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Xiu-Yang Jiang, Zhi-Cheng Liu, Li Fang, Sheng-Jiao Yan* and Jun Lin*

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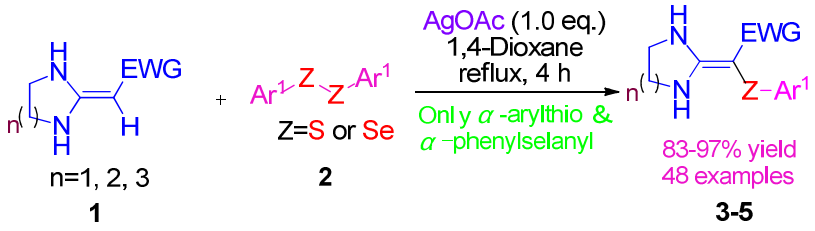

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A novel silver (I)-mediated direct coupling reaction using heterocyclic ketene aminals (HKAs) and diaryl dichalcogenides for the construction of C(sp^2)-S and C(sp^2)-Se bonds was reported. The transformation involves a variety of functionalized substrates, leading to *α*-arylthio and *α*-phenylselanyl HKAs in a mild, facile and efficient way with high regioselectivity and excellent yields. The broad scope of the starting materials enhanced the chemo-diversity of the target materials, thus affording a number of potential applications in the synthesis of heterocycles and its relevant medicinal chemistry.

Introduction

A transition-metal-catalyzed coupling reaction for the formation of carbon-heteroatom bonds is one of the most active contemporary topics in modern synthetic chemistry.[1] The development of concise and sustainable procedures as well as the discovery of novel and efficient transition-metal catalysts have been a driving force in the construction of selective synthetic methods. Among the plethoric formalism of carbon-heteroatom bonds, sp^2 hybrid carbon-chalcogen bonds,[2] in particular, have enjoyed prominent standing in fields such as total synthesis,[3] medicinal chemistry,[4] organometallic chemistry,[5] chemical biology,[6] and supramolecular chemistry.[7] Despite remarkable progress in direct transition-metal catalyzed coupling reactions of aromatic systems with chalcogen,[8] olefin systems with chalcogen have been hardly explored.[9]

In the past few decades, stereoselective and regioselective synthesis focusing on heterocycles that frequently found in natural products, pharmaceuticals, and dyes has played a significant role in many chemical branches, leading to the rapid development of widely used synthons. For example, there is a lot of research effort conducted on HKAs for concise and efficient access to highly functionalized target materials, as interest in HKAs-related transformations is steadily growing.[10-18] The structure of HKAs is showed as Fig 1. Due to the conjugation of electro-donating amino groups and the electron-withdrawing carbonyl group, the double bond (C=C) of HKAs is highly polarized.[18] This leads to higher electron density of the *α*-carbon (C3) than that of the secondary amino groups (N1 and N5). Consequently, the substituted targets of the *α*-carbon have been obtained with high selectivity *via* alkylation,[19]

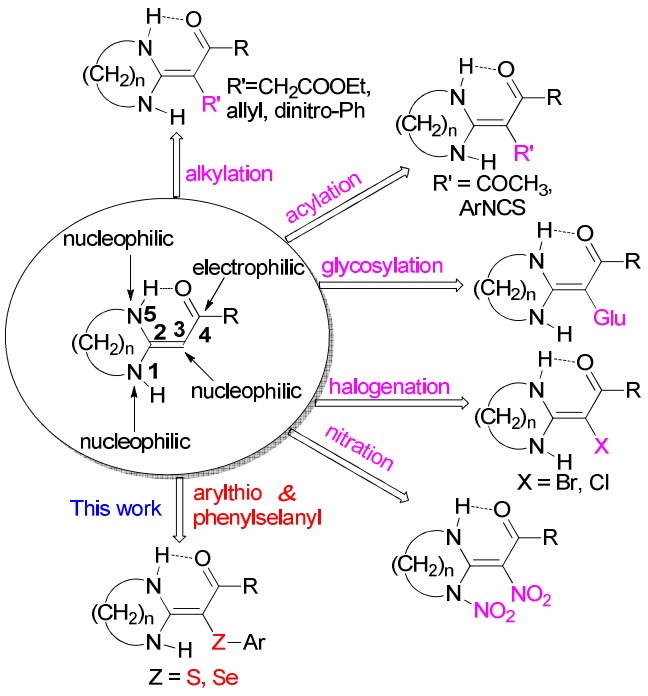

Fig. 1 The regioselective reactions of the *α*-carbon of HKAs

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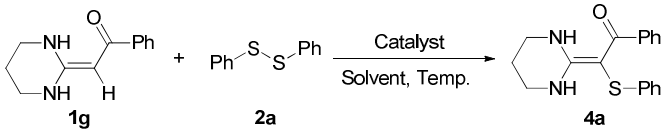
acylation,[20] glycosation,[21] halogenations,[22] and nitration reactions.[23] However, to the best of our knowledge, no information is available on the formation of C-chalcogen bonds *via* the coupling reaction of HKAs with chalcogen. Herein, we report the first example of an AgOAc mediated direct coupling reaction of HKAs **1** with diaryl dichalcogenides **2** that leads to the regioselective functionalization of the α-carbon with excellent yields (83–98%) by a facile post-treatment protocol. The scope of the reaction encompasses HKAs and diaryl dichalcogenides bearing different sized rings, substitution patterns, and functional groups, which suggests that these novel synthons will be suitable for further synthesis of diverse heterocyclic architectures.

Results and Discussion

As an initial entry point, we screened the optimum conditions for the coupling reaction to synthesize 1-phenyl-2-(phenylthio)-2-(tetrahydropyrimidin-2(1H)-ylidene)ethan-1-one **4a** using HKA **1g** and 1,2-di-phenyl disulfane **2a** as the model substrates (Table 1). No reaction occurred without the addition of a catalyst at room temperature or refluxing temperature even after 24 hours (Table 1, entries 1 and 2). However, when AgOAc (1.0 mol%) was added to refluxed 1,4-dioxane, the yield of **4a** reached 95% (Table 1, entries 3 and 4). Subsequently, trials

Table 1. Optimization of the reaction conditions[a]



1g 2a 4a

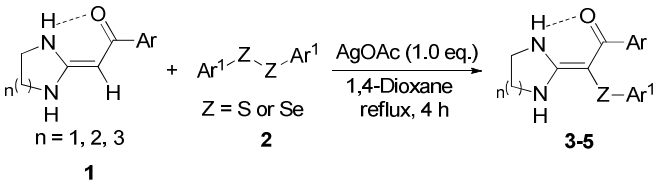
Entry	Cat. [concn. /mol%]	Solvent	t (^{0} C)	Yield[b](%)
1[c]	–	1,4-Dioxane	r. t.	N. R.
2[c]	–	1,4-Dioxane	reflux	N. R.
3	AgOAc (1.0)	1,4-Dioxane	r. t.	32
4	AgOAc (1.0)	1,4-Dioxane	reflux	95
5	$PdCl_2$ (1.0)	1,4-Dioxane	reflux	61
6	*t*-BuOK (1.0)	1,4-Dioxane	reflux	N. R.
7	Cs_2CO_3 (1.0)	1,4-Dioxane	reflux	N. R.
8	K_2CO_3 (1.0)	1,4-Dioxane	reflux	N. R.
9	piperidine (1.0)	1,4-Dioxane	reflux	N. R.
10	Et_3N (1.0)	1,4-Dioxane	reflux	N. R.
11	*p*-MBSA (1.0)	1,4-Dioxane	reflux	N. R.
12	TFA (1.0)	1,4-Dioxane	reflux	N. R.
13	HAc (1.0)	1,4-Dioxane	reflux	N. R.
14	AgOAc (1.3)	1,4-Dioxane	reflux	95
15	AgOAc (0.7)	1,4-Dioxane	reflux	87
16	AgOAc (0.5)	1,4-Dioxane	reflux	79
17	AgOAc (0.3)	1,4-Dioxane	reflux	68
18	AgOAc (1.0)	Toluene	reflux	91
19	AgOAc (1.0)	DMF	reflux	77
20	AgOAc (1.0)	EtOH	reflux	72
21	AgOAc (1.0)	CH_3CN	reflux	51
22	$AgNO_3$ (1.0)	1,4-Dioxane	reflux	N. R.
23	Ag_2CO_3 (1.0)	1,4-Dioxane	reflux	90
24	AgOTf (0.5)	1,4-Dioxane	reflux	93

[a] Reactions were carried out using **1g** (1.0 mmol), **2a** (1.0 mmol), catalyst, and solvent (10 mL) for 4 hours.
[b] Isolated yield, N. R. = no reaction.
[c] Prolonged the duration of the reaction to 24 hours.

with $PdCl_2$ as well as other basic (*t*-BuOK, Cs_2CO_3, K_2CO_3, piperidine, and Et_3N) or acidic (*p*-MBSA, TFA, and HAc) catalysts were screened, but the results demonstrated that only $PdCl_2$ could slightly promote the reaction (Table 1, entries 5–13). We also attempted to change the AgOAc loading to 1.3 mol%, 0.7 mol%, 0.5 mol%, and 0.3 mol%, but the yields of **4a** were nearly the same as that with 1.0 mol%, or even sacrificed. Therefore the results showed that AgOAc (1.0 mol%) was the best (Table 1, entries 14–17). Further screening of solvents (toluene, DMF, EtOH, and CH_3CN) indicated that the prospective product could be obtained with the highest yield (91%) (Table 1, entries 18–21) in toluene, but for the purposes of concise post-treatment and higher yield, 1,4-dioxane remained the most suitable reaction medium. Encourage by these results, other silver salts including $AgNO_3$, $AgCO_3$ and AgOTf were checked (Table 1, entries 22–24). Hence, the optimum conditions included HKAs **1** (1.0 mol) and diaryl dichalcogenides **2** (1.0 mol) in 1,4-dioxane (10 mL) at reflux temperature for 4 hours with AgOAc (1.0 mol%) as the catalyst (Table 1, entries 4 vs 23–24).

With the optimized reaction conditions in hand, we focused on the evaluation of the substrate scope (Table 2). A wide range of substituted HKAs **1a**–**1p** with three distinctively sized diazaheterocycles were employed to react with diaryl disulfides **2a**–**2f** or diphenyl diselenide **2g** separately under the optimized conditions to afford the corresponing α-arylthio or α-phenylselanyl HKAs **3**–**5** in good yields. At first, we examined the scope of substrates **1**. It was observed that the substituent group (Ar) on the HKAs had a certain influence on the yields. The system with an electron-donating group (OMe or Me) on the aryl ring reacted faster and gave higher yields than those with no substituent (H) or an electron-withdrawing group (F or Cl) (*e.g.* Table 2, entries 1−6). Notably, the reaction involving substrates with *ortho*-Cl always showed the lowest yield, which should be attributed to the electronic effect and steric hindrance (Table 2, entries 6, 22, and 33). On the other hand, as the diazaheterocycle is far away from the reactive α-position, the size of it (n) almost has no distinct effect on the yields of target materials (*e.g.* Table 2, entries 1, 17, and 34). Additionally, further exploration of the substrate scope referred to diaryl dichalcogenides **2** that mainly examined the impact of hetero-atoms (Z) and the substituent group (Ar^1) on the yields of target molecules. Obviously, compounds **2**, which has an electronegative element (S), gave higher yields than the relatively electropositive one (Se) (*e.g.* Table 2, entries 1 and 12). The substituents on the diaryl disulfides **2a–2f** exhibited trend in terms of the yields of target products, *i.e.*, *p*-OMe ≈ *p*-Me > *p*-H > *p*-Cl > *m*-F > *m*-diCl (*e.g.* Table 2, entries 17 and 23−27). Similarly, the influence of substrates **2** can be explained by the electronic and the steric effect as well. In brief, these results confirmed that the substituent groups (Ar and Ar^1) and the heteroatoms (Z) were the most significant influencing factors for this type of direct coupling reaction which can be used to synthesize α-arylthio or α-phenylselanyl HKAs **3**–**5**.

Table 2. Substrate scope of silver(I)-mediated coupling reaction of HKAs **1a-p** with diaryl dichalcogenides **2a-g**[a]

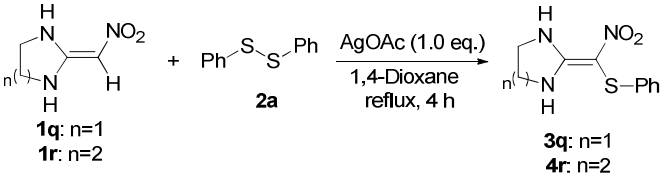


Entry	**1** (n/Ar)	**2** (Z/Ar[1])	Product	Yield[b](%)
1	**1a** (1/Ph)	**2a** (S/Ph)	**3a**	94
2	**1b** (1/*p*-OMePh)	**2a** (S/Ph)	**3b**	97
3	**1c** (1/*p*-MePh)	**2a** (S/Ph)	**3c**	94
4	**1d** (1/*p*-FPh)	**2a** (S/Ph)	**3d**	93
5	**1e** (1/*p*-ClPh)	**2a** (S/Ph)	**3e**	89
6	**1f** (1/*o*-ClPh)	**2a** (S/Ph)	**3f**	85
7	**1a** (1/Ph)	**2b** (S/*p*-OMePh)	**3g**	94
8	**1a** (1/Ph)	**2c** (S/*p*-MePh)	**3h**	95
9	**1a** (1/Ph)	**2d** (S/*p*-ClPh)	**3i**	90
10	**1a** (1/Ph)	**2e** (S/*m*-diClPh)	**3j**	84
11	**1a** (1/Ph)	**2f** (S/*m*-FPh)	**3k**	88
12	**1a** (1/Ph)	**2g** (Se/Ph)	**3l**	91
13	**1b** (1/*p*-OMePh)	**2g** (Se/Ph)	**3m**	93
14	**1c** (1/*p*-MePh)	**2g** (Se/Ph)	**3n**	91
15	**1d** (1/*p*-FPh)	**2g** (Se/Ph)	**3o**	87
16	**1e** (1/*p*-ClPh)	**2g** (Se/Ph)	**3p**	88
17	**1g** (2/Ph)	**2a** (S/Ph)	**4a**	95
18	**1h** (2/*p*-OMePh)	**2a** (S/Ph)	**4b**	98
19	**1i** (2/*p*-MePh)	**2a** (S/Ph)	**4c**	96
20	**1j** (2/*p*-FPh)	**2a** (S/Ph)	**4d**	92
21	**1k** (2/*p*-ClPh)	**2a** (S/Ph)	**4e**	90
22	**1l** (2/*o*-ClPh)	**2a** (S/Ph)	**4f**	87
23	**1g** (2/Ph)	**2b** (S/*p*-OMePh)	**4g**	95
24	**1g** (2/Ph)	**2c** (S/*p*-MePh)	**4h**	96
25	**1g** (2/Ph)	**2d** (S/*p*-ClPh)	**4i**	93
26	**1g** (2/Ph)	**2e** (S/*m*-diClPh)	**4j**	85
27	**1g** (2/Ph)	**2f** (S/*m*-FPh)	**4k**	92
28	**1g** (2/Ph)	**2g** (Se/Ph)	**4l**	92
29	**1h** (2/*p*-OMePh)	**2g** (Se/Ph)	**4m**	95
30	**1i** (2/*p*-MePh)	**2g** (Se/Ph)	**4n**	94
31	**1j** (2/*p*-FPh)	**2g** (Se/Ph)	**4o**	90
32	**1k** (2/*p*-ClPh)	**2g** (Se/Ph)	**4p**	86
33	**1l** (2/*o*-ClPh)	**2g** (Se/Ph)	**4q**	83
34	**1m** (3/Ph)	**2a** (S/Ph)	**5a**	92
35	**1n** (3/*p*-MePh)	**2a** (S/Ph)	**5b**	93
36	**1o** (3/*p*-FPh)	**2a** (S/Ph)	**5c**	90
37	**1p** (3/*p*-ClPh)	**2a** (S/Ph)	**5d**	87
38	**1m** (3/Ph)	**2b** (S/*p*-OMePh)	**5e**	96
39	**1m** (3/Ph)	**2c** (S/*p*-MePh)	**5f**	95
40	**1m** (3/Ph)	**2d** (S/*p*-ClPh)	**5g**	91
41	**1m** (3/Ph)	**2e** (S/*m*-diClPh)	**5h**	83
42	**1m** (3/Ph)	**2f** (S/*m*-FPh)	**5i**	88
43	**1m** (3/Ph)	**2g** (Se/Ph)	**5j**	90
44	**1n** (3/*p*-MePh)	**2g** (Se/Ph)	**5k**	93
45	**1o** (3/*p*-FPh)	**2g** (Se/Ph)	**5l**	86
46	**1p** (3/*p*-ClPh)	**2g** (Se/Ph)	**5m**	85

[a] Reaction conditions: **1** (1.0 mmol) and **2** (1.0 mmol) were added in 1,4-dioxane (10 mL) in the presence of AgOAc (1.0 equiv.), then refluxed in a round-bottom flask for 4 hours.
[b] Isolated yield.

Finally, the scope of this synthetic protocol was evaluated for other HKAs (**1q–1r**). The results are shown in Scheme 1 and demonstrate that **1q–1r** are also the good substitutes in this synthetic procedure (Scheme 1).

It is also worth noting that the purification for all of the target products only required recrystallization rather than column chromatography. This easy post-treatment protocol makes this methodology facile, practical, and rapid to execute.



Scheme 1. Preparation of α-arylthio-substituted HKAs.

All compounds were characterized by IR, ^{1}H NMR, ^{13}C NMR, and HRMS spectroscopy. The outcome of the regioselective direct coupling reaction was confirmed by X-ray diffraction analysis of selected single crystal of **3g** (Fig 2, CCDC949284).

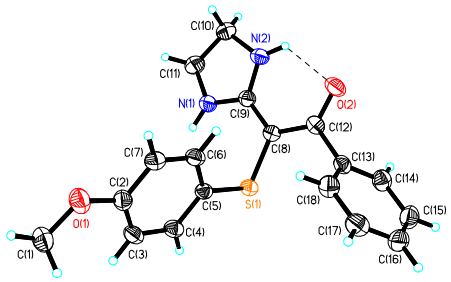
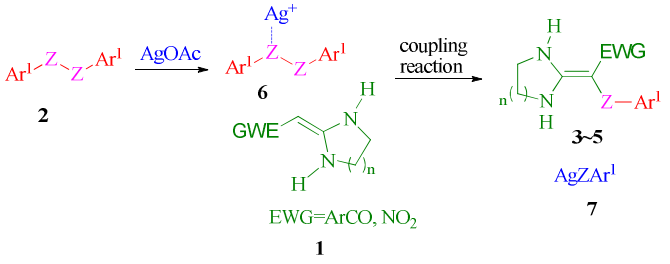


Fig. 2 ORTEP view of the molecular structure of **3g** (thermal ellipsoids are drawn at 30% probability).

In combination with known facts,[24] a plausible mechanism for this reaction is depicted in Scheme 2. Initially, the Ag^{+} derived from AgOAc coordinates with equivalent chalcogens of diaryl dichalcogenides **2** to give **6**. Subsequent the coupling reaction of the α-carbon of HKAs **1** with the non-complexed heteroatom of **6** contributs to C-Z (S or Se) bond formation and affords target materials **3–5** and **7**. The outcome of the coupling reaction is the direct synthesis of a sp^2 hybrid carbon-chalcogen bond *in situ*.



Scheme 2. Plausible mechanism for the synthesis of target materials **3-5**.

Conclusions

In conclusion, we have developed the first protocol for the direct coupling reaction of HKAs with diaryl dichalcogenides in a remarkably mild, facile, and efficient way that covers a wide range of functionalized substrates, thus allowing *in situ*

transformation of a variety of HKAs to α-arylthio and α-phenylselanyl target compounds in excellent yields with high regioselectivity. The developed method can be applied to sp^2 hybrid carbon-chalcogen bond formation reactions in several other olefin systems. We are currently exploring the biological activity of the recently generated compounds as well as their potential application in the synthesis of novel heterocycles.

Experimental Section

General information: All compounds were fully characterized by spectroscopic data. The NMR spectra were recorded on a Bruker DRX500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) or DRX400 (^{1}H: 400 MHz, ^{13}C: 100 MHz); chemical shifts (δ) are expressed in ppm, J values are given in Hz, and deuterated $CDCl_3$ was used as the solvent. IR spectra were recorded on a FT-IR Thermo Nicolet Avatar 360 using KBr pellets. The reactions were monitored by thin layer chromatography (TLC) using silica gel GF_{254}. The melting points were determined on an XT-4A melting point apparatus and are uncorrected. HRMs were performed on an Agilent LC/Msd TOF instrument. All chemicals and solvents were used as received without further purification unless otherwise stated. The raw material **1** was synthesised according to the literature.[25] The materials **3a–3g** were purchased from Aldrich Corporation Limited.

General Procedure for the Synthesis of 3–5: To a 25 ml round-bottom flask, HKAs **1** (1 mmol), 1,2-diphenyldiselane **2** (1 mmol), AgOAc (1 mmol) in dioxane (15 mL) were added. The resulting mixture was heated to reflux and stirred until all starting diphenyldiselane was consumed, as evidenced by TLC. After cooling to room temperature, the solid AgOAc was removed by filtration. The organic layer was then concentrated under reduced pressure to yield crude product. The crude compound was then purified by recrystallization with ethyl acetate and petroleum to afford compounds **3–5** as a white solid. Products **3–5** were further identified by FT-IR, NMR and HRMS, being in good agreement with the assigned structures.

2-(Imidazolidin-2-ylidene)-1-phenyl-2-(phenylthio) ethanone (3a): White solid, yield 94%; mp 202–204 °C; IR (KBr): 3194, 1573, 1482, 1373, 1299, 735 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.53 (t, J = 8.8 Hz, 2H, NCH_2), 3.88 (t, J = 8.8 Hz, 2H, NCH_2), 5.78 (br, 1H, NH), 7.06–7.39 (m, ArH, 10H), 9.91 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 42.6, 45.8, 76.1, 124.7, 125.0, 127.4, 127.7, 129.1, 129.3, 141.0, 142.6, 168.7, 194.1; HRMS (TOF ES$^+$): m/z calcd for $C_{17}H_{16}N_2NaOS$ [(M+Na$^+$)], 319.0876; found, 319.0874.

2-(Imidazolidin-2-ylidene)-1-(4-methoxyphenyl)-2-(phenylthio)ethan-one (3b): White solid, yield 97%; mp 176–177 °C; IR (KBr): 3366, 3269, 1576, 1369, 1241, 732 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.57 (t, J = 8.9 Hz, 2H, NCH_2), 3.75 (s, 3H, CH_3), 3.90 (t, J = 8.9 Hz, 2H, NCH_2), 5.72 (br, 1H, NH), 6.74 (t, J = 8.6 Hz, 2H, ArH), 7.06–7.26 (m, 5H, ArH), 7.45 (t, J = 8.6 Hz, 2H, ArH), 9.95 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 42.6, 45.8, 55.6, 75.6, 112.9, 124.6, 125.0, 129.3, 129.6, 134.9, 141.0, 160.6, 168.9, 193.2; HRMS (TOF ES$^+$): m/z calcd for $C_{18}H_{18}N_2NaO_2S$ [(M+Na$^+$)], 349.0981; found, 349.0971.

2-(Imidazolidin-2-ylidene)-2-(phenylthio)-1-(*p*-tolyl)ethanone (3c): White solid, yield 94%; mp 213–214 °C; IR (KBr): 3416, 3285, 1579, 1531, 1365, 1298, 744 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.28 (s, 3H, CH_3), 3.57 (t, J = 8.8 Hz, 2H, NCH_2), 3.91 (t, J = 8.8 Hz, 2H, NCH_2), 5.72 (br, 1H, NH), 7.02 (d, J = 7.8 Hz, 2H, ArH), 7.06–7.33 (m, ArH, 7H), 9.94 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.8, 42.6, 45.8, 75.9, 124.7, 124.9, 127.5, 128.4, 129.3, 139.1, 139.7, 141.0, 168.7, 194.1; HRMS (TOF ES$^+$): m/z calcd for $C_{18}H_{18}N_2NaOS$ [(M+Na$^+$)], 333.1032; found, 333.1027.

1-(4-Fluorophenyl)-2-(imidazolidin-2-ylidene)-2-(phenylthio)ethanone (3d): White solid, yield 93%; mp 182–183 °C; IR (KBr): 3305, 1580, 1532, 1370, 1303, 743 cm^{-1}; ^{1}H NMR (500MHz,$CDCl_3$): δ = 3.50–3.57 (m, 2H, NCH_2), 3.85–3.89 (m, 2H, NCH_2), 5.80 (br, 1H, NH), 6.84–7.41 (m, 9H, ArH), 9.86 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$) : δ = 42.6, 45.8, 75.9, 114.5 (d, J = 20.0 Hz), 124.6, 125.1, 129.4, 129.7, 138.6, 140.7, 163.4 (d, J = 245.0 Hz), 168.7, 192.7; HRMS (TOF ES$^+$): m/z calcd for $C_{17}H_{15}FN_2NaOS$ [(M+Na$^+$)], 337.0781; found, 337.0783.

1-(4-Chlorophenyl)-2-(imidazolidin-2-ylidene)-2-(phenylthio)ethanone (3e): White solid, yield 89%; mp 200–202 °C; IR (KBr): 3413, 3267, 1579, 1532, 1370, 1306, 742 cm^{-1}; ^{1}H NMR (500 MHz,$CDCl_3$): δ = 3.56 (t, J = 8.9 Hz, 2H, NCH_2), 3.90 (t, J = 8.9 Hz, 2H, NCH_2), 5.80 (br, 1H, NH), 7.06–7.34 (m, 9H, ArH), 9.85 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 42.6, 45.8, 76.0, 124.6, 125.2, 127.9, 129.0, 129.4, 134.9, 140.6, 140.9, 168.7, 192.6; HRMS (TOF ES$^+$): m/z calcd for $C_{17}H_{15}ClN_2NaOS$ [(M+Na$^+$)], 353.0486; found, 353.0486.

1-(2-Chlorophenyl)-2-(imidazolidin-2-ylidene)-2-(phenylthio)ethanone (3f): White solid, yield 85%; mp 194–195 °C; IR (KBr): 3193, 1582, 1540, 1482, 1381, 1299, 747 cm^{-1}; ^{1}H NMR (500 MHz,$CDCl_3$): δ = 3.58 (t, J = 8.9 Hz, 2H, NCH_2), 3.92 (t, J = 8.9 Hz, 2H, NCH_2), 5.80 (br, 1H, NH), 7.05–7.30 (m, 9H, ArH), 9.74 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 42.5, 45.7, 125.1, 126.3, 127.6, 129.0, 129.5, 130.6, 140.2, 142.2, 168.0, 192.1; HRMS (TOF ES$^+$): m/z calcd for $C_{17}H_{15}ClN_2NaOS$ [(M+Na$^+$)], 353.0486; found, 353.0485.

2-(Imidazolidin-2-ylidene)-2-((4-methoxyphenyl)thio)-1-phenylethan-one (3g): White solid, yield 94%; mp 218–220 °C; IR (KBr): 3403, 3304, 1589, 1533, 1482, 1367, 1298, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.55 (t, J = 8.9 Hz, 2H, NCH_2), 3.70 (s, 3H, CH_3), 3.88 (t, J = 8.9 Hz, 2H, NCH_2), 5.82 (br, 1H, NH), 6.78–7.40 (m, 9H, ArH), 9.87 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 42.6, 45.8, 55.8, 115.1, 126.4, 127.1, 127.4, 127.7, 129.1, 131.6, 142.7, 157.9, 168.8, 194.1; HRMS (TOF ES$^+$): m/z calcd for $C_{18}H_{19}N_2O_2S$ [(M+H$^+$)], 327.1162; found, 327.1168.

2-(Imidazolidin-2-ylidene)-1-phenyl-2-(*p*-tolylselanyl) ethanone (3h): White solid, yield 95%; mp 196–197 °C; IR (KBr): 3424, 3318, 1578, 1359, 1298, 702 cm^{-1}; ^{1}H NMR (500 MHz,$CDCl_3$): δ = 2.29 (s, 3H, $ArCH_3$), 3.49–3.53 (m, 2H, NCH_2), 3.85–3.88 (m, 2H, NCH_2), 5.77 (br, 1H, NH), 7.01–7.41 (m, 9H, ArH), 9.91 (br, 1H, NH); ^{13}C NMR (125 MHz,

$CDCl_3$): δ = 21.3, 42.6, 45.8, 76.4, 124.8, 127.4, 127.7, 129.1, 130.1, 134.7, 137.4, 142.7, 168.7, 194.0; HRMS (TOF ES^+): m/z calcd for $C_{18}H_{19}N_2OS$ [$(M+H^+)$], 311.1213; found, 311.1216.

2-((4-Chlorophenyl)selanyl)-2-(imidazolidin-2-ylidene)-1-phenylethan-one (3i): White solid, yield 90%; mp 211–213 °C; IR (KBr): 3200, 1581, 1377, 1299, 705 cm^{-1}; ^1H NMR (500 MHz,$CDCl_3$): δ = 3.58 (t, J = 8.7 Hz, 2H, NCH_2), 3.91 (t, J = 8.7 Hz, 2H, NCH_2), 5.73 (br, 1H, NH), 7.03–7.37 (m, 9H, ArH), 9.90 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 42.6, 45.8, 75.8, 126.0, 127.3, 127.7, 129.2, 129.3, 130.7, 139.6, 142.4, 168.6, 194.2; HRMS (TOF ES^+): m/z calcd for $C_{17}H_{16}ClN_2OS$ [$(M+H^+)$], 331.0666; found, 331.0663.

2-((3,5-Dichlorophenyl)selanyl)-2-(imidazolidin-2-ylidene) -1-phenyleth-anone (3j): White solid, yield 84%; mp 213–214 °C; IR (KBr): 3208, 1575, 1377, 1300, 793 cm^{-1}; ^1H NMR (500 MHz,$CDCl_3$): δ = 3.55–3.61 (m, 2 H, NCH_2), 3.89–3.94 (m, 2 H, NCH_2), 5.76 (br, 1 H, NH), 6.95–7.34 (m, 8H, ArH), 9.89 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 42.6, 45.8, 74.7, 122.7, 125.2, 127.2, 127.8, 129.3, 135.8, 142.2, 145.3, 168.3, 194.1; HRMS (TOF ES^+): m/z calcd for $C_{17}H_{15}Cl_2N_2OS$ [$(M+H^+)$], 365.0277; found, 365.0258.

2-((3-Fluorophenyl)selanyl)-2-(imidazolidin-2-ylidene)-1-phenylethan-one (3k): White solid, yield 88%; mp 204–205 °C; IR (KBr): 3423, 3305, 1581, 1367, 1299, 733 cm^{-1}; ^1H NMR (500 MHz,$CDCl_3$): δ = 3.53 (t, J = 8.8 Hz, 2 H, NCH_2), 3.88 (t, J = 8.8 Hz, 2 H, NCH_2), 5.79 (br, 1 H, NH), 6.73–7.36 (m, 9H, ArH), 9.89 (br, 1 H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 42.6, 45.8, 75.5, 111.5 (d, J = 23.7Hz), 111.9 (d, J = 21.3 Hz), 112.0, 120.3, 127.3, 127.8, 129.2, 130.6, 144.0, 163.2 (d, J = 245.0Hz), 168.5, 194.1; HRMS (TOF ES^+): m/z calcd for $C_{17}H_{16}FN_2OS$ [$(M+H^+)$], 315.0962; found, 315.0965.

2-(Imidazolidin-2-ylidene)-1-phenyl-2-(phenylselanyl)eth-anone (3l): White solid, yield 91%; mp 161–163 °C; IR (KBr): 3409, 3310, 1573, 1368, 1297, 728 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 3.48–3.52 (m, 2H, NCH_2), 3.86–3.90 (m, 2H, NCH_2), 5.78 (br, 1H, NH), 7.11–7.34 (m, 10H, ArH), 9.98 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ= 42.5, 46.0, 73.9, 125.8, 127.3, 127.5, 127.6, 128.9, 129.5, 135.7, 143.7, 168.5, 194.2; HRMS (TOF ES^+): m/z calcd for $C_{17}H_{16}N_2NaOSe$ [$(M+Na^+)$], 367.0320; found, 367.0315.

2-(Imidazolidin-2-ylidene)-1-(4-methoxyphenyl)-2-(phen-ylselanyl)ethanone (3m): White solid, yield 93%; mp 144–146 °C; IR (KBr): 3309, 1603, 1347, 818, 737 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 3.57–3.61 (m, 2H, NCH_2), 3.78 (s, 3H, OCH_3), 3.93–3.96 (m, 2H, NCH_2), 5.77 (br, 1H, NH), 6.75–7.43 (m, 9H, ArH), 10.04 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 42.6, 46.0, 55.6, 73.5, 112.9, 125.8, 127.4, 129.5, 129.6, 135.8, 135.9, 160.5, 168.7, 193.5; HRMS (TOF ES^+): m/z calcd for $C_{18}H_{19}N_2O_2Se$ [$(M+H^+)$] 375.0606; found, 375.0601.

2-(Imidazolidin-2-ylidene)-2-(phenylselanyl)-1-(*p*-tolyl)-ethanone (3n): White solid, yield 91%; mp: 205–207 °C; IR (KBr): 3391, 3252, 1572, 1529, 1366, 1300, 733 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.12 (s, $ArCH_3$), 3.55–3.66 (m, 2H, NCH_2), 3.88–3.95 (m, 2H, NCH_2), 5.74 (br, 1H, NH), 6.74 (d, J = 8.6 Hz, 2H, ArH), 7.12–7.27 (m, 5H, ArH), 7.39 (d, J = 8.6 Hz, 2H, ArH), 10.02 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 42.6, 46.0, 55.6, 67.5, 112.8, 125.8, 127.4, 129.5, 129.6, 135.8, 135.9, 160.5, 168.7, 193.5; HRMS (TOF ES^+): m/z calcd for $C_{18}H_{19}Na_2OSe$ [$(M+H^+)$], 359.0657; found, 359.0661.

1-(4-Fluorophenyl)-2-(imidazolidin-2-ylidene)-2-(phenyl-selanyl)ethan-one (3o): White solid, yield 87%; mp 167–169 °C; IR (KBr): 3412, 3312, 1575, 1525, 1367, 1298, 726 cm^{-1}; ^1H NMR (500 MHz,$CDCl_3$): δ = 3.53–3.58 (m, 2H, NCH_2), 3.90–3.94 (m, 2H, NCH_2), 5.81 (br, 1H, NH), 6.85–6.90 (m, 2H, ArH), 7.14–7.15 (m, 1H, ArH), 7.22–7.37 (m, 6H, ArH), 9.96 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 42.5, 46.0, 73.7, 114.5 (d, J = 20.0 Hz), 126.0, 127.4, 129.6, 129.6, 135.5, 139.6, 163.2 (d, J = 246.3 Hz), 168.6, 192.9; HRMS (TOF ES^+): m/z calcd for $C_{17}H_{16}FN_2OSe$ [$(M+H^+)$], 363.0406; found, 363.0412.

1-(4-Chlorophenyl)-2-(imidazolidin-2-ylidene)-2-(phenyl-selanyl)ethan-one (3p): White solid, yield 88%; mp 184–186 °C; IR (KBr): 3405, 3263, 1576, 1528, 1369, 1305, 736 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 3.56–3.60 (m, 2H, NCH_2), 3.91–3.96 (m, 2H, NCH_2), 5.77 (br, 1H, NH), 7.13–7.28 (m, 9H, ArH), 9.95 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 42.5, 46.0, 73.7, 126.0, 127.3, 127.8, 128.9, 129.6, 134.7, 135.4, 141.9, 168.6, 192.8; HRMS (TOF ES^+): m/z calcd for $C_{17}H_{16}ClN_2OSe$ [$(M+H^+)$], 379.0111;found, 379.0103.

2-(Nitro(phenylthio)methylene)imidazolidine (3q): White solid, yield 88%; mp 163.5–164 °C; IR (KBr): 3350, 3256, 1576, 1392, 1335, 738 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 3.75–3.79 (m, 2H, NCH_2), 3.95–4.00 (m, 2H, NCH_2), 5.83 (br, 1H, NH), 7.13–7.17 (m, 3H, ArH), 7.24–7.28 (m, 2H, ArH), 8.83(br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 43.1, 45.6, 98.4, 125.6, 125.9, 129.1, 136.1, 163.3; HRMS (TOF ES^+): m/z calcd for $C_{10}H_{11}N_3NaO_2S$ [$(M+Na^+)$], 260.0464;found, 260.0462.

1-Phenyl-2-(phenylthio)-2-(tetrahydropyrimdin-2(1*H*)-ylidene)ethan-one (4a): White solid, yield 95%; mp 167–1689 °C; IR (KBr): 3352, 3279, 1586, 1344, 1205, 742 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.79–1.82 (m, 2H, NCH_2), 3.27–3.43 (m, 4H, NCH_2), 6.49 (br, 1H, NH), 7.04–7.08 (m, 3H, ArH), 7.15–7.18 (m, 4H, ArH), 7.24–7.28 (m, 2H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.4, 38.8, 39.5, 78.4, 124.7, 125.0, 126.8, 127.7, 128.5, 129.2, 141.0, 143.9, 160.8, 193.0; HRMS (TOF ES^+): m/z calcd for $C_{18}H_{19}N_2OS$ [$(M+H^+)$], 311.1213; found, 211.1209.

1-(4-Methoxyphenyl)-2-(phenylthio)-2-(tetrahydropyrimi-din-2(1*H*)-ylidene)ethanone (4b): White solid, yield 98%; mp 177–178 °C; IR (KBr): 3364, 3050, 1585, 1344, 1241, 735 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.93–1.96 (m, 2H, CH_2), 3.30–3.35 (m, 2H, NCH_2), 3.43–3.49 (m, 2H, NCH_2), 3.74 (s, 3H, OCH_3), 6.49 (br, 1H, NH), 6.71 (d, J = 7.3 Hz, 2H, ArH), 7.08–7.26 (m, 5H, ArH), 7.33 (d, J = 7.3 Hz, 2H, ArH), 12.05 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.4, 38.8, 39.5, 55.5, 112.9, 124.6, 125.0, 128.9, 129.3, 136.3, 141.1, 160.0, 160.9, 192.4; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{21}N_2O_2S$ [$(M+H^+)$], 341.1318; found, 341.1316.

2-(Phenylthio)-2-(tetrahydropyrimidin-2(1*H*)-ylidene)-1-(*p*-tolyl)ethan-one (4c): White solid, yield 96%; mp 175–177 °C; IR (KBr): 3330, 3052, 1584, 1339, 1164, 746 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.88–1.92 (m, 2H, NCH_2), 2.26 (s, 3H, $ArCH_3$), 3.25–3.29 (m, 2H, NCH_2), 3.40–3.47 (m, 2H, NCH_2), 6.48 (br, 1H, NH), 6.98 (d, J = 7.6 Hz, 2H, ArH), 6.97–7.12 (m, 3H, ArH), 7.22–7.25 (m, 4H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.4, 21.8, 38.8, 39.5, 78.2, 124.6, 125.0, 127.0, 128.3, 129.2, 138.3, 141.1, 160.8, 193.0; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{21}N_2OS$, [$(M+H^+)$], 325.1369; found, 325.1365.

1-(4-Fluorophenyl)-2-(phenylthio)-2-(tetrahydropyrimidin-2(1*H*)-ylid-ene)ethanone (4d): White solid, yield 92%; mp 122–124 °C; IR (KBr): 3322, 3060, 1586, 1343, 1210, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.93–1.99 (m, 2H, CH_2), 3.39–3.43 (m, 4H, NCH_2), 6.51 (br, 1H, NH), 6.83–7.32 (m, 9H, ArH), 11.92 (br, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.0, 39.0, 39.0, 77.9, 114.1 (d, J = 26.3 Hz), 124.2, 124.7, 128.6 (d, J = 8.0 Hz), 128.9, 139.4, 140.3, 160.4, 162.5 (d, J = 245.0 Hz), 191.3; HRMS (TOF ES^+): m/z calcd for $C_{18}H_{17}FN_2NaOS$ [$(M+Na^+)$], 351.0938; found, 351.0637.

1-(4-Chlorophenyl)-2-(phenylthio)-2-(tetrahydropyrimidin-2(1*H*)-ylid-ene)ethanone (4e): White solid, yield 90%; mp 180–181 °C; IR (KBr): 330, 3052, 1584, 1339, 1164, 746 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.95–1.98 (m, 2H, CH_2), 3.39–3.44 (m, 4H, NCH_2), 6.52 (br, 1H, NH), 7.07–7.48 (m, 9H, ArH), 11.85 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.4, 39.1, 39.1, 78.5, 124.6, 125.2, 127.9, 128.5, 129.3, 134.2, 140.6, 142.2, 160.8, 191.6; HRMS (TOF ES^+): m/z calcd for $C_{18}H_{17}ClN_2NaOS$ [$(M+Na^+)$], 367.0642; found, 367.0637.

1-(2-Chlorophenyl)-2-(phenylthio)-2-(tetrahydropyrimidin-2(1*H*)-ylid-ene)ethanone (4f): White solid, yield 87%; mp 163–165 °C; IR (KBr): 3261, 1593, 1341, 1210, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.95–1.99 (m, 2H, CH_2), 3.38–3.44 (m, 4H, NCH_2), 7.00–7.28 (m, 9H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.9, 38.7, 38.7, 79.5, 124.5, 124.7, 125.9, 126.9, 128.4, 128.6, 129.1, 130.1, 139.7, 142.4, 160.0, 189.9; HRMS (TOF ES^+): m/z calcd for $C_{18}H_{17}ClN_2NaOS$ [$(M+Na^+)$], 367.0642; found, 367.0635.

2-((4-Methoxyphenyl)selanyl)-1-phenyl-2-(tetrahydropyrimidin-2(1*H*)-ylidene)ethanone (4g): White solid, yield 95%; mp 174–176 °C; IR (KBr): 3368, 3187, 1592, 1354, 1232, 743 cm^{-1}; ^1H NMR (400 MHz, CDCl3): δ = 1.93–1.96 (m, 2H, CH_2), 3.35–3.45 (m, 4H, NCH_2), 3.76 (s, 3H, OCH_3), 6.56 (br, 1H, NH), 6.78–7.31 (m, 9H, ArH), 11.93 (br, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.1, 38.9, 38.9, 55.5, 79.2, 114.7, 125.8, 126.6, 127.3, 128.1, 131.4, 143.6, 157.5, 160.5, 192.6; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{21}N_2O_2S$ [$(M+H^+)$], 341.1318; found, 341.1319.

1-Phenyl-2-(tetrahydropyrimidin-2(1*H*)-ylidene)-2-(*p*-tolylselanyl)eth-anone (4h): White solid, yield 96%; mp 213–214 °C; IR (KBr): 3369, 1593, 1342, 1208, 800 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.94–1.97 (m, 2H, CH_2), 2.29 (s, 3H, $ArCH_3$), 3.31–3.34 (m, 2H, NCH_2), 3.45–3.49 (m, 2H, NCH_2), 6.51 (br, 1H, NH), 6.99–7.32 (m, 9H, ArH), 11.97 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.4, 21.3, 38.8, 39.5, 78.7, 124.7, 126.9, 127.6, 128.4, 130.0, 134.7, 137.4, 143.9, 160.8, 193.0; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{21}N_2OS$ [$(M+H^+)$], 325.1369; found, 325.1364.

2-((4-Chlorophenyl)selanyl)-1-phenyl-2-(tetrahydropyrimidin-2(1*H*)-ylidene)ethanone (4i): White solid, yield 93%; mp 210–211 °C; IR (KBr): 3360, 1588, 1344, 1210, 809 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.93–1.96 (m, 2H, CH_2), 3.33–3.36 (m, 2H, NCH_2), 3.44–3.47 (m, 2H, NCH_2), 6.43 (br, 1H, NH), 7.00–7.27 (m, 9H, ArH), 11.89 (br, 1H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.4, 38.8, 39.5, 78.1, 125.9, 126.7, 127.7, 128.6, 129.3, 130.7, 139.6, 143.7, 160.7, 193.1; HRMS (TOF ES^+): m/z calcd for $C_{18}H_{18}ClN_2OS$ [$(M+H^+)$], 345.0823, found, 345.0829.

2-((3,5-Dichlorophenyl)selanyl)-1-phenyl-2-(tetrahydropyrimidin-2(1*H*) -ylidene)ethanone (4j): White solid, yield 85%; mp 223–225 °C; IR (KBr): 3276, 3067, 1596, 1334, 1214, 786 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.96–2.01 (m, 2H, CH_2), 3.34–3.38 (m, 2H, NCH_2), 3.46–3.50 (m, 2H, NCH_2), 6.35 (br, 1H, NH), 6.94–7.27 (m, 8H, ArH), 11.89 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.3, 38.8, 39.6, 122.7, 125.2, 126.7, 127.8, 128.7, 135.8, 143.5, 145.3, 160.5, 193.4; HRMS (TOF ES^+): m/z calcd for $C_{18}H_{17}Cl_2N_2OS$ [$(M+H^+)$], 379.0433; found, 379.0437.

2-((4-Fluorophenyl)selanyl)-1-phenyl-2-(tetrahydropyrimidin-2(1*H*)-ylidene)ethanone (4k): White solid, yield 92%; mp 181–183 °C; IR (KBr): 3283, 1590, 1342, 1210, 780 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.95–1.98 (m, 2H, CH_2), 3.32–3.36 (m, 2H, NCH_2), 3.67–3.72 (m, 2H, NCH_2), 6.43 (br, 1H, NH), 6.73–7.29 (m, 9H, ArH), 11.93 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.4, 38.8, 39.5, 111.5 (d, J = 23.8 Hz), 112.0 (d, J = 21.3 Hz), 120.3, 123.1, 126.8, 127.7, 128.6, 130.5, 143.9, 160.7, 163.6 (d, J = 246.3 Hz), 164.8, 193.2; HRMS (TOF ES^+): m/z calcd for $C_{18}H_{18}FN_2OS$ [$(M+H^+)$], 329.1118; found, 329.1118.

1-Phenyl-2-(phenylselanyl)-2-(tetrahydropyrimidin-2(1*H*) -ylidene)ethanone (4l): White solid, yield 92%; mp 162–164 °C; IR (KBr): 3353, 1587, 1343, 741 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.94–1.98 (m, 2H, CH_2), 3.32–3.37 (m, 2H, NCH_2), 3.46–3.50 (m, 2H, NCH_2), 6.57 (br, ^1H, NH), 7.15–7.31 (m, 10H, ArH), 12.12 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.0, 38.5, 39.2, 77.8, 125.3, 126.3, 126.8, 127.1, 127.7, 129.0, 135.3, 144.6, 160.1, 192.6; HRMS (TOF ES^+): m/z calcd for $C_{18}H_{19}N_2OSe$ [$(M+H^+)$], 359.0657, found, 359.0668.

1-(4-Methoxyphenyl)-2-(phenylselanyl)-2-(tetrahydropyrimidin-2(1*H*)-ylidene)ethanone (4m): White solid, yield 95%; mp 154–156 °C; IR (KBr): 3353, 1581, 1344, 1240, 799 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.90–1.95 (m, 2H, CH_2), 3.33–3.45 (m, 4H, NCH_2), 3.73 (s, 3H, OCH_3), 6.53 (br, 1H, NH), 6.69–7.29 (m, 9H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.5, 39.2, 39.8, 55.5, 112.8, 125.8, 127.3, 128.8, 129.5, 135.9, 137.6, 159.9, 160.8, 192.5; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{21}N_2O_2Se$ [$(M+H^+)$], 389.0763; found, 389.0768.

2-(Phenylselanyl)-2-(tetrahydropyrimidin-2(1*H*)-ylidene)-1-(*p*-tolyl)-ethanone (4n): White solid, yield 94%; mp 157–159 °C; IR (KBr): 3363, 3325, 1582, 1341, 1207, 742 cm^{-1}; ^1H

NMR (500 MHz, $CDCl_3$): δ = 1.94–1.97 (m, 2H, CH_2), 2.31 (s, 3H, $ArCH_3$), 3.34–3.47 (m, 4H, NCH_2), 6.56 (br, 1H, NH), 7.01–7.30 (m, 9H, ArH), 12.17 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.5, 21.8, 39.0, 39.7, 78.1, 125.8, 126.9, 127.3, 128.3, 129.5, 135.9, 138.0, 142.2, 160.7, 193.2; HRMS (TOF ES$^+$): m/z calcd for $C_{19}H_{21}N_2OSe$ [(M+H$^+$)], 373.0814; found, 373.0817.

1-(4-Fluorophenyl)-2-(phenylselanyl)-2-(tetrahydropyrim-idin-2(1*H*)-ylidene)ethanone (4o): White solid, yield 90%; mp 139–140 °C; IR (KBr): 3322, 1582, 1346, 1210, 740 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.93–1.98 (m, 2H, CH_2), 3.40–3.47 (m, 4H, NCH_2), 6.59 (br, 1H, NH), 6.85–7.30 (m, 9H, ArH), 12.07 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.4, 39.6, 40.9, 78.5, 114.4 (d, J = 21.3 Hz), 125.9, 127.2, 128.9, 129.6, 135.6, 141.1, 160.7, 163.8, 191.8; HRMS (TOF ES$^+$): m/z calcd for $C_{18}H_{18}FN_2OSe$ [(M+H$^+$)], 377.0563; found, 377.0565.

1-(4-Chlorophenyl)-2-(phenylselanyl)-2-(tetrahydropyrim-idin-2(1*H*)-ylidene)ethanone (4p): White solid, yield 86%; mp 176–177 °C; IR (KBr): 3319, 3057, 1581, 1345, 1205, 740 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.91–1.94 (m, 2H, CH_2), 3.36–3.41 (m, 4H, NCH_2), 6.58 (br, 1H, NH), 7.12–7.25 (m, 9H, ArH), 11.98 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.4, 39.4, 39.4, 78.3, 126.0, 127.2, 127.8, 128.4, 129.6, 133.9, 135.5, 143.4, 160.6, 191.6; HRMS (TOF ES$^+$): m/z calcd for $C_{18}H_{18}ClN_2OSe$ [(M+H$^+$)], 393.0265; found, 393.0267.

1-(2-Chlorophenyl)-2-(imidazolidin-2-ylidene)-2-(phenyl-selanyl)ethan-one (4q): White solid, yield 83%; mp 151–153 °C; IR (KBr): 3350, 1589, 1350, 1211, 747 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.89–1.93 (m, 2H, CH_2), 3.28–3.32 (m, 2H, NCH_2), 3.41–3.45 (m, 2H, NCH_2), 6.49 (br, 1H, NH), 6.99–7.24 (m, 9H, ArH), 11.78 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.4, 39.0, 39.6, 79.8, 125.9, 126.4, 127.7, 128.7, 129.4, 130.5, 134.9, 144.0, 160.2, 190.1; HRMS (TOF ES$^+$): m/z calcd for $C_{18}H_{17}ClN_2NaOSe$ [(M+Na$^+$)], 415.0087, found, 415.0083.

2-(Nitro(phenylthio)methylene)hexahydropyrimidine (4r): White solid, yield 90%; mp 152.5–153 °C; IR (KBr): 3284, 1585, 1356, 1200, 1127, 738 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.93–1.98 (m, 2H, CH_2), 3.42–3.47 (m, 4H, NCH_2), 7.11–7.15 (m, 3H, ArH), 7.22–7.26 (m, 2H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.0, 39.0, 39.0, 100.8, 125.5, 125.9, 129.1, 135.7, 155.7; HRMS (TOF ES$^+$): m/z calcd for $C_{11}H_{13}N_3NaO_2S$ [(M+Na$^+$)], 274.0621; found, 274.0619.

2-(1,3-Diazepan-2-ylidene)-1-phenyl-2-(phenylthio)ethan-one (5a): White solid, yield 92%; mp 177–178 °C; IR (KBr): 3363, 1594, 1343, 1202, 742 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.75–1.81 (m, 4H, CH_2CH_2), 3.20–3.23 (m, 2H, NCH_2), 3.45–3.48 (m, 2H, NCH_2), 6.55 (br, 1H, NH), 7.08–7.31 (m, 10H, ArH), 12.14 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.0, 28.3, 45.5, 46.3, 81.6, 124.8, 125.1, 126.9, 127.6, 128.7, 129.3, 140.9, 143.9, 170.7, 194.2; HRMS (TOF ES$^+$): m/z calcd for $C_{19}H_{21}N_2OS$ [(M+H$^+$)], 325.1369; found, 325.1368.

2-(1,3-Diazepan-2-ylidene)-2-(phenylselanyl)-1-(*p*-tolyl)-ethanone (5b): White solid, yield 93%; mp 157–158 °C; IR (KBr): 3317, 2932, 1605, 1349, 1200, 741 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.73–1.80 (m, 4H, CH_2CH_2), 2.29 (s, 3H, $ArCH_3$), 3.18–3.20 (m, 2H, NCH_2), 3.43–3.47 (m, 2H, NCH_2), 6.54 (br, 1H, NH), 7.01 (d, J = 7.7 Hz, 2H), 7.00–7.13 (m, 3H, ArH), 7.24–7.27 (m, 3H, ArH), 12.20 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.8, 28.1, 28.3, 45.5, 46.3, 81.4, 124.8, 125.1, 127.1, 128.3, 128.3, 129.3, 138.6, 141.0, 170.8, 194.2; HRMS (TOF ES$^+$): m/z calcd for $C_{20}H_{23}N_2OS$ [(M+H$^+$)], 339.1526, found, 339.1518.

2-(1,3-Diazepan-2-ylidene)-1-(4-fluorophenyl)-2-(phenyl-thio)ethanone (5c): White solid, yield 90%; mp 124–125 °C; IR (KBr): 3331, 3060, 1591, 1348, 1207, 847, 740 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$); δ = 1.76–1.84 (m, 4H, CH_2CH_2), 3.22–3.26 (m, 2H, NCH_2), 3.46–3.50 (m, 2H, NCH_2), 6.59 (br, 1H, NH), 6.85–6.91 (m, 2H, ArH), 7.09–7.14 (m, 3H, ArH), 7.25–7.29 (m, ArH, 2H), 7.33–7.36 (m, ArH, 2H), 12.12 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.0, 28.2, 45.5, 46.3, 81.5, 114.4 (d, J = 21.3 Hz), 124.7, 125.2, 129.2, 129.4, 139.9, 140.6, 163.0 (d, J = 245.0 Hz), 170.7, 192.80; HRMS (TOF ES$^+$): m/z calcd for $C_{19}H_{19}FN_2NaOS$ [(M+Na$^+$)], 365.1094; found, 365.1087.

1-(4-Chlorophenyl)-2-(1,3-diazepan-2-ylidene)-2-(phenyl-thio)ethanone (5d): White solid, yield 87%; mp 156–157 °C; IR (KBr): 3325, 3053, 1594, 1349, 1202, 833, 744 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.68–1.81 (m, 4H, CH_2CH_2), 3.20–3.3.24 (m, 2H, NCH_2), 3.67–3.70 (m, 2H, NCH_2), 6.56 (br, 1H, NH), 7.05–7.25 (m, 9H, ArH), 12.06 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.9, 28.2, 45.5, 46.3, 81.5, 124.7, 125.3, 127.8, 128.5, 129.4, 134.4, 140.5, 142.2, 170.6, 192.7; HRMS (TOF ES$^+$): m/z calcd for $C_{19}H_{20}ClN_2OS$ [(M+H$^+$)], 359.0979; found, 359.0975.

2-(1,3-Diazepan-2-ylidene)-2-((4-methoxyphenyl)thio)-1-phenylethan-one (5e): White solid, yield 96%; mp 171–172 °C; IR (KBr): 3316, 2930, 1600, 1342, 1238, 816 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.75–1.79 (m, 4H, CH_2CH_2), 3.19–3.23 (m, 2H, NCH_2), 3.42–3.47 (m, 2H, NCH_2), 3.76 (s, 3H, OCH_3), 6.64 (br, 1H, NH), 6.80 (d, J = 8.5 Hz), 6.98 (d, J = 8.5 Hz), 7.18–7.26 (m, 3H, ArH), 7.28–7.32 (m, 2H, ArH), 12.11 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.0, 28.3, 45.5, 46.3, 55.8, 82.8, 115.1, 126.3, 126.9, 127.6, 128.6, 131.5, 144.0, 157.9, 170.8, 194.1; HRMS (TOF ES$^+$): m/z calcd for $C_{20}H_{23}N_2O_2S$ [(M+H$^+$)], 355.1475; found, 355.147.

2-(1,3-Diazepan-2-ylidene)-1-phenyl-2-(*p*-tolylthio)ethan-one (5f): White solid, yield 95%; mp 175–177 °C; IR (KBr): 3334, 3046, 1600, 1345, 1200, 800 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.75–1.81 (m, 4H, CH_2CH_2), 2.30 (s, 3H, $ArCH_3$), 3.19–3.23 (m, 2H, NCH_2), 3.42–3.48 (m, 2H, NCH_2), 6.58 (br, 1H, NH), 6.98 (d, J = 8.2 Hz, 2H, ArH), 7.06 (d, J = 8.2 Hz, 2H, ArH), 7.17–7.32 (m, 5H, ArH), 12.14(br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.3, 28.0, 28.3, 45.5, 46.3, 81.9, 124.8, 126.9, 127.6, 128.6, 130.1, 134.8, 137.2, 143.9, 170.7, 194.1; HRMS (TOF ES$^+$): m/z calcd for $C_{20}H_{23}N_2OS$ [(M+H$^+$)], 339.1526; found, 339.1527.

2-((4-Chlorophenyl)thio)-2-(1,3-diazepan-2-ylidene)-1-phenylethanone (5g): White solid, yield 91%; mp 200–202 °C; IR (KBr): 3318, 1603, 1346, 1199, 803 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.74–182 (m, 4H, CH_2CH_2), 3.21–3.23 (m, 2H, NCH_2), 3.45–3.48 (m, 2H, NCH_2), 6.48 (br, 1H, NH), 7.00 (d, J = 8.6 Hz, 2H, ArH), 7.17 –7.28 (m, 7H, ArH), 12.1 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.9, 28.2, 45.5, 46.3, 81.2, 126.0, 126.7, 127.7, 128.8, 129.4, 130.8, 139.5, 143.7, 170.5, 194.2; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{20}ClN_2OS$ [$(M+H^+)$], 359.0979; found, 359.0982.

2-(1,3-Diazepan-2-ylidene)-2-((3,5-dichloro phenyl)thio)-1-phenyleth-anone (5h): White solid, yield 83%; mp 139–141 °C; IR (KBr): 3308, 1561, 1348, 1206, 791 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$); δ = 1.79–1.84 (m, 4H, CH_2CH_2), 3.24–3.28 (m, 2H, NCH_2), 3.47–3.50 (m, 2H, NCH_2), 6.38 (br, 1H, NH), 6.91 (s, 2H, ArH), 7.04 (s, 1H, ArH), 7.20–7.27 (m, 5H, ArH), 12.07 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.8, 28.1, 45.4, 46.3, 80.0, 122.7, 125.3, 126.6, 127.8, 128.9, 135.8, 143.5, 145.1, 170.1, 194.3; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{19}Cl_2N_2OS$ [$(M+H^+)$], 393.0590; found, 393.0596.

2-(1,3-Diazepan-2-ylidene)-2-((4-fluorophenyl)thio)-1-phenylethanone (5i): White solid, yield 88%, mp 188–189 °C; IR (KBr): 3255, 1556, 1354, 1210, 776 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.75–1.83 (m, 4H, CH_2CH_2), 3.19–3.23 (m, 2H, NCH_2), 3.42–3.47 (m, 2H, NCH_2), 6.48 (br, 1H, NH), 6.74–6.86 (m, 3H, ArH), 7.15–7.83 (m, 6H, ArH), 12.09 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.9, 28.2, 45.5, 46.3, 111.5 (d, J = 23.8 Hz), 112.0 (d, J = 21.3 Hz), 120.4, 126.8, 127.3, 127.7, 128.7, 128.8, 130.6, 143.7, 163.8 (d, J = 246.3 Hz), 170.4, 194.2; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{20}FN_2OS$ [$(M+H^+)$], 343.1275; found, 343.1271.

2-(1,3-Diazepan-2-ylidene)1-phenyl-2-(phenylselanyl)ethanone (5j): White solid, yield 90%; mp 154–156 °C; IR (KBr): 3347, 1593, 1342, 1202, 737 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.72–1.77 (m, 4H, CH_2CH_2), 3.15–3.19 (m, 2H, CH_2), 3.42–3.46 (m, 2H, CH_2), 6.53 (br, 1H, NH), 7.12–7.28 (m, 10H, ArH), 12.17 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.2, 28.2, 45.7, 46.4, 81.6, 125.9, 126.8, 127.5, 127.6, 128.5, 129.5, 135.7, 145.0, 170.7, 194.4; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{21}N_2OSe$ [$(M+H^+)$], 373.0814; found, 373.0816.

2-(1,3-Diazepan-2-ylidene)-2-(phenylselanyl)-1-(*p*-tolyl)-ethanone (5k): White solid, yield 93%, mp 125–127 °C; IR (KBr): 3308, 1603, 1346, 1204, 818, 736 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.72–1.77 (m, 4H, CH_2CH_2), 3.15–3.18 (m, 2H, NCH_2), 3.41–3.45 (m, 2H, NCH_2), 6.50 (br, 1H, NH), 7.00 (d, J = 7.4 Hz, 2H, ArH), 7.13–7.26 (m, 7H, ArH), 12.19 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.8, 28.1, 28.2, 45.7, 46.5, 81.5, 125.9, 127.0, 127.4, 128.3, 129.5, 135.8, 138.5, 142.1, 170.8, 194.5; HRMS (TOF ES^+): m/z calcd for $C_{20}H_{23}N_2OSe$ [$(M+H^+)$], 387.0970; found, 387.0970.

2-(1,3-Diazepan-2-ylidene)-1-(4-fluorophenyl)-2-(phenylselanyl)ethan-one (5l): White solid, yield 86%; mp 137–138 °C; IR (KBr): 3319, 3053, 1598, 1349, 1207, 841, 737 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.73–1.80 (m, 4H, CH_2CH_2), 2.17 (s, 3H, ArH), 3.18–3.22 (m, 2H, NCH_2), 3.43–3.48 (m, 2H, NCH_2), 6.54 (br, 1H, NH), 6.86 (t, J = 8.5 Hz, 2H, ArH), 7.17–7.30 (m, 7H, ArH), 12.14 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.0, 28.2, 45.6, 46.5, 81.5, 114.4 (d, J = 21.3 Hz), 126.0, 127.4, 129.0, 129.6, 135.5, 141.0, 163.0 (d, J = 245.0 Hz), 170.7, 193.1; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{20}FN_2Ose$ [$(M+H^+)$], 391.0719; found, 391.0718.

1-(4-Chlorophenyl)-2-(1,3-diazepan-2-ylidene)-2-(phenylselanyl)ethan-one (5m): White solid, yield 85%; mp 141–143 °C; IR (KBr): 3315, 3064, 1590, 1346, 1203, 739 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.77–1.83 (m, 4H, CH_2CH_2), 3.22–3.25 (m, 2H, NCH_2), 3.46–3.50 (m, 2H, NCH_2), 6.58 (br, 1H, NH), 7.14–7.33 (m, 9H, ArH), 12.15 (br, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.0, 28.0, 45.6, 46.4, 81.5, 126.1, 127.4, 127.8, 128.4, 129.6, 134.3, 135.4, 143.4, 170.6, 192.9; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{20}ClN_2OSe$ [$(M+H^+)$], 407.0424; found, 407.0416.

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