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ABSTRACT

In order to address the need for consistency and generality in chemical methods developed for detection of latent fingerprints on paper substrates, a practical protocol was developed using 1,2-indanedione-based bi-functional reagents. A series of novel bi-functional reagents were designed and synthesized using a concise, five-step sequence. An optimized development condition that is tailored to the type of paper substrate that requires processing was discovered, allowing potential application in practical criminal work where evidence processing is an irreversible process. The study also provided an insight to the underlying mechanism of interaction between the bi-functional reagent and fingerprint residue.

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1. Introduction

Latent (hidden or invisible) fingerprint detection on paper substrates is a crucial component in criminal investigations, and is used widely in forensic science due to the fact that society relies heavily on such cellulosic materials (official documents, currency printing, packaging, etc.).¹ When a fingerprint is deposited on a paper substrate, amino acids present in natural skin secretions bind to the cellulose of the paper preserving either a visible or latent impression of the friction ridge patterns. Latent fingerprints are the most common, yet problematic type of evidence found at crime scenes, since they require special methods for development and visualization. Over the years, significant amount of research has been devoted to the discovery and development of chemical methods based on the detection of amino acids present in natural skin secretions.¹ Although a wide variety of chemical reagents (ninhydrin, 1,2-indanedione, 1,8-diazafluoren-9-one) have been identified from this collective effort,^{1,2} over 50% of all fingerprints³ still escape detection. Existing chemical methods rely on a stoichiometric reaction between the detection reagent and an amino acid, thus setting an upper limit to sensitivity. Furthermore, latent fingerprints often do not contain adequate quantities of amino acids, and their composition may vary depending on numerous factors, such as an individual's general health, diet, gender and age.¹ As a result, even the most sensitive chemical reagents do not always produce a sufficiently clear image.

To remedy this limitation, attention has been directed toward utilizing nanotechnology in the development process.^{1b,3-4} In particular, the versatility of surface modification of nanoparticles has been exploited, allowing precise targeting of various components present in fingerprint residues.³⁻⁴ In terms of increasing sensitivity, a process that employs metastable silver colloid solution, silver physical developer (Ag-PD),^{1b,5} has been used as a post-treatment enhancement of gold nanoparticle (AuNP) treated fingerprint deposits on paper substrates, which is a form of multi-metal deposition (MMD).^{1b,1d,6} Another common development method is single-metal deposition (SMD),^{1b,1d,7} in which the enhancement of AuNP treated fingerprint residues occurs via reinforcement with gold colloids in aqueous solution rather than with silver. Although development techniques that employ nanotechnology have been rapidly evolving, sensitivity still remains a tough challenge. For example, current developed processes display inconsistent results amongst various protocols, even for the same type of nanoparticles.³ The precise underlying mechanisms involved in the interaction between the AuNPs (or any other nanoparticles) and the fingerprint residue is yet to be elucidated, most likely due to the complex composition of the fingerprint residue.⁸ Thus far, the mechanism was broadly assumed to be a simple ionic interaction between the negatively charged citrate stabilized AuNPs and the positively charged amino acids of the fingerprint residue at low pH.^{3,5-8} The surprising lack of mechanistic study in this field was brought to attention only recently.⁸ Understanding the precise chemical interaction required for latent fingerprint detection on paper

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substrates is essential in developing protocols that will allow consistent results to be obtained. Moreover, in terms of practical criminal investigation, it is important to be able to choose the optimal development conditions amongst the numerous methods that are in existence, since once the evidence is chemically processed, it cannot be reprocessed.

We have been investigating the mechanism⁹ and application of various 1,2-indanedione analogues in detection of latent fingerprints since our first discovery of the chemical reagent in 1997.^{2e-f} Because of its highly fluorescent properties upon interaction with fingerprint residue, 1,2-indanedione rapidly became a standard reagent in forensic laboratories around the world.^{1b} However, due to limitations set by the stoichiometric nature of the reaction, the variability in the amino acid (or sweat) content on a given fingerprint residue, and the need of using specialized equipment (such as lasers) for visualization, the focus of our recent research efforts has been shifted to application of the well-established 1,2-indanedione interaction with amino acids in fingerprint residues^{2,10} as a platform to utilize nanotechnology as a promising alternative. We have recently reported the viability of using a bi-functional reagent containing a 1,2-indanedione motif that is appended by a ten-carbon alkylthiol chain, following the basic principle of MMD (Scheme 1).¹¹ In order to address the challenging issue of achieving consistency in the development of latent fingerprints as well as elucidating the underlying mechanism between the functionalized AuNPs and fingerprint residues, a thorough investigation of the novel method was deemed crucial. Herein, we wish to report a practical, generalized protocol of using 1,2-indanedione functionalized AuNPs for detection of latent fingerprints on various types of paper substrates and an insight to the mechanism of the interaction.

Scheme 1. Latent fingerprint development using 1,2-indanedione based bi-functional reagent.

2. Results and discussion

Although the modified MMD protocol using a ten-carbon chain bi-functional reagent produced acceptable fingerprint images on paper substrates, the contrast was often poor and inconsistent results were obtained when using sebum-rich (lipids and other hydrophobic substances naturally present in skin) fingerprint deposits. Therefore, an assortment of 1,2-indanedione-based bi-functional reagents that varied in chain lengths was generated to study the resulting chemical effects during the interaction between the reagent and the fingerprint residue, which would ultimately allow the development of a generalized procedure.

2.1. Synthesis of 1,2-indanedione analogues

The synthesis of 1,2-indanedione analogues was achieved using a concise, four-step procedure (Scheme 2).¹¹ Commercially available 5-chloro-1-indanone was treated with the requisite potassium alkyltrifluoroborate salt using the Suzuki-Miyaura cross-coupling reaction to afford the corresponding chain coupled product **7-12** in acceptable yields. **In line with our previous findings,¹¹ 2-dicyclohexylphosphino-2',6'-diisopropoxybiphenyl (RuPhos) was the ligand of choice for all the substrates.** Slight variability in yields was observed for the cross-coupling reaction, possibly due to the different side chain lengths. In general, longer side chains afforded modest yields in comparison to shorter ones. Subsequent displacement of the tosylate moiety with potassium thioacetate generated intermediates **13-18** in good yields. Formation of the oxime (**19-24**), followed by conversion to the desired 1,2-indanedione analogues **25-30** was accomplished using a variation of previously developed methods^{2e-f,9} in quantitative yields without requiring the use of silica gel chromatography purification steps. Not surprisingly, in some cases, a negligible amount of the thiol 1,2-indanedione derivative was observed under the acidic aqueous conditions employed in the last step. The mixture of major and minor 1,2-indanedione products was carried onto the next step of AuNP functionalization, since in situ removal of the thiol protecting group occurs naturally during ligand exchange.^{3,12}

Scheme 2. Synthesis of 1,2-indanedione derivatives **25-30**.

*Synthesis of **13** was achieved using a Mitsunobu reaction (see experimental details).

2.2. Synthesis of bi-functional reagents

Finally, AuNPs stabilized by dodecyltrimethylammonium bromide (DDAB) was synthesized following a modification of a known procedure,¹³ and subsequently functionalized via ligand exchange with 1,2-indanedione analogues **19-24** to afford the corresponding bi-functional reagents. UV-Vis spectroscopy and TEM were used to determine both relative particle size and degree of aggregation of functionalized AuNPs.¹⁴ UV-Vis spectra showed clear shifts in gold plasmon band after ligand exchange with respect to the as-prepared DDAB capped AuNP colloids, indicating changes in the AuNP environment (Figure 1a). The relative extent of peak broadening and red/blue shift in gold plasmon band that were observed from changes in chain length of

bi-functional reagents were reasonable considering the corresponding interparticle separation of AuNPs (Figure 1a). Generally, with shorter ligand chain lengths, separation between particles become smaller (exhibited as aggregation or even fusion), which increases the electromagnetic coupling between the particles and results in larger shifts.^{13,15} For example, the relative degree of aggregation appeared to be more pronounced for three-, five-, and eight-carbon bi-functional derivatives over others, which was implied by either increase in peak broadening or appearance of second absorbance around >700 nm (Figure 1a). TEM images of the bi-functional reagents also showed relative degrees of aggregation, where the most pronounced difference was observed between eight-carbon derivative and twelve-carbon derivative (Figure 1b,c).

Figure 1. a) UV—Vis absorption spectrum comparing various bi-functional reagents synthesized (notation on spectrum indicates carbon chain length). As-is AuNP is the as-prepared DDAB stabilized AuNPs. As-is AuNP $\lambda_{\text{max}} = 567$ nm, 3cAuNP $\lambda_{\text{max}} = 555$ nm, 5cAuNP $\lambda_{\text{max}} = 557$ nm, 8cAuNP $\lambda_{\text{max}} = 576$ nm, 10cAuNP $\lambda_{\text{max}} = 557$ nm, 12cAuNP $\lambda_{\text{max}} = 557$ nm, 14cAuNP $\lambda_{\text{max}} = 542$ nm. All measurements taken in dimethyl sulfoxide. b) TEM image of 8cAuNP. c) TEM image of 12cAuNP.

2.3. Application of bi-functional reagents

Application of these reagents in the development of latent fingerprints on paper was examined next following the initially developed conditions.¹¹ In order to determine and compare the relative efficiency of the bi-functional reagents in detecting amino acids, a controlled amino acid substrate system was designed as a model system. A stamp with an intricate snowflake engraved design was coated with a diluted solution of L-leucine and subsequently stamped gently on a Whatman® filter paper (Figure 2). To eliminate the possibility of obtaining misleading results,⁸ the stamped paper substrate (print invisible to the naked eye) was left to age for at least 2 days and then processed by

immersing the paper in a solution of the requisite bi-functional reagent for 1 min. Subsequent water rinse followed by post-treatment with standard Ag-PD solution for <10 s gave rise to visible marks (Figure 2). Since AuNPs that are functionalized with polar ligands (such as ligands containing a carboxylic acid¹⁶ or an acyl moiety³) have been shown to readily bind to cellulose of the paper via hydrogen-bonding interactions, it was crucial to obtain selective preferential binding with the fingerprint residue over the interaction with cellulose in order to achieve good image contrast after development.

In all cases, a positive mark was obtained, in which the silver deposition was more apparent on the mark in comparison to the background. This result strongly suggests the preferential interaction of the bi-functional reagent with the amino acid regardless of chain length. Furthermore, of the bi-functional reagents tested, the eight-carbon chain derivative produced the most pronounced image after processing, while the ten-carbon chain derivative afforded better contrast against the background. Taken together, these results suggest that there is an optimal chain length for the detection of amino acids on paper.

Figure 2. Model system for determining bi-functional reagent efficiency in detecting amino acids on paper substrate. Visible images obtained from L-leucine (0.0075 M in 30% dioxane in water mixture) treated stamp stamped on a Whatman® filter paper, which was cut in half, where each half was treated with different bi-functional reagent chain derivative (0.01% w/v in dimethyl sulfoxide) followed by water rinse then post-enhancement with Ag-PD. The bi-functional reagent indicating carbon chain length used is shown under each half image. The bottom right image where the right half was treated with Ag-PD only was used as the control.

With this promising result in hand, we then tested the bi-functional reagents on various types of paper substrates bearing fingerprint deposits. Thickness of paper gave a remarkable difference in reactivity and subsequently observed contrast (Figure 3). For instance, consistent with observations on the model system, for thicker Whatman® filter paper substrates (180-190 μm in thickness), the ten-carbon chain derivative gave the best results in terms of contrast (Figure 3a), with the twelve-carbon chain giving almost similar results (Figure 3b). Eight-carbon chain derivative however, resulted in poor contrast, although the rate of silver deposition during Ag-PD treatment seemed the fastest and in greatest quantity. However, with much thinner copy paper substrates (100 μm in thickness), the five-carbon chain derivative afforded the best image (Figure 3c), and the eight-carbon chain derivative following was a close second (Figure 3d). Optimal post-treatment enhancement conditions were also identified depending on the thickness of the paper

substrate. Ag-PD worked well for thicker Whatman® filter paper substrates (Figure 3a-b), while SMD worked better for thinner copy paper substrates (Figure 3c-d). For thinner paper, Ag-PD gave rise to images with poor contrast, while for thicker paper substrates, SMD offered almost no image enhancement, but rather, the difference was significantly augmented by Ag-PD.

Figure 3. Latent fingerprints on different types of paper developed using various bi-functional reagents (0.01% w/v in dimethyl sulfoxide) followed by water rinse and subsequent enhancement with Ag-PD or SMD. a) Whatman® filter paper, treated with the ten-carbon chain bi-functional reagent followed by Ag-PD. b) Whatman® filter paper, treated with the twelve-carbon chain derivative, followed by Ag-PD. c) Standard copy paper, treated with the five-carbon chain derivative followed by SMD. d) Standard copy paper, treated with the eight-carbon chain derivative with no enhancement (no SMD or Ag-PD).

A correlation between the relative aggregation of the bi-functional reagent and the thickness of the paper could explain the obtained results. For thicker paper substrates, relatively less aggregated AuNPs (ten- and twelve-carbon derivatives) produced good image contrast, while for thinner paper, more aggregated particles (five- and eight-carbon derivatives) worked better. However, there is a window of optimal chain lengths for different type of paper substrates. For example, the shortest, and thus most aggregated three-carbon chain derivative displayed poor image contrast, suggesting significantly decreased specificity for both thick and thin paper substrates. The longest, thus relatively less aggregated fourteen-carbon chain derivative gave rise to weak prints on thicker paper substrates, and almost no visible prints for thinner paper. Interestingly, in some cases, for thinner paper substrates, the reaction between the five- or eight-carbon chain derivatives and fingerprint deposits was so rapid and facile that visible prints with good contrast appeared without the need for the second enhancement step (Figure 3d).

In terms of mechanism of binding, the well-established reaction between 1,2-indanedione and amino acids^{2,10} appeared to be the main reaction pathway. For example, reliable and consistent results that were in good agreement with the present findings were obtained with eccrine-rich fingerprints, while inconsistent results were obtained using sebum-rich fingerprints. In order to prove the efficacy of the bi-functional reagents in detecting latent fingerprints, a split-print comparison¹⁻² was

conducted (Figure 4). For the split-print comparison, a fingertip was intentionally charged with eccrine secretions (e.g. saliva), and evenly distributed on the surface. The fingertip was then stamped onto a paper substrate and aged for at least 2 days. The paper was then cut in half and processed using different conditions keeping concentration and reaction time consistent. The optimized protocol for thicker filter paper using the twelve-carbon derivative performed significantly better in all cases when compared side by side with other known conditions. For instance, at the optimized reaction time, Ag-PD alone did not afford clear fingerprints (Figure 4a). When AuNPs that lack 1,2-indanedione moiety were used, relatively weak prints lacking in detail were observed, which could be attributed to the normal electrostatic interaction^{1,8} between the AuNP and amino acid component of the fingerprint residue (Figure 4b). There have been reports on the importance of acidity (~pH 3) with regards to obtaining quality prints.^{8,18} To test this hypothesis in the current system, one half of the filter paper that has eccrine-rich fingerprint deposit was pretreated with a 2.5 w/v% malic acid aqueous solution (pH = 2.29 at 21.7 °C) for 10 min, air-dried, and processed using the twelve-carbon reagent (Figure 4c). No significant difference in the obtained fingerprint image was apparent, thus suggesting that the acidity may not necessarily play a role in the current system. Finally, latent fingerprints that were unintentionally charged and aged over a one month period were detected on paper used for official documents (100% cotton paper, 150 μ m in thickness) using the twelve-carbon chain derivative, following the developed protocol for thicker paper substrates (Figure 4d), further supporting the efficiency and practicality of the bi-functional reagents.¹⁷

Figure 4. Latent fingerprints developed using the twelve-carbon chain derivative (0.01% w/v in dimethyl sulfoxide) followed by water rinse, then Ag-PD. a) On Whatman® filter paper, left half processed with twelve-carbon derivative for 2 min then Ag-PD <5 sec, right half with Ag-PD only 2 min. b) On Whatman® filter paper, left half processed with twelve-carbon derivative for 2 min then Ag-PD <5 sec, right half with citrate-capped AuNPs (avg. diameter 60 nm, same concentration) for 2 min then Ag-PD <5 sec. c) On Whatman® filter paper, left half processed with twelve-carbon derivative for 2 min then Ag-PD <5 sec, right half paper pretreated with 2.5% w/v malic acid in water for 10 min then processed with twelve-carbon derivative for 2 min then Ag-PD <5 sec. d) On 100% cotton paper used for official documents (a.k.a. resume paper), >1 month old fingerprint, processed with the twelve-carbon chain derivative for 3 min, then Ag-PD <5 sec.

3. Conclusions

In summary, a practical, generalized protocol was developed for latent fingerprint detection on paper substrates using 1,2-indanedione-based bi-functional reagents. A series of novel bi-functional reagents were designed and successfully synthesized using a concise, five-step protocol in the process. The present optimized protocol displayed efficiency and gave consistent results. When compared to existing chemical detection methods, the development process was very fast, where clearly visible prints with good image contrast was obtained in less than 20 min. The developed latent fingerprints that were obtained were of sufficient quality to be recorded using a standard iPhone camera (iPhone 5S), eliminating the use of specialized equipment. Furthermore, results obtained from this study gave insight to the underlying mechanism of the interaction between the bi-functional reagent and fingerprint residue. Overall, the study provided a generalized development condition tailored to the type of paper substrate that requires processing for latent fingerprints, allowing potential application in cases where sensitive detection reagents are needed.

4. Experimental section

All reactions were performed under an argon atmosphere except where otherwise noted. Solvents were purchased from Fisher Scientific and dried via an alumina column. Anhydrous toluene in Acrosecal bottle was used without further purification prior to use. Milli-Q (18 M Ω) water (Millipore; Billerica, MA, USA) was used for the synthesis of gold nanoparticles. Flash chromatography was carried out on Merck silica gel 60 (240–400 mesh) using the solvent conditions listed under individual experiments. Analytical thin-layer chromatography was performed on Merck silica gel (60F-254) plates (0.25 mm). Visualization of thin-layer chromatography plates was effected with ultraviolet light or phosphomolybdic acid (PMA) stain. Melting points ($^{\circ}\text{C}$) are uncorrected. Proton magnetic resonance spectra (^1H NMR), Carbon magnetic resonance spectra (^{13}C NMR), Fluorine magnetic resonance spectra (^{19}F NMR), and Boron magnetic spectra (^{11}B NMR) were performed on a Bruker NMR operating at 500, 125, 470, and 128 MHz respectively. All ^{11}B chemical shifts were referenced to external $\text{BF}_3\cdot\text{OEt}_2$ (0.0 ppm) with a negative sign indicating an upfield shift. Infrared spectra (IR) were obtained on a Perkin-Elmer 281-B spectrometer or a Bruker Alpha-P spectrometer. High resolution mass spectra (HRMS) were obtained on a Micromass Autospec or a Waters LCTOF-Xe premier. Ultraviolet absorption spectroscopy (UV-Vis) was performed on a JASCO V-650 spectrophotometer (JASCO Analytical Instruments; Easton, MD, USA) equipped with a JASCO PC-734R multichannel Peltier using quartz cells with 1 cm path lengths. Transmission electron microscopy (TEM) was performed using a JEOL 1400 microscope operating at 120 keV. Scanning electron microscopy (SEM) was performed on a JEOL 7500F HRSEM operating at 5.0 kV. All other starting materials and reagents were purchased from Sigma-Aldrich, TCI, Acros, or Strem and were used without further purification unless specified. Silver physical developer (Ag-PD) solution was purchased from Arrowhead Scientific Inc. Fingerprint images were taken with a standard iPhone 5S camera.

Synthesis of potassium alkyltrifluoroborate side chains

4.1. Potassium trifluoro(3-hydroxypropyl)borate (1)

Synthesized following known literature method.¹⁹ White solid. mp 175 $^{\circ}\text{C}$. ^1H NMR spectra obtained was in good agreement with the reported spectra.¹⁹ ^1H NMR: (500 MHz, DMSO- d_6) δ 3.90 (t, J = 5.4 Hz, 1H), 3.24 (td, J = 7.4, 5.6 Hz, 2H), 1.32–1.26 (m, 2H), -0.13–0.18 (m, 2H).

4.2 Potassium trifluoro(5-(tosyloxy)pentyl)borate (2)

General Procedure A. To a stirred solution of 4-penten-1-ol (0.6 mL, 5.81 mmol) in anhydrous CH_2Cl_2 (11 mL) was added triethylamine (1.21 mL, 8.71 mmol) followed by DMAP (28 mg, 0.232 mmol) and TsCl (1.1 g, 5.81 mmol). The resulting mixture was stirred at room temperature overnight. The reaction was diluted with water (10 mL) and extracted with chloroform (10 mL, three times). The combined organic layers were washed with aqueous sat. NH_4Cl (10 mL), separated, dried over MgSO_4 , filtered, and concentrated. Silica gel column chromatography purification (20% EtOAc/Hexanes) afforded the corresponding known tosylate²⁰ (31) as an oil (1.19 g, 86%).

A 50 mL round-bottomed flask was charged with $[\text{Ir}(\text{cod})\text{Cl}]_2$ (50 mg, 0.074 mmol), dppe (59 mg, 0.148 mmol), and a stir bar in a glove box. The flask was then removed and to it was added a solution of the tosylate (1.19 g, 4.95 mmol) in anhydrous CH_2Cl_2 (17 mL) via cannula addition. The resulting mixture was brought to 0 $^{\circ}\text{C}$, followed by dropwise addition of pinacolborane (1.07 mL, 7.43 mmol). The reaction mixture was left to stir and allowed to warm to room temperature overnight. The reaction was quenched by water (5 mL), stirred for 5 min, and the resulting mixture was separated. The aqueous layer was extracted with diethyl ether (15 mL, three times). The combined organic layers were dried over MgSO_4 , filtered, and concentrated. Purification by silica gel chromatography (20% EtOAc/Hexanes) afforded **5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl 4-methylbenzenesulfonate (36)** as an oil (1.64 g, 90%). R_f 0.5 (20% EtOAc/Hex); ^1H NMR: (500 MHz, CDCl_3) δ 7.80 (d, J = 8.3 Hz, 2H), 7.35 (dd, J = 8.6, 0.6 Hz, 2H), 4.03 (t, J = 6.6 Hz, 2H), 2.46 (s, 3H), 1.64 (dq, J = 13.9, 6.7 Hz, 2H), 1.40–1.29 (m, 4H), 1.24 (s, 12H), 0.74 (t, J = 7.6 Hz, 2H); ^{13}C NMR: (125 MHz, CDCl_3) δ 144.6, 133.3, 129.8, 127.9, 83.0, 70.7, 28.6, 27.9, 24.8, 23.4, 21.6; ^{11}B NMR (128.4 MHz, CDCl_3) δ 33.08; IR (cm^{-1}): 2978, 2933, 2864, 1598, 1462, 1362, 1321, 1188, 1177, 1145, 1098, 967, 937, 844, 815, 664, 577, 555; HRMS (ESI) m/z calculated for $\text{C}_{18}\text{H}_{29}\text{BO}_5\text{S}$ ($M + \text{Na}$) $^+$: 391.1730, found: 391.1726.

To a stirred solution of **36** in acetonitrile (5 mL) was added aqueous potassium bifluoride, 4.5 M KHF_2 (aq.) (4.5 mL). The resulting mixture was stirred at room temperature for 1 h. The solution was concentrated, and left under reduced pressure overnight. Hot acetonitrile (50 mL) was added to the solid and the solution was filtered by hot gravity filtration (or alternatively, Soxhlet extraction). The filtrate was evaporated, re-dissolved in small amount of cold diethyl ether (5 mL) and filtered to afford the desired potassium alkyl trifluoroborate salt (**2**) in 96% yield: White solid. mp 158 $^{\circ}\text{C}$. ^1H NMR: (500 MHz, acetone- d_6) δ 7.77 (d, J = 8.2 Hz, 2H), 7.48 (d, J = 7.9 Hz, 2H), 3.96 (t, J = 6.6 Hz, 2H), 2.42 (s, 3H), 1.53–1.46 (m, 2H), 1.16–1.09 (m, 4H), 1.08–1.02 (m, 2H); ^{13}C NMR: (125 MHz, acetone- d_6) δ 145.2, 133.1, 130.6, 127.9, 71.9, 29.03, 28.92, 25.49, 25.48, 21.6; ^{11}B NMR (128.4 MHz, acetone- d_6) δ 5.24; ^{19}F NMR (470.8 MHz, acetone- d_6) δ -136.79; IR (cm^{-1}): 2920, 2856, 1599, 1354, 1332, 1308, 1293, 1273, 1251, 1190, 1174, 1095, 1069, 1020, 944, 914, 883, 838, 809, 779, 723, 705, 689, 665, 567, 552; HRMS (ESI) m/z

calculated for $C_{12}H_{17}BO_3F_3S$ ($M - K^+$): 309.0937, found: 309.0944.

4.3. Potassium trifluoro(8-(tosyloxy)octyl)borate (3)

General procedure A was followed using the known corresponding tosylate (oct-7-en-1-yl 4-methylbenzenesulfonate)²⁰ in the first step and **8-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)octyl 4-methylbenzenesulfonate (37)** in the second step: Colorless oil. R_f 0.65 (20% EtOAc/Hex); 1H NMR: (500 MHz, $CDCl_3$) δ 7.79 (d, J = 8.31 Hz, 2H), 7.35 (d, J = 8.51 Hz, 2H), 4.04-4.00 (m, 2H), 2.45 (s, 3H), 1.69-1.59 (m, 4H), 1.39-1.22 (m, 20H), 0.75 (t, J = 7.82 Hz, 2H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 144.5, 133.1, 129.7, 127.8, 82.8, 70.6, 32.1, 31.6, 29.0, 28.9, 28.8, 28.7, 25.2, 24.7, 23.8, 22.5, 21.5, 14.0; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ 33.68; IR (cm^{-1}): 2977, 2928, 2857, 1598, 1495, 1466, 1363, 1320, 1272, 1213, 1188, 1177, 1145, 1098, 1019, 966, 936, 845, 815, 664, 577, 555; HRMS (ESI) m/z calculated for $C_{21}H_{35}BO_5S$ ($M + H$): 411.2377, found: 411.2372. The desired potassium alkyl trifluoroborate salt (**3**) was obtained in 77% yield: White solid. mp >200 °C. 1H NMR: (500 MHz, acetone- d_6) δ 7.81 (d, J = 8.18 Hz, 2H), 7.50 (d, J = 8.29 Hz, 2H), 4.05 (t, J = 6.41 Hz, 2H), 2.47 (s, 3H), 1.63 (dt, J = 14.26, 6.90 Hz, 2H), 1.38-1.15 (m, 10H), 0.88 (t, J = 7.05 Hz, 2H); ^{13}C NMR: (125 MHz, acetone- d_6) δ 145.7, 134.6, 130.9, 128.7, 83.5, 71.6, 32.9, 32.5, 26.1, 25.3, 25.29, 25.25, 24.8, 23.3, 21.5, 14.4; ^{11}B NMR (128.4 MHz, acetone- d_6) δ 6.03; ^{19}F NMR (470.8 MHz, acetone- d_6) δ -136.81; IR (cm^{-1}): 2916, 2850, 1362, 1175, 1095, 964, 944, 835, 810, 720, 669, 650; HRMS (ESI) m/z calculated for $C_{15}H_{23}BF_3O_3S$ ($M - K^+$): 351.1413, found: 351.1406.

4.4. Potassium trifluoro(10-(tosyloxy)decyl)borate (4)¹¹

General procedure A was followed to obtain the title compound, which was characterized in our previous report.¹¹ 1H NMR and ^{13}C NMR spectra obtained were in good agreement with the reported spectra: 1H NMR: (500 MHz, acetone- d_6) δ 7.84-7.81 (m, 2H), 7.52-7.49 (m, 2H), 4.06 (dt, J = 10.63, 5.0 Hz, 2H), 2.47 (s, 3H), 1.66-1.60 (m, 2H), 1.29-1.18 (m, 14H), 0.15-0.12 (m, 2H); ^{13}C NMR: (125 MHz, acetone- d_6) δ 145.8, 134.5, 130.9, 128.7, 74.8, 71.6, 34.6, 30.8, 30.5, 26.6, 26.1, 25.3, 25.2, 21.6.

4.5. Potassium trifluoro(12-(tosyloxy)dodecyl)borate (5)

General procedure A was followed using the known corresponding tosylate (1-(tosyloxy)dodec-11-ene)²¹ in the first step and **12-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)dodecyl 4-methylbenzenesulfonate (39)** in the second step: Colorless oil. R_f 0.34 (10% EtOAc/Hex); 1H NMR: (500 MHz, $CDCl_3$) δ 7.72 (d, J = 8.32 Hz, 2H), 7.32 (d, J = 8.51 Hz, 2H), 4.00 (t, J = 6.54 Hz, 2H), 2.43 (s, 3H), 1.61 (dt, J = 14.43, 7.00 Hz, 2H), 1.40-1.17 (m, 30H), 0.74 (t, J = 7.77, 2H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 144.4, 133.2, 129.6, 127.7, 82.7, 70.5, 32.2, 29.5, 29.4, 29.3, 29.2, 28.8, 28.7, 25.2, 24.7, 23.8, 21.4; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ 33.68; IR (cm^{-1}): 2977, 2925, 2853, 1598, 1466, 1364, 1319, 1212, 1188, 1176, 1145, 1098, 1019, 966, 912, 846, 814, 790, 763, 732, 688, 665, 651, 641, 625; HRMS (ESI) m/z calculated for $C_{25}H_{43}BO_5S$ ($M + Na$): 489.2822, found: 489.2825. The desired potassium alkyl trifluoroborate salt (**5**) was obtained in 88% yield: White solid. mp >200 °C. 1H NMR: (500 MHz, DMSO- d_6) δ 7.78 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 7.9 Hz, 2H), 4.00 (t, J = 6.2 Hz, 2H), 2.43 (s, 3H), 1.53 (t, J = 6.7 Hz, 2H), 1.19 (s, 18H), -0.04-0.10 (m, 2H); ^{13}C NMR: (125 MHz, DMSO- d_6) δ 144.8, 132.5, 130.1, 127.5, 70.8, 33.1, 29.4, 29.2, 29.1, 28.9, 28.8, 28.1, 28.0, 25.6, 24.6, 21.0; ^{11}B NMR (128.4 MHz, DMSO- d_6) δ 6.42; ^{19}F NMR

(470.8 MHz, DMSO- d_6) δ -136.82; IR (cm^{-1}): 2917, 2850, 1598, 1468, 1363, 1298, 1248, 1188, 1175, 1096, 1021, 965, 946, 918, 836, 809, 793, 720, 669, 642, 626. HRMS (ESI) m/z calculated for $C_{19}H_{31}BF_3O_3S$ ($M - K^+$): 407.2042, found: 407.2039.

4.6. Potassium trifluoro(14-(tosyloxy)tetradecyl)borate (6)

General procedure A was followed using tetradec-13-en-1-yl 4-methylbenzenesulfonate (**35**) in the first step and **14-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)tetradecyl 4-methylbenzenesulfonate (40)** in the second step: Colorless oil. R_f 0.67 (20% EtOAc/Hex); 1H NMR: (500 MHz, $CDCl_3$) δ 7.80 (d, J = 7.80 Hz, 2H), 7.35 (d, J = 7.98 Hz, 2H), 4.05-4.02 (m, 2H), 2.46 (s, 3H), 1.67-1.61 (m, 2H), 1.41 (ddd, J = 12.36, 6.78, 6.30 Hz, 2H), 1.30-1.22 (m, 32H), 0.77 (t, J = 7.75 Hz, 2H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 144.5, 133.3, 129.7, 129.5, 127.8, 127.0, 82.8, 70.6, 41.9, 32.4, 29.6, 29.58, 29.55, 29.4, 29.38, 29.36, 28.9, 28.7, 25.3, 24.7, 23.9, 21.5, 14.1; IR (cm^{-1}): 2977, 2925, 2854, 1598, 1466, 1367, 1321, 1188, 1177, 1145, 1097, 1020, 966, 814, 714, 663, 577, 554; HRMS (ESI) m/z calculated for $C_{27}H_{47}BO_5S$ ($M + H$): 494.3316, found: 495.3318. The desired potassium alkyl trifluoroborate salt (**6**) was obtained in 60% yield: White solid. mp. >200 °C. 1H NMR: (500 MHz, DMSO- d_6) δ 7.78 (d, J = 8.2 Hz, 2H), 7.48 (d, J = 7.8 Hz, 2H), 4.00 (t, J = 6.3 Hz, 2H), 2.42 (s, 3H), 1.57-1.52 (m, 2H), 1.21-1.16 (m, 22H), -0.06-0.12 (m, 2H); ^{13}C NMR: (125 MHz, DMSO- d_6) δ 144.7, 132.5, 130.1, 127.5, 89.7, 84.5, 70.8, 33.1, 29.4, 29.2, 29.1, 29.0, 28.9, 28.8, 28.7, 28.1, 28.0, 25.6, 24.9, 24.6, 21.0; ^{11}B NMR (128.4 MHz, acetone) δ 4.63; ^{19}F NMR (470.8 MHz, DMSO- d_6) δ -136.83; IR (cm^{-1}): 2916, 2850, 1364, 1176, 1095, 965, 923, 835, 809, 793, 719, 670. HRMS (ESI) m/z calculated for $C_{21}H_{35}BO_3F_3SK$ ($M - F$) + $(CH_3O)^-$: 447.2561, found: 447.2552.

4.7. 5-(3-Hydroxypropyl)2,3-dihydro-1H-inden-1-one (7)

General Procedure B. A microwave tube was charged with 5-chloro-1-indanone (50 mg, 0.3 mmol), **1** (50.3 mg, 0.303 mmol), $Pd(OAc)_2$ (1.3 mg, 0.006 mmol), RuPhos (5.6 mg, 0.012 mmol), K_2CO_3 (124 mg, 0.9 mmol), and a stir bar. The cap was sealed, and evacuated and purged with Ar (3 cycles). Degassed toluene:H₂O mixture (1.2 mL) was then added to the microwave tube via syringe and the resulting reaction mixture was heated to 90 °C for 36 h. (For larger scale operation, the reaction was set up in a glove box.) H₂O (1 mL) was added to the reaction, stirred for 5 min, and the resulting layers were separated. The aqueous layer was extracted with ethyl acetate (2 mL, three times). The organic layers were combined, dried over Na_2SO_4 , filtered, and concentrated. Purification by silica gel chromatography (50% EtOAc/Hexanes) afforded the coupled product **7** in 84% yield as an amorphous solid. R_f 0.21 (50% EtOAc/Hex); 1H NMR: (500 MHz, $CDCl_3$) δ 7.69-7.68 (m, 1H), 7.32-7.29 (m, 1H), 7.21 (d, J = 7.82 Hz, 1H), 3.70 (t, J = 6.33 Hz, 2H), 3.11 (t, J = 5.84 Hz, 2H), 2.81 (t, J = 7.74 Hz, 2H), 2.68 (dd, J = 7.75, 3.98 Hz, 2H), 1.96-1.91 (m, 2H), 1.85-1.77 (m, 1H); ^{13}C NMR: (125 MHz, $CDCl_3$) 206.7, 155.8, 149.8, 135.2, 128.0, 126.5, 123.7, 61.9, 36.4, 33.9, 32.5, 25.7; IR (cm^{-1}): 3413, 2929, 2864, 1705, 1609, 1438, 1404, 1332, 1288, 1246, 1231, 1104, 1056, 1033, 834, 815; HRMS (ESI) m/z calculated for $C_{12}H_{14}O_2$ ($M + H$): 191.1071, found: 191.1072.

4.8. 5-(1-Oxo-2,3-dihydro-1H-inden-5-yl)pentyl 4-methylbenzenesulfonate (8)

General procedure B was followed using **2** to afford the desired compound in 70% yield. Yellow amorphous solid. R_f 0.23 (20% EtOAc/Hex); 1H NMR: (500 MHz, $CDCl_3$) δ 7.78 (d, J = 8.30 Hz, 2H), 7.67 (d, J = 7.85 Hz, 1H), 7.36-7.34 (m, 2H), 7.25

(s, 1H), 7.15 (d, $J = 7.86$ Hz, 1H), 4.03 (t, $J = 6.41$ Hz, 2H), 3.11 (t, $J = 5.86$ Hz, 2H), 2.70-2.65 (m, 4H), 2.45 (s, 3H), 1.76-1.59 (m, 4H), 1.45-1.36 (m, 2H); ^{13}C NMR: (125 MHz, CDCl_3) 206.5, 155.7, 149.8, 144.6, 135.1, 133.1, 129.7, 127.9, 127.8, 126.8, 123.6, 70.2, 36.8, 36.0, 30.4, 28.6, 25.6, 24.9, 21.6; IR (cm^{-1}): 2932, 2860, 1708, 1608, 1494, 1440, 1403, 1357, 1281, 1188, 1176, 1097, 1030, 948, 903, 815, 663, 576, 554; HRMS (ESI) m/z calculated for $\text{C}_{21}\text{H}_{24}\text{O}_4\text{S}$ ($\text{M} + \text{H}$) $^+$: 373.1474, found: 373.1473.

4.9. 8-(1-Oxo-2,3-dihydro-1H-inden-5-yl)octyl 4-methylbenzenesulfonate (**9**)

General procedure B was followed using **3** to afford the desired compound in 65% yield. Yellow amorphous solid. R_f 0.24 (20% EtOAc/Hex); ^1H NMR: (500 MHz, CDCl_3) δ 7.80 (d, $J = 8.2$ Hz, 2H), 7.68 (d, $J = 7.8$ Hz, 1H), 7.35 (d, $J = 8.2$ Hz, 2H), 7.19 (d, $J = 7.9$ Hz, 1H), 4.03 (t, $J = 6.5$ Hz, 2H), 3.12 (t, $J = 5.9$ Hz, 2H), 2.68 (dd, $J = 10.3, 4.8$ Hz, 4H), 2.46 (s, 3H), 1.64 (dq, $J = 14.4, 7.2$ Hz, 4H), 1.35-1.25 (m, 9H); ^{13}C NMR: (125 MHz, CDCl_3) 206.5, 155.6, 150.5, 144.5, 135.0, 133.2, 129.7, 127.9, 127.8, 126.3, 123.5, 70.5, 36.3, 36.2, 31.1, 29.1, 29.0, 28.8, 28.7, 25.6, 25.2, 21.5; IR (cm^{-1}): 2928, 2856, 1709, 1608, 1495, 1441, 1403, 1359, 1289, 1229, 1188, 1176, 1097, 1030, 941, 815, 664, 577, 555; HRMS (ESI) m/z calculated for $\text{C}_{24}\text{H}_{30}\text{O}_4\text{S}$ ($\text{M} + \text{H}$) $^+$: 414.1943, found: 414.1943.

4.10. 10-(1-Oxo-2,3-dihydro-1H-inden-5-yl)decyl 4-methylbenzenesulfonate (**10**)¹¹

General procedure B was followed to obtain the title compound in 70% yield, which was characterized in our previous report.¹¹ ^1H NMR and ^{13}C NMR spectra obtained were in good agreement with the reported spectra: ^1H NMR: (500 MHz, CDCl_3) δ 7.70, (d, $J = 8.27$ Hz, 2H), 7.64 (d, $J = 7.85$ Hz, 1H), 7.32 (d, $J = 8.29$ Hz, 2H), 7.26 (s, 1H), 7.17 (d, $J = 7.85$ Hz, 1H), 4.00 (t, $J = 6.50$ Hz, 2H), 3.08 (t, $J = 5.82$ Hz, 2H), 2.68-2.64 (m, 4H), 2.42 (s, 3H), 1.65 (dt, $J = 14.25, 6.95$ Hz, 4H), 1.29-1.21 (m, 12H); ^{13}C NMR: (125 MHz, CDCl_3) 206.5, 155.6, 150.6, 144.5, 134.8, 133.0, 129.6, 127.8, 127.6, 126.2, 123.3, 70.5, 36.3, 36.2, 31.1, 29.2, 29.1, 29.0, 28.7, 28.6, 25.5, 25.1, 21.4.

4.11. 12-(1-Oxo-2,3-dihydro-1H-inden-5-yl)dodecyl 4-methylbenzenesulfonate (**11**)

General procedure B was followed using **5** to afford the desired compound in 38% yield. White amorphous solid. R_f 0.39 (20% EtOAc/Hex); ^1H NMR: (500 MHz, CDCl_3) δ 7.80 (d, $J = 8.0$ Hz, 2H), 7.68 (d, $J = 7.9$ Hz, 1H), 7.35 (d, $J = 8.2$ Hz, 2H), 7.20 (d, $J = 7.8$ Hz, 1H), 4.04-4.02 (m, 2H), 3.12 (t, $J = 5.8$ Hz, 2H), 2.71-2.68 (m, 4H), 2.46 (s, 3H), 1.69-1.62 (m, 4H), 1.32-1.23 (m, 17H); ^{13}C NMR: (125 MHz, CDCl_3) 206.6, 155.6, 150.7, 144.5, 135.0, 133.2, 129.7, 127.9, 127.8, 126.3, 123.5, 70.6, 36.3, 31.2, 29.5, 29.45, 29.4, 29.3, 29.2, 28.8, 28.7, 25.6, 25.2, 21.5; IR (cm^{-1}): 2977, 2922, 2849, 1704, 1607, 1470, 1434, 1393, 1356, 1323, 1296, 1281, 1246, 1186, 1173, 1097, 1030, 949, 837, 815, 670, 576, 556, 532; HRMS (ESI) m/z calculated for $\text{C}_{28}\text{H}_{38}\text{O}_4\text{S}$ ($\text{M} + \text{H}$) $^+$: 471.2569, found: 471.2550.

4.12. 14-(1-Oxo-2,3-dihydro-1H-inden-5-yl)tetradecyl 4-methylbenzenesulfonate (**12**)

General procedure B was followed using **6** to afford the desired compound in 51% yield. White amorphous solid. R_f 0.45 (20% EtOAc/Hex); ^1H NMR: (500 MHz, CDCl_3) δ 7.79 (d, $J = 8.3$ Hz, 2H), 7.67 (d, $J = 7.8$ Hz, 1H), 7.36-7.34 (m, 2H), 7.28 (d, $J = 0.8$ Hz, 1H), 7.19 (d, $J = 7.9$ Hz, 1H), 4.02 (t, $J = 6.5$ Hz, 2H), 3.11 (t, $J = 5.9$ Hz, 2H), 2.71-2.67 (m, 4H), 2.45 (s, 3H), 1.69-1.59 (m, 6H), 1.36-1.18 (m, 18H); ^{13}C NMR: (125 MHz,

CDCl_3) 206.6, 155.6, 150.7, 144.5, 134.9, 133.1, 129.7, 127.9, 126.3, 123.4, 70.6, 36.3, 31.2, 29.6, 29.5, 29.47, 29.41, 29.39, 29.3, 29.2, 28.8, 28.7, 25.6, 25.2, 21.5; IR (cm^{-1}): 2917, 2851, 1712, 1607, 1472, 1433, 1360, 1228, 1186, 1171, 1095, 1030, 977, 955, 832, 807, 794, 719, 689, 668, 644; HRMS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{42}\text{O}_4\text{S}$ ($\text{M} + \text{Na}$) $^+$: 521.2702, found: 521.2698.

4.13. S-(3-(1-Oxo-2,3-dihydro-1H-inden-5-yl)propyl) ethanethioate (**13**)

To a stirred solution of **7** (48 mg, 0.252 mmol) in anhydrous THF (2.5 mL) was added triphenylphosphine (99 mg, 0.378 mmol), diethyl azodicarboxylate (60 μL , 0.378 mmol), and thioacetic acid (36 μL , 0.505 mmol). The resulting mixture was left to stir at room temperature for 20 h. Upon completion, the reaction mixture was concentrated under vacuum to afford the crude product as a yellow oil. Purification by silica gel chromatography (30% EtOAc/Hexanes) afforded **13** as a yellow oil (53 mg, 84%). R_f 0.51 (30% EtOAc/Hex); ^1H NMR: (500 MHz, CDCl_3) δ 7.68 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.29 (s, 1H), 7.19 (d, $J = 7.8$ Hz, 1H), 3.11 (t, $J = 5.4$ Hz, 2H), 2.90 (td, $J = 7.2, 1.7$ Hz, 2H), 2.79-2.76 (m, 2H), 2.70-2.67 (m, 2H), 2.35 (d, $J = 2.1$ Hz, 3H), 1.97-1.91 (m, 2H); ^{13}C NMR: (125 MHz, CDCl_3) 206.5, 195.6, 155.8, 148.8, 135.4, 128.0, 126.5, 123.8, 36.4, 35.2, 31.0, 30.7, 28.5, 25.7; IR (cm^{-1}): 2925, 2859, 1709, 1609, 1439, 1354, 1331, 1281, 1230, 1134, 1103, 1032, 953, 837, 815, 626; HRMS (ESI) m/z calculated for $\text{C}_{14}\text{H}_{16}\text{O}_2\text{S}$ ($\text{M} + \text{Na}$) $^+$: 271.0762, found: 271.0769.

4.14. S-(5-(1-Oxo-2,3-dihydro-1H-inden-5-yl)pentyl) ethanethioate (**14**)

General Procedure C. To a stirred solution of **8** (780 mg, 2.09 mmol) in anhydrous acetonitrile (131 mL) was added potassium thioacetate (478 mg, 4.19 mmol) in one portion. The resulting mixture was then brought to 60 $^\circ\text{C}$ and left to stir overnight. The reaction was quenched by addition of H_2O (100 mL), and extracted with CH_2Cl_2 (100 mL, three times). Organic layers were then combined, washed with brine (100 mL), dried over Na_2SO_4 , filtered, and concentrated. Purification by silica gel chromatography (25% EtOAc/Hexanes) afforded **14** in 91% yield as a yellow oil. R_f 0.39 (20% EtOAc/Hex); ^1H NMR: (500 MHz, CDCl_3) δ 7.65 (d, $J = 7.8$ Hz, 1H), 7.26 (s, 1H), 7.16 (dd, $J = 7.8, 0.6$ Hz, 1H), 3.09 (t, $J = 5.9$ Hz, 2H), 2.84 (t, $J = 7.3$ Hz, 2H), 2.69-2.64 (m, 4H), 2.30 (s, 3H), 1.68-1.56 (m, 4H), 1.43-1.37 (m, 2H); ^{13}C NMR: (125 MHz, CDCl_3) 206.6, 195.9, 155.7, 150.2, 135.1, 127.9, 126.4, 123.6, 36.4, 36.1, 30.68, 30.63, 29.3, 28.9, 28.3, 25.7; IR (cm^{-1}): 2930, 2857, 1710, 1608, 1435, 1353, 1330, 1284, 1230, 1134, 1104, 1030, 956, 813, 627, 586; HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{20}\text{O}_2\text{S}$ ($\text{M} + \text{H}$) $^+$: 277.1262, found: 277.1264.

4.15. S-(8-(1-Oxo-2,3-dihydro-1H-inden-5-yl)octyl) ethanethioate (**15**)

General procedure C was followed using **9** to afford the desired compound in 98% yield. Yellow oil. R_f 0.65 (30% EtOAc/Hex); ^1H NMR: (500 MHz, CDCl_3) δ 7.65 (d, $J = 7.8$ Hz, 1H), 7.26 (s, 1H), 7.17 (d, $J = 7.8$ Hz, 1H), 3.09 (t, $J = 5.7$ Hz, 2H), 2.84 (t, $J = 7.3$ Hz, 2H), 2.66 (q, $J = 6.7$ Hz, 4H), 2.30 (s, 3H), 1.62 (q, $J = 7.1$ Hz, 2H), 1.55 (quintet, $J = 7.2$ Hz, 2H), 1.31-1.23 (m, 8H); ^{13}C NMR: (125 MHz, CDCl_3) 206.3, 195.7, 155.5, 150.4, 134.9, 127.8, 126.2, 123.4, 36.3, 36.2, 31.0, 30.4, 30.0, 29.3, 29.1, 29.0, 28.9, 28.8, 28.5, 25.5; IR (cm^{-1}): 3009, 2926, 2854, 1694, 1608, 1439, 1353, 1330, 1282, 1245, 1230, 1192, 1133, 1105, 1030, 954, 886, 835, 814, 763, 724, 673, 627, 586; HRMS (ESI) m/z calculated for $\text{C}_{19}\text{H}_{26}\text{O}_2\text{S}$ ($\text{M} + \text{H}$) $^+$: 319.1732, found: 319.1729.

4.16. *S*-(10-(1-Oxo-2,3-dihydro-1H-inden-5-yl)decyl) ethanethioate (**16**)¹¹

General procedure C was followed to obtain the title compound in 84% yield, which was characterized in our previous report.¹¹ ¹H NMR and ¹³C NMR spectra obtained were in good agreement with the reported spectra: ¹H NMR: (500 MHz, CDCl₃) δ 7.67 (d, *J* = 7.9 Hz, 1H), 7.28 (s, 1H), 7.19 (d, *J* = 7.9 Hz, 1H), 3.11 (t, *J* = 5.8 Hz, 2H), 2.86 (t, *J* = 7.4 Hz, 2H), 2.69–2.66 (m, 4H), 2.32 (s, 3H), 1.63 (dt, *J* = 14.7, 7.4 Hz, 2H), 1.56 (dq, *J* = 14.3, 7.0 Hz, 2H), 1.31 (dd, *J* = 21.5, 15.0 Hz, 10H); ¹³C NMR: (125 MHz, CDCl₃) 206.5, 195.9, 155.6, 150.6, 134.9, 127.9, 126.2, 123.4, 36.3, 31.2, 30.5, 29.4, 29.3, 29.1, 29.0, 28.9, 28.7, 25.6.

4.17. *S*-(12-(1-Oxo-2,3-dihydro-1H-inden-5-yl)dodecyl) ethanethioate (**17**)

General procedure C was followed using **11** to afford the desired compound in 93% yield. Amorphous solid. *R*_f 0.63 (20% EtOAc/Hex); ¹H NMR: (500 MHz, CDCl₃) δ 7.69 (d, *J* = 7.8 Hz, 1H), 7.29 (s, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 3.13 (dd, *J* = 7.6, 4.1 Hz, 2H), 2.88 (t, *J* = 7.4 Hz, 2H), 2.72–2.69 (m, 4H), 2.34 (s, 3H), 1.72–1.62 (m, 2H), 1.61–1.54 (m, 2H), 1.37–1.28 (m, 16H); ¹³C NMR: (125 MHz, CDCl₃) 206.6, 196.0, 155.6, 150.7, 135.0, 128.0, 126.3, 123.5, 36.4, 31.2, 30.6, 29.6, 29.5, 29.49, 29.43, 29.2, 29.1, 29.0, 28.8, 25.7; IR (cm⁻¹): 2917, 2851, 1701, 1686, 1607, 1470, 1443, 1352, 1334, 1295, 1273, 1231, 1193, 1135, 1106, 1031, 959, 903, 818, 766, 719, 639; HRMS (ESI) *m/z* calculated for C₂₃H₃₄O₂S (M + Na)⁺: 397.2177, found: 397.2177.

4.18. *S*-(14-(1-Oxo-2,3-dihydro-1H-inden-5-yl)tetradecyl) ethanethioate (**18**)

General procedure C was followed using **12** to afford the desired compound in 94% yield. Amorphous solid. *R*_f 0.5 (20% EtOAc/Hex); ¹H NMR: (500 MHz, CDCl₃) δ 7.69 (d, *J* = 7.8 Hz, 1H), 7.29 (s, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 3.12 (dd, *J* = 5.9, 5.7 Hz, 2H), 2.88 (t, *J* = 7.4 Hz, 2H), 2.71–2.69 (m, 4H), 2.34 (s, 3H), 1.71–1.62 (m, 2H), 1.61–1.55 (m, 4H), 1.38–1.27 (m, 18H); ¹³C NMR: (125 MHz, CDCl₃) 206.6, 196.0, 155.6, 150.8, 135.0, 128.0, 126.3, 123.5, 36.4, 31.3, 30.6, 29.6, 29.56, 29.53, 29.49, 29.46, 29.2, 29.15, 29.11, 28.8, 25.7; IR (cm⁻¹): 2916, 2849, 1701, 1686, 1607, 1469, 1442, 1428, 1234, 1120, 1030, 958, 818, 654; HRMS (ESI) *m/z* calculated for C₂₅H₃₈O₂S (M + Na)⁺: 425.2490, found: 425.2498.

4.19. *S*-(3-(2-(hydroxyimino)-1-oxo-2,3-dihydro-1H-inden-5-yl)propyl) ethanethioate (**19**)

General Procedure D. To a stirred solution of **13** (53 mg, 0.213 mmol) in anhydrous CH₂Cl₂ (0.85 mL) at –20 °C was added TMSCl (27 μL, 0.213 mmol) followed by drop-wise addition of isoamy nitrite (29 μL, 0.213 mmol). The resulting mixture was left to stir at –20 °C for 1 h. The reaction was quenched by addition of H₂O (1 mL), and the layers were separated. The aqueous layer was extracted with CH₂Cl₂ (3 mL, three times), and the organic layers were combined. The organic layer was washed with brine (1 mL), dried over MgSO₄, filtered, and concentrated to afford the oxime **19** in quantitative yield as an off-white amorphous solid. *R*_f 0.18 (40% EtOAc/Hex); ¹H NMR: (500 MHz, CDCl₃) δ 7.82 (d, *J* = 7.9 Hz, 1H), 7.35 (s, 1H), 7.28 (s, 1H), 3.85 (s, 2H), 2.92 (t, *J* = 7.2 Hz, 2H), 2.81 (dd, *J* = 9.9, 5.4 Hz, 2H), 2.37 (s, 3H), 1.97 (dt, *J* = 14.9, 7.4 Hz, 2H); ¹³C NMR: (125 MHz, CDCl₃) δ 195.9, 189.05, 155.3, 150.9, 147.4, 136.0, 128.7, 126.6, 124.8, 35.5, 30.83, 30.68, 28.47, 28.31; IR (cm⁻¹): 3250, 2938, 1729, 1689, 1656, 1614, 1438, 1407, 1350, 1333, 1304, 1293, 1274, 1141, 1108, 1040, 947, 925,

907, 833, 774, 763, 730, 691, 629; HRMS (ESI) *m/z* calculated for C₁₄H₁₅NO₃S (M + H)⁺: 278.0850, found: 278.0851.

4.20. *S*-(5-(2-(hydroxyimino)-1-oxo-2,3-dihydro-1H-inden-5-yl)pentyl) ethanethioate (**20**)

General procedure D was followed using **14** to afford the desired compound in quantitative yield. Light yellow amorphous solid. *R*_f 0.3 (40% EtOAc/Hex); ¹H NMR: (500 MHz, CDCl₃) δ 7.82 (d, *J* = 7.9 Hz, 1H), 7.34 (s, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 3.85 (s, 2H), 2.88 (t, *J* = 7.3 Hz, 2H), 2.73 (t, *J* = 7.7 Hz, 2H), 2.34 (s, 3H), 1.73–1.60 (m, 5H), 1.47–1.42 (m, 2H); ¹³C NMR: (125 MHz, CDCl₃) δ 196.1, 189.2, 155.4, 152.3, 147.4, 135.8, 128.7, 126.5, 124.7, 36.4, 30.67, 30.56, 29.3, 28.9, 28.32, 28.26; IR (cm⁻¹): 3497, 3386, 2925, 2858, 1707, 1688, 1649, 1608, 1491, 1340, 1279, 1139, 1112, 1043, 948, 922, 910, 843; HRMS (ESI) *m/z* calculated for C₁₆H₁₉NO₃S (M + Na)⁺: 328.0983, found: 328.0993.

4.21. *S*-(8-(2-(hydroxyimino)-1-oxo-2,3-dihydro-1H-inden-5-yl)octyl) ethanethioate (**21**)

General procedure D was followed using **15** to afford the desired compound in quantitative yield. Light yellow amorphous solid. *R*_f 0.36 (40% EtOAc/Hex); ¹H NMR: (500 MHz, CDCl₃) δ 7.82 (d, *J* = 7.9 Hz, 1H), 7.33 (s, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 3.85 (s, 2H), 2.87 (t, *J* = 7.4 Hz, 2H), 2.72 (t, *J* = 7.7 Hz, 2H), 2.34 (s, 3H), 1.69–1.63 (m, 2H), 1.60–1.54 (m, 2H), 1.34–1.28 (m, 9H); ¹³C NMR: (125 MHz, CDCl₃) 196.2, 189.0, 155.4, 152.6, 147.2, 135.7, 128.6, 126.4, 124.6, 36.6, 31.0, 30.6, 29.4, 29.2, 29.1, 29.0, 28.9, 28.6, 28.2; IR (cm⁻¹): 3247, 2922, 2852, 1726, 1686, 1655, 1608, 1469, 1434, 1407, 1332, 1302, 1273, 1126, 1109, 1037, 959, 946, 924, 905, 832, 773, 755, 691, 634; HRMS (ESI) *m/z* calculated for C₁₉H₂₅NO₃S (M + Na)⁺: 370.1453, found: 370.1453.

4.22. *S*-(10-(2-(hydroxyimino)-1-oxo-2,3-dihydro-1H-inden-5-yl)decyl) ethanethioate (**22**)¹¹

General procedure D was followed to obtain the title compound in quantitative yield, which was characterized in our previous report.¹¹ ¹H NMR and ¹³C NMR spectra obtained were in good agreement with the reported spectra: ¹H NMR: (500 MHz, CDCl₃) δ 7.81 (d, *J* = 7.9 Hz, 1H), 7.33 (s, 1H), 7.26 (d, *J* = 7.9 Hz, 1H), 3.85 (s, 2H), 2.87 (t, *J* = 7.4 Hz, 2H), 2.71 (t, *J* = 7.7 Hz, 2H), 2.34 (s, 3H), 1.66 (dq, *J* = 13.8, 6.9 Hz, 3H), 1.60–1.54 (m, 3H), 1.34–1.28 (m, 11H); ¹³C NMR: (125 MHz, CDCl₃) 196.2, 189.2, 155.3, 152.8, 147.3, 135.6, 128.7, 126.4, 124.5, 36.6, 31.1, 30.6, 29.4, 29.37, 29.34, 29.2, 29.1, 29.0, 28.7, 28.2.

4.23. *S*-(12-(2-(hydroxyimino)-1-oxo-2,3-dihydro-1H-inden-5-yl)dodecyl) ethanethioate (**23**)

General procedure D was followed using **17** to afford the desired compound in quantitative yield. Off-white amorphous solid. *R*_f 0.5 (40% EtOAc/Hex); ¹H NMR: (500 MHz, CDCl₃) δ 7.82 (d, *J* = 7.9 Hz, 1H), 7.34 (s, 1H), 7.26 (s, 1H), 3.85 (s, 2H), 2.88 (t, *J* = 7.4 Hz, 2H), 2.72 (t, *J* = 7.7 Hz, 2H), 2.34 (s, 3H), 1.70–1.64 (m, 2H), 1.60–1.54 (m, 2H), 1.36–1.27 (m, 17H); ¹³C NMR: (125 MHz, CDCl₃) 196.2, 189.0, 155.4, 152.7, 147.2, 135.7, 128.7, 126.4, 124.5, 36.6, 31.1, 30.6, 29.53, 29.5, 29.46, 29.42, 29.3, 29.2, 29.1, 29.0, 28.7, 28.2; IR (cm⁻¹): 3258, 2916, 2851, 1726, 1685, 1655, 1610, 1581, 1470, 1406, 1353, 1332, 1303, 1272, 1113, 1037, 960, 922, 906, 832, 755, 756, 689, 640; HRMS (ESI) *m/z* calculated for C₂₃H₃₃NO₃S (M + Na)⁺: 426.2079, found: 426.2081.

4.24. *S*-(14-(2-(hydroxyimino)-1-oxo-2,3-dihydro-1H-inden-5-yl)tetradecyl) ethanethioate (**24**)

General procedure D was followed using **18** to afford the desired compound in quantitative yield. Off-white amorphous solid. R_f 0.53 (40% EtOAc/Hex); ^1H NMR: (500 MHz, CDCl_3) δ 7.81 (d, J = 7.8 Hz, 1H), 7.33 (s, 1H), 7.28 (d, J = 2.7 Hz, 1H), 3.85 (s, 2H), 2.87 (t, J = 7.2 Hz, 2H), 2.72 (t, J = 7.3 Hz, 2H), 2.33 (s, 3H), 1.67-1.63 (m, 2H), 1.60-1.54 (m, 2H), 1.34-1.32 (m, 21H); ^{13}C NMR: (125 MHz, CDCl_3) 196.2, 189.1, 155.3, 152.7, 147.3, 135.7, 128.7, 126.4, 124.5, 36.6, 31.1, 30.6, 29.57, 29.53, 29.4, 29.3, 29.2, 29.1, 29.0, 28.7, 28.2; IR (cm^{-1}): 3252, 2916, 2849, 1726, 1685, 1655, 1609, 1470, 1435, 1353, 1332, 1303, 1270, 1139, 1120, 1037, 959, 923, 907, 833, 774, 754, 690, 663, 639; HRMS (ESI) m/z calculated for $\text{C}_{25}\text{H}_{37}\text{NO}_3\text{S}$ ($\text{M} + \text{Na}$) $^+$: 454.2392, found: 454.2387.

4.25. *S*-(3-(1,2-dioxo-2,3-dihydro-1H-inden-5-yl)propyl)ethanethioate (25**)**

General Procedure E. To a stirred solution of **19** (30 mg, 0.108 mmol) in CH_2Cl_2 (1 mL) was added aqueous formaldehyde (37% in water, 48 μL) followed by conc. HCl (96 μL). The resulting mixture was stirred at room temperature overnight. The reaction was quenched with cold H_2O (1 mL), and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 mL, three times), and the organic layers were combined. The organic layer was washed with brine (1 mL), dried over MgSO_4 , filtered, and concentrated to afford **25** and a minor amount of thioacetate removed thiol, which was used without further purification. Light yellow amorphous solid. R_f 0.3 (50% EtOAc/Hex); ^1H NMR: (500 MHz, CDCl_3) δ 7.84 (d, J = 7.9 Hz, 1H), 7.39 (s, 1H), 7.32 (d, J = 7.8 Hz, 1H), 3.61 (s, 2H), 2.92 (t, J = 7.2 Hz, 2H), 2.83 (t, J = 7.7 Hz, 2H), 2.35 (s, 3H), 1.97 (dt, J = 14.9, 7.4 Hz, 2H); ^{13}C NMR: (125 MHz, CDCl_3) δ 200.2, 195.6, 186.5, 152.7, 147.0, 135.3, 129.3, 127.1, 125.8, 36.6, 35.7, 30.71, 30.67, 28.4; IR (cm^{-1}): 2923, 2853, 1765, 1719, 1688, 1610, 1438, 1391, 1354, 1329, 1298, 1262, 1204, 1135, 1121, 1090, 948, 835, 749, 669, 627, 566; HRMS (ESI) m/z calculated for $\text{C}_{14}\text{H}_{14}\text{O}_3\text{S}$ ($\text{M} + \text{Na}$) $^+$: 285.0570, found: 285.0561.

4.26. *S*-(5-(1,2-dioxo-2,3-dihydro-1H-inden-5-yl)pentyl)ethanethioate (26**)**

General procedure E was followed using **20** to afford the desired compound in quantitative yield. Yellow amorphous solid. R_f 0.52 (40% EtOAc/Hex); ^1H NMR: (500 MHz, CDCl_3) δ 7.84 (d, J = 7.9 Hz, 1H), 7.37 (s, 1H), 7.31 (d, J = 7.9 Hz, 1H), 3.60 (s, 2H), 2.87 (t, J = 7.3 Hz, 2H), 2.75 (t, J = 7.7 Hz, 2H), 2.33 (s, 3H), 1.74-1.60 (m, 6H), 1.48-1.41 (m, 4H); ^{13}C NMR: (125 MHz, CDCl_3) 200.2, 195.8, 186.4, 154.0, 146.9, 135.1, 129.2, 126.9, 125.7, 36.6, 36.5, 30.5, 30.3, 29.2, 28.7, 28.2; IR (cm^{-1}): 2932, 2858, 1764, 1719, 1688, 1609, 1437, 1391, 1353, 1263, 1134, 949, 837, 752, 627; HRMS (ESI) m/z calculated for $\text{C}_{16}\text{H}_{18}\text{O}_3\text{S}$ ($\text{M} + \text{H}$) $^+$: 291.1055, found: 291.1060.

4.27. *S*-(8-(1,2-dioxo-2,3-dihydro-1H-inden-5-yl)octyl)ethanethioate (27**)**

General procedure E was followed using **21** to afford the desired compound in quantitative yield. Yellow oil. R_f 0.6 (40% EtOAc/Hex); ^1H NMR: (500 MHz, CDCl_3) δ 7.83 (d, J = 7.9 Hz, 1H), 7.37 (s, 1H), 7.31 (d, J = 8.0 Hz, 1H), 3.60 (s, 2H), 2.85 (t, J = 7.4 Hz, 2H), 2.74 (t, J = 7.7 Hz, 2H), 2.32 (s, 3H), 1.70-1.64 (m, 3H), 1.56 (dt, J = 14.6, 7.3 Hz, 3H), 1.35 (dd, J = 13.3, 5.8 Hz, 6H); ^{13}C NMR: (125 MHz, CDCl_3) 200.3, 195.9, 186.4, 154.4, 146.8, 135.1, 129.2, 126.9, 125.6, 36.8, 36.5, 30.8, 30.5, 29.4, 29.1, 29.0, 28.9, 28.8, 28.6; IR (cm^{-1}): 3520, 2421, 3354, 3050, 2921, 2852, 2254, 1900, 1768, 1714, 1613, 1580, 1468, 1434, 1386, 1354, 1329, 1304, 1261, 1203, 1118, 1099, 951, 824,

755, 724, 667, 632; HRMS (ESI) m/z calculated for $\text{C}_{19}\text{H}_{24}\text{O}_3\text{S}$ ($\text{M} + \text{H}$) $^+$: 333.1524, found: 333.1521.

4.28. *S*-(10-(1,2-dioxo-2,3-dihydro-1H-inden-5-yl)decyl)ethanethioate (28**)¹¹**

General procedure E was followed to obtain the title compound in quantitative yield, which was characterized in our previous report.¹¹ ^1H NMR and ^{13}C NMR spectra obtained were in good agreement with the reported spectra: ^1H NMR: (500 MHz, CDCl_3) δ 7.86 (d, J = 7.9 Hz, 1H), 7.38 (s, 1H), 7.33 (d, J = 7.9 Hz, 1H), 3.61 (s, 2H), 2.89-2.86 (m, 2H), 2.76 (t, J = 7.7 Hz, 2H), 2.34 (s, 3H), 1.72-1.64 (m, 3H), 1.62-1.54 (m, 3H), 1.38-1.28 (m, 10H); ^{13}C NMR: (125 MHz, CDCl_3) 200.3, 196.0, 186.4, 154.6, 146.8, 135.1, 129.2, 126.9, 125.7, 36.9, 36.6, 30.9, 30.6, 29.5, 29.49, 29.45, 249.41, 29.3, 29.2, 29.1, 29.0, 28.7; IR (cm^{-1}): 2918, 2850, 1766, 1716, 1694, 1611, 1469, 1434, 1384, 1353, 1328, 1304, 1267, 1136, 1118, 951, 8223, 718, 630; HRMS (ESI) m/z calculated for $\text{C}_{23}\text{H}_{32}\text{O}_3\text{S}$ ($\text{M} + \text{Na}$) $^+$: 411.1970, found: 411.1973.

4.29. *S*-(12-(1,2-dioxo-2,3-dihydro-1H-inden-5-yl)dodecyl)ethanethioate (29**)**

General procedure E was followed using **23** to afford the desired compound in quantitative yield. R_f 0.71 (40% EtOAc/Hex); ^1H NMR: (500 MHz, CDCl_3) δ 7.85 (d, J = 7.9 Hz, 1H), 7.38 (s, 1H), 7.33-7.32 (m, 1H), 3.61 (s, 2H), 2.87 (t, J = 7.3 Hz, 2H), 2.75 (t, J = 7.7 Hz, 2H), 2.34 (s, 3H), 1.71-1.65 (m, 3H), 1.60-1.54 (m, 3H), 1.36-1.27 (m, 14H); ^{13}C NMR: (125 MHz, CDCl_3) 200.4, 196.0, 186.4, 154.6, 146.8, 135.1, 129.2, 126.9, 125.7, 36.9, 36.5, 30.9, 30.6, 29.5, 29.49, 29.45, 249.41, 29.3, 29.2, 29.1, 29.0, 28.7; IR (cm^{-1}): 2918, 2850, 1766, 1716, 1694, 1611, 1469, 1434, 1384, 1353, 1328, 1304, 1267, 1136, 1118, 951, 8223, 718, 630; HRMS (ESI) m/z calculated for $\text{C}_{23}\text{H}_{32}\text{O}_3\text{S}$ ($\text{M} + \text{Na}$) $^+$: 411.1970, found: 411.1973.

4.30. *S*-(14-(1,2-dioxo-2,3-dihydro-1H-inden-5-yl)tetradecyl)ethanethioate (30**)**

General procedure E was followed using **24** to afford the desired compound in quantitative yield. R_f 0.7 (40% EtOAc/Hex); ^1H NMR: (500 MHz, CDCl_3) δ 7.85 (d, J = 8.0 Hz, 1H), 7.38 (s, 1H), 7.33 (d, J = 8.0 Hz, 1H), 3.61 (s, 2H), 2.87 (t, J = 7.4 Hz, 2H), 2.75 (t, J = 7.7 Hz, 2H), 2.33 (s, 3H), 1.71-1.54 (m, 8H), 1.36-1.27 (m, 16H); ^{13}C NMR: (125 MHz, CDCl_3) 200.4, 196.0, 186.4, 154.6, 146.8, 135.1, 129.2, 126.9, 125.7, 36.9, 36.5, 30.9, 30.6, 29.6, 29.5, 29.47, 29.43, 29.3, 29.2, 29.1, 29.0, 28.7; IR (cm^{-1}): 2919, 2849, 1765, 1719, 1693, 1610, 1470, 1437, 1385, 1351, 1328, 1262, 1118, 948, 823, 718, 630; HRMS (ESI) m/z calculated for $\text{C}_{25}\text{H}_{36}\text{O}_3\text{S}$ ($\text{M} + \text{Na}$) $^+$: 439.2283, found: 439.2278.

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Supplementary Material

Supplementary data associated with this article can be found, in the online version.