A Facile and Practical Solvent-Free One-Pot Synthesis of (*Z*)-4-Methylene-3-selenaquinoline Derivatives from *o*-Ethynylanilines and Isoselenocyanates[1]

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Abstract: Heating of *o*-ethynylanilines with isoselenocyanates directly resulted in the 6-*exo-dig* mode ring-closure reaction of the adducts to give the (*Z*)-2-imino-4-methylene-3-selenaquinolines in moderate to good yields. Based on this convenient, solvent-free, catalyst-free method, several 3-selenaquinoline derivatives (3,1-benzoselenazines) were easily obtained in one pot. Successful application of the microwave-assisted synthesis of these compounds was also investigated.

Key words: *o*-ethynyaniline, isoselenocyanate, 3-selenaquinoline, 6-*exo* mode cyclization, microwave

Selenium-containing heterocycles are of significant general interest not only because of their attractive chemical properties and reactivities, but also because of their pharmaceutical applications.[2] In particular, 1,3-selenazines,[3] which are six-membered heterocyclic compounds containing two heteroatoms, nitrogen and selenium, display significant antibacterial activity against both Gram-negative and Gram-positive bacteria and potential anti-tumor effects against human cancer cell. In general, it is difficult to construct the six-membered 1,3-selenazine skeleton. Monocyclic 1,3-selenazines have been mainly prepared using selenoamides,[4] selenoureas[5] or related compounds.[6] To the best of our knowledge, only three papers[7] are available on the synthesis of the benzene-ring-fused 4-selenaisoquinoline derivatives, which were obtained by cyclization of *o*-selenocyanatobenzoyl chloride with HCl. However, there is no report on the preparation of their isomers, i.e., 3-selenaquinolines.

Isoselenocyanates,[8] which are easy to prepare and are relatively stable and safe to handle and store, have recently been used as a powerful tool for the synthesis of various selenium-containing heterocycles. It has been shown that the reaction of bifunctional nucleophiles with isoselenocyanates produced several five- to seven-membered selenium-containing heterocycles. For examples, Koketsu and co-workers have described the synthesis of 2-imino-1,3-oxaselenolanes[9] and 1,3-oxaselenepanes[10] by the reactions of isoselenocyanates with 2-bromoethanol and 4-bromobutanol, respectively. The synthesis of the 1,3-selenazepanes using isoselenocyanates and 5-chlorobutylamines has been reported by Heimgartner and co-workers.[11] 1,3-Selenazolidines were also obtained by the reaction of isoselenocyanates and the propargylamines[12] or nitrile compounds.[13]

In the meantime, tandem addition–cyclizations of *o*-ethynylanilines with the aryl isocyanates[14] and isothiocyanates[15] were reported by Wu and co-workers in 2008. The former is a palladium(II) chloride catalyzed reaction to give indole derivatives[14] via the 5-*endo-dig* mode cyclization of the adducts. The latter provided the synthesis of the 1,3-benzothiazines[15] by the silver-catalyzed reaction of anilines and also, mainly, aryl isothiocyanates.

On the other hand, we have previously disclosed the syntheses of selenium-containing heterocycles using intramolecular ring closure of selenols, which were generated by the reaction of aryl (alkyl) halides with sodium hydrogen selenide (NaHSe) or aryllithium and elemental selenium, with an ethynyl moiety as the synthetic strategy.[16] Very recently, the intramolecular cyclization of alkyneselenols, generated in situ from selenolactones and ethynyllithium, was also reported.[17] In this paper, we now describe the practical solvent-free, catalyst-free, one-pot preparation of selenaquinoline derivatives by intramolecular cyclization of selenols, which used isoselenocyanates as the selenium source.

A preliminary survey to optimize the reaction conditions was first carried out. One mole of the *o*-ethynylaniline **1a** with a butyl group at the triple bond was refluxed with 1.2 equivalents of cyclohexyl isoselenocyanate (**2A**), the secondary aliphatic isoselenocyanate, in benzene (5 mL) for 72 hours to afford the 2-imino-3-selenaquinoline **3Aa** in only 2% yield. The starting material was recovered in 36% yield along with an unidentified complex mixture (Table 1, entry 1). When **1a** was similarly heated under refluxed conditions in nonpolar solvents, such as toluene, xylene, or mesitylene, the desired compound **3Aa** was isolated in 8–27% yields. An increase in the reaction temperature tends to increase the yields of the products, while refluxing in mesitylene (~160 °C) produced **3Aa** in a low yield due to the instability of the isoselenocyanate **2A** (entries 2–4).

The addition of triethylamine in *o*-xylene also did not give a good result (entry 5). The use of polar solvents, e.g., pyridine, dioxane, DMF, and DMSO, at 100 °C or 130 °C reduced the yields of the products (entries 6–9). Increasing the concentration of *o*-ethynylaniline (**1a**) by ten times with cyclohexyl isoselenocyanate (**2A**) in xylene for 6.5

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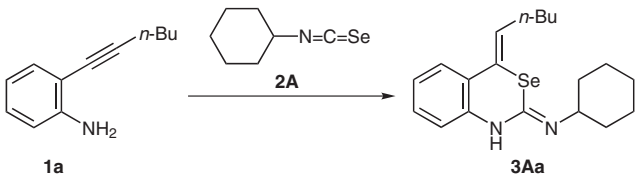
Table 1 Reaction of *o*-(Hex-1-ynyl)aniline (**1a**) with Cyclohexyl Isoselenocyanate (**2A**)



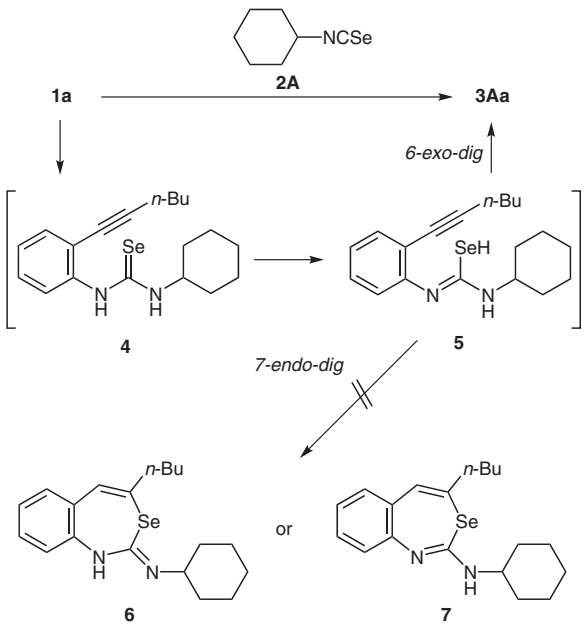
1a **3Aa**

Entry	Conditions	Substrate concentration (M)[a]	Recovery[b] (%)	Yield[b] (%)
1	benzene, reflux, 72 h	0.2	36	2
2	toluene, reflux, 72 h	0.2	21	12
3	*o*-xylene, reflux, 72 h	0.2	27	27
4	mesitylene, reflux, 9 h	0.2	46	8
5	*o*-xylene, Et_3N, reflux, 72 h	0.2	24	3
6	pyridine, reflux, 72 h	0.2	24	8
7	dioxane, reflux, 72 h	0.2	22	6
8	DMF, 130 °C, 31 h	0.2	34	1
9	DMSO, 130 °C, 72 h	0.2	25	6
10	xylene, 130 °C, 6.5 h	2	-	52
11	neat, 130 °C, 4 h	–	-	88

[a] Using substrate **1a** (1.0 mmol), **2A** (1.2 mmol), and solvent (5 mL), except entries 10 and 11.
[b] Isolated yield.

hours at 130 °C gave the 3-selenaquinoline **3Aa** in 52% yield (entry 10). Furthermore, the solvent-free reaction of *o*-ethynylaniline (**1a**) with isoselenocyanate **2A** at 130 °C afforded **3Aa** in 88% yield as the sole product (entry 11).

A possible mechanism for the formation of 2-imino-3-selenaquinoline **3Aa** from *o*-ethynylaniline (**1a**) with isoselenocyanate **2A** is shown in Scheme 1. The initial adduct, 1-cyclohexyl-3-phenylselenourea **4**, undergoes tautomerism to form the iminoselenol **5**. The regio- and stereoselective intramolecular cyclization of the resulting selenol **5** with the triple bond proceeds via the 6-*exo-dig* mode to give the successful 3-selenaquinoline **3**. No 7-*endo-dig* mode cyclization products **6** or **7** were obtained in this case.



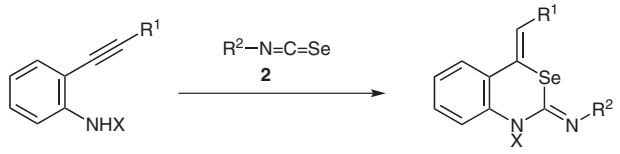
Scheme 1

Next, the extension of this tandem addition–ring closure reaction of the *o*-ethynylanilines **1b–f** having an alkyl, phenyl, or trimethylsilyl group at the ethynyl moiety and a few types of isoselenocyanates **2B–D** was carried out (Table 2). The *o*-ethynylaniline (**1a**) was similarly refluxed with 1.2 equivalents of butyl isoselenocyanate (**2B**), the primary aliphatic isoselenocyanate, in xylene (method I) for 22 hours to give the desired (butylimino)-3-selenaquinoline **3Ba** in 44% yield (entry 3). The reaction of **1a** with isoselenocyanate **2B** under solvent-free conditions (method II) gave **3Ba** in 62% yield (entry 4). However, *tert*-butyl isoselenocyanate (**2C**), a tertiary aliphatic isoselenocyanate, reacted with *o*-ethynylaniline (**1a**) under both the conditions of methods I and II to give a complex mixture without producing any characterized products (entries 5 and 6). When the *o*-ethynylaniline (**1a**) was heated with phenyl isoselenocyanate (**2D**) under the conditions of methods I and II to give 2-(phenylimino)-3-selenaquinoline **3Da** in 33% and 41% yields, respectively (entries 7 and 8). Therefore, the reaction of the several types of *o*-ethynylanilines **1b–f** with cyclohexyl isoselenocyanate (**2A**) under the conditions of method II was

next examined. In these cases, the 2-(cyclohexyimino)-3-selenaquinolines **3Ab–f** with an alkylidene or benzylidene group at C4 were produced in moderate yields (entries 9–13), and the 2-(phenylimino)-3-selenaquinoline **3Dd** was also obtained in 87% yield by using phenyl isoselenocyanate (**2D**) instead of **2A** (entry 14). In contrast, both the *N*-methyl- **8a** and *N*-benzyl-*o*-ethynylanilines (**9a**) did not react with the isoselenocyanates **2** to produce the corresponding 3-selenaquinolines **10** and **11**. The first step, the nucleophilic addition of the anilines **8** and **9** to the isoselenocyanates **2A–D** did not occur under the conditions of method I; the starting isoselenocyanates **2A–D** were recovered (entries 15 and 16). The secondary amines **8** and **9** may be unable to attack the sp carbon of the isoselenocyanate **2** due to steric hindrance of the N-substituent and ethynyl moiety at the *ortho* position in spite of higher electrophilicity than that of the primary anilines **1**. Similarly, the steric bulky *tert*-butyl isoselenocyanate (**2C**) decomposed under the same conditions without forming the corresponding adducts.

On the other hand, solvent-free[18] and microwave-assisted synthesis[19] has gained popularity in recent years, by reducing the reaction time from hours to minutes and increasing the yields. Thus, this construction of the 3-selenaquinoline framework was finally successfully attempted using the microwave synthesis instead of traditional heating in the solvent or solvent-free systems (method I or II) described above. After several unsuccessful evaluations of the method, we determined the optimized reaction conditions. The results obtained by the microwave irradiation are summarized in Table 3. These results clearly indicate the following benefits: (1) this mi-

Table 2 4-Methylene-3-selenaquinolines **3**



1 X = H
8 X = Me
9 X = Bn

a R^1 = *n*-Bu
b R^1 = Me
c R^1 = *t*-Bu
d R^1 = Ph
e R^1 = TMS
f R^1 = H

A R^2 = *c*-Hex
B R^2 = *n*-Bu
C R^2 = *t*-Bu
D R^2 = Ph

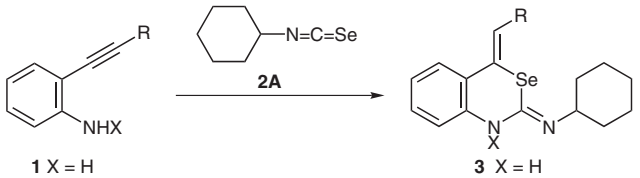
3 X = H
10 X Me
11 X = Bn

Entry	X	R^1	R^2	Method[a]	Time (h)	Product	Yield[b] (%)
1	H	Bu	*c*-Hex	I	6.5	**3Aa**	52
2	H	Bu	*c*-Hex	II	4	**3Aa**	88
3	H	Bu	Bu	I	22	**3Ba**	44
4	H	Bu	Bu	II	7	**3Ba**	62
5	H	Bu	*t*-Bu	I	7	**3Ca**	0[c]
6	H	Bu	*t*-Bu	II	7	**3Ca**	0[c]
7	H	Bu	Ph	I	3.5	**3Da**	43
8	H	Bu	Ph	II	3.5	**3Da**	51
9	H	Me	*c*-Hex	II	8	**3Ab**	63
10	H	*t*-Bu	*c*-Hex	II	11	**3Ac**	53
11	H	Ph	*c*-Hex	II	13	**3Ad**	68
12	H	TMS	*c*-Hex	II	20	**3Ae**	47
13	H	H	*c*-Hex	II	16	**3Af**	51
14	H	Ph	Ph	II	2.5	**3Dd**	87
15	Me	Bu	*c*-Hex	II	20	**10Aa**	0[d]
16	Bn	Bu	*c*-Hex	II	20	**11Aa**	0[d]

[a] Method I: xylene, reflux; method II: neat, 130 °C.
[b] Isolated yield.
[c] Decomposed.
[d] No reaction.

crowave reaction efficiently proceeded and was completed even when the reaction time was reduced from one hour to almost within 30 minutes; (2) solvent-free system; and (3) the products were obtained directly by short chromatography purification.

Table 3 Microwave Synthesis of 4-Methylene-3-selenaquinolines **3A**



1 X = H
8 X = Me
9 X = Bn

3 X = H
10 X Me
11 X = Bn

Entry	X	R	Time (min)	Product	Yield[a] (%)
1	H	Bu	25	**3Aa**	87
2	H	Me	26	**3Ab**	54
3	H	*t*-Bu	34	**3Ac**	59
4	H	Ph	48	**3Ad**	72
5	H	TMS	26	**3Ae**	53
6	H	H	28	**3Af**	46
7	Me	Bu	40	**10Aa**	0[b]
8	Bn	Bu	40	**11Aa**	0[b]

[a] Isolated yield.
[b] Decomposed.

The structures of these 3-selenaquinoline **3** were elucidated from MS, ^{1}H and ^{13}C NMR spectra, and elemental analyses, and finally established by single-crystal X-ray studies using of phenyl derivative **3Dd** (Figure 1).[20]

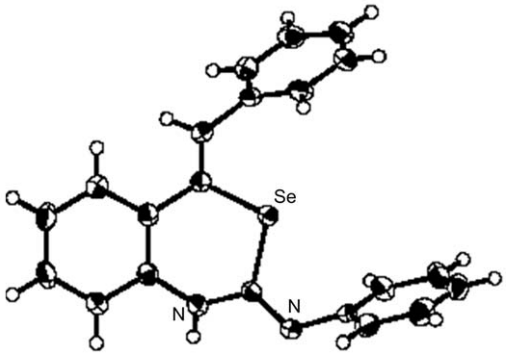


Figure 1 ORTEP drawing of **3Dd** with 50% probability level

In conclusion, we have developed the practical one-pot preparation of (*Z*)-methylene-3-selenaquinolines by the solvent-free, catalyst-free reaction of *o*-ethynylanilines and isoselenocyanates.

The microwave heating was performed in The CEM Focused Microwave™ Synthesis System (CEM Corporation). Melting points were measured on a Yanagimoto micromelting point hot stage apparatus and are uncorrected. IR spectra were recorded on a Horiba FT-720 spectrophotometer. MS and HRMS spectra were recorded on a Jeol SX-102A instrument. NMR spectra were recorded on a Jeol ECP-500 (500 MHz) spectrometer ($CDCl_3$ or DMSO-d_6, TMS internal standard).

All ethynylanilines, *o*-(hex-1-ynyl)aniline (**1a**),[21] *o*-(prop-1-ynyl)aniline (**1b**),[22] *o*-(3,3-dimethylbut-1-ynyl)aniline (**1c**),[23] *o*-(phenylethynyl)aniline (**1d**),[22] *o*-[(trimethylsilyl)ethynyl]aniline (**1e**),[23,24] and *o*-ethynylaniline (**1f**)[22,23] were prepared by literature methods. Cyclohexyl isoselenocyanate (**2A**),[25] butyl isoselenocyanate (**2B**),[25] *tert*-butyl isoselenocyanate (**2C**),[25] and phenyl isoselenocyanate (**2D**)[26] were also prepared by literature methods.

(*Z*)-2-Imino-4-methylene-1,2,3,4-tetrahydro-3-selenaquinolines 3; General Procedures

Method I: A mixture of aniline **1** (1 mmol) and isoselenocyanate **2** (1.2 mmol) in *o*-xylene (0.5 mL) was heated at 130 °C for 3.5–22 h. The mixture was evaporated and the residue was chromatographed (silica gel) to give **3**.

Method II: A mixture of aniline **1** (1 mmol) and isoselenocyanate **2** (1.2 mmol) was heated at 130 °C without solvent for 3.5–20 h. The mixture was chromatographed (silica gel) to give **3**.

Method III: Aniline **1** (1 mmol), isoselenocyanate **2** (1.2 mmol), and a stirrer bar were added to a vial microwave tube. The vial was sealed with a septum and subjected to microwave irradiation at 115 °C for 25–48 min. The mixture was chromatographed (silica gel) to give **3**.

(*Z*)-2-(Cyclohexylimino)-4-pentylidene-1,2,3,4-tetrahydro-3-selenaquinoline (3Aa)

Yellow prisms; mp 99–101 °C (*n*-hexane).

IR (KBr): 3238 (NH), 1603 cm^{-1} (C=N).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.3 Hz, 3 H), 1.14–1.28 (m, 3 H), 1.34–1.52 (m, 6 H), 1.58–1.67 (m, 1 H), 1.70–1.78 (m, 2 H), 2.05–2.14 (m, 2 H), 2.24 (dt, *J* = 7.2, 7.2 Hz, 2 H), 3.94–4.05 (m, 1 H) (all H_{Bu} and H_{Cy}), 4.48–4.67 (br, 1 H, NH), 6.26 (t, *J* = 7.2 Hz, 1 H, H_{olefin}), 7.04 (ddd, *J* = 7.7, 6.4, 1.4 Hz, 1 H), 7.12 (dd, *J* = 8.0, 1.4 Hz, 1 H), 7.23 (ddd, *J* = 8.0, 6.4, 1.4 Hz, 1 H), 7.33 (dd, *J* = 7.7, 1.4 Hz, 1 H) (all H_{Ph}).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0 (q), 22.4 (t), 24.9 (t), 25.7 (t), 31.1 (t), 31.3 (t), 33.5 (t), 51.6 (d), 122.1 (s), 123.5 (d), 124.6 (d), 125.3 (s), 126.3 (d), 128.7 (d), 130.8 (d), 146.1 (s), 147.9 (s).

MS (EI): *m*/*z* (%) = 362 (M^+, 100), 360 (50), 224 (81), 199 (48).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{26}N_2{}^{80}Se$: 362.1262; found: 362.1269.

(*Z*)-2-(Butylimino)-4-pentylidene-1,2,3,4-tetrahydro-3-selenaquinoline (3Ba)

Yellow oil.

IR (neat): 3402 (NH), 1610 cm^{-1} (C=N).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.2 Hz, 3 H), 0.96 (t, *J* = 7.3 Hz, 3 H), 1.34–1.51 (m, 6 H), 1.57–1.64 (m, 2 H), 2.24 (dt, *J* = 7.2, 7.2 Hz, 2 H), 3.53 (*J* = 7.1 Hz, 2 H) (all H_{Bu}, 2 Bu), 6.26 (t, *J* = 7.2 Hz, 1 H, H_{olefin}), 7.05 (ddd, *J* = 7.7, 7.2, 1.4 Hz, 1 H), 7.14 (dd, *J* = 8.0, 1.4 Hz, 1 H), 7.23 (ddd, *J* = 8.0, 7.2, 1.5 Hz, 1 H), 7.34 (dd, *J* = 7.7, 1.5 Hz, 1 H) (all H_{Ph}).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8 (q), 14.0 (q), 20.1 (t), 22.4 (t), 31.15 (t), 31.23 (t), 31.8 (t), 42.8 (t), 122.2 (s), 123.7 (d), 124.7 (d), 125.2 (s), 126.4 (d), 128.7 (d), 131.0 (d), 146.1 (s), 148.9 (s).

MS (EI): *m*/*z* = 336 (M^+, 100), 334 (51), 293 (38), 255 (59), 227 (42), 224 (38).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{24}N_2{}^{80}Se$: 336.1105; found: 336.1104.

(*Z*)-4-Pentylidene-2-(phenylimino)-1,2,3,4-tetrahydro-3-selenaquinoline (3Da)
Orange prisms; mp 102–104 °C (*n*-hexane).

IR (KBr): 3434 (NH), 1631 cm^{-1} (C=N).

^1H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.3 Hz, 3 H), 1.28–1.38 (m, 2 H), 1.38–1.47 (m, 2 H), 2.18 (dt, *J* = 7.2, 7.2 Hz, 2 H) (all H_{Bu}), 3.31–3.98 (br, 1 H, NH), 6.24 (t, *J* = 7.2 Hz, 1 H, H_{olefin}), 6.90 (d, *J* = 8.0 Hz, 1 H), 7.02 (ddd, *J* = 7.8, 6.4, 1.3 Hz, 1 H), 7.09–7.17 (m, 2 H), 7.25–7.30 (m, 2 H), 7.30–7.36 (m, 3 H) (all H_{Ph}).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0 (q), 22.3 (t), 31.1 (t), 31.2 (t), 121.9 (d), 122.2 (d), 123.0 (s), 123.5 (d), 124.0 (s), 124.1 (d), 125.0 (d), 128.7 (d), 129.0 (d), 131.9 (d), 141.4 (s), 144.3 (s), 148.8 (s).

MS (EI): *m*/*z* = 356 (M^+, 72), 354 (37), 300 (40), 275 (100), 231 (45).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{20}N_2{}^{80}Se$: 356.0793; found: 356.0792.

(*Z*)-2-(Cyclohexylimino)-4-ethylidene-1,2,3,4-tetrahydro-3-selenaquinoline (3Ab)
Yellow oil.

IR (neat): 3392 (NH), 1610 cm^{-1} (C=N).

^1H NMR (500 MHz, $CDCl_3$): δ = 1.11–1.24 (m, 3 H), 1.33–1.44 (m, 2 H), 1.57–1.64 (m, 1 H), 1.67–1.75 (m, 2 H), 2.02–2.13 (m, 2 H), 3.93–4.04 (m, 1 H) (all H_{Cy}), 1.86 (d, *J* = 6.8 Hz, 3 H, CH_3), 4.50–4.78 (br, 1 H, NH), 6.30 (q, *J* = 6.8 Hz, 1 H, H_{olefin}), 7.02 (ddd, *J* = 7.7, 7.1, 1.1 Hz, 1 H), 7.13 (dd, *J* = 8.0, 1.1 Hz, 1 H), 7.22 (ddd, *J* = 8.0, 7.1, 1.3 Hz, 1 H), 7.31 (dd, *J* = 7.7, 1.3 Hz, 1 H) (all H_{Ph}).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.9 (q), 24.9 (t), 25.6 (t), 33.4 (t), 51.6 (d), 122.1 (s), 123.5 (d), 124.5 (d), 124.9 (d), 126.3 (d), 126.5 (s), 128.7 (d), 146.0 (s), 147.7 (s).

MS (EI): *m*/*z* = 320 (M^+, 60), 318 (31), 238 (45), 236 (23), 158 (100), 130 (35).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{20}N_2{}^{80}Se$: 320.0792; found: 320.0793.

(*Z*)-2-(Cyclohexylimino)-4-(2,2-dimethylpropylidene)-1,2,3,4-tetrahydro-3-selenaquinoline (3Ac)
Yellow oil.

IR (neat): 3435 (NH), 1608 cm^{-1} (C=N).

^1H NMR (500 MHz, $CDCl_3$): δ = 1.10 (s, 9 H, *t*-Bu), 1.15–1.24 (m, 3 H), 1.33–1.45 (m, 2 H), 1.58–1.66 (m, 1 H), 1.68–1.77 (m, 2 H), 2.04–2.13 (m, 2 H), 3.90–4.00 (m, 1 H) (all H_{Cy}), 4.18–4.92 (br, 1 H, NH), 6.00 (s, 1 H, H_{olefin}), 6.99 (ddd, *J* = 8.0, 7.4, 1.3 Hz, 1 H), 7.10 (dd, *J* = 8.0, 1.1 Hz, 1 H), 7.22 (ddd, *J* = 7.7, 7.4, 1.1 Hz, 1 H), 7.31 (dd, *J* = 7.7, 1.3 Hz, 1 H) (all H_{Ph}).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.8 (t), 25.6 (t), 31.0 (q), 33.5 (t), 35.7 (s), 51.9 (d), 121.4 (s), 121.7 (d), 124.4 (s, × 2), 124.9 (d), 127.7 (d), 128.8 (d), 148.7 (s), 149.5 (d).

MS (EI): *m*/*z* = 362 (M^+, 100), 360 (52), 305 (49), 224 (45).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{26}N_2{}^{80}Se$: 362.1262; found: 362.1251.

(*Z*)-4-Benzylidene-2-(cyclohexylimino)-1,2,3,4-tetrahydro-3-selenaquinoline (3Ad)
Yellow prisms; mp 146–147 °C (*n*-hexane).

IR (KBr): 3390 (NH), 1616 cm^{-1} (C=N).

^1H NMR (500 MHz, $CDCl_3$): δ = 1.07–1.24 (m, 3 H), 1.30–1.45 (m, 2 H), 1.54–1.78 (m, 3 H), 1.96–2.10 (m, 2 H), 3.92–4.04 (m, 1 H) (all H_{Cy}), 4.29–4.60 (br, 1 H, NH), 7.06–7.14 (m, 1 H), 7.17 (dd, *J* = 8.0, 1.4 Hz, 1 H), 7.22–7.43 (m, 7 H), 7.45 (dd, *J* = 7.9, 1.5 Hz, 1 H) (all H_{olefin} and H_{Ph}).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.7 (t), 25.6 (t), 33.3 (t), 51.4 (d), 122.2 (s), 123.6 (d), 125.9 (d), 126.5 (d), 127.6 (s), 127.7 (d), 128.1 (d), 129.1 (d), 129.4 (d), 129.8 (d), 137.0 (s), 146.0 (s), 147.2 (s).

MS (EI): *m*/*z* = 382 (M^+, 100), 380 (50), 300 (60), 299 (41), 220 (52), 219 (92).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{21}H_{22}N_2{}^{80}Se$: 382.0949; found: 382.0956.

(*Z*)-2-(Cyclohexylimino)-4-[(trimethylsilyl)methylene]-1,2,3,4-tetrahydro-3-selenaquinoline (3Ae)
Orange oil.

IR (neat): 3338 (NH), 1614 cm^{-1} (C=N).

^1H NMR (500 MHz, $CDCl_3$): δ = 0.23 (s, 9 H, TMS), 1.14–1.27 (m, 3 H), 1.33–1.46 (m, 2 H), 1.58–1.66 (m, 1 H), 1.68–1.77 (m, 2 H), 2.03–2.13 (m, 2 H), 3.89–4.01 (m, 1 H) (all H_{Cy}), 4.23–4.94 (br, 1 H, NH), 6.56 (s, 1 H, H_{olefin}), 7.03 (ddd, *J* = 7.6, 7.4, 1.4 Hz, 1 H), 7.10 (dd, *J* = 8.0, 1.4 Hz, 1 H), 7.21–7.26 (m, 1 H), 7.44 (dd, *J* = 7.6, 1.4 Hz, 1 H) (all H_{Ph}).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –0.42 (q), 24.8 (t), 25.6 (t), 33.5 (t), 51.8 (d), 123.1 (s), 123.6 (d), 124.0 (d), 126.6 (d), 129.5 (d), 130.8 (d), 141.3 (s), 145.9 (s), 148.6 (s).

MS (EI): *m*/*z* = 378 (M^+, 100), 376 (52), 296 (55), 281 (47), 215 (85), 73 (67).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{26}N_2{}^{80}Se$: 378.1031; found: 378.1029.

(*Z*)-2-(Cyclohexylimino)-4-methylene-1,2,3,4-tetrahydro-3-selenaquinoline (3Af)
Yellow oil.

IR (neat): 3384 (NH), 1614 cm^{-1} (C=N).

^1H NMR (500 MHz, $CDCl_3$): δ = 1.14–1.28 (m, 3 H), 1.34–1.47 (m, 2 H), 1.59–1.68 (m, 1 H), 1.70–1.78 (m, 2 H), 2.04–2.12 (m, 2 H), 3.90–4.02 (m, 1 H) (all H_{Cy}), 4.25–4.85 (br, 1 H, NH), 5.40 and 5.99 (each d, *J* = 1.1 Hz, 1 H, H_{olefin}), 7.06 (ddd, *J* = 8.0, 7.2, 1.4 Hz, 1 H), 7.14 (dd, *J* = 8.0, 1.1 Hz, 1 H), 7.24–7.29 (m, 1 H), 7.46 (dd, *J* = 7.7, 1.1 Hz, 1 H) (all H_{Ph}).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.8 (t), 25.6 (t), 33.5 (t), 51.7 (d), 115.4 (t), 120.9 (s), 123.59 (d), 123.63 (d), 126.6 (d), 129.7 (d), 133.2 (s), 146.4 (s), 148.1 (s).

MS (EI): *m*/*z* = 306 (M^+, 38), 224 (63), 196 (63), 144 (98), 116 (95), 55 (100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{18}N_2{}^{80}Se$: 306.0636; found: 306.0640.

(*Z*)-4-Benzylidene-2-(phenylimino)-1,2,3,4-tetrahydro-3-selenaquinoline (3Dd)
Colorless prisms; mp 214–215 °C ($CHCl_3$).

IR (KBr): 3448 (NH), 1626 cm^{-1} (C=N).

^1H NMR (500 MHz, DMSO-d_6): δ = 7.02 (dd, *J* = 7.3, 7.3 Hz, 1 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 7.31 (dd, *J* = 8.2, 7.6 Hz, 2 H), 7.61–7.63 (m, 2 H), 7.79–7.86 (m, 2 H) (all H_{Ph}), 7.34–7.48 (m, 6 H, H_{Ph}, H_{olefin}), 9.57 (s, 1 H, NH).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 119.5 (d), 121.6 (s), 122.6 (d), 124.5 (d), 125.7 (d), 126.7 (s), 127.8 (d), 128.2 (d), 128.3 (d), 128.7 (d), 129.0 (d), 129.5 (d), 130.3 (d), 136.6 (s), 140.5 (s), 144.1 (s), 144.9 (s).

MS (EI): *m/z* = 376 (M^+, 70), 295 (100), 193 (10), 77 (10).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{21}H_{16}N_2{}^{80}Se$: 376.0479; found: 376.0479.

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References

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(20) Single crystals of **3Dd** were obtained from solns of $CHCl_3$ after slow evaporation of the solvent at r.t. Diffraction data were collected on a Bruker Apex-II CCD. The structure analysis is based on 2629 observed reflections with $I > 2.00\sigma(I)$ and 217 variable parameters; colorless prisms, $C_{21}H_{16}N_2Se$, FW = 375.32, 233 K, monoclinic, space group $P2_1/n$, a = 10.3882(7) Å, b = 8.3928(5) Å, c = 19.432(1) Å, β = 91.164(1)°, V = 1693.9(2) Å^3, Z = 4, R = 0.0288, R_w = 0.0759, GOF = 1.037. The supplementary crystallographic data for **3Dd** (CCDC-773220) can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/products/csd/request/request.php4.

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