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Two-Step Synthesis of Unsymmetrical Diaryl Sulfides via Electrophilic Thiolation of Non-Functionalized (Hetero)arenes

Marvin J. Böhm, Christopher Golz, Isabelle Rüter and Manuel Alcarazo*[a]

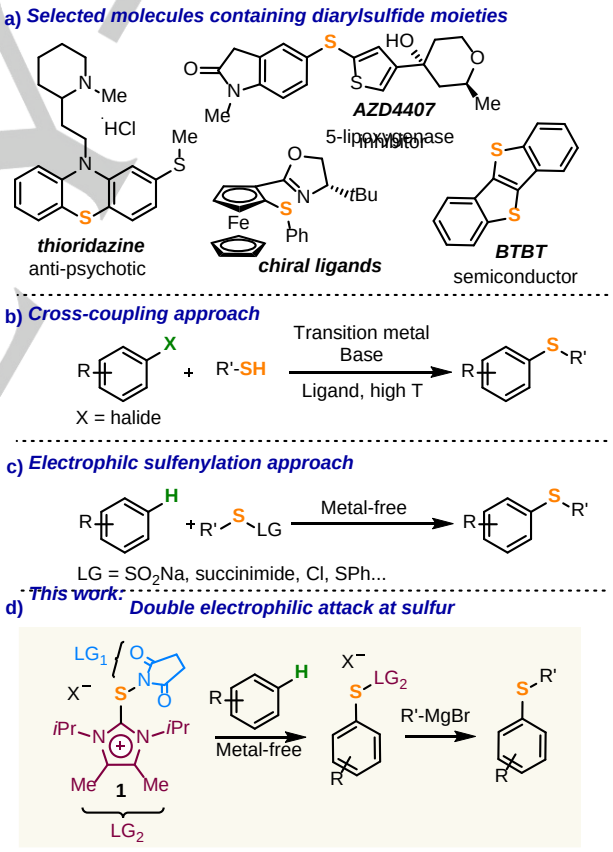
Abstract: This article reports the efficient preparation of a series of unsymmetrically substituted thioethers through a two-step procedure consisting of an initial metal-free C-H sulfenylation of electron-rich (hetero)arenes with newly prepared succinylthioimidazolium salts. Subsequent reaction of the arylthioimidazolium intermediates with Grignards affords the desired thioethers. The synthetic protocol described is modular, scalable and highly yielding, and provides access to sulfides that are not easy to obtain through the existing methodologies. Importantly, no prefunctionalization of the initial (hetero)arene is required.

Introduction

The abundance of natural products in which sulfur-containing moieties are present,[1] together with the number of applications that organosulfur compounds have found in seemly unrelated fields such as drug development,[2] organic materials,[3] ligand design[4] or polymer science,[5] makes versatile methods to introduce sulfur containing moieties in organic molecules of enormous synthetic interest (Scheme 1a). Among these, the metal-catalysed cross-coupling reaction between thiols and organic halides has attracted considerable attention since it allows the synthesis of unsymmetrically substituted aryl sulfides from easy available thiols and aryl halides or pseudohalides.[6] Many advances have been achieved in this reaction, being probably the replacement of the originally used Pd- and Ir-based catalysts[7] by more abundant first row transition metals the most prominent one (Scheme 1b).[8] Despite of this success the employment of metal catalysts is not always exempt of problems; they often suffer from the necessity of pre-functionalised substrates and, if they are used at late stages of a synthesis, the possibility of contamination of the final product with toxic metal impurities is a serious issue.[9]

Metal-free alternatives for the synthesis of diaryl sulfides have also been described. Very often these reactions consist of the attack of sulfur electrophiles to (hetero)arenes through a typical electrophilic aromatic substitution mechanism affording the products of C-H sulfenylation.[10] This approach avoids any pre-functionalization on the ring which suffers the electrophilic attack; however, because most of the electrophilic sulfur reagents available, namely, *N*-thiosuccinimides,[11] sulfonyl chlorides,[12] sodium sulfinates[13] or sulfonium triflates[14] lack of enough reactivity, the scope of the transformation is limited to electron rich aromatic substrates. It is also of note that these sulfenylation protocols very often require the preparation of a new reagent for each [R-S$^+$] moiety to be transferred to an organic group (Scheme 1c).

Having recognized the advantages, but also the limitations of metal-free approaches, we hypothesised about the possible development of a generally applicable an easy to handle [S^{+2}] synthon, which might be used for the preparation of a broad family of unsymmetrically substituted thioethers by consecutive reaction with two different nucleophiles. Herein, we bring into practice that idea by the synthesis and use of succinyl-thioimidazolium salts **1**. As it is described below, compound **1** is able to react with a broad range of unfunctionalized (hetero)aromatic rings via C-H sulfenylation to afford arylthio-imidazolium salts. Reaction of these intermediates with Grignards of different structures delivers the desired thioethers in moderate to excellent yields (Scheme 1d).



Scheme 1. The importance of unsymmetrical diaryl sulfides and different approaches towards their synthesis.

Results and Discussion

Synthesis of succinylthioimidazolium salts. Inspired by the oxidation of imidazole derived thione **2** by halogens to afford dihalosulfuranes **3**,[15] and recognizing the ability of the

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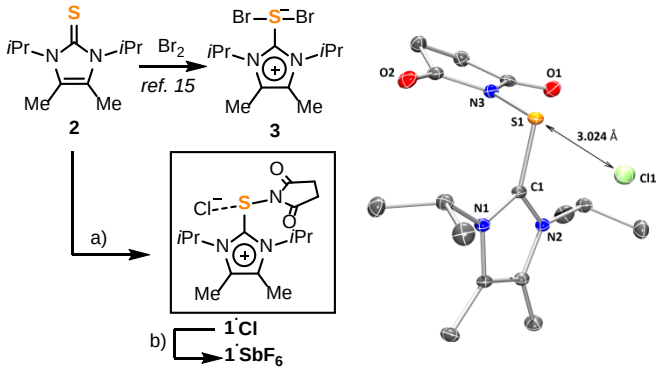
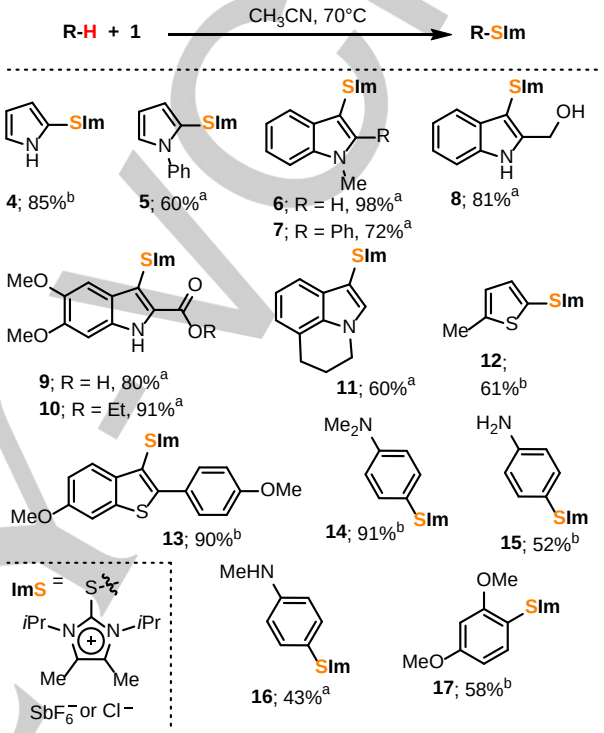
succinimide group to carry out the umpolung of the moieties bonded to its nitrogen atom, we initially tested the oxidation of thiourea **2** with *N*-chlorosuccinimide as a source for the desired [S^{+2}] synthon. To our satisfaction this reaction afforded succinylthioimidazolium salt **1·Cl** in excellent yield as a slightly hygroscopic yellow solid, whose solid state structure was determined by X-ray diffraction (Scheme 2).[16] Anion exchange to hexafluoroantimonate with an excess of $NaSbF_6$ allows the isolation of **1·SbF$_6$**, a crystalline material which is easier to handle. This synthetic route towards **1·SbF$_6$** has been scaled up to multigram quantities without compromising the yield of the product.



Scheme 2. Synthesis and molecular structure of succinylthioimidazolium chloride **1·Cl**. Reagents and conditions: a) NCS (1.0 equiv.), CH_2Cl_2, r.t., 98%; b) $NaSbF_6$ (1.5 equiv.), CH_2Cl_2, r.t., 92%.

In the solid state compound **1·Cl** adopts a slightly distorted T-shape. The N3-S1-Cl1 distribution is nearly linear (178.0°), being the chloride anion slightly bent onto the top of the positively charged imidazolium moiety (Cl1-S1-C1 angle 78.6°). It is also worth noting that while the N3-S1 bond distance (1.724(9) Å) corresponds to the typical one between these two elements,[17] the S1-Cl1 interatomic distance (3.024(4) Å) is 15% shorter than the sum of the van der Waals radii Cl-S (3.55 Å). The hypercoordination of the S-atom in **1** is a direct consequence of its very strong electrophilic character in that particular environment.

Synthesis of arylthioimidazolium salts. Once an efficient synthesis was available for **1**, the following studies were focused on establishing its reactivity towards aromatic structures. Initially, 1-methylindole was used as model substrate. To our delight, the product of direct sulfenylation **4** was isolated in 98% yield when the reaction was performed in acetonitrile at 70 °C (See the Supporting Information for the optimization details). At lower temperatures and employing other solvents the reaction was sluggish, probably due to the lower solubility of salt **1·SbF$_6$** under these conditions. The scope and generality of the reaction was subsequently investigated (Scheme 3). We were glad to see that the electrophilic sulfenylation proceeds with a variety of other electron rich aromatics, including substituted pyrroles **4-5**, indoles **6-11**, (benzo)thiophenes **12-13**, anilines **14-16**, and even anisole derivatives **17**. Only one product was detected in all cases, being the regioselectivity determined by the electronics of the substrate. The sulfenylation protocol does not seems to be affected by ethers, esters, amides or even acidic or basic functionalities already present in the substrates such as free alcohols, carboxylic acids or unprotected amino groups. Unfortunately, under the optimized conditions only traces of the desired products were obtained when furans, benzofurans or anisole were employed as nucleophiles. This still remains as the main limitation of the method.



Scheme 3. Substrate scope of the electrophilic C-H sulfenylation; [a] **1·Cl** was employed as sulfenylation reagent followed by anion exchange with $NaSbF_6$; [b] **1·SbF$_6$** was employed as sulfenylation reagent.

Figure 1 depicts the X-ray structures of compounds **8** and **13** (See the Supplementary Information for the analysis of **4**, **6**, **7**, **9**, **10**, **11**, **14** and **16**).[16] All these salts feature similar attributes; namely, an angular geometry with C4-S1-C1 bond angles in between 100.0 and 105.0°, and C1-S1 bond distances in the range of 1.740-1.770 Å as expected for single C-S bonds.

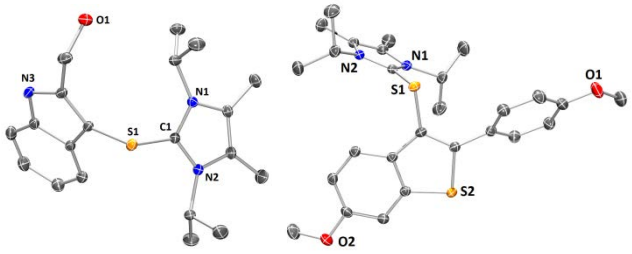
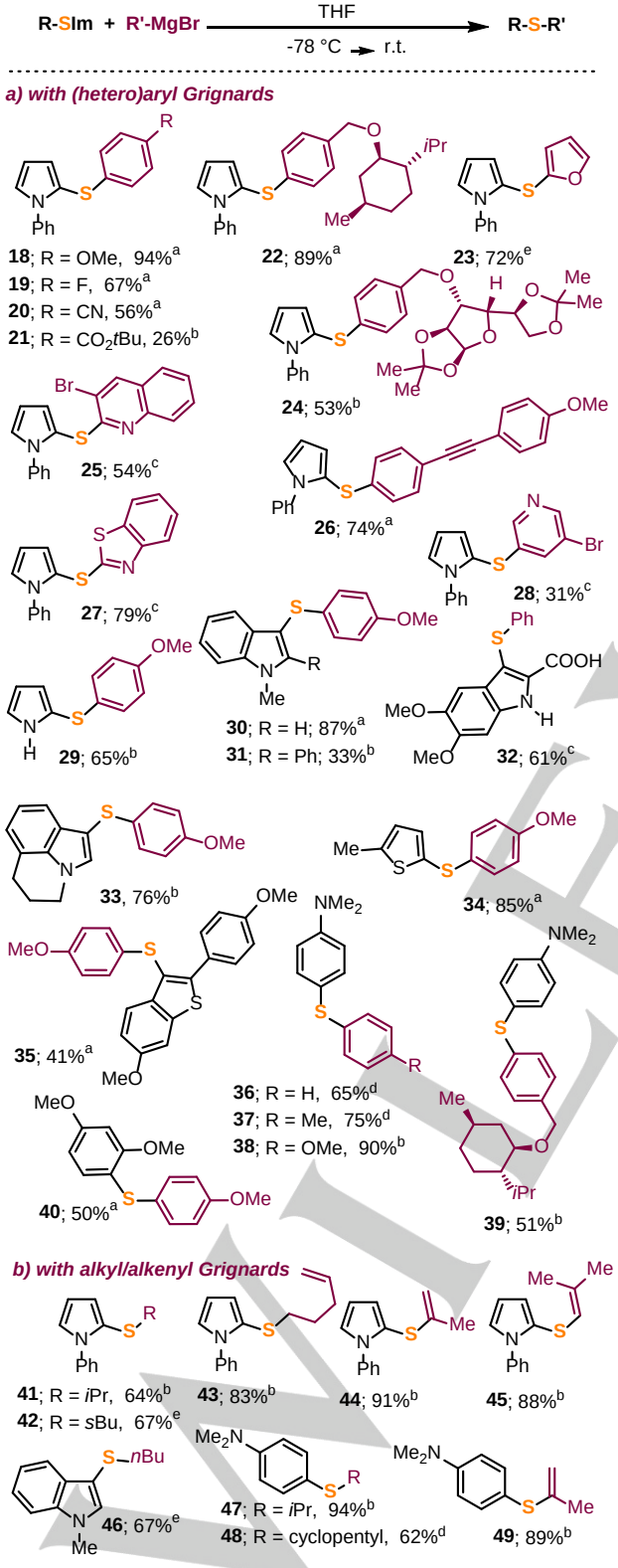


Figure 1. Molecular structures of compounds **8** (left) and **13** (right). Anisotropic displacement parameter shown at 50% probability level. Hydrogen atoms and hexafluoroantimonate anions omitted for clarity.[16]

Synthesis of unsymmetrical diaryl sulfides. With this selection of arylthioimidazolium salts in hand, we started a preliminary exploration to identify possible nucleophiles that could attack at the sulfur atom of these molecules and promote the release of the *N*-heterocyclic carbene, with the concomitant formation of the desired diaryl-, alkenyl(aryl)-, or akyl(aryl)sulfide. After some screening (see the Supporting Information for the optimization details), it was gratifying to find that a variety of Grignard reagents were suitable for that transformation, and afforded in satisfactory yields a complete set of structurally differentiated thioethers containing aryl-, heteroaryl-, alkenyl- and/or alkyl-substituents directly attached to the sulfur atom **18-49** (Scheme 4).[18] As standard conditions 1.5 equivalents of the desired organo-magnesium reagent in THF were used; note however that if acidic protons were present in the initial imidazolium thioether, such as in the case of unprotected pyrrole **29** or indole ring **32**, then additional equivalents of the organometallic nucleophile were employed.



Scheme 4. Substrate scope of the reaction of imidazolium sulfides with Grignards. All yields are of isolated products. Reaction conditions: [a] 1.5 equiv. Grignard; [b] 2.9 equiv. Grignard; [c] 2.9 equiv. Grignard, LiCl, [d] 5.0 equiv. Grignard; [e] 1.5 equiv. R-Li.

The functional group tolerance of this two-step synthesis is inevitably limited by the high reactivity of the Grignard reagents used. These are necessary to displace the carbene moiety from arylthioimidazolium salts **4-17**. All our attempts to use softer organozinc reagents for this step were unsuccessful. On the other hand it is noteworthy that the employment of Grignards prepared following Knochel conditions partially alleviates this inconvenient and allows the accommodation of additional functionalities on the final thioether.[19] Hence, nitriles **20**, esters **21** or even pyridine derivatives **25** and **28**, which may be easily modified in subsequent steps, could be installed as substituents. Liberation of the carbene, either free or more probably as a Mg complex could be confirmed by the detection of the corresponding selenourea when the reaction mixtures are quenched with excess of Se powder. Figure 2 shows the molecular diagrams of compounds **27** and **32** obtained by X-ray diffraction experiments; they confirm the expected connectivity (For the solid state structures of sulfides **19**, **20, 26** and **31** see the Supplementary Information).

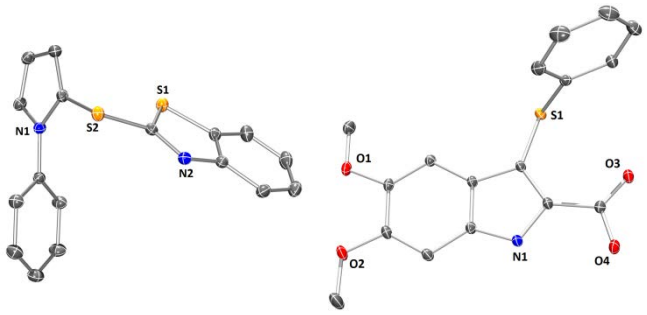
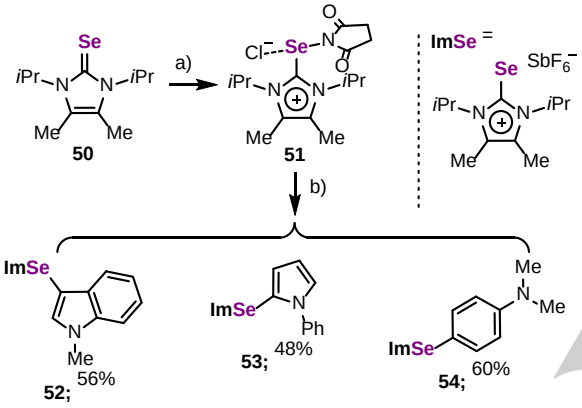


Figure 2. Molecular structures of compounds **27** (left) and **32** (right). Anisotropic displacement parameter shown at 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity.[16]

Keen to underscore the utility of the synthetic method described, we turned our attention to studying its possible extension to the preparation of diaryl substituted selenides. With this idea in mind selenourea **50** was subjected to oxidation with *N*-chlorosuccinimide to afford succinylselenoimidazolium salt **51·Cl** as an orange solid in excellent yield.[20] Interestingly, when this compound was made react with electron rich arenes (*N,N*-dimethylamino benzene) or heteroarenes (*N*-methylindole, *N*-phenylpyrrol), the corresponding products of electrophilic selenylation **52-54** were isolated in moderate yields as pale yellow solids, which could be handled in air for short times without evident decomposition (Scheme 5). As in the sulfenylation case the reaction is regioselective, being only the most electron rich carbon atom of the substrate the one that suffers the electrophilic substitution.



Scheme 5. Synthesis of **51** and substrate scope of the electrophilic C-H selenylation. All yields are of isolated products. Reaction conditions: [a] NCS, CH_3CN, rt, quant.; [b]Arene (1.0 equiv.), CH_3CN, 70 °C, 19h, and then $NaSbF_6$.

The unambiguous establishment of the connectivity of **54** was possible by X-ray analysis. Suitable single crystals were grown by slow diffusion of diethyl ether into a saturated dichloromethane solution of this salt (Figure 3). In the solid state the Se centre of **54** features an acuter angle around (C4-Se1-C1, 99.82°) if compared with those of **8** and **13**, which probably derives from the decreased tendency towards hybridization of the heavier atoms in a group. A short contact between F1 and Se1 was additionally observed (3.209(1)Å); this is surely a consequence of the high electrophilicity of the selenium atom in this compound.[18]

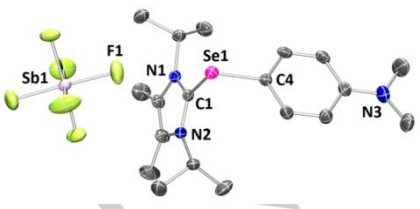
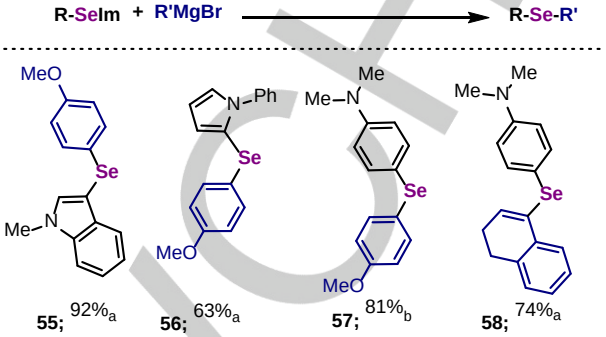


Figure 3. Molecular structures of compounds **54**. Anisotropic displacement parameter shown at 50% probability level. Hydrogen atoms and solvent molecules omitted for clarity. [16]

Finally, the reaction of **52-54** with Grignards proceeded in a similar manner to that observed for the sulfide analogues allowing the isolation of asymmetrically substituted diaryl selenides. Following this procedure compounds **55-58** were prepared as illustrative examples (Scheme 6).



Scheme 6. Substrate scope of the reaction of imidazolium selenides with Grignards. All yields are of isolated products. Reaction conditions: [a] 1.5 equiv. Grignard, THF, -78 °C→r.t.; [b]2.9 equiv. Grignard, THF, -78 °C→r.t.

Conclusions

This article describes a general and efficient protocol for the electrophilic C-H sulfenylation or selenylation of a variety of (hetero)arenes by using inexpensive succinylthio- or succinyl-selenoimidazolium salts as sulfur or selenium sources. Subsequent reaction of these salts with Grignards affords asymmetrically substituted organic sulfides and selenides of different structures. A total of 35 examples are provided. We conclude from these experiments that succinylthio- or succinylselenoimidazolium salts behave as efficient [S^{+2}]- and [Se^{+2}]-synthons, respectively.

Experimental Section

Synthesis of 1·Cl: *N*-Chlorosuccinimide (134mg, 1.00 mmol) was added to a solution of **2** (212 mg, 1.00 mmol) in DCE (10 mL) and the yellow solution obtained was stirred for two hours at rt. After this the solvent was removed *in vacuo* and **1·Cl** was isolated as a light yellow solid (346 mg, 1.00 mmol, 98%). ^{1}H NMR (300 MHz, CD_2Cl_2, ppm) δ = 1.62 (d, *J* = 7.0 Hz, 12H), 2.39 (s, 6H), 2.78 (s, 4H), 6.20 (hept, *J* = 7.1 Hz, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2, ppm) δ = 11.2, 21.5, 29.3, 44.5, 54.6, 130.4, 177.0; IR (ATR, cm^{-1}): 2971, 2941, 1773, 1714, 1610, 1470, 1445, 1422, 1391, 1372, 1346, 1287, 1250, 1216, 1179, 1161, 1132, 1113, 1092, 1010, 943, 906, 869, 820, 802, 752, 664, 644; HRMS (ESI-pos.) *calcd. for* $C_{15}H_{24}N_3O_2S$ [M^+]: 310.1584, *found*: 310.1584.

Synthesis of 1·SbF$_6$: $NaSbF_6$ (1.94 g, 7.50 mmol, 1.5 equiv.) was added to a solution of **1·Cl** (1.73 g, 5.00 mmol) in MeCN (50 mL) and the yellow suspension obtained was stirred for five hours. After this, the solvent was removed *in vacuo* and the remaining solid extracted with DCM (4 x 50 ml). The organic phases were combined and the solvent was removed to afford the desired compound **1·SbF$_6$** as a yellow solid (2.51 g, 4.57 mmol, 92%). ^{1}H NMR (300 MHz, CD_2Cl_2, ppm) δ = 1.57 (d, *J* = 7.2 Hz, 12H), 2.41 (s, 6H), 2.85 (s, 4 H, 7H), 6.23 (sept, *J* = 7.2 Hz, 2H); ^{13}C NMR (126 MHz, CD_2Cl_2, ppm) δ = 11.2, 21.6, 29.3, 55.1, 132.9, 133.5, 176.7; IR (ATR, cm^{-1}): 2993, 1736, 1597, 1458, 1421, 1397, 1376, 1291, 1270,

1236, 1215, 1131, 1092, 1004, 819, 749; HRMS (ESI-pos.) *calcd. for* $C_{15}H_{24}N_3O_2S$ [M^+]: 310.1584, *found*: 310.1584 .

Representative synthesis of arylthioimidazolium salts. Synthesis of 4: Pyrrole (27 mg, 0.4 mmol) was added to a solution of **1•SbF$_6$** (262 mg, 0.480 mmol, 1.2 equiv.) in MeCN (4 mL) and the yellow solution obtained heated to 70 °C for 16 h. After this all volatiles were removed *in vacuo,* the remaining orange oil was dissolved in DCM (4 mL) and washed with sat. aq. $NaSbF_6$ (4 mL) for 5 min. After separation of the two phases the organic layer was dried over $MgSO_4$ and concentrated. Crude **4** was purified through column chromatography (DCM:MeOH; 100:0→95:5) to afford **4** as a yellow foam (175 mg, 0.34 mmol, 85%). ^{1}H NMR (300 MHz, CD_2Cl_2, ppm) δ = 1.54 (d, *J* = 7.2 Hz, 12H), 2.34 (s, 6H), 5.50 (hept, *J* = 7.2 Hz, 2H), 6.20 – 6.26 (m, 1H), 6.46 – 6.52 (m, 1H), 6.95 – 7.03 (m, 1H), 9.37 (s, 1H); ^{13}C NMR (126 MHz, CD_2Cl_2, ppm) δ = 10.9, 21.4, 109.3, 111.4, 118.9, 124.8, 130.3, 136.2; IR (ATR, cm^{-1}): 3181, 2716, 1772, 1715, 1621, 1603, 1377, 1070, 1051, 714, 649, 608; HRMS (ESI-pos.) *calcd. for* $C_{15}H_{24}N_3S$ [M^+]: 278.1685, *found*: 278.1686; (ESI-neg.) *calcd. for* SbF_6^- [M^-]: 234.8948, *found*: 234.8951.

Compound 5: Yellow solid, 60%. ^{1}H NMR (300 MHz, CD_2Cl_2 ppm) δ = 1.34 (d, *J* = 7.1 Hz, 12H), 2.29 (s, 6H), 5.00 (hept, *J* = 7.1 Hz, 2H), 6.40 (dd, *J* = 3.9, 3.0 Hz, 1H), 6.68 (dd, *J* = 3.9, 1.7 Hz, 1H), 7.13 (dd, *J* = 3.0, 1.8 Hz, 1H), 7.33 – 7.39 (m, 2H), 7.49 – 7.62 (m, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2, ppm) δ = 10.8, 21.3, 53.8, 111.7, 112.6, 121.9, 126.5, 128.9, 129.4, 130.4, 130.5, 135.8, 138.7; IR (ATR, cm^{-1}): 2994, 1496, 1455, 1437, 1414, 1377, 1319, 1207, 1137, 1110, 1087, 1039, 768, 725, 700, 656, 615, 603; HRMS (ESI-pos.) *calcd. for* $C_{21}H_{28}N_3S$ [M^+]: 354.1998, *found*: 354.2000; (ESI-neg.) *calcd. for* SbF_6^- [M^-]: 234.8948, *found*: 234.8951.

Compound 6: Yellow foam, 75%. ^{1}H NMR (300 MHz, CD_2Cl_2, ppm) δ = 1.48 (d, *J* = 7.1 Hz, 12H), 2.33 (s, 6H), 3.84 (s, 3H), 5.54 – 5.66 (m, 2H), 7.27 – 7.39 (m, 2H), 7.40 (s, 1H), 7.43 – 7.47 (m, 1H), 7.61 – 7.66 (m, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2, ppm) δ = 10.8, 21.3, 33.9, 53.6, 95.6, 111.4, 118.3, 122.2, 123.9, 128.8, 130.1, 135.8, 137.6, 138.0; IR (ATR, cm^{-1}): 2988, 2363, 1621, 1458, 1417, 1376, 1244, 1113, 738, 657, 631; HRMS (ESI-pos.) *calcd. for* $C_{20}H_{28}N_3S$ [M^+]: 342.1998, *found*: 342.1999; (ESI-neg.) *calcd. for* SbF_6^- [M^-]: 234.8948, *found*: 234.8952.

Compound 7: Yellow foam, 72%. ^{1}H NMR (400 MHz, CD_2Cl_2, ppm) δ = 1.22 (d, *J* = 7.1 Hz, 12H), 2.26 (s, 6H), 3.68 (s, 3H), 5.12 (hept, *J* = 7.1 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.38 – 7.45 (m, 3H), 7.54 (dd, *J* = 18.7, 8.0 Hz, 2H), 7.60 – 7.66 (m, 3H); ^{13}C NMR (126 MHz, CD_2Cl_2, ppm) δ = 11.0, 21.2, 32.5, 53.7, 94.8, 111.6, 118.1, 122.8, 124.4, 128.7, 129.6, 129.7, 129.9, 130.8, 131.1, 137.9, 138.2, 146.9; IR (ATR, cm^{-1}): 2994, 2942, 1693, 1622, 1465, 1445, 1427, 1396, 1378, 1338, 1294, 1236, 1218, 1157, 1135, 1112, 1020, 803, 745, 710, 650; HRMS (ESI-pos.) *calcd. for* $C_{26}H_{32}N_3S$ [M^+]: 418.2311, *found*: 418.2310; (ESI-neg.) *calcd. for* SbF_6^- [M^-]: 234.8948, *found*: 234.8952.

Compound 8: Black foam, 81%. ^{1}H NMR (600 MHz, CD_2Cl_2, ppm) δ = 1.38 (d, *J* = 7.1 Hz, 12H), 2.31 (s, 6H), 4.91 (s, 2H), 5.39 – 5.46 (m, 2H), 7.23 – 7.31 (m, 2H), 7.46 – 7.48 (m, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 9.45 (s, 1H); ^{13}C NMR (126 MHz, CD_2Cl_2, ppm) δ = 11.0, 21.2, 53.7, 56.8, 93.7, 113.2, 117.5, 122.4, 124.1, 128.9, 129.9, 135.7, 137.9, 144.0; IR (ATR, cm^{-1}): 3392, 2983, 1709, 1619, 1448, 1422, 1395, 1376, 1344, 1327, 1293, 1269, 1230, 1216, 1191, 1174, 1151, 1139, 1113, 1074, 1030, 1010, 749, 653; HRMS (ESI-pos.) *calcd. for* $C_{20}H_{28}N_3OS$ [M^+]: 358.1948, *found*: 358.1953; (ESI-neg.) *calcd. for* SbF_6^- [M^-]: 234.8948, *found*: 234.8951.

Compound 9: White powder, 80%. ^{1}H NMR (400 MHz, CD_2Cl_2, ppm) δ = 1.35 (d, *J* = 7.1 Hz, 12H), 2.34 (s, 6H), 3.21 (s, 2H), 3.85 (d, *J* = 1.3 Hz, 3H), 3.91 (d, *J* = 1.0 Hz, 3H), 5.32 – 5.39 (m, 2H), 6.75 (s, 1H), 7.05 (d, *J* = 1.8 Hz, 1H);^{13}C NMR (126 MHz, CD_2Cl_2, ppm) δ = 11.1, 21.3, 56.6, 56.8, 95.9, 98.9, 102.5, 121.9, 127.7, 129.7, 131.5, 138.4, 148.4, 151.4, 161.3; IR (ATR, cm^{-1}): 3255, 1667, 1632, 1621, 1514, 1447, 1425, 1404, 1394, 1375, 1273, 1252, 1206, 1178, 1153, 1112, 1005, 850, 719; HRMS (ESI-pos.) *calcd. for* $C_{22}H_{30}N_3O_4S$ [M^+]: 432.1952, *found*: 432.1947.

Compound 10: Brown foam, 94%. ^{1}H NMR (400 MHz, CD_2Cl_2, ppm) δ = 1.36 – 1.41 (m, 15H), 2.37 (s, 6H), 3.83 (s, 3H), 3.89 (s, 3H), 4.35 (q, *J* = 7.2 Hz, 2H), 5.33 – 5.39 (m, 2H), 6.56 (s, 1H), 7.05 (s, 1H); ^{13}C NMR (101 MHz, CD_2Cl_2, ppm) δ = 11.0, 14.6, 21.3, 54.1, 56.6, 56.7, 62.2, 95.6, 98.8, 104.6, 121.4, 126.0, 130.1, 131.3, 137.4, 148.7, 152.0, 159.7; IR (ATR, cm^{-1}): 3415, 2358, 1696, 1515, 1454, 1341, 1263, 1241, 1209, 1180, 1157, 1113, 1033, 1019, 1004, 832, 653; HRMS (ESI-pos.) *calcd. for* $C_{24}H_{34}N_3O_4S$ [M^+]: 460.2265, *found*: 460.2266; (ESI-neg.) *calcd. for* SbF_6^- [M^-]: 234.8948, *found*: 234.8950.

Compound 11: Yellow foam, 60%. ^{1}H NMR (300 MHz, CD_2Cl_2, ppm) δ = 1.49 (d, *J* = 7.1 Hz, 12H), 2.15 – 2.27 (m, 2H), 2.33 (s, 6H), 2.99 (t, *J* = 6.1 Hz, 2H), 4.15 – 4.24 (m, 2H), 5.53 – 5.76 (m, 2H), 7.03 (dd, *J* = 7.2, 1.0 Hz, 1H), 7.18 (dd, *J* = 8.0, 7.1 Hz, 1H), 7.41 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.43 (s, 1H); ^{13}C NMR (126 MHz, CD_2Cl_2, ppm) δ = 10.8, 21.4, 23.3, 24.9, 45.4, 53.7, 95.1, 115.5, 120.7, 122.6, 124.1, 126.6, 129.9, 133.1, 134.8, 138.2; IR (ATR, cm^{-1}): 2941, 1620, 1505, 1467, 1448, 1383, 1325, 1247, 1219, 1168, 1135, 1110, 1034, 906, 827, 786, 750, 653, 601; HRMS (ESI-pos.) *calcd. for* $C_{22}H_{30}N_3S$ [M^+]: 342.1998, *found*: 342.1999; (ESI-neg.) *calcd. for* SbF_6^- [M^-]: 234.8948, *found*: 234.8951.

Compound 12: Yellow foam, 61%. ^{1}H NMR (300 MHz, CD_2Cl_2, ppm) δ = 1.58 (d, *J* = 7.1 Hz, 12H), 2.39 (s, 6H), 2.47 (d, *J* = 1.1 Hz, 3H), 5.48 (hept, *J* = 7.1 Hz, 2H), 6.76 – 6.79 (m, 1H), 7.23 (d, *J* = 3.7 Hz, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2, ppm) δ = 10.9, 16.1, 21.4, 54.1, 121.7, 127.4, 131.0, 137.2, 149.2; IR (ATR, cm^{-1}): 1422, 1396, 1377, 1218, 1138, 1113, 1093, 1070, 954, 803, 712, 653, 604; HRMS (ESI-pos.) *calcd. for* $C_{16}H_{25}N_2S_2$ [M^+]: 309.1454, *found*: 309.1454; (ESI-neg.) *calcd. for* SbF_6^- [M^-]: 234.8948, *found*: 234.8950.

Compound 13: Yellow foam, 90%. ^{1}H NMR (300 MHz, CD_2Cl_2, ppm) δ = 1.28 (d, *J* = 7.1 Hz, 12H), 2.27 (s, 6H), 3.88 (s, 3H), 3.89 (s, 3H), 5.06 (hept, *J* = 7.1 Hz, 2H), 7.05 – 7.11 (m, 2H), 7.11 – 7.15 (m, 1H), 7.37 (d, *J* = 2.3 Hz, 1H), 7.45 (d, *J* = 8.9 Hz, 1H), 7.49 – 7.54 (m, 2H); ^{13}C NMR (126 MHz, CD_2Cl_2, ppm) δ = 10.9, 21.0, 53.9, 56.1, 56.3, 106.2, 112.1, 115.2, 116.3, 122.4, 124.4, 130.7, 131.7, 133.2, 135.9, 140.1, 149.2, 159.0, 161.7; IR (ATR, cm^{-1}): 2939, 1605, 1529, 1477, 1462, 1440, 1421, 1397, 1378, 1300, 1290, 1248, 1215, 1176, 1112, 1063, 1030, 958, 850, 838, 805, 767, 735, 711, 652, 607; HRMS (ESI-pos.) *calcd. for* $C_{27}H_{33}N_2O_2S_2$ [M^+]: 481.1978, *found*: 481.1980; (ESI-neg.) *calcd. for* SbF_6^- [M^-]: 234.8948, *found*: 234.8950.

Compound 14: Blue foam, 90%. ^{1}H NMR (300 MHz, CD_2Cl_2, ppm) δ = 1.51 (d, *J* = 7.1 Hz, 12H), 2.38 (s, 6H), 2.96 (s, 6H), 5.35 – 5.50 (m, 2H), 6.64 – 6.70 (m, 2H), 7.15 – 7.22 (m, 2H); ^{13}C NMR (126 MHz, CD_2Cl_2, ppm) δ = 10.9, 21.5, 40.5, 53.9, 112.4, 113.9, 130.4, 133.4, 137.6, 152.0; IR (ATR, cm^{-1}): 2940, 1596, 1505, 1470 1444, 1426, 1393, 1373, 1360, 1219, 1198, 1172, 1141, 1113, 947, 809, 654, 608; HRMS (ESI-pos.) *calcd. for* $C_{19}H_{30}N_3S$ [M^+]: 332.2155, *found*: 332.2155; (ESI-neg.) *calcd. for* SbF_6^- [M^-]: 234.8948, *found*: 234.8950.

Compound 15: Yellow oil, 52%. ^{1}H NMR (300 MHz, CD_2Cl_2, ppm) δ = 1.49 (d, *J* = 7.1 Hz, 12H), 2.37 (s, 6H), 4.12 (s, 2H), 5.35 (sept, *J* = 7.1 Hz, 2 H), 6.69 (m, 2H), 7.09 (m, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2, ppm) δ =

10.8, 21.3, 53.8, 115.2, 116.8, 130.5, 133.4, 137.1, 149.6; IR (ATR, cm^{-1}): 3506, 3407, 2984, 2945, 1620, 1595, 1500, 1415, 1305, 835, 655; HRMS (ESI-pos.) *calcd. for* $C_{17}H_{26}N_3S$ [M^+]: 304.1851, *found*: 304.1842; (ESI-neg.) *calcd. for* SbF_6^- [M^-]: 234.8948, *found*: 234.8948.

Synthesis of 16: White foam, 43%. ^{1}H NMR (300 MHz, CD_2Cl_2, ppm) δ = 1.50 (d, *J* = 7.1 Hz, 12H), 2.37 (s, 6H), 2.80 (s, 3H), 4.29 (s, 1H), 5.33 – 5.46 (m, 2H), 6.57 – 6.64 (m, 2H), 7.10 – 7.17 (m, 2H); ^{13}C NMR (101 MHz, CD_2Cl_2, ppm) δ = 10.7, 21.3, 30.5, 53.7, 114.1, 130.4, 133.7, 151.6; IR (ATR, cm^{-1}): 3438, 2988, 1597, 1509, 1448, 1421, 1397, 1377, 1327, 1216, 1186, 1112, 823, 752; HRMS (ESI-pos.) *calcd. for* $C_{18}H_{28}N_3S$ [M^+]: 318.1998, *found*: 318.2003; (ESI-neg.) *calcd. for* SbF_6^- [M^-]: 234.8948, *found*: 234.8948.

Synthesis of 17: White solid, 58%. ^{1}H NMR (300 MHz, CD_2Cl_2, ppm) δ = 1.48 (d, *J* = 7.1 Hz, 12H), 2.38 (s, 6H), 3.82 (s, 3H), 3.83 (s, 3H), 5.39 (hept, *J* = 7.1 Hz, 2H), 6.52 – 6.61 (m, 2H), 7.24 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (126 MHz, CD_2Cl_2, ppm) δ = 11.0, 21.5, 54.0, 56.4, 57.0, 100.5, 107.5, 130.6, 134.4, 136.6, 159.9, 163.8; IR (ATR, cm^{-1}): 2945, 2358, 1603, 1590, 1488, 1454, 1437, 1416, 1314, 1286, 1210, 1159, 1116, 1074, 1034, 828, 798, 653; HRMS (ESI-pos.) *calcd. for* $C_{19}H_{29}N_2O_2S$ [M^+]: 349.1944, *found*: 349.1947; (ESI-neg.) *calcd. for* SbF_6^- [M^-]: 234.8948, *found*: 234.8948.

Representative synthesis of diaryl-, aryl(alkenyl)-, and aryl(alkyl) sulfides. Synthesis of 18: Compound **5** (60.2 mg, 0.102 mmol) was dissolved in THF (1.0 mL) and cooled to -78 °C. Then, a solution of *p*-methoxyphenylmagnesium bromide (0.5 M in THF, 306 µL, 0.153 mmol, 1.5 equiv.) was added drop wise and the mixture allowed to warm up to r.t. overnight. The reaction was then quenched with sat. NH_4Cl (5 mL) and extracted with DCM (3 x 20 mL). Evaporation of the combined organic phases afforded crude **18**, which was subsequently purified by column chromatography (Hexane:ethylacetate; 80:20). White solid (26.9 mg, 0.10 mmol, 94%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ = 3.74 (s, 3H), 6.35 (dd, *J* = 3.6, 3.0 Hz, 1H), 6.69 – 6.72 (m, 1H), 6.71 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 7.03 (dd, *J* = 3.0, 1.8 Hz, 1H), 7.20 – 7.25 (m, 2H), 7.30 – 7.38 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ = 55.5, 109.5, 114.6, 120.5, 126.2, 126.7, 127.5, 128.7, 129.3, 129.4, 139.7, 158.3; IR (ATR, cm^{-1}): 2958, 2828, 2360, 1597, 1488, 1455, 1449, 1434, 1393, 1322, 1291, 1240, 1204, 1180, 1176, 1162, 1138, 1105, 1088, 1074, 1030, 1003, 962, 821, 808, 796, 762, 724, 692, 651, 636, 619, 605; HRMS (EI-pos.) *calcd. for* $C_{17}H_{15}NOS$ [M^+]: 281.0874, *found*: 281.0871.

Compound 19: White solid, 67% yield. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ = 6.39 (dd, *J* = 3.6, 3.0 Hz, 1H), 6.74 (dd, *J* = 3.6, 1.8 Hz, 1H), 6.82 – 6.95 (m, 4H), 7.07 (dd, *J* = 3.0, 1.8 Hz, 1H), 7.19 – 7.24 (m, 2H), 7.31 – 7.35 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 109.6, 115.9 (d, J_{C-F} = 22.0 Hz), 119.2, 121.1, 126.5, 126.6, 127.6, 128.6 (d, J_{C-F} = 7.9 Hz), 128.7, 133.9, 133.9, 139.4, 161.2 (d, J_{C-F} = 244.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$, ppm) δ = -117.3; IR (ATR, cm^{-1}): 3048, 2360, 1586, 1487, 1434, 1394, 1317, 1216, 1156, 1134, 1088, 1034, 1010, 822, 806, 763, 749, 730, 722, 692, 649, 617, 604; HRMS (EI-pos.) *calcd. for* $C_{16}H_{12}FNS$ [M^+]: 269.0674, *found*: 269.0671.

Compound 20: Colorless oil, 65%. ^{1}H NMR (300 MHz, CD_3CN, ppm) δ = 6.46 (dd, *J* = 3.7, 3.0 Hz, 1H), 6.77 (dd, *J* = 3.7, 1.8 Hz, 1H), 6.91 – 6.98 (m, 2H), 7.24 – 7.41 (m, 6H), 7.45 – 7.52 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 108.4, 110.2, 115.8, 118.9, 122.3, 125.5, 126.3, 127.5, 127.9, 128.9, 132.3, 139.0, 147.1; IR (neat, cm^{-1}): 3048, 2225, 1590, 1498, 1482, 1455, 1434, 1394, 1319, 1139, 1077, 1036, 1014, 961, 912, 820, 763, 728, 692, 645, 620, 607; HRMS (EI-pos.) *calcd. for* $C_{17}H_{12}N_2S$ [M^+]: 276.0721, *found*: 276.0716.

Compound 21: Colorless oil, 26%. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ = 1.56 (s, 12H), 6.42 (dd, *J* = 3.7, 3.0 Hz, 1H), 6.76 (dd, *J* = 3.7, 1.8 Hz, 1H), 6.90 – 6.95 (m, 2H), 7.13 (dd, *J* = 3.0, 1.8 Hz, 1H), 7.20 – 7.22 (m, 2H), 7.28 – 7.34 (m, 3H), 7.75 – 7.79 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 28.4, 81.0, 110.0, 117.0, 122.0, 124.8, 126.3, 127.1, 127.7, 128.8, 129.8, 139.3, 145.8, 165.5; IR (neat, cm^{-1}): 2978, 2928, 1707, 1590, 1498, 1456, 1435, 1392, 1366, 1318, 1306, 1290, 1255, 1162, 1139, 1118, 1107, 1090, 1035, 1012, 960, 847, 759, 724, 690, 620; HRMS (ESI-pos.) *calcd. for* $C_{21}H_{28}NO_2S$ [M+H]: 352.1366, *found*: 352.1364.

Compound 22: Colourless oil, 89%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 0.69 (d, *J* = 6.9 Hz, 3H), 0.82 – 1.01 (m, 9H), 1.22 – 1.40 (m, 2H), 1.56 – 1.70 (m, 2H), 2.12 – 2.19 (m, 1H), 2.20 – 2.31 (m, 1H), 3.13 (td, *J* = 10.5, 4.1 Hz, 1H), 4.30 (d, *J* = 11.4 Hz, 1H), 4.56 (d, *J* = 11.4 Hz, 1H), 6.39 (t, *J* = 3.3 Hz, 1H), 6.71 – 6.76 (m, 1H), 6.90 – 6.95 (m, 2H), 7.06 – 7.12 (m, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.20 – 7.25 (m, 2H), 7.27 – 7.36 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 16.2, 21.1, 22.5, 23.4, 25.6, 31.7, 34.7, 40.4, 48.4, 70.1, 78.8, 109.7, 118.5, 121.6, 126.1, 126.4, 126.6, 127.5, 128.6, 128.8, 136.4, 138.6, 139.6; IR (neat, cm^{-1}): 2952, 2918, 2866, 1598, 1498, 1455, 1434, 1319, 1105, 1086, 1073, 1053, 1036, 1015, 834, 804, 760, 721, 692; HRMS (EI-pos.) *calcd. for* $C_{27}H_{33}NOS$ [M^+]: 419.2283, *found*: 419.2275.

Compound 23: Light yellow oil, 69%. ^{1}H NMR (500 MHz, CD_2Cl_2, ppm) δ = 6.07 (dd, *J* = 3.3, 0.9 Hz, 1H), 6.23 – 6.28 (m, 2H), 6.63 (dd, *J* = 3.7, 1.8 Hz, 1H), 6.97 (dd, *J* = 3.0, 1.8 Hz, 1H), 7.33 – 7.37 (m, 3H), 7.39 – 7.49 (m, 3H); ^{13}C NMR (126 MHz, CD_2Cl_2, ppm) δ = 109.7, 111.9, 115.5, 119.6, 119.7, 126.5, 127.4, 128.1, 129.3, 140.0, 145.4, 146.0; IR (neat, cm^{-1}): 1715, 1597, 1498, 1456, 1435, 1391, 1367, 1319, 1213, 1205, 1151, 1136, 1111, 1087, 1073, 1059, 1035, 1004, 958, 905, 880, 762, 720, 692, 656, 634, 615; HRMS (ESI-pos.) *calcd. for* $C_{14}H_{11}NOS$ [M+Na]: 264.0454, *found*: 264.0462.

Compound 24: White solid, 76%.Analyticaly pure material could only be obtained after purification by HPLC with an Agilent Zorbax SB-C18 column using solvent gradient (CH_3CN:H_2O; 65:35 → 100:0). ^{1}H NMR (300 MHz, CD_2Cl_2, ppm) δ = 1.28 (s, 3H), 1.32 (s, 3H), 1.38 (s, 3H), 1.45 (s, 3H), 3.87 – 3.95 (m, 2H), 4.00 – 4.06 (m, 1H), 4.07 – 4.15 (m, 1H), 4.22 – 4.31 (m, 1H), 4.45 – 4.63 (m, 3H), 5.83 (d, *J* = 3.7 Hz, 1H), 6.40 (dd, *J* = 3.6, 3.0 Hz, 1H), 6.72 (dd, *J* = 3.6, 1.8 Hz, 1H), 6.86 – 6.93 (m, 2H), 7.07 - 7.14(m, 3H), 7.20 – 7.39 (m, 5H); ^{13}C NMR (126 MHz, CD_2Cl_2, ppm) δ = 25.8, 26.6, 27.1, 27.2, 67.7, 72.3, 73.2, 81.7, 82.3, 83.1, 105.8, 109.3, 110.1, 112.1, 118.6, 121.9, 126.3, 126.8, 127.1, 127.9, 128.8, 129.1, 135.5, 139.5, 139.9; IR (ATR, cm^{-1}): 2917, 2360, 2341, 1595, 1559, 1498, 1456, 1432, 1380, 1372, 1320, 1252, 1214, 1164, 1121, 1075, 1017, 849, 761, 720, 693, 672, 653; HRMS *calcd.* (EI-pos.) *for* $C_{29}H_{33}NO_6S$ [M^+]: 524.2101, *found*: 524.2085.

Compound 25: White solid, 54%. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ = 6.48 (dd, *J* = 3.6, 3.0 Hz, 1H), 6.76 (dd, *J* = 3.7, 1.8 Hz, 1H), 7.16 – 7.26 (m, 3H), 7.39 – 7.44 (m, 3H), 7.56 – 7.61 (m, 2H), 7.71 – 7.74 (m, 1H), 8.06 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 109.8, 114.9, 116.5, 121.2, 126.1, 126.4, 126.5, 127.1, 127.2, 127.3, 128.4, 128.6, 129.7, 137.9, 139.9, 146.7, 159.2; IR (ATR, cm^{-1}): 3054, 1541, 1495, 1485, 1365, 1321, 1144, 1133, 1111, 1091, 1036, 954, 906, 878, 863, 769, 748, 719, 693, 686, 676, 649, 601; HRMS (EI-pos.) *calcd. for* $C_{19}H_{13}BrN_2S$ [M^+]: 379.9983, *found*: 379.9983.

Compound 26: White solid, 74%. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ = 3.82 (s, 3H), 6.43 (dd, *J* = 3.7, 2.9 Hz, 1H), 6.78 (dd, *J* = 3.7, 1.8 Hz, 1H), 6.86 – 6.92 (m, 4H), 7.12 (dd, *J* = 3.0, 1.8 Hz, 1H), 7.21 – 7.24 (m, 2H), 7.30 – 7.35 (m, 5H), 7.42 – 7.48 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 55.5, 87.9, 89.6, 109.8, 114.1, 115.4, 117.7, 120.4, 121.7,

125.7, 126.4, 126.8, 127.6, 128.7, 131.8, 133.0, 139.4, 139.8, 159.6; IR (ATR, cm^{-1}): 1604, 1509, 1498, 1456, 1436, 1396, 1319, 1286, 1244, 1179, 1172, 1138, 1106, 1031, 1011, 820, 763, 728, 694, 621; HRMS (EI-pos.) *calcd. for* $C_{25}H_{19}NOS$ $[M^+]$: 381.1187, *found*: 381.1186.

Compound 27: White solid, 79%. ^1H NMR (300 MHz, CD_3CN, ppm) δ = 6.50 (dd, *J* = 3.8, 3.0 Hz, 1H), 6.93 (dd, *J* = 3.8, 1.8 Hz, 1H), 7.24 – 7.34 (m, 2H), 7.35 – 7.44 (m, 7H), 7.70 – 7.75 (m, 1H), 7.76 – 7.80 (m, 1H); ^{13}C NMR (126 MHz, CD_3CN, ppm) δ 111.3, 116.0, 122.3, 122.5, 123.8, 125.3, 127.2, 127.5, 129.1, 129.6, 129.9, 136.3, 139.7, 155.1, 173.2; IR (ATR, cm^{-1}): 3054, 2925, 1591, 1495, 1464, 1454, 1428, 1390, 1319, 1237, 1141, 1078, 1068, 1001, 958, 916, 765, 754, 726, 720, 691, 672, 617; HRMS (EI-pos.) *calcd. for* $C_{17}H_{12}N_2S_2$ $[M^+]$: 308.0442, *found*: 308.0449.

Compound 28: Colourless oil, 64%. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ = 6.39 – 6.43 (m, 1H), 6.77 (ddd, *J* = 3.7, 1.8, 0.3 Hz, 1H), 7.12 (ddd, *J* = 3.0, 1.8, 0.3 Hz, 1H), 7.19 – 7.23 (m, 2H), 7.29 (td, *J* = 2.0, 0.3 Hz, 1H), 7.32 – 7.40 (m, 3H), 8.02 (s, 1H), 8.32 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 110.2, 115.6, 122.0, 126.5, 127.5, 128.0, 128.9, 136.2, 139.0, 144.9, 147.1; IR (neat, cm^{-1}): 3007, 2951, 2844, 1541, 1409, 1369, 1311, 1106, 1085, 1061, 1005, 983, 951, 875, 752, 686, 645; HRMS (EI-pos.) *calcd. for* $C_{15}H_{11}BrN_2S$ $[M^+]$: 329.9826, *found*: 329.9821.

Compound 29: White solid, 65%. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ = 3.76 (s, 3H), 6.28 (ddd, *J* = 3.4, 2.5 Hz, 1H), 6.54 (ddd, *J* = 3.4, 2.5, 1.5 Hz, 1H), 6.76 – 6.85 (m, 2H), 6.86 – 6.93 (m, 1H), 7.05 – 7.12 (m, 2H), 8.26 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 55.5, 110.4, 114.8, 117.7, 117.8, 121.5, 128.9, 129.3, 158.4; IR (ATR, cm^{-1}): 3366, 2939, 2836, 1590, 1574, 1490, 1461, 1440, 1405, 1284, 1236, 1174, 1108, 1088, 1074, 1024, 1007, 928, 820, 795, 724, 656, 636, 622; HRMS (ESI-pos.) *calcd. for* $C_{11}H_{11}NOS$ [M+H]: 206.0634, *found*: 206.0630.

Compound 30: White solid, 87%. ^1H NMR (500 MHz, $CDCl_3$, ppm) δ = 3.73 (s, 3H), 3.83 (s, 3H), 6.69 – 6.78 (m, 2H), 7.09 – 7.17 (m, 2H), 7.13 – 7.20 (m, 1H), 7.25 – 7.33 (m, 1H), 7.32 (s, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 33.3, 55.5, 102.6, 109.7, 114.5, 119.8, 120.4, 122.5, 128.5, 129.8, 130.1, 134.5, 137.5, 157.8; IR (ATR, cm^{-1}): 2934, 2831, 1592, 1572, 1509, 1489, 1458, 1440, 1420, 1354, 1334, 1315, 1284, 1237, 1172, 1154, 1125, 1111, 1089, 1028, 1008, 820, 796, 766, 739, 637, 624, 610; HRMS (EI-pos.) *calcd. for* $C_{16}H_{15}NOS$ $[M^+]$: 269.0869; *found*: 269.0873.

Compound 31: White solid, 33%. ^1H NMR (300 MHz, CD_3CN, ppm) δ = 3.68 (s, 3H), 3.70 (s, 3H), 6.70 – 6.76 (m, 2H), 6.92 – 6.98 (m, 2H), 7.11 – 7.19 (m, 1H), 7.30 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.48 – 7.57 (m, 7H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 31.9, 55.5, 101.5, 109.8, 114.3, 114.5, 119.9, 120.9, 122.8, 127.8, 128.1, 128.3, 128.7, 129.9, 130.8, 137.6, 145.5, 157.5; IR (ATR, cm^{-1}): 2922, 2852, 1490, 1460, 1436, 1379, 1285, 1277, 1238, 1176, 1034, 1024, 1011, 824, 815, 797, 737, 697, 620; HRMS (EI-pos.) *calcd. for* $C_{22}H_{19}NOS$ $[M^+]$: 345.1178, *found*: 345.1187.

Synthesis of 32: White solid, 61%. ^1H NMR (400 MHz, CD_2Cl_2, ppm) δ = 3.77 (s, 3H), 3.89 (s, 3H), 6.92 (d, *J* = 2.6 Hz, 2H), 7.16 – 7.29 (m, 5H), 9.53 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 56.3, 56.4, 94.5, 100.9, 108.0, 123.0, 126.7, 127.5, 128.5, 129.4, 131.7, 135.4, 147.8, 151.6, 161.5; IR (ATR, cm^{-1}): 2921, 1671, 1632, 1579, 1508, 1476, 1462, 1437, 1258, 1228, 1205, 1173, 1149, 1086, 1049, 1021, 1004, 913, 836, 797, 735, 689, 663; HRMS (ESI-pos.) *calcd. for* $C_{17}H_{15}NO_4S$ [M+Na]: 352.0614, *found*: 352.0610.

Compound 33: White solid, 76%. ^1H NMR (300 MHz, CD_2Cl_2, ppm) δ 2.20 – 2.31 (m, 2H), 3.00 (dd, *J* = 6.7, 5.5 Hz, 2H), 3.72 (s, 3H), 4.13 – 4.27 (m, 2H), 6.72 – 6.75 (m, 2H), 6.93 – 7.04 (m, 2H), 7.11 – 7.15 (m, 2H), 7.30 – 7.36 (m, 2H); ^{13}C NMR (126 MHz, CD_2Cl_2, ppm) δ = 23.5, 25.1, 45.0, 55.8, 102.5, 114.8, 117.1, 119.8, 121.1, 123.0, 127.7, 129.1, 130.6, 132.3, 135.4, 158.3; IR (ATR, cm^{-1}): 2932, 1591, 1490, 1460, 1439, 1379, 1363, 1323, 1284, 1240, 1174, 1163, 1153, 1103, 1030, 958, 822, 777, 748, 608; HRMS (ESI-pos.) *calcd. for* $C_{18}H_{17}NOS$ [M+H]: 296.1104, *found*: 296.1094.

Compound 34: Colorless oil, 85%. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 2.46 (d, *J* = 1.1 Hz, 3H), 3.77 (s, 3H), 6.67 (dt, *J* = 3.5, 1.1 Hz, 1H), 6.79 – 6.85 (m, 2H), 7.05 (d, *J* = 3.5 Hz, 1H), 7.24 – 7.28 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 15.9, 55.5, 114.7, 125.9, 129.1, 130.6, 130.7, 134.9, 145.3, 158.8; IR (neat, cm^{-1}): 2917, 2831, 1592, 1573, 1490, 1459, 1439, 1285, 1241, 1212, 1172, 1160, 1104, 1065, 1030, 1006, 953, 822, 794, 637, 625; HRMS (EI-pos.) *calcd. for* $C_{12}H_{12}OS_2$ $[M^+]$: 236.0330, *found*: 236.0324.

Compound 35: White solid, 41%. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ = 3.72 (s, 3H), 3.84 (s, 3H), 3.87 (s, 3H), 6.71 – 6.76 (m, 2H), 6.93 – 7.05 (m, 4H), 7.29 – 7.32 (m, 1H), 7.61 – 7.70 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 55.5, 55.5, 55.8, 105.0, 114.0, 114.8, 114.8, 118.4, 124.5, 126.2, 128.2, 128.5, 131.0, 135.2, 137.4, 139.4, 146.1, 157.9, 160.0; IR (ATR, cm^{-1}): 2934, 2832, 1603, 15712, 1557, 1524, 1490, 1471, 1436, 1402, 1299, 1285, 1113, 1062, 985, 905, 820, 803, 766, 731, 647, 636, 621; HRMS (EI-pos.) *calcd. for* $C_{23}H_{20}O_2S_2$ $[M^+]$: 408.0854, *found*: 408.0854.

Compound 36: Colorless oil, 65%. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ = 3.00 (s, 6H), 6.69 – 6.75 (m, 2H), 7.05 – 7.13 (m, 3H), 7.14 – 7.25 (m, 2H), 7.38 – 7.42 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ = 40.5, 113.1, 117.6, 125.1, 127.0, 128.9, 136.3, 140.4, 150.8; IR (neat, cm^{-1}): 2880, 1678, 1592, 1551, 1504, 1475, 1439, 1355, 1314, 1260, 1224, 1193, 1167, 1129, 1100, 1085, 1063, 1023, 998, 944, 906, 811, 765, 736, 689, 644, 621, 610; HRMS (ESI-pos.) *calcd. for* $C_{14}H_{15}NS$ [M+H]: 230.0998, *found*: 230.0999.

Compound 37: Colorless oil, 75%. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ = 2.29 (s, 3H), 2.98 (s, 6H), 6.66 – 6.74 (m, 2H), 7.00 – 7.09 (m, 4H), 7.34 – 7.40 (m, 2H).[21]

Compound 38: White solid, 90%. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ = 2.86 (s, 6H), 3.67 (s, 3H), 6.53 – 6.61 (m, 2H), 6.67 – 6.73 (m, 2H), 7.06 – 7.13 (m, 2H), 7.18 – 7.27 (m, 2H);^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ = 40.5, 55.4, 113.1, 114.7, 120.6, 129.7, 131.0, 134.4, 137.4, 150.2, 158.4; IR (ATR, cm^{-1}): 2855, 1590, 1488, 1453, 1357, 1281, 1230, 1194, 1029, 808, 629; HRMS (EI-pos.) *calcd. for* $C_{15}H_{17}NOS$ $[M^+]$: 259.1031, *found*: 259.1024.

Compound 39: White solid, 51%. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ = 0.71 (d, *J* = 6.9 Hz, 3H), 0.86 – 1.01 (m, 9H), 1.22 – 1.44 (m, 2H), 1.64 (ddt, *J* = 12.6, 9.7, 3.2 Hz, 2H), 2.17 (dtd, *J* = 12.2, 3.8, 1.9 Hz, 1H), 2.27 (hd, *J* = 7.0, 2.8 Hz, 1H), 2.99 (s, 6H), 3.14 (td, *J* = 10.6, 4.2 Hz, 1H), 4.32 (d, *J* = 11.4 Hz, 1H), 4.58 (d, *J* = 11.4 Hz, 1H), 6.67 – 6.73 (m, 2H), 7.08 – 7.13 (m, 2H), 7.17 – 7.22 (m, 2H), 7.34 – 7.40 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 16.3, 21.2, 22.6, 23.5, 25.7, 31.8, 34.8, 40.5, 40.5, 48.5, 77.2, 78.8, 113.1, 118.1, 127.3, 128.4, 135.8, 136.2, 139.1, 150.6; IR (ATR, cm^{-1}): 2950, 2917, 2865, 1593, 1505, 1491, 1444, 1356, 1224, 1193, 1169, 1103, 1082, 1066, 1014, 945, 806, 656; HRMS (EI-pos.) *calcd. for* $C_{25}H_{35}NOS$ $[M^+]$: 397.2439, *found*: 397.2436.

Compound 40: White solid, 65%. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 3.79 (s, 3H), 3.80 (s, 3H), 3.84 (s, 3H), 6.40 – 6.46 (m, 1H), 6.49 (d, *J* = 2.6 Hz, 1H), 6.82 – 6.86 (m, 2H), 7.08 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.25 –

7.30 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 55.5, 55.6, 56.1, 99.2, 105.3, 114.8, 115.9, 126.4, 132.7, 133.4, 158.8, 158.9, 160.7; IR (ATR, cm^{-1}): 2937, 2833, 1589, 1573, 1490, 1459, 1436, 1410, 1300, 1280, 1240, 1206, 1161, 1159, 1102, 1008, 933, 917, 821, 794, 635, 622; HRMS (EI-pos.) *calcd. for* $C_{15}H_{16}O_3S$ [M^+]: 276.0820, *found*: 276.0825.

Compound 41: Colorless oil, 64%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ = 1.02 (d, *J* = 6.7 Hz, 6H), 2.72 (hept, *J* = 6.7 Hz, 1H), 6.29 (dd, *J* = 3.5, 2.9 Hz, 1H), 6.54 (dd, *J* = 3.6, 1.8 Hz, 1H), 7.00 (dd, *J* = 2.9, 1.8 Hz, 1H), 7.32 – 7.49 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 23.1, 40.5, 108.9, 120.1, 121.6, 125.6, 126.8, 127.2, 128.7, 140.1; IR (neat, cm^{-1}): 2958, 2921, 2858, 1597, 1498, 1455, 1432, 1363, 1319, 1237, 1153, 1133, 1089, 1073, 1050, 1034, 959, 761, 718, 616, 607; HRMS (EI-pos.) *calcd. for* $C_{13}H_{15}NS$ [M^+]: 217.0925, *found*: 217.0923.

Compound 42: Yellow oil, 67%. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ = 0.75 (t, *J* = 7.4 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H), 1.22 – 1.29 (m, 1H), 1.30 – 1.40 (m, 1H), 2.46 (h, *J* = 6.8 Hz, 1H), 6.28 (dd, *J* = 3.6, 2.9 Hz, 1H), 6.54 (dd, *J* = 3.6, 1.8 Hz, 1H), 7.00 (dd, *J* = 3.0, 1.8 Hz, 1H), 7.34 – 7.41 (m, 4H), 7.42 – 7.46 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 11.5, 20.6, 29.4, 47.3, 108.9, 120.2, 121.3, 125.5, 126.9, 127.2, 128.6, 140.1; IR (neat, cm^{-1}): 2961, 2920, 1597, 1515, 1498, 1455, 1432, 1374, 1319, 1133, 1089, 1072, 1035, 958, 797, 761, 717, 692, 621, 607; HRMS (EI-pos.) *calcd. for* $C_{14}H_{17}NOS$ [M^+]: 231.1082, *found*: 231.1088.

Compound 43: Colorless oil, 83%. ^{1}H NMR (300 MHz, CD_2Cl_2, ppm) δ = 1.44 (p, *J* = 7.3 Hz, 3H), 1.92 – 2.02 (m, 2H), 2.38 (d, *J* = 7.1 Hz, 2H), 4.87 – 4.89 (m, 1H), 4.91 – 4.95 (m, 1H), 5.67 (ddt, *J* = 15.9, 10.7, 6.7 Hz, 1H), 6.26 (dd, *J* = 3.6, 3.0 Hz, 1H), 6.49 (dd, *J* = 3.6, 1.8 Hz, 1H), 6.98 (dd, *J* = 3.0, 1.8 Hz, 1H), 7.34 – 7.51 (m, 5H); ^{13}C NMR (126 MHz, CD_2Cl_2, ppm) δ = 28.9, 32.8, 37.2, 109.4, 115.2, 119.2, 122.5, 125.7, 127.0, 127.7, 129.1, 138.3, 140.4; IR (neat, cm^{-1}): 2926, 1718, 1639, 1597, 1516, 1498, 1455, 1433, 1393, 1319, 1295, 1273, 1257, 1205, 1174, 1133, 1089, 1073, 1034, 1000, 990, 958, 910, 879, 824,797, 761, 717, 692, 661, 641, 619, 606; HRMS (ESI-pos.) *calcd. for* $C_{15}H_{17}NS$ [M+H]: 244.1154, *found*: 244.1157.

Compound 44: Colorless oil, 91%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ = 1.77 – 1.81 (m, 3H), 4.47 – 4.49 (m, 1H), 4.87 – 4.90 (m, 1H), 6.34 (dd, *J* = 3.6, 2.9 Hz, 1H), 6.63 (dd, *J* = 3.6, 1.8 Hz, 1H), 7.06 (dd, *J* = 3.0, 1.8 Hz, 1H), 7.32 – 7.45 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 22.2, 108.7, 109.5, 118.7, 121.1, 126.1, 127.4, 128.7, 139.7, 143.3; IR (neat, cm^{-1}): 2955, 1596, 1489, 1456, 1448, 1433, 1393, 1320, 1290, 1240, 1204, 1180, 1172, 1161, 1137, 1105, 1087, 1029, 1003, 821, 808, 795, 761, 725, 691, 650, 635, 619; HRMS (EI-pos.) *calcd. for* $C_{13}H_{13}NS$ [M^+]: 215.0769, *found*: 215.0767.

Compound 45: Colourless oil, 88%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 1.64 (dd, *J* = 1.2, 0.5 Hz, 3H), 1.66 – 1.69 (m, 3H), 5.55 – 5.58 (m, 1H), 6.30 (dd, *J* = 3.6, 3.0 Hz, 1H), 6.53 (dd, *J* = 3.6, 1.8 Hz; 1H), 6.98 (dd, *J* = 2.9, 1.8 Hz, 1H), 7.33 – 7.48 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 19.3, 25.1, 109.2, 117.4, 119.4, 122.3, 125.1, 126.6, 127.2, 128.7, 134.9, 139.8; IR (neat, cm^{-1}): 2909, 1597, 1498, 1454, 1434, 1371, 1319, 1299, 1133, 1088, 1072, 1060, 1034, 959, 798, 760, 716, 692, 664, 619, 606; HRMS (ESI-pos.) *calcd. for* $C_{14}H_{15}NS$ [M+H]: 230.0998, *found*: 230.0995.

Compound 46: Colorless oil, 64%. ^{1}H NMR (300 MHz, CD_2Cl_2, ppm) δ = 0.79 (t, 3H), 1.25 – 1.34 (m, 4H), 1.45 – 1.57 (m, 2H), 2.59 – 2.69 (m, 2H), 3.34 (s, 3H), 7.13 – 7.37 (m, 4H), 7.71 (ddd, *J* = 7.6, 1.5, 0.8 Hz, 1H); ^{13}C NMR (126 MHz, CD_2Cl_2, ppm) δ = 14.1, 22.3, 32.6, 33.4, 37.0, 104.4, 110.1, 119.7, 120.2, 122.5, 130.6, 134.4, 137.8; IR (neat, cm^{-1}): 3057, 2917, 1512, 1488, 1476, 1462, 1419, 1329, 1315, 1241, 1204, 1152, 1133, 1100, 1077, 1012, 883, 762, 735, 710; HRMS (ESI-pos.) *calcd. for* $C_{13}H_{17}NS$ [M+H]: 220.1154, *found*: 220.1151.

Compound 47: Colourless oil, 94%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 1.23 (d, *J* = 6.7 Hz, 6H), 2.96 (s, 6H), 3.11 (hept, *J* = 6.7 Hz, 1H), 6.60 – 6.72 (m, 2H), 7.30 – 7.42 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = 23.4, 40.0, 40.6, 112.6, 119.8, 136.1, 150.2; IR (neat, cm^{-1}): 2956, 2922, 2860, 1592, 1502, 1443, 1350, 1224, 1193, 1167, 1153, 1130, 1100, 1060, 1049, 945, 811; HRMS (EI-pos.) *calcd. for* $C_{11}H_{17}NS$ [M^+]: 195.1082, *found*: 195.1089.

Compound 48: Colourless oil, 62%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ = 1.50 – 1.64 (m, 4H), 1.69 – 1.81 (m, 2H), 1.84 – 2.01 (m, 2H), 2.95 (s, 6H), 3.29 – 3.41 (m, 1H), 6.60 – 6.70 (m, 2H), 7.32 – 7.39 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ = 24.7, 33.5, 40.6, 48.8, 112.8, 121.3, 135.1, 150.1; IR (neat, cm^{-1}): 2952, 2799, 1593, 1502, 1443, 1350, 1223, 1192, 1167, 945, 810; HRMS (ESI-pos.) *calcd. for* $C_{13}H_{19}NS$ [M+H]: 222.1311, *found*: 222.1317.

Compound 49: White solid, 89%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ = 1.96 (dd, *J* = 1.4, 0.8 Hz, 3H), 2.98 (s, 6H), 4.57 (s, 1H), 4.93 (q, *J* = 1.4 Hz, 1H), 6.63 – 6.73 (m, 2H), 7.31 – 7.39 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ = 22.8, 40.4, 108.4, 112.8, 117.3, 136.4, 144.0, 150.8; IR (ATR, cm^{-1}): 2914, 1594, 1551, 1505, 1481, 1444, 1356, 1315, 1288, 1225, 1189, 1169, 1129, 1101, 1063, 1001, 846, 922, 853, 813, 766, 716, 616; HRMS (EI-pos.) *calcd. for* $C_{11}H_{15}NS$ [M^+]: 193.0925, *found*: 193.0920.

Synthesis of 51: 2-Selenoimidazoline (75.0 mg, 0.289 mmol) and *N*-chlorosuccinimide (38.6 mg, 0.289 mmol) were dissolved in MeCN (2 mL) and the mixture was stirred for 5 min at r.t. Removal of the solvents *in vacuo* afforded **51** as a light yellow solid (114 mg, 0.289 µmol, quantitative). ^{1}H NMR (400 MHz, CD_2Cl_2, ppm) δ = 1.48 – 1.70 (m, 12H), 2.36 (s, 6H), 2.61 (s, 4H), 6.03 (hept, *J* = 7.0 Hz, 2H); ^{13}C NMR (101 MHz, CD_2Cl_2, ppm) δ 10.9, 21.3, 30.1, 56.1, 129.0, 142.8, 180.6; IR (ATR, cm^{-1}): 2176, 2037, 2029, 1983, 1969, 1707, 1594, 1511, 1360, 1178, 670, 658, 634, 624; HRMS (ESI-pos.) *calcd. for* $C_{15}H_{24}N_3O_2S$ [M^+]: 358.1029, *found*: 358.1031.

Representative synthesis of arylselenoimidazolium salts. Synthesis of 52: *N*-Methylindole (87 µL, 91 mg, 0.694 mmol) was added to a solution of **51** (273 mg, 0.694 mmol.) in MeCN (5 mL) and the mixture stirred at 70 °C for 17 h. Removal of the volatiles afforded a red solid, which was dissolved in DCM (5 mL) and washed with sat. aq. $NaSbF_6$ (3.0 mL). After separation of the two phases, the organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. Crude **52** was purified by column chromatography (DCM:MeOH; 100:0→95:5). Yellow foam (244 mg, 0.390 mmol, 56%). ^{1}H NMR (300 MHz, CD_2Cl_2, ppm) δ = 1.47 (d, *J* = 7.1 Hz, 12H), 2.32 (s, 6H), 3.85 (s, 3H), 5.63 (s, 2H), 7.26 – 7.38 (m, 2H), 7.41 – 7.46 (m, 2H), 7.59 – 7.64 (m, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2, ppm) δ = 10.9, 21.4, 33.9, 55.2, 92.2, 111.2, 119.1, 122.1, 123.8, 129.7, 130.5, 136.9, 137.7; IR (ATR, cm^{-1}): 2964, 2924, 2901, 1433, 1398, 1385, 1359, 1344, 1324, 1229, 1198, 1162, 1145, 1121, 1091, 945, 760, 602; HRMS (ESI-pos.) *calcd. for* $C_{20}H_{28}N_3Se$ [M^+]: 390.1444, *found*: 390.1461; (ESI-neg.) *calcd. for* SbF_6^- [M^-]: 234.8948, fou*nd*: 234.8957.

Compound 53: Yellow solid, 48%. ^{1}H NMR (300 MHz, CD_2Cl_2, ppm) δ 1.32 (d, *J* = 7.1 Hz, 12H), 2.29 (s, 6H), 5.02 (hept, *J* = 7.1 Hz, 2H), 6.41 (dd, *J* = 3.8, 3.0 Hz, 1H), 6.74 (dd, *J* = 3.8, 1.8 Hz, 1H), 7.13 (dd, *J* = 3.0, 1.7 Hz, 1H), 7.30 – 7.35 (m, 2H), 7.48 – 7.60 (m, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2, ppm) δ = 10.8, 21.3, 55.2, 109.6, 111.9, 123.6, 126.6, 129.0, 129.2, 130.2, 130.8, 139.5; IR (ATR, cm^{-1}): 3089, 3033, 2961, 2903, 1767, 1747, 1605, 1509, 1439, 1405, 1384, 1334, 1305, 1234, 1195,

1147, 1133, 1121, 1098, 1082, 914, 756, 716, 710, 618; HRMS (ESI-pos.) *calcd. for* $C_{21}H_{28}N_3Se$ [M^+]: 402.1444, *found*: 402.1456; (ESI-neg.) *calcd. for* SbF_6^- [M^-]: 234.8948, *found*: 234.8954.

Compound 54: Orange solid, 60%. ^{1}H NMR (300 MHz, CD_2Cl_2, ppm) δ = 2.36 (s, 6H), 2.96 (s, 6H), 5.47 (s, 2H), 6.65 (d, *J* = 8.9 Hz, 2H), 7.34 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (101 MHz, CD_2Cl_2, ppm) δ = 10.9, 21.5, 40.4, 55.2, 109.4, 114.0, 130.7, 136.0, 152.1; IR (ATR, cm^{-1}): 2984, 2943, 2887, 2816, 1715, 1619, 1590, 1508, 1464, 1445, 1417, 1363, 1332, 1318, 1264, 1217, 1198, 1174, 1138, 1112, 1076, 1067, 991, 953, 945, 906, 815, 750, 738, 711, 653; HRMS (ESI-pos.) *calcd. for* $C_{19}H_{30}N_3Se$ [M^+]: 380.1600, *found*: 380.1595; (ESI-neg.) *calcd. for* SbF_6^- [M^-]: 234.8948, *found*: 234.8957.

Representative synthesis of diarylselenides. Synthesis of 55: *p*-Methoxyphenylmagnesium bromide (0.5 M in THF, 1.08 mL, 0.540 mmol, 1.5 equiv.) was added dropwise to a suspension of **52** (225 mg, 0.360 mmol) in THF (2.0 mL) at -78 °C. and the mixture allowed to warm up to r.t. overnight. The orange solution thus obtained was quenched with sat. NH_4Cl (5 mL) and extracted with DCM (3 x 20 mL). The combined organic phases were dried over $MgSO_4$, concentrated *in vacuo* and the residue was purified by column chromatography (Hexane:DCM; 80:20→0:100) to obtain **55** as a white solid (104.6 mg, 0.331 mmol, 92%). ^{1}H NMR (300 MHz, CD_2Cl_2, ppm) δ = 3.71 (s, 3H), 3.83 (s, 3H), 6.71 (d, *J* = 8.8 Hz, 2H), 7.14 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.23 – 7.29 (m, 3H), 7.35 (s, 1H), 7.36 – 7.41 (m, 1H), 7.59 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (101 MHz, CD_2Cl_2, ppm) δ = 33.5, 55.8, 97.8, 110.2, 115.2, 120.6, 120.7, 122.8, 124.2, 131.0, 131.9, 135.8, 138.1, 159.1; ^{77}Se NMR (76 MHz, CD_2Cl_2, ppm) δ = 196.9; IR (ATR, cm^{-1}): 2939, 1598, 1578, 1497, 1281, 1157, 1118, 1016, 831, 817, 810, 796; HRMS (ESI-pos.) *calcd. for* $C_{16}H_{15}NOSe$ [M+H]: 318.0392, *found*: 318.0388.

Synthesis of 56: Colourless oil, 63%. ^{1}H NMR (300 MHz, CD_2Cl_2, ppm) δ = 3.74 (s, 3H), 6.33 (dd, *J* = 3.6, 2.9 Hz, 1H), 6.66 (dd, *J* = 3.6, 1.8 Hz, 1H), 6.72 (d, *J* = 8.8 Hz, 2H), 7.02 – 7.09 (m, 3H), 7.18 – 7.23 (m, 2H), 7.31 – 7.39 (m, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2, ppm) δ 55.8, 110.3, 115.3, 116.4, 120.9, 121.9, 124.0, 126.7, 127.3, 128.0, 129.1, 130.2, 132.4, 141.0, 159.4; ^{77}Se NMR (76 MHz, CD_2Cl_2, ppm) δ = 262.4; IR (ATR, cm^{-1}): 3050, 2979, 2944, 2915, 1578, 1471, 1444, 1396, 1306, 1207, 1094, 1079, 1011, 795, 776, 745, 704, 610; HRMS (ESI-pos.) *calcd. for* $C_{17}H_{15}NOSe$ [M+H]: 330.0392, *found*: 330.0387.

Synthesis of 57: White solid, 81%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ = 2.95 (s, 6H), 3.77 (s, 3H), 6.64 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ = δ 40.5, 55.4, 113.4, 115.0, 116.0, 123.7, 133.3, 135.7, 150.3, 158.9; ^{77}Se NMR (MHz, $CDCl_3$, ppm) δ = 380.0; IR (ATR, cm^{-1}): 2951, 2918, 2865, 1593, 1505, 1491, 1444, 1357, 1194, 1102, 1083, 1065, 1015, 807; HRMS (ESI-pos.) *calcd. for* $C_{15}H_{17}NOSe$ [M+H]: 308.0549, *found*: 308.0541.

Synthesis of 58: White solid, 74%. ^{1}H NMR (300 MHz, CD_2Cl_2, ppm) δ = 2.27 – 2.36 (m, 2H), 2.78 (t, *J* = 8.0 Hz, 2H), 2.93 (s, 6H), 6.20 (t, *J* = 4.7 Hz, 1H), 6.61 – 6.68 (m, 2H), 7.09 – 7.20 (m, 3H), 7.35 – 7.43 (m, 2H), 7.50 – 7.59 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ = δ 25.7, 28.5, 40.7, 113.6, 114.3, 126.3, 126.9, 127.8, 127.9, 130.8, 133.0, 134.8, 135.8, 136.9, 150.7; ^{77}Se NMR (MHz, $CDCl_3$, ppm) δ = 345.8; IR (ATR, cm^{-1}): 1587, 1503, 1480, 1446, 1424, 1358, 1315, 1277, 1260, 1228, 1195, 1170, 1083, 1066, 1043, 1029, 1015, 953, 935, 809, 779, 758, 729, 690; HRMS (ESI-pos.) *calcd. for* $C_{18}H_{19}N_1Se$ [M+H]: 330.0756; *found*: 330.0750.

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[1] (a) M. Kvasnika, M. Urban, N. J. Dickinson, J. Sarek, *Nat. Prod. Rep.* **2015**, *32*, 1303-1330; (b) D. Meng, W. Chen, W. Zhao, *J. Nat. Prod.* **2007**, *70*, 824-829; (c) M. R. Prinsep, *Stud. Nat. Prod. Chem.* **2003**, *28*, 617-751

[2] M. Feng, B. Tang, S. H. Liang, X. Jiang, *Curr. Top. Med. Chem.* **2016**, *16*, 1200-1216.

[3] (a) D. A. Boyd, *Angew. Chem. Int. Ed.* **2016**, *55*, 15486-15502; (b) D. Wu, W. Pisula, M. C. Haberecht, X. Feng, K. Müllen, *Org. Lett.* **2009**, *11*, 5686-5689; (c) S. M. Yang, J. J. Shie, J. M. Fang, S. K. Nandy, Y. Y. Chang, *J. Org. Chem.* **2002**, *67*, 5208-5215.

[4] (a) J. C. Carretero, *Chem. Commun.* **2011**, *47*, 2207-2211; (b) *Chiral Sulfur Ligands in Asymmetric Catalysis,* H. Pellisier, RSC Catalysis Series 2, Cambridge **2009**.

[5] (a) A. Kausar, S. Zulfiqar, M. I. Sarwar, *Pol. Rev.* **2014**, *54,* 185-267; (b) A. S. Rahate, K. R. Nemade, S. A. Waghuley, *Rev. Chem. Eng.* **2013**, *29*, 471-489; (c) N. Spassky, *Phosphorus Sulfur Silicon Relat. Elem.* **1993,** *74*, 71-92.

[6] C. C. Eichman, J. P. Stambuli, *Molecules*, **2011**, *16*, 590-608.

[7] For selected references: (a) G. Bastug, S. P. Nolan, *J. Org. Chem.* **2013**, *78*, 9303-9308; (b) M. Sayah, M. G. Organ, *Chem. Eur. J.* **2011**, *17*, 11719-11722; (c) M. Arisawa, T. Suzuki, T. Ishikawa, M. Yamaguchi, *J. Am. Chem. Soc.* **2008,** *130*, 12214-12215; (d) M. A. Fernández-Rodríguez, Q. Shen, J. F. Hartwig, *J. Am. Chem. Soc.* **2006**, *128*, 2180-2181; (e) M. Murata, S. L. Buchwald, *Tetrahedron*, **2004**, *60*, 7397-7403.

[8] For selected references: (a) Z. Qiao, N. Gea, X. Jiang, *Chem. Commun.* **2015**, *51*, 10295-10298; (b) X. B. Xu, J. Liu, J. J. Zhang, Y. W. Wang, Y. Peng, *Org. Lett.* **2013**, *15*, 550-553; (c) Y. Zhang, K. C. Ngeow, J. Y. Ying, *Org. Lett.* **2007**, *9*, 3495-3498; (d) O. Baldovino-Pantaleón, S. Hernández-Ortega, D. Morales-Morales, *Adv. Synth. Catal.,* **2006**, *348,* 236-242; (e) Y. C. Wong, T. T. Jayanth, C. H. Cheng, *Org. Lett.* **2006**, *8*, 5613-5616.

[9] See the "*Q3D Elemental Impurities Guidance for Industry*." U. S. Department of Health and Human Service, **2015**.

[10] C. L. Sun, Z. J. Shi, *Chem. Rev.* **2014**, *114*, 9219-9280.

[11] (a) T. Hostier, V. Ferey, G. Ricci, D. Gómez-Pardo, J. Cossy, *Chem. Commun.* **2015**, *51*, 13898-13901; (b) T. Hostier, V. Ferey, G. Ricci, D. Gomez-Pardo, J. Cossy, *Org. Lett.* **2015***, 17,* 3898−3901; (c) M. Tudge, M. Tamiya, C. Savarin, G. R. Humphrey, *Org. Lett.* **2006, 8,** 565-568.

[12] Q. Wu, D. Zhao, X. Qin, J. Lan, J. You, *Chem. Commun.* **2011**, *47*, 9188-9190.

[13] (a) F. Xiao, H. Xie, S. Liu, G. J. Deng, *Adv. Synth. Catal.,* **2014**, *356,* 364-368; (b) F. Xiao, S. Chen, J. Tian, H. Huang, Y. Liu, G. J. Deng, *Green Chem.* **2016**, *18*, 1538-1546.

[14] J. A. Fernández-Salas, A. P. Pulis, D. J. Procter, *Chem. Commun.* **2016**, *52*, 12364-12367.

[15] a) G. Talavera, J. Peña, M. Alcarazo, *J. Am. Chem. Soc.* **2015**, *137*, 8704-8707; b) H. W. Roesky, U. N. Nehete, S. Singh, H. Schmidt, Y. G. Shermolovich, *Main Group. Chem.* **2005**, *1*, 11-21; c) N. Kuhn, H. Bohnen, J. Fahl, D. Bläser, R. Boese, *Chem. Ber.* **1996**, *127*, 1579-

1586; d) A. J. Arduengo, E. M. Burgess, *J. Am. Chem. Soc.* **1977**, *99*, 2376-2378.

[16] CCDC 1842202 (**1•Cl**), 1842214 (**4**), 1842208 (**6**), 1842198 (**7**), 1842205 (**8**), 1842207 (**9**), 1742205 (**10**), 1842213 (**11**), 1842199 (**13**), 1842200 (**14**), 1842204 (**16**), 1842211(**19**), 1842209 (**20**), 1842201 (**26**), 1842212 (**27**), 1842203 (**32**), 1844013 (**54**) and 1843380 (**SI-1**) contain the supplementary crystallographic data for this article. This data can be obtained free of charge from the Cambridge Chrystallographic Data Centre via www.ccdc.cam.uk/data_request/cif.

[17] „*Structure Correlation*" H. B. Bürgi, J. D. Dunitz, Ed. Wiley **1994**. Apendix A: pages 752-858.

[18] J. Peña, G. Talavera, B. Waldecker, M. Alcarazo, *Chem. Eur. J.* **2017**, *23*, 75-78.

[19] a) A. Krasovskiy, V. Krasovskaya, P. Knochel. *Angew. Chem. Int. Ed.* **2006**, 45, 2958-2961; b) A. Krasovskiy, P. Knochel, *Angew. Chem. Int. Ed.* **2004**, *43*, 3333-3336.

[20] For the synthesis of **50** see: N. Kuhn, G. Henkel, T. Kratz, *Z. Naturforsch. B.* **1993**, *48*, 973-977.

[21] Analytical data were in agreement with those reported: S. K. R. Parumala, R. K. Peddinti *Green Chem.* **2015**, 17, 4068-4073.

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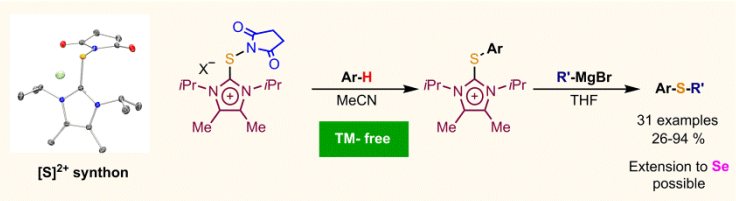

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