

Supporting Information

Aerial Oxygen-Driven Selenocyclization of *o*-Vinylanilides Mediated by Coupled Fe³⁺/Fe²⁺ and I₂/I⁻ Redox Cycles

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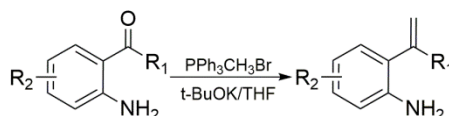
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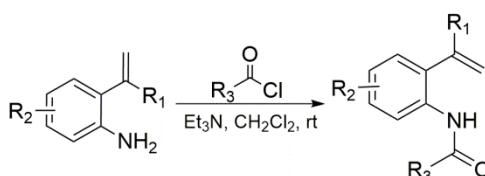
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1. General synthetic procedures and characterization of *o*-vinylanilides

1.1 General synthetic procedures^[1]



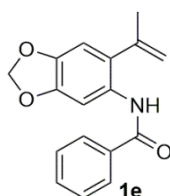
Step 1: To a mixture of 2-aminoacetophenones (22.2 mmol), methyltriphenylphosphonium bromide (33.3 mmol) was added potassium *t*-butylate (1.0 M in THF, 34 mL) under argon atmosphere. The reaction was stirred overnight at ambient temperature. The reaction solution was concentrated *in vacuo* and redissolved in ethyl acetate (20 mL). The ethyl acetate solution was washed with saturated aqueous NaHCO₃ (20 mL). The organic phase was dried over anhydrous MgSO₄ and concentrated *in vacuo*. Flash column chromatography afforded desired *o*-aminostyrene intermediates.



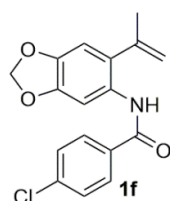
Step 2: To a solution of 2-aminostyrenes (18.9 mmol) and Et₃N (28.3 mmol) in CH₂Cl₂ (60 mL) was added benzoylchloride (22.7 mmol) at 0 °C. The reaction was stirred for 3 h at ambient temperature. The reaction solution was concentrated *in vacuo*. Flash column chromatography afforded *o*-vinylanilides (**1a–1o**) in pure form.

The characterization data of known *o*-vinylanilides (**1a–1d** and **1i–1o**) are in agreement with previous reports^[2–5].

1.2 Characterization of new *o*-vinylanilides (**1e–1h**)

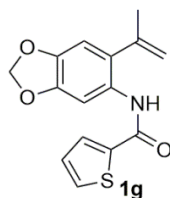


***N*-(6-(Prop-1-en-2-yl)benzo[*d*][1,3]dioxol-5-yl)benzamide (1e):** a white solid; mp 77–80 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.36 (br, 1H), 8.04 (s, 1H), 7.82 (t, *J* = 7.4 Hz, 2H), 7.57–7.47 (m, 3H), 6.67 (s, 1H), 5.97 (s, 2H), 5.45 (s, 1H), 5.09 (s, 1H), 2.08 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.8, 146.8, 143.9, 143.2, 135.0, 131.7, 128.8, 128.2, 127.1, 126.8, 116.9, 107.4, 103.1, 101.3, 24.5; IR (KBr): ν_{max} 3717, 2663, 1948, 1529, 1307, 1244, 1188, 1131, 1040, 904, 846 cm⁻¹; HRMS (ESI⁺): *m/z* calcd for C₁₇H₁₆NO₃ [M+H]⁺ 282.1125; found 282.1128.

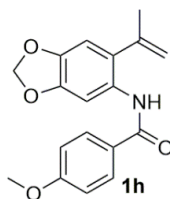


4-Chloro-*N*-(6-(prop-1-en-2-yl)benzo[*d*][1,3]dioxol-5-yl)benzamide (1f): a white solid;

mp 83–85 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.30 (br, 1H), 8.01 (s, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 6.68 (s, 1H), 5.99 (s, 1H), 5.46 (s, 2H), 5.08 (s, 1H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.8, 146.9, 144.1, 143.3, 138.0, 133.4, 129.1, 128.3, 127.9, 127.2, 116.9, 107.4, 103.1, 101.3, 24.5; IR (KBr): ν_{max} 3716, 2919, 1532, 1529, 1360, 1261, 1191, 1131, 1037, 904, 846 cm^{-1} ; HRMS (ESI+): m/z calcd for $\text{C}_{17}\text{H}_{15}\text{ClNO}_3$ $[\text{M}+\text{H}]^+$ 316.0735; found 316.0731.

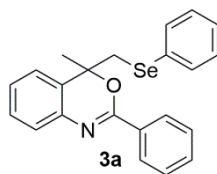


N-(6-(Prop-1-en-2-yl)benzo[d][1,3]dioxol-5-yl)thiophene-2-carboxamide (1g): a white solid; mp 91–93 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.22 (br, 1H), 7.98 (s, 1H), 7.54–7.50 (m, 2H), 7.13 (t, J = 4.0 Hz, 1H), 6.67 (s, 1H), 5.98 (s, 2H), 5.47 (s, 1H), 5.09 (s, 1H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.3, 146.8, 144.0, 143.2, 139.6, 130.4, 128.1, 127.8, 127.0, 116.9, 115.4, 107.3, 103.1, 101.3, 100.5, 97.8, 24.5; IR (KBr): ν_{max} 3678, 2895, 1654, 1505, 1424, 1357, 1240, 1182, 1132, 1038, 860, 728 cm^{-1} ; HRMS (ESI+): m/z calcd for $\text{C}_{15}\text{H}_{14}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$ 288.0689; found 288.0690.



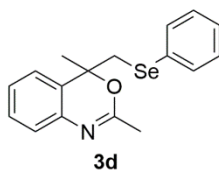
4-Methoxy-N-(6-(prop-1-en-2-yl)benzo[d][1,3]dioxol-5-yl)benzamide (1h): a white solid; mp 75–77 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.26 (bs, 1H), 8.03 (s, 1H), 7.79 (t, J = 8.7 Hz, 2H), 6.99 (t, J = 8.7 Hz, 2H), 6.67 (d, 1H), 5.98 (s, 1H), 5.45 (s, 1H), 5.09 (s, 1H), 3.89 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 164.4, 162.4, 146.8, 143.8, 143.4, 132.8, 128.7, 127.0, 116.8, 114.0, 107.3, 103.1, 101.2, 55.4, 24.5; IR (KBr): ν_{max} 3716, 2862, 1650, 1594, 1505, 1483, 1426, 1360, 1292, 1239, 1182, 1094, 1038, 934, 861 cm^{-1} ; HRMS (ESI+): m/z calcd for $\text{C}_{18}\text{H}_{18}\text{NO}_4$ $[\text{M}+\text{H}]^+$ 312.1230; found 312.1231.

2. Characterization of known selenylated benzoxazines^[6,7]

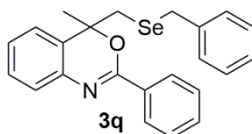


4-Methyl-2-phenyl-4-((phenylselanyl)methyl)-4H-benzo[d][1,3]oxazine (3a): a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 8.01 (d, J = 8.0 Hz, 2H), 7.53 (t, J = 8.0 Hz, 1H), 7.45 (t, J = 8.0 Hz, 2H), 7.42–7.40 (m, 2H), 7.36 (d, J = 8.0 Hz, 1H), 7.34–7.30 (m, 1H), 7.24–7.20 (m, 2H), 7.19–7.15 (m, 3H), 3.74 (d, J = 12.0 Hz, 1H), 3.57 (d, J = 12.0 Hz, 1H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 155.3, 138.9, 131.1, 130.7, 132.6, 131.5, 128.2, 129.0, 128.8, 128.5,

127.4, 127.2, 126.8, 124.9, 123.9, 80.3, 27.3; IR (KBr): $\nu_{\max}$ 3422, 3064, 3031, 2951, 1692, 1588, 1570, 1523, 1455, 1400, 1340, 1252, 1177, 1136, 1092, 1043, 1013, 989, 899, 832, 755 cm^{-1} ; HRMS (ESI⁺): m/z calcd for $\text{C}_{22}\text{H}_{20}\text{NOSe}$ $[\text{M}+\text{H}]^+$ 394.0706; found 394.0710.



2,4-Dimethyl-4-phenylselenomethyl-4H-benzo[d][1,3]oxazine (3d): a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.42–7.40 (m, 2H), 7.26–7.20 (m, 4H), 7.11 (d, $J = 7.4$ Hz, 2H), 7.03 (d, $J = 7.0$ Hz, 1H), 3.46 (d, $J = 12.9$ Hz, 1H), 3.24 (d, $J = 12.9$ Hz, 1H), 1.92 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.8, 138.4, 133.4, 130.6, 129.2, 129.1, 128.1, 127.2, 126.4, 124.5, 123.2, 79.9, 40.6, 27.2, 21.6; IR (KBr): $\nu_{\max}$ 3422, 3065, 3031, 2949, 1692, 1587, 1570, 1528, 1455, 1411, 1345, 1255, 1180, 1135, 1092, 1047, 1020, 999, 879, 852, 753 cm^{-1} ; HRMS(ESI⁺): m/z calcd for $\text{C}_{17}\text{H}_{18}\text{NOSe}$ $[\text{M}+\text{H}]^+$ 331.0475; found 331.0477.



4-((benzylselenanyl)methyl)-4-methyl-2-phenyl-4H-benzo[d][1,3]oxazine (3q): a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 8.13 (d, $J = 8.0$ Hz, 2H), 7.57–7.50 (m, 3H), 7.35–7.23 (m, 6H), 7.14 (t, $J = \text{Hz}$, 3H), 3.63–3.57 (m, 2H), 3.19 (d, $J = 12.0$ Hz, 1H), 3.04 (d, $J = 12.0$ Hz, 1H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 155.4, 139.3, 138.5, 132.3, 131.8, 129.2, 129.0, 128.9, 128.6, 128.5, 127.7, 126.9, 126.7, 124.8, 123.9, 80.5, 35.0, 27.9, 26.8; IR (KBr): $\nu_{\max}$ 3750, 2956, 2853, 1645, 1578, 1545, 1445, 1445, 1315, 125, 1245, 1178, 1045, 1087, 1082, 955, 829, 770 cm^{-1} ; HRMS (ESI⁺): m/z calcd for $\text{C}_{23}\text{H}_{22}\text{NOSe}$ $[\text{M}+\text{H}]^+$ 408.0862; found 408.0869.



4-Methyl-4-((methylselenanyl)methyl)-2-phenyl-4H-benzo[d][1,3]oxazine (3r): a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 8.11 (d, $J = 8.0$ Hz, 2H), 7.57–7.54 (m, 1H), 7.50 (d, $J = 8.0$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.24–7.20 (m, 2H), 3.22 (d, $J = 16.0$ Hz, 1H), 3.08 (d, $J = 16.0$ Hz, 1H), 1.80–1.77 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 155.3, 138.4, 132.3, 131.7, 129.2, 128.9, 128.6, 127.6 ($\times 2$), 126.8, 124.7, 123.9, 80.7, 36.8, 26.9, 5.9; IR (KBr): $\nu_{\max}$ 3750, 2956, 2853, 1645, 1578, 1545, 1445, 1445, 1315, 125, 1245, 1178, 1045, 1087, 1082, 955, 829, 770 cm^{-1} ; HRMS (ESI⁺): m/z calcd for $\text{C}_{17}\text{H}_{18}\text{NOSe}$ $[\text{M}+\text{H}]^+$ 332.0549; found 332.0550.

3. Qualitative chromogenic assays for control redox reactions without *o*-vinylanilide

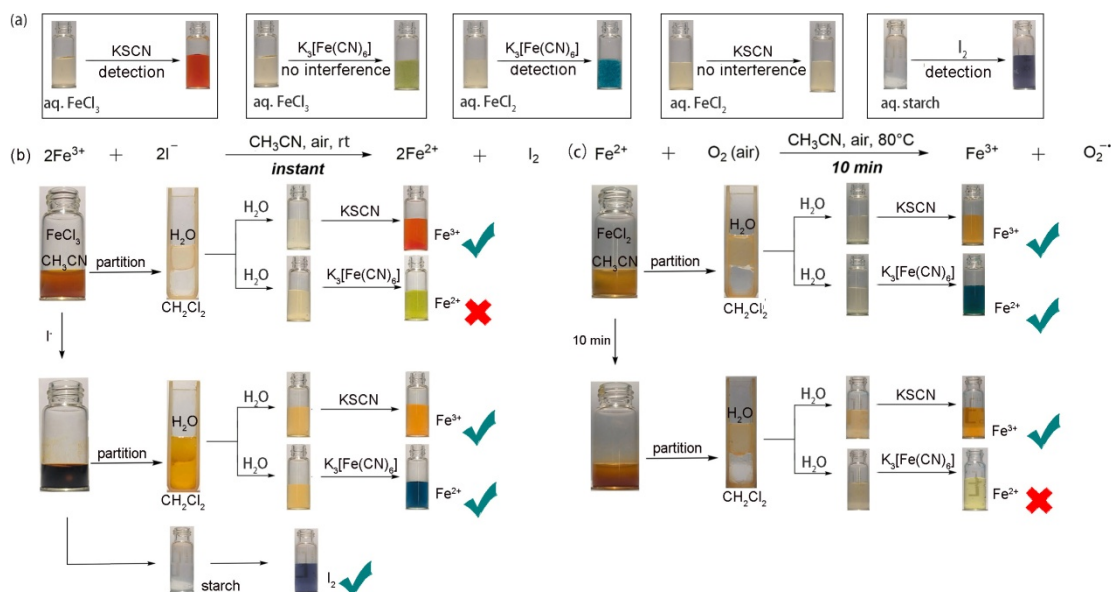


Figure S1. (a) General methods for chromogenic detection of Fe^{3+} , Fe^{2+} , and $\text{I}_2^{a,b}$; (b) Qualitative chromogenic assay for the reaction of Fe^{3+} and I^- in CH_3CN ; (c) qualitative chromogenic assay for the reaction of Fe^{2+} and aerial O_2 in CH_3CN . ^aConditions for qualitative detection of Fe^{3+} and Fe^{2+} : $[\text{Fe}^{3+}]$ and $[\text{Fe}^{2+}] = 0.005 \text{ M}$, $[\text{KSCN}] = [\text{K}_3\text{Fe}(\text{CN})_6] = 0.1 \text{ M}$, and $\text{KSCN} = 3 \text{ eq.}/\text{K}_3\text{Fe}(\text{CN})_6 = 1.5 \text{ eq.}$ ^bConditions for qualitative detection of I_2 : $[\text{I}_2] = 0.005 \text{ M}$; $[\text{starch}] = 10 \text{ mg/mL}$.

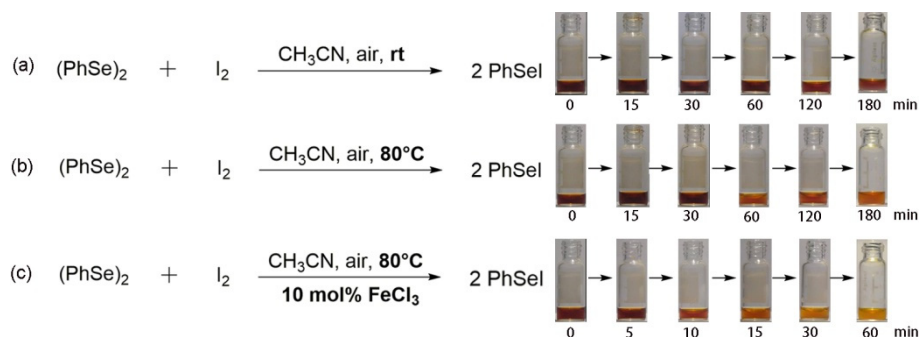


Figure S2. The reaction of I_2 with PhSeSePh at ambient temperature (a), 80°C (b), and 80°C with 10 mol% FeCl_3 (c).

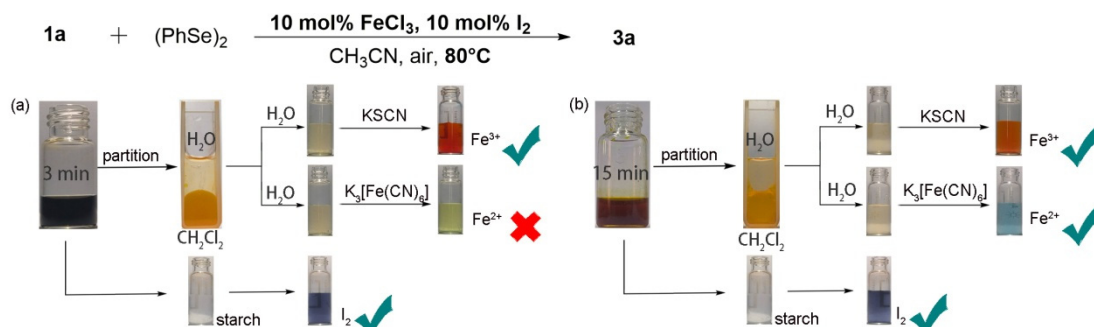


Figure S3. The chromogenic assay for the monitoring the changes of key redox species at 3 min (a) and 15 min (b) during the reaction process.

4. ^1H and ^{13}C spectra of new *o*-vinylanilides

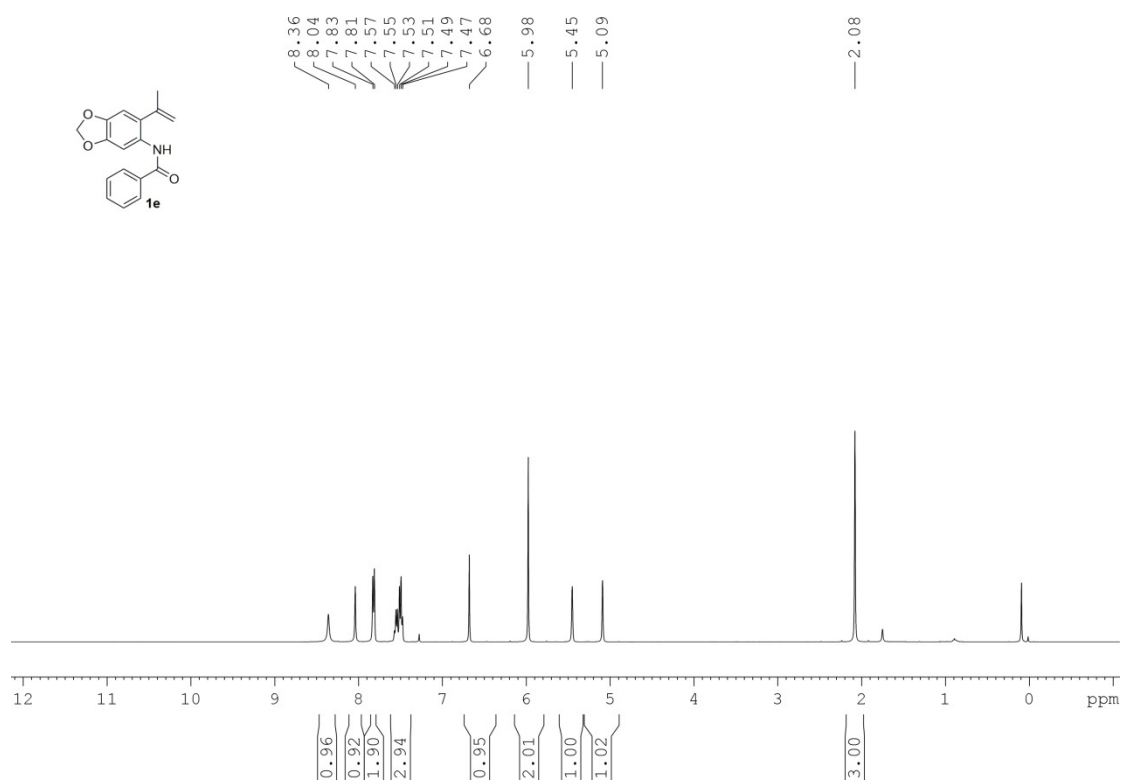


Figure S4. ^1H NMR spectrum of **1e**

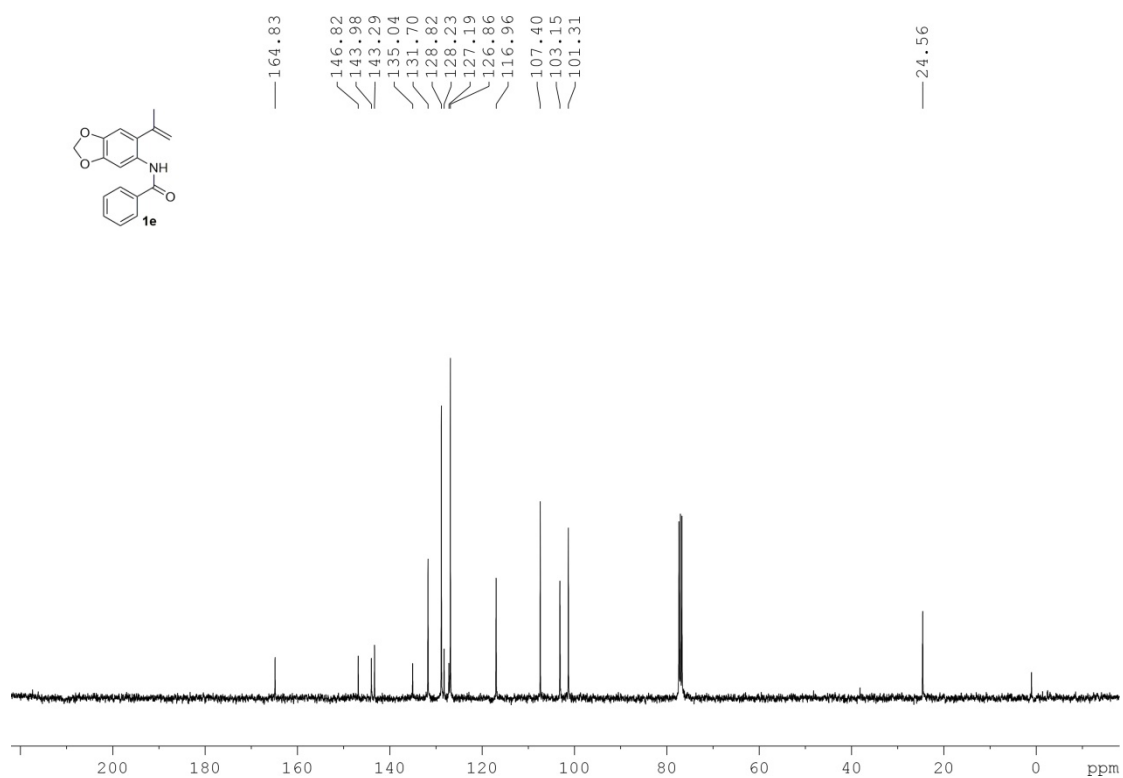


Figure S5. ^{13}C NMR spectrum of **1e**

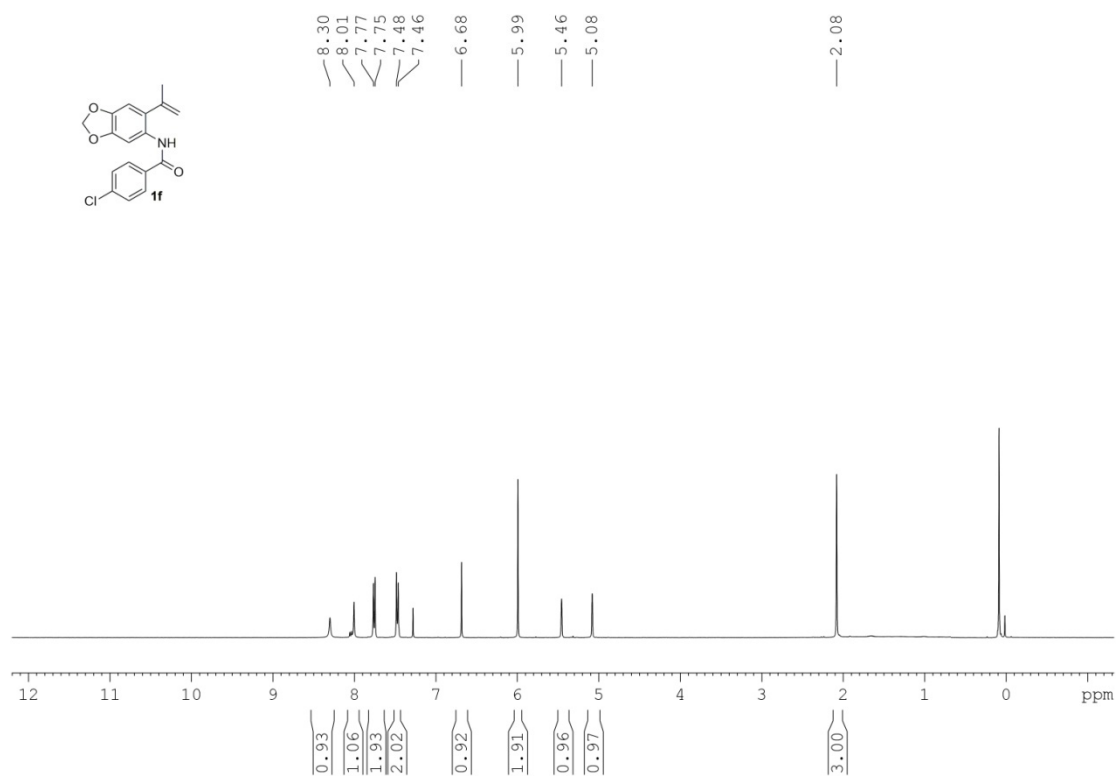


Figure S6. ^1H NMR spectrum of **1f**

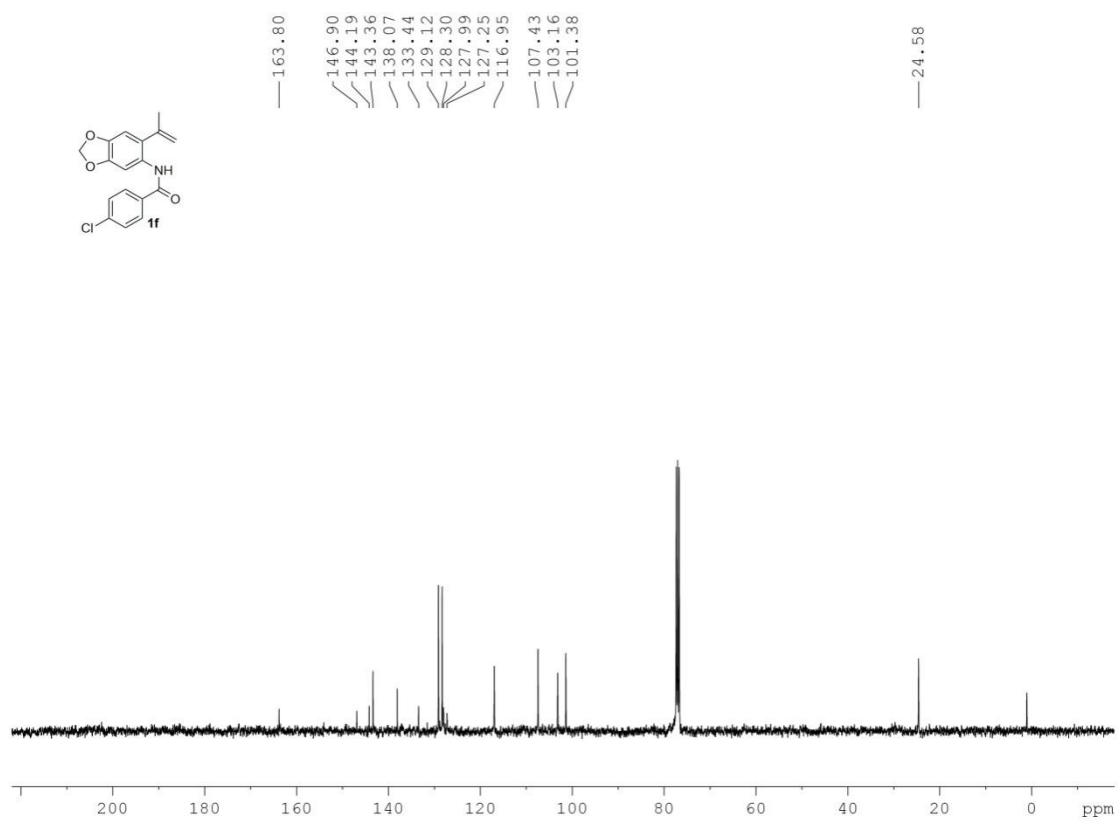


Figure S7. ^{13}C NMR spectrum of **1f**

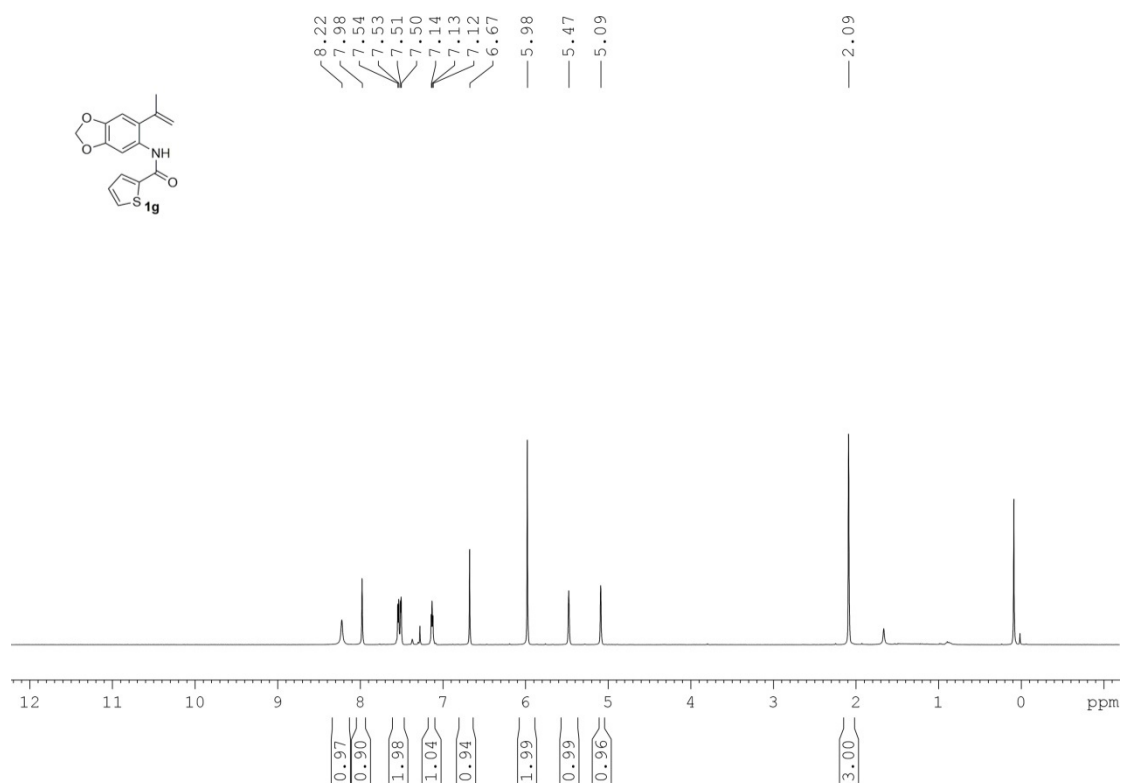


Figure S8. ¹H NMR spectrum of **1g**

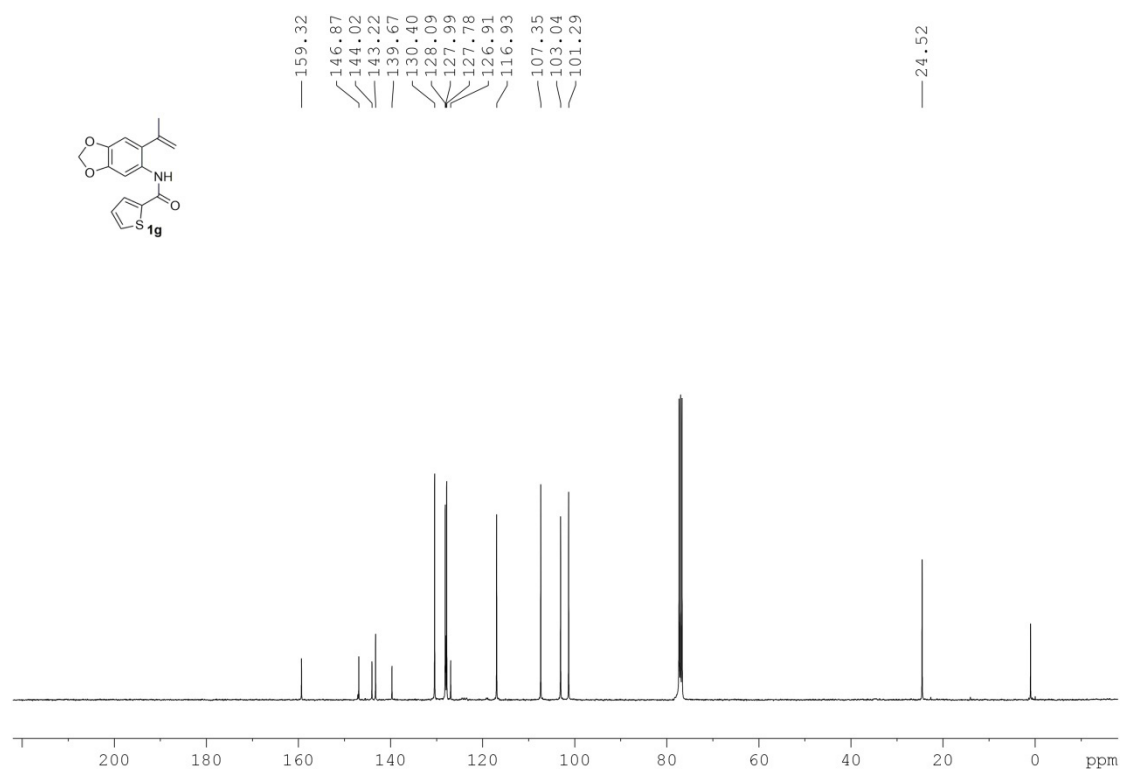


Figure S9. ¹³C NMR spectrum of **1g**

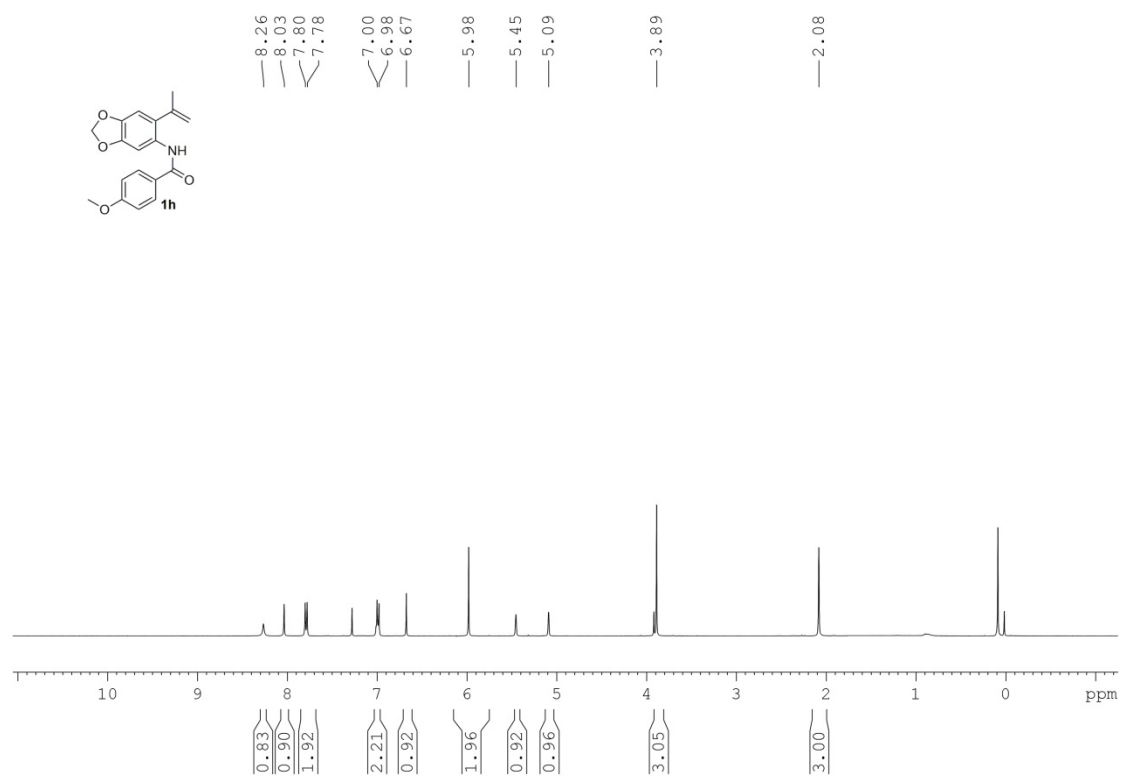


Figure S10. ¹H NMR spectrum of **1h**

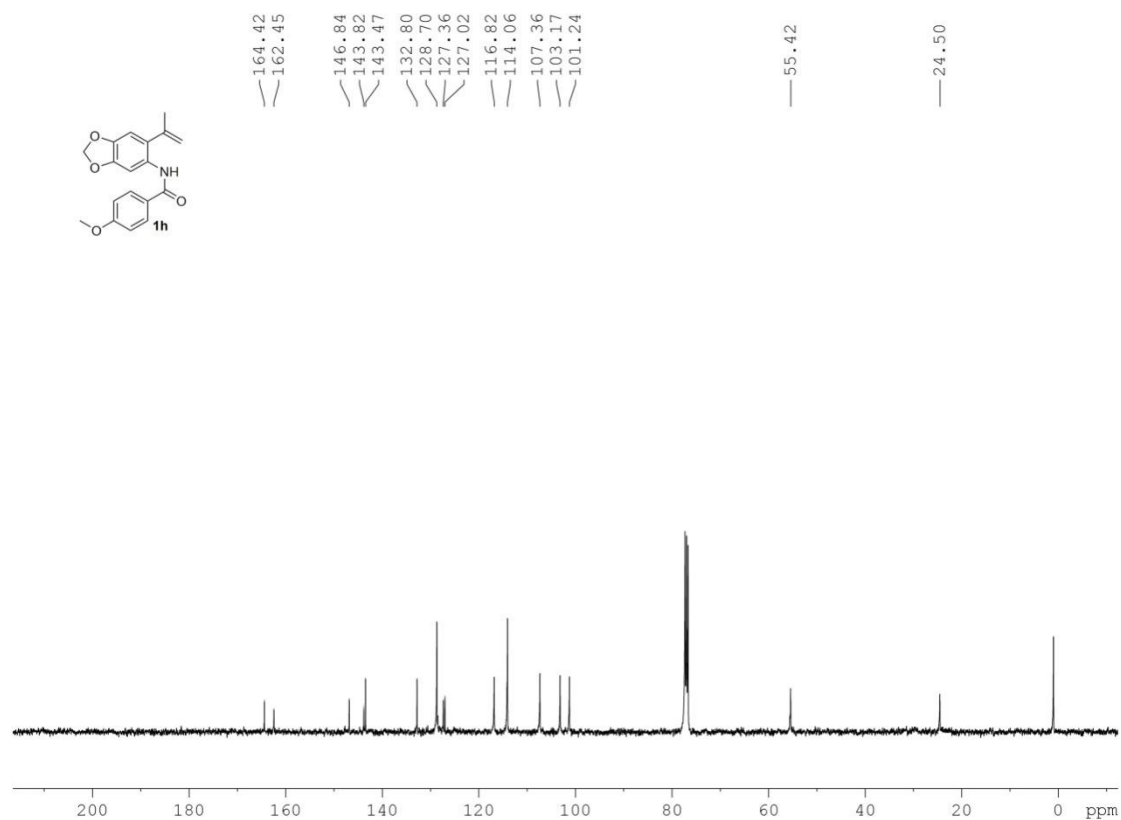


Figure S11. ¹³C NMR spectrum of **1h**

5. ^1H and ^{13}C spectra of selenylated benzoxazines

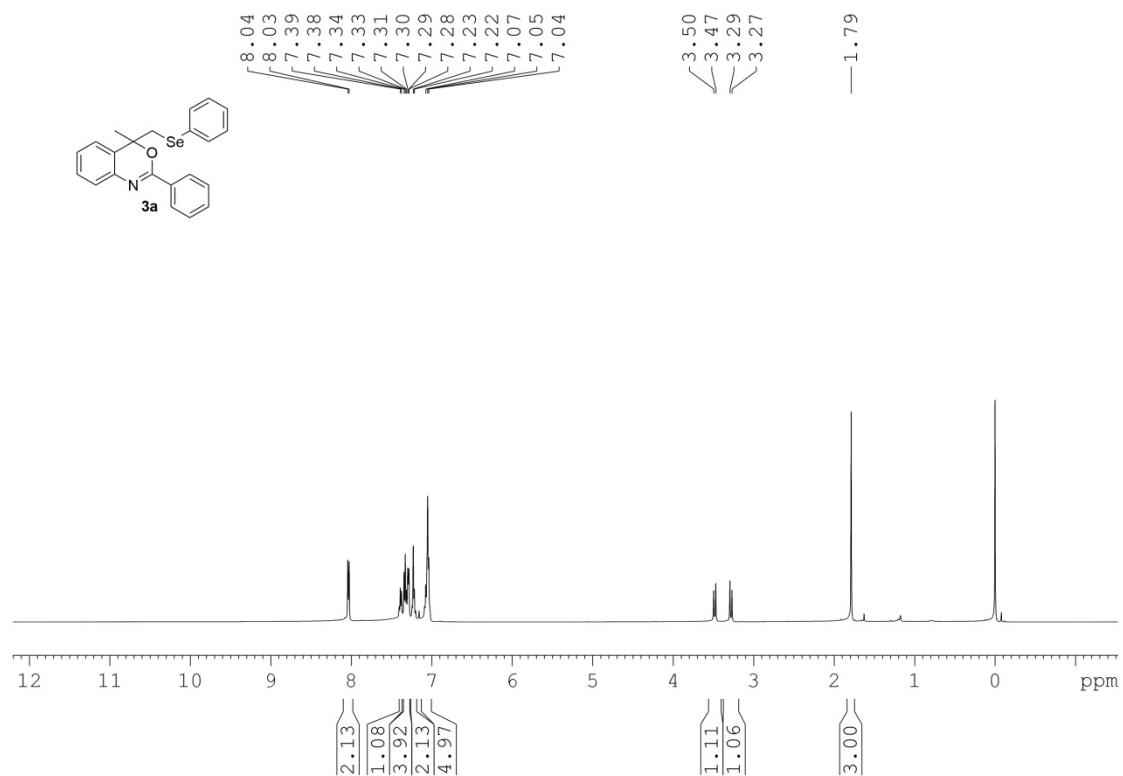


Figure S12. ^1H NMR spectrum of **3a**

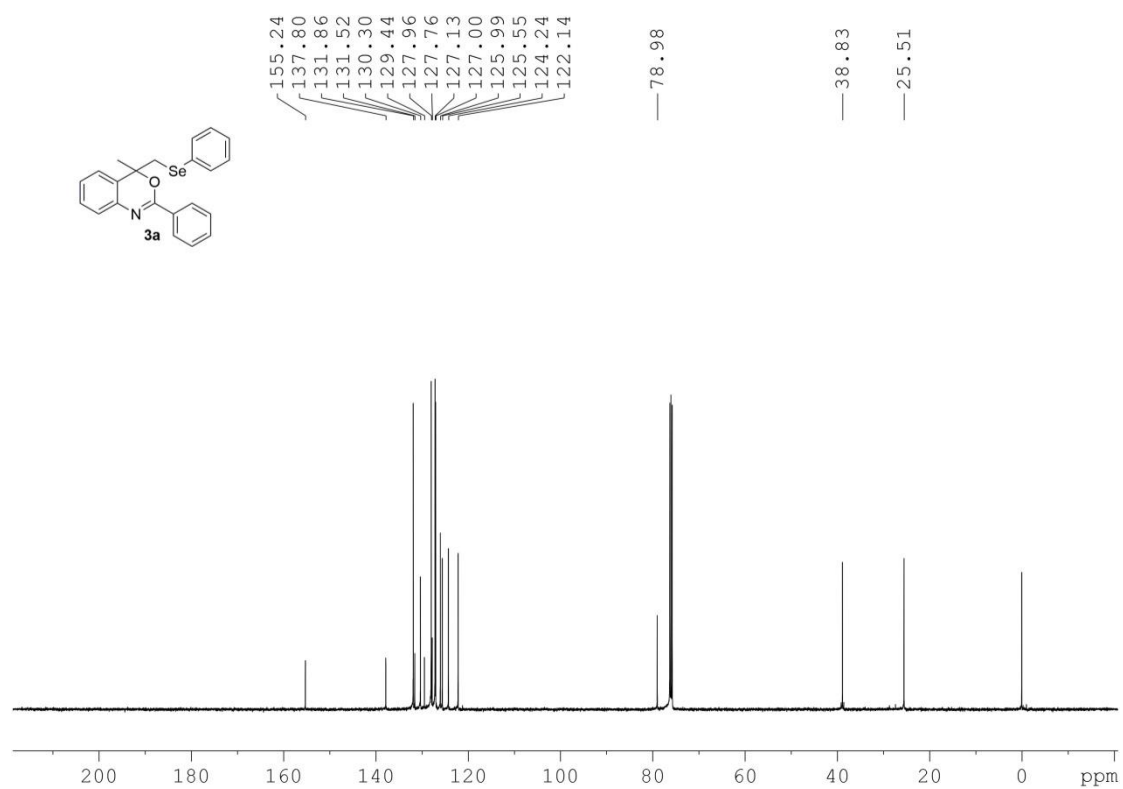


Figure S13. ^{13}C NMR spectrum of **3a**

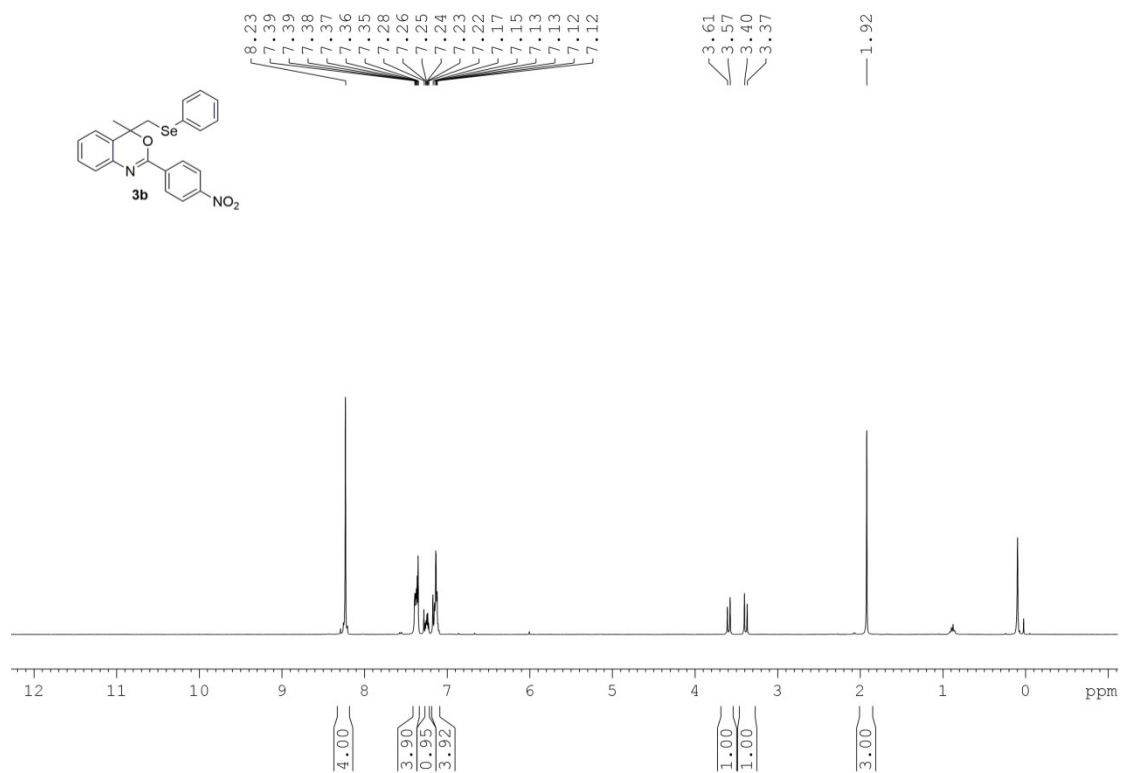


Figure S14. ¹H NMR spectrum of **3b**

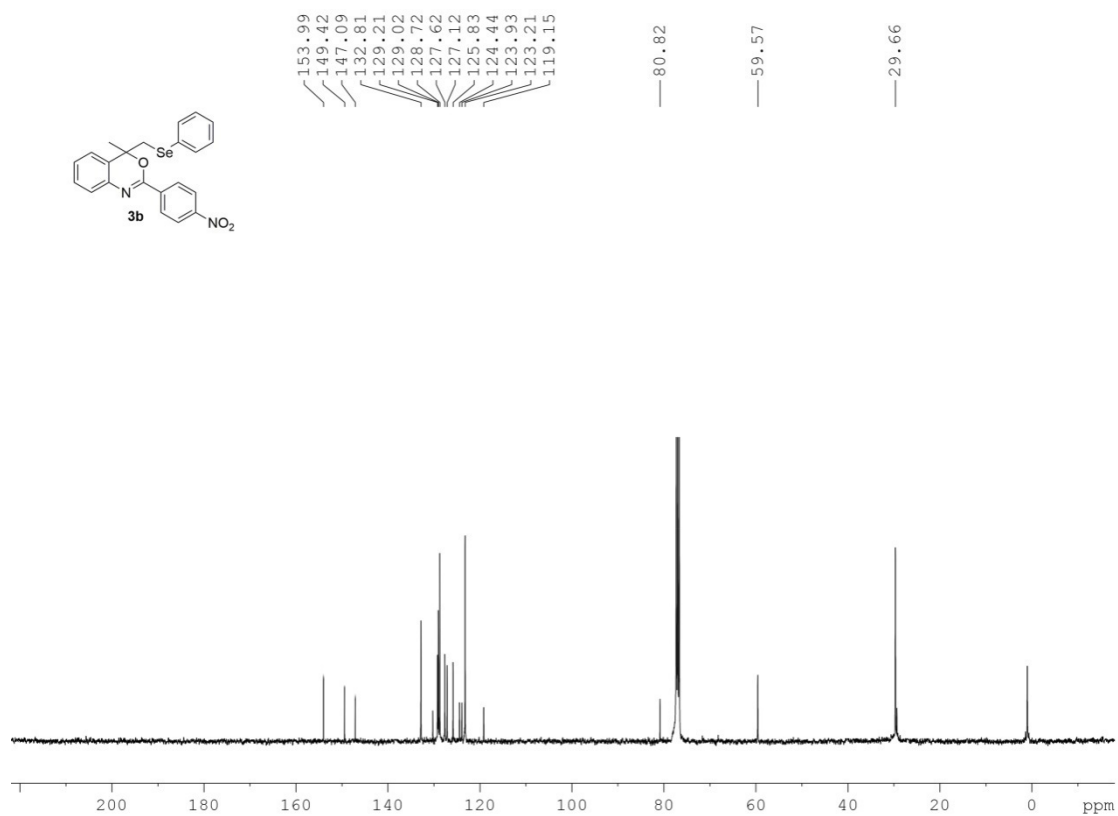


Figure S15. ¹³C NMR spectrum of **3b**

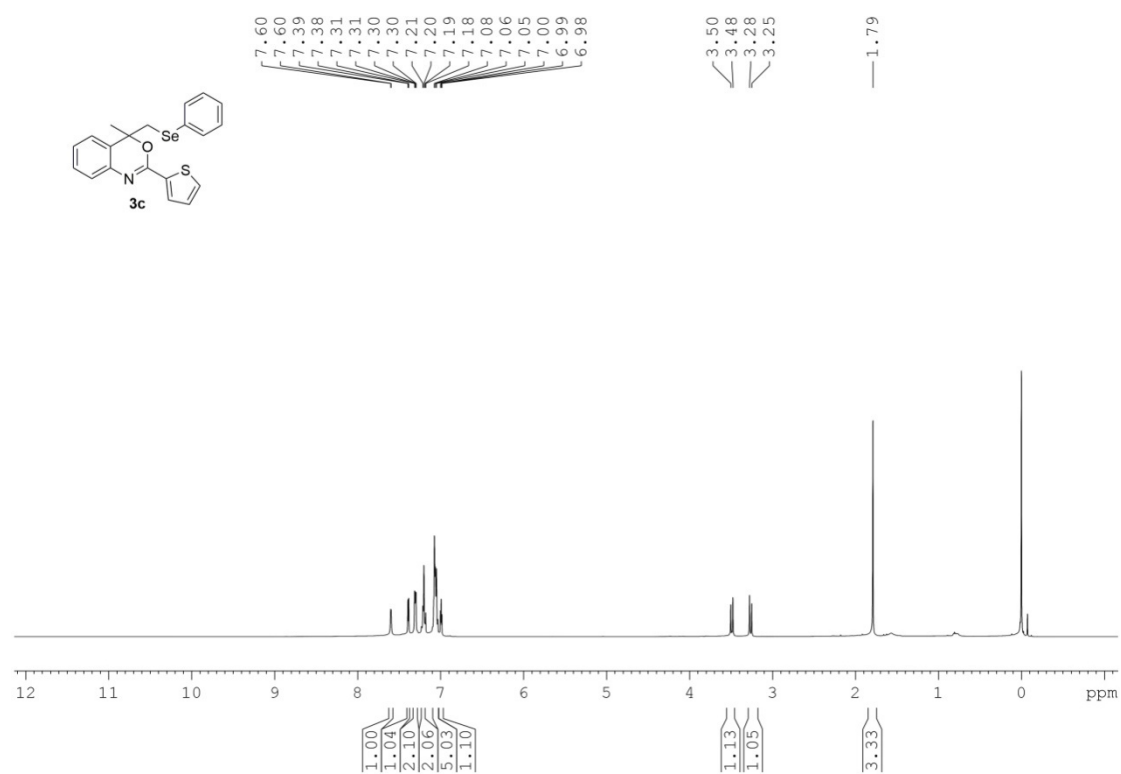


Figure 16. ¹H NMR spectrum of **3c**

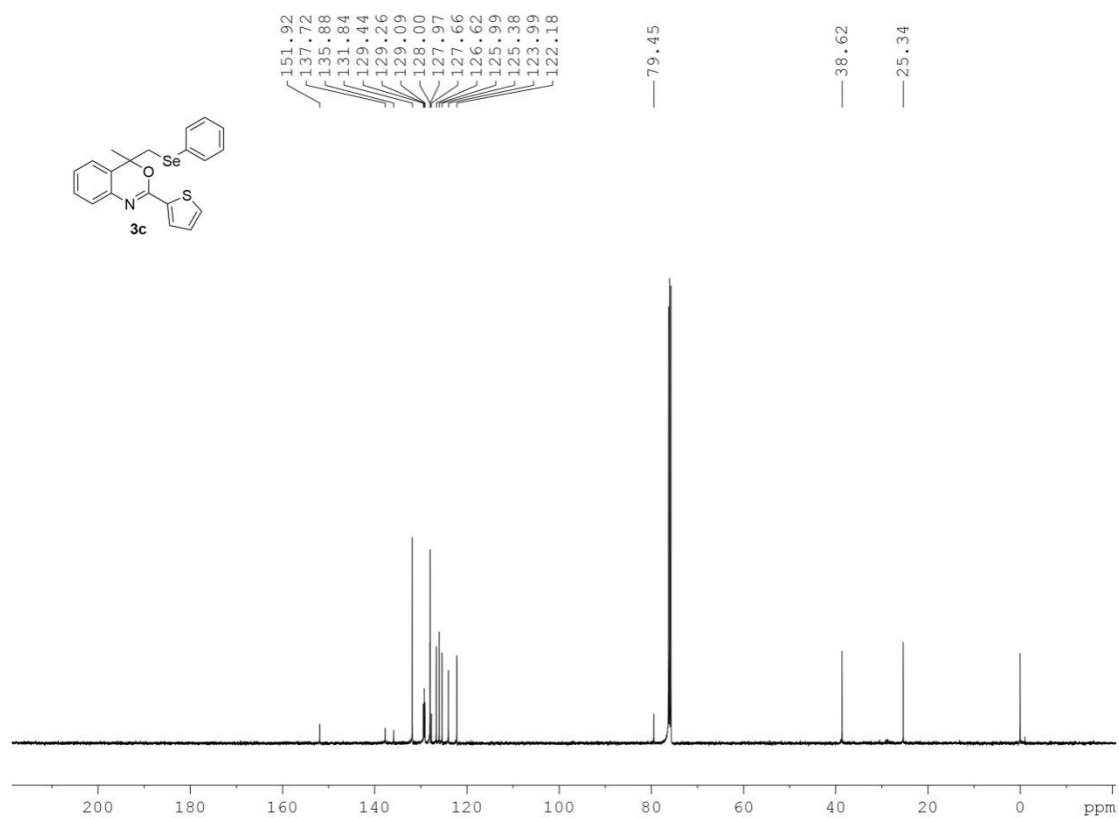


Figure S17. ¹³C NMR spectrum of **3c**

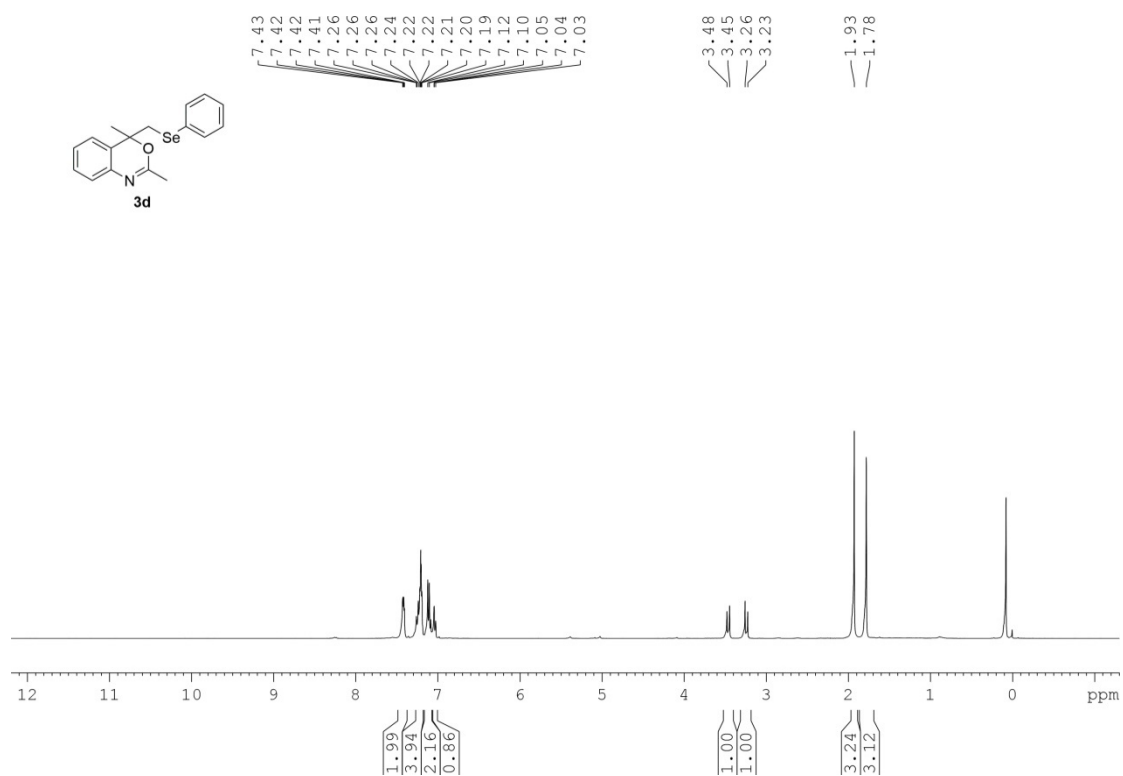


Figure 18. ¹H NMR spectrum of 3d

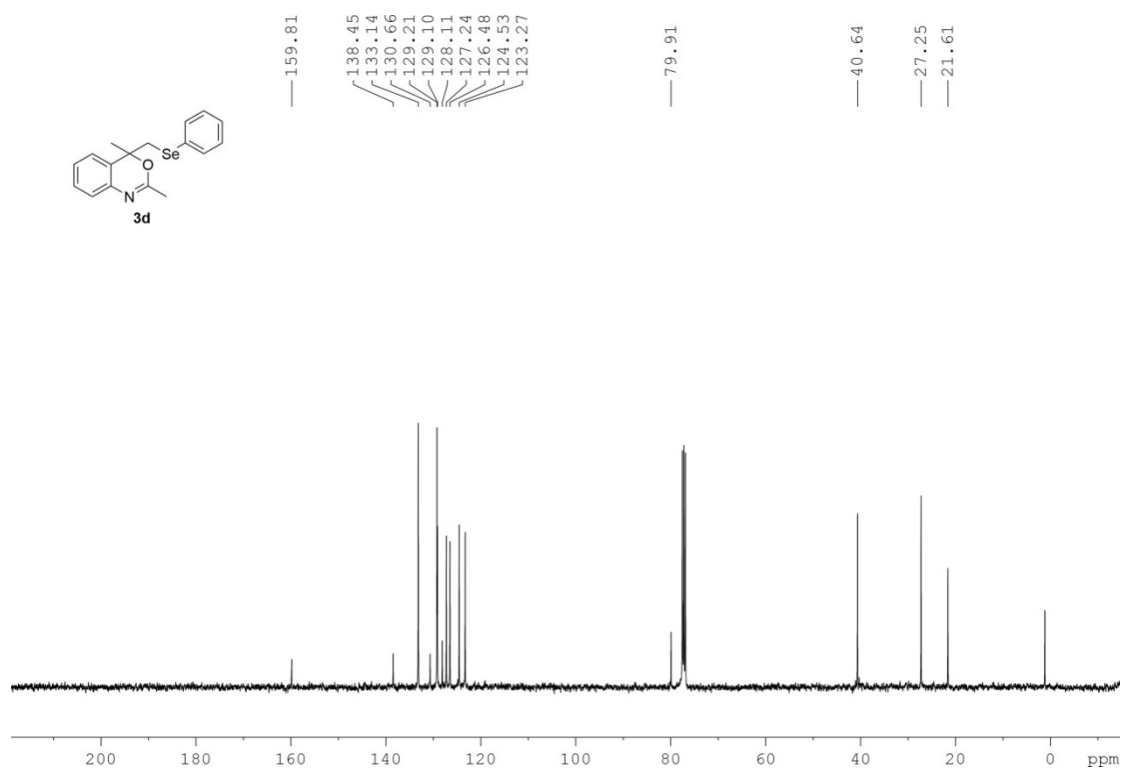


Figure S19. ¹³C NMR spectrum of 3d

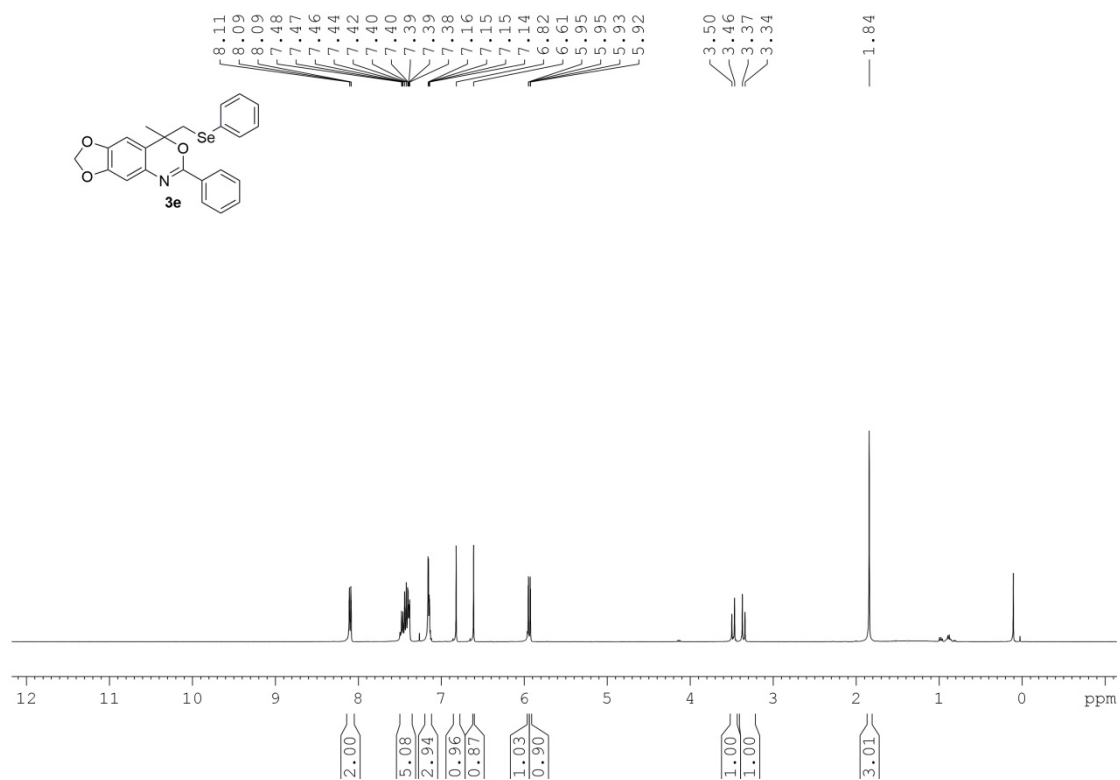


Figure S20. ¹H NMR spectrum of **3e**

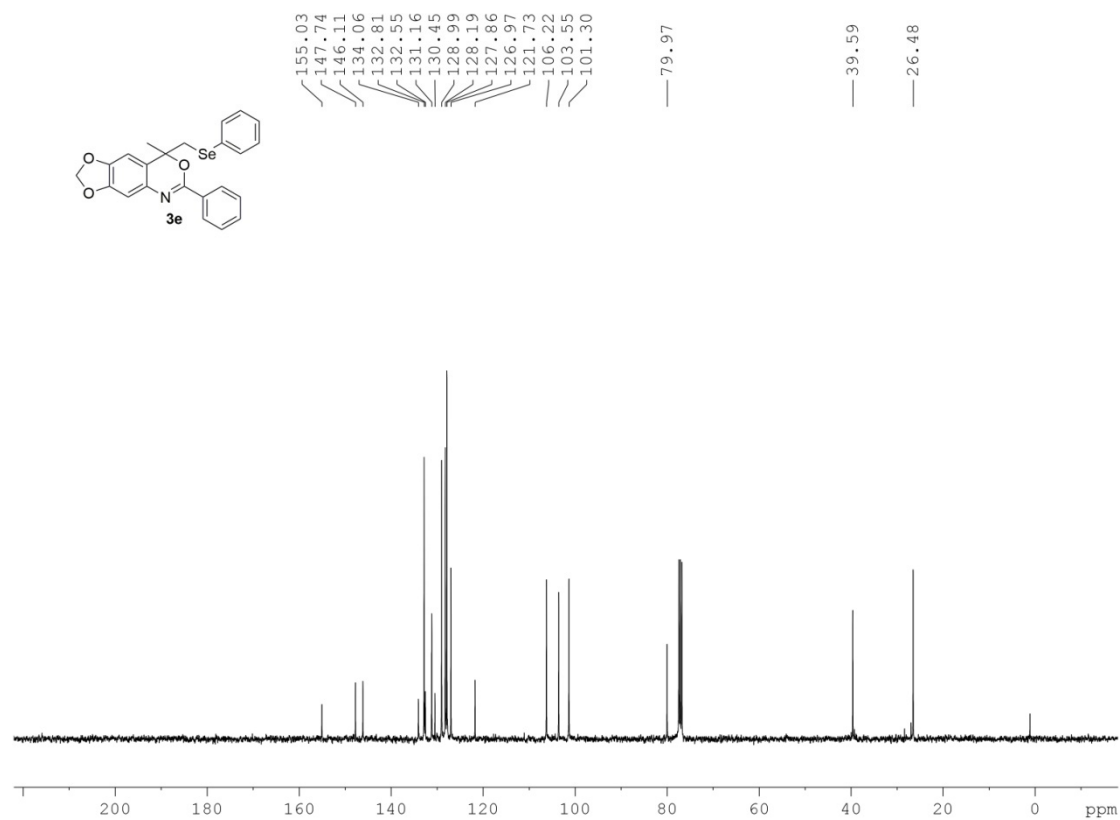


Figure S21. ¹³C NMR spectrum of **3e**

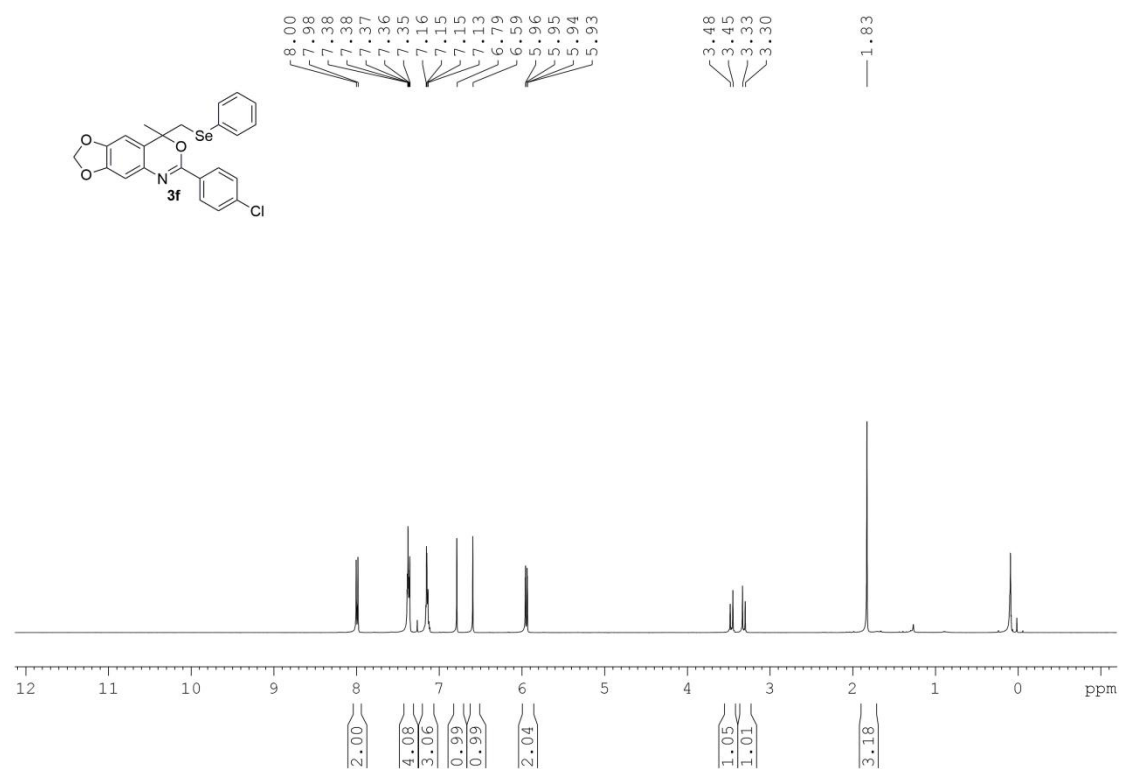


Figure S22. ¹H NMR spectrum of **3f**

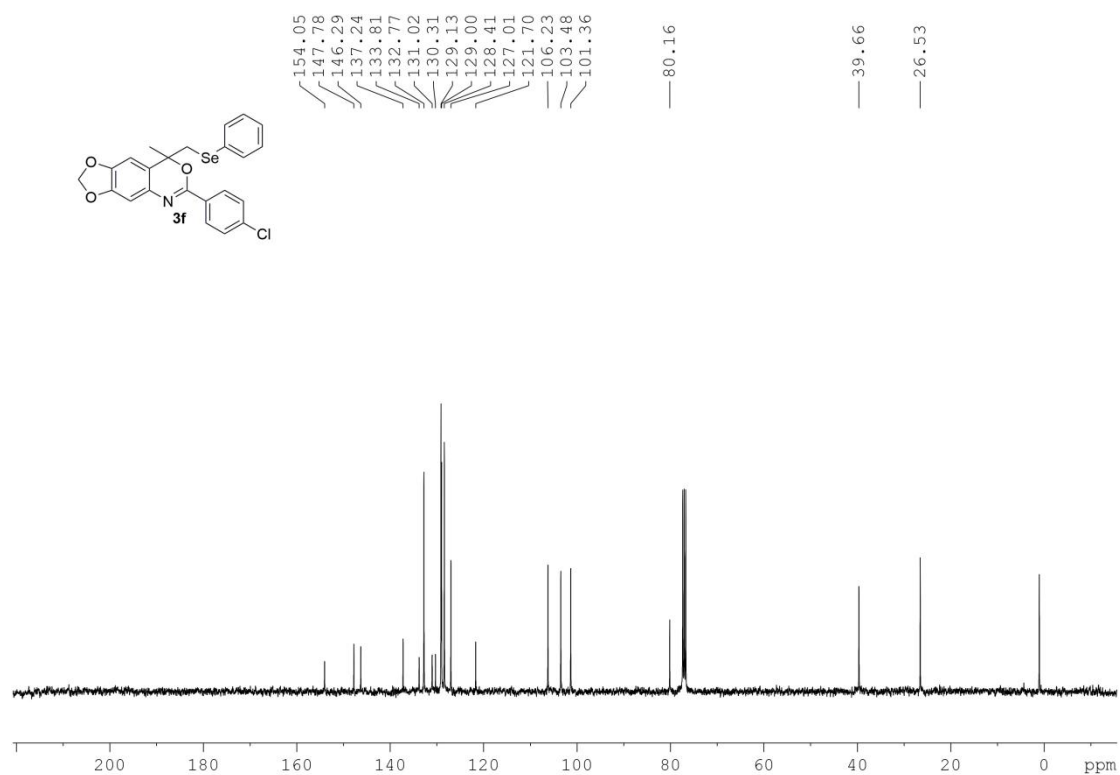


Figure S23. ¹³C NMR spectrum of **3f**

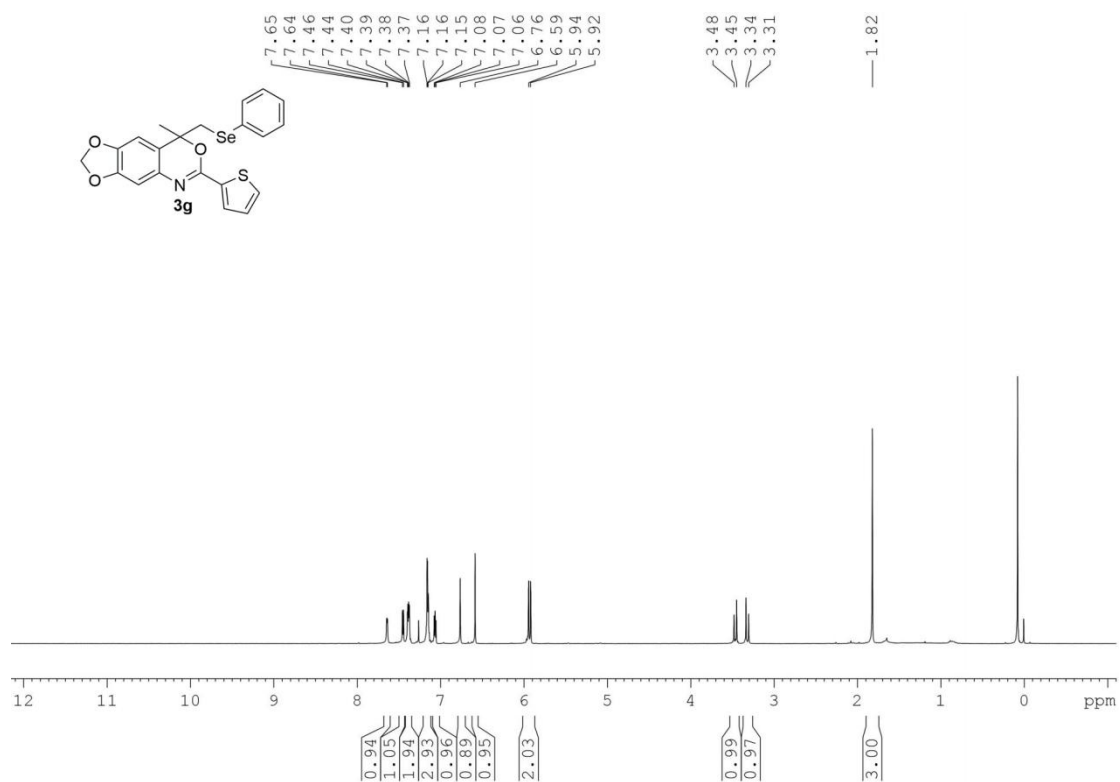


Figure S24. ¹H NMR spectrum of **3g**

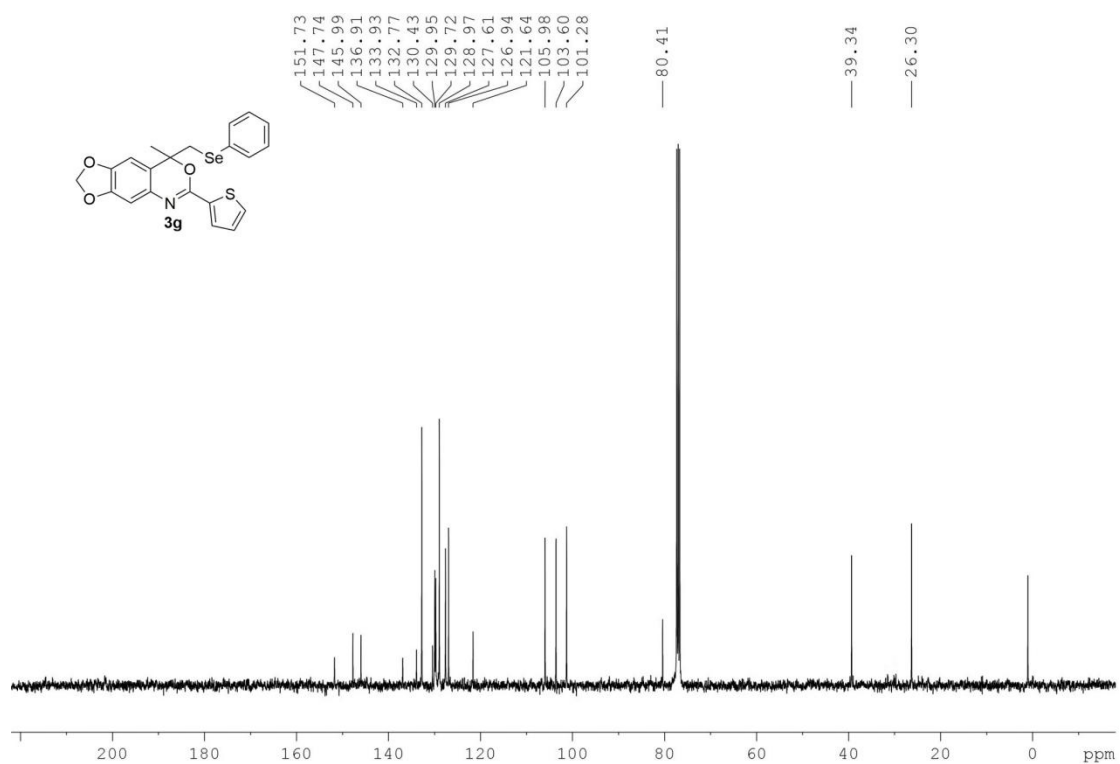


Figure S25. ¹³C NMR spectrum of **3g**

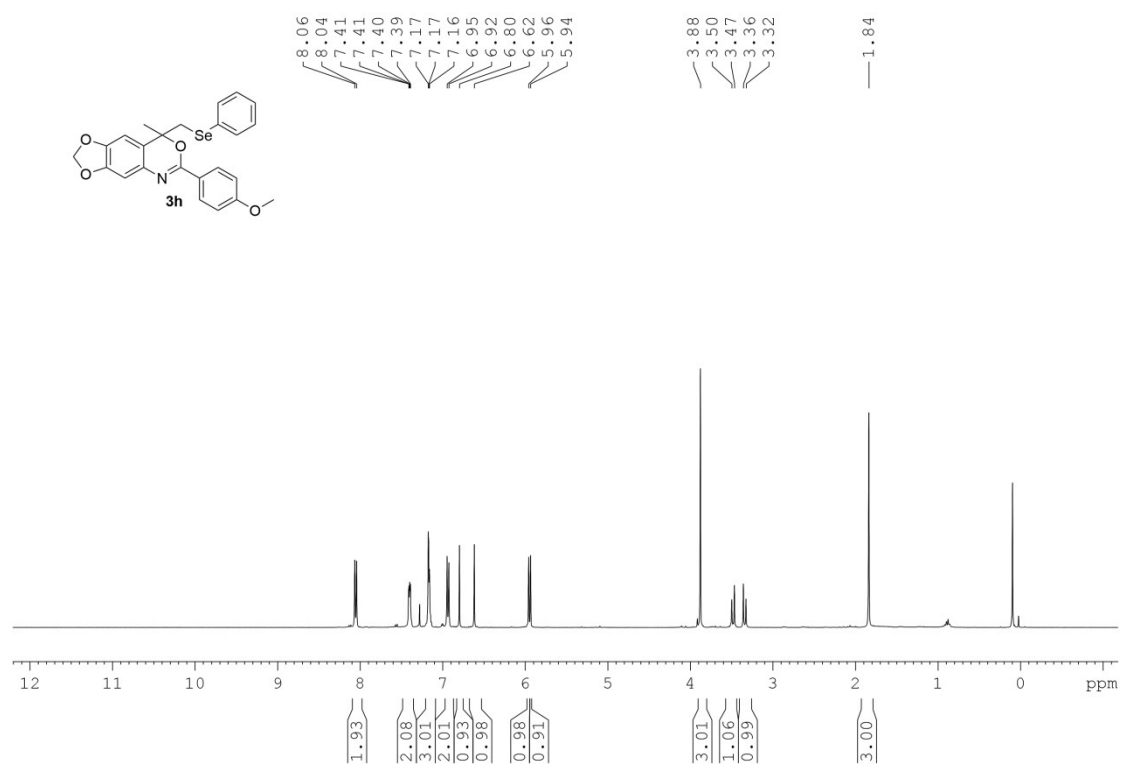


Figure S26. ¹H NMR spectrum of **3h**

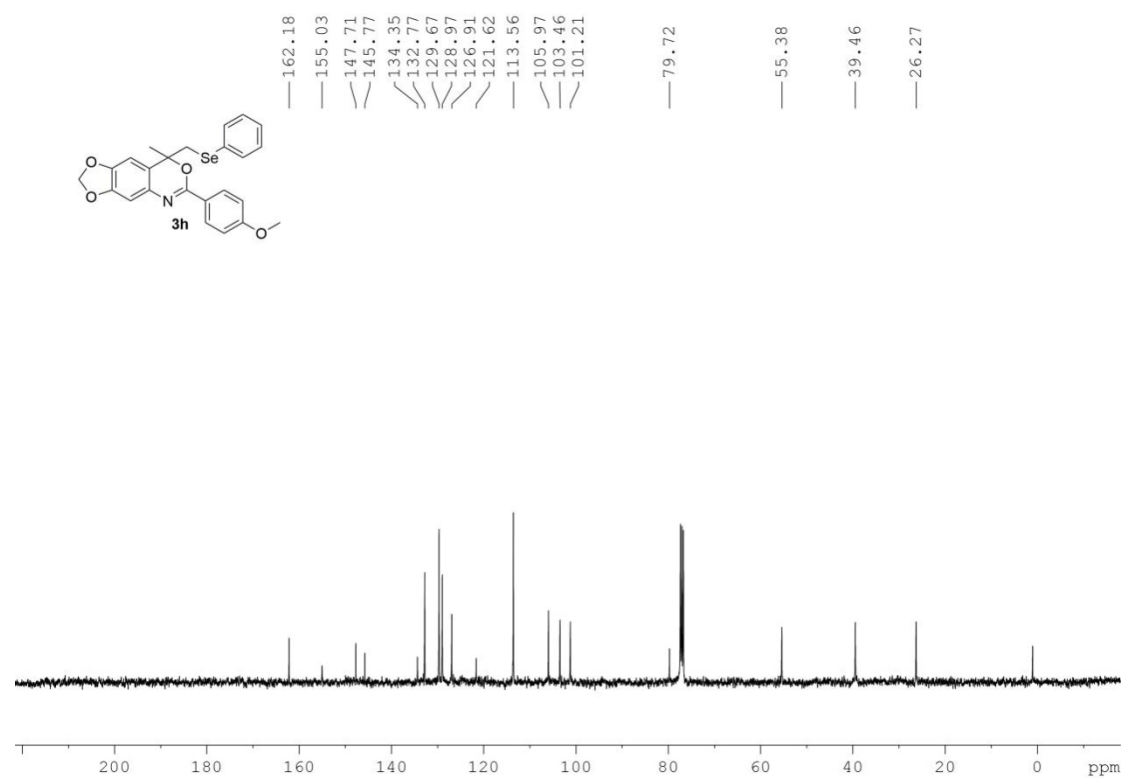


Figure S27. ¹³C NMR spectrum of **3h**

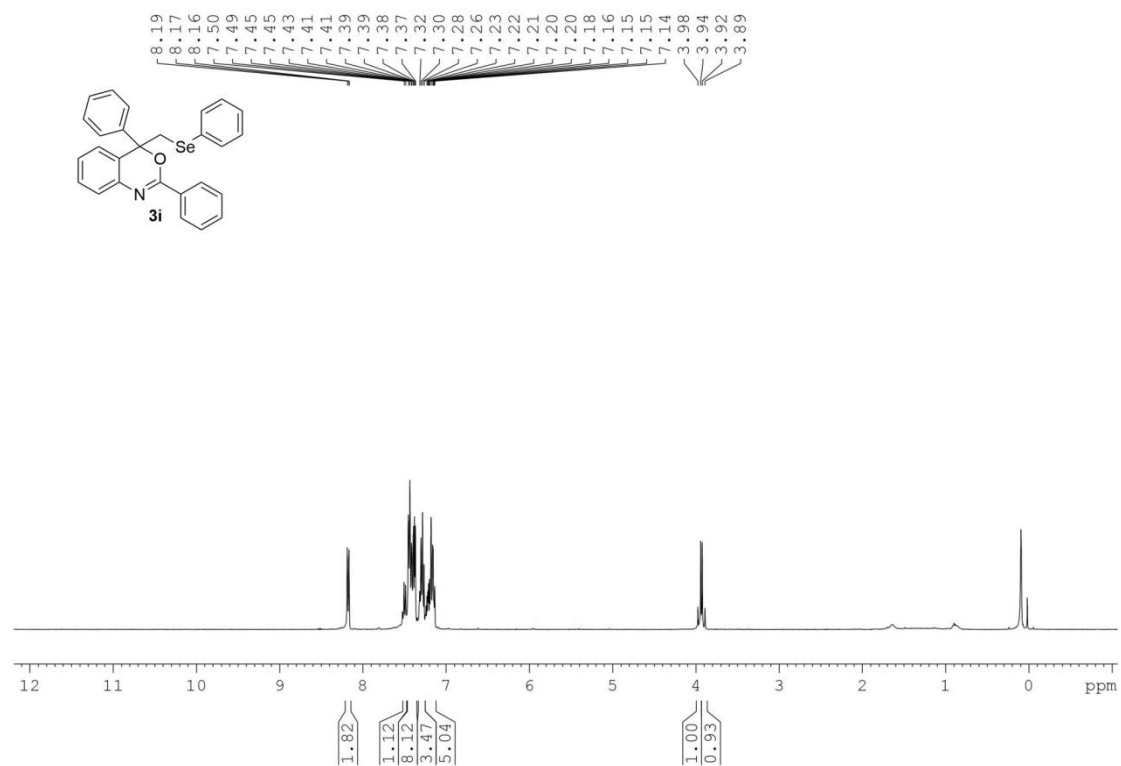


Figure S28. ¹H NMR spectrum of **3i**

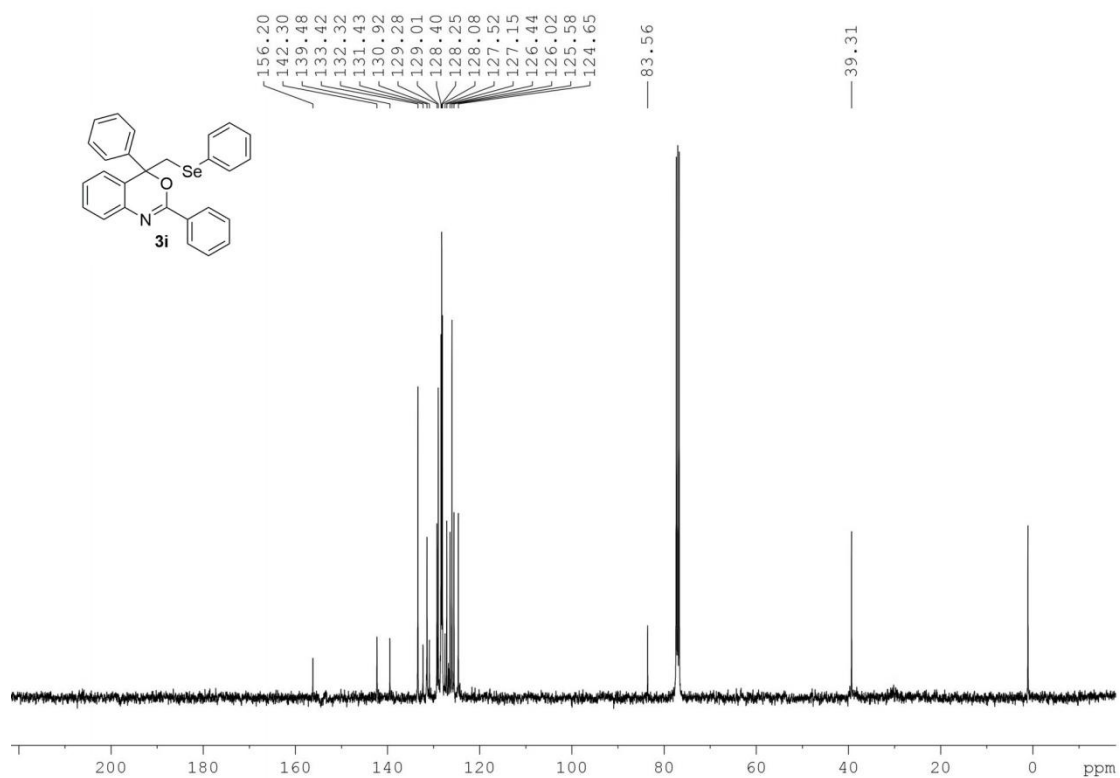


Figure S29. ¹³C NMR spectrum of **3i**

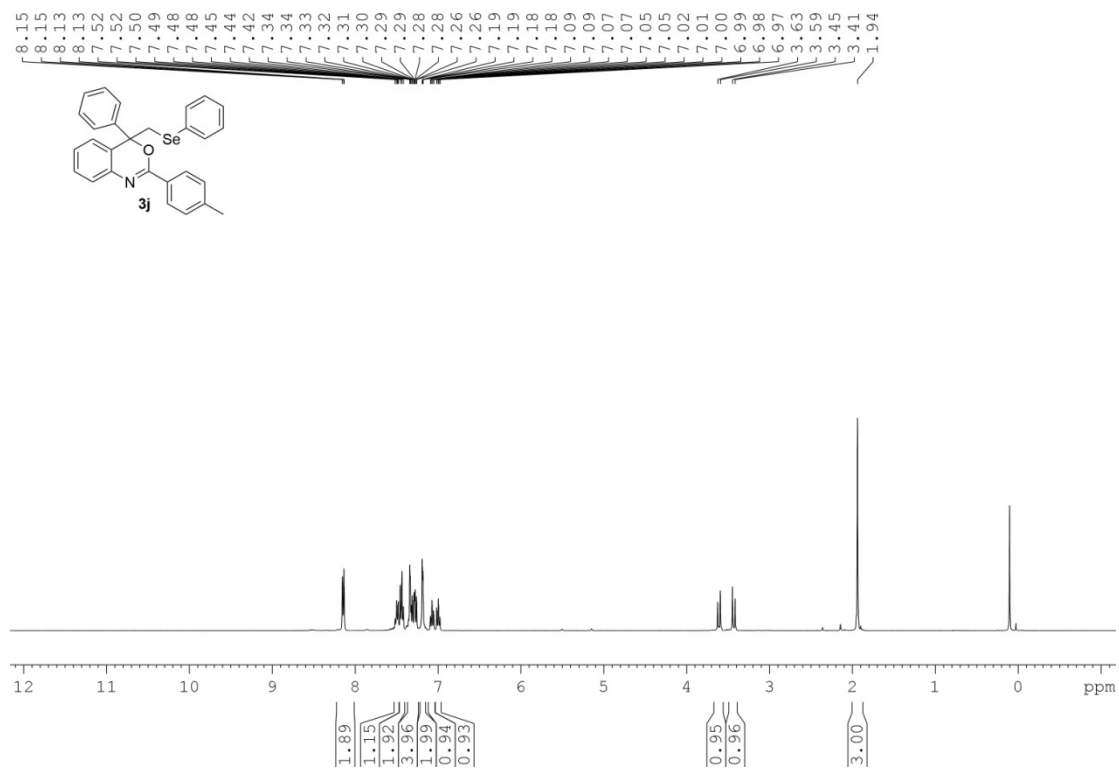


Figure S30. ¹H NMR spectrum of **3j**

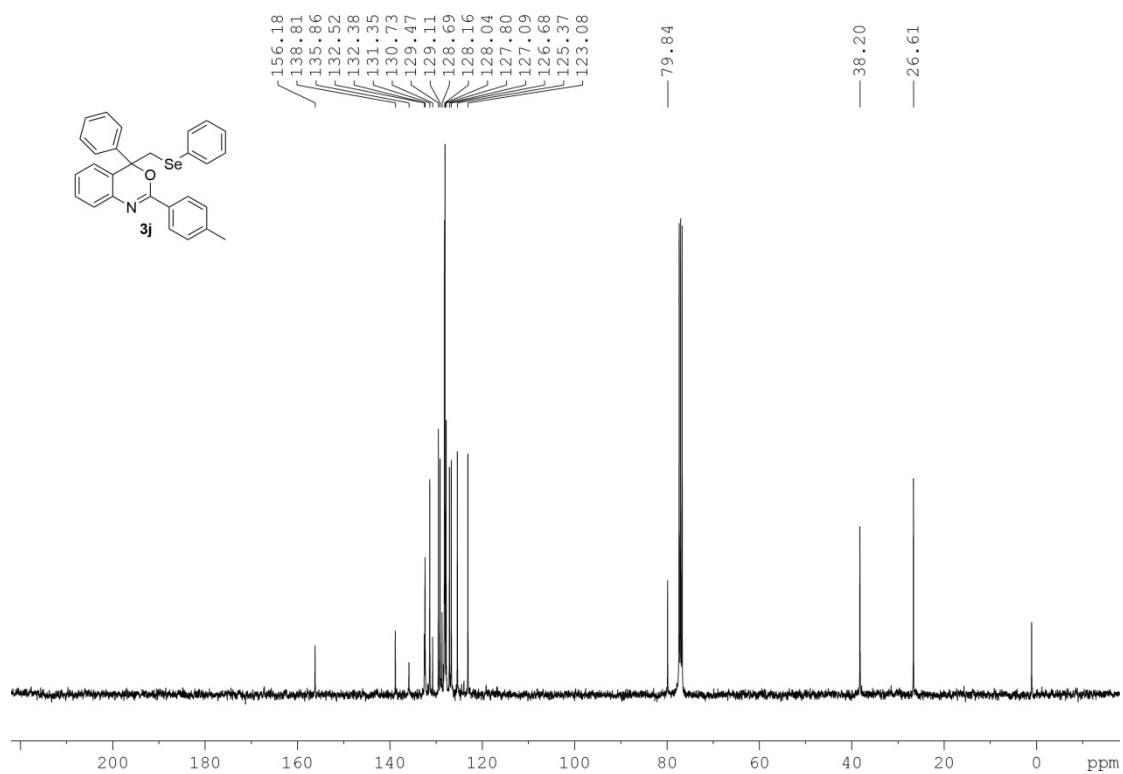


Figure S31. ¹³C NMR spectrum of **3j**

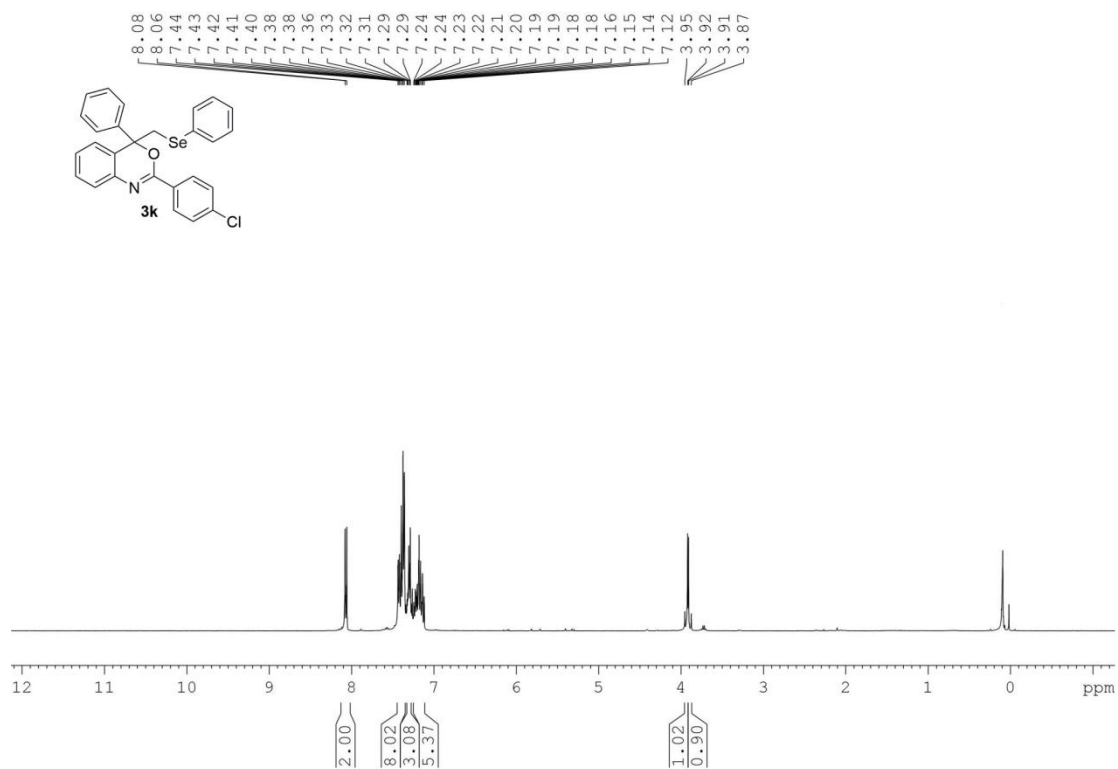


Figure S32. ¹H NMR spectrum of **3k**

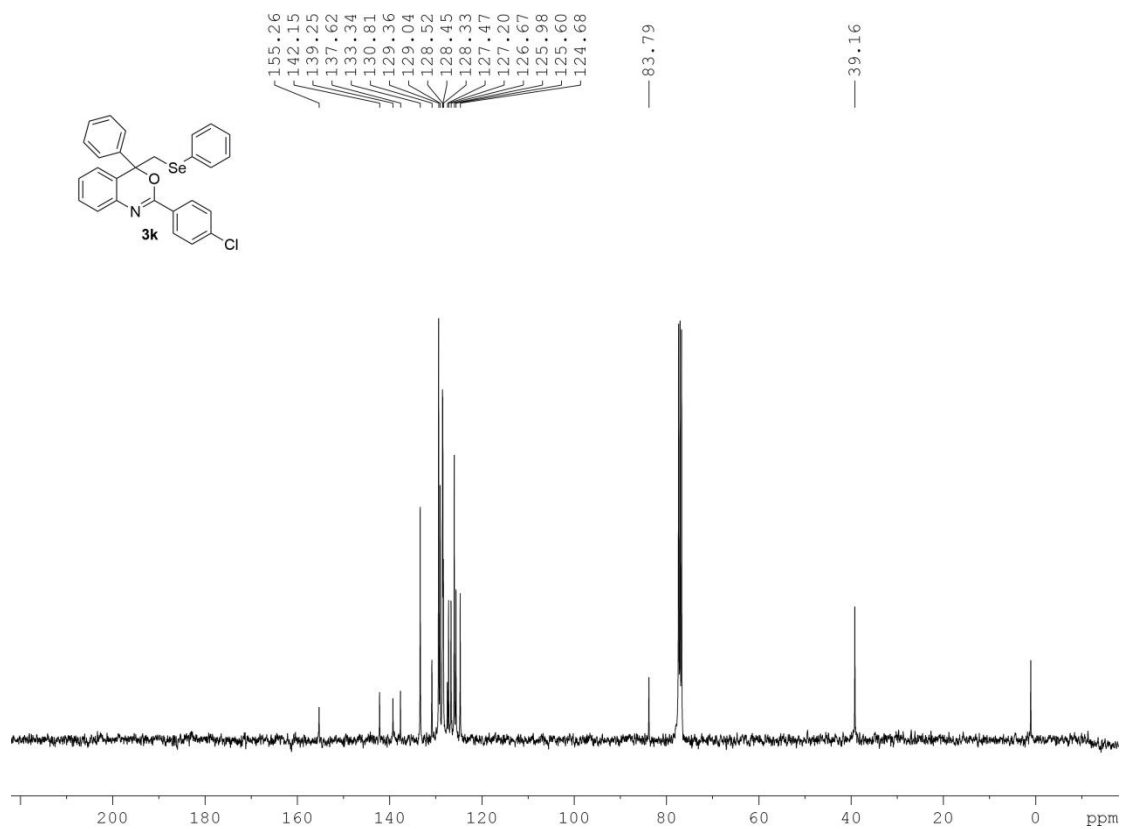


Figure S33. ¹³C NMR spectrum of **3k**

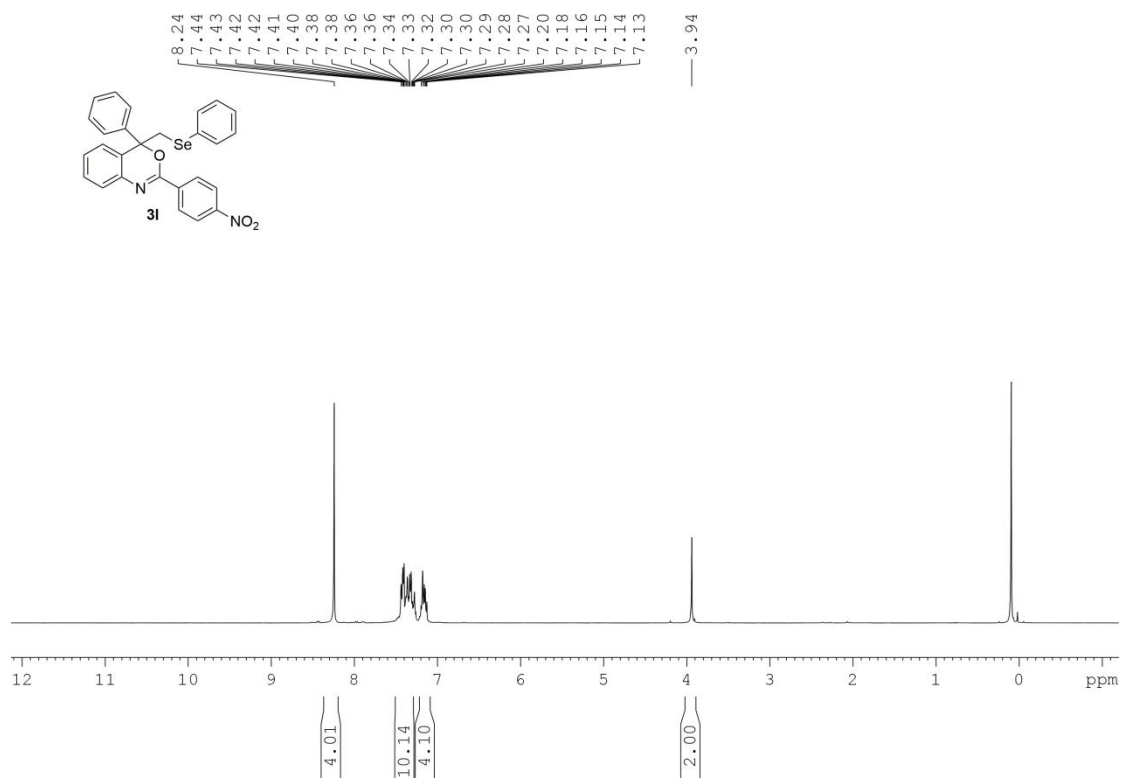


Figure S34. ¹H NMR spectrum of **3l**

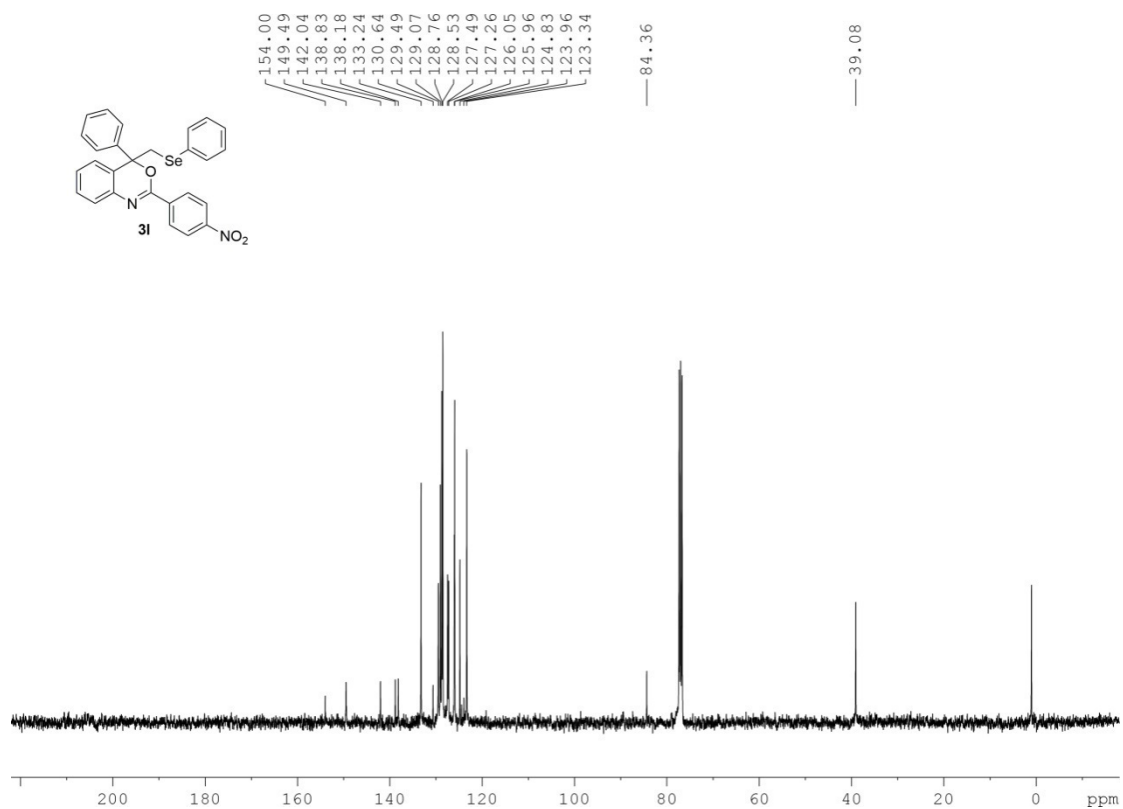


Figure S35. ¹³C NMR spectrum of **3l**

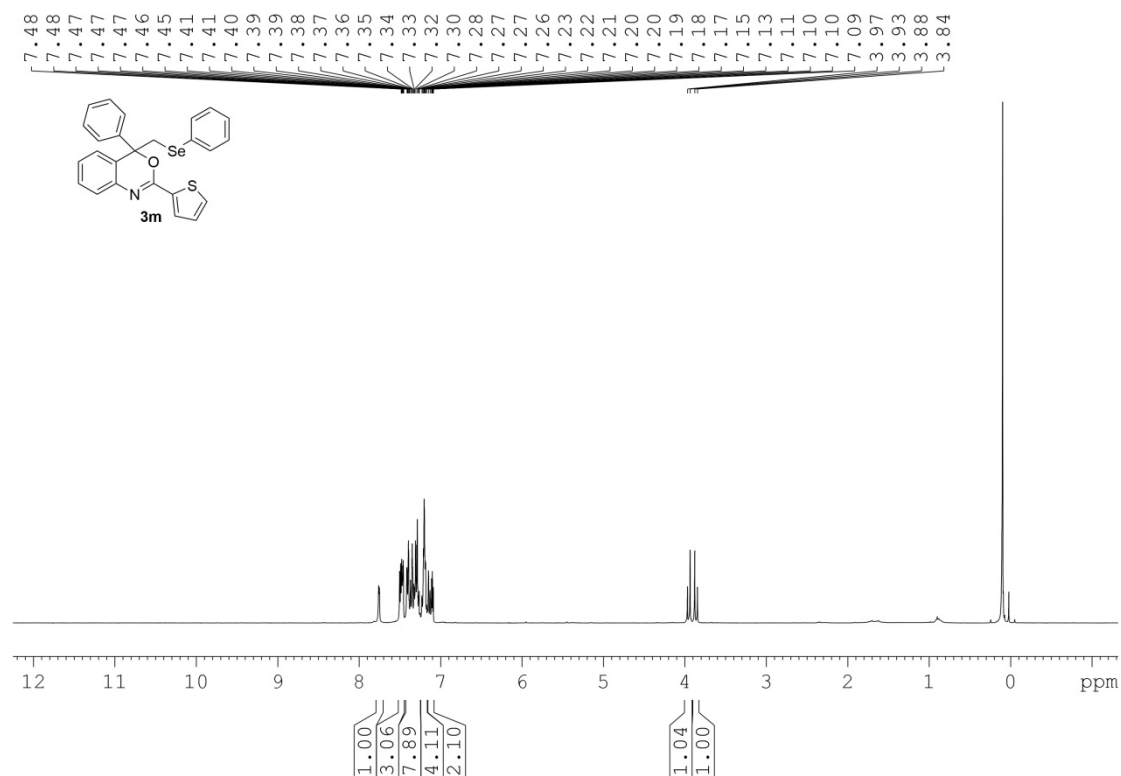


Figure S36. ¹H NMR spectrum of **3m**

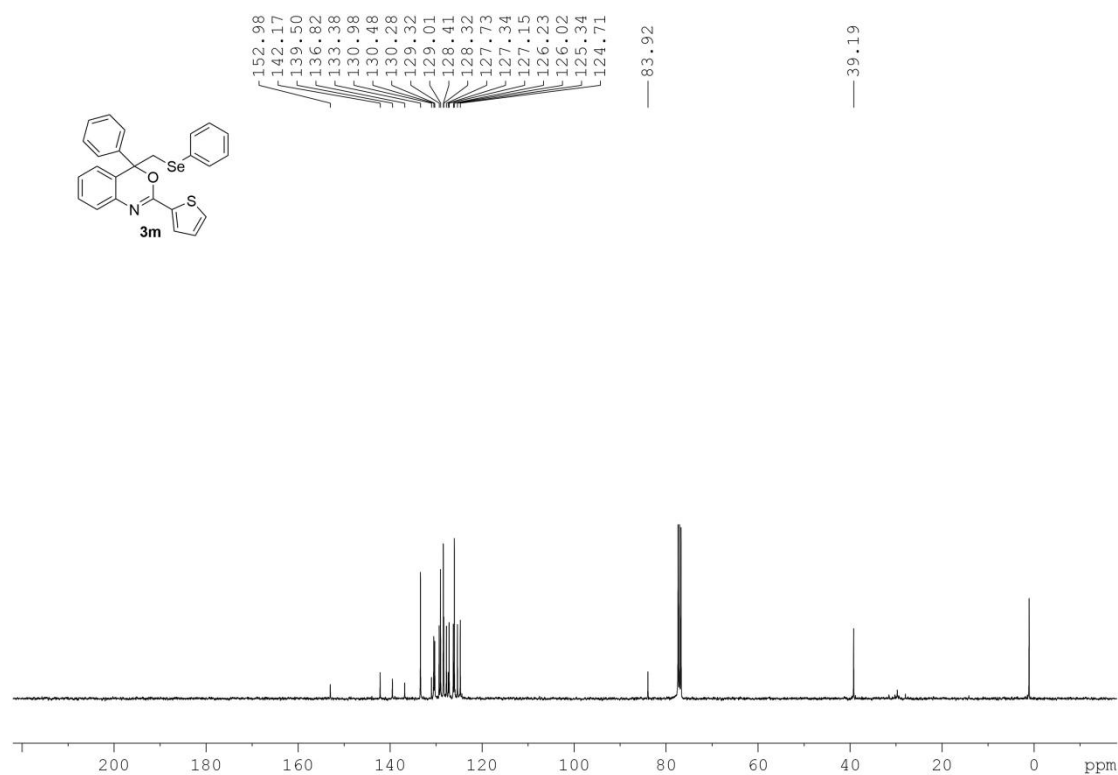


Figure S37. ¹³C NMR spectrum of **3m**

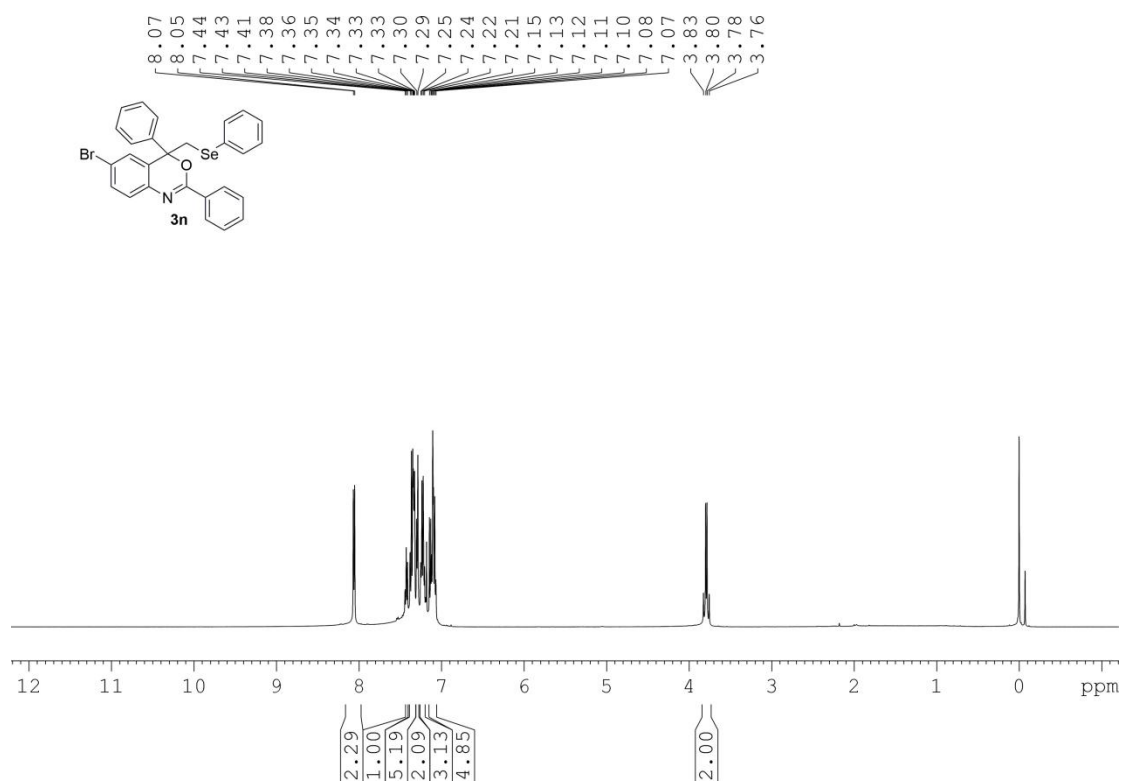


Figure S38. ¹H NMR spectrum of **3n**

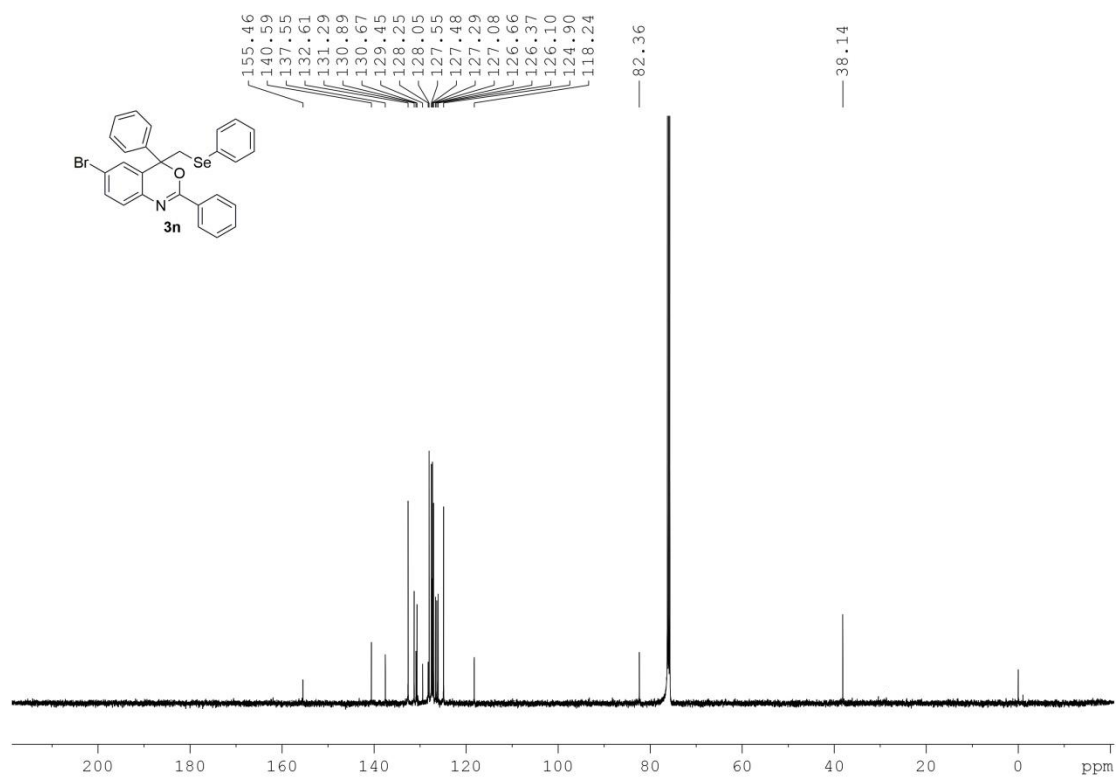


Figure S39. ¹³C NMR spectrum of **3n**

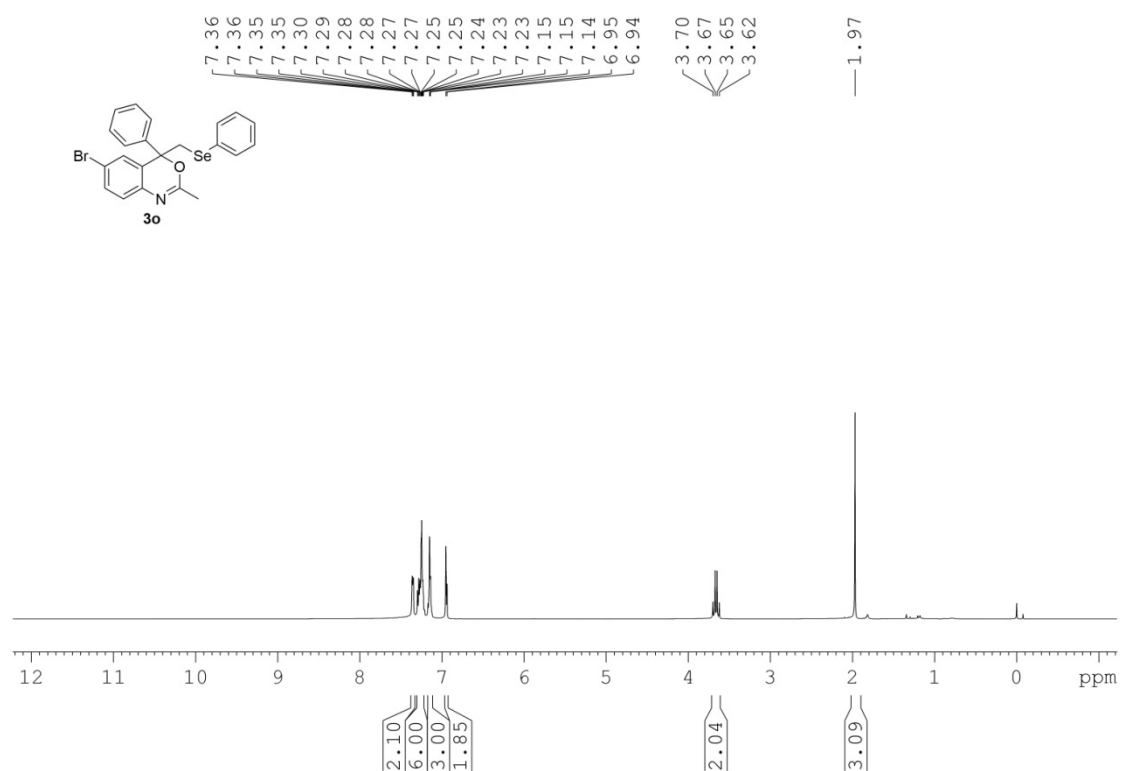


Figure S40. ¹H NMR spectrum of **3o**

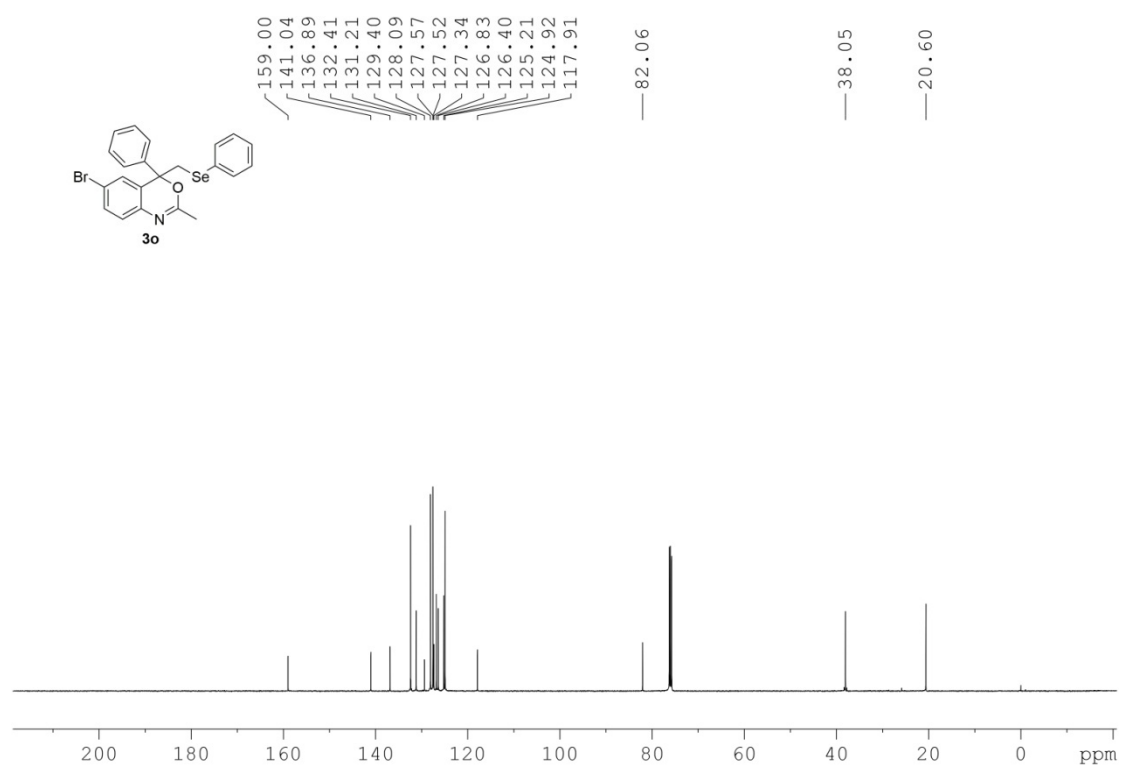


Figure S41. ¹³C NMR spectrum of **3o**

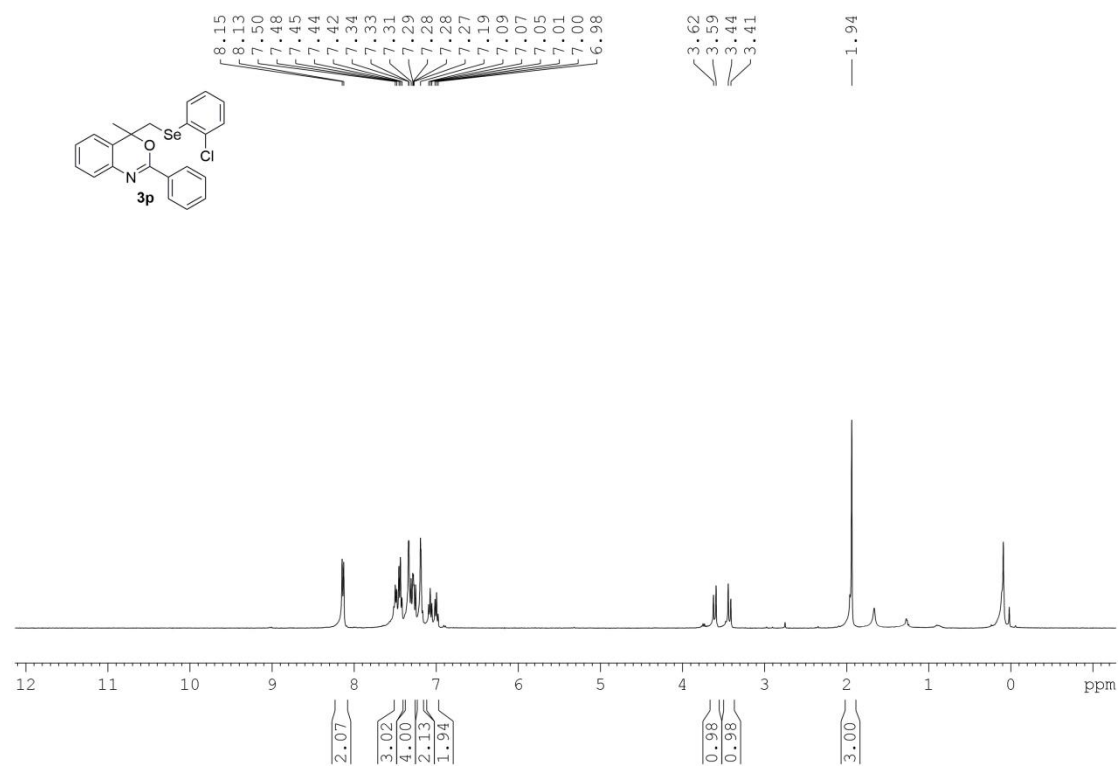


Figure S42. ¹H NMR spectrum of **3p**

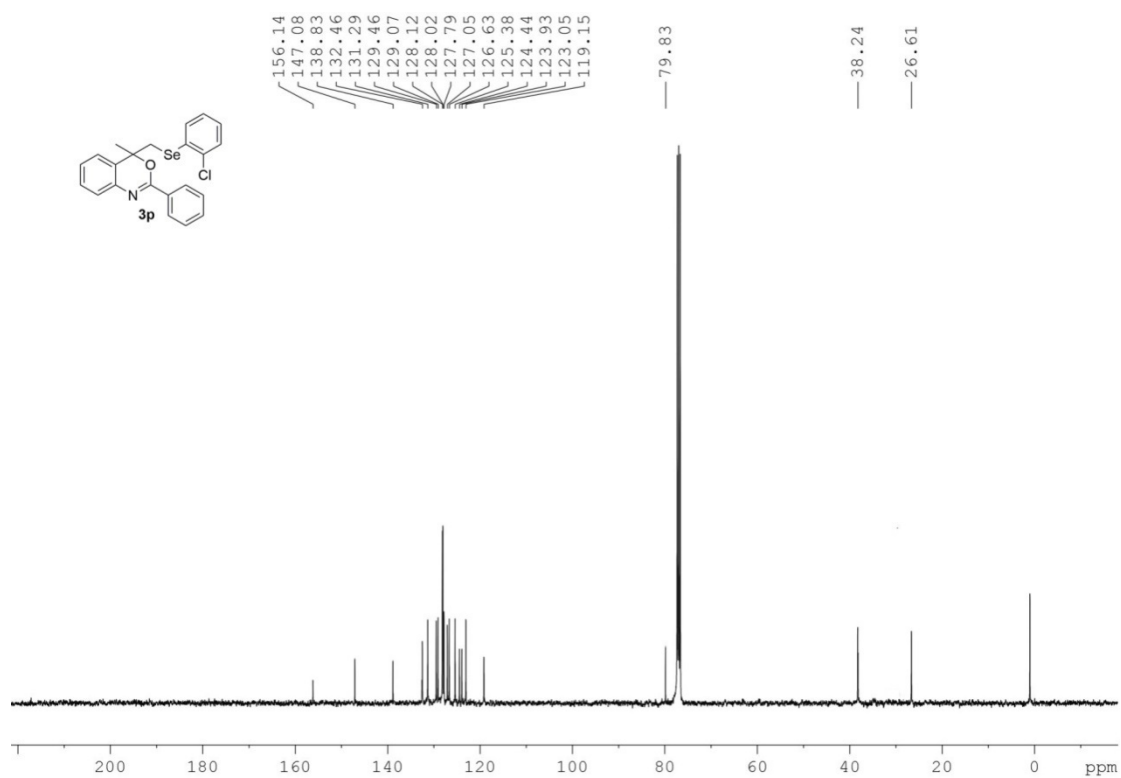


Figure S43. ¹³C NMR spectrum of **3p**

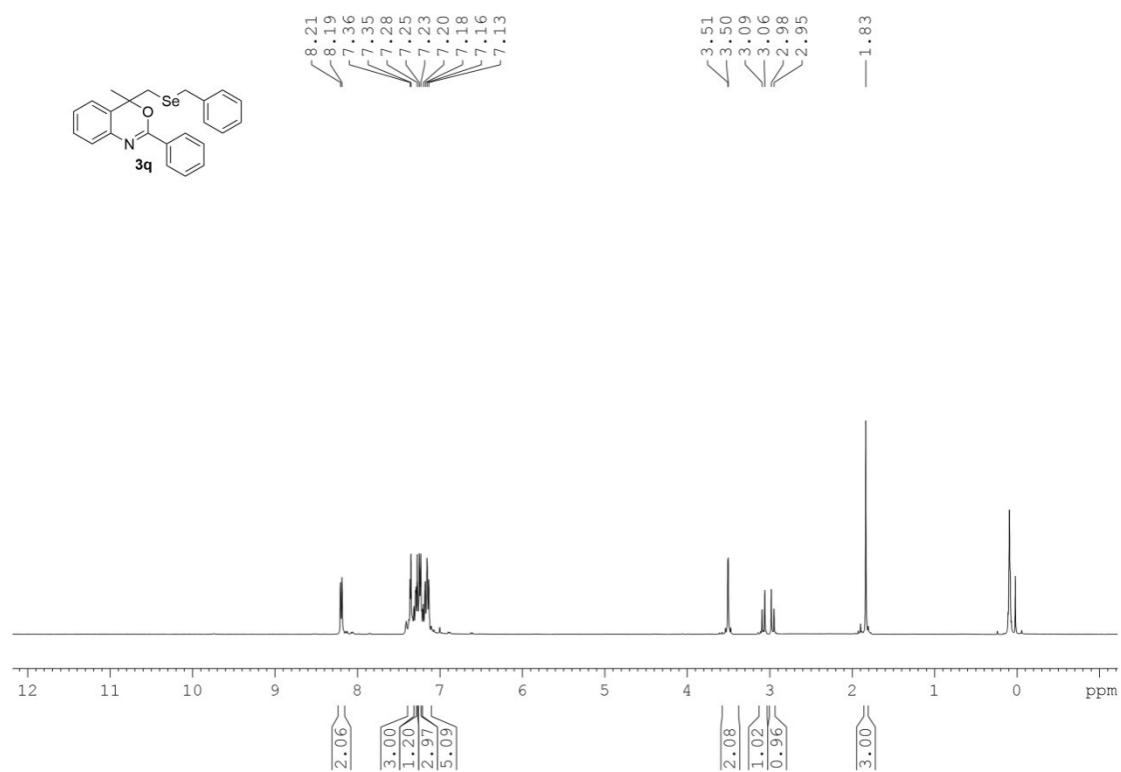


Figure S44. ^1H NMR spectrum of **3q**

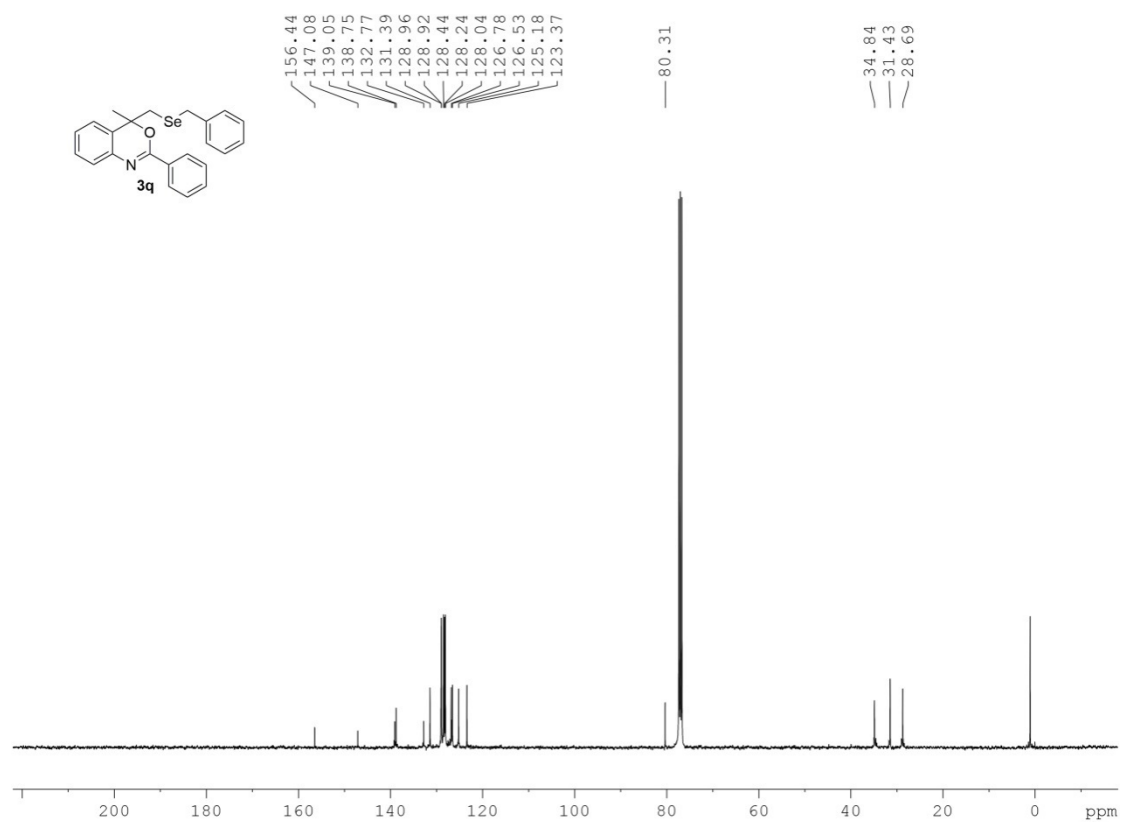


Figure S45. ^{13}C NMR spectrum of **3q**

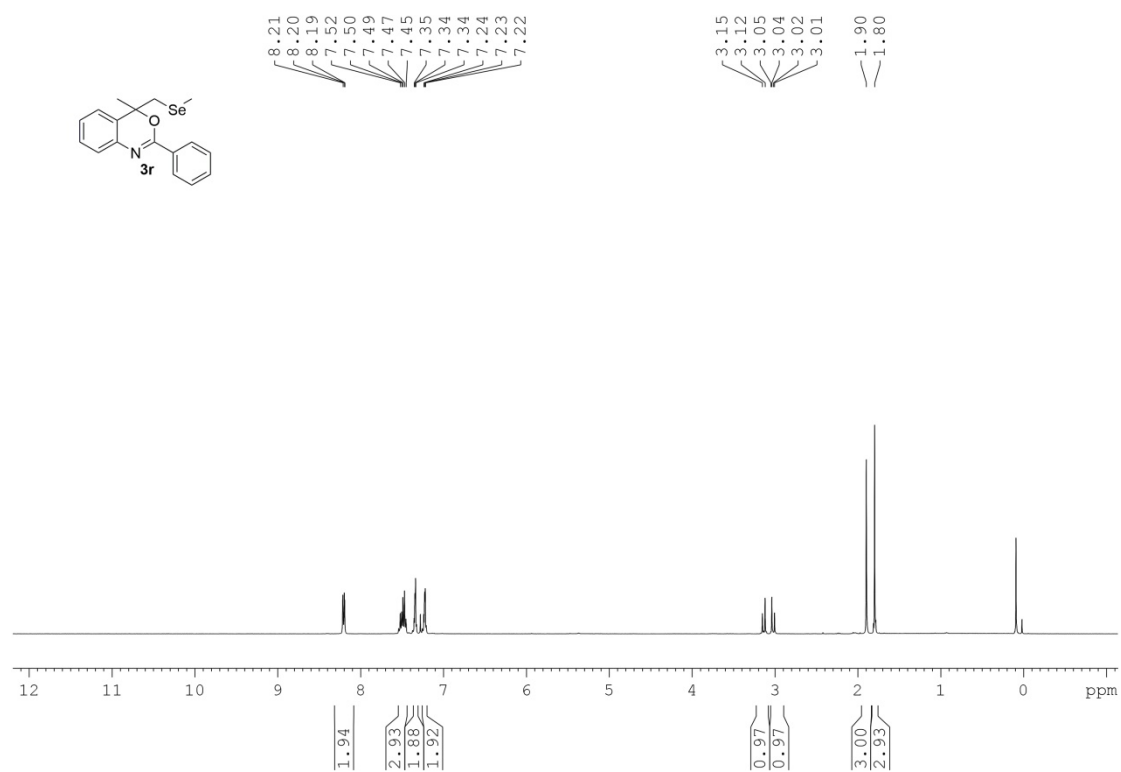


Figure S46. ¹H NMR spectrum of **3r**

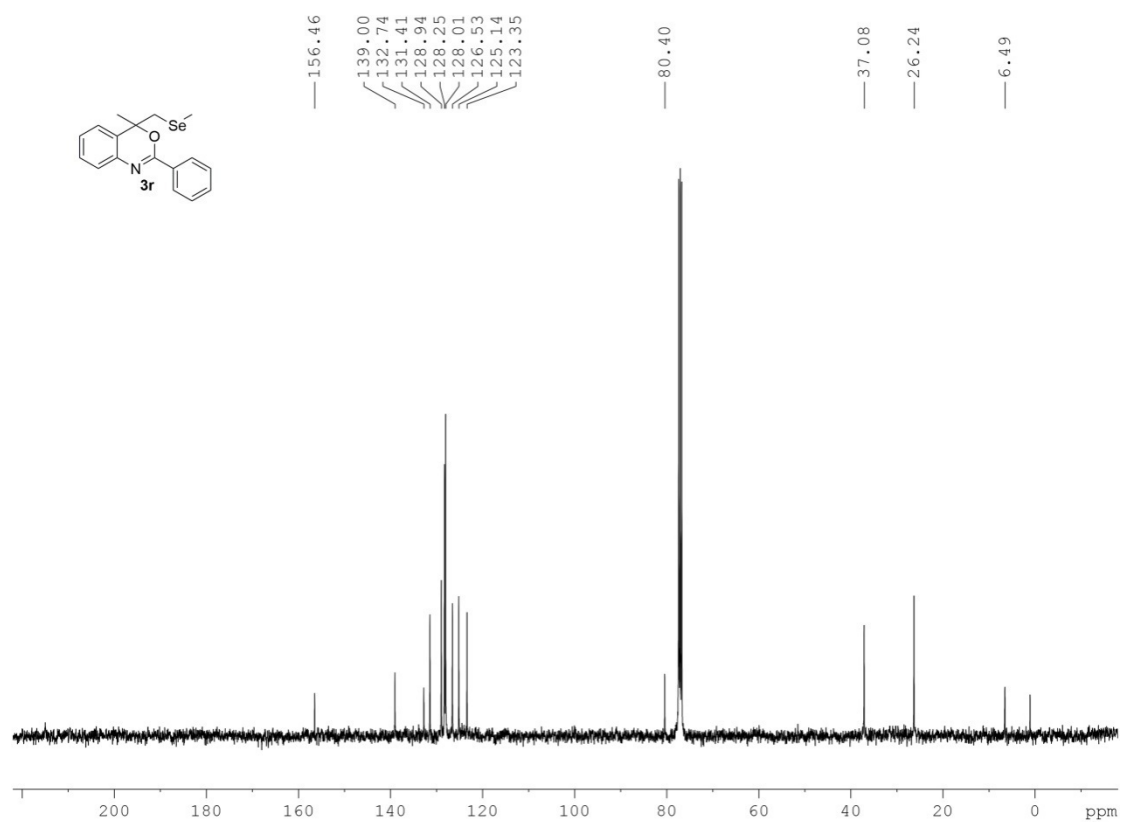


Figure S47. ¹³C NMR spectrum of **3r**

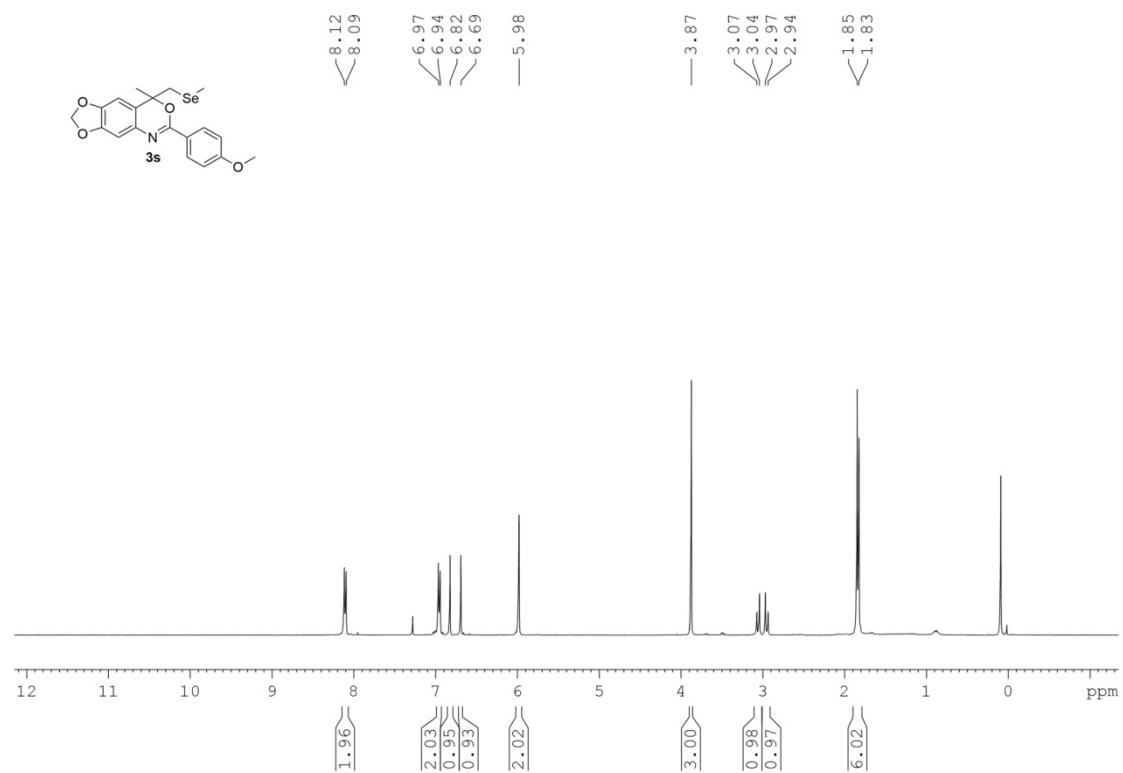


Figure S48. ^1H NMR spectrum of **3s**

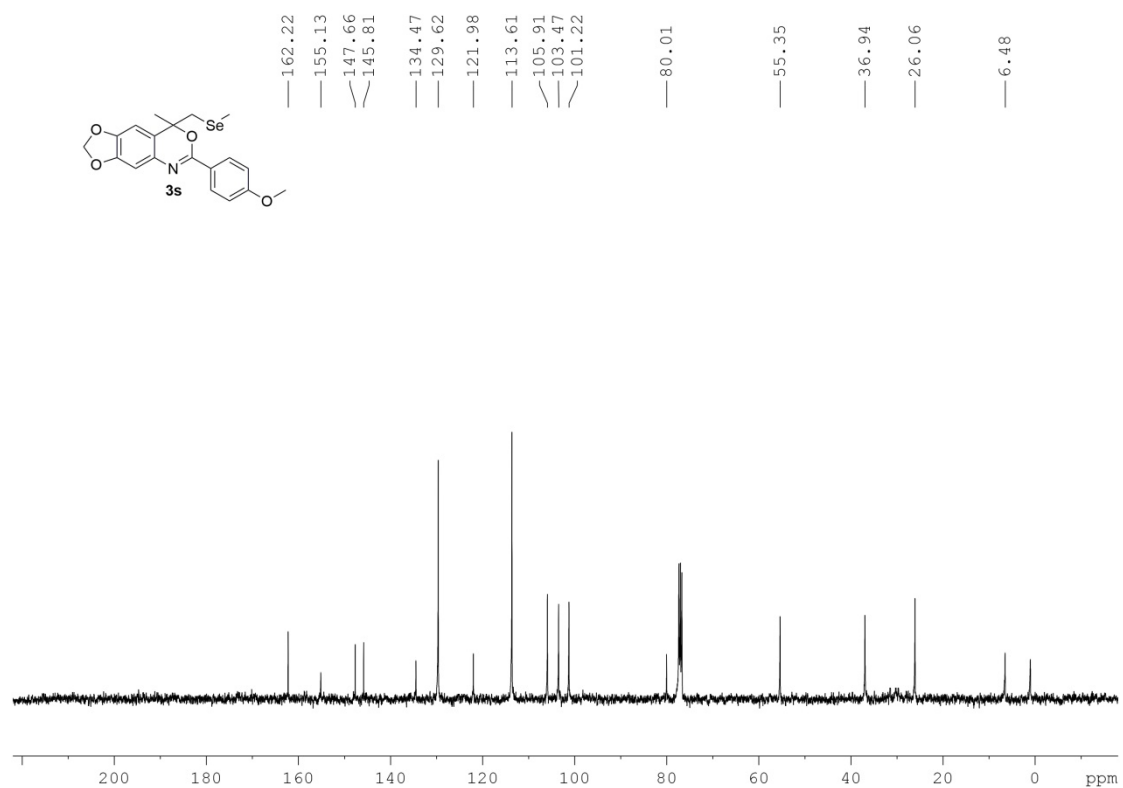


Figure S49. ^{13}C NMR spectrum of **3s**

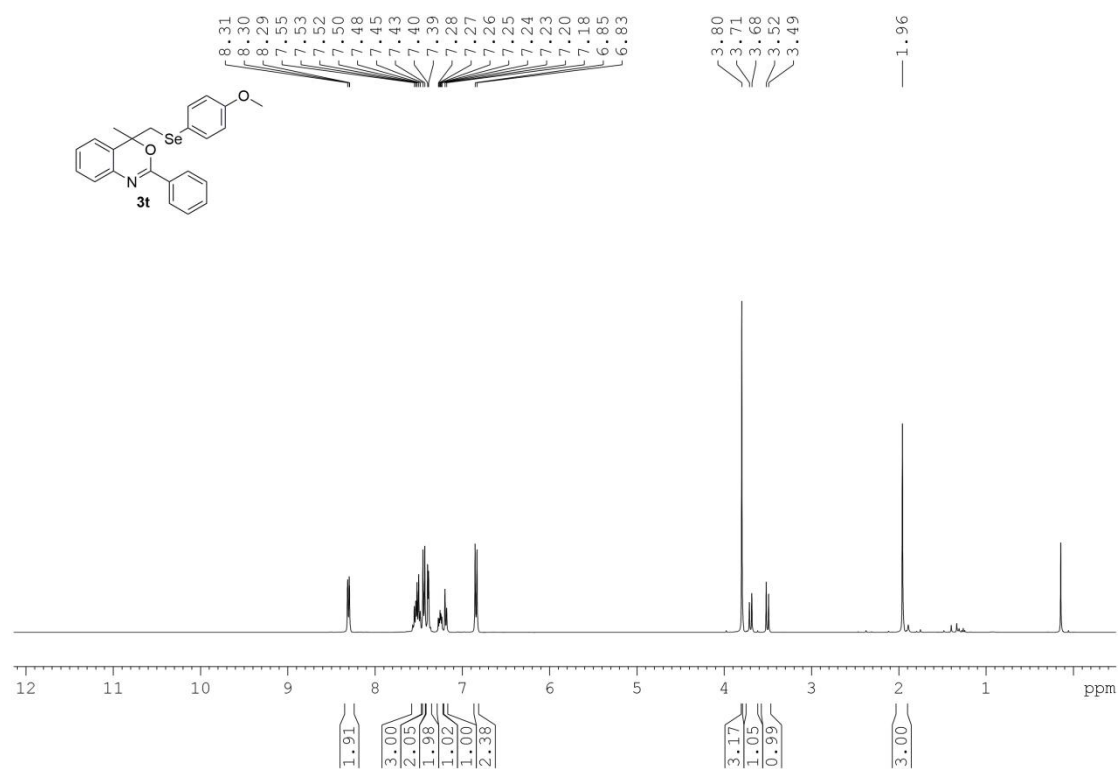


Figure S50. ¹H NMR spectrum of **3t**

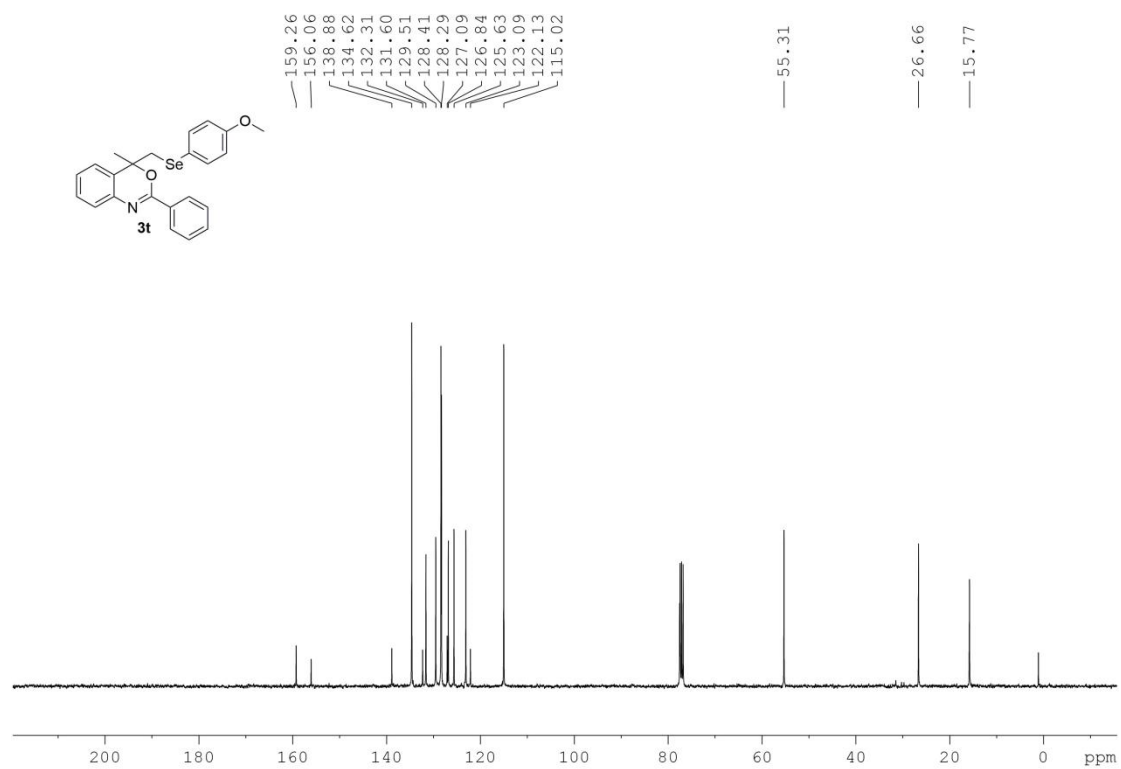


Figure S51. ¹³C NMR spectrum of **3t**

6. References

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