Dehydroxyselenocyanation of Alcohols Under Grinding Condition

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Supporting Information

Contents

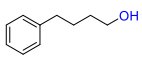
1. General Information

Unless otherwise noted, reagents and solvents were purchased from commercial suppliers (such as Energy Chemical Corporation, Bide Pharm etc.) and used without further purification. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded at 25 ^{o}C on a Bruker Advance 400 M NMR or 500 M NMR spectrometers ($CDCl_3$, DMSO – d_6 as solvent). HMBC spectra were recorded at 25 ^{o}C on a Bruker Avance III HD 700 MHz NMR spectrometers ($CDCl_3$ as solvent). Chemical shifts of ^{1}H, ^{19}F, ^{31}P, ^{77}Se and ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.00) and relative to the signal of $SiMe_4$ (δ 0.00 singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); p (pentent); m (multiplets), etc. Coupling constants are reported as a J value in Hertz (Hz). The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ H = 7.26 ppm, δ C = 77.16 ppm, DMSO – d_6 : δ H = 2.50 ppm, δ C = 39.52 ppm,). The high resolution mass spectrum (HRMS) were recorded on an Agilent (Q–TOF6520) unit with an ESI source. IR spectra were measured on a Shimadzu IRAffinnity–1s spectrometer. Melting points were measured on a binocular microscope XT4A melting point apparatus (uncorrected). Flash chromatography was performed using 200–300 mesh silica gel with the indicated solvent system. The alkaline potassium permanganate solution used as the color reagent is prepared by dissolving 1.5 g of potassium permanganate, 10 g of potassium carbonate, and 0.125 g of sodium hydroxide in 200 mL of distilled water.

2.Starting Materials

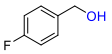
Table S1. Substrate scope of this work

Seleno/thiocyanated reagents **1**[1–5] and alcohols **2x**[6], **2an**[7], **2ao**[8] were prepared according to published procedures, **2w**, **2y** and **2ad** were prepared according to the General Procedure (Section 3, 3.1). The remaining substrates are all commercially available.



2a

2b



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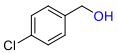

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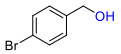

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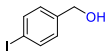

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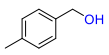

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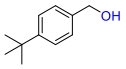

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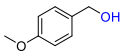

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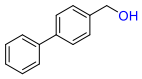

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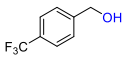

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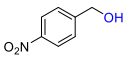

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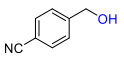
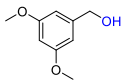


2m

2n

2o



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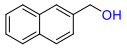

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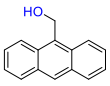
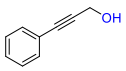


2r

2s

2t



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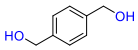

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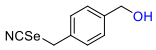
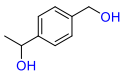
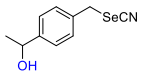


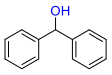
2w/3v



2x



2y/3x

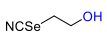


2z

2aa

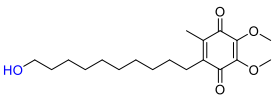
2ab

2ac



2ad/3ac

2ae



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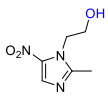

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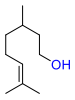

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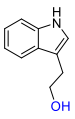

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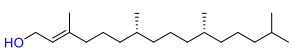

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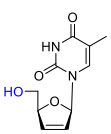

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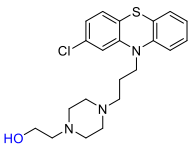
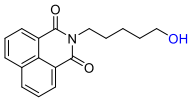


2al

2am



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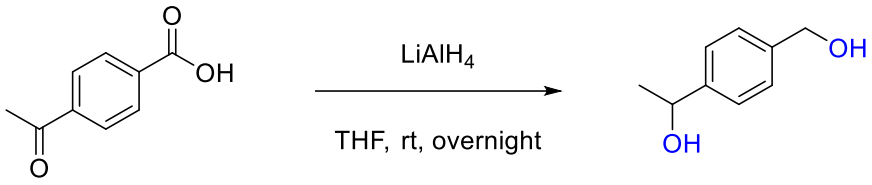
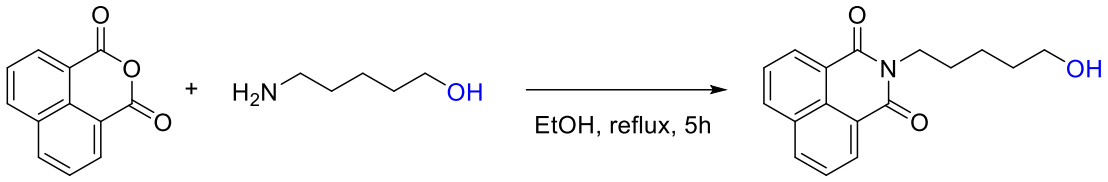
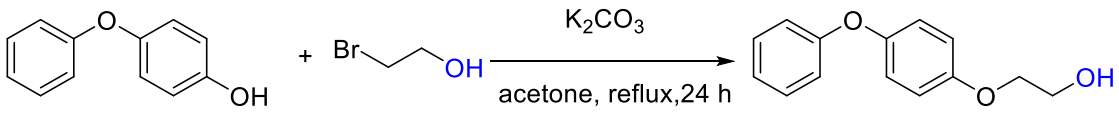


Add a solution of 4–acetylbenzoic acid (1 g, 6.10 mmol, 1.0 equiv) in THF (6 mL) to a solution of $LiAlH_4$ 1 M in THF (691 mg, 18.29 mmol, 3.0 equiv) cooled at 0 °C. Stir the mixture at 0 °C for 12 hours. Add water (5 mL), NaOH 1 M (1.3 mL) to the mixture. Filter the resulting suspension and purified by column chromatography (eluent: PE/EA = 2:1) to obtain **2x** in 90% yield.



Heat a suspension of 1,8–naphthalic anhydride (1.98 g, 10.0 mmol, 1.0 equiv) and 5–amino–1–pentanol (1.34 g, 13.0 mmol, 1.3 equiv) in absolute EtOH (90 mL) under reflux for 5 hours. Remove the solvent under reduced pressure. Wash the residue by ethanol and then purified by column chromatography (eluent: PE/EA = 3:1) to obtain the product **2an**.



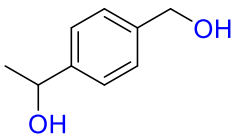
To a solution of 4–Phenoxyphenol (1.86 g, 10 mmol, 1.0 equiv), Potassium carbonate (6.9 g, 50 mmol, 5 equiv), and acetone (25 mL) was added 2–Bromoethanol (3.72 g, 30 mmol, 3.0 equiv). The resulting mixture was stirred and refluxed at 90°C for 24 h under nitrogen. The mixture was poured into 30 mL water solution and extracted with ethyl acetate (EtOAc) (3×10 mL). The combined organic layers were washed with brine (40 mL) and dried over anhydrous Na_2SO_4. The organic layer was concentrated in vacuo to obtain the crude mixture, which was purified by silica gel flash chromatography (eluent: PE/EA = 5:1) to obtain the product **2ao**.

The synthetic methods for compounds **2w**, **2y** and **2ad** are described in

Section 3, 3.1.

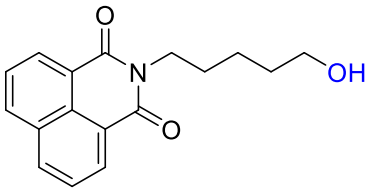
Spectra of Starting Materials

α–Methyl–1,4–benzenedimethanol (**2x**)



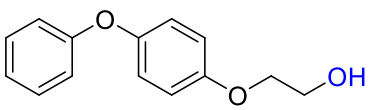
Colorless liquid; 90% yield; eluent: PE/EA = 2:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 4H), 4.91 (q, J = 6.5 Hz, 1H), 4.69 (s, 2H), 1.75 (s, 2H), 1.50 (d, J = 6.5 Hz, 3H) ppm. Spectra are consistent with literature data[1].

2–(5–Hydroxypentyl)–1*H*–benz[de]isoquinoline–1,3(2*H*)–dione (**2an**)



White solid; 78% yield; eluent: PE/EA = 3:1; mp. 93–95 °C (lit. mp. 94–96 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (dd, J = 7.3, 1.2 Hz, 2H), 8.21 (dd, J = 8.3, 1.2 Hz, 2H), 7.75 (dd, J = 8.2, 7.3 Hz, 2H), 4.23 – 4.16 (m, 2H), 3.67 (t, J = 6.5 Hz, 2H), 1.84 – 1.74 (m, 2H), 1.67 (m, 2H), 1.51 (m, 2H) ppm. Spectra and melting point are consistent with literature data[2].

2–(4–Phenoxyphenoxy)ethanol (**2ao**)



White solid; 57% yield; eluent: PE/EA = 5:1. mp. 120–122 °C (lit. mp. 120–122 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.09 – 6.89 (m, 7H), 4.08 (dd, J = 5.2, 3.8 Hz, 2H), 3.97 (dd, J = 5.2, 3.8 Hz, 2H), 2.05 (br, 1H) ppm. Spectra and melting point are consistent with literature data[3].

The spectral data for compounds **2w**, **2y**, and **2ad** are provided in Section 6.

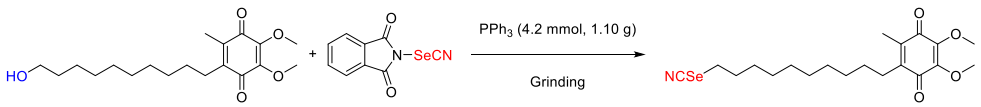
3. General Experimental Procedures

3.1 General Procedures

Add selenocyanation reagent **1a** (0.22 mmol) and triphenylphosphine (0.21 mmol) to an oven–dried ceramic mortar with a diameter of 60 mm. After shaking to mix thoroughly, add alcohol (0.20 mmol). Then, use a ceramic pestle to quickly grind the mixture until the system changes into an orange to red paste. Grinding is completed after 2 minutes. Without quenching, transfer the paste to a chromatography column to obtain the product. As a significant amount of unpleasant odor is released during the grinding process, it is recommended that all operations should be carried out in a fume hood.

3.2 Gram–Scale Reactions and Derivatization of Products

3.2.1 Gram–Scale Reaction



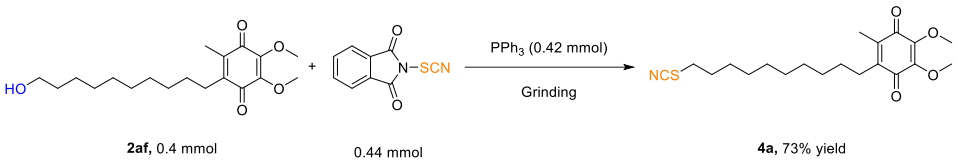
4 mmol
1.35 g

4.4 mmol
1.11 g

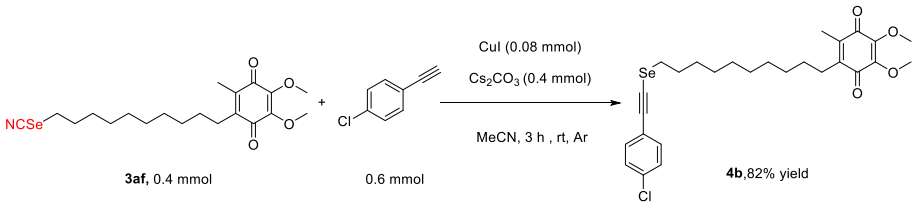
80% yield
1.37 g

Add *N*–selenocyanatophthalimide (4.4 mmol, 1.11 g, 1.1 equiv) and triphenylphosphine (4.2 mmol, 1.10 g, 1.05 equiv) to an oven–dried ceramic mortar with a diameter of 90 mm. After shaking to mix thoroughly, add **2af** (4.0 mmol, 1.35 g, 1.0 equiv). Then, use a ceramic pestle to quickly grind the mixture until the system changes into a red paste. Grinding is completed after 2 minutes. Without quenching, transfer the paste to a chromatography column (eluent: PE/EA = 10:1) to obtain the product **3af** resulting in 80% yield (1.37 g).

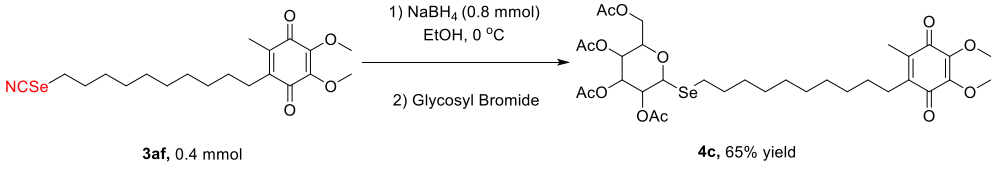
3.2.2 Derivatization of Products



Add *N*–thiocyanatophthalimide (0.44 mmol, 89.8 mg, 1.1 equiv) and triphenylphosphine (0.42 mmol, 110mg, 1.05 equiv) to an oven–dried ceramic mortar with a diameter of 60 mm. After shaking to mix thoroughly, add **2af** (0.4 mmol, 135.2 mg, 1.0 equiv). Then, use a ceramic pestle to quickly grind the mixture until the system changes into a red paste. Grinding is completed after 2 minutes. Without quenching, transfer the paste to a chromatography column (eluent: PE/EA = 5:1) to obtain the product **4a** resulting in 73% yield (110.7 mg).



To a 25 mL Schlenk tube charged with CuI (15.2 mg, 0.08 mmol, 0.2 equiv) and Cs_2CO_3 (130.4 mg, 0.4 mmol, 1.0 equiv) in acetonitrile (2.0 mL) under an argon atmosphere at room temperature was added **3af** (170.9 mg, 0.4 mmol, 1.0 equiv). Then, (4–chlorophenyl) acetylene (81.6 mg, 0.6 mmol, 1.5 equiv) was added. The reaction was stirred for 3 h. The solution was concentrated in vacuo to get the crude product, which was purified by flash chromatography (eluent: PE/EA = 15:1) to obtain the product **4b** resulting in 82% yield (175.8 mg).

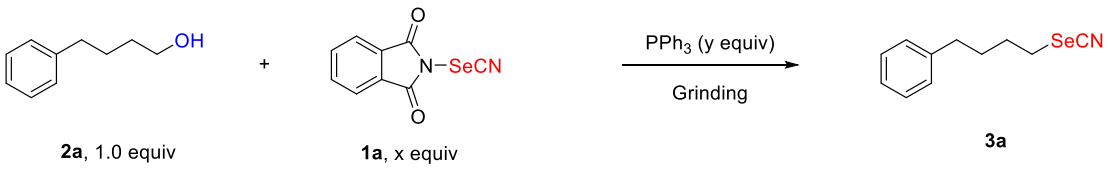


To a 25 mL Schlenk tube were added **3af** (170.9 mg, 0.4 mmol, 1.00 equiv) and EtOH (4.0 mL). Then $NaBH_4$ (30.4 mg, 0.8 mmol, 2.0 equiv) was added at 0 °C. After stirring 10 minutes, the glycosyl bromide was added (247.2 mg, 0.6 mmol, 1.5 equiv) and the reaction mixture was stirred at room temperature for 4 h. The mixture was poured into aq. sat. NH_4Cl (30 mL), and extracted with DCM (2×10 mL). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, and

concentrated under reduced pressure. The residue was purified by column chromatography (PE/EA = 3:1) to afford the product **4c** resulting in 65% yield (190.4 mg).

4. Optimization of Reaction Conditions

Table S2. Investigation of the Ratio between SeCN Source and Phosphine.[a,b,c]

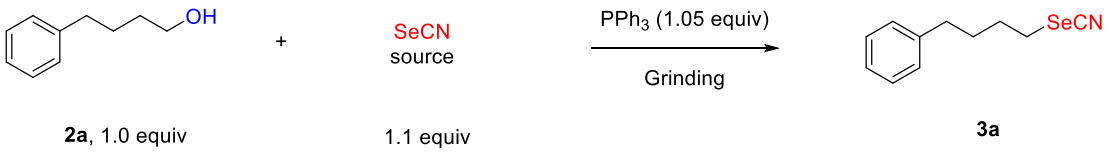


2a, 1.0 equiv　　**1a**, x equiv　　**3a**

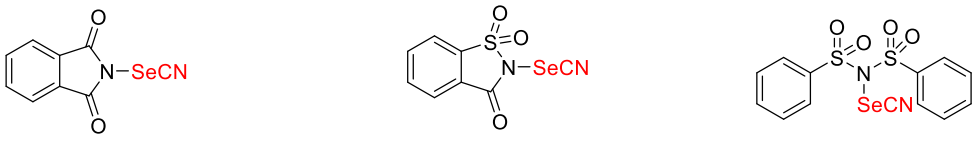
Entry	x	y	Yield(%)[b]
1	1.5	1.3	71
2	1.3	1.1	75
3	1.1	1.05	86
4	1.05	1.0	73
5	1.05	1.1	66
6	0.8	0.8	51
7[c]	1.1	1.05	80

[a] Standard Conditions: 4–phenylbutan–1–ol (**2a**, 0.2 mmol,1.0 equiv, 30.2 mg), *N*–Selenocyanatophthalimide (**1a**, x equiv), triphenylphosphine (y equiv) to an oven–dried ceramic mortar with a diameter of 60 mm. Then, use a ceramic pestle to quickly grind the mixture until the system changes into an orange paste. [b] Isolated yield. [c] Agate mortars were used instead of ceramic mortars.

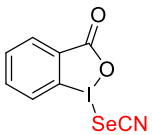
Table S3. Optimization of the SeCN Source[a,b]



2a, 1.0 equiv　　1.1 equiv　　**3a**



1a　　**1b**　　**1c**



1d

KSeCN

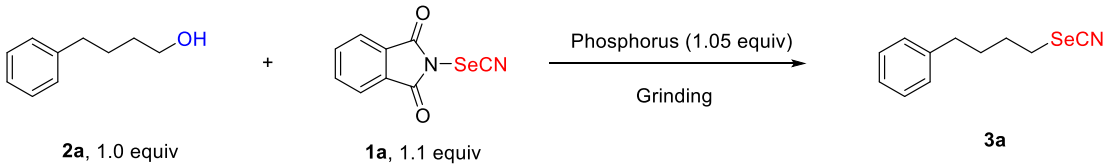
1e

Entry	–SeCN source	Yield (%)[b]

1	**1b**	69
2	**1c**	62
3	**1d**	43
4	**1e**	NR

[a] Standard Conditions: 4–phenylbutan–1–ol (**2a**, 0.2 mmol, 1.0 equiv, 30.2 mg), SeCN source (**1**, 0.22 mmol, 1.1 equiv), triphenylphosphine (55.0 mg, 0.21 mmol, 1.05 equiv) to an oven–dried ceramic mortar with a diameter of 60 mm. Then, use a ceramic pestle to quickly grind the mixture until the system changes into an orange paste. [b] Isolated yield.

Table S4. Optimization of the Phosphorus [a,b]

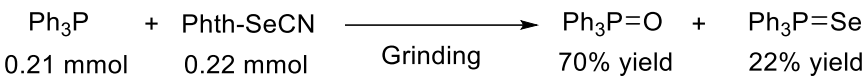


2a, 1.0 equiv **1a**, 1.1 equiv **3a**

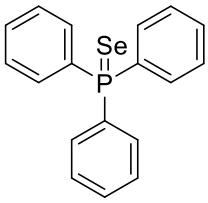
Entry	Phosphorus	Yield(%)[b]
1	PPh_3 (1.05 equiv)	86
2	PCy_3 (1.05 equiv)	NR
3	$P(4-CF_3C_6H_4)_3$ (1.05 equiv)	48
4	$P(4-OMeC_6H_4)_3$ (1.05 equiv)	29

[a] Standard Conditions: 4–phenylbutan–1–ol (**2a**, 0.2 mmol, 1.0 equiv, 30.2 mg), *N*–Selenocyanatophthalimide (**1a**, 50.4 mg, 0.22 mmol, 1.1 equiv), phosphorus (0.21 mmol, 1.05 equiv) to an oven–dried ceramic mortar with a diameter of 60 mm. Then, use a ceramic pestle to quickly grind the mixture until the system changes into an orange paste. [b] Isolated yield.

During some experiments, an impurity exhibiting similar polarity to the target product was detected. This impurity was subsequently identified as triphenylphosphine selenide by comparison with a standard spectrum. To investigate the origin of this byproduct, control experiments were performed.

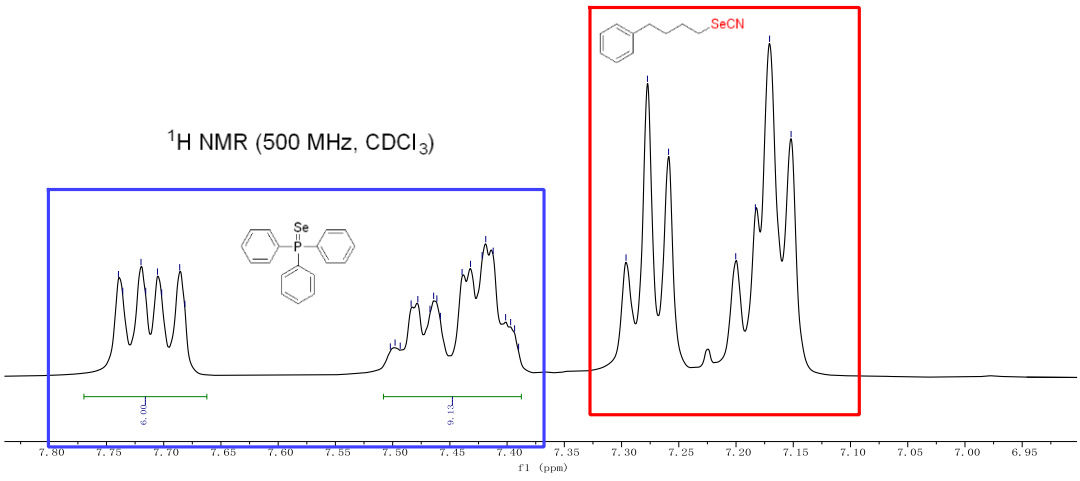


The experiments revealed that triphenylphosphine selenide could be formed by simply grinding triphenylphosphine and **1a** together, even without the addition of the substrate.

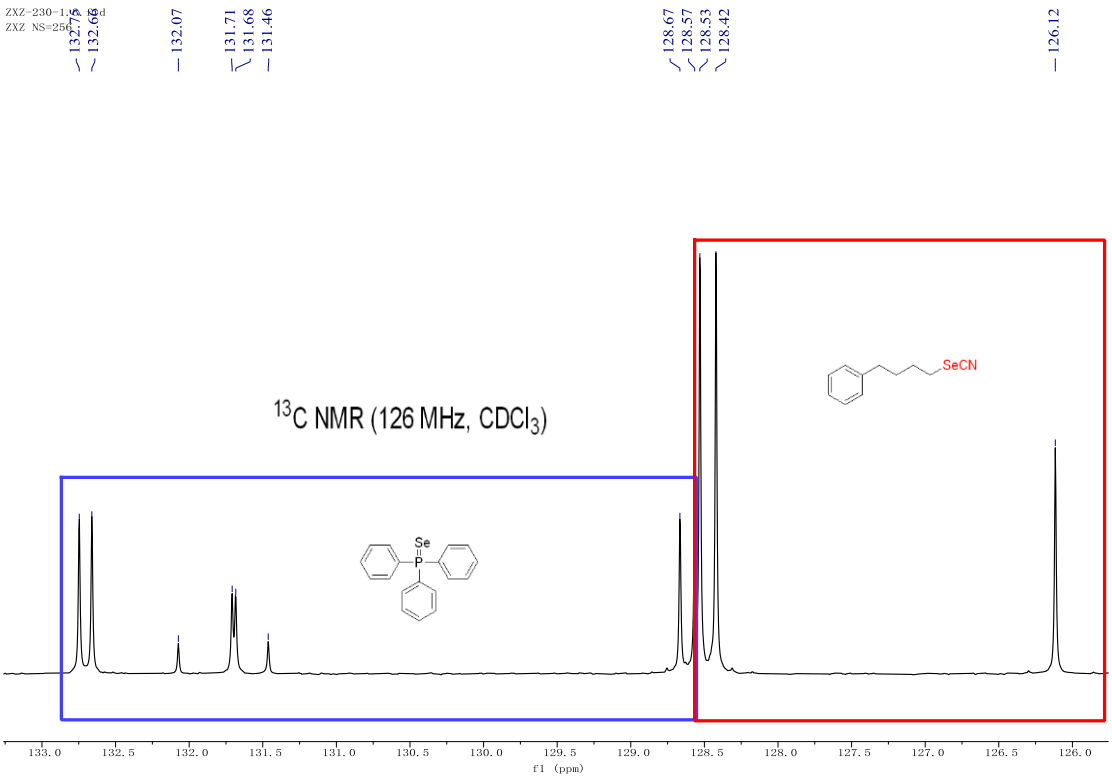


The identification of the byproduct triphenylphosphine selenide was accomplished through comprehensive spectroscopic characterization including ^{1}H (500 MHz, $CDCl_3$), ^{13}C (126 MHz, $CDCl_3$), ^{31}P (162 MHz, $CDCl_3$), and ^{77}Se (76 MHz, $CDCl_3$) NMR analyses, complemented HRMS. The spectrum was compared with the reference spectrum reported in the literature.[9] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 6H), 7.50 – 7.39 (m, 9H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.7 (d, J = 11.3 Hz), 131.8 (d, J = 76.9 Hz), 131.7 (d, J = 3.8 Hz), 128.6 (d, J = 12.6 Hz) ppm. ^{31}P NMR (162 MHz) δ 35.3(p, J = 13.7 Hz) ppm. ^{77}Se NMR (76 MHz) δ –265.9 (d, J = 736.2 Hz) ppm. HRMS *m/z*: calcd. for $C_{18}H_{16}PSe$ $[M + H]^+$ 343.0155, found 343.0142.

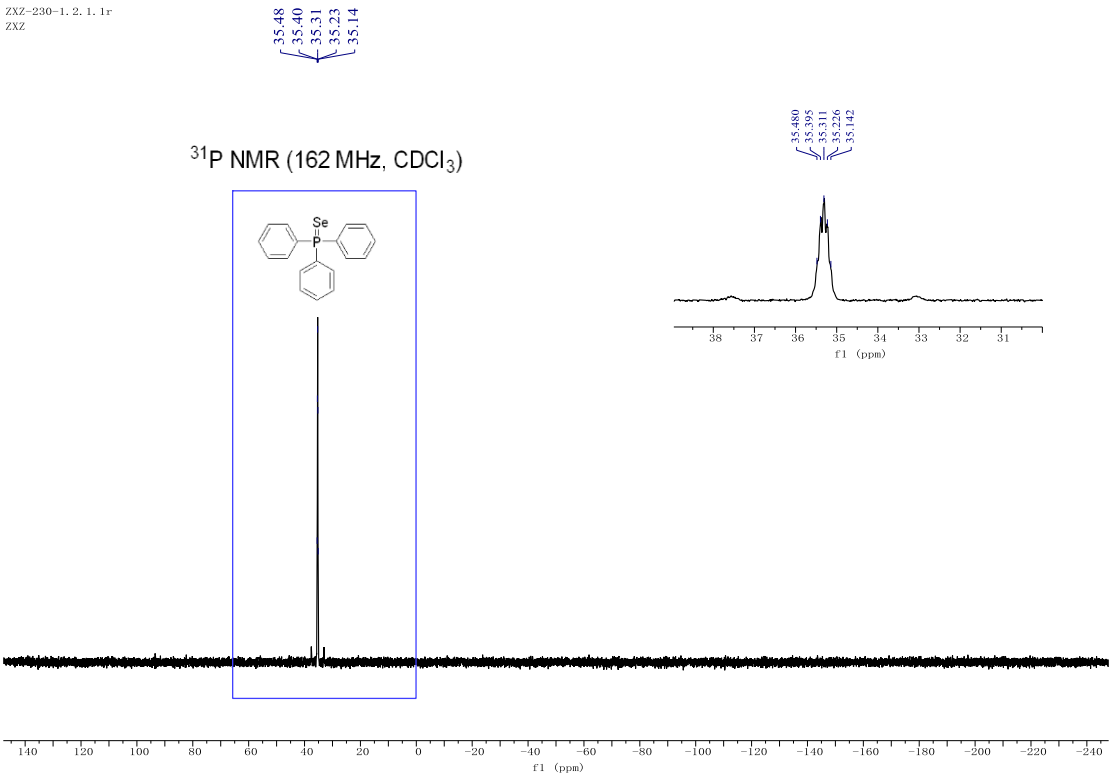
The mixed ^{1}H NMR spectrum of **3a** and triphenylphosphine selenide.



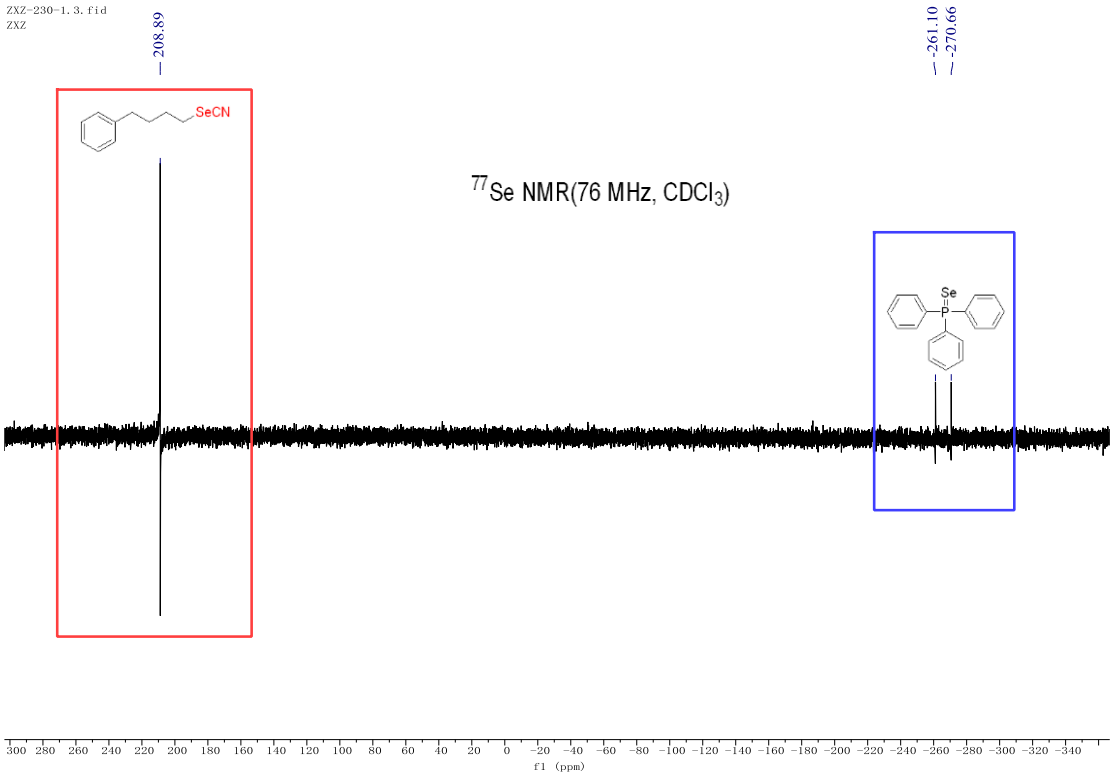
The mixed ^{13}C NMR spectrum of **3a** and triphenylphosphine selenide.



The mixed ^{31}P NMR spectrum of **3a** and triphenylphosphine selenide.

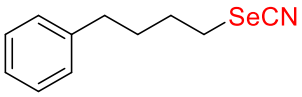


The mixed ^{77}Se NMR spectrum of **3a** and triphenylphosphine selenide.


ZXZ-230-1.3.fid
ZXZ
208.89
-261.10
-270.66
SeCN
Se
P
77Se NMR(76 MHz, CDCl3)
300 280 260 240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300 -320 -340
f1 (ppm)

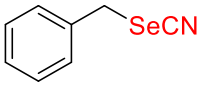
5. Characterization Data and Spectra of Products

(4–selenocyanatobutyl)benzene (**3a**)



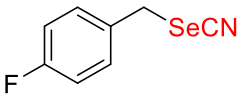
Following the general procedure (eluent: PE/EA = 10:1), **3a** was obtained in 86% yield (41.1 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (t, J = 7.5 Hz, 2H), 7.23 – 7.15 (m, 3H), 3.04 (t, J = 7.3 Hz, 2H), 2.66 (t, J = 7.6 Hz, 2H), 1.93 (p, J = 7.3 Hz, 2H), 1.77 (p, J = 7.6 Hz, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 141.4, 128.5, 128.4, 126.1, 101.5, 35.1, 30.8, 30.4, 29.4 ppm. ^{77}Se NMR (76 MHz, $CDCl_3$): δ 208.89. HRMS *m/z*: calcd. for $C_{11}H_{14}NSe$ $[M + H]^+$ 240.0291, found 240.0287.

(selenocyanatomethyl)benzene (**3b**)



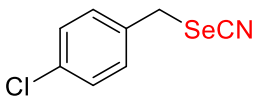
Following the general procedure (eluent: PE/EA = 10:1), **3b** was obtained in 81% yield (31.9 mg) as white solid. mp. 70–72 °C (lit. mp. 71–72 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 – 7.32 (m, 5H), 4.31 (s, 2H) ppm, ^{13}C NMR (126 MHz, $CDCl_3$): δ 135.4, 129.2, 129.0, 128.7, 101.9, 32.8 ppm. Spectra and melting point were consistent with literature data[10].

1–fluoro–4–(selenocyanatomethyl)benzene (**3c**)



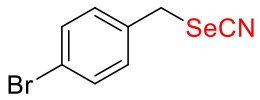
Following the general procedure (eluent: PE/EA = 10:1), **3c** was obtained in 77% yield (33.1 mg) as white solid. mp. 64–66 °C (lit. mp. 64–65 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.06 (t, J = 8.6 Hz, 2H), 4.27 (s, 2H) ppm, ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.8 (d, J = 249.1 Hz), 131.4 (d, J = 3.2 Hz), 130.8 (d, J = 8.7 Hz), 116.2 (d, J = 22.1 Hz), 101.7, 31.8 ppm, ^{19}F NMR (471 MHz, $CDCl_3$) δ –112.30 (m, 1F) ppm. Spectra and melting point were consistent with literature data[11].

1–chloro–4–(selenocyanatomethyl)benzene (**3d**)



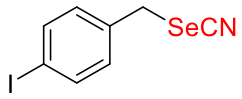
Following the general procedure (eluent: PE/EA = 10:1), **3d** was obtained in 82% yield (37.9 mg) as white solid. mp. 57–58 °C (lit. mp. 58–59 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 4.24 (s, 2H) ppm, ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.7, 134.1, 130.3, 129.4, 101.6, 31.9 ppm. Spectra and melting point were consistent with literature data[11].

1–bromo–4–(selenocyanatomethyl)benzene (**3e**)



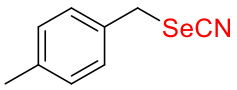
Following the general procedure (eluent: PE/EA = 10:1), **3e** was obtained in 75% yield (41.3 mg) as white solid. mp. 63–65 °C (lit. mp. 63–64 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.49 (d, J = 8.5, 2H), 7.25 – 7.23 (d, J = 8.5, 2H), 4.22 (s, 2H) ppm, ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.7, 132.4, 130.6, 122.9, 101.5, 31.9 ppm. Spectra and melting point were consistent with literature data[10].

1–iodo–4–(selenocyanatomethyl)benzene (**3f**)



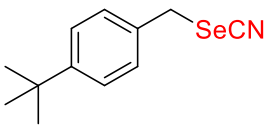
Following the general procedure (eluent: PE/EA = 5:1), **3f** was obtained in 70% yield (45.2 mg) as white solid. mp:78–80 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.68 (d, J = 8.4 Hz, 2H), 7.15 – 7.08 (d, J = 8.4 Hz, 2H), 4.22 (s, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.3, 135.2, 130.7, 101.4, 94.5, 32.0 ppm. HRMS *m/z*: calcd. for C_7H_6I $[M - SeCN]^+$ 216.9509, found 216.9505.

1–methyl–4–(selenocyanatomethyl)benzene (**3g**)



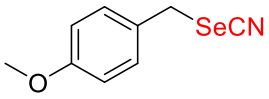
Following the general procedure (eluent: PE/EA = 10:1), **3g** was obtained in 72% yield (30.4 mg) as white solid. mp. 45–47 °C (lit. mp. 45–46 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 2H), 7.18 (d, J = 7.8 Hz, 2H), 4.29 (s, 2H), 2.36 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.7, 132.3, 129.9, 129.0, 102.1, 32.9, 21.3 ppm. Spectra and melting point were consistent with literature data[10].

1–(tert–butyl)–4–(selenocyanatomethyl)benzene (**3h**)



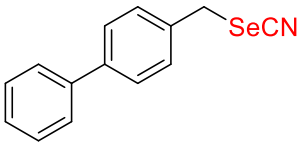
Following the general procedure (eluent: PE/EA = 10:1), **3h** was obtained in 63% yield (31.9 mg) as white solid. mp. 90–91 °C (lit. mp. 89–90°C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 4.31 (s, 2H), 1.33 (s, 9H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.9, 131.2, 127.7, 125.1, 101.1, 33.7, 31.7, 30.2 ppm. Spectra and melting point were consistent with literature data[10].

1–methoxy–4–(selenocyanatomethyl)benzene (**3i**)



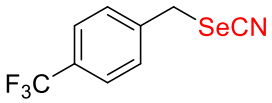
Following the general procedure (eluent: PE/EA = 8:1), **3i** was obtained in 77% yield (35.0 mg) as yellow solid. mp. 53–54 °C (lit. mp. 52–54 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.25 (d, J = 8.7 Hz, 2H), 6.92 – 6.85 (d, J = 8.7 Hz, 2H), 4.30 (s, 2H), 3.81 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9, 130.4, 127.2, 114.6, 102.2, 55.4, 32.9 ppm. Spectra and melting point were consistent with literature data[12].

4–(selenocyanatomethyl)–1,1'–biphenyl (**3j**)



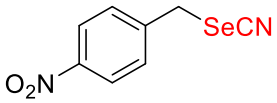
Following the general procedure (eluent: PE/EA = 10:1), **3j** was obtained in 70% yield (38.2 mg) as white solid. mp. 175–176 °C (lit. mp. 174–175 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.53 (m, 4H), 7.48 – 7.41 (m, 4H), 7.40 – 7.33 (m, 1H), 4.36 (s, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.7, 140.2, 134.3, 129.5, 128.9, 127.9, 127.7, 127.1, 101.9, 32.7 ppm. Spectra and melting point were consistent with literature data[10].

1–(selenocyanatomethyl)–4–(trifluoromethyl)benzene (**3k**)



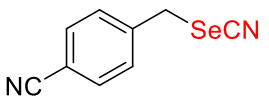
Following the general procedure (eluent: PE/EA = 8:1), **3k** was obtained in 52% yield (27.6 mg) as pink solid. mp. 54–55 °C (lit. mp. 54–55 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 4.29 (s, 2H) ppm. ^{19}F NMR (471 MHz, CDCl3) δ –62.74 (s, 3F) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.8, 130.8 (q, J = 32.7 Hz), 129.4, 126.1 (q, J = 3.8 Hz), 123.8 (q, J = 272.6 Hz), 101.1, 31.5 ppm. Spectra and melting point were consistent with literature data[11].

1–nitro–4–(selenocyanatomethyl)benzene (**3l**)



Following the general procedure (eluent: PE/EA = 5:1), **3l** was obtained in 45% yield (21.8 mg) as white solid. mp. 122–123°C (lit. mp. 122–124 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 – 8.22 (d, J = 8.9 Hz, 2H), 7.58 – 7.52 (m, 2H), 4.31 (s, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 143.1, 129.9, 124.4, 100.6, 31.0 ppm. Spectra and melting point were consistent with literature data[10].

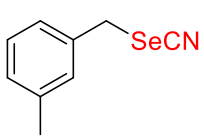
4–(selenocyanatomethyl)benzonitrile (**3m**)



Following the general procedure (eluent: PE/EA = 3:1), **3m** was obtained in 51% yield (22.6 mg) as white solid. mp.

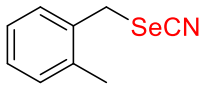
135–137 °C (lit. mp. 136–137 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 4.27 (s, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 133.1, 129.9, 118.4, 112.8, 101.0, 31.6 ppm. Spectra were consistent with literature data[10].

1–methyl–3–(selenocyanatomethyl)benzene (**3n**)



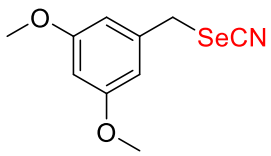
Following the general procedure (eluent: PE/EA = 10:1), **3n** was obtained in 68% yield (28.7 mg) as white solid. mp. 53–54°C (lit. mp. 55.5–56.5 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.13 (m, 4H), 4.27 (s, 2H), 2.35 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.0, 135.3, 129.7, 129.5, 129.1, 126.1, 102.1, 32.9, 21.4 ppm. Spectra and melting point were consistent with literature data[11].

1–methyl–2–(selenocyanatomethyl)benzene (**3o**)



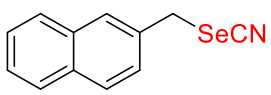
Following the general procedure (eluent: PE/EA = 10:1), **3o** was obtained in 59% yield (24.9 mg) as white solid. mp. 30–32°C (lit. mp. 29–30 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.17 (m, 4H), 4.36 (s, 2H), 2.41 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.8, 132.9, 131.1, 130.2, 129.2, 126.8, 101.8, 31.5, 19.2 ppm. Spectra and melting point were consistent with literature data[10].

1,3–dimethoxy–5–(selenocyanatomethyl)benzene (**3p**)



Following the general procedure (eluent: PE/EA = 5:1), **3p** was obtained in 70% yield (36.0 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.50 (d, J = 2.2 Hz, 2H), 6.42 (t, J = 2.3 Hz, 1H), 4.24 (s, 2H), 3.80 (s, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.2, 137.4, 106.9, 102.0, 100.7, 55.5, 33.0 ppm. HRMS (ESI) *m/z*: calcd. for $C_{10}H_{12}NO_2Se$ $[M + H]^+$ 258.0033, found 258.0028. IR (KBr) 2947, 2872, 2149(SeCN), 1207 cm^{-1}.

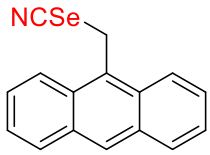
2–(selenocyanatomethyl)naphthalene (**3q**)



Following the general procedure (eluent: PE/EA = 10:1), **3q** was obtained in 78% yield (38.5 mg) as white solid. mp. 114–116 °C (lit. mp. 115–116 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 4H), 7.51 – 7.49 (m, 2H), 7.45–7.43 (d, J = 8.4 Hz, 1H), 4.45 (s, 2H) ppm. ^{13}C NMR (126

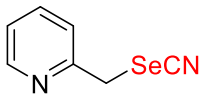
MHz, $CDCl_3$) δ 133.2, 133.1, 132.7, 129.2, 128.2, 128.0, 127.8, 126.8, 126.8, 126.3, 101.9, 33.4 ppm. Spectra and melting point were consistent with literature data[10].

9–(selenocyanatomethyl)anthracene (**3r**)



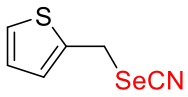
Following the general procedure (eluent: PE/EA = 10:1), **3r** was obtained in 69% yield (41.0 mg) as yellow solid. mp:163–165 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.49 (s, 1H), 8.25 – 8.24 (d, J = 7.5, 2H), 8.05 – 8.03 (d, J = 7.5, 2H), 7.64–7.67 (m, 2H), 7.53 – 7.50 (m, 2H), 5.48 (s, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 131.5, 130.0, 129.7, 129.6, 127.4, 125.5, 124.3, 123.1, 102.3, 26.8 ppm. HRMS (ESI) *m/z*: calcd. for $C_{16}H_{12}NSe$ $[M + H]^+$ 298.0135, found 298.0142.

2–(selenocyanatomethyl)pyridine (**3s**)



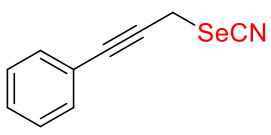
Following the general procedure (eluent: PE/EA = 3:1), **3s** was obtained in 44% yield (17.4 mg) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (dt, J = 5.0, 1.3 Hz, 1H), 7.73 (td, J = 7.7, 1.8 Hz, 1H), 7.35 (d, J = 7.8 Hz, 1H), 7.30 – 7.23 (m, 1H), 4.55 (s, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.4, 149.4, 137.1, 123.1, 122.3, 103.1, 34.5 ppm. HRMS (ESI) *m/z*: calcd. for $C_7H_7N_2Se$ $[M + H]^+$ 198.9774, found 198.9761.

2–(selenocyanatomethyl)thiophene (**3t**)



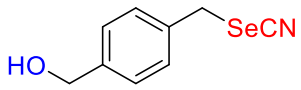
Following the general procedure (eluent: PE/EA = 3:1), **3t** was obtained in 62% yield (25.2 mg) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 – 7.25 (d, J = 6.4, 1H), 7.07 – 7.06 (m, 1H), 6.93 – 6.90 (dd, J_1 = 4.4, J_2 = 6.4, 1H), 4.50 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.3, 127.6, 126.5, 126.1, 100.9, 25.9. Spectra were consistent with literature data[13].

(3–selenocyanatoprop–1–yn–1–yl)benzene (**3u**)



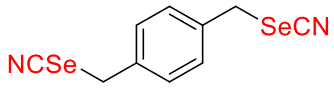
Following the general procedure (eluent: PE/EA = 8:1), **3u** was obtained in 65% yield (28.7 mg) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.38 – 7.28 (m, 3H), 4.01 (s, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.0, 129.1, 128.4, 121.8, 101.0, 87.7, 82.3, 15.8 ppm. HRMS (ESI) *m/z*: calcd. for $C_{10}H_8NSe$ $[M + H]^+$ 221.9822, found 221.9815.

(4–(selenocyanatomethyl)phenyl)methanol (**3v**)



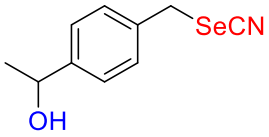
Following the general procedure (eluent: PE/EA = 3:1), the reaction scale was expanded to 0.5 mmol. **3v** was obtained in 73% yield (82.9 mg) as white solid. mp:69–71 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (m, 4H), 4.61 (s, 2H), 4.26 (s, 2H), 2.62 (s, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 134.8, 129.2, 127.6, 102.3, 64.5, 32.6 ppm. HRMS (ESI) *m/z*: calcd. for $C_9H_{10}NOSe$ $[M + H]^+$ 227.9928, found 227.9930.

1,4–bis(selenocyanatomethyl)benzene (**3w**)



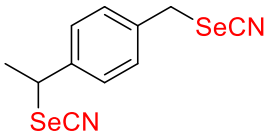
Following the general procedure (eluent: PE/EA = 3:1), synthesize **3w** through the following two routes, with the first being: using **2v** as the substrate, a one–pot two–step method was employed, adding 1.05 equivalents of triphenylphosphine and 1.1 equivalents of selenium cyanide reagent in two portions, resulting in a 47% yield (29.7 mg). Alternatively, the purified **3v** obtained after separation can be used as the substrate to synthesize **3w**, resulting in a 71% yield (47.4 mg). If a purer product cannot be obtained, one may attempt to wash the solid with dichloromethane, as the product has a relatively low solubility in dichloromethane. However, this may lead to the loss of trace amounts of the product. mp. 153–154 °C (lit. mp. 152–155 °C). ^{1}H NMR (500 MHz, DMSO – d_6) δ 7.37 (s, 4H), 4.32 (s, 4H) ppm. ^{13}C NMR (126 MHz, DMSO – d_6) δ 138.4, 129.6, 105.4, 32.8 ppm. Spectra and melting point were consistent with literature data[14].

1–(4–(selenocyanatomethyl)phenyl)ethan–1–ol (**3x**)



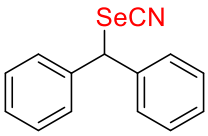
Following the general procedure (eluent: PE/EA = 3:1), the reaction scale was expanded to 0.5 mmol, **3x** was obtained in 66% yield (79.5 mg) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (q, J = 8.2 Hz, 4H), 4.87 (q, J = 6.5 Hz, 1H), 4.28 (s, 2H), 2.20 (s, 1H), 1.47 (d, J = 6.5 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.5, 134.5, 129.2, 126.2, 102.1, 69.9, 32.6, 25.2 ppm. The HMBC spectrum, displayed in Part 6, indicated a coupling interaction between the hydrogen atoms on the α – carbon of the primary alcohol and the carbon center in the selenocyanate substituent. HRMS (ESI) *m/z*: calcd. for $C_{10}H_{12}NOSe$ $[M + H]^+$ 242.0084, found 242.0080.

1–(1–selenocyanatoethyl)–4–(selenocyanatomethyl)benzene (**3y**)



Following the general procedure (eluent: PE/EA = 3:1), synthesize **3y** through the following two routes, with the first being: using **2x** as the substrate, a one–pot two–step method was employed, adding 1.05 equivalents of triphenylphosphine and 1.1 equivalents of selenium cyanide reagent in two portions, resulting in a 23% yield (15.2 mg). Alternatively, the purified **3x** obtained after separation can be used as the substrate to synthesize **3y**, resulting in a 43% yield (28.4 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 4.89 (q, J = 7.0 Hz, 1H), 4.27 (s, 2H), 2.03 (d, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.3, 136.4, 129.7, 127.9, 102.3, 101.7, 44.9, 32.1, 22.6 ppm. HRMS (ESI) *m/z*: calcd. for $C_{11}H_{11}N_2Se_2$ $[M + H]^+$ 330.9253, found 330.9253.

(selenocyanatomethylene)dibenzene (**3z**)

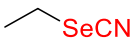


Following the general procedure (eluent: PE/EA = 20:1), **3z** was obtained in 41% yield (22.4 mg) as pink solid. mp. 48–50 °C (lit. mp. 48–49 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 4H), 7.33 – 7.26 (m, 4H), 7.26 – 7.21 (m, 2H), 6.04 (s, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.8, 128.1, 127.6, 127.5, 101.7, 53.5 ppm. Spectra and melting point were consistent with literature data[15].

Selenocyanatomethane (**3aa**)

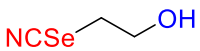
Following the general procedure (eluent: pentane/DCM = 15:1, Use alkaline potassium permanganate as a chromogenic reagent), the reaction scaled of 0.5 mmol, rotary evaporation was performed at 0 °C, **3aa** was obtained in 53% yield (32.1 mg) as colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.51(s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 102.0, 8.5 ppm. HRMS (ESI) *m/z*: calcd. for C_2H_4NSe $[M + H]^+$ 121.9509, found 121.9500.

Selenocyanatoethane (**3ab**)



Following the general procedure (eluent: pentane/DCM = 15:1, Use alkaline potassium permanganate as a chromogenic reagent), the reaction scaled of 0.5 mmol, rotary evaporation was performed at 0 °C, **3ab** was obtained in 62% yield (41.9 mg) as colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.08 (q, J = 7.5 Hz, 2H), 1.68 (t, J = 7.4 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 101.3, 23.4, 16.5 ppm. HRMS (ESI) *m/z*: calcd. for C_3H_6NSe $[M + H]^+$ 135.9665, found 135.9673.

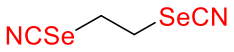
2–selenocyanatoethan–1–ol (**3ac**)



Following the general procedure (eluent: PE/EA = 2:1, Use alkaline

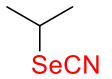
potassium permanganate as a chromogenic reagent), the reaction scaled of 0.5 mmol, **3ac** was obtained in 69% yield (52.1 mg) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.06 (m, 2H), 3.30 – 3.21 (m, 2H), 2.32 (br, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 101.5, 61.3, 32.2 ppm. Spectra were consistent with literature data[16].

1,2–diselenocyanatoethane (**3ad**)



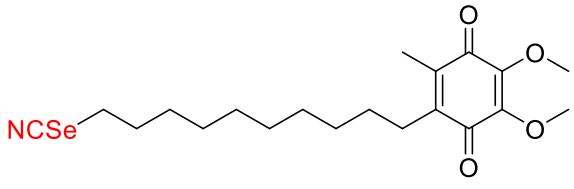
Following the general procedure (eluent: PE/EA = 5:1, Use alkaline potassium permanganate as a chromogenic reagent), synthesize **3ad** through the following two routes, with the first being: using **2ac** as the substrate, a one–pot two–step method was employed, adding 1.05 equivalents of triphenylphosphine and 1.1 equivalents of selenium cyanide reagent in two portions, resulting in a 44% yield (21.1 mg). Alternatively, the purified **3ac** obtained after separation can be used as the substrate to synthesize **3ad**, resulting in a 75% yield (36.0 mg) as brown solid. mp. 110-111 ºC (lit. mp. 112 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.46 – 3.44(m, 4H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 105.1, 30.0 ppm. HRMS (ESI) *m/z*: calcd. for $C_4H_5N_2Se_2$ $[M + H]^+$ 240.8783, found 240.8788. Spectra were consistent with literature data[17]

2–selenocyanatopropane (**3ae**)



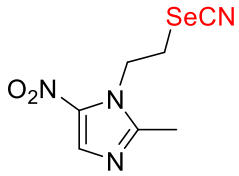
Following the general procedure (eluent: pentane/DCM = 15:1, Use alkaline potassium permanganate as a chromogenic reagent), the reaction scaled of 0.5 mmol, rotary evaporation was performed at 0 °C, **3ae** was obtained in 38% yield (28.3 mg) as colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.74 (p, *J* = 6.8 Hz, 1H), 1.65 (d, *J* = 6.8 Hz, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 101.5, 38.3, 25.0 ppm. HRMS (ESI) *m/z*: calcd. for C_4H_8NSe $[M + H]^+$ 149.9822 find 149.9815.

2,3–dimethoxy–5–methyl–6–(10–selenocyanatodecyl)cyclohexa–2,5–diene–1,4–dion e (**3af**)



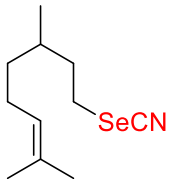
Following the general procedure (eluent: PE/EA = 10:1), **3af** was obtained in 84% yield (71.7 mg) as orange oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.99 (s, 6H), 3.07 (t, *J* = 7.4 Hz, 2H), 2.45 (t, *J* = 7.5 Hz, 2H), 2.01 (s, 3H), 1.90 (p, *J* = 7.4 Hz, 2H), 1.47 – 1.25 (m, 14H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.7, 184.1, 144.3, 144.3, 143.0, 138.6, 101.6, 61.1, 30.8, 29.7, 29.7, 29.3, 29.3, 29.3, 29.1, 28.8, 28.7, 26.3, 11.9 ppm. HRMS (ESI) *m/z*: calcd. for $C_{20}H_{30}NO_4Se$ $[M + H]^+$ 428.1340, found 428.1340.

2–methyl–5–nitro–1–(2–selenocyanatoethyl)–1*H*–imidazole (**3ag**)



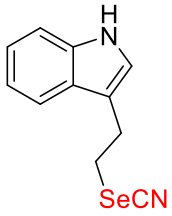
Following the general procedure (eluent: PE/EA = 3:1), **3ag** was obtained in 69% yield (35.9 mg) as brown oil. ^{1}H NMR (500 MHz, DMSO – d_6) δ 8.05 (s, 1H), 4.67 (t, J = 6.6 Hz, 2H), 3.45 (t, J = 6.6 Hz, 2H), 2.52 (s, 3H) ppm. ^{13}C NMR (126 MHz, DMSO – d_6) δ 151.8, 138.9, 133.6, 104.9, 46.4, 29.2, 14.6 ppm. HRMS (ESI) *m/z*: calcd. for $C_7H_9N_4O_2Se$ $[M + H]^+$ 260.9891, found 260.9882.

2,6–dimethyl–8–selenocyanatooct–2–ene (**3ah**)



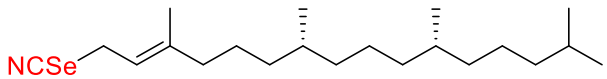
Following the general procedure (eluent: PE/EA = 20:1; Use alkaline potassium permanganate as a chromogenic reagent), **3ah** was obtained in 82% yield (40.2 mg) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.08 (m, 1H), 3.14 – 3.00 (m, 2H), 2.08 – 1.85 (m, 3H), 1.77 – 1.55 (m, 8H), 1.40 – 1.33 (m, 1H), 1.25 – 1.18 (m, 1H), 0.94(d, J = 6.6 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ: 131.8, 124.2, 101.5, 37.9, 36.5, 32.4, 27.6, 25.7, 25.3, 19.0, 17.7 ppm. HRMS (ESI) *m/z*: calcd. for $C_{11}H_{20}NSe$ $[M + H]^+$ 246.0761, found 246.0759.

3–(2–selenocyanatoethyl)–1*H*–indole (**3ai**)



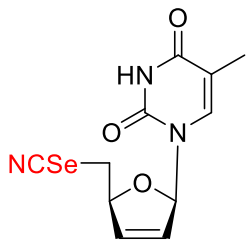
Following the general procedure (eluent: PE/EA = 3:1), **3ai** was obtained in 58% yield (29.0 mg) as pink oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.56 (d, J = 7.9 Hz, 1H), 7.36 (d, J = 8.1 Hz, 1H), 7.24 – 7.18 (m, 1H), 7.14 (td, J = 7.5, 1.0 Hz, 1H), 3.34 (m, 4H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.4, 126.7, 122.6, 122.5, 119.8, 118.4, 112.9, 111.6, 102.1, 30.5, 26.8 ppm. HRMS (ESI) m/z: calcd. for $C_{11}H_{11}N_2Se$ $[M + H]^+$ 251.0087, found 251.0088.

(7*R*,11*R*, *E*)–3,7,11,15–tetramethyl–1–selenocyanatohexadec–2–ene (**3aj**)



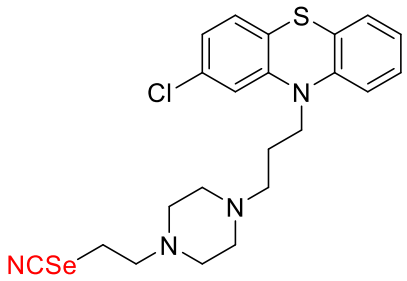
Following the general procedure (eluent: PE/EA = 20:1; Use alkaline potassium permanganate as a chromogenic reagent), **3aj** was obtained in 78% yield (60.1 mg) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.47 – 5.38 (t, J = 8.5 Hz, 1H), 3.82 (d, J = 8.4 Hz, 2H), 2.14 – 1.98 (m, 2H), 1.74 (s, 2H), 1.58 – 1.00 (m, 20H), 0.91 – 0.82 (m, 12H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.6, 117.1, 102.0, 39.9, 39.4, 37.4, 37.4, 37.3, 36.5, 32.8, 32.7, 28.0, 27.8, 25.1, 24.8, 24.5, 22.7, 22.7, 19.8, 19.7, 16.2 ppm. HRMS (ESI) *m/z*: calcd. for $C_{21}H_{40}NSe$ $[M + H]^+$ 386.2326, found 386.2322.

5–methyl–1–((2*R*,5*S*)–5–(selenocyanatomethyl)–2,5–dihydrofuran–2–yl)pyrimidine–2,4(1*H*,3*H*)–dione (**3ak**)



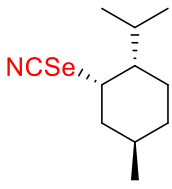
Following the general procedure (eluent: PE/EA = 1:1), **3ak** was obtained in 59% yield (36.9 mg) as pink solid. ^{1}H NMR (500 MHz, DMSO – d_6) δ 11.35 (s, 1H), 7.26 (s, 1H), 6.82 (s, 1H), 6.48 (d, J = 5.8 Hz, 1H), 6.09 (d, J = 4.9 Hz, 1H), 5.05 (s, 1H), 3.38 (dd, J = 12.9, 5.1 Hz, 1H), 3.32 – 3.26 (m, 1H), 1.78 (s, 3H) ppm. ^{13}C NMR (126 MHz, DMSO – d_6) δ 163.8, 150.8, 136.1, 135.2, 126.6, 109.7, 104.5, 89.4, 84.4, 33.0, 12.1 ppm. HRMS *m/z*: calcd. for $C_{11}H_{12}N_3O_3Se$ $[M + H]^+$ 314.0044, found 314.0040.

2–chloro–10–(3–(4–(2–selenocyanatoethyl)piperazin–1–yl)propyl)–10*H*–phenothiazine (**3al**)



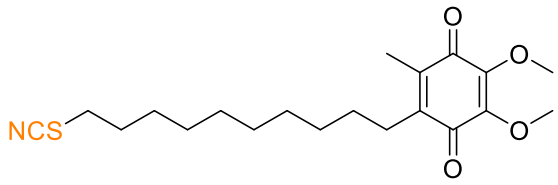
Following the general procedure (eluent: EA), **3al** was obtained in 72% yield (70.8 mg) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 – 7.08 (m, 2H), 7.01 (d, J = 8.1 Hz, 1H), 6.96 – 6.82 (m, 4H), 3.89 (t, J = 6.8 Hz, 2H), 3.46 (t, J = 6.5 Hz, 2H), 2.74 (t, J = 6.6 Hz, 2H), 2.58 – 2.30 (m, 10H), 1.91 (p, J = 6.9 Hz, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.5, 144.5, 133.2, 127.9, 127.5, 127.4, 124.8, 123.5, 122.9, 122.3, 115.9, 115.8, 104.8, 55.2, 54.3, 52.9, 52.6, 45.2, 30.2, 24.2. HRMS (ESI) *m/z*: calcd. for $C_{22}H_{26}ClN_4SSe$ $[M + H]^+$ 493.0732, found 493.0730.

(1*S*,4*R*)–1–isopropyl–4–methyl–2–selenocyanatocyclohexane (**3am**)



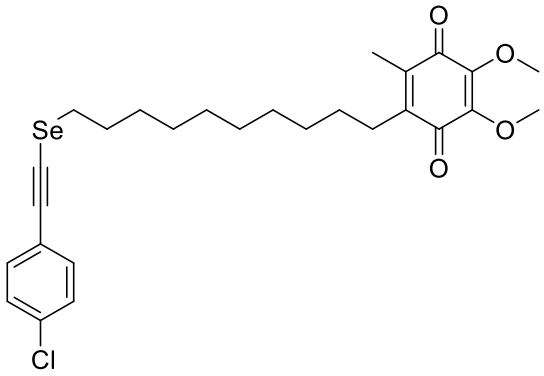
Following the general procedure (eluent: PE; Use alkaline potassium permanganate as a chromogenic reagent), the reaction scaled of 0.4 mmol, **3am** was obtained in 27% yield (26.4 mg) as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.40 (td, J = 11.7 Hz, 3.9 Hz, 1H), 2.46 – 2.38 (m, 1H), 2.12 – 1.99 (m, 1H), 1.83 – 1.72 (m, 2H), 1.59 (m, 1H), 1.55 – 1.45 (m, 2H), 1.15 – 1.08 (m, 1H), 1.17 – 1.06 (m, 1H), 1.09 – 0.98 (m, 6H), 0.79 (d, J = 6.9 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 101.5, 52.1, 48.1, 45.6, 34.7, 34.2, 29.9, 25.2, 21.9, 21.3, 15.0 ppm. HRMS (ESI) *m/z*: calcd. for $C_{11}H_{20}NSe$ $[M + H]^+$ 246.0761, found 246.0755.

2,3–dimethoxy–5–methyl–6–(10–thiocyanatodecyl)cyclohexa–2,5–diene–1,4–dione (**4a**)



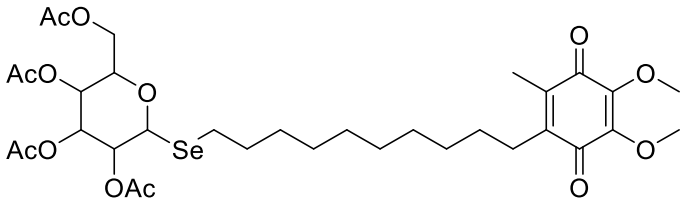
Following the general procedure (eluent: PE/EA = 5:1), **4a** was obtained in 73% yield (56.1 mg) as red oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.95 (s, 6H), 2.92 (t, J = 7.3 Hz, 2H), 2.44 – 2.38 (m, 2H), 1.98 (s, 3H), 1.79 (p, J = 7.4 Hz, 2H), 1.45 – 1.33 (m, 2H), 1.36 – 1.23 (m, 14H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.8, 184.3, 144.5, 144.4, 143.2, 138.8, 112.5, 61.3, 34.2, 30.0, 29.9, 29.5, 29.4, 29.4, 29.0, 28.8, 28.1, 26.5, 12.0 ppm. HRMS (ESI) *m/z*: calcd. for $C_{20}H_{30}NO_4S$ $[M + H]^+$ 380.1896, found 380.1900.

2–(10–(((4–chlorophenyl)ethynyl)selanyl)decyl)–5,6–dimethoxy–3–methylcyclohexa–2,5–diene–1,4–dione (**4b**)



Following the general procedure (eluent: PE/EA = 5:1), **4b** was obtained in 82% yield (175.8 mg) as orange oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 7.26 (m, 2H), 3.99 (s, 6H), 2.87 (t, J = 7.3 Hz, 2H), 2.45(t, J = 7.5 Hz, 2H), 2.01 (s, 3H), 1.85 (p, J = 7.4 Hz, 2H), 1.47 – 1.25 (m, 14H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.7, 184.2, 144.3, 144.3, 143.1, 138.7, 133.9, 132.7, 128.6, 122.2, 98.3, 72.0, 61.1, 30.1, 29.8, 29.7, 29.4, 29.4, 29.3, 29.3, 29.0, 28.7, 26.4, 11.9 ppm. HRMS (ESI) *m/z*: calcd. for $C_{27}H_{34}ClO_4S$ $[M + H]^+$ 537.1311, found 537.1306.

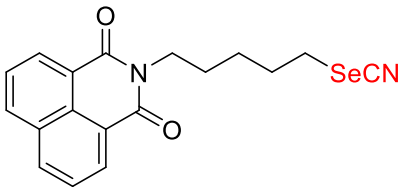
2–(acetoxymethyl)–6–((10–(4,5–dimethoxy–2–methyl–3,6–dioxocyclohexa–1,4–dien–1–yl)decyl)selanyl)tetrahydro–2*H*–pyran–3,4,5–triyl triacetate (**4c**)



Following the general procedure (eluent: PE/EA = 2:1), **4c** was obtained in 65% yield (190.3 mg) as orange oil

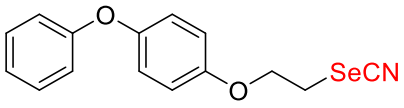
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.20 (t, J = 9.3 Hz, 1H), 5.09 (td, J = 9.6, 7.0 Hz, 2H), 4.72 (d, J = 10.2 Hz, 1H), 4.24 (m, 1H), 4.17 – 4.08 (m, 1H), 3.99 (s, 6H), 3.70 (ddd, J = 10.1, 4.9, 2.4 Hz, 1H), 2.82 – 2.66 (m, 2H), 2.45 (t, J = 7.5 Hz, 2H), 2.10 – 1.99 (m, 15H), 1.74 – 1.65 (m, 2H), 1.43 – 1.23 (m, 14H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.7, 184.1, 170.6, 170.2, 169.4, 169.4, 144.3, 144.3, 143.0, 138.6, 77.4, 76.9, 73.8, 72.8, 70.8, 68.3, 62.2, 61.1, 30.3, 29.8, 29.8, 29.5, 29.4, 29.3, 29.1, 28.7, 26.4, 23.8, 20.8, 20.7, 20.6, 20.6, 11.9 ppm. HRMS (ESI) *m/z*: calcd. for $C_{33}H_{49}O_{13}Se$ $[M + H]^+$ 733.2338, found 733.2344.

2–(5–selenocyanatopentyl)–1H–benzo[de]isoquinoline–1,3(2*H*)–dione (**5a**)



Following the general procedure (eluent: PE/EA = 5:1), **5a** was obtained in 78% yield (58.0 mg) as white solid. mp. 124–125 ºC (lit. mp. 126–127 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (m, 1H), 8.21 (m, 1H), 7.75 (t, J = 7.8 Hz, 1H), 4.20 (t, J = 7.4 Hz, 1H), 3.09 (t, J = 7.4 Hz, 1H), 2.00 (p, J = 7.5 Hz, 1H), 1.81 (p, J = 7.7 Hz, 1H), 1.59 (p, J = 6.4 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2, 134.0, 131.6, 131.3, 128.1, 127.0, 122.6, 101.5, 39.9, 30.4, 29.4, 27.2, 26.6 ppm. Spectra were consistent with literature data[7].

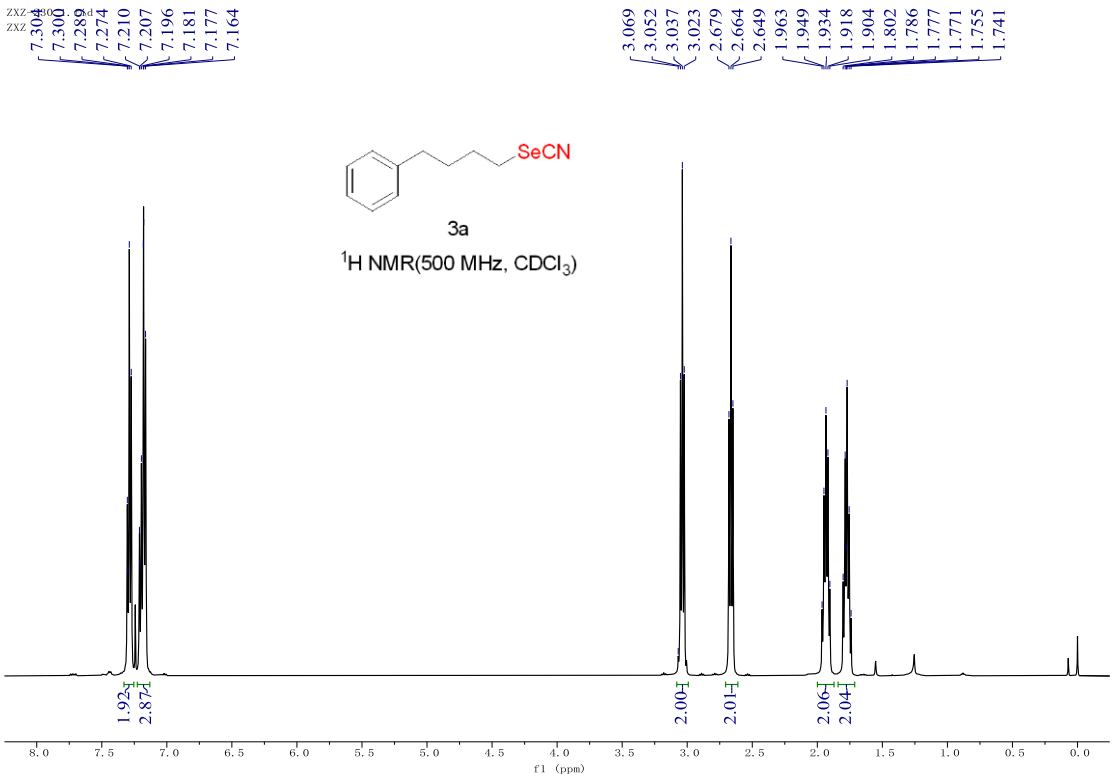
1–phenoxy–4–(2–selenocyanatoethoxy)benzene (**5b**)



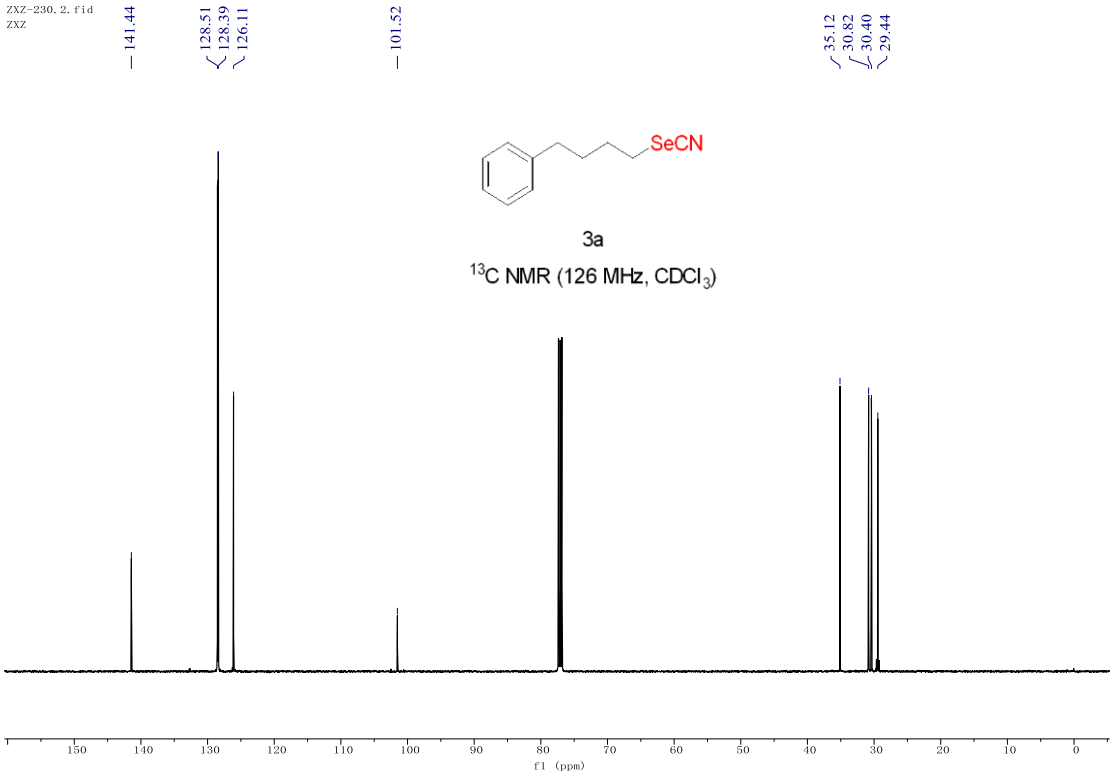
Following the general procedure (eluent: PE/EA = 5:1), **5b** was obtained in 69% yield (44.0 mg) as white solid. mp. 52–54 ºC (lit. mp. 54 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.06 (tt, J = 7.3, 1.1 Hz, 1H), 7.00 – 6.87 (m, 6H), 4.36 (t, J = 6.0 Hz, 2H), 3.42 (t, J = 6.0 Hz, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 154.0, 151.3, 129.7, 122.8, 120.8, 117.9, 115.9, 101.2, 67.1, 28.2 ppm. Spectra were consistent with literature data[14].

6. Copies of ^{1}H, ^{13}C, ^{19}F and HMBC NMR Spectra

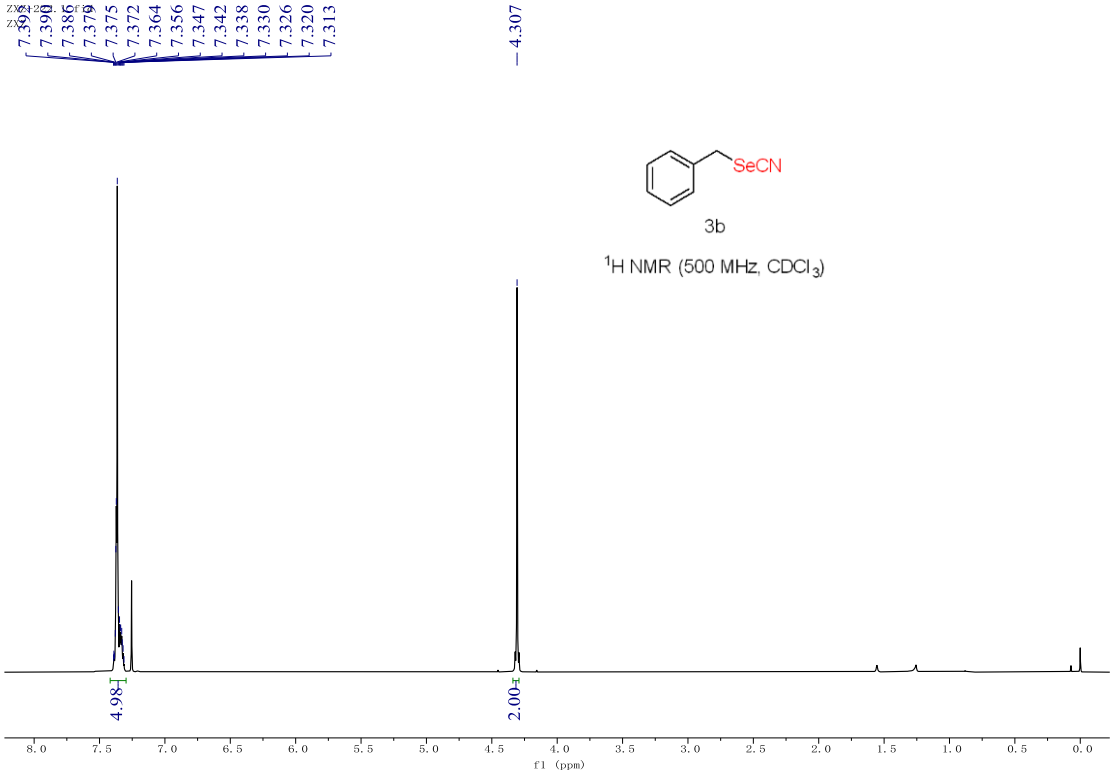
^{1}H NMR of **3a**



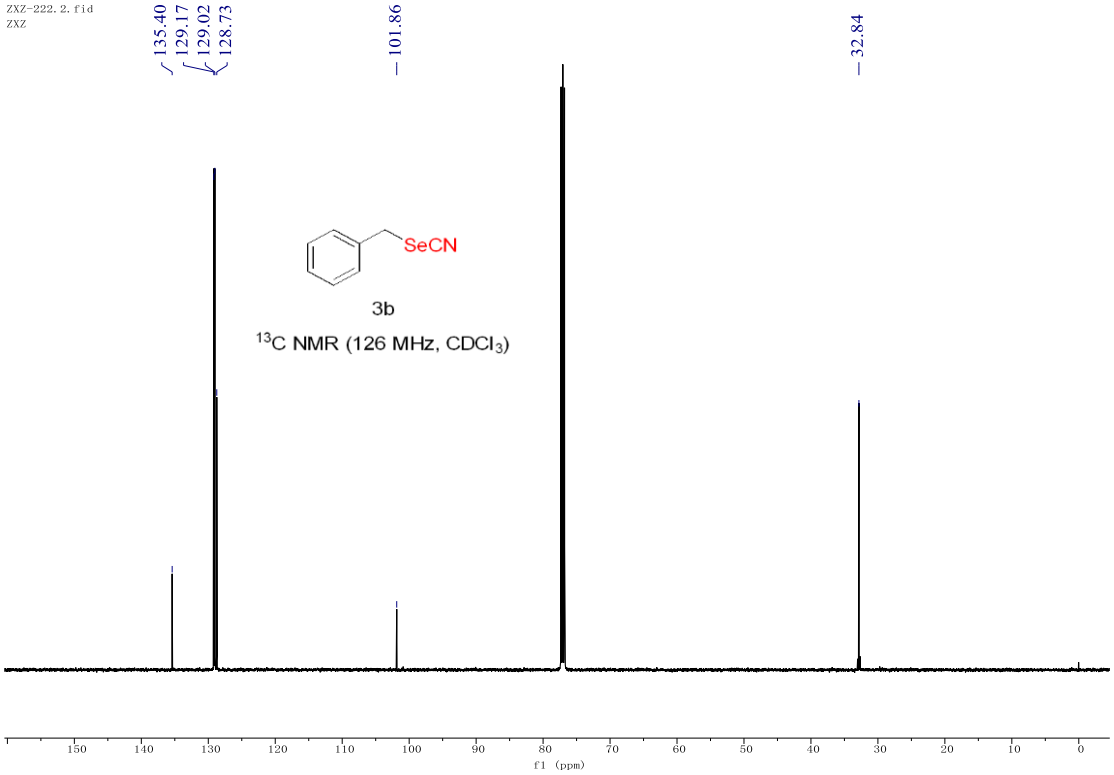
^{13}C NMR of **3a**



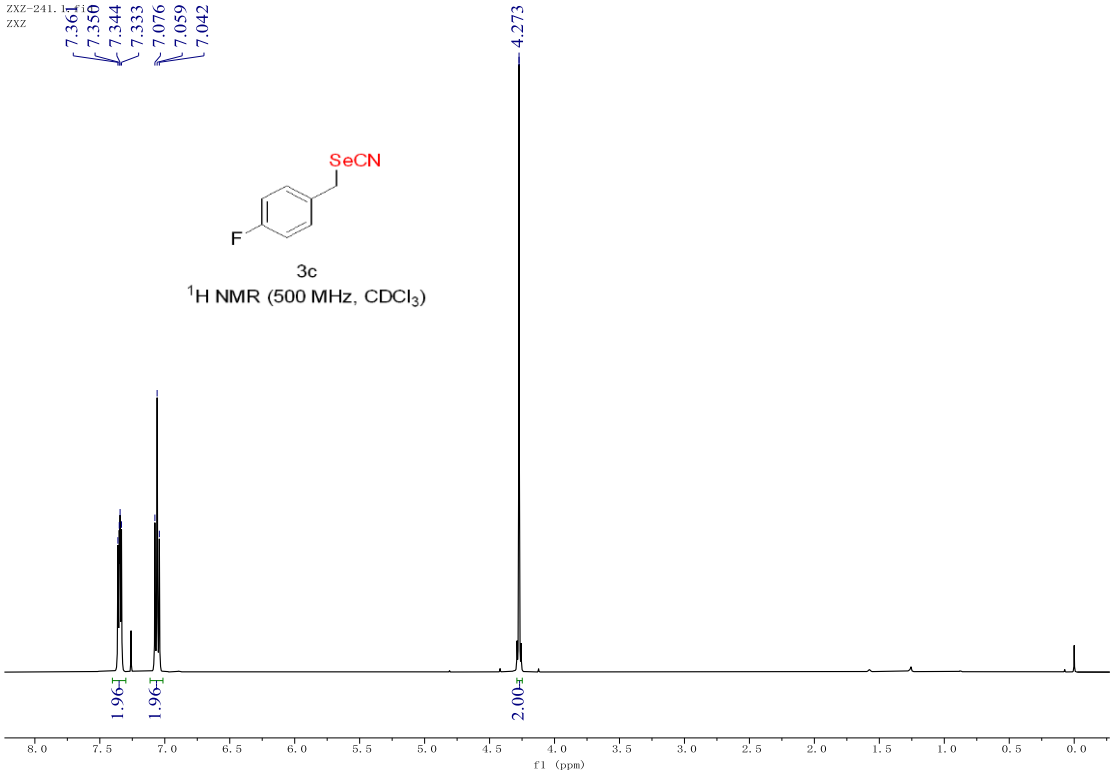
^{1}H NMR of **3b**



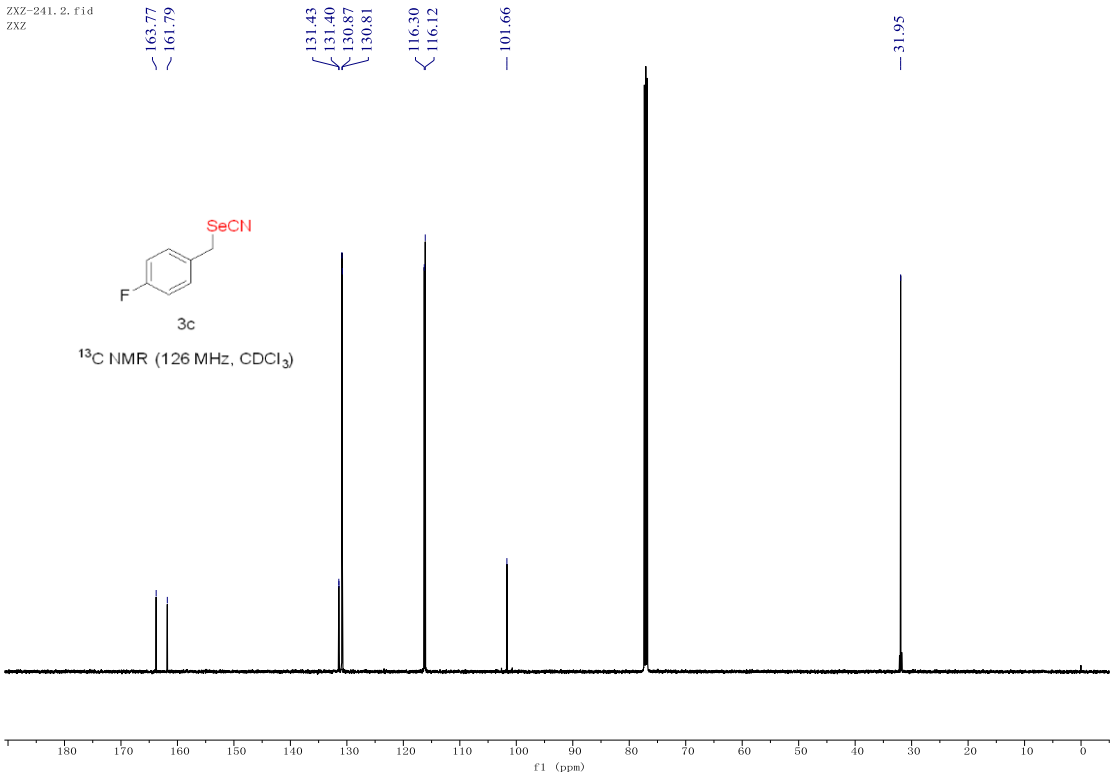
^{13}C NMR of **3b**



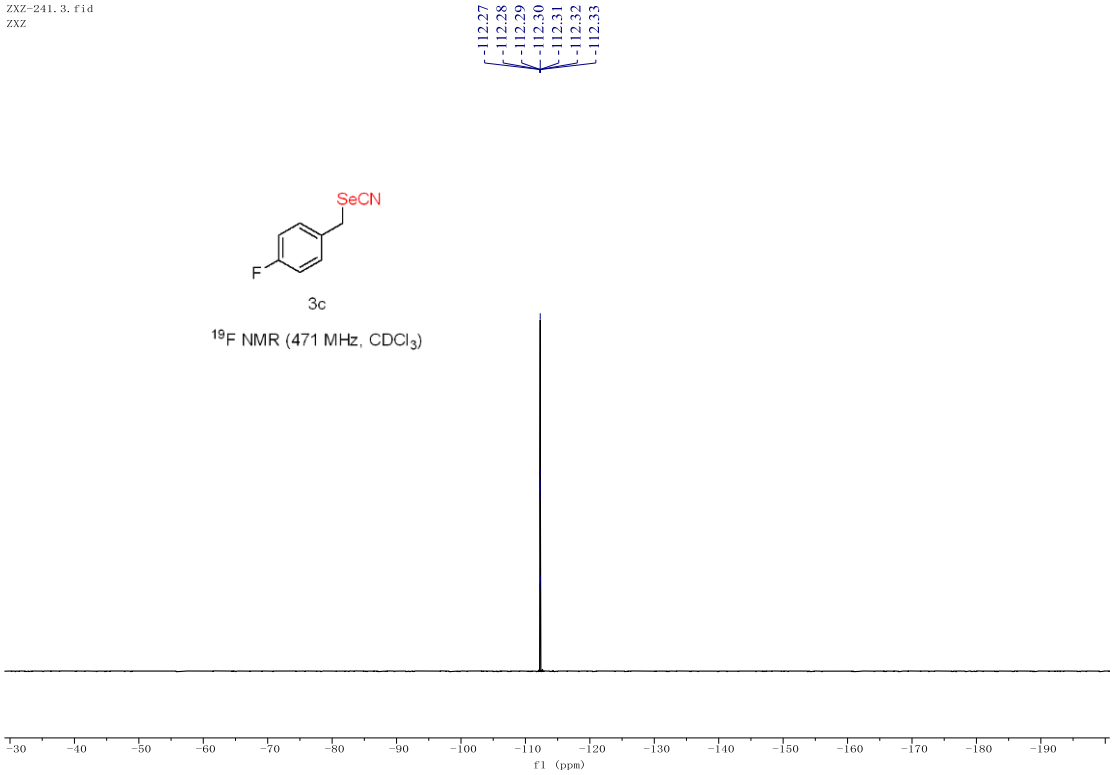
^{1}H NMR of **3c**



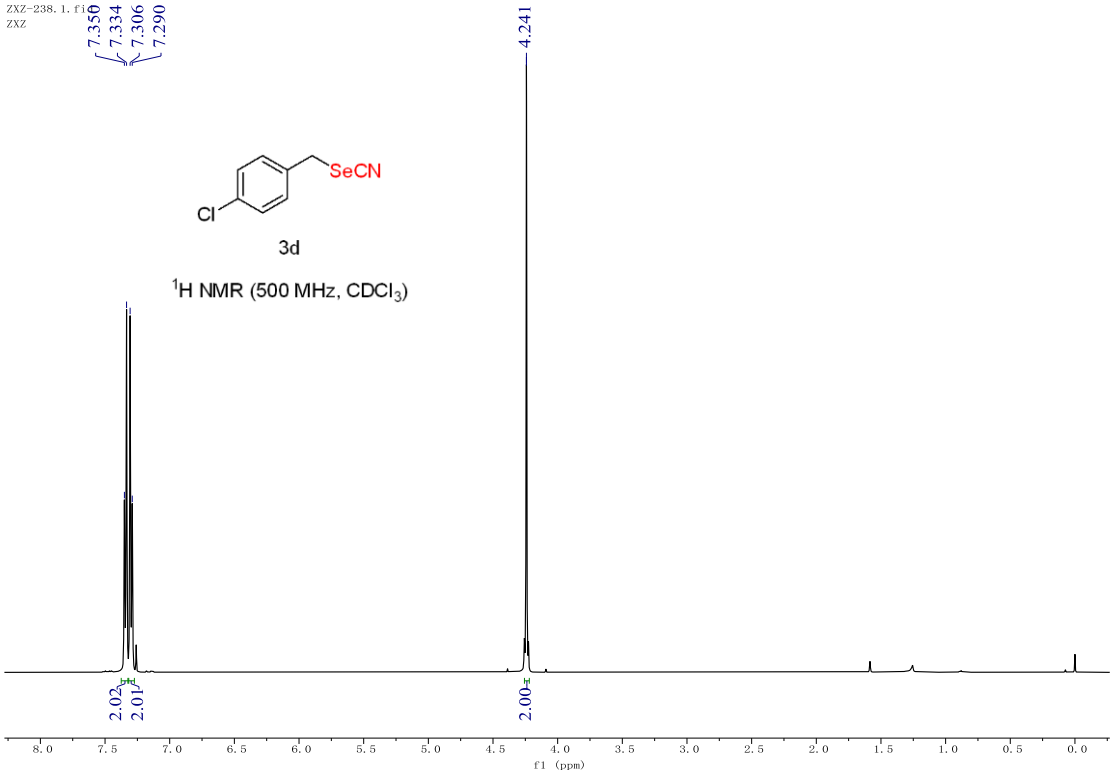
^{13}C NMR of **3b**



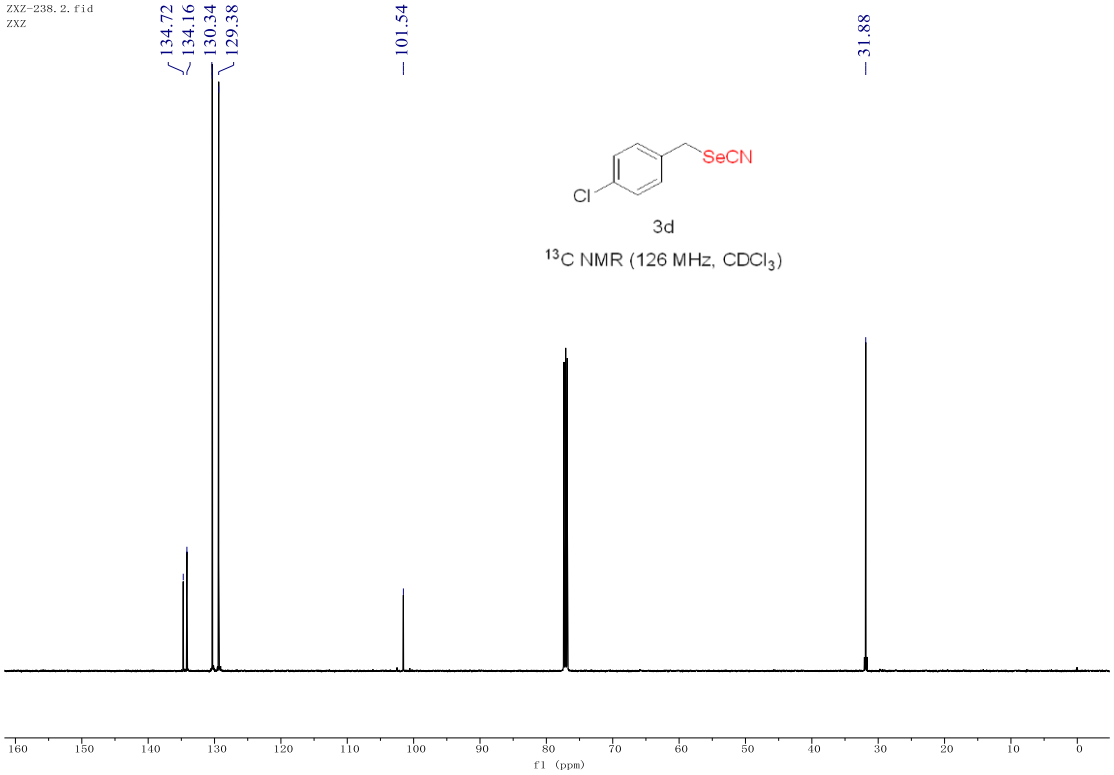
^{19}F NMR of **3c**



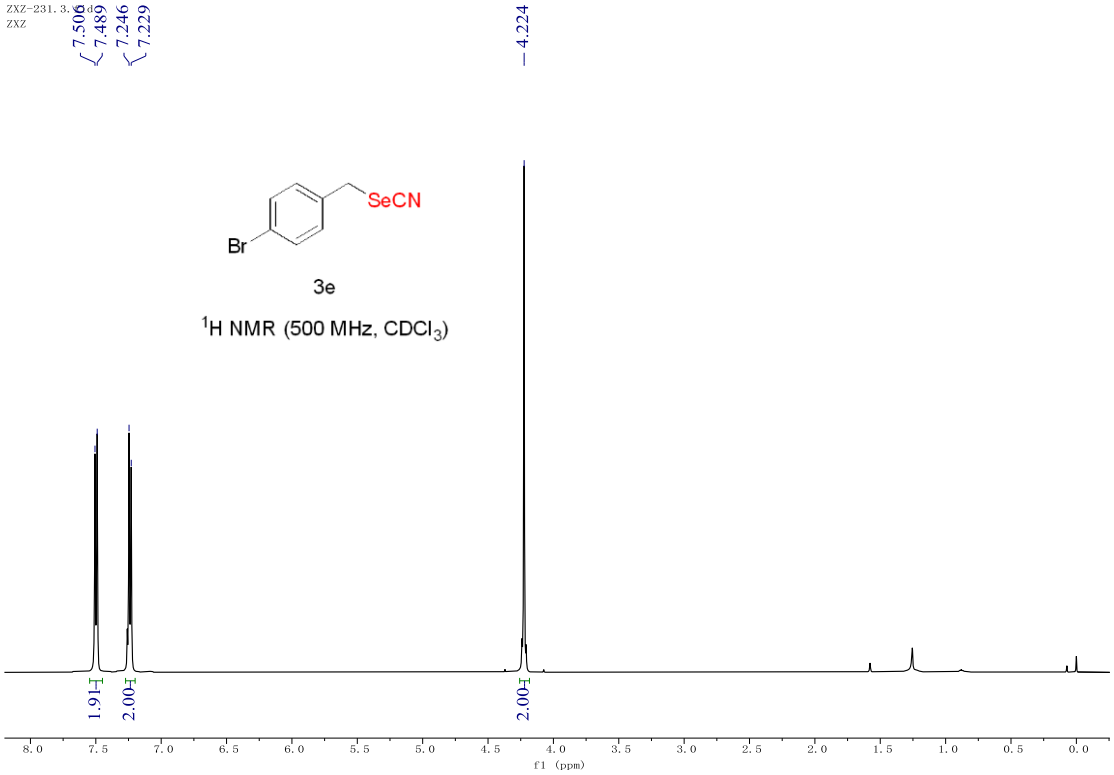
^{1}H NMR of **3d**



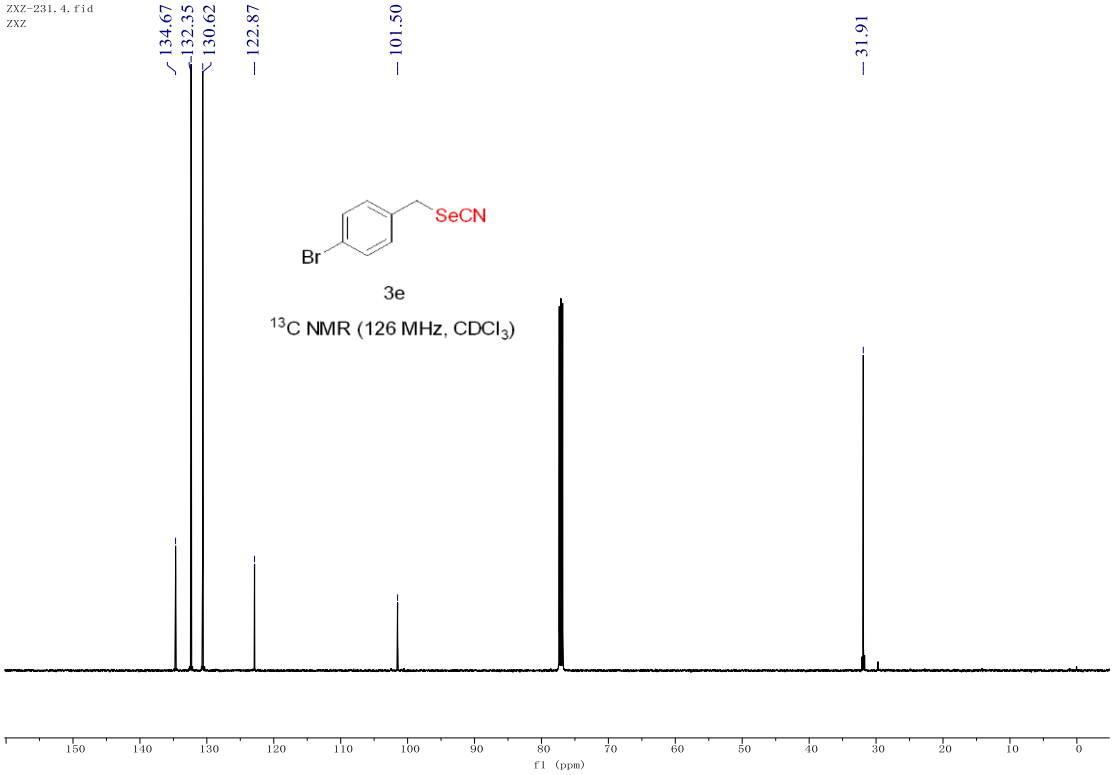
^{13}C NMR of **3d**



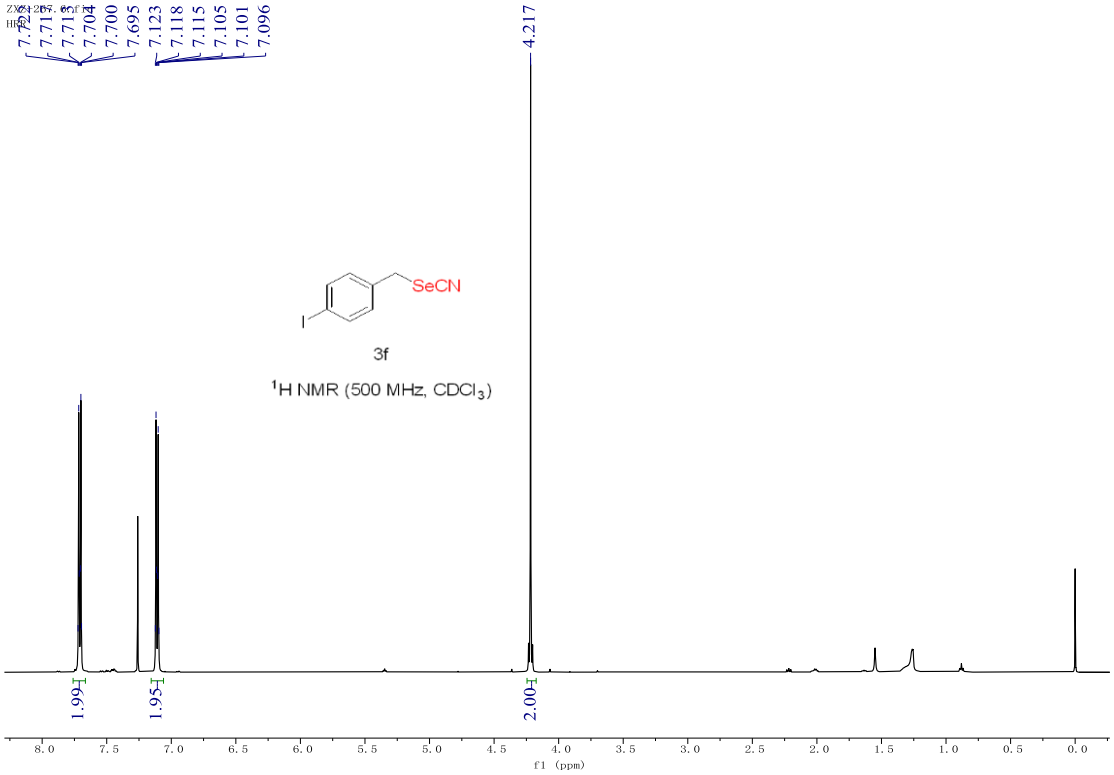
^{1}H NMR of **3e**



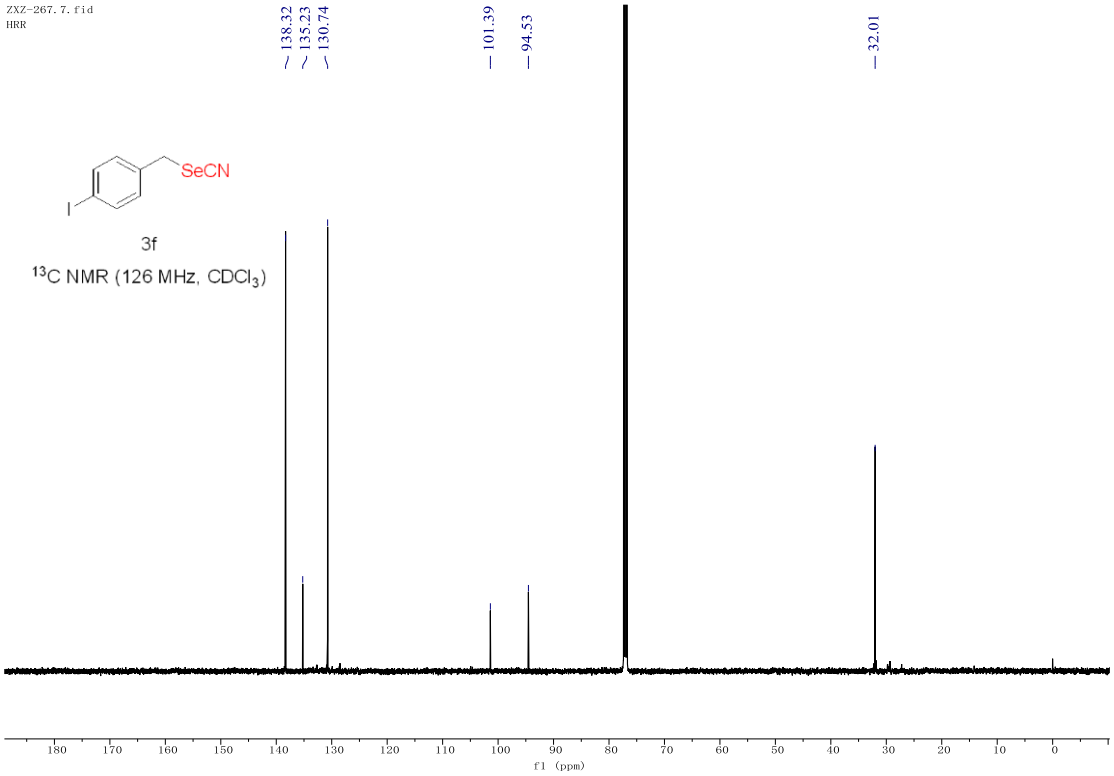
^{13}C NMR of **3e**



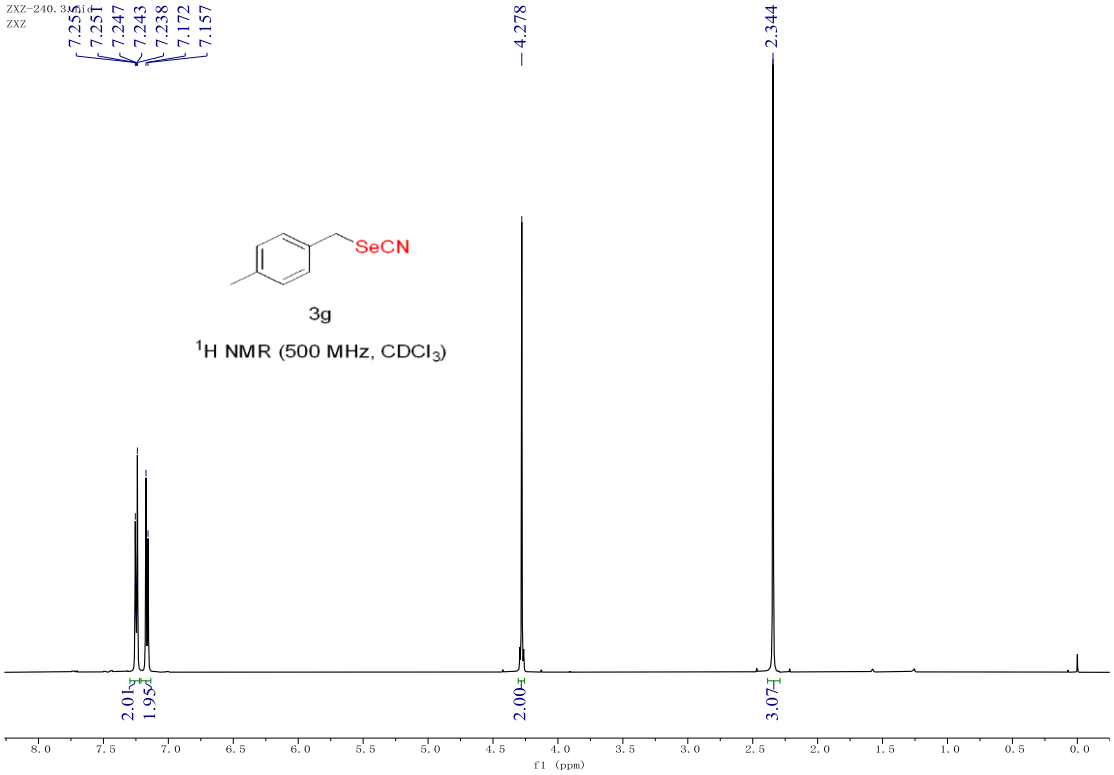
^{1}H NMR of **3f**



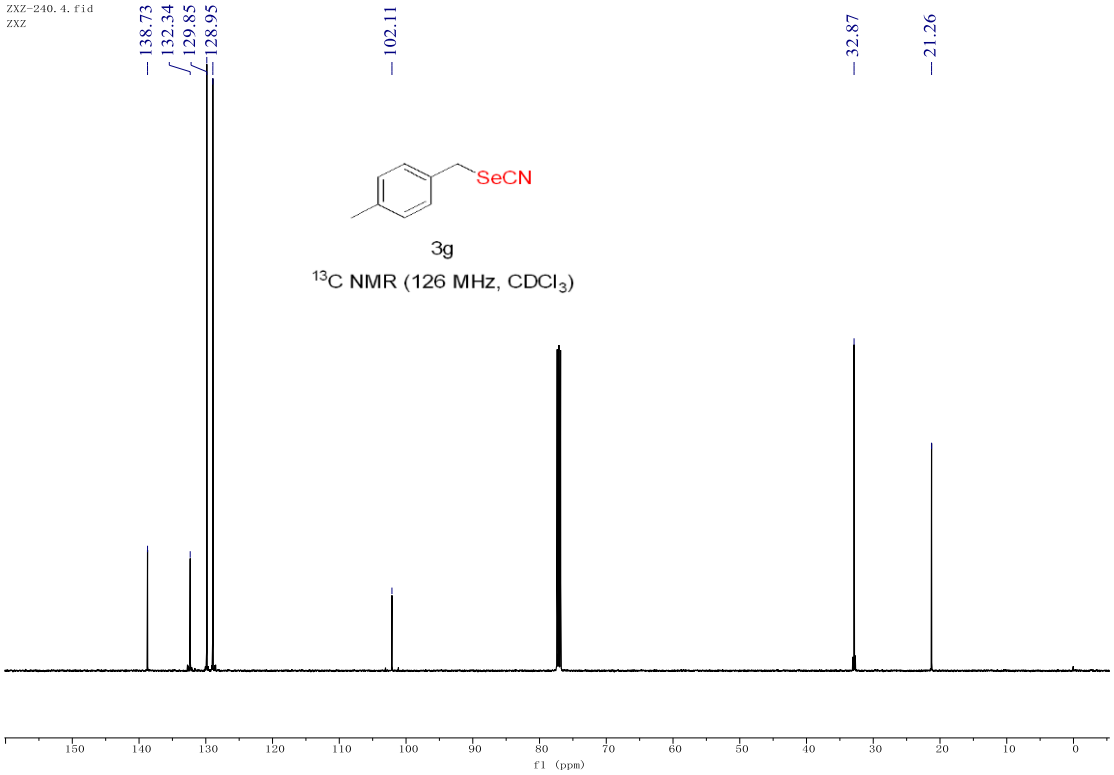
^{13}C NMR of **3f**



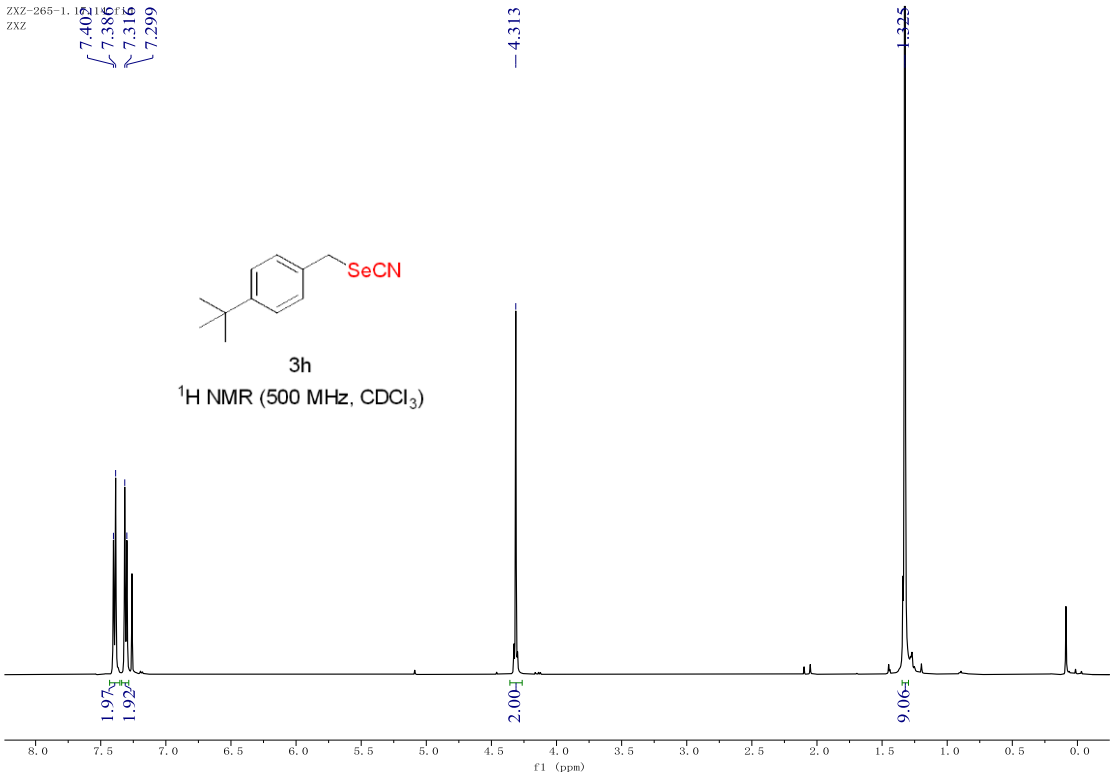
^{1}H NMR of **3g**



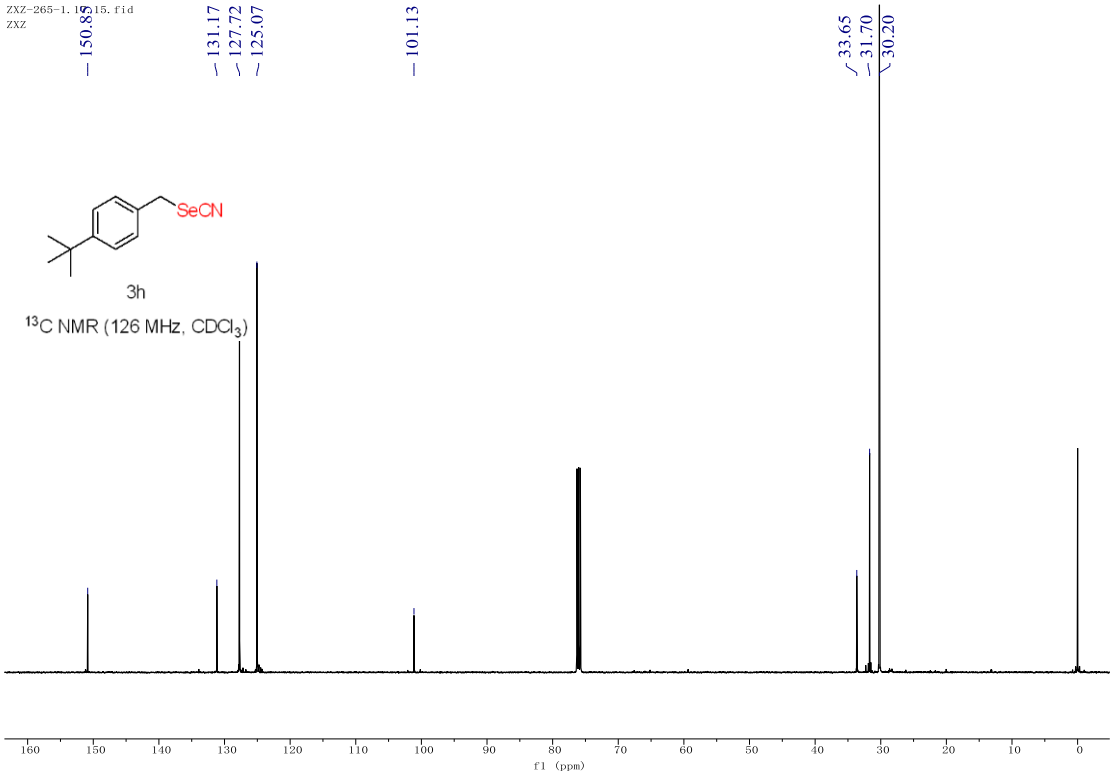
^{13}C NMR of **3g**



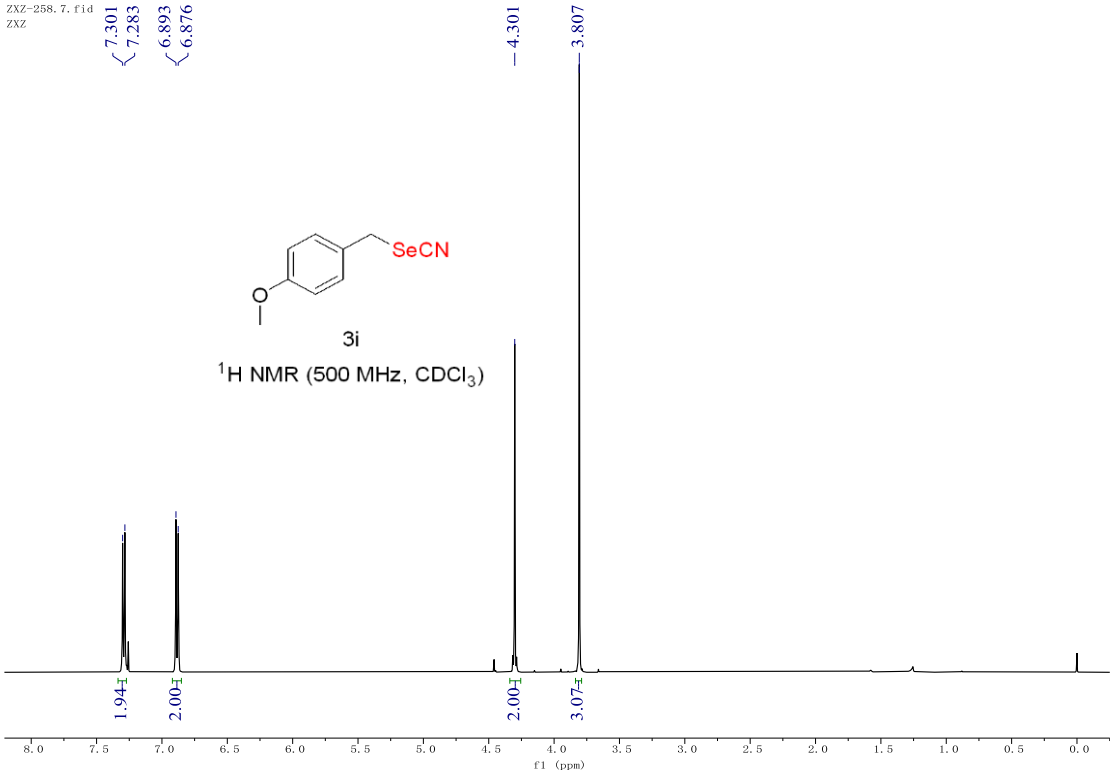
^{1}H NMR of **3h**



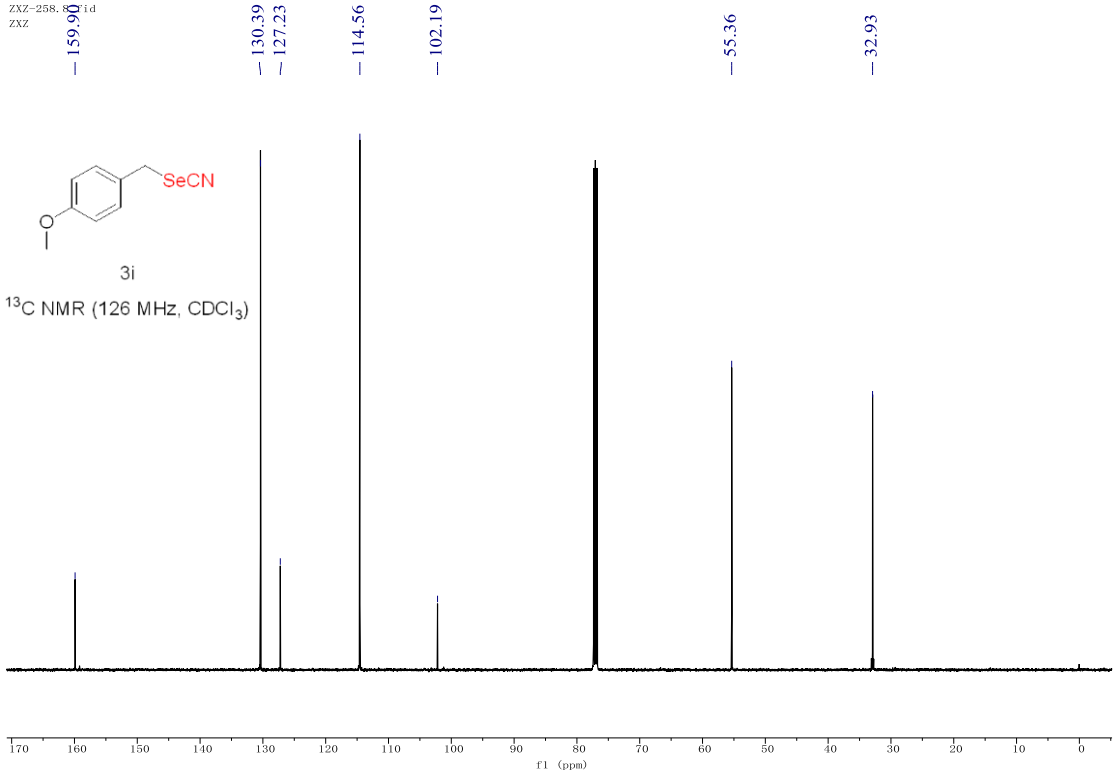
^{13}C NMR of **3h**



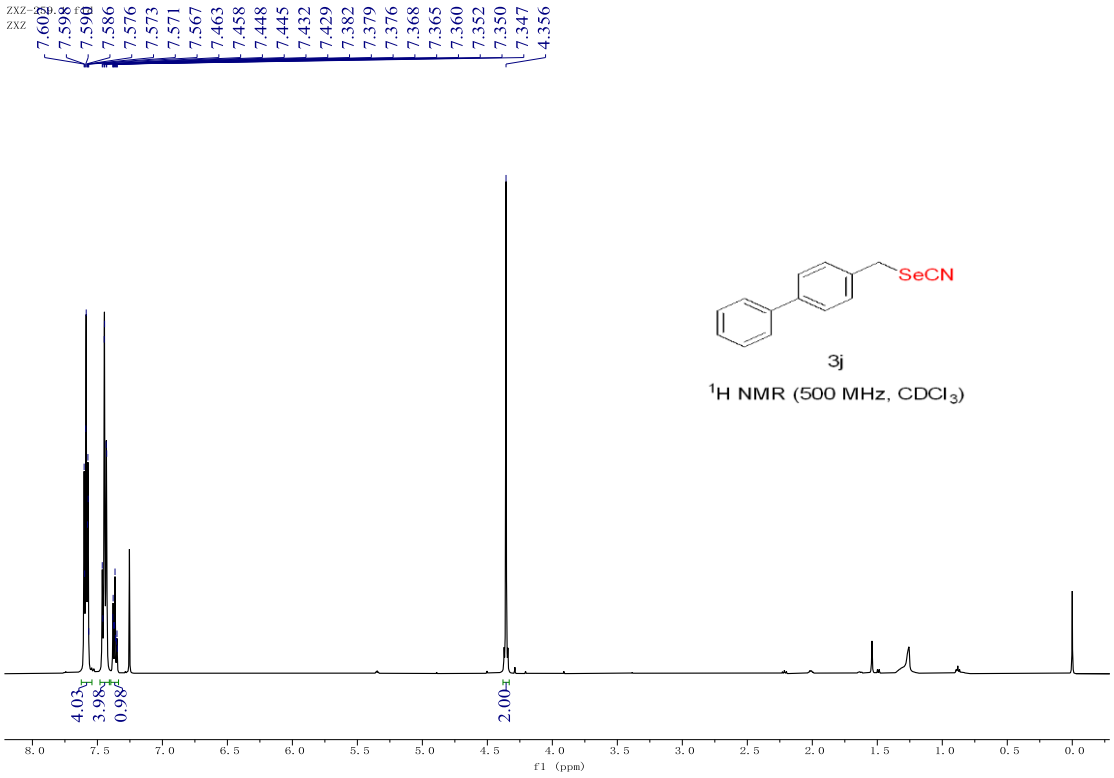
^{1}H NMR of **3i**



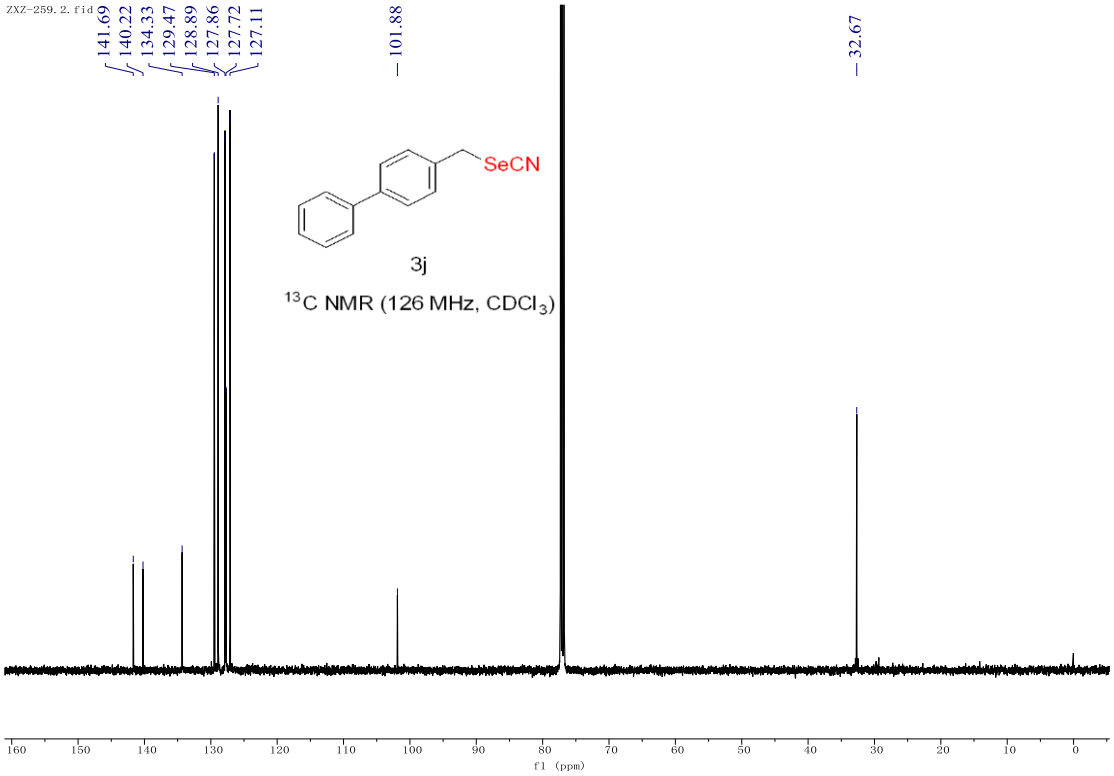
^{13}C NMR of **3i**



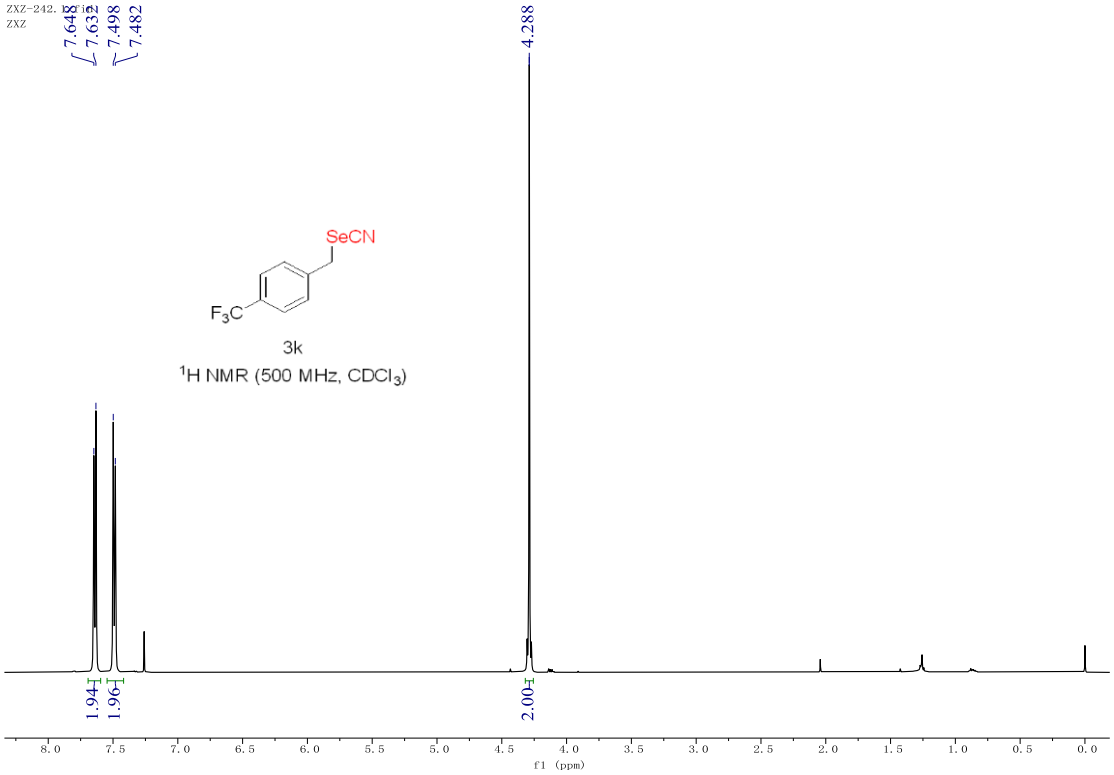
^{1}H NMR of **3j**



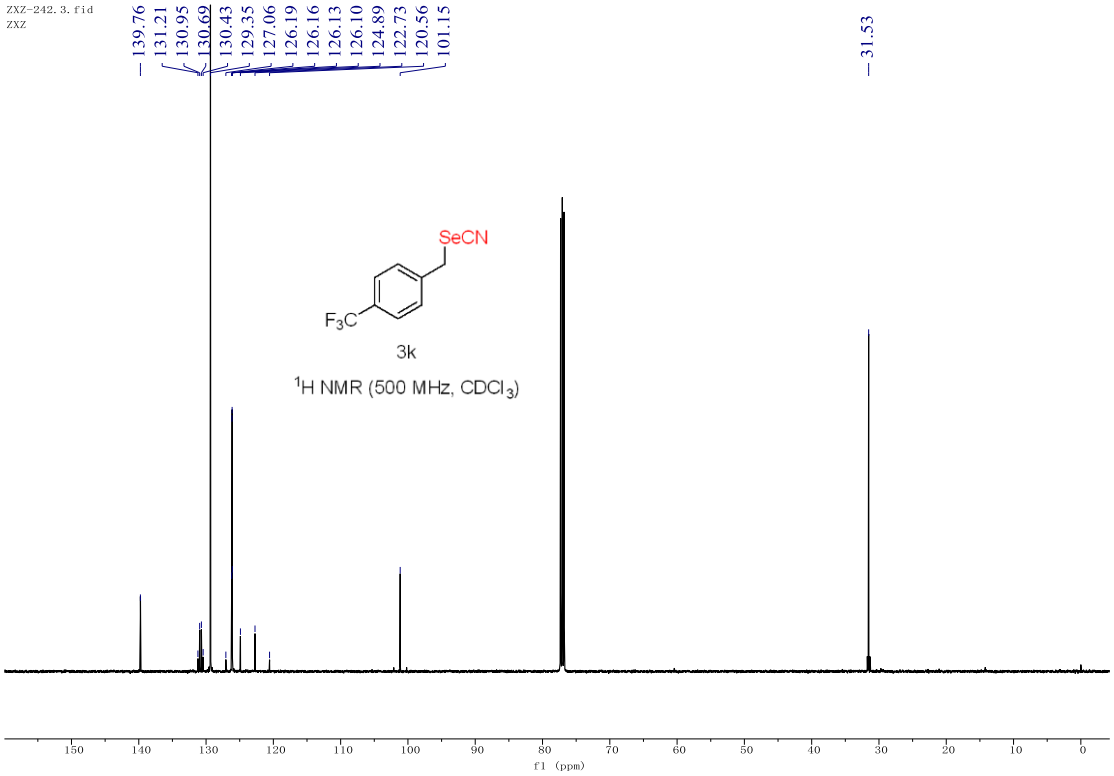
^{13}C NMR of **3j**



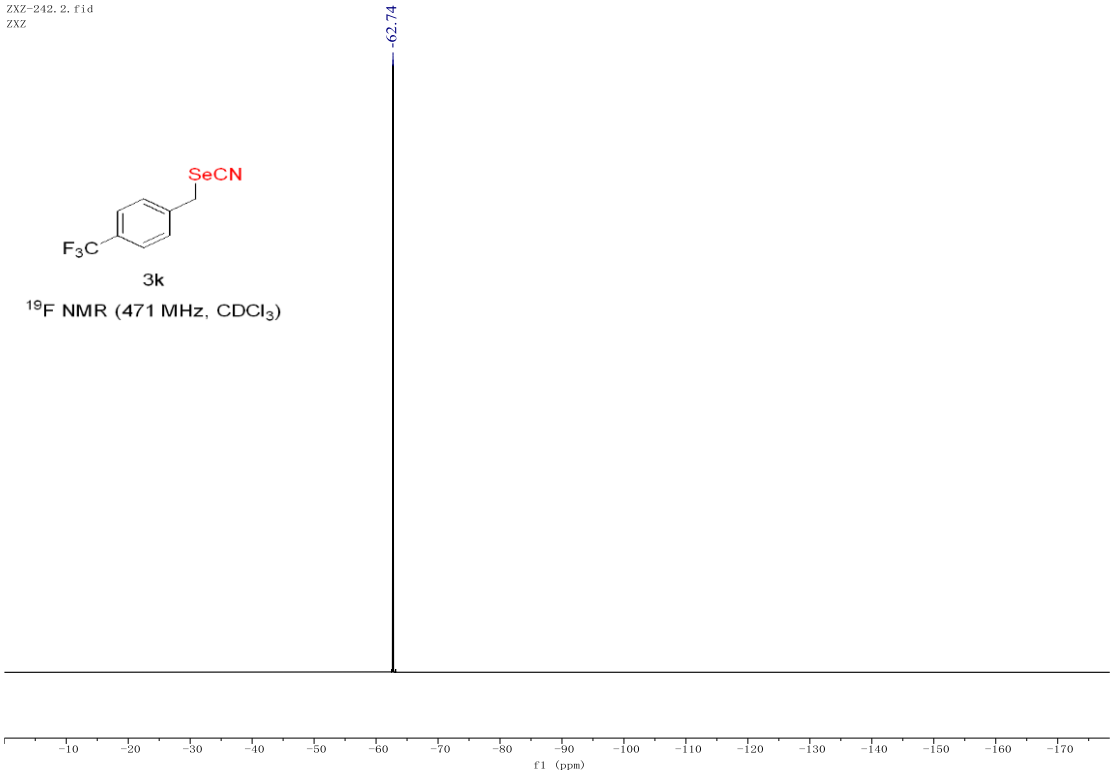
^{1}H NMR of **3k**



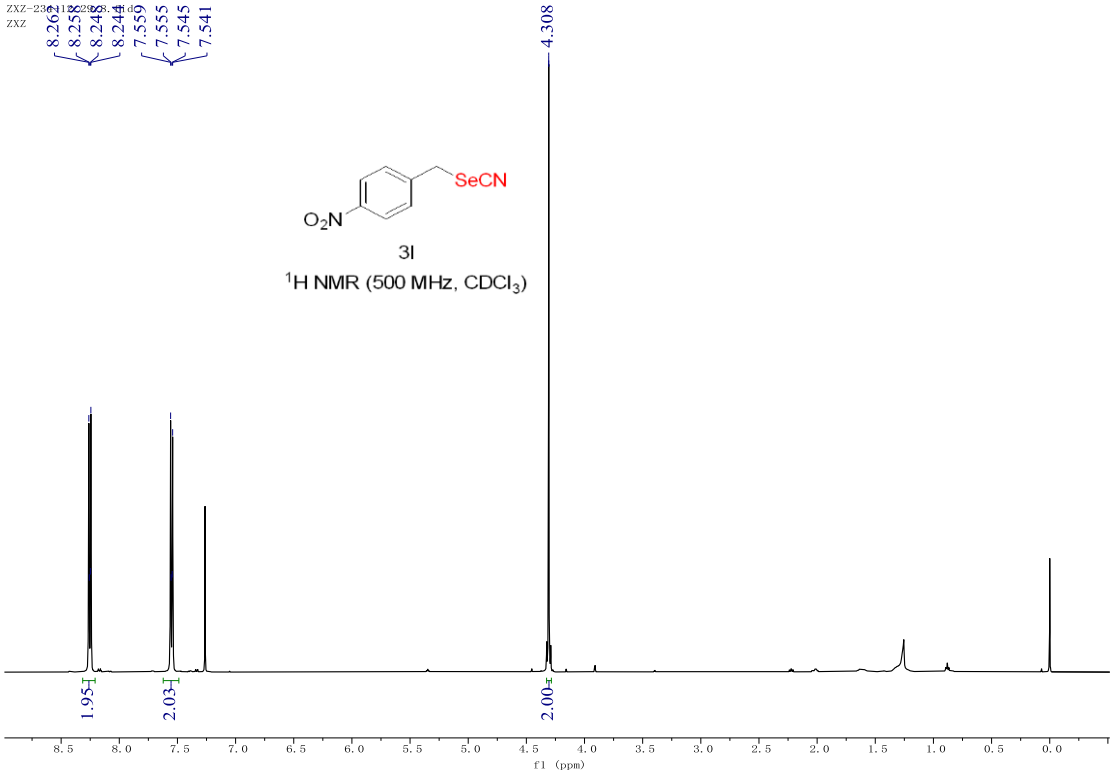
^{13}C NMR of **3k**



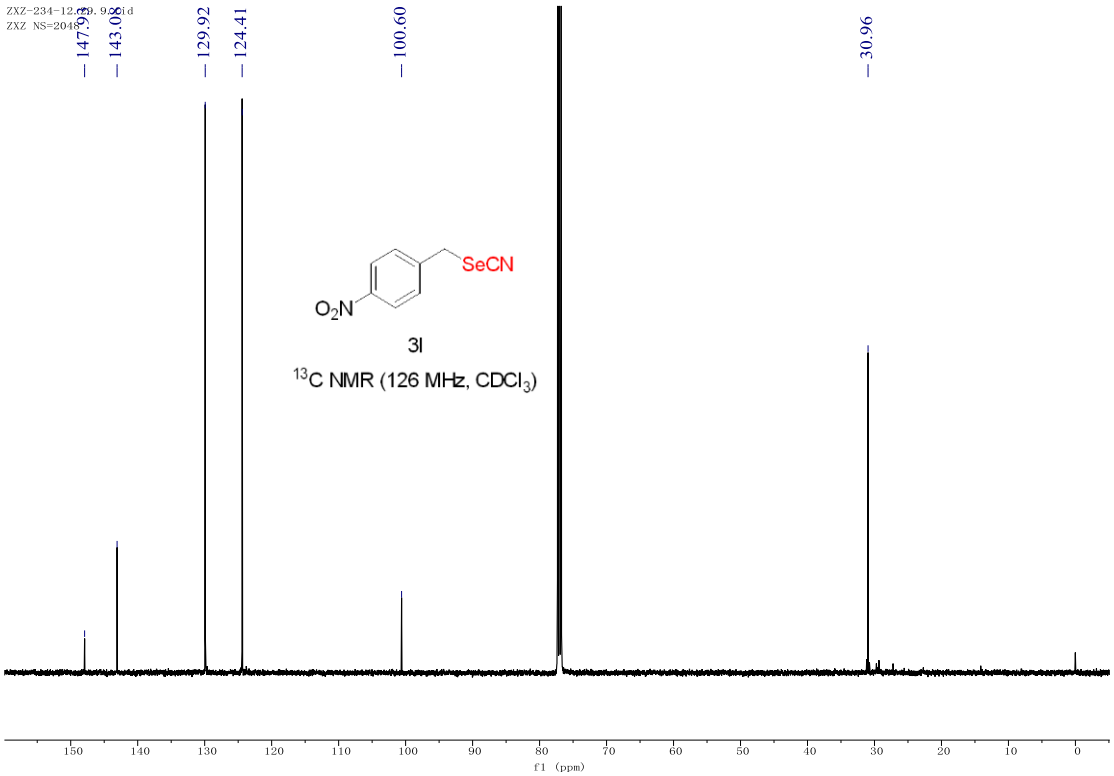
^{19}F NMR of **3k**



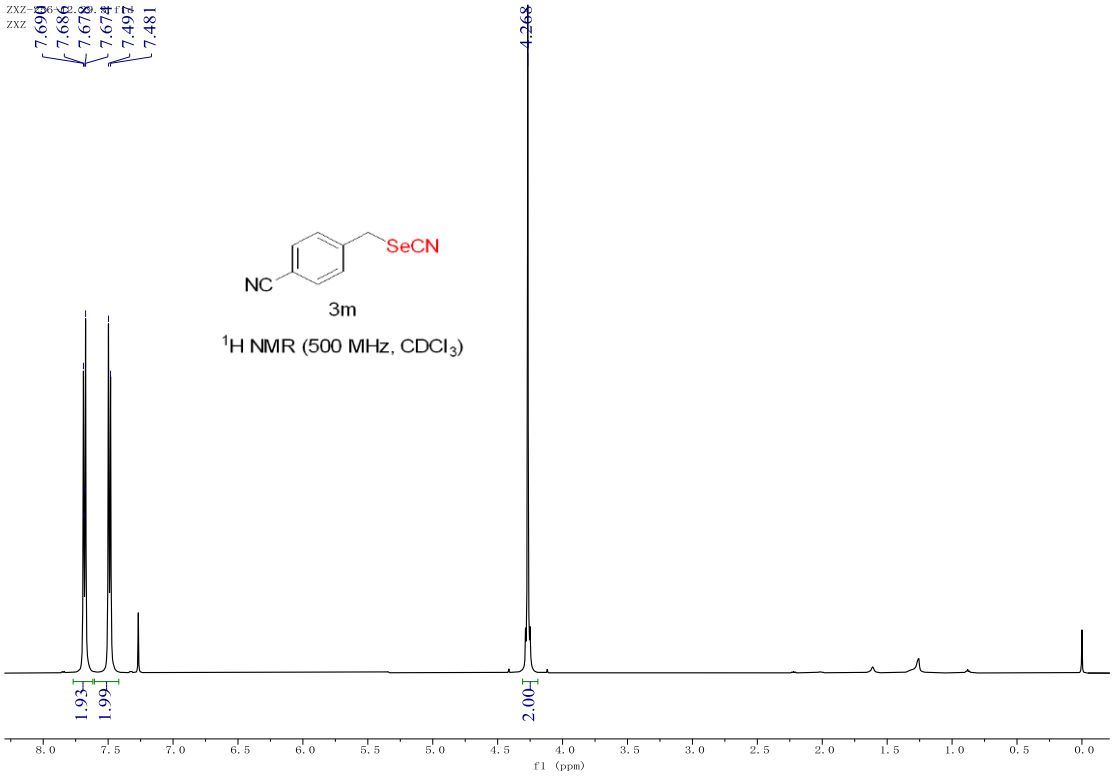
^{1}H NMR of **3l**



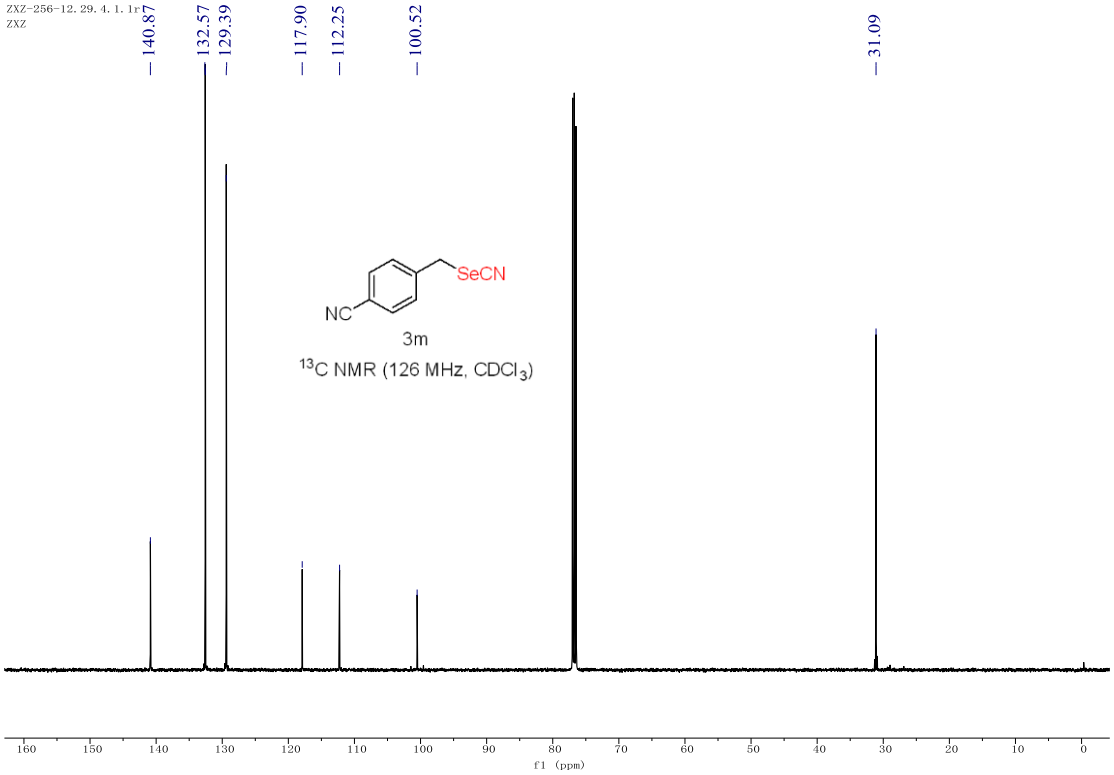
^{13}C NMR of **3l**



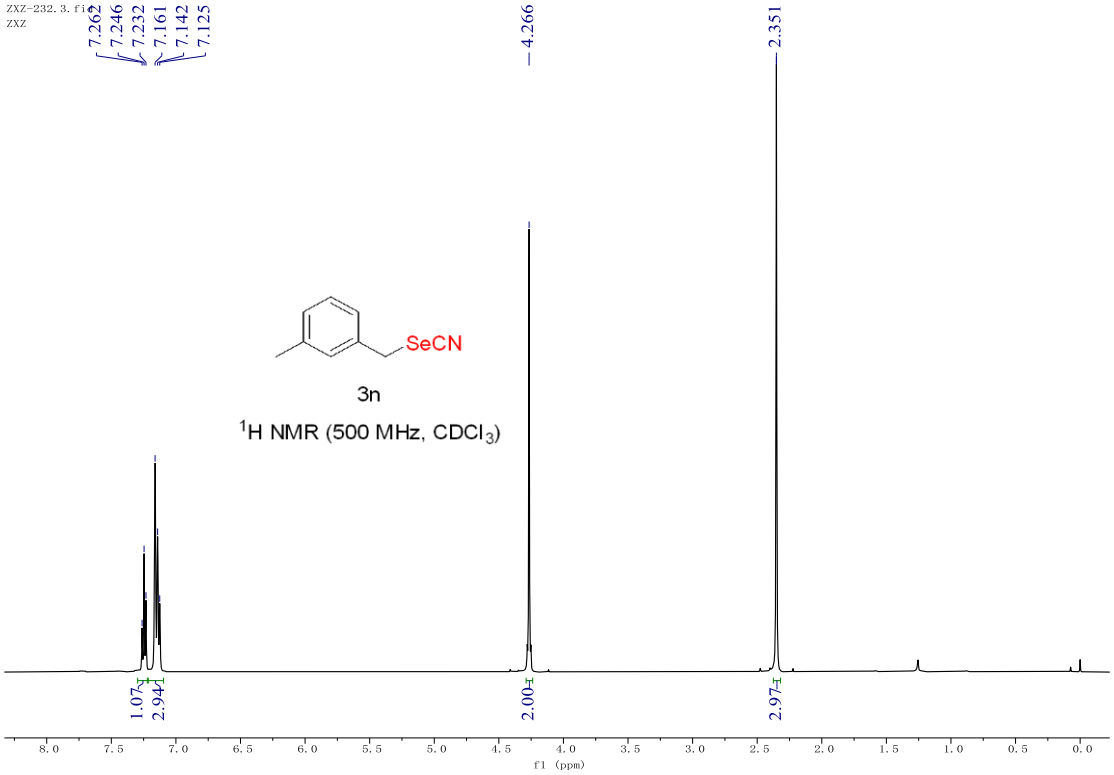
^{1}H NMR of **3m**



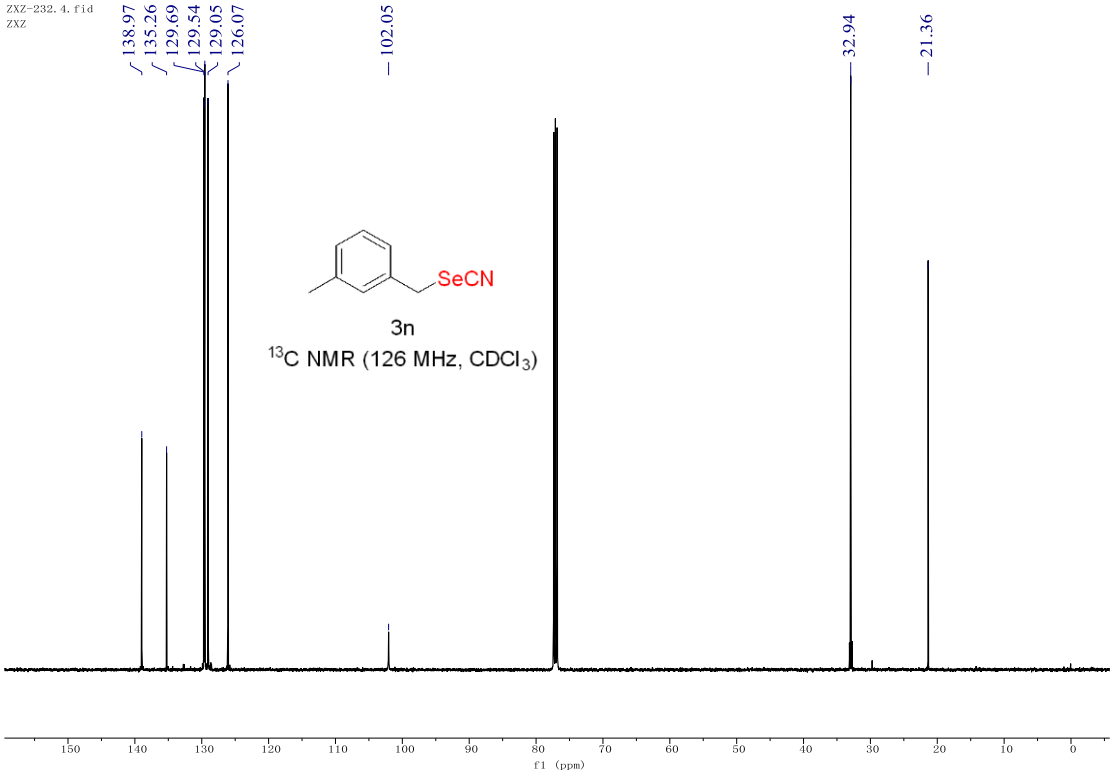
^{13}C NMR of **3m**



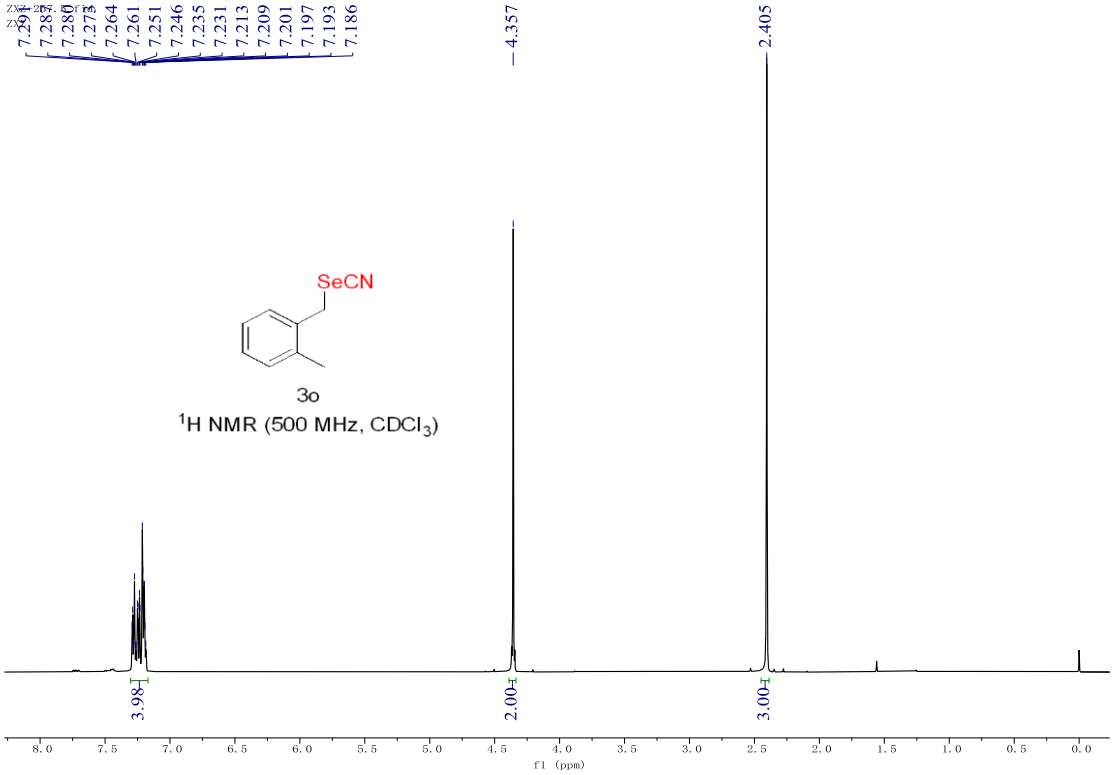
^{1}H NMR of **3n**



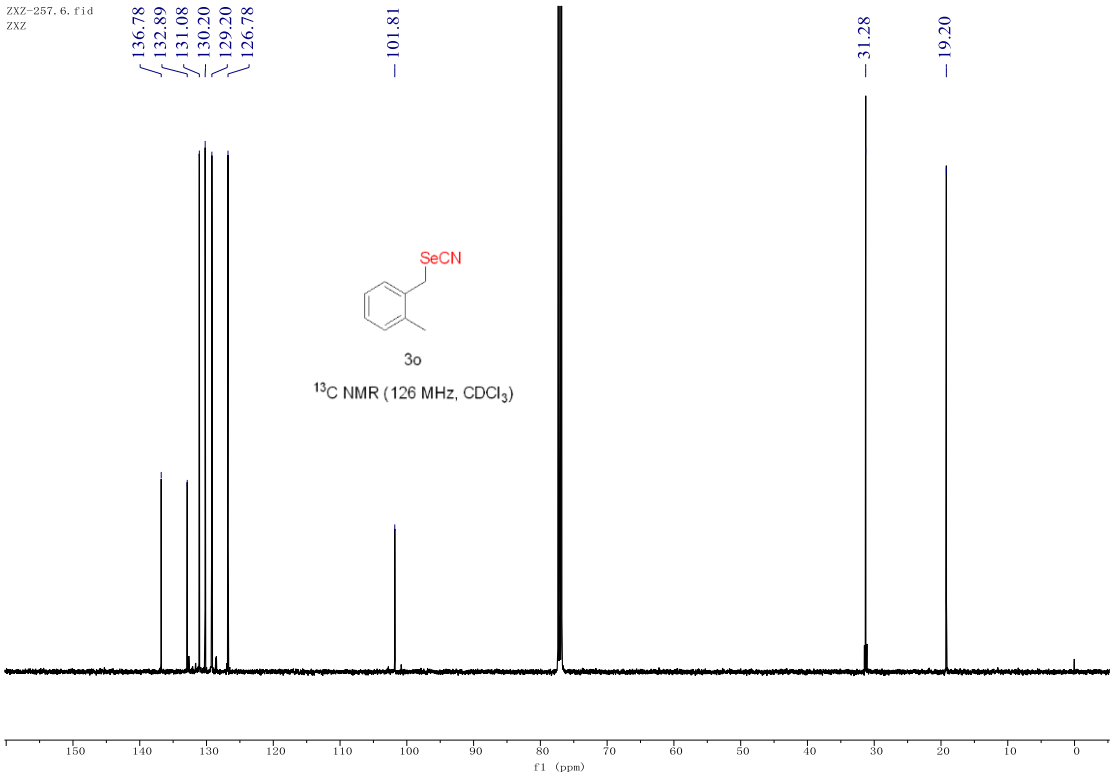
^{13}C NMR of **3n**



^{1}H NMR of **3o**



^{13}C NMR of **3**



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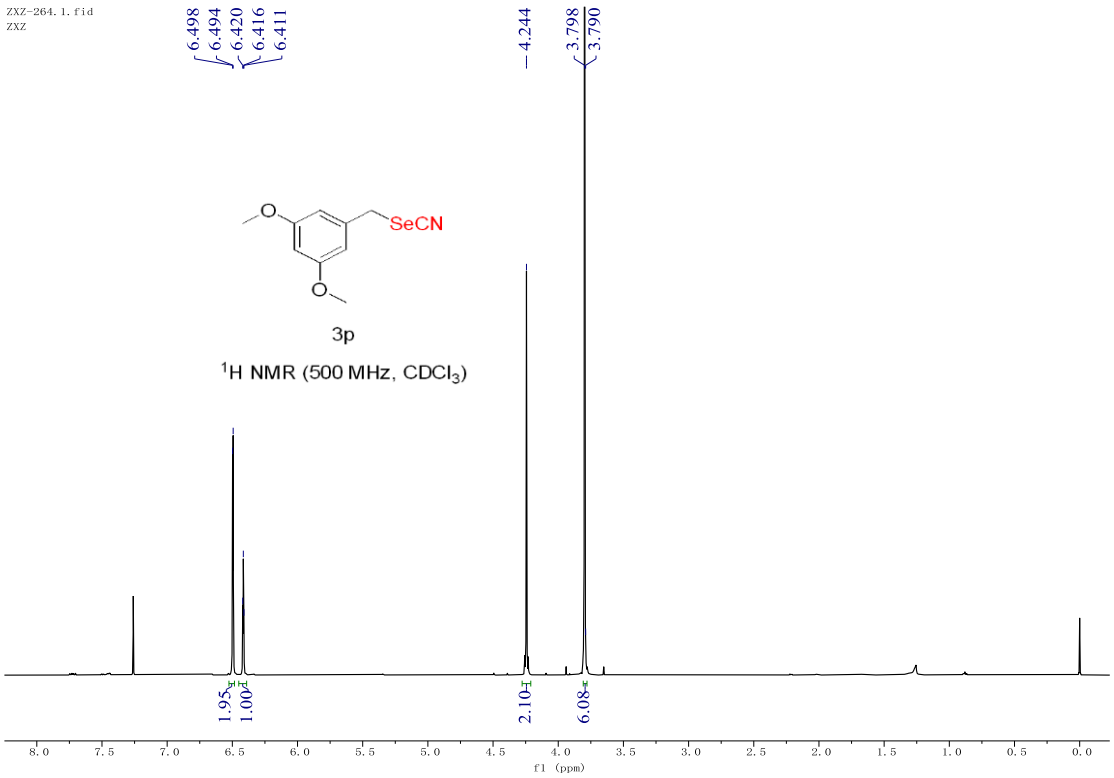
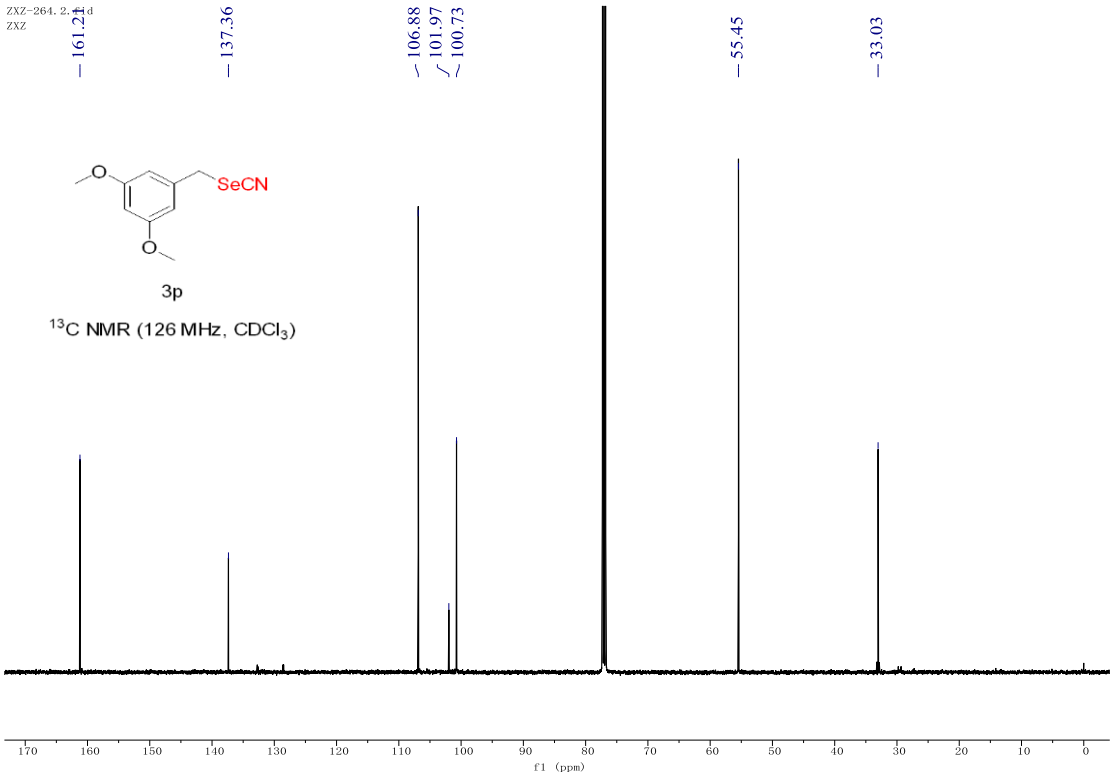
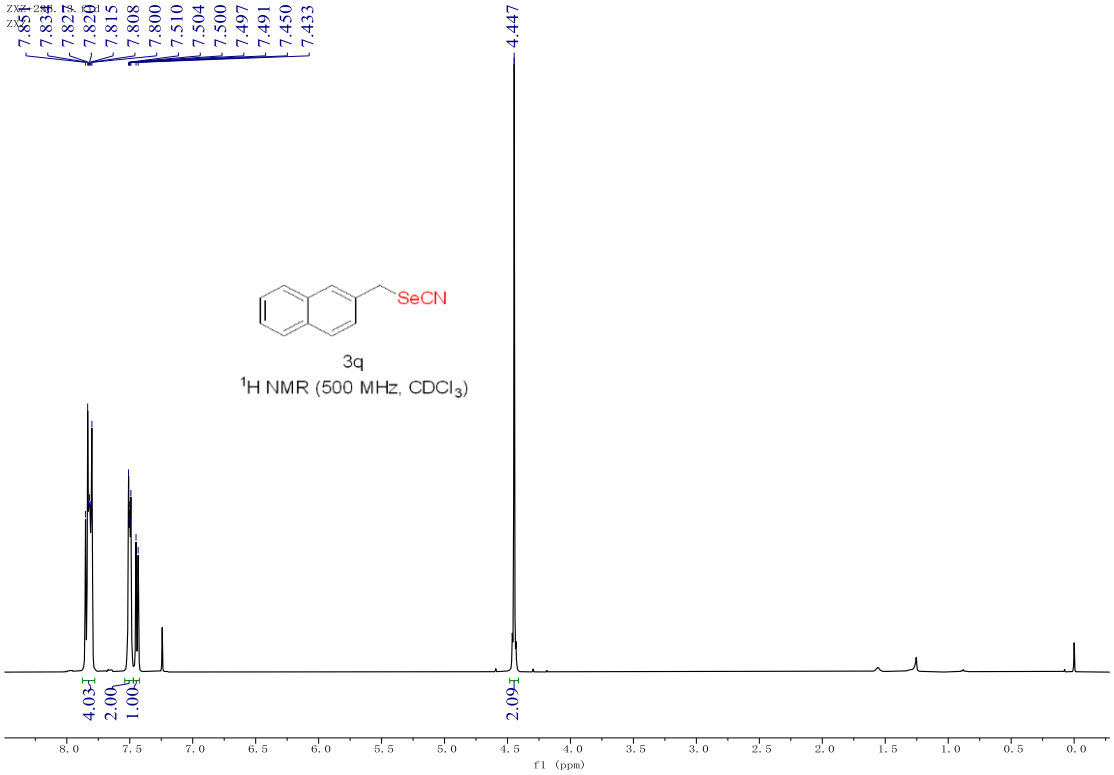


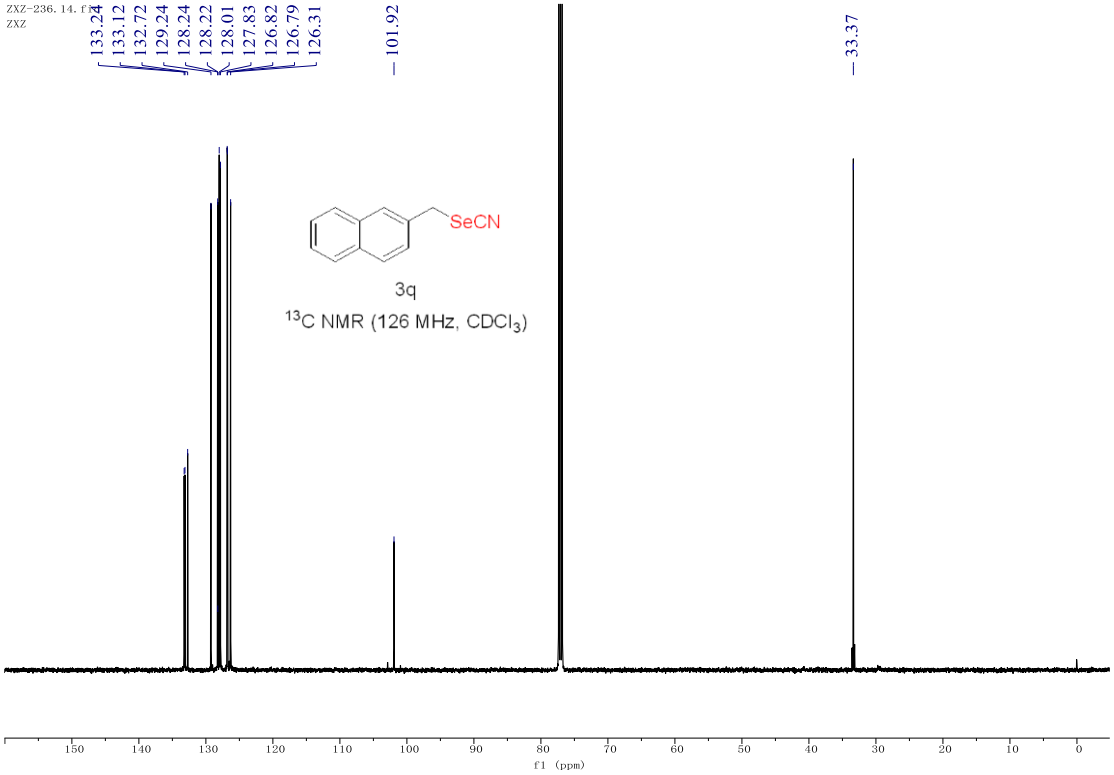
^{13}C NMR of **3p**



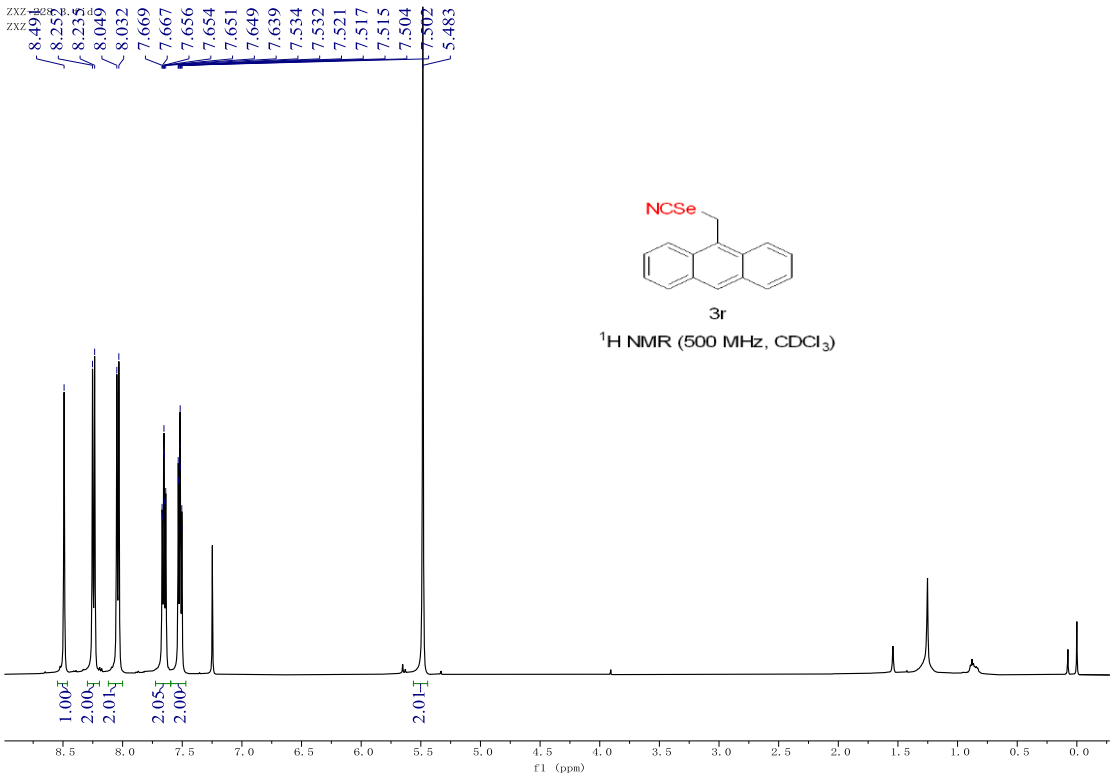
^{1}H NMR of **3q**



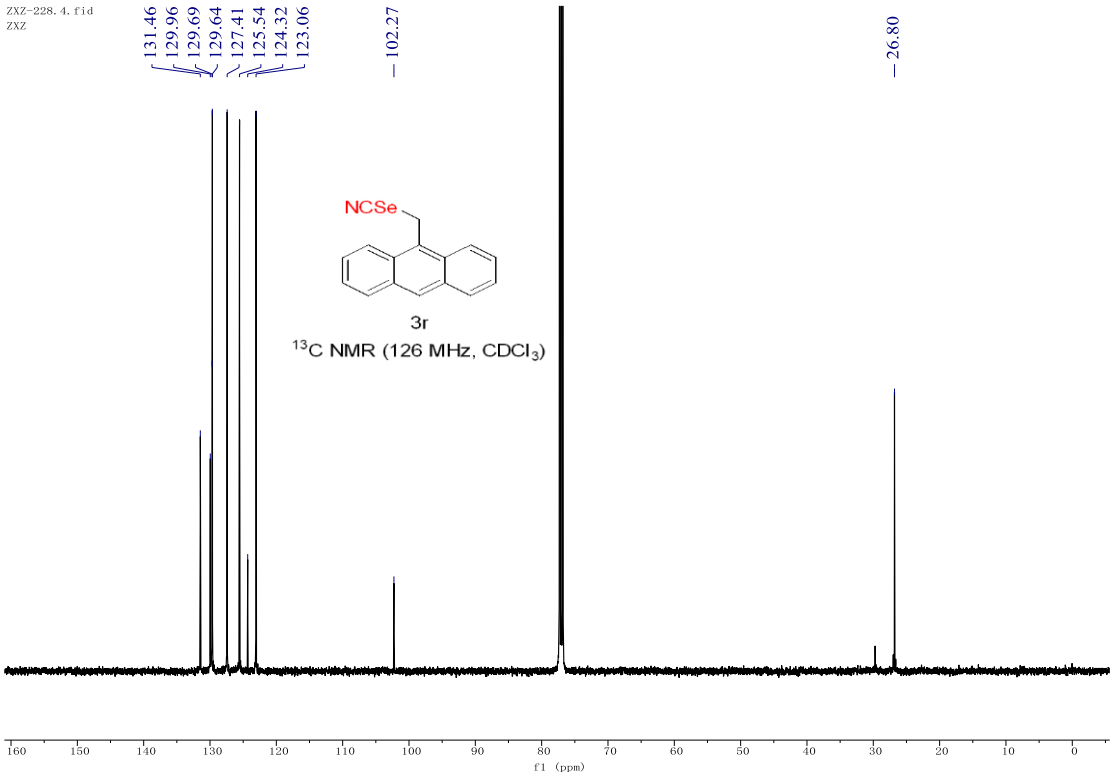
^{13}C NMR of **3q**



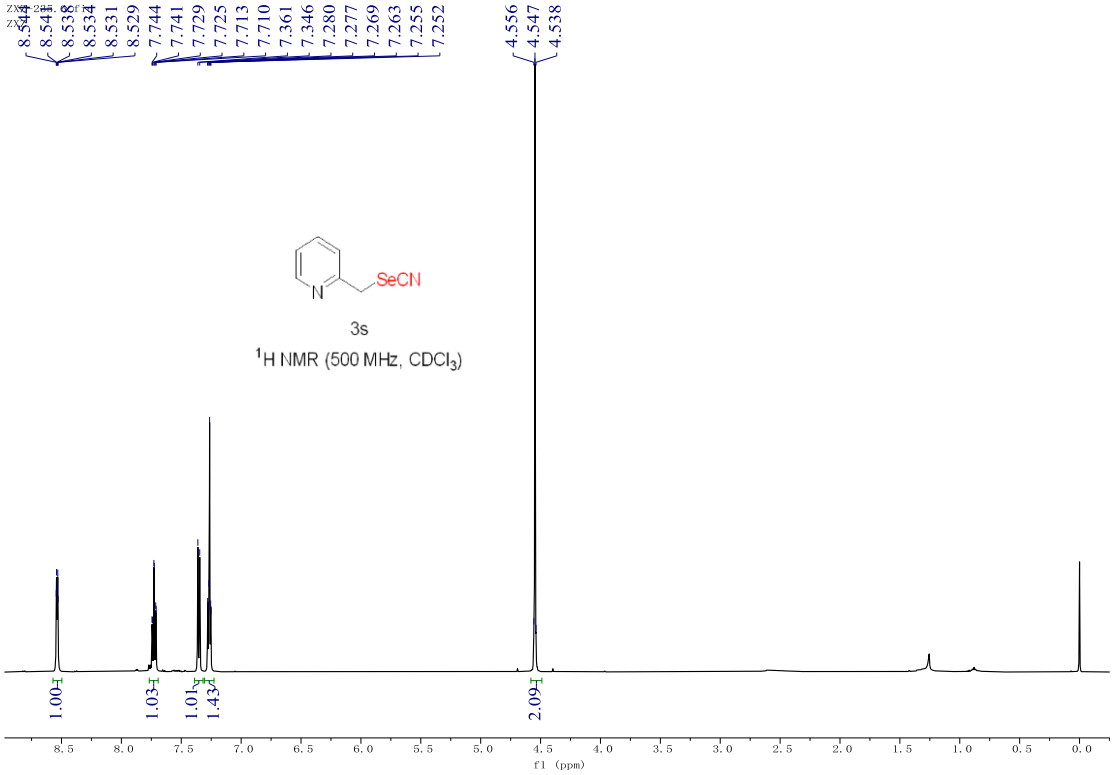
^{1}H NMR of **3r**



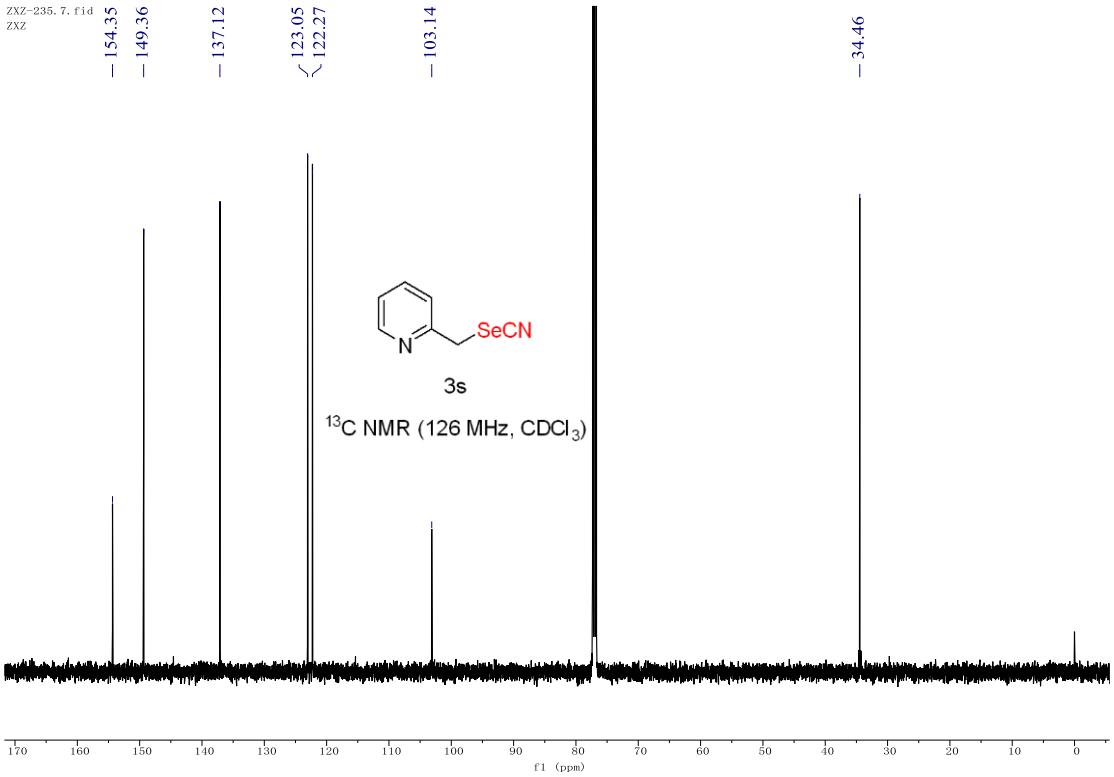
^{13}C NMR of **3r**



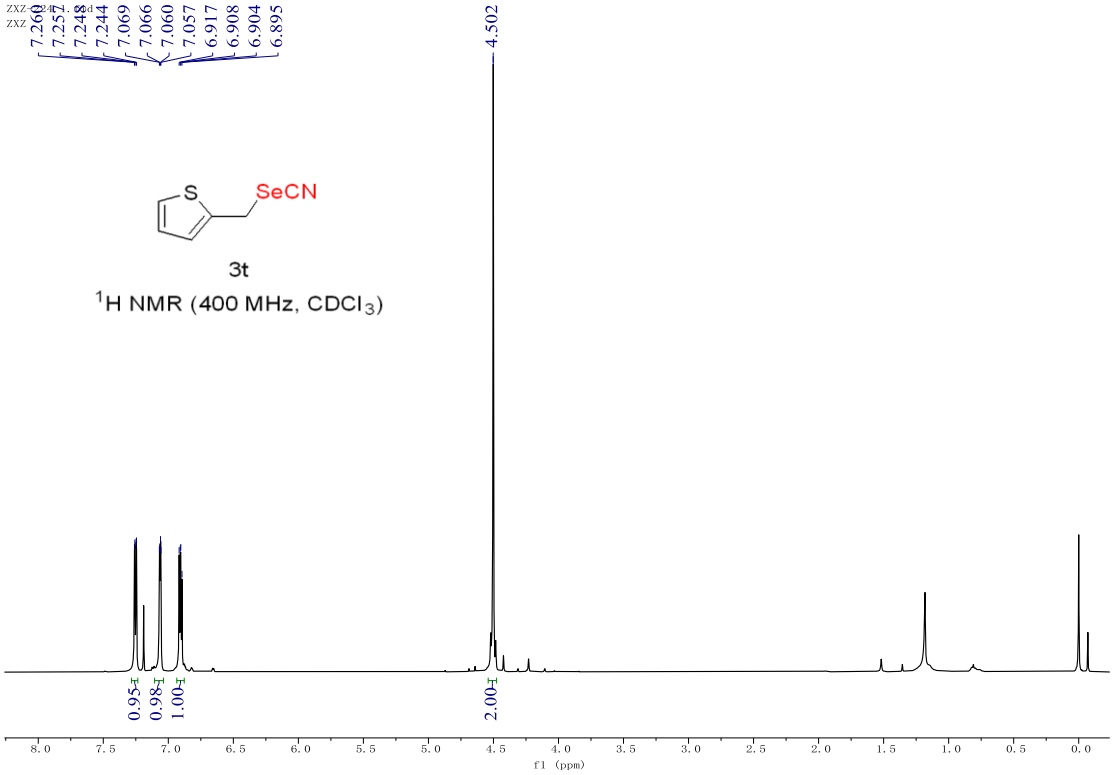
^{1}H NMR of **3s**



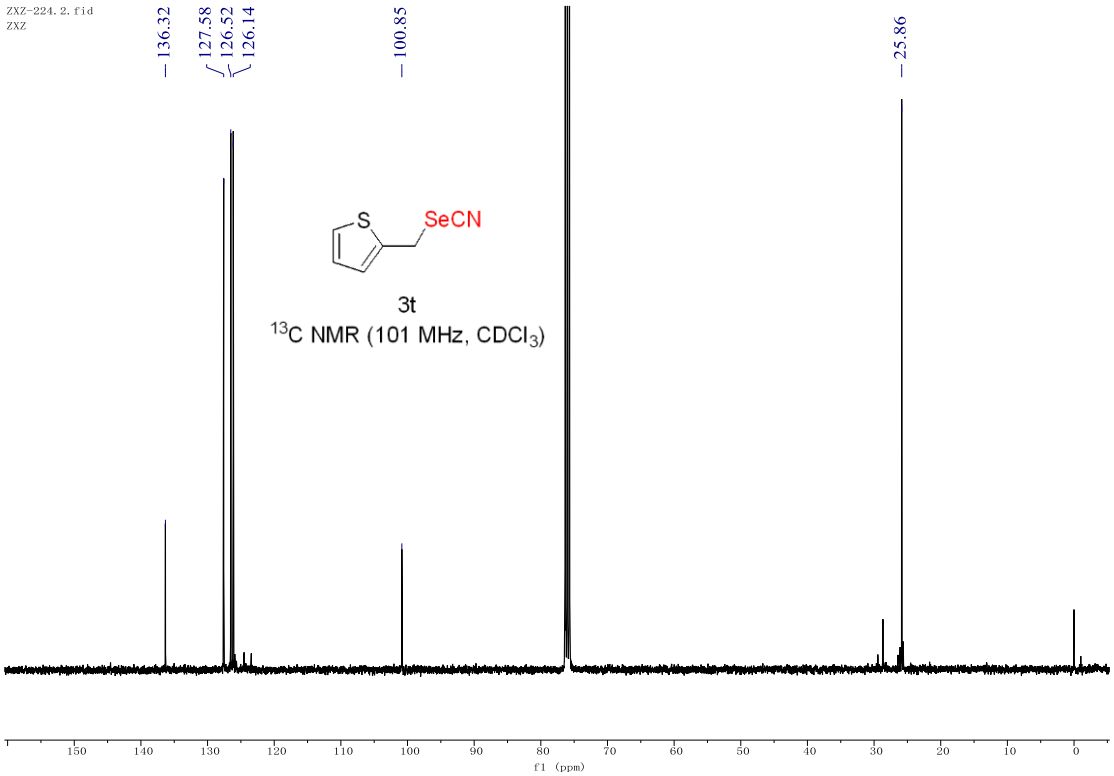
^{13}C NMR of **3s**



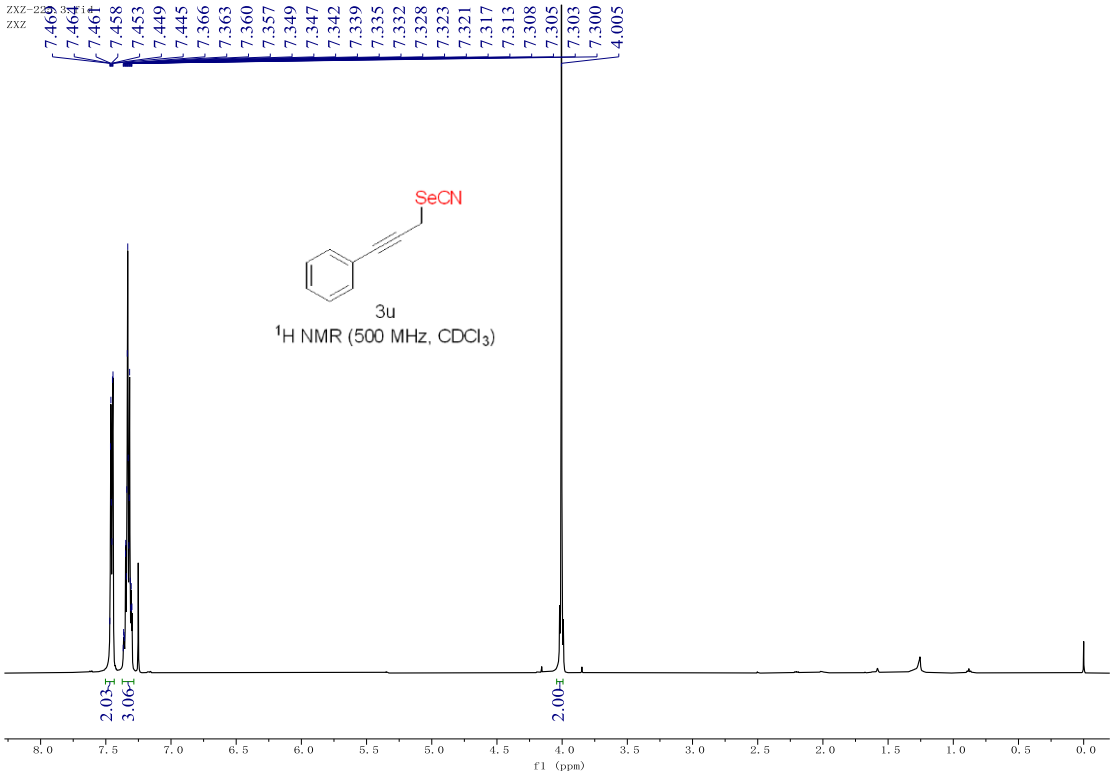
^{1}H NMR of **3t**



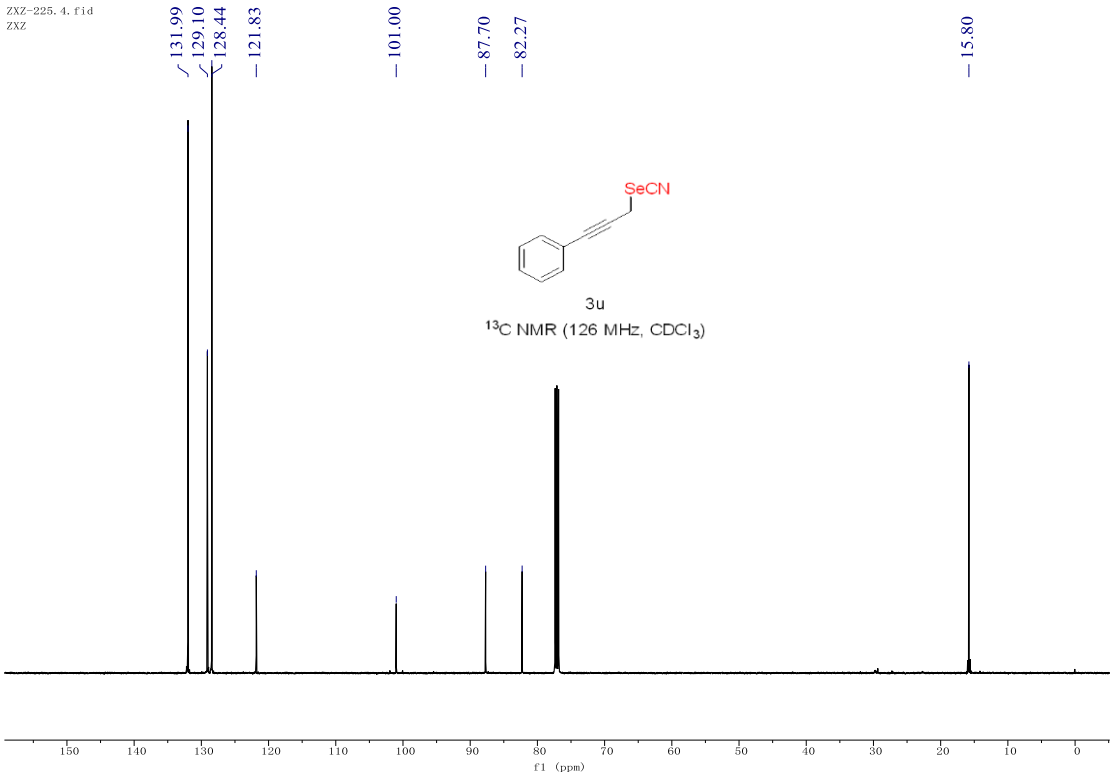
^{13}C NMR of **3t**



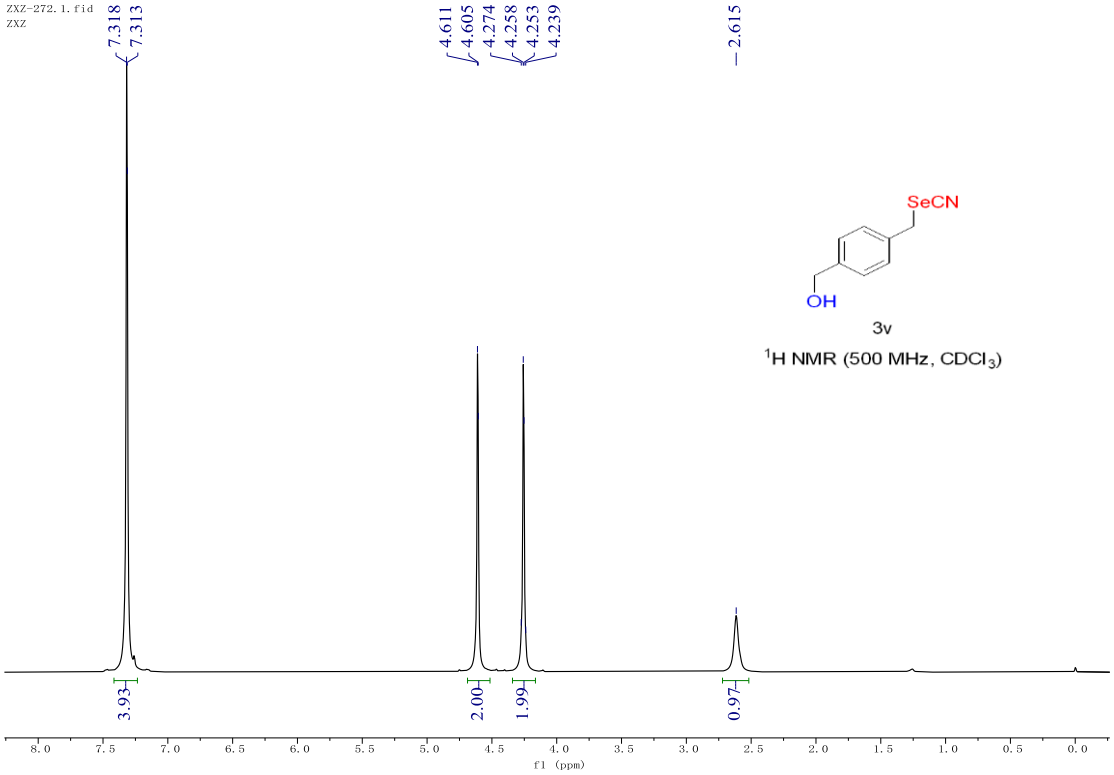
^{1}H NMR of **3u**



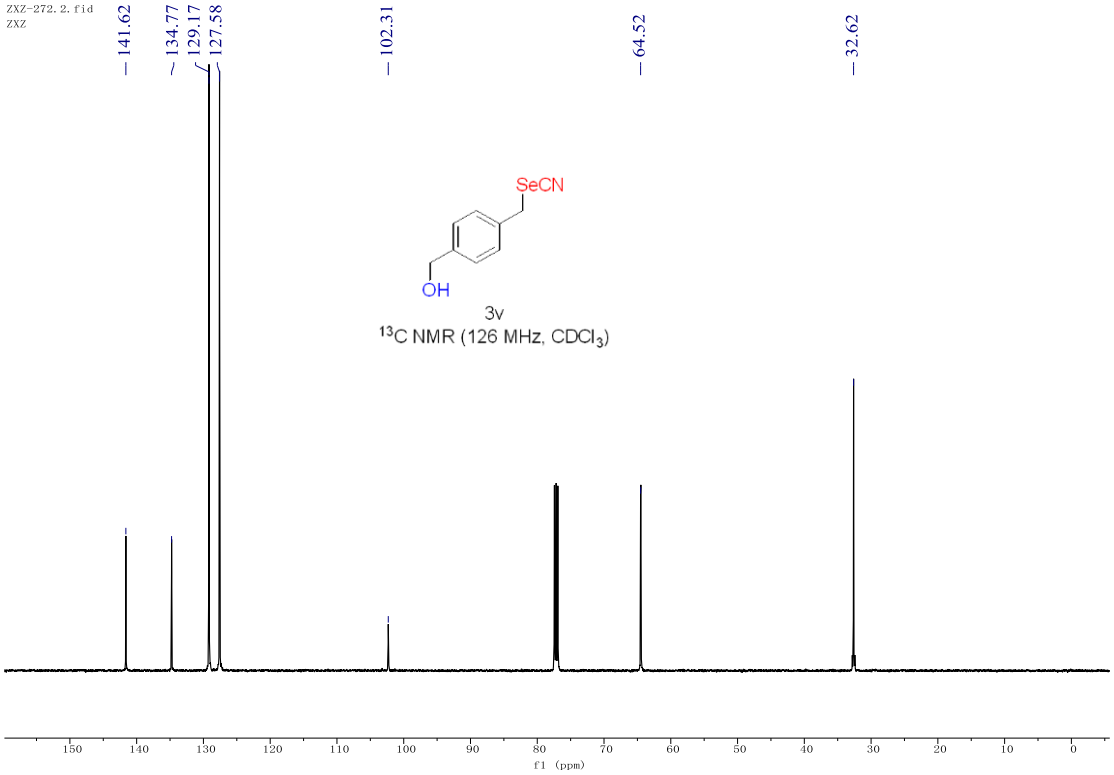
^{13}C NMR of **3u**



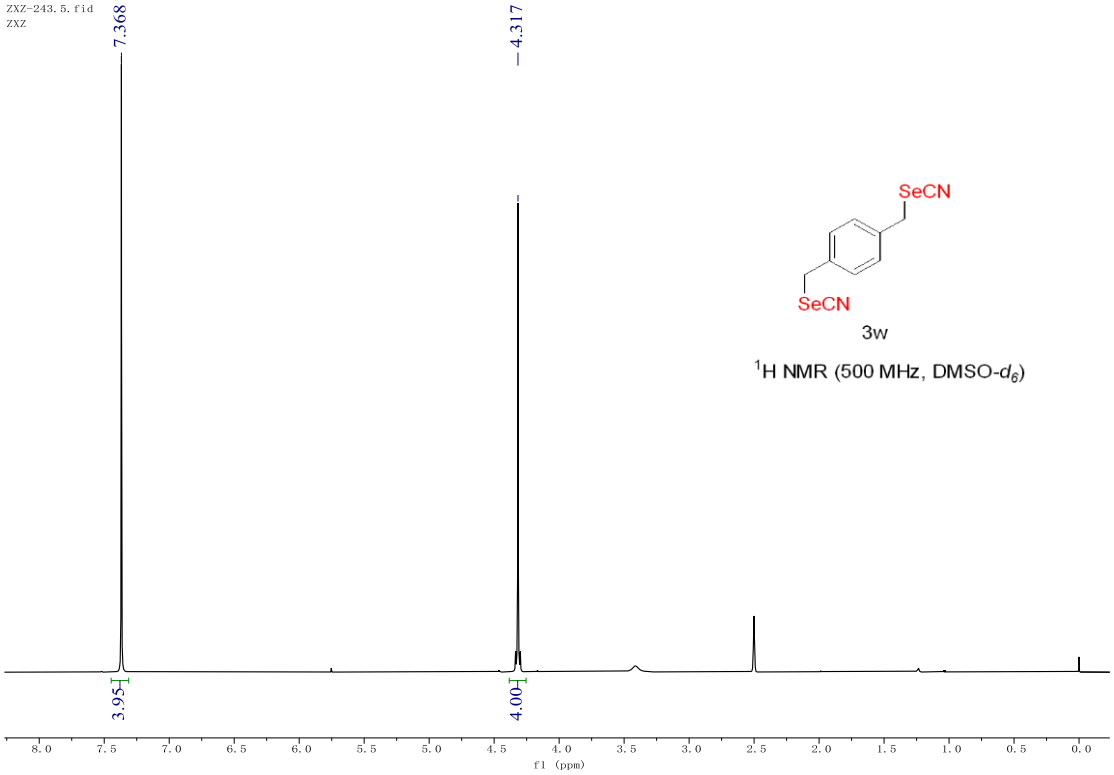
^{1}H NMR of **3v**



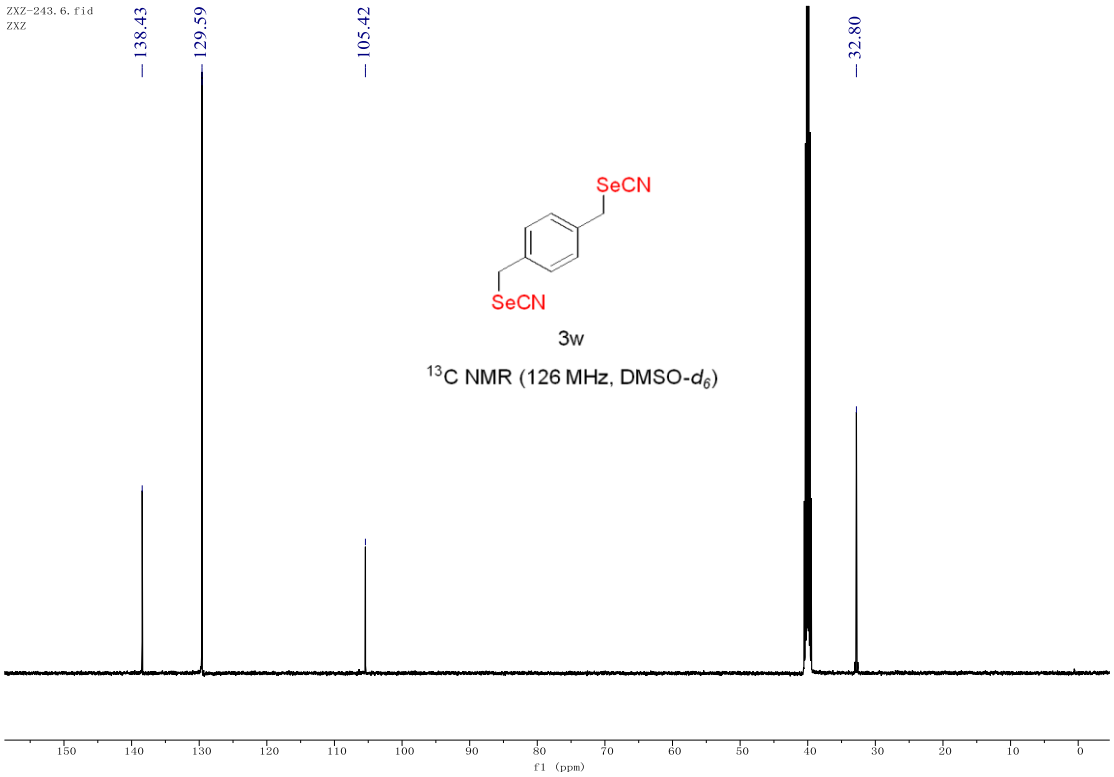
^{13}C NMR of **3v**



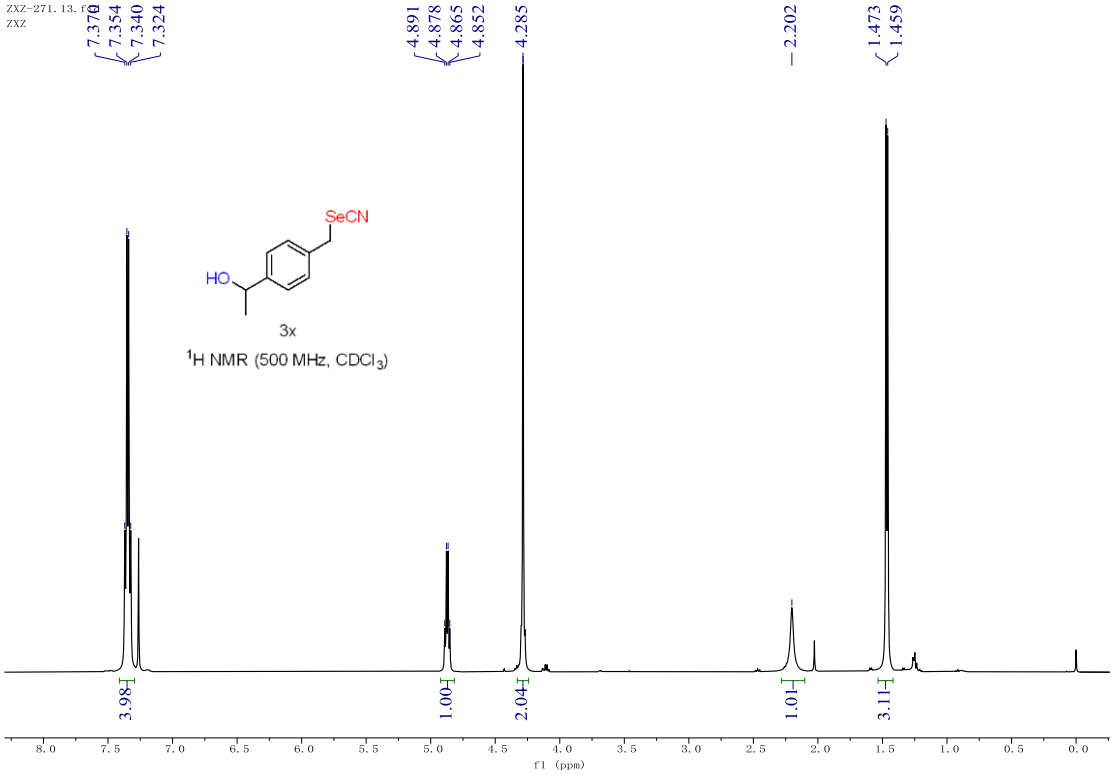
^{1}H NMR of **3w**



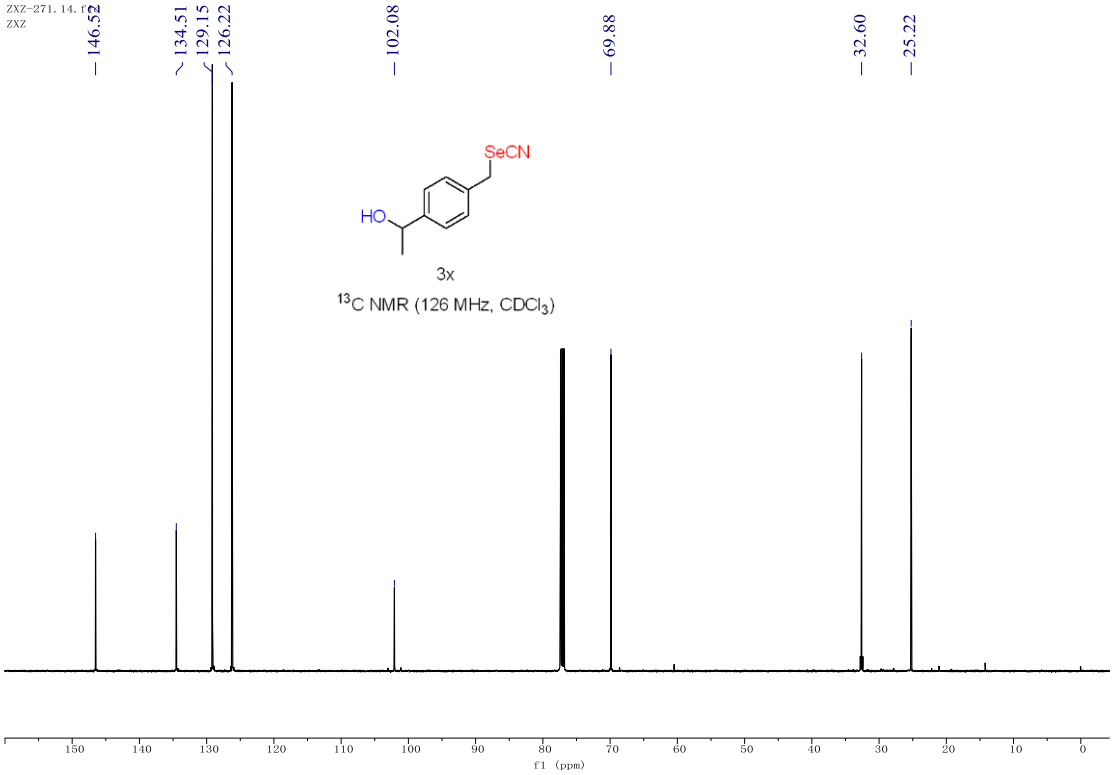
^{13}C NMR of **3w**



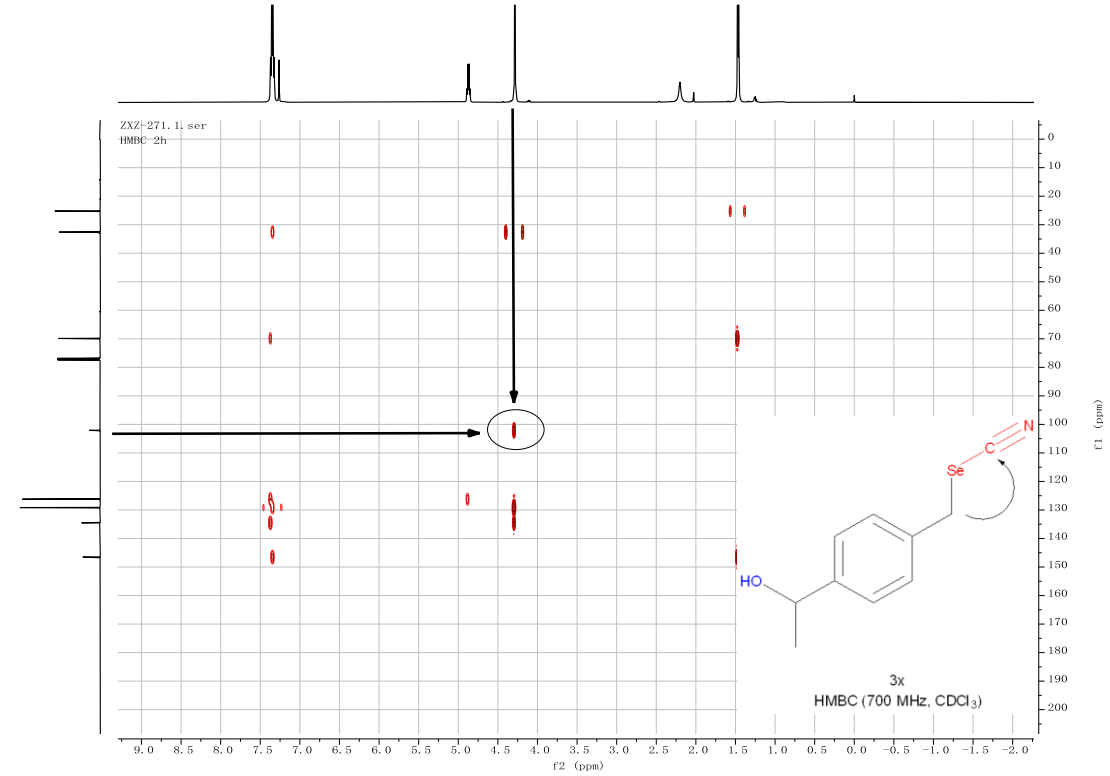
^{1}H NMR of **3x**



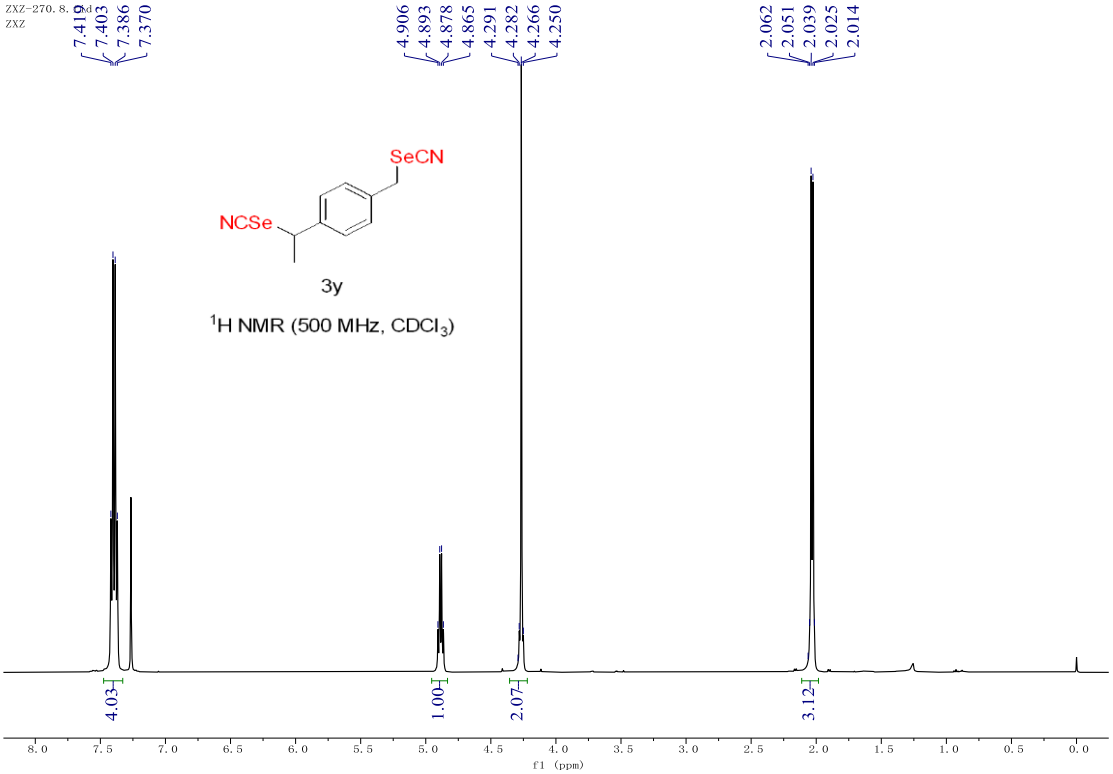
^{13}C NMR of **3x**



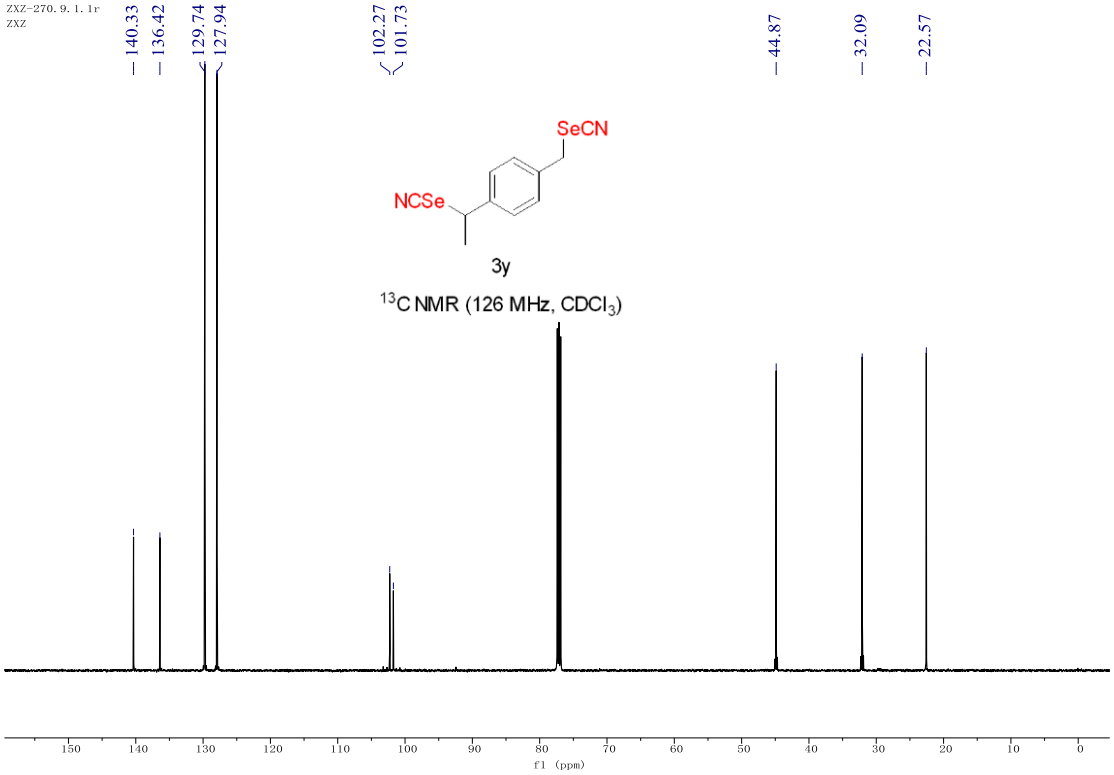
HMBC NMR of **3x**



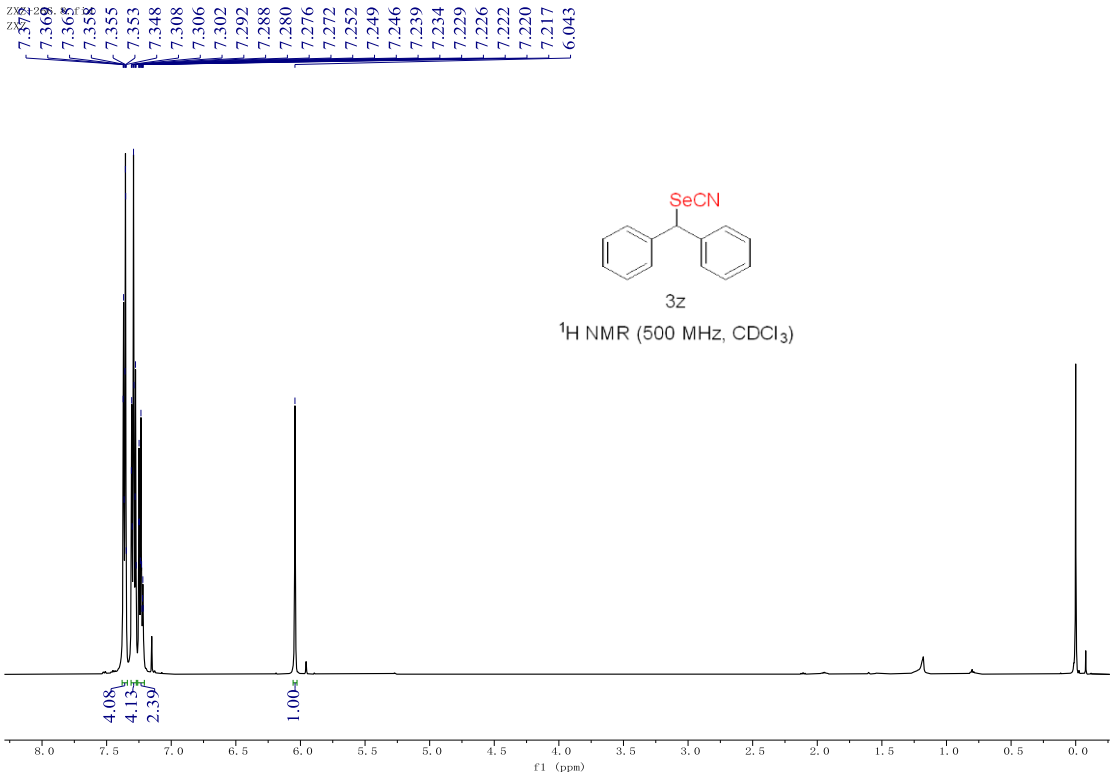
^{1}H NMR of **3y**



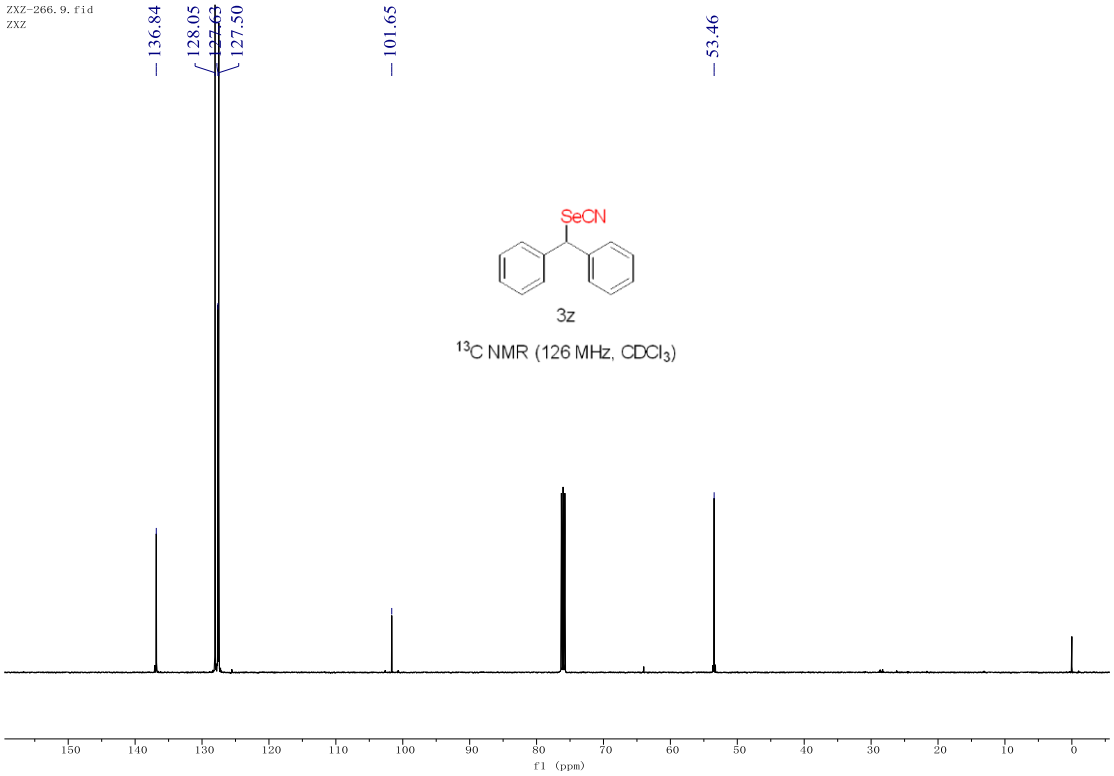
^{13}C NMR of **3y**



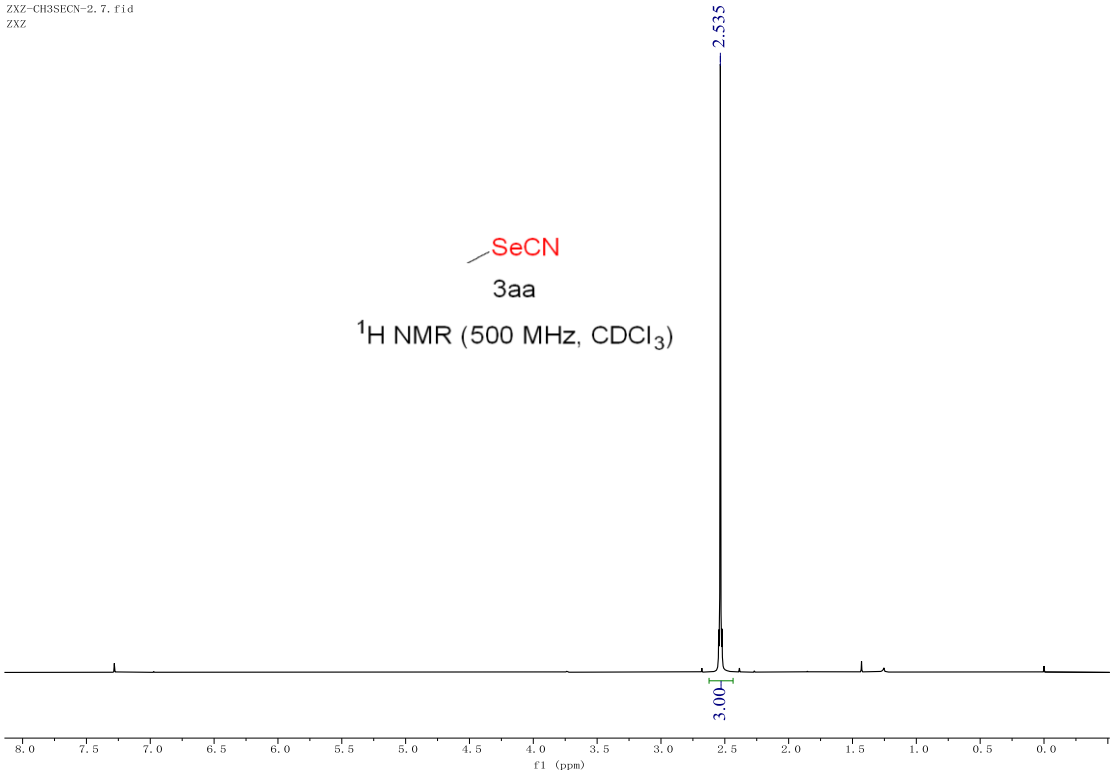
^{1}H NMR of **3z**



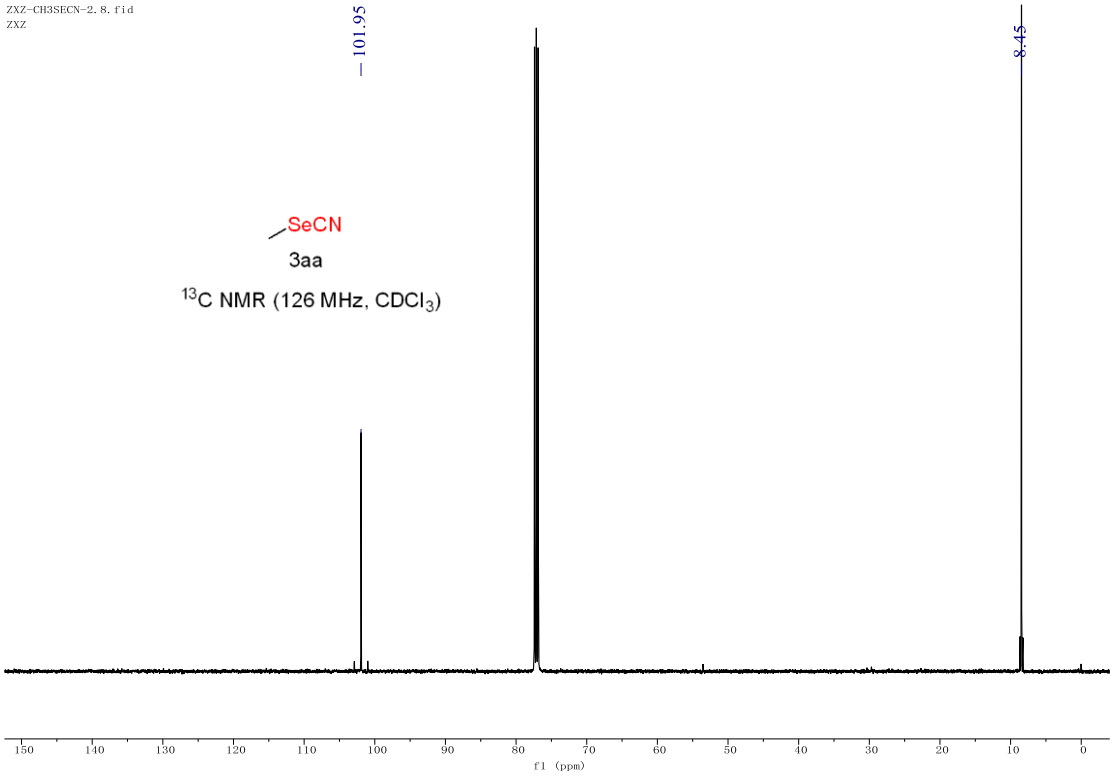
^{13}C NMR of **3z**



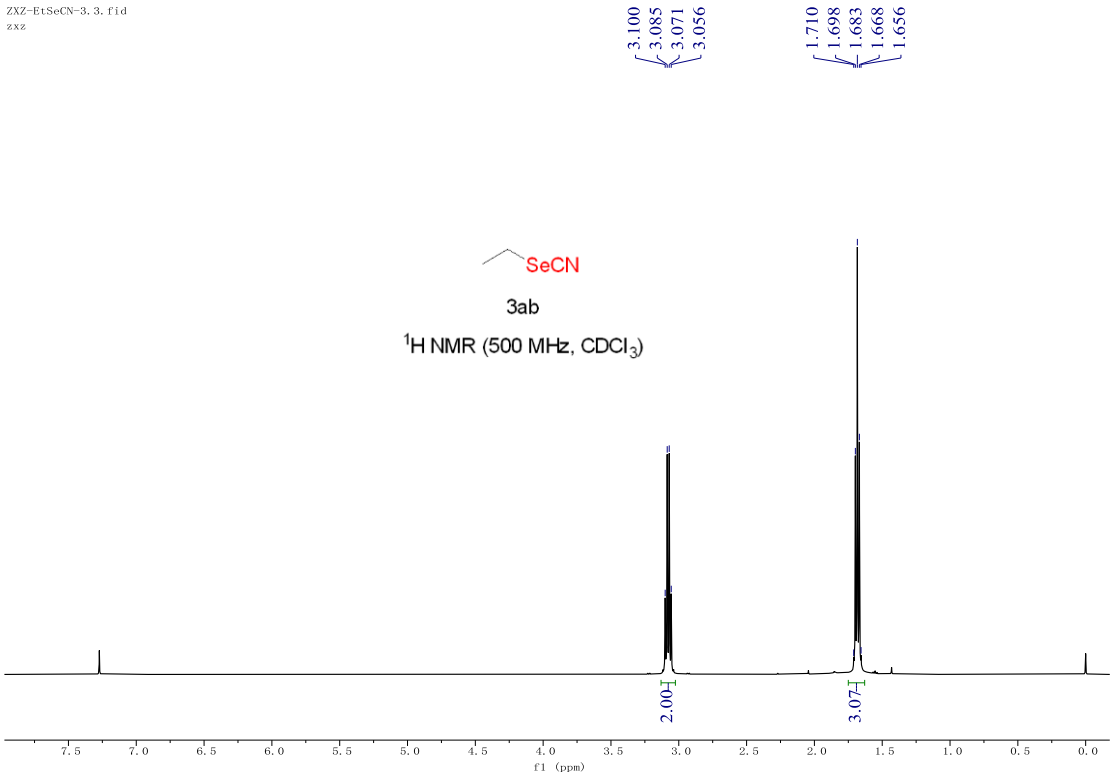
^{1}H NMR of **3aa**



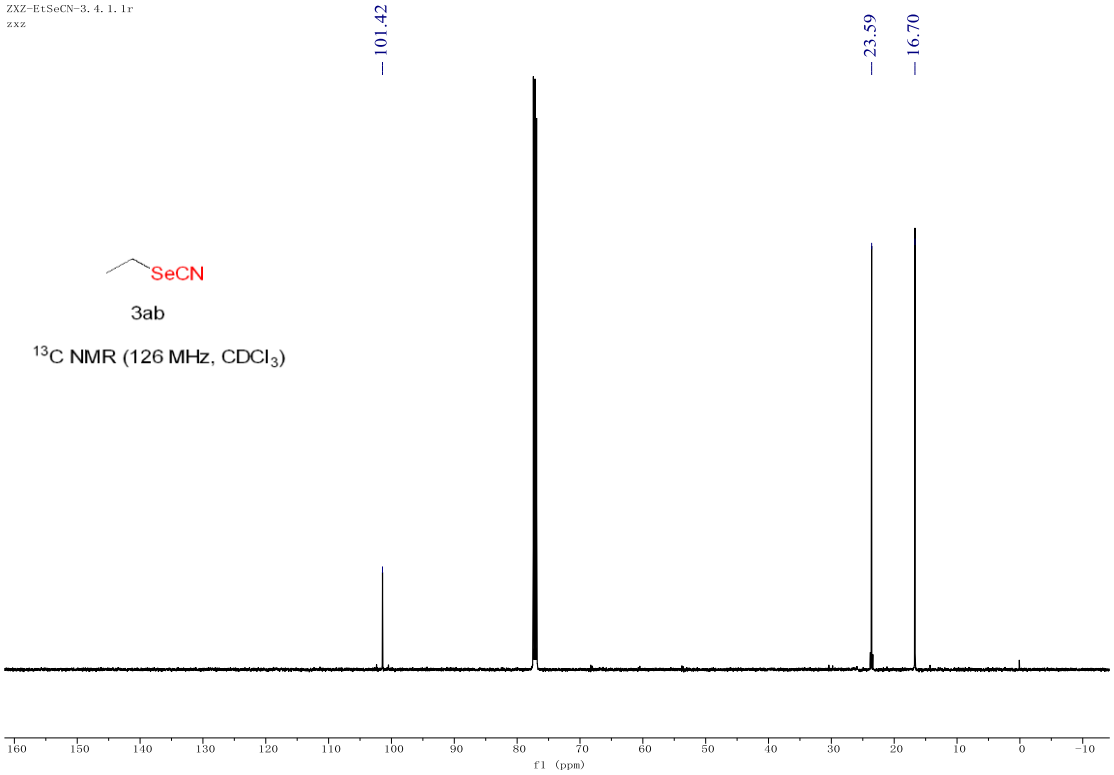
^{13}C NMR of **3aa**



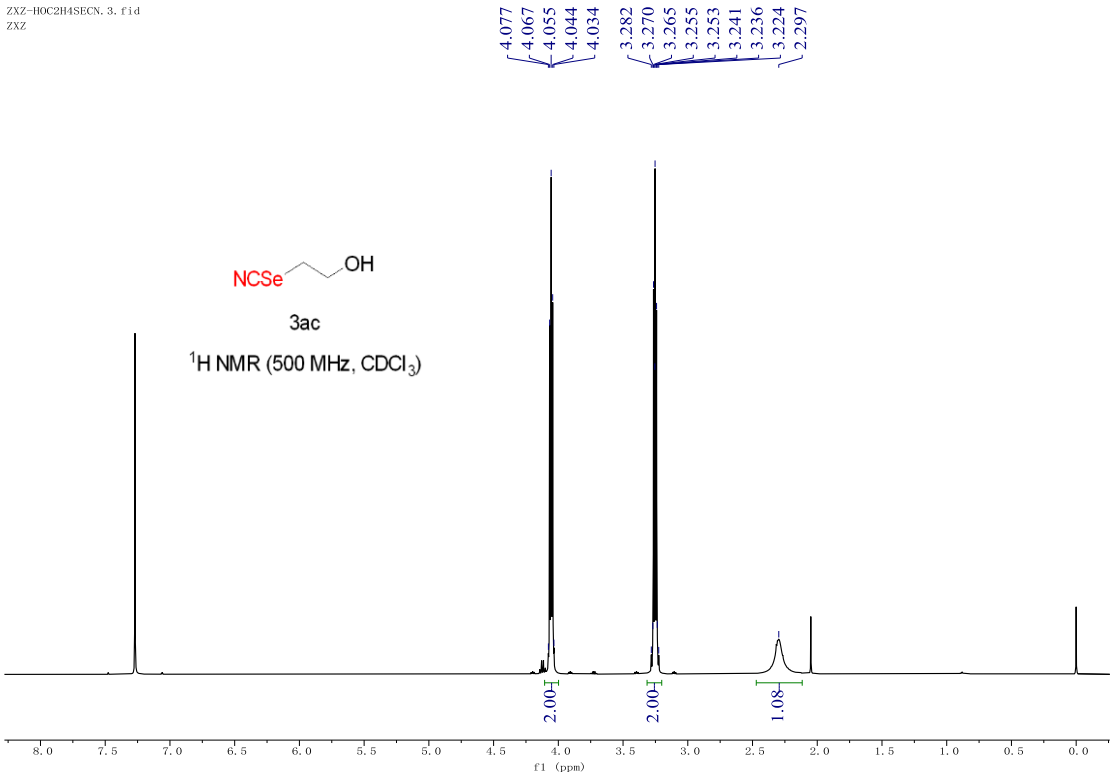
^{1}H NMR of **3ab**



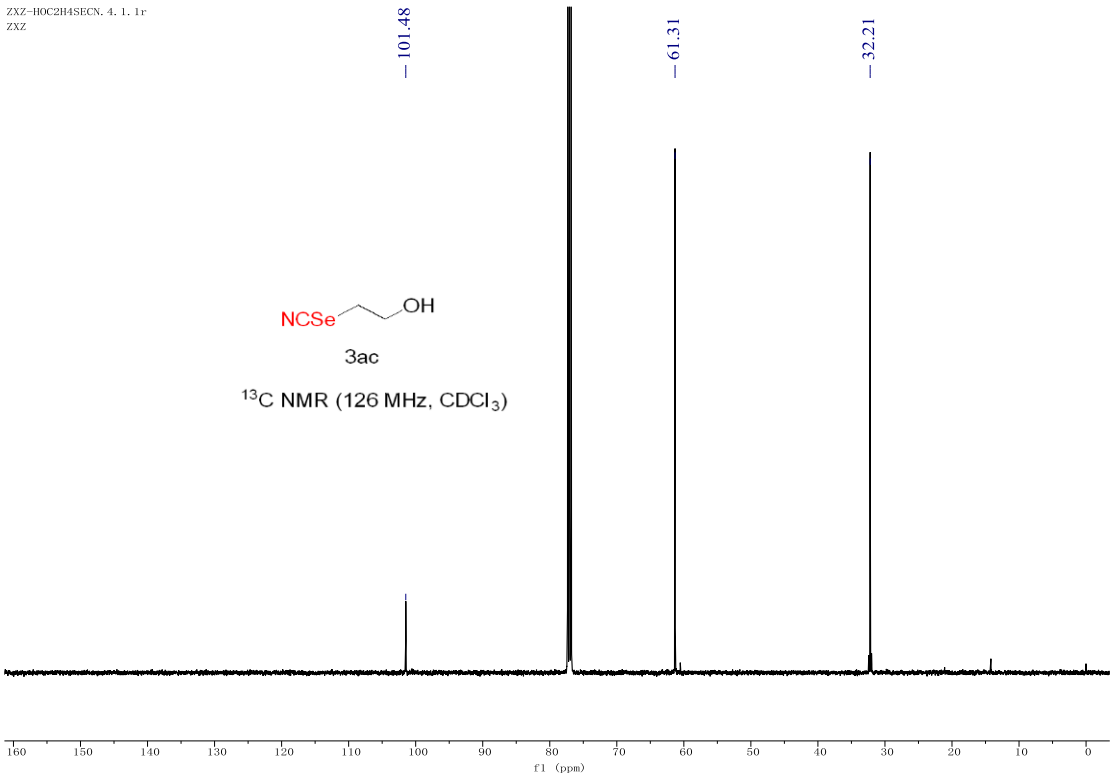
^{13}C NMR of **3ab**



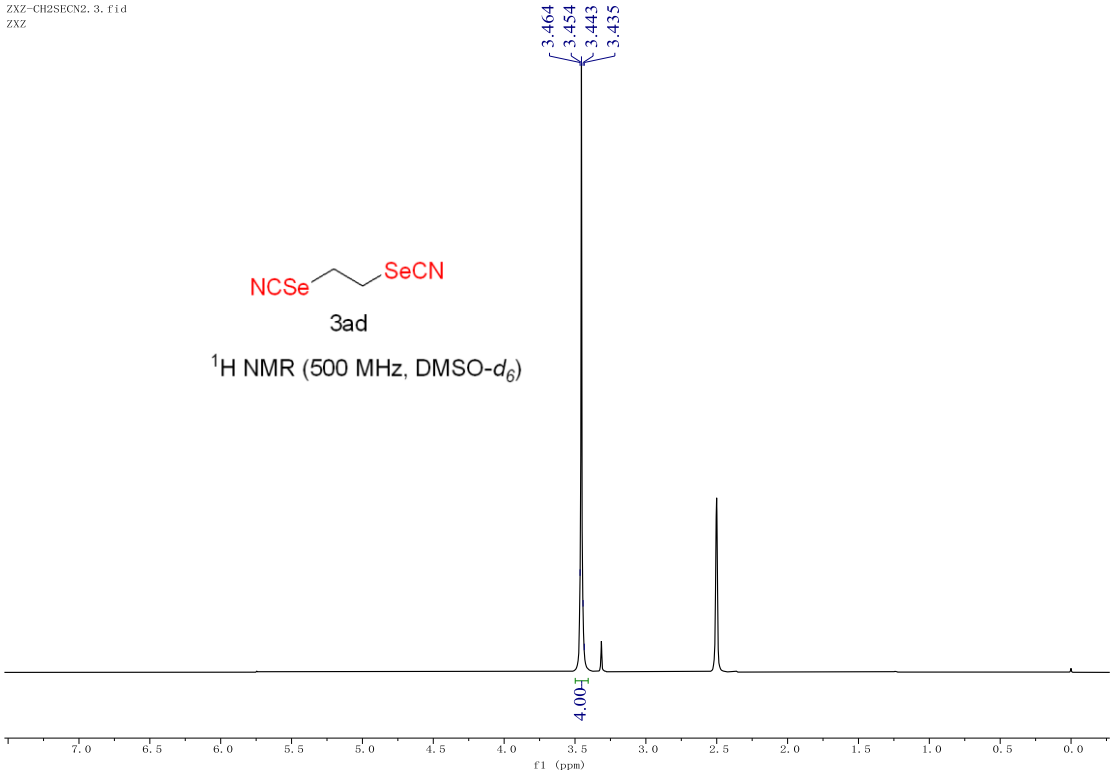
^{1}H NMR of **3ac**



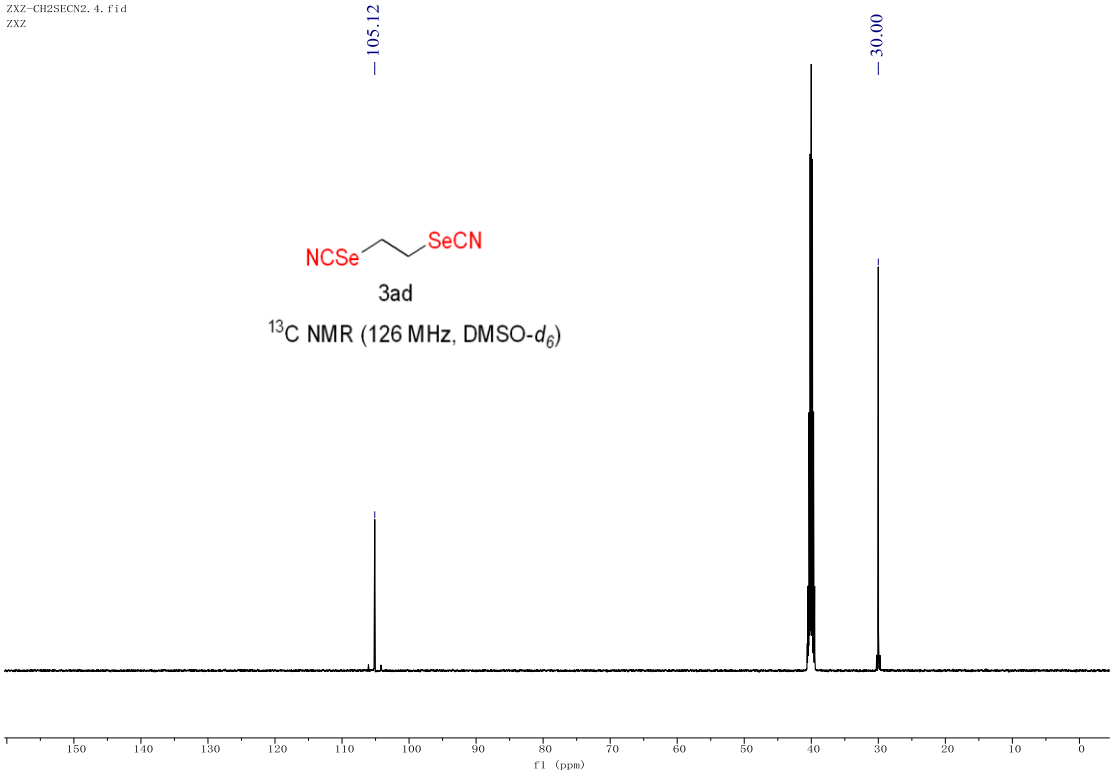
^{13}C NMR of **3ac**



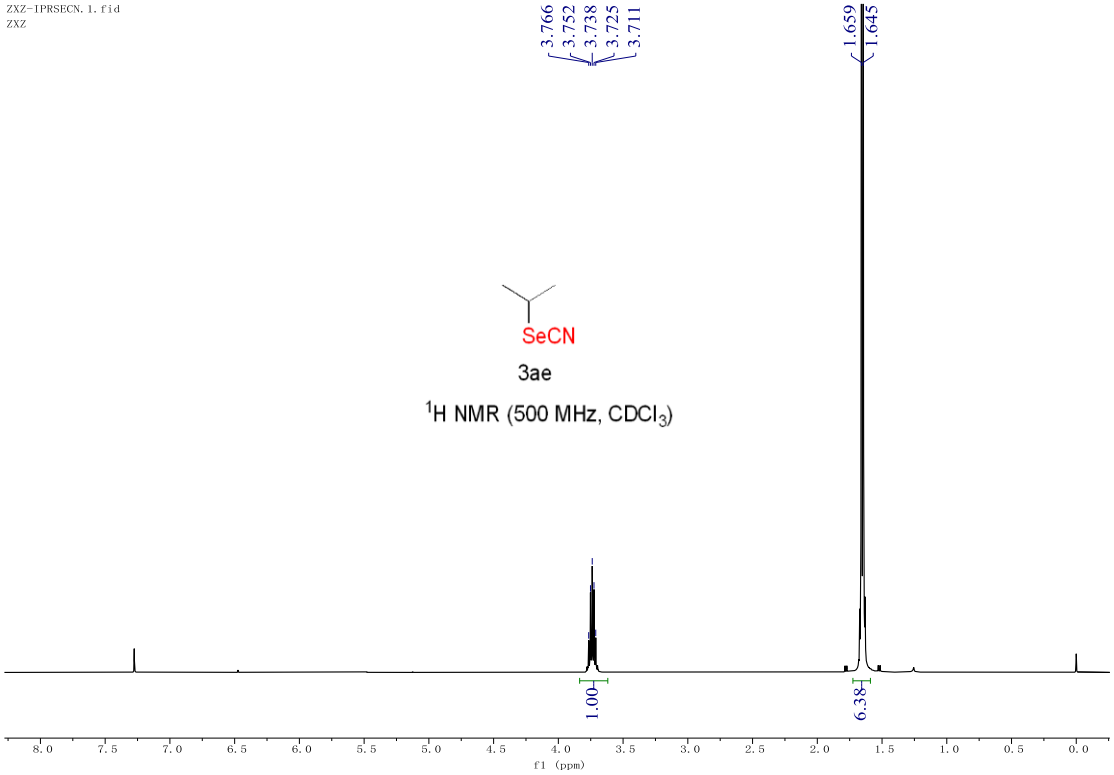
^{1}H NMR of **3ad**



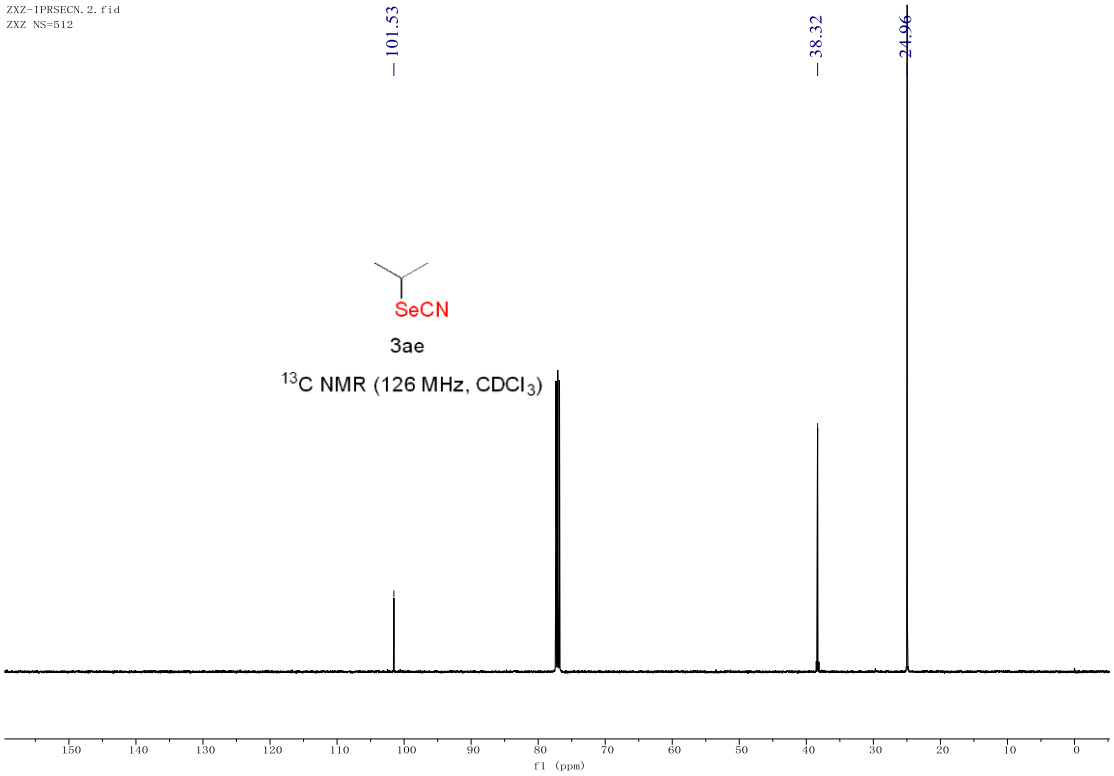
^{13}C NMR of **3ad**



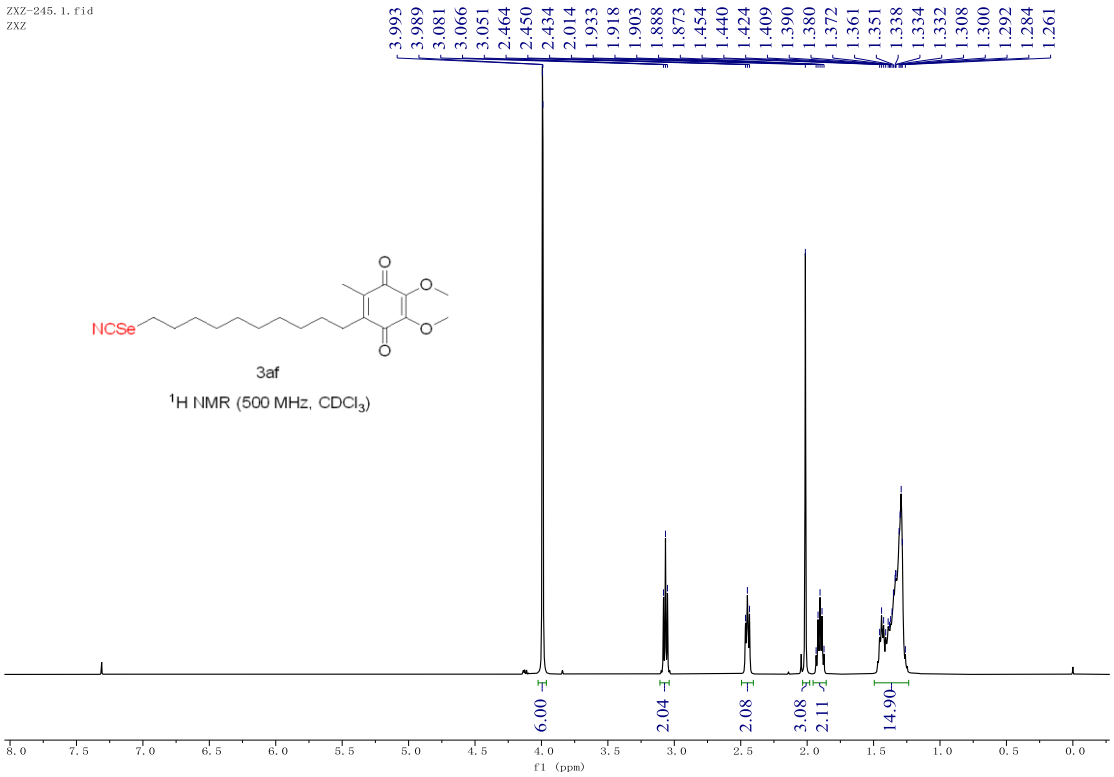
^{1}H NMR of **3ae**



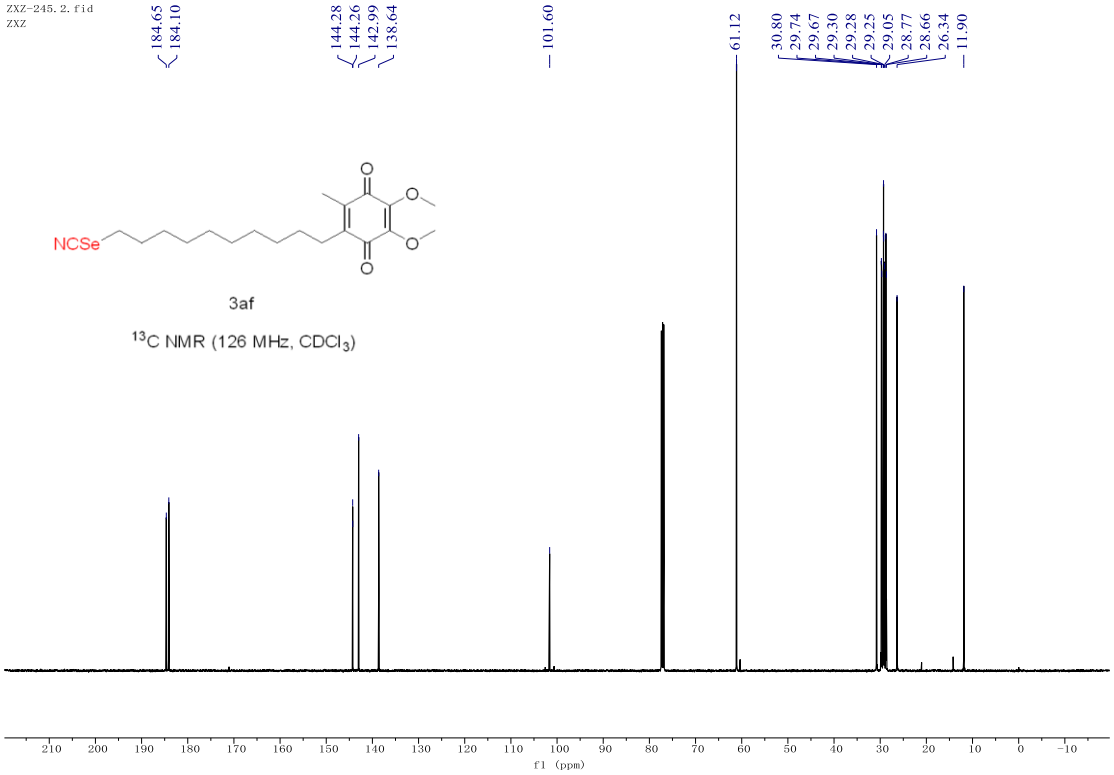
^{13}C NMR of **3ae**



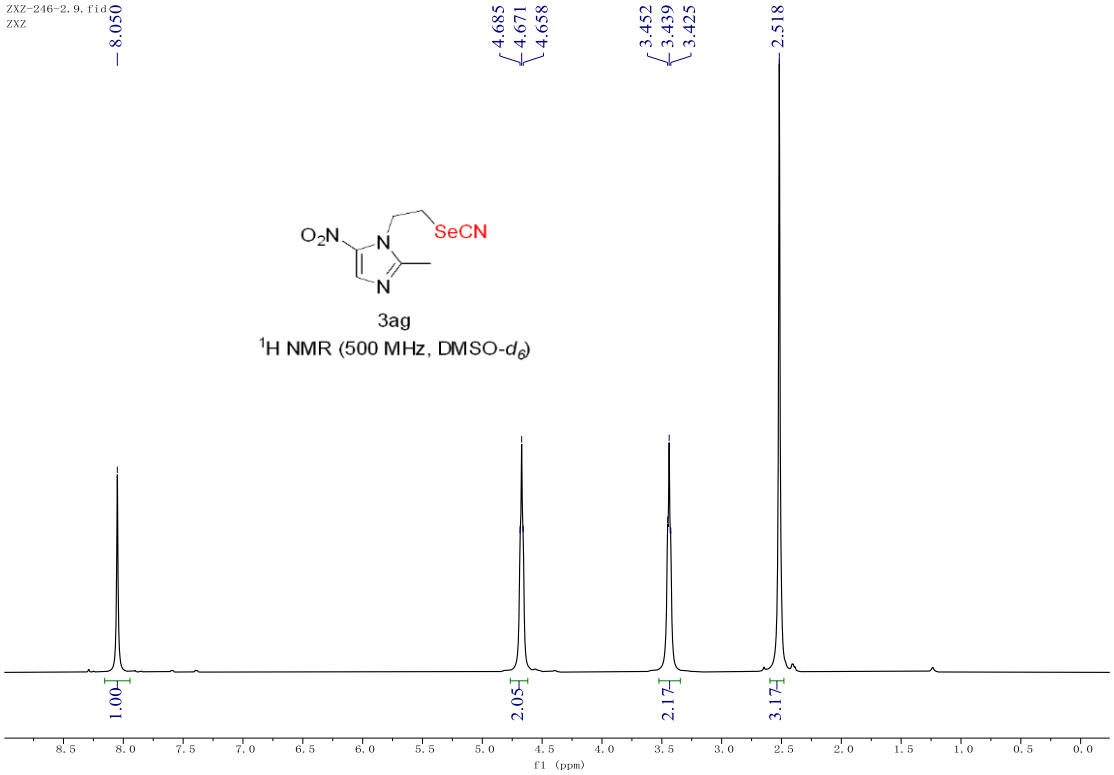
^{1}H NMR of **3af**



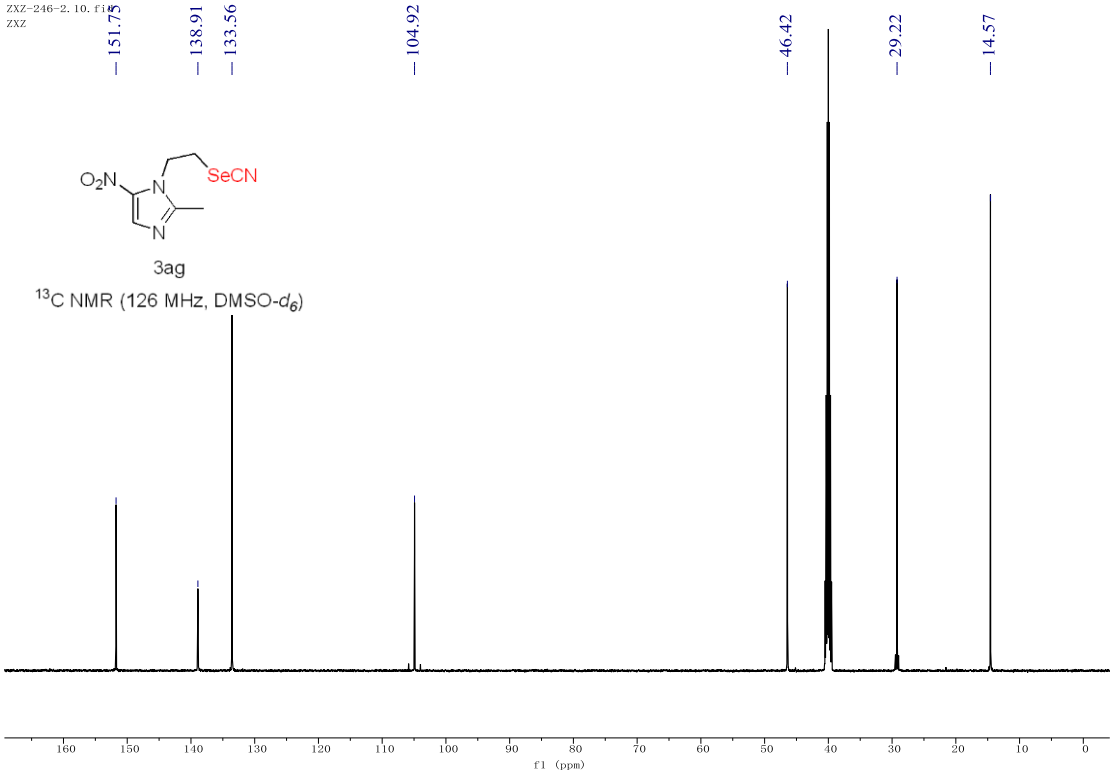
^{13}C NMR of **3af**



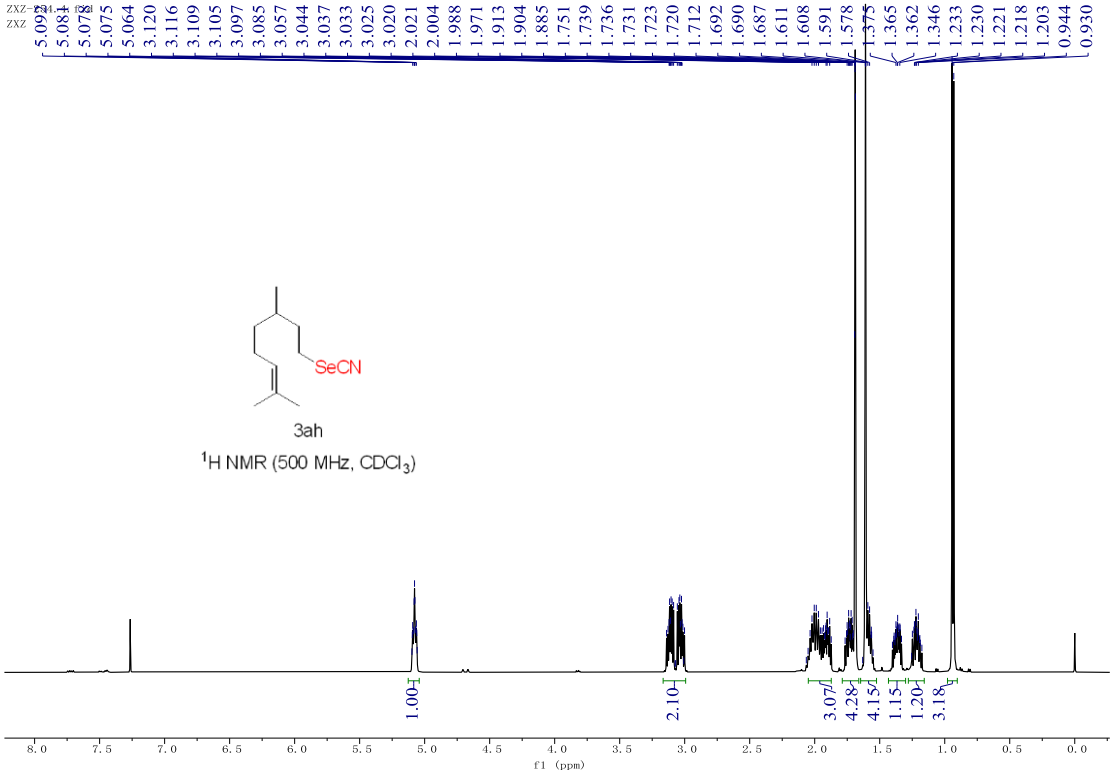
^{1}H NMR of **3ag**



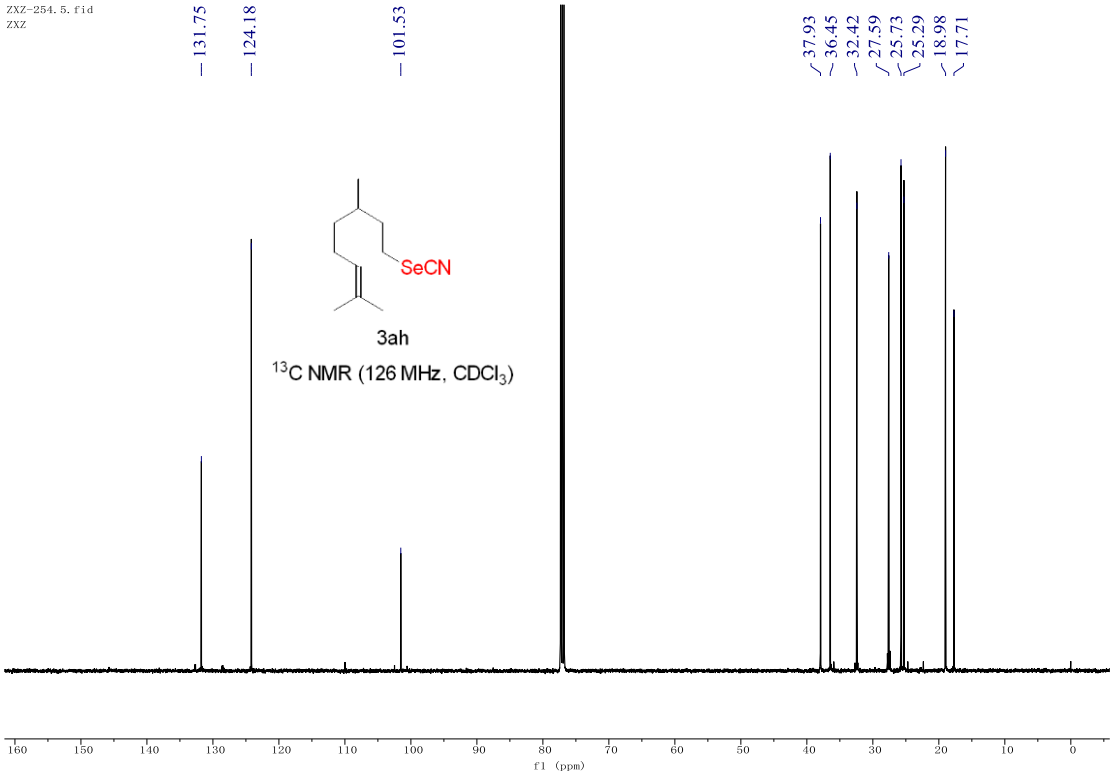
^{13}C NMR of **3ag**



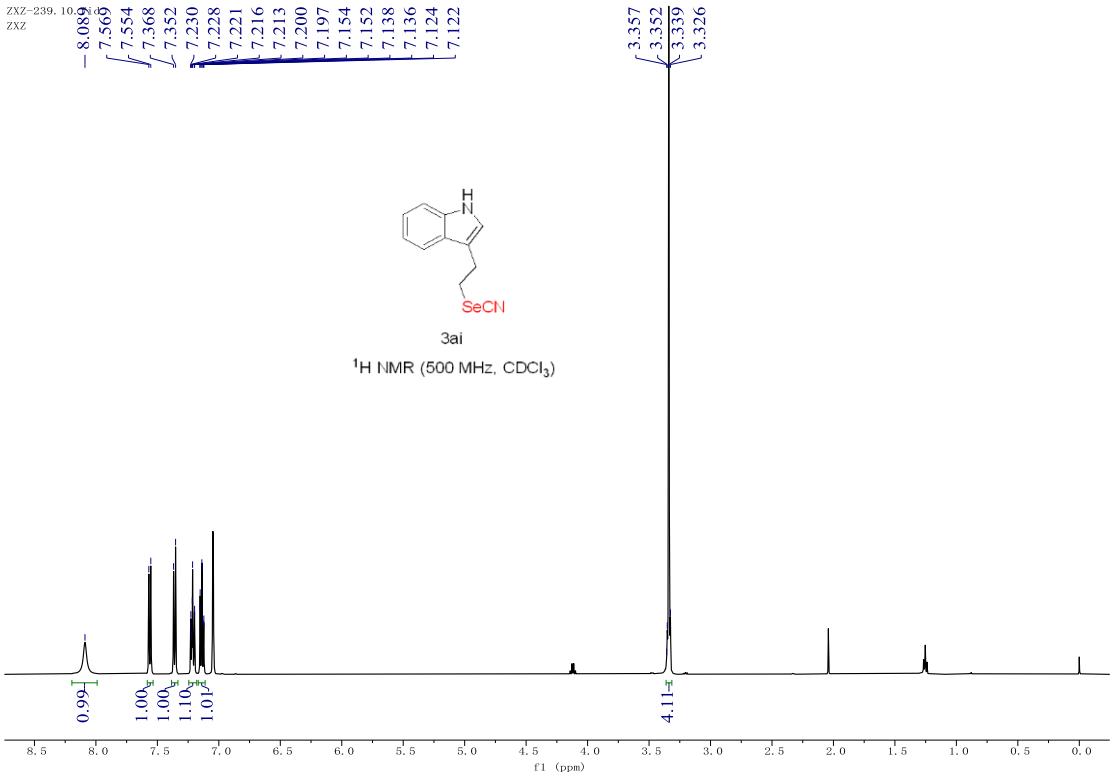
^{1}H NMR of **3ah**



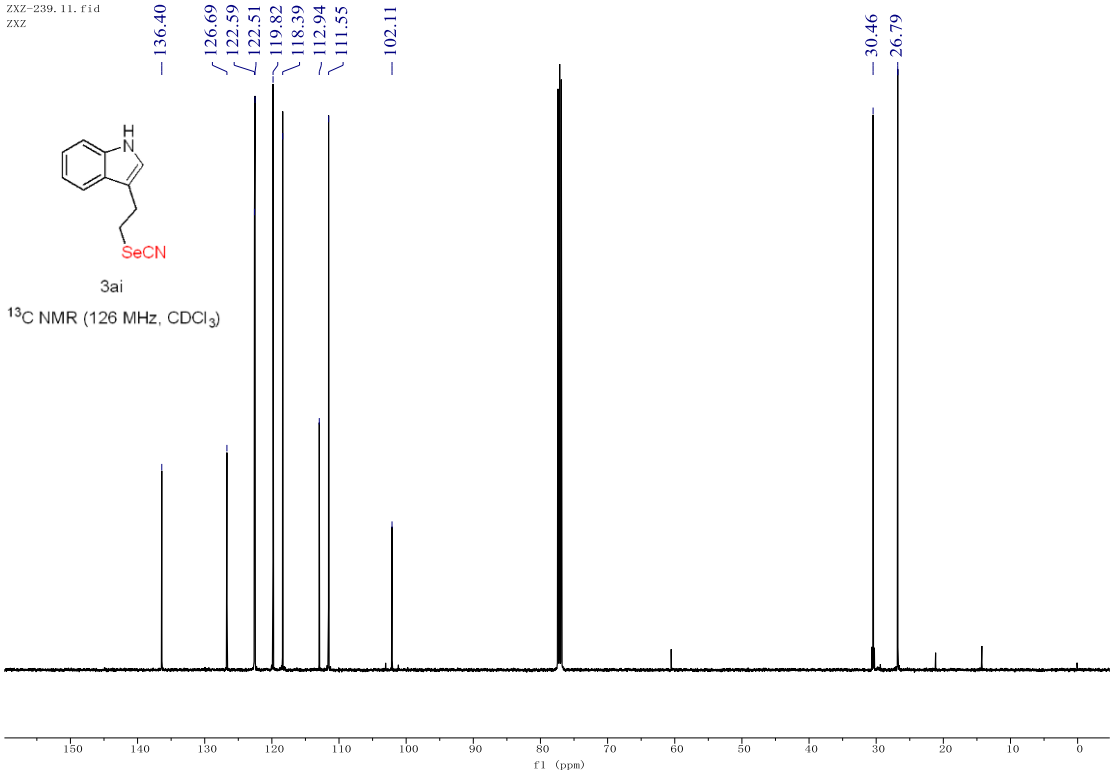
^{13}C NMR of **3ah**



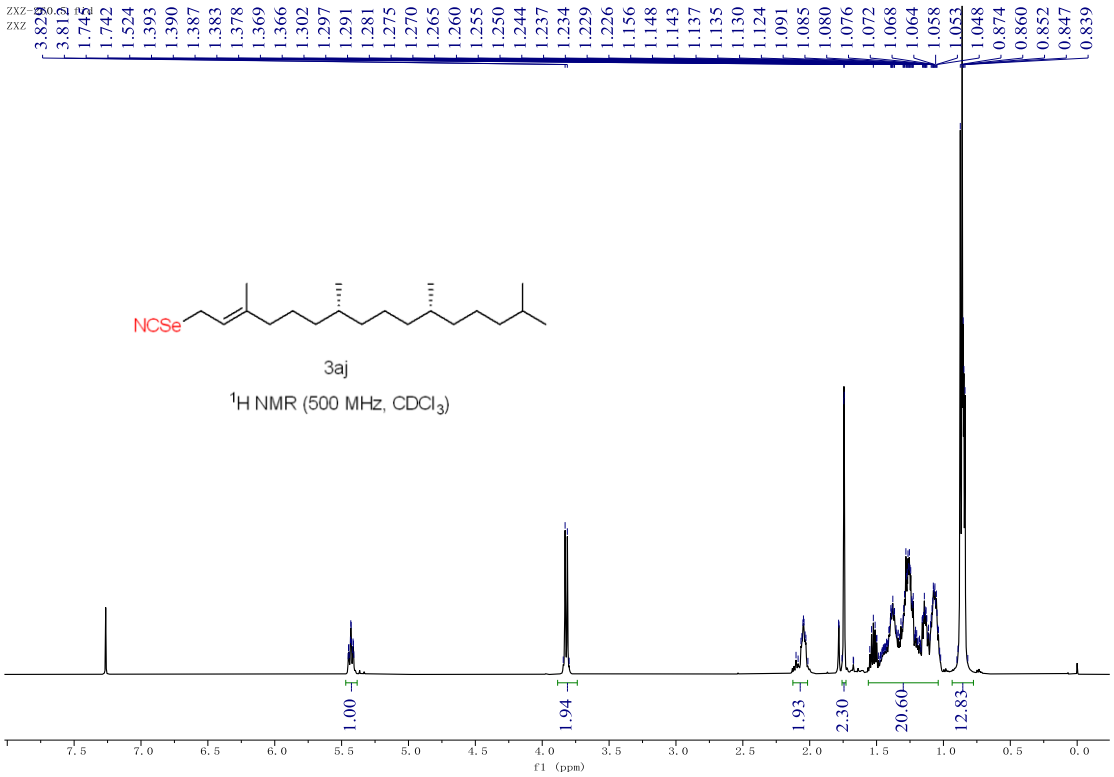
^{1}H NMR of **3ai**



^{13}C NMR of **3ai**



^{1}H NMR of **3aj**



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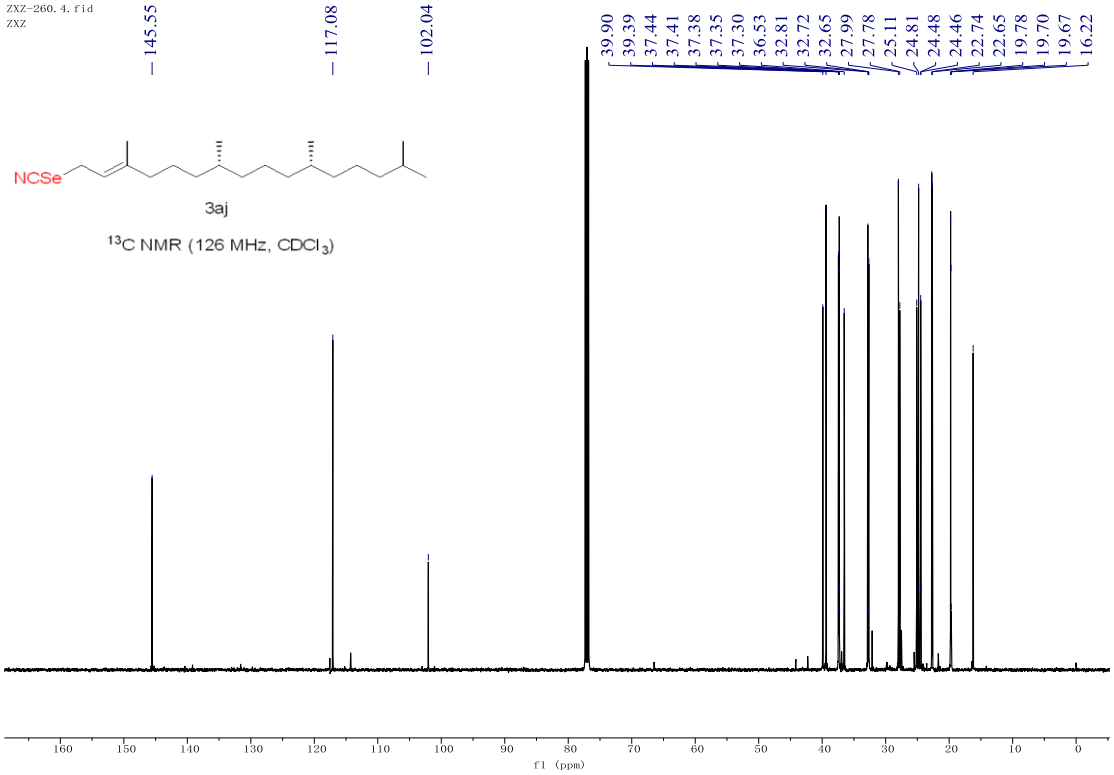
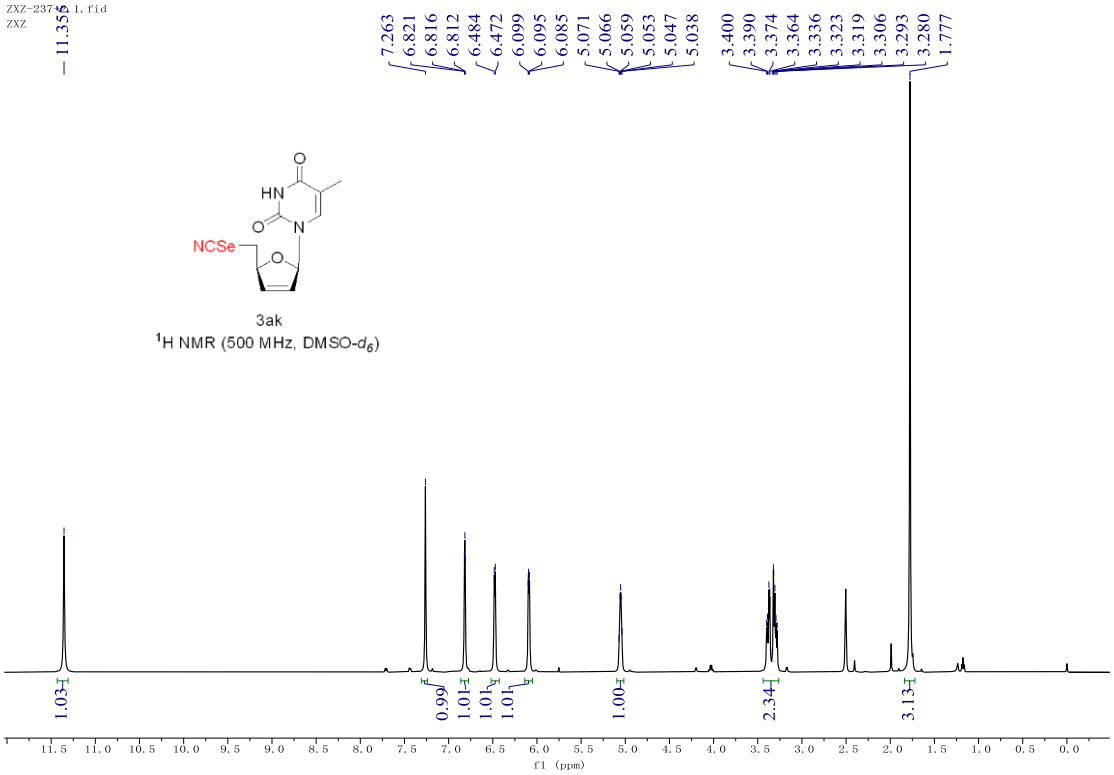
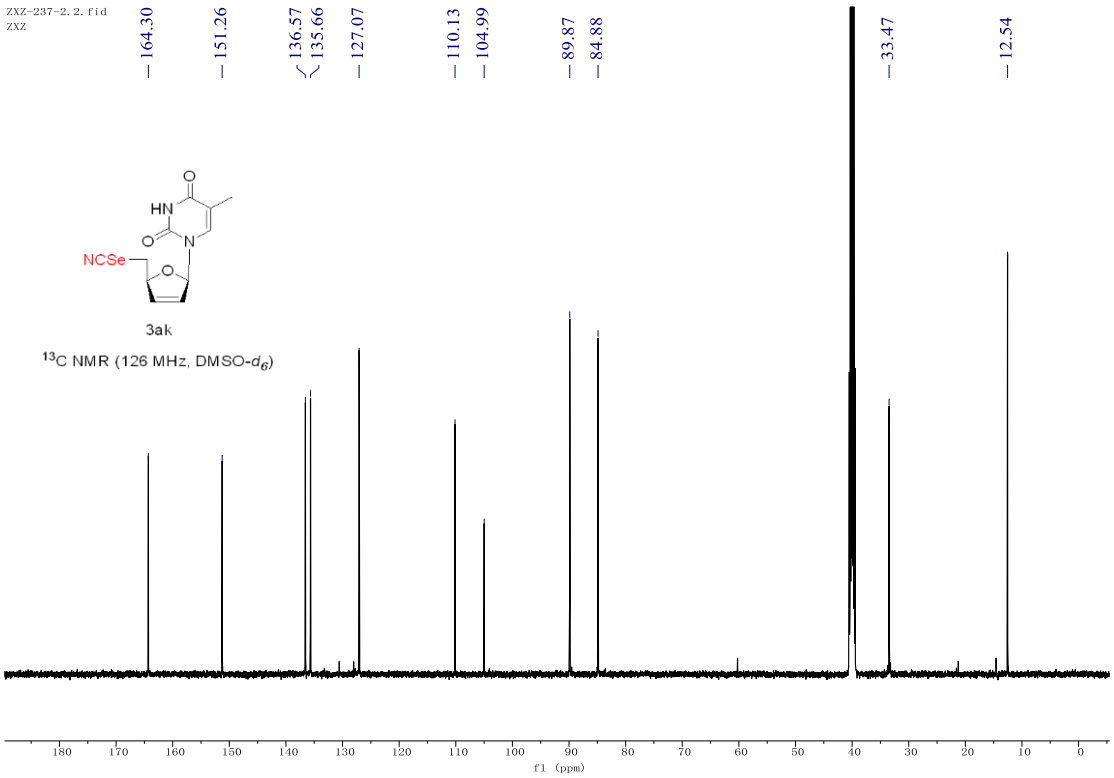


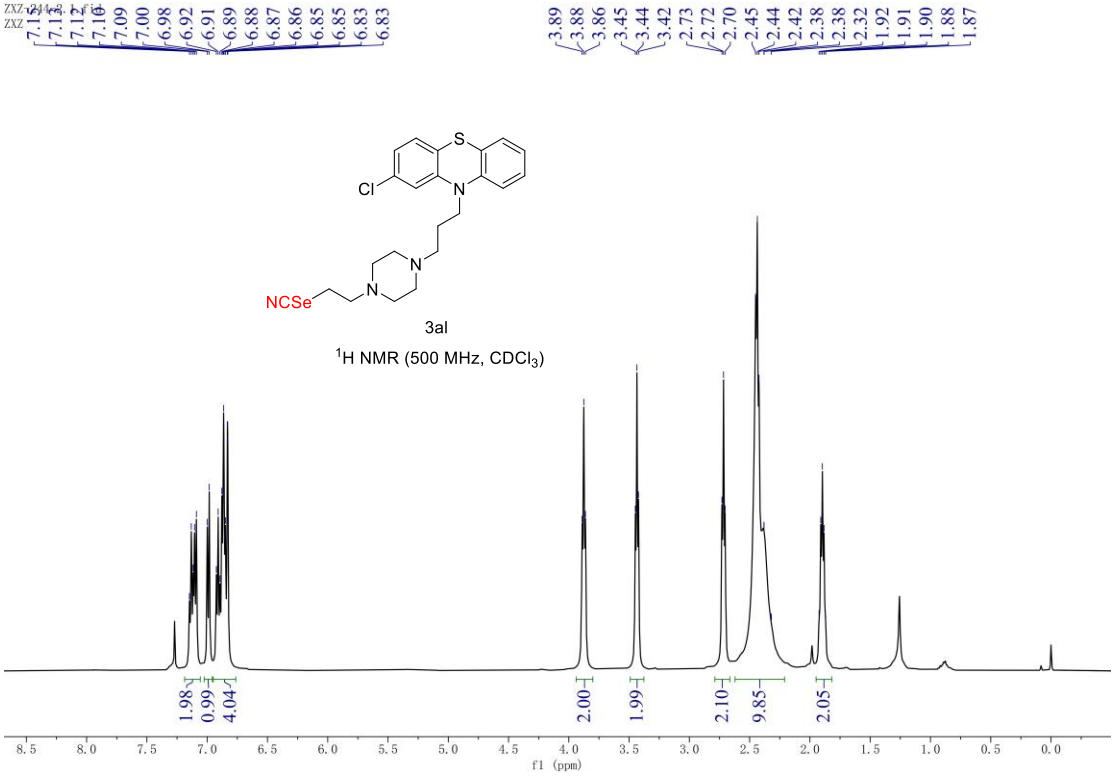
^{1}H NMR of **3ak**



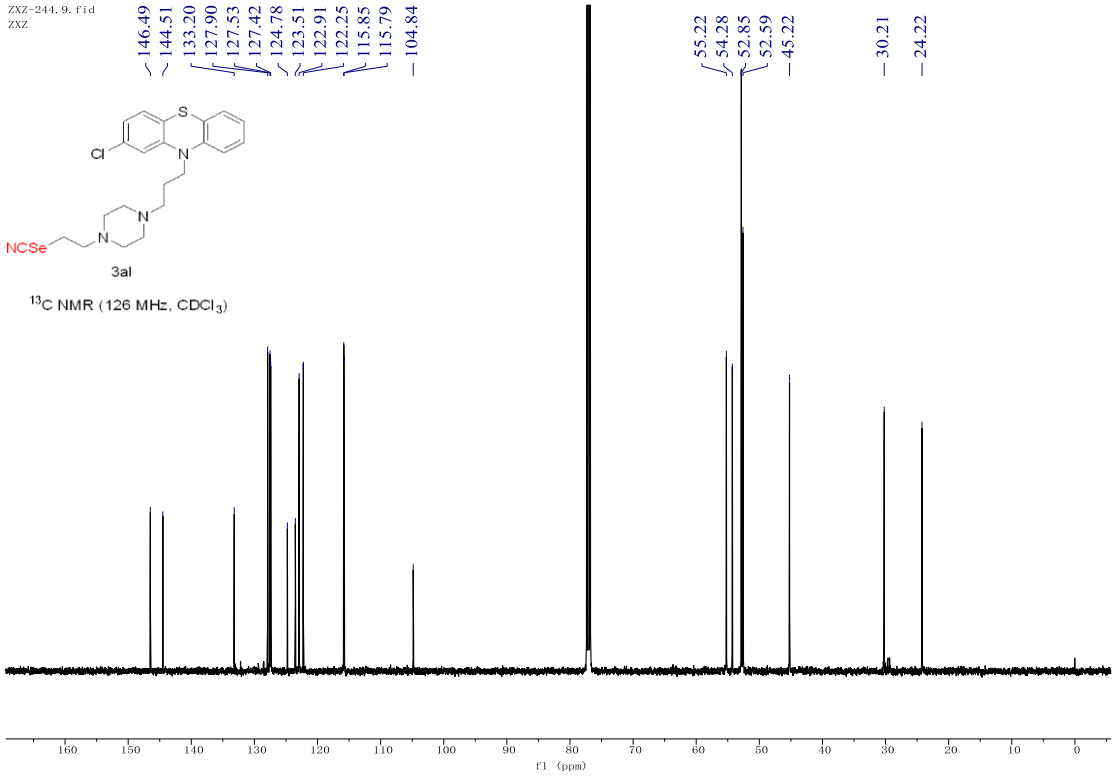
^{13}C NMR of **3ak**



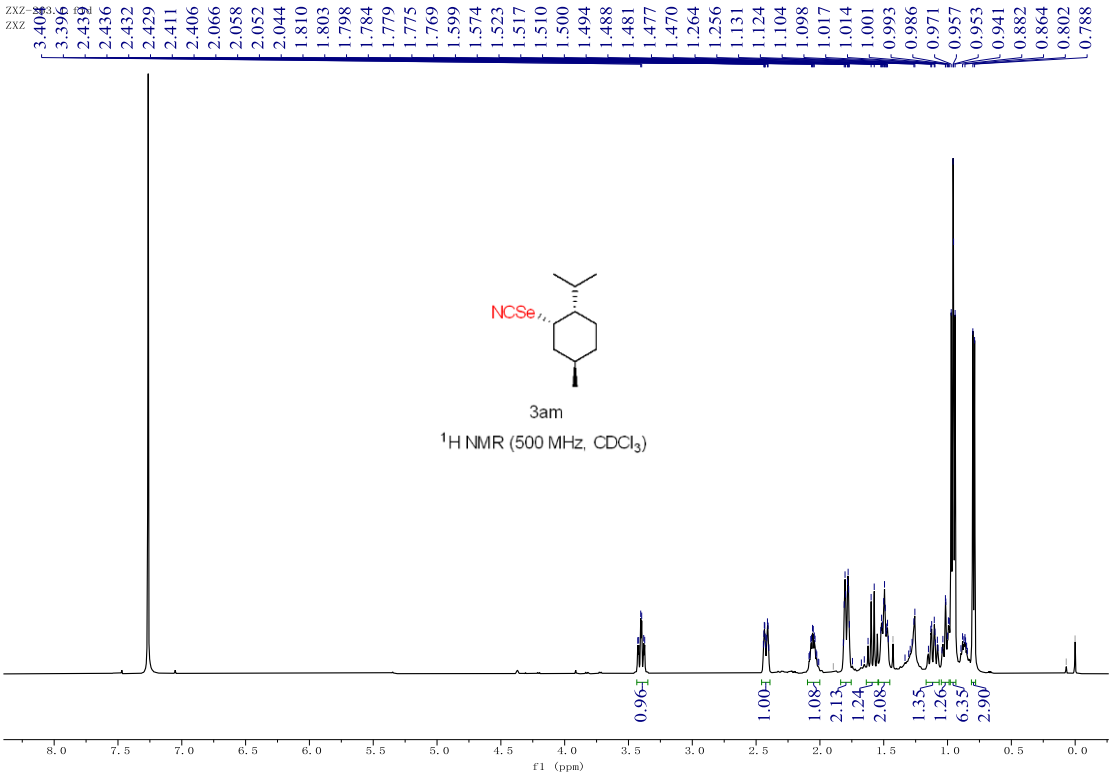
^{1}H NMR of **3al**



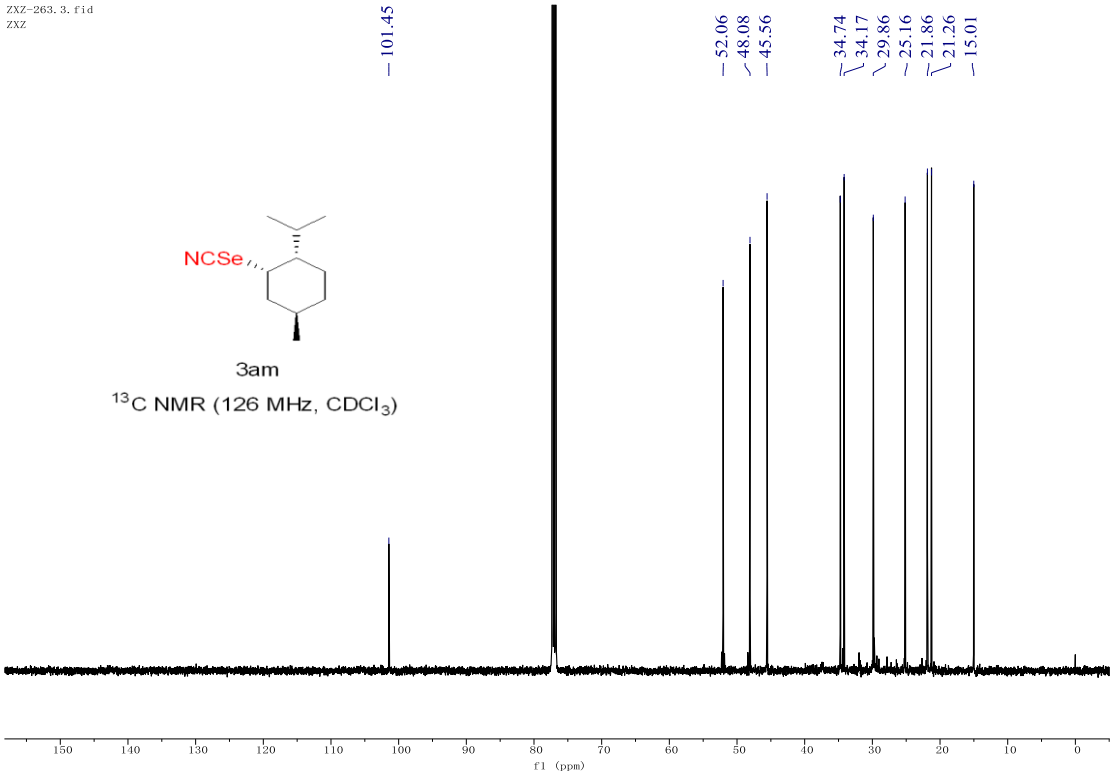
^{13}C NMR of **3al**



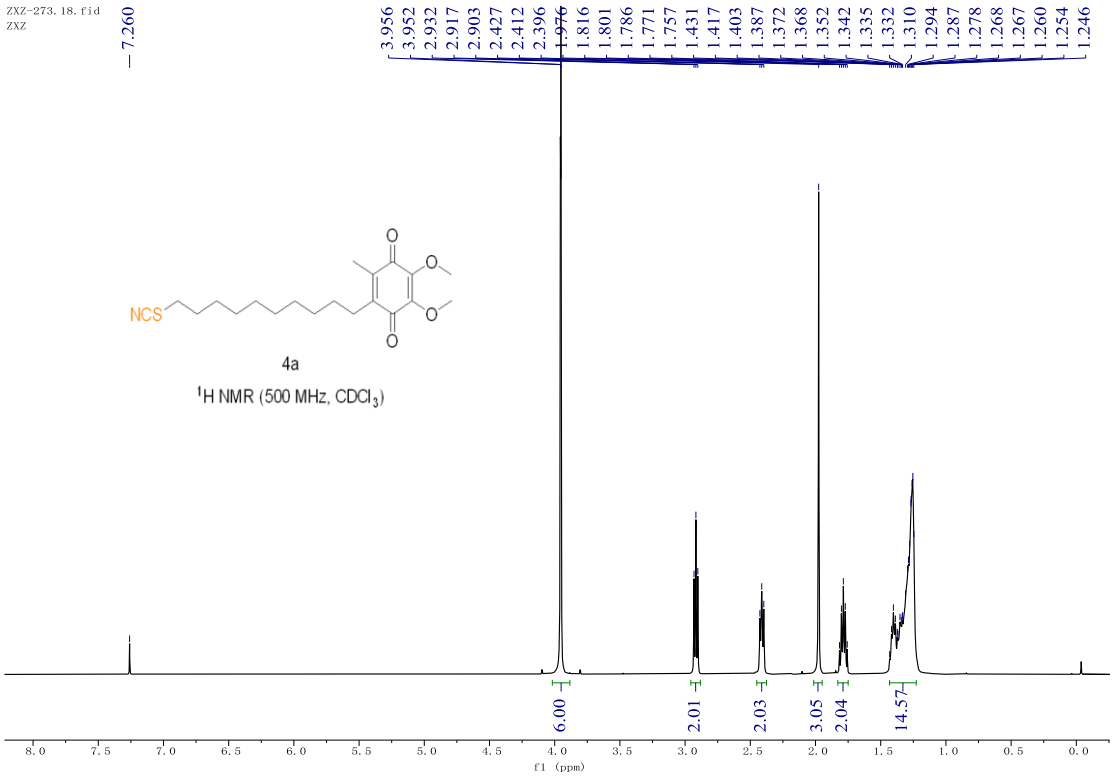
^{1}H NMR of **3am**



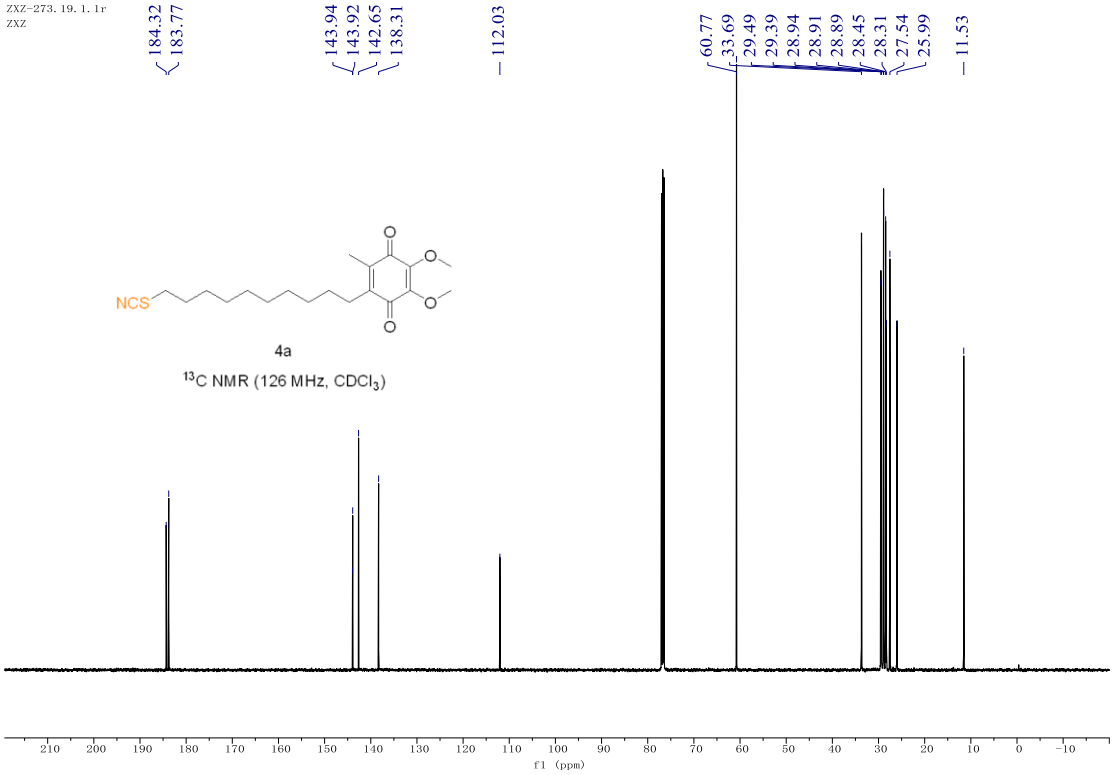
^{13}C NMR of **3am**



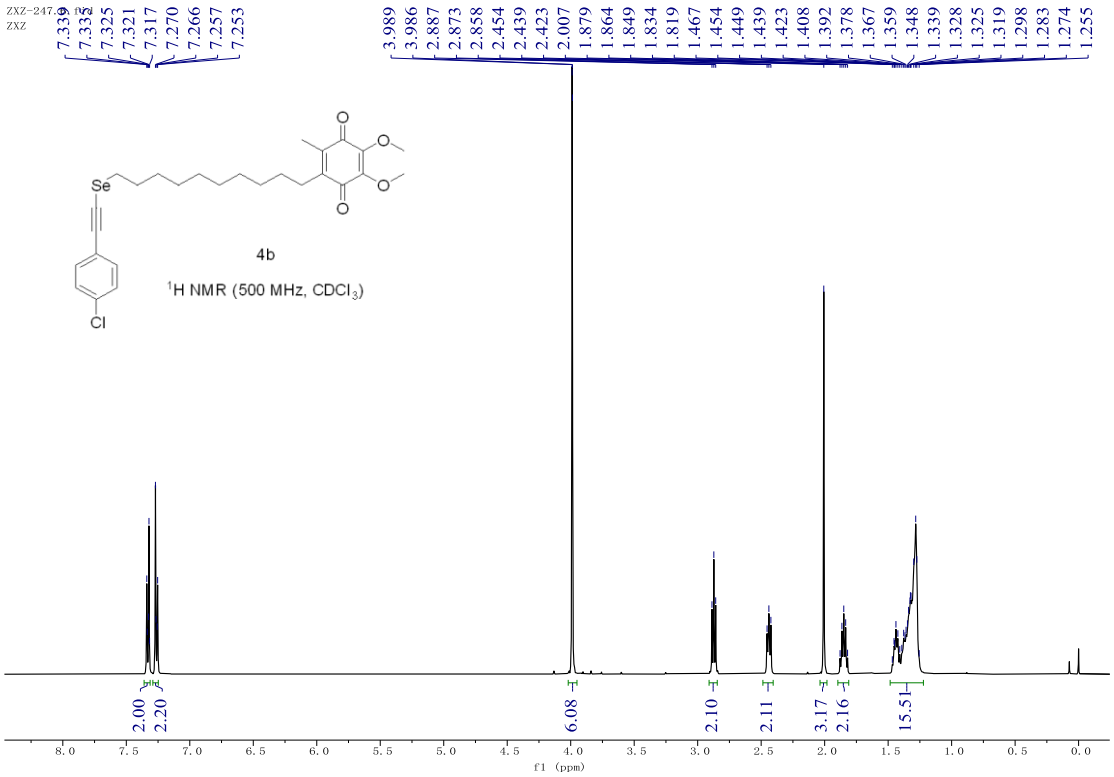
^{1}H NMR of **4a**



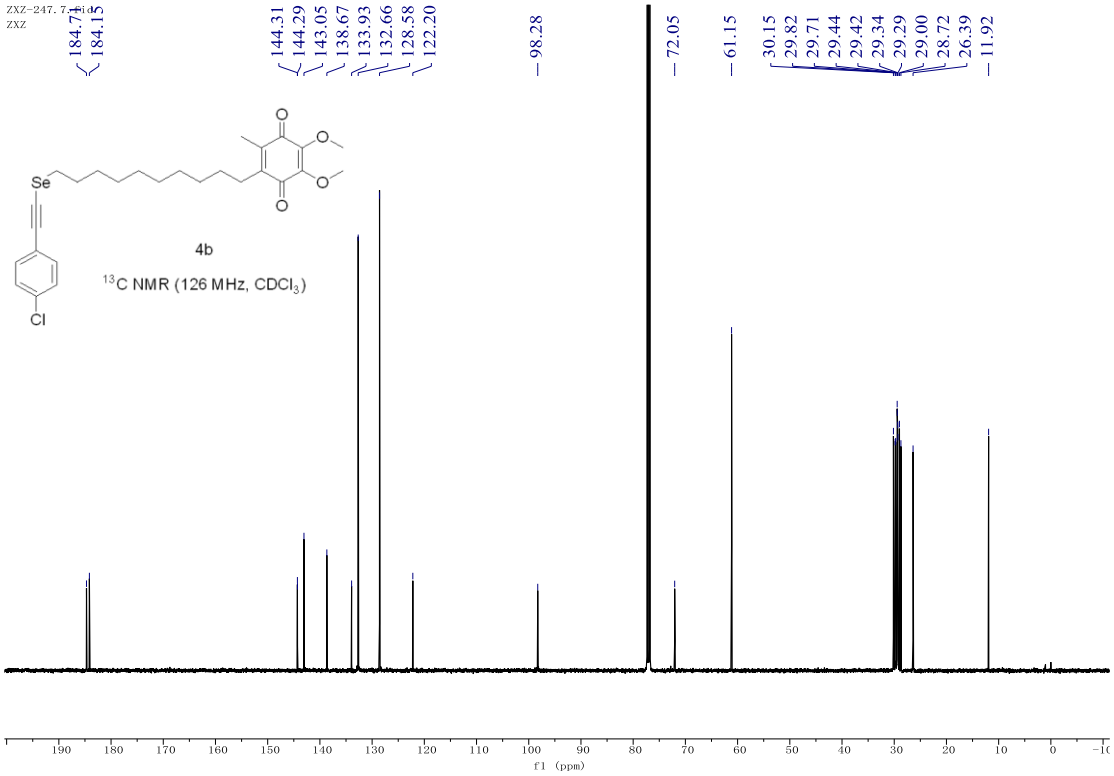
^{13}C NMR of **4a**



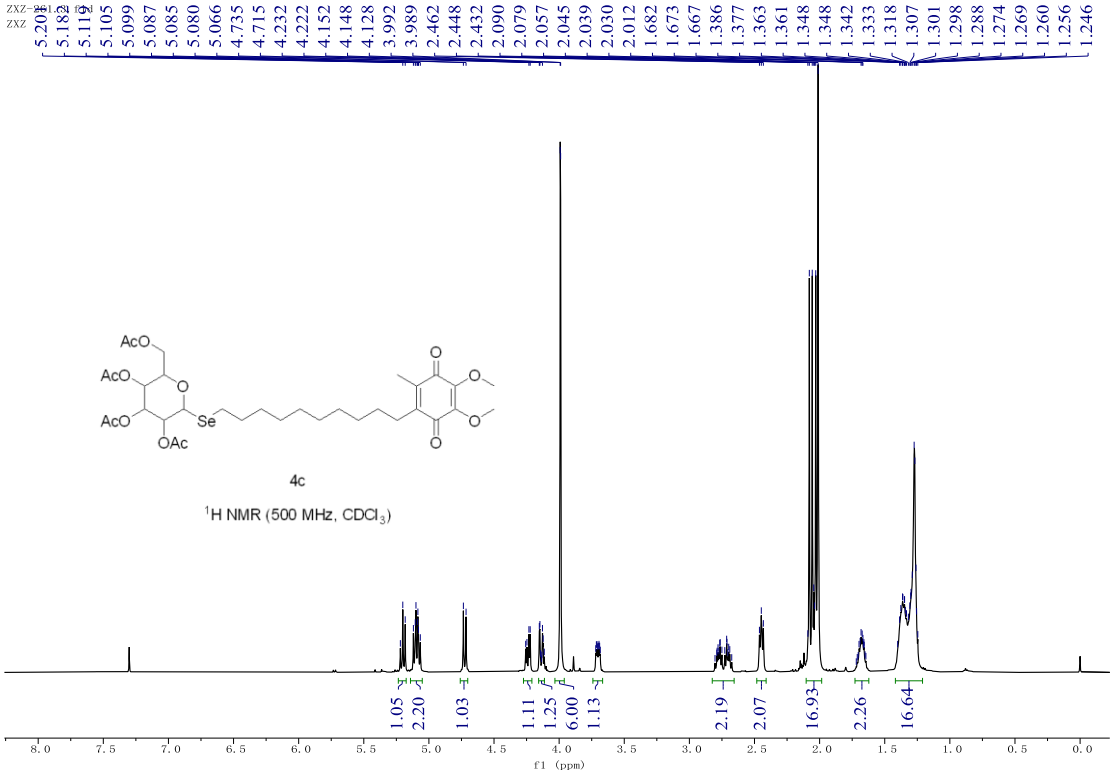
^{1}H NMR of **4b**



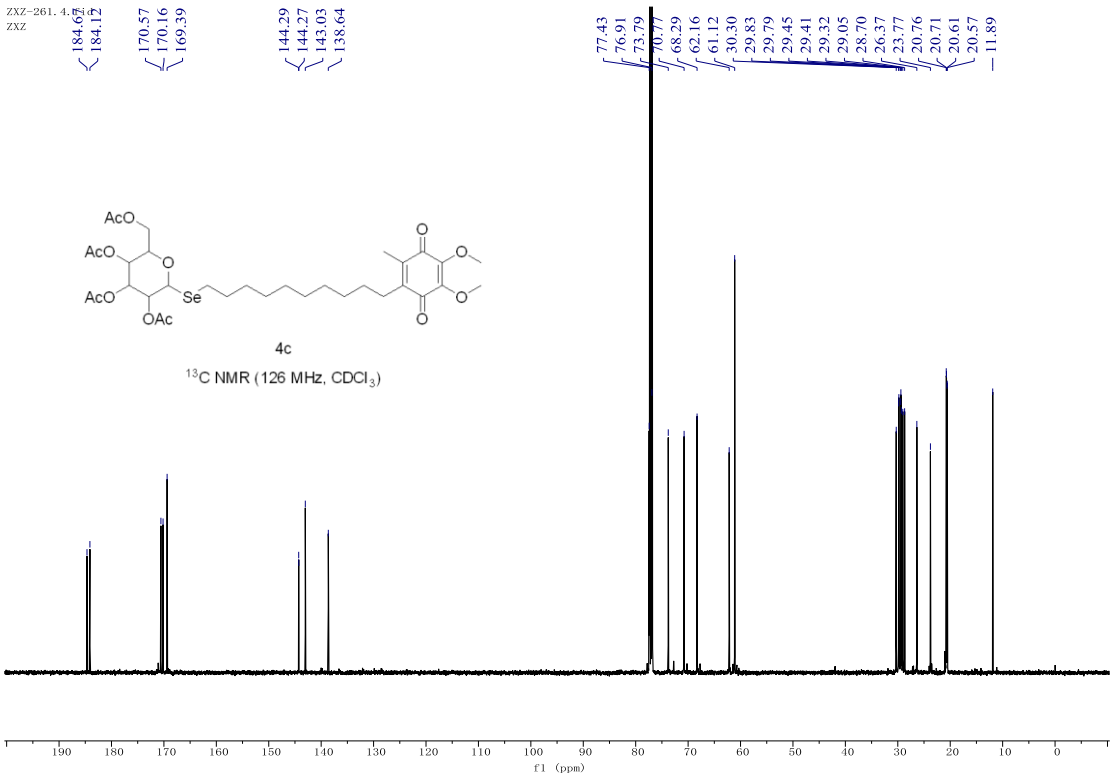
^{13}C NMR of **4b**



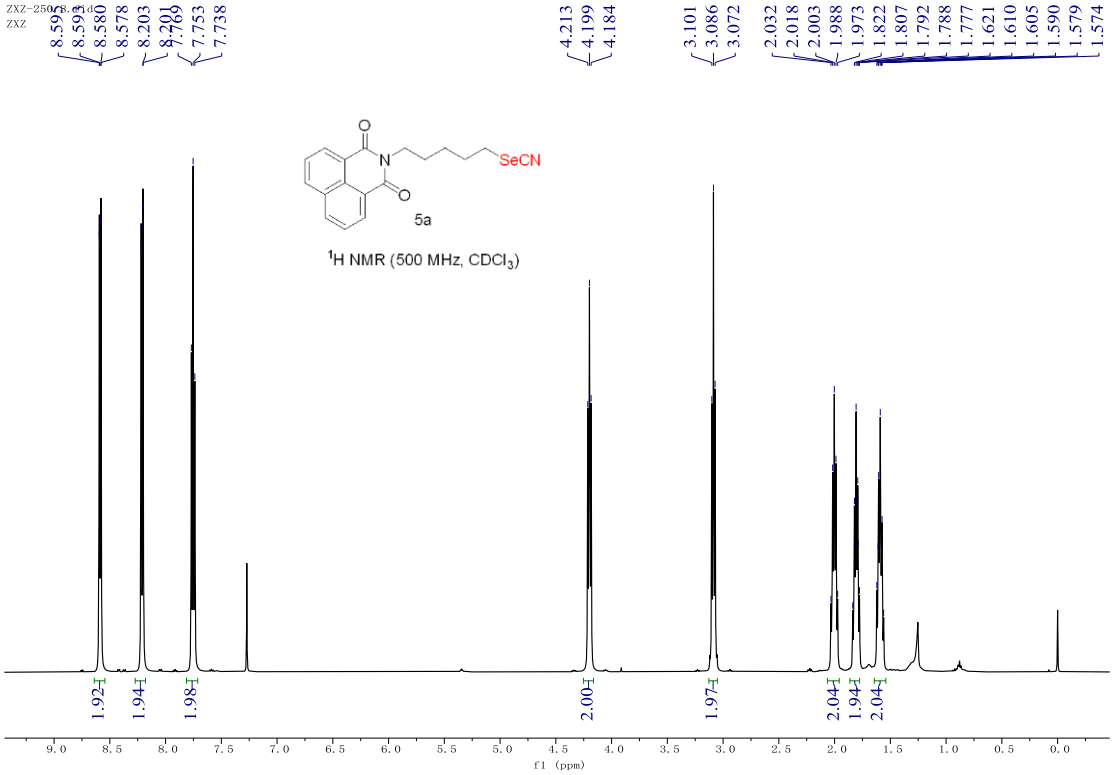
^{1}H NMR of **4c**



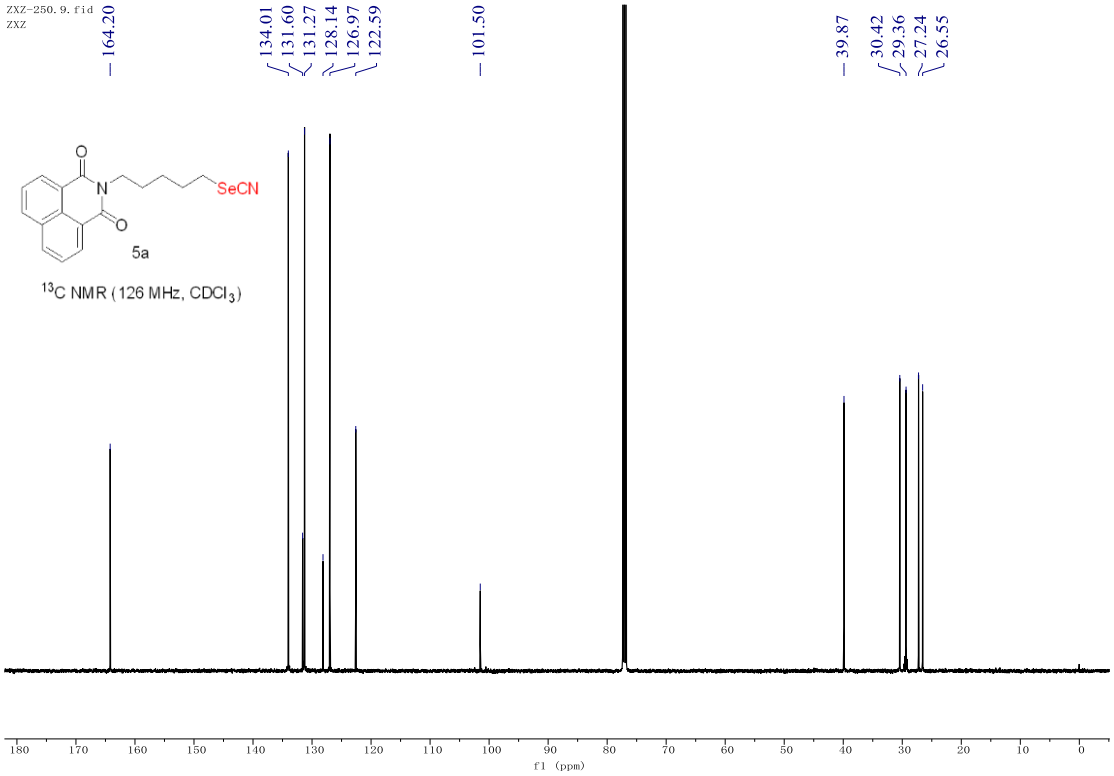
^{13}C NMR of **4c**



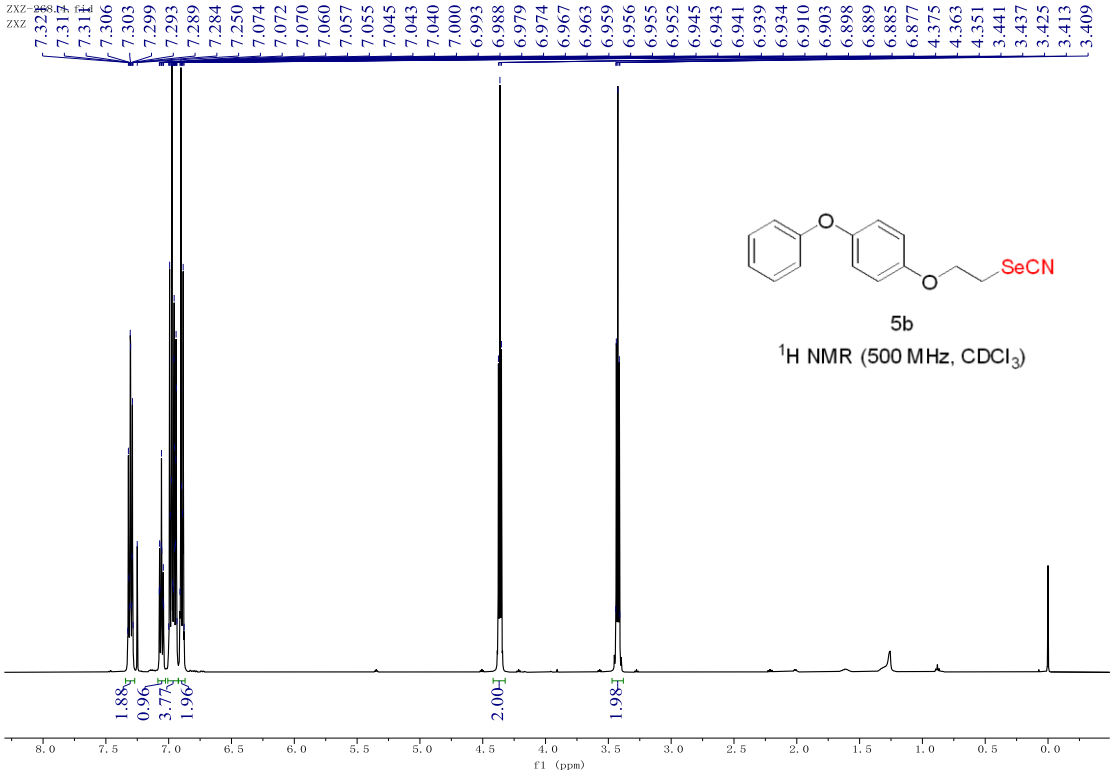
^{1}H NMR of **5a**



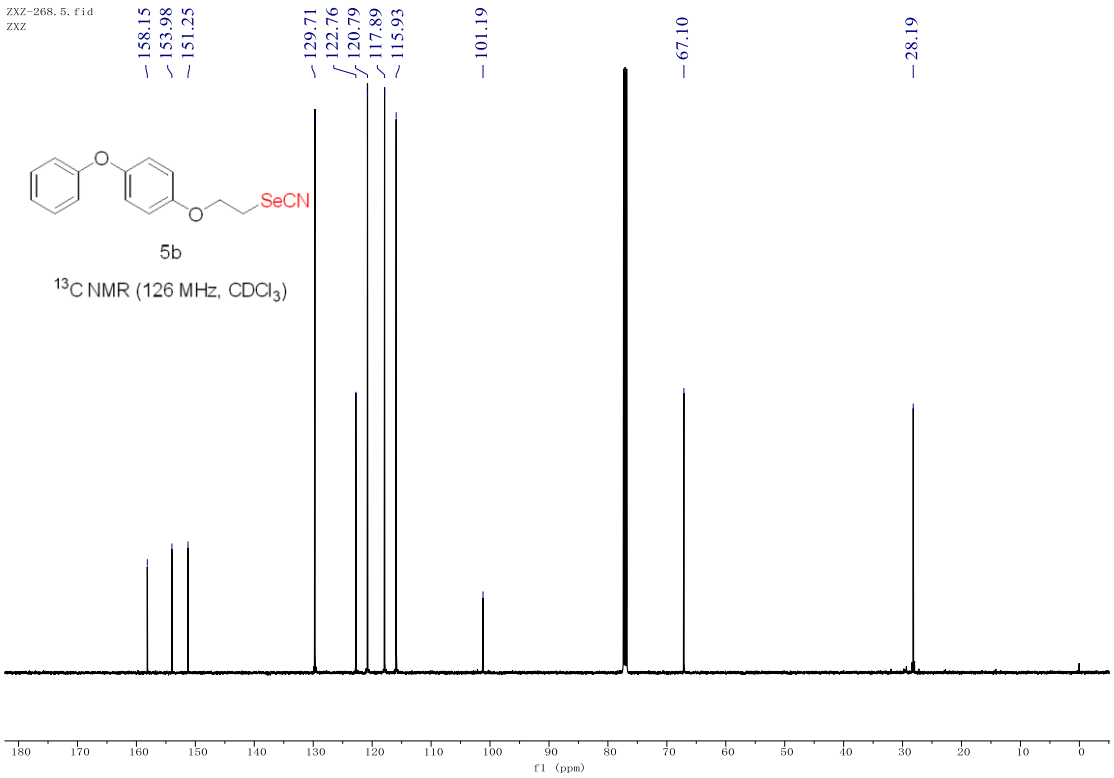
^{13}C NMR of **5a**



^{1}H NMR of **5b**



^{13}C NMR of **5b**


ZXZ-268.5.fid
ZXZ
158.15
153.98
151.25
129.71
122.76
120.79
117.89
115.93
101.19
67.10
28.19
SeCN
5b
13C NMR (126 MHz, CDCl3)
f1 (ppm)

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