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Straightforward and direct access to β-seleno- amines and sulfonylamides *via* the controlled addition of phenylselenomethyllithium ($LiCH_2SePh$) to imines

Raffaele Senatore [a], Monika Malik [a], Saad Touqeer [a], Roberta Listro [b], Simona Collina [b], Wolfgang Holzer [a], Vittorio Pace [a, c, *]

[a] Department of Pharmaceutical Chemistry, University of Vienna, Althanstrasse 14, 1090, Vienna, Austria
[b] Department of Drug Sciences, University of Pavia, Via Taramelli 6, 27100, Pavia, Italy
[c] Department of Chemistry, University of Turin, Via P. Giuria 7, 10125, Turin, Italy

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Dedicated to Prof. Dr. Nuno Maulide for his outstanding contributions to the art of Synthesis.

ABSTRACT

The transfer of a α-methyl phenylseleno carbanion to variously functionalized *N*-aryl and *N*-sulfonyl imines is reported. The fast selenium-lithium exchange conducted on a diselenoacetal with *n*-BuLi enables the generation of the attacking homologative nucleophile under chemoselective conditions preserving concomitant potentially sensitive functionalities to the lithiating conditions. Uniformly high yields were observed, thus establishing a valuable and conceptually simple approach to the title compounds.

1. Introduction

Embodying selenium containing groups into an organic skeleton profoundly influences the physical-chemical features of the resulting scaffold, thus complementing the reach and well-established portfolio of (stereoselective) transformations these organometallics offer [1]. Indeed, there is a continuous and growing interest towards the biological properties displayed by organoselenium analogues whose structures are frequently encountered in enzymes governing important metabolic cascades (*e.g.* selenoprotein P, glutathione peroxidase, *inter alia*) [2]. Additionally, recent uses of selenium-based pharmacologically active substances emerged as valuable tools for treating important diseases, as exemplified by ebselen, thus further increasing the potential of such a chalcogen-containing motifs [3]. Evidently, the simultaneous derivatization of organoselenium species with additional functionalities expands the chemical space and the overall versatility of the so obtained materials. In this sense, including a nitrogen-centered group in a relevant position may represent an effective strategy for tuning pivotal molecular properties (*e.g.* solubility, cell permeability, metabolic parameters *etc.*) or, by focusing on pure synthetic aspects, it enables selective chemistries *en route* to more complex architectures [4]. In fact, the proper activation of these β-seleno amine-type manifolds results in a versatile technique for assembling different aza-cycles such as aziridines [5a, 5b, 5c] or diastereomerically enriched 2,4-disubstituted pyrrolidines [6]. This applicative significance merged with the potential exhibited in different areas including material science and drug design, [7a, 7b] motivated the development of variously oriented tactics for the construction of the motif. In recent years, the amino- or amido-selenation of olefins – *i.e.* the simultaneous installation into the sp^2-hydridized C–C bond of both the selenium atom and the nitrogenated moiety - emerged as an attractive and practical solution. Mechanistically, the electrophilic organoselenium agent generates a seleniranium ion susceptible of nucleophilic attack by the *N*-containing partner. The protocol manifests strong dependence on the nature and level of substitution of the competent olefin, as well as, on the nucleophilicity of the attacking amine or amide groups. As a consequence, the adequate modulation – *via* ionic[8], electrochemical [9] or radical [10] pathway - of these events becomes critical for the successful outcome of the targeted strategy. A logically distinct approach involves the ring opening of an aziridine with an *in situ* generated selenium anion [11]. It

* Corresponding author. Department of Chemistry, University of Turin, Via P. Giuria 7, 10125, Turin, Italy.
E-mail addresses: vittorio.pace@univie.ac.at, vittorio.pace@unito.it (V. Pace).
https://drugsynthesis.univie.ac.at/-Twitter:@LabPace (V. Pace)

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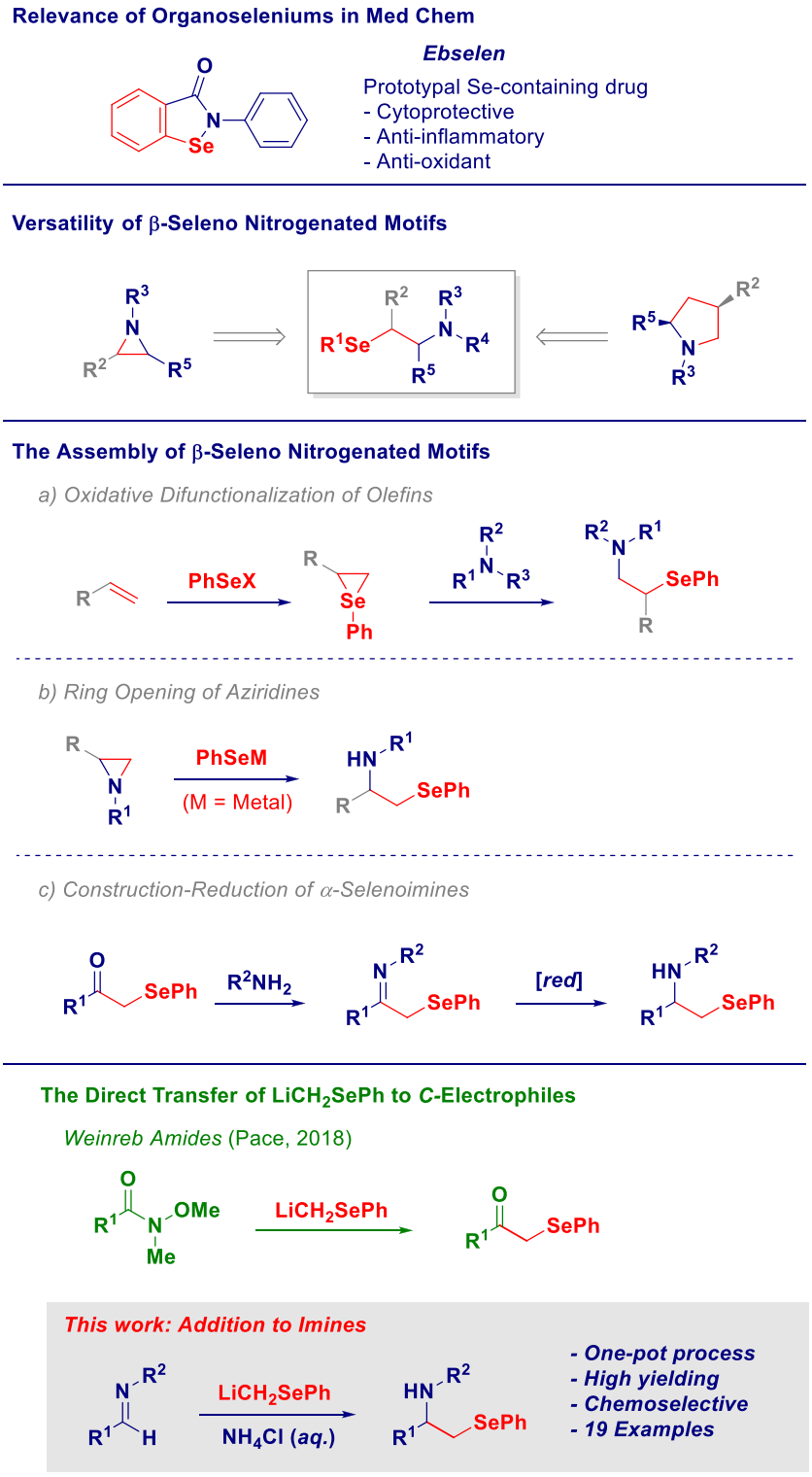
0040-4020/

appears conceivable that using these highly valuable synthons may pose severe limitations in terms of costs. Alternatively, Outurquin proposed a two-steps methodology paved on forming highly unstable and difficult to purify α-selenoimines (from the corresponding ketones) followed by the controlled reduction to the desired compounds [5a,12] (see Scheme 1)

Inspired by our work on homologation of carbon electrophiles with α-substituted methyllithiums (LiCHXY) [13,14], in 2018 we reported a general approach for introducing substituted seleniummethyl fragments – *i.e.* $RSeCH_2$ – onto Weinreb amides [13k,14a]. The strategy paved on the generation of the carbanion from a diselenoacetal [15] by adapting seminal Reich's studies [16],



Scheme 1. General context of the presented work.

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documented high versatility and chemoselectivity. We reasoned that delivering this Se-centered carbanion [17] to a given imine would produce the β-seleno nitrogenated adduct through a conceptually intuitive and novel approach. To the best of our knowledge, the employment of C–C bond forming operations for producing the title compounds is still unprecedented and, herein we disclose our findings.

2. Results and discussion

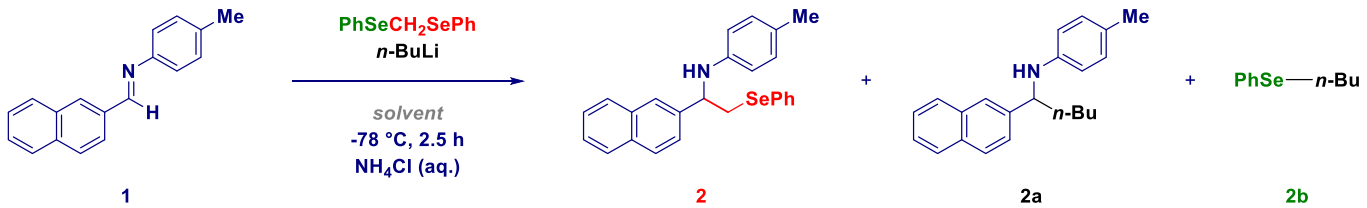
We selected the naphthyl-substituted imine **1** as the model compound for accomplishing the formal homologation with the lithiated α-methyl seleno carbanion ($LiCH_2SePh$). As anticipated, a convenient source of this species was individuated in the diselenoacetal [15a] ($PhSeCH_2SePh$) which undergoes an extremely fast selenium-lithium exchange upon treatment with *n*-BuLi. Evidently, the genesis of the requested carbanion is accompanied by the formation of the interconversion product – the selenoether *n*-BuSePh (**2b**) – which guarantees a quantitative estimation of the process. The optimization study revealed the adaptability of the conditions established for preparing α-selenoketones starting from Weinreb amides:[14a] $PhSeCH_2SePh$ (1.3 equiv), *n*-BuLi (1.25 equiv) in Et_2O at −78 °C under non-Barbier type conditions (Table 1). Although the initial experiment showed the formation of the expected β-selenoamine **2** in a reasonably good 70% yield, a noticeable amount of the aminic compound **2a** generated by the direct attack of *n*-BuLi to the azomethinic carbon was detected (entry 1). With the aim of improving the yield of **2**, we briefly screened the effect of additional parameters: *i*) the simple switching to THF as the reaction medium did not alter significantly the **2**:**2a** ratio (entry 2); *ii*) decreasing the lithiation time was detrimental in agreement with our previous study on Weinreb amides (entries 3–4); *iii*) the use of alternative ethereal-type solvents such as 2-MeTHF [18a, 18b, 18c] and CPME [19] significantly decreased the efficiency (entries 5–6); *iv*) pleasingly, the progressive increase of the loading of Se-carbanion enables to maximize the yield up to 93%, being practically undetectable the formation of the side product **2a** (entries 7–8); *v*) using a smaller excess of diselenoacetal (2.0 equiv) compared to the lithiating agent (1.90 equiv) guarantees the full generation of $LiCH_2SePh$ and, thus to skip the concomitant, undesired attack of *n*-BuLi to **1**.

With the optimal conditions in hand, we then explored the scope of the transformation (Scheme 2). A series of variously functionalized *N*-aryl imines easily undergoes the transformation giving the expected β-phenylseleno adducts in high yields. The substitution on the aromatic ring of the starting *N*-phenyl-type aldimines was perfectly tolerated: the presence of electron-donating functionalities such as methoxy at different positions did not alter the efficiency of the methodology. Analogously, potentially sensitive halogens – including the reactive bromo-derivatives (**5** and **8**) - could be introduced on the nucleus yielding the corresponding seleno-amines. The chemoselectivity of the approach is further illustrated in the case of the nitrile-bearing compound **10**, in which this electrophilic group was preserved by the nucleophilic attack. Switching to heteroaromatic aldimines was also possible, as documented by the 2-furyl (**12**) derivative. The nature of the *N*-imine group can be conveniently shifted to a sulfonyl-analogue in order to prepare β-seleno sulfonyl imides (**13**–**19**). Interestingly, our approach constitutes an effective solution for accessing **14** whose previous synthesis through the ring-opening of an aziridine was affected by limited regiocontrol.[11] A comparable chemoselective profile was observed: halogen-containing groups – such as chlorine, fluoro, trifluoromethyl and bromo – maintain unaltered the productivity of the homologative technique. Similarly, poly- (naphthyl, **13**) or heteroaromatic (2-furyl, **18** – 2-thienyl, **19**) benzensulfonylimines acted as competent starting materials without affecting the chemical integrity of these systems.

3. Conclusions

In conclusion, we have developed a straightforward and versatile methodology for the transfer of a selenium-centered methyllithium carbanion to variously functionalized imines. The selective lithiation of a diselenoacetal ($PhSeCH_2SePh$) smoothly provides the homologating agent ($LiCH_2SePh$) which can be easily released to the electrophilic azomethinic partners. The high degree of chemoselectivity, as well as the very good to excellent yields observed, make this conceptually intuitive strategy of wide and general applicability.

Table 1
Model Reaction: Optimization.



Entry	Solvent	$LiCH_2SePh$ (equiv)	Lithiation time (min)	Ratio 2:2a	Yield of 2 (%)[a]
1[b]	Et_2O	1.25	60	76:24	70
2	THF	1.25	60	78:22	73
3	THF	1.25	45	75:25	68
4	THF	1.25	30	77:23	64
5	2-MeTHF	1.25	60	65:45	50
6	CPME	1.25	60	71:29	58
7	THF	1.60	60	93:7	84
8	***THF***	***1.90***	***60***	***>99:1***	***93***
9[c]	THF	1.90	60	95:5	90

[a] Isolated yield.
[b] **2a** was isolated in 19% yield.
[c] $PhSeCH_2SePh$ (1.90 equiv) and *n*-BuLi (1.90 equiv) were used.

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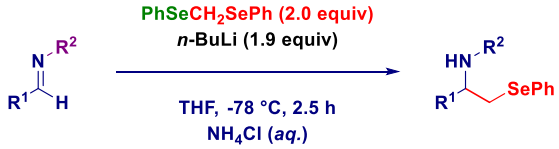
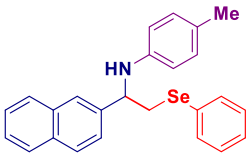
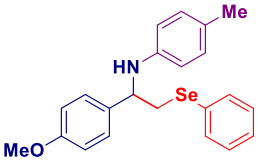
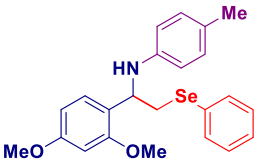


N-Aryl Imines


2 (93 %)


3 (88 %)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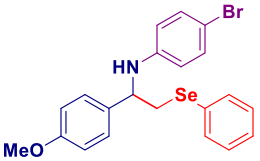
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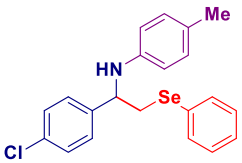
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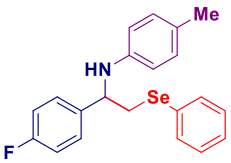
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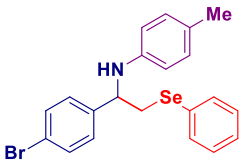
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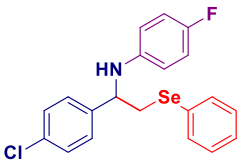
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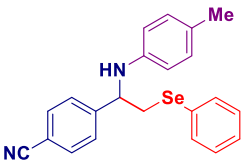
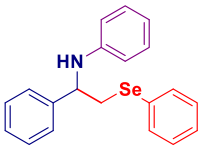
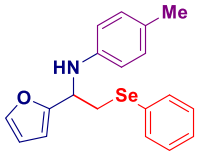
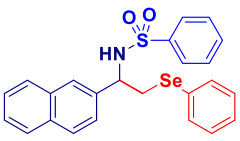
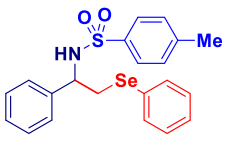

10 (92 %)

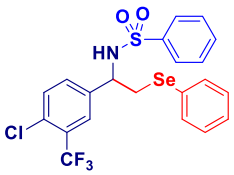

11 (89 %)

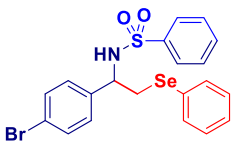

12 (86 %)

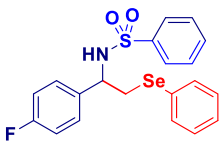
N-Sulfonyl Imines

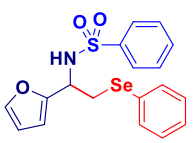

13 (89 %)

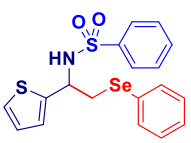

14 (91 %)


15 (85 %)


16 (90 %)


17 (92 %)


18 (87 %)


19 (90 %)

Scheme 2. Scope of the protocol.

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3.1. Experimental Part

3.1.1. Instrumentation and general analytical methods

Melting points were determined on a Reichert–Kofler hot-stage microscope and are uncorrected. Mass spectra were obtained on a Shimadzu QP 1000 instrument (EI, 70 eV) and on a Bruker maXis 4G instrument (ESI-TOF, HRMS). ^{1}H, ^{13}C, ^{19}F, ^{15}N and ^{77}Se NMR spectra were recorded with a Bruker Avance III 400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, 376 MHz for ^{19}F, 40 MHz for ^{15}N and 76 MHz for ^{77}Se) at 297 K using a directly detecting broadband observe (BBFO) probe. The center of the (residual) solvent signal was used as an internal standard which was related to TMS with δ 7.26 ppm (^{1}H in $CDCl_3$), δ 77.0 ppm (^{13}C in $CDCl_3$). ^{19}F NMR spectra were referenced via the Ξ ratio (absolute referencing). ^{15}N NMR spectra (gs-HMBC, gs-HSQC) were referenced against neat, external nitromethane. ^{77}Se spectra were referenced against diphenyldiselane (δ Ph_2Se_2 463 ppm). Spin-spin coupling constants (J) are given in Hz.

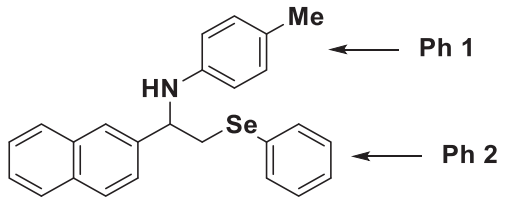
In nearly all cases, full and unambiguous assignment of all resonances was performed by combined application of standard NMR techniques, such as APT, HSQC, HMBC, HSQCTOCSY, COSY and NOESY experiments.

THF was distilled over Na/benzophenone. Chemicals were purchased from SigmaAldrich, Acros, Alfa Aesar and TCI Europe. Solutions were evaporated under reduced pressure with a rotary evaporator. TLC was carried out on aluminium sheets precoated with silica gel 60F254 (Merchery-Nagel, Merk); the spots were visualised under UV light (λ = 254 nm) and/or $KMnO_4$ (aq.) was used as revealing system.

3.1.2. General procedure

To a solution of 1,1'-(methylenediselanyl)dibenzene (2.0 equiv) in dry THF (2 mL) a 2.5 M solution of *n*-BuLi in hexanes (1.9 equiv) was added dropwise at −78 °C under argon and the reaction mixture was stirred at −78 °C for 1 h. Then, a solution of the starting imine (1.0 equiv) in dry THF (1 mL) was added and the mixture was stirred at −78 °C for 2.5 h before quenching with sat. aqueous NH_4Cl. The mixture was exhaustively extracted with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The product was obtained after purification by column chromatography on silica gel (*n*-hexane:EtOAc).

3.1.3. 4-methyl-N-[1-(2-naphthyl)-2-(phenylselanyl)ethyl]aniline (2)



By Following the general procedure, starting from 1,1'-(methylenediselanyl)dibenzene (0.652 g, 2.0 mmol, 2.0 equiv) in dry THF (2 mL), *n*-BuLi (2.5 M, 0.76 mL, 1.9 mmol, 1.9 equiv) and 4-methyl-*N*-(naphthalen-2-ylmethylene)aniline (0.245 g, 1.0 mmol, 1.0 equiv) in dry THF (1 mL), compound **2** was obtained in 93% yield (0.387 g) as colourless oil after purification by column chromatography on silica gel (*n*-hexane:EtOAc 99:1).

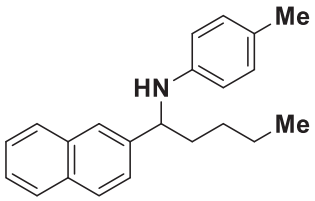
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (m, 1H, Naph H-1), 7.80 (m, 2H, Naph), 7.78 (m, 1H, Naph), 7.54 (m, 2H, Ph 2 H-2,6), 7.47 (m, 1H, Naph H-3), 7.46 (m, 1H, Naph), 7.45 (m, 1H, Naph), 7.27 (m, 1H, Ph 2 H-4), 7.26 (m, 2H, Ph 2 H-2,6), 6.87 (m, 2H, Ph 1 H-3,5), 6.43 (m, 2H, Ph 1 H-2,6), 4.59 (dd, ^{3}J = 8.9 Hz, ^{3}J = 4.6 Hz, 1H, CH), 4.5 (brs, 1H, NH), 3.44 (dd, ^{2}J = 12.6 Hz, ^{3}J = 4.6 Hz, 1H, CH_2), 3.28 (dd, ^{2}J = 12.6 Hz, ^{3}J = 8.9 Hz, 1H, CH_2), 2.18 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7 (Ph 1 C-1), 140.3 (Naph C-2), 133.55 (Ph 2 C-2,6), 133.51 (Naph 8a), 133.0 (Naph 4a), 129.6 (Ph 1 C-3,5), 129.3 (Ph 2 C-1), 129.2 (Ph 2 C-3,5), 128.6 (Naph), 127.9 (Naph), 127.7 (Naph), 127.5 (Ph 2 C-4), 127.1 (Ph 1 C-4), 126.1 (Naph), 125.7 (Naph), 125.2 (Naph C-1), 124.4 (Naph C-3), 114.0 (Ph 1 C-2,6), 58.4 (CH), 36.4 (CH_2), 20.3 (CH_3).

^{77}Se NMR (76 MHz, $CDCl_3$): δ 267.3 (m).

HRMS (ESI), *m/z* $[M + H]^+$ calcd. for $C_{25}H_{24}NSe$: 418.1068; found: 418.1057.

3.1.4. 4-methyl-N-[1-(2-naphthyl)pentyl]aniline (2a)



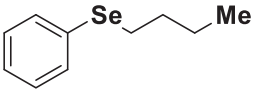
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (m, 3H, Naph H-4,5,8), 7.81 (s, 1H, Naph H-1), 7.50 (m, 1H, Naph H-3), 7.47 (m, 1H, Naph H-6), 7.45 (m, 1H, Naph H-7), 6.89 (m, 2H, Ph H-3,5), 6.50 (m, 2H, Ph H-2,6), 4.44 (m, 1H, CH), 3.9–4.4 (brs, 1H, NH), 2.18 (s, 3H, CH_3), 1.88 (m, 2H, $C\underline{H}_2CH_2CH_2CH_3$), 1.37 (m, 2H, $CH_2C\underline{H}_2CH_2CH_3$), 1.36 (m, 2H, $CH_2CH_2C\underline{H}_2CH_3$), 0.90 (t, ^{3}J = 7.0 Hz, 3H, $CH_2CH_2CH_2C\underline{H}_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2 (Ph C-1), 142.0 (Naph C-2), 133.5 (Naph C-8a), 132.8 (Naph C-4a), 129.6 (Ph C-3,5), 128.3 (Naph), 127.8 (Naph), 127.6 (Naph), 126.4 (Ph C-4), 125.9 (Naph C-6), 125.4 (Naph C-7), 125.1 (Naph C-1), 124.8 (Naph C-3), 113.5 (Ph C-2,6), 58.8 (CH), 38.6 ($\underline{C}H_2CH_2CH_2CH_3$), 28.5 ($CH_2\underline{C}H_2CH_2CH_3$), 22.6 ($CH_2CH_2\underline{C}H_2CH_3$), 20.3 ($CH_3$), 14.0 ($CH_2CH_2CH_2\underline{C}H_3$).

^{15}N NMR (40 MHz, $CDCl_3$): δ −305.4.

HRMS (ESI), *m/z* $[M + H]^+$ calcd. for $C_{22}H_{26}N$: 304.2060; found: 304.2057.

3.1.5. Butyl phenyl selenide (2b)14a



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (m, 2H, Ph H-2,6), 7.25 (m, 2H, Ph H-3,5), 7.23 (m, 1H, Ph H-4), 2.92 (m, 2H, $C\underline{H}_2CH_2CH_2CH_3$), 1.69 (m, 2H, $CH_2C\underline{H}_2CH_2CH_3$), 1.43 (m, 2H, $CH_2CH_2C\underline{H}_2CH_3$), 0.91 (t, ^{3}J = 7.4 Hz, 3H, $CH_2CH_2CH_2C\underline{H}_3$).

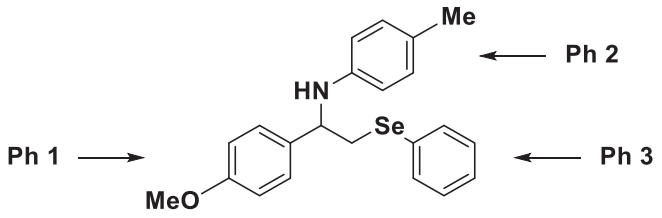
^{13}C NMR (100 MHz, $CDCl_3$): δ 132.3 (Ph C-2,6), 130.7 (Ph C-1), 129.0 (Ph C-3,5), 126.6 (Ph C-4), 32.2 ($CH_2\underline{C}H_2CH_2CH_3$), 27.6 ($\underline{C}H_2CH_2CH_2CH_3$), 22.9 ($CH_2CH_2\underline{C}H_2CH_3$), 13.5 ($CH_2CH_2CH_2\underline{C}H_3$).

^{d}Se NMR (76 MHz, $CDCl_3$): δ 290.5

HRMS (ESI), *m/z* $[M + H]^+$ calcd. for $C_{10}H_{15}Se$: 215.0333; found: 215.0336.

Please cite this article as: R. Senatore et al., Straightforward and direct access to β-seleno- amines and sulfonylamides *via* the controlled addition of phenylselenomethyllithium ($LiCH_2SePh$) to imines, Tetrahedron, https://doi.org/10.1016/j.tet.2020.131220

3.1.6. N-[1-(4-methoxyphenyl)-2-(phenylselanyl)ethyl]-4-methylaniline (3)



By Following the general procedure, starting from 1,1'-(methylenediselanyl)dibenzene (0.652 g, 2.0 mmol, 2.0 equiv) in dry THF (2 mL), *n*-BuLi (2.5 M, 0.76 mL, 1.9 mmol, 1.9 equiv) and *N*-(4-methoxybenzylidene)-4-methylaniline (0.225 g, 1.0 mmol, 1.0 equiv) in dry THF (1 mL), compound **3** was obtained in 88% yield (0.348 g) as colourless oil after purification by column chromatography on silica gel (*n*-hexane:EtOAc 9:1).

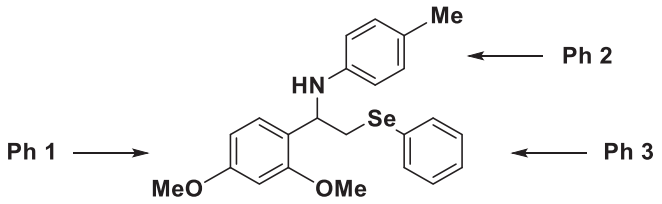
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (m, 2H, Ph 3 H-2,6), 7.26 (m, 3H, Ph 3 H-3,4,5), 7.25 (m, 2H, Ph 1 H-2,6), 6.88 (m, 2H, Ph 2 H-3,5), 6.83 (m, 2H, Ph 1 H-3,5), 6.40 (m, 2H, Ph 2 H-2,6), 4.39 (dd, ^{3}J = 8.4 Hz, ^{3}J = 5.1 Hz, 1H, CH), 4.0–4.8 (brs, 1H, NH), 3.78 (s, 3H, OCH_3), 3.33 (dd, ^{2}J = 12.5 Hz, ^{3}J = 5.1 Hz, 1H, CH_2), 3.22 (m, 1H, CH_2), 2.18 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9 (Ph 1 C-4), 144.9 (Ph 2 C-1), 134.6 (Ph 1 C-1), 133.4 (Ph 3 C-2,6), 129.5 (Ph 2 C-3,5), 129.4 (Ph 3 C-1), 129.2 (Ph 3C −3,5), 127.5 (Ph 1 C-2,6), 127.4 (Ph 3 C-4), 127.2 (Ph 2 C-4), 114.1 (Ph 1 C-3,5, Ph 2 C-2,6), 57.7 (CH), 55.2 (OCH_3), 36.4 (CH_2), 20.4 (CH_3).

^{77}Se NMR (76 MHz, $CDCl_3$): δ 265.0 (m).

HRMS (ESI), *m/z* $[M + H]^+$ calcd. for $C_{22}H_{24}NOSe$: 398.1018; found: 398.1016.

3.1.7. N-[1-(2,4-dimethoxyphenyl)-2-(phenylselanyl)ethyl]-4-methylaniline (4)



By Following the general procedure, starting from 1,1'-(methylenediselanyl)dibenzene (0.652 g, 2.0 mmol, 2.0 equiv) in dry THF (2 mL), *n*-BuLi (2.5 M, 0.76 mL, 1.9 mmol, 1.9 equiv) and *N*-(2,4-dimethoxybenzylidene)-4-methylaniline (0.255 g, 1.0 mmol, 1.0 equiv) in dry THF (1 mL), compound **4** was obtained in 83% yield (0.354 g) as brown oil after purification by column chromatography on silica gel (*n*-hexane:EtOAc 99:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (m, 2H, Ph 3 H-2,6), 7.24 (m, 3H, Ph 3 H-3,4,5), 7.21 (d, ^{3}J = 8.4 Hz, 1H, Ph 1 H-6), 6.89 (m, 2H, Ph 2 H-3,5), 6.43 (d, ^{4}J = 2.4 Hz, 1H, Ph 1 H-3), 6.39 (m, 3H, Ph 1 H-5, Ph 2 H-2,6), 4.78 (dd, ^{3}J = 8.3 Hz, ^{3}J = 4.8 Hz, 1H, CH), 4.38 (brs, 1H, NH), 3.82 (s, 3H, 2-OCH_3), 3.77 (s, 3H, 4-OCH_3), 3.45 (dd, ^{2}J = 12.4 Hz, ^{3}J = 4.8 Hz, 1H, CH_2), 3.22 (dd, ^{2}J = 12.4 Hz, ^{3}J = 8.3 Hz, 1H, CH_2), 2.19 (s, 3H, CH_3).

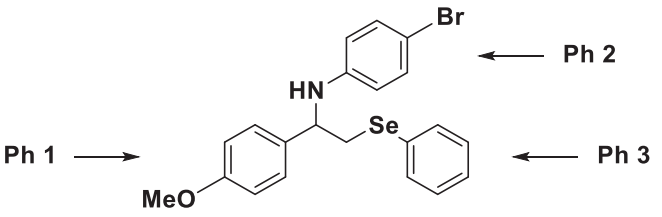
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0 (Ph 1 C-4), 157.6 (Ph 1 C-2), 144.8 (Ph 2 C-1), 132.9 (Ph 3 C-2,6), 130.2 (Ph 3 C-1), 129.5 (Ph 2 C-3,5), 128.9 (Ph 3 C-3,5), 128.0 (Ph 1 C-6), 126.9 (Ph 3 C-4), 126.6 (Ph 2 C-4), 122.2 (Ph 1 C-1), 113.8 (Ph 2 C-2,6), 104.1 (Ph 1 C-5), 98.7 (Ph 1 C-3), 55.3 (4-OCH_3), 55.2 (2-OCH_3), 53.0 (CH), 34.2 (CH_2), 20.3 (CH_3).

^{77}Se NMR (76 MHz, $CDCl_3$): δ 263.3 (m).

^{15}N NMR (40 MHz, $CDCl_3$): δ −308.0.

HRMS (ESI), *m/z* $[M + H]^+$ calcd. for $C_{23}H_{26}NO_2Se$: 428.1123; found: 428.1120.

4-bromo-*N*-[1-(4-methoxyphenyl)-2-(phenylselanyl)ethyl]aniline (5)



By Following the general procedure, starting from 1,1'-(methylenediselanyl)dibenzene (0.652 g, 2.0 mmol, 2.0 equiv) in dry THF (2 mL), *n*-BuLi (2.5 M, 0.76 mL, 1.9 mmol, 1.9 equiv) and 4-bromo-*N*-(4-methoxybenzylidene)aniline (0.290 g, 1.0 mmol, 1.0 equiv) in dry THF (1 mL), compound **5** was obtained in 85% yield (0.392 g) as yellow oil after purification by column chromatography on silica gel (*n*-hexane:EtOAc 98:2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (m, 2H, Ph 3 H-2,6), 7.28 (m, 1H, Ph 3 H-4), 7.27 (m, 2H, Ph 3 H-3,5), 7.22 (m, 2H, Ph 1 H-2,6), 7.13 (m, 2H, Ph 2 H-3,5), 6.84 (m, 2H, Ph 1 H-3,5), 6.30 (m, 2H, Ph 2 H-2,6), 4.34 (dd, ^{3}J = 8.8 Hz, ^{3}J = 4.6 Hz, 1H, CH), 3.8–5.0 (brs, 1H, NH), 3.78 (s, 3H, OCH_3), 3.32 (dd, ^{2}J = 12.6 Hz, ^{3}J = 4.6 Hz, 1H, CH_2), 3.15 (dd, ^{2}J = 12.6 Hz, ^{3}J = 8.8 Hz, 1H, CH_2).

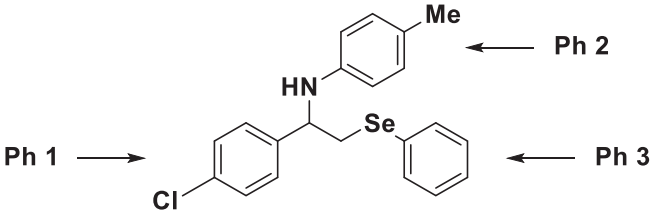
^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1 (Ph 1 C-4), 146.0 (Ph 2 C-1), 134.0 (Ph 1 C-1), 133.6 (Ph3 C-2,6), 131.7 (Ph 2 C-3,5), 129.3 (Ph 3 C-3,5), 129.0 (Ph 3 C-1), 127.6 (Ph 3 C-4), 127.3 (Ph 1 C-2,6), 115.3 (Ph 2 C-2,6), 114.2 (Ph 1 C-3,5), 109.5 (Ph 2 C-4), 57.2 (CH), 55.2 (OCH_3), 36.4 (CH_2).

^{77}Se NMR (76 MHz, $CDCl_3$): δ 265.9 (m).

^{15}N NMR (40 MHz, $CDCl_3$): δ −303.9.

HRMS (ESI), *m/z* $[M + Na]^+$ calcd. for $C_{21}H_{20}BrNNaOSe$: 483.9786; found: 483.9785.

3.1.8. N-[1-(4-chlorophenyl)-2-(phenylselanyl)ethyl]-4-methylaniline (6)



By Following the general procedure, starting from 1,1'-(methylenediselanyl)dibenzene (0.652 g, 2.0 mmol, 2.0 equiv) in dry THF (2 mL), *n*-BuLi (2.5 M, 0.76 mL, 1.9 mmol, 1.9 equiv) and *N*-(4-chlorobenzylidene)-4-methylaniline (0.229 g, 1.0 mmol, 1.0 equiv) in dry THF (1 mL), compound **6** was obtained in 87% yield (0.349 g) as brown oil after purification by column chromatography on silica gel (*n*-hexane:EtOAc 99:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (m, 2H, Ph 3 H-2,6), 7.27 (m, 7H, Ph 1 H-2,3,5,6, Ph 3 H-3,4,5), 6.90 (m, 2H, Ph 2 H-3,5), 6.35 (m, 2H, Ph 2 H-2,6), 4.40 (dd, ^{3}J = 8.8 Hz, ^{3}J = 4.6 Hz, 1H, CH), 4.36 (brs, 1H, NH), 3.32 (dd, ^{2}J = 12.6 Hz, ^{3}J = 4.5 Hz, 1H, CH_2), 3.16 (dd, ^{2}J = 12.6 Hz, ^{3}J = 8.8 Hz, 1H, CH_2), 2.20 (s, 3H, CH_3).

Please cite this article as: R. Senatore et al., Straightforward and direct access to β-seleno- amines and sulfonylamides *via* the controlled addition of phenylselenomethyllithium ($LiCH_2SePh$) to imines, Tetrahedron, https://doi.org/10.1016/j.tet.2020.131220

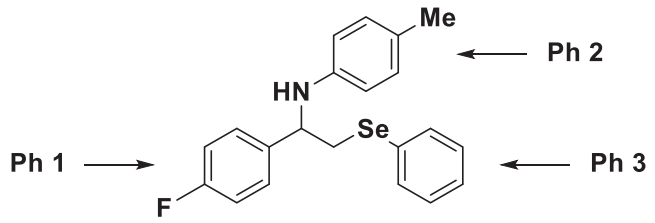
^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4 (Ph 2 C-1), 141.3 (Ph 1 C-1), 133.6 (Ph 3 C-2,6), 133.0 (Ph 1 C-4), 129.6 (Ph 2 C-3,5), 129.3 (Ph 3 C-3,5), 129.0 (Ph 3 C-1), 128.9 (Ph 1 C-3,5), 127.7 (Ph1 C-2,6), 127.6 (Ph 3 C-4), 127.3 (Ph 2 C-4), 113.9 (Ph 2 C-2,6), 57.4 (CH), 36.4 (CH_2), 20.3 (CH_3).

^{77}Se NMR (76 MHz, $CDCl_3$): δ 266.0 (m).

^{15}N NMR (40 MHz, $CDCl_3$): δ −307.1.

HRMS (ESI), *m/z* $[M + H]^+$ calcd. for $C_{21}H_{21}ClNSe$: 402.0522; found: 402.0523.

3.1.9. N-[1-(4-fluorophenyl)-2-(phenylselanyl)ethyl]-4-methylaniline (7)



By Following the general procedure, starting from 1,1'-(methylenediselanyl)dibenzene (0.652 g, 2.0 mmol, 2.0 equiv) in dry THF (2 mL), *n*-BuLi (2.5 M, 0.76 mL, 1.9 mmol, 1.9 equiv) and *N*-(4-fluorobenzylidene)-4-methylaniline (0.213 g, 1.0 mmol, 1.0 equiv) in dry THF (1 mL), compound **7** was obtained in 92% yield (0.353 g) as yellow oil after purification by column chromatography on silica gel (*n*-hexane:EtOAc 99:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (m, 2H, Ph 3 H-2,6), 7.30 (m, 2H, Ph 1 H-2,6), 7.27 (m, 1H, Ph 3 H-4), 7.26 (m, 2H, Ph 3 H-3,5), 6.98 (m, 2H, Ph 1 H-3,5), 6.89 (m, 2H, Ph 2 H-3,5), 6.36 (m, 2H, Ph 2 H-2,6), 4.41 (dd, ^3J = 8.7 Hz, ^3J = 4.8 Hz, 1H, CH), 4.35 (brs, 1H, NH), 3.32 (dd, ^2J = 12.6 Hz, ^3J = 4.8 Hz, 1H, CH_2), 3.18 (dd, ^2J = 12.6 Hz, ^3J = 8.7 Hz, 1H, CH_2), 2.19 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1 (d, $^1J_{C,F}$ = 245.5 Hz, Ph 1 C-4), 144.4 (Ph 2 C-1), 138.3 (d, $^4J_{C,F}$ = 3.1 Hz, Ph 1 C-1), 133.5 (Ph 3 C-2,6), 129.6 (Ph 2 C-3,5), 129.3 (Ph 3 C-3,5), 129.1 (Ph 3 C-1), 127.9 (d, $^3J_{C,F}$ = 8.0 Hz, Ph 1 C-2,6), 127.5 (Ph 3 C-4), 127.4 (Ph 2 C-4), 115.6 (d, $^2J_{C,F}$ = 21.4 Hz, Ph 1 C-3,5), 114.0 (Ph 2 C-2,6), 57.5 (CH), 36.5 (CH_2), 20.3 (CH_3).

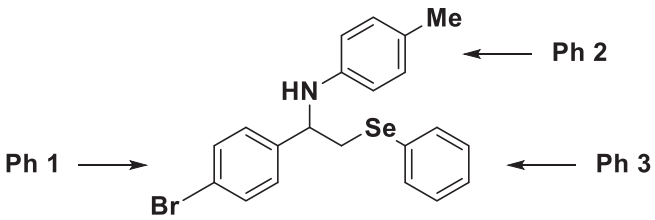
^{77}Se NMR (76 MHz, $CDCl_3$): δ 265.6 (m).

^{19}F NMR (376 MHz, $CDCl_3$): δ −115.2 (m).

^{15}N NMR (40 MHz, $CDCl_3$): δ −312.9.

HRMS (ESI), *m/z* $[M + H]^+$ calcd. for $C_{21}H_{21}FNSe$: 386.0818; found: 386.0812.

3.1.10. N-[1-[4-bromophenyl)-2-(phenylselanyl)ethyl]-4-methylaniline (8)



By Following the general procedure, starting from 1,1'-(methylenediselanyl)dibenzene (0.652 g, 2.0 mmol, 2.0 equiv) in dry THF (2 mL), *n*-BuLi (2.5 M, 0.76 mL, 1.9 mmol, 1.9 equiv) and *N*-(4-bromobenzylidene)-4-methylaniline (0.274 g, 1.0 mmol, 1.0 equiv) in dry THF (1 mL), compound **8** was obtained in 86% yield (0.383 g) as yellowish oil after purification by column chromatography on silica gel (*n*-hexane:EtOAc 98:2).

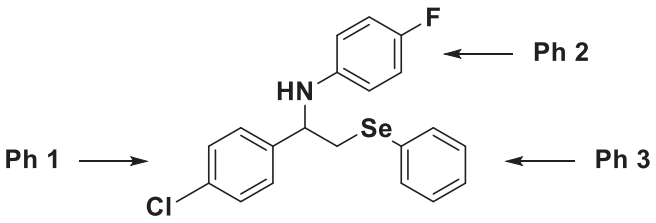
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (m, 2H, Ph 3 H-2,6), 7.40 (m, 2H, Ph 1 H-3,5), 7.27 (m, 1H, Ph 3 H-4), 7.26 (m, 2H, Ph 3 H-3,5), 7.21 (m, 2H, Ph 1 H-2,6), 6.89 (m, 2H, Ph 2 H-3,5), 6.36 (m, 2H, Ph 2 H-2,6), 4.37 (dd, ^3J = 8.6 Hz, ^3J = 4.8 Hz, 1H, CH), 4.0−5.0 (brs, 1H, NH), 3.32 (dd, ^2J = 12.6 Hz, ^3J = 4.8 Hz, 1H, CH_2), 3.18 (dd, ^2J = 12.6 Hz, ^3J = 8.6 Hz, 1H, CH_2), 2.19 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 144.0 (Ph 2 C-1), 141.6 (Ph 1 C-1), 133.6 (Ph 3 C-2,6), 131.8 (Ph 1 C-3,5), 129.6 (Ph 2 C-3,5), 129.3 (Ph 3 C-3,5), 129.0 (Ph 3 C-1), 128.2 (Ph 1 C-2,6), 127.6 (Ph 2 C-4, Ph 3 C-4), 121.2 (Ph 1 C-4), 114.2 (Ph 2 C-2,6), 57.8 (CH), 36.1 (CH_2), 20.4 (CH_3).

^{77}Se NMR (76 MHz, $CDCl_3$): δ 266.5 (m).

HRMS (ESI), *m/z* $[M + H]^+$ calcd. for $C_{21}H_{21}BrNSe$: 446.0017; found: 446.0021.

3.1.11. N-[1-(4-chlorophenyl)-2-(phenylselanyl)ethyl]-4-fluoroaniline (9)



By Following the general procedure, starting from 1,1'-(methylenediselanyl)dibenzene (0.652 g, 2.0 mmol, 2.0 equiv) in dry THF (2 mL), *n*-BuLi (2.5 M, 0.76 mL, 1.9 mmol, 1.9 equiv) and N-(4-chlorobenzylidene)-4-fluoroaniline (0.233 g, 1.0 mmol, 1.0 equiv) in dry THF (1 mL), compound **9** was obtained in 88% yield (0.356 g) as yellowish oil after purification by column chromatography on silica gel (*n*-hexane:EtOAc 98:2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (m, 2H, Ph 3 H-2,6), 7.27 (m, 7H, Ph 1 H-2,3,5,6, Ph 3 H-3,4,5), 6.78 (m, 2H, Ph 2 H-3,5), 6.35 (m, 2H, Ph 2 H-2,6), 4.31 (dd, ^3J = 8.9 Hz, ^3J = 4.5 Hz, 1H, CH), 4.0−4.9 (brs, 1H, NH), 3.32 (dd, ^2J = 12.7 Hz, ^3J = 4.5 Hz, 1H, CH_2), 3.14 (dd, ^2J = 12.7 Hz, ^3J = 8.9 Hz, 1H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2 (d, $^1J_{C,F}$ = 235.9 Hz, Ph 2 C-4), 142.9 (Ph 2 C-1), 140.8 (Ph 1 C-1), 133.7 (Ph 3 C-2,6), 133.3 (Ph 1 C-4), 129.3 (Ph 3 C-3,5), 129.0 (Ph 1 C-3,5), 128.7 (Ph 3 C-1), 127.7 (Ph 1 C-2,6, Ph 3 C-4), 115.6 (d, $^2J_{C,F}$ = 22.4 Hz, Ph 2 C-3,5), 114.8 (m, Ph 2 C-2,6), 58.0 (CH), 36.2 (CH_2).

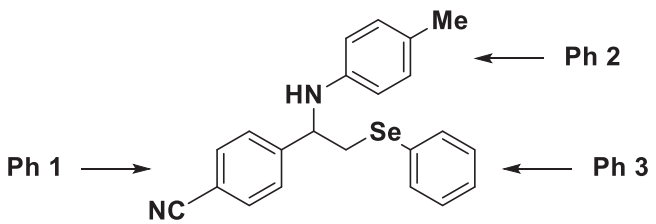
^{77}Se NMR (76 MHz, $CDCl_3$): δ 266.6 (m).

^{19}F NMR (376 MHz, $CDCl_3$): δ −127.0 (m).

^{15}N NMR (40 MHz, $CDCl_3$): δ −307.9.

HRMS (ESI), *m/z* $[M + H]^+$ calcd. for $C_{20}H_{18}ClFNSe$: 406.0272; found: 406.0270.

3.1.12. 4-{1-[(4-methylphenyl)amino]-2-(phenylselanyl)ethyl} benzonitrile (10)



Please cite this article as: R. Senatore et al., Straightforward and direct access to β-seleno- amines and sulfonylamides *via* the controlled addition of phenylselenomethyllithium ($LiCH_2SePh$) to imines, Tetrahedron, https://doi.org/10.1016/j.tet.2020.131220

By Following the general procedure, starting from 1,1'-(methylenediselanyl)dibenzene (0.652 g, 2.0 mmol, 2.0 equiv) in dry THF (2 mL), *n*-BuLi (2.5 M, 0.76 mL, 1.9 mmol, 1.9 equiv) and 4-((*p*-tolylimino)methyl)benzonitrile (0.220 g, 1.0 mmol, 1.0 equiv) in dry THF (1 mL), compound **10** was obtained in 92% yield (0.360 g) as yellowish oil after purification by column chromatography on silica gel (*n*-hexane:EtOAc 99:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (m, 2H, Ph 1 H-2,6), 7.49 (m, 2H, Ph 3 H-2,6), 7.45 (m, 2H, Ph 1 H-3,5), 7.28 (m, 1H, Ph 3 H-4), 7.26 (m, 2H, Ph 3 H-3,5), 6.89 (m, 2H, Ph 2 H-3,5), 6.32 (m, 2H, Ph 2 H-2,6), 4.44 (dd, ^3J = 8.7 Hz, ^3J = 4.5 Hz, 1H, CH), 4.1–4.9 (brs, 1H, NH), 3.32 (dd, ^2J = 12.8 Hz, ^3J = 4.5 Hz, 1H, CH_2), 3.16 (dd, ^2J = 12.8 Hz, ^3J = 8.7 Hz, 1H, CH_2), 2.19 (s, 3H, CH_3).

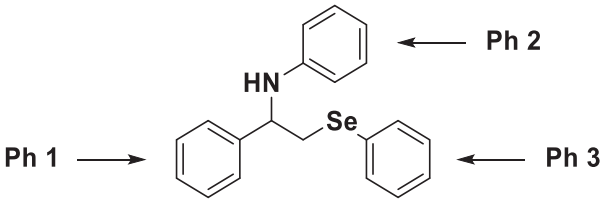
^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3 (Ph 1 C-4), 143.9 (Ph 2 C-1), 133.7 (Ph 3 C-2,6), 132.6 (Ph 1 C-2,6), 129.7 (Ph 2 C-3,5), 129.3 (Ph 3 C-3,5), 128.6 (Ph 3 C-1), 127.8 (Ph 2 C-4, Ph 3 C-4), 127.3 (Ph 1 C-3,5), 118.7 (C≡N), 114.0 (Ph 2 C-2,6), 111.3 (Ph 1 C-1), 57.9 (CH), 35.9 (CH_2), 20.3 (CH_3).

^{77}Se NMR (76 MHz, $CDCl_3$): δ 267.8.

^{15}N NMR (40 MHz, $CDCl_3$): δ −308.3.

HRMS (ESI), *m/z* $[M + H]^+$ calcd. for $C_{22}H_{21}N_2Se$: 393.0864; found: 393.0866.

3.1.13. N-[1-phenyl-2-(phenylselanyl)ethyl]aniline (11)



By Following the general procedure, starting from 1,1'-(methylenediselanyl)dibenzene (0.652 g, 2.0 mmol, 2.0 equiv) in dry THF (2 mL), *n*-BuLi (2.5 M, 0.76 mL, 1.9 mmol, 1.9 equiv) and *N*-benzylideneaniline (0.181 g, 1.0 mmol, 1.0 equiv) in dry THF (1 mL), compound **11** was obtained in 89% yield (0.313 g) as yellow solid after purification by column chromatography on silica gel (*n*-hexane:EtOAc 99:1).

mp: 125–127 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (m, 2H, Ph 3 H-2,6), 7.35 (m, 2H, Ph 1 H-2,6), 7.31 (m, 2H, Ph 1 H-3,5), 7.27 (m, 3H, Ph 3 H-3,4,5), 7.25 (m, 1H, Ph 1 H-4), 7.07 (m, 2H, Ph 2 H-3,5), 6.67 (m, 1H, Ph 2 H-4), 6.45 (m, 2H, Ph 2 H-2,6), 4.46 (dd, ^3J = 8.8 Hz, ^3J = 4.7 Hz, 1H, CH), 4.3–4.7 (brs, 1H, NH), 3.37 (dd, ^2J = 12.6 Hz, ^3J = 4.7 Hz, 1H, CH_2), 3.22 (dd, ^2J = 12.6 Hz, ^3J = 8.8 Hz, 1H, CH_2).

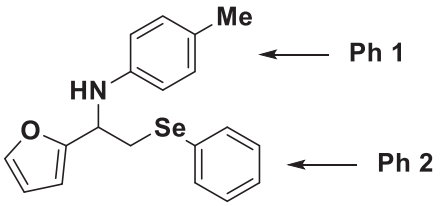
^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0 (Ph 2 C-1), 142.6 (Ph 1 C-1), 133.5 (Ph 3 C-2,6), 129.3 (Ph 3 C-1), 129.2 (Ph 3 C-3,5), 129.0 (Ph 2 C-3,5), 128.8 (Ph 1 C-3,5), 127.53 (Ph 3 C-4), 127.49 (Ph 1 C-4), 126.3 (Ph 1 C-2,6), 117.8 (Ph 2 C-4), 113.8 (Ph 2 C-2,6), 57.9 (CH), 36.4 (CH_2).

^{77}Se NMR (76 MHz, $CDCl_3$): δ 266.7 (m)

^{15}N NMR (40 MHz, $CDCl_3$): δ −305.1.

HRMS (ESI), *m/z* $[M + H]^+$ calcd. for $C_{20}H_{20}NSe$: 354.0755; found: 354.0751.

3.1.14. N-[1-(2-furyl)-2-(phenylselanyl)ethyl]-4-methylaniline (12)



By Following the general procedure, starting from 1,1'-(methylenediselanyl)dibenzene (0.652 g, 2.0 mmol, 2.0 equiv) in dry THF (2 mL), *n*-BuLi (2.5 M, 0.76 mL, 1.9 mmol, 1.9 equiv) and *N*-(furan-2-ylmethylene)-4-methylaniline (0.185 g, 1.0 mmol, 1.0 equiv) in dry THF (1 mL), compound **12** was obtained in 86% yield (0.306 g) as yellow oil after purification by column chromatography on silica gel (*n*-hexane:EtOAc 99:1).

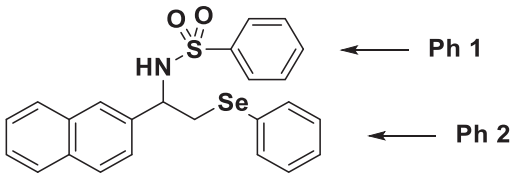
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (m, 2H, Ph 2 H-2,6), 7.30 (dd, ^3J = 1.8 Hz, ^4J = 0.9 Hz, 1H, Furyl H-5), 7.25 (m, 3H, Ph 2 H-3,4,5), 6.93 (m, 2H, Ph 1 H-3,5), 6.45 (m, 2H, Ph 1 H-2,6), 6.27 (dd, ^3J = 3.2 Hz, ^3J = 1.8 Hz, 1H, Furyl H-4), 6.19 (m, 1H, Furyl H-3), 4.68 (m, 1H, CH), 4.03–4.30 (brs, 1H, NH), 3.40 (dd, ^2J = 12.5 Hz, ^3J = 6.5 Hz, 1H, CH_2), 3.36 (dd, ^2J = 12.5 Hz, ^3J = 6.3 Hz, 1H, CH_2), 2.21 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6 (Furyl C-2), 144.1 (Ph 1 C-1), 141.8 (Furyl C-5), 133.4 (Ph 2 C-2,6), 129.7 (Ph 1 C-3,5), 129.5 (Ph 2 C-1), 129.1 (Ph 2 C-3,5), 127.6 (Ph 1 C-4), 127.3 (Ph 2 C-4), 114.0 (Ph 1 C-2,6), 110.3 (Furyl C-4), 106.8 (Furyl C-3), 52.4 (CH), 32.9 (CH_2), 20.4 (CH_3).

^{77}Se NMR (76 MHz, $CDCl_3$): δ 262.2 (m).

HRMS (ESI), *m/z* $[M + H]^+$ calcd. for $C_{19}H_{20}NOSe$: 358.0705; found: 358.0707.

3.1.15. N-(1-(naphthalen-2-yl)-2-(phenylselanyl)ethyl) benzenesulfonamide (13)



By Following the general procedure, starting from 1,1'-(methylenediselanyl)dibenzene (0.652 g, 2.0 mmol, 2.0 equiv) in dry THF (2 mL), *n*-BuLi (2.5 M, 0.76 mL, 1.9 mmol, 1.9 equiv) and *N*-(naphthalen-2-ylmethylene)benzenesulfonamide (0.295 g, 1.0 mmol, 1.0 equiv) in dry THF (1 mL), compound **13** was obtained in 89% yield (0.414 g) as colourless oil after purification by column chromatography on silica gel (*n*-hexane:EtOAc 9:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (m, 1H, Naph H-5), 7.67 (m, 1H, Naph H-8), 7.63 (m, 1H, Naph H-4), 7.61 (m, 2H, Ph 1 H-2,6), 7.46 (m, 1H, Naph H-1), 7.45 (m, 2H, Naph H-6, Naph H-7), 7.38 (m, 1H, Ph 1 H-4), 7.37 (m, 2H, Ph 2 H-2,6), 7.24 (m, 3H, Ph 1 H-3,5, Ph 2 H-4), 7.22 (m, 2H, Ph 2 H-3,5), 7.14 (m, 1H, Naph H-3), 5.43 (d, ^3J = 5.5 Hz, 1H, NH), 4.58 (m, 1H, CH), 3.32 (dd, ^2J = 12.8 Hz, ^3J = 7.3 Hz, 1H, CH_2), 3.25 (dd, ^2J = 12.8 Hz, ^3J = 6.4 Hz, 1H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ 139.9 (Ph1 C-1), 136.4 (Naph C-2), 133.3 (Ph 2 C-2,6), 132.96 (Naph C-8a), 132.94 (Naph C-4a), 132.4 (Ph 1 C-4), 129.3 (Ph 2 C-3,5), 128.7 (Ph 1 C-3,5), 128.52 (Naph C-4), 128.51 (Ph 2 C-1), 127.9 (Naph C-8), 127.59 (Ph 2 C-4), 127.77 (Naph C-5), 127.1 (Ph 1 C-2,6), 126.3 (Naph C-7), 126.2 (Naph C-6), 126.1 (Naph C-1), 124.0 (Naph C-3), 57.3 (CH), 35.0 (CH_2).

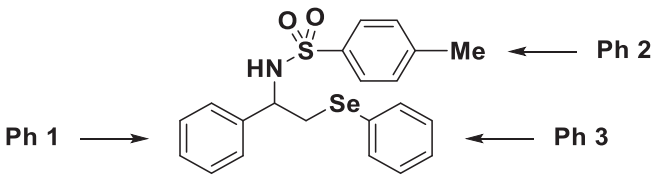
Please cite this article as: R. Senatore et al., Straightforward and direct access to β-seleno- amines and sulfonylamides *via* the controlled addition of phenylselenomethyllithium ($LiCH_2SePh$) to imines, Tetrahedron, https://doi.org/10.1016/j.tet.2020.131220

^{77}Se NMR (76 MHz, $CDCl_3$): δ 257.8 (m).

^{15}N NMR (40 MHz, $CDCl_3$): δ −271.7.

HRMS (ESI), *m/z* $[M + H]^+$ calcd. for $C_{24}H_{22}NO_2SSe$: 468.0531; found: 468.0532.

3.1.16. 4-methyl-N-[1-phenyl-2-(phenylselanyl)ethyl] benzenesulfonamide (14)[11]



By Following the general procedure, starting from 1,1'-(methylenediselanyl)dibenzene (0.652 g, 2.0 mmol, 2.0 equiv) in dry THF (2 mL), *n*-BuLi (2.5 M, 0.76 mL, 1.9 mmol, 1.9 equiv) and *N*-benzylidene-4-methylbenzenesulfonamide (0.261 g, 1.0 mmol, 1.0 equiv) in dry THF (1 mL), compound **14** was obtained in 91% yield (0.391 g) as white solid after purification by column chromatography on silica gel (*n*-hexane:EtOAc 99:1).

mp: 92−93 °C (lit. 92−93 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (m, 2H, Ph 2 H-2,6), 7.34 (m, 2H, Ph 3 H-2,6), 7.26 (m, 1H, Ph 3 H-4), 7.22 (m, 2H, Ph 3 H-3,5), 7.20 (m, 2H, Ph 1 H-3,5), 7.19 (m, 1H, Ph 1 H-4), 7.12 (m, 2H, Ph 2 H-3,5), 7.06 (m, 2H, Ph 1 H-2,6), 5.27 (m, 1H, NH), 4.37 (m, 1H, CH) 3.24 (dd, ^2J = 12.8Hz, ^3J = 7.2Hz, 1H, CH_2), 3.16 (dd, ^2J = 12.8 Hz, ^3J = 6.4 Hz, 1H, CH_2), 2.37 (s, 3H, CH_3).

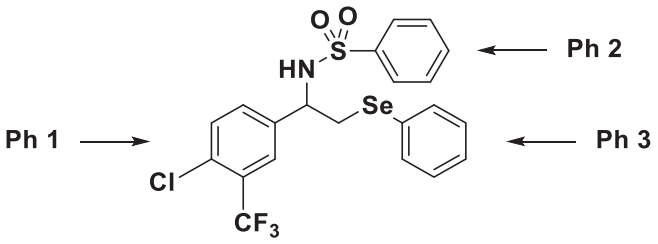
^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2 (Ph 2 C-4), 139.5 (Ph 1 C-1), 136.9 (Ph 2 C-1), 133.2 (Ph 3 C-2,6), 129.4 (Ph 2 C-3,5), 129.2 (Ph 3 C-3,5), 128.7 (Ph 3 C-1), 128.5 (Ph 1 C-3,5), 128.0 (Ph 1 C-4), 127.5 (Ph 3 C-4), 127.2 (Ph 2 C-2,6), 126.6 (Ph 1 C-2,6), 57.1 (CH), 35.1 (CH_2), 21.5 (CH_3).

^{77}Se NMR (76 MHz, $CDCl_3$): δ 256.8 (m)

^{15}N NMR (40 MHz, $CDCl_3$): δ −271.4.

HRMS (ESI), *m/z* $[M + Na]^+$ calcd. for $C_{21}H_{21}NNaO_2SSe$: 454.0350; found: 454.0342.

3.1.17. N-{1-[4-chloro-3-(trifluoromethyl)phenyl]-2-(phenylselanyl)ethyl} benzensulfonamide (15)



By Following the general procedure, starting from 1,1'-(methylenediselanyl)dibenzene (0.652 g, 2.0 mmol, 2.0 equiv) in dry THF (2 mL), *n*-BuLi (2.5 M, 0.76 mL, 1.9 mmol, 1.9 equiv) and *N*-(4-chloro-3-(trifluoromethyl)benzylidene)benzenesulfonamide (0.347 g, 1.0 mmol, 1.0 equiv) in dry THF (1 mL), compound **15** was obtained in 85% yield (0.440 g) as yellow solid after purification by column chromatography on silica gel (*n*-hexane:EtOAc 99:1).

mp: 125−126 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (m, 2H, Ph 2 H-2,6), 7.50 (m, 1H, Ph 2 H-4) 7.35 (m, 2H, Ph 2 H-3,5), 7.32 (m, 2H, Ph 3 H-2,6), 7.28 (m, 1H, Ph 3 H-4), 7.25 (m, 1H, Ph 1 H-5), 7.23 (m, 1H, Ph 1 H-2), 7.22 (m, 2H, Ph 3 H-3,5), 7.18 (m, 1H, Ph 1 H-6), 5.43 (d, ^3J = 5.0 Hz, 1H, NH), 4.45 (m, 1H, CH) 3.11 (d, ^3J = 6.6 Hz, 2H, CH_2).

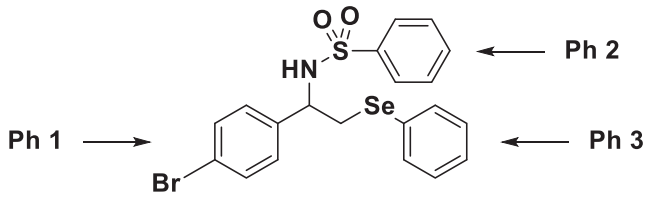
^{13}C NMR (100 MHz, $CDCl_3$): δ 139.7 (Ph 2 C-1), 138.5 (Ph 1 C-1), 133.7 (Ph 3 C-2,6), 132.9 (Ph 2 C-4), 131.8 (q, $^3J_{C,F}$ = 1.9 Hz, Ph 1 C-4), 131.4 (Ph 1 C-5), 131.3 (Ph 1 C-6), 129.4 (Ph 3 C-3,5), 128.9 (Ph 2 C-3,5), 128.3 (q, $^2J_{C,F}$ = 31.5 Hz, Ph 1 C-3), 128.1 (Ph 3 C-4), 127.6 (Ph 3 C-1), 127.1 (Ph 2 C-2,6), 125.9 (q, $^3J_{C,F}$ = 5.4 Hz, Ph 1 C-2), 122.4 (q, $^1J_{C,F}$ = 273.7 Hz, CF_3), 56.2 (CH), 34.9 (CH_2).

^{19}F NMR (376 MHz, $CDCl_3$): δ −62.7 (s, CF_3).

^{15}N NMR (40 MHz, $CDCl_3$): δ −272.8.

HRMS (ESI), *m/z* $[M + Na]^+$ calcd. for $C_{21}H_{17}ClF_3NNaO_2SSe$: 541.9678; found: 541.9691.

3.1.18. N-[1-(4-bromophenyl)-2-(phenylselanyl)ethyl] benzenesulfonamide (16)



By Following the general procedure, starting from 1,1'-(methylenediselanyl)dibenzene (0.652 g, 2.0 mmol, 2.0 equiv) in dry THF (2 mL), *n*-BuLi (2.5 M, 0.76 mL, 1.9 mmol, 1.9 equiv) and *N*-(4-bromobenzylidene)benzenesulfonamide (0.324 g, 1.0 mmol, 1.0 equiv) in dry THF (1 mL), compound **16** was obtained in 90% yield (0.445 g) as white solid after purification by column chromatography on silica gel (*n*-hexane:EtOAc 99:1).

mp: 124−125 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (m, 2H, Ph 2 H-2,6), 7.50 (m, 1H, Ph 2 H-4), 7.35 (m, 2H, Ph 2 H-3,5), 7.33 (m, 2H, Ph 3 H-2,6), 7.27 (m, 1H, Ph 3 H-4), 7.27 (m, 2H, Ph 1 H-3,5), 7.22 (m, 2H, Ph 3 H-3,5), 6.91 (m, 2H, Ph 1 H-2,6), 5.37 (d, ^3J = 5.5 Hz, 1H, NH), 4.35 (m, 1H, CH), 3.16 (dd, ^2J = 12.9 Hz, ^3J = 7.4 Hz, 1H, CH_2), 3.11 (dd, ^2J = 12.9 Hz, ^3J = 6.2 Hz, 1H, CH_2).

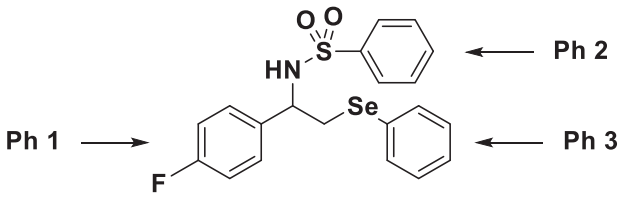
^{13}C NMR (100 MHz, $CDCl_3$): δ 139.8 (Ph 2 C-1), 138.4 (Ph 1 C-1), 133.4 (Ph 3 C-2,6), 132.6 (Ph 2 C-4), 131.6 (Ph 1 C-3,5), 129.4 (Ph 3 C-3,5), 128.9 (Ph 2 C-3,5), 128.4 (Ph 1 C-2,6), 128.2 (Ph 3 C-1), 127.8 (Ph 3 C-4), 127.1 (Ph 2 C-2,6), 122.0 (Ph 1 C-4), 56.6 (CH), 34.9 (CH_2).

^{77}Se NMR (76 MHz, $CDCl_3$): δ 257.9 (m).

^{15}N NMR (40 MHz, $CDCl_3$): δ −272.2.

HRMS (ESI), *m/z* $[M + H]^+$ calcd. for $C_{20}H_{19}BrNO_2SSe$: 495.9480; found: 495.9476.

3.1.19. N-[1-(4-fluorophenyl)-2-(phenylselanyl)ethyl] benzenesulfonamide [17]



By Following the general procedure, starting from 1,1'-(methylenediselanyl)dibenzene (0.652 g, 2.0 mmol, 2.0 equiv) in dry THF (2 mL), *n*-BuLi (2.5 M, 0.76 mL, 1.9 mmol, 1.9 equiv) and *N*-(4-fluorobenzylidene)benzenesulfonamide (0.263 g, 1.0 mmol, 1.0 equiv) in dry THF (1 mL), compound **17** was obtained in 92% yield

Please cite this article as: R. Senatore et al., Straightforward and direct access to β-seleno- amines and sulfonylamides *via* the controlled addition of phenylselenomethyllithium ($LiCH_2SePh$) to imines, Tetrahedron, https://doi.org/10.1016/j.tet.2020.131220

(0.399 g) as yellowish solid after purification by column chromatography on silica gel (*n*-hexane:EtOAc 98:2).

mp: 99–102 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (m, 2H, Ph 2 H-2,6), 7.48 (m, 1H, Ph 2 H-4), 7.35 (m, 2H, Ph 3 H-2,6), 7.34 (m, 2H, Ph 2 H-3,5), 7.27 (m, 1H, Ph 3 H-4), 7.23 (m, 2H, Ph 3 H-3,5), 7.00 (m, 2H, Ph 1 H-2,6), 6.83 (m, 2H, Ph 1 H-3,5), 5.38 (d, 1H, ^3J = 5.4 Hz, 1H, NH), 4.38 (m, 1H, CH), 3.18 (dd, ^2J = 12.9 Hz, ^3J = 7.4 Hz, 1H, CH_2), 3.12 (dd, ^2J = 12.9 Hz, ^3J = 6.3 Hz, 1H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3 (d, $^1J_{C,F}$ = 247.0 Hz, Ph 1 C-4), 139.9 (Ph 2 C-1), 135.1 (d, $^4J_{C,F}$ = 3.2 Hz, Ph 1 C-1), 133.4 (Ph 3 C-2,6), 132.6 (Ph 2 C-4), 129.3 (Ph 3 C-3,5), 128.8 (Ph 2 C-3,5), 128.4 (d, $^3J_{C,F}$ = 8.3 Hz, Ph 1 C-2,6), 128.3 (Ph 3 C-1), 127.7 (Ph 3 C-4), 127.1 (Ph 2 C-2,6), 115.4 (d, $^2J_{C,F}$ = 21.6 Hz, Ph 1 C-3,5), 56.5 (CH), 35.1 (CH_2).

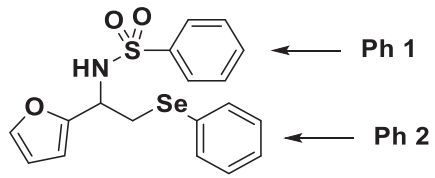
^{77}Se NMR (76 MHz, $CDCl_3$): δ 258.0 (m).

^{19}F NMR (376 MHz, $CDCl_3$): δ −113.9 (m).

^{15}N NMR (40 MHz, $CDCl_3$): δ −271.6.

HRMS (ESI), *m/z* $[M + Na]^+$ calcd. for $C_{20}H_{18}FNNaO_2SSe$: 458.0100; found: 458.0108.

3.1.20. N-[1-(2-furyl)-2-(phenylselanyl)ethyl]benzenesulfonamide (18)



By Following the general procedure, starting from 1,1'-(methylenediselanyl)dibenzene (0.652 g, 2.0 mmol, 2.0 equiv) in dry THF (2 mL), *n*-BuLi (2.5 M, 0.76 mL, 1.9 mmol, 1.9 equiv) and *N*-(furan-2-ylmethylene)benzenesulfonamide (0.235 g, 1.0 mmol, 1.0 equiv) in dry THF (1 mL), compound **18** was obtained in 87% yield (0.353 g) as yellowish oil after purification by column chromatography on silica gel (*n*-hexane:EtOAc 9:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (m, 2H, Ph 1 H-2,6), 7.50 (m, 1H, Ph 1 H-4), 7.39 (m, 2H, Ph 1 H-3,5), 7.39 (m, 2H, Ph2 H-2,6), 7.25 (m, 1H, Ph 2 H-4), 7.24 (m, 2H, Ph 2 H-3,5), 7.11 (dd, ^3J = 1.8 Hz, ^4J = 0.8 Hz, 1H, Furyl H-5), 6.12 (dd, ^3J = 3.3 Hz, ^3J = 1.8 Hz, 1H, Furyl H-4), 5.99 (m, 1H, Furyl H-3), 5.30 (d, ^3J = 8.0 Hz, 1H, NH), 4.63 (m, 1H, CH), 3.36 (dd, ^2J = 12.7 Hz, ^3J = 5.7 Hz, 1H, CH_2), 3.17 (dd, ^2J = 12.7 Hz, ^3J = 7.3 Hz, 1H, CH_2).

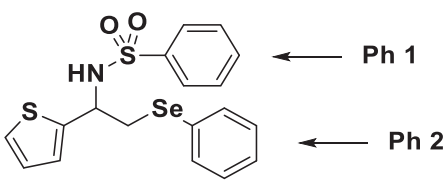
^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2 (Furyl C-2), 142.2 (Furyl C-5), 140.2 (Ph 1 C-1), 133.2 (Ph 2 C-2,6), 132.5 (Ph 1 C-4), 129.2 (Ph 2 C-3,5), 128.9 (Ph 1 C-3,5), 128.8 (Ph 2 C-1), 127.4 (Ph 2 C-4), 127.0 (Ph 1 C-2,6), 110.2 (Furyl C-4), 108.0 (Furyl C-3), 51.4 (CH), 32.5 (CH_2).

^{77}Se NMR (76 MHz, $CDCl_3$): δ 260.3 (m).

^{15}N NMR (40 MHz, $CDCl_3$): δ −274.5.

HRMS (ESI), *m/z* $[M + Na]^+$ calcd. for $C_{18}H_{17}NNaO_3SSe$: 429.9987; found: 429.9987.

3.1.21. N-[2-(phenylselanyl)-1-(2-thienyl)ethyl] benzenesulfonamide (19)



By Following the general procedure, starting from 1,1'-(methylenediselanyl)dibenzene (0.652 g, 2.0 mmol, 2.0 equiv) in dry THF (2 mL), *n*-BuLi (2.5 M, 0.76 mL, 1.9 mmol, 1.9 equiv) and *N*-(thiophen-2-ylmethylene)benzenesulfonamide (0.251 g, 1.0 mmol, 1.0 equiv) in dry THF (1 mL), compound **19** was obtained in 90% yield (0.379 g) as yellowish oil after purification by column chromatography on silica gel (*n*-hexane:EtOAc 9:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (m, 2H, Ph 1 H-2,6), 7.50 (m, 1H, Ph 1 H-4), 7.42 (m, 2H, Ph 2 H-2,6), 7.37 (m, 2H, Ph 1 H-3,5), 7.27 (m, 1H, Ph 2 H-4), 7.26 (m, 2H, Ph 2 H-3,5), 7.12 (dd, ^3J = 5.1 Hz, ^4J = 1.2 Hz, 1H, Th H-5), 6.81 (dd, ^3J = 5.1 Hz, ^3J = 3.5 Hz, 1H, Th H-4), 6.74 (m, 1H, Th H-3), 5.31 (d, ^3J = 6.8 Hz, 1H, NH), 4.79 (m, 1H, CH), 3.40 (dd, ^2J = 12.8 Hz, ^3J = 6.0 Hz, 1H, CH_2), 3.20 (dd, ^2J = 12.8 Hz, ^3J = 6.7 Hz, 1H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1 (Th C-2), 140.0 (Ph 1 C-1), 133.3 (Ph 2 C-2,6), 132.6 (Ph 1 C-4), 129.3 (Ph 2 C-3,5), 128.9 (Ph 1 C-3,5), 128.8 (Ph 2 C-1), 127.6 (Ph 2 C-4), 127.1 (Ph 1 C-2,6), 126.7 (Th C-4), 125.5 (Th C-3), 125.4 (Th C-5), 53.1 (CH), 35.7 (CH_2).

^{77}Se NMR (76 MHz, $CDCl_3$): δ 259.0 (m).

^{15}N NMR (40 MHz, $CDCl_3$): δ −268.8.

HRMS (ESI), *m/z* $[M + H]^+$ calcd. for $C_{18}H_{18}NO_2S_2Se$: 423.9939; found: 423.9936.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2020.131220.

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