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A Transition-Metal-Free and Base-Mediated Carbene Insertion into Sulfur-Sulfur and Selenium-Selenium Bonds: An Easy Access to Thio- and Selenoacetals

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Abstract: A transition-metal-free and base-mediated carbene insertion across sulfur-sulfur and selenium-selenium bonds has been developed by employing *N*-tosylhydrazone as a stable and safe carbene precursor. The ylide formation from carbene followed by Stevens rearrangement are considered to be the key steps. This thiol and selenol-free protocol delivers thioacetals and selenoacetals in good to excellent yields in short reaction time with good functional group tolerance. A one-pot synthesis involving in situ generation of tosylhydrazone has also been demonstrated.

Keywords: Carbene insertion; *N*-tosylhydrazones; Transition-metal-free; Thioacetals; Selenoacetals

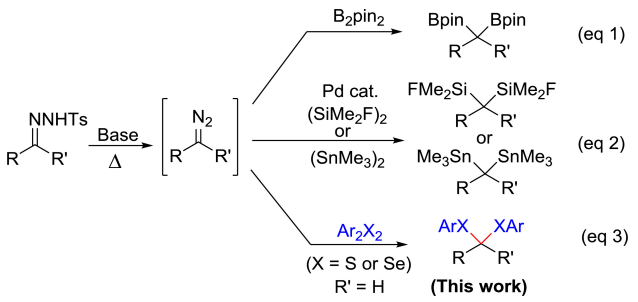
Carbene insertion reactions have proven to be a highly versatile and powerful strategy for the formation of C–C and C-hetero bonds.[1] During the past decades, catalytic, thermal and photochemical assisted carbene insertions on C–H bond have been well studied and have become carbene's representative reactions.[2] Quite apart from many C–H insertion reactions, carbenes undergo insertion into an array of X–H bonds where X is N, Si, O, S, Se, P or halogen.[3] Diazo compounds are widely employed as precursors for the generation of carbene species. However, diazo compounds which are not bearing any electron-withdrawing groups often present a challenge with respect to their uncertain explosive and instability nature.[4] In this context, *N*-tosylhydrazones have emerged as alternative and safe carbene precursors where non-stabilized transient diazo compounds could be generated in situ by base-mediated thermolysis.[5] *N*-tosylhydrazones have been extensively utilized in metal catalyzed cross-coupling reactions.[6] Subsequently, some unprecedented transformation involving metal-free reductive coupling of *N*-tosylhydrazones have been developed by Barlunga *et al.* and others.[7]

On the other hand, the remarkable stability of thioacetals under acidic or basic conditions makes them as a versatile protecting group and as a key intermediate in various natural product synthesis.[8] Noteworthy examples are dehydrogliotoxin[8a] and lignans.[8b] However, traditional methods for the synthesis of thioacetals were associated with the drawback of handling of thiol or dithiol which are known for their foul odour.[9] Some progress has been made for the thiol-free synthesis of thioacetals using tributylphosphine,[10a] methylthiotrimethylsilane[10b] and In-TMSCl[10c] independently. Nevertheless, these attempts are often suffer from the generation of phosphine oxide as inevitable byproduct, removal of this material is experimentally tedious and silane reagents are highly moisture sensitive as well as expensive.

Conversely, the reaction between carbene and disulfides has received less attention.[11] Fu *et al.* applied rhodium catalyzed carbene insertion approach into S–S bond to obtain thioacetals by employing *N*-sulfonyl-1,2,3-triazoles and diaryldisulfides.[12] In recent years, insertion using *N*-tosylhydrazones into homonuclear bonds, have gained great interest as these tactic enable the synthesis of gem-metallated and non-metallated compounds.

In 2012, Wang and co-workers reported the first example of carbon insertion utilizing *N*-tosylhydrazones across the B–B bond under metal-free conditions (Scheme 1, eq 1).[13] Most recently, the same group has developed an attractive protocol to access geminal bis(silane) and geminal bis(stannane) derivatives through carbene insertion into Si–Si and Sn–Sn bonds using palladium catalyst (Scheme 1, eq 2).[14] In continuing our study of employing *N*-tosylhydrazone as a carbene precursor,[15] herein we report a metal-free, base mediated carbene insertion into S–S and Se–Se bonds using *N*-tosylhydrazones to synthesize

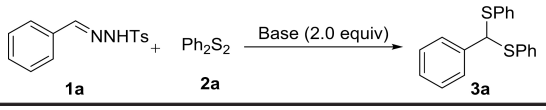
thio- and selenoacetals under thiol and selenol-free conditions (Scheme 1, eq 3).



Scheme 1. Insertion into homonuclear bonds using *N*-tosylhydrazones.

We began the exploration of this insertion process by using benzaldehyde derived *N*-tosylhydrazone **1a** as model substrate with diphenyldisulfide **2a**. The reaction was carried out with 1 equiv. of **2a** in the presence of 2 equiv. of KO^{t}Bu as a base in 1,4-dioxane at 100 °C. To our delight, the expected product bis (phenylthio)acetal **3a** was isolated in 45% yield (Table 1, entry 1). The use of 1.5 equiv. of Ph_2S_2 provided 73% yield of the product (entry 2).

Table 1. Optimization of reaction conditions.[a]



Entry	Base	Solvent	Temp (°C)	Time (h)	Yield[b] (%)
1	KO^{t}Bu	Dioxane	100	15	45[c]
2	KO^{t}Bu	Dioxane	100	12	73
3	KO^{t}Bu	Dioxane	100	10	72[d]
4	NaOEt	Dioxane	100	16	18
5	K_2CO_3	Dioxane	100	18	trace
6	Et_3N	Dioxane	100	18	trace
7	KO^{t}Bu	THF	100	12	51
8	KO^{t}Bu	Toluene	100	12	35
9	KO^{t}Bu	CH_3CN	100	12	50
10	KO^{t}Bu	DMF	100	30 min	81
11	KO^{t}Bu	DMSO	100	10 min	89
12	KO^{t}Bu	DMSO	90	20 min	80
13	KO^{t}Bu	DMSO	110	5 min	88
14	–	DMSO	100	24	nr[e]

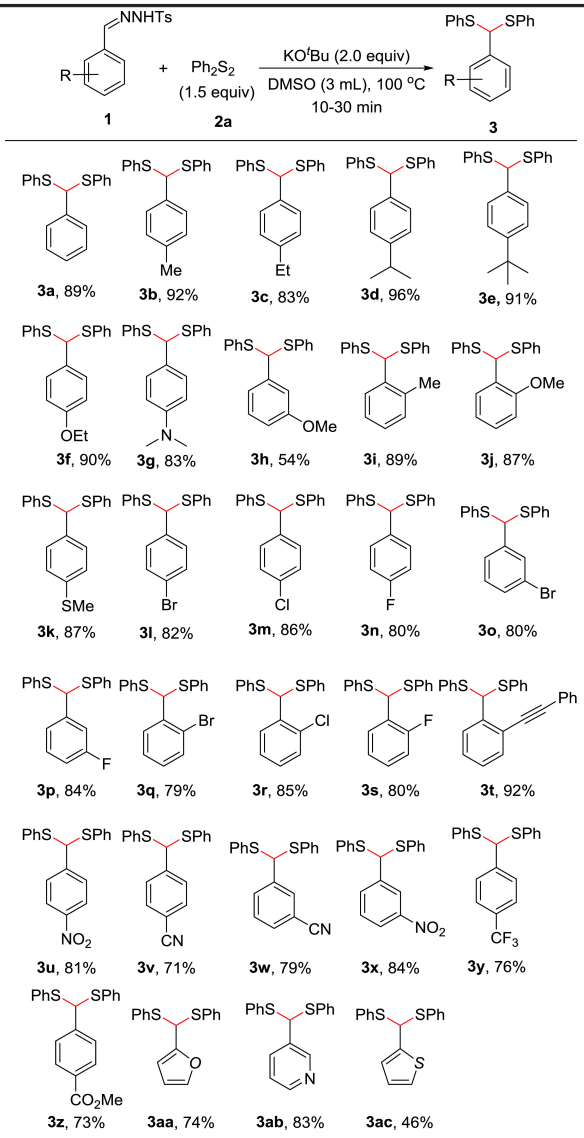
[a] Reaction conditions: **1a** (0.5 mmol, 1.0 equiv.), **2a** (1.5 equiv.), base (2.0 equiv.) and solvent (2 mL).
[b] Isolated yield.
[c] 1.0 equiv. of **2a** was used.
[d] 3.0 equiv. of TBAC was used.
[e] nr = no reaction.

The addition of phase transfer catalyst which is typically used to accelerate the decomposition of *N*-tosylhydrazone to diazo species has no effect on the reaction as the addition of 3 equiv. of TBAC (*n*-tetrabutylammoniumchloride) led to a similar yield (entry 3). Further screening of bases to improve the efficacy of the reaction was not beneficial (entries 4–6). Then, we observed that solvent significantly influenced the yield of the insertion reaction. Solvents such as THF, toluene and acetonitrile were investigated but they were less effective than 1,4-dioxane (entries 7–9). Interestingly, a dramatic change in the reaction rate was observed when the reaction was carried out in DMF, thus the product was isolated in 81% yield within 30 min (entry 10). Pleasingly, DMSO stood out to be a better choice as it gave the desired product in 89% yield within 10 min (entry 11). Further attempts to decrease the reaction temperature were not beneficial as it provided the product with reduced yield and took longer reaction time (entry 12). The reaction proceeded faster at higher temperature but yield was not improved (entry 13). A blank reaction was performed without adding base. As expected, there was no reaction and both the reactants were remained as such (entry 14).[16]

With this optimized reaction conditions, we then proceeded to explore the scope of the reaction and results are summarized in Table 2. Initially, a series of *N*-tosylhydrazones were employed as substrates in this insertion reaction. Reaction conditions were found to be general regardless of the steric and electronic nature of substrates as the wide range of *N*-tosylhydrazones underwent reaction smoothly to provide the corresponding bis(arylthio)acetals in good to excellent yields. Electron-donating group containing substrates furnished the insertion product in good yield irrespective of the relative position (**3b–k**). Halogen-substituted *N*-tosylhydrazones found to be suitable substrates and corresponding isolated products can undergo further derivatizations (**3l–s**). Phenylethynyl substituted tosylhydrazone also proceeded well and afforded the product in 92% yield (**3t**). As with the electron withdrawing substituents like nitro, cyano and CF_3 groups, the outcome were fruitful (**3u–y**). Notably, sensitive functional group like ester was also well tolerated under the reaction conditions (**3z**). *N*-tosylhydrazones containing heterocycle units such as 2-furyl, 3-pyridyl and 2-thiophene were also underwent conversion and provided satisfactory yields (**3aa–ac**). However, aliphatic aldehyde and ketone derived *N*-tosylhydrazones failed to afford desired product under the optimized reaction conditions.

Next, substrate scope with respect to diaryl disulfides was investigated and results are shown in Table 3. Electron-donating group containing diaryldisulfides underwent insertion smoothly and afforded the product in good yields (**3ad–af**). Strong electron-

Table 2. Reaction of various *N*-tosylhydrazone with diphenyl disulfide.[a,b]

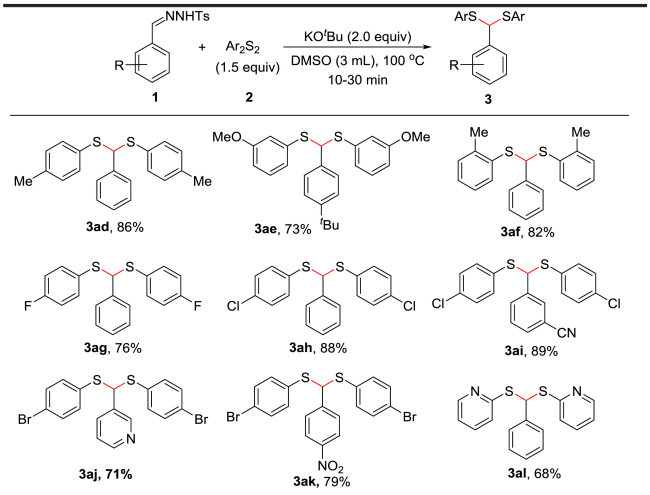


[a] Reaction conditions: **1** (1.0 mmol), **2 a** (1.5 mmol) and KO^{t}Bu (2.0 equiv.) in DMSO (3 mL) at 100 °C for 10–30 min.
[b] Isolated yields.

withdrawing group (F) and weak electron-withdrawing substituents (Cl and Br) could also be employed as suitable substrates affording the corresponding products (**3ag–ak**) in moderate to good yields. Substrate bearing pyridine moiety was also compatible with reaction conditions, giving **3al** in 68% isolated yield. The insertion rection was unsuccessful when bis(4-nitrophenyl) disulphide was used as substrate.

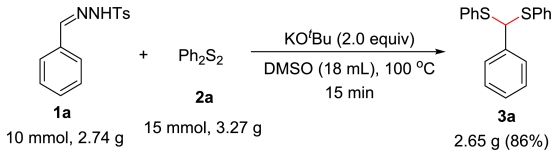
A scale-up reaction was performed to showcase the synthetic utility of this new methodology. To our delight, reaction of *N*-tosylhydrazone **1 a** with diphenyldisulfide **2 a** under the standard condition provided

Table 3. Reaction of various diaryl disulfides with *N*-tosylhydrazones.[a,b]



[a] Reaction conditions: **1** (1.0 mmol), **2** (1.5 mmol) and KO^{t}Bu (2.0 equiv.) in DMSO (3 mL) at 100 °C for 10–30 min.
[b] Isolated yields.

the product in 86 % yield within 15 minutes (Scheme 2).

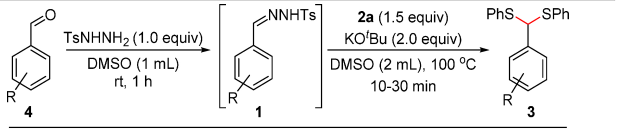


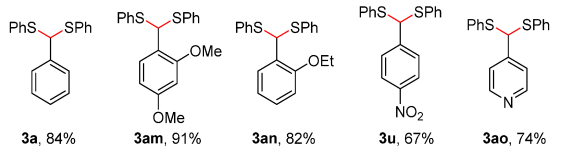
Scheme 2. Gram-scale synthesis.

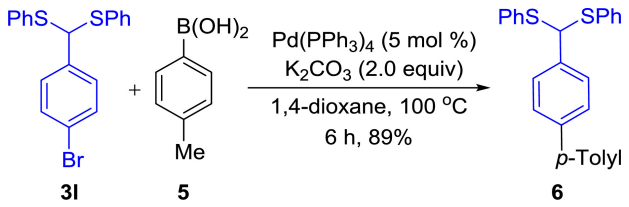
The successful carbene insertion into S–S bond prompted to investigate this transformation in a one-pot manner where tosylhydrazone could be generated in situ from corresponding aldehyde and tosylhydrazide. This process would be step economic as it avoids isolation of intermediate *N*-tosylhydrazone. At first, benzaldehyde and tosylhydrazide were stirred at room temperature in DMSO for 1 h. Then Ph_2S_2 and KO^{t}Bu were added and the reaction was heated at 100 °C. As expected, the reaction proceeded well in one-pot condition and comparable yield was observed. Few more substrates were employed in this reaction conditions and the results are shown in Table 4.

To validate the stability of bis(arylthio)acetal, **3l** was subjected to palladium catalyzed cross-coupling reaction with arylboronic acid **5** (Scheme 3). Thioacetal undergone the arylation and corresponding product **6** was obtained in good yield. Notably, the thioacetal group was very stable and remained unaffected.

Table 4. One-pot reaction through in situ synthesis of *N*-tosylhydrazones.



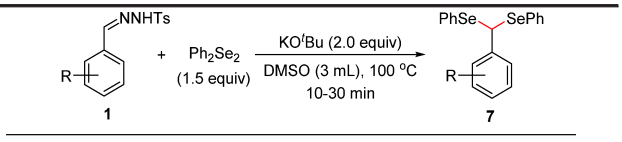


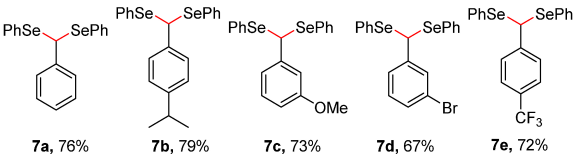


Scheme 3. Derivatization of thioacetal.

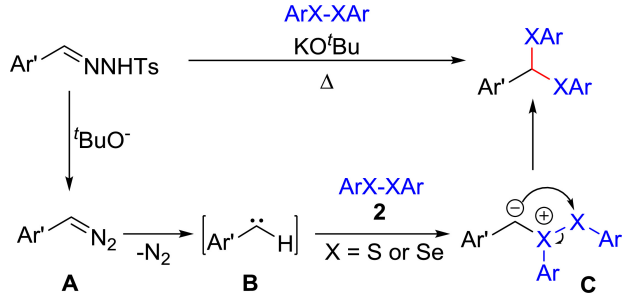
After exploration of carbene insertion into S–S bond, we turned our attention to Se–Se bond since selenoacetals found utility in various areas including organo-selenium chemistry.[17] Diphenyldiselenide was subjected under the optimized reaction conditions. As anticipated, carbene insertion proceeded smoothly to provide bis(phenylseleno)acetals **7** in good yields. Substrates bearing electron donating groups (**7b** and **7c**), halogen and withdrawing groups were well tolerated and gave the desired product in moderate yields (**7d** and **7e**) (Table 5).

Table 5. Carbene insertion across Se–Se bond.



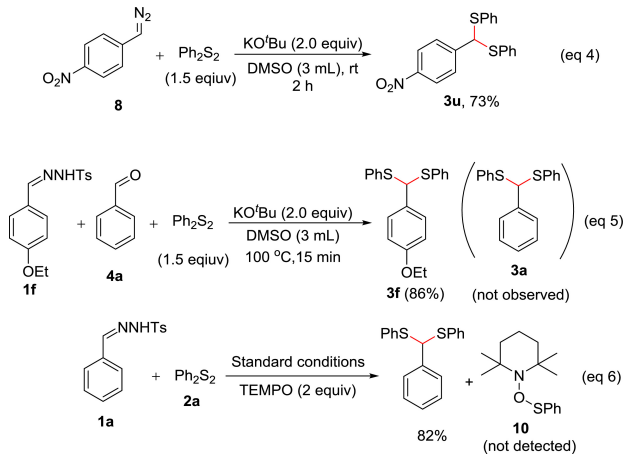


A possible reaction mechanism for the metal-free carbene insertion reaction is shown in Scheme 4. Initially, diazo compound **A** could be generated in situ from corresponding tosylhydrazone upon heating with base through Bamford–Stevens reaction. Thermally induced exclusion of N_2 would lead to the formation of free carbene species[7a] **B** which upon reacting with **2** forms an ylide intermediate **C**. Finally, 1,2-migration or Stevens rearrangement of **C** with X–X bond cleavage affords the desired product.



Scheme 4. Possible reaction pathway.

To cast light on the reaction mechanism of this insertion process, few control experiments were carried out (Scheme 5). Pre-formed diazo compound **8** was subjected to insertion reaction at room temperature and the corresponding thioacetal **3u** was obtained as a sole product (Scheme 5, eq 4). This result proves that the reaction proceeds via diazo intermediate **A**. But, the same reaction did not proceed without base which shows that base is necessary not only for diazo compound **A** formation, it is also essential for subsequent steps as well.[18] Next, diazo intermediate could be decomposed into aldehyde which can undergo deoxygenative thioacetalization with disulfides. To check this hypothesis, a competitive experiment was designed between benzaldehyde **4a** and *p*-ethoxybenzaldehyde derived tosylhydrazone **1f** (Scheme 5, eq 5). However, formation of **3a** was not detected by ^{1}HNMR analysis of crude reaction mixture and **3f** was isolated with 86% yield. It clearly supports that the reaction does not proceed via deoxygenative thioacetalization. To examine the



Scheme 5. Control experiments.

possibility of whether a sulfur radical (ArS•) is involved in the insertion process,[11d] a radical trapping experiment was carried out (Scheme 5, eq 6). The addition of 2 equiv. of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) under our standard reaction conditions had no effect, as the inserted product **3a** was isolated in 82% yield. Hence, we propose that insertion mainly proceeds through formation of ylide **C**.[11b]

In conclusion, a new procedure involving carbene insertion into S–S and Se–Se bonds have been developed using *N*-tosylhydrazone as a safe, stable and readily synthesizable carbene precursor. This protocol paves a way to synthesize thio- and selenoacetals under thiol and selenol-free conditions in good to excellent yields. This new protocol features with short reaction time, high functional group tolerance and wide substrate scope. Scale-up reaction and one-pot synthesis involving in situ generation of tosylhydrazone were demonstrated to show the applicability of this protocol.

Experimental Section

General information

All reactions were carried out in oven-dried reaction tubes. Reactions were monitored by thin-layer chromatography (TLC) using Merck silica gel 60 F_{254} precoated plates (0.25 mm) and visualized by UV fluorescence quenching using appropriate mixture of ethyl acetate and hexanes. Aluminium oxide (neutral) was purchased from Thermo Fisher scientific and used for column chromatography using hexanes and ethyl acetate mixture as eluent. All the reactions were carried out in temperature controlled IKA magnetic stirrers. ^{1}H and ^{13}CNMR spectra were recorded on a Bruker 400 MHz and 500 MHz (100 MHz and 125 MHz for ^{13}C) instrument. ^{1}HNMR spectra were reported relative to residual $CDCl_3$ (δ 7.26 ppm) and DMSO-d_6 (δ 2.50 ppm). When the residual peak overlapping with compound, spectra was reported to residual TMS. ^{13}CNMR were reported relative to $CDCl_3$ (δ 77.16 ppm). Chemical shifts were reported in parts per million and multiplicities are as indicated: s (singlet), d (doublet), t (triplet), q (quartet), sep (septet) and m (multiplet). Coupling constants, *J* are reported in Hertz. Melting points were recorded on a Guna capillary melting point apparatus and uncorrected. Infrared spectra were recorded on a FTIR 4000 Series Spectrometer using KBr. The wave numbers of recorded IR signals are quoted in cm^{-1}. High resolution mass spectra (HRMS) were recorded on Waters-Q-Tof Micro mass spectrometer. Diaryl disulfides[19] and *N*-tosylhydrazones[15b] were synthesized using a reported literature procedure.

General procedure for carbene insertion into S–S bond to synthesis of thioacetals 3

Under open atmosphere, *N*-tosylhydrazone **1** (1.0 mmol), diaryl disulfide **2** (1.5 mmol) and KO^{t}Bu (2.0 mmol) were successively added to oven dried reaction tube. DMSO (3 mL) was added and closed with glass-stopper. The reaction tube was then immersed in a 100 °C pre-heated oil bath. The reaction was heated with stirring till complete consumption of **1**. Upon cooling down to room temperature, water was added to the reaction mixture and extracted with ethyl acetate (3×5 mL). Brine wash (1×10 mL) was given to the combined organic extractions and dried over anhydrous Na_2SO_4. Removal of solvent and neutral alumina column separation of crude using hexanes and ethyl acetate mixture (49:1) afforded the corresponding bis(arylthio)acetal **3**.

(Phenylmethylene)bis(phenylsulfane)[12] **(3a):** 275 mg, 89% yield; colourless oil; R_f 0.71 (2% ethyl acetate in hexanes); ^{1}HNMR ($CDCl_3$, 400 MHz) δ 5.42 (s, 1H), 7.19–7.25 (m, 9H), 7.30–7.37 (m, 6H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 60.5, 127.9, 128.0, 128.2, 128.6, 129.0, 132.6, 134.6, 139.7; FTIR (neat) 691, 742, 1024, 1438, 1479, 1581, 3025 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{19}H_{16}S_2Na$: 331.0591; found 331.0591.

(*p*-Tolylmethylene)bis(phenylsulfane)[12] **(3b):** 297 mg, 92% yield; white solid; mp 56–58 °C; R_f 0.41 (2% ethyl acetate in hexanes); ^{1}HNMR ($CDCl_3$, 400 MHz) δ 2.30 (s, 3H), 5.41 (s, 1H), 7.07 (d, J=8.0 Hz, 2H), 7.19–7.25 (m, 6H), 7.26 (d, J=8.0 Hz, 2H), 7.31–7.36 (m, 4H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 21.3, 60.3, 127.8, 127.9, 128.9, 129.3, 132.4, 134.9, 136.8, 138.0; FTIR (KBr) 689, 736, 1024, 1438, 1479, 3019 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{20}H_{19}S_2$: 323.0928; found 323.0925.

((4-Ethylphenyl)methylene)bis(phenylsulfane)[12] **(3c):** 280 mg, 83% yield; colourless oil; R_f 0.40 (2% ethyl acetate in hexanes); ^{1}HNMR ($CDCl_3$, 400 MHz) δ 1.25 (t, J=7.6 Hz, 3H), 2.66 (q, J=7.6 Hz, 2H), 5.46 (s, 1H), 7.14 (d, J=8.0 Hz, 2H), 7.24–7.30 (m, 6H), 7.33 (d, J=8.0 Hz, 2H), 7.35–7.42 (m, 4H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 15.5, 28.7, 60.4, 127.8, 127.9, 128.1, 128.9, 132.5, 135.0, 137.0, 144.3; FTIR (neat) 688, 737, 840, 1024, 1438, 1479, 2964, 3057 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{21}H_{20}S_2Na$: 359.0904; found 359.0896.

((4-*Iso*propylphenyl)methylene)bis(phenylsulfane) (3d): 337 mg, 96% yield; colorless semi solid; R_f 0.45 (2% ethyl acetate in hexanes); ^{1}HNMR ($CDCl_3$, 400 MHz) δ 1.26 (d, J=6.8 Hz, 6H), 2.91 (sep, J=6.8 Hz, 1H), 5.46 (s, 1H), 7.16 (d, J=8.0 Hz, 2H), 7.24–7.29 (m, 6H), 7.31–7.35 (m, 2H), 7.35–7.40 (m, 4H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 24.0, 33.9, 60.4, 126.7, 127.8, 127.9, 128.9, 132.5, 135.0, 137.1, 148.9; FTIR (neat) 689, 736, 1024, 1438, 1479, 1582, 2869, 2959, 3057 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{22}H_{23}S_2$: 351.1241; found 351.1222.

((4-(*Tert*-butyl)phenyl)methylene)bis(phenylsulfane) (3e): 332 mg, 91% yield; colourless oil; R_f 0.32 (2% ethyl acetate in hexanes); ^{1}HNMR ($CDCl_3$, 400 MHz) δ 1.21 (s, 9H), 5.35 (s, 1H), 7.12–7.16 (m, 6H), 7.19–7.21 (m, 4H), 7.24–7.28 (m, 4H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 31.4, 34.7, 60.4, 125.6, 127.6, 127.7, 128.9, 132.4, 135.0, 136.7, 151.2; FTIR (neat) 689, 736, 1024, 1267, 1479, 1582, 2984, 3057 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{23}H_{24}S_2Na$: 387.1217; found 387.1203.

((4-Ethoxyphenyl)methylene)bis(phenylsulfane) (3f): 318 mg, 90% yield; white solid; mp 74–76 °C; R_f 0.29 (2% ethyl acetate in hexanes); ^{1}HNMR ($CDCl_3$, 400 MHz) δ 1.43 (t, J = 7.2 Hz, 3H), 4.04 (q, J = 7.2 Hz, 2H), 5.47 (s, 1H), 6.80–6.85 (m, 2H), 7.23–7.31 (m, 6H), 7.31–7.35 (m, 2H), 7.36–7.42 (m, 4H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 14.9, 59.9, 63.6, 114.5, 127.8, 128.9, 129.2, 131.6, 132.5, 134.9, 158.8; FTIR (KBr) 687, 738, 1024, 1245, 1508, 1607, 2926, 2677, 3067 cm^{-1}; HRMS (m/z): $[M+Na]^+$ calcd for $C_{21}H_{20}OS_2Na$: 375.0853; found 375.0828.

4-(Bis(phenylthio)methyl)-*N*,*N*-dimethylaniline (3g): 292 mg, 83% yield; white solid; mp 124–126 °C; R_f 0.39 (5% ethyl acetate in hexanes); ^{1}HNMR ($CDCl_3$, 400 MHz) δ 2.97 (s, 6H), 5.47 (s, 1H), 6.66 (d, J = 8.8 Hz, 2H), 7.22–7.34 (m, 8H), 7.35–7.42 (m, 4H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 40.6, 60.0, 112.3, 127.0, 127.5, 128.9 (for 2C), 132.1, 135.5, 150.4; FTIR (KBr) 680, 727, 1065, 1362, 1524, 1612, 2892, 3052 cm^{-1}; HRMS (m/z): $[M+Na]^+$ calcd for $C_{21}H_{21}NS_2Na$: 374.1013; found 374.1026.

((3-Methoxyphenyl)methylene)bis(phenylsulfane)[12] **(3h):** 183 mg, 54% yield; colourless oil; R_f 0.32 (2% ethyl acetate in hexanes); ^{1}HNMR ($CDCl_3$, 400 MHz) δ 3.78 (s, 3H), 5.43 (s, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.92–7.01 (m, 2H), 7.21 (t, J = 8.0 Hz, 1H), 7.24–7.32 (m, 6H), 7.35–7.43 (m, 4H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 55.4, 60.6, 113.2, 114.2, 120.4, 127.9, 129.0, 129.6, 132.7, 134.7, 141.3, 159.7; FTIR (neat) 688, 739, 1262, 1437, 1488, 1590, 2835, 3056 cm^{-1}; HRMS (m/z): $[M+Na]^+$ calcd for $C_{20}H_{18}OS_2Na$: 361.0697; found 361.0663.

(*o*-Tolylmethylene)bis(phenylsulfane) (3i): 287 mg, 89% yield; colourless oil; R_f 0.40 (2% ethyl acetate in hexanes); ^{1}HNMR ($CDCl_3$, 400 MHz) δ 2.30 (s, 3H), 5.66 (s, 1H), 7.06–7.11 (m, 1H), 7.11–7.17 (m, 2H), 7.19–7.25 (m, 6H), 7.29–7.36 (m, 4H), 7.58–7.67 (m, 1H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 19.4, 57.2, 126.6, 127.8, 128.0, 128.4, 129.0, 130.5, 132.4, 135.0, 135.2, 137.5; FTIR (neat) 687, 737, 1024, 1265, 1437, 1481, 1582, 3064 cm^{-1}; HRMS (m/z): $[M+H]^+$ calcd for $C_{20}H_{19}S_2$: 323.0928; found 323.0916.

((2-Methoxyphenyl)methylene)bis(phenylsulfane) (3j): 295 mg, 87% yield; colourless oil; R_f 0.32 (2% ethyl acetate in hexanes); ^{1}HNMR ($CDCl_3$, 400 MHz) δ 3.82 (s, 3H), 6.13 (s, 1H), 6.86 (d, J = 8.4 Hz, 1H), 6.95 (t, J = 7.6 Hz, 1H), 7.22–7.30 (m, 7H), 7.37–7.43 (m, 4H), 7.57–7.62 (m, 1H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 52.6, 55.8, 110.8, 120.9, 127.5, 128.0, 128.8, 129.0, 129.2, 132.1, 135.2, 155.8; FTIR (neat) 689, 744, 1024, 1245, 1437, 1487, 2835, 3062 cm^{-1}; HRMS (m/z): $[M+Na]^+$ calcd for $C_{20}H_{18}OS_2Na$: 361.0697; found 361.0696.

((4-(Methylthio)phenyl)methylene)bis(phenylsulfane) (3k): 309 mg, 87% yield; off white solid; mp 88–90 °C; R_f 0.32 (2% ethyl acetate in hexanes); ^{1}HNMR ($CDCl_3$, 400 MHz) δ 2.38 (s, 3H), 5.32 (s, 1H), 7.02–7.10 (m, 2H), 7.12–7.23 (m, 8H), 7.23–7.31 (m, 4H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 15.8, 60.1, 116.4, 128.0, 128.4, 129.0, 132.6, 134.6, 136.5, 138.5; FTIR (KBr) 688, 749, 1024, 1087, 2920, 3069 cm^{-1}; HRMS (m/z): $[M+K]^+$ calcd for $C_{20}H_{18}S_3K$: 393.0208; found 393.0197.

((4-Bromophenyl)methylene)bis(phenylsulfane)[12] **(3l):** 318 mg, 82% yield; white solid; mp 92–94 °C; R_f 0.73 (2% ethyl acetate in hexanes); ^{1}HNMR ($CDCl_3$, 400 MHz) δ 5.40 (s, 1H), 7.22–7.32 (m, 8H), 7.34–7.44 (m, 6H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 59.9, 122.0, 128.2, 129.1, 129.7, 131.7, 132.9, 134.1, 138.9; FTIR (KBr) 700, 750, 1025, 1484, 1590, 1642, 3042 cm^{-1}; HRMS (m/z): $[M+H]^+$ calcd for $C_{19}H_{16}BrS_2$: 386.9877; found 386.9874.

((4-Chlorophenyl)methylene)bis(phenylsulfane)[12] **(3m):** 295 mg, 86% yield; white solid; 68–70 °C; R_f 0.55 (2% ethyl acetate in hexanes); ^{1}HNMR ($CDCl_3$, 400 MHz) δ 5.37 (s, 1H), 7.19–7.28 (m, 10H), 7.30–7.35 (m, 4H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 59.9, 128.2, 128.7, 129.1, 129.4, 132.9, 133.8, 134.1, 138.4; FTIR (KBr) 647, 689, 719, 1015, 1438, 1475, 3047 cm^{-1}; HRMS (m/z): $[M+K]^+$ calcd for $C_{19}H_{15}ClS_2K$: 380.9941; found 380.9939.

((4-Fluorophenyl)methylene)bis(phenylsulfane)[12] **(3n):** 261 mg, 80% yield; white solid; mp 48–50 °C; R_f 0.55 (2% ethyl acetate in hexanes); ^{1}HNMR ($CDCl_3$, 400 MHz) δ 5.40 (s, 1H), 6.89–6.96 (m, 2H), 7.21–7.26 (m, 6H), 7.28–7.35 (m, 6H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 59.8, 115.5 (d, J = 21 Hz), 128.1, 129.0, 129.7 (d, J = 8 Hz), 132.9, 134.3, 135.6 (d, J = 4 Hz), 162.4 (d, J = 246 Hz); FTIR (KBr) 688, 739, 842, 1024, 1222, 1506, 3064 cm^{-1}; HRMS (m/z): $[M+H]^+$ calcd for $C_{19}H_{16}FS_2$: 327.0677; found 327.0670.

((3-Bromophenyl)methylene)bis(phenylsulfane) (3o): 310 mg, 80% yield; colourless oil; R_f 0.35 (2% ethyl acetate in hexanes); ^{1}HNMR ($CDCl_3$, 400 MHz) δ 5.38 (s, 1H), 7.15 (t, J = 8.0 Hz, 1H), 7.26–7.32 (m, 7H), 7.34–7.40 (m, 5H), 7.51 (t, J = 1.6 Hz, 1H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 60.1, 122.5, 126.6, 128.3, 129.1, 130.0, 131.1, 131.2, 133.0, 134.0, 142.1; FTIR (neat) 689, 737, 1024, 1438, 1478, 1583, 3056 cm^{-1}; HRMS (m/z): $[M+H]^+$ calcd for $C_{19}H_{16}BrS_2$: 386.9877; found 386.9864.

((3-Fluorophenyl)methylene)bis(phenylsulfane) (3p): 275 mg, 84% yield; colourless oil; R_f 0.68 (2% ethyl acetate in hexanes); ^{1}HNMR ($CDCl_3$, 400 MHz) 5.38 (s, 1H), 6.91 (tdd, J = 8.4, 2.4, 1.2 Hz, 1H), 7.06–7.12 (m, 2H), 7.16–7.21 (m, 1H). 7.21–7.26 (m, 6H), 7.31–7.36 (m, 4H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 60.1, 115.0 (d, J = 22 Hz), 115.1 (d, J = 21 Hz), 123.7 (d, J = 3 Hz), 128.2, 129.1, 130.0 (d, J = 9 Hz), 132.9, 134.1, 142.4 (d, J = 7 Hz), 162.8 (d, J = 245 Hz); FTIR (neat) 689, 739, 1251, 1440, 1480, 1586, 3059 cm^{-1}; HRMS (m/z): $[M+Na]^+$ calcd for $C_{19}H_{15}FS_2Na$: 349.0497; found 349.0475.

((2-Bromophenyl)methylene)bis(phenylsulfane) (3q): 306 mg, 79% yield; colourless oil; R_f 0.48 (2% ethyl acetate in hexanes); ^{1}HNMR ($CDCl_3$, 400 MHz) δ 6.07 (s, 1H), 7.12 (td, J = 7.6, 1.6 Hz, 1H), 7.24–7.30 (m, 7H), 7.37–7.43 (m, 4H), 7.54 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.72–7.79 (m, 1H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 58.8, 123.7, 127.9, 128.0, 129.0, 129.5, 130.2, 132.4, 132.8, 134.3, 138.6; FTIR (neat) 689, 739, 1024, 1438, 1479, 1582, 3056 cm^{-1}; HRMS (m/z): $[M+H]^+$ calcd for $C_{19}H_{16}BrS_2$: 386.9877; found 386.9870.

((2-Chlorophenyl)methylene)bis(phenylsulfane) (3r): 292 mg, 85% yield; colourless oil; R_f 0.48 (2% ethyl acetate in hexanes); ^{1}HNMR ($CDCl_3$, 400 MHz) δ 6.03 (s, 1H), 7.13–7.21 (m, 2H), 7.21–7.25 (m, 6H), 7.28–7.32 (m, 1H), 7.33–7.37 (m, 4H) 7.68 (dd, J = 8.0, 2.0 Hz, 1H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 56.1, 127.3, 128.0, 129.0, 129.2, 129.5, 130.0, 132.5, 132.9, 134.3, 137.1; FTIR (neat) 688, 742, 1024, 1438, 1468,

1479, 1582, 3061 cm^{-1}; HRMS (*m/z*): $[M+K]^+$ calcd for $C_{19}H_{15}ClS_2K$: 380.9941; found 380.9918.

((2-Fluorophenyl)methylene)bis(phenylsulfane) (3s): 262 mg, 80% yield; colourless oil; R_f 0.42 (2% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.91 (s, 1H), 6.97–7.05 (m, 1H), 7.12 (td, *J* = 7.6, 1.2 Hz, 1H), 7.21–7.26 (m, 1H), 7.26–7.32 (m, 6H), 7.39–7.45 (m, 4H), 7.61 (td, *J* = 7.6, 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 52.4 (d, *J* = 2 Hz), 115.3 (d, *J* = 22 Hz), 124.4 (d, *J* = 4 Hz), 127.1 (d, *J* = 13 Hz), 128.1, 129.0, 129.6, 129.7 (d, *J* = 4 Hz), 132.7, 134.2, 159.2 (d, *J* = 243 Hz); FTIR (neat) 689, 748, 1024, 1237, 1484, 1583, 2924, 3057 cm^{-1}; HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{19}H_{15}FS_2Na$: 349.0497; found 349.0468.

((2-(Phenylethynyl)phenyl)methylene)bis(phenylsulfane) (3t): 376 mg, 92% yield; pale yellow oil; R_f 0.42 (2% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 6.29 (s, 1H), 7.20–7.25 (m, 6H), 7.25–7.29 (m, 1H), 7.31–7.39 (m, 4H), 7.9–7.45 (m, 6H), 7.52 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.74–7.82 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 57.6, 87.0, 95.3, 122.1, 123.1, 127.6, 127.9, 128.0, 128.5, 128.7, 128.9, 129.0, 131.7, 131.9, 132.1, 135.1, 141.3; FTIR (neat) 689, 756, 1024, 1438, 1479, 1492, 1582, 3054 cm^{-1}; HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{27}H_{20}S_2Na$: 431.0904; found 431.0874.

((4-Nitrophenyl)methylene)bis(phenylsulfane) (3u): 287 mg, 81% yield; pale yellow oil; R_f 0.42 (5% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.46 (s, 1H), 7.24–7.32 (m, 6H), 7.34–7.39 (m, 4H), 7.44–7.50 (m, 2H), 8.04–8.14 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 60.0, 123.8, 128.7, 128.9, 129.2, 133.2, 133.4, 147.3, 147.4; FTIR (neat) 689, 739, 1024, 1109, 1344, 1517, 2925, 3068 cm^{-1}; HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{19}H_{15}NO_2S_2Na$: 376.0442; found 376.0428.

4-(Bis(phenylthio)methyl)benzonitrile (3v): 237 mg, 71% yield; colourless oil; R_f 0.29 (5% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.42 (s, 1H), 7.25–7.32 (m, 6H), 7.33–7.38 (m, 4H), 7.39–7.44 (m, 2H), 7.52–7.57 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 60.2, 111.7, 118.6, 128.6, 128.7, 129.2, 132.3, 133.3, 133.4, 145.2; FTIR (neat) 688, 743, 850, 1024, 1438, 1478, 2228, 2924, 3055 cm^{-1}; HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{20}H_{15}NS_2Na$: 356.0544; found 356.0564.

3-(Bis(phenylthio)methyl)benzonitrile (3w): 264 mg, 79% yield; colourless oil; R_f 0.32 (5% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.31 (s, 1H), 7.16–7.22 (m, 6H), 7.22–7.31 (m, 5H), 7.42 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.45–7.51 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 59.8, 112.5, 118.5, 128.6, 129.2, 129.4, 131.5, 131.6, 132.4, 133.3, 133.4, 141.5; FTIR (neat) 688, 742, 1024, 1438, 1479, 1581, 2230, 3058 cm^{-1}; HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{20}H_{15}NS_2Na$: 356.0544; found 356.0529.

((3-Nitrophenyl)methylene)bis(phenylsulfane) (3x): 297 mg, 84% yield; pale yellow oil; R_f 0.39 (5% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.40 (s, 1H), 7.16–7.22 (m, 6H), 7.24–7.30 (m, 4H), 7.34 (t, *J* = 8.8 Hz, 1H), 7.58 (dt, *J* = 8.0, 1.6 Hz, 1H), 8.00 (ddd, *J* = 8.0, 1.6, 0.8 Hz, 1H), 8.05 (t, *J* = 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 59.9, 123.0, 123.1, 128.7, 129.2, 129.5, 133.3, 133.4, 134.0, 142.1, 148.2; FTIR (neat) 689, 739, 1024, 1351, 1526, 2924, 3066 cm^{-1}; HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{19}H_{15}NO_2S_2Na$: 376.0442; found 376.0447.

((4-(Trifluoromethyl)phenyl)methylene)bis(phenylsulfane) (3y): 287 mg, 76% yield; white solid; mp 76–78 °C; R_f 0.32 (2% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 500 MHz) δ 5.34 (s, 1H), 7.11–7.19 (m, 6H), 7.20–7.28 (m, 4H), 7.34 (d, *J* = 6.4 Hz, 2H), 7.41 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 60.1, 124.1 (q, *J* = 270 Hz), 125.5 (q, *J* = 3.75 Hz), 128.3, 128.4, 129.1, 130.1 (q, *J* = 32.5 Hz), 133.0, 133.8, 143.9; FTIR (KBr) 688, 733, 1071, 1109, 1161, 1331, 1438, 2919, 3069 cm^{-1}; HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{20}H_{15}F_3S_2Na$: 399.0465; found 399.0491.

Methyl-4-(bis(phenylthio)methyl)benzoate (3z): 268 mg, 73% yield; white solid; mp 66–68 °C; R_f 0.26 (2% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.93 (s, 3H), 5.45 (s, 1H), 7.24–7.30 (m, 6H), 7.33–7.39 (m, 4H), 7.39–7.43 (m, 2H), 7.92–7.98 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 52.3, 60.3, 128.1, 128.3, 129.1, 129.8, 129.9, 133.1, 133.9, 144.9, 166.8; FTIR (KBr) 689, 741, 1019, 1108, 1277, 1435, 1702, 3057 cm^{-1}; HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{21}H_{18}O_2S_2Na$: 389.0646; found 389.0660.

2-(Bis(phenylthio)methyl)furan (3aa): 221 mg, 74% yield; pale yellow oil; R_f 0.39 (2% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.47 (s, 1H), 6.16 (d, *J* = 3.2 Hz, 1H), 6.24 (dd, *J* = 3.2, 3.2 Hz, 1H), 7.26–7.30 (m, 6H), 7.35–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 53.3, 109.1, 110.6, 128.3, 129.0, 133.2, 133.8, 142.6, 151.4; FTIR (neat) 688, 739, 1024, 1438, 1479, 1582, 2924, 3055 cm^{-1}; HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{17}H_{14}OS_2Na$: 321.0384; found 321.0382.

3-(Bis(phenylthio)methyl)pyridine (3ab): 257 mg, 83% yield; colourless oil; R_f 0.48 (30% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.34 (s, 1H), 7.07–7.14 (m, 1H), 7.14–7.21 (m, 6H), 7.21–7.31 (m, 4H), 7.58–7.66 (m, 1H), 8.32–8.40 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 58.0, 123.4, 128.5, 129.1, 133.3, 133.5, 135.4, 135.8, 149.1, 149.3; FTIR (neat) 690, 749, 1024, 1420, 1478, 1573, 3053 cm^{-1}; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{18}H_{16}NS_2$: 310.0724; found 310.0721.

2-(Bis(phenylthio)methyl)thiophene (3ac): 145 mg, 46% yield; pale yellow oil; R_f 0.32 (2% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.72 (s, 1H), 6.88 (dd, *J* = 4.8, 3.8 Hz, 1H), 6.97 (d, *J* = 3.6 Hz, 1H), 7.25 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.28–7.33 (m, 6H), 7.39–7.46 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.9, 125.9, 126.6, 126.7, 128.2, 129.0, 132.9, 134.3, 143.8; FTIR (neat) 690, 749, 1024, 1420, 1478, 1573, 3053 cm^{-1}; HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{17}H_{14}S_3Na$: 337.0155; found 337.0164.

(Phenylmethylene)bis(*p*-tolylsulfane) (3ad): 290 mg, 86% yield; white solid; mp 64–66 °C; R_f 0.47 (2% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 6H), 5.31 (s, 1H), 7.00–7.07 (m, 4H), 7.18–7.26 (m, 7H), 7.28–7.34 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.3, 61.4, 128.0, 128.5, 129.7, 131.0, 133.3, 134.8, 138.1, 140.1; FTIR (KBr) 697, 808, 1017, 1450, 1490, 2974, 3059 cm^{-1}; HRMS (*m/z*): $[M+Na]^+$ calcd for $C_{21}H_{20}S_2Na$: 359.0904; found 359.0919.

((4-(*Tert*-butyl)phenyl)methylene)bis((3-methoxyphenyl)sulfane) (3ae): 311 mg, 73% yield; colourless oil; R_f 0.49 (5% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.31 (s, 9H), 3.70 (s, 6H), 5.47 (s, 1H), 6.78 (ddd, *J* = 8.0, 2.4, 0.8

Hz, 2H), 6.83–6.87 (m, 2H), 6.96–7.01 (m, 2H), 7.13–7.20 (m, 2H), 7.30–7.32 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.4, 34.7, 55.3, 59.9, 114.0, 117.0, 124.4, 125.6, 127.7, 129.7, 136.1, 136.8, 151.2, 159.7; FTIR (neat) 686, 773, 1041, 1246, 1477, 1588, 2960 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{25}H_{28}O_2S_2Na$: 447.1428; found 447.1423.

(Phenylmethylene)bis(*o*-tolylsulfane) (3af): 277 mg, 82% yield; colourless oil; R_f 0.55 (2% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H), 5.29 (s, 1H), 7.03–7.10 (m, 2H), 7.11–7.16 (m, 4H), 7.21–7.28 (m, 3H), 7.31–7.41 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.7, 60.1, 126.5, 127.9, 128.0, 128.1, 128.6, 130.4, 133.2, 134.1, 140.1, 140.3; FTIR (neat) 699, 751, 1061, 1468, 1588, 2921, 3059 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{21}H_{20}S_2Na$: 359.0904; found 359.0895.

(Phenylmethylene)bis((4-fluorophenyl)sulfane) (3ag): 262 mg, 76% yield; colourless oil; R_f 0.57 (2% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.23 (s, 1H), 6.89–6.96 (m, 4H), 7.22–7.26 (m, 5H), 7.27–7.34 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 62.2, 116.2 (d, J=22 Hz), 127.9, 128.3, 128.6, 129.2 (d, J=3 Hz), 135.9 (d, J=8 Hz), 139.4, 163.0 (d, J=247 Hz); FTIR (neat) 698, 826, 1012, 1452, 1589, 2924, 3063 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{19}H_{15}F_2S_2$: 345.0583; found 345.0582.

(Phenylmethylene)bis((4-chlorophenyl)sulfane)[12] **(3ah):** 332 mg, 88% yield; colourless oil; R_f 0.38 (2% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.33 (s, 1H), 7.16–7.18 (m, 1H), 7.18–7.23 (m, 6H), 7.23–7.27 (m, 4H), 7.28–7.32 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 60.9, 127.9, 128.5, 128.7, 129.1, 132.6, 134.3, 134.4, 139.0; FTIR (neat) 697, 819, 1012, 1388, 1474, 1572, 2919, 3058 cm^{-1}; $[M+Na]^+$ calcd for $C_{19}H_{14}Cl_2S_2Na$: 398.9811; found 398.9801.

3-(Bis((4-chlorophenyl)thio)methyl)benzonitrile (3ai): 359 mg, 89% yield; colourless oil; R_f 0.50 (10% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.30 (s, 1H), 7.20–7.26 (m, 8H), 7.35–7.41 (m, 1H), 7.48–7.56 (m, 2H), 7.58–7.61 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 60.2, 112.9, 118.4, 129.5, 129.6, 131.4, 131.5, 132.0, 132.3, 134.8, 135.2, 140.9; FTIR (neat) 687, 822, 1013, 1093, 1475, 2231, 2924, 3060 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{20}H_{13}NCl_2S_2Na$: 423.9764; found 423.9760.

3-(Bis((4-bromophenyl)thio)methyl)pyridine (3aj): 332 mg, 71% yield; colourless oil; R_f 0.48 (20% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.34 (s, 1H), 7.16–7.24 (m, 5H), 7.33–7.42 (m, 4H), 7.60–7.69 (m, 1H), 8.41–8.51 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 58.1, 123.2, 123.6, 132.2, 132.4, 134.9, 135.0, 135.4, 149.1, 149.7; FTIR (neat) 709, 812, 1008, 1472, 2919, 3058 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{18}H_{14}NBr_2S_2$: 465.8934; found 465.8927.

((4-Nitrophenyl)methylene)bis((4-bromophenyl)sulfane) (3ak): 404 mg, 79% yield; yellow solid; mp 92–94 °C; R_f 0.46 (10% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.36 (s, 1H), 7.16–7.22 (m, 4H), 7.35–7.42 (m, 4H), 7.44 (d, J=8.4 Hz, 2H), 8.12 (d, J=8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 60.0, 123.4, 124.0, 128.8, 132.0, 132.5, 135.0, 146.4, 147.6; FTIR (KBr) 732, 817, 1009, 1346, 1520, 2924, 3069 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{19}H_{14}NO_2S_2Br_2$: 509.8833; found 509.8831.

2,2′-((Phenylmethylene)bis(sulfanediyl))dipyridine (3al): 212 mg, 68% yield; colourless oil; R_f 0.40 (15% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.92–7.00 (m, 2H), 7.03 (s, 1H), 7.12–7.34 (m, 5H), 7.40–7.49 (m, 2H), 7.56–7.72 (m, 2H), 8.38–8.49 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 51.0, 120.3, 122.6, 128.0, 128.3, 128.6, 136.4, 140.0, 149.7, 158.0; FTIR (neat) 698, 985, 1117, 1560, 2992, 3046 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{17}H_{14}N_2S_2Na$: 333.0496; found 333.0498.

General procedure for one-pot reaction through in situ synthesis of *N*-tosylhydrazones

To a rapidly stirred suspension of tosylhydrazide (1.0 mmol) in DMSO (1 mL), aldehyde (1.0 mmol) was added dropwise (solid aldehydes were added as portion wise) and the mixture was stirred at room temperature for 1 h. Diphenyl disulfide **2a** (1.5 mmol), K_2CO_3 (2.0 mmol) and DMSO (2 mL) were added successively in open atmosphere. Reaction tube was stoppered and heated to 100 °C in pre-heated oil bath. Reaction was monitored by TLC. After completion of reaction, reaction mixture was cooled to room temperature, water was added and extracted with EtOAc (3×5 mL). Brine wash (1×5 mL) was given to combined organic extractions and dried over Na_2SO_4. Solvent was evaporated and the crude mixture was purified by column chromatography using alumina (neutral) and hexanes/ethyl acetate (49:1) as eluent to afford the corresponding product.

((2,4-Dimethoxyphenyl)methylene)bis(phenylsulfane) (3am): 336 mg, 91% yield; colourless oil; R_f 0.39 (2% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.80 (s, 3H), 3.81 (s, 3H), 6.04 (s, 1H), 6.42 (d, J=2.4 Hz, 1H), 6.45 (dd, J=8.8, 2.4 Hz, 1H), 7.20–7.29 (m, 6H), 7.34–7.41 (m, 4H), 7.50 (d, J=8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 52.2, 55.5, 55.8, 98.5, 104.8, 120.5, 127.3, 128.8, 129.8, 131.9, 135.5, 157.0, 160.7; FTIR (neat) 688, 740, 1026, 1164, 1290, 1615, 2947, 3060 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{21}H_{20}O_2S_2Na$: 391.0802; found 391.0805.

((2-Ethoxyphenyl)methylene)bis(phenylsulfane) (3an): 290 mg, 82% yield; colourless oil; R_f 0.32 (2% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.42 (t, J=6.8 Hz, 3H), 4.04 (q, J=6.8 Hz, 2H), 6.15 (s, 1H), 6.84 (d, J=8.4 Hz, 1H), 6.90–6.97 (m, 1H), 7.19–7.29 (m, 7H), 7.36–7.43 (m, 4H), 7.58–7.65 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.0, 52.7, 64.1, 111.7, 120.8, 127.4, 128.2, 128.8, 129.0, 129.1, 131.9, 135.5, 155.2; FTIR (neat) 689, 753, 1024, 1248, 1478, 1582, 2978, 3057 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{21}H_{20}OS_2Na$: 375.0853; found 375.0854.

4-(Bis(phenylthio)methyl)pyridine (3ao): 229 mg, 74% yield; pale yellow oil; R_f 0.55 (30% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.33 (s, 1H), 7.20–7.24 (m, 2H), 7.27–7.31 (m, 6H), 7.33–7.39 (m, 4H), 8.47–8.53 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 59.6, 122.7, 128.6, 129.2, 133.3, 148.7, 150.0, 151.1; FTIR (neat) 687, 738, 1023, 1438, 1476, 1577, 2919, 3069 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{18}H_{16}NS_2$: 310.0724; found 310.0717.

General procedure for carbene insertion into Se-Se bond to synthesis of selenoacetal 7

Under open atmosphere, *N*-tosylhydrazone **1** (1.0 mmol), diphenyl diselenide (1.5 mmol) and KO^{t}Bu (2.0 mmol) were successively added to oven dried reaction tube. DMSO (3 mL) was added and closed with glass-stopper. The reaction tube was then immersed in a 100 °C pre-heated oil bath. The reaction was heated with stirring till complete consumption of **1**. Generally reaction completes within 30 minutes. Upon cooling down to room temperature, water was added to the reaction mixture and extracted with ethyl acetate (3×5 mL). Brine wash (1×5 mL) was given to the combined organic extractions and dried over anhydrous Na_2SO_4. Removal of solvent and neutral alumina column separation of crude using hexanes and ethyl acetate mixture (49:1) afforded the corresponding bis(phenylseleno)acetal **7**.

(Phenylmethylene)bis(phenylselane) (7a): 306 mg, 76% yield; pale yellow oil; R_f 0.32 (2% ethyl acetate in hexanes); ^{1}HNMR ($CDCl_3$, 400 MHz) δ 5.47 (s, 1H), 7.13–7.20 (m, 7H), 7.20–7.27 (m, 4H), 7.38–7.44 (m, 4H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 43.9, 127.6, 128.1, 128.2, 128.4, 129.0, 131.1, 134.7, 141.3; FTIR (neat) 693, 737, 1022, 1065, 1265, 1475, 1577, 3025, 3054 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{19}H_{16}Se_2Na$: 426.9480; found 426.9471.

((4-*Iso*propylphenyl)methylene)bis(phenylselane) (7b): 352 mg, 79% yield; pale yellow oil; R_f 0.29 (2% ethyl acetate in hexanes); ^{1}HNMR ($CDCl_3$, 400 MHz) δ 1.20 (d, *J*=6.4 Hz, 6H), 2.84 (sep, *J*=6.4 Hz, 1H), 5.48 (s, 1H), 7.05 (d, *J*=6.8 Hz, 2H), 7.15–7.27 (m, 8H), 7.41 (d, *J*=7.2 Hz, 4H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 24.1, 33.9, 44.0, 126.5, 127.9, 128.1, 129.0, 131.4, 134.6, 138.7, 148.4; FTIR (neat) 685, 735, 1022, 1475, 1574, 2959, 3053 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{22}H_{22}Se_2Na$: 468.9949; found 468.9950.

((3-Methoxyphenyl)methylene)bis(phenylselane) (7c): 316 mg, 73% yield; pale yellow oil; R_f 0.29 (2% ethyl acetate in hexanes); ^{1}HNMR ($CDCl_3$, 400 MHz) δ 3.74 (s, 3H), 5.48 (s, 1H), 6.74 (ddd, *J*=8.4, 2.8, 1.2 Hz, 1H), 6.84 (t, *J*=2.0 Hz, 1H), 6.89 (dt, *J*=7.6, 1.2 Hz, 1H), 7.15 (t, *J*=8.0 Hz, 1H), 7.21–7.32 (m, 6H), 7.44–7.50 (m, 4H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 43.9, 55.3, 113.2, 113.8, 120.4, 128.2, 129.1, 129.4, 131.2, 134.7, 142.9, 159.5; FTIR (neat) 696, 738, 1022, 1263, 1486, 1598, 2936, 3055 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{20}H_{18}OSe_2Na$: 456.9586; found 456.9614.

((3-Bromophenyl)methylene)bis(phenylselane)[10c] **(7d):** 323 mg, 67% yield; pale yellow oil; R_f 0.32 (2% ethyl acetate in hexanes); ^{1}HNMR ($CDCl_3$, 400 MHz) δ 5.38 (s, 1H), 7.04 (t, *J*=8.0 Hz, 1H), 7.15 (dt, *J*=8.0, 1.2 Hz, 1H), 7.19–7.30 (m, 7H), 7.35 (t, *J*=1.6 Hz, 1H), 7.39–7.44 (m, 4H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 42.7, 122.3, 126.7, 128.6, 129.2, 129.9, 130.5, 130.6, 131.2, 135.0, 143.7; FTIR (neat) 687, 739, 1021, 1067, 1436, 1474, 1571, 2922, 3054 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{19}H_{16}BrSe_2$: 482.8766; found 482.8738.

((4-(Trifluoromethyl)phenyl)methylene)bis(phenylselane) (7e): 339 mg, 72% yield; pale yellow solid; mp 58–60 °C; R_f 0.32 (2% ethyl acetate in hexanes); ^{1}HNMR ($CDCl_3$, 400 MHz) δ 5.47 (s, 1H), 7.17–7.25 (m, 4H), 7.26–7.31 (m, 2H), 7.31–7.36 (m, 2H), 7.38–7.45 (m, 6H); ^{13}CNMR ($CDCl_3$, 125 MHz) δ 42.7, 124.1 (q, *J*=270 Hz), 125.4 (q, *J*=3.75 Hz), 128.4, 128.6, 129.2, 129.5 (q, *J*=32.5 Hz), 130.4, 135.0, 145.5; FTIR (KBr) 689, 740, 846, 1066, 1322, 1475, 2923, 3061 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{20}H_{16}F_3Se_2$: 472.9535; found 472.9565.

Procedure for synthesis of 6:

Under open atmosphere, ((4-bromophenyl)methylene)bis (phenylsulfane) **3l** (0.5 mmol), *p*-tolylboronic acid **5** (1.5 mmol), $Pd(PPh_3)_4$ (5 mol%) and K_2CO_3 (1.0 mmol) were successively added to oven dried reaction tube. Degassed 1,4-dioxane (3 mL) was added and closed with glass-stopper. The reaction tube was then immersed in a 100 °C pre-heated oil bath. The reaction was heated with stirring till complete consumption of **3l**. The reaction progression was monitored by TLC. After 6 h, reaction mixture was cooled down to room temperature. Water was added to the reaction mixture and extracted with ethyl acetate (3×5 mL). Brine wash (1×5 mL) was given to the combined organic extractions and dried over anhydrous Na_2SO_4. Removal of solvent and neutral alumina column separation of crude using hexanes and ethyl acetate mixture (49:1) afforded coupled product **6**.

((4′-Methyl-[1,1′-biphenyl]-4-yl)methylene)bis(phenylsulfane) (6): 178 mg, 89% yield; white solid; mp 100–102 °C; R_f 0.29 (2% ethyl acetate in hexanes); ^{1}HNMR ($CDCl_3$, 400 MHz) δ 2.31 (s, 3H), 5.39 (s, 1H), 7.14–7.19 (m, 8H), 7.27–7.32 (m, 4H), 7.32–7.36 (m, 2H), 7.37–7.44 (m, 4H); ^{13}CNMR ($CDCl_3$, 100 MHz) δ 21.3, 60.4, 127.0, 127.1, 127.9, 128.4, 129.0, 129.6, 132.7, 134.7, 137.4, 137.7, 138.5, 140.9; FTIR (KBr) 688, 751, 815, 1024, 1186, 1438, 1493, 2853, 2920, 3066 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{26}H_{22}S_2Na$: 421.1061; found 421.1061.

Synthesis of 1-(diazomethyl)-4-nitrobenzene 8:

A reported procedure was followed to synthesize 1-(diazomethyl)-4-nitrobenzene.[20] 4-Nitrobenzaldehye (10.0 mmol) was taken in 50 mL single necked round bottomed flask. 10 mL ethanol and hydrazine monohydrate (15.0 mmol) were added. The reaction mixture was refluxed. Reaction was monitored by TLC. After 12 h, reaction mixture was allowed to cool to room temperature. The yellow colored crystal formation was observed. Ethanol was removed by filtration under vacuum to get yellow crystals as a desired product in 74% yield (1.23 g). ^{1}H and ^{13}C data were in well agreement with the literature data. (4-Nitrobenzylidene) hydrazine was taken to next step without further purification.

(4-Nitrobenzylidene)hydrazine (165 mg, 1.0 mmol) and $MgSO_4$ (482 mg, 4.0 mmol) were taken in dry DCM (3 mL) under inert atmosphere. The reaction mixture was cooled to 0 °C. Then activated manganese dioxide (345 mg, 4.0 mmol) was added slowly. After addition, reaction mixture was stirred at same temperature for 2 h. Reaction mixture was passed through a small pad of celite and 2 mL of DCM was used for washing. Solvent was removed under vacuum (water bath temperature was maintained at 25 °C in rotatory evaporator) to get pure diazo compound as a yellow color solid **8** in 56% yield (92 mg). Diazo compound was used to

next step without purification due to its facile decomposition. (*Caution*: Appropriate precaution must be taken while synthesizing the above mentioned diazo compound as it prone to undergo facile decomposition).

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References

[1] a) M. P. Doyle, M. A. McKervey, T. Ye, *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*: *From Cyclopropanes to Ylides*, Wiley, Newyork, **1998**; b) H. M. L. Davies, R. E. J. Beckwith, *Chem. Rev.* **2003**, *103*, 2861–2904; c) H. M. L. Davies, J. R. Manning, *Nature* **2008**, *451*, 417–424; d) Y. Xia, Y. Zhang, J. Wang, *ACS Catal.* **2013**, *3*, 2586–2598.

[2] For reviews see: a) M. P. Doyle, R. Duffy, M. Ratnikov, L. Zhou, *Chem. Rev.* **2010**, *110*, 704–724; b) A. Ford, A. Ring, C. N. Slattery, A. R. Maguire, H. Miel, M. A. McKervey, *Chem Rev* **2015**, *115*, 9981–10080; c) F. Hu, Y. Xia, C. Ma, Y. Zhang, J. Wang, *Chem. Commun.* **2015**, *51*, 7986–7995; For selected examples of C–H insertion, see: d) D. Sole, F. Mariani, M. L. Bennasar, I. Fernandez, *Angew. Chem.*, *Int. Ed.* **2016**, *55*, 6467–6470.

[3] a) F. Zaragoza Dorwald, *Metal Carbenes in Organic Synthesis*, Wiley-VCH, Germany, **1998**; b) S.-F. Zhu, Q.-L. Zhou, *Acc. Chem. Res.* **2012**, *45*, 1365–1377; c) D. Gillingham, N. Fei, *Chem. Soc. Rev.* **2013**, *42*, 4918–4931.

[4] a) J. C. Cain,. *Diazo Chemistry-Synthesis and Reactions*, Merchant Books, **2006**; b) J. R. Fulton, V. K. Aggarwal, J. de Vicente, *Eur. J. Org. Chem.* **2005**, 1479–1492.

[5] W. R. Bamford, T. S. Stevens, *J. Chem. Soc.* **1952**, 4735–4740.

[6] For selected reviews, see: a) J. Barluenga, C. Valdes, *Angew. Chem.*, *Int. Ed.* **2011**, *50*, 7486–7500; b) Z. Shao, H. Zhang, *Chem. Soc. Rev.* **2012**, *41*, 560–572; c) Q. Xiao, Y. Zhang, J. Wang, *Acc. Chem. Res.* **2013**, *46*, 236–247. For selected publications see: d) V. K. Aggarwal, E. Alonso, I. Bae, G. Hynd, K. M. Lydon, M. J. Palmer, M. Patel, M. Porcelloni, J. Richardson, R. A. Stenson, J. R. Studley, J.-L. Vasse, C. L. Winn, *J. Am. Chem. Soc.* **2003**, *125*, 10926–10940; e) J. Barluenga, P. Moriel, C. Valdes, F. Aznar, *Angew. Chem.*, *Int. Ed.* **2007**, *46*, 5587–5590; f) X. Zhao, G. Wu, Y. Zhang, J. Wang, *J. Am. Chem. Soc.* **2011**, *133*, 3296–3299; g) L. Wu, X. Zhang, Q.-Q. Chen, A.-K. Zhou, *Org. Biomol. Chem.* **2012**, *10*, 7859–7862; h) A. Khanna, C. Maung, K. R. Johnson, T. T. Luong, D. L. Van Vranken, *Org. Lett.* **2012**, *14*, 3233–3235; i) P.-X. Zhou, L. Zheng, J.-W. Ma, Y.-Y. Ye, X.-Y. Liu, P.-F. Xu, Y.-M. Liang, *Chem. - Eur. J.* **2014**, *20*, 6745–6751; j) X. S. Shang, N. T. Li, H. X. Siyang, P. N. Liu, *J. Org. Chem.* **2015**, *80*, 4808–4815.

[7] a) J. Barluenga, M. Tomas-Gamasa, F. Aznar, C. Valdes, *Nat. Chem.* **2009**, *1*, 494–499; b) J. Barluenga, M. Tomas-Gamasa, F. Aznar, C. Valdes, *Angew. Chem.*, *Int. Ed.* **2010**, *49*, 4993–4996; c) Q. Ding, B. Cao, J. Yuan, X. Liu, Y. Peng, *Org. Biomol. Chem.* **2011**, *9*, 748–751; d) X. Li, Y. Feng, L. Lin, G. Zou, *J. Org. Chem.* **2012**, *77*, 10991–10995; e) Z. Liu, H. Tan, L. Wang, T. Fu, Y. Xia, Y. Zhang, J. Wang, *Angew. Chem.*, *Int. Ed.* **2015**, *54*, 3056–3060; f) G. Wu, Y. Deng, H. Luo, J. Zhou, T. Li, Y. Zhang, J. Wang, *Chem. Commun.* **2016**, *52*, 5266–5268; g) C. Zhu, J. Li, P. Chen, W. Wu, Y. Ren, H. Jiang, *Org. Lett.* **2016**, *18*, 1470–1473.

[8] a) Y. Kishi, T. Fukuyama, S. Nakatsuka, *J. Amer. Chem. Soc.* **1973**, *95*, 6492–6493; b) N. Rehnberg, G. Magnusson, *J. Org. Chem.* **1990**, *55*, 4340–4349; c) Y. Mori, Y. Kohchi, M. Suzuki, S. Carmeli, R. E. Moore, G. M. L. Patterson, *J. Org. Chem.* **1991**, *56*, 631–637; d) S. D. Rychnovsky, *Chem. Rev.* **1995**, *95*, 2021–2040; e) A. B. Smith III, S. M. Condon, J. A. McCauley, *Acc. Chem. Res.* **1998**, *31*, 35–46; f) S. Oh, I. H. Jeong, C. M. Ahn, W.-S. Shin, S. Lee, *Bioorg. Med. Chem.* **2004**, *12*, 3783–3790; g) A. B. Smith, III, C. M. Adams, *Acc. Chem. Res.* **2004**, *37*, 365–377; h) K. Benda, W. Regenhardt, E. Schaumann, G. Adiwidjaja, *Eur. J. Org. Chem.* **2009**, 1016–1021.

[9] a) Y. Kamitori, M. Hojo, R. Masuda, T. Kimura, T. Yoshida, *J. Org. Chem.* **1986**, *51*, 1427–1431; b) H. Tani, K. Masumoto, T. Inamasu, H. Suzuki, *Tetrahedron Lett.* **1991**, *32*, 2039–2042; c) S. Muthusamy, S. A. Babu, C. Gunanathan, *Tetrahedron Lett.* **2001**, *42*, 359–362; d) S. Kanta De, *Adv. Synth. Catal.* **2005**, *347*, 673–676; e) A. T. Khan, T. Parvin, L. H. Choudhury, *Synthesis* **2006**, 2497–2502; f) C. Wiles, P. Watts, S. J. Haswell, *Tetrahedron Lett.* **2007**, *48*, 7362–7365.

[10] a) M. Tazaki, M. Takagi, *Chem. Lett.* **1979**, 767–770; b) D. A. Evans, L. K. Truesdale, K. G. Grimm, S. L. Nesbitt, *J. Am. Chem. Soc.* **1977**, *99*, 5009–5017; c) B. C. Ranu, A. Saha, T. Mandal, *Tetrahedron* **2009**, *65*, 2072–2078.

[11] a) W. Ando, Y. Kumamoto, T. Takata, *Tetrahedron Lett.* **1985**, *26*, 5187–5190; b) A. Alberti, D. Griller, A. S. Nazran, G. F. Pedulli, *J. Am. Chem. Soc.* **1986**, *108*, 3024–3028; c) Y. Kawamura, K. Akitomo, M. Oe, T. Horie, M. Tsukayama, *Tetrahedron Lett.* **1997**, *38*, 8989–8992; d) Y. Zheng, R. Bian, X. Zhang, R. Yao, L. Qiu, X. Bao, X. Xu, *Eur. J. Org. Chem.* **2016**, 3872–3877; e) I. Ojima, K. Kondo, *Bull. Chem. Soc. Jap.* **1973**, *46*, 1539–1545; f) K. Kondo, I. Ojima, *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1490–1500.

[12] a) H. Zhang, H. Wang, H. Yang, H. Fu, *Org. Biomol. Chem.* **2015**, *13*, 6149–6153.

[13] a) H. Li, L. Wang, Y. Zhang, J. Wang, *Angew. Chem.*, *Int. Ed.* **2012**, *51*, 2943–2946; b) H. Li, X. Shangguan, Z. Zhang, S. Huang, Y. Zhang, J. Wang, *Org. Lett.* **2014**, *16*, 448–451.

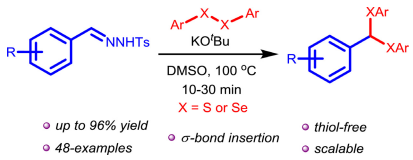
[14] Z. Liu, H. Tan, T. Fu, Y. Xia, D. Qiu, Y. Zhang, J. Wang, *J. Am. Chem. Soc.* **2015**, *137*, 12800–12803.

[15] a) D. Ganapathy, G. Sekar, *Org. Lett.* **2014**, *16*, 3856–3859; b) D. Arunprasath, P. Muthupandi, G. Sekar, *Org. Lett.* **2015**, *17*, 5448–5451.

[16] See the supporting information for detailed optimization.

[17] a) T. Wirth, *Organoselenium Chemistry*: *Synthesis And Reactions*, Wiley-VCH, KGaA, Germany, **2012**; b) G. Mugesh, W.-W. du Mont, H. Sies, *Chem. Rev.* **2001**, *101*, 2125–2179.
[18] When the reaction was carried out in the absence of base, diazo compound and disulfide were remained unreactive even after 24h under our optimized reaction conditions. Upon addition of base, formation of product was observed. We believe that the base initiates the decomposition of diazo compound into free carbene through rapid nitrogen extrusion.
[19] H. Ghafuri, M. M. Hashemi, *J. Sulfur Chem.* **2009**, *30*, 578–580.
[20] F. Friscourt, C. J. Fahrni, G.-J. Boons, *Chem. - Eur. J.* **2015**, *21*, 13996–14001.

A Transition-Metal-Free and Base-Mediated Carbene Insertion into Sulfur-Sulfur and Selenium-Selenium Bonds: An Easy Access to Thio- and Selenoacetals



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