Deuterated Methylselenylating Reagents Design for Diverse Se-Methyl-d₃ Scaffolds Construction

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1. Supplementary Methods

General information. 1 H and 13 C NMR spectra were recorded on a Bruker AscendTM 400 (400 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: 1 H (CDCl₃ δ 7.26; DMSO- d_6 δ 2.50; CD₃OD δ 3.30), 13 C (CDCl₃ δ 77.16; DMSO- d_6 δ 39.5; CD₃OD δ 49.10). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. For thin layer chromatography (TLC), Huanghai precoated TLC plates (GF254) were used, and compounds were visualized with a UV light at 254 nm. High resolution mass spectra (HRMS) were obtained on an Agilent 1290II-6545 spectrometer. Melting point (MP) was obtained on Hanon MP-430. Column chromatography was performed with silica gel (200-300 mesh ASTM) and Aluminum oxide active (FCP 100-200 mesh ASTM). The photoreactor SSSTECH-AL₁ was used. In particular, Energy Chemical's dry ethanol was used. Unless otherwise noted, commercially available reagents purchased from Adamas-beta, TCI, Rhawn or Energy Chemical and were used as received.

2. Synthesis of The Starting Materials

- 1) General Procedure for The Synthesis of Sodium Sulfinate were Prepared according to the literature^[1,14].
- 2) General Procedure for The Synthesis of Diazonium Salts were Prepared according to The Literature^[2].
- 3) General Procedure for The Synthesis of of Allenes were Prepared according to The Literature^[8,15-17].
- 4) General Procedure for The Synthesis of Styrene Derivatives were Prepared according to The Literature^[10].
- 5) General Procedure for The Synthesis of [1.1.1]Propellane Derivatives were Prepared According to The Literature^[11].

3. Optimization of The Reaction Conditions

Supplementary Table 1. Optimization of Deuterated Methylselenylating Reagents^{a,b,c,d,e}

	Electro	onditions A: ophile (1.1 eq se (2.0 equiv.	1	1				
CD ₃ C	OD ——	IF. 0 °C to r.t.	/ → [CD ₃ OL	.g ——		Conditions C:		
(1.0 eq SI- 1	uiv.,	11, 0 0 10 1.1.	SI-2			ToISO ₂ Na (Z equ	ıiv.)	
				_	→ (CD ₃) ₂ Se ₂	Oxidant (W equi	——>ToISC	SeCD ₃
			Condition: NaBH ₄ (X e		SI-4	DCM, 0 °C to r.t.,	12 h	1
		E	EtOH (dry, Y				(all case	s > 99% D)
		Se —— SI-3	DMF, 90 °C	C, 3 h				
Entry	Electrophil	e Base	X (equiv.)	Y (equiv	.) Z (equiv.)	Oxidant (W equiv.)	Yield (%) ^d	D-inc. (%)
1	TsCl	NaOH	1.0	4.0	1.0	PhI(OAc) ₂ (1.1)	57	>99
2	Tf_2O	NaOH	1.0	4.0	1.0	PhI(OAc) ₂ (1.1)	30	>99
3	MsCI	NaOH	1.0	4.0	1.0	PhI(OAc) ₂ (1.1)	trace	>99
4	TsCI	Pyridine	1.0	4.0	1.0	PhI(OAc) ₂ (1.1)	35	>99
5	TsCl	TEA	1.0	4.0	1.0	PhI(OAc) ₂ (1.1)	27	>99
6	TsCl	2,6-Lutidine	1.0	4.0	1.0	PhI(OAc) ₂ (1.1)	30	>99
7	TsCl	NaOH	1.25	5.0	1.0	PhI(OAc) ₂ (1.1)	56	>99
8	TsCl	NaOH	0.75	3.0	1.0	PhI(OAc) ₂ (1.1)	60	>99
9	TsCl	NaOH	0.6	2.4	1.0	PhI(OAc) ₂ (1.1)	62 ^e	>99
10	TsCl	NaOH	0.5	2.0	1.0	PhI(OAc) ₂ (1.1)	62	>99
11	TsCl	NaOH	0.4	1.6	1.0	PhI(OAc) ₂ (1.1)	52	>99
12	TsCl	NaOH	0.6	2.4	1.0	NBS (1.1)	trace	>99
13	TsCl	NaOH	0.6	2.4	1.0	NIS (1.1)	trace	>99
14	TsCl	NaOH	0.6	2.4	1.0	NCS (1.1)	trace	>99
15	TsCl	NaOH	0.6	2.4	1.0	DMP (1.1)	12	>99
16	TsCI	NaOH	0.6	2.4	2.0	PhI(OAc) ₂ (1.0)	60	>99
17	TsCl	NaOH	0.6	2.4	3.0	PhI(OAc) ₂ (1.0)	59	>99
18	TsCl	NaOH	0.6	2.4	4.0	PhI(OAc) ₂ (1.0)	55	>99
19	TsCl	NaOH	0.6	2.4	0.9	PhI(OAc) ₂ (1.0)	54	>99
20	TsCl	NaOH	0.6	2.4	0.8	PhI(OAc) ₂ (1.0)	49	>99
21	TsCl	NaOH	0.6	2.4	1.0	$PhI(OAc)_2$ (2.0)	59	>99
22	TsCl	NaOH	0.6	2.4	1.0	PhI(OAc) ₂ (3.0)	58	>99
23	TsCl	NaOH	0.6	2.4	1.0	PhI(OAc) ₂ (1.1)	62	>99
24	TsCl	NaOH	0.6	2.4	1.0	PhI(OAc) ₂ (1.2)	62	>99
25	TsCl	NaOH	0.6	2.4	1.0	PhI(OAc) ₂ (1.3)	61	>99
26 ^f	TsCl	NaOH	0.6	2.4	1.0	PhI(OAc) ₂ (1.2)	31	93
27 ^g	TsCI	NaOH	0.6	2.4	1.0	PhI(OAc) ₂ (1.2)	52	98
28 ^h	TsCl	NaOH	0.6	2.4	1.0	PhI(OAc) ₂ (1.2)	61	98
28 ⁱ	TsCl	NaOH	0.6	2.4	1.0	PhI(OAc) ₂ (1.2)	50	>99

^aReaction condition **A**: **SI-1** (0.1 mmol, 1.0 equiv.), NaOH (0.2 mmol, 2.0 equiv.) were added to THF, then TsCl (0.11 mmol, 1.1 equiv.) was added to the mixture at 0 °C, then the mixture at r.t. for 12 h. ^bReaction condition **B**: **SI-3** (0.1 mmol, 1.0 equiv.), NaBH₄ (0.6 mmol, 0.6 equiv.) and dry EtOH (0.24 mmol, 2.4 equiv.) were added to DMF (1.0 mL) at 90 °C for 3 h, then TsOCD₃ (0.1 mmol, 1.0 equiv.) was added to the mixture at 90 °C for 12 h. ^cReaction condition **C**: TolSO₂Na (0.1 mmol, 1.0 equiv.) was added to **SI-4** (crude in 1.0 mL DCM), then PhI(OAc)₂ (0.11 mmol, 1.1 equiv.) in DCM (1.0 mL) was added to the mixture at 0 °C, then reaction at 25 °C for 16 h. ^dYield based on ¹H NMR. ^eIsolated yield. ^fStep II: 1 h. ^gStep II: 1.5 h. ^hStep II: 2 h. ⁱStep II: 5 h.

Step I: the aqueous solution (0.5 mL) of NaOH (10 mmol, 2 equiv.) was added to the mixture of CD₃OD (5 mmol, 1 equiv.) and THF (0.5 mL) at 0 °C, then TsCl (5.5 mmol, 1.1 equiv.) dissolved in THF (1.25 mL) was added to the mixture at 0 °C, the reaction mixture was stirred at 25 °C for 10 h. After the reaction was completed, the mixture was concentrated in vacuo, and then water (10 mL) was added to the residue, followed by processes of extraction using EtOAc (10 mLx3), concentration, and desiccation to give the crude TsOCD₃.

Step II: to a Schlenk tube containing Se powder (5 mmol, 1.0 equiv.) and NaBH₄ (3.0 mmol, 0.6 equiv.), and DMF (5.0 mL) were added dried EtOH (12 mmol, 2.4 equiv.), the reaction mixture was stirred at 90 °C for 30 min. The crude TsOCD₃ was then added to the mixture at 90 °C for 3 h. After the reaction was completed, the mixture was cooled to room temperature, which was then quenched by water (20 mL). The organic phase was subsequently extracted with CH₂Cl₂ (10 mLx5), and dried over anhydrous Na₂SO₄, leading to obtaining crude CD₃SeSeCD₃.

Step III: to a three-necked flask containing RSO₂Na (5.0 mmol, 1.0 equiv.), and crude CD₃SeSeCD₃ in CH₂Cl₂ were dropwise added a cooled mixture (0 °C) of PhI(OAc)₂ (5.5 mmol, 1.1 equiv.) and CH₂Cl₂ (15 mL), the reaction mixture was stirred at 25 °C for 12 h. After the reaction was complete, the reaction mixture was quenched by water (50 mL), the organic layer was then dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue was purified by silica gel column chromatography to afford the SeCD₃ reagents **1**.

Supplementary Table 2. Optimization of Difunctionalized Reactions of Olefins^{a,b,c}

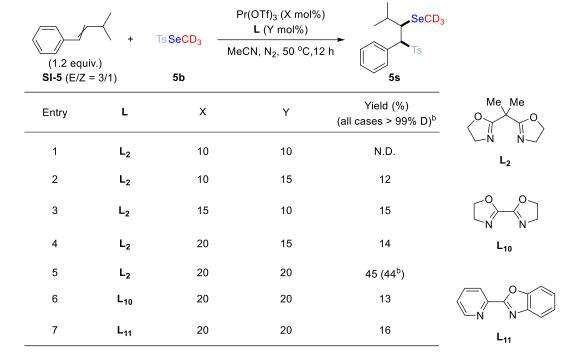
4a		1		(All cases > 99% D)		
Entry	Solvent	Temp. (°C)	Cat.	L	Yield (%) ^b	
1	CCI ₄	50	Pr(OTf) ₃	L ₈	24	
2	DCE	50	$Pr(OTf)_3$	L ₈	35	
3	Dioxane	50	Pr(OTf) ₃	L ₈	19	
4	PhMe	50	Pr(OTf) ₃	L ₈	ND	
5	DMF	50	$Pr(OTf)_3$	L ₈	29	
6	DMSO	50	Pr(OTf) ₃	L ₈	34	
7	MeCN	50	Pr(OTf) ₃	L ₈	68	
8	MeCN	50	Sc(OTf) ₃	L ₈	58	
9	MeCN	50	La(OTf) ₃	L ₈	63	
10	MeCN	50	Ga(OTf) ₃	L ₈	15	
11	MeCN	50	Er(OTf) ₃	L ₈	20	
12	MeCN	50	$Eu(OTf)_3$	L ₈	48	
13	MeCN	50	Dy(OTf) ₃	L ₈	55	
14	MeCN	50	$Lu(OTf)_3$	L ₈	41	
15	MeCN	60	$Pr(OTf)_3$	L ₈	60	
16	MeCN	70	$Pr(OTf)_3$	L ₈	57	
17	MeCN	40	$Pr(OTf)_3$	L ₈	51	
18	MeCN	30	$Pr(OTf)_3$	L ₈	43	
19	MeCN	50	$Pr(OTf)_3$	L ₇	83	
20	MeCN	50	$Pr(OTf)_3$	L ₇	90 (84) ^c	
21	MeCN	50	$Pr(OTf)_3$	L ₉	81	
22	MeCN	50	$Pr(OTf)_3$	L_{5}	65	
23	MeCN	50	$Pr(OTf)_3$	L_3	76	
24 25	MeCN MeCN	50 50	$Pr(OTf)_3$ $Pr(OTf)_3$	L ₁ L ₅	91 (89) ^c 74	
Me Me	Me N= Me	Me Me	CI	CI	N N=	
Me	N—Me	t Bu t Bu t Bu t	Br N	Br _	L ₅	

^aReaction conditions: styrenes (0.1 mmol, 1.0 equiv.), TsSeCD₃ (0.12 mmol, 1.2 equiv.), Cat. (0.01 mmol, 10 mol%) and L (0.01 mmol, 10 mol%) were added to MeCN (0.25 mL) at temperature for 12 h. ^bYield based on ¹H NMR. ^cIsolated yield.

To a three-necked flask containing RSO_2SeCD_3 (0.24 mmol, 1.2 equiv.), $Pr(OTf)_3$ (0.02 mmol, 10 mol%), **L** (0.02 mmol, 10 mol%) in MeCN (0.5 mL) were added olefin (0.2 mmol, 1.0 equiv.), the reaction mixture was stirred at 50 °C for 12 h,

which was then quenched by water. The organic layer was subsequently extracted with EtOAc, washed with brine, and dried over anhydrous Na₂SO₄. The residue was purified by silica gel column chromatography to afford the SeCD₃ reagents **5a**.

Supplementary Table 3. Optimization of Difunctionalized Reactions of Olefins^{a,b,c,d}



^aReaction conditions: styrenes (0.1 mmol, 1.0 equiv.), TsSeCD₃ (0.12 mmol, 1.2 equiv.), Pr(OTf)₃ (0.01 mmol, 20 mol%) and L (0.01 mmol, 20 mol%) were added to MeCN (0.25 mL) at 50 °C for 12 h. ^bYield based on ¹H NMR. ^cIsolated yield. ^ddr > 20:1

To a three-necked flask containing TsSeCD₃ (0.24 mmol, 1.2 equiv.), Pr(OTf)₃ (0.04 mmol, 20 mol%), **L** (0.04 mmol, 10 mol%) in MeCN (0.5 mL) were added olefin (0.2 mmol, 1.0 equiv.), the reaction mixture was stirred at 50 °C for 12 h, which was then quenched by water. The organic layer was subsquently extracted with EtOAc, washed with brine, and dried over anhydrous Na₂SO₄. The residue was purified by silica gel column chromatography to afford the conpound **5s**.

Supplementary Table 4. Optimization The Reaction Conditions of Nucleophilic Selenium Deuterium Methylation. a,b,c

Entry	Solvent	Base	Temp. (°C)	X (equiv.)	Yield (%) ^b
1	THF	Cs ₂ CO ₃	50	1.0	65
2	DMF	Cs_2CO_3	50	1.0	67
3	MeOH	Cs_2CO_3	50	1.0	76 ^c
4	DMSO	Cs_2CO_3	50	1.0	21
5	DCE	Cs_2CO_3	50	1.0	48
6	MeOH	NaOH	50	1.0	26
7	MeOH	NaO ^t Bu	50	1.0	41
8	MeOH	TEA	50	1.0	trace
9	MeOH	DBU	50	1.0	trace
10	MeOH	Cs_2CO_3	30	1.0	53
11	MeOH	Cs_2CO_3	40	1.0	61
12	MeOH	Cs_2CO_3	60	1.0	75
13	MeOH	Cs_2CO_3	50	0.9	71
14	MeOH	Cs_2CO_3	50	1.1	76

^aReaction conditions: **8a** (0.2 mmol, 1.0 equiv.), 5**a** (0.2 mmol, 1.0 equiv.) and Cs₂CO₃ (0.2 mmol, 1.0 equiv.) were added to solvent (0.5 mL) at 50 °C for 12 h. ^bYield based on ¹H NMR. ^cIsolated yield.

To a dried Schlenk tube containing **5a** (0.2 mmol, 1.0 equiv.), agents **8** (0.2 mmol, 1.0 equiv.), and Cs₂CO₃ (0.2 mmol, 1.0 equiv.) were added MeOH (0.5 mL), the reaction mixture was stirred at 50 °C for 12 h, which was then quenched by water. The organic layer was then extracted with EtOAc, washed with brine, and dried over anhydrous Na₂SO₄. The residue was purified by silica gel column chromatography to afford the SeCD₃ reagents **10**.

4. Deuterated Selenomethylation with Various Reagents

4.1 General Procedure for The Synthesis of Products 2a, 2b and 2c¹

To a dry Schlenk tube containing **1b** (0.2 mmol, 1.0 equiv.), NiBr₂ (0.01 mmol, 5.0 mol%), **L**₄ (0.015 mmol, 7.5 mol%) and alkyl bromides (0.22 mmol, 1.1 equiv.) were added DMF/MeCN (2:3, 1.0 mL). the mixture was stirred at 110 °C for 10 h, which was then quenched by water. The organic layer was then extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄. The residue was purified by silica gel column chromatography to afford the product.

4.2 General Procedure for The Synthesis of Products 2d, 2e and 2f²

TsSeCD₃ +
$$R^+$$
 $R^ R^+$ R^+ R^+

To a dry Schlenk tube containing **1b** (0.3 mmol, 1.5 equiv.), Eosin Y (0.01 mmol, 5.0 mol%), K₃PO₄ (0.4 mmol, 2.0 equiv.) and diazonium salts (0.2 mmol, 1.0 equiv.) were added MeOH (1.5 mL), the reaction mixture was stirred at room temperature for 12 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄. The residue was purified by silica gel column chromatography to afford the product.

4.3 General Procedure for The Synthesis of Products 2g, 2h and 2i³

To a dry Schlenk tube containing **1b** (0.24 mmol, 1.2 equiv.), Cu(OAc)₂ (0.02 mmol, 10 mol%), **L**₁ (0.02 mmol, 10 mol%), Cs₂CO₃ (0.2 mmol, 1.0 equiv.) and arylboronic acids (0.2 mmol, 1.0 equiv.) were added THF (1.0 mL), the reaction mixture was stirred at room temperature for 12 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄. The residue was purified by silica gel column chromatography to afford the product.

4.4 General Procedure for The Synthesis of Products 2j, 2k, 2l and 2m⁴

TsSeCD₃ +
$$\frac{\text{CuSO}_4 \text{ (5 mol\%)}}{\text{NaHCO}_3 \text{ (2.0 equiv.)}}$$

NeOH, r.t., 12 h

2j R = Br

2k R = CHO

2l R = 3-OBn

2m R = 3-OH

To a dry Schlenk tube containing **1b** (0.2 mmol, 1.0 equiv.), CuSO₄ (0.01 mmol, 5.0 mol%), NaHCO₃ (0.4 mmol, 2.0 equiv.) and aryl borates (0.3 mmol, 1.2 equiv.) were added MeOH (1.5 mL), the reaction mixture was stirred at room temperature for 12 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄. The residue was purified by silica gel column chromatography to afford the product.

4.5 General Procedure for The Synthesis of Products 2n, 2o and 2p⁵

To a dry Schlenk tube containing **1b** (0.3 mmol, 1.5 equiv.), CuI (0.01 mmol, 5.0 mol%), Xantphos (0.012 mmol, 6.0 mol%) and alkynes (0.2 mmol, 1.0 equiv.) were added DMSO (2.0 mL), the mixture was stirred at room temperature for 10 h, which was then quenched by water. After the reaction was complete, the reaction was quenched by water, the organic layer was then extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄. The product was obtained by column chromatography.

4.6 General Procedure for The Synthesis of Products 2q, 2r and 2s⁶

TsSeCD₃ + R
$$\longrightarrow$$
 \longrightarrow \longrightarrow \longrightarrow SeCD₃

THF, 0 °C to r.t., N₂, 12 h

2q R = Ph
2r R = Me
2s R = CF₃

To a dry Schlenk tube containing alkynes (0.2 mmol, 1.0 equiv.) was added THF (0.2 mL), then LiHMDS (0.22 mmol, 1.1 equiv.) was dropwise added to the mixture, the mixture was stirred at -78 °C for 10 min, then **1b** dissolved in THF (0.2 mL) were added to the mixture at room temperature for 12 h. After the reaction was complete, the reaction was quenched with NH₄Cl aqueous solution, the organic layer was then extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄. The product was obtained by column chromatography.

4.7 General Procedure for The Synthesis of Products 2t and 2u⁷

To a dry Schlenk tube containing **1b** (0.2 mmol, 1.0 equiv.), indole (0.24 mmol, 1.2 equiv.) were added EtOH (1.0 mL), the mixture was stirred at room temperature for 24 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with dichloromethane, washed with brine, dried over anhydrous Na₂SO₄. The product was obtained by column chromatography.

4.8 General Procedure for The Synthesis of Product 2v⁶

TsSeCD₃ +
$$CI$$
 $TMPMgCI·LiCI (1.1 equiv.)$ $THF, r.t., N_2, 1 h$ CI $SeCD_3$ CI

To a dry Schlenk tube containing 2,5-dichlorothiophene (0.2 mmol, 1.0 equiv.) in THF (0.2 mmol) were added TMPMgCl·LiCl (0.22 mmol, 1.1 equiv.) at room temperature for 30 min, then **1b** (0.22 mmol, 1.1 equiv.) was added to the mixture at room temperature for 30 min. After the reaction was complete, the reaction was quenched with NH₄Cl aqueous solution, the organic layer was then extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄. The product was obtained by column chromatography.

4.9 General Procedure for The Synthesis of Products 2w, 2x and 2y⁶

TsSeCD₃ +
$$\frac{Cs_2CO_3 (1.5 \text{ equiv.})}{DCE, \text{ r.t., } 12 \text{ h}}$$
 $\frac{Cs_2CO_3 (1.5 \text{ equiv.})}{DCE, \text{ r.t., } 12 \text{ h}}$ $\frac{R^2}{R^2}$ $\frac{2w R^1 = CI, R^2 = OMe}{2x R^1 = CI, R^2 = O^tBu}$ $\frac{2v R^1 = OMe, R^2 = OMe}{R^2}$

To a dry Schlenk tube containing **1b** (0.22 mmol, 1.1 equiv.), β -ketoester oxindoles (0.2 mmol, 1.0 equiv.) and Cs₂CO₃ (0.3 mmol, 1.5 equiv.) were added DCE (3.0 mL), the mixture was stirred at room temperature for 12 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with dichloromethane, washed with brine, dried over anhydrous Na₂SO₄. The product was obtained by column chromatography.

4.10 General Procedure for The Synthesis of Products 2z and 2aa-2ac⁶

To a dry Schlenk tube containing **1b** (0.22 mmol, 1.1 equiv.) in DCM (0.5 mL) were added thiol (0.2 mmol, 1.0 equiv.), TEA (0.2 mmol, 1.0 equiv.) and DCM (0.5 mL), the mixture was stirred at room temperature for 4 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with dichloromethane, washed with brine, dried over anhydrous Na₂SO₄. The product was obtained by column chromatography.

4.11 General Procedure for The Synthesis of Product 2ad⁶

TsSeCD₃ +
$$\frac{H}{N}$$
 $\frac{n_{\text{BuLi (1.1 equiv.)}}}{\text{THF, 0 °C to r.t., 12 h}}$ 2ad

To a dry Schlenk tube containing diphenylamine (0.2 mmol, 1.0 equiv.) in THF (1.2 mL) were added ⁿBuLi (0.22 mmol, 1.1 equiv.), the mixture was stirred at -78 °C for 1 h, then **1b** (0.24 mmol, 1.2 equiv.) was added to the mixture at room temperature for 12 h. After the reaction was complete, the reaction was quenched with NH₄Cl aqueous solution, the organic layer was then extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄. The product was obtained by column chromatography.

4.12 General Procedure for The Synthesis of Product 2ae⁶

To a dry Schlenk tube containing diphenylphosphine oxide (0.2 mmol, 1.0 equiv.) in THF (2.0 mL) were added LiHMDS (0.22 mmol, 1.1 equiv.), the mixture was stirred at -78 °C for 15 min, then **1b** (0.24 mmol, 1.2 equiv.) was added to the mixture at room temperature for 12 h. After the reaction was complete, the reaction was quenched with NH₄Cl aqueous solution, the organic layer was then extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄. The product was obtained by column chromatography.

4.13 General Procedure for The Synthesis of Product 3a⁸

To a dry Schlenk tube containing **1b** (0.2 mmol, 1.0 equiv.), allenes (0.24 mmol, 1.2 equiv.) in DCM (1.0 mL) were added DABCO (0.02 mmol, 10 mol%), the mixture stirred at -30 °C for 10 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with dichloromethane, washed with brine, dried over anhydrous Na₂SO₄. The product was obtained by column chromatography.

4.14 General Procedure for The Synthesis of Product 3b⁸

To a dry Schlenk tube containing **1b** (0.2 mmol, 1.0 equiv.), allenes (0.24 mmol, 1.2 equiv.) in DCM (1.0 mL) were added DABCO (0.02 mmol, 10 mol%), the mixture stirred at -30 °C for 10 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with dichloromethane, washed with brine, dried over anhydrous Na₂SO₄. The product was obtained by column chromatography.

4.15 General Procedure for The Synthesis of Product 3c⁸

To a dry Schlenk tube containing **1a** (0.2 mmol, 1.0 equiv.), allenes (0.24 mmol, 1.2 equiv.) in DCM (1.0 mL) were added DABCO (0.02 mmol, 10 mol%), the mixture stirred at -30 °C for 10 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with dichloromethane, washed with brine, dried over anhydrous Na₂SO₄. The product was obtained by column chromatography.

4.16 General Procedure for The Synthesis of Product $3d^8$

To a dry Schlenk tube containing **1b** (0.2 mmol, 1.0 equiv.), allenes (0.24 mmol, 1.2 equiv.) in DCM (1.0 mL) were added DABCO (0.02 mmol, 10 mol%), the mixture stirred at -30 °C for 10 h, then DBU (0.4 mmol, 2.0 equiv.) was added to the mixture at -30 °C for 4 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with dichloromethane, washed with

brine, dried over anhydrous Na₂SO₄. The product was obtained by column chromatography.

4.17 General Procedure for The Synthesis of Product 3e⁸

To a dry Schlenk tube containing **1b** (0.2 mmol, 1.0 equiv.), allenes (0.24 mmol, 1.2 equiv.) in DCM (1.0 mL) were added DABCO (0.02 mmol, 10 mol%), the mixture stirred at -30 °C for 10 h, then DBU (0.4 mmol, 2.0 equiv.) was added to the mixture at -30 °C for 4 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with dichloromethane, washed with brine, dried over anhydrous Na₂SO₄. The product was obtained by column chromatography.

4.18 General Procedure for The Synthesis of Products 3f, 3g and 3h⁹

To a dry Schlenk tube containing Ir(ppy)₃ (0.04 mmol, 2.0 mol%), NaO'Bu (0.1 mmol, 0.5 equiv.) and **1b** (0.4 mmol, 2.0 equiv.) were added DCM (1.0 mL), the mixture was stirred at room temperature and with 12 W blue LED lamp under N₂ for 12 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with dichloromethane, washed with brine, dried over anhydrous Na₂SO₄. The product was obtained by column chromatography.

4.19 General Procedure for The Synthesis of Product 3i¹⁰

To a dry Schlenk tube containing **1b** (0.2 mmol, 1.0 equiv.), Ru(bpy)₃Cl₂ (0.005 mmol, 2.5 mol%), PPh₃AuNTf₂ (0.04 mmol, 20 mol%), Styrene (0.4 mmol, 2.0 equiv.) in DCE (2.0 mL) were added DABCO (0.02 mmol, 10 mol%), the mixture was stirred at room temperature and with 12 W blue LED lamp under N₂ for 12 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with dichloromethane, washed with brine, dried over anhydrous Na₂SO₄. The product was obtained by column chromatography.

4.20 General Procedure for The Synthesis of Products 3j-3n¹¹

To a dry Schlenk tube containing **1j**, **1k**, **1l**, **1m** or **1n** (0.3 mmol, 1.5 equiv.), Esion Y (0.004 mmol, 2.0 mol%) and [1.1.1]Propellane (0.2 mmol, 1.0 equiv.) were added THF (2.0 mL), the mixture was stirred at room temperature and with 12 W blue LED lamp under N₂ for 12 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with dichloromethane, washed with brine, dried over anhydrous Na₂SO₄. The product was obtained by column chromatography.

4.21 General Procedure for The Synthesis of Product 3011

To a dry Schlenk tube containing **10** (0.3 mmol, 1.5 equiv.), Esion Y (0.004 mmol, 2.0 mol%) and [1.1.1]Propellane (0.2 mmol, 1.0 equiv.) were added THF (2.0 mL), the mixture was stirred at room temperature and with 12 W blue LED lamp under N₂ for 12 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with dichloromethane, washed with brine, dried over anhydrous Na₂SO₄. The product was obtained by column chromatography.

4.22 General Procedure for The Synthesis of Product 3p¹¹

TolSO₂Se¹³CH₃ +
$$\frac{\text{Esion Y (2.0 mol\%)}}{\text{THF, r.t., N2, 12 h}}$$
 TolO₂S $\frac{\text{Se}^{13}\text{CH}_3}{\text{Sl-23}}$ Sl-23

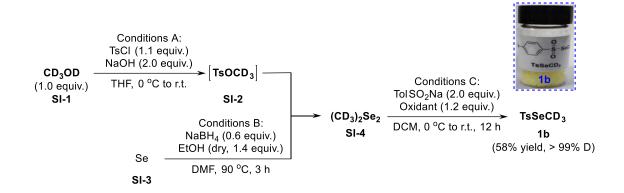
To a dry Schlenk tube containing **1p** (0.3 mmol, 1.5 equiv.), Esion Y (0.004 mmol, 2.0 mol%) and [1.1.1]Propellane (0.2 mmol, 1.0 equiv.) were added THF (2.0 mL), the mixture was stirred at room temperature and with 12 W blue LED lamp under N₂ for 12 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with dichloromethane, washed with brine, dried over anhydrous Na₂SO₄. The product was obtained by column chromatography.

4.23 General Procedure for The Synthesis of Product 11

To a dry Schlenk tube containing **5a** (0.3 mmol, 1.5 equiv.), Cs₂CO₃ (0.3 mmol, 1.0 equiv.) and acrylates or propenone (0.2 mmol, 1.0 equiv.) were added MeOH (0.5 mL), the mixture was stirred at 50 °C for 12 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with dichloromethane, washed with brine, dried over anhydrous Na₂SO₄. The product was obtained by column chromatography.

5. Gram-Scale Operation

5.1 Grams Scale Procedure for The Synthesis of Product 1b



Step I: The aqueous solution (6.5 mL) of NaOH (130 mmol, 2 equiv) was added to the mixture of CD₃OD (65 mmol, 1 equiv.) and THF (6.5 mL) at 0 °C, then TsCl (71.5 mol, 1.1 equiv.) dissolved in THF (16.25 mL) was added to the mixture at 0 °C, the reaction mixture was stirred at 25 °C for 10 h. After the reaction was completed, the mixture was concentrated in vacuo, and then water (150 mL) was added to the residue, followed by processes of extraction using EtOAc (50 mLx3), concentration, and desiccation to give the crude TsOCD₃.

Step II: To a Schlenk tube containing Se powder (65 mmol, 1.0 equiv.) and NaBH₄ (39 mmol, 0.6 equiv.), and DMF (65 mL) were added dried EtOH (156 mmol, 2.4 equiv.), the reaction mixture was stirred at 90 °C for 30 min. The crude TsOCD₃ was then added to the mixture at 90 °C for 3 h. After the reaction was completed, the mixture was cooled to room temperature, which was then quenched by water (200 mL). The organic phase was subsequently extracted with CH₂Cl₂ (50 mLx5), and dried over anhydrous Na₂SO₄, leading to obtaining crude CD₃SeSeCD₃.

Step III: To a three-necked flask containing RSO₂Na (65 mmol, 1.0 equiv.), and crude CD₃SeSeCD₃ in CH₂Cl₂ were dropwise added a cooled mixture (0 °C) of

PhI(OAc)₂ (71.5 mmol, 1.1 equiv.) and CH₂Cl₂ (150 mL), the reaction mixture was stirred at 25 °C for 12 h. After the reaction was complete, the reaction mixture was quenched by water (200 mL), the organic layer was then dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue was purified by silica gel column chromatography to afford the SeCD₃ reagents 1.

5.2 Grams Scale Procedure for The Synthesis of Product 2g

To a dry Schlenk tube containing **1b** (1.67 g, 6.6 mmol, 1.2 equiv.), Cu(OAc)₂ (0.099 g, 0.55 mmol, 10 mol%), 2,2'-bpy (0.085 g, 0.55 mmol, 10 mol%), Cs₂CO₃ (1.79 g, 5.5 mmol, 1.0 equiv.) and arylboronic acids (1.08 g, 5.5 mmol, 1.0 equiv.) were added THF (30 mL), the mixture was stirred at room temperature for 12 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄. The product **2g** was obtained in 1.15g with 83% yield via column chromatography.

5.3 Grams Scale Procedure for The Synthesis of Product 5a

To a three-necked flask containing TsSeCD₃ (5.3 g, 21.2 mmol, 1.2 equiv.), Pr(OTf)₃ (1.0 g, 1.76 mmol, 10 mol%), **L**₁ (0.41 g, 1.76 mmol, 10 mol%) in MeCN (4.4 mL) were added olefin (0.2 mL, 17.6 mmol, 1.0 equiv.), the reaction mixture was stirred at 50 °C for 12 h, which was then quenched by water. The organic layer was

subsquently extracted with EtOAc, washed with brine, and dried over anhydrous Na₂SO₄. The product **5a** was obtained in 5.1g with 81% yield via column chromatography.

5.4 Grams Scale Procedure for The Synthesis of Product 10a

To a dried Schlenk tube containing 7**a** (2.61 g, 7.3 mmol, 1.0 equiv.), agents **8** (1.54 g, 7.3 mmol, 1.0 equiv.), and Cs₂CO₃ (2.37 g, 7.3 mmol, 1.0 equiv.) were added MeOH (12 mL), the reaction mixture was stirred at 50 °C for 12 h, which was then quenched by water. The organic layer was then extracted with EtOAc, washed with brine, and dried over anhydrous Na₂SO₄. The product **11a** was obtained in 1.1g with 65% yield via column chromatography.

5.4 Characterization of Products.

The title compound **1a** was isolated as a yellow solid (64% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (40:1). (Rf 0.5, petroleum ether/ethyl acetate = 10:1). D-inc. >99% (determined by ¹H NMR). MP: 25.2-26.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.87-7.83 (m, 2H), 7.64-7.58 (m, 1H), 7.58-7.48 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 146.2, 133.7, 129.3, 126.4, 12.8-11.9 (m, C-D₃) HRMS (ESI) m/z Calcd for [C₇H₅D₃O₂SSeNa, M + Na]⁺: 261.9491; Found: 261.9496.

The title compound **1b** was isolated as a yellow solid (62% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (40:1). (Rf 0.5, petroleum ether/ethyl acetate = 10:1). D-inc. >99% (determined by ¹H NMR). MP: 30.6-32.1 °C. ¹H NMR (400 MHz, CDCl₃)
$$\delta$$
 7.76 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 2.45

(s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 144.8, 143.7, 129.9, 126, 21.7, 12.7-11.8 (m, C-D₃). **HRMS** (ESI) m/z Calcd for [C₈H₇D₃O₂SSeNa, M + Na]⁺: 275.9647; Found: 275.9644.

The title compound **1c** was isolated as a yellow solid (60% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (40:1). (Rf 0.5, petroleum

ether/ethyl acetate = 10:1). D-inc. >99% (determined by ¹H NMR). MP: 65.7-67.9 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, J = 8.7 Hz, 2H), 7.54 (d, J = 8.6 Hz, 2H), 1.35 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 157.7, 143.6, 126.5, 126.3, 35.4, 31.2, 12.5-12.3 (m, C-D₃). HRMS (ESI) m/z Calcd for [C₁₁H₁₃D₃O₂SSeNa, M + Na]⁺: 318.0117; Found: 318.0121.

The title compound **1d** was isolated as a yellow solid (64% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30:1). (Rf 0.5, petroleum

ether/ethyl acetate = 7:1). D-inc. >99% (determined by ¹H NMR). MP: 71.4-73.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, J = 9.0 Hz, 2H), 6.98 (d, J = 9.0 Hz, 2H), 3.88 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.6, 138.3, 128.9, 114.3, 55.9, 12.6-11.8 (m, C-D₃). HRMS (ESI) m/z Calcd for [C₇H₅D₃O₃SSeNa, M + Na]⁺: 291.9596; Found: 291.9600.

The title compound **1e** was isolated as a yellow solid (63% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (40:1). (Rf 0.5, petroleum

ether/ethyl acetate = 10:1). D-inc. >99% (determined by ${}^{1}H$ NMR). MP: 111.5-112.7 ${}^{\circ}C$. ${}^{1}H$ NMR (400 MHz, CDCl₃) δ 6.95 (s, 2H), 2.69 (s, 6H), 2.31 (s, 3H). ${}^{13}C$ NMR (100 MHz, CDCl₃) δ 143.7, 140.2, 138.7, 132.3, 23.0, 21.2, 11.2 (m, C-D₃). HRMS (ESI) m/z Calcd for [C₁₀H₁₁D₃O₂SSeNa, M + Na]⁺: 303.9960; Found: 303.9961.

The title compound **1f** was isolated as a yellow solid (61% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (40:1). (Rf 0.5, petroleum

ether/ethyl acetate = 10:1). D-inc. >99% (determined by ${}^{1}\mathbf{H}$ NMR). MP: 56.0-58.4 °C. ${}^{1}\mathbf{H}$ NMR (400 MHz, CDCl₃) δ 8.40 (d, J = 2.0 Hz, 1H), 7.99 (d, J = 8.5 Hz, 2H), 7.92 (d, J = 8.0 Hz, 1H), 7.87 (dd, J = 8.8, 2.0 Hz, 1H), 7.72-7.59 (m, 2H). ${}^{13}\mathbf{C}$ NMR (100 MHz, CDCl₃) δ 143.0, 135.2, 131.8, 129.9, 129.2, 129.5, 128.1, 128.0, 127.9, 121.7, 13.0-12.3 (m, C-D₃). HRMS (ESI) m/z Calcd for [C₁₁H₇D₃O₂SSeNa, M + Na]⁺: 311.9647; Found: 311.9644.

The title compound **1g** was isolated as a yellow solid (57% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (40:1). (Rf 0.5, petroleum

ether/ethyl acetate = 10:1). D-inc. >99% (determined by ¹H NMR). MP: 40.8-42.5 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.94-7.84 (m, 2H), 7.27-7.17 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 165.4 (d, ¹ J_{C-F} = 256.7 Hz), 142.3 (d, ⁴ J_{C-F} = 3.1 Hz), 129.3 (d, ³ J_{C-F} = 9.6 Hz), 116.4 (d, ² J_{C-F} = 22.9 Hz), 12.7-12.3 (m, C-D₃). ¹⁹F NMR (376 MHz, CDCl₃) δ 103.1. HRMS (ESI) m/z Calcd for [C₇H₄D₃FO₂SSeNa, M + H]⁺: 257.9577; Found: 257.9576.

The title compound **1h** was isolated as a yellow solid (61% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (40:1). (Rf 0.5, petroleum

ether/ethyl acetate = 10:1). D-inc. >99% (determined by ¹H NMR). MP: 27.4-29.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.88-7.74 (m, 2H), 7.61-7.45 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 144.8, 140.3, 129.6, 128.0, 12.8-12.3 (m, C-D₃). HRMS (ESI) m/z Calcd for [C₇H₄D₃FO₂SSeNa, M + Na]⁺: 295.9101; Found: 295.9106.

The title compound 1i was isolated as a yellow solid (61% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (40:1). (Rf 0.5, petroleum ether/ethyl acetate = 10:1). D-inc. >99% (determined by ¹H NMR). MP: 35.7-37.6 °C. ¹**H NMR** (400 MHz, CDCl₃) δ 7.74 (d, J = 8.8 Hz, 2H), 7.69 (d, J = 8.8 Hz, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 145.3, 132.0, 128.9, 128.0, 12.6-12.3 (m, C-D₃). **HRMS** (ESI) m/z Calcd for $[C_7H_4D_3BrO_2SSeNa, M + Na]^+$: 339.8596; Found: 339.8591.

The title compound 1j was isolated as a yellow solid (62% SO₂SeCD₃ yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (40:1). (Rf 0.5, petroleum ether/ethyl acetate = 10:1). D-inc. >99% (determined by ¹H NMR). MP: 25.7-27.3 °C. ¹**H NMR** (400 MHz, CDCl₃) δ 7.90 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 8.6 Hz, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 146.0, 138.6, 127.8, 100.5, 12.8-12.3 (m, C-D₃). **HRMS** (ESI) m/z Calcd for [C₇H₄D₃IO₂SSeNa, M + Na]⁺: 387.8457; Found: 387.8461.

The title compound 1k was isolated as a yellow solid (62% SO₂SeCD₃ yield) through flash chromatography on silica gel eluting with 1k petroleum ether/ethyl acetate (40:1). (Rf 0.5, petroleum ether/ethyl acetate = 10:1). D-inc. >99% (determined by ¹H NMR). MP: 95.7-97.4 °C. ¹**H NMR** (400 MHz, CDCl₃) δ 8.40 (d, J = 8.8 Hz, 2H), 8.06 (d, J = 8.8 Hz, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 151.1, 150.4, 127.8, 124.8, 13.2-12.8 (m, C-D₃). **HRMS** (ESI) m/z Calcd for $[C_7H_4D_3NO_4SSeNa, M + Na]^+$: 306.9342; Found: 306.9344.

The title compound 11 was isolated as a yellow solid (57% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (40:1). (Rf 0.5, petroleum ether/ethyl acetate = 10:1). D-inc. >99% (determined by ¹H NMR). MP: 34.8-36.5 °C.

¹**H NMR** (400 MHz, CDCl₃) δ 8.01 (d, J = 8.3 Hz, 2H), 7.83 (d, J = 8.3 Hz, 2H). ¹³**C**

NMR (100 MHz, CDCl₃) δ 149.4, 135.2 (q, ${}^{2}J_{C-F}$ = 33.2 Hz), 127.1, 126.6 (q, ${}^{3}J_{C-F}$ = 3.7 Hz), 123.2 (d, ${}^{1}J_{C-F}$ = 273.1 Hz), 13.0-12.5 (m, C-D₃). ¹⁹**F NMR** (376 MHz, CDCl₃) δ -63.1. **HRMS** (ESI) m/z Calcd for [C₈H₄D₃F₃O₂SSeNa, M + H]⁺: 307.9545; Found: 307.9545.

The title compound **Im** was isolated as a yellow solid (56% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.5, petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by **1H NMR**). **MP**: 112.4-114.5 °C.

¹**H NMR** (400 MHz, CDCl₃) δ 9.13 (dd, J = 4.3, 1.8 Hz, 1H), 8.31 (dd, J = 7.4, 1.5 Hz, 1H), 8.27 (dd, J = 8.3, 1.8 Hz, 1H), 8.07 (dd, J = 8.1, 1.5 Hz, 1H), 7.62 (t, J = 7.8 Hz, 1H), 7.57 (dd, J = 8.3, 4.2 Hz, 1H). ¹³**C NMR** (100 MHz, CDCl₃) δ 151.2, 143.5, 142.8, 136.6, 134.0, 129.3, 128.6, 125.2, 122.6, 13.7-13.3 (m, C-D₃). **HRMS** (ESI) m/z Calcd for [C₁₀H₆D₃NO₂SSeNa, M + Na]⁺: 312.9600; Found: 312.9605.

EtSO₂SeCD₃
1n

The title compound **1n** was isolated as a yellow solid (58% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (40:1). (Rf 0.5, petroleum ether/ethyl acetate = 10:1).

D-inc. >99% (determined by ¹**H NMR**). ¹**H NMR** (400 MHz, CDCl₃) δ 3.35 (q, J = 7.4 Hz, 2H), 1.39 (t, J = 7.3 Hz, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 59.6, 12.6-11.7 (m, C-D₃), 8.7. **HRMS** (ESI) m/z Calcd for [C₃H₆D₃O₂SSe, M + H]⁺: 191.9671; Found: 191.9672.

The title compound **10** was isolated as a yellow solid (58% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (40:1). (Rf 0.5, petroleum ether/ethyl acetate = 10:1). D-inc. >99% (determined by ¹H

NMR). ¹**H NMR** (400 MHz, CDCl₃) δ 2.80 (d, J = 12.4 Hz, 1H), 2.43 (d, J = 12.4 Hz, 1H), 2.39-2.26 (m, 1H), 2.11-2.04 (m, 1H), 2.01-1.94 (m, 2H), 1.85 (d, J = 18.4 Hz,

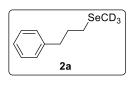
1H), 1.60 (d, J = 9.2 Hz, 1H), 1.36 (t, J = 9.1 Hz, 1H), 1.01 (s, 3H), 0.87 (s, 3H). ¹³C **NMR** (100 MHz, CDCl₃) δ 217.7, 61.3, 48.1, 43.6, 43.3, 27.9, 26.9, 22.4, 20.2, 20.1, 6.7-6.2 (m, C-D₃). **HRMS** (ESI) m/z Calcd for [C₁₁H₁₅D₃O₃SSeNa, M + Na]⁺: 336.0222; Found: 336.0224.

The title compound **1p** was isolated as a white solid (51% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (6:1). (Rf 0.4, petroleum ether/ethyl acetate = 3:1). D-inc. >99% (determined by ¹H

NMR). ¹**H NMR** (400 MHz, CDCl₃) δ 7.63 (m, J = 8.3, 2.2 Hz, 1H), 7.59 (d, J = 2.1 Hz, 1H), 7.49 - 7.36 (m, 1H), 2.99 (m, 2H), 2.52 (m, 1H), 2.47 - 2.41 (m, 1H), 2.35 (m, 1H), 2.22 - 2.12 (m, 1H), 2.12 - 2.04 (m, 2H), 2.00 (m, 1H), 1.71 - 1.58 (m, 2H), 1.58 - 1.45 (m, 3H), 0.92 (s, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 220.4, 146.3, 143.9, 138.3, 126.7, 126.3, 123.8, 50.5, 47.9, 44.7, 37.7, 35.8, 31.6, 29.5, 26.1, 25.6, 21.6, 13.9. **HRMS** (ESI) m/z Calcd for [C₁₉H₂₁D₃O₃SSe, M + H]⁺:416.0872 ; Found: 416.0873.

The title compound **1q** was isolated as a yellow solid (56% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (40:1). (Rf 0.5, petroleum

ether/ethyl acetate = 10:1). D-inc. >99% (determined by ${}^{1}H$ NMR). ${}^{1}H$ NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 2.76-2.40 (m, 6H). ${}^{13}C$ NMR (100 MHz, CDCl₃) δ 144.7, 143.5, 129.8, 126.5, 56.3, 12.8 (s, ${}^{13}C$ -H₃). HRMS (ESI) m/z Calcd for [${}^{13}C_{1}C_{7}H_{10}O_{2}SSeNa$, M + Na]⁺: 273.9498; Found: 273.9502.



The title compound **2a** was isolated as a colorless oil (74% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99%

(determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 7.29 (dd, J = 8.1, 6.9 Hz, 2H), 7.23-7.14 (m, 3H), 2.72 (t, J = 7.4 Hz, 2H), 2.55 (t, J = 7.4 Hz, 2H), 2.11-1.89 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 141.7, 128.6, 128.5, 126.0, 36.0, 31.8, 24.8. **HRMS** (ESI) m/z Calcd for $[C_{10}H_{13}D_3Se, M + H]^+$: 218.0522; Found: 218.0528.

SeCD₃ 2b

The title compound **2b** was isolated as a colorless oil (75% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99% (determined by ¹H

NMR). ¹**H NMR** (400 MHz, CDCl₃) δ 2.45 (d, J = 6.8 Hz, 2H), 1.91-1.79 (m, 2H), 1.77-1.67 (m, 2H), 1.67-1.59 (m, 1H), 1.54-1.40 (m, 1H), 1.33-1.20 (m, 2H), 1.18-1.07 (m, 1H), 1.03-0.88 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 38.4, 34.0, 33.4, 26.3, 26.2. **HRMS** (ESI) m/z Calcd for [C₈H₁₃D₃SeNa, M + Na]⁺: 218.0503; Found: 218.0510.

The title compound 2c was isolated as a colorless oil (80% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99% (determined by ¹**H NMR**). ¹**H NMR** (400 MHz, CDCl₃) δ 7.04 (d, J = 1.9 Hz, 1H), 6.94 (dd, J = 8.1, 2.0 Hz, 1H), 6.71 (d, J = 8.1 Hz, 1H), 4.55 (t, J = 8.7 Hz, 2H), 3.19(t, J = 8.7 Hz, 2H), 2.93-2.85 (m, 2H), 2.79-2.72 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 158.8, 133.5, 128.0, 127.3, 125.1, 125.0, 109.2, 71.4, 36.4, 29.9, 27.1. **HRMS** (ESI) m/z Calcd for $[C_{11}H_{11}D_3OSeNa, M + Na]^+$: 246.0471; Found: 246.0472.

The title compound 2d was isolated as a colorless oil (80% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99%

(determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, J = 8.8 Hz, 2H), 7.46 (d, J = 8.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 137.6, 129.5, 128.1 (q, ${}^{2}J_{C-F}$ = 32.8 Hz), 125.8 (q, ${}^{3}J_{C-F}$ = 3.7 Hz), 124.3 (q, ${}^{1}J_{C-F}$ = 271.8 Hz). ${}^{19}F$ NMR (376 MHz, CDCl₃) δ -62.5. **HRMS** (ESI) m/z Calcd for [C₈H₄D₃F₃SeNa, M + Na]⁺: 265.9751; Found: 265.9755.

$$\begin{bmatrix} \mathsf{Bn} \\ \mathsf{N} \\ \mathsf{Et} \end{bmatrix} \mathsf{SeCD}_3$$

The title compound **2e** was isolated as a colorless oil (86% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99%

(determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.20 (m, 4H), 7.19-7.10 (m, 3H), 6.52 (d, J = 8.3 Hz, 2H), 4.43 (s, 2H), 3.39 (q, J = 7.1 Hz, 2H), 1.12 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 147.8, 139.0, 134.4, 128.7, 127.0, 126.5, 115.5, 112.9, 54.0, 45.4, 12.2. **HRMS** (ESI) m/z Calcd for [C₁₆H₁₆D₃NSeNa, M + Na]⁺: 331.0763; Found: 331.0763.

The title compound **2f** was isolated as a colorless oil (91% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (40/1). (Rf 0.7, petroleum ether/ethyl acetate = 20:1). D-inc. >99% (determined by ¹H NMR). ¹H NMR (400

MHz, CDCl₃) δ 7.41 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H). ¹³C **NMR** (100 MHz, CDCl₃) δ 158.9, 133.5, 121.5, 114.9, 55.4. **HRMS** (ESI) m/z Calcd for $[C_8H_7D_3OSeNa, M + Na]^+$: 227.9977; Found: 227.9980.

The title compound 2g was isolated as a white solid (88% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99% (determined by ¹H

NMR). **MP**: 103.1-105.1 °C. ¹**H NMR** (400 MHz, CDCl₃) δ 7.61-7.56 (m, 2H), 7.50 (s, 4H), 7.44 (dd, J = 8.5, 6.9 Hz, 2H), 7.40-7.32 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 140.6, 139.2, 131.0, 130.8, 129.0, 127.8, 127.4, 127.0. **HRMS** (ESI) m/z Calcd for $[C_{13}H_9D_3SeNa, M + Na]^+$: 274.0190; Found: 274.0197.

$$\begin{array}{c|c}
\hline
O_2N & SeCD_3 \\
\hline
\mathbf{2h} \\
\end{array}$$

The title compound **2h** was isolated as a yellow solid (70% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.5, petroleum ether/ethyl acetate = 10:1). D-inc. >99% (determined by ¹H NMR). MP: 39.0-41.2 °C. ¹**H NMR** (400 MHz, CDCl₃) δ 8.09 (d, J = 8.9 Hz, 2H), 7.45 (d, J = 8.9 Hz, 2H). ¹³C **NMR** (100 MHz, CDCl₃) δ 145.8, 143.5, 128.7, 123.9. **HRMS** (ESI) m/z Calcd for $[C_7H_7D_3NO_2SeNa, M + Na]^+$: 242.9723; Found: 242.9724.

The title compound 2i was isolated as a yellow solid (80% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.5, petroleum ether/ethyl acetate = 10:1). D-inc. >99% (determined by ¹H NMR). MP: 91.2-93.0 °C. ¹**H NMR** (400 MHz, CDCl₃) δ 7.37 (d, J = 8.7 Hz, 2H), 7.27 (d, J = 7.2 Hz, 2H), 6.50 (s, 1H), 1.51 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 152.8, 137.2, 132.2, 124.7, 119.4, 80.8, 28.4. **HRMS** (ESI) m/z Calcd for $[C_{12}H_{14}D_3NO_2Se, M + Na]^+$: 313.0505; Found: 313.0501.

The title compound 2j was isolated as a yellow solid (82% yield) SeCD₃ through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99% (determined by ¹H NMR). MP: 46.8-48.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.34 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 132.1, 132.0, 130.8, 120.2. HRMS (ESI) m/z Calcd for [C₇H₄D₃BrSeNa, M + Na]⁺: 275.8977; Found: 275.8984.

The title compound **2k** was isolated as a colorless oil (81% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.6, petroleum ether). D-inc. >99% (determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 9.93 (s, 1H), 7.73 (d, J =8.3 Hz, 2H), 7.48 (d, J = 8.3 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 191.7, 142.6,

134.0, 130.1, 128.9. **HRMS** (ESI) m/z Calcd for [C₈H₅D₃OSeNa, M + Na]⁺: 225.9826; Found: 225.9830.

BnO SeCD₃ 21

The title compound 21 was isolated as a white solid (80% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.6, petroleum ether). D-inc. >99% (determined by ¹H

NMR). **MP**: 36.8-38.1 °C. ¹**H NMR** (400 MHz, CDCl₃) δ 7.47-7.43 (m, 2H), 7.42-7.38 (m, 2H), 7.37-7.31 (m, 1H), 7.18 (t, J = 7.9 Hz, 1H), 7.07-7.04 (m, 1H), 7.04-6.99 (m, 1H), 6.87-6.76 (m, 1H), 5.06 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 159.2, 136.9, 133.1, 129.9, 128.8, 128.2, 127.7, 122.7, 116.7, 112.6, 70.1. **HRMS** (ESI) m/z Calcd for $[C_{14}H_{13}D_3OSeNa, M + Na]^+$: 304.0296; Found: 304.0292.

SeCD₃ 2m

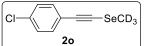
The title compound 2m was isolated as a yellow oil (83% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.5, petroleum ether/ethyl acetate = 20:1). D-inc. >99% (determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 7.48 (m, 1H), 7.16 (m, 1H),

6.91 (m, 1H), 6.73 (m, 1H), 6.44 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 156.3, 136.6, 131.1, 121.0, 116.7, 114.5, 9.7-8.4 (m, C-D₃). HRMS (ESI) m/z Calcd for $[C_7H_5D_3OSe, M + H]^+$: 192.00001; Found: 192.00001.

$$\operatorname{\mathsf{Br}}$$
 $\operatorname{\mathsf{SeCD}}_3$ $\operatorname{\mathsf{2n}}$

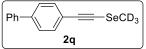
The title compound 2n was isolated as a yellow oil (80% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99%

(determined by ${}^{1}H$ NMR). MP: 36.8-38.1 ${}^{\circ}C$. ${}^{1}H$ NMR (400 MHz, CDCl₃) δ 7.34 (d, J = 8.6 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 133.0, 131.6, 122.5, 122.4, 97.3, 73.0, 9.5-9.1 (m, C-D₃). HRMS (ESI) m/z Calcd for $[C_9H_4D_3BrSeNa, M + Na]^+$: 299.8977; Found: 299.8969.



The title compound **20** was isolated as a yellow oil (71% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99% (determined by ¹H NMR). ¹**H NMR** (400 MHz, CDCl₃) δ 7.40 (t, J = 1.8 Hz, 1H), 7.31-7.25 (m, 2H), 7.25-7.19 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 134.2, 131.4, 129.6, 129.6, 128.4, 125.3, 97.0, 73.3, 9.6-9.1 (m, C-D₃). **HRMS** (ESI) m/z Calcd for [C₉H₄D₃ClSeK, M + K]⁺: 271.9221; Found: 271.9229.

The title compound **2p** was isolated as a yellow oil (91% SeCD₃ MeO yield) through flash chromatography on silica gel eluting 2p with petroleum ether. (Rf 0.5, petroleum ether). D-inc. >99% (determined by ¹H **NMR**). ¹**H NMR** (400 MHz, CDCl₃) δ 7.37 (d, J = 8.7 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 159.7, 133.4, 115.7, 114.0, 98.0, 69.2, 55.4, 9.9-0.1 (m, C-D₃). **HRMS** (ESI) m/z Calcd for $[C_{10}H_7D_3OSeNa, M + Na]^+$: 251.9977; Found: 251.9976.



yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99% (determined by 1 H NMR). MP: 86.0-67.1 °C. 1 H NMR (400 MHz, CDCl₃) δ 7.59 (dd, J = 8.3, 1.3 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.45 (t, J = 7.7Hz, 2H), 7.39-7.33 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 140.9, 140.4, 132.1, 128.9, 127.7, 127.1, 127.1, 122.5, 98.2, 72.0. HRMS (ESI) m/z Calcd for $[C_{15}H_9D_3SeNa, M + Na]^+$: 298.0185; Found: 298.0193.

The title compound 2q was isolated as a yellow solid (80%

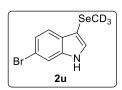
The title compound **2r** was isolated as a yellow oil (71%) SeCD₃ Me 2r yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99% (determined by ¹H **NMR**). ¹**H NMR** (400 MHz, CDCl₃) δ 7.32 (d, J = 8.2 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 2.34 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 138.4, 131.7, 129.1, 120.5, 98.4, 70.2, 21.6, 9.6 (m, C-D₃). **HRMS** (ESI) m/z Calcd for $[C_{10}H_7D_3SeNa, M + Na]^+$: 236.0034; Found: 236.0042.

The title compound 2s was isolated as a yellow oil (80%) -SeCD₃ yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99% (determined by ¹H **NMR**). ¹**H NMR** (400 MHz, CDCl₃) δ 7.55 (d, J = 8.2 Hz, 2H), 7.49 (d, J = 8.2 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 131.6, 129.7 (q, ${}^{2}J_{C-F}$ = 32.6 Hz), 127.4 (d, ${}^{4}J_{C-F}$ = 1.6 Hz), 125.3 (q, ${}^{3}J_{C-F}$ = 3.9 Hz), 121.4 (q, ${}^{1}J_{C-F}$ = 272.0 Hz), 9.6-9.1 (m, C-D₃). ¹⁹**F NMR** (376 MHz, CDCl₃) δ -62.8. **HRMS** (ESI) m/z Calcd for [C₁₀H₅D₃F₃Se, M + H]+: 267.9926; Found: 267.9934.

SeCD₃ 2t

through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.6, petroleum ether/ethyl acetate = 10:1). D-inc. >99% (determined by 1 H NMR). 1 H NMR (400 MHz, CDCl₃) δ 8.13 (s, 1H), 7.62 (d, J = 8.1 Hz, 1H), 7.25 (d, J = 2.5 Hz, 1H), 7.19 (d, J = 1.4 Hz, 1H), 7.05(d, J = 7.4 Hz, 1H), 2.48 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 136.9, 132.7, 128.6, 128.0, 127.8, 122.3, 119.8, 111.4, 21.8, 8.9-8.5 (m, C- D_3). **HRMS** (ESI) m/z Calcd for $[C_{10}H_9D_3NSe, M + H]^+$: 229.0318; Found: 229.0316.

The title compound 2t was isolated as a yellow oil (78% yield)



The title compound **2u** was isolated as a yellow solid (75% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.6, petroleum ether/ethyl acetate = 10:1). D-inc. >99% (determined by ¹H NMR). MP: 53.2-55.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.26 (s, 1H), 7.83 (d, J = 2.0 Hz, 1H), 7.30-7.24 (m, 2H), 7.20 (d, J =8.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 134.9, 131.7, 130.5, 125.6, 122.8, 113.9,

112.9, 99.7, 9.0 (m, C-D₃). **HRMS** (ESI) m/z Calcd for [C₉H₅D₃BrNSeNa, M + Na]⁺: 314.9086; Found: 314.9090.

SeCD₂

The title compound 2v was isolated as a yellow oil (65% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.6, petroleum ether/ethyl acetate = 10:1). D-inc. >99% (determined by ${}^{1}H$ NMR). ${}^{1}H$ NMR (400 MHz, CDCl₃) δ 6.74 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 129.1, 127.1, 125.7, 123.5. **HRMS** (ESI) m/z Calcd for [C₅HD₃Cl₂SSeNa, M + Na]⁺: 271.8662; Found: 271.8653.

The title compound 2w was isolated as a yellow solid (91%

The title compound 2x was isolated as a yellow solid (89%

yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.5, petroleum ether/ethyl acetate = 10:1). D-inc. >99% (determined by ¹H NMR). MP: 96.9-98.1 °C. ¹**H NMR** (400 MHz, CDCl₃) δ 7.74 (d, J = 8.1 Hz, 1H), 7.45-7.37 (m, 2H), 3.98 (d, J= 18.5 Hz, 1H), 3.82 (s, 3H), 3.13 (d, J = 18.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 194.7, 170.0, 151.1, 141.9, 132.5, 129.1, 126.6, 126.5, 53.5, 49.5, 38.6. **HRMS** (ESI) m/z Calcd for $[C_{12}H_8D_3ClO_3SeNa, M + Na]^+$: 343.9642; Found: 343.9644.

O^tBu Σ_{eCD_3} CI

yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.5, petroleum ether/ethyl acetate = 10:1). D-inc. >99% (determined by ¹H NMR). MP: 80.6-82.0 °C. ¹**H NMR** (400 MHz, CDCl₃) δ 7.72 (d, J = 8.1 Hz, 1H), 7.43-7.34 (m, 2H), 3.92 (d, J = 8.1 Hz, 1H), 7.43-7.34 (m, J = 8.1 Hz, 1H) = 18.4 Hz, 1H), 3.07 (d, J = 18.4 Hz, 1H), 1.49 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 195.20, 168.30, 151.2, 141.6, 132.8, 128.9, 126.4, 126.4, 83.2, 50.5, 38.7, 28.0, 6.2 (m, C-D₃). **HRMS** (ESI) m/z Calcd for $[C_{15}H_{14}D_3ClO_3SeNa, M + Na]^+$: 386.0112; Found: 386.0113.

The title compound **2y** was isolated as a yellow solid (78% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1). (Rf 0.6, petroleum

ether/ethyl acetate = 5:1). D-inc. >99% (determined by ${}^{1}H$ NMR). MP: 80.5-82.1 °C. ${}^{1}H$ NMR (400 MHz, CDCl₃) δ 7.72 (d, J = 8.5 Hz, 1H), 6.92 (m, 1H), 6.83 (d, J = 2.3 Hz, 1H), 3.94 (d, J = 18.3 Hz, 1H), 3.86 (s, 3H), 3.78 (s, 3H), 3.12 (d, J = 18.2 Hz, 1H). ${}^{13}C$ NMR (100 MHz, CDCl₃) δ 195.1, 170.5, 165.8, 152.9, 127.0, 127.0, 116.1, 109.4, 55.8, 53.3, 50.1, 39.1. HRMS (ESI) m/z Calcd for [C₁₃H₁₁D₃O₄SeNa, M + Na]⁺: 340.0138; Found: 340.0142.

The title compound **2z** was isolated as a yellow oil (86% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99% (determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 2.79 (t, J = 7.4 Hz, 2H), 1.72-1.61 (m, 2H), 1.39 (d, J = 7.2 Hz, 2H), 1.34-1.20 (m, 16H), 0.88 (t, J = 6.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 38.0, 32.1, 30.7, 29.8, 29.8, 29.7, 29.7, 29.5, 29.4, 28.6, 22.8, 14.3. **HRMS** (ESI) m/z Calcd for [C₁₃H₂₅D₃SSeNa, M + Na]⁺: 322.1163; Found: 322.1161.

The title compound **2aa** was isolated as a yellow solid (81% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1). (Rf 0.5, petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by 1 H NMR). MP: 39.7-41.3 °C. 1 H NMR (400 MHz, CDCl₃) δ 8.09 (d, J = 9.0 Hz, 2H), 7.61 (d, J = 9.0 Hz, 2H). 13 C NMR (100 MHz, CDCl₃) δ 146.2, 145.9, 127.7, 124.2, 12.9 (m, C-D₃). HRMS (ESI) m/z Calcd for [C₇H₄D₃NO₂SSeNa, M + Na]⁺: 274.9443; Found: 274.9445.

The title compound **2ab** was isolated as a yellow oil (89% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (6:1). (Rf 0.6, petroleum ether/ethyl

acetate = 3:1). D-inc. >99% (determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 5.33 (d, J = 8.2 Hz, 1H), 4.65-4.53 (m, 1H), 3.76 (s, 3H), 3.34-3.12 (m, 2H), 1.44 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 171.5, 155.2, 80.3, 53.7, 52.7, 39.9, 28.4. **HRMS** (ESI) m/z Calcd for $[C_{10}H_{16}D_3NO_4SSeNa, M + Na]^+$: 355.0281; Found: 355.0281.

SSeCD₃

The title compound **2ac** was isolated as a yellow oil (89% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (6:1). (Rf 0.4, petroleum ether/ethyl

acetate = 3:1). D-inc. >99% (determined by 1H NMR). ¹H NMR (400 MHz, CDCl₃) δ 6.38 (d, J = 7.8 Hz, 1H), 4.87 (m, 1H), 3.76 (s, 3H), 3.46 - 2.95 (m, 2H), 2.04 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.0, 169.8, 52.6, 52.4, 39.2, 23.1, 12.8-12.3 (m, C-D₃). HRMS (ESI) m/z Calcd for [C₆H₈D₃NO₃SSe, M + K]+: 298.9445; Found: 298.9446.

 Ph_N SeCD₃ Ρ'n 2ad

The title compound 2ad was isolated as a yellow oil (51% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.7, petroleum ether). D-inc. >99% (determined by ¹H **NMR**). ¹**H NMR** (400 MHz, DMSO- d_6) δ 7.32 (dd, J = 8.6, 7.2 Hz, 4H), 7.14 (dd, J= 8.7, 1.2 Hz, 4H), 7.08-7.01 (m, 2H). ¹³C **NMR** (100 MHz, DMSO- d_6) δ 148.2, 129.3, 122.8, 121.8. **HRMS** (ESI) m/z Calcd for $[C_{13}H_{10}D_3NSeNa, M + Na]^+$: 289.0294; Found: 289.0291.

Ph P D₃CSe Ph

The title compound 2ae was isolated as a yellow oil (54% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (40:1). (Rf 0.6, petroleum ether/ethyl acetate = 20:1).

D-inc. >99% (determined by 1 H NMR). 1 H NMR (400 MHz, CDCl₃) δ 7.97-7.82 (m, 4H), 7.57-7.51 (m, 2H), 7.50-7.44 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 133.4, 132.5, 132.5, 132.3, 131.7, 131.6, 128.9, 128.8. ³¹**P NMR** (162 MHz, CDCl₃) δ 44.3. **HRMS** (ESI) m/z Calcd for $[C_{13}H_{10}D_3OPSeNa, M + Na]^+$: 289.0294; Found: 289.0291.

The title compound **3a** was isolated as a yellow oil (72% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1). (Rf 0.5, petroleum ether/ethyl acetate =

5:1). D-inc. >99% (determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 8.35 (s, 1H), 7.83 - 7.77 (m, 2H), 7.66 (d, J = 8.3 Hz, 2H), 7.59 - 7.53 (m, 1H), 7.42 (t, J = 7.8 Hz, 2H), 7.23 - 7.15 (m, 2H), 4.02 (s, 2H), 2.35 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 192.3, 144.3, 144.1, 136.1, 136.0, 133.6, 132.7, 129.8, 128.7, 128.2, 128.2, 38.9, 21.7. **HRMS** (ESI) m/z Calcd for [C₁₈H₁₅D₃O₃SSe, M + H]⁺: 398.0332; Found: 398.0332.

The title compound **3b** was isolated as a yellow solid (80% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1). (Rf 0.6, petroleum

ether/ethyl acetate = 5:1). D-inc. >99% (determined by ${}^{1}H$ NMR). MP: 113.5-115.1 ${}^{\circ}C$. ${}^{1}H$ NMR (400 MHz, CDCl₃) δ 7.63 (d, J = 8.3 Hz, 2H), 7.23 (m, 5H), 7.21 - 7.17 (m, 3H), 7.15 (m, 2H), 7.11 (d, J = 8.1 Hz, 2H), 6.51 (s, 1H), 6.57 (s, 1H), 6.37 (s, 1H), 4.42 (s, 1H), 2.30 (s, 3H). ${}^{13}C$ NMR (100 MHz, CDCl₃) δ 168.2, 146.1, 145.0, 139.5, 139.4, 135.8, 130.0, 129.1, 128.6, 128.5, 128.2, 128.2, 127.2, 127.0, 78.4, 78.4, 34.1, 21.8. HRMS (ESI) m/z Calcd for [C₂₅H₂₁D₃O₄SSeNa, M + Na]⁺: 504.0822; Found: 504.0820.

The title compound **3c** was isolated as a yellow oil (72% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.6, petroleum

ether/ethyl acetate = 5:1). D-inc. >99% (determined by 1 H NMR). 1 H NMR (400 MHz, CDCl₃) δ 7.77 (s, 1H), 7.75 (s, 1H), 7.41-7.36 (m, 5H), 7.36-7.33k (m,

5H), 7.33-7.28 (m, 2H), 7.09 (q, J = 1.5 Hz, 1H), 6.93 (s, 1H), 2.45 (s, 3H), 2.26 (s, 1H), 2.26 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 163.6, 155.2, 145.5, 139.5, 134.2, 130.3, 128.9, 128.8, 128.6, 128.3, 127.7, 124.9, 124.9, 78.1, 21.8, 13.5. **HRMS** (ESI) m/z Calcd for $[C_{25}H_{21}D_3O_4SSeNa, M + Na]^+$: 504.0822; Found: 504.0825.

$$\begin{array}{c|c} \hline \\ Ph & O & O & Ph \\ \hline \\ O & & SeCD_3 \\ \hline & 3d \\ \hline \end{array}$$

The title compound 3d was isolated as a yellow solid (71% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.6, petroleum

ether/ethyl acetate = 5:1). D-inc. >99% (determined by ¹H NMR). MP: 97.5-99.0 °C. ¹**H NMR** (400 MHz, CDCl₃) δ 7.86-7.77 (m, 2H), 7.53 (t, J = 7.5 Hz, 1H), 7.39 (t, J =7.8 Hz, 2H), 7.34-7.27 (m, 6H), 7.27-7.23 (m, 2H), 7.20 (dd, J = 1.9, 1.9 Hz, 2H), 6.71 (s, 1H), 6.64 (s, 1H), 6.47 (s, 1H), 4.47 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 168.2, 145.9, 139.4, 139.3, 138.8, 133.9, 129.5, 129.4, 128.6, 128.5, 128.3, 128.2, 127.2, 127.1, 78.5, 78.5, 34.0, 6.0-5.8 (m, C-D₃). HRMS (ESI) m/z Calcd for $[C_{24}H_{19}D_3O_4SSeNa, M + Na]^+: 512.0485;$ Found: 512.0489.

through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.6, petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 8.3 Hz, 2H), 7.42 - 7.31 (m, 3H), 7.29 (s, 1H), 7.27 (d, J = 2.1 Hz, 2H), 7.25 (s, 1H), 6.72 - 6.68 (m, 1H), 6.47 (d, J = 1.0 Hz, 1H), 5.00 (q, J = 1.0 Hz) 12.4 Hz, 2H), 4.38 (s, 1H), 2.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 169.3, 146.1, 145.0, 135.8, 135.2, 130.0, 129.1, 128.7, 128.6, 128.5, 128.2, 67.5, 34.2, 21.8. **HRMS**

(ESI) m/z Calcd for $[C_{25}H_{21}D_3O_4SSeNa, M + Na]^+$: 450.0334; Found: 450.0337.

The title compound **3f** was isolated as a yellow solid (65% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.6, petroleum

The title compound **3e** was isolated as a yellow oil (80% yield)

ether/ethyl acetate = 5:1). D-inc. >99% (determined by ¹H NMR). MP: 120.7-122.0 °C. ¹**H NMR** (400 MHz, CDCl₃) δ 7.43 (d, J = 8.3 Hz, 2H), 7.15 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.2 Hz, 2H), 6.39 (s, 1H), 2.38 (s, 3H), 2.36 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 156.5, 143.8, 139.5, 139.1, 132.5, 129.5, 128.7, 128.3, 127.7, 124.4, 21.7, 21.6. **HRMS** (ESI) m/z Calcd for [C₁₇H₁₅D₃O₂SSeNa, M + Na]+: 392.0273; Found: 392.0274.

The title compound **3g** was isolated as a yellow solid (60% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.6, petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by ¹H NMR). MP: 148.5-150.0 °C. ¹**H NMR** (400 MHz, CDCl₃) δ 7.54-7.35 (m, 4H), 7.18 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.1 Hz, 2H), 6.42 (s, 1H), 2.39 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 154.6, 144.2, 138.8, 134.3, 131.3, 130.0, 129.6, 127.7, 125.3, 123.8, 21.8. **HRMS** (ESI) m/z Calcd for $[C_{16}H_{12}D_3BrO_2SSeNa, M + Na]^+$: 455.9222; Found: 455.9221.

through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.6, petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by ¹H NMR). MP: 100.7-101.9 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, J = 8.3 Hz, 2H), 7.37-7.31 (m, 1H), 7.31-7.26 (m, 2H), 7.17-7.11 (m, 4H), 6.44 (s, 1H), 2.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 156.3, 143.8, 139.0, 135.4, 129.5, 129.4, 128.4, 128.0, 127.7, 124.9, 21.7. HRMS (ESI) m/z Calcd for $[C_{16}H_{13}D_3O_2SSeNa, M + Na]^+$: 378.0117; Found: 378.0119.

The title compound 3i was isolated as a yellow oil (70% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1). (Rf 0.6, petroleum ether/ethyl acetate =

The title compound **3h** was isolated as a yellow solid (67% yield)

5:1). D-inc. >99% (determined by ¹H NMR). MP: 70.8-72.4 °C. ¹H NMR (400 MHz,

CDCl₃) δ 7.48 (d, J = 8.3 Hz, 2H), 7.15-7.09 (m, 5H), 7.07 (dd, J = 7.0, 3.0 Hz, 2H), 4.40 (dd, J = 4.0, 4.0 Hz, 1H), 3.94 (dd, J = 10.6, 10.6 Hz, 1H), 3.70 (dd, J = 4.0, 4.0 Hz, 1H), 2.35 (s, 3H). ¹³C **NMR** (100 MHz, CDCl₃) δ 144.5, 138.9, 136.4, 129.6, 128.6, 128.1, 127.7, 127.4, 61.8, 35.6, 21.6. **HRMS** (ESI) m/z Calcd for [C₁₆H₁₅D₃O₂SSeNa, M + Na]⁺: 380.0273; Found: 380.0273.

$$\begin{array}{c|c}
 & O \\
 & SeCD_3 \\
 & O \\
 & 3j
\end{array}$$

The title compound **3j** was isolated as a yellow oil (91% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1). (Rf 0.5,

petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by ${}^{1}\mathbf{H}$ NMR). ${}^{1}\mathbf{H}$ NMR (400 MHz, CDCl₃) δ 7.72 (d, J = 8.9 Hz, 2H), 7.36 (d, J = 8.9 Hz, 2H), 2.46 (s, 3H), 2.19 (s, 6H). ${}^{13}\mathbf{C}$ NMR (100 MHz, CDCl₃) δ 145.0, 133.8, 130.0, 128.7, 54.0, 53.6, 31.1, 21.8. HRMS (ESI) m/z Calcd for [C₁₃H₁₃D₃O₂SSeNa, M + Na]⁺: 342.0224; Found: 342.0224.

The title compound **3k** was isolated as a white solid (88% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1). (Rf 0.5,

petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by ¹H NMR). MP: 91.4-93.8 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 8.9 Hz, 2H), 7.01 (d, J = 8.9 Hz, 2H), 3.87 (s, 3H), 2.17 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 164.0, 130.8, 128.2, 114.6, 55.8, 53.9, 53.7, 31.1, 3.3-2.9 (m, C-D₃). HRMS (ESI) m/z Calcd for [C₁₃H₁₃D₃O₃SSeNa, M + Na]⁺: 358.0066; Found: 358.0070.

The title compound **31** was isolated as a white oil (80% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1). (Rf 0.5, petroleum

ether/ethyl acetate = 5:1). D-inc. >99% (determined by ${}^{1}H$ NMR). ${}^{1}H$ NMR (400 MHz, CDCl₃) δ 8.44 (d, J = 1.8 Hz, 1H), 8.00 (d, J = 8.6 Hz, 2H), 7.94 (d, J = 8.1 Hz,

1H), 7.81 (m, 1H), 7.67 (m, 2H), 2.23 (s, 6H). ¹³C **NMR** (100 MHz, CDCl₃) δ 135.5, 133.8, 132.2, 130.5, 129.5, 128.1, 127.8, 123.3, 54.1, 53.7, 31.2. HRMS (ESI) m/z Calcd for [C₁₆H₁₃D₃O₂SSe, M + H]⁺:378.0117 ; Found: 378.0120.

$$\begin{array}{c|c} \hline \\ Br & & \\ &$$

The title compound **3m** was isolated as a white oil (77% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1). (Rf 0.6,

petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by 1 H NMR). 1 H NMR (400 MHz, CDCl₃) δ 7.71 (s, 4H), 2.20 (s, 3H). 13 C NMR (100 MHz, CDCl₃) δ 135.81, 132.7, 130.2, 129.4, 54.0, 53.5, 31.1. HRMS (ESI) m/z Calcd for [C₁₂H₁₀D₃BrO₂SSe, M + H]⁺: 383.9246; Found: 383.9246.

$$\begin{array}{c|c} \hline \\ O_2 N - & & \\ & S \\ & S \\ & O \\ & 3n \\ \end{array}$$
 SeCD₃

The title compound **3n** was isolated as a white solid (86% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1). (Rf 0.5,

petroleum ether/ethyl acetate = 4:1). D-inc. >99% (determined by 1 H NMR). MP: 153.7-155.2 °C. 1 H NMR (400 MHz, CDCl₃) δ 8.41 (d, J = 8.7 Hz, 2H), 8.06 (d, J = 8.7 Hz, 2H), 2.23 (s, 6H). 13 C NMR (100 MHz, CDCl₃) δ 151.1, 142.7, 130.2, 124.6, 54.1, 53.5, 31.3. HRMS (ESI) m/z Calcd for [C₁₃H₁₀D₃NO₄SSeNa, M + Na]⁺: 372.9811; Found: 372.9814.

The title compound **30** was isolated as a white oil (83% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1). (Rf 0.5, petroleum ether/ethyl acetate = 3:1). D-inc. >99%

(determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 7.59 - 7.54 (m, 2H), 7.45 (d, J = 8.2 Hz, 1H), 3.07 - 2.87 (m, 2H), 2.52 (dd, J = 18.7, 8.7 Hz, 1H), 2.47 - 2.40 (m, 1H), 2.34 (m, , 1H), 2.20 (s, 6H), 2.17 - 2.10 (m, 1H), 2.07 (m, 2H), 2.02 - 1.96 (m, 1H), 1.64 (m, 3H), 1.57 - 1.40 (m, 4H), 0.92 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 220.3, 146.5, 138.2, 134.1, 129.0, 126.4, 125.9, 54.0, 53.6, 50.6, 47.9, 44.7, 37.7, 35.9,

31.6, 31.1, 29.4, 26.1, 25.6, 21.7, 14.0. **HRMS** (ESI) m/z Calcd for $[C_{24}H_{27}D_3O_3SSeNa, M + H]^+$: 482.1269; Found: 482.1274.

The title compound **3p** was isolated as a yellow oil (94% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1). (Rf 0.5,

petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 2.43 (s, 3H), 2.17 (s, 6H), 1.93 (d, J = 142.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 145.0, 133.7, 129.9, 128.6, 53.9, 53.5, 31.1, 21.7, 3.6 (s, ¹³C-H₃). HRMS (ESI) m/z Calcd for [13 C₁C₁₂H₁₆D₃O₂SSeNa, M + Na]⁺: 342.9928; Found: 342.9929.

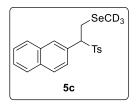
The title compound **5a** was isolated as a white solid (89% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.6, petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by ¹H NMR). MP: 65.4-66.9 °C. ¹H

NMR (400 MHz, CDCl₃) δ 7.42 (d, J = 8.3 Hz, 2H), 7.37-7.32 (m, 1H), 7.29 (t, J = 3.9 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 6.9 Hz, 2H), 4.29 (dd, J = 3.4, 3.4 Hz, 1H), 3.48 (dd, J = 3.4, 3.4 Hz, 1H), 3.26 (dd, J = 3.4, 3.4 Hz, 1H), 2.41 (s, 3H). ¹³C **NMR** (100 MHz, CDCl₃) δ 144.9, 134.1, 132.0, 130.0, 129.6, 129.3, 129.3, 128.6, 72.6, 21.8, 21.7. **HRMS** (ESI) m/z Calcd for [C₁₆H₁₅D₃O₂SSeNa, M + Na]⁺: 380.0273; Found: 380.0270.

The title compound **5b** was isolated as a white solid (91% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.6, petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by ¹H

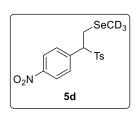
NMR). **MP**: 71.4-73.0 °C. ¹**H NMR** (400 MHz, CDCl₃) δ 7.41 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.2 Hz, 2H), 4.23 (dd, J

= 3.4, 3.4 Hz, 1H), 3.41 (dd, J = 3.5, 3.4 Hz, 1H), 3.20 (t, J = 3.5, 3.4 Hz, 1H), 2.38 (s, 3H), 2.31 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 144.8, 139.2, 134.1, 129.8, 129.5, 129.3, 129.2, 128.7, 72.1, 21.8, 21.4, 5.3-4.6 (m, C-D₃). **HRMS** (ESI) m/z Calcd for [C₁₇H₁₇D₃O₂SSeNa, M + Na]⁺: 394.0430; Found: 394.0431.



The title compound **5c** was isolated as a white solid (85% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.6, petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by ¹H

NMR). **MP**: 93.0-95.0 °C. ¹H **NMR** (400 MHz, CDCl₃) δ 7.77-7.69 (m, 1H), 7.68-7.61 (m, 2H), 7.49 (d, J = 1.9 Hz, 1H), 7.43-7.35 (m, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.6, 1.9 Hz, 1H), 7.03 (d, J = 8.1 Hz, 2H), 4.38 (dd, J = 3.4, 3.4 Hz, 1H), 3.44 (dd, J = 3.4, 3.4 Hz, 1H), 3.28 (dd, J = 3.4, 3.4 Hz, 1H,), 2.25 (s, 3H). ¹³C **NMR** (100 MHz, CDCl₃) δ 144.9, 133.9, 133.4, 132.9, 130.0, 129.5, 129.3, 129.1, 128.3, 128.2, 127.7, 126.8, 126.5, 126.4, 72.5, 21.7, 21.6, 4.9-4.7 (m, C-D₃). **HRMS** (ESI) m/z Calcd for [C₂₀H₁₇D₃O₂SSeNa, M + Na]⁺: 430.0430; Found: 430.0432.



The title compound **5d** was isolated as a white solid (77% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1). (Rf 0.5, petroleum ether/ethyl acetate = 4:1). D-inc. >99% (determined by ¹H NMR).

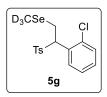
MP: 88.5-90.3 °C. ¹**H NMR** (400 MHz, CDCl₃) δ 7.41 (dd, J = 8.4 Hz, 8.4 Hz, 4H), 7.22 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.5 Hz, 2H), 4.22 (dd, J = 3.4, 3.4 Hz, 1H), 3.42 (dd, J = 3.4, 3.5 Hz, 1H), 3.16 (dd, J = 3.4, 3.5 Hz, 1H), 2.41 (s, 3H). ¹³C **NMR** (100 MHz, CDCl₃) δ 145.3, 133.8, 131.9, 131.6, 131.1, 129.8, 129.3, 123.7, 71.8, 21.9, 21.5. **HRMS** (ESI) m/z Calcd for [C₁₆H₁₄D₃NO₄SSeNa, M + Na]⁺: 425.0130; Found: 425.0132.

The title compound **5e** was isolated as a white solid (85% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.6, petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by ¹H

NMR). **MP**: 90.8-92.0 °C. ¹H **NMR** (400 MHz, CDCl₃) δ 7.41 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.5 Hz, 2H), 4.22 (dd, J = 3.5 3.5 Hz, 1H), 3.41 (dd, J = 3.5, 3.5 Hz, 1H), 3.15 (dd, J = 3.5, 3.5 Hz, 1H), 2.40 (s, 3H). ¹³C **NMR** (100 MHz, CDCl₃) δ 145.2, 133.8, 131.8, 131.5, 131.1, 129.7, 129.2, 123.6, 71.8, 21.8, 21.5. **HRMS** (ESI) m/z Calcd for [C₁₆H₁₅D₃BrO₂SSe, M + H]⁺: 435.9559; Found: 435.9558.

The title compound **5f** was isolated as a white solid (81% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.6, petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by ¹H NMR). MP: 123.0-125.4 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, J = 8.3 Hz, 2H), 7.26-7.20 (m, 2H), 7.19 (s, 1H), 7.07-6.98 (m, 1H), 6.94 - 6.90 (m, 1H), 6.90 - 6.85 (m, 1H), 4.25 (dd, J = 3.4, 3.4 Hz, 1H), 3.43 (dd, J = 3.5, 3.4 Hz, 1H), 3.17 (dd, J = 3.5, 3.4 Hz, 1H), 2.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.6 (d, ${}^{1}J_{C-F} = 247.1$ Hz), 145.2, 134.5 (d, ${}^{3}J_{C-F} = 7.6$ Hz), 133.8, 130.1 (d, ${}^{3}J_{C-F} = 8.3$ Hz), 129.7, 129.2, 125.8, 116.8 (d, ${}^{2}J_{C-F} = 22.6$ Hz), 116.3 (d, ${}^{2}J_{C-F} = 20.9$ Hz), 72.0, 21.8, 21.6. ¹⁹F NMR (376 MHz, CDCl₃) δ - 112.1. HRMS (ESI) m/z Calcd for [C₁₆H₁₄D₃FO₂SSeNa, M + Na]⁺: 398.0179; Found: 398.0184.



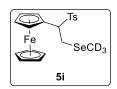
The title compound **5g** was isolated as a white solid (80% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.6, petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by **1H NMR**). **MP**: 88.1-90.8 °C. **1H**

NMR (400 MHz, CDCl₃) δ 7.62 (dd, J = 7.8, 1.6 Hz, 1H), 7.44 (d, J = 8.3 Hz, 2H), 7.32 (td, J = 7.5, 1.7 Hz, 1H), 7.28 - 7.22 (m, 1H), 7.20 (dd, J = 1.7, 1.6 Hz, 1H), 7.17

(d, J = 7.7 Hz, 2H), 5.09 (dd, J = 3.5, 3.5 Hz, 1H), 3.52 (dd, J = 3.5, 3.6 Hz, 1H), 3.20 (dd, J = 3.5, 3.6 Hz, 1H), 2.39 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 145.1, 136.6, 134.6, 130.6, 130.3, 129.7, 129.6, 129.2, 127.3, 66.2, 21.9, 21.7, 5.3-4.4 (m, C-D₃). HRMS (ESI) m/z Calcd for [C₁₆H₁₄D₃ClO₂SSeNa, M + Na]⁺: 413.9884; Found: 413.9885.

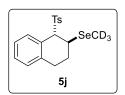
The title compound **5h** was isolated as a white solid (80% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.6, petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by ¹H

NMR). **MP**: 151.3-153.0 °C. ¹**H NMR** (400 MHz, CDCl₃) δ 7.68 (d, J = 7.3 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 7.12 (d, J = 7.6 Hz, 2H), 4.27 (dd, J = 3.4, 3.4 Hz, 1H), 3.46 (dd, J = 3.5, 3.4 Hz, 1H), 3.21 (dd, J = 3.5, 3.4 Hz, 1H), 2.38 (s, 3H), 1.33 (s, 12H). ¹³C **NMR** (100 MHz, CDCl₃) δ 144.8, 134.9, 134.8, 134.0, 129.5, 129.2, 129.2, 84.0, 72.6, 25.0, 24.9, 21.7, 21.6, 5.1-4.7 (m, C-D₃). **HRMS** (ESI) m/z Calcd for [C₂₂H₂₆D₃BO₄SSeNa, M + Na]⁺: 506.1131; Found: 506.1129.



The title compound **5i** was isolated as a yellow oil (76% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.6, petroleum ether/ethyl acetate =

5:1). D-inc. >99% (determined by ¹**H NMR**). ¹**H NMR** (400 MHz, CDCl₃) δ 7.36 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 4.17 (s, 5H), 4.16-4.12 (m, 3H), 4.06 (q, J = 1.7 Hz, 1H), 3.92 (q, J = 1.6 Hz, 1H) 3.34 (dd, J = 6.1, 6.1 Hz, 1H), 3.02 (dd, J = 5.6, 5.7 Hz, 1H), 2.38 (s, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 144.7, 133.3, 129.7, 129.2, 81.0, 70.7, 69.4, 69.2, 68.7, 68.6, 67.2, 22.3, 21.7, 6.9-6.4 (m, C-D₃). **HRMS** (ESI) m/z Calcd for [C₂₀H₁₉D₃FeO₂SSeNa, M + Na]⁺: 487.9936; Found: 487.9939.



The title compound **5j** was isolated as a white solid (74% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.6, petroleum ether/ethyl acetate =

5:1). D-inc. >99% and diastereoselectivity >20:1 (determined by ¹H NMR). MP: 98.1-100.7 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, J = 8.3 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 1.4 Hz, 1H), 7.03 (dd, J = 7.9, 1.3 Hz, 1H), 6.98 (t, J = 7.5, 1.4 Hz, 1H), 6.88 (dd, J = 7.8, 1.4 Hz, 1H), 4.40 (d, J = 1.5 Hz, 1H), 3.96-3.77 (m, 1H), 2.87-2.71 (m, 1H), 2.68-2.58 (m, 1H), 2.52-2.40 (m, 1H), 2.34 (s, 3H), 1.84-1.72 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 145.0, 138.3, 134.6, 132.2, 129.7, 129.3, 129.2, 128.9, 125.6, 125.4, 70.9, 33.5, 25.9, 24.9, 21.7, 4.5-3.8 (m, C-D₃). HRMS (ESI) m/z Calcd for [C₁₈H₁₇D₃O₂SSeNa, M + Na]⁺: 406.0430; Found: 406.0427.

SeCD₃

The title compound **5k** was isolated as a white solid (81% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.6, petroleum ether/ethyl acetate =

5:1). D-inc. >99% and diastereoselectivity >20:1 (determined by ¹H NMR). MP: 79.5-81.6 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.17 (d, J = 8.3 Hz, 2H), 7.03-6.97 (m, 2H), 6.93 (d, J = 2.3 Hz, 2H), 6.90 (d, J = 4.8 Hz, 1H), 6.84-6.81 (m, 1H), 4.40 (s, 1H), 3.88-3.65 (m, 1H), 3.11 (dd, J = 8.0, 8.0 Hz, 1H), 2.46 (d, J = 17.5 Hz, 1H), 2.11 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 145.1, 144.2, 133.8, 133.0, 129.8, 129.6, 129.3, 127.5, 127.1, 124.9, 79.0, 39.5, 35.9, 21.8, 4.1-3.7 (m, C-D₃). HRMS (ESI) m/z Calcd for [C₁₇H₁₅D₃O₂SSeNa, M + Na]⁺: 392.0273; Found: 392.0274.



The title compound **51** was isolated as a white solid (71% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.4, petroleum ether/ethyl acetate = 10:1). D-

inc. >99% and diastereoselectivity >20:1 (determined by ^{1}H NMR). MP: 95.7-97.0 $^{\circ}$ C. ^{1}H NMR (400 MHz, CDCl₃) δ 7.30 (d, J = 8.4 Hz, 2H), 7.23-7.17 (m, 1H), 7.17-7.08 (m, 4H), 7.04 (d, J = 8.0 Hz, 2H), 4.15 (d, J = 10.2 Hz, 1H), 4.00-3.85 (m, 1H), 2.31 (s, 3H), 1.97 (d, J = 6.8 Hz, 3H). 13 C NMR (100 MHz, CDCl₃) δ 144.2, 136.2, 134.2, 130.1, 129.2, 128.9, 128.7, 128.4, 34.0, 29.9, 22.1, 21.7. HRMS (ESI) m/z Calcd for [C₁₇H₁₇D₃O₂SSeNa, M + Na]⁺: 394.0430; Found: 394.0435.

The title compound **5m** was isolated as a colorless oil (75% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.5, petroleum ether/ethyl acetate = 5:1). D-inc. >99% and diastereoselectivity >20:1 (determined by

¹**H NMR**). ¹**H NMR** (400 MHz, CDCl₃) δ 7.31 (d, J = 8.3 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.2 Hz, 2H), 6.67 (d, J = 9.0 Hz, 2H), 4.10 (d, J = 10.0 Hz, 1H), 3.96-3.85 (m, 1H), 3.74 (s, 3H), 2.31 (s, 3H), 1.93 (d, J = 6.7 Hz, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 159.9, 144.1, 136.2, 131.2, 129.2, 128.6, 125.9, 113.6, 76.6, 55.3, 34.1, 22.0, 21.7. **HRMS** (ESI) m/z Calcd for [C₁₈H₁₉D₃O₃SSeNa, M + Na]⁺: 424.0535; Found: 424.0536.

The title compound **5n** was isolated as a colorless oil (65% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1). (Rf 0.5, petroleum ether/ethyl acetate = 3:1). D-inc. >99% and

diastereoselectivity >20:1 (determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 1H NMR (400 MHz,) δ 7.46 (d, J = 7.3 Hz, 2H), 7.15 (d, J = 7.4 Hz, 2H), 6.95 (d, J = 2.0 Hz, 1H), 6.83 (d, J = 8.8 Hz, 1H), 6.72 (d, J = 8.2 Hz, 1H), 4.30 (d, J = 3.5 Hz, 1H), 4.06 - 3.96 (m, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 2.34 (s, 3H), 1.74 (d, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 149.5, 148.4, 144.4, 135.6, 129.4, 128.5, 124.1, 122.3, 113.7, 110.5, 75.0, 56.0, 55.8, 32.3, 21.6, 18.3, 5.0-3.7 (m, C-D₃). HRMS (ESI) m/z Calcd for [C₁₈H₁₉D₃O₃SSeNa, M + Na]⁺: 424.0535; Found: 424.0536.

The title compound **50** was isolated as a white solid (83% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.4, petroleum ether/ethyl acetate = 10:1).

D-inc. >99% and diastereoselectivity >20:1 (determined by ¹H NMR).

MP: 95.7-97.0 °C. ¹**H NMR** (400 MHz, Chloroform-d) δ 7.39 (d, J = 7.7 Hz, 1H),

7.30 (d, J = 7.6 Hz, 1H), 7.26 - 7.15 (m, 1H), 7.07 (d, J = 8.0 Hz, 1H), 4.29 (d, J = 2.8 Hz, 1H), 3.98 (qd, J = 7.1, 3.3 Hz, 1H), 2.27 (s, 3H), 1.66 (d, J = 7.1 Hz, 3H). 13 C **NMR** (100 MHz, Chloroform-d) δ 144.4, 135.7, 131.1, 130.3, 129.4, 128.9, 128.6, 128.2, 75.6, 32.0, 21.6, 18.2, 5.3-3.0 (m, C-D₃). **HRMS** (ESI) m/z Calcd for [C₁₇H₁₇D₃O₂SSeNa, M + Na]⁺: 394.0430; Found: 394.0435.

D₃CSe, Et
Ts

The title compound **5p** was isolated as a white solid (46% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.4, petroleum ether/ethyl acetate = 10:1).

D-inc. >99% and diastereoselectivity >20:1 (determined by ${}^{1}H$ NMR). ${}^{1}H$ NMR (400 MHz, CDCl₃) δ 7.31 (d, J = 8.1 Hz, 2H), 7.16 (m, 5H), 7.04 (d, J = 8.0 Hz, 2H), 4.28 (d, J = 9.3 Hz, 1H), 3.74 (m, 1H), 2.30 (s, 3H), 2.25 (m, 1H), 2.06 (dp, J = 14.6, 7.3 Hz, 1H) 1.17 (t, J = 7.2 Hz, 3H). ${}^{13}C$ NMR (100 MHz, CDCl₃) δ 144.4, 135.7, 131.1, 130.3, 129.4, 128.9, 128.6, 128.2, 75.6, 32.0, 21.6, 18.2. **HRMS** (ESI) m/z Calcd for [C₁₇H₁₇D₃O₂SSe, M + Nal⁺:394.0430; Found:394.0429



The title compound **5q** was isolated as a colorless oil (58% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30:1). (Rf 0.5, petroleum ether/ethyl acetate = 15:1).

D-inc. >99% and diastereoselectivity >20:1 (determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 7.37 (d, J = 7.9 Hz, 2H), 7.32 - 7.26 (m, 2H), 7.23 - 7.13 (m, 3H), 7.06 (d, J = 8.0 Hz, 2H), 4.37 (d, J = 3.8 Hz, 1H), 3.64 (dt, J = 11.6, 3.3 Hz, 1H), 2.48 (dqd, J = 14.5, 7.2, 2.7 Hz, 1H), 2.26 (s, 3H), 1.56 - 1.33 (m, 1H), 1.02 (t, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 144.4, 135.8, 131.3, 130.7, 129.4, 128.8, 128.6, 128.1, 76.6, 41.6, 24.1, 21.6, 13.1, 3.1-2.5 (m, C-D₃). HRMS (ESI) m/z Calcd for [C₁₈H₁₉D₃O₂SSeNa, M + H]⁺: 380.0826; Found: 380.0826.



The title compound **5r** was isolated as a colorless oil (53% yield) through flash chromatography on silica gel eluting with petroleum

ether/ethyl acetate (30:1). (Rf 0.5, petroleum ether/ethyl acetate = 15:1). D-inc. >99% and diastereoselectivity = 10:1 (determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 6.8 Hz, 2H), 7.23 (d, J = 7.0 Hz, 1H), 7.19 (d, J = 7.5 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 4.37 (d, J = 3.6 Hz, 1H), 3.79-3.68(m, 1H), 2.43-2.34 (m, 1H), 2.28 (s, 3H), 1.69-1.51 (m, 1H), 1.48-1.33 (m, 2H), 0.91 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 144.5, 135.7, 131.4, 130.6, 129.4, 128.9, 128.6, 128.2, 76.5, 39.3, 32.8, 21.7, 21.6, 13.8, 6.7-6.3 (m, C-D₃). **HRMS** (ESI) m/z Calcd for $[C_{19}H_{21}D_3O_2SSeNa, M + Na]^+$: 438.0692; Found: 438.0693.

D₃CSe /Pr 5s

flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.5, petroleum ether/ethyl acetate = 10:1). Dinc. >99% and diastereoselectivity >20:1 (determined by ¹H NMR). MP: 111.0-113.4 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, J = 8.3 Hz, 2H), 7.26-7.14 (m, 5H), 7.08 (d, J = 8.1 Hz, 2H), 4.46 (d, J = 8.1 Hz, 1H), 3.58 (dd, J = 2.2, 2.2 Hz, 1H), 2.31 (s, J = 2.2, 2.2 Hz3H), 2.01-1.86 (m, 1H), 1.07 (d, J = 6.6 Hz, 3H), 0.53 (d, J = 6.6 Hz, 3H). ¹³C NMR $(100 \text{ MHz}, \text{CDCl}_3) \delta 144.0, 136.5, 133.1, 130.2, 129.2, 128.6, 128.5, 76.2, 49.0, 30.0,$ 22.4, 21.7, 17.8, 2.6 (m, C-D₃). **HRMS** (ESI) m/z Calcd for [C₁₉H₂₁D₃O₂SSeNa, M + Na]+: 438.0692; Found: 438.0691.

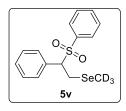
The title compound 5s was isolated as a white solid (44% yield) through

The title compound **5t** was isolated as a colorless oil (53% yield)



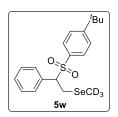
through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30:1). (Rf 0.5, petroleum ether/ethyl acetate = 15:1). D-inc. >99% and diastereoselectivity = 7:1 (determined by ¹H NMR). ¹H **NMR** (400 MHz, CDCl₃) δ 7.37 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 7.0 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 7.18 (d, J = 7.8 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 4.36 (d, J = 3.6 Hz, 1H), 3.83-3.57 (m, 1H), 2.49-2.38 (m, 1H), 2.27 (s, 3H), 1.58-1.22 (m, 5H), 0.90-0.78 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 144.5, 135.8, 131.5, 130.7, 129.5, 128.9, 128.6, 128.2, 76.6, 39.5, 30.6, 30.4, 22.5, 21.7, 14.2. HRMS (ESI) m/z Calcd for $[C_{20}H_{23}D_3O_2SSeNa, M + Na]^+: 452.0848$; Found: 452.0852.

The title compound **5u** was isolated as a white solid (81% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.5, petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by ¹H NMR). MP: 131.9-133.4 ¹**H NMR** (400 MHz, CDCl₃) δ 7.33 (d, J = 7.9 Hz, 2H), 7.24 (t, J = 6.8 Hz, 1H), 7.18 (t, J = 7.4 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 7.06 (d, J = 7.6 Hz, 2H), 4.21 (dd, J = 7.8 Hz, 2H), 4.21 (dd, J = 7.8= 12.3, 3.4 Hz, 1H), 3.45 - 3.34 (m, 1H), 3.24 - 3.12 (m, 1H), 2.31 (s, 3H), 1.77 (d, J = 1)141.7 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 144.8, 133.9, 131.9, 129.9, 129.4, 129.1, 129.1, 128.5, 72.4, 21.7, 5.5 (s, ¹³C-H₃). **HRMS** (ESI) m/z Calcd for $[C_{15}^{13}CH_{18}O_2SSeNa, M + Na]^+$: 378.0124; Found: 378.0131.



The title compound 5v was isolated as a white solid (85% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.5, petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by ¹H NMR). ¹H NMR (400 MHz,

CDCl₃) δ 7.58-7.46 (m, 3H), 7.36 (t, J = 7.7 Hz, 2H), 7.32-7.26 (m, 1H), 7.23 (dd, J =8.3, 6.5 Hz, 2H), 7.11 (d, J = 7.4 Hz, 2H), 4.29 (dd, J = 3.4, 3.4 Hz, 1H), 3.46 (dd, J =3.4, 3.5 Hz, 1H), 3.25 (dd, J = 3.4, 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 136.9, 133.8, 131.7, 129.8, 129.2, 129.05, 128.8, 128.5, 72.4, 21.4, 5.1-4.7 (m, C-D₃). **HRMS** (ESI) m/z Calcd for $[C_{15}H_{13}D_3O_2SSeNa, M + Na]^+$: 382.0066; Found: 382.0067.



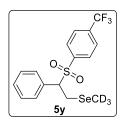
The title compound 5w was isolated as a white solid (89% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.5, petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by ¹H NMR). MP: 67.0-69.2 °C. ¹H

NMR (400 MHz, CDCl₃) δ 7.44 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.6 Hz, 2H), 7.33-7.27 (m, 1H), 7.23 (t, J = 7.5 Hz, 2H), 7.12 (d, J = 7.2 Hz, 2H), 4.27 (dd, J = 3.4, 3.4 Hz, 1H), 3.43 (dd, J = 3.4, 3.5 Hz, 1H), 3.24 (dd, J = 3.4, 3.5 Hz, 1H), 1.29 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 157.8, 133.9, 131.8, 129.9, 129.2, 129.0, 128.4, 125.8, 72.4, 35.3, 31.1, 21.5, 5.1-4.6 (m, C-D₃). **HRMS** (ESI) m/z Calcd for [C₁₉H₂₁D₃O₂SSeNa, M + Na]⁺: 438.0692; Found: 438.0691.

OMe
OSO
SeCD3

The title compound 5x was isolated as a white solid (85% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.5, petroleum ether/ethyl acetate = 4:1). D-inc. >99% (determined by ${}^{1}H$ NMR). MP: 95.2-97.0 °C. ${}^{1}H$ NMR (400 MHz, CDCl₃) δ 7.37 (d, J = 8.9

Hz, 2H), 7.29-7.24 (m, 1H), 7.21 (t, J = 7.3 Hz, 2H), 7.08 (d, J = 7.0 Hz, 2H), 6.78 (d, J = 8.9 Hz, 2H), 4.21 (dd, J = 3.4, 3.4 Hz, 1H), 3.78 (s, 3H), 3.41 (dd, J = 3.4, 3.5 Hz, 1H), 3.19 (dd, J = 3.4, 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 163.8, 132.1, 131.3, 129.9, 129.2, 128.5, 128.4, 114.0, 72.6, 55.7, 21.6, 5.1-4.7 (m, C-D₃). HRMS (ESI) m/z Calcd for [C₁₆H₁₅D₃O₃SSeNa, M + Na]⁺: 396.0222; Found: 396.0221.



The title compound **5y** was isolated as a white solid (81% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.5, petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by **1H NMR**). **MP**: 64.0-65.1 °C.

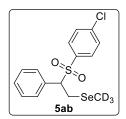
¹H NMR (400 MHz, CDCl₃) δ 7.60 (s, 4H), 7.32-7.26 (m, 1H), 7.22 (t, J = 7.5 Hz, 2H), 7.08 (d, J = 6.5 Hz, 2H), 4.28 (dd, J = 3.4, 3.5 Hz, 1H), 3.46 (dd, J = 3.5, 3.5 Hz, 1H), 3.23 (dd, J = 3.5, 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 140.6, 135.4 (q, ${}^{2}J_{C-F} = 33.2$ Hz), 131.3, 129.9, 129.7, 129.6, 128.8, 125.9 (q, ${}^{3}J_{C-F} = 3.7$ Hz), 123.1 (q, ${}^{1}J_{C-F} = 273.1$ Hz), 72.7, 21.0, 5.3-4.8 (m, C-D₃). ¹⁹F NMR (376 MHz, CDCl₃) δ -63.2. HRMS (ESI) m/z Calcd for [C₁₆H₁₂D₃F₃O₂SSeNa, M + Na]⁺: 433.9991; Found: 433.9996.

$$\begin{array}{c|c} & \mathsf{NO}_2 \\ & &$$

The title compound **5z** was isolated as a white solid (80% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1). (Rf 0.4, petroleum ether/ethyl acetate = 3:1). D-inc. >99% (determined by 1 H NMR). MP: 115.9-116.4 °C. 1 H NMR (400 MHz, CDCl₃) δ 8.12 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 8.8 Hz, 2H), 7.30-7.23 (m, 1H), 7.19 (t, J = 7.2 Hz, 2H), 7.05 (d, J = 7.2 Hz, 2H), 4.27 (dd, J = 3.4, 3.4 Hz, 1H), 3.45 (dd, J = 3.4, 3.5 Hz, 1H), 3.21 (dd, J = 3.4, 3.5 Hz, 1H). 13 C NMR (100 MHz, CDCl₃) δ 150.7, 142.9, 131.1, 130.5, 129.8, 129.8, 128.9, 123.9, 72.8, 20.8, 5.1-4.7 (m, C-D₃). HRMS (ESI) m/z Calcd for $[C_{15}H_{12}D_3NO_4SSeNa, M + Na]^+$: 410.9968; Found: 410.9965.

The title compound **5aa** was isolated as a white solid (85% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.5, petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by ¹H NMR).

MP: 83.5-85.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.46-7.39 (m, 2H), 7.2 -7.22 (m, 1H), 7.19 (t, J = 7.6 Hz, 2H), 7.04 (d, J = 7.2 Hz, 2H), 6.97 (t, J = 8.5 Hz, 2H), 4.21 (dd, J = 3.4, 3.4 Hz, 1H), 3.41 (dd, J = 3.4, 3.5 Hz, 1H), 3.18 (dd, J = 3.4, 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 165.8 (d, J = 256.8 Hz), 132.9 (d, J = 3.2 Hz), 131.9 (d, J = 9.7 Hz), 131.7, 129.8, 129.4, 128.6, 116.1 (d, J = 22.6 Hz), 72.7, 21.2, 5.2-4.7 (m, C-D₃). ¹⁹F NMR (376 MHz, CDCl₃) δ -103.1. HRMS (ESI) m/z Calcd for [C₁₅H₁₃D₃FO₂SSe, M + H]⁺: 362.0203; Found: 362.0205.



The title compound **5ab** was isolated as a white solid (89% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.5, petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by ¹H NMR). MP: 111.0-112.1 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, J = 8.6 Hz, 2H), 7.29-7.23 (m, 3H), 7.19 (t, J = 7.4 Hz, 2H), 7.05 (d, J = 6.9 Hz, 2H), 4.21 (dd, J = 3.4, 3.4 Hz, 1H), 3.40 (dd, J = 3.4 3.4 Hz, 1H), 3.18 (dd, J = 3.4 3.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 140.6,

135.4, 131.6, 130.5, 129.9, 129.4, 129.1, 128.7, 72.6, 21.1, 5.2-4.7 (m, C-D₃). **HRMS** (ESI) m/z Calcd for [C₁₅H₁₂D₃ClO₂SSeNa, M + Na]⁺: 399.9727; Found: 399.9732.

The title compound **5ac** was isolated as a white solid (85% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.5, petroleum ether/ethyl acetate =

5:1). D-inc. >99% (determined by ¹H NMR). MP: 95.1-97.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, J = 8.6 Hz, 2H), 7.29-7.24 (m, 3H), 7.20 (t, J = 7.3 Hz, 2H), 7.06 (d, J = 7.3 Hz, 2H), 4.22 (dd, J = 3.4, 3.4 Hz, 1H), 3.40 (dd, J = 3.4, 3.4 Hz, 1H), 3.18 (dd, J = 3.4, 3.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 136.0, 132.1, 131.5, 130.6, 129.9, 129.4, 129.2, 128.7, 72.6, 21.1, 5.2-4.8 (m, C-D₃). HRMS (ESI) m/z Calcd for [C₁₅H₁₂D₃BrO₂SSeNa, M + Na]⁺: 443.9222; Found: 443.9225.

The title compound **5ad** was isolated as a white solid (81% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.5, petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by ¹H NMR). MP: 118.4-120.1 °C.

¹**H NMR** (400 MHz, CDCl₃) δ 7.66 (d, J = 8.6 Hz, 2H), 7.28-7.23 (m, 1H), 7.20 (t, J = 7.4 Hz, 2H), 7.12 (d, J = 8.5 Hz, 2H), 7.05 (d, J = 7.0 Hz, 2H), 4.21 (dd, J = 3.5, 3.5 Hz, 1H), 3.39 (dd, J = 3.5, 3.4 Hz, 1H), 3.17 (dd, J = 3.5, 3.4 Hz, 1H). ¹³**C NMR** (100 MHz, CDCl₃) δ 138.1, 136.7, 131.5, 130.4, 129.9, 129.5, 128.7, 102.0, 72.6, 21.2, 5.1-4.7 (m, C-D₃). **HRMS** (ESI) m/z Calcd for [C₁₅H₁₂D₃IO₂SSeNa, M + Na]⁺: 491.9083; Found: 491.9081.

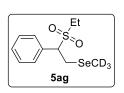
The title compound **5ae** was isolated as a white solid (83% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.5, petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by 1 H NMR). MP: 118.2-120.0 ${}^{\circ}$ C. 1 H NMR (400 MHz, CDCl₃) δ

8.12 (d, J = 1.8 Hz, 1H), 7.89-7.76 (m, 3H), 7.64 (t, J = 7.4 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.46 (dd, J = 8.6, 1.9 Hz, 1H), 7.29 (t, J = 7.3 Hz, 1H), 7.21 (t, J = 7.5 Hz, 2H), 7.14 (d, J = 7.2 Hz, 2H), 4.39 (dd, J = 3.4, 3.4 Hz, 1H), 3.51 (dd, J = 3.4, 3.5 Hz, 1H), 3.30 (dd, J = 3.4, 3.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 135.3, 133.9, 131.9, 131.8, 131.2, 130.0, 129.4, 129.4, 129.3, 128.9, 128.6, 128.0, 127.7, 123.6, 72.6, 21.5, 5.2-4.8 (m, C-D₃). HRMS (ESI) m/z Calcd for [C₁₉H₁₅D₃O₂SSeNa, M + Na]⁺: 416.0273; Found: 416.0271.

$$\begin{array}{|c|c|c|}\hline \\ O_{S}S_{O} & N \\\hline \\ SeCD_{3} \\\hline \\ \mathbf{5af} \\\hline \end{array}$$

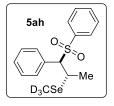
The title compound **5af** was isolated as a white solid (78% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.5, petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by ¹H

NMR). **MP**: 138.1-140.0 °C. ¹**H NMR** (400 MHz, CDCl₃) δ 9.20 (d, J = 4.5 Hz, 1H), 8.23 (dd, J = 12.3, 7.8 Hz, 2H), 7.99 (d, J = 8.1 Hz, 1H), 7.59 (dd, J = 8.4, 7.3 Hz, 1H), 7.48 (t, J = 7.8 Hz, 1H), 7.19 (d, J = 7.6 Hz, 2H), 7.15 (d, J = 6.6 Hz, 1H), 7.11 (d, J = 7.4 Hz, 2H), 5.84 (dd, J = 3.5, 3.5 Hz, 1H), 3.56-3.47 (m, 1H), 3.37 (dd, J = 3.5, 3.5 Hz, 1H). ¹³C **NMR** (100 MHz, CDCl₃) δ 151.6, 144.3, 136.9, 135.1, 134.4, 132.9, 132.2, 129.8, 129.0, 128.7, 128.4, 122.4, 70.3, 21.7, 5.2-4.8 (m, C-D₃). **HRMS** (ESI) m/z Calcd for [C₁₈H₁₄D₃NO₂SSeNa, M + Na]⁺: 417.0226; Found: 417.0227.



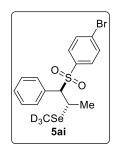
The title compound **5ag** was isolated as a colorless oil (81% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). (Rf 0.5, petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by ¹H NMR). ¹H NMR (400 MHz,

CDCl₃) δ 7.49-7.43 (m, 2H), 7.43-7.39 (m, 3H), 4.26 (dd, J = 3.4, 3.4 Hz, 1H), 3.47 (dd, J = 3.4, 3.4 Hz, 1H), 3.19 (dd, J = 3.4, 3.4 Hz, 1H), 2.88-2.55 (m, 2H), 1.25 (t, J = 7.5 Hz, 3H). ¹³C **NMR** (100 MHz, CDCl₃) δ 132.6, 129.6, 129.5, 129.3, 69.0, 45.4, 21.5, 6.3, 5.2-4.7 (m, C-D₃). **HRMS** (ESI) m/z Calcd for [C₁₁H₁₅D₃O₂SSe, M + H]⁺: 312.0246; Found: 312.0241.



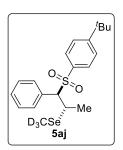
The title compound **5ah** was isolated as a white solid (81% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.5, petroleum ether/ethyl acetate =

10:1). D-inc. >99% and diastereoselectivity >20:1 (determined by ¹H NMR). MP: 111.9-113.4 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.45 (t, J = 9.8 Hz, 3H), 7.28 (t, J = 7.2 Hz, 2H), 7.22 (t, J = 6.1 Hz, 1H), 7.19 - 7.09 (m, 4H), 4.21 (d, J = 10.2 Hz, 1H), 4.02 - 3.92 (m, 1H), 2.01 (d, J = 6.7 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 138.9, 133.9, 133.2, 129.9, 128.8, 128.6, 128.5, 128.3, 33.8, 22.0. HRMS (ESI) m/z Calcd for [C₁₆H₁₅D₃O₂SSeNa M + Na]⁺: 380.0279; Found: 380.0281.



The title compound **5ai** was isolated as a white solid (81% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.5, petroleum ether/ethyl acetate = 10:1). D-inc. >99% and diastereoselectivity >20:1 (determined by 1 H NMR). MP: 140.8-142.0 °C. 1 H NMR (400 MHz, CDCl₃) δ

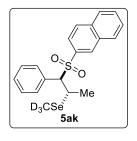
7.32 (d, J = 8.3 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 7.1 Hz, 1H), 7.10 (t, J = 7.4 Hz, 2H), 7.05 (d, J = 7.7 Hz, 2H), 4.10 (d, J = 10.2 Hz, 1H), 3.92 - 3.80 (m, 1H), 1.90 (d, J = 6.8 Hz, 3H). ¹³C **NMR** (100 MHz, CDCl₃) δ 138.1, 133.7, 131.8, 130.1, 130.0, 129.1, 128.6, 128.5, 77.7, 33.7, 22.0. **HRMS** (ESI) m/z Calcd for $[C_{16}H_{14}D_3BrO_2SSeNa, M + Na]^+$: 457.9384; Found: 457.9381.



The title compound **5aj** was isolated as a white solid (81% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.5, petroleum ether/ethyl acetate = 10:1). D-inc. >99% and diastereoselectivity >20:1 (determined by **1H NMR**). **MP**: 104.8-106.1 °C. **1H NMR** (400 MHz, CDCl₃) δ

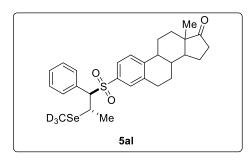
7.33 (d, J = 8.3 Hz, 2H), 7.27 - 7.22 (m, 2H), 7.21 - 7.15 (m, 1H), 7.14 - 7.04 (m, 4H), 4.15 (d, J = 10.2 Hz, 1H), 3.99 - 3.87 (m, 1H), 1.97 (d, J = 6.8 Hz, 3H), 1.24 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 157.2, 135.9, 134.2, 129.9, 128.7, 128.5, 128.2, 125.4, 77.6, 35.2, 33.7, 31.0, 22.0. HRMS (ESI) m/z Calcd for [$C_{20}H_{23}D_3O_2SSeNa$, M + Na]⁺: 436.0905; Found: 436.0911.



The title compound **5ak** was isolated as a white solid (81% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.5, petroleum ether/ethyl acetate = 10:1). D-inc. >99% and diastereoselectivity >20:1 (determined by ¹H NMR). MP:

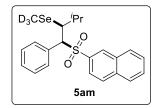
147.8-149.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.11 - 8.00 (m, 2H), 7.77 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 8.6 Hz, 1H), 7.58 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.37 (dd, J = 8.7, 1.9 Hz, 1H), 7.17 - 7.10 (m, 3H), 7.09 - 7.01 (m, 2H), 4.28 (d, J = 10.0 Hz, 1H), 4.05 - 3.93 (m, 1H), 2.01 (d, J = 6.9 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 136.0, 134.8, 133.9, 131.8, 130.5, 130.0, 129.3, 129.1, 128.8, 128.4, 128.2, 127.8, 127.3, 123.2, 77.5, 33.8, 22.0. HRMS (ESI) m/z Calcd for [C₂₀H₁₇D₃O₂SSeNa, M + Na]⁺: 430.0435; Found: 430.0434.



The title compound **5al** was isolated as a white oil (81% yield) through flash chromatography on silica gel eluting with petroleum ether/DCM (5:1). (Rf 0.5, petroleum ether/ethyl acetate = 10:1). D-inc. >99% and diastereoselectivity

=1:1 (determined by ¹H NMR). MP: 147.8-149.1 °C.¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, J = 5.0 Hz, 1H), 7.23 (d, J = 2.0 Hz, 1H), 7.19 (d, J = 3.6 Hz, 1H), 7.17 - 7.11 (m, 5H), 7.10 - 6.96 (m, 1H), 4.13 (dd, J = 10.1, 2.8 Hz, 1H), 3.97 - 3.86 (m, 1H), 2.77 (dd, J = 9.4, 6.4 Hz, 0H), 2.66 (dd, J = 17.1, 10.2 Hz, 1H), 2.49 (dd, J = 18.9, 8.7 Hz, 1H), 2.33 (dd, J = 6.5, 3.9 Hz, 1H), 2.22 (dd, J = 9.6, 4.8 Hz, 1H), 2.11 (dd, J = 18.7, 9.0 Hz, 1H), 2.07 - 2.00 (m, 2H), 1.96 (t, J = 8.0 Hz, 5H), 1.69 - 1.56 (m, 1H), 1.45 (td, J = 11.0, 9.5, 5.9 Hz, 4H), 0.88 (d, J = 1.9 Hz, 3H). ¹³C NMR (100MHz,

CDCl₃) δ 220.4, 145.6, 137.2, 136.0, 134.2, 130.0, 129.3, 128.7, 128.1, 125.8, 125.6, 77.5, 50.5, 47.8, 44.5, 37.6, 35.8, 33.6, 31.4, 28.8, 26.0, 25.5, 21.9, 21.6, 13.8. **HRMS** (ESI) m/z Calcd for [C₂₈H₃₁D₃O₃SSe, M + H]⁺: 534.1582; Found: 534.1583.



The title compound **5am** was isolated as a white solid (50% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (40:1). (Rf 0.5, petroleum ether/ethyl acetate = 20:1). D-inc. >99% and

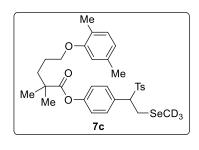
diastereoselectivity >20:1 (determined by ${}^{1}H$ NMR). MP: 171.3-173.4 ${}^{\circ}C$. ${}^{1}H$ NMR (400 MHz, CDCl₃) δ 8.09 (d, J = 1.8 Hz, 1H), 7.64 (d, J = 8.7 Hz, 1H), 7.56 - 7.40 (m, 3H), 7.24 - 7.13 (m, 2H), 7.13 - 6.94 (m, 3H), 4.51 (d, J = 8.3 Hz, 1H), 3.57 (dd, J = 8.2, 2.2 Hz, 1H), 1.89 (m, 1H), 1.02 (d, J = 6.6 Hz, 3H), 0.49 (d, J = 6.6 Hz, 3H). ${}^{13}C$ NMR (100 MHz, CDCl₃) δ 136.6, 134.9, 133.0, 131.9, 130.4, 130.2, 129.3, 129.0, 128.7, 128.5, 128.5, 127.9, 127.4, 76.5, 49.1, 30.1, 22.3, 17.8. HRMS (ESI) m/z Calcd for [C₂₂H2₁D₃O₂SSe, M + H]⁺:436.0923; Found:436.0927.

The title compound **7a** was isolated as a colorless oil (71% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (6:1).

(Rf 0.5, petroleum ether/ethyl acetate = 3:1). D-inc. >99% and diastereoselectivity = 10:1 (determined by 1 H NMR). 1 H NMR (400 MHz, CDCl₃) δ 7.93 (dd, J = 8.2, 1.4 Hz, 2H), 7.39 (d, J = 7.9 Hz, 2H), 7.21 (dd, J = 11.7, 7.9 Hz, 4H), 5.75 (d, J = 8.3 Hz, 1H), 5.43 - 4.98 (m, 3H), 4.49 (dd, J = 12.3, 2.3 Hz, 1H), 4.41 - 4.21 (m, 2H), 4.04 - 3.90 (m, 1H), 3.53 - 3.41 (m, 1H), 3.27 - 3.12 (m, 1H), 2.39 (s, 3H), 2.11 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H). 13 C NMR (100 MHz, CDCl₃) δ 170.2, 169.4, 169.0, 165.6, 145.2, 137.5, 133.7, 130.1, 130.0, 129.9, 129.7, 129.1, 91.8, 72.9, 72.7, 72.2, 70.2, 68.1, 62.4, 21.8, 21.7, 21.3, 20.9, 20.7, 20.7. HRMS (ESI) m/z Calcd for $[C_{31}H_{33}D_{3}O_{13}SSeNa, M + Na]^{+}$: 754.1128; Found: 754.1128.

The title compound **7b** was isolated as a yellow oil (80% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1). (Rf 0.5, petroleum ether/ethyl acetate = 5:1). D-inc. >99% and diastereoselectivity >20:1 (determined by ¹H NMR). ¹H

NMR (400 MHz, CDCl₃) δ 7.37 (d, J = 8.0 Hz, 2H), 7.23-7.11 (m, 6H), 4.27 (dd, J = 3.4, 3.4 Hz, 1H), 3.77 (d, J = 15.0 Hz, 1H), 3.43 (dd, J = 3.5, 3.5 Hz, 1H), 3.19 (s, 1 H), 3.14 (dd, J = 3.5, 3.5 Hz, 1H), 2.58-2.41 (m, 2H), 2.37 (s, 3H), 2.14 (t, J = 4.6 Hz, 1H), 2.11-2.01 (m, 1H), 1.96 (d, J = 18.5 Hz, 1H), 1.76-1.62 (m, 1H), 1.50-1.39 (m, 1H), 1.13 (s, 3H), 0.89 (s, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 214.0, 149.6, 145.2, 133.5, 131.4, 131.1, 129.6, 129.1, 122.1, 71.7, 58.1, 48.0, 47.8, 42.8, 42.5, 26.9, 25.1, 21.7, 21.4, 20.0, 19.8, 5.0 (m, C-D₃) **HRMS** (ESI) m/z Calcd for [C₂₆H₂₉D₃O₆S₂SeNa, M + Na]⁺: 610.0886; Found: 610.0890.



The title compound **7c** was isolated as a colorless oil (60% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (6:1). (Rf 0.5, petroleum ether/ethyl acetate = 3:1). D-inc. >99% (determined by ¹H NMR). MP: 91.3-92.8 °C. ¹H NMR

(400 MHz, CDCl₃) δ 7.41 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 7.9 Hz, 2H), 7.14 (d, J = 8.1 Hz, 2H), 7.01 (d, J = 7.2 Hz, 1H), 6.95 (d, J = 8.2 Hz, 2H), 6.67 (d, J = 7.5 Hz, 1H), 6.63 (s, 1H), 4.27 (dd, J = 3.4, 3.4 Hz, 1H), 3.99 (d, J = 5.1 Hz, 2H), 3.46 (dd, J = 3.5, 3.5 Hz, 1H), 3.18 (dd, J = 3.5, 3.5 Hz, 1H), 2.40 (s, 3H), 2.31 (s, 4H), 2.17 (s, 4H), 1.87 (s, 4H), 1.36 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 176.0, 156.9, 151.7, 145.0, 136.6, 133.8, 130.9, 130.4, 129.6, 129.2, 126.9, 123.6, 121.7, 120.8, 111.9, 71.9, 67.7, 42.6, 37.2, 25.3, 25.2, 21.8, 21.6, 21.5, 15.9. **HRMS** (ESI) m/z Calcd for [C₃₁H₃₅D₃O₅SSeNa, M + Na]⁺: 628.1691; Found: 628.1695.

The title compound **7d** was isolated as a white solid (61% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1). (Rf 0.5, petroleum ether/ethyl acetate = 1:1). Dinc. >99% (determined by 1 H NMR). MP: 174.3-176.2 °C. 1 H NMR (400 MHz, CDCl₃) δ 7.67 (d, J

= 8.4 Hz, 2H), 7.49 (s, 2H), 7.47 (s, 1H), 7.41 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.3 Hz, 2H), 6.94 (d, J = 2.5 Hz, 1H), 6.86 (d, J = 9.0 Hz, 1H), 6.70 (dd, J = 2.5, 2.4 Hz, 1H), 4.21 (dd, J = 3.4, 3.5 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 2H), 3.37 (dd, J = 3.5, 3.4 Hz, 1H), 3.14 (dd, J = 3.5, 3.4 Hz, 1H), 2.43 (s, 1H), 2.38 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 168.5, 168.4, 156.4, 145.0, 139.8, 138.4, 136.8, 133.9, 133.5, 131.3, 131.0, 130.6, 130.2, 129.6, 129.4, 129.2, 127.6, 119.7, 115.3, 112.4, 112.3, 100.0, 71.7, 55.9, 33.4, 29.8, 21.8, 21.7, 13.5. HRMS (ESI) m/z Calcd for [C₃₅H₃₀D₃ClN₂O₅SSeNa, M + Na]⁺: 734.1050; Found: 734.1052.

The title compound **7e** was isolated as a white solid (75% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1). (Rf 0.5, petroleum ether/ethyl acetate = 5:1). D-

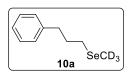
inc. >99% (determined by ¹H NMR). MP: 88.8-90.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, J = 8.2 Hz, 2H), 7.29 (s, 2H), 7.26 (d, J = 3.2 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 4.24 (dd, J = 3.5, 3.4 Hz, 1H), 3.92 (q, J = 7.1 Hz, 1H), 3.45 (dd, J = 3.5, 3.4 Hz, 1H), 3.16 (dd, J = 3.5, 3.4 Hz, 1H), 2.47 (d, J = 7.2 Hz, 2H), 2.38 (d, J = 1.2 Hz, 3H), 1.93 - 1.79 (m, 1H), 1.59 (d, J = 7.2 Hz, 3H), 0.91 (d, J = 6.6 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 172.9, 151.5, 145.0, 141.0, 137.1, 133.8, 130.8, 129.6, 129.6, 129.4, 129.2, 127.3, 121.6, 71.9, 45.3, 45.1, 30.3, 29.8, 22.5, 21.7, 21.6, 18.6. HRMS (ESI) m/z Calcd for [C₂₈H₂₉D₃O₄SSeNa, M + Na]⁺: 570.1273; Found: 570.1274.

The title compound **7f** was isolated as a white solid (78% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1). (Rf 0.5, petroleum ether/ethyl acetate = 5:1). D-inc. >99% (determined by ¹H

NMR). **MP**: 136.4-138.1 °C. ¹H **NMR** (400 MHz, CDCl₃) δ 7.35 (q, J = 7.4, 6.7 Hz, 5H), 7.17 (dd, J = 7.8, 5.4 Hz, 3H), 7.13 (d, J = 8.7 Hz, 2H), 7.06 - 6.95 (m, 4H), 6.75 (s, 1H), 6.59 (dd, J = 8.3, 1.2 Hz, 1H), 4.27 (dd, J = 3.4, 3.4 Hz, 1H), 4.04 (s, 2H), 3.47 (dd, J = 3.5, 3.4 Hz, 1H), 3.19 (dd, J = 3.5, 3.4 Hz, 1H), 2.38 (s, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 170.2, 151.1, 145.0, 142.7, 137.7, 133.7, 131.1, 130.9, 129.7, 129.5, 129.1, 128.9, 128.4, 124.3, 123.6, 122.3, 121.7, 118.5, 71.9, 38.7, 21.7, 21.4. **HRMS** (ESI) m/z Calcd for [C₃₀H₂₄D₃Cl₂NO₄SSeNa, M + Na]⁺: 673.0289; Found: 673.0292.

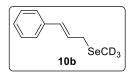
The title compound **7g** was isolated as a white solid (67% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1). (Rf 0.5, petroleum ether/ethyl acetate = 5:1). D-inc. >99% and

diastereoselectivity >20:1 (determined by ¹H NMR). MP: 142.4-144.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, J = 8.0 Hz, 2H), 7.33-7.27 (m, 3H), 7.20-7.10 (m, 3H), 7.07 (d, J = 8.0 Hz, 2H), 7.03-6.98 (m, 2H), 6.90 (d, J = 8.6 Hz, 2H), 6.74 (s, 1H), 6.67-6.54 (m, 1H), 4.14 (d, J = 10.1 Hz, 1H), 4.01 (s, 2H), 3.93-3.80 (m, 1H), 2.31 (s, 3H), 1.96 (d, J = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 170.2, 150.8, 144.4, 142.7, 137.7, 135.8, 131.9, 131.1, 131.0, 129.5, 129.4, 129.0, 128.6, 128.4, 124.4, 123.7, 122.4, 121.5, 118.6, 76.8, 38.7, 33.9, 22.1, 21.7. HRMS (ESI) m/z Calcd for [C₃₁H₂₆D₃Cl₂NO₄SSeK, M + K]⁺: 703.0179; Found: 703.0182.



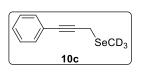
The title compound **10a** was isolated as a colorless oil (81% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99%

(determined by ¹**H NMR**). ¹**H NMR** (400 MHz, CDCl₃) δ 7.25-7.19 (m, 2H), 7.16-7.08 (m, 3H), 2.64 (t, J = 7.6 Hz, 2H), 2.48 (t, J = 7.4 Hz, 2H), 2.02-1.84 (m, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 141.7, 128.6, 128.5, 126.0, 35.9, 31.8, 24.8. **HRMS** (ESI) m/z Calcd for [C₁₀H₁₁D₃O₂SSeNa, M + Na]⁺: 218.0522; Found: 218.0528.



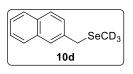
The title compound **10b** was isolated as a colorless oil (91% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99%

(determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 7.42-7.36 (m, 2H), 7.35-7.29 (m, 2H), 7.26-7.20 (m, 1H), 6.42-6.21 (m, 2H), 3.32 (d, J = 7.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 136.9, 131.5, 128.7, 127.6, 126.5, 126.4, 26.8, 3.4-3.0 (m, C-D₃). HRMS (ESI) m/z Calcd for [C₁₀H₉D₃SeNa, M + Na]⁺: 238.0190; Found: 238.0195.



The title compound **10c** was isolated as a yellow oil (95% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99%

(determined by ¹**H NMR**). ¹**H NMR** (400 MHz, CDCl₃) δ 7.47-7.38 (m, 2H), 7.34-7.27 (m, 3H), 3.43 (s, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 131.8, 128.4, 128.2, 123.4, 86.3, 83.3, 9.3, 4.7-4.3 (m, C-D₃). **HRMS** (ESI) m/z Calcd for [C₁₀H₇D₃SeNa, M + Na]⁺: 236.0034; Found: 236.0030.



The title compound **10d** was isolated as a colorless oil (89% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99%

(determined by 1 H NMR). 1 H NMR (400 MHz, CDCl₃) δ 7.88-7.75 (m, 3H), 7.66 (d,

J = 1.8 Hz, 1H), 7.55-7.40 (m, 3H), 3.90 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 136.7, 133.33, 132.5, 128.5, 127.8, 127.7, 127.4, 127.1, 126.3, 125.8, 28.6, 4.0-3.5 (m, C-D₃). **HRMS** (ESI) m/z Calcd for [C₁₂H₉D₃SeNa, M + Na]⁺: 262.0190; Found: 262.0197.

yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99% (determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 7.29 (t, J = 7.5 Hz, 2H), 7.19 (d, J = 8.1 Hz, 3H), 2.64 (t, J = 6.9 Hz, 2H), 2.56 (t, J = 6.5 Hz, 2H), 1.80-1.66 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 142.3, 128.5, 128.4, 125.8, 35.5, 31.6, 29.8, 25.2. **HRMS** (ESI) m/z Calcd for $[C_{11}H_{13}D_3SeNa, M + Na]^+$: 254.0503; Found: 254.0509.

The title compound 10f was isolated as a colorless oil (82% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99% (determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 6.43

The title compound 10e was isolated as a colorless oil (80%)

(d, J = 2.3 Hz, 2H), 6.32 (s, 1H), 3.78 (s, 6H), 3.67 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 160.8, 141.6, 106.9, 98.8, 55.4, 28.6. **HRMS** (ESI) m/z Calcd for $[C_{10}H_{11}D_3O_2SeNa, M + Na]^+$: 272.0245; Found: 272.0247.

The title compound 10g was isolated as a colorless oil (85% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). (Rf 0.7, petroleum ether/ethyl acetate = 20:1). D-inc. >99% (determined by 1 H NMR). 1 H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.3 Hz, 2H, 7.26 (d, J = 8.3 Hz, 2H), 3.83 (s, 3H), 3.68 (s, 2H).¹³C NMR (100) MHz, CDCl₃) δ 167.0, 144.9, 129.9, 128.9, 128.6, 52.2, 27.8. **HRMS** (ESI) m/z Calcd for $[C_{10}H_9D_3O_2SeNa, M + Na]^+$: 270.0083; Found: 270.0085.

The title compound 10h was isolated as a colorless oil (73% yield) through flash chromatography on silica gel eluting with petroleum ether). (Rf 0.5, petroleum ether). D-inc. >99%

(determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 7.04 (d, J = 1.9 Hz, 1H), 6.94 (dd, J = 1.9, 2.0 Hz, 1H), 6.71 (d, J = 8.1 Hz, 1H), 4.55 (t, J = 8.7 Hz, 2H), 3.19(t, J = 8.7 Hz, 2H), 3.04-2.84 (m, 2H), 2.82-2.67 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 158.7, 133.4, 127.9, 127.2, 125.0, 125.0, 109.2, 71.3, 36.4, 29.9, 27.0, 3.7-3.0 (m, C-D₃). **HRMS** (ESI) m/z Calcd for $[C_{11}H_{11}D_3OSeNa, M + Na]^+$: 268.0290; Found: 268.0291.

The title compound **10i** was isolated as a colorless oil (90% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (40:1). (Rf 0.6, petroleum ether/ethyl acetate = 20:1). D-inc. >99% (determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 7.97 (s, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.37 (d, J = 8.1 Hz, 1H), 7.26-7.17 (m, 1H), 7.19-7.10 (m, 1H), 7.05 (d, J = 2.3 Hz, 1H), 3.16 (t, J = 7.9 Hz, 2H), 2.90 (t, J = 1.6 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 136.4, 127.2, 122.2, 121.6 (d, J = 2.1 Hz), 119.5, 118.8, 115.9, 111.3, 26.6, 25.7. **HRMS** (ESI) m/z Calcd for

 $[C_{11}H_{10}D_3NSeK, M + K]^+$: 281.0033; Found: 281.0037.

The title compound 10j was isolated as a colorless oil (76% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.4, petroleum ether). Dinc. >99% (determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 7.97 (s, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.37 (d, J = 8.1 Hz, 1H), 7.26-7.17 (m, 1H), 7.19-7.10 (m, 1H), 7.05 (d, J = 2.3 Hz, 1H), 3.16 (t, J = 7.9 Hz, 2H), 2.90 (t, J = 1.6 Hz, 2H). ¹³C **NMR** (100 MHz, CDCl₃) δ 136.4, 127.2, 122.2, 121.6 (d, J = 2.1 Hz), 119.5, 118.8, 115.9, 111.3, 26.6, 25.7. **HRMS** (ESI) m/z Calcd for $[C_{11}H_{10}D_3NSeK, M + K]^+$: 281.0033; Found: 281.0037.

The title compound **10k** was isolated as a colorless oil (81% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.4, petroleum ether). D-inc. >99% (determined by ¹H NMR). ¹H NMR (400

MHz, CDCl₃) δ 8.13 (d, J = 8.7 Hz, 1H), 7.88 (dd, J = 7.9, 1.6 Hz, 1H), 7.85 - 7.78 (m, 1H), 7.58 - 7.48 (m, 3H), 7.47 - 7.41 (m, 1H), 4.96 (s, 2H), 3.58 (t, J = 5.7 Hz, 2H), 2.53 (t, J = 6.8 Hz, 2H), 1.76 (dd, J = 6.6, 3.5 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 134.0, 133.8, 131.8, 128.6, 128.6, 126.4, 126.2, 125.8, 125.3, 124.1, 71.5, 69.8, 30.0, 27.0, 25.0, 3.6-3.4 (m, C-D₃). **HRMS** (ESI) m/z Calcd for [C₁₅H₁₅D₃OSeNa, M + Na]⁺: 320.0609; Found: 320.0610.

The title compound **10l** was isolated as a colorless oil (76% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.4, petroleum ether). D-inc. >99%

(determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 6.84 (s, 2H), 3.77 (t, J = 5.7 Hz, 2H), 2.64 (t, J = 6.9 Hz, 2H), 2.26 (s, 9H), 2.00-1.83 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 153.7, 133.0, 130.6, 129.4, 71.7, 30.7, 27.1, 25.1, 20.8, 16.3, 3.7-3.3 (m, C-D₃). HRMS (ESI) m/z Calcd for [C₁₄H₁₉D₃OSeNa, M + Na]⁺: 312.0916; Found: 312.0921.

The title compound **10m** was isolated as a colorless oil (76% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.4, petroleum ether). D-inc. >99%

(determined by ¹**H NMR**). ¹**H NMR** (400 MHz, CDCl₃) δ 7.07-6.93 (m, 1H), 6.77-6.62 (m, 1H), 6.61-6.49 (m, 1H), 4.01 (t, J = 6.0 Hz, 2H), 2.60 (t, J = 7.0 Hz, 2H), 2.00-1.77 (m, 4H). ¹³**C NMR** (100 MHz, CDCl₃) δ 158.8 (dd, ¹ $J_{C-F} = 241.9$, 2.6 Hz),

149.0 (d, ${}^{1}J_{C-F} = 235.2 \text{ Hz}$), 147.8 (dd, ${}^{3}J_{C-F} = 4.1$, 2.7 Hz), 116.2 (dd, ${}^{2}J_{C-F} = 20.7$, 10.3 Hz), 106.4 (dd, ${}^{2}J_{C-F}$ = 23.8, 6.9 Hz), 102.6 (d, ${}^{2}J_{C-F}$ = 28.0 Hz), 68.9, 29.2, 26.6, 24.8, 3.7-3.3 (m, C-D₃). ¹⁹**F NMR** (376 MHz, CDCl₃) δ -116.78 (d, J = 14.8 Hz), -140.45 (d, J = 14.8 Hz). **HRMS** (ESI) m/z Calcd for $[C_{11}H_{11}D_3F_2OSeNa, M + Na]^+$: 306.0258; Found: 306.0257.

The title compound 10n was isolated as a colorless oil (79% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (40:1). (Rf 0.4,

petroleum ether/ethyl acetate = 20:1). D-inc. >99% (determined by ¹H NMR). ¹H **NMR** (400 MHz, CDCl₃) δ 6.83 (s, 4H), 3.93 (t, J = 5.6 Hz, 2H), 3.76 (s, 3H), 2.99-2.50 (m, 2H), 1.93-1.78 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 153.8, 153.2, 115.4, 114.7, 67.9, 55.8, 29.6, 26.8, 24.9, 3.7-3.2 (m, C-D₃). **HRMS** (ESI) m/z Calcd for $[C_{12}H_{15}D_3O_2SeNa, M + Na]^+$: 277.0660; Found: 277.0661.

The title compound 100 was isolated as a colorless oil (79% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.5, petroleum ether). D-inc. >99% (determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.22 (m, 2H), 6.99-6.93 (m, 1H), 6.93-6.88 (m, 2H), 4.22 (t, J = 7.1 Hz, 2H), 2.89 (t, J = 7.1 Hz, 2H). ¹³C **NMR** (100 MHz, CDCl₃) δ 158.5, 129.6, 121.1, 114.7, 68.2, 23.5. **HRMS** (ESI) m/z

The title compound **10p** was isolated as a colorless oil (79%) yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.5, petroleum ether). D-inc. >99%

(determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 7.37 (d, J = 8.9 Hz, 2H), 6.78 (d, J = 9.0 Hz, 2H), 4.17 (t, J = 7.1 Hz, 2H), 2.87 (t, J = 7.1 Hz, 2H). ¹³C NMR

Calcd for $[C_9H_9D_3OSeNa, M + Na]^+$: 242.0134; Found: 242.0137.

(100 MHz, CDCl₃) δ 157.7, 132.4, 116.5, 113.2, 68.5, 23.3. **HRMS** (ESI) m/z Calcd for [C₉H₈D₃BrOSeNa, M + Na]⁺: 319.9239; Found: 319.9240.

The title compound **10q** was isolated as a colorless oil (76% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (40:1). (Rf 0.5, petroleum

ether/ethyl acetate = 20:1). D-inc. >99% (determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 6.99-6.85 (m, 4H), 4.26 (t, J = 7.3 Hz, 2H), 4.08 (q, J = 7.0 Hz, 2H), 2.92 (t, J = 7.3 Hz, 2H), 1.44 (t, J = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 149.0, 148.3, 121.7, 121.0, 114.2, 113.5, 69.7, 64.5, 23.3, 15.0. HRMS (ESI) m/z Calcd for [C₁₁H₁₄D₃O₂Se, M + H]⁺: 264.0577; Found: 264.0580.

The title compound **10r** was isolated as a colorless oil (86% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether. D-

inc. >99% (determined by ¹**H NMR**). ¹**H NMR** (400 MHz, CDCl₃) δ 7.53 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 3.31-3.22 (m, 2H), 2.82-2.69 (m, 2H). ¹³**C NMR** (100 MHz, CDCl₃) δ 141.2 (d, ⁴ J_{C-F} = 1.5 Hz), 128.6 (d, ² J_{C-F} = 18.7 Hz), 128.1, 125.9 (q, ³ J_{C-F} = 3.8 Hz), 121.5 (q, ¹ J_{C-F} = 271.8 Hz), 33.3, 23.4, 4.2-3.8 (m, C-D₃). ¹⁹**F NMR** (376 MHz, CDCl₃) δ -62.4. **HRMS** (ESI) m/z Calcd for [C₁₀H₈D₃F₃SSeNa, M + Na]⁺: 325.9779; Found: 325.9779.

The title compound **10s** was isolated as a colorless oil (68% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether.

D-inc. >99% (determined by ¹**H NMR**). ¹**H NMR** (400 MHz, CDCl₃) δ 6.81 - 6.74 (m, 2H), 6.64-6.53 (m, 1H), 2.95 (t, J = 6.6 Hz, 2H), 2.55 (t, J = 6.6 Hz, 2H), 1.93-1.70 (m, 4H). ¹³**C NMR** (100 MHz, CDCl₃) δ 163.1 (q, ${}^{I}J_{C-F}$ = 249.9, 13.3 Hz), 141.2 (d, ${}^{3}J_{C-F}$ = 9.9 Hz), 110.3 (dd, ${}^{2}J_{C-F}$ = 19.6 Hz), 101.0 (t, ${}^{2}J_{C-F}$ = 25.4 Hz), 32.3, 29.1,

28.7, 24.5. ¹⁹**F NMR** (376 MHz, CDCl₃) δ -109.5. **HRMS** (ESI) m/z Calcd for $[C_{11}H_{11}D_3F_2SSeNa, M + Na]^+$: 322.0035; Found: 322.0040.



The title compound **10t** was isolated as a white solid (74% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99% (determined by ¹H

NMR). **MP**: 61.4-63.9 °C. ¹**H NMR** (400 MHz, CDCl₃) δ 2.36 (d, J = 2.9 Hz, 6H), 2.10 (t, J = 3.9 Hz, 3H), 1.72 (t, J = 3.1 Hz, 6H). ¹³**C NMR** (100 MHz, CDCl₃) δ 67.0, 49.4, 35.6, 32.7. **HRMS** (ESI) m/z Calcd for [C₁₁H₁₅D₃SeNa, M + Na]⁺: 256.0660; Found: 256.0669.

The title compound **10u** was isolated as a colorless oil (68% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (40:1). (Rf 0.6, petroleum ether/ethyl acetate = 20:1). D-inc. >99% (determined by ¹H

NMR). ¹**H NMR** (400 MHz, CDCl₃) δ 7.43 (d, J = 2.6 Hz, 1H), 7.08 (dd, J = 2.5, 2.5 Hz, 1H), 7.00-6.88 (m, 3H), 6.62 (d, J = 8.8 Hz, 1H), 3.93 (t, J = 6.0 Hz, 2H), 2.46 (t, J = 7.3 Hz, 2H), 1.80-1.66 (m, 2H), 1.64-1.51 (m, 2H). ¹³C **NMR** (100 MHz, CDCl₃) δ 152.7, 151.0, 142.9, 130.8, 130.3, 127.8, 127.7, 124.3, 122.4, 121.1, 117.7, 114.7, 68.5, 29.1, 26.3, 24.7, 3.4-3.0 (m, C-D₃). **HRMS** (ESI) m/z Calcd for [C₁₇H₁₄D₃Cl₃O₂SeNa, M + Na]⁺: 463.9545; Found: 463.9550.

The title compound **10v** was isolated as a colorless oil (71% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (40:1). (Rf 0.6, petroleum ether/ethyl acetate = 20:1). D-inc. >99%

(determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 1H NMR (400 MHz, Chloroform-d) δ 7.43 (d, J = 2.5 Hz, 1H), 7.08 (dd, J = 8.8, 2.5 Hz, 1H), 7.00-6.88 (m, 3H), 6.62 (d, J = 8.8 Hz, 1H), 3.93 (t, J = 6.0 Hz, 2H), 2.54-2.38 (m, 2H), 2.10 (s, 1H),

1.81-1.67 (m, 4H), 1.59 (q, J = 7.5 Hz, 3H). ¹³C **NMR** (100 MHz, CDCl₃) δ 13C NMR (101 MHz, Chloroform-d) δ 152.67, 151.03, 142.91, 130.79, 130.27, 127.82, 127.67, 124.30, 122.42, 121.11, 117.68, 114.74, 68.54, 29.06, 26.30, 24.82, 4.04 (s, ¹³C-H₃). **HRMS** (ESI) m/z Calcd for [C₁₆¹³CH₁₇Cl₃O₂SeNa, M + Na]⁺: 461.9391; Found: 461.9394.

The title compound **10w** was isolated as a colorless oil (68% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1). (Rf 0.6, petroleum ether/ethyl acetate = 5:1). D-inc. >99%

(determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 5.84 (d, J = 3.7 Hz, 1H), 4.50 (d, J = 3.7 Hz, 1H), 4.31-4.22 (m, 1H), 4.12-4.01 (m, 2H), 3.95 (dd, J = 8.6, 5.7 Hz, 1H), 3.82 (d, J = 3.0 Hz, 1H), 3.66-3.56 (m, 1H), 3.55-3.46 (m, 1H), 2.51 (t, J = 7.1 Hz, 2H), 1.79-1.57 (m, 4H), 1.46 (s, 3H), 1.39 (s, 3H), 1.32 (s, 3H), 1.28 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 111.7, 108.9, 105.3, 82.5, 82.1, 81.2, 72.4, 69.9, 67.3, 29.8, 26.8, 26.8, 26.7, 26.2, 25.4, 24.9, 5.8-3.2 (m, C-D₃). HRMS (ESI) m/z Calcd for [C₁₈H₂₉D₃O₅SeNa, M + Na]⁺: 434.1501; Found: 434.1504.

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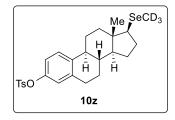
The title compound **10x** was isolated as a colorless oil (50% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.6,

petroleum ether/ethyl acetate = 10:1). D-inc. >99% (determined by ${}^{1}\mathbf{H}$ NMR). ${}^{1}\mathbf{H}$ NMR (400 MHz, CDCl₃) δ 3.64 (q, J = 5.1, 4.2 Hz, 2H), 2.71-2.50 (m, 4H), 2.16 (s, 3H), 2.11 (s, 3H), 2.07 (s, 3H), 1.95-1.88 (m, 4H), 1.86-1.69 (m, 2H), 1.54-1.45 (m, 2H), 1.35-1.17 (m, 14H), 1.17-0.98 (m, 8H), 0.85 (dd, J = 10.0, 6.7 Hz, 12H). ${}^{13}\mathbf{C}$ NMR (100 MHz, CDCl₃) δ 148.2, 147.7, 127.8, 125.8, 122.8, 117.5, 77.2, 76.8, 74.7, 72.3, 39.3, 37.4, 37.4, 37.3, 32.7, 32.7, 31.2, 30.5, 28.0, 24.8, 24.4, 23.9, 22.7, 22.6,

21.0, 20.6, 19.7, 19.7, 12.7, 11.9, 11.8. **HRMS** (ESI) m/z Calcd for [C₃₃H₅₅D₃O₂SeNa, M + Na]⁺: 592.3688; Found: 592.3690.

The title compound **10y** was isolated as a green oil (75% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1). (Rf 0.5, petroleum ether/ethyl acetate = 5:1). D-inc. >99%

(determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 7.05 (d, J = 8.7 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 4.03 (q, J = 7.0 Hz, 2H), 3.66 (t, J = 7.3 Hz, 2H), 2.51 (t, J = 7.2 Hz, 2H), 1.80 (s, 3H), 1.71-1.62 (m, 2H), 1.62-1.53 (m, 2H), 1.43 (t, J = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 170.9, 158.4, 135.6, 129.2, 115.3, 63.8, 48.5, 28.1, 27.5, 24.9, 22.9, 14.9. **HRMS** (ESI) m/z Calcd for [C₁₅H₂₀D₃NO₂SeNa, M + Na]⁺: 355.0975; Found: 355.0977.



The title compound **10z** was isolated as a colorless oil (68% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.4, petroleum ether/ethyl acetate = 10:1). D-inc. >99%

(determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H), 7.03 (d, J = 8.7 Hz, 1H), 6.54 (dd, J = 8.4, 2.8 Hz, 1H), 6.47 (d, J = 3.2 Hz, 1H), 4.77 (s, 1H), 4.27 (dd, J = 9.1, 7.7 Hz, 1H), 2.80-2.62 (m, 2H), 2.39 (s, 3H), 2.18-2.08 (m, 1H), 2.07-1.99 (m, 1H), 1.97-1.84 (m, 1H), 1.79-1.70 (m, 1H), 1.70-1.54 (m, 2H), 1.40-1.22 (m, 4H), 1.13-0.98 (m, 2H), 0.75 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 153.5, 144.6, 138.1, 134.2, 132.2, 129.8, 127.9, 126.6, 115.3, 112.8, 90.0, 49.0, 43.7, 43.4, 38.5, 36.1, 29.5, 27.8, 27.1, 26.0, 23.1, 21.8, 11.8. HRMS (ESI) m/z Calcd for [C₂₆H₂₉D₃O₃SeNa, M + Na]⁺: 530.1323; Found: 530.1324.

The title compound **11a** was isolated as a colorless oil (82% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1). (Rf 0.5, petroleum ether). D-inc. >99%

(determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 6.9 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 3.41 (t, J = 7.3 Hz, 2H), 2.92 (t, J = 7.5 Hz, 2H), 3.41 (t, J = 7.5 Hz, J = 7.5 7.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 198.8, 136.6, 133.3, 128.7, 128.1, 39.7, 18.4. **HRMS** (ESI) m/z Calcd for $[C_{10}H_9D_3OSeNa, M + Na]^+$: 254.0139; Found: 254.0140.

The title compound 11b was isolated as a colorless oil (82% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.5, petroleum ether/ethyl acetate = 10:1). D-inc. >99% (determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 7.42-7.30 (m, 5H), 5.15 (s, 2H), 2.78 (s, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 172.2, 135.8, 128.7, 128.4, 128.4, 66.6, 35.5, 18.8, 3.8-3.5 (m, C-D₃). **HRMS** (ESI) m/z Calcd for $[C_{11}H_{11}D_3O_2SeNa, M + Na]^+$: 284.0240; Found:

284.0245.

The title compound 11c was isolated as a colorless oil (81% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.5, petroleum

ether/ethyl acetate = 10:1). D-inc. >99% (determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 7.49-7.32 (m, 2H), 7.28-7.19 (m, 1H), 7.15-7.05 (m, 2H), 2.98 (t, J =6.4 Hz, 2H), 2.88 (t, J = 7.1 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 170.9, 150.7, 129.5, 126.0, 121.6, 35.6, 18.7, 4.1-3.7 (m, C-D₃). HRMS (ESI) m/z Calcd for $[C_{10}H_9D_3O_2SeNa, M + Na]^+$: 270.0083; Found: 270.0080.

The title compound 11d was isolated as a colorless oil (78% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.5, petroleum ether/ethyl acetate = 10:1). D-inc. >99% (determined by ${}^{1}\mathbf{H}$ NMR). ${}^{1}\mathbf{H}$ NMR (400 MHz, CDCl₃) δ 7.20 (d, J = 8.1 Hz, 2H), 7.01 (d, J = 8.5 Hz, 2H), 2.96 (t, J = 6.5 Hz, 2H), 2.87 (t, J = 7.1 Hz, 2H), 2.64 (q, J = 7.6 Hz, 2H), 1.23 (t, J = 7.6 Hz, 3H). ${}^{13}\mathbf{C}$ NMR (100 MHz, CDCl₃) δ 171.2, 148.6, 142.0, 128.9, 121.3, 35.6, 28.4, 18.8, 15.7, 4.1-3.7 (m, C-D₃). **HRMS** (ESI) m/z Calcd for [C₁₂H₁₃D₃O₂SeNa, M + Na]⁺: 298.0396; Found: 298.0394.

The title compound **11e** was isolated as a colorless oil (58% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1). (Rf 0.5, petroleum ether/ethyl acetate = 5:1). D-inc. >99%

(determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 5.88 (d, J = 3.7 Hz, 1H), 5.27 (d, J = 2.4 Hz, 1H), 4.54 (d, J = 3.6 Hz, 1H), 4.21 (d, J = 2.6 Hz, 2H), 4.12-4.07 (m, 1H), 4.05-4.00 (m, 1H), 2.77 (s, 4H), 1.52 (s, 3H), 1.41 (s, 3H), 1.32 (s, 3H), 1.31 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.1, 112.5, 109.5, 105.2, 83.4, 79.9, 76.5, 72.5, 67.4, 35.4, 27.0, 26.9, 26.3, 25.4, 18.7. **HRMS** (ESI) m/z Calcd for [C₁₇H₂₅D₃O₆SeNa, M + Na]⁺: 434.1132; Found: 434.1130.

The title compound **11f** was isolated as a colorless oil (71% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). (Rf 0.6, petroleum ether/ethyl acetate = 10:1). D-inc. >99% (determined by ¹H

NMR). ¹**H NMR** (400 MHz, CDCl₃) δ 4.76-4.65 (m, 1H), 2.80-2.72 (m, 2H), 2.73-2.65 (m, 2H), 2.09-1.94 (m, 1H), 1.93-1.80 (m, 1H), 1.75-1.62 (m, 2H), 1.55-1.42 (m, 1H), 1.43-1.30 (m, 1H), 1.14-0.96 (m, 2H), 0.92-0.86 (m, 7H), 0.75 (d, J = 7.0 Hz, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 172.0, 74.7, 47.1, 41.0, 35.9, 34.3, 31.5, 26.4, 23.5, 22.2, 20.9, 19.1, 16.4. **HRMS** (ESI) m/z Calcd for [C₁₄H₂₃D₃O₂SeNa, M + Na]⁺: 332.1179; Found: 332.1176

6. General Procedure for Derivatization of 2g

6.1 Oxidative Derivatization of 2g.

To a dry Schlenk tube containing **2g** (0.2 mmol, 1.0 equiv.), ^mCPBA (0.22 mmol, 1.1 equiv.) and DCM (2.0 mL) at room temperature and for 8 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with dichloromethane, washed with brine, dried over anhydrous Na₂SO₄. The product **15a** was obtained with 58% yield via column chromatography.

To a dry Schlenk tube containing **2g** (0.2 mmol, 1.0 equiv.), ^mCPBA (0.4 mmol, 2.0 equiv.) and DCM (2.0 mL) at room temperature and for 4 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with dichloromethane, washed with brine, dried over anhydrous Na₂SO₄. The product **15b** was obtained with 85% yield via column chromatography.

6.2 Characterization of Products.

The title compound **15a** was isolated as a white solid (58% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (40/1). (Rf 0.5, petroleum ether/ethyl acetate = 10/1). D-inc. >99% (determined by ¹H NMR). MP: 25.2-26.3 °C. ¹H NMR (400 MHz, CDCl₃)
$$\delta$$
 8.07 (d, J = 8.1 Hz, 2H), 7.84 (d, J = 8.1 Hz, 2H), 7.59 (d, J = 7.4 Hz, 2H), 7.55-7.38 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 147.66,

140.91, 138.80, 129.29, 129.05, 128.97, 127.51, 127.10. **HRMS** (ESI) m/z Calcd for [C₁₃H9D₃OSeNa, M + Na]⁺: 280.0241; Found: 280.0242.

The title compound **19b** was isolated as a white solid (85% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (40/1). (Rf 0.5, petroleum ether/ethyl acetate = 10/1). D-inc. >99% (determined by ¹H NMR). MP: 40.2-42.8 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, J = 8.1 Hz, 2H), 7.71 (d, J = 8.1 Hz, 2H), 7.56 (d, J = 8.1 Hz, 2H), 7.43 (m, 2H), 7.36 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 144.45, 140.28, 139.66, 129.01, 128.42, 128.20, 127.27, 126.03. HRMS (ESI) m/z

Calcd for $[C_{13}H_9D_3O_2Se, M + H]^+$: 282.0198; Found: 282.0198.

7. Application of Se-methyl- d_3 reagent

7.1 A Formal Vinyl C-H Sulfonylation and a Nucleophilic Deuterated Methylselenylation via Application Relay Strategy

Procedure: To a dry Schlenk tube containing **12** (0.3 mmol, 1.0 equiv.), **5b** (0.36 mmol, 1.2 equiv.), Pr(OTf)₃ (0.03 mmol, 10 mol%), **L**₁ (0.03 mmol, 10 mol%) and MeCN (1.5 mL) at 50 °C and for 10 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with dichloromethane, washed with brine, dried over anhydrous Na₂SO₄. The product **13** was obtained with 78% yield via column chromatography.

To a dry Schlenk tube containing **13** (0.2 mmol, 1.0 equiv.), Cs₂CO₃ (0.2 mmol, 1.0 equiv.) and MeOH (0.5 mL) at 50 °C and for 10 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with dichloromethane, washed with brine, dried over anhydrous Na₂SO₄. The product **14** was obtained with 65% yield via column chromatography.

7.2 General Procedure for The Synthesis of Drug Analogues¹²

7.2.1 Synthesis of Thioripyridazine Analogues

Step I: To a dry Schlenk tube containing **16** (0.3 mmol, 1.0 equiv.) and TsCl (0.348 mmol, 1.16 equiv.) were added pyridine (0.2 mL), the mixture was stirred at room temperature and for 2 h. After the reaction was complete, the reaction was quenched with 0.2 M HCl, the organic layer was then extracted with EtOAc, wash the organic layer with saturated NaHCO₃ solution and brine, dried over anhydrous Na₂SO₄. The product **SI-24** was obtained with 77% yield via column chromatography.

Step II: To a dry Schlenk tube containing 2-chloro phenothiazine (0.3 mmol, 1.0 equiv.) and NaH (0.36 mmol, 1.2 equiv.) in DMF (7.5 mL) were added **SI-24** (0.372 mmol, 1.24 equiv.) and NaI (0.03 mmol, 10 mol%), the mixture was stirred at 0 °C for 30 min. After the reaction was complete, the reaction was quenched with NH₄Cl aqueous solution, the organic layer was then extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄. The product **SI-25** was obtained with 70% yield via column chromatography.

Step III: To a dry Schlenk tube containing **SI-25** (0.3 mmol, 1.0 equiv.) was added TFA/DCM (0.9 mL, 1:2), the mixture was stirred at room temperature and for 12 h. After the reaction was complete, the reaction was quenched with NaHCO₃ aqueous solution, the organic layer was then extracted with dichloromethane, washed with brine, dried over anhydrous Na₂SO₄. The product **SI-26** was obtained with 90% yield via column chromatography.

Step IV: To a dry Schlenk tube containing **SI-26** (0.3 mmol, 1.0 equiv.) and Formaldehyde aqueous solution (0.6 mmol, 2.0 equiv.) were added THF (10 mL), the mixture was stirred at room temperature and for 30 min, then NaBH(OAc)₃ (0.9 mmol, 3.0 equiv.) was added to the mixture at room temperature for 24 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄. The product **17** was obtained with 95% yield via column chromatography.

Step V: To a dry Schlenk tube containing **17** (0.3 mmol, 1.0 equiv.), B₂(OH)₄ (0.6 mmol, 2.0 equiv.), XPhos-Pd-G (0.003 mmol, 1.0 mol%), XPhos (0.006 mmol, 2.0 mol%) and KOAc (0.9 mmol, 3.0 equiv.) were added EtOH (1.5 mL), the mixture was stirred at 80 °C for 12 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄. The product **18** was obtained with 81% yield via column chromatography.

Step VI: To a dry Schlenk tube containing **18** (0.3 mmol, 1.0 equiv.), Cu(OAc)₂ (0.03 mmol, 10 mol% equiv.), **L**₁ (0.03 mmol, 10 mol%), Cs₂CO₃ (0.3 mmol, 1.0 equiv.) and TsSeCD₃ (0.36 mmol, 1.2 equiv.) were added THF (1.0 mL), the mixture was stirred at room temperature for 14 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄. The product **19** was obtained with 81% yield via column chromatography.

7.2.2. Synthesis of Ranolazine Analogues¹³

Step I: To a dry Schlenk tube containing **20** (10 mmol, 1.0 equiv.) and Piperazine (40 mmol, 4.0 equiv.) were added EtOH (20 mL), the mixture was stirred under reflux and for 4 h. After the reaction was complete, the reaction was quenched with saturated NaHCO₃, the organic layer was then extracted with EtOAc, wash the obrine, dried over anhydrous Na₂SO₄. The crude product **SI-29** was obtained with 83% yield.

Step II: To the magnetically stirred mixture of **SI-29** (8 mmol) in water (16 mL) at 22 °C was epichlorohydrine (8.4 mmol,1.05 equiv.) and stirring was continued for 2h followed by addition of **2m** (1.97 g,10.4 mmol, 1.3 equiv.) and the stirring continued at 90 °C for 5 h. The reaction mixture was cooled to rt and neutralized with NaHCO₃:(until the effervescence ceases). The mixture was cooled to 0-5 °C and diluted with 1:1 methanol and acetone (20 mL). The solid that precipitated out (2-3 h) was filtered, washed with chilled methanol (5 mL), and dried to get analytically pure ranolazine analogues **21** (3.3 g, 84%).

7.3 Characterization of Products.

The title compound 13 was isolated as a colorless oil (78% yield) through flash chromatography on silica gel eluting

with petroleum ether/ethyl acetate (30:1). (Rf 0.4, petroleum ether/ethyl acetate = 10:1). D-inc. >99% (determined by ^{1}H NMR). ^{1}H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 8.4 Hz, 1H), 7.35 (d, J = 8.3 Hz, 1H), 7.15 (dd, J = 17.6, 8.2 Hz, 2H), 4.54 (d, J = 6.0 Hz, 1H), 4.27 (dd, J = 12.3, 3.4 Hz, 1H), 3.57 (t, J = 6.0 Hz, 1H), 3.40 (dd, J = 12.5, 3.5 Hz, 1H), 3.17 (d, J = 12.4 Hz, 1H), 2.33 (s, 2H). ^{13}C NMR (100 MHz, CDCl₃) δ 165.5, 145.2, 137.6, 133.8, 130.2, 130.1, 129.8, 129.7, 129.1, 72.2, 64.5, 28.8, 21.7, 21.4. HRMS (ESI) m/z Calcd for [C₁₉H₁₈D₃O₄SSeBrNa, M + Na]⁺: 529.9590; Found: 529.9587.

The title compound **14** was isolated as a colorless oil (58% yield) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30:1). (Rf 0.4, petroleum to 10:1). D-inc. >99% (determined by **1H NMR**). **1H NMR** (400)

ether/ethyl acetate = 10:1). D-inc. >99% (determined by ${}^{1}\mathbf{H}$ NMR). ${}^{1}\mathbf{H}$ NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 6.67 (s, 1H), 5.99 (s, 1H), 4.52 (t, J = 7.3 Hz, 2H), 2.85 (t, J = 7.2 Hz, 2H), 2.37 (s, 3H). ${}^{13}\mathbf{C}$ NMR (100 MHz, CDCl₃) δ 165.8, 150.5, 144.8, 137.3, 135.4, 130.8, 129.8, 129.6, 129.2, 128.5, 126.5, 64.7, 22.8, 21.7. **HRMS** (ESI) m/z Calcd for [C₁₉H₁₇D₃O₄SSeNa, M + Na]⁺: 450.0328; Found: 450.0329.

The title compound **18** was isolated as a white solid (80% yield) through flash chromatography on Aluminum oxide active eluting with DCM/methanol (10:1). (Rf 0.3, DCM/methanol = 10:1). **MP**: 162.5-164.2 °C. ¹**H NMR** (400 MHz, CD₃OD) δ 7.27 - 7.07 (m, 4H), 6.99 (m, 2H), 6.89 (m,

1H), 4.23 - 3.88 (m, 2H), 3.34 (s, 2H), 3.04 (m, 1H), 2.76 (m, 1H), 2.55 (m, 1H), 2.35 (m, 4H), 1.88 (dd, J = 14.7, 3.9 Hz, 1H), 1.78 (dq, J = 9.9, 5.4, 4.6 Hz, 1H), 1.74 - 1.59 (m, 3H), 1.54 - 1.42 (m, 1H), 1.37 (td, J = 11.1, 10.6, 3.6 Hz, 1H). ¹³**C NMR** (100 MHz, CDCl₃) δ 146.7, 144.8, 129.3, 128.4, 128.3, 127.0, 123.4, 122.0, 116.8, 78.5, 63.9, 56.9, 44.6, 41.6, 30.2, 29.2, 24.9, 24.9, 23.4. **HRMS** (ESI) m/z Calcd for [C₂₀H₂₅BN₂O₂S, M + H]⁺: 368.1843; Found: 368.1845.

The title compound **19** was isolated as a yellow solid (85% yield) through flash chromatography on silica gel eluting with DCM/methanol (50:1). (Rf 0.4, DCM/methanol = 20:1). D-inc. >99% (determined by **1H NMR**). **1H NMR** (400 MHz, CDCl₃) δ 7.15 (m, 2H), 7.02 (d, J = 8.1 Hz, 1H), 6.93 (m, 1H), 6.91 - 6.81 (m, 3H), 3.93 (ddd, J = 14.0, 8.6, 5.4 Hz, 1H), 3.82 (ddd, J =

14.1, 8.9, 6.0 Hz, 1H), 2.86 (dt, J = 11.8, 4.1 Hz, 2H), 2.23 (s, 3H), 2.13 (dq, J = 8.7, 5.8 Hz, 3H), 1.89 (ddd, J = 11.8, 8.2, 5.3 Hz, 1H), 1.72 (dt, J = 13.9, 4.0 Hz, 2H), 1.61 (dq, J = 9.5, 5.3, 4.4 Hz, 2H), 1.25 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 146.7, 144.6, 133.4, 128.0, 127.7, 127.5, 125.2, 123.9, 123.0, 122.4, 116.0, 62.2, 56.9, 44.0, 42.9, 30.7, 29.8, 25.5, 24.1. **HRMS** (ESI) m/z Calcd for [C₂₁H₂₃D₃N₂SSeH, M + H]⁺: 422.1243; Found: 422.1245.

The title compound **21** was isolated as a yellow solid (89% yield) through flash chromatography on silica gel eluting with DCM/methanol (40:1). (Rf 0.5, DCM/methanol = 20:1). D-inc. >99% (determined by 1 H NMR). 1 H NMR (400 MHz, CDCl₃) δ 8.64 (s, 1H), 7.24 - 7.13 (m, 2H), 7.12 - 7.05 (m, 3H), 6.95 (m, 1H), 6.84 (d, J = 8.1 Hz, 1H),

4.19 - 4.12 (m, 1H), 4.12 - 4.02 (m, 2H), 3.21 (s, 2H), 2.76 (d, J = 7.3 Hz, 6H), 2.70 - 2.57 (m, 4H), 2.23 (s, 6H). ¹³C **NMR** (100 MHz, CDCl₃) δ 168.4, 156.0, 135.0, 133.6, 128.3, 128.3, 127.2, 126.7, 122.2, 122.0, 111.7, 71.1, 65.9, 61.6, 60.7, 53.7, 53.6, 18.7. **HRMS** (ESI) m/z Calcd for [C₂₄H₃₀D₃N₃O₃SeNa, M + Na]⁺: 517.1768; Found: 517.1771.

8. Mechanism study Difunctionalized Reactions of Se-methyl-d₃ Reagents

with Olefins via Pr-Catalysis

8.1 Radical Trapping Experiments

General procedure: To a three-port flask containing TsSeCD₃ (0.24 mmol, 1.2 equiv.), Pr(OTf)₃ (0.02 mmol, 10 mol%), **L**₁ (0.02 mmol, 10 mol%), stilbene or THB (0.4 mmol, 2.0 equiv.) in MeCN (0.5 mL) were added styrene (0.2 mmol, 1.0 equiv.), the mixture stirred at 50 °C for 12 h. The product 5**a** was obtained with 81% yield via column chromatography, no radical capture products were detected.

8.2 Cation Capture Experiments

General procedure: To a three-port flask containing TsSeCD₃ (0.24 mmol, 1.2 equiv.), Pr(OTf)₃ (0.02 mmol, 10 mol%), **L**₁ (0.02 mmol, 10 mol%), EtOH (2.0 mmol, 10 equiv.) in MeCN (0.5 mL) were added styrene (0.2 mmol, 1.0 equiv.), the mixture stirred at 50 °C for 12 h. The product **5a** was obtained with 50% yield via column chromatography, the product **SI-31** was obtained with 41% yield via column chromatography.

Ts
$$\frac{\text{Pr(OTf)}_3 (10 \text{ mol\%})}{\text{L } (10 \text{ mol\%})}$$
 $\frac{\text{L } (10 \text{ mol\%})}{\text{MeCN, } 50 \text{ °C, } 12 \text{ h}}$ $\frac{\text{OEt}}{\text{SeCD}_3}$ $\frac{\text{SI-29} (\text{n.d.})}{\text{SI-29} (\text{n.d.})}$

General procedure: To a dry Schlenk tube containing EtOH (2.0 mmol, 10 equiv.), Pr(OTf)₃ (0.02 mmol, 10 mol%), **L**₁ (0.02 mmol, 10 mol%), in MeCN (0.5 mL) were added **5a** (0.2 mmol, 1.0 equiv.), the mixture was stirred at 50 °C for 12 h. After the reaction was complete, the reaction was quenched with water, the organic layer was then extracted with dichloromethane, washed with brine, dried over anhydrous Na₂SO₄. The result after reaction was tested by GC-MS.

8.3 Olefins Isomerization Experiments

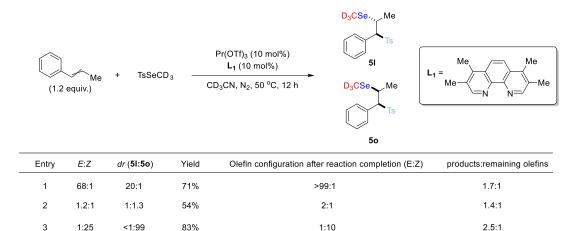
Supplementary Table 5. Olefins Isomerization Experiments

General procedure: To a dry Schlenk tube containing $Pr(OTf)_3$ (0.02 mmol, 10 mol%), L_1 or L_2 (0.02 mmol, 10 mol%), in CD_3CN (0.4 mL) were added styrene (0.2 mmol, 1.0 equiv.), the mixture stirred at 50 °C for 12 h. After the reaction was complete, the reaction system was filtered. The olefin configuration after reaction was tested through in-situ NMR.

^a Pr(OTf)₃ (10 mol%), **L**₁ (10 mol%)

8.4 Mechanism Verification Experiments 15,16,17

Supplementary Table 6. Mechanism Verification Experiments-1



General procedure: To a dry Schlenk tube containing TsSeCD₃ (0.24 mmol, 1.2 equiv.), Pr(OTf)₃ (0.02 mmol, 10 mol%), **L**₁ (0.02 mmol, 10 mol%), in CD₃CN (0.4 mL) were added styrene (0.2 mmol, 1.0 equiv.), the mixture stirred at 50 °C for 12 h. After the reaction was complete, the reaction system was filtered and the product was obtained via column chromatography. The remaining olefin configuration after reaction was tested through in-situ ¹H NMR.

Supplementary Table 7. Mechanism Verification Experiments-2

Entry	E:Z	dr (51:50)	Yield	Olefin configuration after reaction completion (E:Z)	products:remaining olefins
1	68:1	20:1	44%	36:1	1:1.45
2	1.2:1	1:1.3	27%	1.52:1	1:1.6
3	1:25	<1:99	50%	1:24	1:1

General procedure: To a dry Schlenk tube containing TsSeCD₃ (0.24 mmol, 1.2 equiv.), Pr(OTf)₃ (0.04 mmol, 20 mol%), **L**₂ (0.04 mmol, 20 mol%), in CD₃CN (0.4 mL) were added styrene (0.2 mmol, 1.0 equiv.), the mixture stirred at 50 °C for 12 h. After the reaction was complete, the reaction system was filtered and the product was obtained via column chromatography. The remaining olefin configuration after reaction was tested through in-situ ¹H NMR.

Supplementary Table 8. Mechanism Verification Experiments-3

Entry	E:Z	dr (5p:5q)	Yield	Olefin configuration after reaction completion (E:Z)	Products:Remaining olefins
1	25:1	25:1	46%	18.83:1	1:1.19
2	1.73:1	1:1.85	48%	6.67:1	1.49:1
3	1:25	<1:99	58%	1:5	1.52:1

General procedure: To a dry Schlenk tube containing TsSeCD₃ (0.24 mmol, 1.2 equiv.), Pr(OTf)₃ (0.04 mmol, 20 mol%), **L**₂ (0.04 mmol, 20 mol%), in CD₃CN (0.4 mL) were added styrene (0.2 mmol, 1.0 equiv.), the mixture stirred at 50 °C for 12 h.

After the reaction was complete, the reaction system was filtered and the product was obtained via column chromatography. The remaining olefin configuration after reaction was tested through in-situ ¹H NMR.

Supplementary Table 9. Mechanism Verification Experiments-4

Entry	E:Z	dr (5r [,] :5r)	Yield	Olefin configuration after reaction completion (E:Z)	products:remaining olefins
1	30:1	2:1	36%	57.5:1	1:2.57
2	1:2	1:10	53%	2.38:1	1.54:1
3	1:12.5	1:20	74%	1:4.5	3.03:1

General procedure: To a dry Schlenk tube containing TsSeCD₃ (0.24 mmol, 1.2 equiv.), Pr(OTf)₃ (0.04 mmol, 20 mol%), **L**₉ (0.04 mmol, 10 mol%), in CD₃CN (0.4 mL) were added styrene (0.2 mmol, 1.0 equiv.), the mixture stirred at 50 °C for 12 h. After the reaction was complete, the reaction system was filtered and the product was obtained via column chromatography. The remaining olefin configuration after reaction was tested through in-situ ¹H NMR.

8.5 Characterization of Products.

The title compound **SI-29** was isolated as a colorless oil (41% yield) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.4, petroleum ether). Dinc. >99% (determined by ¹H NMR). ¹H NMR (400 MHz,

CDCl₃) δ 7.45 - 6.99 (m, 5H), 4.36 (dd, J = 7.8, 5.6 Hz, 1H), 3.31 (dd, J = 7.0, 3.8 Hz, 2H), 2.88 (dd, J = 12.5, 7.9 Hz, 1H), 2.63 (dd, J = 12.6, 5.6 Hz, 1H), 1.11 (t, J = 7.1 Hz, 3H). ¹³C **NMR** (100 MHz, CDCl₃) δ 141.9, 128.4, 127.8, 126.6, 82.6, 64.5, 32.7,

15.3. **HRMS** (ESI) m/z Calcd for $[C_{11}H_{13}D_3OSeK, M + K]^+$: 286.0816.0328; Found: 286.0816.

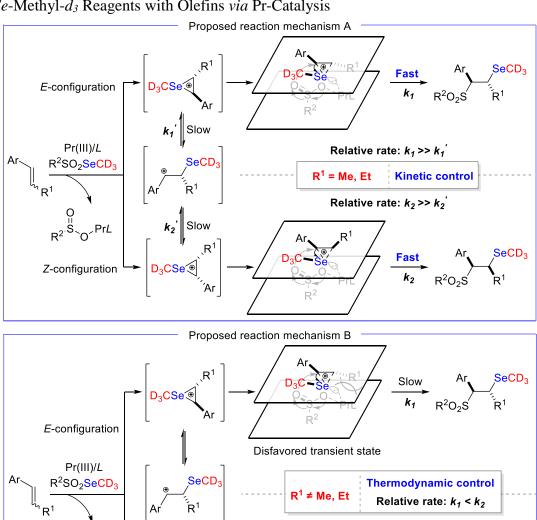
8.6 Proposed Mechanisms of Difunctionalized Reactions of Se-methyl- d_3 Reagents with Olefins via Pr-Catalysis

To elucidate the mechanistic details of the lanthanides-catalyzed difunctionalization, a series of control experiments were carried out (see the Supplementary 8.1 & 8.2 for details). At first, radical trapping reagents, such as stilbene and BHT, were introduced into the reaction under standard conditions, without altering the course of the transformation (see the Supplementary 8.2 for details). These results excluded the possibility of a radical reaction route. Secondly, upon the addition of ten equivalents of ethanol to the standard reaction mixture, the ethoxy-substituted compound SI-30 was obtained with 41% yield, accompanied by the generation of **5a** with 50% yield (see the Supplementary 8.2 for details). Furthermore, the product 5a could not be transformed to SI-30 with ethanol as nucleophile under the standard conditions. These results indicated the possible mechanism involved a cationic reaction route. Subsequent experiments on olefin isomerization indicated that all different kinds of olefins would not undergo isomerization (see the Supplementary 8.2 for details).

Due to different structural configurations of the products (eg: **51**, **50**, and **5am**) obtained from various alkenes, we believe that there might be multiple reaction routes involved. To further illuminate the stereoselectivity of the reaction, the E- β -methylstyrene (E:Z=68:1), mixed (E/Z)- β -methylstyrenes (E:Z=1.2:1), and Z- β -methylstyrene (E:Z=1:25) were subjected to their respective transformations, in which \mathbf{L}_1 was employed as ligand, and acetonitrile- d_3 was used as the solvent instead of acetonitrile (see the Supplementary Table **6** for details). As a result, the E- β -methylstyrene and Z- β -methylstyrene each converted to its respective product **51** (77% yield, 20:1 dr) and **50** (83% yield, >99:1 dr) with excellent dr value, and the olefin residues maintained their original configurations at a high ratio. Mixed β -

methylstyrenes with an E/Z ratio of 1.25:1 would transform to a mixture of 51 and 50 in 54% yield with a ratio of 1:1.3, while the ratio of the olefin residues reached a ratio of 2:1. Given that the two configurations of olefins do not convert into each other, these results revealed that the stereochemistry of the product depends on the configuration of the parent alkene, and the reaction rate of Z- β -methylstyrenes is faster than that of E-isomer. To validate these findings, the $E-\beta$ -methylstyrene, mixed (E/Z)- β -methylstyrenes, and Z- β -methylstyrene were each utilized individually in their respective reactions, with L2 being changed as the ligand (see the Supplementary Table 7 for details). Besides the reaction yields, the outcomes of the reactions with the three olefin types, encompassing both product configurations and the remaining unreacted olefin geometries, aligned closely with those previously obtained utilizing ligand L₁. These further confirmed that the diffunctionalization of β -methylstyrenes might be determined by the intrinsic properties of the substrate. Further experiments indicated that β -ethylstyrenes exhibit reaction characteristics akin to those observed for β -methylstyrenes (see the Supplementary Table 8 for details). When the alkenes bearing carbon chains extending beyond β -ethylstyrenes were employed, the reaction pathway might differ, due to our observation that mixture olefins predominantly produce one specific diastereoisomer as the predominant product (Figure 6, 5r, 5s and **5t**). Likewise, the *E-\beta-n*-propylstyrene (E:Z=30:1), mixed (E/Z)- β -n-propylstyrenes (E:Z = 1:2), and β -n-propylstyrene (Z:E = 12.5:1) with a high Z-ratio were successively loaded into this transformation process by using L₂ as ligand (see the Supplementary Table 8 for details). Resultantly, the β -n-propylstyrene with a high Zratio generated $5\mathbf{r}$ as the major product in 74% yield with excellent dr value (20:1 dr), and the configuration ratio of the olefin residue was decreased to 4.5:1 (Z/E). Mixed β -n-propylstyrene with an E/Z ratio of 1:2 would form **5r** in 53% yield with high dr value, while the ratio of the olefin residues was changed to 2.38:1 (E/Z). The $E-\beta-n$ propylstyrene was transformed to the product 5r with low efficiency (36% yield) and poor dr value (2:1 dr), while the configuration ratio of the olefin residue was increased to 57.5:1 (E/Z). Given that the two configurations of olefins do not convert into each other, these experiments demonstrated that they might produce interconvertible intermediates throughout the difunctionalized process, and that the reactivity of $Z-\beta-n$ -propylstyrene is higher than the $E-\beta-n$ -propylstyrene.

Supplementary Figure 1. Proposed Mechanisms of Difunctionalized Reactions of *Se*-Methyl-*d*₃ Reagents with Olefins *via* Pr-Catalysis



Based on experiments and literature precedents, tentative mechanisms to elucidate the stereoselectivity of the difunctionalizations were proposed. First, benzenesulfono selenoate was activated by Lewis acid $Pr(OTf)_3$, and then reacted with a β -alkylstyrene to generate a selenonium ion with specific configuration from

Z-configuration

Favored transient state

Fast

 R^2O_2S

Major Product

SeCD₃

the related styrene. When the β -alkyl-styrenes (alkyl = Me and Et) with minimal steric hindrance were used as substrates, the transformation is likely a kinetically controlled process, meaning that the reaction rate at which sulfinate attacks selenonium ions to yield the corresponding products is significantly greater than the rate of interconversion among selenonium ions. Therefore, the difunctionalization of E- or Zolefin results in the selective synthesis of the desired products with distinct configuration (see the Supplementary Figure 1 proposed reactions mechanism a for details). When the β -alkyl-styrenes (alkyl \neq Me and Et) exhibiting enhanced steric bulk were used as substrates, the selenonium ions formed from the E- or Z-olefin can be interconvertible as well, and the configuration of the desired product was determined by the thermodynamic process that sulfinate prefers to attack the selenonium ion yielding from Z-olefin which contains smaller steric hindrance. Therefore, Z-olefin can obtain the desired product with single configuration in high efficiency, and mixed olefin produce the product with high diastereoselectivity, while E-olefin obtains the target product in poor yield and low diastereoselectivity (see the Supplementary Figure 1 proposed reactions mechanism **b** for details).

9. References

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10. X-ray Crystallography Analysis

Supplementary Figure 2. Single-Crystal X-ray Crystallography of **5ak** (CCDC 2355211)



checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

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Hall group	-P 2ybc	-P 2ybc			
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Dx,g cm-3	1.495	1.495			
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Mu (mm-1)	2.636	2.636			
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F000'	822.15				
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The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

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Alert level G

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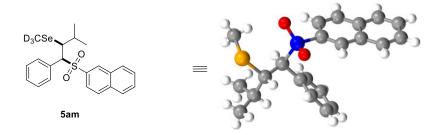
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PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large

Please Check 5.20 Why ?

- O ALERT level A Most likely a serious problem resolve or explain
- O ALERT level B A potentially serious problem, consider carefully 2 ALERT level C Check. Ensure it is not caused by an omission or oversight
- 3 ALERT level G General information/check it is not something unexpected
- 2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
- 2 ALERT type 2 Indicator that the structure model may be wrong or deficient 1 ALERT type 3 Indicator that the structure quality may be low
- O ALERT type 4 Improvement, methodology, query or suggestion O ALERT type 5 Informative message, check

Supplementary Figure 3. Single-Crystal X-ray Crystallography of **5am** (CCDC 2385432)



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You have not supplied any structure factors. As a result the full set of tests cannot be run.

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Hall group	P 2ac 2ab	P 2ac 2ab	
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Sum formula	C22 H24 O2 S Se	C22 H24 C	02 S Se
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Dx,g cm-3	1.441	1.440	
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F000'	886.25		
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Alert level B

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Author Response: Low data quality.

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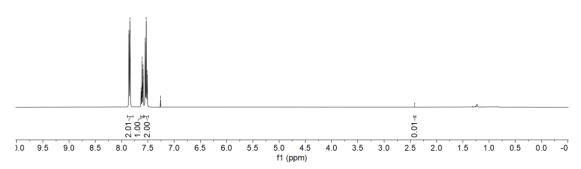
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0 ALERT level A = Most likely a serious problem - resolve or explain
1 ALERT level B = A potentially serious problem, consider carefully
8 ALERT level C = Check. Ensure it is not caused by an omission or oversight
7 ALERT level G = General information/check it is not something unexpected
3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
3 ALERT type 2 Indicator that the structure model may be wrong or deficient 3 ALERT type 3 Indicator that the structure quality may be low
A ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check
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11. ¹H, ¹³C, ¹⁹F, ³¹P, ²H Spectrum of Compounds

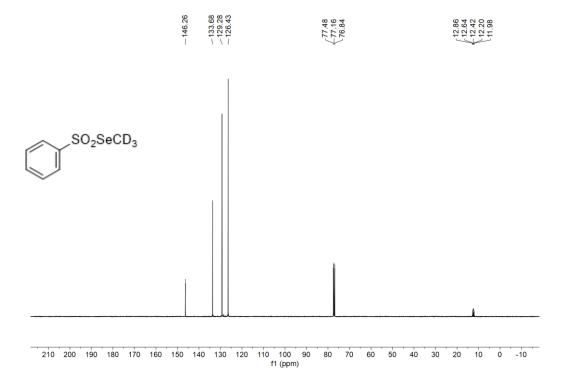
11.1 NMR Spectra of Deuterated Methylselenylating Reagents

Supplementary Figure 4. ¹H NMR Spectrum of 1a (400 MHz, CDCl₃)

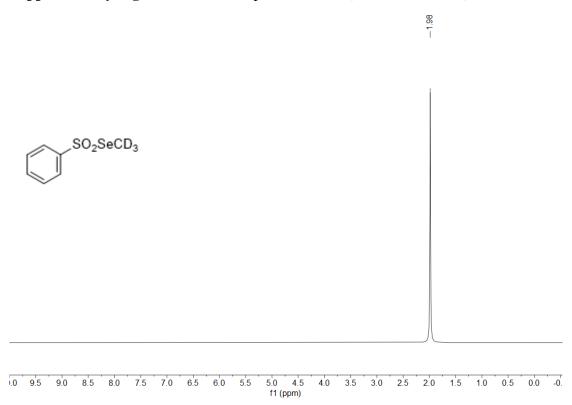
SO₂SeCD₃



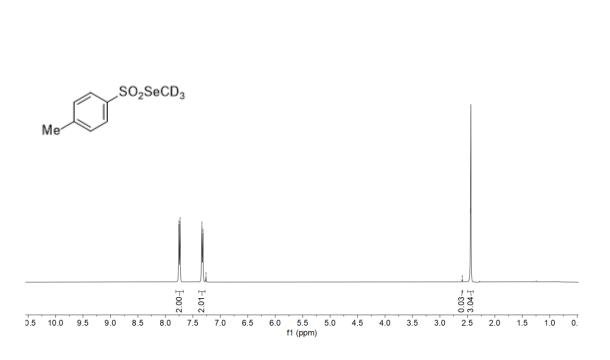
Supplementary Figure 5. ¹³C NMR Spectrum of 1a (100 MHz, CDCl₃)



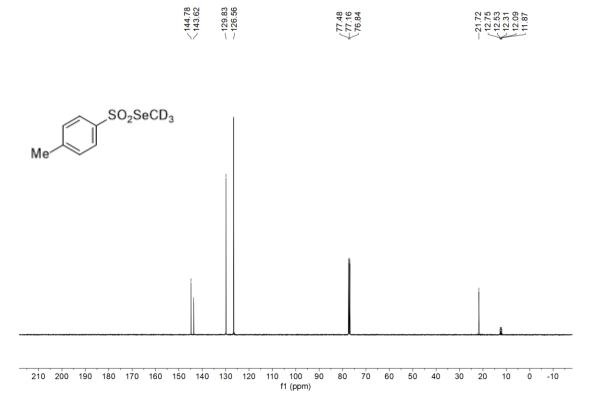




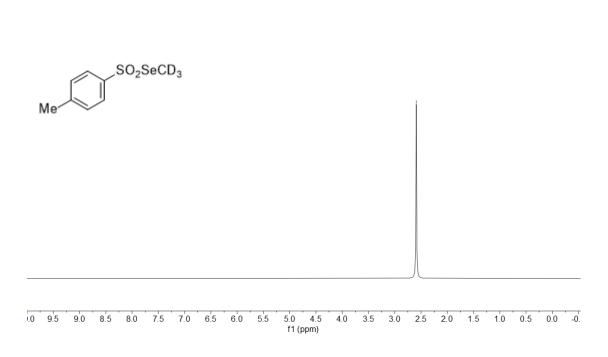
Supplementary Figure 7. ¹H NMR Spectrum of 1b (400 MHz, CDCl₃)



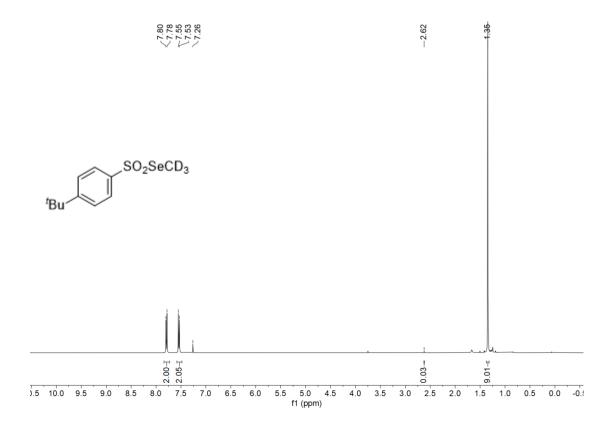
Supplementary Figure 8. ¹³C NMR Spectrum of 1b (100 MHz, CDCl₃)



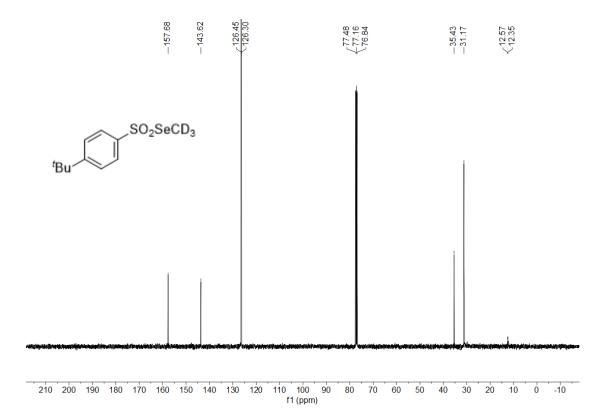
Supplementary Figure 9. ²H NMR Spectrum of 1b (100 MHz, CHCl₃)



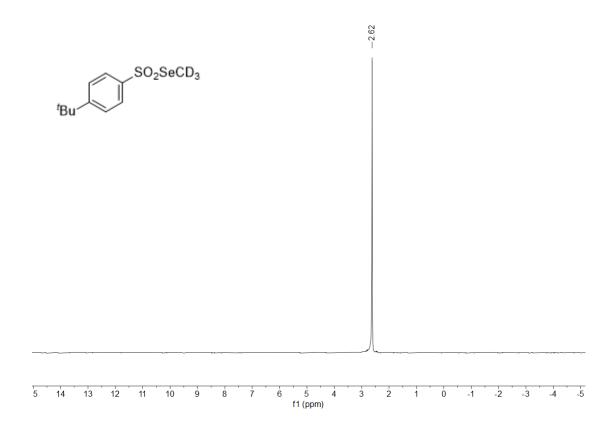
Supplementary Figure 10. ¹H NMR Spectrum of 1c (400 MHz, CDCl₃)



Supplementary Figure 11. ¹³C NMR Spectrum of 1c (100 MHz, CDCl₃)

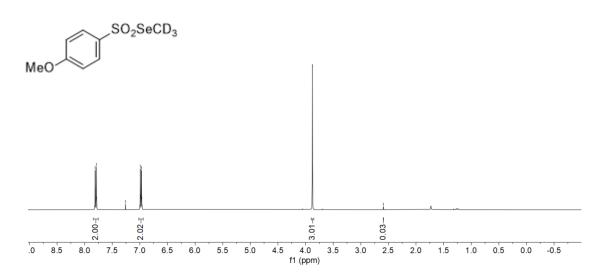


Supplementary Figure 12. ²H NMR Spectrum of 1c (100 MHz, CHCl₃)

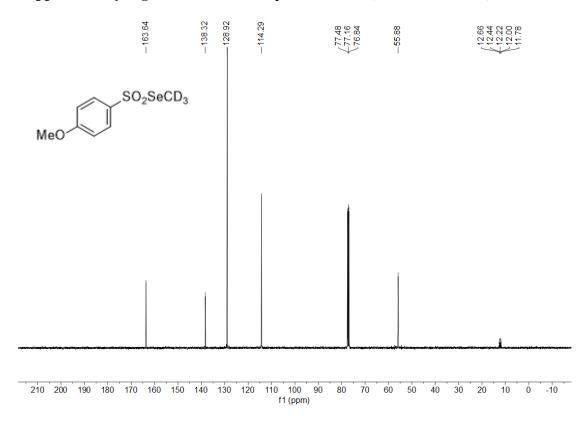


Supplementary Figure 13. ¹H NMR Spectrum of 1d (400 MHz, CDCl₃)

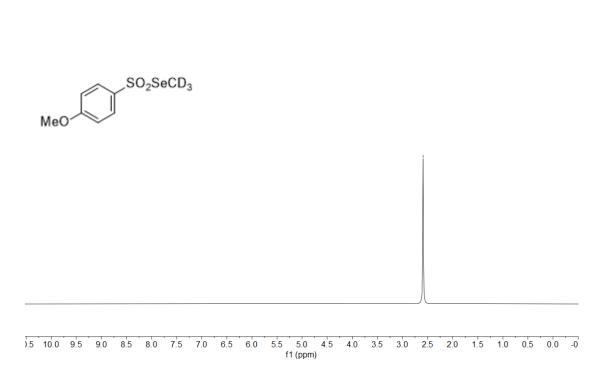




Supplementary Figure 14. ¹³C NMR Spectrum of **1d** (100 MHz, CDCl₃)

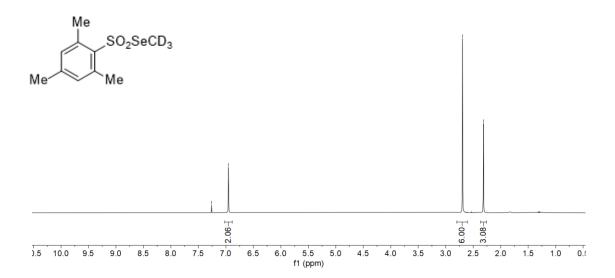


Supplementary Figure 15. ²H NMR Spectrum of 1d (100 MHz, CHCl₃)

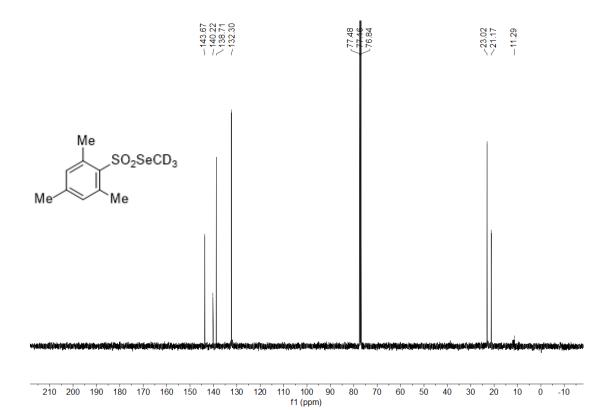


Supplementary Figure 16. ¹H NMR Spectrum of 1e (400 MHz, CDCl₃)



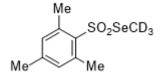


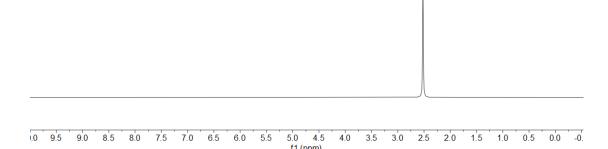
Supplementary Figure 17. ¹³C NMR Spectrum of **1e** (100 MHz, CDCl₃)



Supplementary Figure 18. ²H NMR Spectrum of 1e (100 MHz, CHCl₃)



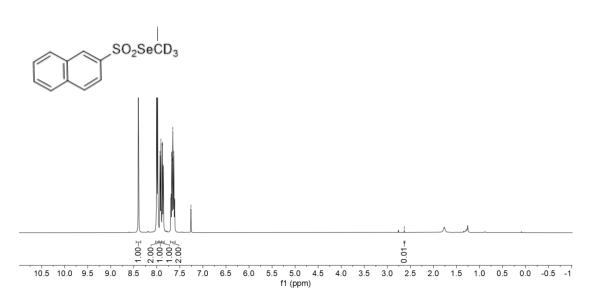




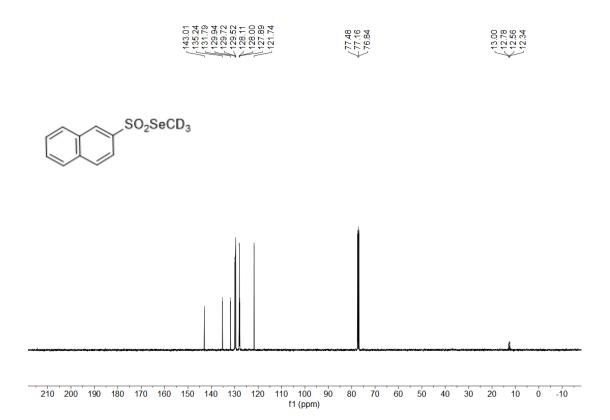
Supplementary Figure 19. ¹H NMR Spectrum of 1f (400 MHz, CDCl₃)

8.40 -8.40 -8.40 -8.40 -7.93 -7.93 -7.93 -7.93 -7.93 -7.93 -7.63 -7.63 -7.65 -7.

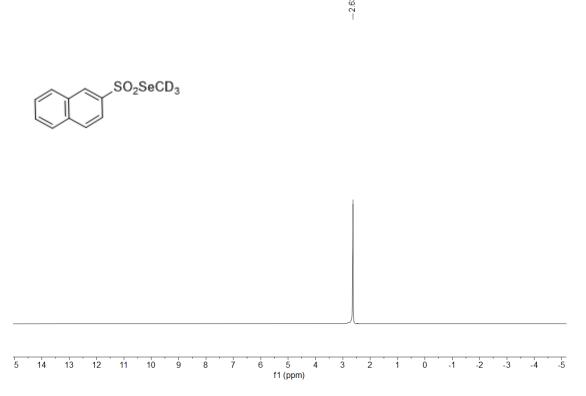
2.63



Supplementary Figure 20. ¹³C NMR Spectrum of 1f (400 MHz, CDCl₃)

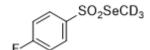


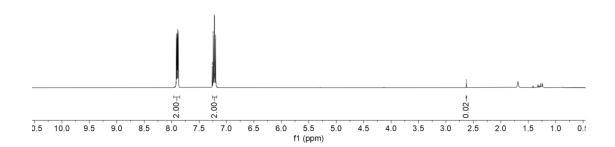
Supplementary Figure 21. ²H NMR Spectrum of 1f (100 MHz, CHCl₃)



Supplementary Figure 22. ¹H NMR Spectrum of 1g (400 MHz, CDCl₃)

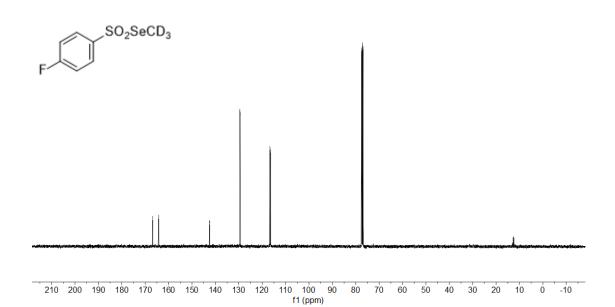






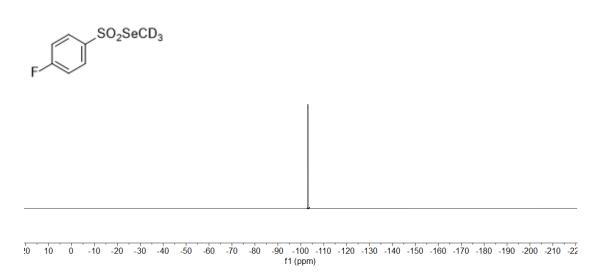
Supplementary Figure 23. ¹³C NMR Spectrum of 1g (100 MHz, CDCl₃)





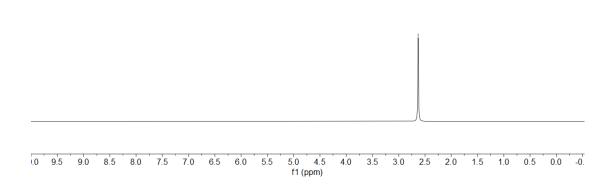






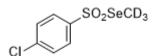
Supplementary Figure 25. ²H NMR Spectrum of 1g (100 MHz, CHCl₃)

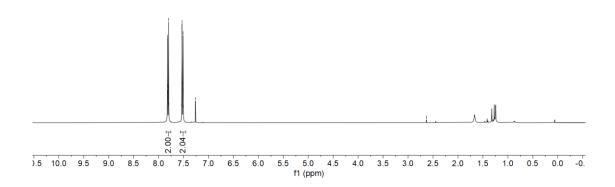
2 63



Supplementary Figure 26. ¹H NMR Spectrum of 1h (400 MHz, CDCl₃)

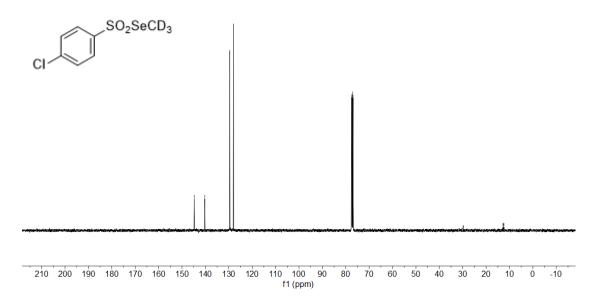






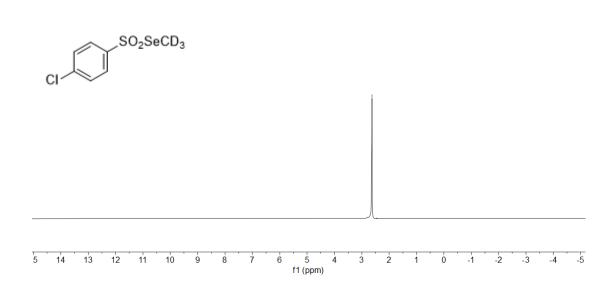
Supplementary Figure 27. ¹³C NMR Spectrum of 1h (100 MHz, CDCl₃)

77.7.48 77.7.48 77.1.68 77.1.68 77.1.16 77.1.16 77.1.16 77.1.16 77.1.16 77.1.16 77.1.16



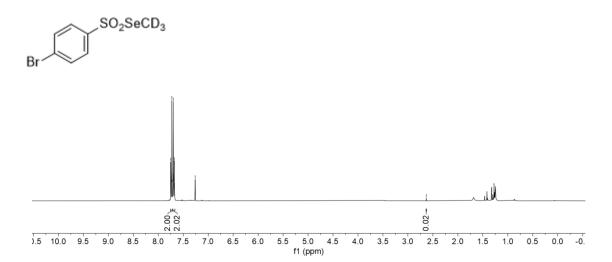
Supplementary Figure 28. ²H NMR Spectrum of 1h (100 MHz, CHCl₃)





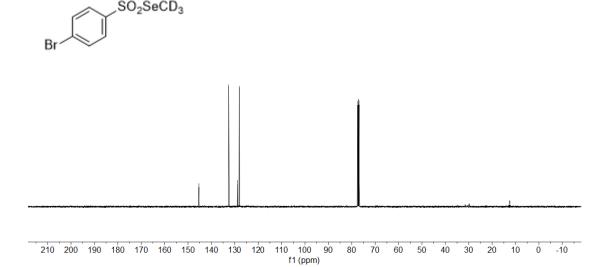
Supplementary Figure 29. ¹H NMR Spectrum of 1i (400 MHz, CDCl₃)





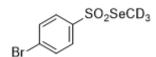
Supplementary Figure 30. ¹³C NMR Spectrum of 1i (100 MHz, CDCl₃)

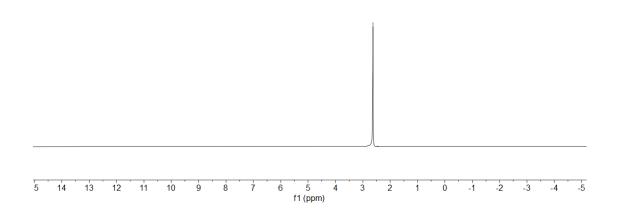




Supplementary Figure 31. ²H NMR Spectrum of 1i (100 MHz, CHCl₃)

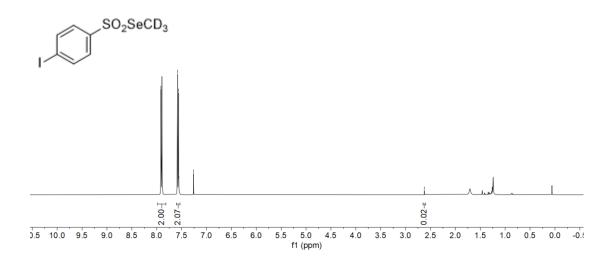






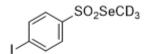
Supplementary Figure 32. ¹H NMR Spectrum of 1j (400 MHz, CDCl₃)

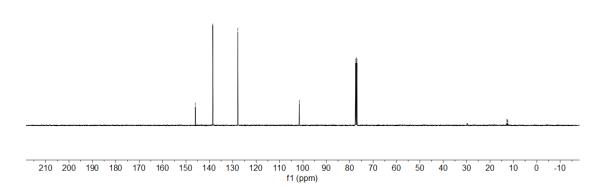




Supplementary Figure 33. ¹³C NMR Spectrum of 1j (100 MHz, CDCl₃)

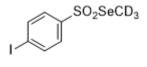
- 145.99 - 138.55 - 127.83 - 101.53 - 12.83 - 12.83 - 12.83

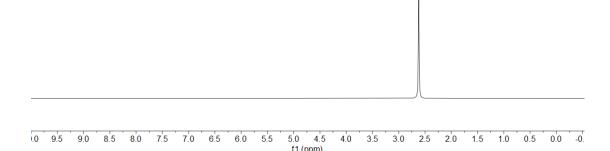




Supplementary Figure 34. ²H NMR Spectrum of 1j (100 MHz, CHCl₃)



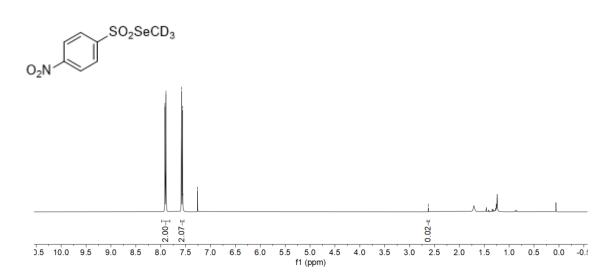




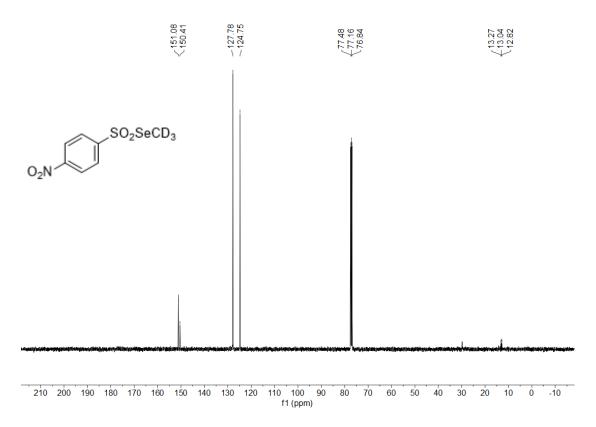
Supplementary Figure 35. ¹H NMR Spectrum of 1k (400 MHz, CDCl₃)

7.92

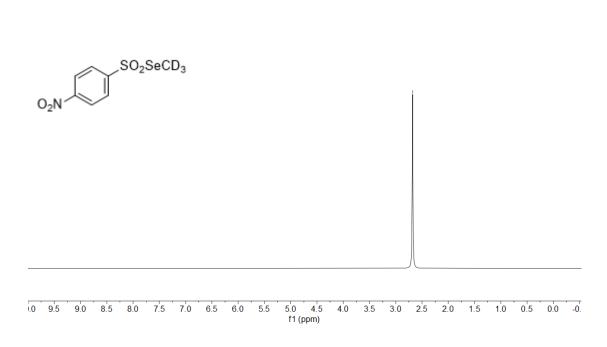




Supplementary Figure 36. ¹³C NMR Spectrum of 1k (100 MHz, CDCl₃)

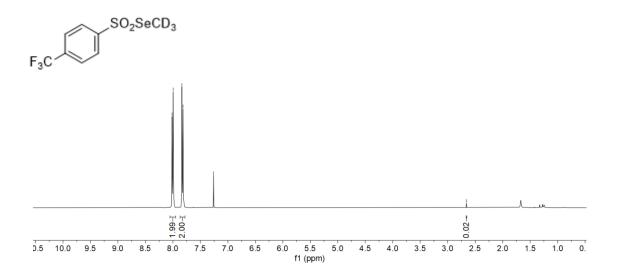


Supplementary Figure 37. ²H NMR Spectrum of 1k (100 MHz, CHCl₃)



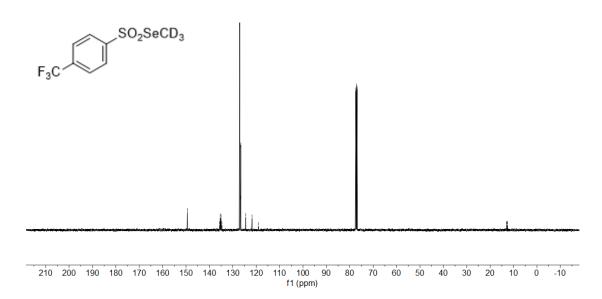
Supplementary Figure 38. ¹H NMR Spectrum of 11 (400 MHz, CDCl₃)



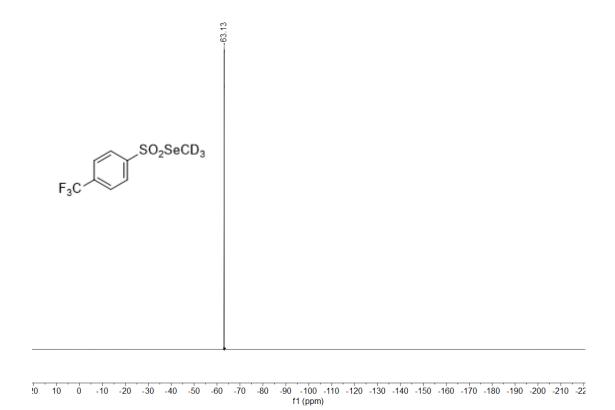


Supplementary Figure 39. ¹³C NMR Spectrum of 11 (100 MHz, CDCl₃)

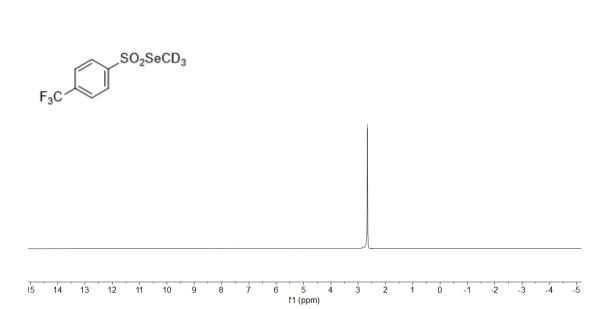




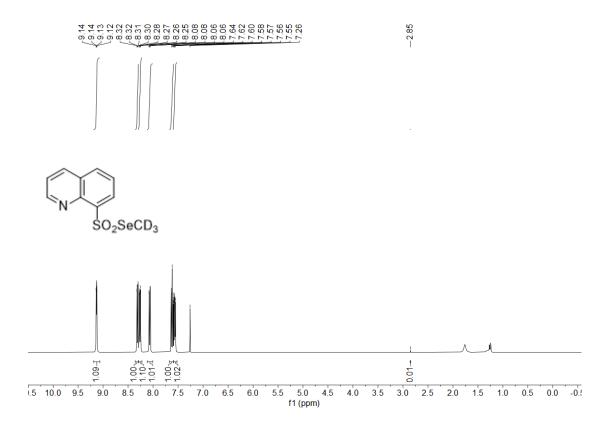
Supplementary Figure 40. ¹⁹F NMR Spectrum of 11 (376 MHz, CDCl₃)



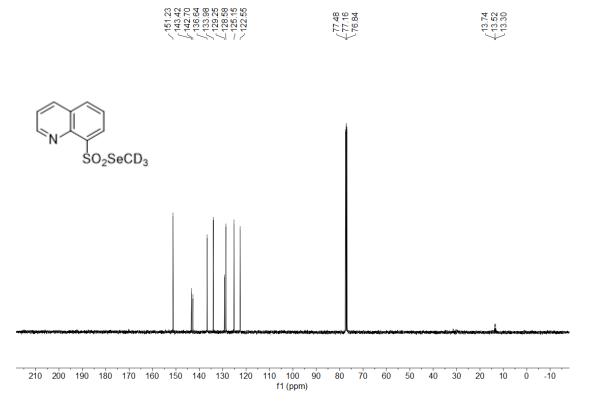
Supplementary Figure 41. ²H NMR Spectrum of 11 (100 MHz, CHCl₃)



Supplementary Figure 42. ¹H NMR Spectrum of 1m (400 MHz, CDCl₃)

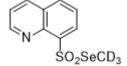


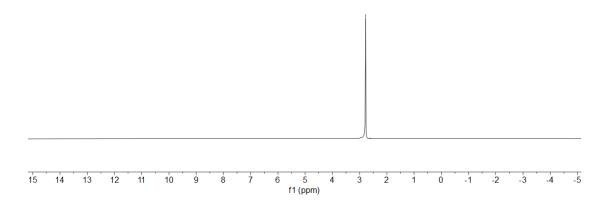
Supplementary Figure 43. ¹³C NMR Spectrum of 1m (100 MHz, CDCl₃)



Supplementary Figure 44. ²H NMR Spectrum of 1m (100 MHz, CHCl₃)

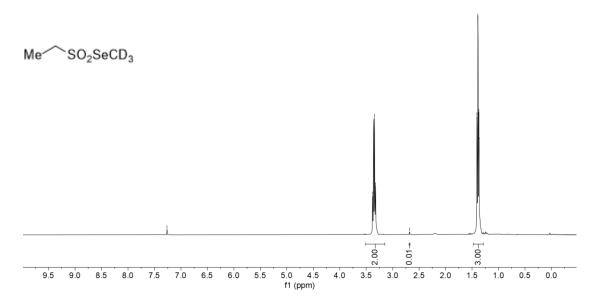




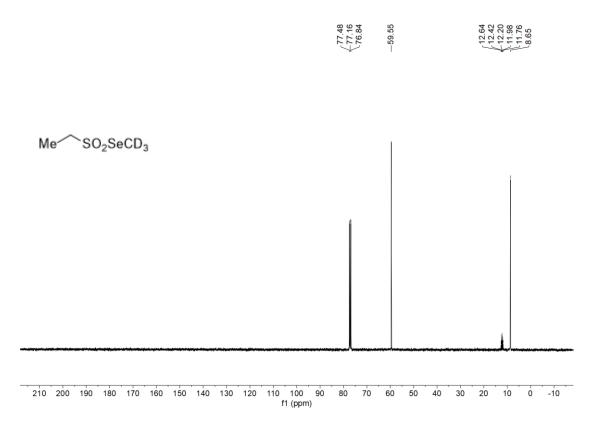


Supplementary Figure 45. ¹H NMR Spectrum of 1n (400 MHz, CDCl₃)

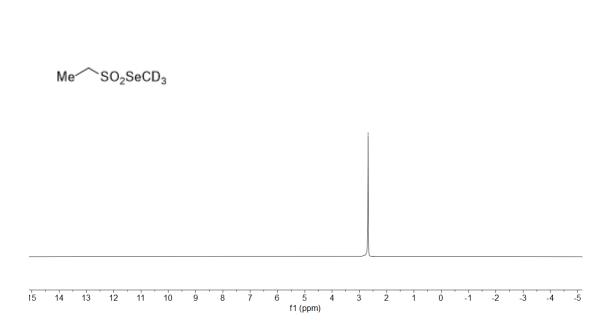
-7.26 3.38 -2.68 2.14 -1.41



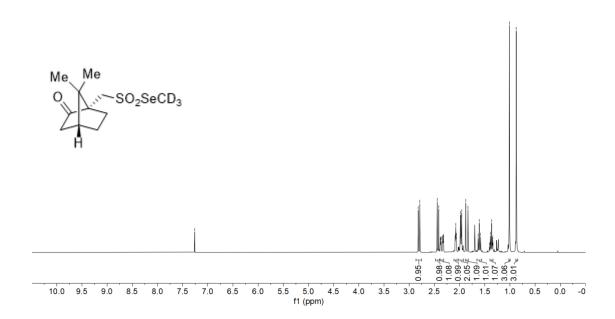
Supplementary Figure 46. ¹³C NMR Spectrum of 1n (100 MHz, CDCl₃)



Supplementary Figure 47. ²H NMR Spectrum of 1n (100 MHz, CHCl₃)



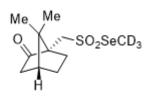
Supplementary Figure 48. ¹H NMR Spectrum of 10 (400 MHz, CDCl₃)

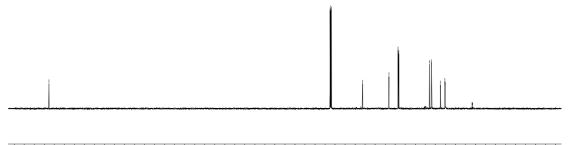


Supplementary Figure 49. ¹³C NMR Spectrum of 10 (100 MHz, CDCl₃)

-217.69

77.48 77.16 76.84 —61.32 —61.32 43.55 43.55 43.55 43.55 43.55 22.39 22.39 22.39 22.39 22.39 66.79 66.28

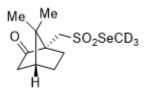


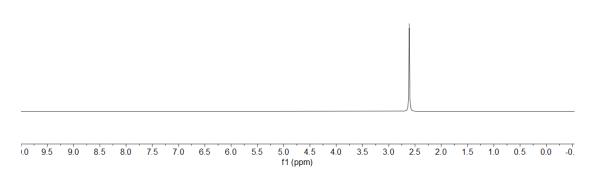


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 f1 (ppm)

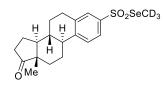
Supplementary Figure 50. ²H NMR Spectrum of 10 (100 MHz, CHCl₃)

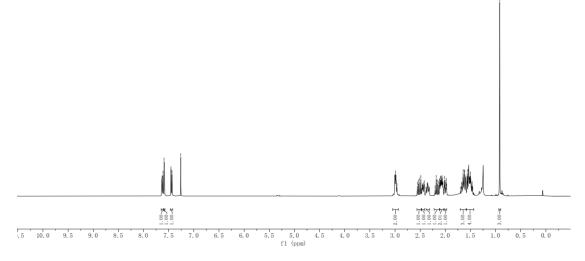
-2.61



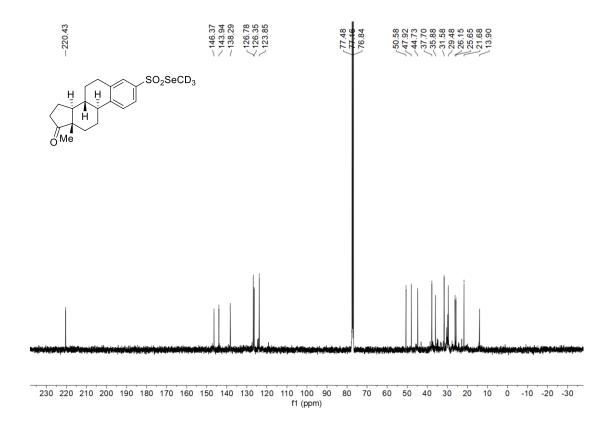


Supplementary Figure 51. 1 H NMR Spectrum of 1p (100 MHz, CDCl₃)

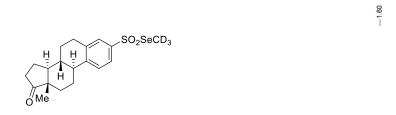


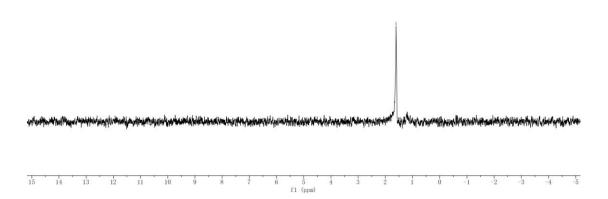


Supplementary Figure 52. ¹³H NMR Spectrum of 1p (100 MHz, CDCl₃)



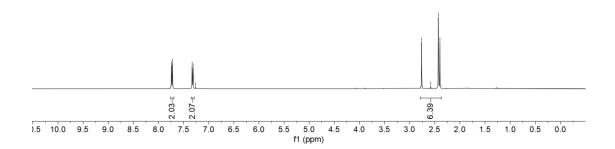
Supplementary Figure 53. ²H NMR Spectrum of 1p (100 MHz, CHCl₃)



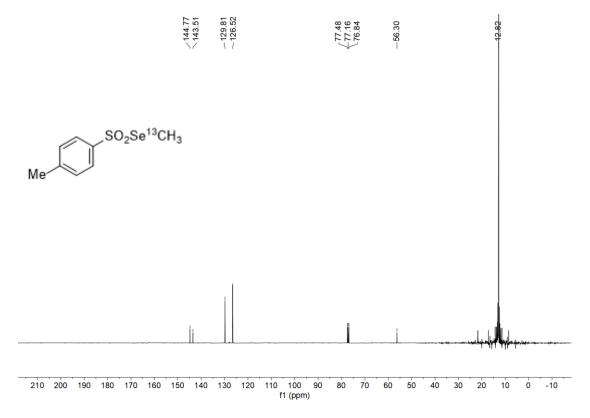


Supplementary Figure 54. ¹H NMR Spectrum of 1q (400 MHz, CDCl₃)



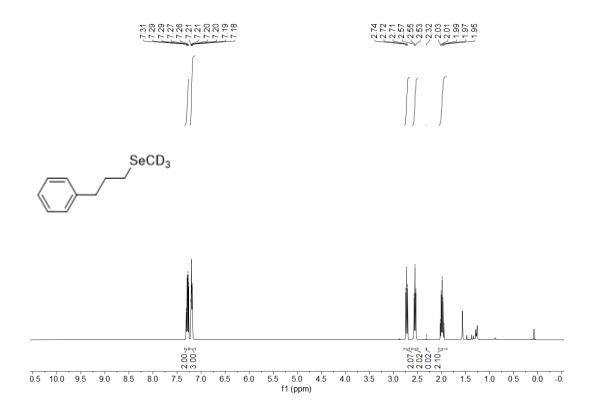


Supplementary Figure 55. ¹³C NMR Spectrum of 1q (100 MHz, CDCl₃)

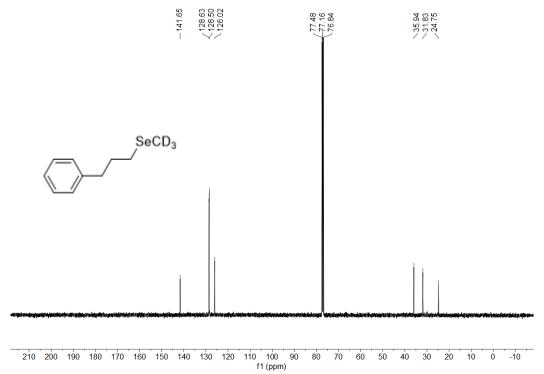


11.2 NMR Spectra of Deuterated Selenomethylation Products

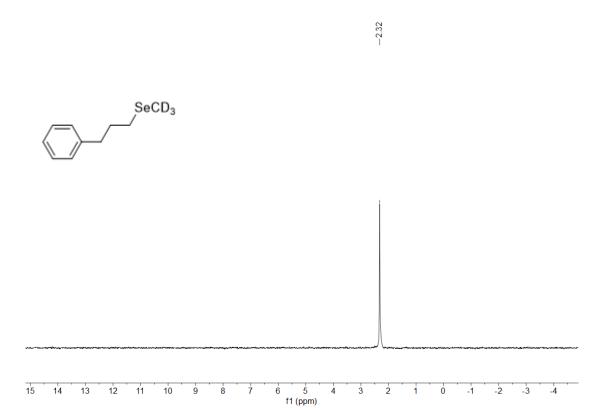
Supplementary Figure 56. ¹H NMR Spectrum of 2a (400 MHz, CDCl₃)



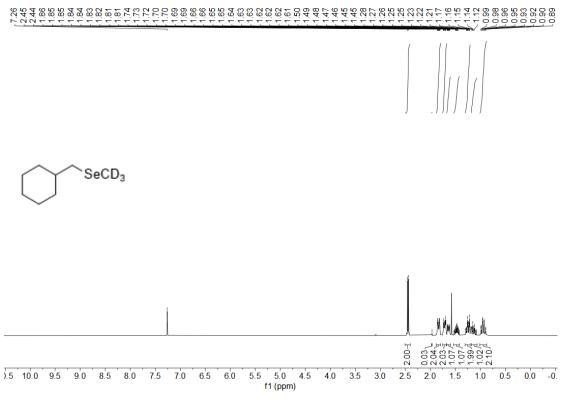
Supplementary Figure 57. ¹³C NMR Spectrum of 2a (100 MHz, CDCl₃)



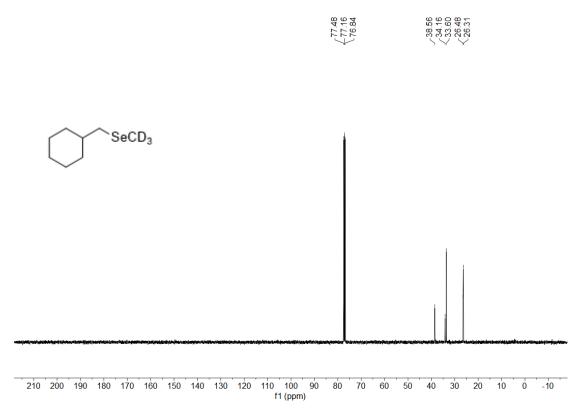
Supplementary Figure 58. ²H NMR Spectrum of 2a (100 MHz, CHCl₃)



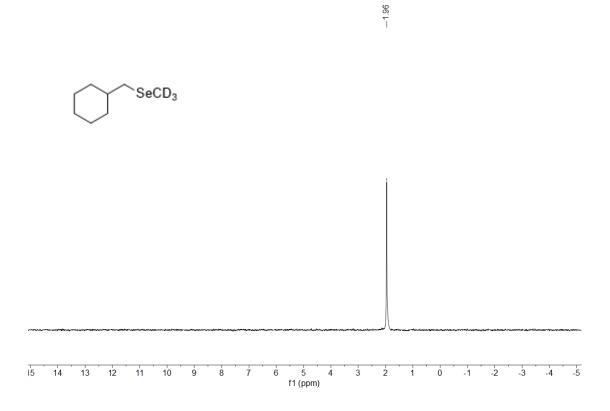
Supplementary Figure 59. ¹H NMR Spectrum of 2b (400 MHz, CDCl₃)



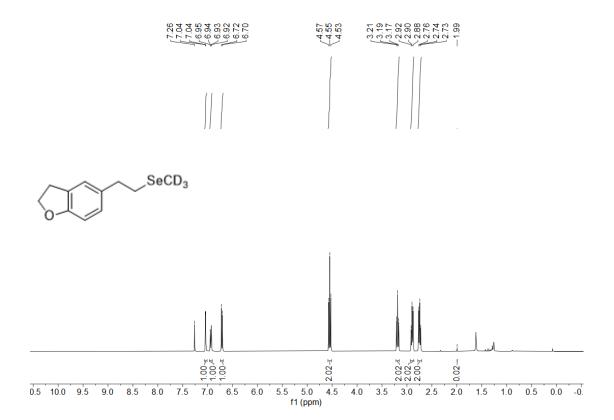
Supplementary Figure 60. ¹³C NMR Spectrum of **2b** (100 MHz, CDCl₃)



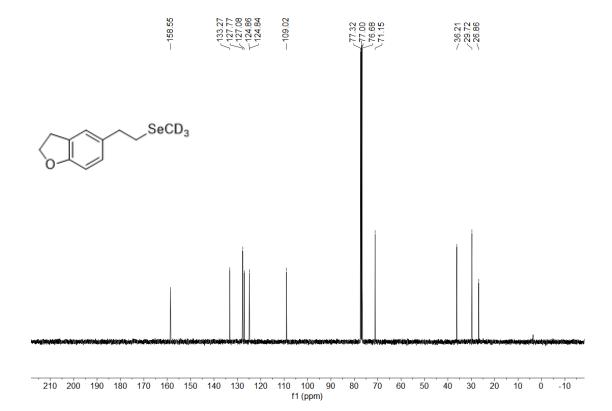
Supplementary Figure 61. ²H NMR Spectrum of 2b (100 MHz, CHCl₃)



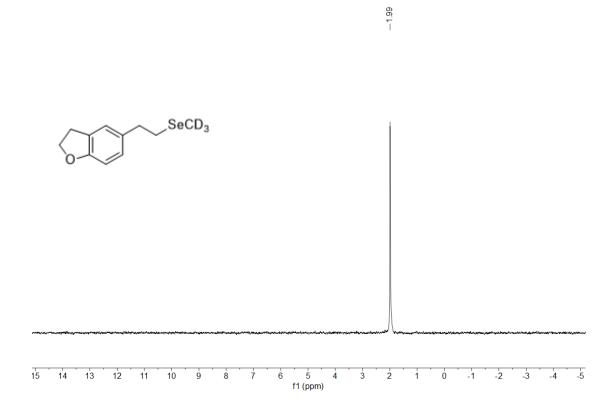
Supplementary Figure 62. ¹H NMR Spectrum of 2c (400 MHz, CDCl₃)



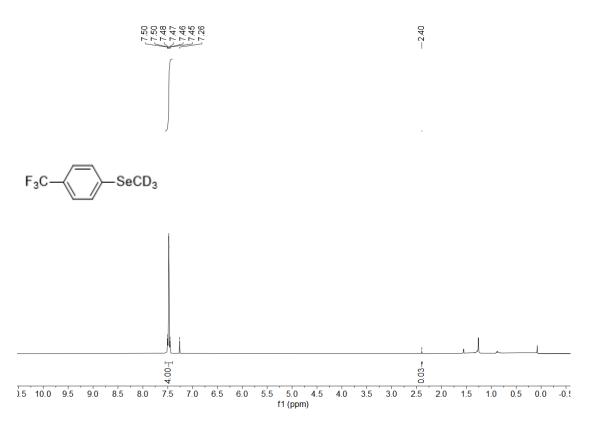
Supplementary Figure 63. ¹³C NMR Spectrum of 2c (100 MHz, CDCl₃)



Supplementary Figure 64. ²H NMR Spectrum of 2c (100 MHz, CHCl₃)

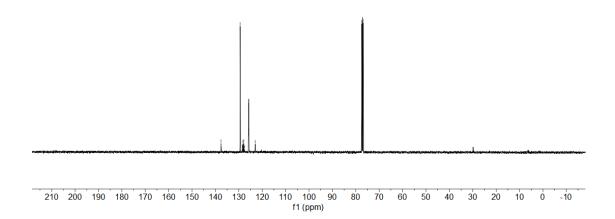


Supplementary Figure 65. ¹H NMR Spectrum of 2d (400 MHz, CDCl₃)

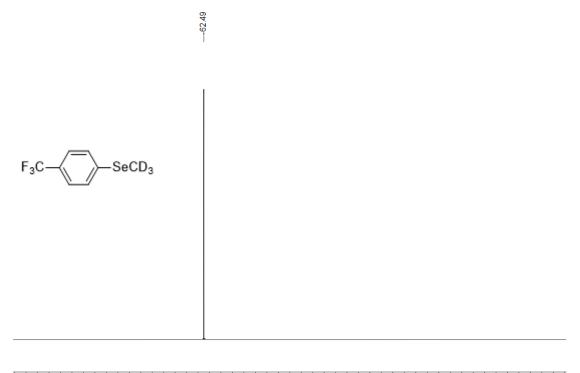


Supplementary Figure 66. ¹³C NMR Spectrum of 2d (100 MHz, CDCl₃)



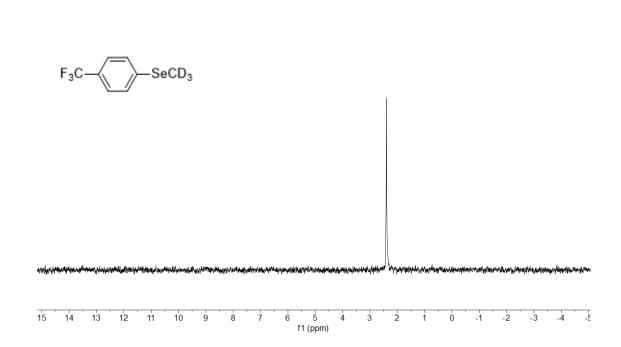


Supplementary Figure 67. ¹⁹F NMR Spectrum of 2d (376 MHz, CDCl₃)

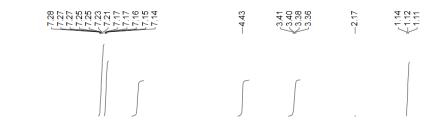


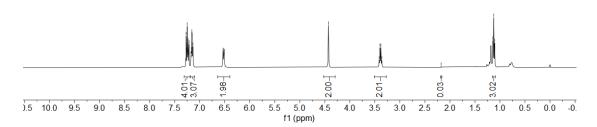
Supplementary Figure 68. ²H NMR Spectrum of 2d (100 MHz, CHCl₃)





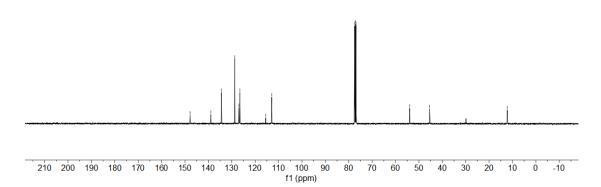
Supplementary Figure 69. ¹H NMR Spectrum of 2e (400 MHz, CDCl₃)





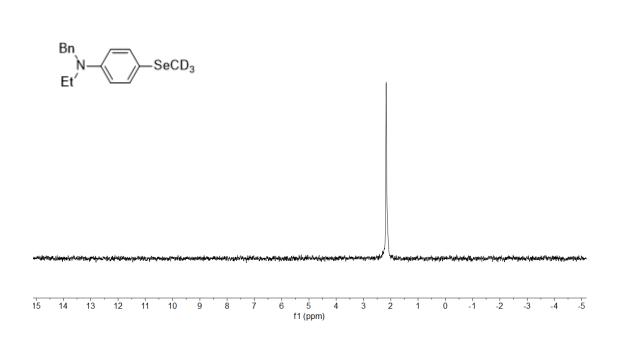
Supplementary Figure 70. ¹³C NMR Spectrum of 2e (100 MHz, CDCl)



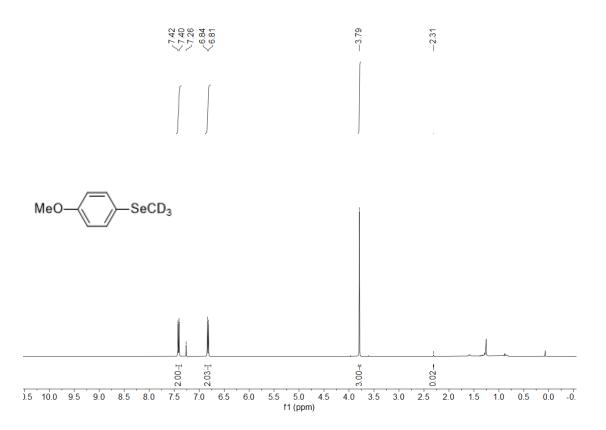


Supplementary Figure 71. ²H NMR Spectrum of 2e (100 MHz, CHCl₃)



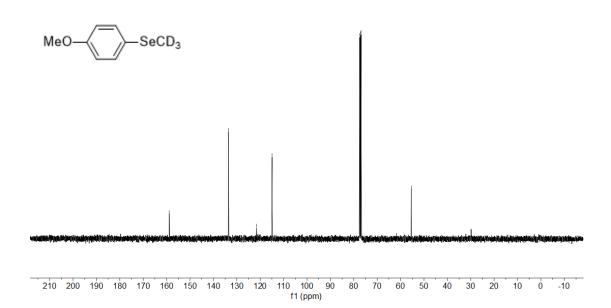


Supplementary Figure 72. ¹H NMR Spectrum of 2f (400 MHz, CDCl₃)

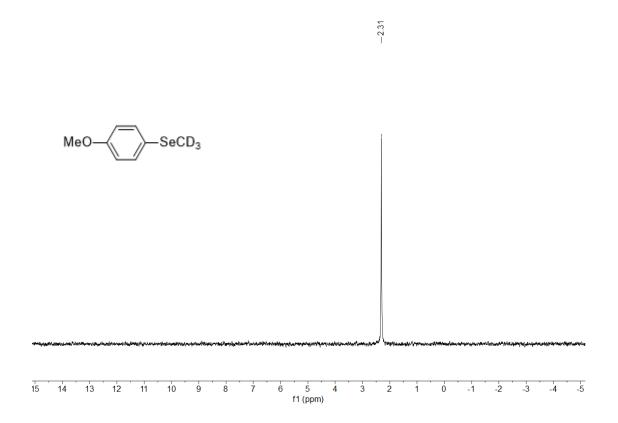


Supplementary Figure 73. ¹³C NMR Spectrum of 2f (100 MHz, CDCl₃)

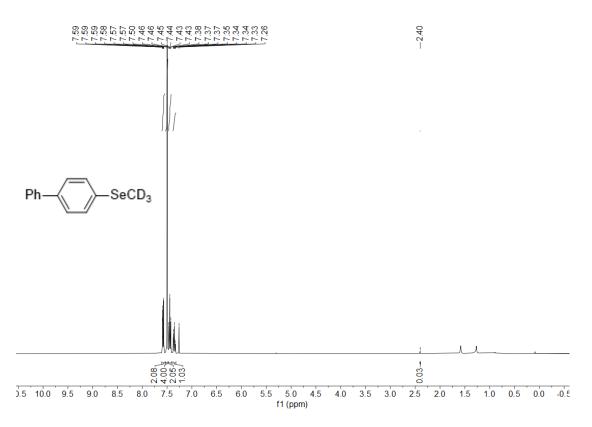




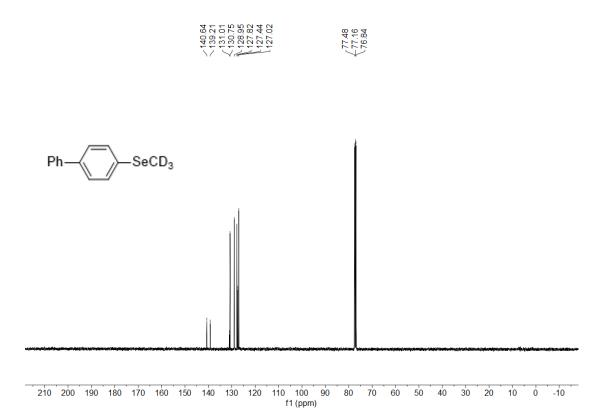
Supplementary Figure 74. ²H NMR Spectrum of 2f (100 MHz, CHCl₃)



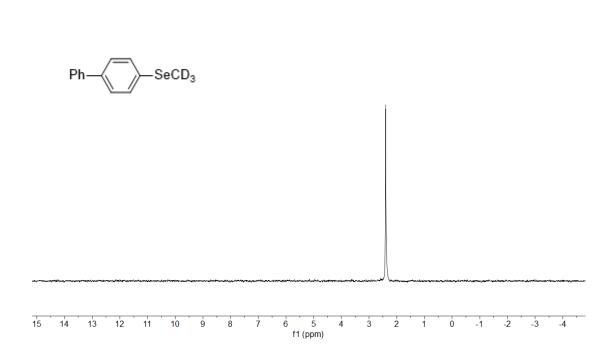
Supplementary Figure 75. ¹H NMR Spectrum of 2g (400 MHz, CDCl₃)



Supplementary Figure 76. ¹³C NMR Spectrum of 2g (100 MHz, CDCl₃)

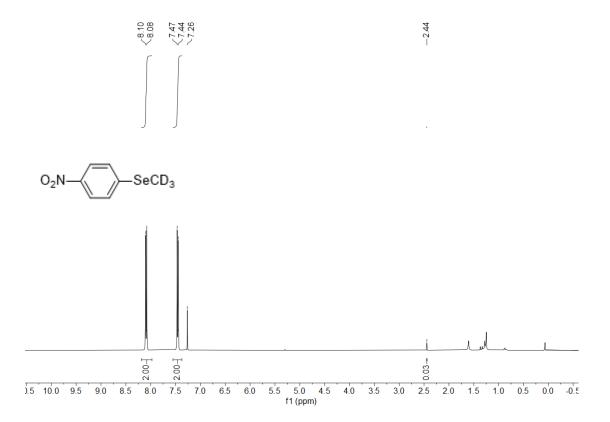


Supplementary Figure 77. ²H NMR Spectrum of 2g (100 MHz, CHCl₃)

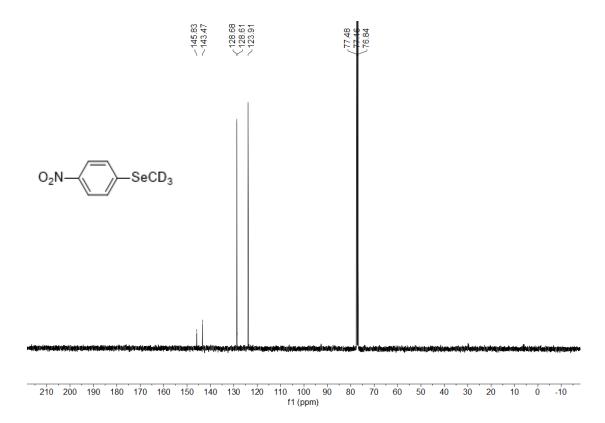


-2.40

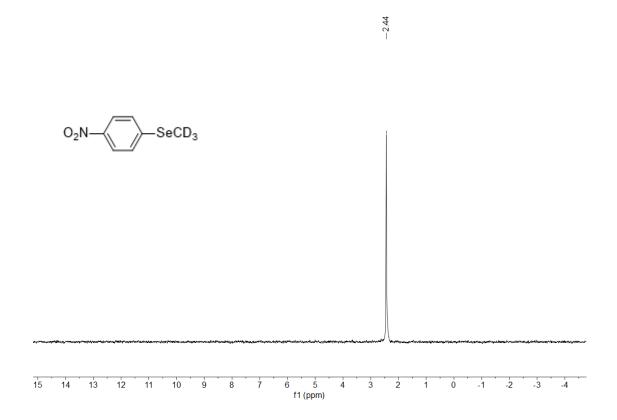
Supplementary Figure 78. ¹H NMR Spectrum of 2h (400 MHz, CDCl₃)



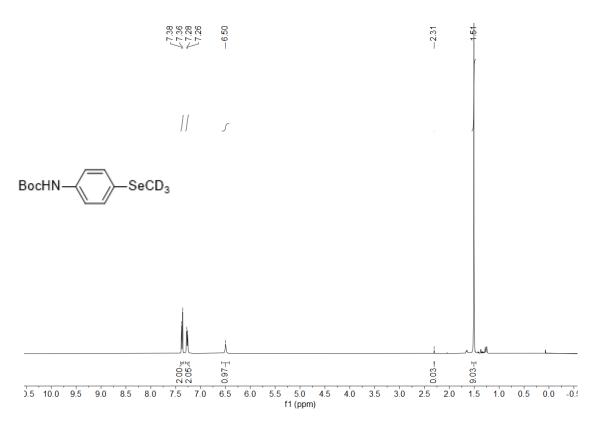
Supplementary Figure 79. ¹³C NMR Spectrum of 2h (100 MHz, CDCl₃)



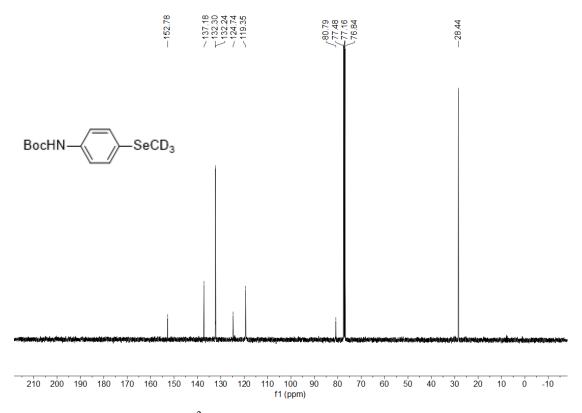
Supplementary Figure 80. ²H NMR Spectrum of 2h (100 MHz, CHCl₃)



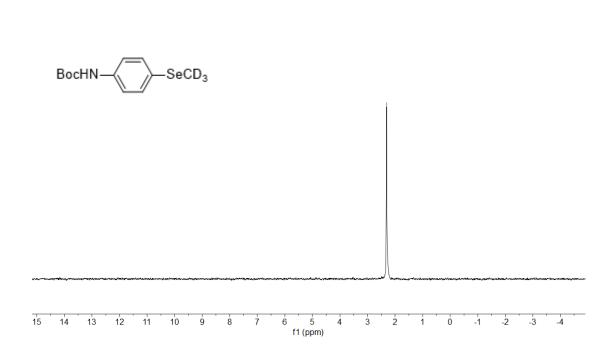
Supplementary Figure 81. ¹H NMR Spectrum of 2i (400 MHz, CDCl₃)



Supplementary Figure 82. ¹³C NMR Spectrum of 2i (100 MHz, CDCl₃)

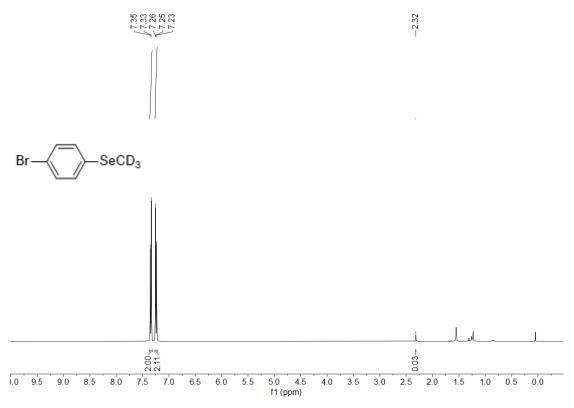


Supplementary Figure 83. ²H NMR Spectrum of 2i (100 MHz, CHCl₃)

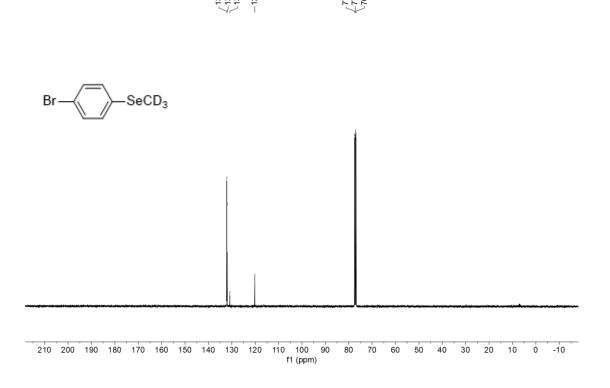


-2.31

Supplementary Figure 84. ¹H NMR Spectrum of 2j (400 MHz, CDCl₃)

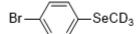


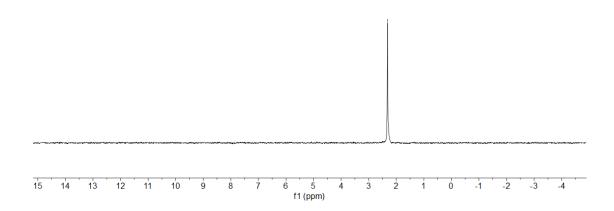
Supplementary Figure 85. ¹³C NMR Spectrum of 2j (100 MHz, CDCl₃)



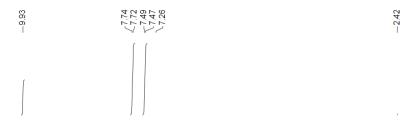
Supplementary Figure 86. ²H NMR Spectrum of 2j (100 MHz, CHCl₃)

-2.32

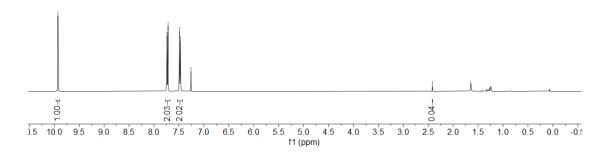




Supplementary Figure 87. ¹H NMR Spectrum of 2k (400 MHz, CDCl₃)

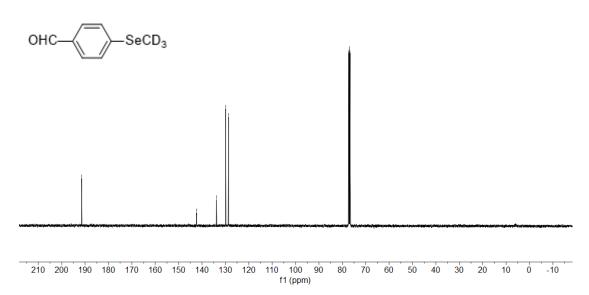






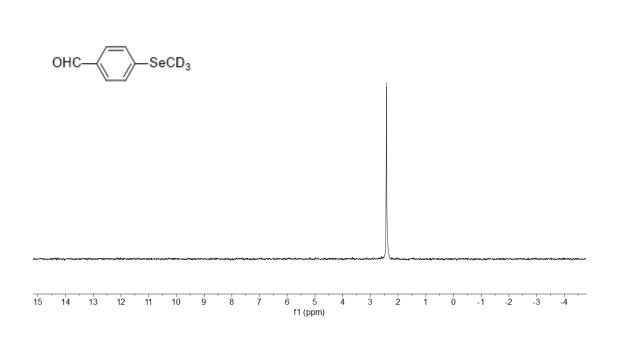
Supplementary Figure 88. ¹³C NMR Spectrum of 2k (100 MHz, CDCl₃)



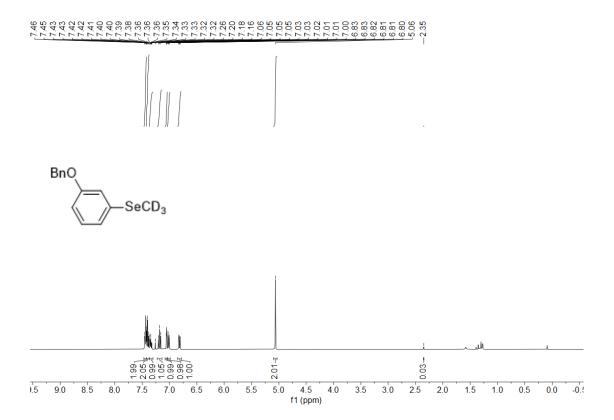


Supplementary Figure 89. ²H NMR Spectrum of 2k (100 MHz, CHCl₃)

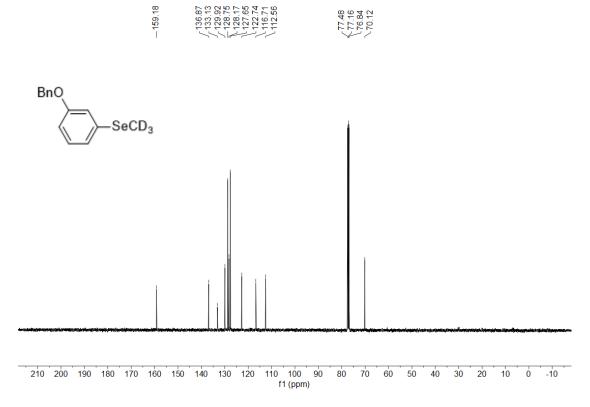




Supplementary Figure 90. ¹H NMR Spectrum of 21 (400 MHz, CDCl₃)

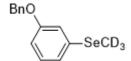


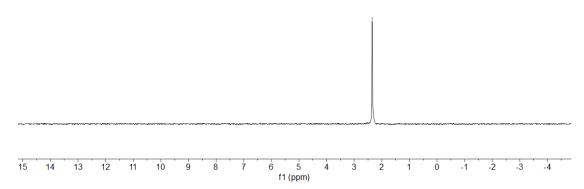
Supplementary Figure 91. ¹³C NMR Spectrum of 2l (100 MHz, CDCl₃)



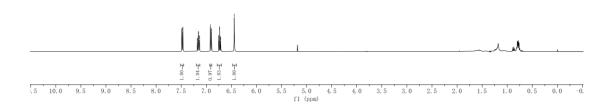
Supplementary Figure 92. ²H NMR Spectrum of 2l (100 MHz, CHCl₃)

-2.35





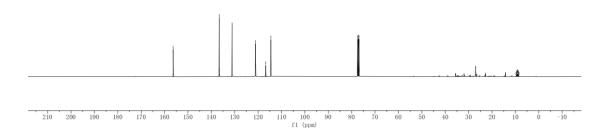
Supplementary Figure 93. ¹H NMR Spectrum of 2m (100 MHz, CHCl₃)



Supplementary Figure 94. ¹H NMR Spectrum of 2m (100 MHz, CHCl₃)

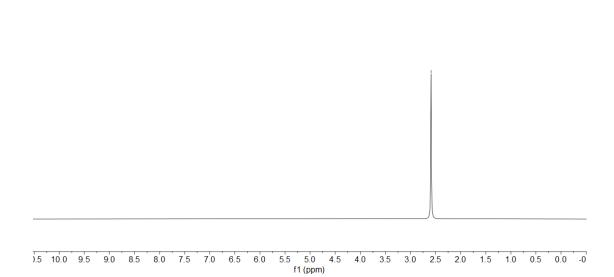




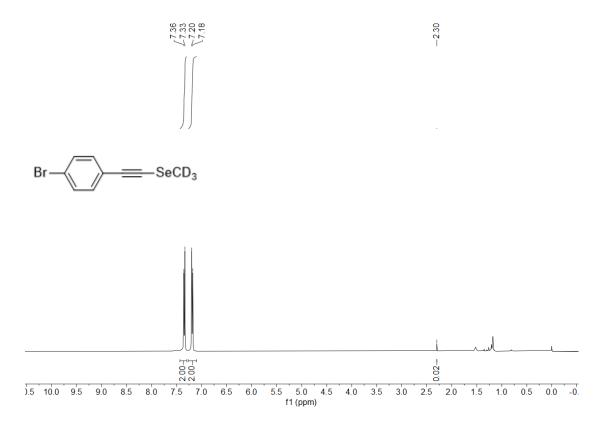


Supplementary Figure 95. ²H NMR Spectrum of 2m (100 MHz, CHCl₃)

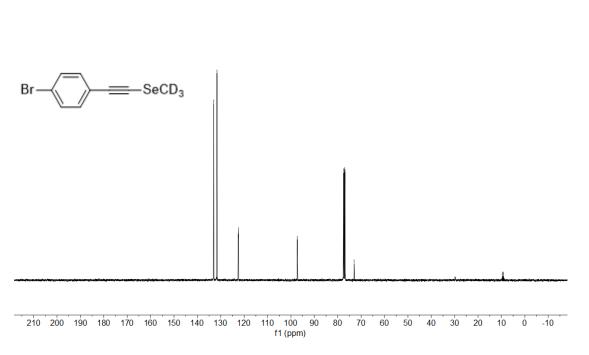




Supplementary Figure 96. ¹H NMR Spectrum of 2n (400 MHz, CDCl₃)

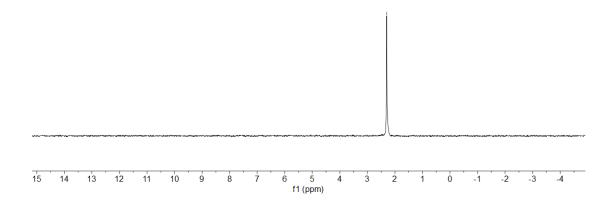


Supplementary Figure 97. ¹³C NMR Spectrum of **2n** (100 MHz, CDCl₃)

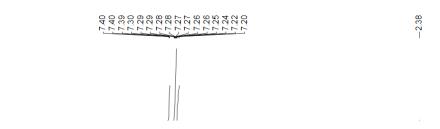


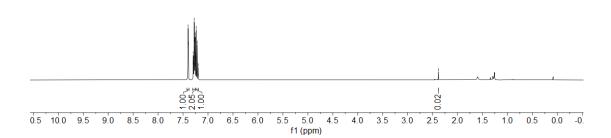
Supplementary Figure 98. ²H NMR Spectrum of 2n (100 MHz, CHCl₃)



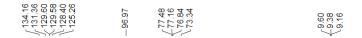


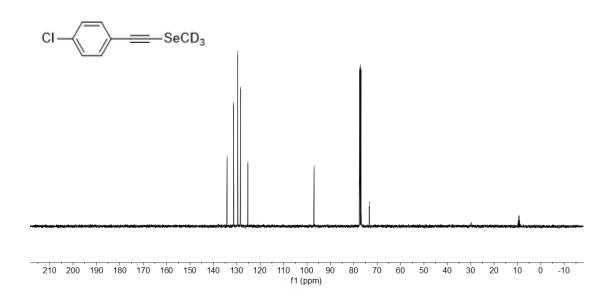
Supplementary Figure 99. ¹H NMR Spectrum of 2o (400 MHz, CDCl₃)





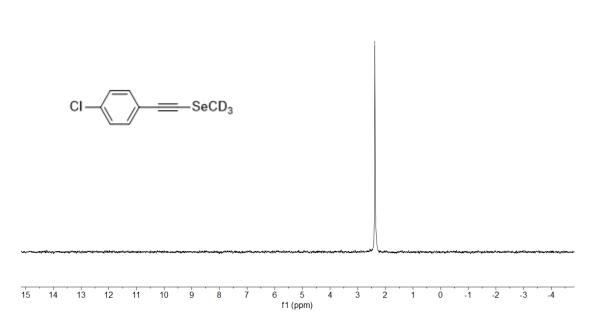
Supplementary Figure 100. ¹³C NMR Spectrum of 20 (100 MHz, CDCl₃)





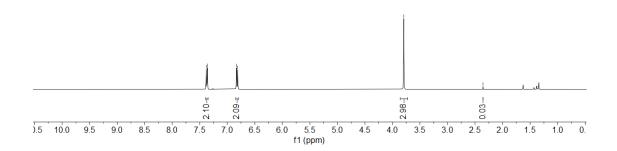
Supplementary Figure 101. ²H NMR Spectrum of 2o (100 MHz, CHCl₃)



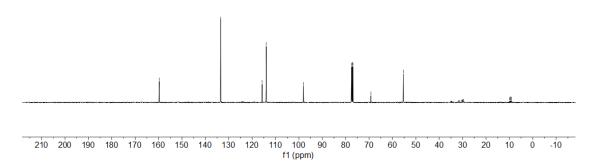


Supplementary Figure 102. ¹H NMR Spectrum of 2p (400 MHz, CDCl₃)

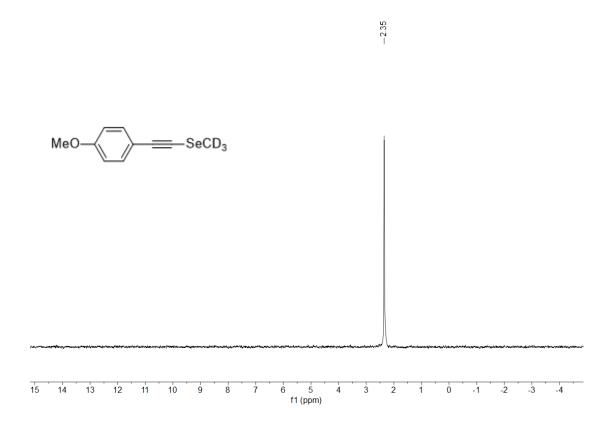




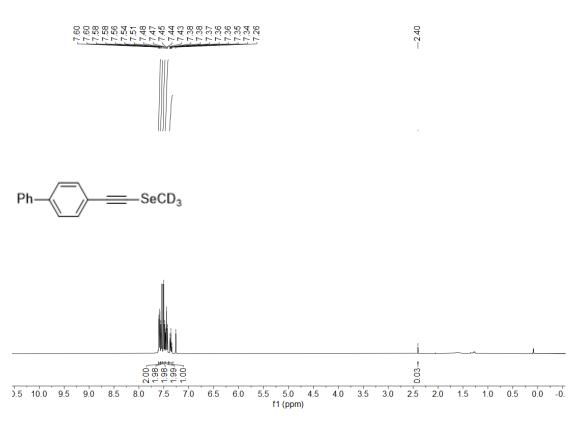
Supplementary Figure 103. ¹³C NMR Spectrum of 2p (100 MHz, CDCl₃)



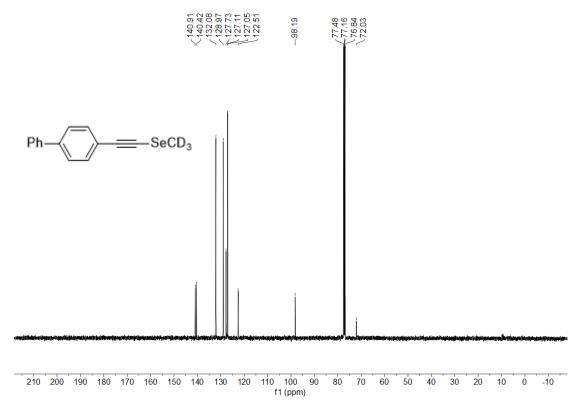
Supplementary Figure 104. ²H NMR Spectrum of 2p (100 MHz, CHCl₃)



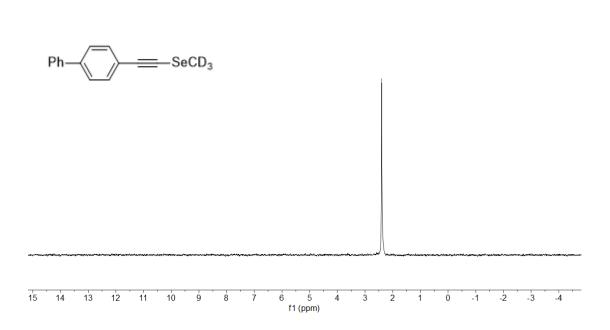
Supplementary Figure 105. ¹H NMR Spectrum of 2q (400 MHz, CDCl₃)



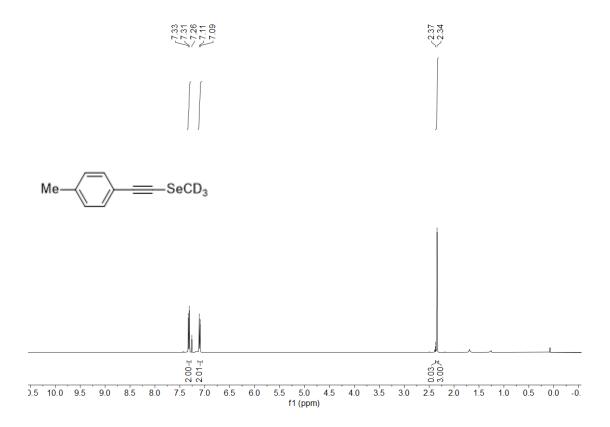
Supplementary Figure 106. ¹³C NMR Spectrum of 2q (100 MHz, CDCl₃)



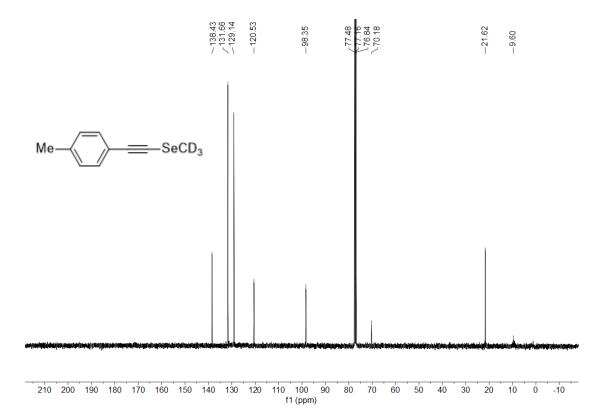
Supplementary Figure 107. ²H NMR Spectrum of 2q (100 MHz, CHCl₃)



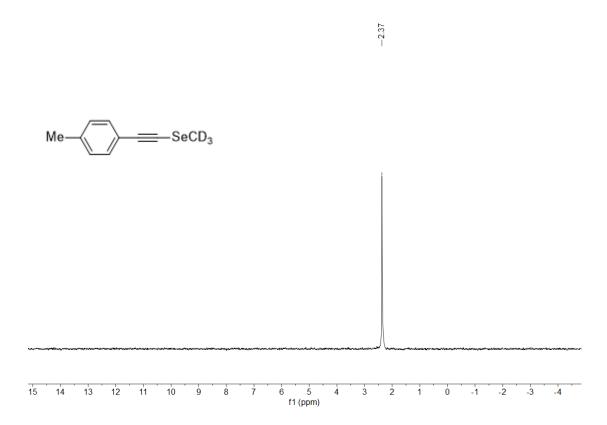
Supplementary Figure 108. ¹H NMR Spectrum of 2r (400 MHz, CDCl₃)



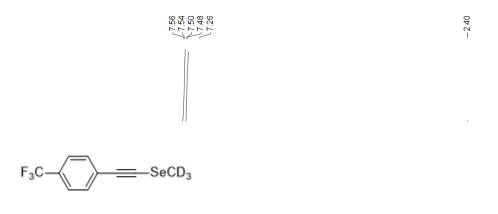
Supplementary Figure 109. ¹³C NMR Spectrum of 2r (100 MHz, CDCl₃)

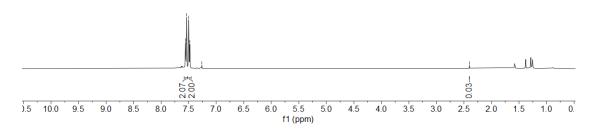


Supplementary Figure 110. ²H NMR Spectrum of 2r (100 MHz, CHCl₃)

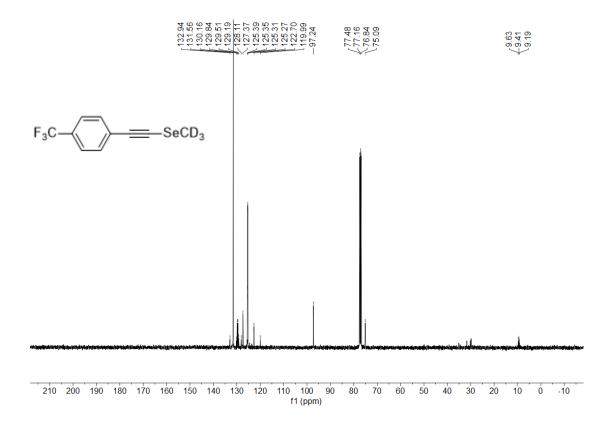


Supplementary Figure 111. ¹H NMR Spectrum of 2s (400 MHz, CDCl₃)





Supplementary Figure 112. ¹³C NMR Spectrum of 2s (100 MHz, CDCl₃)

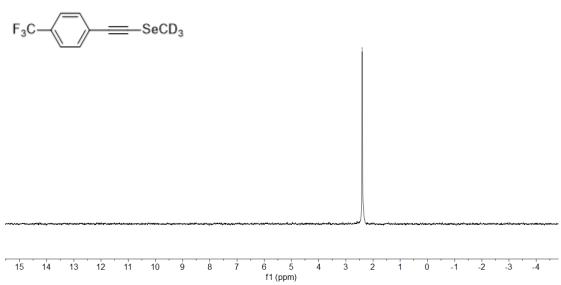


Supplementary Figure 113. ¹⁹F NMR Spectrum of 2s (376 MHz, CDCl₃)

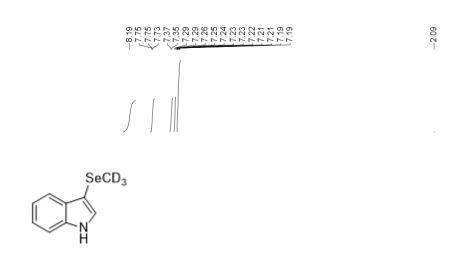


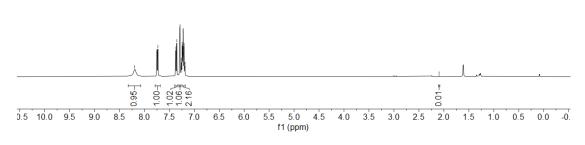
Supplementary Figure 114. ²H NMR Spectrum of 2s (100 MHz, CHCl₃)



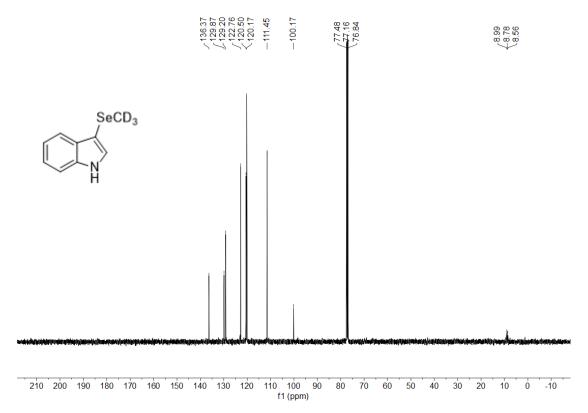


Supplementary Figure 115. ¹H NMR Spectrum of 2t (400 MHz, CDCl₃)

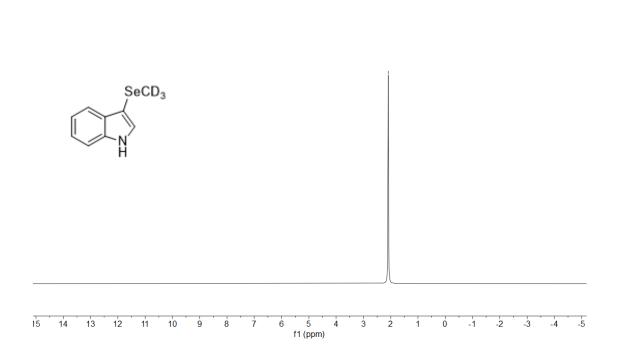




Supplementary Figure 116. ¹³C NMR Spectrum of 2t (100 MHz, CDCl₃)

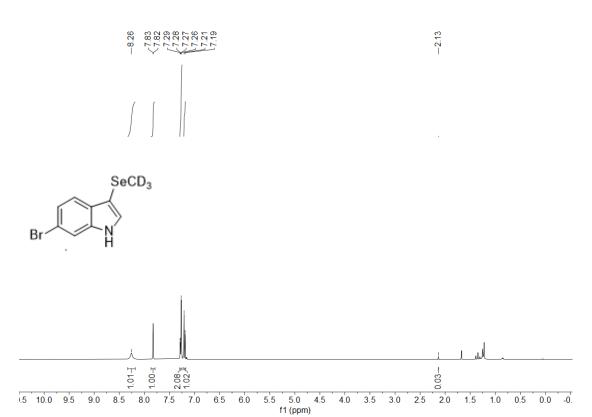


Supplementary Figure 117. ²H NMR Spectrum of 2t (100 MHz, CHCl₃)



-2.09

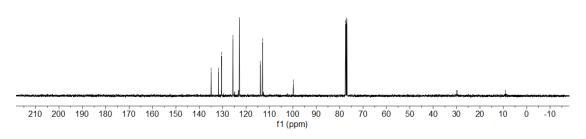
Supplementary Figure 118. ¹H NMR Spectrum of 2u (400 MHz, CDCl₃)



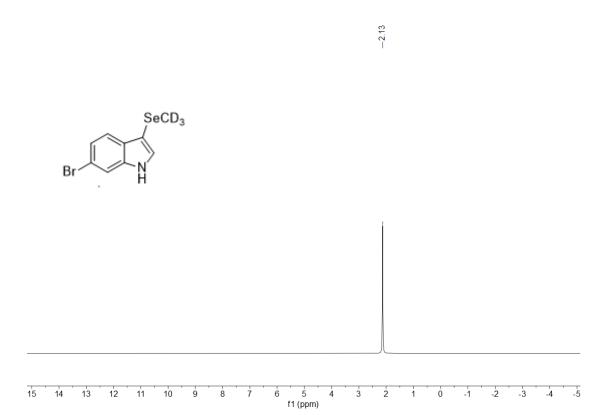
Supplementary Figure 119. ¹³C NMR Spectrum of 2u (100 MHz, CDCl₃)

7.134.94 7.131.75 7.12.78 7.12.93 7.13.90 7.13.90 7.77.48 7.77.16 7.77.16 7.77.16

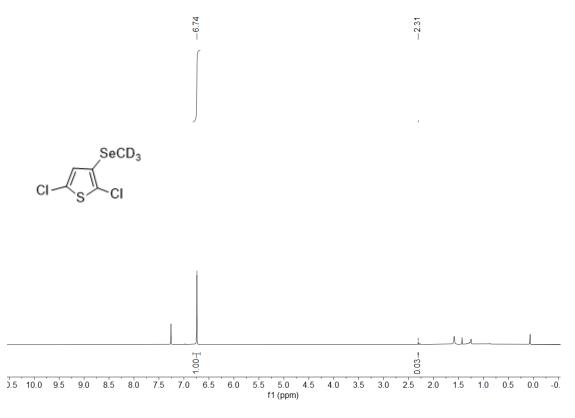
$$\mathsf{Br} \overset{\mathsf{SeCD_3}}{\overset{\mathsf{N}}{\underset{\mathsf{H}}{\bigvee}}}$$



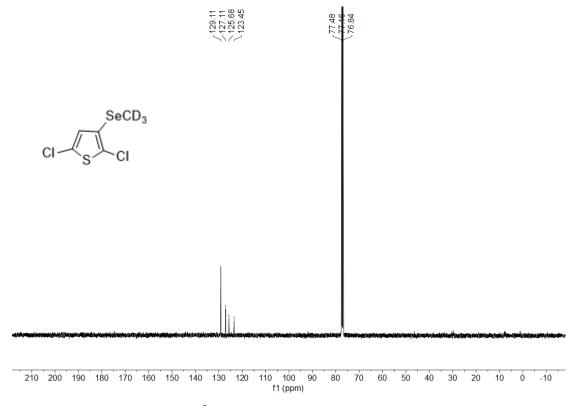
Supplementary Figure 120. ²H NMR Spectrum of 2u (100 MHz, CHCl₃)



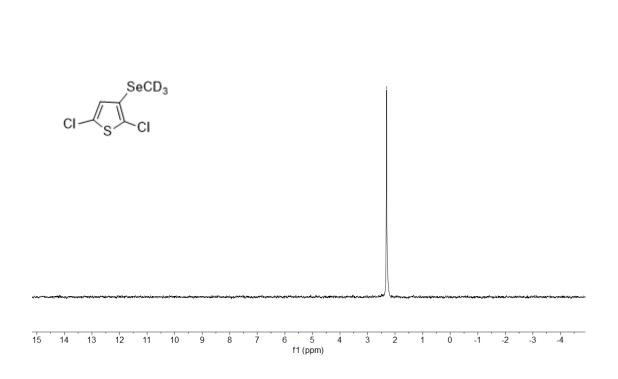
Supplementary Figure 121. ¹H NMR Spectrum of 2v (400 MHz, CDCl₃)



Supplementary Figure 122. ¹³C NMR Spectrum of 2v (100 MHz, CDCl₃)

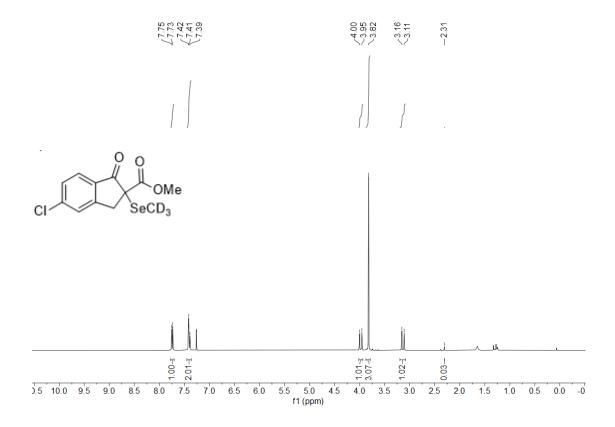


Supplementary Figure 123. ²H NMR Spectrum of 2v (100 MHz, CHCl₃)

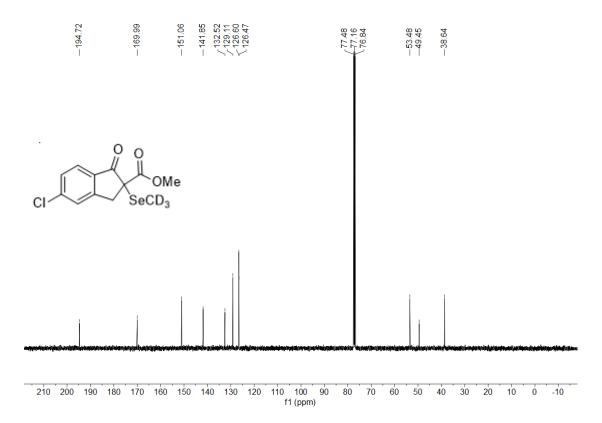


-2.31

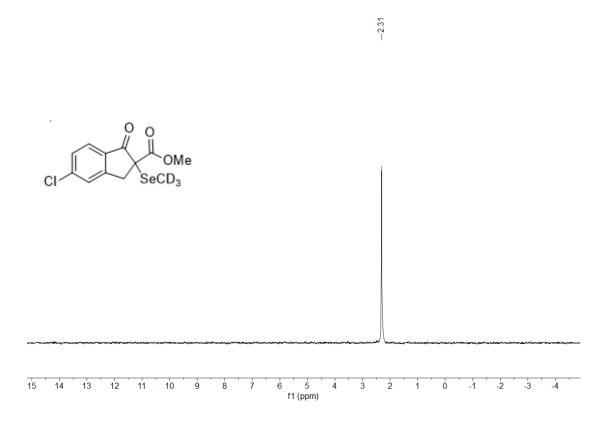
Supplementary Figure 124. ¹H NMR Spectrum of 2w (400 MHz, CDCl₃)



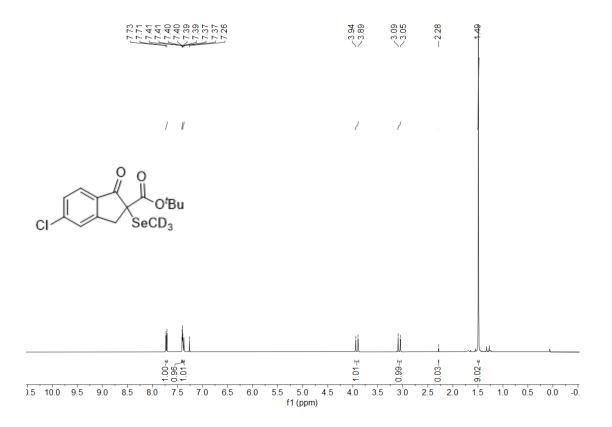
Supplementary Figure 125. ¹³C NMR Spectrum of 2w (100 MHz, CDCl₃)



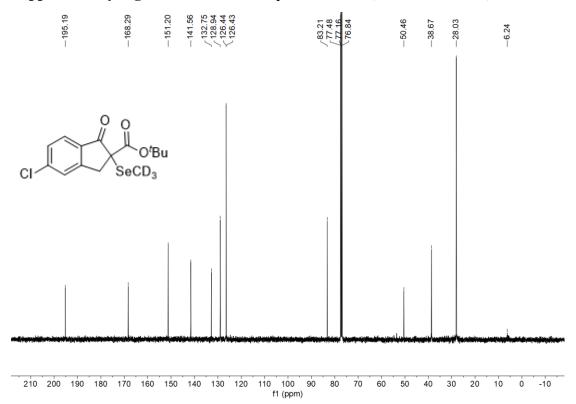
Supplementary Figure 126. ²H NMR Spectrum of 2w (100 MHz, CHCl₃)



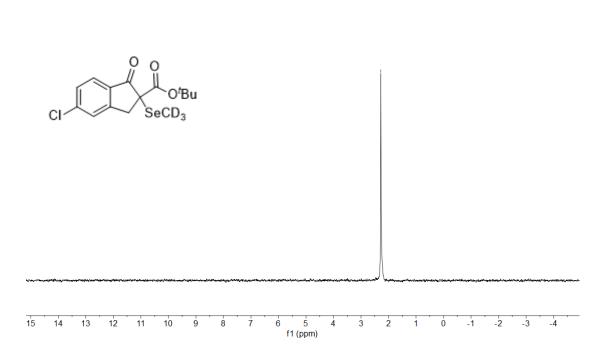
Supplementary Figure 127. ¹H NMR Spectrum of 2x (400 MHz, CDCl₃)



Supplementary Figure 128. ¹³C NMR Spectrum of 2x (100 MHz, CDCl₃)



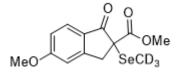
Supplementary Figure 129. ²H NMR Spectrum of 2x (100 MHz, CHCl₃)

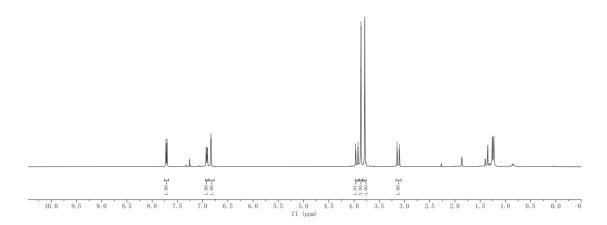


Supplementary Figure 130. ¹H NMR Spectrum of 2y (400 MHz, CDCl₃)

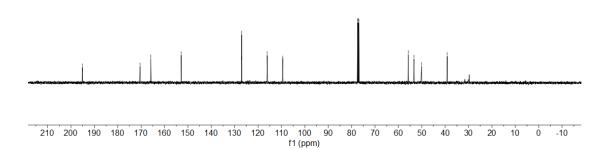


3.97 3.86 3.86 3.78 3.78 3.15 3.15



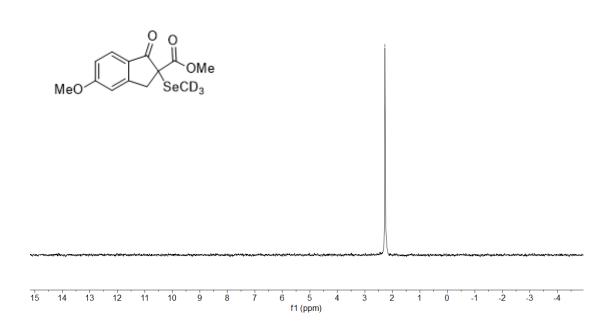


Supplementary Figure 131. ¹³C NMR Spectrum of 2y (100 MHz, CDCl₃)

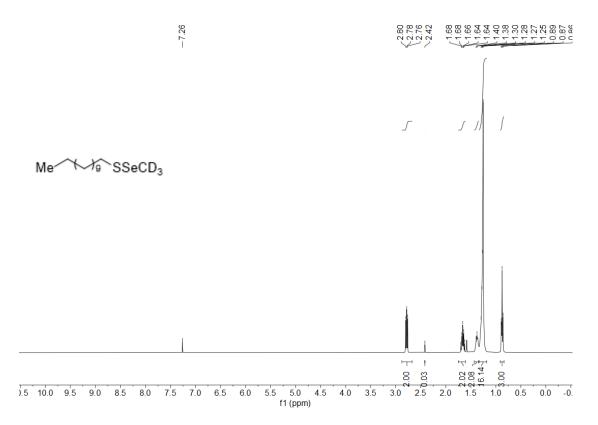


Supplementary Figure 132. ²H NMR Spectrum of 2y (100 MHz, CHCl₃)





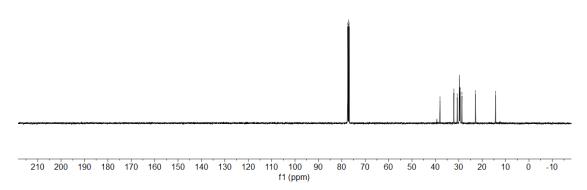
Supplementary Figure 133. ¹H NMR Spectrum of 2z (400 MHz, CDCl₃)



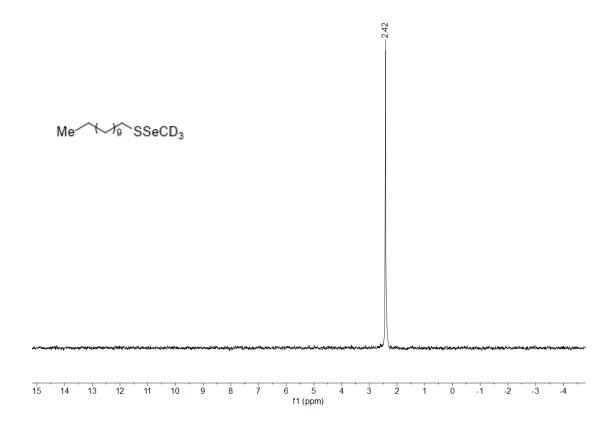
Supplementary Figure 134. ¹³C NMR Spectrum of 2z (100 MHz, CDCl₃)



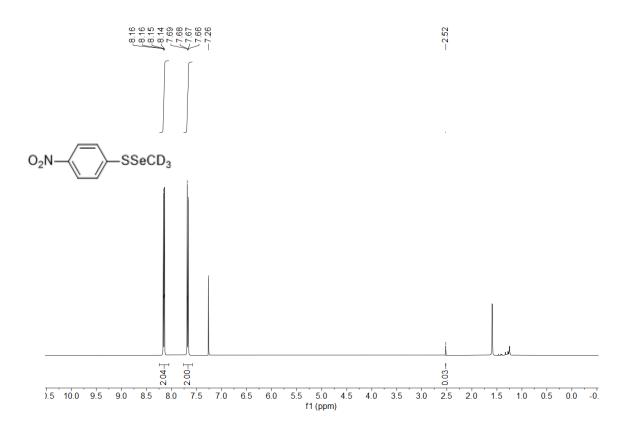




Supplementary Figure 135. ²H NMR Spectrum of 2z (100 MHz, CHCl₃)

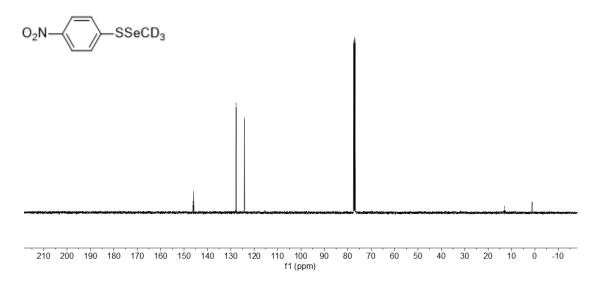


Supplementary Figure 136. ¹H NMR Spectrum of 2aa (400 MHz, CDCl₃)

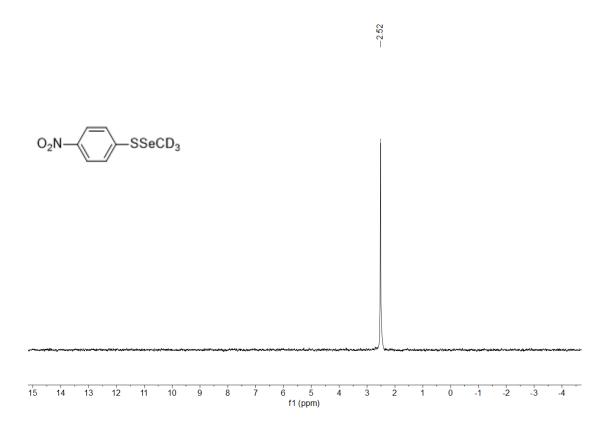


Supplementary Figure 137. ¹³C NMR Spectrum of 2aa (100 MHz, CDCl₃)

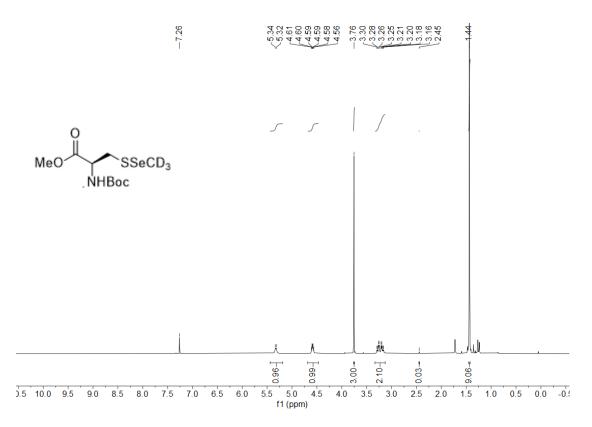




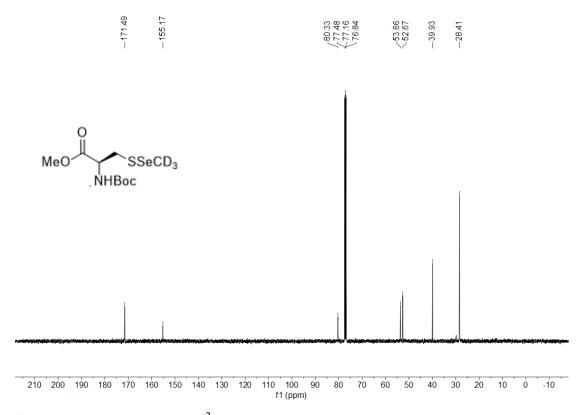
Supplementary Figure 138. ²H NMR Spectrum of 2aa (100 MHz, CHCl₃)



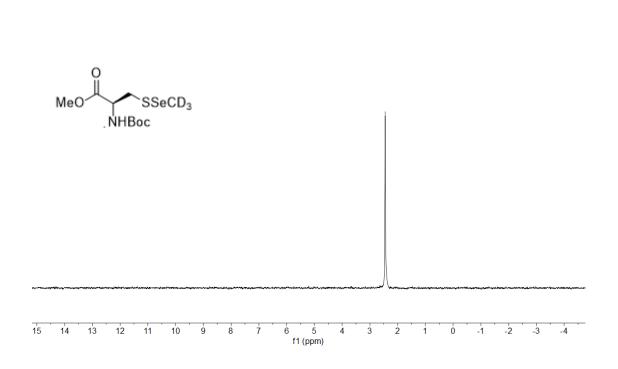
Supplementary Figure 139. ¹H NMR Spectrum of 2ab (400 MHz, CDCl₃)



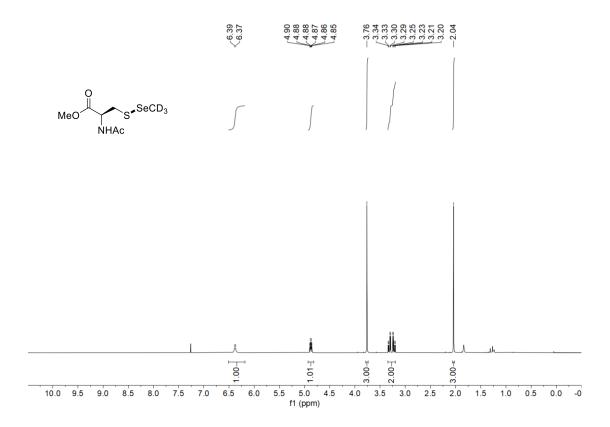
Supplementary Figure 140. ¹³C NMR Spectrum of 2ab (100 MHz, CDCl₃)



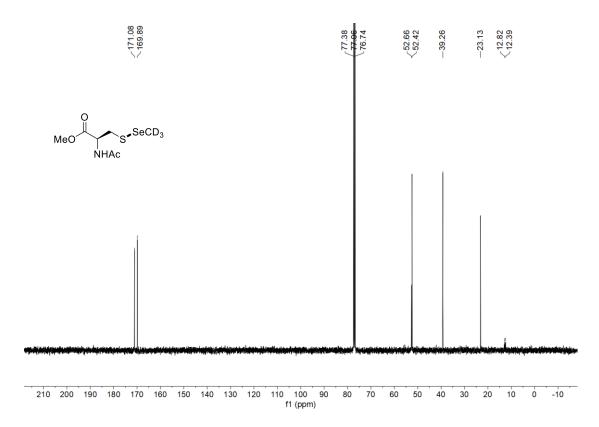
Supplementary Figure 141. ²H NMR Spectrum of 2ab (100 MHz, CHCl₃)



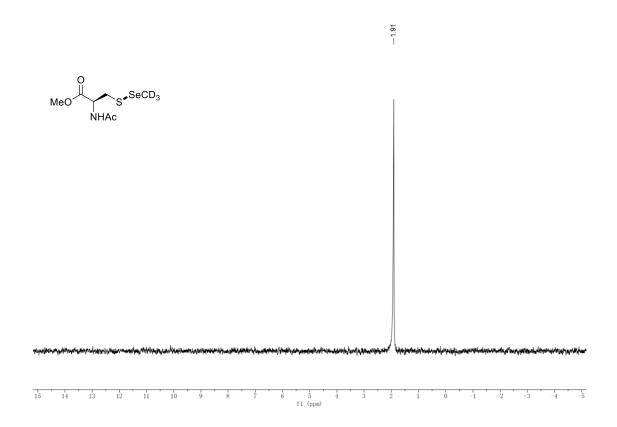
Supplementary Figure 142. ¹H NMR Spectrum of 2ac (400 MHz, CDCl₃)



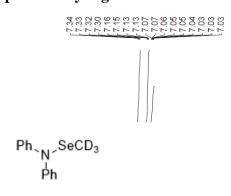
Supplementary Figure 143. ¹³C NMR Spectrum of 2ac (100 MHz, CDCl₃)

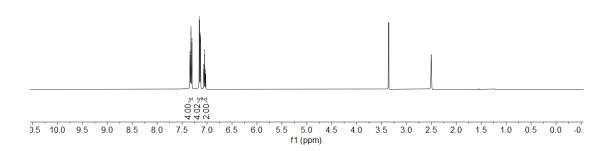


Supplementary Figure 144. ²H NMR Spectrum of 2ac (100 MHz, CHCl₃)

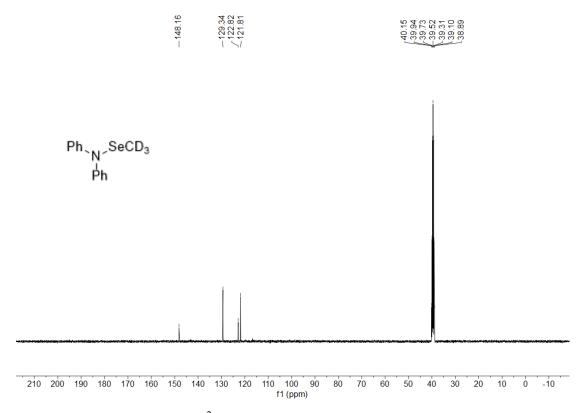


Supplementary Figure 145. ¹H NMR Spectrum of **2ad** (400 MHz, DMSO-*d*₆)

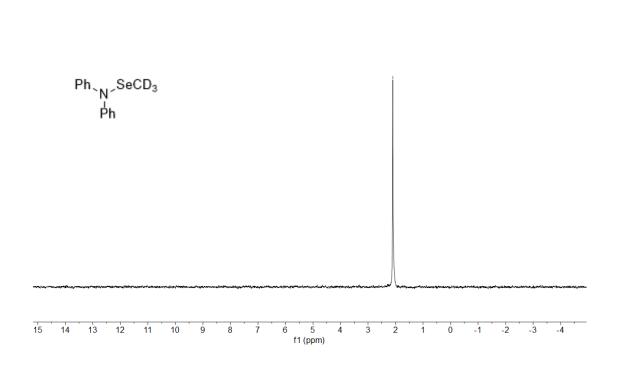




Supplementary Figure 146. ¹³C NMR Spectrum of 2ad (100 MHz, CDCl₃)

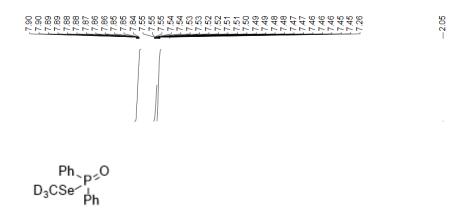


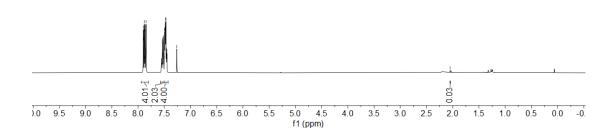
Supplementary Figure 147. ²H NMR Spectrum of 2ad (100 MHz, CHCl₃)



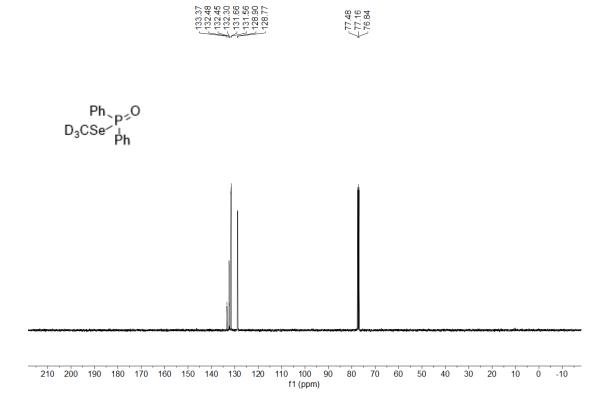
-2.10

Supplementary Figure 148. ¹H NMR Spectrum of 2ae (400 MHz, CDCl₃)

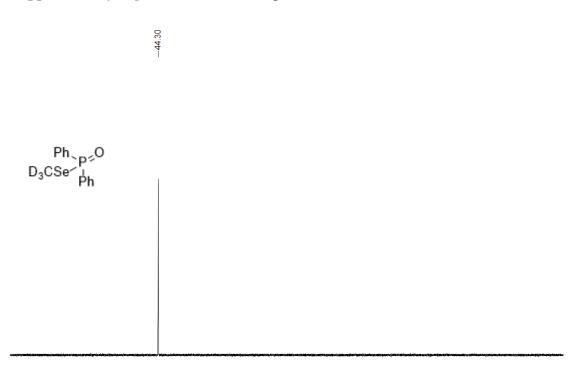




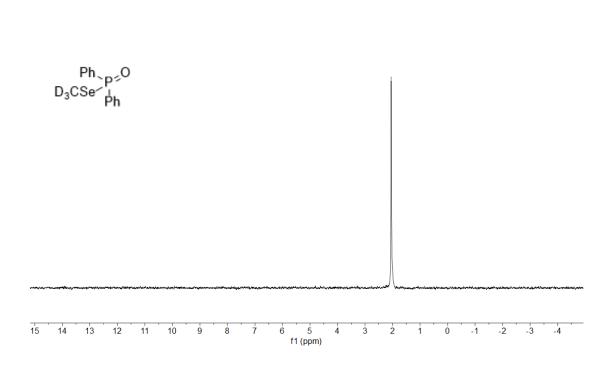
Supplementary Figure 149. ¹³C NMR Spectrum of 2ae (100 MHz, CDCl₃)





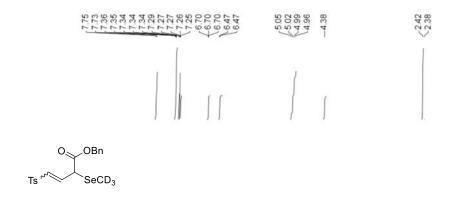


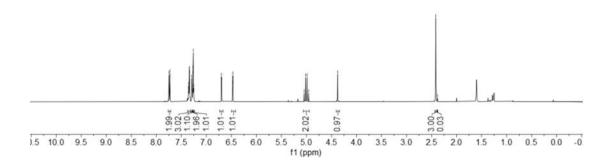
Supplementary Figure 151. ²H NMR Spectrum of 2ae (100 MHz, CHCl₃)



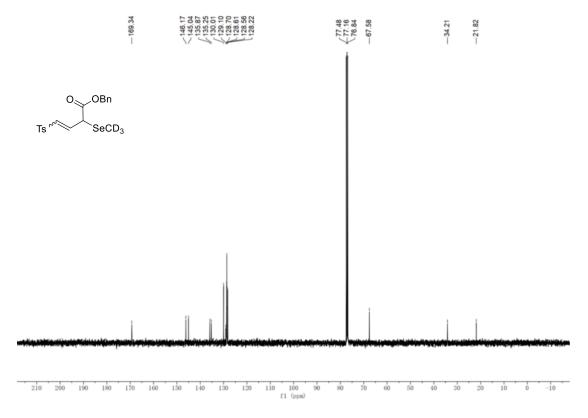
-2.05

Supplementary Figure 152. ¹H NMR Spectrum of 3a (400 MHz, CDCl₃)

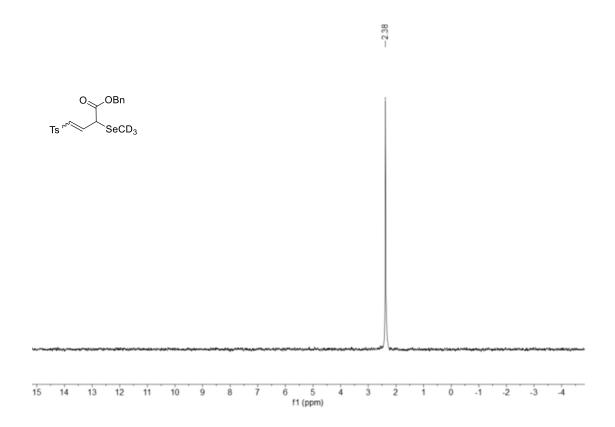




Supplementary Figure 153. ¹³C NMR Spectrum of 3a (100 MHz, CDCl₃)

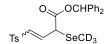


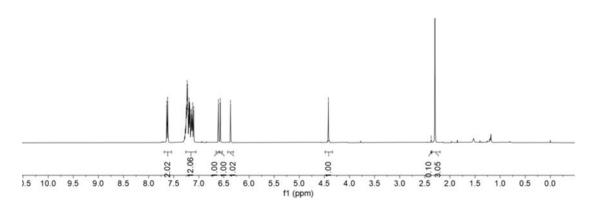
Supplementary Figure 154. ²H NMR Spectrum of 3a (100 MHz, CHCl₃)



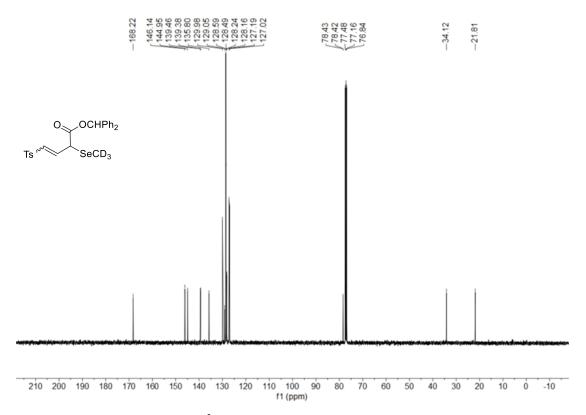
Supplementary Figure 155. ¹H NMR Spectrum of 3b (400 MHz, CDCl₃)



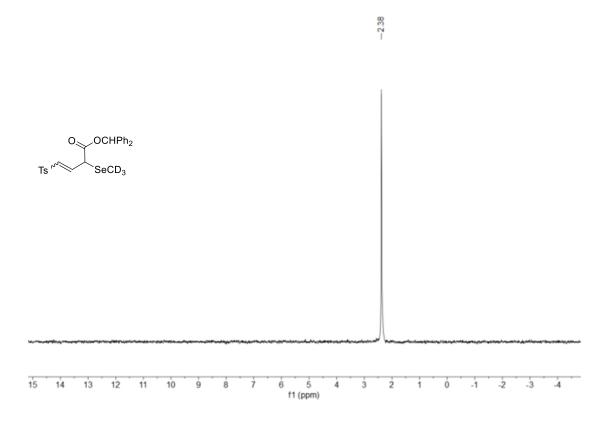




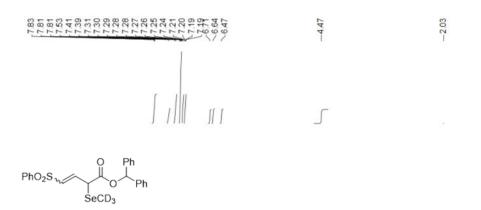
Supplementary Figure 156. ¹³C NMR Spectrum of 3b (100 MHz, CDCl₃)

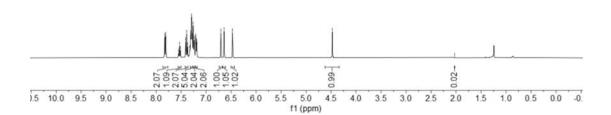


Supplementary Figure 157. ²H NMR Spectrum of 3b (100 MHz, CHCl₃)



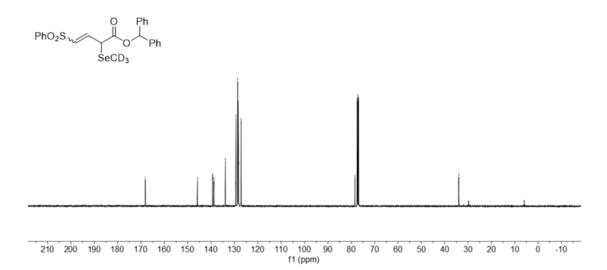
Supplementary Figure 158. ¹H NMR Spectrum of 3c (400 MHz, CDCl₃)





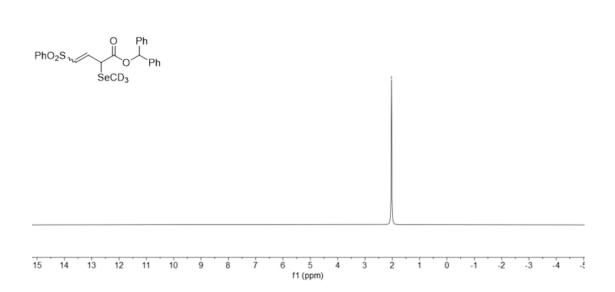
Supplementary Figure 159. ¹³C NMR Spectrum of 3c (100 MHz, CDCl₃)



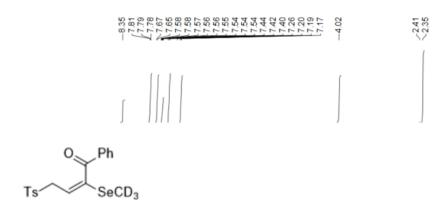


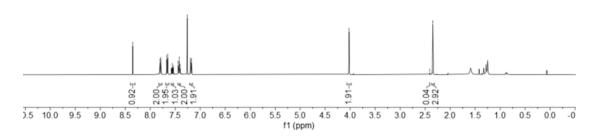
Supplementary Figure 160. ²H NMR Spectrum of 3c (100 MHz, CHCl₃)



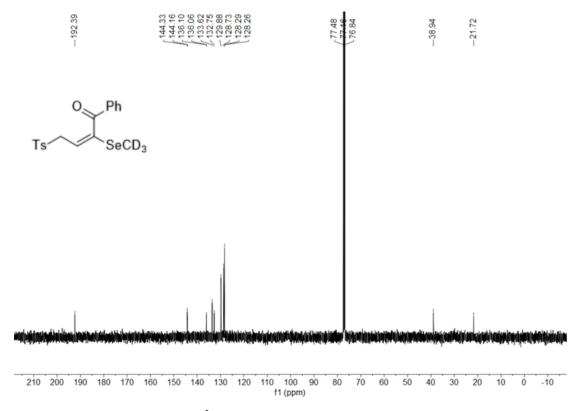


Supplementary Figure 161. ¹H NMR Spectrum of 3d (400 MHz, CDCl₃)

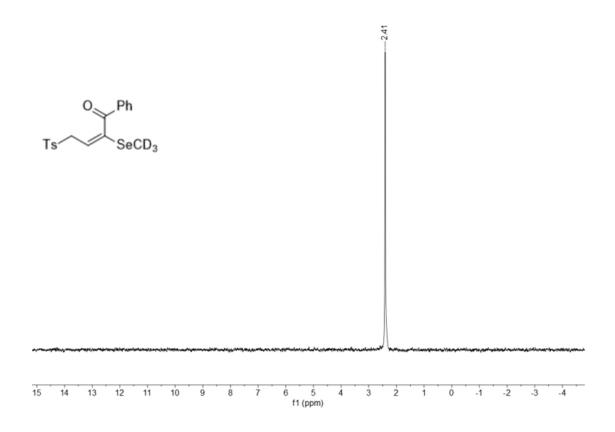




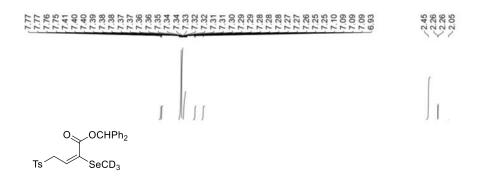
Supplementary Figure 162. ¹³C NMR Spectrum of 3d (100 MHz, CDCl₃)

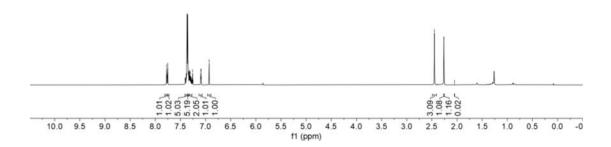


Supplementary Figure 163. ²H NMR Spectrum of 3d (100 MHz, CHCl₃)



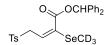
Supplementary Figure 164. ¹H NMR Spectrum of **3e** (400 MHz, CDCl₃)

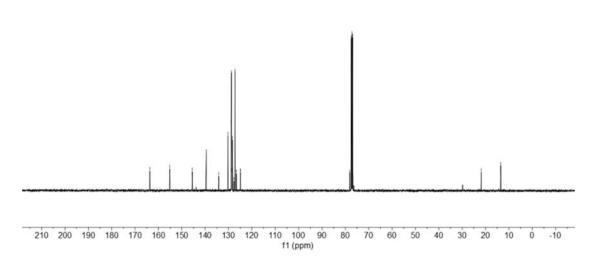




Supplementary Figure 165. ¹³C NMR Spectrum of 3e (100 MHz, CDCl₃)

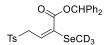


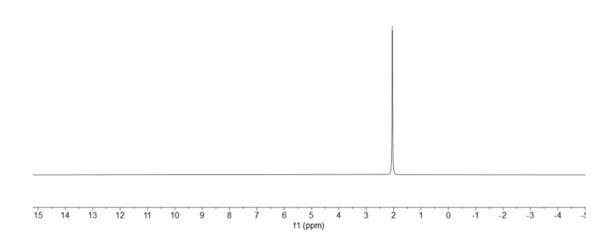




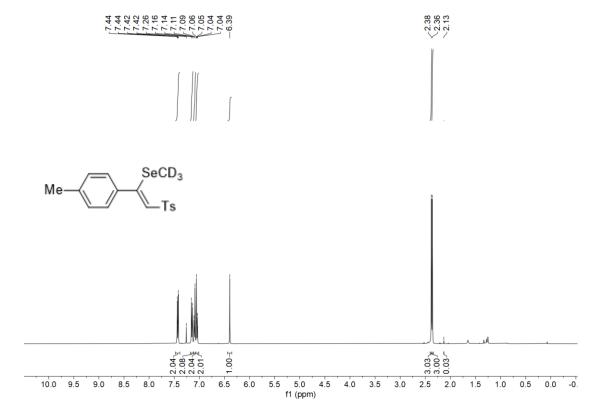




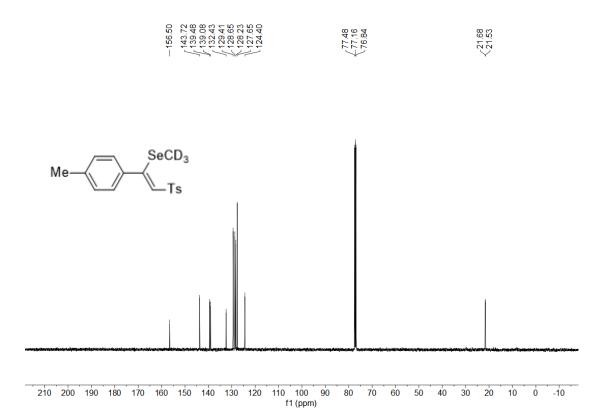




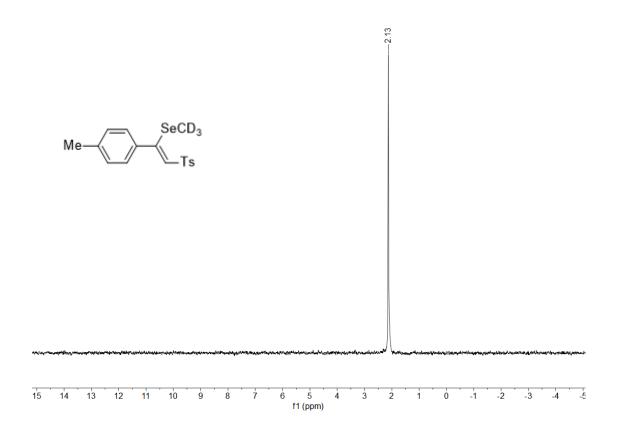
Supplementary Figure 167. ¹H NMR Spectrum of 3f (400 MHz, CDCl₃)



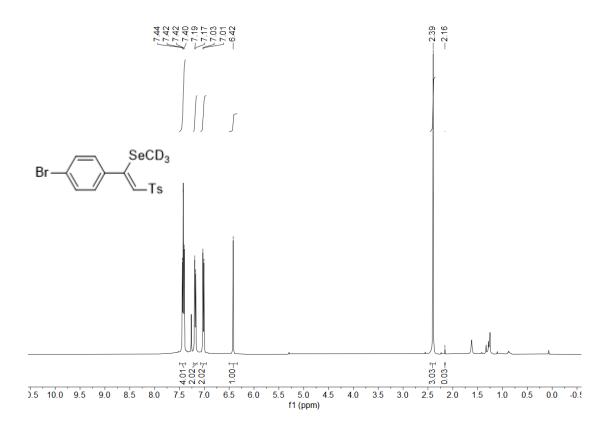
Supplementary Figure 168. ¹³C NMR Spectrum of 3f (100 MHz, CDCl₃)



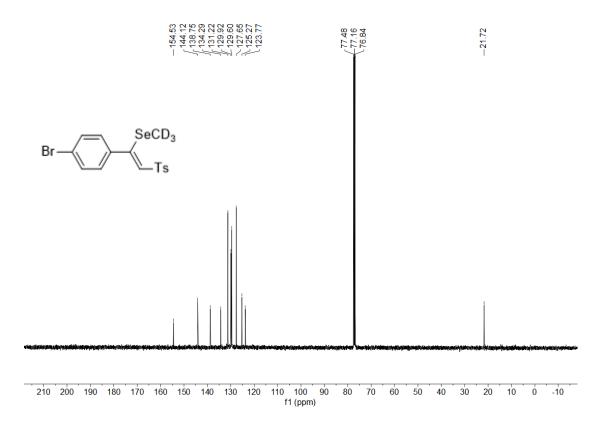
Supplementary Figure 169. ²H NMR Spectrum of 3f (100 MHz, CHCl₃)



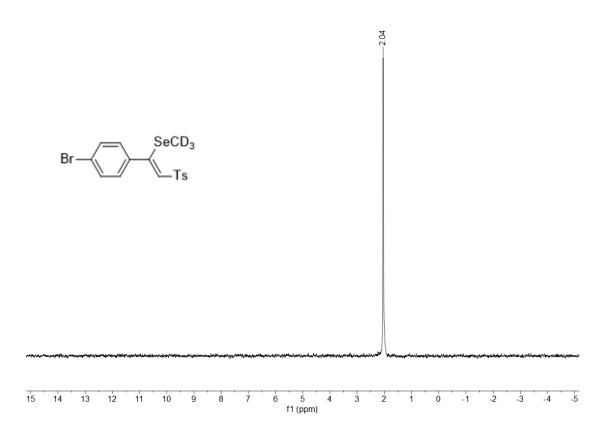
Supplementary Figure 170. ¹H NMR Spectrum of 3g (400 MHz, CDCl₃)



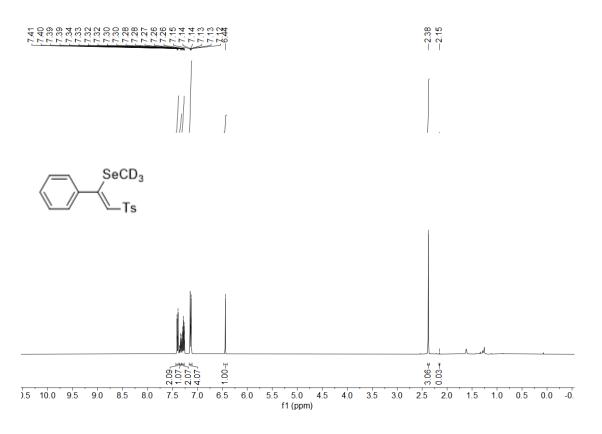
Supplementary Figure 171. ¹³C NMR Spectrum of 3g (100 MHz, CDCl₃)



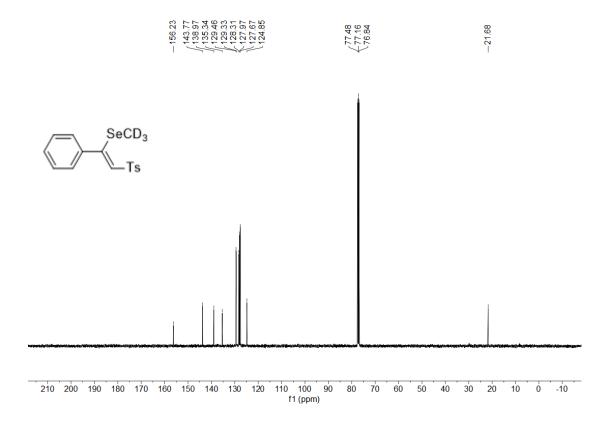
Supplementary Figure 172. ²H NMR Spectrum of 3g (100 MHz, CHCl₃)



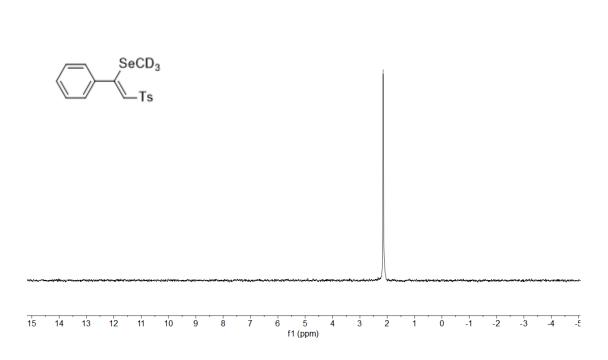
Supplementary Figure 173. ¹H NMR Spectrum of 3h (400 MHz, CDCl₃)



Supplementary Figure 174. ¹³C NMR Spectrum of 3h (100 MHz, CDCl₃)

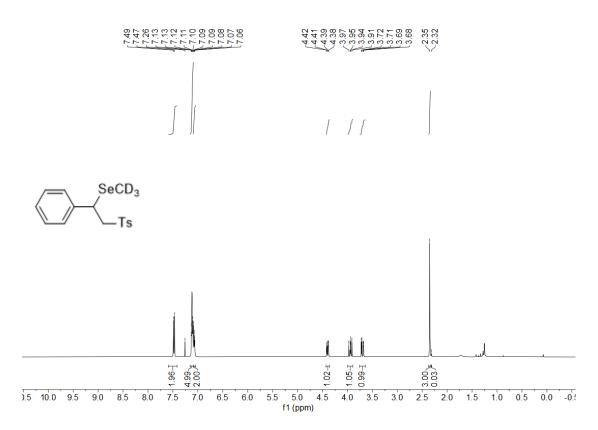


Supplementary Figure 175. ²H NMR Spectrum of 3h (100 MHz, CHCl₃)



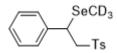
-2.15

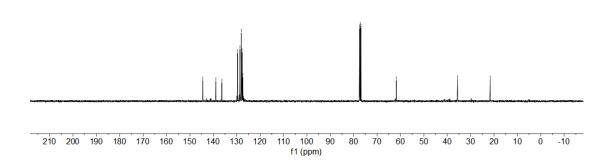
Supplementary Figure 176. ¹H NMR Spectrum of **3i** (400 MHz, CDCl₃)



Supplementary Figure 177. ¹³C NMR Spectrum of 3i (100 MHz, CDCl₃)

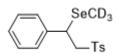


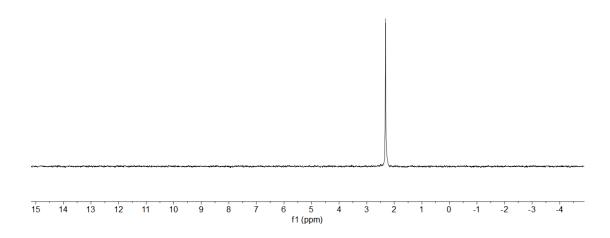




Supplementary Figure 178. ²H NMR Spectrum of **3i** (100 MHz, CHCl₃)



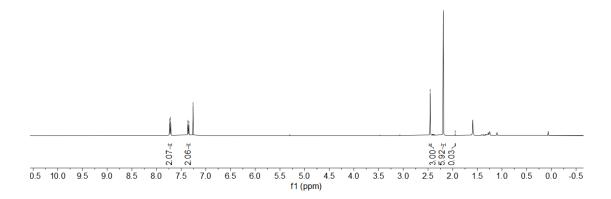




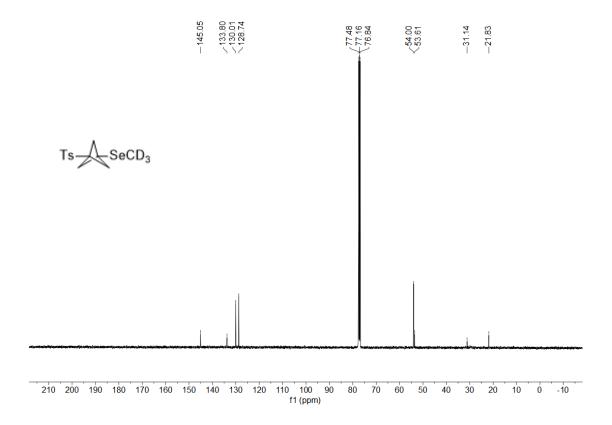
Supplementary Figure 179. ¹H NMR Spectrum of 3j (400 MHz, CDCl₃)



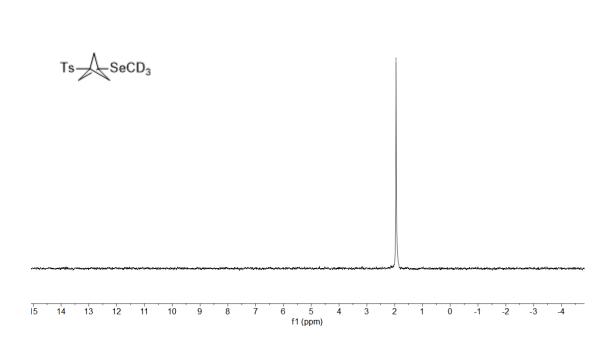




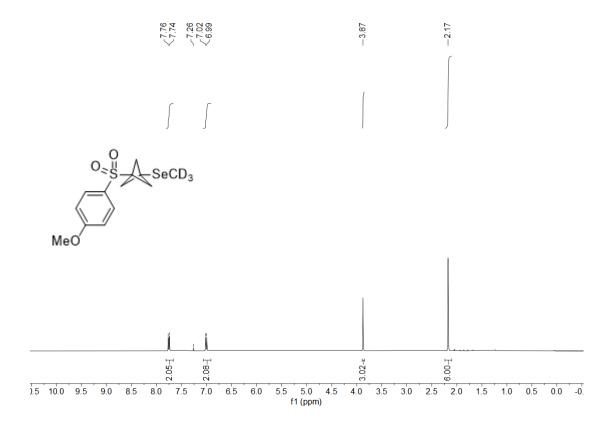
Supplementary Figure 180. ¹³C NMR Spectrum of 3j (100 MHz, CDCl₃)



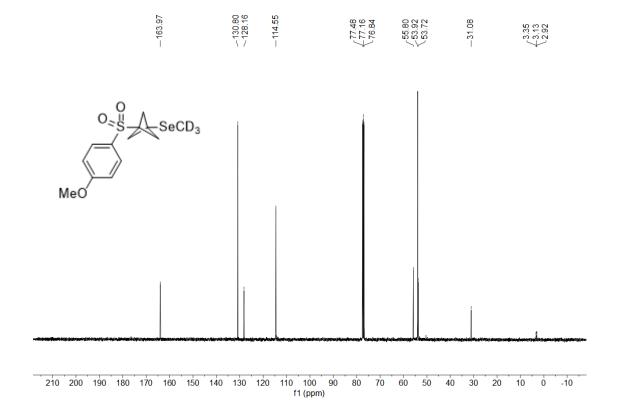
Supplementary Figure 181. ²H NMR Spectrum of 3j (100 MHz, CHCl₃)



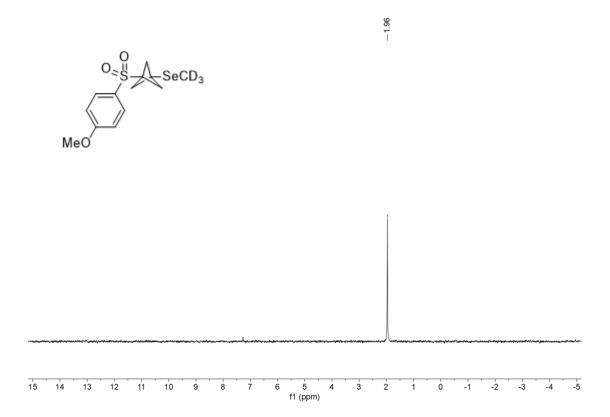
Supplementary Figure 182. 1 H NMR Spectrum of 3k (400 MHz, CDCl₃)



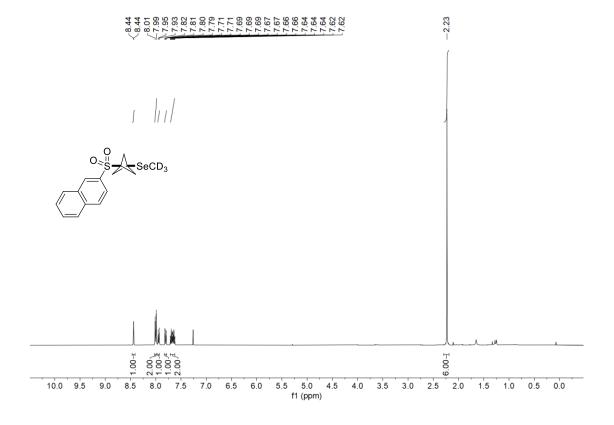
Supplementary Figure 183. ¹³C NMR Spectrum of 3k (400 MHz, CDCl₃)



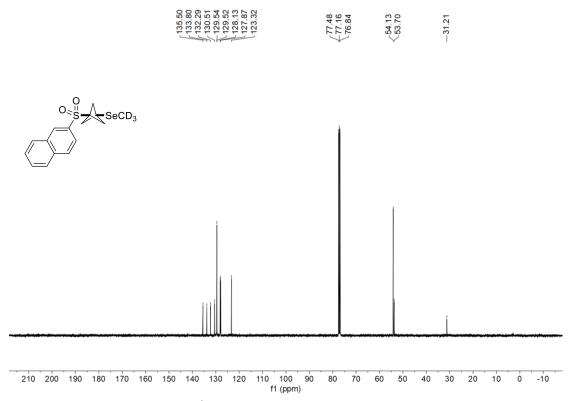
Supplementary Figure 184. ²H NMR Spectrum of 3k (100 MHz, CHCl₃)



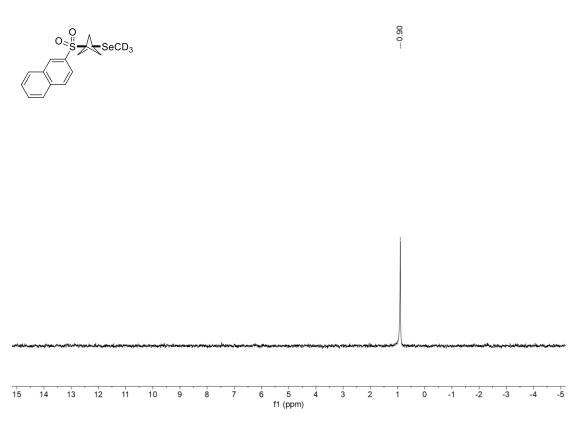
Supplementary Figure 185. ¹H NMR Spectrum of **3l** (400 MHz, CDCl₃)



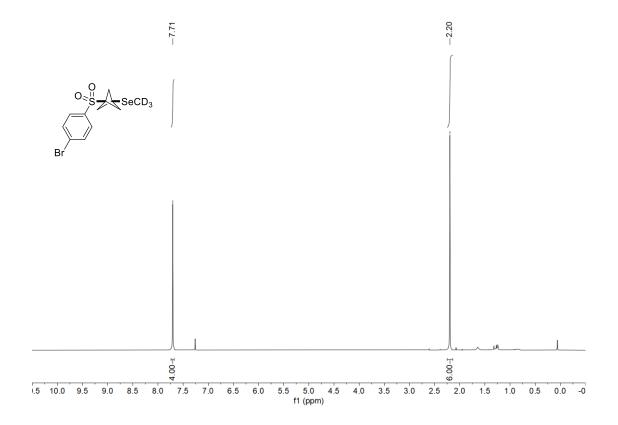
Supplementary Figure 186. ¹³C NMR Spectrum of 3l (100 MHz, CDCl₃)



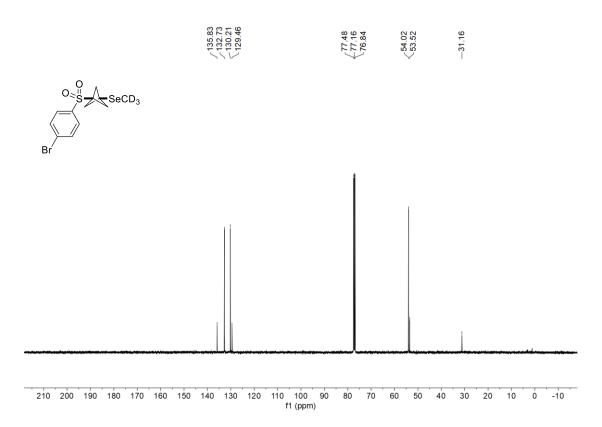
Supplementary Figure 187. ²H NMR Spectrum of 3l (100 MHz, CHCl₃)



Supplementary Figure 188. 1 H NMR Spectrum of 3m (400 MHz, CDCl $_3$)

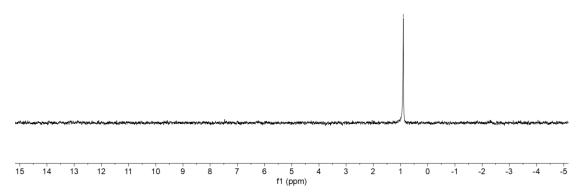


Supplementary Figure 189. ¹³C NMR Spectrum of 3m (100 MHz, CDCl₃)

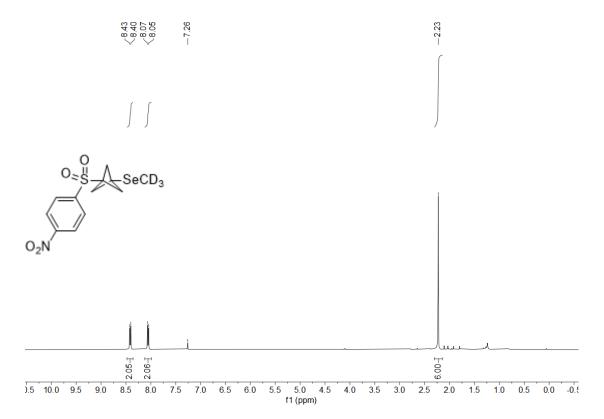


Supplementary Figure 190. ²H NMR Spectrum of 3m (100 MHz, CHCl₃)



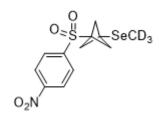


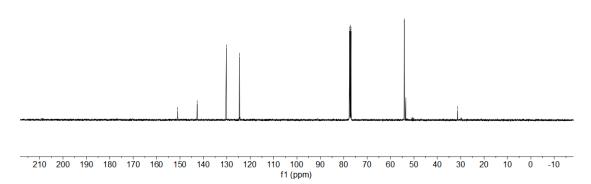
Supplementary Figure 191. ¹H NMR Spectrum of 3n (400 MHz, CDCl₃)



Supplementary Figure 192. ¹³C NMR Spectrum of **3n** (100 MHz, CDCl₃)



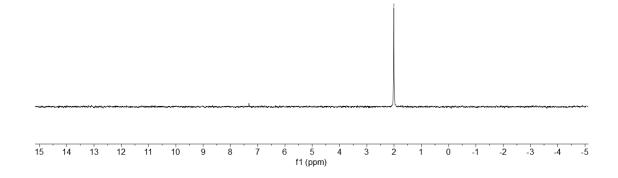




Supplementary Figure 193. ²H NMR Spectrum of 3n (100 MHz, CHCl₃)

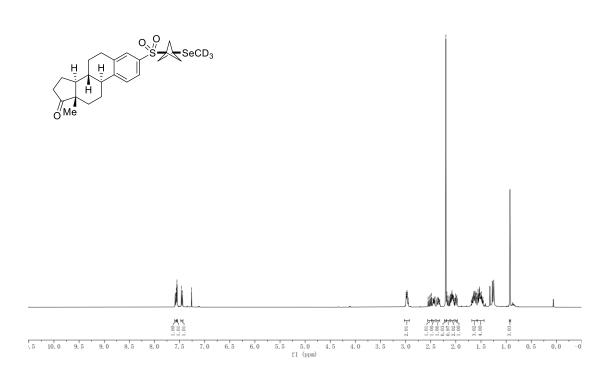
-2.01

$$O_{\approx}$$
 SeCD₃

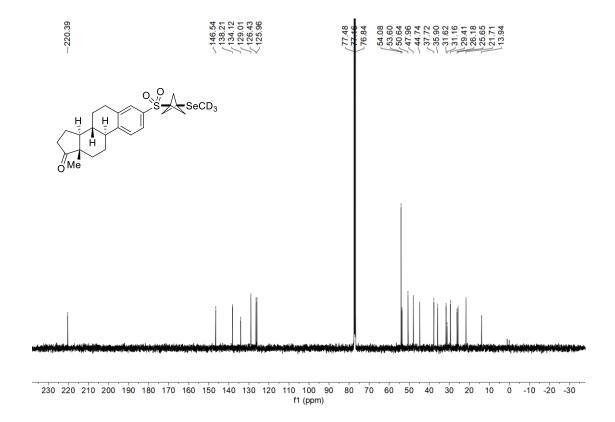


Supplementary Figure 194. ¹H NMR Spectrum of 3o (400 MHz, CDCl₃)

$\frac{1}{2}$

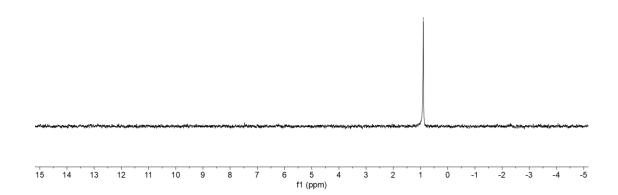


Supplementary Figure 195. ¹³C NMR Spectrum of 3o (100 MHz, CDCl₃)

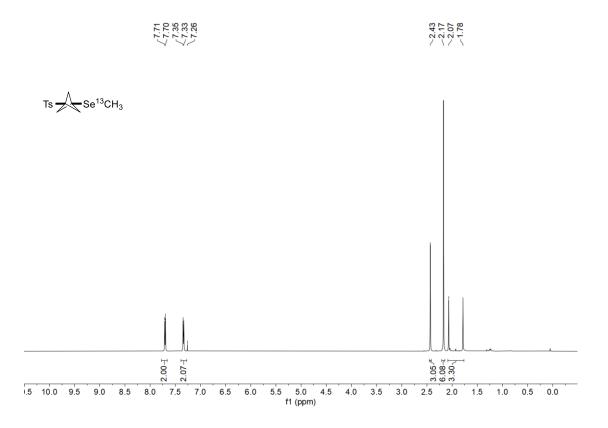


Supplementary Figure 196. ²H NMR Spectrum of **30** (100 MHz, CHCl₃)

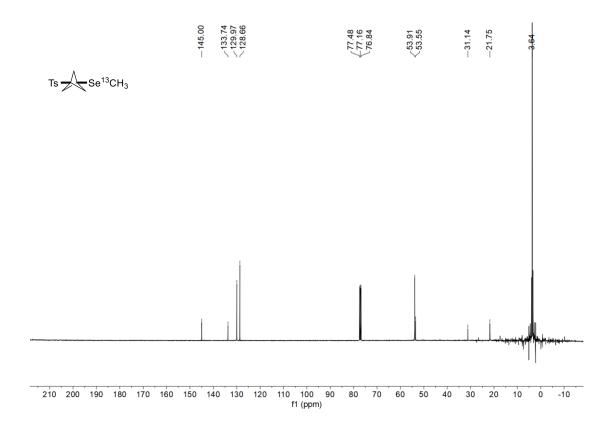




Supplementary Figure 197. ¹H NMR Spectrum of 3p (400 MHz, CDCl₃)

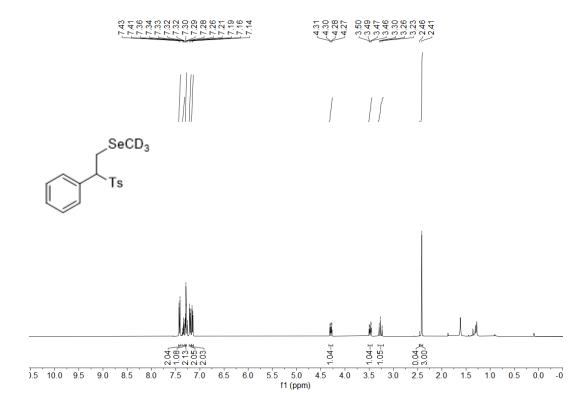


Supplementary Figure 198. ¹³C NMR Spectrum of 3p (100 MHz, CHCl₃)

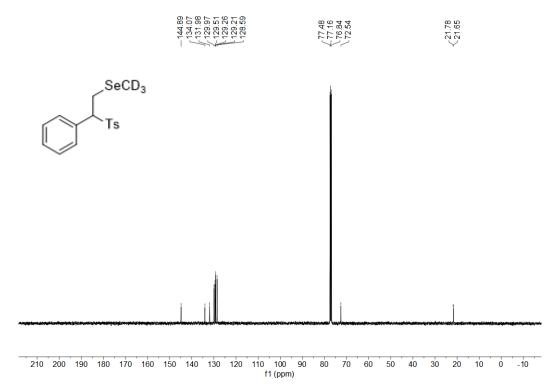


11.3 NMR Spectra of Difunctionalized Products

Supplementary Figure 199. ¹H NMR Spectrum of 5a (400 MHz, CDCl₃)

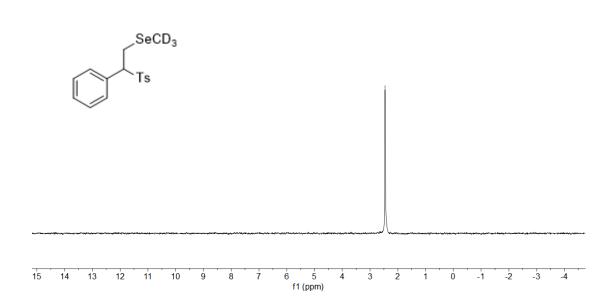


Supplementary Figure 200. ¹³C NMR Spectrum of 5a (100 MHz, CDCl₃)

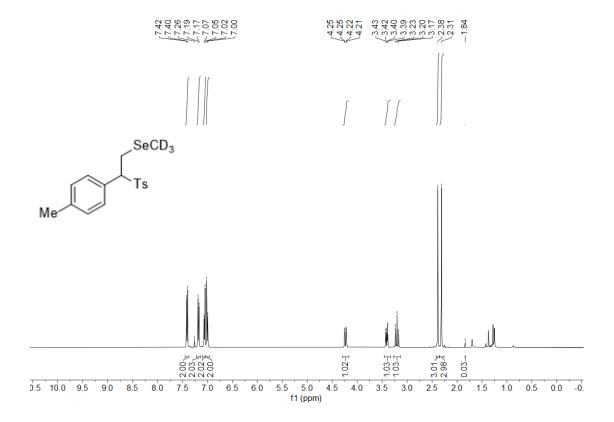


Supplementary Figure 201. ²H NMR Spectrum of **5a** (100 MHz, CHCl₃)

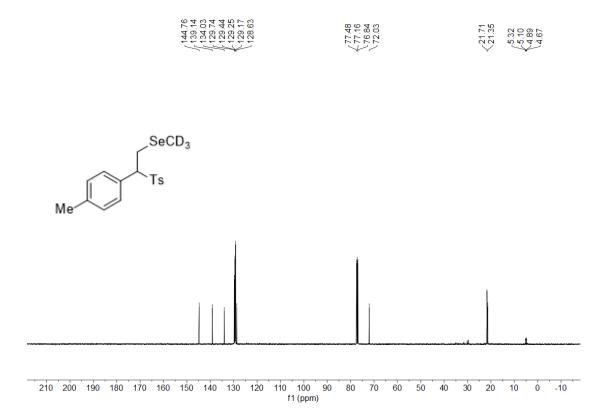




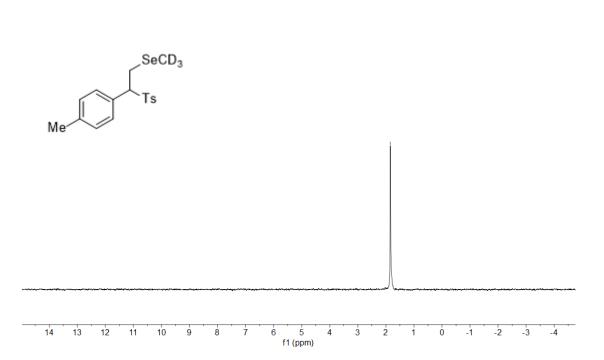
Supplementary Figure 202. ¹H NMR Spectrum of **5b** (400 MHz, CDCl₃)



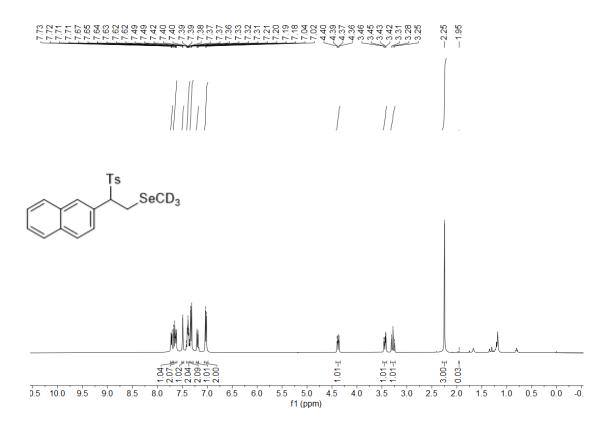
Supplementary Figure 203. ¹³C NMR Spectrum of 5b (100 MHz, CDCl₃)



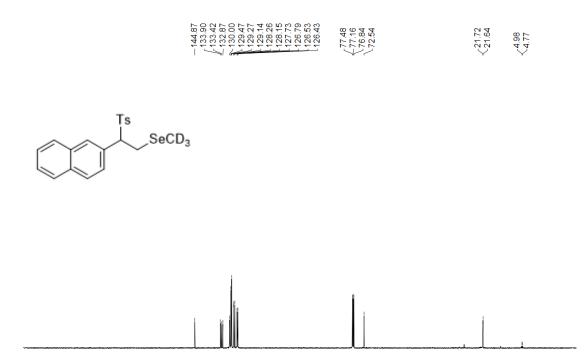
Supplementary Figure 204. ²H NMR Spectrum of 5b (100 MHz, CHCl₃)



Supplementary Figure 205. ¹H NMR Spectrum of 5c (400 MHz, CDCl₃)

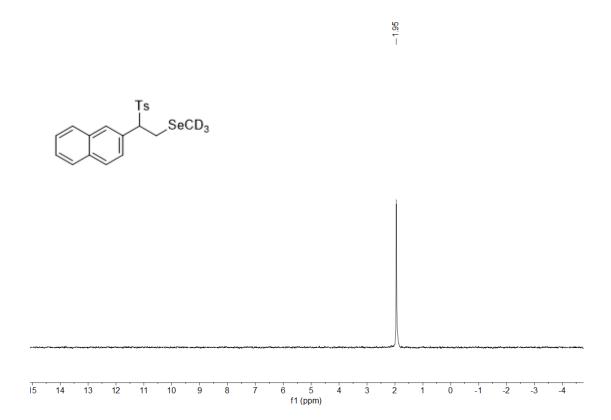


Supplementary Figure 206. ¹³C NMR Spectrum of 5c (100 MHz, CDCl₃)

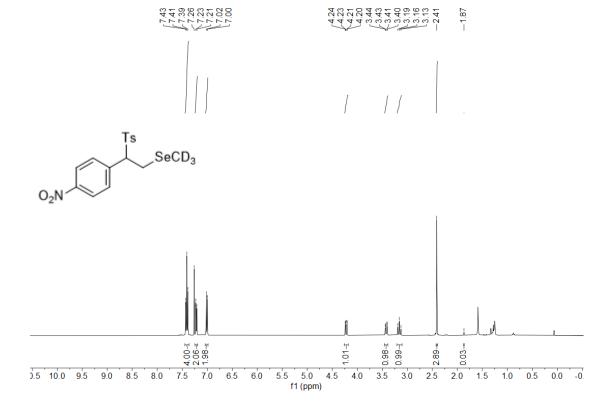


210 200 190 180 170 160 150 140 130 120 110 100 90 f1 (ppm)

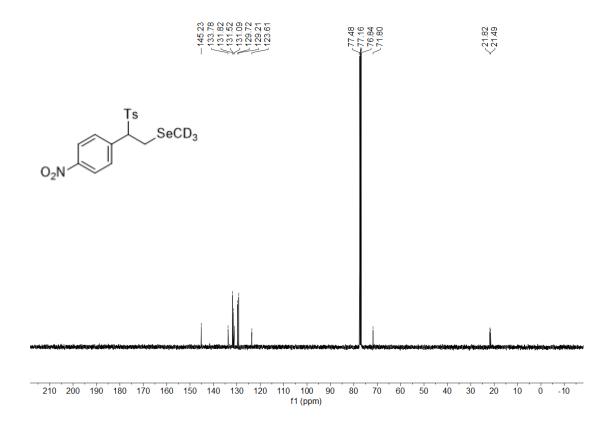
Supplementary Figure 207. ²H NMR Spectrum of **5c** (100 MHz, CHCl₃)



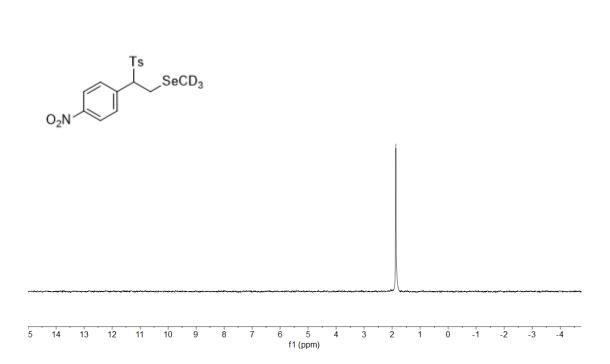
Supplementary Figure 208. ¹H NMR Spectrum of 5d (400 MHz, CDCl₃)



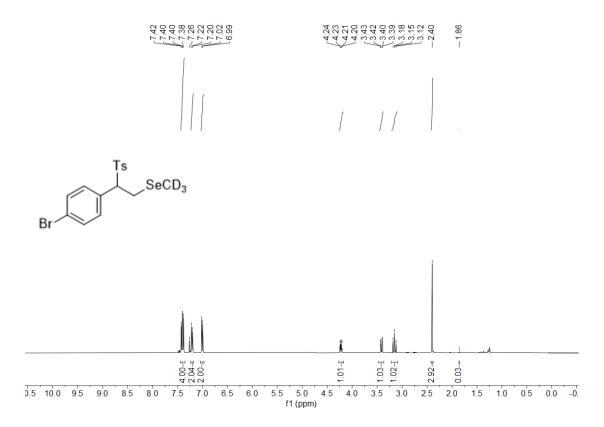
Supplementary Figure 209. ¹³C NMR Spectrum of 5d (100 MHz, CDCl₃)



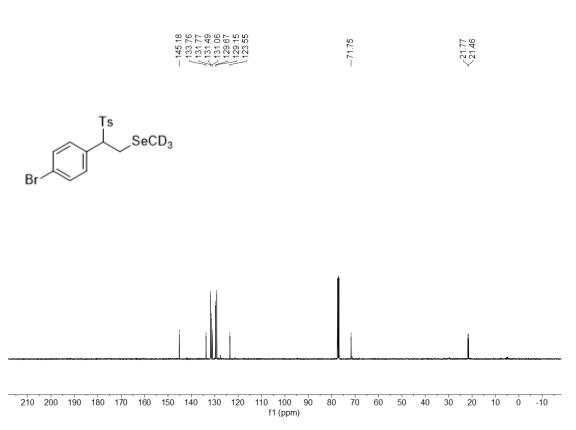
Supplementary Figure 210. ²H NMR Spectrum of 5d (100 MHz, CHCl₃)



Supplementary Figure 211. ¹H NMR Spectrum of 5e (400 MHz, CDCl₃)

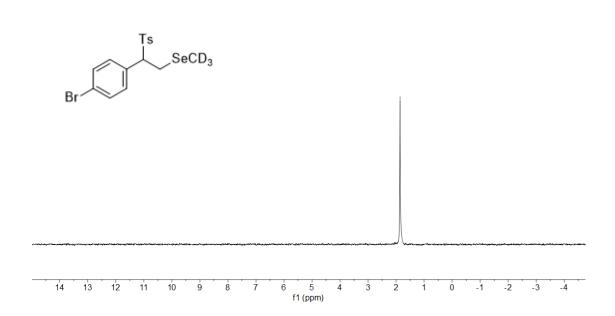


Supplementary Figure 212. ¹³C NMR Spectrum of **5e** (100 MHz, CDCl₃)

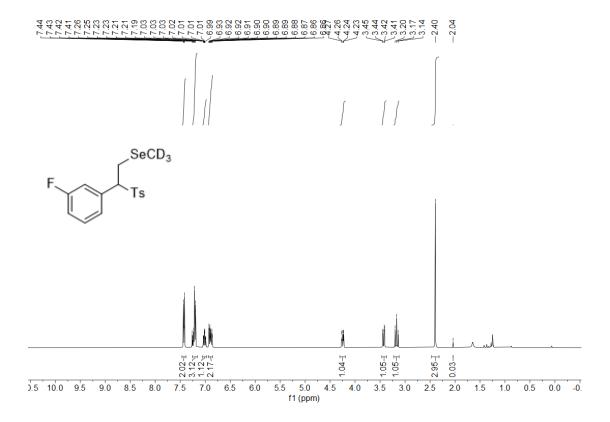


Supplementary Figure 213. ²H NMR Spectrum of **5e** (100 MHz, CHCl₃)

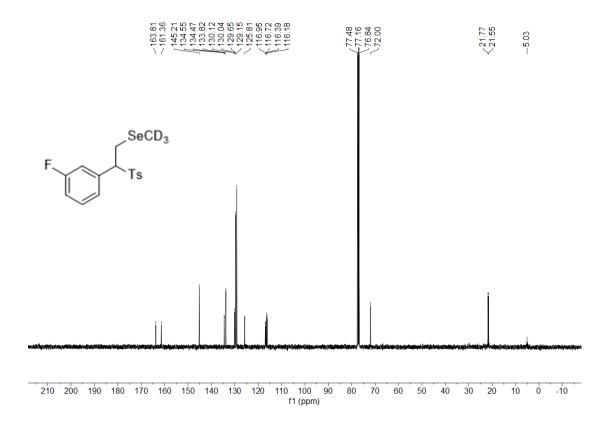




Supplementary Figure 214. ¹H NMR Spectrum of **5f** (400 MHz, CDCl₃)

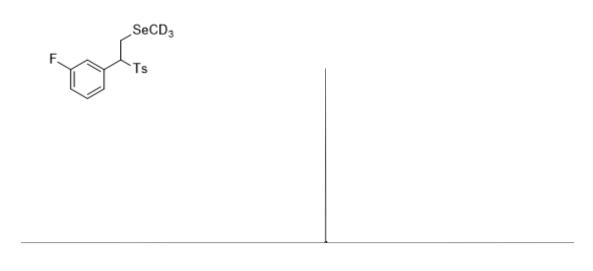


Supplementary Figure 215. ¹³C NMR Spectrum of 5f (100 MHz, CDCl₃)

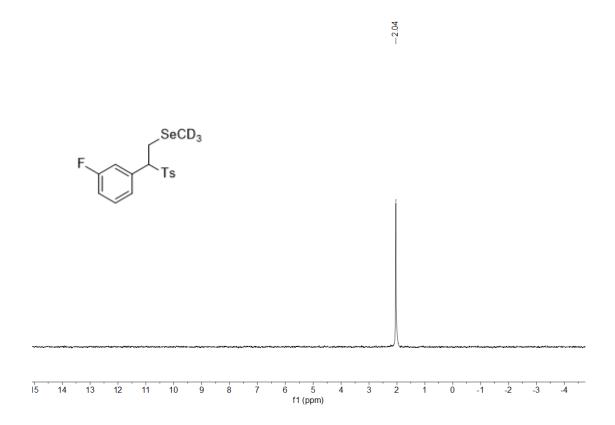


Supplementary Figure 216. ²H NMR Spectrum of 5f (100 MHz, CHCl₃)

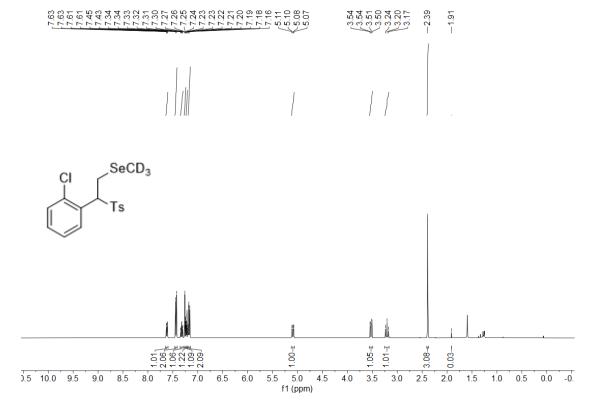
-112.12



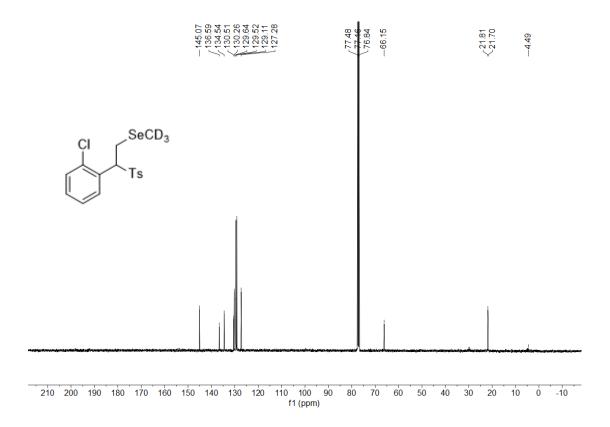
Supplementary Figure 217. ²H NMR Spectrum of 5f (100 MHz, CDCl₃)



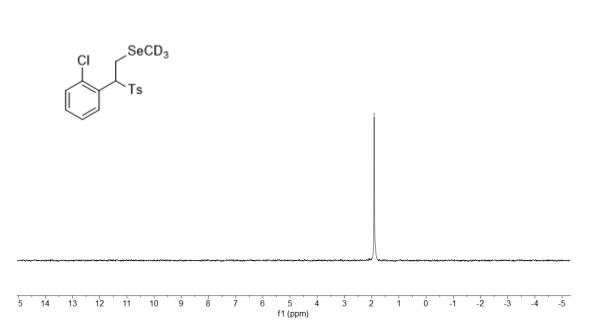
Supplementary Figure 218. ¹H NMR Spectrum of 5g (400 MHz, CDCl₃)



Supplementary Figure 219. ¹³C NMR Spectrum of 5g (100 MHz, CDCl₃)

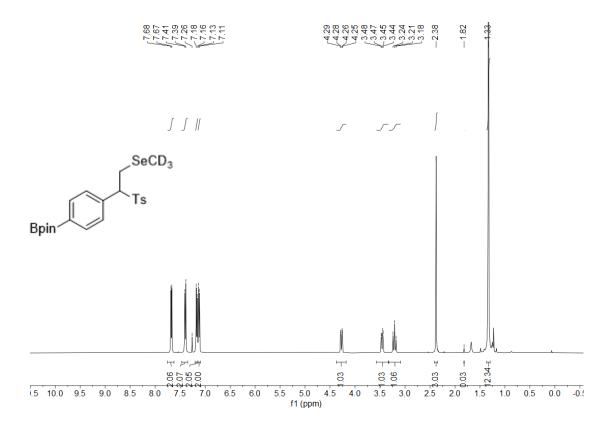


Supplementary Figure 220. ²H NMR Spectrum of 5g (100 MHz, CHCl₃)

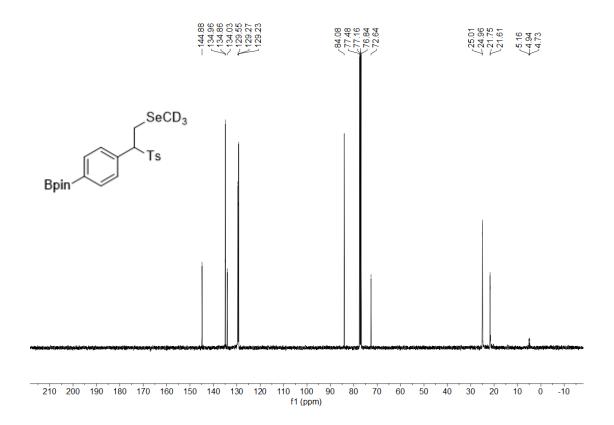


1.91

Supplementary Figure 221. ¹H NMR Spectrum of 5h (400 MHz, CDCl₃)

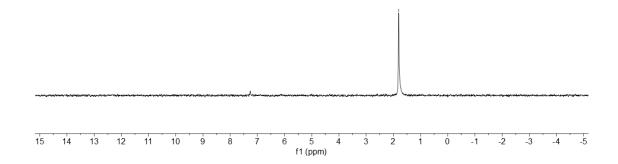


Supplementary Figure 222. ¹³C NMR Spectrum of 5h (100 MHz, CDCl₃)

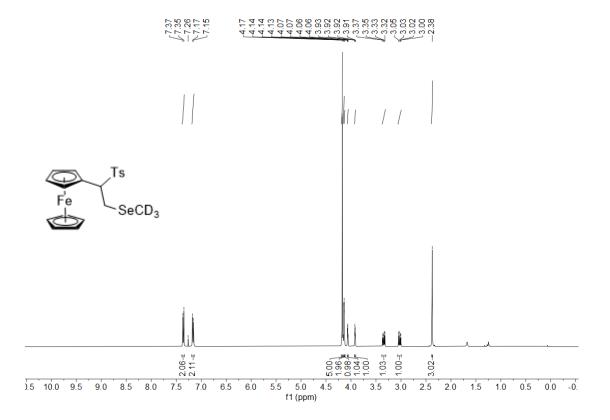


Supplementary Figure 223. ²H NMR Spectrum of **5h** (100 MHz, CHCl₃)

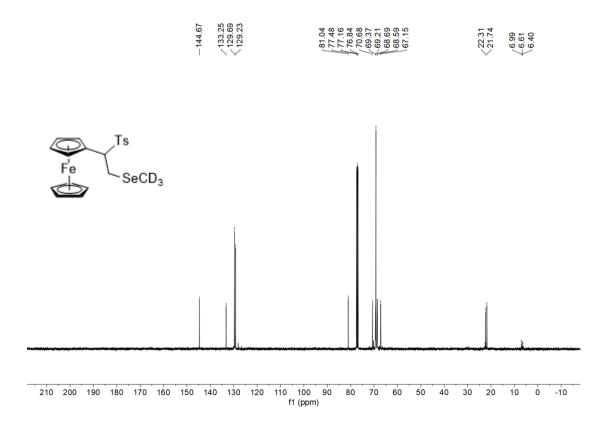
1.81



Supplementary Figure 224. ¹H NMR Spectrum of **5i** (400 MHz, CDCl₃)

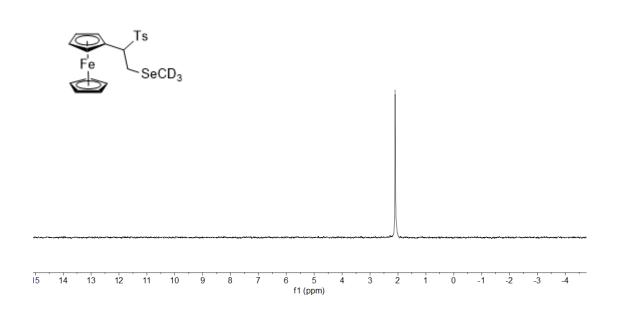


Supplementary Figure 225. ¹³C NMR Spectrum of 5i (100 MHz, CDCl₃)

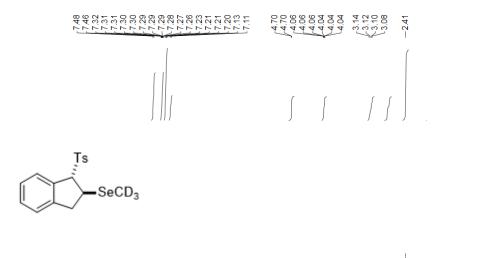


Supplementary Figure 226. ²H NMR Spectrum of 5i (100 MHz, CHCl₃)



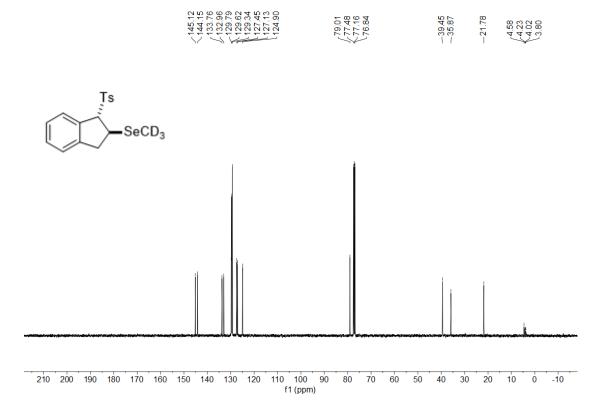


Supplementary Figure 227. ¹H NMR Spectrum of 5j (400 MHz, CDCl₃)



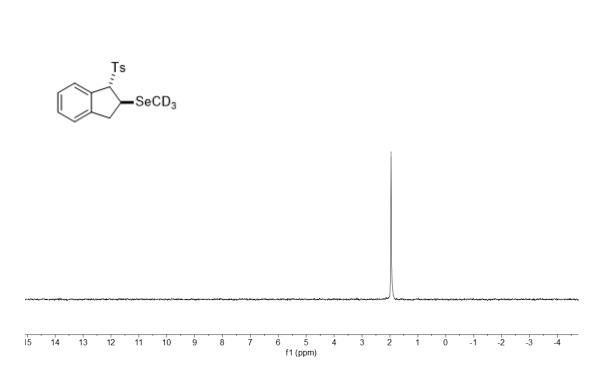
2.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0 f1 (ppm)

Supplementary Figure 228. ¹³C NMR Spectrum of 5j (100 MHz, CDCl₃)

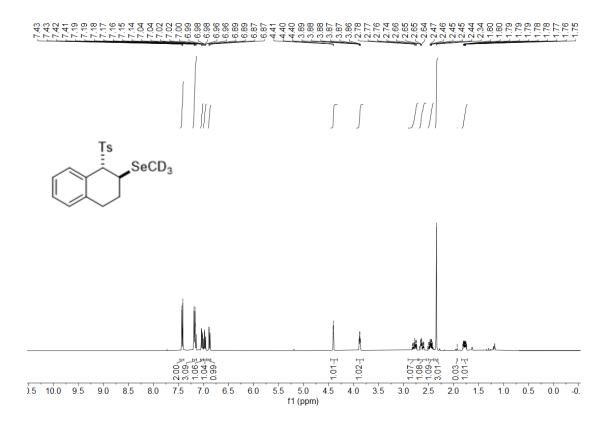


Supplementary Figure 229. ²H NMR Spectrum of **5j** (100 MHz, CHCl₃)

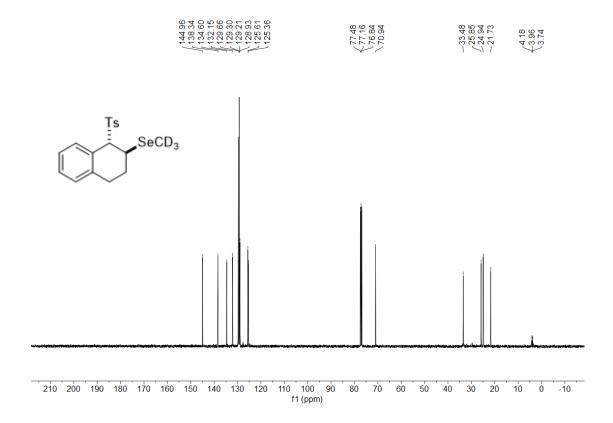




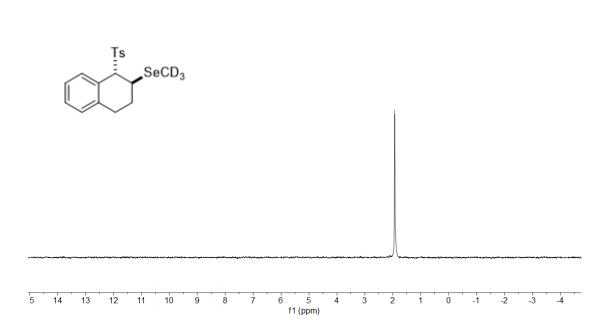
Supplementary Figure 230. ¹H NMR Spectrum of 5k (400 MHz, CDCl₃)



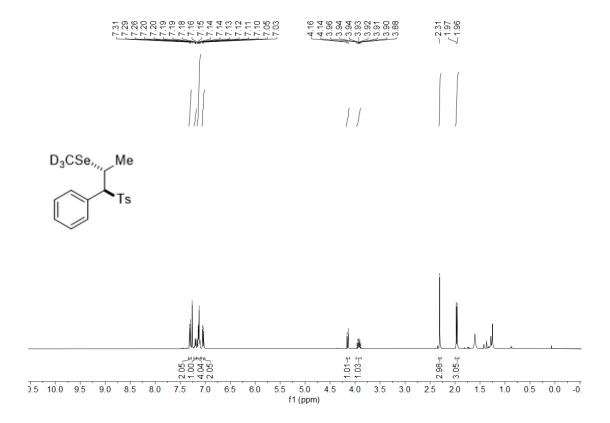
Supplementary Figure 231. ¹³C NMR Spectrum of 5k (100 MHz, CDCl₃)



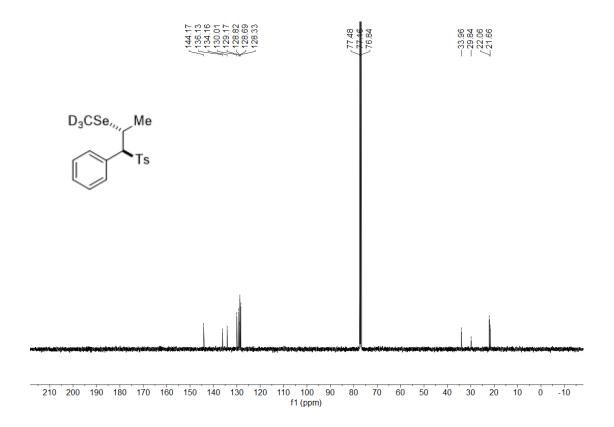
Supplementary Figure 232. ²H NMR Spectrum of 5k (100 MHz, CHCl₃)



Supplementary Figure 233. ¹H NMR Spectrum of 5l (400 MHz, CDCl₃)

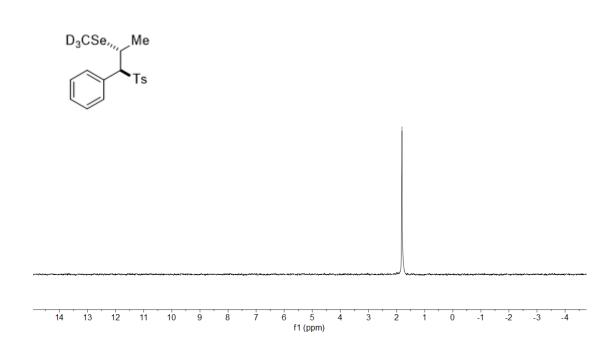


Supplementary Figure 234. ¹³C NMR Spectrum of 5l (100 MHz, CDCl₃)

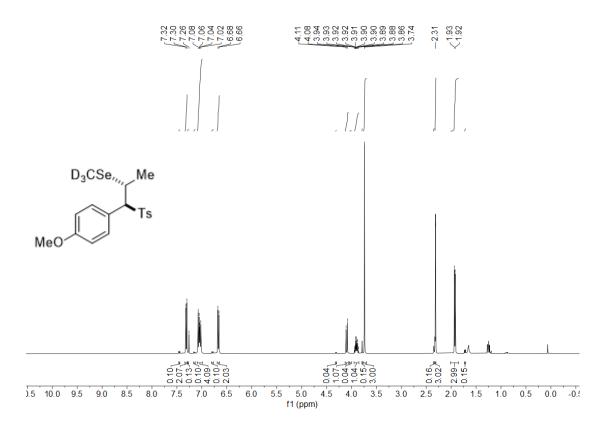


Supplementary Figure 235. ²H NMR Spectrum of **5l** (100 MHz, CHCl₃)



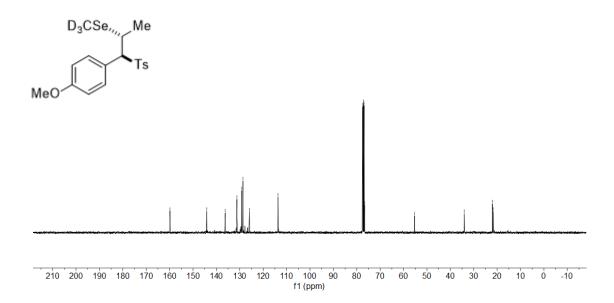


Supplementary Figure 236. ¹H NMR Spectrum of 5m (400 MHz, CDCl₃)



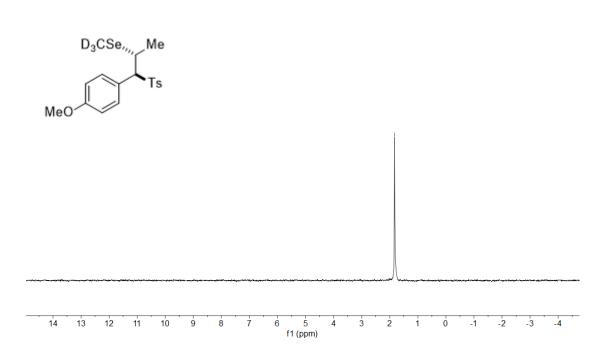
Supplementary Figure 237. ¹³C NMR Spectrum of 5m (100 MHz, CDCl₃)



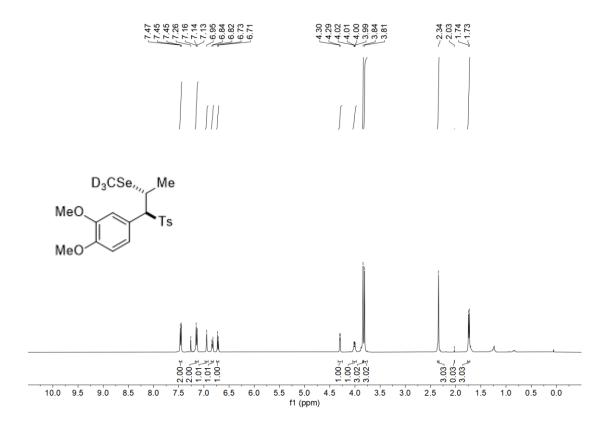


Supplementary Figure 238. ²H NMR Spectrum of 5m (100 MHz, CHCl₃)

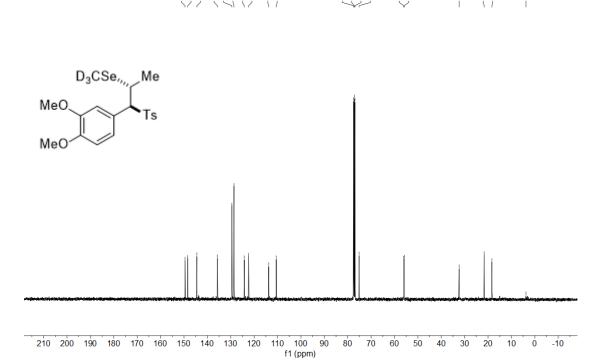
-1.83



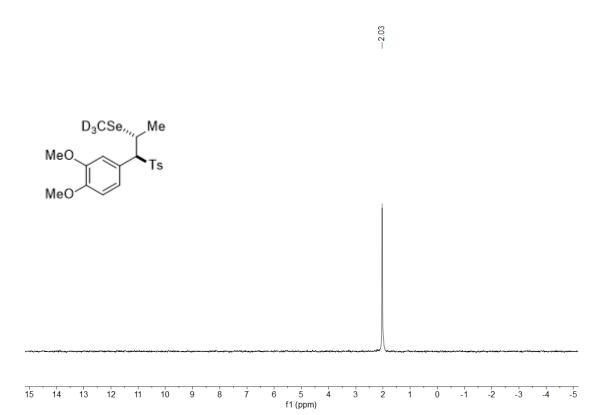
Supplementary Figure 239. ¹H NMR Spectrum of 5n (400 MHz, CDCl₃)



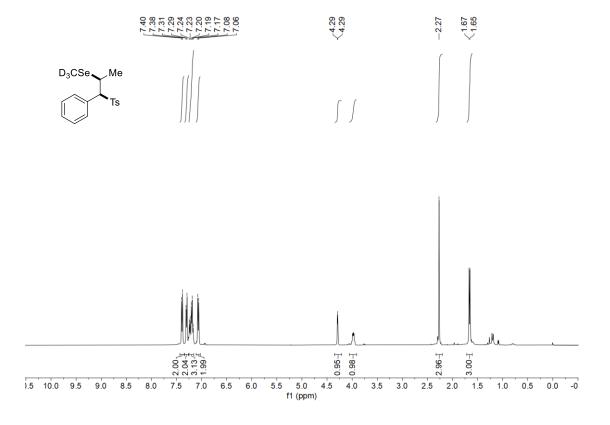
Supplementary Figure 240. ¹³C NMR Spectrum of 5n (100 MHz, CDCl₃)



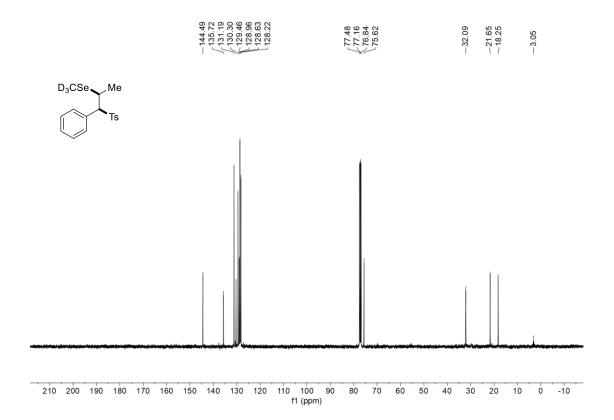
Supplementary Figure 241. ²H NMR Spectrum of 5n (100 MHz, CHCl₃)



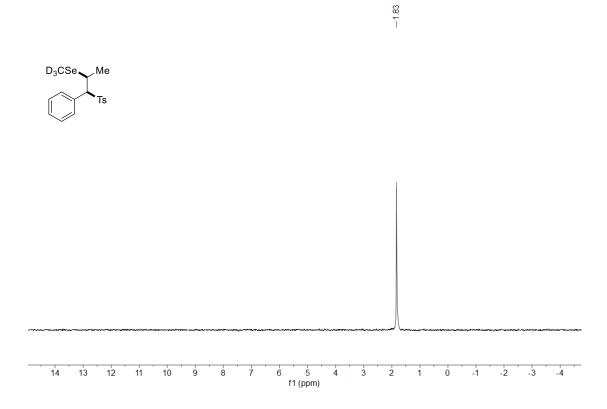
Supplementary Figure 242. ¹H NMR Spectrum of 50 (400 MHz, CDCl₃)



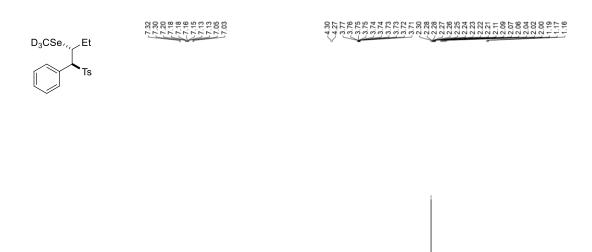
Supplementary Figure 243. ¹³C NMR Spectrum of 50 (400 MHz, CDCl₃)



Supplementary Figure 244. ²H NMR Spectrum of 50 (100 MHz, CHCl₃)



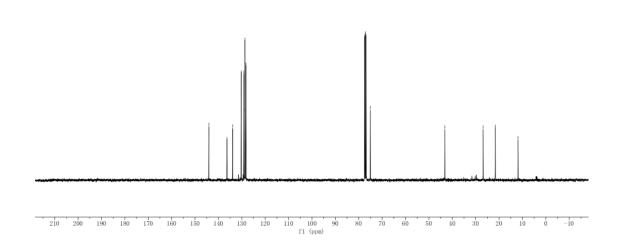
Supplementary Figure 245. ¹H NMR Spectrum of 5p (400 MHz, CDCl₃)



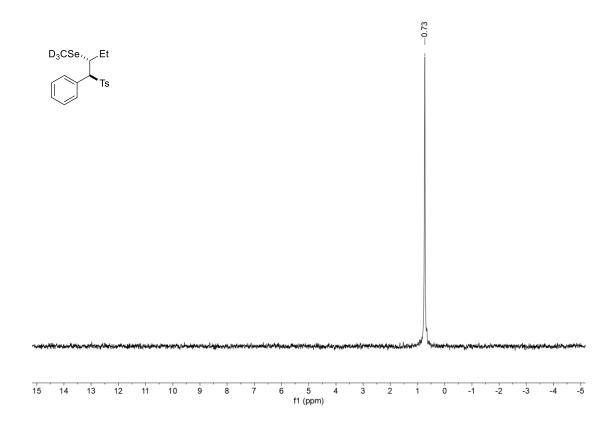
5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.

Supplementary Figure 246. ¹³C NMR Spectrum of 5p (400 MHz, CDCl₃)

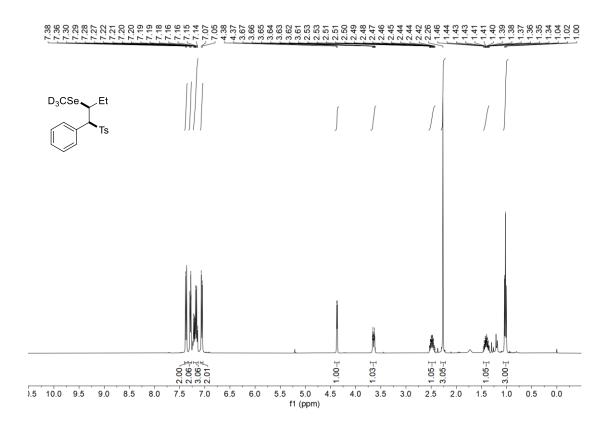




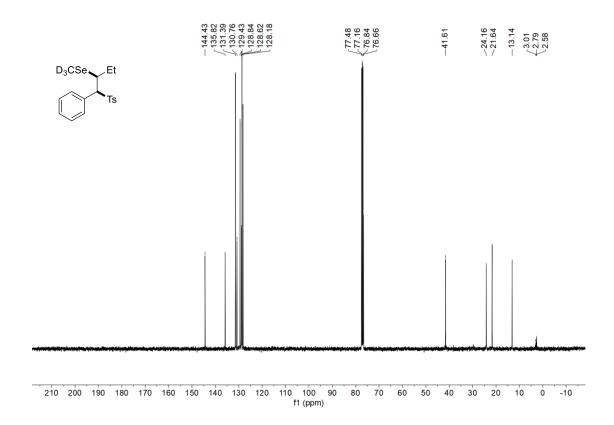
Supplementary Figure 247. ²H NMR Spectrum of **5p** (100 MHz, CHCl₃)



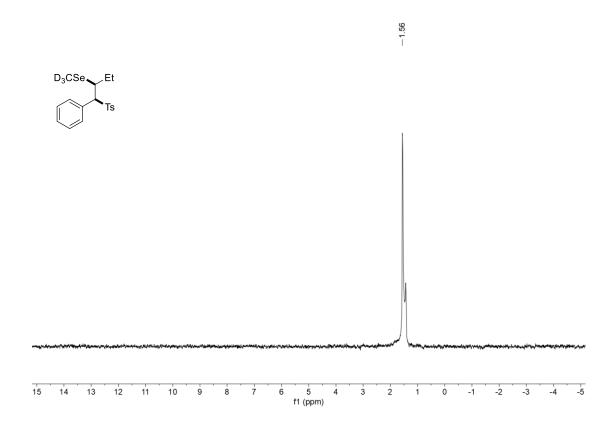
Supplementary Figure 248. ¹H NMR Spectrum of 5q (400 MHz, CDCl₃)



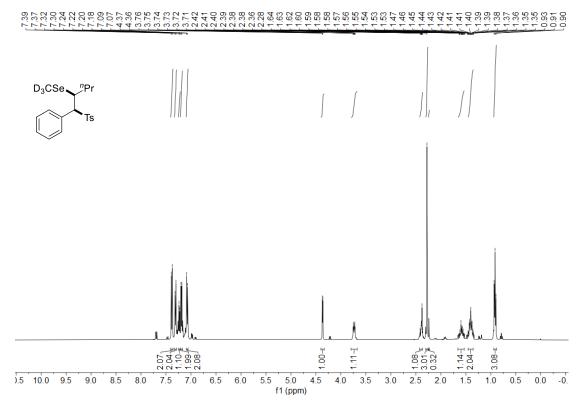
Supplementary Figure 249. ¹H NMR Spectrum of 5q (400 MHz, CDCl₃)

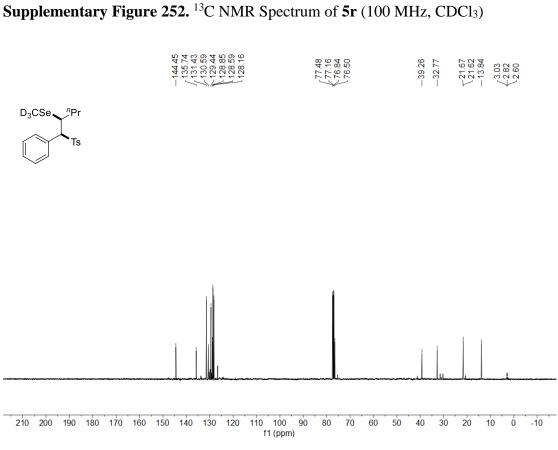


Supplementary Figure 250. ²H NMR Spectrum of 5q (100 MHz, CHCl₃)

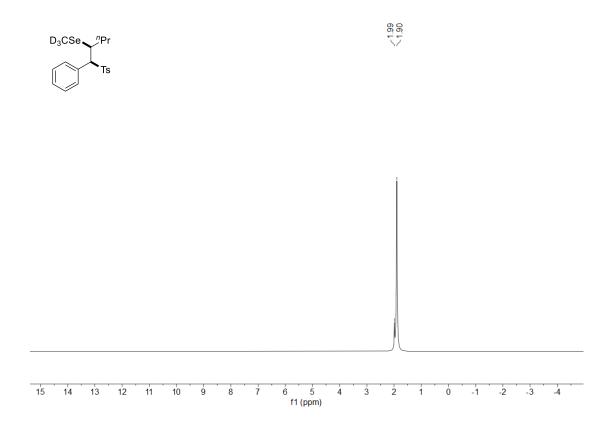


Supplementary Figure 251. ¹H NMR Spectrum of **5r** (400 MHz, CDCl₃)

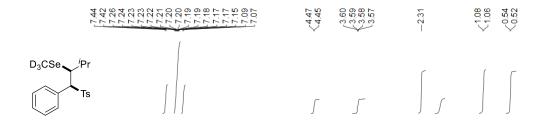


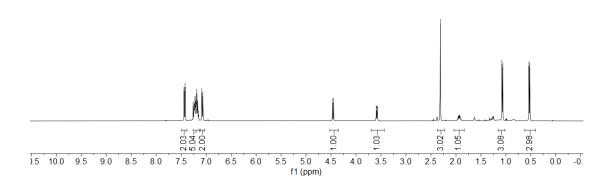


Supplementary Figure 253. ²H NMR Spectrum of 5r (100 MHz, CHCl₃)

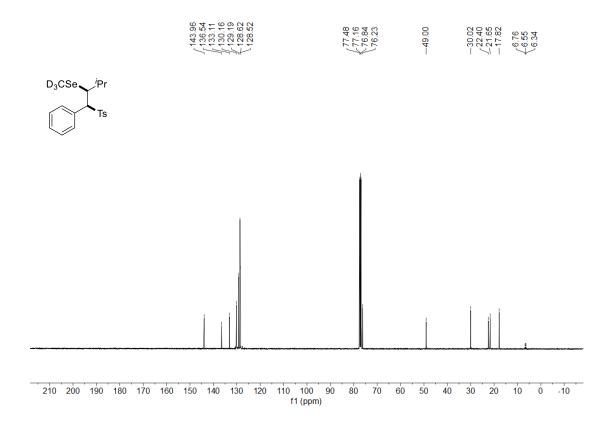


Supplementary Figure 254. ¹H NMR Spectrum of 5s (400 MHz, CDCl₃)

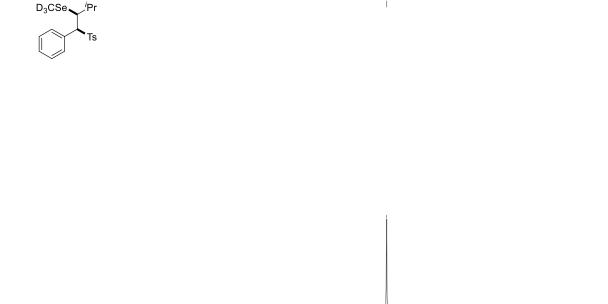




Supplementary Figure 255. ¹³C NMR Spectrum of 5s (100 MHz, CDCl₃)

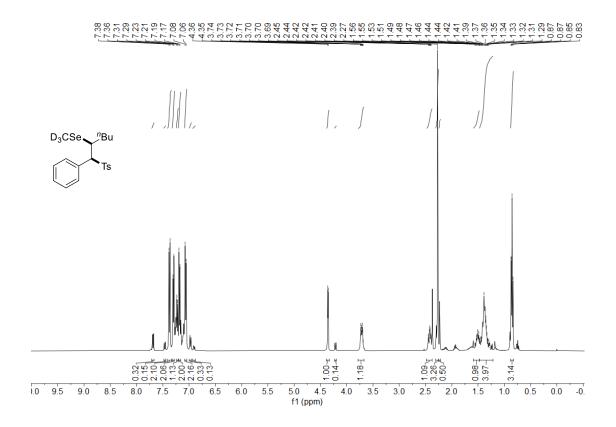


Supplementary Figure 256. ²H NMR Spectrum of 5s (100 MHz, CHCl₃)

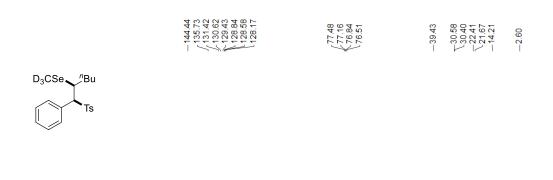


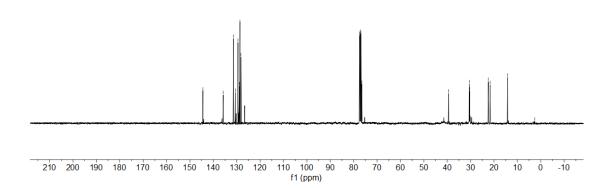
f1 (ppm)

Supplementary Figure 257. ¹H NMR Spectrum of 5t (400 MHz, CDCl₃)

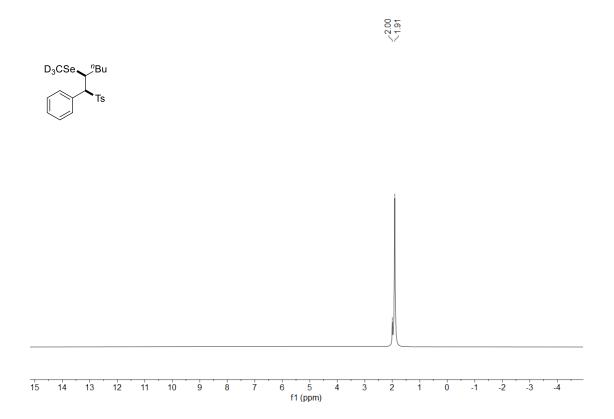


Supplementary Figure 258. ¹³C NMR Spectrum of 5t (100 MHz, CDCl₃)

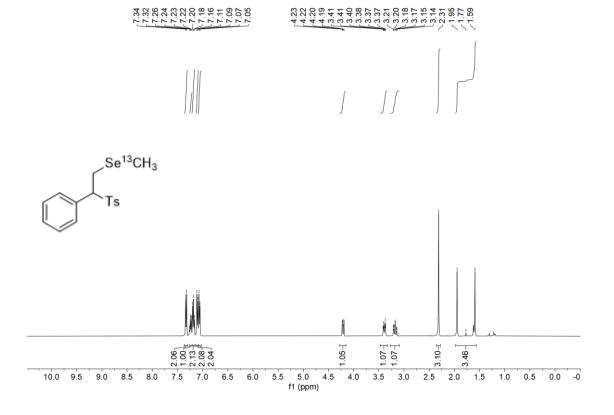




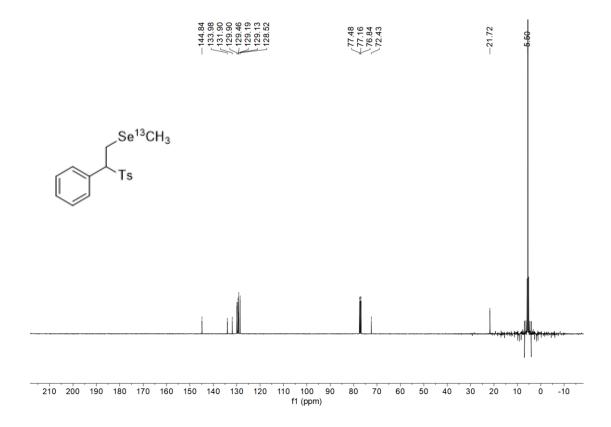
Supplementary Figure 259. ²H NMR Spectrum of **5t** (100 MHz, CHCl₃)



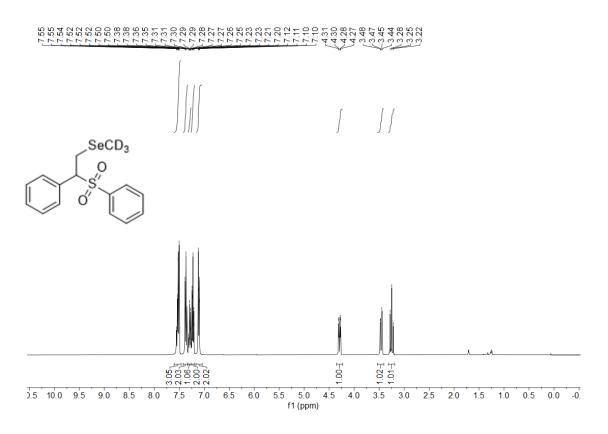
Supplementary Figure 260. ¹H NMR Spectrum of 5u (400 MHz, CDCl₃)



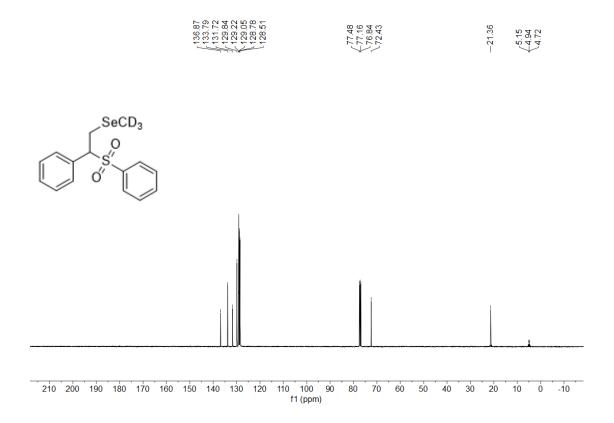
Supplementary Figure 261. ¹³C NMR Spectrum of 5u (100 MHz, CDCl₃)



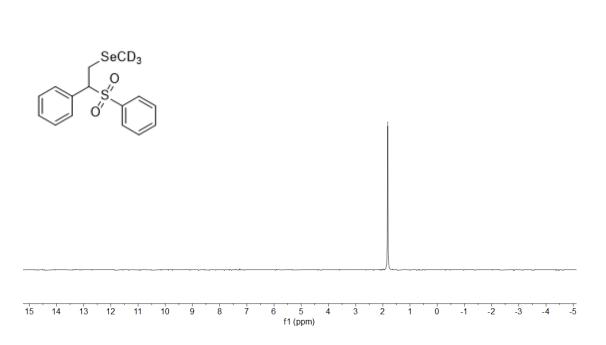
Supplementary Figure 262. ¹H NMR Spectrum of 5v (400 MHz, CDCl₃)



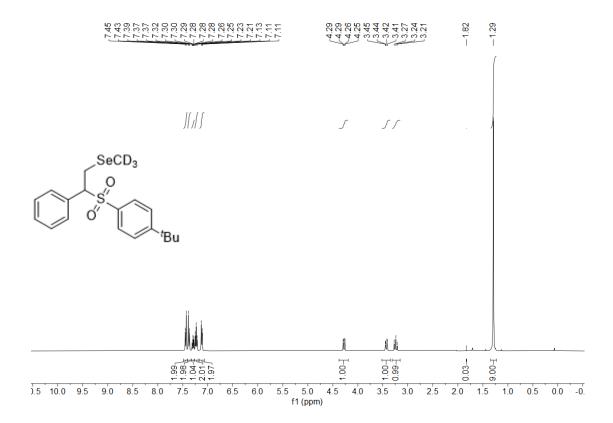
Supplementary Figure 263. ¹³C NMR Spectrum of 5v (100 MHz, CDCl₃)



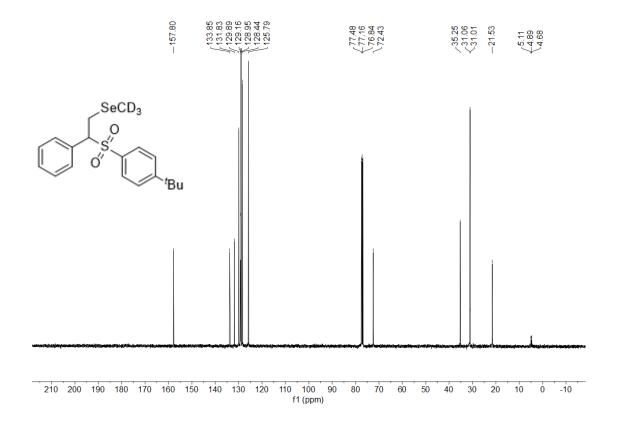
Supplementary Figure 264. ²H NMR Spectrum of 5v (100 MHz, CHCl₃)



Supplementary Figure 265. ¹H NMR Spectrum of 5w (400 MHz, CDCl₃)

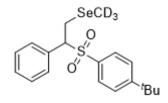


Supplementary Figure 266. ¹³C NMR Spectrum of 5w (100 MHz, CDCl₃)



Supplementary Figure 267. ²H NMR Spectrum of **5w** (100 MHz, CHCl₃)

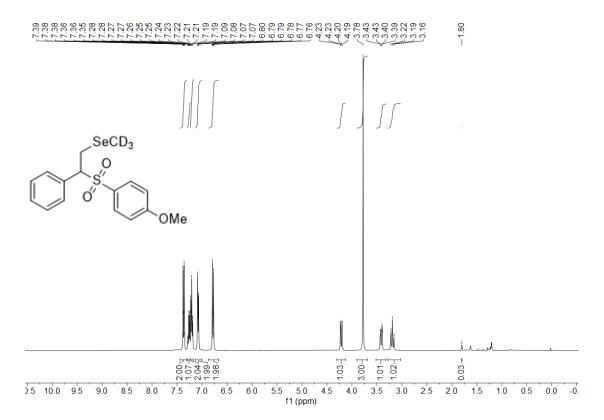




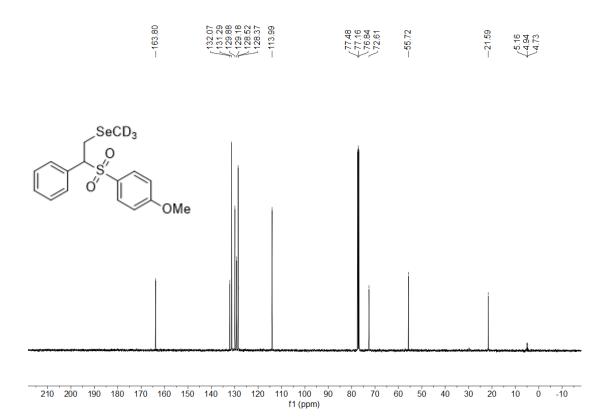


15.0 14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 f1 (ppm)

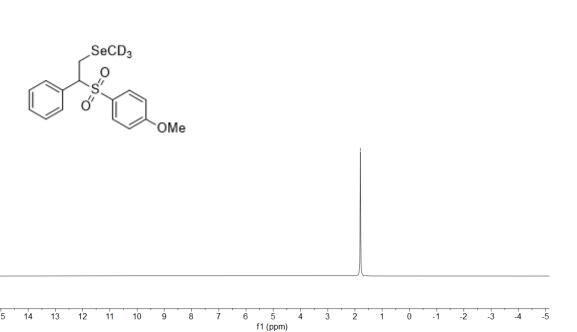
Supplementary Figure 268. ¹H NMR Spectrum of 5x (400 MHz, CDCl₃)



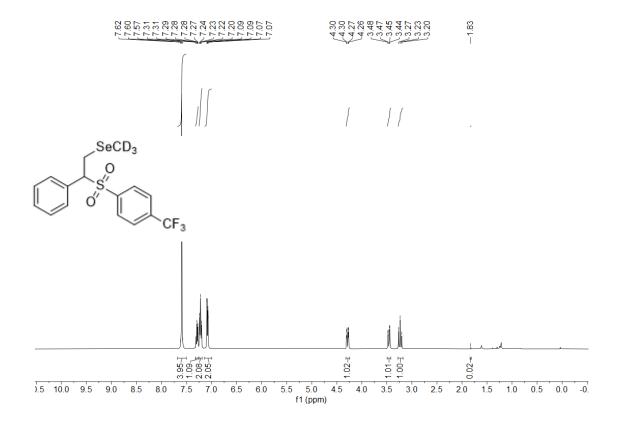
Supplementary Figure 269. ¹³C NMR Spectrum of 5x (100 MHz, CDCl₃)



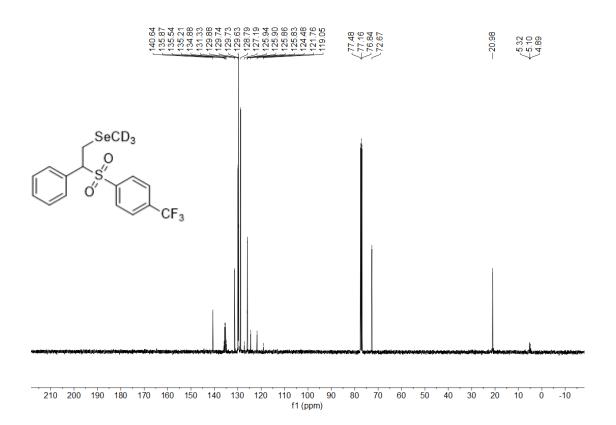
Supplementary Figure 270. ²H NMR Spectrum of 5x (100 MHz, CHCl₃)



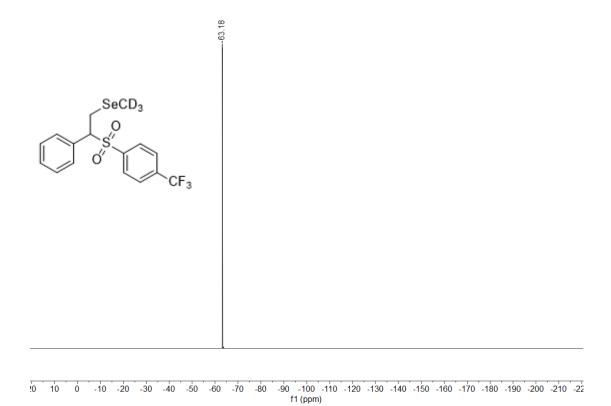
Supplementary Figure 271. ¹H NMR Spectrum of **5y** (400 MHz, CDCl₃)



Supplementary Figure 272. ¹³C NMR Spectrum of 5y (100 MHz, CDCl₃)

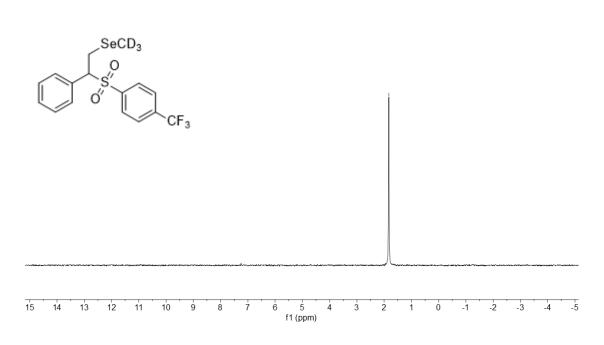


Supplementary Figure 273. ¹⁹F NMR Spectrum of 5y (376 MHz, CDCl₃)

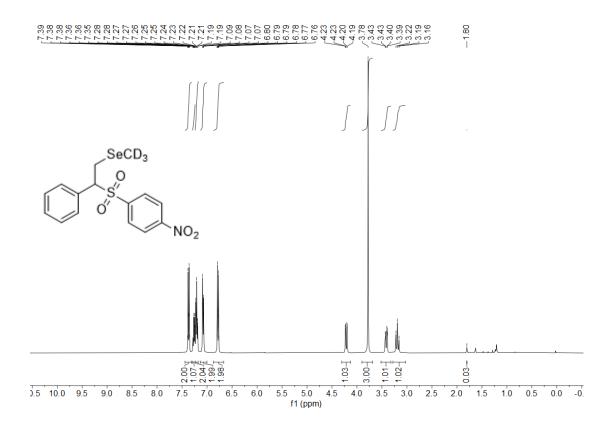


Supplementary Figure 274. ²H NMR Spectrum of 5y (100 MHz, CHCl₃)

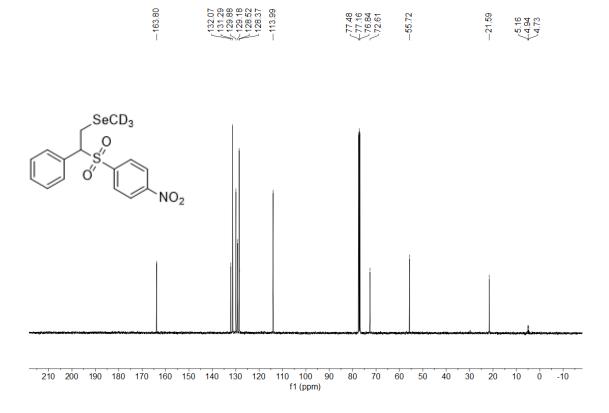




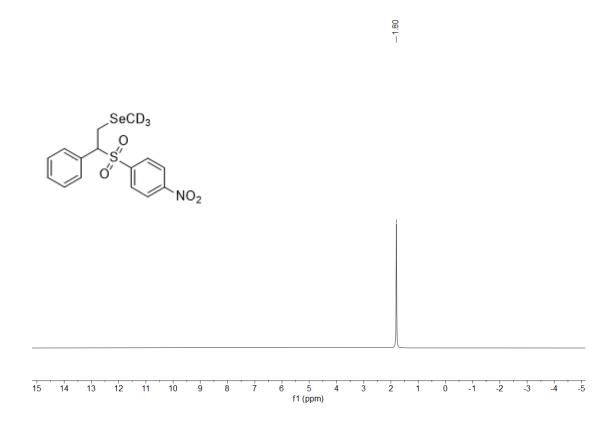
Supplementary Figure 275. ¹H NMR Spectrum of **5z** (400 MHz, CDCl₃)



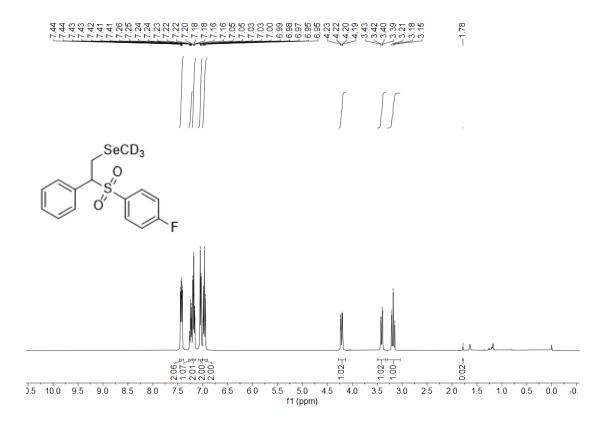
Supplementary Figure 276. ¹³C NMR Spectrum of 5z (100 MHz, CDCl₃)



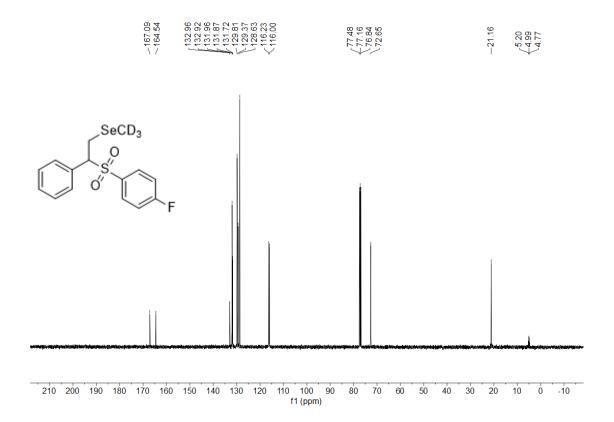
Supplementary Figure 277. ²H NMR Spectrum of **5z** (100 MHz, CHCl₃)



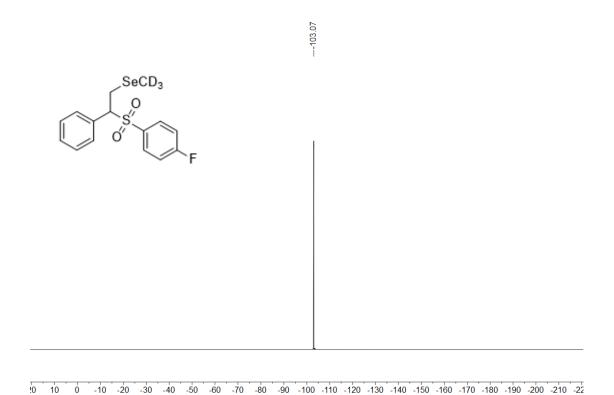
Supplementary Figure 278. ¹H NMR Spectrum of 5aa (400 MHz, CDCl₃)



Supplementary Figure 279. ¹³C NMR Spectrum of 5aa (100 MHz, CDCl₃)

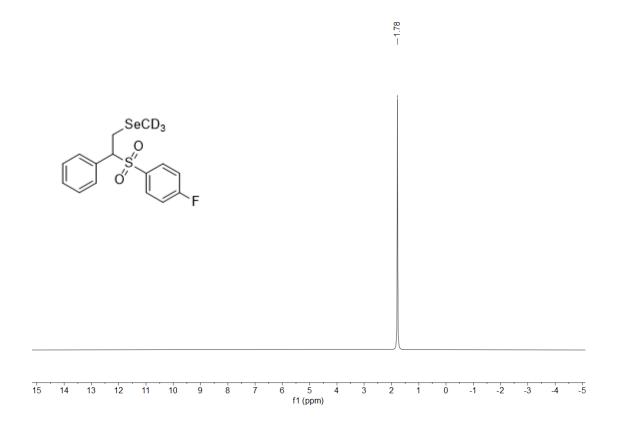


Supplementary Figure 280. ¹⁹F NMR Spectrum of 5aa (376 MHz, CDCl₃)

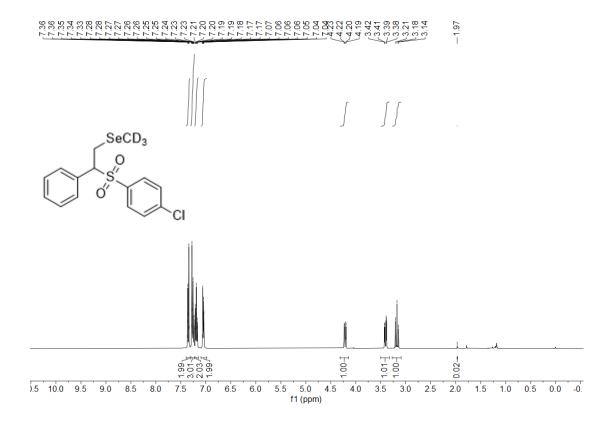


f1 (ppm)

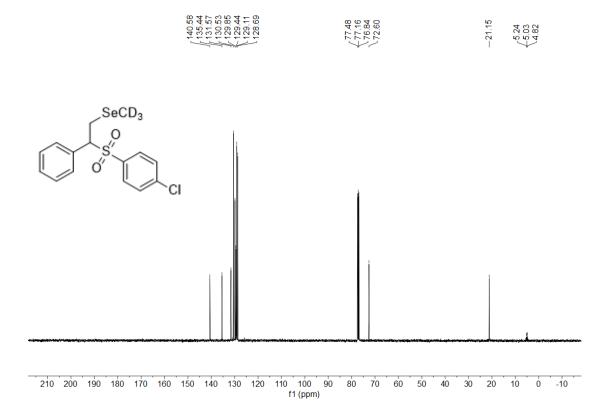
Supplementary Figure 281. ²H NMR Spectrum of **5aa** (100 MHz, CHCl₃)



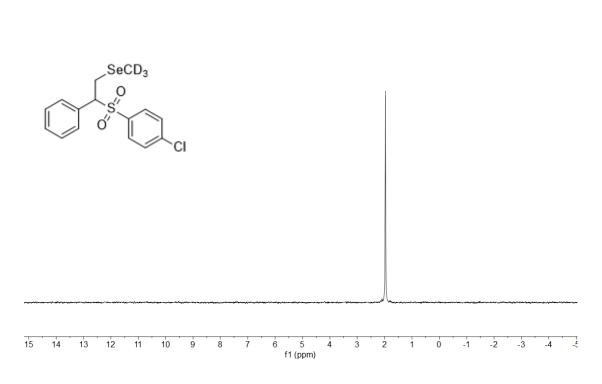
Supplementary Figure 282. ¹H NMR Spectrum of 5ab (400 MHz, CDCl₃)



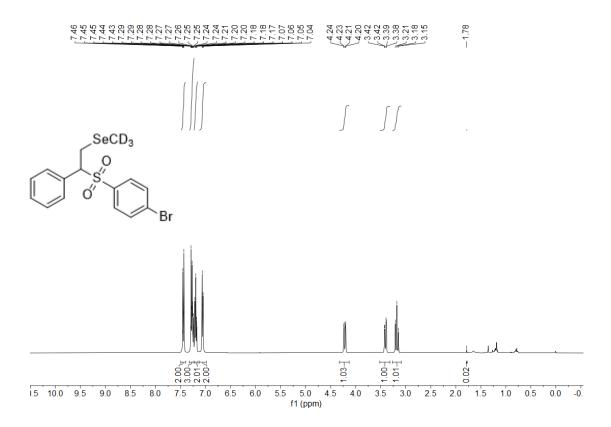
Supplementary Figure 283. ¹³C NMR Spectrum of 5ab (100 MHz, CDCl₃)



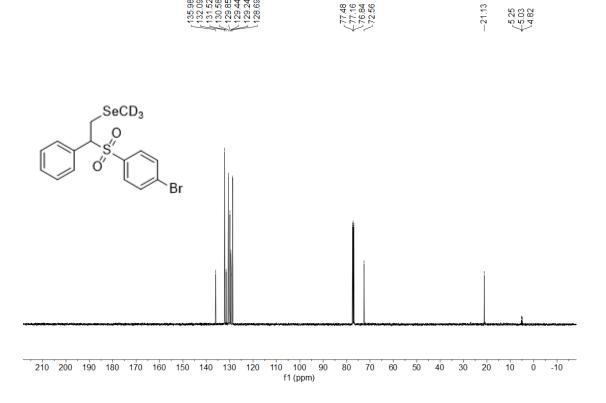
Supplementary Figure 284. ²H NMR Spectrum of 5ab (100 MHz, CHCl₃)



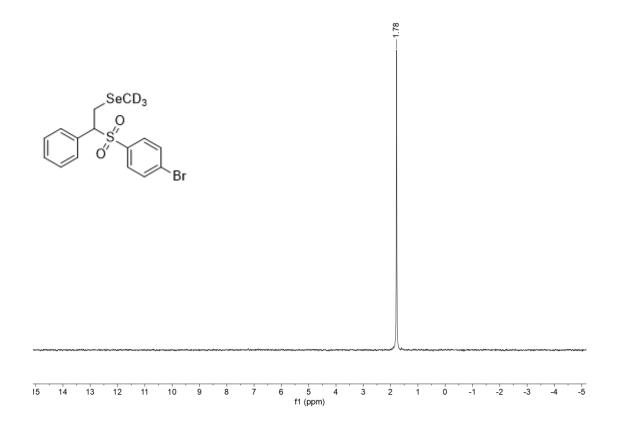
Supplementary Figure 285. ¹H NMR Spectrum of 5ac (400 MHz, CDCl₃)



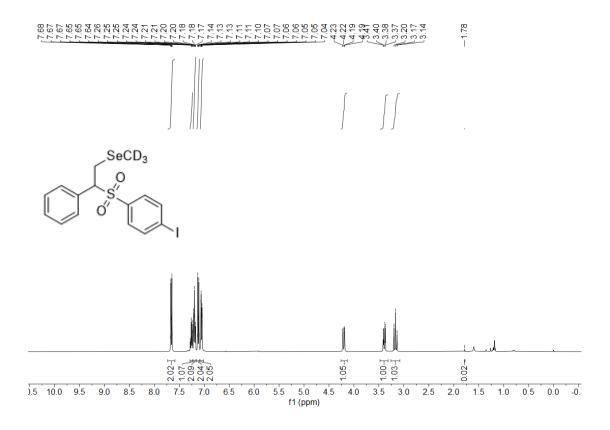
Supplementary Figure 286. ¹³C NMR Spectrum of 5ac (100 MHz, CDCl₃)



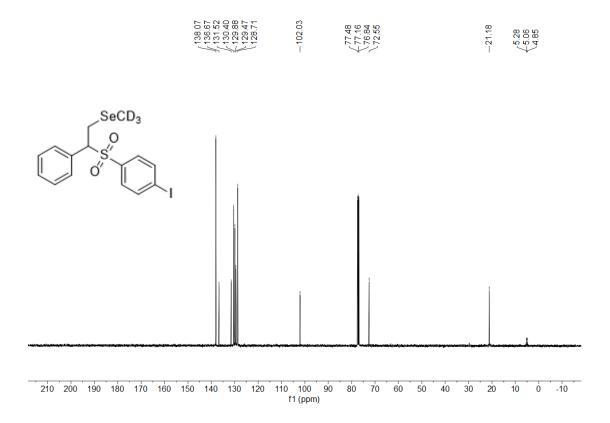
Supplementary Figure 287. ²H NMR Spectrum of **5ac** (100 MHz, CHCl₃)



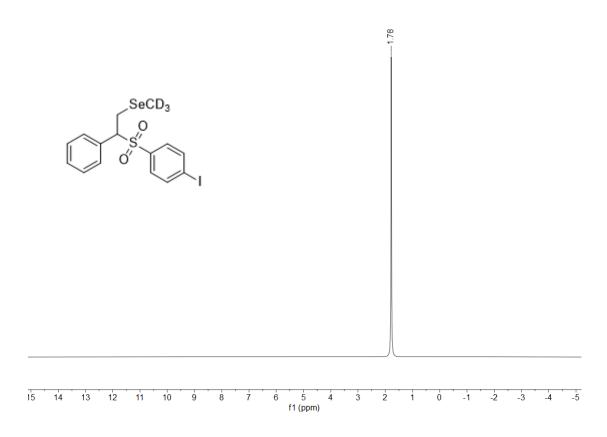
Supplementary Figure 288. ¹H NMR Spectrum of 5ad (400 MHz, CDCl₃)



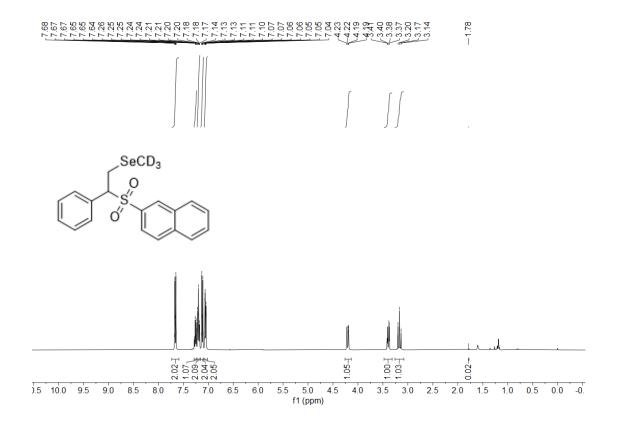
Supplementary Figure 289. ¹³C NMR Spectrum of 5ad (100 MHz, CDCl₃)



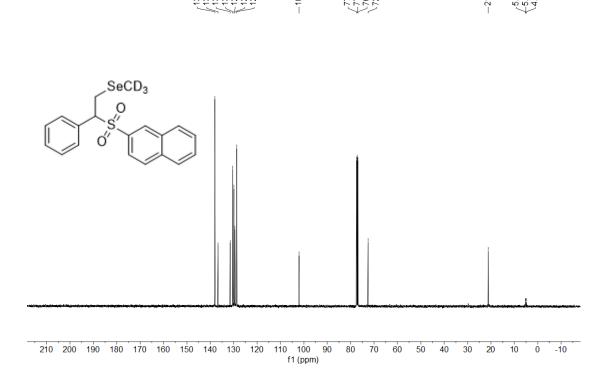
Supplementary Figure 290. ²H NMR Spectrum of 5ad (100 MHz, CHCl₃)



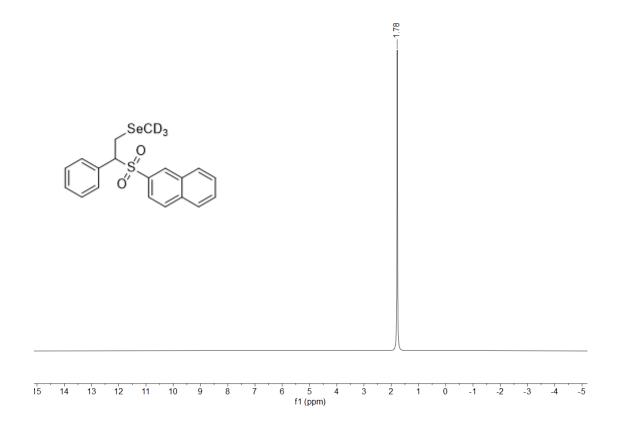
Supplementary Figure 291. ¹H NMR Spectrum of **5ae** (400 MHz, CDCl₃)



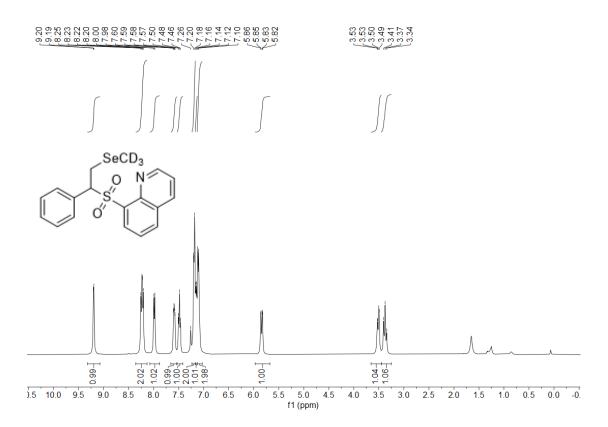
Supplementary Figure 292. ¹³C NMR Spectrum of 5ae (100 MHz, CDCl₃)



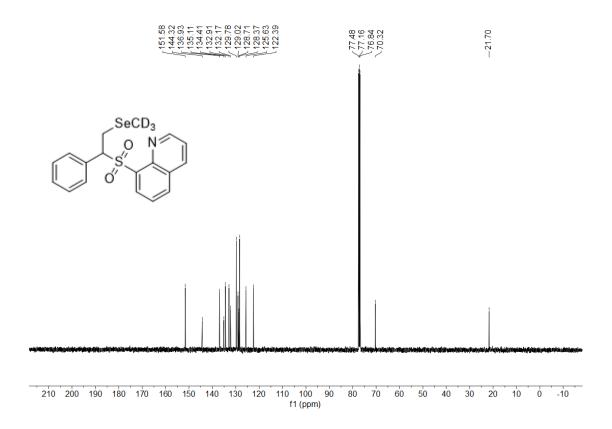
Supplementary Figure 293. ²H NMR Spectrum of **5ae** (100 MHz, CHCl₃)



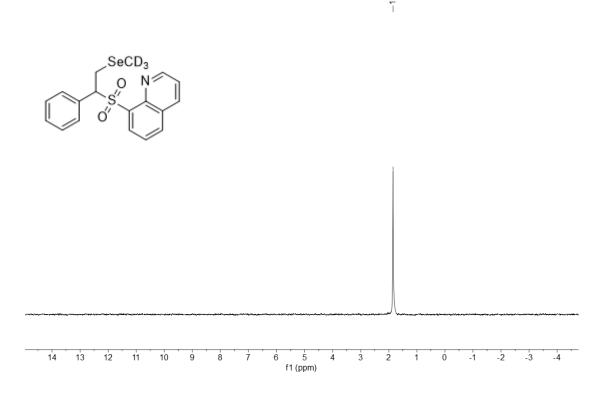
Supplementary Figure 294. ¹H NMR Spectrum of 5af (400 MHz, CDCl₃)



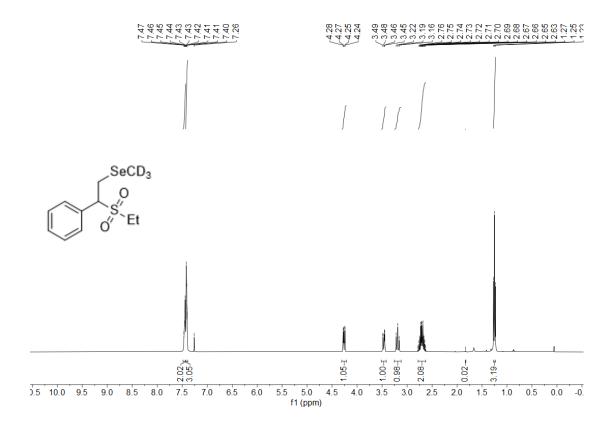
Supplementary Figure 295. ¹³C NMR Spectrum of 5af (100 MHz, CDCl₃)



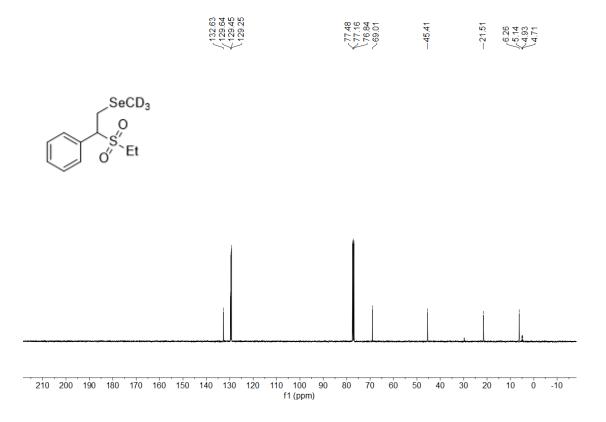
Supplementary Figure 296. ²H NMR Spectrum of 5af (100 MHz, CHCl₃)



Supplementary Figure 297. ¹H NMR Spectrum of 5ag (400 MHz, CDCl₃)

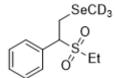


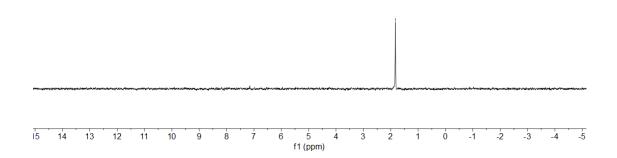
Supplementary Figure 298. ¹³C NMR Spectrum of 5ag (100 MHz, CDCl₃)



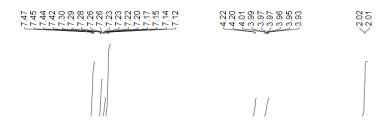
Supplementary Figure 299. ²H NMR Spectrum of **5ag** (100 MHz, CHCl₃)

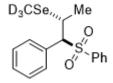


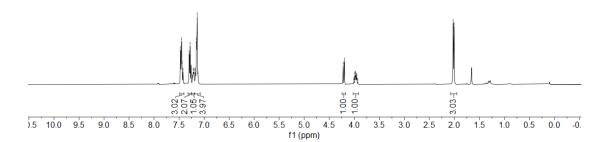




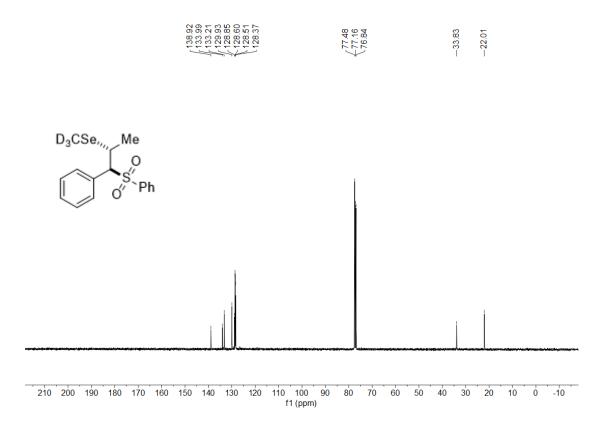
Supplementary Figure 300. ¹H NMR Spectrum of 5ah (400 MHz, CDCl₃)



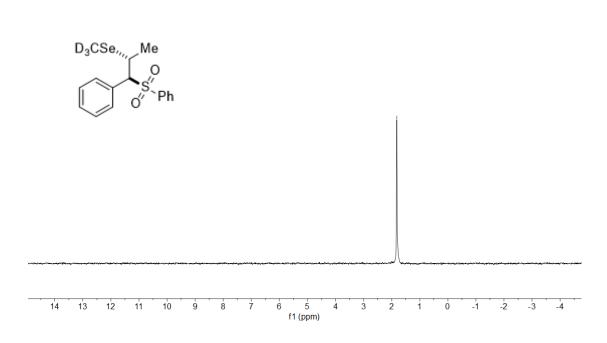




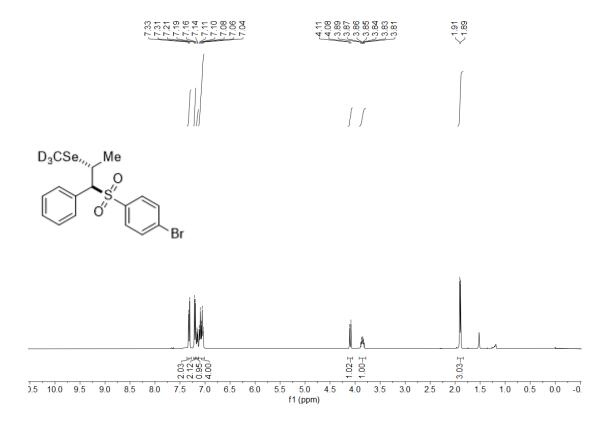
Supplementary Figure 301. ¹³C NMR Spectrum of 5ah (100 MHz, CDCl₃)



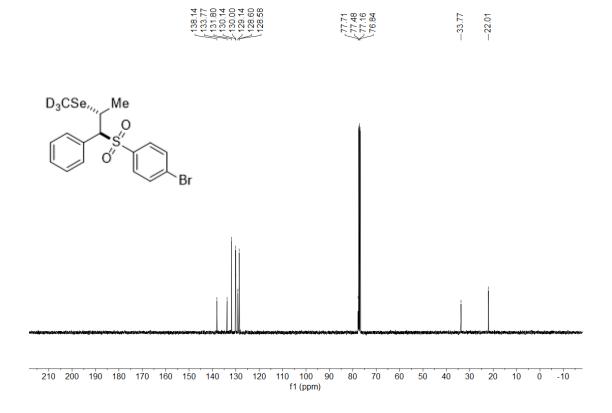
Supplementary Figure 302. ²H NMR Spectrum of 5ah (100 MHz, CHCl₃)



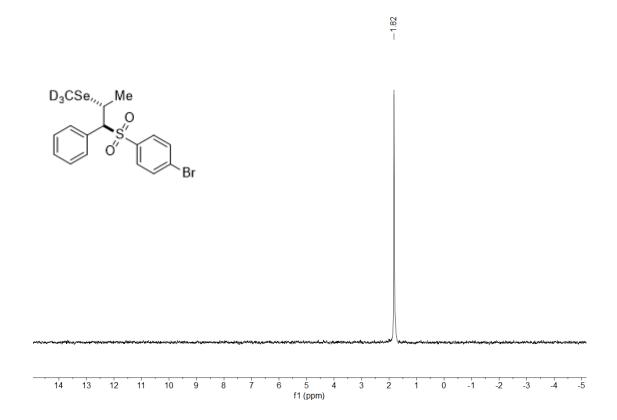
Supplementary Figure 303. ¹H NMR Spectrum of **5ai** (400 MHz, CDCl₃)



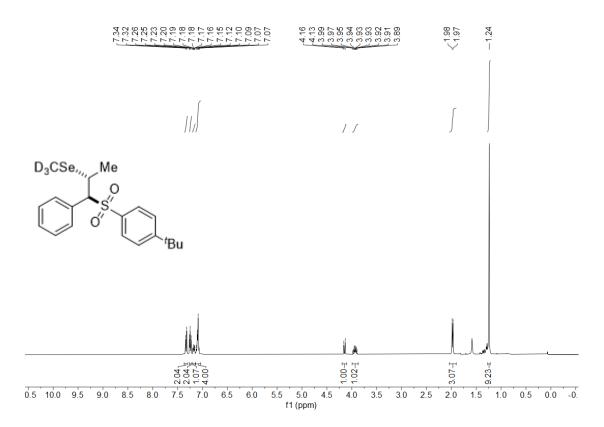
Supplementary Figure 304. ¹³C NMR Spectrum of 5ai (100 MHz, CDCl₃)



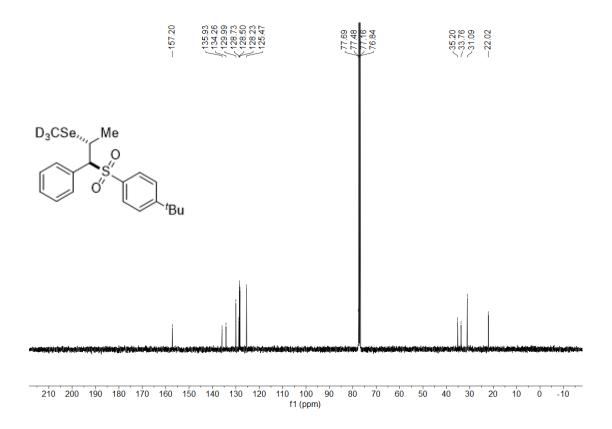
Supplementary Figure 305. ²H NMR Spectrum of **5ai** (100 MHz, CHCl₃)



Supplementary Figure 306. ¹H NMR Spectrum of 5aj (400 MHz, CDCl₃)

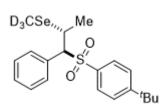


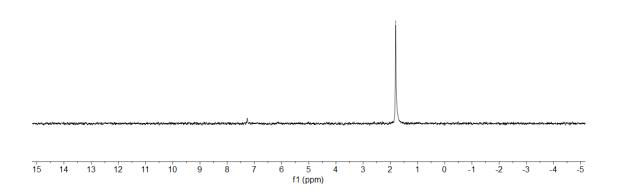
Supplementary Figure 307. ¹³C NMR Spectrum of 5aj (100 MHz, CDCl₃)



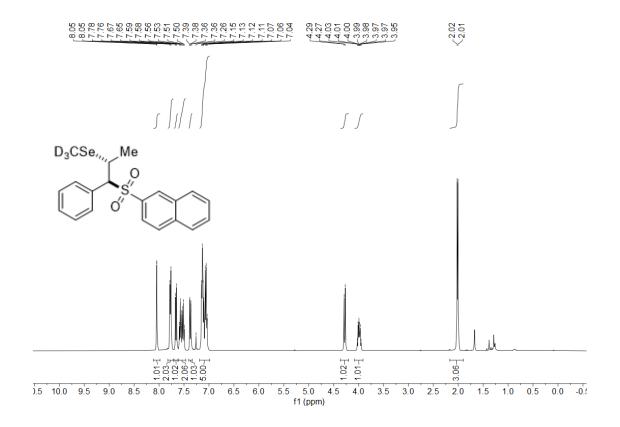
Supplementary Figure 308. ²H NMR Spectrum of 5aj (100 MHz, CHCl₃)

1.81

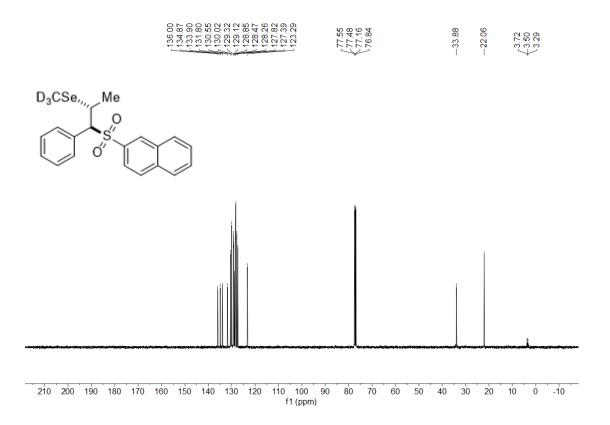




Supplementary Figure 309. ¹H NMR Spectrum of 5ak (400 MHz, CDCl₃)

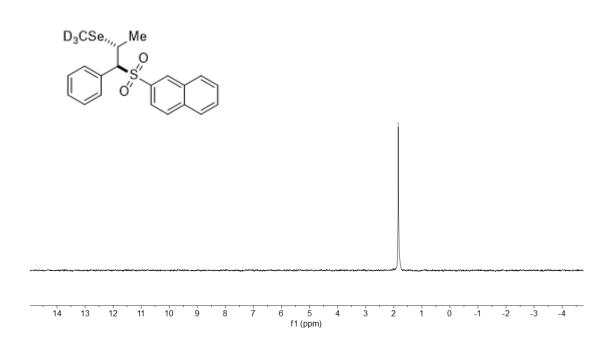


Supplementary Figure 310. ¹³C NMR Spectrum of 5ak (100 MHz, CDCl₃)

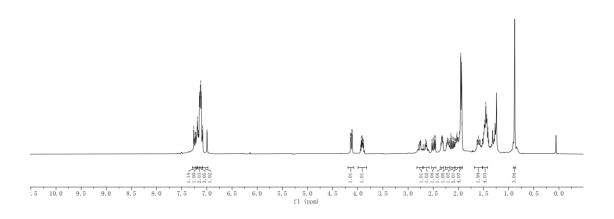


Supplementary Figure 311. ²H NMR Spectrum of **5ak** (100 MHz, CHCl₃)

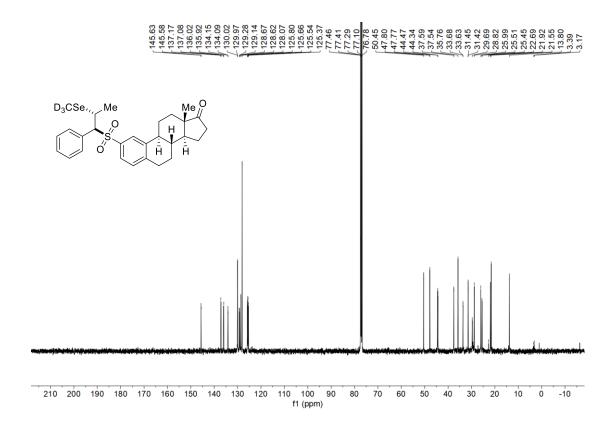




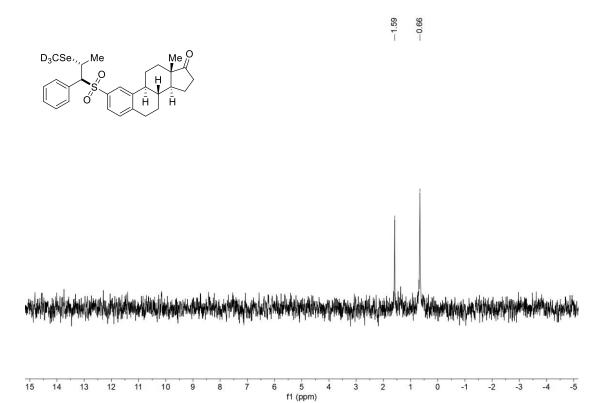
Supplementary Figure 312. ¹H NMR Spectrum of **5al** (400 MHz, CDCl₃)



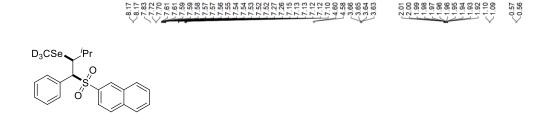
Supplementary Figure 313. ¹³C NMR Spectrum of 5al (400 MHz, CDCl₃)

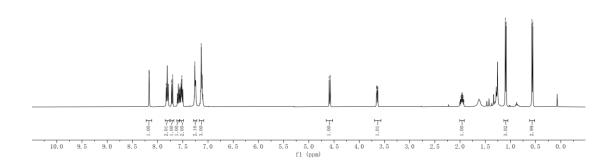


Supplementary Figure 314. ²H NMR Spectrum of 5al (100 MHz, CHCl₃)

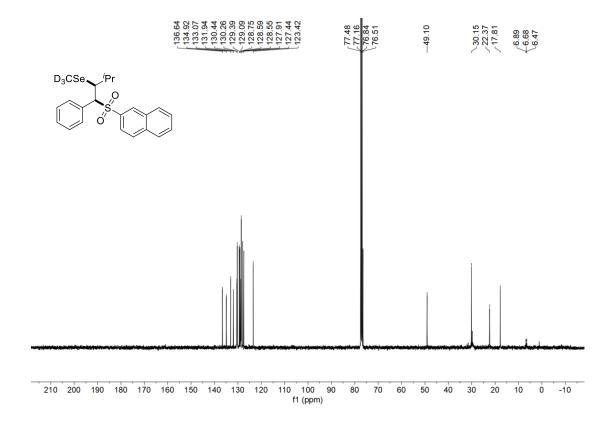


Supplementary Figure 315. ¹H NMR Spectrum of **5am** (400 MHz, CDCl₃)

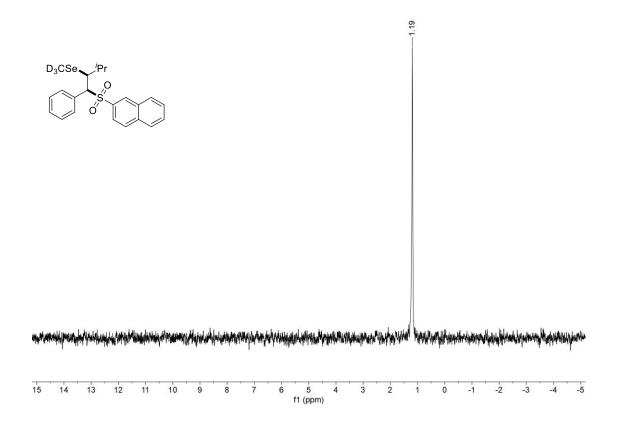




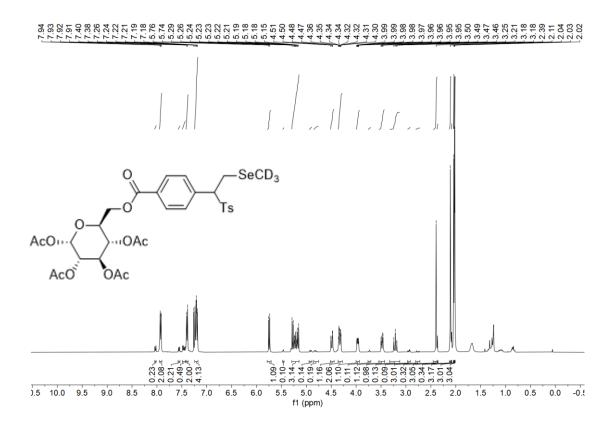
Supplementary Figure 316. ¹³C NMR Spectrum of 5am (100 MHz, CDCl₃)



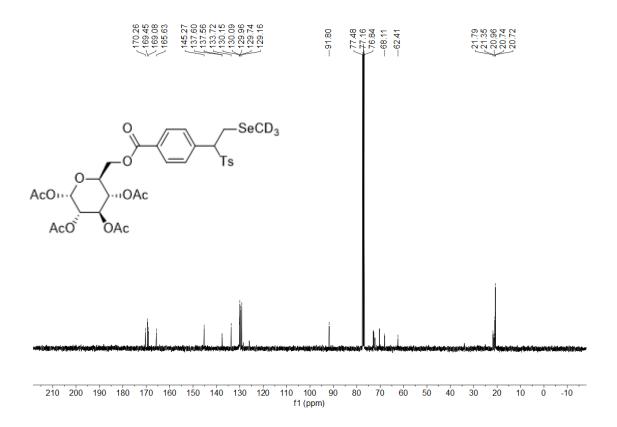
Supplementary Figure 317. ²H NMR Spectrum of **5am** (100 MHz, CHCl₃)



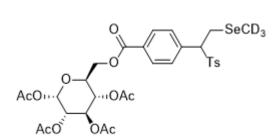
Supplementary Figure 318. ¹H NMR Spectrum of 7a (400 MHz, CDCl₃)

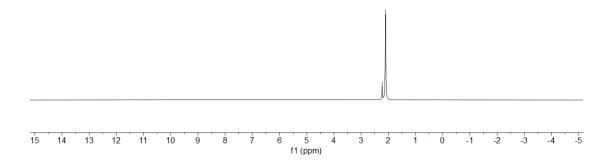


Supplementary Figure 319. ¹³C NMR Spectrum of 7a (100 MHz, CDCl₃)

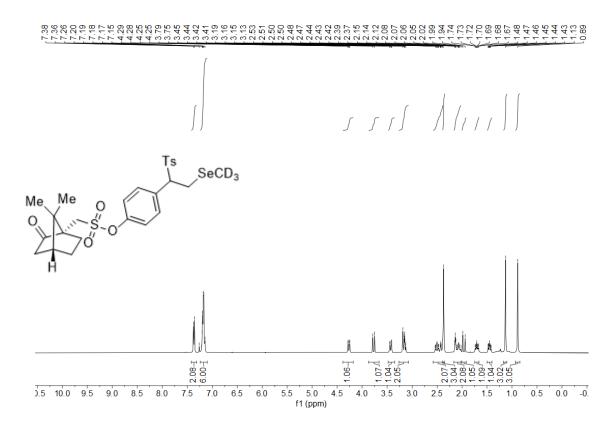


Supplementary Figure 320. ²H NMR Spectrum of 7a (100 MHz, CHCl₃)

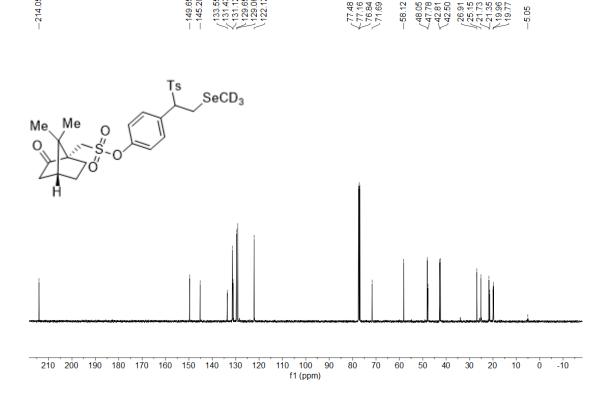




Supplementary Figure 321. ¹H NMR Spectrum of **7b** (400 MHz, CDCl₃)

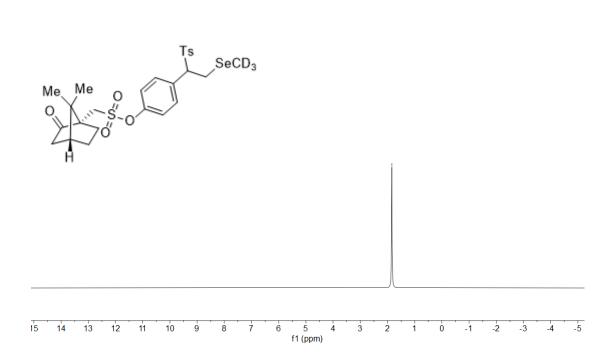


Supplementary Figure 322. ¹³C NMR Spectrum of 7b (100 MHz, CDCl₃)

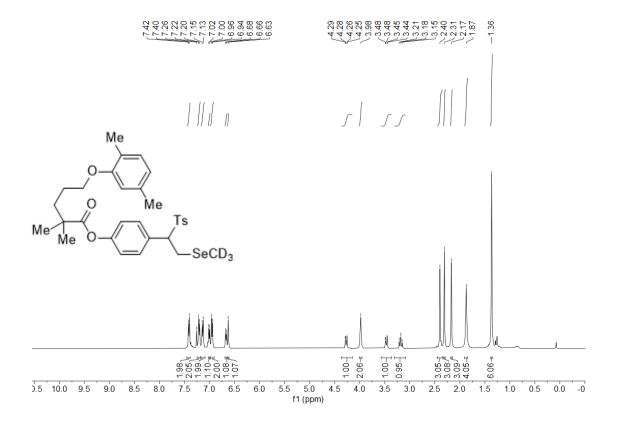


Supplementary Figure 323. ²H NMR Spectrum of 7b (100 MHz, CHCl₃)

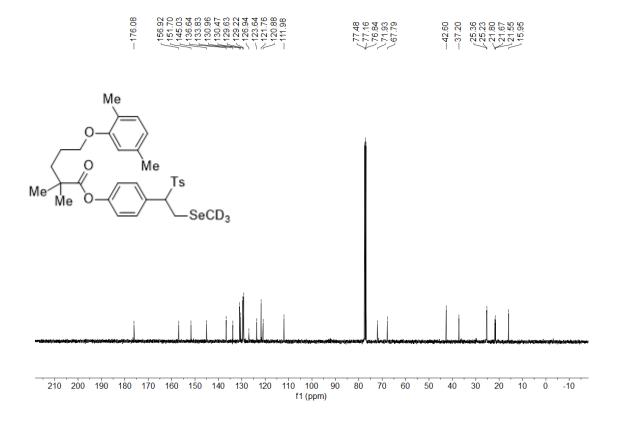




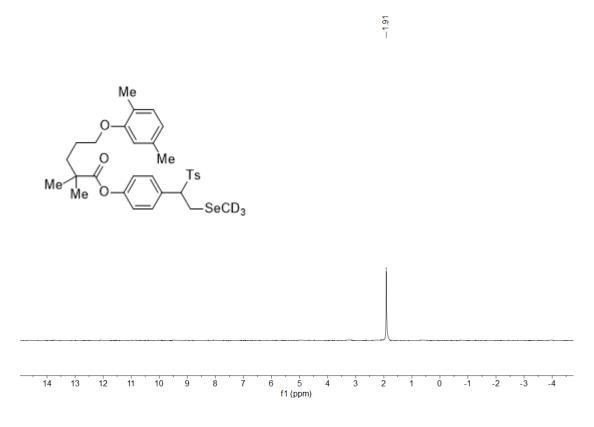
Supplementary Figure 324. ¹H NMR Spectrum of 7c (400 MHz, CDCl₃)



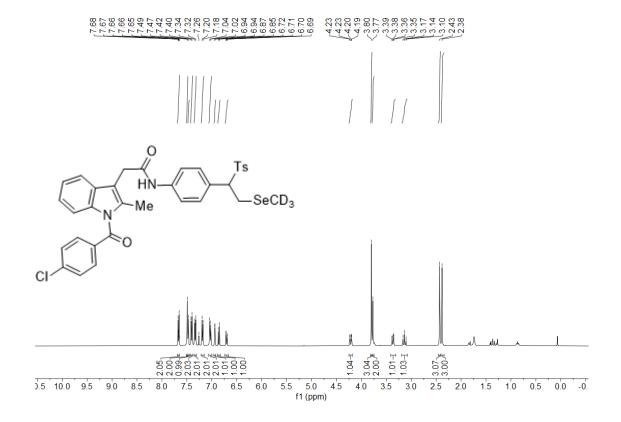
Supplementary Figure 325. ¹³C NMR Spectrum of 7c (100 MHz, CDCl₃)



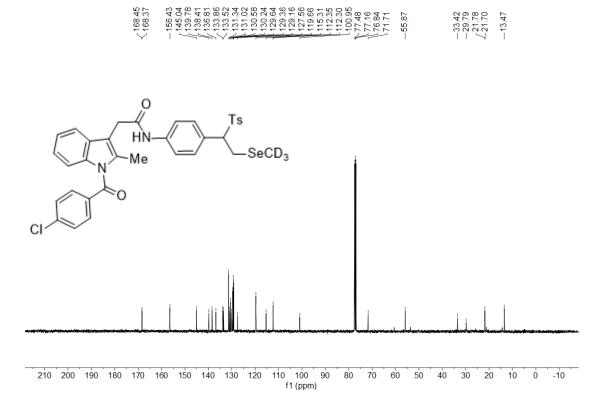
Supplementary Figure 326. ²H NMR Spectrum of 7c (100 MHz, CHCl₃)



Supplementary Figure 327. ¹H NMR Spectrum of **7d** (400 MHz, CDCl₃)

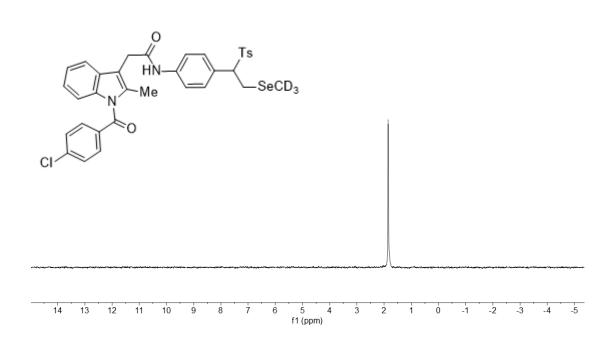


Supplementary Figure 328. ¹³C NMR Spectrum of 7d (100 MHz, CDCl₃)

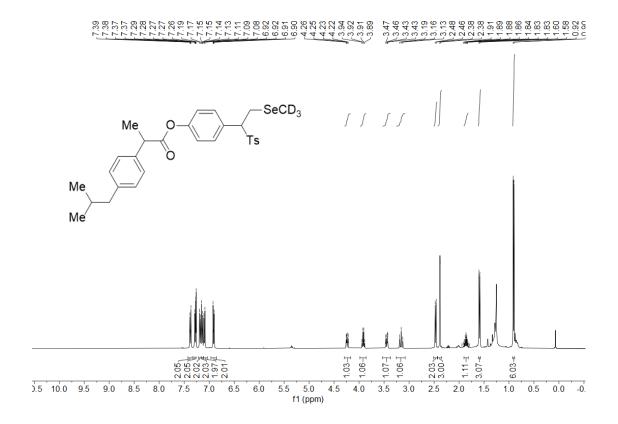


Supplementary Figure 329. ²H NMR Spectrum of **7d** (100 MHz, CHCl₃)

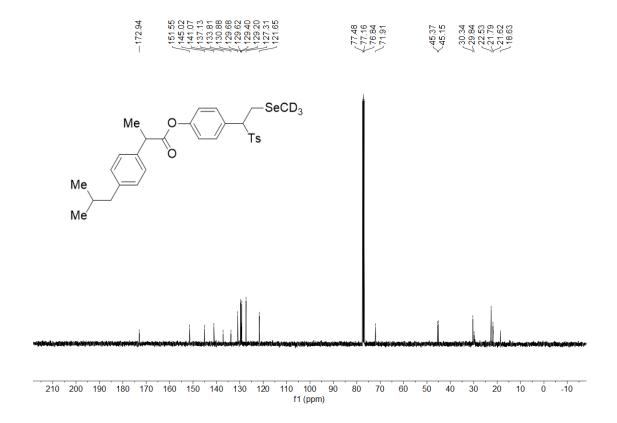




Supplementary Figure 330. ¹H NMR Spectrum of 7e (400 MHz, CDCl₃)

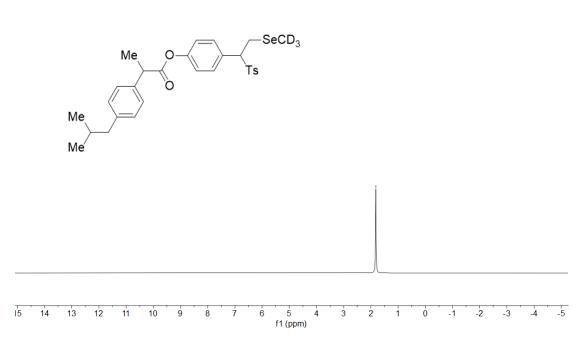


Supplementary Figure 331. ¹³C NMR Spectrum of 7e (100 MHz, CDCl₃)

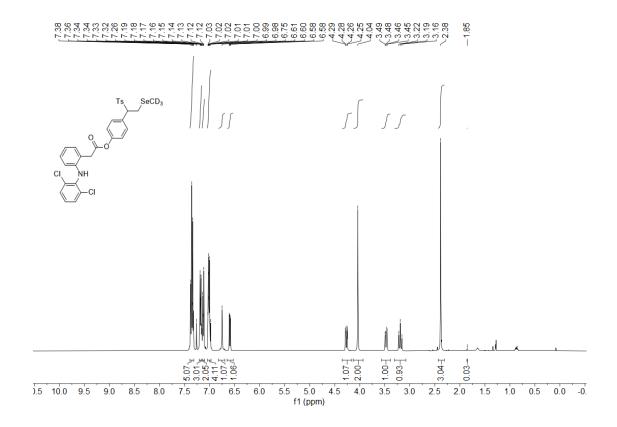


Supplementary Figure 332. ²H NMR Spectrum of 7e (100 MHz, CHCl₃)

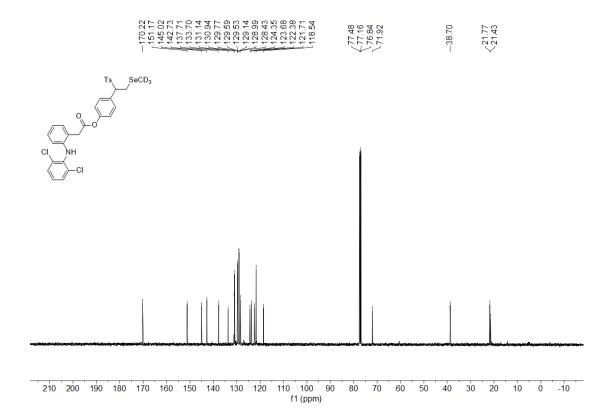
-1.82



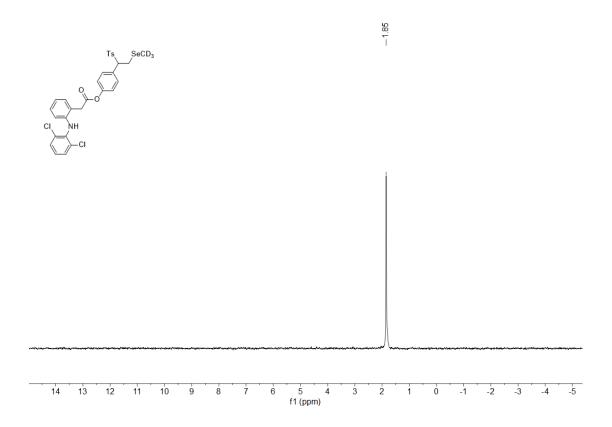
Supplementary Figure 333. ¹H NMR Spectrum of 7f (400 MHz, CDCl₃)



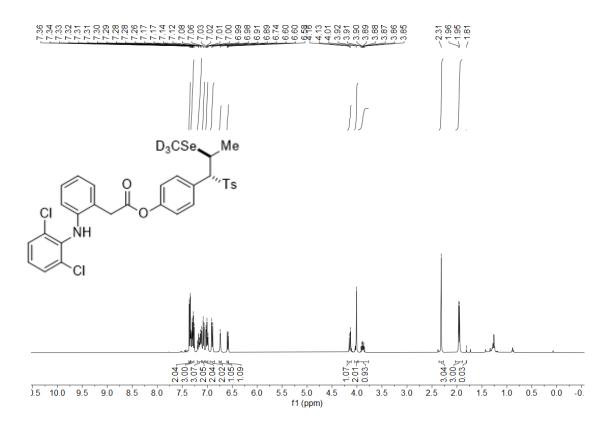
Supplementary Figure 334. ¹³C NMR Spectrum of 7f (100 MHz, CDCl₃)



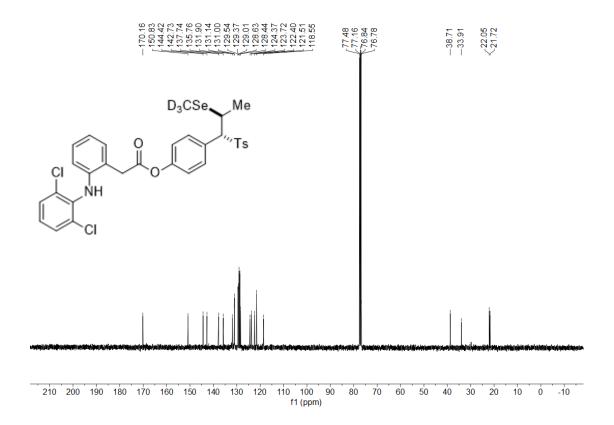
Supplementary Figure 335. ²H NMR Spectrum of **7f** (100 MHz, CHCl₃)



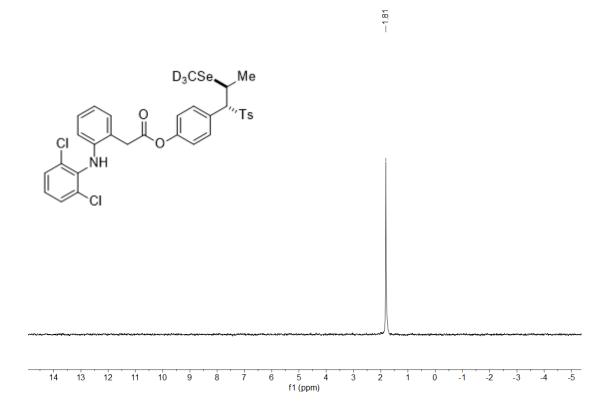
Supplementary Figure 336. ¹H NMR Spectrum of 7g (400 MHz, CDCl₃)



Supplementary Figure 337. ¹³C NMR Spectrum of **7g** (100 MHz, CDCl₃)

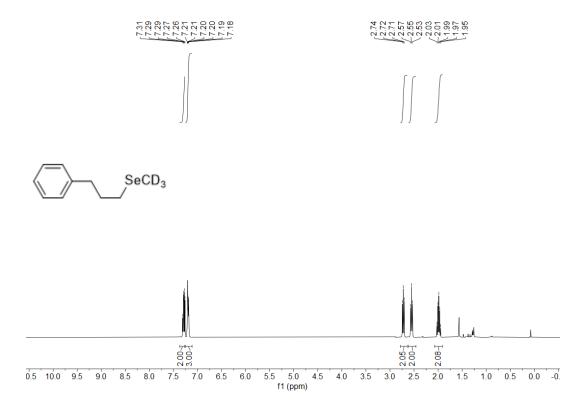


Supplementary Figure 338. ²H NMR Spectrum of 7g (100 MHz, CHCl₃)

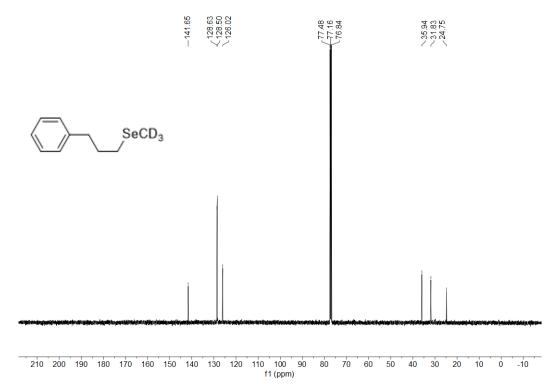


11.4 NMR Spectra of Nucleophilic Selenium Deuterated Methylation Products

Supplementary Figure 339. ¹H NMR Spectrum of 10a (400 MHz, CDCl₃)

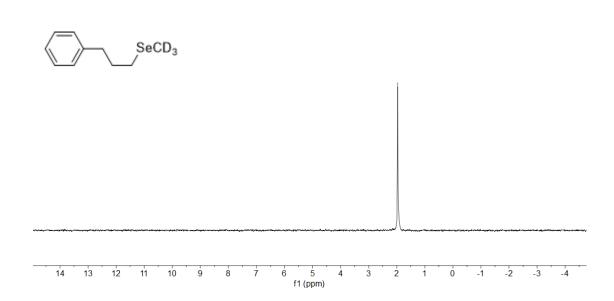


Supplementary Figure 340. ¹³C NMR Spectrum of 10a (100 MHz, CDCl₃)

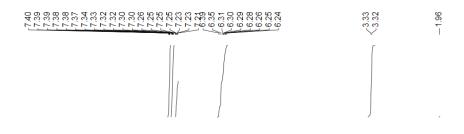


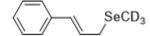
Supplementary Figure 341. ²H NMR Spectrum of **10a** (100 MHz, CHCl₃)

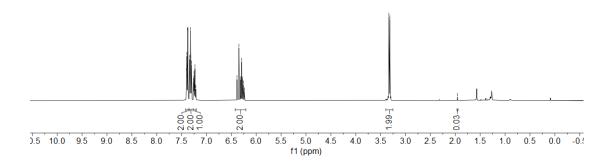




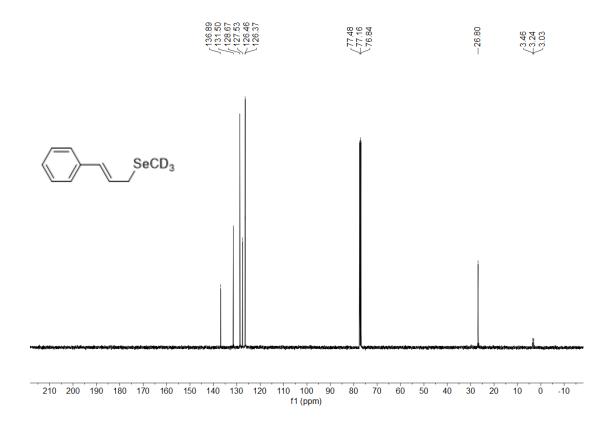
Supplementary Figure 342. ¹H NMR Spectrum of **10b** (400 MHz, CDCl₃)



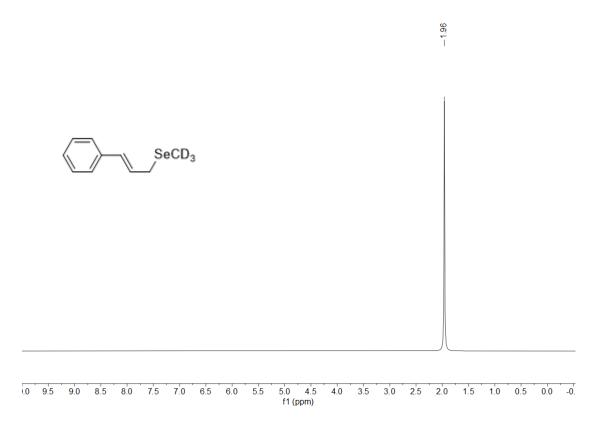




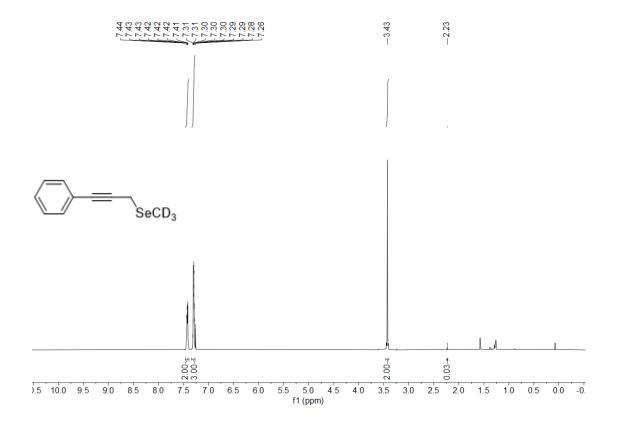
Supplementary Figure 343. ¹³C NMR Spectrum of 10b (100 MHz, CDCl₃)



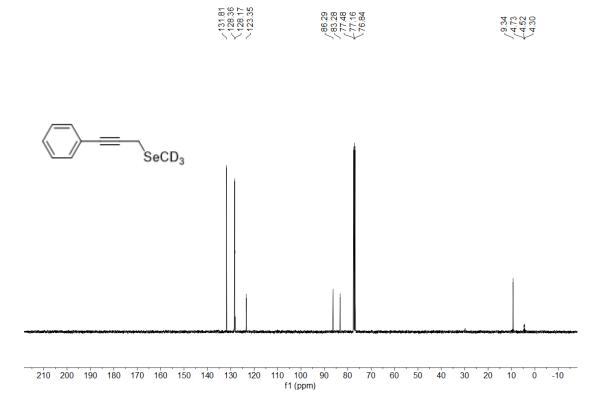
Supplementary Figure 344. ²H NMR Spectrum of 10b (100 MHz, CHCl₃)



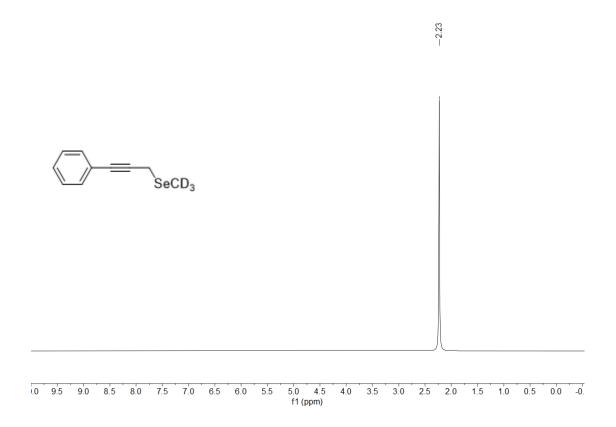
Supplementary Figure 345. ¹H NMR Spectrum of **10c** (400 MHz, CDCl₃)



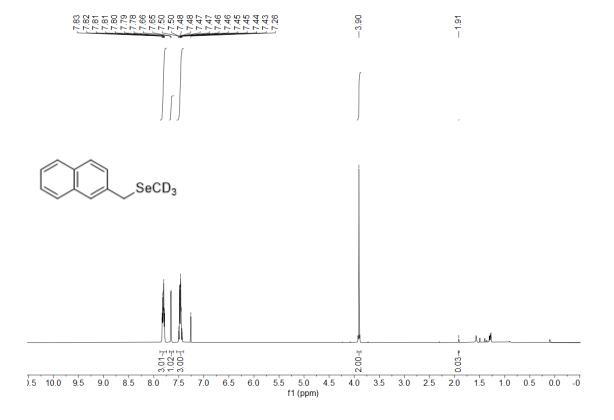
Supplementary Figure 346. ¹³C NMR Spectrum of 10c (100 MHz, CDCl₃)



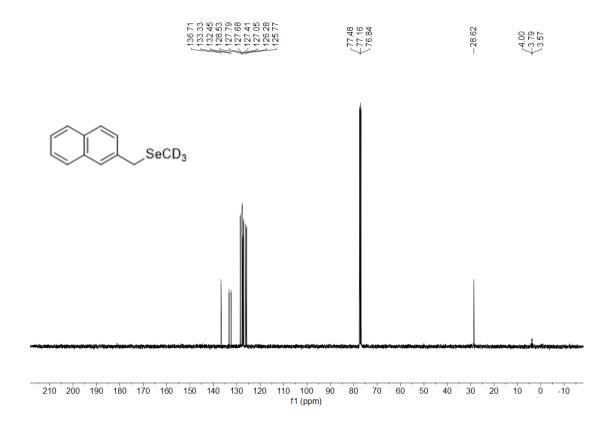
Supplementary Figure 347. ²H NMR Spectrum of **10c** (100 MHz, CHCl₃)



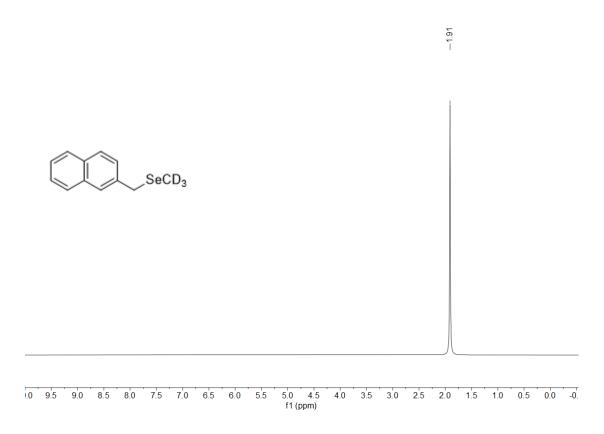
Supplementary Figure 348. ¹H NMR Spectrum of **10d** (400 MHz, CDCl₃)



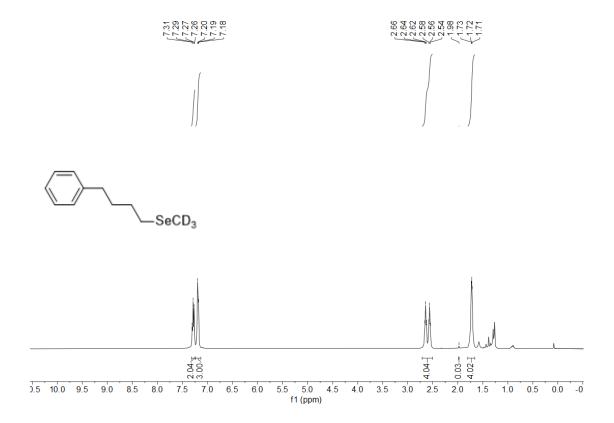
Supplementary Figure 349. ¹³C NMR Spectrum of 10d (100 MHz, CDCl₃)



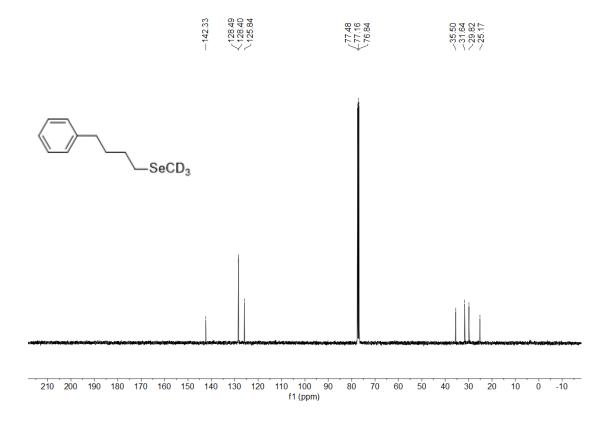
Supplementary Figure 350. ²H NMR Spectrum of 10d (100 MHz, CHCl₃)



Supplementary Figure 351. ¹H NMR Spectrum of **10e** (400 MHz, CDCl₃)

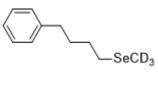


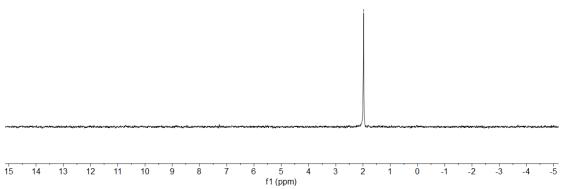
Supplementary Figure 352. ¹³C NMR Spectrum of 10e (100 MHz, CDCl₃)



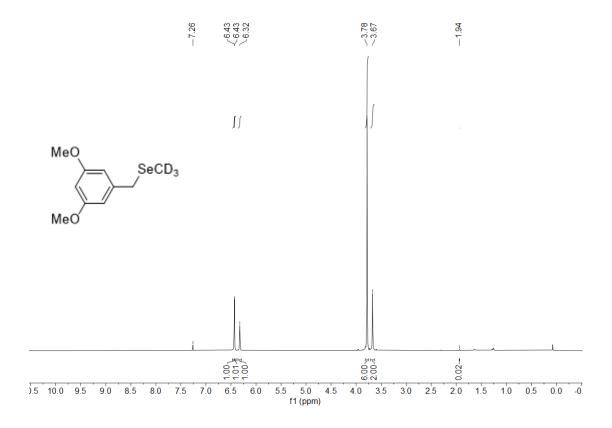
Supplementary Figure 353. ²H NMR Spectrum of 10e (100 MHz, CHCl₃)

-1.98

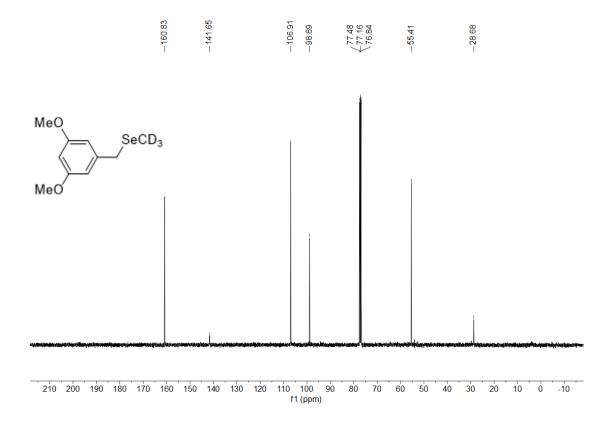




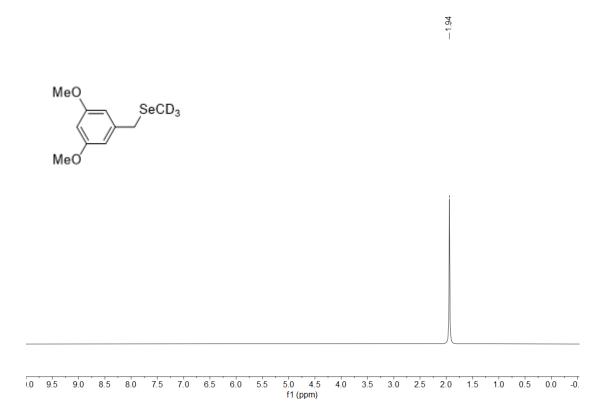
Supplementary Figure 354. 1 H NMR Spectrum of 10f (400 MHz, CDCl₃)



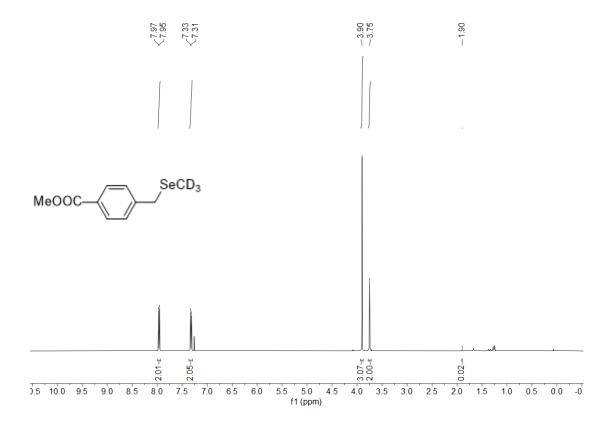
Supplementary Figure 355. ¹³C NMR Spectrum of **10f** (100 MHz, CDCl₃)



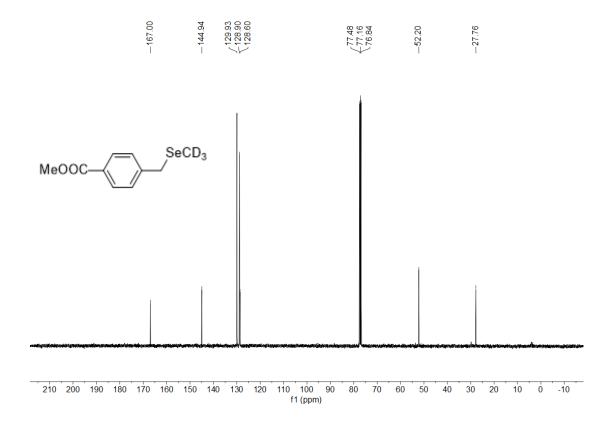
Supplementary Figure 356. ²H NMR Spectrum of 10f (100 MHz, CHCl₃)



Supplementary Figure 357. ¹H NMR Spectrum of 10g (400 MHz, CDCl₃)

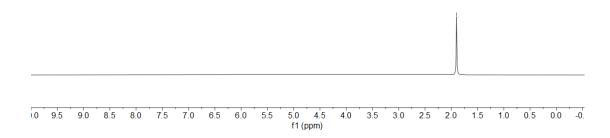


Supplementary Figure 358. ¹³C NMR Spectrum of 10g (100 MHz, CDCl₃)

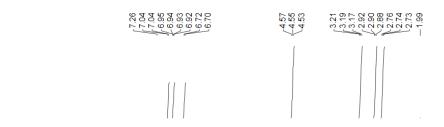


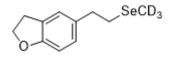
Supplementary Figure 359. ²H NMR Spectrum of 10g (100 MHz, CHCl₃)

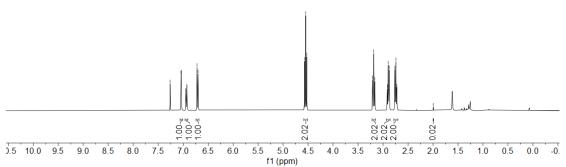




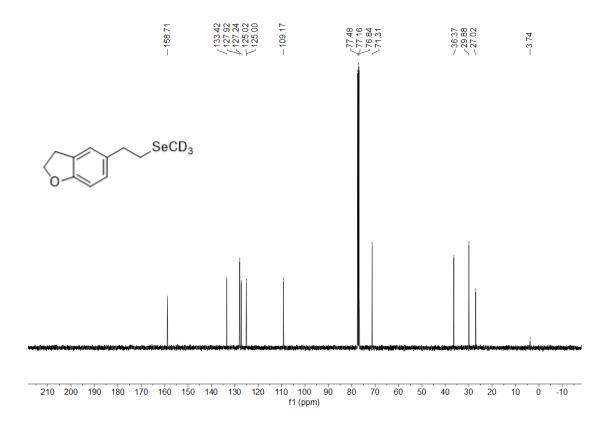
Supplementary Figure 360. ¹H NMR Spectrum of 10h (400 MHz, CDCl₃)





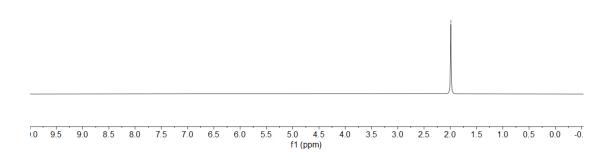


Supplementary Figure 361. ¹³C NMR Spectrum of 10h (100 MHz, CDCl₃)

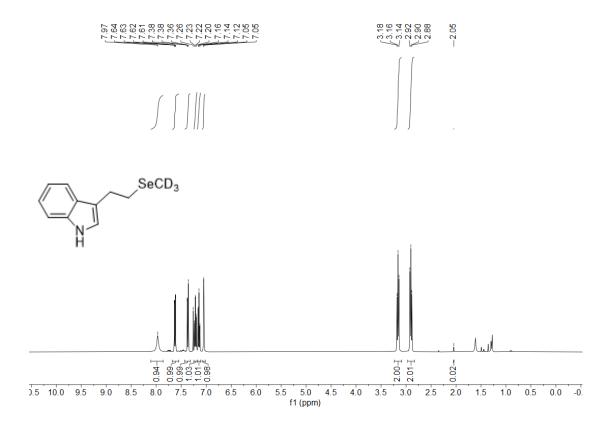


Supplementary Figure 362. ²H NMR Spectrum of 10h (100 MHz, CHCl₃)

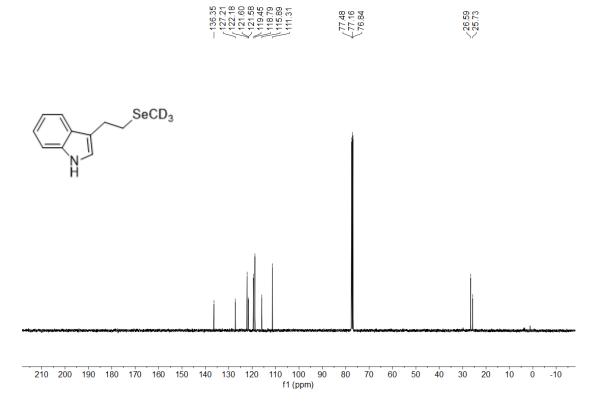
1.99



Supplementary Figure 363. ¹H NMR Spectrum of **10i** (400 MHz, CDCl₃)

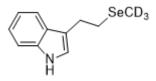


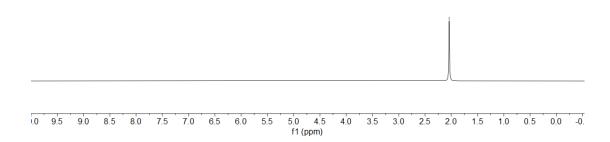
Supplementary Figure 364. ¹³C NMR Spectrum of 10i (100 MHz, CDCl₃)



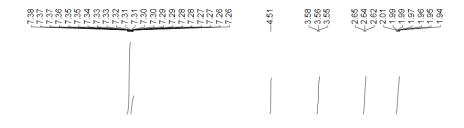
Supplementary Figure 365. ²H NMR Spectrum of **10i** (100 MHz, CHCl₃)

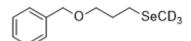


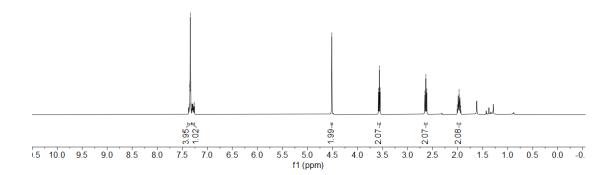




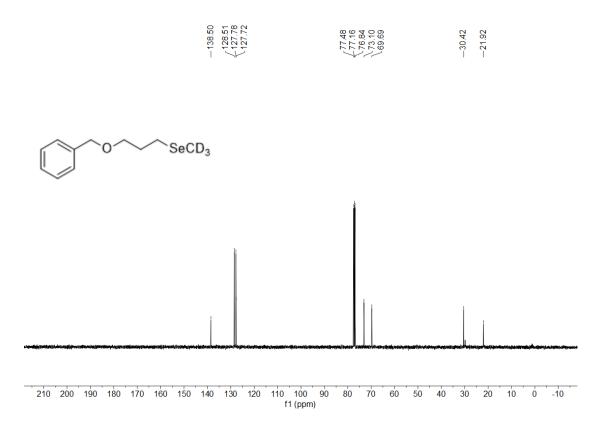
Supplementary Figure 366. ¹H NMR Spectrum of 10j (400 MHz, CDCl₃)



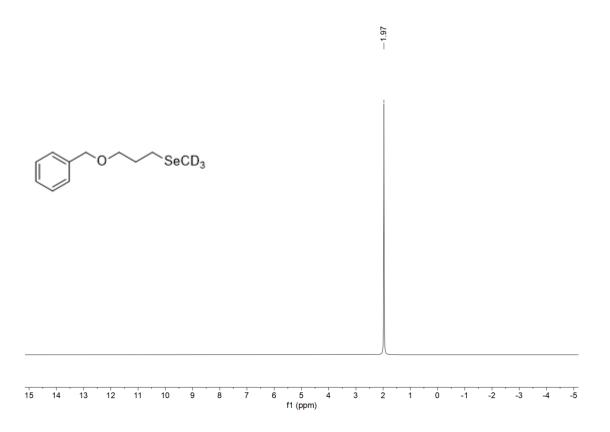




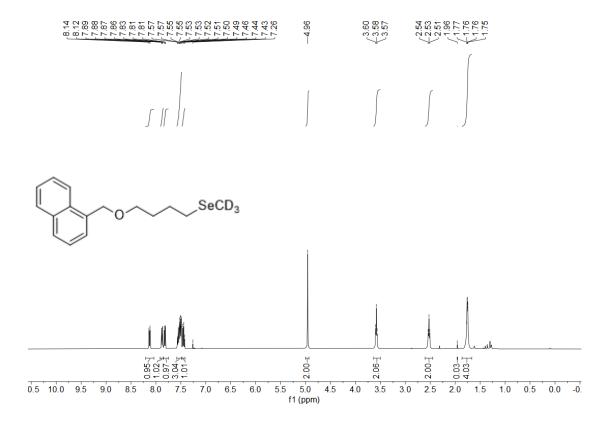
Supplementary Figure 367. ¹³C NMR Spectrum of 10j (100 MHz, CDCl₃)



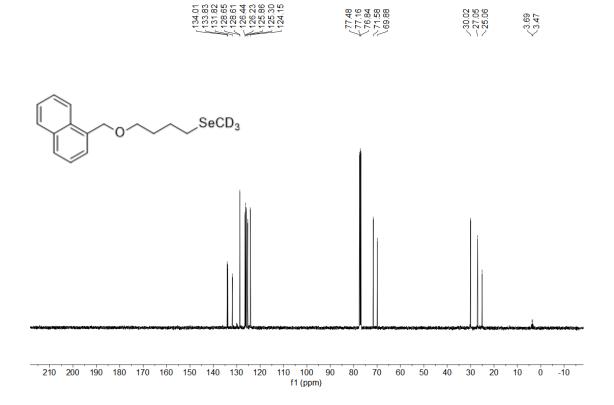
Supplementary Figure 368. ²H NMR Spectrum of 10j (100 MHz, CHCl₃)



Supplementary Figure 369. ¹H NMR Spectrum of **10k** (400 MHz, CDCl₃)

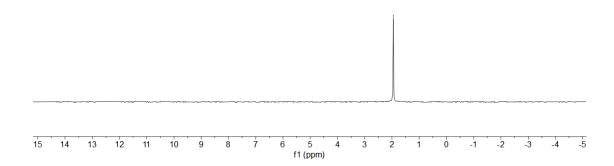


Supplementary Figure 370. ¹³C NMR Spectrum of 10k (100 MHz, CDCl₃)

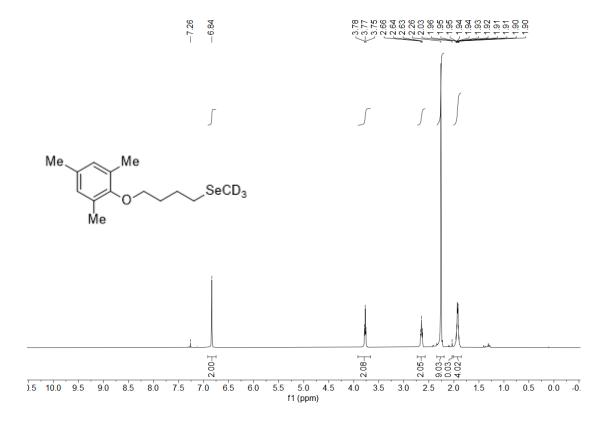


Supplementary Figure 371. ²H NMR Spectrum of 10k (100 MHz, CHCl₃)

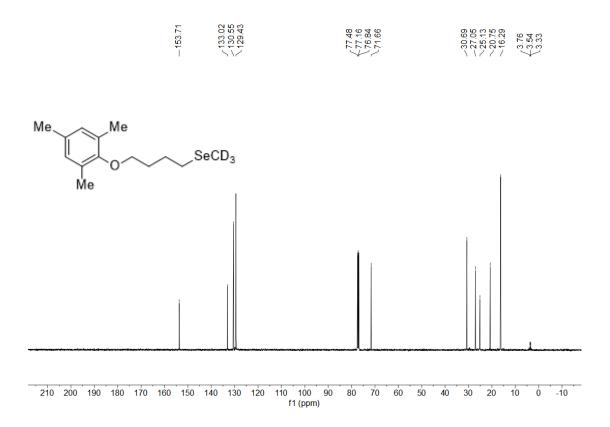
-1.95



Supplementary Figure 372. ¹H NMR Spectrum of 10l (400 MHz, CDCl₃)



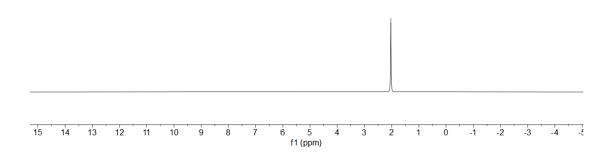
Supplementary Figure 373. ¹³C NMR Spectrum of 10l (100 MHz, CDCl₃)



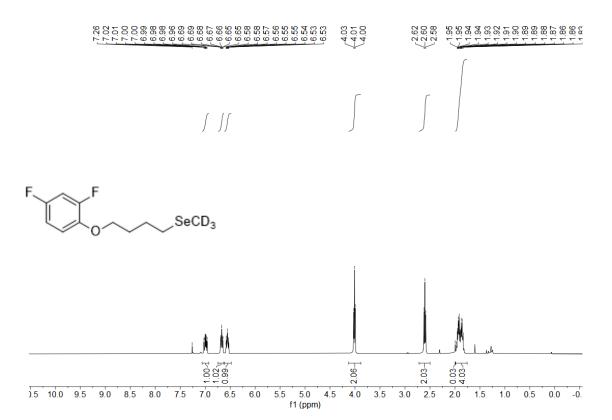
Supplementary Figure 374. ²H NMR Spectrum of 10l (100 MHz, CHCl₃)



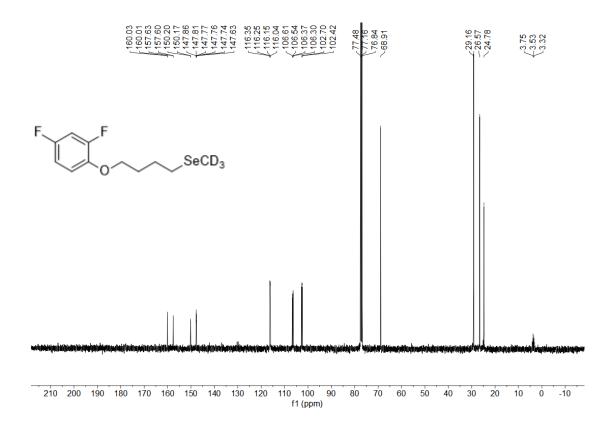
$$Me$$
 O
 $SeCD_3$



Supplementary Figure 375. ¹H NMR Spectrum of 10m (400 MHz, CDCl₃)

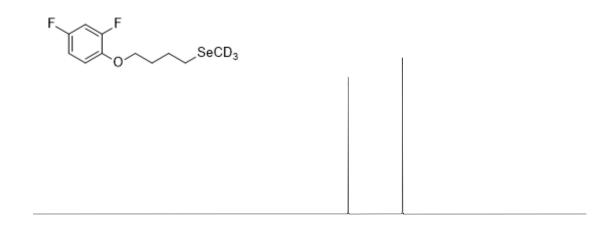


Supplementary Figure 376. ¹³C NMR Spectrum of 10m (100 MHz, CDCl₃)



Supplementary Figure 377. ¹⁹F NMR Spectrum of 10m (376 MHz, CDCl₃)

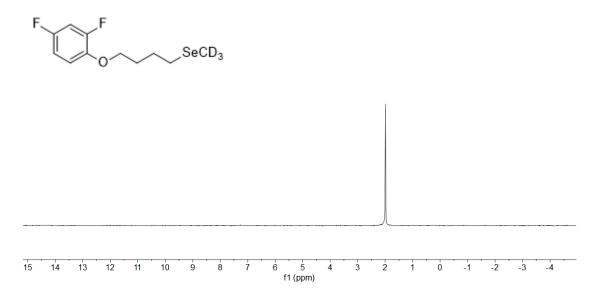




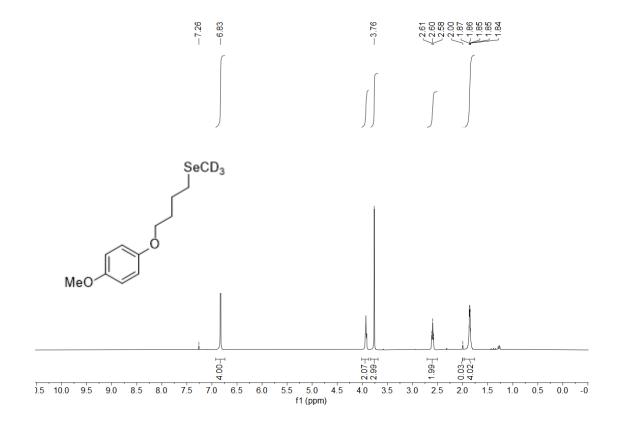
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22 f1 (ppm)

Supplementary Figure 378. ²H NMR Spectrum of 10m (100 MHz, CHCl₃)

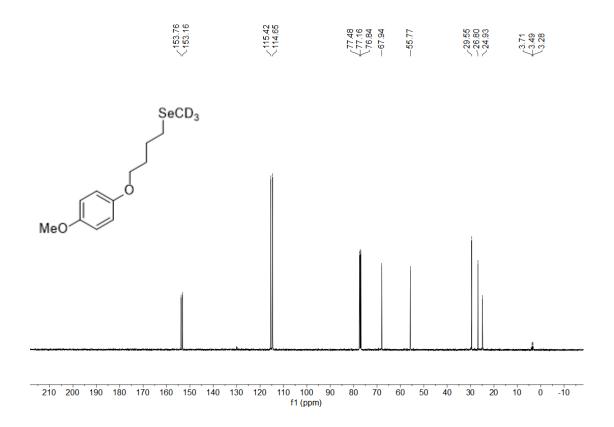
9



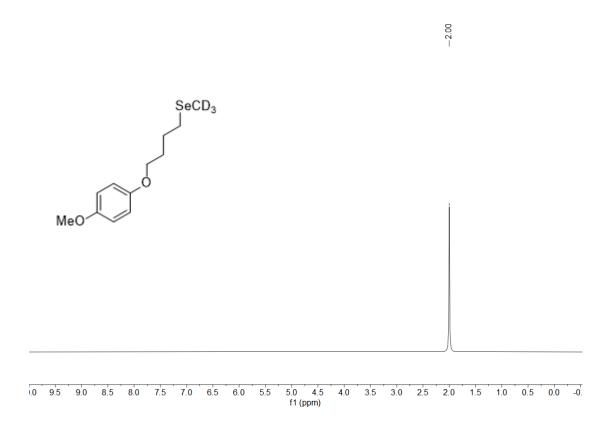
Supplementary Figure 379. ¹H NMR Spectrum of 10n (400 MHz, CDCl₃)



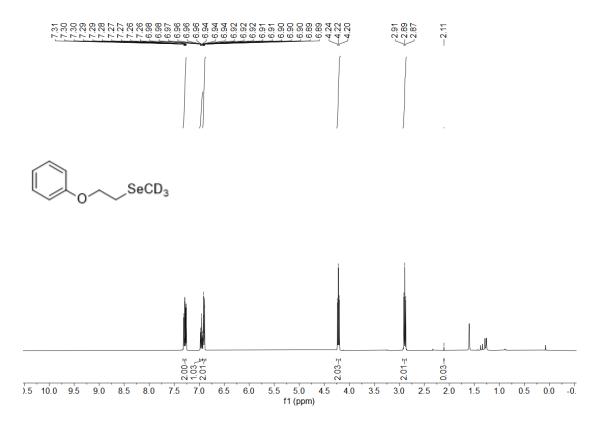
Supplementary Figure 380. ¹³C NMR Spectrum of 10n (100 MHz, CDCl₃)



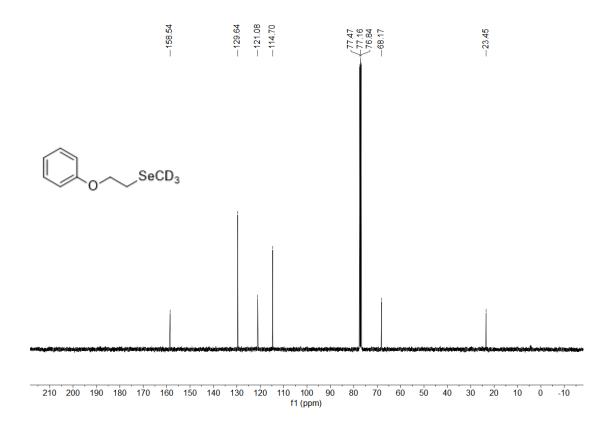
Supplementary Figure 381. ²H NMR Spectrum of 10n (100 MHz, CHCl₃)



Supplementary Figure 382. ¹H NMR Spectrum of 10o (400 MHz, CDCl₃)

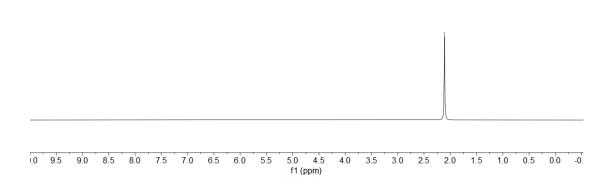


Supplementary Figure 383. ¹³C NMR Spectrum of 10o (100 MHz, CDCl₃)

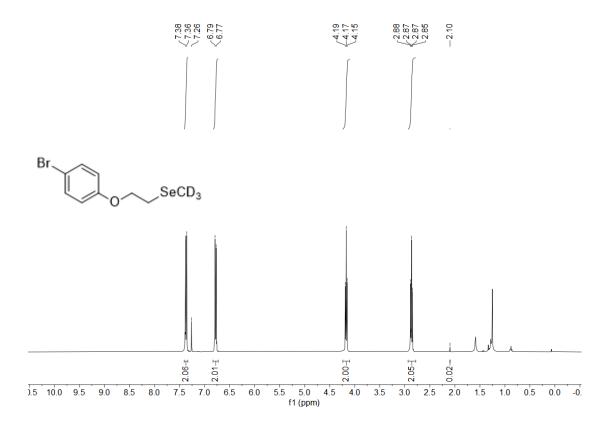


Supplementary Figure 384. ²H NMR Spectrum of 10o (100 MHz, CHCl₃)

-2 11

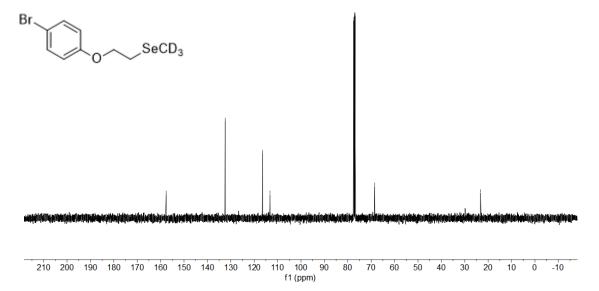


Supplementary Figure 385. ¹H NMR Spectrum of 10p (400 MHz, CDCl₃)



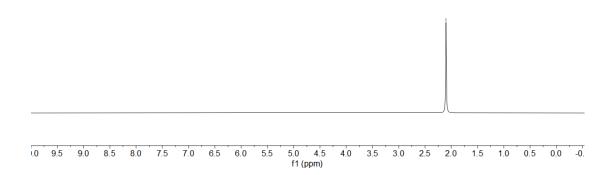
Supplementary Figure 386. ¹³C NMR Spectrum of 10p (100 MHz, CDCl₃)



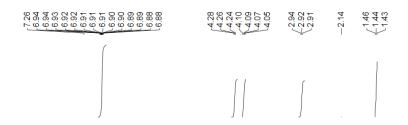


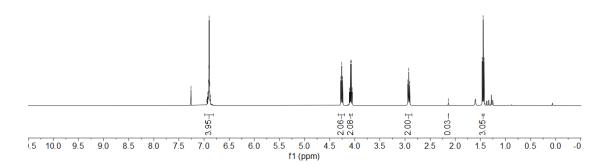
Supplementary Figure 387. ²H NMR Spectrum of 10p (100 MHz, CHCl₃)

-2.10

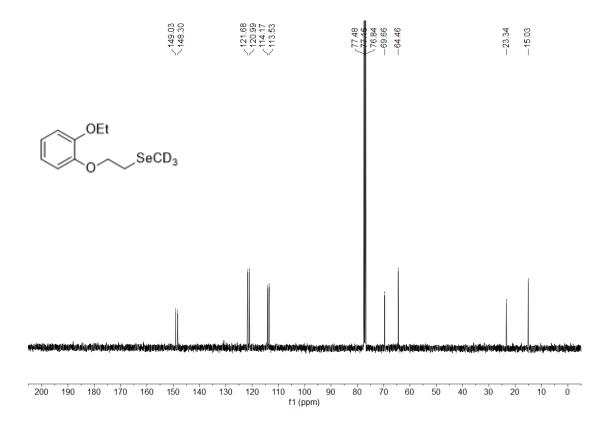


Supplementary Figure 388. ¹H NMR Spectrum of 10q (400 MHz, CDCl₃)



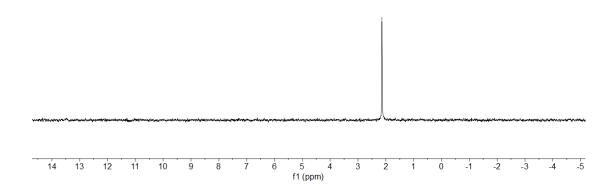


Supplementary Figure 389. 13 C NMR Spectrum of 10q (100 MHz, CDCl₃)

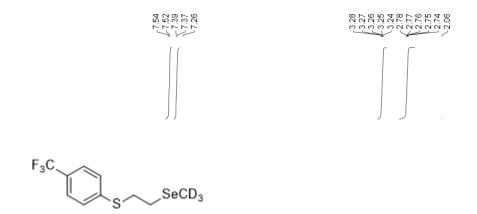


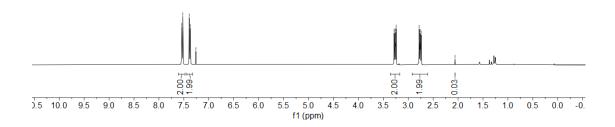
Supplementary Figure 390. ²H NMR Spectrum of 10q (100 MHz, CHCl₃)

1

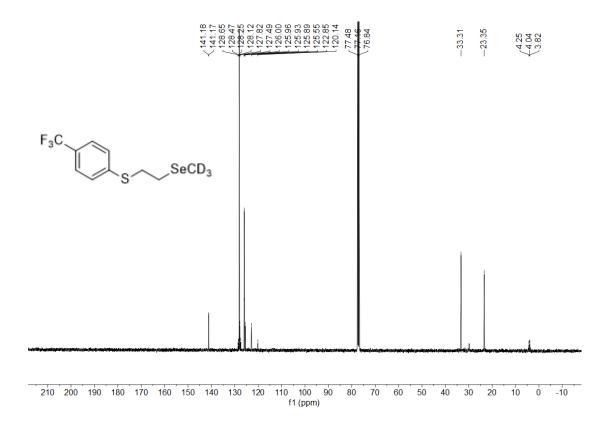


Supplementary Figure 391. ¹H NMR Spectrum of 10r (400 MHz, CDCl₃)

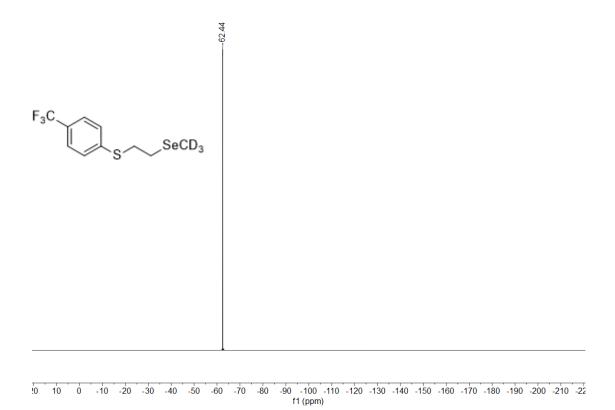




Supplementary Figure 392. ¹³C NMR Spectrum of 10r (100 MHz, CDCl₃)

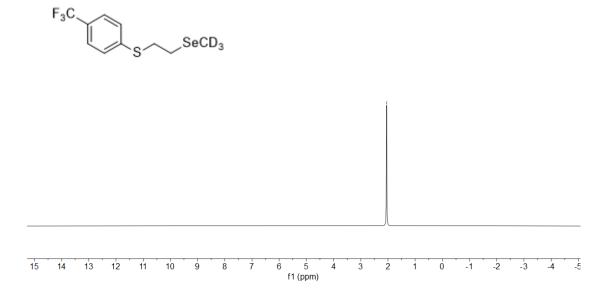


Supplementary Figure 393. ¹⁹F NMR Spectrum of 10r (376 MHz, CDCl₃)

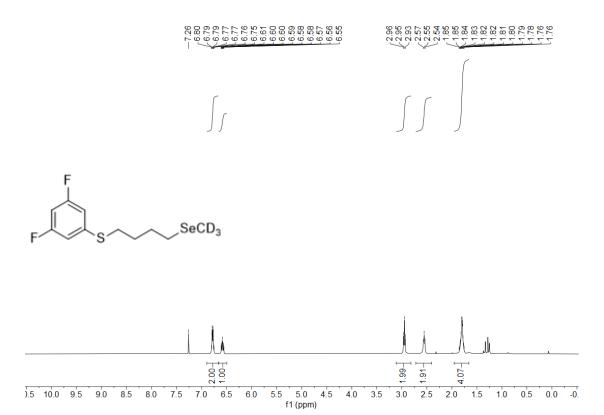


Supplementary Figure 394. ²H NMR Spectrum of 10r (100 MHz, CHCl₃)

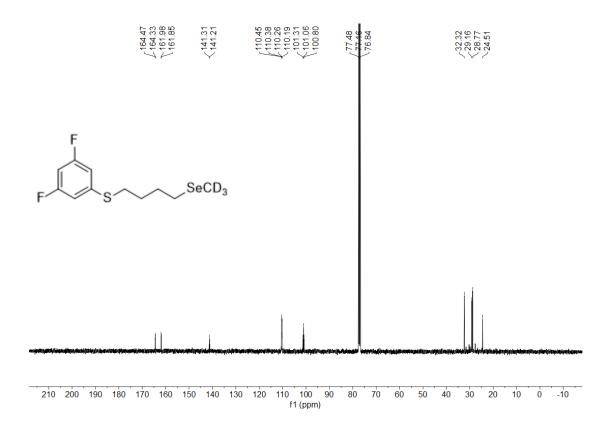




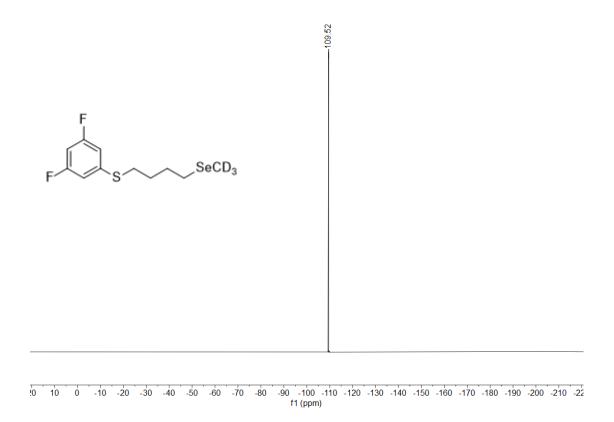
Supplementary Figure 395. ¹H NMR Spectrum of 10s (400 MHz, CDCl₃)



Supplementary Figure 396. ¹³C NMR Spectrum of 10s (100 MHz, CDCl₃)

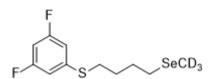


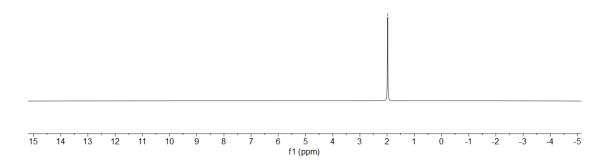
Supplementary Figure 397. ¹⁹F NMR Spectrum of 10s (376 MHz, CDCl₃)



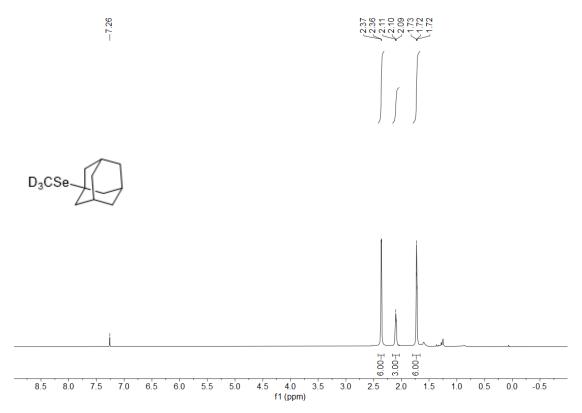
Supplementary Figure 398. ²H NMR Spectrum of 10s (100 MHz, CHCl₃)

1.9

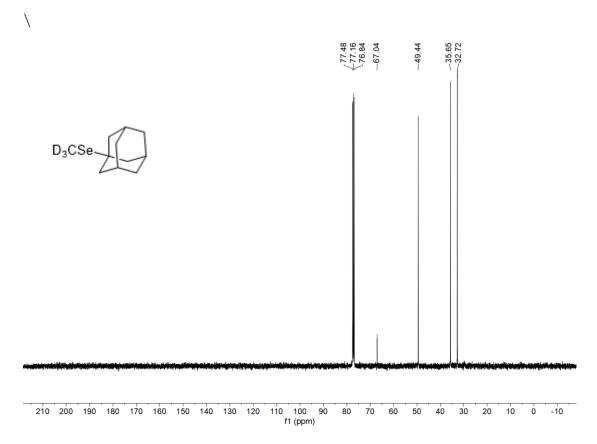




Supplementary Figure 399. 1 H NMR Spectrum of 10t (400 MHz, CDCl₃)



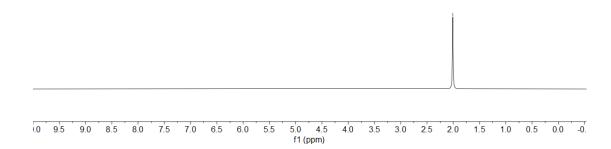
Supplementary Figure 400. ¹³C NMR Spectrum of 10t (100 MHz, CDCl₃)



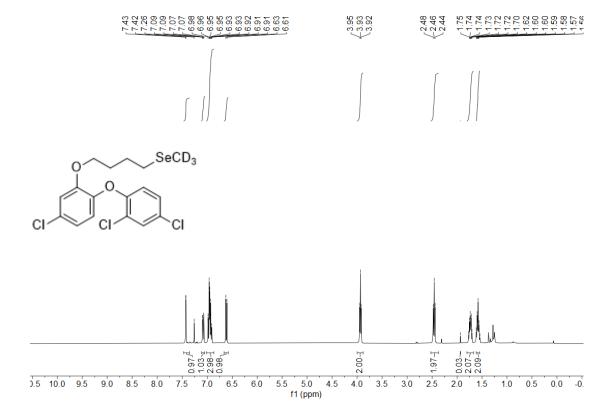
Supplementary Figure 401. ²H NMR Spectrum of 10t (100 MHz, CHCl₃)



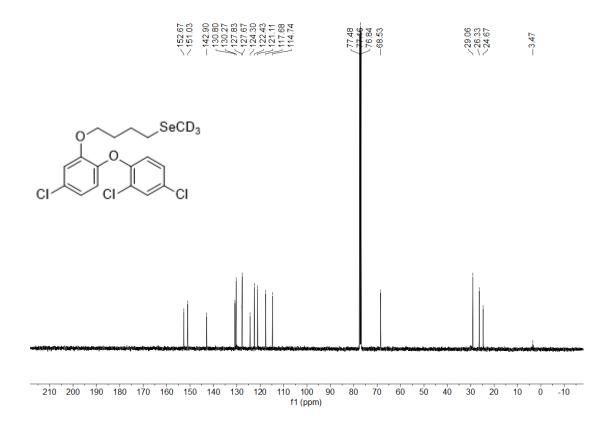




Supplementary Figure 402. ¹H NMR Spectrum of 10u (400 MHz, CDCl₃)

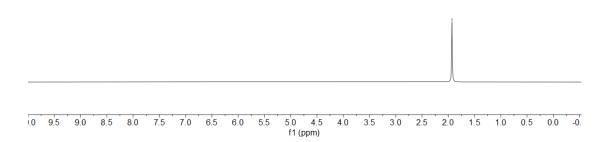


Supplementary Figure 403. ¹³C NMR Spectrum of 10u (100 MHz, CDCl₃)

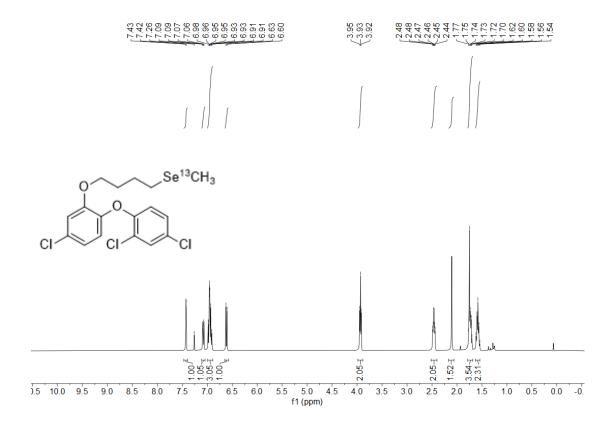


Supplementary Figure 404. ²H NMR Spectrum of 10u (100 MHz, CHCl₃)

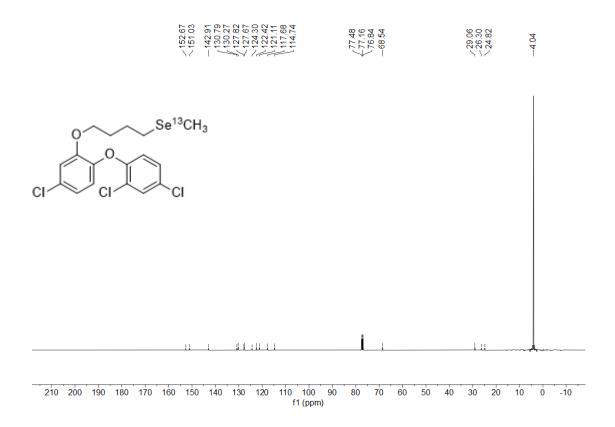
9



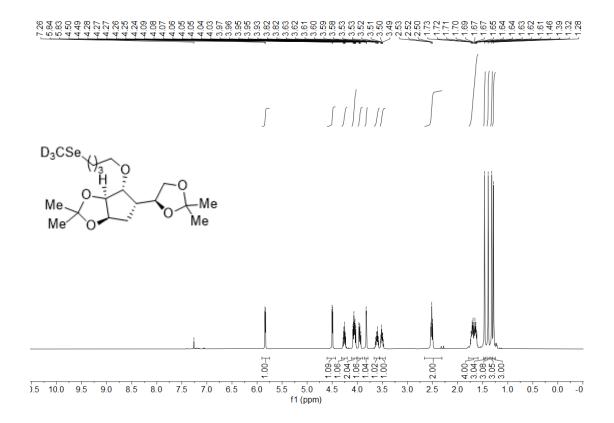
Supplementary Figure 405. ¹H NMR Spectrum of 10v (400 MHz, CDCl₃)



Supplementary Figure 406. ¹³C NMR Spectrum of 10v (100 MHz, CDCl₃)

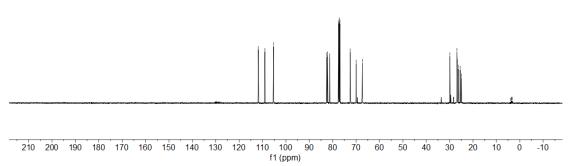


Supplementary Figure 407. ¹H NMR Spectrum of 10w (400 MHz, CDCl₃)



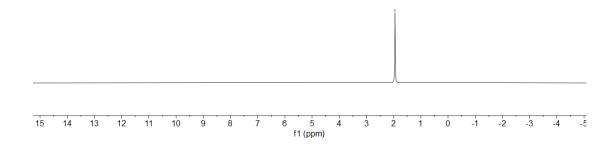
Supplementary Figure 408. ¹³C NMR Spectrum of 10w (100 MHz, CDCl₃)



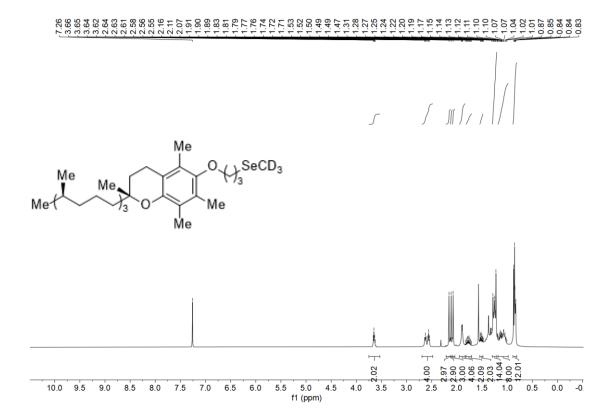


Supplementary Figure 409. ²H NMR Spectrum of **10w** (100 MHz, CHCl₃)

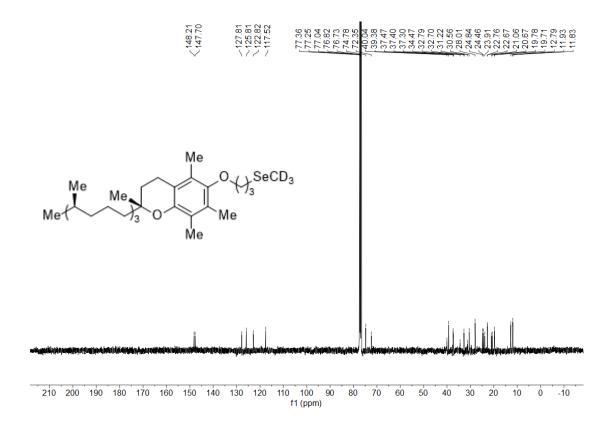
-1.95



Supplementary Figure 410. ¹H NMR Spectrum of 10x (400 MHz, CDCl₃)



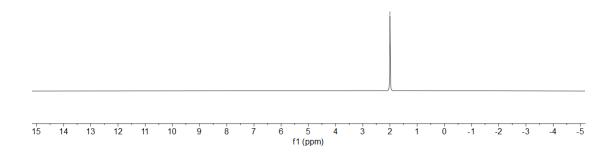
Supplementary Figure 411. ¹³C NMR Spectrum of 10x (100 MHz, CDCl₃)



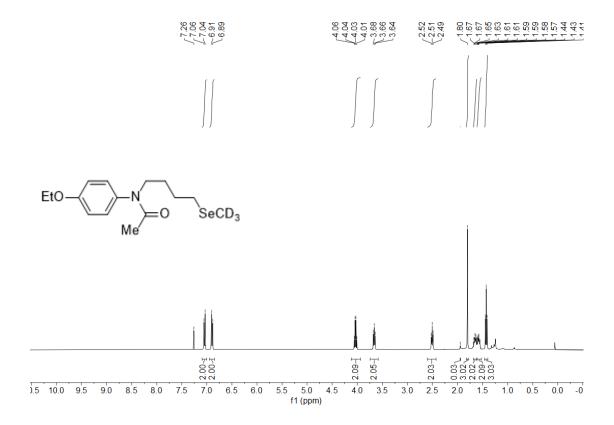
Supplementary Figure 412. ²H NMR Spectrum of 10x (100 MHz, CHCl₃)

-2.00

$$\begin{array}{c} \text{Me} \\ \text{Me} \\$$

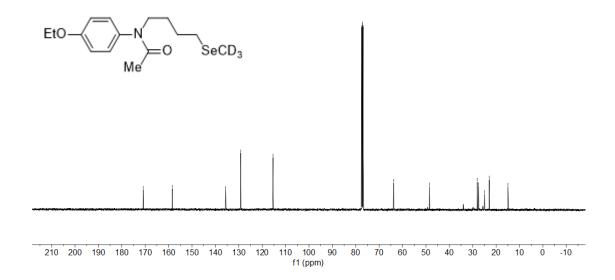


Supplementary Figure 413. ¹H NMR Spectrum of 10y (400 MHz, CDCl₃)



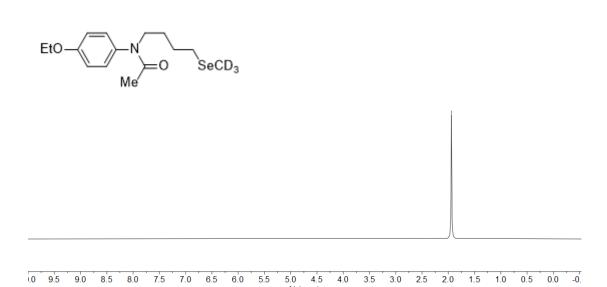
Supplementary Figure 414. ¹³C NMR Spectrum of 10y (100 MHz, CDCl₃)



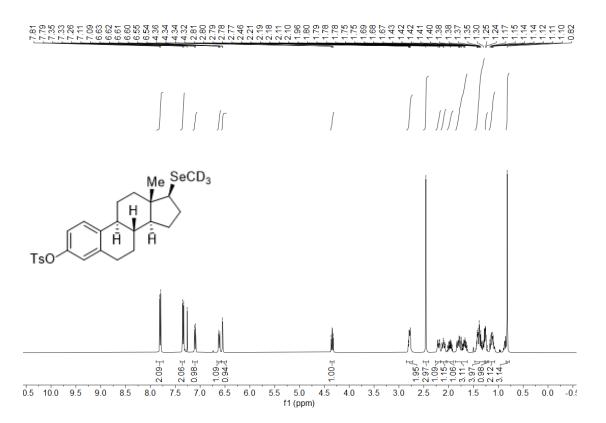


Supplementary Figure 415. ²H NMR Spectrum of 10y (100 MHz, CHCl₃)

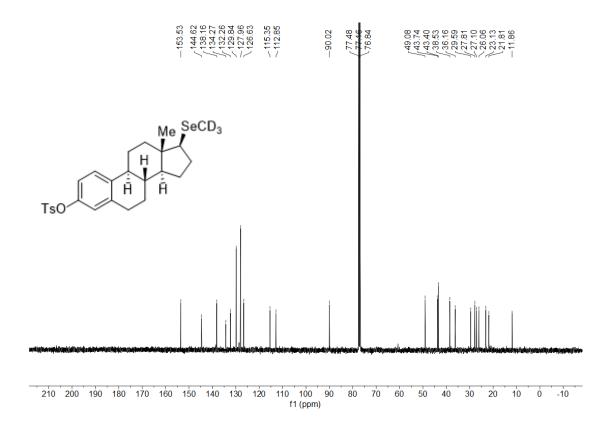
1.94



Supplementary Figure 416. ¹H NMR Spectrum of 10z (400 MHz, CDCl₃)

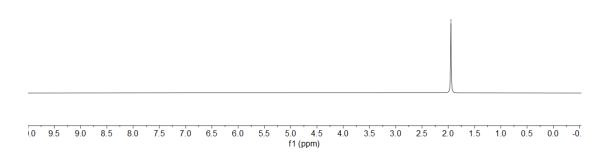


Supplementary Figure 417. ¹³C NMR Spectrum of 10z (100 MHz, CDCl₃)

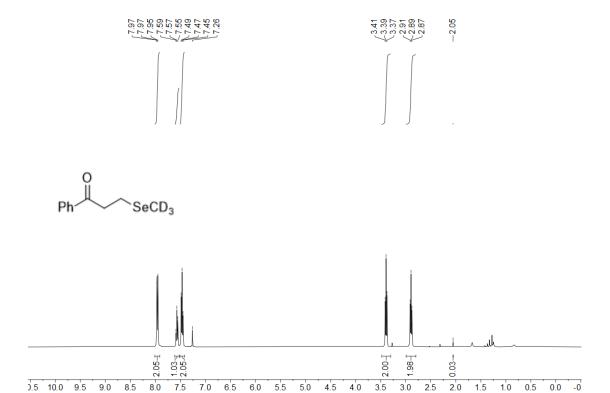


Supplementary Figure 418. ²H NMR Spectrum of 10z (100 MHz, CHCl₃)

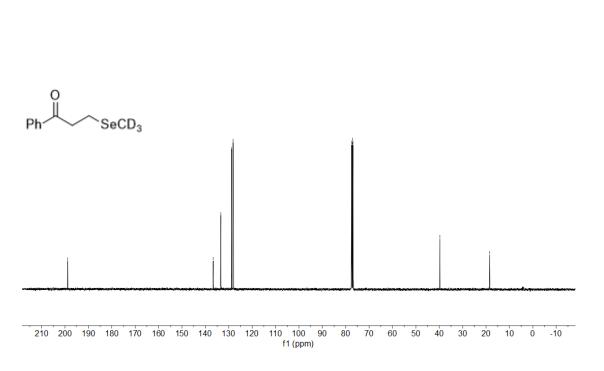
-1.95



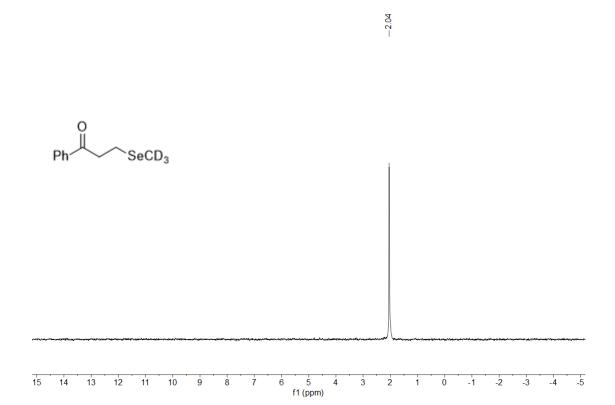
Supplementary Figure 419. ¹H NMR Spectrum of 11a (400 MHz, CDCl₃)



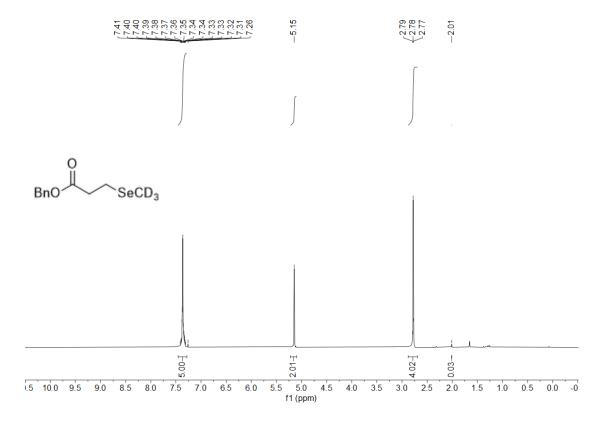
Supplementary Figure 420. ¹³C NMR Spectrum of 11a (100 MHz, CDCl₃)



Supplementary Figure 421. ²H NMR Spectrum of **11a** (100 MHz, CHCl₃)

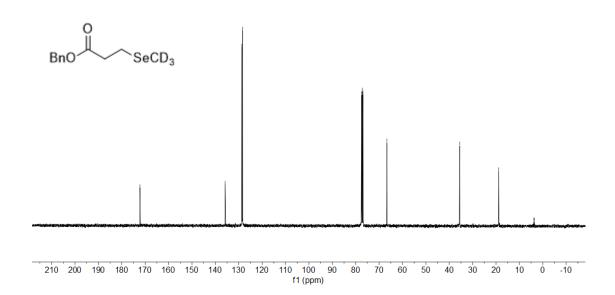


Supplementary Figure 422. ¹H NMR Spectrum of 11b (400 MHz, CDCl₃)



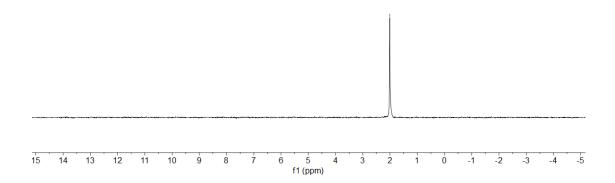
Supplementary Figure 423. ¹³C NMR Spectrum of 11b (100 MHz, CDCl₃)



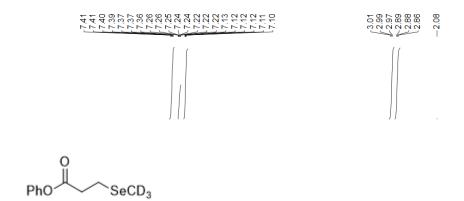


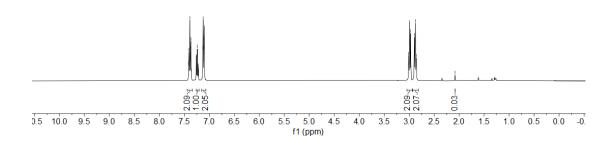
Supplementary Figure 424. ²H NMR Spectrum of 11b (100 MHz, CHCl₃)

-2.0



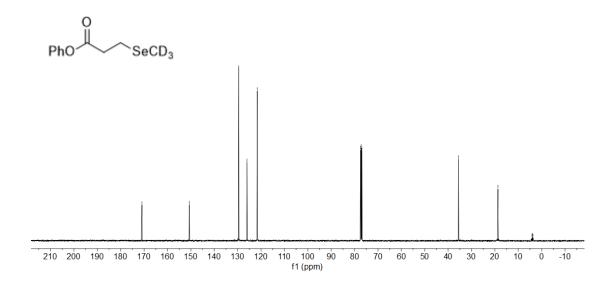
Supplementary Figure 425. ¹H NMR Spectrum of **11c** (400 MHz, CDCl₃)





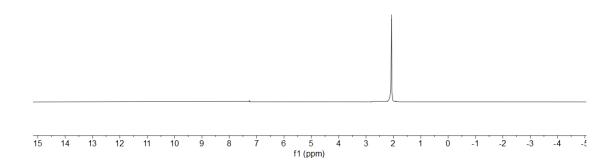
Supplementary Figure 426. ¹³C NMR Spectrum of 11c (100 MHz, CDCl₃)

170.93	150.65	129.52 125.99 121.60	77.48 77.16	35.55	18.69	4.14 3.93 3.71
1	1	1 / 1		1	1	



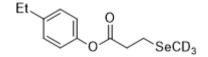
Supplementary Figure 427. ²H NMR Spectrum of **11c** (100 MHz, CHCl₃)

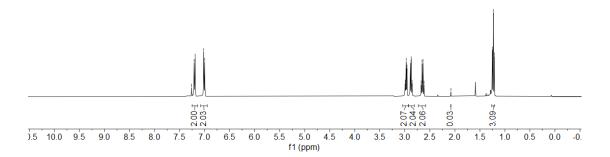
-2.07



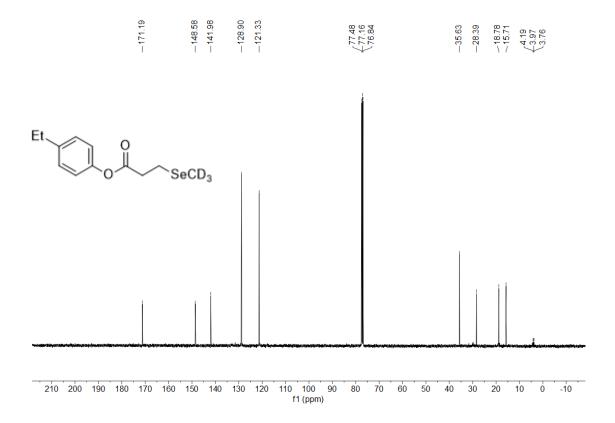
Supplementary Figure 428. ¹H NMR Spectrum of 11d (400 MHz, CDCl₃)



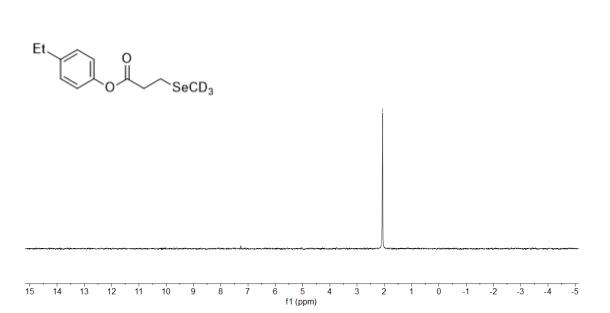




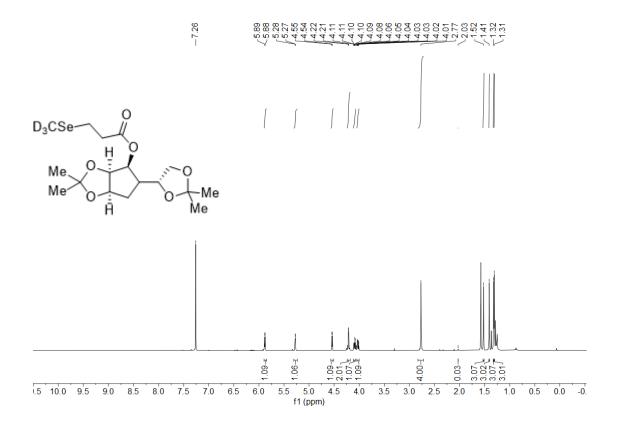
Supplementary Figure 429. ¹³C NMR Spectrum of 11d (100 MHz, CDCl₃)



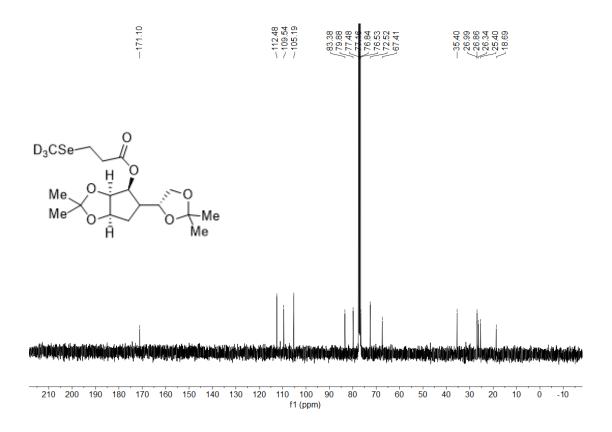
Supplementary Figure 430. ²H NMR Spectrum of 11d (100 MHz, CHCl₃)



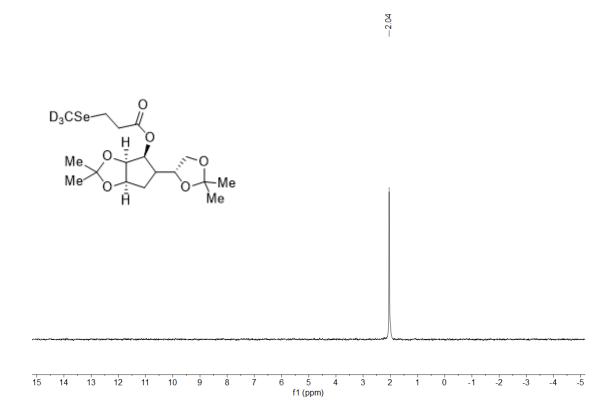
Supplementary Figure 431. ¹H NMR Spectrum of **11e** (400 MHz, CDCl₃)



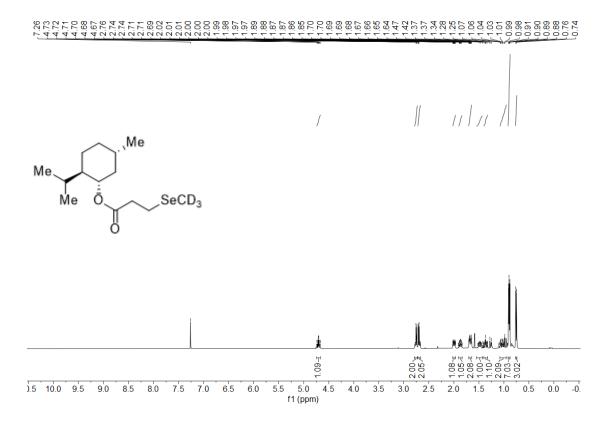
Supplementary Figure 432. ¹³C NMR Spectrum of 11e (100 MHz, CDCl₃)



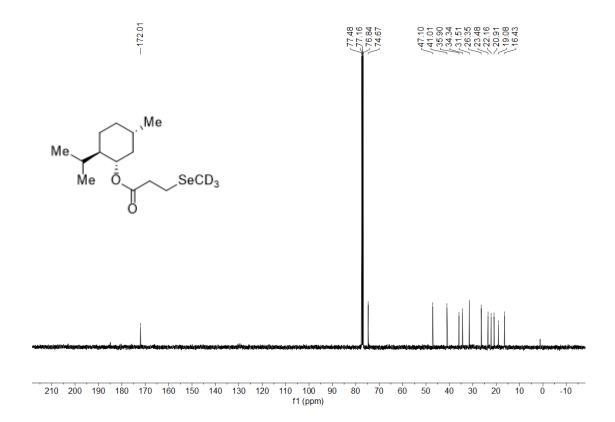
Supplementary Figure 433. ²H NMR Spectrum of **11e** (100 MHz, CHCl₃)



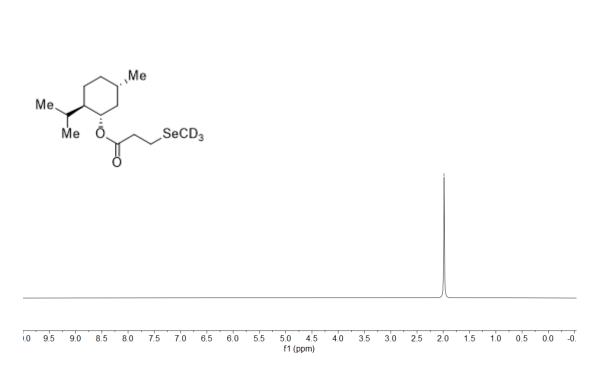
Supplementary Figure 434. ¹H NMR Spectrum of 11f (400 MHz, CDCl₃)



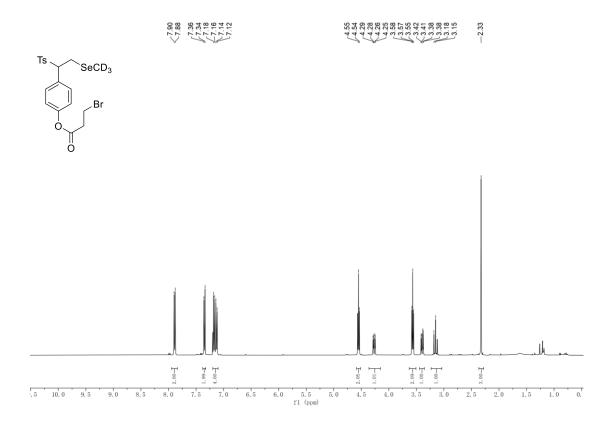
Supplementary Figure 435. ¹³C NMR Spectrum of 11f (100 MHz, CDCl₃)



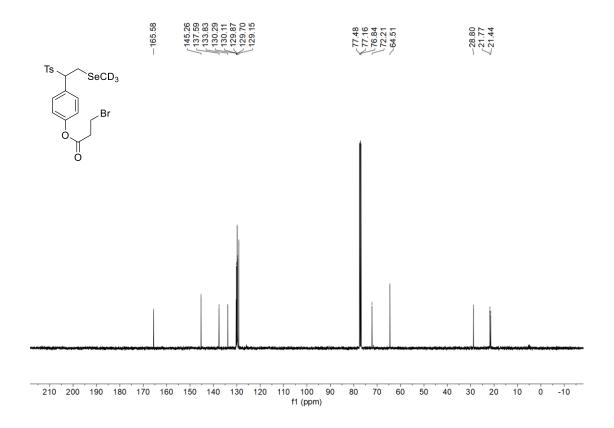
Supplementary Figure 436. ²H NMR Spectrum of 11f (100 MHz, CHCl₃)



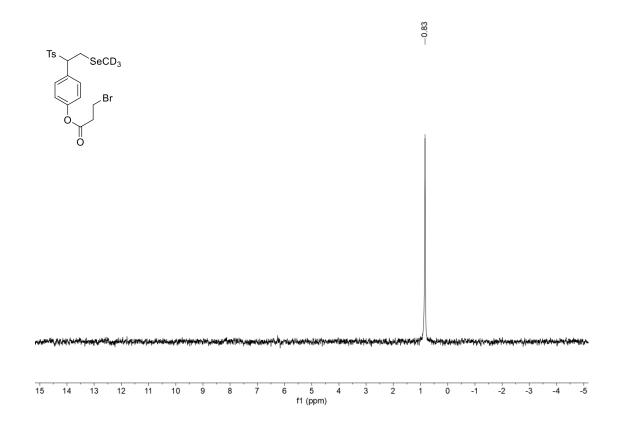
Supplementary Figure 437. ¹H NMR Spectrum of 13 (100 MHz, CHCl₃)



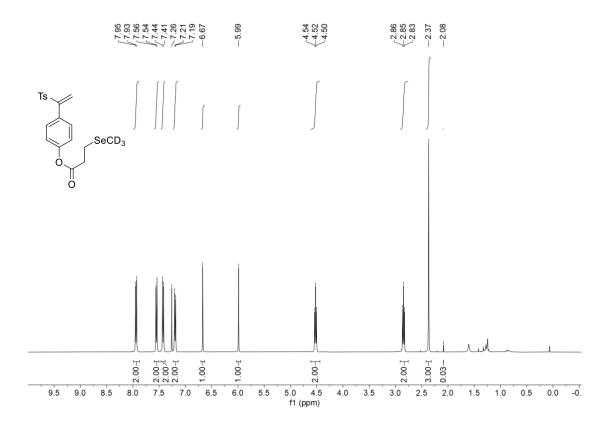
Supplementary Figure 438. ¹³C NMR Spectrum of 13 (100 MHz, CHCl₃)



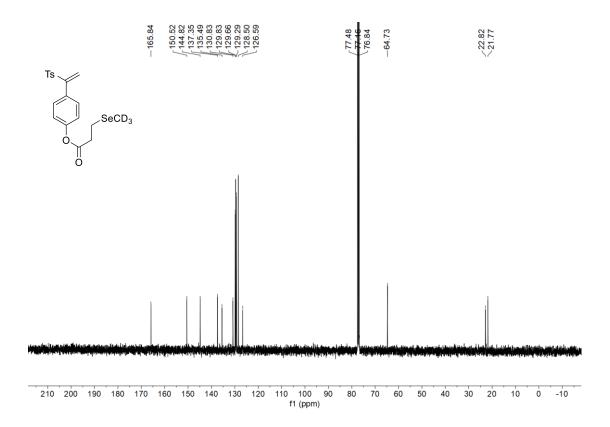
Supplementary Figure 439. ²H NMR Spectrum of **13** (100 MHz, CHCl₃)



Supplementary Figure 440. ¹H NMR Spectrum of 14 (400 MHz, CDCl₃)

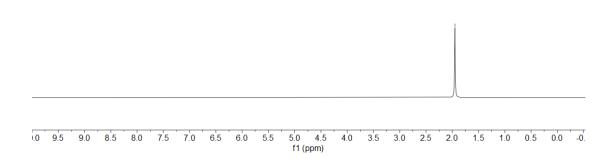


Supplementary Figure 441. ¹³C NMR Spectrum of **14** (100 MHz, CDCl₃)

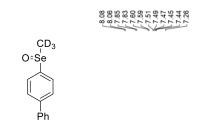


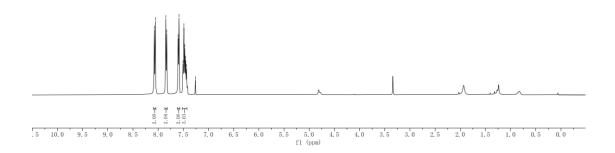
Supplementary Figure 442. ²H NMR Spectrum of 14 (100 MHz, CHCl₃)



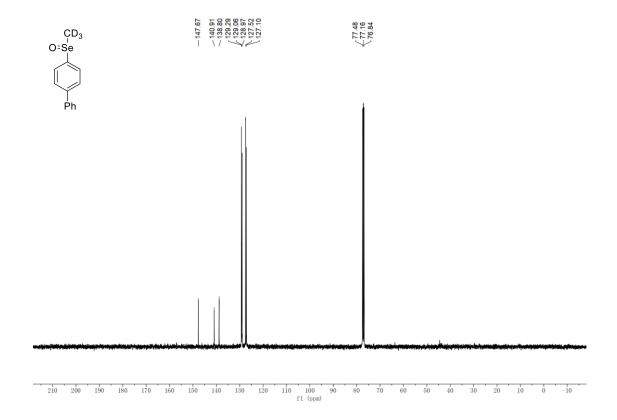


Supplementary Figure 443. ¹H NMR Spectrum of 15a (400 MHz, CDCl₃)

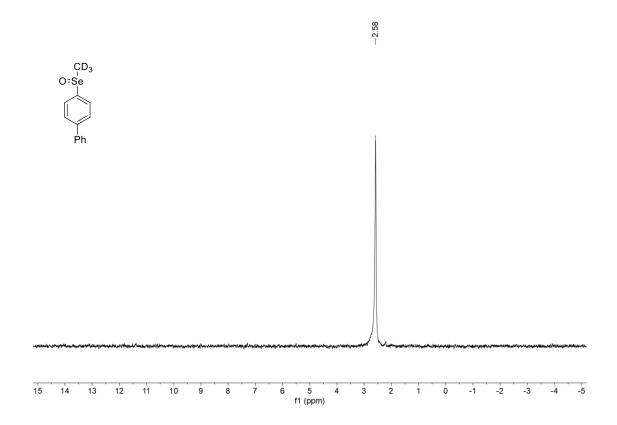




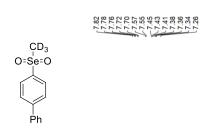
Supplementary Figure 444. ¹³C NMR Spectrum of 15a (400 MHz, CDCl₃)

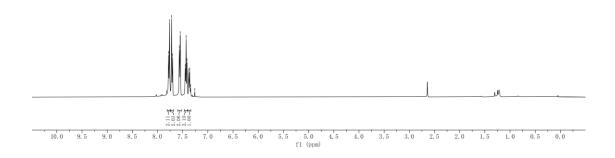


Supplementary Figure 445. ²H NMR Spectrum of 15a (100 MHz, CHCl₃)

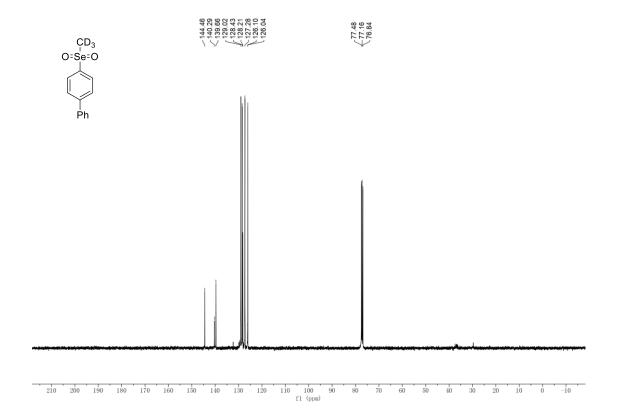


Supplementary Figure 446. ¹H NMR Spectrum of **15b** (400 MHz, CDCl₃)

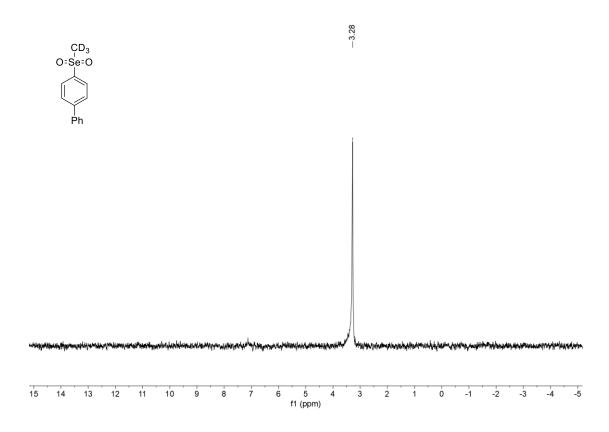




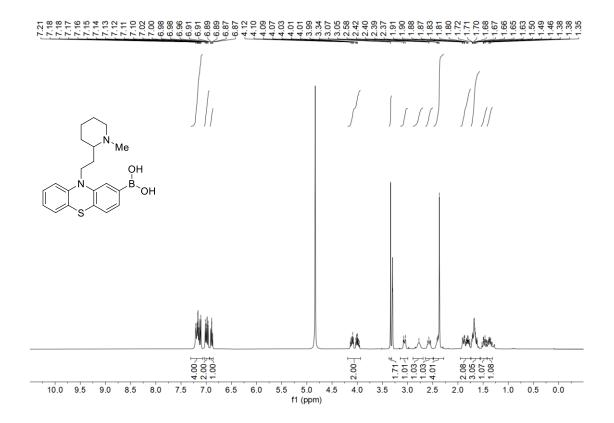
Supplementary Figure 447. ¹³C NMR Spectrum of 15b (100 MHz, CDCl₃)



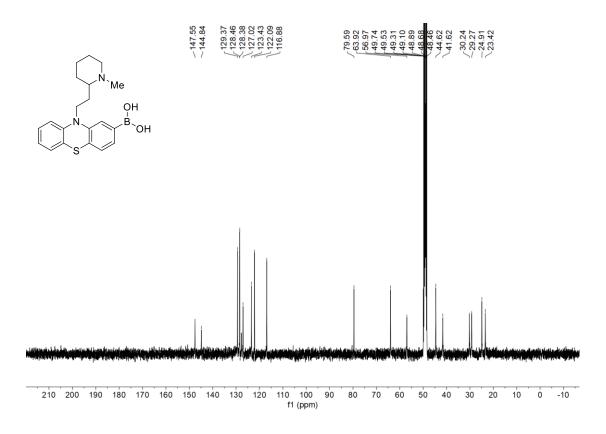
Supplementary Figure 448. ²H NMR Spectrum of 15b (100 MHz, CHCl₃)



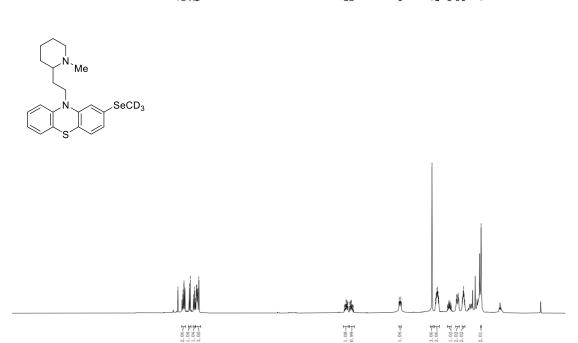
Supplementary Figure 449. ¹H NMR Spectrum of **18** (400 MHz, CD₃OD)



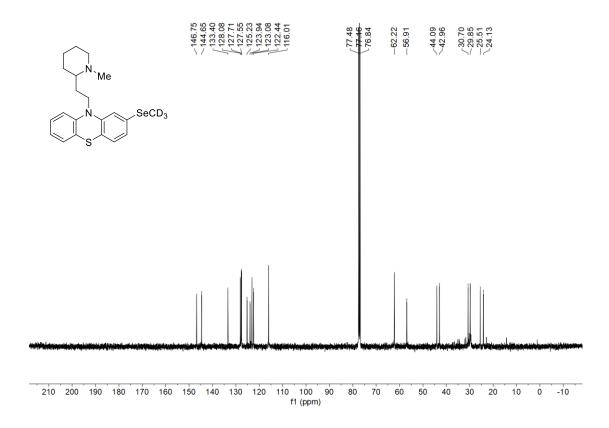
Supplementary Figure 450. ¹³C NMR Spectrum of 18 (100 MHz, CD₃OD)



Supplementary Figure 451. ¹H NMR Spectrum of 19 (400 MHz, CDCl₃)

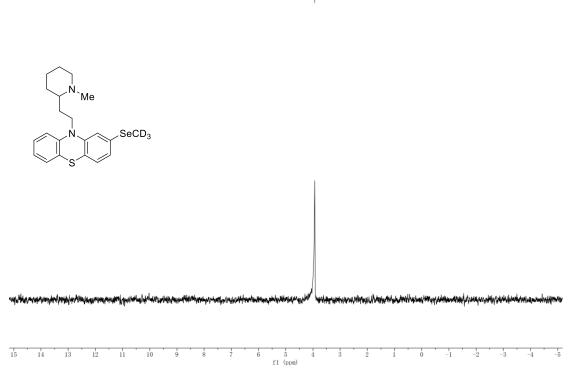


Supplementary Figure 452. ¹³C NMR Spectrum of 19 (100 MHz, CDCl₃)

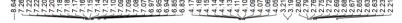


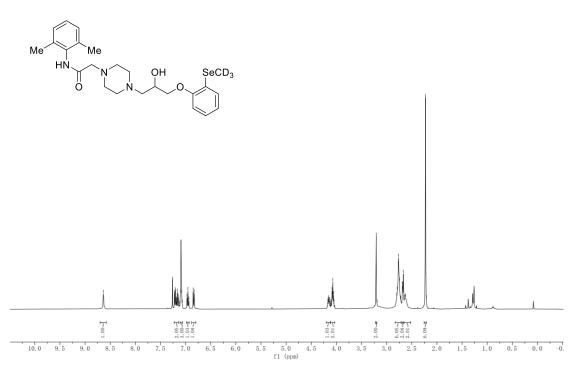
Supplementary Figure 453. ²H NMR Spectrum of **19** (100 MHz, CHCl₃)



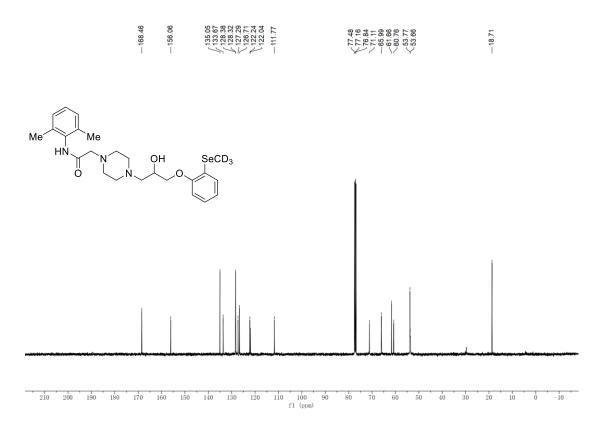


Supplementary Figure 454. ¹H NMR Spectrum of 21 (400 MHz, CDCl₃)

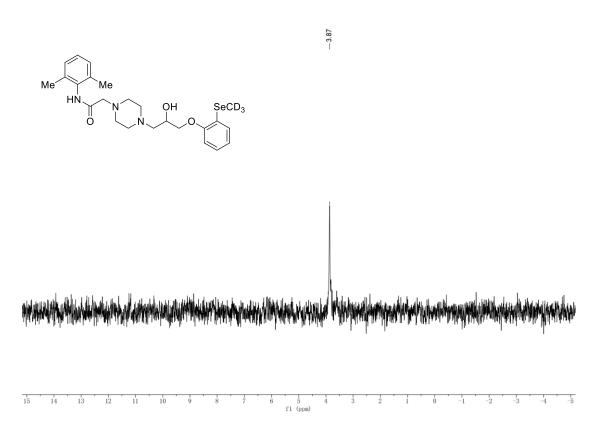




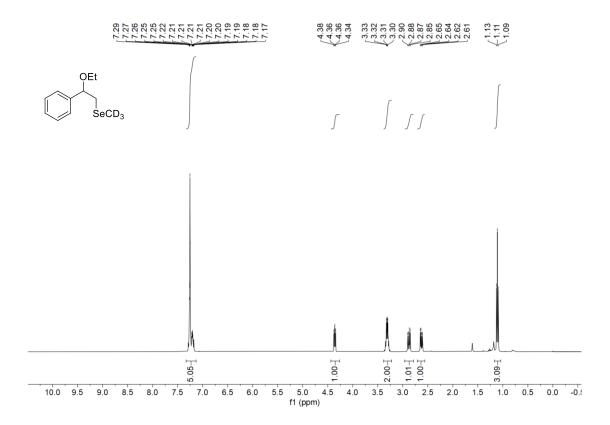
Supplementary Figure 455. ¹³C NMR Spectrum of 19 (100 MHz, CDCl₃)



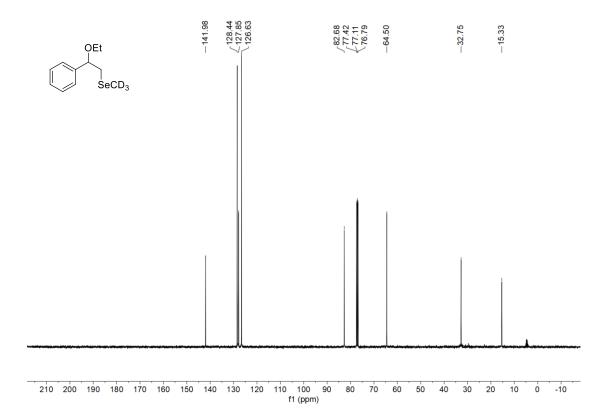
Supplementary Figure 456. ²H NMR Spectrum of 19 (100 MHz, CHCl₃)



Supplementary Figure 457. ¹H NMR Spectrum of S1-29 (400 MHz, CDCl₃)

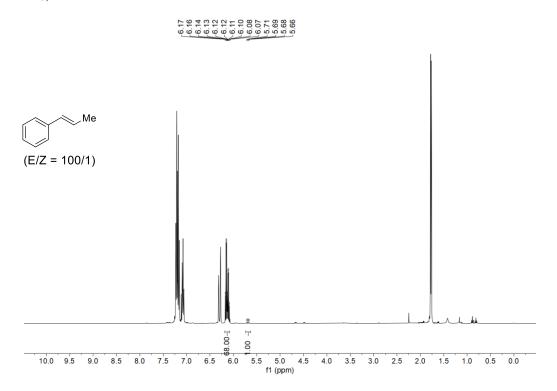


Supplementary Figure 458. ¹³C NMR Spectrum of S1-29 (100 MHz, CDCl₃)

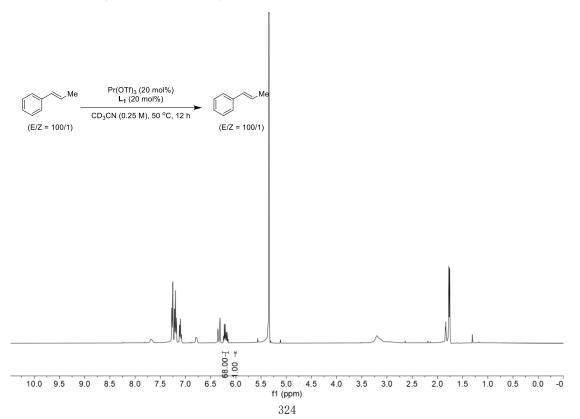


11.5 NMR Spectra of Control Experiments of Mechanisms

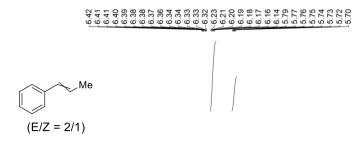
Supplementary Figure 459. ¹H NMR Spectrum of (*E*)- β -Methylstyrene (400 MHz, CDCl₃)

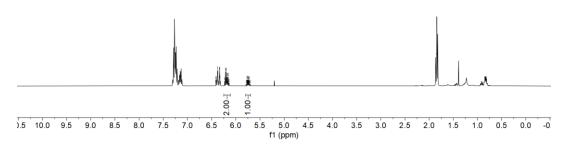


Supplementary Figure 460. ¹H NMR Spectrum of Control Experiments of Mechanism-1 (400 MHz, CDCl₃)

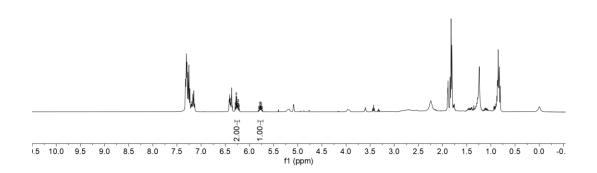


Supplementary Figure 461. ¹H NMR Spectrum of Mix β-Methylstyrene (400 MHz, CDCl₃)

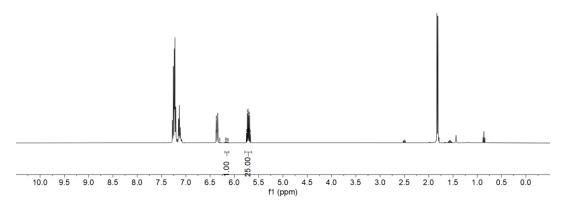




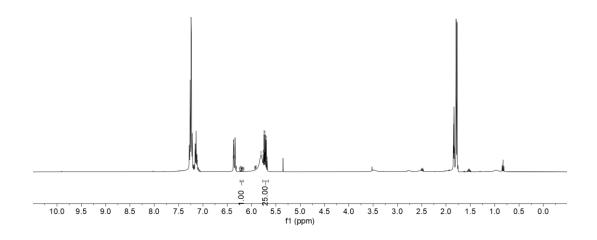
Supplementary Figure 462. ¹H NMR Spectrum of Control Experiments of Mechanism-2 (400 MHz, CDCl₃)



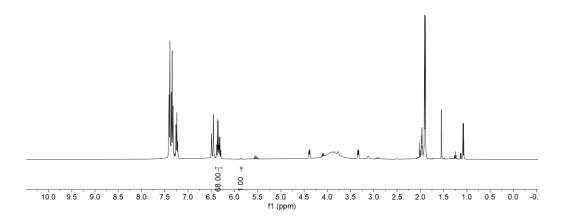
Supplementary Figure 463. ¹H NMR Spectrum of (*Z*)- β -Methylstyrene (400 MHz, CDCl₃)



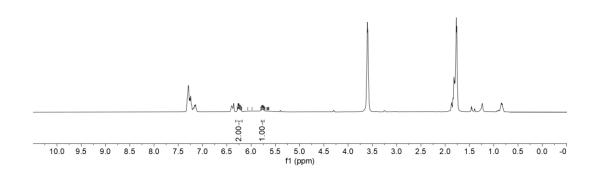
Supplementary Figure 464. ¹H NMR Spectrum of Control Experiments of Mechanism-3 (400 MHz, CDCl₃)



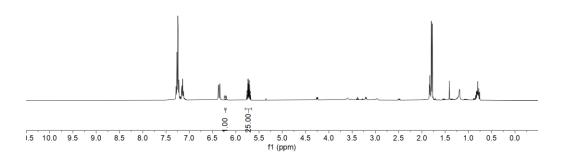
Supplementary Figure 465. ¹H NMR Spectrum of Control Experiments of Mechanism-4 (400 MHz, CDCl₃)



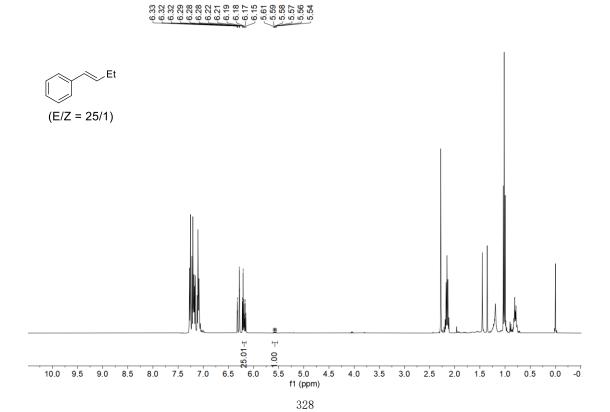
Supplementary Figure 466. ¹H NMR Spectrum of Control Experiments of Mechanism-5 (400 MHz, CDCl₃)



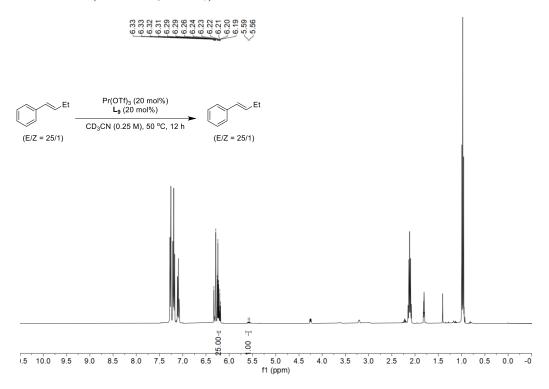
Supplementary Figure 467. ¹H NMR Spectrum of Control Experiments of Mechanism-6 (400 MHz, CDCl₃)



Supplementary Figure 468. ¹H NMR Spectrum of (*E*)- β -Ethylstyrene (400 MHz, CDCl₃)

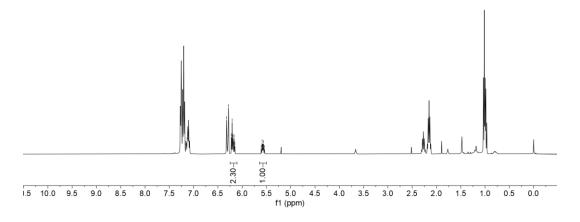


Supplementary Figure 469. ¹H NMR Spectrum of Control Experiments of Mechanism-7 (400 MHz, CDCl₃)

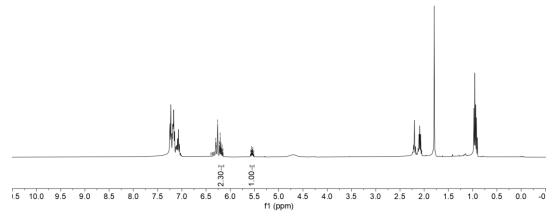


Supplementary Figure 470. ¹H NMR Spectrum of Mix β -Ethylstyrene (400 MHz, CDCl₃)

$$Et$$
 $(E/Z = 2.3/1)$

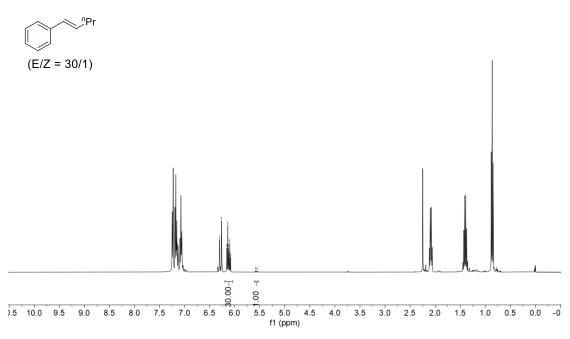


Supplementary Figure 471. ¹H NMR Spectrum of Control Experiments of Mechanism-8 (400 MHz, CDCl₃)



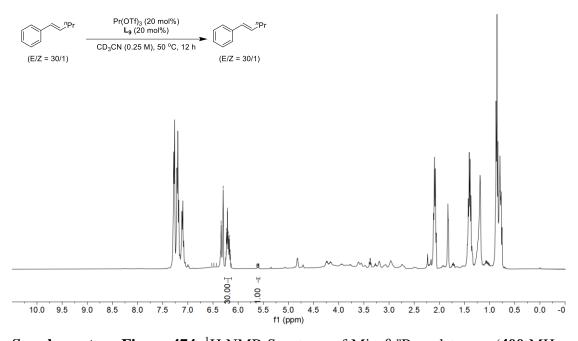
Supplementary Figure 472. ¹H NMR Spectrum of (*E*)- β -ⁿPropylstyrene (400 MHz, CDCl₃)





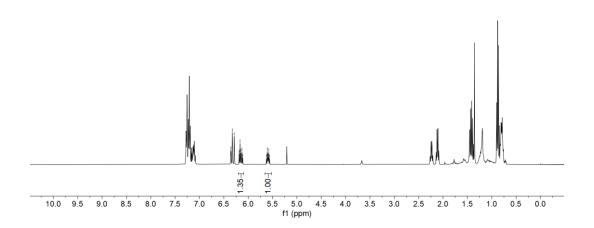
Supplementary Figure 473. ¹H NMR Spectrum of Control Experiments of Mechanism-9 (**400** MHz, CDCl₃)

6.5.5 6.

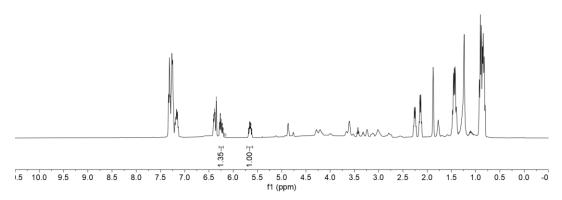


Supplementary Figure 474. ¹H NMR Spectrum of Mix β -ⁿPropylstyrene (**400** MHz, CDCl₃)

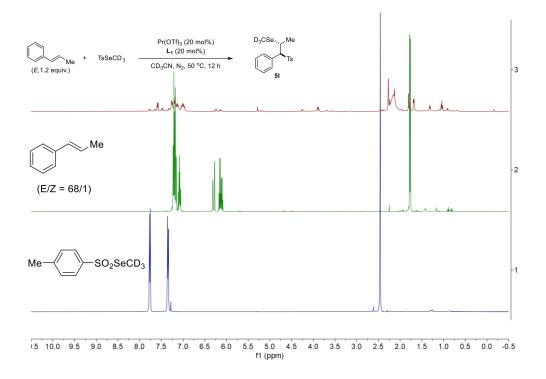
$$^{n}Pr$$
(E/Z = 1.35/1)



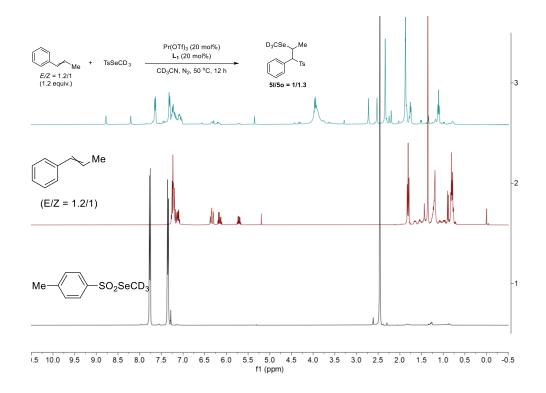
Supplementary Figure 475. ¹H NMR Spectrum of Control Experiments of Mechanism-10 (400 MHz, CDCl₃)



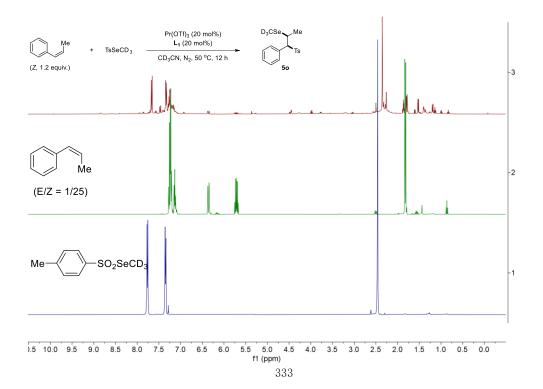
Supplementary Figure 476. ¹H NMR Spectrum of Mechanism Verification Experiments-1-1 (400 MHz, CDCl₃)



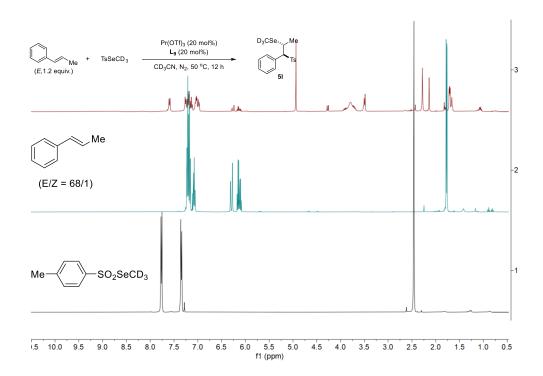
Supplementary Figure 477. ¹H NMR Spectrum of Mechanism Verification Experiments-1-2 (400 MHz, CDCl₃)



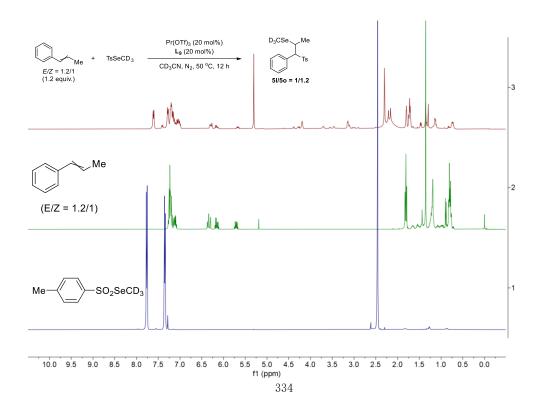
Supplementary Figure 478. ¹H NMR Spectrum of Mechanism Verification Experiments-1-3 (400 MHz, CDCl₃)



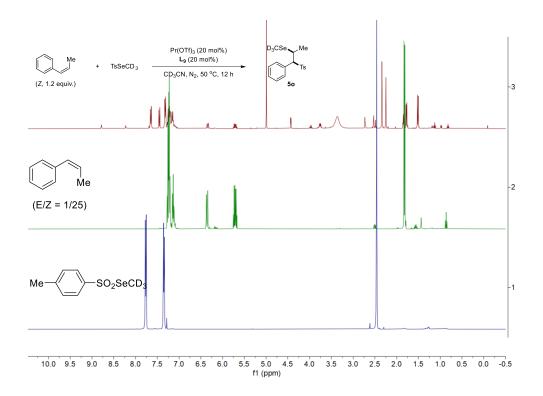
Supplementary Figure 479. ¹H NMR Spectrum of Mechanism Verification Experiments-2-1 (400 MHz, CDCl₃)



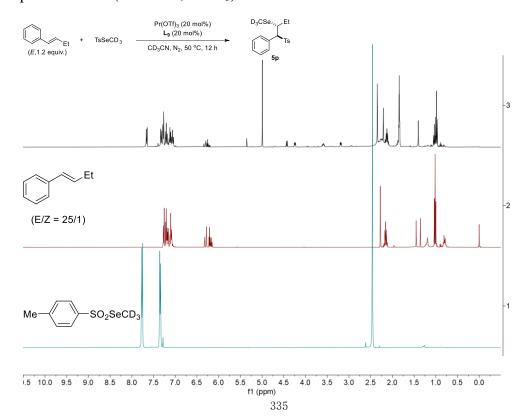
Supplementary Figure 480. ¹H NMR Spectrum of Mechanism Verification Experiments-2-2 (400 MHz, CDCl₃)



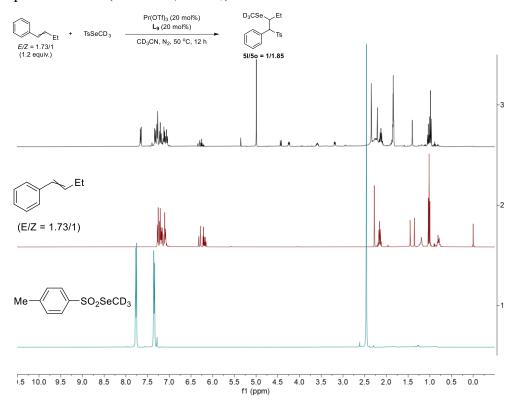
Supplementary Figure 481. ¹H NMR Spectrum of Mechanism Verification Experiments-2-3 (400 MHz, CDCl₃)



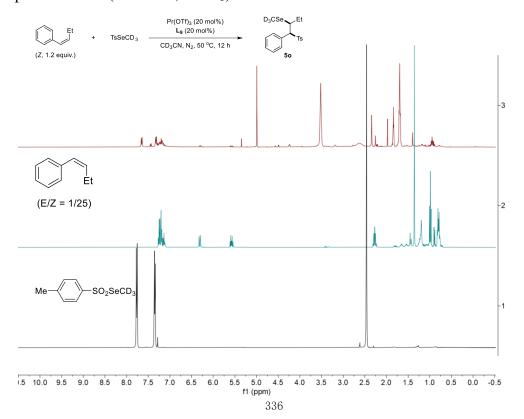
Supplementary Figure 482. ¹H NMR Spectrum of Mechanism Verification Experiments-3-1 (400 MHz, CDCl₃)



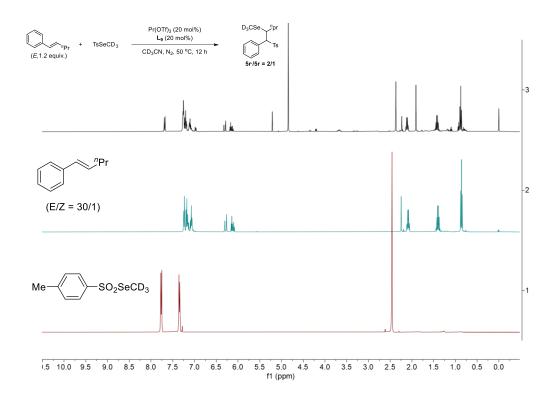
Supplementary Figure 483. ¹H NMR Spectrum of Mechanism Verification Experiments-3-2 (400 MHz, CDCl₃)



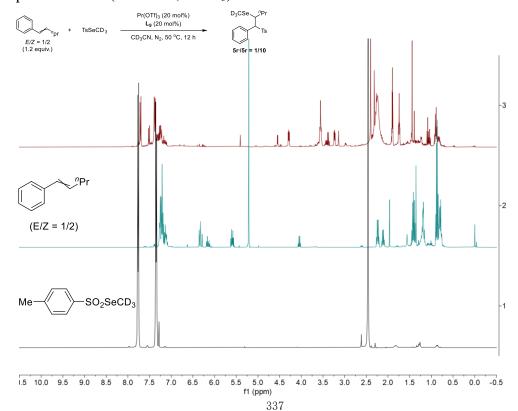
Supplementary Figure 484. ¹H NMR Spectrum of Mechanism Verification Experiments-3-3 (400 MHz, CDCl₃)



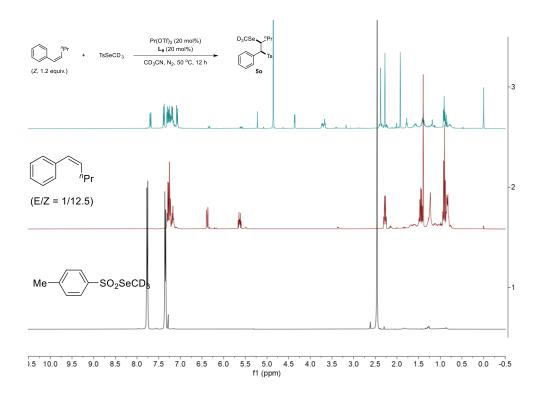
Supplementary Figure 485. ¹H NMR Spectrum of Mechanism Verification Experiments-4-1 (400 MHz, CDCl₃)



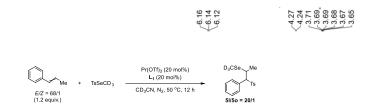
Supplementary Figure 486. ¹H NMR Spectrum of Mechanism Verification Experiments-4-2 (400 MHz, CDCl₃)

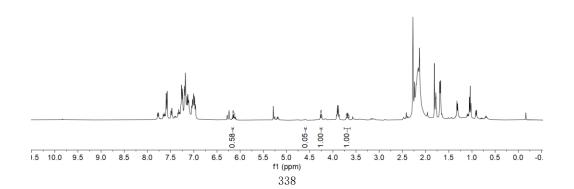


Supplementary Figure 487. ¹H NMR Spectrum of Mechanism Verification Experiments-4-3 (400 MHz, CDCl₃)

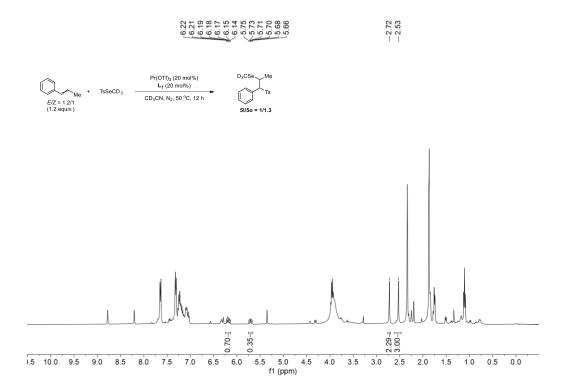


Supplementary Figure 488. In-situ ¹H NMR Spectrum of Mechanism Verification Experiments-1-1 (400 MHz, CDCl₃)

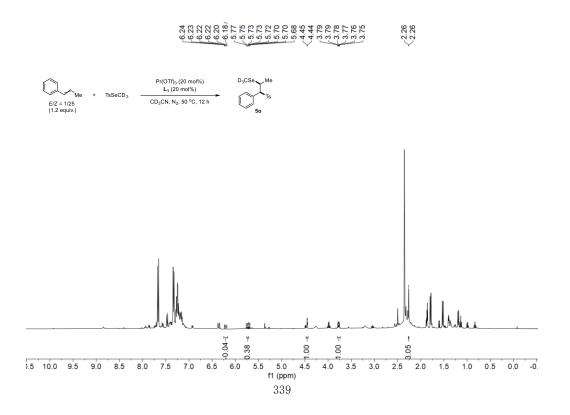




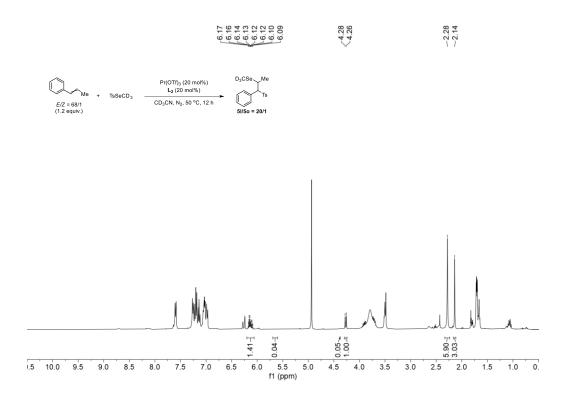
Supplementary Figure 489. In-situ ¹H NMR Spectrum of Mechanism Verification Experiments-1-2 (400 MHz, CDCl₃)



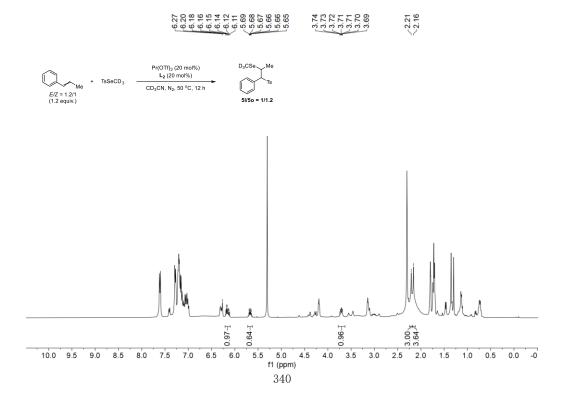
Supplementary Figure 490. In-situ ¹H NMR Spectrum of Mechanism Verification Experiments-1-3 (400 MHz, CDCl₃)



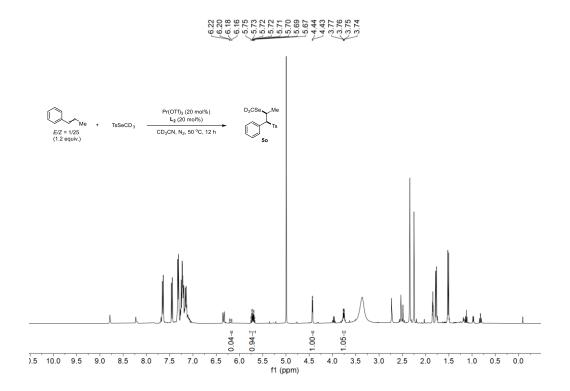
Supplementary Figure 491. In-situ ¹H NMR Spectrum of Mechanism Verification Experiments-2-1 (400 MHz, CDCl₃)



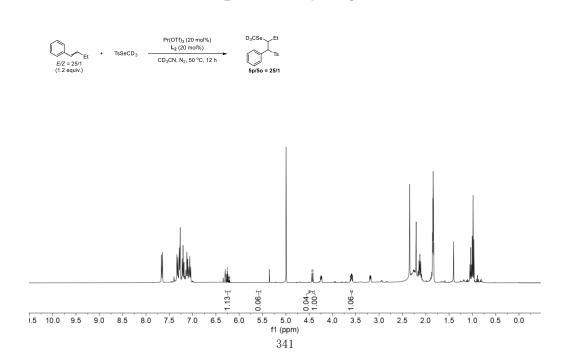
Supplementary Figure 492. In-situ ¹H NMR Spectrum of Mechanism Verification Experiments-2-2 (400 MHz, CDCl₃)



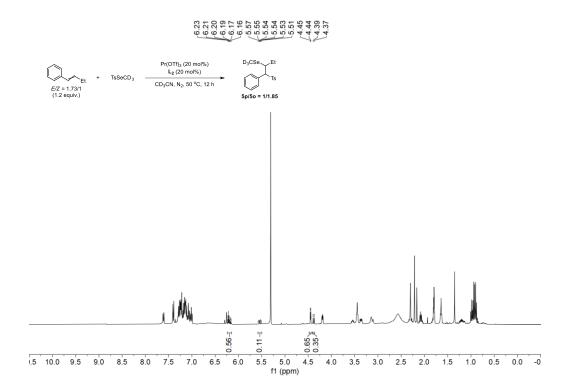
Supplementary Figure 493. In-situ ¹H NMR Spectrum of Mechanism Verification Experiments-2-3 (400 MHz, CDCl₃)



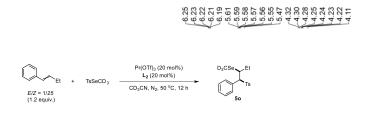
Supplementary Figure 494. In-situ ¹H NMR Spectrum of Mechanism Verification Experiments-3-1 (400 MHz, CDCl₃)

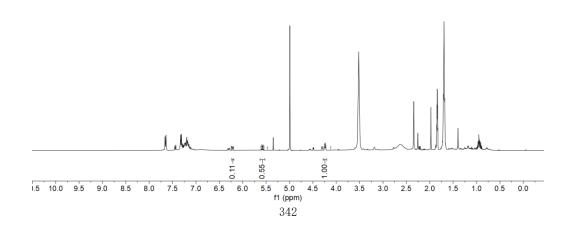


Supplementary Figure 495. In-situ ¹H NMR Spectrum of Mechanism Verification Experiments-3-2 (400 MHz, CDCl₃)

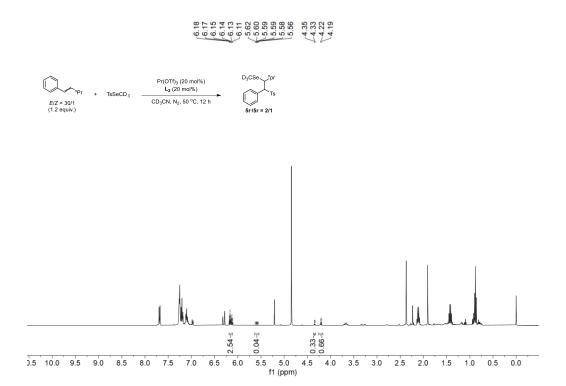


Supplementary Figure 496. In-situ ¹H NMR Spectrum of Mechanism Verification Experiments-3-3 (400 MHz, CDCl₃)

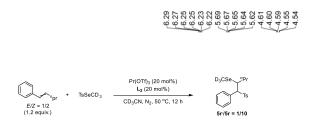


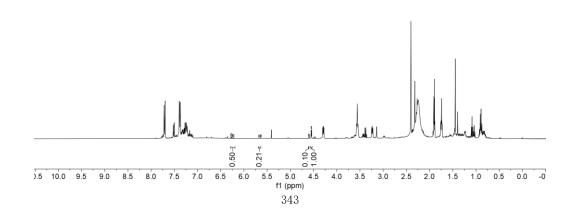


Supplementary Figure 497. In-situ ¹H NMR Spectrum of Mechanism Verification Experiments-4-1 (400 MHz, CDCl₃)



Supplementary Figure 498. In-situ ¹H NMR Spectrum of Mechanism Verification Experiments-4-2 (400 MHz, CDCl₃)





Supplementary Figure 499. In-situ ¹H NMR Spectrum of Mechanism Verification Experiments-4-3 (400 MHz, CDCl₃)

