

Supporting information for

Radical-mediated Carboselenation of Terminal Alkynes under Mild
Conditions

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Experimental procedures and analytical data

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1. General information

All commercial reagents and available compounds were obtained from Energy Chemical, Sinopharm Chemical Reagent Co., Ltd and TCI, and used without further purification. ^1H and ^{13}C NMR spectra were recorded on Varian 400 MHz NMR spectrometer using CDCl_3 as solvent and TMS as an internal standard. High-resolution mass spectra (HRMS) were recorded on a Bruker solariX FT-ICR mass spectrometer. Reactions were monitored using thin-layer chromatography (TLC) on commercial silica gel plates (GF 254), and were performed under UV light (254 nm). All the new products were further characterized by high resolution mass spectra (ESI-QTOF).

2. General procedure for the synthesis of (E)- γ -Seleno-Substituted Allyl Nitriles

0.2 mmol scale: A 10 mL tube was charged with alkyne **1** (0.20 mmol), azobis **2** (0.12 mmol) and diorganyl diselenides **3** (0.11 mmol) in DCE (1.5 mL), and then the contents were reacted in a sealed tube under air at 80 °C (oil bath) for 18 hours. Upon completion, the solvent was removed to give crude product, which was further purified by flash chromatography on silica gel (petroleum ether (30-60°C)/ethylacetate as eluent) to give the pure product **4** or **5**.

5 mmol scale: A 10 mL tube was charged with alkyne **1a** (5 mmol), AIBN (6 mmol) and PhSeSePh (5.1 mmol) in DCE (5 mL), and then the contents were reacted in a sealed tube under air at 80 °C (oil bath) for 18 hours. Upon completion, the solvent was removed to give crude product, which was further purified by flash chromatography on silica gel (petroleum ether (30-60°C)/ethylacetate = 40:1, v/v) to give the pure product **4a** (0.96g, yield 58%).

3. General procedure for the synthesis of **6**^[1]

A mixture of **4a** (0.2 mmol) and H_2SO_4 (6.0 eq) in MeOH (1 mL) was vigorously stirred at 50 °C (oil bath) for 18 h under an air atmosphere. Then the solvent was evaporated under reduced pressure and 1 mL of water added into the mixture. The aqueous solution was extracted with ethyl acetate (2 mL × 3) and the combined

organic layer was washed with saturated ammonium chloride, dried with anhydrous MgSO₄, filtered, the solvent was removed to give crude product, which was further purified by flash chromatography on silica gel (petroleum ether (30-60°C)/ethylacetate = 40:1, v/v) to give product **6** as a colorless oil (37.4 mg, yield 85%).

4. General procedure for the synthesis of **7**^[2]

A mixture of **4a** (0.2 mmol) and Br₂ (4.0 eq) in DCM (2 mL) was vigorously stirred at 50 °C (oil bath) for 3 h under an air atmosphere. Then the solvent were evaporated under reduced pressure and 1 mL of water added into the mixture. The aqueous solution was extracted with ethyl acetate (2 mL × 3) and the combined organic layer was washed with saturated ammonium chloride, dried with anhydrous MgSO₄, filtered, the solvent was removed to give crude product, which was further purified by flash chromatography on silica gel (petroleum ether (30-60°C)/ethylacetate = 20:1, v/v) to give product **7** as a colorless oil (47.3 mg, yield 95%).

5. Details of control experiment

Radical trapping: A 10 mL tube was charged with 1,1-diphenylethene **8** (0.20 mmol), AIBN (0.12 mmol) and PhSeSePh (0.11 mmol) in DCE (1.5 mL), and then the contents were reacted under air at 80 °C (oil bath) for 18 hours. Upon completion, the solvent was removed to give crude product, which was further purified by flash chromatography on silica gel (petroleum ether (30-60°C)/ethylacetate = 40:1, v/v) to give the pure product **9**.

Deuterium labeling reaction: A 10 mL tube was charged with **1a-D** (0.20 mmol), AIBN (0.12 mmol) and PhSeSePh (0.11 mmol) in DCE (1.5 mL), and then the contents were reacted under air at 80 °C (oil bath) for 18 hours. Upon completion, the solvent was removed to give crude product, which was further purified by flash chromatography on silica gel (petroleum ether (30-60°C)/ethylacetate = 40:1, v/v) to give the pure product **4a-D** (78% yield). ¹H NMR (400 MHz, CDCl₃): δ= 7.48 (d, *J*=

7.2 Hz, 2H), 7.26-7.27 (m, 8H), 1.34 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ = 138.0, 137.3, 135.7, 135.6, 130.0, 129.2, 129.1, 128.5, 128.4, 128.0, 123.1, 33.4, 29.0.

6. X-Ray crystallographic studies

Single crystals of compounds **4o** was grown in DCM at room temperature and the X-ray diffraction studies were carried out on a SMART APEX diffractometer with graphite-monochromated Cu radiation ($\lambda = 1.54184 \text{ \AA}$).

Compound	4o
CCDC number	2144293
Empirical formula	$\text{C}_{24} \text{H}_{21} \text{NSe}$
Formula weight	402.38
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$\text{P}2_1/\text{c}$
a/ \AA	20.1987(11)
b/ \AA	5.8074(4)
c/ \AA	34.9086(14)
$\alpha/^\circ$	90
$\beta/^\circ$	97.666(5)
$\gamma/^\circ$	90
Volume/ \AA^3	4058.2(4)
Z	8
$\rho_{\text{calc}}/\text{cm}^3$	1.317
μ/mm^{-1}	6.092
F(000)	1648
Crystal size/mm ³	0.12 × 0.13 × 0.14
Radiation	Cu K α ($\lambda = 1.54184$)
2 Θ range for data collection/°	3.6350 to 71.868
Index ranges	-23 ≤ h ≤ 24, -4 ≤ k ≤ 7, -42 ≤ l ≤ 29
Reflections collected	7308
Independent reflections	2918 [$\text{R}_{\text{int}} = 0.0708$, $\text{R}_{\text{sigma}} = 0.0877$]
Data/restraints/parameters	3876/34/213
Goodness-of-fit on F ²	1.055
Final R indexes [I>=2σ (I)]	$\text{R}_1 = 0.0303$, $\text{wR}_2 = 0.0372$
Final R indexes [all data]	$\text{R}_1 = 0.1959$, $\text{wR}_2 = 0.2192$
Largest diff. peak/hole / e \AA^{-3}	0.73/-0.99

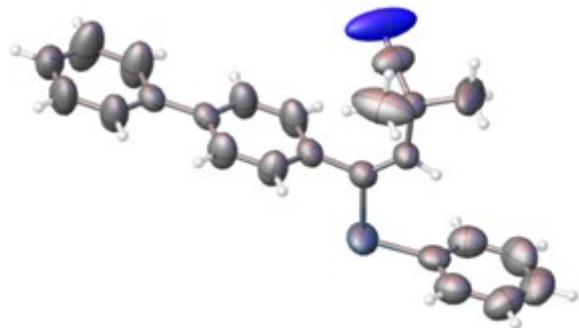
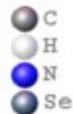
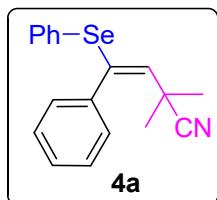


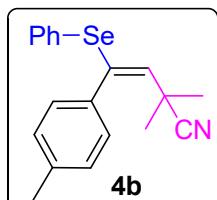
Figure S1. Perspective view of **4o** with thermal ellipsoids at 50% probability level

7. Analytical data



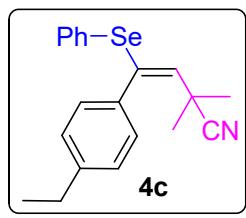
(*E*)-2,2-dimethyl-4-phenyl-4-(phenylselanyl)but-3-enenitrile (**4a**).

Yellow solid, yield 52.0 mg (79%); m.p. 56.2-56.5 °C; TLC (petroleum ether: AcOEt=40:1), R_f = 0.32. ^1H NMR (400 MHz, CDCl_3): δ (ppm) = 7.48 (d, J = 7.6 Hz, 2H), 7.28-7.30 (m, 8H), 5.62 (s, 1H), 1.34 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) = 138.1, 137.3, 135.7, 130.0, 129.3, 129.1, 128.6, 128.5, 128.4, 128.0, 123.3, 33.4, 29.0. IR (ATR): 2237.0, 1623.3, 1575.9, 1066.1, 820.6, 744.4, 690.4 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{18}\text{H}_{17}\text{NSe}$, $[\text{M}+\text{H}]^+$ 328.0599; Found 328.0605.

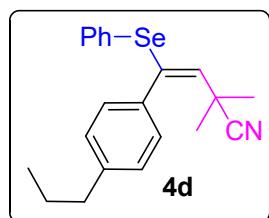


(*E*)-2,2-dimethyl-4-(phenylselanyl)-4-(p-tolyl)but-3-enenitrile (**4b**).

White solid, yield 55.2 mg (81%); m.p. 87.5-88.1 °C; TLC (petroleum ether: AcOEt=30:1), R_f = 0.40. ^1H NMR (400 MHz, CDCl_3): δ (ppm) = 7.49 (d, J = 7.2 Hz, 2H), 7.28 (t, J = 7.6 Hz, 3H), 7.16 (d, J = 7.6 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 5.55 (s, 1H), 2.32 (s, 3H), 1.32 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) = 138.4, 138.3, 135.6, 134.4, 129.8, 129.3, 129.0, 128.8, 128.7, 128.4, 123.3, 33.3, 29.0, 21.4. IR (ATR): 2234.4, 1621.9, 1592.3, 1069.9, 825.0, 760.8, 696.0 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{19}\text{H}_{19}\text{NSe}$, $[\text{M}+\text{H}]^+$ 342.0755; Found 342.0762.

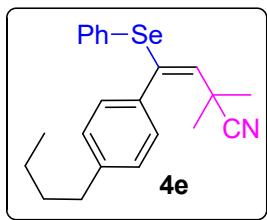


$(\text{E})\text{-4-(4-ethylphenyl)-2,2-dimethyl-4-(phenylselanyl)but-3- enenitrile}$ (**4c**). Colorless oil, yield 56.8 mg (80%); m.p. 45.1-46.0 °C; TLC (petroleum ether: AcOEt=40:1), R_f = 0.35. ^1H NMR (400 MHz, CDCl_3): δ (ppm) = 7.49 (d, J = 6.4 Hz, 2H), 7.24-7.30 (m, 3H), 7.18 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 5.54 (s, 1H), 2.61 (q, J = 7.6 Hz, 2H), 1.31 (s, 6H), 1.21 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) = 144.6, 138.6, 135.6, 134.6, 129.5, 129.3, 129.0, 128.8, 128.5, 127.5, 123.4, 33.3, 28.9, 28.6, 15.4. IR (ATR): 2231.6, 1619.7, 1577.2, 1065.2, 819.2, 744.9, 692.6 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{20}\text{H}_{21}\text{NSe}$, $[\text{M}+\text{H}]^+$ 356.0912; Found 356.0921.

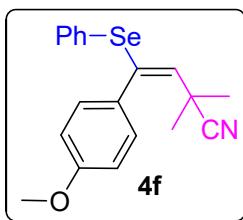


$(\text{E})\text{-2,2-dimethyl-4-(phenylselanyl)-4-(4-propylphenyl)but-3- enenitrile}$ (**4d**). Colorless oil, yield 61.2 mg (83%); TLC (petroleum ether: AcOEt=40:1), R_f = 0.35. ^1H NMR (400 MHz, CDCl_3): δ = 7.47 (d, J = 6.8 Hz, 2H), 7.22-7.29 (m, 3H), 7.16 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 5.56 (s, 1H), 2.55 (t, J = 7.6 Hz, 2H), 1.58-1.63 (m, 2H), 1.31 (s, 6H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ = 143.0, 138.6, 135.7, 134.6, 129.5, 129.2, 129.0, 128.8, 128.4,

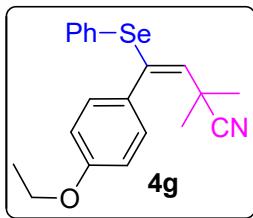
128.1, 123.4, 37.7, 33.4, 28.9, 24.3, 13.7. IR (ATR): 2232.5, 1604.3, 1577.9, 1065.1, 826.2, 738.6, 690.6 cm⁻¹. HRMS (ESI-QTOF) Calcd for C₂₁H₂₃NSe, [M+H]⁺ 370.1068; Found 370.1075.



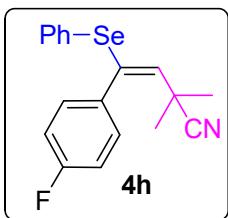
(*E*)-4-(4-butylphenyl)-2,2-dimethyl-4-(phenylselanyl)but-3-enenitrile (**4e**). Colorless oil, yield 46.0 mg (60%); TLC (petroleum ether: AcOEt=40:1), R_f = 0.32. ¹H NMR (400 MHz, CDCl₃): δ= 7.47 (d, J= 6.8 Hz, 2H), 7.23-7.29 (m, 3H), 7.16 (d, J= 6.4 Hz, 2H), 7.08 (d, J= 6.4 Hz, 2H), 5.56 (s, 1H), 2.56-2.59 (m, 2H), 1.55-1.57 (m, 2H), 1.28-1.32 (m, 8H), 0.92 (t, J=7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ= 143.2, 135.7, 134.5, 129.4, 129.2, 129.0, 128.4, 128.0, 123.4, 35.4, 33.4, 33.3, 28.9, 22.2, 14.0. IR (ATR): 2232.5, 1604.4, 1575.9, 1065.5, 820.6, 738.6, 690.5 cm⁻¹. HRMS (ESI-QTOF) Calcd for C₂₂H₂₅NSe, [M+H]⁺ 384.1225; Found 384.1230.



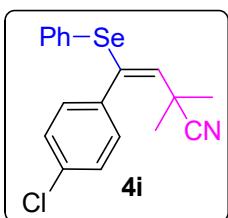
(*E*)-4-(4-methoxyphenyl)-2,2-dimethyl-4-(phenylselanyl)but-3-enenitrile (**4f**). White solid, yield 53.5 mg (75%); m.p. 90.1-90.5 °C; TLC (petroleum ether: AcOEt=20:1), R_f = 0.48. ¹H NMR (400 MHz, CDCl₃): δ= 7.48 (d, J= 6.0 Hz, 2H), 7.26-7.29 (m, 3H), 7.20 (d, J= 8.4 Hz, 2H), 6.81 (d, J= 8.8 Hz, 2H), 5.57 (s, 1H), 3.78 (s, 3H), 1.33 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ= 159.5, 138.3, 135.5, 130.5, 129.9, 129.2, 128.4, 123.0, 113.4, 55.2, 33.3, 29.0. IR (ATR): 2232.0, 1623.8, 1570.4, 1063.9, 815.6, 746.2, 692.8 cm⁻¹. HRMS (ESI-QTOF) Calcd for C₁₉H₁₉NOSe, [M+H]⁺ 358.0705; Found 358.0713.



(E)-4-(4-ethoxyphenyl)-2,2-dimethyl-4-(phenylselanyl)but-3-enenitrile (4g). White solid, yield 53.4 mg (72%); m.p. 74.2-74.8 °C; TLC (petroleum ether: AcOEt=20:1), $R_f = 0.51$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.48$ (d, $J = 6.0$ Hz, 2H), 7.26-7.27 (m, 3H), 7.19 (d, $J = 8.4$ Hz, 2H), 6.90 (d, $J = 6.8$ Hz, 2H), 5.57 (s, 1H), 3.97-4.03 (s, 2H), 1.37-1.40 (m, 3H), 1.33 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 159.0, 138.4, 135.5, 130.5, 129.9, 129.2, 128.4, 123.4, 114.9, 63.3, 33.3, 29.0, 14.8$. IR (ATR): 2233.7, 1623.3, 1576.0, 1046.3, 825.3, 740.3, 690.8 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{20}\text{H}_{21}\text{NOSe}$, $[\text{M}+\text{H}]^+$ 372.0861; Found 372.0864.

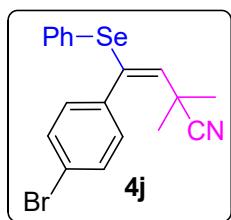


(E)-4-(4-fluorophenyl)-2,2-dimethyl-4-(phenylselanyl)but-3-enenitrile (4h). White solid, yield 42.8 mg (62%); m.p. 83.8-84.5 °C; TLC (petroleum ether: AcOEt=40:1), $R_f = 0.40$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.45$ (d, $J = 7.2$ Hz, 2H), 7.18-7.30 (m, 5H), 6.96 (t, $J = 8.4$ Hz, 2H), 5.65 (s, 1H), 1.35 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 162.5$ (d, $J=250$ Hz), 137.1, 135.7, 133.2, 131.0, 130.9, 130.8, 129.3, 128.6, 128.3, 123.0, 115.0 (d, $J=27$ Hz), 33.3, 29.1; ^{19}F NMR (376 MHz, CDCl_3): $\delta = -112.6$. IR (ATR): 2236.7, 1623.4, 1575.3, 1066.5, 823.0, 747.7, 693.7 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{18}\text{H}_{16}\text{NFSe}$, $[\text{M}+\text{H}]^+$ 346.0505; Found 346.0512.



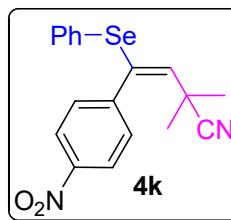
(E)-4-(4-chlorophenyl)-2,2-dimethyl-4-(phenylselanyl)but-3-enenitrile (4i). White solid, yield 53.4 mg (74%); m.p. 103.8-104.5 °C; TLC (petroleum ether:

AcOEt=30:1), $R_f = 0.41$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.44$ (d, $J = 6.8$ Hz, 2H), 7.23-7.30 (m, 5H), 7.15 (d, $J = 8.4$ Hz, 2H), 5.68 (s, 1H), 1.35 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 136.9, 135.8, 135.6, 134.3, 131.1, 130.4, 129.3, 128.7, 128.3, 123.0, 33.3, 29.0$. IR (ATR): 2237.2, 1623.3, 1588.3, 1065.7, 820.6, 742.5, 690.7 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{18}\text{H}_{16}\text{NCISe}$, $[\text{M}+\text{H}]^+$ 362.0209; Found 362.0215.



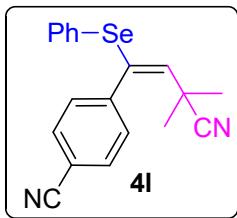
(E) -4-(4-bromophenyl)-2,2-dimethyl-4-(phenylselanyl)but-3-enenitrile (**4j**).

White solid, yield 52.6 mg (65%); m.p. 107.7-108.5 °C; TLC (petroleum ether: AcOEt=40:1), $R_f = 0.42$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.44$ (d, $J = 7.2$ Hz, 2H), 7.39 (d, $J = 8.0$ Hz, 2H), 7.24-7.31 (m, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 5.68 (s, 1H), 1.35 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 136.9, 136.3, 135.6, 131.2, 131.1, 130.7, 129.3, 128.7, 128.2, 123.0, 122.5, 33.3, 29.0$. IR (ATR): 2236.4, 1633.2, 1581.5, 1068.3, 807.2, 745.7, 690.4 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{18}\text{H}_{16}\text{NBrSe}$, $[\text{M}+\text{H}]^+$ 405.9704; Found 405.9709.



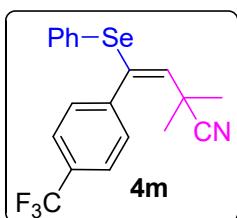
(E) -2,2-dimethyl-4-(4-nitrophenyl)-4-(phenylselanyl)but-3-enenitrile (**4k**).

Yellow solid, yield 46.1 mg (62%); m.p. 144.5-145.6 °C; TLC (petroleum ether: AcOEt=20:1), $R_f = 0.18$. ^1H NMR (400 MHz, CDCl_3): $\delta = 8.09$ (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 7.2$ Hz, 2H), 7.21-7.33 (m, 5H), 5.85 (s, 1H), 1.40 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 147.3, 144.2, 135.7, 135.1, 132.7, 130.0, 129.4, 129.0, 127.5, 123.2, 122.4, 33.5, 29.1$. IR (ATR): 2234.9, 1623.3, 1592.2, 1065.9, 825.1, 742.5, 692.1 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2\text{Se}$, $[\text{M}+\text{H}]^+$ 373.0450; Found 373.0456.

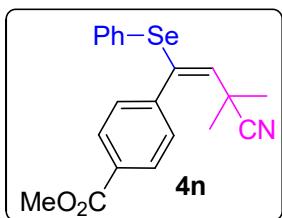


(E)-4-(3-cyano-3-methyl-1-(phenylselanyl)but-1-en-1-yl)benzonitrile (4l).

White solid, yield 38.7 mg (55%); m.p. 130.1-131.4 °C; TLC (petroleum ether: AcOEt=20:1), $R_f = 0.20$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.51$ (d, $J = 8.0$ Hz, 2H), 7.39 (d, $J = 7.2$ Hz, 2H), 7.21-7.30 (m, 5H), 5.80 (s, 1H), 1.38 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 147.3, 142.2, 135.7, 135.6, 132.2, 131.7, 129.8, 128.0, 123.5, 118.5, 112.0, 33.5, 29.1$. IR (ATR): 2227.9, 1623.3, 1547.1, 1066.2, 822.4, 742.0, 690.5 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{19}\text{H}_{16}\text{N}_2\text{Se}$, $[\text{M}+\text{H}]^+$ 353.0551; Found 353.0549.

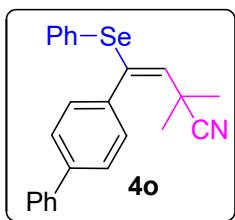


(E)-2,2-dimethyl-4-(phenylselanyl)-4-(trifluoromethyl)phenylbut-3-enenitrile (4m). White solid, yield 48.2 mg (61%); m.p. 72.0-73.0 °C; TLC (petroleum ether: AcOEt=40:1), $R_f = 0.32$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.51$ (d, $J = 7.6$ Hz, 2H), 7.43 (d, $J = 7.6$ Hz, 2H), 7.23-7.32 (m, 5H), 5.75 (s, 1H), 1.35 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 141.1, 136.5, 135.8, 131.5, 129.4, 128.9, 127.9, 124.9$ (q, $J = 3$ Hz), 122.9, 33.4, 29.0; ^{19}F NMR (376 MHz, CDCl_3): $\delta = -62.7$. IR (ATR): 2237.0, 1621.3, 1575.6, 1063.5, 825.8, 739.2, 691.5 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{19}\text{H}_{16}\text{NF}_3\text{Se}$, $[\text{M}+\text{H}]^+$ 396.0473; Found 396.0482.

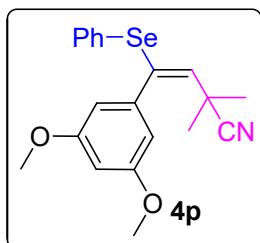


(E)-methyl 4-(3-cyano-3-methyl-1-(phenylselanyl)but-1-en-1-yl)benzoate (4n). White solid, yield 46.2 mg (60%); m.p. 145.1-146.5 °C; TLC (petroleum ether: AcOEt=20:1), $R_f = 0.23$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.92$ (d, $J = 8.0$ Hz, 2H), 7.42 (d, $J = 7.2$ Hz, 2H), 7.22-7.28 (m, 5H), 5.76 (s, 1H), 3.88 (s, 3H),

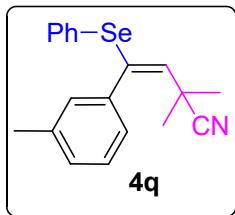
1.35 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ = 166.6, 142.1, 136.8, 135.7, 131.4, 129.3, 129.2, 129.1, 128.7, 122.8, 52.1, 33.5, 29.0. IR (ATR): 2230.8, 1715.3, 1623.5, 1575.9, 1066.1, 818.1, 744.3, 692.8 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{19}\text{H}_{20}\text{NO}_2\text{Se}$, $[\text{M}+\text{H}]^+$ 386.0654; Found 386.0658.



(E)-4-((1,1'-biphenyl)-4-yl)-2,2-dimethyl-4-(phenylselanyl)but-3-enenitrile (4o). Yellow solid, yield 56.4 mg (70%); m.p. 137.4-138.0 °C; TLC (petroleum ether: AcOEt=40:1), R_f = 0.34. ^1H NMR (400 MHz, CDCl_3): δ = 7.59 (d, J = 8.0 Hz, 2H), 7.50-7.54 (m, 4H), 7.43 (t, J =7.6 Hz, 2H), 7.25-7.36 (m, 6H), 5.66 (s, 1H), 1.36 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ = 141.0, 140.3, 138.2, 136.4, 135.7, 130.2, 129.5, 129.3, 128.7, 128.6, 128.5, 127.5, 127.0, 126.6, 123.4, 33.4, 29.0. IR (ATR): 2237.5, 1623.3, 1575.8, 1072.1, 816.5, 735.0, 690.4 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{24}\text{H}_{21}\text{NSE}$, $[\text{M}+\text{H}]^+$ 404.0912; Found 404.0914.



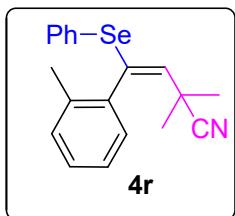
(E)-4-(3,5-dimethoxyphenyl)-2,2-dimethyl-4-(phenylselanyl)but-3-enenitrile (4p). Colorless oil, yield 40.2 mg (52%); TLC (petroleum ether: AcOEt=20:1), R_f = 0.28. ^1H NMR (400 MHz, CDCl_3): δ = 7.51 (d, J = 6.4 Hz, 2H), 7.28-7.30 (m, 3H), 6.42 (s, 2H), 6.36 (s, 1H), 5.55 (s, 1H), 3.74 (s, 6H), 1.33 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ = 160.2, 139.2, 138.5, 135.8, 129.6, 129.3, 128.6, 128.5, 123.6, 107.1, 100.8, 55.4, 33.3, 28.7. IR (ATR): 2237.0, 1623.3, 1588.1, 1062.5, 834.8, 739.9, 690.3 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{20}\text{H}_{21}\text{NO}_2\text{Se}$, $[\text{M}+\text{H}]^+$ 388.0810; Found 388.0817.



(E)-2,2-dimethyl-4-(phenylselanyl)-4-(m-tolyl)but-3-enenitrile (4q).

Colorless oil, yield 54.5 mg (80%); TLC (petroleum ether: AcOEt=30:1), $R_f = 0.35$.

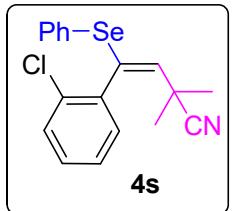
^1H NMR (400 MHz, CDCl_3): $\delta = 7.49$ (d, $J = 6.8$ Hz, 2H), 7.27-7.31 (m, 3H), 7.17 (t, $J = 7.6$ Hz, 1H), 7.07-7.08 (m, 3H), 5.53 (s, 1H), 2.30 (s, 3H), 1.32 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 138.4, 137.6, 137.2, 135.7, 129.7, 129.5, 129.2, 129.1, 128.7, 128.5, 127.8, 126.2, 123.3, 33.4, 29.0, 21.4$. IR (ATR): 2232.3, 1623.3, 1578.0, 1065.2, 822.2, 738.9, 690.5 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{19}\text{H}_{19}\text{NSe}$, $[\text{M}+\text{H}]^+$ 342.0755; Found 342.0760.



(E)-2,2-dimethyl-4-(phenylselanyl)-4-(o-tolyl)but-3-enenitrile (4r).

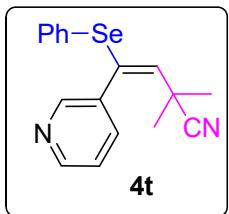
Colorless oil, yield 53.2 mg (78%); TLC (petroleum ether: AcOEt=30:1), $R_f = 0.36$.

^1H NMR (400 MHz, CDCl_3): $\delta = 7.48$ (d, $J = 7.2$ Hz, 2H), 7.32 (t, $J = 6.8$ Hz, 1H), 7.26 (t, $J = 7.2$ Hz, 2H), 7.19 (t, $J = 7.2$ Hz, 2H), 7.07 (t, $J = 7.2$ Hz, 1H), 6.97 (d, $J = 7.2$ Hz, 1H), 5.50 (s, 1H), 2.37 (s, 3H), 1.31 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 137.7, 136.4, 136.2, 135.9, 130.2, 129.4, 129.2, 128.8, 128.7, 128.6, 128.1, 125.2, 122.5, 33.8, 28.7, 28.3, 19.8$. IR (ATR): 2233.1, 1623.3, 1577.5, 1065.1, 820.6, 739.5, 690.6 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{19}\text{H}_{19}\text{NSe}$, $[\text{M}+\text{H}]^+$ 342.0755; Found 342.0764.

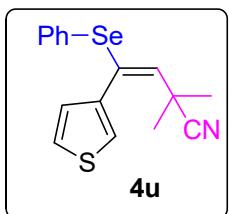


(E)-4-(2-chlorophenyl)-2,2-dimethyl-4-(phenylselanyl)but-3-

enenitrile (4r). Yellow oil, yield 48.3 mg (67%); TLC (petroleum ether: AcOEt=40:1), $R_f = 0.30$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.49$ (d, $J = 7.6$ Hz, 2H), 7.19-7.35 (m, 5H), 7.11 (t, $J = 7.6$ Hz, 1H), 7.02 (t, $J = 7.2$ Hz, 1H), 5.72 (s, 1H), 1.39 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 136.2, 135.7, 133.7, 133.1, 132.0, 130.8, 129.8, 129.5, 129.1, 128.8, 128.0, 126.1, 122.4, 34.1, 29.0, 27.5$. IR (ATR): 2236.0, 1623.3, 1577.5, 1055.2, 820.6, 739.5, 690.4 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{18}\text{H}_{16}\text{NClSe}$, $[\text{M}+\text{H}]^+$ 362.0209; Found 362.0211.

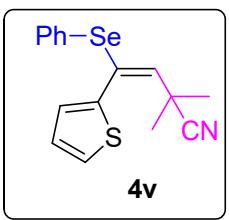


(*E*)-2,2-dimethyl-4-(phenylselanyl)-4-(pyridin-3-yl)but-3-enenitrile (**4t**). Yellow solid, yield 39.3 mg (60%); m.p. 80.1-81.2 °C; TLC (petroleum ether: AcOEt=4:1), $R_f = 0.46$. ^1H NMR (400 MHz, CDCl_3): $\delta = 8.45$ (d, $J = 3.2$ Hz, 1H), 8.38 (s, 1H), 7.52 (d, $J = 7.6$ Hz, 1H), 7.42 (t, $J = 6.8$ Hz, 2H), 7.17-7.29 (m, 3H), 5.82 (s, 1H), 1.40 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 149.3, 149.2, 136.5, 135.7, 133.7, 133.4, 132.9, 129.4, 128.8, 127.7, 122.8, 122.6, 33.6, 29.2$. IR (ATR): 2232.5, 1623.3, 1578.2, 1064.2, 820.6, 743.5, 691.0 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{Se}$, $[\text{M}+\text{H}]^+$ 329.0551; Found 329.0559.

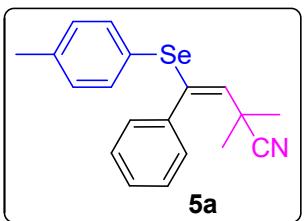


(*E*)-2,2-dimethyl-4-(phenylselanyl)-4-(thiophen-3-yl)but-3-enenitrile (**4u**). Yellow oil, yield 46.6 mg (70%); TLC (petroleum ether: AcOEt=40:1), $R_f = 0.21$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.45$ (d, $J = 6.8$ Hz, 1H), 7.24-7.29 (m, 4H), 7.15 (s, 1H), 7.04 (t, $J = 4.8$ Hz, 1H), 5.69 (s, 1H), 1.37 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 137.1, 135.3, 132.8, 131.9, 129.2, 128.7, 128.4, 128.3, 125.5, 125.2, 123.2, 33.3, 28.9$. IR (ATR): 2232.7, 1623.3, 1577.6, 1065.5, 840.5, 737.2, 689.9 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{16}\text{H}_{15}\text{NSSe}$, $[\text{M}+\text{H}]^+$ 334.0163;

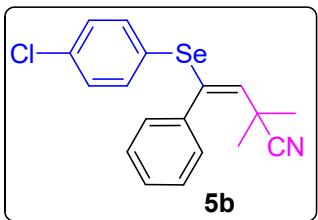
Found 334.0170.



(E)-2,2-dimethyl-4-(phenylselanyl)-4-(thiophen-2-yl)but-3-enenitrile (**4v**). Yellow solid, yield 43.9 mg (66%); m.p. 64.5-65.1 °C; TLC (petroleum ether: AcOEt=40:1), $R_f = 0.25$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.49$ (d, $J=7.2$ Hz, 2H), 7.27-7.34 (m, 4H), 7.04 (d, $J=3.2$ Hz, 1H), 6.93 (t, $J=4.0$ Hz, 1H), 5.74 (s, 1H), 1.44 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 138.4$, 135.0, 133.6, 129.9, 129.3, 129.2, 129.1, 128.4, 127.3, 126.8, 122.7, 33.6, 29.0. IR (ATR): 2231.2, 1623.3, 1577.6, 1066.1, 820.6, 738.2, 688.1 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{16}\text{H}_{15}\text{NSSe}$, $[\text{M}+\text{H}]^+$ 334.0163; Found 334.0177.

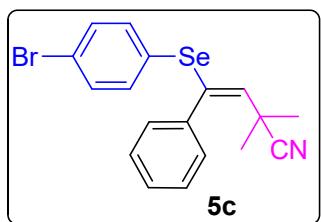


(E)-2,2-dimethyl-4-phenyl-4-(p-tolylselanyl)but-3-enenitrile (**5a**). Yellow solid, yield 55.9 mg (82%); m.p. 58.1-58.5 °C; TLC (petroleum ether: AcOEt=40:1), $R_f = 0.34$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.38$ (d, $J=6.8$ Hz, 2H), 7.28-7.29 (m, 5H), 7.08 (d, $J=7.6$ Hz, 2H), 5.51 (s, 1H), 2.34 (s, 3H), 1.34 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 138.8$, 138.5, 137.4, 135.9, 130.1, 129.1, 129.0, 128.4, 128.0, 124.9, 123.2, 33.4, 29.0, 21.1. IR (ATR): 2237.2, 1623.3, 1577.2, 1063.1, 815.5, 746.8, 692.4 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{19}\text{H}_{19}\text{NSe}$, $[\text{M}+\text{H}]^+$ 342.0755; Found 342.0762.

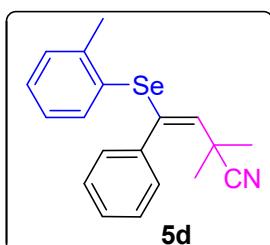


(E)-4-((4-chlorophenyl)selanyl)-2,2-dimethyl-4-phenylbut-3-enenitrile (**5b**). Yellow solid, yield 51.2 mg (71%); m.p. 62.0-63.0 °C; TLC

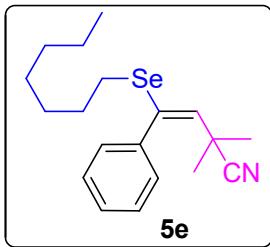
(petroleum ether: AcOEt=40:1), $R_f = 0.35$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.36$ (d, $J = 8.4$ Hz, 2H), 7.19-7.28 (m, 7H), 5.69 (s, 1H), 1.36 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 137.8, 137.0, 136.9, 134.9, 130.7, 129.4, 129.1, 128.6, 128.1, 126.7, 123.0, 33.4, 29.0$. IR (ATR): 2235.6, 1622.3, 1575.9, 1069.0, 821.5, 729.2, 695.0 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{18}\text{H}_{16}\text{NCISe}$, $[\text{M}+\text{H}]^+$ 362.0209; Found 362.0214.



(E)-4-((4-bromophenyl)selanyl)-2,2-dimethyl-4-phenylbut-3-enenitrile (5c). Yellow solid, yield 56.5 mg (70%); m.p. 67.0-67.5 °C; TLC (petroleum ether: AcOEt=40:1), $R_f = 0.32$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.35$ (d, $J = 8.4$ Hz, 3H), 7.28-7.30 (m, 5H), 7.22 (d, $J = 2.4$ Hz, 1H), 5.69 (s, 1H), 1.36 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 137.6, 137.1, 132.3, 130.9, 129.1, 128.6, 128.2, 128.1, 127.4, 123.1, 122.9, 33.5, 29.0$. IR (ATR): 2235.2, 1622.4, 1593.7, 1070.9, 817.9, 759.4, 694.2 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{18}\text{H}_{16}\text{NBrSe}$, $[\text{M}+\text{H}]^+$ 405.9704; Found 405.9709.

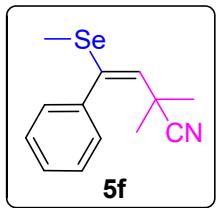


(E)-2,2-dimethyl-4-phenyl-4-(o-tolylselanyl)but-3-enenitrile (5d). Colorless oil, yield 51.8 mg (76%); TLC (petroleum ether: AcOEt=40:1), $R_f = 0.35$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.56$ (d, $J = 7.6$ Hz, 1H), 7.26-7.30 (m, 7H), 7.11 (s, 1H), 5.31 (s, 1H), 2.49 (s, 3H), 1.31 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 142.2, 137.4, 137.3, 130.4, 129.5, 129.3, 128.9, 128.5, 128.0, 126.8, 123.2, 33.4, 29.0, 22.6$. IR (ATR): 2232.0, 1623.3, 1592.8, 1072.0, 820.6, 748.7, 696.3 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{19}\text{H}_{19}\text{NSe}$, $[\text{M}+\text{H}]^+$ 342.0755; Found 342.0763.



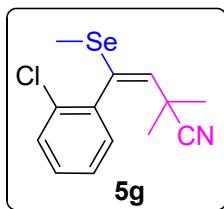
(E)-4-(heptylselanyl)-2,2-dimethyl-4-phenylbut-3-enenitrile

(5e). Colorless oil, yield 25.8 mg (76%); TLC (petroleum ether: AcOEt=40:1), $R_f = 0.41$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.30\text{-}7.38$ (m, 5H), 5.78 (s, 1H), 2.41 (t, $J=7.6$ Hz, 2H), 1.55-1.57 (m, 2H), 1.38 (s, 6H), 1.22-1.28 (m, 10H), 0.85-0.88 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 137.6, 129.8, 129.1, 128.4, 128.1, 123.3, 33.4, 31.6, 30.0, 29.8, 29.2, 28.7, 26.5, 22.6, 14.1$. IR (ATR): 2232.8, 1623.3, 1575.9, 1072.2, 820.6, 764.4, 697.1 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{19}\text{H}_{27}\text{NSe}$, $[\text{M}+\text{H}]^+$ 350.1381; Found 350.1388.



(E)-2,2-dimethyl-4-(methylselanyl)-4-phenylbut-3-enenitrile.

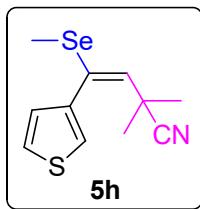
Colorless oil, yield 25.8 mg (65%); TLC (petroleum ether: AcOEt=40:1), $R_f = 0.36$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.30\text{-}7.39$ (m, 5H), 5.61 (s, 1H), 1.94 (s, 3H), 1.39 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 136.9, 129.0, 128.5, 128.2, 127.6, 127.1, 123.3, 33.4, 29.2, 7.0$. IR (ATR): 2231.7, 1623.3, 1575.9, 1072.3, 820.6, 761.9, 696.2 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{13}\text{H}_{15}\text{NSe}$, $[\text{M}+\text{H}]^+$ 266.0442; Found 266.0447.



(E)-2,2-dimethyl-4-(methylselanyl)-4-phenylbut-3-enenitrile.

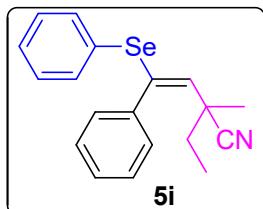
Colorless oil, yield 34.7 mg (58%); TLC (petroleum ether: AcOEt=40:1), $R_f = 0.31$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.41$ (d, $J=3.6$ Hz, 1H), 7.26-7.31 (m, 3H), 5.70 (s, 1H), 1.96 (s, 3H), 1.43 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 135.6, 133.2, 131.8, 130.9, 129.9, 129.7, 126.5, 123.5, 34.0, 29.2, 27.7, 6.7$. IR (ATR):

2234.2, 1623.3, 1587.8, 1055.4, 852.8, 745.1, 690.9 cm⁻¹. HRMS (ESI-QTOF) Calcd for C₁₃H₁₄NClSe, [M+H]⁺ 300.0053; Found 300.0058.



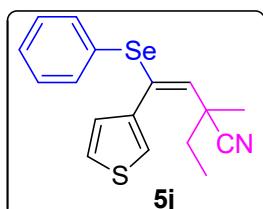
(E)-2,2-dimethyl-4-(methylselanyl)-4-(thiophen-3-yl)but-3-enenitrile

(5h). Yellow oil, yield 37.9 mg (70%); TLC (petroleum ether: AcOEt=40:1), R_f = 0.31. ¹H NMR (400 MHz, CDCl₃): δ= 7.36 (d, J=2.0 Hz, 1H), 7.29 (s, 1H), 7.08 (d, J=4.8 Hz, 1H), 5.64 (s, 1H), 1.95 (s, 3H), 1.41 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ= 137.1, 131.7, 129.2, 128.4, 125.6, 125.0, 123.4, 33.3, 29.0, 7.0. IR (ATR): 2231.1, 1618.1, 1575.9, 1077.8, 842.7, 767.8, 696.6 cm⁻¹. HRMS (ESI-QTOF) Calcd for C₁₁H₁₃NSSe, [M+H]⁺ 272.0007; Found 272.0009.



(E)-2-ethyl-2-methyl-4-phenyl-4-(phenylselanyl)but-3-enenitrile

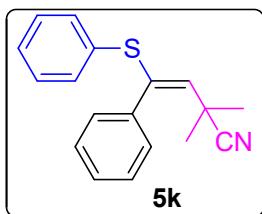
(5i). Yellow solid, yield 51.2 mg (75%); m.p. 60.0-60.8 °C; TLC (petroleum ether: AcOEt=40:1), R_f = 0.32. ¹H NMR (400 MHz, CDCl₃): δ= 7.49 (d, J= 7.2 Hz, 2H), 7.25-7.28 (m, 8H), 5.47 (s, 1H), 1.59 (q, J=6.8 Hz, 2H), 1.31 (s, 6H), 0.98 (t, J=7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ= 138.0, 137.3, 135.8, 129.3, 129.1, 128.6, 127.9, 122.0, 38.8, 35.0, 26.6, 9.5. IR (ATR): 2232.5, 1624.5, 1575.9, 1064.8, 823.6, 745.3, 690.7 cm⁻¹. HRMS (ESI-QTOF) Calcd for C₁₉H₁₉NSe, [M+H]⁺ 342.0755; Found 342.0763.



(E)-2-ethyl-2-methyl-4-(phenylselanyl)-4-(thiophen-3-yl)but-3-

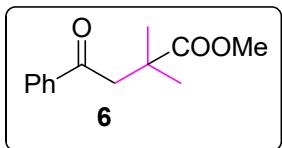
enenitrile (5j). White solid, yield 47.2 mg (68%); m.p. 48.5-49.0 °C; TLC

(petroleum ether: AcOEt=40:1), $R_f = 0.30$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.47$ (d, $J=7.2$ Hz, 2H), 7.25-7.30 (m, 4H), 7.12 (s, 1H), 7.03 (d, $J=4.8$ Hz, 1H), 5.57 (s, 1H), 1.62 (q, $J=7.2$ Hz, 2H), 1.34 (s, 6H), 0.99 (t, $J=7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 137.1, 135.4, 132.6, 131.3, 129.2, 128.8, 128.5, 128.4, 125.4, 125.2, 122.0, 38.8, 34.9, 26.5, 9.5$. IR (ATR): 2234.2, 1623.3, 1574.5, 1067.1, 841.9, 760.8, 687.3 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{17}\text{H}_{17}\text{NSSe}$, $[\text{M}+\text{H}]^+$ 348.0320; Found 348.0326.

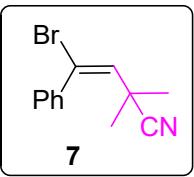


(E)-2,2-dimethyl-4-phenyl-4-(phenylthio)but-3-enenitrile (5k).

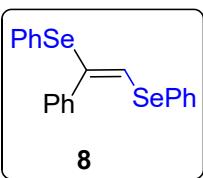
Yellow solid, yield 36.3 mg (65%); m.p. 37.5-38.0 °C; TLC (petroleum ether: AcOEt=40:1), $R_f = 0.30$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.20\text{-}7.37$ (m, 10H), 5.53 (s, 1H), 1.36 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 136.1, 135.7, 133.8, 132.1, 130.5, 129.6, 129.1, 128.7, 128.4, 128.0, 123.2, 32.7, 29.2$. IR (ATR): 2236.5, 1625.3, 1581.1, 1072.4, 841.5, 743.5, 690.2 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{18}\text{H}_{17}\text{NS}$, $[\text{M}+\text{H}]^+$ 280.1154; Found 280.1161.



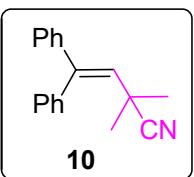
methyl 2,2-dimethyl-4-oxo-4-phenylbutanoate (6). White solid, yield 37.4 mg (85%); m.p. 46.0-47.0 °C; TLC (petroleum ether: AcOEt=20:1), $R_f = 0.42$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.94$ (d, $J=7.6$ Hz, 2H), 7.56 (t, $J=7.2$ Hz, 1H), 7.45 (t, $J=7.6$ Hz, 2H), 3.67 (s, 3H), 3.30 (s, 2H), 1.32 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 197.6, 177.9, 136.9, 133.1, 128.6, 127.9, 52.0, 48.6, 40.0, 25.8$. IR (ATR): 1727.2, 1679.8, 1580.3, 1076.4, 818.8, 759.5, 688.3 cm^{-1} . Spectral data were in accordance with the literature.^[3]



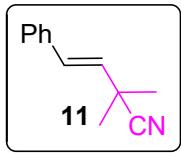
(E)-4-bromo-2,2-dimethyl-4-phenylbut-3-enenitrile (7). Colorless oil, yield 47.3 mg (95%); TLC (petroleum ether: AcOEt=40:1), $R_f = 0.28$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.50$ (d, $J=4.0$ Hz, 2H), 7.35-7.36 (m, 3H), 6.08 (s, 1H), 1.69 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 139.7, 130.5, 129.3, 128.7, 128.4, 127.6, 124.6, 33.4, 27.7$. IR (ATR): 2234.8, 1621.7, 1575.9, 1076.5, 822.1, 758.8, 692.1 cm^{-1} . HRMS (ESI-QTOF) Calcd for $\text{C}_{12}\text{H}_{12}\text{NBr}$, $[\text{M}+\text{H}]^+$ 250.0226; Found 250.0235.



(E)-(1-phenylethene-1,2-diyl)bis(phenylselane) (8). Colorless oil, yield 28.2 mg (34%); TLC (petroleum ether: AcOEt=40:1), $R_f = 0.79$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.44$ -7.50 (m, 6H), 7.22-7.35 (m, 9H), 9.09 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 139.6, 133.1, 132.1, 129.3, 128.7, 128.3, 127.5, 127.4, 126.0$. IR (ATR): 1623.7, 1576.9, 1073.5, 824.5, 758.6, 692.5 cm^{-1} . Spectral data were in accordance with the literature.^[4]



2,2-dimethyl-4,4-diphenylbut-3-enenitrile (10). Colorless oil, yield 13.4 mg (27%); TLC (petroleum ether: AcOEt=40:1), $R_f = 0.33$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.42$ (d, $J=6.4$ Hz, 2H), 7.22-7.31 (m, 8H), 5.86 (s, 1H), 1.49 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 130.0, 128.9, 128.3, 128.1, 127.9, 127.2, 126.0, 32.4, 29.5$. IR (ATR): 2235.0, 1623.1, 1575.2, 1074.4, 776.7, 734.9, 695.5 cm^{-1} . Spectral data were in accordance with the literature.^[5]



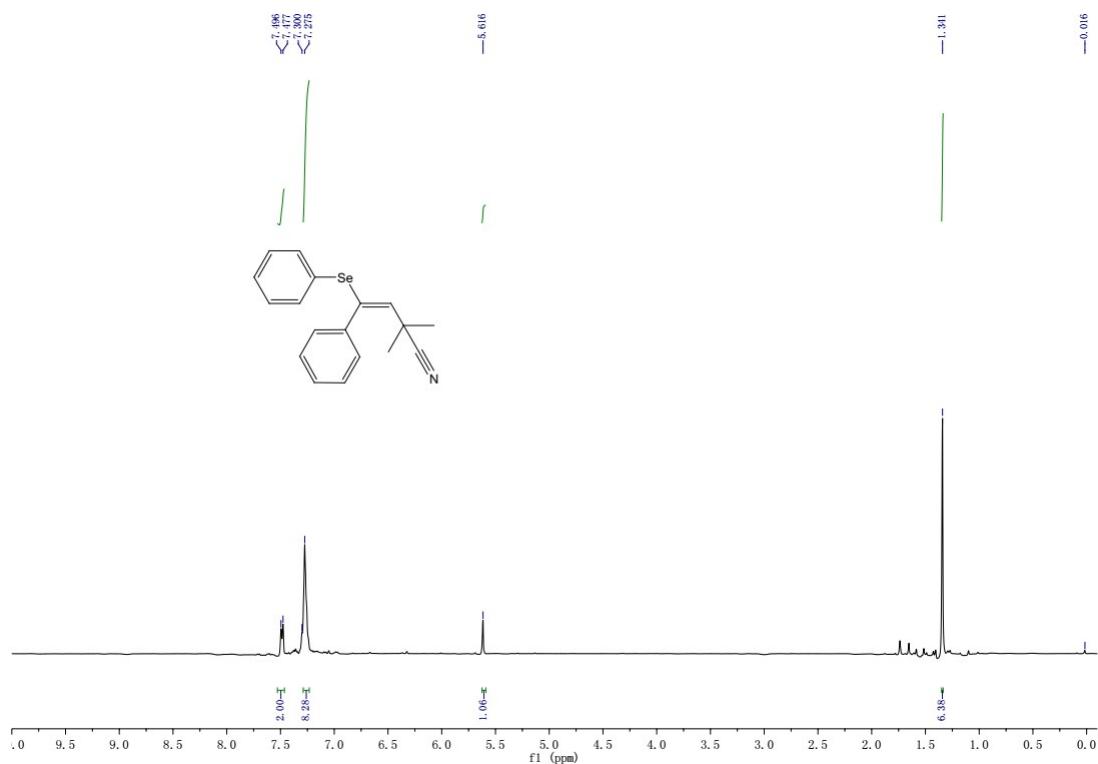
(*E*)-2,2-dimethyl-4-phenylbut-3-enenitrile (**11**). Yellow oil; TLC (petroleum ether: AcOEt=40:1), $R_f = 0.23$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.26\text{--}7.41$ (m, 5H), 6.76 (d, $J=16.0$ Hz, 1H), 6.04 (d, $J=16.0$ Hz, 1H), 1.55 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 135.7$, 130.4, 129.8, 128.7, 128.2, 126.6, 123.5, 35.0, 27.7. IR (ATR): 2235.5, 1599.2, 1073.7, 748.4, 692.4 cm^{-1} . Spectral data were in accordance with the literature.^[6]

8. References

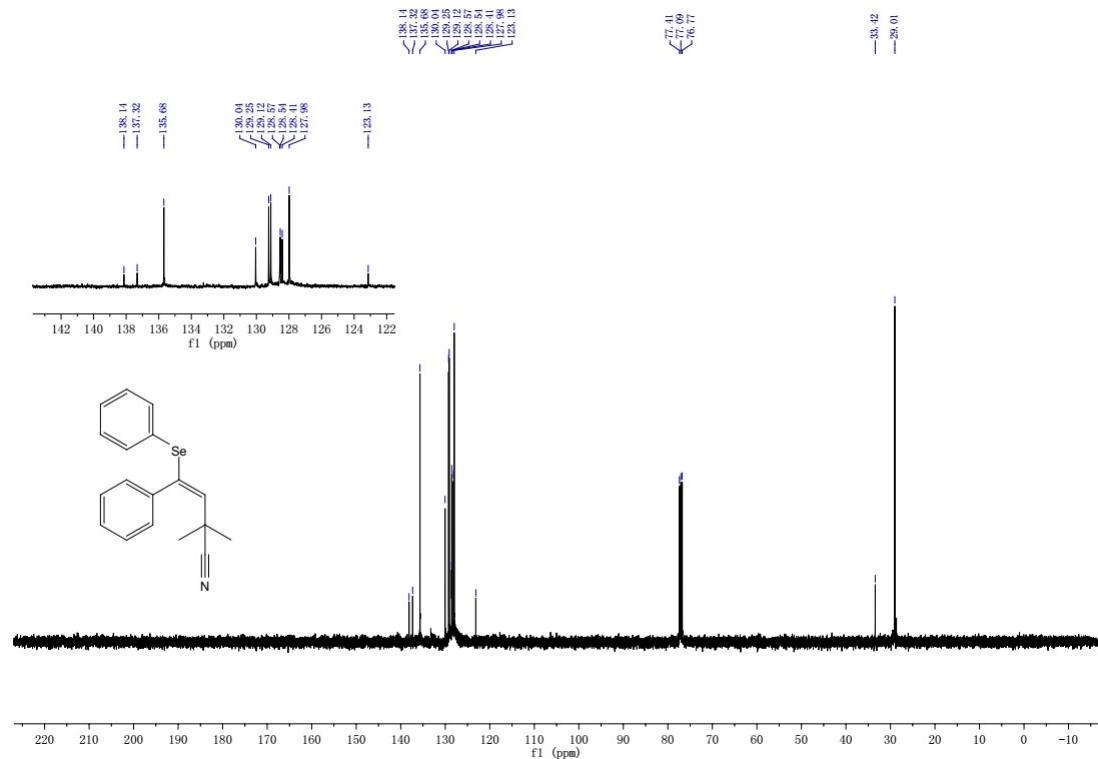
- (1) Xuyang Yan, Hongchi Liu, Shenquan Wei, Hanmin Huang, *Org. Lett.*, **2020**, 22, 6794-6798.
- (2) Jean C. Kazmierczak, Ana M. S. Recchi, Fabiane Gritzenco, Everton B. Balbom, Thiago Barcellos, Adriane Sperança, Benhur Godoi, *Eur. J. Org. Chem.*, **2017**, 6382-6389.
- (3) Ran Ding, Zhi-Dao Huang, Zheng-Li Liu, Tian-Xiang Wang, Yun-He Xu, Teck-Peng Loh, *Chem. Commun.*, **2016**, 52, 5617-5620.
- (4) Andressa C. H. Weber, Felipe L. Coelho,^[a] Ricardo F. Affeldt, Paulo H. Schneider, *Eur. J. Org. Chem.* **2018**, 6738–6742.
- (5) Shan Tang, Yichang Liu, Xinlong Gao, Pan Wang, Pengfei Huang, Aiwen Lei, *J. Am. Chem. Soc.*, **2018**, 140, 6006-6013.
- (6) Zhong-zhong Cao, Zhiwen Nie, Tonglin Yang, Miaodong Su, Hui Li, Wei-ping Luo, Qiang Liu, Can-Cheng Guo, *J. Org. Chem.*, **2020**, 85, 3287-3296.

9. Copies of NMR spectra

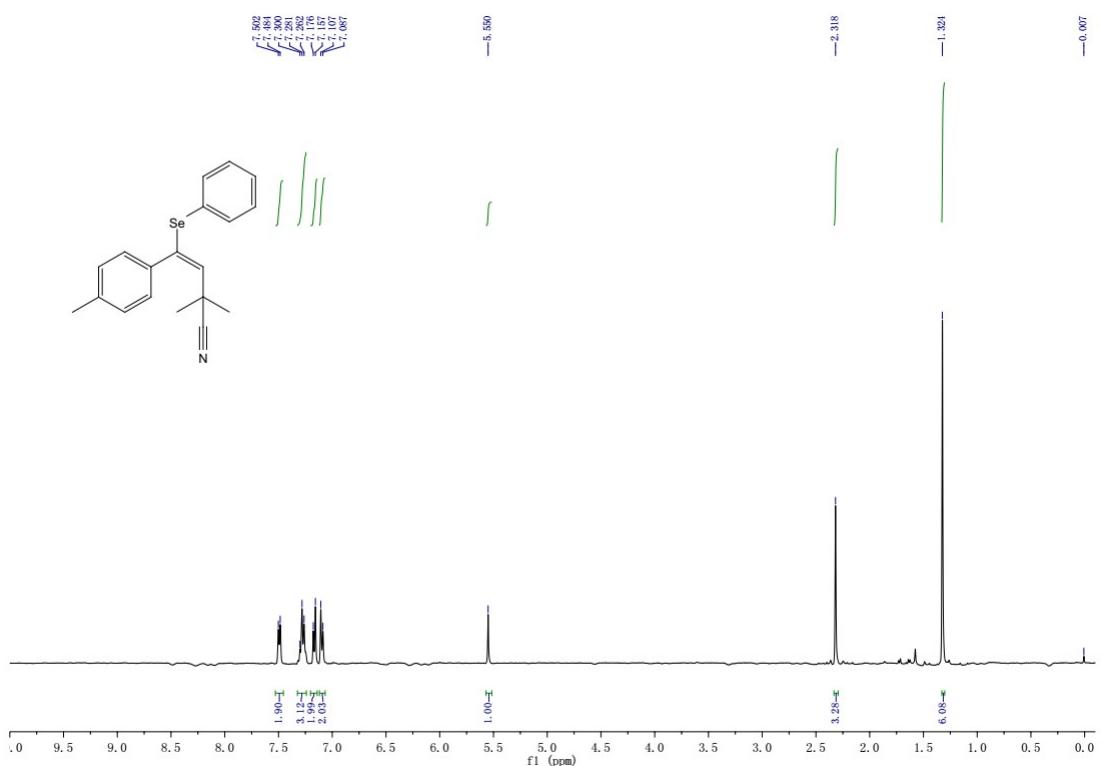
400 MHz ^1H NMR for compound 4a



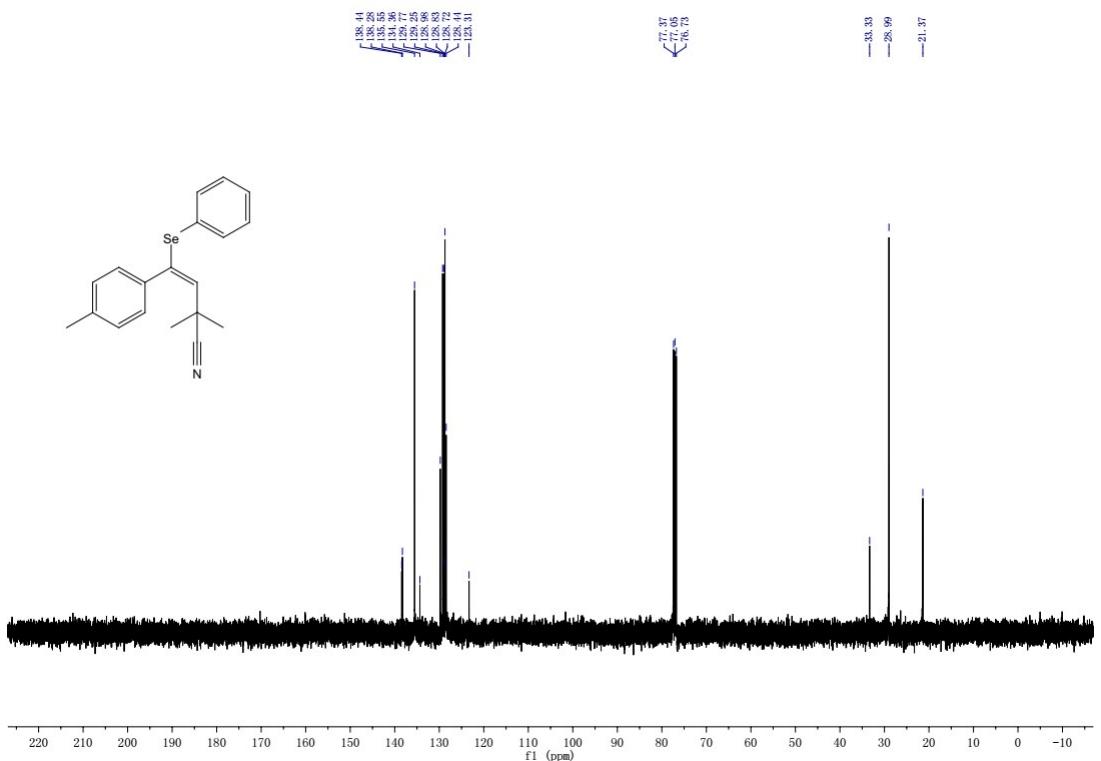
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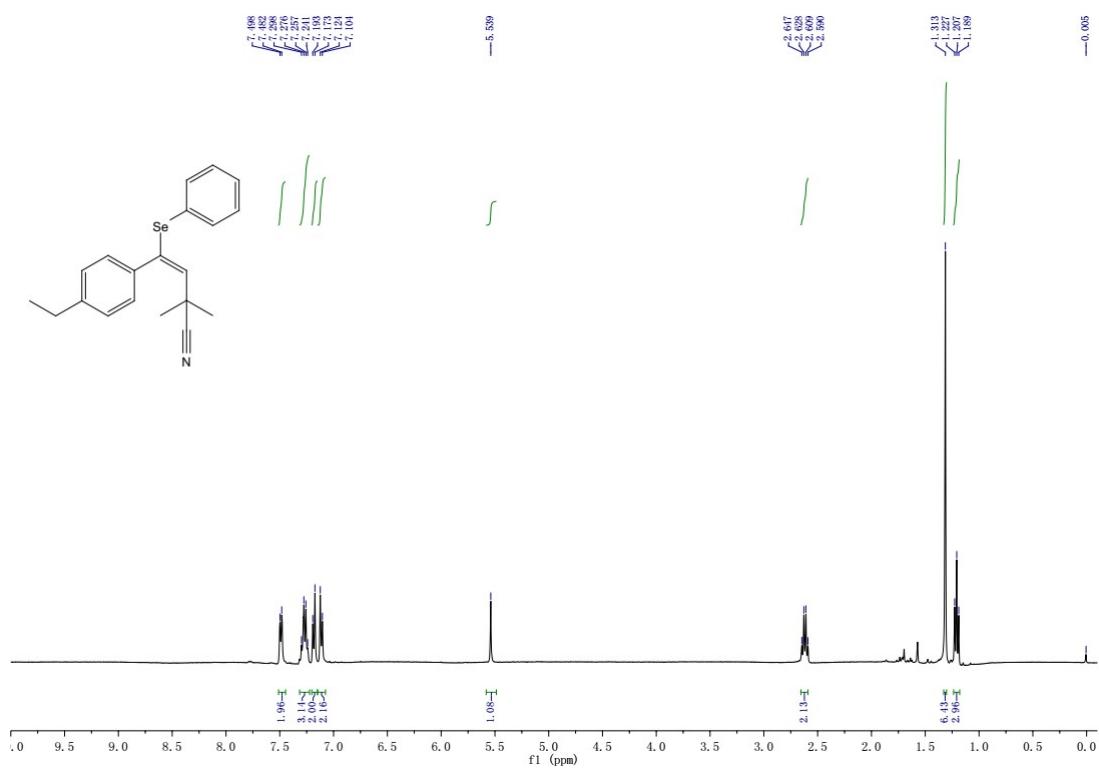
400 MHz ^1H NMR for compound **4b**



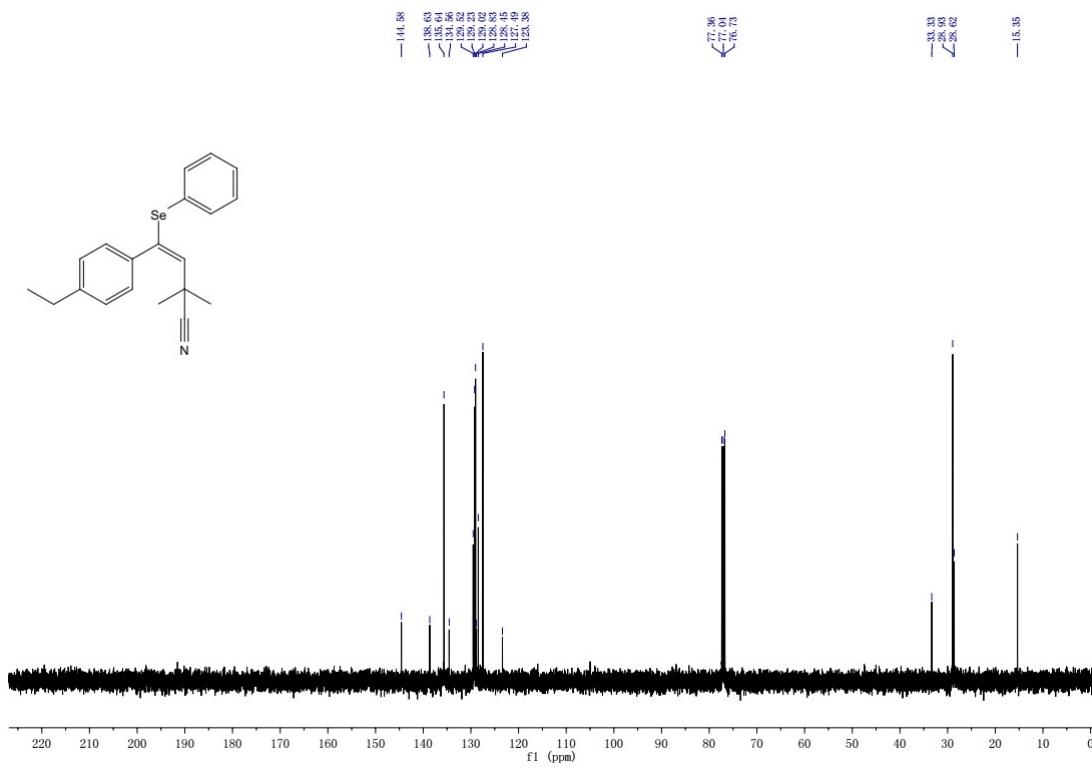
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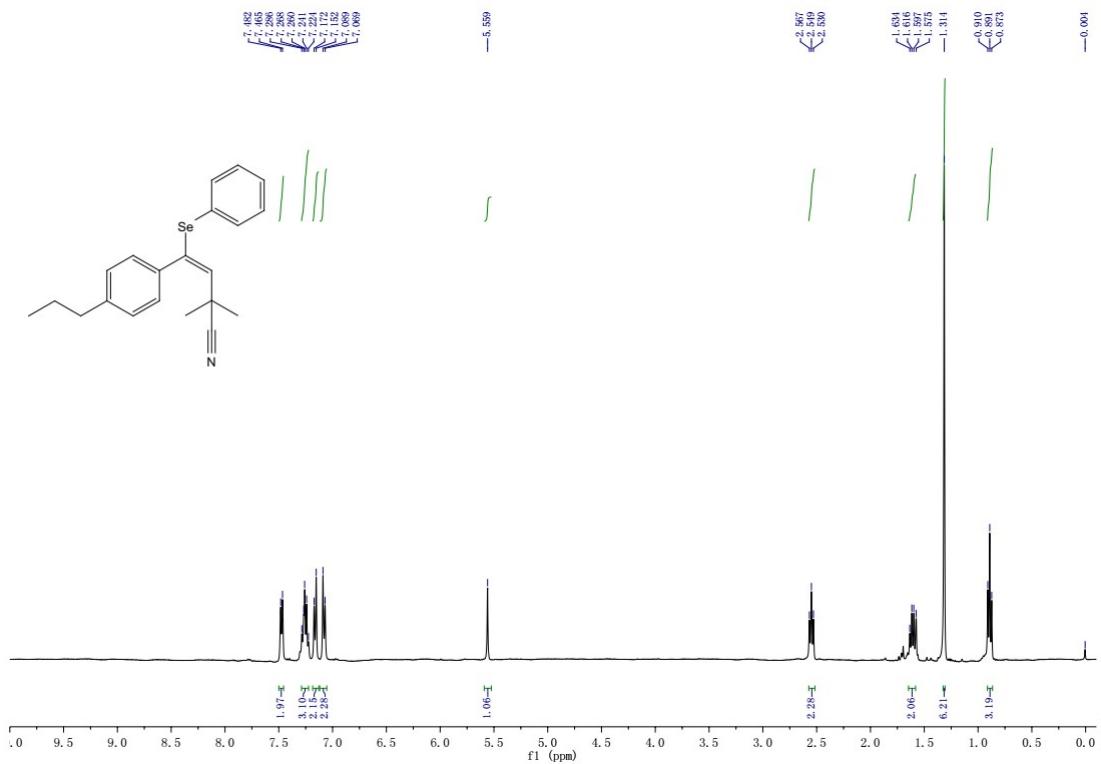
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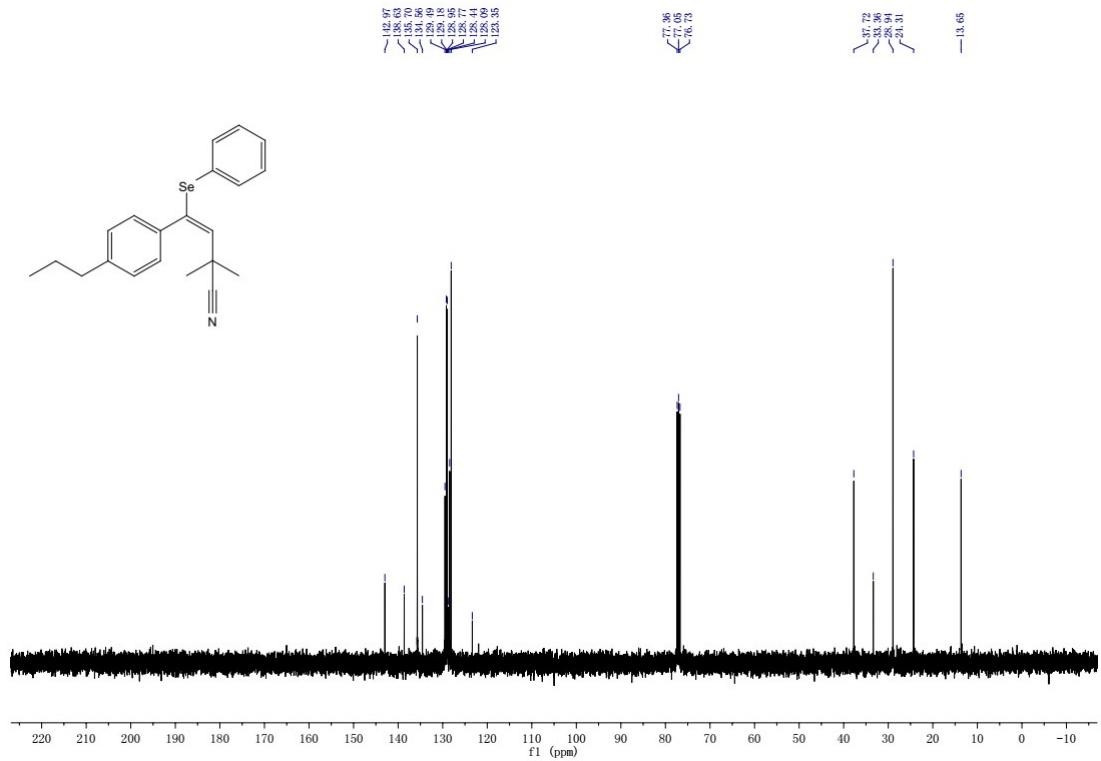
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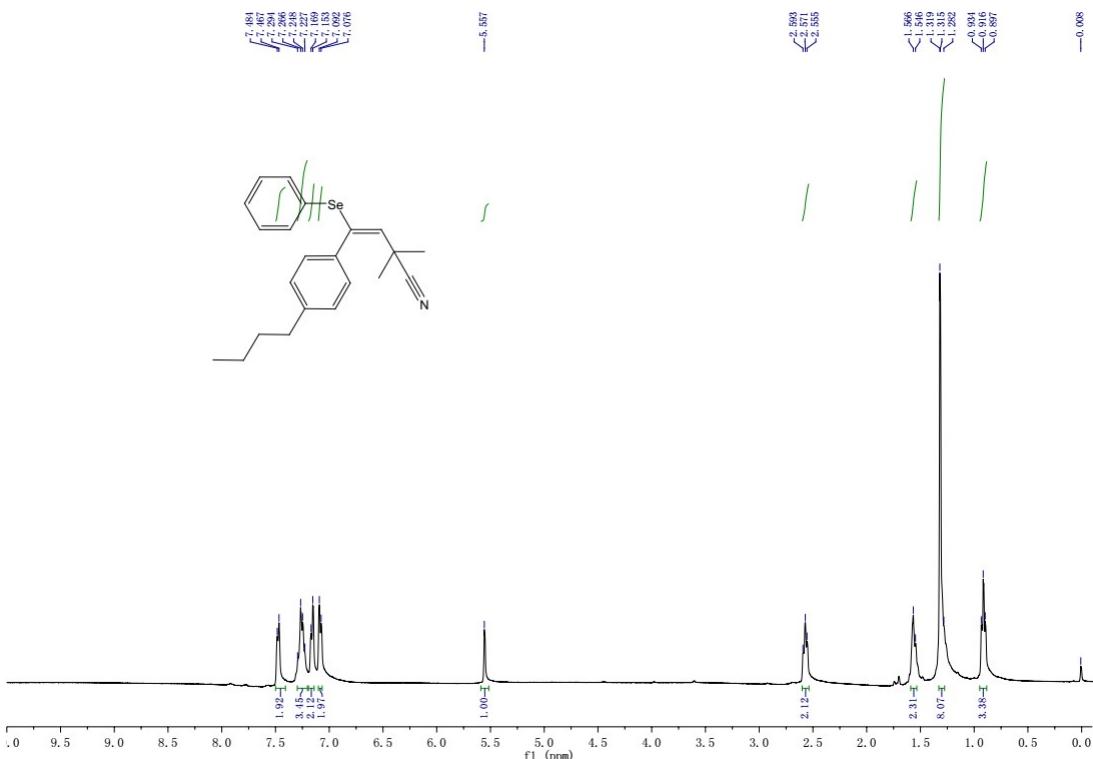
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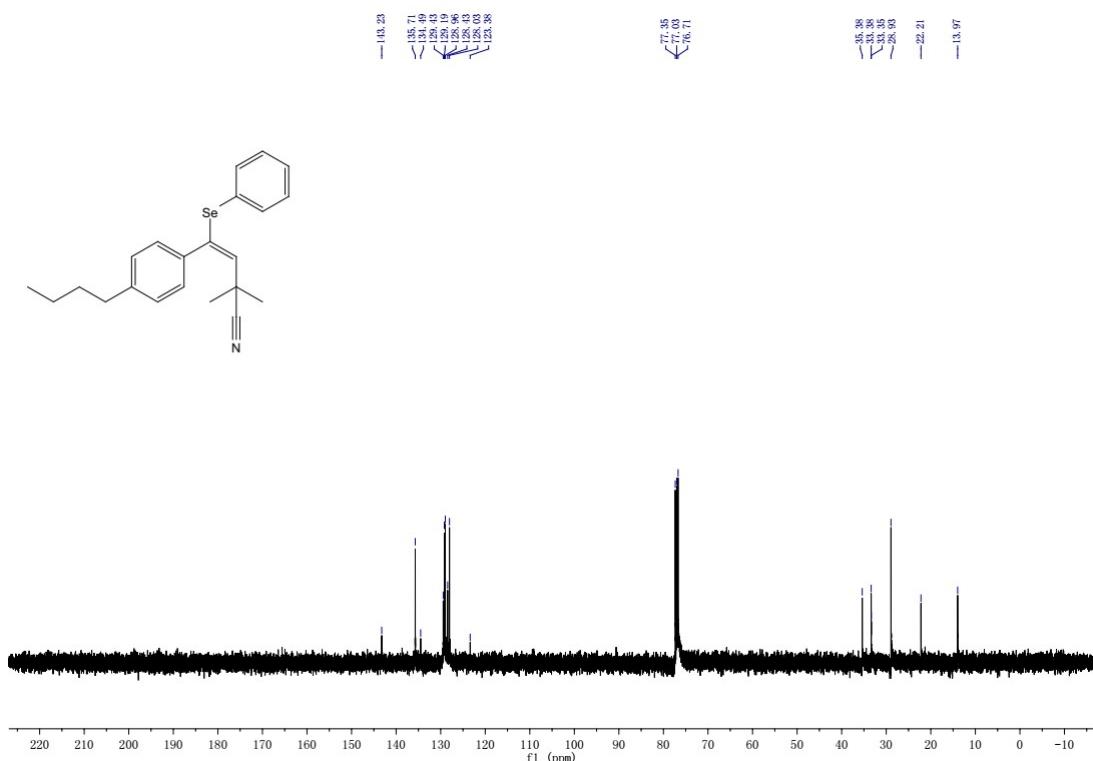
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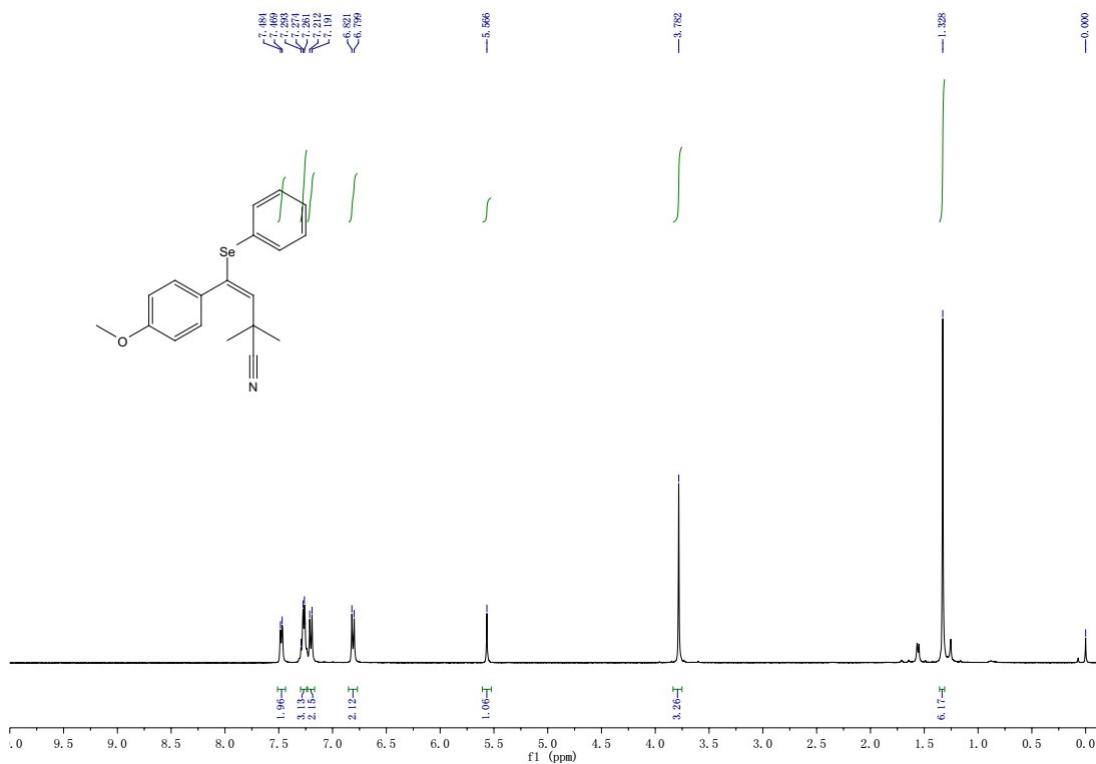
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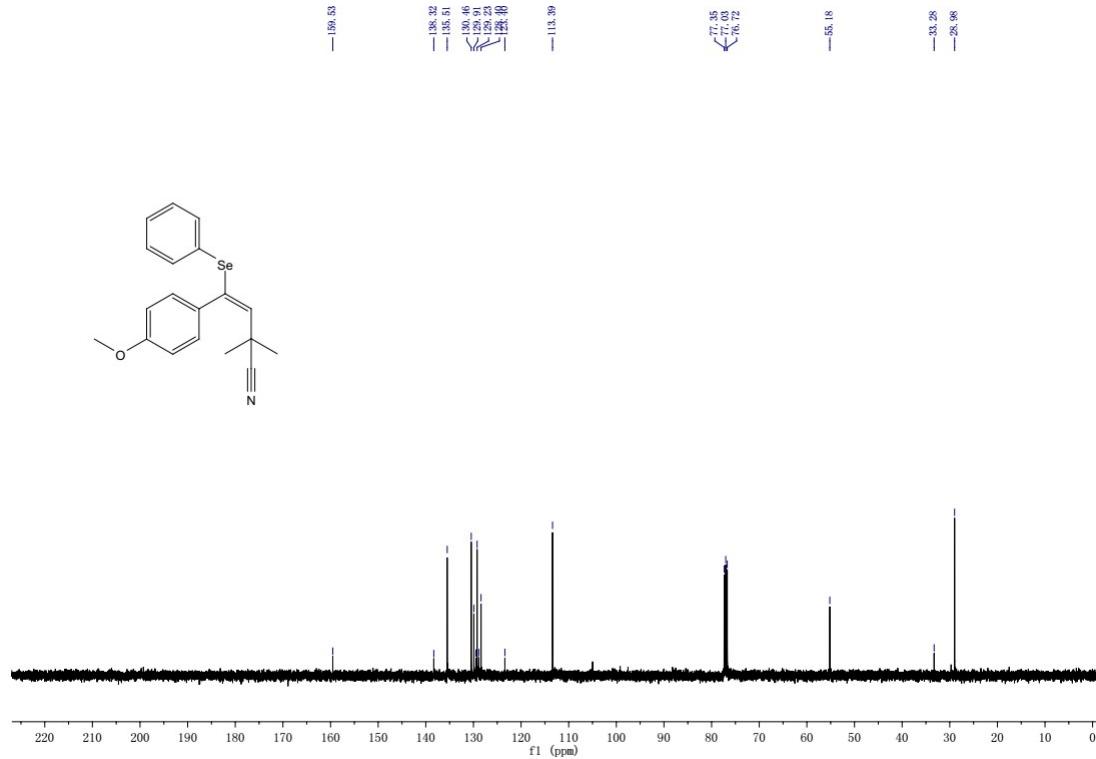
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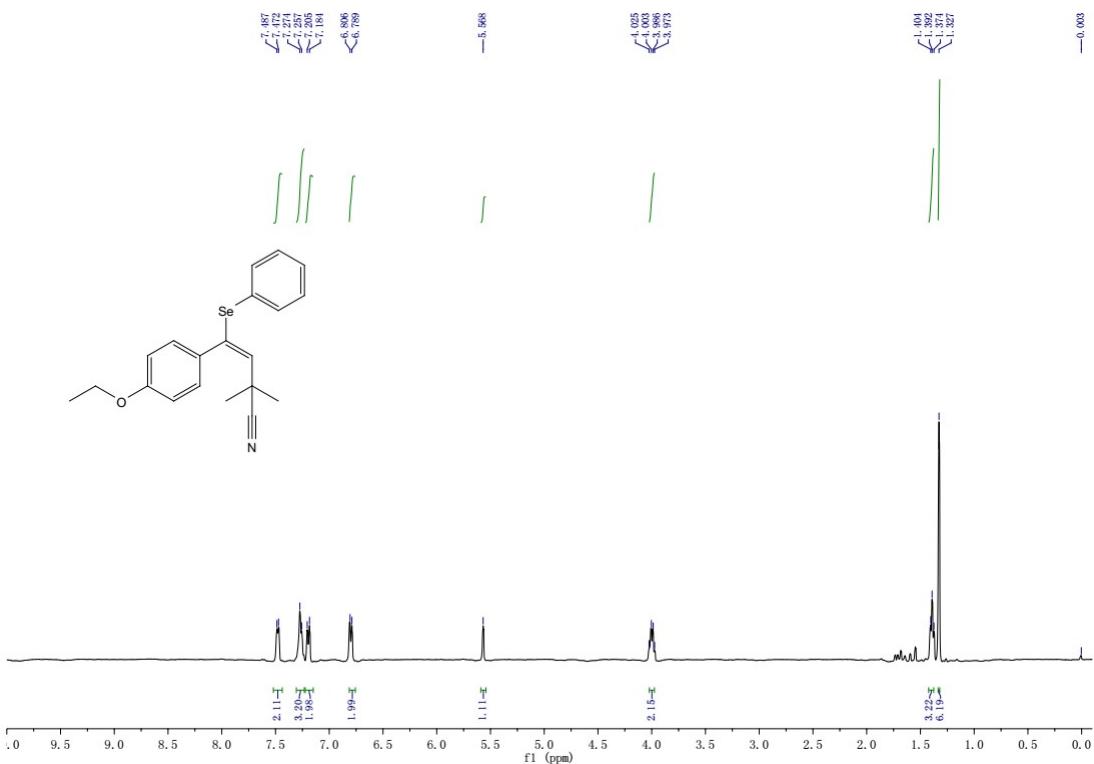
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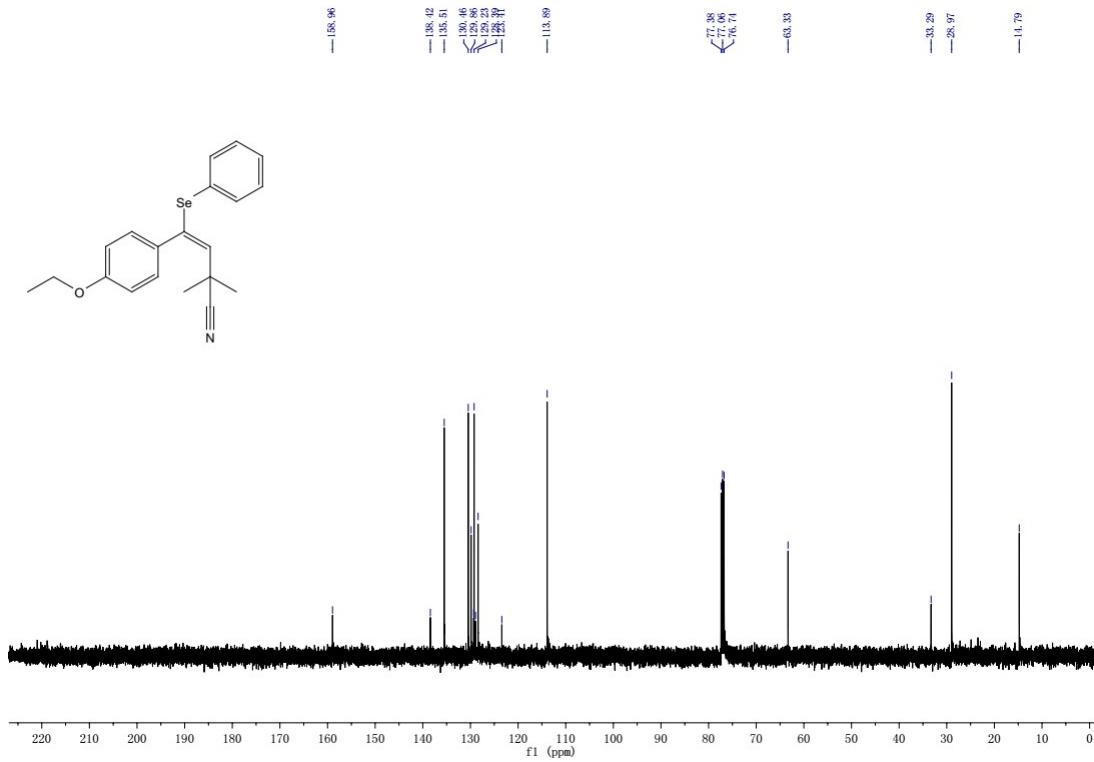
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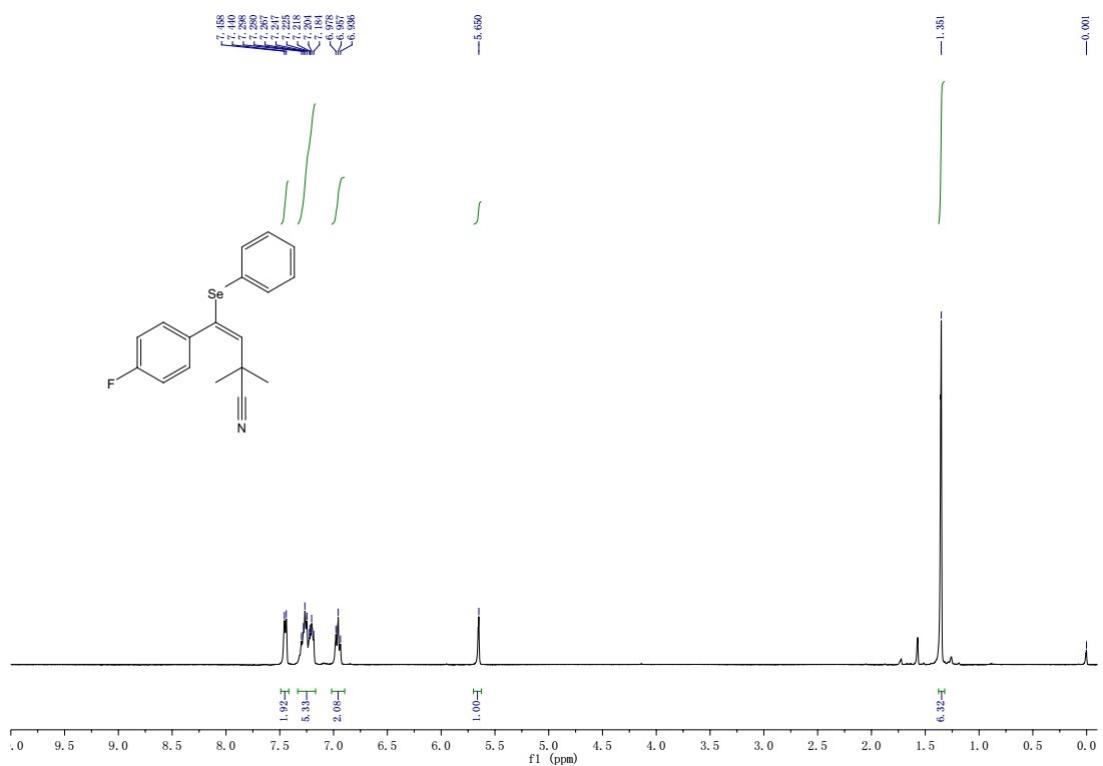
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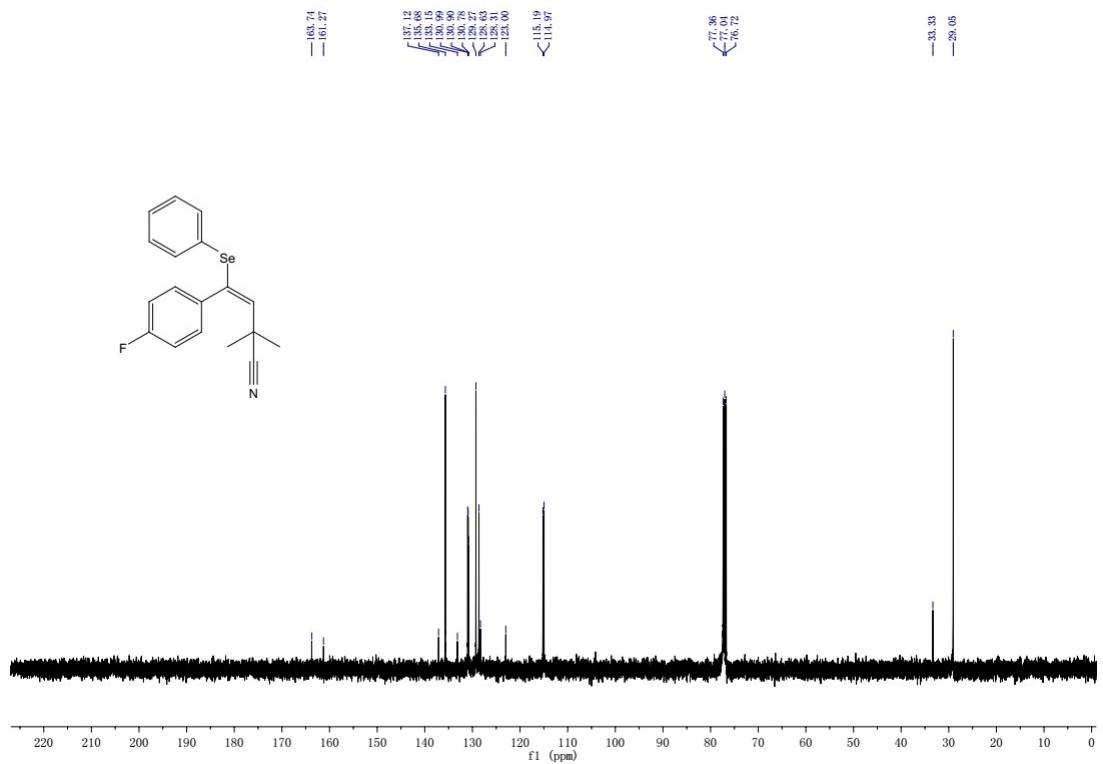
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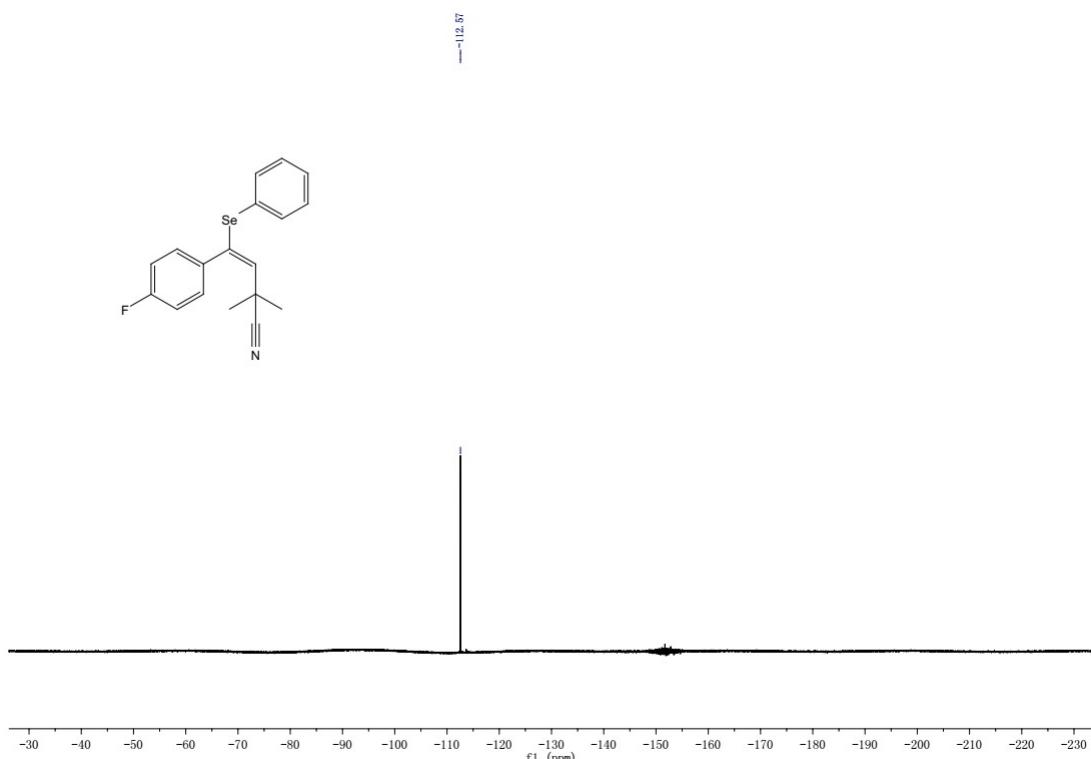
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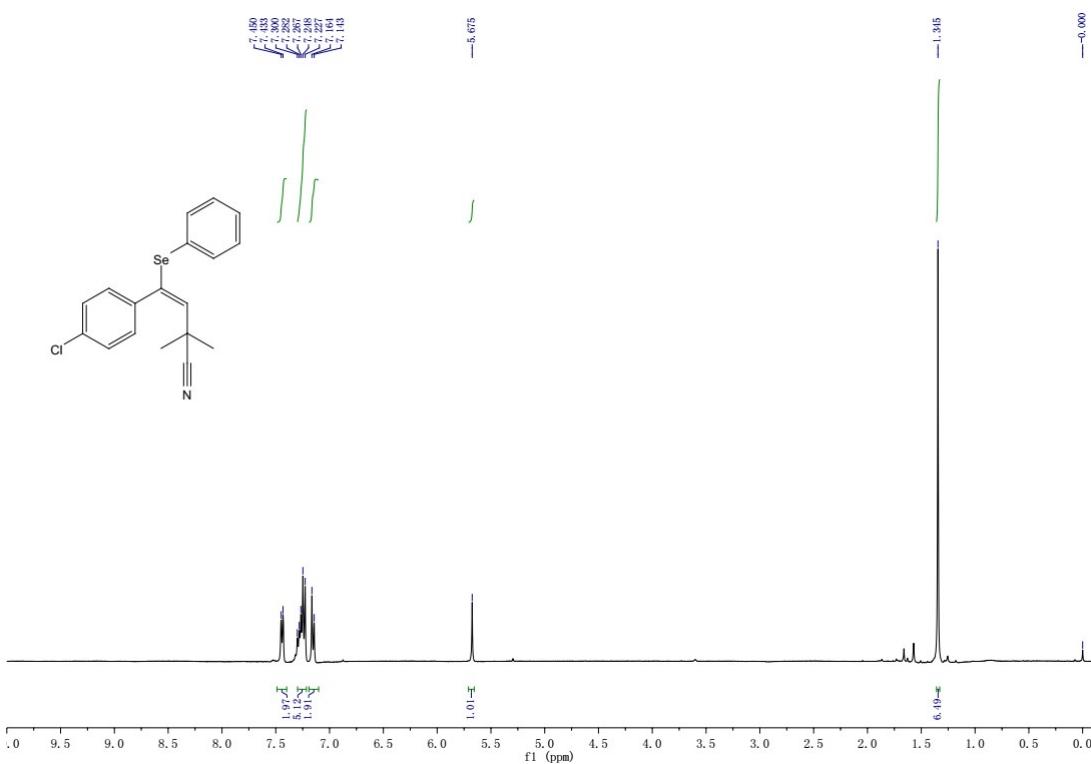
100 MHz ^{13}C NMR for compound **4h**



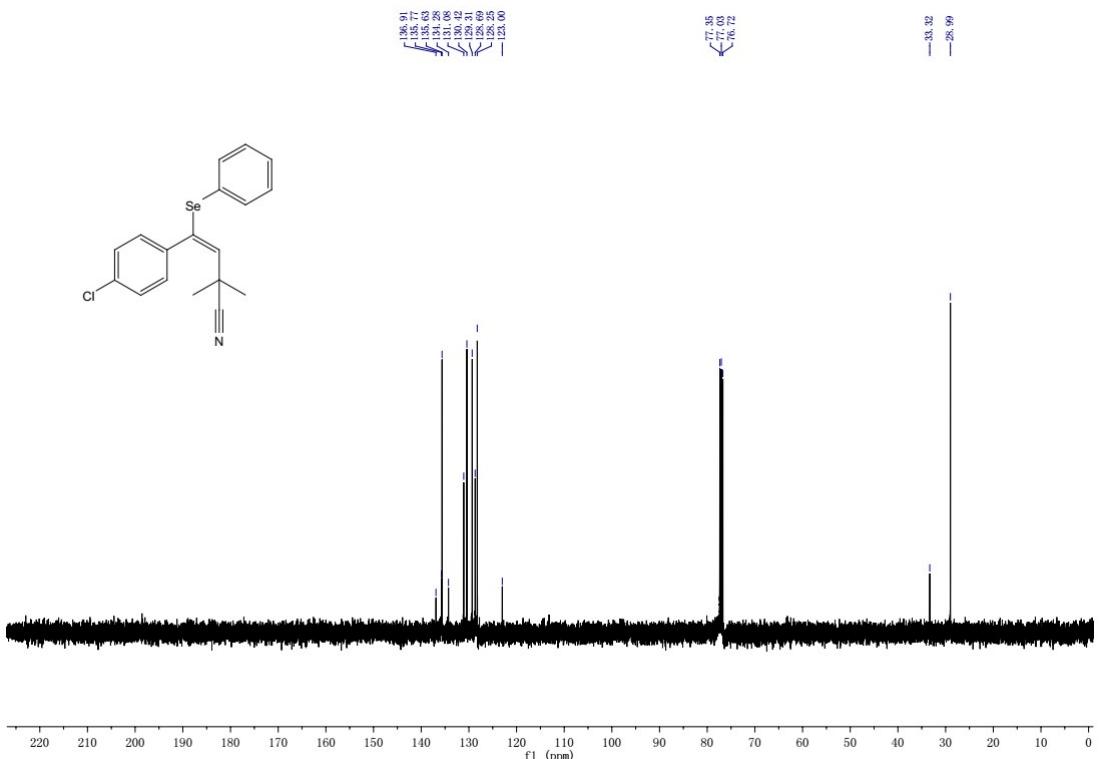
376 MHz ^{19}F NMR for compound **4h**



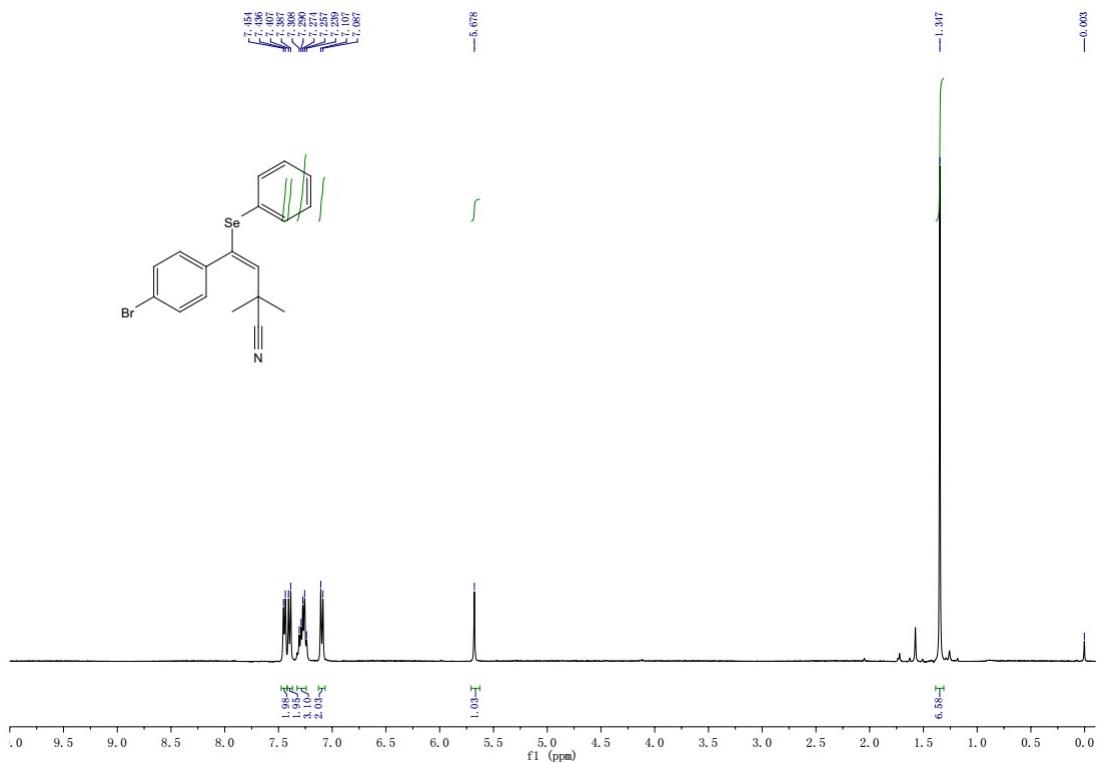
400 MHz ^1H NMR for compound **4i**



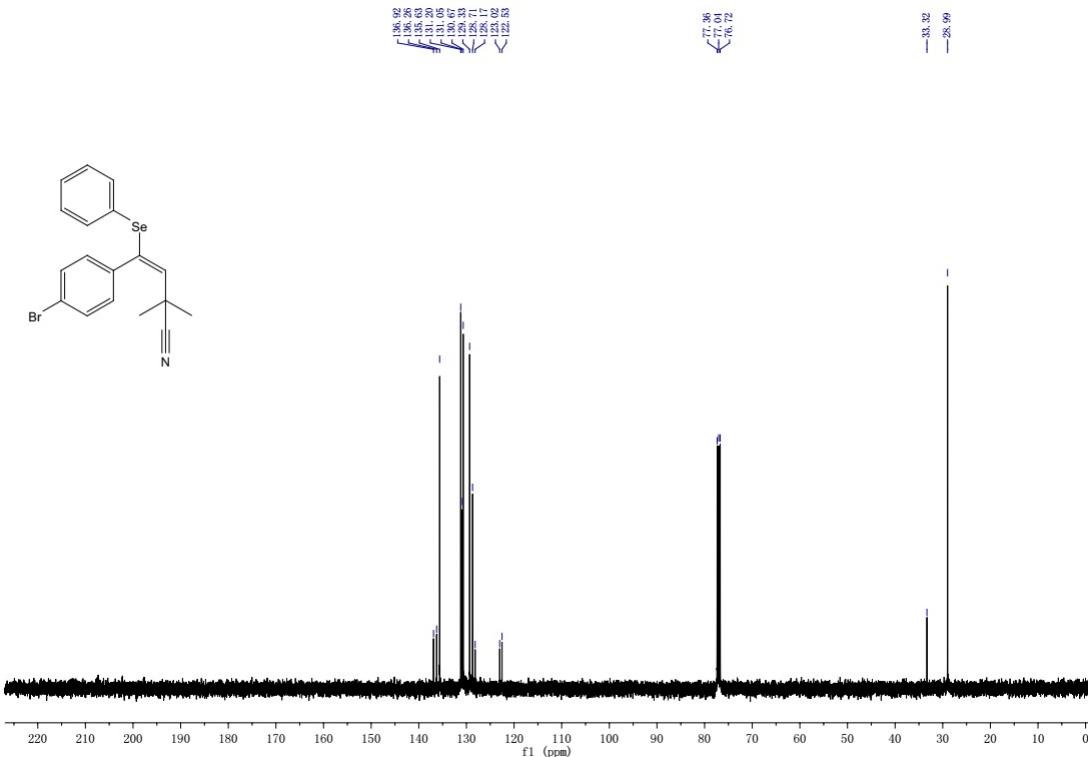
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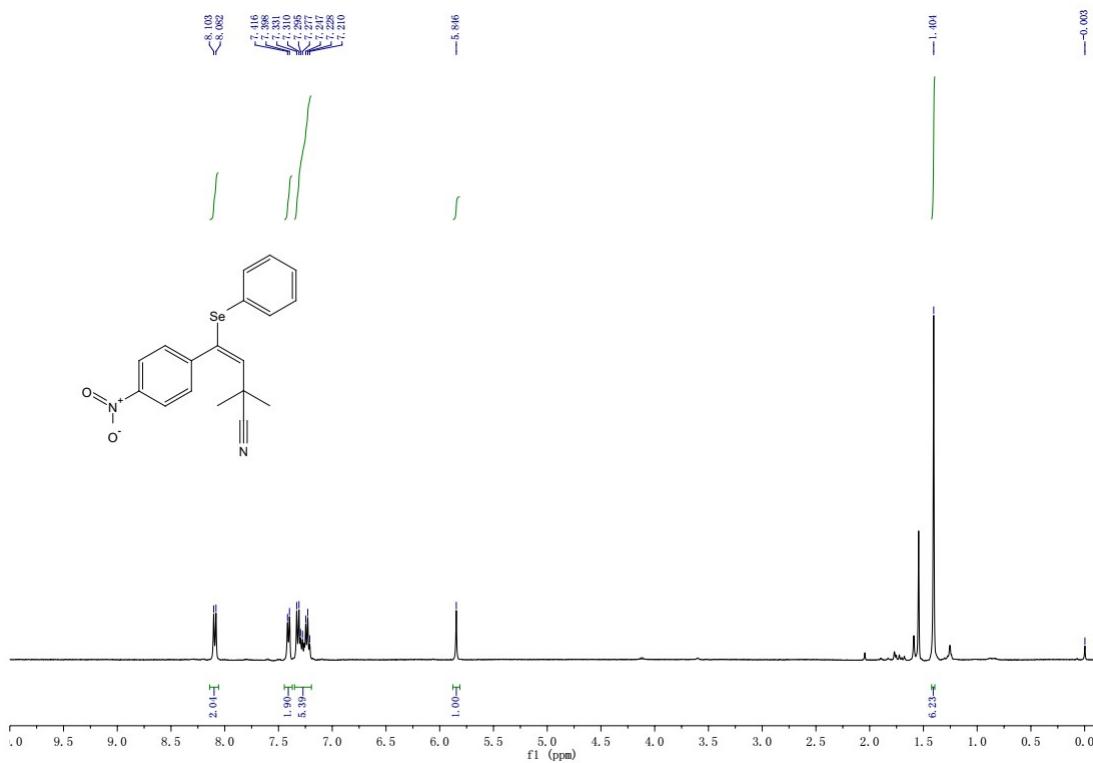
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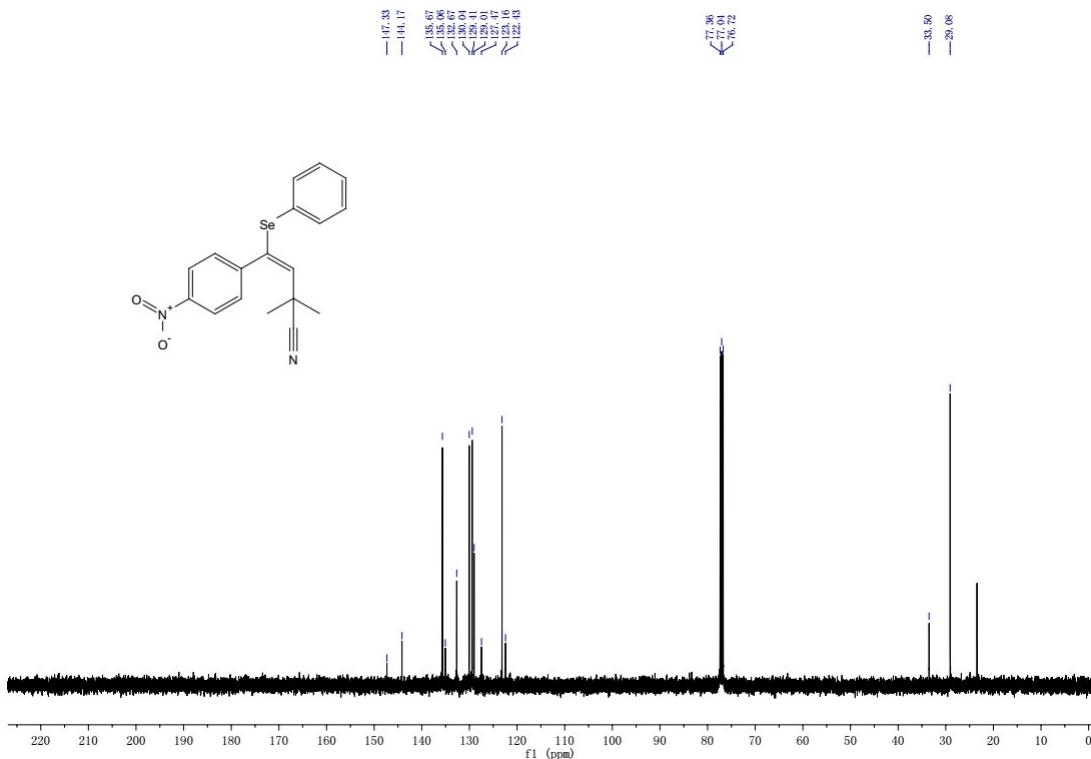
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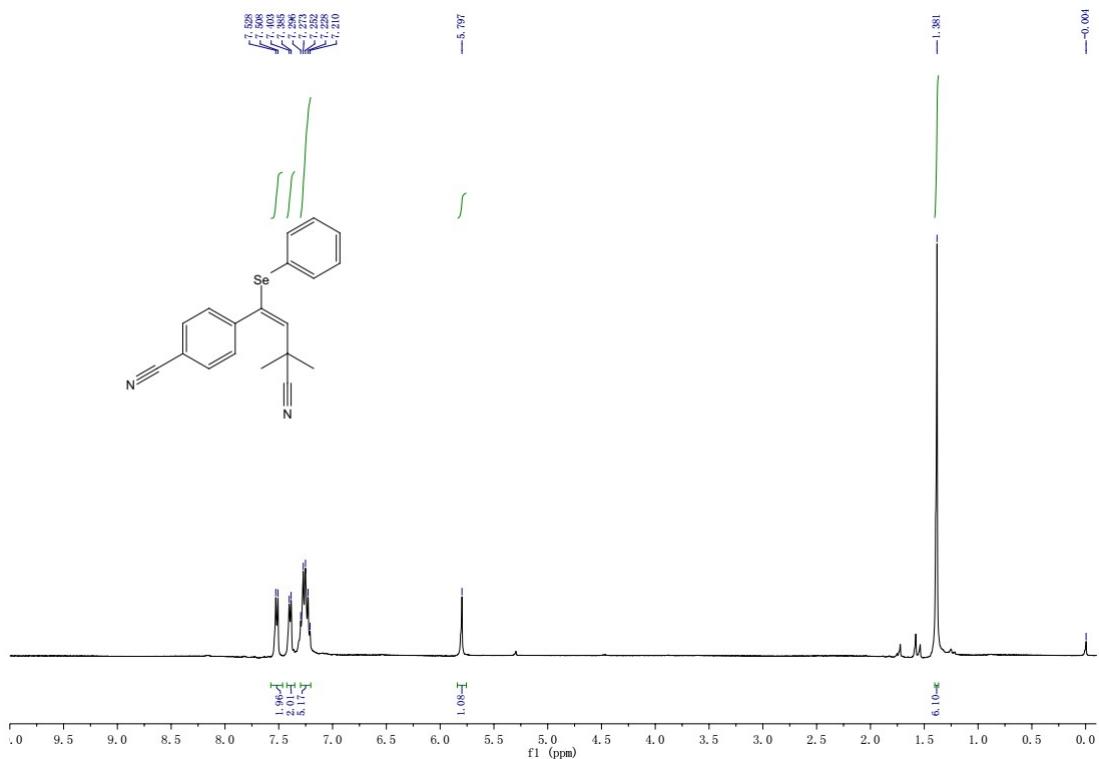
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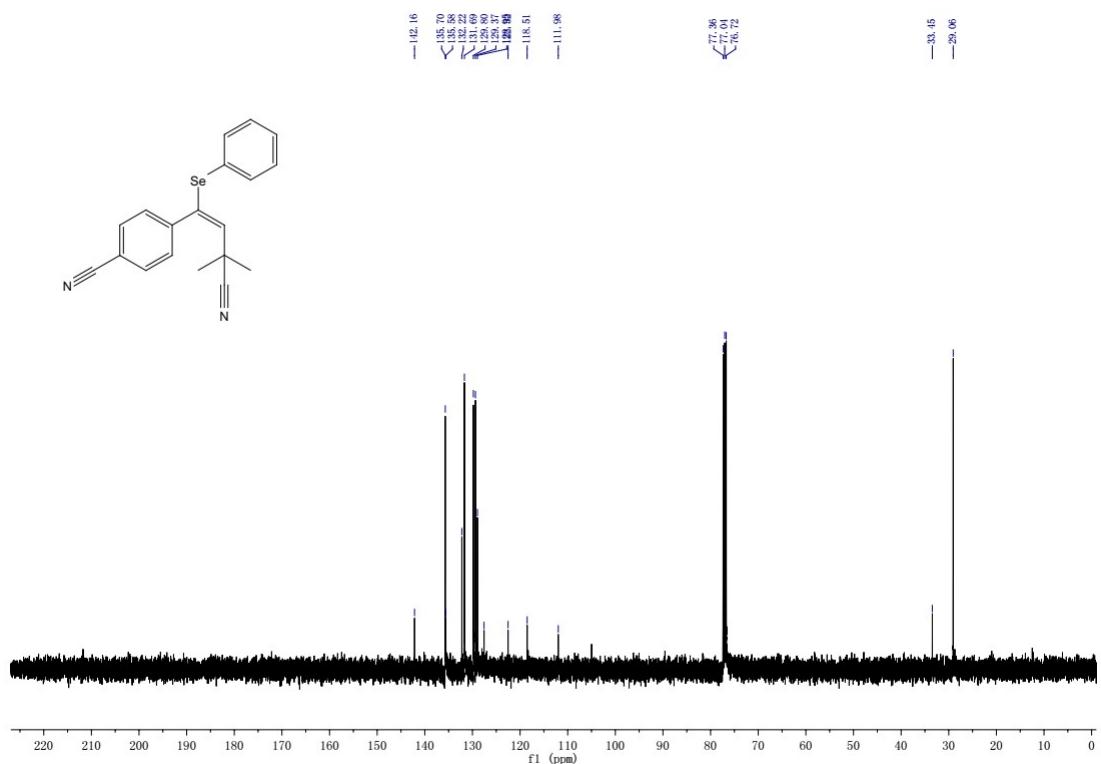
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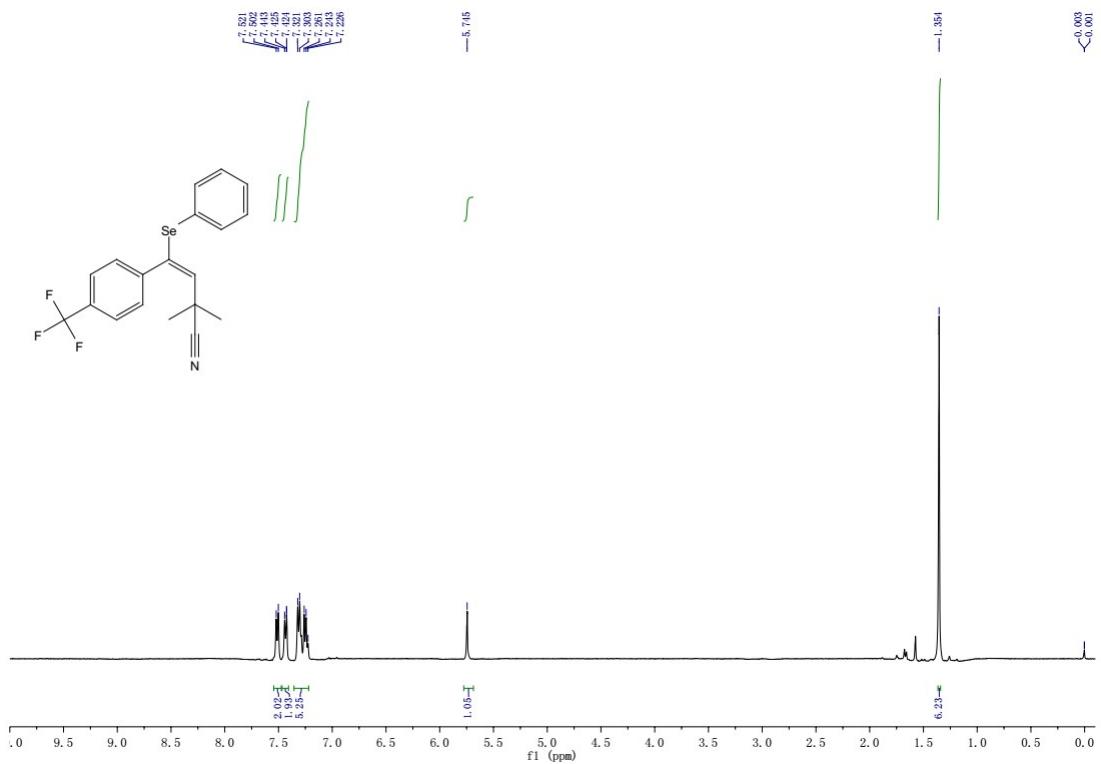
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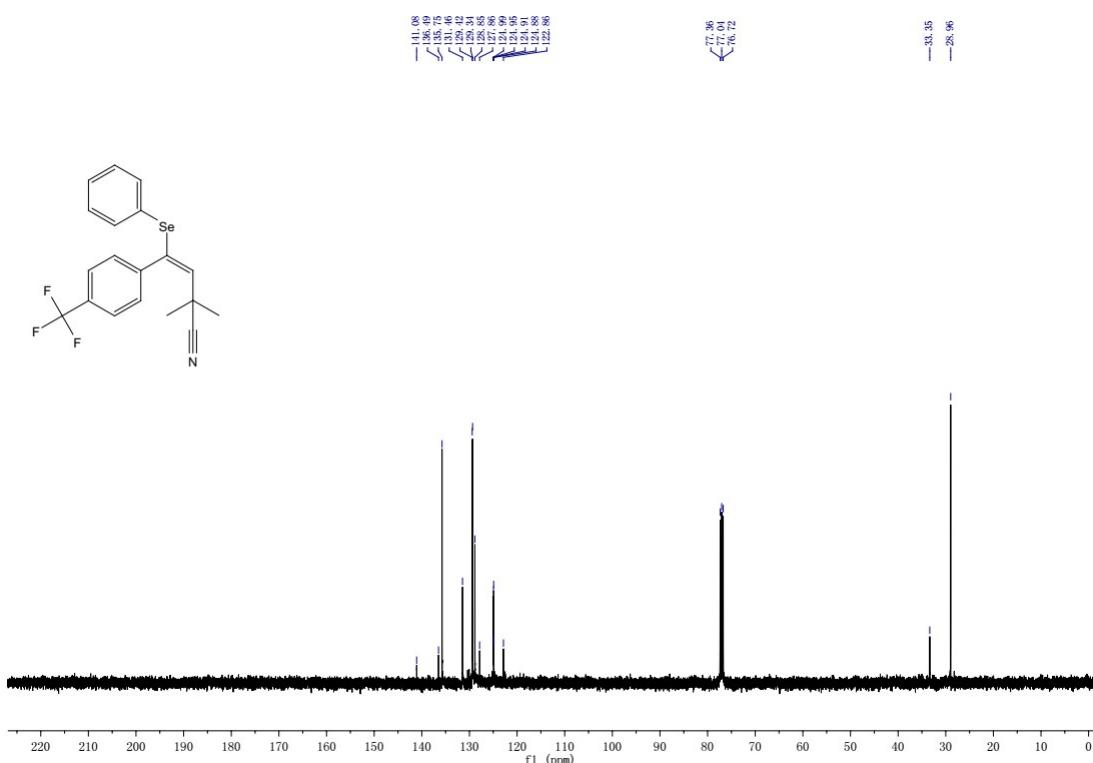
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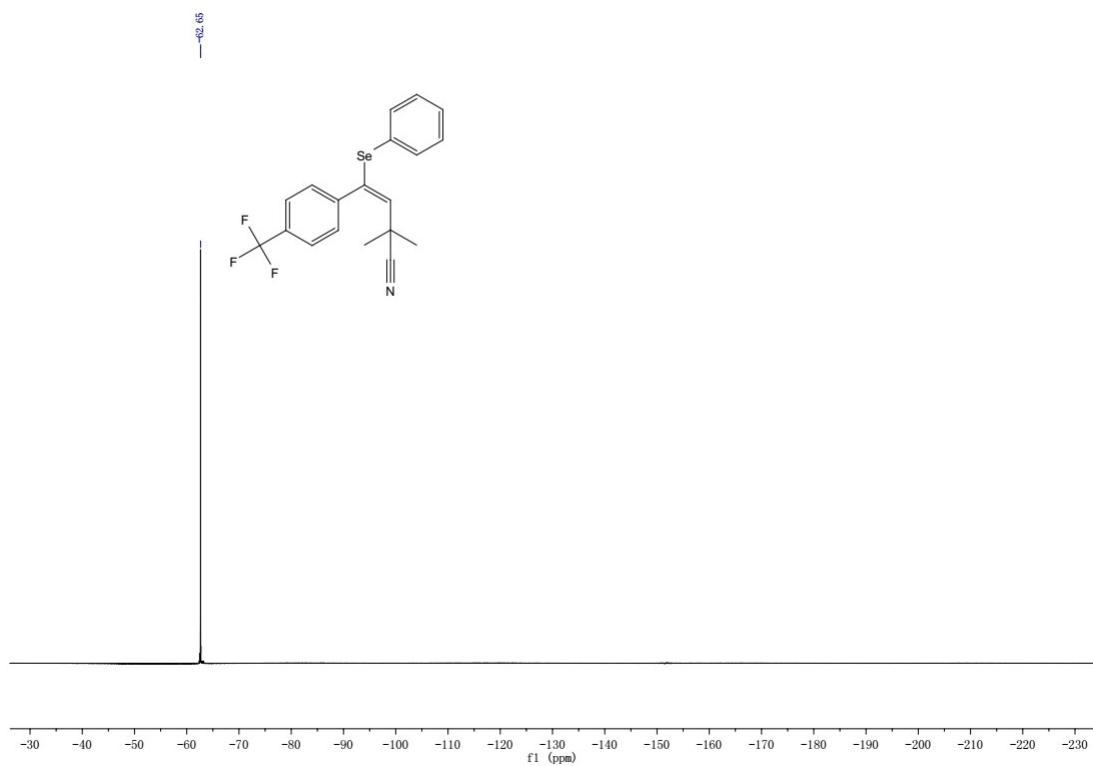
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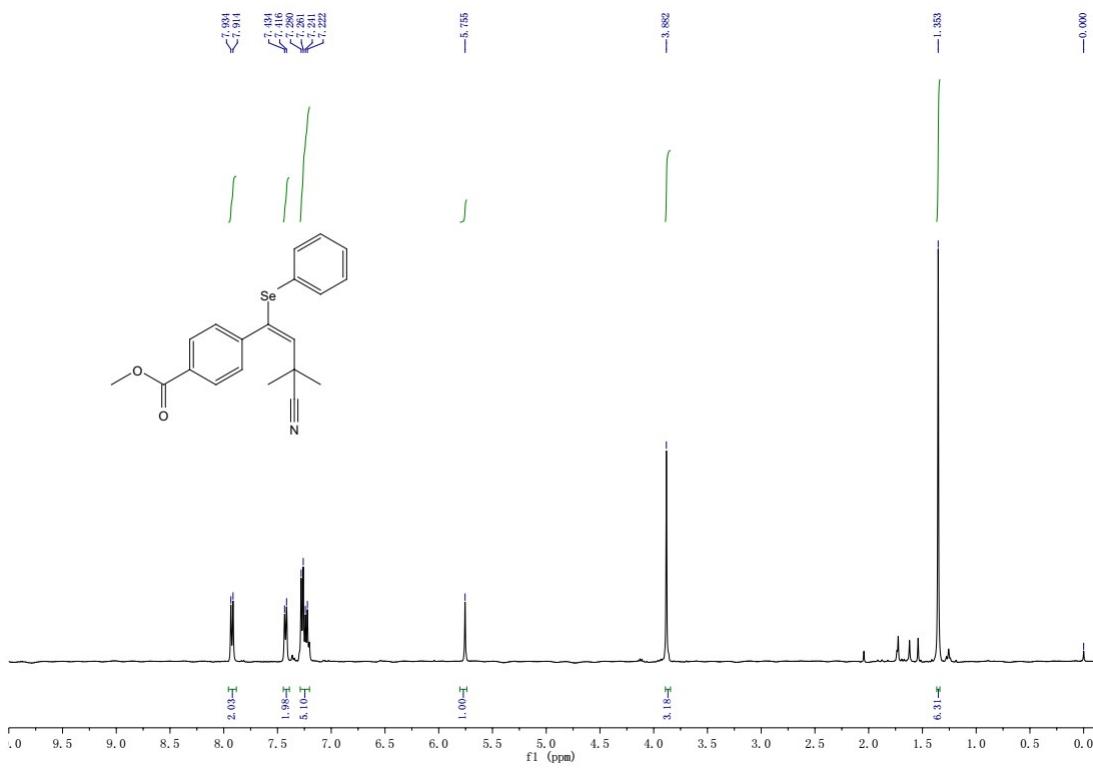
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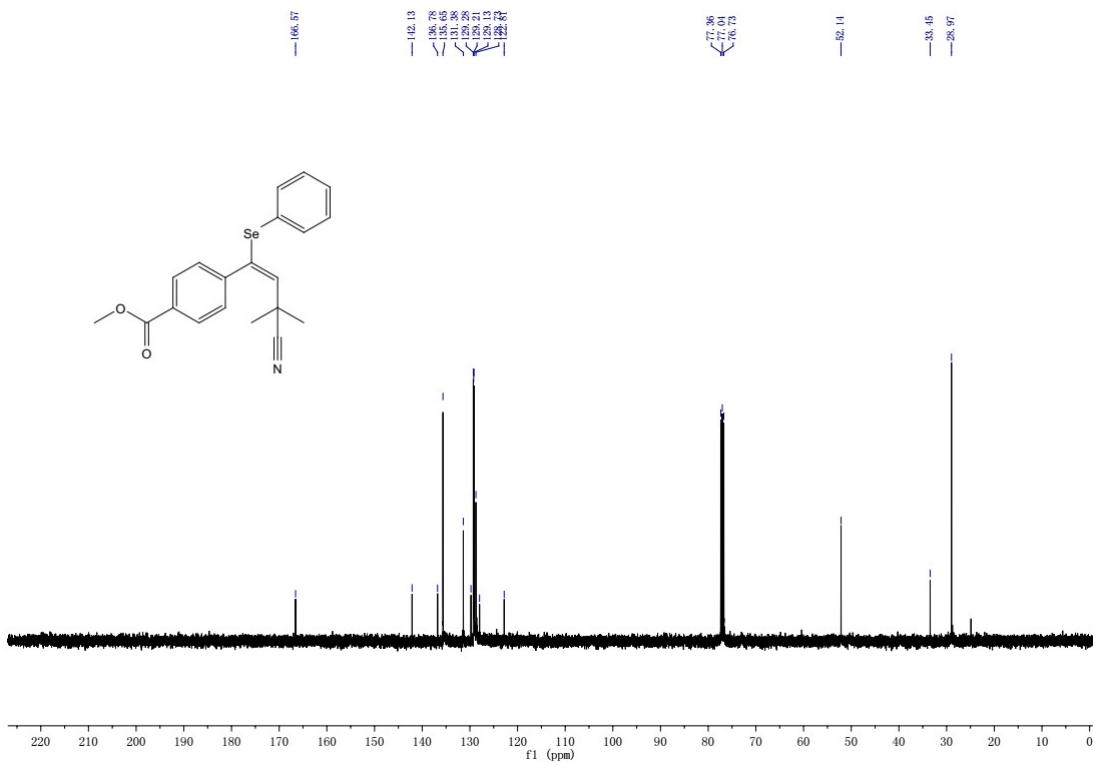
376 MHz ^{19}F NMR for compound **4m**



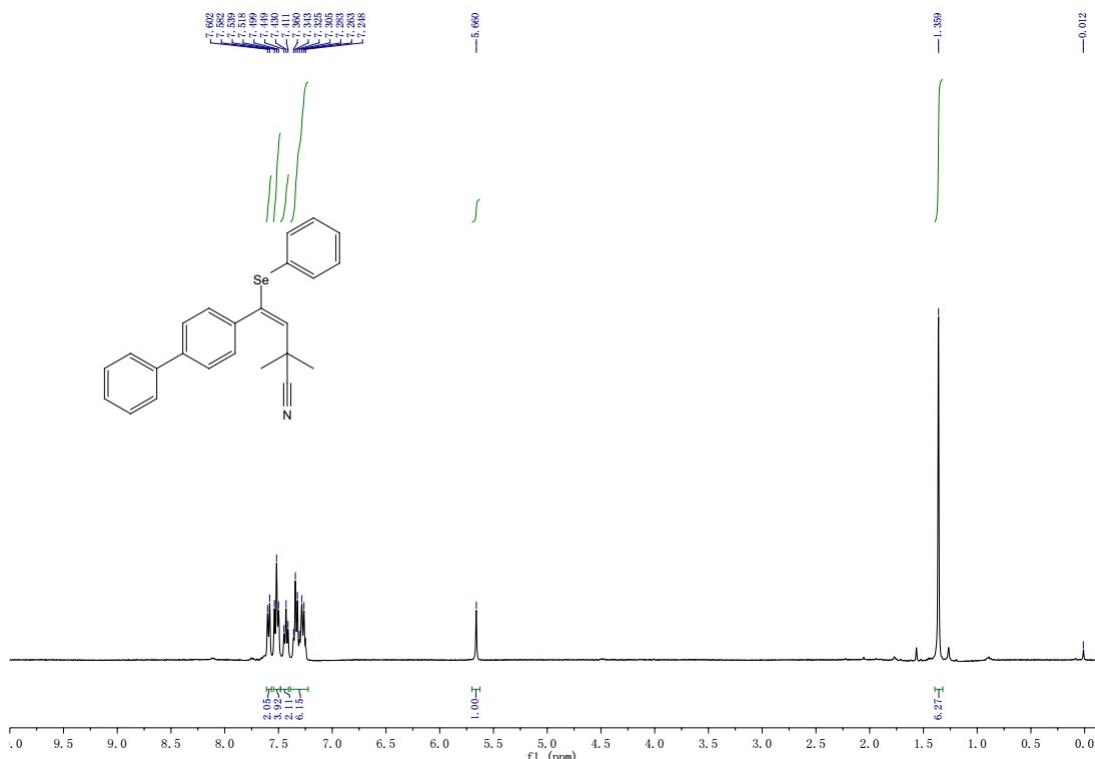
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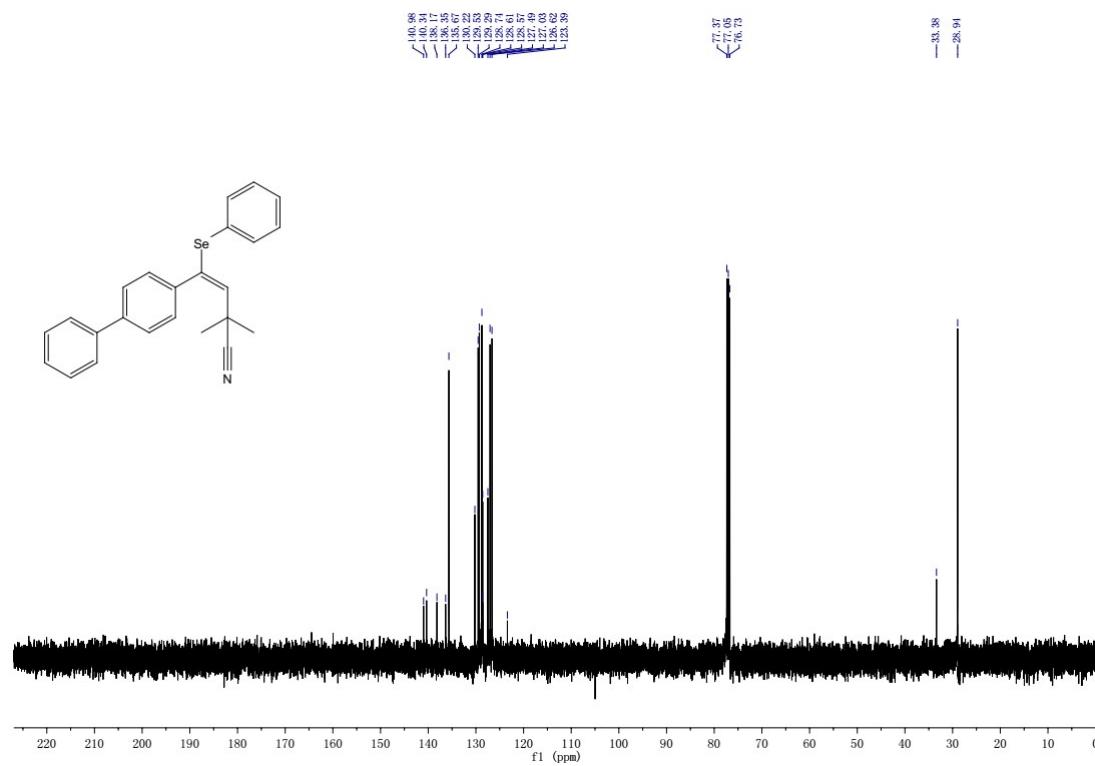
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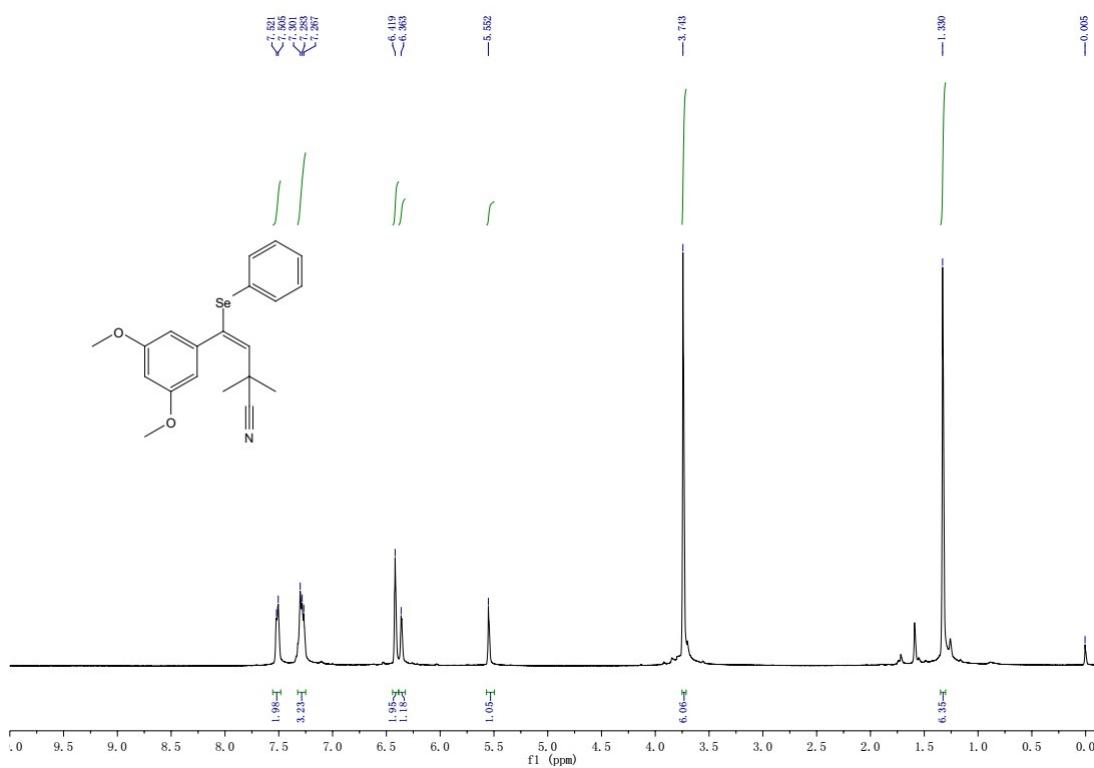
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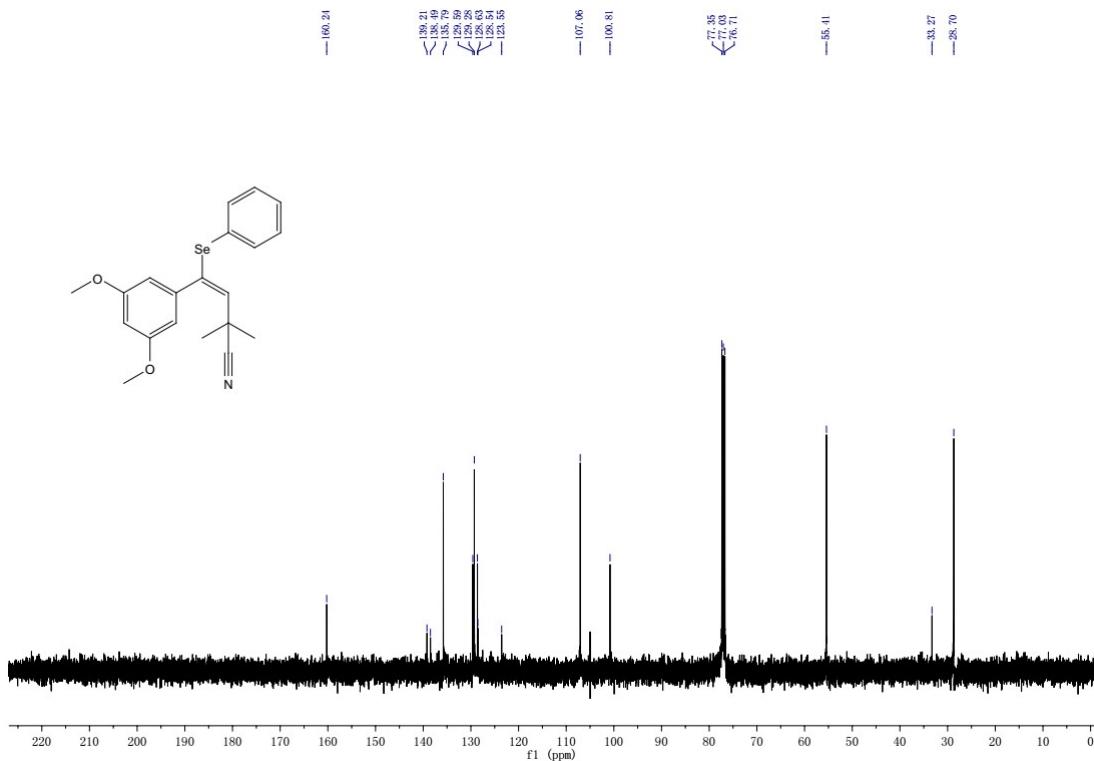
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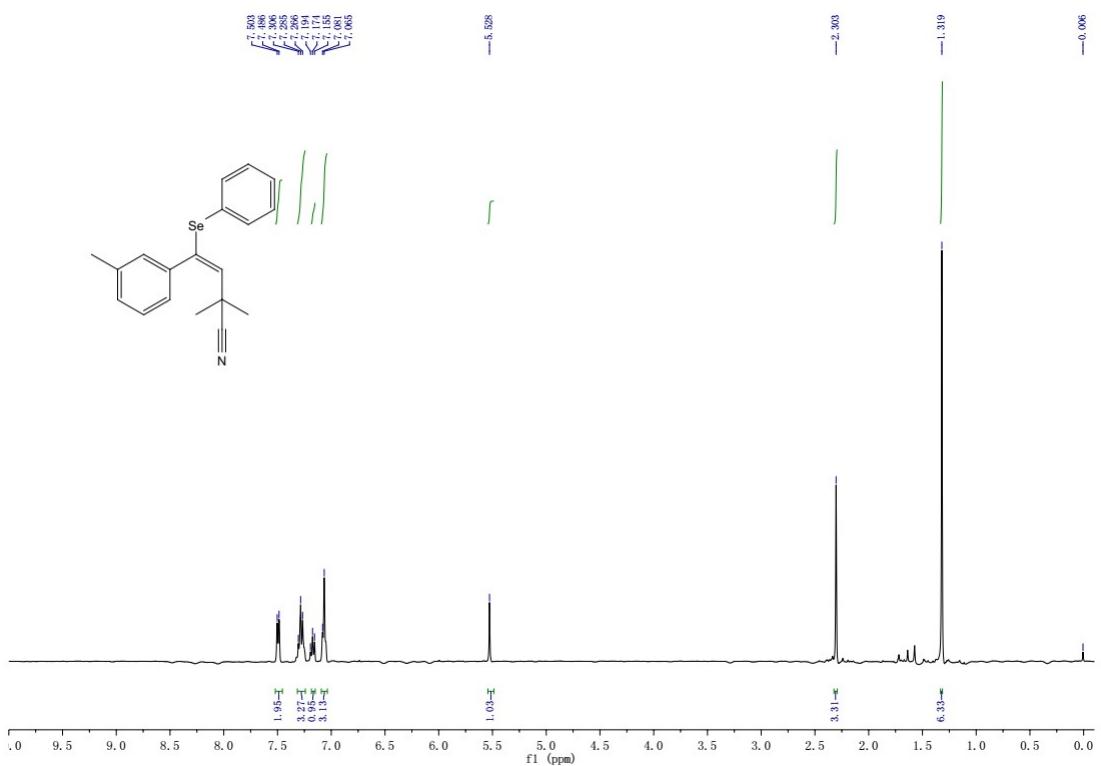
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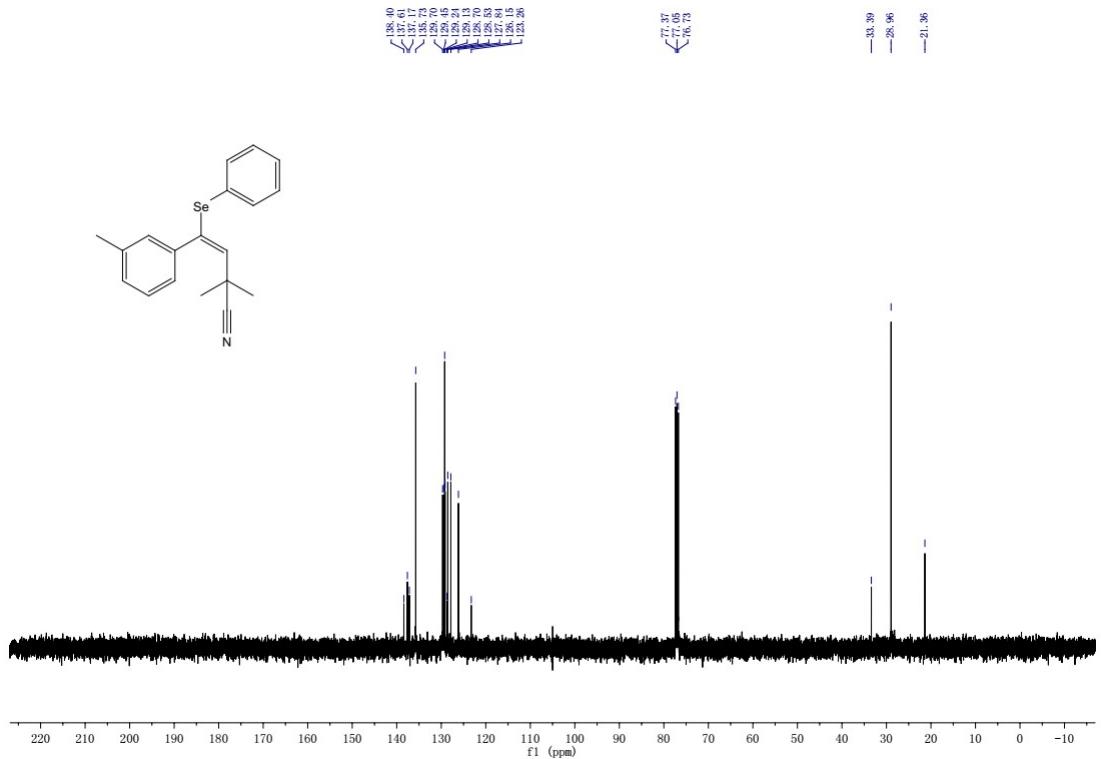
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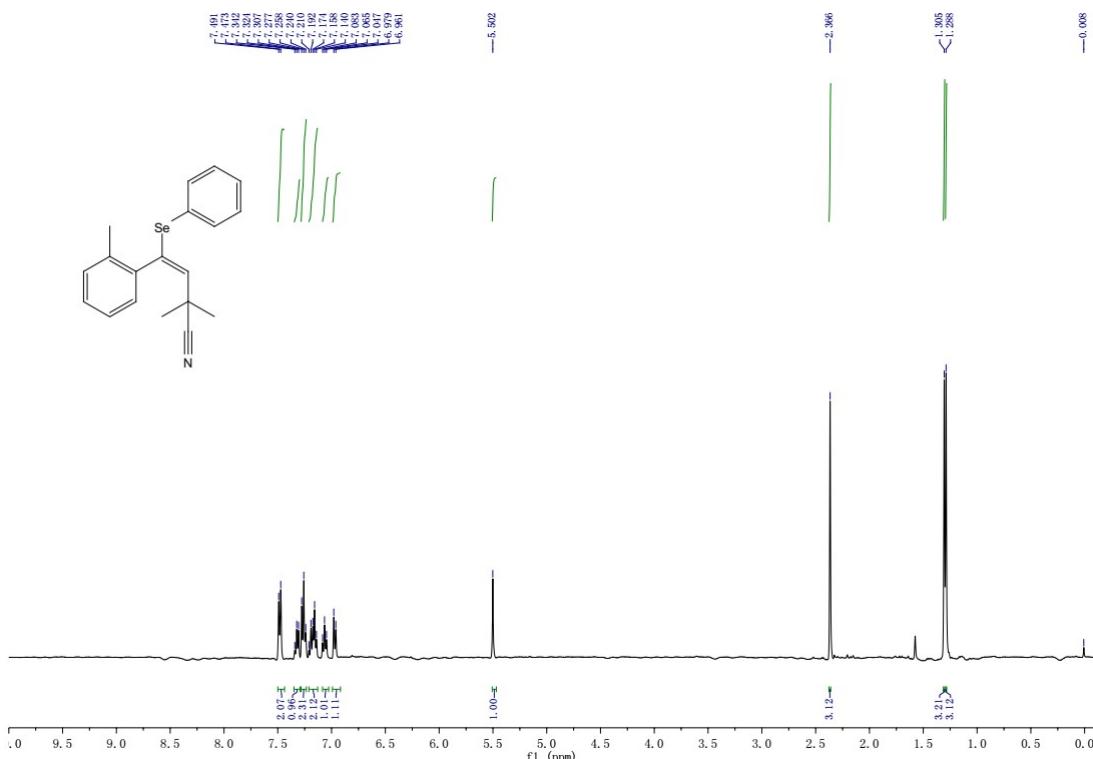
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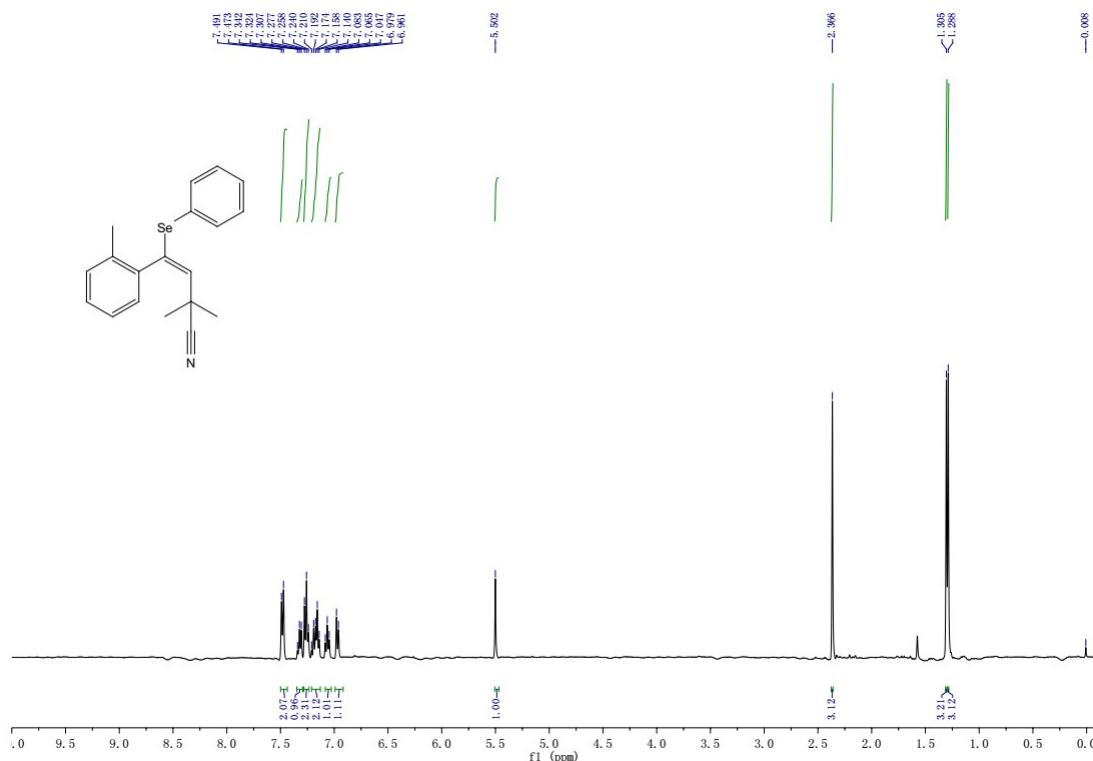
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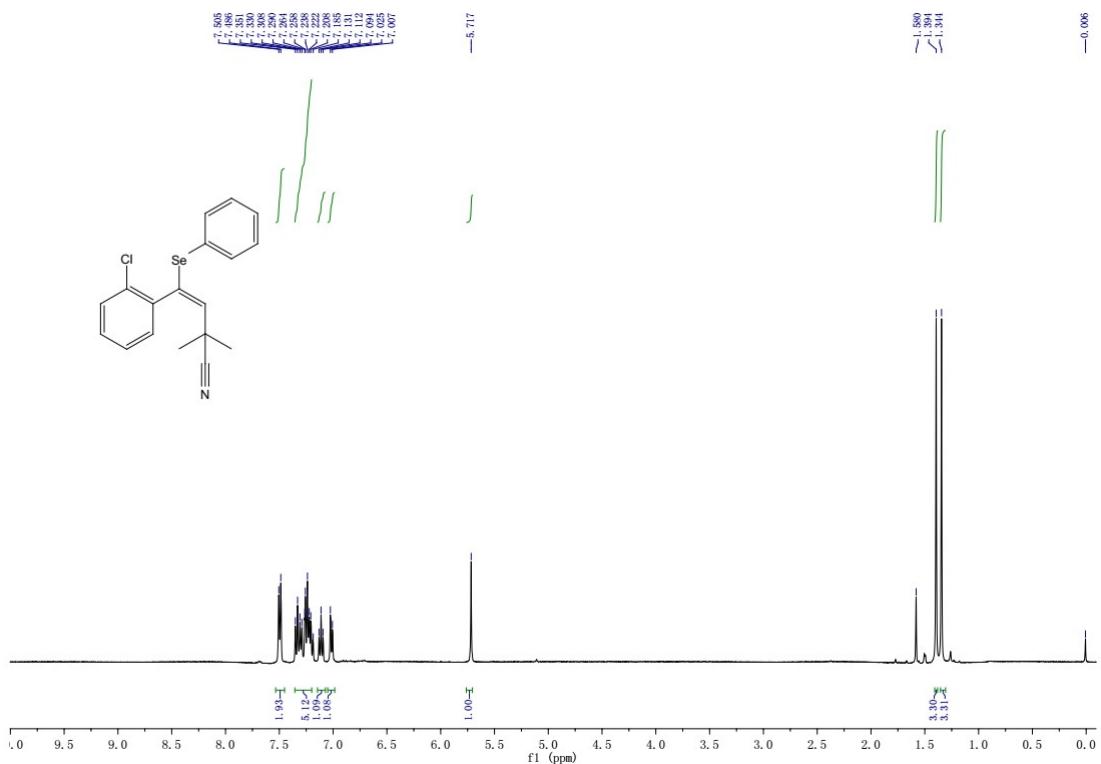
400 MHz ^1H NMR for compound 4r



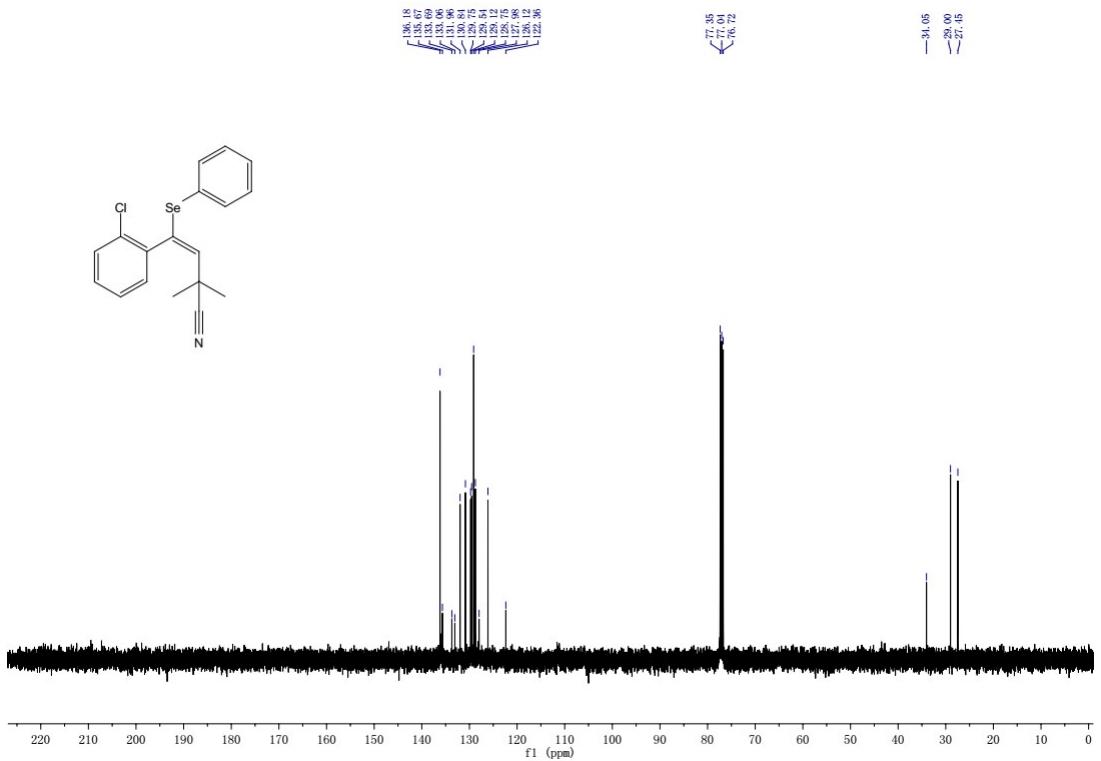
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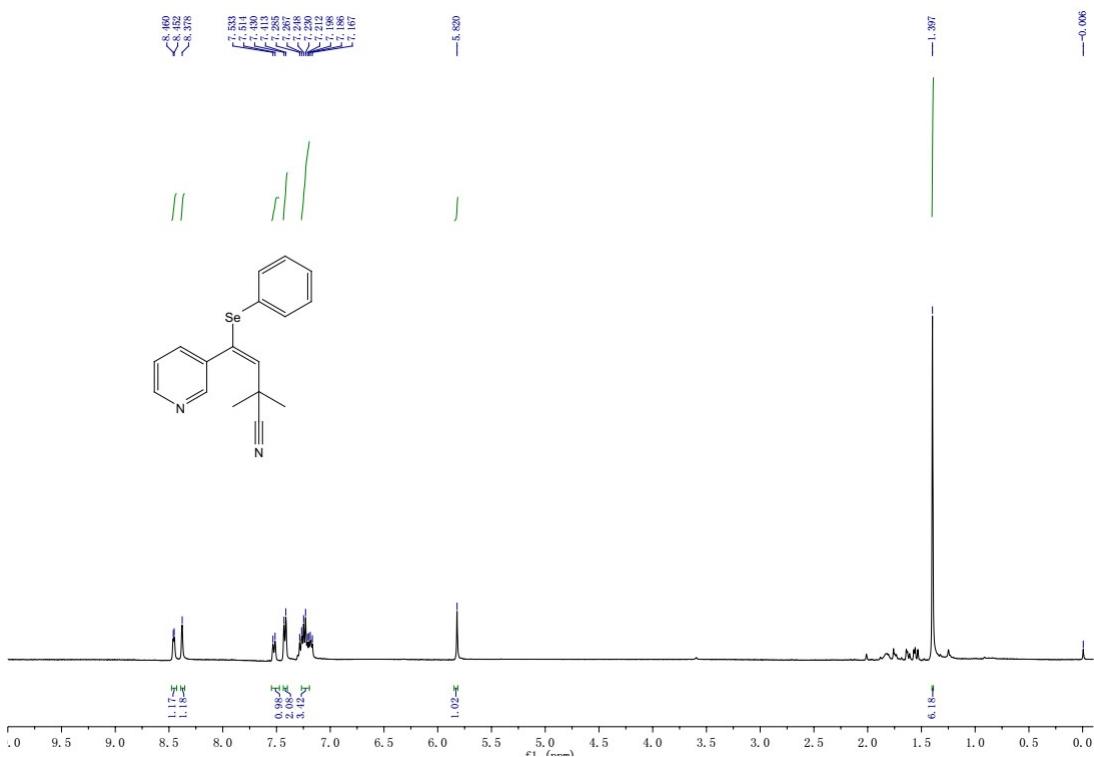
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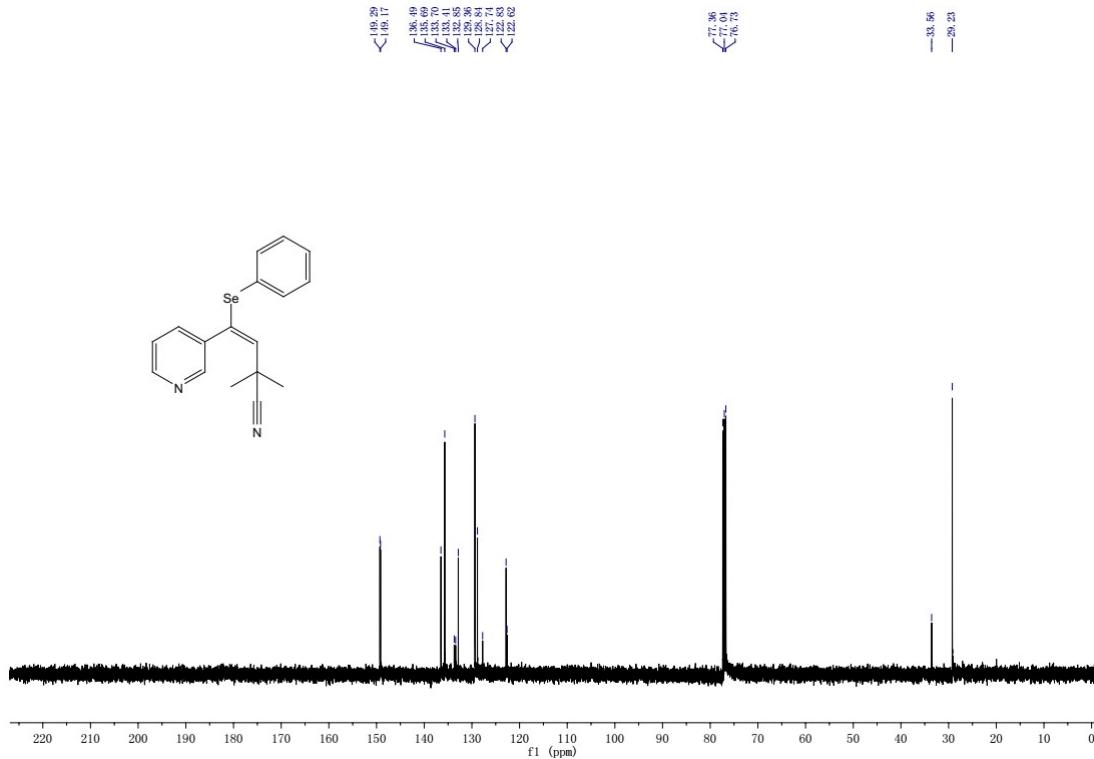
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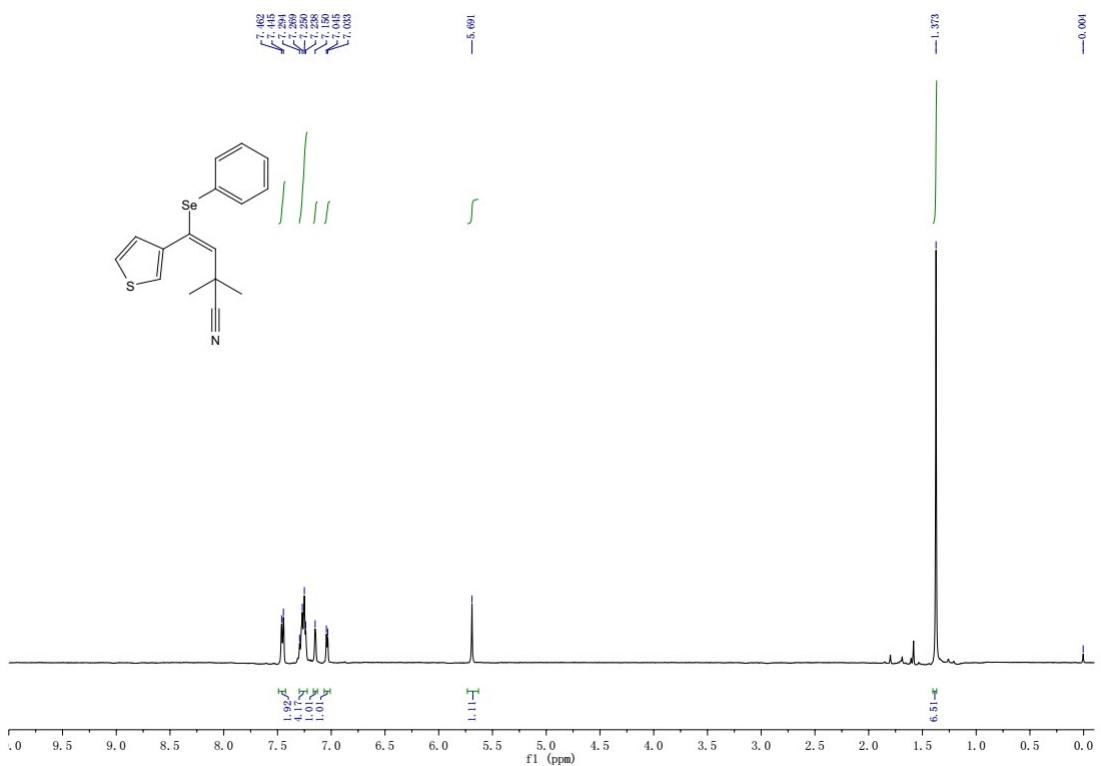
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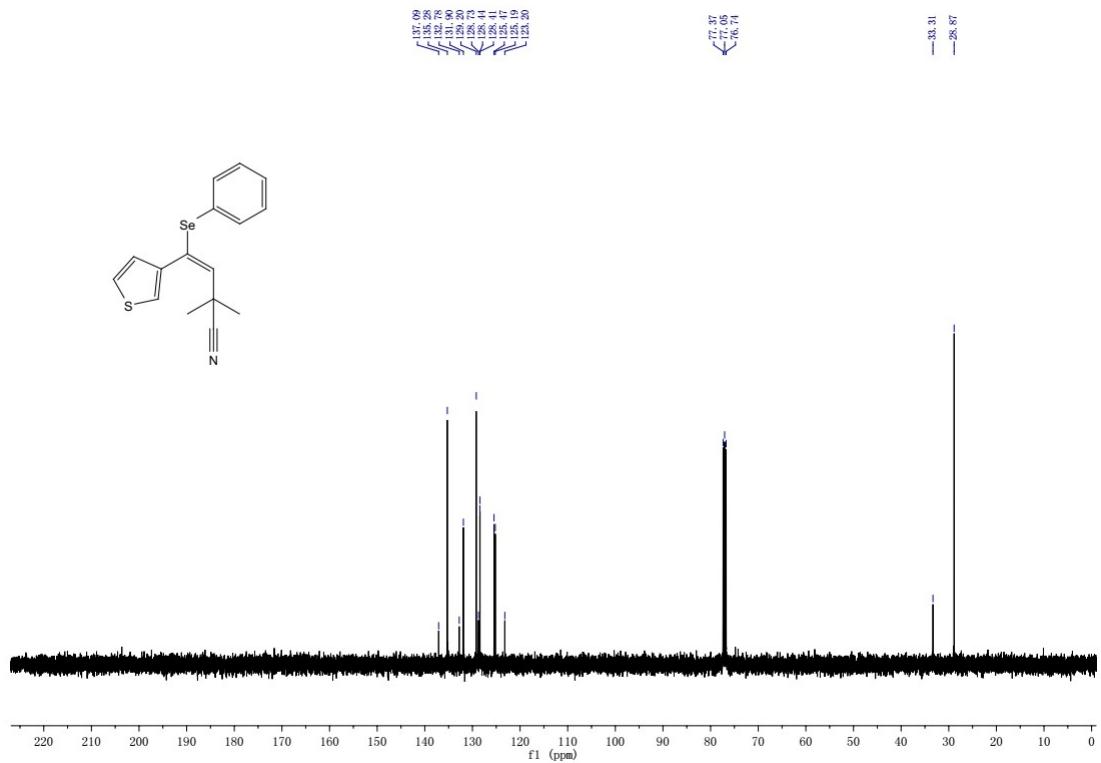
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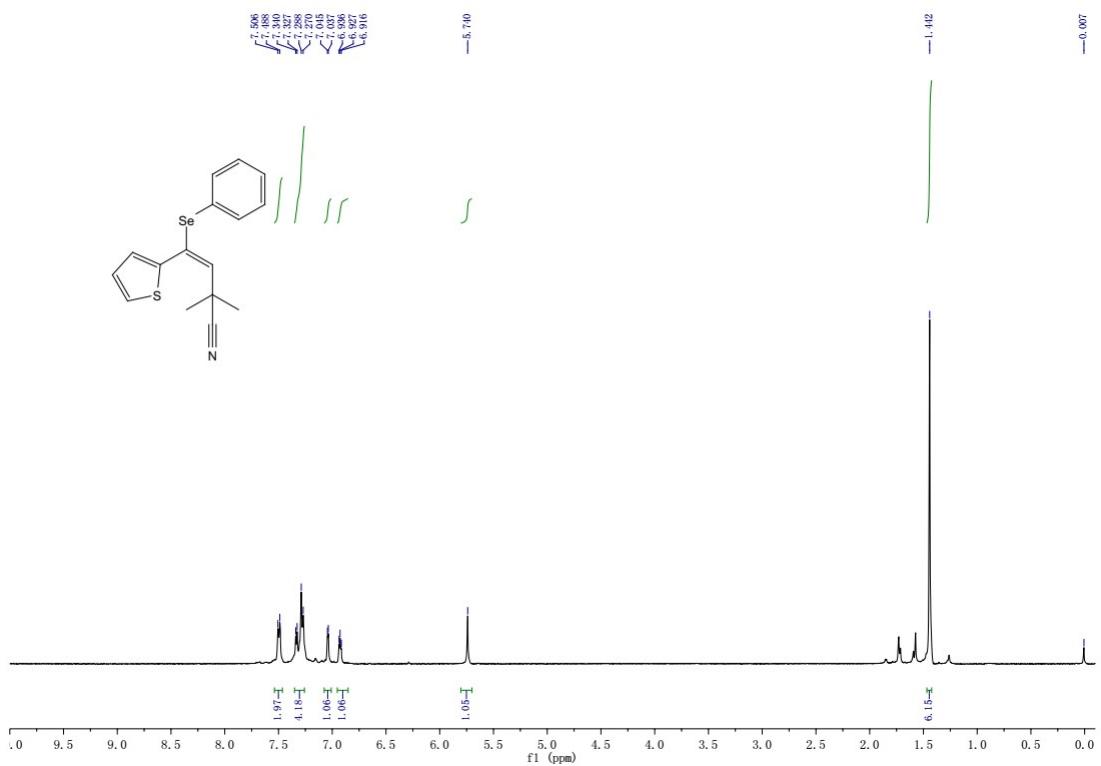
400 MHz ^1H NMR for compound **4u**



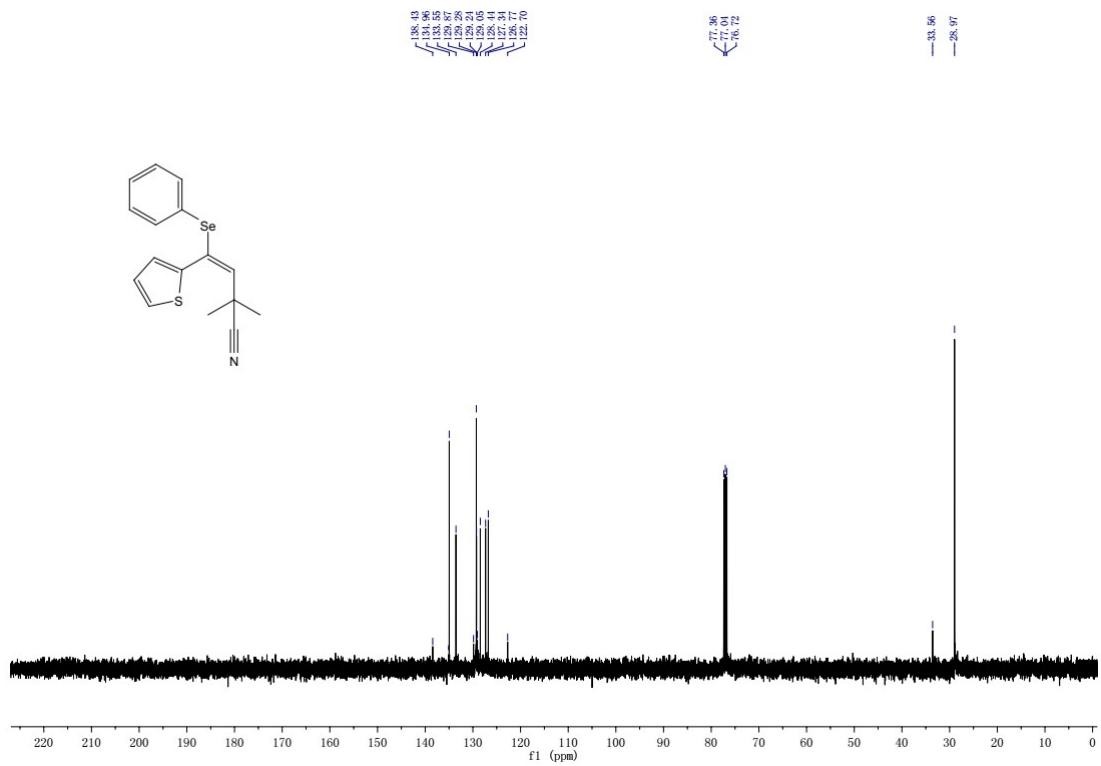
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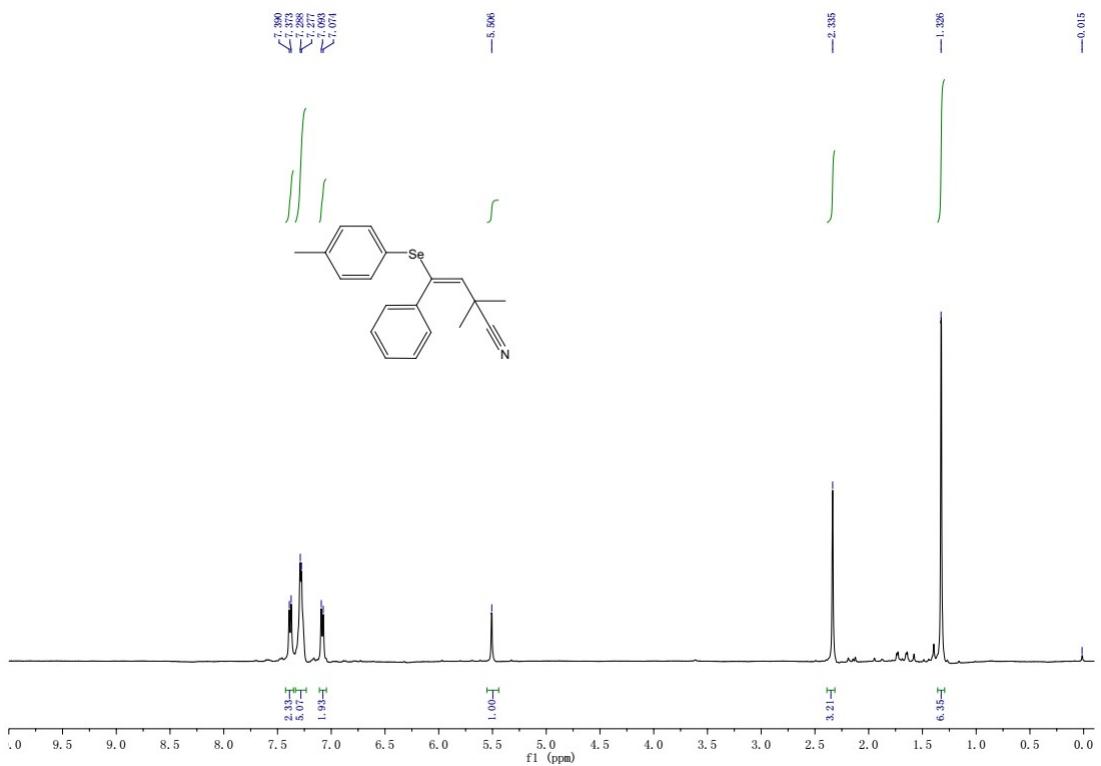
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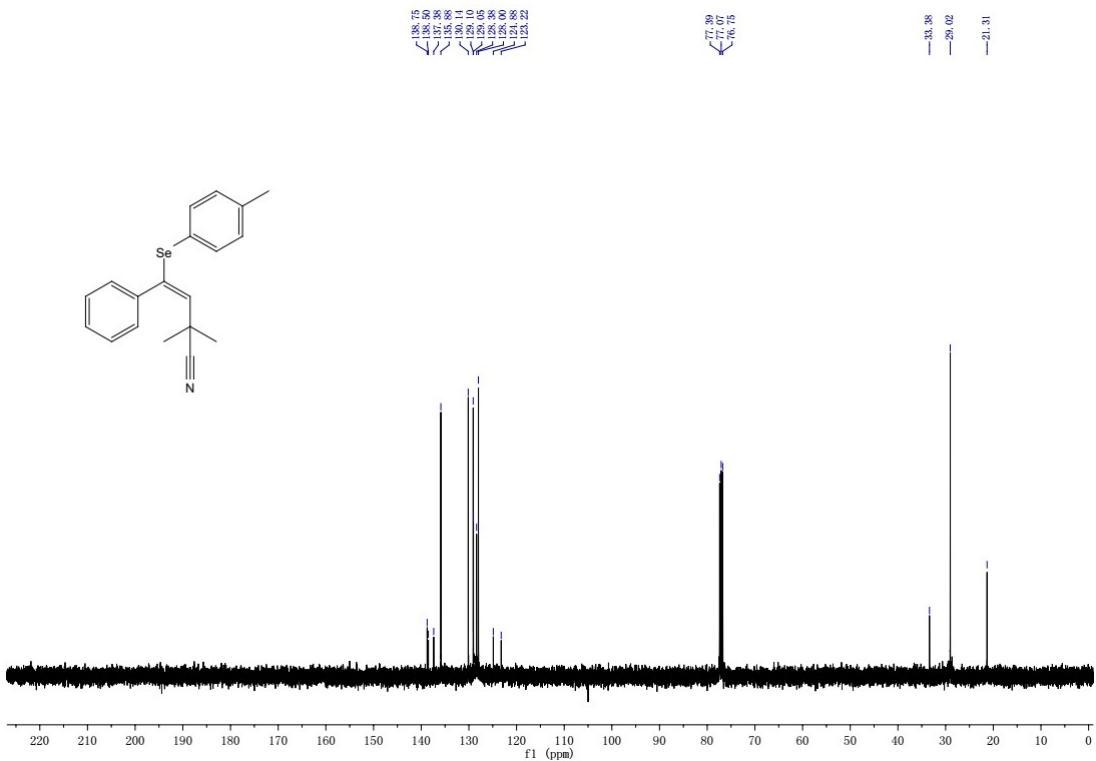
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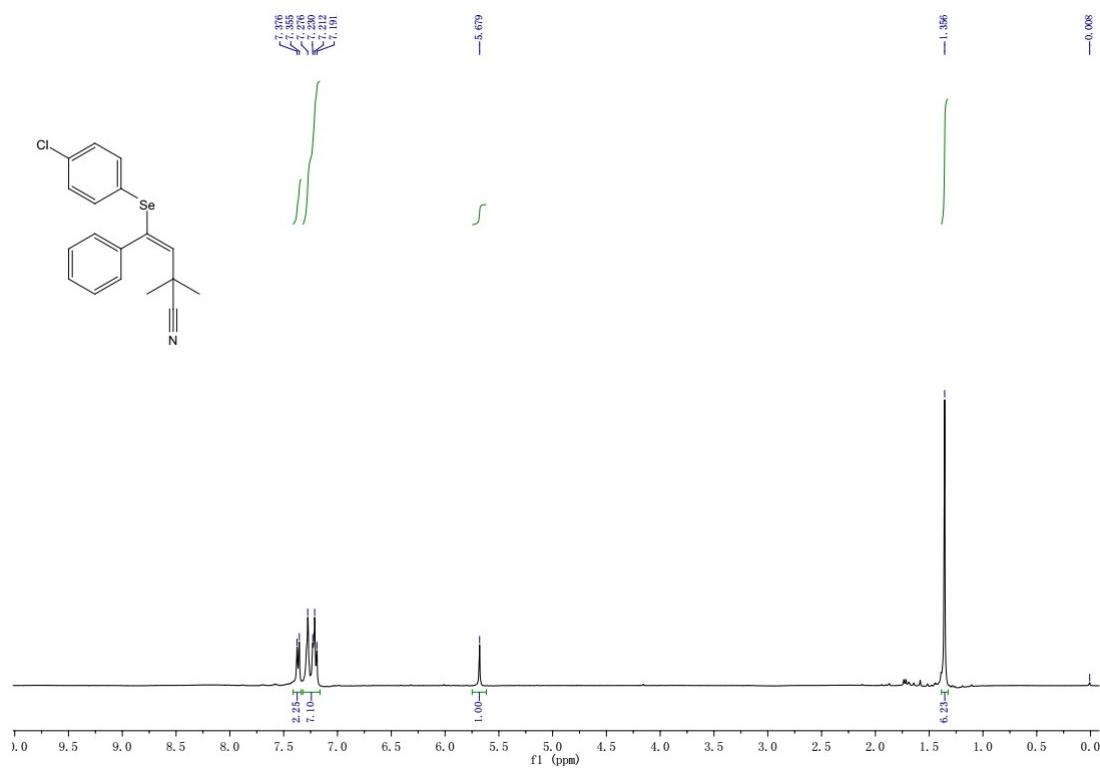
400 MHz ^1H NMR for compound **5a**



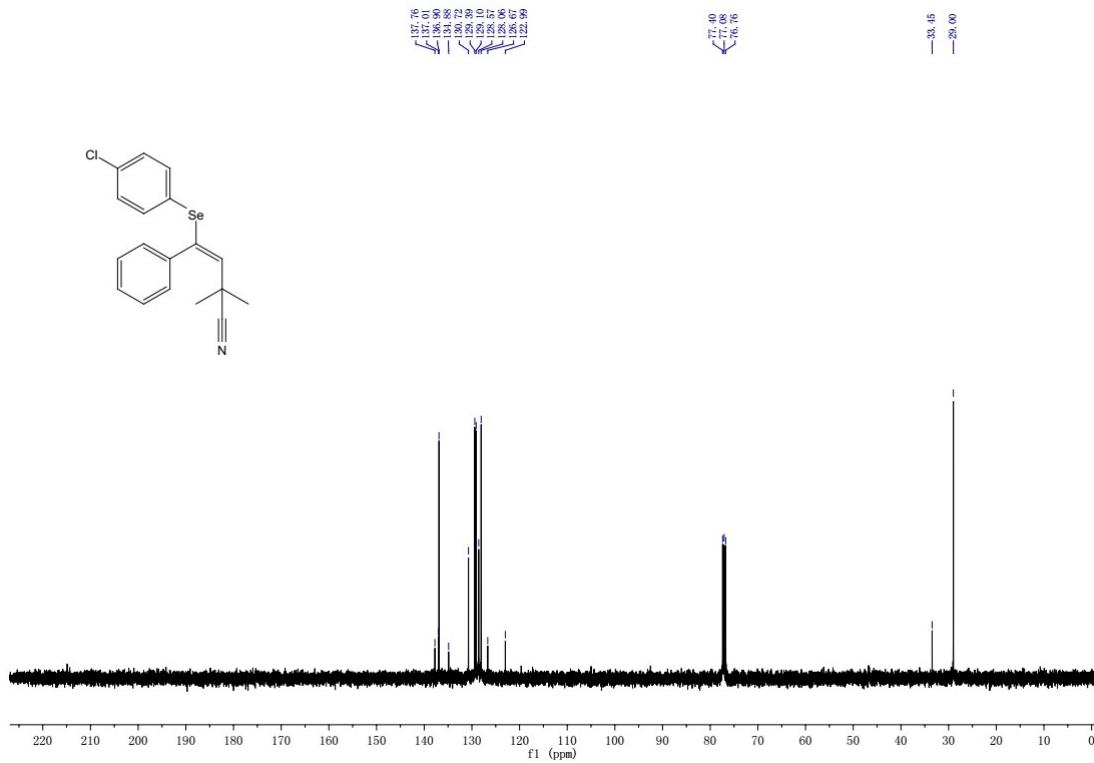
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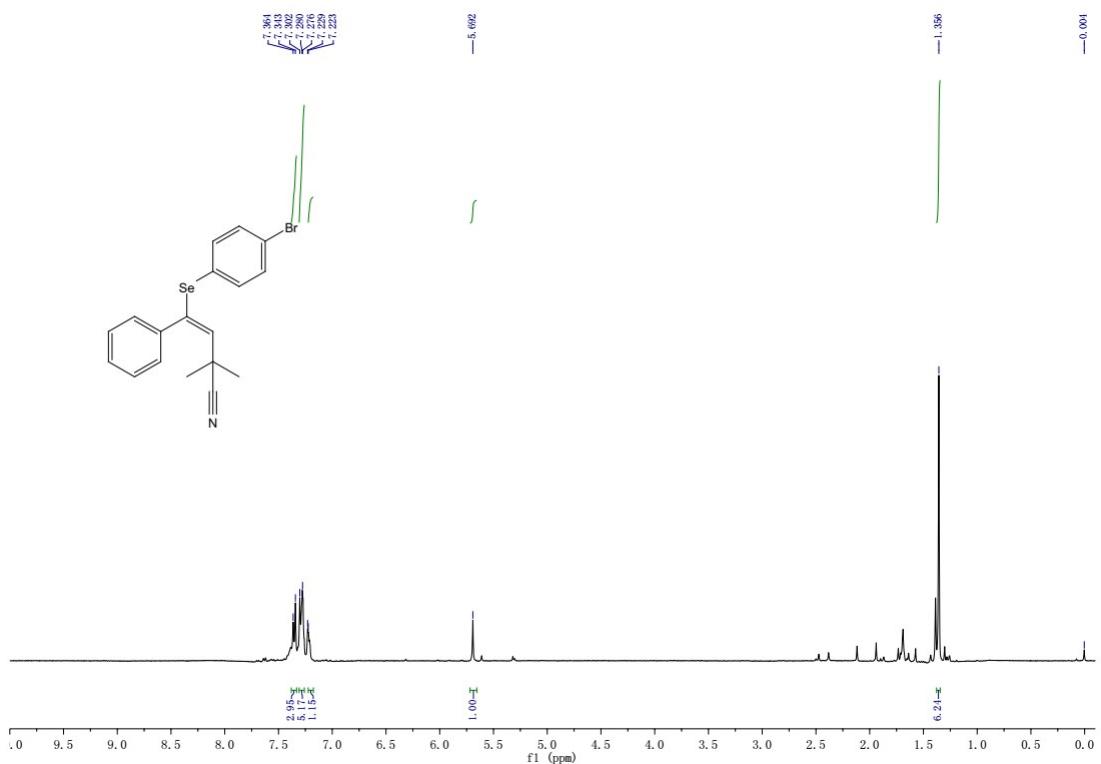
400 MHz ^1H NMR for compound **5b**



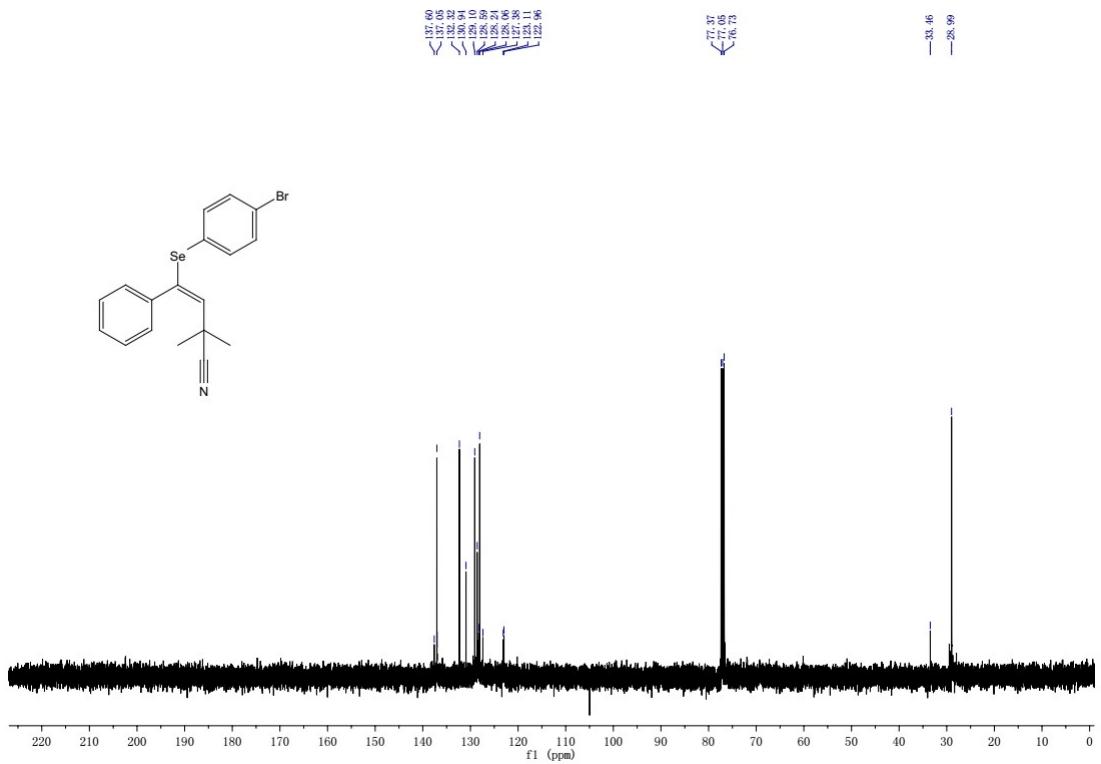
100 MHz ^{13}C NMR for compound **5b**



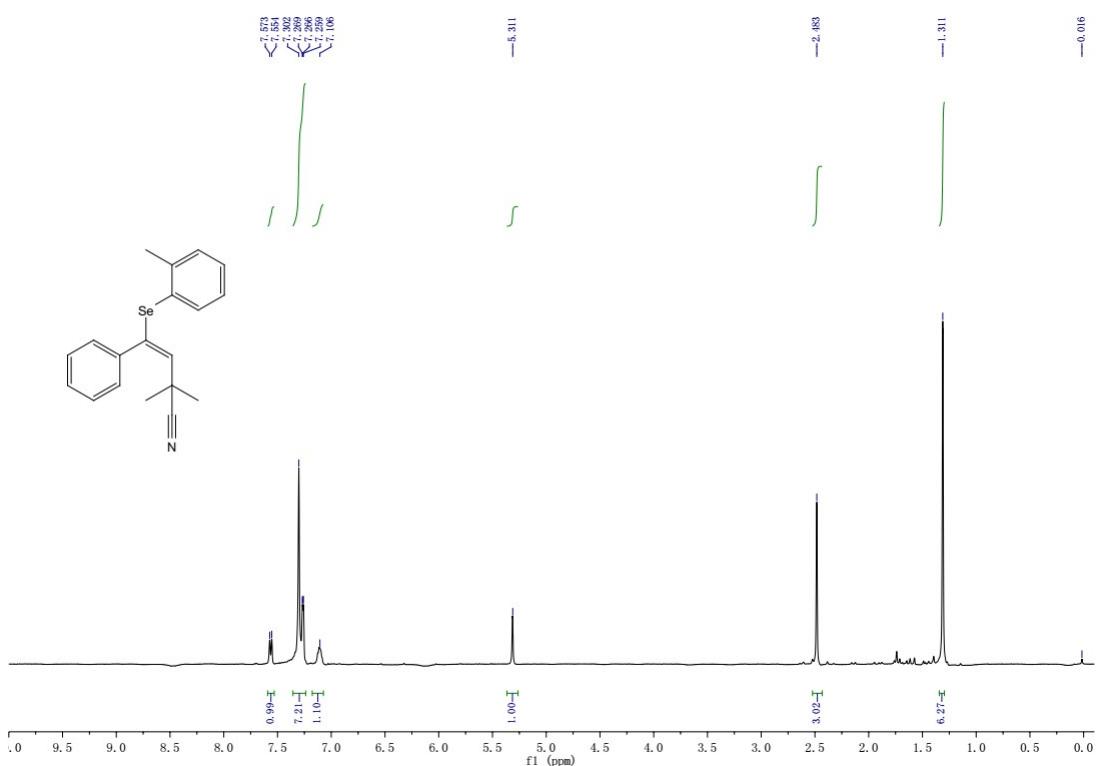
400 MHz ^1H NMR for compound **5c**



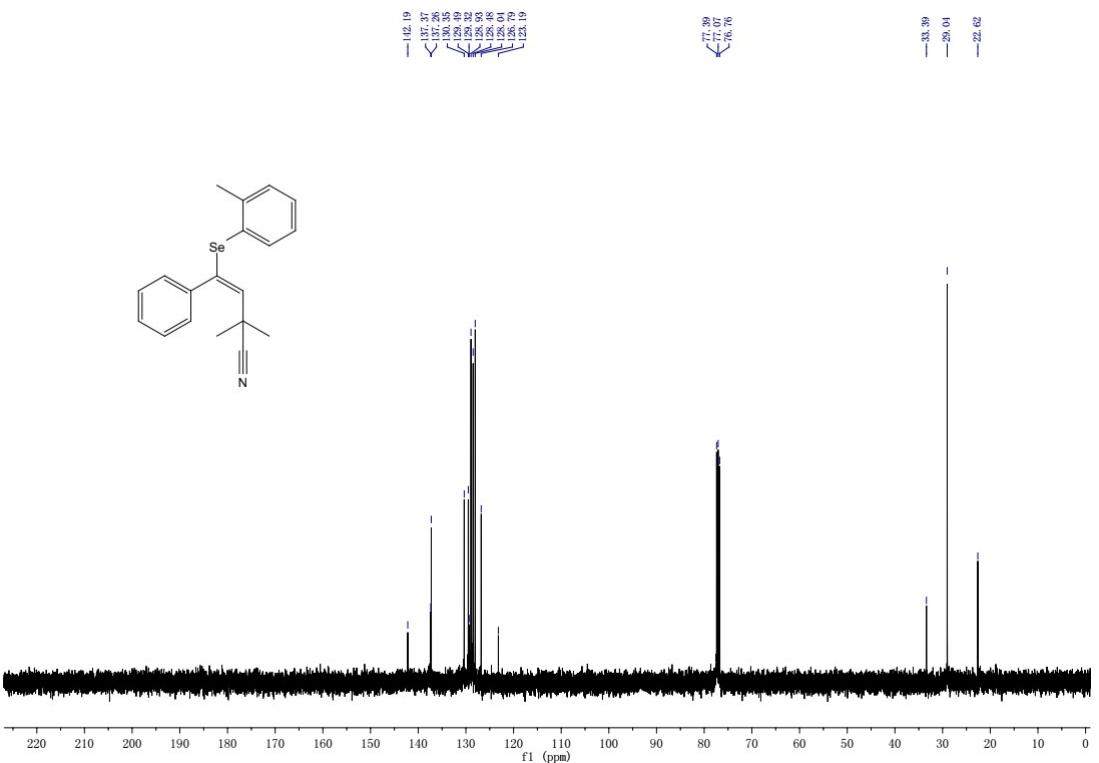
100 MHz ^{13}C NMR for compound **5c**



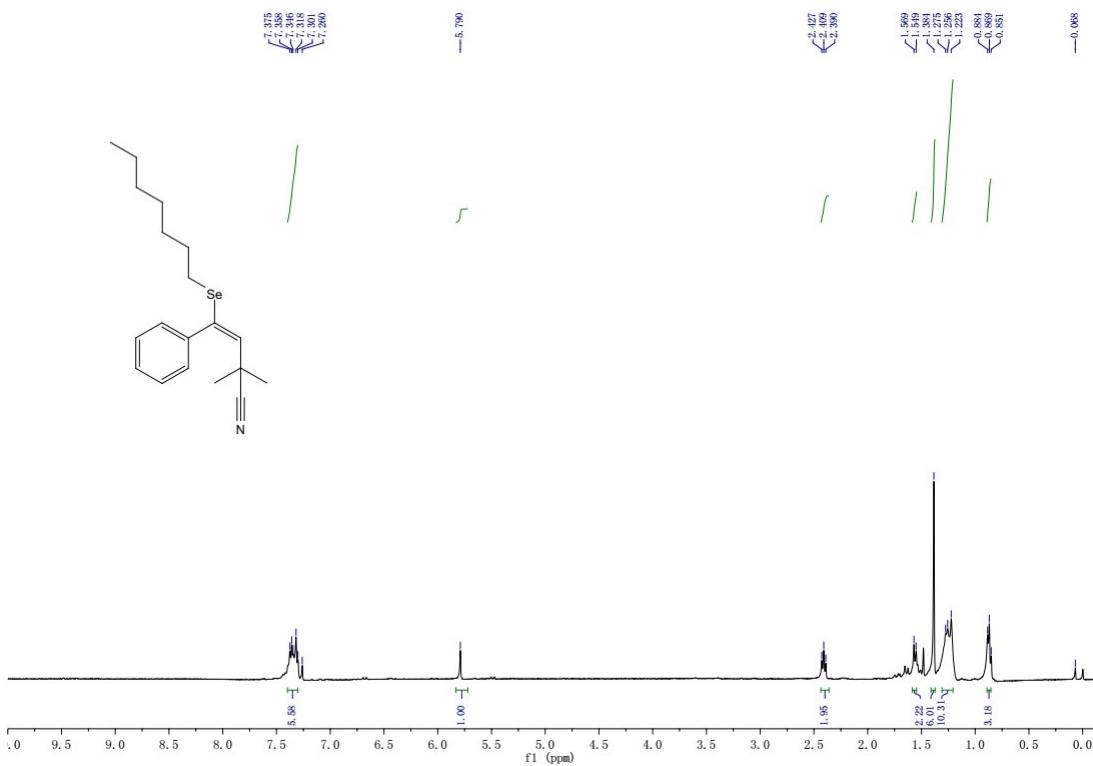
400 MHz ^1H NMR for compound **5d**



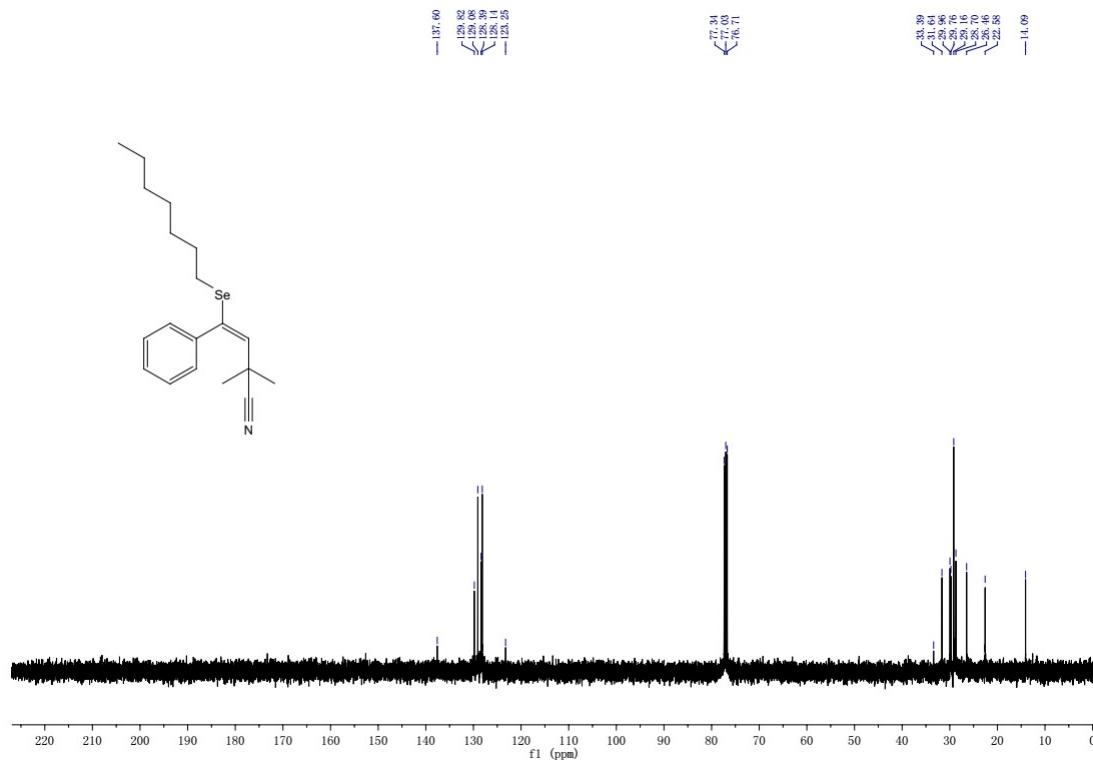
100 MHz ^{13}C NMR for compound **5d**



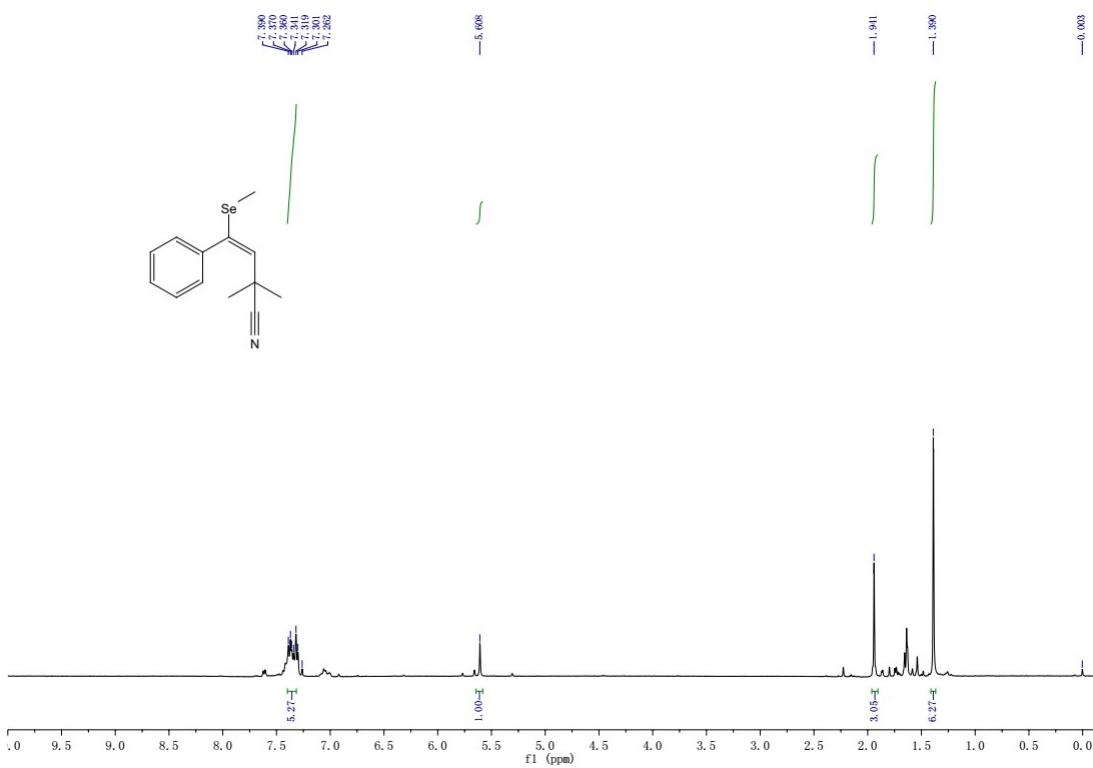
400 MHz ^1H NMR for compound **5e**



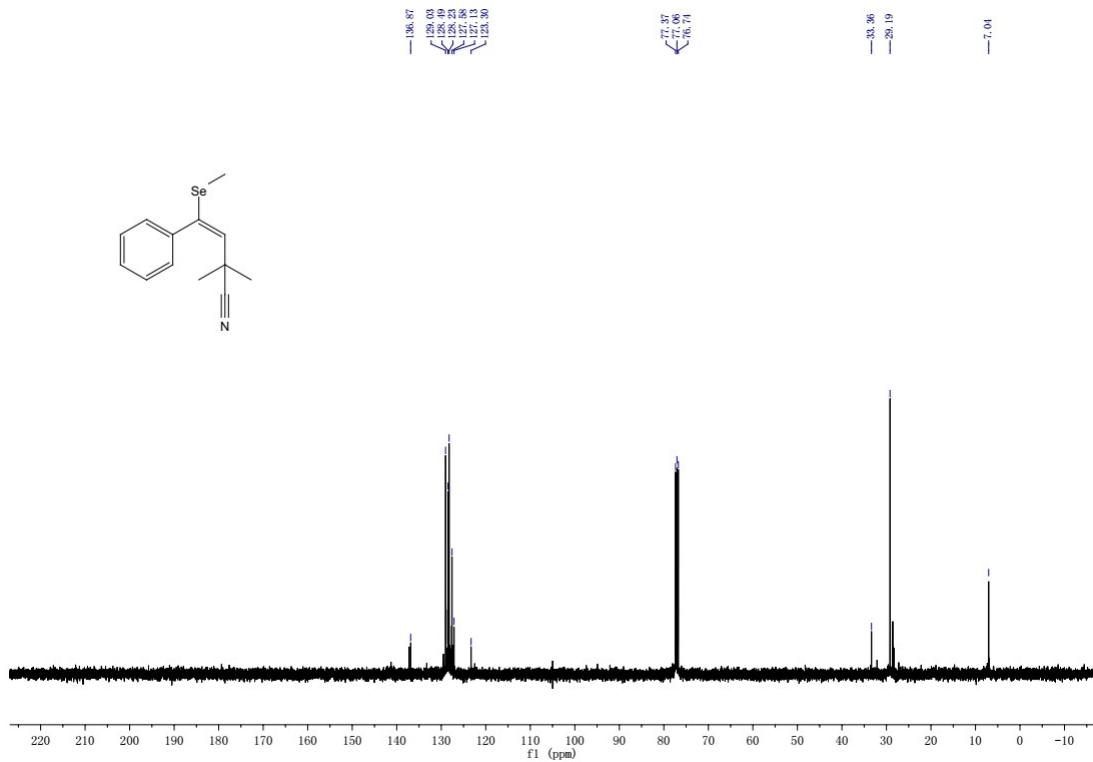
100 MHz ^{13}C NMR for compound **5e**



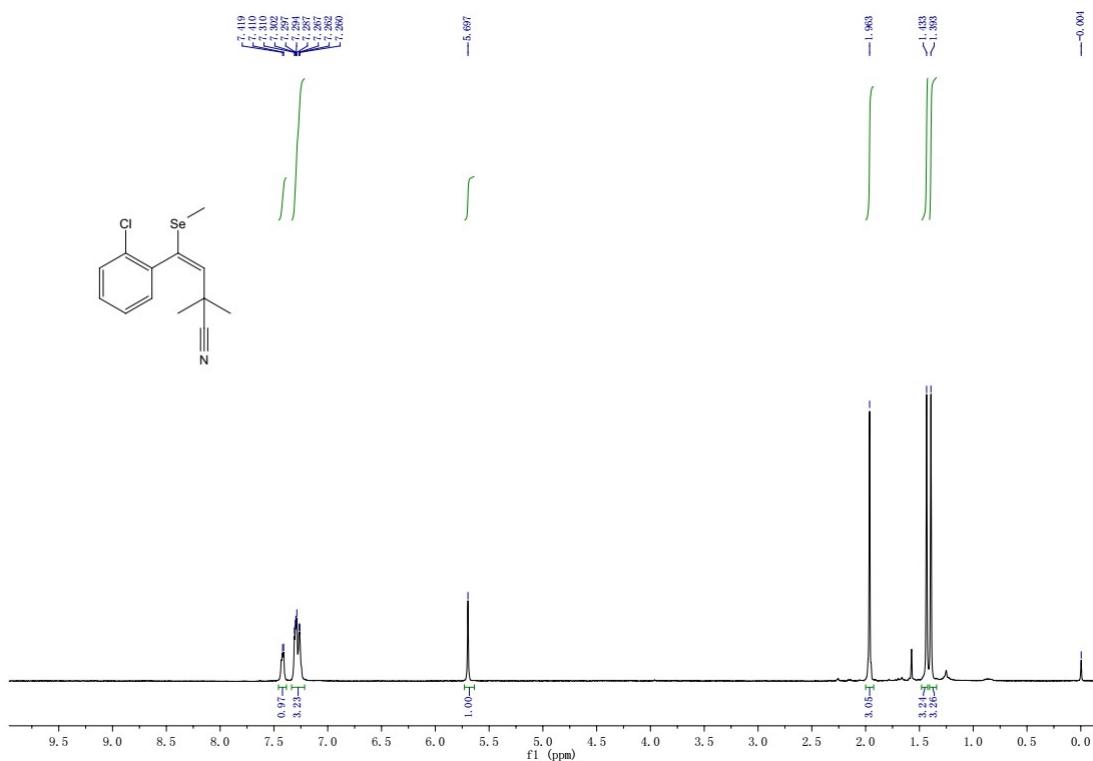
400 MHz ^1H NMR for compound 5f



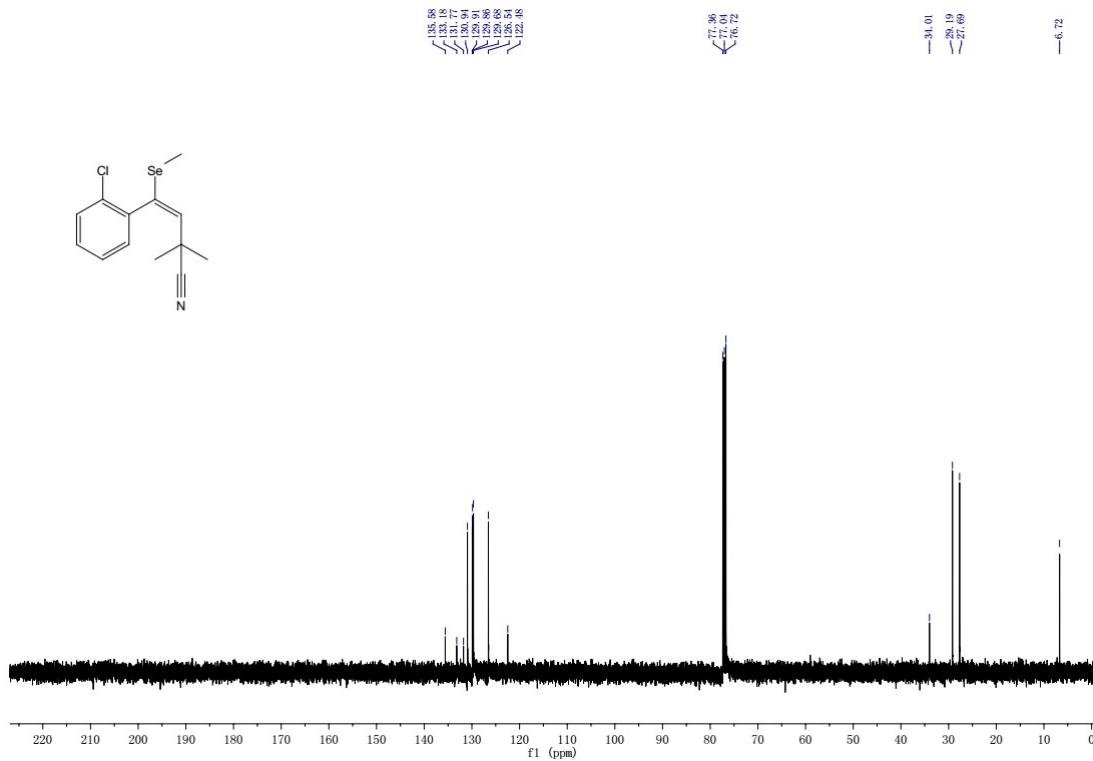
100 MHz ^{13}C NMR for compound 5f



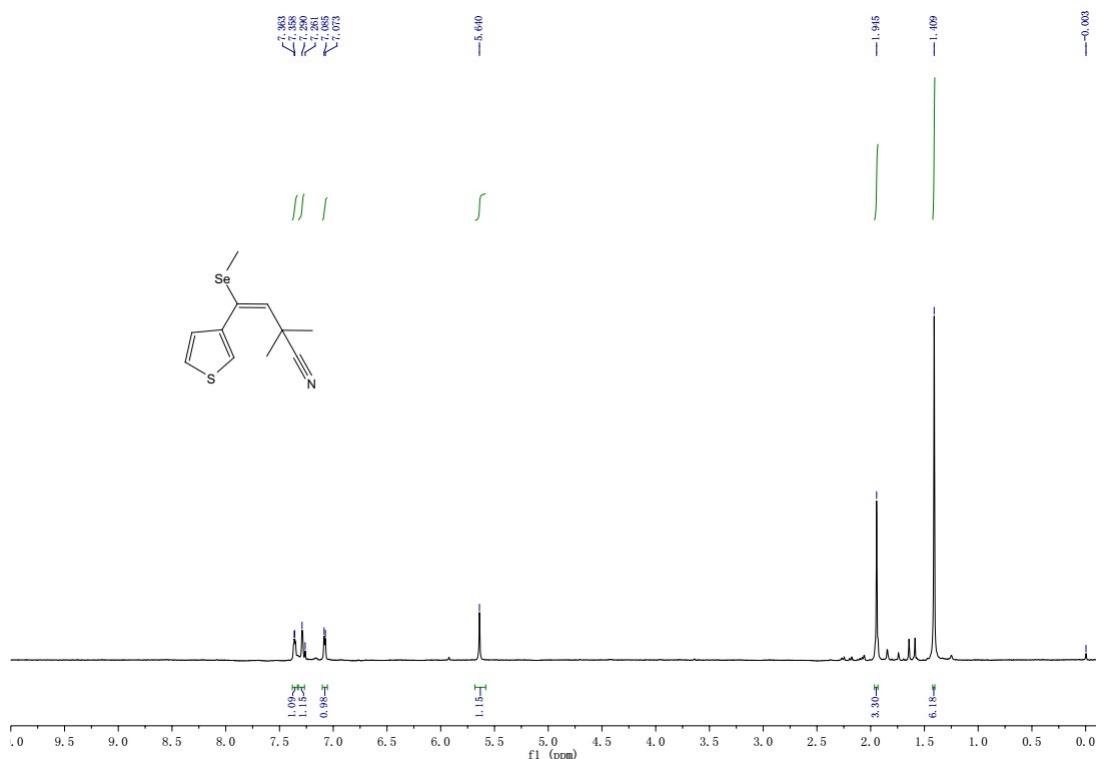
400 MHz ^1H NMR for compound **5g**



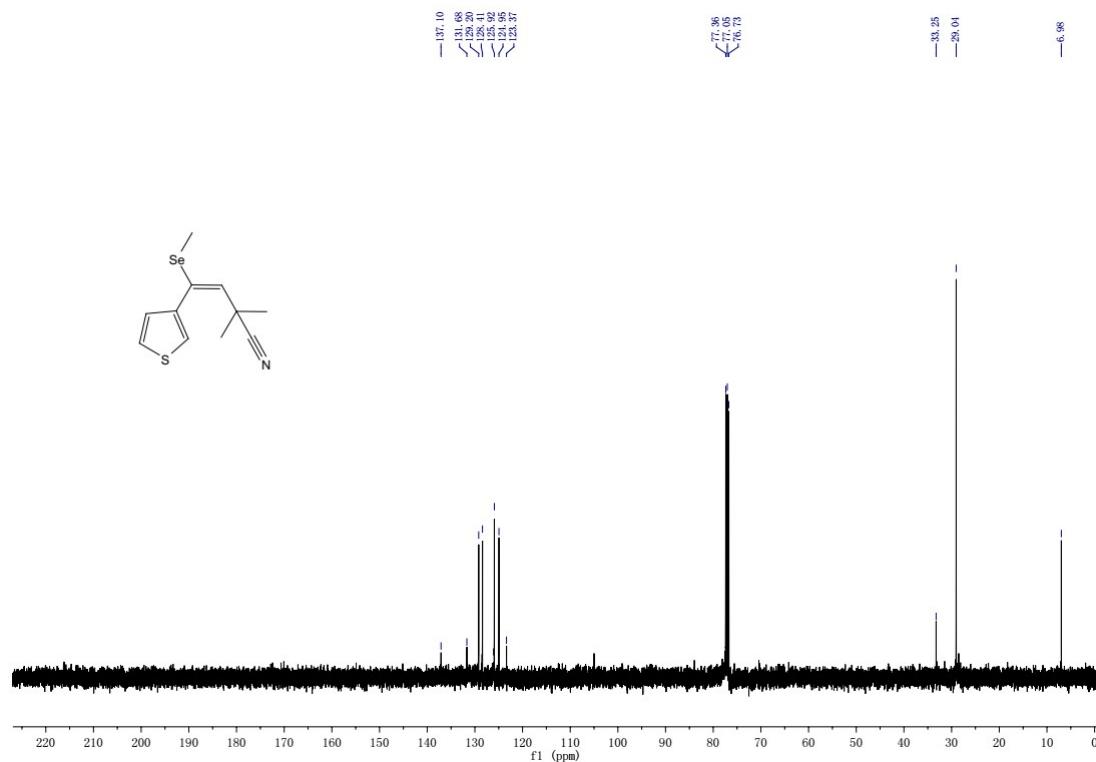
100 MHz ^{13}C NMR for compound **5g**



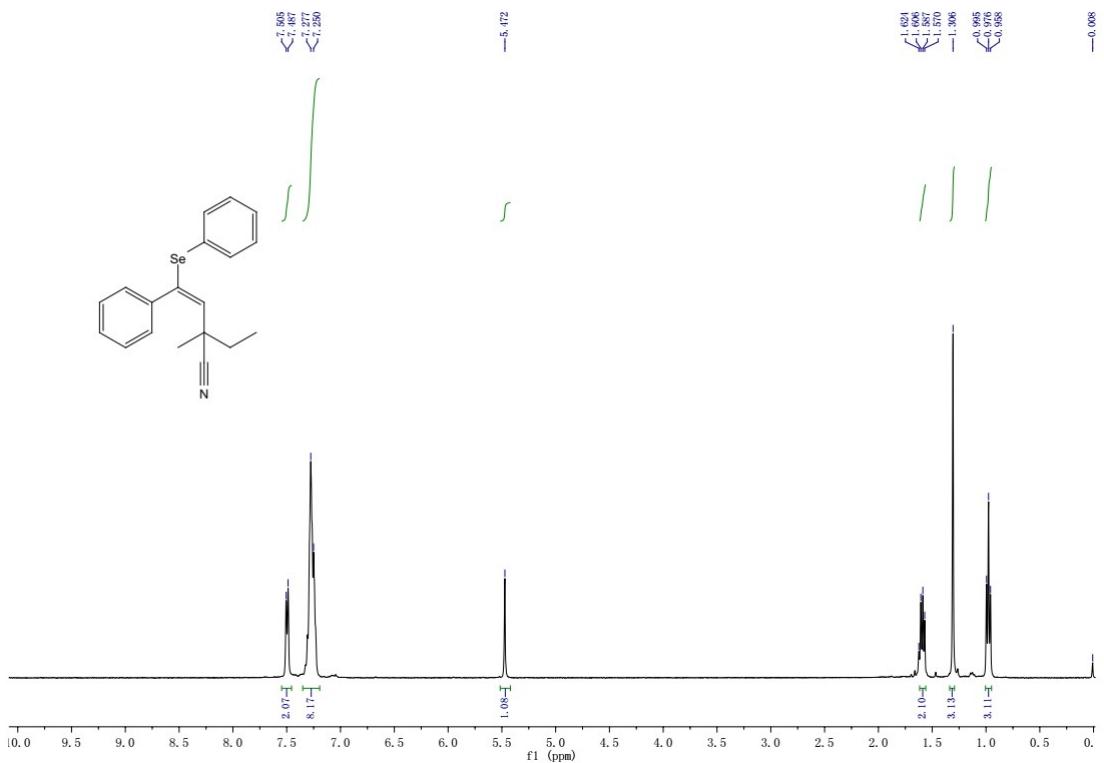
400 MHz ^1H NMR for compound **5h**



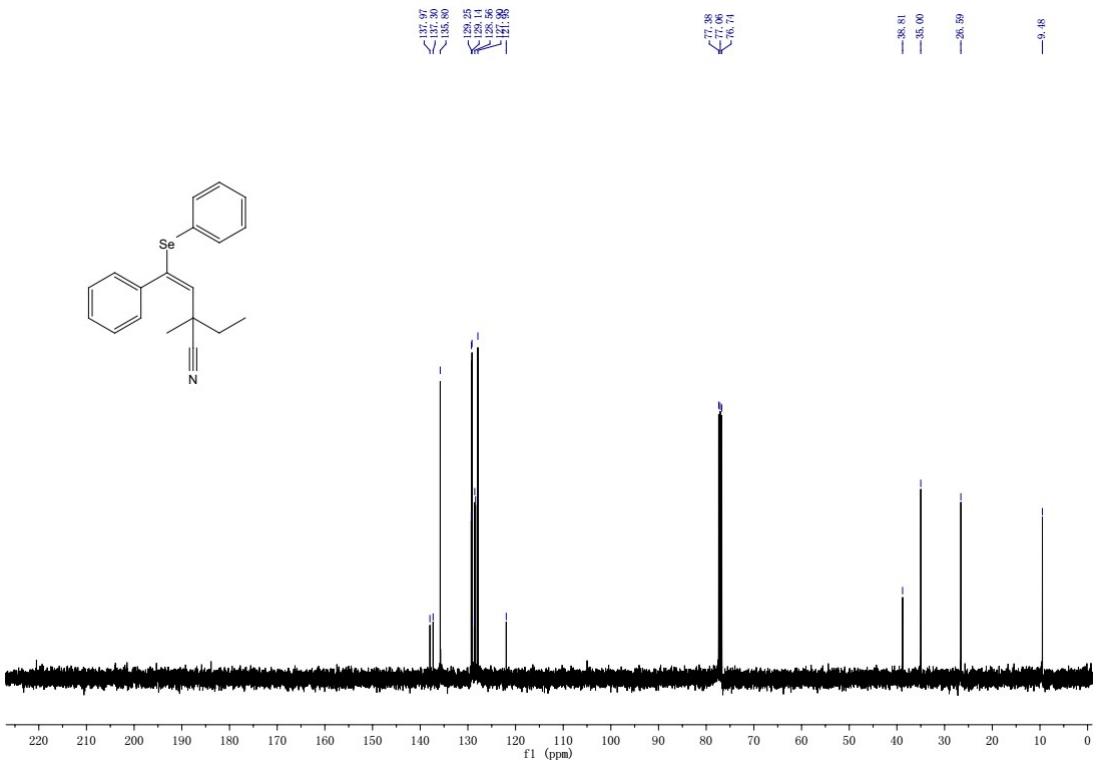
100 MHz ^{13}C NMR for compound **5h**



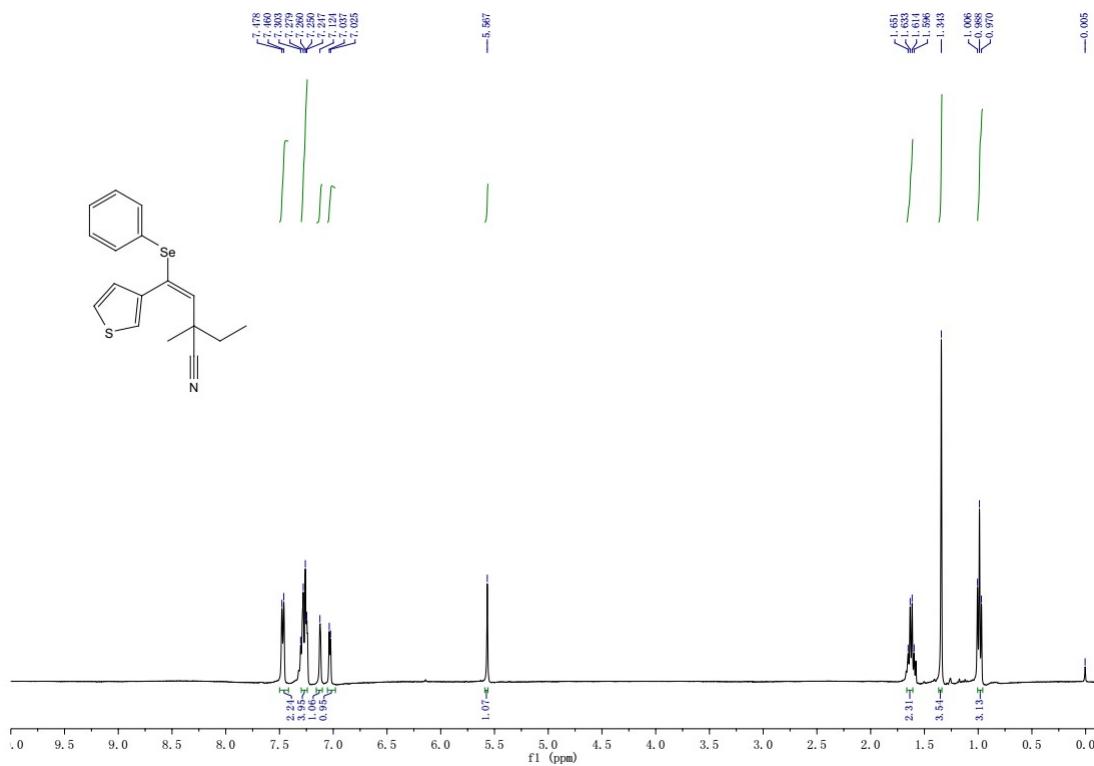
400 MHz ^1H NMR for compound 5i



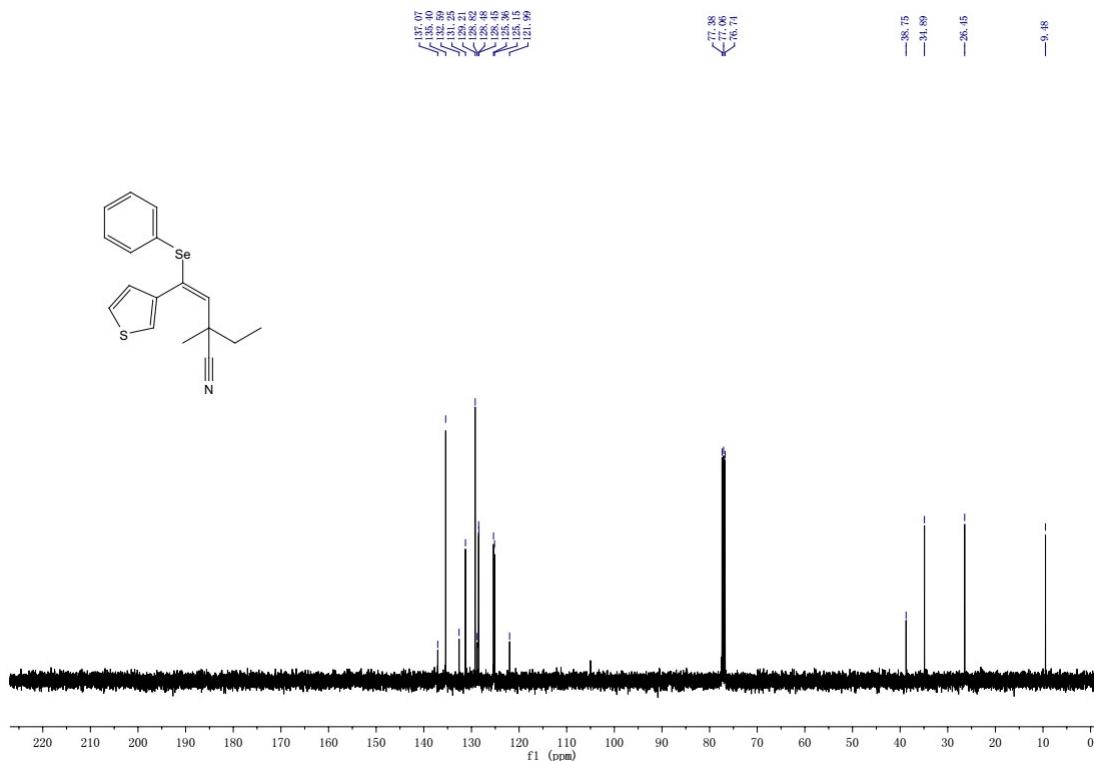
100 MHz ^{13}C NMR for compound 5i



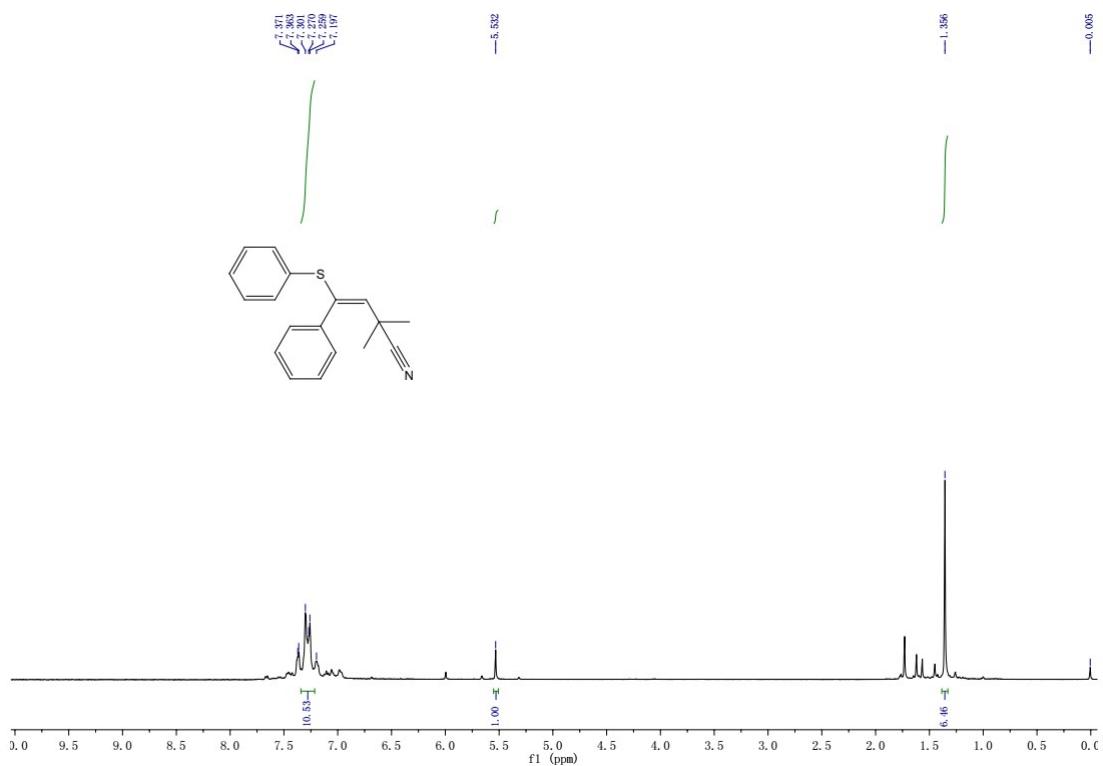
400 MHz ^1H NMR for compound 5j



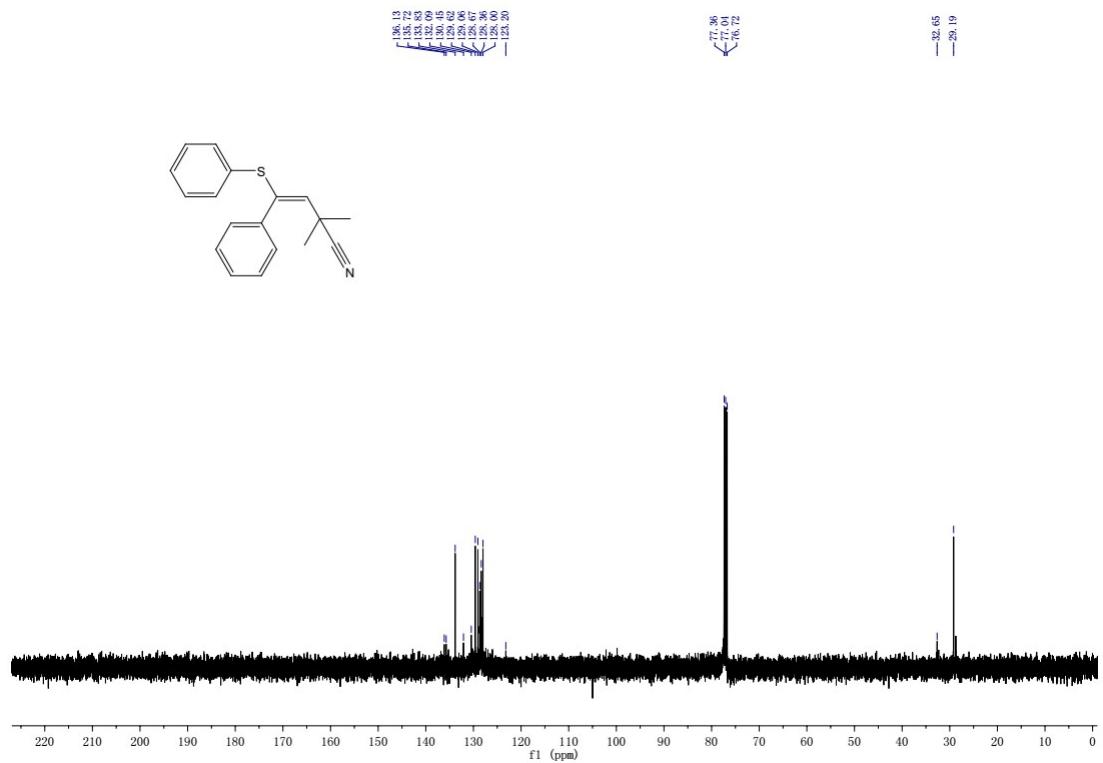
100 MHz ^{13}C NMR for compound 5j



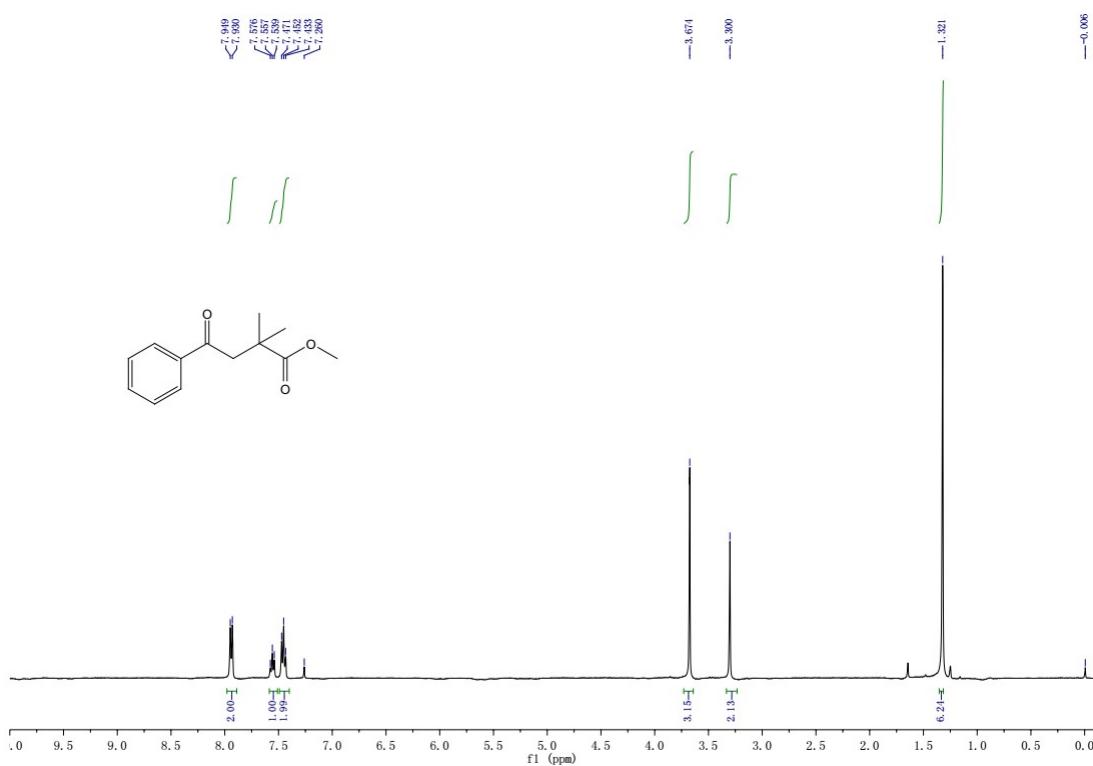
400 MHz ^1H NMR for compound **5k**



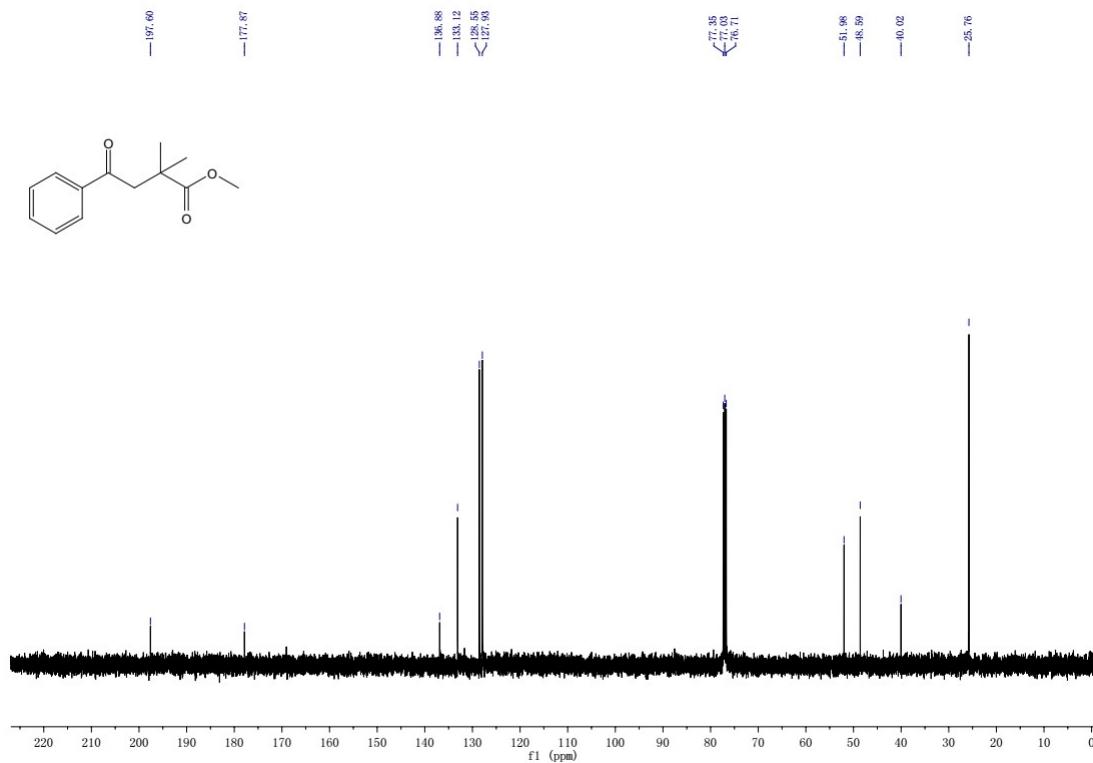
100 MHz ^{13}C NMR for compound **5k**



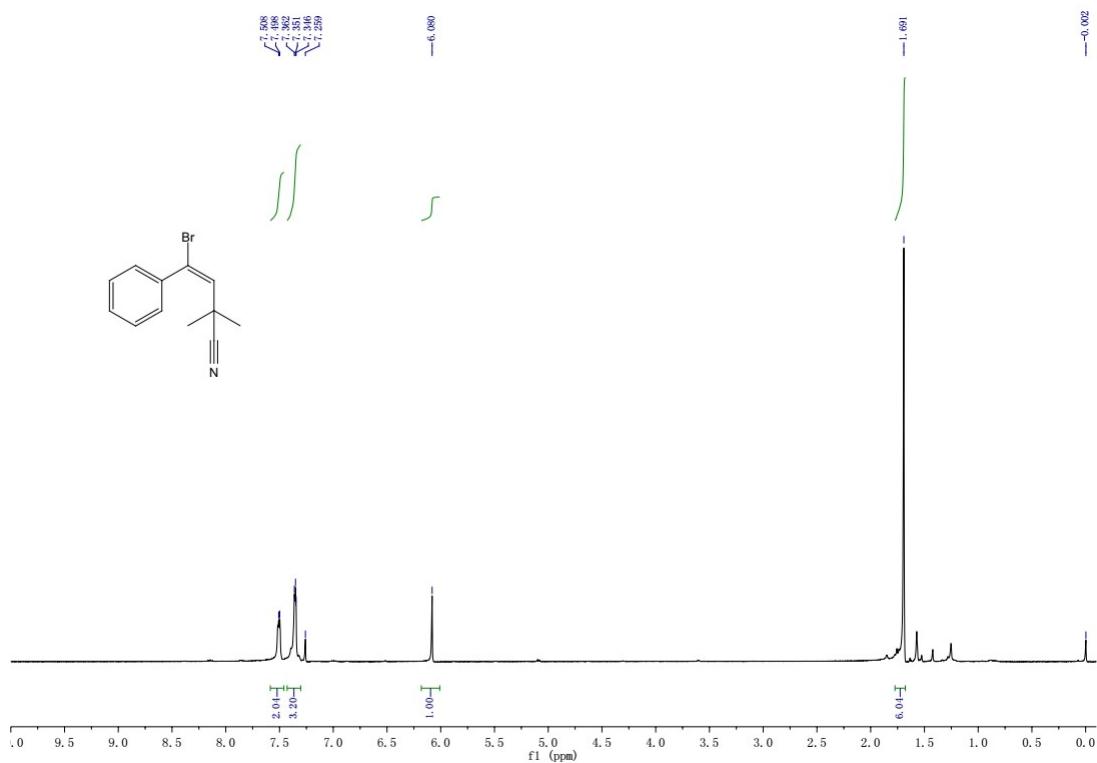
400 MHz ^1H NMR for compound 6



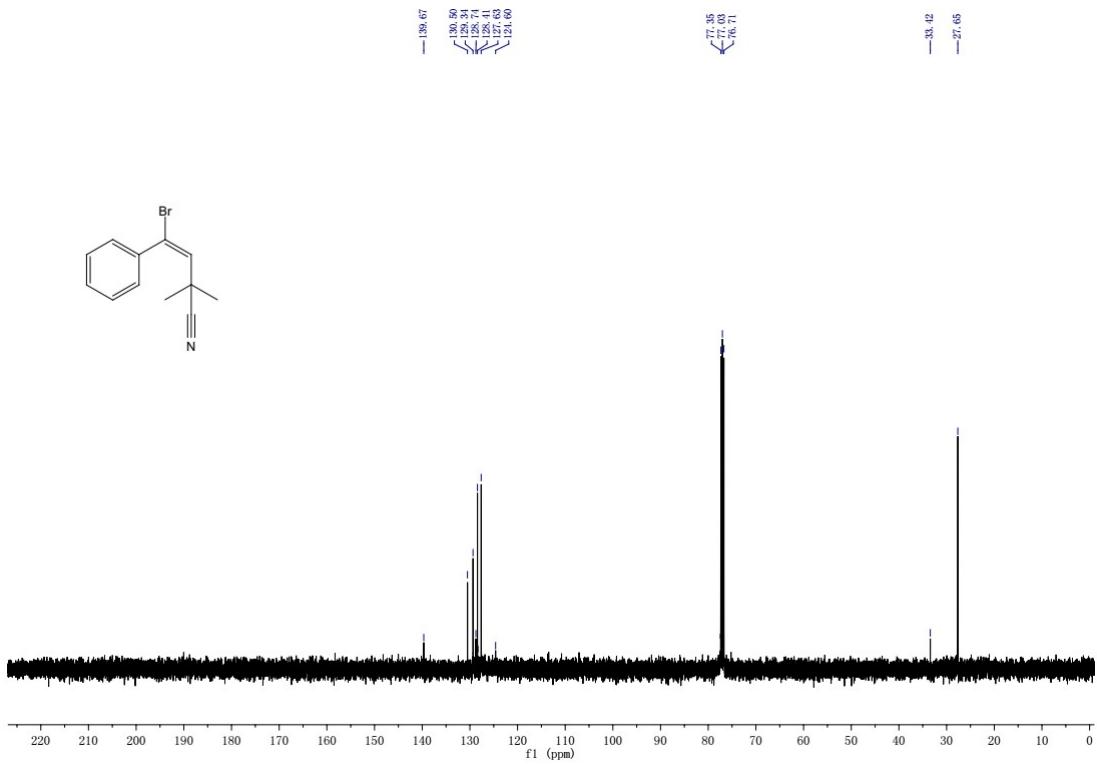
100 MHz ^{13}C NMR for compound 6



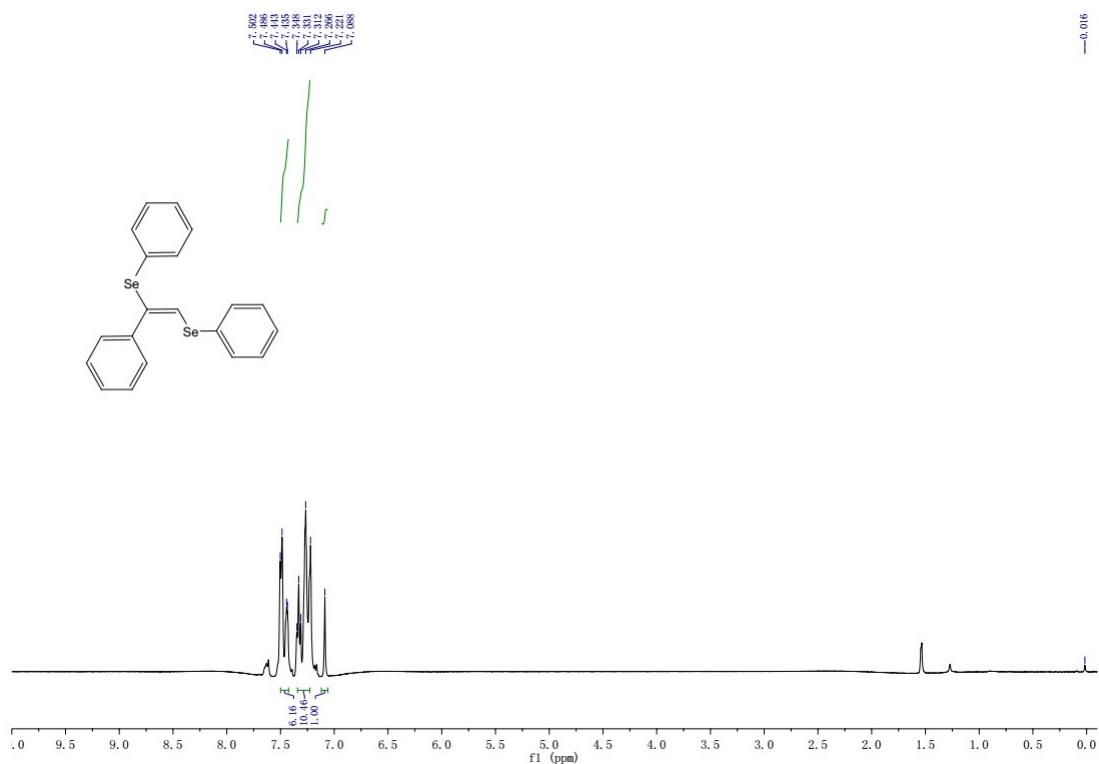
400 MHz ^1H NMR for compound 7



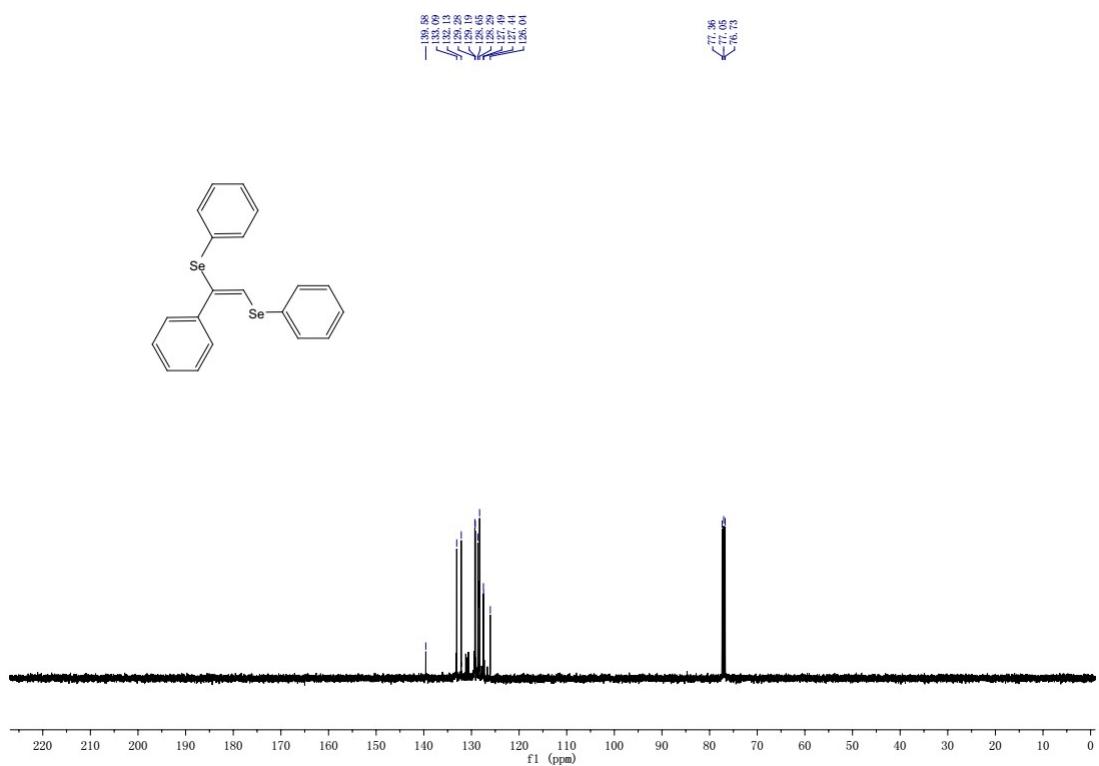
100 MHz ^{13}C NMR for compound 7



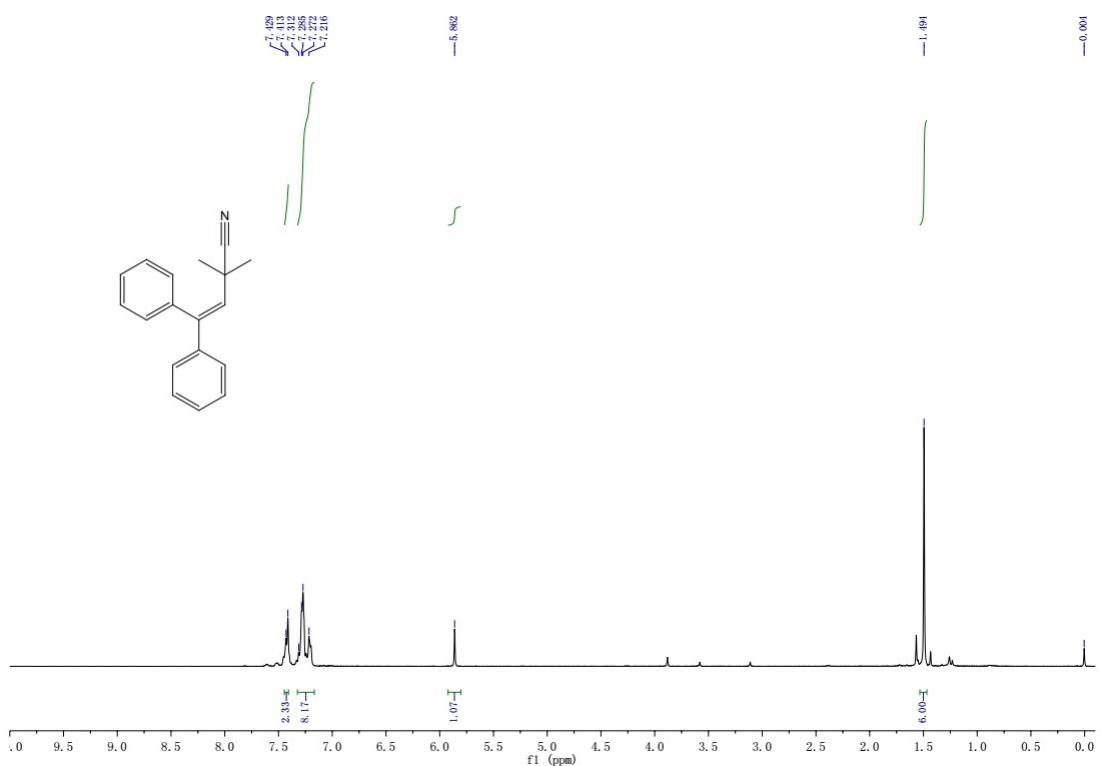
400 MHz ^1H NMR for compound 8



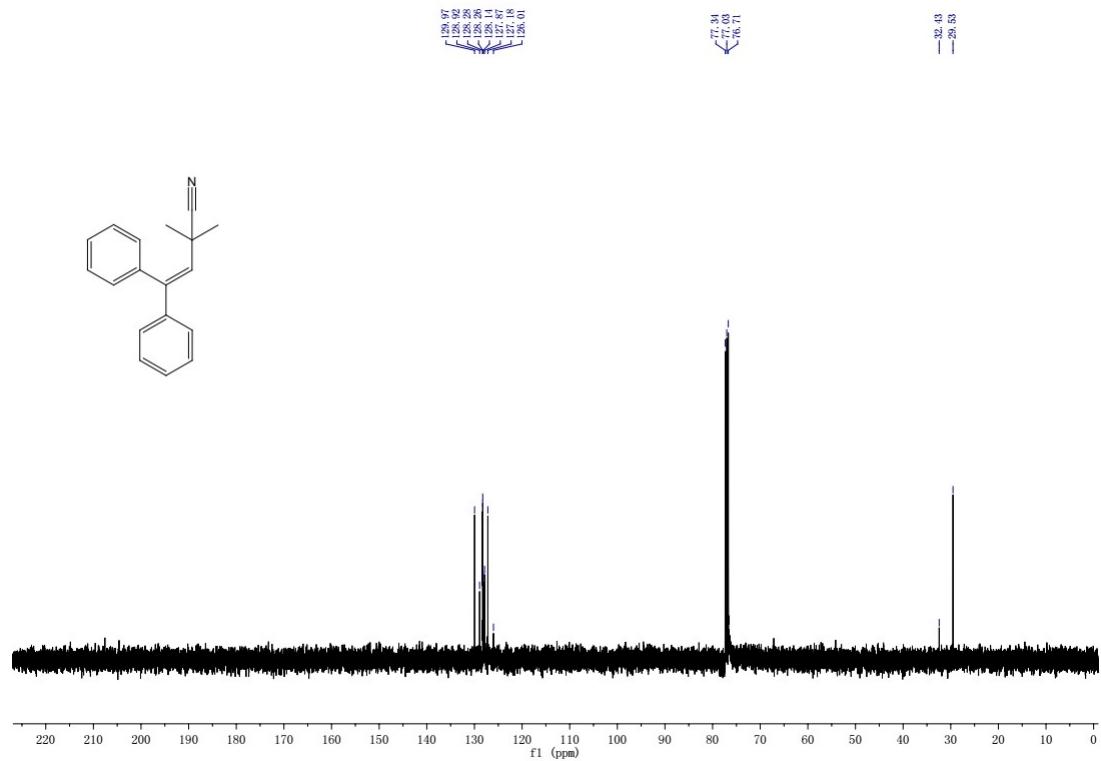
100 MHz ^{13}C NMR for compound 8



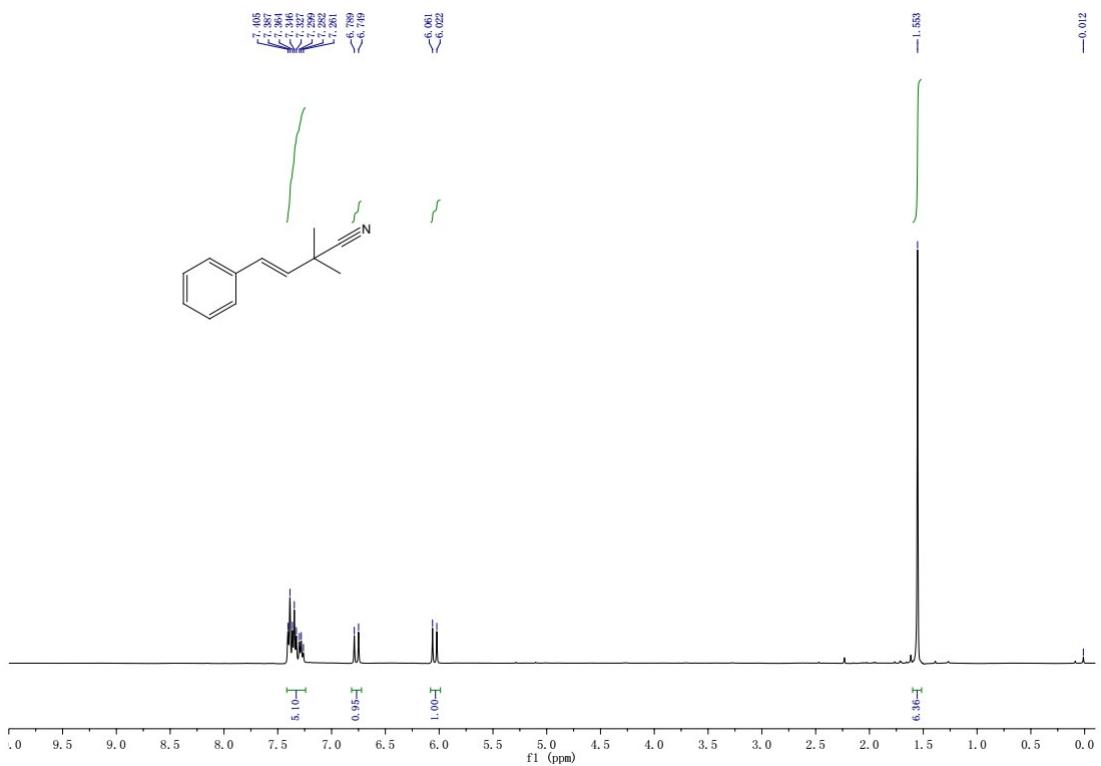
400 MHz ^1H NMR for compound **10**



100 MHz ^{13}C NMR for compound **10**



400 MHz ^1H NMR for compound 11



100 MHz ^{13}C NMR for compound 11

