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A new facile synthetic method for the construction of 1,3-oxathiolan-2-ylidenes

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Abstract

A new, convenient and efficient synthetic method for the construction of 1,3-oxathiolan-2-ylidenes via sodium borohydride reduction of the addition product of dithiocarbamic acid esters with α-bromoketones under basic conditions is reported. This method is general and applicable to a range of systems.

1,3-Oxathiolan-2-ylidenes having an exocyclic imine group can be used in organic synthesis for the preparation of biologically active compounds.[1] These heterocycles were initially prepared by the reaction of alkylthiocyanates or acetyl and benzoyl isothiocyanates with epoxides,[2] and subsequently by the 1,3-cycloaddition of heterocumulenes, such as isothiocyanates with oxiranes under various reaction conditions.[3,4] The basic skeleton of 1,3-oxathiolan-2-ylidenes is unstable and has been isolated as its *N*-acyl or *N*-carbamoyl derivatives.[5] Taking advantage of the faster alkylation of the thiocyano group compared to the intramolecular cyclisation of 2-hydroxythiocyanates, an alternative strategy for the synthesis of *N*-alkyl-1,3-oxathiolan-2-ylidenes has been achieved from 2-hydroxythiocyanates and 1-adamantyl or tertiary butylalcohols.[6] In all these cases, the *N*-alkyl-1,3-oxathiolan-2-ylidenes exist as a mixture of cis/trans isomers around the imine double bond. In another strategy, 2-methylbut-3-yn-2-ol reacts with benzyl isothiocyanate to give the oxathiolan-2-ylidene moiety having an exocyclic double bond obtained by intramolecular attack of sulfur on the terminal acetylene.[7] Reactions of lithiated salts of dithioalkylimines with carbonyl compounds give the oxathiolan-2-ylidene skeleton.[8] The synthesis of 2-imino-5-chloro-1,3-oxathiolanes, 2-imino-1,3-oxathioles and 1,3-thiazolin-2-ones from *N*-aryl and *N*-alkyl-*S*-chloroisothiocarbamoyl chlorides and ketones has been reported.[9]

However, the drawbacks using the above-strategies are the requirement of expensive and specially designed substrates, reagents and catalysts and elevated temperatures. The use of polar solvents is accompanied by undesirable reactions such as trimerization of the isocyanate. Aromatic and aliphatic isothiocyanates usually do not give oxathiolan-2-ylidenes because of the facile conversion to 2-oxazolidinones in the presence of oxiranes.[10] Unlike in the synthesis of *N*-aryl-1,3-oxathiolan-2-ylidenes the reaction of isocyanates with oxiranes catalysed by Lewis acids cannot be used for the preparation of *N*-alkyl derivatives.[11] 1,3-Oxathiolan-2-ylidenes are formed only by the cycloaddition of activated isothiocyanates such as acetyl and benzoyl isothiocyanates with oxiranes.

During the formation of thiazolidine-2-imine, the sulfur atom of the thiourea attacks the bromomethyl carbon of the α-bromoketone.[12] Taking cues from the reactivity of thioureas,[12] the leaving ability of a thiol attached to an imine functionality[13] and the α-brominating ability of ketones using 1,1′-(ethane-1,2-diyl)dipyridinium bistribromide (EDPBT)[14] we envisaged a retrosynthetic scheme for the construction of 1,3-oxathiolan-2-ylidenes (Scheme 1).

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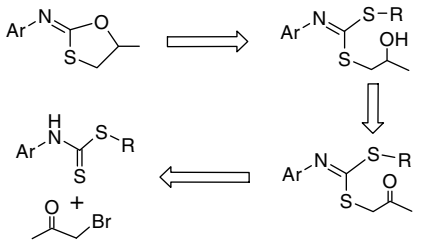


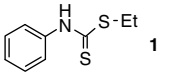
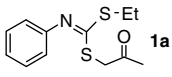
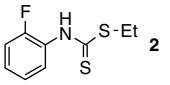
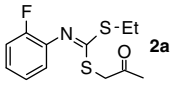
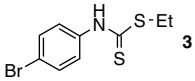
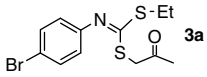
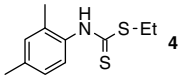
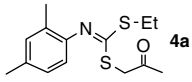
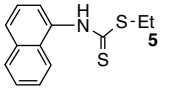
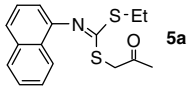
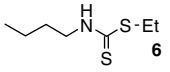
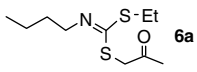
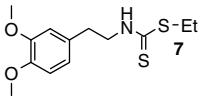
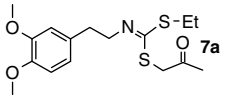
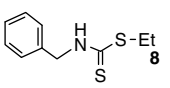
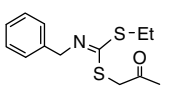
Scheme 1. Retrosynthetic analysis of oxathiolan-2-ylidenes.

As expected, the dithiocarbamic acid ester **1** (Table 1, Scheme 1) reacted with the α-bromoketone formed by the reaction of acetone with EDPBT in the presence of triethylamine to give the addition product **1a** containing a carbonyl functionality within 0.5 h at room temperature.[20] Similarly, various other adducts **2a**–**8a** of different dithiocarbamic acid esters **2**–**8** were prepared employing this strategy in good yields as shown in Table 1.

Haloketones, such as 3-bromo-4-methyl-pentane-2-one, 2-bromo-1-phenyl-ethanone, 2-bromo-cyclohexanone and 1-bromo-1-(4-methoxy-phenyl)-propan-2-one, were prepared from their parent ketones using EDPBT.[14] These α-haloketones were then reacted with dithiocarbamic acid esters **1** and **5** in the presence of triethylamine in acetonitrile to provide adducts **9a**–**12a** as shown in Table 2. Adducts **1a**–**12a** were obtained exclusively as their *Z*-isomer. S-Alkylation of dithiocarbamic acid esters involves base (triethylamine)-mediated abstraction of the NH proton, hence an E_2 type of reaction which will be favourable if the NH and C=S are *anti* to each other. We have shown in an analogous system having a thioimido or a thioamido functionality, during the formation of the thiazole-2-imine, the imine double bonds were found to have the *Z*-conformation (eight crystal structures).[12] Further no diastereomeric products could be detected even in ^{1}H NMR of the crude. Adducts **9a**, **11a** and **12a** were obtained as racemic products since they were prepared from the corresponding racemic bromo compounds.

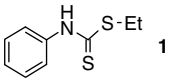
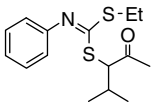
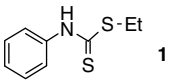
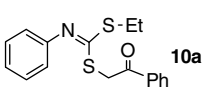
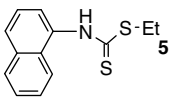
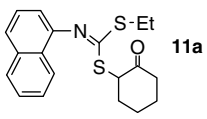
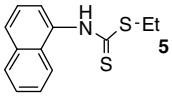
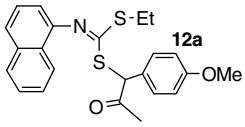
Having successfully achieved the first step in our strategy we then attempted to reduce the adduct **1a** using sodium borohydride in a methanolic medium. The carbonyl group of **1a** was reduced selectively without affecting the imine functionality. The reduced product[15] was isolated and characterised, however, it slowly cyclised to give the 1,3-oxathiolan-2-ylidene **1b** with concomitant liberation of odorous mercaptoethanol at room temperature. However, by performing the reduction of **1a** in methanolic KOH, the carbonyl reduction was faster and complete cyclisation was achieved by carrying out the reaction at 60 °C.[21] When the leaving group was changed from –SEt to –SMe or $-SCH_2Ph$ the reaction rate and yield were found to be similar. Keeping in mind the cost factors, and the ease of preparation and handling, we used –SEt as the leaving group for all the other substrates.

Table 1
S-Alkylation[a] of dithiocarbamic acid esters

Substrate	Product[b]	Yield[c] (%)
 **1**	 **1a**	82
 **2**	 **2a**	78
 **3**	 **3a**	94
 **4**	 **4a**	95
 **5**	 **5a**	81
 **6**	 **6a**	80
 **7**	 **7a**	86
 **8**	 **8a**	78

[a] Reactions were monitored by TLC.
[b] Confirmed by IR, ^{1}H and ^{13}C NMR.[22]
[c] Isolated yield.

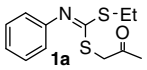
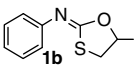
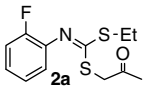
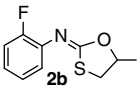
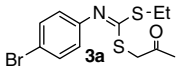
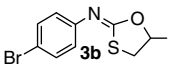
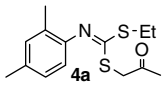
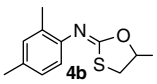
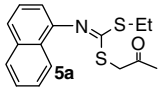
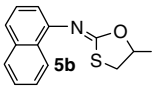
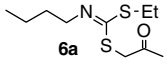
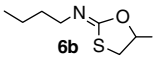
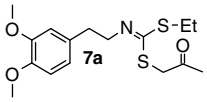
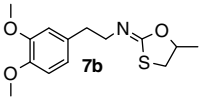
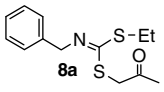
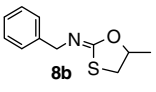
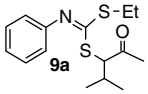
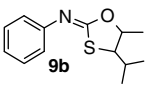
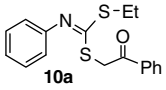
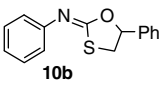
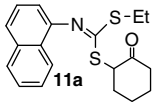
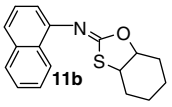
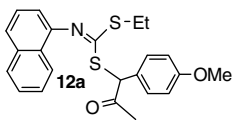
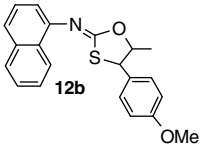
Table 2
S-Alkylation[a] of dithiocarbamic acid esters

Substrate	Product[b]	Yield[c] (%)
 **1**	 **9a**	75
 **1**	 **10a**	80
 **5**	 **11a**	75
 **5**	 **12a**	60

[a] Reactions were monitored by TLC.
[b] Confirmed by IR, ^{1}H and ^{13}C NMR.[22]
[c] Isolated yield.

The versatility of this synthetic method is demonstrated with substrates **1a**–**12a** as shown in Table 3. Although quantitative conversion was observed by GC and from the crude yield, the isolated product yield was much lower.

Table 3
Formation[a] of 1,3-oxathiolan-2-ylidene

Substrate	Product[b]	Time (h)	Yield[c] (%)
 **1a**	 **1b**	5	67
 **2a**	 **2b**	3	55
 **3a**	 **3b**	1	67
 **4a**	 **4b**	3	54
 **5a**	 **5b**	5	55
 **6a**	 **6b**	2	55
 **7a**	 **7b**	2	56
 **8a**	 **8b**	2	69
 **9a**	 **9b**	1	45
 **10a**	 **10b**	1	50
 **11a**	 **11b**	2	45
 **12a**	 **12b**	1	40

[a] Reactions were monitored by TLC.
[b] Confirmed by IR, ^{1}H and ^{13}C NMR.[22]
[c] Isolated yield.

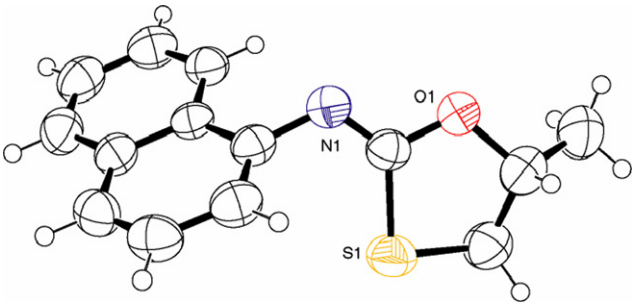


Fig. 1. ORTEP view of **5b** with the atom-numbering scheme.

Compared to the aryl systems **1a**–**5a**, the alkyl **6a**, veratryl **7a** and benzyl **8a** systems reacted faster. This observation is comparable to the cycloaddition of $PhCH_2NCS$ and PhNCS, where the latter is more reactive than the former towards cycloaddition with propylene oxide.[4] The presence of the 1,3-oxathiolan-2-ylidene skeleton is shown in the single crystal X-ray structure of **5b**,[16–19] Figure 1. The versatility of this methodology has been demonstrated successfully using ketones other than acetone as shown with substrates **9a**–**12a** giving the corresponding 1,3-oxathiolan-2-ylidenes **9b**–**12b** in moderate yields (Table 3). Products **1b**–**8b** and **10b** were obtained as racemic mixtures whereas products **9b**, **11b** and **12b** were obtained as diastereomeric mixtures.

In conclusion, this Letter reports an efficient method for the S-alkylation of dithiocarbamic acid esters with α-bromoketones under basic conditions. Subsequently, we developed an efficient synthetic method for the construction of 1,3-oxathiolan-2-ylidenes by reduction of the addition product of dithiocarbamic acid esters with α-bromoketones. This method is convenient in terms of simplicity and general applicability.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.02.103.

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15. *(Z)*-Ethyl 2-hydroxypropyl phenyldithioimidocarbonate: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27 (m, 6H), 3.04 (m, 4H), 3.20 (br s, 1H), 4.11 (br s, 1H), 6.86 (d, 2H, $J = 7.2$ Hz), 7.09 (t, 1H, $J = 7.6$ Hz), 7.30 (t, 2H, $J = 8.0$ Hz). IR (KBr): 3364, 3059, 2970, 2927, 2870, 1651, 1574, 1485, 1448, 1261, 1207, 1165, 1107, 1071, 946, 762, 695 cm^{-1}.
16. *Crystallographic description of* **5b**: Crystal dimensions (mm): $0.28 \times 0.20 \times 0.17$. $C_{14}H_{13}NOS$, $M_r = 243.31$. Monoclinic, space group $P2(1)/n$; $a = 7.8987(2)$ Å, $b = 14.0972(4)$ Å, $c = 11.5295(3)$ Å; $\alpha = 90.00°$, $\beta = 106.7410(10)°$, $\gamma = 90.00°$, $V = 1229.39(6)$ Å^3; $Z = 4$; $\rho_{cal} = 1.315$ mg/m^3; $\mu(mm^{-1}) = 0.245$; $F(000) = 512$; Reflections collected/unique = 3047/2281; refinement method = full-matrix least-squares on F^2; final R indices $[I > 2\sigma_I]$ $R1 = 0.0579$, $wR2 = 0.1306$, R indices (all data) $R1 = 0.0414$, $wR2 = 0.1155$; goodness of fit = 1.033. CCDC number for compound **5b** is CCDC 676901. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.
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20. *General procedure for S-alkylation: (Z)-Ethyl 2-oxopropyl phenyldithioimidocarbonate* (**1a**): 1,1′-(Ethane-1,2-diyl)dipyridinium bistribromide EDPBT (3 mmol) was added to acetone (5 mL) and the mixture stirred for 10 min, during this period the bromination of acetone was complete as judged from the disappearance of the orange colour of EDPBT and precipitating out of the spent reagent 1,1′-(ethane-1,2-diyl)dipyridinium dibromide (EDPDB). The supernatant containing the bromo ketone was then filtered into a solution of phenyldithiocarbamic acid ethyl ester **1** (5 mmol) in acetone (5 mL) and triethylamine (10 mmol) and was stirred at room temperature. The reaction was complete within 0.5 h as judged from the TLC. After completion of the reaction, the solvent was evaporated and ethyl acetate (20 mL) was added. The ethyl acetate layer was washed with a saturated solution of $NaHCO_3$, dried over anhydrous Na_2SO_4, concentrated under reduced pressure and purified over silica gel to give an 82% yield of (*Z*)-ethyl 2-oxopropyl phenyldithioimidocarbonate (**1a**).
21. *General procedure for the reductive cyclisation of (Z)-ethyl 2-oxopropyl phenyldithioimidocarbonate* (**1a**) *to rac-N*-[(2*Z*)-5-methyl-1,3-oxathiolan-2-ylidene]aniline (**1b**): To a solution of (*Z*)-ethyl 2-oxopropyl phenyldithioimidocarbonate (**1a**) (0.762 g, 3 mmol) in methanol (5 mL) was added KOH (0.168 g, 3 mmol) followed by portion-wise addition of sodium borohydride (0.057 g, 1.5 mmol) over a period of 5 min at 0 °C. After stirring for 0.5 h, the reaction mixture was heated at 60 °C for 5 h. The progress of the reaction was monitored by TLC. After completion of the reaction, methanol was evaporated and the product was extracted with ethyl acetate (2×25 mL). The organic layer was separated and dried over anhydrous sodium sulphate and concentrated. Further purification was accomplished by column chromatography over a short column of basic alumina using a mixture of hexane and ethyl acetate as eluent. The product, *rac-N*-[(2*Z*)-5-methyl-1,3-oxathiolan-2-ylidene]aniline (**1b**), was obtained in 67% yield.
22. *Spectral data of selected compounds*: (*Z*)-Ethyl 2-oxopropyl phenyldithioimidocarbonate **1a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (t, 3H,$J = 7.6$ Hz), 2.30 (s, 3H), 3.07 (q, 2H, $J = 7.6$ Hz), 3.90 (s, 2H), 6.83 (d, 2H, $J = 7.6$ Hz), 7.09 (m, 1H), 7.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.8, 26.6, 29.3, 42.0, 120.4, 124.3, 129.1, 149.3, 161.1, 202.3. IR (KBr): 3058, 2968, 2927, 1718, 1577, 1354, 1208, 1151, 943, 762, 695 cm^{-1}. HRMS (ESI), MH^+, found 254.3959, $C_{12}H_{16}NOS_2$ requires 254.3965. (*Z*)-Ethyl 2-oxopropyl 2-Fluorophenyldithioimidocarbonate **2a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (t, 3H, $J = 7.2$ Hz), 2.28 (s, 3H), 3.08 (q, 2H, $J = 7.2$ Hz), 3.91 (s, 2H), 6.84 (br s, 1H), 7.03 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.7, 26.8, 29.0, 41.9, 116.1, 122.4, 124.3, 125.4, 136.9, 151.5, 154.0, 163.7, 202.3. IR (KBr): 3061, 2971, 2930, 2873, 1715, 1574, 1485, 1451, 1355, 1239, 1151, 1102, 950, 850, 756, 727, 577 cm^{-1}. HRMS (ESI): MH^+, found 272.3865, $C_{12}H_{15}FNOS_2$ requires 272.3870. *rac-N*-[(2*Z*)-5-Methyl-1,3-oxathiolan-2-ylidene]aniline **1b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.54 (d, 3H, $J = 6.4$ Hz), 3.05 (app. t, 1H, $J = 9.2$ Hz), 3.36 (dd, 1H, $J_1 = 10.8$ Hz, $J_2 = 5.6$ Hz), 4.75 (m, 1H), 6.96 (d, 2H, $J = 7.2$ Hz), 7.10 (t, 1H, $J = 7.2$ Hz), 7.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.1, 37.7, 78.6, 121.3, 124.1, 129.0, 149.0, 163.6. IR (KBr): 3057, 3030, 2980, 2935, 2855, 1651, 1593, 1488, 1159, 1102, 1022, 949, 770, 697, 658, 593 cm^{-1}. HRMS (ESI): MH^+, found 194.2749, $C_{10}H_{12}NOS$ requires 194.2757. *rac*-2-Fluoro-*N*-[(2*Z*)-5-methyl-1,3-oxathiolan-2-ylidene]aniline **2b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.50 (d, 3H, $J = 6.0$ Hz), 3.05 (app. t, 1H, $J = 10.0$ Hz), 3.35 (dd, 1H, $J_1 = 10.8$ Hz, $J_2 = 5.6$ Hz), 4.76 (m, 1H), 6.94 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.3, 38.2, 79.8, 116.2, 116.4, 123.4, 124.5, 125.4, 136.9, 153.1, 155.5, 163.3. IR (KBr): 3033, 2977, 2927, 2869, 1651, 1488, 1453, 1242, 1161, 1097, 1024, 950, 836, 755, 653, 588 cm^{-1}. HRMS (ESI): MH^+, found 212.2667, $C_{10}H_{11}FNOS$ requires 212.2674.*rac*-4-Bromo-*N*-[(2*Z*)-5-methyl-1,3-oxathiolan-2-ylidene]aniline **3b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.55 (d, 3H, $J = 6.4$ Hz), 3.09 (app. t, 1H, $J = 10.0$ Hz), 3.41 (dd, 1H,

$J_1 = 10.8$ Hz, $J_2 = 5.6$ Hz), 4.77 (m, 1H), 6.85 (d, 2H, $J = 8.4$ Hz), 7.42 (d, 2H, $J = 8.4$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.3, 38.0, 79.1, 117.3, 123.3, 132.2, 148.2, 164.3. IR (KBr): 2991, 2935, 1680, 1634, 1486, 1388, 1250, 1163, 1096, 958, 835, 605 cm^{-1}. HRMS (ESI): MH^+, found 273.1665, $C_{10}H_{11}BrNOS$ requires 273.1670. *rac*-2,4-Dimethyl-*N*-[(2*Z*)-5-methyl-1,3-oxathiolan-2-ylidene]aniline **4b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.45 (d, 3H, $J = 6.0$ Hz), 2.17 (s, 3H), 2.29 (s, 3H), 3.05 (app. t, 1H, $J = 10.0$ Hz), 3.35 (dd, 1H, $J_1 = 10.9$ Hz, $J_2 = 5.2$ Hz), 4.75 (m, 1H), 6.75 (d, 1H, $J = 7.6$ Hz), 6.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.9, 19.3, 21.0, 37.9, 79.0, 120.4, 127.3, 130.0, 131.4, 133.9, 145.6, 163.2. IR (KBr): 2979, 2923, 2865, 1651, 1497, 1454, 1382, 1239, 1162, 1092, 1024, 951, 821, 634 cm^{-1}. HRMS (ESI): MH^+, found 222.3117, $C_{12}H_{16}NOS$ requires 222.3113. *rac*-*N*-[(2*Z*)-5-Methyl-1,3-oxathiolan-2-ylidene]naphthalene-1-amine **5b**: Crystalline solid, mp 87–89 °C ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.59 (d, 3H, $J = 6.0$ Hz), 3.05 (app. t, 1H, J = 10.0 Hz), 3.36 (dd, 1H, $J_1 = 10.8$ Hz, $J_2 = 6.0$ Hz), 4.83 (m, 1H), 7.00 (d, 1H, $J = 7.2$ Hz), 7.43 (m, 3H), 7.61 (d, 1H, $J = 8.4$ Hz), 7.81 (d, 1H, $J = 7.2$ Hz), 8.05 (d, 1H, $J = 8.0$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.5, 38.0, 79.3, 115.9, 123.9, 124.5, 125.7, 126.0, 126.4, 127.8, 128.0, 134.4, 146.0, 164.1. IR (KBr): 3016, 2926, 2861, 1657, 1496, 1451, 1402, 1095, 1050, 875, 824, 804, 687, 605 cm^{-1}. HRMS (ESI): MH^+, found 244.3302, $C_{14}H_{14}NOS$ requires 244.3307. *rac*-*N*-[(2*Z*)-5-Methyl-1,3-oxathiolan-2-ylidene] *n*-butylamine **6b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, 3H, $J = 7.2$ Hz), 1.33 (m, 2H), 1.43 (d, 3H, $J = 6.0$ Hz), 1.52 (m, 2H), 3.01–3.07 (m, 3H) 3.33 (dd, 1H, $J_1 = 10.8$ Hz, $J_2 = 5.2$ Hz),4.53 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 19.1, 20.4, 32.9, 37.6, 53.5, 79.9, 161.0. IR (KBr): 2950, 2935, 2873, 1680, 1542, 1460, 1383, 1168, 1076, 748, 636 cm^{-1}. HRMS (ESI): MH^+, found 174.2859, $C_8H_{16}NOS$ requires 174.2865. *rac*-2-(3,4-Dimethoxyphenyl)-*N*-[(2*Z*-5-methyl-1,3-oxathiolan-2-ylidene]ethanamine **7b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39 (d, 3H, $J = 6.4$ Hz), 2.78 (t, 2H, $J = 7.6$ Hz), 2.94 (app. t, 1H, $J = 9.6$ Hz), 3.28 (m, 3H), 3.78 (s, 3H), 3.80 (s, 3H), 4.57 (m, 1H), 6.71 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.3, 37.0, 37.8, 51.0, 55.8, 56.0, 77.6, 111.3, 112.3, 120.9, 132.9, 147.5, 148.8, 162.2. IR (KBr): 2935, 2832, 1696, 1675, 1516, 1460, 1271, 1020, 748 cm^{-1}. HRMS (ESI): MH^+, found 282.3821, $C_{14}H_{20}NO_3S$ requires 282.3829. *rac*-*N*-[(2*Z*)-5-methyl-1,3-oxathiolan-2-ylidene]phenylmethanamine **8b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.47 (d, 3H, $J = 6.0$ Hz), 3.05 (app. t, 1H, $J = 9.6$ Hz), 3.38 (dd, 1H, $J_1 = 10.8$ Hz, $J_2 = 5.6$ Hz), 4.35 (d, 2H, $J = 6.8$ Hz), 4.61 (m, 1H), 7.28 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.3, 38.0, 57.5, 80.5, 126.8, 127.7, 128.4, 139.7, 162.8. IR (KBr): 3027, 2978, 2931, 2869, 1663, 1452, 1352, 1156, 1122, 1089, 1051, 1022, 929, 735, 699, 641 cm^{-1}. HRMS (ESI): MH^+, found 208.3035, $C_{11}H_{14}NOS$ requires 208.3037. *rac*-*N*-[(2*Z*)-4-Isopropyl-5-methyl-1,3-oxathiolan-2-ylidene]aniline (diastereomeric mixture) **9b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (m, 6H), 1.40 (d, 3H, $J = 6.0$ Hz), 1.90 (m, 1H), 3.31 (m, 1H), 4.52 (m, 1H), 6.99 (m, 2H), 7.11 (t, 1H, $J = 7.2$ Hz), 7.32 (t, 2H,$J = 7.6$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.5, 20.0, 21.3, 31.3, 61.9, 80.9, 121.6, 124.2, 129.2, 149.5, 163.4. IR (KBr): 3054, 2963, 2868, 1651, 1595, 1544, 1447, 1315, 1229, 1110, 1064, 948, 769, 696, 642 cm^{-1}. HRMS (ESI): MH^+, found 236.3509, $C_{13}H_{18}NOS$ requires 236.3513. *rac*-*N*-[(2*Z*)-5-Phenyl-1,3-oxathiolan-2-ylidene]aniline **10b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.29 (app. t, 1H,$J = 10.8$ Hz), 3.53 (dd, 1H, $J_1 = 10.8$ Hz, $J_2 = 4.8$ Hz), 5.53 (app. t, 1H, $J = 6$ Hz), 6.81 (s, 2H), 6.94-6.99 (m, 3H), 7.16–7.57 (m, 5H).^{13}C NMR (100 MHz, $CDCl_3$): δ 38.7, 83.4, 118.9, 121.6, 123.7, 126.1, 128.9, 129.5, 138.1, 154.3, 163.9. IR (KBr): 3054, 2950, 1648, 1604, 1541, 1497, 1445, 1314, 1229, 1067, 754, 694 cm^{-1}. HRMS (ESI): MH^+, found 254.3466, $C_{15}H_{14}NOS$ requires 256.3477. *rac*-*N*-[(2*Z*)-Hexahydro-1,3-benzoxathiol-2-ylidene]naphthalene-1-amine (diastereomeric mixture) **11b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12–1.55 (m, 4H), 1.79 (m, 2H), 2.30 (m, 2H), 3.39 (m, 1H), 4.56 (m, 1H), 6.91 (m, 1H), 7.20–7.84 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.1, 20.4, 23.6, 28.0, 47.1, 81.5, 115.8, 121.0, 123.5, 124.6, 126.7, 128.1, 128.6, 128.8, 134.3, 145.9, 164.4. IR (KBr): 3054, 2937, 2859, 1650, 1574, 1536, 1504, 1393, 1358, 1259, 1184, 1114, 1013, 964, 907, 774, 729, 642 cm^{-1}. HRMS (ESI): MH^+, found 284.4013, $C_{17}H_{18}NOS$ requires 284.4013. *rac*-*N*-[{2*Z*}-4-(4-Methoxyphenyl)-5-methyl-1,3-oxathiolan-2-ylidene] naphthalene-1-amine (diastereomeric mixture) **12b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (m, 3H), 3.62 (s, 3H), 4.46 (d, 1H, $J = 5.6$ Hz), 4.86 (m, 1H), 6.71 (t, 2H, $J = 8.4$), 7.00 (m, 2H), 7.13 (m, 1H), 7.30 (m, 1H), 7.38 (m, 2H), 7.50 (d, 1H, $J = 8.4$ Hz), 7.70 (m, 1H), 8.07 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.5, 54.8, 55.5, 82.5, 114.2, 115.9, 123.8, 124.6, 125.7, 126.0, 126.4, 128.3, 128.4, 128.9, 129.6, 134.4, 145.9, 159.8, 164.2. IR (KBr): 3056, 2961, 2836, 1651, 1574, 1512, 1462, 1393, 1304, 1248, 1179, 1073, 1032, 943, 802, 777, 734, 654 cm^{-1}. HRMS (ESI): MH^+, found 350.4549, $C_{21}H_{20}NO_2S$ requires 350.4545.