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**Supporting Information**

# Molybdenum (V)-mediated switching of the C($sp^2$)-Se bond of phenylselenyl-functionalized arenes or heterocycles under mild conditions

Ming Zhang,† Beifang Nian,† Zhibang Wu, Jianhua Guo, Zhuo Chen, Caifeng Yuan, Xuankun Huang, Yiwen Shen, Hongbin Zhang,* E Tang*

Key Laboratory of Medicinal Chemistry for Natural Resource, Ministry of Education, Yunnan Provincial Center for Research & Development of Natural Products, School of Chemical Science and Technology, Yunnan University, Kunming 650091, China.

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## 1. General information

Unless otherwise noted, all other reagents and starting materials were purchased from commercial source and used without further purification. Thin layer chromatography was carried out on $GF_{254}$ plates (0.25 mm layer thickness). Flash chromatography was performed with 200-300 mesh silica gels. Reactions were monitored by TLC and visualized by a dual short wave/long wave UV lamp. $^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra were recorded on Bruker Avance 400, 500, or 600 MHz spectrophotometers. Chemical shifts in $^{1}H$ NMR spectra were reported in parts per million (ppm) on the δ scale. Data for $^{1}H$ NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, br. s = broad singlet), coupling constant in Herts (Hz) and integration. Data for $^{13}C$ NMR spectra were reported in terms of chemical shift in ppm. ESI-MS was taken on Agilent 1100 HPLC-TOF spectrometer. GC-MS was taken on FINNIgAN TRACEDSQ spectrometer.

**Substrates (1a-36a, 1d-12d) were prepared according to literature procedures.[1-8]**

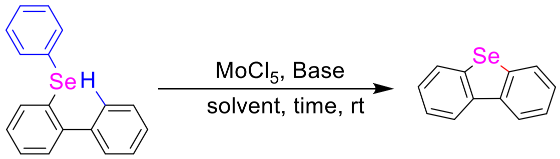
## 2. Optimization of the reaction conditions

### 2.1 Optimization of the reaction conditions for the synthesis of compounds c

We selected 2-phenylseleno-1,1'-biphenyl (**1a**) as a test substrate with $MoCl_5$ as an oxidant and trimethylamine (TEA) as a base for this dephenylization and ring-closing reaction. To our delight, the desired dibenzoselenophene compound **1c** was obtained at room temperature with a yield of 12% (Table 1, entry 1). The reaction conditions were then optimized, and the results were summarized in Table 1. The yield of **1c** increased with the increase in the amount of $MoCl_5$ (entries 2-4). 47% was the best yield when 5.0 equiv. of $MoCl_5$ was used (entry 3). Solvent and base screening revealed that the reaction can proceed smoothly in the presence of ethylenediamine (EDA), NaH, and EtONa to obtain **1c** in 32-76% yields (entries 5-7), and the desired product was obtained when the reaction was carried out in DMSO, DMF, THF, EtOH,

$CH_3CN$, toluene, ethyl acetate (EA), and diethyl ether (9-42%, entries 8-15), although the reaction yields were unsatisfactory. A significant improvement in the yield was observed when DCM and *t*-BuOK were employed as the reaction solvent and base, respectively, and **1c** was obtained in 92% yield (entry 16). The low solubility of $MoCl_5$ and *t*-BuOK in petroleum ether (PE) leads to a trace amount of the product (entry 17). The yield decreased significantly when the reaction time was shortened from 6 h to 3 h or less amount of *t*-BuOK was used (entries 18 and 22); the yield remained unchanged when the reaction time was extended or more base was employed (entries 19 and 24). Product **1c** was not observed in the absence of $MoCl_5$ or the base (entries 20 and 21). Only a 26% yield of **1c** was obtained when a mixture of 2.5 equiv. of $MoCl_5$ and 2.5 equiv. of $TiCl_4$ was used (entry 22).

**Table 1** Optimization of the dephenylization and ring-closing reaction condition of 2-phenylseleno-1,1'-biphenyl (**1a**)



**1a** **1c**

| Entry | $MoCl_5$ (equiv) | Solvent$^h$ | Base | Yield of **1c**$^b$ (%) |
|---|---|---|---|---|
| 1 | 1.0 | DCM | TEA | 12 |
| 2 | 2.0 | DCM | TEA | 29 |
| 3 | 5.0 | DCM | TEA | 47 |
| 4 | 7.5 | DCM | TEA | 46 |
| 5 | 5.0 | DCM | EDA | 32 |
| 6 | 5.0 | DCM | NaH | 67 |
| 7 | 5.0 | DCM | EtONa | 76 |
| 8 | 5.0 | DMSO | *t*-BuOK | 30 |
| 9 | 5.0 | DMF | *t*-BuOK | 28 |
| 10 | 5.0 | THF | *t*-BuOK | 22 |
| 11 | 5.0 | EtOH | *t*-BuOK | 9 |
| 12 | 5.0 | $CH_3CN$ | *t*-BuOK | 15 |
| 13 | 5.0 | Toluene | *t*-BuOK | 42 |
| 14 | 5.0 | EA | *t*-BuOK | 10 |
| 15 | 5.0 | $Et_2O$ | *t*-BuOK | 10 |

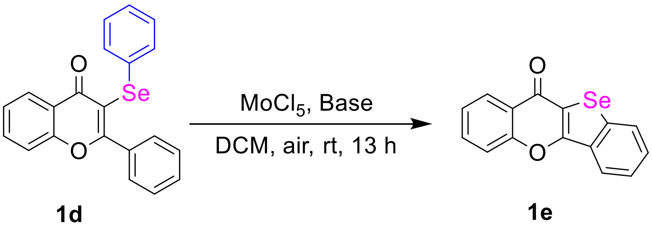
|  |  |  |  |  |
|---|---|---|---|---|
| 16 | 5.0 | DCM | *t*-BuOK | 92 |
| 17 | 5.0 | PE | *t*-BuOK | trace |
| 18[c] | 5.0 | DCM | *t*-BuOK | 67 |
| 19[d] | 5.0 | DCM | *t*-BuOK | 92 |
| 20 | – | DCM | *t*-BuOK | nr |
| 21 | 5.0 | DCM | – | 0 |
| 22[e] | 2.5 | DCM | *t*-BuOK | 26 |
| 23[f] | 5.0 | DCM | *t*-BuOK | 69 |
| 24[g] | 5.0 | DCM | *t*-BuOK | 92 |

[a]Reaction conditions: **1a** (0.2 mmol), $MoCl_5$, base (5.0 equiv.), solvent (3 mL) in the air at room temperature for 6 h. [b]Isolated yield. [c,d]The reaction was performed for 3.0 h[c] and 7.5 h[d] respectively. [e]2.5 Equiv. of $MoCl_5$ and 2.5 equiv. of $TiCl_4$ were added.[f,g] 4.0[f] And 6.0[g] equiv. of *t*-BuOK were added. [h]EA, PE, TEA, and EDA are ethyl acetate, petroleum ether, triethylamine, and ethylenediamine, respectively.

## 2.2 Optimization of the reaction conditions for the synthesis of compounds e

We selected 3-phenylselanyl flavone (**1d**) as a test substrate with $MoCl_5$ (5.0 equiv.) and *t*-BuOK (5.0 equiv.) for this dephenylization and ring-closing reaction. The desired product 5a,10a-dihydro-11*H*-benzo[4,5]selenopheno[3,2-*b*]chromen-11-one (**1e**) was obtained at room temperature with a yield of 20% (Table 2, entry 1). A better yield of 57% was obtained when the amounts of $MoCl_5$ and *t*-BuOK were increased to 10.0 equiv. Then, we screened the following bases, including NaH, EtONa, EDA, and TEA, to obtain **1e** in 32-71% yields (Table 2, entries 3-6). TEA is a better base than *t*-BuOK for the reaction of **1d** (Table 2, entry 3). Neither increasing nor decreasing the amounts of TEA and $MoCl_5$ resulted in a higher yield of **1e** (entries 7-11).

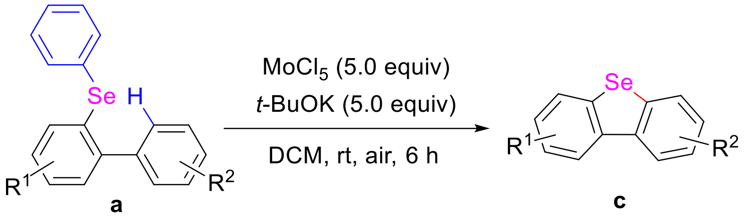
**Table 2** Optimization of the dephenylization and ring-closing reaction conditions of 3-phenylselanyl flavone (**1d**)



| Entry | $MoCl_5$ (equiv) | Base | Yield of 1**e**[b] (%) |
|---|---|---|---|
| 1 | 5.0 | *t*-BuOK | 20 |
| 2 | 10 | t-BuOK | 57 |
| 3 | 10 | TEA | 71 |
| 4 | 10 | NaH | 32 |
| 5 | 10 | EtONa | 45 |
| 6 | 10 | EDA | 62 |
| 7 | 1.0 | TEA | 6 |
| 8 | 2.0 | TEA | 18 |
| 9 | 5.0 | TEA | 48 |
| 10 | 7.5 | TEA | 65 |
| 11 | 12 | TEA | 70 |

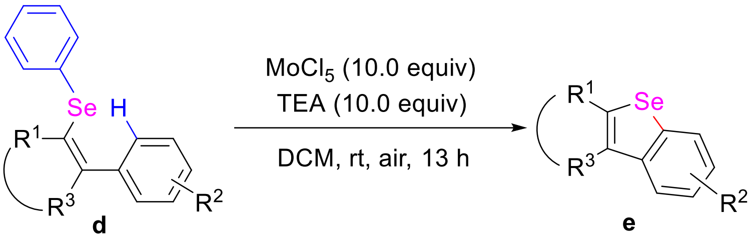
[a]Reaction conditions: **1d** (0.2 mmol), DCM (3 mL) in the air at room temperature for 13 h, using the same equivalent of base and $MoCl_5$. [b]Isolated yield.

## 3. Synthesis of compounds c



To a reaction tube containing **a** (0.2 mmol) of DCM (3.0 mL) was added $MoCl_5$ (1.0 mmol, 27.3 mg). Stir at room temperature for 5 hours. Monitor the progress of the reaction by TLC. After the reaction is complete, add *t*-BuOK (1.0 mmol, 112 mg) and continue stirring for 1 h. Filter the reaction solution through a short pad of silica gel quickly. Dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 500/1, V/V) to afford compounds **c**.

## 4. Synthesis of compounds e

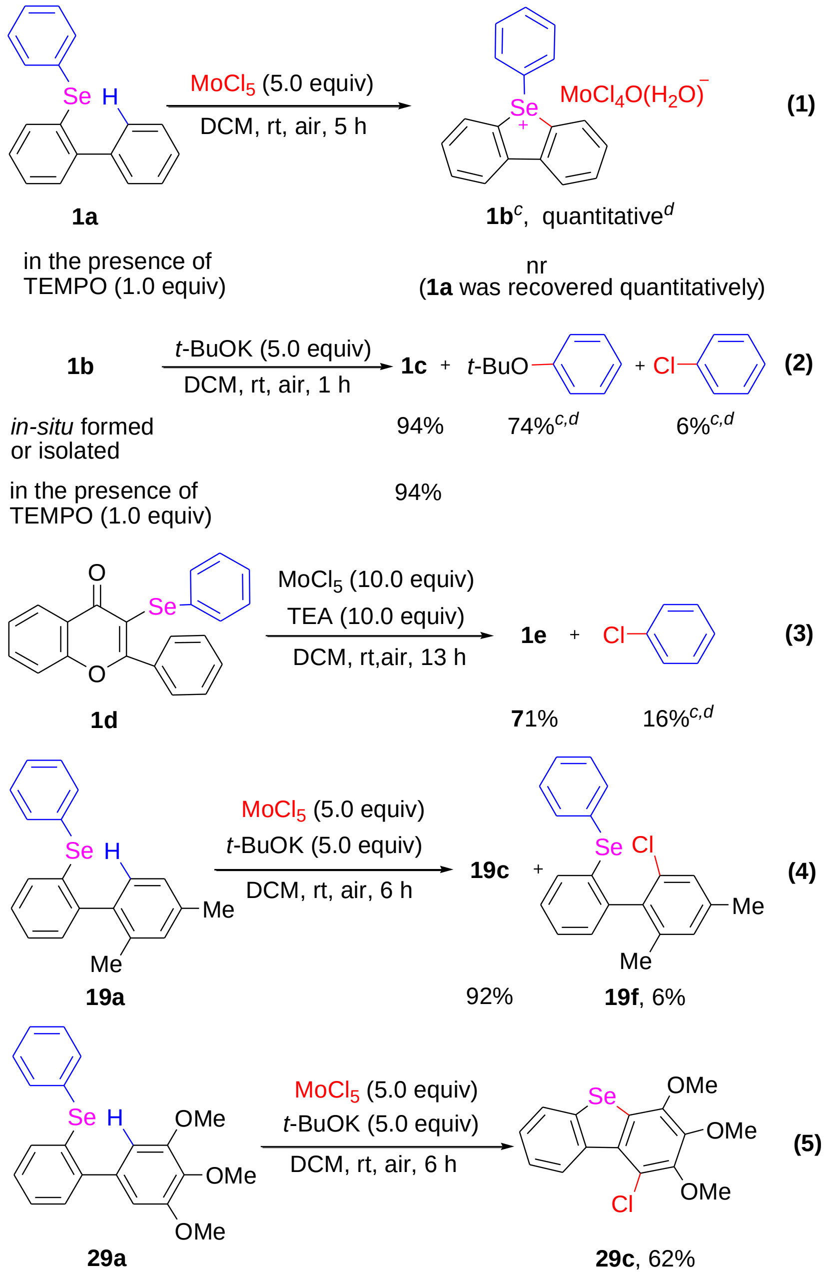


To a reaction tube containing **d** (0.2 mmol) in DCM (3.0 mL) was added $MoCl_5$ (2.0 mmol, 54.6 mg). Stir at room temperature for 5 hours. Monitor the progress of the reaction by TLC. After the reaction is complete, add TEA (2.0 mmol, 0.28 mL) and continue stirring for 1 h. Quickly filter the reaction solution through a short pad of silica gel. Dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1, V/V) to afford the compound **e**.

## 5. Control experiments

In order to clarify the mechanism of Mo-mediated dephenylization and intramolecular oxidative C($sp^2$)-Se coupling reaction of phenyl selenides, we performed some control experiments (Scheme 1). In the absence of the base, substrate **1a** reacted with 5.0 equiv. of $MoCl_5$ at room temperature in the air for 5 h. A selenonium cation (**1b**) was observed by HRMS and isolated quantitatively by HPLC, and the major product **1b** was the $[MoOCl_4]^-$ anion with an associated selenonium cation [Scheme 1, (1)], whose structure was confirmed as $[PhSeAr_2]^+[MoOCl_4(H_2O)]^-$ by the X-ray crystallographic analysis of pale green crystals grown from **1b** (Manuscript, Scheme 4), and no doubt the result of ingress of adventitious water during crystallization. The water O is trans to Mo=O. A similar structure of this anion has been reported previously.[14] If **1b** was treated with 5 equiv. of *t*-BuOK, product **1c** would yield a 94% yield. Phenyl *tert*-butyl ether and chlorobenzene, as key by-products, were observed by HRMS analysis and isolated by HPLC in 74% and 6% yields, respectively [Scheme 1, (2)]. Chlorobenzene was also obtained by HPLC with a yield of 16% in the reaction of **1d** [Scheme 1, (3)]. The three experiments indicated that the product-forming step of this reaction lies in a Mo-mediated oxidative coupling of selenide and a subsequent SN

**Scheme 1.** Control experiments[a,b]



[a]Reaction conditions: **a** (0.2 mmol), $MoCl_5$ (5.0 equiv.), *t*-BuOK (5.0 equiv.), DCM (3 mL), and at room temperature. [b]Isolated yield. [c]Detected by HRMS [d] Isolated by HPLC [acetonitrile: $H_2O$ (vol./vol) = 90 : 10, 1.5 mL/min, monitoring at 254 nm by UV spectroscopy].

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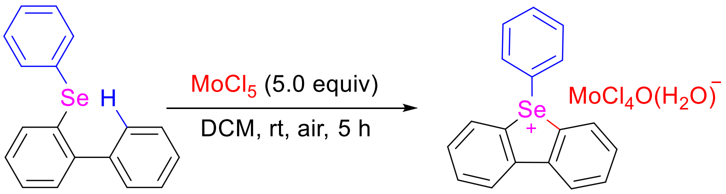
substitution reaction. This process can also be verified from the reaction in which the by-product **19f** was obtained with a yield of 6%. This is the result of a chlorine anion attacking intermediate **19b** as a nucleophile to lead to the cleavage of the C($sp^2$)-Se bond [Scheme 1, (4)]. When using a substrate bearing multiple strong electron-donating groups on the benzene ring, the chloro-functionalized dibenzo[b,d]selenonene **29c** was obtained in 62% yield by two attacks of $Cl^-$ ions to the selenonium intermediate [Scheme 1, (5)]. Furthermore, 1.0 equiv. of 2,2,6,6-tetramethylpipe-ridinooxy (TEMPO) shut down the reaction of **1a** but not of **1b**, implying that only the formation of **1b** from **1a** proceeds *via* the radical pathway [Scheme 1, (1) and (2)].

## 5.1 Reaction of 1a with $MoCl_5$ [Scheme 1, (1)]

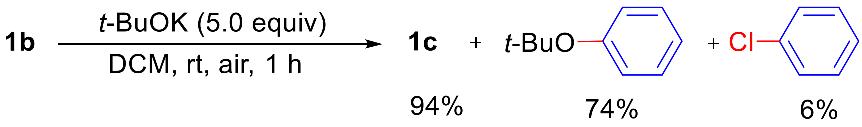


**1a**

**1b**, quantitative

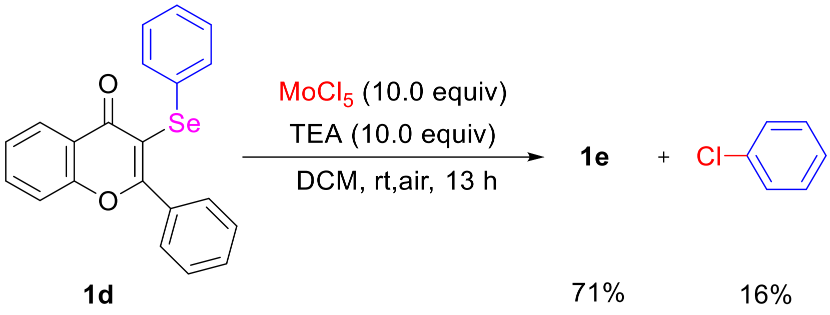
To a reaction tube containing **1a** (0.2 mmol, 61.9 mg) in DCM (3.0 mL) was added $MoCl_5$ (1.0 mmol, 27.3 mg). Stir at room temperature for 5 hours. Monitor the progress of the reaction by TLC. After substrate **1a** is completely transformed, filter the mixture. Compound **1b** was obtained quantitatively, and it can be further purified by recrystallization of petroleum ether and dichloromethane.

## 5.2 Reaction of 1b with *t*-BuOK [Scheme 1, (2)]



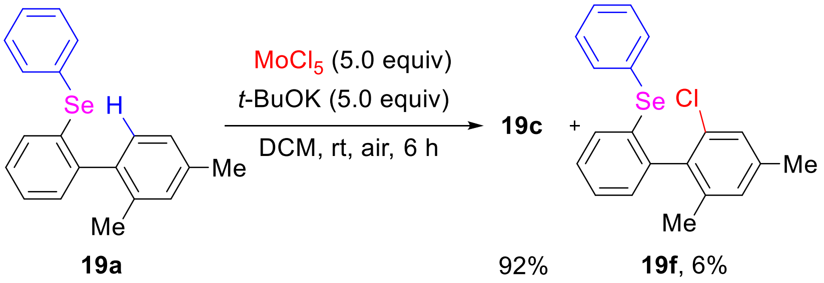
Dissolve **1b** (1.0 mmol, 580.0 mg in DCM (5.0 mL), add *t*-BuOK (5.0 mmol, 560 mg) and stirring at room temperature for 1 h. Filter the reaction solution through a short pad of silica gel quickly. Dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The mixture was purified on an Agilent HPLC 1260 system using acetonitrile: $H_2O$ (90:10 vol./vol.) as mobile phase and flow rate of 1.5 mL/min with monitoring at 254 nm to give chlorobenzene and 1,1-dimethylethoxybenzene in 6% and 74% yields, respectively.

### 5.3 Reaction of 1d with $MoCl_5$ [Scheme 1, (3)]



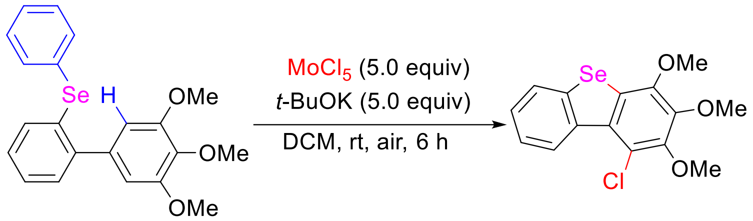
To a reaction tube containing **1d** (0.5 mmol, 188.6 mg) in DCM (3.0 mL) was added $MoCl_5$ (5.0 mmol, 54.6 mg). Stir at room temperature for 5 h. Monitor the progress of the reaction by TLC. After the reaction is complete, add TEA (5.0 mmol, 0.28 mL) and continue stirring for 1 h. Filter the reaction solution through a short pad of silica gel quickly. Dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The mixture was purified on an Agilent HPLC 1260 system using acetonitrile: $H_2O$ (90:10 vol./vol.) as mobile phase and flow rate of 1.5 mL/min with monitoring at 254 nm to give chlorobenzene in 16% yield.

### 5.4 Reaction of 19a with $MoCl_5$ [Scheme 1, (4)]



To a reaction tube containing **19a** (0.2 mmol, 67.5 mg) in DCM (3.0 mL) was added $MoCl_5$ (1.0 mmol, 27.3 mg). Stir at room temperature for 5 h. Monitor the progress of the reaction by TLC. After the reaction is complete, add *t*-BuOK (1.0 mmol, 112 mg) and continue stirring for 1 h. Filter the reaction solution through a short pad of silica gel quickly. Dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 600/1, V/V) to afford compound **19c** and **19f** in 92% and 6% yields, respectively.

### 5.5 Reaction of 29a with $MoCl_5$ [Scheme 1, (5)]



**29a** **29c**, 62%

To a reaction tube containing **29a** (0.2 mmol, 79.9 mg) in DCM (3.0 mL) was added $MoCl_5$ (1.0 mmol, 27.3 mg). Stir at room temperature for 5 h. Monitor the progress of the reaction by TLC. After the reaction is complete, add *t*-BuOK (1.0 mmol, 112 mg) and continue stirring for 1 h. Filter the reaction solution through a short pad of silica gel quickly. Dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 300/1, V/V) to afford compound **29c** in 62% yield.

### 5.6 Reaction of 1a with $MoCl_5$ and TEMPO [Scheme 1, (6)]

$$\mathbf{1a} \xrightarrow[\substack{\text{TEMPO (1.0 equiv)} \\ \text{DCM, rt, air, 5 h}}]{\text{MoCl}_5\text{ (5.0 equiv)}} \text{NR}$$

To a reaction tube containing **1a** (0.2 mmol, 61.9 mg) in DCM (3.0 mL) was added $MoCl_5$ (1.0 mmol, 27.3 mg) and TEMPO (0.2 mmol, 31.3 mg). Stir at room temperature for 5 h. Monitor the progress of the reaction by TLC. The substrate **1a** has not been consumed, and no new products have appeared. Quickly filter the reaction solution through a short pad of silica gel. Dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 500/1, V/V) to afford **1a** quantitatively.

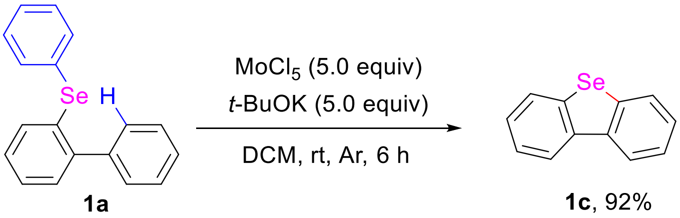
### 5.7 Reaction of 1b with $MoCl_5$ and TEMPO [Scheme 1, (7)]

$$\mathbf{1b} \xrightarrow[\substack{\text{TEMPO (1.0 equiv)} \\ \text{DCM, rt, air, 1 h}}]{t\text{-BuOK (5.0 equiv)}} \underset{94\%}{\mathbf{1c}}$$

Dissolve **1b** (0.2 mmol, 116.0 mg) in DCM (2.0 mL), add TEMPO (0.2 mmol, 31.3 mg) and *t*-BuOK (1.0 mmol, 112 mg) and stirring at room temperature for 1 h.

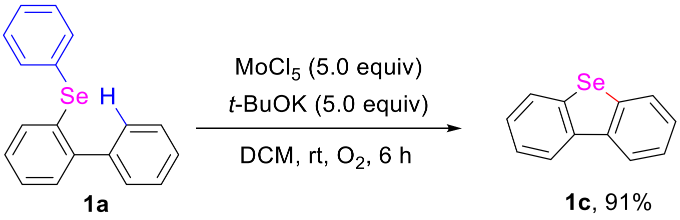
Monitor the progress of the reaction by TLC. After the reaction is complete, quickly filter the reaction solution through a short pad of silica gel. Dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 500/1, V/V) to afford compound **1c** in 94% yield.

### 5.8 Reaction of 1a under an argon atmosphere



**1a** (0.2 mmol, 61.9 mg) and $MoCl_5$ (1.0 mmol, 27.3 mg) were added to a two-necked flask under an argon atmosphere. Then DCM (3 mL) was injected into the bottle. Stir at room temperature for 5 h. Monitor the progress of the reaction by TLC. After the reaction is complete, add dissolved *t*-BuOK (1.0 mmol, 112 mg) and continue stirring for 1 h. Quickly filter the reaction solution through a short pad of silica gel. Dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 500/1, V/V) to afford compound **1c**.

### 5.8 Reaction of 1a under an oxygen atmosphere



**1a** (0.2 mmol, 61.9 mg) and $MoCl_5$ (1.0 mmol, 27.3 mg) were added to a two-necked flask under an oxygen atmosphere. Then DCM (3 mL) was injected into the bottle. Stir at room temperature for 5 h. Monitor the progress of the reaction by TLC. After the reaction is complete, add dissolved *t*-BuOK (1.0 mmol, 112 mg) and continue stirring for 1 h. Quickly filter the reaction solution through a short pad of silica gel.

Dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 500/1, V/V) to afford compound **1c**.

## 6. Mechanistic investigations

### 6.1 Mass spectrometry for intermediate 1b

To a reaction tube containing **1a** (0.2 mmol, 61.9 mg) in DCM (3.0 mL) was added $MoCl_5$ (1.0 mmol, 27.3 mg). Stir at room temperature for 5 h. Monitor the progress of the reaction by TLC. After the reaction is complete, product **1b** can be detected by ESI. HR-ESI-MS (m/z): calcd. for $C_{18}H_{13}Se^+$ $[M+H]^+$ 309.0177, found 309.0171.

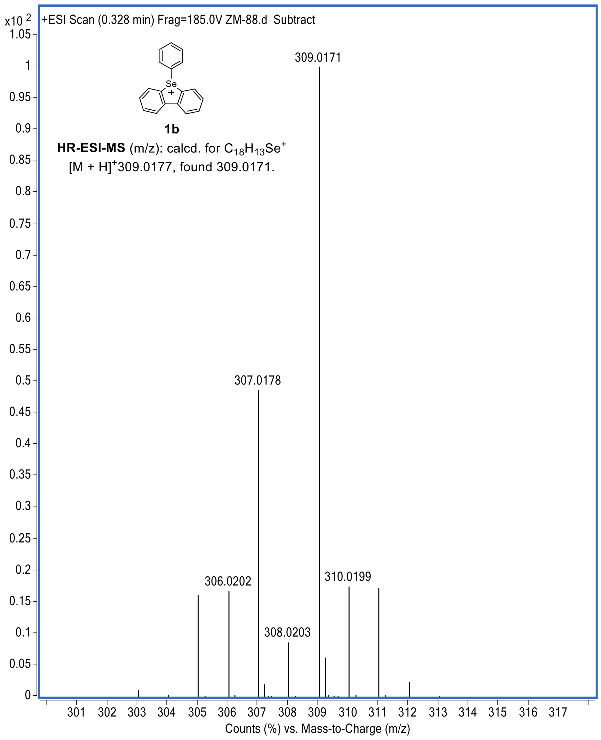
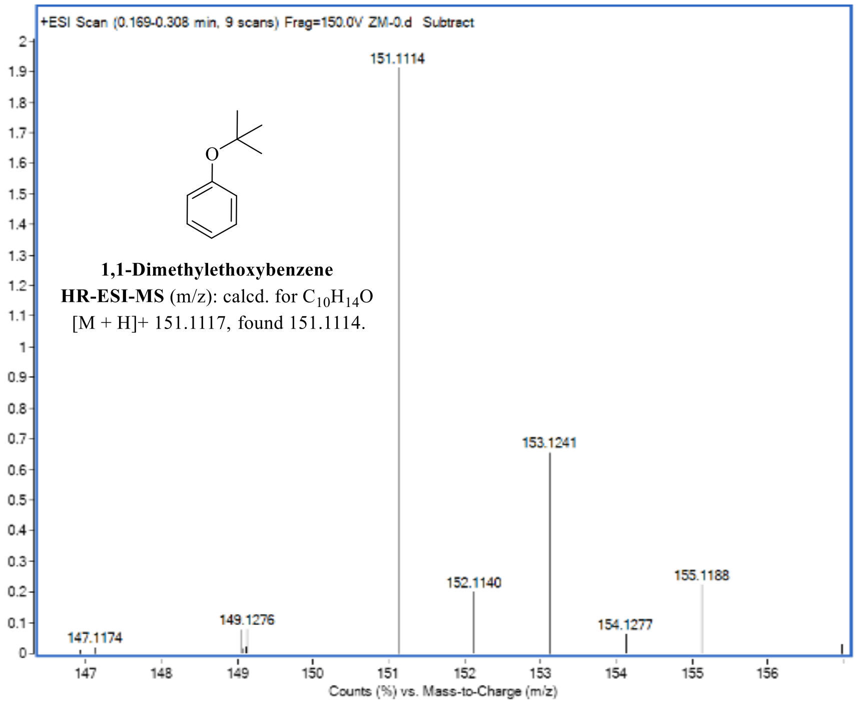


**Figure S1.** Mass spectrum of **1b**.

### 6.2 Mass spectrometry for 1,1-dimethylethoxybenzene.

To a reaction tube containing **1a** (0.2 mmol) in DCM (3.0 mL) was added $MoCl_5$ (1.0 mmol, 27.3 mg). Stir at room temperature for 5 h. Monitor the progress of the reaction by TLC. After the reaction is complete, add *t*-BuOK (1.0 mmol, 112 mg) and continue stirring for 1 h. After the reaction is complete, quickly filter the reaction solution through a short pad of silica gel. Dried over $MgSO_4$, filtered, and concentrated under reduced pressure. 1,1-Dimethylethoxybenzene can be detected by ESI. HR-ESI-MS (m/z): calcd. for $C_{10}H_{14}O$ $[M+H]^+$ 151.1117, found 151.1114.



**1,1-Dimethylethoxybenzene**
**HR-ESI-MS** (m/z): calcd. for $C_{10}H_{14}O$
[M + H]+ 151.1117, found 151.1114.

**Figure S2.** Mass spectrum of 1,1-dimethylethoxybenzene.

### 6.3 Mass spectrometry for the chlorobenzene yielded from 1b

To a reaction tube containing **1b** (0.2 mmol, 116 mg) in DCM (2.0 mL) was added *t*-BuOK (1.0 mmol, 112 mg) and stirring for 1 h. After the reaction is complete, quickly filter the reaction solution through a short pad of silica gel. Dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Chlorobenzene can be detected by EI. GC-MS (EI): calcd. for $C_6H_5Cl$ $[M^+]$ 112; found 112.

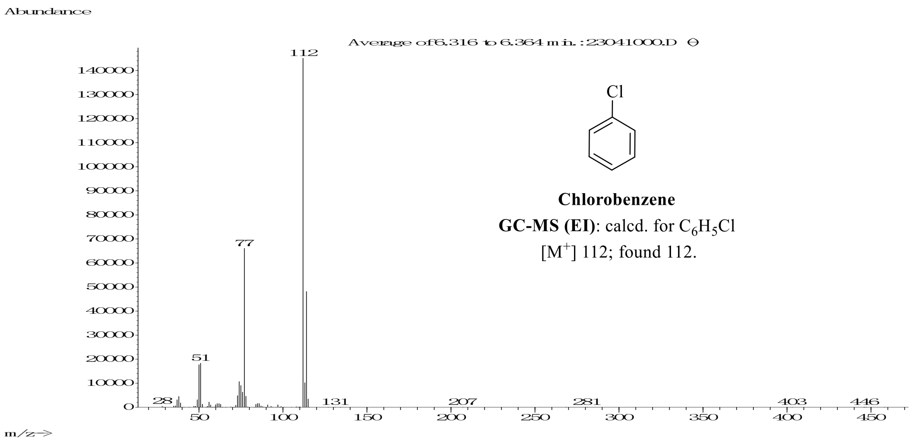


**Figure S3.** Mass spectrum of chlorobenzene yielded from **1b**

## 6.4 Mass spectrometry for the chlorobenzene yielded from 1d

To a reaction tube containing **1d** (0.2 mmol, 75.4 mg) in DCM (3.0 mL) was added $MoCl_5$ (2.0 mmol, 54.6 mg). Stir at room temperature for 5 h. Monitor the progress of the reaction by TLC. After the reaction is complete, add TEA (2.0 mmol, 0.28 mL) and continue stirring for 1 h. Quickly filter the reaction solution through a short pad of silica gel. Dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Chlorobenzene can be detected by EI. GC-MS (EI): calcd. for $C_6H_5Cl$ [$M^+$] 112; found 112.

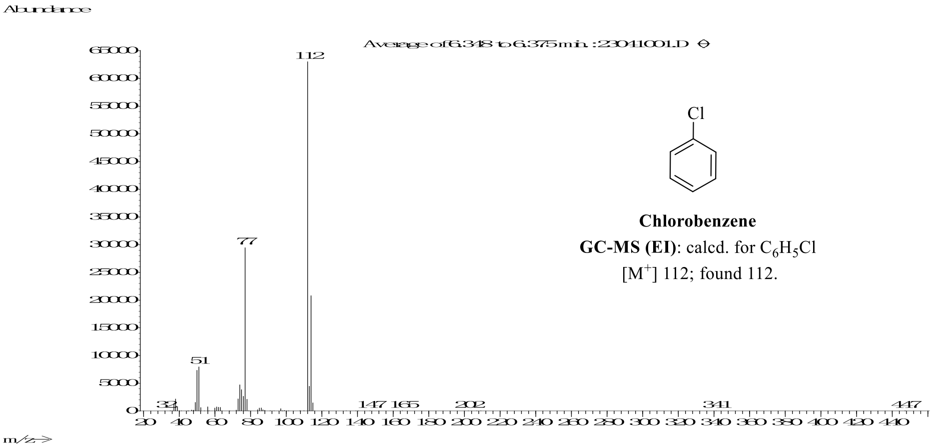
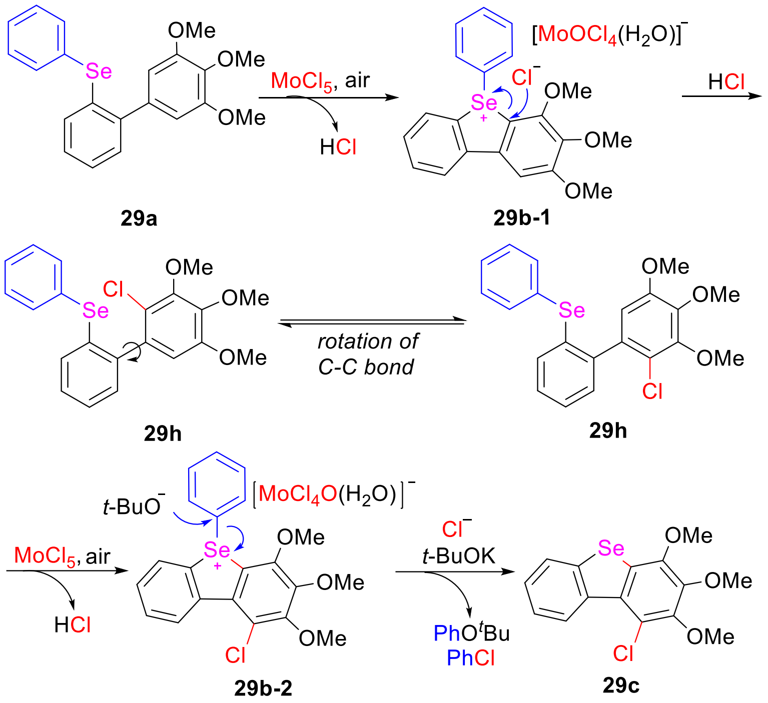


**Figure S4.** Mass spectrum of chlorobenzene from yielded from **1d**

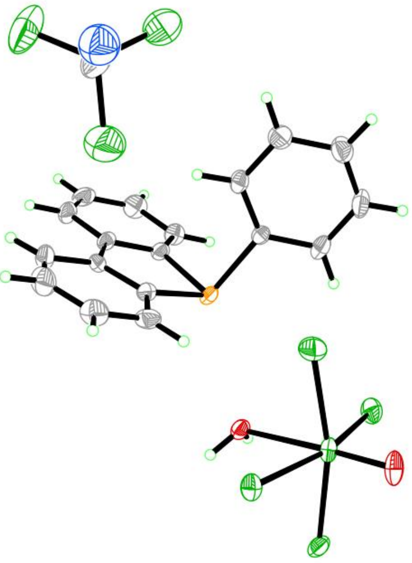
## 6.5 Proposed mechanism for the formation of compound 29c.



Compound **29a** was initially catalyzed by $MoCl_5$ to form intermediate **29b-1**. **29b-1** was attacked by the chloride anion to form compound **29h**. After the rotation of the C-C bond, the conformer formed by **29h** favors the formation of intermediate **29b-2**. The addition of *t*-BuOK leads to the selective cleavage of C($sp^2$)-Se bond, compound **29c** was finally formed *via* dephenylation reaction.

## 7. X-ray structure of compounds 1b and 8e.

### 7.1 X-ray structure of compound 1b.



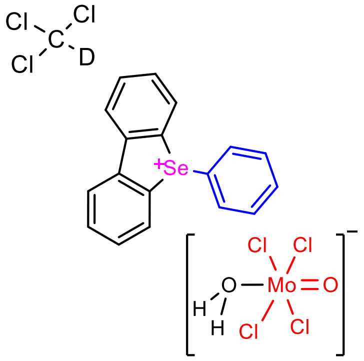


**Table 1.** Crystal Data and Structure Refinement for **1b**.

| | |
|---|---|
| Identification code | **1b** |
| Empirical formula | $C_{19}H_{15}DCl_7MoO_2Se$ |
| Formula weight | 700.37 |
| Temperature | 150.00 K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Triclinic, P-1 |
| Unit cell dimensions | a = 8.2075(12) Å α = 103.403(5)°.<br>b = 12.1341(16) Å β = 90.813(6)°.<br>c = 13.2766(19) Å γ = 98.443(5)°. |
| Volume | 1270.7(3) Å$^3$ |
| Z, Calculated density | 2, 1.831 Mg/m$^3$ |
| Absorption coefficient | 2.699 mm$^{-1}$ |
| F(000) | 682 |
| Crystal size | 0.18 × 0.15 × 0.1 mm |
| Theta range for data collection | 2.059 to 25.000°. |
| Limiting indices | -9<=h<=9, -14<=k<=14, -15<=l<=15 |
| Reflections collected / unique | 15684 / 4475 [R(int) = 0.0607] |
| Completeness to theta = 25.000 | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7457 and 0.5719 |
| Refinement method | Full-matrix least-squares on F$^2$ |

| | |
|---|---|
| Data/restraints/parameters | 4475 / 48 / 272 |
| Goodness-of-fit on F$^2$ | 0.984 |
| Final R indices [I>2α(I)] | R1 = 0.0572, wR2 = 0.1433 |
| R indices (all data) | R1 = 0.0792, wR2 = 0.1569 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 1.715 and -1.560 e. Å$^{-3}$ |

**Table 2.** Atomic coordinates ( × 10$^4$) and equivalent isotropic displacement parameters (Å$^2$ × 10$^3$) for **1b**.

U(eq) is defined as one-third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Mo(1) | 8312(1) | 11590(1) | 1528(1) | 38(1) |
| Cl(1) | 7599(3) | 10891(2) | 2945(2) | 60(1) |
| O(2) | 7856(6) | 9633(4) | 672(4) | 35(1) |
| Cl(3) | 5483(2) | 11387(2) | 1030(2) | 49(1) |
| Cl(4) | 8957(2) | 11768(2) | -198(2) | 45(1) |
| Cl(5) | 11013(2) | 11180(2) | 1737(1) | 42(1) |
| O(1) | 8657(7) | 12974(4) | 2087(5) | 58(2) |
| Se(1) | 5099(1) | 7730(1) | 1454(1) | 32(1) |
| C(1) | 4197(8) | 8414(5) | 2738(5) | 30(1) |
| C(2) | 4165(8) | 7914(6) | 3569(6) | 40(2) |
| C(3) | 3469(10) | 8437(7) | 4467(6) | 51(2) |
| C(4) | 2863(11) | 9465(7) | 4508(6) | 55(2) |
| C(5) | 2906(11) | 9932(7) | 3676(7) | 56(2) |
| C(6) | 3573(9) | 9423(6) | 2761(6) | 45(2) |
| C(7) | 4021(8) | 6165(5) | 1223(5) | 34(2) |
| C(8) | 2444(9) | 5769(6) | 840(6) | 42(2) |
| C(9) | 1892(11) | 4592(7) | 696(7) | 54(2) |
| C(10) | 2936(11) | 3885(7) | 924(6) | 52(2) |
| C(11) | 4516(11) | 4298(6) | 1311(6) | 46(2) |
| C(12) | 5094(9) | 5465(5) | 1477(5) | 34(2) |
| C(13) | 6729(9) | 6065(6) | 1896(5) | 36(2) |
| C(14) | 8016(10) | 5580(7) | 2239(6) | 51(2) |
| C(15) | 9462(10) | 6292(9) | 2640(7) | 62(2) |
| C(16) | 9703(9) | 7458(8) | 2702(7) | 56(2) |
| C(17) | 8437(9) | 7947(7) | 2346(6) | 45(2) |
| C(18) | 6976(8) | 7237(6) | 1976(5) | 34(2) |
| Cl(6) | 8102(7) | 6955(4) | 5106(3) | 142(2) |
| Cl(7) | 5389(6) | 6834(4) | 6342(3) | 126(1) |
| Cl(8) | 7274(6) | 5011(3) | 6027(3) | 137(2) |
| C(19) | 7343(13) | 6460(7) | 6161(7) | 96(4) |
| D(19) | 8065 | 6871 | 6788 | 116 |

**Table 3.** Bond lengths [Å] and angles [°] for **1b**.

| | |
|---|---|
| Mo(1)-Cl(1) | 2.286(2) |
| Mo(1)-O(2) | 2.355(4) |
| Mo(1)-Cl(3) | 2.3673(19) |
| Mo(1)-Cl(4) | 2.4097(19) |
| Mo(1)-Cl(5) | 2.3680(18) |
| Mo(1)-O(1) | 1.651(5) |
| O(2)-H(2A) | 0.8926 |
| O(2)-H(2B) | 0.8928 |
| Se(1)-C(1) | 1.924(7) |
| Se(1)-C(7) | 1.927(6) |
| Se(1)-C(18) | 1.909(6) |
| C(1)-C(2) | 1.376(9) |
| C(1)-C(6) | 1.390(9) |
| C(2)-H(2) | 0.9500 |
| C(2)-C(3) | 1.387(11) |
| C(3)-H(3) | 0.9500 |
| C(3)-C(4) | 1.399(11) |
| C(4)-H(4) | 0.9500 |
| C(4)-C(5) | 1.352(12) |
| C(5)-H(5) | 0.9500 |
| C(5)-C(6) | 1.389(12) |
| C(6)-H(6) | 0.9500 |
| C(7)-C(8) | 1.360(10) |
| C(7)-C(12) | 1.399(9) |
| C(8)-H(8) | 0.9500 |
| C(8)-C(9) | 1.400(11) |
| C(9)-H(9) | 0.9500 |
| C(9)-C(10) | 1.375(12) |
| C(10)-H(10) | 0.9500 |
| C(10)-C(11) | 1.367(12) |
| C(11)-H(11) | 0.9500 |
| C(11)-C(12) | 1.390(10) |
| C(12)-C(13) | 1.464(10) |
| C(13)-C(14) | 1.401(10) |
| C(13)-C(18) | 1.385(9) |
| C(14)-H(14) | 0.9500 |
| C(14)-C(15) | 1.380(13) |
| C(15)-H(15) | 0.9500 |
| C(15)-C(16) | 1.382(13) |
| C(16)-H(16) | 0.9500 |
| C(16)-C(17) | 1.398(11) |
| C(17)-H(17) | 0.9500 |
| C(17)-C(18) | 1.380(10) |
| Cl(6)-C(19) | 1.736(8) |

| | |
|---|---|
| Cl(7)-C(19) | 1.735(9) |
| Cl(8)-C(19) | 1.719(8) |
| C(19)-D(19) | 1.0000 |
| | |
| Cl(1)-Mo(1)-O(2) | 82.99(12) |
| Cl(1)-Mo(1)-Cl(3) | 89.52(8) |
| Cl(1)-Mo(1)-Cl(4) | 164.04(8) |
| Cl(1)-Mo(1)-Cl(5) | 89.00(8) |
| O(2)-Mo(1)-Cl(3) | 80.58(13) |
| O(2)-Mo(1)-Cl(4) | 81.06(12) |
| O(2)-Mo(1)-Cl(5) | 81.34(12) |
| Cl(3)-Mo(1)-Cl(4) | 88.41(7) |
| Cl(3)-Mo(1)-Cl(5) | 161.90(7) |
| Cl(5)-Mo(1)-Cl(4) | 88.07(7) |
| O(1)-Mo(1)-Cl(1) | 99.2(2) |
| O(1)-Mo(1)-O(2) | 177.8(3) |
| O(1)-Mo(1)-Cl(3) | 99.6(2) |
| O(1)-Mo(1)-Cl(4) | 96.8(2) |
| O(1)-Mo(1)-Cl(5) | 98.4(2) |
| Mo(1)-O(2)-H(2A) | 110.4 |
| Mo(1)-O(2)-H(2B) | 110.7 |
| H(2A)-O(2)-H(2B) | 103.3 |
| C(1)-Se(1)-C(7) | 101.1(3) |
| C(18)-Se(1)-C(1) | 100.0(3) |
| C(18)-Se(1)-C(7) | 87.0(3) |
| C(2)-C(1)-Se(1) | 121.3(5) |
| C(2)-C(1)-C(6) | 122.9(7) |
| C(6)-C(1)-Se(1) | 115.9(5) |
| C(1)-C(2)-H(2) | 120.7 |
| C(1)-C(2)-C(3) | 118.5(6) |
| C(3)-C(2)-H(2) | 120.7 |
| C(2)-C(3)-H(3) | 120.4 |
| C(2)-C(3)-C(4) | 119.2(7) |
| C(4)-C(3)-H(3) | 120.4 |
| C(3)-C(4)-H(4) | 119.6 |
| C(5)-C(4)-C(3) | 120.8(8) |
| C(5)-C(4)-H(4) | 119.6 |
| C(4)-C(5)-H(5) | 119.3 |
| C(4)-C(5)-C(6) | 121.4(7) |
| C(6)-C(5)-H(5) | 119.3 |
| C(1)-C(6)-H(6) | 121.5 |
| C(5)-C(6)-C(1) | 117.1(7) |
| C(5)-C(6)-H(6) | 121.5 |
| C(8)-C(7)-Se(1) | 125.5(5) |

| | |
|---|---|
| C(8)-C(7)-C(12) | 123.6(6) |
| C(12)-C(7)-Se(1) | 110.9(5) |
| C(7)-C(8)-H(8) | 121.4 |
| C(7)-C(8)-C(9) | 117.2(7) |
| C(9)-C(8)-H(8) | 121.4 |
| C(8)-C(9)-H(9) | 119.9 |
| C(10)-C(9)-C(8) | 120.2(8) |
| C(10)-C(9)-H(9) | 119.9 |
| C(9)-C(10)-H(10) | 119.1 |
| C(9)-C(10)-C(11) | 121.9(7) |
| C(11)-C(10)-H(10) | 119.1 |
| C(10)-C(11)-H(11) | 120.3 |
| C(10)-C(11)-C(12) | 119.4(7) |
| C(12)-C(11)-H(11) | 120.3 |
| C(7)-C(12)-C(13) | 114.9(6) |
| C(11)-C(12)-C(7) | 117.8(7) |
| C(11)-C(12)-C(13) | 127.3(6) |
| C(14)-C(13)-C(12) | 126.8(7) |
| C(18)-C(13)-C(12) | 115.1(6) |
| C(18)-C(13)-C(14) | 118.1(7) |
| C(13)-C(14)-H(14) | 120.8 |
| C(15)-C(14)-C(13) | 118.5(8) |
| C(15)-C(14)-H(14) | 120.8 |
| C(14)-C(15)-H(15) | 118.5 |
| C(14)-C(15)-C(16) | 122.9(7) |
| C(16)-C(15)-H(15) | 118.5 |
| C(15)-C(16)-H(16) | 120.5 |
| C(15)-C(16)-C(17) | 119.1(8) |
| C(17)-C(16)-H(16) | 120.5 |
| C(16)-C(17)-H(17) | 121.1 |
| C(18)-C(17)-C(16) | 117.7(7) |
| C(18)-C(17)-H(17) | 121.1 |
| C(13)-C(18)-Se(1) | 111.9(5) |
| C(17)-C(18)-Se(1) | 124.4(5) |
| C(17)-C(18)-C(13) | 123.6(6) |
| Cl(6)-C(19)-D(19) | 108.3 |
| Cl(7)-C(19)-Cl(6) | 107.1(5) |
| Cl(7)-C(19)-D(19) | 108.3 |
| Cl(8)-C(19)-Cl(6) | 114.2(5) |
| Cl(8)-C(19)-Cl(7) | 110.6(6) |
| Cl(8)-C(19)-D(19) | 108.3 |

Symmetry transformations used to generate equivalent atoms:

**Table 3.** Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **1b**.

(The anisotropic displacement factor exponent takes the form: -2 pi$^2$ [ h$^2$ a*$^2$ U11 + ... + 2 h k a* b* U12 ])

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Mo(1) | 42(1) | 27(1) | 43(1) | 4(1) | -2(1) | 12(1) |
| Cl(1) | 74(1) | 69(1) | 44(1) | 21(1) | 15(1) | 20(1) |
| O(2) | 43(3) | 25(2) | 38(3) | 9(2) | 3(2) | 3(2) |
| Cl(3) | 43(1) | 52(1) | 54(1) | 14(1) | -1(1) | 19(1) |
| Cl(4) | 62(1) | 33(1) | 46(1) | 20(1) | 7(1) | 7(1) |
| Cl(5) | 40(1) | 38(1) | 48(1) | 5(1) | -4(1) | 10(1) |
| O(1) | 69(4) | 31(3) | 67(4) | -8(3) | -8(3) | 19(3) |
| Se(1) | 34(1) | 27(1) | 38(1) | 16(1) | 0(1) | 4(1) |
| C(1) | 31(3) | 25(3) | 33(3) | 7(3) | 0(3) | 0(3) |
| C(2) | 37(4) | 40(4) | 47(4) | 14(3) | -3(3) | 15(3) |
| C(3) | 53(5) | 61(5) | 46(5) | 19(4) | 2(4) | 17(4) |
| C(4) | 71(6) | 52(5) | 43(5) | 4(4) | 4(4) | 24(4) |
| C(5) | 73(6) | 34(4) | 63(5) | 7(4) | 1(4) | 24(4) |
| C(6) | 47(4) | 34(4) | 58(5) | 20(4) | -3(4) | 9(3) |
| C(7) | 41(4) | 26(3) | 34(4) | 8(3) | 5(3) | 3(3) |
| C(8) | 42(4) | 37(4) | 43(4) | 5(3) | -2(3) | 2(3) |
| C(9) | 51(5) | 46(5) | 58(5) | 6(4) | -1(4) | -5(4) |
| C(10) | 70(6) | 32(4) | 50(5) | 12(4) | 16(4) | -4(4) |
| C(11) | 68(5) | 25(3) | 44(4) | 5(3) | 9(4) | 12(3) |
| C(12) | 48(4) | 25(3) | 28(3) | 5(3) | 3(3) | 4(3) |
| C(13) | 44(4) | 37(4) | 31(4) | 11(3) | 13(3) | 19(3) |
| C(14) | 61(5) | 49(5) | 51(5) | 18(4) | 9(4) | 29(4) |
| C(15) | 45(5) | 85(7) | 67(6) | 28(5) | -2(4) | 28(5) |
| C(16) | 31(4) | 77(6) | 60(5) | 22(5) | -6(4) | 5(4) |
| C(17) | 34(4) | 53(5) | 50(5) | 20(4) | 7(3) | -2(3) |
| C(18) | 33(4) | 37(4) | 36(4) | 13(3) | 5(3) | 7(3) |
| Cl(6) | 199(4) | 121(3) | 114(3) | 34(2) | 54(3) | 39(3) |
| Cl(7) | 155(3) | 159(4) | 93(2) | 61(2) | 4(2) | 63(3) |
| Cl(8) | 213(5) | 72(2) | 134(3) | 27(2) | -34(3) | 43(3) |
| C(19) | 182(13) | 49(6) | 55(6) | -1(5) | -16(7) | 28(7) |

**Table 4.** Hydrogen coordinates ( × 10$^4$) and isotropic displacement parameters (Å$^2$ × 10$^3$) for **1b**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2A) | 8785 | 9417 | 408 | 53 |
| H(2B) | 7174 | 9509 | 114 | 53 |
| H(2) | 4610 | 7226 | 3529 | 48 |
| H(3) | 3404 | 8101 | 5046 | 62 |
| H(4) | 2417 | 9840 | 5128 | 66 |
| H(5) | 2471 | 10624 | 3719 | 67 |
| H(6) | 3600 | 9750 | 2176 | 54 |

| | | | | |
|---|---|---|---|---|
| H(8) | 1746 | 6269 | 678 | 50 |
| H(9) | 793 | 4282 | 440 | 65 |
| H(10) | 2547 | 3087 | 809 | 62 |
| H(11) | 5213 | 3793 | 1465 | 55 |
| H(14) | 7897 | 4780 | 2198 | 61 |
| H(15) | 10329 | 5967 | 2883 | 74 |
| H(16) | 10716 | 7921 | 2984 | 67 |
| H(17) | 8576 | 8741 | 2357 | 55 |

**Table 5.** Torsion angles [°] for **1b**.

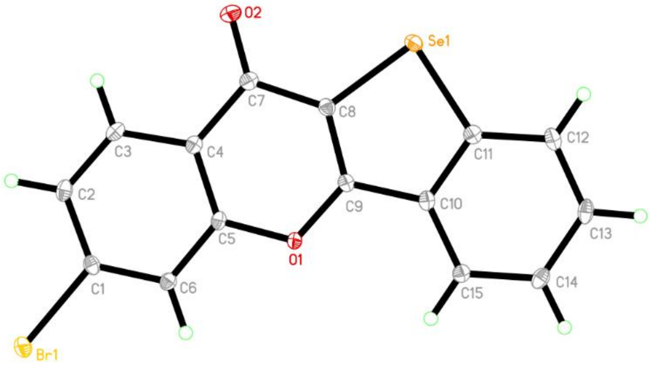
| | |
|---|---|
| Se(1)-C(1)-C(2)-C(3) | -178.7(6) |
| Se(1)-C(1)-C(6)-C(5) | 179.7(6) |
| Se(1)-C(7)-C(8)-C(9) | 178.1(6) |
| Se(1)-C(7)-C(12)-C(11) | -177.4(5) |
| Se(1)-C(7)-C(12)-C(13) | 2.6(7) |
| C(1)-C(2)-C(3)-C(4) | -1.6(12) |
| C(2)-C(1)-C(6)-C(5) | 0.5(11) |
| C(2)-C(3)-C(4)-C(5) | 2.0(14) |
| C(3)-C(4)-C(5)-C(6) | -1.1(14) |
| C(4)-C(5)-C(6)-C(1) | -0.2(13) |
| C(6)-C(1)-C(2)-C(3) | 0.4(11) |
| C(7)-C(8)-C(9)-C(10) | -0.9(12) |
| C(7)-C(12)-C(13)-C(14) | 178.0(7) |
| C(7)-C(12)-C(13)-C(18) | -0.1(9) |
| C(8)-C(7)-C(12)-C(11) | 1.1(10) |
| C(8)-C(7)-C(12)-C(13) | -178.9(6) |
| C(8)-C(9)-C(10)-C(11) | 1.2(13) |
| C(9)-C(10)-C(11)-C(12) | -0.3(12) |
| C(10)-C(11)-C(12)-C(7) | -0.9(10) |
| C(10)-C(11)-C(12)-C(13) | 179.2(7) |
| C(11)-C(12)-C(13)-C(14) | -2.1(12) |
| C(11)-C(12)-C(13)-C(18) | 179.8(7) |
| C(12)-C(7)-C(8)-C(9) | -0.2(11) |
| C(12)-C(13)-C(14)-C(15) | -178.1(7) |
| C(12)-C(13)-C(18)-Se(1) | -2.4(7) |
| C(12)-C(13)-C(18)-C(17) | -179.6(6) |
| C(13)-C(14)-C(15)-C(16) | -1.0(13) |
| C(14)-C(13)-C(18)-Se(1) | 179.3(5) |
| C(14)-C(13)-C(18)-C(17) | 2.1(11) |
| C(14)-C(15)-C(16)-C(17) | -0.1(14) |
| C(15)-C(16)-C(17)-C(18) | 2.1(12) |
| C(16)-C(17)-C(18)-Se(1) | -180.0(6) |
| C(16)-C(17)-C(18)-C(13) | -3.1(11) |
| C(18)-C(13)-C(14)-C(15) | 0.0(11) |

Symmetry transformations used to generate equivalent atoms:

**Table 6.** Hydrogen bonds for **1b** [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|

## 7.2 X-ray structure of compound 8e.



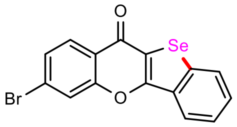


**Table 7.** Sample and crystal data for **8e**.

| | |
|---|---|
| Identification code | **8e** |
| Chemical formula | $C_{15}H_7BrO_2Se$ |
| Formula weight | 378.08 g/mol |
| Wavelength | 0.71073 Å |
| Crystal size | 0.200 × 0.230 × 0.250 mm |
| Crystal system | monoclinic |
| Space group | P 1 21/c 1 |
| Unit cell dimensions | a = 12.133(2) Å α = 90° |
| | b = 7.2784(13) Å β = 107.078(6)° |
| | c = 14.645(2) Å γ = 90° |
| Volume | 1236.3(4) $Å^3$ |
| Z | 4 |
| Density (calculated) | 2.031 $g/cm^3$ |
| Absorption coefficient | 6.261 $mm^{-1}$ |
| F(000) | 728 |

**Table 8.** Data collection and structure refinement for **8e**.

| | |
|---|---|
| Theta range for data collection | 2.91 to 28.30° |
| Index ranges | -16<=h<=16, -9<=k<=9, -19<=l<=18 |

| | |
|---|---|
| Reflections collected | 28000 |
| Independent reflections | 3075 [R(int) = 0.0754] |
| Max. and min. transmission | 0.7457 and 0.4644 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXT 2014/5 (Sheldrick, 2014) |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Refinement program | SHELXL 2018/3 (Sheldrick, 2015) |
| Function minimized | $\Sigma$ w($Fo^2$ - $Fc^2$)$^2$ |
| Data/restraints/parameters | 3075 / 0 / 173 |
| Goodness-of-fit on F2 | 1.035 |
| Δ/σmax | 0.002 |
| Final R indices | Final R indices R1 = 0.0238, wR2 = 0.0510 |
| | all data R1 = 0.0286, wR2 = 0.0524 |
| Weighting scheme | w=1/[$\sigma^2$($Fo^2$)+1.0174P] |
| | where P=($Fo^2$+2$Fc^2$)/3 |
| Extinction coefficient | 0.0035(5) |
| Largest diff. peak and hole | 0.433 and -0.344 eÅ$^{-3}$ |
| R.M.S. deviation from mean | 0.083 eÅ$^{-3}$ |

**Table 9.** Atomic coordinates and equivalent isotropic atomic displacement parameters (Å2) for **8e**.

U(eq) is defined as one-third of the trace of the orthogonalized Uij tensor.

| | x/a | y/b | z/c | U(eq) |
|---|---|---|---|---|
| Br1 | 0.95752(2) | 0.41201(3) | 0.88627(2) | 0.02247(8) |
| Se1 | 0.54838(2) | 0.73159(3) | 0.31459(2) | 0.01810(7) |
| O1 | 0.63159(11) | 0.64876(19) | 0.59855(9) | 0.0143(3) |
| O2 | 0.80504(13) | 0.5569(2) | 0.39823(11) | 0.0256(3) |
| C1 | 0.89515(17) | 0.4628(3) | 0.75414(14) | 0.0164(4) |
| C2 | 0.95954(17) | 0.4209(3) | 0.69190(15) | 0.0187(4) |
| C3 | 0.91270(17) | 0.4595(3) | 0.59644(15) | 0.0175(4) |
| C4 | 0.80300(17) | 0.5389(3) | 0.56071(14) | 0.0151(4) |
| C5 | 0.74101(16) | 0.5752(3) | 0.62559(14) | 0.0143(4) |
| C6 | 0.78684(17) | 0.5398(3) | 0.72313(14) | 0.0156(4) |
| C7 | 0.75350(17) | 0.5810(3) | 0.45807(14) | 0.0172(4) |
| C8 | 0.63850(17) | 0.6553(3) | 0.43663(14) | 0.0155(4) |
| C9 | 0.58449(16) | 0.6873(3) | 0.50454(14) | 0.0141(4) |
| C10 | 0.47183(16) | 0.7696(3) | 0.47303(14) | 0.0144(4) |
| C11 | 0.43638(17) | 0.8046(3) | 0.37441(14) | 0.0164(4) |
| C12 | 0.32984(18) | 0.8862(3) | 0.32950(15) | 0.0191(4) |
| C13 | 0.25993(17) | 0.9315(3) | 0.38544(16) | 0.0200(4) |
| C14 | 0.29407(17) | 0.8977(3) | 0.48430(15) | 0.0184(4) |
| C15 | 0.39931(16) | 0.8168(3) | 0.52818(14) | 0.0156(4) |

**Table 10.** Bond lengths (Å) for **8e**.

|  |  |  |  |
|---|---|---|---|
| Br1-C1 | 1.896(2) | Se1-C8 | 1.884(2) |
| Se1-C11 | 1.896(2) | O1-C5 | 1.377(2) |
| O1-C9 | 1.356(2) | O2-C7 | 1.230(2) |
| C1-C2 | 1.397(3) | C1-C6 | 1.377(3) |
| C2-H2 | 0.95 | C2-C3 | 1.375(3) |
| C3-H3 | 0.95 | C3-C4 | 1.404(3) |
| C4-C5 | 1.399(3) | C4-C7 | 1.478(3) |
| C5-C6 | 1.396(3) | C6-H6 | 0.95 |
| C7-C8 | 1.442(3) | C8-C9 | 1.362(3) |
| C9-C10 | 1.438(3) | C10-C11 | 1.404(3) |
| C10-C15 | 1.401(3) | C11-C12 | 1.399(3) |
| C12-H12 | 0.95 | C12-C13 | 1.381(3) |
| C13-H13 | 0.95 | C13-C14 | 1.406(3) |
| C14-H14 | 0.95 | C14-C15 | 1.381(3) |
| C15-H15 | 0.95 |  |  |

**Table 11**. Bond angles (°) for **8e**.

|  |  |  |  |
|---|---|---|---|
| C8-Se1-C11 | 86.52(9) | C9-O1-C5 | 117.10(15) |
| C2-C1-Br1 | 119.43(15) | C6-C1-Br1 | 118.17(15) |
| C6-C1-C2 | 122.40(18) | C1-C2-H2 | 120.8 |
| C3-C2-C1 | 118.39(18) | C3-C2-H2 | 120.8 |
| C2-C3-H3 | 119.1 | C2-C3-C4 | 121.80(18) |
| C4-C3-H3 | 119.1 | C3-C4-C7 | 121.49(18) |
| C5-C4-C3 | 117.67(18) | C5-C4-C7 | 120.84(17) |
| O1-C5-C4 | 122.89(17) | O1-C5-C6 | 115.23(17) |
| C6-C5-C4 | 121.88(18) | C1-C6-C5 | 117.84(18) |
| C1-C6-H6 | 121.1 | C5-C6-H6 | 121.1 |
| O2-C7-C4 | 123.73(18) | O2-C7-C8 | 124.09(19) |
| C8-C7-C4 | 112.18(17) | C7-C8-Se1 | 124.87(14) |
| C9-C8-Se1 | 111.88(15) | C9-C8-C7 | 123.17(18) |
| O1-C9-C8 | 123.80(17) | O1-C9-C10 | 119.30(17) |
| C8-C9-C10 | 116.90(18) | C11-C10-C9 | 112.39(17) |
| C15-C10-C9 | 128.00(18) | C15-C10-C11 | 119.61(18) |
| C10-C11-Se1 | 112.32(15) | C12-C11-Se1 | 126.18(16) |
| C12-C11-C10 | 121.49(19) | C11-C12-H12 | 121.1 |
| C13-C12-C11 | 117.78(19) | C13-C12-H12 | 121.1 |
| C12-C13-H13 | 119.2 | C12-C13-C14 | 121.51(19) |
| C14-C13-H13 | 119.2 | C13-C14-H14 | 119.8 |
| C15-C14-C13 | 120.42(19) | C15-C14-H14 | 119.8 |
| C10-C15-H15 | 120.4 | C14-C15-C10 | 119.19(18) |
| C14-C15-H15 | 120.4 |  |  |

**Table 12.** Torsion angles (°) for **8e**.

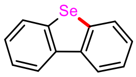
|  |  |  |  |
|---|---|---|---|
| Br1-C1-C2-C3 | -179.80(15) | Br1-C1-C6-C5 | -179.38(14) |

| | | | |
|---|---|---|---|
| Se1-C8-C9-O1 | -178.59(14) | Se1-C8-C9-C10 | 0.4(2) |
| Se1-C11-C12-C13 | -179.41(15) | O1-C5-C6-C1 | 178.76(17) |
| O1-C9-C10-C11 | 178.67(16) | O1-C9-C10-C15 | -0.6(3) |
| O2-C7-C8-Se1 | -1.1(3) | O2-C7-C8-C9 | -177.5(2) |
| C1-C2-C3-C4 | -0.1(3) | C2-C1-C6-C5 | 0.4(3) |
| C2-C3-C4-C5 | -1.1(3) | C2-C3-C4-C7 | 179.62(18) |
| C3-C4-C5-O1 | -178.45(17) | C3-C4-C5-C6 | 2.0(3) |
| C3-C4-C7-O2 | -2.8(3) | C3-C4-C7-C8 | 177.79(18) |
| C4-C5-C6-C1 | -1.6(3) | C4-C7-C8-Se1 | 178.35(14) |
| C4-C7-C8-C9 | 1.9(3) | C5-O1-C9-C8 | 0.9(3) |
| C5-O1-C9-C10 | -178.12(16) | C5-C4-C7-O2 | 178.0(2) |
| C5-C4-C7-C8 | -1.5(3) | C6-C1-C2-C3 | 0.4(3) |
| C7-C4-C5-O1 | 0.8(3) | C7-C4-C5-C6 | -178.75(18) |
| C7-C8-C9-O1 | -1.7(3) | C7-C8-C9-C10 | 177.26(18) |
| C8-Se1-C11-C10 | 0.05(15) | C8-Se1-C11-C12 | 179.44(19) |
| C8-C9-C10-C11 | -0.4(3) | C8-C9-C10-C15 | -179.67(19) |
| C9-O1-C5-C4 | -0.4(3) | C9-O1-C5-C6 | 179.17(16) |
| C9-C10-C11-Se1 | 0.2(2) | C9-C10-C11-C12 | -179.27(18) |
| C9-C10-C15-C14 | 179.05(19) | C10-C11-C12-C13 | -0.1(3) |
| C11-Se1-C8-C7 | -177.04(18) | C11-Se1-C8-C9 | -0.25(15) |
| C11-C10-C15-C14 | -0.2(3) | C11-C12-C13-C14 | 0.2(3) |
| C12-C13-C14-C15 | -0.3(3) | C13-C14-C15-C10 | 0.3(3) |
| C15-C10-C11-Se1 | 179.51(14) | C15-C10-C11-C12 | 0.1(3) |

**Table 13.** Hydrogen bond distances (Å) and angles (°) for **8e**.

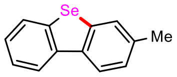
| | **Donor-H** | **Acceptor-H** | **Donor-Acceptor** | **Angle** |
|---|---|---|---|---|
| C6-H6...Se1 | 0.95 | 3.05 | 3.900(2) | 150.4 |
| C12-H12...O2 | 0.95 | 2.58 | 3.484(3) | 158.9 |

## 8. Characterization of products.



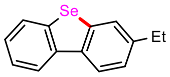
**Dibenzoselenophene (1c)**

Purification by PTLC ($R_f = 0.56$ in petroleum ether) afforded **1c** as a yellow solid (43.4 mg, 94% yield). Mp = 53-55°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.14 (dd, *J* = 7.9, 1.3 Hz, 2H), 7.86 (td, *J* = 7.6, 1.2 Hz, 2H), 7.47 (td, *J* = 7.6, 1.2 Hz, 2H), 7.40 (td, *J* = 7.6, 1.4 Hz, 2H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 139.3, 138.3, 126.8, 126.1, 124.8, 122.8. $^{77}$Se NMR (114 MHz, Chloroform-*d*) δ = 450.5. IR (KBr, cm$^{-1}$): ν 2955, 2930, 1570, 1434, 1423, 1327, 1261, 1221, 1038, 1002, 896, 861, 729, 632; GC-MS (EI): calcd. for $C_{12}H_8Se$ [M$^+$] 231.9; found 232.0.



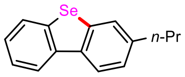
**3-Methyldibenzo[*b,d*]selenophene (2c)**

Purification by PTLC ($R_f = 0.52$ in petroleum ether) afforded **2c** as a yellow solid (40.2 mg, 82% yield). Mp = 73.5-75°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.01 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.82 – 7.75 (dd, 1H), 7.62 (s, 1H), 7.37 (td, *J* = 7.5, 1.2 Hz, 1H), 7.32 – 7.25 (m, 1H), 7.21 (d, *J* = 1.5 Hz, 1H), 2.41 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 139.5, 138.9, 138.4, 137.0, 135.9, 126.4, 126.3, 126.2, 126.1, 124.8, 122.5, 122.5, 21.6. IR (KBr, cm$^{-1}$): ν 2976, 2943, 1583, 1456， 1346, 1286, 1247, 1057, 1036, 885, 757, 664; GC-MS (EI): calcd. for $C_{13}H_{10}Se$ [M$^+$]245.9; found 246.0.



**3-Ethyldibenzo[*b,d*]selenophene (3c)**

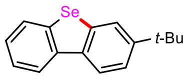
Purification by PTLC ($R_f = 0.50$ in petroleum ether) afforded **3c** as a yellow solid (49.2 mg, 90% yield). Mp = 43-45.6°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.07 (dd, *J* = 7.9, 1.3 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.71 (s, 1H), 7.43 (td, *J* = 7.6, 1H), 7.35 (td, *J* = 7.6, 1.3 Hz, 1H), 7.29 (dd, *J* = 8.1, 1.5 Hz, 1H), 2.77 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 143.5, 139.5, 139.0, 138.4, 136.1, 126.4, 126.1, 125.2, 125.0, 124.8, 122.6, 122.6, 29.0, 15.8. IR (KBr, cm$^{-1}$): ν 2967, 2955, 2867, 1587, 1456, 1446, 1367, 1283, 1257, 1046, 1034, 936, 876, 744, 657; GC-MS (EI): calcd. for $C_{14}H_{12}Se$ [M$^+$] 260.0; found 260.1.



**3-Propyldibenzo[*b,d*]selenophene (4c)**

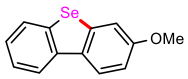
Purification by PTLC ($R_f = 0.45$ in petroleum ether) afforded **4c** as a yellow oily liquid (50.8 mg, 93% yield). $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 7.8 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.71 (s, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H) , 7.29 (dd, *J* = 8.1, 1.5 Hz, 1H), 2.73 (t, *J* = 7.6 Hz, 2H), 1.82 –

1.66 (m, 2H), 1.01 (td, *J* = 7.3, 1.5 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 141.8, 138.9, 138.3, 136.0, 126.4, 126.0, 125.7, 125.6, 124.7, 122.5, 122.5, 38.0, 24.6, 13.8. IR (KBr, cm$^{-1}$): ν 2975, 2937, 2853, 1563, 1474, 1463, 1375, 1297, 1263, 1057, 1053, 958, 883, 755, 681; GC-MS (EI): calcd. for $C_{15}H_{14}Se$ $[M^+]$ 274.0; found 274.1.



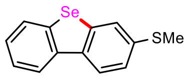
### 3-(*Tert*-butyl)dibenzo[*b,d*]selenophene (5c）

Purification by PTLC ($R_f$ = 0.45 in petroleum ether) afforded **5c** as a yellow solid (51.7 mg, 90% yield). Mp = 63.8-65.5°C. $^1$H NMR (500 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 7.9 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.92 (s, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 1.43 (s, 9H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 150.4, 138.3, 139.4, 139.2, 135.8, 126.4, 126.1, 124.8, 122.8, 122.6, 122.5, 122.4, 35.1, 31.5. IR (KBr, cm$^{-1}$): ν 2963, 2945, 2855, 1739, 1572, 1435, 1376, 1247, 1228, 991, 812, 745, 717; GC-MS (EI): calcd. for $C_{16}H_{16}Se$ $[M^+]$ 288.0; found 288.1.



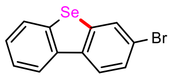
### 3-Methoxydibenzo[*b,d*]selenophene (6c)

Purification by PTLC ($R_f$ = 0.40 in petroleum ether) afforded **6c** as a yellow solid (45.9 mg, 85% yield). Mp = 67-69°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.00 (dd, *J* = 8.5, 2.5 Hz, 2H), 7.83 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.43 (td, *J* = 7.6, 1.3 Hz, 1H), 7.38 (d, *J* = 2.4 Hz, 1H), 7.32 (td, *J* = 7.6, 1.3 Hz, 1H), 7.05 (dd, *J* = 8.7, 2.4 Hz, 1H), 3.90 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 159.0, 140.7, 138.4, 138.2, 131.7, 125.9, 125.8, 124.9, 123.4, 122.1, 113.4, 109.5, 55.6. IR (KBr, cm$^{-1}$): ν 2973, 2929, 1555, 1486, 1457, 1437, 1256, 1214, 1068, 1012, 776, 751, 721,682; GC-MS (EI): calcd. for $C_{13}H_{10}OSe$ $[M^+]$ 261.9; found 262.0.



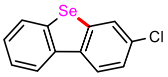
### Dibenzo[*b,d*]selenophen-3-yl(methyl)sulfane (7c)

Purification by PTLC ($R_f$ = 0.36 in petroleum ether) afforded **7c** as a white solid (49.3 mg, 89% yield). Mp = 95-97°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 7.9 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 1.8 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.41 – 7.30 (m, 2H), 2.57 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 140.2, 138.9, 138.0, 137.7, 135.6, 126.7, 126.1, 125.0, 124.0, 123.1, 122.8, 122.6, 16.2. IR (KBr, cm$^{-1}$): ν 2965, 2913, 1543, 1472, 1442, 1419, 1237, 1191, 1043, 1002, 767, 734, 705, 664; GC-MS (EI): calcd. for $C_{13}H_{10}SSe$ $[M^+]$ 277.9; found 278.0.



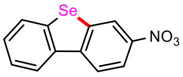
### 3-Bromodibenzo[*b,d*]selenophene (8c)

Purification by PTLC ($R_f$ = 0.48 in petroleum ether) afforded 8c as a yellow solid (55.2 mg, 89% yield). Mp = 83.5-86°C. $^{1}$H NMR (500 MHz, Chloroform-*d*) δ 8.09 – 8.01 (m, 1H), 7.98 (d, *J* = 4.9 Hz, 1H), 7.90 (ddd, *J* = 11.3, 8.4, 4.1 Hz, 1H), 7.84 (d, *J* = 7.1 Hz, 1H), 7.53 (t, *J* = 7.0 Hz, 1H), 7.44 (td, *J* = 7.4, 2.8 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 140.8, 139.3, 137.4, 137.2, 128.6, 128.2, 127.3, 126.0, 125.1, 123.9, 122.9, 120.6. IR (KBr, cm$^{-1}$): ν 3032, 2904, 1554, 1439, 1413, 1365, 1189, 1045, 1001, 842, 788, 731, 705, 683, 657; GC-MS (EI): calcd. for $C_{12}H_7BrSe$ [M$^+$] 309.9; found 310.0.



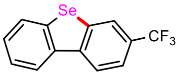
### 3-Chlorodibenzo[*b,d*]selenophene (9c)

Purification by PTLC ($R_f$ = 0.32 in petroleum ether) afforded **9c** as a yellow solid (46.8 mg, 88% yield). Mp = 53-55.5°C. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.08 (dd, *J* = 7.8, 1.3 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.90 – 7.81 (m, 2H), 7.47 (td, *J* = 7.6, 1.2 Hz, 1H), 7.45 – 7.38 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 140.4, 139.3, 137.4, 136.8, 132.7, 127.1, 126.1, 125.7, 125.5, 125.1, 123.5, 122.9. IR (KBr, cm$^{-1}$): ν 3067, 2957, 2865, 1589, 1466, 1445, 1408, 1275, 1242, 1112, 1055, 841, 803, 776, 738; GC-MS (EI): calcd. for $C_{12}H_7ClSe$ [M$^+$] 265.9; found 266.0.



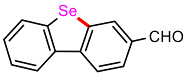
### 3-Nitrodibenzo[*b,d*]selenophene (10c)

Purification by PTLC ($R_f$ = 0.32 in petroleum ether) afforded **10c** as a yellow solid (47.5 mg, 86% yield). Mp = 140-142°C. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.77 (d, *J* = 2.1 Hz, 1H), 8.31 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.20 (d, *J* = 8.1 Hz, 2H), 7.94 (d, *J* = 7.1 Hz, 1H), 7.59 – 7.49 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 146.1, 143.4, 141.8, 139.5, 136.3, 128.7, 126.4, 125.6, 124.3, 122.9, 121.9, 120.2. IR (KBr, cm$^{-1}$): ν 3089, 2976, 1679, 1493, 1486, 1467, 1255, 1263, 1134, 1069, 853, 783, 705; GC-MS (EI): calcd. for $C_{12}H_7NO_2Se$ [M$^+$] 276.9; found 277.0.



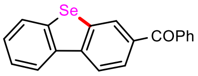
### 3-(Trifluoromethyl)dibenzo[*b,d*]selenophene (11c)

Purification by PTLC ($R_f$ = 0.28 in petroleum ether) afforded **11c** as a yellow solid (52.0 mg, 87% yield). Mp = 74.2-76°C. $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.15 (s, 3H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.48 (t, *J* = 9.0 Hz, 2H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 141.1, 140.4, 139.4, 137.0, 128.7 (q, *J* = 32.3 Hz), 128.0, 126.2, 125.6, 125.3, 124.1 (d, *J* = 233.6 Hz), 123.2 (q, *J* = 4.1 Hz), 122.9, 121.7 (q, *J* = 3.6 Hz). IR (KBr, cm$^{-1}$): ν 3376, 2997, 1366, 1275, 1189, 1145, 1098, 1067, 901, 843, 758, 719; GC-MS (EI): calcd. for $C_{13}H_7F_3Se$ [M$^+$] 299.9; found 300.0.



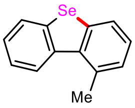
### Dibenzo[*b,d*]selenophene-3-carbaldehyde (12c)

Purification by PTLC ($R_f$ = 0.36 in petroleum ether/EtOAc/$CH_2Cl_2$ = 15:1:1) afforded **12c** as a yellow solid (41.5 mg, 80% yield). Mp = 103-105°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 10.05 (s, 1H), 8.34 (d, *J* = 1.5 Hz, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 8.15 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.91 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.87 (dd, *J* = 6.8, 1.2 Hz, 1H), 7.43 (ddd, *J* = 9.1, 7.4, 1.5 Hz, 2H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 190.5, 142.3, 140.4, 138.7, 136.1, 133.7, 127.4, 127.3, 125.3, 124.8, 124.3, 123.0, 122.2. IR (KBr, cm$^{-1}$): ν 3205, 2955, 1768, 1597, 1542, 1475, 1423, 1367, 1256, 1021, 822, 775, 734; GC-MS (EI): calcd. for $C_{13}H_8OSe$ [M$^+$] 259.9; found 260.0.



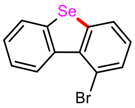
**Dibenzo[*b,d*]selenophen-3-yl(phenyl)methanone (13c)**

Purification by PTLC ($R_f$ = 0.32 in petroleum ether) afforded **13c** as a yellow solid (54.9 mg, 82% yield). Mp = 123-125°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.34 (d, *J* = 1.5 Hz, 1H), 8.21 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.93 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.87 – 7.84 (m, 2H), 7.65 – 7.60 (m, 1H), 7.55 – 7.50 (m, 3H), 7.49 – 7.44 (m, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 196.1, 141.7, 141.0, 139.1, 137.8, 137.3, 135.7, 132.5, 130.1, 128.4, 128.0, 126.8, 126.3, 125.2, 123.8, 122.5. IR (KBr, cm$^{-1}$): ν 3205, 3015, 1778, 1536, 1513, 1443, 1417, 1331, 1213, 1075, 863, 734, 702; GC-MS (EI): calcd. for $C_{19}H_{12}OSe$ [M$^+$] 336.0; found 336.1.



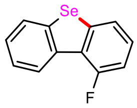
**1-Methyldibenzo[*b,d*]selenophene (15c)**

Purification by PTLC ($R_f$ = 0.48 in petroleum ether) afforded **15c** as a yellow solid (42.1 mg, 86% yield). Mp = 79.8-81.6°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.78 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.47 (td, *J* = 8.1, 1.2 Hz, 1H), 7.38 (td, *J* = 8.1, 1.2 Hz, 1H), 7.29 (td, *J* = 8.1, 1.2 Hz, 1H), 7.24 (s, 1H), 2.92 (dd, *J* = 7.2, 1.8 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 139.9, 139.6, 139.6, 136.4, 136.2, 128.1, 126.8, 126.1, 126.1, 125.9, 124.6, 123.9, 23.5. IR (KBr, cm$^{-1}$): ν 3023, 2901, 2827, 1537, 1487, 1175, 1067, 1012, 878, 787, 745; GC-MS (EI): calcd. for $C_{13}H_{10}Se$ [M$^+$] 245.9; found 246.0.



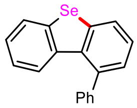
**1-Bromodibenzo[*b,d*]selenophene (16c)**

Purification by PTLC ($R_f$ = 0.45 in petroleum ether) afforded **16c** as a yellow solid (52.7 mg, 85% yield). Mp = 91-93°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 9.31 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.91 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.87 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.71 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.52 (td, *J* = 8.3, 7.8, 1.4 Hz, 1H), 7.46 (td, *J* = 7.5, 1.4 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 141.8, 139.9, 137.8, 135.1, 131.2, 127.4, 127.2, 126.7, 125.8, 125.2, 124.3, 119.6. IR (KBr, cm$^{-1}$): ν 3022, 3014, 1644, 1443, 1423, 1376, 1207, 1063, 1042, 863, 775, 751, 724, 698, 663; GC-MS (EI): calcd. for $C_{12}H_7BrSe$ [M$^+$] 309.9; found 310.0.



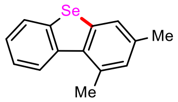
### 1-Fluorodibenzo[*b,d*]selenophene (17c)

Purification by PTLC ($R_f$ = 0.26 in petroleum ether) afforded **17c** as a white crystal (45.8 mg, 92% yield). Mp = 70-72°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.54 – 8.41 (m, 1H), 7.93 – 7.86 (m, 1H), 7.66 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.46 – 7.40 (m, 1H), 7.34 (td, *J* = 8.0, 5.0 Hz, 1H), 7.17 (dddd, *J* = 11.6, 8.1, 2.3, 1.2 Hz, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 160.7 (d, *J* =252.4 Hz), 141.1 (d, *J* = 3.4 Hz), 138.8, 136.1 (d, *J* = 4.7 Hz), 128.8 (d, *J* = 59.7 Hz), 127.3 (d, *J* = 7.9 Hz), 127.0 (d, *J* = 12.6 Hz), 126.9, 125.6, 125.3, 121.7 (d, *J* = 3.9 Hz), 111.6 (d, *J* = 20.9 Hz). IR (KBr, cm$^{-1}$): ν 3043, 2953, 1667, 1574, 1412, 1363, 1237, 1042, 1017, 834, 763, 734, 712, 683, 647; GC-MS (EI): calcd. for $C_{12}H_7FSe$ [M$^+$] 249.9; found 250.0.



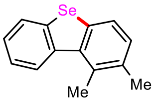
### 1-Phenyldibenzo[*b,d*]selenophene (18c)

Purification by PTLC ($R_f$ = 0.46 in petroleum ether) afforded **18c** as a yellow oily liquid (54.7 mg, 89% yield). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.88 (dt, *J* = 7.9, 1.2 Hz, 1H), 7.82 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.48 (dt, *J* = 4.6, 2.6 Hz, 3H), 7.40 (ddd, *J* = 5.2, 3.2, 1.8 Hz, 2H), 7.36 (td, *J* = 7.3, 6.8, 1.2 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.02 (td, *J* = 3.3, 1.4 Hz, 2H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 141.9, 140.9, 140.1, 139.6, 138.4, 135.3, 129.1, 128.8, 127.7, 126.8, 126.3, 125.9, 125.7, 125.2, 124.2. IR (KBr, cm$^{-1}$): ν 3035, 2942, 2845, 1466, 1435, 1423, 1353, 1226, 1063, 998, 795, 718, 667; GC-MS (EI): calcd. for $C_{18}H_{12}Se$ [M$^+$] 308.0; found 308.1.



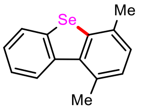
### 1,3-Dimethyldibenzo[*b,d*]selenophene (19c)

Purification by PTLC ($R_f$ = 0.42 in petroleum ether) afforded **19c** as a yellow solid (47.7 mg, 92% yield). Mp = 111.7-114°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.32 (d, *J* = 8.1 Hz, 1H), 7.89 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.57 (s, 1H), 7.42 (td, *J* = 7.5, 1.2 Hz, 1H), 7.34 (td, *J* = 7.5, 1.2 Hz, 1H), 7.06 (s, 1H), 2.86 (s, 3H), 2.43 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 140.2, 139.6, 139.2, 136.2, 135.7, 134.0, 129.6, 126.3, 126.1, 125.5, 124.6, 124.0, 23.3, 21.2. IR (KBr, cm$^{-1}$): ν 3105, 2956, 2974, 1783, 1647, 1467, 1434, 1256, 1086, 1061, 875, 782, 734, 679; GC-MS (EI): calcd. for $C_{14}H_{12}Se$ [M$^+$] 260.0; found 260.1.



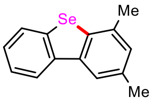
**1,2-Dimethyldibenzo[*b,d*]selenophene (20c)**

Purification by PTLC ($R_f$ = 0.50 in petroleum ether) afforded **20c** as a yellow solid (85% yield). Mp = 48-50°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.45 (d, *J* = 8.2 Hz, 1H), 7.91 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.46 (td, *J* = 8.0, 1.2 Hz, 1H), 7.37 (td, *J* = 8.0, 1.2 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 2.84 (s, 3H), 2.49 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 139.9, 139.7, 137.2, 136.8, 134.8, 133.6, 128.8, 127.2, 126.2, 125.7, 124.4, 123.2, 20.9, 18.2. IR (KBr, cm$^{-1}$): ν 3063, 2947, 2863, 1667, 1634, 1453, 1423, 1274, 1073, 1035, 834, 763, 742, 693, 653; GC-MS (EI): calcd. for $C_{14}H_{12}Se$ [M$^+$] 260.0; found 260.1.



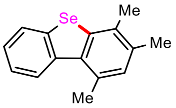
**1,4-Dimethyldibenzo[*b,d*]selenophene (21c)**

Purification by PTLC ($R_f$ = 0.42 in petroleum ether) afforded **21c** as a yellow oily liquid (37.8 mg, 73% yield). $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.41 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.47 (td, *J* = 8.3, 7.8, 1.5 Hz, 1H), 7.38 (td, *J* = 8.3, 7.8, 2H), 7.20 (d, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 2.90 (s, 3H), 2.54 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 141.3, 140.4, 139.2, 133.4, 133.0, 132.2, 128.6, 126.6, 126.1, 126.1, 125.7, 124.6, 23.1, 22.4. IR (KBr, cm$^{-1}$): ν 3045, 2976, 2967, 1756, 1683, 1461, 1298, 1067, 1045, 867, 796, 634; GC-MS (EI): calcd. for $C_{14}H_{12}Se$ [M$^+$] 260.0; found 260.1.



**2,4-Dimethyldibenzo[*b,d*]selenophene (22c)**

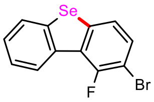
Purification by PTLC ($R_f$ = 0.52 in petroleum ether) afforded **22c** as a yellow solid (45.1 mg, 87% yield). Mp = 43-45.5°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.08 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.78 (s, 1H), 7.43 (td, *J* = 7.6, 1.2 Hz, 1H), 7.35 (td, *J* = 7.5, 1.4 Hz, 1H), 7.07 (s, 1H), 2.51 (s, 3H), 2.48 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 139.3, 138.9, 138.2, 137.2, 135.1, 134.5, 128.5, 126.5, 126.1, 124.7, 123.0, 120.6, 22.4, 21.3. IR (KBr, cm$^{-1}$): ν 3096, 2913, 1775, 1668, 1434, 1413, 1243, 1075, 1047, 886, 774, 762, 663; GC-MS (EI): calcd. for $C_{14}H_{12}Se$ [M$^+$] 260.0; found 260.1.



**1,3,4-Trimethyldibenzo[*b,d*]selenophene (23c)**

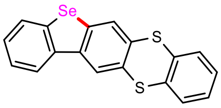
Purification by PTLC ($R_f$ = 0.43 in petroleum ether) afforded **23c** as a yellow oily liquid

(45.3 mg, 83% yield). $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.33 (d, *J* = 8.2 Hz, 1H), 7.91 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.44 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.34 (td, *J* = 7.5, 1.3 Hz, 1H), 7.07 (s, 1H), 2.84 (s, 3H), 2.45 (s, 3H), 2.39 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 140.8, 139.1, 134.2, 133.7, 133.1, 131.0, 130.2, 126.2, 125.9, 125.3, 124.6, 22.9, 19.9, 19.7. IR (KBr, cm$^{-1}$): ν 3024, 2965, 2835, 1634, 1623, 1565, 1423, 1412, 1283, 1083, 1046, 883, 763, 721, 678, 613; GC-MS (EI): calcd. for $C_{15}H_{14}Se$ [M$^+$] 274.0; found 274.1.



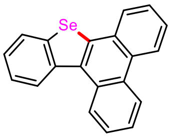
**2-Bromo-1-fluorodibenzo[*b,d*]selenophene (24c)**

Purification by PTLC ($R_f$ = 0.22 in petroleum ether) afforded **24c** as a yellow solid (42.6 mg, 65% yield). Mp = 83-84.3°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.44 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.88 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.55 – 7.48 (m, 3H), 7.44 (td, *J* = 7.6, 1.4 Hz, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 156.8 (d, *J* =252.9 Hz), 140.0 (d, *J* = 4.6 Hz), 139.4, 135.4 (d, *J* = 5.4 Hz), 130.6, 127.9 (d, *J* = 15.3 Hz), 127.4 (d, *J* = 1.2 Hz), 127.1 (d, *J* = 13 Hz), 125.7, 125.5, 122.6 (d, *J* = 4.6 Hz), 105.1 (d, *J* = 20.8 Hz). IR (KBr, cm$^{-1}$): ν 3168, 3023, 1631, 1525, 1474, 1364, 1248, 1067, 1028, 867, 823, 731, 711, 623, 606; GC-MS (EI): calcd. for $C_{12}H_6FBrSe$ [M$^+$] 327.9; found 328.0.



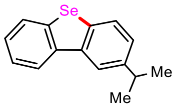
**Benzo[4,5]selenopheno[2,3-*b*]thianthrene (25c)**

Purification by PTLC ($R_f$ = 0.24 in petroleum ether) afforded **25c** as a yellow solid (45.8 mg, 62% yield). Mp = 108.3-110°C. $^1$H NMR (600 MHz, Chloroform-*d*) δ 9.52 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.69 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.61 – 7.54 (m, 3H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.33 – 7.27 (m, 2H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 139.1, 138.9, 137.0, 136.4, 135.4, 134.0, 133.9, 132.5, 128.5, 127.6, 127.5, 127.3, 126.8, 125.9, 125.8, 124.9, 124.0, 123.8. IR (KBr, cm$^{-1}$): ν 3035, 3007, 1645, 1423, 1331, 1067, 898, 764, 725, 606; GC-MS (EI): calcd. for $C_{18}H_{10}S_2Se$ [M$^+$] 369.9; found 370.0.



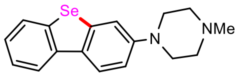
**Benzo[*b*]phenanthro[9,10-*d*]selenophene (26c)**

Purification by PTLC ($R_f$ = 0.26 in petroleum ether) afforded **26c** as a yellow solid (60.2 mg, 91% yield). Mp = 107.6-110°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 9.06 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.89 – 8.80 (m, 2H), 8.72 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.07 (dd, *J* = 7.9, 1.4 Hz, 1H), 8.00 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.79 – 7.63 (m, 4H), 7.61 – 7.57 (m, 1H), 7.44 (td, *J* = 7.5, 1.2 Hz, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 141.5, 140.6, 139.9, 131.0, 130.7, 130.2, 130.1, 129.3, 127.5, 127.4, 127.2, 126.6, 126.3, 125.7, 125.4, 125.2, 124.2, 123.9, 123.3. IR (KBr, cm$^{-1}$): ν 3035, 2873, 2869, 1454, 1422, 1407, 1376, 1254, 1031, 972, 714, 656, 623; GC-MS (EI): calcd. for $C_{20}H_{12}Se$ [M$^+$] 332.0; found 332.1.



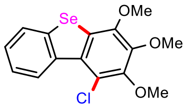
**2-Isopropyldibenzo[*b,d*]selenophene (27c)**

Purification by PTLC ($R_f$ = 0.56 in petroleum ether) afforded **27c** as a yellow oily liquid (46.4 mg, 85% yield). $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 8.0 Hz, 1H), 8.00 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 3.08 (p, *J* = 7.0 Hz, 1H), 1.36 (d, *J* = 6.9 Hz, 6H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 144.8, 138.6, 137.3, 135.3, 125.6, 125.1, 124.9, 124.8, 123.7, 121.7, 119.5, 33.2, 23.3. GC-MS (EI): calcd. for $C_{15}H_{14}Se$ [M$^+$] 274.0; found 274.1.



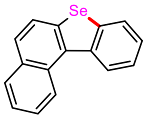
**1-(Dibenzo[*b,d*]selenophen-3-yl)-4-methylpiperazine (28c)**

Purification by PTLC ($R_f$ = 0.28 in petroleum ether/EtOAc = 5:1) afforded **28c** as a brown solid (36.2 mg, 55% yield). Mp = 98-91°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.97 (dd, *J* = 8.4, 4.8 Hz, 2H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 2.3 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.08 (dd, *J* = 8.8, 2.3 Hz, 1H), 3.32 (t, *J* = 5.0 Hz, 4H), 2.63 (t, *J* = 5.0 Hz, 4H), 2.38 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 150.6, 140.9, 138.5, 138.2, 130.7, 125.9, 125.5, 124.8, 123.1, 121.9, 114.7, 111.8, 55.1, 49.2, 46.1.GC-MS (EI): calcd. for $C_{17}H_{18}N_2Se$ [M$^+$] 330.0; found 330.1.



**1-Chloro-2,3,4-trimethoxydibenzo[*b,d*]selenophene (29c)**

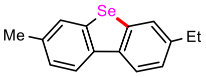
Purification by PTLC ($R_f$ = 0.30 in petroleum ether) afforded **29c** as a yellow oily liquid (45.9 mg, 62% yield). $^1$H NMR (400 MHz, Chloroform-*d*) δ 9.06 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.1 Hz, 1H), 4.08 (s, 3H), 4.03 (s, 3H), 3.98 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 149.3, 147.5, 144.2, 139.5, 138.5, 130.1, 129.9, 127.1, 126.6, 125.9, 124.7, 120.6, 61.5, 61.3, 60.8. HR-ESI-MS (*m/z*): calcd. for $C_{13}H_{16}O_3SeCl$ [M+H]$^+$ 356.9791, found 356.9788.



**Benzo[*b*]naphtho[1,2-*d*]selenophene (32c)**

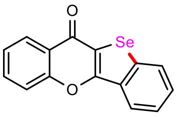
Purification by PTLC ($R_f$ = 0.32 in petroleum ether) afforded **32c** as a yellow solid

(51.7 mg, 92% yield). Mp = 93-95°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 9.05 (dd, *J* = 8.5, 1.0 Hz, 1H), 8.91 (dd, *J* = 8.3, 0.7 Hz, 1H), 8.05 (dd, *J* = 7.6, 1.5 Hz, 1H), 8.01 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.72 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.59 (tdd, *J* = 7.9, 7.1, 1.2 Hz, 2H), 7.44 (ddd, *J* = 8.2, 7.2, 1.2 Hz, 1H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 140.4, 139.9, 139.6, 132.4, 131.7, 131.7, 129.5, 127.7, 127.0, 126.6, 126.5, 125.4, 125.1, 124.9, 123.9, 123.3. GC-MS (EI): calcd. for $C_{16}H_{10}Se$ [M$^+$] 281.9; found 282.0.



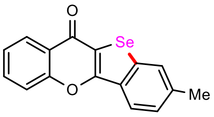
### 3-Ethyl-7-methyldibenzo[*b,d*]selenophene (35c)

Purification by PTLC ($R_f$ = 0.54 in petroleum ether) afforded **35c** as a yellow oily liquid (48.6 mg, 89% yield). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.97 (t, *J* = 8.4 Hz, 2H), 7.68 (dd, *J* = 9.1, 1.2 Hz, 2H), 7.32 – 7.21 (m, 2H), 2.77 (q, *J* = 7.6 Hz, 2H), 2.48 (s, 3H), 1.32 (t, *J* = 7.6 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 143.0, 139.1, 139.1, 136.5, 136.1, 135.9, 126.2, 126.2, 125.1, 125.0, 122.3, 122.2, 29.0, 21.6, 15.8. GC-MS (EI): calcd. for $C_{15}H_{14}Se$ [M$^+$] 274.0; found 274.1.



### 11*H*-Benzo[4,5]selenopheno[3,2-*b*]chromen-11-one (1e)

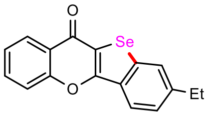
Purification by PTLC ($R_f$ = 0.35 in petroleum ether/EtOAc = 10:1) afforded **1e** as a yellow solid (42.4 mg, 71% yield). Mp = 197-201°C. $^1$H NMR (600 MHz, Chloroform-*d*) δ 8.38 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.27 – 8.19 (m, 1H), 8.02 – 7.90 (m, 1H), 7.78 (td, *J* = 7.8, 6.9, 1.7 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.51 (t, *J* = 7.5 Hz, 1H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 174.6, 156.2, 155.6, 139.9, 133.9, 132.2, 129.4, 126.9, 126.0, 125.5, 125.2, 124.4, 122.5, 121.6, 118.1. IR (KBr, cm$^{-1}$): ν 3887, 3843, 3836, 3614, 3573, 3405, 2936, 2814, 1561, 1505, 1489, 1278, 1254, 1146, 913, 823, 804, 743; HR-ESI-MS (*m/z*): calcd. for $C_{15}H_8O_2Se$ [M+H]$^+$ 300.9762, found 300.9758.



### 8-Methyl-11*H*-benzo[4,5]selenopheno[3,2-*b*]chromen-11-one (2e)

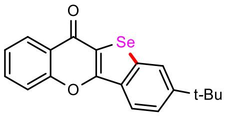
Purification by PTLC ($R_f$ = 0.38 in petroleum ether/EtOAc = 10:1) afforded **2e** as a yellow solid (42.5 mg, 68% yield). Mp = 158-160°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.33 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.74 – 7.69 (m, 2H), 7.61 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.45 (td, *J* = 7.5, 7.0, 1.1 Hz, 1H), 7.30 (dd, *J* = 8.1, 1.4 Hz, 1H), 2.47 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 174.4, 156.1, 155.6, 140.3, 140.1, 133.6, 129.7, 127.1, 126.8, 125.9, 125.0, 123.9, 122.4, 120.6, 118.0, 21.9. IR (KBr, cm$^{-1}$): ν 3943, 3867, 3624, 3589, 3418, 2923, 2856, 1513, 1487, 1289, 1256, 1165, 923, 804; HR-ESI-MS (*m/z*): calcd. for $C_{16}H_{10}O_2Se$ [M+H]$^+$ 314.9919, found

314.9920.



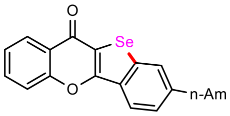
**8-Ethyl-11*H*-benzo[4,5]selenopheno[3,2-*b*]chromen-11-one(3e)**

Purification by PTLC ($R_f$ = 0.42 in petroleum ether/EtOAc = 10:1) afforded **3e** as a yellow solid (40.6 mg, 62% yield). Mp = 117.5-120°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.34 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 7.80 – 7.68 (m, 2H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.39 – 7.33 (m, 1H), 2.79 (q, *J* = 7.6 Hz, 2H), 1.32 (t, *J* = 7.6 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 174.4, 156.1, 155.7, 146.6, 140.3, 133.6, 130.0, 126.1, 125.9, 125.6, 125.0, 124.1, 122.5, 120.7, 118.0, 29.3, 15.4. IR (KBr, cm$^{-1}$): ν 3916, 3863, 3842, 3605, 3475, 3447, 2979, 2964, 2891, 1675, 1586, 1558, 1365, 1234, 1227, 1168, 984, 874, 725, 683; HR-ESI-MS (*m/z*): calcd. for $C_{17}H_{12}O_2Se$ [M+H]$^+$ 329.0075, found 329.0073.



**8-(*Tert*-butyl)-11*H*-benzo[4,5]selenopheno[3,2-*b*]chromen-11-one (4e)**

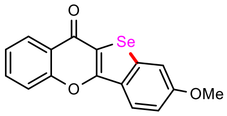
Purification by PTLC ($R_f$ = 0.36 in petroleum ether/EtOAc = 10:1) afforded **4e** as a yellow solid (49.7 mg, 70% yield). Mp = 111-113°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.36 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 1.6 Hz, 1H), 7.75 (ddd, *J* = 8.6, 7.0, 1.7 Hz, 1H), 7.66 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.60 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.48 (td, *J* = 8.1, 7.5, 1.2 Hz, 1H), 1.42 (s, 9H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 174.4, 156.2, 155.7, 153.5, 140.3, 133.6, 129.7, 126.0, 125.0, 123.9, 123.7, 123.2, 122.5, 121.0, 118.0, 35.5, 31.3. IR (KBr, cm$^{-1}$): ν 3912, 3883, 3827, 3646, 3602, 3522, 3487, 3434, 2964, 2913, 2864, 1644, 1608, 1561, 1517, 1463, 1306, 1264, 1217, 1110, 937, 874, 822, 756, 694; HR-ESI-MS (*m/z*): calcd. for $C_{19}H_{16}O_2Se$ [M+H]$^+$ 357.0388, found 357.0387.



**8-Pentyl-11*H*-benzo[4,5]selenopheno[3,2-*b*]chromen-11-one (5e)**

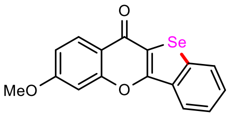
Purification by PTLC ($R_f$ = 0.32 in petroleum ether/EtOAc = 10:1) afforded **5e** as a yellow solid (26.6 mg, 36% yield). Mp = 83.7-85°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.37 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 2.76 (t, *J* = 7.8 Hz, 2H), 1.71 (p, *J* = 7.4 Hz, 2H), 1.39 – 1.33 (m, 4H), 0.91 (t, *J* = 6.6 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 174.5, 156.2, 155.8, 145.4, 140.2, 133.6, 130.0, 126.6, 126.3, 126.0, 125.0, 124.1, 122.5, 120.7, 118.0, 36.3, 31.5, 31.0, 22.5, 14.0. IR (KBr, cm$^{-1}$): ν 3954, 3889, 3863, 3647, 3534, 3487, 2968, 2926, 2867, 1658, 1667, 1589, 1543, 14755, 1367, 1258, 1252, 1103, 934, 862, 852, 769, 692; HR-ESI-MS (*m/z*):

calcd. for $C_{20}H_{18}O_2Se$ $[M+H]^+$ 371.0545, found 371.0547.



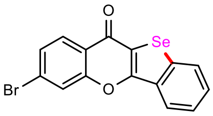
**8-Methoxy-11*H*-benzo[4,5]selenopheno[3,2-*b*]chromen-11-one (6e)**

Purification by PTLC ($R_f$ = 0.42 in petroleum ether/EtOAc = 10:1) afforded **6e** as a yellow solid (28.3 mg, 43% yield). Mp = 207.7-210°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.36 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.09 (d, *J* = 8.8 Hz, 1H), 7.74 (td, *J* = 7.8, 7.0, 1.7 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 2.3 Hz, 1H), 7.13 (dd, *J* = 8.8, 2.3 Hz, 1H), 3.93 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 174.1, 161.3, 156.1, 155.7, 142.0, 133.5, 125.9, 125.5, 125.2, 125.0, 122.5, 119.3, 117.9, 115.3, 109.5, 55.8. IR (KBr, cm$^{-1}$): ν 3926, 3854, 3837, 3622, 3469, 2977, 2958, 2889, 1672, 1593, 1516, 1378, 1246, 1223, 1172, 965, 803, 726, 678; HR-ESI-MS (*m/z*): calcd. for $C_{16}H_{10}O_3Se$ $[M+H]^+$ 330.9868, found 330.9867.



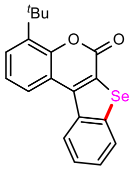
**3-Methoxy-11*H*-benzo[4,5]selenopheno[3,2-*b*]chromen-11-one (7e)**

Purification by PTLC ($R_f$ = 0.38 in petroleum ether/EtOAc = 10:1) afforded **7e** as a yellow solid (30.2 mg, 46% yield). Mp = 175.7-180°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 9.3 Hz, 1H), 8.18 – 8.09 (m, 1H), 7.97 – 7.88 (m, 1H), 7.53 – 7.49 (m, 2H), 7.03 (d, *J* = 8.1 Hz, 2H), 3.95 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 173.9, 164.3, 158.0, 155.1, 139.6, 132.2, 129.1, 127.3, 126.8, 125.3, 124.1, 121.7, 116.4, 114.2, 100.5, 55.9. HR-ESI-MS (*m/z*): calcd. for $C_{16}H_{10}O_3Se$ $[M+H]^+$ 330.9868, found 330.9865.



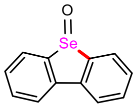
**3-Bromo-11*H*-benzo[4,5]selenopheno[3,2-*b*]chromen-11-one (8e)**

Purification by PTLC ($R_f$ = 0.48 in petroleum ether/EtOAc = 10:1) afforded **8e** as a yellow solid (39.3 mg, 52% yield). Mp = 95.5-98°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 8.5 Hz, 1H), 8.21 – 8.13 (m, 1H), 7.96 (dt, *J* = 7.4, 3.5 Hz, 1H), 7.87 (s, 1H), 7.61 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.58 – 7.53 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 173.7, 156.2, 155.3, 140.1, 131.8, 129.6, 128.8, 128.0, 127.4, 126.9, 125.6, 124.3, 121.9, 121.3, 121.2. IR (KBr, cm$^{-1}$): ν 3907, 3876, 3863, 3614, 3582, 3405, 2814, 1569, 1510, 1489, 1278, 1254, 1152, 913, 823, 757; HR-ESI-MS (*m/z*): calcd. for $C_{15}H_7O_2SeBr$ $[M+H]^+$ 378.8867, found 378.8867.



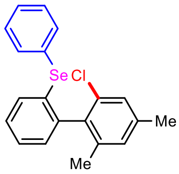
**4-(*Tert*-butyl)-6*H*-benzo[4,5]selenopheno[2,3-*c*]chromen-6-one (9e)**

Purification by PTLC ($R_f = 0.48$ in petroleum ether/EtOAc = 10:1) afforded **9e** as a yellow solid (37.6 mg, 53% yield). Mp = 68-70°C. $^1$H NMR (600 MHz, Chloroform-*d*) δ 8.74 (d, *J* = 8.2 Hz, 1H), 8.48 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 7.9 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 1.59 (s, 9H). $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 157.4, 150.7, 144.1, 141.7, 138.1, 137.1, 127.5, 127.0, 126.7, 126.6, 126.0, 124.9, 123.0, 120.7, 118.6, 34.4, 29.1. IR (KBr, cm$^{-1}$): ν 3955, 3847, 3832, 3654, 3527, 3498, 3442, 2979, 2962, 2835, 1645, 1610, 1564, 1521, 1472, 1309, 1272, 1217, 1124, 939, 878, 822, 764, 681; HR-ESI-MS (*m/z*): calcd. for $C_{19}H_{16}O_2Se$ $[M+H]^+$ 357.0388, found 357.0388.



**Dibenzo[*b,d*]selenophene 5-oxide (1g)**

Purification by PTLC ($R_f = 0.48$ in DCM/MeOH = 10:1) afforded **1g** as a yellow solid (109.9 mg, 89% yield). Mp = 192-195°C. $^1$H NMR (400 MHz, Methanol-*d₄*) δ 7.95 (d, *J* = 7.7 Hz, 2H), 7.91 (dd, *J* = 7.7, 1.2 Hz, 2H), 7.61 (td, *J* = 7.6, 1.2 Hz, 2H), 7.47 (td, *J* = 7.6, 1.2 Hz, 2H). $^{13}$C NMR (101 MHz, Methanol-d4) δ 144.9, 141.0, 132.7, 129.9, 128.5, 123.3.



**(2'-Chloro-4',6'-dimethyl-[1,1'-biphenyl]-2-yl)(phenyl)selane (19f)**

Purification by PTLC ($R_f = 0.45$ in petroleum ether) afforded **19f** as a yellow solid (4.5 mg, 6% yield).Mp = 182.6-185°C. $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.33 (d, *J* = 8.2 Hz, 1H), 7.90 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.58 (s, 1H), 7.52 – 7.42 (m, 3H), 7.35 (td, *J* = 7.6, 1.3 Hz, 1H), 7.27 (dd, *J* = 4.9, 1.8 Hz, 3H), 7.07 (s, 1H), 2.88 (s, 3H), 2.44 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 140.2, 139.6, 139.2, 136.2, 135.7, 134.0, 133.0, 131.2, 129.6, 129.3, 127.3, 126.3, 126.1, 125.5, 124.6, 124.0, 23.3, 21.1. GC-MS (EI): calcd. for $C_{20}H_{17}SeCl$ $[M^+]$ 372; found 372.

## 9. References.

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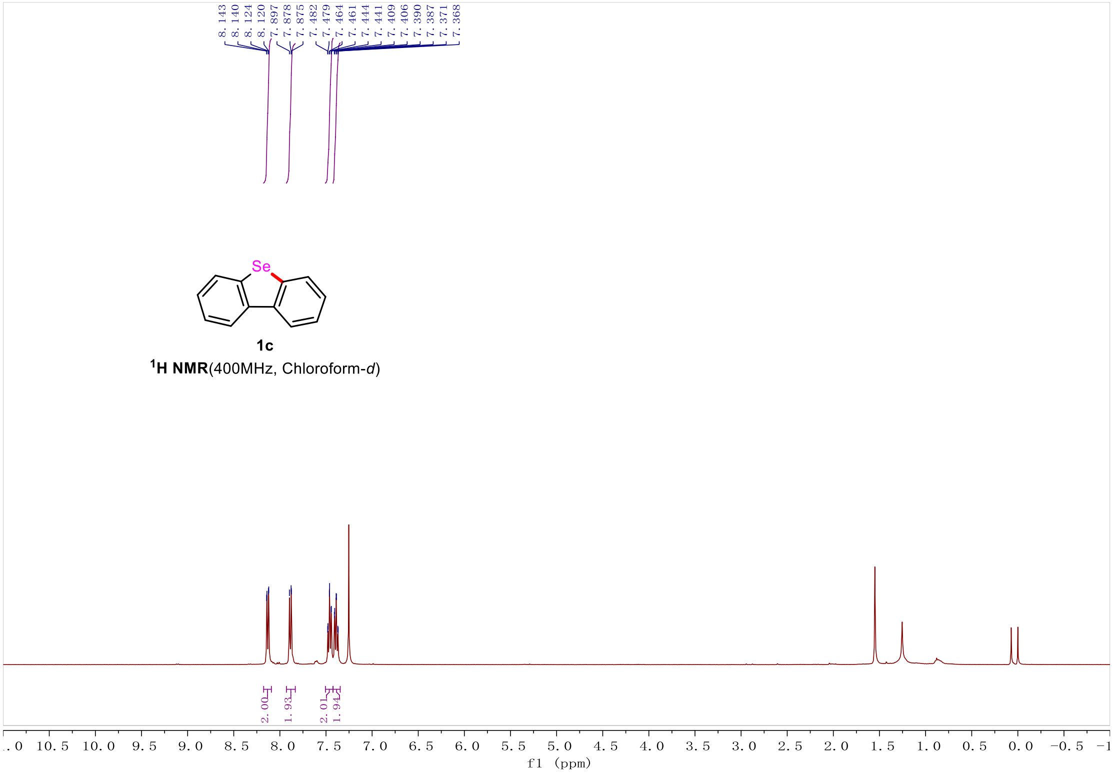
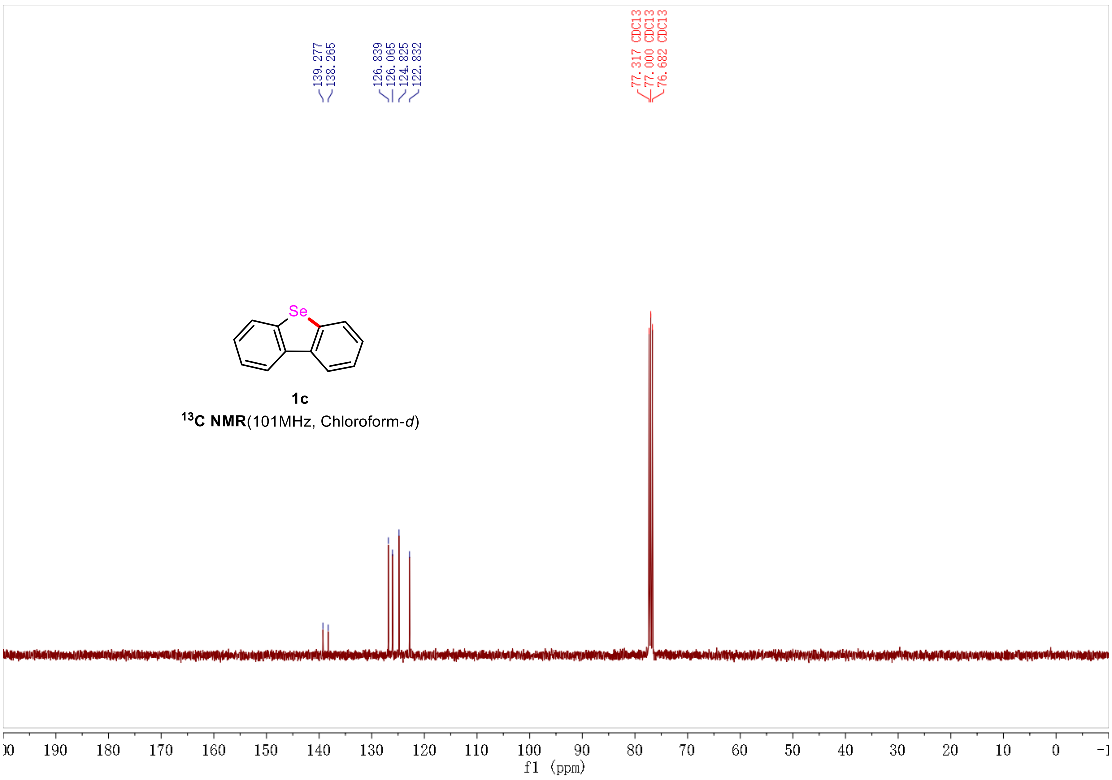
# 10. Copies of NMR spectra.



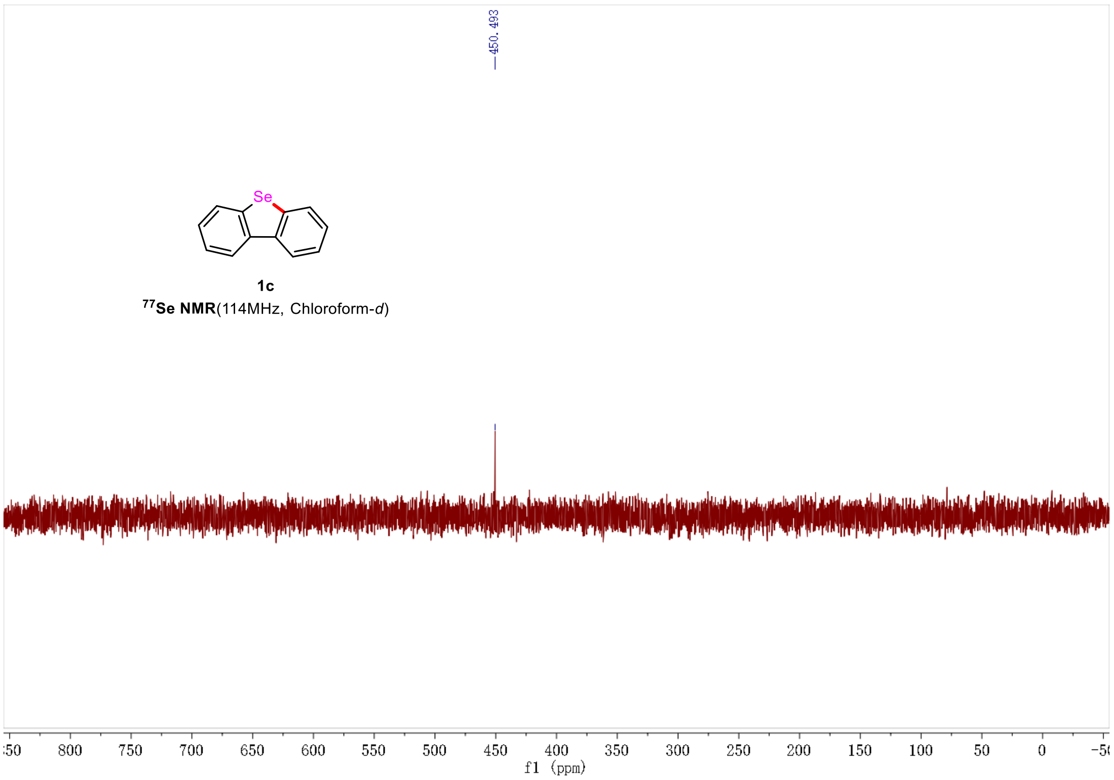
**1c**

**$^1$H NMR**(400MHz, Chloroform-*d*)

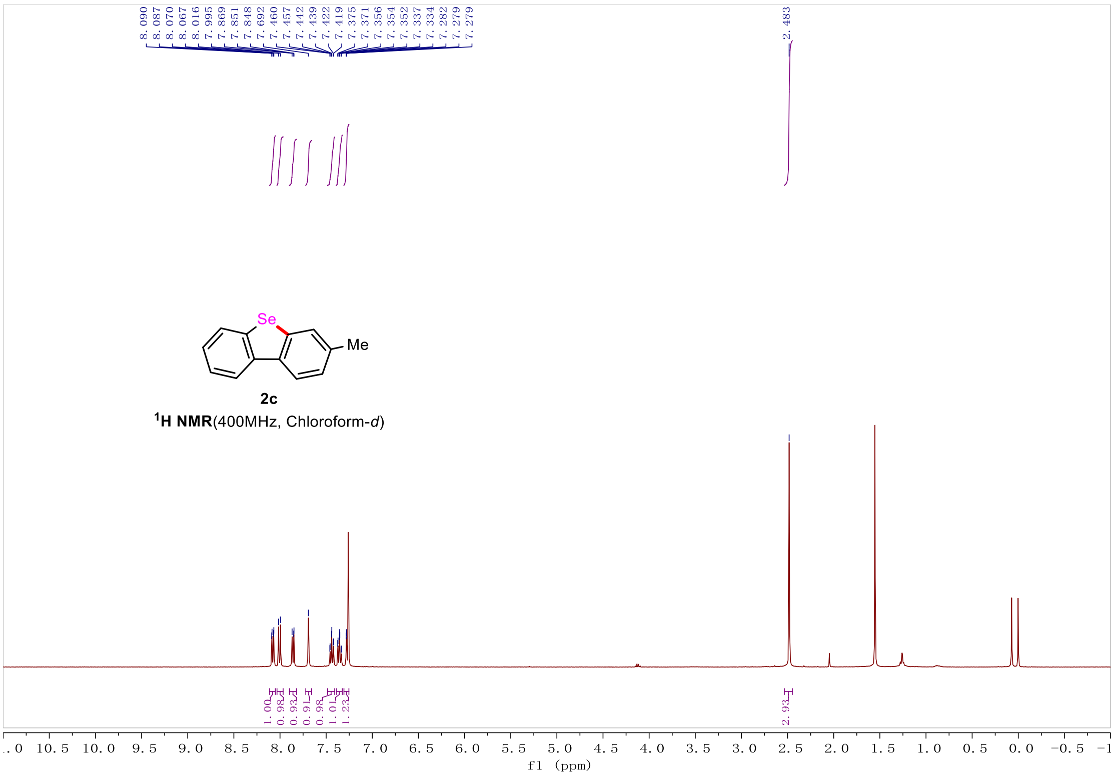


**1c**

**$^{13}$C NMR**(101MHz, Chloroform-*d*)


**1c**

$^{77}$**Se NMR**(114MHz, Chloroform-*d*)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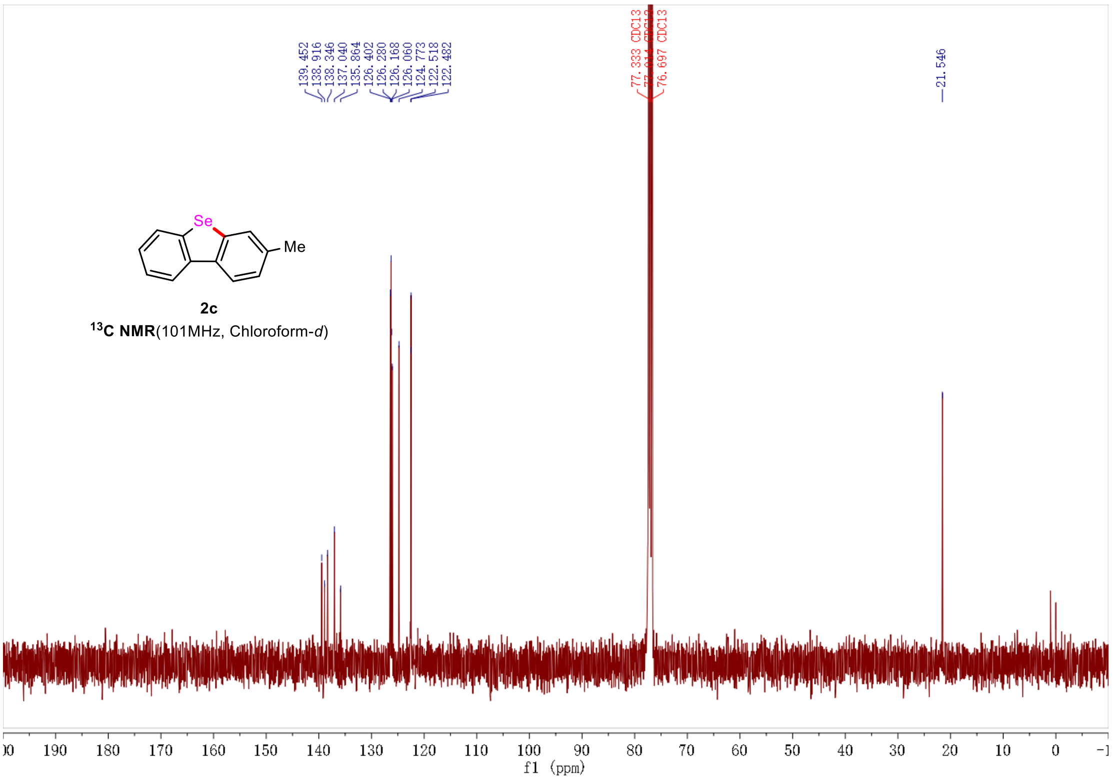
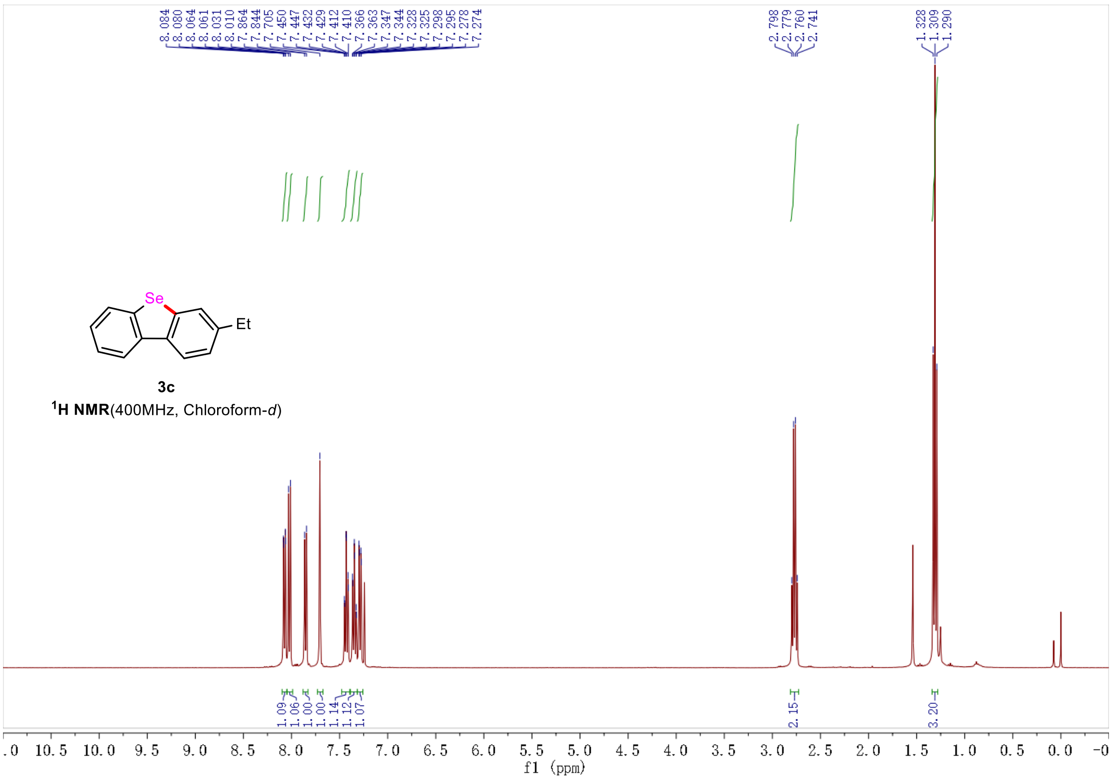
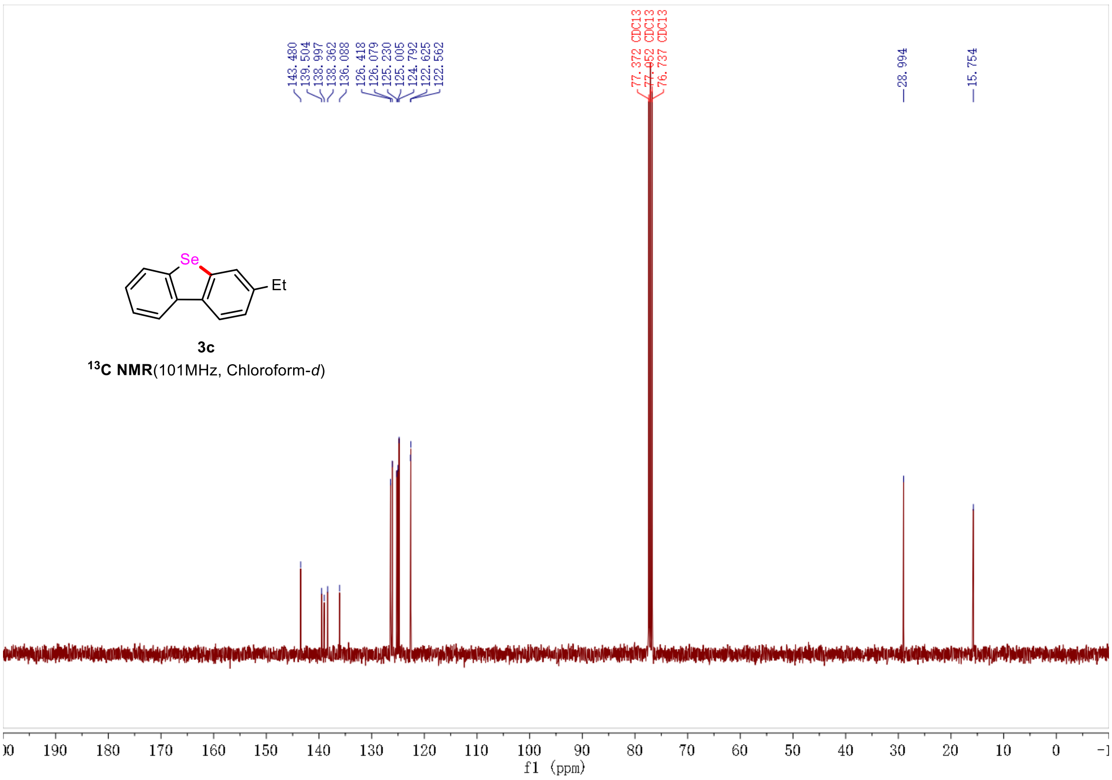
8.070
8.067
8.016
7.995
7.869
7.851
7.848
7.692
7.460
7.457
7.442
7.439
7.422
7.419
7.375
7.371
7.356
7.354
7.352
7.337
7.334
7.282
7.279
7.279
2.483
Se
Me
2c
1H NMR(400MHz, Chloroform-d)
1.00
0.98
0.93
0.91
0.98
1.01
1.23
2.93
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


139.452
138.916
138.346
137.040
135.864
126.402
126.280
126.168
126.060
124.773
122.518
122.482
77.333 CDCl3
76.697 CDCl3
21.546
Se
Me
2c
13C NMR(101MHz, Chloroform-d)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)



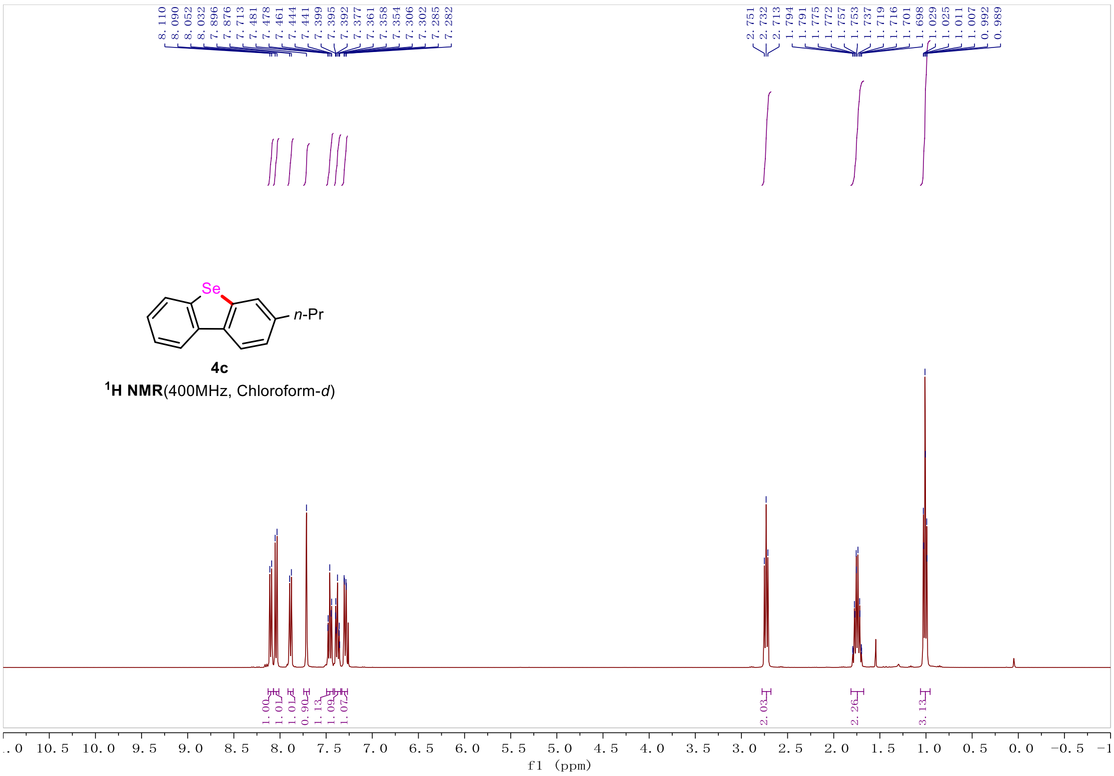
**3c**

**$^1$H NMR**(400MHz, Chloroform-*d*)



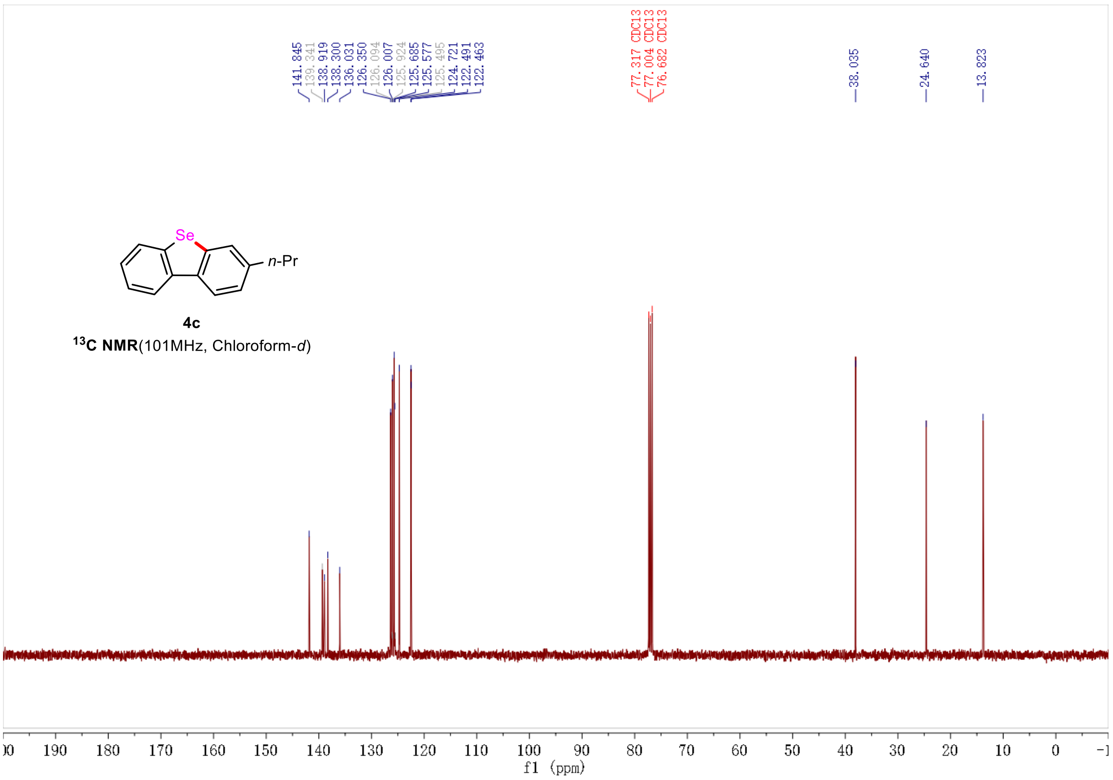
**3c**

**$^{13}$C NMR**(101MHz, Chloroform-*d*)



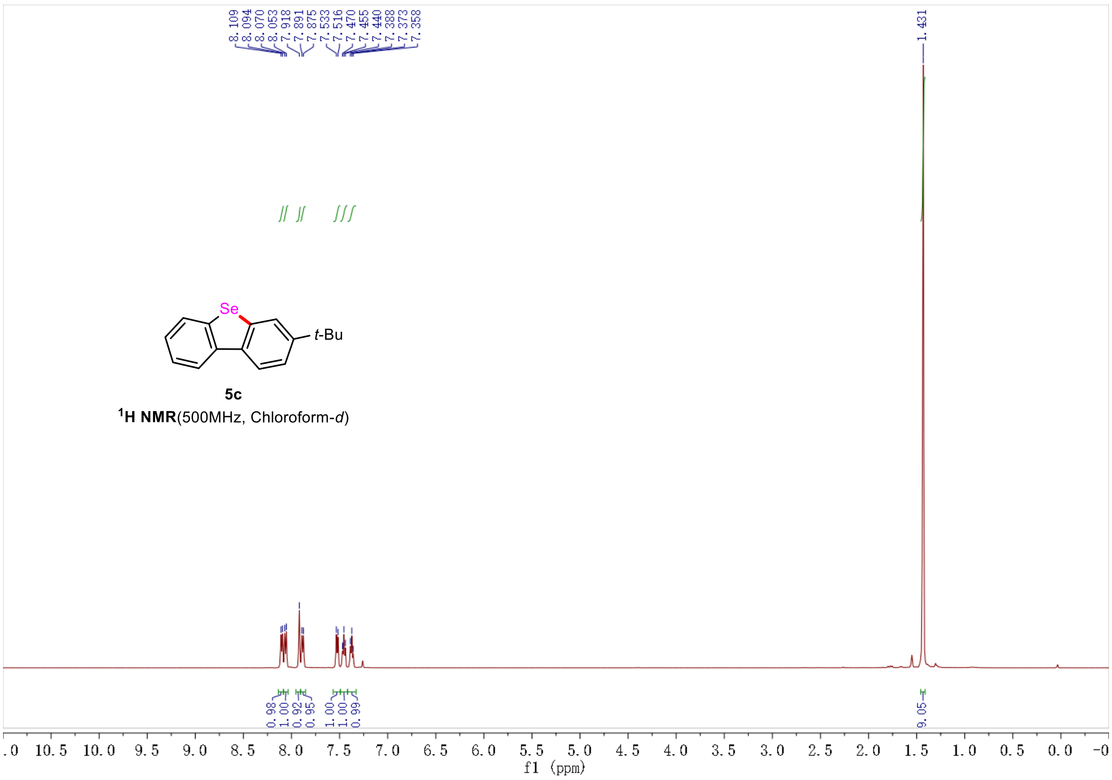
4c

**$^1$H NMR**(400MHz, Chloroform-*d*)



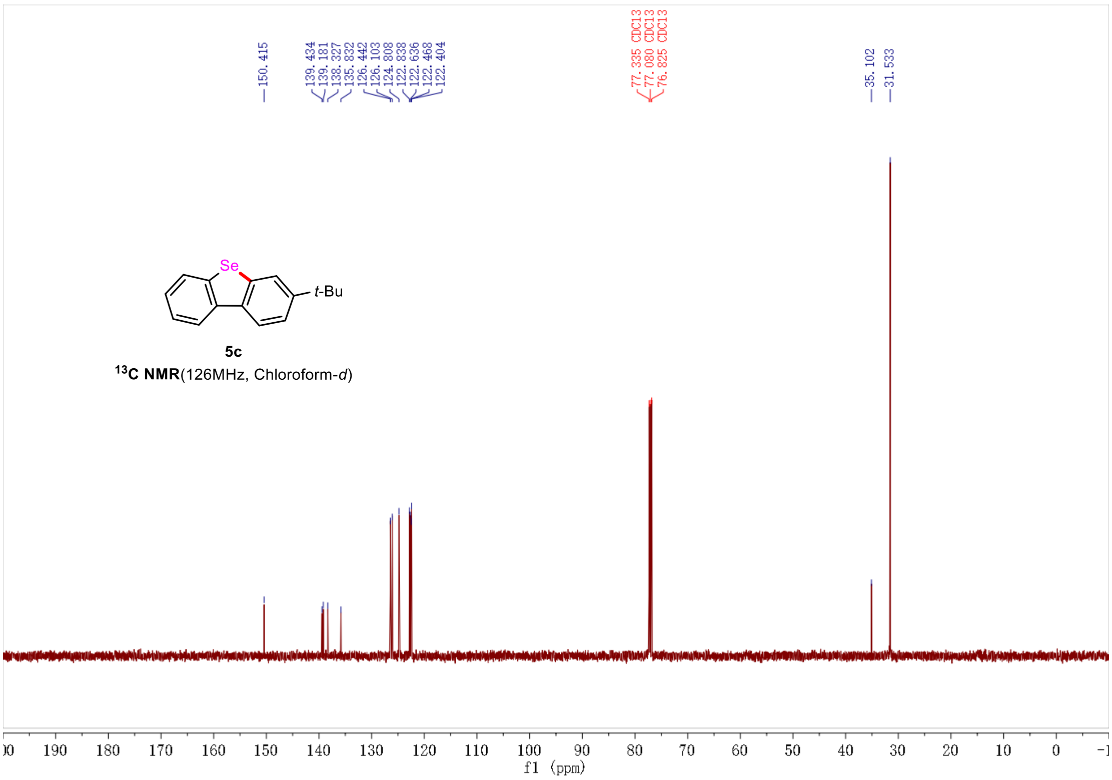
4c

**$^{13}$C NMR**(101MHz, Chloroform-*d*)



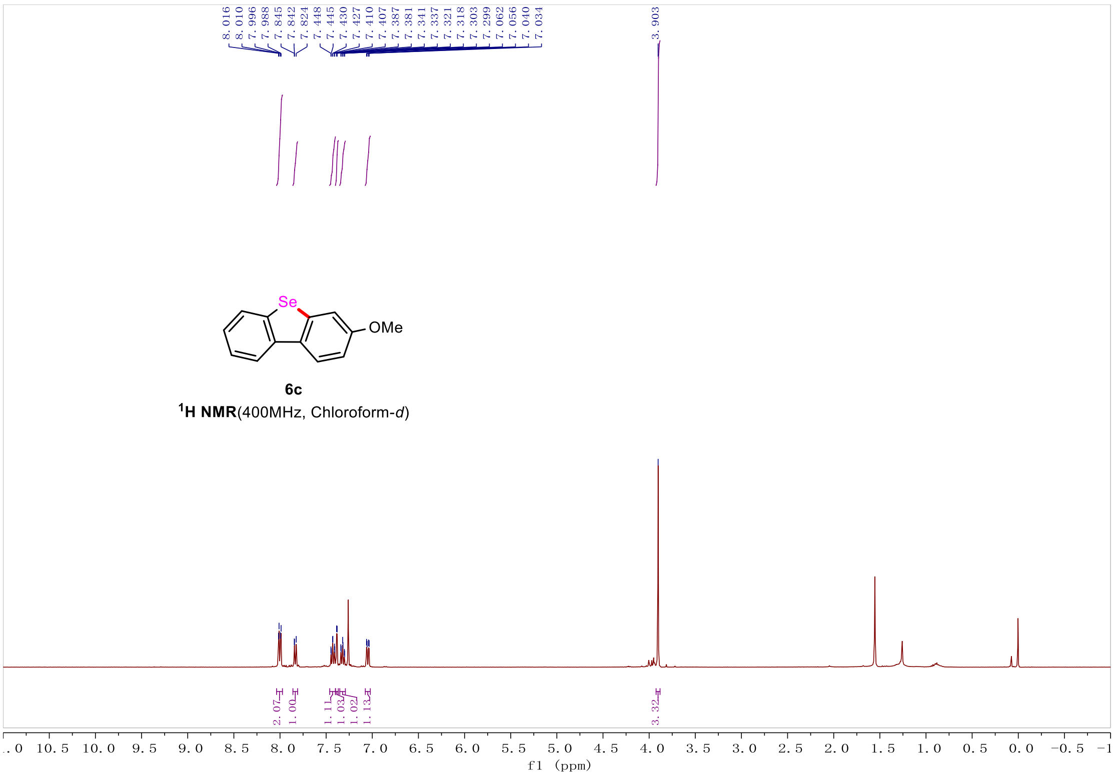
**5c**

**$^1$H NMR**(500MHz, Chloroform-*d*)



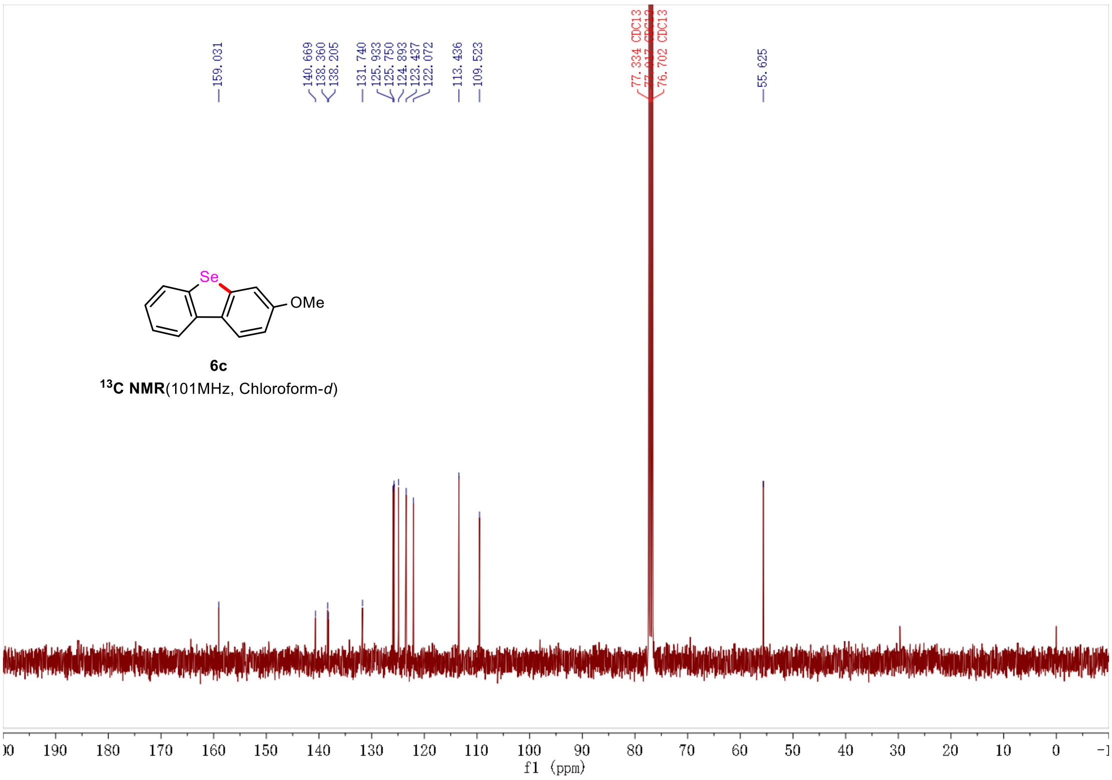
**5c**

**$^{13}$C NMR**(126MHz, Chloroform-*d*)



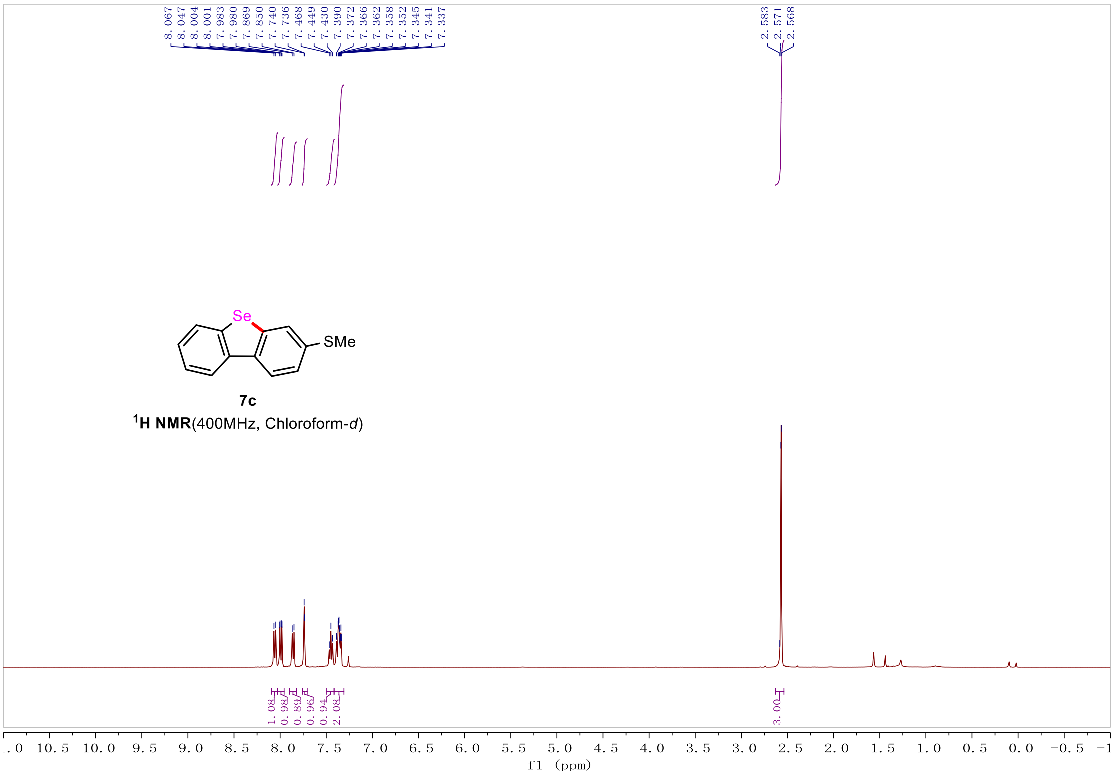
**6c**

$^1$**H NMR**(400MHz, Chloroform-*d*)



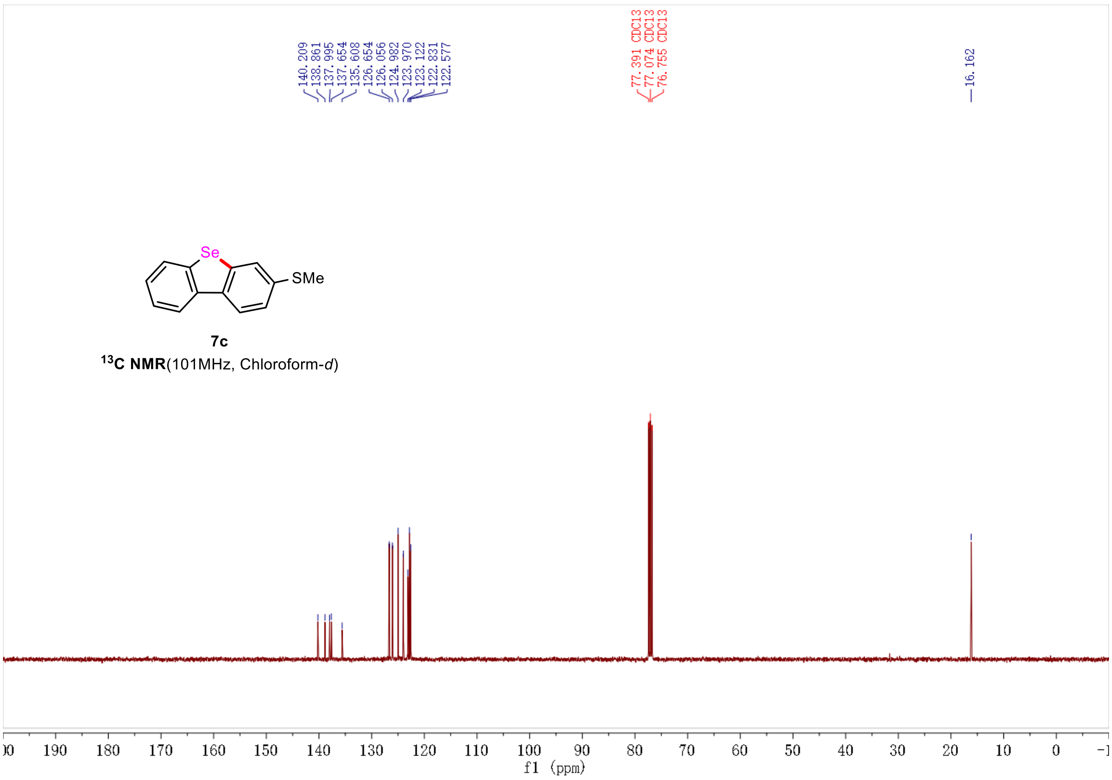
**6c**

$^{13}$**C NMR**(101MHz, Chloroform-*d*)



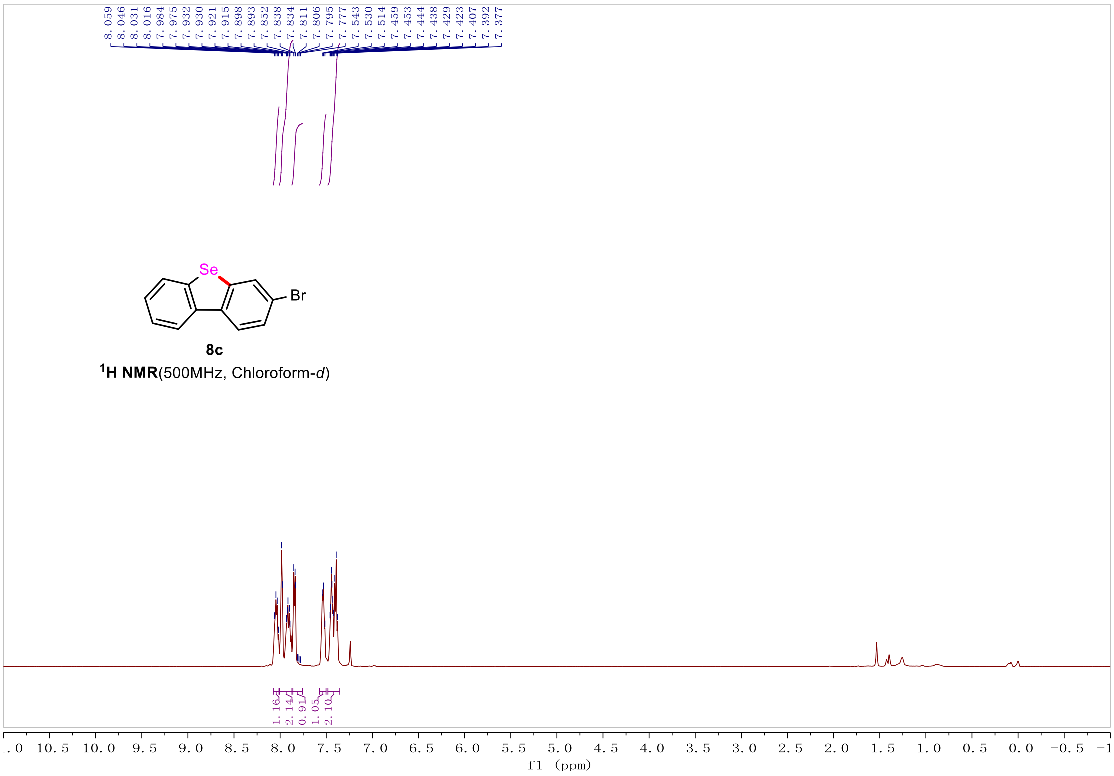
**7c**

$^{1}$**H NMR**(400MHz, Chloroform-*d*)



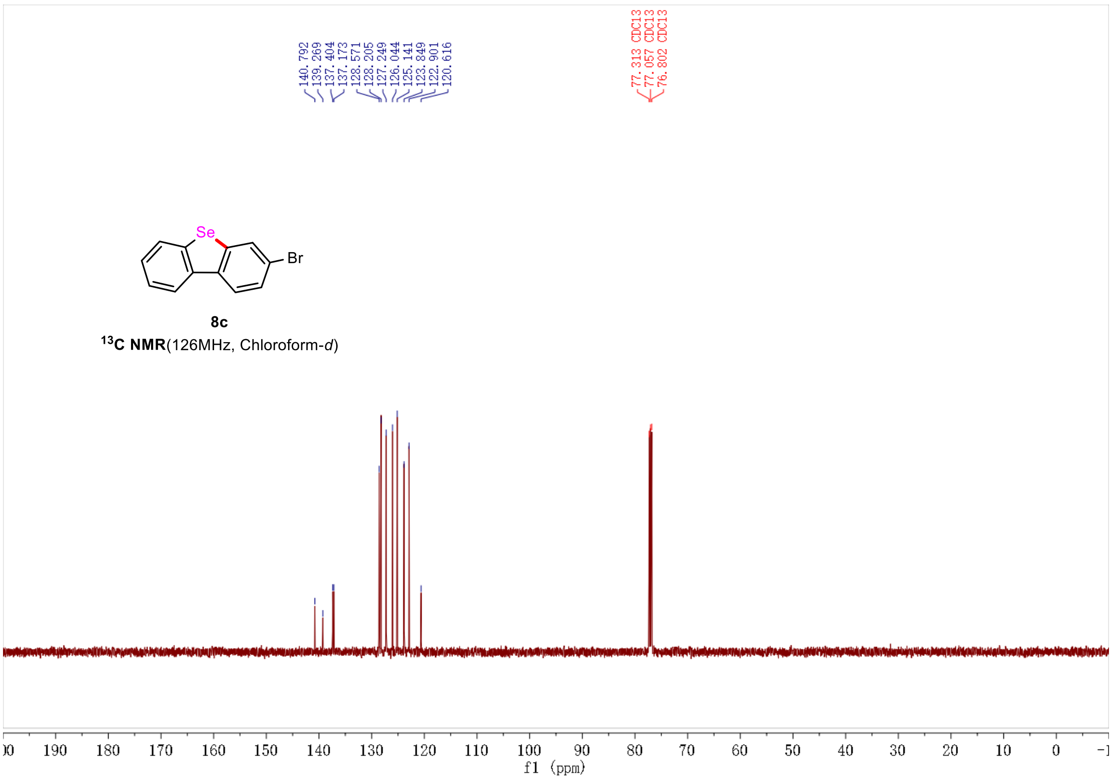
**7c**

$^{13}$**C NMR**(101MHz, Chloroform-*d*)



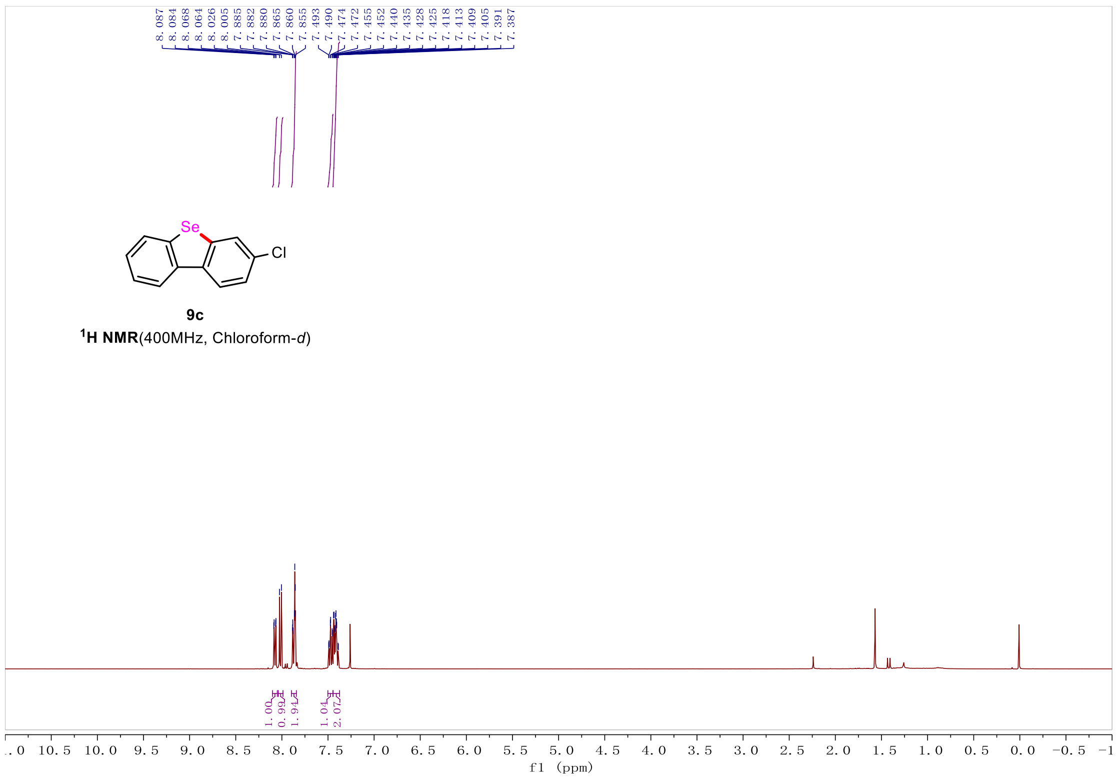
**8c**

**$^1$H NMR**(500MHz, Chloroform-*d*)



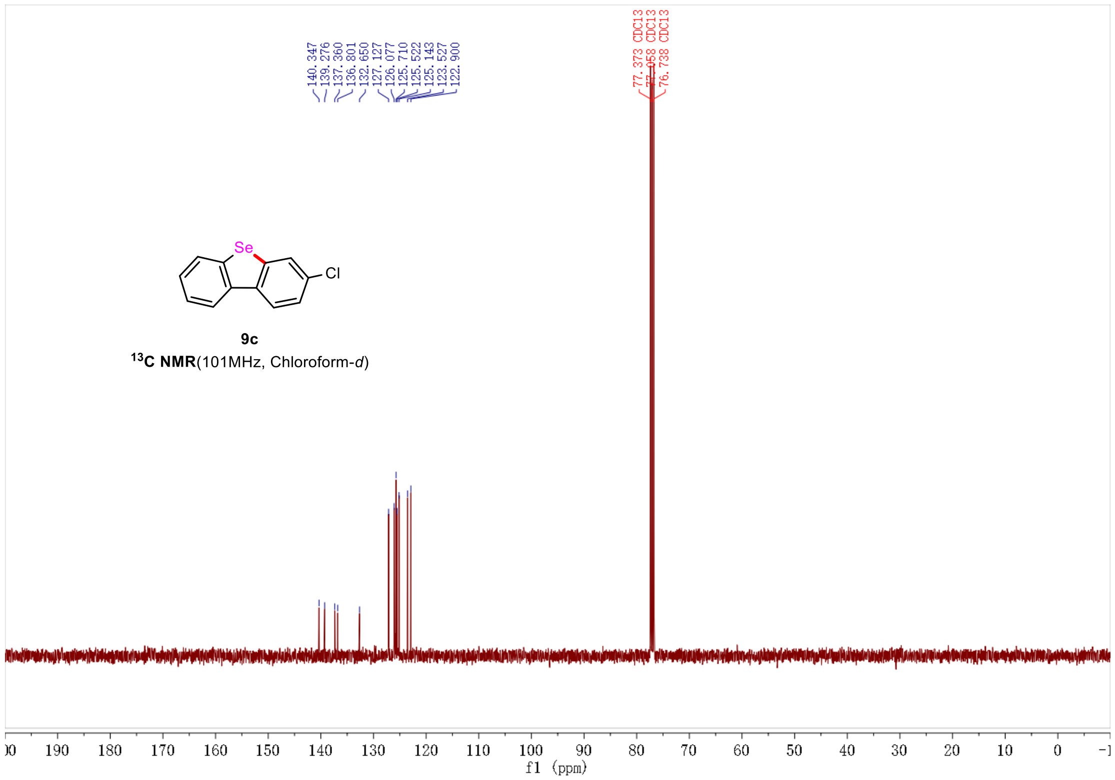
**8c**

**$^{13}$C NMR**(126MHz, Chloroform-*d*)



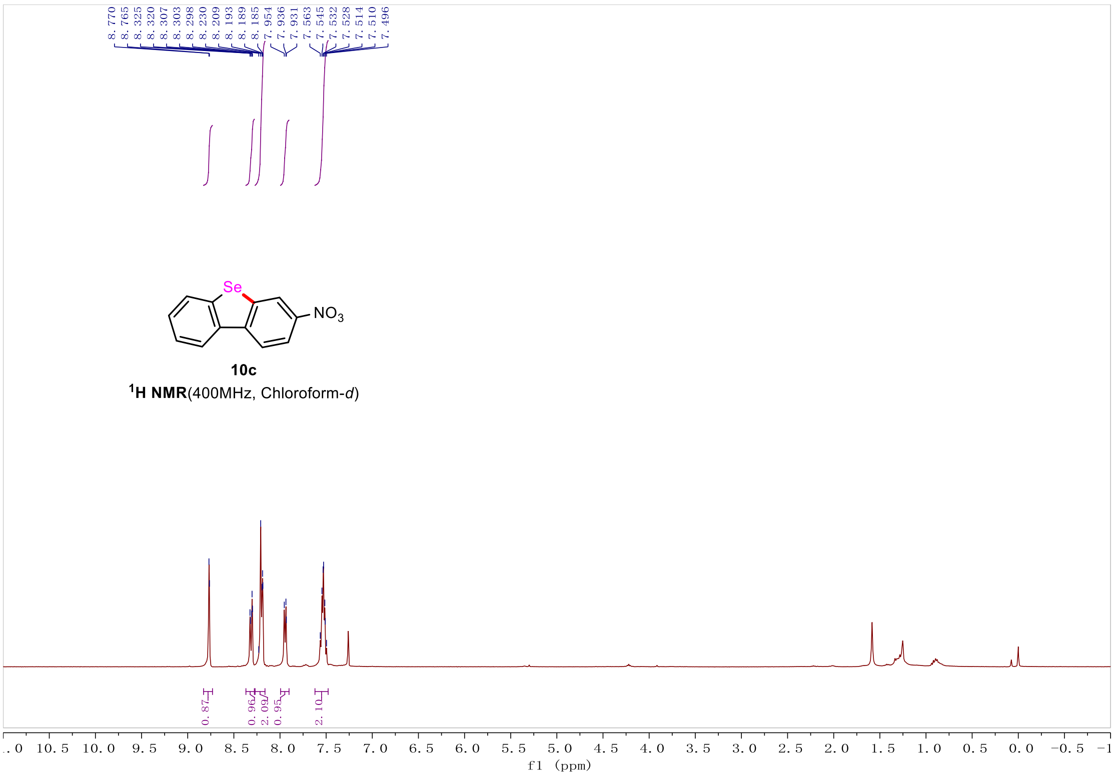
**9c**

**$^1$H NMR**(400MHz, Chloroform-*d*)



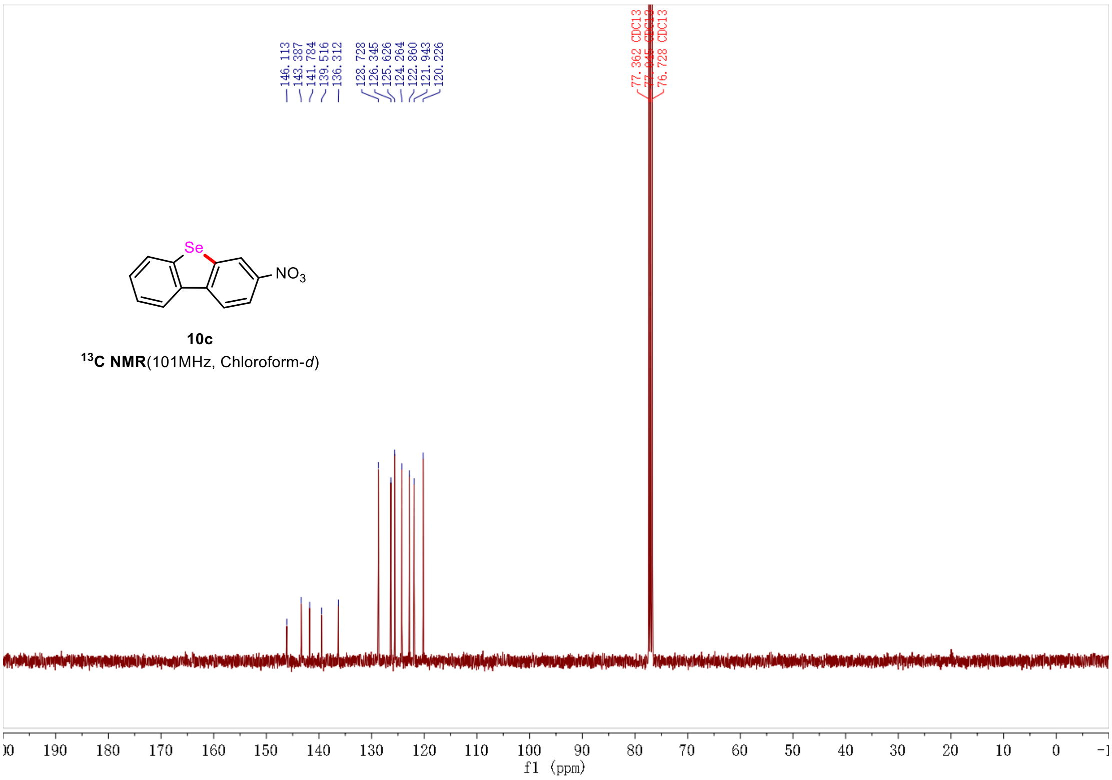
**9c**

**$^{13}$C NMR**(101MHz, Chloroform-*d*)



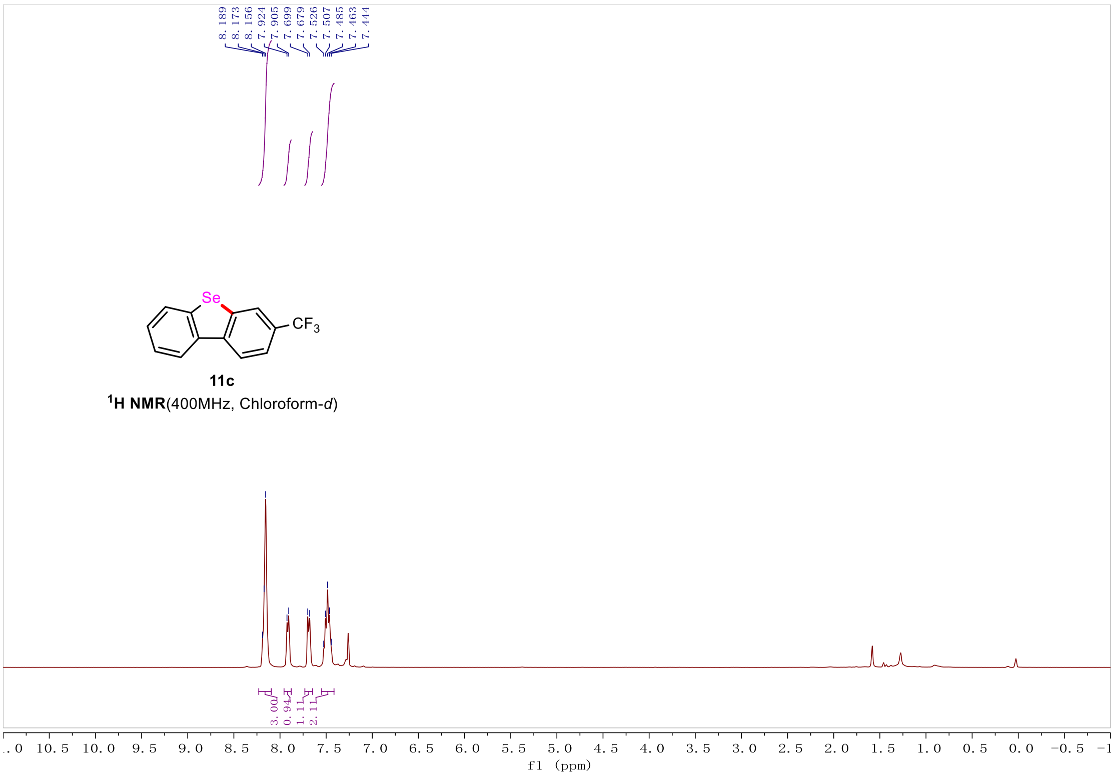
**10c**

$^{1}$**H NMR**(400MHz, Chloroform-*d*)

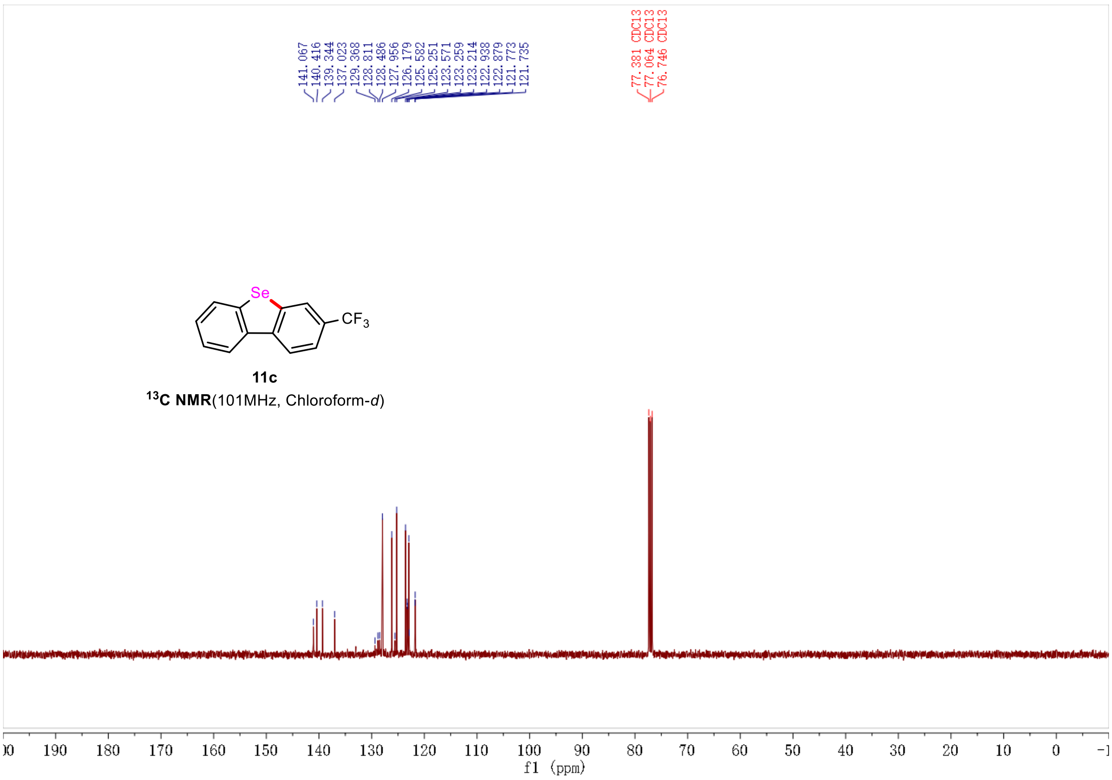


**10c**

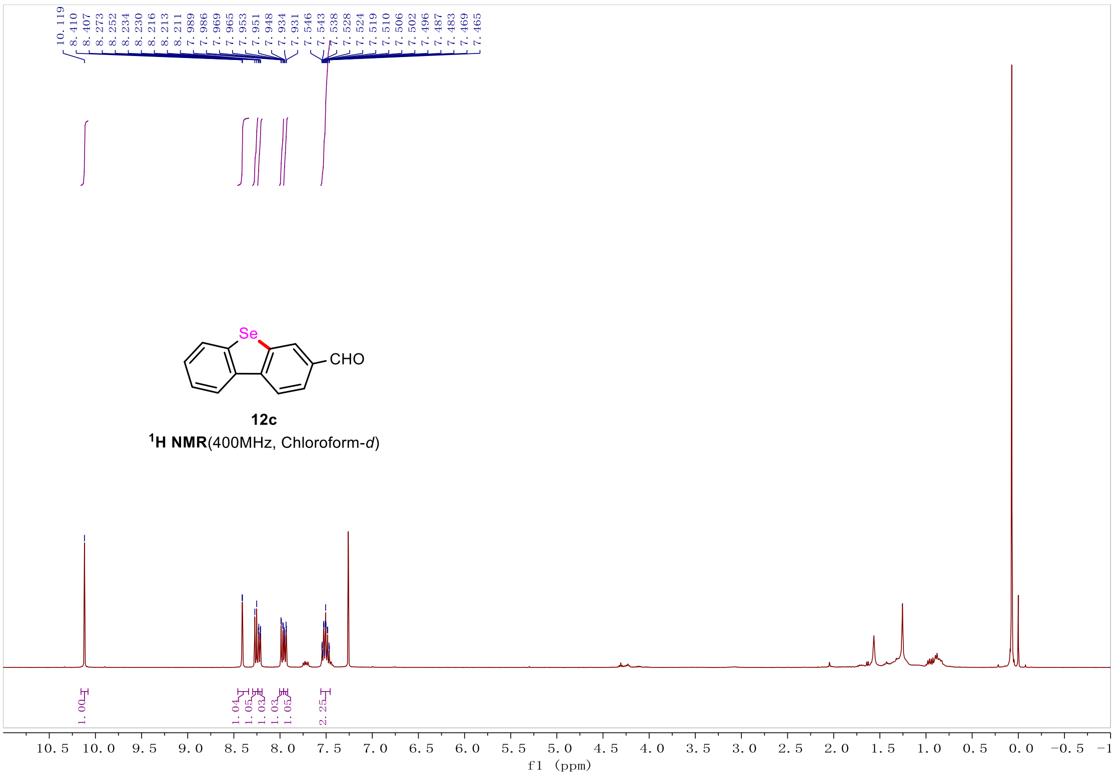
$^{13}$**C NMR**(101MHz, Chloroform-*d*)


11c

$^{1}$H **NMR**(400MHz, Chloroform-*d*)

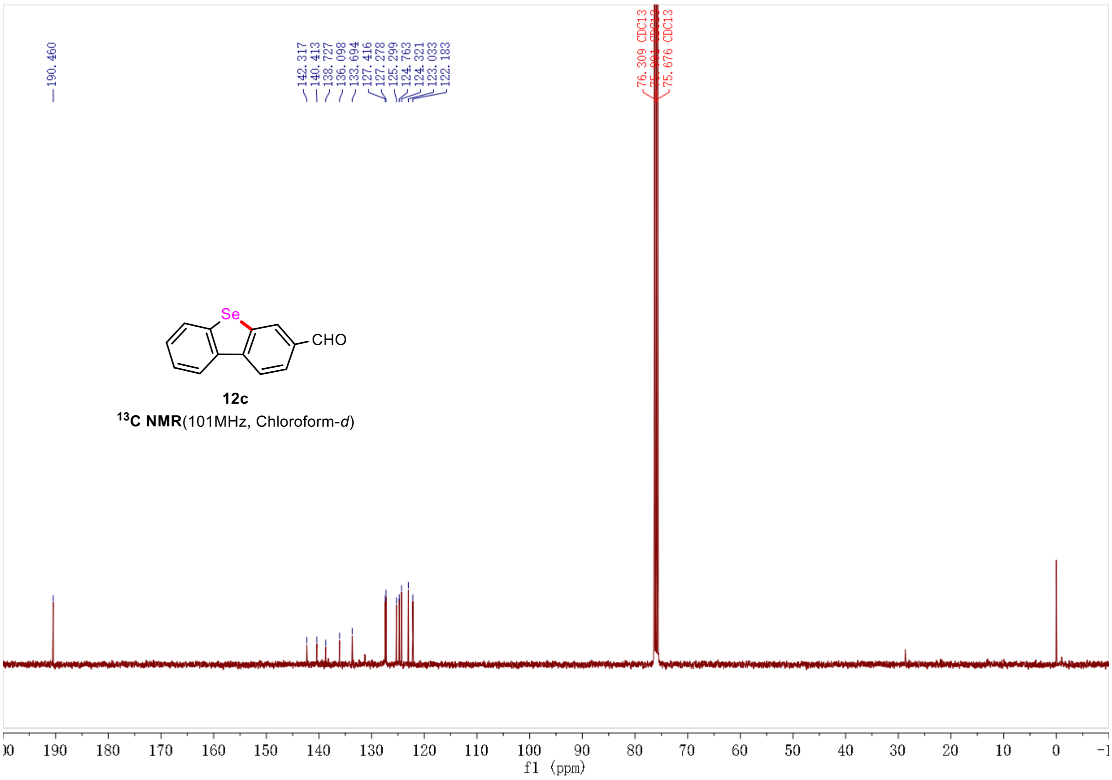

11c

$^{13}$C **NMR**(101MHz, Chloroform-*d*)



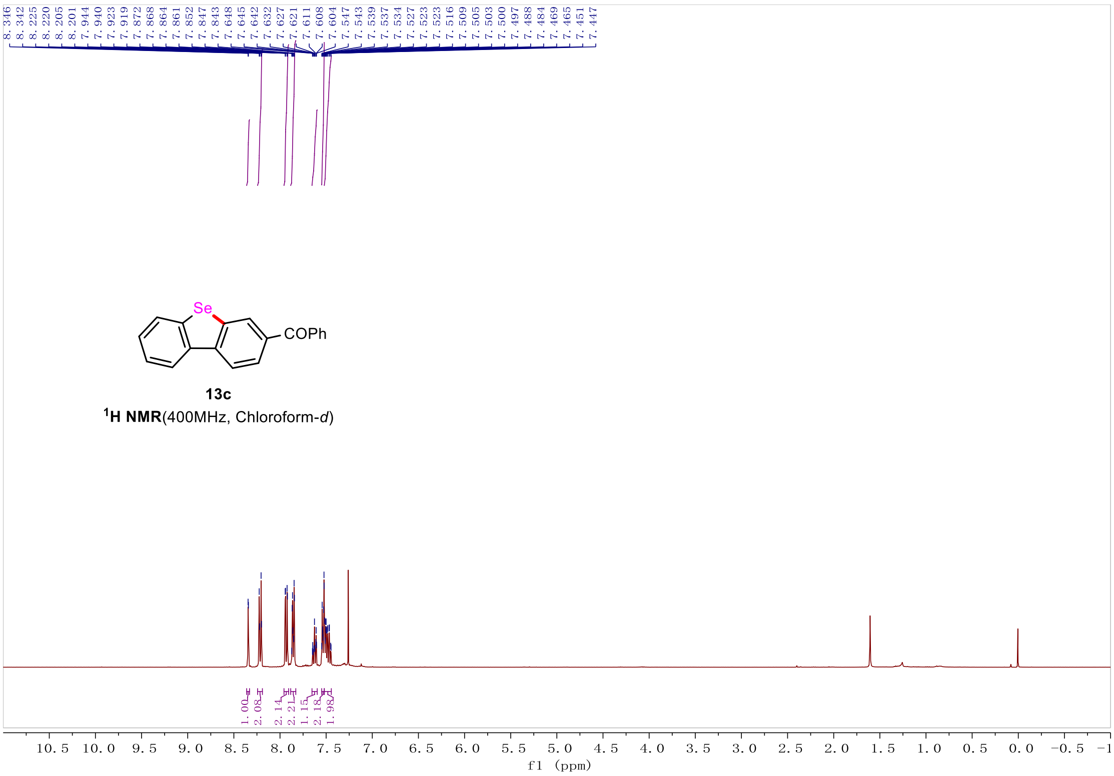
**12c**

**$^1$H NMR**(400MHz, Chloroform-*d*)



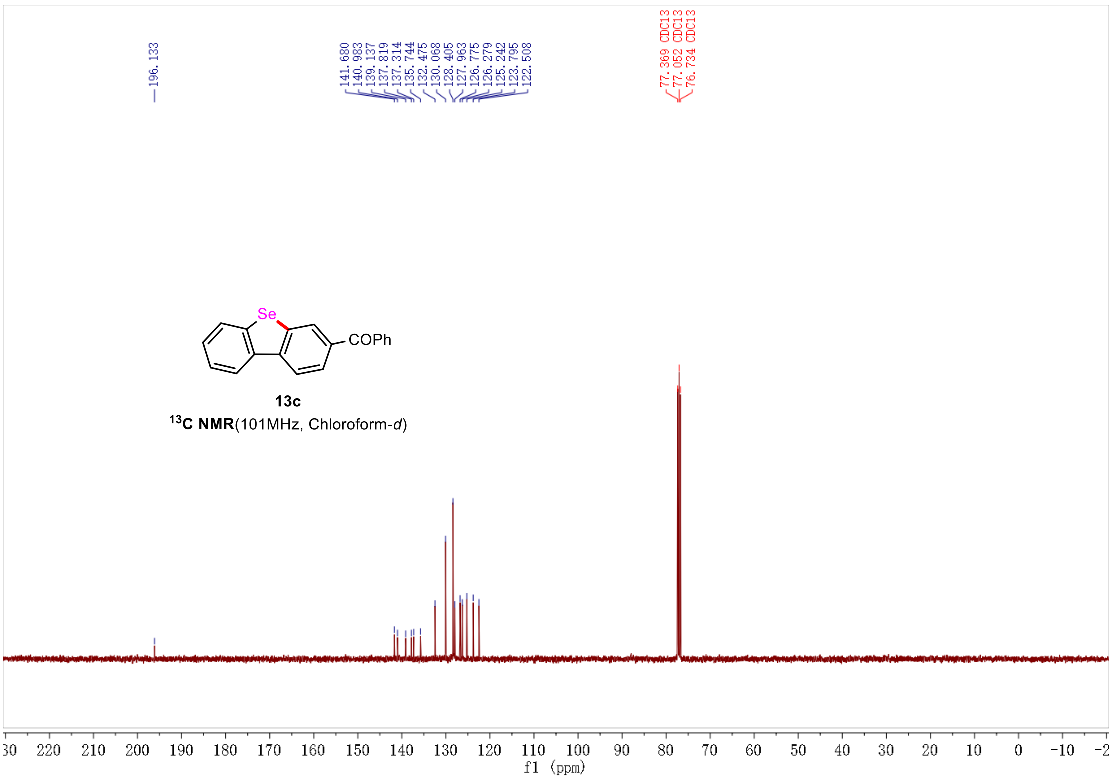
**12c**

**$^{13}$C NMR**(101MHz, Chloroform-*d*)



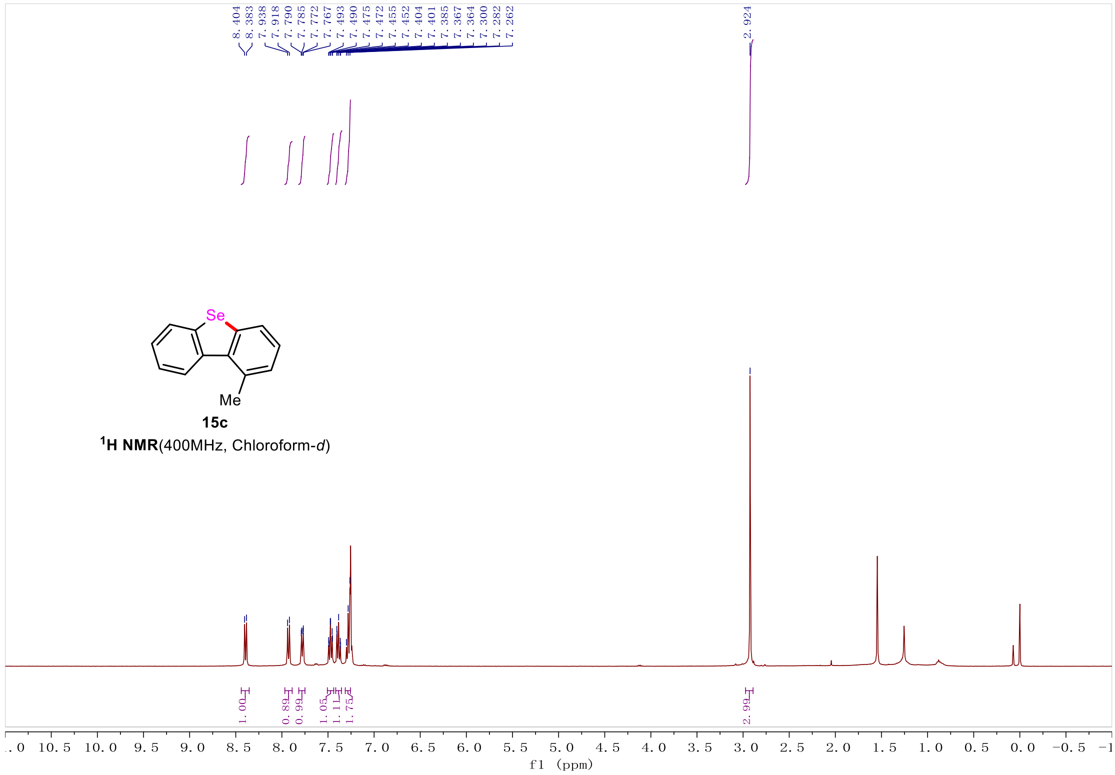
**13c**

**$^1$H NMR**(400MHz, Chloroform-*d*)



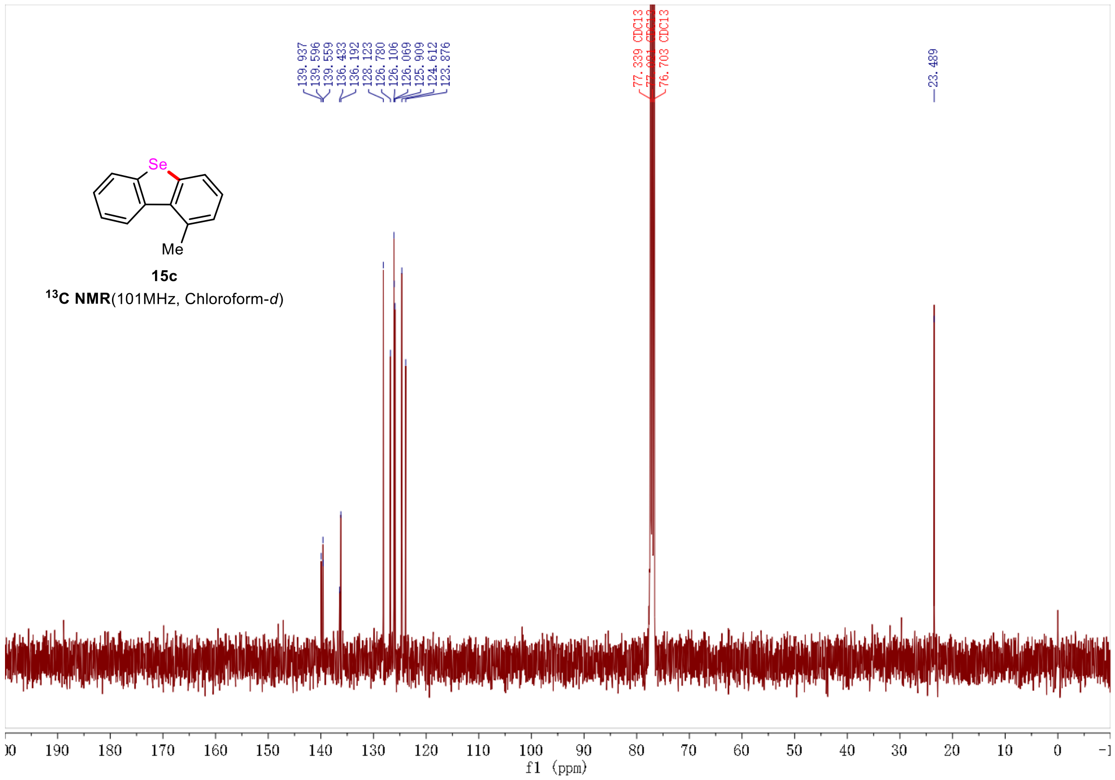
**13c**

**$^{13}$C NMR**(101MHz, Chloroform-*d*)



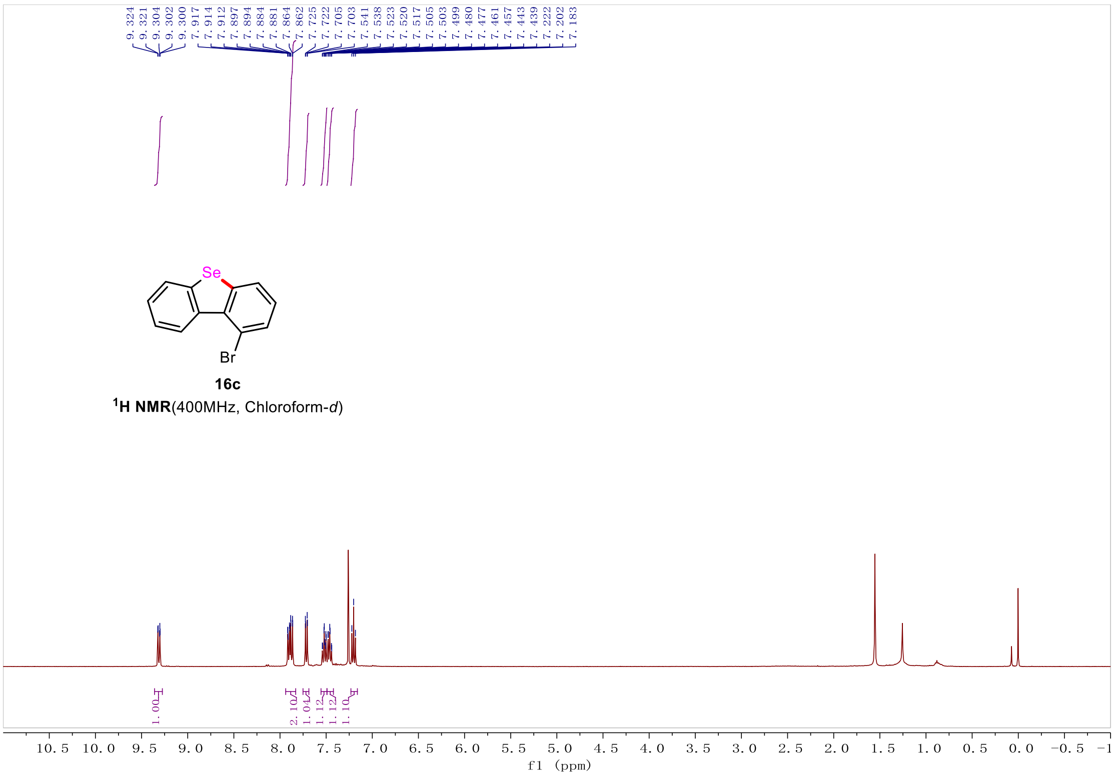
**15c**

**$^1$H NMR**(400MHz, Chloroform-*d*)



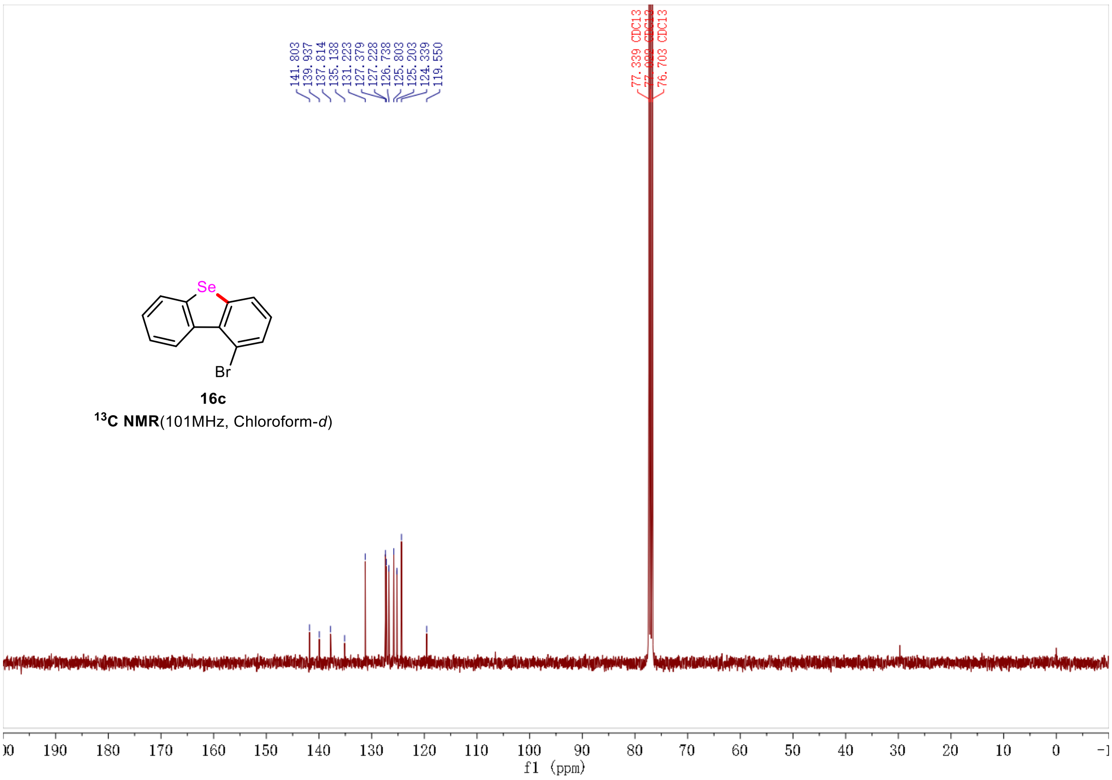
**15c**

**$^{13}$C NMR**(101MHz, Chloroform-*d*)



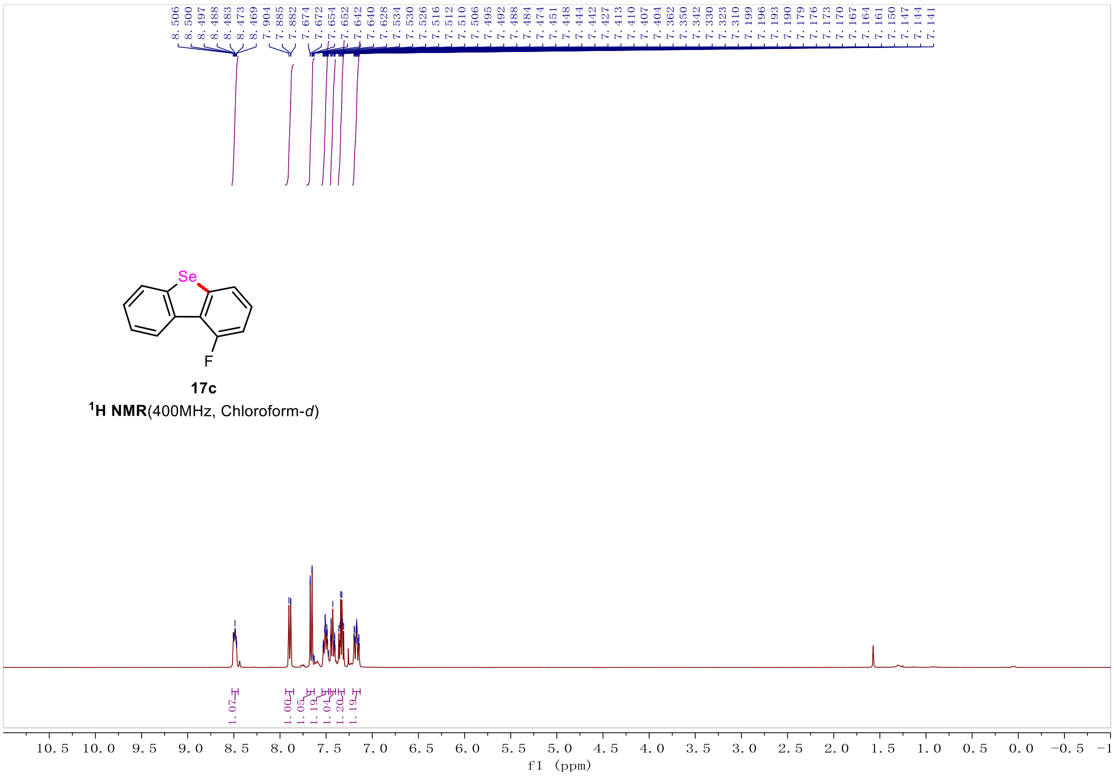
**16c**

$^1$**H NMR**(400MHz, Chloroform-*d*)



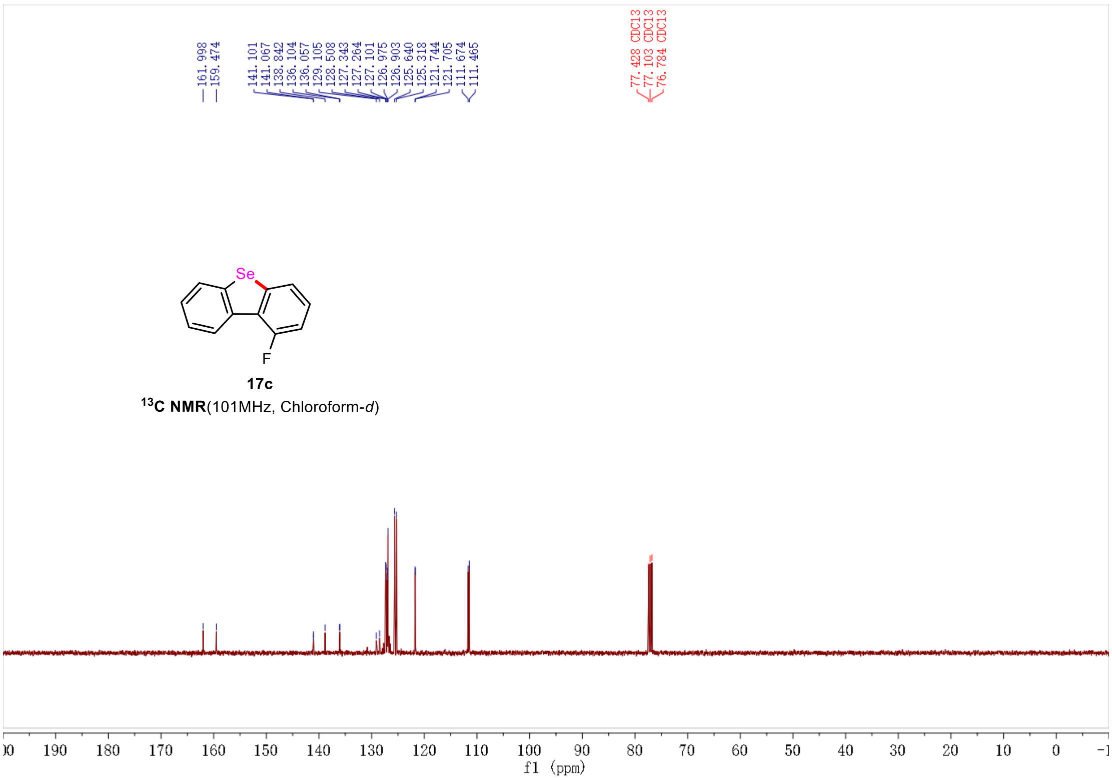
**16c**

$^{13}$**C NMR**(101MHz, Chloroform-*d*)



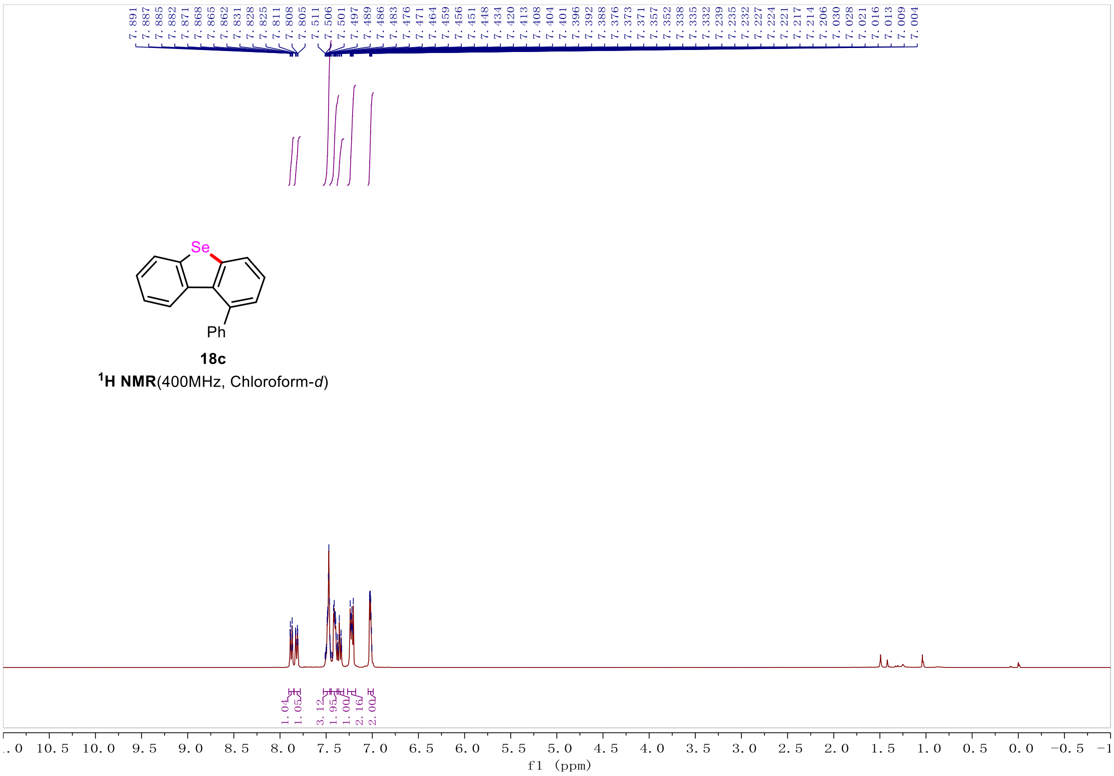
**17c**

$^1$**H NMR**(400MHz, Chloroform-*d*)



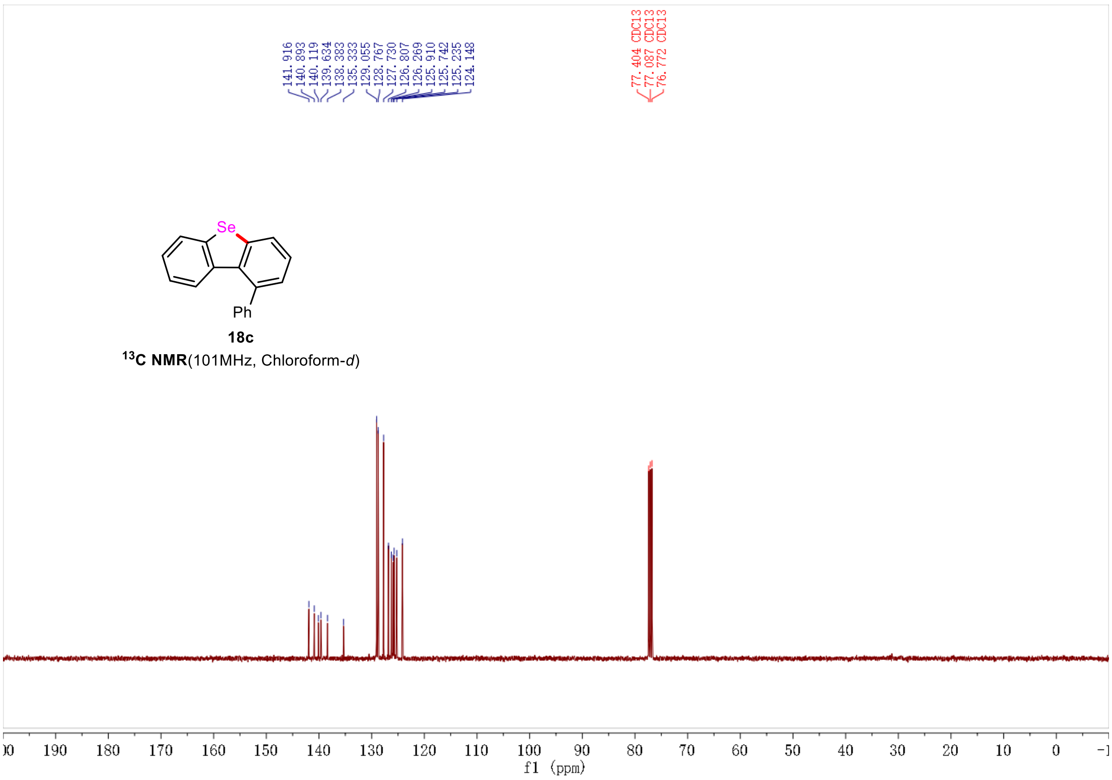
**17c**

$^{13}$**C NMR**(101MHz, Chloroform-*d*)



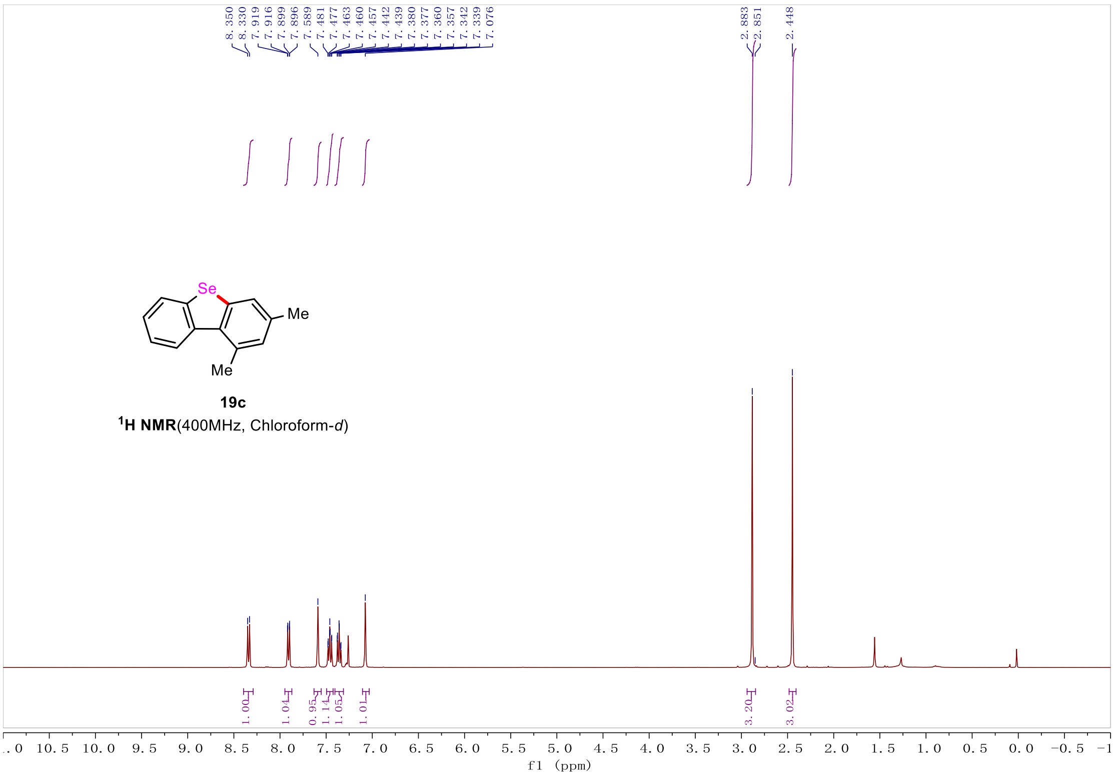
**18c**

**$^1$H NMR**(400MHz, Chloroform-*d*)



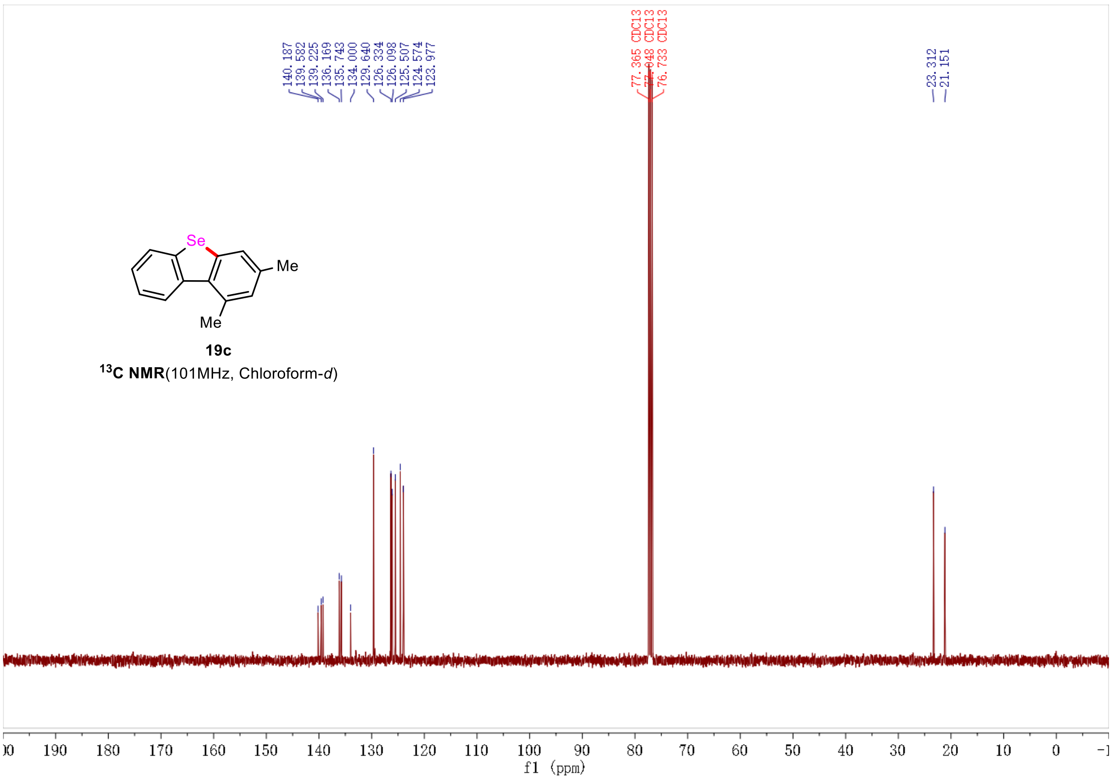
**18c**

**$^{13}$C NMR**(101MHz, Chloroform-*d*)



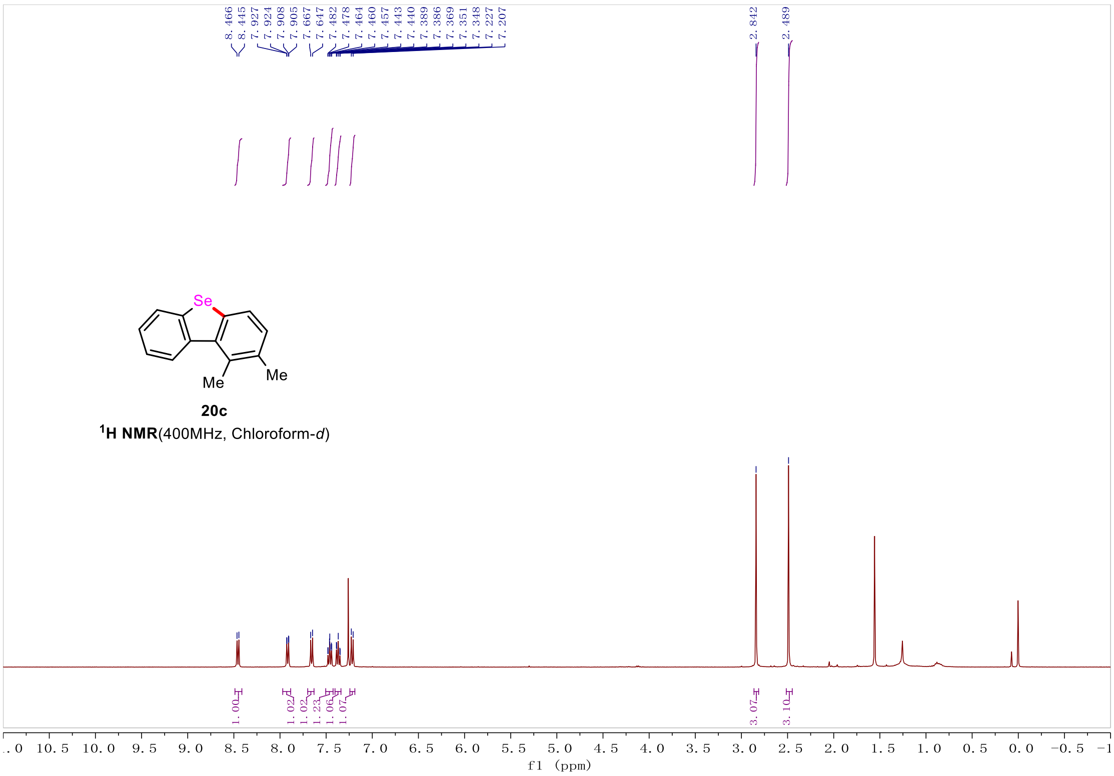
**19c**

$^1$**H NMR**(400MHz, Chloroform-*d*)



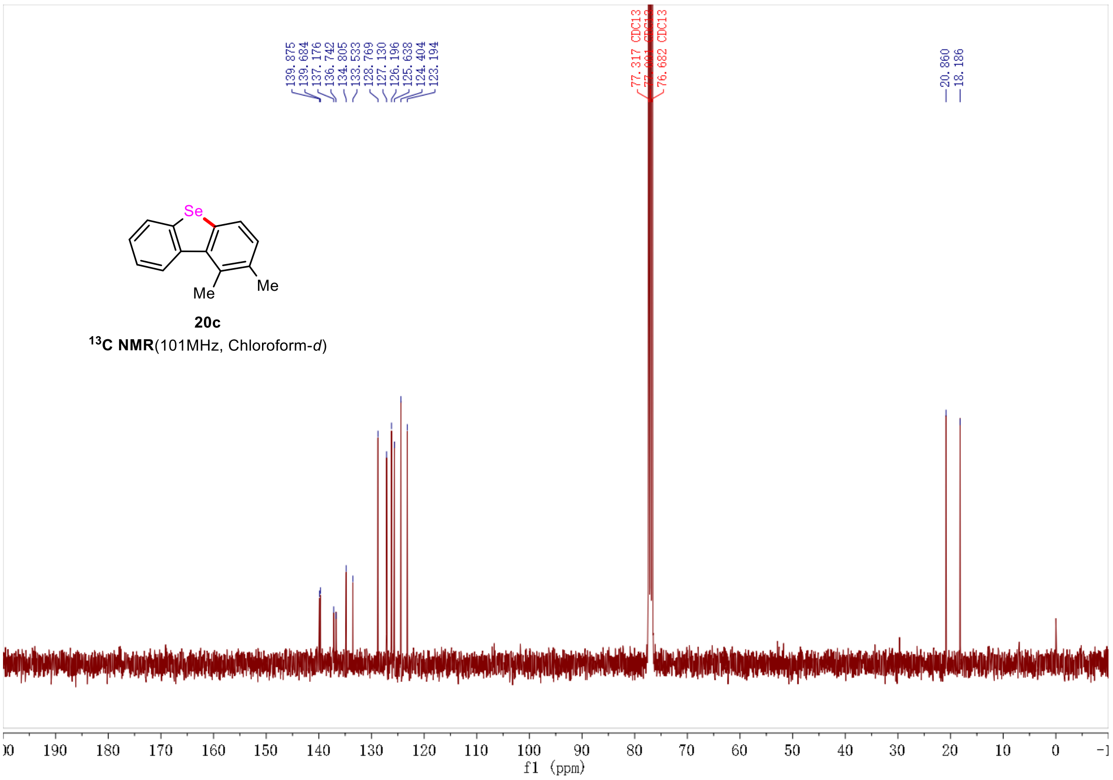
**19c**

$^{13}$**C NMR**(101MHz, Chloroform-*d*)



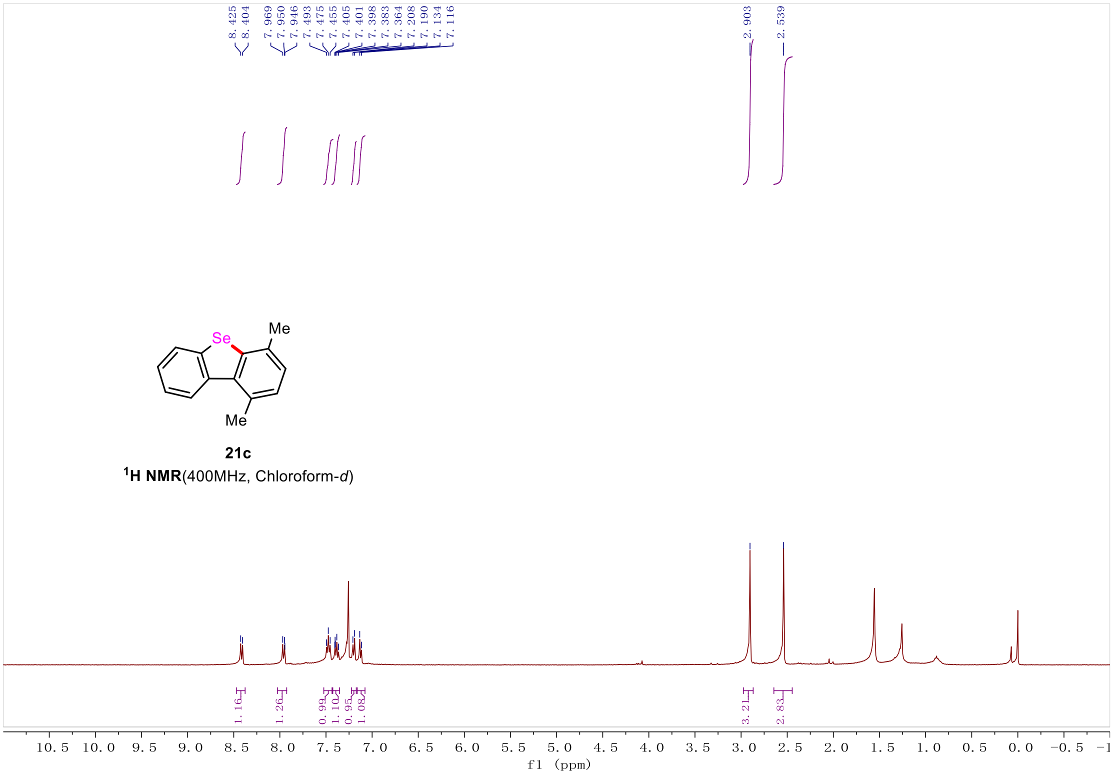
**20c**

**$^1$H NMR**(400MHz, Chloroform-*d*)



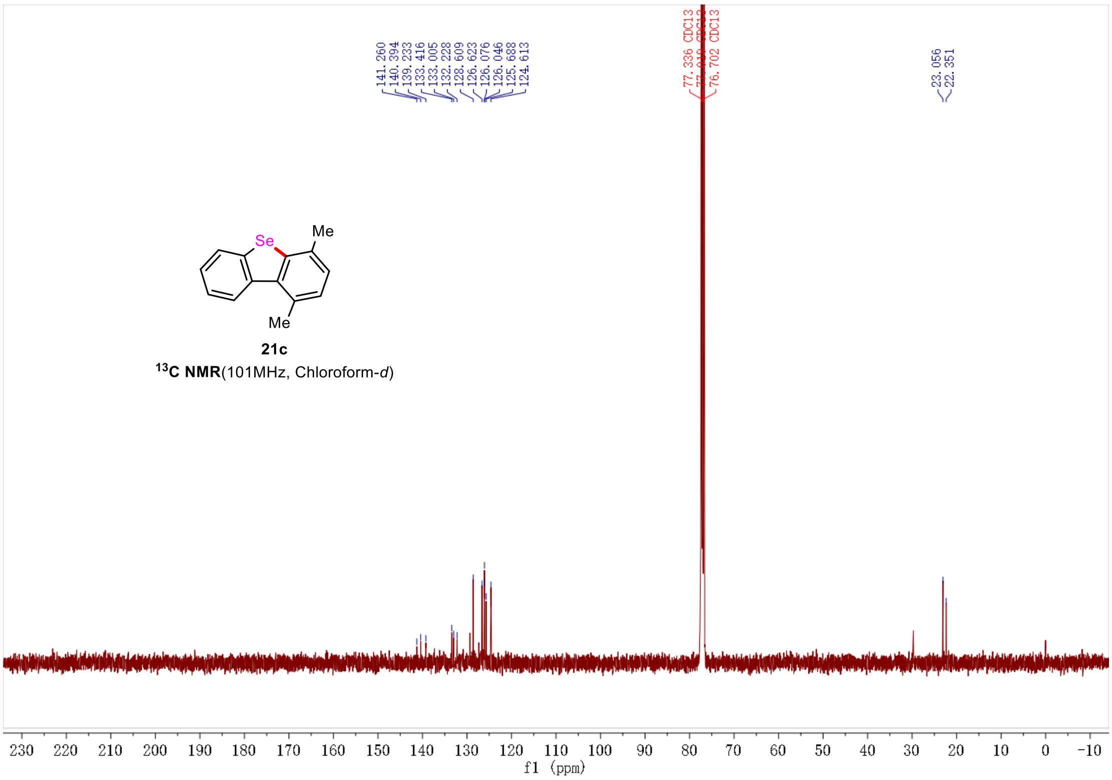
**20c**

**$^{13}$C NMR**(101MHz, Chloroform-*d*)



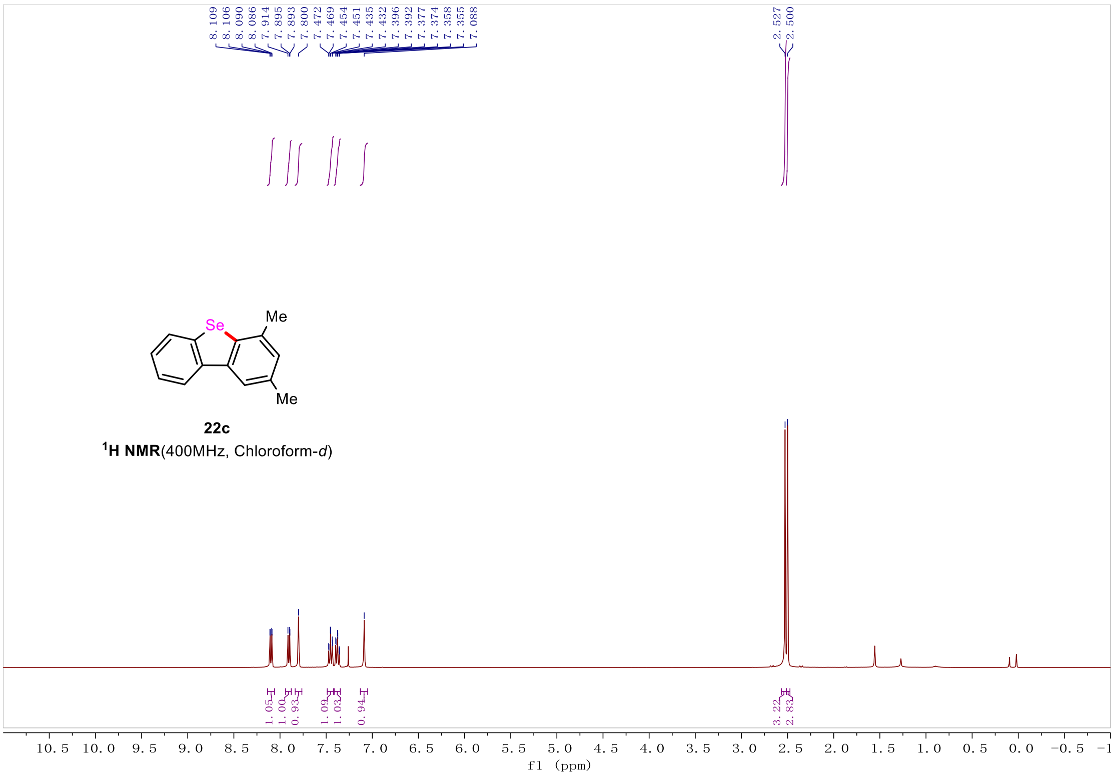
**21c**

$^{1}$**H NMR**(400MHz, Chloroform-*d*)



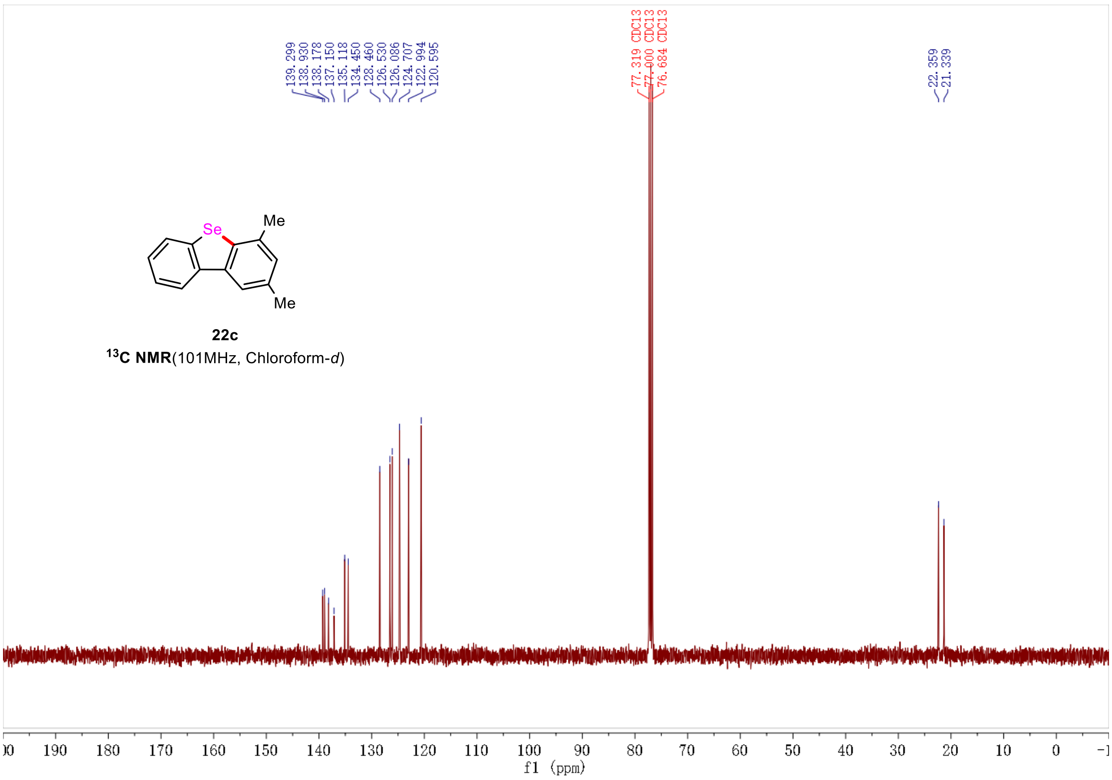
**21c**

$^{13}$**C NMR**(101MHz, Chloroform-*d*)



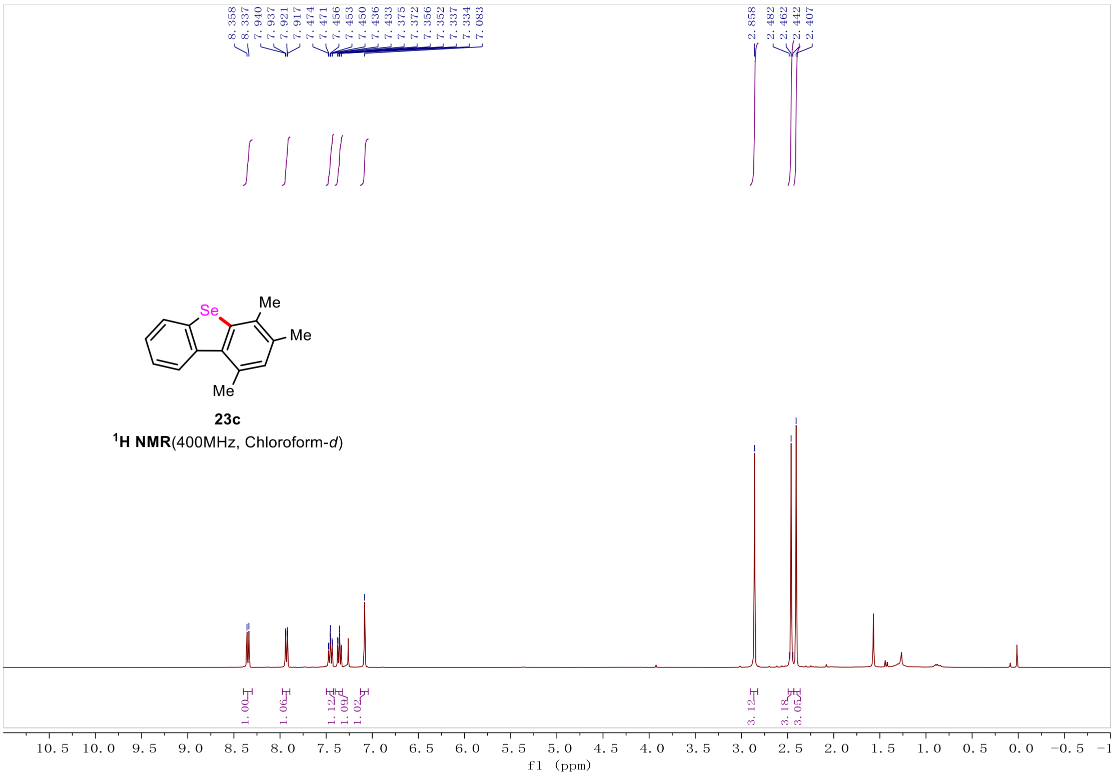
**22c**

$^{1}$**H NMR**(400MHz, Chloroform-*d*)



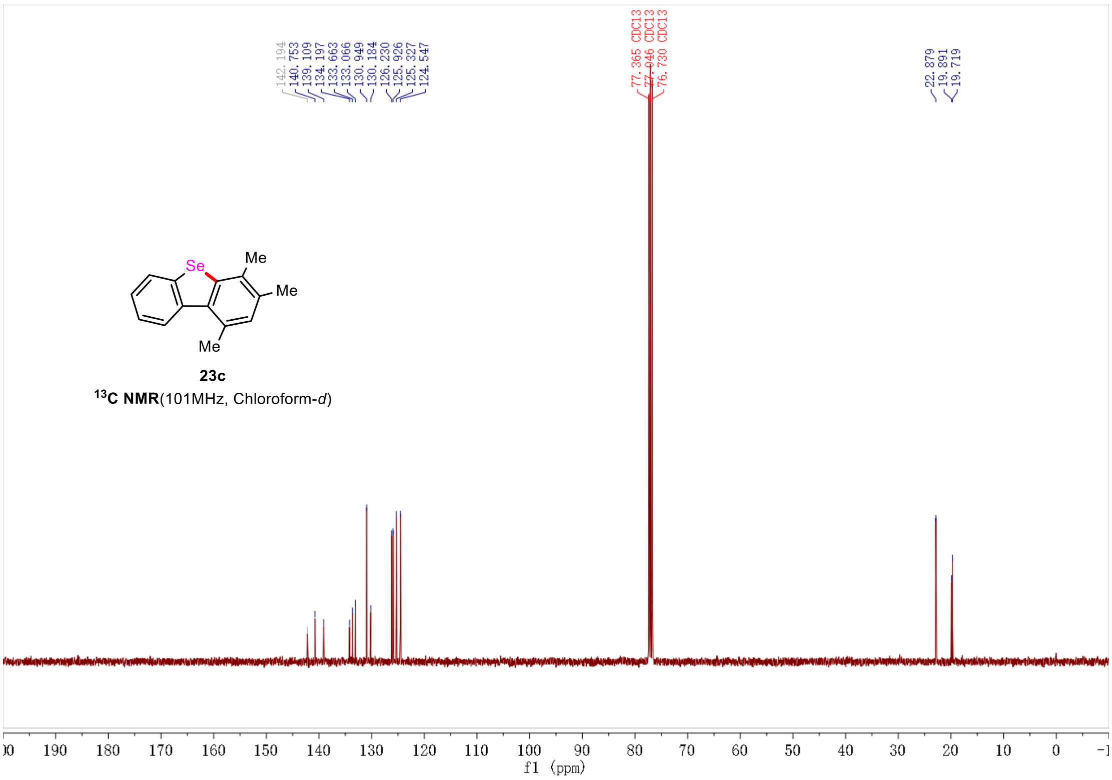
**22c**

$^{13}$**C NMR**(101MHz, Chloroform-*d*)



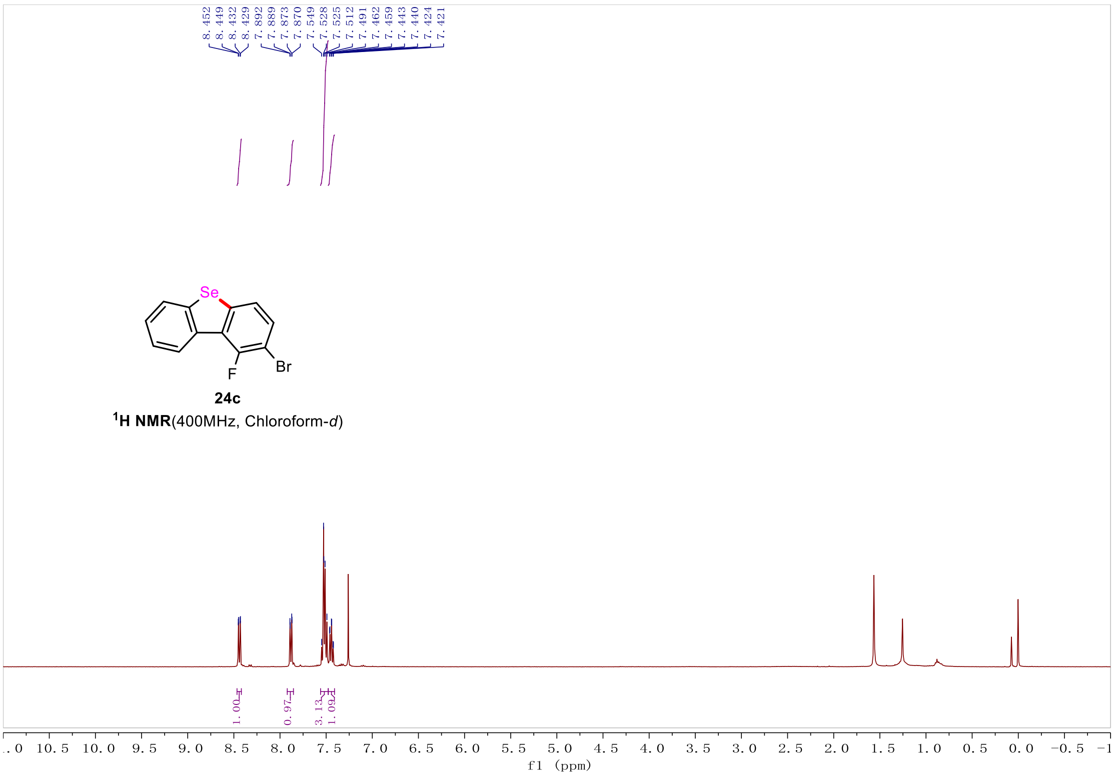
**23c**

$^{1}$**H NMR**(400MHz, Chloroform-*d*)



**23c**

$^{13}$**C NMR**(101MHz, Chloroform-*d*)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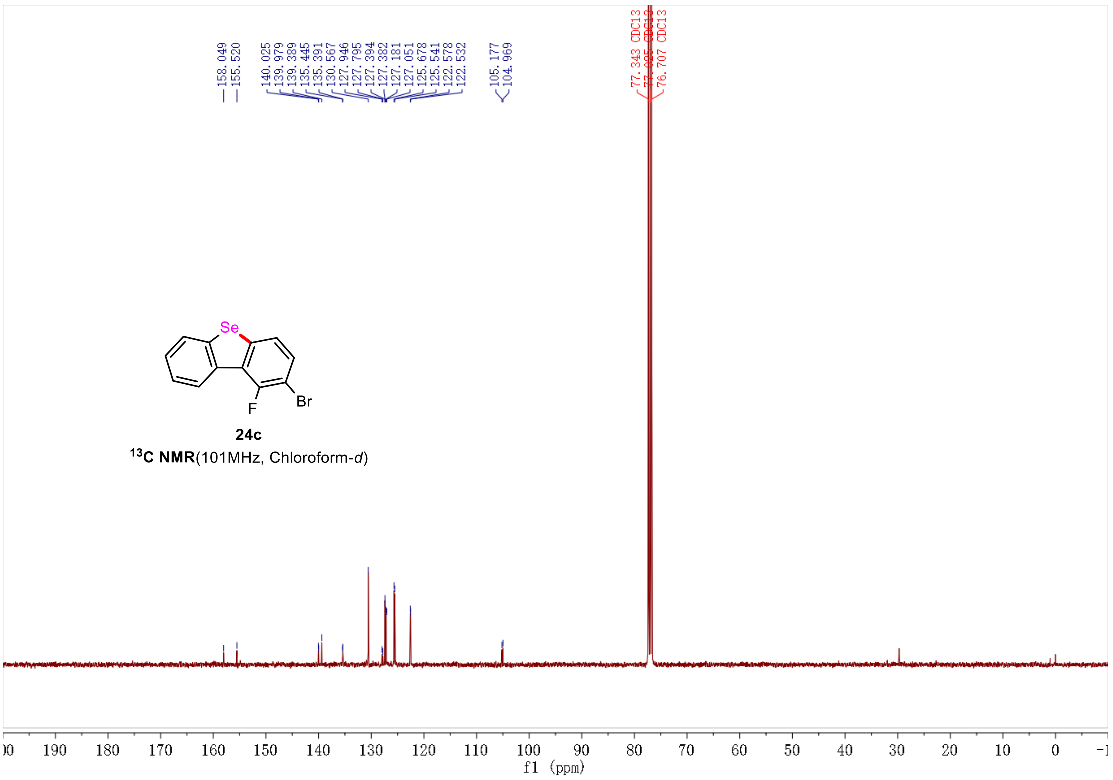
8.449
8.432
8.429
7.892
7.889
7.873
7.870
7.549
7.528
7.525
7.512
7.491
7.462
7.459
7.443
7.440
7.424
7.421
Se
F
Br
24c
$^1$H NMR(400MHz, Chloroform-*d*)
1.00
0.97
3.13
1.09
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)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139.979
139.389
135.445
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130.567
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127.795
127.394
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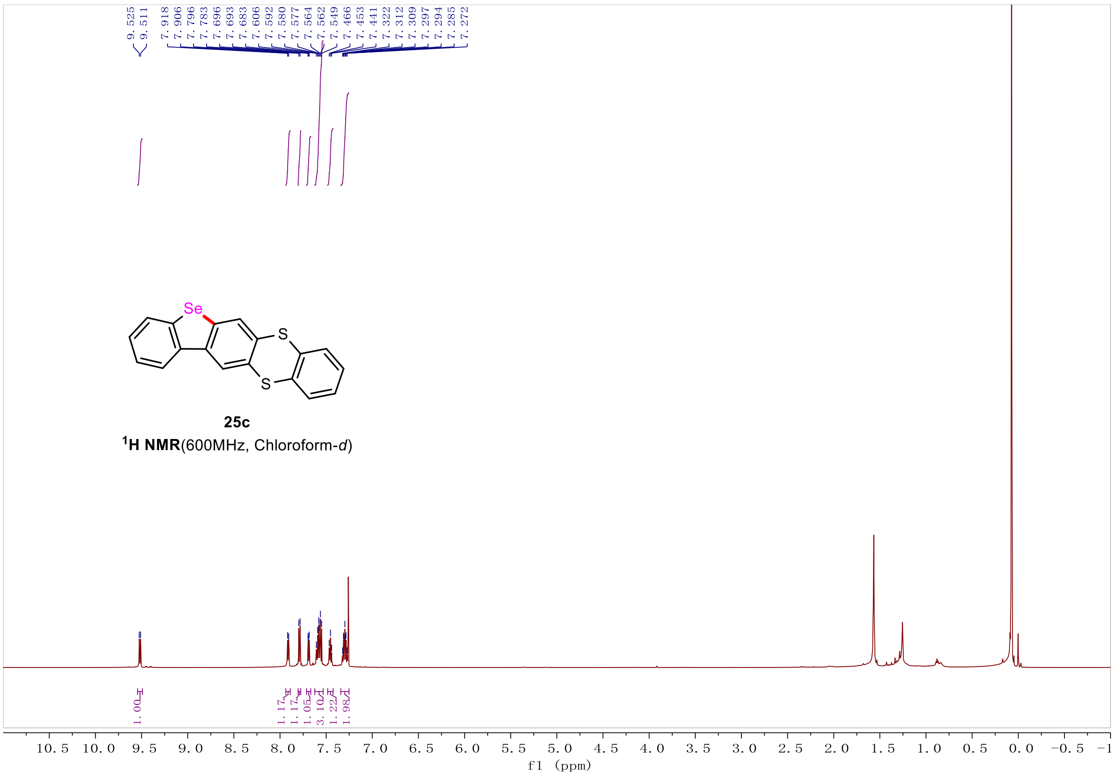
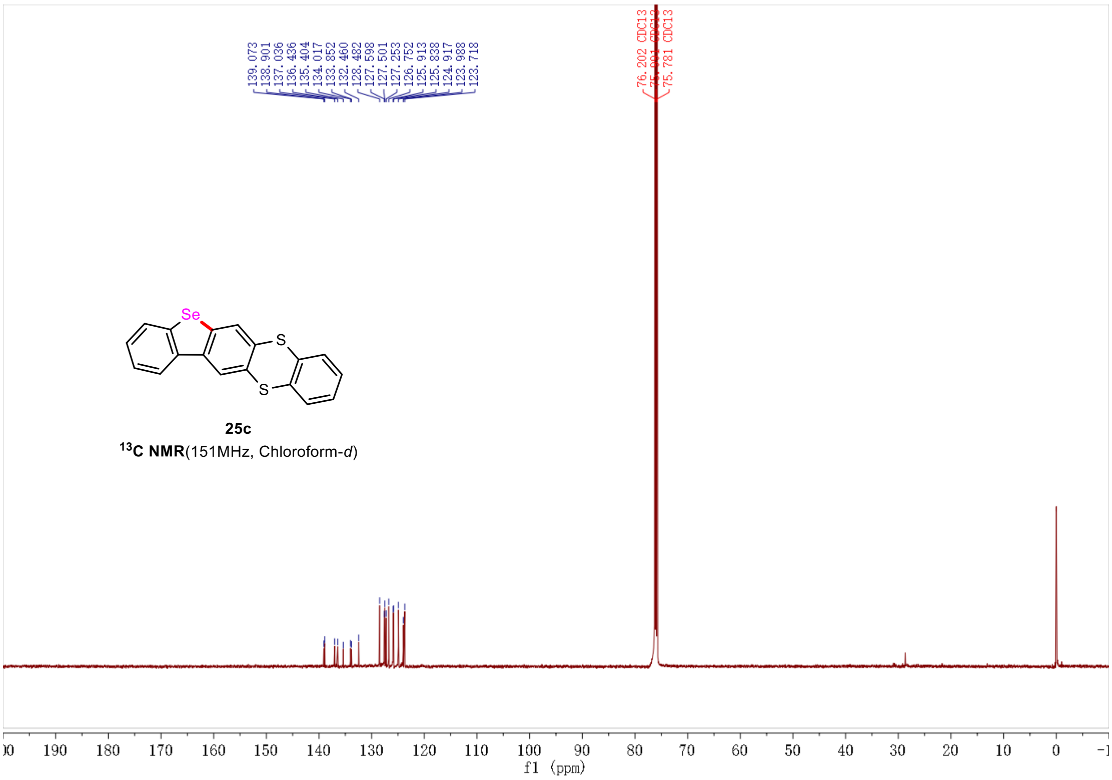
127.181
127.051
125.678
125.541
122.578
122.532
105.177
104.969
77.343 CDCl3
77.025 CDCl3
76.707 CDCl3
Se
F
Br
24c
$^{13}$C NMR(101MHz, Chloroform-*d*)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)



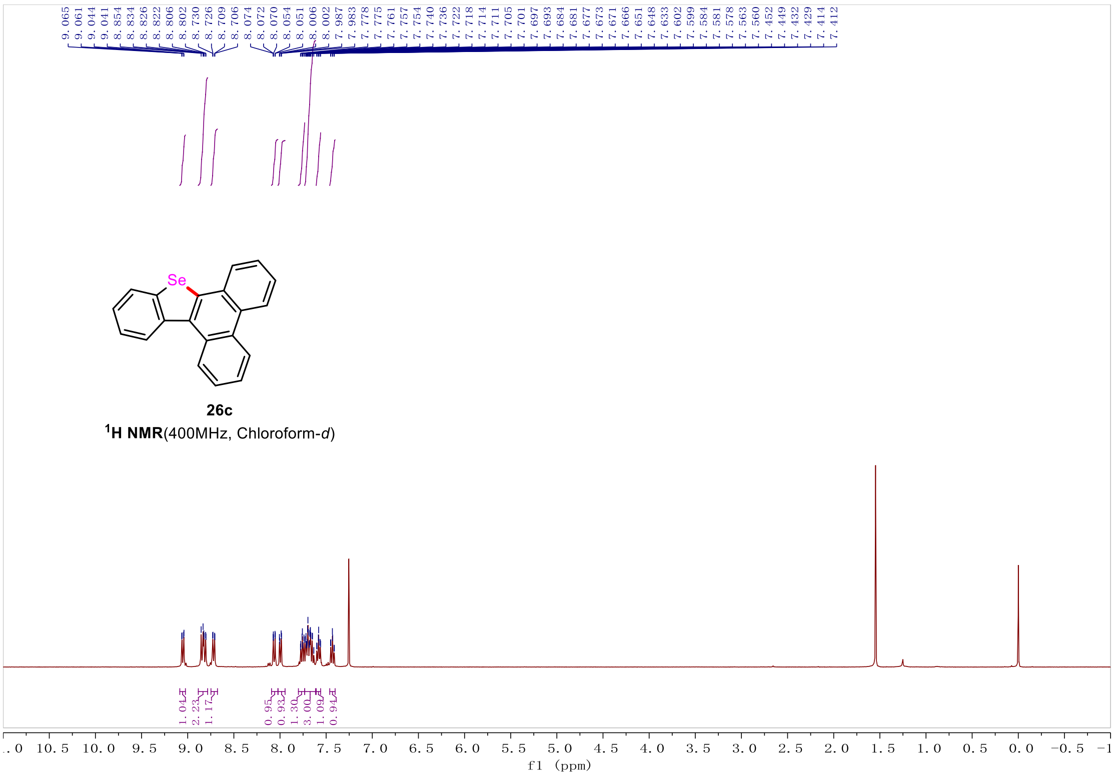
**25c**

**$^1$H NMR**(600MHz, Chloroform-*d*)



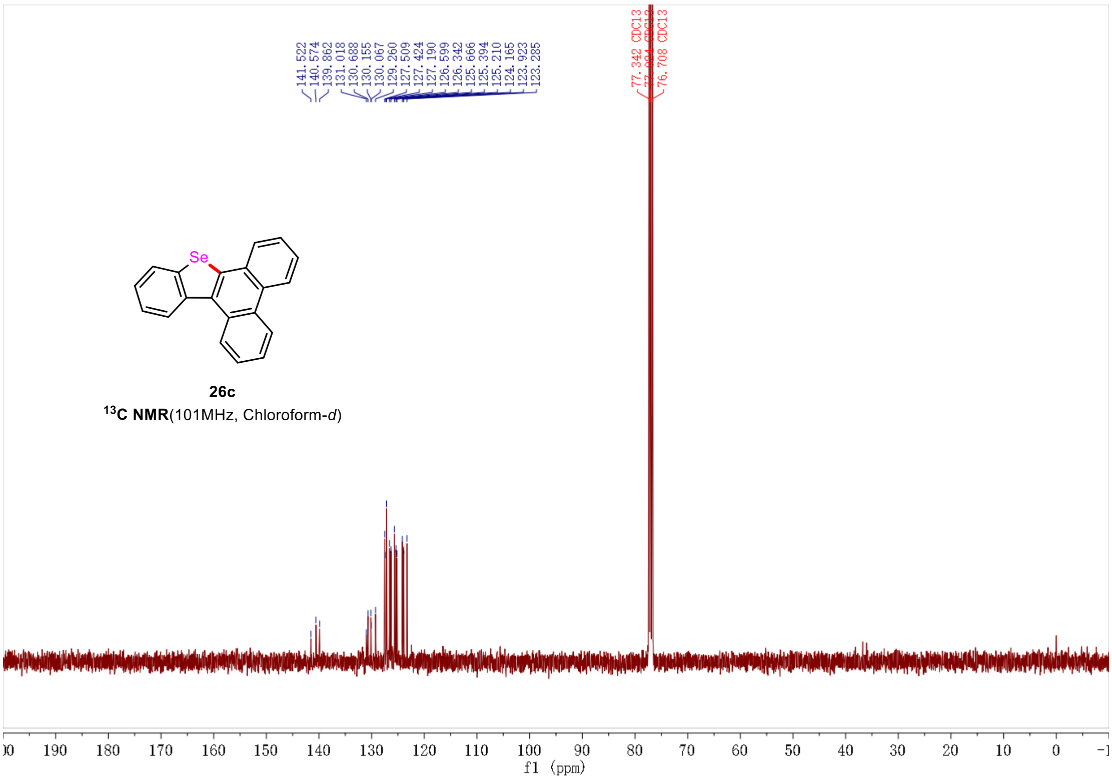
**25c**

**$^{13}$C NMR**(151MHz, Chloroform-*d*)



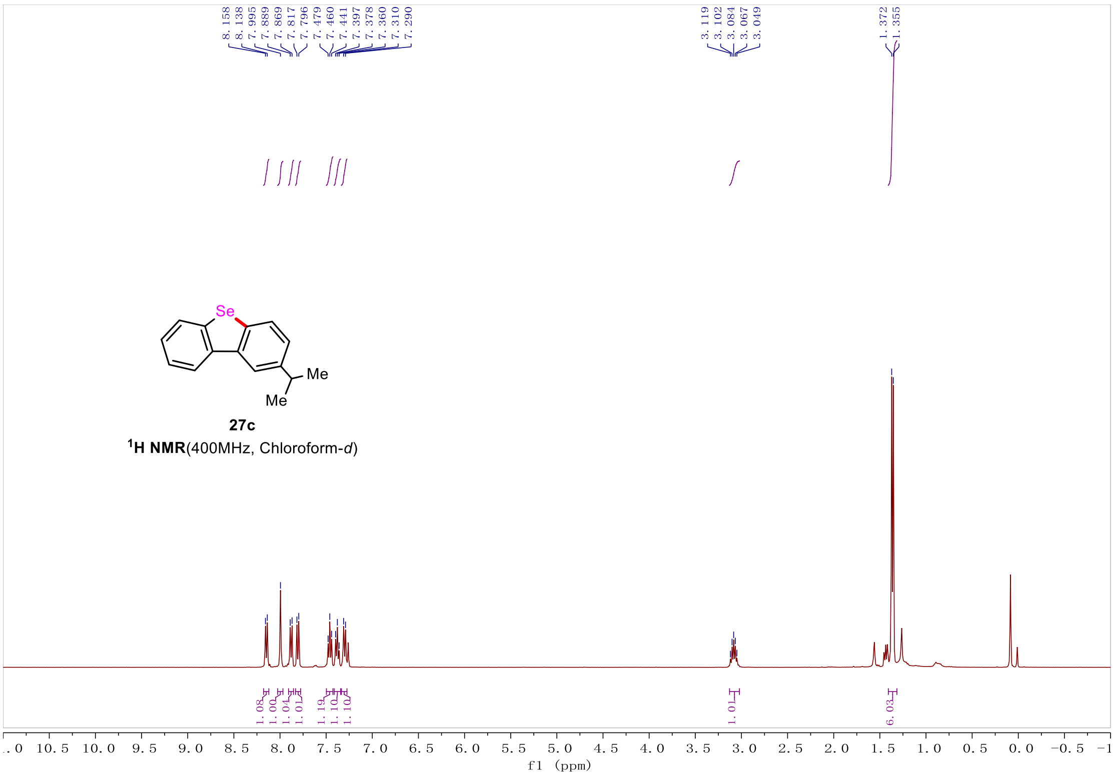
**26c**

**$^1$H NMR**(400MHz, Chloroform-*d*)

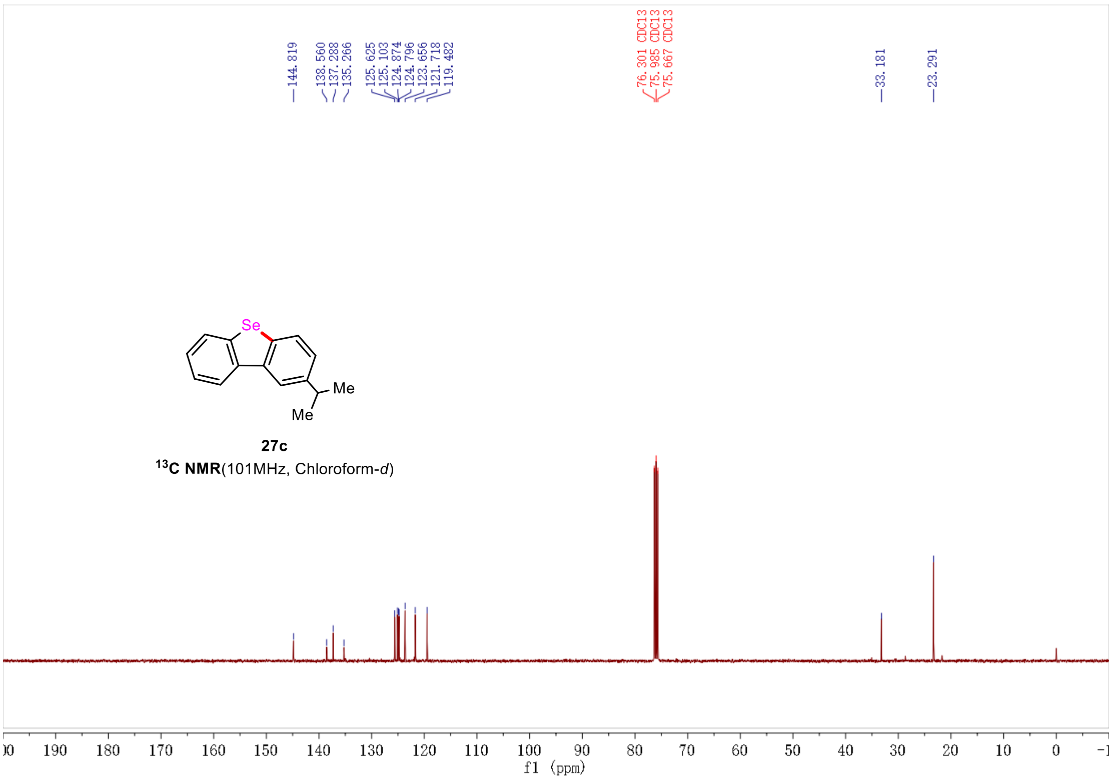


**26c**

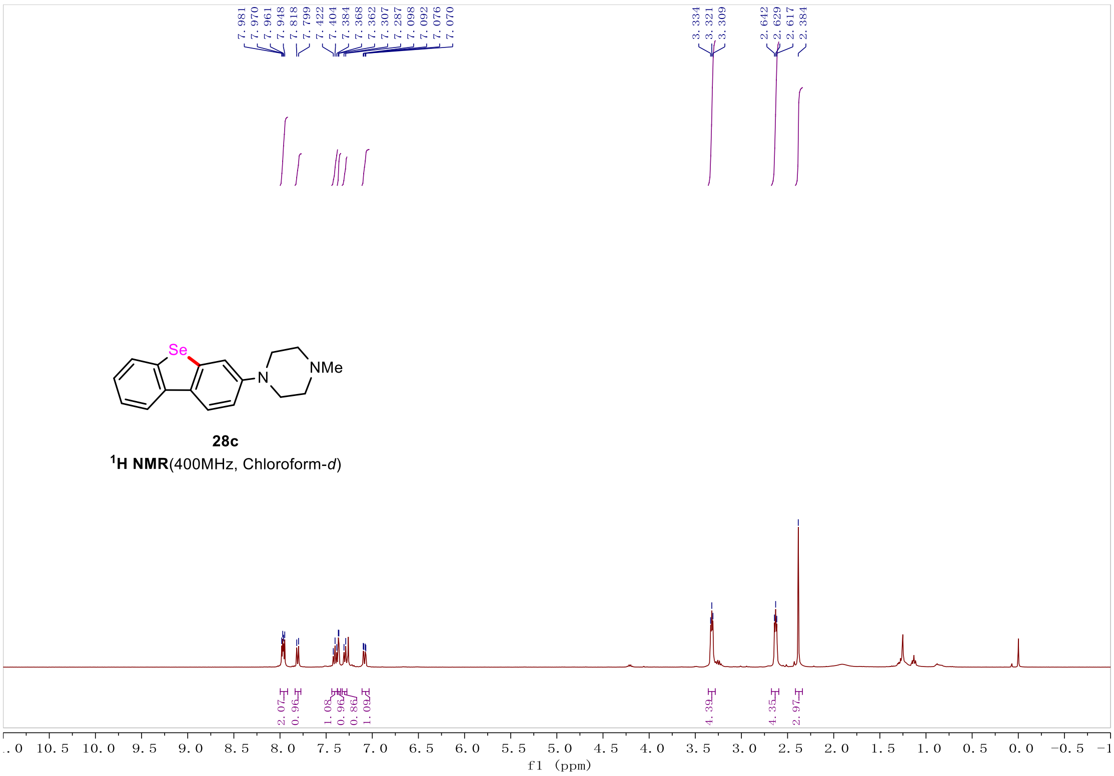
**$^{13}$C NMR**(101MHz, Chloroform-*d*)


**27c**

**$^1$H NMR**(400MHz, Chloroform-*d*)

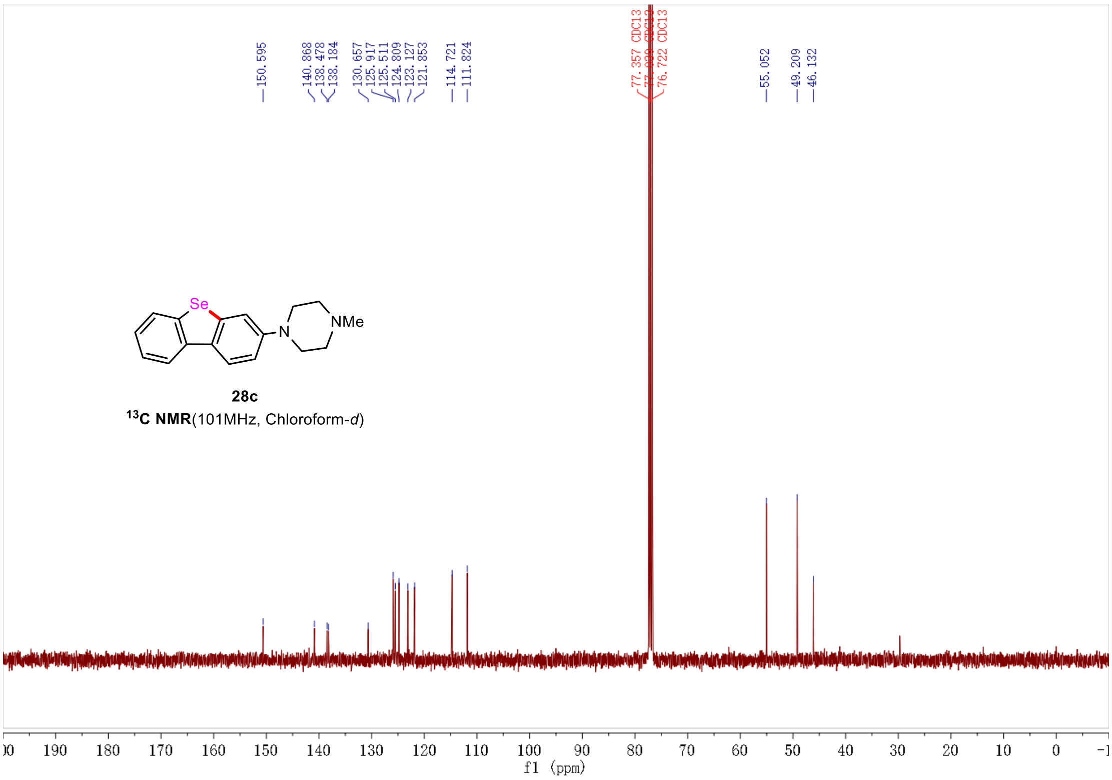

**27c**

**$^{13}$C NMR**(101MHz, Chloroform-*d*)



**28c**

$^1$**H NMR**(400MHz, Chloroform-*d*)



**28c**

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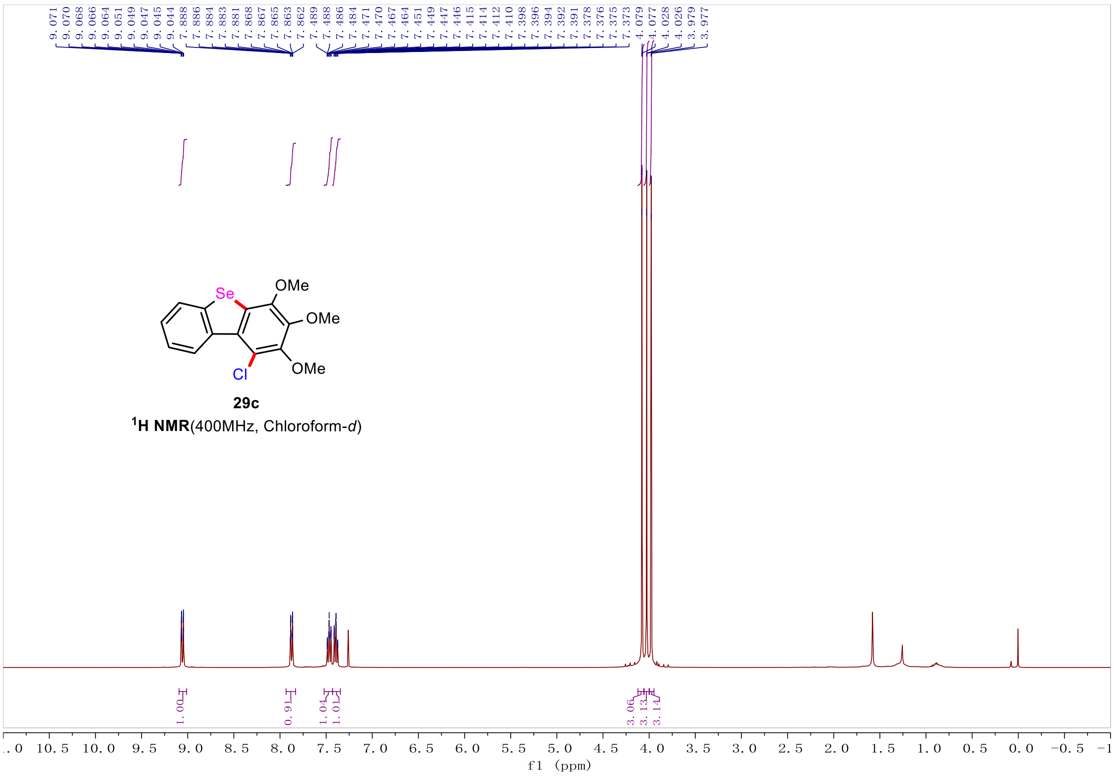
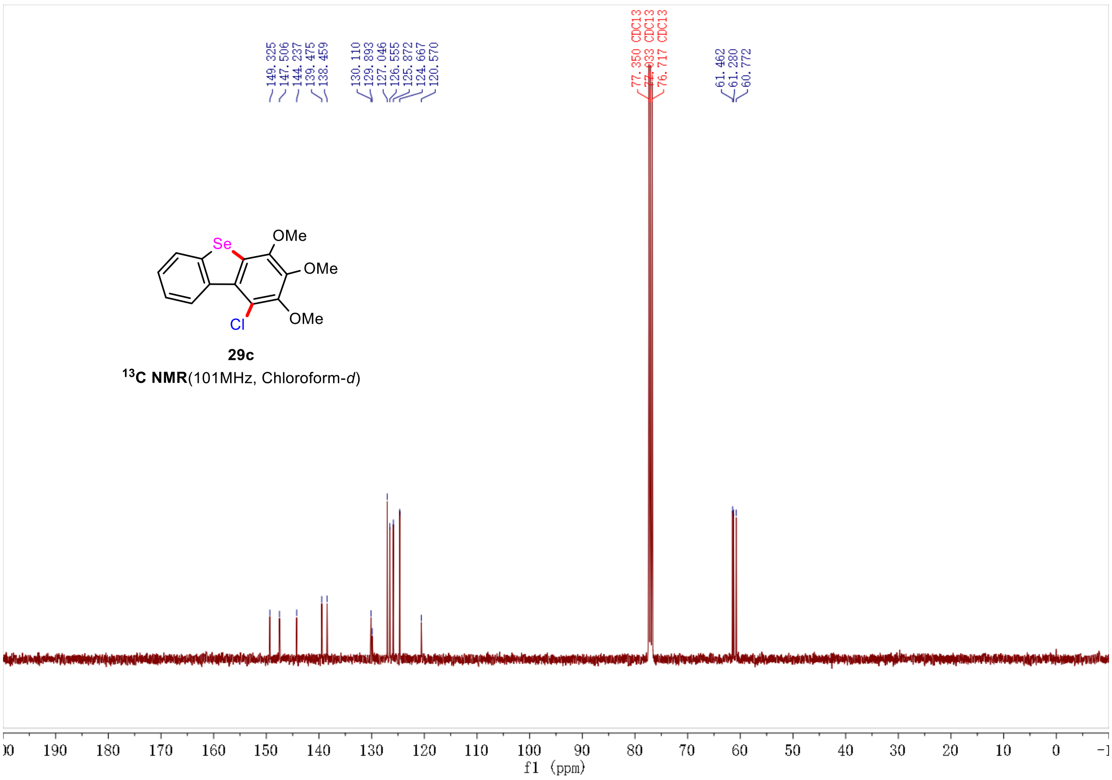


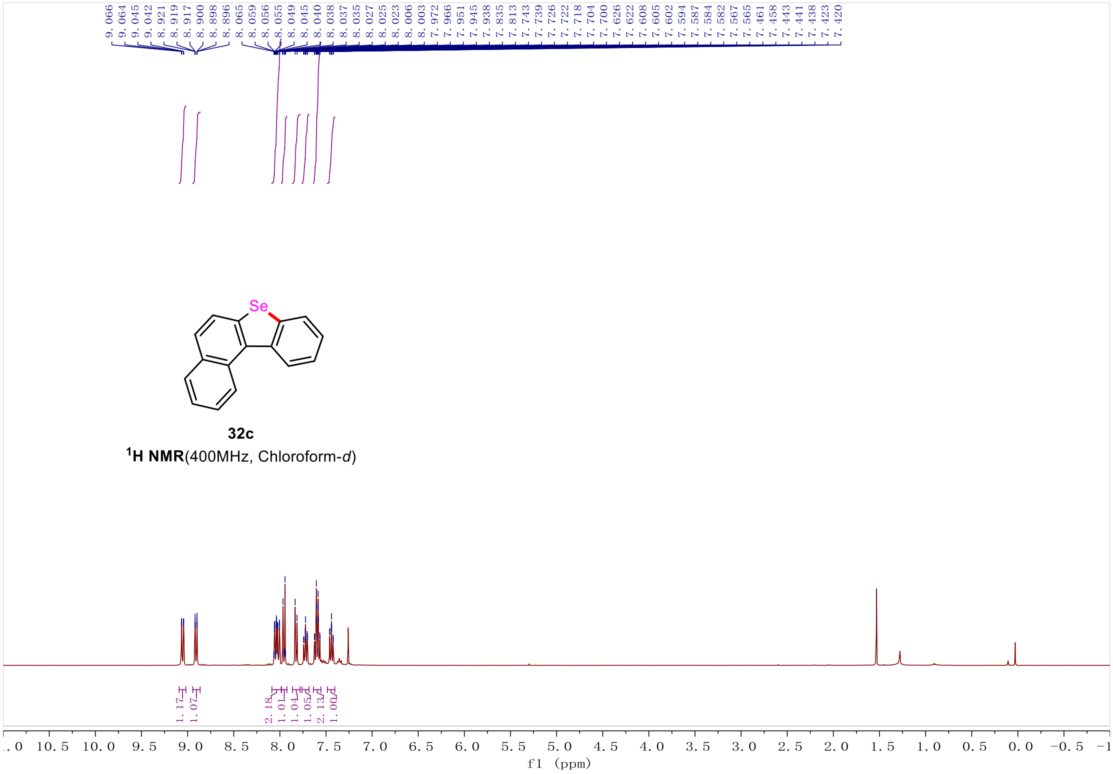
**29c**

**$^{1}$H NMR**(400MHz, Chloroform-*d*)



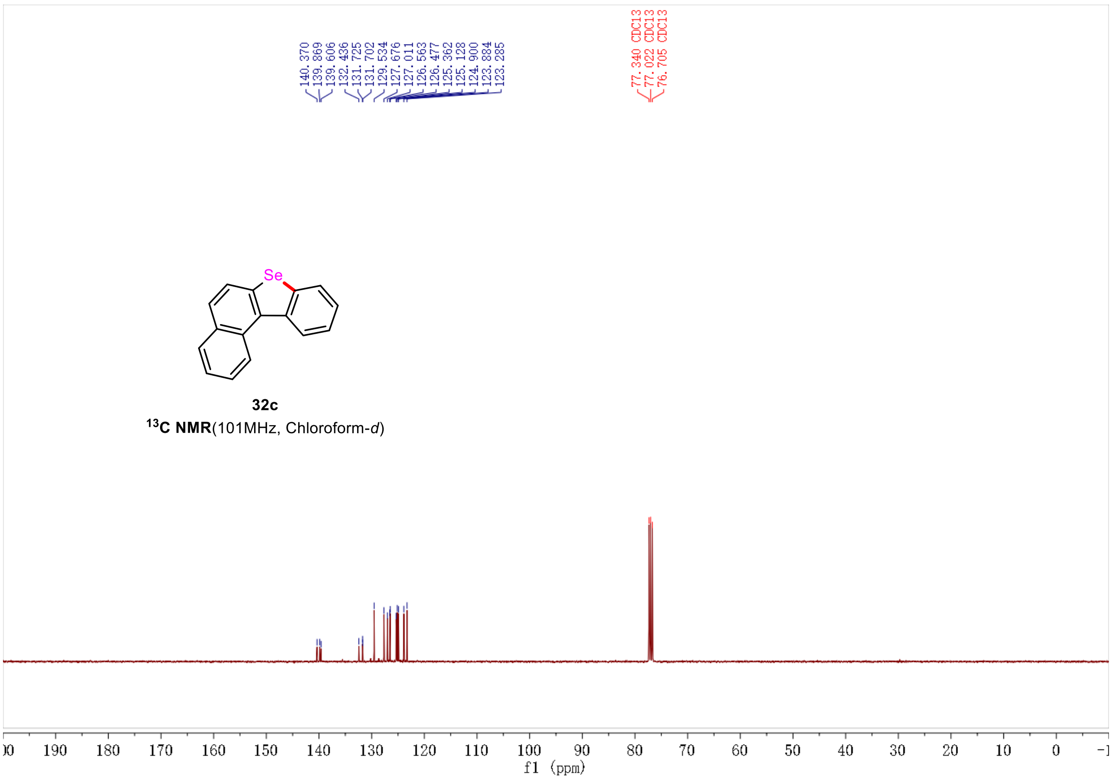
**29c**

**$^{13}$C NMR**(101MHz, Chloroform-*d*)



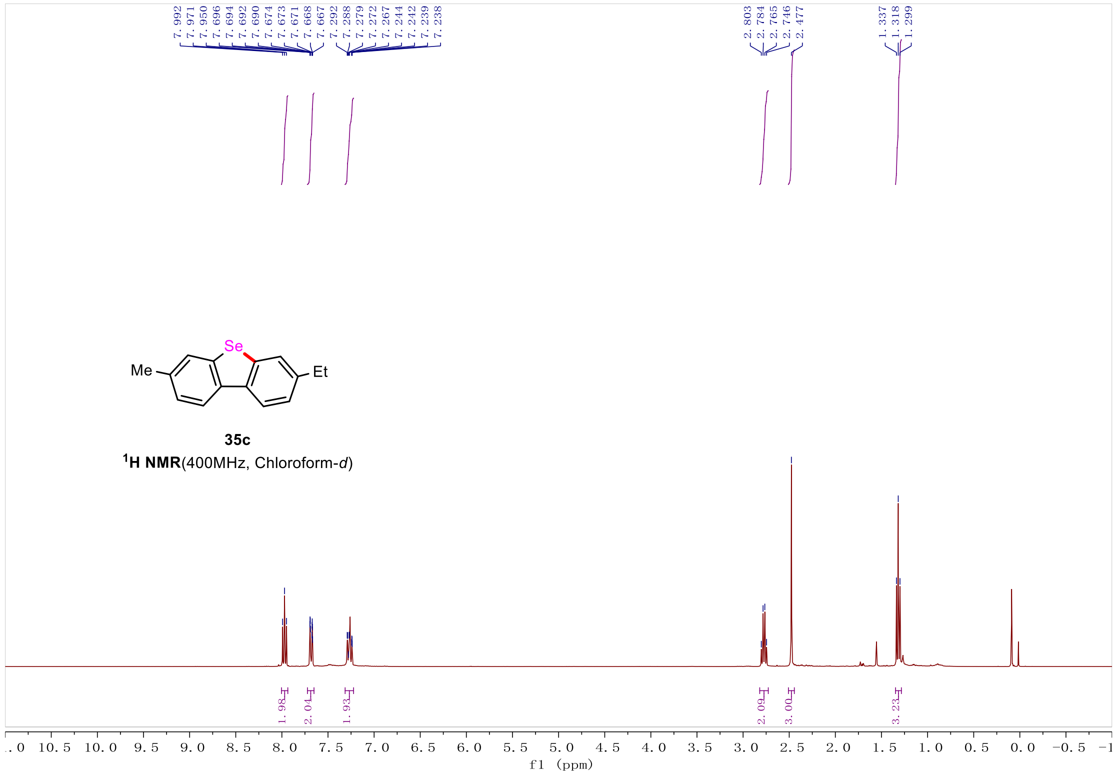
**32c**

$^1$**H NMR**(400MHz, Chloroform-*d*)



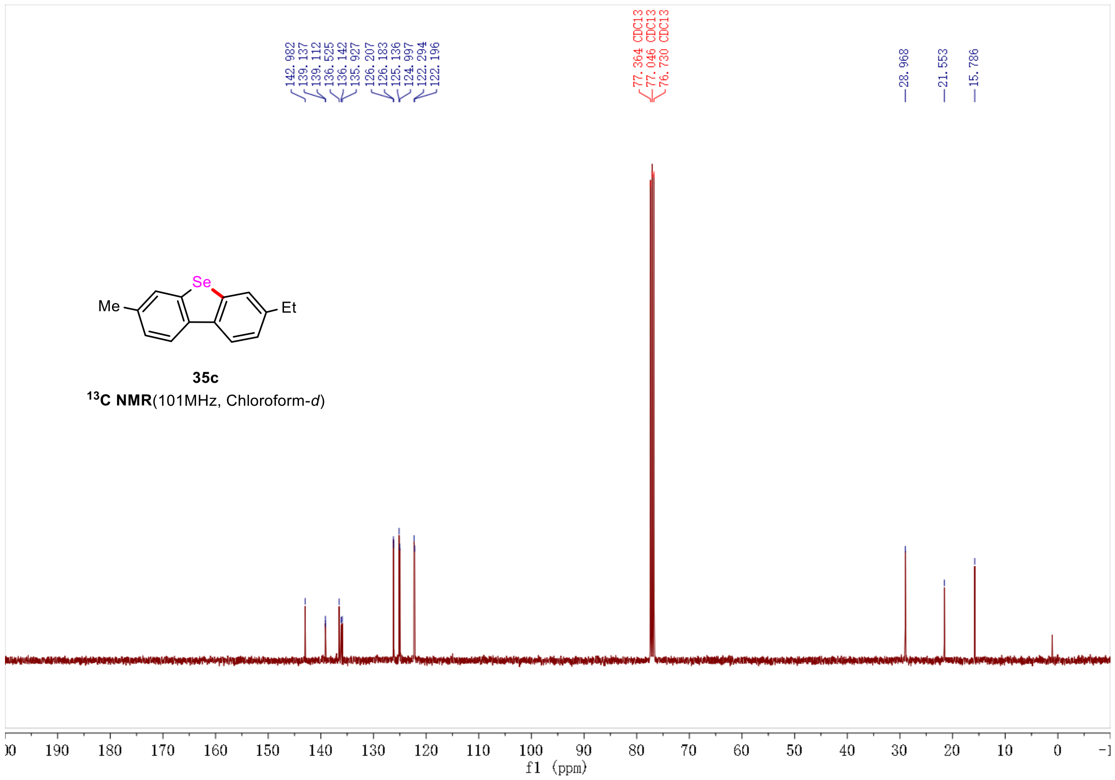
**32c**

$^{13}$**C NMR**(101MHz, Chloroform-*d*)



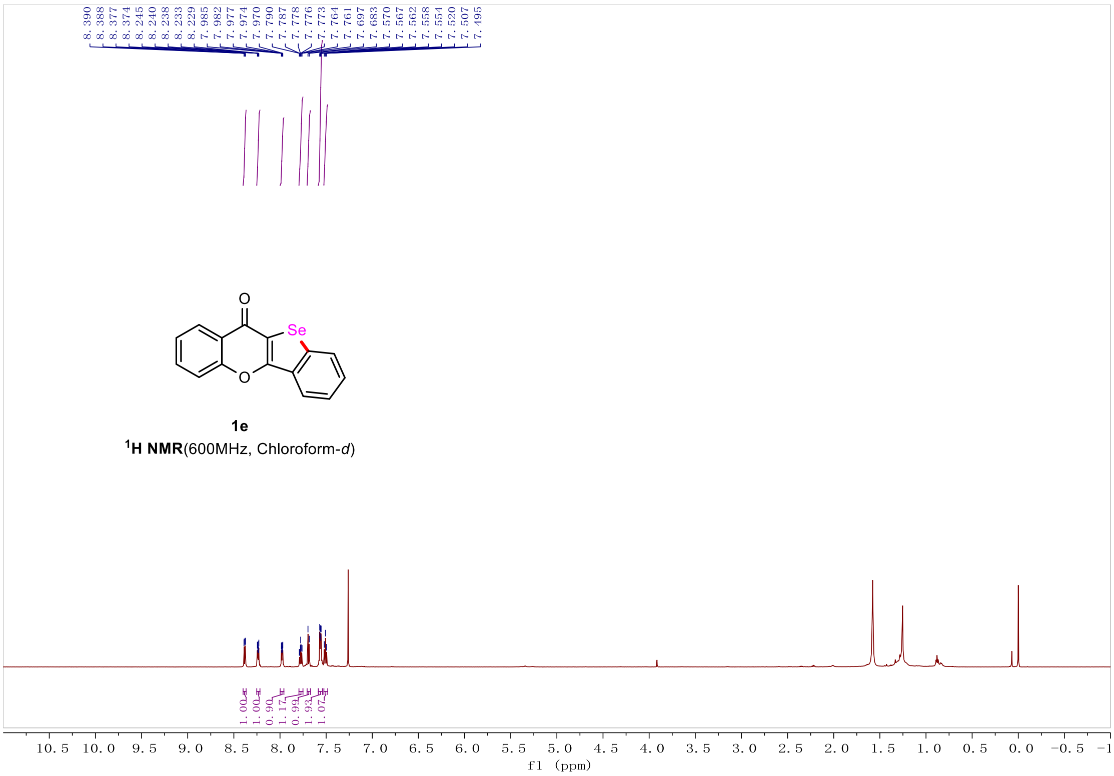
**35c**

**$^1$H NMR**(400MHz, Chloroform-*d*)



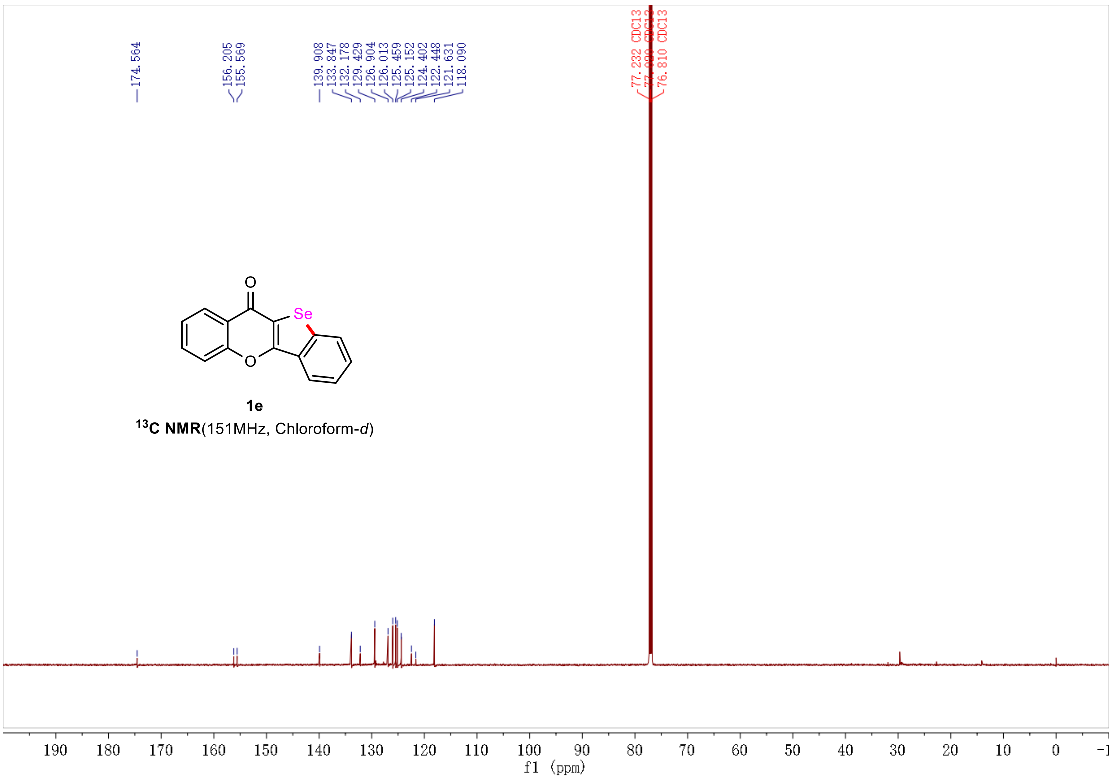
**35c**

**$^{13}$C NMR**(101MHz, Chloroform-*d*)



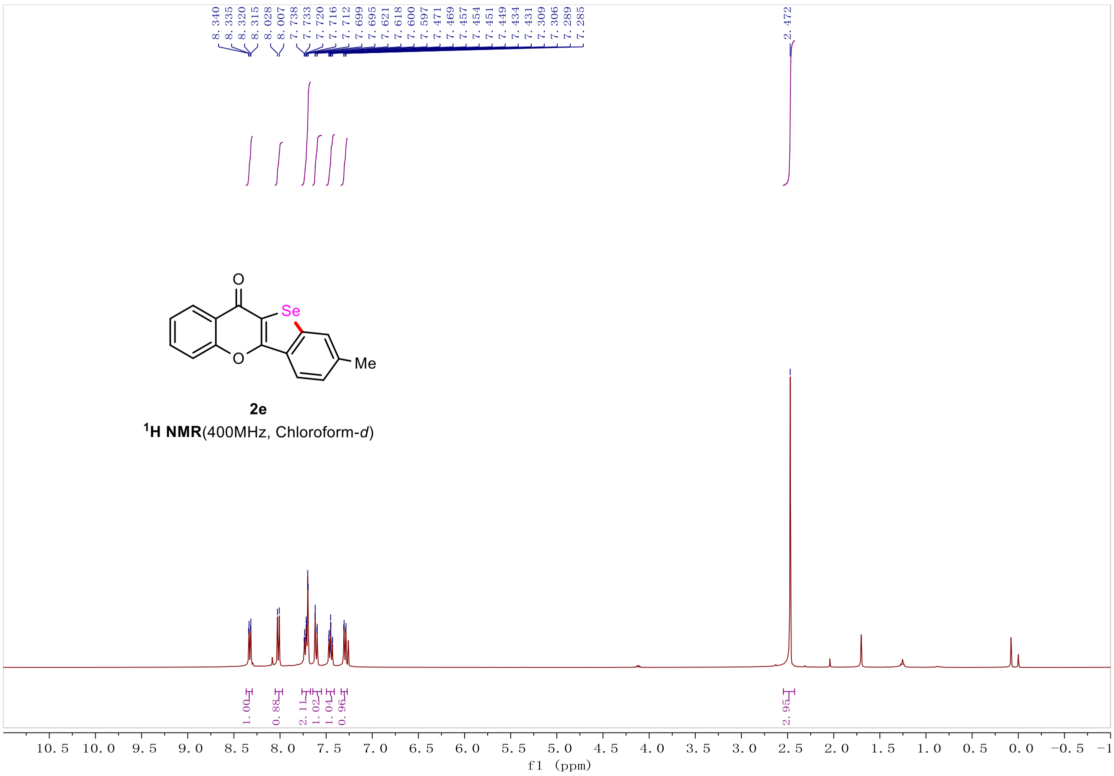
**1e**

**$^1$H NMR**(600MHz, Chloroform-*d*)



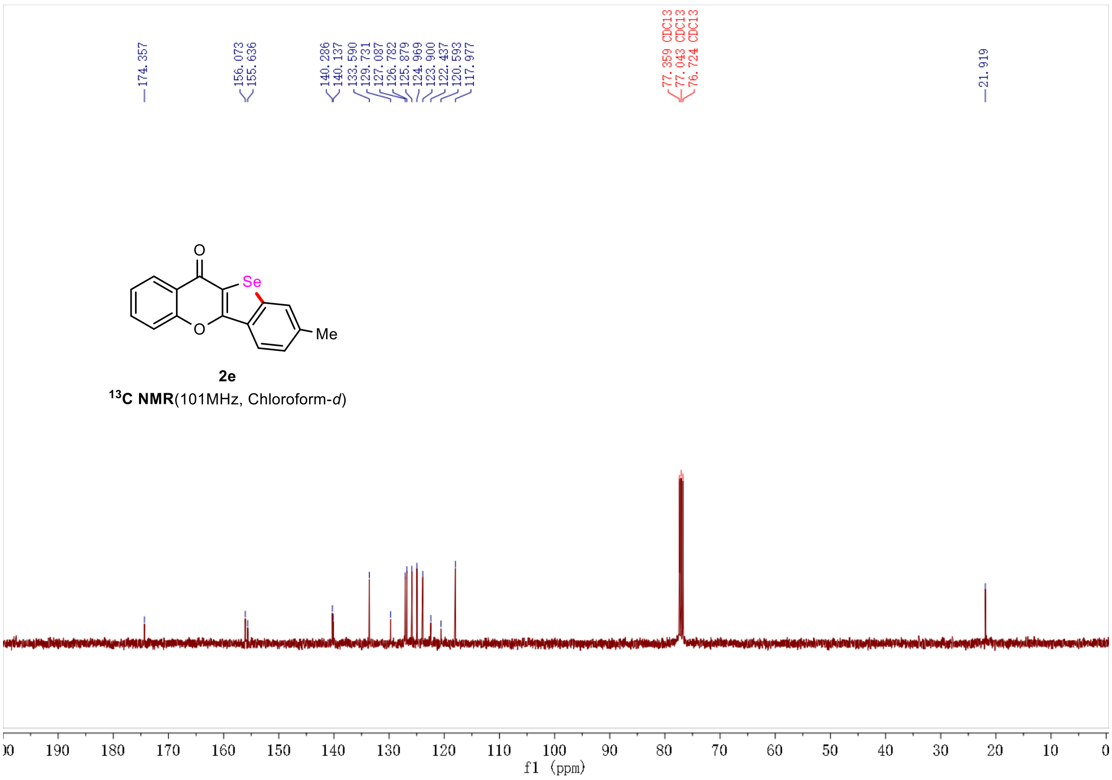
**1e**

**$^{13}$C NMR**(151MHz, Chloroform-*d*)



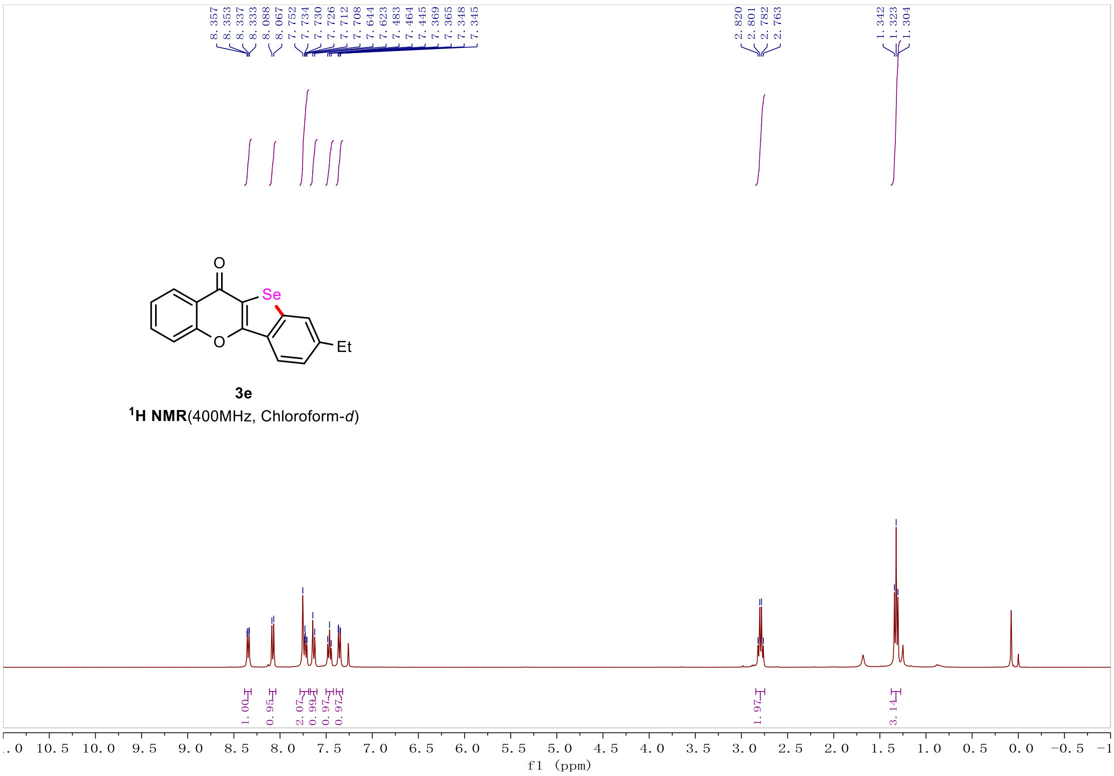
2e

$^{1}$**H NMR**(400MHz, Chloroform-*d*)



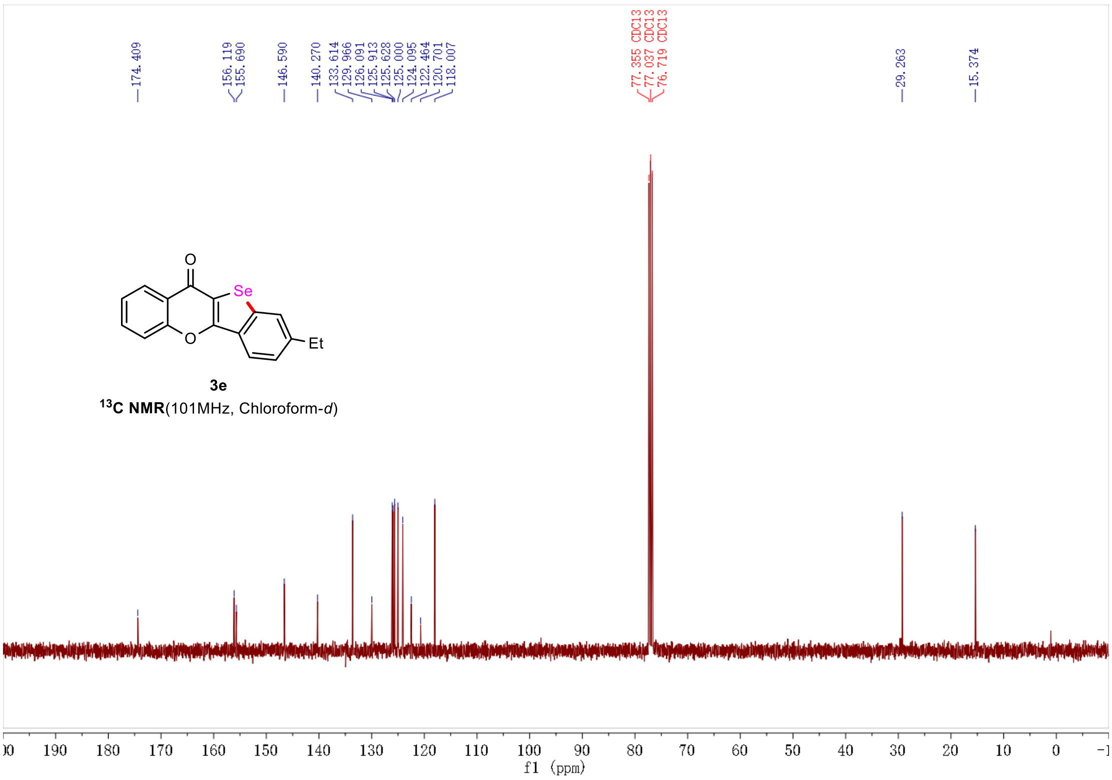
2e

$^{13}$**C NMR**(101MHz, Chloroform-*d*)



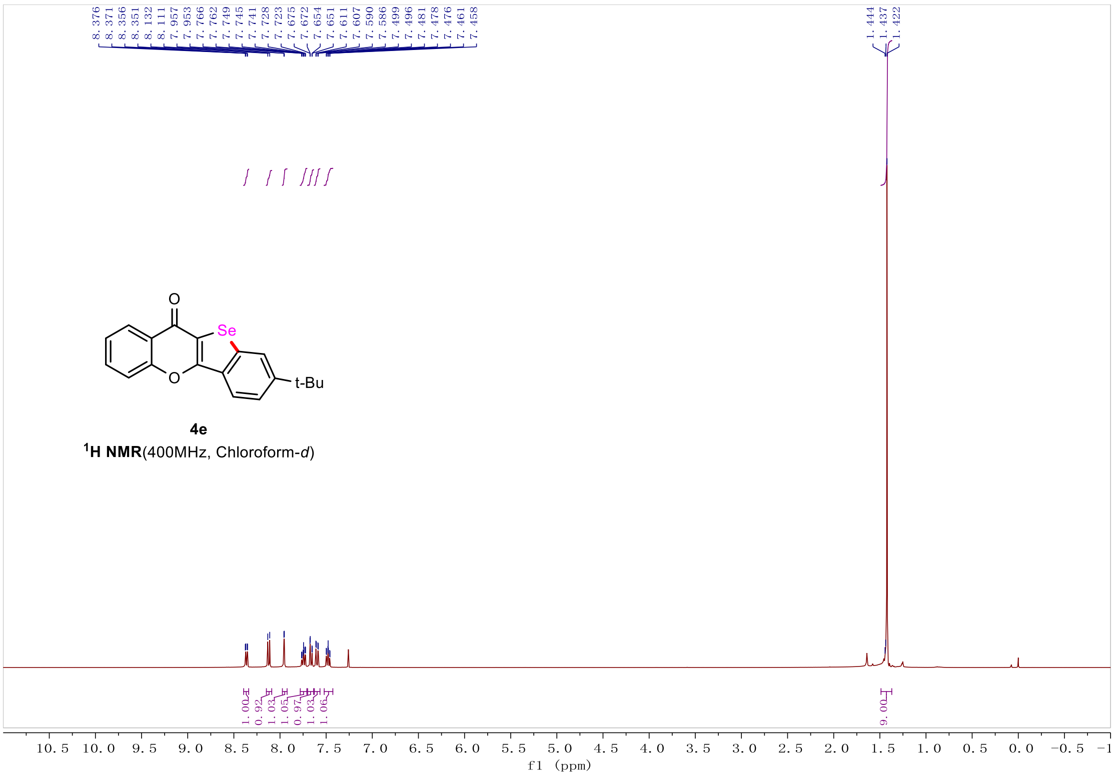
**3e**

**$^{1}$H NMR**(400MHz, Chloroform-*d*)



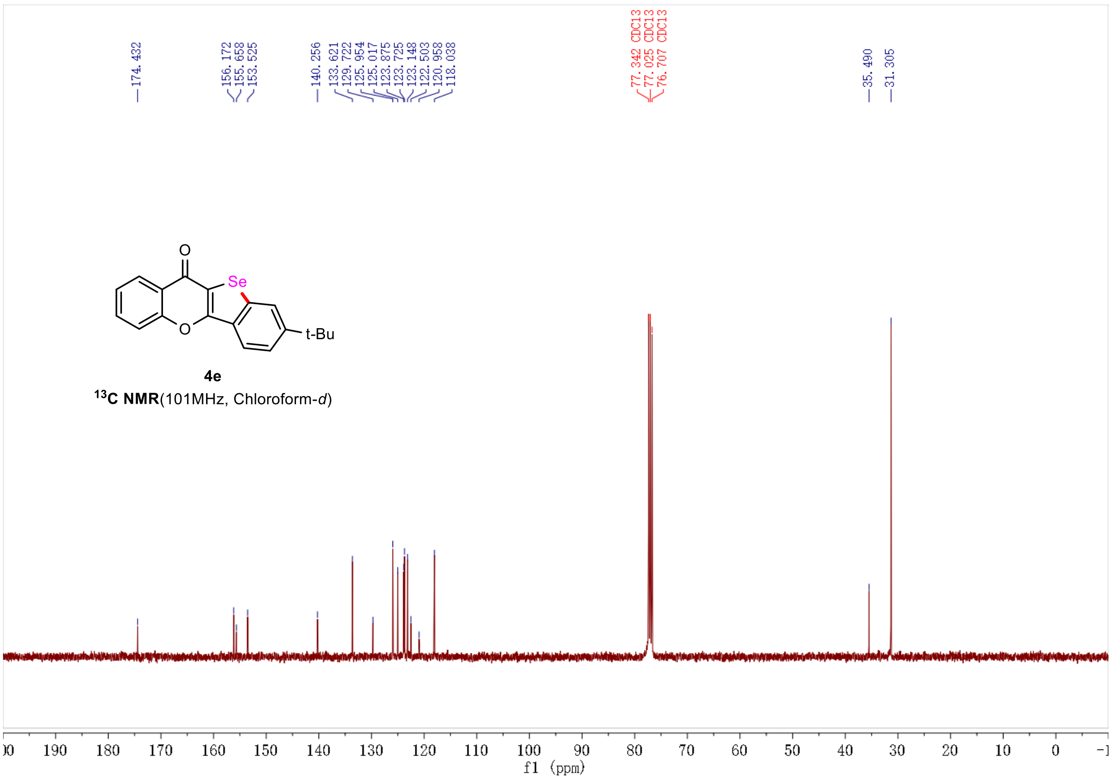
**3e**

**$^{13}$C NMR**(101MHz, Chloroform-*d*)



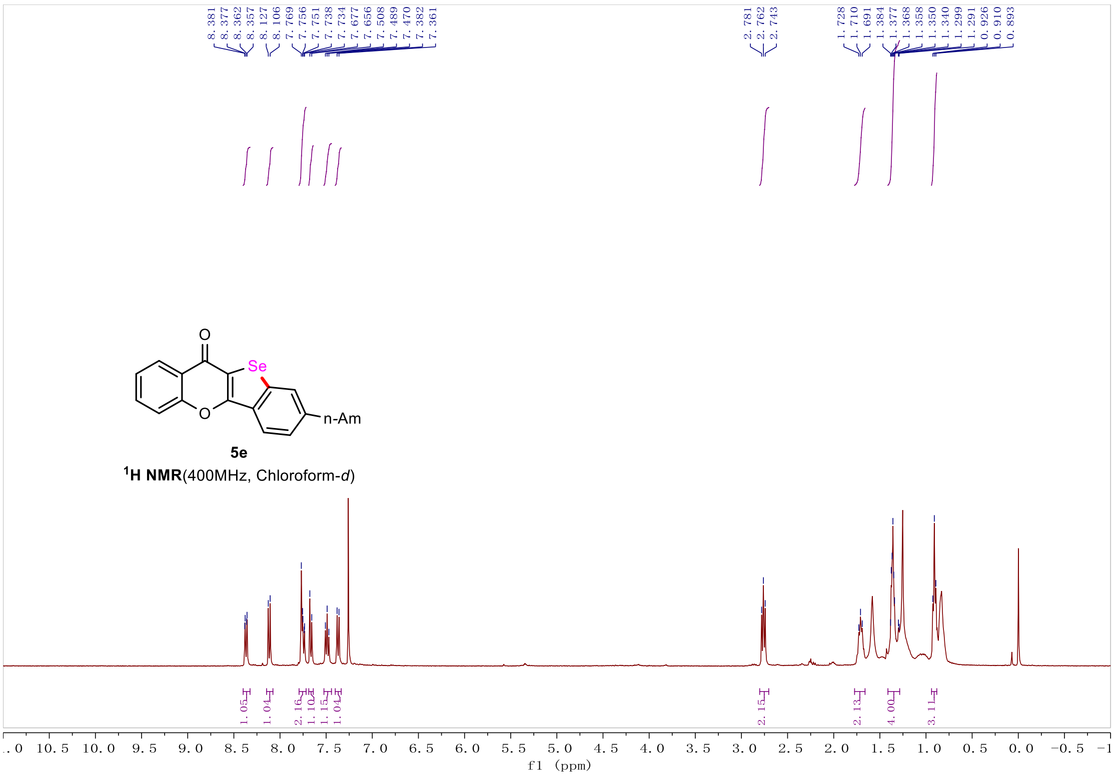
**4e**

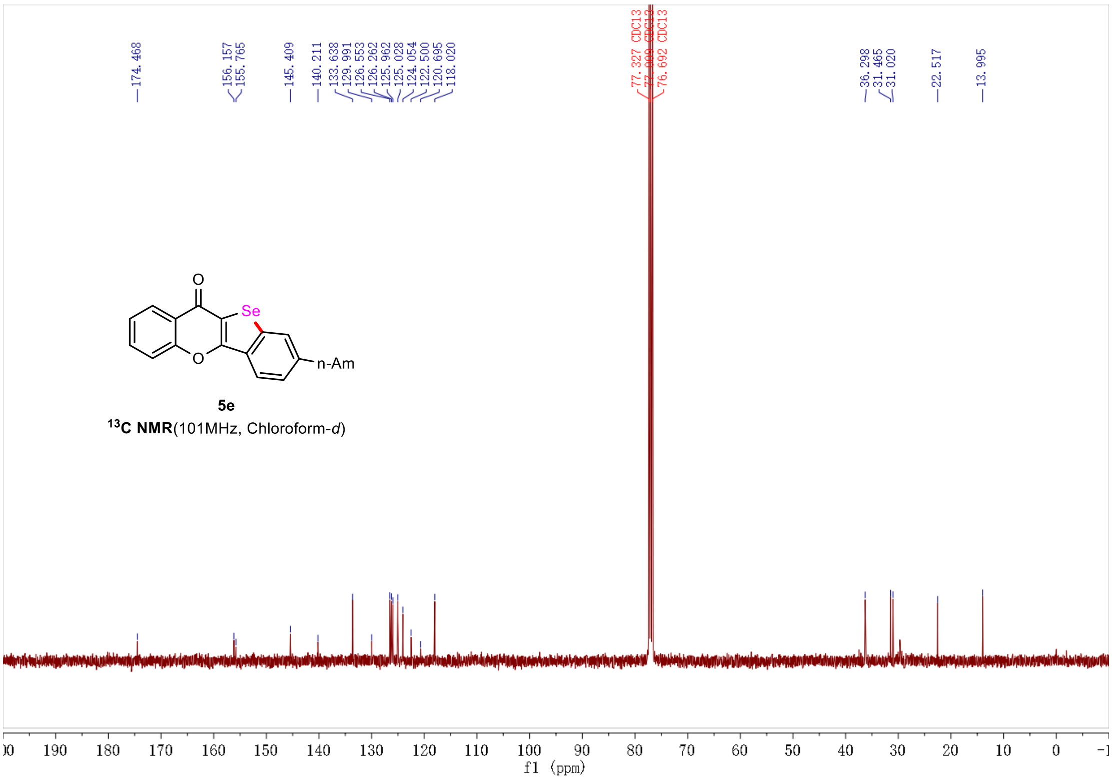
**$^1$H NMR**(400MHz, Chloroform-*d*)

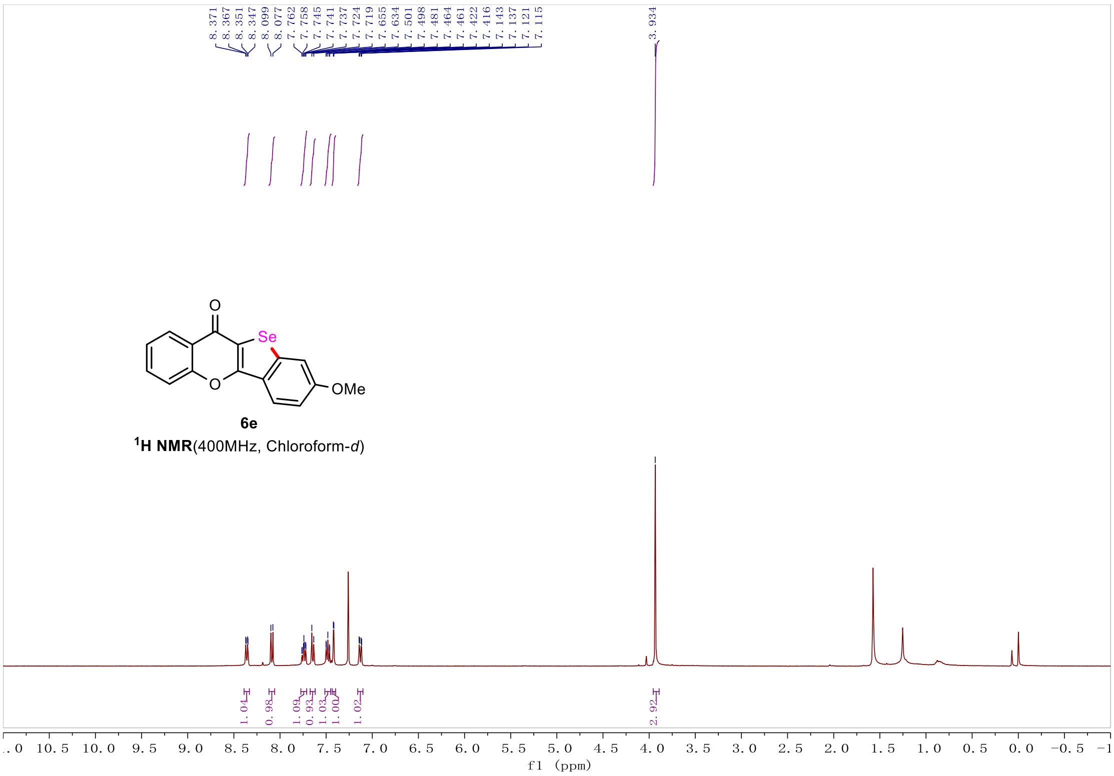


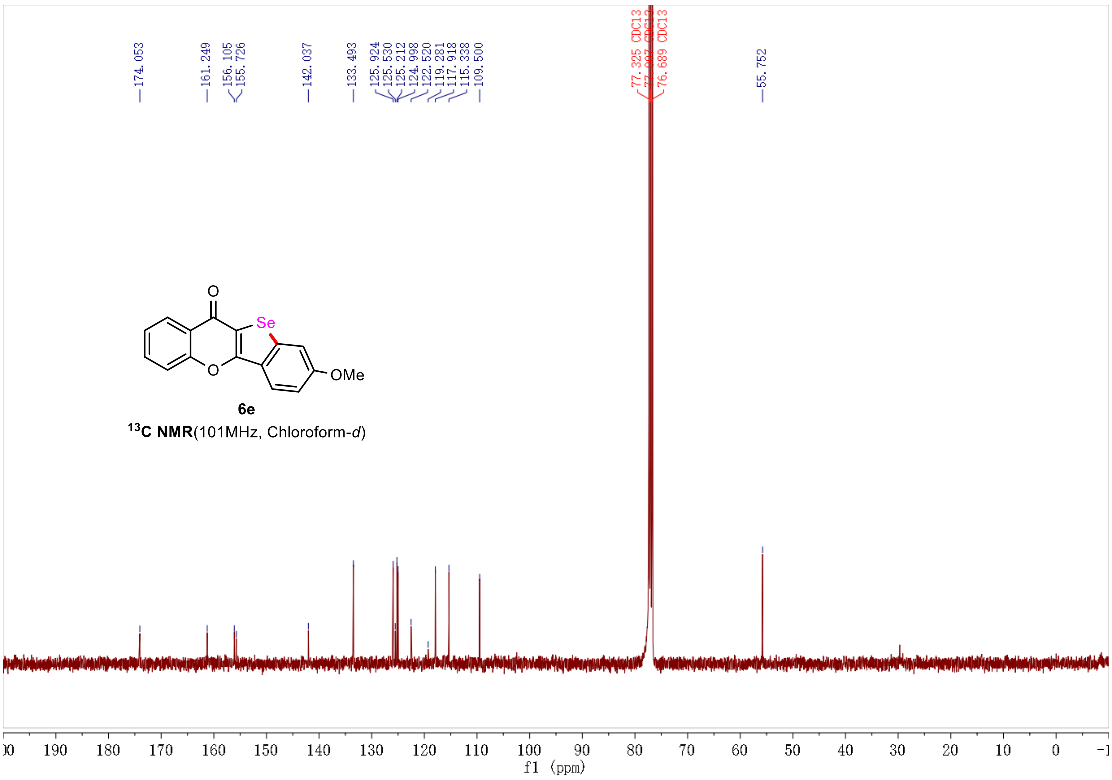
**4e**

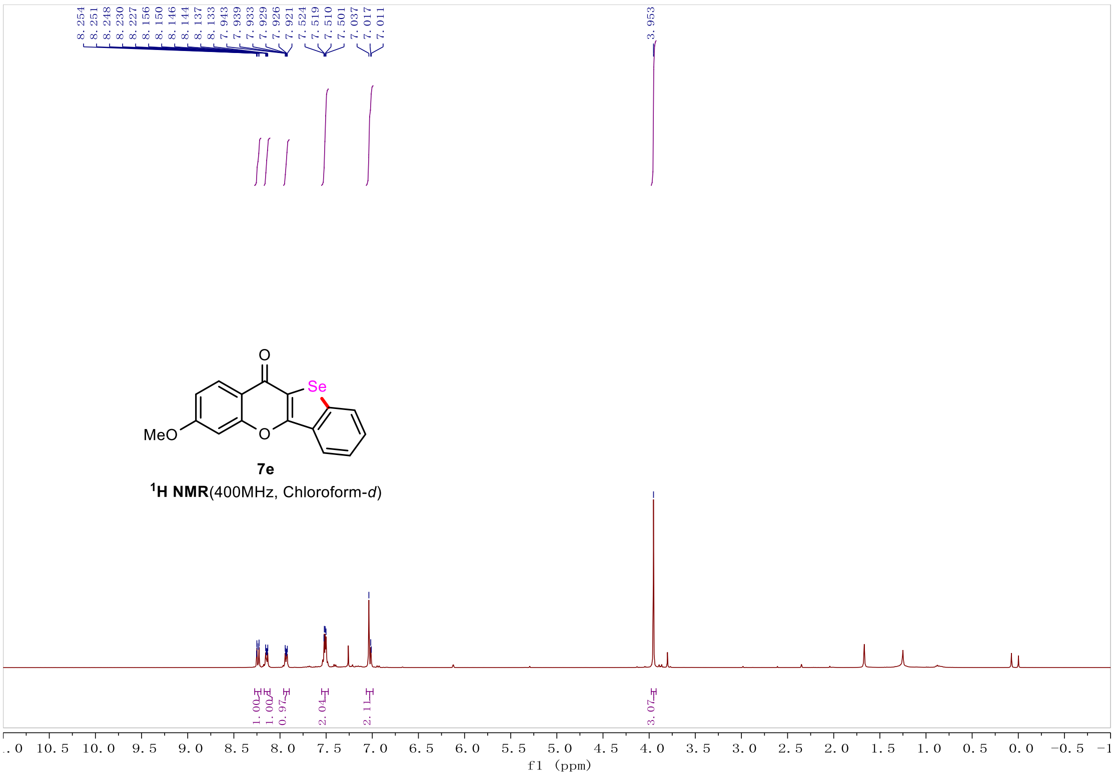
**$^{13}$C NMR**(101MHz, Chloroform-*d*)


8.381
8.377
8.362
8.357
8.127
8.106
7.769
7.756
7.751
7.738
7.734
7.677
7.656
7.508
7.489
7.470
7.382
7.361
2.781
2.762
2.743
1.728
1.710
1.691
1.384
1.377
1.368
1.358
1.350
1.340
1.299
1.291
0.926
0.910
0.893
O
Se
O
n-Am
5e
1H NMR(400MHz, Chloroform-d)
1.05
1.04
2.16
1.10
1.15
1.04
2.15
2.13
4.00
3.11
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


174.468
156.157
155.765
145.409
140.211
133.638
129.991
126.553
126.262
125.962
125.028
124.054
122.500
120.695
118.020
77.327 CDCl3
77.009 CDCl3
76.692 CDCl3
36.298
31.465
31.020
22.517
13.995
O
Se
O
n-Am
5e
13C NMR(101MHz, Chloroform-d)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

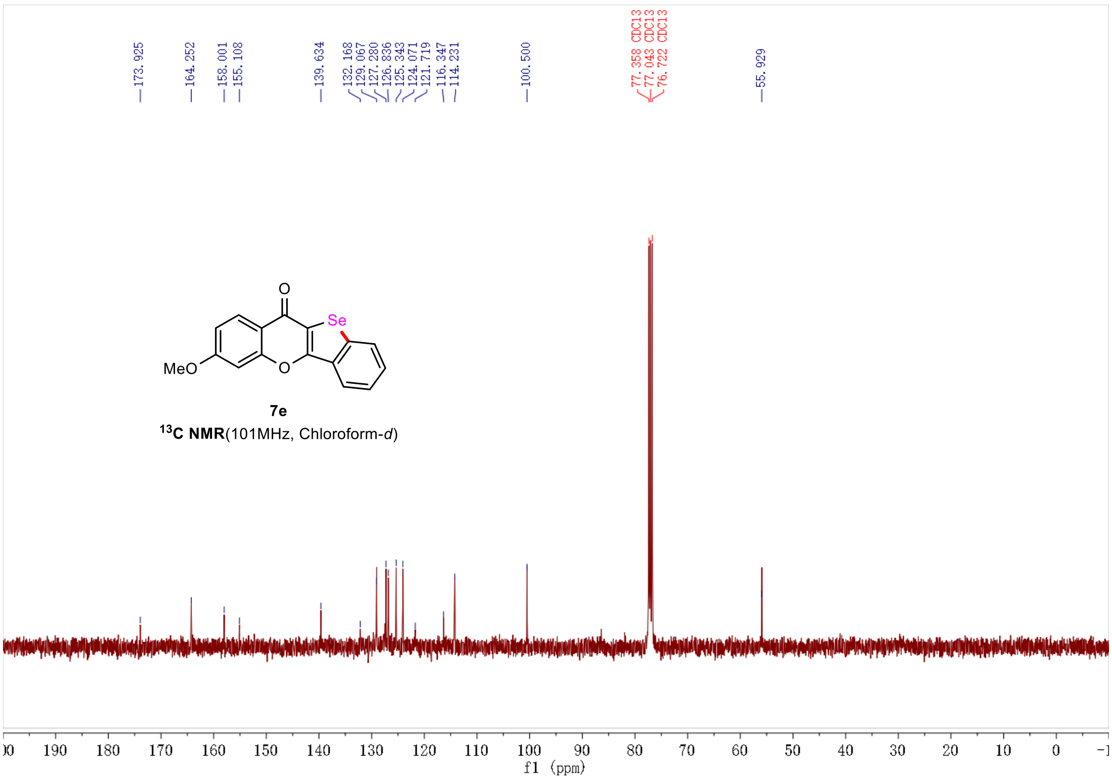

8.371
8.367
8.351
8.347
8.099
8.077
7.762
7.758
7.745
7.741
7.737
7.724
7.719
7.655
7.634
7.501
7.498
7.481
7.464
7.461
7.422
7.416
7.143
7.137
7.121
7.115
3.934
O
Se
O
OMe
6e
1H NMR(400MHz, Chloroform-d)
1.04
0.98
1.09
0.93
1.03
1.00
1.02
2.92
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


174.053
161.249
156.105
155.726
142.037
133.493
125.924
125.530
125.212
124.998
122.520
119.281
117.918
115.338
109.500
77.325 CDCl3
77.007 CDCl3
76.689 CDCl3
55.752
O
Se
O
OMe
6e
13C NMR(101MHz, Chloroform-d)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



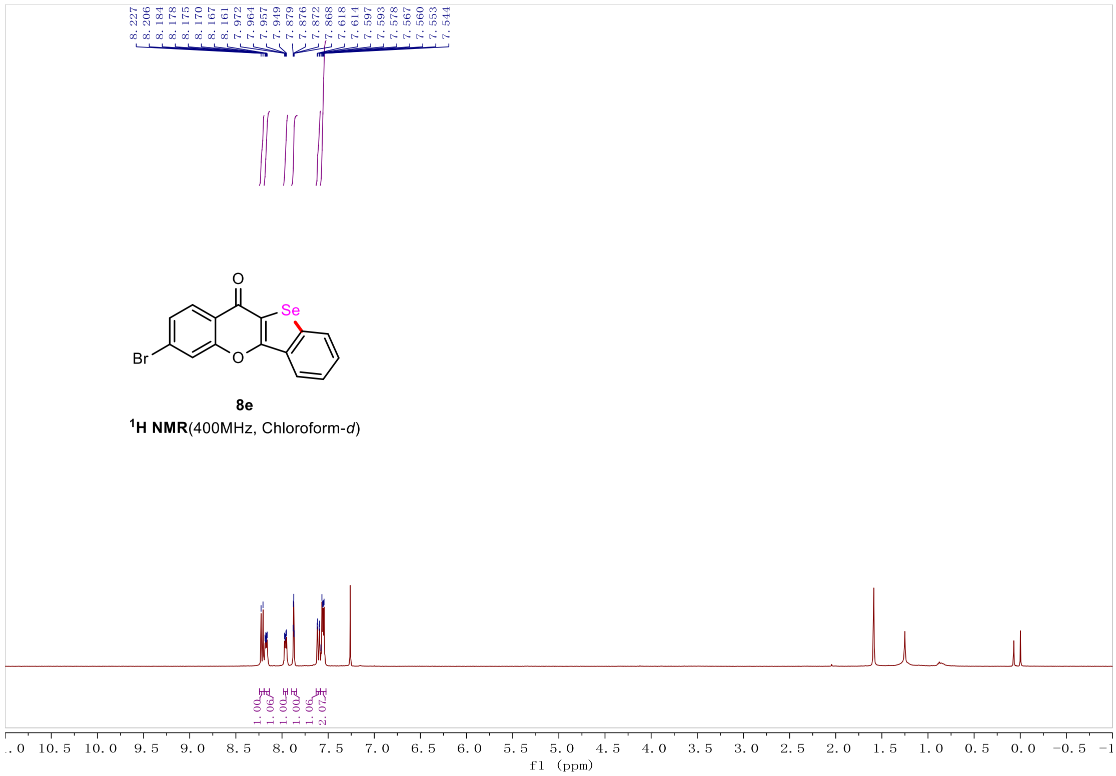
**7e**

$^{1}$**H NMR**(400MHz, Chloroform-*d*)



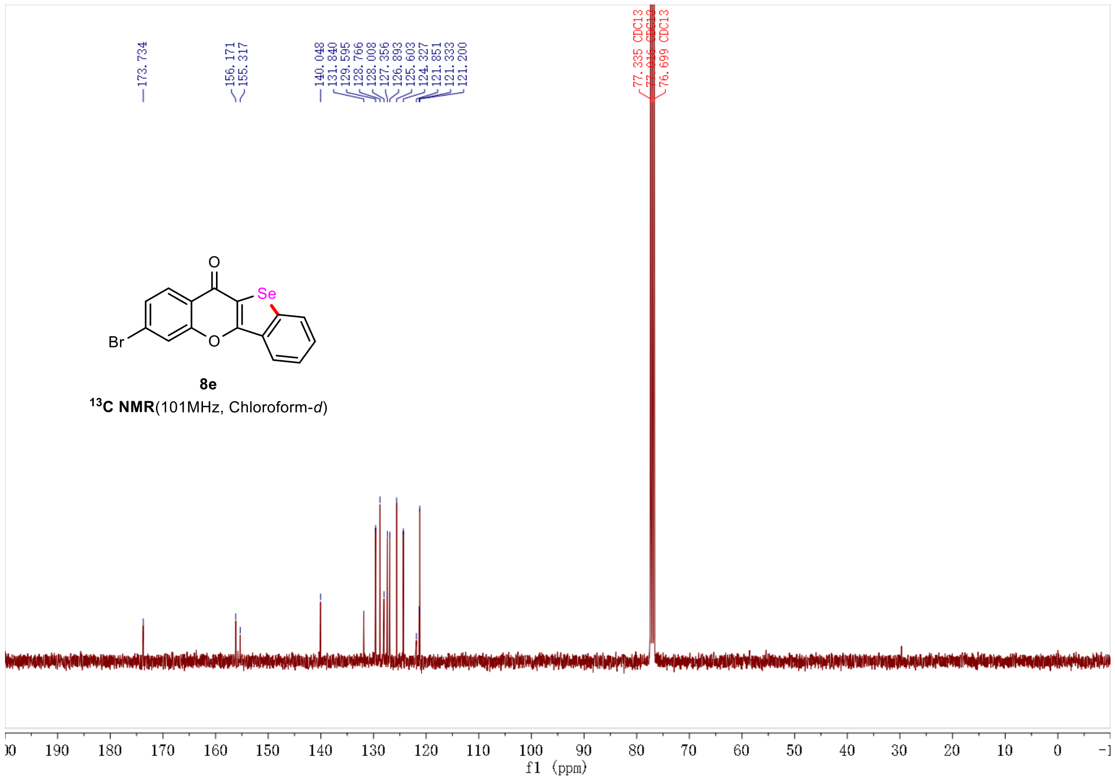
**7e**

$^{13}$**C NMR**(101MHz, Chloroform-*d*)



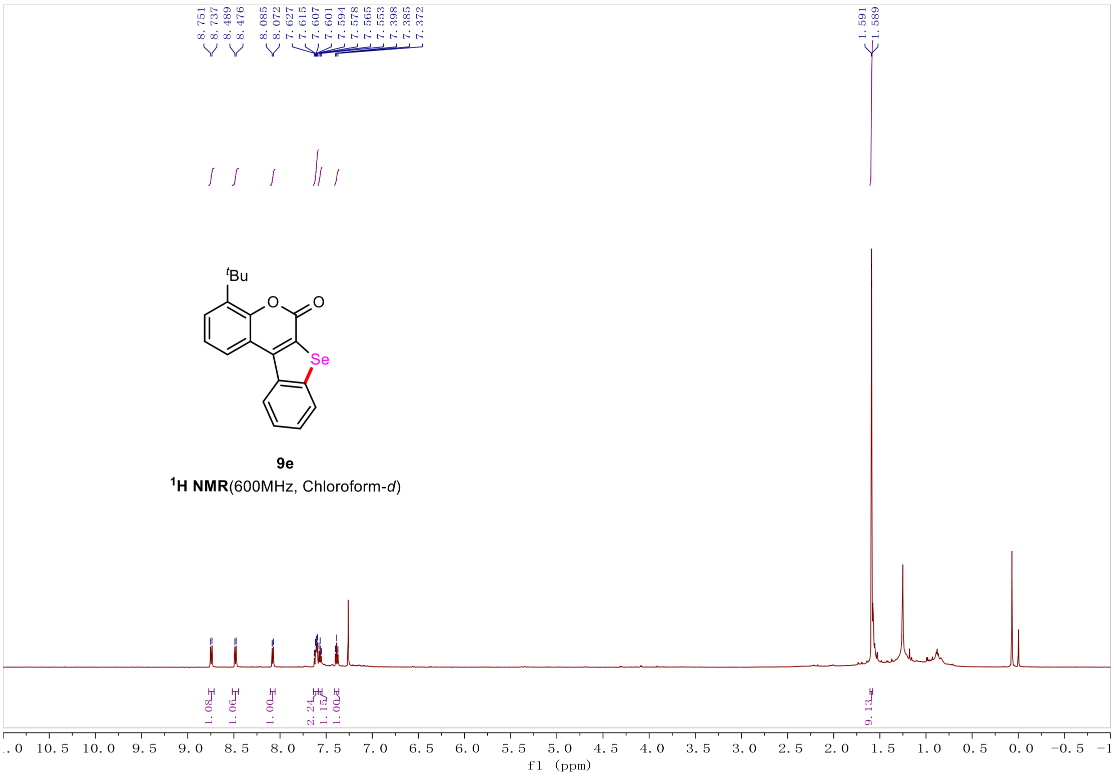
**8e**

**$^{1}$H NMR**(400MHz, Chloroform-*d*)



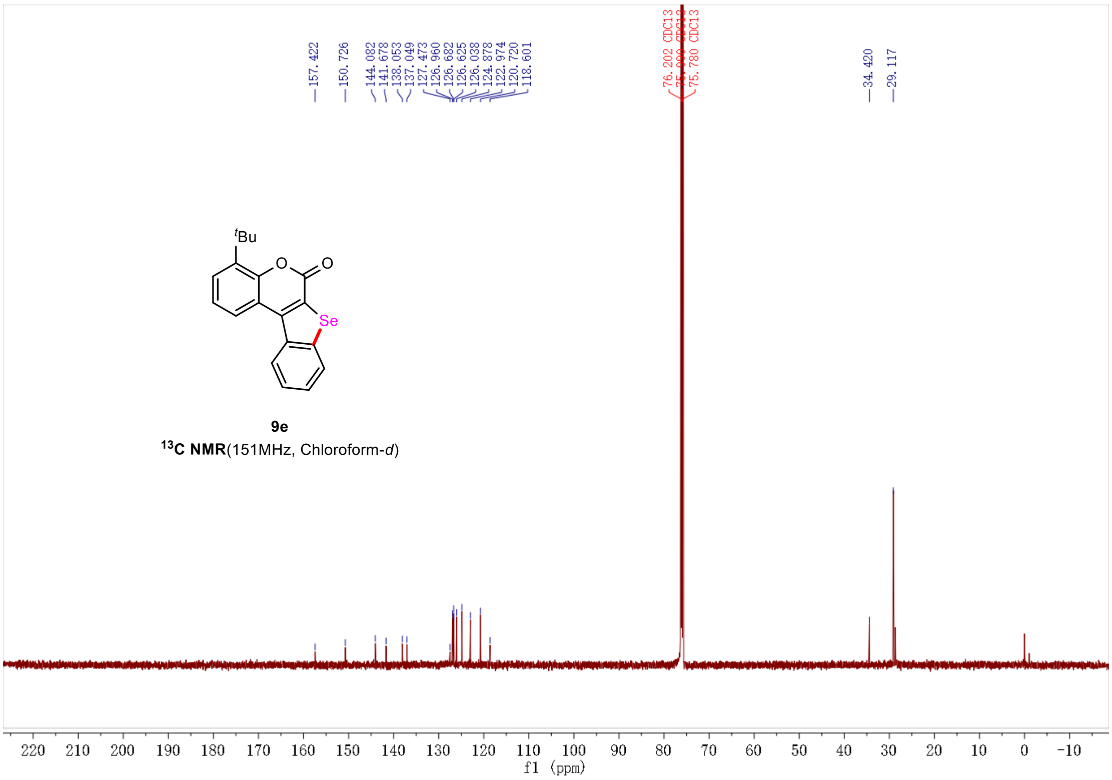
**8e**

**$^{13}$C NMR**(101MHz, Chloroform-*d*)



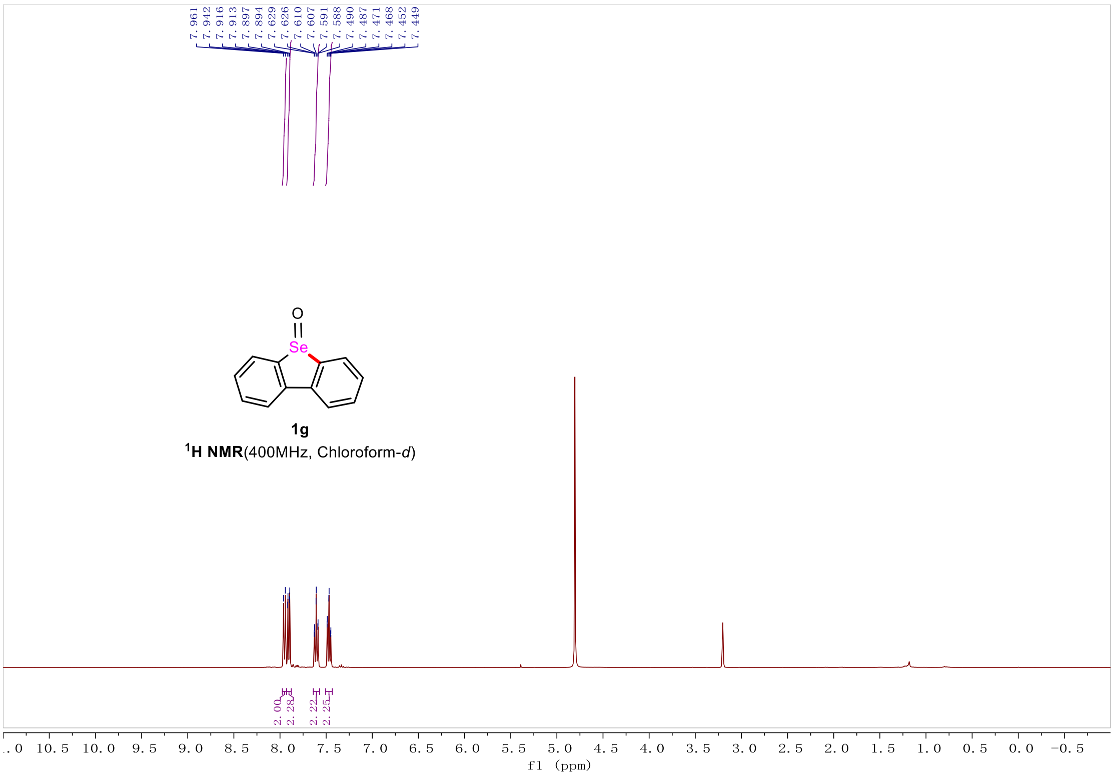
**9e**

**$^1$H NMR**(600MHz, Chloroform-*d*)



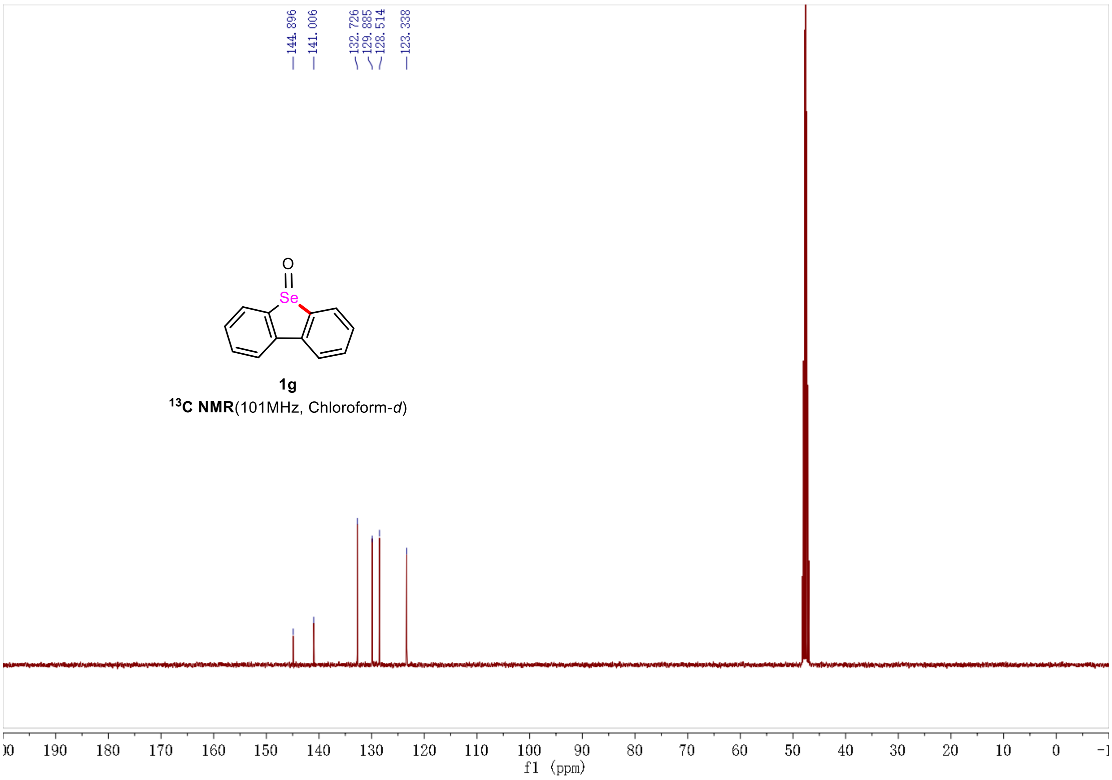
**9e**

**$^{13}$C NMR**(151MHz, Chloroform-*d*)



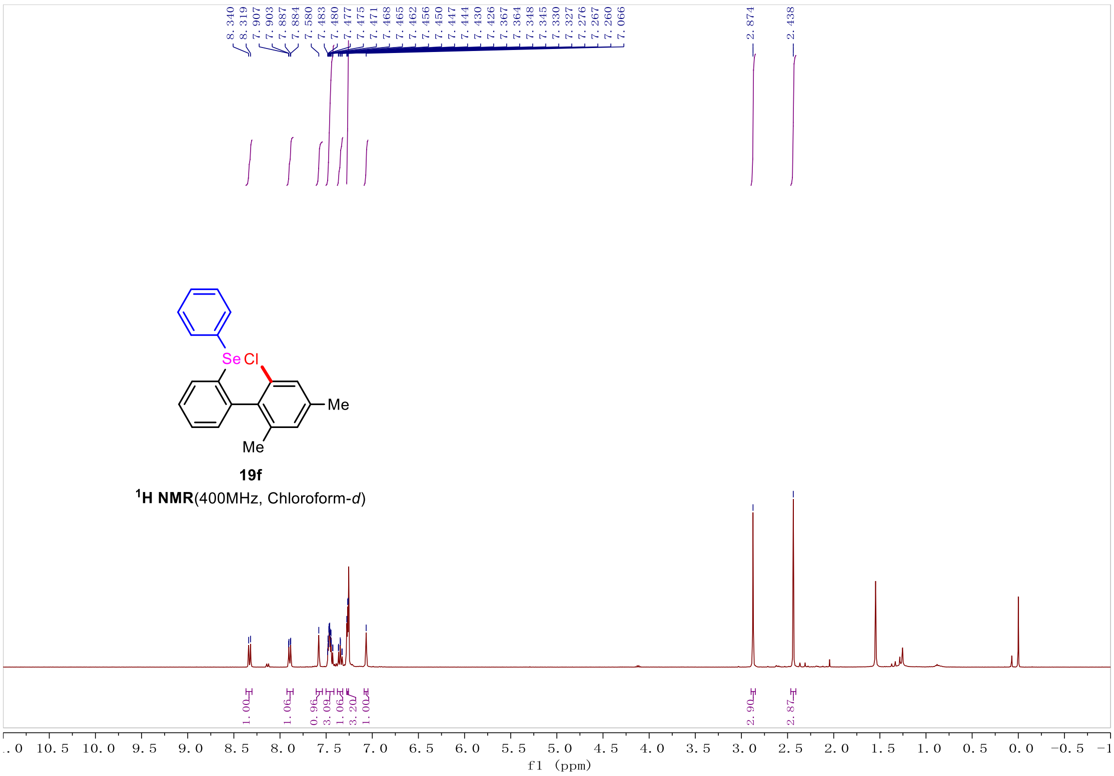
**1g**

**$^1$H NMR**(400MHz, Chloroform-*d*)



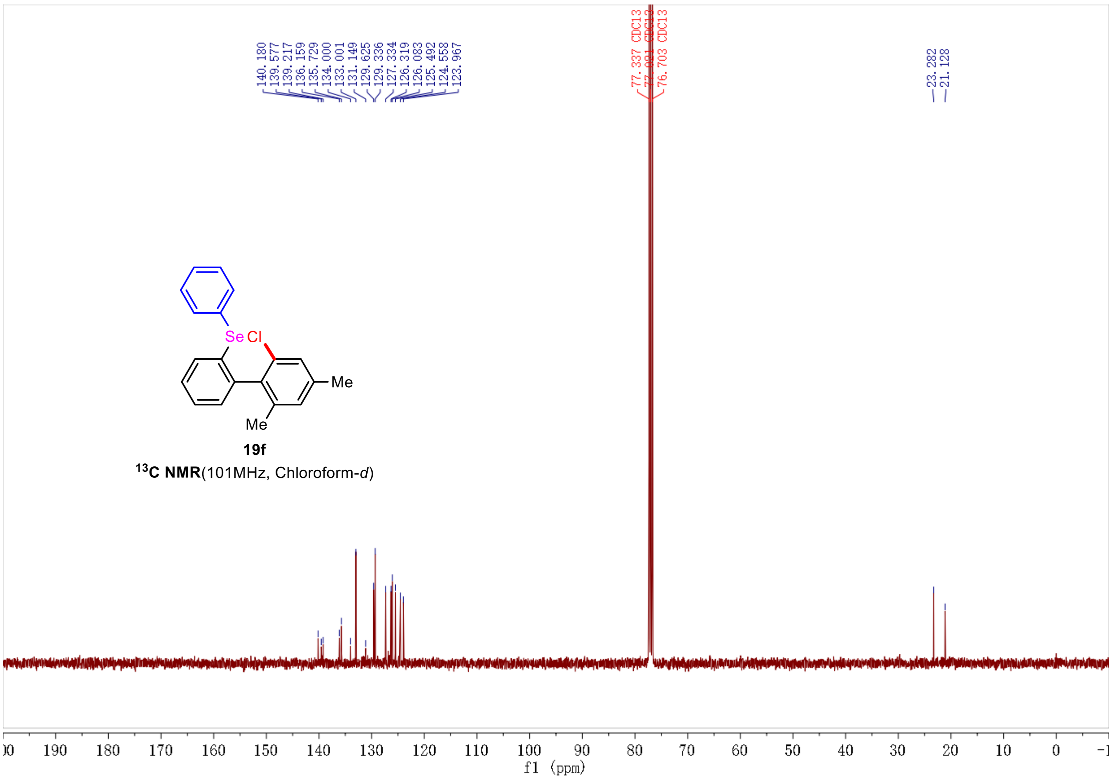
**1g**

**$^{13}$C NMR**(101MHz, Chloroform-*d*)



**19f**

$^1$**H NMR**(400MHz, Chloroform-*d*)



**19f**

$^{13}$**C NMR**(101MHz, Chloroform-*d*)