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A Microwave-Assisted Synthesis of Julolidine-9-carboxamide Derivatives and Their Conversion to Chalcogenoxanthones via Directed Metalation

Jason J. Holt, Brandon D. Calitree, Josiah Vincek, Michael K. Gannon, II, and Michael R. Detty*

Department of Chemistry, The State University of New York at Buffalo, Buffalo, New York 14260-3000

mdetty@buffalo.edu

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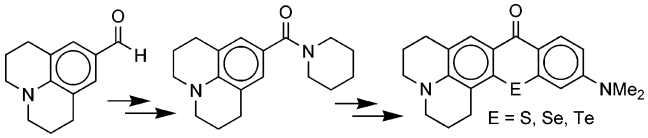
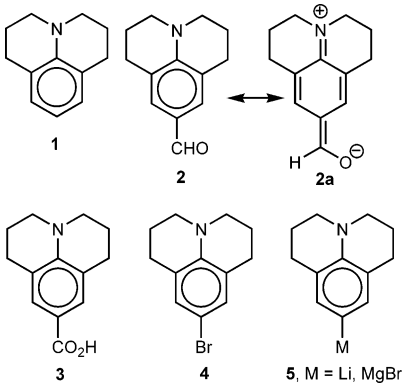


9-Formyljulolidine was oxidized via a microwave-assisted Willgerodt−Kindler reaction to the *N*-piperidine or *N*-morpholine julolidine-9-thioamide. 9-Formyl-1,1,7,7-tetramethyljulolidine gave the corresponding *N*-piperidine tetramethyljulolidine-9-thioamide. The thioamides were converted to the corresponding carboxamides with trifluoroacetic anhydride. The amide group directed ortho-metalation in the julolidine system, but not in the tetramethyljulolidine system. The resulting anion was captured by dichalcogenide electrophiles. The resulting products were converted to chalcogenoxanthones with phosphorus oxychloride and triethylamine ($POCl_3/Et_3N$).

Julolidine (**1**, Chart 1) is an intriguing chemical structure. While **1** is chemically an aniline derivative with two *N*-alkyl substituents forming rings back to the aromatic ring, the fused rings lock the nitrogen lone-pair of electrons into conjugation with the aromatic ring leading to unusual reactivity. The aromatic ring is activated to electrophilic attack and Vilsmeier−Haack formylation of **1** gives 9-formyljulolidine (**2**) in >90% yield.[1,2] The conformational rigidity gives an electron-rich ring for electrophilic attack. However, the oxidation of the aldehyde **2** to the carboxylic acid **3** and to other carboxylic acid derivatives proved to be problematic due to contributions from resonance form **2a**. The conformational rigidity of the julolidyl system also complicates efforts to convert 9-bromojulolidine (**4**)[2] to carboxylic acid **3** via the corresponding organolithium or organomagnesium derivatives **5**. The Grignard reagent does not form while metal−halogen exchange between *n*-BuLi and **4** gives only 50% conversion.[3]

CHART 1



The one method we have found to yield **3** successfully was a silver oxide catalyzed oxidation,[2] which gave **3** reproducibly, but in only 10−15% isolated yield, not the ~60% yields reported by Smith and Yu.[4] We sought a general, reproducible means to oxidize **2** to the carboxylic acid oxidation state. We were also interested in using amide derivatives of **3** in directed metalation reactions to prepare chalcogenoxanthones incorporating the julolidine ring. Directed metalation reactions of derivatives of **3** have not been described.

Several thioamides have been prepared from aldehydes, S, and morpholine by using a microwave-assisted Willgerodt−Kindler (W-K) reaction.[5] Other amines gave products of amine oxidation. We report that 9-formyl julolidine (**2**) is oxidized with S and piperidine as well as morpholine by using microwave-assisted W-K reactions. Reaction of **2** with piperidine and S in *N*,*N*-dimethylformamide (DMF) with microwave irradiation gave thioamide **6** in 91−93% isolated yield (Scheme 1). The reaction mixture in a sealed microwave vessel was irradiated at 400 W for 30 min. The temperature of the reaction was held at 200 °C. Under similar conditions, treating **2** with morpholine and S gave thioamide **7** in 73−75% isolated yield. These reactions have been run successfully on a 1−3-g scale. Diethylamine did not give any of the diethylthioamide under these conditions.

The W-K reaction also proceeded as a strictly thermal reaction. The reaction of **2** with piperidine and S in DMF at 153 °C for 30 min also gave **6**, but in only 71−78% isolated yields. The evolution of H_2S gas was also apparent from the strong odor associated with the reaction. In the microwave-assisted reaction, both the sealed reaction vessel and the microwave effect itself would lead to increased pressure, which might limit the evolution of H_2S leading to the higher yields in the microwave-assisted W-K reactions.

The slow addition of trifluoroacetic anhydride[6] to thioamides **6** or **7** in CH_2Cl_2 at room temperature (Scheme 1) gave amides

* To whom correspondence should be addressed: Phone: (716) 645-6800, ext 2200. Fax: (716) 645-6963.

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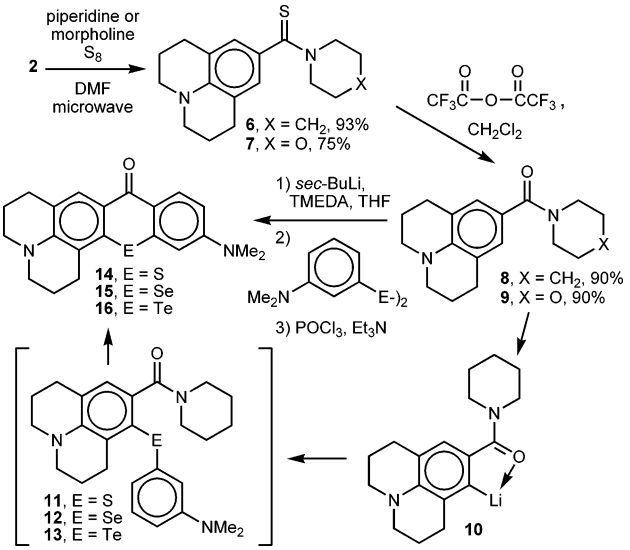
SCHEME 1



8 and **9**, respectively, in 90% isolated yield. The same transformation was also accomplished by using copper nitrate hexahydrate in CH_2Cl_2,[7] but yields were lower (~80%).

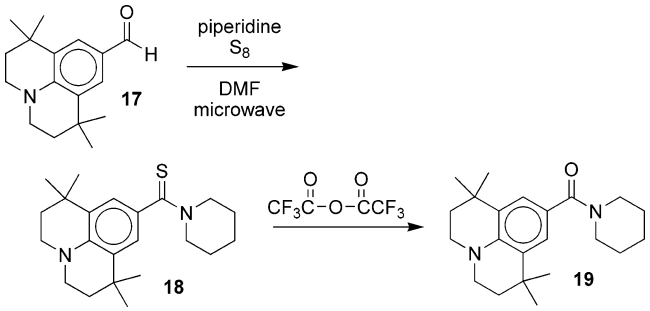
The two-step conversion of **2** to the carboxamide derivatives gave overall yields of 84% for **8** and 70% for **9**. This method represents a reliable means for oxidation of **2** to the carboxylic acid oxidation state and provides amides that can be examined in directed metalation reactions.

Metalation of **8** with *sec*-BuLi/tetramethylenediamine (TMEDA) in THF at −78 °C presumably gives anion **10** (Scheme 1). The addition of bis(3-dimethylaminophenyl) disulfide, diselenide, or ditelluride[8] to **10** gave the diarylchalcogenides **11** and **12** as oils and diaryltelluride **13** in 30% yield as a crystalline solid (and recovered **8** in 16% yield). Both **11** and **12** were chromatographically inseparable from small quantities of unreacted **8** under a variety of conditions. Typically, the mixtures consisted of 93−97% **11** with 3−7% of **8** and 85−90% **12** with 10−15% **8**. The use of more forcing conditions or excess *sec*-BuLi gave reduced yields. The mixtures were used in the cyclization step without further purification.

The **8**/**11** mixture or the **8**/**12** mixture reacted with $POCl_3$/Et_3N[8a] to give the chalcogenoxanthones **14** and **15**, respectively, as well as unreacted **8**, which was readily separated by chromatography on silica gel at this stage. The yields for **14** and **15** were each 72% for the cyclization of **11** or **12**. Telluride **13** reacted with $POCl_3$/Et_3N[8a] to give telluroxanthone **16** in 76% isolated yield. Importantly, the 2,3,6,7-tetrahydro-1*H*,5*H*-benzo(*i*,*j*)quinolizine ring system (i.e., the julolidyl system) appears to be stable (a) to *sec*-BuLi/TMEDA and (b) to the $POCl_3$/Et_3N cyclization conditions.

Directed metalation reactions were unsuccessful with morpholino amide **9**. In this system, the morpholine ring appeared to react with the *sec*-BuLi/TMEDA and none of the chalcogenide products related in structure to **11**−**13** were detected.

SCHEME 2



The microwave-assisted W-K reaction[5] was also applied to the oxidation of 9-formyl tetramethyljulolidine **17**.[9] Reaction of **17** with piperidine and S in DMF with microwave irradiation gave thioamide **18** in 69% isolated yield (Scheme 2). The slow addition of trifluoroacetic anhydride[6] to **18** in CH_2Cl_2 at room temperature gave amide **19** in 72% isolated yield. All of our attempts thus far to do directed metalation reactions with **19** and diaryl dichalcogenides have only returned unreacted **19**.

In summary, we have described a reliable, two-step procedure for oxidizing 9-formyl julolidine (**2**) to julolidine-9-carboxamide derivatives **8** and **9** and for oxidizing 9-formyl tetramethyljulolidine (**17**) to tetramethyljulolidine-9-carboxamide derivative **19** as well as the first directed metalation reactions of a julolidine 9-carboxamide derivative. Directed metalation of **8** with *sec*-BuLi proceeds to give anion **10**, which has been captured by dichalcogenide electrophiles. Chalcogenides **11**−**13** are cyclized with $POCl_3$/Et_3N to give chalcogenoxanthones **14**−**16**. The chalcogenoxanthones **14**−**16** serve as precursors to chalcogenoxanthylium dyes based on **14**−**16**, which are of potential interest as photosensitizers for photodynamic therapy[10] and as stimulators/inhibitors of *P*-glycoprotein.[11]

Experimental Section

Microwave-Assisted W-K Reaction. Microwave reactions were run in a sealed 80 mL microwave reaction vial. The reaction was subjected to 25% power at the 400 W setting with an upper temperature limit of 200 °C for 30 min followed by cooling for 25 min. 9-Formyl julolidine[1] (**2**, 3.00 g, 15.0 mmol) or 9-formyl tetramethyljulolidine[9] (**17**, 4.00 g, 15.5 mmol), S (1.20 g, 3.8 mmol), and piperidine (4.44 mL, 45.0 mmol) in 7.5 mL of DMF were treated in this manner. The resulting red solution was cooled to ambient temperature and poured into 100 mL of cold water. For **8**, the resulting yellow precipitate was collected by filtration and was then washed with water (2 × 30 mL) and hexanes (2 × 30 mL). The precipitate was then dissolved in CH_2Cl_2, and the resulting solution was dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel, then eluted with 1:9 ether−CH_2Cl_2 to give 4.17 g (93%) of **6** as a yellow solid. For **18**, the aqueous mixture was extracted with CH_2Cl_2 (3 × 100 mL) and the combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by chromatography on silica gel, then eluted with 1:9 ether−CH_2Cl_2 to give 3.8 g (69%) of **18** as a yellow-brown oil. Sulfur (0.40 g, 13 mmol),

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2 (1.00 g, 5.0 mmol), and morpholine (1.31 mL, 15.0 mmol) were treated as described to give 1.08 g (72%) of **7**.

For **6**: mp 173−175 °C dec; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 6.74 (s, 2 H), 4.24 (br m, 2 H), 3.66 (br m, 2 H), 3,17 (t, 4 H, J = 6 Hz), 2.71 (t, 4 H, J = 6 Hz), 1.94 (m, 4 H), 1.72 (br m, 2 H), 1.75−1.50 (br m, 4 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 201.3, 143.9, 130.5, 126.0, 120.5, 51.8 (br), 50.2, 28.0, 26.5 (br), 24.7, 22.2; IR (KBr) 2933, 2852, 1603, 1506, 1476, 1438, 1311, 1233, 1208, 1170, 1133, 1025, 1006 cm^{-1}; HRMS (ESI) *m*/*z* 300.1650 (calcd for $C_{18}H_{24}N_2S^+$ 300.1655).

For **7**: mp 129−131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 2 H), 4.50−3.90 (br m, 4 H), 3.90−3.60 (br m, 4 H), 3.18 (t, 4 H, J = 6 Hz), 2.72 (t, 4 H, J = 6 Hz), 1.95 (t×t, 4 H, J = 5.8, 6.4 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 202.6, 144.1, 128.8, 126.3, 120.2, 66.8, 52.1(br), 49.9, 27.7, 21.7; IR (KBr) 2931, 1601, 1507, 1457, 1312, 1227, 1208, 1155, 1112, 1025 cm^{-1}; HRMS (ESI) *m*/*z* 303.1525 (calcd for $C_{17}H_{22}N_2OS + H^+$ 303.1526). Anal. Calcd for $C_{17}H_{22}N_2OS$: C, 67.51; H, 7.33; N, 9.26. Found: C, 67.26; H, 7.22; N, 9.17.

For **18**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (s, 2 H), 4.30 (br s, 2 H), 3.68 (br s, 2 H), 3.18 (t, 4 H, J = 6 Hz), 1.74 (t, 4 H, J = 6 Hz), 1.73 (br m, 6 H), 1.26 (s, 12 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 202.0, 141.5, 129.6, 128.9, 123.4, 52.2 (br), 46.6, 36.4, 32.2, 30.9, 26.3 (br), 24.4; IR (film on NaCl) 2934, 2855, 1600, 1510 cm^{-1}; HRMS (ESI) *m*/*z* 357.2358 (calcd for $C_{22}H_{32}N_2S + H^+$ 357.2359).

Thermal W-K Reactions. 9-Formyl julolidine[1] (**2**, 0.500 g, 2.48 mmol) and S (0.200 g, 6.21 mmol) were suspended in 3.2 mL of dry DMF. Piperdine (0.74 mL, 7.4 mmol) was added to the stirred mixture and the resulting mixture was heated at 153 °C for 30 min. The reaction mixture was cooled to ambient temperature and was poured into 30 mL of CH_2Cl_2. The resulting solution was washed with water (2 × 10 mL) and brine (2 × 10 mL), then was concentrated under reduced pressure. The crude product was recrystallized from CH_2Cl_2/MeOH to give 0.595 g (71%) to 0.645 g (78%) of **6** as yellow crystals. On this scale, the microwave-assisted W-K reaction gave 0.780 g (93%) of **6** following recrystallization.

Procedure for Thioamide to Amide Conversion. Trifluoroacetic anhydride (0.28 mL, 2.0 mmol, 1.2 equiv) was added slowly over a period of 5 min to thioamide **6**, **7**, or **18** (1.7 mmol, 1 equiv) in dry CH_2Cl_2 (10 mL). A red color that persisted was observed upon addition of the trifluoroacetic anhydride. The reaction mixture was stirred at room temperature for 1 h and was then washed with an equal volume of aqueous 10% Na_2CO_3. The organic fraction was dried over $MgSO_4$ and concentrated to yield a red oil. The amides **8** and **9** were purified via chromatography on silica gel eluted with 10% ether in CH_2Cl_2 to give 0.43 g (90%) of **8** and 0.43 g (90%) of **9** as yellow oils, and 0.56 g (72%) of **19** as a yellow solid. Products were stored at −20 °C due to discoloration upon standing at room temperature.

For **8**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 (s, 2H), 3.56 (br m, 4H), 3.17 (t, 4H, J = 6.0 Hz), 2.73 (t, 4H, J = 6.5 Hz), 1.95 (m, 4H), 1.66 (m, 2H), 1.57 (br m, 4H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 171.2, 144.2, 126.8, 122.7, 120.6, 50.1, 46.5 (br), 28.0, 26.5, 25.1, 22.2; IR (film on NaCl) 2933, 2852, 1609, 1513 cm^{-1}; HRMS (ESI) *m*/*z* 285.1963 (calcd for $C_{18}H_{24}N_2O + H^+$ 285.1961).

For **9**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89 (s, 2 H), 3.70−3.63 (br m, 8 H), 3.18 (t, 4 H, J = 6 Hz), 2.72 (t, 4 H, J = 6 Hz), 1.95 (q, 4 H, J = 6 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 171.5, 144.3, 126.9, 120.8, 120.4, 67.0, 49.8, 45.9 (br), 27.7, 21.7; IR (film on NaCl) 3487, 2928, 2846, 1606, 1516 cm^{-1}; HRMS (ESI) *m*/*z* 286.1675 (calcd for $C_{17}H_{22}N_2O_2^+$ 286.1676).

For **19**: mp 151−154 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (s, 2 H), 3.56 (br s, 4 H), 3.18 (t, 4 H, J = 6 Hz), 1.74 (t, 4 H, J = 6 Hz), 1.71−1.64 (br m, 2 H), 1.63−1.56 (br m, 4 H), 1.27 (s, 12 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 171.8, 141.7 129.2, 123.9, 122.0, 46.7, 46.4 (br), 36.5, 32.2, 31.0, 26.1, 24.8; IR (film on NaCl) 2932, 2854, 1623, 1606, 1517 cm^{-1}; HMRS (ESI) *m*/*z* 341.2585 (calcd for $C_{22}H_{32}N_2O + H^+$ 341.2587).

Procedure for Lithiation of 8 and Formation of 11−13. Amide **8** (1.10 g, 3.87 mmol, 1 equiv) and TMEDA (0.584 mL, 3.87 mmol, 1 equiv) were dissolved in dry THF (80 mL) in a flame-dried flask under argon. The resulting solution was cooled to −78 °C and *sec*-butyllithium in THF (3.44 mL of a 1.24 M solution, 4.26 mmol, 1.1 equiv) was then added over 3 min. The reaction was stirred for 10 min and bis(3-dimethylaminophenyl) disulfide (1.19 g, 3.87 mmol), diselenide (1.50 g, 3.87 mmol), or ditelluride (1.92 g, 3.87 mmol) in dry THF (20 mL) was added. The resulting mixture was stirred at −78 °C for 0.5 h and then warmed to room temperature with stirring overnight. The reaction was then quenched with saturated NH_4Cl (100 mL) and extracted with ether (3 × 50 mL). The organic extracts were combined, washed with brine (2 × 40 mL), dried over $MgSO_4$, and concentrated. The crude products were purified via chromatography on silica gel eluting with 5% EtOAc/CH_2Cl_2 to give 1.11 g of a 97:3 mixture of **11** to **8** (60% yield of **11**), 0.82 g of an 85:15 mixture of **12** to **8** (37% yield of **12**), and 0.46 g (30%) of **13** as a yellow solid, mp 72−76 °C, as well as 0.18 g (16%) of unreacted **8**.

For **11**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (t, 1H, J = 10.0 Hz), 6.72 (s, 1H), 6.58 (s, 1H), 6.45 (d, 1H, J = 9.0 Hz), 6.36 (d, 1H, J = 9.5 Hz), 3.76−3.68 (m, 1H), 3.62−3.54 (m, 1H), 3.24−3.12 (m, 3H), 3.12−3.02 (m, 3H), 2.88 (s, 6H), 2.83 (t, 1H, J = 7.5 Hz), 2.75 (t, 3H, J = 8.0 Hz), 1.95 (sextet, 2H, J = 7.5 Hz), 1.85 (quintet, 2H, J = 8.0 Hz), 1.62−1.46 (m, 4H), 0.92−0.80 (m, 2H); HRMS (ESI) *m*/*z* 435.2342 (calcd for $C_{26}H_{33}ON_3S^+$ 435.2344).

For **12**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 (t, 1H, J = 8.0 Hz), 6.70−6.69 (m, 2H), 6.50−6.48 (m, 2H), 3.76−3.70 (m, 1H), 3.62−3.54 (m, 1H), 3.26−3.15 (m, 3H), 3.15−3.04 (m, 3H), 2.87 (s, 6H), 2.81 (q, 2H, J = 6.5 Hz), 2.78−2.70 (m, 2H), 2.00−1.92 (m, 2H), 1.84 (quintet, 2H, J = 6.0 Hz), 1.68−1.48 (m, 4H), 1.31 (qt, 2H, J = 5.5 Hz); HRMS (ESI) *m*/*z* 484.1859 (calcd for $C_{26}H_{33}ON_3{}^{80}Se + H^+$ 484.1862)

For **13**: ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C) δ 6.95 (t, 1 H, J = 8 Hz), 6.88 (d, 1H, J = 2.5 Hz), 6.74 (d, 1 H, J = 8 Hz), 6.69 (s, 1 H), 6.52 (d×d, 1 H, J = 2.5, 8 Hz), 3.64 (br s, 2H), 3.27 (br s, 2 H), 3.16 (t, 2 H, J = 6 Hz), 3.06 (t, 2 H, J = 6 Hz), 2.85 (s, 6 H), 2.83 (br s, 2 H), 2.74 (t, 2 H, J = 6 Hz), 1.94 (quintet, 2 H, J = 6 Hz), 1.83 (quintet, 2 H, J = 6 Hz), 1.60 (br s, 4 H), 1.42 (br s, 2 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 172.0, 151.0, 143.1, 134.0, 129.5, 127.5, 124.2, 123.4, 122.7, 119.0, 117.6, 114.1, 111.1, 50.0, 49.4, 48.5, 42.6, 40.4, 33.8, 27.9, 26.5, 25.4, 24.6, 22.4, 21.7; IR (KBr) 2926, 2853, 1623, 1584, 1554 cm^{-1}; HRMS (ESI) *m*/*z* 534.1748 (calcd for $C_{26}H_{34}N_3O^{130}Te + H^+$ 534.1759).

Cyclization of 11−13. To the **8**/**11** (0.45 g, 1.0 mmol of **11**) or **8**/**12** mixture (0.53 g, 1.0 mmol of **12**) in dry acetonitrile (30 mL) was added Et_3N (1.67 mL, 12.0 mmol) followed by $POCl_3$ (1.12 mL, 12.0 mmol). The resulting mixture was stirred for 1 h at room temperature and was then heated to 80 °C for 2 h. The reaction was stopped by the addition of 1 N NaOH (100 mL). The organic products were extracted with CH_2Cl_2 (3 × 25 mL) and the combined organic extracts were washed with brine (2 × 25 mL), dried over $MgSO_4$, and concentrated. The crude product was purified via chromatography on SiO_2 eluted with 5% EtOAc/CH_2Cl_2 to separate unreacted **8** from chalcogenoxanthones **14** and **15**. Both **14** and **15** were recrystallized from CH_3CN to give 0.251 g (72%) of **14** and 0.285 g (72%) of **15**. Compound **13** (0.408 g, 0.769 mmol) in dry acetonitrile (25 mL) was treated with triethylamine (1.29 mL, 9.22 mmol) and phosphorus oxychloride (0.86 mL, 9.2 mmol) as described to give 0.26 g (76%) of **16** as a yellow solid following recrystallization from CH_3CN.

For **14**: mp 236−237 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, 1 H, J = 9.0 Hz), 8.11 (s, 1 H), 6.78 (d×d, 1 H, J = 2.5, 9.0 Hz), 6.63 (d, 1 H, J = 2.5 Hz), 3.27 (t, 2 H, J = 6.0 Hz), 3.26 (t, 2 H, J = 5.5 Hz), 3.07 (s, 6H), 2.86 (t, 2 H, J = 6.0 Hz), 2.77 (t, 2 H, J = 6.5 Hz), 2.07 (m, 2 H), 1.98 (m, 2 H); ^{13}C NMR

(75.5 MHz, $CDCl_3$) δ 178.1, 151.6, 145.6, 138.7, 135.0, 130.6, 127.9, 120.2, 118.7, 118.3, 112.7, 111.2, 105.6, 50.3, 49.4, 40.0, 27.7, 24.1, 21.5, 21.2; IR (KBr) 2934, 2833, 2361, 2343, 1591, 1508, 1416, 1355, 1331, 1306, 1175, 1077 cm^{-1}; HRMS (ESI) *m*/*z* 351.1518 (calcd for $C_{21}H_{22}N_2OS + H^+$ 351.1526).

For **15**: mp 243−245 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, 1 H, J = 9.2 Hz), 8.18 (s, 1H), 6.77 (d×d, 1 H, J = 2.6, 9.2 Hz), 6.73 (d, 1 H, J = 2.6 Hz), 3.28 (m, 4 H), 3.07 (s, 6 H), 2.86 (t, 2 H, J = 6.4 Hz), 2.71 (t, 2 H, J = 6.8 Hz), 2.07 (q, 2 H, J = 6.8 Hz), 2.00 (q, 2 H, J = 6.4 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 180.1, 151.5, 145.7, 136.3, 134.1, 132.0, 129.7, 120.2-(2), 120.2(8), 119.7, 114.6, 111.4, 108.0, 50.2, 49.4, 40.0, 27.6, 25.7, 21.5, 21.4; IR (KBr) 2926, 2843, 2366, 1589, 1572, 1509, 1410, 1303, 1174, 1062 cm^{-1}; HRMS (ESI) *m*/*z* 399.0965 (calcd for $C_{21}H_{22}N_2O^{80}Se + H^+$ 399.0970). Anal. Calcd for $C_{21}H_{22}N_2$-OSe: C, 63.47; H, 5.58; N, 7.05. Found: C, 63.39; H, 5.67; N, 7.02.

For **16**: mp 229−231 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, 1 H, J = 9.5 Hz), 8.25 (s, 1 H), 6.83 (d, 1 H, J = 2.5 Hz), 6.74 (d×d, 1 H, J = 2.5, 9.5 Hz), 3.26 (t, 4 H, J = 6.75 Hz), 3.05 (s, 6 H), 2.86 (t, 2 H, J = 6.5 Hz), 2.58 (t, 2 H, J = 6.5 Hz), 2.11−2.05 (m, 2H), 2.00−1.95 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 184.0, 151.3, 145.9, 133.5, 131.7, 123.3, 122.80, 122.75, 121.8, 120.7, 118.3, 113.6, 112.0, 50.1, 49.6, 39.9, 29.8, 27.5, 21.7, 21.5; IR (KBr) 2927, 2850, 1584, 1506 cm^{-1}; HRMS (ESI) *m*/*z* 449.0868 (calcd for $C_{21}H_{22}N_2O^{130}Te + H^+$ 449.0867). Anal. Calcd for $C_{21}H_{22}N_2OTe$: C, 56.55; H, 4.97; N, 6.28. Found: C, 56.52; H, 5.00; N, 6.14.

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Supporting Information Available: General methods and ^1H and ^{13}C NMR spectra of compounds **6**−**9**, **13**−**16**, **18**, and **19** and ^1H NMR spectra for the **11**/**8** and **12**/**8** mixtures. This material is available free of charge via the Internet at http://pubs.acs.org.

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