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Study of a 1,6-hydride shift in an open chain of hydroxylactam-triarylcabinols

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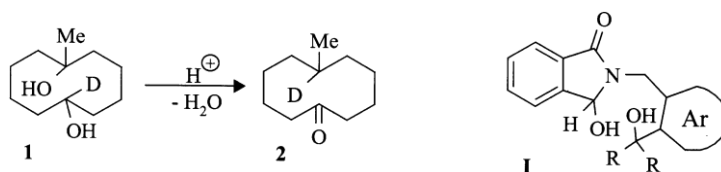
Abstract - Hydroxylactam-alcohols **5a,b,d** (isoindole series), under acidic treatment gave phthalimides **7a,b,d** via a hydride shift induced by an intramolecular π -stacking (benzene-benzene or benzene-thiophene interaction) which did not occur in **10a** (succinimide series).

The pinacol rearrangement is a well-known reaction and it has been demonstrated that the hydrogen has a greater migratory aptitude than a phenyl group. Although direct nucleophilic rearrangement over distances greater than 1,2 are rare, a shift across a ring of 8-11 members^{1,2} is still possible as exemplified with cyclodecanediol **1**³ (Scheme 1).

Based on these observations we intended to study structures of type **I**, because during our investigations on the synthesis of polyheterocycles containing an isoindole moiety, we have prepared hydroxylactam-alcohols **5a-d**. Actually, in an acidic medium the hydroxylactam is a precursor of an *N*-acyliminium ion,⁴ and the triarylcabinol can also give a carbocation. Consequently, it was reasonable to investigate the possibilities of a hydrogen migration from the hydroxylactam to the carbinol.

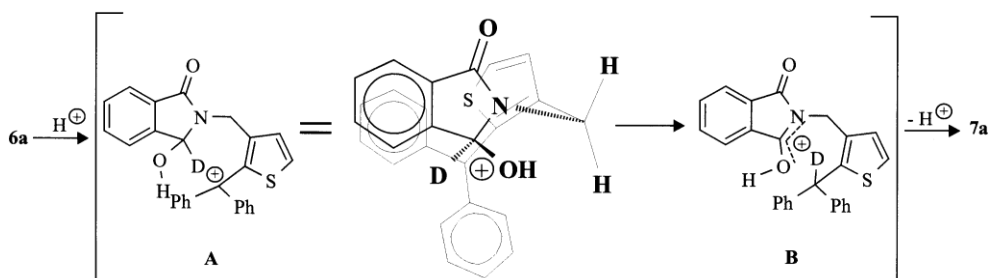
In a diol, as might be expected, the leaving hydroxy group is the one which leads to the more

stable carbocation. We have recently described that an *N*-acyliminium ion reacts easily with an alcohol or a thiol.⁵ Thus from compound **5a**, we expected either the formation of an ether or a nucleophilic pinacol rearrangement if the geometry of the structure permits the transfer of an atom similar to the one observed in cyclodecanediol **1**. The starting hydroxylactam-alcohols **5a-c** were obtained in good yields by reducing the phthalimide-esters **3a-b**^{6,7} with sodium borohydride and by subsequent addition of an excess of phenylmagnesium bromide (Scheme 2). Thus, when **5a** was subjected to a catalytic amount of *p*-toluenesulfonic acid (PTSA) in refluxing toluene for 2 h, a mixture of ether **6a** (80%) and imide **7a** (20%) was formed. Compounds **5a**, **6a** and **7a** were easily differentiated by the analysis of their NMR (¹H and ¹³C) spectra. Due to the presence of a stereogenic center, methylene protons (N-CH₂) and carbon atoms of the two phenyl groups are not equivalent for **5a** and **6a** in contrast to **7a**. When a catalytic amount of trifluoroacetic acid (TFA) in place of PTSA was used during 30 min, we observed the ether **6a** accompanied with traces of **7a**. The imide **7a** was obtained from **5a** or **6a** as the sole product when the reaction was carried out for 2 days with an excess of TFA. This behavior was similar to a pinacol rearrangement. To prove that the product **7a** resulted of a hydrogen migration we prepared the deuterated hydroxylactam **5a**. The latter resulted of the reduction of **4a** in the presence of deuterated sodium borohydride. The deuterated compound **5a** gave the deuterated phthalimide **7a**. A NMR analysis revealed the absence of hydrogen in the α -position to the two phenyl groups compared to that observed in the non-deuterated product **7a** ($\delta = 6.22$ ppm). The hydrogen migration can be rationalized as depicted in Scheme 3. The more stable carbocation **A** was first formed, followed by a transfer of deuterium which led to a new carbocation **B** stabilized by both a nitrogen and an oxygen atom. Finally, loss of a proton provided phthalimide **7a**. This hydride transfer was supposed to be due to the geometry of the carbocation **A**.



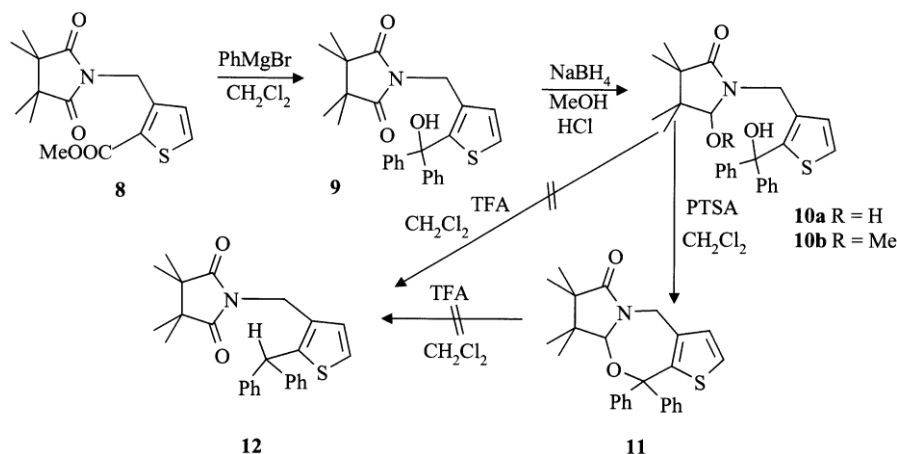
Scheme 1.

single product because the imide **12** (TFA, dichloromethane) was not observed. In the latter case there is no π - π interaction and furthermore the imide is shielded by the four methyl groups.



Scheme 3.

As another example we prepared the oxazepine **6d** and the imide **7d** from diol **5d**. This diol resulted from the action of 6 equiv. of thien-2-ylmagnesium bromide onto the ester **4a**. The replacement of the two benzene rings (**5a,b**) by two thiophene rings (**5d**) has modified the π - π interaction. Actually the hydride transfer was carried out in two days for **5a,b** while after seven days only 35% of **5d** had reacted with the formation of 13% of **7d** accompanied with degradation products. Furthermore, as in benzene series we did not observe a reaction between the *N*-acyliminium ion and one of the two thiophene rings whatever the conditions of the reaction (temperature, time).



Scheme 4.

In conclusion we have described an interesting hydride transfer between a hydroxylactam and an alcohol in a non-cyclic product. A π -stacking in the intermediate carbocation seems to be necessary for this transfer. Further studies are in progress to investigate scope and limitations of this new type of hydrogen migration.

2. Experimental

2.1. General

Melting points are uncorrected. The infrared spectra of solids (potassium bromide) were recorded on a Perkin- Elmer FTIR paragon 1000 spectrometer. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 (200 MHz) instrument in deuteriochloroform solution and chemical shifts (δ) are expressed in ppm relative to internal TMS. Thin layer chromatography was performed on precoated plates of silica gel 60 F254 (Merck) and the spots visualized using an ultraviolet lamp or iodine vapor. E. Merck silica gel 60 F (70-300 mesh) was used for column chromatography. The elemental analyses were carried out by the microanalysis laboratory of INSA at Rouen, F 76130 Mt. St. Aignan, France. Compounds **4a,b** were prepared as indicated in Refs. 6 and 7.

2.1.1. 2,3-Dihydro-3-hydroxy-2-[2-(diphenylhydroxymethyl)thien-3-ylmethyl]-1H-isoindol-1-one (5a). To a freshly prepared solution of phenylmagnesium bromide (60 mL of 1M solution in ether) in dry dichloromethane (60 mL) was added portionwise solid hydroxylactam **4a** (3.03 g, 10 mmol) at room temperature with stirring. Stirring was continued for 3 h. The solution was then carefully poured into a 10% solution of ammonium chloride. The mixture was decanted and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried on magnesium sulfate and filtered. The solution was concentrated under reduced pressure. The residue was chromatographed on silica gel (dichloromethane until the biphenyl was removed, then dichloromethane/acetone 90/10). The diol was recrystallized from ethanol to furnish pure product **5a**. Yield 56%; mp 162°C; IR: 3368 (OH), 3330 (OH), 1660 (C=O) cm^{-1} ; ^1H NMR: δ 4.14 (d, $J=15$ Hz, 1H, CH_2), 4.22 (s, 1H, OH), 4.49 (d, $J=15$ Hz, 1H, CH_2), 5.59 (s, 1H, OH), 5.67 (s, 1H, CH), 6.98 (d, $J=5$ Hz, 1H, $\text{H}_{\text{thiophene}}$), 7.03 (d, $J=5$ Hz, 1H, $\text{H}_{\text{thiophene}}$), 7.06-7.63 (m, 14H, H_{arom}); ^{13}C NMR: δ 37.2 (CH_2), 79.0 (C), 81.5 (CH), 123.2 (CH), 123.3 (CH), 124.5 (CH), 127.2 (2 CH), 127.5 (2 CH), 127.6 (CH), 127.7 (CH), 127.9 (4 CH), 129.7 (CH), 130.5 (CH), 131.2 (C), 132.3 (CH), 134.3 (C), 143.1 (C), 146.7 (C), 147.0 (C), 148.5 (C), 167.3 (CO). Anal. Calcd for $\text{C}_{26}\text{H}_{21}\text{NO}_3\text{S}$: C, 73.05; H, 4.95; N, 3.28. Found: C, 72.78; H, 4.89; N, 3.34.

2.1.2. 2,3-Dihydro-3-hydroxy-2-[2-(diphenylhydroxymethyl)phenylmethyl]-1H-

isoindol-1-one (5b). This compound was prepared from **4b** using the same procedure as for **5a**. Yield 59%; mp 118°C; IR: 3306 (OH), 1680 (C=O) cm⁻¹; ¹H NMR: δ 4.40 (d, *J*=15 Hz, 1H, CH₂), 4.63 (d, *J*=15 Hz, 1H, CH₂), 4.73 (d, *J*=7 Hz, 1H, OH), 5.59 (d, *J*=7 Hz, 1H, CH), 6.56 (d, *J*=8 Hz, 1H, H_{arom}), 6.92-7.52 (m, 16H, H_{arom}), 7.61 (d, *J*=7 Hz, 1H, H_{arom}); ¹³C NMR: δ 41.2 (CH₂), 81.2 (CH), 82.9 (C), 123.0 (2 CH), 126.3 (CH), 127.0 (CH), 127.1 (CH), 127.3 (2 CH), 127.7 (2 CH), 127.8 (2 CH), 127.9 (2 CH), 128.2 (CH), 129.3 (CH), 129.8 (CH), 131.3 (CH), 131.4 (C), 131.9 (CH), 137.1 (C), 143.0 (C), 144.2 (C), 146.9 (C), 147.0 (C), 167.5 (CO). Anal. Calcd for C₂₈H₂₃NO₃: C, 79.79; H, 5.50; N, 3.32. Found: C, 79.34; H, 5.62; N, 3.15.

2.1.3. 2,3-Dihydro-3-hydroxy-2-[2-(di(thien-2-yl)hydroxymethyl)thien-3-ylmethyl]-1H-isoindol-1-one (5d). This compound was prepared from **4a** using the same procedure as for **5a,b** but with 2-thienylmagnesium bromide. Yield 64%; mp 202°C; IR: 3422 (OH), 1656 (C=O) cm⁻¹; ¹H NMR: δ 3.50 (s broad, 1H, N-C-OH), 4.37 (d, *J*=15 Hz, 1H, CH₂), 4.64 (d, *J*=15 Hz, 1H, CH₂), 5.70 (s broad, 1H, N-CH), 6.46 (s broad, 1H, OH), 6.80-6.98 (m, 4H, H_{thiophene}), 7.01 (d, *J*=5 Hz, 1H, H₃), 7.08 (d, *J*=5 Hz, 1H, H₂), 7.18-7.58 (m, 5H, 3H_{arom}+2H_{thiophene}), 7.64 (d, *J*=7 Hz, 1H, H_{arom}); ¹³C NMR: δ 37.5 (CH₂), 74.4 (C), 81.2 (CH), 122.4 (CH), 123.6 (CH), 124.0 (CH), 125.6 (CH), 125.7 (2 CH), 125.8 (CH), 126.5 (2 CH), 129.1 (CH), 129.4 (CH), 131.1 (C), 132.1 (CH), 135.4 (C), 145.0 (C), 145.8 (C), 152.1 (C), 152.2 (C), 166.6 (CO). Anal. Calcd for C₂₂H₁₇NO₃S₃: C, 60.11; H, 3.90; N, 3.19. Found: C, 60.02; H, 3.85; N, 3.24.

2.1.4. 4,12-Dihydro-12,12-diphenylthieno[3',2':5,6][1,3]oxazepino[2,3-*a*]isoindol-6(10bH)-one (6a). A solution of compound **5a** (10 mmol), a catalytic amount of PTSA in dichloromethane (20 mL) was stirred for 30 min (reaction was monitored by TLC). The solution was washed successively with a saturated sodium hydrogen carbonate solution, then with water and was dried (magnesium sulfate) and filtered. The solution was concentrated under reduced pressure and the residue was recrystallized from ethanol to furnish pure **6a**: Yield 88%; mp 178°C; IR: 1707 (C=O) cm⁻¹; ¹H NMR: δ 4.19 (d, *J*=16 Hz, 1H, H₄), 5.36 (d, *J*=16 Hz, 1H, H₄), 6.01 (s, 1H, H_{10b}), 7.05 (d, *J*=5 Hz, 1H, H₃), 7.11 (d, *J*=5 Hz, 1H, H₂), 7.20-7.57 (m, 13H, H_{arom}), 7.78 (d, *J*=7 Hz, 1H, H₇); ¹³C NMR: δ 40.8 (CH₂), 84.7 (CH), 86.3 (C), 123.2 (CH), 123.5 (CH), 124.7 (CH), 127.5 (2 CH), 127.8 (2 CH), 128.0 (CH), 128.7 (CH), 128.8 (2 CH), 129.1 (CH), 129.4 (2 CH), 129.6 (CH), 131.7 (C), 132.0 (CH), 135.3 (C), 141.4 (C), 142.6 (C), 144.7 (C), 146.6 (C), 166.5 (CO). Anal. Calcd for C₂₆H₁₉NO₂S: C,

76.26; H, 4.68; N, 3.42. Found: C, 75.89; H, 4.81; N, 3.28.

2.1.5. 5,13-Dihydro-5,5-diphenylisoindolo[1,2-*c*][2,4]benzoxazepin-11(6*aH*)-one (6*b*).

This compound was prepared from **5b** using the same procedure as for **5a**. Yield 93%; mp 175°C; IR: 1677 (C=O) cm⁻¹; ¹H NMR: δ 4.48 (d, *J*= 15 Hz, 1H, H₅), 4.65 (d, *J*=15 Hz, 1H, H₅), 6.21 (s, 1H, H_{11b}), 6.61 (d, *J*=8 Hz, 1H, H_{arom}), 7.05-7.61 (m, 16H, H_{arom}), 7.78 (d, *J*=6 Hz, 1H, H₈); ¹³C NMR: δ 45.8 (CH₂), 83.3 (CH), 89.1 (C), 123.0 (CH), 123.0 (CH), 127.2 (CH), 127.4 (3 CH), 127.7 (2 CH), 127.9 (CH), 128.2 (2 CH), 128.5 (CH), 129.1 (2 CH), 129.3 (CH), 130.2 (CH), 131.4 (CH), 131.6 (CH), 132.2 (C), 135.3 (C), 142.1 (C), 142.2 (C), 142.4 (C), 145.7 (C), 165.8 (CO). Anal. Calcd for C₂₈H₂₁NO₂: C, 83.35; H, 5.25; N, 3.47. Found: C, 82.93; H, 5.40; N, 3.32.

2.1.6. 4,12-Dihydro-12,12-di(thien-2-yl)thieno[3',2':5,6][1,3]oxazepino[2,3-*a*]isoindol-

6(10*bH*)-one (6*d*). This compound was prepared from **5d** using the same procedure as for **6a**. Yield 100%; mp 217°C; IR: 1703 (C=O) cm⁻¹; ¹H NMR: δ 4.34 (d, *J*=16 Hz, 1H, H₄), 5.34 (d, *J*=16 Hz, 1H, H₄), 6.14 (s, 1H, H_{10b}), 6.80 (dd, *J*=4 and 2 Hz, 1H, H_{thiophene}), 6.87-6.94 (m, 2H, H₃+H_{thiophene}), 6.95-7.07 (m, 2H, H_{thiophene}), 7.14 (d, *J*=5 Hz, 1H, H₂), 7.27 (dd, *J*=5 and 1Hz, 1H, H_{thiophene}), 7.40-7.59 (m, 4H, 3H_{arom}+H_{thiophene}), 7.78 (d, *J*=6 Hz, 1H, H₇); ¹³C NMR: δ 40.9 (CH₂), 82.1(C), 84.5 (CH), 123.4 (CH), 123.4 (CH), 124.9 (CH), 125.5 (CH), 126.2 (CH), 126.7 (CH), 126.9 (CH), 128.6 (CH), 129.0 (CH), 129.7 (CH), 130.0 (CH), 131.6 (C), 132.1 (CH), 134.5 (C), 142.2 (C), 144.4 (C), 146.0 (C), 150.2 (C), 166.7 (CO). Anal. Calcd for C₂₂H₁₅NO₂S₃: C, 62.68; H, 3.59; N, 3.32. Found: C, 62.88; H, 3.68; N, 3.46.

2.1.7. 2,3-Dihydro-2-[2-(hydroxy-diphenylmethyl)thien-3-ylmethyl]-1*H*-isoindole-1,3-

dione (7*a*). Compound **7a** was synthesized using the same procedure as for the synthesis of **6a** (starting from **5a** or **6a**) but with 1mL of TFA in place of PTSA and with a reaction time of 2 days: Yield 90%; mp 150°C; IR: 1718 (C=O) cm⁻¹; ¹H NMR: δ 4.62 (s, 2H, CH₂), 6.22 (s, 1H, CH), 7.02-7.26 (m, 12H, H_{arom}), 7.57-7.67 (m, 2H, H_{phthalimide}), 7.67-7.78 (m, 2H, H_{phthalimide}); ¹³C NMR: δ 34.5 (CH₂), 49.2 (CH), 123.0 (2 CH), 123.8 (CH), 126.5 (2 CH), 128.2 (4 CH), 128.7 (4 CH), 129.5 (CH), 131.8 (2 C), 132.1 (C), 133.7 (2 CH), 143.7 (2 C), 145.8 (C), 167.8 (2 CO). Anal. Calcd for C₂₆H₁₉NO₂S: C, 76.26; H, 4.68; N, 3.42. Found: C, 75.82; H, 4.61; N, 3.25.

2.1.8. 2,3-Dihydro-2-[2-(hydroxy-diphenylmethyl)phenylmethyl]-1*H*-isoindole-1,3-dione

(7b). Compound **7b** was synthesized using the same procedure as for the synthesis of **7a** (starting from **5b** or **6b**). Yield 96%; mp 176°C; IR: 1710 (C=O) cm⁻¹; ¹H NMR: δ 4.77 (s, 2H, CH₂), 6.21 (s, 1H, CH), 6.76-6.90 (m, 1H, H_{arom}), 6.97-7.46 (m, 13H, H_{arom}), 7.56-7.69 (m, 2H, H_{phthalimide}), 7.69-7.81 (m, 2H, H_{phthalimide}); ¹³C NMR: δ 39.2 (CH₂), 52.3 (CH), 123.2 (2 CH), 126.2 (2 CH), 126.7 (CH), 127.8 (CH), 128.3 (4 CH), 129.6 (4 CH), 130.0 (CH), 130.2 (CH), 131.9 (2 C), 133.8 (2 CH), 134.4 (C), 141.9 (C), 143.6 (2 C), 168.1 (2 CO). Anal. Calcd for C₂₈H₂₁NO₂: C, 83.35; H, 5.25; N, 3.47. Found: C, 82.99; H, 5.05; N, 3.39.

2.1.9. 2,3-Dihydro-2-[2-(hydroxy-di(thien-2-yl)methyl)thien-3-ylmethyl]-1H-isoindole-1,3-dione (7d). Compound **7d** was synthesized using the same procedure as for the synthesis of **7a** (starting from **5d** or **6d**) but the reaction time was 6 days: Yield 28%; mp 159°C; IR: 1713 (C=O) cm⁻¹; ¹H NMR: δ 4.76 (s, 2H, CH₂), 6.72 (s, 1H, CH), 6.84-6.95 (m, 4H, H_{thiophene}), 7.05-7.15 (m, 2H, H_{thiophene}), 7.18 (dd, *J*=5 and 2 Hz, 2H, H_{thiophene}), 7.64-7.75 (m, 2H, H_{phthalimide}), 7.76-7.86 (m, 2H, H_{phthalimide}); ¹³C NMR: δ 34.3 (CH₂), 40.0 (CH), 123.2 (2 CH), 124.0 (CH), 124.7 (2 CH), 126.0 (2 CH), 126.4 (2 CH), 129.4 (CH), 131.9 (2 C), 132.1 (C), 133.8 (2 CH), 145.5 (C), 147.1 (2 C), 167.8 (2 CO). Anal. Calcd for C₂₂H₁₅NO₂S₃: C, 62.68; H, 3.59; N, 3.32. Found: C, 62.78; H, 3.59; N, 3.24.

2.1.10. 3,3,4,4-Tetramethyl-1-[2-carbomethoxythien-3-ylmethyl]succinimide (8). A mixture of tetramethylsuccinimide (1.55 g, 10 mmol), crown ether 18-C-6 (0.01 g), potassium carbonate (1.52 g, 11 mmol), potassium iodide (0.166 g, 1 mmol), and dry toluene was stirred for 10 min. A solution of methyl 3-bromomethylthiophene-2-carboxylate (2.82 g, 12 mmol) in toluene (10 mL) was added dropwise. The mixture was refluxed for 24 h. After cooling, the mixture was filtrated on celite and was then concentrated under reduced pressure. The residue was recrystallized from ethanol to furnish pure **8** with a yield of 79%, mp 154°C; IR: 1696 (C=O) cm⁻¹; ¹H NMR: δ 1.10 (s, 12H, 4CH₃), 3.83 (s, 3H, OCH₃), 5.02 (s, 2H, CH₂), 6.77 (d, *J*=5 Hz, 1H, H_{thiophene}), 7.36 (d, *J*=5 Hz, 1H, H_{thiophene}). Anal. Calcd for C₁₅H₁₉NO₄: C, 58.23; H, 6.19; N, 4.53. Found: C, 58.04; H, 6.15; N, 4.35.

2.1.11. 3,3,4,4-Tetramethyl-1-[2-(diphenylhydroxymethyl)thien-3-ylmethyl]succinimide (9). This compound was obtained as an oil with a yield of 74%, ¹H NMR: δ 1.10 (s, 12H, 4CH₃), 4.30 (s, 2H, CH₂), 6.20 (s, 1H, OH), 6.82 (d, *J*=5 Hz, 1H, H_{thiophene}), 7.04 (d, *J*=5 Hz, 1H, H_{thiophene}), 7.19-7.57 (m, 10H, H_{phenyl}); ¹³C NMR: δ 21.2 (4 CH₃), 36.5 (CH₂), 46.9 (2 C), 124.9 (CH), 127.2 (4 CH), 127.3 (2 CH), 127.7 (4 CH), 128.6 (CH), 132.5 (C), 147.3 (2 C),

149.5 (C), 183.2 (2 CO).

2.2. Reduction of imide **9**, formation of **10a+10b**

To a mixture of imide **9** (1.73 g, 4 mmol) in dry methanol (40 mL) at 0°C was added sodium borohydride (0.9 g, 24 mmol) by portions. To this mixture were added five drops of ethanolic hydrochloric acid solution (prepared from nine drops of concentrated hydrochloric acid in ethanol (15 mL) at regular intervals (10 min). The reaction was monitored by TLC. The excess of sodium borohydride was decomposed by careful addition of cold water (15 mL) and diluted hydrochloric acid. Sodium hydrogen carbonate was added and the solvent was evaporated. The residue was dissolved in a mixture of dichloromethane/water. The organic layer was dried on magnesium sulfate and was then concentrated under reduced pressure giving a mixture of **10a/10b** (85/15) in a 95% yield.

2.2.1. 3,3,4,4-Tetramethyl-1-[2-(diphenylhydroxymethyl)thien-3-ylmethyl]succinamidal (10a). ¹H NMR: δ 0.84 (s, 3H, CH₃), 0.88 (s, 3H, CH₃), 0.89 (s, 3H, CH₃), 1.03 (s, 3H, CH₃), 3.82 (m, 1H, OH), 4.04 (d, *J*=15 Hz, 1H, CH₂), 4.32 (d, *J*=15 Hz, 1H, CH₂), 4.53 (d, *J*=5 Hz, CH), 5.45 (s, 1H, OH), 6.97 (d, *J*=5 Hz, 1H, H_{thiophene}), 7.05 (d, *J*=5 Hz, 1H, H_{thiophene}), 7.21-7.60 (m, 10H, H_{phenyl}); ¹³C NMR: δ 17.4 (CH₃), 19.5 (CH₃), 22.4 (CH₃), 23.1(CH₃), 38.2 (CH₂), 42.4 (C), 46.0 (C), 78.9 (CH), 88.6 (C), 124.3 (CH), 127.2 (2 CH), 127.4 (2 CH), 127.5 (CH), 127.6 (CH), 127.8 (2 CH), 127.9 (2 CH), 130.0 (CH), 134.8 (C), 146.8 (C), 147.0 (C), 147.8 (C), 180.0 (CO).

2.2.2. 5-Methoxy-3,3,4,4-tetramethyl-1-[2-(diphenylhydroxymethyl)thien-3-ylmethyl]succinamidal (10b). ¹H NMR: δ 0.85 (s, 3H, CH₃), 0.89 (s, 3H, CH₃), 0.94 (s, 3H, CH₃), 1.01 (s, 3H, CH₃), 3.44 (s, 3H, OCH₃), 4.04 (d, *J*=15 Hz, 1H, CH₂), 4.14 (d, *J*=15 Hz, 1H, CH₂), 4.20 (s, 1H, OH), 6.98 (d, *J*=5 Hz, 1H, H_{thiophene}), 7.03 (d, *J*=5 Hz, 1H, H_{thiophene}), 7.16-7.52 (m, 10H, H_{phenyl}).

2.2.3. 4,7,8,10-tetrahydro-7,7,8,8-tetramethyl-10,10-di-phenylpyrrolo[2,1-*b*]thieno[3,2-*e*][1,3]oxazepin-6(8*aH*)-one (11). This compound was prepared from the mixture of **10a** and **10b** using the same procedure as for the synthesis of **6a,b**. Yield 100%; mp 157°C; IR: 1665 (C=O) cm⁻¹; ¹H NMR: δ 0.80 (s, 3H, CH₃), 0.98 (s, 3H, CH₃), 1.09 (s, 3H, CH₃), 1.31 (s, 3H, CH₃), 3.85 (d, *J*=15 Hz, 1H, CH₂), 4.66 (s, 1H, CH), 5.14 (d, *J*=15 Hz, 1H, CH₂), 6.88-7.10

(m, 2H, H_{thiophene}), 7.12-7.46 (m, 10H, H_{phenyl}); ¹³C NMR: δ 17.8 (CH₃), 18.4 (CH₃), 24.4 (CH₃), 25.6 (CH₃), 41.0 (CH₂), 42.8 (C), 45.3 (C), 86.6 (C), 92.4 (CH), 124.5 (CH), 127.5 (2 CH), 127.7 (2 CH), 127.8 (CH), 128.4 (CH), 128.5 (2 CH), 128.9 (CH), 129.5 (2 CH), 136.3 (C), 141.9 (C), 144.6 (C), 147.2 (C), 179.0 (CO). Anal. Calcd for C₂₆H₂₇NO₂S: C, 74.79; H, 6.52; N, 3.35. Found: C, 74.35; H, 6.64; N, 3.31.

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