Supporting Information

Palladium-Catalyzed C-H Trifluoromethylselenolation of Arenes with [Me_4N][$SeCF_3$]

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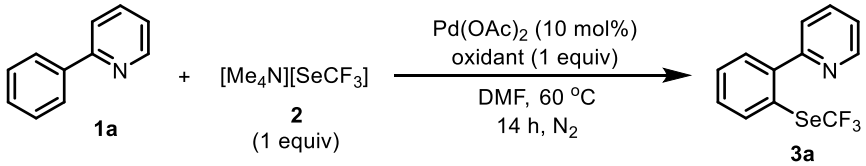
Table of contents

1. General information.

All reactions were carried out under a nitrogen atmosphere. Unless otherwise specified, NMR spectra were recorded in $CDCl_3$ 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) or $PhOCF_3$ (-58 ppm for ^{19}F NMR) as an internal or external standard. The HPLC experiments were carried out on a Wufeng LC-100 II instrument (column: Shodex, C18, 5 μm, 4.6 × 250 mm), and the yields of product were determined by using the corresponding pure compound as an external standard. 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, m = multiplet. Melting points were measured and uncorrected. MS experiments were performed on a TOF-Q ESI instrument. $[Me_4N][SeCF_3]$ was synthesized according to the literature.[1] Pyridine derivatives and their analogues (**1d-1f**,[2] **1g**,[3] **1i**,[4] **1j**,[2] **1l**,[5] **1o**,[6] **1w**,[7] **1x**,[8] **1z**,[9] **4b**,[10] **4d**,[11] **4e**,[12] and **4f**[13]) were prepared according to the literatures. Solvents were purified according to the literature.[14] Other reagents used in the reactions were all purchased from the commercial sources and used without further purification.

2. Screening of the optimal conditions for the reactions of 2-phenylpyridine (1a) with $[Me_4N][SeCF_3]$ (2).

Table S1. $Pd(OAc)_2$-Catalyzed C-H trifluoromethylselenolation of **1a** with **2** in the presence of different oxidants.[a]

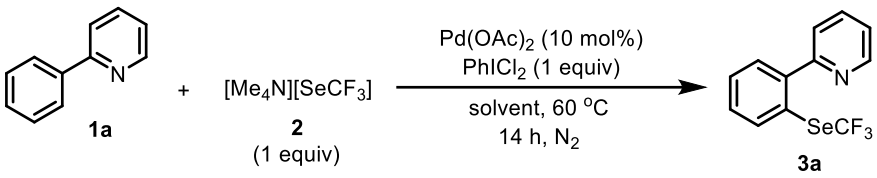


Entry	Oxidant	Yield (**3a**, %)
1	NBS	33
2	NCS	3
3	NIS	0
4	NHS	0
5	NFSI	0
6	$PhI(OAc)_2$	1

7	$PhICl_2$	53
8	$K_2S_2O_8$	0
9	TCCA	1
10	BPO	0
11	Selectflour	5
12	DDQ	21
13	*t*-BuOCl	0
14	*m*-CPBA	0
15	$KMnO_4$	0
16	$Cu(OAc)_2$	0
17	PIFA	4
18	$AgNO_3$	0

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.2 mmol), oxidant (0.2 mmol), $Pd(OAc)_2$ (0.02 mmol), DMF (2 mL), N_2, 60 °C, 14 h. Yields were determined by ^{19}F NMR using $PhOCF_3$ (32.4 mg, 0.2 mmol) as an internal standard.

Table S2. $Pd(OAc)_2$-Catalyzed C-H trifluoromethylselenolation of **1a** with **2** in different solvents.[a]

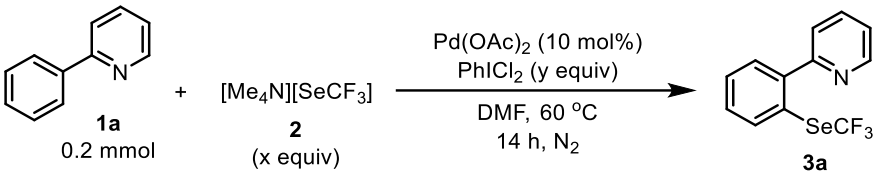


Entry	Solvent	Yield (**3a**, %)
1	THF	5
2	CH_3CN	24
3	DME	6
4	DCM	3
5	DMF	48
6	toulene	10
7	DMAc	40
8	1.4-dioxane	7

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.2 mmol), $PhICl_2$ (0.2 mmol), $Pd(OAc)_2$

(0.02 mmol), solvent (2 mL), N_2, 60 °C, 14 h. Yields were determined by HPLC using 2-(2-((trifluoromethyl)selanyl)phenyl)pyridine (**3a**) as an external standard (t_R = 5.00 min, λ_{max} = 240 nm, water / methanol = 20 / 80 (v / v)).

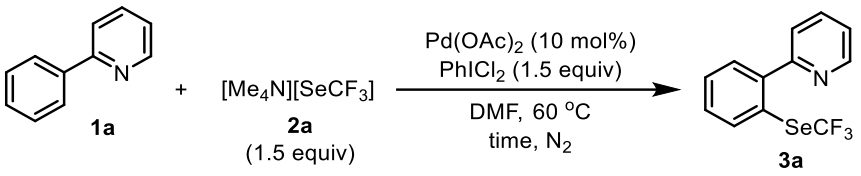
Table S3. $Pd(OAc)_2$-Catalyzed C-H trifluoromethylselenolation of **1a** with **2** at different reactant ratios.[a]



Entry	**1a**:**2**:$PhICl_2$	Yield (**3a**, %)
1	1:1:1	48
2	1:1.2:1	55
3	1:1.2:1.2	61
4	1:1.5:1	39
5	1:1.5:1.5	69
6	1:2:1	trace
7	1:2:1.5	45
8	1:2:2	64

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.2, 0.24, 0.3, 0.4 mmol), $PhICl_2$ (0.2, 0.24, 0.3, 0.4 mmol), $Pd(OAc)_2$ (0.02 mmol), DMF (2 mL), N_2, 60 °C, 14 h. Yields were determined by HPLC using 2-(2-((trifluoromethyl)selanyl)phenyl)pyridine (**3a**) as an external standard (t_R = 5.00 min, λ_{max} = 240 nm, water / methanol = 20 / 80 (v / v)).

Table S4. $Pd(OAc)_2$-Catalyzed C-H trifluoromethylselenolation of **1a** with **2** for different times.[a]

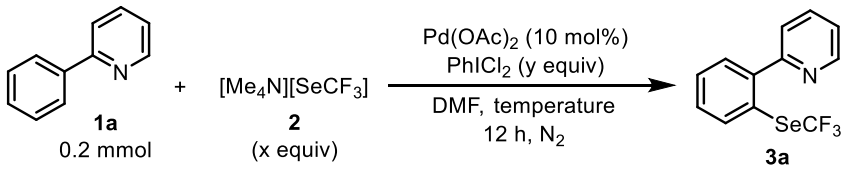


Entry	Time (h)	Yield (**3a**, %)
1	2	47
2	6	63

3	10	65
4	12	68
5	14	69
6	18	68
7	22	68

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol), $PhICl_2$ (0.3 mmol), $Pd(OAc)_2$ (0.02 mmol), DMF (2 mL), N_2, 60 °C. Yields were determined by HPLC using 2-(2-((trifluoromethyl)selanyl)phenyl)pyridine (**3a**) as an external standard (t_R = 5.00 min, λ_{max} = 240 nm, water / methanol = 20 / 80 (v / v)).

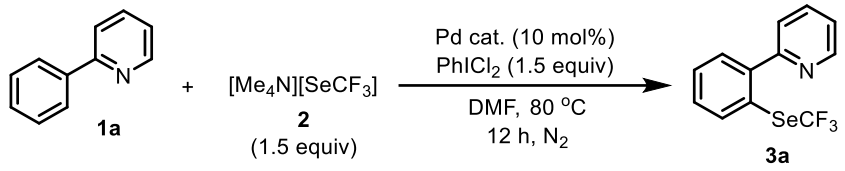
Table S5. $Pd(OAc)_2$-Catalyzed C-H trifluoromethylselenolation of **1a** with **2** at different temperatures.[a]



Entry	**1a**:**2**:$PhICl_2$	Temperature (°C)	Yield (**3a**, %)
1	1:1.5:1.5	40	39
2	1:1.5:1.5	60	69
3	1:1.5:1.5	80	74, 79[b], 74[c]
4	1:2:2	80	82, 89 (91)[c]
5	1:1.5:1.5	90	76
6	1:1.5:1.5	100	83 (86)
7	1:1.5:1.5	110	81
8	1:1.5:1.5	120	69

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 or 0.4 mmol), $PhICl_2$ (0.3 or 0.4 mmol), DMF (2 mL), $Pd(OAc)_2$ (0.02 mmol), N_2, 12 h. Yields were determined by HPLC using 2-(2-((trifluoromethyl)selanyl)phenyl)pyridine (**3a**) as an external standard (t_R = 5.00 min, λ_{max} = 240 nm, water / methanol = 20 / 80 (v / v)). Isolated yield is depicted in the parenthesis. [b] 24 h. [c] 36 h.

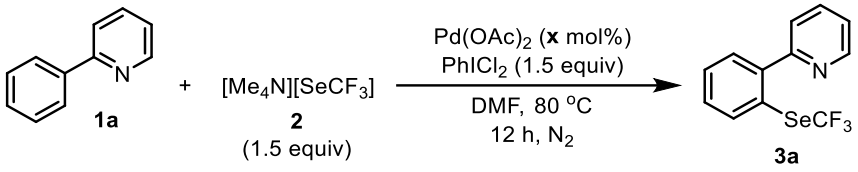
Table S6. C-H Trifluoromethylselenolation of **1a** with **2** in the presence of different Pd-catalysts.[a]



Entry	Pd cat.	Yield (**3a**, %)
1	$Pd(OAc)_2$	74
2	$Pd(CF_3COO)_2$	48
3	$Pd_2(dba)_3$	39
4	$Pd(dppf)Cl_2$	15
5	$Pd(dba)_2$	53
6	$Pd(PPh_3)_2Cl_2$	22
7	$Pd(amphos)_2Cl_2$	16
8	$Pd(CH_3CN)_2Cl_2$	64
9	$PdCl_2$	62

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $PhICl_2$ (0.3 mmol), DMF (2 mL), N_2, 80 °C, 12 h. Yields were determined by HPLC using 2-(2-((trifluoromethyl)selanyl)phenyl)pyridine (**3a**) as an external standard (t_R = 5.00 min, λ_{max} = 240 nm, water / methanol = 20 / 80 (v / v)).

Table S7. $Pd(OAc)_2$-Catalyzed C-H trifluoromethylselenolation of **1a** with **2** at different catalyst loadings.[a]



Entry	x	Yield (**3a**, %)
1	5	63
2	10	74
3	15	72
4	20	74

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $PhICl_2$ (0.3 mmol), DMF (2 mL), N_2, 80 °C, 12 h. Yields were determined by HPLC using 2-(2-((trifluoromethyl)selanyl)phenyl)pyridine (**3a**) as an external standard (t_R = 5.00

min, λ_{max} = 240 nm, water / methanol = 20 / 80 (v / v)).

3. General procedures for the Pd-catalyzed C-H trifluoromethylselenolation.

Procedure A: In a nitrogen-filled glovebox, a sealed tube was charged with 2-phenylpyridine or its derivative (**1**, 0.2 mmol), $[Me_4N][SeCF_3]$ (**2**, 66.6 mg, 0.3 mmol), $Pd(OAc)_2$ (4.49 mg, 0.02 mmol), and DMF (1 mL) with stirring. Then a DMF (1 mL) solution of $PhICl_2$ (82.5 mg, 0.3 mmol) was added. The mixture was reacted at 100 °C for 12 h, cooled to room temperature, quenched with H_2O, and diluted with ethyl acetate (20 mL). The organic solution was washed with H_2O (3 × 10 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 a mixture of petroleum ether/dichloromethane or petroleum ether/ethyl acetate as eluents to give the trifluoromethylselenolated product.

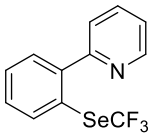
Procedure B: In a nitrogen-filled glovebox, a sealed tube was charged with 2-phenylpyridine or its derivative (**1**, 0.2 mmol), $[Me_4N][SeCF_3]$ (**2**, 88.8 mg, 0.4 mmol), $Pd(OAc)_2$ (4.49 mg, 0.02 mmol), and DMF (1 mL) with stirring. Then a DMF (1 mL) solution of $PhICl_2$ (110 mg, 0.4 mmol) was added. The mixture was reacted at 80 °C for 36 h, cooled to room temperature, quenched with H_2O, and diluted with ethyl acetate (20 mL). The organic solution was washed with H_2O (3 × 10 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 a mixture of petroleum ether/dichloromethane or petroleum ether/ethyl acetate as eluents to give the trifluoromethylselenolated product.

Procedure C: In a nitrogen-filled glovebox, a sealed tube was charged with arene (**4**, 0.2 mmol), $[Me_4N][SeCF_3]$ (**2**, 88.8 mg, 0.4 mmol), $Pd(OAc)_2$ (4.49 mg, 0.02 mmol), DMF (1 mL), and a DMF (1 mL) solution of $PhICl_2$ (82.5 mg, 0.3 mmol) with stirring. Then TFA (1mL) were added outside glovebox under N_2. The mixture was reacted at 100 °C for 12 h, cooled to room temperature, quenched with H_2O, and diluted with ethyl acetate (20 mL). The organic solution was washed with H_2O (3 × 10 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 a mixture of petroleum ether/dichloromethane or petroleum ether/ethyl acetate as eluents to give the trifluoromethylselenolated product.

Procedure D: In a nitrogen-filled glovebox, a sealed tube was charged with arene (**4**,

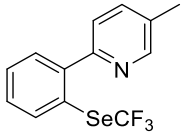
0.2 mmol), $[Me_4N][SeCF_3]$ (**2**, 132.9 mg, 0.6 mmol), $Pd(OAc)_2$ (4.49 mg, 0.02 mmol), and DMF (1 mL) with stirring. Then a DMF (1 mL) solution of $PhICl_2$ (165 mg, 0.6 mmol) was added. The mixture was reacted at 100°C for 36 h, cooled to room temperature, quenched with H_2O, and diluted with ethyl acetate (20 mL). The organic solution was washed with H_2O (3 × 10 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 a mixture of petroleum ether/dichloromethane or petroleum ether/ethyl acetate as eluents to give the trifluoromethylselenolated product.

2-(2-((Trifluoromethyl)selanyl)phenyl)pyridine (**3a**)



Procedure A: 52.1 mg, 86% yield. **Procedure B**: 55.1 mg, 91% yield. Light yellow oil, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (dm, *J* = 4.9 Hz, 1H), 7.90-7.89 (m, 1H), 7.83-7.75 (m, 3H), 7.43-7.38 (m, 2H), 7.28 (m, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.7 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.4, 145.9, 137.8, 136.0, 130.5, 128.6, 127.6, 127.3, 126.3, 123.2 (q, *J* = 338.5 Hz), 121.4, 120.3. IR (KBr): 3059, 3016, 1591, 1575, 1560, 1480, 1469, 1438, 1428, 1303, 1265, 1101, 1074, 1029, 1019, 997, 961, 947, 794, 749, 666, 625 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{12}H_9F_3NSe]^+$ ($[M + H]^+$): 303.9847; found: 303.9852.

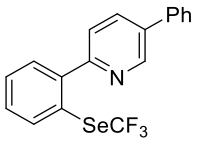
3-Methyl-2-(2-((trifluoromethyl)selanyl)phenyl)pyridine (**3b**)



Procedure A: 40.0 mg, 63% yield. **Procedure B**: 42.5 mg, 67% yield. Light yellow oil, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (m, 1H), 7.87 (dm, *J* = 7.1 Hz, 1H), 7.76 (dd, *J* = 7.2, 2.2 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.62 (dm, *J* = 8.1 Hz, 1H), 7.41-7.35 (m, 2H), 2.39 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.8 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.9, 147.3, 139.0, 137.7, 132.3, 131.5 (q, *J* = 2.0 Hz),

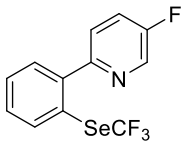
129.3, 128.4, 128.1 (q, J = 1.6 Hz), 127.4, 124.3 (q, J = 338.8 Hz), 120.9, 18.2. IR (KBr): 3062, 3012, 2959, 2925, 2867, 1599, 1589, 1576, 1559, 1492, 1467, 1439, 1381, 1305, 1259, 1249, 1226, 1100, 1073, 1037, 1019, 832, 770, 738, 726, 665, 640 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{13}H_{11}F_3NSe]^+$ ($[M + H]^+$): 318.0003; found: 318.0011.

5-Phenyl-2-(2-((trifluoromethyl)selanyl)phenyl)pyridine (**3c**)



Procedure A: 43.2 mg, 57% yield. **Procedure B**: 46.3 mg, 61% yield. Light yellow solid, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. M.p.: 138.2-139.5 ^oC. ^1H NMR (500 MHz, $CDCl_3$) δ 8.92 (dd, J = 2.3, 0.7 Hz, 1H), 8.02 (dd, J = 8.3, 2.3 Hz, 1H), 7.91 (dm, J = 7.2 Hz, 1H), 7.85-7.83 (m, 2H), 7.66-7.63 (m, 2H), 7.52 (tm, J = 7.3 Hz, 2H), 7.46-7.39 (m, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.7 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.2, 145.3, 138.6, 137.1, 135.4, 135.4, 131.6 (q, J = 2.0 Hz), 129.6, 129.2, 128.6, 128.4, 127.4, 127.1, 124.3 (q, J = 339.2 Hz), 121.3. IR (KBr): 3067, 3031, 1592, 1580, 1478, 1465, 1448, 1429, 1368, 1331, 1310, 1267, 1234, 1163, 1130, 1106, 1074, 1030, 1018, 1006, 933, 913, 849, 784, 758, 744, 730, 712, 696, 664, 639 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{18}H_{13}F_3NSe]^+$ ($[M + H]^+$): 380.0160; found: 380.0170.

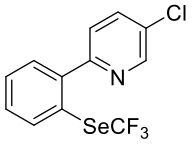
5-Fluoro-2-(2-((trifluoromethyl)selanyl)phenyl)pyridine (**3d**)



Procedure A: 35.3 mg, 55% yield. **Procedure B**: 34.6 mg, 54% yield. Light yellow oil, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. ^1H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, J = 2.8 Hz, 1H), 7.88 (d, J = 7.2 Hz, 1H), 7.74-7.69 (m, 2H), 7.54 (td, J = 8.4, 2.8 Hz, 1H), 7.44-7.38 (m, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.1 (s, 3F), -127.9 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8 (d, J = 258.0 Hz), 153.4 (d, J = 4.0 Hz), 139.1, 135.7 (d, J = 24.4 Hz), 132.5 (q, J = 1.8 Hz), 129.6, 128.9, 127.9, 127.5, 124.1 (d, J = 18.9 Hz), 123.8 (q, J =336.9 Hz), 123.0 (d, J = 4.5 Hz). IR (KBr): 3063, 1683, 1587, 1490, 1468, 1440, 1386, 1260,

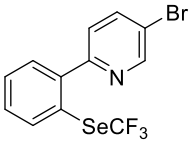
1233, 1099, 1074, 1034, 1018, 908, 838, 772, 739, 660, 633 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{12}H_8F_4NSe]^+$ ($[M + H]^+$): 321.9753; found: 321.9753.

5-Chloro-2-(2-((trifluoromethyl)selanyl)phenyl)pyridine (**3e**)



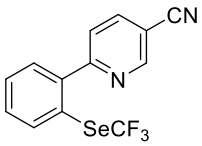
Procedure A: 39.1 mg, 58% yield. **Procedure B**: 36.4 mg, 54% yield. White solid, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. M.p.: 77.8-79.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (d, *J* = 2.1 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.79 (dd, *J* = 8.5. 2.4 Hz, 1H), 7.73-7.72 (m, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.45-7.39 (m, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.2 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.0, 146.3, 138.7, 136.9, 132.4 (q, *J* = 1.7 Hz), 131.2, 129.9, 128.9, 127.8, 127.7 (q, *J* = 1.3 Hz), 123.9 (q, *J* = 337.1 Hz), 122.5. IR (KBr): 3073, 2963, 1668, 1589, 1579, 1552, 1481, 1464, 1436, 1376, 1366, 1305, 1261, 1235, 1138, 1097, 1073, 1031, 1012, 947, 918, 835, 801, 771, 739, 687, 632 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{12}H_8ClF_3NSe]^+$ ($[M + H]^+$): 335.9525; found: 335.931.

5-Bromo-2-(2-((trifluoromethyl)selanyl)phenyl)pyridine (**3f**)



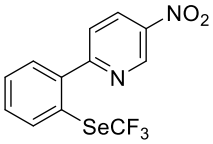
Procedure A: 31.2 mg, 41% yield. **Procedure B**: 33.5 mg, 44% yield. White solid, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. M.p.: 76.7-78.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (d, *J* = 2.1 Hz, 1H), 7.93 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.89-7.87 (m, 1H), 7.74-7.72 (m, 1H), 7.63 (d, *J* = 8.5, 1H), 7.44-7.39 (m, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.2 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.3, 148.5, 139.7, 138.7, 132.4, 129.9, 128.9, 127.8, 127.7, 123.9 (q, *J* = 337.9 Hz), 122.9, 119.8. IR (KBr): 3068, 1666, 1588, 1574, 1548, 1479, 1463, 1432, 1364, 1304, 1259, 1233, 1173, 1138, 1094, 1071, 1031, 1018, 1007, 948, 921, 834, 771, 740, 729, 680, 648, 631 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{12}H_8BrF_3N^{82}Se]^+$ ($[M + H]^+$): 383.8954; found: 383.8949.

6-(2-((Trifluoromethyl)selanyl)phenyl)nicotinonitrile (**3h**)



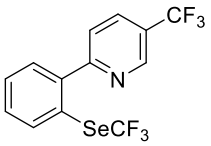
Procedure A: 19.7 mg, 30% yield. **Procedure B**: 21.0 mg, 32% yield. Light yellow solid, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. M.p.: 104.5-105.9 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (dd, *J* = 2.0, 0.7 Hz, 1H), 8.08 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.93-7.90 (m, 1H), 7.87 (dd, *J* = 8.3, 0.7 Hz, 1H), 7.80-7.77 (m, 1H), 7.50-7.46 (m, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.0 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 150.3, 140.0, 138.2, 132.9 (q, *J* = 1.6 Hz), 130.9, 129.5, 128.3, 128.1, 123.7 (q, *J* = 337.6 Hz), 121.8, 116.4, 108.4. IR (KBr): 3107, 3075, 2923, 2231, 1696, 1593, 1569, 1548, 1503, 1484, 1466, 1437, 1427, 1396, 1375, 1309, 1261, 1240, 1136, 1105, 1086, 1070, 1033, 1017, 869, 854, 801, 781, 745, 640 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{13}H_8F_3N_2Se]^+$ ($[M + H]^+$): 328.9799; found: 328.9809.

5-Nitro-2-(2-((trifluoromethyl)selanyl)phenyl)pyridine (**3i**)



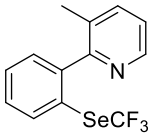
Procedure A: 14.6 mg, 21% yield. **Procedure B**: 15.3 mg, 22% yield. Yellow solid, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. M.p.: 118.8-119.3 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.51 (m, 1H), 8.61 (dm, *J* = 8.7 Hz, 1H), 7.95-7.92 (m, 2H), 7.83 (m, 1H), 7.51-7.48 (m, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.0 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.0, 143.2, 142.9, 138.0, 133.0 (q, *J* = 1.8 Hz), 132.1, 131.1, 129.8, 128.5 (q, *J* = 1.6 Hz), 128.2, 123.6 (q, *J* = 336.6 Hz), 122.0. IR (KBr): 3140, 3094, 2924, 1590, 1569, 1519, 1480, 1468, 1432, 1391, 1370, 1339, 1313, 1275, 1093, 1070, 1019, 1001, 874, 786, 741, 630 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{12}H_8F_3N_2O_2Se]^+$ ($[M + H]^+$): 348.9698; found: 348.9706.

5-(Trifluoromethyl)-2-(2-((trifluoromethyl)selanyl)phenyl)pyridine (**3j**)



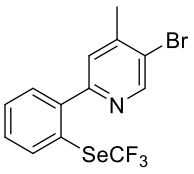
Procedure A: 31.2 mg, 42% yield. **Procedure B**: 33.4 mg, 45% yield. Light yellow solid, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. M.p.: 101.9-103.5 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (m, 1H), 8.06 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.92 (m, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.81-7.79 (m, 1H), 7.48-7.44 (m, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.2 (s, 3F), -62.3 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 144.5 (q, *J* = 4.2 Hz), 138.5, 134.2 (q, *J* = 3.4 Hz), 132.6 (q, *J* = 1.8 Hz), 130.5, 129.4, 128.2 (q, *J* = 1.1 Hz), 127.9, 125.0 (q, *J* = 33.6 Hz), 123.8 (q, *J* = 337.1 Hz), 121.5, 121.3 (q, *J* = 272.6 Hz). IR (KBr): 3061, 1609, 1578, 1562, 1498, 1469, 1443, 1393, 1329, 1308, 1264, 1171, 1128, 1099, 1086, 1073, 1032, 1017, 936, 847, 735, 672 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{13}H_8F_6N^{82}Se]^+$ ($[M + H]^+$): 373.9722; found: 373.9716.

3-Methyl-2-(2-((trifluoromethyl)selanyl)phenyl)pyridine (**3k**)



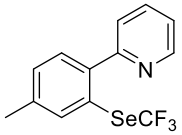
Procedure A: 40.0 mg, 63% yield. **Procedure B**: 44.3 mg, 70% yield. Light yellow oil, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 4.6, 0.8 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.63 (dm, *J* = 7.7 Hz, 1H), 7.48-7.39 (m, 3H), 7.24 (dd, *J* = 7.7, 4.8 Hz, 1H), 2.24 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -35.4 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1, 146.2, 144.2, 138.6, 135.8, 131.3, 129.9, 129.0, 129.0, 125.0 (q, *J* = 1.3 Hz), 123.0 (q, *J* = 333.8 Hz), 122.9, 19.4. IR (KBr): 3057, 2960, 2928, 2859, 1584, 1572, 1446, 1431, 1422, 1383, 1299, 1260, 1225, 1184, 1100, 1075, 1019, 911, 828, 793, 781, 751, 658, 627 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{13}H_{11}F_3NSe]^+$ ($[M + H]^+$): 318.0003; found: 318.0007.

5-Bromo-4-methyl-2-(2-((trifluoromethyl)selanyl)phenyl)pyridine (**3l**)



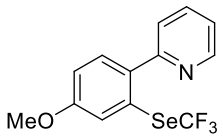
Procedure A: 52.9 mg, 67% yield. **Procedure B**: 62.3 mg, 79% yield. White solid, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. M.p.: 80.6-81.7 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.89-7.86 (m, 1H), 7.72-7.70 (m, 1H), 7.59 (s, 1H), 7.42-7.39 (m, 2H), 2.48 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.2 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.6, 148.9, 148.0, 138.8, 132.2 (q, *J* = 1.8 Hz), 129.7, 128.8, 127.8 (q, *J* = 1.5 Hz), 127.7, 124.0 (q, *J* = 337.6 Hz), 123.8, 122.6, 26.6. IR (KBr): 2958, 2924, 1626, 1587, 1538, 1478, 1467, 1436, 1381, 1365, 1309, 1250, 1202, 1097, 1055, 1034, 1025, 910, 865, 770, 726, 676 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{13}H_{10}BrF_3N^{82}Se]^+$ ($[M + H]^+$): 397.9110; found: 397.9109.

2-(4-Methyl-2-((trifluoromethyl)selanyl)phenyl)pyridine (**3m**)



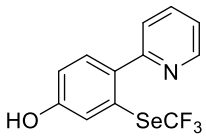
Procedure A: 44.3 mg, 70% yield. **Procedure B**: 48.1 mg, 76% yield. Light yellow oil, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (dm, *J* = 4.9 Hz, 1H), 7.78 (td, *J* = 7.8, 1.8 Hz, 1H), 7.76 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.70 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.25 (m, 1H), 7.21 (dm, *J* = 8.0 Hz, 1H), 2.43 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.7 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.5, 146.9, 139.9, 137.0, 136.2, 132.1 (q, *J* = 1.9 Hz), 128.4, 128.3, 128.2 (q, *J* = 1.6 Hz), 124.3 (q, *J* = 338.6 Hz), 122.1, 121.1, 21.4. IR (KBr): 3057, 3018, 2923, 2863, 1592, 1573, 1470, 1429, 1395, 1310, 1301, 1261, 1221, 1101, 1074, 1019, 999, 849, 825, 779, 744, 727, 629 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{13}H_{11}F_3NSe]^+$ ($[M + H]^+$): 318.0003; found: 318.0009.

5-Methoxy-2-(2-((trifluoromethyl)selanyl)phenyl)pyridine (**3n**)



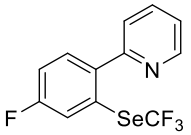
Procedure A: 44.0 mg, 66% yield. **Procedure B**: 55.3 mg, 83% yield. White solid, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. M.p.: 112.2-113.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.6 Hz, 1H), 7.77 (td, *J* = 8.0, 1.7 Hz, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.42 (d, *J* = 2.0 Hz, 1H), 7.22 (m, 1H), 6.94 (dd, *J* = 8.7, 2.5 Hz, 1H), 3.87 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -38.2 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 156.1, 146.7, 137.0, 131.1, 130.0 (q, *J* = 1.2 H), 129.3, 124.5 (q, *J* = 339.9 Hz), 121.7, 120.5, 116.5 (q, *J* = 1.8 Hz), 113.2, 55.5. IR (KBr): 3019, 2965, 2925, 2842, 1598, 1573, 1560, 1471, 1444, 1429, 1288, 1186, 1108, 1083, 1070, 1032, 1013, 996, 860, 822, 781, 743, 723, 628 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{13}H_{11}F_3NOSe]^+$ ([M + H]$^+$): 333.9952; found: 333.9955.

4-(Pyridin-2-yl)-3-((trifluoromethyl)selanyl)phenol (**3o**)



Procedure A: 45.9 mg, 72% yield. **Procedure B**: 47.8 mg, 75% yield. Light yellow solid, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. M.p.: 112.9-113.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (dm, *J* = 5.0 Hz, 1H), 7.80 (td, *J* = 7.8, 1.7 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.28 (m, 1H), 7.25 (d, *J* = 2.0 Hz, 1H), 6.78 (dd, *J* = 8.5, 2.5 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.3 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.3, 157.1, 146.9, 137.4, 132.7, 130.2, 127.5, 123.7 (q, *J* = 338.1 Hz), 122.3, 122.2, 120.7, 116.1. IR (KBr): 3289, 3085, 1596, 1586, 1566, 1490, 1469, 1366, 1284, 1243, 1216, 1154, 1101, 1002, 874, 820, 784, 757, 636 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{12}H_9F_3NOSe]^+$ ([M + H]$^+$): 317.9863; found: 317.9861.

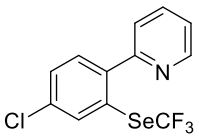
2-(4-Fluoro-2-((trifluoromethyl)selanyl)phenyl)pyridine (**3p**)



Procedure A: 19.9 mg, 31% yield. **Procedure B**: 21.2 mg, 33% yield. Light yellow oil, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (dm, *J* = 4.9 Hz, 1H), 7.84-7.77

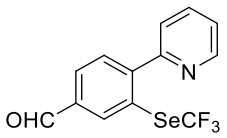
(m, 2H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.61 (dd, *J* = 9.4, 2.5 Hz, 1H), 7.29 (m, 1H), 7.11 (td, *J* = 8.5, 2.5 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -38.5 (s, 3F), -110.8 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.9 (d, *J* = 252.0 Hz), 155.5, 146.8, 137.2, 134.5 (d, *J* = 2.4 Hz), 130.7 (m), 129.7 (d, *J* = 8.7 Hz), 124.3 (q, *J* = 339.8 Hz), 122.4, 120.9, 118.3 (dq, *J* = 25.0, 2.2 Hz), 114.3 (d, *J* = 21.8 Hz). IR (KBr): 3063, 3020, 1593, 1566, 1489, 1470, 1432, 1308, 1271, 1252, 1218, 1101, 1067, 1021, 873, 824, 779, 743, 728, 630 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{12}H_8F_4NSe]^+$ ($[M + H]^+$): 321.9753; found: 321.9759.

2-(4-Chloro-2-((trifluoromethyl)selanyl)phenyl)pyridine (**3q**)



Procedure A: 26.3 mg, 39% yield. **Procedure B**: 27.6 mg, 41% yield. White solid, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. M.p.: 89.9-91.1 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (dm, *J* = 4.9 Hz, 1H), 7.85-7.82 (m, 2H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.38 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.31 (m, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -38.2 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.5, 147.0, 137.3, 137.0, 135.7, 131.0 (q, *J* = 2.0 Hz), 130.2 (q, *J* = 2.0 Hz), 129.2, 127.4, 124.2 (q, *J* = 339.3 Hz), 122.7, 121.1. IR (KBr): 3126, 3052, 3022, 1592, 1574, 1547, 1466, 1430, 1417, 1382, 1307, 1255, 1117, 1090, 1068, 1017, 855, 823, 792, 776, 701, 630 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{12}H_8ClF_3N^{78}Se]^+$ ($[M + H]^+$): 335.9465; found: 335.9472.

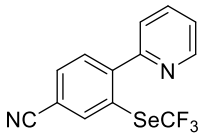
6-(2-((Trifluoromethyl)selanyl)phenyl)nicotinaldehyde (**3r**)



Procedure A: 28.5 mg, 43% yield. **Procedure B**: 31.8 mg, 48% yield. Light yellow solid, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. M.p.: 96.0-97.6 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.7 (s, 1H), 8.72 (dt, *J* = 4.8, 1.2 Hz, 1H), 8.34 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.92-7.85 (m, 3H), 7.37 (m, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.9 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.1, 155.2, 147.2, 143.6, 137.4, 136.7, 133.4 (q, *J* = 2.1 Hz), 130.0 (q, *J* =

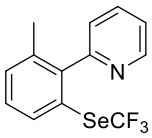
1.8 Hz), 129.0, 127.5, 124.2 (q, J = 339.3 Hz), 123.4, 121.9. IR (KBr): 3363, 3077, 3019, 1697, 1591, 1576, 1552, 1471, 1434, 1369, 1314, 1255, 1211, 1115, 1095, 1068, 1003, 866, 781, 746, 710, 631 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{13}H_9F_3NOSe]^+$ ([M + H]$^+$): 331.9796; found: 331.9801.

4-(Pyridin-2-yl)-3-((trifluoromethyl)selanyl)benzonitrile (**3s**)



Procedure A: 21.0 mg, 32% yield. **Procedure B**: 22.9 mg, 35% yield. Yellow solid, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. M.p.: 118.5-119.7 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (dm, J = 4.9 Hz, 1H), 8.15 (d, J = 0.8 Hz, 1H), 7.95-7.91 (m, 2H), 7.87 (dm, J = 8.0 Hz, 1H), 7.71 (dd, J = 8.1, 1.5 Hz, 1H), 7.42 (m, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -38.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.6, 147.2, 142.2, 137.6, 134.4, 130.5, 130.4, 128.7, 124.0 (q, J = 339.7 Hz), 123.6, 121.7, 117.9, 113.5. IR (KBr): 2231, 1590, 1574, 1468, 1428, 1387, 1259, 1201, 1144, 1126, 1093, 1071, 1019, 1001, 878, 835, 785, 719, 632 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{13}H_8F_3N_2{}^{78}Se]^+$ ([M + H]$^+$): 326.9807; found: 326.9809.

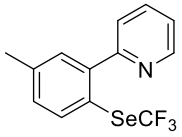
2-(2-Methyl-6-((trifluoromethyl)selanyl)phenyl)pyridine (**3u**)



Procedure A: 43.7 mg, 69% yield. **Procedure B**: 42.4 mg, 67% yield. Light yellow liquid, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (m, 1H), 7.78 (td, J = 7.7, 1.8 Hz, 1H), 7.74 (d, J = 7.5 Hz, 1H), 7.34 (d, J = 6.9 Hz, 1H), 7.32-7.29 (m, 3H), 2.17 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -35.7 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 149.2, 144.8, 137.6, 136.2, 133.9, 131.8, 129.0, 124.6, 124.4 (q, J = 1.2 Hz), 122.7 (q, J = 333.5 Hz), 122.5, 20.9. IR (KBr): 3057, 3002, 2961, 2928, 1591, 1567, 1477, 1449, 1436, 1419, 1382, 1281, 1121, 1094, 1065, 1027, 991, 842, 777, 749, 737, 662, 621 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{13}H_{11}F_3NSe]^+$ ([M + H]$^+$):

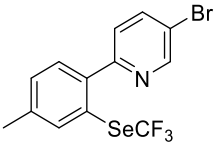
318.0003; found: 318.0012.

2-(5-Methyl-2-((trifluoromethyl)selanyl)phenyl)pyridine (**3v**)



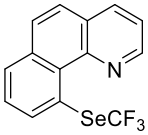
Procedure A: 46.9 mg, 74% yield. **Procedure B**: 45.0 mg, 71% yield. Light yellow liquid, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (dm, *J* = 4.8 Hz, 1H), 7.79 (td, *J* = 7.8, 1.7 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.58 (s, 1H), 7.27 (m, 1H), 7.22 (dd, *J* = 8.2, 1.4 Hz, 1H), 2.42 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.5 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 147.3, 139.7, 137.7, 136.9, 132.1 (q, *J* = 1.7 Hz), 130.5, 129.6, 124.1 (q, *J* = 1.6 Hz), 124.1 (q, *J* = 338.2 Hz), 122.3, 121.7, 21.0. IR (KBr): 3022, 2923, 1591, 1573, 1559, 1477, 1429, 1398, 1381, 1313, 1261, 1101, 1075, 1023, 1003, 960, 882, 812, 786, 744, 725, 645, 630 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{13}H_{11}F_3NSe]^+$ ($[M + H]^+$): 318.0003; found: 318.0000.

5-Bromo-2-(4-methyl-2-((trifluoromethyl)selanyl)phenyl)pyridine (**3w**)



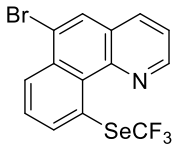
Procedure A: 56.0 mg, 71% yield. **Procedure B**: 58.5 mg, 74% yield. White solid, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. M.p.: 118.0-119.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, *J* = 2.1 Hz, 1H), 7.89 (m, 1H), 7.68 (s, 1H), 7.62-7.58 (m, 2H), 7.22 (d, *J* = 7.9 Hz, 1H), 2.43 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.2 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.6, 143.6, 135.5, 134.8, 131.1, 128.0 (q, *J* = 1.7 Hz), 123.9, 123.9, 122.8 (q, *J* = 1.6 Hz), 119.2 (q, *J* = 337.4 Hz), 117.9, 114.6, 16.6. IR (KBr): 3033, 2923, 1601, 1575, 1463, 1366, 1305, 1238, 1221, 1123, 1098, 1071, 1010, 910, 837, 810, 750, 725, 638 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{13}H_{10}BrF_3N^{82}Se]^+$ ($[M + H]^+$): 397.9110; found: 397.9110.

10-((Trifluoromethyl)selanyl)benzo[*h*]quinolone (**3x**)



Procedure A: 52.3 mg, 80% yield. **Procedure B**: 54.3 mg, 83% yield. Yellow solid, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. M.p.: 105.1-106.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 (dd, *J* = 4.5, 1.6 Hz, 1H), 8.20 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.69-7.64 (m, 2H), 7.55 (dd, *J* = 8.0, 4.5 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -40.4 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.7, 144.8, 135.5, 135.1, 129.4, 129.3 (q, *J* = 1.3 Hz), 128.6, 128.5, 127.3 (q, *J* = 2.5 Hz), 126.9, 126.2, 125.3 (q, *J* = 343.0 Hz), 125.2, 121.4. IR (KBr): 3047, 2924, 2854, 1621, 1586, 1561, 1496, 1464, 1445, 1420, 1408, 1332, 1194, 1153, 1106, 1086, 918, 891, 832, 817, 757, 711, 644 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{14}H_9F_3NSe]^+$ ($[M + H]^+$): 327.9847; found: 327.9854.

6-Bromo-10-((trifluoromethyl)selanyl)benzo[*h*]quinolone (**3y**)

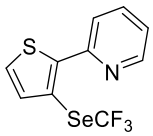


Procedure A: 42.9 mg, 53% yield. **Procedure B**: 42.0 mg, 52% yield. White solid, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. M.p.: 136.0-136.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.02 (m, 1H), 8.64 (m, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 7.7 Hz, 1H), 7.77 (m, 1H), 7.70-7.66 (m, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -40.4 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.0, 145.5, 135.5, 135.1, 131.6, 129.8 (q, *J* = 1.7 Hz), 129.2, 128.0, 127.8 (q, *J* = 2.6 Hz), 126.2, 125.4, 125.2 (q, *J* = 342.9 Hz), 122.2, 119.5. IR (KBr): 3023, 2923, 2853, 1597, 1560, 1482, 1417, 1400, 1261, 1217, 1208, 1091, 942, 893, 859, 794, 769, 716, 647 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{14}H_8BrF_3NSe]^+$ ($[M + H]^+$): 405.8952; found: 405.8953.

2-Methyl-10-((trifluoromethyl)selanyl)benzo[*h*]quinolone (**3z**)

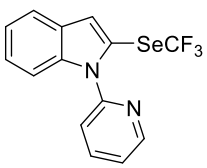
Procedure A: 27.9 mg, 41% yield. **Procedure B**: 29.2 mg, 43% yield. Light yellow solid, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. M.p.: 115.3-117.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 2.89 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -40.6 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.4, 145.1, 135.8, 135.2, 129.3 (q, *J* = 1.7 Hz), 128.6, 128.3, 127.4, 127.1 (q, *J* = 2.6 Hz), 126.1, 125.4 (q, *J* = 344.6 Hz), 125.1, 124.8, 122.0, 23.5. IR (KBr): 3044, 2955, 2924, 2854, 1622, 1608, 1589, 1561, 1509, 1495, 1446, 1371, 1261, 1209, 1143, 1118, 1109, 1090, 920, 840, 816, 758, 714 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{15}H_{11}F_3NSe]^+$ ($[M + H]^+$): 342.0003; found: 342.0013.

2-(3-((Trifluoromethyl)selanyl)thiophen-2-yl)pyridine (**3aa**)



Procedure A: 40.1 mg, 65% yield. **Procedure B**: 49.4 mg, 80% yield. Light yellow oil, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.8 Hz, 1H), 7.73 (td, *J* = 7.7, 1.6 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 5.3 Hz, 1H), 7.28 (d, *J* = 5.3 Hz, 1H), 7.17 (m, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.9 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.7, 147.7, 137.0, 136.1 (q, *J* = 1.1 Hz), 129.9 (q, *J* = 2.2 Hz), 126.7, 124.2 (q, *J* = 337.8 Hz), 121.6 (q, *J* = 1.4 Hz), 121.4, 120.3. IR (KBr): 3099, 3010, 2928, 1589, 1567, 1499, 1472, 1440, 1293, 1265, 1172, 1153, 1102, 1009, 987, 876, 779, 738, 712, 621 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{10}H_7F_3NSSe]^+$ ($[M + H]^+$): 309.9411; found: 309.9416.

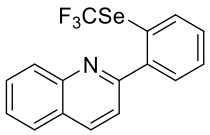
1-(Pyridin-2-yl)-2-((trifluoromethyl)selanyl)-1*H*-indole (**3ab**)



Procedure A: 30.0 mg, 44% yield. **Procedure B**: 15.6 mg, 23% yield. Light yellow oil, a mixture of petroleum ether/dichloromethane/trichloromethane = 10/5/1 (v/v/v)

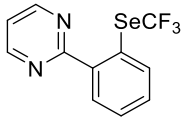
as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.5 Hz, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 8.06 (s, 1H), 7.89 (t, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.40-7.34 (m, 2H), 7.28-7.26 (m, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -36.9 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.4, 149.3, 138.7, 135.5, 134.4, 132.0, 124.3, 122.6, 122.2 (q, *J* = 335.6 Hz), 121.3, 120.5, 115.2, 113.0, 96.3 (q, *J* = 1.6 Hz). IR (KBr): 3146, 3054, 3021, 2925, 1592, 1580, 1519, 1471, 1437, 1362, 1342, 1318, 1229, 1148, 1093, 1016, 773, 759, 746, 732, 645 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{14}H_{10}F_3N_2Se]^+$ ($[M + H]^+$): 342.9956; found: 342.9968.

2-(2-((Trifluoromethyl)selanyl)phenyl)quinolone (**5a**)



Procedure A: 23.3 mg, 33% yield. **Procedure B**: 14.8 mg, 21% yield. White solid, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. M.p.: 92.5-94.5 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.7 Hz, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 7.98-7.94 (m, 2H), 7.90 (d, *J* = 8.6 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.78 (tm, *J* = 7.0 Hz, 1H), 7.59 (tm, *J* = 7.0 Hz, 1H), 7.48-7.43 (m, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -38.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.1, 146.0, 138.6, 137.4, 131.3 (q, *J* = 2.0 Hz), 130.4, 130.0, 129.0, 128.3, 127.7, 127.2, 127.1, 126.9, 124.5 (q, *J* = 339.4 Hz), 118.9. IR (KBr): 3056, 2924, 1618, 1601, 1578, 1508, 1467, 1439, 1426, 1323, 1278, 1146, 1118, 1086, 1044, 1025, 1012, 966, 816, 758, 744, 710, 650 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{16}H_{11}F_3NSe]^+$ ($[M + H]^+$): 354.0003; found: 354.0009.

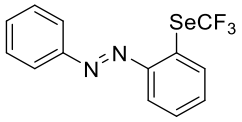
2-(2-((Trifluoromethyl)selanyl)phenyl)pyrimidine (**5b**)



Procedure A: 13.4 mg, 22% yield. **Procedure B**: 10.3 mg, 17% yield. **Procedure C**: 33.4 mg, 55% yield. White solid, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. M.p.: 59.1-60.4 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (d, *J* = 4.9 Hz, 2H), 8.56 (dd, *J* = 7.3, 2.2 Hz, 1H), 7.85 (d, *J* = 7.4 Hz, 1H), 7.48-7.42 (m, 2H), 7.25 (t, *J* = 4.9 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -38.3

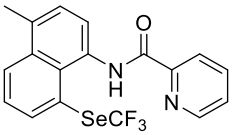
(s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.4, 156.1, 135.9, 131.4, 130.7, 130.3 (q, *J* = 1.6 Hz), 130.1 (q, *J* = 2.3 Hz), 127.0, 124.4 (q, *J* = 338.8 Hz), 119.0. IR (KBr): 3044, 2927, 2855, 1713, 1571, 1553, 1449, 1418, 1262, 1247, 1107, 1083, 1025, 814, 802, 752, 727, 648, 630 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{11}H_8F_3N_2Se]^+$ ($[M + H]^+$): 304.9799; found: 304.9808.

1-Phenyl-2-(2-((trifluoromethyl)selanyl)phenyl)diazene (**5c**)



Procedure A: 21.8 mg, 33% yield. **Procedure B**: 13.8 mg, 21% yield. **Procedure C**: 29.0 mg, 44% yield. Orange oil, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.98-7.95 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.56-7.50 (m, 4H), 7.45 (td, *J* = 8.0, 1.6 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -38.0 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.8, 150.4, 131.9, 131.5, 130.2 (q, *J* = 2.1 Hz), 129.4, 129.2, 127.7, 124.1 (q, *J* = 1.5 Hz), 123.8 (q, *J* = 340.9 Hz), 122.8. IR (KBr): 3065, 2926, 1587, 1561, 1476, 1455, 1445, 1300, 1270, 1230, 1101, 1055, 1030, 920, 861, 769, 728, 714, 684 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{13}H_{10}F_3N_2Se]^+$ ($[M + H]^+$): 330.9956; found: 330.9959.

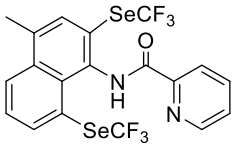
N-(4-Methyl-8-((trifluoromethyl)selanyl)naphthalen-1-yl)picolinamide (**5d**)



Procedure A (36 h): 11.3 mg, 14% yield. **Procedure C**: 8.3 mg, 10% yield. Light yellow solid, a mixture of petroleum ether/ethyl acetate = 10/1 (v/v) as eluents for column chromatography. M.p.: 116.3-117.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.85 (s, 1H), 8.71 (d, *J* = 3.8 Hz, 1H), 8.31 (d, *J* = 7.8 Hz, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 8.05 (d, *J* = 7.1 Hz, 1H), 7.93 (td, *J* = 7.6, 1.1 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.53-7.46 (m, 3H), 2.74 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.0 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.3, 150.1, 148.3, 139.0, 137.5, 135.0, 134.2, 130.8, 129.5, 128.0, 127.4, 126.5, 126.4, 125.5, 122.9 (q, *J* = 334.2 Hz), 122.8, 118.1, 20.3. IR (KBr): 3295, 3083, 2966, 2924, 2852, 1681, 1591, 1572, 1521, 1496, 1430, 1335,

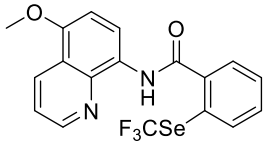
1268, 1134, 1102, 1055, 833, 811, 762, 745, 692, 622 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{18}H_{14}F_3N_2OSe]^+$ ($[M + H]^+$): 411.0218; found: 411.0226.

N-(4-Methyl-2,8-bis((trifluoromethyl)selanyl)naphthalen-1-yl)picolinamide (**5d'**)



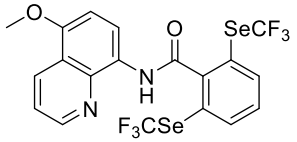
Procedure A (36 h): 12.1 mg, 11% yield. **Procedure C**: 11.1 mg, 10% yield. Light yellow solid, a mixture of petroleum ether/ethyl acetate = 10/1 (v/v) as eluents for column chromatography. M.p.: 118.1-119.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.52 (s, 1H), 8.77 (d, *J* = 4.6 Hz, 1H), 8.29 (d, *J* = 7.8 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 7.3 Hz, 1H), 7.95 (td, *J* = 7.7, 1.4 Hz, 1H), 7.89 (s, 1H), 7.58-7.53 (m, 2H), 2.76 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -34.9 (s, 3F), 36.9 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5, 148.9, 148.6, 137.6, 136.7, 136.2, 135.9, 133.8, 133.6, 131.4, 127.2, 127.0, 126.9, 124.7 (q, *J* = 1.1 Hz), 123.1, 122.9 (q, *J* = 334.9 Hz), 122.9 (q, *J* = 333.7 Hz), 121.2 (q, *J* = 1.0 Hz), 20.2. IR (KBr): 3264, 3059, 2954, 2928, 2854, 1678, 1591, 1572, 1483, 1464, 1429, 1171, 1141, 1109, 999, 869, 828, 796, 753, 697, 682, 620 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{19}H_{13}F_6N_2OSe_2]^+$ ($[M + H]^+$): 558.9257; found: 558.9260.

N-(5-Methoxyquinolin-8-yl)-2-((trifluoromethyl)selanyl)benzamide (**5e**)[15]



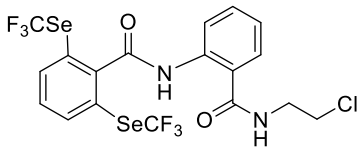
Procedure A (36 h): 26.4 mg, 31% yield. **Procedure C**: 11.1 mg, 13% yield. White solid, a mixture of petroleum ether/ethyl acetate = 10/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.5 (s, 1H), 8.33 (d, *J* = 4.0 Hz, 1H), 8.77 (d, *J* = 8.5 Hz, 1H), 8.60 (dm, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 7.5 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.54-7.45 (m, 3H), 6.87 (d, *J* = 8.6 Hz, 1H), 4.01 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -36.8 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.3, 149.9, 147.9, 138.3, 133.7, 131.0, 130.5 (q, *J* = 2.0 Hz), 130.4, 129.0 (q, *J* = 1.4 Hz), 126.6, 126.4, 126.3, 122.8 (q, *J* = 335.7 Hz), 119.9, 119.5, 116.0, 103.2, 54.8.

N-(5-Methoxyquinolin-8-yl)-2,6-bis((trifluoromethyl)selanyl)benzamide (**5e'**)[15]



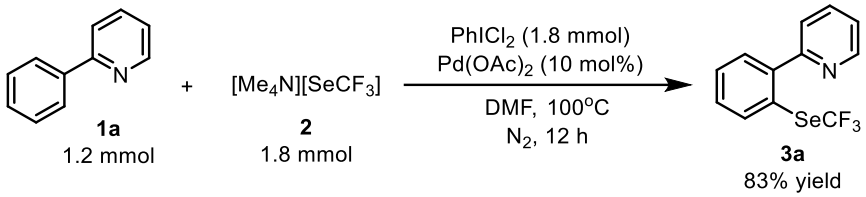
Procedure A (36 h): 24.1 mg, 21% yield. **Procedure C**: 25.2 mg, 22% yield. Light yellow solid, a mixture of petroleum ether/ethyl acetate = 10/1 (v/v) as eluents for column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.82 (d, *J* = 8.6 Hz, 1H), 8.75 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.60 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.80 (d, *J* = 7.9 Hz, 2H), 7.51 (t, *J* = 7.9 Hz, 1H), 7.44 (dd, *J* = 8.4, 4.2 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -35.2 (s, 6F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.8, 151.2, 148.9, 139.5, 139.3, 131.2, 130.9, 127.2, 122.3 (q, *J* = 334.4 Hz), 122.1, 122.1, 120.9, 120.6, 117.4, 104.2, 55.9.

N-(2-((2-Chloroethyl)carbamoyl)phenyl)-2,6-bis((trifluoromethyl)selanyl)benzamide (**5f**)



Procedure A: 43.1 mg, 36% yield. **Procedure B**: 44.2 mg, 37% yield. **Procedure D**: 56.2 mg, 47% yield. White solid, a mixture of petroleum ether/dichloromethane = 3/1 (v/v) as eluents for column chromatography. M.p.: 179.5-181.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.22 (s, 1H), 8.71 (d, *J* = 8.3 Hz, 1H), 7.96 (d, *J* = 7.9 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.69 (s, 1H), 3.73 (m, 2H), 3.67 (t, *J* = 5.0 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -35.1 (s, 6F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.8, 165.4, 149.1, 139.8, 138.5, 133.1, 130.9, 126.7, 124.0, 122.3 (q, *J* = 333.7 Hz), 122.1, 121.5, 120.9, 43.5, 41.6. IR (KBr): 3310, 3168, 3106, 2987, 2913, 2845, 1635, 1603, 1540, 1492, 1444, 1364, 1326, 1302, 1290, 1271, 1256, 1195, 1188, 1126, 1100, 941, 915, 863, 783, 755, 737, 693, 667 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{18}H_{14}ClF_6N_2O_2Se_2]^+$ ($[M + H]^+$): 598.8973; found: 598.8977.

An example of the scale-up C-H trifluoromethylselenolation.

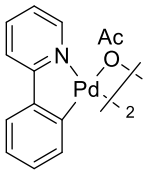


In a nitrogen-filled glovebox, a sealed round-bottom flask was charged with 2-phenylpyridine (**1a**, 186.2 mg, 1.2 mmol), $[Me_4N][SeCF_3]$ (**2**, 398.7mg, 1.8 mmol), $Pd(OAc)_2$ (27.0 mg, 0.12 mmol), and DMF (6 mL) with stirring. Then a DMF (6 mL) solution of $PhICl_2$ (492.9 mg, 1.8 mmol) was added. The mixture was reacted at 100 °C for 12 h, cooled to room temperature, quenched with H_2O, and diluted with ethyl acetate (60 mL). The organic solution was washed with H_2O (3 × 20 mL), dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether/dichloromethane (3/1 (v/v)) as eluents to give 300.5 mg (83% yield) of **3a** as a light yellow oil.

4. Control experiments for mechanistic insights

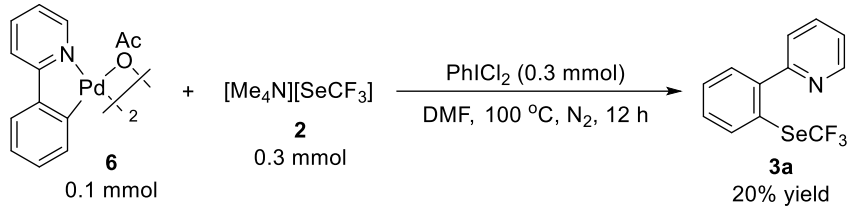
4.1. Synthesis of 2-phenylpyridyl palladium acetate dimer (6)[16]

To a solution of 2-phenylpyridine (**1a**, 0.346 g, 2.23 mmol) in CH_2Cl_2 (22 mL) was added $Pd(OAc)_2$ (0.50 g, 2.23 mmol) with vigorous stirring. The mixture was reacted at room temperature for 3 h and concentrated to dryness under reduced pressure. The residue was washed with ethyl ether (3 × 5 mL) and dried under vacuum to afford the title compound as an orange-yellow solid (0.7 g, 99% yield).



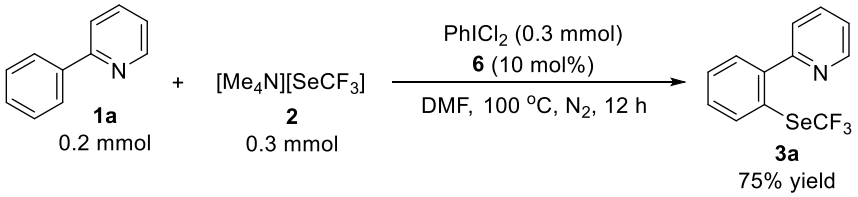
2-Phenylpyridyl palladium acetate dimer (**6**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 5.4 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 7.3 Hz, 2H), 6.87-6.79 (m, 6H), 6.45 (t, *J* = 6.6 Hz, 2H), 2.26 (s, 6H).

4.2. Trifluoromethylselenolation of 6 with 2 under the standard conditions



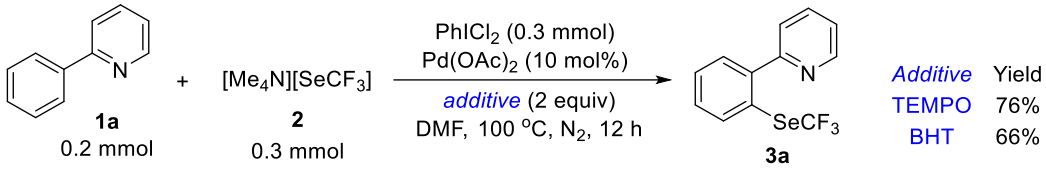
In a nitrogen-filled glovebox, a sealed tube was charged with compound **6** (64.0 mg, 0.1 mmol), $[Me_4N][SeCF_3]$ (**2**, 66.6 mg, 0.3 mmol), and DMF (1 mL) with stirring. Then a DMF (1 mL) solution of $PhICl_2$ (82.5 mg, 0.3 mmol) was added. The mixture was reacted at 100°C for 12 h, cooled to room temperature, quenched with H_2O, and diluted with ethyl acetate (20 mL). The organic solution was washed with H_2O (3 × 10 mL), dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether/dichloromethane (3/1 (v/v)) as eluents to give 12.1 mg (20% yield) of **3a** as a light yellow oil.

4.3. C-H Trifluoromethylselenolation of 1a with 2 in the presence of 6 under the standard conditions



In a nitrogen-filled glovebox, a sealed tube was charged with 2-phenylpyridine (**1a**, 31.4 mg, 0.2 mmol), $[Me_4N][SeCF_3]$ (**2**, 66.6 mg, 0.3 mmol), compound **6** (12.8 mg, 0.02 mmol), and DMF (1 mL) with stirring. Then a DMF (1 mL) solution of $PhICl_2$ (82.5 mg, 0.3 mmol) was added. The mixture was reacted at 100°C for 12 h, cooled to room temperature, quenched with H_2O, and diluted with ethyl acetate (20 mL). the organic solution was washed with H_2O (3 × 10 mL), dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether/dichloromethane (3/1 (v/v)) as eluents to give 45.5 mg (75% yield) of **3a** as a light yellow oil.

4.4. Pd-Catalyzed C-H trifluoromethylselenolation of 1a with 2 in the presence of radical traps under the standard conditions



In a nitrogen-filled glovebox, a sealed tube was charged with 2-phenylpyridine (**1a**, 31.4 mg, 0.2 mmol), $[Me_4N][SeCF_3]$ (**2**, 66.6 mg, 0.3 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO, 62.5 mg, 0.40 mmol) or 2,6-di-*tert*-butyl-4-methylphenol (BHT, 88.1 mg, 0.4 mmol), and DMF (1 mL) with stirring. Then a DMF (1 mL) solution of $PhICl_2$ (82.5 mg, 0.3 mmol) was added. The mixture was reacted at 100 °C for 12 h, cooled to room temperature, quenched with H_2O, and diluted with ethyl acetate (20 mL). The organic solution was washed with H_2O (3 × 10 mL), dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of petroleum ether/dichloromethane (3/1 (v/v)) as eluents to give 46.1 mg (TEMPO, 76% yield) or 40.1 mg (BHT, 66%) of **3a** as a light yellow oil.

4.5. ^{19}F NMR analyses of the standard reaction mixtures at different times.

Procedure: In a nitrogen-filled glovebox, a sealed tube was charged with 2-phenylpyridine (**1a**, 0.2 mmol), $[Me_4N][SeCF_3]$ (**2a**, 0.3 mmol), $Pd(OAc)_2$ (0.02 mmol), and DMF (1 mL) with stirring. Then a DMF (1 mL) solution of $PhICl_2$ (0.3 mmol) was added. The mixture was reacted at 100 °C for 1 h, 2 h, 4 h, 8 h, or 12 h and analyzed by ^{19}F NMR using $PhOCF_3$ as an internal standard.

Figure 1. ^{19}F NMR spectrum of the standard reaction mixture for 1 h (24.8 mg of $PhOCF_3$ (0.153 mmol) was used as an internal standard)

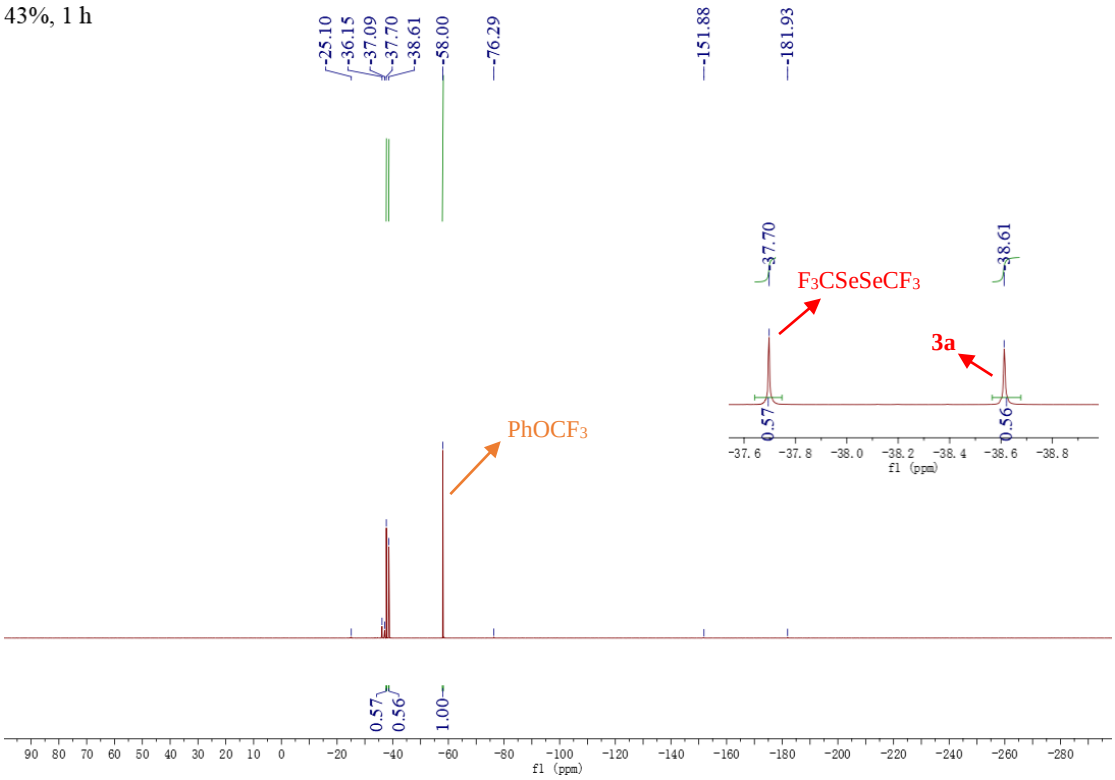


Figure 2. ^{19}F NMR spectrum of the standard reaction mixture for 2 h (24.5 mg of $PhOCF_3$ (0.151 mmol) was used as an internal standard)

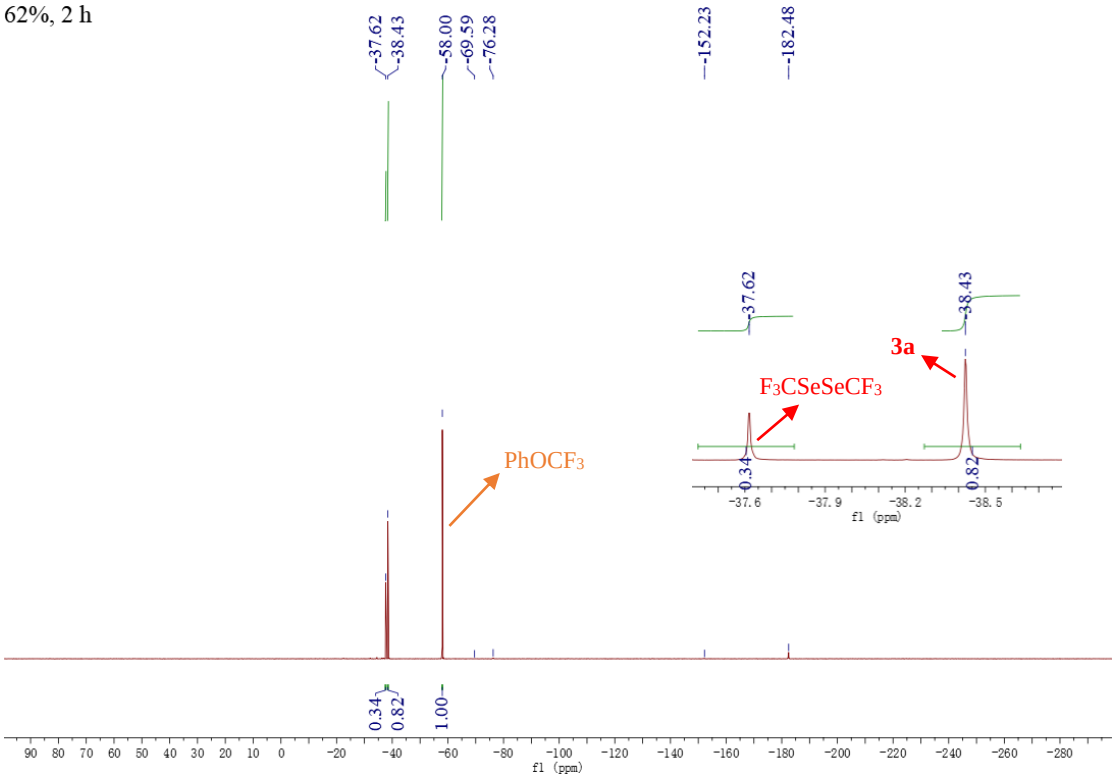


Figure 3. ^{19}F NMR spectrum of the standard reaction mixture for 4 h (25.1 mg of

$PhOCF_3$ (0.155 mmol) was used as an internal standard)

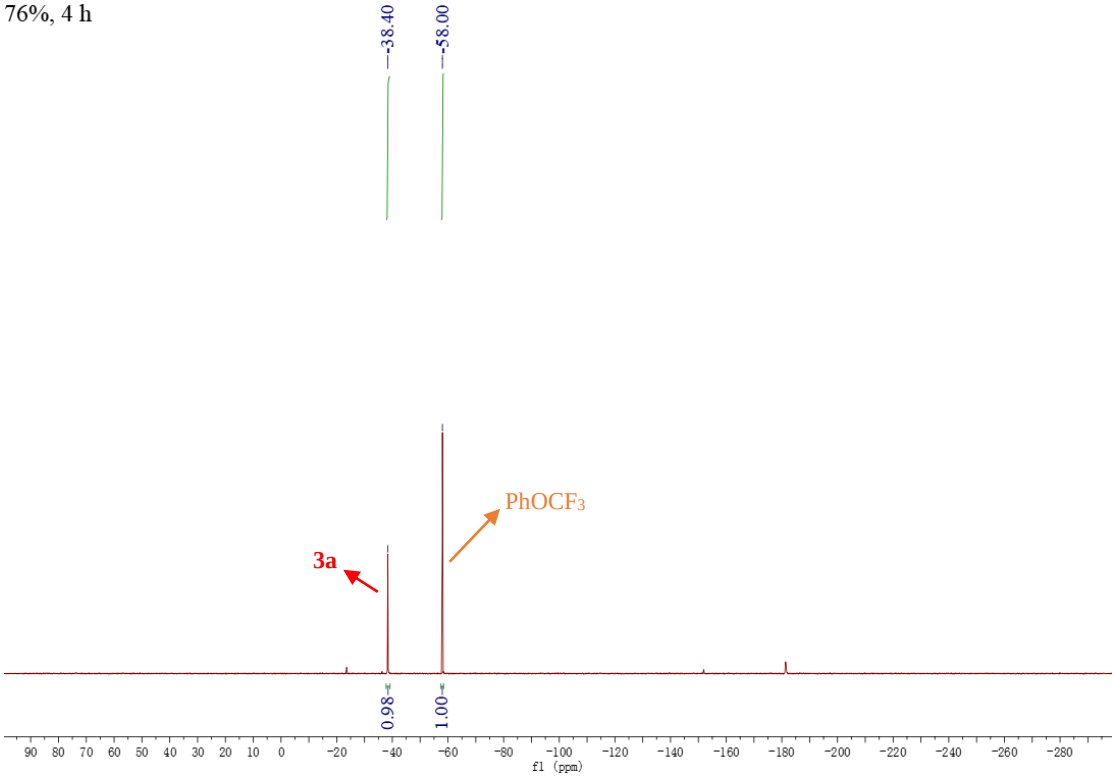


Figure 4. ^{19}F NMR spectrum of the standard reaction mixture for 8 h (25.9 mg of $PhOCF_3$ (0.160 mmol) was used as an internal standard)

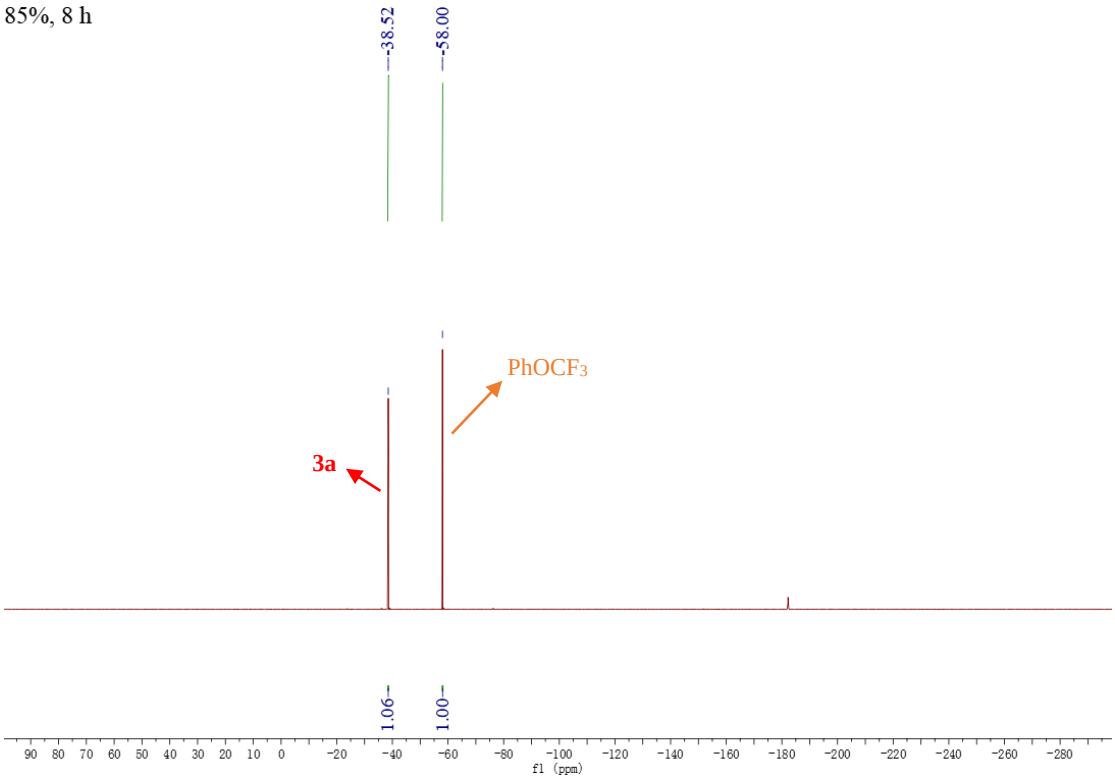


Figure 5. ^{19}F NMR spectrum of the standard reaction mixture for 12 h (23.2 mg of $PhOCF_3$ (0.143 mmol) was used as an internal standard)

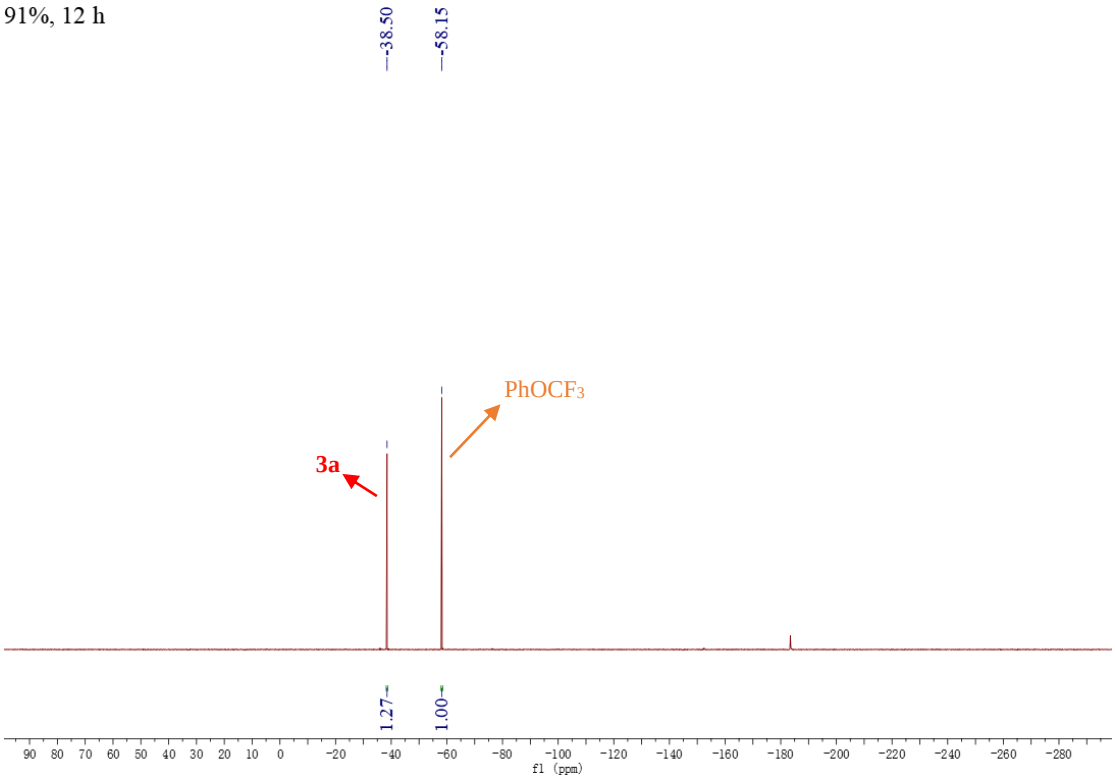
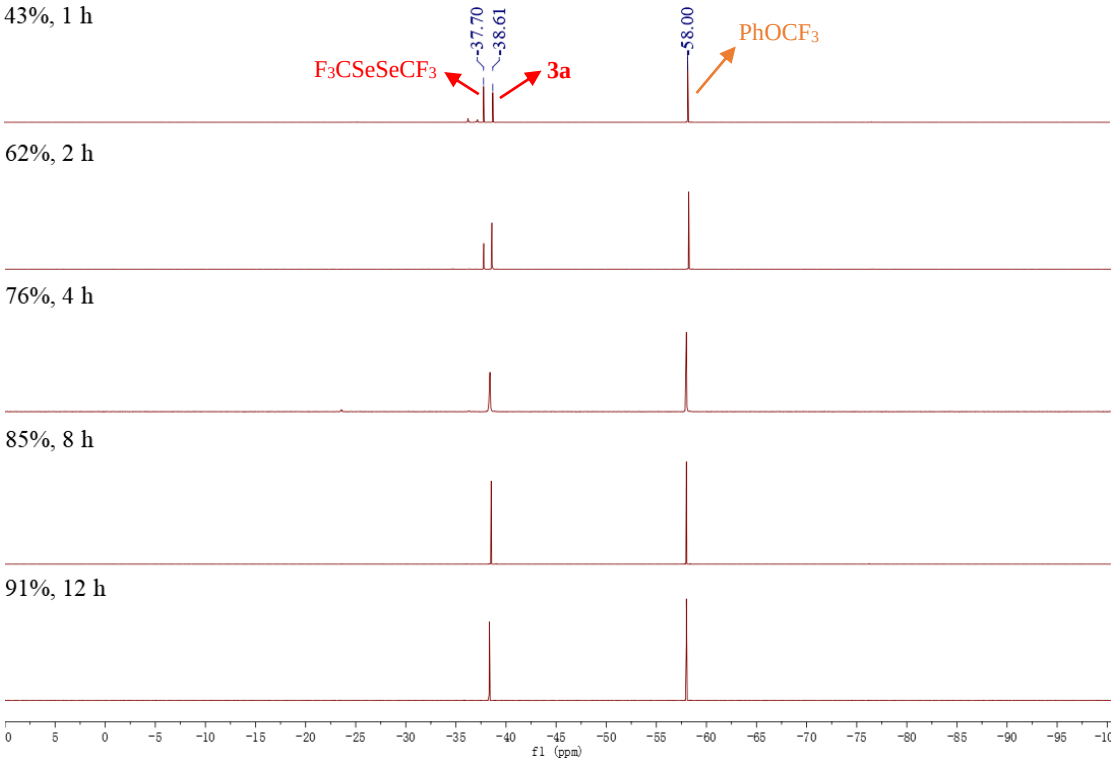
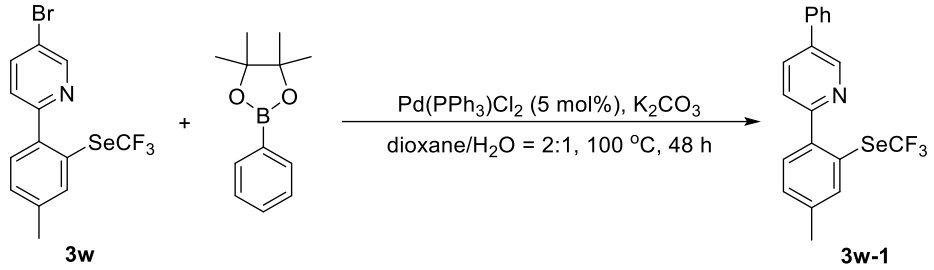


Figure 6. The combination of ^{19}F NMR spectra in **Figures 1-5**

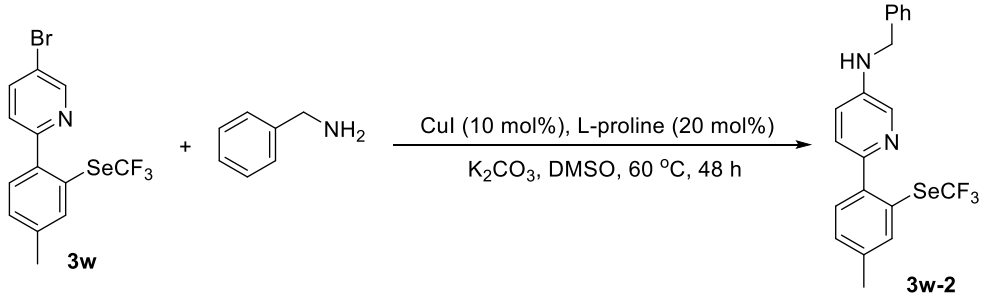


5. Second functionalization of the product.

Using **3w** as an example (The below reaction conditions were not fully optimized)



Procedure: Under a N_2 atmosphere, an oven-dried Schlenk flask was charged with 5-bromo-2-(4-methyl-2-((trifluoromethyl)selanyl)phenyl)pyridine (**3w**, 39.5 mg, 0.1 mmol), $Pd(PPh_3)_2Cl_2$ (3.5 mg, 0.005mmol), K_2CO_3 (27.6 mg, 0.2 mmol), phenylboronic acid pinacol ester (26.5 mg, 0.13 mmol), dioxane (0.8 mL), and H_2O (0.4 ml) with stirring. The mixture was reacted at 100 °C for 48 h, cooled to room temperature, and concentrated under the reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether/ethyl acetate = 20/1 (v/v) as eluents to give 20.0 mg of 2-(4-methyl-2-((trifluoromethyl) selanyl)phenyl)-5-phenylpyridine (**3w-1**) as a light yellow solid (50% yield). M.p.: 85.2-86.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.89 (d, *J* = 1.8 Hz, 1H), 8.00 (dd, *J* = 8.3, 2.3 Hz, 1H). 7.82 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.69 (s, 1H), 7.64 (m, 2H), 7.51 (t, *J* = 7.3 Hz, 2H), 7.43 (m, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 2.44 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.7 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.3, 145.3, 139.9, 137.2, 135.9, 135.4, 135.1, 132.1, 129.2, 128.4, 128.3, 128.3, 128.2, 127.1, 126.9 (q, *J* = 336.1 Hz), 121.1, 21.4. IR (KBr): 3063, 3028, 2959, 2923, 2852, 1646, 1595, 1468, 1447, 1368, 1262, 1107, 1076, 1017, 1005, 971, 848, 822, 773, 750, 728, 714, 695 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{19}H_{15}F_3NSe]^+$ ($[M + H]^+$): 394.0316; found: 394.0323.



Procedure: In a nitrogen-filled glovebox, a tube was charged with

5-bromo-2-(4-methyl-2-((trifluoromethyl)selanyl)phenyl)pyridine (**3w**, 39.5 mg, 0.1 mmol), *L*-proline (2.3 mg, 0.02 mmol), CuI (2.0 mg, 0.01 mmol), K_2CO_3 (27.6 mg, 0.2 mmol), phenylmethanamine (16.1 mg, 0.15 mmol), and DMSO (1 mL) with stirring. The mixture was reacted at 60 °C for 48 h, cooled to room temperature, quenched with H_2O, and diluted with ethyl acetate (5 mL). The organic solution was washed with H_2O (3 × 5 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 a mixture of petroleum ether/ethyl acetate = 5/1 (v/v) as eluents to give 13.3 mg of *N*-benzyl-6-(4-methyl-2-((trifluoromethyl)selanyl)phenyl)pyridin-3-amine (**3w-2**) as a light yellow liquid (31% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 2.7 Hz, 1H), 7.60 (s, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.53 (d, *J* = 8.7 Hz, 1H), 7.38 (m, 4H), 7.32 (m, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.00 (dd, *J* = 8.6, 2.8 Hz, 1H), 4.41 (d, *J* = 5.2 Hz, 2H), 4.25 (brs, 1H), 2.39 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -37.7 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2, 142.9, 138.3, 138.2, 136.5, 132.3, 131.7, 128.9, 128.1, 127.7, 127.4, 127.4, 127.1 (q, *J* = 1.2 Hz), 124.3 (q, *J* = 332.8 Hz), 121.5, 120.1, 47.9, 21.3. IR (KBr): 3355, 3028, 2922, 2852, 1594, 1572, 1555, 1500, 1489, 1464, 1386, 1300, 1215, 1124, 1092, 1025, 1005, 921, 876, 839, 820, 756, 708, 639 cm^{-1}. HRMS-ESI (m/z) calcd. for $[C_{20}H_{18}F_3N_2Se]^+$ ($[M + H]^+$): 423.0582; found: 423.0593.

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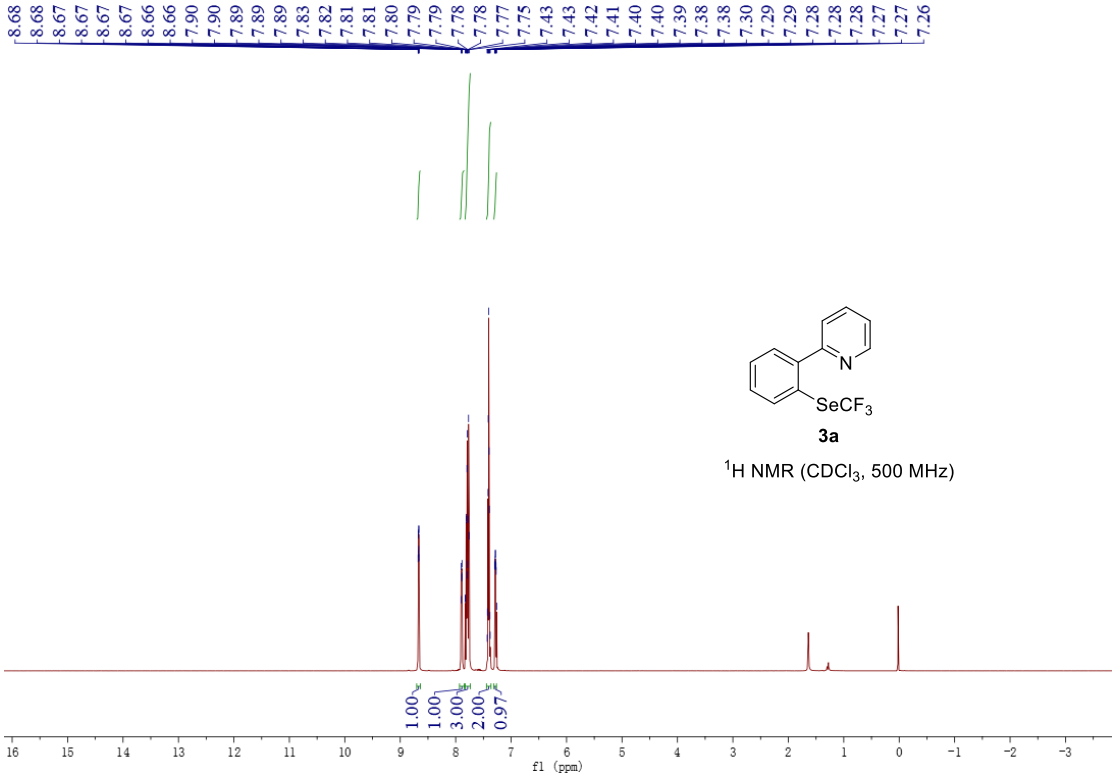
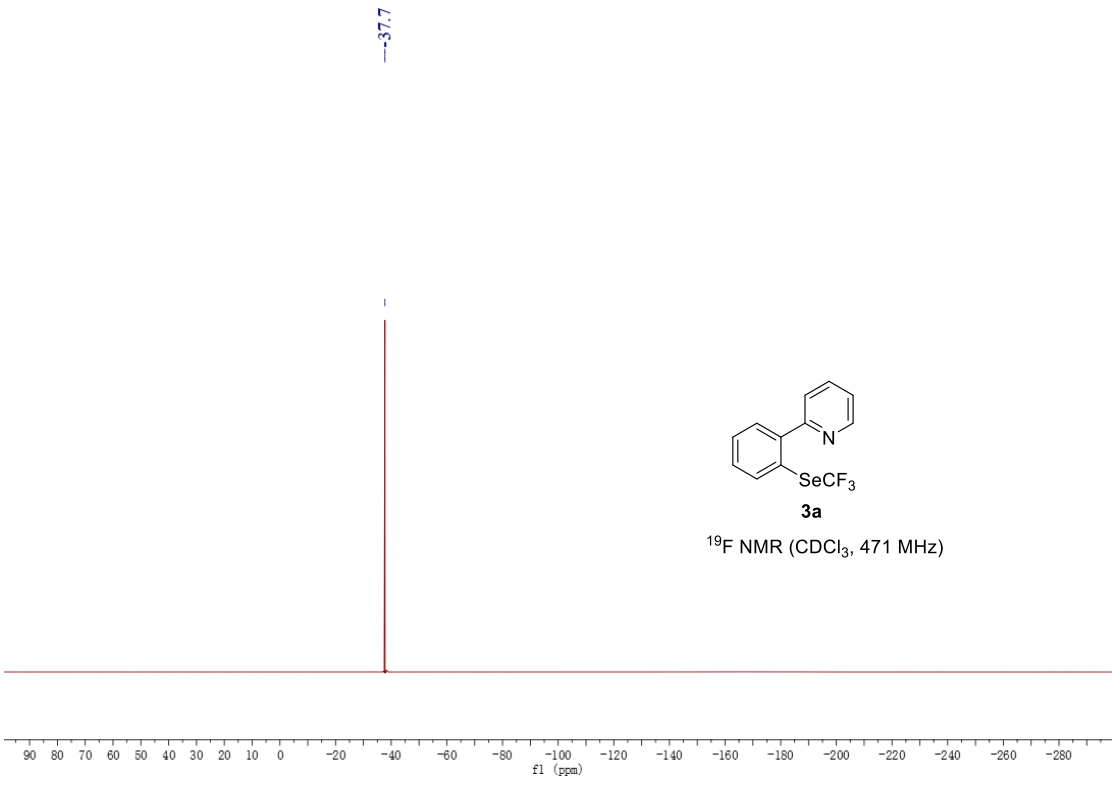
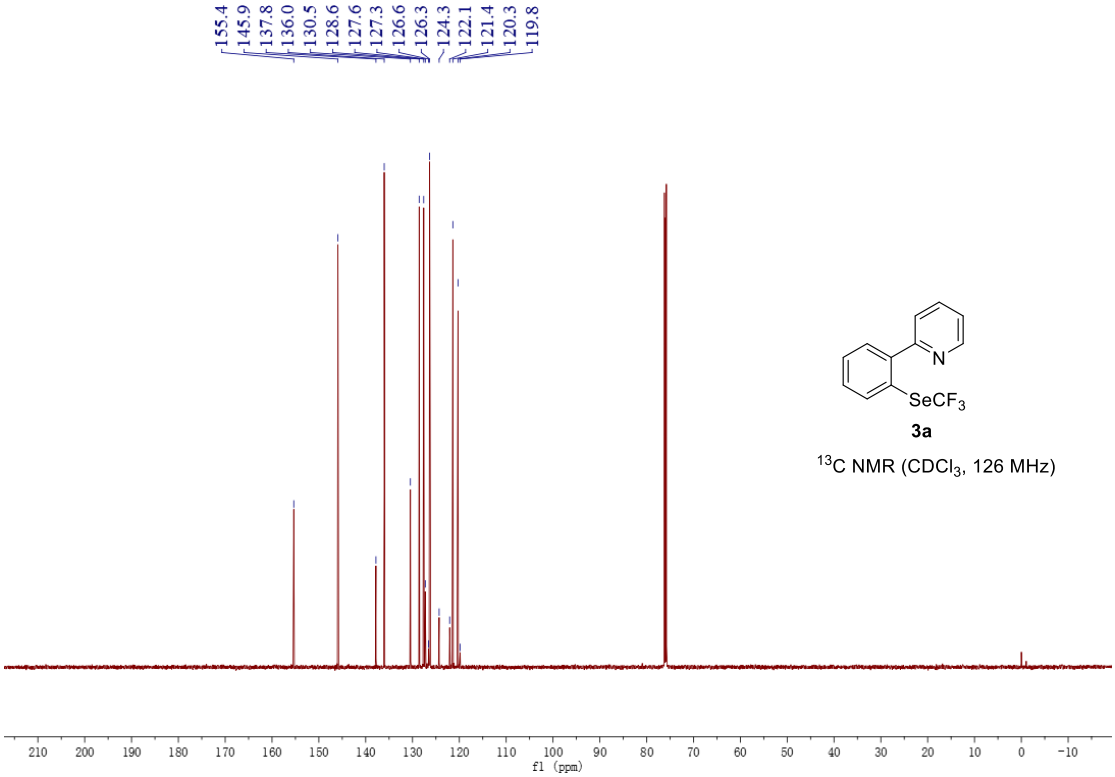
6. NMR spectra of the products

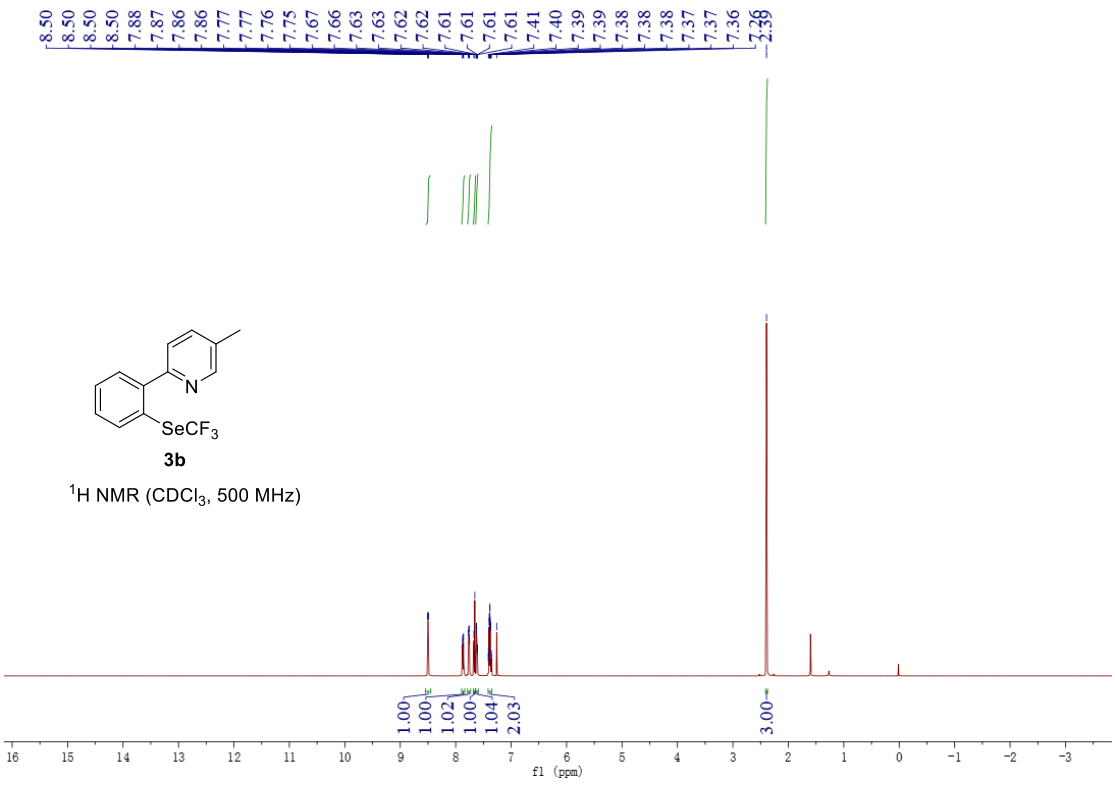






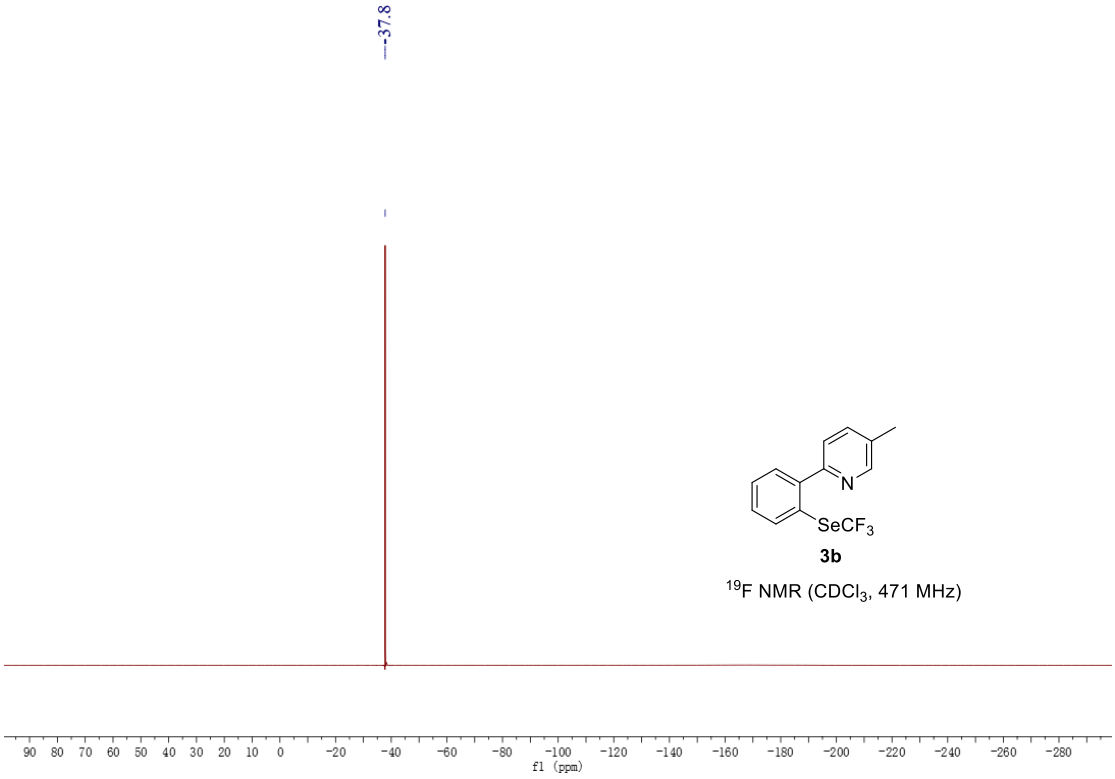
3a

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



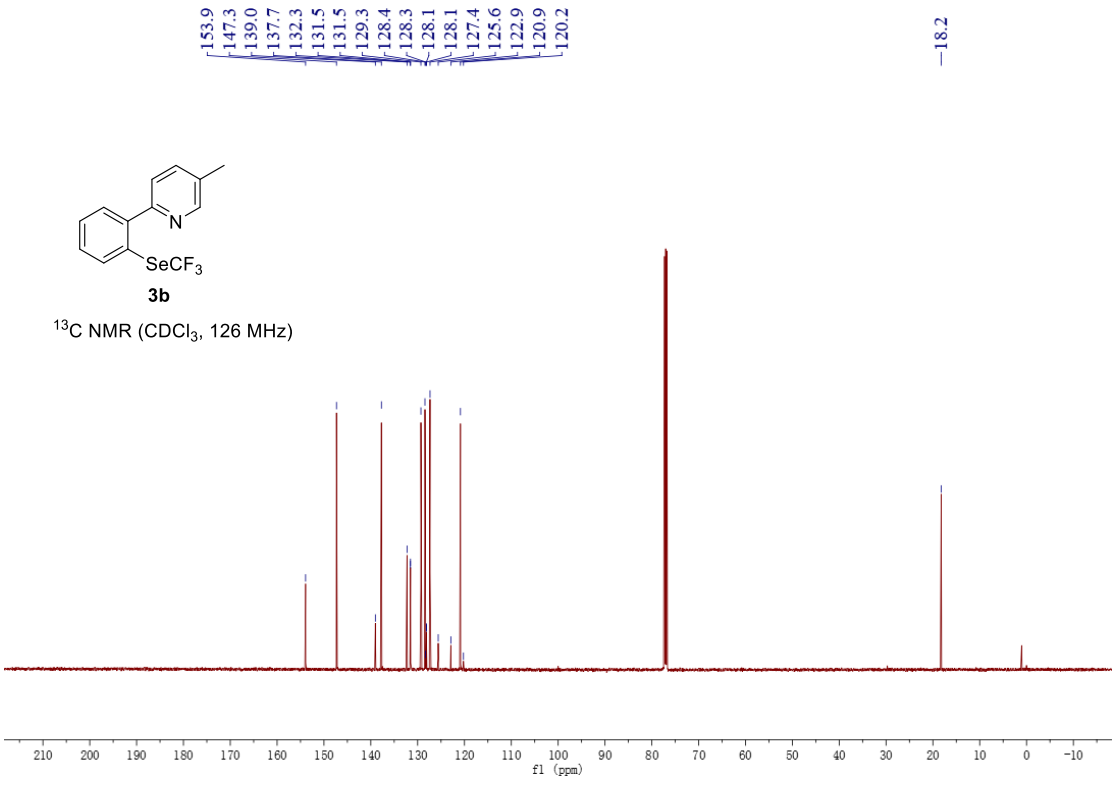
3b

^{1}H NMR ($CDCl_3$, 500 MHz)



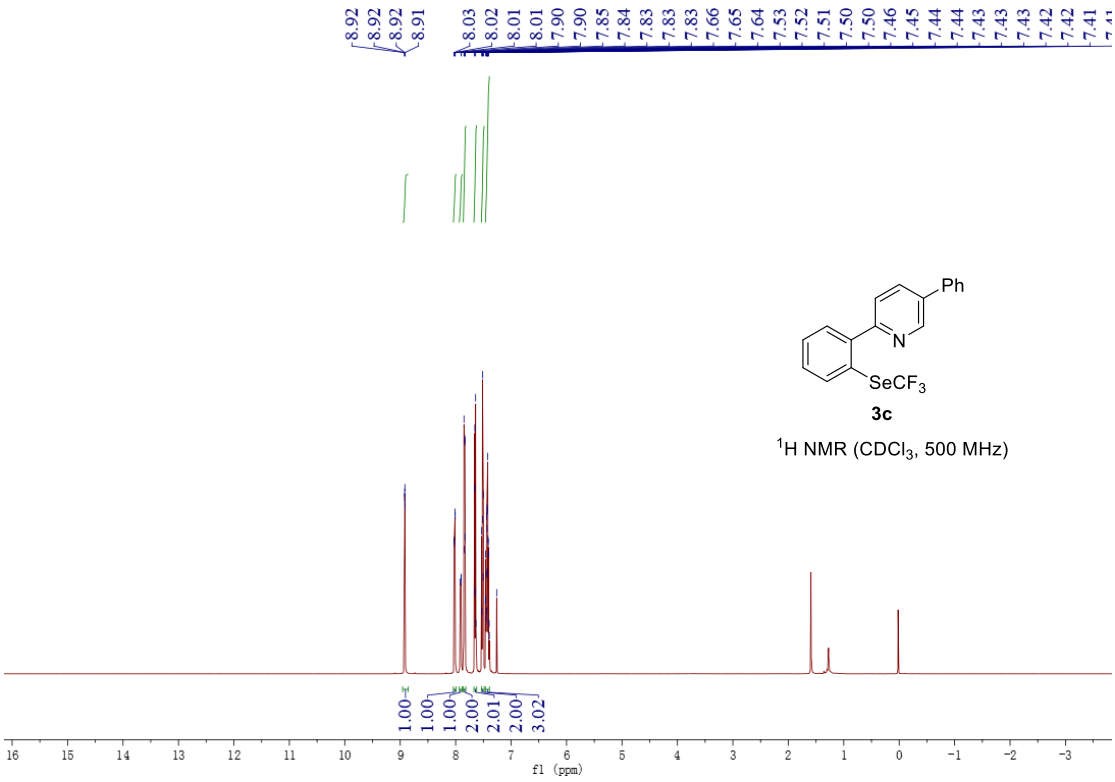
3b

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



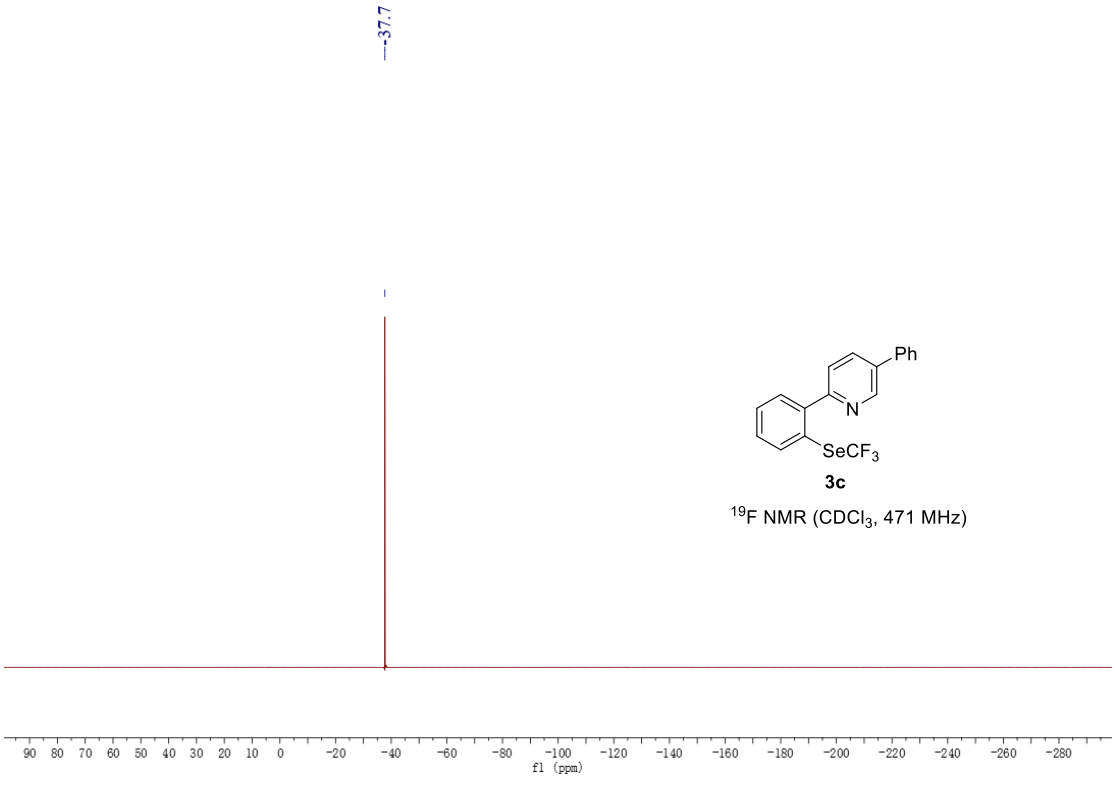
3b

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



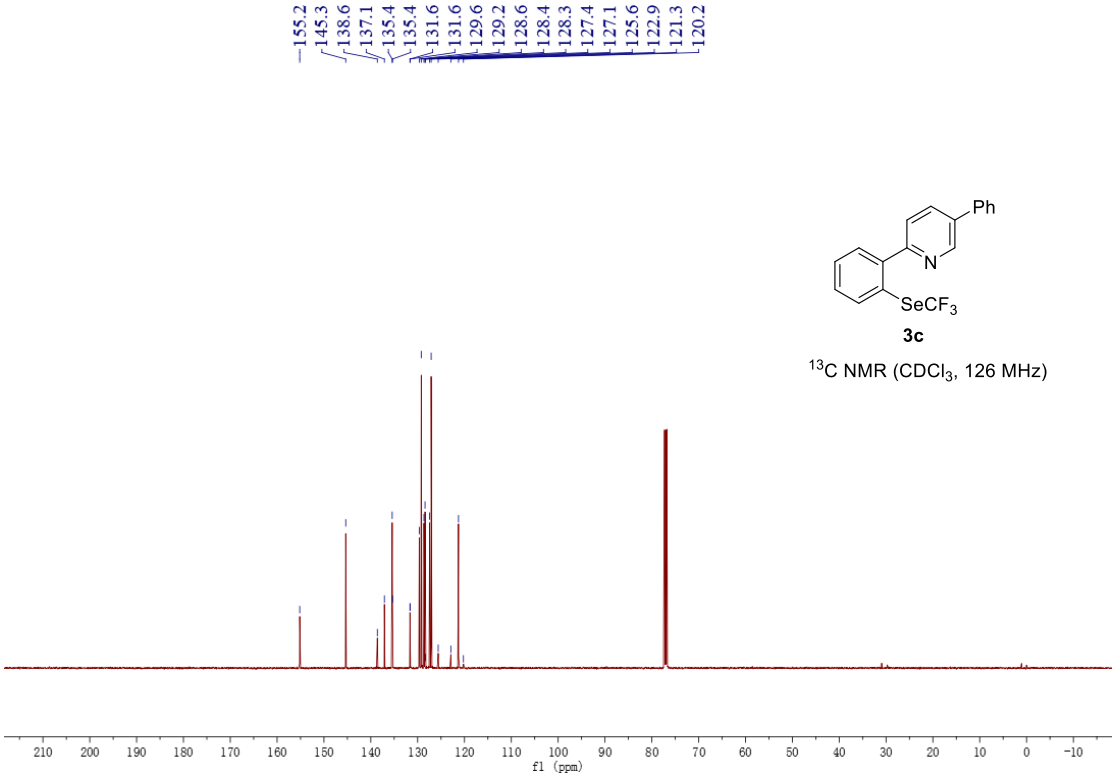
3c

^{1}H NMR ($CDCl_3$, 500 MHz)



3c

^{19}F NMR ($CDCl_3$, 471 MHz)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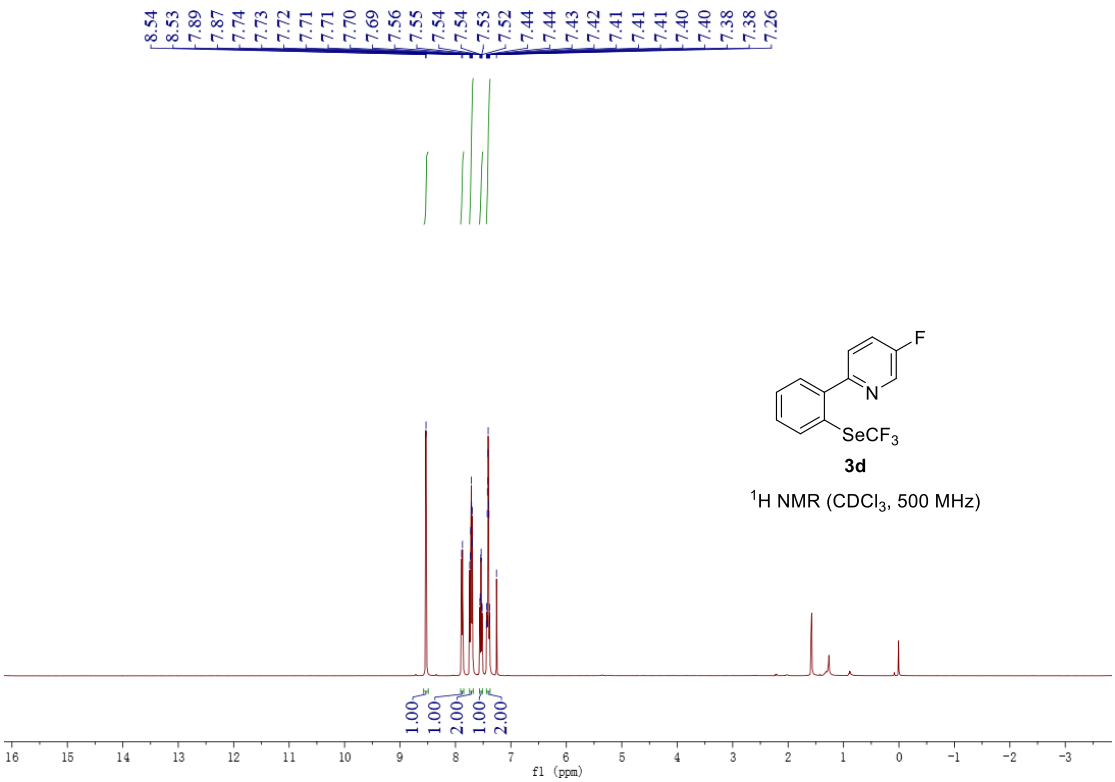
138.6
137.1
135.4
135.4
131.6
131.6
129.6
129.2
128.6
128.4
128.3
127.4
127.1
125.6
122.9
121.3
120.2
Ph
N
SeCF3
3c
13C NMR (CDCl3, 126 MHz)
f1 (ppm)


8.54
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7.72
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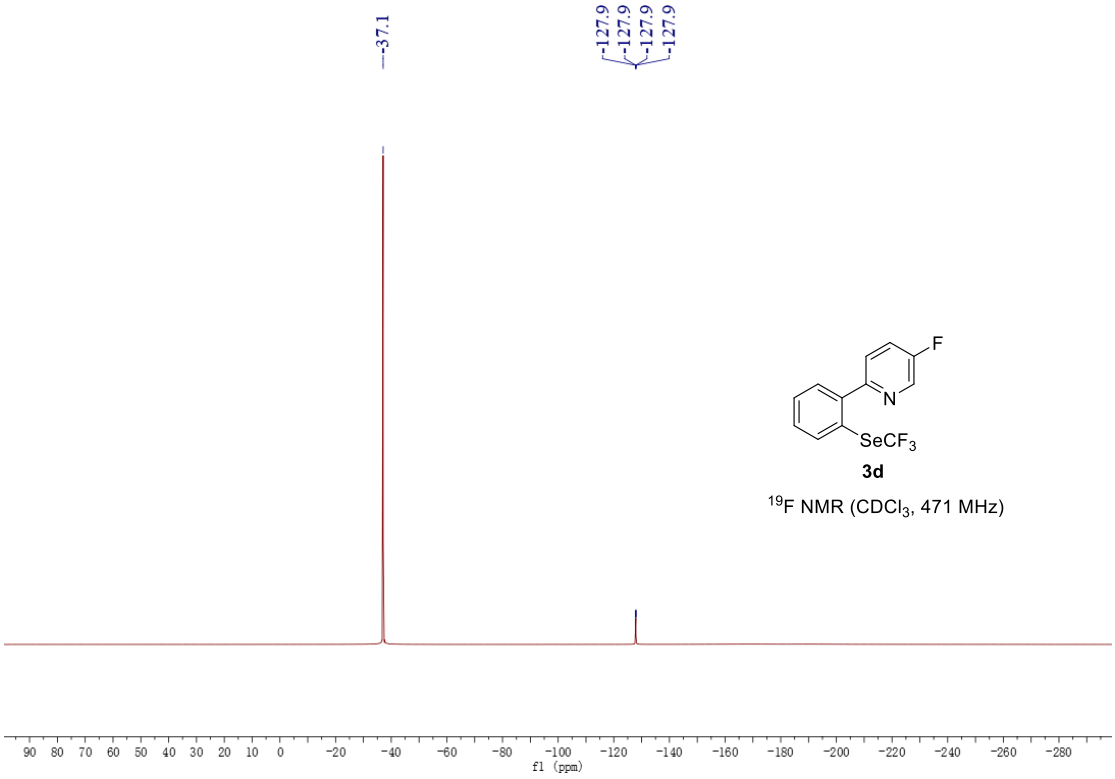
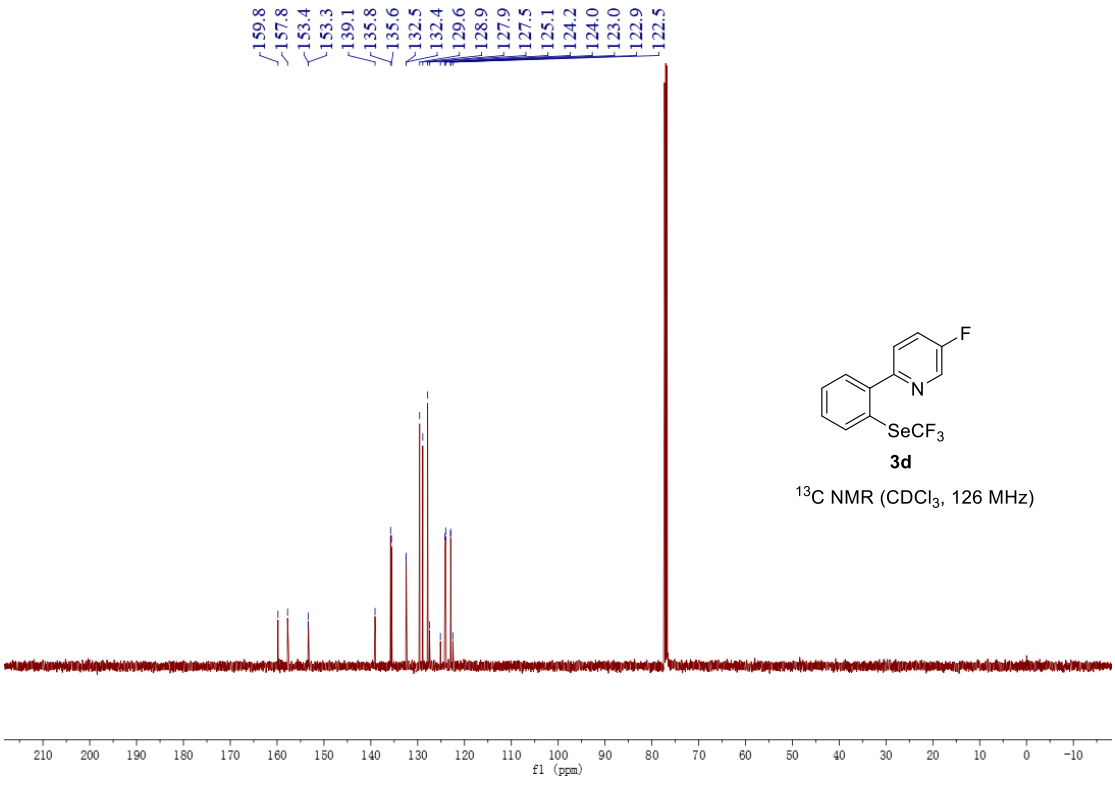
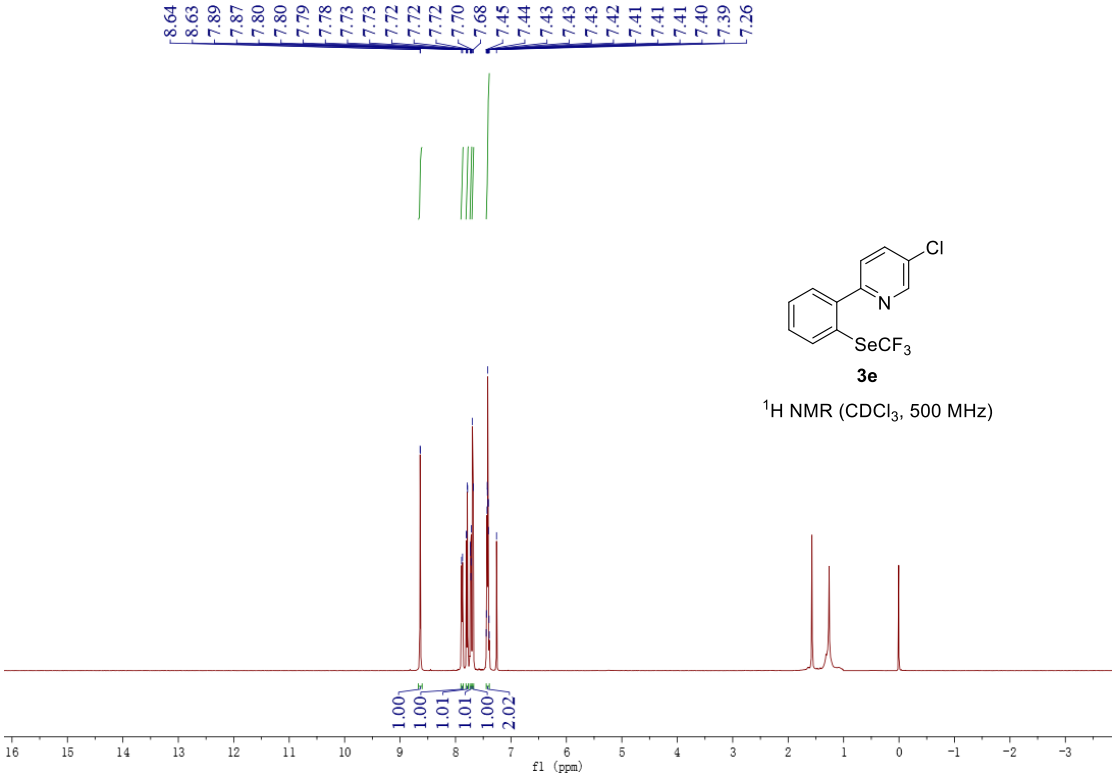
7.69
7.56
7.55
7.54
7.54
7.53
7.52
7.44
7.44
7.43
7.42
7.41
7.41
7.41
7.40
7.40
7.38
7.38
7.26
F
N
SeCF3
3d
1H NMR (CDCl3, 500 MHz)
1.00
1.00
2.00
1.00
2.00
f1 (ppm)

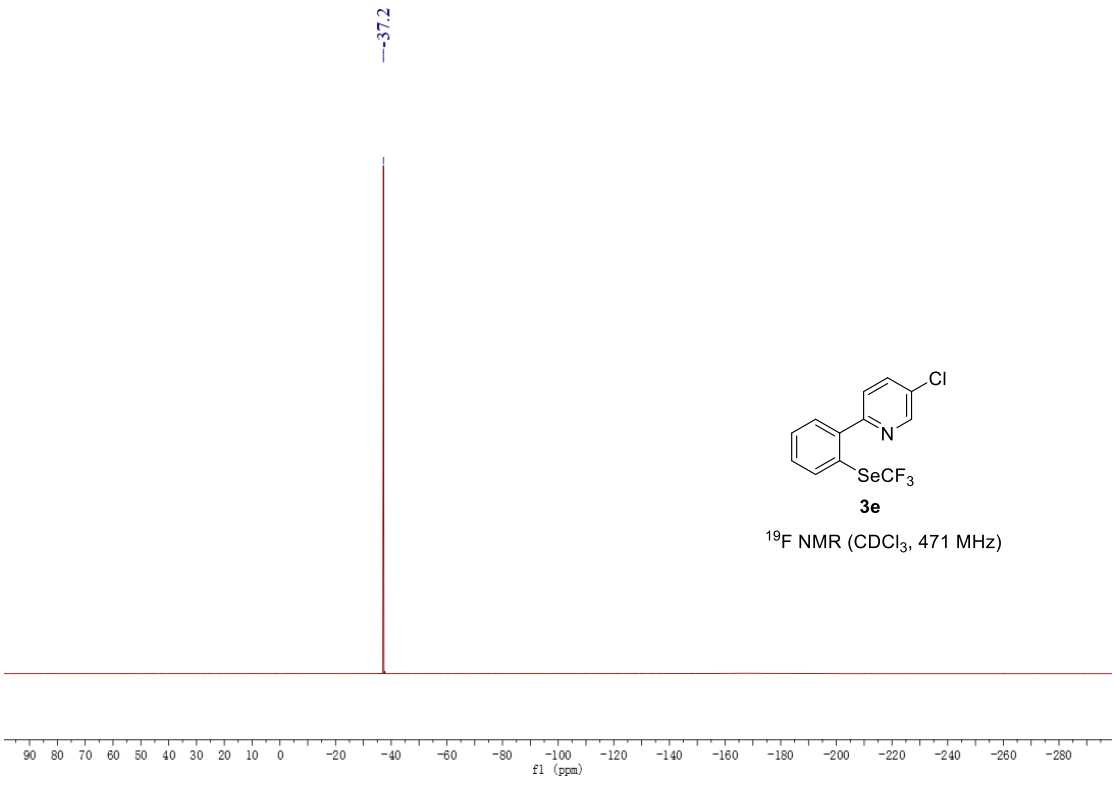

-37.1
-127.9
-127.9
-127.9
-127.9
F
N
SeCF3
3d
19F NMR (CDCl3, 471 MHz)
f1 (ppm)


159.8
157.8
153.4
153.3
139.1
135.8
135.6
132.5
132.4
129.6
128.9
127.9
127.5
125.1
124.2
124.0
123.0
122.9
122.5
F
N
SeCF3
3d
13C NMR (CDCl3, 126 MHz)
f1 (ppm)



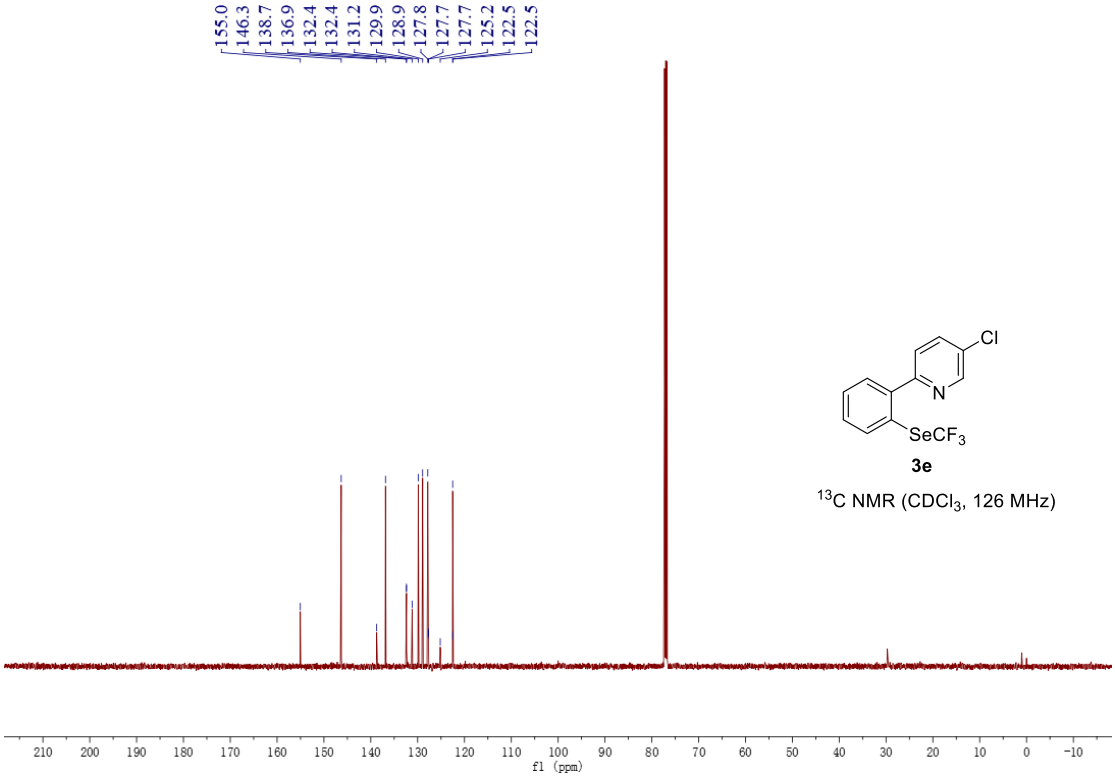
3e

^{1}H NMR ($CDCl_3$, 500 MHz)



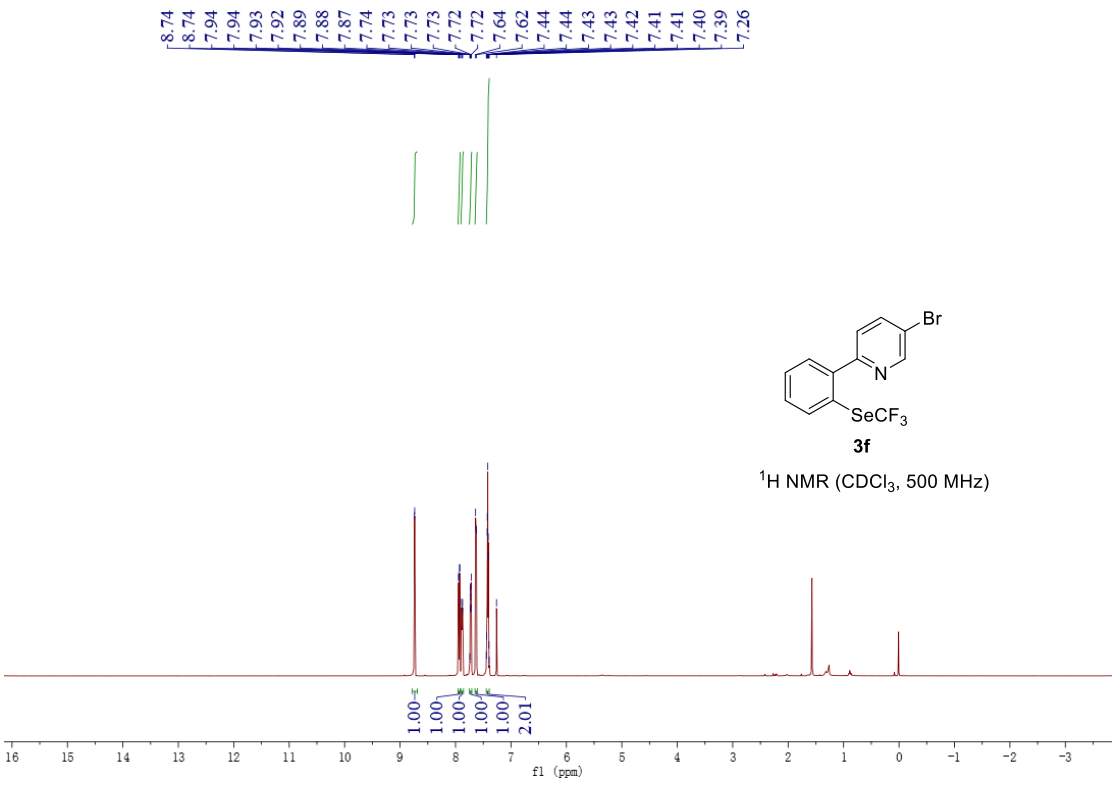
3e

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



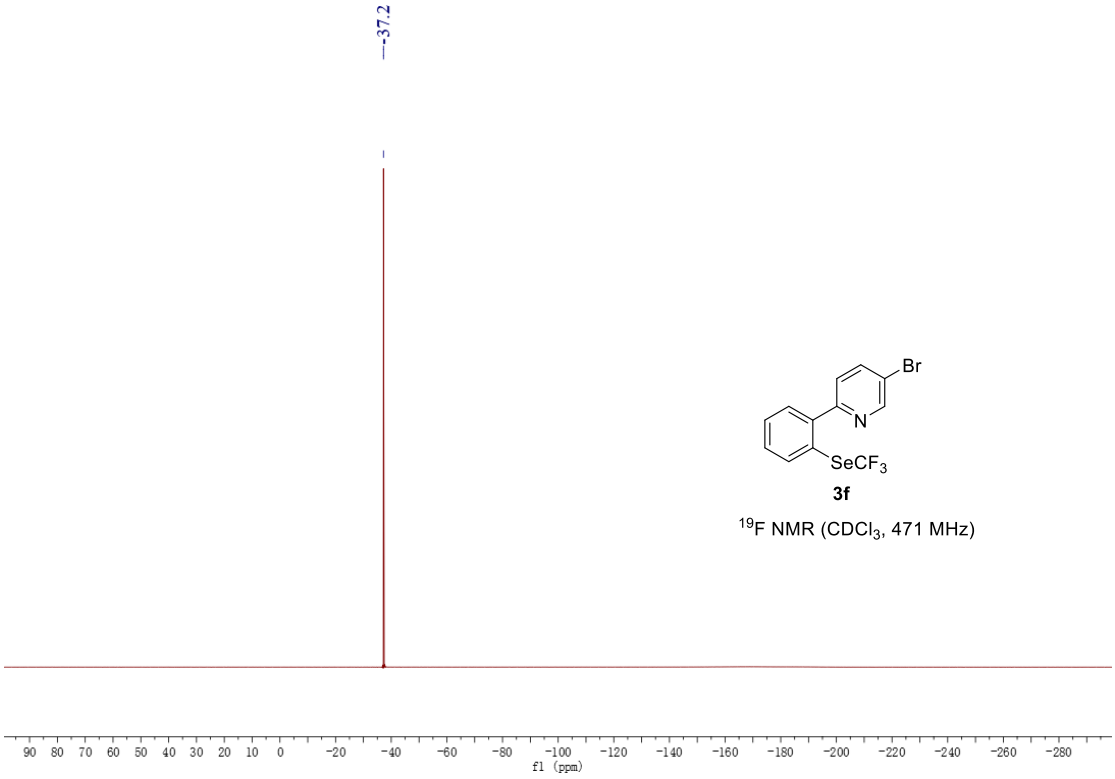
3e

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



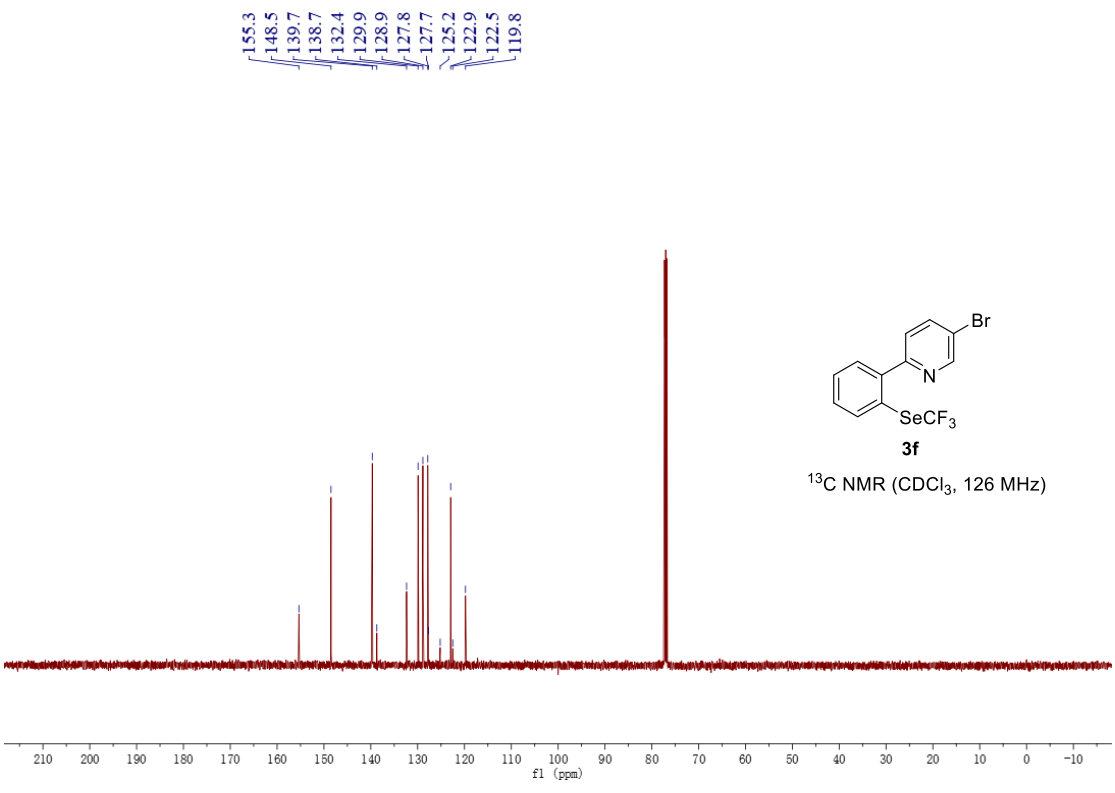
3f

^{1}H NMR ($CDCl_3$, 500 MHz)



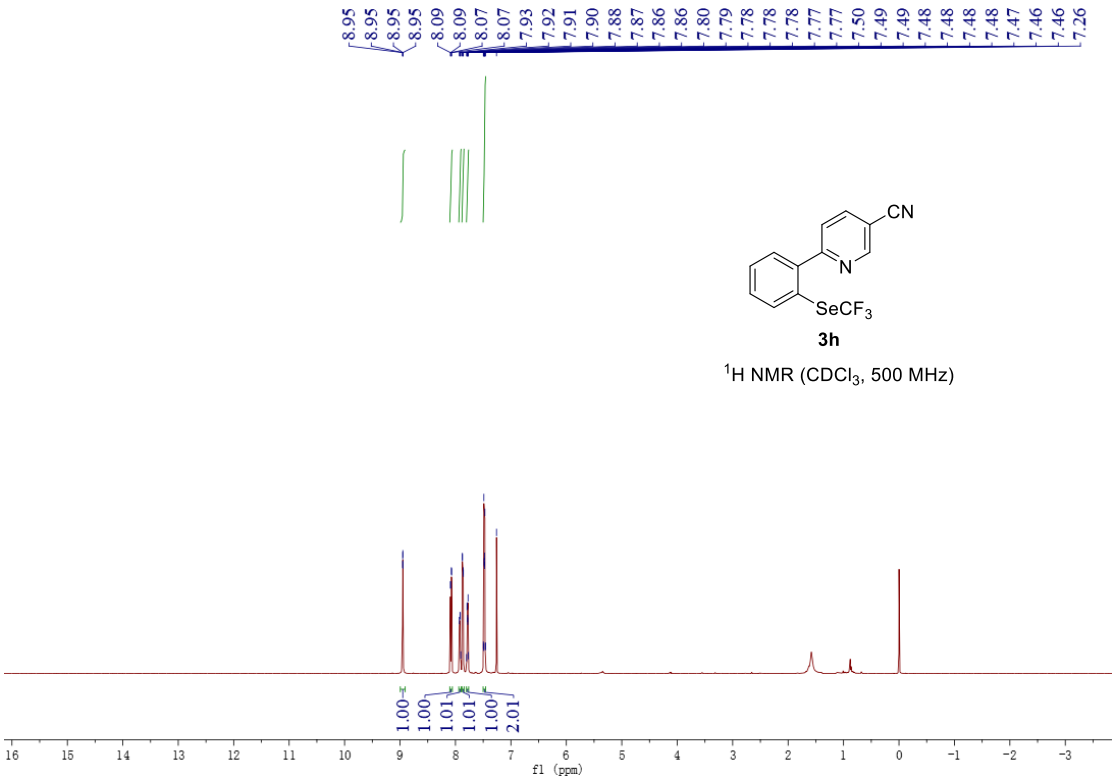
3f

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



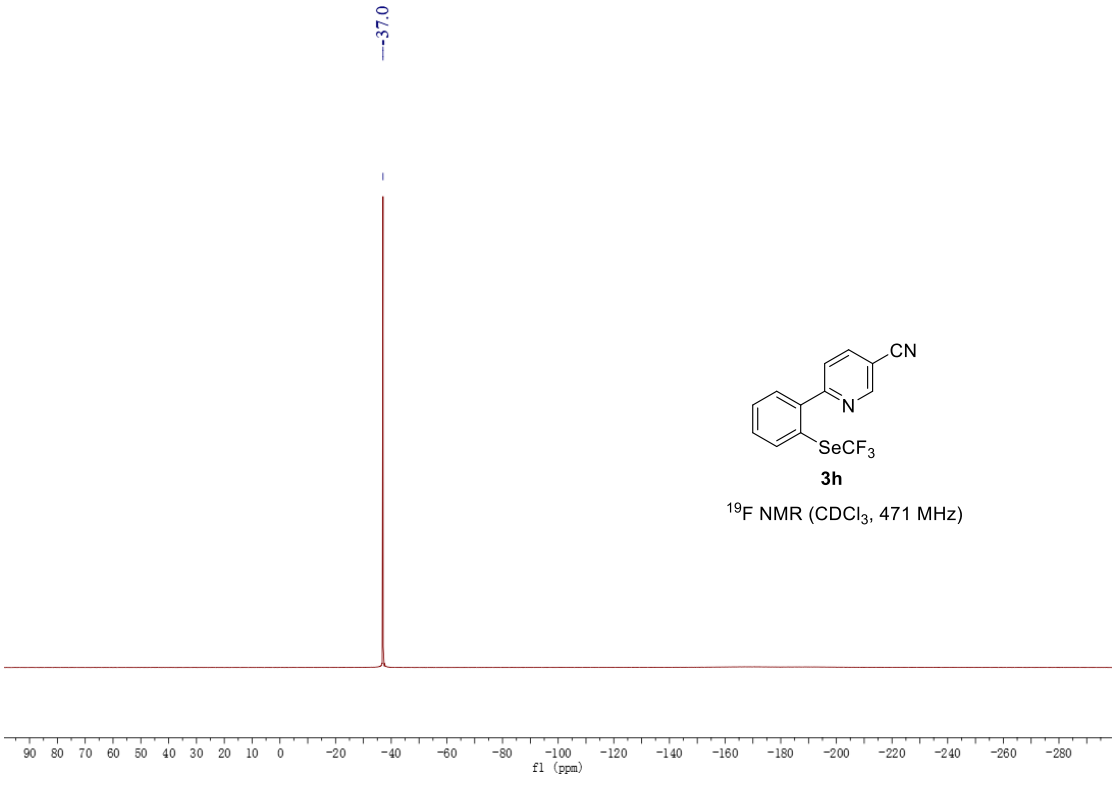
3f

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



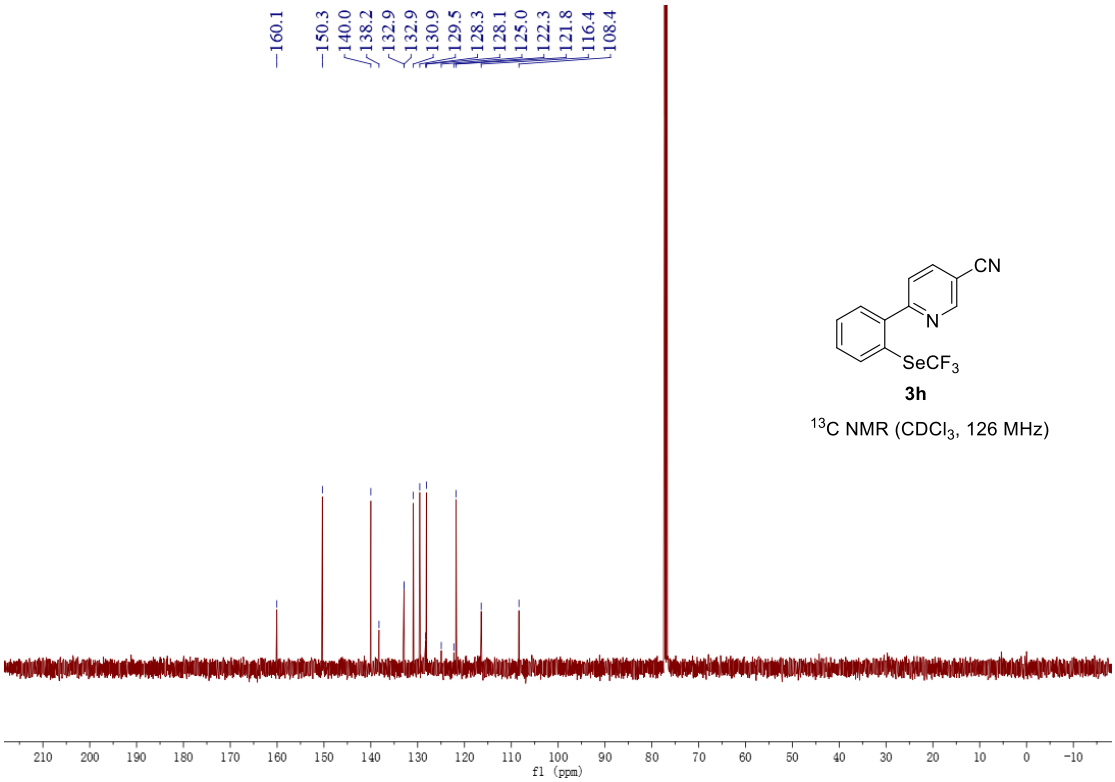
3h

^{1}H NMR ($CDCl_3$, 500 MHz)



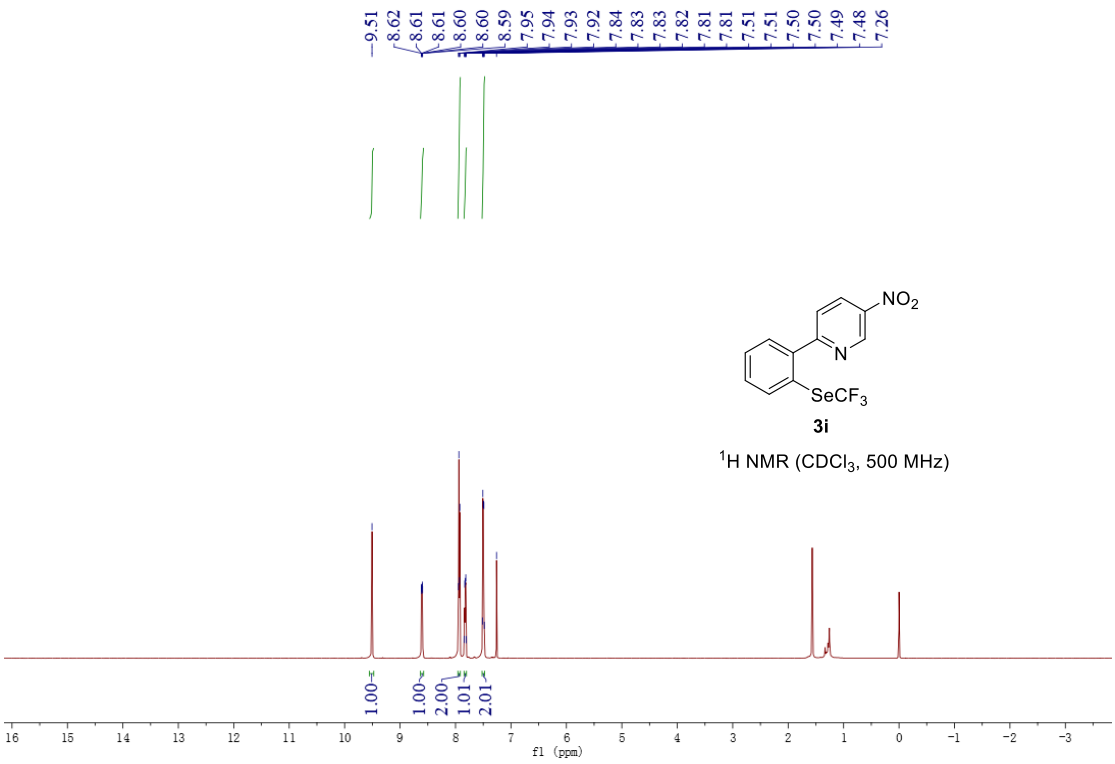
3h

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



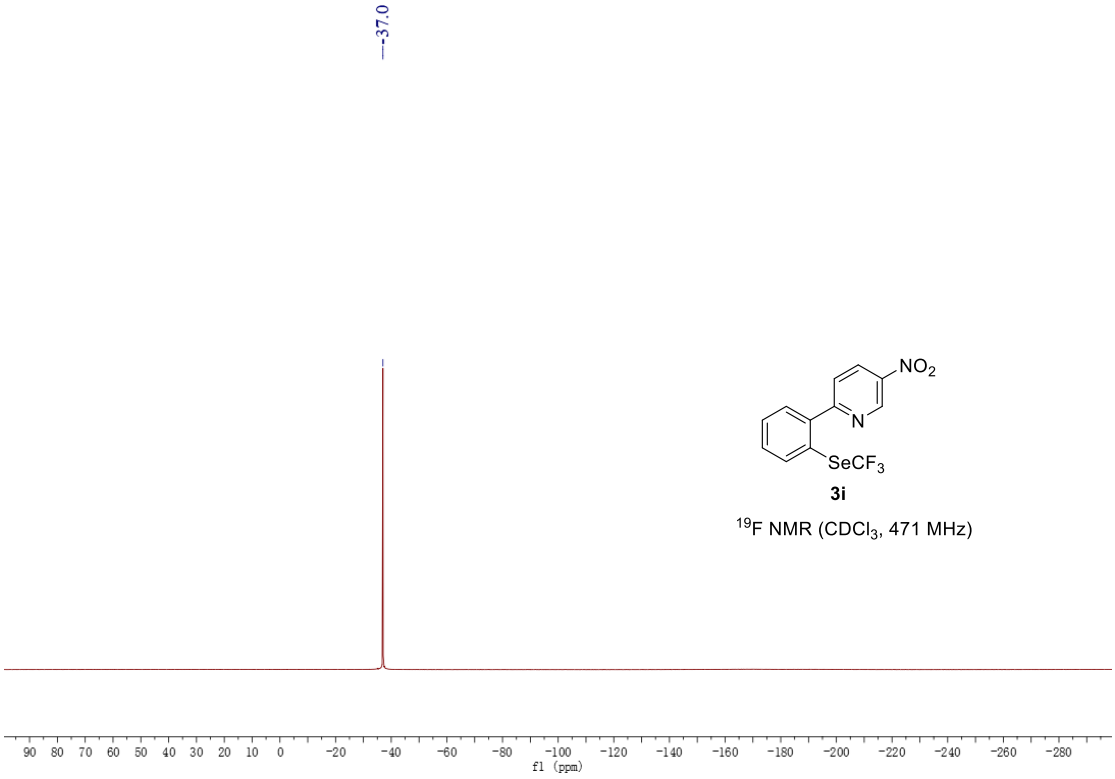
3h

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



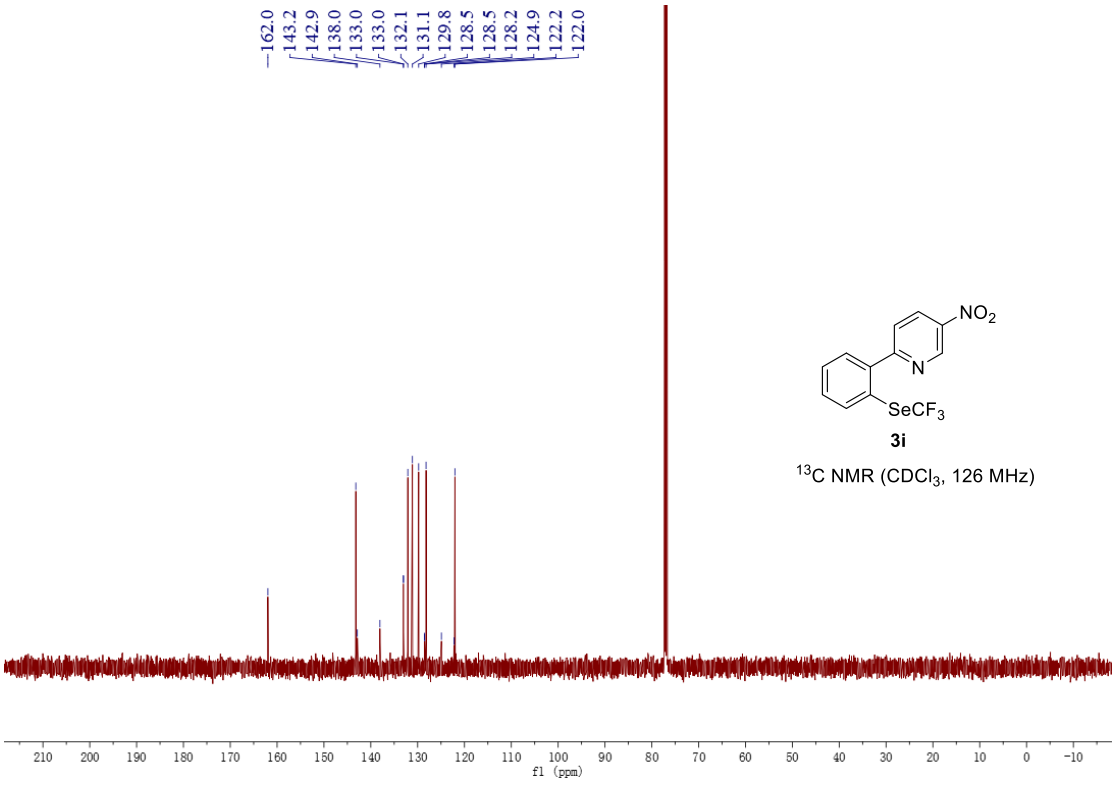
3i

^{1}H NMR ($CDCl_3$, 500 MHz)



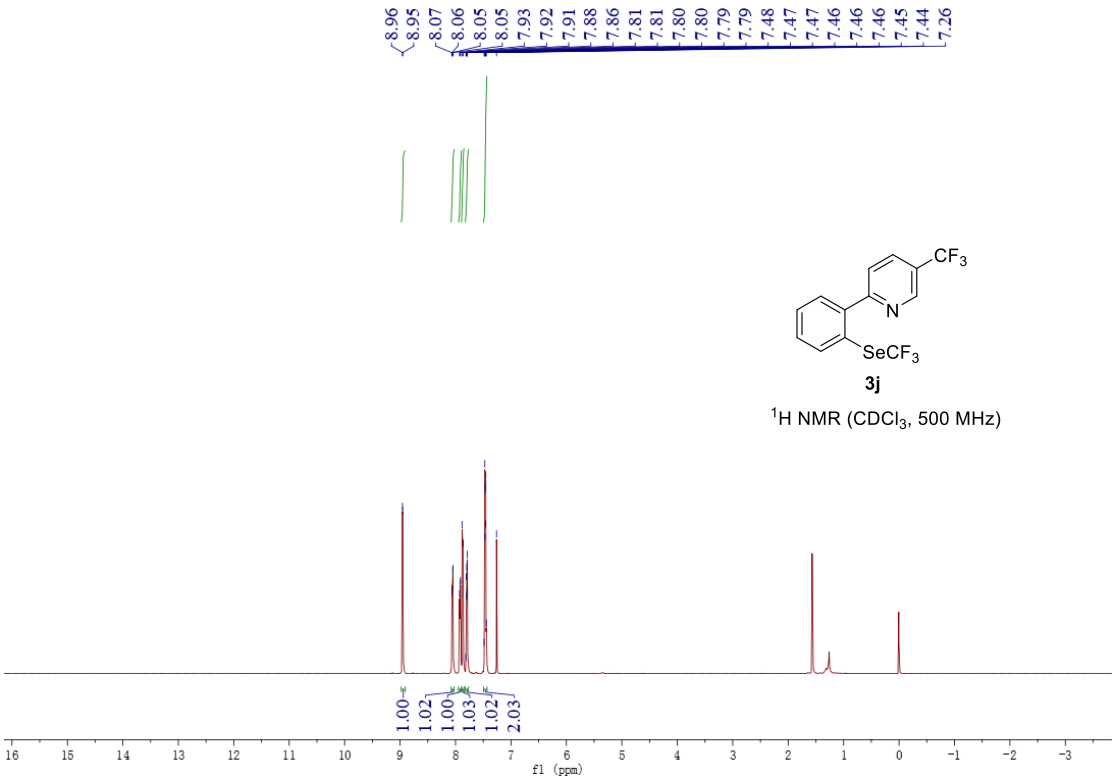
3i

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



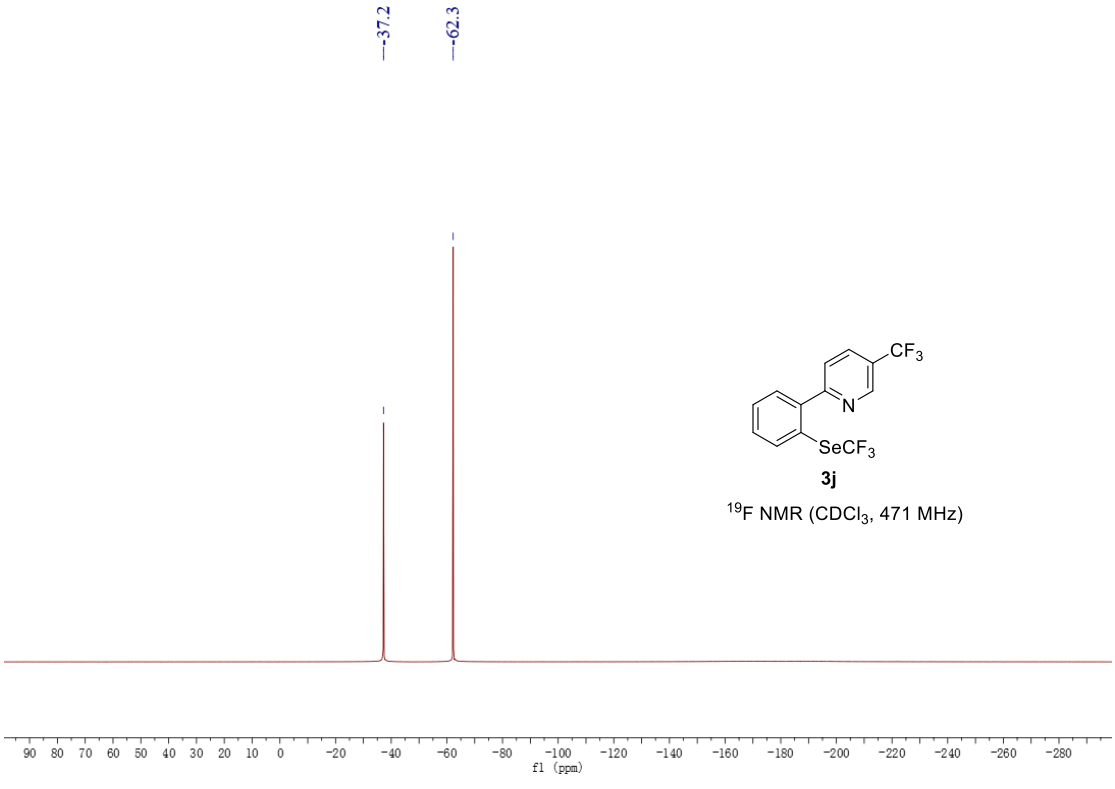
3i

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



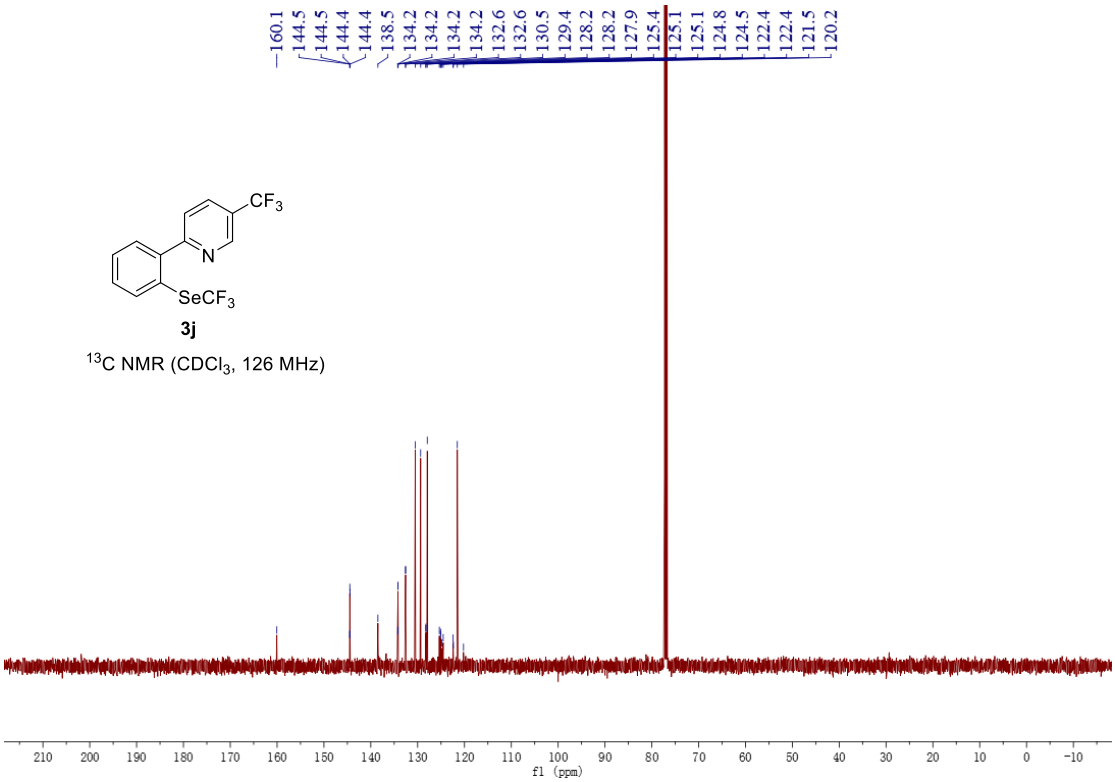
3j

^{1}H NMR ($CDCl_3$, 500 MHz)



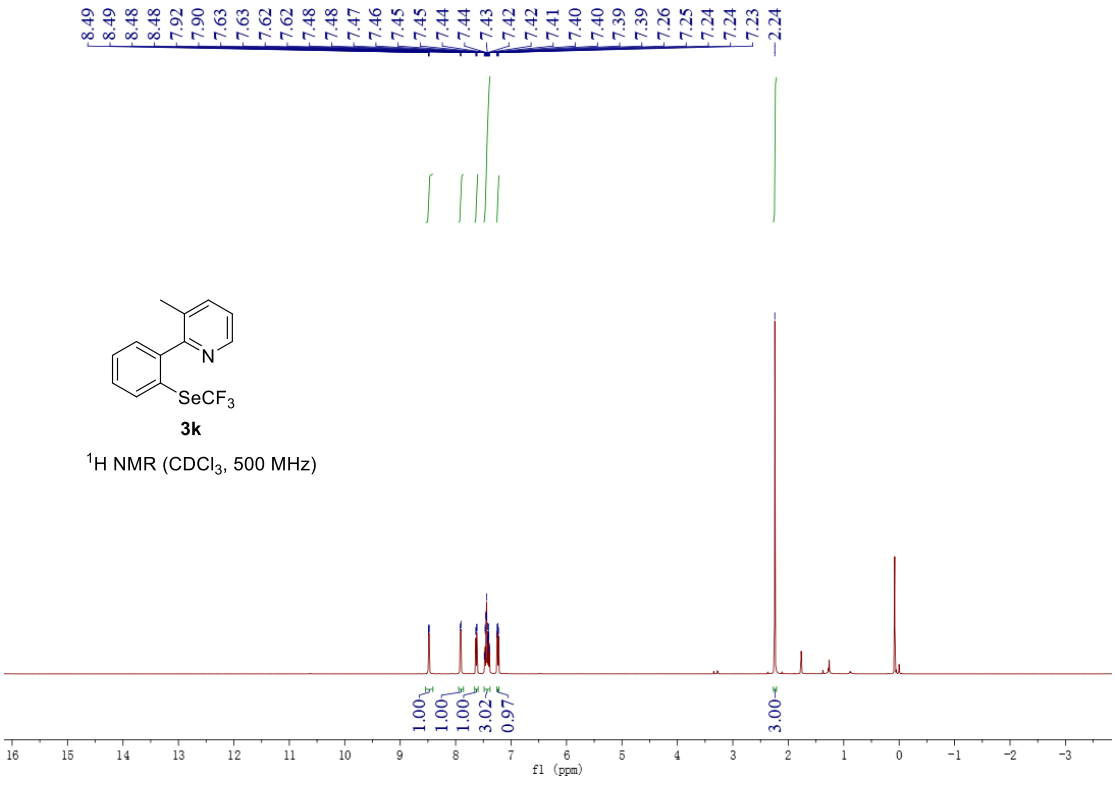
3j

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



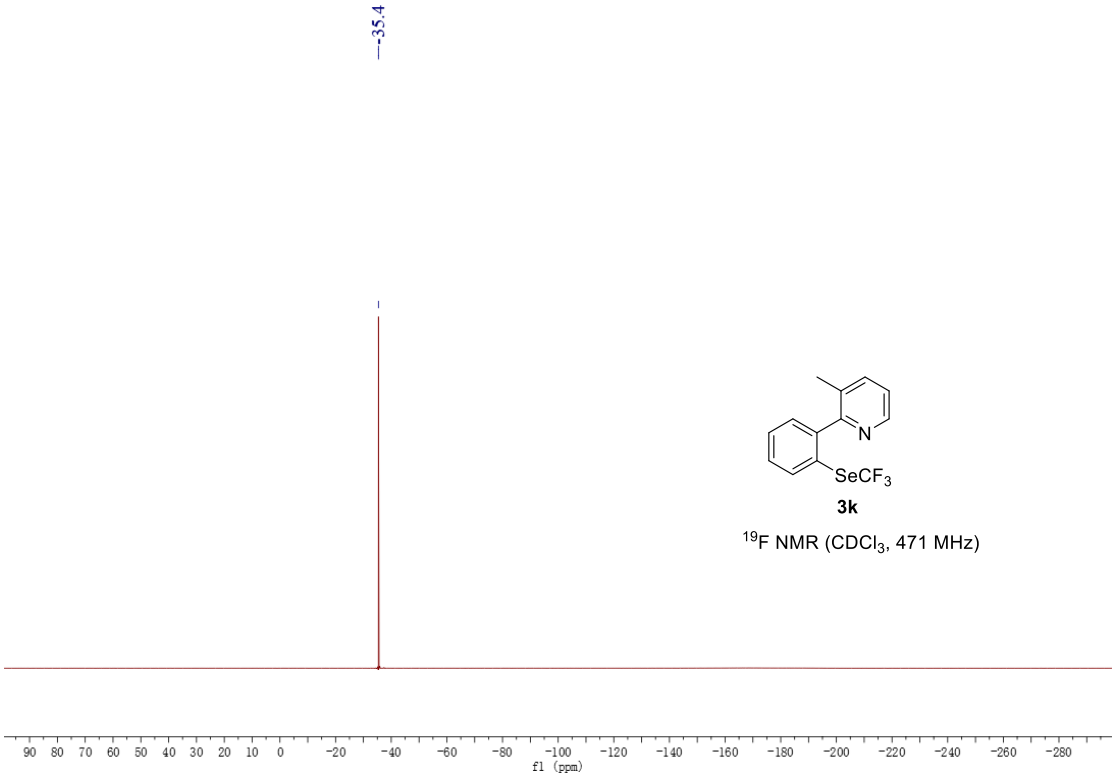
3j

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



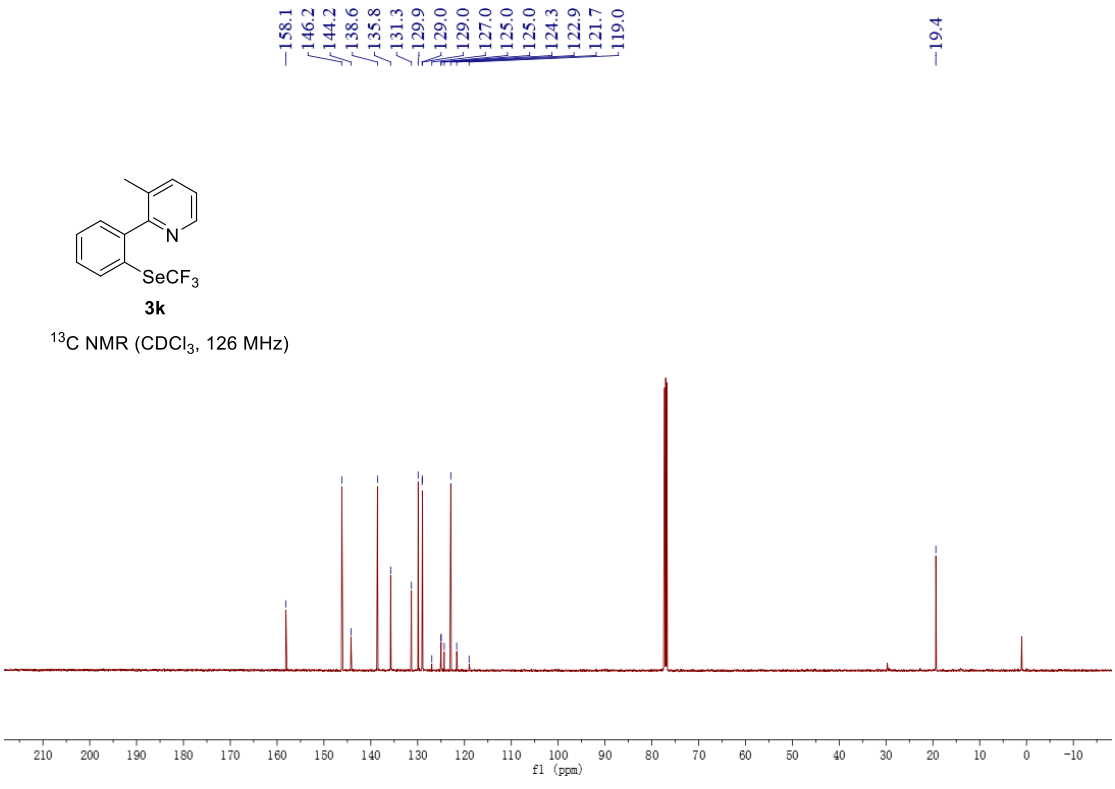
3k

^{1}H NMR ($CDCl_3$, 500 MHz)



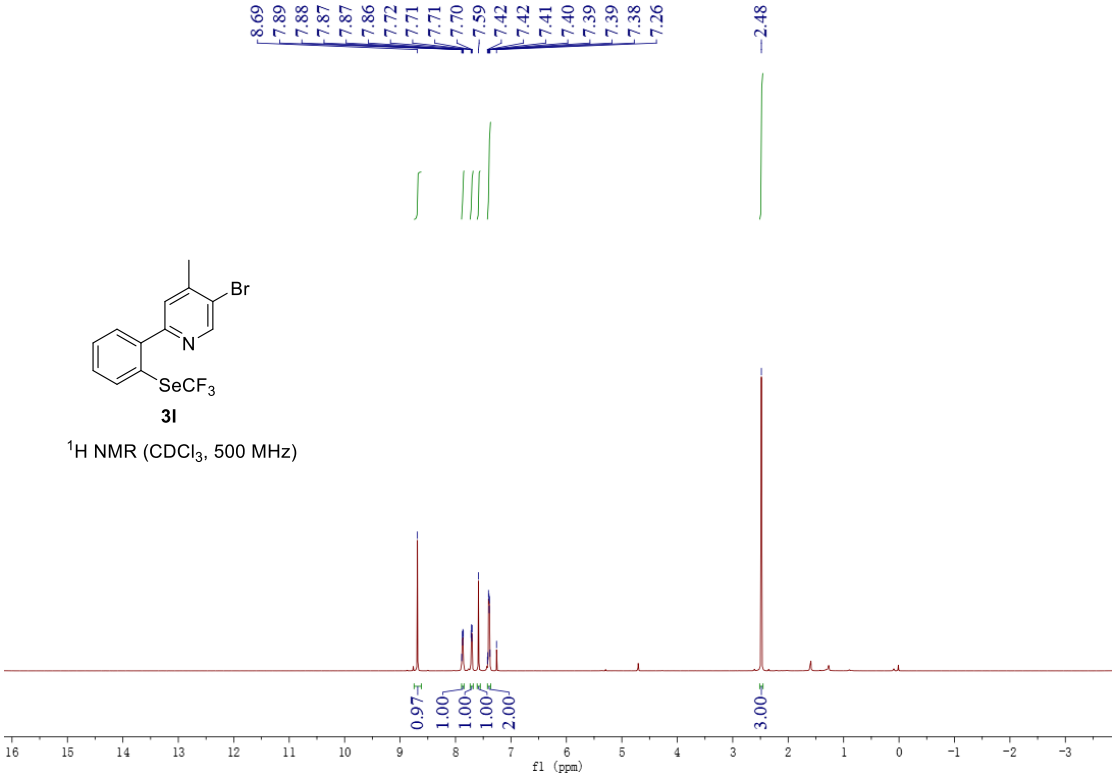
3k

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



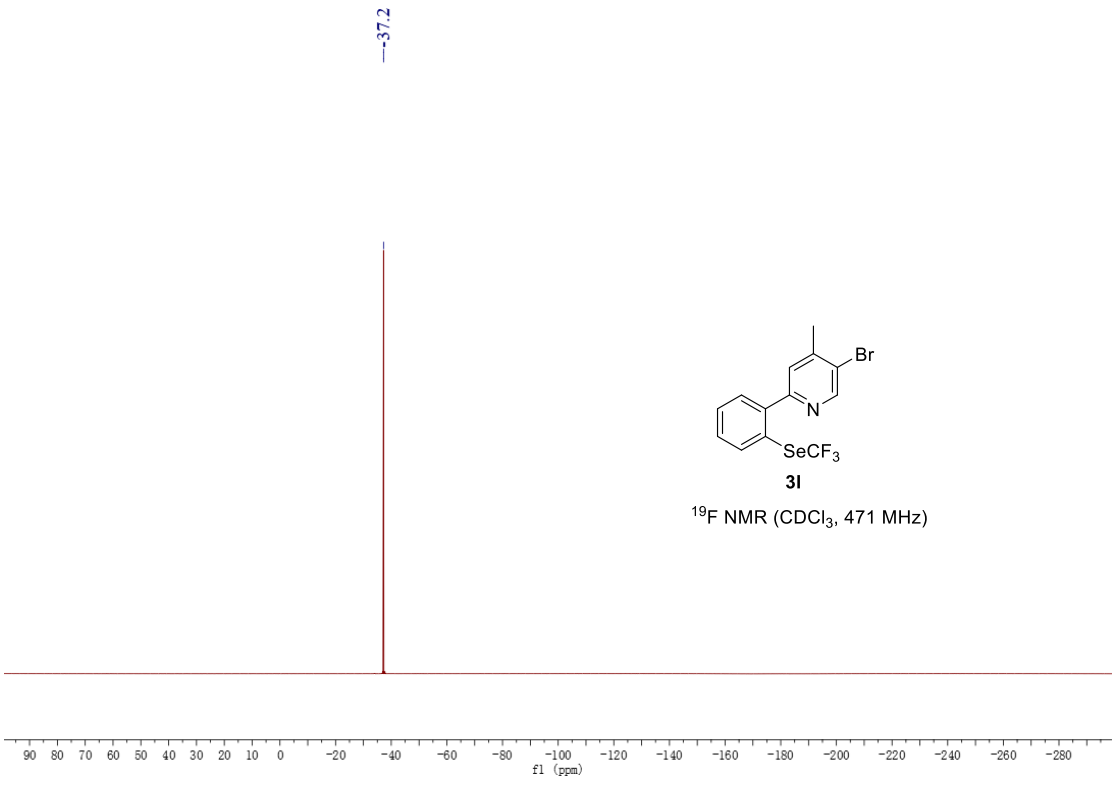
3k

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



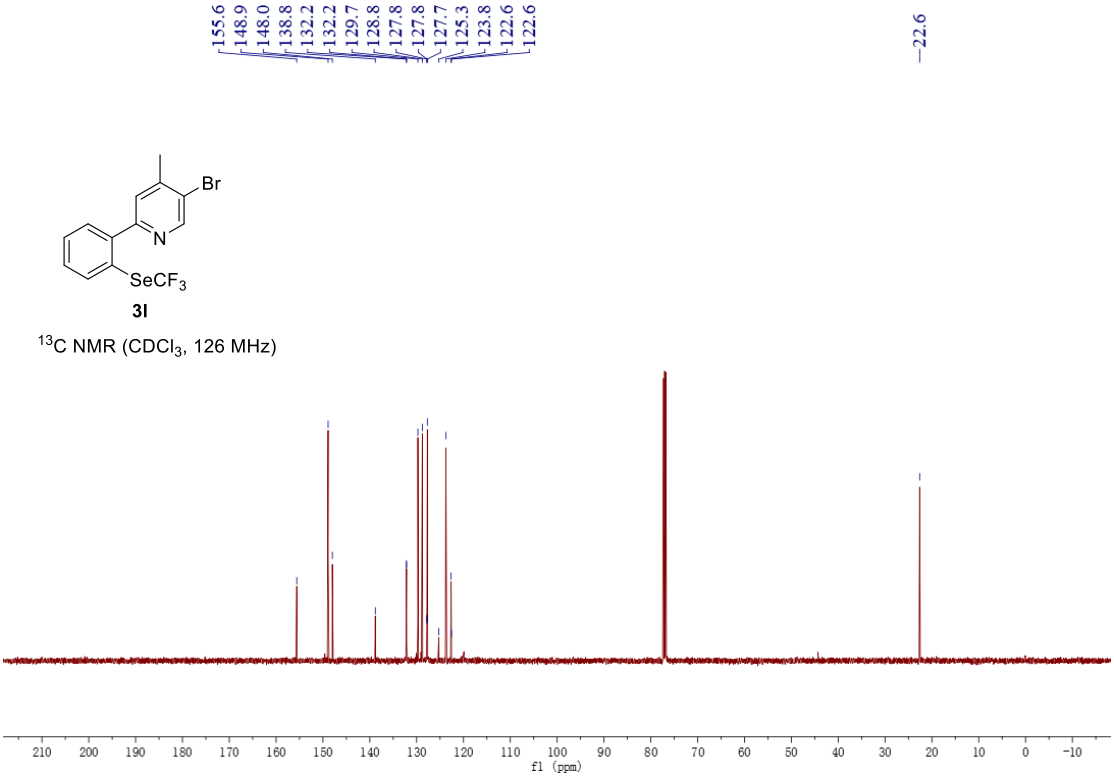
3l

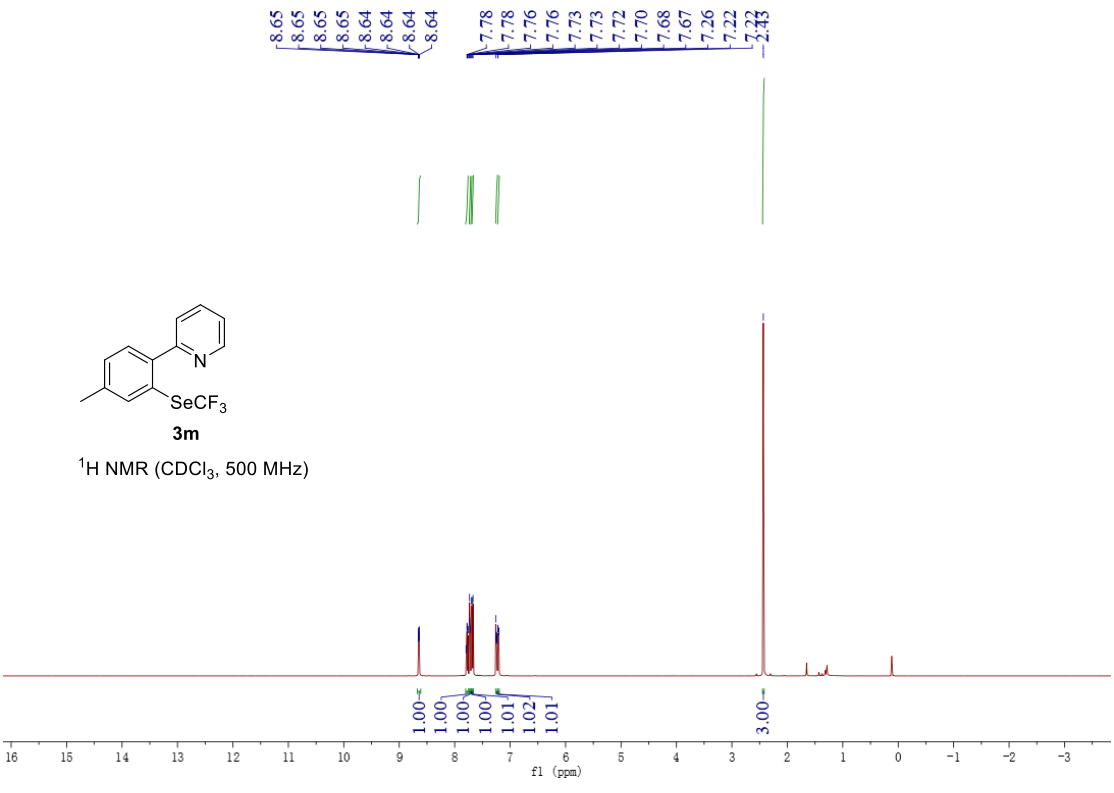
^{1}H NMR ($CDCl_3$, 500 MHz)

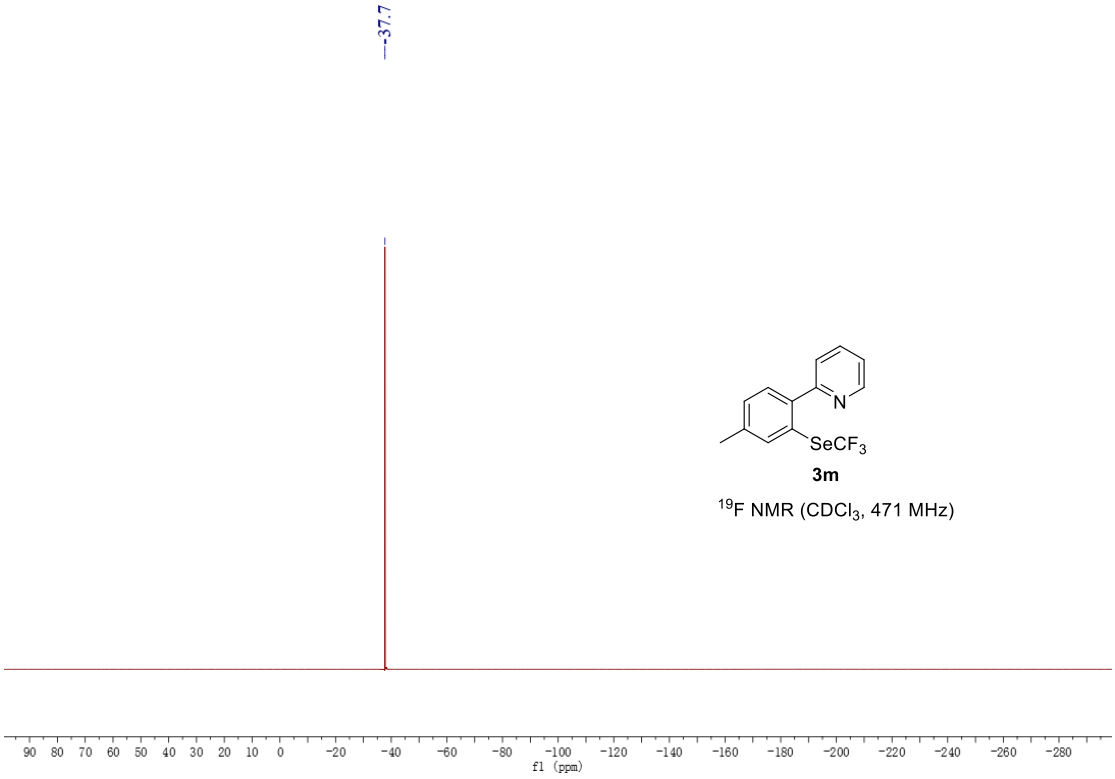


3l

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

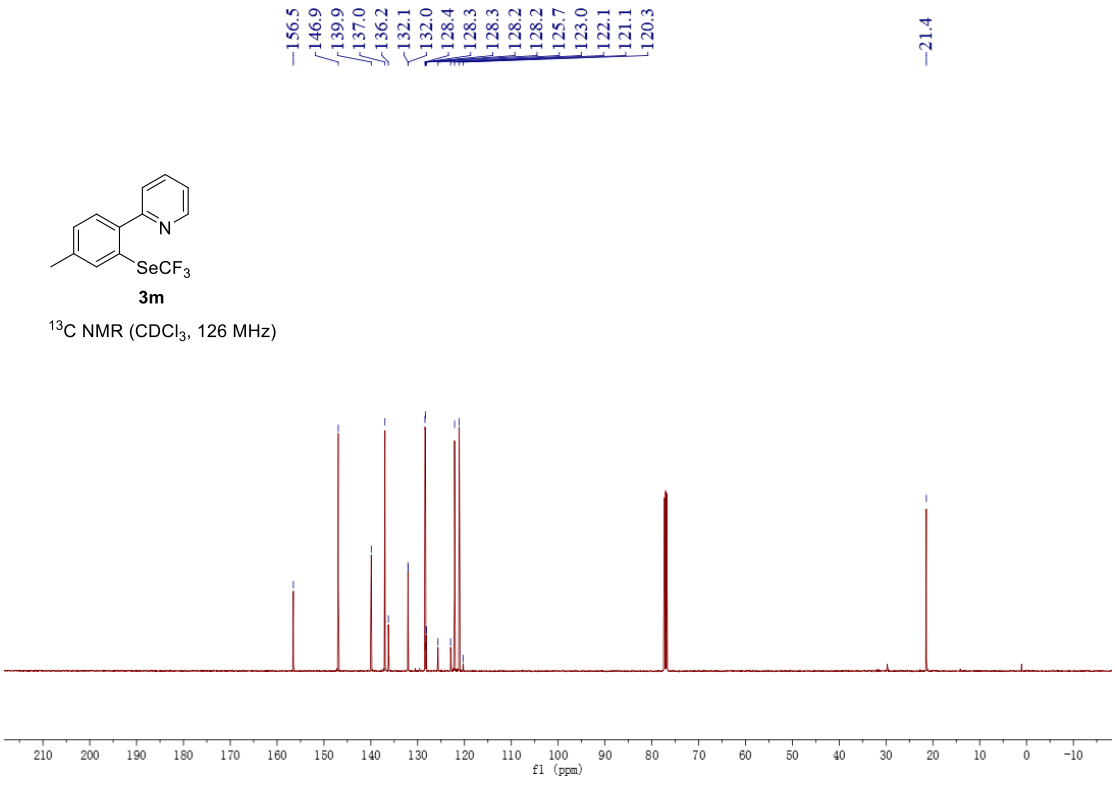

155.6
148.9
148.0
138.8
132.2
132.2
129.7
128.8
127.8
127.8
127.7
125.3
123.8
122.6
122.6
22.6
Br
N
SeCF3
3l
13C NMR (CDCl3, 126 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.65
8.65
8.65
8.65
8.64
8.64
8.64
8.64
7.78
7.78
7.76
7.76
7.73
7.73
7.72
7.70
7.68
7.67
7.26
7.22
2.43
N
SeCF3
3m
1H NMR (CDCl3, 500 MHz)
1.00
1.00
1.00
1.01
1.02
1.01
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)



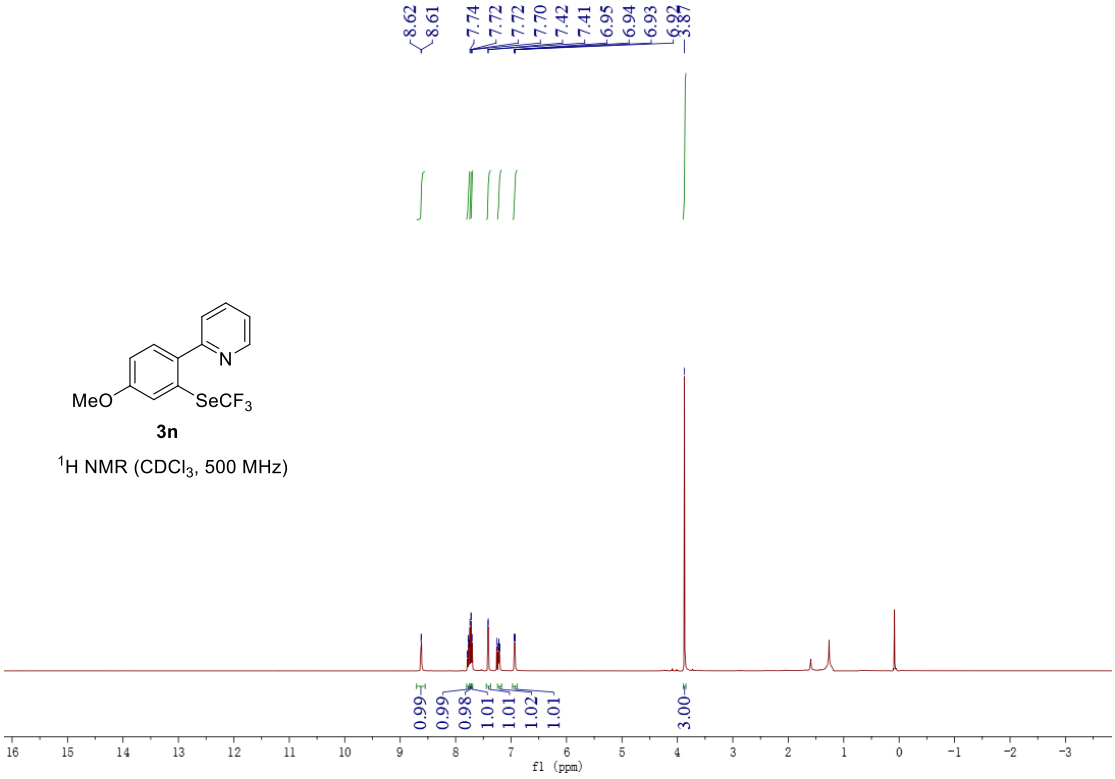
3m

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



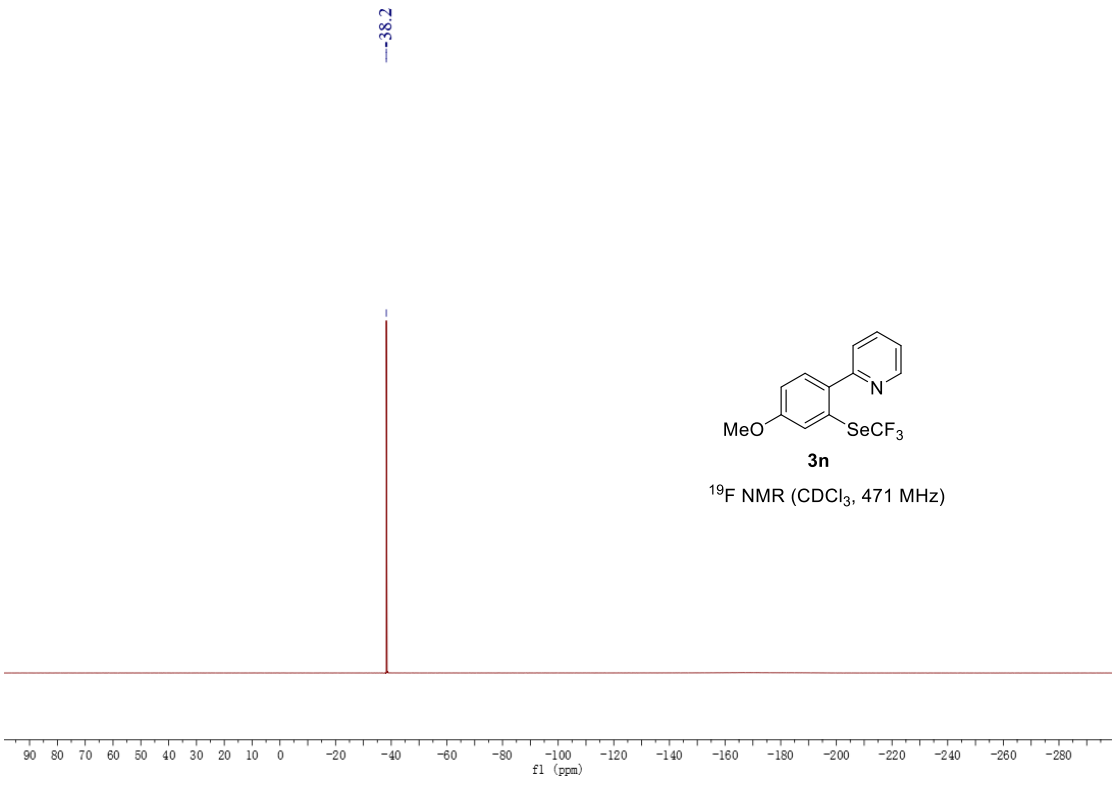
3m

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



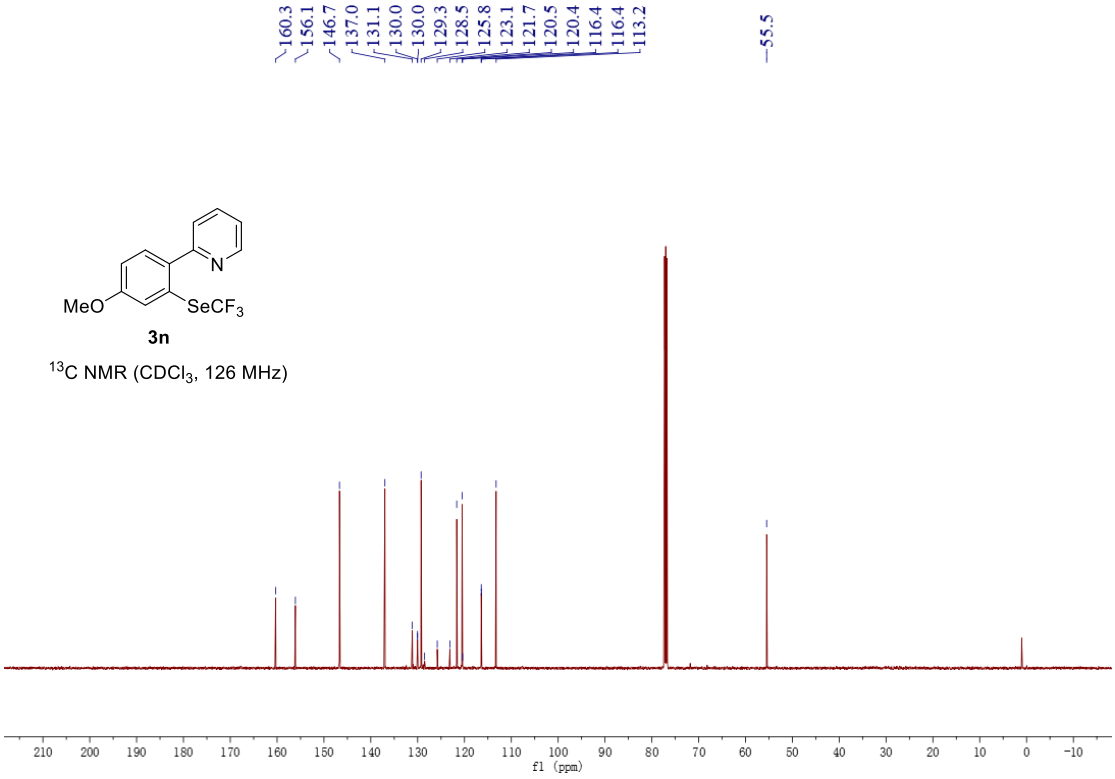
3n

^{1}H NMR ($CDCl_3$, 500 MHz)



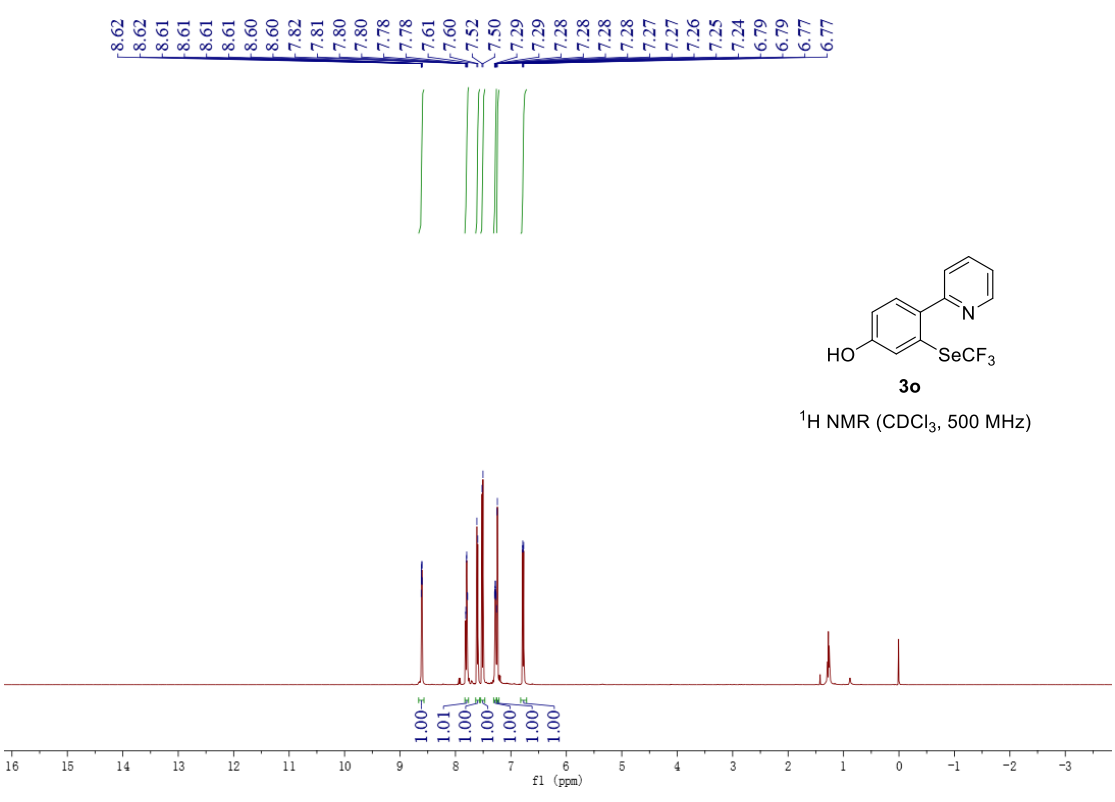
3n

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



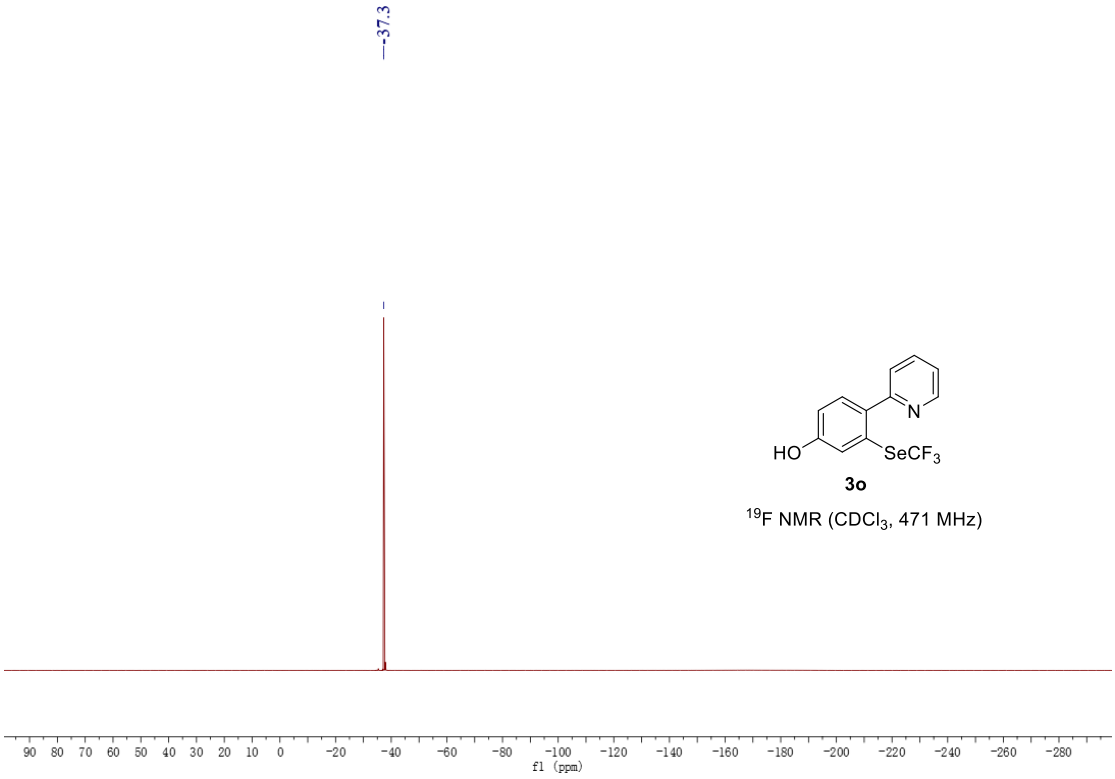
3n

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



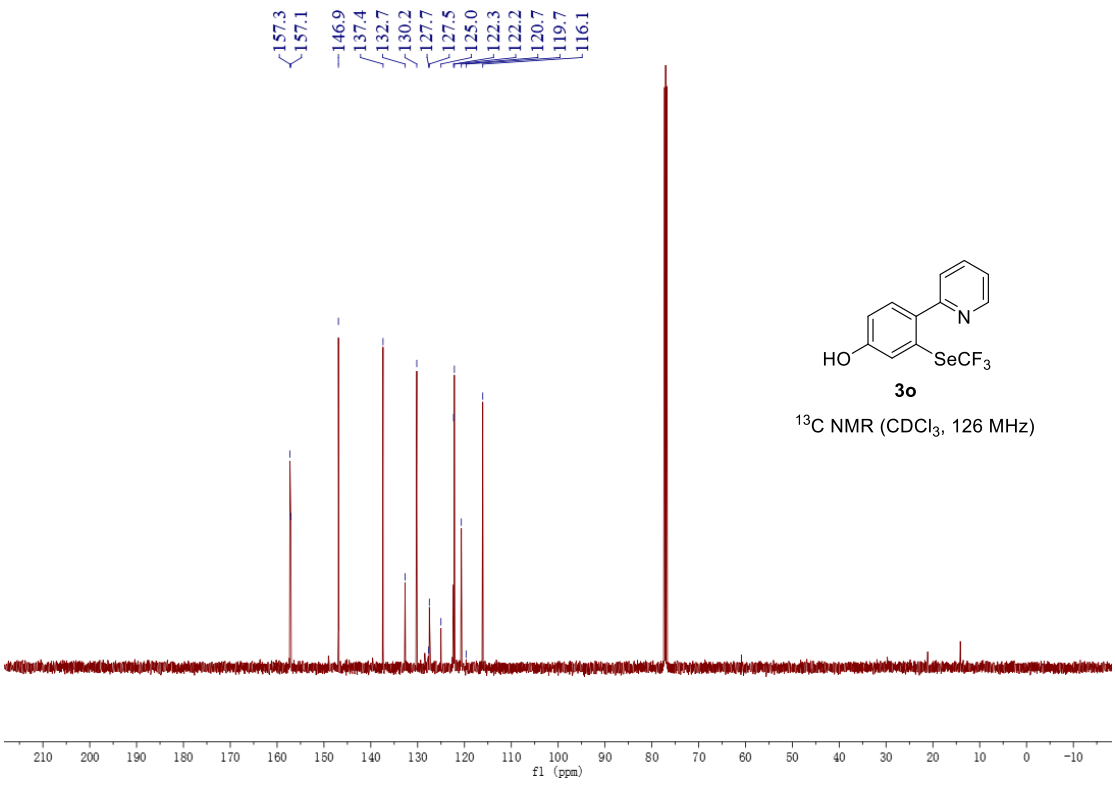
3o

^{1}H NMR ($CDCl_3$, 500 MHz)



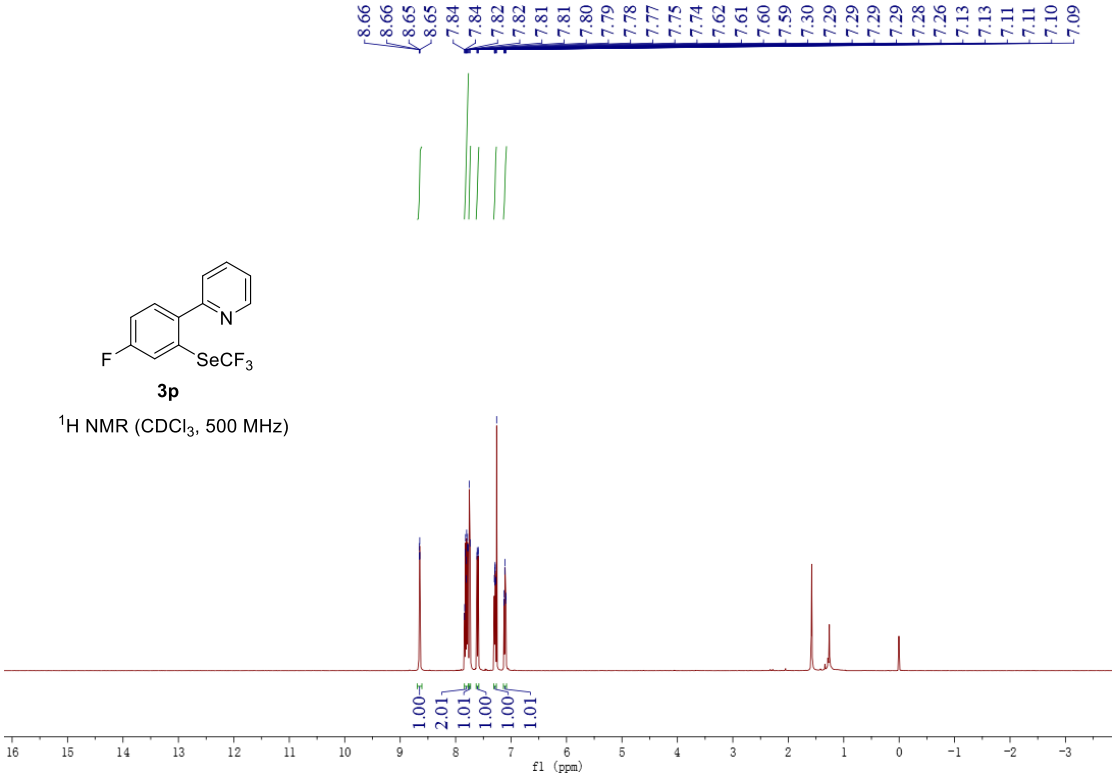
3o

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



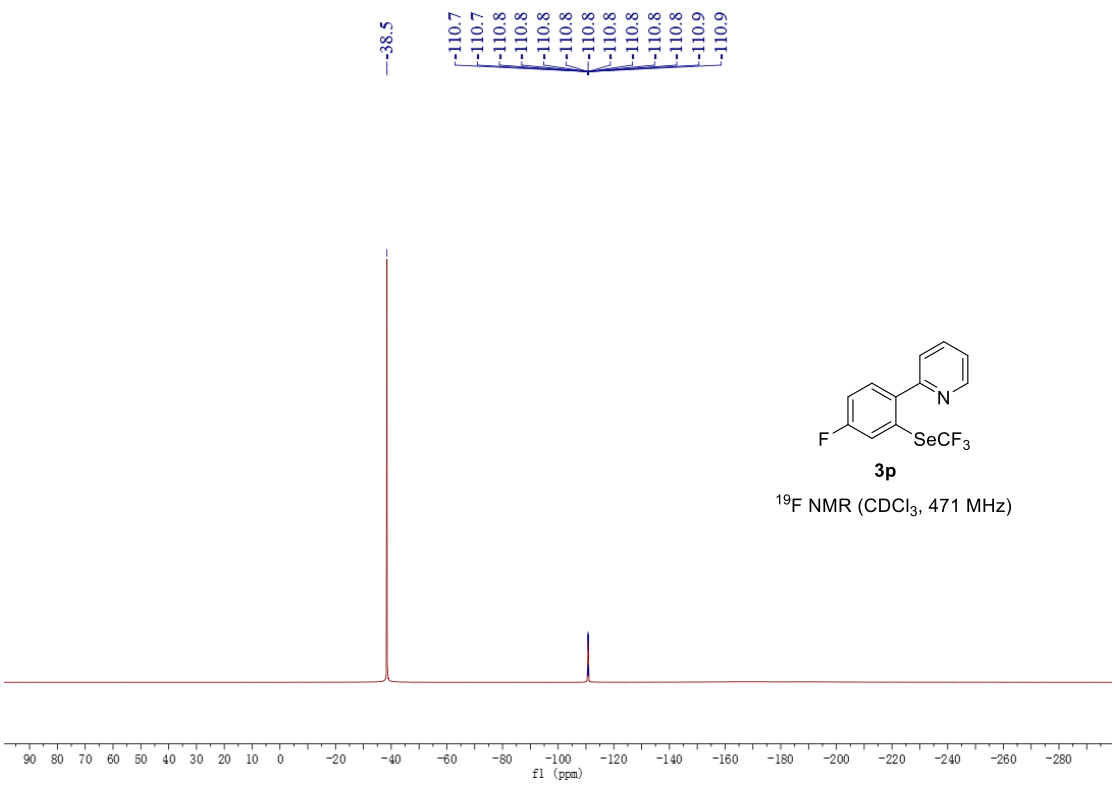
3o

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



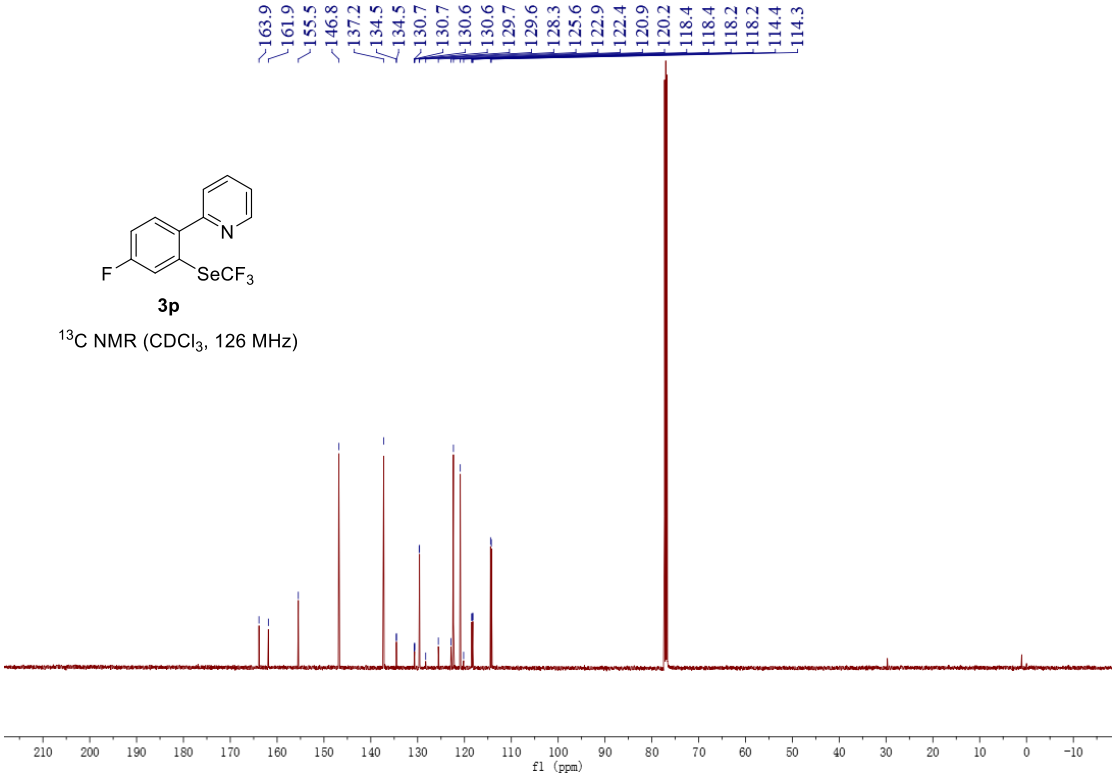
3p

^{1}H NMR ($CDCl_3$, 500 MHz)



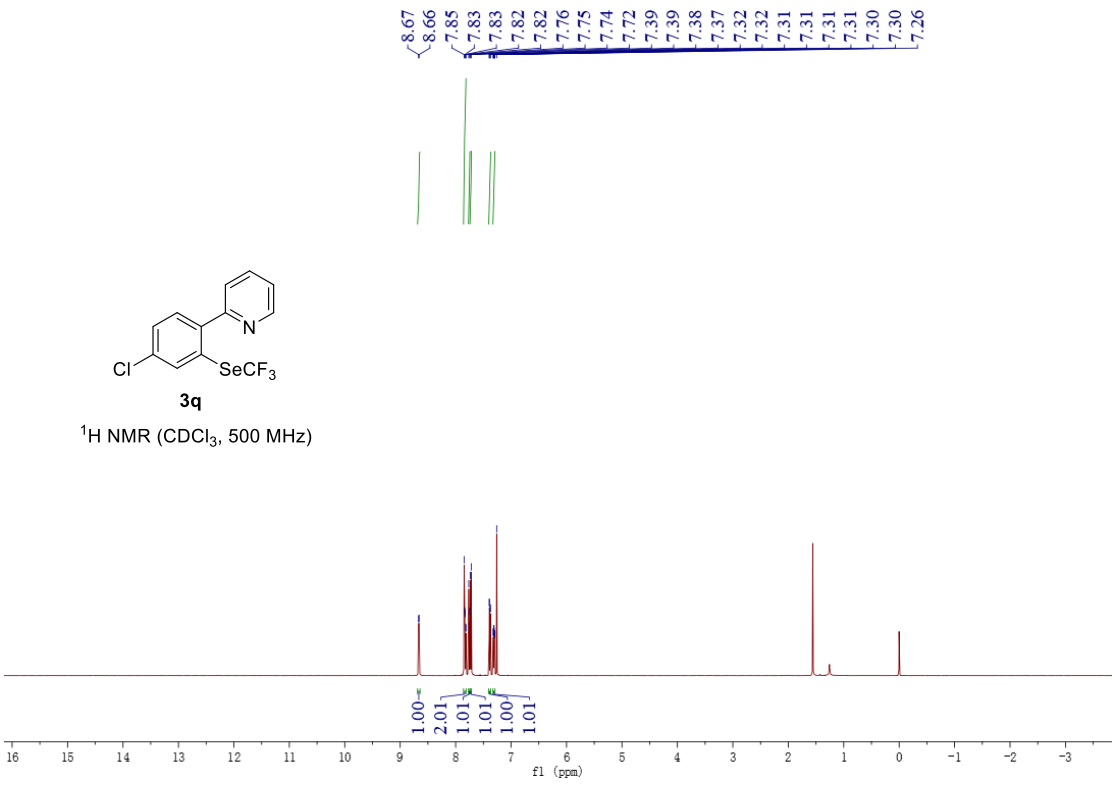
3p

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



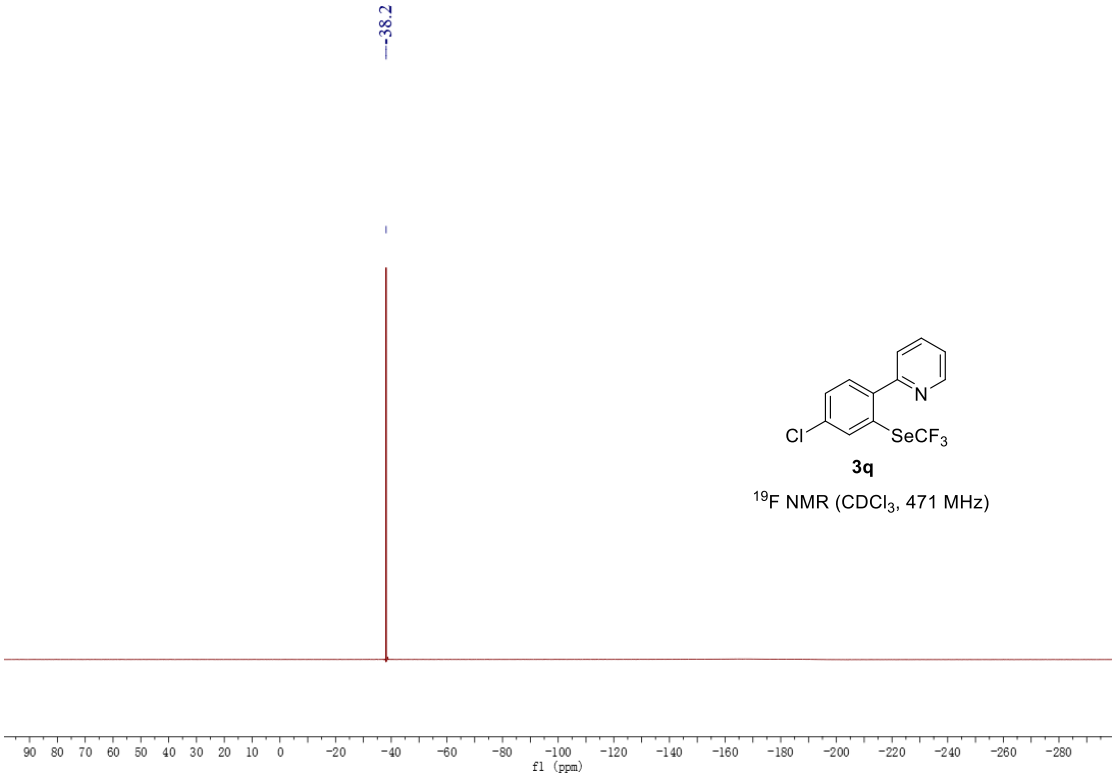
3p

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



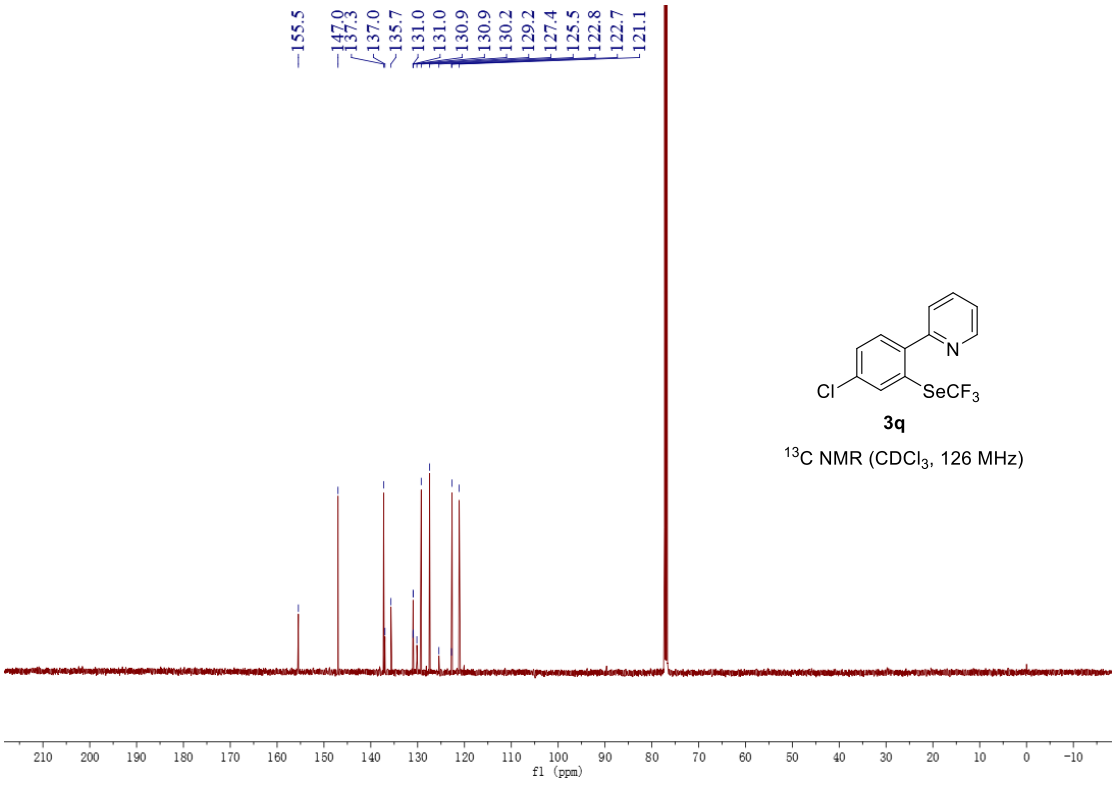
3q

^{1}H NMR ($CDCl_3$, 500 MHz)



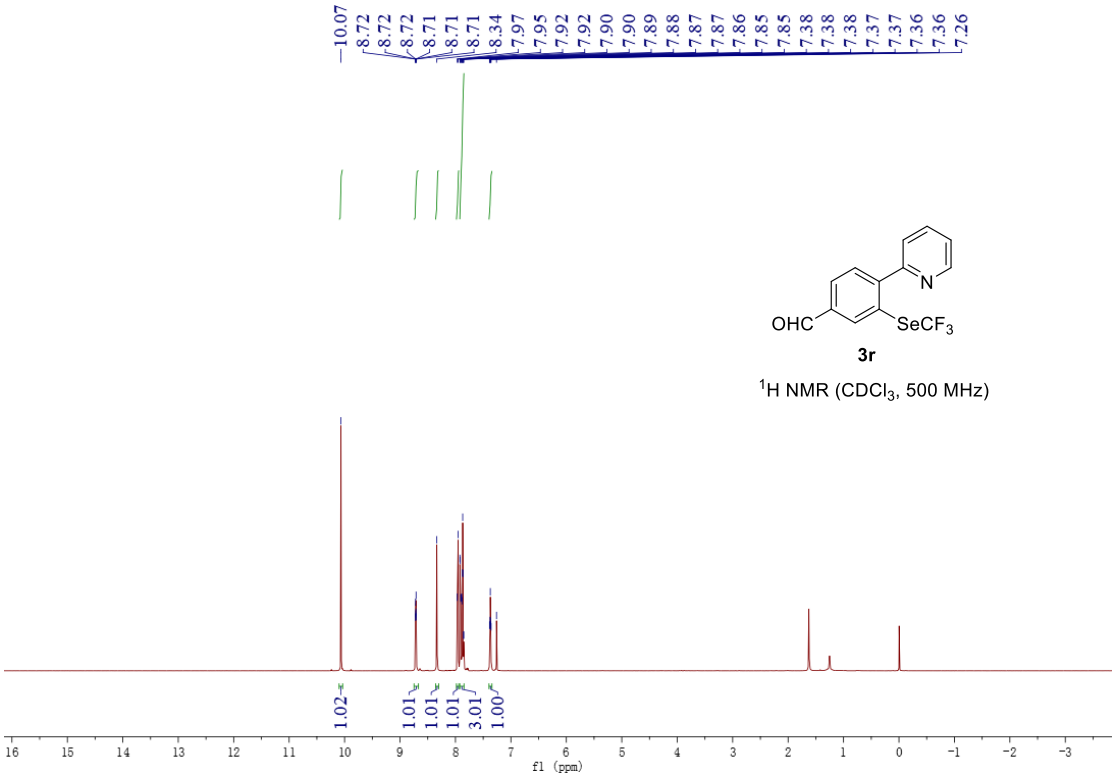
3q

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



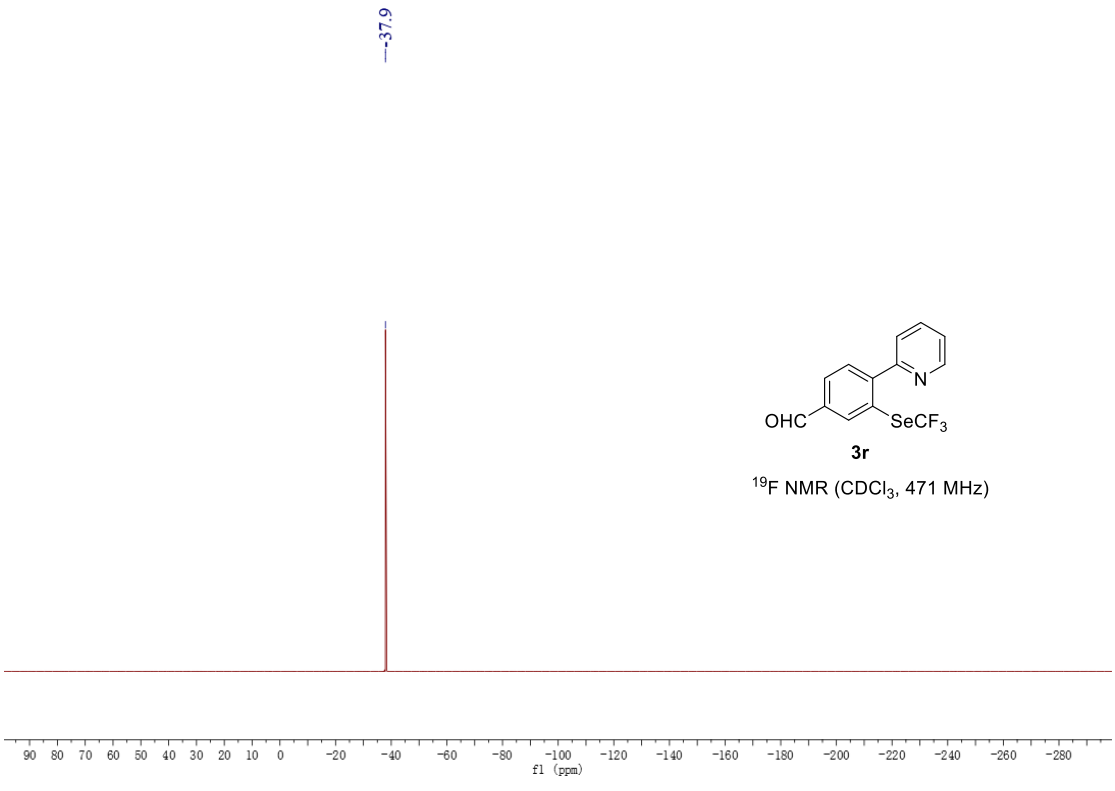
3q

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



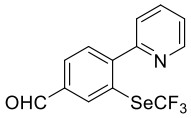
3r

^{1}H NMR ($CDCl_3$, 500 MHz)



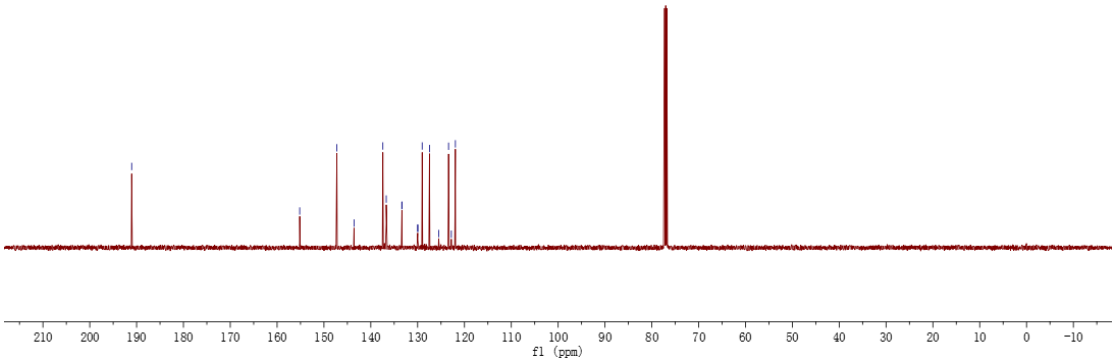
3r

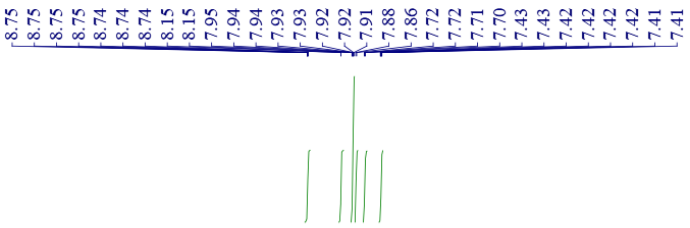
^{19}F NMR ($CDCl_3$, 471 MHz)

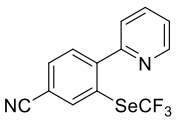


3r

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

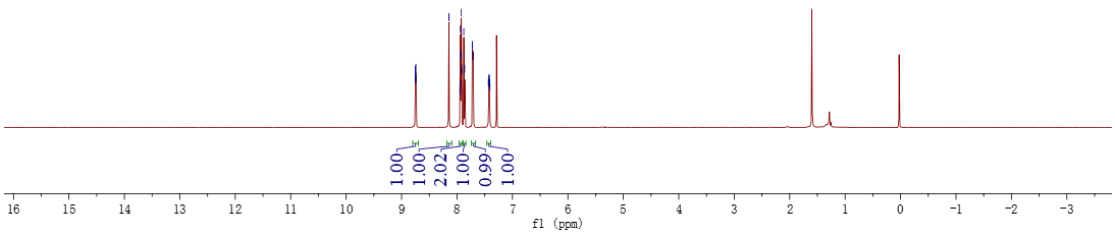


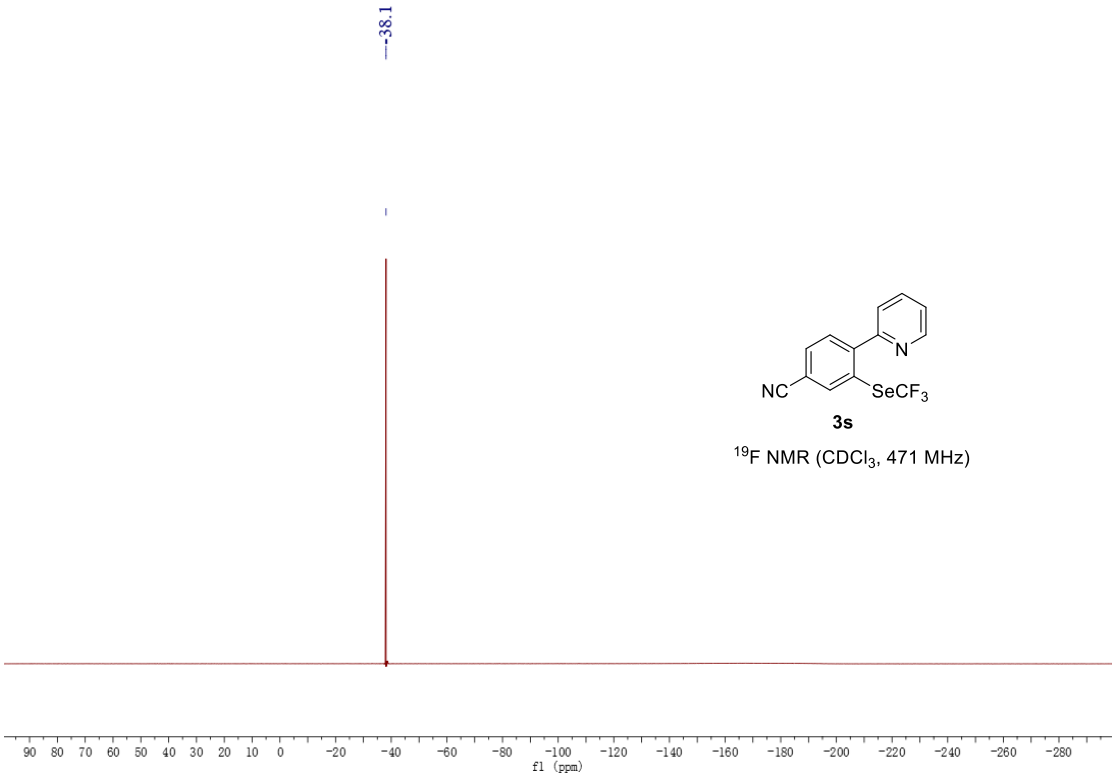




3s

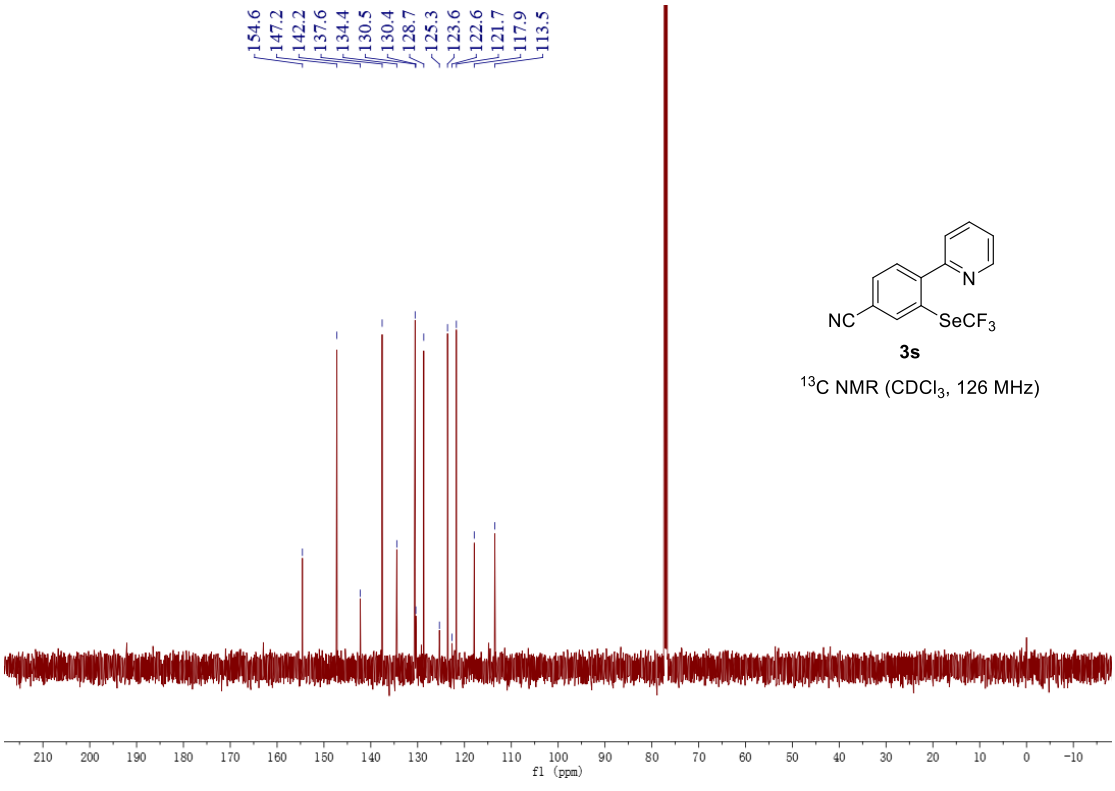
^{1}H NMR ($CDCl_3$, 500 MHz)





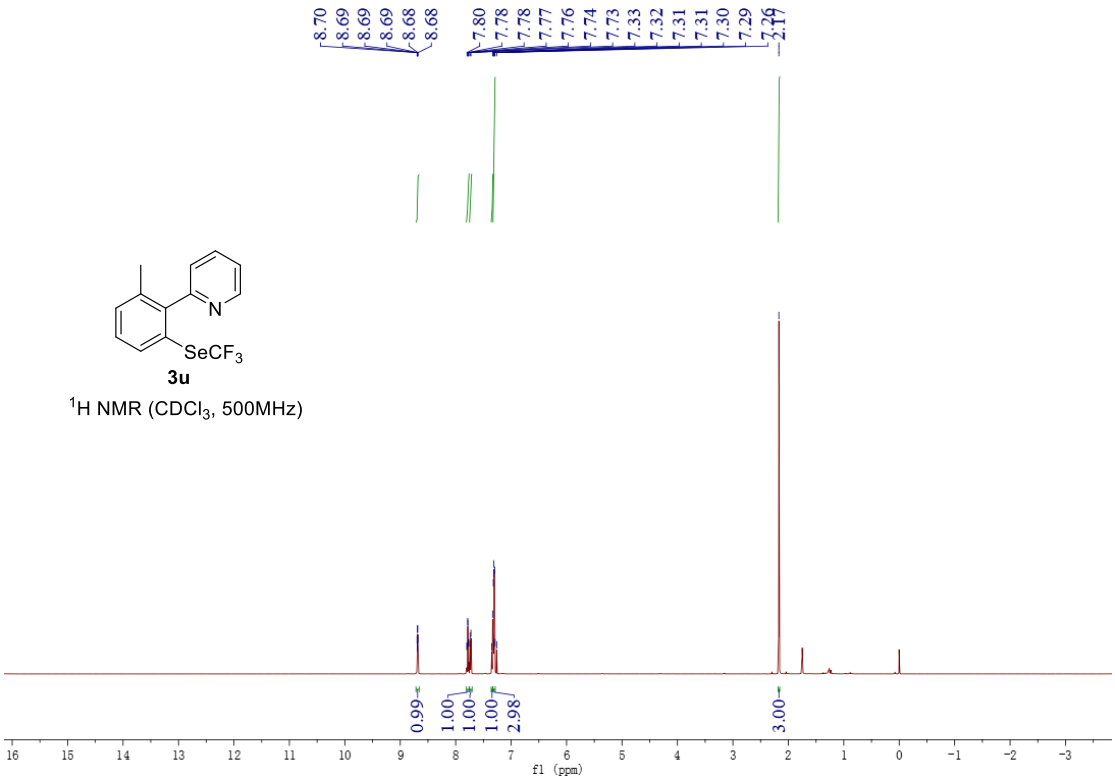
3s

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



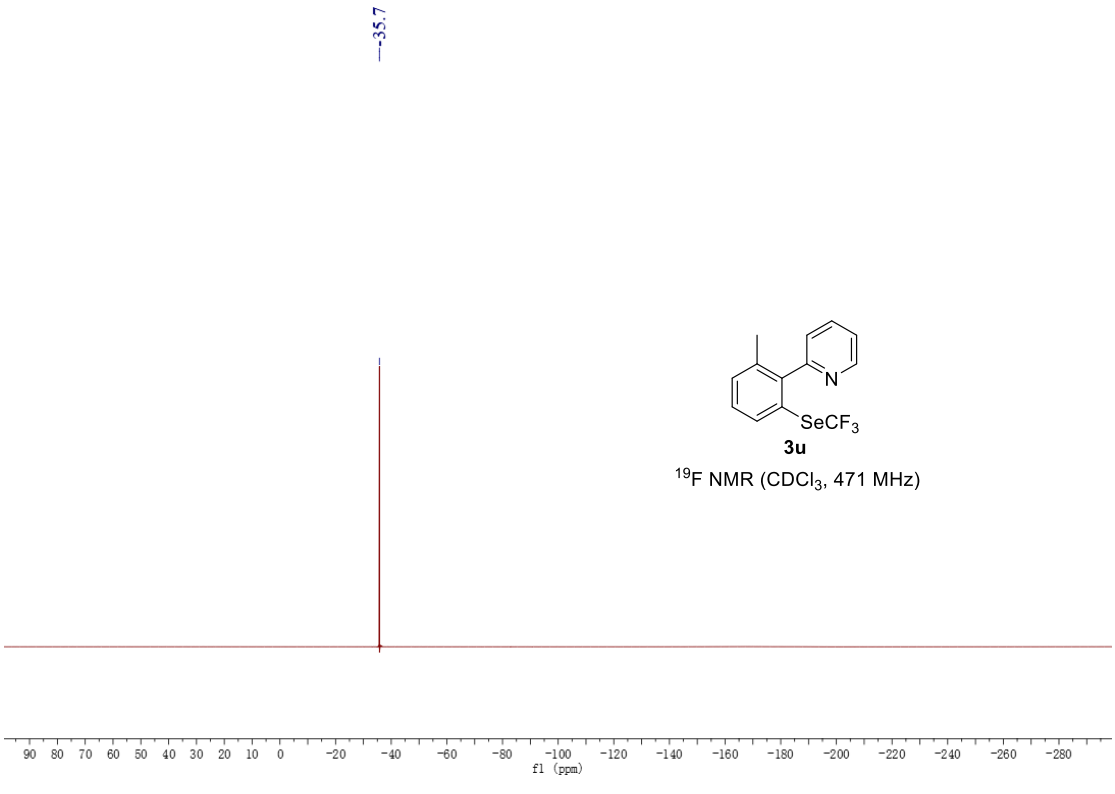
3s

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



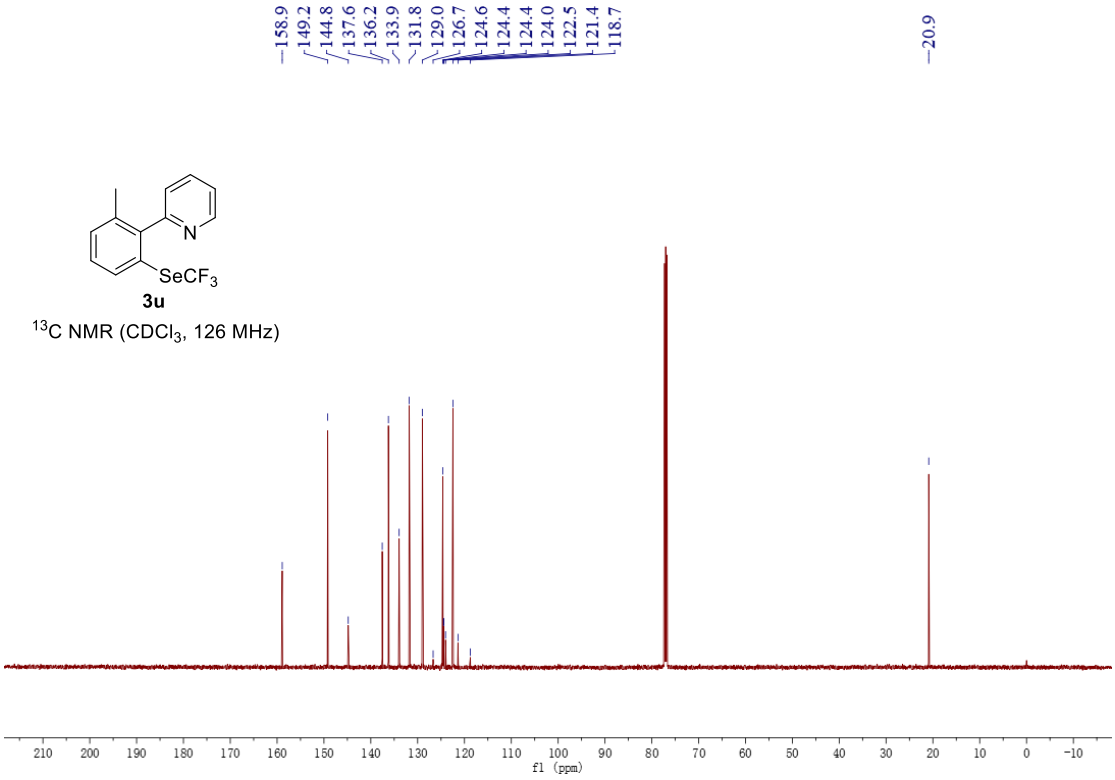
3u

^{1}H NMR ($CDCl_3$, 500MHz)



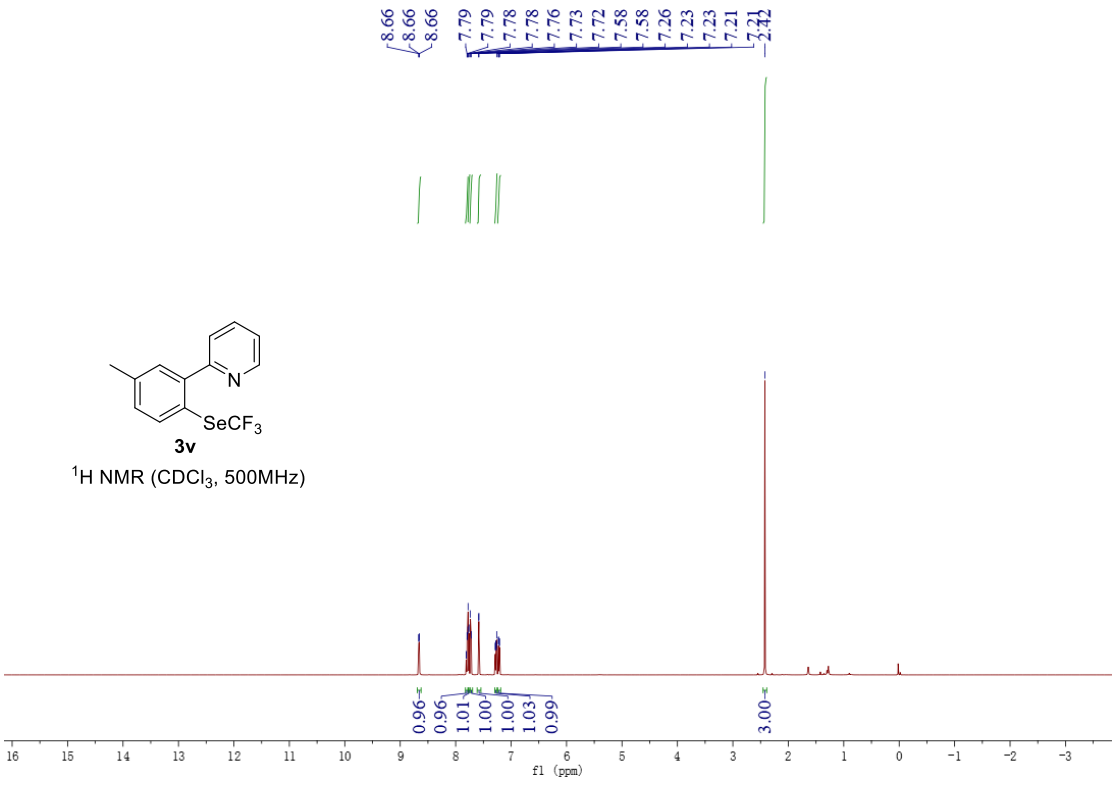
3u

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



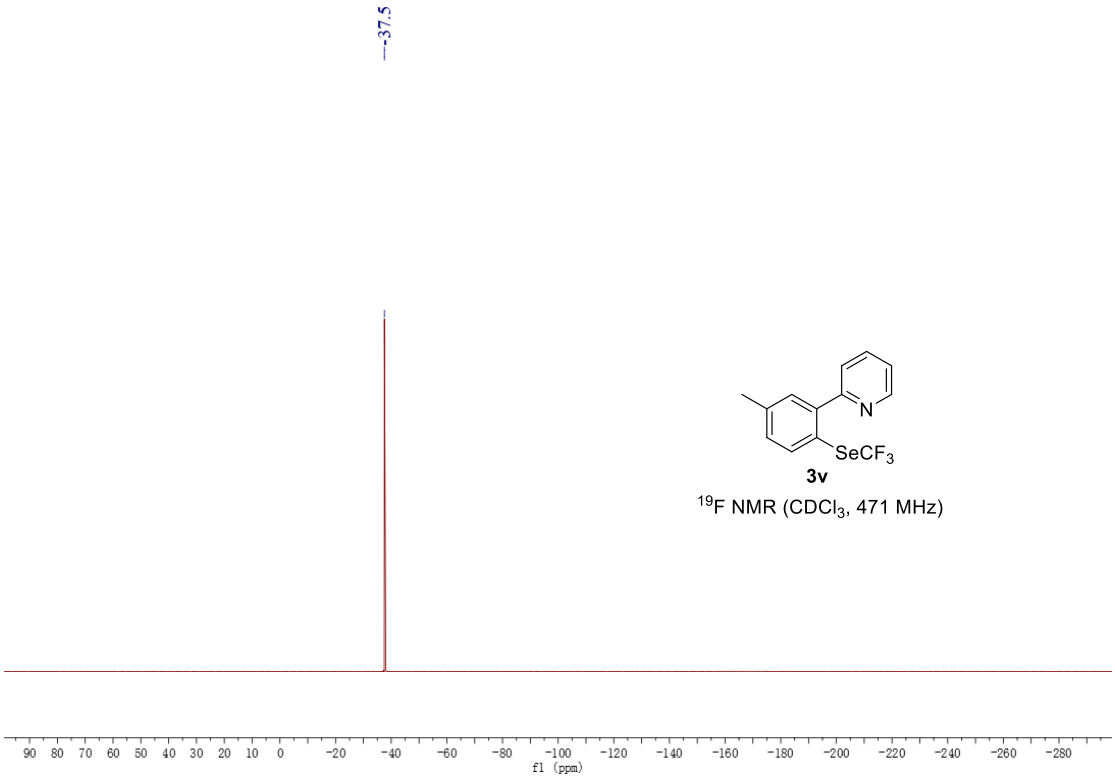
3u

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



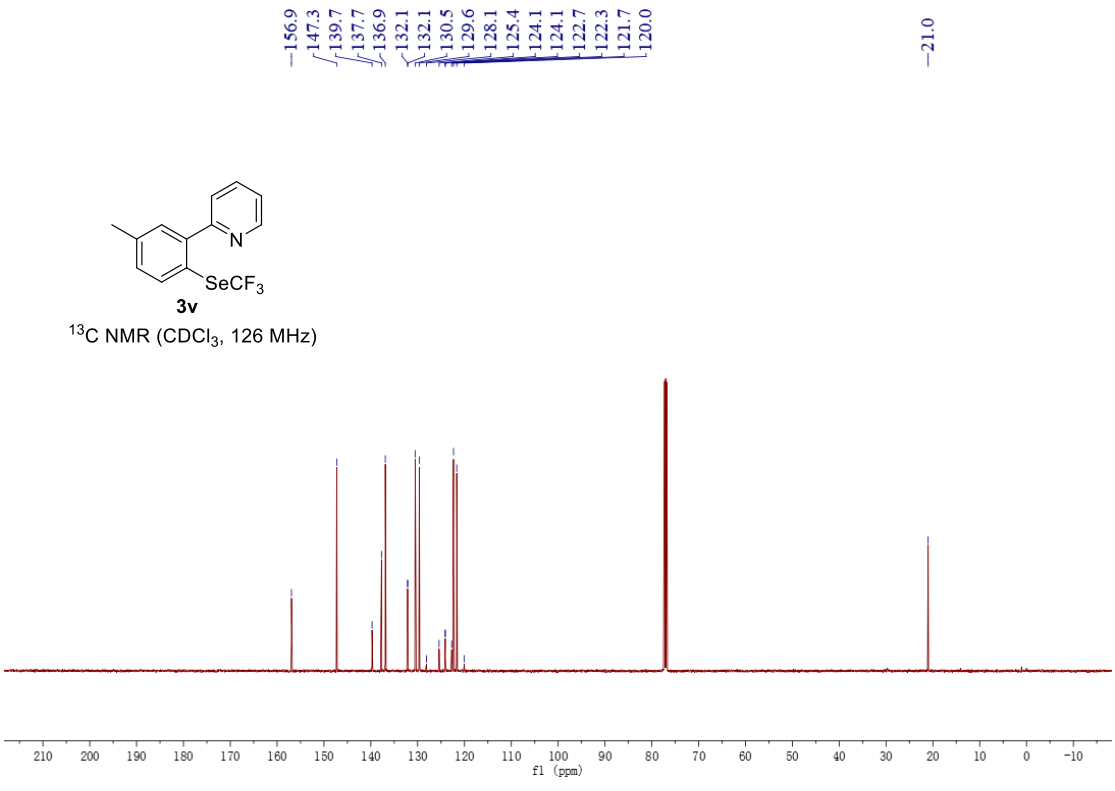
3v

^{1}H NMR ($CDCl_3$, 500MHz)



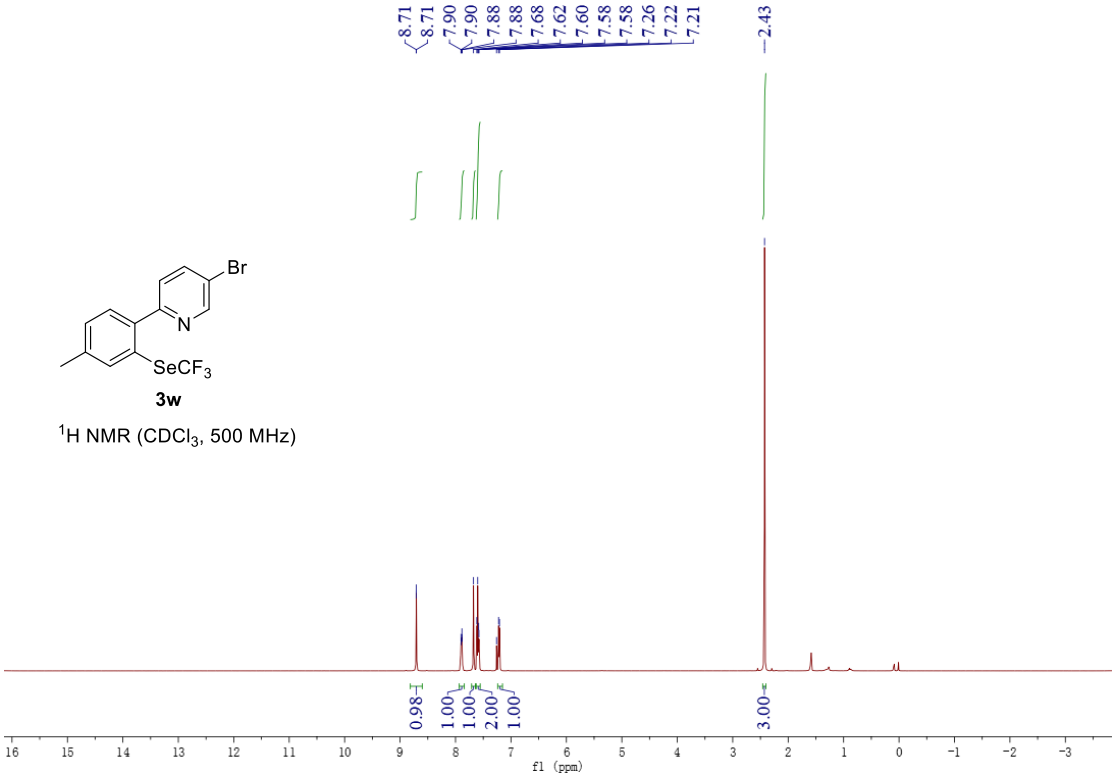
3v

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



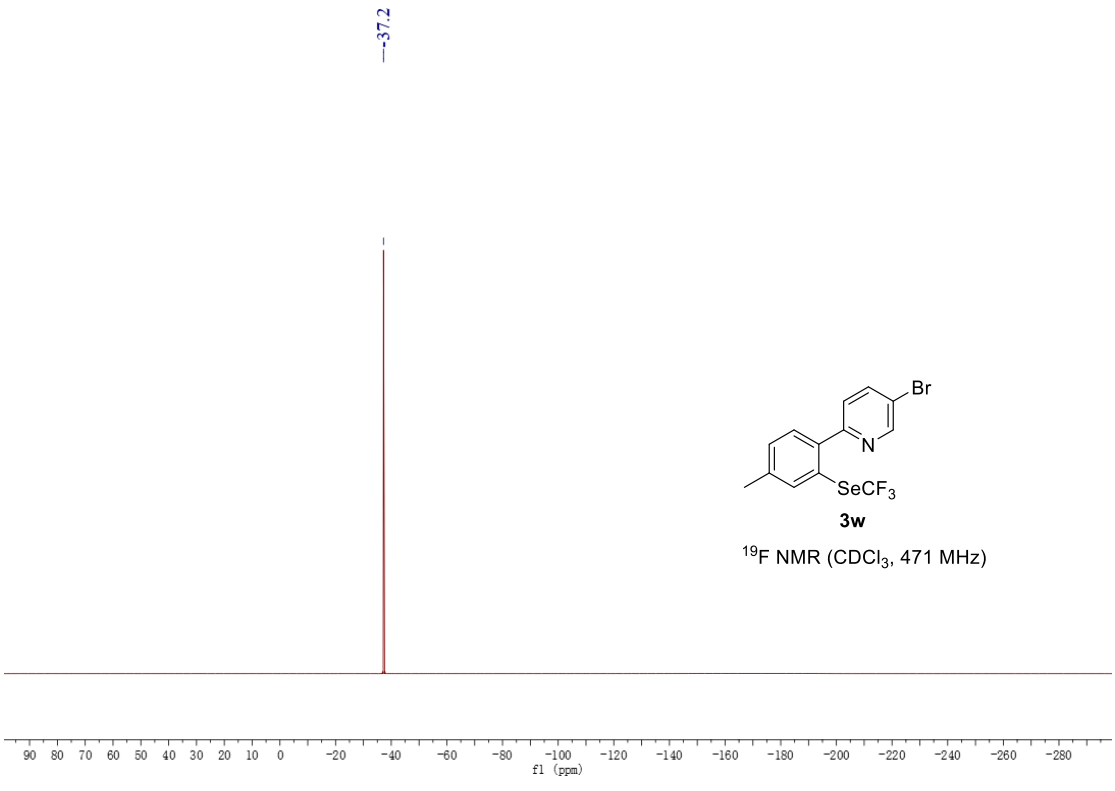
3v

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



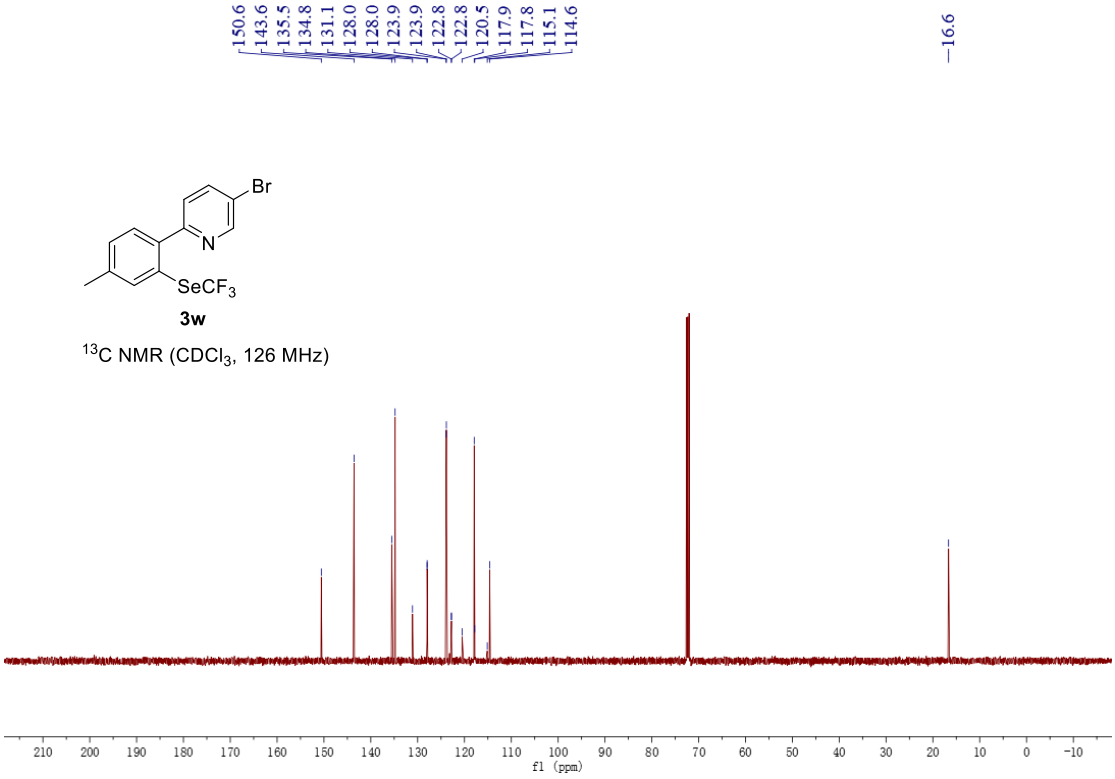
3w

^{1}H NMR ($CDCl_3$, 500 MHz)



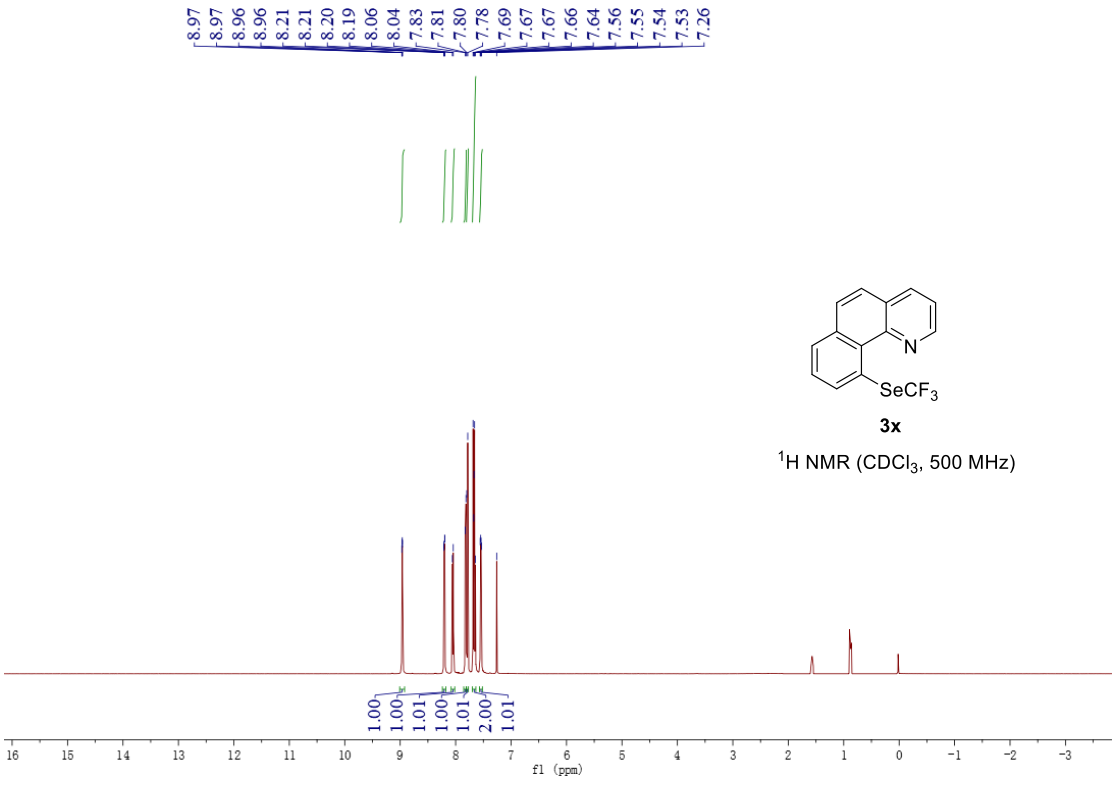
3w

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



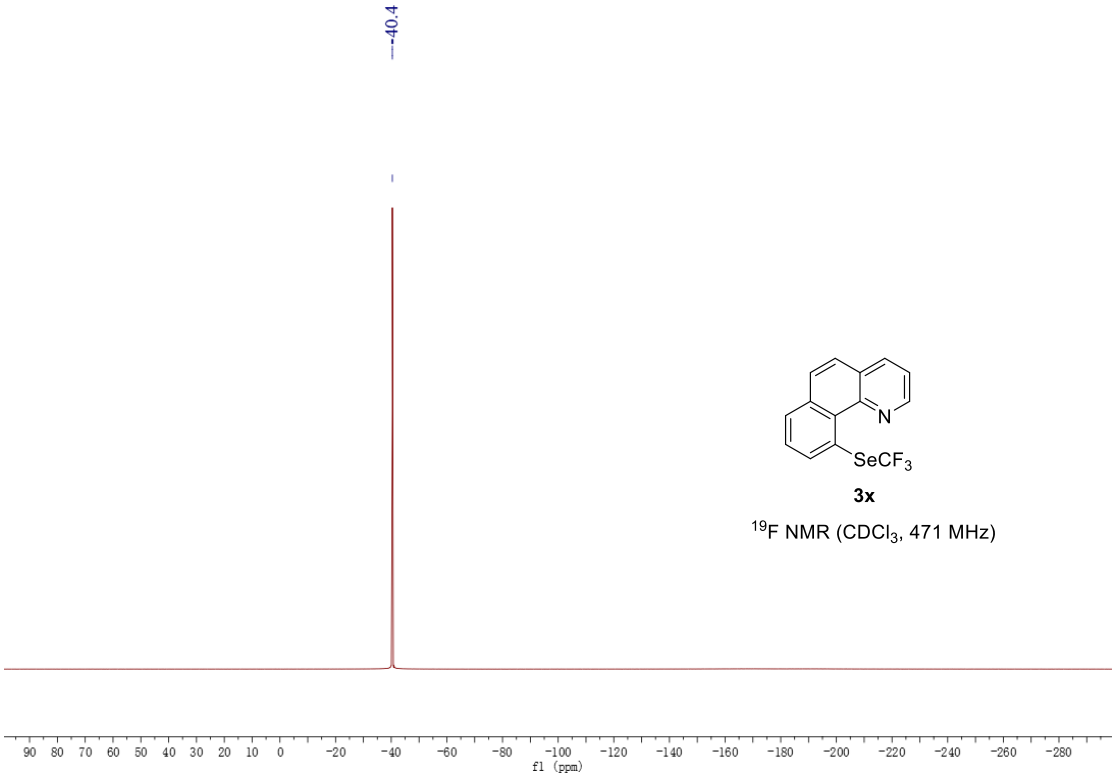
3w

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



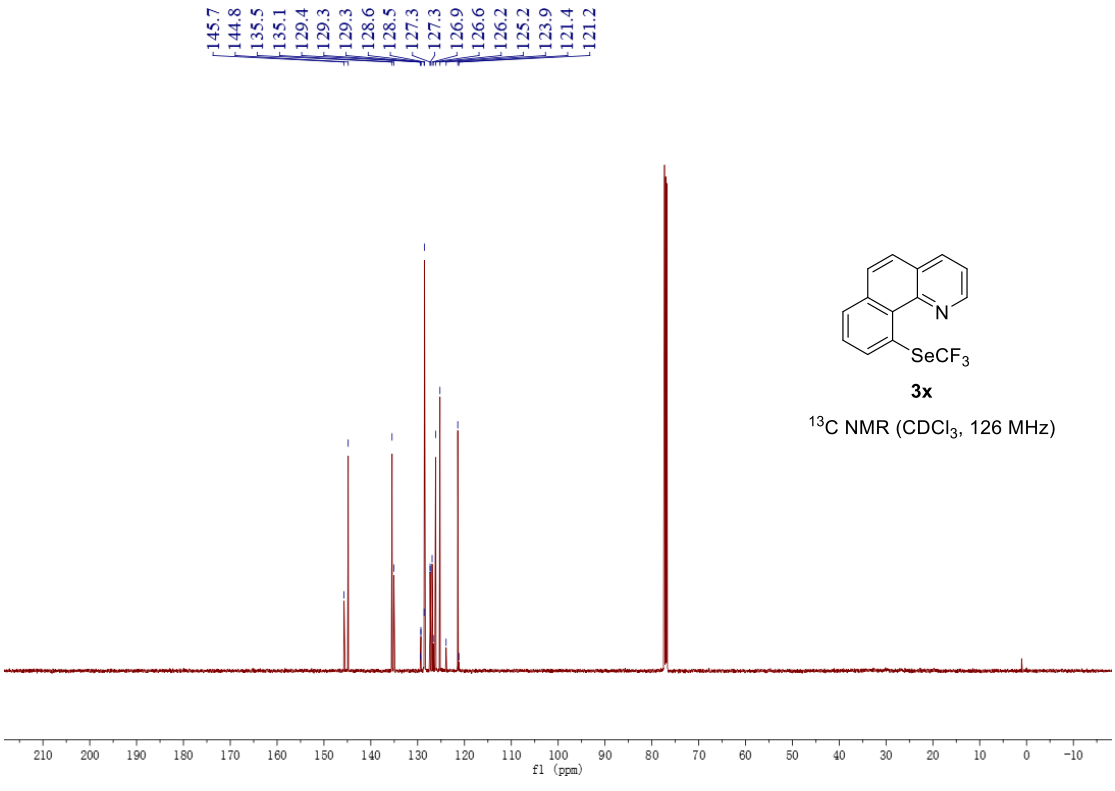
3x

^{1}H NMR ($CDCl_3$, 500 MHz)



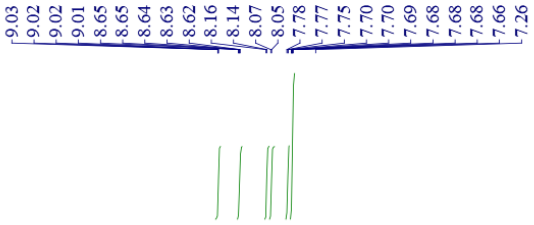
3x

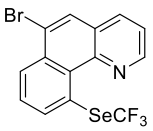
^{19}F NMR ($CDCl_3$, 471 MHz)



3x

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





3y

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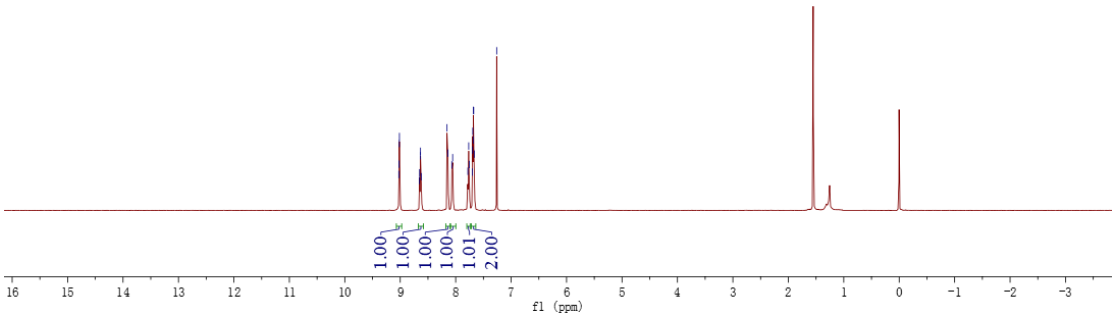
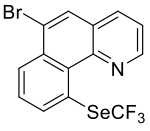
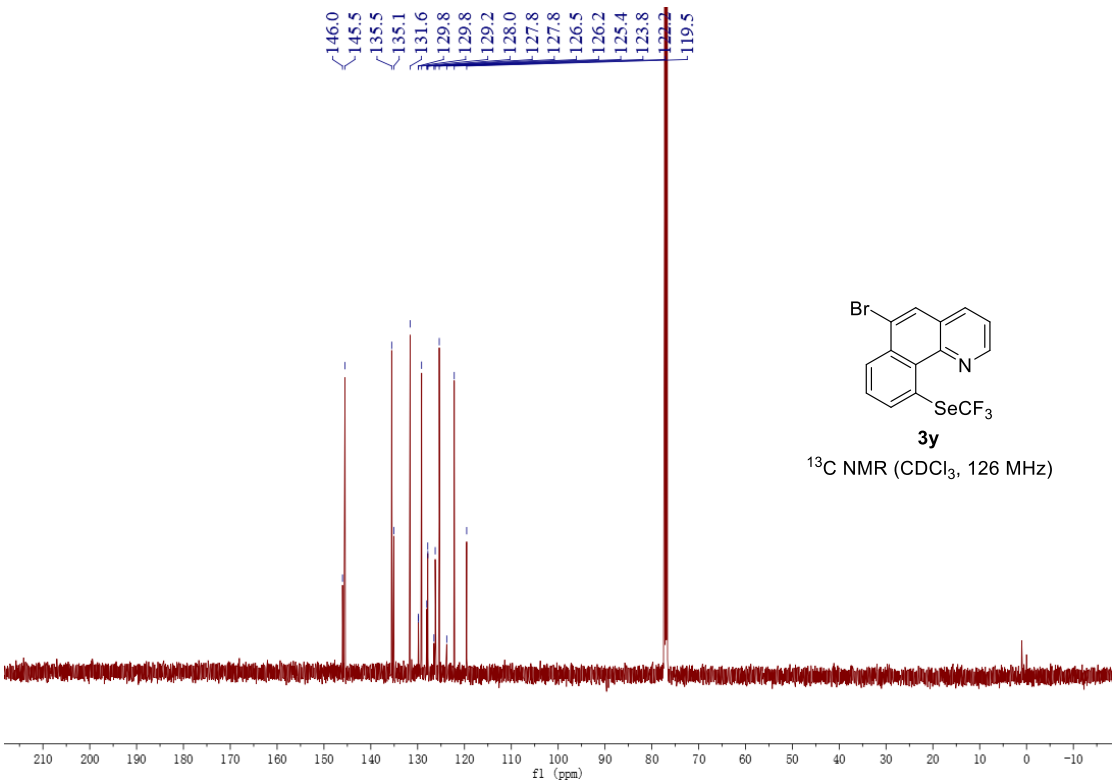




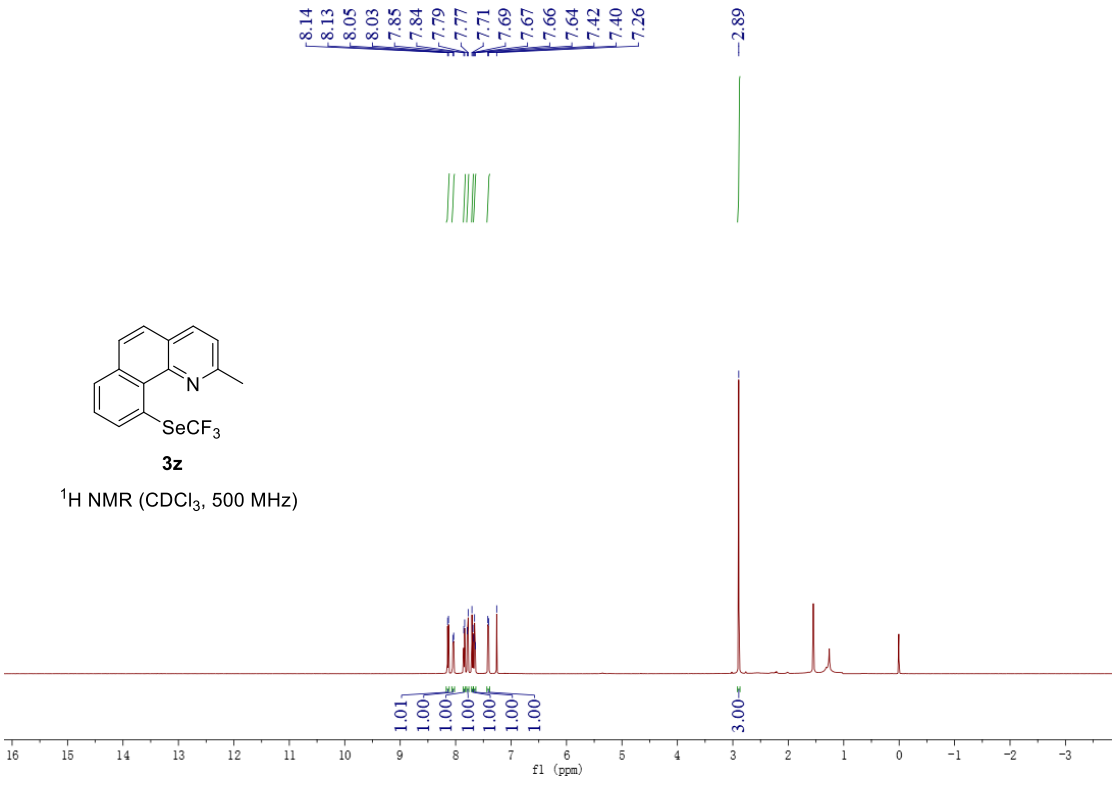
3y

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



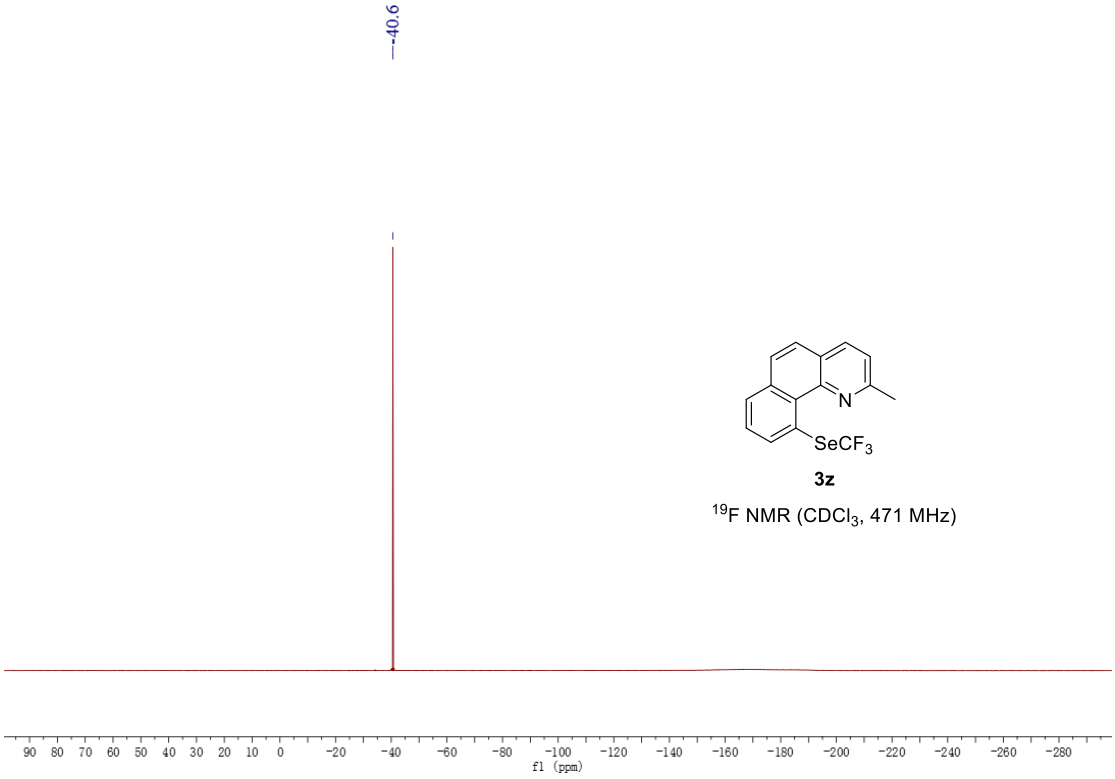
3y

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



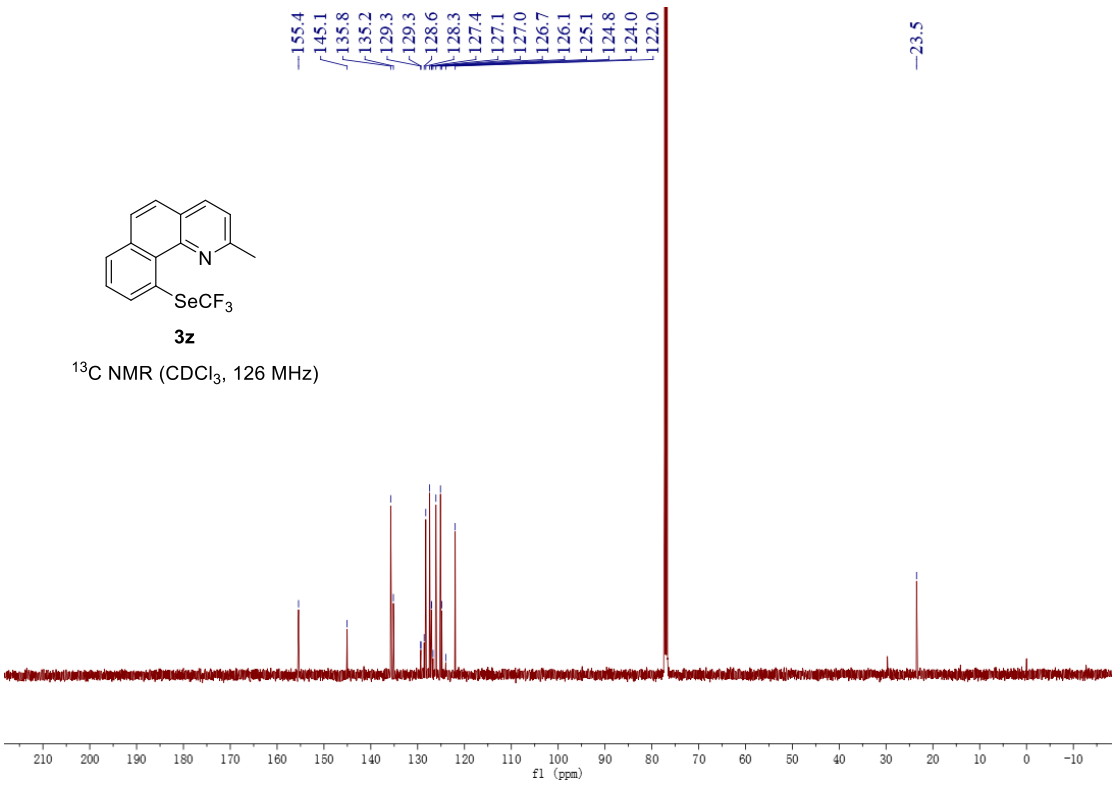
3z

^{1}H NMR ($CDCl_3$, 500 MHz)



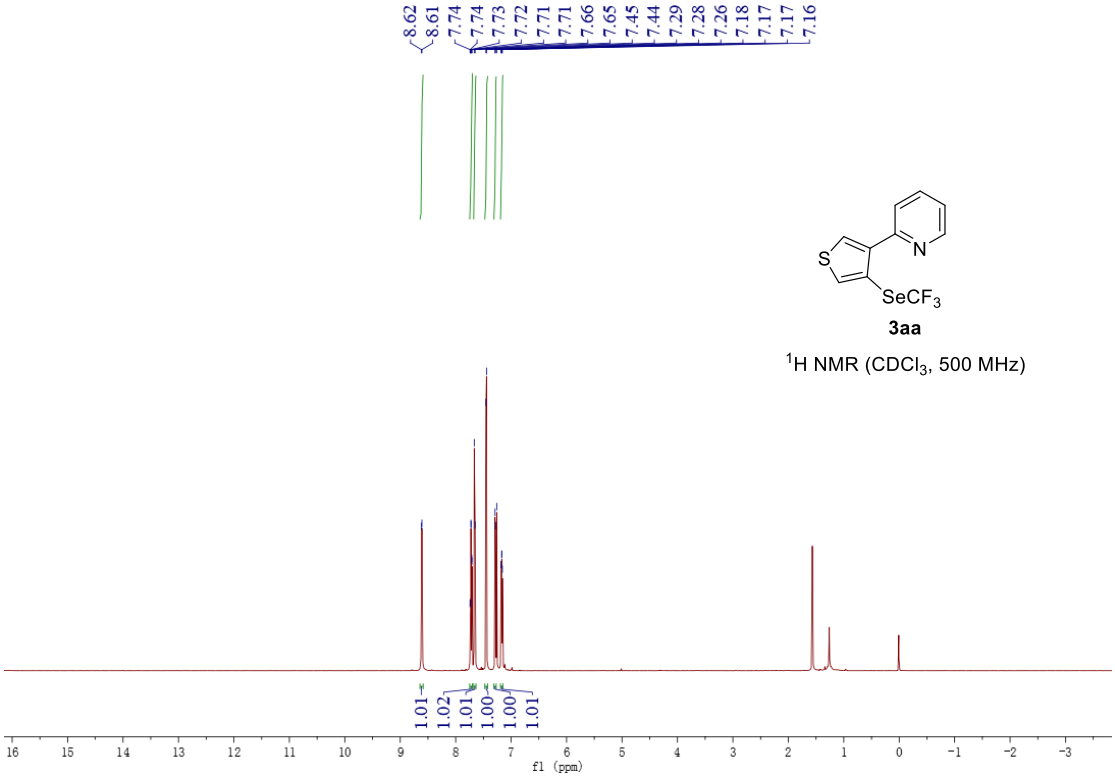
3z

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



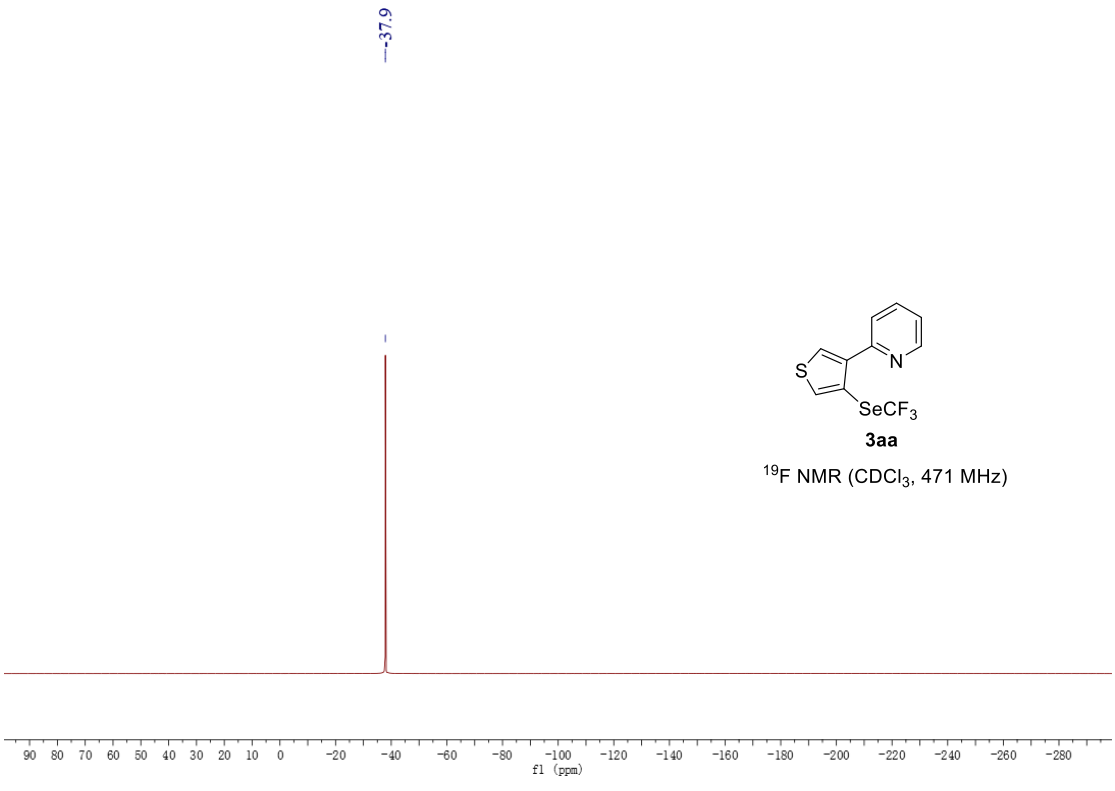
3z

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



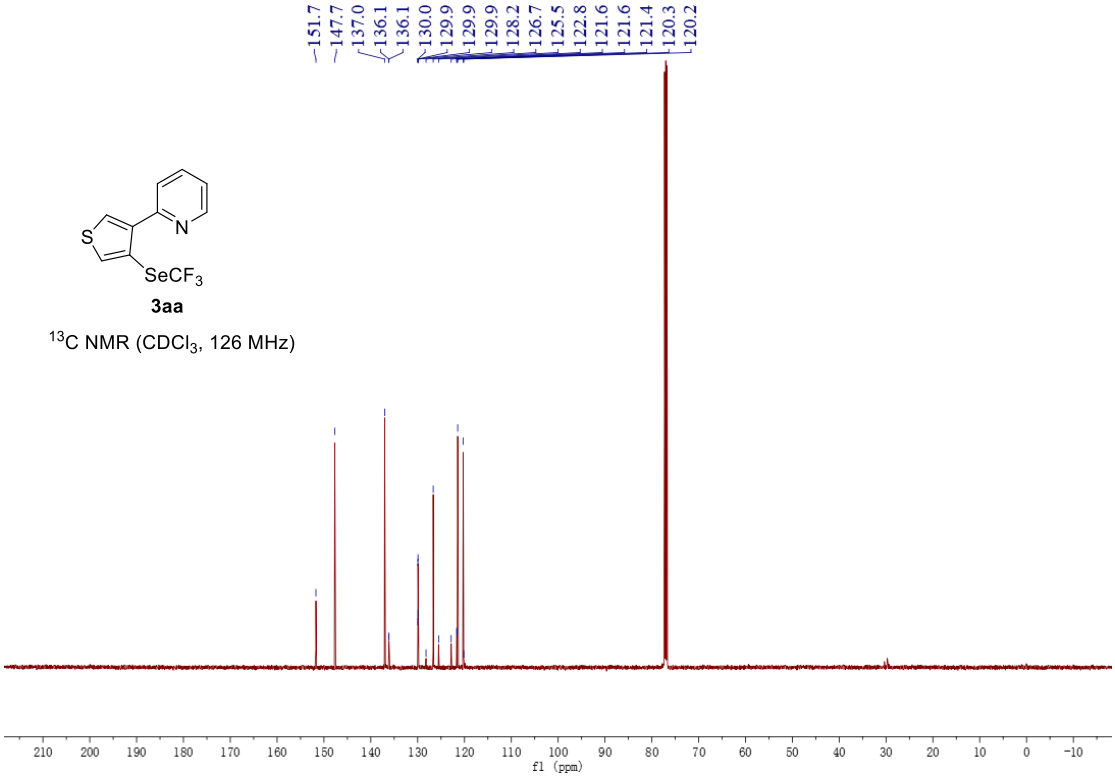
3aa

^{1}H NMR ($CDCl_3$, 500 MHz)



3aa

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



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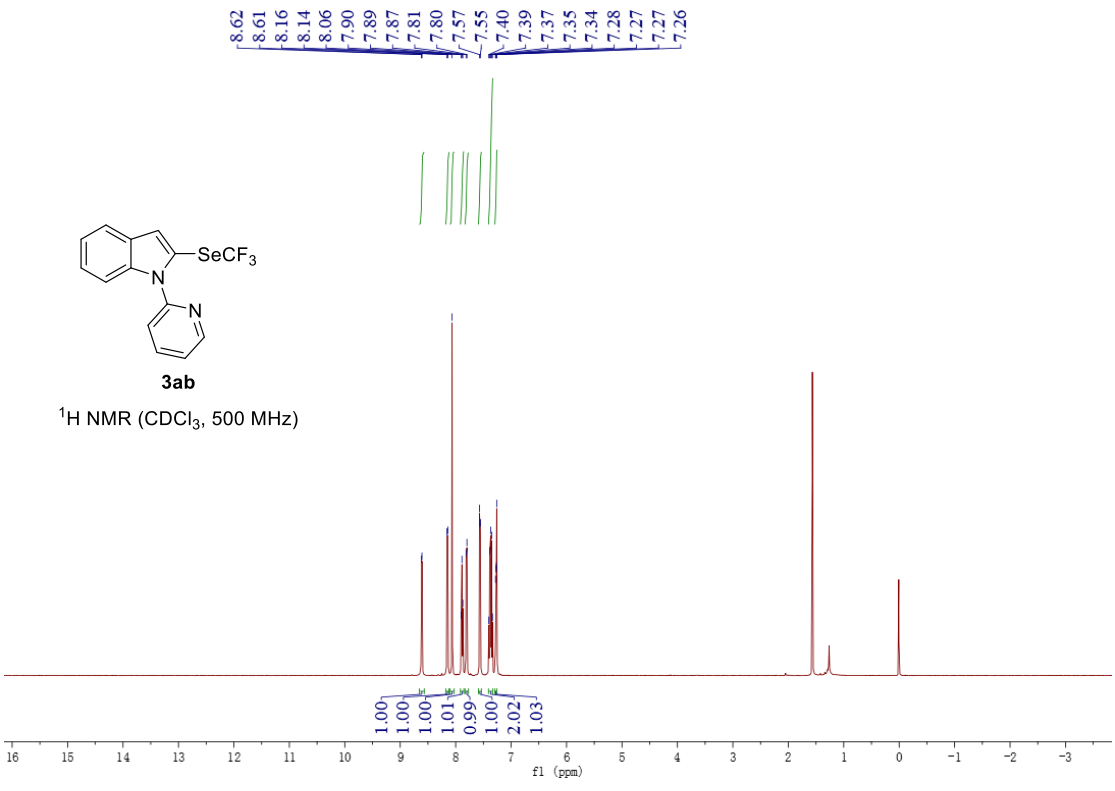

3ab

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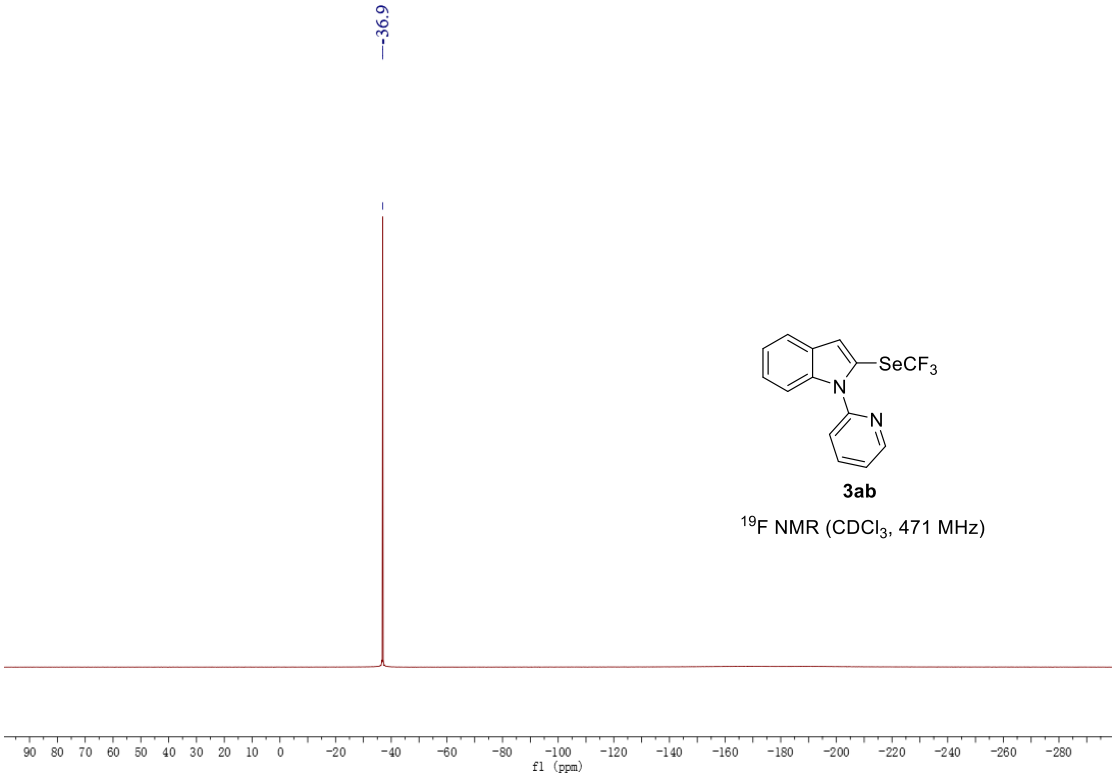

3ab

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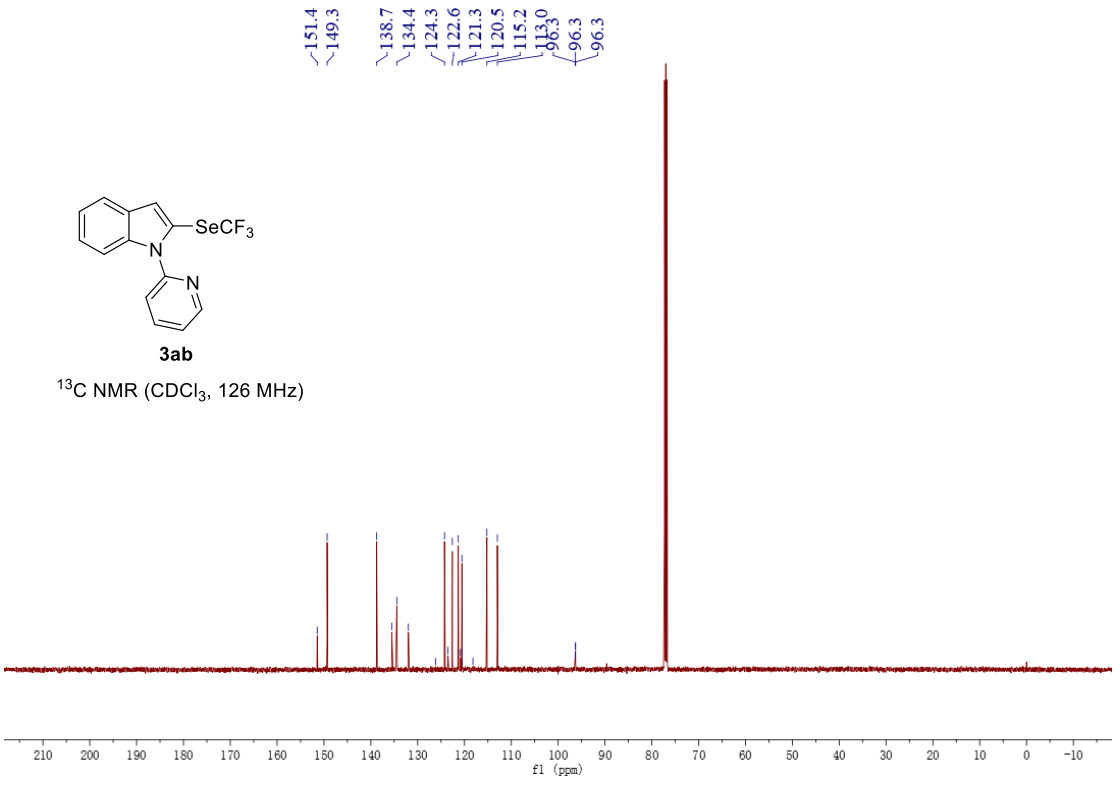
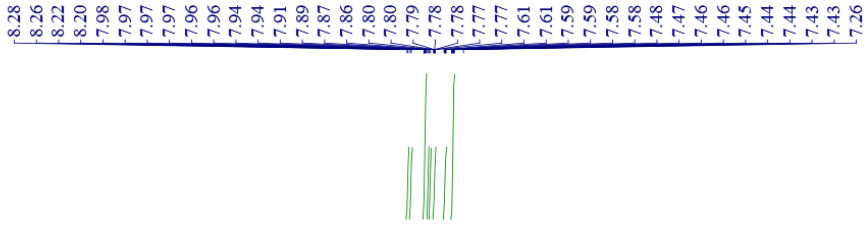
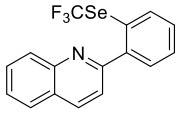


3ab

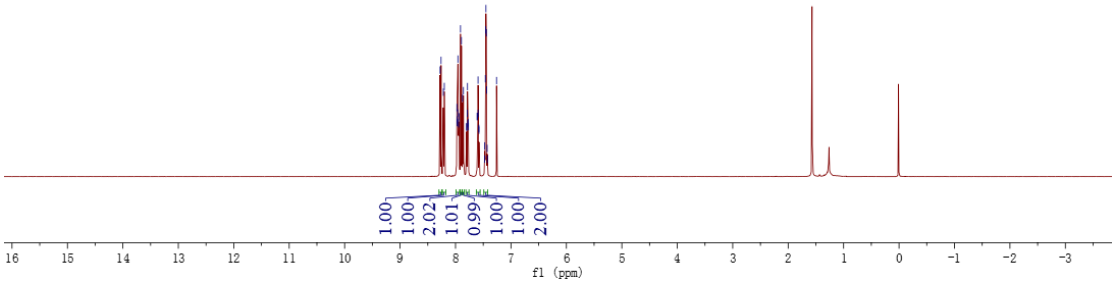
^{13}C NMR ($CDCl_3$, 126 MHz)

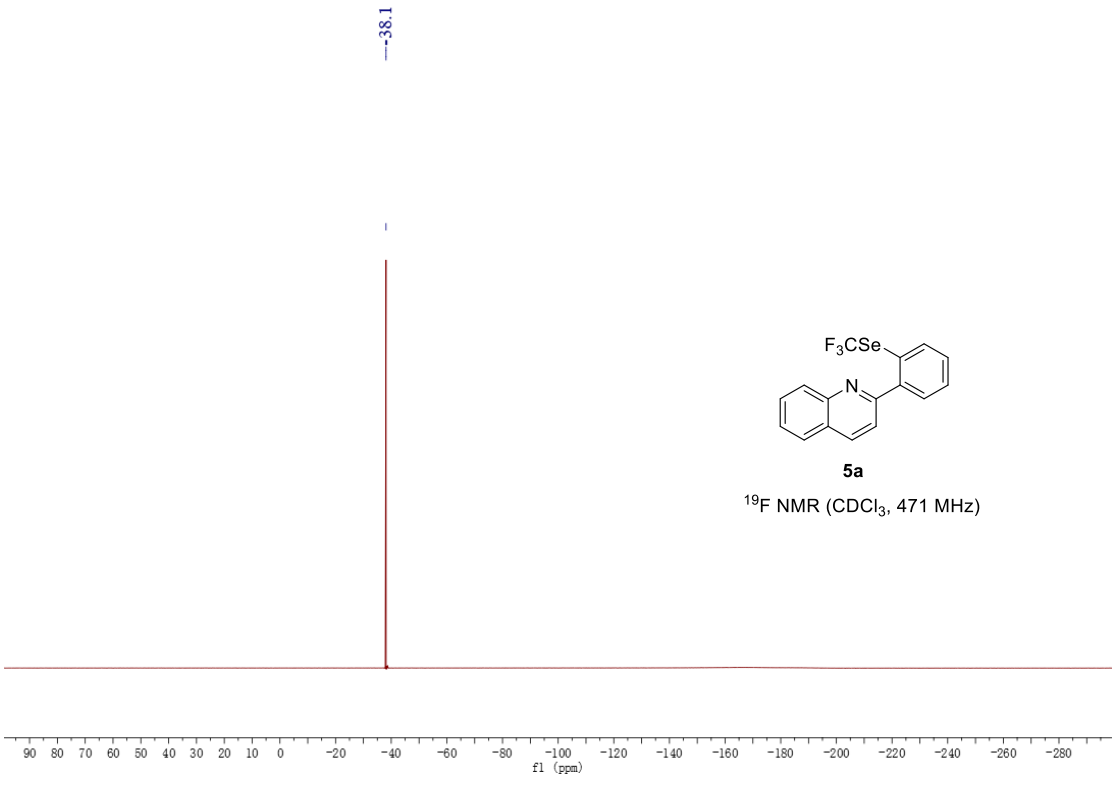




5a

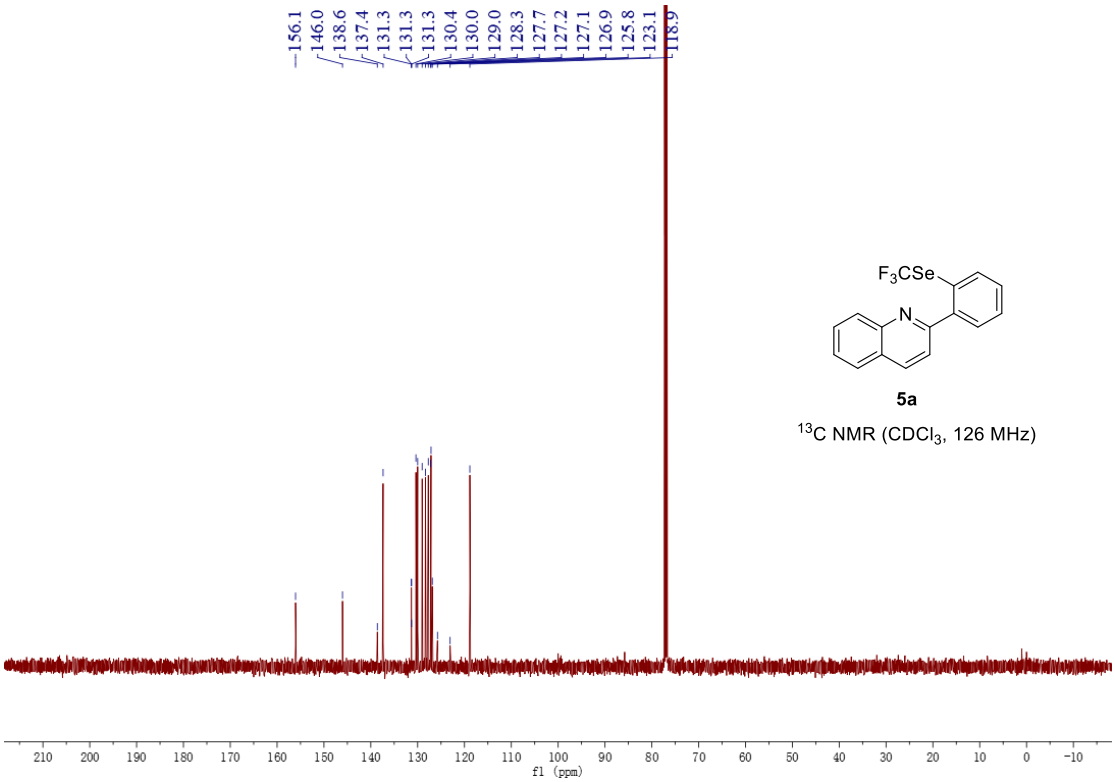
^{1}H NMR ($CDCl_3$, 500 MHz)





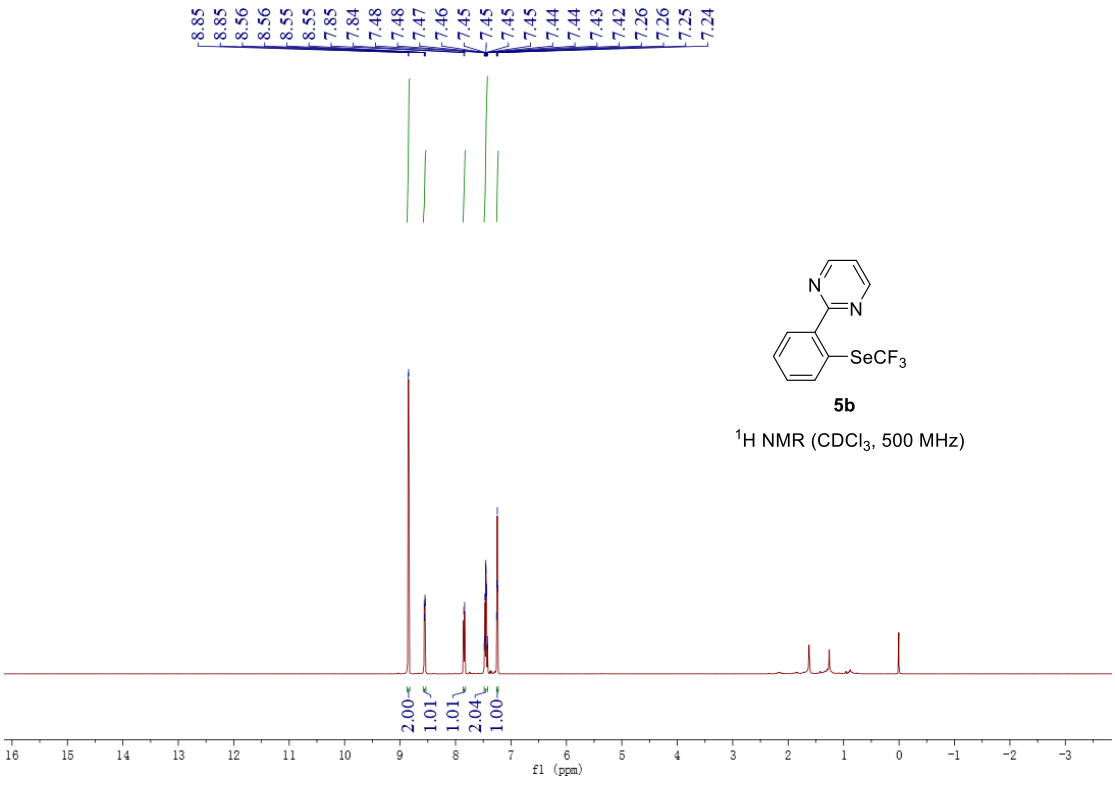
5a

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



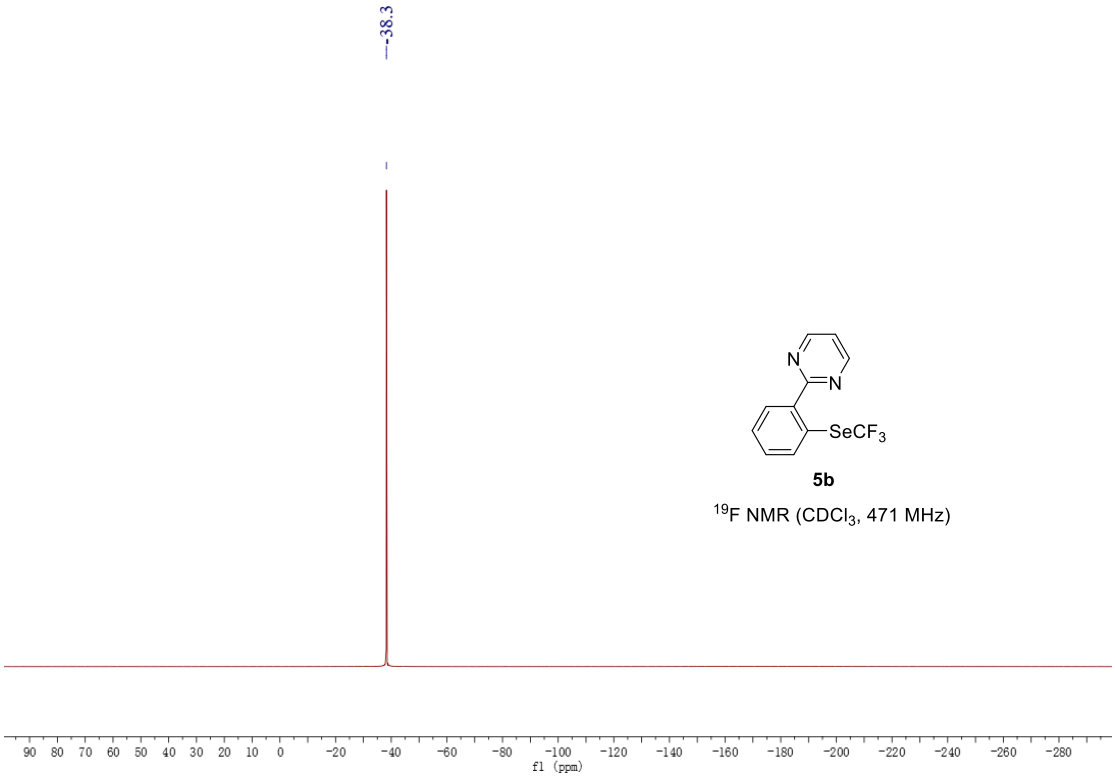
5a

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



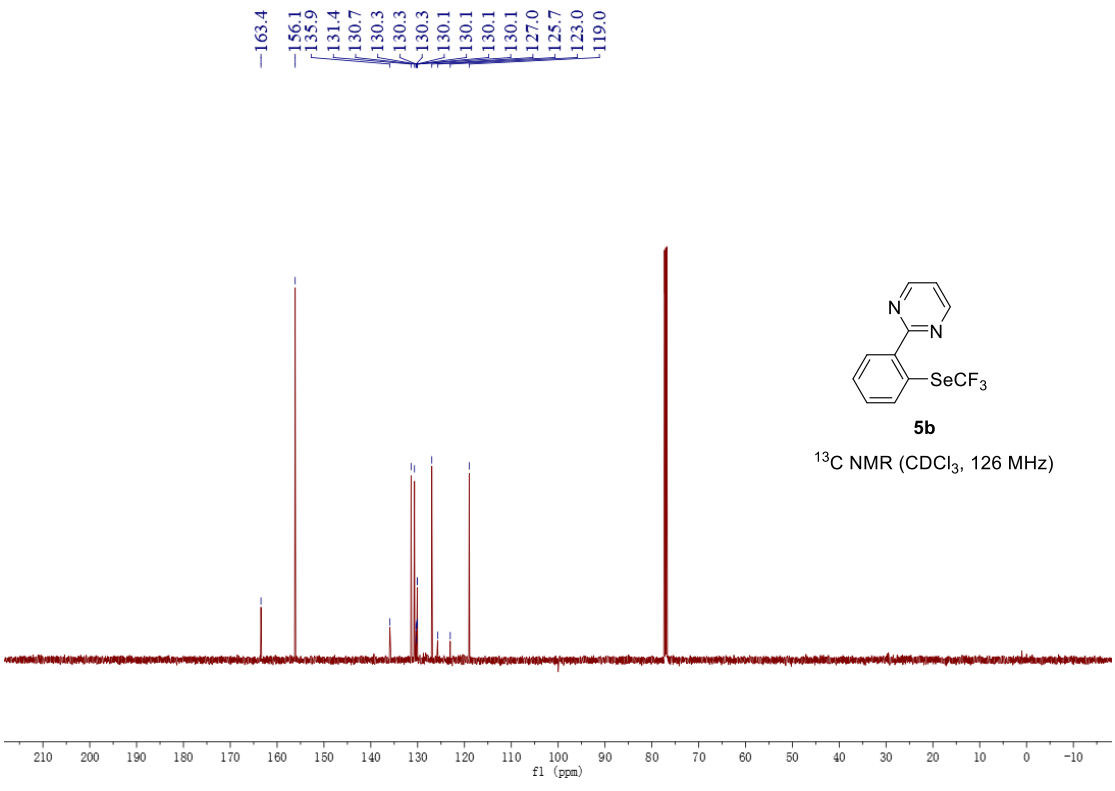
5b

^{1}H NMR ($CDCl_3$, 500 MHz)



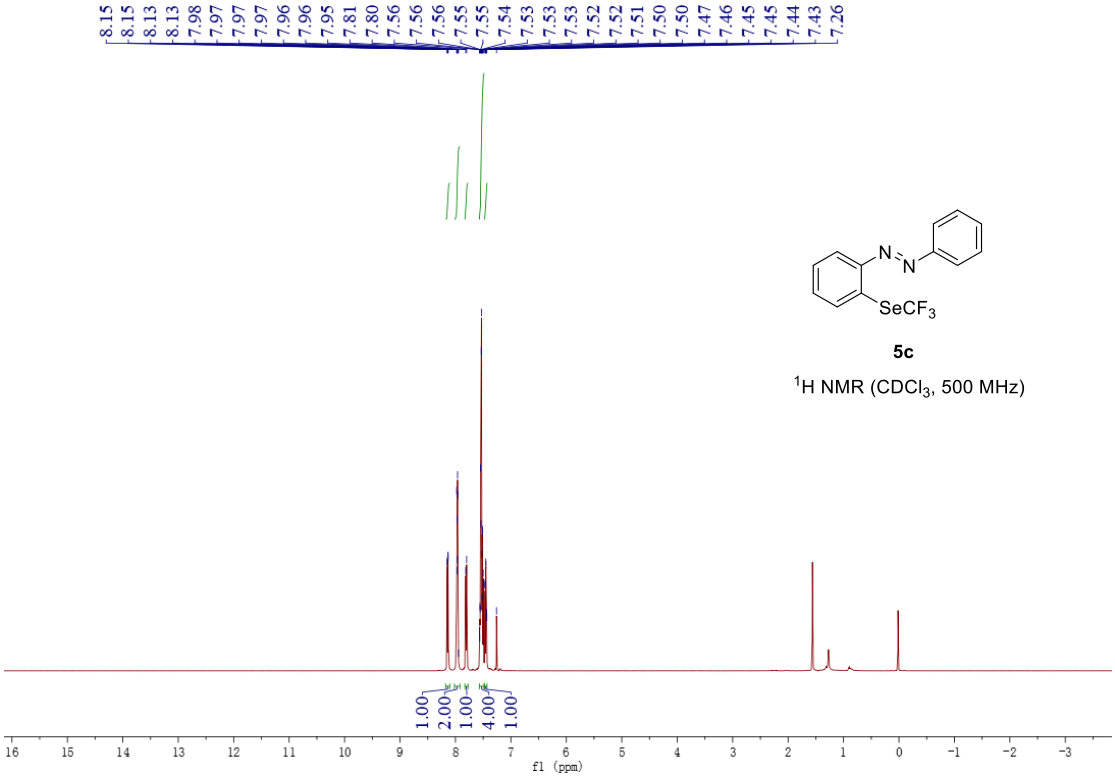
5b

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



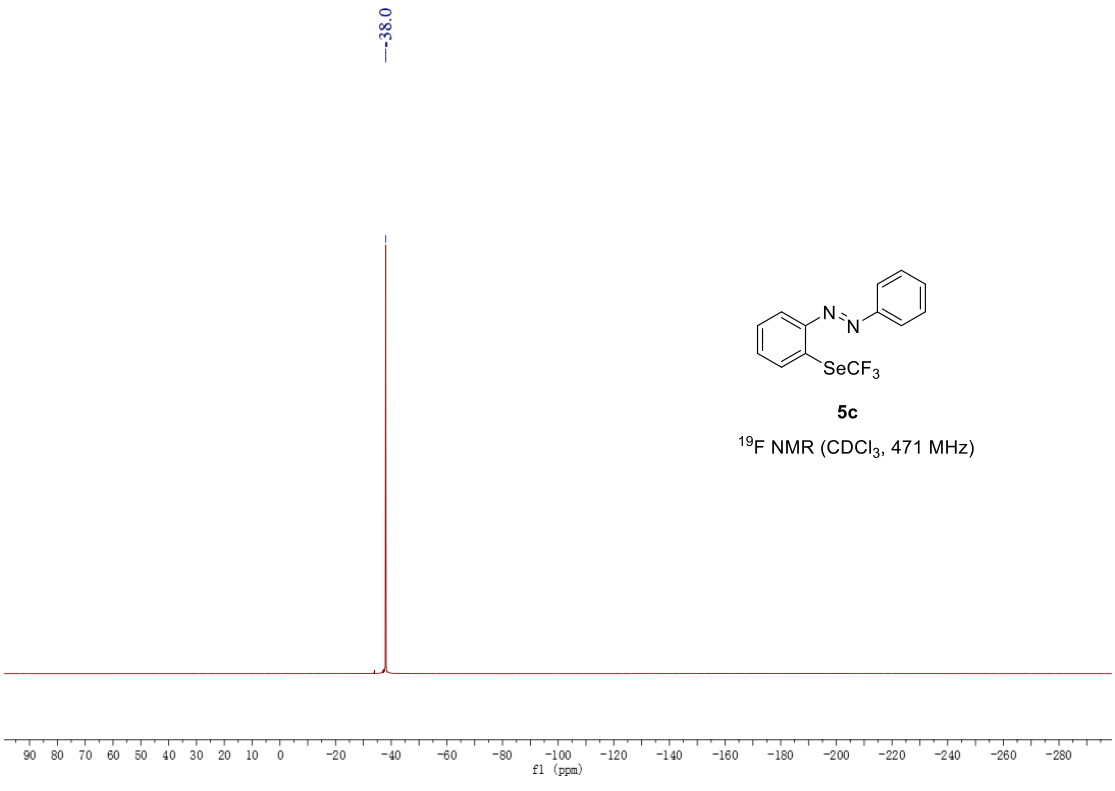
5b

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



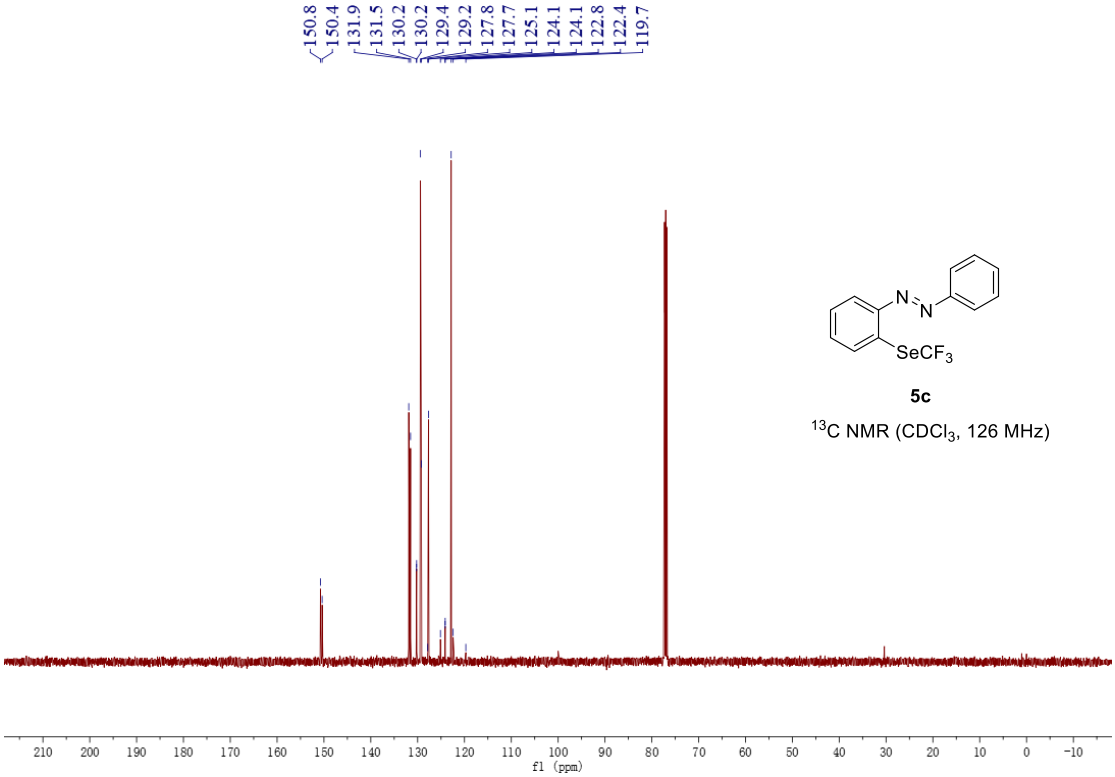
5c

^{1}H NMR ($CDCl_3$, 500 MHz)



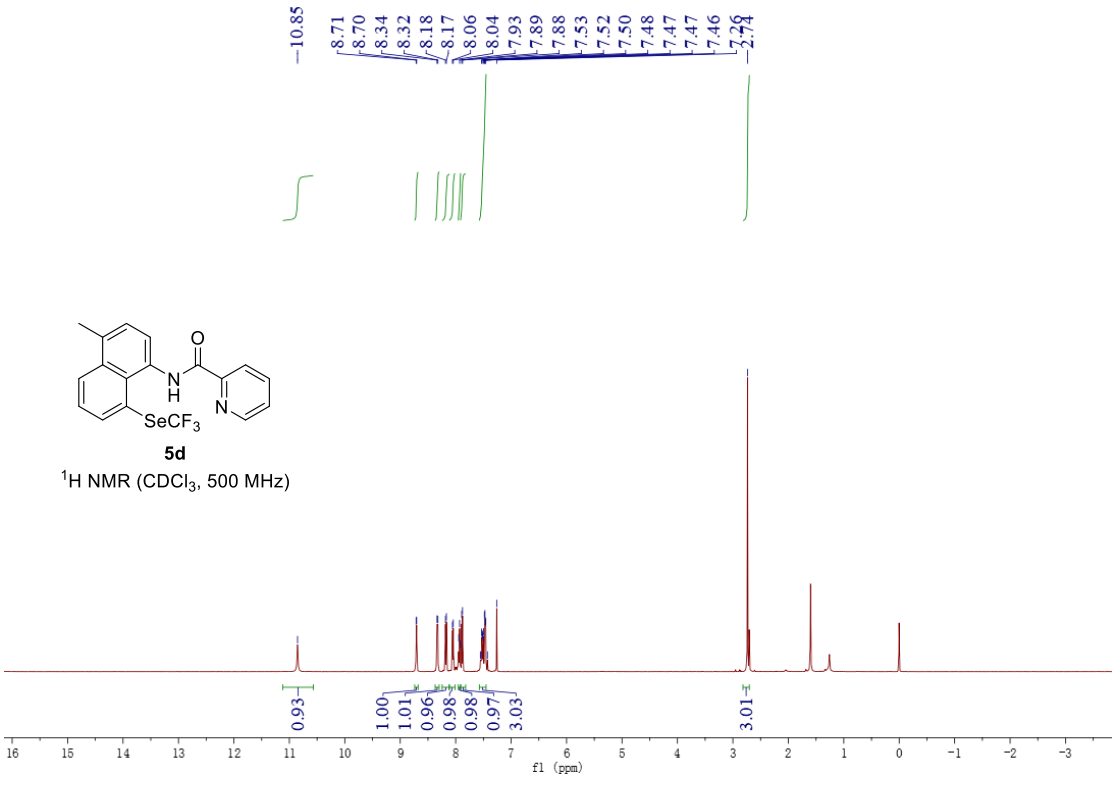
5c

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



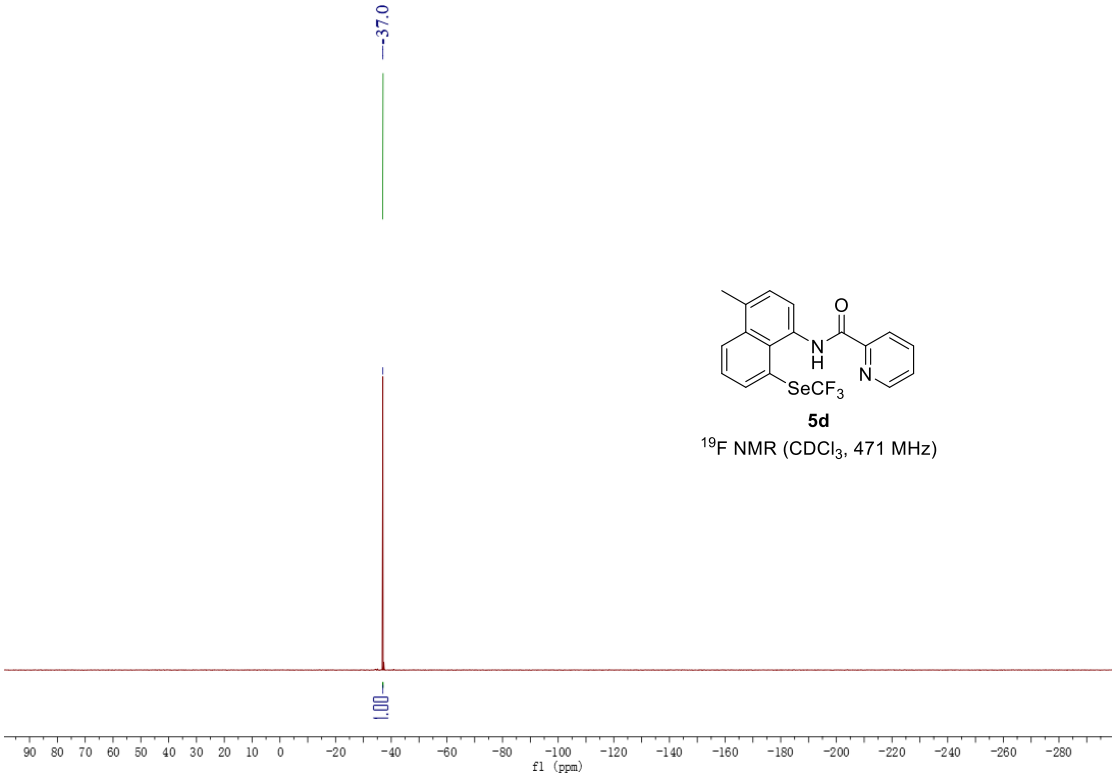
5c

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



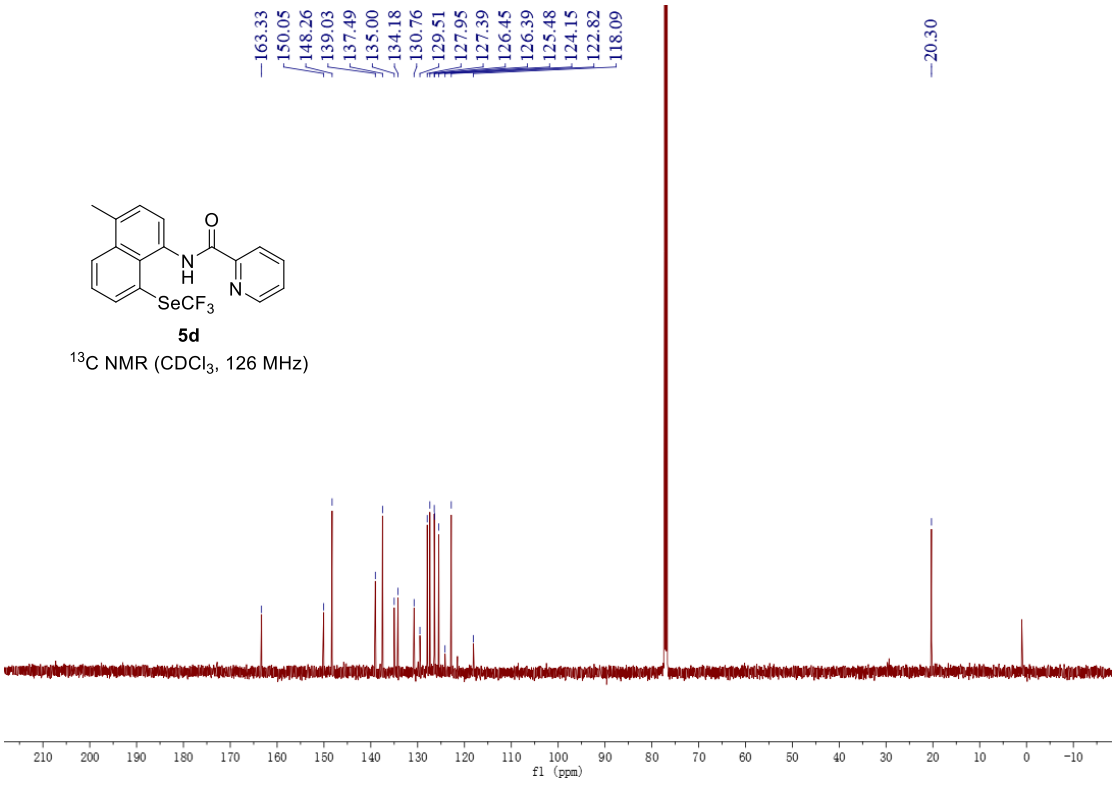
5d

^{1}H NMR ($CDCl_3$, 500 MHz)



5d

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



5d

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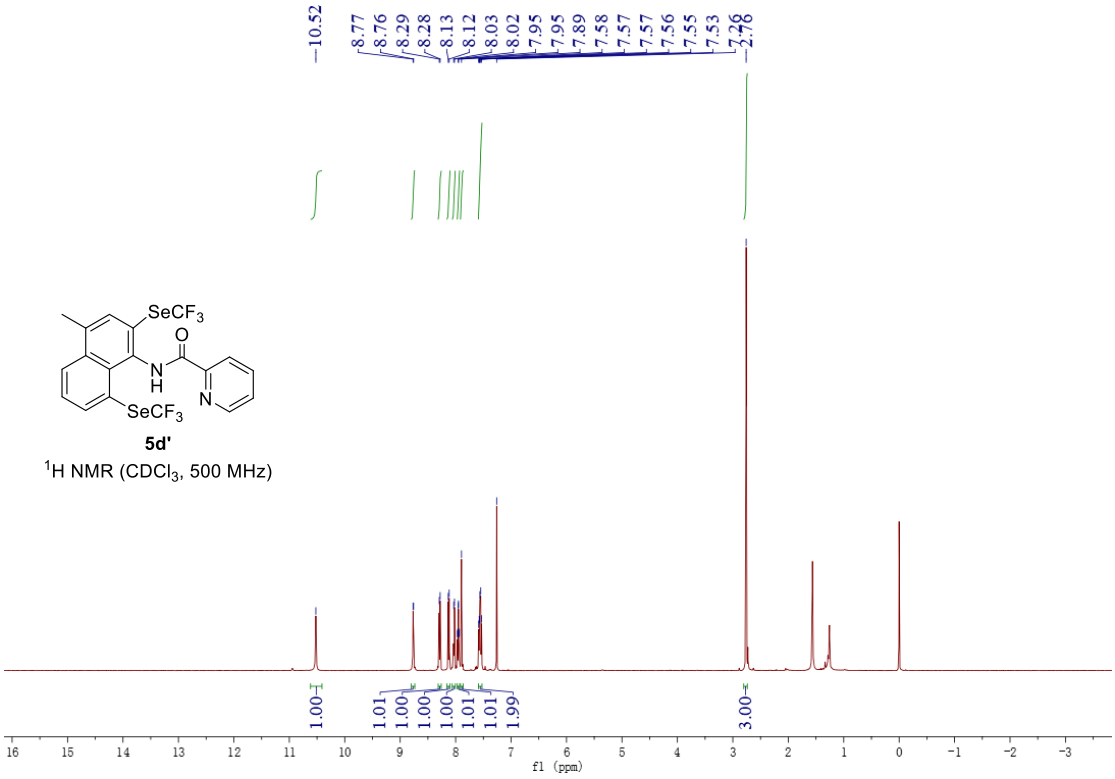
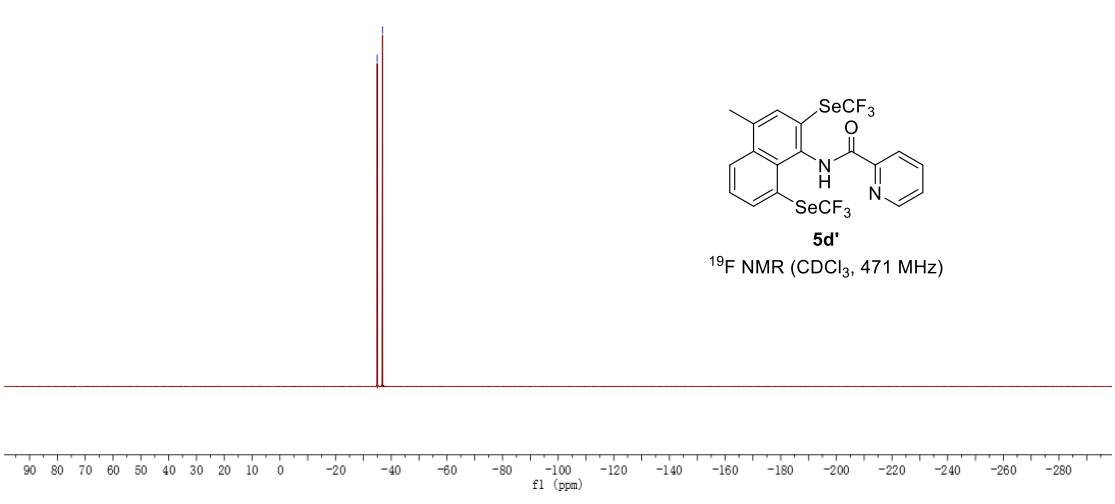


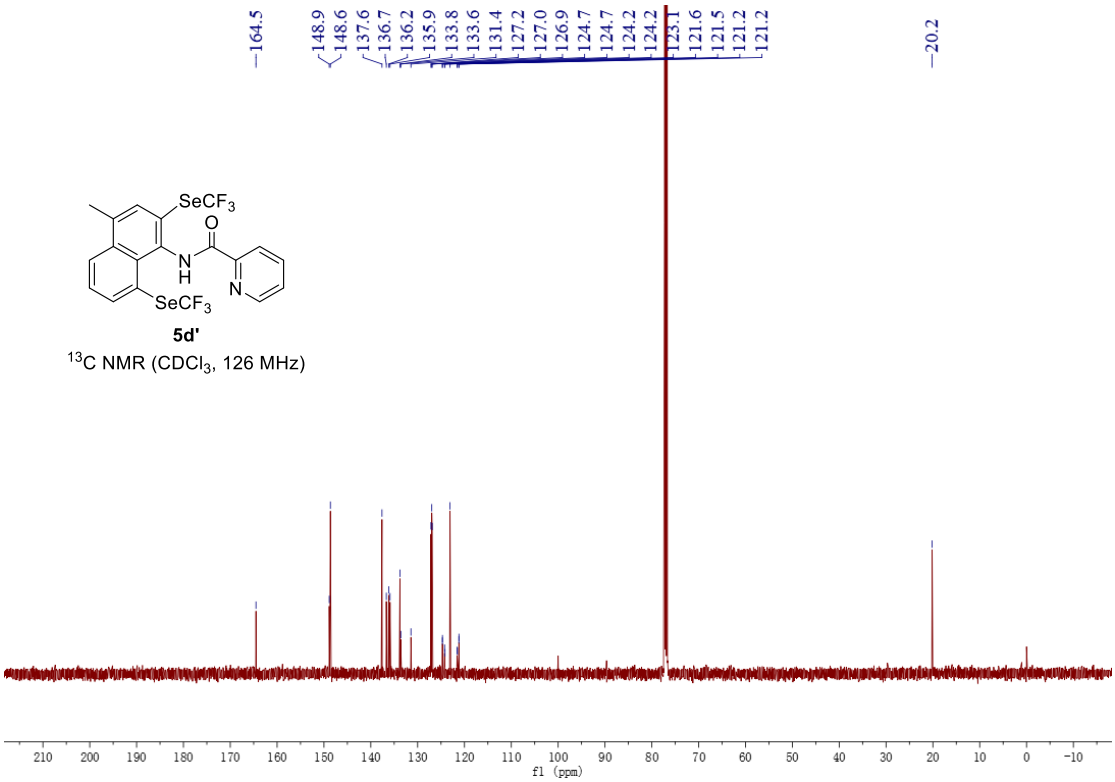
5d'

^{1}H NMR ($CDCl_3$, 500 MHz)



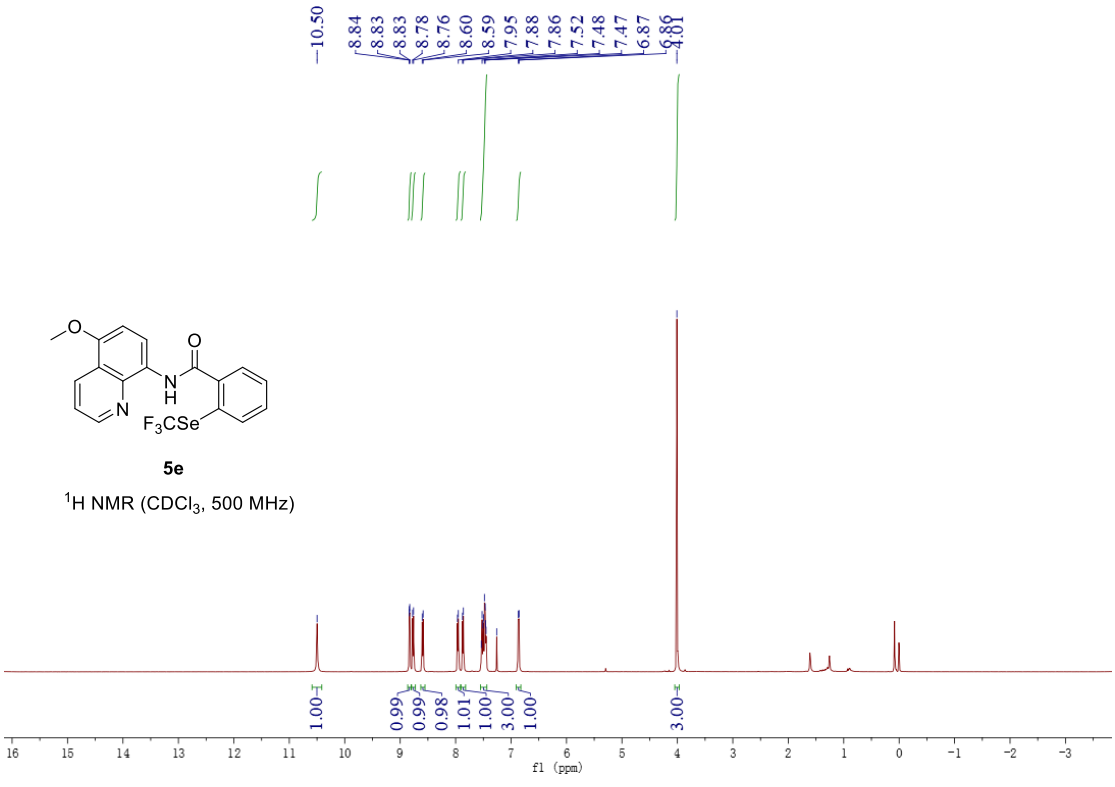
5d'

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



5d'

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



5e

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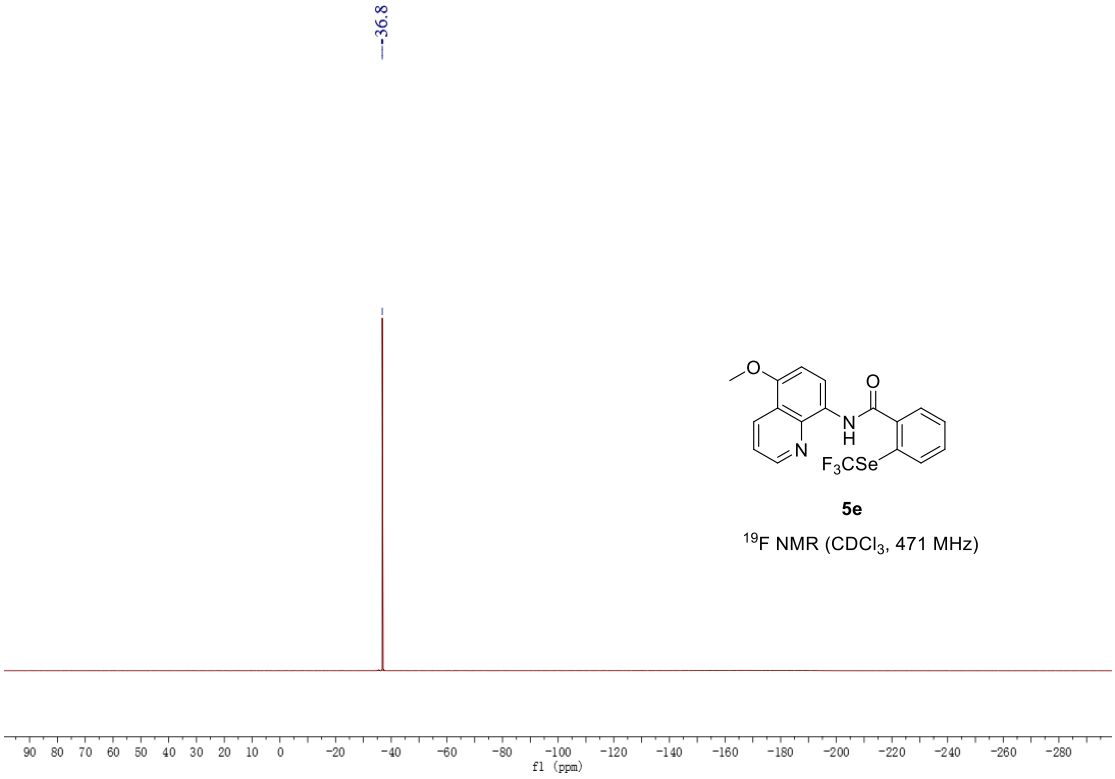

5e

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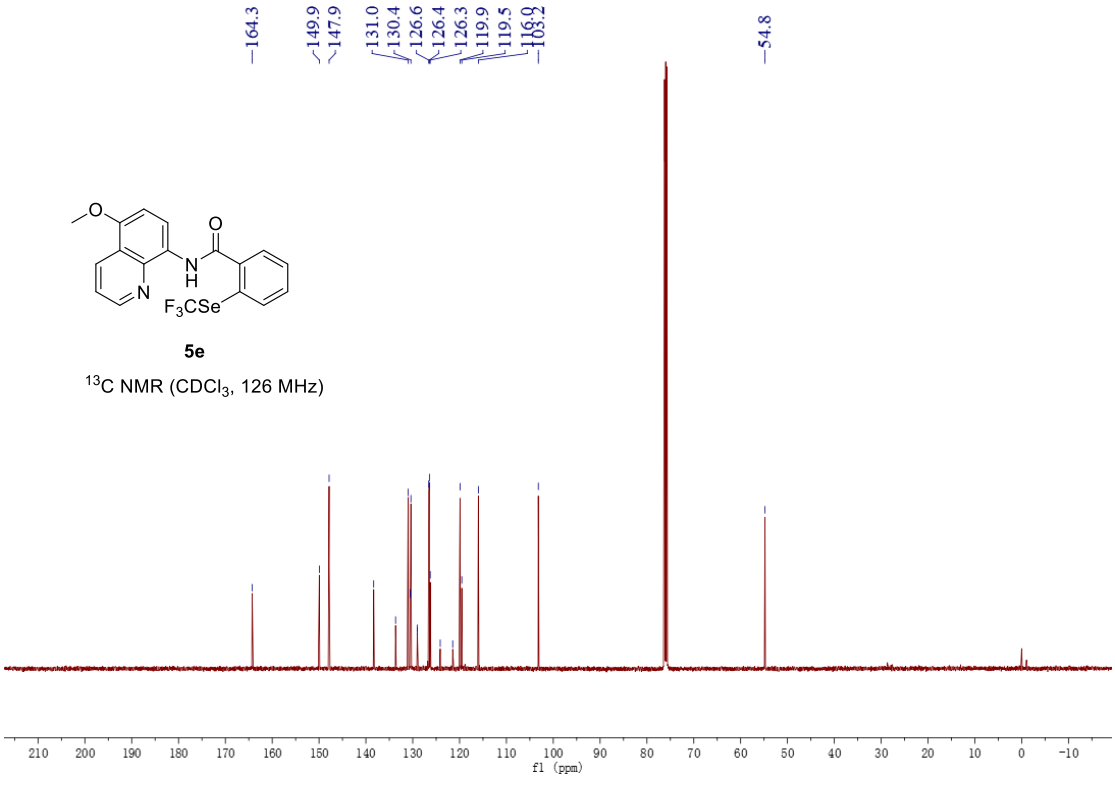

5e

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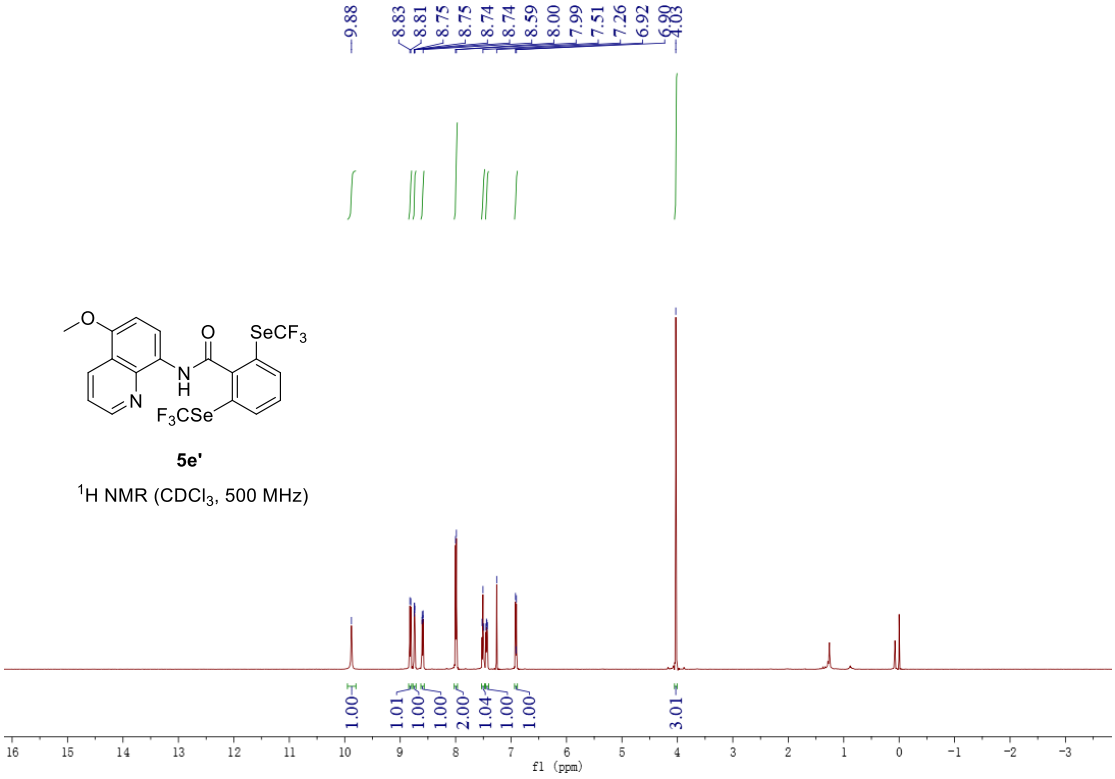

5e'

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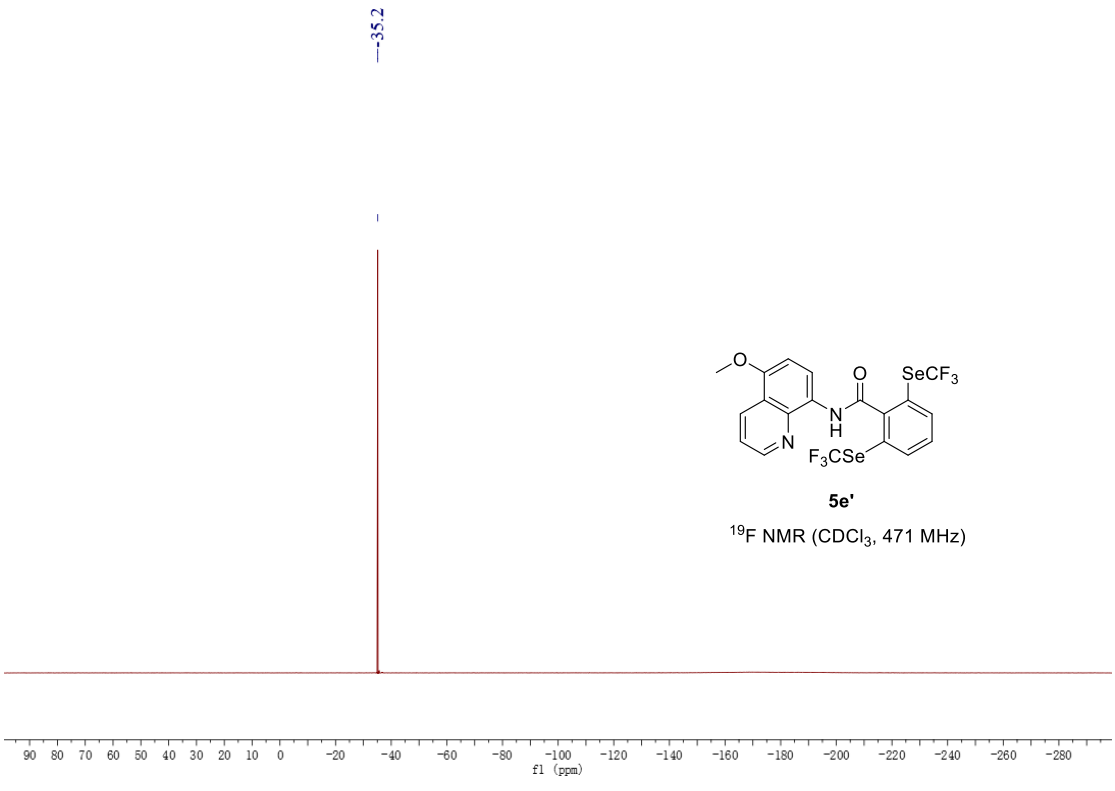
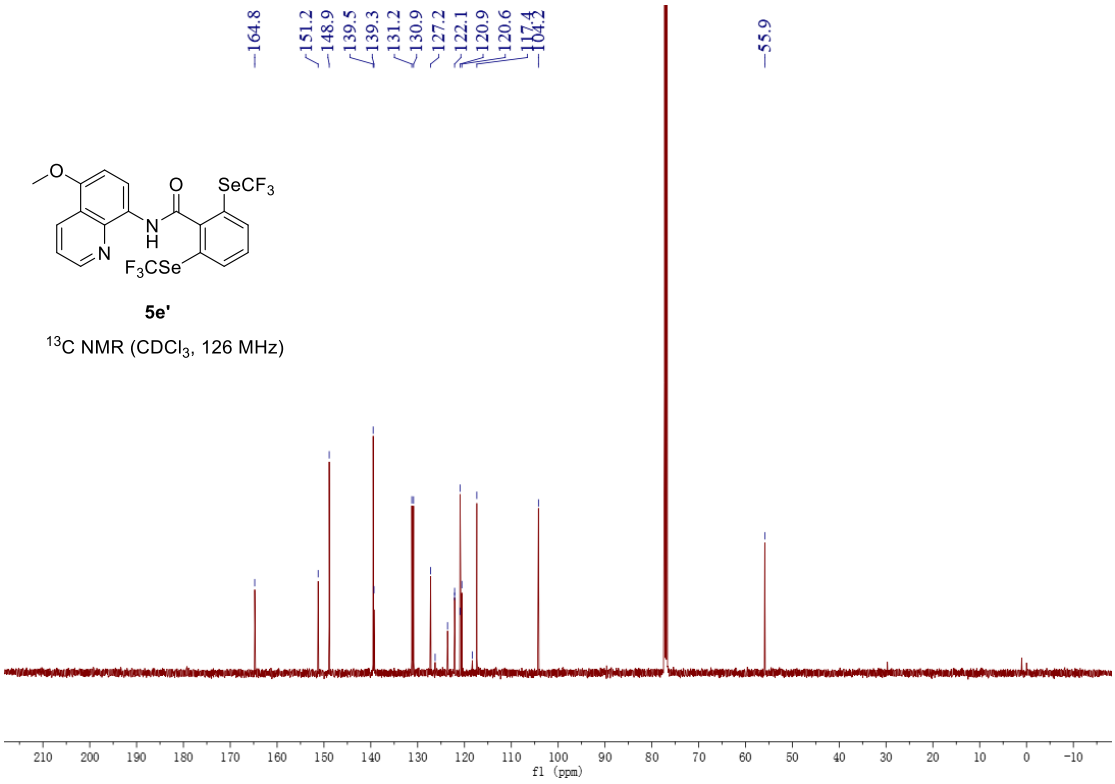


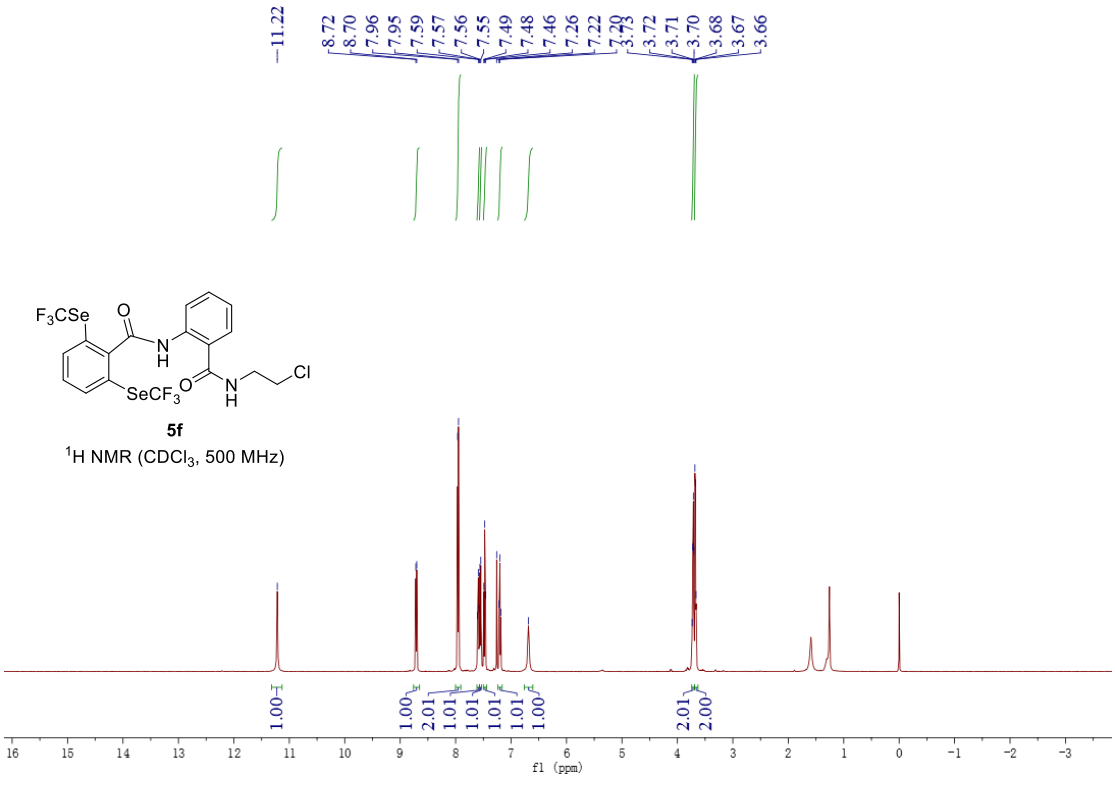
5e'

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



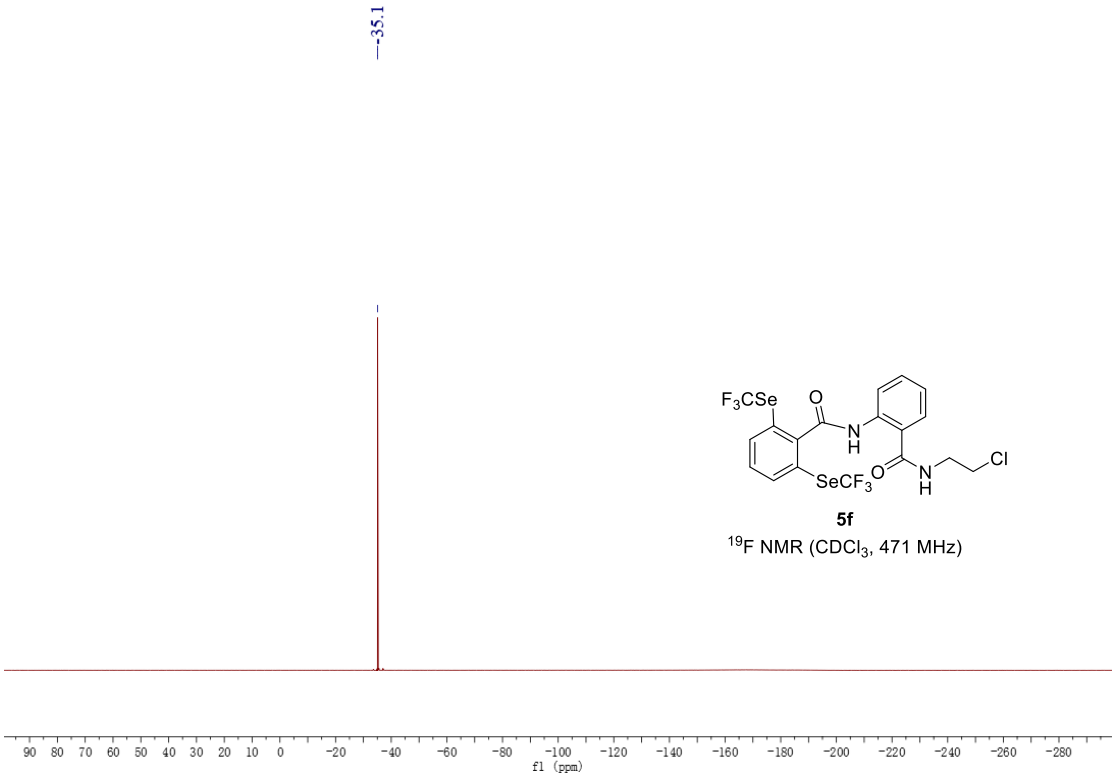
5e'

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



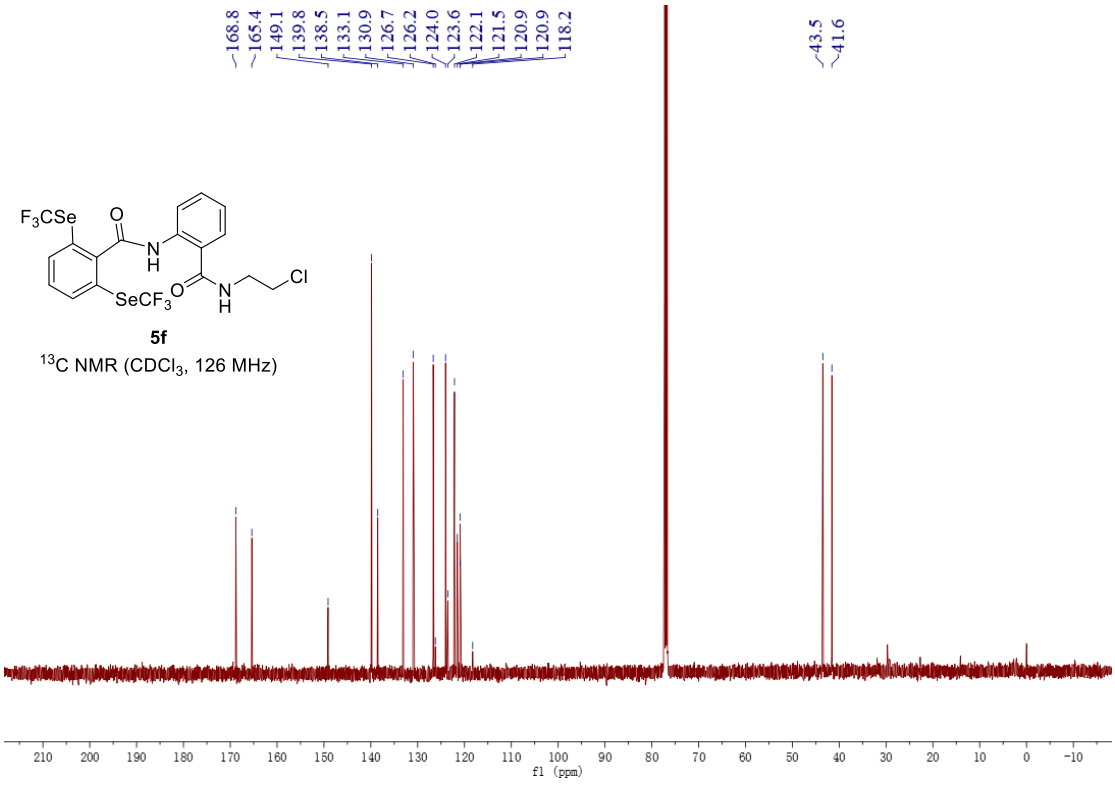
5f

^{1}H NMR ($CDCl_3$, 500 MHz)



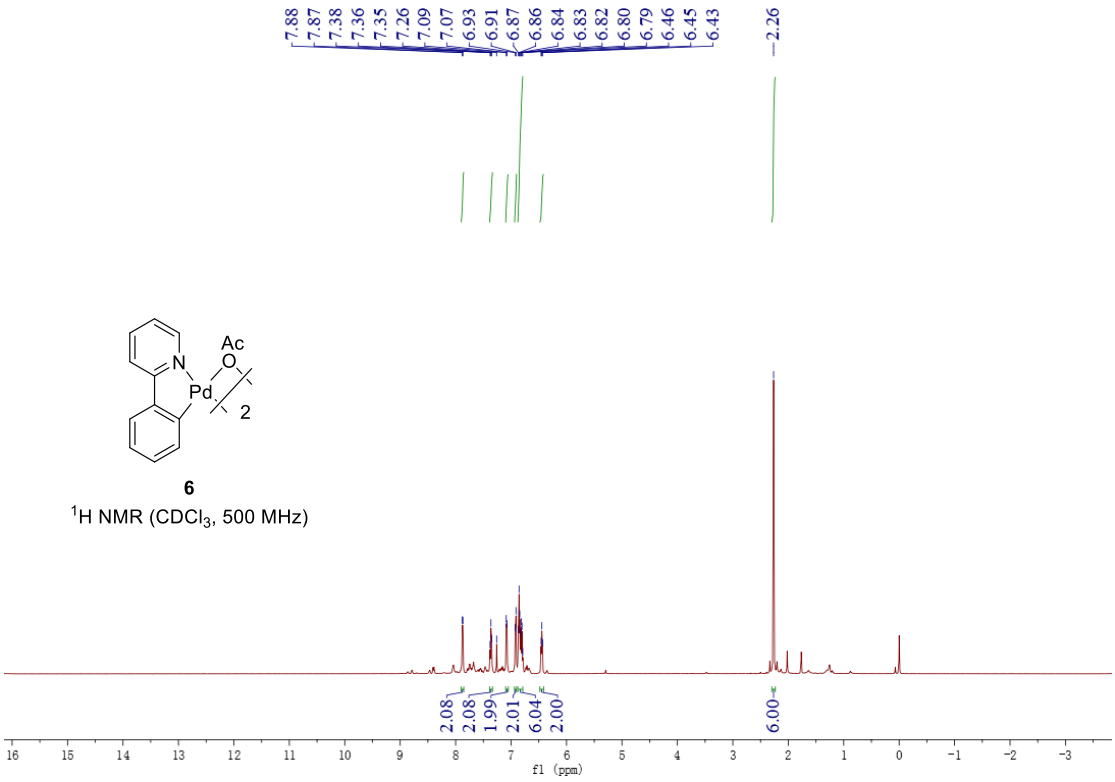
5f

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



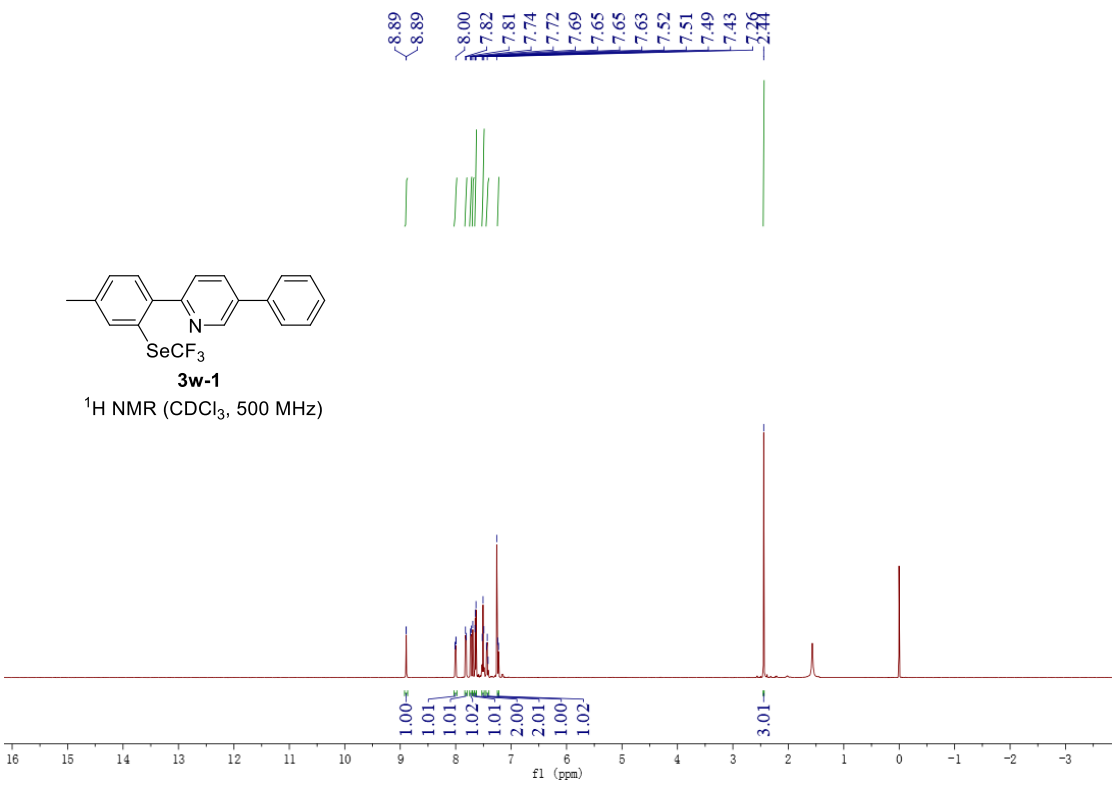
5f

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



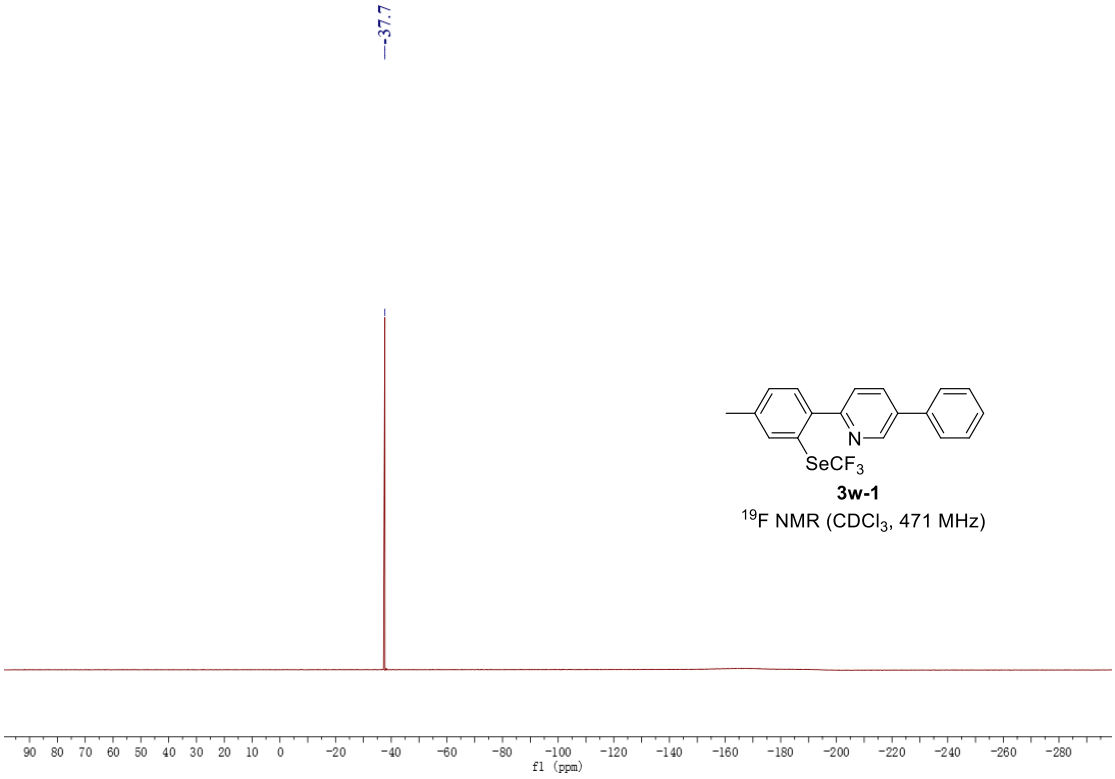
6

^{1}H NMR ($CDCl_3$, 500 MHz)



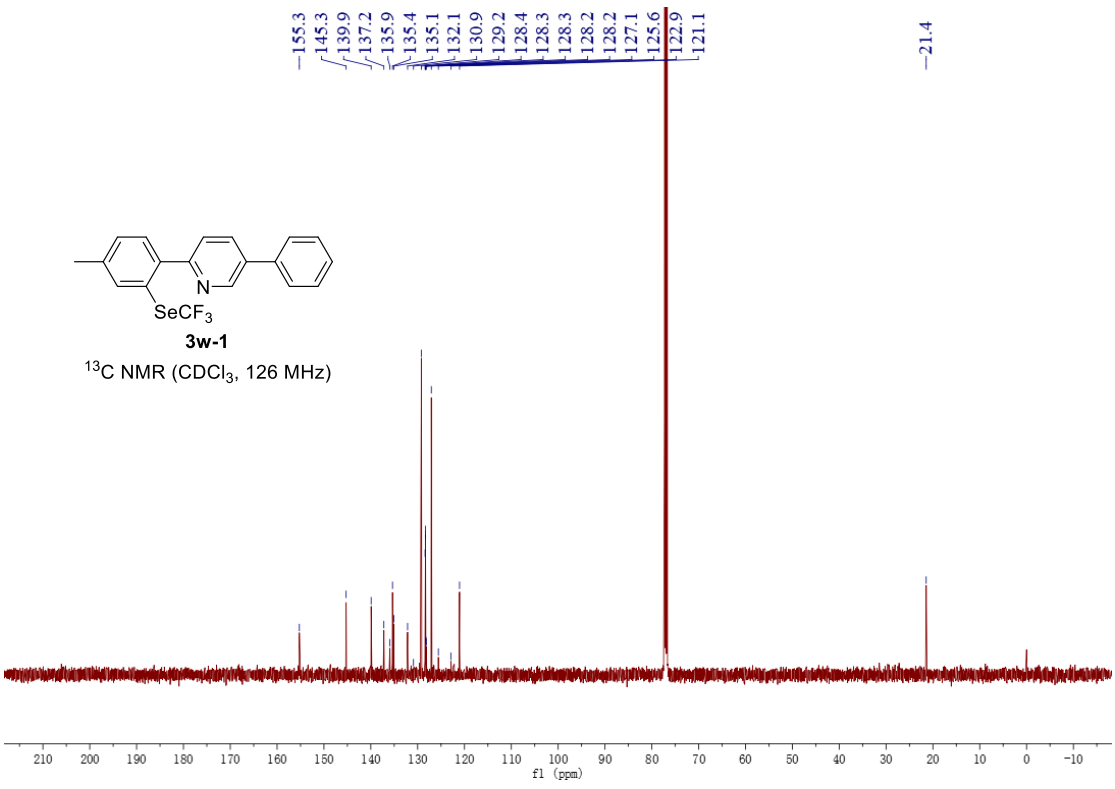
3w-1

^{1}H NMR ($CDCl_3$, 500 MHz)



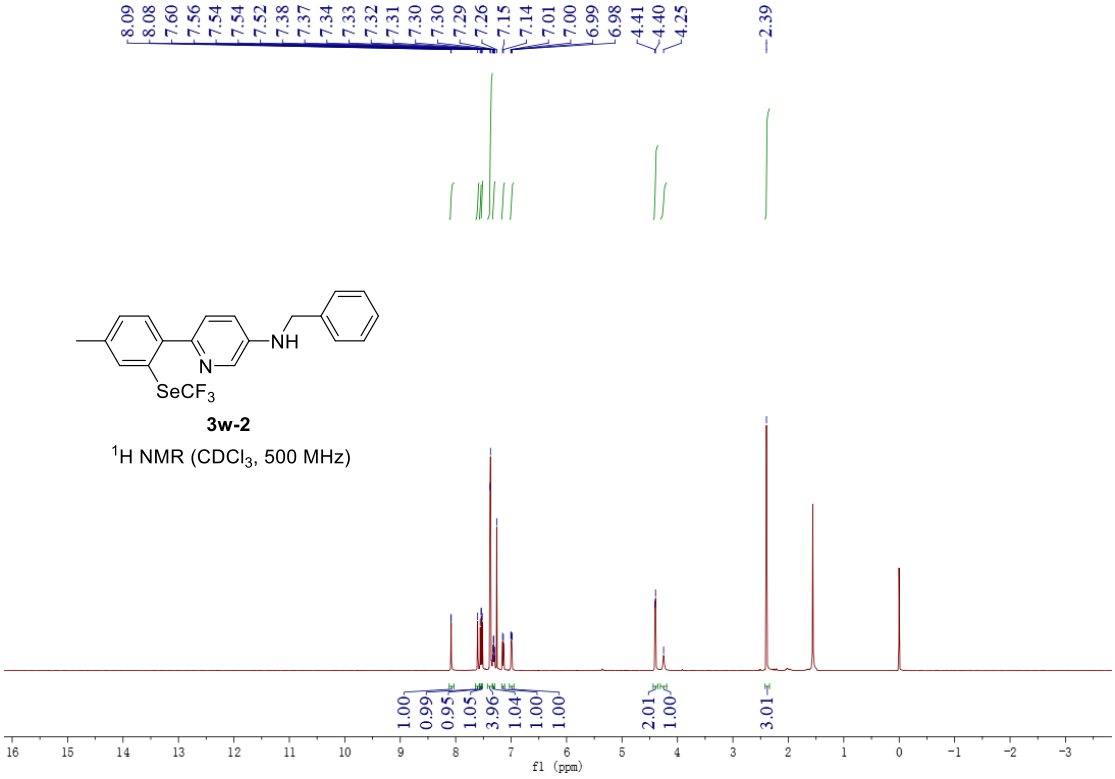
3w-1

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



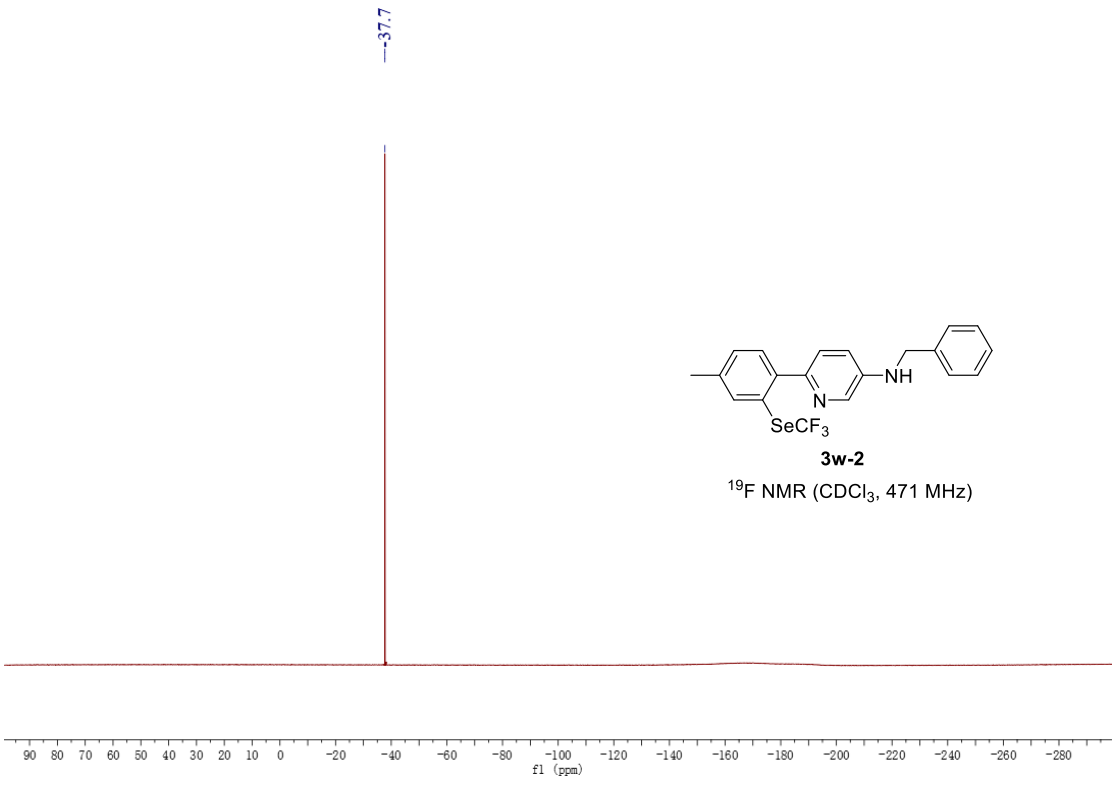
3w-1

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



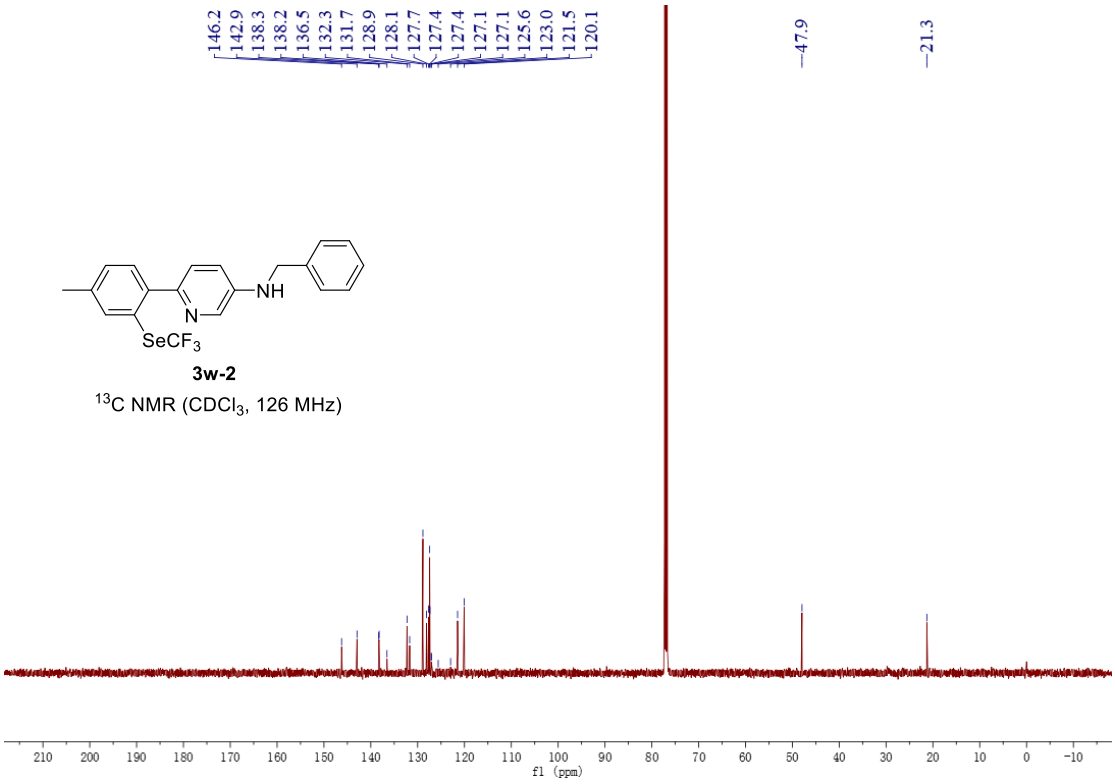
3w-2

^{1}H NMR ($CDCl_3$, 500 MHz)



3w-2

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



3w-2

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