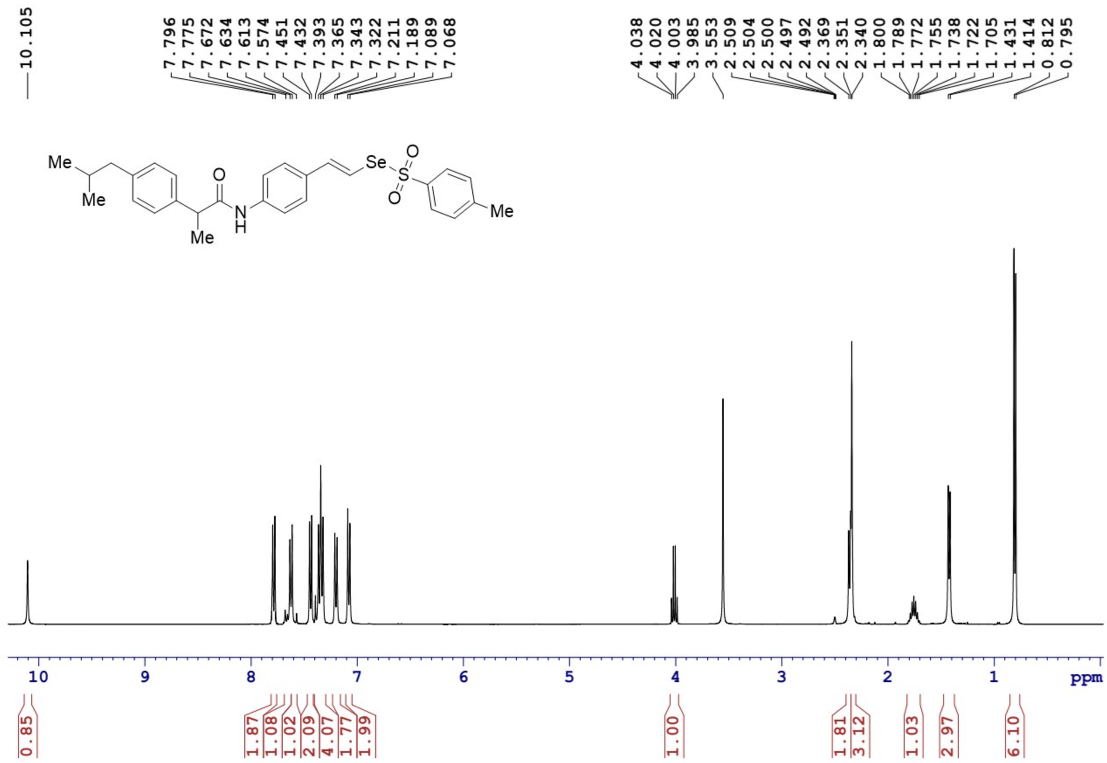
3ao-^{13}C NMR (100 MHz, DMSO-d_6)



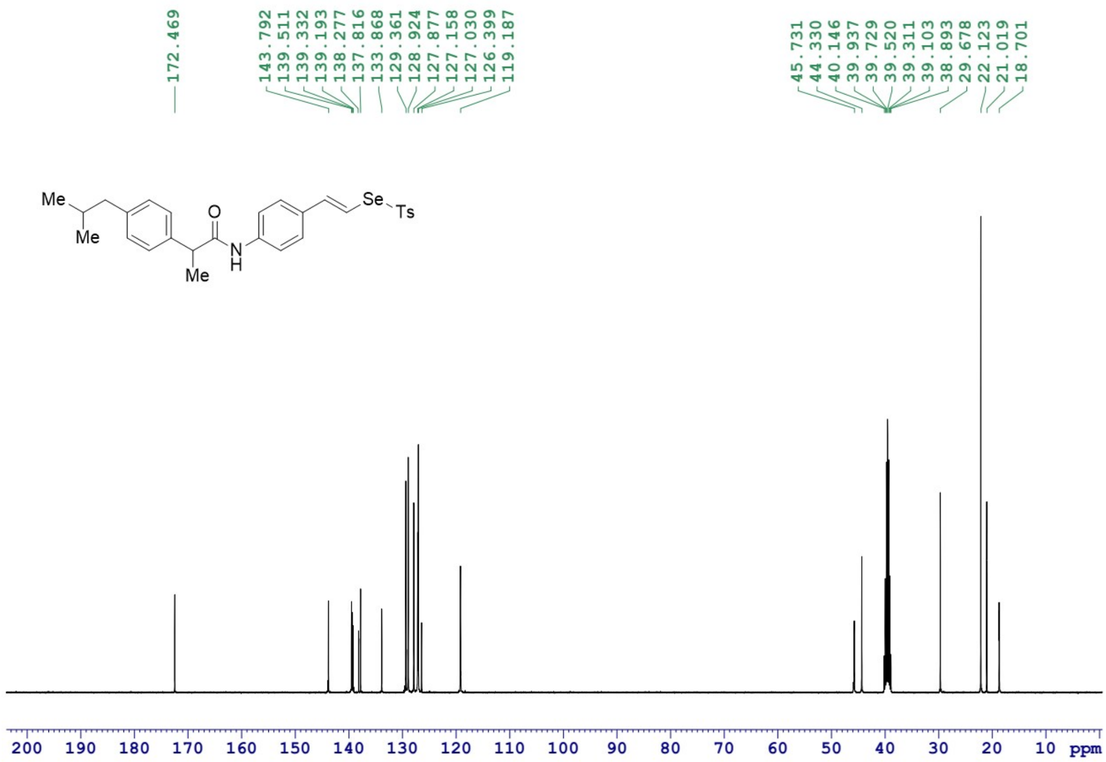
3ap-^{1}H NMR (400 MHz, DMSO-d_6)



3ap-^{13}C NMR (100 MHz, DMSO-d_6)



3aq-^{1}H NMR (400 MHz, DMSO-d_6)



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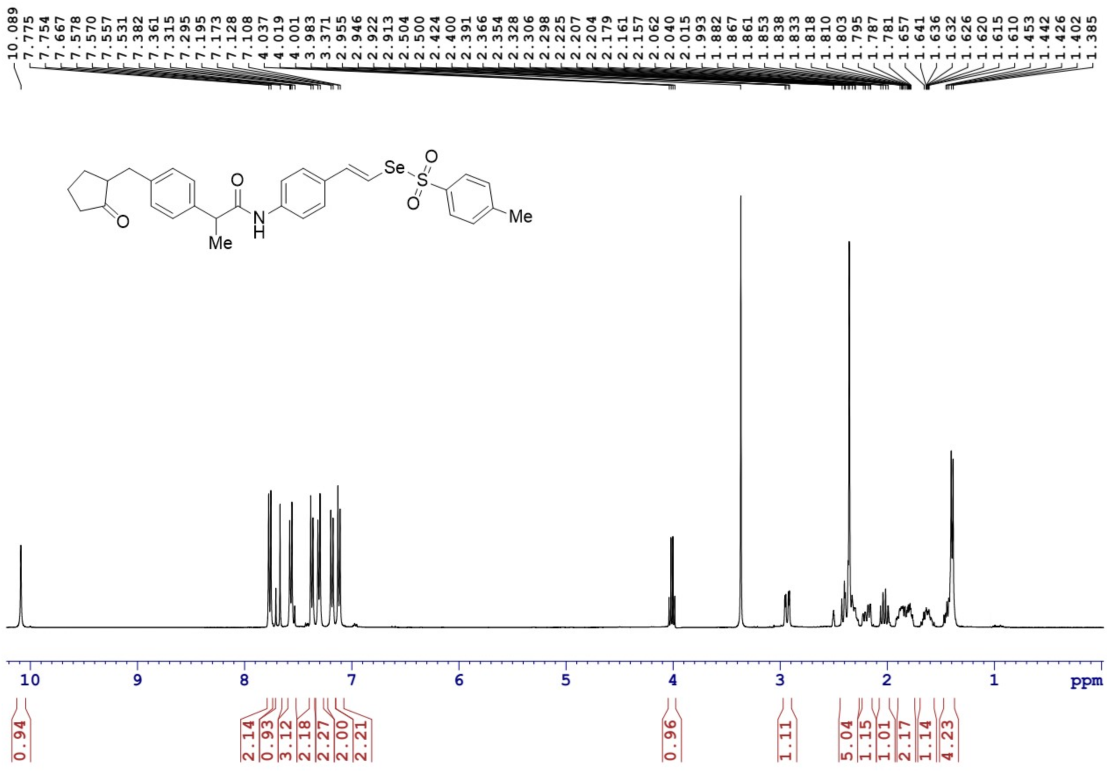
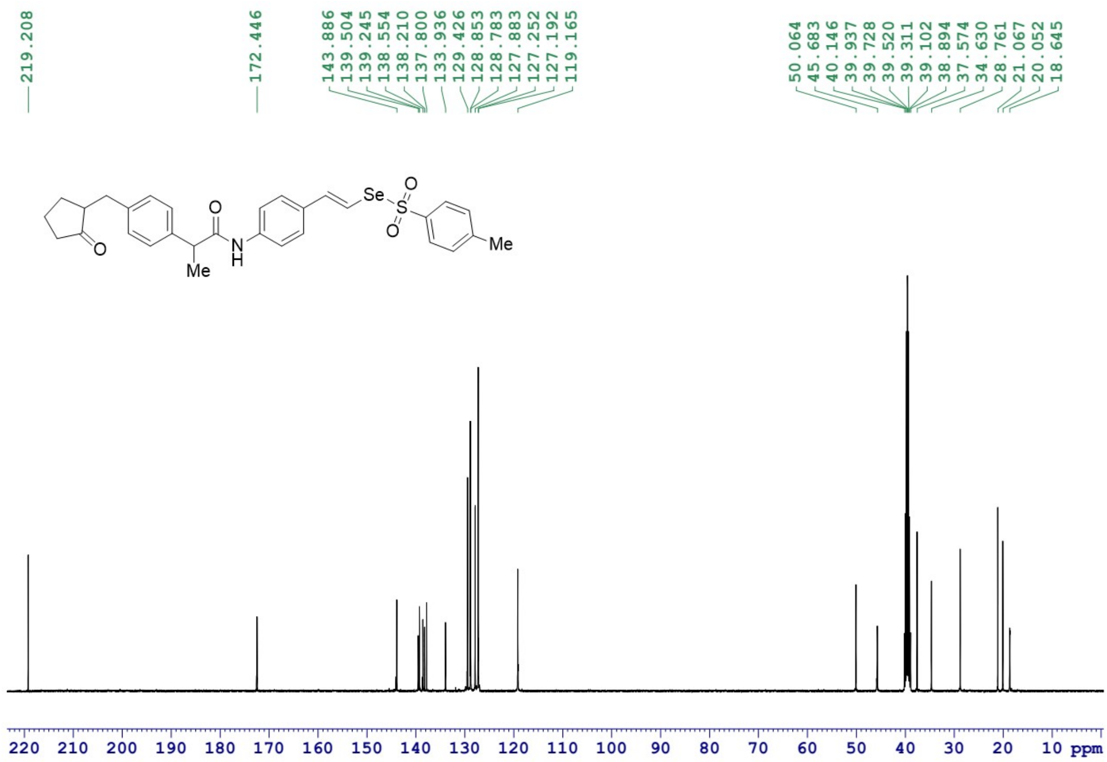


3ar-^{1}H NMR (400 MHz, DMSO-d_6)



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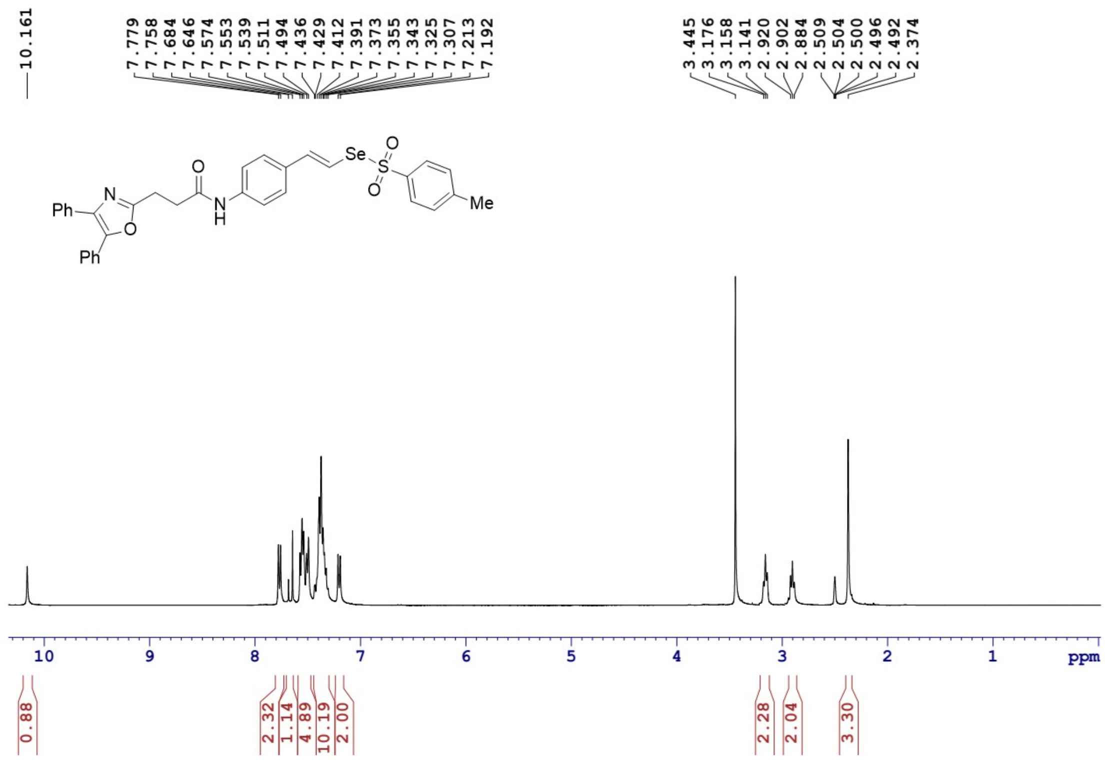

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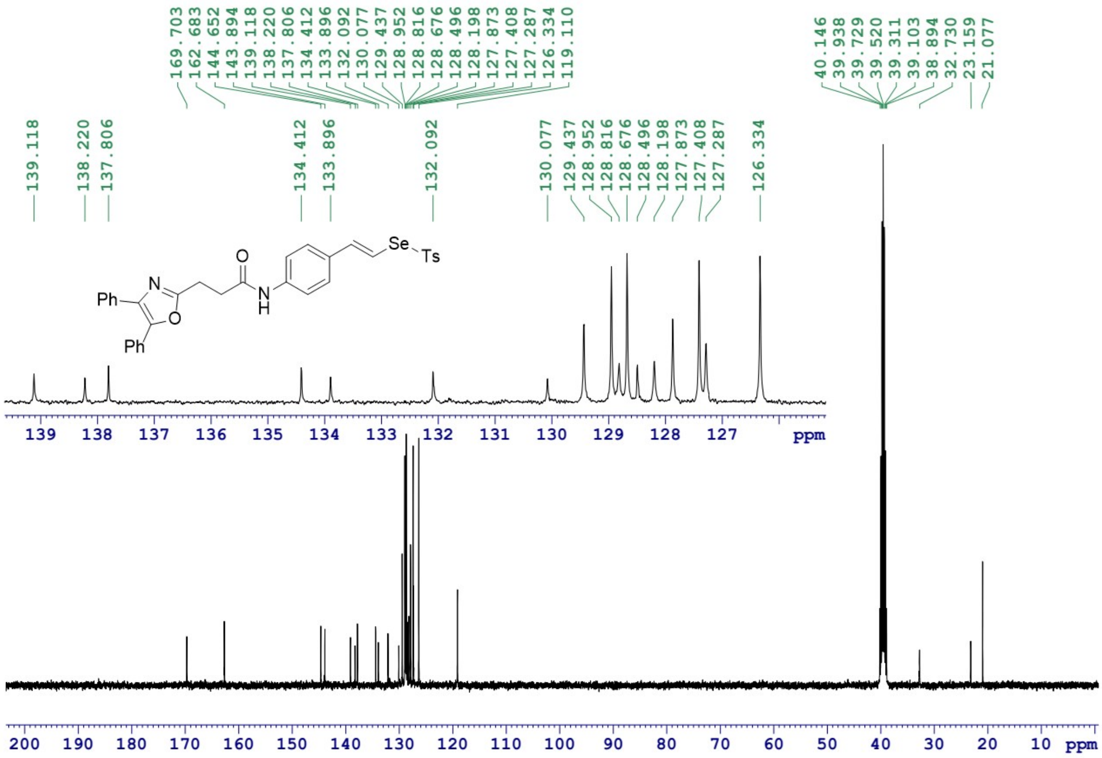

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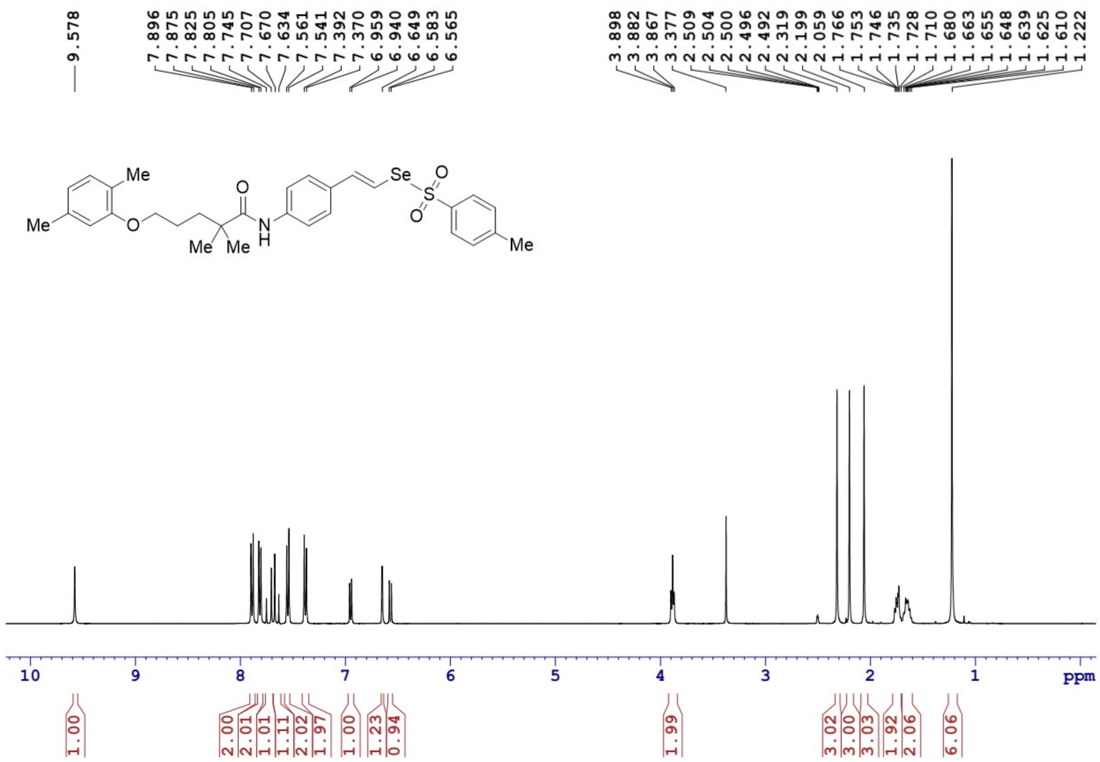

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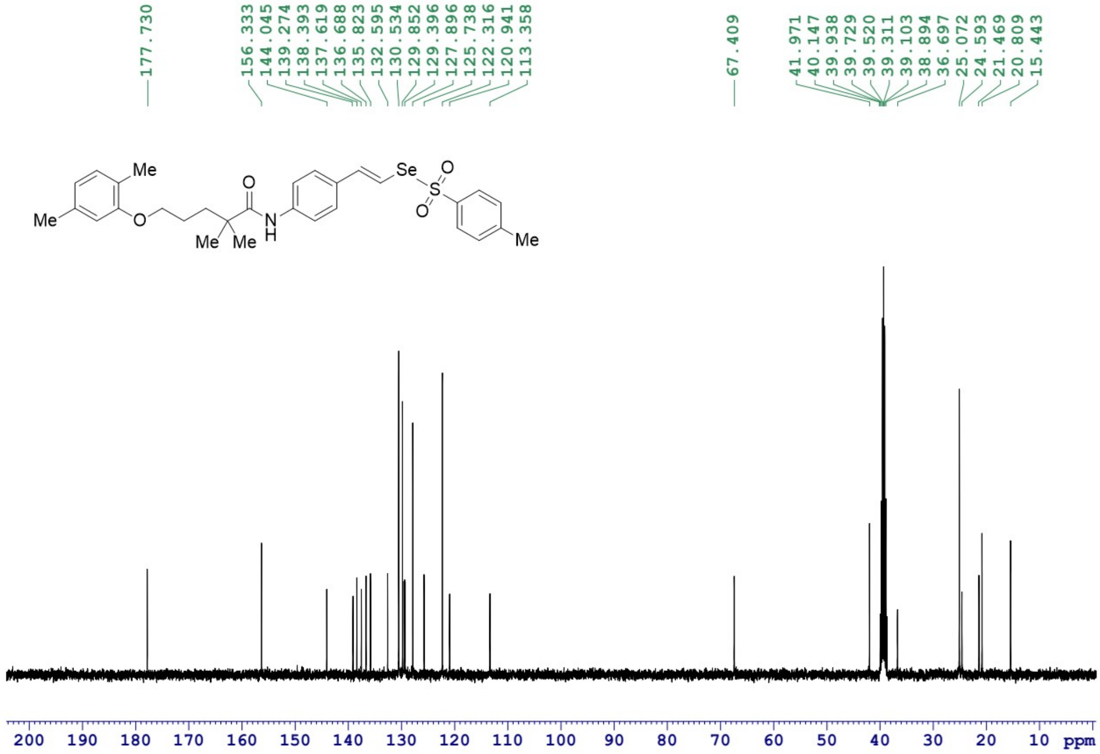

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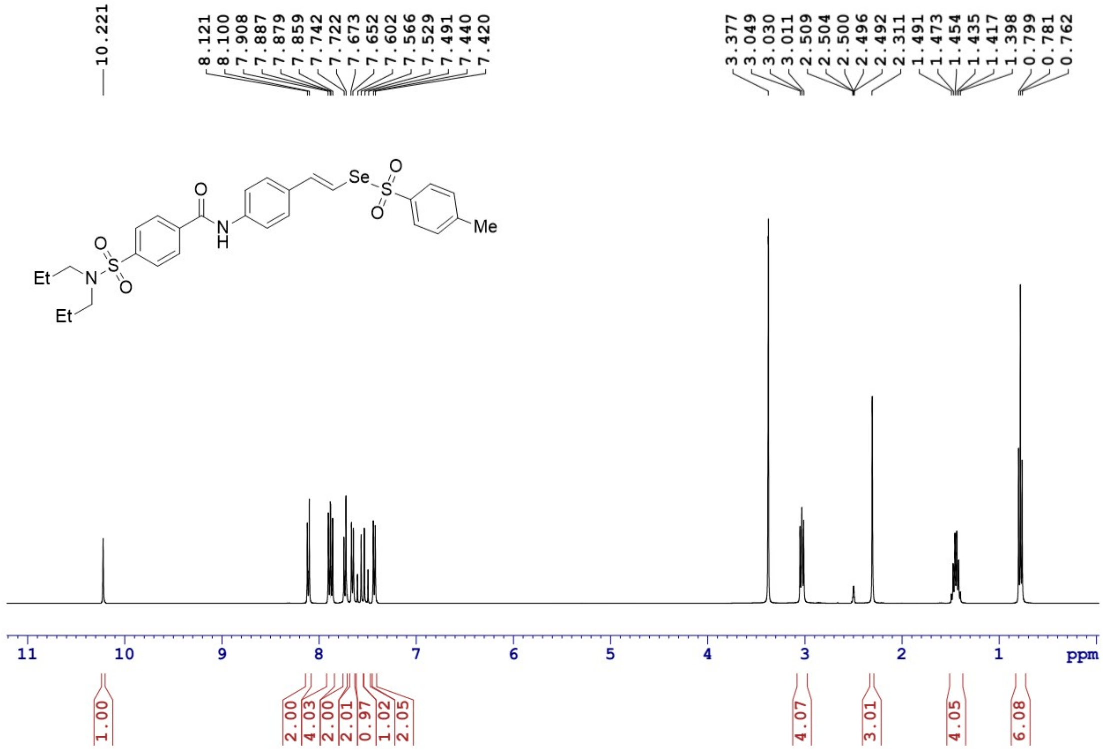

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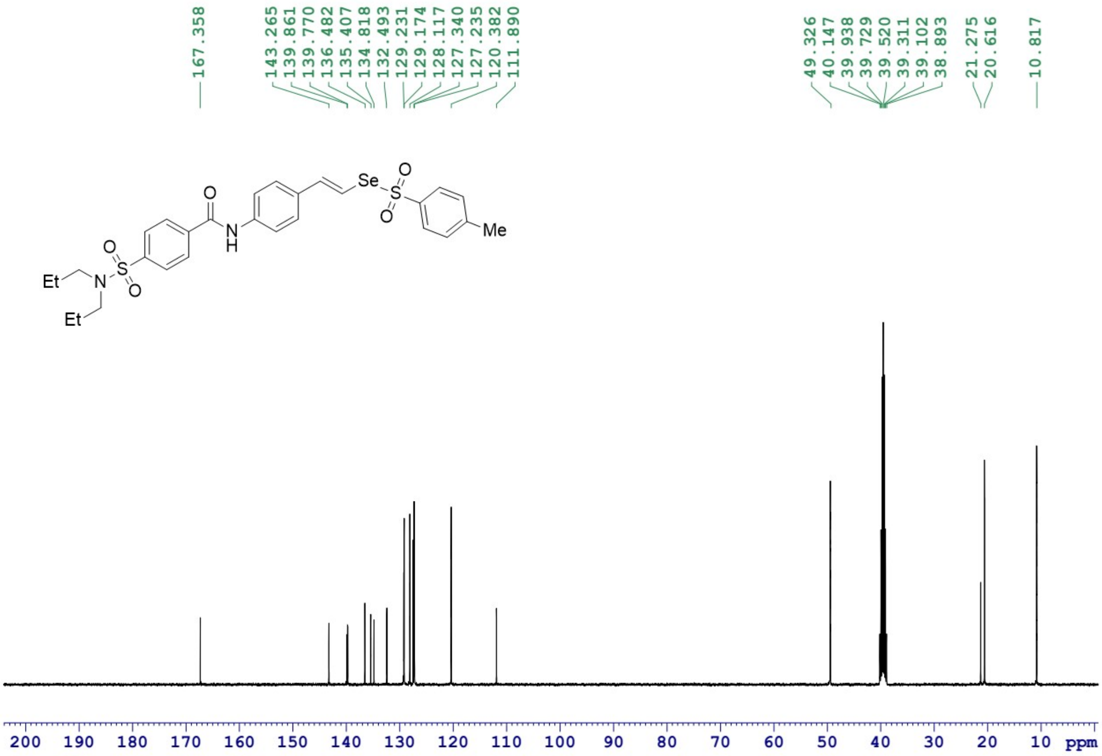

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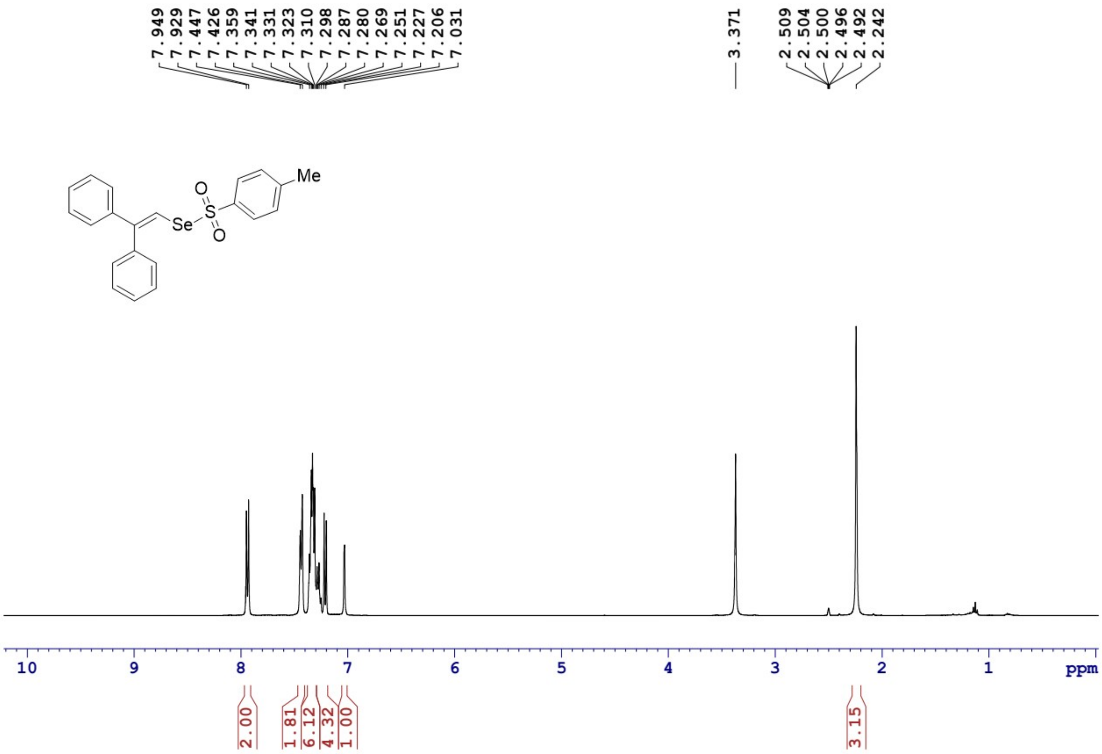

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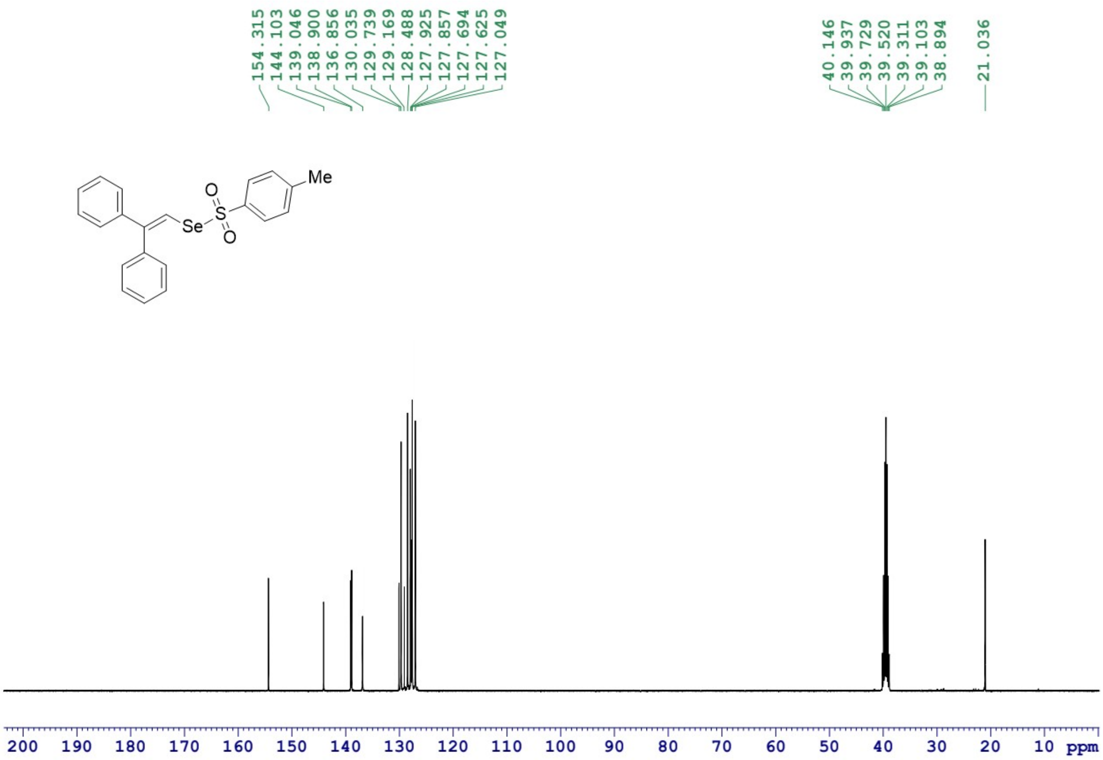

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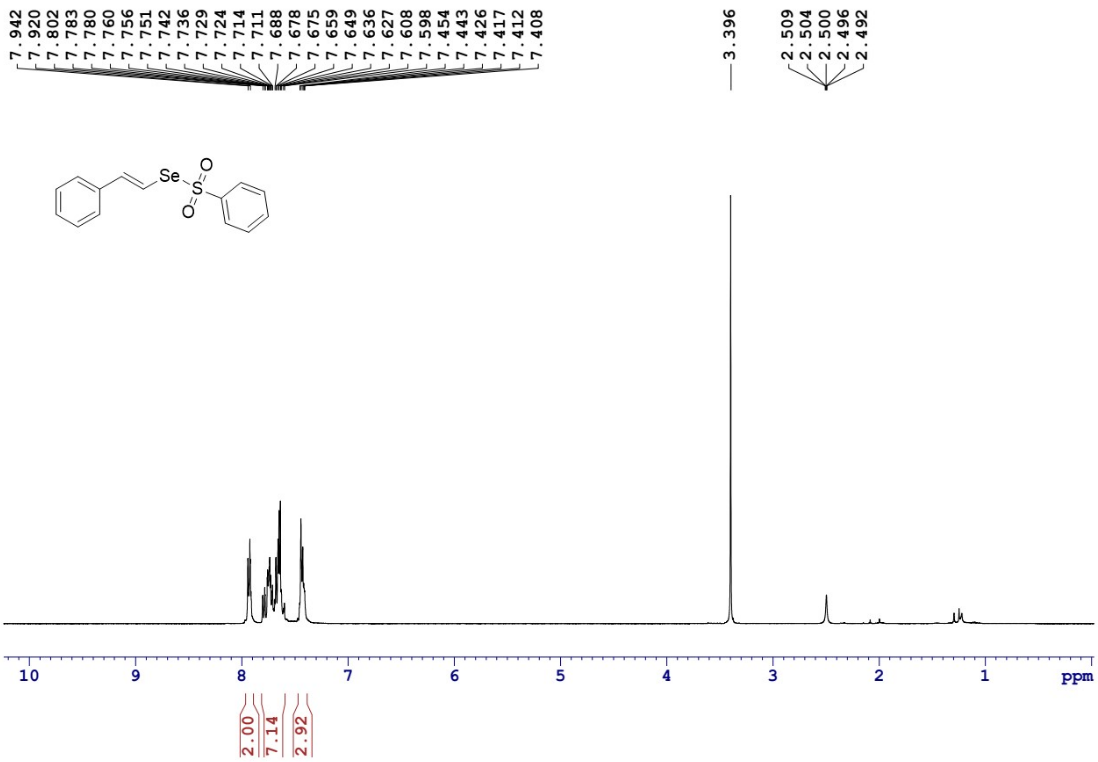

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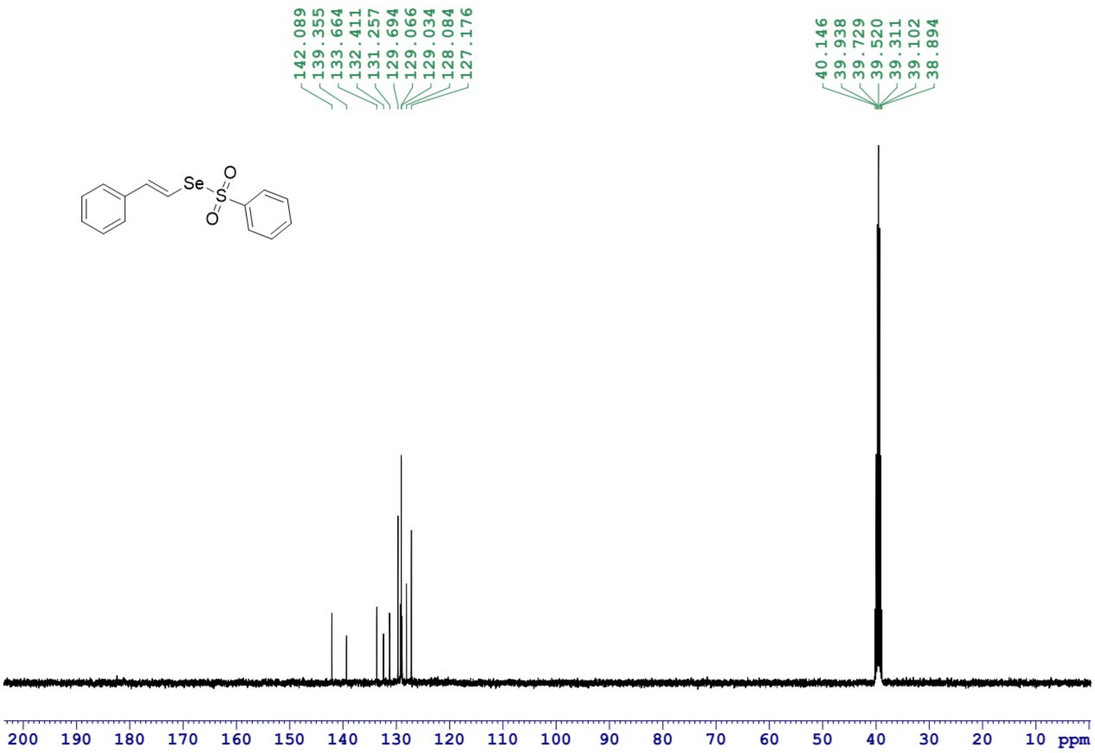
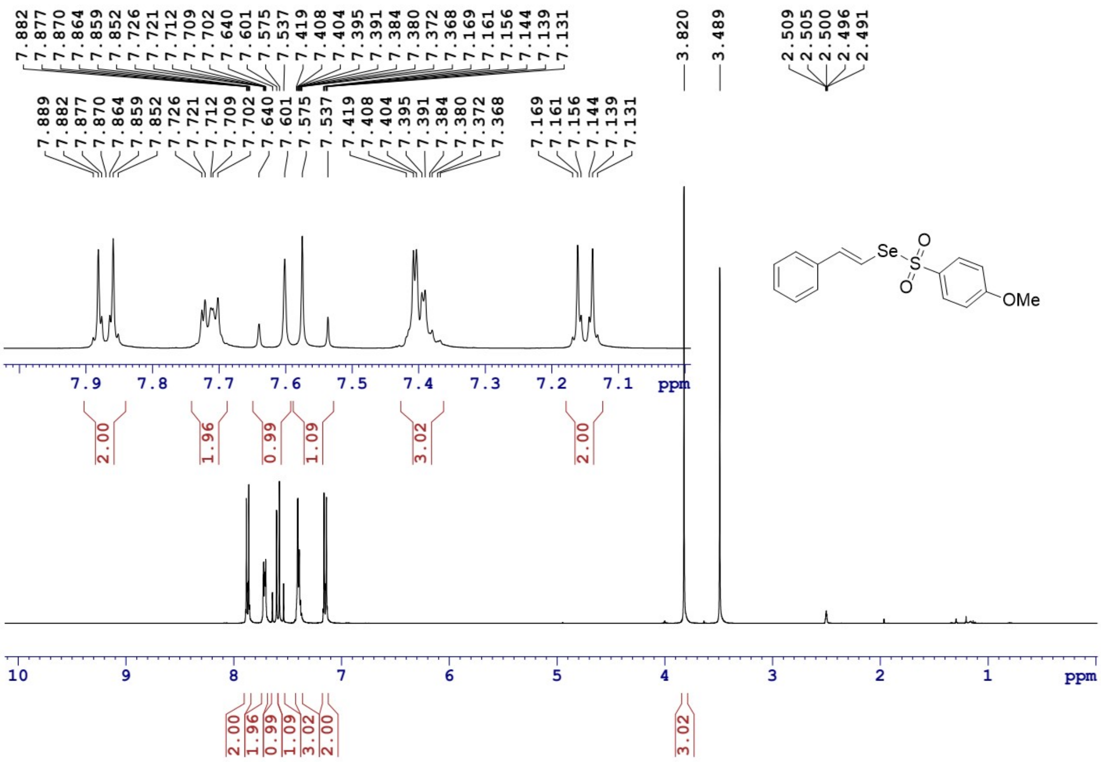


3ba-^{13}C NMR (100 MHz, DMSO-d_6)



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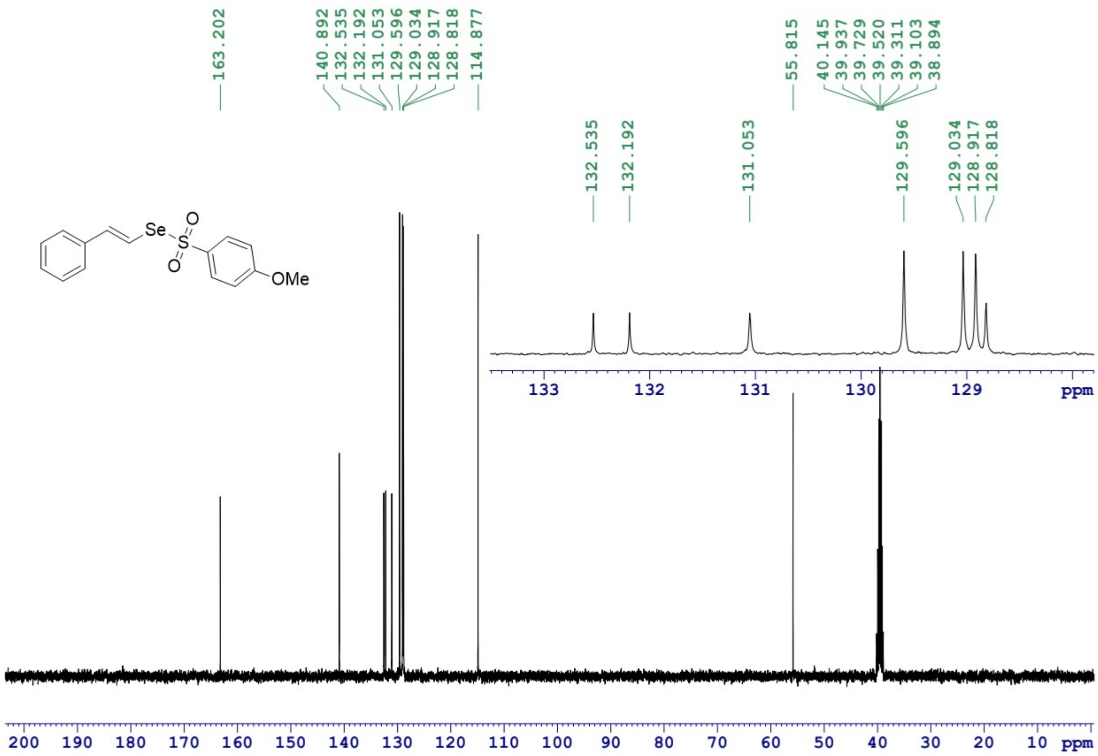

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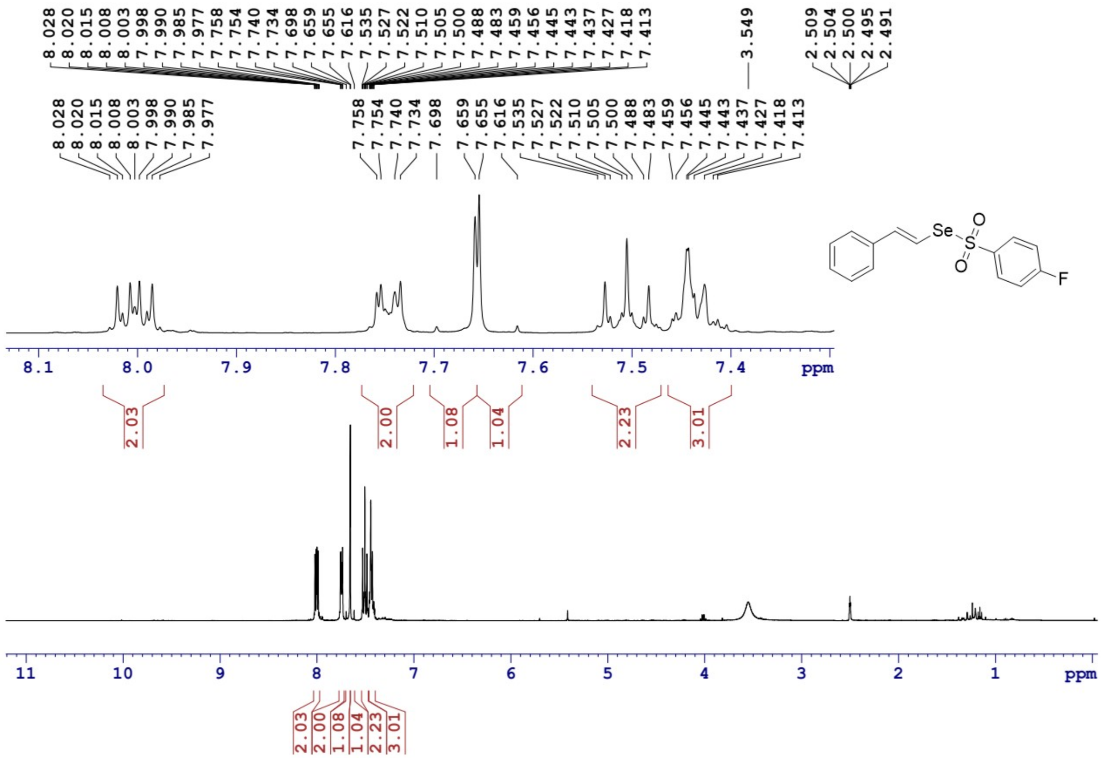

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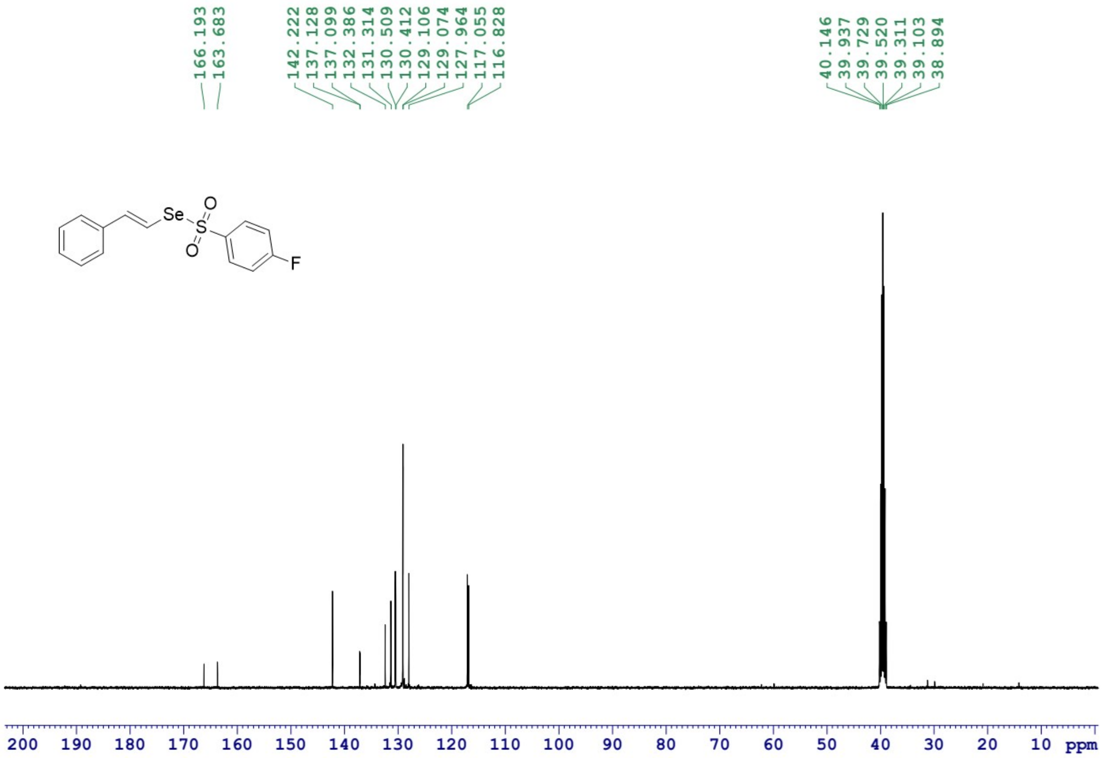
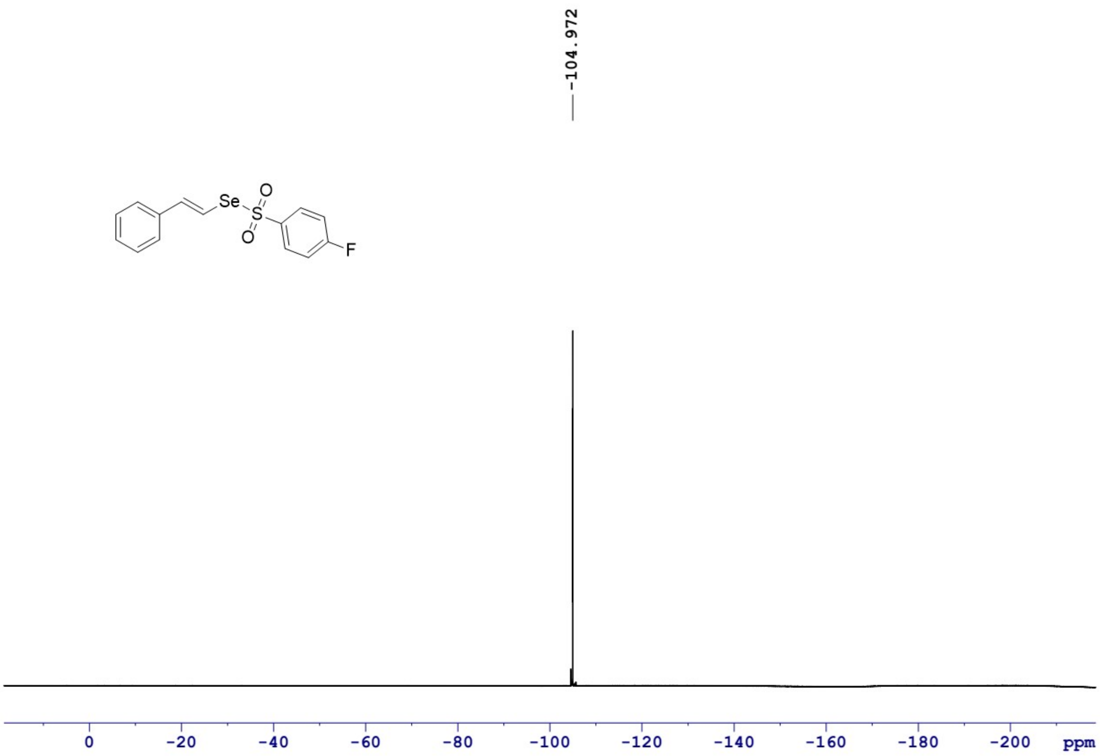
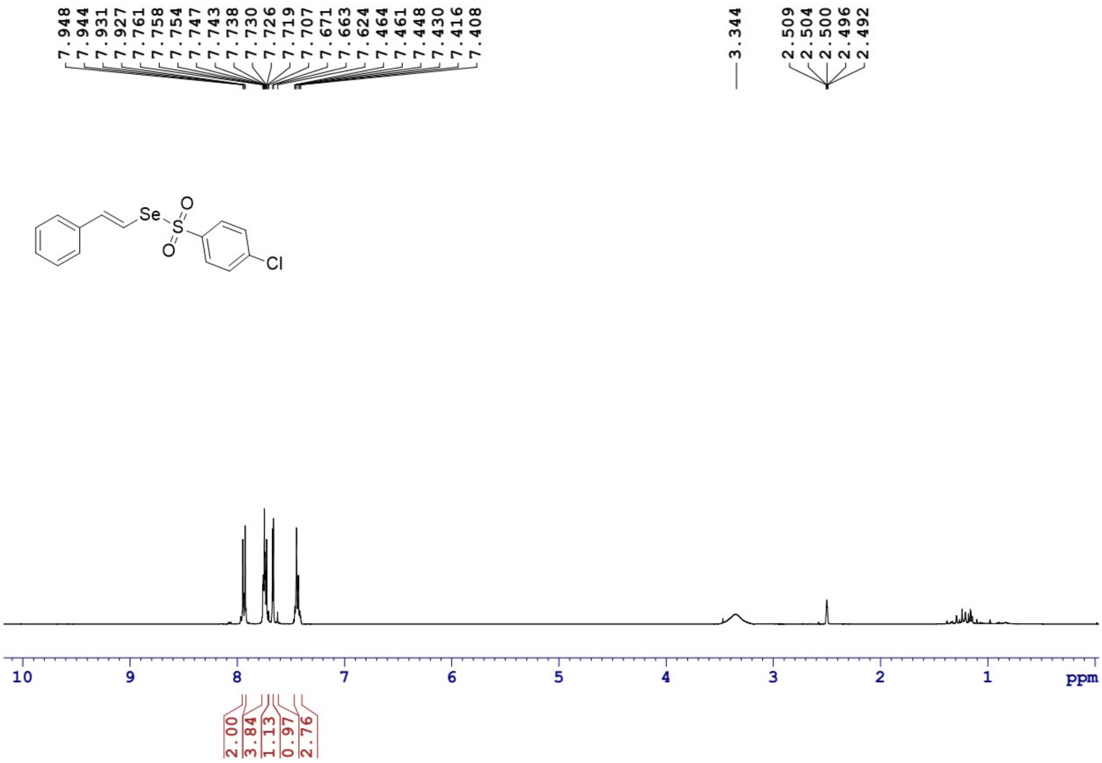


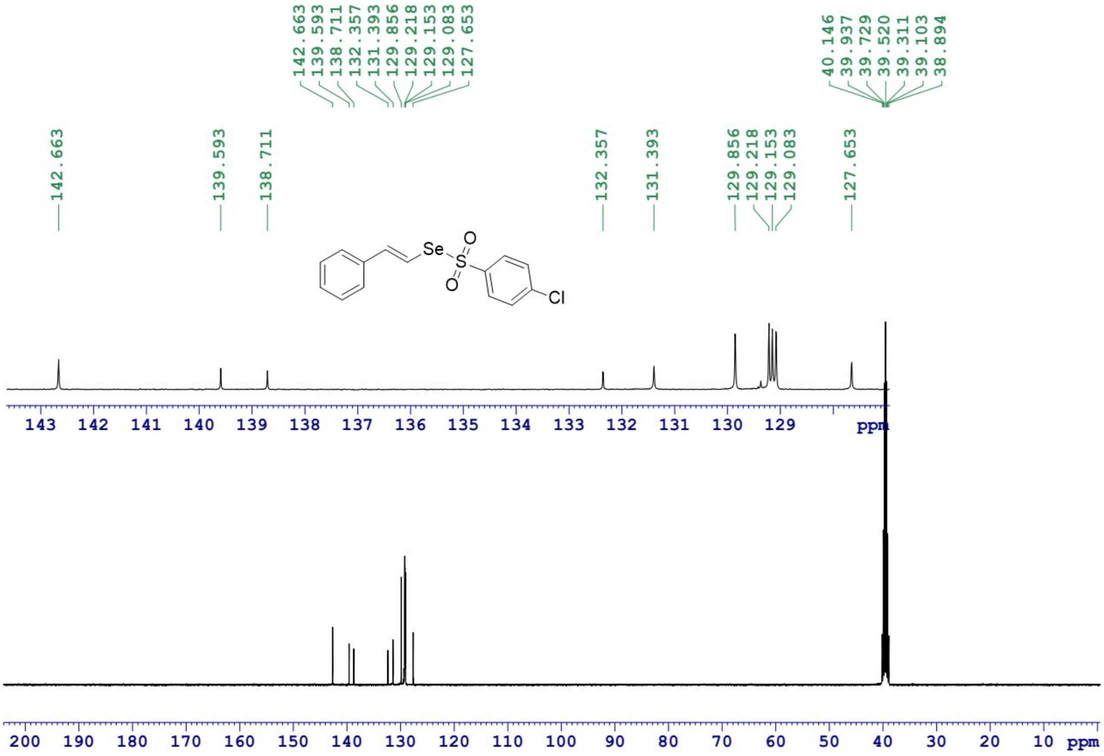
3da-^{13}C NMR (100 MHz, DMSO-d_6)



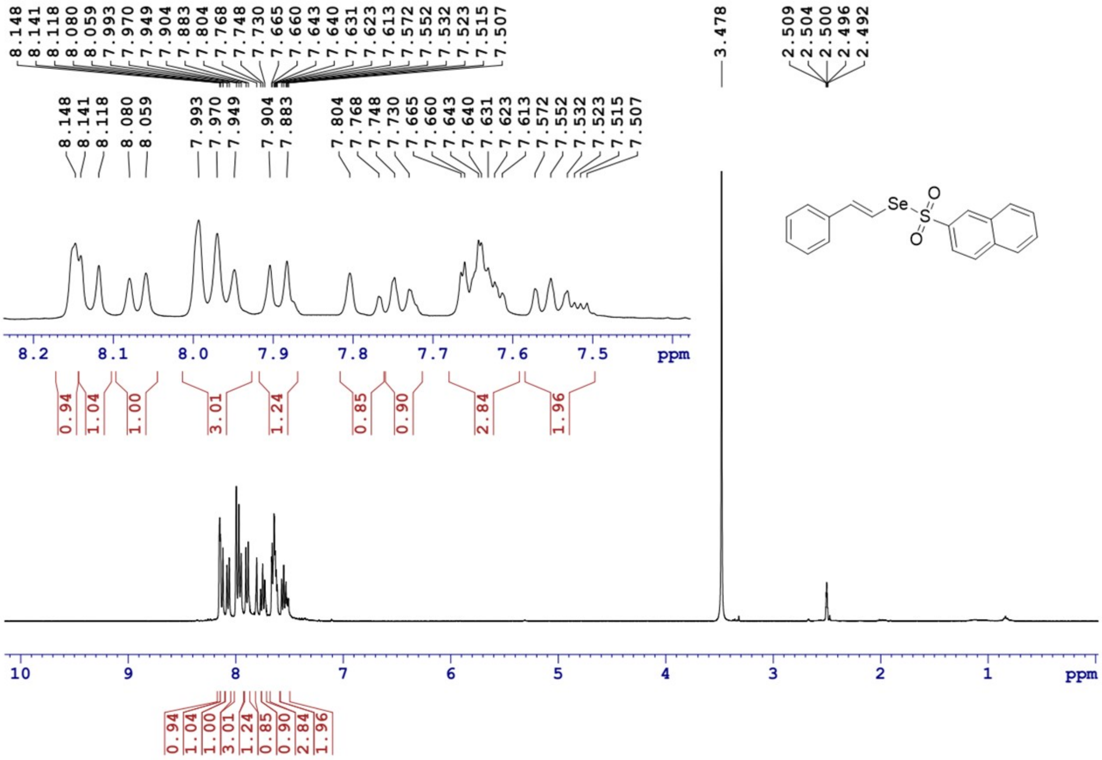
3da-^{19}F NMR (376.8 MHz, DMSO-d_6)



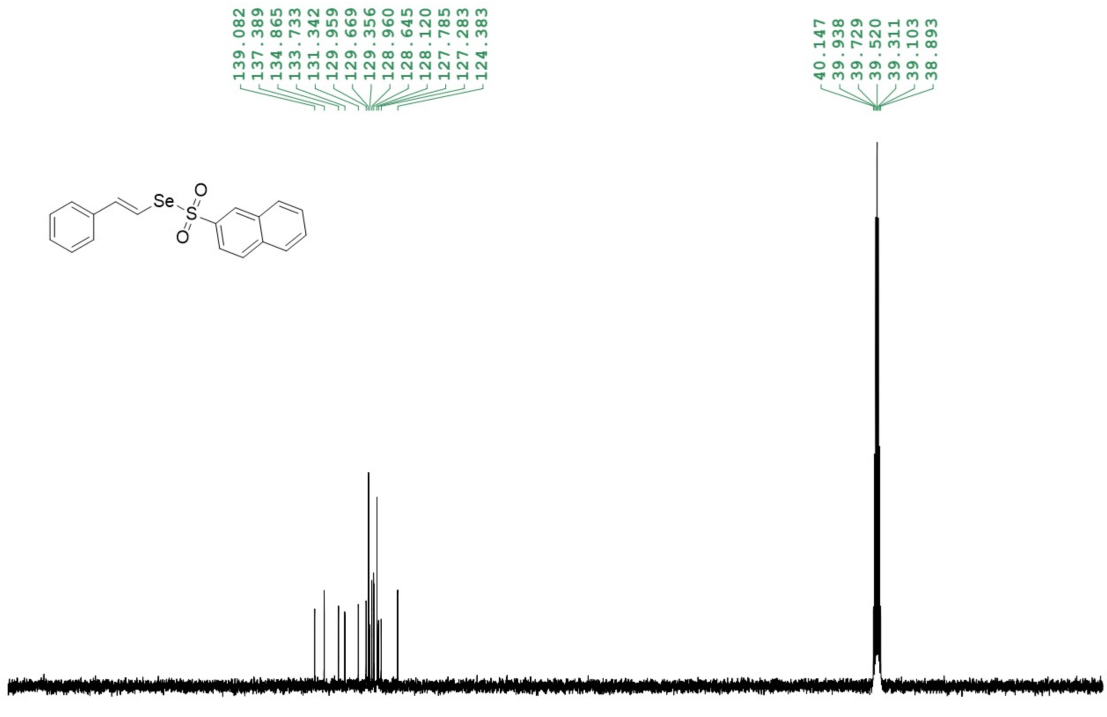
3ea-^{1}H NMR (400 MHz, DMSO-d_6)



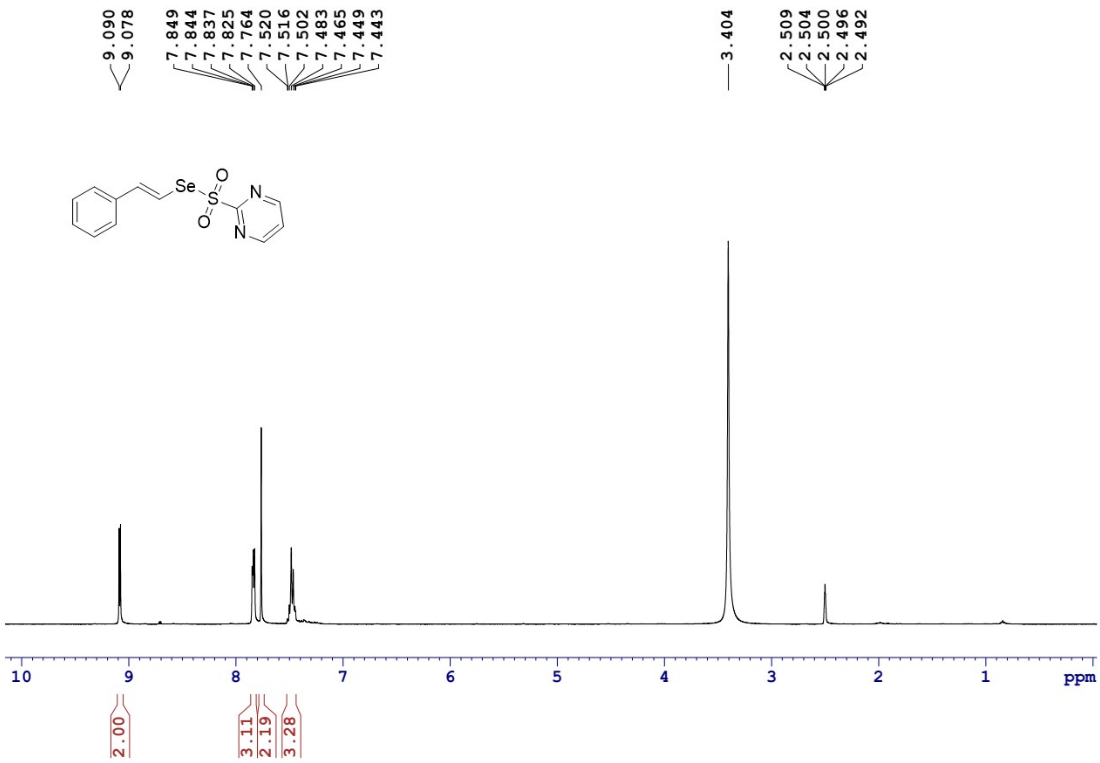
3ea-^{13}C NMR (100 MHz, DMSO-d_6)



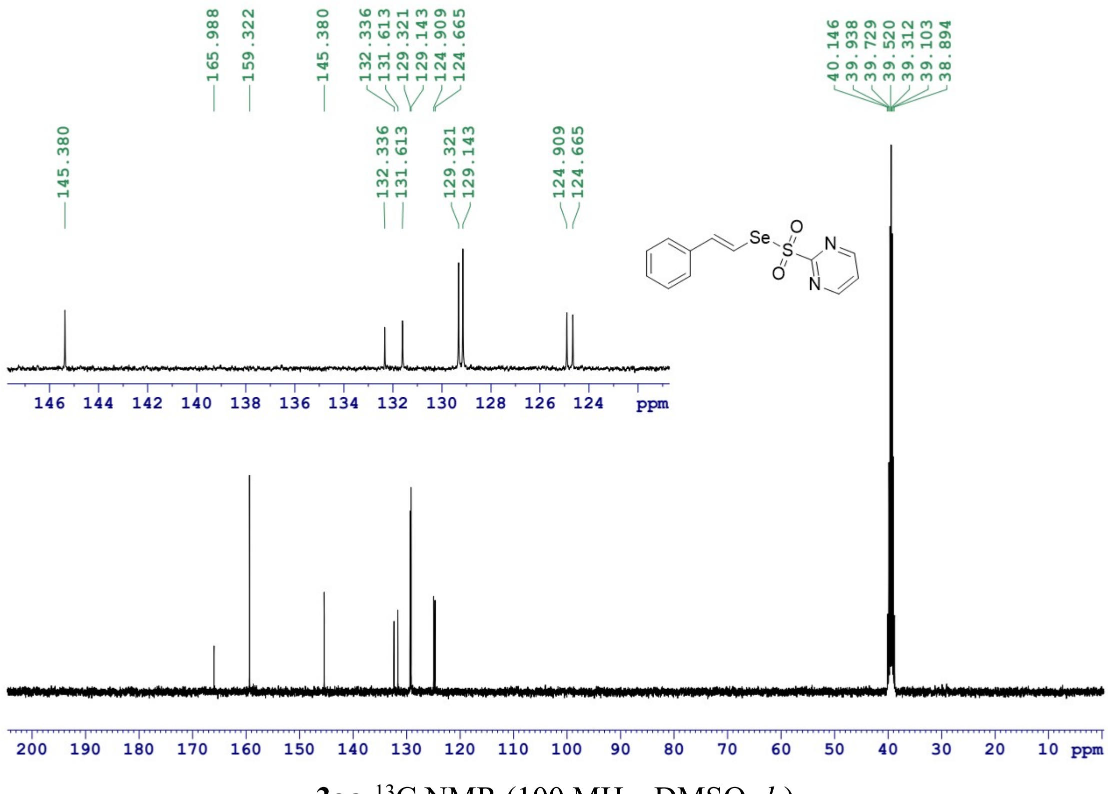
3fa-^{1}H NMR (400 MHz, DMSO-d_6)



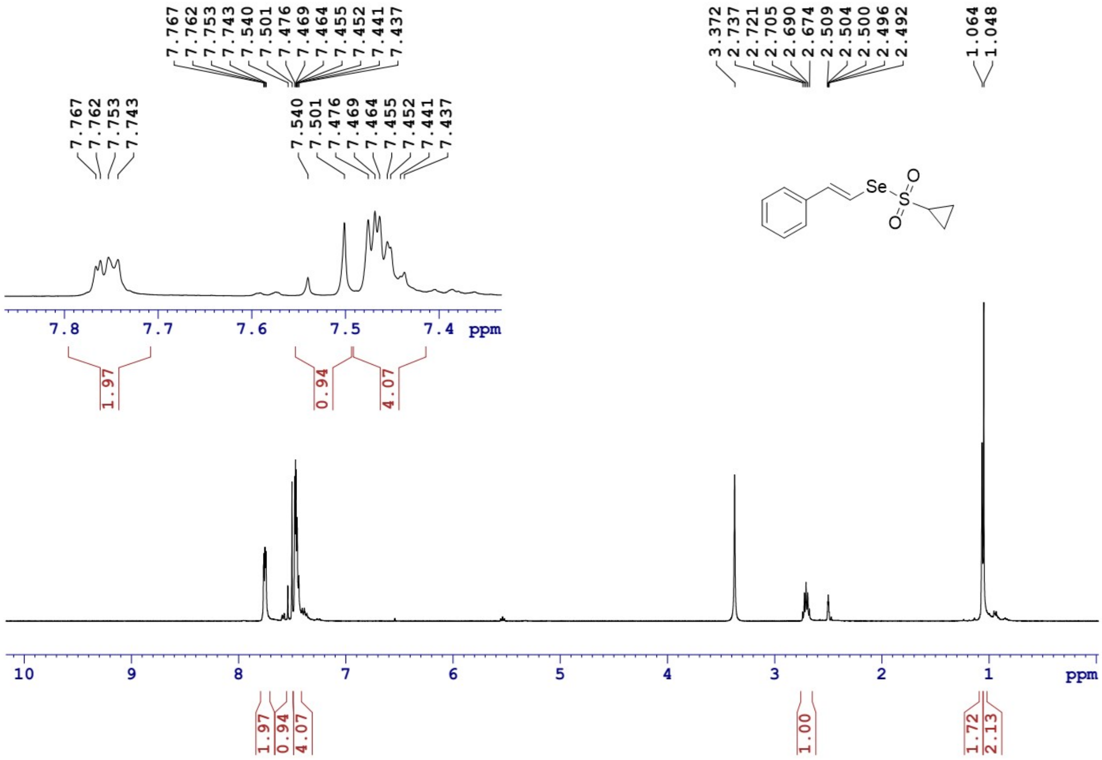
3fa-^{13}C NMR (100 MHz, DMSO-d_6)



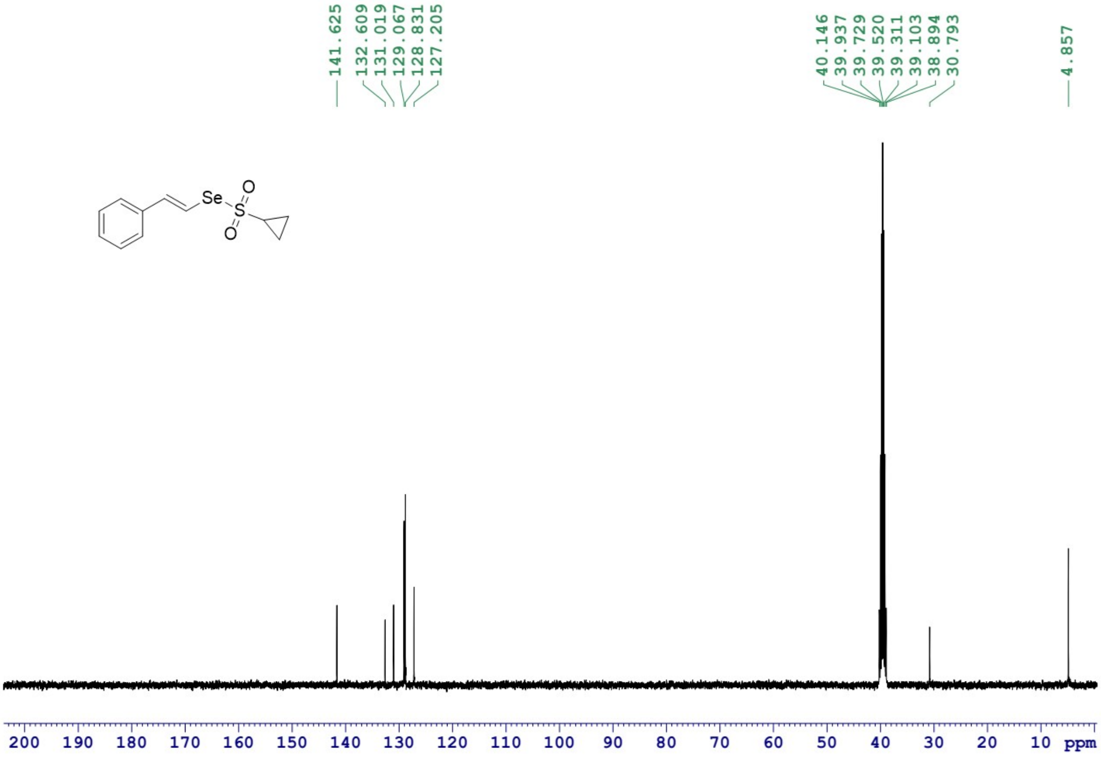
3ga-1H NMR (400 MHz, DMSO-d_6)



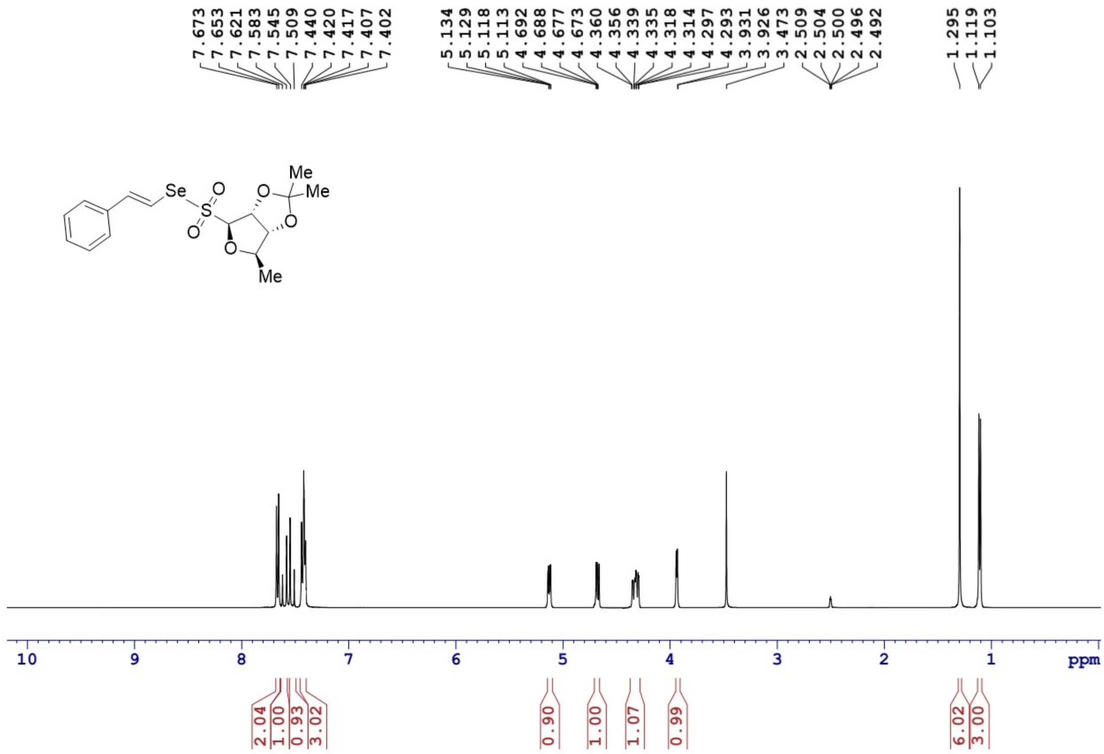
3ga-13C NMR (100 MHz, DMSO-d_6)



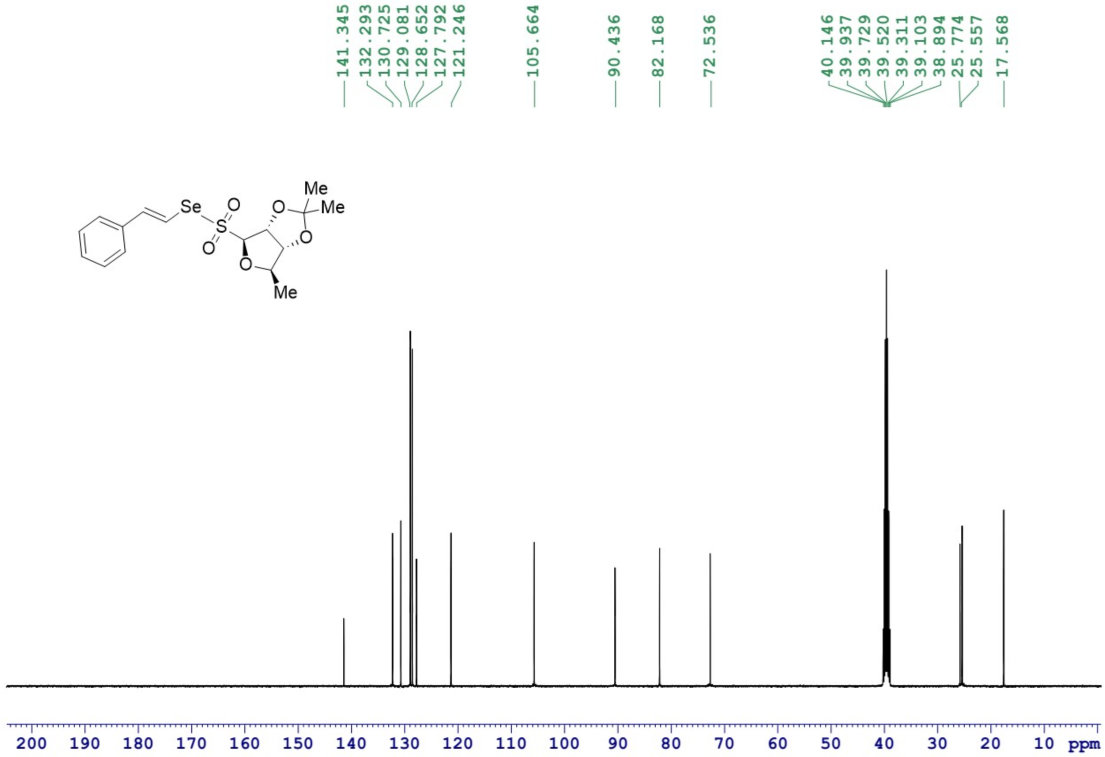
3ha-¹H NMR (400 MHz, DMSO-d_6)



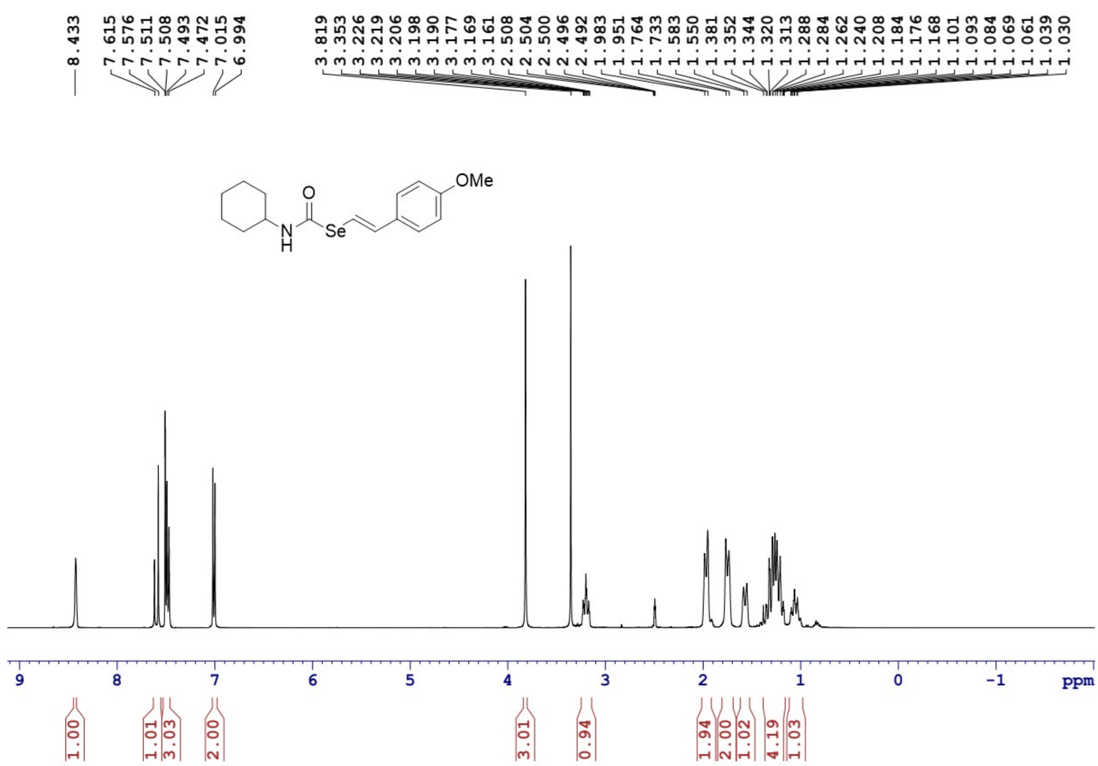
3ha-^{13}C NMR (100 MHz, DMSO-d_6)



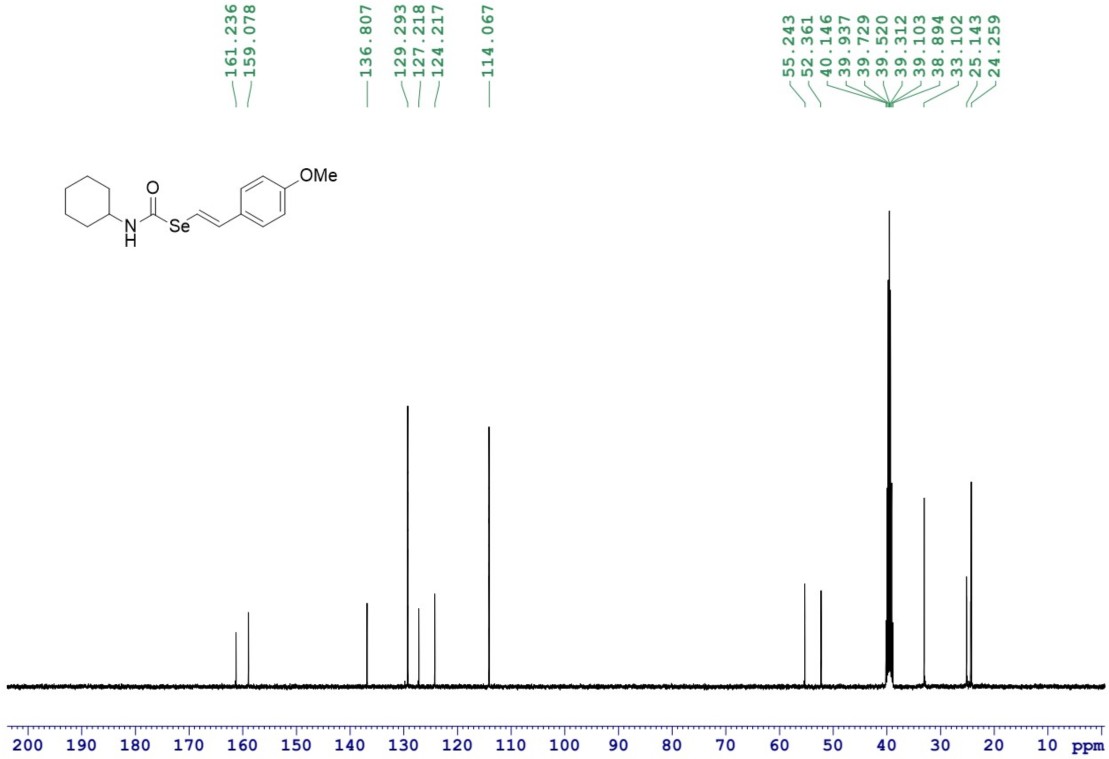
3ia-^{1}H NMR (400 MHz, DMSO-d_6)



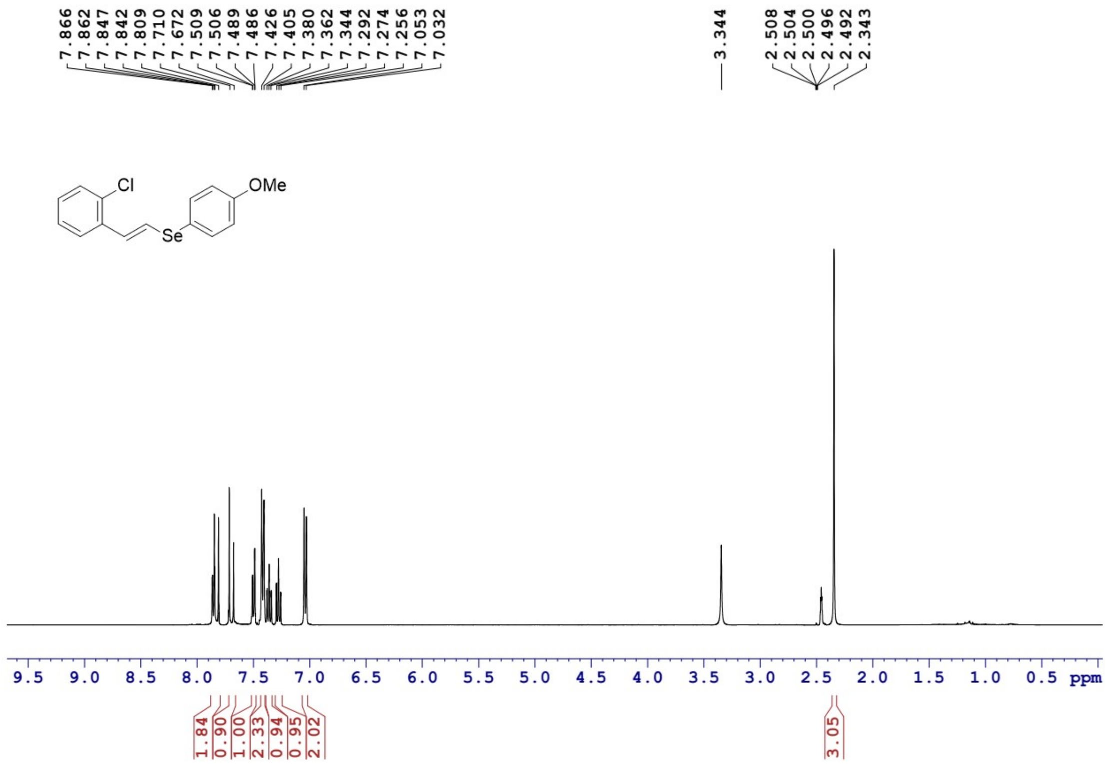
3ia-^{13}C NMR (100 MHz, DMSO-d_6)



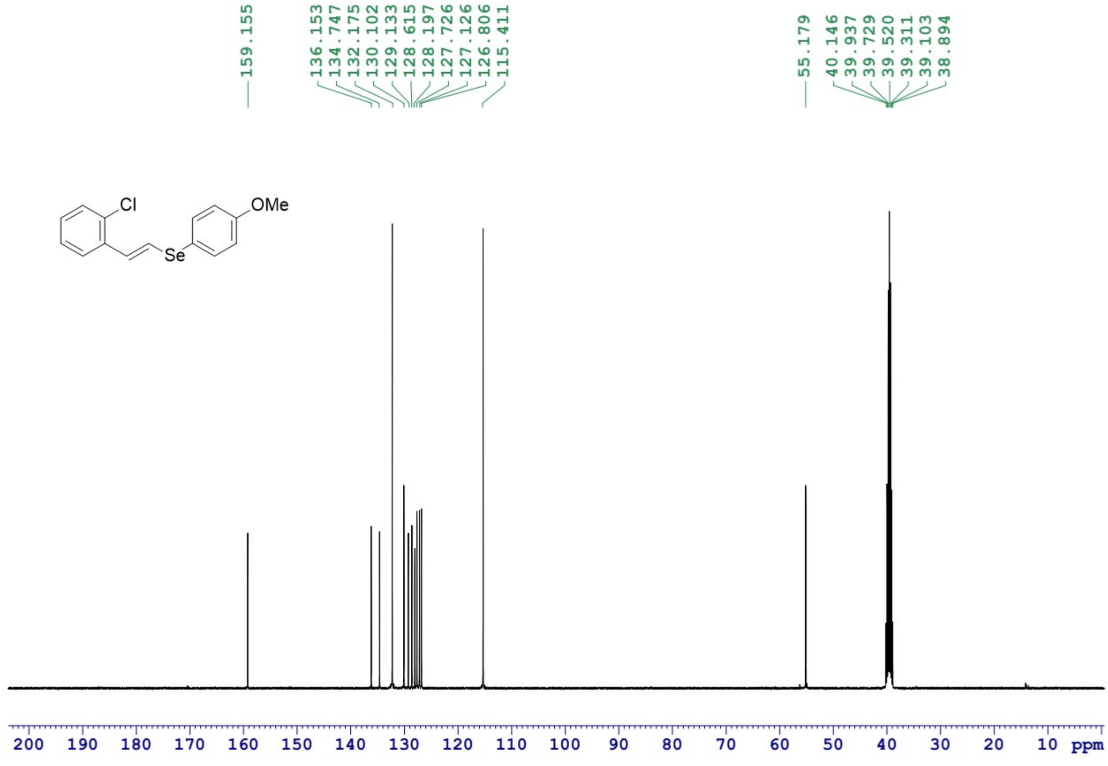
4aa-^{1}H NMR (400 MHz, DMSO-d_6)



4aa-^{13}C NMR (100 MHz, DMSO-d_6)



4ab-[1]H NMR (400 MHz, DMSO-d_6)



4ab-[13]C NMR (100 MHz, DMSO-d_6)