

Supporting Information

Cu-Mediated Arylselenylation of Aryl Halides with Trifluoromethyl Aryl Selenonium Ylides

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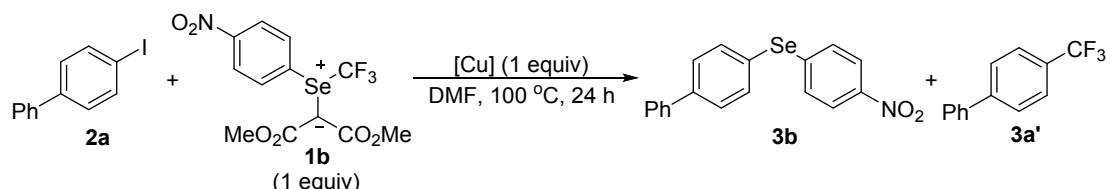
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1. General information

All reactions were carried out under a nitrogen atmosphere unless otherwise stated. The NMR spectra were recorded in CDCl_3 or CD_3COCD_3 on a 500 MHz (for ^1H), 471 MHz (for ^{19}F), and 126 MHz (for ^{13}C) spectrometer. All chemical shifts were reported in ppm relative to TMS (0 ppm for ^1H NMR) and PhOCF_3 (58.0 ppm for ^{19}F NMR) as an internal or external standard, respectively. The coupling constants were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. The HPLC experiments were carried out on a Wufeng LC-100 II instrument (column: Shodex, C18, 5 μm , 4.6 \times 250 mm), and the HPLC yields of the products were determined by using the corresponding pure compounds as the external standards. Melting points were measured and uncorrected. MS experiments were performed on a TOF-Q ESI or EI instrument. Trifluoromethyl aryl selenium ylides (**1a-b¹** and **1f-j¹**), dimethyl 2-(phenylselanyl)malonate (**4**,² and aryl trifluoromethyl selenoethers³ (starting materials for the synthesis of **1**) were synthesized according to the literatures. Solvents were purified according to the literature.⁴ Other reagents used in the reactions were all purchased from the commercial sources and used without further purification.

2. Screening the optimal reaction conditions for **1b** and **2a**

Table S1. Reaction of **2a** with **1b** in the presence of different Cu-catalysts.^a

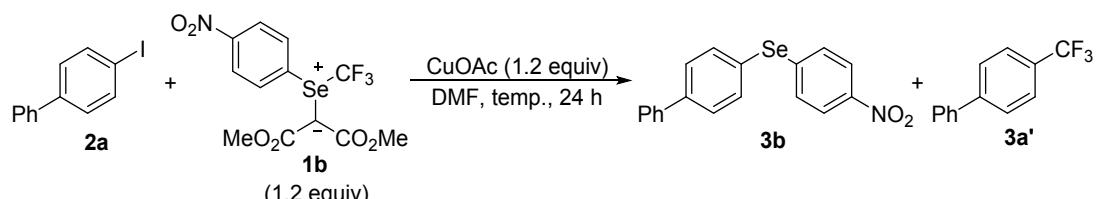


Entry	Catalyst	Yield (3b , %) ^b	Yield (3a' , %) ^b
1	CuI	8	4
2	CuCl	27	10
3	CuBr	16	7
4	CuOAc	54	6
5	CuSCN	5	0
6	CuCN	18	3
7	CuOTf	40	6

8	$\text{Cu}(\text{OAc})_2$	45	0
9	CuSO_4	36	0
10	$\text{Cu}(\text{acac})_2$	44	2
11	Cu	48	3

^a Reaction conditions: a mixture of **2a** (0.2 mmol), **1b** (0.2 mmol), and catalysts (0.2 mmol) in DMF (2 mL) was reacted at 100 °C for 24 h. ^b Yields were determined by HPLC ($\lambda = 253$ nm, $\text{H}_2\text{O}/\text{CH}_3\text{OH} = 15:85$ (v/v)) using [1,1'-biphenyl]-4-yl(4-nitrophenyl)selane (**3b**, $t_{\text{R}} = 15.24$ min) and 4-(trifluoromethyl)-1,1'-biphenyl (**3a'**, $t_{\text{R}} = 8.54$ min) as external standards, respectively.

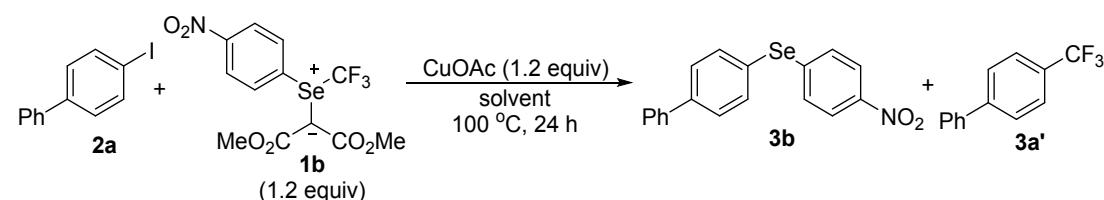
Table S2. CuOAc-Catalyzed reaction of **2a** with **1b** at different temperature.^a



Entry	Temp. (°C)	Yield (3b , %) ^b	Yield (3a' , %) ^b
1	r.t.	0	1
2	60	trace	8
3	80	38	6
4	100	56	6

^a Reaction condition: a mixture of **2a** (0.2 mmol), **1b** (0.24 mmol), and CuOAc (0.24 mmol) in DMF (2 mL) was reacted at different temperature for 24 h. ^b Yields were determined by HPLC ($\lambda = 253$ nm, $\text{H}_2\text{O}/\text{CH}_3\text{OH} = 15:85$ (v/v)) using [1,1'-biphenyl]-4-yl(4-nitrophenyl)selane (**3b**, $t_{\text{R}} = 15.24$ min) and 4-(trifluoromethyl)-1,1'-biphenyl (**3a'**, $t_{\text{R}} = 8.54$ min) as external standards, respectively.

Table S3. CuOAc-Catalyzed reaction of **2a** with **1b** in different solvents.^a

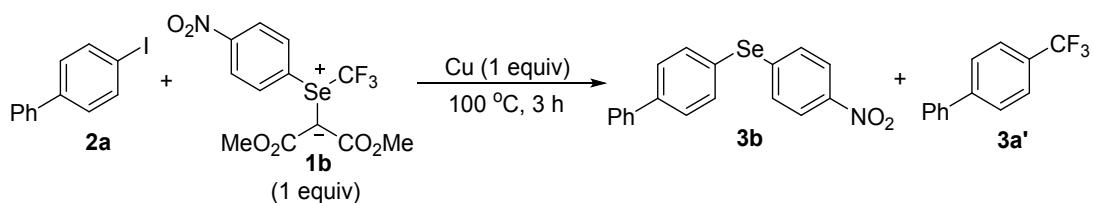


Entry	Solvent	Yield (3b , %) ^b	Yield (3a' , %) ^b
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1	DMSO	64	2
2	1,4-dioxane	trace	2
3	toluene	11	0
4	CH ₃ CN	60	2
5	DCE	16	0
6	DMF	56	6
7	NMP	52	8

^a Reaction condition: a mixture of **2a** (0.2 mmol), **1b** (0.24 mmol), and CuOAc (0.24 mmol) in solvent (2 mL) was stirred at 100 °C for 24 h. ^b Yields were determined by HPLC ($\lambda = 253$ nm, H₂O/CH₃OH = 15:85 (v/v)) using [1,1'-biphenyl]-4-yl(4-nitrophenyl)selane (**3b**, $t_R = 15.24$ min) and 4-(trifluoromethyl)-1,1'-biphenyl (**3a'**, $t_R = 8.54$ min) as external standards, respectively.

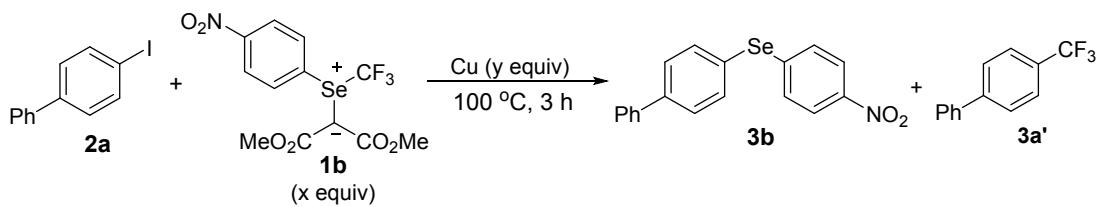
Table S4. The Cu-catalyzed reaction of **2a** with **1b** in different solvent.^a



Entry	Solvent	Yield (3b , %) ^b	Yield (3a' , %) ^b
1	DMSO	42	3
2	CH ₃ CN	15	6
3	DMF	54	3

^a Reaction condition: a mixture of **2a** (0.2 mmol), **1b** (0.2 mmol), and Cu (0.2 mmol) in solvent (2 mL) was reacted at 100 °C for 3 h. ^b Yields were determined by HPLC ($\lambda = 253$ nm, $\text{H}_2\text{O}/\text{CH}_3\text{OH} = 15:85$ (v/v)) using [1,1'-biphenyl]-4-yl(4-nitrophenyl)selane (**3b**, $t_{\text{R}} = 15.24$ min) and 4-(trifluoromethyl)-1,1'-biphenyl (**3a'**, $t_{\text{R}} = 8.54$ min) as external standards, respectively.

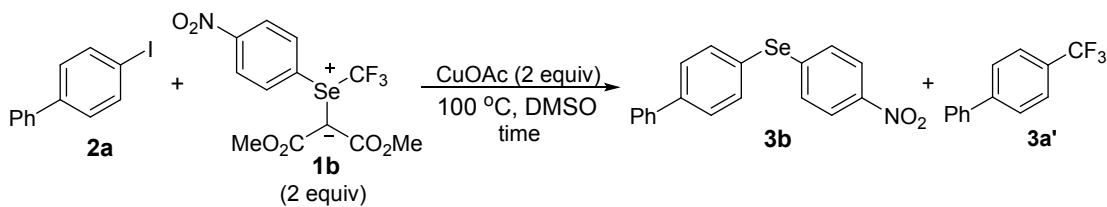
Table S5. The effects of molar ratios of **2a**, **1a** and Cu on the reaction.^a



Entry	[2a]:[1b]:[Cu]	Yield (3b, %) ^b	Yield (3a', %) ^b
1	1:1.2:1.2	49	3
2	1:1.2:2	56	3
3	1:1.5:1.5	60	12
4	1:2:2	84, 81 ^c	6
5 ^d	1:2:2	84	7
6	1:2:3	62	9
7	1:2:2.5	59	7
8	1:2:1.5	56	7
9	2:1:2	48	7
10 ^e	1:2:2	14	9
11 ^f	1:2:2	68	10
12 ^g	1:2:2	0	trace
13^h	1:2:2	92	4
14	1:2.5:2.5	72	7
15	1:3.5:2	58	10

^a Reaction condition: a mixture of **2a** (0.2 mmol), **1b** (x equiv), and Cu (y equiv) in DMF (2 mL) was reacted at 100 °C for 3 h. ^b Yields were determined by HPLC ($\lambda = 253$ nm, $\text{H}_2\text{O}/\text{CH}_3\text{OH} = 15:85$ (v/v)) using [1,1'-biphenyl]-4-yl(4-nitrophenyl)selane (**3b**, $t_{\text{R}} = 15.24$ min) and 4-(trifluoromethyl)-1,1'-biphenyl (**3a'**, $t_{\text{R}} = 8.54$ min) as external standards, respectively. ^c Isolated yield. ^d 6 h. ^e CuOAc. ^f CuOAc, 24 h. ^g CuSCN. ^h CuOAc, DMSO, 24 h.

Table S6. Reaction of **2a**, **1b** and CuOAc with different times.^a



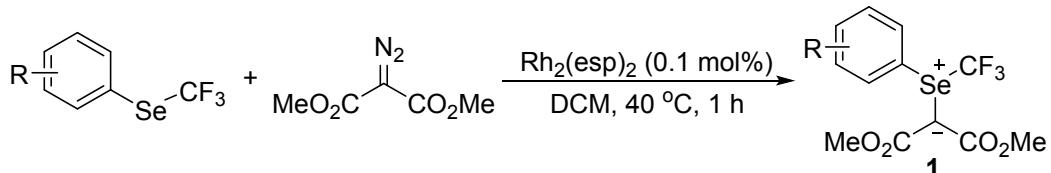
Entry	Time (h)	Yield (3b , %) ^b	Yield (3a' , %) ^b
1	3	29	4
2	6	46	4
3	12	51	4
4	16	69	4
5	20	94, 94^c	5
6	24	92	4
7	36	93	5

^a Reaction condition: a mixture of **2a** (0.2 mmol), **1b** (0.4 mmol), and CuOAc (0.4 mmol) in DMSO (2 mL) was reacted at 100 °C for 3-36 h.

^b Yields were determined by HPLC ($\lambda = 253$ nm, $\text{H}_2\text{O}/\text{CH}_3\text{OH} = 15:85$ (v/v)) using [1,1'-biphenyl]-4-yl(4-nitrophenyl)selane (**3b**, $t_{\text{R}} = 15.24$ min) and 4-(trifluoromethyl)-1,1'-biphenyl (**3a'**, $t_{\text{R}} = 8.54$ min) as external standards, respectively.

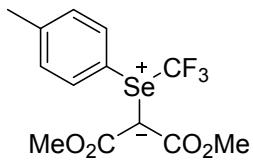
^c Isolated yield.

3. Typical procedures for the synthesis of trifluoromethyl aryl selenium ylide 1



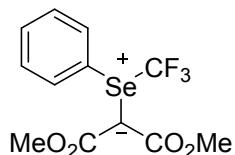
Procedure A: In a nitrogen-filled glovebox, an oven-dried flask was charged with *p*-tolyl(trifluoromethyl)selane (1.20 g, 5.0 mmol), Rh₂(esp)₂ (3.8 mg, 0.005 mmol), and CH₂Cl₂ (40 mL) with stirring. A solution of diazomalonate (0.948 g, 6.0 mmol) in CH₂Cl₂ (10 mL) was added slowly at room temperature during a period of 30 min. The mixture was heated at 40 °C for 1 h, cooled to room temperature, and concentrated to dryness under the reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (1:1 (v/v)) as eluents to give 0.846 g of **1c** as a white solid (91%).

Dimethyl 2-(*p*-tolyl(trifluoromethyl)-λ⁴-selanylidene)malonate (**1c**)



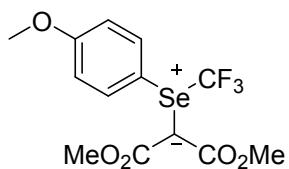
M.p.: 102-103 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.51 (d, $J = 8.1$ Hz, 2H), 7.36 (d, $J = 8.1$ Hz, 2H), 3.70 (s, 6H), 2.43 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ -45.3 (s, 3F). ^{13}C NMR (126 MHz, CDCl_3) δ 166.1, 143.5, 131.3, 128.7, 123.6, 120.5 (q, $J = 357.3$ Hz), 64.9, 51.4, 21.4. IR (KBr): 3077, 3023, 2959, 2851, 1744, 1690, 1649, 1587, 1488, 1440, 1322, 1231, 1210, 1170, 1075, 1056, 1040, 940, 808, 758, 741 cm^{-1} . HRMS-ESI (m/z) calcd for $\text{C}_{13}\text{H}_{14}\text{F}_3\text{O}_4\text{Se}$ ($[\text{M} + \text{H}]^+$): 371.0004; Found: 370.9998.

Dimethyl 2-(phenyl(trifluoromethyl)- λ^4 -selanylidene)malonate (**1a**)



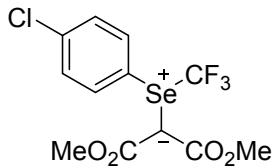
Light yellow solid (0.801 g, 90%), a mixture of petroleum ether and ethyl acetate (1:1 (v/v)) as eluents for column chromatography. M.p.: 78-80 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.67-7.58 (m, 5H), 3.73 (s, 6H). ^{19}F NMR (471 MHz, CDCl_3) δ -44.9 (s, 3F). ^{13}C NMR (126 MHz, CDCl_3) δ 166.1, 132.5, 130.6, 128.7, 127.0, 120.5 (q, $J = 357.6$ Hz), 64.8, 51.5. IR (KBr): 3090, 3074, 3018, 2960, 2850, 1748, 1697, 1648, 1479, 1440, 1325, 1233, 1205, 1169, 1074, 1055, 999, 941, 759, 741, 685 cm^{-1} . HRMS-ESI (m/z) calcd for $\text{C}_{12}\text{H}_{12}\text{F}_3\text{O}_4\text{Se}$ ($[\text{M} + \text{H}]^+$): 356.9847; Found: 356.9857.

Dimethyl 2-((4-methoxyphenyl)(trifluoromethyl)- λ^4 -selanylidene)malonate (**1d**)¹



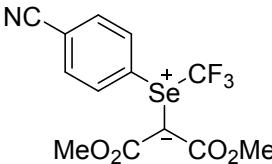
Light yellow oil (0.924 g, 96%), a mixture of petroleum ether and ethyl acetate (1:1 (v/v)) as eluents for column chromatography. ^1H NMR (500 MHz, CDCl_3) δ 7.58 (d, $J = 8.9$ Hz, 2H), 7.05 (d, $J = 8.9$ Hz, 2H), 3.86 (s, 3H), 3.70 (s, 6H). ^{19}F NMR (471 MHz, CDCl_3) δ -45.8 (s, 3F). ^{13}C NMR (126 MHz, CDCl_3) δ 166.2, 163.1, 131.0, 120.5 (q, $J = 357.7$ Hz), 117.1, 116.1, 65.4, 55.7, 51.4.

Dimethyl 2-((4-chlorophenyl)(trifluoromethyl)- λ^4 -selanylidene)malonate (**1e**)



White solid (0.317 g, 68%), a mixture of petroleum ether and ethyl acetate (1:1 (v/v)) as eluents for column chromatography. M.p.: 113-115 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.60-7.55 (m, 4H), 3.71 (s, 6H). ^{19}F NMR (471 MHz, CDCl_3) δ -44.7 (s, 3F). ^{13}C NMR (126 MHz, CDCl_3) δ 166.0, 139.5, 130.9, 130.2, 125.1, 120.5 (q, $J = 357.6$ Hz), 65.1, 51.6. IR (KBr): 3098, 3083, 3013, 2994, 2950, 2911, 2843, 1684, 1630, 1439, 1394, 1336, 1239, 1197, 1186, 1161, 1100, 1076, 1005, 813, 764, 737 cm^{-1} . HRMS-ESI (m/z) calcd for $\text{C}_{12}\text{H}_{11}\text{ClF}_3\text{O}_4\text{Se}$ ([M + H] $^+$): 390.9458; Found: 390.9452.

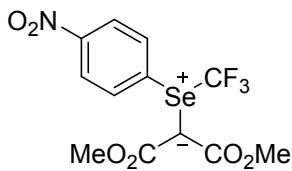
Dimethyl 2-((4-cyanophenyl)(trifluoromethyl)- λ^4 -selanylidene)malonate (**1g**)



White solid (0.537 g, 94%), a mixture of petroleum ether and ethyl acetate (1:1 (v/v)) as eluents for column chromatography. M.p.: 125-127 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.86 (d, $J = 8.4$ Hz, 2H), 7.77 (d, $J = 8.4$ Hz, 2H), 3.72 (s, 6H). ^{19}F NMR (471 MHz, CDCl_3) δ -43.6 (s, 3F). ^{13}C NMR (126 MHz, CDCl_3) δ 165.9, 133.8, 130.2, 127.7, 125.7, 121.8, 120.5 (q, $J = 357.5$ Hz), 65.0, 51.6. IR (KBr): 3093, 3071, 2949, 2849, 2236, 1678, 1633, 1440, 1326, 1244, 1196, 1187, 1163, 1083, 1053, 1009, 957, 825, 761, 738 cm^{-1} . HRMS-ESI (m/z) calcd for $\text{C}_{13}\text{H}_{11}\text{F}_3\text{O}_4\text{Se}$ ([M + H] $^+$): 381.9800; Found: 381.9802.

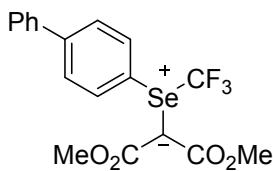
Procedure B: In a nitrogen-filled glovebox, an oven-dried flask was charged with aryl trifluoromethylselenoether (1 equiv), $\text{Rh}_2(\text{esp})_2$ (0.1 mol%), and CH_2Cl_2 with stirring. A solution of diazomalonate (1.2 equiv) in CH_2Cl_2 was added slowly at room temperature during a period of 30 min. The mixture was heated at 40 °C for 1 h, cooled to room temperature, and concentrated to dryness under the reduced pressure. The residue was purified by crystallization from layering a solution of the crude product in dichloromethane with diethyl ether to afford the desired product (**1b**, **1f**, and **1h-j**).

Dimethyl 2-((4-nitrophenyl)(trifluoromethyl)- λ^4 -selanylidene)malonate (**1b**)¹



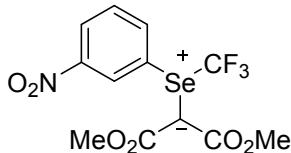
Yellow solid (3.2 g, 80%). M.p.: 113-115 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.42 (d, $J = 8.7$ Hz, 2H), 7.85 (d, $J = 8.7$ Hz, 2H), 3.74 (s, 6H). ^{19}F NMR (471 MHz, CDCl_3) δ -43.5 (s, 3F). ^{13}C NMR (126 MHz, CDCl_3) δ 165.7, 150.3, 133.7, 130.0, 125.3, 120.5 (q, $J = 358.5$ Hz), 65.4, 51.8.

Dimethyl 2-((1,1'-biphenyl)-4-yl(trifluoromethyl)- λ^4 -selanylidene)malonate (**1f**)¹



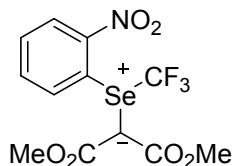
White solid (0.450 g, 52%). M.p.: 122-124 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.77 (d, $J = 8.3$ Hz, 2H), 7.70 (d, $J = 8.3$ Hz, 2H), 7.58 (d, $J = 7.5$ Hz, 2H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.43 (t, $J = 7.2$ Hz, 1H), 3.73 (s, 6H). ^{19}F NMR (471 MHz, CDCl_3) δ -44.9 (s, 3F). ^{13}C NMR (126 MHz, CDCl_3) δ 166.1, 145.7, 138.9, 129.3, 129.2, 129.1, 128.7, 127.3, 125.4, 120.5 (q, $J = 357.0$ Hz), 64.9, 51.5.

Dimethyl 2-((3-nitrophenyl)(trifluoromethyl)- λ^4 -selanylidene)malonate (**1h**)¹



Grey solid (0.442 g, 73%). M.p.: 127-129 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.50-8.47 (m, 2H), 7.99 (d, $J = 8.1$ Hz, 1H), 7.82 (t, $J = 8.1$ Hz, 1H), 3.74 (s, 6H). ^{19}F NMR (471 MHz, CDCl_3) δ -43.7 (s, 3F). ^{13}C NMR (126 MHz, CDCl_3) δ 165.8, 149.1, 134.4, 131.5, 128.9, 127.2, 124.2, 120.5 (q, $J = 358.8$ Hz), 65.4, 51.8.

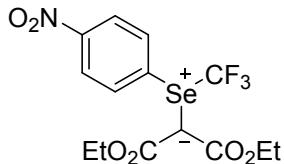
Dimethyl 2-((2-nitrophenyl)(trifluoromethyl)- λ^4 -selanylidene)malonate (**1i**)¹



Yellow solid (0.777 g, 53%). M.p.: 116-118 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.52

(dd, $J = 7.8, 1.3$ Hz, 1H), 7.97 (dd, $J = 7.9, 1.3$ Hz, 1H), 7.91 (td, $J = 7.8, 1.5$ Hz, 1H), 7.86 (td, $J = 7.9, 1.5$ Hz, 1H), 3.70 (s, 6H). ^{19}F NMR (471 MHz, CDCl_3) δ -42.7 (s, 3F). ^{13}C NMR (126 MHz, CDCl_3) δ 166.1, 146.3, 135.7, 133.8, 132.3, 126.7, 122.9, 120.5 (q, $J = 357.2$ Hz), 65.2, 51.6.

Diethyl 2-((4-nitrophenyl)(trifluoromethyl)- λ^4 -selanylidene)malonate (**1j**)

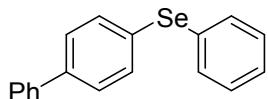


Yellow solid (0.483 g, 23%). M.p.: 123-125 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.41 (d, $J = 8.6$ Hz, 2H), 7.86 (d, $J = 8.6$ Hz, 2H), 4.18 (q, $J = 7.1$ Hz, 4H), 1.23 (t, $J = 7.1$ Hz, 6H). ^{19}F NMR (471 MHz, CDCl_3) δ -43.6 (s, 3F). ^{13}C NMR (126 MHz, CDCl_3) δ 165.4, 150.2, 134.0, 130.0, 125.2, 120.5 (q, $J = 358.9$ Hz), 65.6, 60.7, 14.4. IR (KBr): 3098, 2982, 2953, 1677, 1638, 1601, 1526, 1478, 1398, 1373, 1347, 1320, 1233, 1203, 1182, 1088, 1070, 1050, 1007, 849, 764, 739, 708 cm⁻¹. HRMS-ESI (m/z) calcd for $\text{C}_{12}\text{H}_{11}\text{F}_3\text{NO}_6\text{Se}$ ([M + H]⁺): 430.0011; Found: 430.0007.

4. General procedure for the synthesis of diaryl selenides **3**

In a nitrogen-filled glovebox, a sealed tube was charged with aryl halides (**2**, 0.2 mmol), trifluoromethyl aryl selenium ylide (**1**, 0.4 mmol), CuOAc (48.8 mg, 0.4 mmol), and DMSO (2 mL) with stirring. The mixture was reacted at 100, 120 or 140 °C for 20 h, cooled to room temperature, and diluted with ethyl acetate (60 mL). The organic solution was washed by water (20 × 3 mL), dried over anhydrous Na_2SO_4 , and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether or a mixture of petroleum ether and ethyl acetate as eluents to give the title compound (**3**).

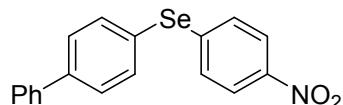
[1,1'-Biphenyl]-4-yl(phenyl)selane (**3a**)⁵



White solid (41.5 mg from 100 °C, 67%; 44.6 mg from 120 °C, 72%), petroleum ether as eluent for column chromatography. M.p.: 64-66 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.59 (d, $J = 7.8$ Hz, 2H), 7.56-7.51 (m, 6H), 7.45 (t, $J = 7.4$ Hz, 2H), 7.37 (m, 1H), 7.33-7.30 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 140.4, 140.3, 133.3, 133.1, 131.1,

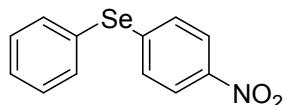
130.3, 129.4, 128.9, 128.0, 127.5, 127.5, 127.0.

[1, 1'-Biphenyl]-4-yl(4-nitrophenyl)selane (**3b**)



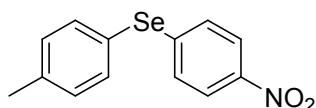
Yellow solid (67.0 mg from **1b**, 94%; 39.1 mg from 4-PhC₆H₄Br (140 °C), 55%; 59.7 mg from **1j**, 84%), a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 95-97 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.06 (d, *J* = 9.0 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.64-7.61 (m, 4H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.43-7.39 (m, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 146.3, 143.8, 142.4, 139.9, 136.2, 129.9, 129.0, 128.7, 128.0, 127.1, 126.1, 124.0. IR (KBr): 3059, 2924, 1574, 1512, 1474, 1343, 1176, 1107, 1060, 1003, 850, 762, 734, 692 cm⁻¹. HRMS-ESI (m/z) calcd for C₁₈H₁₄NO₂Se ([M + H]⁺): 356.0184; Found: 356.0178.

(4-Nitrophenyl)(phenyl)selane (**3c**)⁶



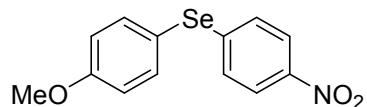
Yellow solid (54.2 mg from C₆H₅I, 97%; 39.0 mg from C₆H₅Br (140 °C), 70%), a mixture of petroleum ether and ethyl acetate (80:1 (v/v)) as eluents for column chromatography. M.p.: 56-58 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.03 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 6.8 Hz, 2H), 7.47-7.40 (m, 3H), 7.36 (d, *J* = 9.0 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 146.2, 144.0, 135.9, 130.1, 129.7, 129.4, 127.2, 124.0.

(4-Nitrophenyl)(*p*-tolyl)selane (**3d**)⁷



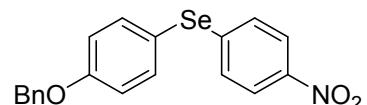
Yellow solid (49.9 mg from 4-CH₃C₆H₄I, 85%; 34.0 mg from 4-CH₃C₆H₄Br (140 °C), 58%), a mixture of petroleum ether and ethyl acetate (80:1 (v/v)) as eluents for column chromatography. M.p.: 82-84 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.01 (d, *J* = 8.9 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 8.9 Hz, 2H), 7.23 (d, *J* = 7.9, 2H), 2.41 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 146.0, 144.8, 139.8, 136.2, 130.9, 129.2, 123.9, 123.3, 21.3.

(4-Methoxyphenyl)(4-nitrophenyl)selane (**3e**)⁶



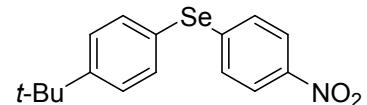
Yellow solid (48.0 mg, 78%; 23.0 mg from 4-MeOC₆H₄Br (140 °C, 20 h), 37%; 32.2 mg from 4-MeOC₆H₄Br (140 °C, 48 h), 52%), a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 88-90 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.01 (d, *J* = 9.0 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 9.0 Hz, 2H), 6.95 (d, *J* = 8.9, 2H), 3.86 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 160.9, 145.9, 145.4, 138.2, 128.7, 123.9, 116.8, 115.8, 55.4.

(4-(Benzylxy)phenyl)(4-nitrophenyl)selane (**3f**)



Yellow solid (48.4 mg, 63%; 47.7 mg from 4-BnOC₆H₄Br (140 °C), 62%), a mixture of petroleum ether and ethyl acetate (20:1 (v/v)) as eluents for column chromatography. M.p.: 107-109 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.02 (d, *J* = 8.9 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 7.1 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.0, 1H), 7.29 (d, *J* = 9.0 Hz, 2H), 7.03 (d, *J* = 8.5 Hz, 2H), 5.12 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 160.1, 146.0, 145.3, 138.2, 136.4, 128.8, 128.7, 128.2, 127.5, 123.9, 117.3, 116.7, 70.2. IR (KBr): 3084, 3063, 3028, 2929, 2876, 2848, 1588, 1573, 1510, 1492, 1359, 1345, 1281, 1242, 1176, 1108, 1079, 1059, 1012, 915, 840, 811, 751, 736, 700, 654 cm⁻¹. HRMS-ESI (m/z) calcd for C₁₉H₁₉N₂O₃Se ([M + NH₄]⁺): 403.0555; Found: 403.0554.

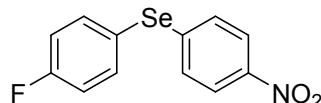
(4-(*Tert*-butyl)phenyl)(4-nitrophenyl)selane (**3g**)



Yellow solid (63.5 mg, 95%; 40.5 mg from 4-*t*-BuC₆H₄Br (140 °C), 60%), a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 66-68 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.03 (d, *J* = 8.9 Hz,

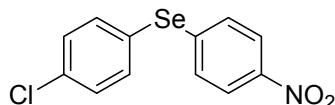
2H), 7.56 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.8, 2H), 1.36 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 152.9, 146.1, 144.4, 135.8, 129.5, 127.2, 123.9, 123.6, 34.8, 31.2. IR (KBr): 3100, 3061, 3027, 2952, 2901, 2867, 1595, 1575, 1509, 1474, 1398, 1341, 1323, 1176, 1113, 1075, 1061, 1009, 853, 838, 827, 739, 678 cm^{-1} . HRMS-ESI (m/z) calcd for $\text{C}_{16}\text{H}_{18}\text{NO}_2\text{Se}$ ([M + H] $^+$): 336.0497; Found: 336.0483.

(4-Fluorophenyl)(4-nitrophenyl)selane (**3h**)⁸



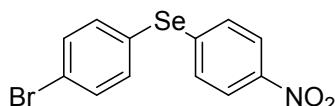
Yellow solid (41.3 mg, 70%), a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 71-73 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.04 (d, J = 9.0 Hz, 2H), 7.64 (m, 2H), 7.32 (d, J = 8.9 Hz, 2H), 7.12 (t, J = 8.7 Hz, 2H). ^{19}F NMR (471 MHz, CDCl_3) δ -110.7 (m, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 163.6 (d, J = 250.5 Hz), 146.3, 143.8, 138.3 (d, J = 8.3 Hz), 129.4, 124.0, 121.8 (d, J = 3.5), 117.4 (d, J = 21.8 Hz).

(4-Chlorophenyl)(4-nitrophenyl)selane (**3i**)⁹



Yellow solid (52.3 mg, 84%), a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 82-84 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.04 (d, J = 8.7 Hz, 2H), 7.56 (d, J = 8.5 Hz, 2H), 7.38-7.35(m, 4H). ^{13}C NMR (126 MHz, CDCl_3) δ 146.4, 143.1, 137.1, 135.9, 130.3, 129.9, 125.5, 124.1.

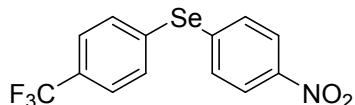
(4-Bromophenyl)(4-nitrophenyl)selane (**3j**)



Yellow solid (39.6 mg, 56%), a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 97-99 °C. ^1H NMR (500 MHz, acetone-d₆) δ 8.14 (d, J = 8.7 Hz, 2H), 7.65 (d, J = 8.6 Hz, 2H), 7.62 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 8.7 Hz, 2H). ^{13}C NMR (126 MHz, acetone-d₆) δ 146.7, 142.4, 137.3, 133.2, 130.5, 126.7, 124.1, 123.4. IR (KBr): 3088, 3019, 2920, 2840, 1912, 1817,

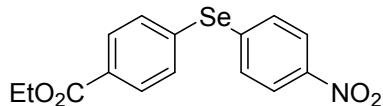
1645, 1574, 1509, 1466, 1341, 1321, 1177, 1109, 1064, 1005, 851, 842, 808, 738, 709, 678 cm⁻¹. HRMS-ESI (m/z) calcd for C₁₂H₉BrNO₂Se ([M + H]⁺): 357.8976; Found: 357.8973.

(4-Nitrophenyl)(4-(trifluoromethyl)phenyl)selane (3k**)**



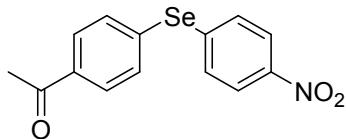
Yellow solid (49.6 mg, 71%), a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 81-83 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.10 (d, *J* = 9.0 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.9 Hz, 2H). ¹⁹F NMR (471 MHz, CDCl₃) δ -62.9 (s, 3F). ¹³C NMR (126 MHz, CDCl₃) δ 146.9, 141.2, 134.7, 133.2, 131.5, 131.0 (q, *J* = 32.8 Hz), 126.7 (q, *J* = 3.7 Hz), 124.3, 123.8 (q, *J* = 272.2 Hz). IR (KBr): 3097, 3068, 2962, 2920, 2850, 1595, 1577, 1508, 1475, 1398, 1341, 1324, 1168, 1123, 1100, 1081, 1065, 1056, 1016, 1009, 958, 852, 835, 817, 737, 690 cm⁻¹. HRMS-ESI (m/z) calcd for C₁₃H₉F₃NO₂Se ([M + H]⁺): 347.9745; Found: 347.9751.

Ethyl 4-((4-nitrophenyl)selanyl)benzoate (3l**)**



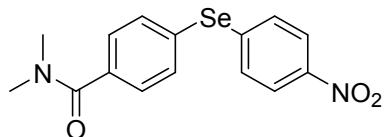
Yellow solid (57.9 mg, 82%; 36.1 mg from 4-EtO₂CC₆H₅Br (140 °C), 60%), a mixture of petroleum ether and ethyl acetate (2:1 (v/v)) as eluents for column chromatography. M.p.: 111-113 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.07 (d, *J* = 8.9 Hz, 2H), 8.01 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.9 Hz, 2H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 165.9, 146.8, 141.6, 134.3, 134.2, 131.4, 130.8, 130.8, 124.2, 61.3, 14.3. IR (KBr): 3090, 3059, 3038, 2979, 2925, 2909, 2850, 1945, 1817, 1702, 1589, 1575, 1517, 1488, 1474, 1400, 1369, 1349, 1287, 1274, 1184, 1106, 1058, 1011, 852, 760, 739, 688, 683 cm⁻¹. HRMS-ESI (m/z) calcd for C₁₅H₁₄NO₄Se ([M + H]⁺): 352.0083; Found: 352.0078.

1-(4-((4-Nitrophenyl)selanyl)phenyl)ethan-1-one (3m**)**



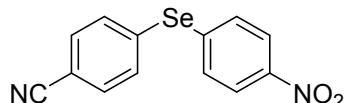
Yellow solid (21.0 mg from CuOAc/DMF/20 h, 33%; 31.2 mg from Cu/DMF/3 h, 49%), a mixture of petroleum ether and ethyl acetate (10:1 (v/v)) as eluents for column chromatography. M.p.: 125-127 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.10 (d, J = 8.9 Hz, 2H), 7.92 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.3 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H), 2.62 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 197.1, 147.0, 141.1, 137.1, 135.1, 134.1, 131.8, 129.5, 124.2, 26.6. IR (KBr): 3085, 3053, 3003, 2958, 2920, 2849, 1681, 1572, 1514, 1477, 1394, 1344, 1319, 1267, 1181, 1105, 1060, 1008, 957, 852, 827, 737, 682 cm^{-1} . HRMS-ESI (m/z) calcd for $\text{C}_{14}\text{H}_{12}\text{NO}_3\text{Se}$ ($[\text{M} + \text{H}]^+$): 321.9977; Found: 321.9983.

N,N-Dimethyl-4-((4-nitrophenyl)selanyl)benzamide (**3n**)



Yellow solid (42.3 mg, 61%), a mixture of petroleum ether and ethyl acetate (2:1 (v/v)) as eluents for column chromatography. M.p.: 97-99 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.04 (d, J = 8.9 Hz, 2H), 7.62 (d, J = 8.1 Hz, 2H), 7.43-7.39 (m, 4H), 3.12 (s, 3H), 3.00 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 170.6, 146.5, 142.6, 137.1, 135.3, 135.2, 130.5, 129.4, 128.6, 39.5, 35.4. IR (KBr): 3077, 3043, 2921, 2850, 1790, 1630, 1593, 1574, 1517, 1472, 1404, 1343, 1264, 1085, 1068, 1009, 851, 828, 736 cm^{-1} . HRMS-ESI (m/z) calcd for $\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_3\text{Se}$ ($[\text{M} + \text{H}]^+$): 351.0242; Found: 351.0250.

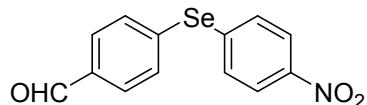
4-((4-Nitrophenyl)selanyl)benzonitrile (**3o**)



Yellow solid (27.2 mg from 4-NCC₆H₄I, 45%; 32.0 mg from 4-NCC₆H₄Br (140 °C), 53%), a mixture of petroleum ether and ethyl acetate (10:1 (v/v)) as eluents for column chromatography. M.p.: 134-136 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.14 (d, J = 8.6 Hz, 2H), 7.62-7.55 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 147.4, 139.4, 136.1, 133.7, 133.0, 132.8, 124.5, 118.1, 112.2. IR (KBr): 3091, 3052, 3023, 2922, 2850,

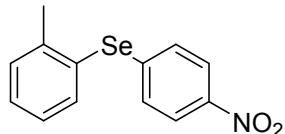
2230, 1921, 1798, 1729, 1655, 1596, 1585, 1574, 1510, 1481, 1346, 1177, 1104, 1059, 1011, 851, 826, 737, 681, 547 cm⁻¹. HRMS-ESI (m/z) calcd for C₁₃H₁₂N₃O₂Se ([M + NH₄]⁺): 322.0089; Found: 322.0082.

4-((4-Nitrophenyl)selanyl)benzaldehyde (**3p**)



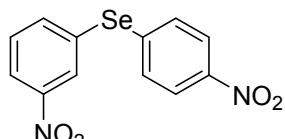
Yellow solid (53.9 mg, 88%), a mixture of petroleum ether and ethyl acetate (10:1 (v/v)) as eluents for column chromatography. M.p.: 135-137 °C. ¹H NMR (500 MHz, CDCl₃) δ 10.02 (s, 1H), 8.13 (d, J = 8.8 Hz, 2H), 7.84 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 8.1 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 191.1, 147.2, 140.2, 137.5, 136.0, 133.8, 132.4, 130.6, 124.3. IR (KBr): 3090, 3054, 2832, 2736, 1696, 1587, 1564, 1508, 1474, 1384, 1346, 1208, 1168, 1104, 1058, 1010, 852, 836, 737, 680 cm⁻¹. HRMS-ESI (m/z) calcd for C₁₃H₁₀NO₃Se ([M + H]⁺): 307.9820; Found: 307.9822.

(4-Nitrophenyl)(*o*-tolyl)selane (**3q**)



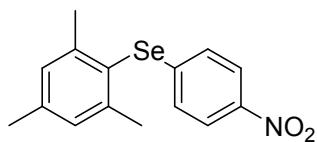
Yellow solid (50.0 mg, 85%), a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 61-63 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.03 (d, J = 8.8 Hz, 2H), 7.65 (d, J = 7.5 Hz, 1H), 7.40-7.38 (m, 2H), 7.28 (d, J = 8.6 Hz, 2H), 7.21 (m, 1H), 2.42 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 146.1, 143.8, 142.4, 137.4, 131.0, 130.2, 129.2, 127.9, 127.4, 124.0, 22.8. IR (KBr): 3087, 3064, 2999, 2957, 2924, 2854, 1594, 1571, 1506, 1475, 1359, 1341, 1317, 1184, 1109, 1064, 1033, 1101, 851, 836, 750, 737, 677 cm⁻¹. HRMS-ESI (m/z) calcd for C₁₃H₁₂NO₂Se ([M + H]⁺): 294.0028; Found: 294.0032.

(3-Nitrophenyl)(4-nitrophenyl)selane (**3r**)



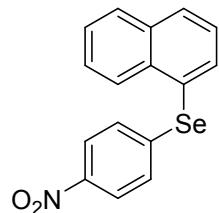
Yellow solid (49.7 mg, 77%), a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 120-122 °C. ¹H NMR (500 MHz, acetone-d₆) δ 8.44 (s, 1H), 8.31 (d, *J* = 8.2 Hz, 1H), 8.17 (d, *J* = 8.7 Hz, 2H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.76 (t, *J* = 7.9 Hz, 1H), 7.70 (d, *J* = 8.6 Hz, 2H). ¹³C NMR (126 MHz, acetone-d₆) δ 148.9, 147.2, 140.7, 140.6, 131.8, 131.2, 130.2, 128.9, 124.3, 123.7. IR (KBr): 3093, 3019, 3075, 2919, 2850, 1648, 1596, 1576, 1525, 1476, 1345, 1184, 1109, 1058, 870, 852, 835, 802, 729, 670 cm⁻¹. HRMS-ESI (m/z) calcd for C₁₂H₉N₂O₄Se ([M + H]⁺): 324.9722; Found: 324.9724.

Mesityl(4-nitrophenyl)selane (**3s**)¹⁰



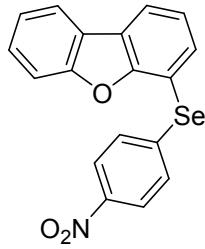
Yellow solid (53.9 mg, 84%), a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 89-91 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.98 (d, *J* = 8.9 Hz, 2H), 7.14 (d, *J* = 8.9 Hz, 2H), 7.06 (s, 2H), 2.42 (s, 6 H), 2.35 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 145.7, 144.8, 143.7, 140.3, 129.4, 127.7, 125.1, 124.0, 24.1, 21.1.

Naphthalen-1-yl(4-nitrophenyl)selane (**3t**)¹¹



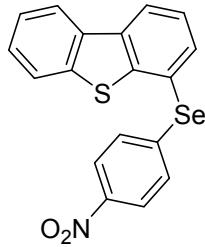
Yellow solid (51.7 mg, 79%), a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 82-84 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.27 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 7.6 Hz, 2H), 7.96 (d, *J* = 8.7 Hz, 2H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.58-7.49 (m, 3H), 7.23 (d, *J* = 8.7 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 146.1, 143.9, 136.8, 134.6, 134.5, 131.2, 129.1, 128.9, 127.7, 126.8, 126.2, 126.0, 123.9.

4-((4-Nitrophenyl)selanyl)dibenzo[b,d]furan (**3u**)



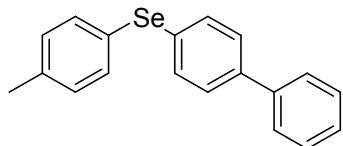
Yellow solid (57.6 mg, 78%), a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 143-145 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.08 (d, $J = 7.6$ Hz, 1H), 8.02-7.98 (m, 3H), 7.71 (d, $J = 7.5$ Hz, 1H), 7.58 (d, $J = 8.2$ Hz, 1H), 7.49 (t, $J = 7.3$ Hz, 1H), 7.41-7.38 (m, 4H). ^{13}C NMR (126 MHz, CDCl_3) δ 156.7, 156.0, 146.4, 142.2, 134.7, 129.9, 127.9, 125.2, 124.1, 124.0, 124.0, 123.3, 122.5, 121.1, 112.0, 109.5. IR (KBr): 3101, 3054, 3019, 2835, 1787, 1664, 1593, 1575, 1503, 1475, 1466, 1447, 1408, 1341, 1318, 1260, 1220, 1183, 1142, 1108, 1066, 1031, 1010, 850, 844, 750, 737 cm^{-1} . HRMS-ESI (m/z) calcd for $\text{C}_{18}\text{H}_{12}\text{NO}_3\text{Se}$ ($[\text{M} + \text{H}]^+$): 369.9977; Found: 369.9977.

4-((4-Nitrophenyl)selanyl)dibenzo[b,d]thiophene (3v)



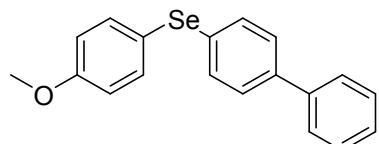
Yellow solid (59.9 mg, 78%), a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 154-156 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.28 (d, $J = 7.9$ Hz, 1H), 8.17 (m, 1H), 8.00 (d, $J = 8.6$ Hz, 2H), 7.83-7.81 (m, 2H), 7.54-7.48 (m, 3H) 7.33 (d, $J = 8.8$ Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 147.3, 146.4, 141.9, 139.3, 136.5, 136.0, 135.2, 129.5, 127.4, 125.7, 124.8, 124.1, 123.1, 122.9, 122.2, 120.3. IR (KBr): 3090, 3060, 2918, 2849, 1642, 1594, 1575, 1509, 1382, 1343, 1246, 1102, 1063, 1045, 1028, 1008, 851, 836, 797, 756, 738, 679 cm^{-1} . HRMS-ESI (m/z) calcd for $\text{C}_{18}\text{H}_{12}\text{NO}_2\text{SSe}$ ($[\text{M} + \text{H}]^+$): 385.9748; Found: 385.9755.

[1,1'-Biphenyl]-4-yl(*p*-tolyl)selane (3w)⁹



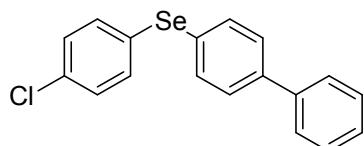
White solid (30.6 mg from 100 °C, 47%; 41.8 mg from 120 °C, 65%), petroleum ether as eluent for column chromatography. M.p.: 98-100 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.58 (d, $J = 8.0$ Hz, 2H), 7.49-7.43 (m, 8H), 7.36 (t, $J = 6.9$ Hz, 1H), 7.15 (d, $J = 7.6$ Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 140.5, 139.9, 137.8, 134.0, 132.4, 131.3, 130.3, 128.8, 127.9, 127.4, 127.0, 126.9, 21.2.

[1,1'-Biphenyl]-4-yl(4-methoxyphenyl)selane (**3x**)⁹



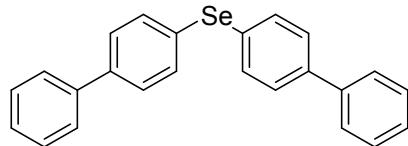
White solid (17.2 mg from 100 °C, 25%; 37.1 mg from 120 °C, 54%), a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 75-77 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.57-7.55 (m, 4H), 7.47-7.40 (m, 6H), 7.34 (t, $J = 7.3$ Hz, 1H), 6.89 (d, $J = 8.7$ Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 159.9, 140.5, 139.5, 136.6, 132.4, 131.3, 128.8, 127.8, 127.3, 126.9, 112.0, 115.2, 55.3.

[1,1'-Biphenyl]-4-yl(4-chlorophenyl)selane (**3y**)⁹



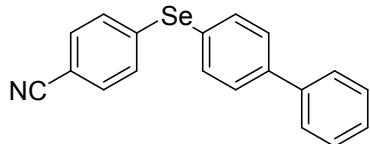
White solid (55.7 mg, 81%), petroleum ether as eluent for column chromatography. M.p.: 119-121 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.61 (d, $J = 7.8$ Hz, 2H), 7.58-7.54 (m, 4H), 7.50-7.45 (m, 4H), 7.40 (t, $J = 7.5$ Hz, 1H), 7.29 (d, $J = 8.4$ Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 140.7, 140.3, 134.2, 133.6, 133.6, 129.7, 129.6, 128.9, 128.2, 127.6, 127.0.

Di([1,1'-biphenyl]-4-yl)selane (**3z**)¹²



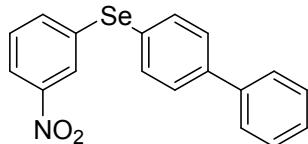
White solid (47.4 mg from 100 °C, 61%; 51.3 mg from 120 °C, 66%), petroleum ether as eluent for column chromatography. M.p.: 177-179 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.61 (d, *J* = 7.6 Hz, 8H), 7.55 (d, *J* = 7.8 Hz, 4H), 7.47 (t, *J* = 7.3 Hz, 4H), 7.38 (t, *J* = 7.3 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 140.4, 140.4, 133.4, 130.2, 128.9, 128.1, 127.5, 127.0.

4-([1,1'-Biphenyl]-4-ylselanyl)benzonitrile (**3aa**)



White solid (63.6 mg, 95%), a mixture of petroleum ether and ethyl acetate (20:1 (v/v)) as eluents for column chromatography. M.p.: 131-133 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 7.5 Hz, 4H), 7.49-7.46 (m, 4H), 7.41-7.39 (m, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 142.1, 140.9, 139.9, 136.0, 132.4, 130.4, 129.0, 128.6, 127.9, 127.1, 126.4, 118.8, 109.8. IR (KBr): 3052, 3028, 2924, 2853, 2227, 1587, 1552, 1481, 1474, 1445, 1391, 1181, 1063, 1016, 1004, 833, 812, 763, 715, 695 cm⁻¹. HRMS-ESI (m/z) calcd for C₁₉H₁₄NSe ([M + H]⁺): 336.0286; Found: 336.0285.

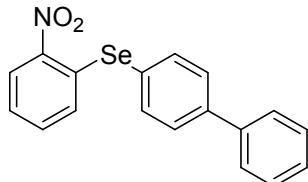
[1,1'-Biphenyl]-4-yl(3-nitrophenyl)selane (**3ab**)



Yellow solid (47.4 mg, 67%), a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 95-97 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.27 (m, 1H), 8.07 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.61-7.58 (m, 4H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.43-7.37 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 148.7, 141.8, 140.0, 137.1, 135.1, 134.8, 129.9, 128.9, 128.6, 127.9, 127.4, 127.1, 125.9, 121.7. IR (KBr): 3098, 3049, 2919, 2855, 1522, 1477, 1346, 1004, 868, 836, 802, 763, 758, 729, 695 cm⁻¹. HRMS-ESI (m/z) calcd for

$C_{18}H_{14}NO_2Se$ ($[M + H]^+$): 356.0184; Found: 356.0188.

[1,1'-Biphenyl]-4-yl(2-nitrophenyl)selane (3ac**)**

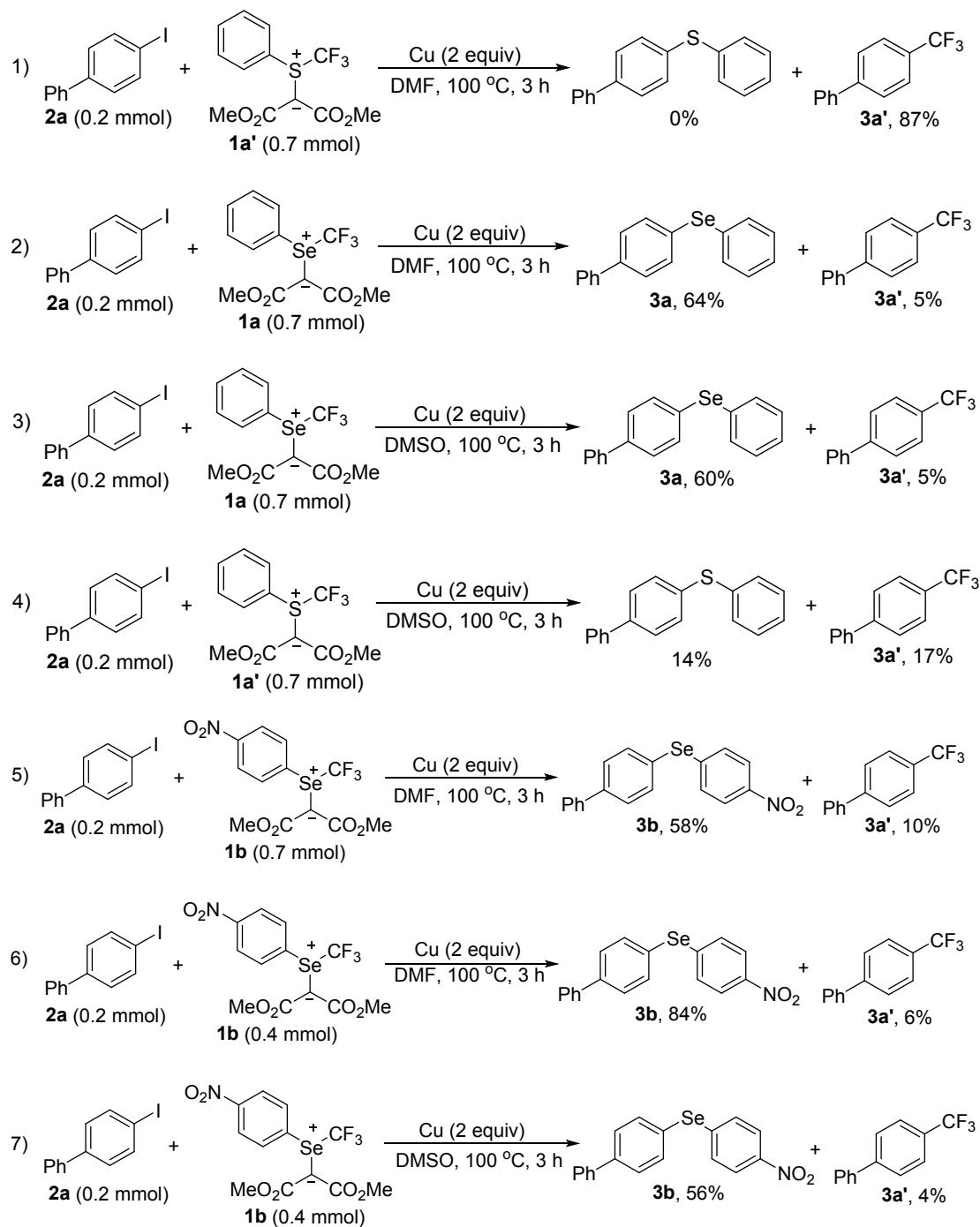


Yellow solid (27.7 mg, 39%), a mixture of petroleum ether and ethyl acetate (40:1 (v/v)) as eluents for column chromatography. M.p.: 121-123 °C. 1H NMR (500 MHz, $CDCl_3$) δ 8.34 (dd, $J = 8.2, 0.9$ Hz, 1H), 7.78 (d, $J = 8.1$ Hz, 2H), 7.69 (d, $J = 8.1$ Hz, 2H), 7.66 (d, $J = 7.5$ Hz, 2H), 7.50 (t, $J = 7.4$ Hz, 2H), 7.41 (t, $J = 7.4$ Hz, 1H), 7.34 (t, $J = 7.6$ Hz, 1H), 7.29 (t, $J = 7.4$ Hz, 1H), 7.10 (d, $J = 8.0$ Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.7, 142.8, 140.0, 137.8, 136.0, 133.7, 130.3, 129.0, 128.7, 128.0, 127.2, 127.0, 126.1, 125.8. IR (KBr): 3055, 3023, 2963, 2921, 2852, 1732, 1633, 1589, 1568, 1508, 1474, 1448, 1331, 1307, 1169, 1097, 1035, 1006, 875, 851, 830, 758, 724, 693 cm^{-1} . HRMS-ESI (m/z) calcd for $C_{18}H_{14}NO_2Se$ ($[M + H]^+$): 356.0184; Found: 356.0189.

5. Control experiments

5.1. Cu-Mediated reactions of **2a** with trifluoromethyl aryl sulfonium ylide and trifluoromethyl aryl selenium ylides under the same conditions.

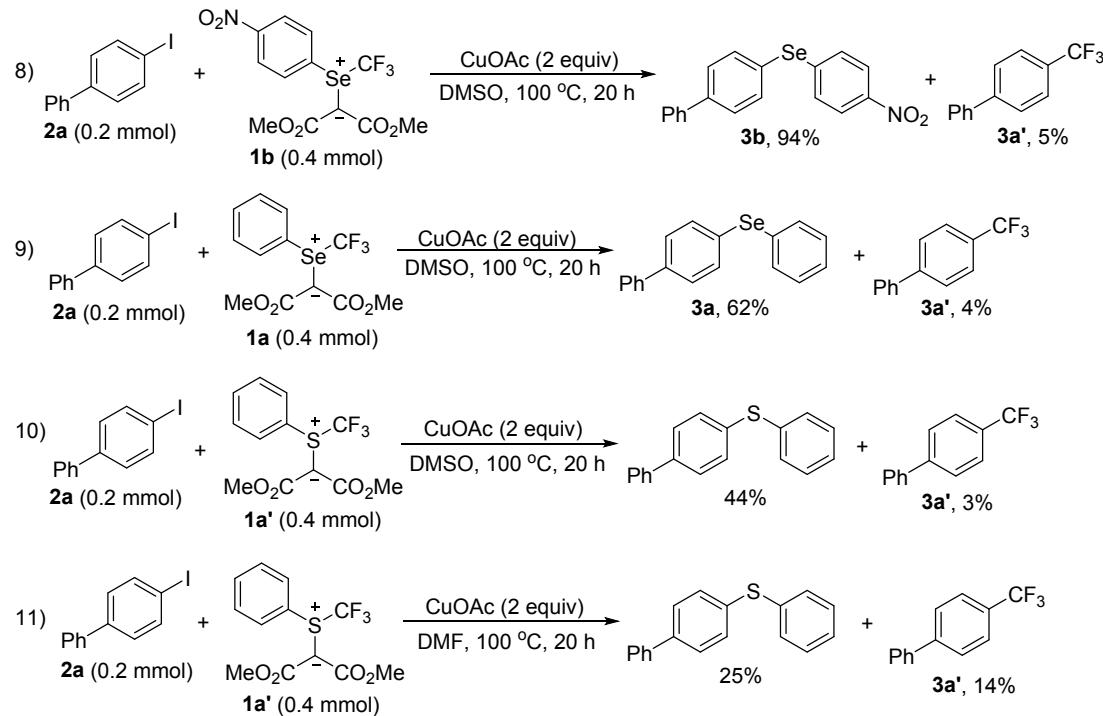
In a nitrogen-filled glovebox, a sealed tube was charged with 4-iodo-1,1'-biphenyl (**2a**, 56.0 mg, 0.2 mmol), **1a'** or **1a** or **1b** (0.4 mmol), Cu (25.6 mg, 0.4 mmol), and DMSO or DMF (2 mL) with stirring. The mixture was reacted at 100 °C for 20 h and cooled to room temperature. The yields of **3a'** and 4- PhC_6H_4SPh or **3a** or **3b** were determined by HPLC ($\lambda = 253$ nm, $H_2O/CH_3OH = 15:85$ (v/v)) using 4-(trifluoromethyl)-1,1'-biphenyl ($t_R = 8.54$ min) and [1,1'-biphenyl]-4-yl(phenyl)sulfane ($t_R = 17.04$ min) or [1,1'-biphenyl]-4-yl(phenyl)selane ($t_R = 18.78$ min) or [1,1'-biphenyl]-4-yl(4-nitrophenyl)selane ($t_R = 15.24$ min) as external standards, respectively.



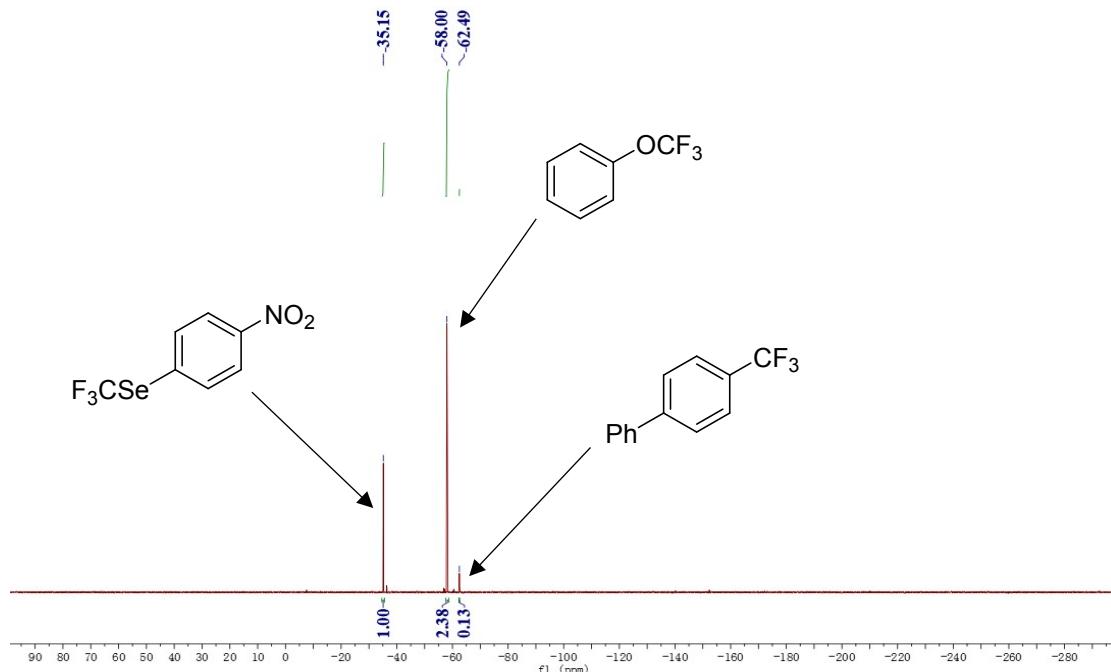
5.2. CuOAc-Mediated reactions of **2a** with trifluoromethyl aryl sulfonium ylide and trifluoromethyl aryl selenium ylides under the same conditions.

In a nitrogen-filled glovebox, a sealed tube was charged with 4-iodo-1,1'-biphenyl (**2a**, 56.0 mg, 0.2 mmol), **1b** or **1a** or **1a'** (0.4 mmol), CuOAc (48.8 mg, 0.4 mmol), and DMSO or DMF (2 mL) with stirring. The mixture was reacted at 100 °C for 20 h and cooled to room temperature. The yields of **3a'** and **3b** or **3a** or 4-*Ph*C₆H₄SPh were determined by HPLC ($\lambda = 253$ nm, H₂O/CH₃OH = 15:85 (v/v)) using 4-

(trifluoromethyl)-1,1'-biphenyl ($t_R = 8.54$ min) and [1,1'-biphenyl]-4-yl(4-nitrophenyl)selane ($t_R = 15.24$ min) or [1,1'-biphenyl]-4-yl(phenyl)selane ($t_R = 18.78$ min) or [1,1'-biphenyl]-4-yl(phenyl)sulfane ($t_R = 17.04$ min) as external standards, respectively.



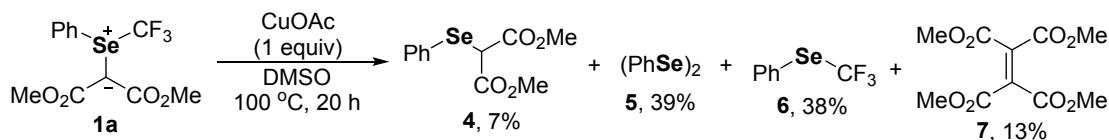
The ^{19}F NMR spectrum of the reaction mixture (equation 8)



29.9 mg of PhOC(F)(F)F was added to the reaction mixture as an internal standard. The yield of 4-(trifluoromethyl)-1,1'-biphenyl was calculated to be 5% and that of (4-

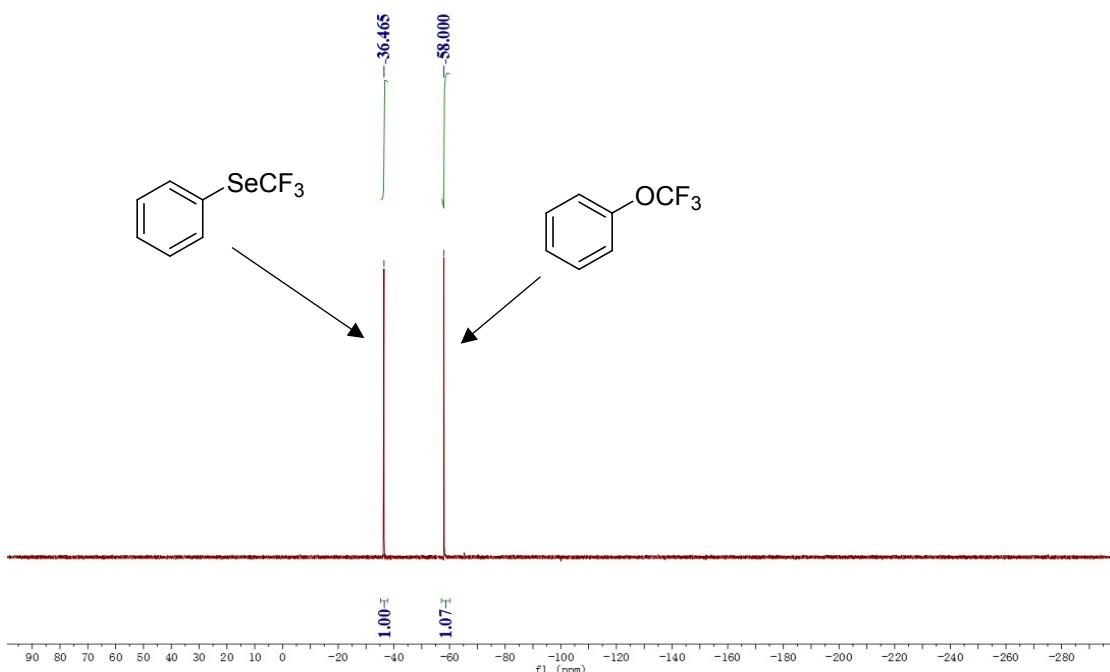
nitrophenyl)(trifluoromethyl)selane was found to be 19% based on PhOCF₃ added.

5.3. CuOAc-Mediated decomposition of **1a** in the absence of aryl halide.

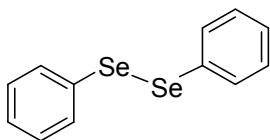


In a nitrogen-filled glovebox, a sealed tube was charged with dimethyl 2-(phenyl(trifluoromethyl)- λ^4 -selanylidene)malonate (**1a**, 71.2 mg, 0.2 mmol), CuOAc (24.4 mg, 0.2 mmol), and DMSO (2 mL) with stirring. The mixture was reacted at 100 °C for 20 h and cooled to room temperature. 13.2 mg of PhOCF₃ was added as an internal standard and the yield of PhSeCF₃ (**6**) was measured by ¹⁹F NMR spectroscopy (38%). The reaction mixture was then diluted by ethyl acetate (60 mL). The organic solution was washed with water (20 × 3 mL), dried over anhydrous Na₂SO₄, and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether and a mixture of petroleum ether and ethyl acetate (40:1 to 10:1 (v/v)) as eluents to give 12.3 mg of **5** (39%), 4.0 mg of **4** (7%), and 3.5 mg of **7** (13%), respectively.

The ¹⁹F NMR spectrum of the reaction mixture (after addition of 13.2 mg PhOCF₃ and before workup)

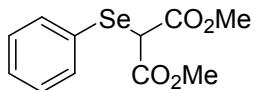


1,2-Diphenyldiselenane (**5**)¹³



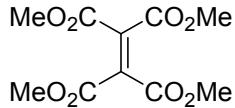
Yellow solid, petroleum ether for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.64 (d, *J* = 7.6 Hz, 4H), 7.31-7.27 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 131.5, 130.9, 129.2, 127.7.

Dimethyl 2-(phenylselanyl)malonate (**4**)²



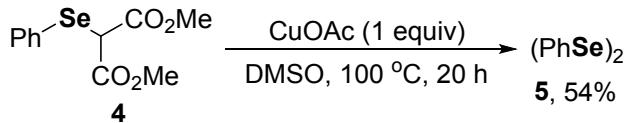
Yellow oil, a mixture of petroleum ether and ethyl acetate (20:1 (v/v)) as eluents for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.66 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.1 Hz, 2H), 4.50 (s, 1H), 3.72 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 167.6, 135.7, 129.3, 129.2, 127.4, 53.1, 45.8.

Tetramethyl ethene-1,1,2,2-tetracarboxylate (**7**)¹⁴



Light yellow solid, a mixture of petroleum ether and ethyl acetate (10:1 (v/v)) as eluents for column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 3.87 (s, 12 H). ¹³C NMR (126 MHz, CDCl₃) δ 162.6, 135.4, 53.4.

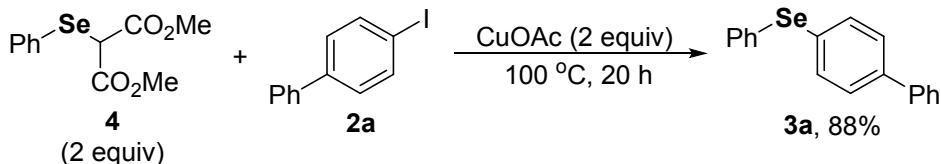
5.4. CuOAc-Mediated decomposition of **4** in the absence of aryl halide.



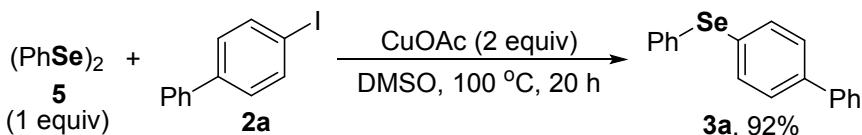
In a nitrogen-filled glovebox, a sealed tube was charged with dimethyl 2-(phenylselanyl)malonate (**4**,² 57.6 mg, 0.2 mmol), CuOAc (24.4 mg, 0.2 mmol), and DMSO (2 mL) with stirring. The mixture was reacted at 100 °C for 20 h, cooled to room temperature, and diluted with ethyl acetate (60 mL). The organic solution was washed with water (20 × 3 mL), dried over anhydrous Na₂SO₄, and concentrated to dryness under reduced pressure. The residue was purified by column chromatography

on silica gel using petroleum ether as eluent to give 17.1 mg of **5** (54%).

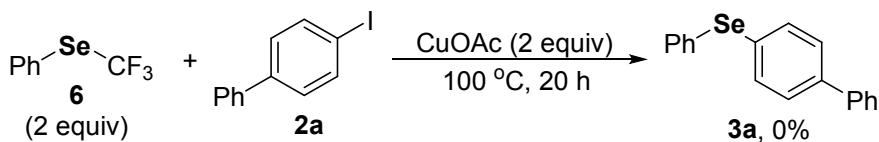
5.5. CuOAc-Mediated reactions of **4**, **5** and **6** with **2a** under the standard conditions.



In a nitrogen-filled glovebox, a sealed tube was charged with dimethyl 2-(phenylselanyl)malonate (**4**,² 115.2 mg, 0.4 mmol), 4-iodo-1,1'-biphenyl (**2a**, 55.6 mg, 0.2 mmol), CuOAc (48.8 mg, 0.4 mmol), and DMSO (2 mL) with stirring. The mixture was reacted at 100 °C for 20 h and cooled to room temperature. The yield of **3a** was determined by HPLC ($\lambda = 253$ nm, H₂O/CH₃OH = 15:85 (v/v)) using [1,1'-biphenyl]-4-yl(phenyl)selane ($t_{\text{R}} = 18.78$ min) as an external standard (88%).

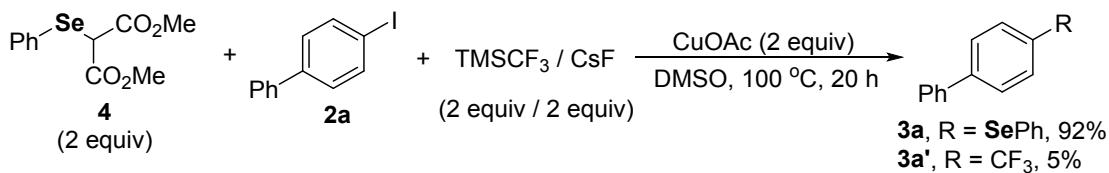


In a nitrogen-filled glovebox, a sealed tube was charged with 1,2-diphenyldiselenane (**5**, 62.8 mg, 0.2 mmol), 4-iodo-1,1'-biphenyl (**2a**, 56.0 mg, 0.2 mmol), CuOAc (48.8 mg, 0.4 mmol), and DMSO (2 mL) with stirring. The mixture was reacted at 100 °C for 20 h and cooled to room temperature. The yield of **3a** was determined by HPLC ($\lambda = 253$ nm, H₂O/CH₃OH = 15:85 (v/v)) using [1,1'-biphenyl]-4-yl(phenyl)selane ($t_{\text{R}} = 18.78$ min) as an external standard (92%).

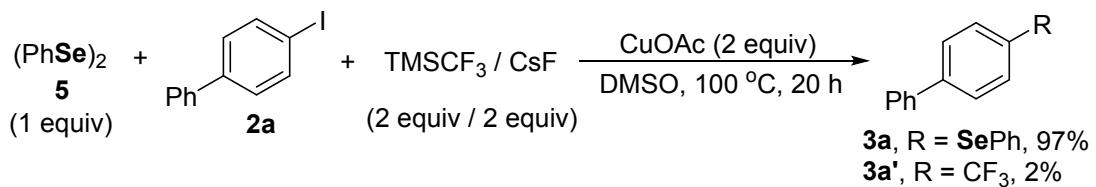


In a nitrogen-filled glovebox, a sealed tube was charged with phenyl(trifluoromethyl)selane (**6**,³ 90.4 mg, 0.4 mmol), 4-iodo-1,1'-biphenyl (**2a**, 55.6 mg, 0.2 mmol), CuOAc (48.8 mg, 0.4 mmol), and DMSO (2 mL) with stirring. The mixture was reacted at 100 °C for 20 h and cooled to room temperature. The yield of **3a** was determined by HPLC ($\lambda = 253$ nm, H₂O/CH₃OH = 15:85 (v/v)) using [1,1'-biphenyl]-4-yl(phenyl)selane ($t_{\text{R}} = 18.78$ min) as an external standard (0%).

5.6. CuOAc-Mediated competitive aryl selenylation and trifluoromethylation.

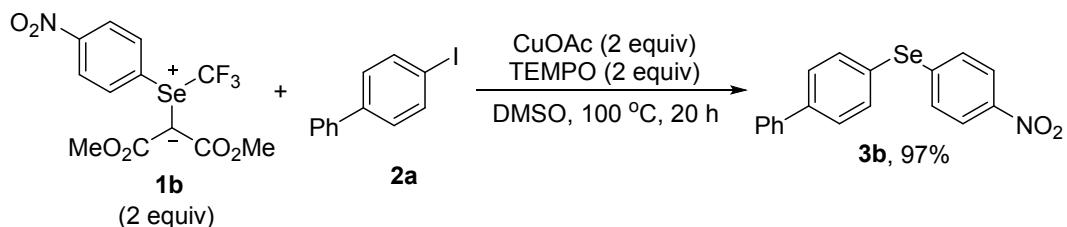


In a nitrogen-filled glovebox, a sealed tube was charged with 4-iodo-1,1'-biphenyl (**2a**, 56.0 mg, 0.2 mmol), (phenylselanyl)malonate (**4**, 115.0 mg, 0.4 mmol) CuOAc (48.8 mg, 0.4 mmol), TMSCF₃ (56.8 mg, 0.4 mmol), CsF (60.8 mg, 0.4 mmol), and DMSO (2 mL) with stirring. The mixture was reacted at 100 °C for 20 h and cooled to room temperature. The yields of **3a'** (5%) and **3a** (92%) were determined by HPLC (λ = 253 nm, H₂O/CH₃OH = 15:85 (v/v)) using 4-(trifluoromethyl)-1,1'-biphenyl (t_R = 8.54 min) and [1,1'-biphenyl]-4-yl(phenyl)selane (t_R = 18.78 min) as external standards, respectively.



In a nitrogen-filled glovebox, a sealed tube was charged with 4-iodo-1,1'-biphenyl (**2a**, 56.0 mg, 0.2 mmol), 1,2-diphenyldiselane (**5**, 62.8 mg, 0.2 mmol), CuOAc (48.8 mg, 0.4 mmol), TMSCF₃ (56.8 mg, 0.4 mmol), CsF (60.8 mg, 0.4 mmol), and DMSO (2 mL) with stirring. The mixture was reacted at 100 °C for 20 h and cooled to room temperature. The yields of **3a'** (2%) and **3a** (97%) were determined by HPLC (λ = 253 nm, H₂O/CH₃OH = 15:85 (v/v)) using 4-(trifluoromethyl)-1,1'-biphenyl (t_R = 8.54 min) and [1,1'-biphenyl]-4-yl(phenyl)selane (t_R = 18.78 min) as external standards, respectively.

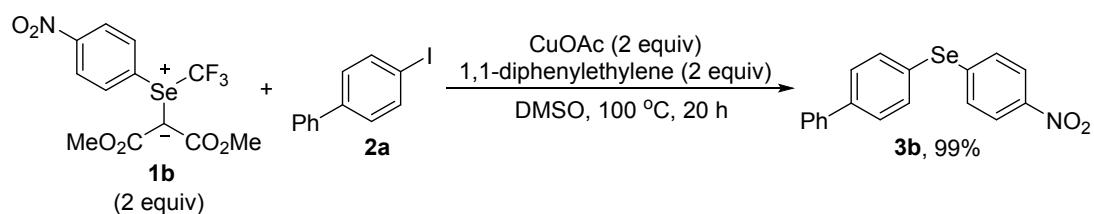
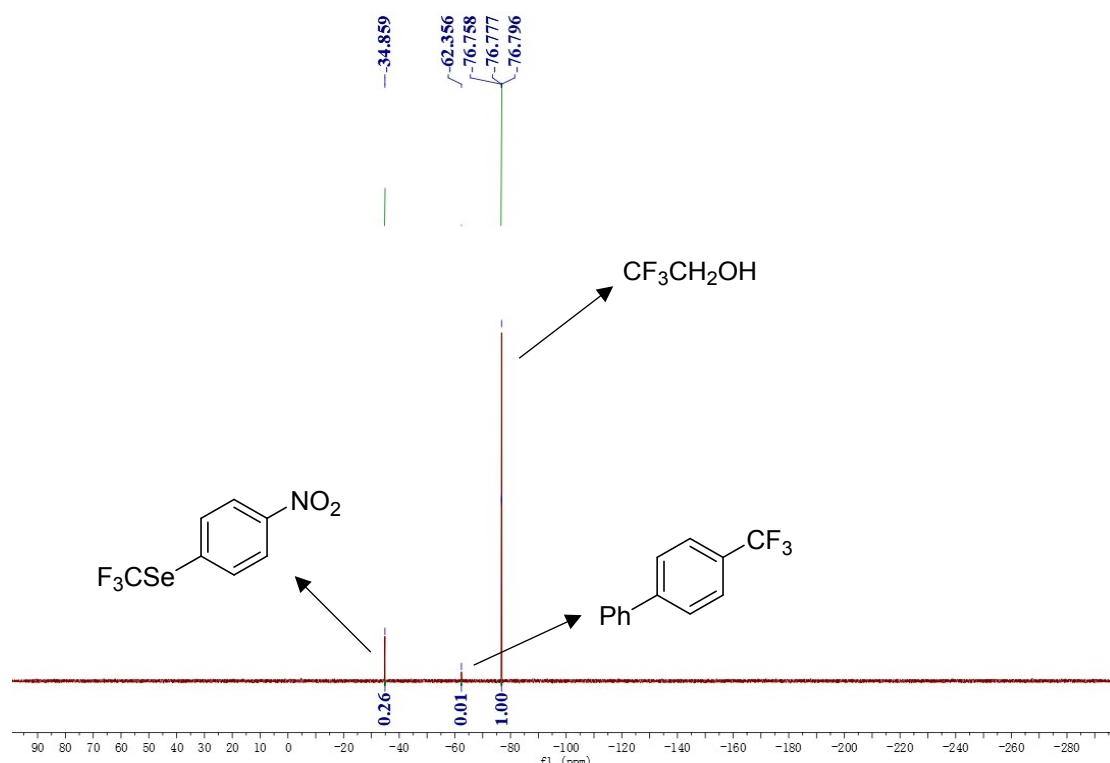
5.7. Cu-Mediated arylselenylation of **2a** by **1b** in the presence of radical traps.



In a nitrogen-filled glovebox, a sealed tube was charged with 4-iodo-1,1'-biphenyl (**2a**,

56.0 mg, 0.2 mmol), **1b** (160.4 mg, 0.4 mmol), CuOAc (48.8 mg, 0.4 mmol), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO, 62.5 mg, 0.4 mmol), and DMSO (2 mL) with stirring. The mixture was reacted at 100 °C for 20 h and cooled to room temperature. The yield of **3b** (97%) was determined by HPLC using [1,1'-biphenyl]-4-yl(4-nitrophenyl)selane ($t_R = 15.24$ min, $\lambda = 253$ nm, H₂O/CH₃OH = 15:85 (v/v)) as an external standard.

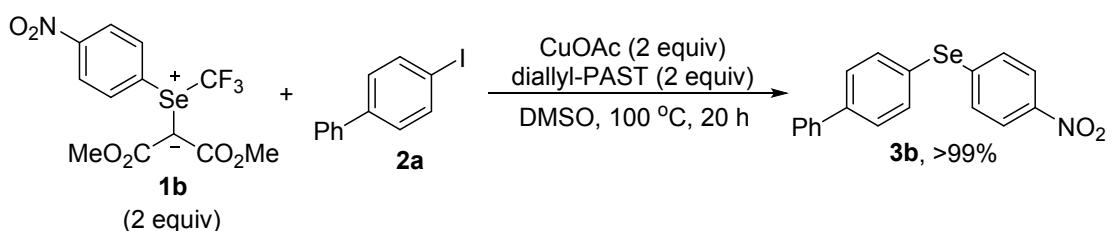
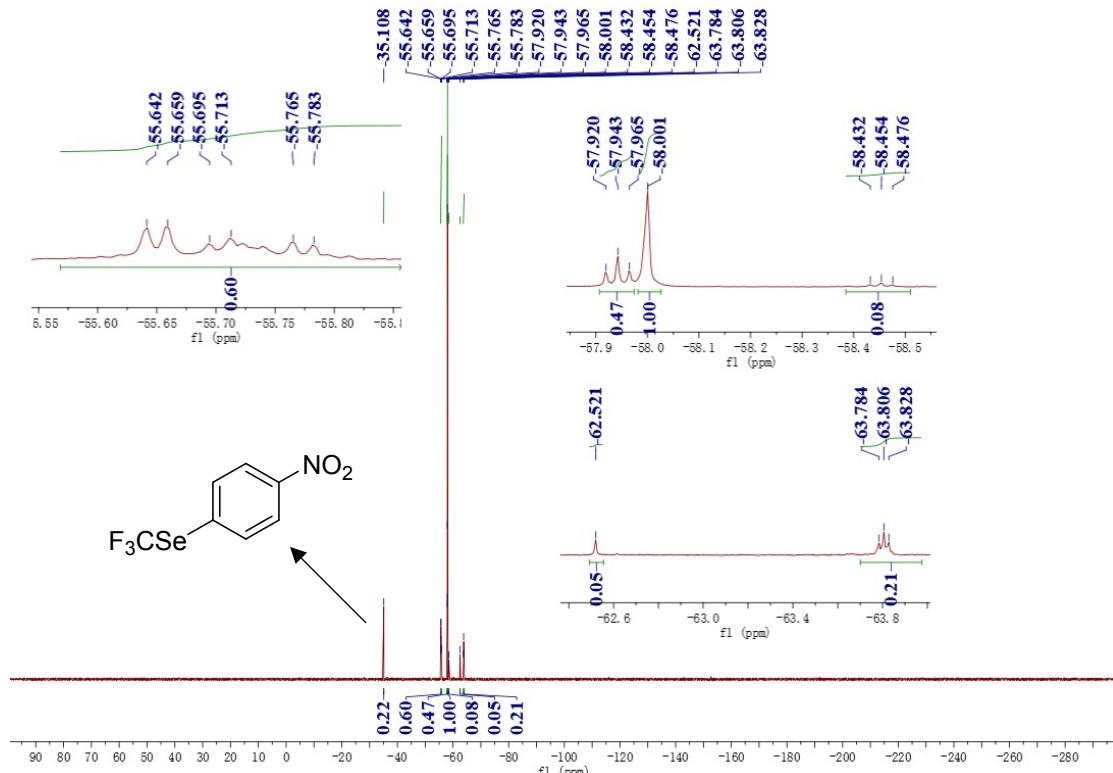
The ¹⁹F NMR spectrum of the reaction mixture (after addition of 21.3 mg CF₃CH₂OH as an internal standard)



In a nitrogen-filled glovebox, a sealed tube was charged with 4-iodo-1,1'-biphenyl (**2a**, 56.0 mg, 0.2 mmol), **1b** (160.4 mg, 0.4 mmol), CuOAc (48.8 mg, 0.4 mmol), 1,1-diphenylethylene (72.1 mg, 0.4 mmol), and DMSO (2 mL) with stirring. The mixture was reacted at 100 °C for 20 h and cooled to room temperature. The yield of **3b** (99%) was determined by HPLC using [1,1'-biphenyl]-4-yl(4-nitrophenyl)selane ($t_R = 15.24$

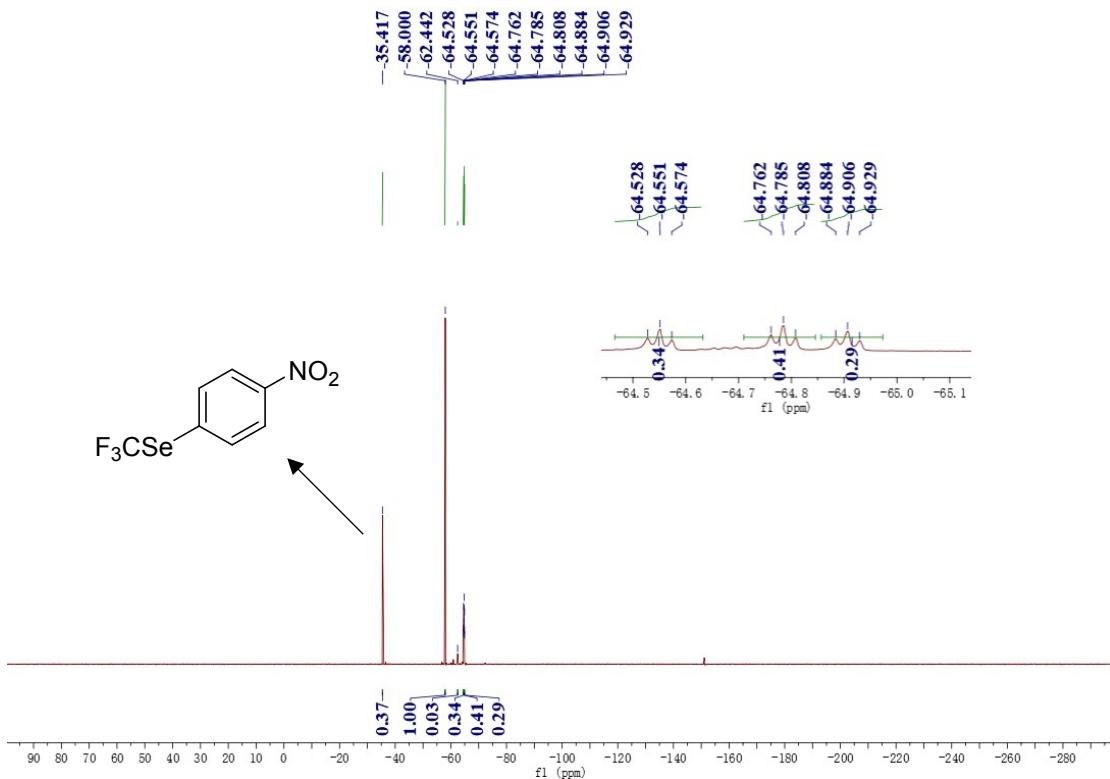
min, $\lambda = 253$ nm, $\text{H}_2\text{O}/\text{CH}_3\text{OH} = 15:85$ (v/v)) as an external standard.

The ^{19}F NMR spectrum of the reaction mixture (after addition of 29.3 mg PhOCF_3 as an internal standard)



In a nitrogen-filled glovebox, a sealed tube was charged with 4-iodo-1,1'-biphenyl (**2a**, 56.0 mg, 0.2 mmol), **1b** (160.4 mg, 0.4 mmol), CuOAc (48.8 mg, 0.4 mmol), N,N-diallyl-4-methylbenzenesulfonamide (diallyl-PAST, 100.5 mg, 0.4 mmol), and DMSO (2 mL) with stirring. The mixture was reacted at 100 °C for 20 h and cooled to room temperature. The yield of **3b** (>99%) was determined by HPLC using [1,1'-biphenyl]-4-yl(4-nitrophenyl)selane ($t_R = 15.24$ min, $\lambda = 253$ nm, $H_2O/CH_3OH = 15:85$ (v/v)) as an external standard.

The ^{19}F NMR spectrum of the reaction mixture (after addition of 32.0 mg PhOCF₃ as an internal standard)

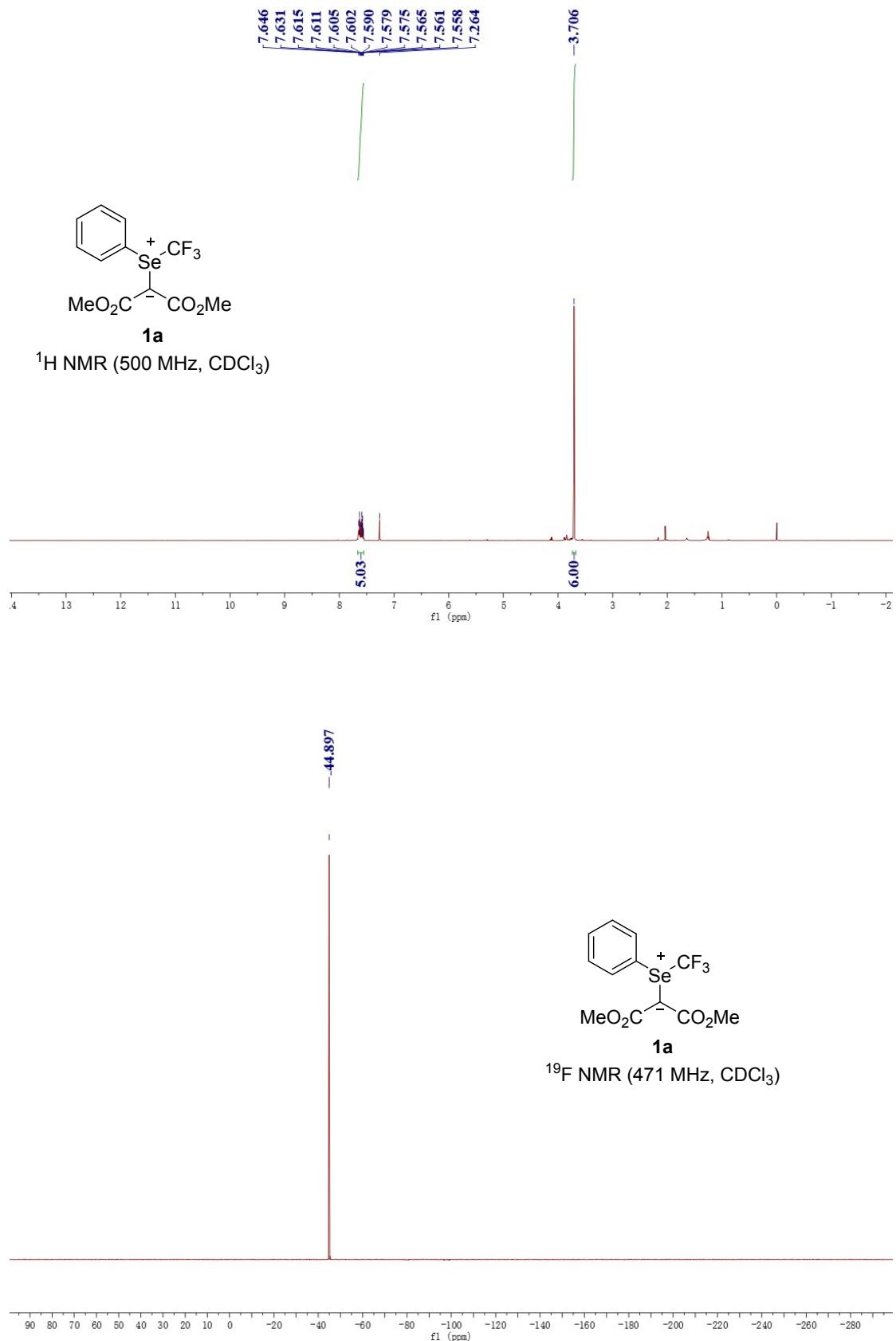


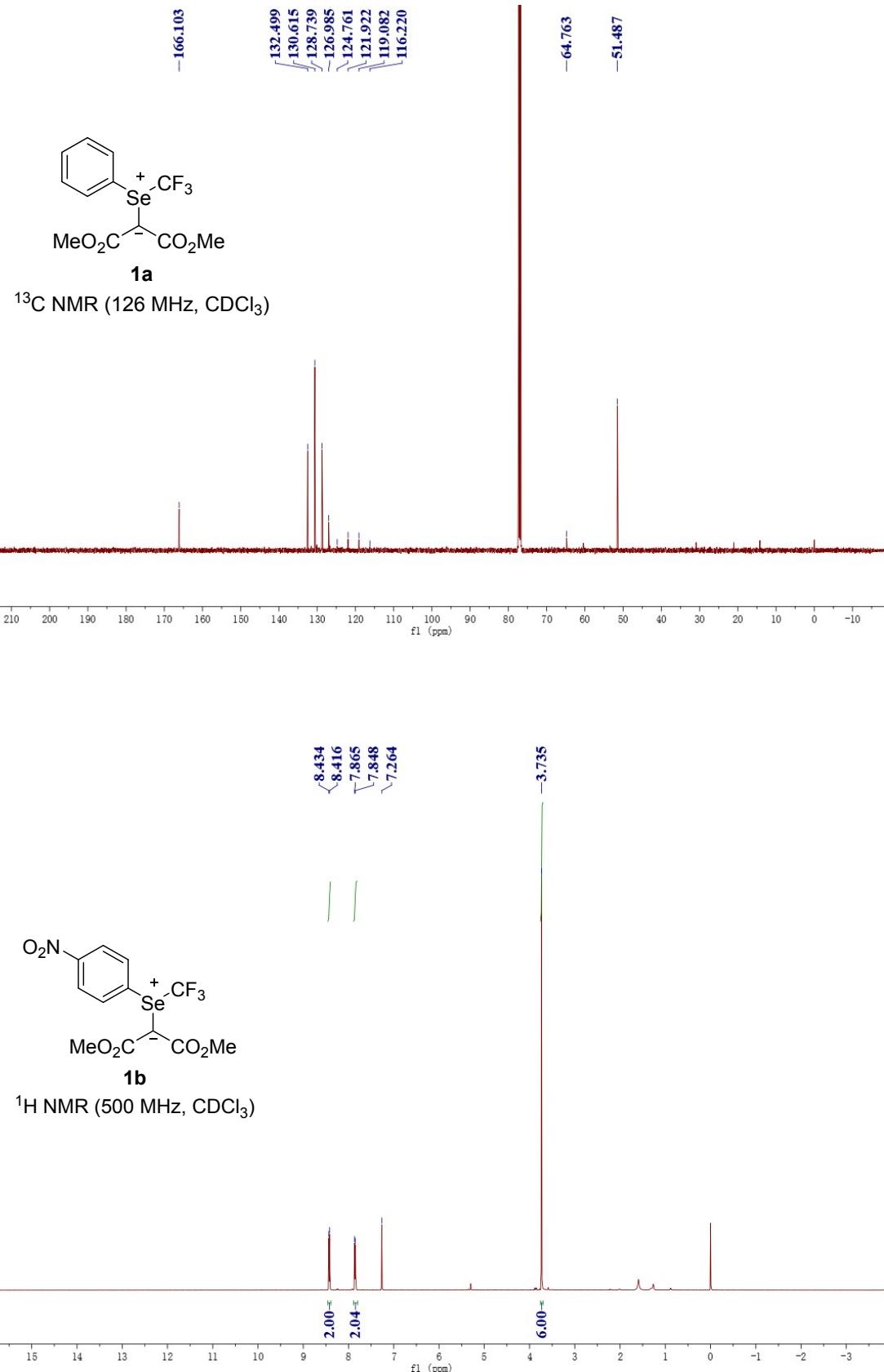
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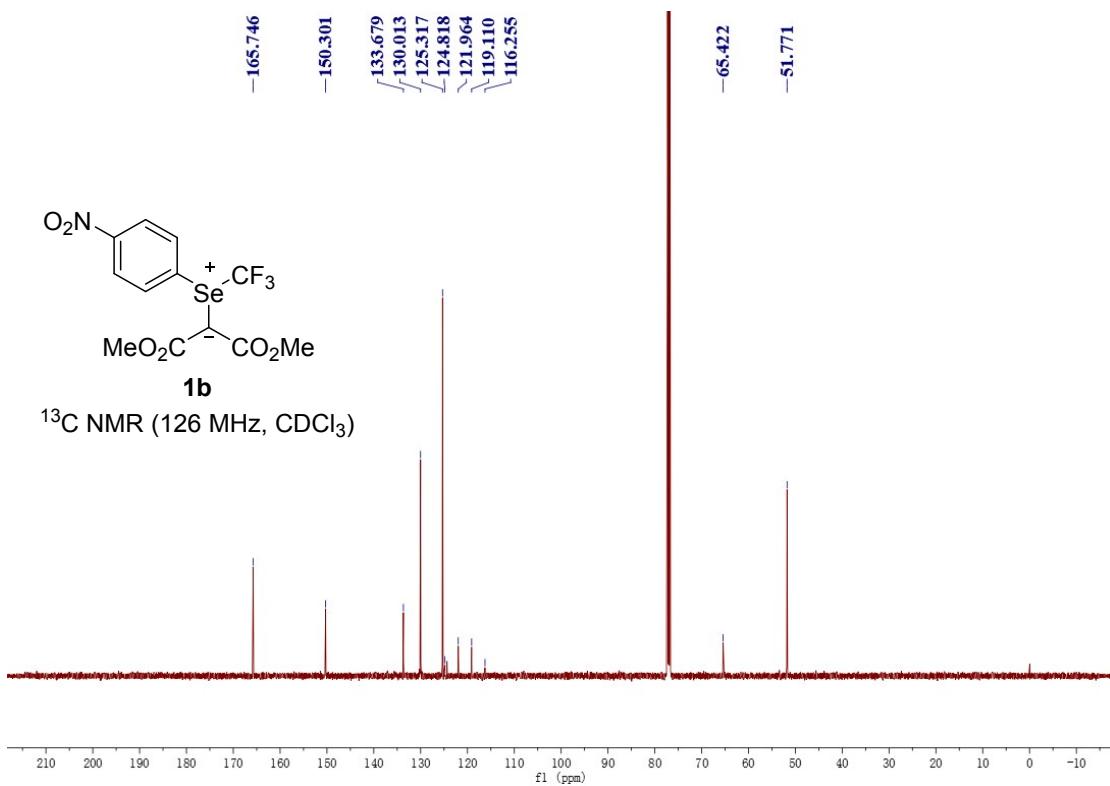
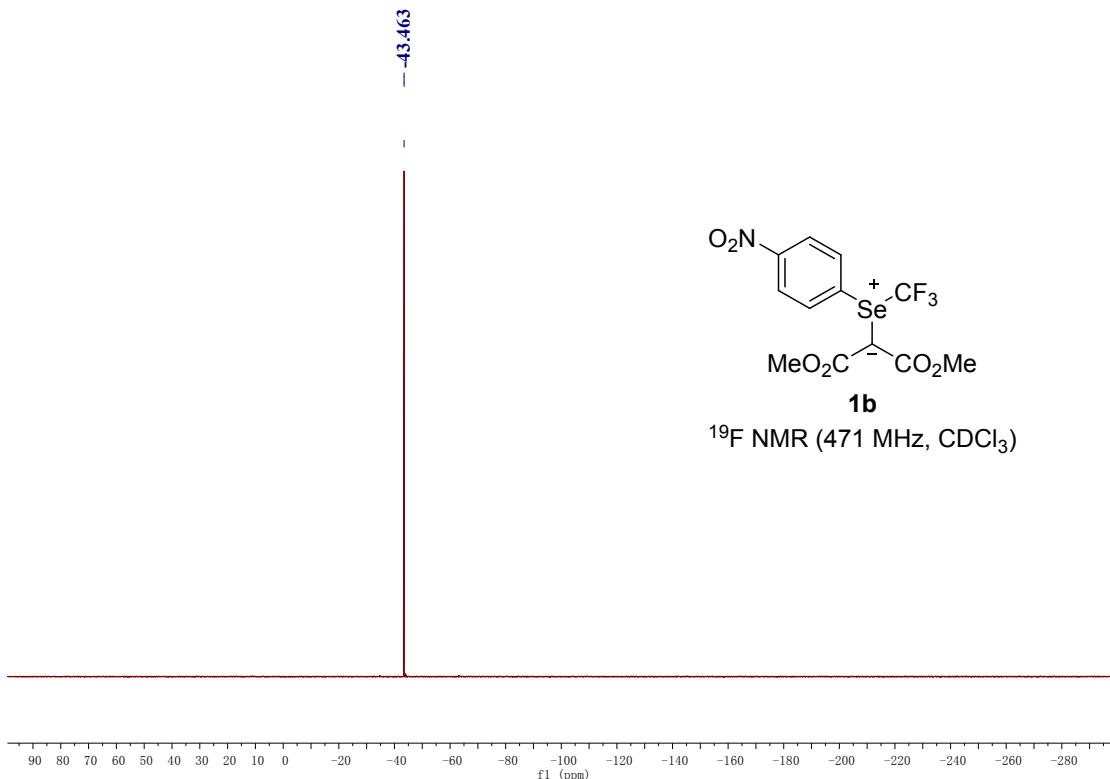
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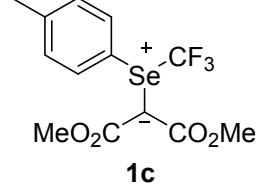
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6. The NMR spectra of 1, 3, 4, 5, 6 and 7

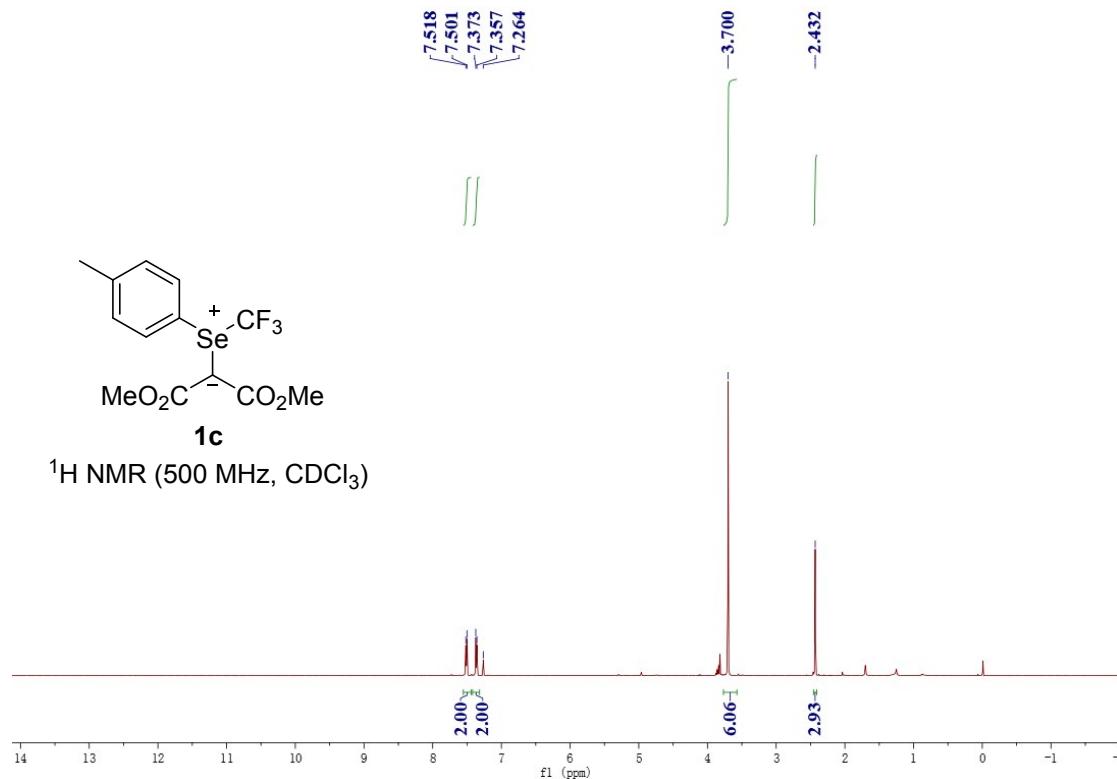




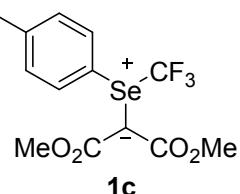




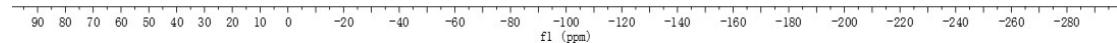
^1H NMR (500 MHz, CDCl_3)

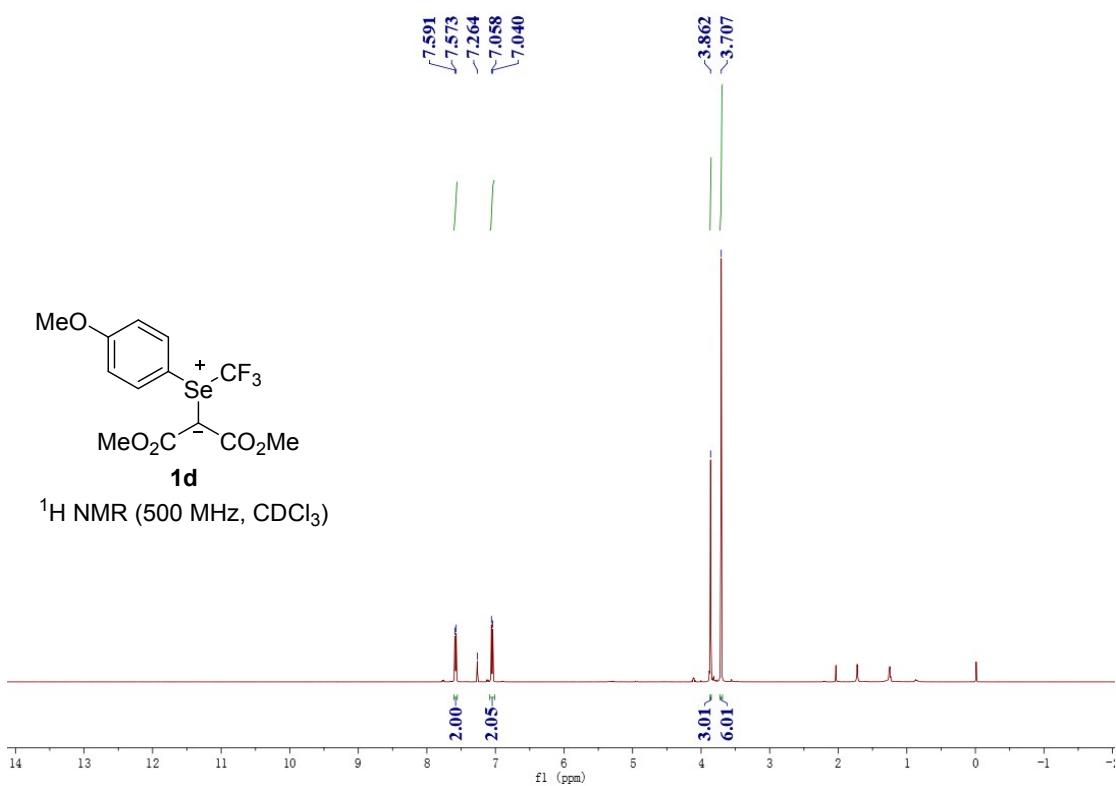
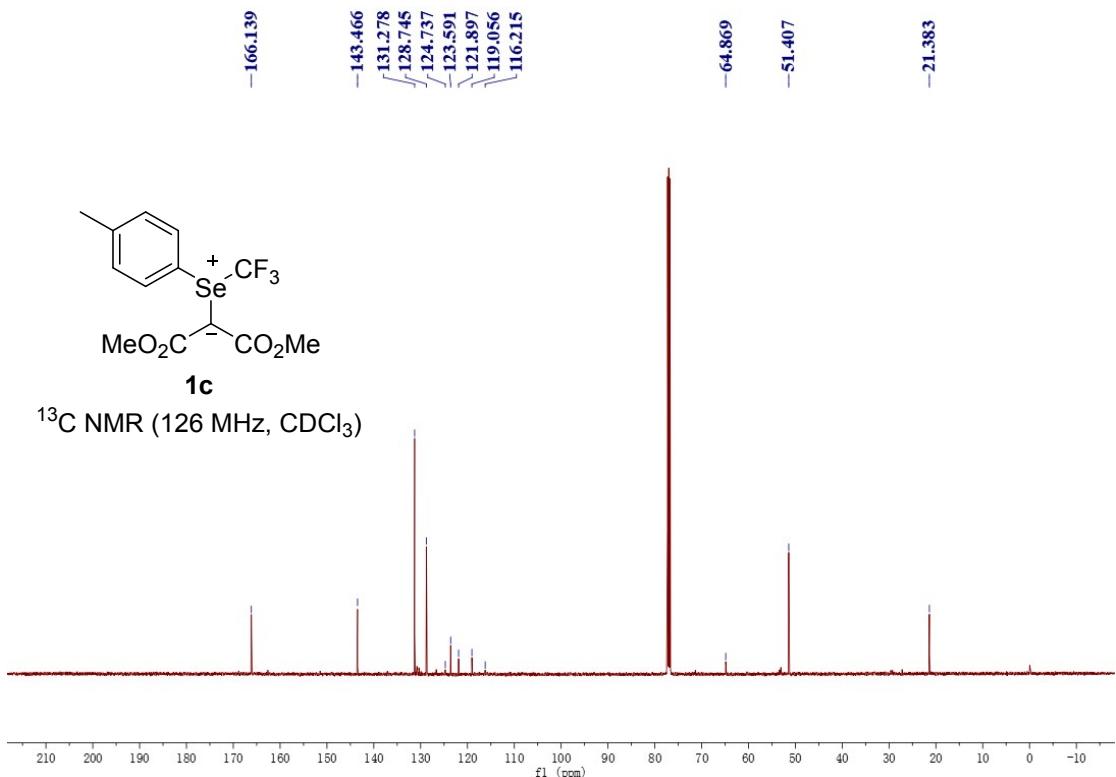


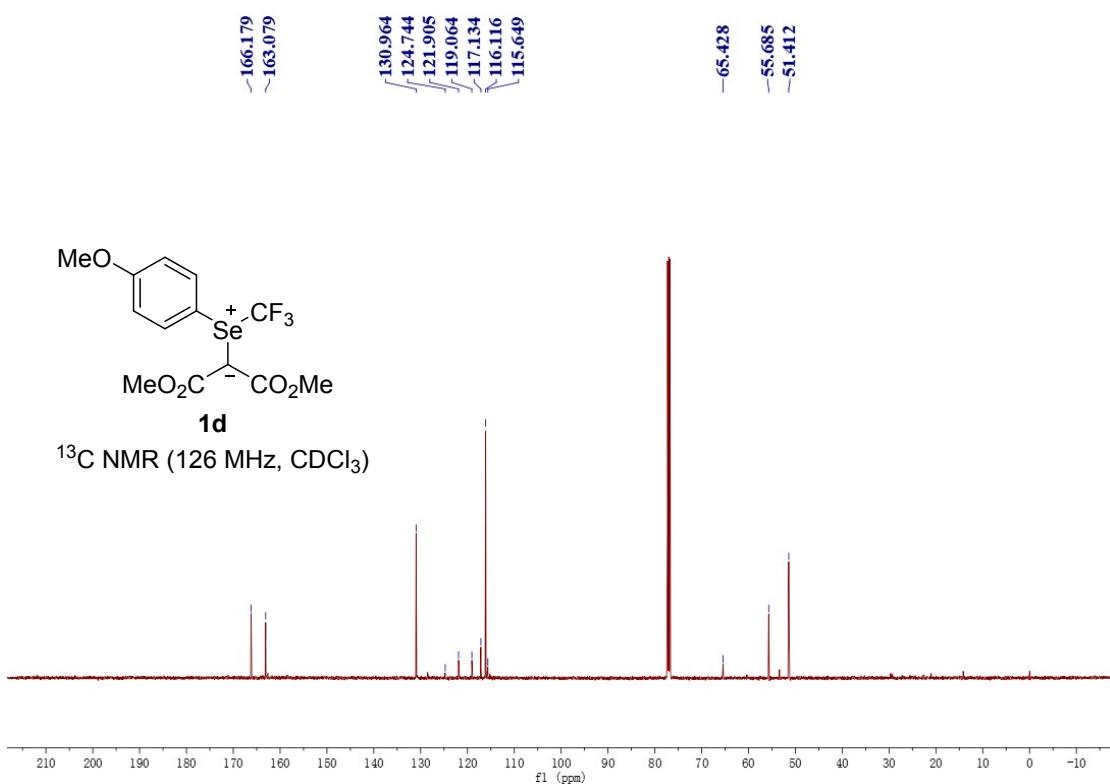
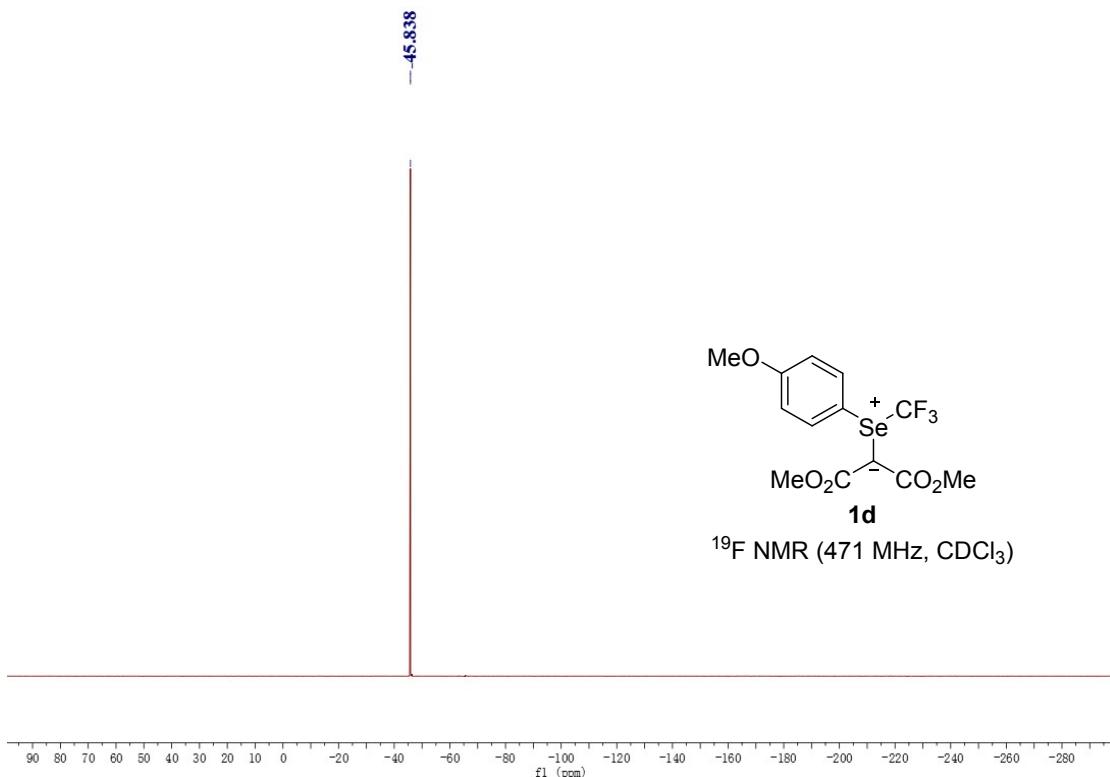
-45.333

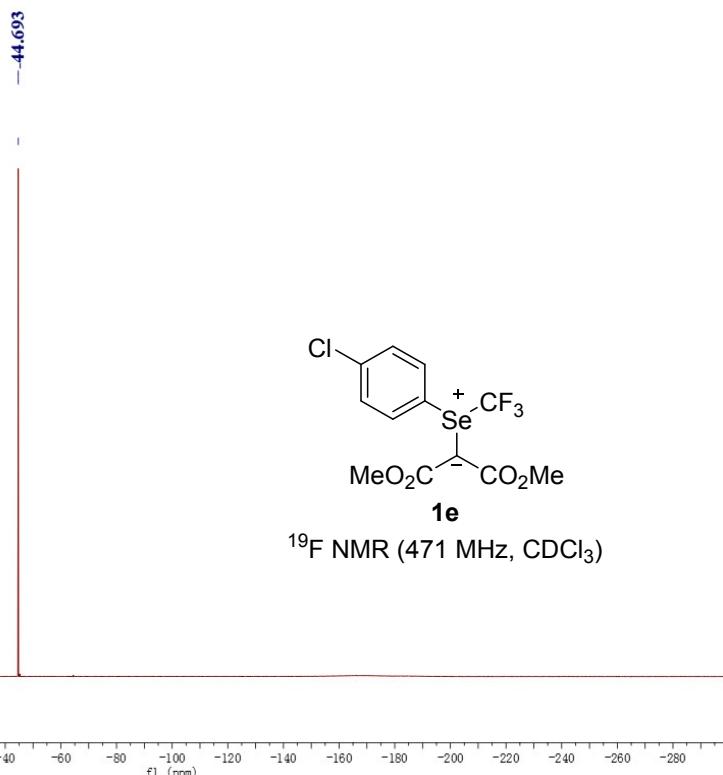
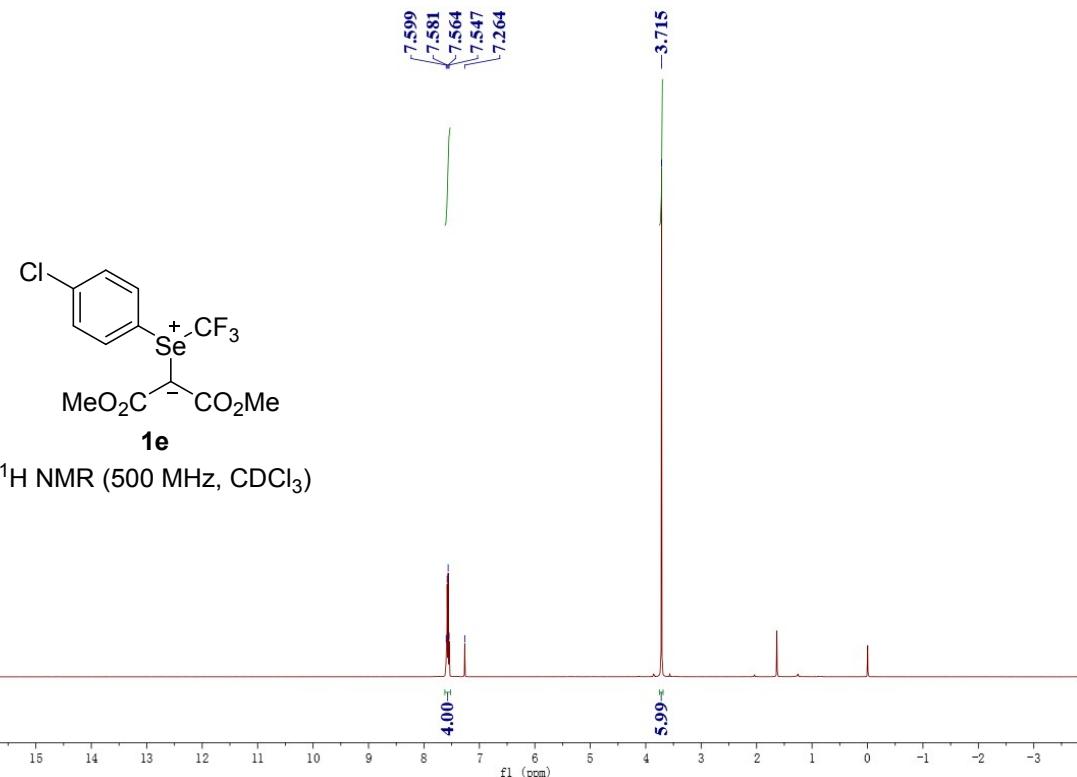


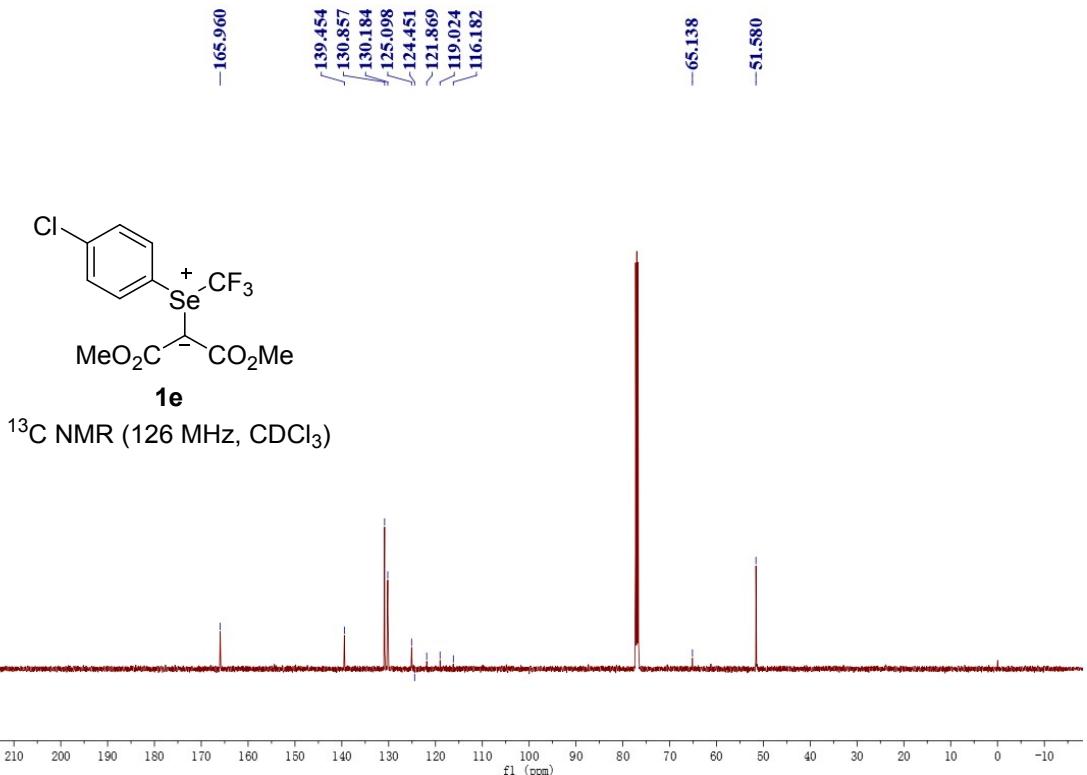
^{19}F NMR (471 MHz, CDCl_3)

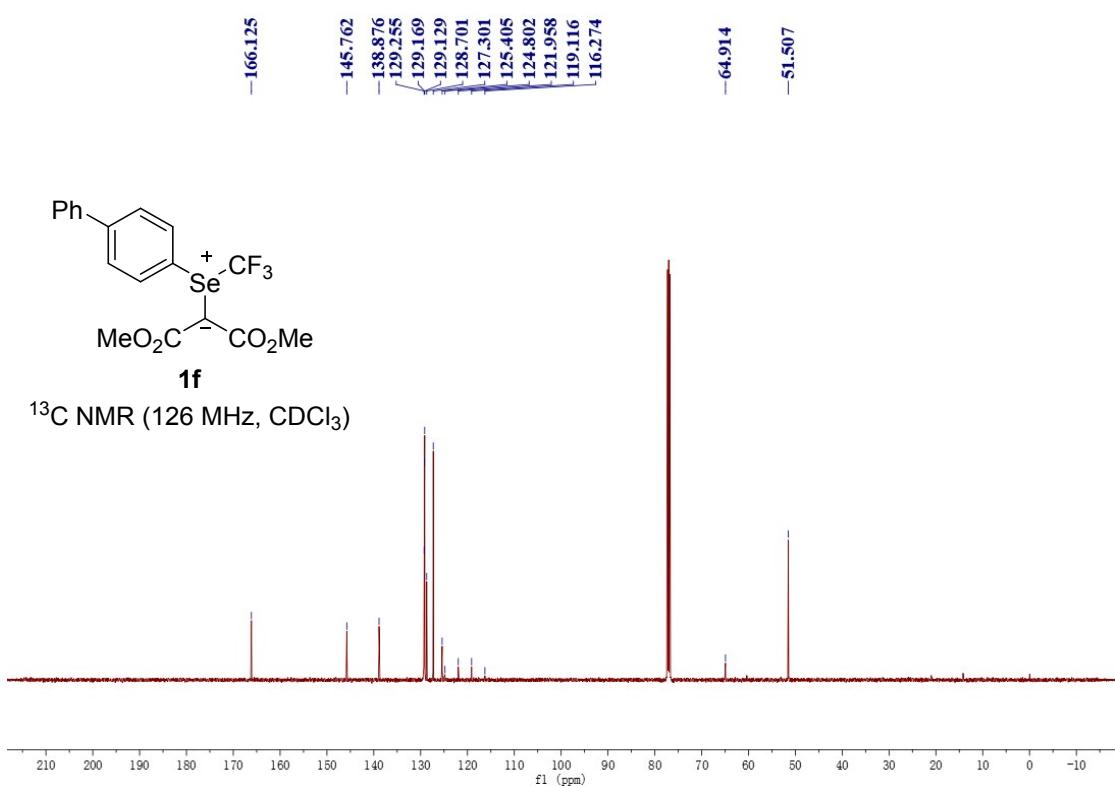
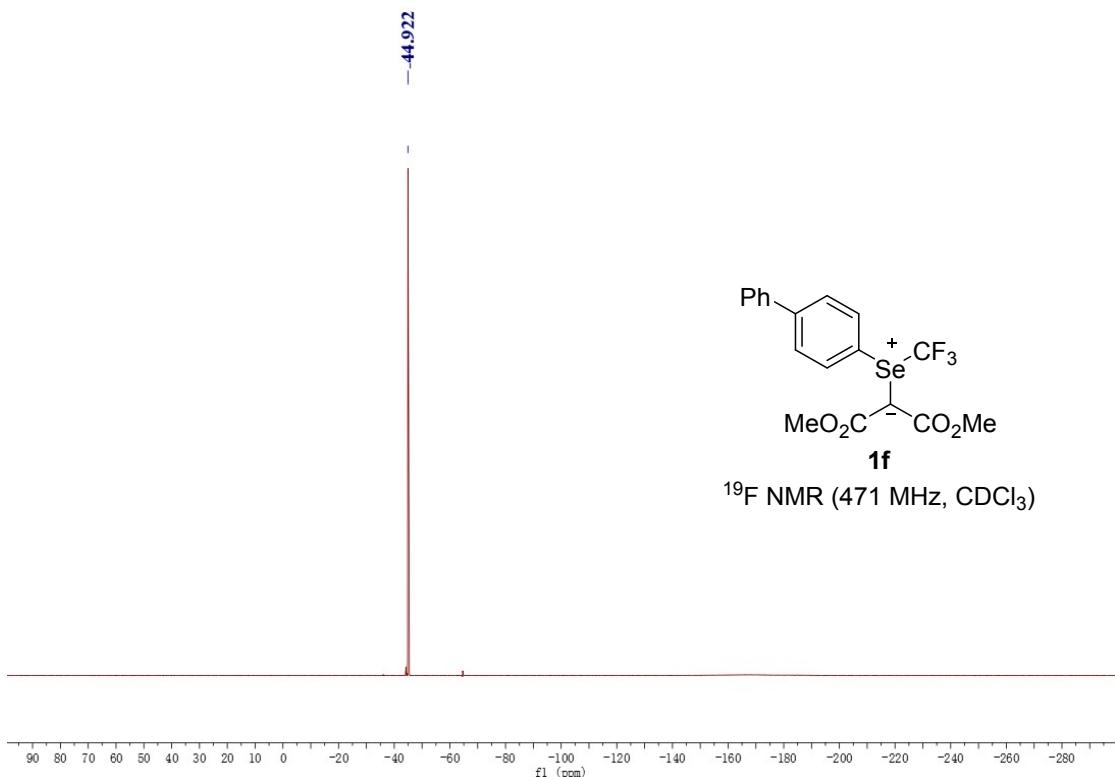


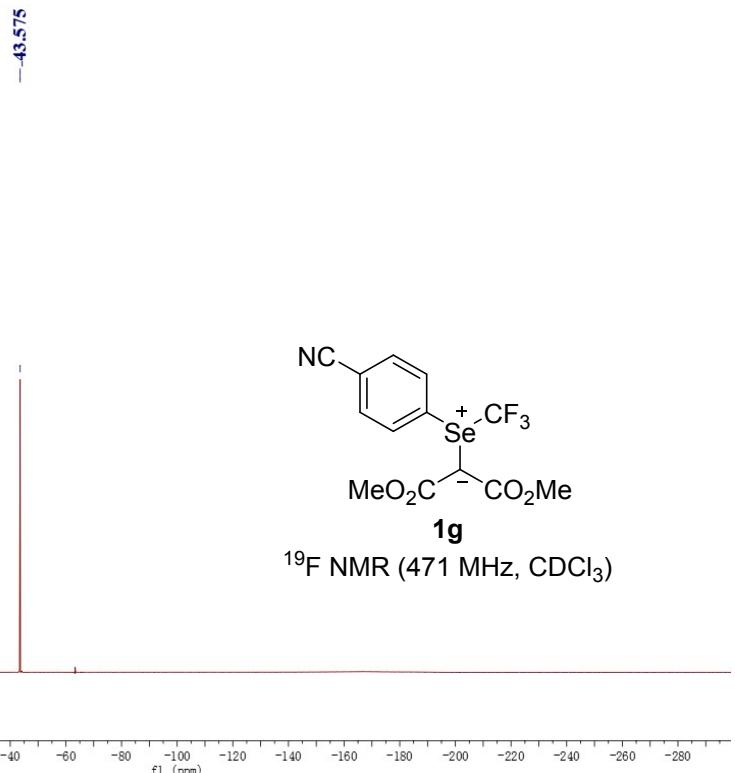
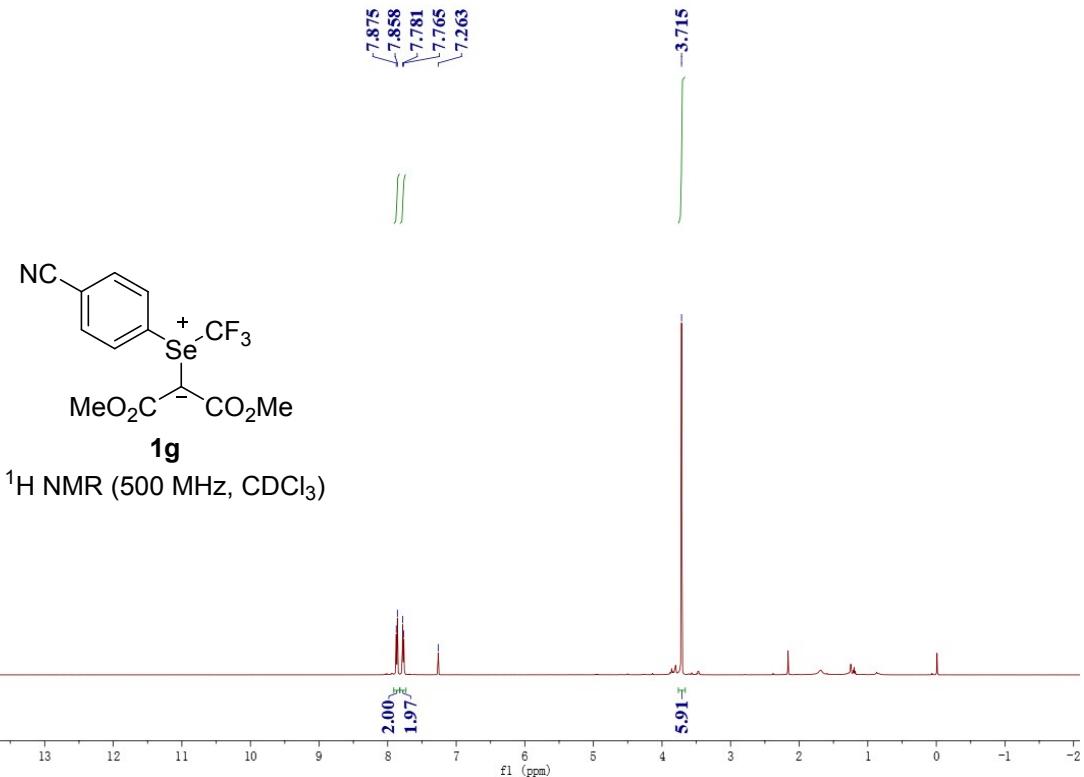


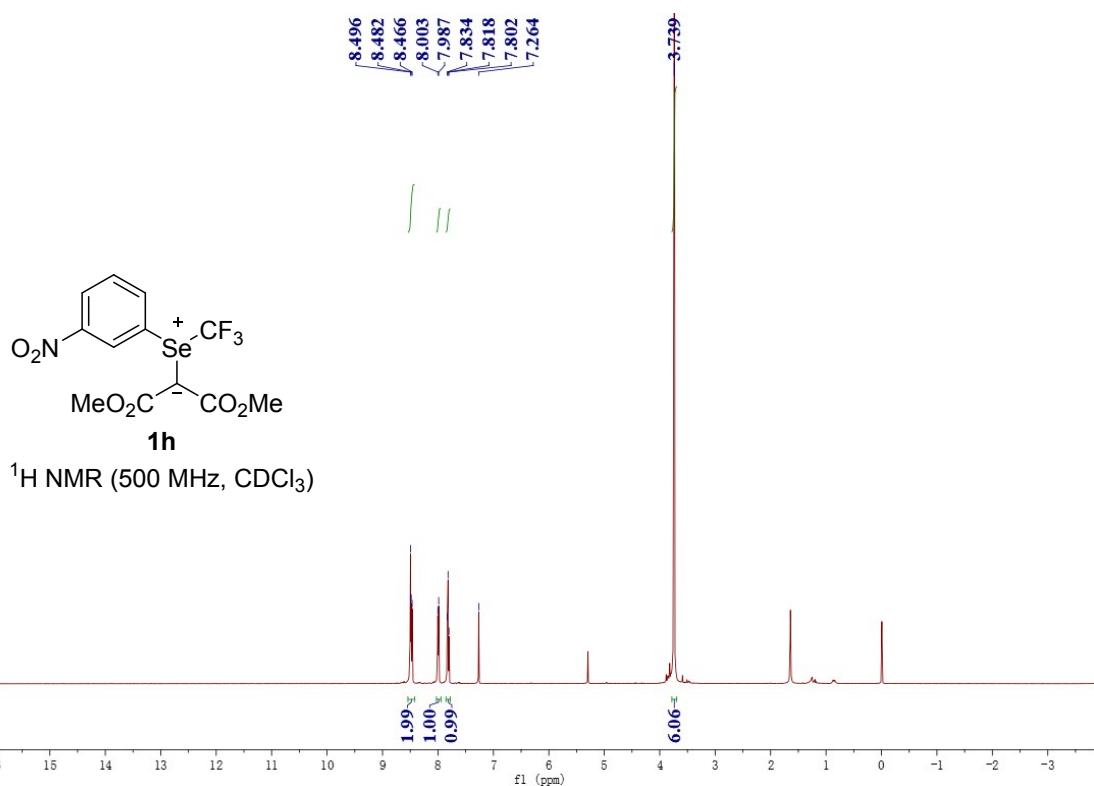
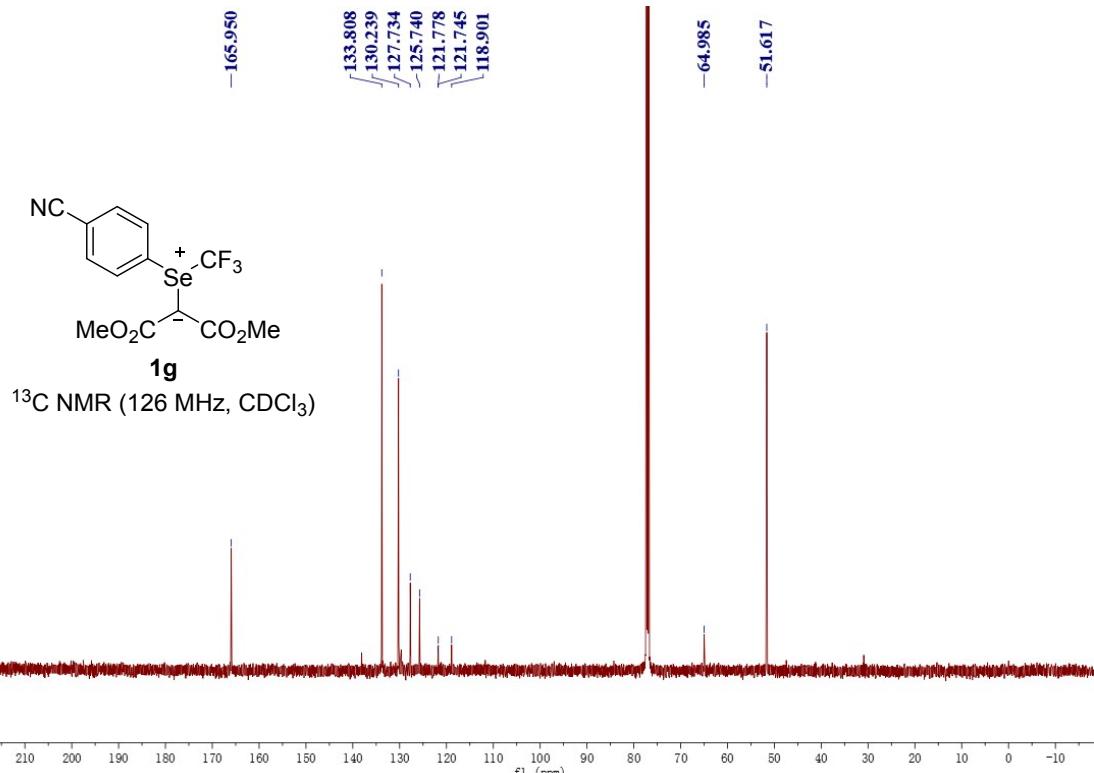


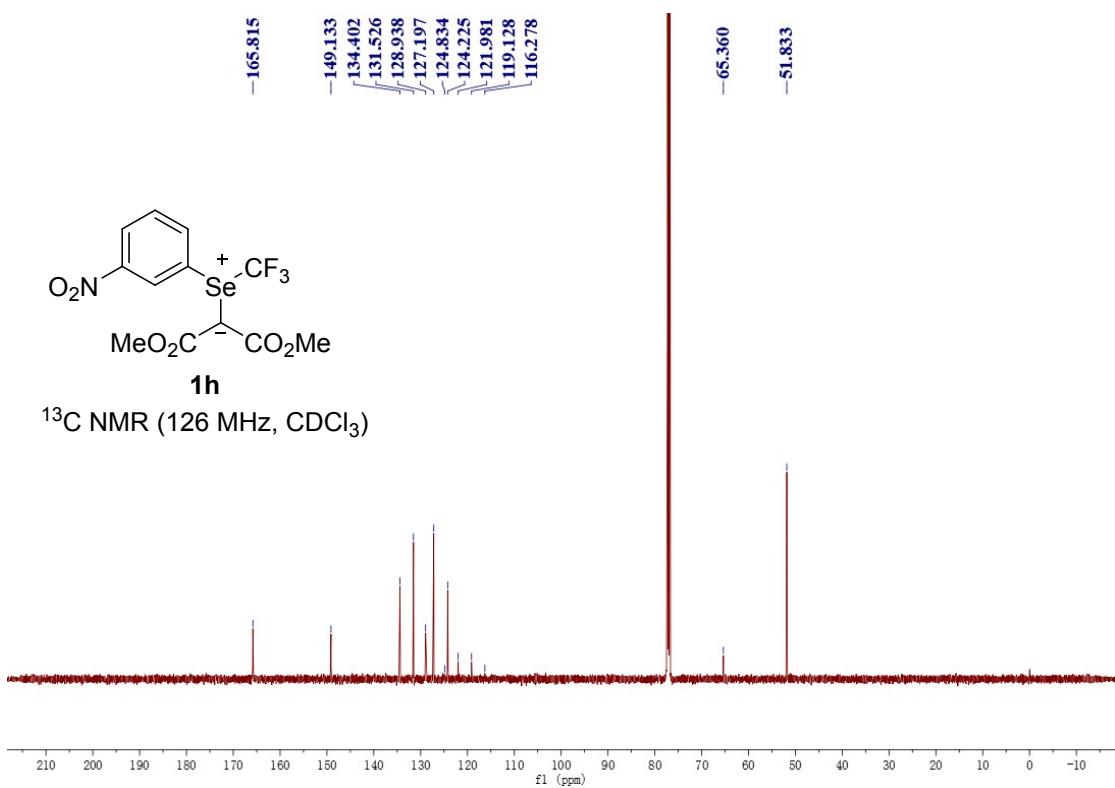
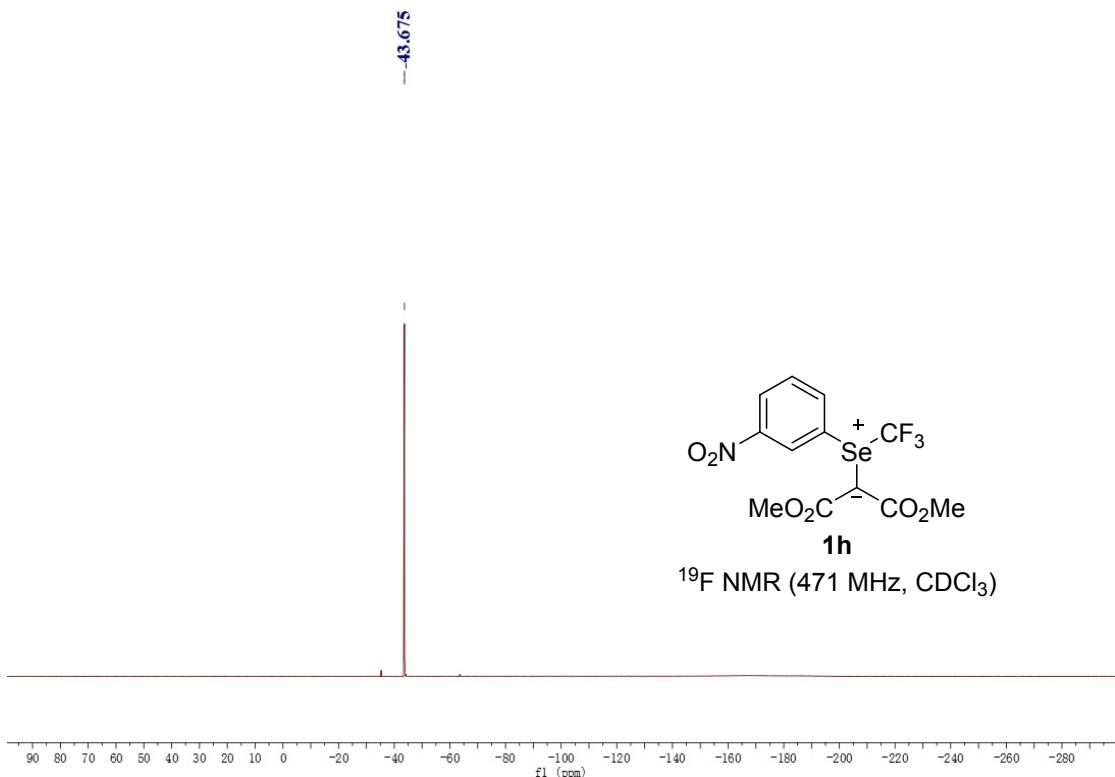


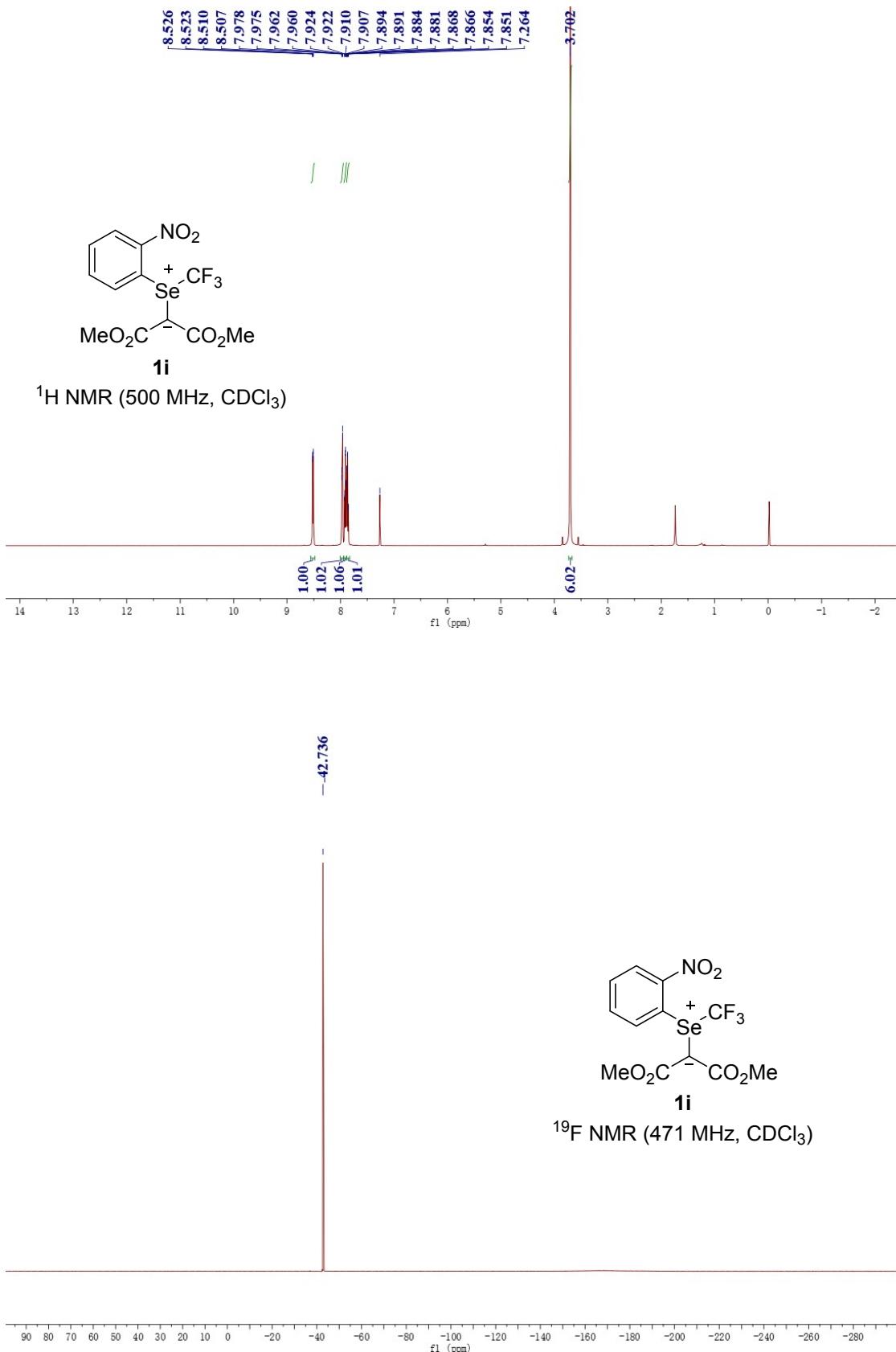


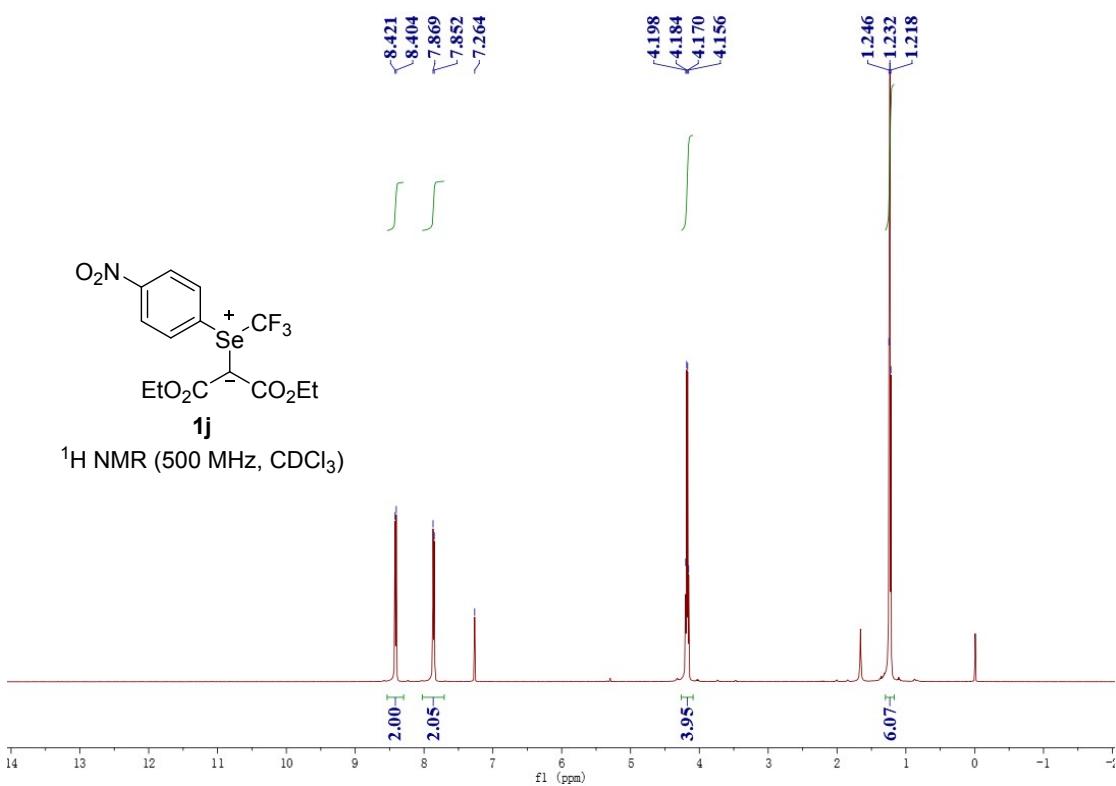
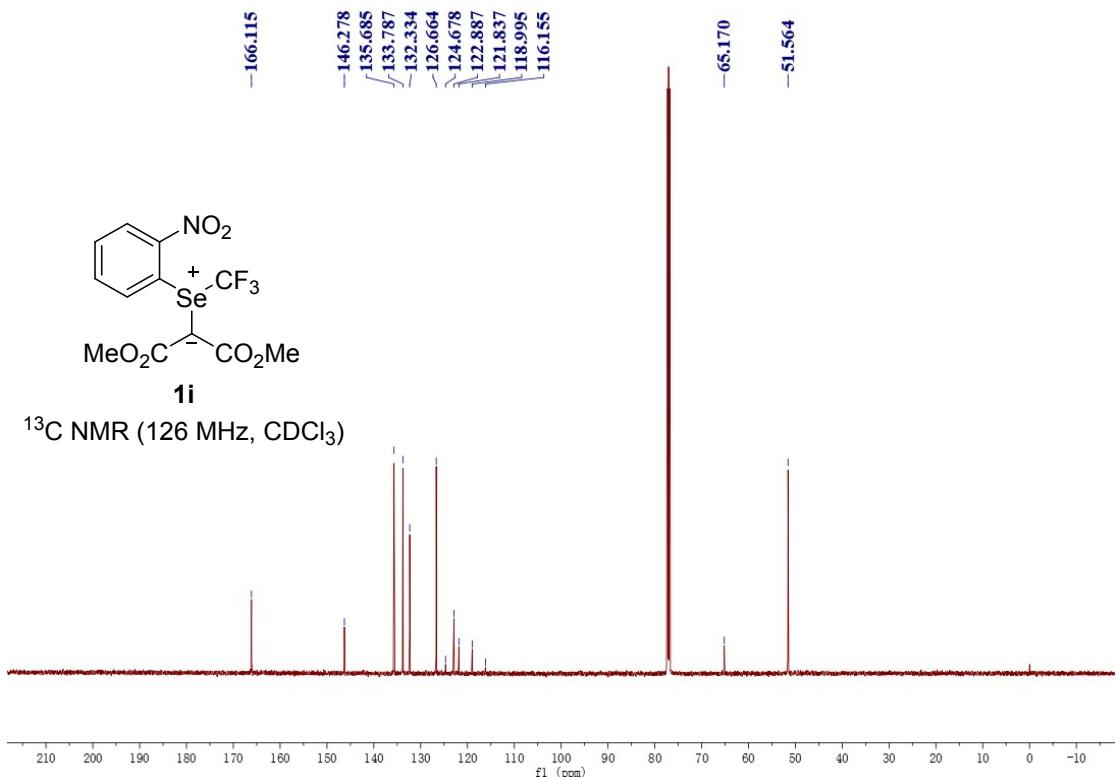


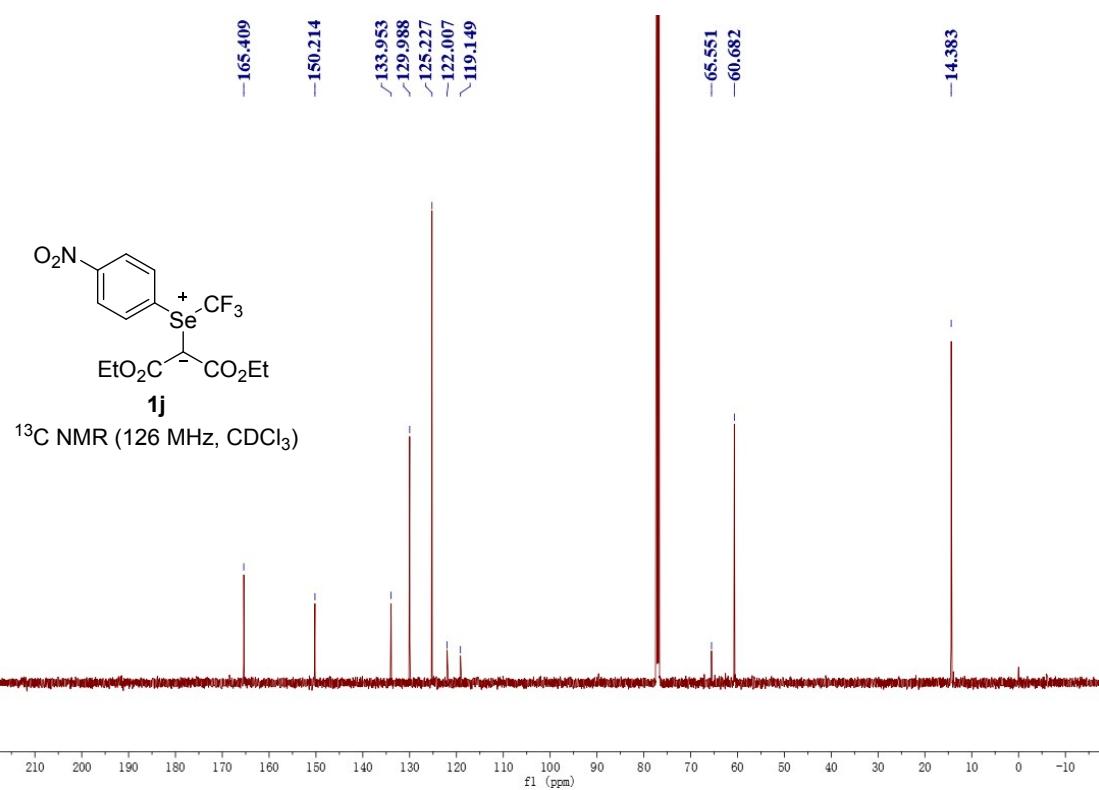
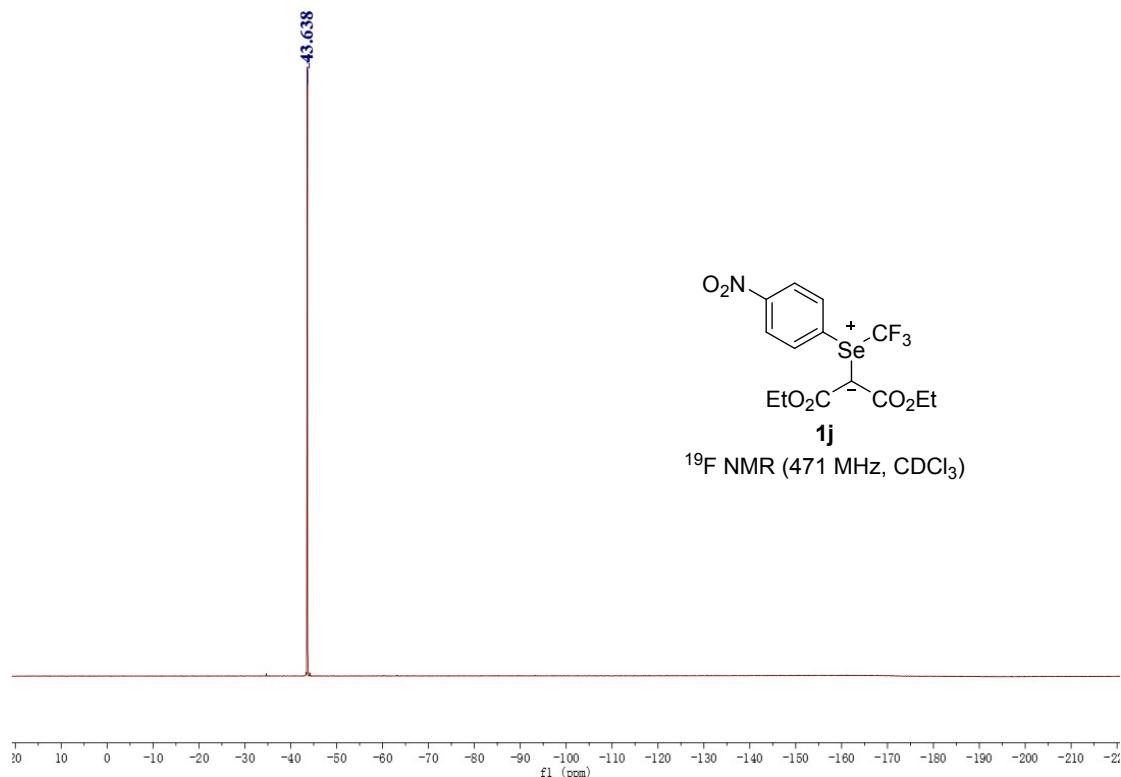


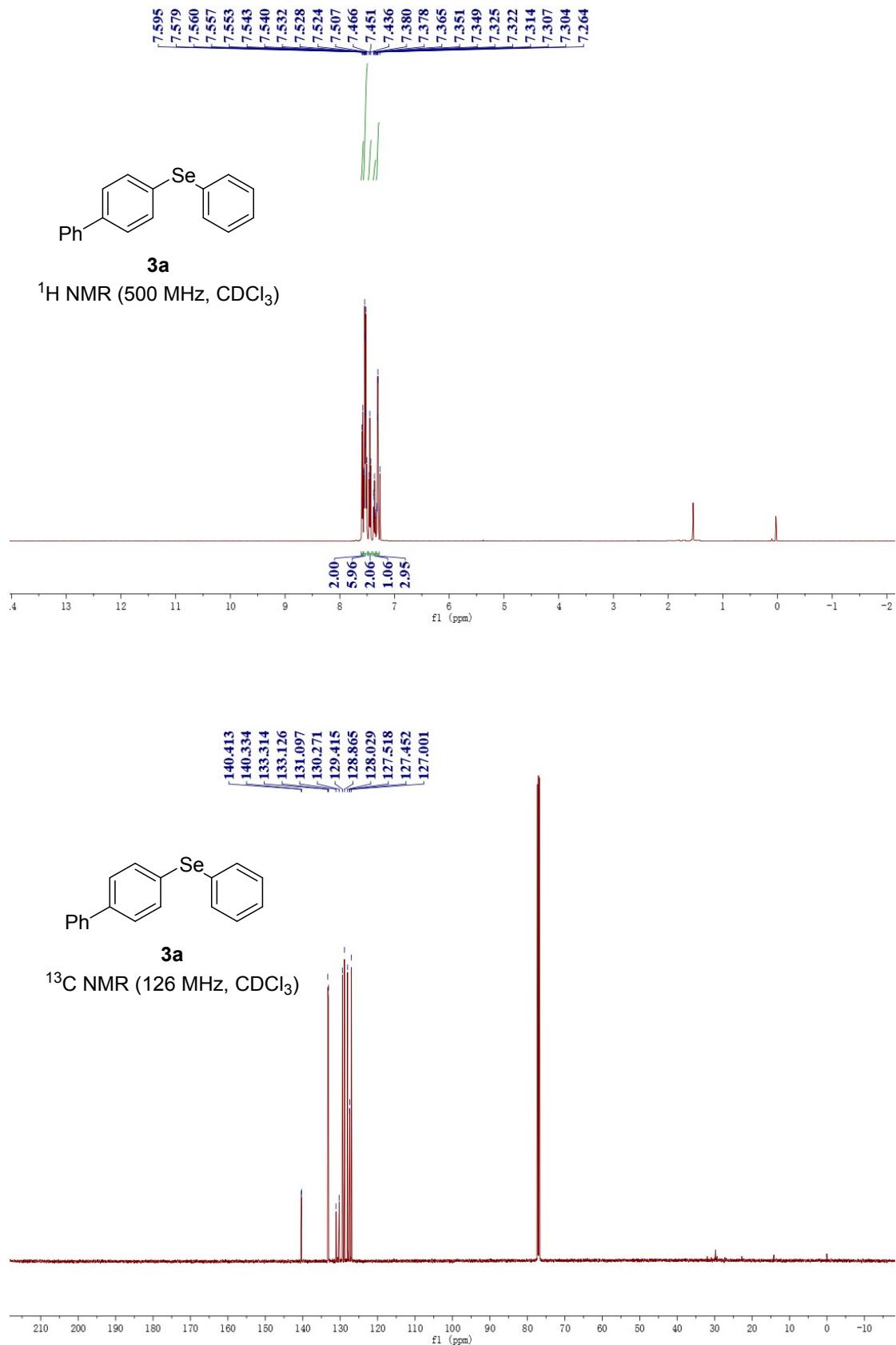


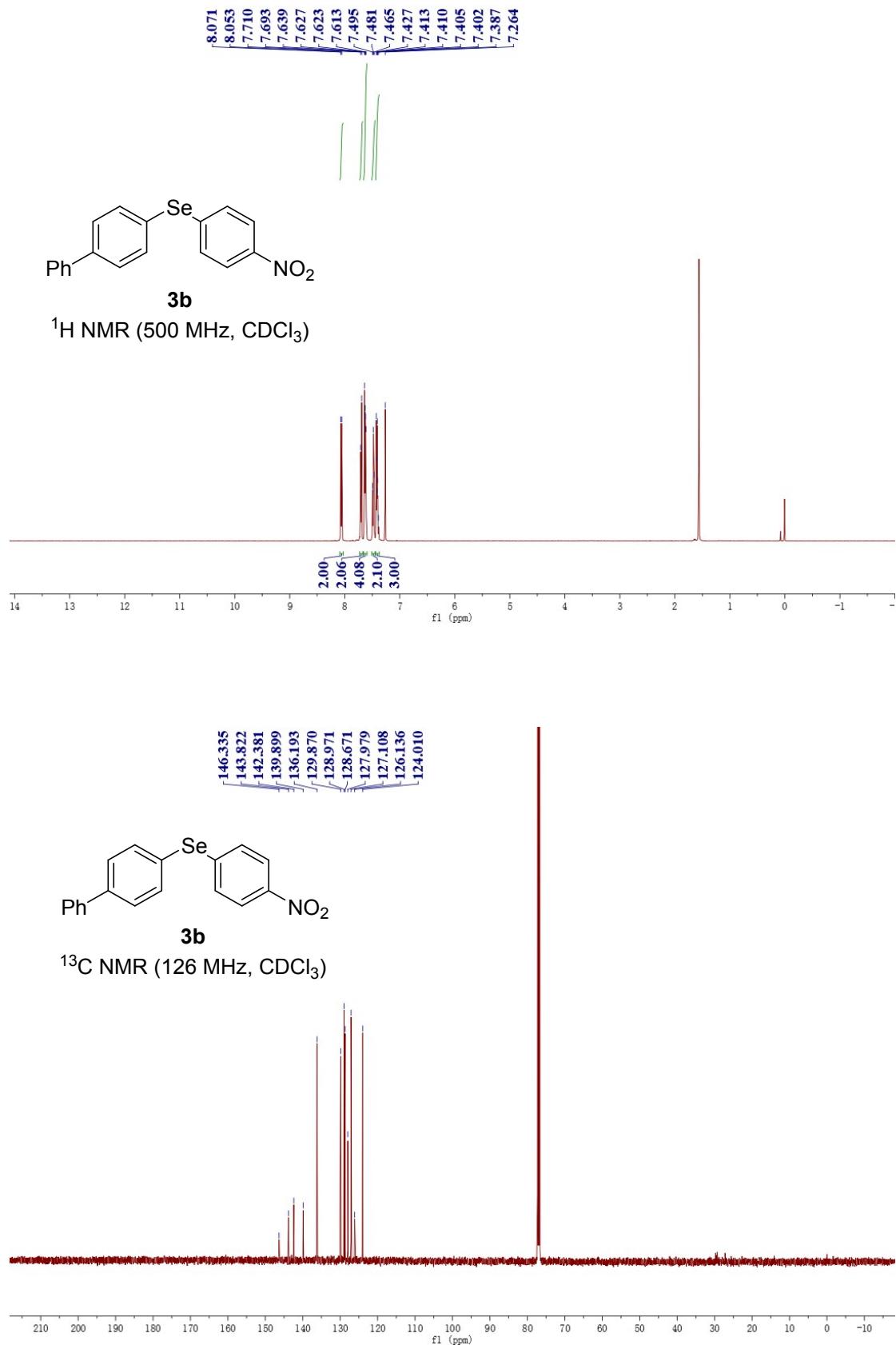


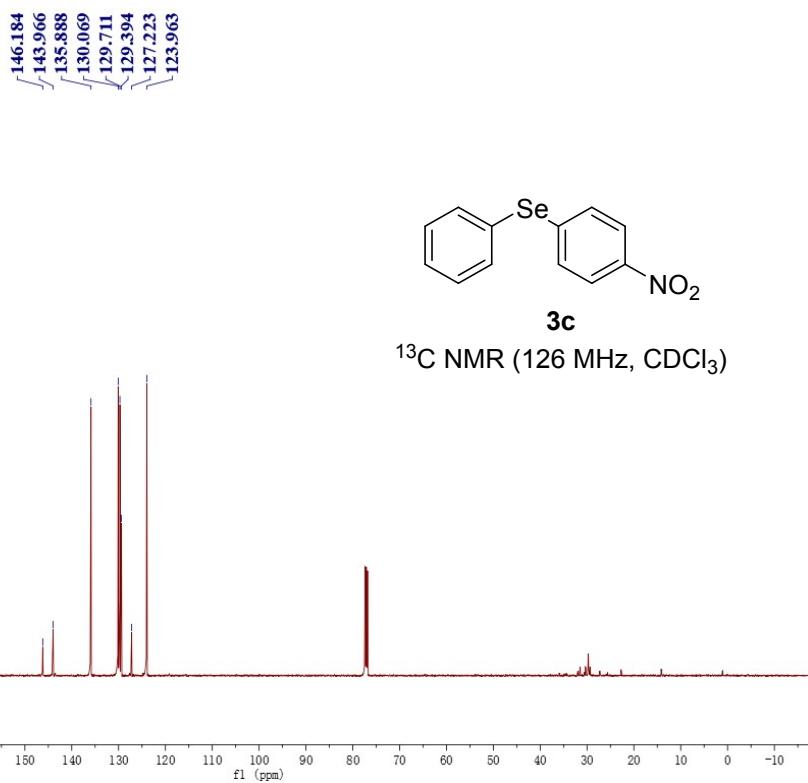
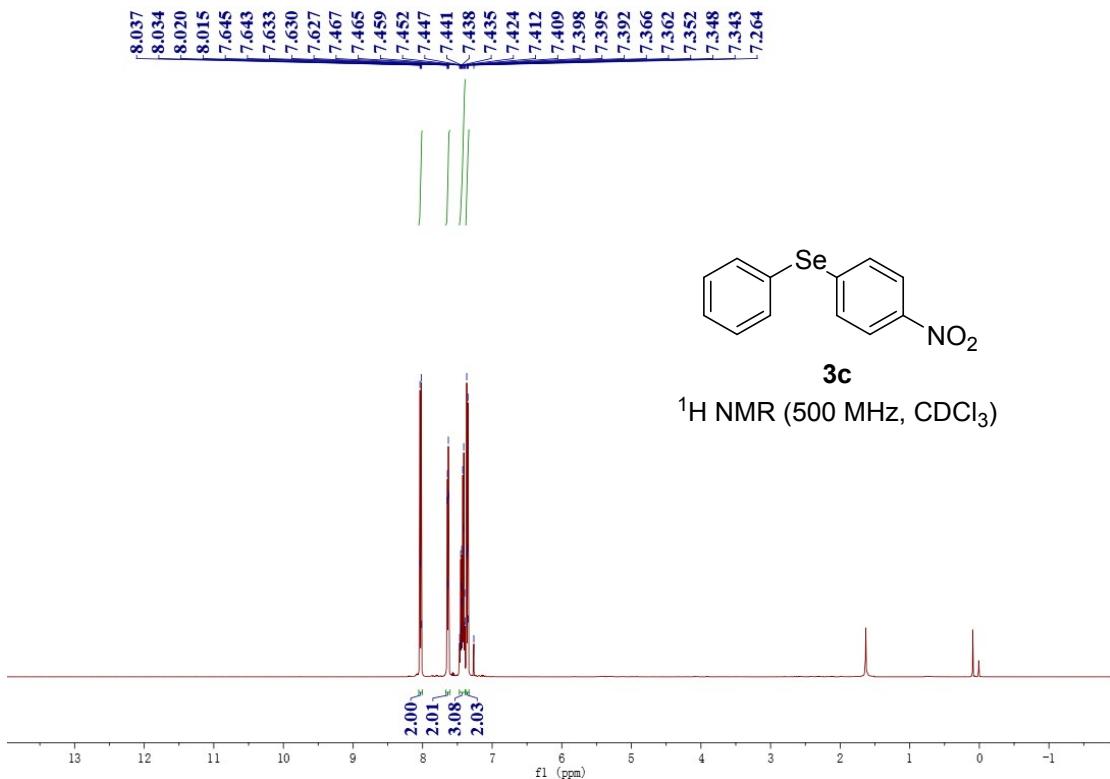


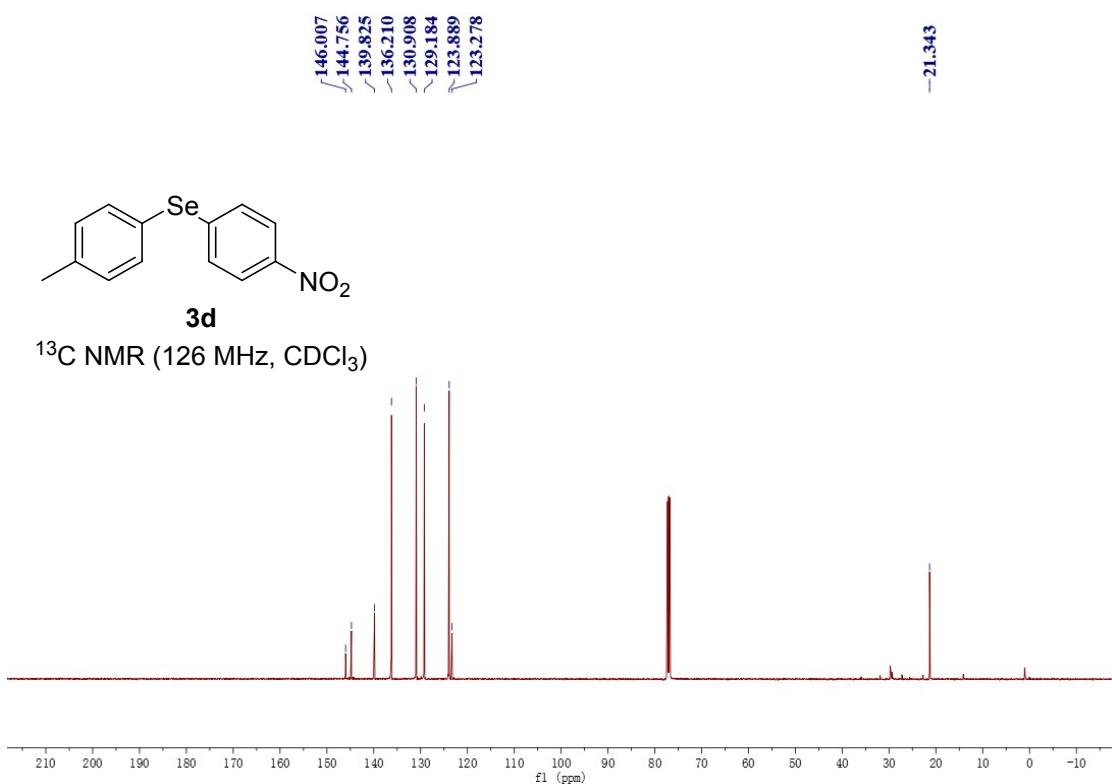
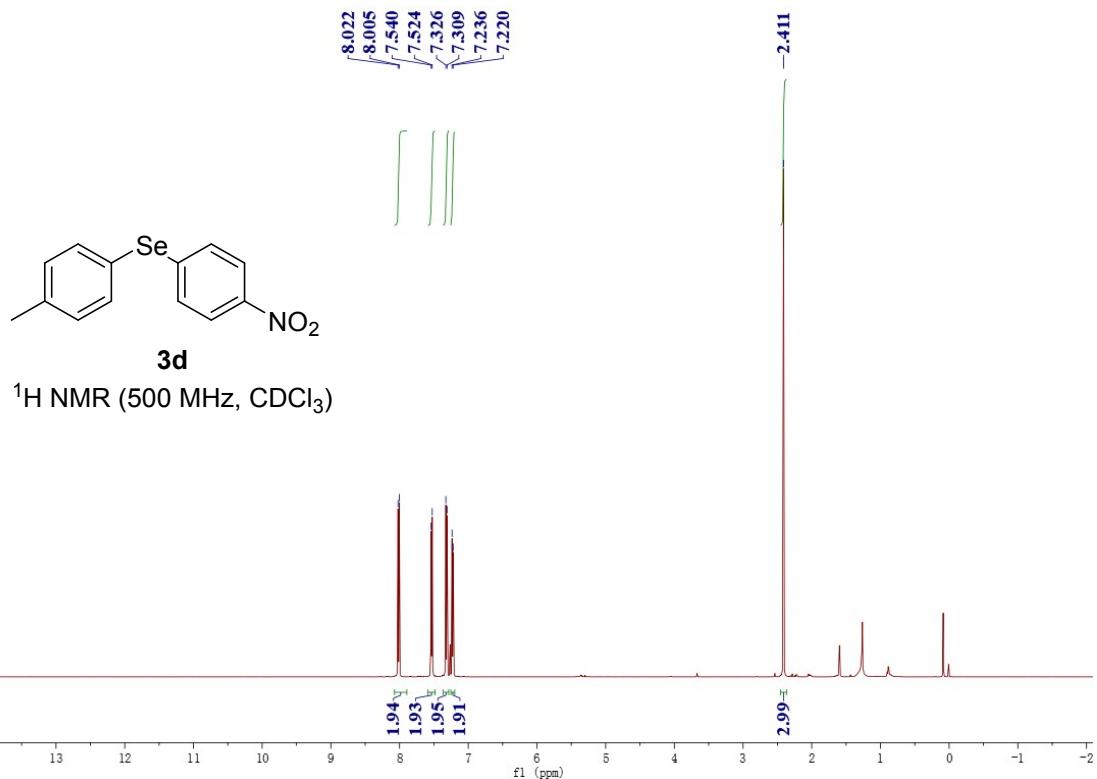


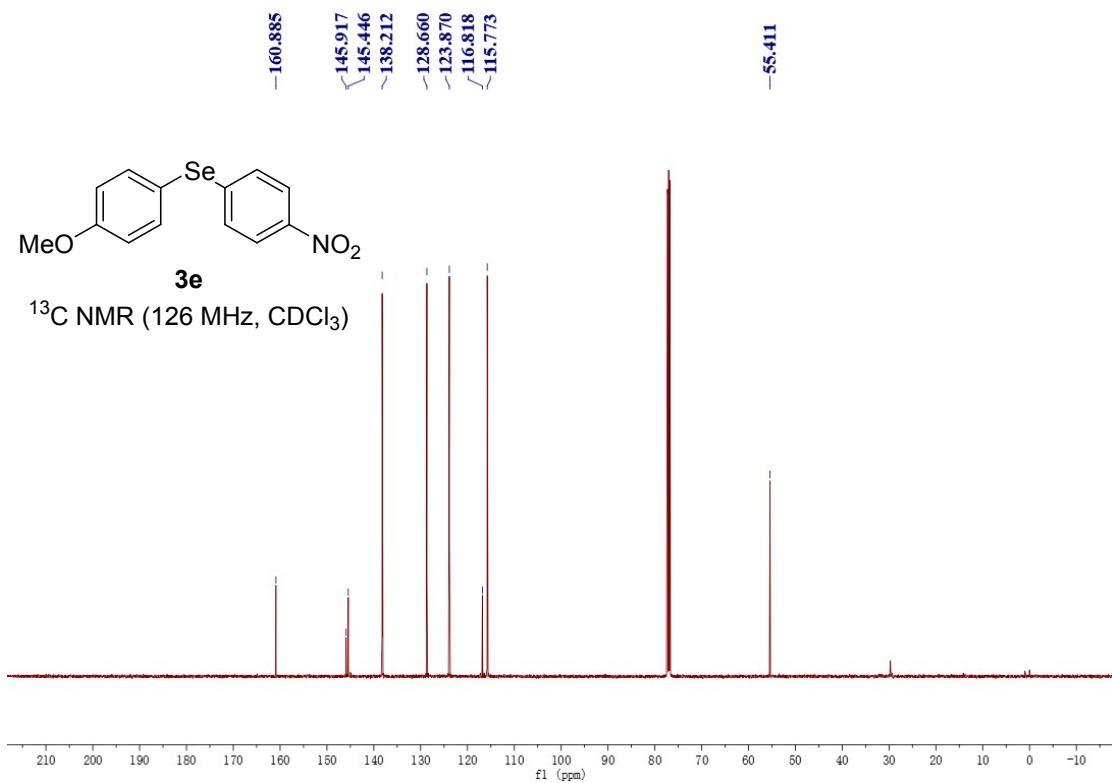
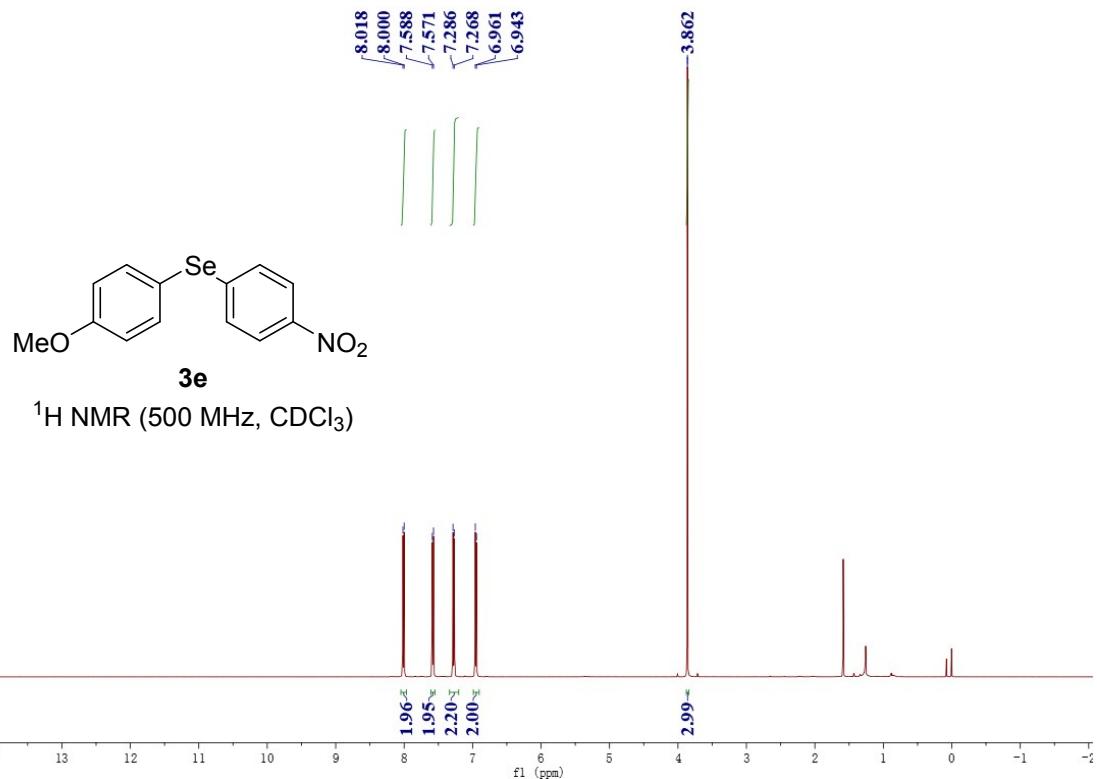


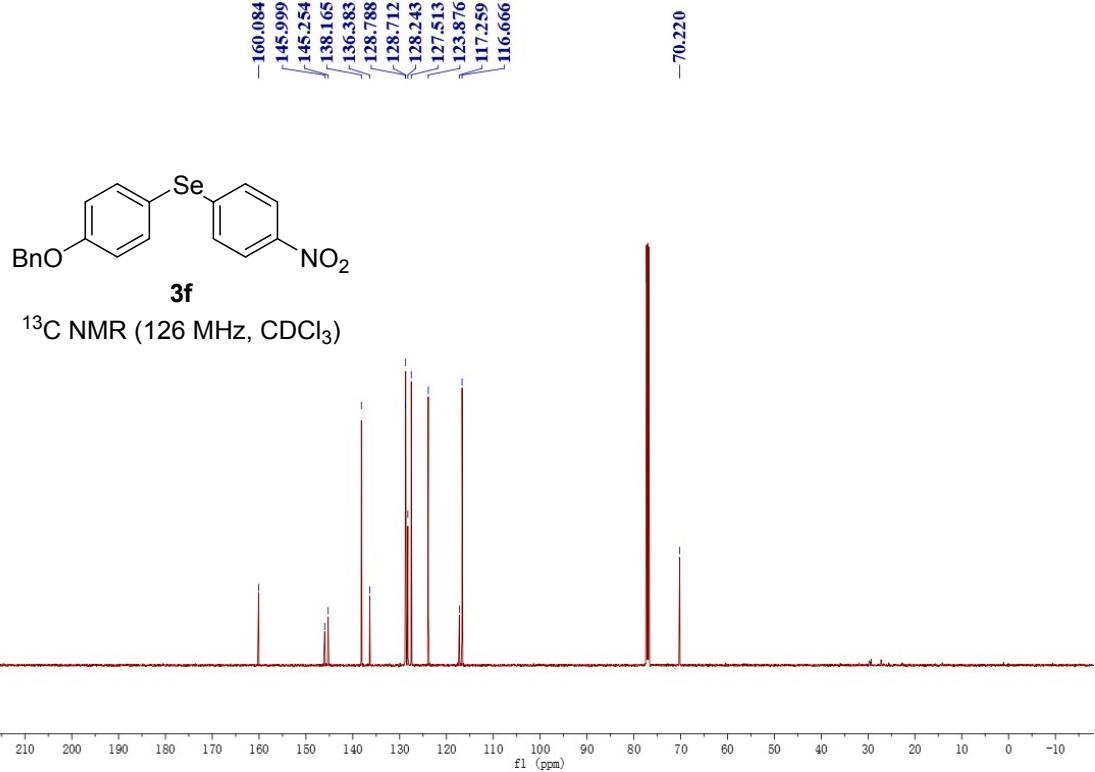
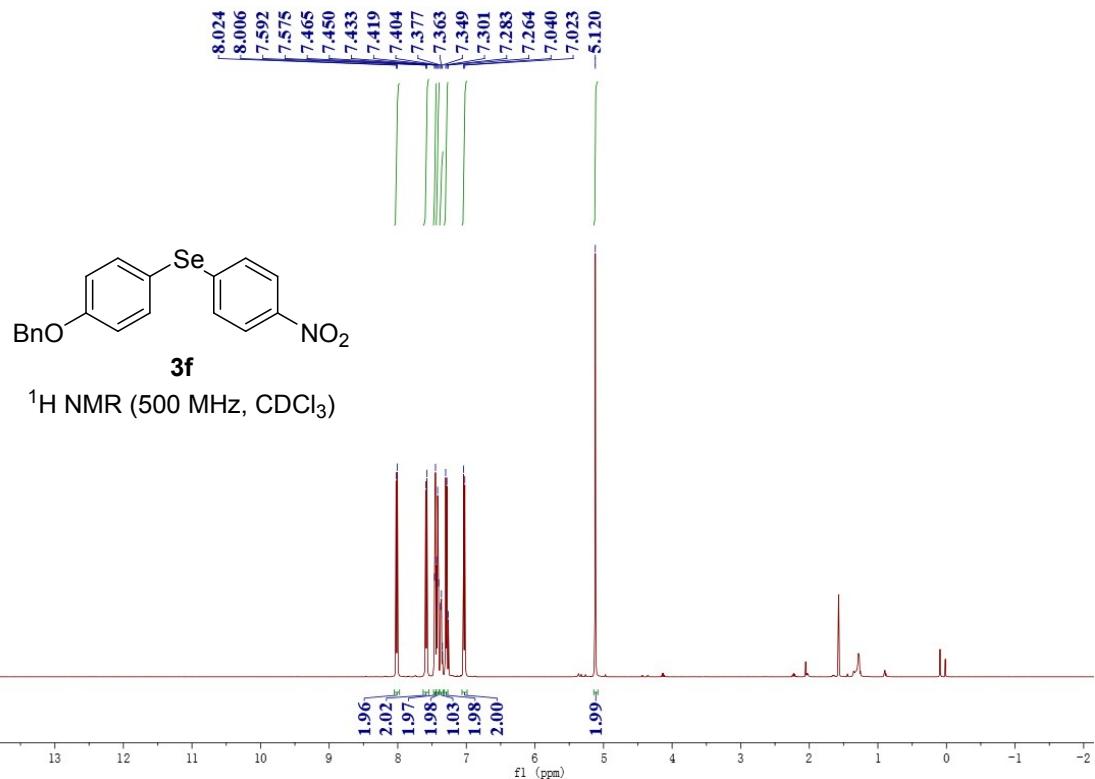


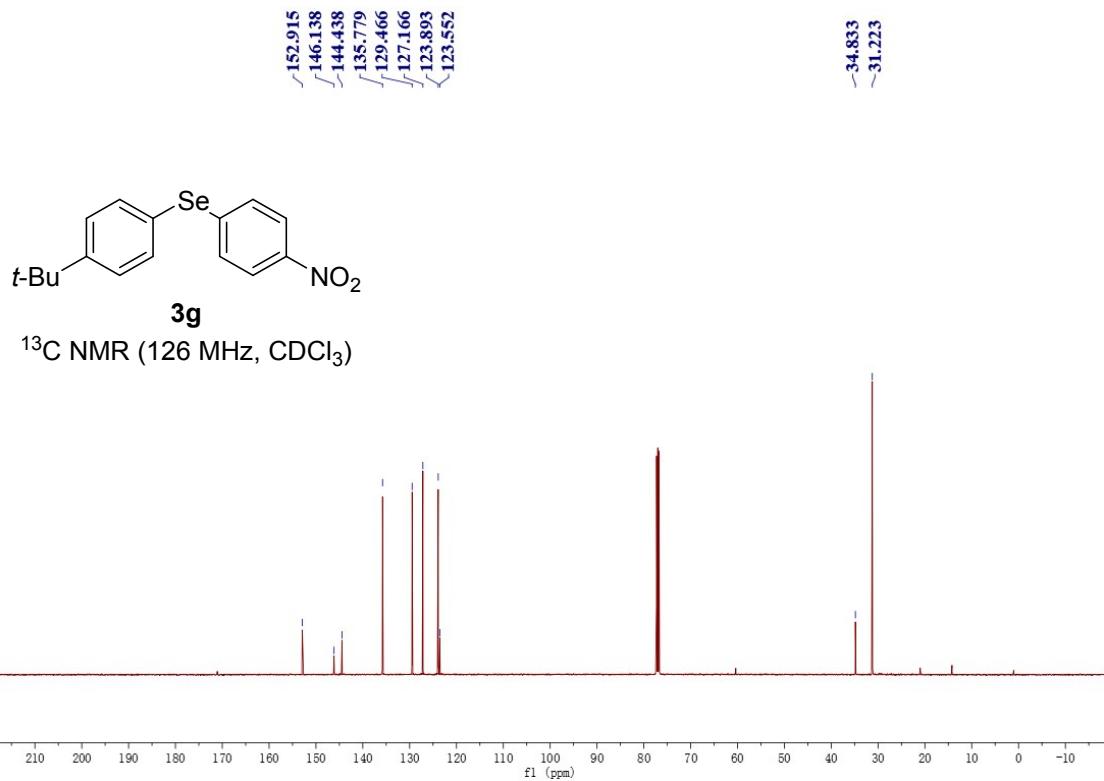
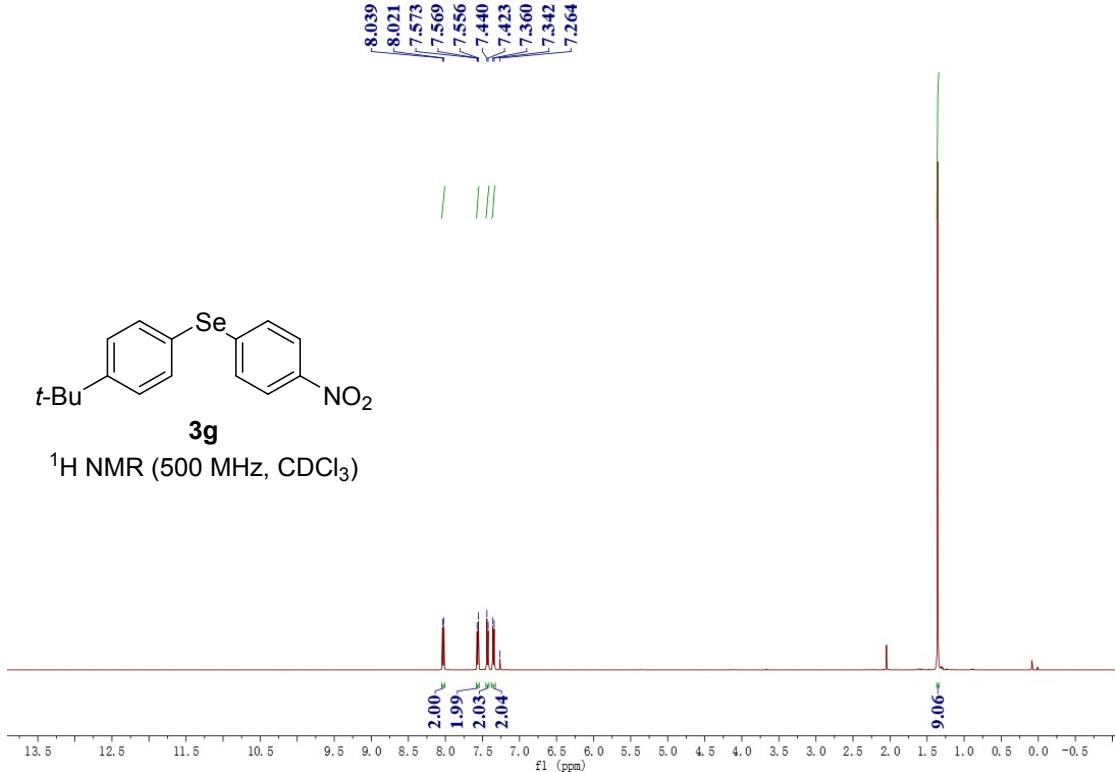


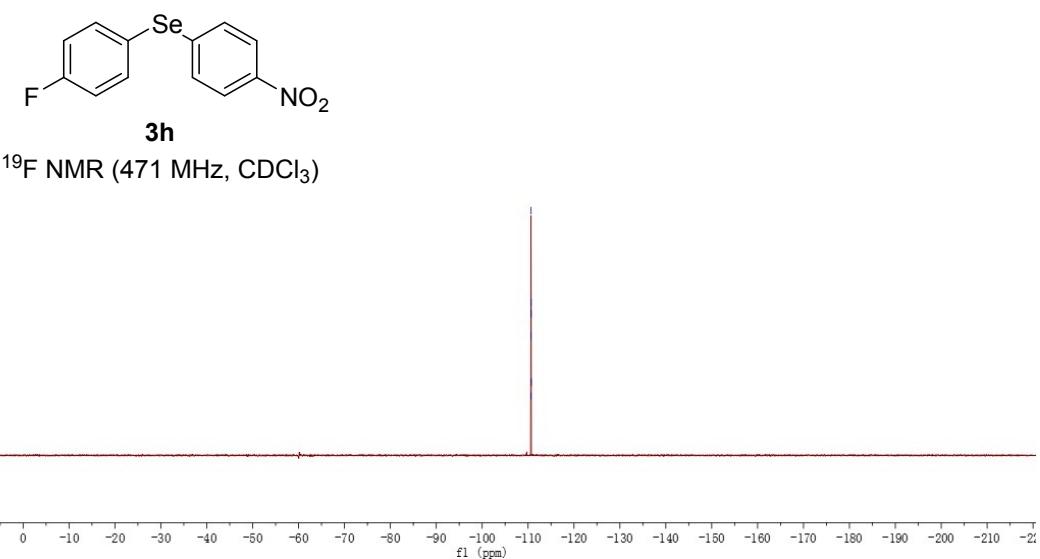
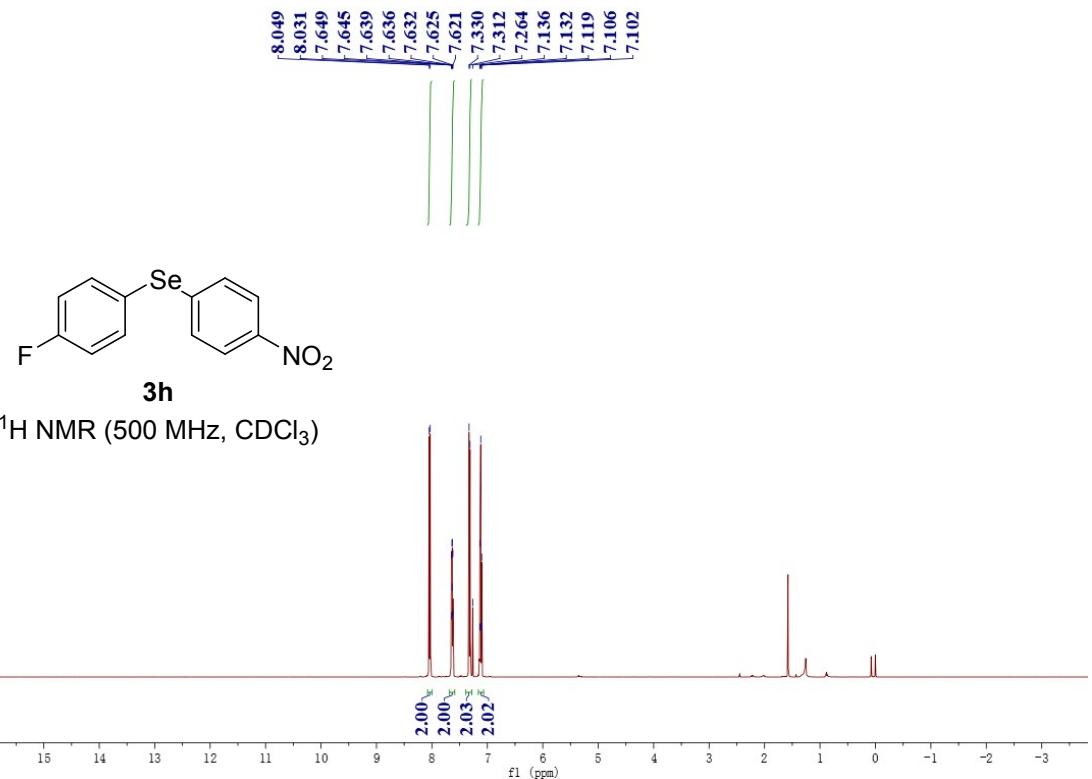


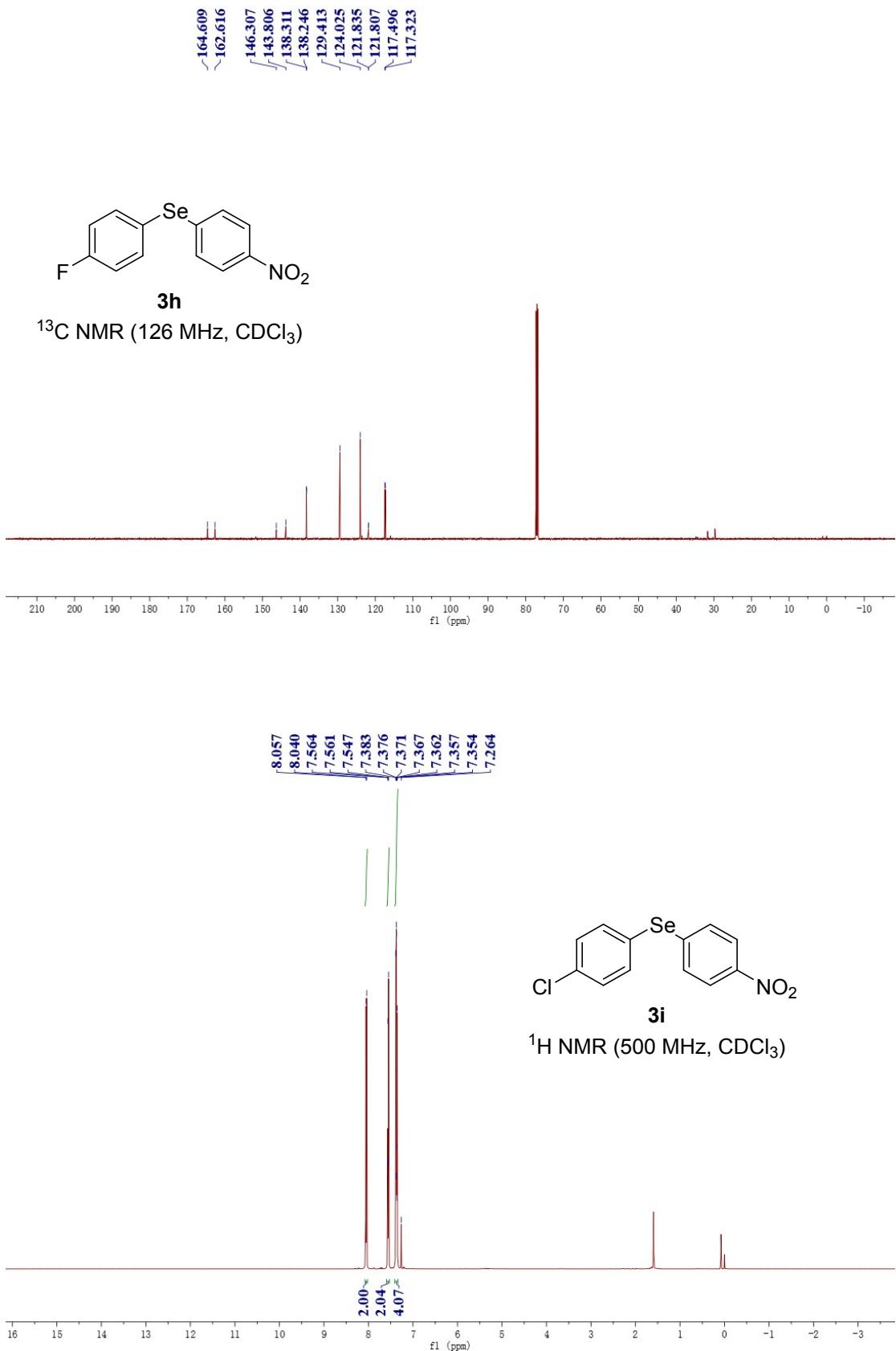




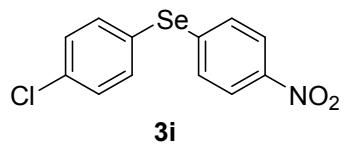




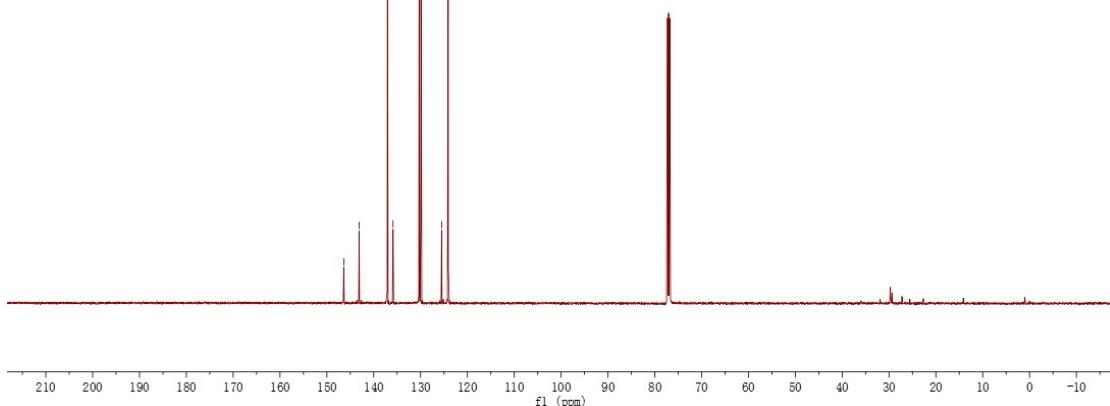




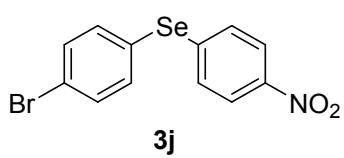
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143.097
137.057
135.876
130.292
129.933
125.507
124.091



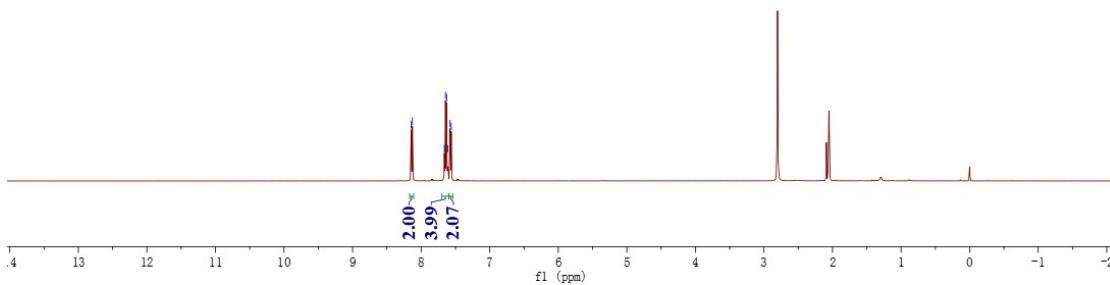
^{13}C NMR (126 MHz, CDCl_3)

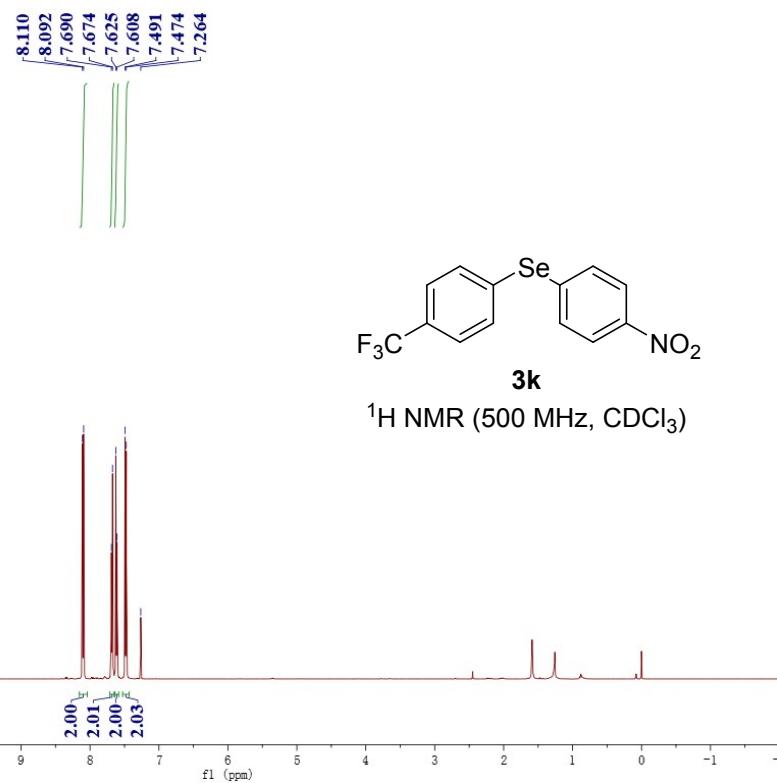
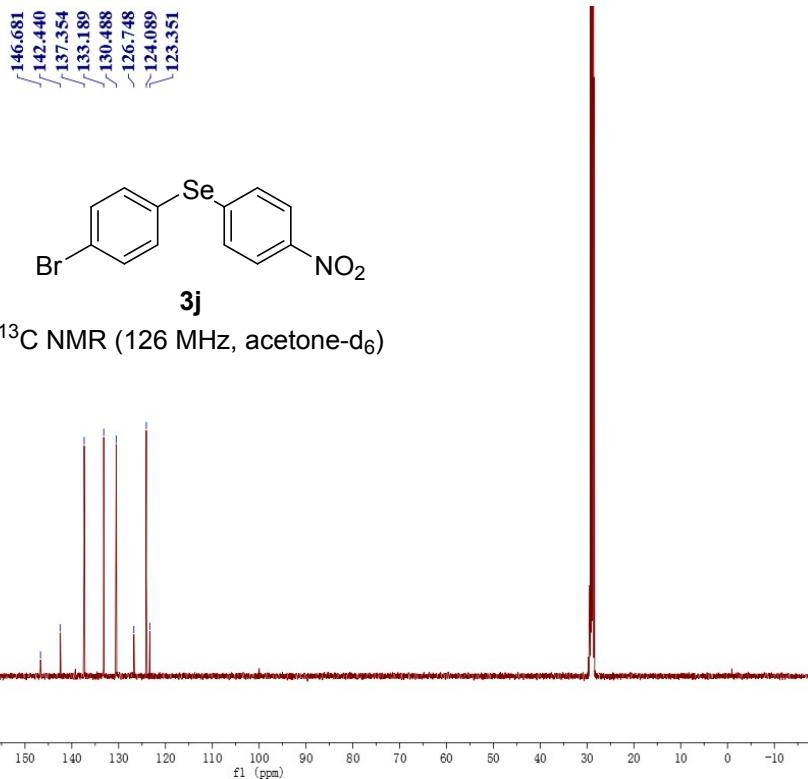


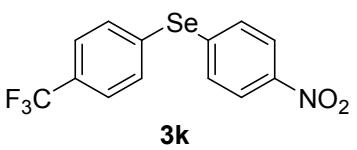
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8.127
7.662
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7.629
7.612
7.578
7.560



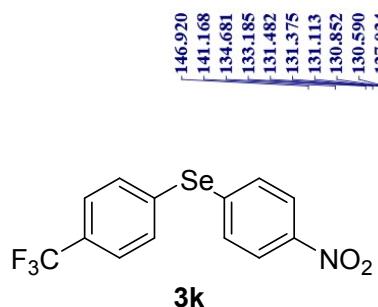
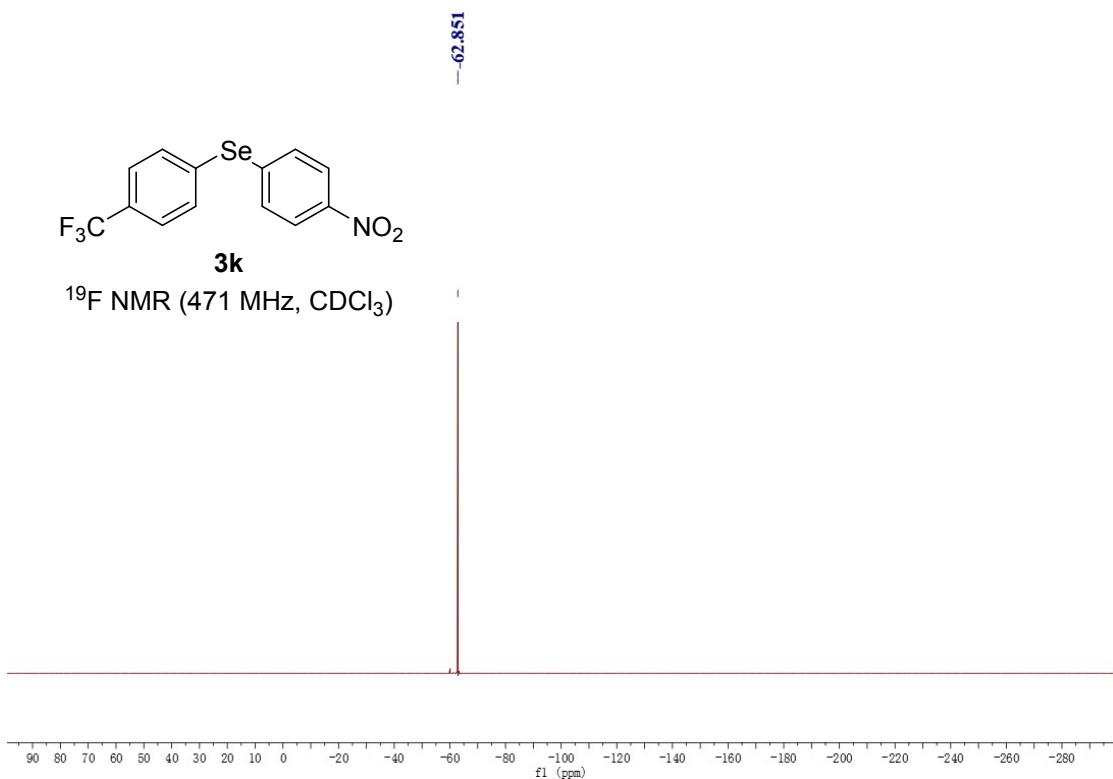
^1H NMR (500 MHz, acetone- d_6)



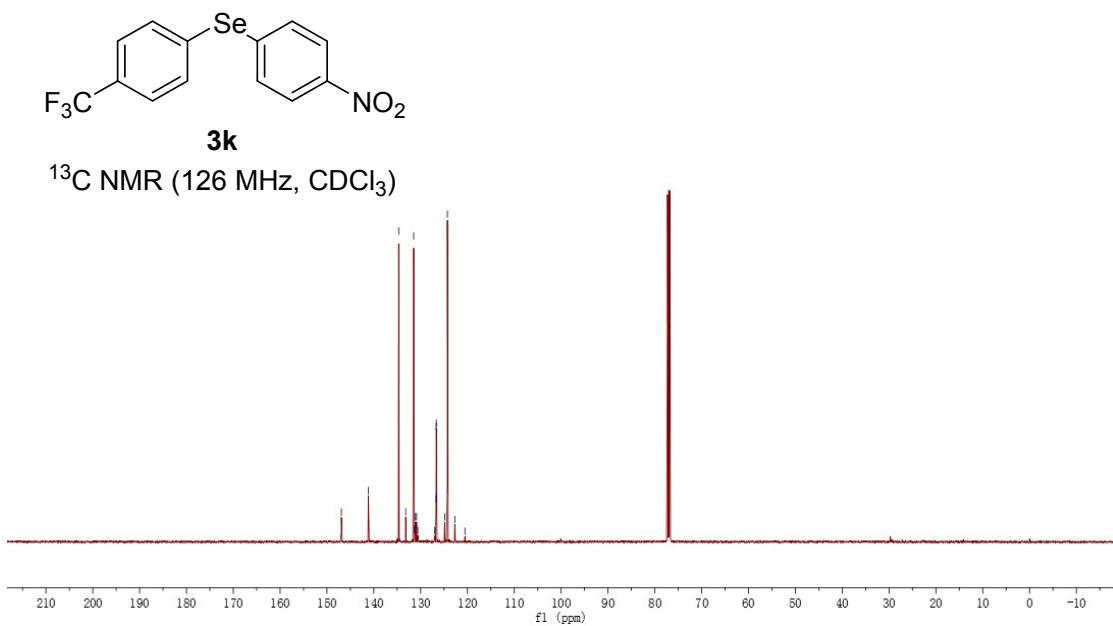


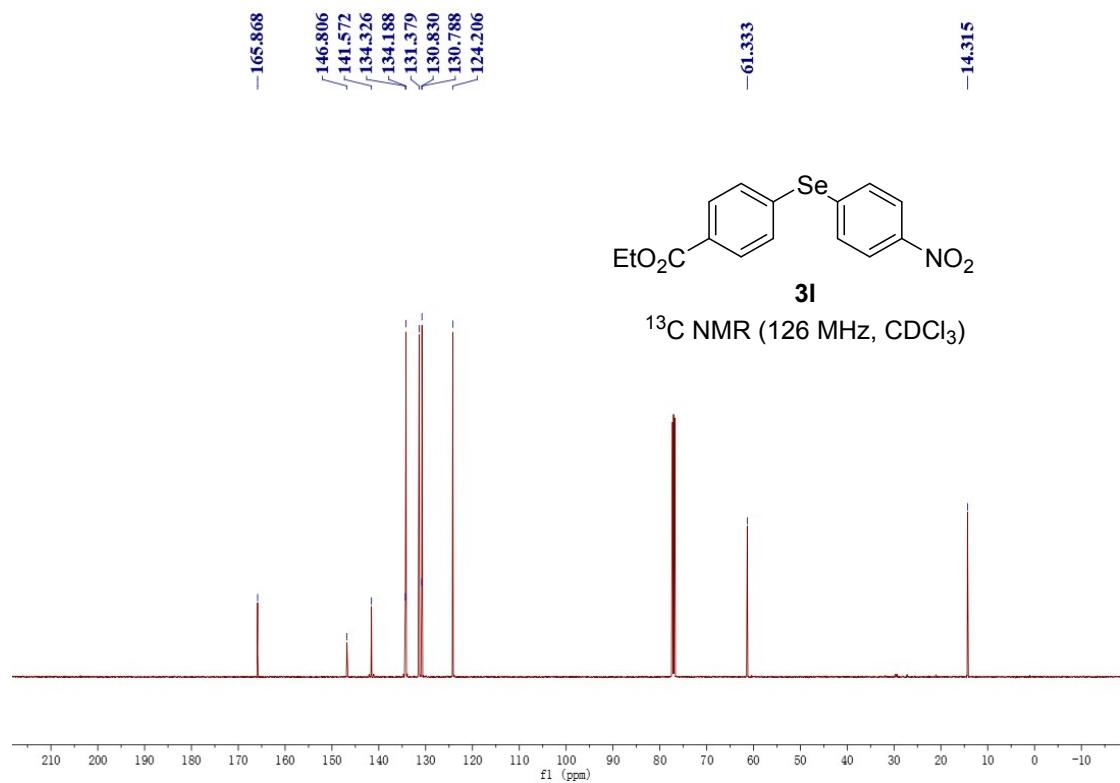
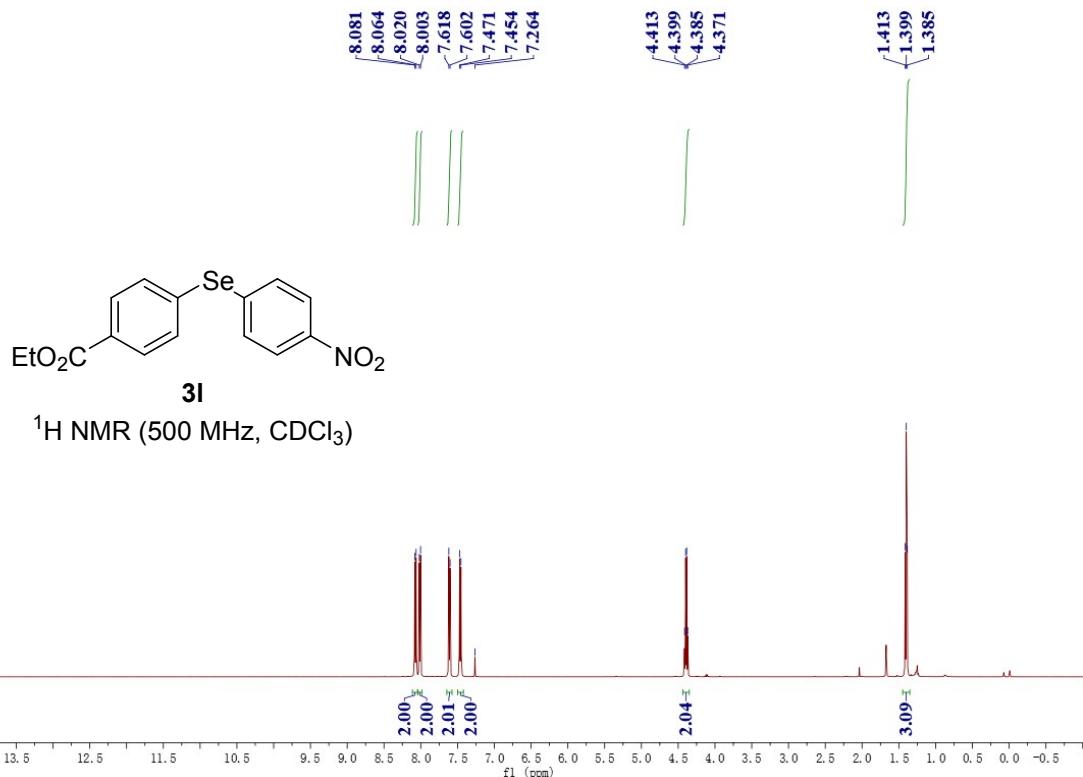


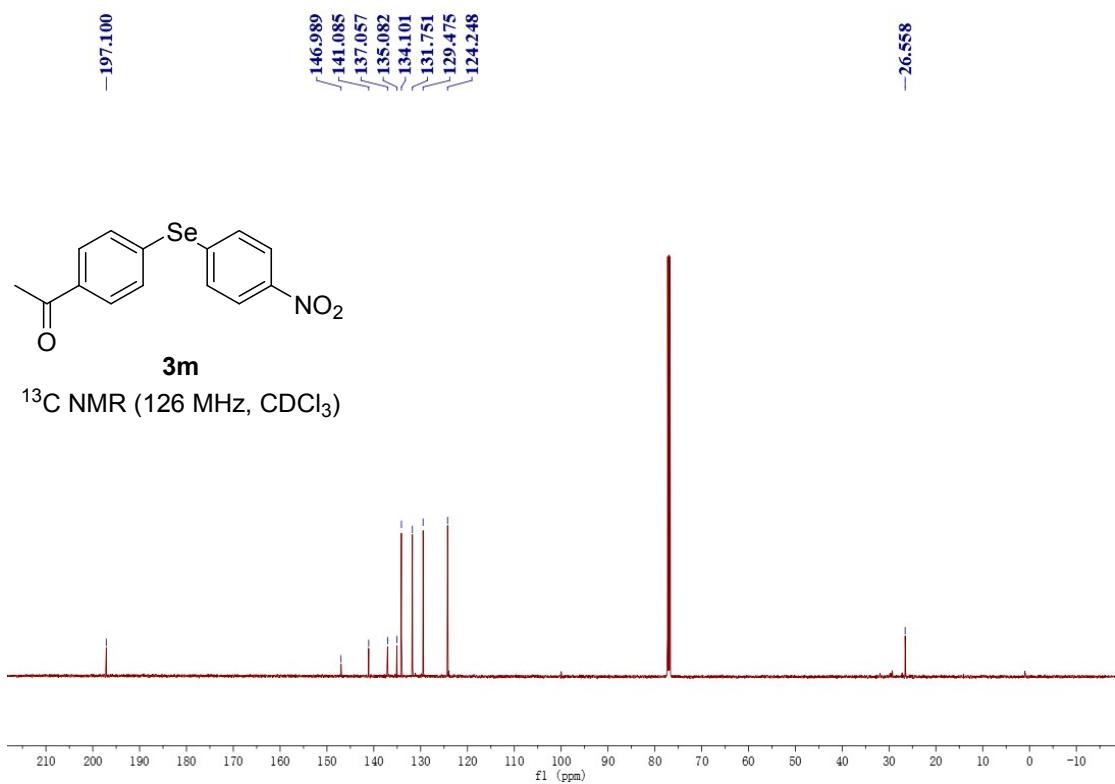
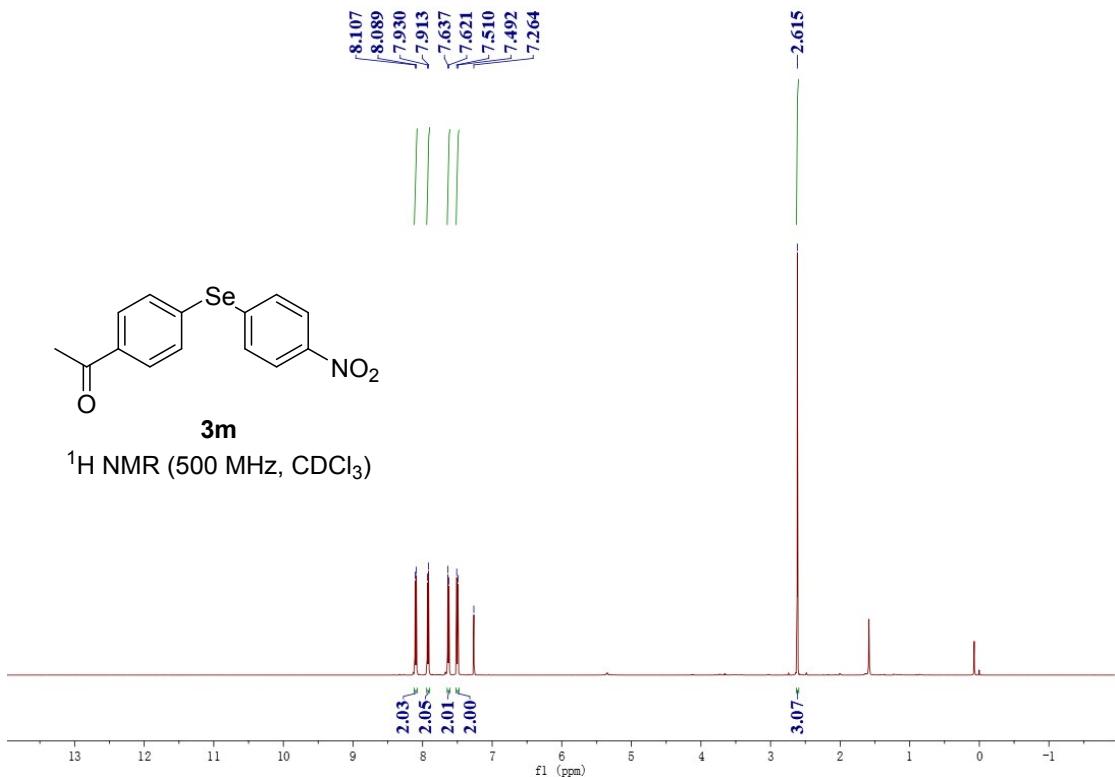
¹⁹F NMR (471 MHz, CDCl₃)

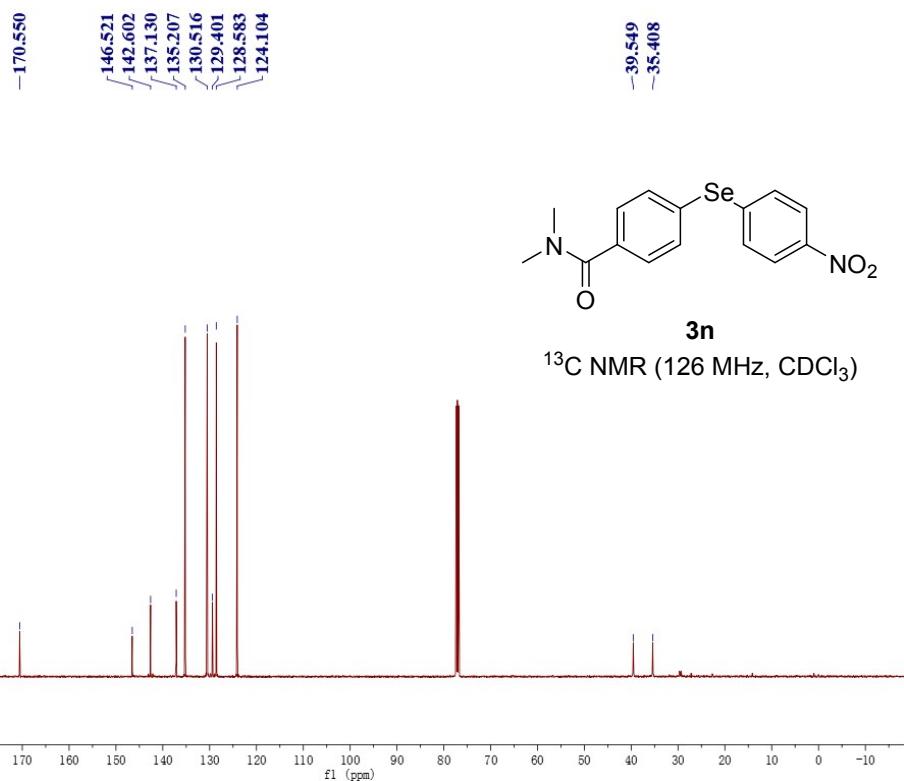
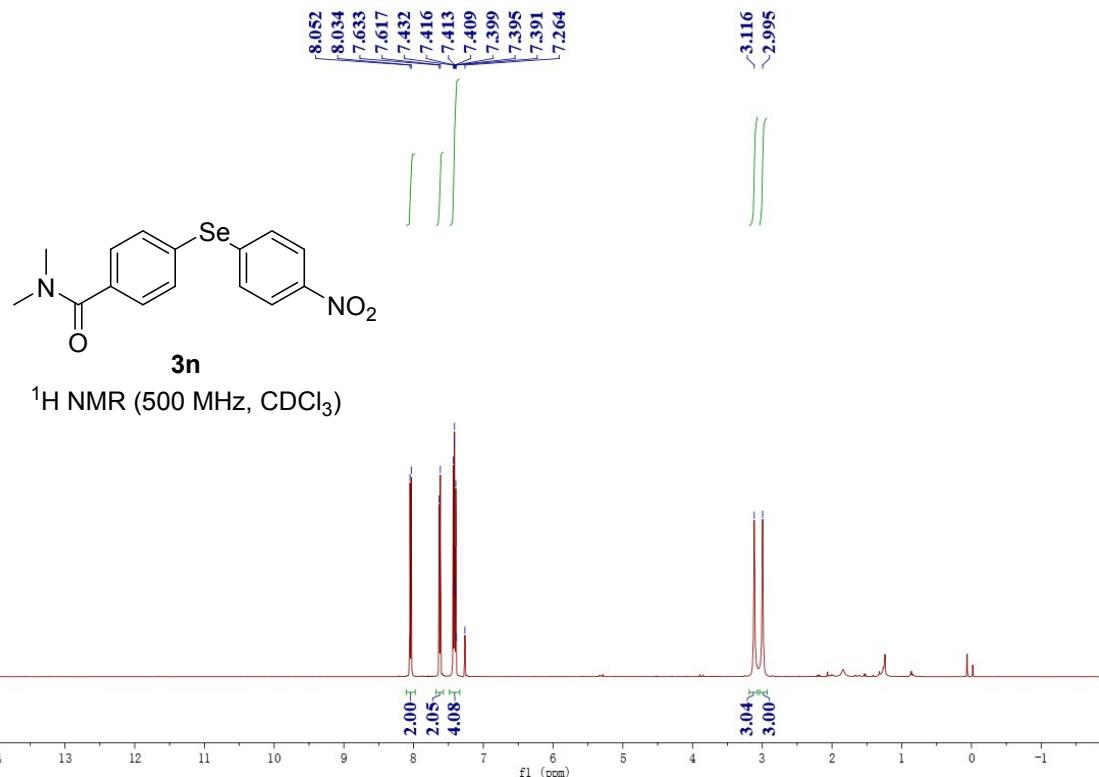


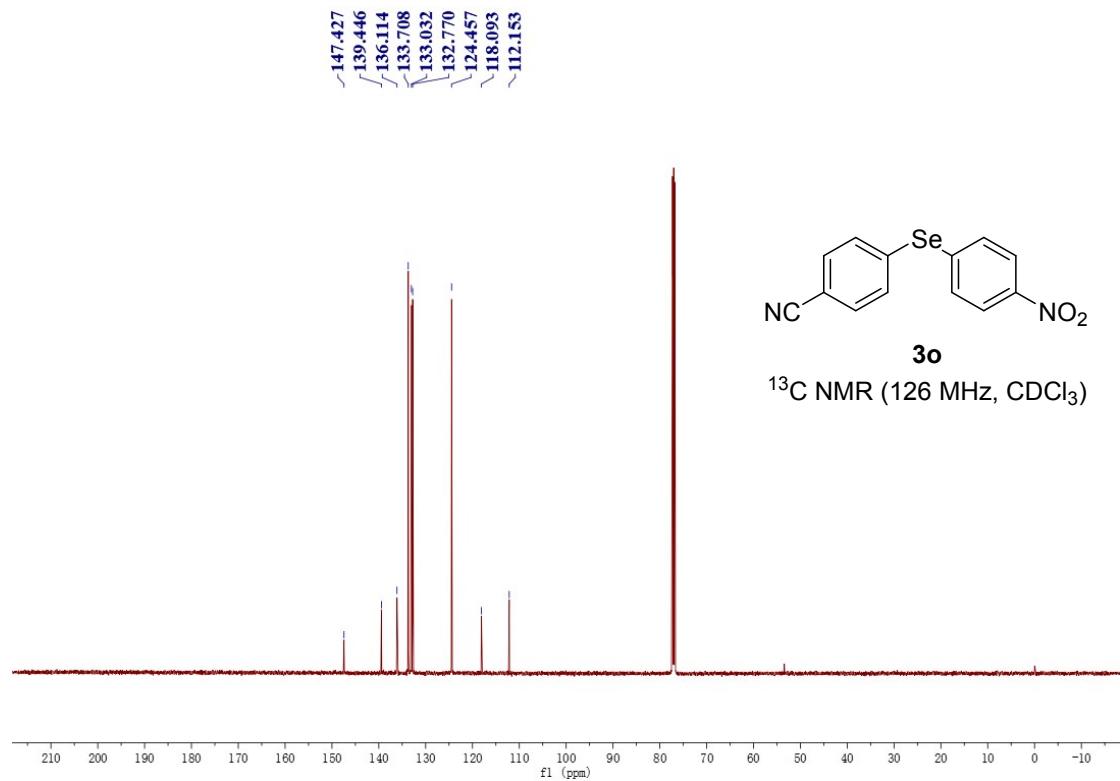
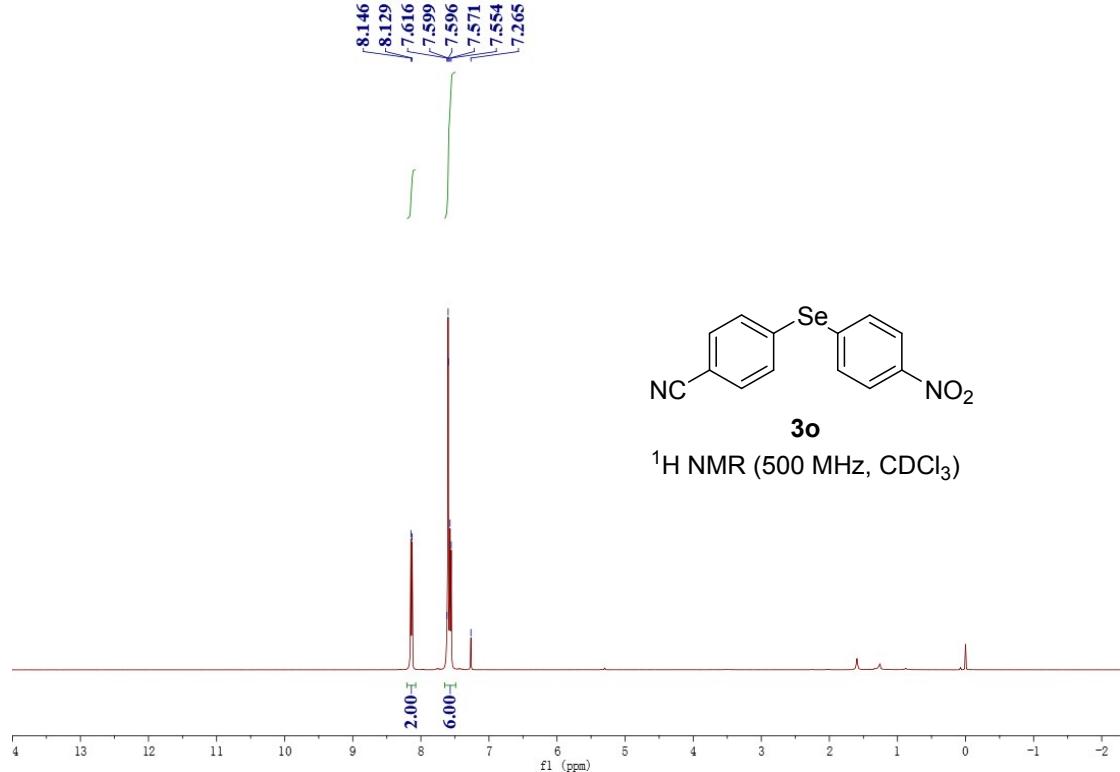
¹³C NMR (126 MHz, CDCl₃)

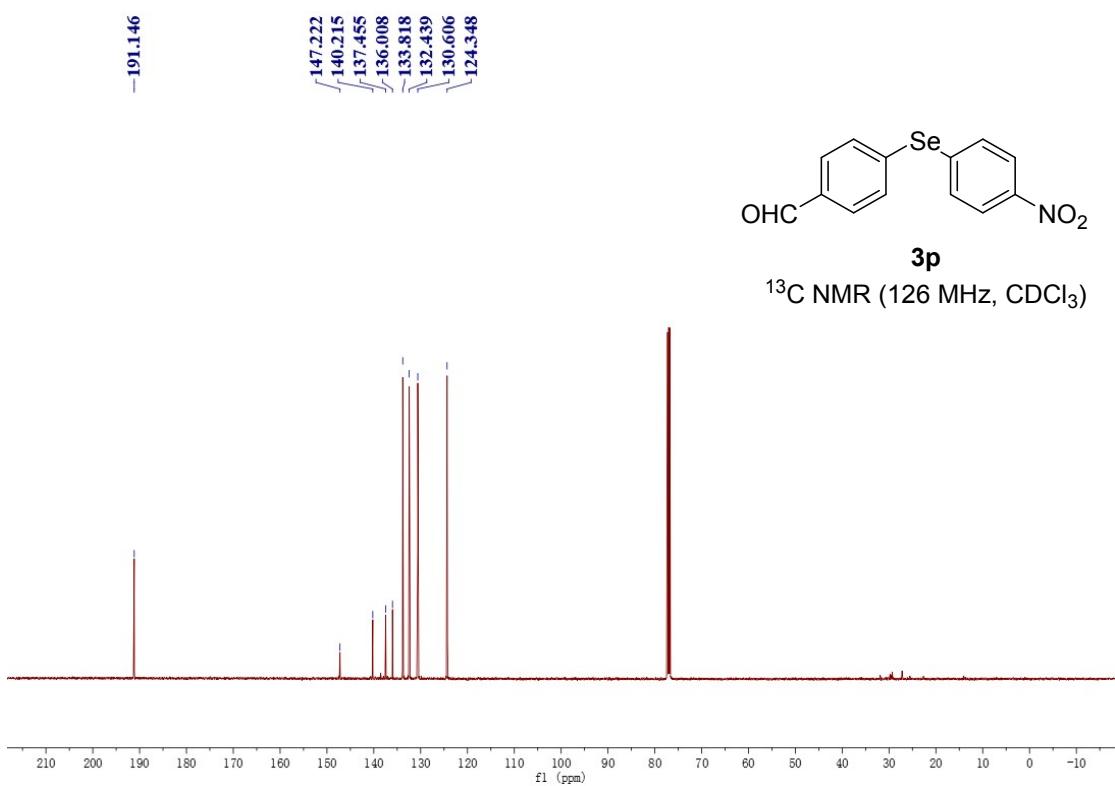
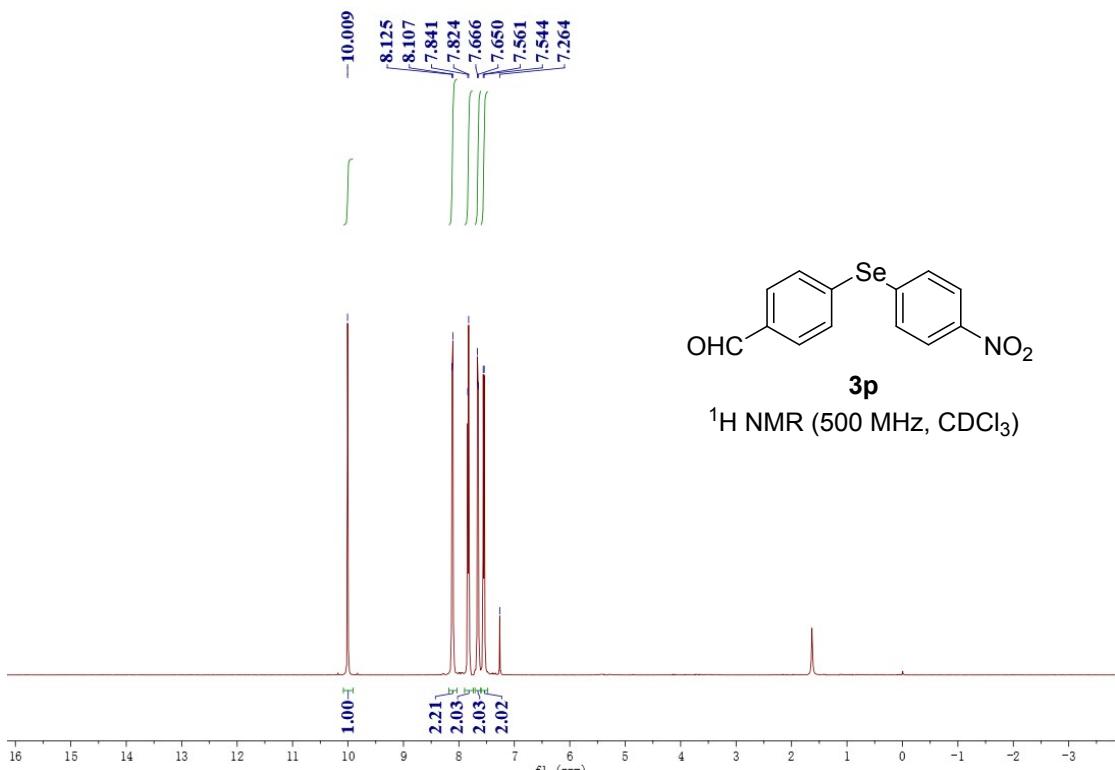


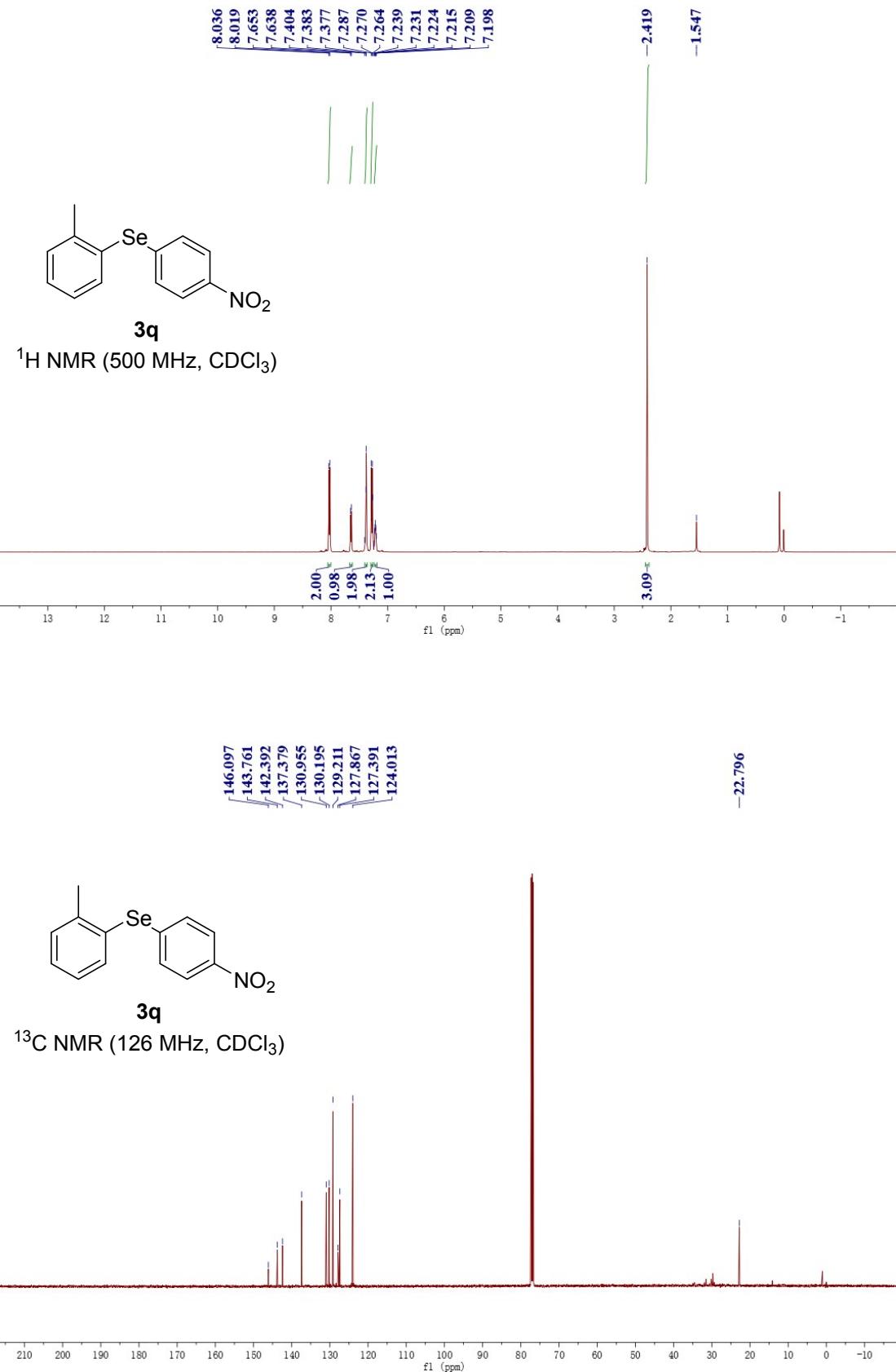


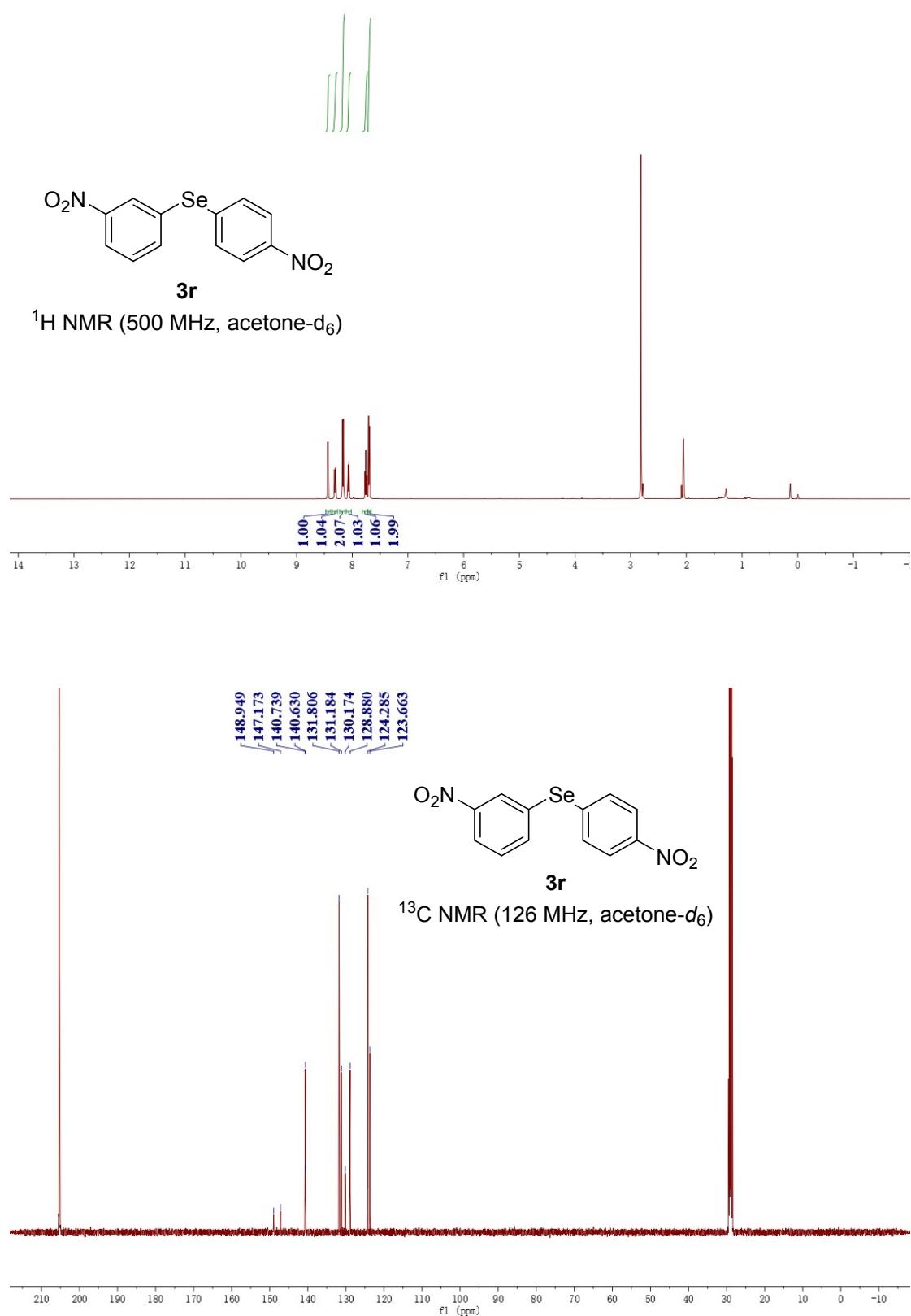


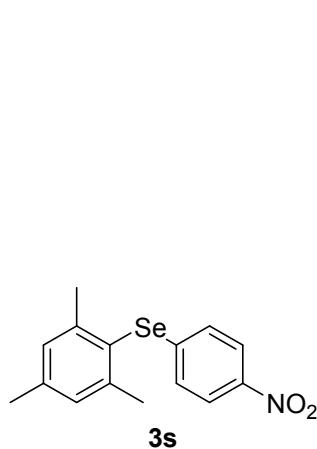




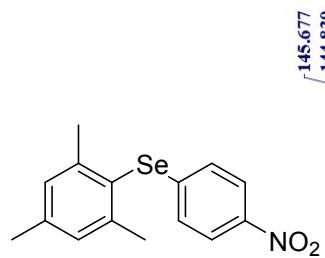
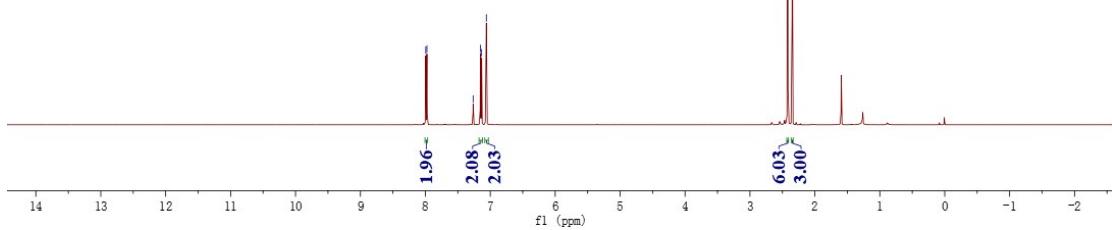




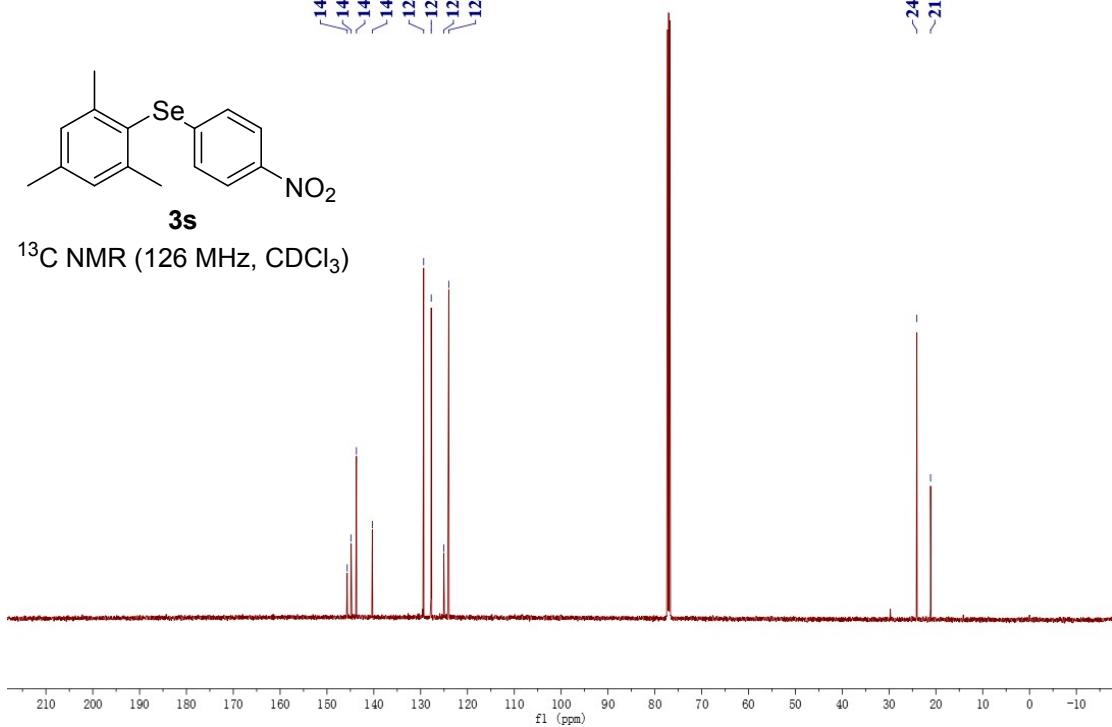


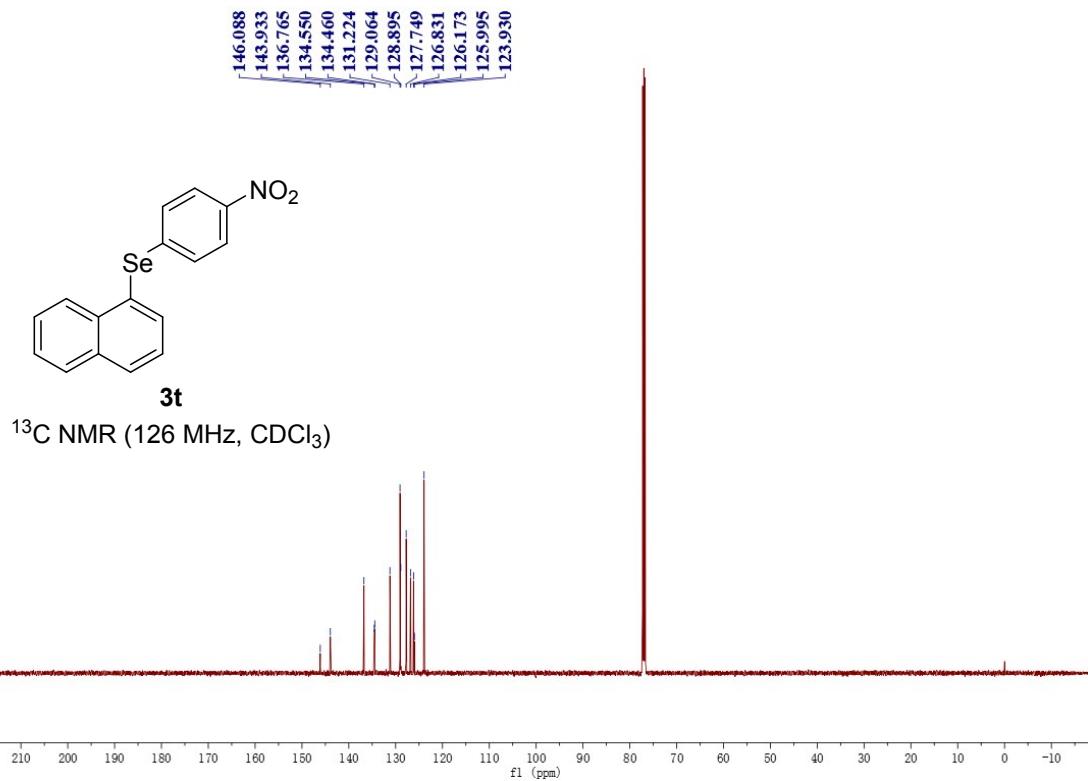
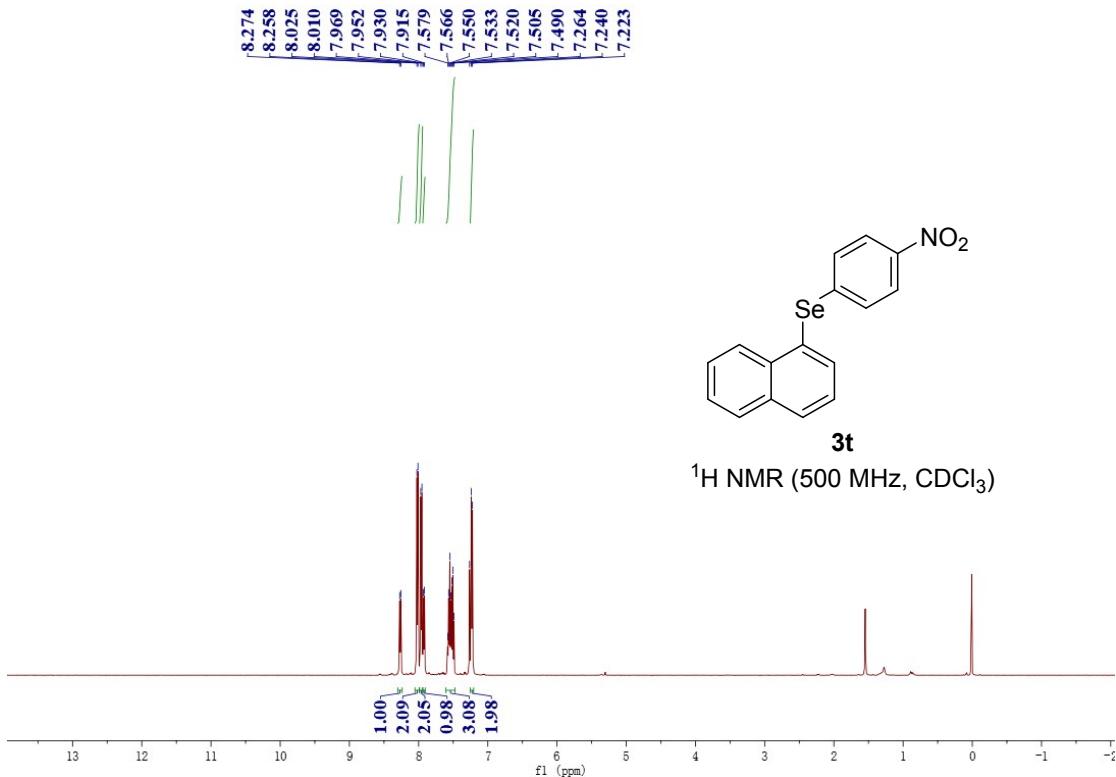


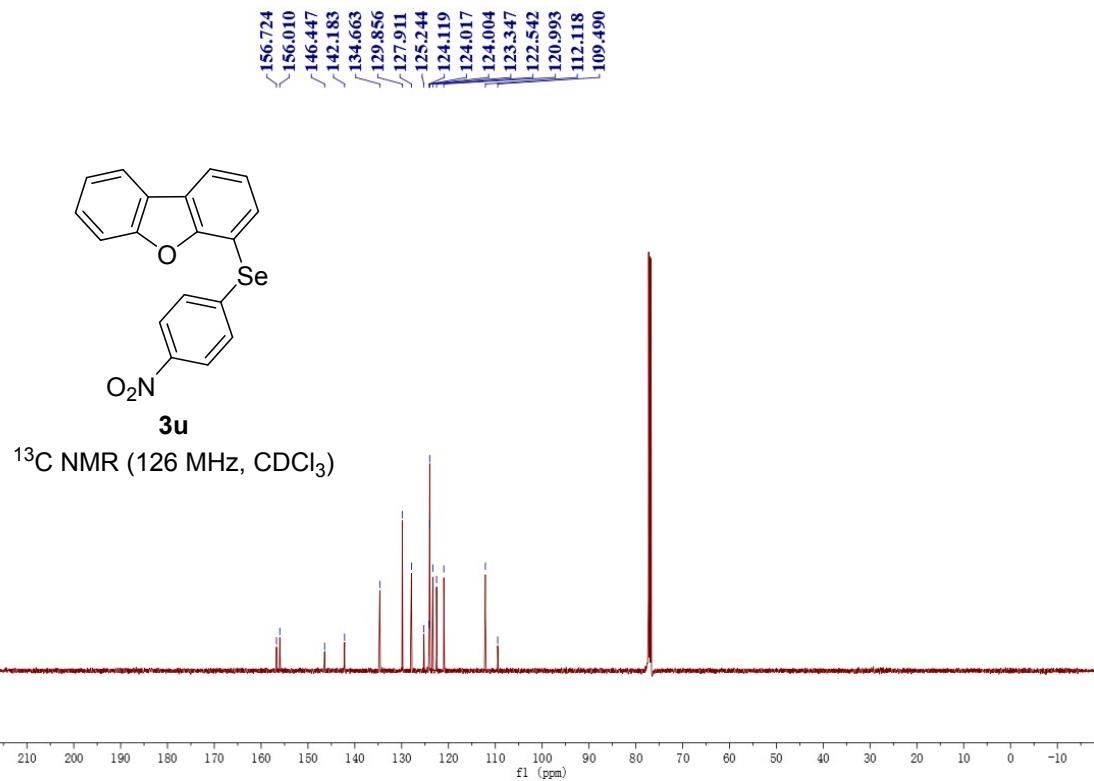
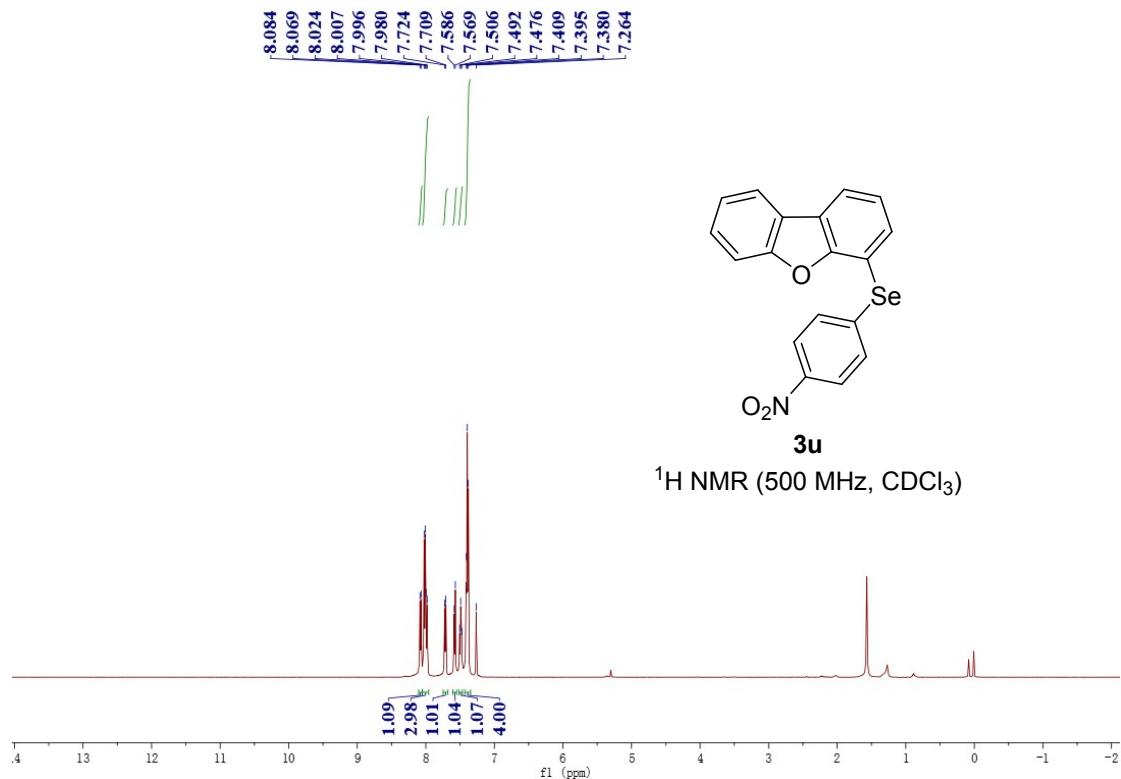
¹H NMR (500 MHz, CDCl₃)

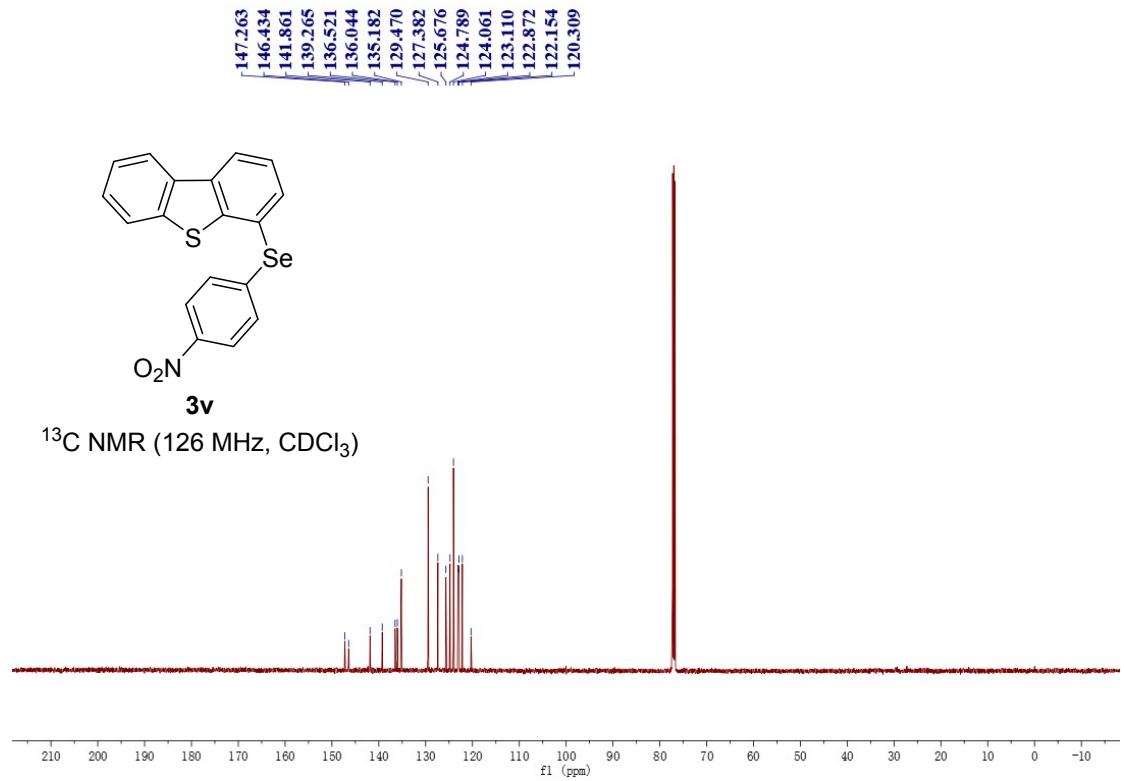
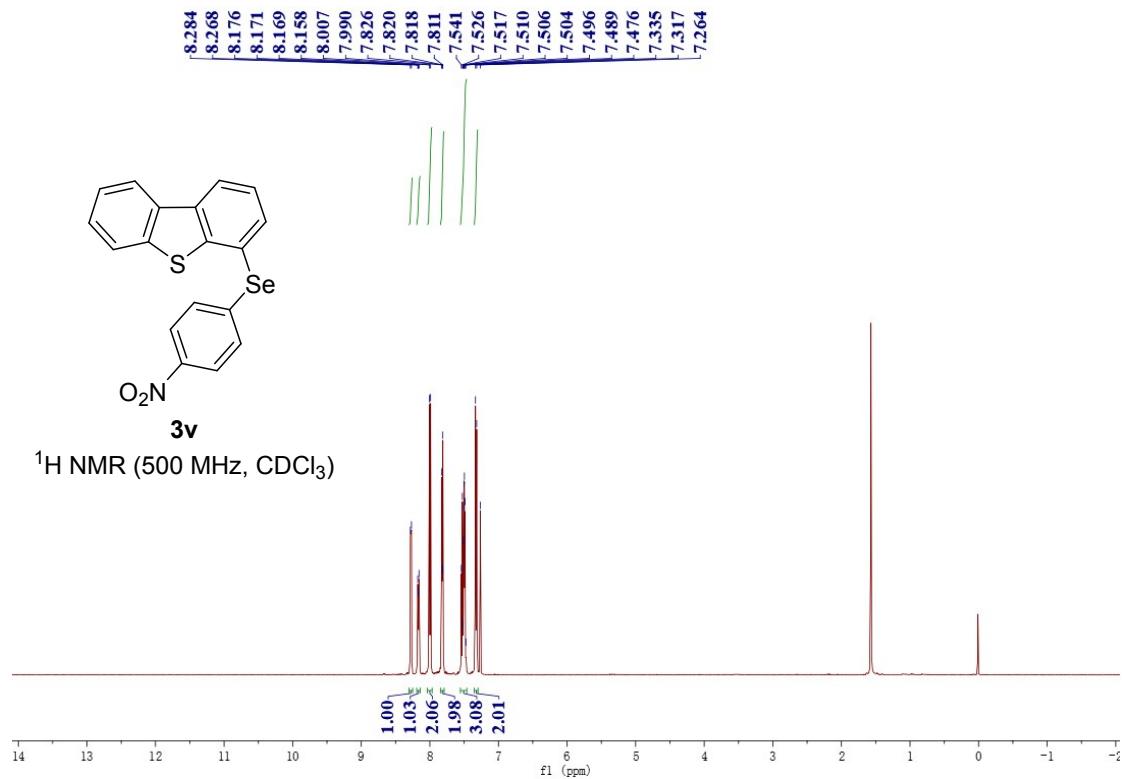


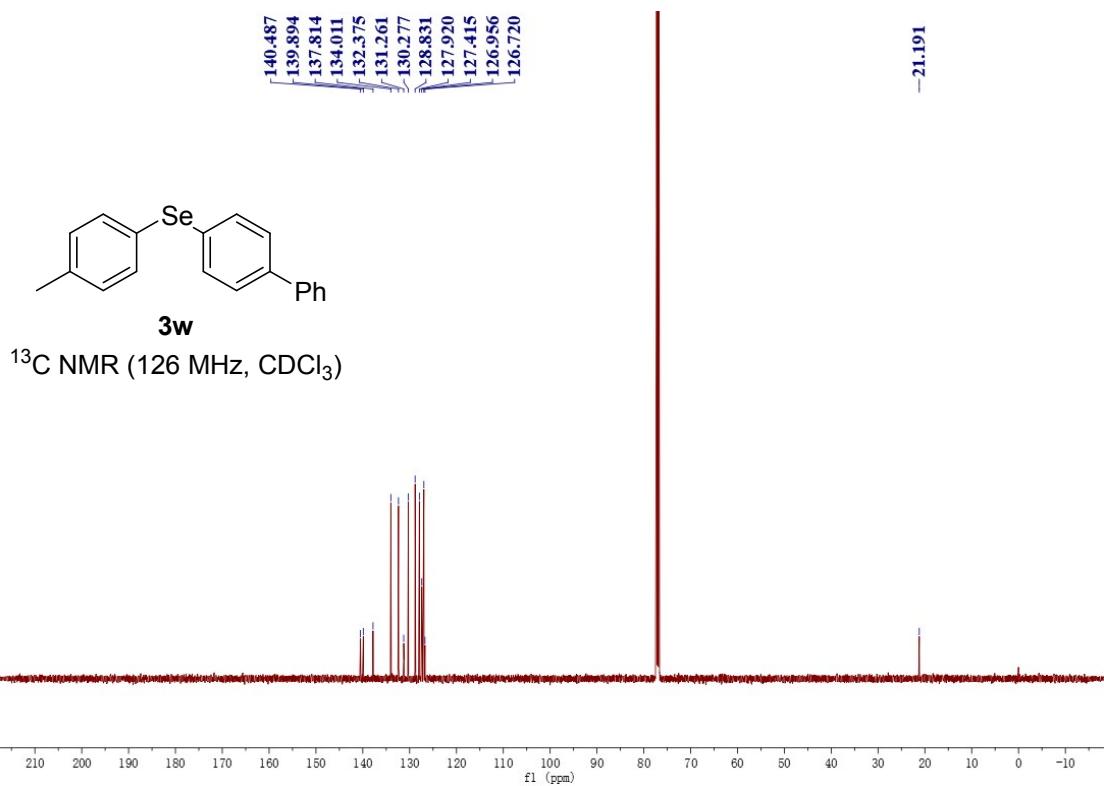
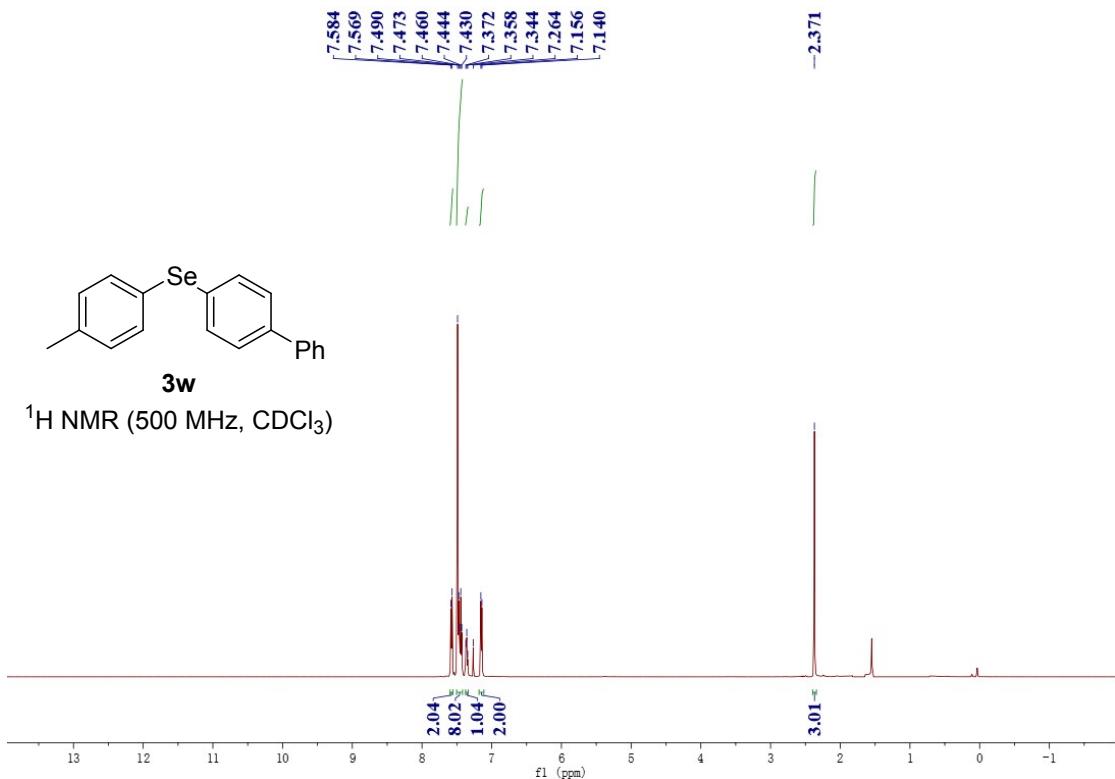
¹³C NMR (126 MHz, CDCl₃)

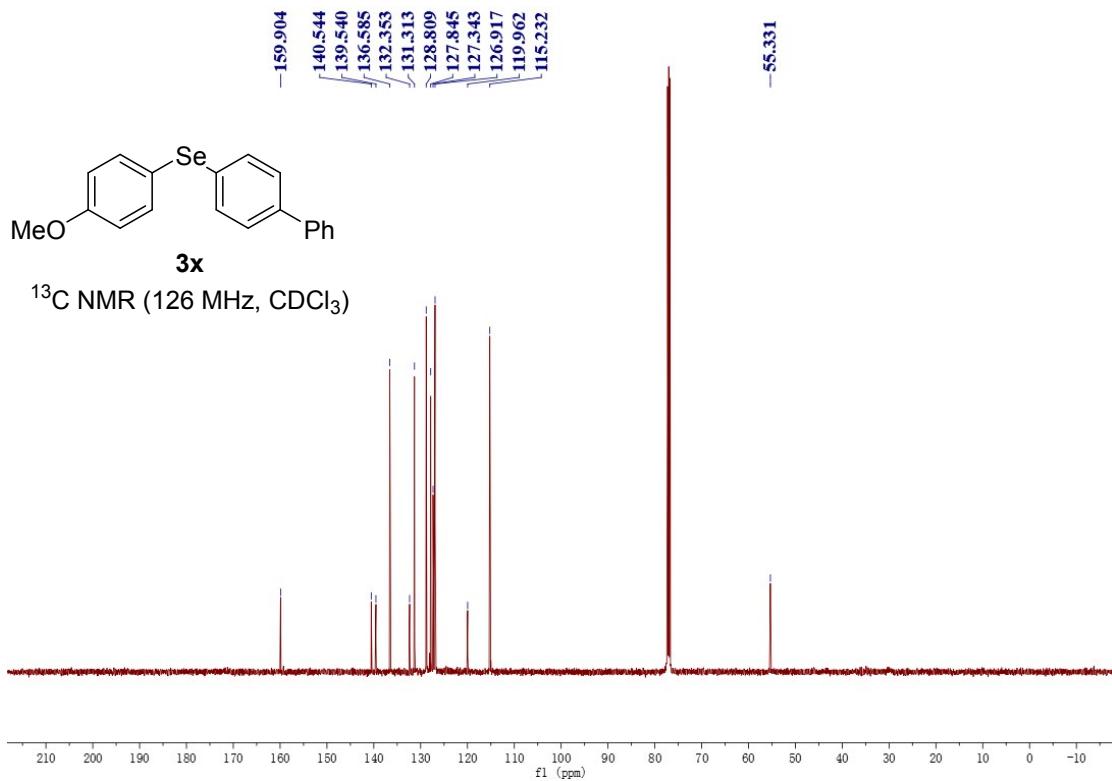
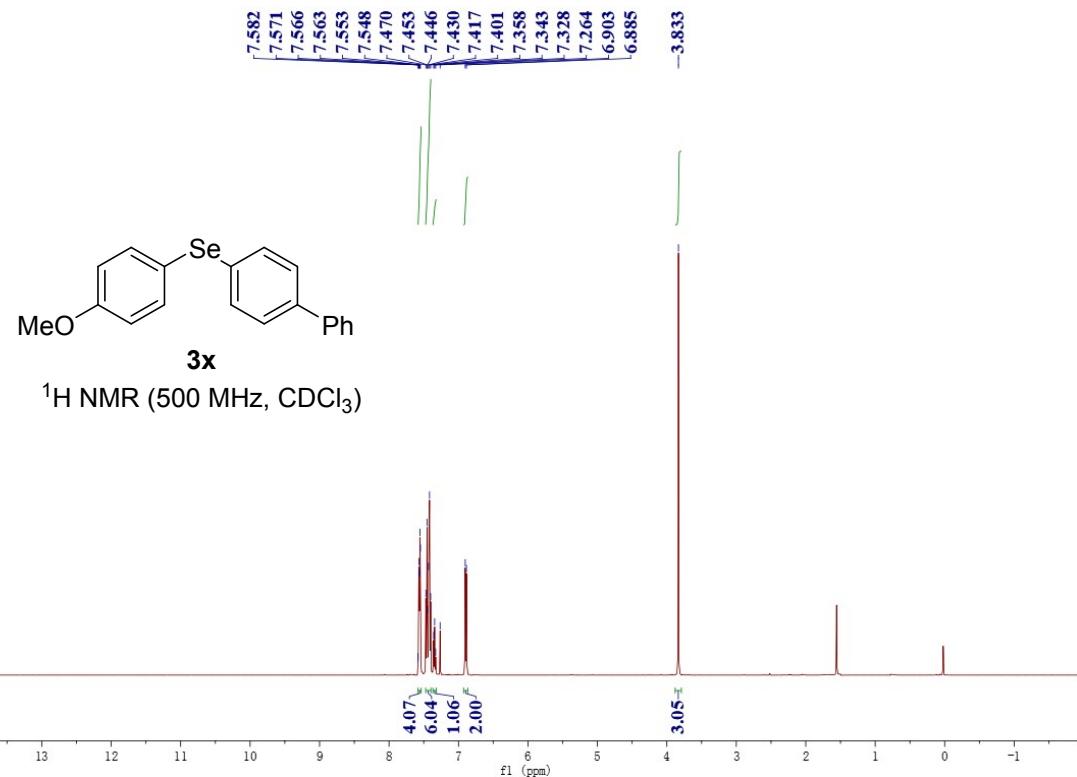


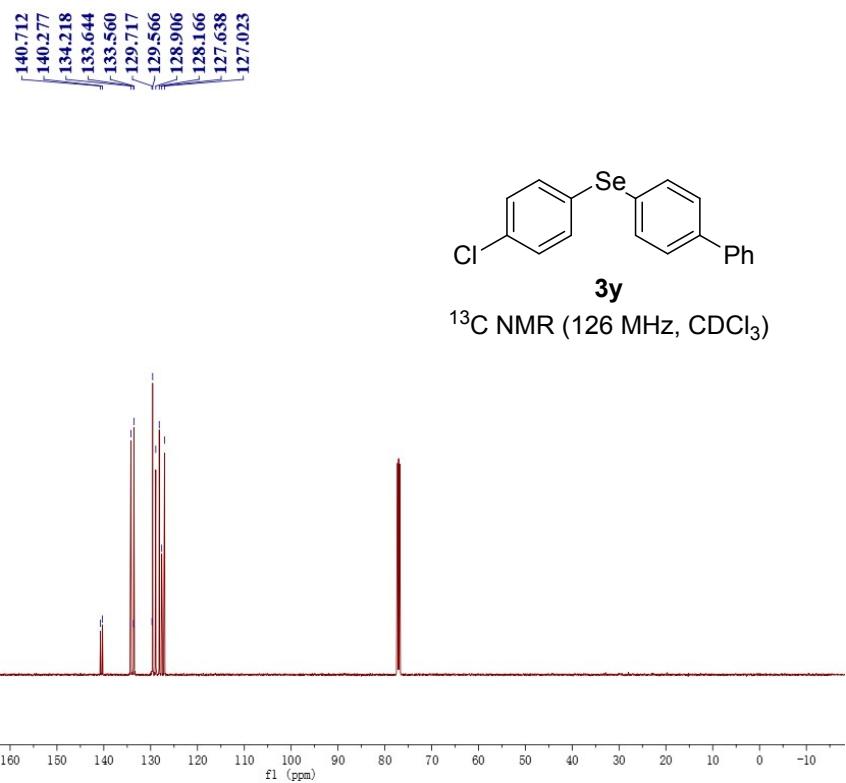
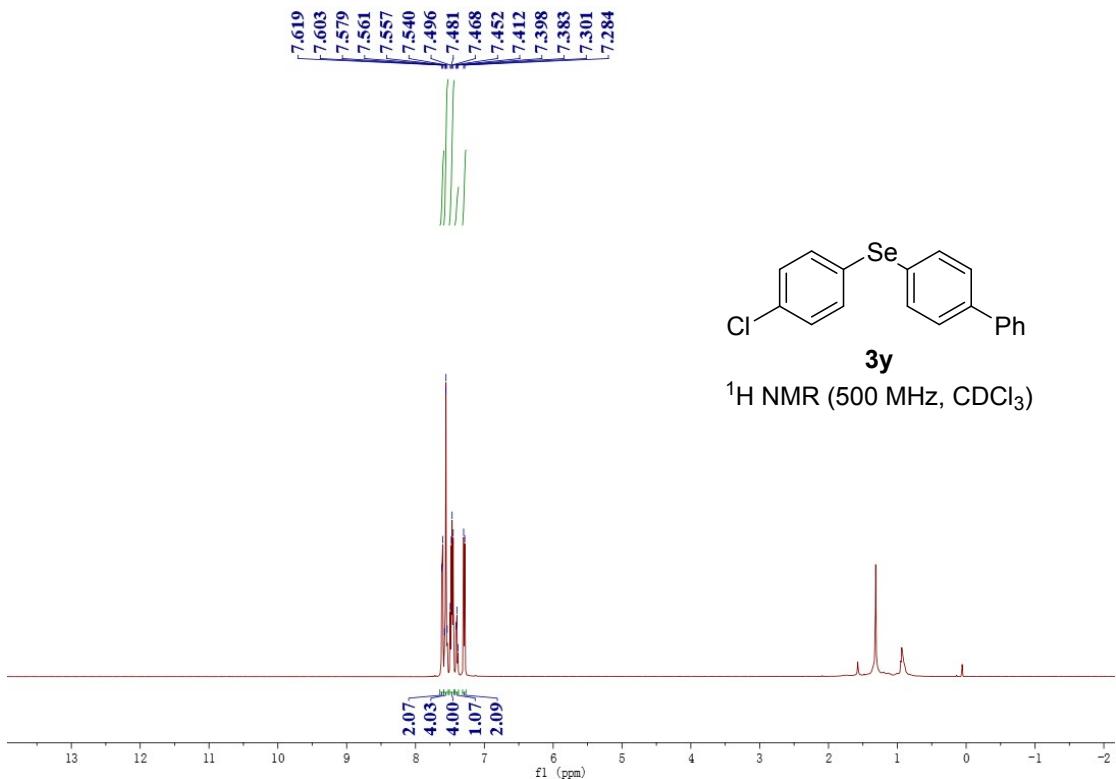


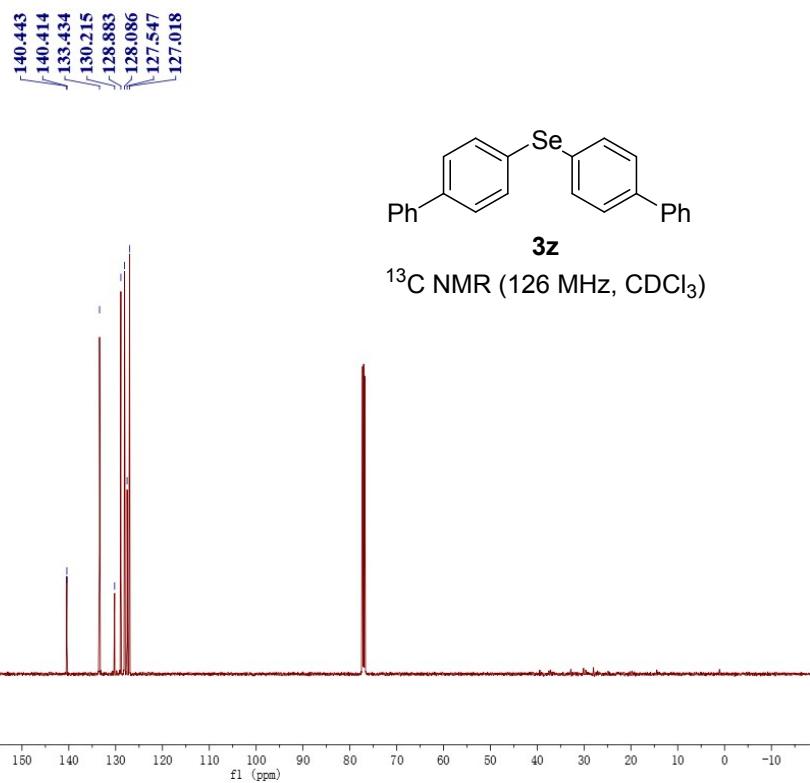
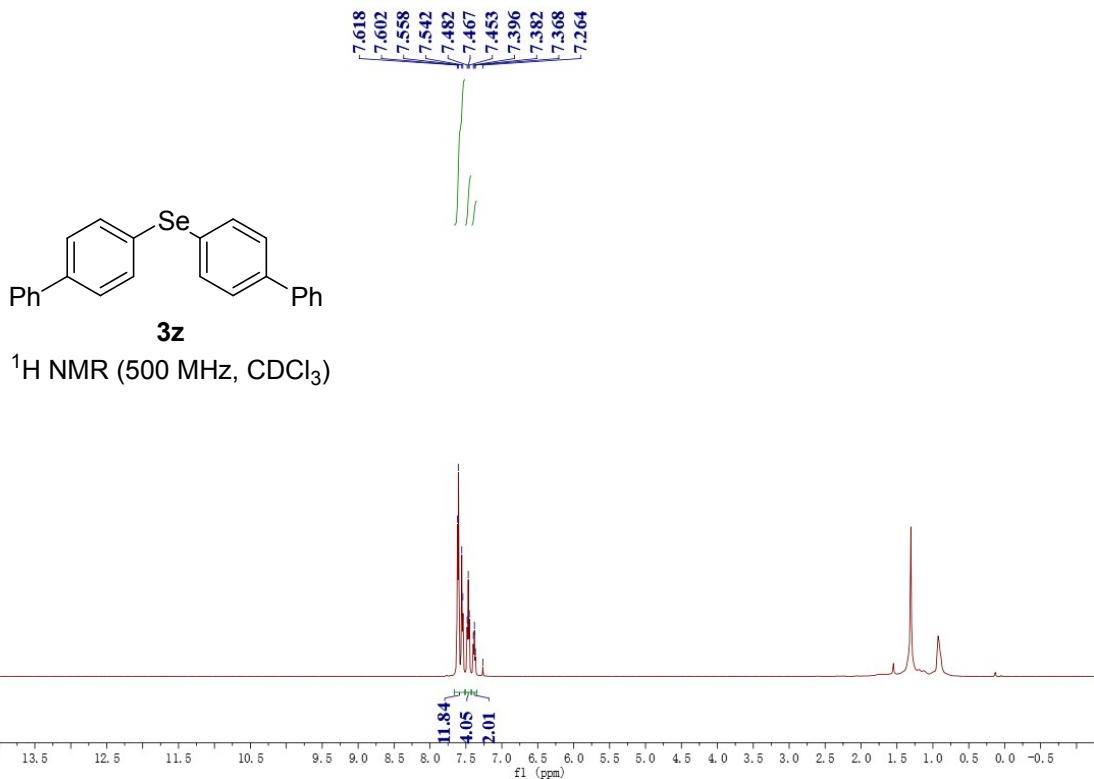


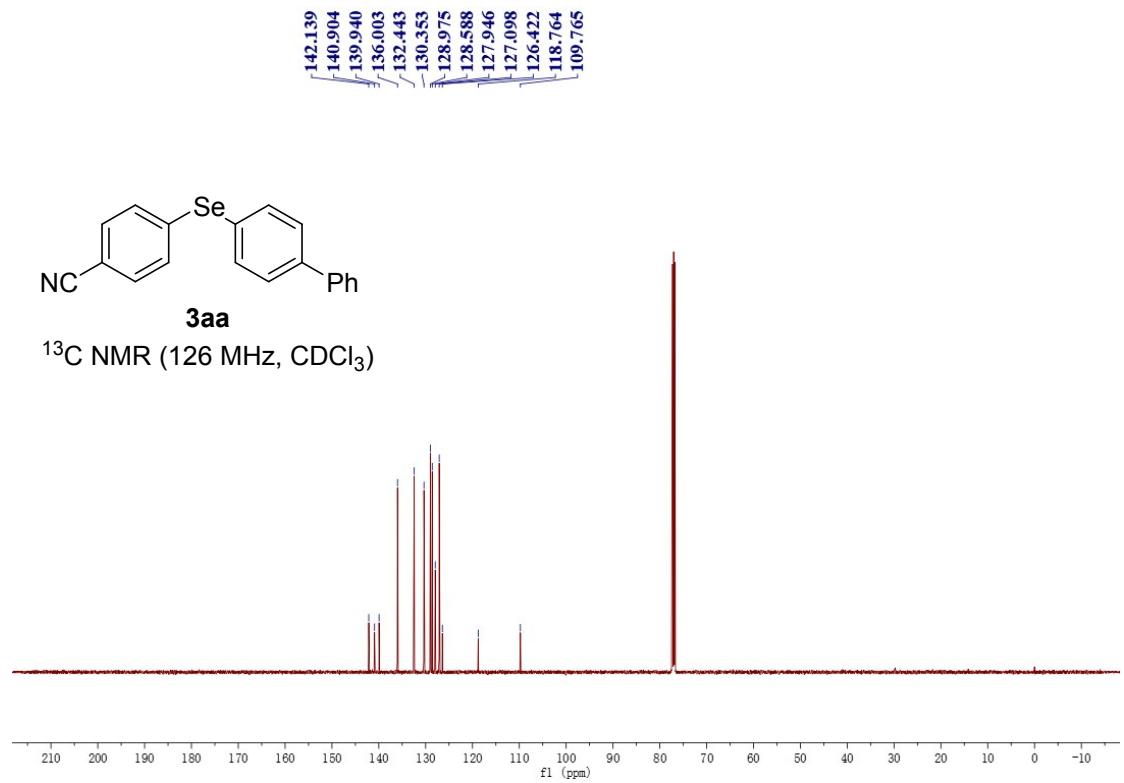
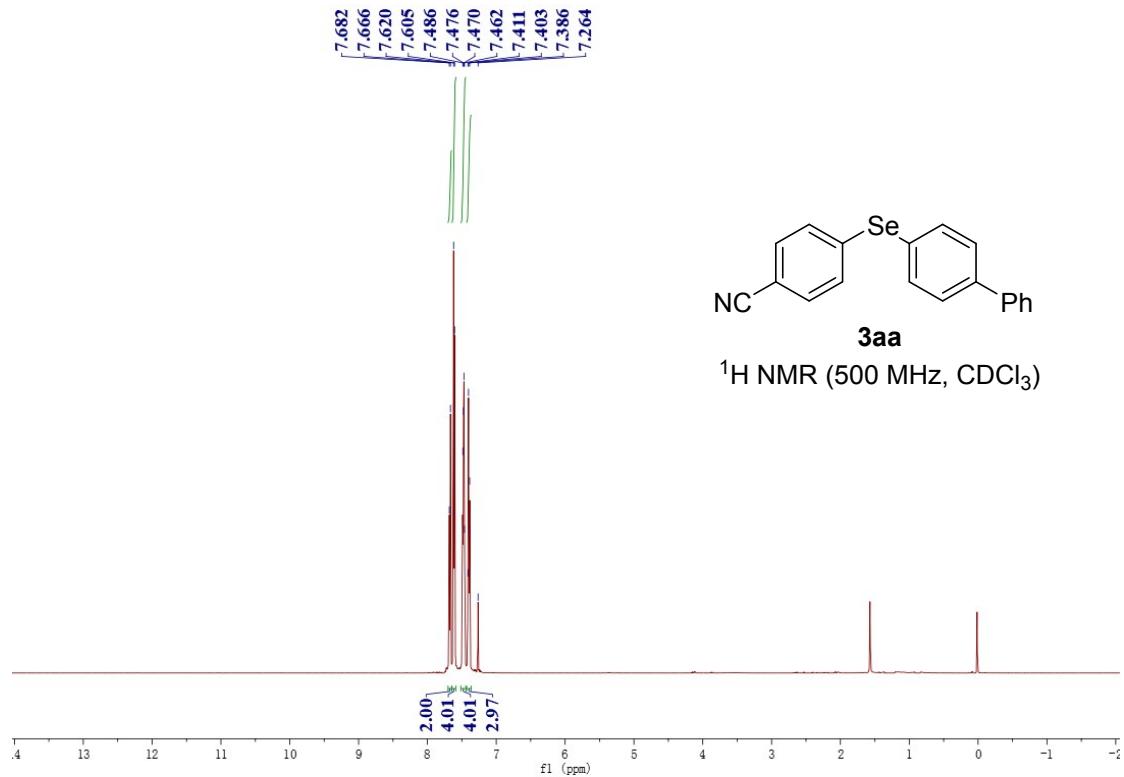


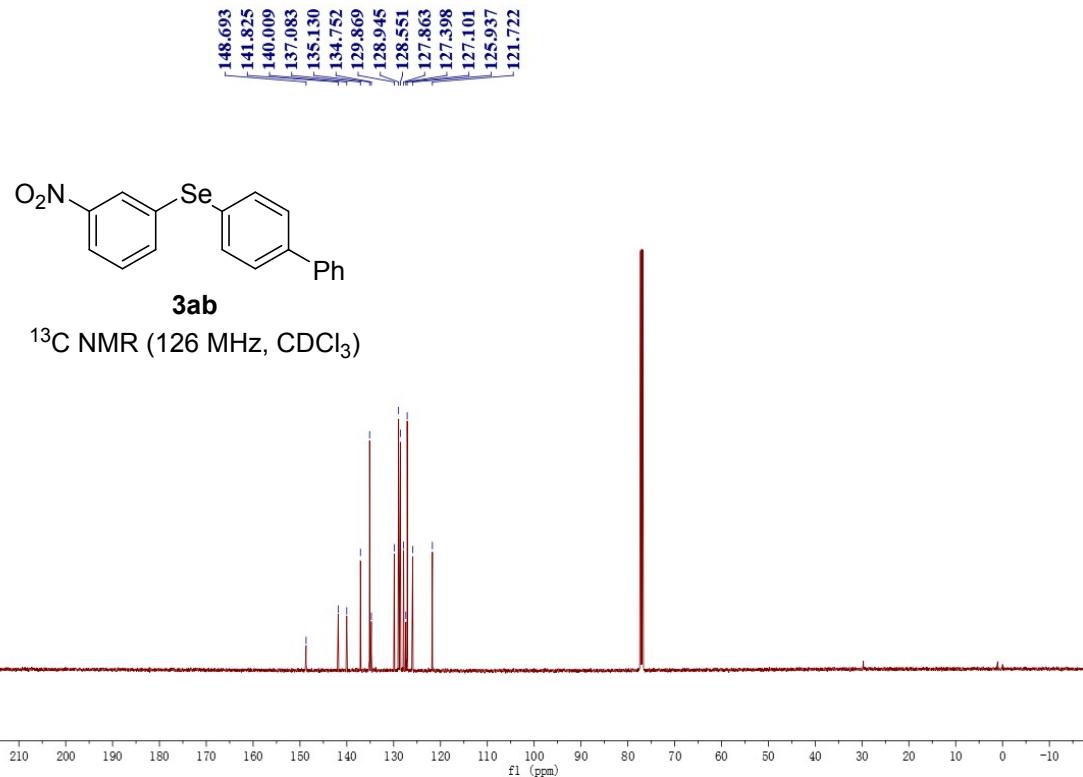
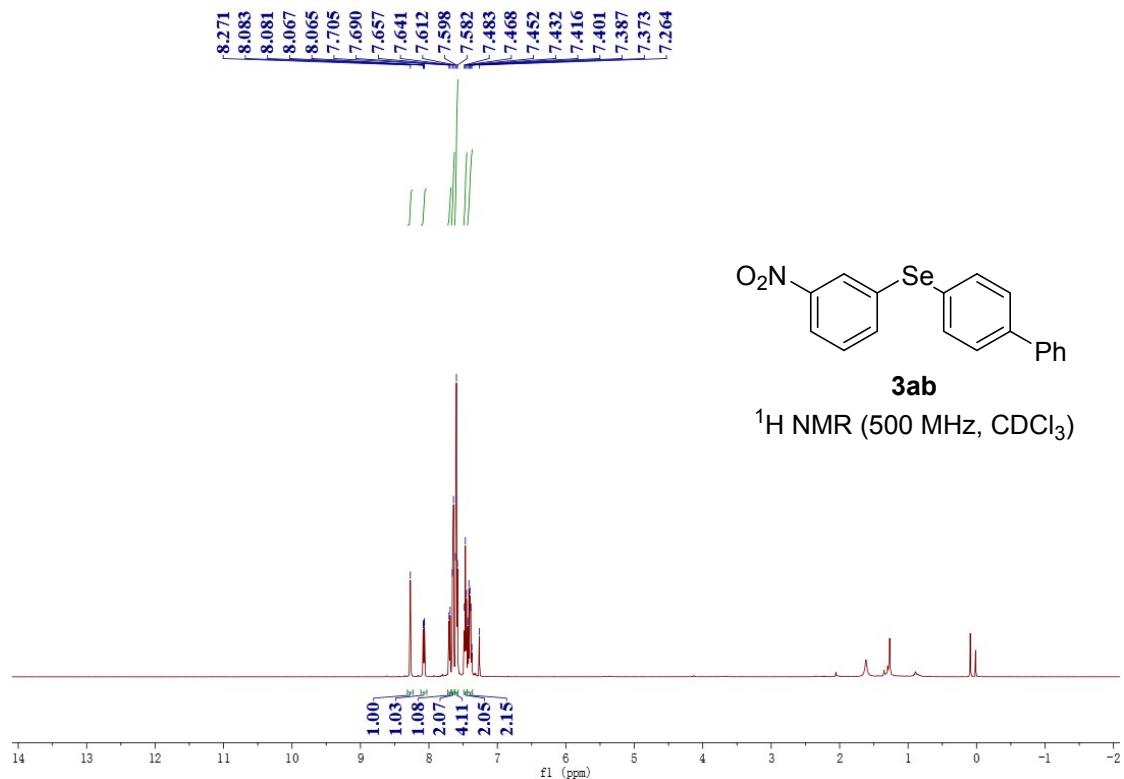


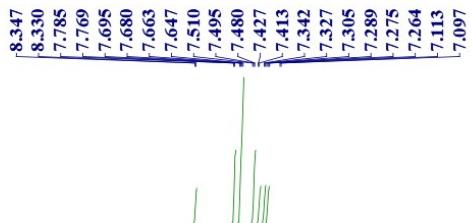




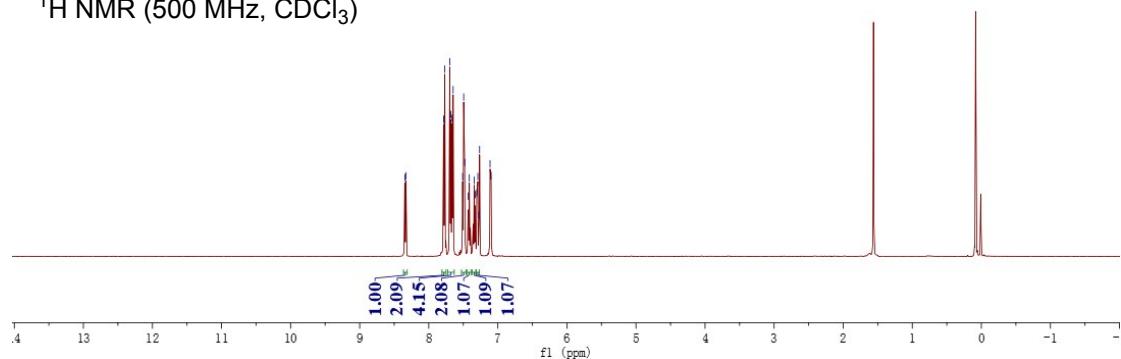




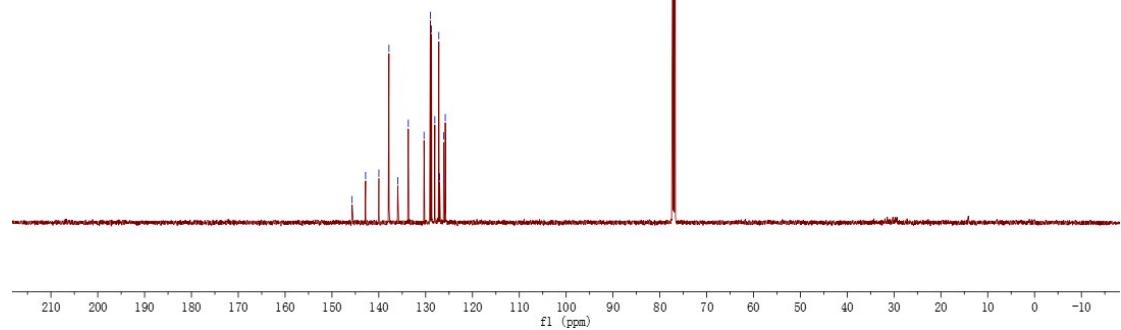


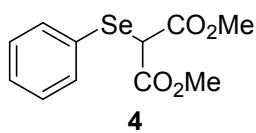


3ac
 ^1H NMR (500 MHz, CDCl_3)

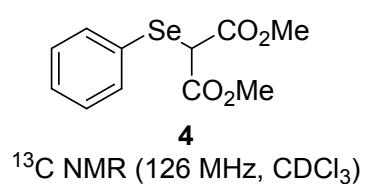
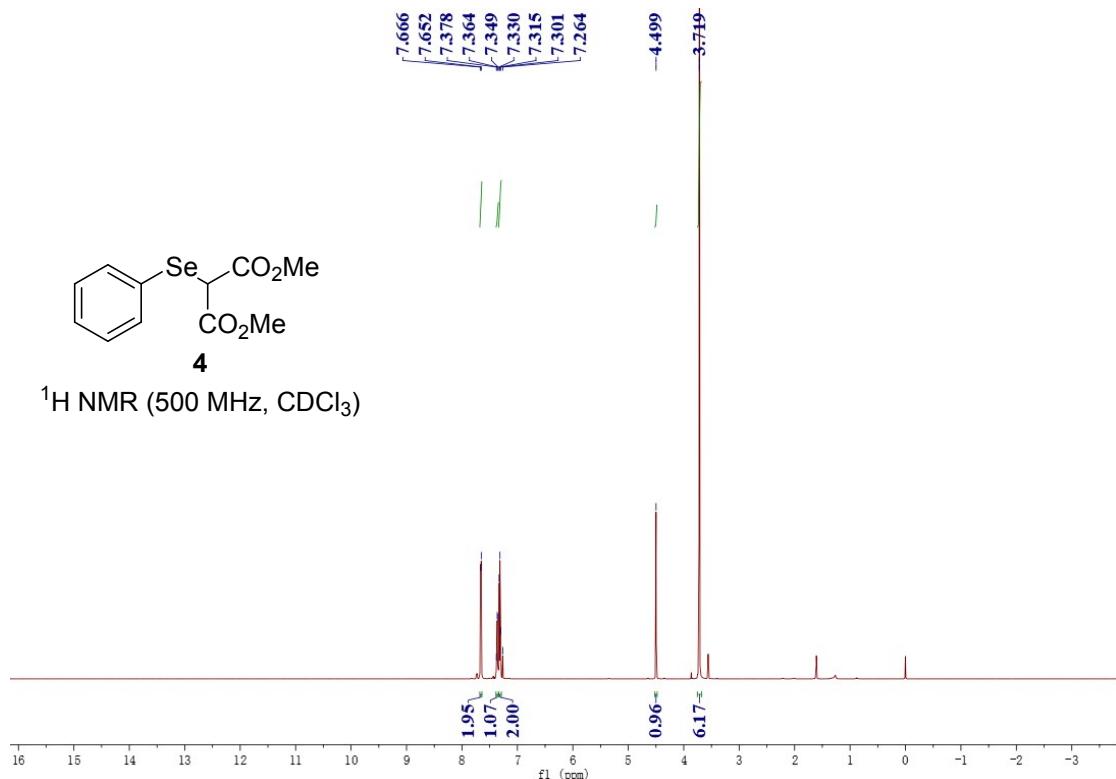


3ac
 ^{13}C NMR (126 MHz, CDCl_3)

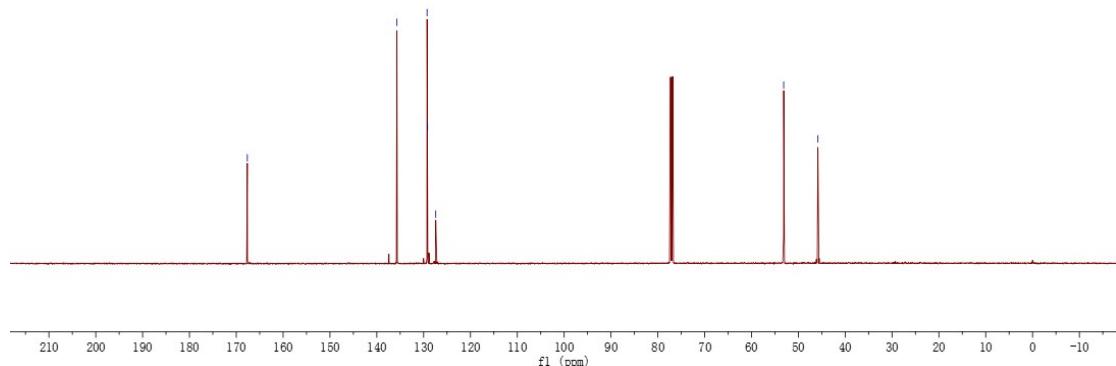


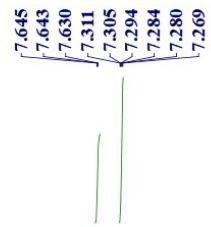


^1H NMR (500 MHz, CDCl_3)

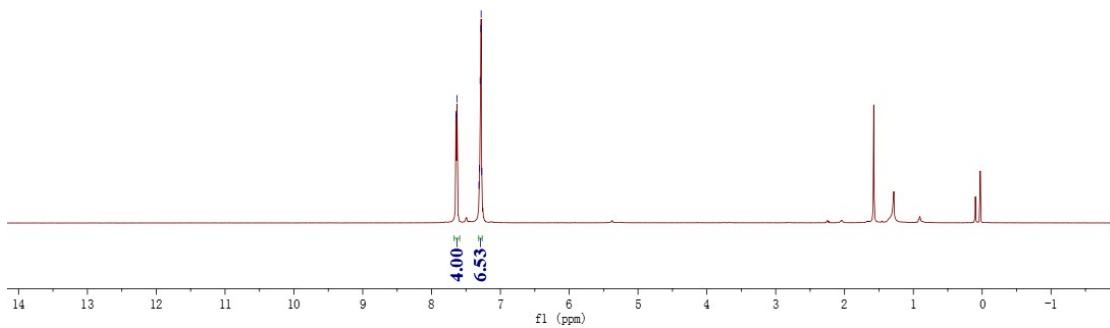


^{13}C NMR (126 MHz, CDCl_3)

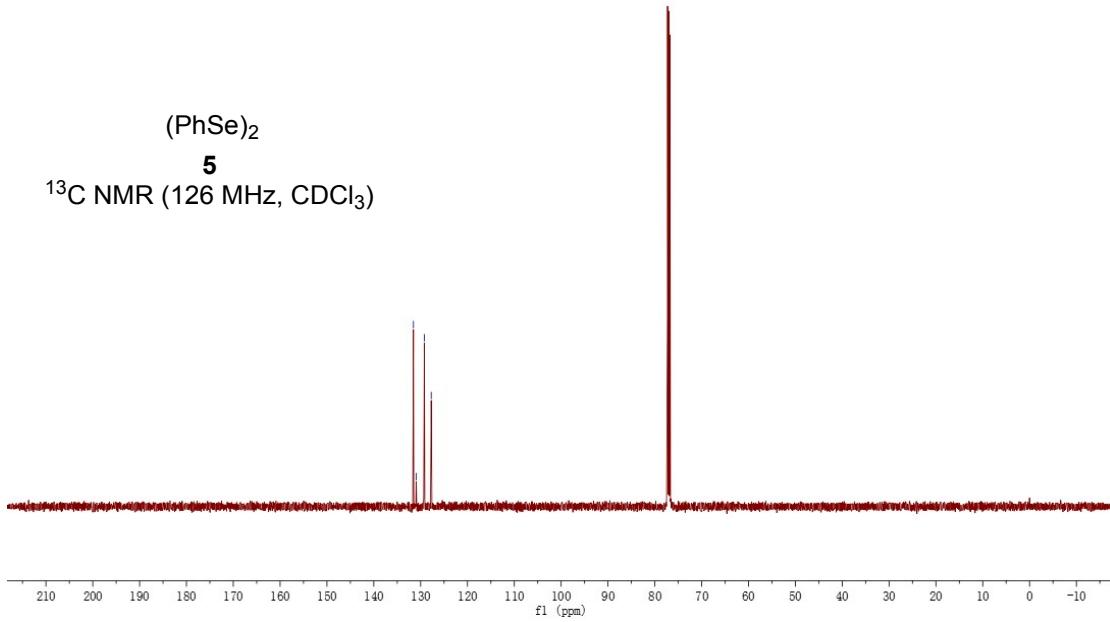


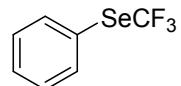
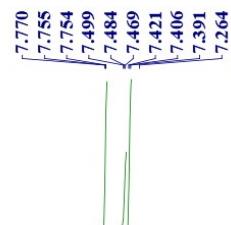


(PhSe)₂
5
¹H NMR (500 MHz, CDCl₃)

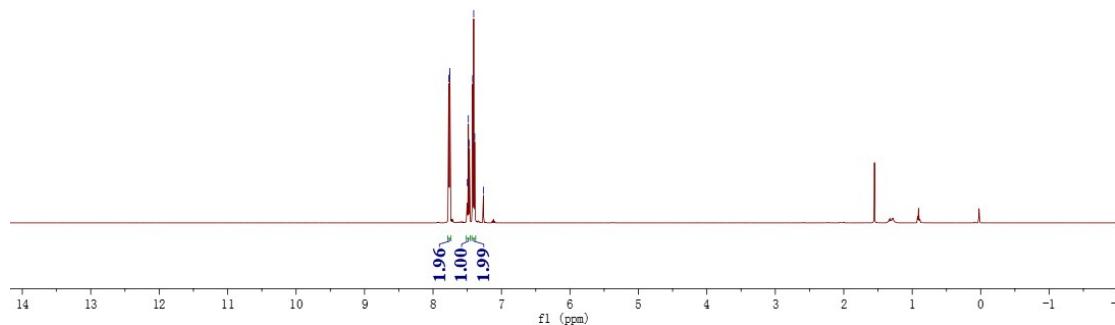


(PhSe)₂
5
¹³C NMR (126 MHz, CDCl₃)

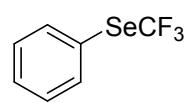




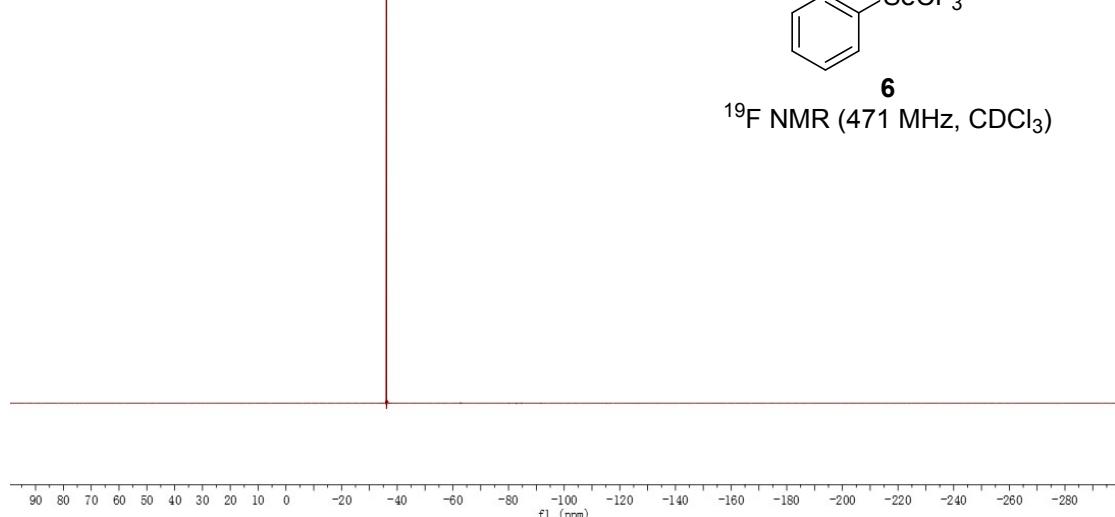
6
1H NMR (500 MHz, CDCl₃)

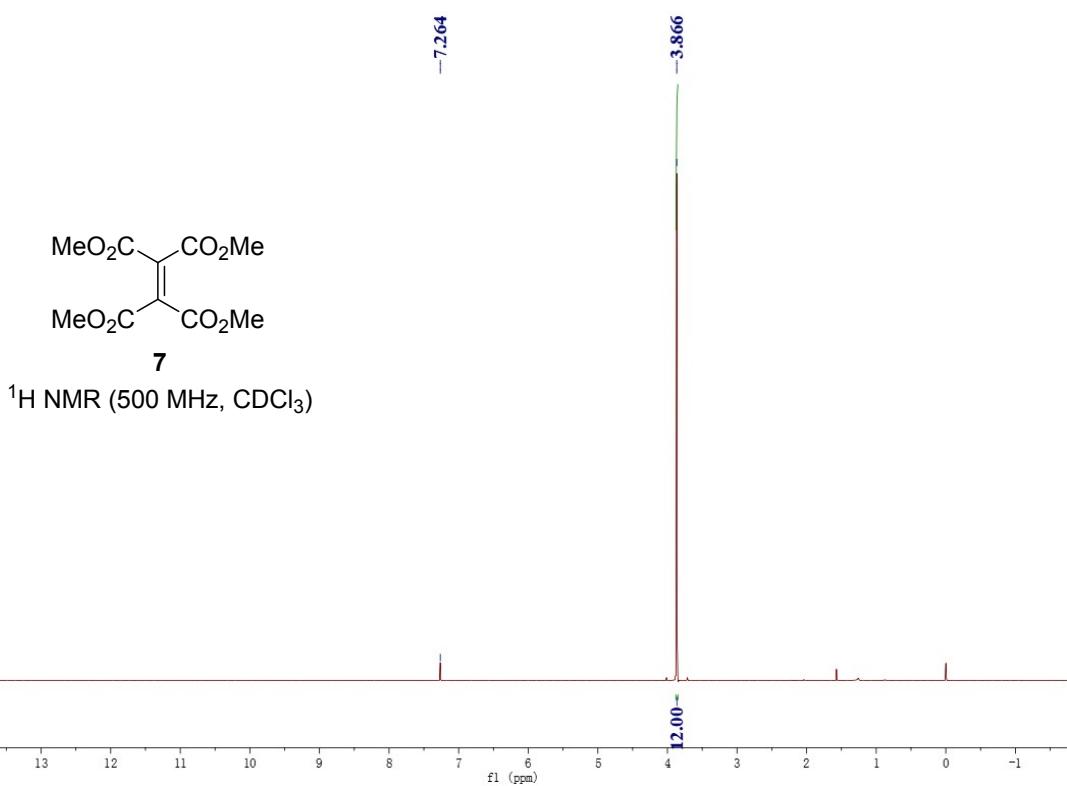
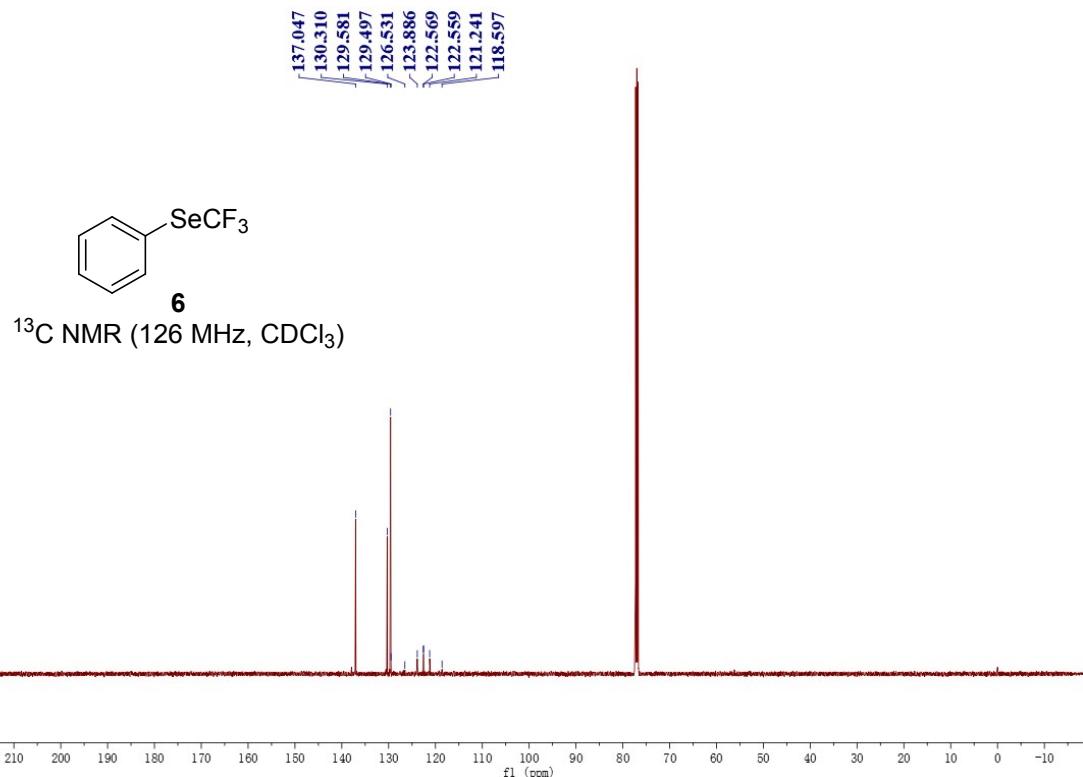


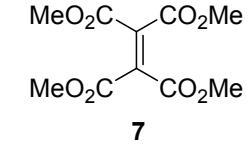
-36.088



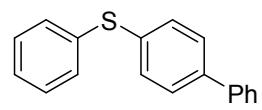
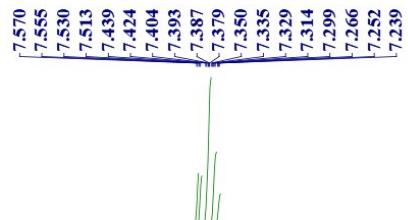
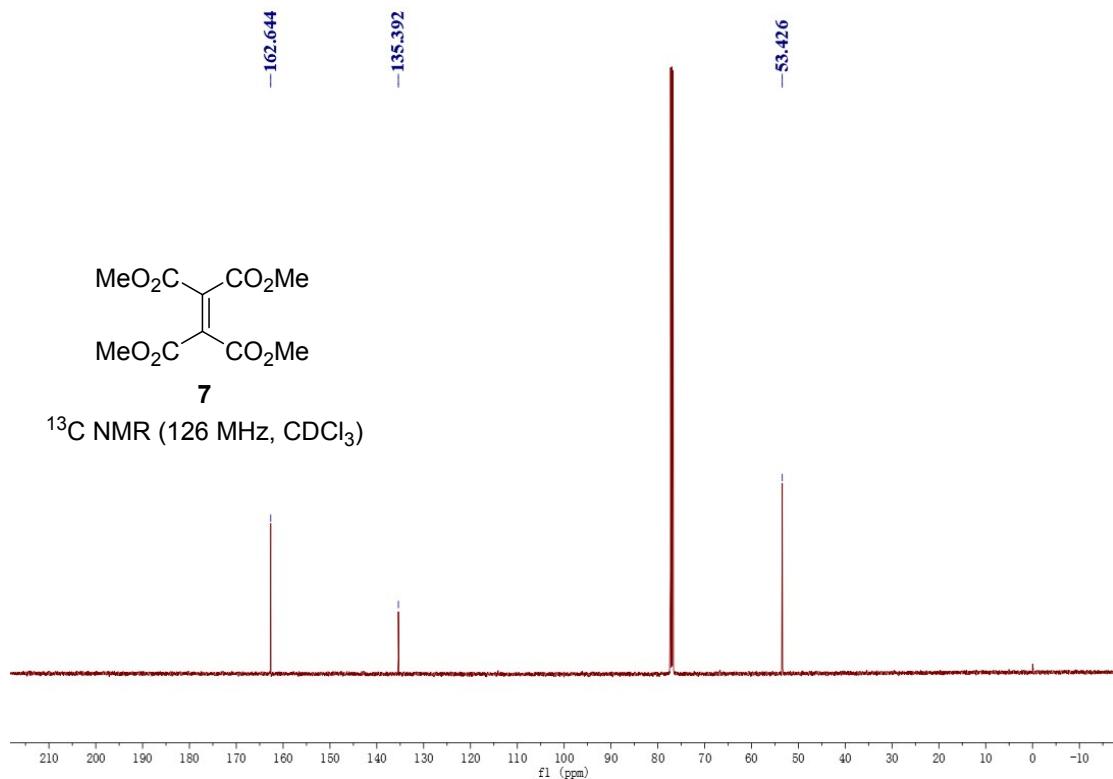
6
19F NMR (471 MHz, CDCl₃)







¹³C NMR (126 MHz, CDCl₃)



¹H NMR (500 MHz, CDCl₃)

