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Synthesis and Properties of Heavy Chalcogen Analogues of the Texas Reds and Related Rhodamines

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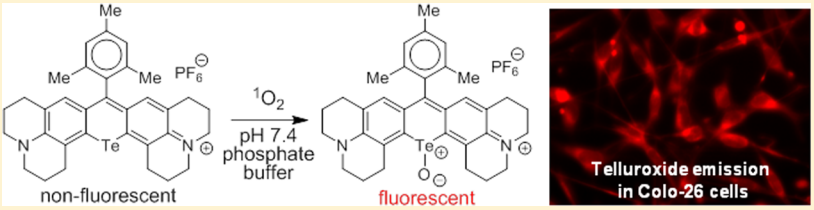
Supporting Information

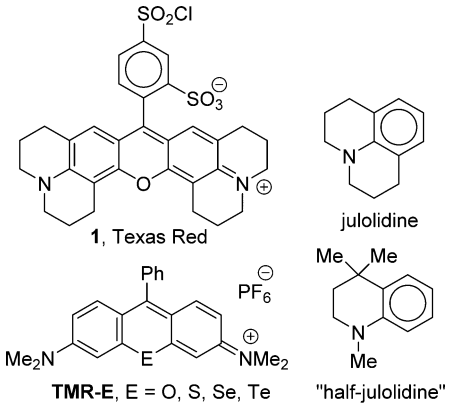


ABSTRACT: Analogues of Texas red incorporating the heavy chalcogens S, Se, and Te atoms in the xanthylium core were prepared from the addition of aryl Grignard reagents to appropriate chalcogenoxanthone precursors. The xanthones were prepared via directed metalation of amide precursors, addition of dichalcogenide electrophiles, and electrophilic cyclization of the resulting chalcogenides with phosphorus oxychloride and triethylamine. The Texas red analogues incorporate two fused julolidine rings containing the rhodamine nitrogen atoms. Analogues containing two "half-julolidine" groups (a trimethyltetrahydroquinoline) and one julolidine and one "half-julolidine" were also prepared. The photophysics of the Texas red analogues were examined. The S-analogues were highly fluorescent, the Se-analogues generated single oxygen ($^1O_2$) efficiently upon irradiation, and the Te-analogues were easily oxidized to rhodamines with the telluroxide oxidation state. The tellurorhodamine telluroxides absorb at wavelengths ≥690 nm and emit with fluorescence maxima >720 nm. A mesityl-substituted tellurorhodamine derivative localized in the mitochondria of Colo-26 cells (a murine colon carcinoma cell line) and was oxidized *in vitro* to the fluorescent telluroxide.

INTRODUCTION

The two fused julolidine rings of the rhodamine Texas red (**1**, Chart 1) lock the N atoms into conjugation with the rhodamine xanthylium core leading to longer wavelengths of absorption. Compound **1** and related structures have found numerous applications, primarily based on their wavelength and efficiency of fluorescence and their flat, rigid nature, which has assisted in binding to biopolymers.[1−12] Analogues of **1** with even longer wavelengths of absorbance and emission have been of interest.[12−14]

Chart 1



We have prepared heavy-atom analogues of the tetramethylrosamines/rhodamines (**TMR-E**, Chart 1)[15−17] and analogues incorporating one julolidine group[18] and, more recently, one "half-julolidine" group (a trimethyltetrahydroquinoline, Chart 1) in the xanthylium core.[19] The introduction of a single fused julolidine or half-julolidine group gives a small increase in absorption maxima (λ_{max}), but larger shifts in λ_{max} are realized by replacing the oxygen atom of the xanthylium core with the heavier chalcogen atoms S, Se, and Te. As the chalcogen atoms increase in size, the resulting rhodamines have decreasing quantum yields of fluorescence (Φ_{FL}) and increasing quantum yields for the generation of triplets and singlet oxygen [$\Phi(^1O_2)$].[15−18] The synthesis of Texas red derivatives incorporating the heavier chalcogen atoms S, Se, and Te should give rhodamine analogues with values of λ_{max} > 600 nm

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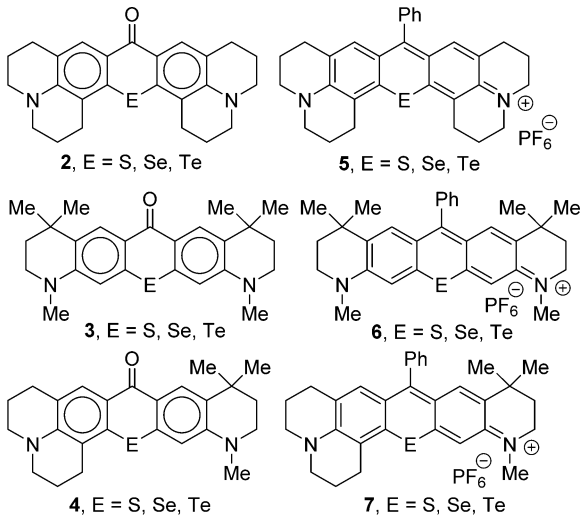
with control of relative yields for fluorescence and triplet production for different applications.

A second observation regarding analogues of **TMR-Te** is the facile oxidation to the telluroxide oxidation state. The rhodamine telluroxides absorb at much longer wavelengths (>60 nm longer) than the reduced forms. Furthermore, the rhodamine telluroxides are highly fluorescent, while the reduced tellurorhodamine/rosamines are nonfluorescent.[20,21] Tellurium-containing derivatives of **1** should be readily oxidized to telluroxides with absorption and emission wavelengths in the near-infrared.

Herein, we describe the synthesis of S-, Se-, and Te-containing analogues of **1** and related compounds via the chalcogenoxanthone precursors **2**−**4** (Chart 2). The Texas red analogues **5**−**7** with a 9-phenyl substituent were then prepared (Chart 2). The S-containing analogues were highly fluorescent, the Se-containing analogues were an order of magnitude less fluorescent and generated singlet oxygen ($^1O_2$) efficiently upon irradiation, and the Te-containing analogues were easily oxidized to the telluroxide oxidation state and absorb at wavelengths >690 nm and emit with fluorescence maxima >720 nm. Preliminary studies also indicate that tellurorhodamines localize in the mitochondria of cells and that *in vitro* oxidation of a tellurorhodamine and emission from the resulting telluroxide can be observed in cells in culture.

Chart 2



RESULTS AND DISCUSSION

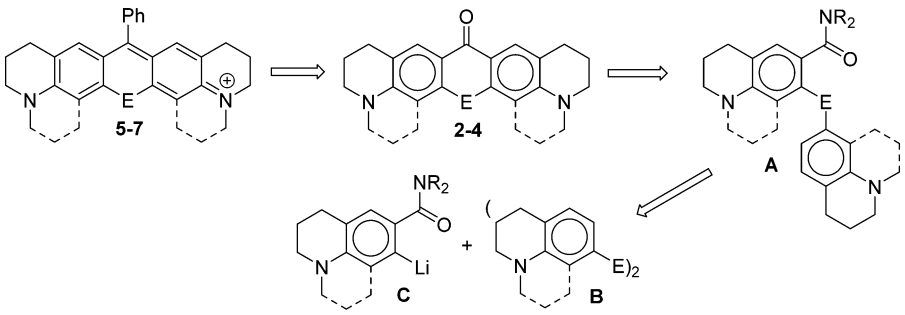
Synthesis. Our synthetic approach is analyzed in Scheme 1. The key to the successful synthesis of **TMR**-related molecules or derivatives incorporating a julolidine or half-julolidine was access to the corresponding chalcogenoxanthones as precursors to the rhodamine analogues.[18,19,22−24] The synthesis of chalcogenoxanthones is similarly key to this work. Texas red analogues such as **5**−**7** can be prepared via the addition of PhMgBr (or other Grignard or organolithium reagents) to chalcogenoxanthones **2**−**4** followed by treatment with acid. Chalcogenoxanthones **2**−**4** can be prepared via electrophilic cyclization of the diaryl chalcogenide intermediates **A** (Scheme 1) under modified Friedel−Crafts conditions. Structures related to **A** have shown a propensity to cyclize *para* to the amino substituent under these conditions.[19,22−24] Intermediates **A** can be prepared via the addition of a diaryl dichalcogenide **B** bearing a *m*-amino substituent to an anion **C** prepared by amide-directed metalation.[19,22−24]

The specific dichalcogenide precursors **B** were prepared as shown in Scheme 2. 3-Bromoaniline (**8**) was converted to 8-bromojulolidine (**9**) using a modification of the literature procedure used to prepare other 8-substituted julolidines.[25] Alkylation of **8** with excess 1-bromo-3-chloropropane at 140 °C in the presence of Na_2CO_3 gave dialkylation of **8** in essentially quantitative yield. The unpurified dialkylation product was isolated by extraction, dried, and then heated at 160 °C in anhydrous DMF for 48 h to give **9**[26] in 68% isolated yield overall. Formation of the Grignard reagent from **9** with Mg turnings in THF proceeded only when the concentration of **9** in THF was at least 2.0 M. At lower concentrations, the Grignard reagent either did not form or formed sluggishly. Elemental S, Se, or Te was then added to the Grignard reagent from **9** to give the corresponding julolidyl dichalcogenides **10** following air oxidation.

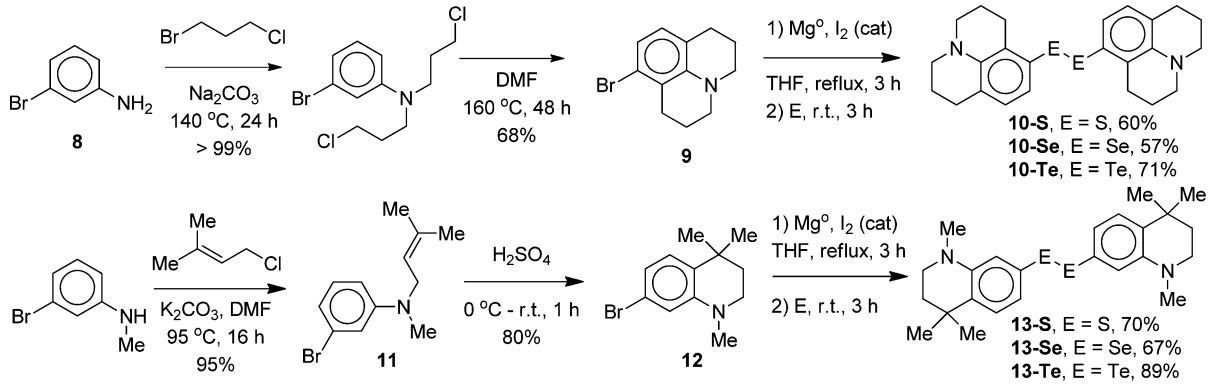
The half-julolidyl analogues **13** were prepared via allylation of commercially available 3-bromo-*N*-methylaniline with 1-chloro-3-methylbut-2-ene in DMF at 95 °C to give aniline **11** in 95% yield (Scheme 2). These conditions are more strenuous than the literature conditions[25] used for the allylation of *N*-methylaniline (1-chloro-3-methylbut-2-ene and K_2CO_3 in CH_3CN at 40 °C) and were necessary to give product formation. Cyclization of **11** with concentrated H_2SO_4 gave tetrahydroquinoline **12**.[27] The Grignard reagent from **12** reacted with elemental S, Se, or Te to give dichalcogenides **13** following air oxidation.

Chalcogenoxanthones **2**−**4** were prepared as shown in Scheme 3. Julolidine-9-carboxamide **14**[22] was treated with *s*-BuLi and TMEDA to give directed *ortho*-lithiation. Treating the resulting anion with a diaryl dichalcogenide **10** gave the

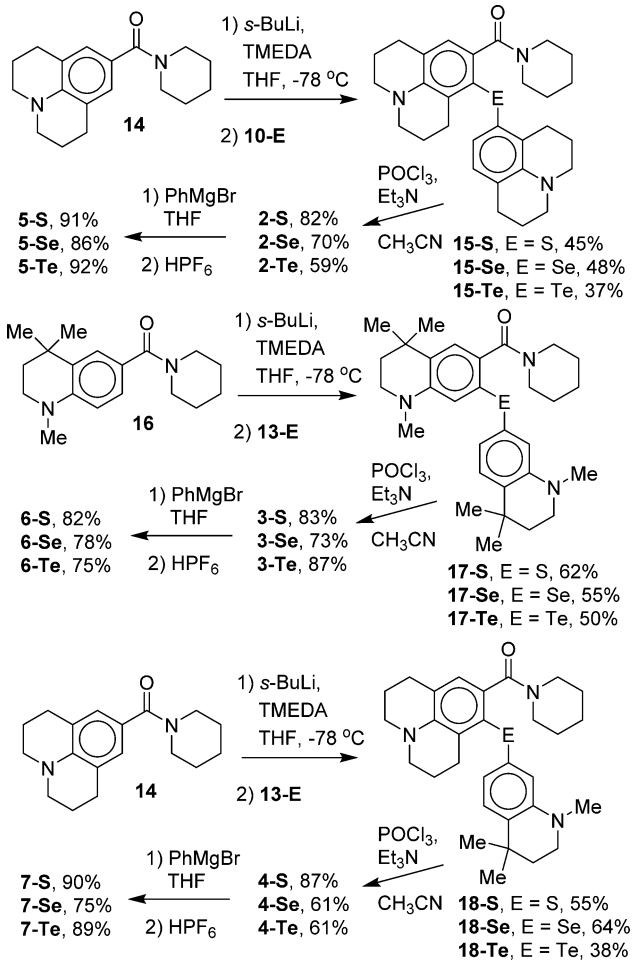
Scheme 1



Scheme 2



Scheme 3



unsymmetrical diaryl chalcogenides **15**, which were cyclized to xanthones **2** with $POCl_3$ and Et_3N in CH_3CN.[23] Similarly, tetrahydroquinoline carboxamide **16**[19] was treated with *s*-BuLi and TMEDA followed by a diaryl dichalcogenide **13** to give the unsymmetrical diaryl chalcogenides **17**, which were cyclized to xanthones **3** with $POCl_3$ and Et_3N in CH_3CN.[23] The unsymmetrical xanthones **4** were prepared from carboxamide **14** and diaryl dichalcogenides **13** via the intermediacy of diaryl chalcogenides **18**. The cyclization of **18** with $POCl_3$ and Et_3N in CH_3CN[23] gave xanthones **4**.

Alternatively, xanthones **4** were prepared from directed metalation of **16** followed by treating the resulting anion with a dichalcogenide **10-E**. This approach gave poorer yields than the procedure shown in Scheme 3.

Compounds **2**−**4** were converted to the Texas red analogues **5**−**7** (Scheme 2) with PhMgBr in THF followed by work up with aqueous HPF_6 (Table 1). Other 9-substituents should be readily introduced using other Grignard or organolithium reagents.[15,16,18−22]

It should be noted that the directed metalation of **16** gave only one regioisomer following the addition of the dichalcogenide electrophile. No product resulting from electrophilic attack at the carbon next to the *gem*-dimethyl substituents was observed. The electrophilic cyclization of intermediates **17** gave only one product−acylation at the *para*-position relative to the amino substituent. The synthetic routes to chalcogenoxanthones **2** and **4** could only lead to one regioisomer in the directed metalation reaction and, for **2**, only one product in the electrophilic cyclization.

Photophysical Properties. Texas red (**1**) has an absorbance maximum, λ_{max}, of 587 nm in MeOH with a molar extinction coefficient, ε, of 8.5×10^4 M^{-1} cm^{-1} (Table 1).[1] The Texas red analogues **5** incorporating the heavier chalcogen analogues have values of λ_{max} at longer wavelengths (594−617 nm, Table 1). For comparison purposes, values of λ_{max} and ε in MeOH for the **TMR-E** analogues (E = O−Se[16] and Te[15]) are also compiled in Table 1. The heavy-chalcogen analogues **5** of the Texas reds are all red-shifted 20−23 nm relative to their corresponding **TMR-E** derivative, and all have values of $\varepsilon \geq 1.24 \times 10^5$ M^{-1} cm^{-1}. Compounds **6** with two half-julolidine groups are red-shifted 8−9 nm relative to the corresponding **TMR-E** analogues, while the red shift of the unsymmetrical dyes **7** is intermediate at 13−16 nm.

Steady-state fluorescence spectra for **5**−**7** were acquired with excitation at 532 nm.[16] The emission maxima (λ_{FL}) and quantum yields for fluorescence (Φ_{FL}) for **TMR-E** (E = O−Se[16] and Te[21]) and dyes **5**−**7** are compiled in Table 1. Values of Φ_{FL} for the S-containing dyes **5-S**, **6-S**, and **7-S** (Φ_F = 0.42−0.53, Table 1) are comparable to Φ_{FL} for **TMR-S** (Φ_F = 0.44).[16] Selenium-containing dyes **5-Se**, **6-Se**, and **7-Se** have values of Φ_{FL} roughly an order of magnitude smaller than their corresponding S-analogues (Φ_{FL} = 0.02−0.06, Table 1), and all are more emissive than **TMR-Se** (Φ_F = 0.009).[16] Fluorescence from all of the Te-containing analogues (**TMR-Te**, **5-Te**, **6-Te**, and **7-Te**) is weak (Φ_{FL} < 0.005, Table 1).

Quantum yields for the generation of $^1O_2$ [$\Phi(^1O_2)$] by **5**−**7** were evaluated using steady-state $^1O_2$ luminescence with **TMR-Se** as a reference [$\Phi(^1O_2)$ = 0.87].[16] In Figure 1, the smoothed luminescence spectra of $^1O_2$ produced by the sensitization of **5-**

Table 1. Synthetic Yields, Absorption Maxima (λ_{max}), and Molar Extinction Coefficients (ε) in CH_3OH, Fluorescence Emission Maxima (λ_{FL}) and Quantum Yields for Fluorescence (Φ_{FL}) in CH_3OH, Quantum Yields for the Generation of Singlet Oxygen [$\Phi(^1O_2)$] in CH_3OH for 5-E–7-E, and Values of λ_{max}, ε, and $\Phi(^1O_2)$ for 19-Se and 20-Se

compd	% yield	λ_{max} (nm)	ε (M^{-1} cm^{-1})	λ_{FL} (nm)	Φ_{FL}[a]	$\Phi(^1O_2)$[a]
TMR-O[b]		550	8.66×10^4	575	0.84	0.08
TMR-S[b]		571	6.26×10^4	599	0.44	0.21
TMR-Se[b]		581	4.4×10^4	608	0.009	0.87
TMR-Te		597[c]	8.1×10^4[c]		<0.005[d]	0.43[d]
1		587[e]	8.5×10^4[e]	615[e]		
5-S	91	594	1.24×10^5	621	0.42	<0.05
5-Se	86	604	1.35×10^5	631	0.06	0.68
5-Te	92	617	1.44×10^5	642	0.002	0.53
6-S	92	579	1.04×10^5	606	0.53	<0.05
6-Se	78	590	1.36×10^5	617	0.03	0.79
6-Te	75	607	1.21×10^5	632	0.002	0.47
7-S	90	587	1.20×10^5	614	0.47	<0.05
7-Se	75	597	1.22×10^5	624	0.02	0.81
7-Te	89	610	1.27×10^5	637	0.003	0.40
19-Se[f]		588	1.26×10^5			0.85
20-Se	74	585	1.35×10^5			0.88

[a]Standard deviation in values is ±3%. [b]Ref 16. [c]Ref 15. [d]Ref 20. [e]Ref 1. [f]Ref 18.

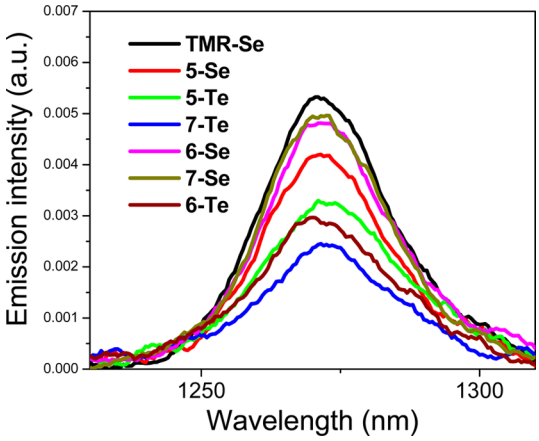


Figure 1. Luminescence of $^1O_2$ sensitized with **TMR-Se**, **5-Se**, **5-Te**, **6-Se**, **6-Te**, **7-Se**, and **7-Te** through excitation at 532 nm (MeOH solutions). Concentrations of all solutions were adjusted to match OD = 0.10 at 532 nm.

Se, **5-Te**, **6-Se**, **6-Te**, **7-Se**, and **7-Te** are compared to the luminescence spectrum of $^1O_2$ produced by the sensitization of **TMR-Se**. Steady-state $^1O_2$ luminescence emission for the S-containing dyes **5-S**, **6-S**, and **7-S** was difficult to extract from the background and the values of $\Phi(^1O_2)$ for the S-containing compounds are considered to be low [$\Phi(^1O_2) < 0.05$]. Values of $\Phi(^1O_2)$ are compiled in Table 1 for **TMR-E** (E = O–Se[16] and Te[23]) derivatives and dyes **5**–**7**.

The Se-containing analogues **TMR-Se**, **5-Se**, **6-Se**, and **7-Se** were found to generate $^1O_2$ more efficiently [$\Phi(^1O_2)$ = 0.68–0.87] than their corresponding Te-containing analogues **TMR-Te**, **5-Te**, **6-Te**, and **7-Te** [$\Phi(^1O_2)$ = 0.40–0.53]. A possible reason for this can be that as the rate of $S_1 \rightarrow T_1$ intersystem crossing increases, the heavy atom simultaneously increases the rate of $T_1 \rightarrow S_0$ nonradiative transition, causing a decrease in the triplet lifetime that, correspondingly, may decrease the efficiency of the sensitization of singlet oxygen.[28,29] The observed intensity of $^1O_2$ luminescence could be also affected by other possible interactions of $^1O_2$, which are different for the Texas red analogues with Se and Te atoms (e.g., possible formation of exciplexes between $^1O_2$ and dye molecules).

In examining the trends observed on the impact of amine structure on $\Phi(^1O_2)$ within the Se-containing dyes, incorporation of the julolidyl fragment lowers $\Phi(^1O_2)$ more than incorporation of the half-julolidyl fragment. Values for **5-Se**, **6-**

Scheme 4

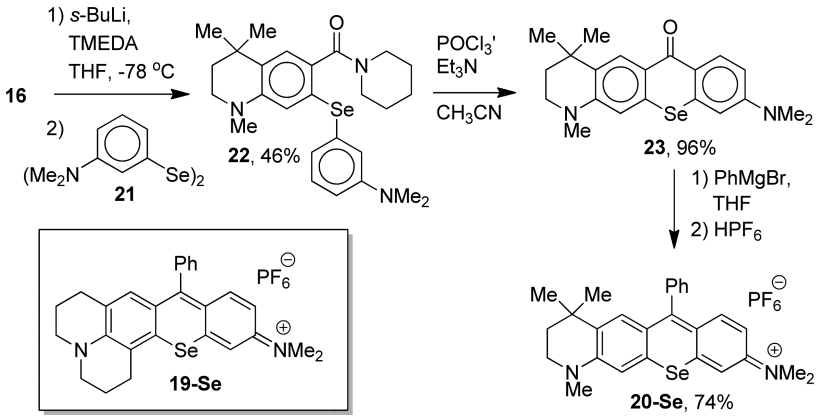
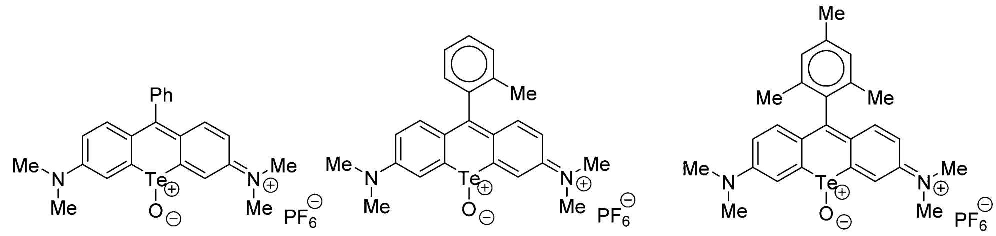


Chart 3



24 25 26

Se, and **7-Se** were compared to **19-Se**[18] incorporating one julolidyl fragment and **20-Se** incorporating one-half-julolidyl fragment.

Compound **20-Se** was prepared as shown in Scheme 4. Lithiation of amide **16** with *s*-BuLi/TMEDA followed by the addition of diselenide **21**[24] gave diaryl selenide **22** in 46% isolated yield as the only observed product. Cyclization of **22** with $POCl_3/Et_3N$ in CH_3CN[23] gave selenoxanthone **23** in 96% yield. The addition of PhMgBr to **23** in THF followed by work-up with aqueous HPF_6 gave selenorhodamine **20-Se** in 74% isolated yield. The luminescence spectrum of $^1O_2$ produced by sensitization with **20-Se** was compared to the luminescence spectrum of $^1O_2$ produced by sensitization of **TMR-Se** to give $\Phi(^1O_2)$ of 0.88 (Table 1). The value of $\Phi(^1O_2)$ for **19-Se** was previously determined to be 0.85.[18]

The selenorhodamine **TMR-Se** has λ_{max} of 581 nm in MeOH, while values of λ_{max} for **19-Se** and **20-Se** were 588 and 585 nm, respectively. The impact of the incorporation of a single julolidyl or half-julolidyl moiety in the chromophore is less than half the change observed in λ_{max} for the incorporation of two. The impact of the incorporation of a single julolidyl or half-julolidyl moiety on $\Phi(^1O_2)$ is even smaller. Values of $\Phi(^1O_2)$ for **TMR-Se** (0.87), **19-Se** (0.85), and **20-Se** (0.88) are essentially identical within the 3% error of the experiments. When both amino groups are constrained in julolidyl or half-julolidyl fragments, values of $\Phi(^1O_2)$ are lower for **5-Se** (0.68) and **6-Se** (0.76) relative to **TMR-Se**, **19-Se**, or **20-Se**.

Oxidation of Tellurorhodamines to Tellurorhodamine Telluroxides. Earlier studies with chalcogenopyrylium dyes show that rates of reaction of $^1O_2$ with the chalcogen atom in the dye chromophore is Te ≫ S > Se.[30] Our recent studies show a rapid oxidation of several tellurorhodamines with $^1O_2$ to give telluroxides **24–26** (Chart 3).[20] We examined the oxidations of **5-Te** and **6-Te** to the corresponding telluroxides in two ways. Photooxidation of 8×10^{-6} M **5-Te** in air-saturated 50% aqueous MeOH containing 0.1 M CF_3CO_2H with 375–800 nm light from a filtered tungsten lamp (50 mW cm^{-2}) gave loss of the chromophore for **5-Te** (λ_{max} 617 nm) and appearance of a new chromophore at 716 nm, which was transiently stable. The oxidation was more conveniently carried out using H_2O_2 as an oxidant as shown in Figure 2. Texas red analogue **5-Te** was oxidized with 3×10^{-3} M H_2O_2 to give presumably the corresponding telluroxide with λ_{max} of 716 nm ($\varepsilon = 1.1 \times 10^5$ M^{-1} cm^{-1} assuming 100% conversion of **5-Te** to telluroxide) with an isosbestic point at 641 nm. The 716 nm chromophore was lost upon standing under the conditions of reaction over a 2-h time period. Attempts to prepare the telluroxide on a milligram scale resulted decomposition to many products.[20]

In our earlier work, tellurorhodamine telluroxides **25** and **26** (Chart 3) substituted with 9-aryl groups with *ortho*-methyl

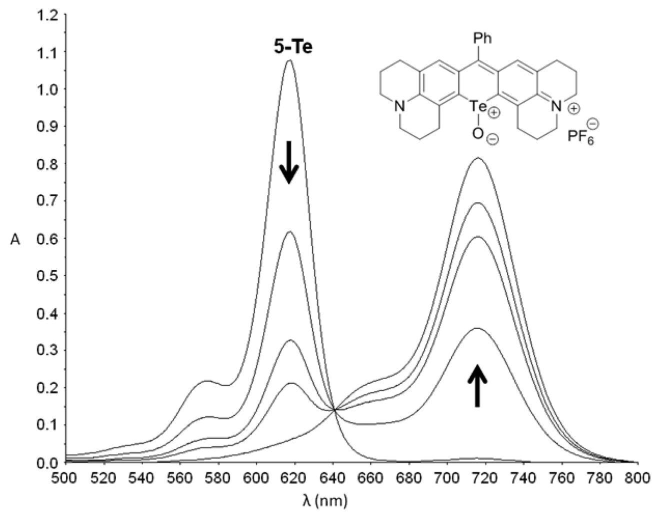


Figure 2. Oxidation of 8×10^{-6} M **5-Te** with 3×10^{-3} M H_2O_2 in 50% aqueous MeOH containing 0.1 M CF_3CO_2H. After an initial scan at 0 s, subsequent scans were taken at 960, 1920, 2400, and 3360 s.

functionality displayed increased hydrolytic stability relative to telluroxide **24** with a 9-phenyl substituent.[20] To this end, 9-mesityltellurorhodamine **27** was prepared in 83% yield by the addition of the Grignard reagent from 2-bromomesitylene to telluroxanthone **2-Te** at ambient temperature in THF followed by work-up with aqueous HPF_6 (Scheme 5). Tellurorhodamine **27** absorbed light with a λ_{max} of 617 nm and ε of 1.65×10^5 M^{-1} cm^{-1} in MeOH (Table 2). Tellurorhodamine **27** was oxidized to telluroxide **28** with 3×10^{-3} M H_2O_2 in either pH 7.4 phosphate buffer or in MeOH containing 0.1 M CF_3CO_2H. Mesityl-substituted telluroxide **28** was stable with no loss of the 704 nm chromophore (Table 2) after several hours at ambient temperature.

Similarly, the addition of the Grignard reagent from 2-bromomesitylene to telluroxanthone **3-Te** at ambient temperature in THF followed by work-up with aqueous HPF_6 gave tellurorhodamine **29** in 56% isolated yield (Scheme 5). Tellurorhodamine **29** absorbed light with a λ_{max} of 606 nm and an ε of 9.66×10^4 M^{-1} cm^{-1} in MeOH (Table 2). Tellurorhodamine **29** was oxidized with 3×10^{-3} M H_2O_2 in either pH 7.4 phosphate buffer or in MeOH containing 0.1 M CF_3CO_2H to give telluroxide **30** with a λ_{max} of 692 nm (Table 2). Telluroxide **30** was less stable than telluroxide **28** and was lost over several hours at ambient temperature in both solvent systems.

On a preparative scale, both **27** and **29** were oxidized in 0.1 M CF_3CO_2D in CD_3OD with H_2O_2 (0.18 M) to allow the acquisition of NMR spectra. For both compounds, ^1H NMR spectra were acquired immediately after the addition of H_2O_2 and showed complete oxidation of the starting tellurorosamine

Scheme 5

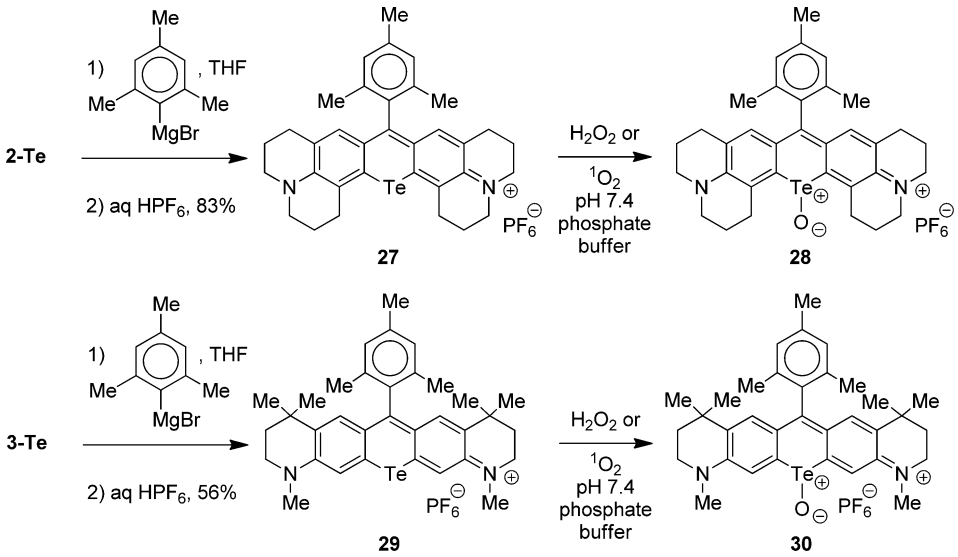


Table 2. Absorption Maxima (λ_{max}), Molar Extinction Coefficients (ε), Fluorescence Maxima (λ_{FL}), and Fluorescence Quantum Yields (Φ_{FL}) for Tellurorhodamine 27 and 29 and Tellurorhodamine Telluroxides 28 and 30

compd	λ_{max} (nm)	ε (M^{-1} cm^{-1})	λ_{FL} (nm)	Φ_{FL}
27[a]	617	1.65×10^5		<0.005
28[b]	704	1.35×10^5	740	0.16
29[a]	606	9.66×10^4		<0.005
30[b]	692	1.65×10^5	720	0.16

[a]In MeOH. [b]In CH_3OH containing 0.1 M CF_3CO_2H.

to telluroxides **28** and **30**. For **28**, no further changes were observed over a 1.5-h period. For **30**, loss of telluroxide signals and the appearance of new products were observed over a 1.5-h period.

Coupling patterns and chemical shifts are similar in the **27**/**28** and **29**/**30** pairs, and ^{1}H NMR spectra for both pairs in 0.1 M CF_3CO_2D in CD_3OD are compiled in the Supporting Information. Both tellurorosamine dyes **27** and **29** gave ^{13}C NMR spectra with the expected 19 (11 aromatic and 8 aliphatic) signals. The ^{13}C NMR spectra of telluroxides **28** and **30** were not as well-defined (Supporting Information). All eight different aliphatic carbons were observed for both compounds, but only 8 aromatic signals for **28** and 10 aromatic signals for **30** were observed. Acquisition of data was limited by the stability of the oxidized product. At higher concentrations of **28**/**30**, the rate of loss of **30** was accelerated suggesting second-order processes for the loss of **30**. Solvent addition/elimination to the telluroxide functionality might also lead to line broadening on near-by carbons.

Both **28** and **30** were highly emissive. The absorption and emission spectra of telluroxides **28** and **30** in MeOH containing 0.1 M CF_3CO_2H are shown in Figure 3. Values of Φ_F for **28** and **30** were both 0.16 (Table 2) using Rhodamine 700 as a known fluorescence standard with $\Phi_F = 0.38$.[31]

Biological Studies: Cellular Oxidation of 27. In our early work examining telluropyrylium dyes as photosensitizers for the photodynamic therapy (PDT) of cancer, we noted mitochondrial fluorescence from the telluroxide oxidation state following irradiation of dye-treated U-251 MG glioblastoma cells.[32,33] Oxidation of the telluropyrylium dyes via self-

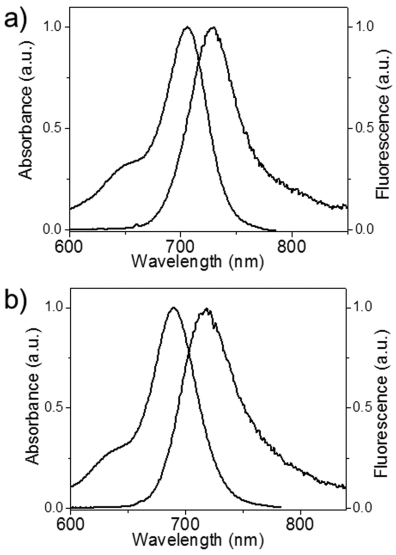


Figure 3. Absorption and fluorescence spectra for (a) tellurorhodamine telluroxide **28** and (b) tellurorhodamine telluroxide **30** in MeOH with 0.1 M CF_3CO_2H.

sensitized generation of singlet oxygen gave telluroxide analogues that absorbed and fluoresced at *shorter* wavelengths than the reduced form. More recent studies with telluride/telluroxide[20,34] and selenide/selenoxide[35] pairs examined fluorescence from the chromophore substituted with telluroxide or selenoxide functionality as a probe for redox cycles in living cells. In the case of telluride/telluroxide pairs based on the rhodamine core, the telluroxide absorbs and fluoresces at wavelengths *longer* than those of the reduced form.[19,20]

In order to examine the viability of tellurorhodamine **27**/telluroxide **28** as a redox pair indicator in cells, Colo-26 cells (a murine colon carcinoma cell line) were incubated first with 0.5 μM MitoTracker Green (**MTG**) for 10 min and then 0.2 μM tellurorhodamine **27** for an additional 5 min (15 min total for **MTG** and 5 min total for **27**). The cells were washed prior to imaging on a fluorescence microscope. The cells were brought to focus using a halogen lamp, which was used at the end of the experiment to generate the transmission microscopy image

shown in Figure 4a. Irradiating the cells with 620 nm light should oxidize nonfluorescent tellurorhodamine **27** (Figure 4b,

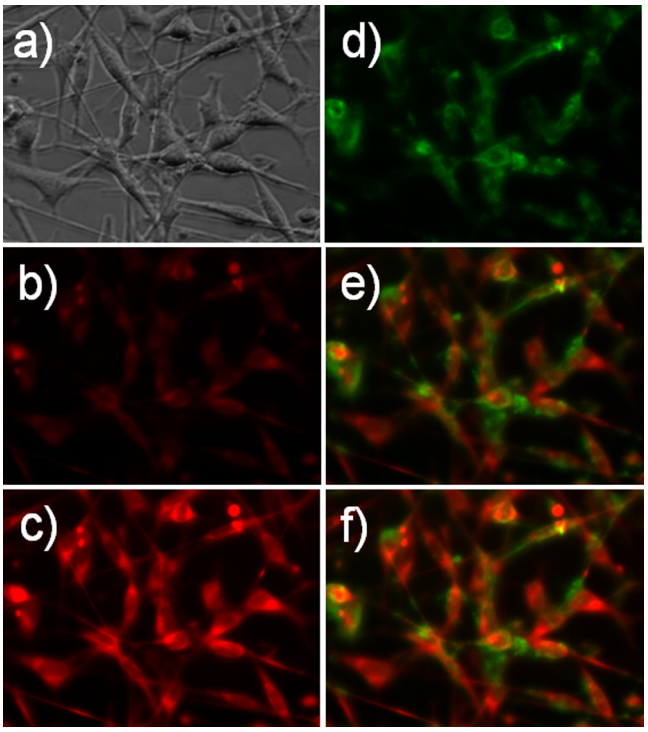


Figure 4. (a) Transmission microscopy image of Colo-26 cells treated with **MTG** and tellurorhodamine **27**. (b) Fluorescence microscopy image of Colo-26 cells before irradiation with 620 ± 30 nm light (t = 0 s). (c) Fluorescence microscopy image of Colo-26 cells from Panel b after 15 s of irradiation with 620 ± 30 nm light (t = 15 s). (d) Fluorescence microscopy image of **MTG** fluorescence in Colo-26 cells (excitation with 470 ± 20 nm light). (e) Overlay of images from panels b and d. (f) Overlay of images from panels c and d.

time = 0 s for 620 nm irradiation) via **27**-sensitized generation of $^1O_2$ to give fluorescent telluroxide **28** (Figure 4c, time = 15 s of irradiation with 620 ± 30 nm light) in the cell. Excitation of the **MTG** (470 ± 20 nm light) is shown in Figure 4d. Figure 4e and f shows the overlays of emission from telluroxide **28** and the **MTG**. The images of Figure 4 clearly indicate that the reduced tellurorhodamine dye **27** is in the Colo-26 cells and that brief irradiation with 620 nm light gives photooxidation of **27** to fluorescent telluroxide **28** in Figure 4c. The overlay of **MTG** emission and telluroxide **28** emission in Figure 4f indicates that tellurorhodamine **28** is at least partially targeted to the mitochondria.

■ CONCLUSIONS

We have successfully prepared heavy-chalcogen analogues of Texas red (**1**) incorporating S, Se, and Te atoms in the xanthylium core. The heavy-chalcogen analogues absorb at longer wavelengths than **1**. The excited state of S-containing analogue **5-S** is highly emissive (Φ_{FL} = 0.42), while the excited state of the Se- and Te-containing derivatives gives intersystem crossing to the triplet with efficient generation of $^1O_2$ [$\Phi(^1O_2)$ = 0.68 for **5-Se** and 0.53 for **5-Te**]. We have also prepared derivatives **6-E** and **7-E** incorporating fused trimethyltetrahydroquinoline (half-julolidine) in the xanthylium core. These derivatives give values of λ_{max} that are intermediate between the **TMR-E** and **5-E** derivatives (Table 1), but their photophysical properties are quite similar to those for **5-E**.

Incorporating a single julolidine or a single half-julolidine into the xanthylium core has little impact on the photophysical properties. Singlet oxygen yields for **TMR-Se**, **19-Se**, and **20-Se** are essentially identical, while values of λ_{max} are between 581 and 587 nm (Table 1).

The tellurium analogues **5-Te** and **6-Te** are easily oxidized with $^1O_2$ or H_2O_2 presumably to the corresponding telluroxides, but the telluroxide derivatives were hydrolytically unstable. Texas red analogues **27** and **29** bearing a 9-mesityl substituent are oxidized to telluroxides **28** and **30**, respectively, which are hydrolytically more stable than the oxidation products of **5-Te** and **6-Te**. Both **28** and **30** are highly fluorescent (Φ_F = 0.16 for both). Tellurorhodamine **27** is oxidized to telluroxide **28** by the self-sensitized generation of $^1O_2$ in cells.

The heavy-chalcogen Texas red analogues can be applied to several biological problems. The mesityl-substituted tellurorhodamine **27** and its corresponding telluroxide **28** represent a redox-related, nonfluorescent/fluorescent pair of molecules that can be observed in cells. Fluorescence from telluroxide **28** or related structures (such as **30**) *in vitro* might allow the tracking of cellular redox processes.[20] The Se-containing analogues **5-Se**, **6-Se**, and **7-Se** as well as related structures have potential as photosensitizers for the photodynamic therapy (PDT) of malignant cells[17,18,36,37] and as photosensitizers for the photodynamic purging of blood-borne viral and bacterial pathogens.[38−40] For applications in PDT, the Se-containing analogues **5-Se**, **6-Se**, and **7-Se** absorb light wavelengths >600 nm, where light penetration of tissue is greatest.[40]

These versatile chromophores can also be applied to problems related to solar energy and solar fuels as has been done with analogues of the **TMR-E** dyes. Appropriate substitution in the 9-position of the chromophores would allow entry into longer-wavelength-absorbing photosensitizers for dye-sensitized solar cells[41,42] and longer-wavelength-absorbing photosensitizers for the solar reduction of protons to hydrogen.[43] In the latter systems, control of excited state lifetime (singlet vs triplet) is important, and the suite of Texas red analogues allows control of both wavelengths of absorption and singlet−triplet yields.

■ EXPERIMENTAL SECTION

Preparation of 8-Bromo-1,2,3,5,6,7-hexahydropyrido[3,2,1-*ij*]quinoline (9).[25,26] 3-Bromoaniline (**8**, 12.7 mL, 116 mmol, 1.0 equiv), sodium carbonate (49.0 g, 465 mmol), and 1-bromo-3-chloropropane (173 mL, 1.74 mol) were heated at 140 °C for 48 h. After cooling to room temperature, water (300 mL) was added, and products were extracted with CH_2Cl_2 (3 × 200 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated. Excess 1-bromo-3-chloropropane was then removed at 45 °C at 1 Torr. The crude dialkylated product was then dissolved in 15 mL of DMF and heated at 160 °C for 48 h. After cooling to room temperature, 1 M NaOH (250 mL) was added. The resulting mixture was extracted with diethyl ether (3 × 250 mL). The combined extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude product was recrystallized from MeOH to give 20.0 g (68.2% overall) of **9** as a white solid, mp 31−32 °C: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 6.73 (d, 1 H, J = 7.5 Hz), 6.63 (d, 1 H, J = 8.5 Hz), 3.18−3.07 (m, 4 H), 2.75 (t, 2 H, J = 6.0 Hz), 2.68 (t, 2 H, J = 6.5 Hz), 2.01−1.90 (m, 4 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 144.5, 127.7, 122.9, 120.6, 120.5, 119.4, 50.0, 49.6, 28.5, 27.6, 21.9, 21.8; HRMS (ESI, HRDFMagSec) m/z 252.0381 (calcd for $C_{12}H_{14}N^{79}Br + H^+$: 252.0382).

Preparation of Bisjulolidyl Disulfide 10-S. Compound **9** (2.77 g, 11.0 mmol) and ground Mg turnings (294 mg, 12.1 mmol) in 5.5 mL of THF were heated at reflux for 3 h. The reaction mixture was cooled to room temperature, and elemental S (388 mg, 12.1 mmol) and an additional 5.5 mL of THF were added. The resulting mixture was stirred at room temperature for 3 h before adding 10 mL of 1.0 M HCl (10 mL) and water (100 mL). The reaction mixture was stirred overnight under air, and the products were then extracted with ether (3 × 250 mL). The combined extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude product was purified via column chromatography on SiO_2 eluted with 0.5:9.5 EtOAc/hexanes (R_f = 0.5) to give 1.35 g (60.3%) of **10-S** as a yellow solid, mp 107−108 °C: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 6.77 (d, 2 H, J = 7.5 Hz), 6.70 (d, 2 H, J = 8.0 Hz), 3.16−3.06 (m, 8 H), 2.83 (t, 4 H, J = 6.0 Hz), 2.70 (t, 4 H, J = 6.0 Hz), 2.00−1.88 (m, 8 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 143.2, 133.0, 126.9, 120.8, 120.4, 116.3, 50.1, 49.5, 27.6, 25.1, 21.8, 21.6; HRMS (ESI, HRDFMagSec) m/z 408.1690 (calcd for $C_{24}H_{28}N_2S_2^+$: 408.1688).

Preparation of Bisjulolidyl Diselenide 10-Se. The procedure described for the preparation of **10-S** was followed using **9** (5.00 g, 19.8 mmol), Mg turnings (530 mg, 12.1 mmol), and elemental Se (1.72 mg, 21.8 mmol) in a total of 20 mL of THF. Work-up as described and purification via chromatography on SiO_2 (0.5:9.5 EtOAc/hexanes) gave 2.84 g (57.0%) of **10-Se** as an orange solid, mp 126−128 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (d, 2 H, J = 7.6 Hz), 6.69 (d, 2 H, J = 8.0 Hz), 3.15−3.07 (m, 8 H), 2.83 (t, 4 H, J = 6.4 Hz), 2.73 (t, 4 H, J = 6.4 Hz), 2.01−1.90 (m, 8 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 143.3, 128.8, 127.2, 121.9, 121.5, 120.5, 50.2, 49.7, 27.7, 27.6, 22.1, 21.9; HRMS (ESI, HRDFMagSec) m/z 505.0649 (calcd for $C_{24}H_{28}N_2{}^{80}Se_2$ + H^+: 505.0656).

Preparation of Bisjulolidyl Ditelluride 10-Te. The procedure described for the preparation of **10-S** was followed using **9** (2.00 g, 7.93 mmol), Mg turnings (212 mg, 8.73 mmol), and elemental Te (1.11 g, 8.73 mmol) in a total of 8 mL of THF. Work-up as described and purification via recrystallization from CH_2Cl_2/hexanes gave 1.70 g (71.4%) of **10-Te** as an orange solid, mp 138−139 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, 2 H, J = 8.0 Hz), 6.59 (d, 2 H, J = 8.0 Hz), 3.15−3.06 (m, 8 H), 2.82 (t, 4 H, J = 6.5 Hz), 2.78 (t, 4 H, J = 6.5 Hz), 2.10−1.90 (m, 8 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 143.5, 128.1, 127.5, 124.6, 122.8, 109.5, 50.4, 50.2, 33.5, 28.1, 23.0, 22.4; HRMS (EI, HRDFMagSec) m/z 604.0354 (calcd for $C_{24}H_{28}N_2{}^{130}Te_2$ + H^+: 604.0350).

Preparation of 3-Bromo-*N*-methyl-*N*-(3-methylbut-2-enyl)-aniline (11). 1-Chloro-3-methylbut-2-ene (5.87 mL, 49.5 mmol, 1.5 equiv) was slowly added to a stirred solution of potassium carbonate (6.84 g, 49.5 mmol, 1.5 equiv) and commercially available 3-bromo-*N*-methylaniline (6.45 g, 33.0 mmol, 1.0 equiv) in DMF (30 mL). The resulting solution was heated to 95 °C for 16 h before it was allowed to cool to ambient temperature. Water (30 mL) was added, and the mixture was extracted with diethyl ether (3 × 100 mL). The combined organic fractions were washed with water (4 × 100 mL), dried over anhydrous magnesium sulfate, vacuum filtered, and concentrated *in vacuo*. The crude products were purified via column chromatography on SiO_2 eluted with 30:70 CH_2Cl_2/hexanes (R_f = 0.60) to give 8.00 g (95.3%) of **11** as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (t, 1 H, J = 8.0 Hz), 6.83 (t, 1 H, J = 2.0 Hz), 6.79 (d, 1 H, J = 8.0 Hz), 6.59 (dd, 1 H, J = 2.0, 8.0 Hz), 5.16 (m, 1 H), 3.87 (d, 2 H, J = 6.5 Hz), 2.88 (s, 3 H), 1.73 (s, 6 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 150.8, 135.1, 130.2, 123.4, 120.1, 118.8, 115.3, 111.1, 50.2, 37.8, 25.7, 17.9; IR (film on NaCl) ν_{max} 2969, 2913, 1953, 1555, 1494, 1450 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 253.0459 (calcd for $C_{12}H_{16}N^{79}Br^+$: 253.0461).

Preparation of 7-Bromo-1,4,4-trimethyl-1,2,3,4-tetrahydroquinoline (12).[27] Concentrated sulfuric acid (23.6 mL) was added dropwise to aniline **11** (7.87 g, 31.0 mmol, 1.0 equiv) at 0 °C. The resulting mixture was warmed to ambient temperature and was stirred for 1 h before it was transferred via pipet into water at 0 °C. Sodium hydroxide pellets were added until the solution was basic to litmus. The mixture was extracted with ether (4 × 100 mL), and the combined organic fractions were dried over anhydrous magnesium sulfate, filtered, and concentrated. The crude product was recrystallized from hot methanol to give 6.26 g (79.5%) of **12** as a brown solid, mp 55−57 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (d, 1 H, J = 8.0 Hz), 6.73 (dd, 1 H, J = 2.0, 8.0 Hz), 6.66 (d, 1 H, J = 2.0 Hz), 3.25 (t, 2 H, J = 6.0 Hz), 2.89 (s, 3 H), 1.73 (t, 2 H, J = 6.0 Hz), 1.25 (s, 6 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 147.1, 130.8, 127.4, 120.7, 118.5, 113.4, 47.8, 39.3, 37.1, 32.1, 30.6; HRMS (EI, HRDFMagSec) m/z 253.0456 (calcd for $C_{12}H_{16}N^{79}Br^+$: 253.0461).

Preparation of Diaryl Sulfide 13-S. Freshly ground magnesium turnings (522 mg, 21.5 mmol, 1.1 equiv) were suspended in a stirred solution of **12** (5.00 g, 19.6 mmol, 1.0 equiv) in THF (30 mL). A crystal of elemental iodine was added, and the resulting solution was heated at reflux for 3 h, then cooled to ambient temperature, and elemental sulfur (628 mg, 19.6 mmol, 1.0 equiv) was added. The resulting solution was stirred at ambient temperature for 3 h, and then a solution of 1 M aqueous HCl (30 mL) was added. The mixture was allowed to stir overnight under air before it was extracted with diethyl ether (3 × 100 mL), and the combined organic fractions were dried over anhydrous magnesium sulfate, filtered, and concentrated. The crude products were purified via column chromatography on SiO_2 eluted with 3:7 CH_2Cl_2/hexanes (R_f = 0.5), to give 2.81 g (70.0%) of **13-S** as a pale yellow solid, mp 66−68 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (d, 2 H, J = 8.0 Hz), 6.81 (dd, 2 H, J = 1.5, 8.0 Hz), 6.72 (d, 2 H, J = 1.5 Hz), 3.21 (t, 4 H, J = 6.0 Hz), 2.84 (s, 6 H), 1.72 (t, 4 H, J = 6.0 Hz), 1.24 (s, 12 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 145.6, 135.6, 130.7, 126.1, 115.6, 110.2, 47.5, 39.1, 37.0, 31.8, 30.7; HRMS (EI, HRDFMagSec) m/z 412.2008 (calcd for $C_{24}H_{32}N_2S_2^+$: 412.2001).

Preparation of Diaryl Diselenide 13-Se. The procedure described for the preparation of **13-S** was followed using **12** (2.00 g, 7.87 mmol), Mg turnings (211 mg, 8.66 mmol), and elemental Se (1.72 g, 21.8 mmol) in a total of 16 mL of THF. Work-up as described followed by purification via column chromatography on SiO_2 eluted with 2:8 CH_2Cl_2/hexanes (R_f = 0.4) and recrystallization from hexanes gave 1.33 g (66.8%) of **13-Se** as an orange solid, mp 76−78 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (d, 2 H, J = 8.0 Hz), 6.92 (dd, 2 H, J = 1.5, 7.5 Hz), 6.82 (d, 2 H, J = 2.0 Hz), 3.20 (t, 4 H, J = 6.0 Hz), 2.82 (s, 6 H), 1.72 (t, 4 H, J = 6.0 Hz), 1.24 (s, 12 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 145.4, 130.8, 129.0, 125.9, 118.9, 113.7, 47.2, 38.8, 36.7, 31.6, 30.8; HRMS (EI, HRDFMagSec) m/z 508.0895 (calcd for $C_{24}H_{32}N_2{}^{80}Se_2^+$: 508.0896).

Preparation of Diaryl Ditelluride 13-Te. The procedure described for the preparation of **13-S** was followed using **12** (2.50 g, 9.84 mmol), Mg turnings (263 mg, 10.8 mmol), and elemental Te (1.72 g, 21.8 mmol) in a total of 20 mL of THF. Workup as described followed by purification via column chromatography on SiO_2 eluted with 2:8 CH_2Cl_2/hexanes (R_f = 0.4) and recrystallization from hexanes gave 2.64 g (88.9%) of **13-Te** as a dark red solid, mp 85−87 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (dd, 2 H, J = 1.5, 7.5 Hz), 6.98 (d, 2 H, J = 1.5 Hz), 6.94 (d, 2 H, J = 8.0 Hz), 3.19 (t, 4 H, J = 6.0 Hz), 2.81 (s, 6 H), 1.72 (t, 4 H, J = 6.0 Hz), 1.24 (s, 12 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 145.6, 131.4, 126.1, 124.8, 119.9, 105.9, 47.4, 39.0, 36.9, 31.7, 30.7; HRMS (ESI, HRDFMagSec) m/z 609.0758 (calcd for $C_{24}H_{32}N_2{}^{130}Te_2$ + H^+: 609.0763).

Preparation of Diaryl Sulfide 15-S. *sec*-Butyllithium (1.14 M in cyclohexane, 3.39 mL, 3.87 mmol) was added dropwise to a stirred solution of TMEDA (576 μL, 3.87 mmol) and amide **14**[17] (1.00 g, 3.52 mmol) in THF (70 mL) at −78 °C. A solution of **10-S** (1.58 g, 3.87 mmol) in THF (70 mL) at −78 °C was added immediately. The resulting mixture was stirred at −78 °C for 3 h and then 15 h at room temperature. A solution of saturated NH_4Cl (25 mL) was added, and the products were extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude product was purified via chromatography on SiO_2 (1:9 Et_2O/DCM, R_f = 0.5) to give 765 mg (44.5%) of **15-S** as a yellow oil: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 6.76 (s, 1 H), 6.60 (d, 1 H, J = 8.0 Hz), 6.01 (d, 1 H, J = 8.0 Hz), 3.78−3.68 (m, 1 H), 3.65−3.54 (m, 1 H), 3.34−3.20 (m, 4 H), 3.18−3.05 (m, 6 H), 2.74−2.62 (m, 8 H), 2.13−1.93 (m, 6 H), 1.92−1.83 (m, 2 H), 1.72−1.53 (m, 4 H), 1.47−1.32 (m, 2 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 168.9,

143.8, 143.5, 134.3, 131.3, 126.9, 126.0, 125.2, 124.8, 122.9, 118.5, 118.2, 113.8, 50.5, 50.1, 49.8, 49.7, 48.1, 42.2, 28.1, 27.8, 26.3, 26.1, 25.8, 25.3, 24.9, 22.5, 22.4, 21.9, 21.8; IR (film on NaCl) 2934, 2854, 1630, 1587, 1488, 1438, 1305, 1202 cm^{-1}; HRMS (EI, HRDFMagSec) m/z 487.2652 (calcd for $C_{30}H_{37}ON_3S^+$: 487.2658).

Preparation of Diaryl Selenide 15-Se. *sec*-Butyllithium (1.03 M in cyclohexane, 1.88 mL, 1.93 mmol), TMEDA (288 μL, 1.93 mmol), amide **14**[17] (500 mg, 1.76 mmol, 1.0 equiv), and **10-Se** (972 mg, 1.93 mmol) in THF (2 × 35 mL) were treated as described for the preparation of **15-S**. Following chromatography on SiO_2 (1:9 Et_2O/DCM, R_f = 0.5), **15-Se** was isolated in 450 mg (47.9%) yield as a yellow oil: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 6.73 (s, 1 H), 6.54 (d, 1 H, J = 8.0 Hz), 6.09 (d, 1 H, J = 8.5 Hz), 3.76−3.68 (m, 1 H), 3.59−3.51 (m, 1 H), 3.29−3.07 (m, 10 H), 2.86−2.71 (m, 6 H), 2.70−2.62 (m, 2 H), 2.08−1.91 (m, 6 H), 1.86 (quintet, 2 H, J = 6.5 Hz), 1.69−1.52 (m, 4 H), 1.42−1.30 (m, 2 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 169.8, 143.9, 143.8, 131.9, 131.4, 127.3, 126.1, 124.8, 123.4, 122.9, 119.8, 119.3, 116.1, 54.2, 50.5, 50.2, 49.9, 48.3, 42.3, 28.6, 28.2, 27.8, 27.0, 26.5, 25.8, 25.0, 22.5, 22.4, 22.3, 22.0; IR (film on NaCl) 2934, 2854, 1627, 1596, 1502, 1461, 1437, 1390, 1316, 1304, 1262, 1211 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 536.2184 (calcd for $C_{30}H_{37}ON_3{}^{80}Se + H^+$: 536.2175).

Preparation of Diaryl Telluride 15-Te. *sec*-Butyllithium (1.08 M in cyclohexane, 3.58 mL, 3.52 mmol), TMEDA (576 μL, 3.87 mmol), amide **14**[17] (1.00 g, 3.52 mmol, 1.0 equiv), and **10-Te** (2.32 g, 3.87 mmol) in THF (2 × 70 mL) were treated as described for the preparation of **15-S**. Following chromatography on SiO_2 (1:9 Et_2O/DCM, R_f = 0.5), **15-Te** was isolated in 763 mg (37.2%) yield as a yellow oil: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 6.75 (s, 1 H), 6.51 (d, 1 H, J = 8.0 Hz), 6.37 (d, 1 H, J = 8.0 Hz), 3.80−3.55 (m, 2 H), 3.40−3.26 (m, 2 H), 3.23 (t, 2 H, J = 6.0 Hz), 3.18−3.05 (m, 6 H), 3.00−2.76 (m, 4 H), 2.74−2.55 (m, 4 H), 2.07−1.92 (m, 6 H), 1.89−1.80 (m, 2 H), 1.75−1.51 (m, 4 H), 1.4−1.38 (m, 2H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 171.3, 143.9, 143.1, 134.3, 127.8, 127.5, 124.5, 123.1, 122.8, 121.5, 120.4, 118.4, 114.2, 50.4, 50.1, 50.0, 49.9, 48.4, 42.5, 33.8, 31.0, 28.1, 27.8, 26.6, 25.7, 24.9, 22.7, 22.4, 22.3, 22.0; IR (film on NaCl) 2934, 2852, 1623, 1582, 1486, 1436, 1388, 1328, 1305, 1202 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 586.2073 (calcd for $C_{30}H_{37}ON_3{}^{130}Te + H^+$: 586.2072).

Preparation of Diaryl Sulfide 17-S. *sec*-Butyllithium (0.94 M in 92:8 cyclohexane/hexanes, 4.09 mL, 3.84 mmol), TMEDA (572 μL, 3.84 mmol), amide **16**[21] (1.00 g, 3.49 mmol), and **13-S** (1.58 g, 3.84 mmol) in THF (2 × 70 mL) were treated as described for the preparation of **15-S**. Following chromatography on SiO_2 (1:9 EtOAc/CH_2Cl_2, R_f = 0.6), **17-S** was isolated in 1.06 g (61.6%) yield as a yellow solid, mp 83−85 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (d, 1 H, J = 8.0 Hz), 7.00 (s, 1 H), 6.68−6.62 (m, 2 H), 6.43 (s, 1 H), 3.66 (br s, 2 H), 3.26−3.04 (m, 6 H), 2.84 (s, 3 H), 2.73 (s, 3 H), 1.76−1.66 (m, 4 H), 1.63−1.44 (m, 6 H), 1.24 (s, 12 H); ^{13}C NMR (MHz, $CDCl_3$) δ 168.8, 145.1, 132.3, 131.1, 130.0, 129.5, 125.6, 125.2, 123.7, 119.2, 113.7, 112.9, 47.5 (br), 47.0, 46.8, 42.1 (br), 38.7, 38.4, 36.6, 36.2, 31.3, 31.2, 30.3, 30.1, 25.4 (br), 24.1; IR (film on NaCl) 2931, 2852, 1630, 1593, 1501, 1467, 1434 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 492.3035 (calcd for $C_{30}H_{41}N_3OS + H^+$: 492.3043).

Preparation of Diaryl Selenide 17-Se. *sec*-Butyllithium (1.19 M in 92:8 cyclohexane/hexanes, 3.23 mL, 3.84 mmol), TMEDA (572 μL, 3.84 mmol), amide **16**[21] (1.00 g, 3.49 mmol), and **13-Se** (1.94 g, 3.84 mmol) in THF (2 × 55 mL) were treated as described for the preparation of **15-S**. Following chromatography on SiO_2 (1:9 Et_2O/CH_2Cl_2, R_f = 0.6), **17-Se** was isolated in 1.04 g (55.3%) yield as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (d, 1 H, J = 7.5 Hz), 6.99 (s, 1 H), 6.86−6.78 (m, 2 H), 6.43 (s, 1 H), 3.44 (br s, 4 H), 3.18 (quintet, 4 H, J = 6.0 Hz), 2.83 (s, 3 H), 2.65 (s, 3 H), 1.71 (t, 2 H, J = 6.0 Hz), 1.68 (t, 2 H, J = 6.0 Hz), 1.64−1.57 (m, 2 H), 1.57−1.48 (m, 4 H), 1.23 (s, 6 H), 1.21 (s, 6 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) 169.6, 145.3, 130.7, 128.9, 128.6, 127.4, 125.8, 124.8, 123.8, 122.1, 116.7, 113.7, 47.1, 46.9, 45.0 (br), 38.7, 38.2, 36.6, 36.3, 31.4, 31.2, 30.3, 30.1, 25.6, 24.2; IR (film on NaCl) 2930, 1627, 1593, 1499, 1467, 1430 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 562.2330 (calcd for $C_{30}H_{41}N_3O^{80}Se + Na^+$: 562.2307).

Preparation of Diaryl Telluride 17-Te. *sec*-Butyllithium (1.19 M in 92:8 cyclohexane/hexanes, 3.23 mL, 2.88 mmol), TMEDA (429 μL, 2.88 mmol), amide **16**[21] (750 mg, 2.62 mmol), and **13-Te** (1.74 g, 2.88 mmol) in THF (55 + 40 mL) were treated as described for the preparation of **15-S**. Following chromatography on SiO_2 (1:19 EtOAc/DCM, R_f = 0.7), **17-Te** was isolated in 764 mg (49.6%) yield as a yellow solid, mp 182−184 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d × d, 1 H, J = 1.0, 7.5 Hz), 7.18 (d, 1 H, J = 1.0 Hz), 7.10−7.04 (m, 2 H), 6.40 (s, 1 H), 3.60−3.53 (m, 4 H), 3.21 (t, 2 H, J = 6.0 Hz), 3.17 (t, 2 H, J = 6.0 Hz), 1.72−1.65 (m, 4 H), 1.65−1.59 (m, 4 H), 1.26 (s, 6 H), 1.21 (s, 6 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 171.5, 145.9, 145.5, 131.5, 128.7, 127.7, 126.1, 125.1, 123.5, 123.4, 119.8, 115.7, 114.2, 47.2, 46.9, 46.4 (br), 38.9, 37.9, 36.7, 36.2, 31.6, 31.1, 30.4, 30.1, 25.9, 24.4; IR (film on NaCl) 2931, 2852, 1591 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 590.2380 (calcd for $C_{30}H_{41}N_3O^{130}Te + H^+$: 590.2385).

Preparation of Diaryl Sulfide 18-S. *sec*-Butyllithium (1.00 M in 92:8 cyclohexane/hexanes, 3.87 mL, 3.87 mmol), TMEDA (577 μL, 3.87 mmol), amide **14**[17] (1.00 g, 3.52 mmol), and **13-S** (1.60 g, 3.87 mmol) in THF (2 × 60 mL) were treated as described for the preparation of **15-S**. Following chromatography on SiO_2 (1:9 Et_2O/CH_2Cl_2, R_f = 0.5), **18-S** was isolated in 992 mg (55.4%) yield as a white solid, mp 141−143 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.94 (d, 1 H, J = 8.0 Hz), 6.69 (s, 1 H), 6.44 (s, 1 H), 6.30 (d, 1 H, J = 8.0 Hz), 3.72−3.65 (m, 1 H), 3.63−3.55 (m, 1 H), 3.22−3.05 (m, 7 H), 3.04−2.89 (m, 2 H), 2.80 (s, 3 H), 2.78−2.68 (m, 3 H), 2.02−1.90 (m, 2 H), 1.87 (quintet, 2 H, J = 6.0 Hz), 1.70 (t, 2 H, J = 6.0 Hz), 1.62−1.44 (m, 4 H), 1.32−1.23 (m, 2 H), 1.20 (s, 3 H), 1.19 (s, 3 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.0, 145.1, 143.2, 134.8, 130.3, 128.2, 125.7, 125.6, 125.2, 124.1, 122.1, 114.6, 109.4, 49.5, 49.1, 47.6, 47.1, 41.7, 38.8, 36.8, 31.2, 30.5, 30.4, 27.4, 25.6, 25.4, 25.0, 24.1, 21.3, 21.2; IR (film on NaCl) 2934, 2853, 1630, 1590, 1552, 1500, 1438 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 490.2878 (calcd for $C_{30}H_{39}N_3OS + H^+$: 490.2887).

Preparation of Diarylselenide 18-Se. *sec*-Butyllithium (1.23 M in 92:8 cyclohexane/hexanes, 3.15 mL, 3.87 mmol), TMEDA (577 μL, 3.87 mmol), amide **14**[17] (1.00 g, 3.52 mmol), and **13-Se** (1.96 g, 3.87 mmol) in THF (2 × 40 mL) were treated as described for the preparation of **15-S**. Following chromatography on SiO_2 eluted with 2:9 EtOAc/CH_2Cl_2, (R_f = 0.5), **18-Se** was isolated in 1.21 g (64.0%) yield as a red solid, mp 55−57 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (d, 1 H, J = 8.0 Hz), 6.68 (s, 1 H), 6.54 (d, 1 H, J = 1.5 Hz), 6.43 (dd, 1 H, J = 1.5, 8.0 Hz), 3.78−3.66 (m, 1 H), 3.62−3.51 (m, 1 H), 3.22−3.12 (m, 5 H), 3.11−3.05 (m, 2 H), 3.04−2.97 (m, 1 H), 2.89−1.89 (m, 2 H), 2.76 (s, 3 H), 2.72−2.68 (m, 2 H), 2.00−1.89 (m, 2 H), 1.82 (m, 2 H), 1.70 (m, 2 H), 1.65−1.43 (m, 4 H), 1.34−1.21 (m, 2 H), 1.20 (s, 3 H), 1.19 (s, 3 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 170.2, 145.7, 143.4, 131.2, 130.4, 129.3, 126.2, 126.0, 124.3, 123.9, 122.4, 117.5, 112.1, 49.9, 49.6, 48.0, 47.6, 42.1, 39.2, 37.2, 31.7, 30.9, 30.8, 28.5, 27.8, 25.9, 25.4, 24.5, 21.9, 21.6; IR (film on NaCl) 2933, 2853, 1628, 1587, 1499 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 537.2254 (calcd for $C_{30}H_{39}N_3O^{80}Se^+$: 537.2253).

Preparation of Diaryltelluride 18-Te. *sec*-Butyllithium (0.94 M in 92:8 cyclohexane/hexanes, 1.23 mL, 1.16 mmol), TMEDA (173 μL, 1.16 mmol), amide **14**[17] (300 mg, 1.05 mmol), and **13-Te** (700 mg, 1.16 mmol) in THF (2 × 40 mL) were treated as described for the preparation of **15-S**. Following chromatography on SiO_2 eluted with 1:9 EtOAc/CH_2Cl_2, (R_f = 0.5), **18-Te** was isolated in 233 mg (37.9%) yield as a light brown solid, mp 81−83 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.90 (d, 1 H, J = 8.0 Hz), 6.72 (s, 1 H), 6.70−6.63 (m, 2 H), 3.66 (br s, 2 H), 3.32−3.10 (m, 7 H), 3.07 (t, 2 H, J = 5.5 Hz), 2.99−2.87 (m, 1 H), 2.79 (s, 3 H), 2.74 (t, 2 H, J = 6.5 Hz), 1.93 (quintet, 2 H, J = 6.0 Hz), 1.83 (quintet, 2 H, J = 6.0 Hz), 1.71 (t, 2 H, J = 5.5 Hz), 1.66−1.50 (m, 4 H), 1.42−1.33 (m, 2 H), 1.21 (s, 6 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 171.7, 145.7, 142.7, 133.6, 130.2, 127.3, 126.3, 123.9, 123.4, 117.7, 114.0, 113.6, 49.7, 49.6, 48.2 (br), 47.4, 42.3 (br), 39.0, 37.0, 33.7, 31.6, 30.7, 27.7, 26.1 (br), 25.2 (br), 24.4, 22.2, 21.4; IR (film on NaCl) 2932, 2852, 1623, 1582, 1546, 1497, 1434 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 588.2231 (calcd for $C_{30}H_{39}N_3O^{130}Te^+$: 588.2228).

Preparation of Bisjulolidyl Thioxanthone 2-S. Phosphorus oxychloride (1.73 mL, 18.6 mmol) was added dropwise to a solution of triethylamine (2.59 mL, 18.6 mmol) and **15-S** (755 mg, 1.55 mmol) in anhydrous CH_3CN (50 mL). The resulting mixture was heated at reflux for 12 h and was then cooled to 0 °C. A solution of 1 M NaOH (10 mL) was added slowly, and the resulting mixture was poured into a stirred solution of cold 1 M NaOH (200 mL). The resulting mixture was stirred for 6 h, and products were then extracted with CH_2Cl_2 (3 × 250 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated. The resulting solid was recrystallized from CH_2Cl_2/hexanes to give 511 mg (82.0%) of **2-S** as a brown solid, mp >250 °C: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.95 (s, 2 H), 3.41−3.10 (m, 8 H), 2.95−2.65 (m, 8 H), 2.14−1.82 (m, 8 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 178.1, 145.8, 134.8, 127.7, 120.7, 118.1, 113.5, 50.6, 49.7, 28.2, 24.5, 21.9, 21.6; IR (film on NaCl) 2932, 1590, 1421, 1331, 1302 cm^{-1}; HRMS [ESI, high-resolution, double focusing magnetic sector (HRDFMagSec)] m/z 403.1845 (calcd for $C_{25}H_{26}O_1N_2S_1$ + H$^+$: 403.1839).

Preparation of Bisjulolidyl Selenoxanthone 2-Se. Phosphorus oxychloride (1.46 mL, 15.7 mmol), triethylamine (2.19 mL, 15.7 mmol), and **15-Se** (700 mg, 1.31 mmol) in anhydrous CH_3CN (30 mL) were treated as described for the preparation of **2-S**. The crude product was recrystallized from CH_2Cl_2/hexanes to give 410 mg (70.0%) of **2-Se** as a brown solid, mp >250 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (s, 2 H), 3.31−3.24 (m, 8 H), 2.86 (t, 4 H, J = 6.5 Hz), 2.79 (t, 4 H, J = 6.5 Hz), 2.08 (quintet, 4 H, J = 6.5 Hz), 1.98 (quintet, 4 H, J = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.3, 145.5, 133.6, 129.3, 120.2, 119.3, 114.6, 50.2, 49.4, 27.6, 25.5, 21.5, 21.3; IR (film on NaCl) 2927, 2834, 1586, 1569, 1540, 1416, 1329, 1301, 1204 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 451.1289 (calcd for $C_{25}H_{26}ON_2{}^{80}Se$ + H$^+$: 451.1283).

Preparation of Bisjulolidyl Telluroxanthone 2-Te. Phosphorus oxychloride (1.44 mL, 15.5 mmol), triethylamine (2.16 mL, 15.5 mmol), and **15-Te** (753 mg, 1.29 mmol) in anhydrous CH_3CN (30 mL) were treated as described for the preparation of **2-S**. The crude product was recrystallized from CH_2Cl_2/hexanes to give 380 mg (59.1%) of **2-Te** as a brown solid, mp >250 °C: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.13 (s, 2 H), 3.51−3.23 (m, 8 H), 2.85 (t, 4 H, J = 6.5 Hz), 2.70 (t, 4 H, J = 6.5 Hz), 2.07 (quintet, 4 H, J = 6.5 Hz), 1.97 (quintet, 4 H, J = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.2, 146.1, 131.4, 122.8, 122.3, 121.3, 118.6, 50.5, 49.9, 30.0, 28.1, 22.2, 21.9; IR (film on NaCl) 2940, 2836, 1583, 1556, 1535, 1504, 1406, 1321, 1292, 1204 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 501.1172 (calcd for $C_{25}H_{26}ON_2{}^{130}Te$ + H$^+$: 501.1180).

Preparation of Bishalf-julolidyl Thioxanthone 3-S. Phosphorus oxychloride (2.36 mL, 25.3 mmol), triethylamine (3.53, 25.3 mmol), and **17-S** (1.04 g, 2.11 mmol) in anhydrous CH_3CN (25 mL) were treated as described for the preparation of **2-S**. The crude product was recrystallized from CH_2Cl_2/hexanes to give 708 mg (82.5%) of **3-S** as a brown solid, mp >250 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (s, 2 H), 6.44 (s, 2 H), 3.38 (t, 4 H J = 6.0 Hz), 3.01 (s, 6 H), 1.76 (t, 4 H, J = 6.0 Hz), 1.35 (s, 12 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 177.5, 147.3, 136.7, 130.3, 125.9, 118.2, 103.4, 47.1, 38.7, 35.9, 31.7, 29.7; IR (film, NaCl) 2957, 1594, 1574, 1520, 1434 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 407.2149 (calcd for $C_{25}H_{30}N_2OS$ + H$^+$: 407.2152).

Preparation of Bishalf-julolidyl Selenoxanthone 3-Se. Phosphorus oxychloride (0.849 mL, 9.11 mmol), triethylamine (1.27 mL, 9.11 mmol), and **17-Se** (409 mg, 0.759 mmol) in anhydrous CH_3CN (15 mL) were treated as described for the preparation of **2-S**. The crude product was recrystallized from CH_2Cl_2/hexanes to give 250 mg (72.5%) of **3-Se** as a brown solid, mp >250 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (s, 2 H), 6.53 (s, 2 H), 3.38 (t, 4 H, J = 6.0 Hz), 3.00 (s, 6 H), 1.75 (t, 4 H, J = 6.0 Hz), 1.34 (s, 12 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 179.5, 147.3, 134.1, 130.5, 127.5, 119.7, 106.2, 47.2, 38.8, 36.0, 31.8, 29.8; IR (film on NaCl) 2955, 1590, 1562, 1517 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 455.1599 (calcd for $C_{25}H_{30}N_2O^{80}Se$ + H$^+$: 455.1596).

Preparation of Bishalf-julolidyl Telluroxanthone 3-Te. Phosphorus oxychloride (1.29 mL, 13.8 mmol), triethylamine (1.92 mL, 13.8 mmol), and **17-Te** (677 mg, 1.15 mmol) in anhydrous CH_3CN (25 mL) were treated as described for the preparation of **2-S**. The crude product was recrystallized from CH_2Cl_2/hexanes to give 507 mg (87.4%) of **3-Te** as a brown solid, mp >250 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (s, 2 H), 6.64 (s, 2 H), 3.36 (t, 4 H, J = 6.0 Hz), 2.98 (s, 6 H), 1.75 (t, 4 H, J = 6.0 Hz), 1.34 (s, 12 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 183.2, 147.1, 131.0, 129.3, 122.6, 118.9, 112.3, 47.2, 38.7, 36.0, 31.7, 29.8; IR (film on NaCl) 2924, 1585 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 505.1500 (calcd for $C_{25}H_{30}N_2O^{130}Te$ + H$^+$: 505.1493).

Preparation of Julolidyl/Half-julolidyl Thioxanthone 4-S. Phosphorus oxychloride (1.72 mL, 18.4 mmol), triethylamine (2.56 mL, 11.0 mmol), and **18-S** (750 mg, 1.53 mmol) in anhydrous CH_3CN (30 mL) were treated as described for the preparation of **2-S**. The crude product was recrystallized from CH_2Cl_2/hexanes to give 538 mg (86.9%) of **4-S** as a brown solid, mp >250 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1 H), 8.10 (s, 1 H), 6.50 (s, 1 H), 3.37 (t, 2 H, J = 6.0 Hz), 3.28−3.21 (m, 4 H), 3.00 (s, 3 H), 2.85 (t, 2 H, J = 6.5 Hz), 2.75 (t, 2 H, J = 6.5 Hz), 2.05 (quintet, 2 H, J = 6.5 Hz), 1.96 (quintet, 2 H, J = 6.5 Hz), 1.75 (t, 2 H, J = 6.0 Hz), 1.35 (s, 6 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 177.5, 147.1, 144.9, 136.3, 134.6, 130.3, 127.4, 125.5, 119.5, 117.8, 117.7, 112.2, 103.7, 49.7, 48.9, 46.9, 38.5, 35.7, 31.6, 29.5, 27.4, 23.7, 21.1, 20.7; IR (film on NaCl) 2931, 1592, 1573, 1513, 1421 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 404.1917 (calcd for $C_{25}H_{28}N_2OS^+$: 404.1917).

Preparation of Julolidyl/Half-julolidyl Selenoxanthone 4-Se. Phosphorus oxychloride (2.46 mL, 26.4 mmol), triethylamine (3.68 mL, 26.4 mmol), and **18-Se** (1.18 g, 2.20 mmol) in anhydrous CH_3CN (40 mL) were treated as described for the preparation of **2-S**. The crude product was recrystallized from CH_2Cl_2/hexanes to give 610 mg (61.4%) of **4-Se** as a brown solid, mp >250 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1 H), 8.14 (s, 1 H), 6.55 (s, 1 H), 3.31 (t, 2 H, J = 6.0 Hz), 3.22−3.13 (m, 4 H), 2.94 (s, 3 H), 2.80 (t, 2 H, J = 6.0 Hz), 2.63 (t, 2 H, J = 6.0 Hz), 2.00 (quintet, 2 H, J = 6.0 Hz), 1.91 (quintet, 2 H, J = 6.0 Hz), 1.70 (t, 2 H, J = 6.0 Hz), 1.32 (s, 6 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 179.8, 147.3, 145.4, 134.1, 133.9, 130.7, 129.4, 127.3, 119.9, 119.5, 119.4, 114.4, 106.3, 50.0, 49.2, 47.2, 38.8, 36.0, 31.8, 29.7, 27.5, 25.5, 21.3, 21.2; IR (film on NaCl) 2930, 1589, 1569, 1514 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 453.1432 (calcd for $C_{25}H_{28}N_2O^{80}Se$ + H$^+$: 453.1440).

Preparation of Julolidyl/Half-julolidyl Telluroxanthone 4-Te. Phosphorus oxychloride (306 μL, 3.28 mmol), triethylamine (457 μL, 3.28 mmol), and **18-Te** (160 mg, 0.273 mmol) in anhydrous CH_3CN (20 mL) were treated as described for the preparation of **2-S**. The crude product was recrystallized from CH_2Cl_2/hexanes to give 83.0 mg (60.6%) of **4-Te** as a brown solid, mp >250 °C: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.47 (s, 1 H), 8.17 (s, 1 H), 6.74 (s, 1 H), 3.32 (t, 2 H, J = 6.0 Hz), 3.26−3.14 (m, 4 H), 2.95 (s, 3 H), 2.83 (t, 2 H, J = 6.3 Hz), 2.53 (t, 2 H, J = 6.3 Hz), 2.06−1.86 (m, 4 H), 1.72 (t, 2 H, J = 6.0 Hz), 1.34 (s, 6 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 183.6, 147.6, 146.0, 131.7, 131.6, 129.0, 122.9, 122.8, 122.7, 120.9, 119.5, 118.6, 112.5, 50.3, 49.8, 47.6, 39.1, 36.5, 32.1, 30.1, 30.0, 27.9, 22.0, 21.8; IR (film on NaCl) 2928, 1583, 1560, 1406, 1304, 1280, 1261, 1207 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 503.1329 (calcd for $C_{25}H_{28}ON_2{}^{130}Te$ + H$^+$: 503.1337).

Preparation of Bisjulolidyl Thiorhodamine 5-S. Phenylmagnesium bromide (1 M in THF, 1.24 mL, 1.24 mmol) was added dropwise to a stirred solution of **2-S** (100 mg, 0.248 mmol) in THF (10 mL), and the resulting mixture was heated at reflux for 16 h and then cooled to ambient temperature. The reaction was quenched by the addition of glacial acetic acid (2 mL) and the resulting mixture was poured into 200 mL of aqueous 10% HPF_6. After stirring for 12 h, the precipitate was collected via filtration and washed with water (30 mL) and diethyl ether (4 × 25 mL) to give 138 mg (91.4%) of **5-S** as a green solid, mp >250 °C: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.63−7.56 (m, 3 H), 7.30−7.23 (m, 2 H), 6.95 (s, 2 H), 3.54−3.44 (m, 8 H), 2.94 (t, 4 H, J = 6.0 Hz), 2.65 (t, 4 H, J = 6.0 Hz), 2.16 (quintet, 4 H, J = 6.0 Hz), 1.95 (quintet, 4 H, J = 6.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 157.3, 148.5, 138.8, 137.0, 132.8, 129.8, 129.2, 128.8, 125.1, 118.6, 114.1, 51.5, 50.5, 28.2, 24.4, 20.8, 20.4; λ_{max} (MeOH) 594 nm

(ε = 1.24 × 10^{-5} M^{-1} cm^{-1}); HRMS (ESI, HRDFMagSec) m/z 463.2203 (calcd for $C_{31}H_{31}N_2S^+$: 463.2202).

Preparation of Bisjulolidyl Selenorhodamine 5-Se. Phenylmagnesium bromide (1 M in THF, 2.23 mL, 2.23 mmol) and **2-Se** (100 mg, 0.223 mmol) in THF (10 mL) were treated as described for the preparation of **5-S** to give 125 mg (85.6%) of **5-Se** as a blue solid, mp >250 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62−7.54 (m, 3 H), 7.28−7.20 (m, 2 H), 6.98 (s, 2 H), 3.56−3.40 (m, 8 H), 2.86 (t, 4 H, J = 6.0 Hz), 2.62 (t, 4 H, J = 6.0 Hz), 2.18 (quintet, 4 H, J = 6.0 Hz), 1.94 (quintet, 4 H, J = 6.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 159.1, 148.3, 141.0, 138.4, 135.1, 129.8, 129.0, 128.7, 124.5, 119.4, 116.5, 51.5, 50.6, 28.1, 26.2, 20.8, 20.6; λ_{max} (MeOH) 604 nm (ε = 1.35 × 10^5 M^{-1} cm^{-1}); HRMS (ESI, HRDFMagSec) m/z 511.1649 (calcd for $C_{31}H_{31}N_2{}^{80}Se^+$: 511.1647).

Preparation of Bisjulolidyl Tellurorhodamine 5-Te. Phenylmagnesium bromide (1 M in THF, 1.00 mL, 1.00 mmol) and **2-Te** (100 mg, 0.201 mmol) in THF (10 mL) were treated as described for the preparation of **5-S** to give 130 mg (92.3%) of **5-Te** as a purple solid, mp >250 °C: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.60−7.51 (m, 3 H), 7.25−7.19 (m, 2 H), 7.09 (s, 2 H), 3.47 (t, 4 H, J = 6.0 Hz), 3.43 (t, 4 H, J = 6.0 Hz), 2.73 (t, 4 H, J = 6.5 Hz), 2.59 (t, 4 H, J = 6.0 Hz), 2.20 (quintet, 4 H, J = 6.0 Hz), 1.93 (quintet, 4 H, J = 6.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 162.2, 147.7, 140.6, 138.1, 135.6, 129.7, 128.6, 128.5, 124.2, 121.5, 121.0, 51.4, 50.7, 30.5, 28.0, 21.0, 20.8; λ_{max} (MeOH) 615 nm (ε = 1.44 × 10^5 M^{-1} cm^{-1}); HRMS (ESI, HRDFMagSec) m/z 561.1540 (calcd for $C_{31}H_{31}N_2{}^{130}Te^+$: 561.1544).

Preparation of Bishalf-julolidyl Thiorhodamine 6-S. Phenylmagnesium bromide (1 M in THF, 2.46 mL, 2.46 mmol) and **3-S** (100 mg, 0.246 mmol) in THF (10 mL) were treated as described for the preparation of **5-S** to give 124 mg (82.1%) of **6-S** as a green solid, mp 252−254 °C: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.68−7.61 (m, 3 H), 7.36−7.30 (m, 2 H), 7.29 (s, 2 H), 7.00 (s, 2 H), 3.58 (t, 4 H, J = 6.0 Hz), 3.24 (s, 6 H), 1.75 (t, 4 H, J = 6.0 Hz), 1.09 (s, 12 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 158.7, 150.5, 142.9, 136.2, 135.1, 130.6, 129.7, 129.6, 128.9, 119.4, 104.6, 48.5, 40.0, 34.6, 32.2, 28.6; λ_{max} (MeOH) 579 nm (ε = 1.04 × 10^5 M^{-1} cm^{-1}); HRMS (ESI, HRDFMagSec) m/z 467.2514 (calcd for $C_{31}H_{35}N_2S^+$: 467.2515).

Preparation of Bishalf-julolidyl Selenorhodamine 6-Se. Phenylmagnesium bromide (1 M in THF, 1.10 mL, 1.10 mmol) and **3-Se** (100 mg, 0.22 mmol) in THF (10 mL) were treated as described for the preparation of **5-S** to give 113 mg (77.9%) of **6-Se** as a green solid, mp 246−248 °C: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.65−7.59 (m, 3 H), 7.33−7.27 (m, 4 H), 7.17 (s, 2 H), 3.55 (t, 4 H, J = 6.0 Hz), 3.23 (s, 6 H), 1.74 (t, 4 H, J = 6.0 Hz), 1.05 (s, 12 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 159.6, 149.6, 144.5, 137.5, 134.1, 132.1, 129.0, 128.5, 127.1, 119.8, 107.9, 48.3, 39.9, 34.5, 31.8, 28.6; λ_{max} (MeOH) 590 nm (ε = 1.36 × 10^5 M^{-1} cm^{-1}); HRMS (ESI, HRDFMagSec) m/z 515.1960 (calcd for $C_{31}H_{35}N_2{}^{80}Se^+$: 515.1960).

Preparation of Bishalf-julolidyl Tellurorhodamine 6-Te. Phenylmagnesium bromide (1 M in THF, 1.98 mL, 1.98 mmol) and **3-Te** (100 mg, 0.198 mmol) in THF (10 mL) were treated as described for the preparation of **5-S** to give 105 mg (75.0%) of **6-Te** as a green solid, mp 250−252 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61−7.55 (m, 3 H), 7.48 (s, 2 H), 7.35 (s, 2 H), 7.25−7.21 (m, 2 H), 3.49 (t, 4 H, J = 6.0 Hz), 3.24 (s, 6 H), 1.71 (t, 4 H, J = 6.0 Hz), 1.00 (s, 12 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 163.5, 149.2, 140.0, 136.0, 135.5, 134.2, 129.3, 129.0, 128.7, 122.1, 114.8, 48.6, 39.9, 34.8, 32.0, 28.6; λ_{max} (MeOH) 607 nm (ε = 1.21 × 10^5 M^{-1} cm^{-1}); HRMS (ESI, HRDFMagSec) m/z 565.1857 (calcd for $C_{31}H_{35}N_2{}^{130}Te^+$: 565.1857).

Preparation of Julolidyl/Half-julolidyl Thiorhodamine 7-S. Phenylmagnesium bromide (1 M in THF, 2.47 mL, 2.47 mmol) and **4-S** (100 mg, 0.247 mmol) in THF (10 mL) were treated as described for the preparation of **5-S** to give 136 mg (90.1%) of **7-S** as a purple solid, mp 249−251 °C: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.66−7.58 (m, 3 H), 7.33−7.27 (m, 2 H), 7.19 (s, 1 H), 7.06 (s, 1 H), 7.03 (s, 1 H), 3.57 (t, 2 H, J = 6.5 Hz), 3.54−3.48 (m, 4 H), 3.22 (s, 3 H), 2.88 (t, 2 H, J = 6.5 Hz), 2.67 (t, 2 H, J = 6.5 Hz), 2.17 (quintet, 2 H, J = 6.0 Hz), 1.96 (quintet, 2 H, J = 6.0 Hz), 1.74 (t, 2 H, J = 6.5 Hz), 1.07 (s, 6 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 157.8, 150.0, 148.9, 141.9, 139.6, 136.6, 134.8, 133.2, 130.2, 129.7, 129.4, 128.8, 125.4, 119.1, 118.8, 113.9, 104.8, 51.5, 50.6, 48.4, 39.8, 34.7, 32.1, 28.6, 28.1, 24.3, 20.7, 20.2; λ_{max} (MeOH) 587 nm (ε = 1.20 × 10^5 M^{-1} cm^{-1}); HRMS (ESI, HRDFMagSec) m/z 465.2358 (calcd for $C_{31}H_{33}N_2S^+$: 465.2359).

Preparation of Julolidyl/Half-julolidyl Selenorhodamine 7-Se. Phenylmagnesium bromide (1 M in THF, 1.11 mL, 1.11 mmol) and **4-Se** (100 mg, 0.222 mmol) in THF (10 mL) were treated as described for the preparation of **5-S** to give 110 mg (75.3%) of **7-Se** as a purple solid, mp 237−239 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65−7.54 (m, 3 H), 7.30−7.23 (m, 2 H), 7.19 (s, 1 H), 7.18 (s, 1 H), 7.10 (s, 1 H), 3.56−3.44 (m, 6 H), 3.21 (s, 3 H), 2.78 (t, 2 H, J = 6.0 Hz), 2.64 (t, 2 H, J = 6.0 Hz), 2.18 (quintet, 2 H, J = 6.0 Hz), 1.95 (quintet, 2 H, J = 6.0 Hz), 1.73 (t, 2 H, J = 6.0 Hz), 1.03 (s, 6 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) 158.7, 149.1, 148.1, 142.6, 141.6, 137.6, 134.9, 133.8, 131.7, 129.0, 128.8, 128.4, 124.3, 119.2, 119.1, 116.2, 107.4, 51.1, 50.2, 48.0, 39.5, 34.4, 31.7, 28.6, 27.6, 25.7, 20.2, 19.9; λ_{max} (MeOH) 597 nm (ε = 1.22 × 10^5 M^{-1} cm^{-1}); HRMS (ESI, HRDFMagSec) m/z 513.1803 (calcd for $C_{31}H_{33}N_2{}^{80}Se^+$: 513.1803).

Preparation of Julolidyl/Half-julolidyl Tellurorhodamine 7-Te. Phenylmagnesium bromide (1 M in THF, 1.00 mL, 1.00 mmol) and **4-Te** (100 mg, 0.200 mmol) in THF (10 mL) were treated as described for the preparation of **5-S** to give 125 mg (88.7%) of **7-Te** as a purple solid, mp >250 °C: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.62−7.54 (m, 3 H), 7.41 (s, 1 H), 7.28 (s, 1 H), 7.27−7.23 (m, 2 H), 7.22 (s, 1 H), 3.53−3.46 (m, 4 H), 3.44 (t, 2 H, J = 6.0 Hz), 3.19 (s, 3 H), 2.67−2.58 (m, 4 H), 2.24−2.17 (m, 2 H), 1.98−1.90 (m, 2 H), 1.71 (t, 2 H, J = 6.0 Hz), 0.99 (s, 6 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 162.9, 148.8, 148.3, 140.3, 138.7, 136.8, 135.1, 135.0, 134.1, 129.6, 128.8, 128.6, 124.5, 122.0, 121.7, 121.6, 114.3, 51.6, 50.9, 48.5, 39.8, 34.9, 32.0, 30.8, 28.7, 27.9, 20.9, 20.7; λ_{max} (MeOH) 610 nm (ε = 1.27 × 10^5 M^{-1} cm^{-1}); HRMS (ESI, HRDFMagSec) m/z 563.1697 (calcd for $C_{31}H_{33}N_2{}^{130}Te^+$: 563.1700).

Preparation of Diaryl Selenide 22. *sec*-Butyllithium (1.00 M in cyclohexane, 0.96 mL, 0.96 mmol), TMEDA (144 μL, 0.964 mmol), amide **16**[19] (0.250 g, 0.873 mmol), and diselenide **21**[22] (0.730 g, 1.83 mmol) in THF (2 × 30 mL) were treated as described for the preparation of **15-S**. The crude product was purified via column chromatography (SiO_2, 4:6 EtOAc/hexanes) to yield 194 mg (45.9%) of **22** as a pale yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (t, 1 H, J = 8.1 Hz), 7.04−6.95 (m, 2 H), 6.90 (d, 1 H, J = 8.1 Hz), 6.64 (dd, 1 H, J = 2.4, 8.1 Hz), 6.48 (s, 1 H), 3.62−3.36 (m, 4 H), 3.19 (t, 2 H, J = 6.0 Hz), 2.91 (s, 6 H), 2.67 (s, 3 H), 1.71 (t, 2 H, J = 6.0 Hz), 1.65 (m, 2 H), 1.58 (m, 4 H), 1.23 (s, 6 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 169.8, 150.7, 145.6, 130.7, 129.4, 129.2, 128.3, 125.2, 124.1, 122.2, 118.1, 114.0, 111.5, 47.1, 45.0 (br), 40.2, 38.5, 36.4, 31.5, 30.3, 25.8, 24.4; IR (film on NaCl) 2933, 2852, 1625, 1590, 1557, 1533, 1493, 1467, 1430, 1347, 1317, 1260 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 486.2018 (calcd for $C_{26}H_{35}N_3O^{80}Se$ + H^+: 486.2018).

Preparation of Selenoxanthone 23. Phosphorus oxychloride (0.380 mL, 4.08 mmol), triethylamine (0.567 mL, 4.07 mmol), and selenide **22** (165 mg, 0.339 mmol) in anhydrous CH_3CN (15 mL) were treated as described for the preparation of **2-S**. The crude product was recrystallized from CH_2Cl_2/hexanes to give 130 mg (95.7%) of **23** as a yellow solid, mp 200−203 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (d, 1 H, J = 9.0 Hz), 8.46 (s, 1 H), 6.76 (dd, 1 H, J = 3.0, 9.0 Hz), 6.67 (d, 1 H, J = 3.0 Hz), 6.54 (s, 1 H), 3.39 (t, 2 H, J = 6.0 Hz), 3.07 (s, 6 H), 3.02 (s, 3 H), 1.76 (t, 2 H, J = 6.0 Hz), 1.35 (s, 6 H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 179.8, 151.6, 147.7, 136.4, 134.4, 132.2, 130.9, 127.8, 120.5, 119.9, 111.3, 107.9, 106.4, 47.5, 40.0, 39.0, 36.2, 32.0, 29.9; IR (film on NaCl) 1590, 1314, 1287 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 401.1126 (calcd for $C_{21}H_{24}N_2O^{80}Se$ + H^+: 401.1127).

Preparation of Half-julolidyl Selenorhodamine 20-Se. Phenylmagnesium bromide (1.0 M in THF, 2.50 mL, 2.50 mmol) and selenoxanthone **23** (200 mg, 0.501 mmol) in THF (20 mL) were treated as described for the preparation of **5-S** to give 225 mg (74.3%) of **20-Se** as a green solid, mp 215−218 °C: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.66−7.59 (m, 2 H), 7.45 (d, 1 H, J = 9.0 Hz), 7.36 (s, 1 H) 7.32−7.27 (m, 3 H), 7.23 (d, 1 H, J = 2.5 Hz), 7.19 (s, 1 H), 6.82 (dd, 1 H, J = 2.5, 9.5 Hz), 3.57 (t, 2 H, J = 6.5 Hz), 3.26 (s, 3 H), 3.23

(s, 6 H), 1.75 (t, 2 H, J = 6.5 Hz), 1.05 (s, 6 H); ^{13}C NMR (500 MHz, CD_2Cl_2) δ 161.3, 153.0, 150.7, 145.4, 145.1, 138.4, 137.6, 135.0, 133.1, 129.5, 128.9, 120.5, 120.0, 114.7, 108.9, 108.3, 48.9, 40.7, 40.3, 34.6, 32.1, 28.5; λ_{max} (CH_3OH) 585 nm (ε = 1.35 × 10^5 M^{-1} cm^{-1}); IR (film on NaCl) 1591, 1509, 1448, 1387, 1356, 1330, 1252, 1211 cm^{-1}; HRMS (ESI, HRDFMagSec) m/z 461.1490 (calcd for $C_{27}H_{29}N_2Se^+$: 461.1497).

Preparation of Tellurorhodamine 27. 2-Bromomesitylene (469 μL, 3.07 mmol) was dissolved in dry THF (1.5 mL) in a round-bottomed flask. Magnesium (82.0 mg, 3.37 mmol) was added and the solution stirred at room temperature until most of the magnesium was consumed. The resulting solution of Grignard reagent was added via cannula to a stirred suspension of **2-Te** (100 mg, 0.204 mmol) in dry THF (10 mL). The resulting solution was heated at reflux for 24 h, cooled to ambient temperature, and poured into 200 mL of an ∼10% aqueous HPF_6 solution. The resulting precipitate was collected via filtration after 12 h of stirring and was washed with water (100 mL) and diethyl ether (100 mL) to give 127 mg (83.0%) of **27** as a dark purple solid, mp >250 °C. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.10 (s, 2 H), 7.03 (s, 2 H), 3.47 (t, 4 H, J = 6.0 Hz), 3.43 (t, 4 H, J = 6.0 Hz), 2.74 (t, 4 H, J = 6.5 Hz), 2.61 (t, 4 H, J = 6.5 Hz), 2.42 (s, 3 H), 2.21 (quintet, 4 H, J = 6.0 Hz), 1.93 (quintet, 4 H, J = 6.5 Hz), 1.80 (s, 6 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 162.4, 147.9, 138.5, 136.6, 136.0, 135.9, 135.4, 128.7, 125.1, 120.9, 120.8, 51.4, 50.7, 30.5, 28.0, 21.2, 21.0, 20.8, 19.7; λ_{max} (MeOH) 617 nm (ε = 1.65 × 10^5 M^{-1} cm^{-1}); HRMS (ESI, HRDFMagSec) m/z 603.2013 (calcd for $C_{34}H_{37}N_2{}^{130}Te^+$: 603.2012).

Oxidation of Tellurorhodamine 27 to Tellurorhodamine Telluroxide 28. Tellurorhodamine **27** (1.5 mg, 0.20 μmol) was dissolved in 0.60 mL of a solution of 0.1 M CF_3CO_2D in CD_3OD in a 5 mm NMR tube. The ^{1}H NMR spectrum of **27** in this solvent system was acquired: δ 7.09 (s, 2 H), 7.07 (s, 2 H), 3.54−3.48 (m, 4 H), 3.47−3.43 (m, 4 H), 2.82−2.74 (m, 4 H), 2.64−2.56 (m, 4 H), 2.42 (s, 3 H), 2.23−2.15 (m, 4 H), 1.98−1.88 (m, 4 H), 1.79 (s, 6 H). To this solution was added 12.5 μL of an 8.8 M solution of H_2O_2 (0.11 mmol, 0.18 M final concentration). The ^{1}H NMR spectrum of the resulting solution was recorded within 3 min of addition of the H_2O_2, and oxidation was complete at this point: ^{1}H NMR (500 MHz, CD_3OD 0.1 M $CF_3C(O)OD$) δ 7.05 (s, 2 H), 6.81 (s, 2 H), 3.75−3.67 (m, 4 H), 3.66−3.60 (m, 4 H), 3.46−3.36 (m, 4 H), 2.58−2.49 (m, 4 H), 2.39 (s, 3 H), 2.29−2.17 (m, 4 H), 2.00−1.86 (m, 4 H), 1.90 (s, 6 H); ^{13}C NMR (500 MHz, 0.1 M $CF_3C(O)OD$ in CD_3OD) δ 151.1, 139.3, 137.2, 136.2, 135.4, 130.1, 128.5, 126.0, 52.0, 51.4, 30.4, 27.3, 20.8, 20.2, 20.1, 18.6; λ_{max} (CH_3OH) 704 nm (ε = 1.35 × 10^5 M^{-1} cm^{-1}); HRMS (ESI, HRDFMagSec) m/z 619.1963 (calcd for $C_{34}H_{37}N_2O^{130}Te^+$: 619.1963).

Preparation of Tellurorhodamine 29. 2-Bromomesitylene (461 μL, 2.98 mmol) was added to a stirred suspension of ground magnesium turnings (79.7 mg, 3.28 mmol) in THF (3 mL). The resulting solution was stirred at ambient temperature for 3 h before it was transferred via cannula to a stirred solution of telluroxanthone **3-Te** (150 mg, 0.298 mmol) at room temperature in THF (5 mL). The mixture was heated at reflux overnight, then cooled to ambient temperature before glacial acetic acid (2 mL) was added. The resulting solution was poured into cold, stirring 10% aqueous HPF_6 (200 mL), and the resulting mixture was stirred for 12 h. The precipitate was collected via filtration and washed with water (50 mL) and hexanes (75 mL), yielding 125 mg (55.8%) of **29** as a blue solid, mp 166−168 °C: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.40 (s, 2 H), 7.39 (s, 2 H), 7.08 (s, 2 H), 3.50 (t, 4 H, J = 6.0 Hz), 3.20 (s, 6 H), 2.44 (s, 3 H), 1.82 (s, 6 H), 1.73 (t, 4 H, J = 6.0 Hz), 1.01 (s, 12 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 164.1, 149.5, 138.9, 135.9, 135.8, 135.6, 135.1, 133.7, 128.7, 121.5, 114.9, 48.5, 39.9, 34.8, 31.9, 28.8, 21.2, 19.5; λ_{max} (CH_3OH) 606 nm (ε = 9.66 × 10^4 M^{-1} cm^{-1}); HRMS m/z 607.2329 (ESI, HRDFMagSec) ($C_{34}H_{41}N_2{}^{130}Te^+$: 607.2326).

Oxidation of Tellurorhodamine 29 to Tellurorhodamine Telluroxide 30. Tellurorhodamine **29** (1.5 mg, 0.20 μmol) was dissolved in 0.60 mL of a solution of 0.1 M CF_3CO_2D in CD_3OD in a 5 mm NMR tube. The ^{1}H NMR spectrum of **29** in this solvent system was acquired: δ 7.73 (s, 2 H), 7.43 (s, 2 H), 7.16 (s, 2 H), 3.54 (t, 4 H, J = 6.0 Hz), 3.21 (s, 4 H), 2.42 (s, 3 H), 1.82 (s, 6 H), 1.82 (t, 4 H, J = 6.0 Hz), 1.00 (s, 6 H). To this solution was added 12.5 μL of an 8.8 M solution of H_2O_2 (0.11 mmol, 0.18 M final concentration). The ^{1}H NMR spectrum of the resulting solution was recorded within 3 min of addition of the H_2O_2, and oxidation was complete at this point: ^{1}H NMR (500 MHz, CD_3OD 0.1 M $CF_3C(O)OD$) δ 8.00 (s, 2 H), 7.19 (s, 2 H), 7.15 (s, 2 H), 3.76 (t, 4 H, J = 6.0 Hz), 3.48 (s, 4 H), 2.42 (s, 3 H), 1.93 (s, 6 H), 1.77 (t, 4 H, J = 6.0 Hz), 1.00 (s, 6 H); ^{13}C NMR (500 MHz, 0.1 M $CF_3C(O)OD$ in CD_3OD) δ 153.4, 140.8, 137.0, 136.8, 135.7, 129.8, 129.4, 123.7, 50.2, 40.8, 35.3, 32.6, 32.3, 28.9, 21.2, 19.6; λ_{max} (CH_3OH) 692 nm (ε = 1.65 × 10^5 M^{-1} cm^{-1}); HRMS (ESI, HRDFMagSec) m/z 623.2279 (calcd for $C_{34}H_{41}N_2O^{130}Te^+$: 623.2276).

Determination of Singlet Oxygen Yields from Singlet Oxygen Phosphorescence Spectroscopy. Generation of singlet oxygen ($^1O_2$) was assessed by its phosphorescence peak at 1270 nm. A spectrometer equipped with a near-infrared photodetector was used for acquisition of the emission spectra in NIR spectral range. A diode-pumped solid-state laser at 532 nm was the excitation source. The emission signal was collected at 90° relative to the exciting laser beam with the use of a 950 nm long-pass filter to attenuate the scattered light and fluorescence from the samples. The samples (methanol solutions of the compounds in quarts cuvettes) were placed in front of the spectrometer entrance slit.

Fluorescence Experiments. Measurements of fluorescence quantum yield were performed on a spectrofluorometer using either fluorescent dye Rhodamine 6G with known Φ_{FL} = 0.93[44] in MeOH for **5-E**−**7-E** or fluorescent dye LD 700 perchlorate (Rhodamine 700) as a reference with known Φ_{FL} = 0.38[31] in MeOH for **27** and **28**.

Cell Experiments. Colo-26, a murine colon carcinoma cell line, was maintained in RPMI 1640 supplemented with 10% fetal calf serum (FCS) and antibiotics at 37 °C, and 5% CO_2. Colo-26 cells were harvested, counted, and seeded at a density of 1.5 × 10^5 cells per well in 0.5 mL of RPMI supplemented medium the night before the assay in a 24-well plate. The day of the assay, the medium was removed from a single well at a time, and 0.5 mL of HBSS was added to the cells. MitoTracker Green (0.25 μL of stock solution and 0.5 μM final concentration) was added to the well, and the plate was incubated for 10 min. Tellurorhodamine **27** (0.2 μM) was added, and the plate was incubated for an additional 5 min (total incubation = 15 min). The HBSS containing tellurorhodamine **27** and MitoTracker Green was removed, and 0.5 mL of fresh HBSS was added.

A camera-equipped fluorescence microscope was used in the cell imaging experiments. Tellurorhodamine **27** and/or telluroxide **28** were excited with 620 ± 30 nm light, and MitoTracker Green was excited with 470 ± 20 nm light. ImageJ software was used to color the images and to give an overlay of images.

■ ASSOCIATED CONTENT

Supporting Information

General experimental procedures and ^{1}H and ^{13}C NMR spectra for **2-E**−**7-E**, **9**, **10-E**, **11**, **12**, **13-E**, **15-E**, **17-E**, **18-E**, **20-E**, **22**, **23**, and **27**−**30**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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