Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Synthesis of 2,5-Disubstituted Selenophenes *via* Copper-Catalyzed Regioselective [2+2+1] Cyclization of Terminal Alkynes and Selenium

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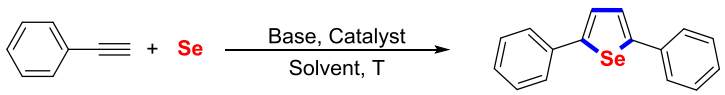
A. General Information

^{1}H and ^{13}C NMR spectra were recorded at 400 MHz NMR spectrometer using $CDCl_3$ as solvent and TMS as an internal standard. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants were reported in Hertz (Hz). IR spectra were obtained with an infrared spectrometer on either potassium bromide pellets or liquid films between two potassium bromide pellets. GC-MS data were obtained using electron ionization. HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). Melting points were measured using a melting point instrument and were uncorrected. TLC was performed using commercially available 100−400 mesh silica gel plates (GF254). X-ray structural analyses were conducted on an X-ray analysis instrument. All the reaction temperatures reported were oil bath temperatures. Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification.

B. Optimization of the Reaction Conditions

Table S1. Optimization of the Reaction Conditions[a]



1a 2 3a

Entry	Catalyst	Base	Solvent	Temp (^{o}C)	Yield (%)[b]
1	CuTC	DBU	Ethanol	130	n.d.
2	CuTC	DBU	*n*-Hexane	130	12
3	CuTC	DBU	THF	130	18
4	CuTC	DBU	CH_3CN	130	23
5	Cu_2O	DBU	CH_3CN	130	12
6	CF_3SO_3Cu	DBU	CH_3CN	130	28
7	CuF_2	DBU	CH_3CN	130	24
8	$(CF_3SO_3)_2Cu$	DBU	CH_3CN	130	25
9	Cu	DBU	CH_3CN	130	37
10	CF_3SO_3Zn	DBU	CH_3CN	130	13
11	$(CF_3SO_3)_3Fe$	DBU	CH_3CN	130	trace

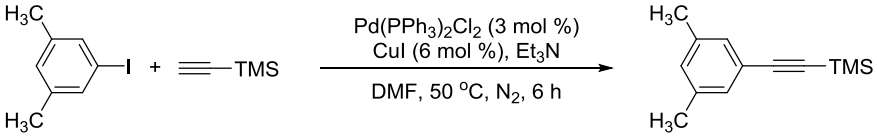
12	Fe	DBU	CH_3CN	130	n.r.
13	CF_3SO_3Ag	DBU	CH_3CN	130	trace
14	Cu	NH_2Na	CH_3CN	130	26
15	Cu	LDA	CH_3CN	130	31
16	Cu	DABCO	CH_3CN	130	n.d.
17	Cu	NaOH	CH_3CN	130	n.d.
18	Cu	$NaHCO_3$	CH_3CN	130	n.d.
19[c]	Cu	DBU	CH_3CN	130	45
20[d]	Cu	DBU	CH_3CN	130	70
21[d,e]	Cu	DBU	CH_3CN	130	76
22[d-f]	Cu	DBU	CH_3CN	130	80
23[d-f]	Cu	DBU	CH_3CN	125	83
24[d-f]	Cu	DBU	CH_3CN	120	**86 (84)**
25[d-f]	Cu	DBU	CH_3CN	115	85

[a]Reaction conditions: Unless otherwise noted, **1a** (0.4 mmol), **2** (0.4 mmol), catalyst (5 mol %), base (0.4 mol), solvent (2.0 mL) under air at 130 °C for 10 h. [b]Monitored by NMR using CH_2Br_2 as the internal standard. Number in parentheses is isolated yield. [c]Under O_2 atmosphere. [d]Under N_2 atmosphere. [e]The reaction time was 7 h. [f]The reaction was carried out with 0.2 mmol base.

C. Experimental Procedure

I. General Procedure for the Synthesis of Substrates 1f, 1j and 1k[1]

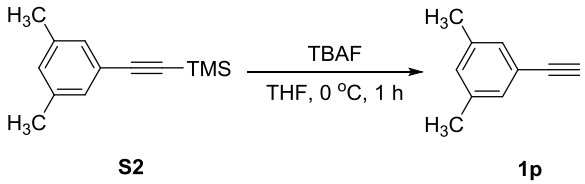
Typical procedure for the preparation of terminal alkyne substrates **1i**, **1n**, **1o**, **1p** and **11**. Using **1p** as the example:



S1 **S2**

To a dried tube was added 1-iodo-3,5-dimethylbenzene (**S1**, 464 mg, 2.0 mmol), trimethylsilylacetylene (310 μL, 2.2 mmol), $Pd(PPh_3)_2Cl_2$ (42.1 mg, 3 mol %), triethylamine (1.0 mL, 7.2 mmol) and DMF (3.5 mL) under N_2. The mixture was stirred and heated at 50 ℃ for 6 h. The reaction mixture was allowed to cool to room temperature and H_2O was added. The aqueous layer was extracted with Et_2O. The combined organic extracts were washed with brine, dried over

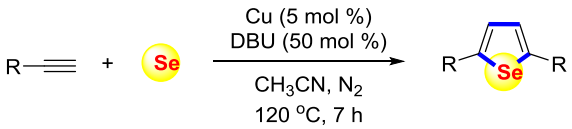
$MgSO_4$, filtered, and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel with hexane to afford 3,5-(dimethylphenylethynyl)trimethylsilane (**S2**, 343.6 mg, 85%) as a yellow oil.



S2 **1p**

To a solution of 3,5-(dimethylphenylethynyl)trimethylsilane (**S2**, 303.2 mg, 1.5 mmol) in THF (1.5 mL) was added TBAF (2 mL, 2 mmol, 1.0 M in THF) at 0 ℃. After stirring for 30 min, the reaction was quenched with saturated aqueous NH_4Cl, and the reaction mixture was extracted with Et_2O. The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel with *n*-hexane to afford 1-ethyl-3,5-dimethyl-benzene (**1p**, 156.1 mg, 80%) as a pale-yellow oil.

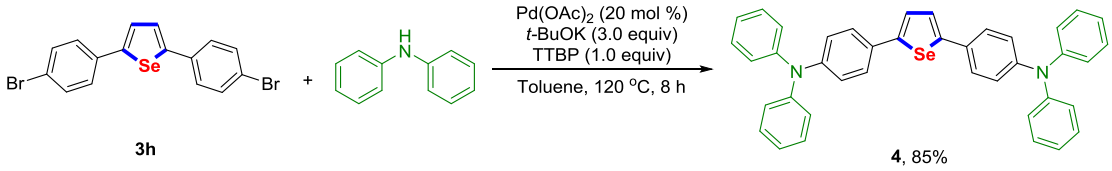
II. General Procedure for the Synthesis of Product 3



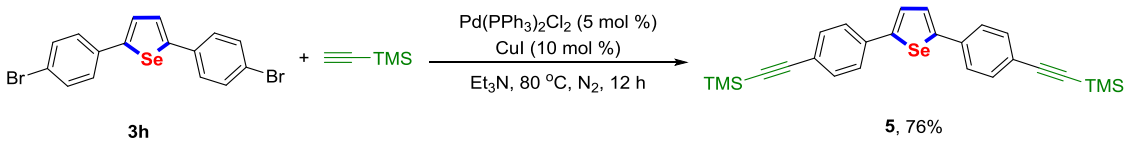
1 **2** **3**

A mixture of alkyne **1** (0.4 mmol), selenium **2** (31.6 mg, 0.4 mmol), Cu (1.3 mg, 5 mol %), DBU (30.6 mg, 0.2 mol) was added to a sealed tube equipped with magnetic stirred bar in 2 mL CH_3CN. The reaction was stirred under N_2 atmosphere at 120 ℃ for 7 h. After the reaction was completed (monitored by TLC), the mixture was cooled to room temperature and saturated aqueous NaCl was added. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layers were concentrated in vacuum. The residue was purified by column chromatography on silica gel with petroleum ether to afford the desired product **3**.

III. Synthetic Procedure for Compounds 4 and 5[2]



A mixture of 2,5-bis(4-bromophenyl)-selenophene (**3h**, 88.4 mg, 0.2 mmol), diphenylamine (347.0 mg,1.2 mmol), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol), *t*-BuOK (67.4 mg, 0.6 mmol) and tri-*tert*-butylphosphine (TTBP) (40.5 mg, 0.2 mmol) in toluene (3 mL) was stirred at 120 ℃ for 7 h under N_2. After the reaction was completed, the mixture was cooled to room temperature. Water was added and the resulting mixture was extracted with CH_2Cl_2 (3 × 30 mL). Then the combined organic layers were dried with $MgSO_4$, filtered, and concentrated in vacuum. The residue was subjected to column chromatography on silica gel with *n*-hexane to afford product **4** as a yellow solid (105 mg, 85% yield).



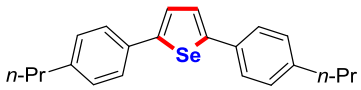
A mixture of 2,5-bis(4-bromophenyl)-selenophene (**3h**, 88.4 mg, 0.2 mmol), trimethylsilylacetylene (161.8 mg, 0.8 mmol), $Pd(PPh_3)_2Cl_2$ (7.1 mg, 0.01 mmol) and CuI (66.3 mg, 3.8 mmol) in Et_3N (3 mL) was stirred at 80 ℃ for 12 h under N_2. After the reaction was completed, the mixture was cooled to room temperature. Water was added and the resulting mixture was extracted with CH_2Cl_2 (3 × 30 mL). Then the combined organic layers were dried with $MgSO_4$, filtered, and concentrated in vacuum. The residue was subjected to column chromatography on silica gel with *n*-hexane to afford product **5** as a yellow oil (72.4 mg, 76% yield).

D. Characterization Data for All Products

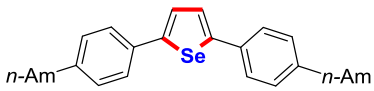
2,5-Diphenylselenophene (3a). White solid (47.7 mg, 84%); m.p. 163.2-164.1 °C; ^{1}H-NMR (400

MHz, $CDCl_3$): δ ppm 7.57 (d, J = 7.4 Hz, 4H), 7.45 (s, 2H), 7.37 (t, J = 7.5 Hz, 4H), 7.28 (t, J = 7.4 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ ppm 149.8, 136.3, 128.9, 127.6, 126.2, 126.1; ν_{max}(KBr)/cm^{-1} 2922, 2852, 1651, 1455, 1267, 1083, 905, 749, 681; HRMS-ESI (m/z): calcd for $C_{16}H_{13}Se$ $[M+H]^+$: 285.0177, found 285.0176.

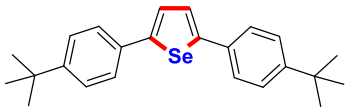
2,5-Bis(4-methylphenyl)-selenophene (3b). White solid (54.3 mg, 87%); m.p. 170.5-171.3 ^{o}C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ ppm 7.46 (d, J = 8.0 Hz, 4H), 7.39 (s, 2H), 7.17 (d, J = 7.9 Hz, 4H), 2.36 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ ppm 149.4, 137.4, 133.6, 129.6, 125.9, 125.6, 21.2; ν_{max}(KBr)/cm^{-1} 2923, 1641, 1453, 1264, 1109, 1016, 793, 542, 497; HRMS-ESI (m/z): calcd for $C_{18}H_{17}Se$ $[M+H]^+$: 313.0490, found 313.0482.



2,5-Bis(4-propylphenyl)-selenophene (3c). White solid (61.7 mg, 84%); m.p. 182.3-183.3 ^{o}C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ ppm 7.47 (d, J = 7.8 Hz, 4H), 7.38 (s, 2H), 7.16 (d, J = 7.8 Hz, 4H), 2.58 (t, J = 7.6 Hz, 4H), 1.65 (h, J = 7.4 Hz, 4H), 0.95 (t, J = 7.3 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ ppm 149.4, 142.2, 133.9, 129.0, 125.9, 125.6, 37.7, 24.4, 13.8; ν_{max}(KBr)/cm^{-1} 2949, 1651, 1459, 1010, 795, 553, 463; HRMS-ESI (m/z): calcd for $C_{22}H_{25}Se$ $[M+H]^+$: 369.1117, found 369.1115.

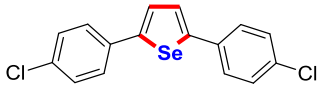


2,5-Bis(4-pentylphenyl)-selenophene (3d). White solid (68.6 mg, 81%); m.p. 191.6-192.5 ^{o}C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ ppm 7.45 (d, J = 7.9 Hz, 4H), 7.35 (s, 2H), 7.14 (d, J = 7.9 Hz, 4H), 2.58 (t, J = 7.6 Hz, 4H), 1.70 – 1.52 (m, 4H), 1.39 – 1.24 (m, 8H), 0.89 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ ppm 149.4, 142.4, 133.9, 128.9, 125.9, 125.6, 35.6, 31.5, 31.0, 22.5, 14.0; ν_{max}(KBr)/cm^{-1} 2929, 2854, 1460, 1265, 1122, 976, 799, 733, 552, 462; HRMS-ESI (m/z): calcd for $C_{26}H_{33}Se$ $[M+H]^+$: 425.1743, found 425.1743.

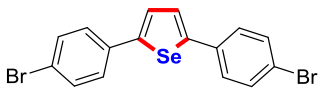


2,5-Bis(4-*tert*-butylphenyl)-selenophene (3e). White solid (51.5 mg, 65%); m.p. 200.7-201.8 ^{o}C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ ppm 7.49 (d, J = 8.2 Hz, 4H), 7.37 (d, J = 8.0 Hz, 6H), 1.33 (s, 18H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ ppm 150.6, 149.3, 133.7, 125.8, 125.7, 34.6, 31.3; ν_{max}(KBr)/cm^{-1} 2956, 2866, 1765, 1508, 1458, 1374, 1262, 753; HRMS-ESI (m/z): calcd for $C_{24}H_{29}Se$ $[M+H]^+$: 397.1430, found 397.1436.

2,5-Bis(4-fluorophenyl)-selenophene (3f). Light yellow solid (51.1 mg, 80%); m.p. 195.1-196.0 ^{o}C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ ppm 7.55 – 7.47 (m, 4H), 7.35 (s, 2H), 7.07 (t, J = 8.6 Hz, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ ppm 162.4 (d, J = 247.7 Hz), 148.6, 132.5, 127.7, 126.2, 115.9 (d, J = 21.8 Hz); ν_{max}(KBr)/cm^{-1} 2924, 2851, 1643, 1463, 1281, 1102, 1019, 811, 682, 543, 465; HRMS-ESI (m/z): calcd for $C_{16}H_{11}F_2Se$ $[M+H]^+$: 321.0000, found 320.9977.

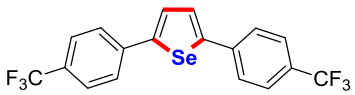


2,5-Bis(4-chlorophenyl)-selenophene (3g). White solid (54.9 mg, 78%); m.p. 198.5-199.5 ^{o}C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ ppm 7.48 (d, J = 8.1 Hz, 4H), 7.41 (s, 2H), 7.34 (d, J = 8.2 Hz, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ ppm 148.8, 134.6, 133.5, 129.1, 127.2, 126.7; ν_{max}(KBr)/cm^{-1} 3392, 2921, 2853, 1458, 1234, 1095, 902, 807, 538, 470; HRMS-ESI (m/z): calcd for $C_{16}H_9Cl_2Se$ $[M]^+$: 351.9325, found 351.9322.

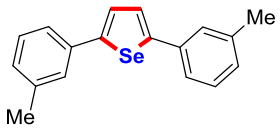


2,5-Bis(4-bromolphenyl)-selenophene (3h). White solid (66.2 mg, 75%); m.p. 221.3-222.1 ^{o}C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ ppm 7.52 – 7.47 (m, 4H), 7.44 – 7.39 (m, 6H); ^{13}C-NMR (100

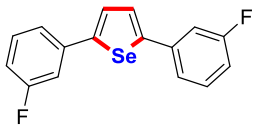
MHz, $CDCl_3$): δ ppm 148.8, 135.1, 132.1, 127.5, 126.7, 121.6; ν_{max}(KBr)/cm^{-1} 2997, 2919, 1765, 1462, 1392, 1261, 806, 754, 446; HRMS-ESI (m/z): calcd for $C_{16}H_9Br_2Se$ $[M-H]^+$: 440.8221, found 440.8210.



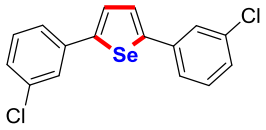
2,5-Bis(4-trifluorolphenyl)-selenophene (3i). Light gray solid (40.3 mg, 48%); m.p. 177.6-178.4 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ ppm 7.68 – 7.62 (m, 8H), 7.56 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ ppm 149.3, 139.3, 129.7 (q, J = 32.7 Hz), 127.8, 126.2, 126.0, 124.1 (q, J = 270.2 Hz); ν_{max}(KBr)/cm^{-1} 2918, 2852, 1407, 1331, 1268, 1124, 835, 801, 756, 592; HRMS-ESI (m/z): calcd for $C_{18}H_{11}F_6Se$ $[M+H]^+$: 419.9852, found 419.9861.



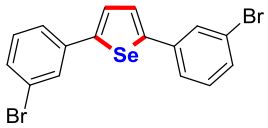
2,5-Bis(3-methylphenyl)-selenophene (3j). White solid (55.5 mg, 89%); m.p. 183.2-184.1 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ ppm 7.41 (s, 2H), 7.36 (d, J = 6.8 Hz, 4H), 7.24 (t, J = 8.0 Hz, 2H), 7.09 (d, J = 7.5 Hz, 2H), 2.38 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ ppm 149.8, 138.5, 136.3, 128.8, 128.4, 126.8, 126.0, 123.2, 21.4; ν_{max}(KBr)/cm^{-1} 2924, 2852, 1591, 1465, 1271, 1026, 878, 776, 685, 534; HRMS-ESI (m/z): calcd for $C_{18}H_{17}Se$ $[M+H]^+$: 313.0490, found: 313.0488.



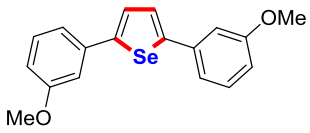
2,5-Bis(3-fluorophenyl)-selenophene (3k). Light yellow solid (52.4 mg, 82%); m.p. 139.6-140.5 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ ppm 7.45 (s, 2H), 7.37 – 7.30 (m, 4H), 7.29 – 7.23 (m, 2H), 7.02 – 6.95 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ ppm 163.1 (d, J = 246.2 Hz), 148.9, 138.2, 130.4, 127.0, 121.9, 114.5 (d, J = 21.3 Hz), 112.7 (d, J = 22.7 Hz); ν_{max}(KBr)/cm^{-1} 2924, 2855, 1650, 1576, 1499, 1264, 1162, 1002, 867, 780, 678, 552, 461; HRMS-ESI (m/z): calcd for $C_{16}H_{11}F_2Se$ $[M+H]^+$: 321.0000, found 320.9977.



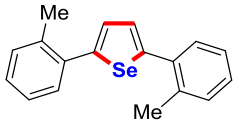
2,5-Bis(3-chlorophenyl)-selenophene (3l). Yellow solid (55.6 mg, 79%); m.p. 115.2-116.1 ^{o}C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ ppm 7.55 (t, J = 1.6 Hz, 2H), 7.46 (s, 2H), 7.43 (dt, J = 7.5, 1.5 Hz, 2H), 7.31 (t, J = 7.7 Hz, 2H), 7.28 – 7.26 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ ppm 148.8, 137.8, 134.9, 130.2, 127.7, 127.1, 125.9, 124.3; ν_{max}(KBr)/cm^{-1} 2920, 2853,1647, 1562, 1464, 1413, 1075, 877, 774, 682; HRMS-ESI (m/z): calcd for $C_{16}H_{10}Cl_2Se$ $[M]^+$: 351.9325, found 351.9321.



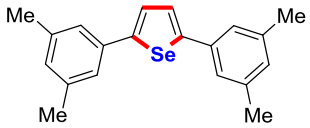
2,5-Bis(3-bromophenyl)-selenophene (3m). White solid (68.6 mg, 78%); m.p. 129.6-130.3 ^{o}C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ ppm 7.70 (s, 2H), 7.50 – 7.39 (m, 6H), 7.27 – 7.21 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ ppm 148.7, 138.0, 130.6, 130.4, 128.8, 127.1, 124.8, 123.1; ν_{max}(KBr)/cm^{-1} 2924, 2855, 1649, 1556, 1463, 969, 871, 771, 682, 473; HRMS-ESI (m/z): calcd for $C_{16}H_9Br_2Se$ $[M-H]^+$: 440.8221, found 440.8211.



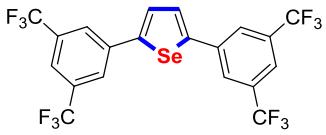
2,5-Bis(3-methoxyphenyl)-selenophene (3n). White solid (52.2 mg, 76%); m.p. 191.3-192.2 ^{o}C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ ppm 7.42 (s, 2H), 7.27 (t, J = 7.9 Hz, 2H), 7.15 (d, J = 7.7 Hz, 2H), 7.09 (s, 2H), 6.83 (d, J = 8.2 Hz, 2H), 3.84 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ ppm 159.9, 149.7, 137.6, 129.9, 126.3, 118.7, 113.0, 111.7, 55.3; ν_{max}(KBr)/cm^{-1} 2934, 2838, 1658, 1474, 1276, 1166, 1046, 759, 688; HRMS-ESI (m/z): calcd for $C_{18}H_{17}O_2Se$ $[M+H]^+$: 345.0389, found 345.0386.



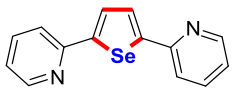
2,5-Bis(3-methylphenyl)-selenophene (3o). Yellow oil (23.0 mg, 37%); ^{1}H-NMR (400 MHz, $CDCl_3$): δ ppm 7.46 – 7.41 (m, 2H), 7.28 – 7.19 (m, 6H), 7.18 (s, 2H), 2.49 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ ppm 149.4, 136.2, 135.6, 130.8, 130.5, 128.7, 127.7, 125.9, 21.3; ν_{max}(KBr)/cm^{-1} 2922, 2857, 1759, 1646, 1463, 1376, 1265, 814, 753; HRMS-ESI (m/z): calcd for $C_{18}H_{17}Se$ $[M+H]^+$: 313.0490, found 313.0487.



2,5-Bis(3,5-dimethylphenyl)-selenophene (3p). White solid (49.6 mg, 73%); m.p. 124.5-125.2 ^{o}C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ ppm 7.39 (s, 2H), 7.18 (s, 4H), 6.91 (s, 2H), 2.33 (s, 12H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ ppm 149.7, 138.4, 136.2, 129.3, 125.9, 123.9, 21.3; ν_{max}(KBr)/cm^{-1} 2926, 2852, 1595, 1458, 1027, 800, 681, 583, 470; HRMS-ESI (m/z): calcd for $C_{20}H_{21}Se$ $[M+H]^+$: 341.0804, found 341.0807.

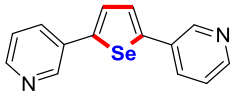


2,5-Bis(3,5-bis(trifluoromethyl)phenyl)selenophene (3q). White solid (46.7 mg, 42%); m.p. 159.6-160.3 ^{o}C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ ppm 7.97 (s, 4H), 7.82 (s, 2H), 7.64 (s, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ ppm 148.3, 137.7, 132.6 (q, J = 33.5 Hz), 128.6, 125.9, 123.1 (q, J = 271.2 Hz), 121.4; ν_{max}(KBr)/cm^{-1} 2919, 2854, 1609, 1458, 1371, 1282, 1121, 1009, 885, 795, 686; HRMS-ESI (m/z): calcd for $C_{20}H_8F_{12}Se$ $[M]^+$: 555.9600, found 555.9606.



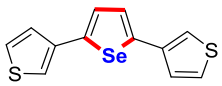
2,5-Bis(2-pyridyl)-selenophene (3r). Brown solid (33.1 mg, 58%); m.p. 170.5-171.1 ^{o}C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ ppm 8.56 (d, J = 4.7 Hz, 2H), 7.81 (s, 2H), 7.72 – 7.65 (m, 4H), 7.19 – 7.11 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ ppm 154.0, 152.8, 150.0, 136.5, 127.3, 122.1, 118.0; ν_{max}(KBr)/cm^{-1} 3634, 2925, 2849, 1650, 1383, 998, 774, 556, 467; HRMS-ESI (m/z): calcd

for $C_{14}H_{11}N_2Se$ $[M+H]^+$: 287.0082, found 287.0078.

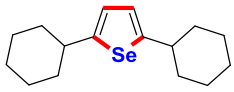


2,5-Bis(3-pyridyl)-selenophene (3s). Brown solid (25.7 mg, 45%); m.p. 114.8-115.6 ^oC; ^1H-NMR (400 MHz, $CDCl_3$): δ ppm 8.85 (s, 2H), 8.55 (d, J = 4.2 Hz, 2H), 7.85 (d, J = 7.9 Hz, 2H), 7.55 (s, 2H), 7.33 (dd, J = 7.9, 4.8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ ppm 148.8, 147.0, 146.8, 133.1, 131.9, 127.6, 123.7; ν_{max}(KBr)/cm^{-1} 2925, 2850, 1709, 1563, 1470, 1407, 1185, 1115, 1023, 796, 699, 546, 462; HRMS-ESI (m/z): calcd for $C_{14}H_{11}N_2Se$ $[M+H]^+$: 287.0082, found 287.0088.

2,5-Bis(2-thienyl)-selenophene (3t). Brown solid (46.7 mg, 79%); m.p. 170.4-171.2 ^oC; ^1H-NMR (400 MHz, $CDCl_3$): δ ppm 7.21 (d, J = 6.6 Hz, 4H), 7.10 (s, 2H), 7.00 (t, J = 4.0 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ ppm 141.0, 139.4, 127.9, 126.4, 124.6, 124.3; ν_{max}(KBr)/cm^{-1} 3058, 1423, 1264, 1051, 803, 737, 691, 441; HRMS-ESI (m/z): calcd for $C_{12}H_9S_2Se$ $[M+H]^+$: 296.9304, found 293.9296.



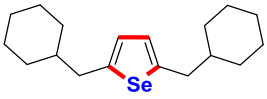
2,5-Bis(3-thienyl)-selenophene (3u) Brown solid (44.3 mg, 75%); m.p. 142.5-143.2 ^oC; ^1H-NMR (400 MHz, $CDCl_3$): δ ppm 7.36 – 7.31 (m, 4H), 7.29 – 7.26 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ ppm 142.9, 137.7, 126.4, 126.1, 125.9, 119.8; ν_{max}(KBr)/cm^{-1} 3081, 2920, 2855, 1759, 1650, 1464, 1238, 960, 765; HRMS-ESI (m/z): calcd for $C_{12}H_9S_2Se$ $[M+H]^+$: 296.9305, found 296.9302.



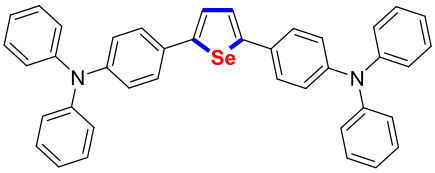
2,5-Dicyclohexylselenophene (3v). Light yellow oil (23.6 mg, 40%); ^1H-NMR (400 MHz, $CDCl_3$): δ ppm 6.74 (s, 2H), 2.81 – 2.68 (m, 2H), 2.04 (d, J = 8.6 Hz, 4H), 1.85 – 1.76 (m, 4H), 1.73

– 1.66 (m, 2H), 1.44 – 1.30 (m, 8H), 1.28 – 1.16 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ ppm 156.8, 123.0, 41.9, 36.3, 26.5, 26.0; ν_{max}(KBr)/cm^{-1} 2923, 2852, 1447, 1266, 1035, 984, 751, 531; HRMS-ESI (m/z): calcd for $C_{16}H_{25}Se$ $[M+H]^+$: 297.1116, found 297.1116.

2,5-Dicyclopropylselenophene (3w). Light yellow oil (13.5 mg, 32%); ^{1}H-NMR (400 MHz, $CDCl_3$): δ ppm 6.69 (s, 2H), 2.09 – 1.99 (m, 2H), 0.98 – 0.91 (m, 4H), 0.68 – 0.61 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ ppm 152.5, 124.3, 13.7, 10.4; ν_{max}(KBr)/cm^{-1} 2921, 2852, 1762, 1645, 1458, 1264, 755; HRMS-ESI (m/z): calcd for $C_{10}H_{13}Se$ $[M+H]^+$: 213.0177, found 213.0175.



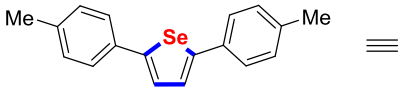
2,5-Bis(cyclohexylmethyl)-selenophene (3x). Light yellow oil (22.7 mg, 35%); ^{1}H-NMR (400 MHz, $CDCl_3$): δ ppm 6.66 (s, 2H), 2.67 (d, J = 7.0 Hz, 2H), 1.78 (d, J = 14.9 Hz, 4H), 1.74 – 1,58 (m, 6H), 1.53 – 1.41 (m, 2H), 1.30 – 1.08 (m, 6H), 1.01 - 0.85 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ ppm 149.2, 126.4, 40.8, 40.7, 33.1, 26.5, 26.2; ν_{max}(KBr)/cm^{-1} 2920, 2850, 1505, 1447, 1347, 1269, 1006, 800, 758, 570; HRMS-ESI (m/z): calcd for $C_{18}H_{29}Se$ $[M+H]^+$: 325.1429, found 325.1427.



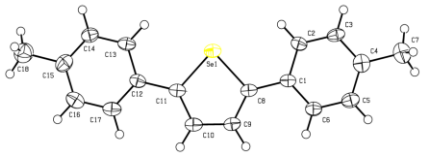
2,5-Di([1,1'-biphenyl]-4-yl)selenophene (4). Yellow solid (37.0 mg, 85%); m.p. 193.7-194.5^{o}C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ ppm 7.41 (d, J = 8.6 Hz, 4H), 7.32 (s, 2H), 7.26 (t, J = 7.9 Hz, 8H), 7.11 (d, J = 7.6 Hz, 8H), 7.03 (t, J = 7.8 Hz, 8H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ ppm 148.6, 147.4, 147.2, 130.5, 129.3, 126.7, 125.3, 124.5, 123.6, 123.1; ν_{max}(KBr)/cm^{-1} 3039, 2922, 2853, 1589, 1490, 1279, 1179, 810, 747, 696, 520; HRMS (ESI, m/z): calcd for $C_{42}H_{32}Se$ $[M+H]^+$: 616.1629, found 616.1633.

E. X-ray Crystallographic Analysis for Product 3b

The X-ray crystallographic structures for **3b**. ORTEP representation with 50% probability thermal ellipsoids. Crystal data have been deposited to CCDC, number 2076234.



3b



CCDC: 2076234

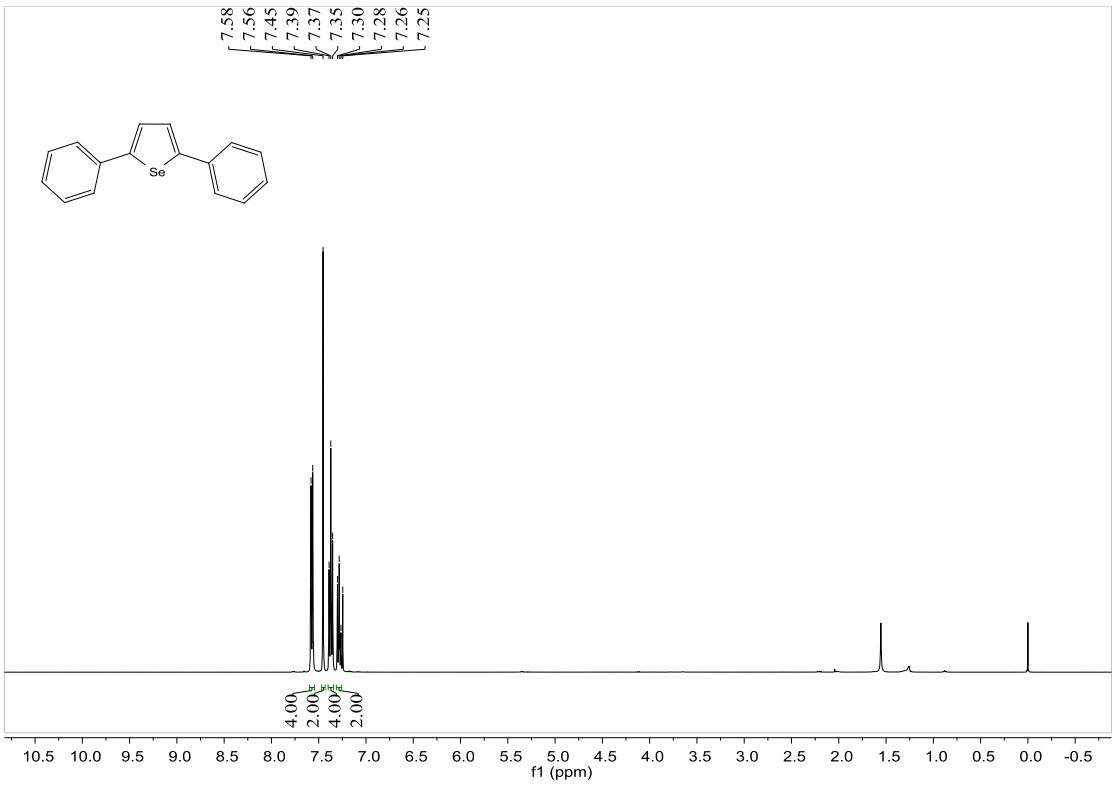
Empirical formula	$C_{18}H_{16}Se$
Formula weight	312.04
Temperature	150.0 K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P21/n
Unit cell dimensions	*a* = 5.8303(2) Å, alpha = 90.00 deg.
	b = 33.0703(13) Å, beta = 90.00 deg.
	c = 14.6045(5) Å, gamma = 90.00 deg.
Volume	2815.89(18) $Å^3$
Z, Calculated density	8, 1.468 g/cm^3
Absorption coefficient	2.650 mm^{-1}
F(000)	1264.0
Crystal size	0.12 × 0.05 × 0.02 mm^3
Theta range for data collection	4.928 to 52.76 deg.
Index ranges	-6≤h≤7, -38≤k≤40, -18≤l≤18
Reflections collected	10638
Independent reflections	1591 [R_{int} = 0.0797, R_{sigma} = 0.0519]
Completeness to theta = 26.380	99.7 %
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1591/79/147
Goodness-of-fit on F^2	1.092
Final *R* indices [*I* > *2sigma(I)*]	R_1 = *0.0396*, wR_2 = *0.0625*
Final *R* indexes [all data]	R_1 = *0.0738*, wR_2 = *0.0758*

F. References

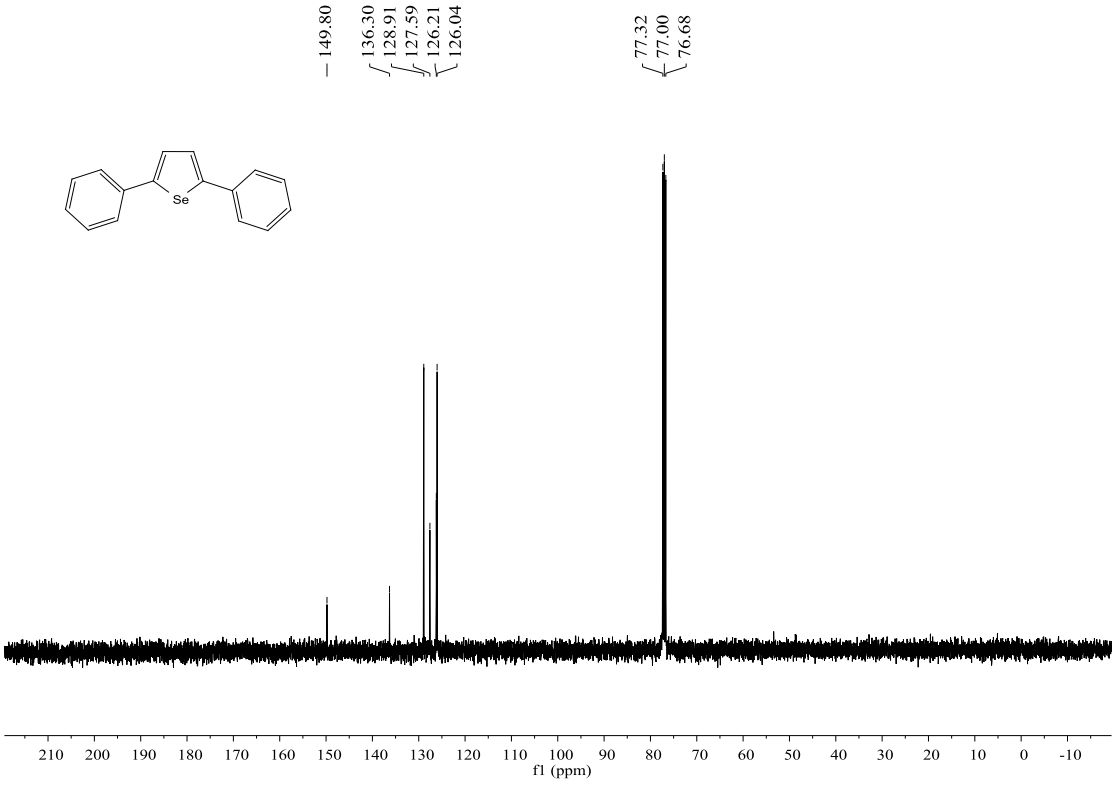
1. A. Elangovan, Y. Wang and T. Ho, *Org. Lett.*, **2003**, *5*, 1841.
2. F. Zhou, C. Li, M. Li, Y. Jin, H. Jiang, Y. Zhang and W. Wu, *Chem. Commun.*, **2021**, *57*, 4799.

G. ^{1}H and ^{13}C NMR Spectra

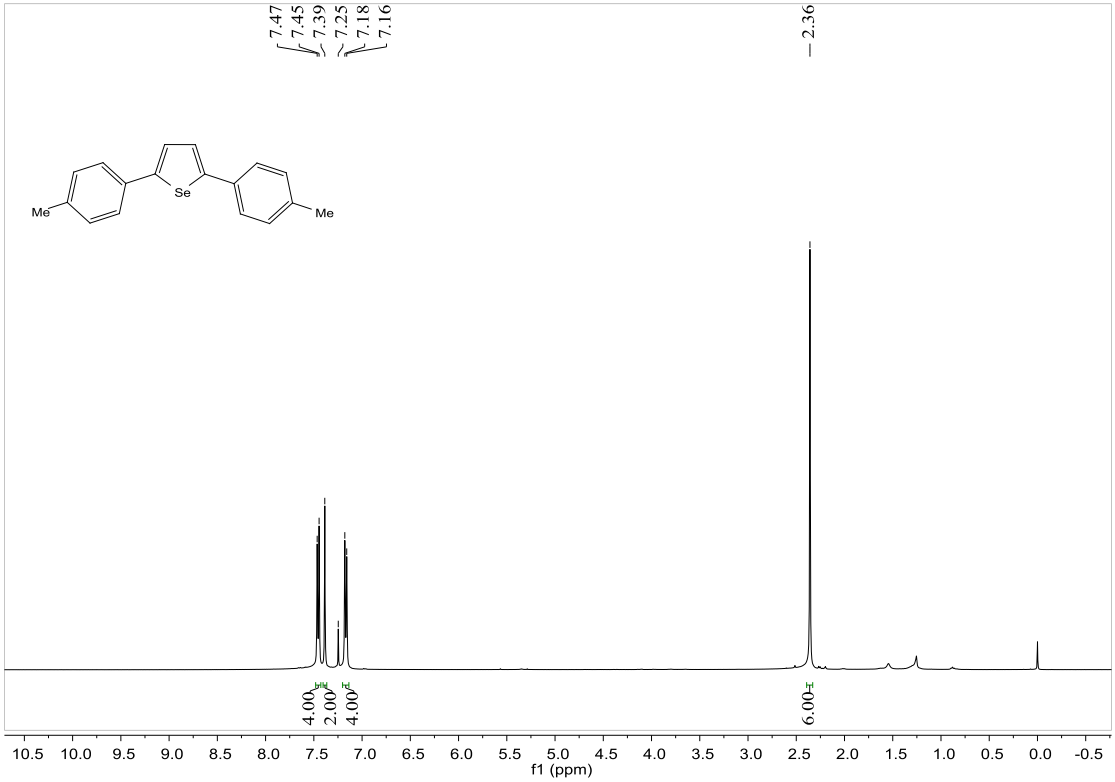
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum for 3a



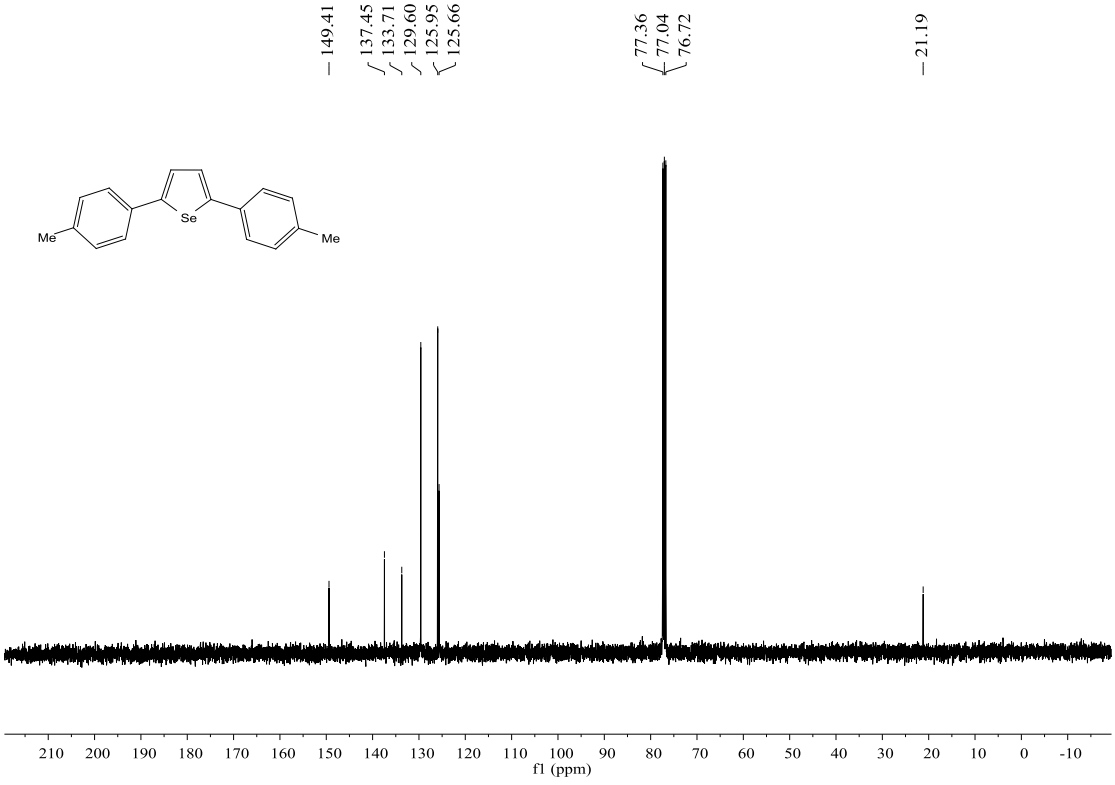
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum for 3a



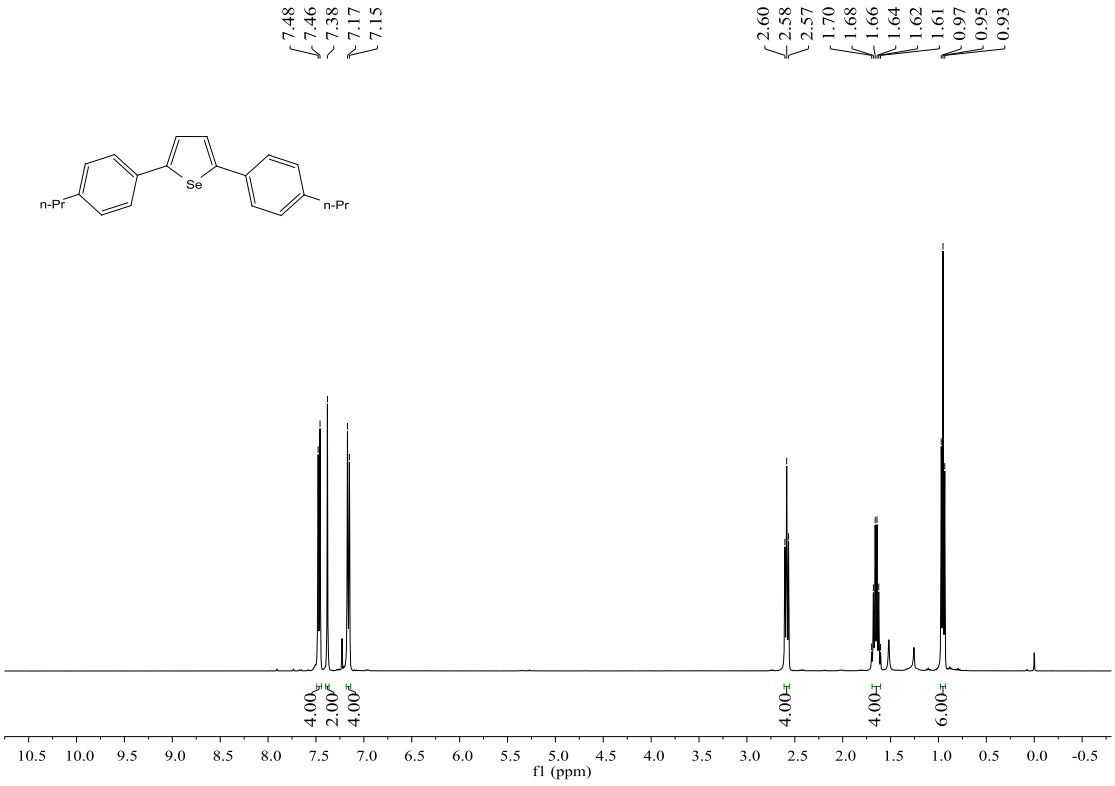
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum for 3b



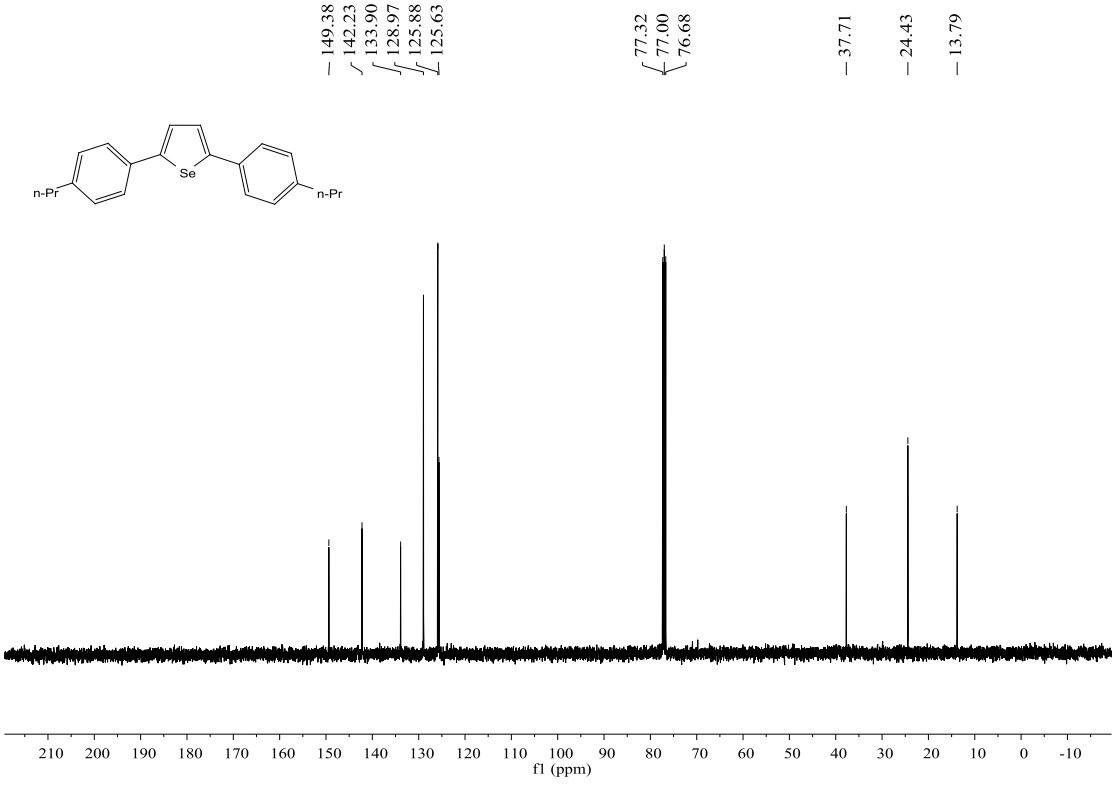
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum for 3b



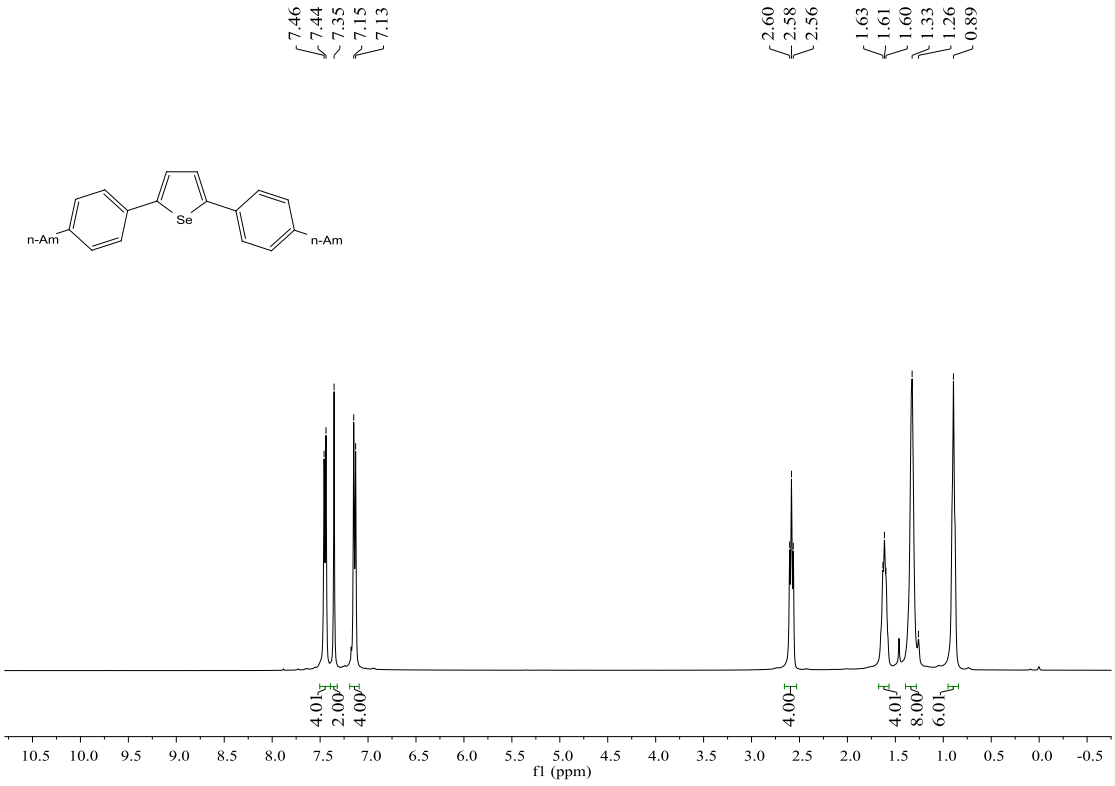
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum for 3c



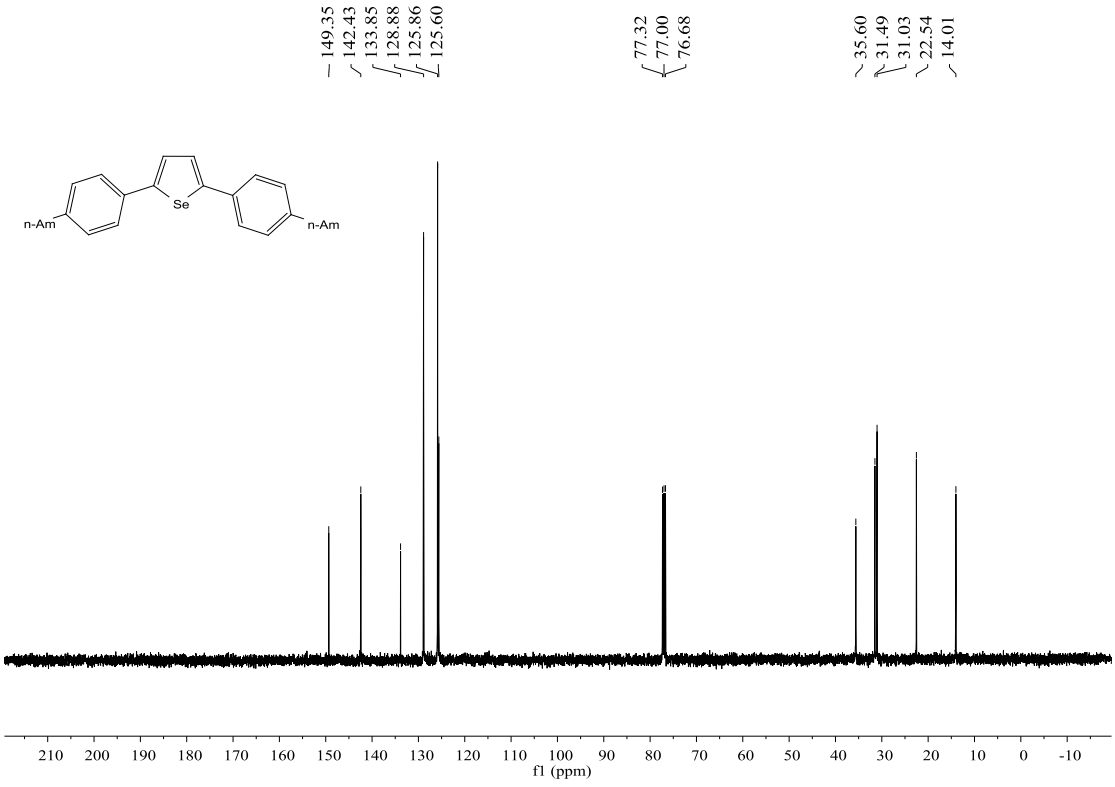
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum for 3c



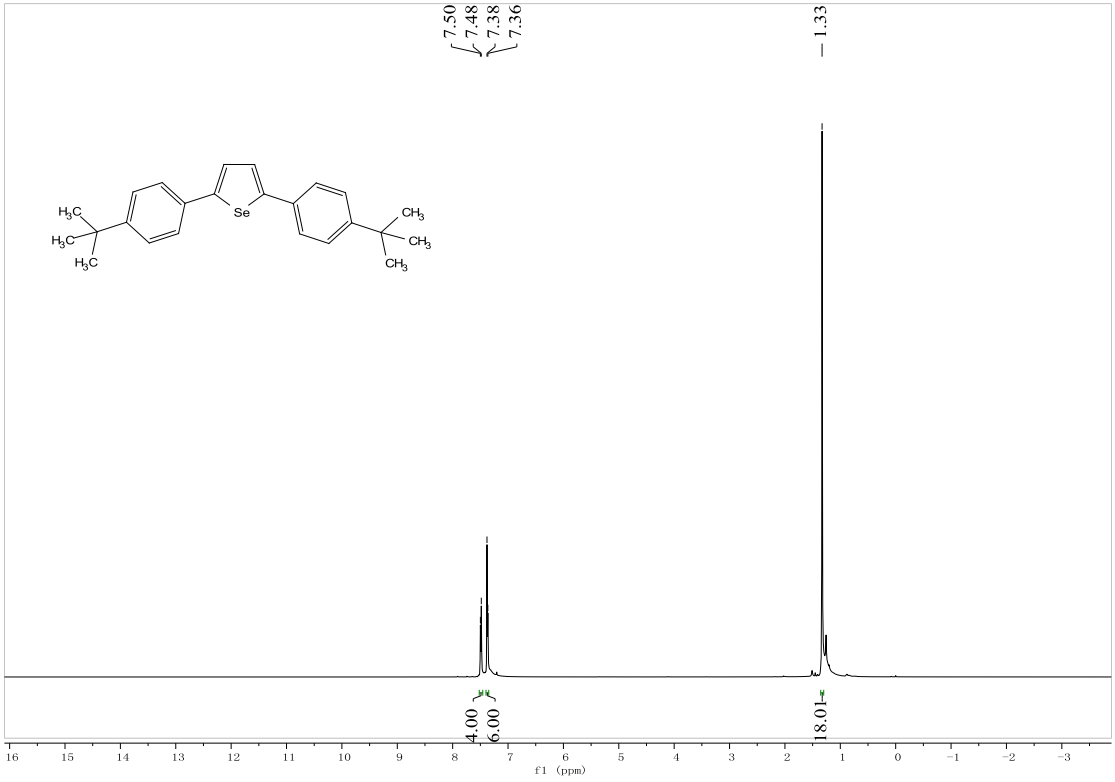
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum for 3d



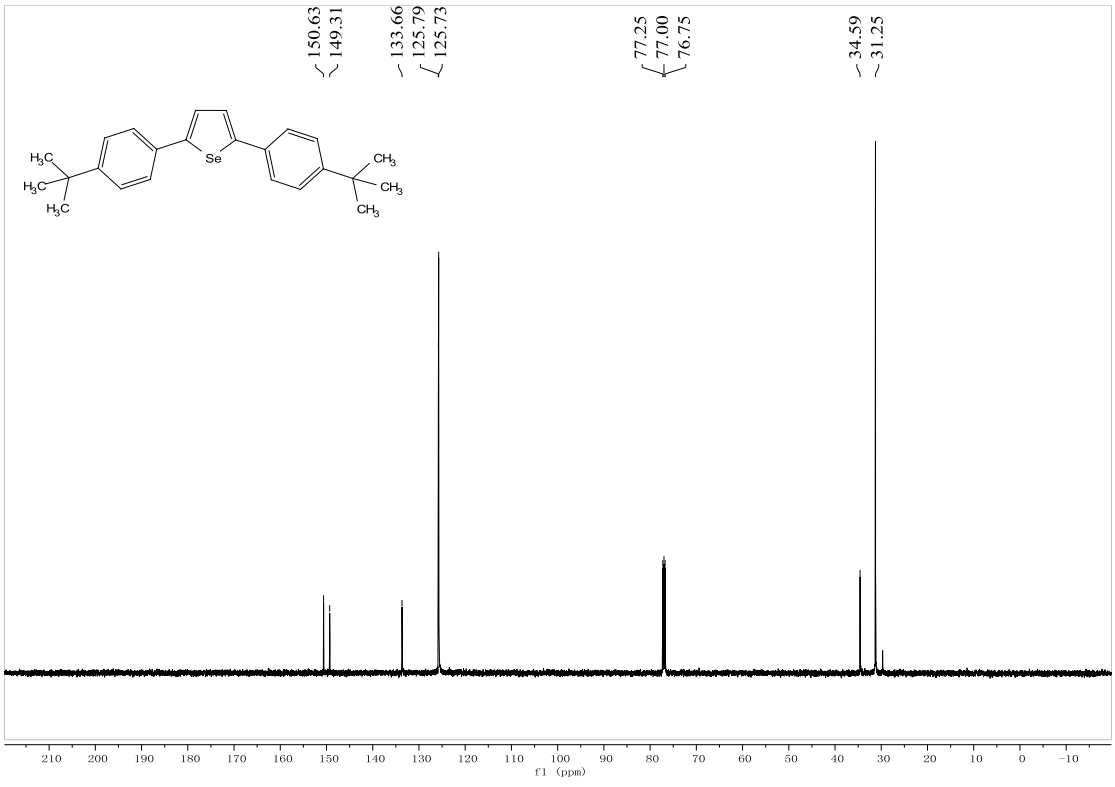
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum for 3d



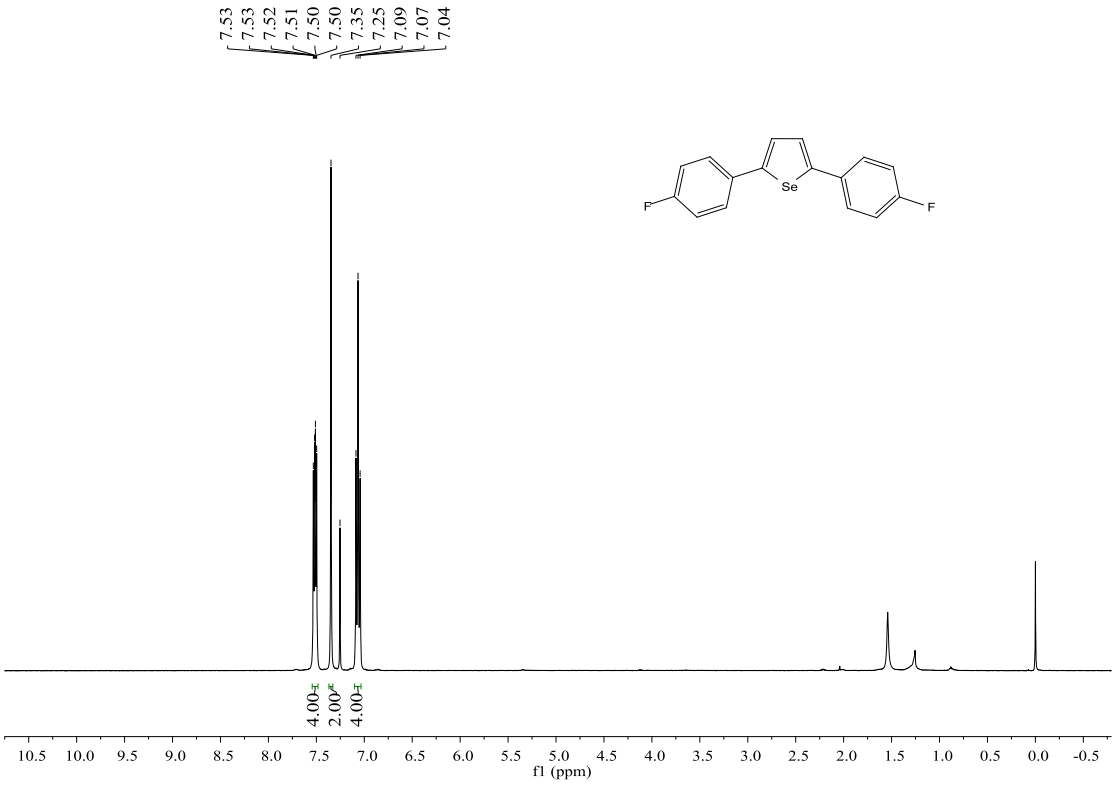
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum for 3e



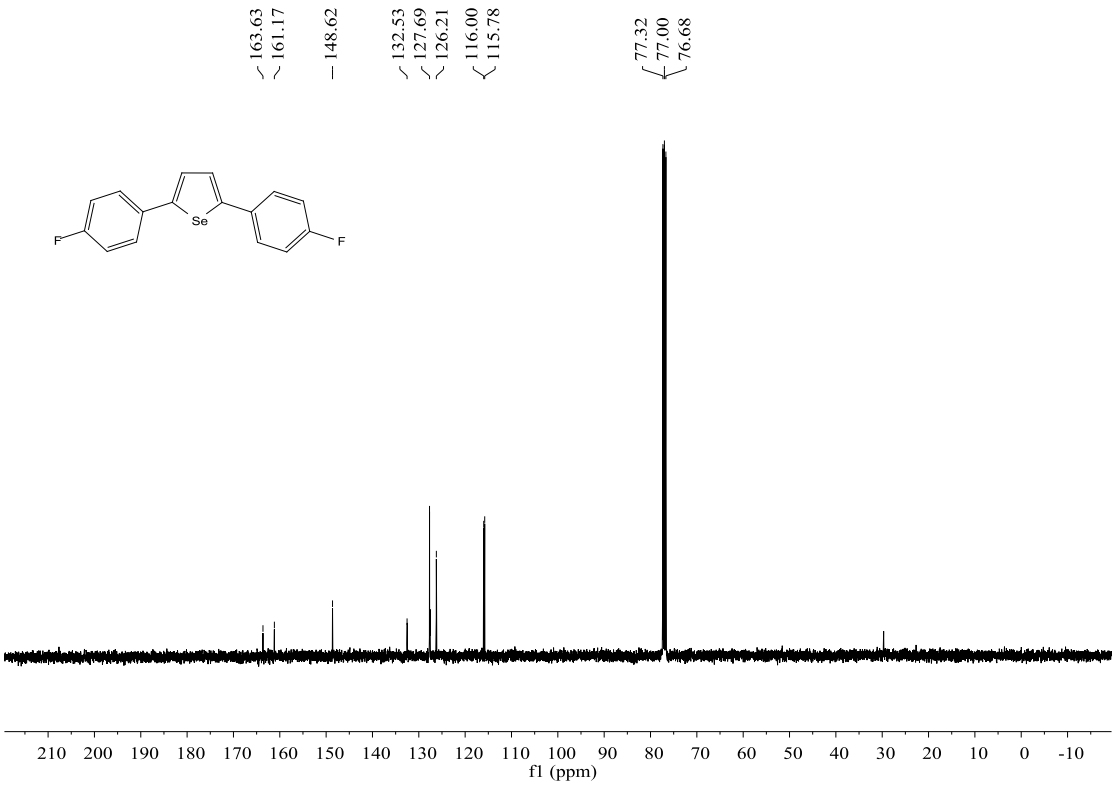
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum for 3e



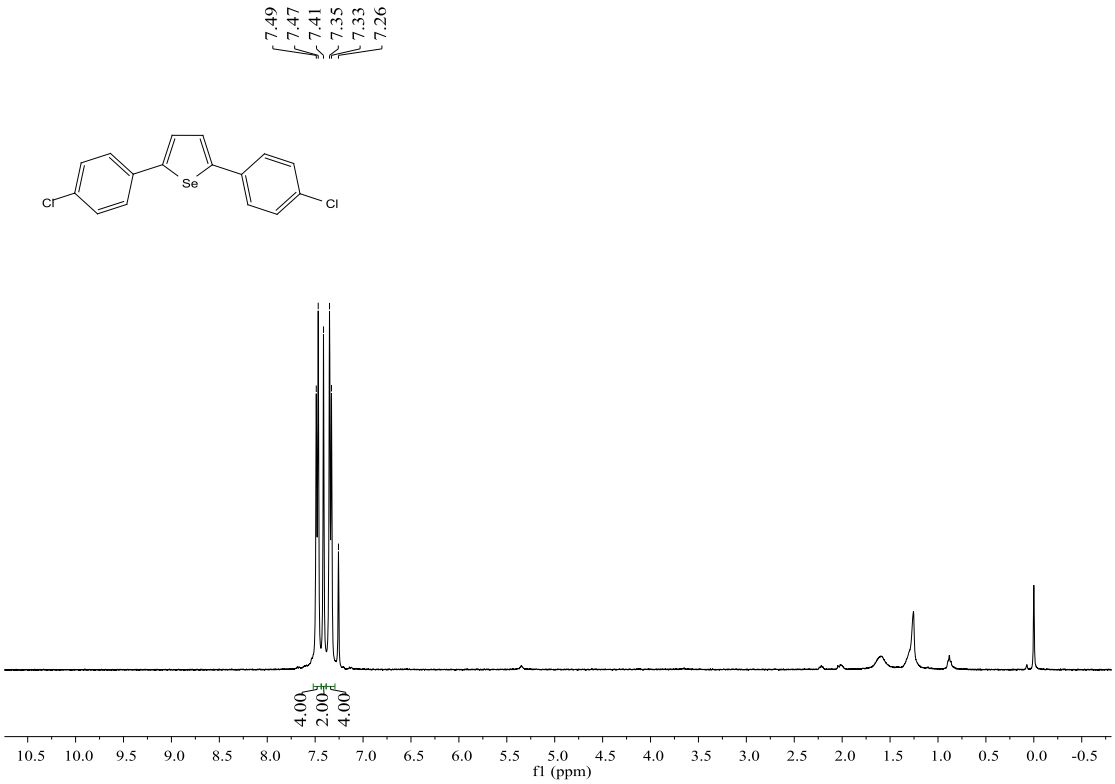
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum for 3f



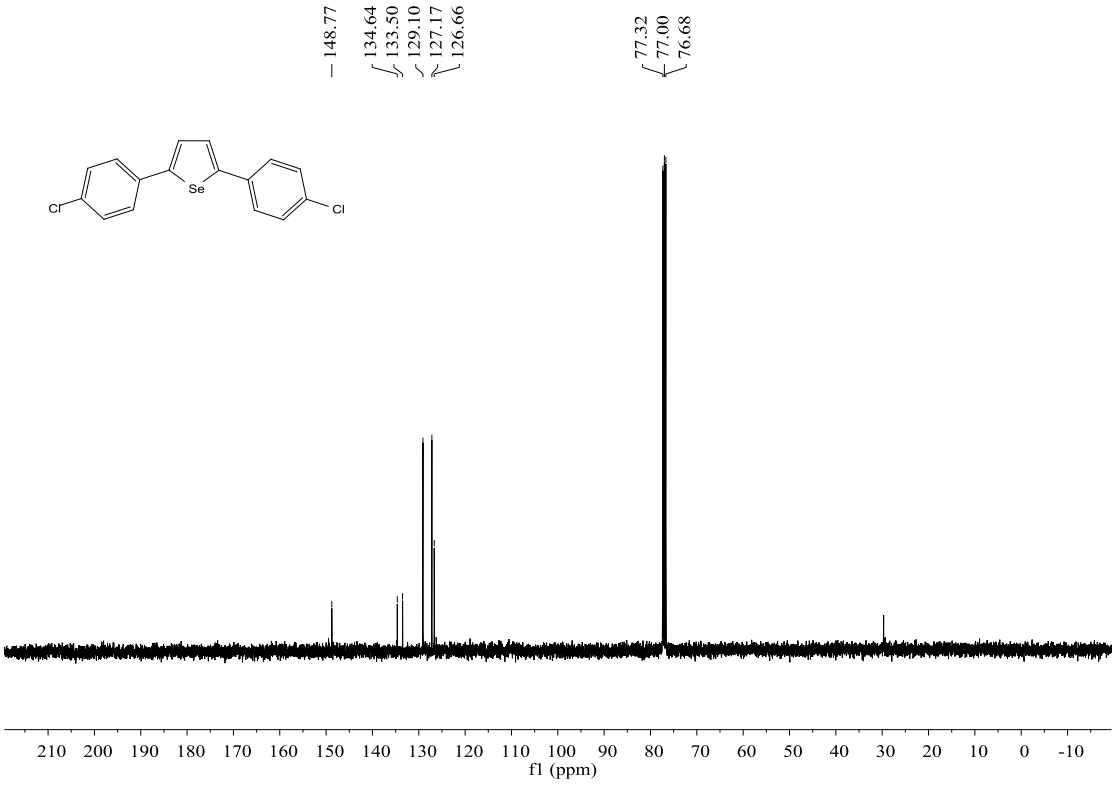
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum for 3f



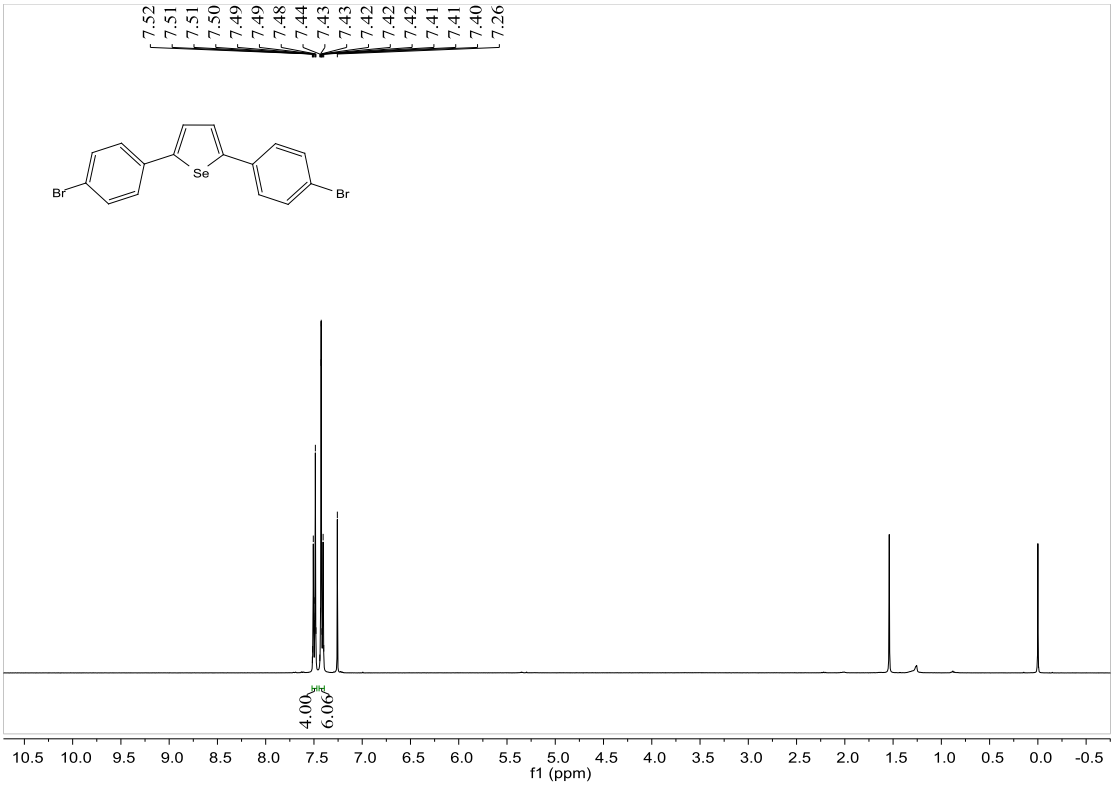
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum for 3g



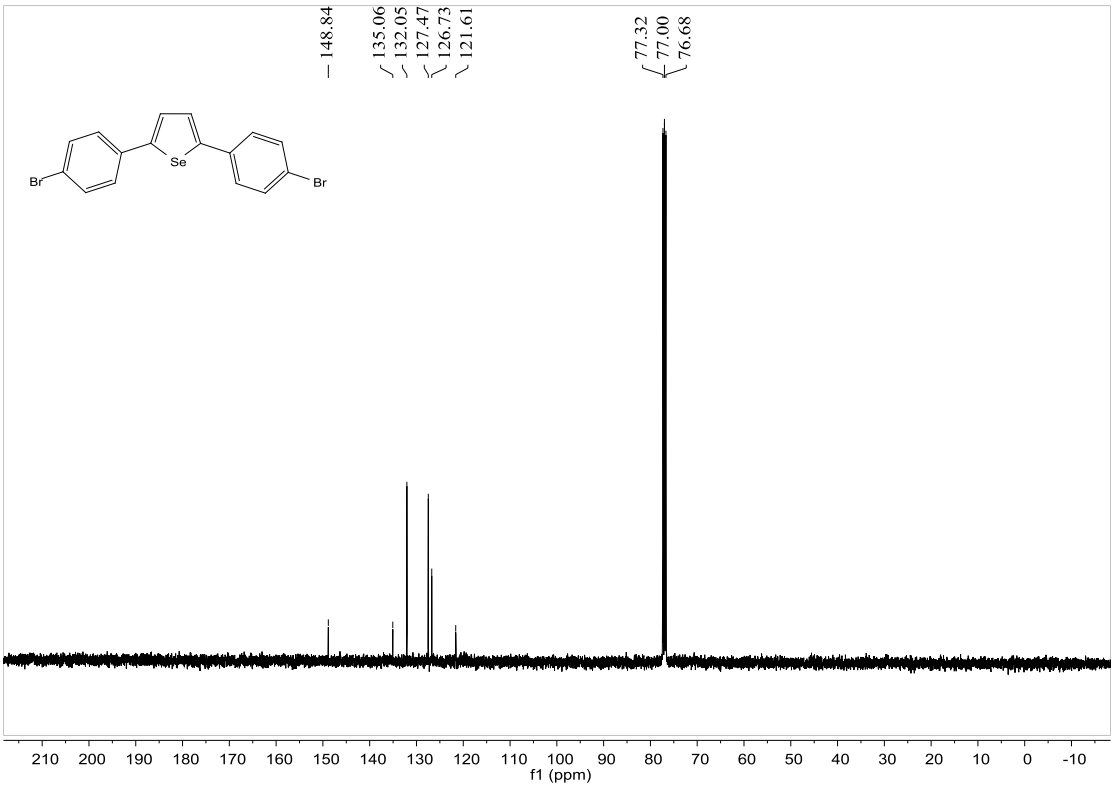
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum for 3g



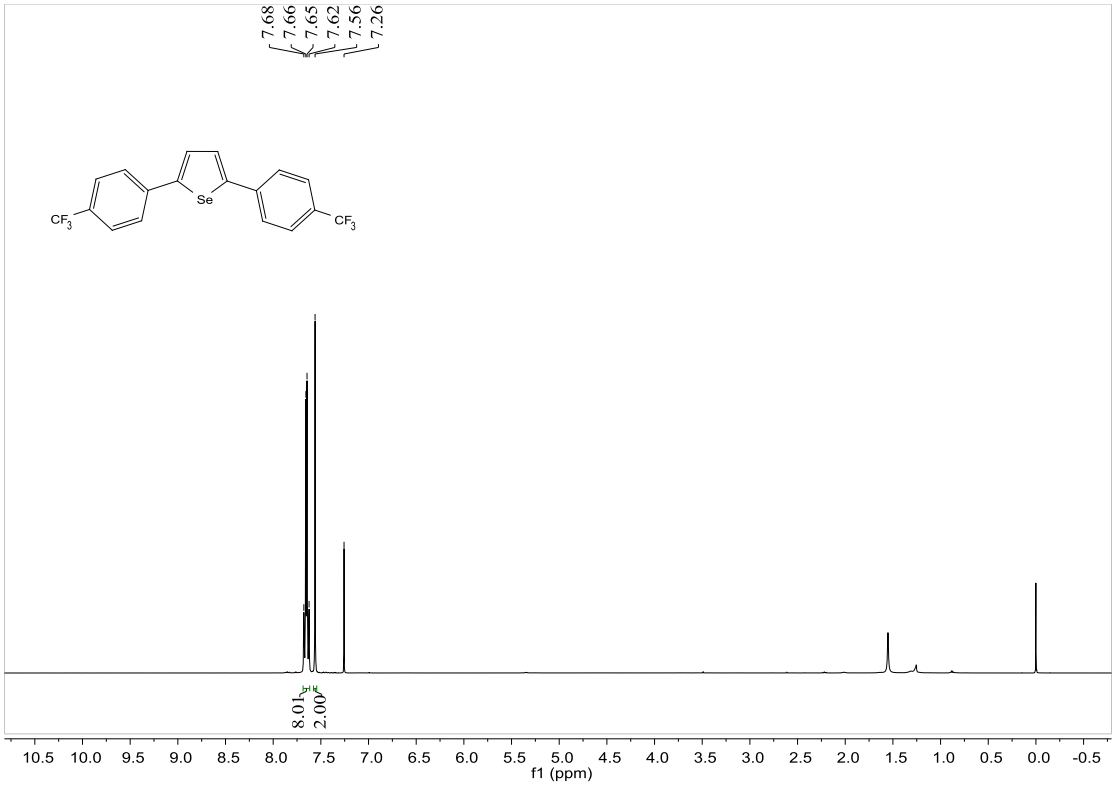
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum for 3h



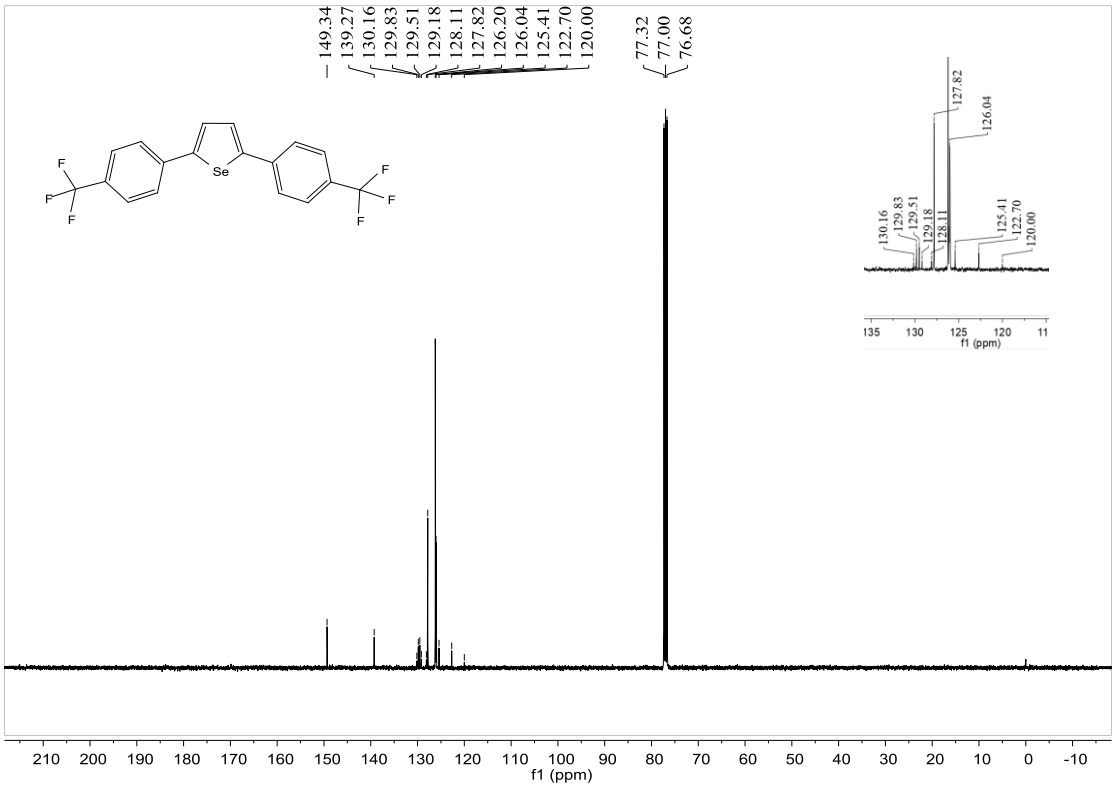
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum for 3h



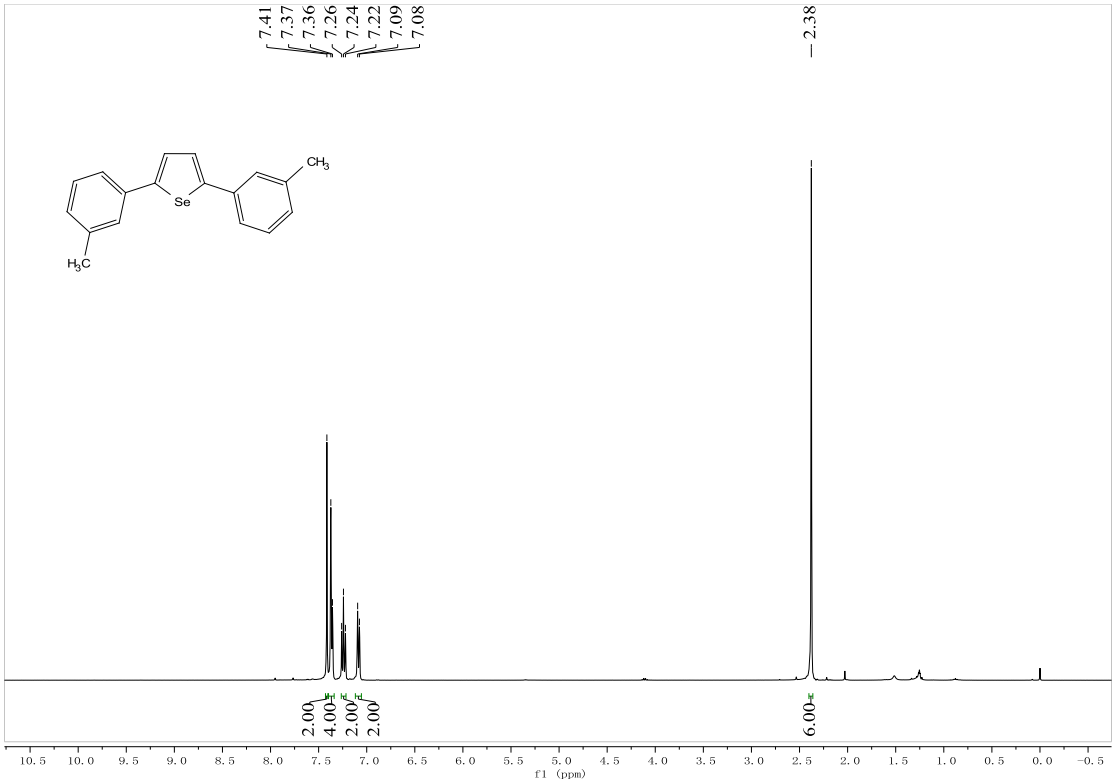
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum for 3i



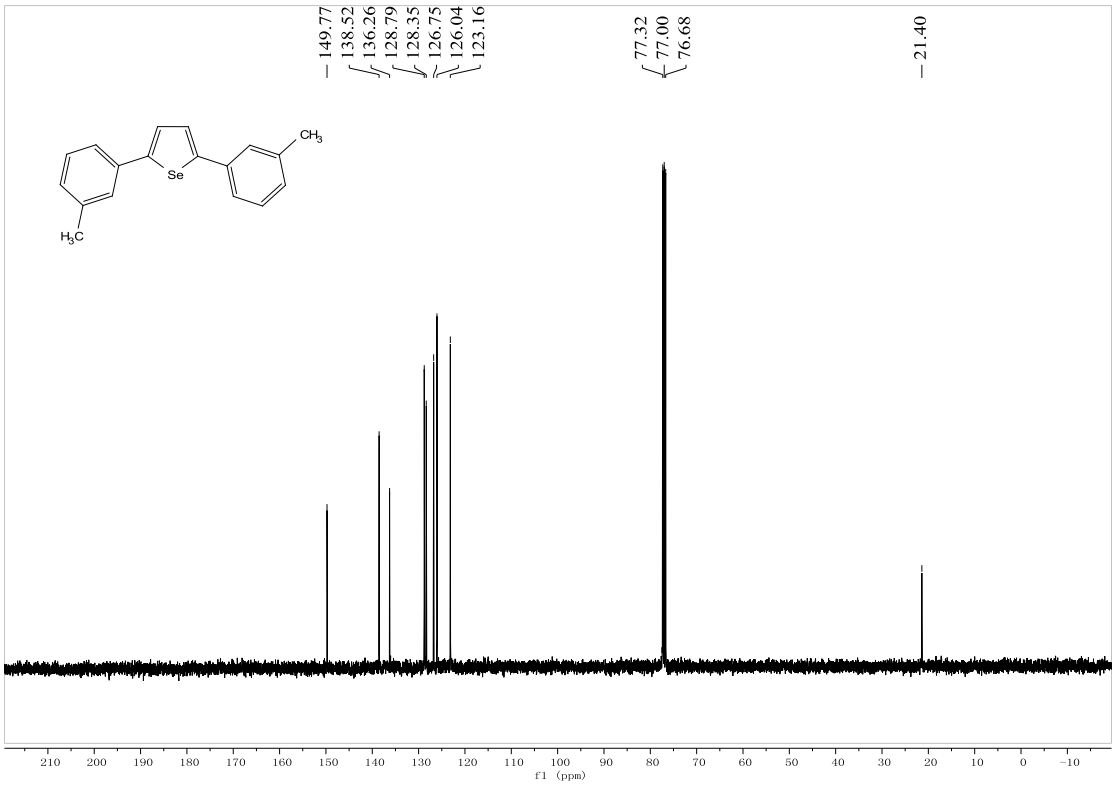
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum for 3i



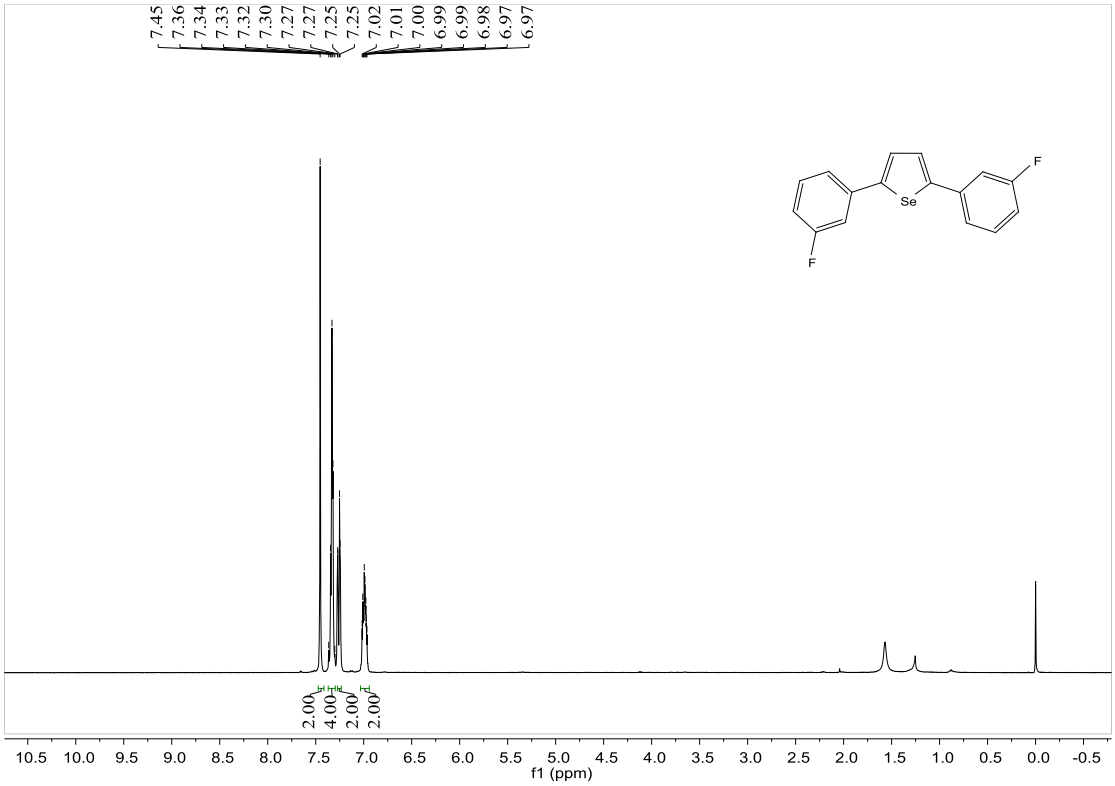
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum for 3j



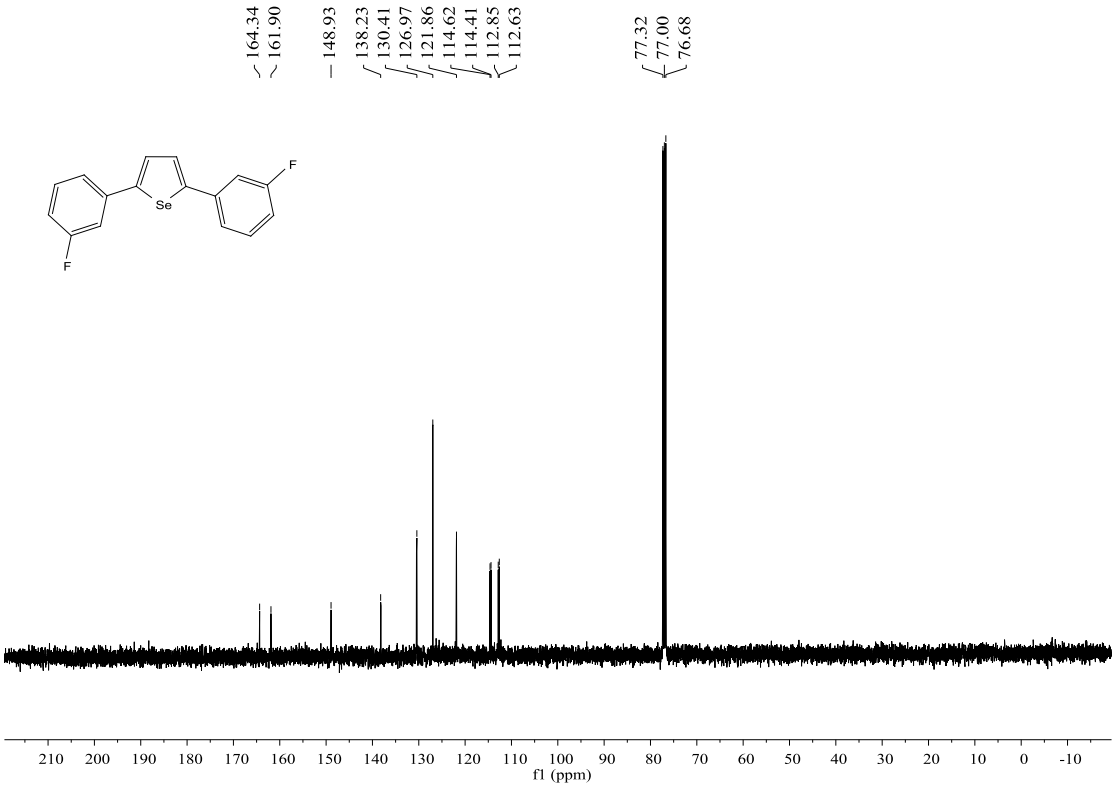
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum for 3j



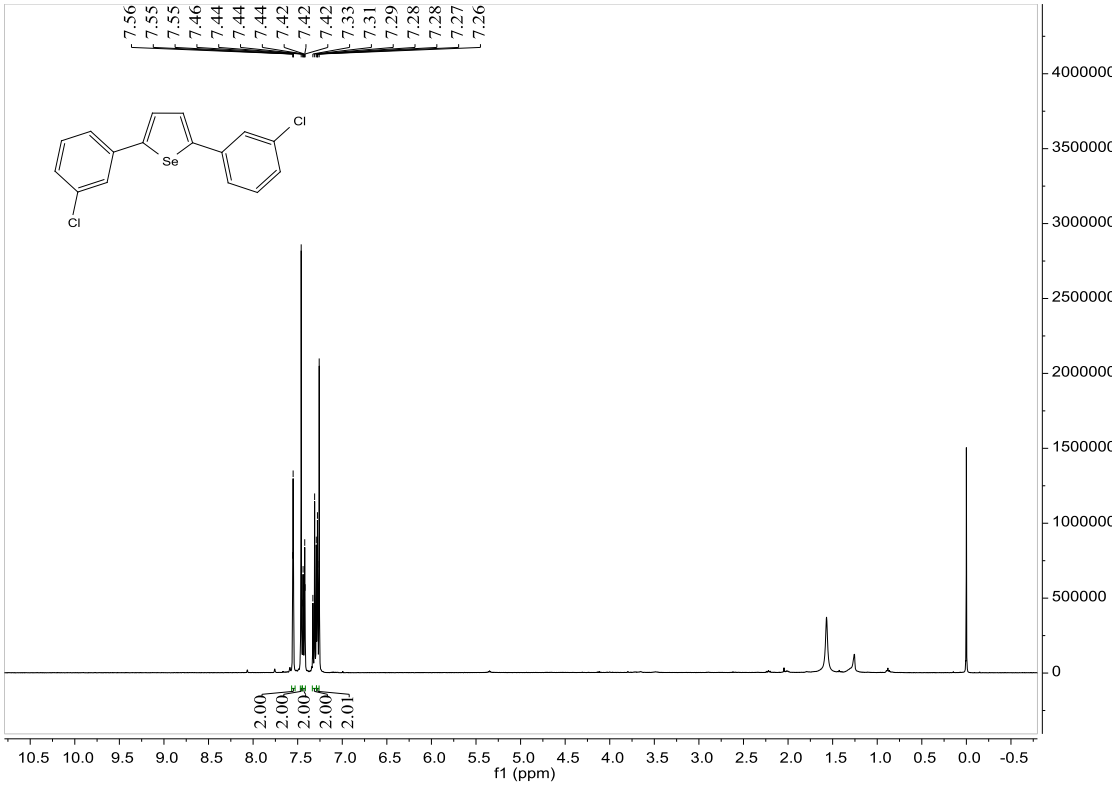
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum for 3k



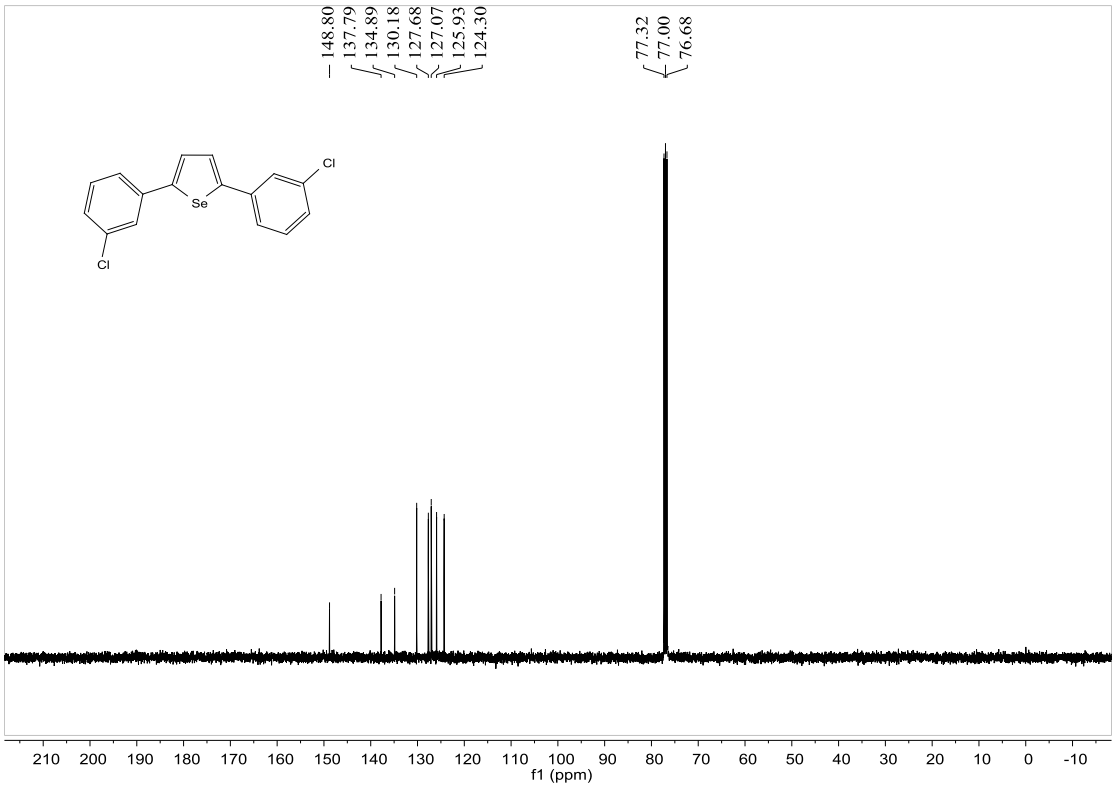
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum for 3k



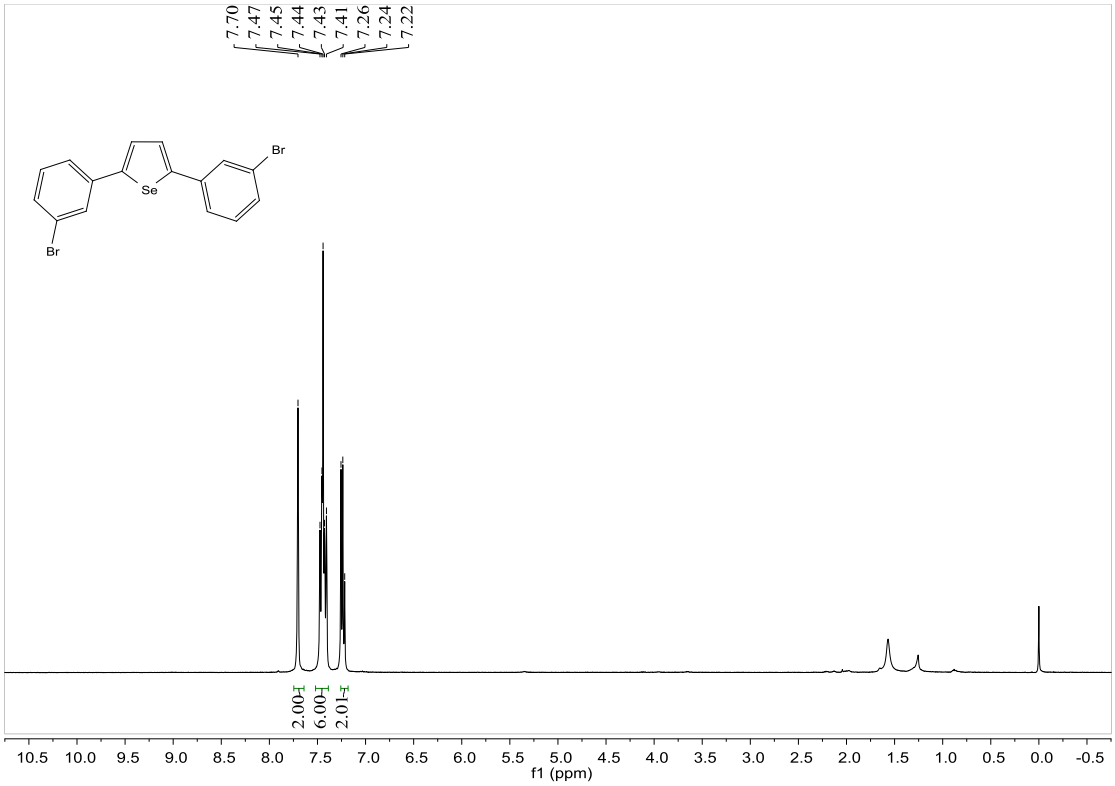
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum for 3l



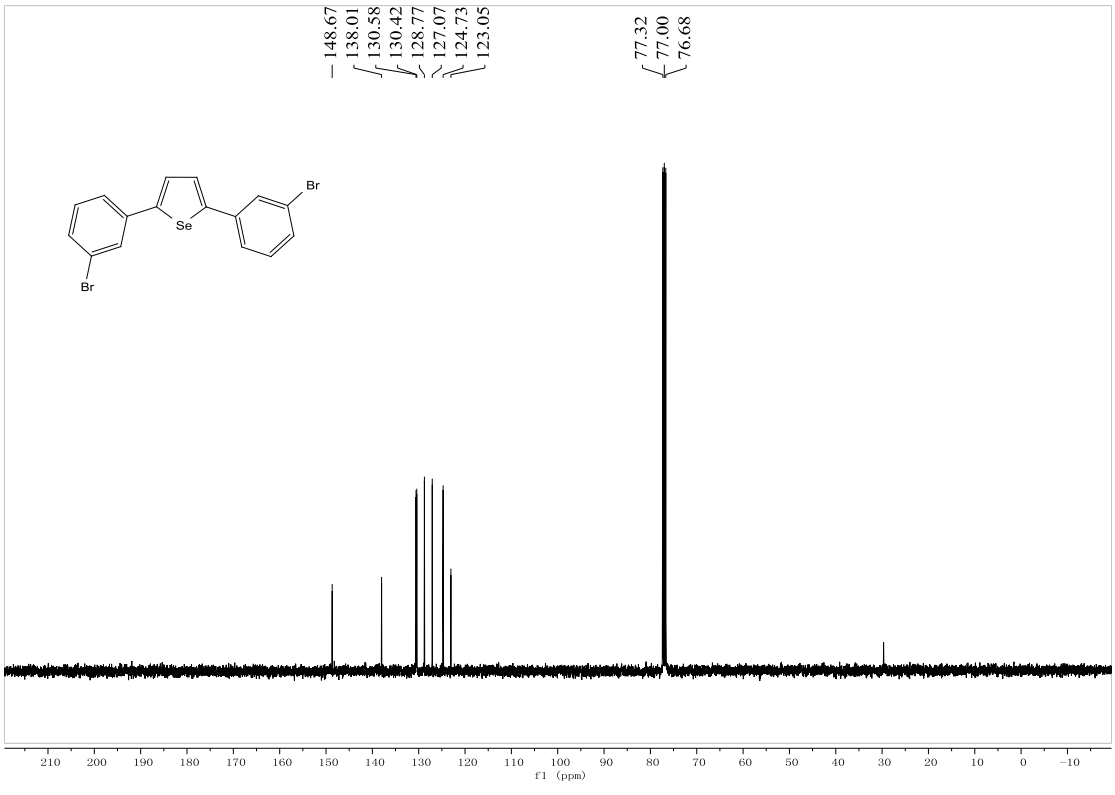
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum for 3l



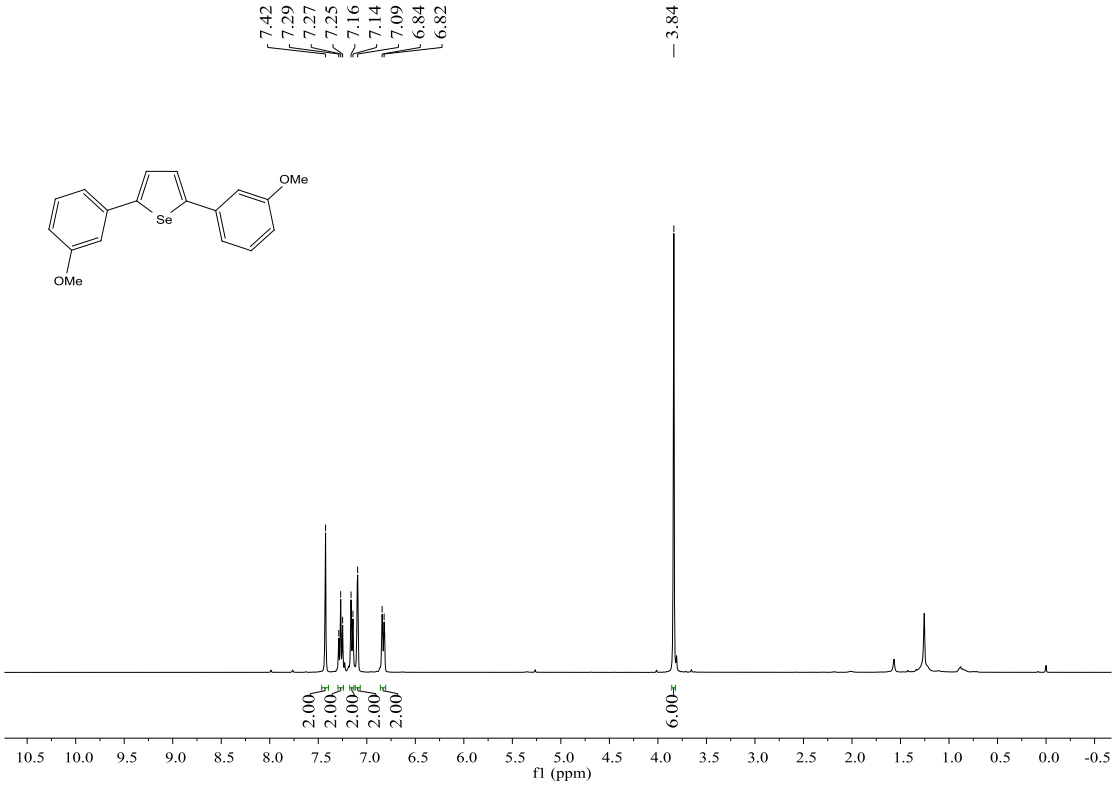
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum for 3m



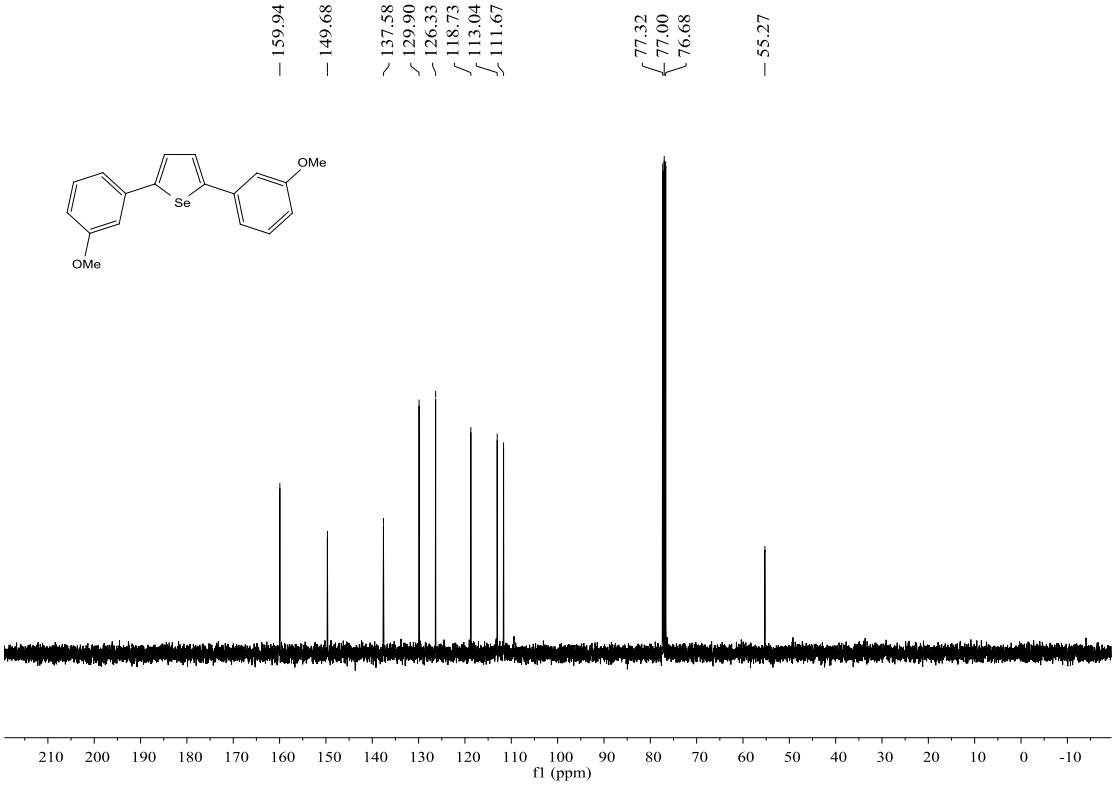
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum for 3m



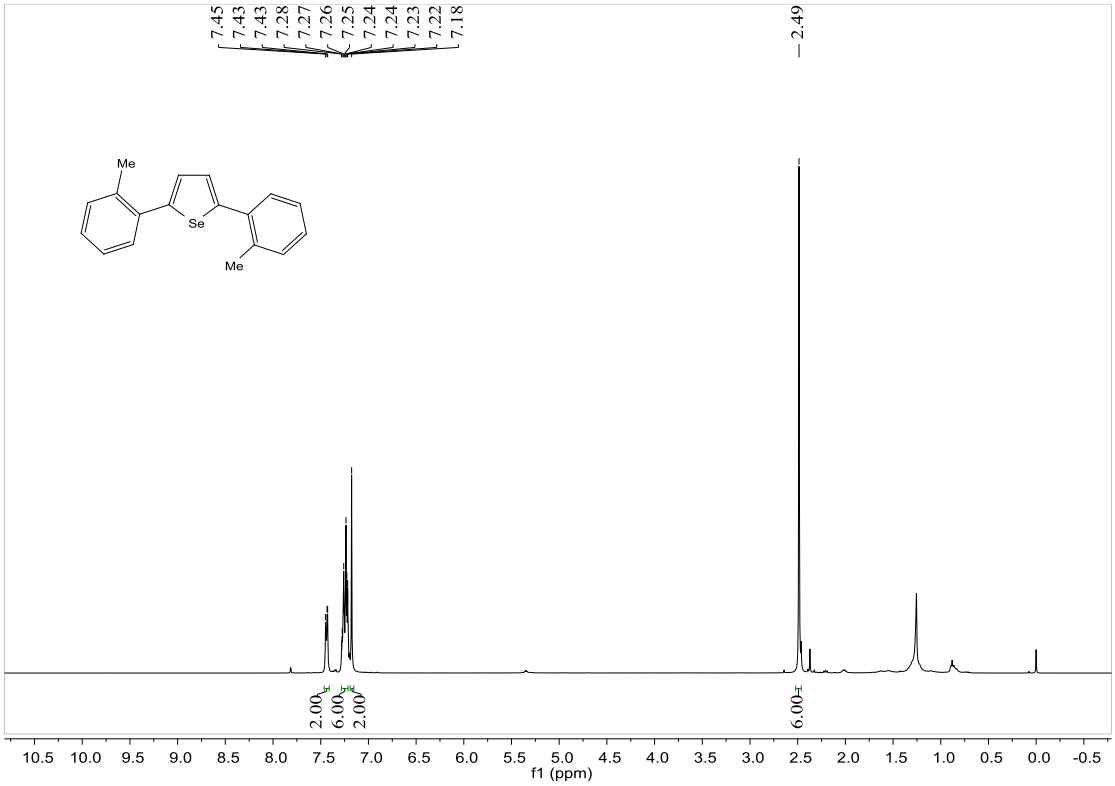
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum for 3n



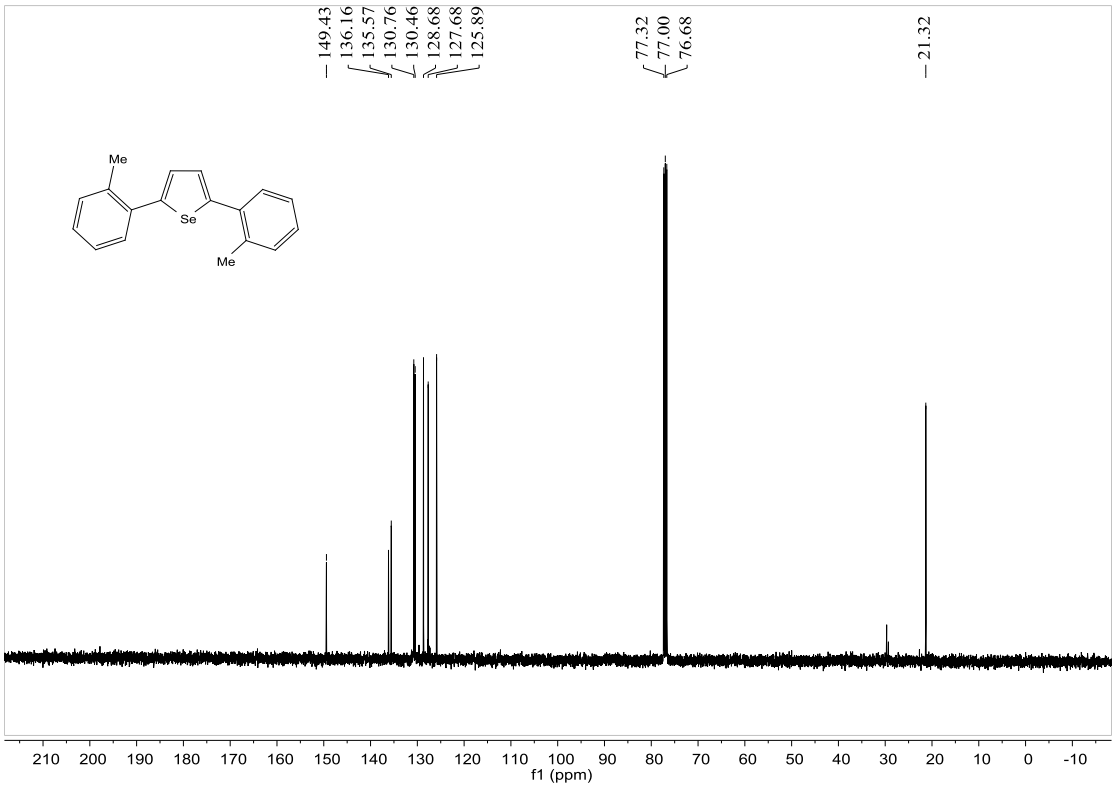
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum for 3n



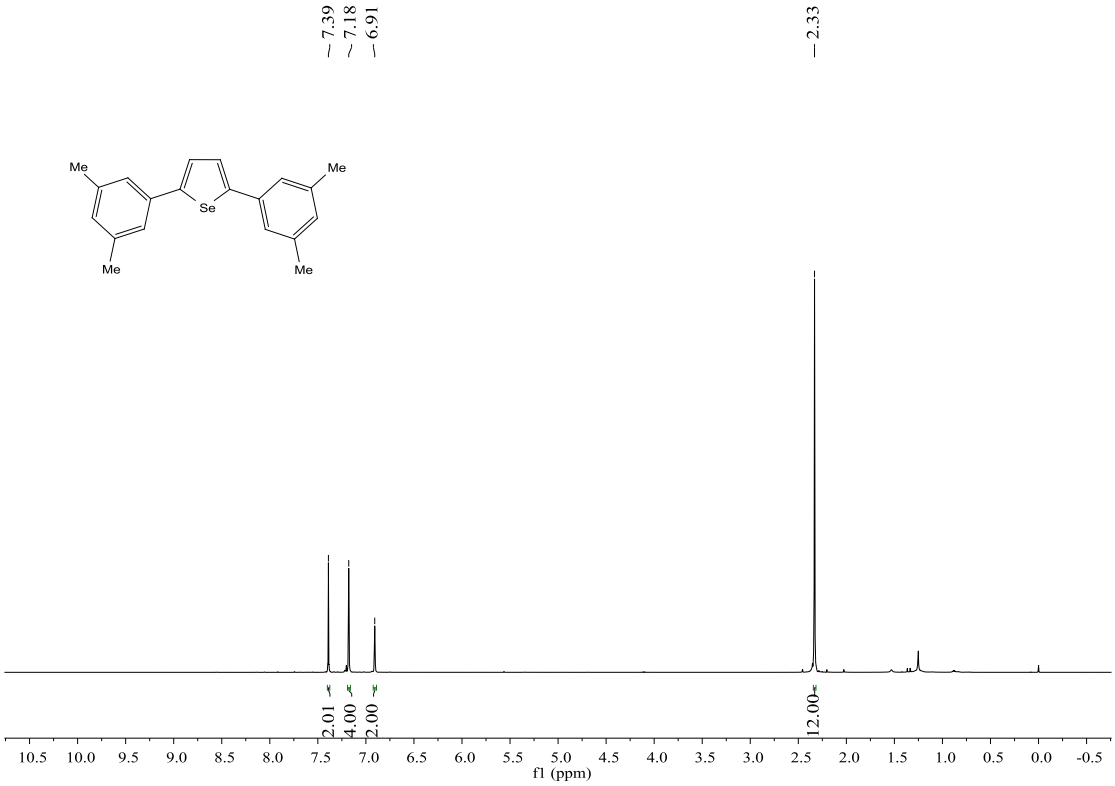
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum for 3o



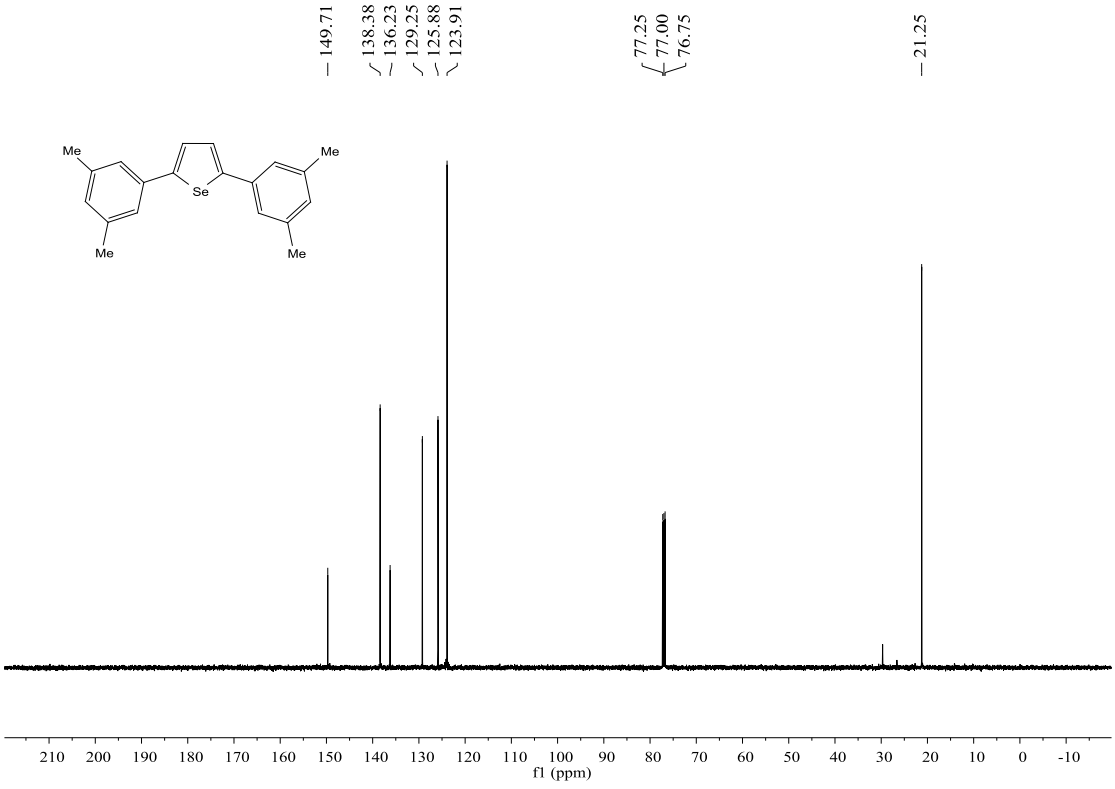
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum for 3o



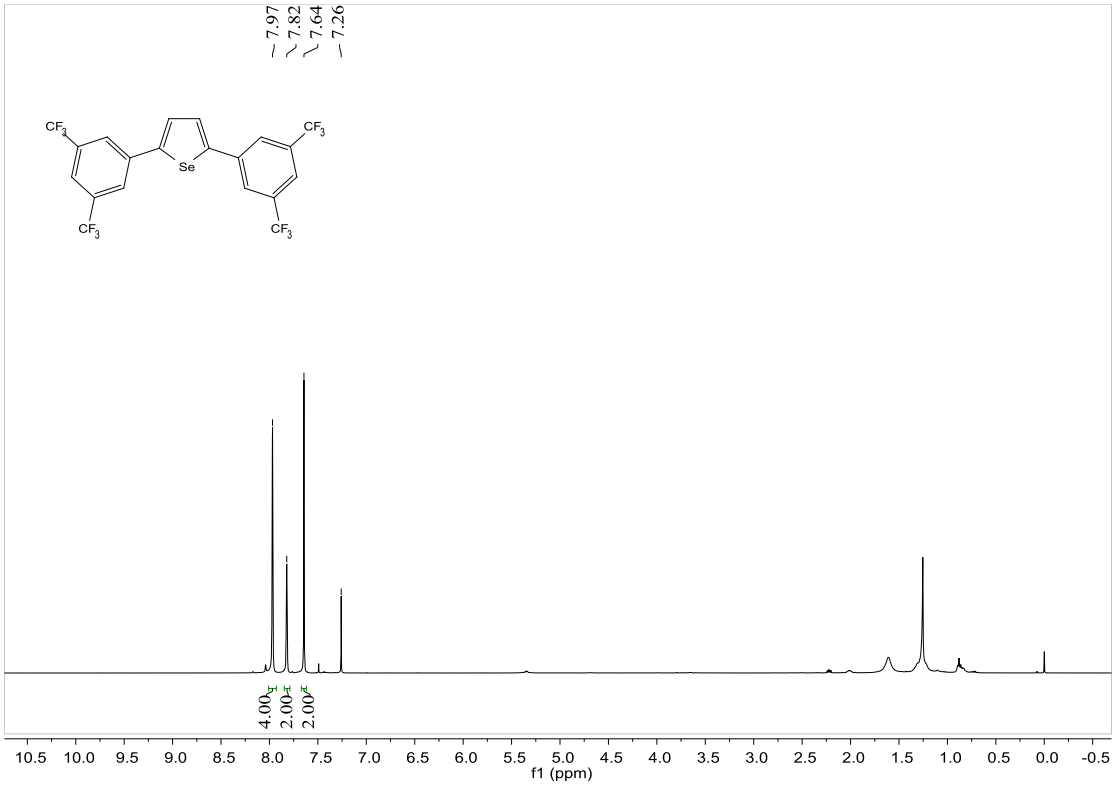
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum for 3p



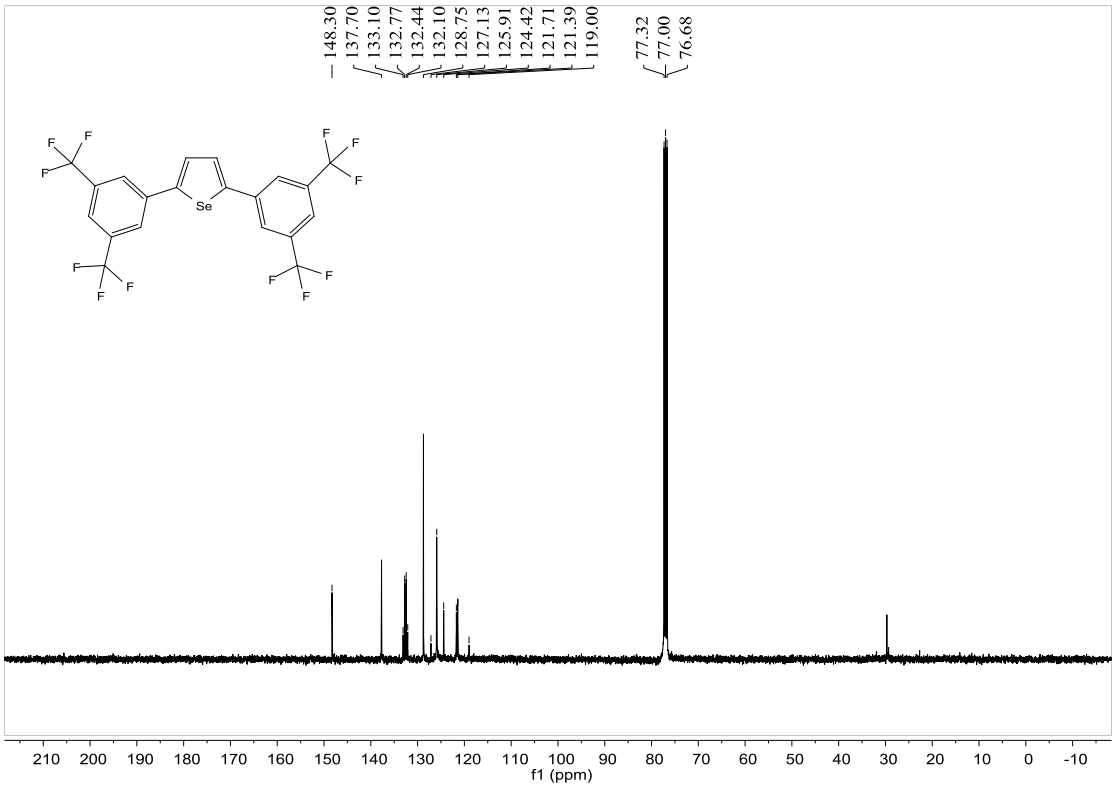
^{13}C-NMR (125 MHz, $CDCl_3$) spectrum for 3p



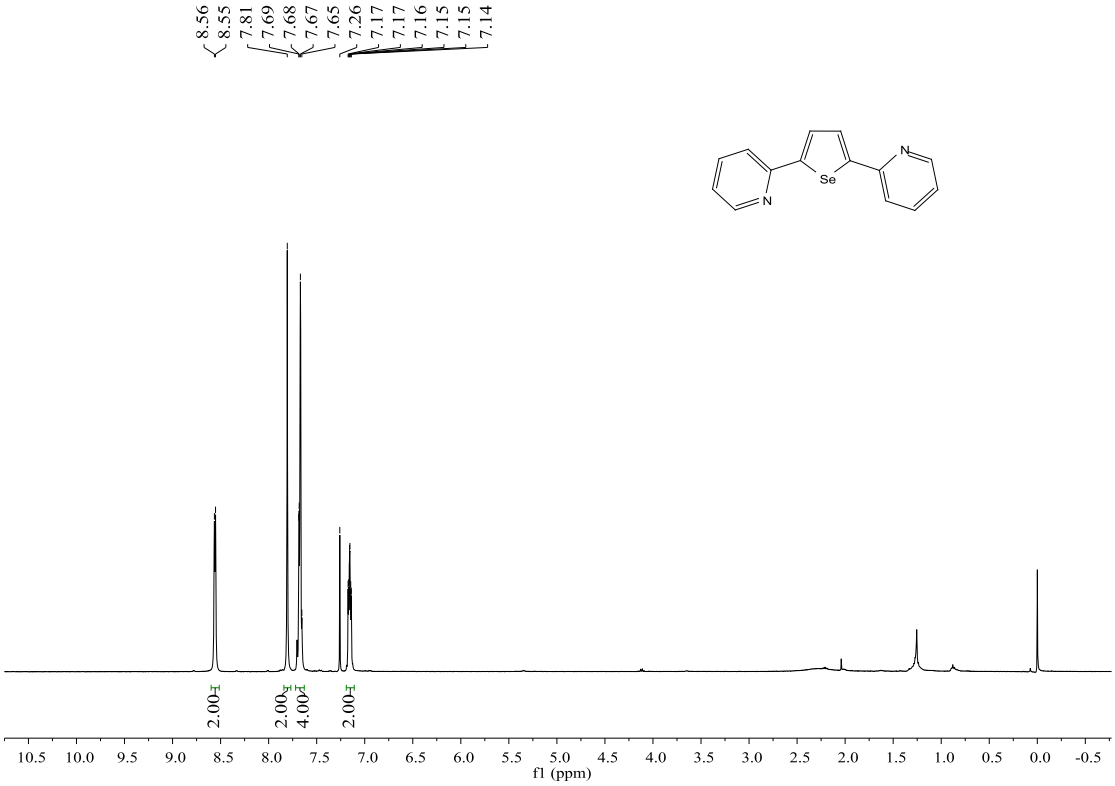
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum for 3q



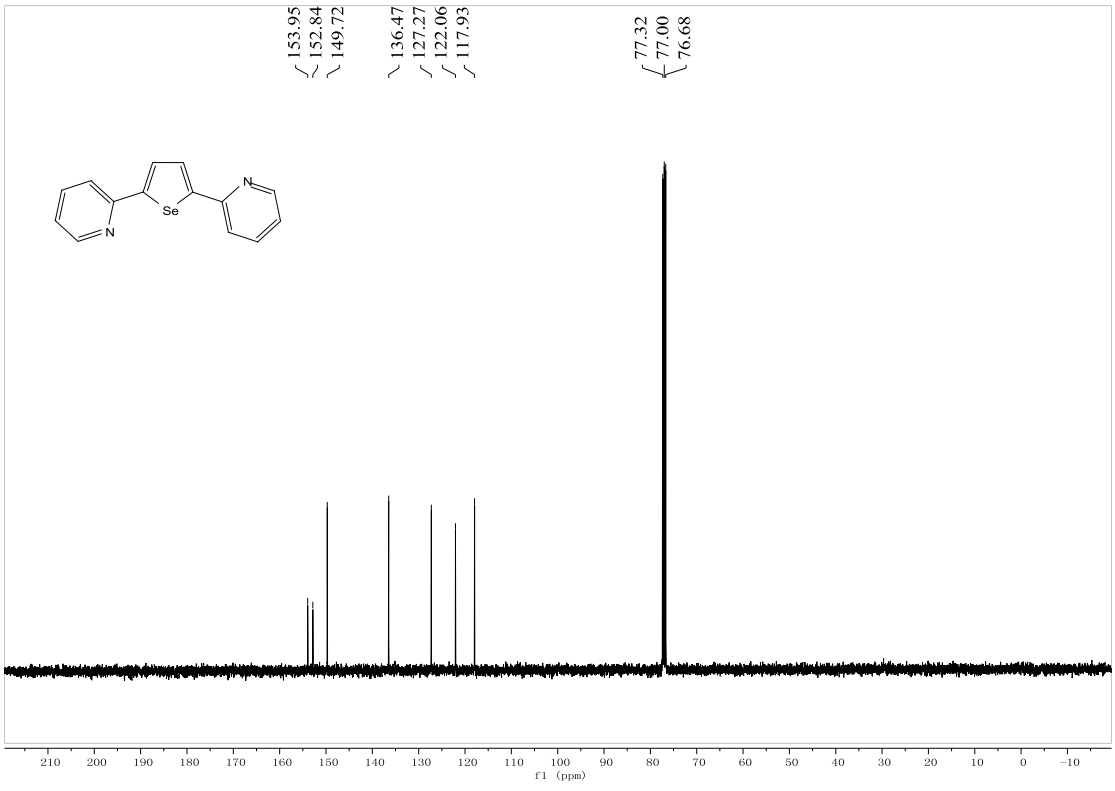
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum for 3q



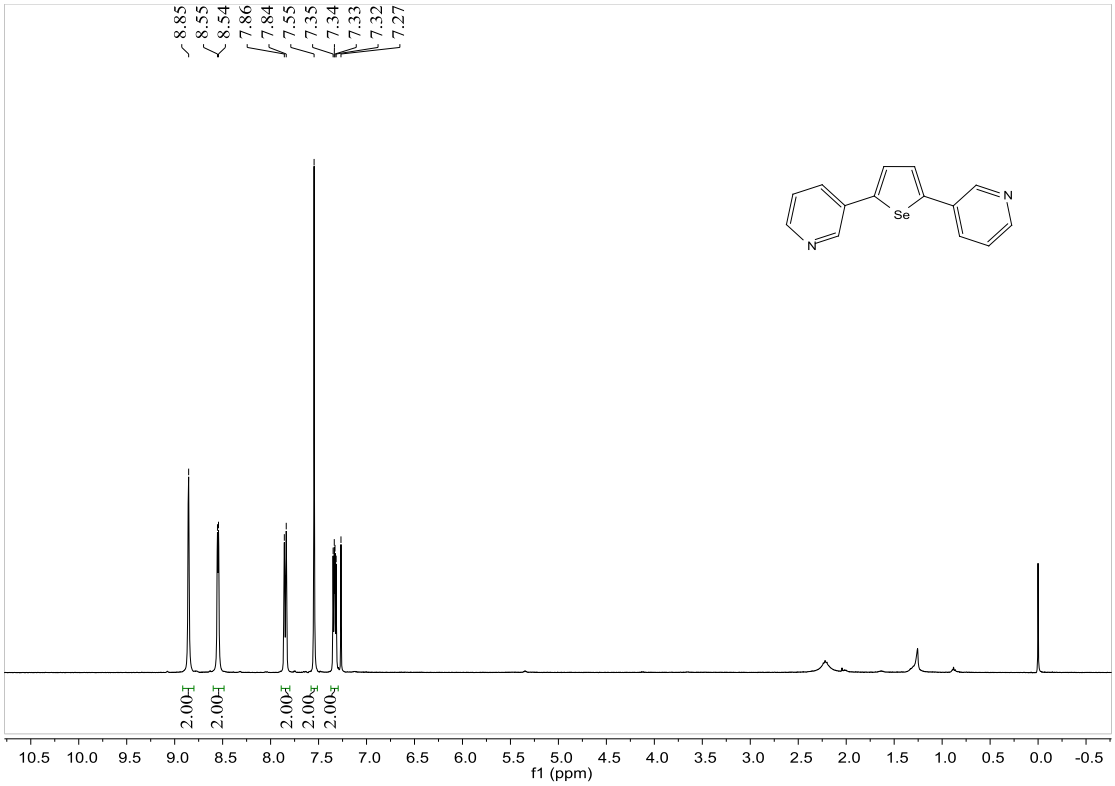
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum for 3r



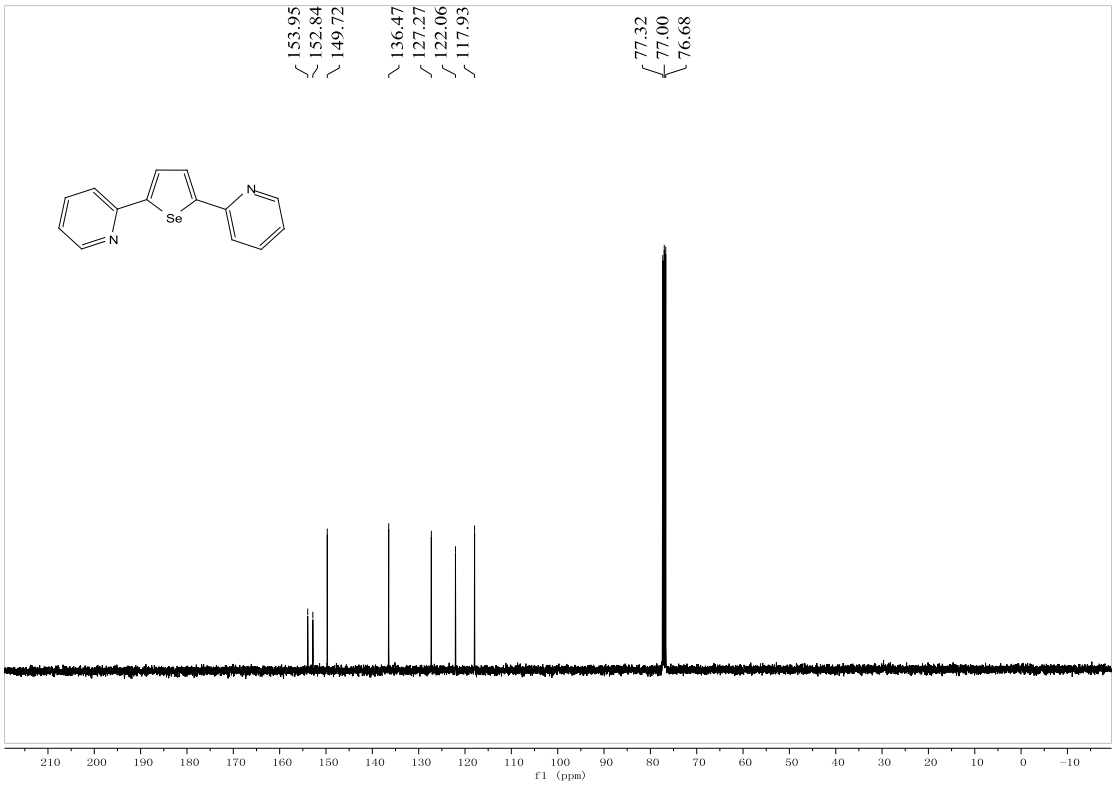
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum for 3r



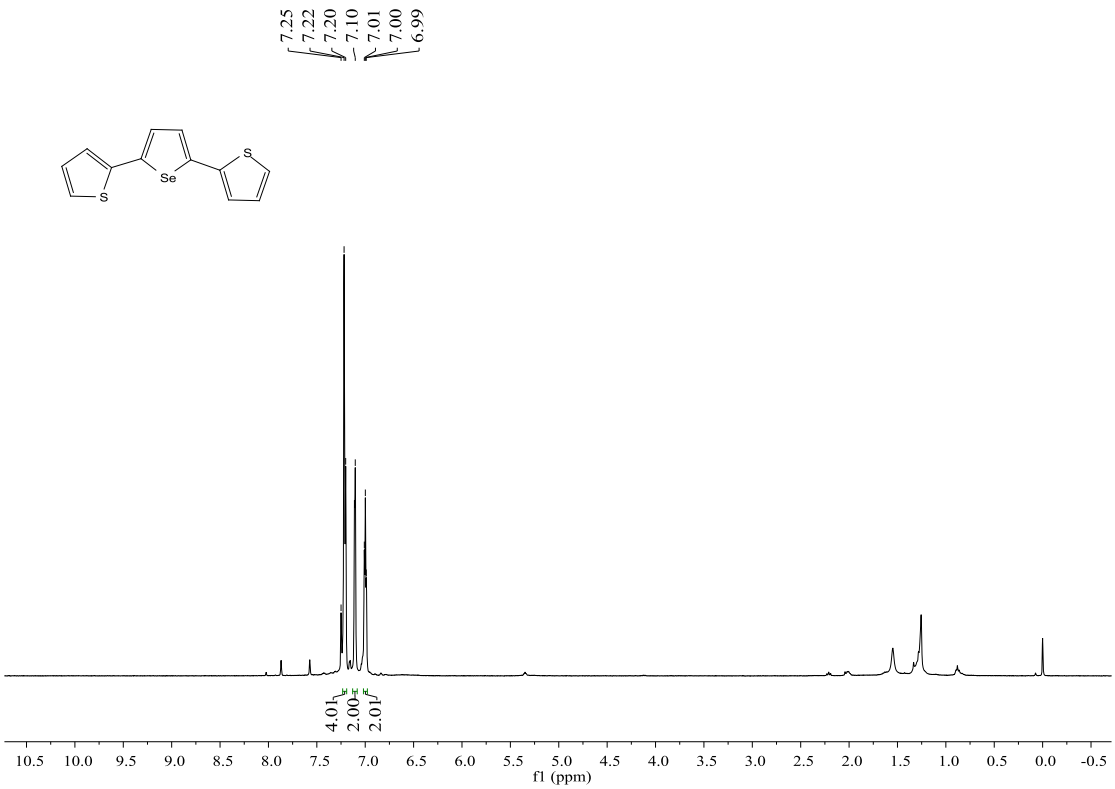
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum for 3s



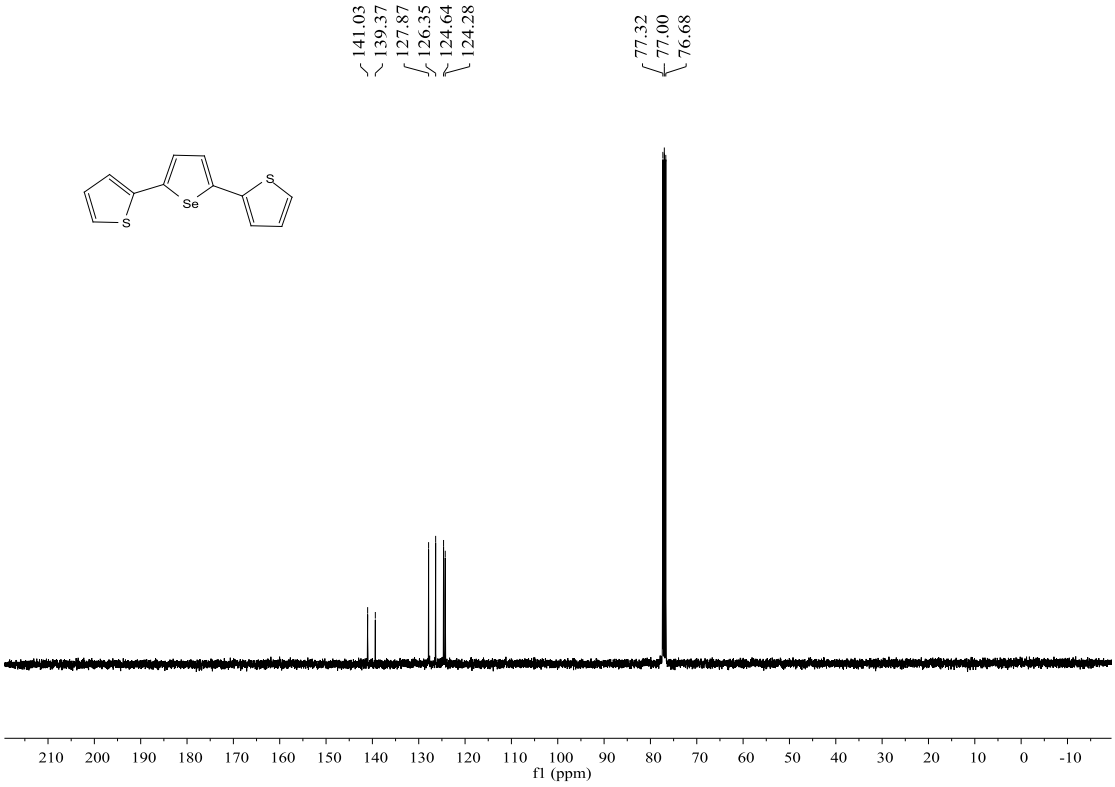
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum for 3s



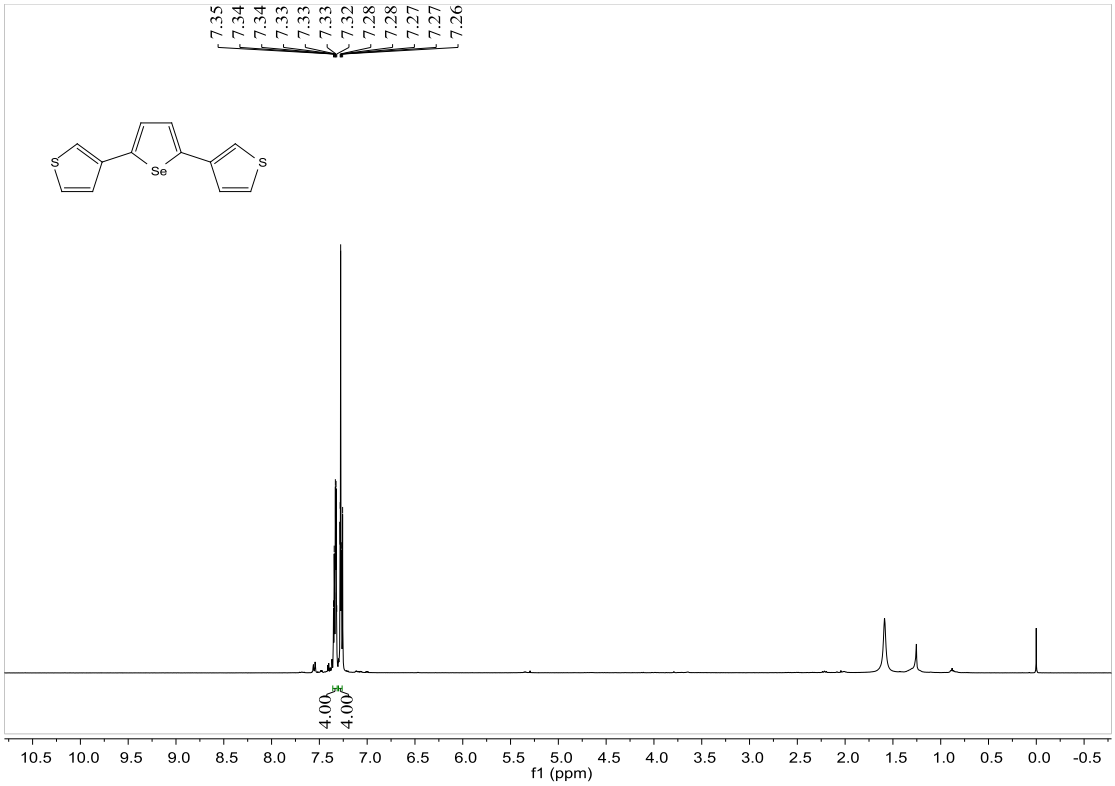
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum for 3t



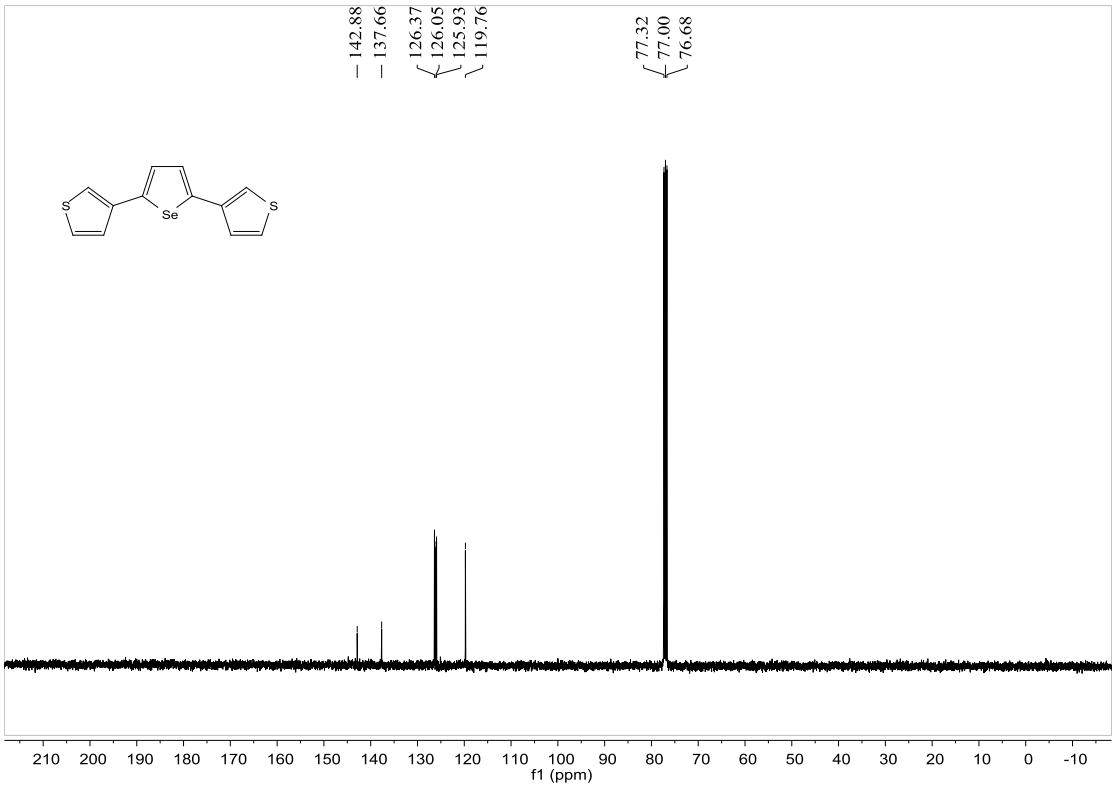
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum for 3t



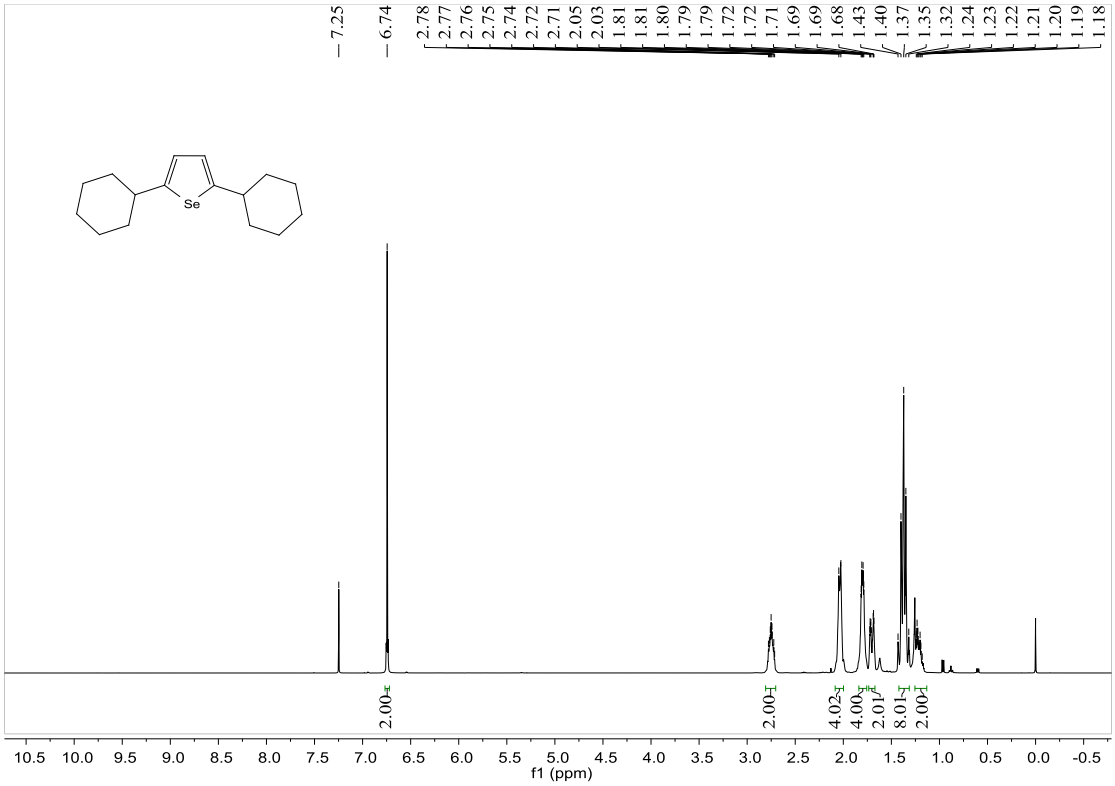
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum for 3u



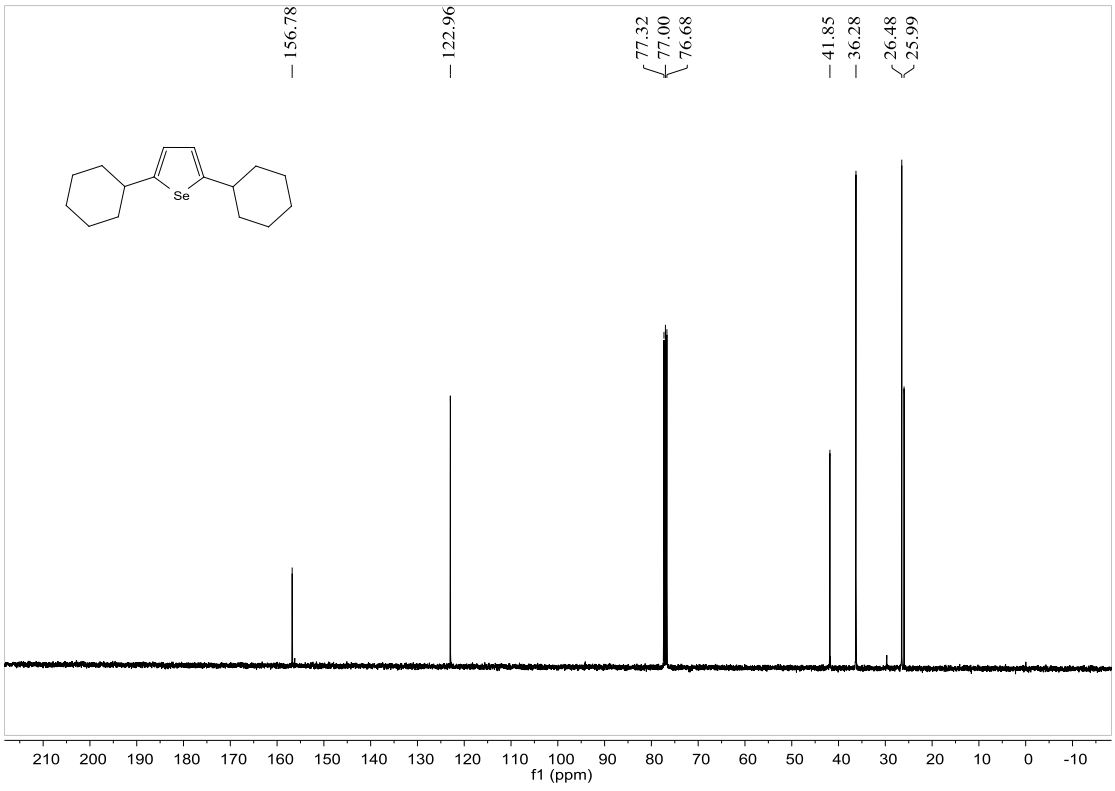
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum for 3u



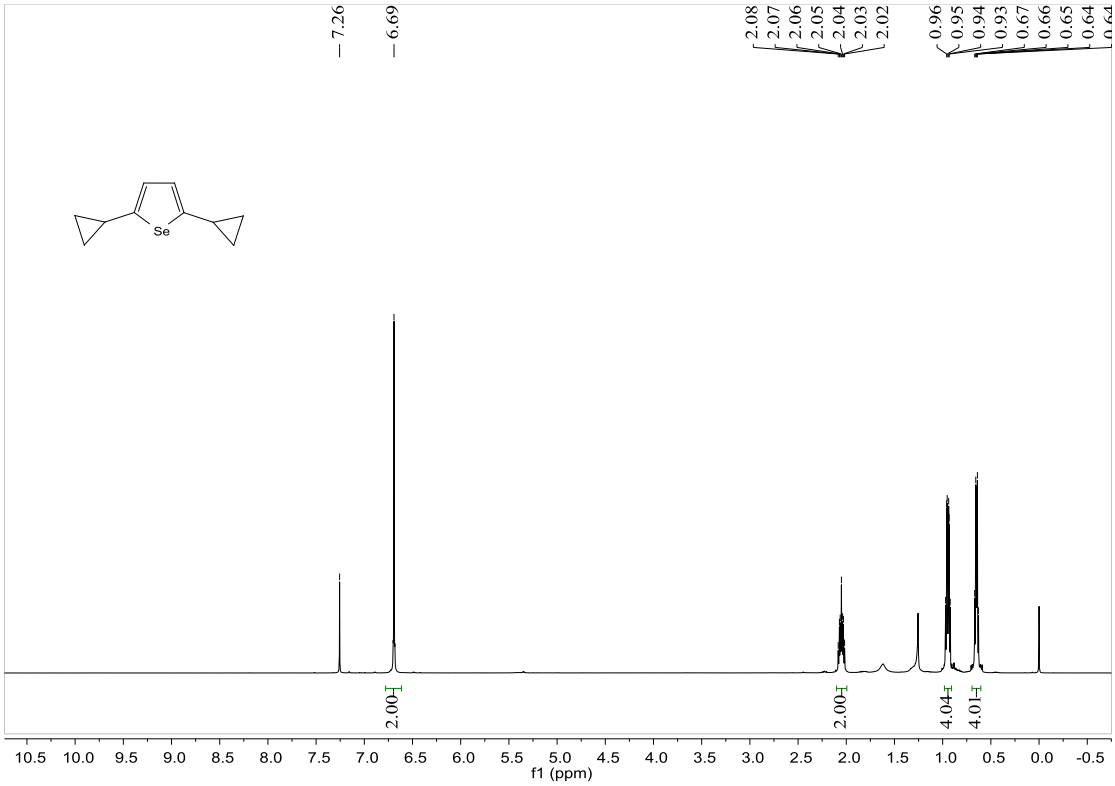
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum for 3v



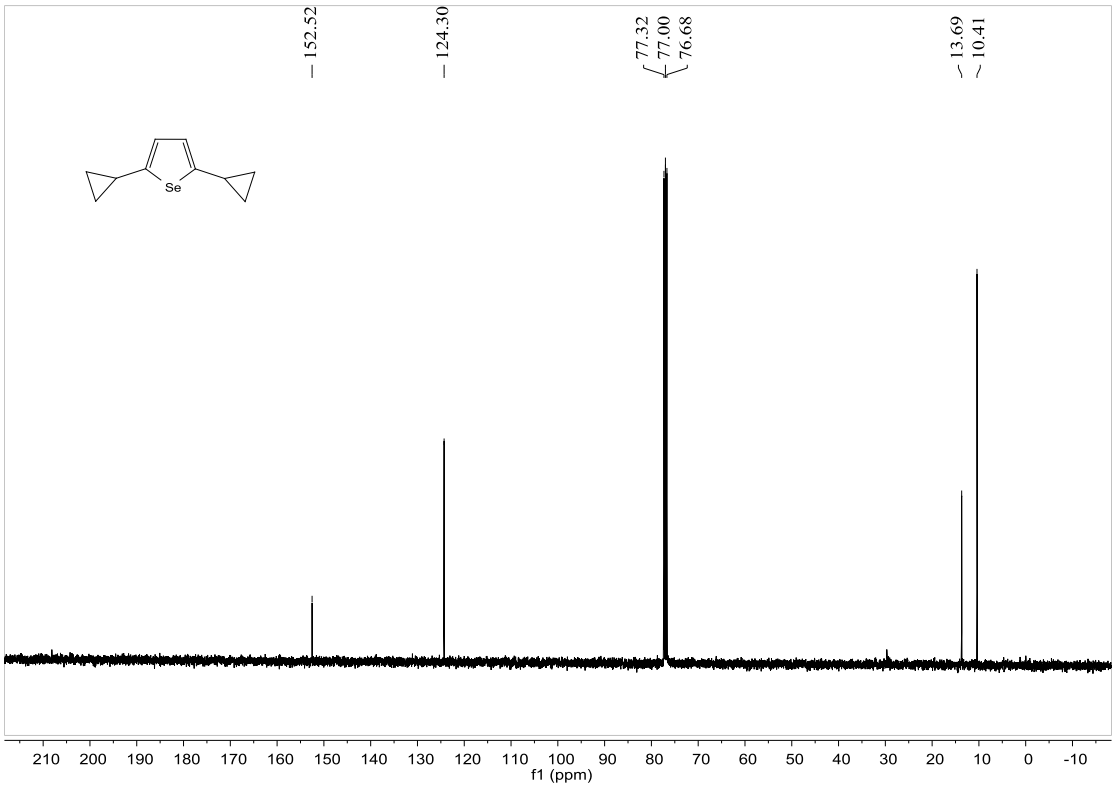
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum for 3v



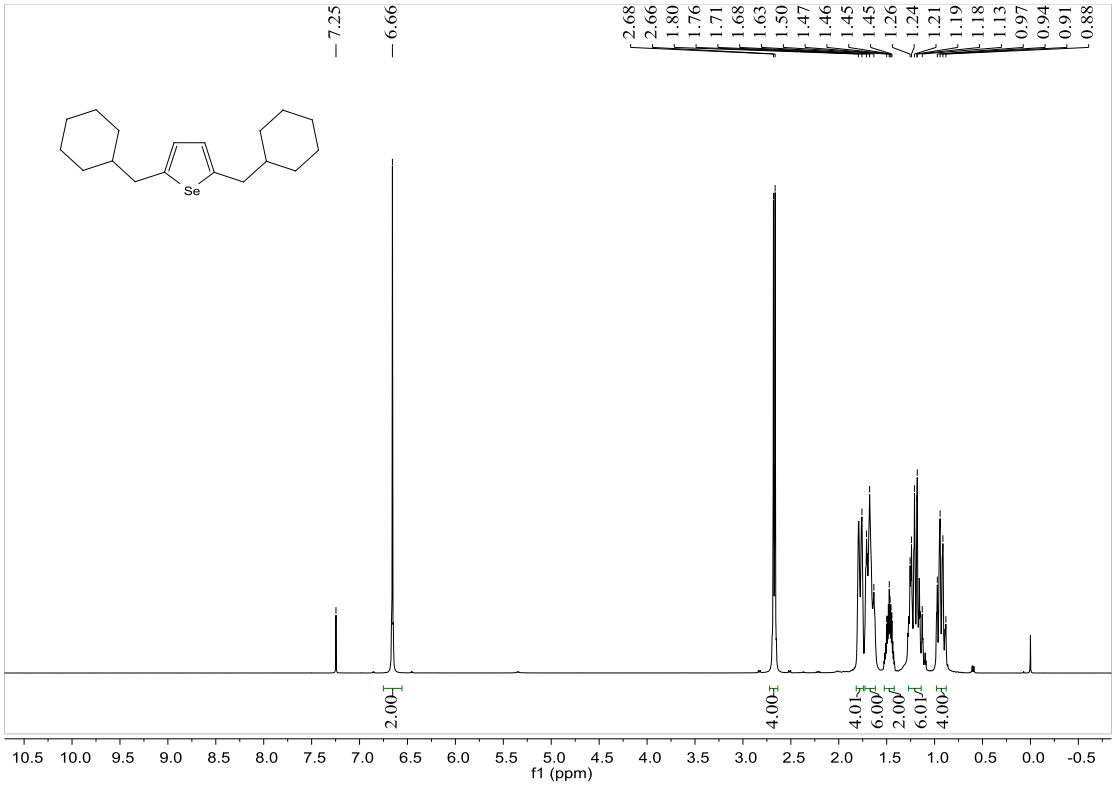
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum for 3w



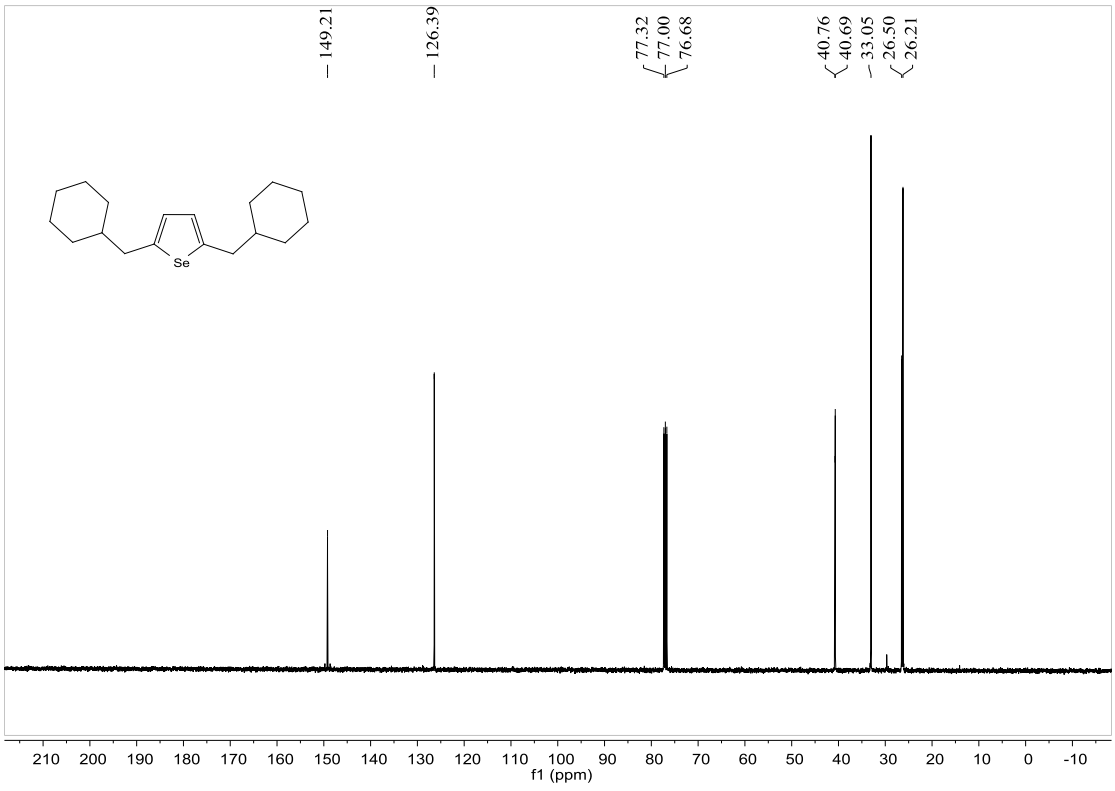
^{13}C-NMR (100 MHz, $CDCl_3$) spectrum for 3w



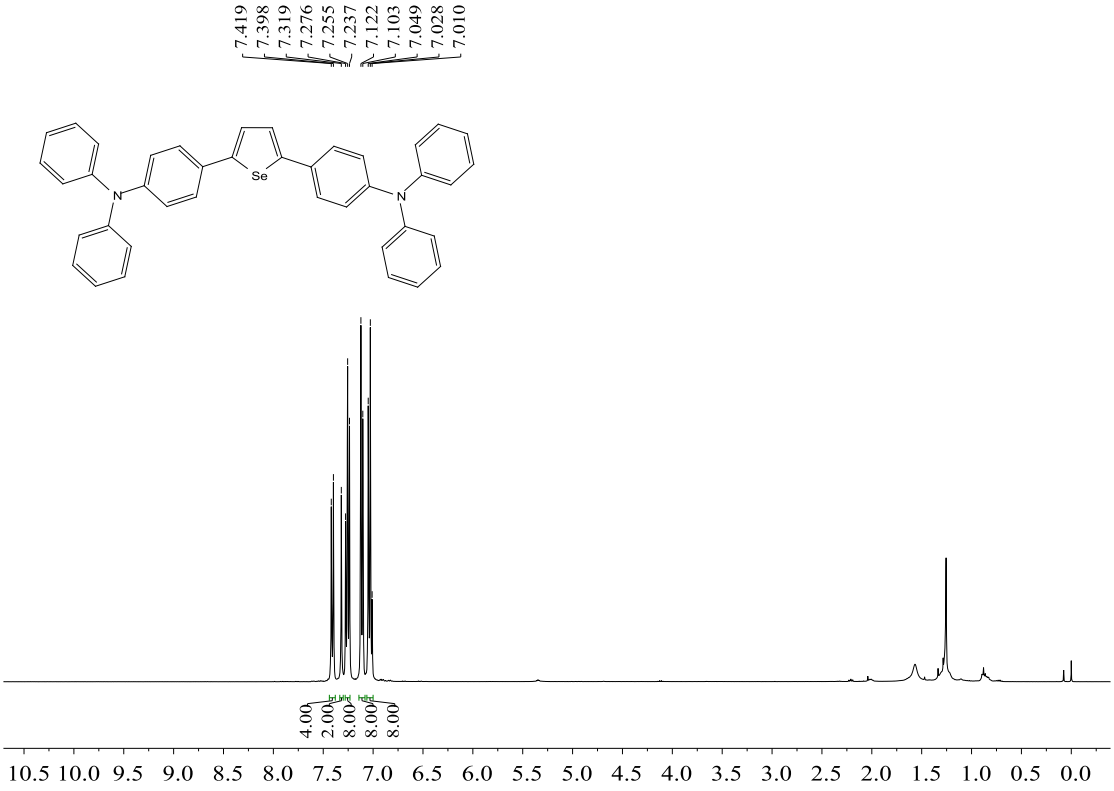
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum for 3x



^{13}C-NMR (100 MHz, $CDCl_3$) spectrum for 3x



^{1}H-NMR (400 MHz, $CDCl_3$) spectrum for 4



^{13}C-NMR (100 MHz, $CDCl_3$) spectrum for 4