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# Synthesis of Weinreb amides *via* Pd-Catalyzed Aminocarbonylation of Heterocyclic-derived Triflates

*A. Deagostino,<sup>†</sup> Paolo Larini,<sup>†</sup> Ernesto G. Occhiato,<sup>‡</sup> Lorena Pizzuto,<sup>†</sup> Cristina Prandi\*<sup>†</sup> and Paolo  
Venturello<sup>†</sup>*

<sup>†</sup>Dipartimento di Chimica Generale ed Organica Applicata, Università di Torino, Corso Massimo  
D'Azeglio, 48, I-10125 Torino, Italy. <sup>‡</sup>Dipartimento di Chimica Organica "U. Schiff", and  
HeteroBioLab, Università di Firenze, Via della Lastruccia 13, I-50019 Sesto Fiorentino, Italy.

[cristina.prandi@unito.it](mailto:cristina.prandi@unito.it)

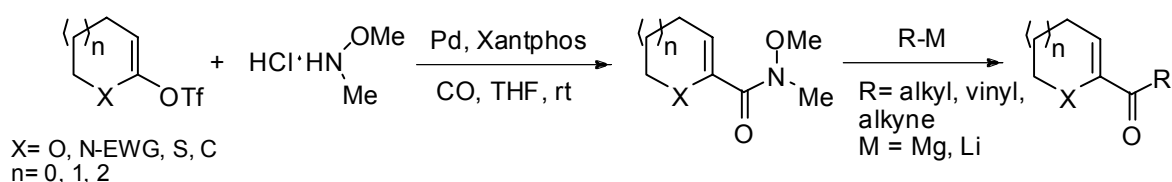
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CORRESPONDING AUTHOR FOOTNOTE Cristina Prandi, Dipartimento di Chimica Generale ed  
Organica Applicata, Università di Torino, Corso Massimo D'Azeglio, 48, I-10125 Torino, Italy

## SYNOPSIS TOC

### Synthesis of Weinreb amides *via* Pd-Catalyzed Aminocarbonylation of Heterocyclic-derived triflates

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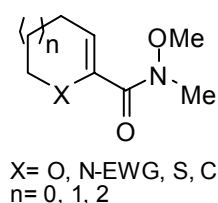


**ABSTRACT:** The direct transformation of lactam-, lactone-, and thiolactone-derived triflates into *N*-methoxy-*N*-methyl or morpholine Weinreb amides has been realized using Pd-catalyzed aminocarbonylation under CO atmospheric pressure and at room temperature. The carbonylative coupling can be efficiently carried out with 2% of catalyst in the presence of Xantphos as a ligand. The amides smoothly react with nucleophiles to afford acylated aza-, oxa- and thio-heterocycles. The proposed methodology could be advantageously exploited for the synthesis of dienones in which one of the double bonds is embedded in a heterocyclic moiety, as useful substrates for Nazarov cyclization.

The *N*-methoxy-*N*-methyl amides, otherwise known as Weinreb amides, are well established pivotal acylating agents in organic chemistry, due to their feature of reacting with organometallic reagents through stable metal-chelated intermediates, thus providing ketones without side products.<sup>1</sup> Since the first report in 1981,<sup>2</sup> the frequency with which they appear in the literature as key intermediates in advanced syntheses has rapidly grown. Weinreb amides are readily prepared starting from acyl chlorides,<sup>3</sup> esters,<sup>4</sup> oxazolidinones/thiazolidinones<sup>5</sup> or carboxylic acids by means of one-pot condensation with *N,O*-dimethylhydroxylamine hydrochloride in the presence of peptide coupling

reagents.<sup>6</sup> Taddei e al.<sup>7</sup> reported the synthesis of Weinreb amides in the presence of 2-chloro-4,6-dimethoxy[1.3.5]triazine (CDMT). The activation of the carboxylic acid has also been accomplished with Deoxo-Fluor fluorinating reagent.<sup>8</sup> Although these methods have been widely used especially in the preparation of *N*-methoxy-*N*-methyl amides of *N*-protected  $\alpha$ -amino acids, most of them require the use of an excess of expensive coupling reagent. Interestingly, sterically hindered carboxylic acids can be converted into Weinreb amides *via* acyl mesylates with good yields, even if the purification may be complicated by the formation of *N*-methoxy-*N*-methylmethansulfonamides as by-product.<sup>9</sup> A one-pot synthesis of  $\alpha$ -siloxy-Weinreb amides from aldehydes has been very recently published.<sup>10</sup> *N*-methoxy-*N*-methyl amides have in addition been prepared using 4,6-pyrimidyl urethane and Grignard reagents.<sup>11</sup> Among palladium catalysis based strategies, Stille cross-coupling between *N*-methoxy-*N*-methylcarbamoyl chloride with vinyl or aryl stannanes turned out to be an alternative to other synthetic methods.<sup>12</sup> An aminocarbonylative coupling of a dioxinone moiety in the presence of dppp has been proposed.<sup>13</sup> Furthermore, Buchwald proposed a new approach based on the aminocarbonylation of aryl bromides, in which the efficiency of the bidentate phosphine Xantphos, known to possess a large bite angle, has been exploited. The scope of the reaction has been extended to electron-deficient, -neutral and -rich aryl bromides.<sup>14</sup> In the context of an ongoing total synthesis project, we were interested in generating the Weinreb amides, whose general structure is represented in Figure 1, from the corresponding triflates. This was due to our recent interest in the Nazarov reaction,<sup>15</sup> which prompted us to investigate new and convenient synthetic sequences leading to conjugated dienones. To our knowledge, up to date there is only one reference which concerns the synthesis of substituted *N*-methoxy-*N*-methyl-3,4-dihydro-2*H*-pyran-6-carboxamide (X = O) using a hetero Diels–Alder cycloaddition catalyzed by bis(oxazoline) copper(II) complexes.<sup>16</sup> We therefore decided to undertake an investigation aimed at evaluating the feasibility of an aminocarbonylative coupling for the syntheses of

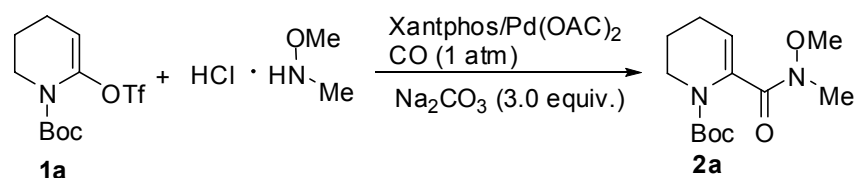
heterocyclic Weinreb amides and identify the optimized reaction conditions in order to establish this as a general method for the synthesis of heterocyclic acylated derivatives.



**Figure 1.** Heterocyclic Weinreb amides

Preliminary studies were conducted on the triflate prepared from *tert*-butyl-2-oxopiperidine-1-carboxylate, according to the literature procedure.<sup>17</sup> The initially chosen conditions were those proposed by Buchwald in his aminocarbonylative coupling of aryl bromides,<sup>14</sup> hence triflate **1a** (Scheme 1) was treated with 2% of Pd(OAc)<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub> (3 equiv.), and Xantphos as the supporting ligand in toluene as a solvent under one atmosphere pressure of CO.

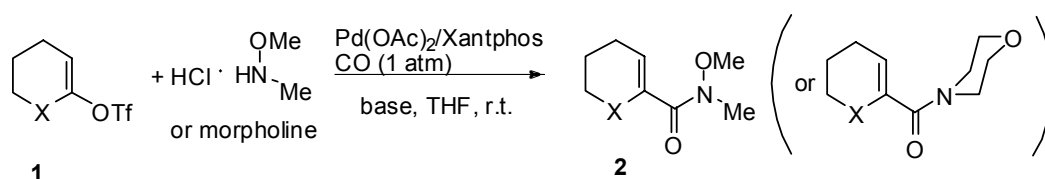
**Scheme 1.** Aminocarbonylative coupling on lactam derived triflate **1a**



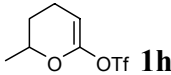
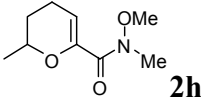
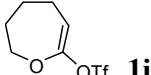
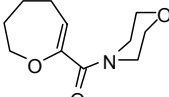
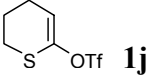
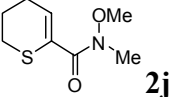
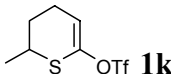
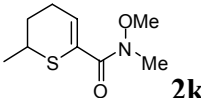
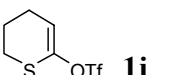
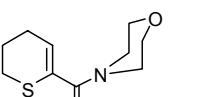
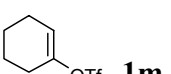
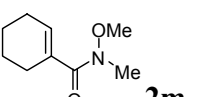
On the basis of the remarkable reactivity of heterocyclic derived triflates in cross-coupling reactions,<sup>18</sup> we decided to perform the reaction at room temperature, and after 3 hours a TLC and a GC control showed the complete disappearance of the starting triflate and a 100% conversion. The amide was recovered with a 55 % yield after workup and flash chromatography purification. With THF as a solvent, the yield of the amide **2a**, after flash chromatography purification rose to 78%. The use of Xantphos proved to be mandatory as experiments conducted with dppp or dppf in the role of ligands gave only a 12% conversion (determined by GC as an average of two runs) after 48 h at room

temperature with dppp (5%). Longer reaction times, various catalyst loadings or different Pd(OAc)<sub>2</sub>/Xantphos ratios did not improve the yield. The optimized experimental conditions were thus applied to the synthesis of a series of heterocyclic Weinreb amides as reported in Table 1.

**TABLE 1.** Synthesis of heterocyclic Weinreb amides



entry	Triflate	Product	yield (%) <sup>a</sup>
1	<b>1a</b>	<b>2a</b>	78
2	<b>1b</b>	<b>2b</b>	75
3	<b>1a</b>	<b>2c</b>	57
4	<b>1d</b>	<b>2d</b>	68
5	<b>1e</b>	<b>2e</b>	64
6	<b>1f</b>	<b>2f</b>	72
7	<b>1g</b>	<b>2g</b>	76

8	 <b>1h</b>	 <b>2h</b>	83
9	 <b>1i</b>	 <b>2i</b>	90
10	 <b>1j</b>	 <b>2j</b>	70 <sup>b</sup>
11	 <b>1k</b>	 <b>2k</b>	68 <sup>b</sup>
12	 <b>1j</b>	 <b>2l</b>	66
13	 <b>1m</b>	 <b>2m</b>	58

Reactions conditions: triflate **1** (1 equiv.), Pd(OAc)<sub>2</sub> 2%, Xantphos 2%, *N*-methoxy-*N*-methyl amine or morpholine (1 equiv.), Na<sub>2</sub>CO<sub>3</sub> (3 equiv.) room temperature overnight under a static atmosphere of CO. <sup>a</sup>Yields refer to flash chromatography purified products. <sup>b</sup>Experiments were conducted with anhydrous DCM and Et<sub>3</sub>N as a base without substantial variations in yield.

Bearing in mind the importance of *N*-protecting groups in determining the reactivity of these intermediates in multistep synthetic sequences, we investigated the feasibility of the aforementioned experimental conditions to the synthesis of a series of lactam-derived *N*-methyl-*N*-methoxy amides. *N*-COOMe and *N*-Tosyl amides **2d** and **2e** were recovered in good yields, and in these cases the crude reaction mixtures could be filtered through a short pad of Celite and directly used for subsequent reactions. Different ring sizes are well tolerated, so that the pyrrolidinone-derived amide **2b** and the

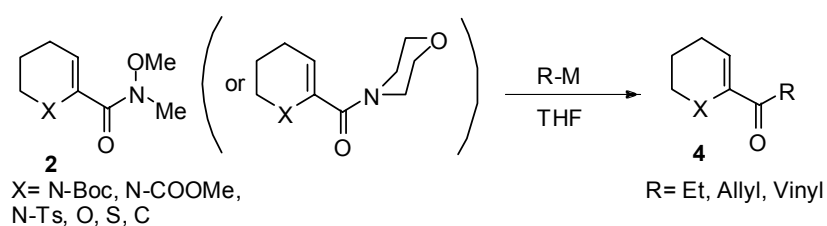
caprolactam-derived amide **2f** were isolated in good yields.<sup>19</sup> The same experimental conditions were applied to the synthesis of lactone-derived amides **2g-i**, and thiolactone-derived amides **2j-l**. Morpholino enamides are reported to successfully replace classical Weinreb amides,<sup>20</sup> as their use is often preferable due to, besides their high reactivity, the low cost of morpholine with respect to *N*-methoxy-*N*-methyl amine hydrochloride. To this end, we envisioned the possibility of using morpholine as an amine in the aminocarbonylative process: under the experimental conditions set up for *N*-methoxy-*N*-methyl amides, morpholino amides **2c**, **2i** and **2l** were obtained in 57%, 90% and 66% yield respectively. Moreover, the procedure could be rewardingly applied to the carbocyclic system as well; a 58% yield of the cyclohexanone-derived amide **2m** was obtained, though in this case a slight amount of carbonylated homocoupling product was detected.

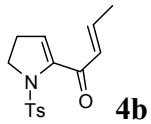
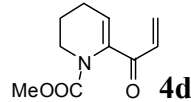
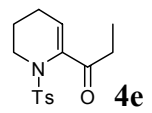
In order to explore the feasibility of the synthesized heterocyclic amides as useful intermediates in multistep syntheses involving acylated synthones, we decided to inspect the reactivity of the amides reported in Table 1 with organometallic reagents, namely Grignard and organolithium reagents. In recent years we have been largely concerned with the study of Nazarov reaction, so that we were particularly interested in new and efficient synthetic routes leading to functionalized divinyl ketones. These arguments strongly influenced the choice of the nucleophiles used to investigate the heterocyclic Weinreb amides potential. First experiments were conducted on nitrogen amides **2a**, **b**, **d** (Table 2) with discouraging results: with carbamates as protecting groups (Boc, COOMe, Cbz) the amides showed an inadequate reactivity and were recovered unchanged (apart from methyl 6-acryloyl-3,4-dihydropyridine-1(2*H*)-carboxylate **4d** obtained in low yield from amide **2d**) even under drastic reaction conditions such as the use of a strong excess of an organometallic reagent (up to 5 equiv. of BuLi, vinyl or ethylmagnesium bromide) or high temperatures. The presence of tosyl as a protecting group determined an enhancement in the reactivity, so that ketone **4e** could be obtained although in low yield. Satisfactory results were at last obtained with allyl magnesium bromide, as ketones **4b** and **4f** were

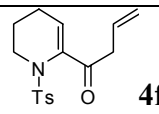
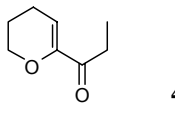
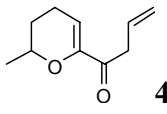
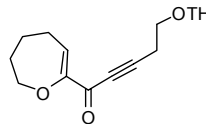
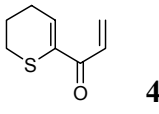
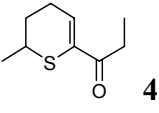
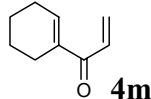


isolated in excellent yields (91% and 90% respectively), although in the course of column chromatography purification a partial isomerization of the terminal double bond occurred. Concerning the unexpected low reactivity of *N*-carbamate protected Weinreb amides, it is noteworthy to underline that the saturated analogue Cbz protected proline-derived Weinreb amide is reported to react with organomagnesium reagents under mild conditions.<sup>7</sup> On the basis of our experimental data we could only presume that both conformational aspects and metal-chelation phenomena due to the carbamate *N*-protecting group are accountable to explain the observed reactivity.<sup>21</sup>

**Table 2.** Conversion of heterocyclic amides into functionalized ketones



<i>entry</i>	<b>Amide</b>	<b>Product</b>	<b>T (°C)</b>	<b>Yield %<sup>a</sup></b>
1	<b>2a</b>	nd	-78 to 80	—
2	<b>2b</b>	 <b>4b</b>	-78	91
3	<b>2c</b>	nd	-78 to 80	—
4	<b>2d</b>	 <b>4d</b>	-78 to rt	21
5	<b>2e</b>	 <b>4e</b>	-78 to rt	38

6	2e		-78	90
7	2g		-78	76
8	2h		-78	78
9	2i		-78	87
10	2j		-78	80
11	2k		-78	72
12	2m		-78	94

The reactions were conducted under an argon atmosphere at  $-78\text{ }^{\circ}\text{C}$ , upon the addition of the amide the temperature was progressively raised on the basis of the TLC control of the reaction progress.

<sup>a</sup>Yields refer to flash chromatography column purification.

Satisfactory results have been obtained with oxygen, thio or carbocycle amides **2g-m**. The reactions with ethyl, allyl or vinyl magnesium bromide all proceeded smoothly at  $-78\text{ }^{\circ}\text{C}$  and afforded quite pure ketones in less than 1 hour. Provided that the sequence is feasible, the vinylation reaction using the commercial available and cheap vinyl magnesium bromide could be considered of remarkable synthetic worth. In the case of amide **2i**, the reaction with THP protected lithium but-3-yn-1-ol efficiently

proceeded at -78 °C and was complete within 30 min, affording the corresponding conjugated enynone **4i** in a 87% yield after flash chromatography purification.

In conclusion, we have reported on the synthesis of a new class of heterocyclic Weinreb amides, under extremely mild and convenient reaction conditions and inexpensive reagents. Lactam-, lactone-, and thiolactone-derived triflates were converted into *N*-methoxy-*N*-methyl or morpholine Weinreb amides by Pd-catalyzed aminocarbonylation in the presence of Xantphos as a ligand. The amides smoothly reacted with nucleophiles to afford acylated aza-, oxa- and thio-heterocycles. This methodology opens the access to interesting functionalized heterocyclic frameworks useful as building blocks in total syntheses.

#### EXPERIMENTAL SECTION:

**General Information.** All solvents were degassed before use in cross-coupling processes. Chromatographic separations were carried out under pressure on silica gel using flash-column techniques;  $R_f$  values refer to TLC carried out on 0.25-mm silica gel plates (Merck F254), with the same eluant indicated for the column chromatography.  $^1\text{H}$  NMR spectra were recorded at 200 MHz. Data were reported as follows: chemical shifts in ppm from tetramethylsilane as an internal standard, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double-doublet, m = multiplet, br = broad), coupling constants (Hz), and assignment.  $^{13}\text{C}$  NMR spectra were measured on a 50 MHz spectrometer with complete proton decoupling. Chemical shifts were reported in ppm from the residual solvent as an internal standard. DEPT and INEPT experiments were performed on a 200 MHz spectrometer. MS spectra were recorded at an ionizing voltage of 70 eV. THF was distilled from Na/benzophenone. Triflates **1a-q** have been synthesised as previously reported.<sup>17</sup> Other simple chemicals were purchased and used as such. The procedures described in this section are representative, and thus the yields may differ from those shown in Tables 1 and 2.

**General Procedure for the Synthesis of *N*-methoxy-*N*-methyl amides **2a**, **2b**, **2d**, **2e**, **2f**, **2g**, **2h**, **2j**, **2k**, and **2m**.** An oven-dried three necked round bottom flask with one tap was equipped with a

magnetic stir bar and was filled with argon. All solid reagents were added by briefly removing the rubber septum under flow of argon: Pd(OAc)<sub>2</sub> (0.02 equiv., 0.02 mmol, 4.50 mg), Xantphos (0.02 equiv., 0.02 mmol, 5.8 mg), *N*-methoxy-*N*-methyl amine hydrochloride (1 equiv., 1 mmol, 97 mg), Na<sub>2</sub>CO<sub>3</sub> (3 equiv. 3 mmol, 318 mg) and THF (10 mL). Then, the reaction was purged for *ca* 10 min with CO(g). A solution of triflate (1 equiv., 1 mmol) in 3 mL of THF was then added. A balloon filled with CO(g) was connected to the reaction vessel and the reaction mixture was stirred at room temperature until complete consumption of the triflate as judged by TLC analysis. The reaction mixture was then diluted with ethyl acetate (*ca* 10 mL), filtered through a plug of celite (eluting with ethyl acetate) and concentrated under reduced pressure. The crude material obtained was purified by flash chromatography on silica gel.

**General Procedure for the Synthesis of morpholino amides 2c, 2i and 2l.** The procedure is the same as that applied to the synthesis of *N*-methoxy-*N*-methyl amides, apart from the use of morpholine (1 equiv. 1 mmol, 87 mg) as an amine.

***N*-Methoxy-*N*-methyl-1-tosyl-4,5-dihydro-1*H*-pyrrole-2-carboxamide (2b).** after purification by flash chromatography with petroleum ether/ethyl acetate 1 : 1 (*R<sub>f</sub>* = 0.22), 232 mg (75 %) of a yellow oil was recovered <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): ppm 7.78 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 5.60 (t, *J* = 1.8 Hz, 1H), 3.75 (s, 3H), 3.68 (t, *J* = 8.7 Hz, 2H), 3.25 (s, 3H), 2.35 (s, 3H), 2.15 (t, *J* = 8.8 Hz, 2H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 173.2; 143.9; 138.3; 132.5; 129.4; 128.1; 119.1; 65.5; 49.2; 47.1; 28.3; 21.4. IR (neat) 3624, 3090, 2937, 1740, 1658, 1387, 1207, 1089, 1029 cm<sup>-1</sup>; MS (*m/z*): 310 (M<sup>+</sup>, 16), 225 (40), 250 (72), 183 (61), 123 (98), 91 (100). Anal. Calcd. for C<sub>14</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>S C, 54.18; H, 5.85; N, 9.03; found C, 54.36; H, 5.65; N, 9.16.

**Benzyl 7-(methoxy(methyl)carbamoyl)-2,3,4,5-tetrahydro-1*H*-azepine-1-carboxylate (2f):** after purification by flash chromatography with petroleum ether/ethyl acetate 2 : 1 (*R<sub>f</sub>* = 0.25), 229 mg (72%) of a yellow oil was recovered <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): ppm 7.23 (s, 5H), 6.07 (t, *J* = 6.4 Hz, 1H), 5.02 (s, 2H), 3.60-3.51 (m, 2H), 3.22 (s, 3H), 2.85 (s, 3H), 2.22-2.17 (m, 2H), 1.75-1.69 (m, 2H), 1.51-1.48 (m, 2H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): 167.7; 153.8; 137.5; 135.8; 130.6; 128.5; 128.18; 127.9;

67.5; 60.1; 48.1; 33.3; 28.8; 27.0; 23.2; MS (m/z): 318 (M<sup>+</sup>, 2), 287 (5), 258 (25), 107 (60), 91 (100).  
Anal. Calcd. for C<sub>17</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>, C, 64.13; H, 6.97; N, 8.80; found C, 64.38; H, 6.85; N, 8.76.

***N*-Methoxy-*N*-methyl-3,4-dihydro-2*H*-pyran-6-carboxamide (2g):** after purification by flash chromatography with petroleum ether/ethyl acetate 3 : 1 (R<sub>f</sub> = 0.3), 130 mg (76 %) of a yellow oil was recovered <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): ppm 5.53 (t, *J* = 4.0 Hz, 1H), 4.07 (t, *J* = 5.1 Hz, 2H), 3.77 (s, 3H), 3.23 (s, 3H), 2.15 (t, *J* = 3.4 Hz, 2H), 1.86 (t, *J* = 3.45 Hz, 2H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 165.6; 147.7; 106.4; 66.1; 61.1; 34.3; 21.6; 20.2. MS (m/z): 171 (M<sup>+</sup>, 15), 111 (75), 83 (10), 55 (100).  
Anal. Calcd. for C<sub>8</sub>H<sub>13</sub>NO<sub>3</sub>, C, 56.13; H, 7.65; N, 8.18; found C, 56.36; H, 7.55; N, 8.16.

***N*-Methoxy-*N*-methyl-3,4-dihydro-2*H*-thiopyran-6-carboxamide (2j):** after purification by flash chromatography with petroleum ether/ethyl acetate 3 : 1 (R<sub>f</sub> = 0.3), 131 mg (70 %) of a yellow oil was recovered <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): ppm 6.33 (t, *J* = 4.3 Hz, 1H), 3.71 (s, 3H), 3.26 (s, 3H), 3.00-2.73 (m, 2H), 2.30 (dd, *J* = 10.6, 6.3 Hz, 2H), 2.01 (m, 2H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 167.4; 127.8; 126.3; 61.2; 33.9; 26.8; 24.0; 21.7; MS (m/z): 187 (M<sup>+</sup>, 39), 127 (100), 99 (88), 71 (65). Anal. Calcd. for C<sub>8</sub>H<sub>13</sub>NO<sub>2</sub>S, C, 51.31; H, 7.00; N, 7.48; S, 17.12; found C, 51.46; H, 7.05; N, 7.24, S, 17.24.

**(3,4-dihydro-2*H*-Thiopyran-6-yl)(morpholino)methanone (2l):** after purification by flash chromatography with petroleum ether/ethyl acetate 3 : 1 (R<sub>f</sub> = 0.3), 140 mg (66 %) of a yellow oil was recovered <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): ppm 5.92 (t, *J* = 4.3, Hz, 1H), 3.73-3.51 (m, 8H), 2.98-2.87 (m, 2H), 2.25 (t, *J* = 5.4 Hz, 2H), 2.01 (t, *J* = 5.4 Hz, 2H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 167.6; 128.4; 122.0; 66.8 (2C); 30.0 (2C); 26.6; 23.4; 21.3; MS (m/z): 213 (M<sup>+</sup>, 100), 180 (18), 128 (60), 99 (86).  
Anal. Calcd. for C<sub>10</sub>H<sub>15</sub>NO<sub>2</sub>S, C, 56.31; H, 7.09; N, 6.57; S, 15.03; found C, 56.31; H, 7.05; N, 6.55, S, 15.45.

**General Procedure for the Synthesis of Heterocyclic Acyl Derivatives 4b, 4d, 4e, 4f, 4g, 4h, 4i, 4j, 4k, 4m.** An oven-dried Shlenck flask equipped with a magnetic stir bar was flame dried and kept under an argon atmosphere. A solution of the appropriate Grignard reagent (2 mmol) in anhydrous THF (5 mL) was introduced and refrigerated at -78 °C with an acetone/liquid nitrogen bath. A solution of the appropriate Weinreb amide was then slowly added. The reaction mixture was stirred and, if necessary

the temperature was progressively raised at room temperature until complete consumption of amide as judged by TLC analysis. The reaction mixture was then diluted with ethyl acetate (~ 10 mL), washed twice with brine, the organic layers were then dried over sodium sulphate and concentrated under reduced pressure. The crude material obtained was purified by flash chromatography on silica gel.

**1-(3,4-Dihydro-2H-thiopyran-6-yl)prop-2-en-1-one (4j):** after purification by flash chromatography with petroleum ether/ethyl acetate 5 : 1 ( $R_f = 0.45$ ), 129 mg (78 %) of a white oil was recovered  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ): ppm 6.98 (t,  $J = 4.8$  Hz, 1H) superimposed to 6.88 (dd,  $J = 17.0, 10.5$  Hz, 1H), 6.32 (dd,  $J = 17.0, 1.2$  Hz, 1H), 5.74 (d,  $J = 10.5$  Hz, 1H), 2.95-2.85 (m, 2H), 2.43 (dd,  $J = 11.2, 5.8$  Hz, 2H), 2.08-1.95 (m, 2H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  187.6; 136.8; 133.9; 129.9 ; 128.9; 26.0; 25.00; 21.2; MS (m/z): 154 ( $\text{M}^+$ , 82), 126 (48), 99 (62), 71 (81), 55(100). Anal. Calcd. for  $\text{C}_{18}\text{H}_{24}\text{O}_3\text{S}$ , C, 67.47; H, 7.55; O, 14.98; S, 10.01 found C, 67.12; H, 7.38; S, 9.98.

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**Supporting Information Available:** Characterization data for compounds **2a**, **2c**, **2d**, **2e**, **2h**, **2i**, **2k**, **2m**, **3**, **4b**, **4d**, **4e**, **4f**, **4g**, **4h**, **4i**, **4k**, **4m** and copies of the  $^1\text{H}$  NMR and  $^{13}\text{C}$  spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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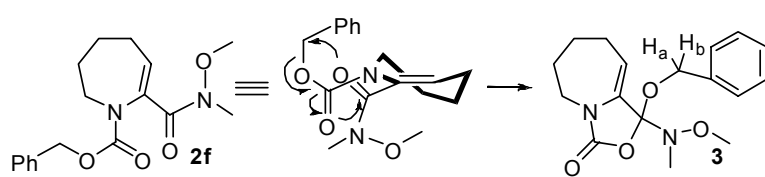
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A similar rearrangement in the presence

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