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ORIGINAL PAPER

Regioselective synthesis of 1,3-oxathiolane-2-imine derivatives

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Abstract An efficient one-pot synthesis of functionalized 1,3-oxathiolane-2-imine derivatives via the reaction of aryl isothiocyanates and oxiranes is developed. This catalytic procedure takes place in the presence of MeONa in THF at 25 °C in good to excellent yields.

Keywords Heterocycles · Oxirane · Methoxide · Aryl isothiocyanate · One-pot synthesis

Introduction

Within the last decades, many transformations of oxiranes have been well developed, and the ring-opening reactions are among the most studied. Most of the ring-opening methods proceeded in the presence of Lewis acids, Lewis bases, Bronsted acids, thioxanthenone-fused azacrown ethers, Schiff base, and porphyrin complexes [1–11]. These smallest of heterocyclic compounds exhibit a synthetically very useful utility in the synthesis of other oxygen-containing heterocyclic compounds [12], 1,2-amino alcohols [13, 14], and alcohols [15]. In many cases, the regioselectivity has been found to be sensitive to the operating opening reactions [16–18], and the methods are limited to the oxiranes bearing a chelate-forming substituent.

1,3-Oxathiolane-2-imine derivatives are highly valuable intermediates in organic synthesis and have been used as core structures for the development of herbicidal agents. The earlier attempts at the synthesis of 1,3-oxathiolane-2-imine derivatives suffered from low yields, harsh conditions, and formation of by-products [19, 20].

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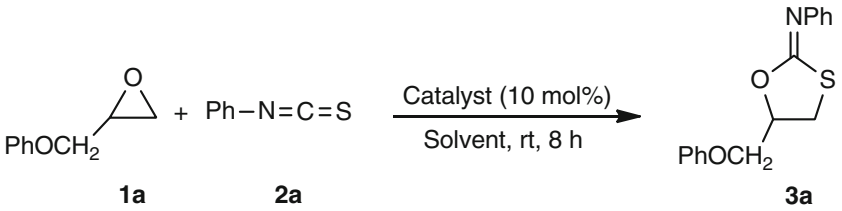
Results and discussion

Herein, we describe an efficient one-pot method for the synthesis of 1,3-oxathiolan-2-imine derivatives **3** from the reaction of oxiranes **1** and aryl isothiocyanates **2** in the presence of a catalytic amount of methoxide at room temperature in acceptable yields.

2-(Phenoxymethyl)oxirane (**1a**) and phenylisothiocyanate (**2a**) were selected as prototypical reaction partners for alkoxide catalyzed one-pot reaction. To explore the optimum reaction conditions, the effects of catalyst and solvent were considered. The solvent had a great impact on the reaction. No product was obtained when the reaction was carried out in MeOH using methoxide as a catalyst (Table 1, entry 10). DMF was found to be unsuccessful for the transformation, too (Table 1, entry 8). Changing the solvent to hexane afforded **3a** in 53 % yield (Table 1, entry 9). The yield of **3a** increased dramatically to 76 and 90 % when CH_2Cl_2 and THF were the solvents, respectively (Table 1, entries 6, 1). Different catalysts were also tested, but MeONa proved to be most effective (Table 1, entry 1). Although *t*-BuONa completely inhibited the reaction, **3a** was achieved in 71 and 41 % yield in the presence of EtONa and *i*-PrONa as catalyst, respectively (Table 1, entries 2, 3). The yield of **3a** remained almost the same upon increasing the catalyst loading to 20 mol% (Table 1, entry 12), but reducing the loading of the catalyst to 5 mol% adversely affected the yield of product (Table 1, entry 13). My investigations for the reaction condition optimization demonstrated that **1a** (1 mmol), **2a** (1 mmol), NaH (10 mol%), and MeOH (1 mmol) in 3 cm^3 THF at

Table 1 Optimization of reaction conditions



1a **2a** **3a**

Entry	Catalyst	Solvent	Yield/%
1	MeONa	THF	90
2	EtONa	THF	71
3	*i*-PrONa	THF	41
4	*t*-BuONa	THF	Trace
5	DMAP	THF	23
6	MeONa	CH_2Cl_2	76
7	MeONa	MeCN	41
8	MeONa	DMF	14
9	MeONa	Hexane	53
10	MeONa	MeOH	–
11	MeONa	Toluene	43
12	MeONa[a]	THF	91
13	MeONa[b]	THF	42

[a] 20 mol% of catalyst was used

[b] 5 mol% of catalyst was used

25 °C for 8 h provided an improved reaction condition for this transformation, and the desired product was achieved in excellent yield.

With the optimized reaction condition in hand, the generality of this transformation was explored, and the results are summarized in Scheme 1. Good yields were obtained from the reaction of oxiranes **1a**, **1e**, and **1f**. The polar effect of the C–O bond bound to the three-membered rings probably increases the electrophilicity of the oxiranes (Scheme 1). Excellent yields were obtained from the reaction of oxirane **1f** derived from cyclohexene and aryl isothiocyanates. In alkyl-substituted oxiranes, only the products formed by the attack of the S-atom of ArNCS at the terminal carbon were detected by ^{1}H NMR. For the phenyl-substituted oxiranes, terminal- and benzylic-attacked products were formed in a ratio of 4:1 caused by the interference of electronic and steric effects (Scheme 1). Structures of compounds **3a**–**3r** were assigned by IR, ^{1}H NMR, ^{13}C NMR, and mass spectral data. Due to the presence of a stereogenic center, the ^{1}H NMR spectrum of **3a** exhibited three multiplets at 3.50–3.59, 4.24–4.35, and 5.01–5.05 ppm arising from two CH_2 and CH protons, respectively. The ^{13}C NMR spectrum of **3a** shows 16 signals, in agreement with the proposed structure. The mass spectrum of **3a** displayed the molecular ion peak at $m/z = 285$.

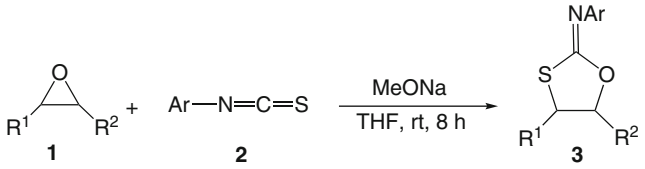
Mechanistically, it is conceivable that the reaction involves the initial formation of anionic adduct **4** from the reaction of methoxide and aryl isothiocyanate. This anionic adduct reacts with oxirane to produce ring-opened intermediate **5**. Ring closure of this intermediate affords **6**, and finally, elimination of methoxide completes the catalytic cycle and gives **3** (Scheme 2). In both oxirane and aryl isothiocyanate derivatives, electron-poor substrates react more efficiently than electron-rich substrates in accordance with the proposed reaction mechanism.

In conclusion, we have described a convenient and efficient one-pot method for the regioselective synthesis of 1,3-oxathiolane-2-imine derivatives. It should be noted that several functional groups such as methyl methacrylate, alkoxy, phenoxy, and cyano could be well tolerated. Further studies are being conducted to develop catalytic cyclization in the presence of aziridine and heterocumulenes.

Experimental

Oxiranes, aryl isothiocyanate derivatives, alcohols, and NaH were obtained from Merck and were used without further purification. Melting points were measured on an

Scheme 1

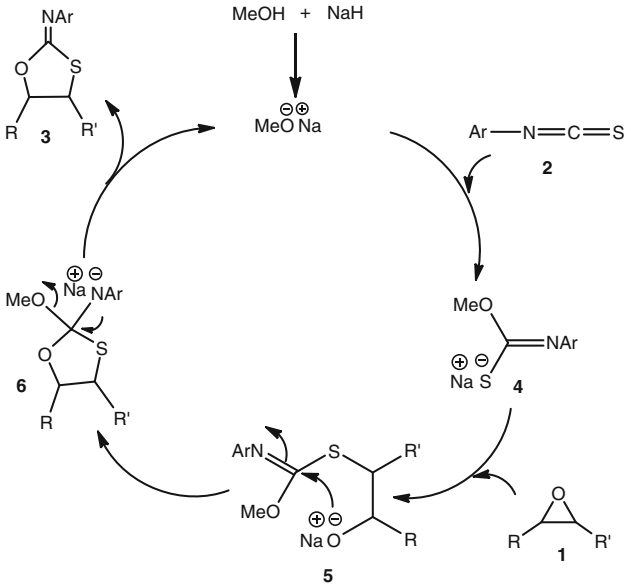


	R^1	R^2
1a	$PhOCH_2$	H
1b	CH_3	H
1c	$(CH_3)_2CHOCH_2$	H
1d	$CH_3CH_2CH_2$	H
1e	$CH_3C(CH_2)COOCH_2$	H
1f	$R^1,R^2 = -(CH_2)_4-$	
1g	Ph	H
1h	4-MeO-C_6H_4	H
1i	4-CN-C_6H_4	H

	Ar
2a	Ph
2b	4-Me-C_6H_4
2c	4-MeO-C_6H_4

	R^1	R^2	Ar
3a	$PhOCH_2$	H	Ph
3b	$PhOCH_2$	H	4-Me-C_6H_4
3c	$PhOCH_2$	H	4-MeO-C_6H_4
3d	CH_3	H	Ph
3e	CH_3	H	4-Me-C_6H_4
3f	CH_3	H	4-MeO-C_6H
3g	$(CH_3)_2CHOCH_2$	H	Ph
3h	$(CH_3)_2CHOCH_2$	H	4-Me-C_6H_4
3i	$(CH_3)_2CHOCH_2$	H	4-MeO-C_6H
3j	$CH_3CH_2CH_2$	H	4-Me-C_6H_4
3k	$CH_3CH_2CH_2$	H	4-MeO-C_6H
3l	$CH_3C(CH_2)COOCH_2$	H	Ph
3m	$CH_3C(CH_2)COOCH_2$	H	4-Me-C_6H_4
3n	R^1, $R^2 = -(CH_2)_4-$		Ph
3o	R^1, $R^2 = -(CH_2)_4-$		4-Me-C_6H_4
3p	Ph	H	Ph
3q	4-MeO-C_6H_4	H	Ph
3r	4-CN-C_6H_4	H	Ph

Scheme 2



Electrothermal-9100 apparatus. IR Spectra: Shimadzu IR-460 spectrometer. ^1H and ^{13}C NMR spectra: Bruker DRX-500 AVANCE instrument in $CDCl_3$ at 500.1 and 125.7 MHz, respectively, δ in ppm, J in Hz. EIMS (70 eV): Finnigan-MAT-8430 mass spectrometer. Elemental analyses (C, H, N) were performed with a Heraeus CHN–O-Rapid analyzer. The results agreed favorably with the calculated values.

General procedure for the preparation of compounds ***3***

To a stirred solution of MeOH (1 mmol) in 3 cm^3 THF as a solvent were added NaH (10 mol%) and aryl isothiocyanate (1 mmol); the mixture was stirred for 15 min at 0 °C. After addition of oxirane (1 mmol) at room temperature, the reaction mixture was stirred for 8 h. After completion of the reaction (monitored by TLC), the solvent was removed under reduced pressure, and the residue was purified by column chromatography (SiO_2; hexane/AcOEt) to afford pure title compounds.

N-[4-(Phenoxymethyl)-1,3-oxathiolan-2-ylidene]benzenamine(**3a**, $C_{16}H_{15}NO_2S$)

The crude product was purified by column chromatography (SiO_2, hexane/EtOAc 8/1, $R_f = 0.39$) affording 0.26 g (90 %) **3a**. M.p.: 118–120 °C; IR (KBr): $\bar{\nu}$ = 3,017, 2,987, 1,629, 1,559, 1,309, 1,148 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 3.50–3.59$ (m, CH_2), 4.24–4.35 (m, CH_2), 5.01–5.05 (m, CH), 6.91 (d, $^3J = 8.2$ Hz, 2CH), 6.96 (d, $^3J = 8.3$ Hz, 2CH), 7.02 (t, $^3J = 7.3$ Hz, CH), 7.16–7.33 (m, 5CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 36.1$ (CH_2), 60.9 (CH_2), 78.9 (CH), 114.6 (2CH), 121.2 (CH),

121.7 (CH), 124.4 (2CH), 129.1 (2CH), 129.6 (2CH), 148.9 (C), 158.0 (C), 161.9 (C) ppm; EI-MS (70 eV): *m/z* (%) = 285 (M^+, 3), 152 (25), 133 (34), 119 (86), 93 (78), 77 (100), 43 (44), 34 (18).

4-Methyl-N-[4-(phenoxymethyl)-1,3-oxathiolan-2-ylidene]benzenamine (**3b**, $C_{17}H_{17}NO_2S$)

The crude product was purified by column chromatography (SiO_2, hexane/EtOAc 8/1, $R_f = 0.32$) affording 0.26 g (86 %) **3b**. M.p.: 127–129 °C; IR (KBr): $\bar{\nu}$ = 3,014, 2,965, 1,621, 1,568, 1,334, 1,142 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.36 (s, Me), 3.49–3.58 (m, CH_2), 4.35–4.48 (m, CH_2), 4.99–5.04 (m, CH), 6.91 (d, ^3J = 8.2 Hz, 2CH), 6.96 (d, ^3J = 8.3 Hz, 2CH), 7.02 (t, ^3J = 7.3 Hz, CH), 7.16 (d, ^3J = 8.2 Hz, 2CH), 7.33 (t, ^3J = 7.9 Hz, 2CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 20.9 (Me), 36.5 (CH_2), 58.9 (CH_2), 77.9 (CH), 114.7 (2CH), 121.0 (CH), 121.7 (2CH), 129.6 (2CH), 129.7 (2CH), 133.9 (C), 146.4 (C), 158.1 (C), 162.6 (C) ppm; EI-MS (70 eV): *m/z* (%) = 299 (M^+, 2), 165 (29), 133 (41), 131 (78), 93 (100), 91 (55), 43 (47), 34 (20).

4-Methoxy-N-[4-(phenoxymethyl)-1,3-oxathiolan-2-ylidene]benzenamine (**3c**, $C_{17}H_{17}NO_3S$)

The crude product was purified by column chromatography (SiO_2, hexane/EtOAc 8/1, $R_f = 0.28$) affording 0.25 g (80 %) **3c**. M.p.: 133–135 °C; IR (KBr): $\bar{\nu}$ = 3,019, 2,967, 1,650, 1,542, 1,314, 1,124 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 3.42–3.55 (m, CH_2), 3.73 (s, OMe), 4.25–4.34 (m, CH_2), 4.91–5.00 (m, CH), 6.77–7.28 (m, 9CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 37.7 (CH_2), 55.4(OMe), 62.9 (CH_2), 77.6 (CH), 114.7 (2CH), 115.3 (2CH), 121.0 (CH), 123.7 (2CH), 129.6 (2CH), 141.3 (C), 156.4 (C), 159.1 (C), 160.1 (C) ppm; EI-MS (70 eV): *m/z* (%) = 315 (M^+, 6), 182 (34), 149 (78), 133 (57), 107 (40), 93 (100), 43 (40), 34 (21).

N-(4-Methyl-1,3-oxathiolan-2-ylidene)benzenamine (**3d**, $C_{10}H_{11}NOS$)

The crude product was purified by column chromatography (SiO_2, hexane/EtOAc 8/1, $R_f = 0.59$) affording 0.16 g (81 %) **3d**. M.p.: 75–77 °C; IR (KBr): $\bar{\nu}$ = 3,011, 2,988, 1,641, 1,556, 1,325, 1,114 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.45 (d, ^3J = 6.5 Hz, Me), 3.30–3.38 (m, CH_2), 4.75–4.84 (m, CH), 7.06 (d, ^3J = 7.8 Hz, 2 CH), 7.11–7.25 (m, 3CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 20.3 (Me), 38.4 (CH_2), 70.3 (CH), 117.1 (2 CH), 120.1 (CH), 125.7 (2 CH), 141.6 (C), 160.1 (C) ppm; EI-MS (70 eV): *m/z* (%) = 193 (M^+, 1), 136 (81), 77 (100), 59 (53), 57 (78), 41 (31), 18 (22).

4-Methyl-N-(4-methyl-1,3-oxathiolan-2-ylidene)benzenamine (**3e**, $C_{11}H_{13}NOS$)

The crude product was purified by column chromatography (SiO_2, hexane/EtOAc 8/1, $R_f = 0.50$) affording 0.16 g (78 %) **3e**. M.p.: 80–82 °C; IR (KBr): $\bar{\nu}$ = 3,023, 2,956, 1,633, 1,593, 1,314, 1,121 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$)): δ = 1.40 (d, ^3J = 6.5 Hz, Me), 1.52 (s, Me), 3.34–3.40 (m, CH_2), 4.69–4.81 (m, CH), 7.00 (d, ^3J = 6.5 Hz, 2 CH), 7.14 (d, ^3J = 7.1 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 21.3 (Me), 24.5 (Me), 39.4 (CH_2), 68.1 (CH), 120.1 (2 CH), 128.7 (2 CH), 136.1 (C), 144.6 (C), 159.3 (C) ppm; EI-MS (70 eV): *m/z* (%) = 207 (M^+, 1), 150 (100), 91 (76), 59 (51), 57 (75), 54 (60), 40 (44), 18 (15).

4-Methoxy-N-(4-methyl-1,3-oxathiolan-2-ylidene)benzenamine(**3f**, $C_{11}H_{13}NO_2S$)

The crude product was purified by column chromatography (SiO_2, hexane/EtOAc 8/1, $R_f = 0.44$) affording 0.16 g (73 %) **3f**. M.p.: 87–90 °C; IR (KBr): $\bar{\nu}$ = 3,012, 2,965, 1,632, 1,576, 1,326, 1,108 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.52 (d, ^3J = 6.2 Hz, Me), 3.46–3.59 (m, CH_2), 3.65 (s, OMe), 4.67–4.79 (m, CH), 6.76 (d, ^3J = 6.9 Hz, 2 CH), 7.27 (d, ^3J = 7.1 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 21.3 (Me), 38.9 (CH_2), 55.6 (OMe), 67.5 (CH), 115.1 (2 CH), 124.6 (2 CH), 141.6 (C), 158.2 (C), 160.3 (C) ppm; EI-MS (70 eV): *m/z* (%) = 223 (M^+, 6), 165 (100), 107 (74), 59 (63), 57 (78), 54 (36), 40 (40), 18 (13).

N-[4-(Isopropoxymethyl)-1,3-oxathiolan-2-ylidene]benzenamine(**3g**, $C_{13}H_{17}NO_2S$)

The crude product was purified by column chromatography (SiO_2, hexane/EtOAc 8/1, $R_f = 0.64$) affording 0.22 g (88 %) **3g**. M.p.: 93–95 °C; IR (KBr): $\bar{\nu}$ = 3,015, 2,988, 1,643, 1,571, 1,321, 1,122 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ = 1.14 (d, ^3J = 6.1 Hz, 2Me), 3.53–3.62 (m, CH_2), 3.83–3.92 (m, CH), 4.11–4.14 (m, CH_2), 4.72–4.79 (m, CH), 7.03 (d, ^3J = 6.9 Hz, 2 CH), 7.10–7.21 (m, 3CH) ppm;^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 21.0 (2Me), 38.3 (CH_2), 63.4 (CH), 69.9 (CH_2), 74.3 (CH), 122.2 (2 CH), 127.6 (CH), 130.3 (2 CH), 149.3 (C), 163.7 (C) ppm; EI-MS (70 eV): *m/z* (%) = 251 (M^+, 5), 192 (58), 135 (85), 116 (44), 77 (100), 59 (67), 57 (51), 54 (32).

N-[4-(Isopropoxymethyl)-1,3-oxathiolan-2-ylidene]-4-methylbenzenamine (**3h**, $C_{14}H_{19}NO_2S$)

The crude product was purified by column chromatography (SiO_2, hexane/EtOAc 8/1, $R_f = 0.57$) affording 0.23 g (85 %) **3h**. M.p.: 101–103 °C; IR (KBr): $\bar{\nu}$ = 3,031, 2,973, 1,652, 1,577, 1,341, 1,142 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ = 1.15 (d, ^3J = 6.7 Hz, 2Me), 2.33 (s, Me), 3.41–3.48 (m, CH_2), 3.79–4.08 (m, 3CH), 4.71–4.83 (m, CH), 7.06 (d, ^3J = 7.8 Hz, 2 CH), 7.25 (d, ^3J = 7.6 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 21.9 (Me), 23.1 (2Me), 37.4 (CH_2), 64.2 (CH), 70.7 (CH_2), 73.3 (CH), 122.3 (2 CH), 129.7 (2 CH), 135.6 (C), 144.5 (C), 160.0

(C) ppm; EI-MS (70 eV): *m/z* (%) = 265 (M^+, 7), 206 (51), 149 (68), 116 (100), 91 (70), 59 (56), 57 (42), 54 (28).

N-[4-(Isopropoxymethyl)-1,3-oxathiolan-2-ylidene]-4-methoxybenzenamine (**3i**, $C_{14}H_{19}NO_3S$)

The crude product was purified by column chromatography (SiO_2, hexane/EtOAc 8/1, $R_f = 0.50$) affording 0.23 g (81 %) **3i**. M.p.: 107–109 °C; IR (KBr): $\bar{\nu}$ = 3,009, 2,967, 1,631, 1,590, 1,311, 1,130 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): $\delta = 1.17$ (d, $^3J = 6.5$ Hz, 2Me), 3.42–3.50 (m, CH_2), 3.74–3.78 (m, CH_2), 3.79 (s, OMe), 3.82–3.85 (m, CH), 4.61–4.67 (m, CH), 6.84 (d, $^3J = 7.1$ Hz, 2 CH), 6.91 (d, $^3J = 7.3$ Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 22.0$ (2Me), 36.5 (CH_2), 55.4 (OMe), 62.3 (CH), 70.3 (CH_2), 73.2 (CH), 115.3 (2 CH), 123.3 (2 CH), 141.3 (C), 157.5 (C), 159.3 (C) ppm; EI-MS (70 eV): *m/z* (%) = 281 (M^+, 5), 222 (51), 165 (100), 116 (63), 107 (75), 59 (58), 54 (27).

4-Methyl-N-(4-propyl-1,3-oxathiolan-2-ylidene)benzenamine(**3j**, $C_{13}H_{17}NOS$)

The crude product was purified by column chromatography (SiO_2, hexane/EtOAc 8/1, $R_f = 0.65$) affording 0.19 g (80 %) **3j**. M.p.: 94–96 °C; IR (KBr): $\bar{\nu}$ = 3,020, 2,964, 1,645, 1,579, 1,313, 1,121 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): $\delta = 1.07$ (t, $^3J = 7.4$ Hz, Me), 1.37–1.69 (m, $2CH_2$), 2.32 (s, Me), 3.47–3.55 (m, CH_2), 4.62–4.76 (m, CH), 7.10 (d, $^3J = 6.9$ Hz, 2 CH), 7.32 (d, $^3J = 7.4$ Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 13.9$ (Me), 17.6 (CH_2), 23.9 (Me), 27.8 (CH_2), 36.8 (CH_2), 67.5 (CH), 122.7 (2 CH), 130.4 (2 CH), 134.5 (C), 147.4 (C), 162.1 (C) ppm; EI-MS (70 eV): *m/z* (%) = 235 (M^+, 7), 202 (58), 149 (100), 91 (64), 86 (71), 59 (60), 57 (43), 54 (26).

4-Methoxy-N-(4-propyl-1,3-oxathiolan-2-ylidene)benzenamine (**3k**, $C_{13}H_{17}NO_2S$)

The crude product was purified by column chromatography (SiO_2, hexane/EtOAc 8/1, $R_f = 0.58$) affording 0.20 g (78 %) **3k**. M.p.: 109–111 °C; IR (KBr): $\bar{\nu}$ = 3,025, 2,977, 1,631, 1,569, 1,341, 1,122 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): $\delta = 1.11$ (t, $^3J = 7.0$ Hz, Me), 1.35–1.62 (m, $2CH_2$), 3.32–3.50 (m, CH_2), 3.65 (s, OMe), 4.61–4.70 (m, CH), 6.81 (d, $^3J = 6.3$ Hz, 2 CH), 7.20 (d, $^3J = 6.9$ Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 14.5$ (Me), 16.3 (CH_2), 28.2 (CH_2), 35.2 (CH_2), 55.4 (OMe), 64.8 (CH), 115.7 (2 CH), 123.4 (2 CH), 140.5 (C), 158.4 (C), 160.1 (C) ppm; EI-MS (70 eV): *m/z* (%) = 251 (M^+, 5), 218 (42), 165 (100), 107 (40), 86 (78), 59 (60), 57 (54), 54 (26).

[2-(Phenylimino)-1,3-oxathiolan-4-yl]methyl methacrylate (**3l**, $C_{14}H_{15}NO_3S$)

The crude product was purified by column chromatography (SiO_2, hexane/EtOAc 8/1, $R_f = 0.33$) affording 0.25 g (91 %) **3l**. M.p.: 110–112 °C; IR (KBr): $\bar{\nu}$ = 3,011, 2,967, 1,731, 1,633, 1,577, 1,345, 1,122 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): $\delta = 1.90$ (s, Me), 3.46–3.55 (m, CH_2), 4.50–4.63 (m, CH_2), 4.91–5.00 (m, CH), 5.64 (m, CH), 6.17 (m, CH), 7.02 (t, $^3J = 7.3$ Hz, CH), 7.16 (d, $^3J = 8.2$ Hz, 2 CH), 7.33 (t, $^3J = 7.9$ Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 18.0$ (Me), 35.3 (CH_2),65.9(CH_2), 76.0 (CH), 122.3 (2 CH), 125.1 (CH_2), 127.3 (CH), 130.1 (2 CH), 137.1 (C), 148.1 (C), 162.2 (C), 168.5 (C) ppm; EI-MS (70 eV): *m/z* (%) = 251 (M^+, 5), 222 (78), 142 (76), 135 (80), 85 (65), 77 (100), 59 (51), 54 (32).

[2-(4-Methylphenylimino)-1,3-oxathiolan-4-yl]methyl methacrylate (**3m**, $C_{15}H_{17}NO_3S$)

The crude product was purified by column chromatography (SiO_2, hexane/EtOAc 8/1, $R_f = 0.30$) affording 0.25 g (87 %) **3m**. M.p.:121–123 °C; IR (KBr): $\bar{\nu}$ = 3,010, 2,977, 1,734, 1,644, 1,573, 1,340, 1,143 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): $\delta = 1.93$ (s, Me), 2.35(s, Me), 3.42–3.63 (m, CH_2), 4.53–4.58 (m, CH_2), 4.85–4.92 (m, CH), 5.60 (m, CH), 6.14 (m, CH), 7.16 (d, $^3J = 7.3$ Hz, 2 CH), 7.33 (d, $^3J = 6.9$ Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 18.2$ (Me), 24.3 (Me), 35.7 (CH_2),65.1(CH_2), 75.2 (CH), 123.1 (2 CH), 124.7(CH_2), 130.1(2 CH), 136.1 (C), 139.1 (C), 149.0 (C), 163.0 (C), 167.2 (C) ppm; EI-MS (70 eV): *m/z* (%) = 251 (M^+, 5), 206 (51), 149 (100), 142 (67), 91 (72), 59 (60), 57 (56), 54 (27).

N-(Hexahydrobenzo[d][1,3]oxathiol-2-ylidene)benzenamine (**3n**, $C_{13}H_{15}NOS$)

The crude product was purified by column chromatography (SiO_2, hexane/EtOAc 8/1, $R_f = 0.69$) affording 0.22 g (93 %) **3n**. M.p.: 168–170 °C; IR (KBr): $\bar{\nu}$ = 3,011, 2,968, 1,629, 1,573, 1,341, 1,119 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ = 1.39–2.14 (m, 8H), 2.56–2.63 (m, CH), 3.54–3.71 (m, CH), 7.13 (t, $^3J = 7.1$ Hz, CH), 7.20 (d, $^3J = 8.2$ Hz, 2 CH), 7.33 (t, $^3J = 7.9$ Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 21.4$ (CH_2), 24.7 (CH_2), 28.2 (CH_2), 35.5 (CH_2), 44.4 (CH), 80.1 (CH), 122.2 (2 CH), 127.6 (CH), 130.4 (2 CH), 147.4 (C), 164.6 (C) ppm; EI-MS (70 eV): *m/z* (%) = 233 (M^+, 4), 135 (100), 98 (67), 77 (85), 70 (54), 59 (60), 54 (20).

N-(Hexahydrobenzo[d][1,3]oxathiol-2-ylidene)-4-methylbenzenamine (**3o**, $C_{14}H_{17}NOS$)

The crude product was purified by column chromatography (SiO_2, hexane/EtOAc 8/1, $R_f = 0.61$) affording 0.22 g (90 %) **3o**. M.p.: 182–184 °C; IR (KBr): $\bar{\nu}$ = 3,028, 2,976, 1,633, 1,565, 1,323, 1,109 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ = 1.44–2.11 (m, 8H), 2.35 (s, Me), 2.64–2.68 (m, CH), 3.63–3.70 (m, CH), 7.14 (d, $^3J = 7.0$ Hz, 2 CH), 7.33 (d, $^3J = 7.2$ Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 21.4$ (CH_2), 23.4 (Me), 24.7 (CH_2),28.2

(CH_2), 30.5 (CH_2), 43.7 (CH), 81.1 (CH), 123.4 (2 CH), 130.1 (2 CH), 136.9 (C), 146.0 (C), 163.0 (C) ppm; EI-MS (70 eV): *m/z* (%) = 247 (M^+, 5), 149 (100), 98 (75), 91 (63), 71 (55), 59 (48), 54 (26).

N-(4-Phenyl-1,3-oxathiolan-2-ylidene)benzenamine (**3p**, $C_{15}H_{13}NOS$)

The crude product was purified by column chromatography (SiO_2, hexane/EtOAc7/1, $R_f = 0.34$) affording 0.20 g (77 %) **3p**. M.p.: 108–110 °C; IR (KBr): $\bar{\nu} = 3{,}051$, 2,917, 1,631, 1,540, 1,312, 1,123 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 3.21$–3.44 (m, CH_2), 4.79–4.83 (dd, $^2J = 10.3$ Hz, $^3J = 5.7$ Hz, CH), 7.13 (t, $^3J = 7.1$ Hz, CH), 7.20 (d, $^3J = 8.2$ Hz, 2 CH), 7.33–7.61 (m, 7CH) ppm;^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 37.1$ (CH_2), 79.3 (CH), 121.6 (2 CH), 126.4 (2 CH), 127.2 (CH), 128.0 (CH), 129.5 (2 CH), 130.9 (2 CH), 137.2 (C), 148.7 (C), 162.2 (C) ppm; EI-MS (70 eV): *m/z* (%) = 255 (M^+, 2), 137 (41), 135 (74), 121 (53), 119 (86), 77 (100), 43 (34).

N-[4-(4-Methoxyphenyl)-1,3-oxathiolan-2-ylidene]benzenamine (**3q**, $C_{16}H_{15}NO_2S$)

The crude product was purified by column chromatography (SiO_2, hexane/EtOAc7/1, $R_f = 0.24$) affording 0.20 g (72 %) **3q**. M.p.: 125–127 °C; IR (KBr): $\bar{\nu} = 3{,}037$, 2,922, 1,632, 1,546, 1,324, 1,136 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 3.23$–3.45 (m, CH_2), 3.65 (s, OMe), 4.72 (dd, $^2J = 9.6$ Hz, $^3J = 5.2$ Hz, CH), 6.75 (d, $^3J = 7.5$ Hz, 2 CH), 7.02 (d, $^3J = 7.5$ Hz, 2 CH), 7.10 (d, $^3J = 7.5$ Hz, 2 CH), 7.14–7.28 (m, 3CH) ppm;^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 37.3$ (CH_2), 55.4 (OMe), 76.4 (CH), 114.0 (2 CH), 122.3 (2 CH), 127.5 (CH), 128.2 (2 CH), 130.4 (2 CH), 134.1 (C), 148.4 (C), 159.3 (C), 162.5 (C) ppm; EI-MS (70 eV): *m/z* (%) = 285 (M^+, 5), 167 (28), 151 (34), 135 (72), 119 (80), 107 (54), 77 (100), 43 (40).

4-[2-(Phenylimino)-1,3-oxathiolan-4-yl]benzonitrile (**3r**, $C_{16}H_{12}N_2OS$)

The crude product was purified by column chromatography (SiO_2, hexane/EtOAc5/1, $R_f = 0.32$) affording 0.22 g (80 %) **3r**. M.p.: 146–149 °C; IR (KBr): $\bar{\nu} = 3{,}041$, 2,938, 2,231, 1,634, 1,547, 1,318, 1,134 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 3.27$–3.50 (m, CH_2), 4.89 (dd, $^2J = 10.1$ Hz, $^3J = 5.6$ Hz, CH), 7.12 (d, $^3J = 7.0$ Hz, 2 CH), 7.15–7.28 (m, 3CH), 7.38 (d, $^3J = 8.1$ Hz, 2 CH), 7.52 (d, $^3J = 8.1$ Hz, 2 CH) ppm;^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 38.3$ (CH_2), 80.3 (CH), 112.5 (C), 116.2 (CN), 122.2 (2 CH), 127.5 (CH), 128.2 (2 CH), 130.1 (2 CH), 133.3 (2 CH), 145.1 (C), 148.4 (C), 164.2 (C) ppm; EI-MS (70 eV): *m/z* (%) = 280 (M^+, 4), 162 (21), 146 (34), 135 (74), 119 (80), 102 (58), 77 (100), 43 (32).

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