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Preparation of tertiary alcohols and γ-lactones from allylsilanes and anhydrides†

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Summary – The $TiCl_4$-mediated reaction of allyltrimethylsilane and anhydrides yields alkyldiallylcarbinols. In the case of the diallylsilane 1,8-bis(trimethylsilyl)octa-2,6-diene and cyclic anhydrides, spiro-lactones resulting from a *gem*-diallylation are obtained with high stereoselectivity.

allylsilane / anhydride / dialkylation

Introduction

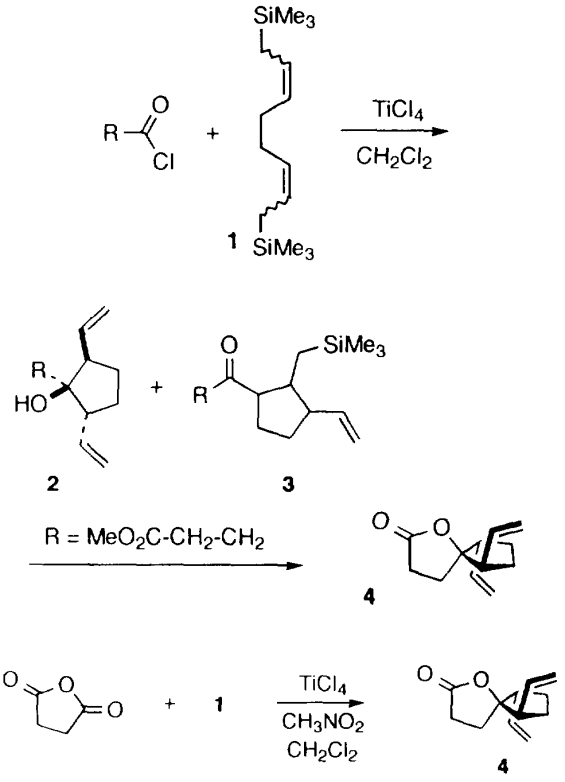
In 1995, Calas first showed that the electrophilic substitution of allylsilanes occurred with an allylic shift [1]. Twenty years later, Calas and Dunoguès demonstrated the regiospecificity of the acylation reaction by the report of a straightforward synthesis of artemisia ketone [2,3]. The *anti* stereospecificity of the reaction was later confirmed by Kumada [4]. The acylation reaction of allylsilanes is now part of the standard synthetic repertoire [5-9].

In 1988, we began the development of the chemistry of 1,8-bis(trimethylsilyl)octa-2,6-diene (BISTRO) **1** for the stereoselective preparation of potentially useful synthetic units [10]. We previously showed that the acylation of **1** with acyl chlorides led to a mixture of (*dl*)-1-alkyl-2,5-divinyl-cylopentanols **2** and cyclopentylketones **3** or the spiro-γ-lactone **4** [11-13]. Compounds **2** and **4** are highly valuable in the synthesis of various substituted steroids or tetracyclic triterpenoids.

Acylation of allylsilanes with anhydrides has received little attention from fundamental and synthetic points of views [5,6,14-16]. We have shown that treatment of succinic anhydride with **1** in the presence of $TiCl_4$ and 4 equiv of nitromethane leads to **4** in a straightforward manner. The yield and the diastereoselectivity of the reaction are both excellent since the only *dl*-isomer is isolated in a 78% yield.

Encouraged by this result, we decided to condense allyltrimethylsilane and acetic anhydride. Tertiary alcohol **5** resulting from a twofold addition of an allyl group was isolated in a fair yield of 59% (alcohol **5** has previously been obtained in 90% yield by addition of allyl Grignard reagent to ethyl acetate [17]).

Using the same procedure, the bis allylic γ-lactone **6** was prepared by reaction of allyltrimethylsilane and succinic anhydride (68% yield). When the reaction is carried out without nitromethane as a co-solvent, **6** is isolated in only 56% yield and a minor spirocyclic compound **7** (one isomer) is detected (11% yield).



† This article is dedicated to Professor Calas, in recognition of his outstanding research in organosilicon chemistry.

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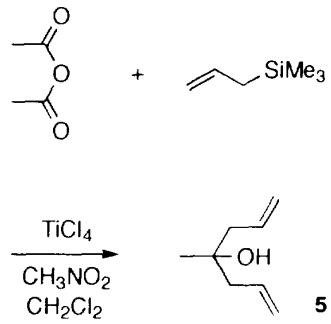
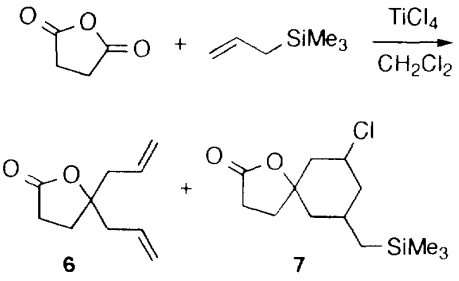
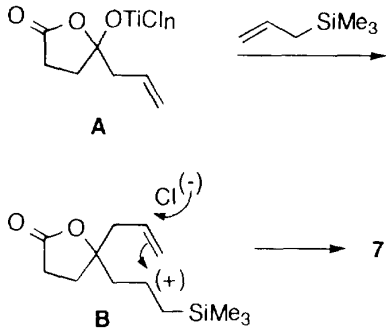


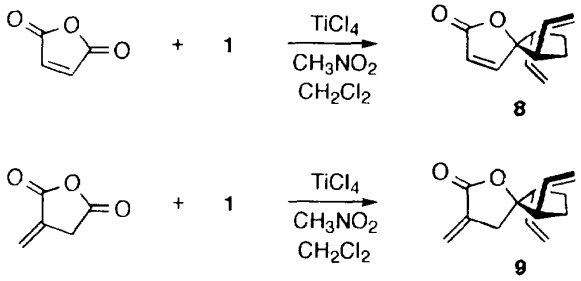


Compound **7** obviously arises from a participation reaction. We assume that the initial addition of allyltrimethylsilane to succinic anhydride affords the intermediate **A**. The second allyltrimethylsilane addition leads to the β-silyl carbocation **B**, which is set up to undergo a carbocationic cyclization process as depicted below :



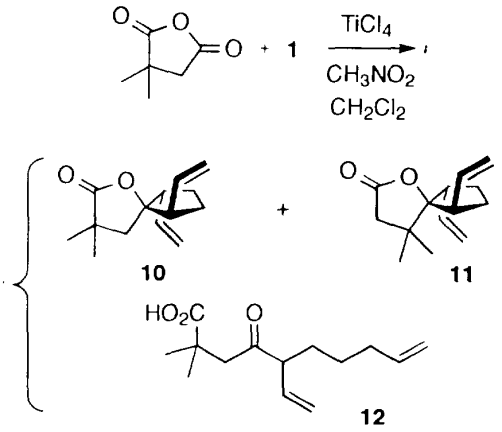
In order to extend the scope and limitations of the spirolactone formation, other anhydrides were tested in this reaction. High diastereoselectivity was also achieved with unsaturated cyclic compounds such as maleic anhydride or itaconic anhydride (methylenesuccinic anhydride). Unfortunately, the yields dramatically decrease to 26 and 13% yields for spirolactones **8** and **9** respectively (the other compounds are hydroxy and keto acids).

Dialkylation of 2,2-dimethylsuccinic anhydride leading to lactone **10** was obtained with high regioselectivity (**10**/**11** = 20:1) but in a 50% moderate yield. Acyclic ketoacid **12** was obtained as a byproduct from

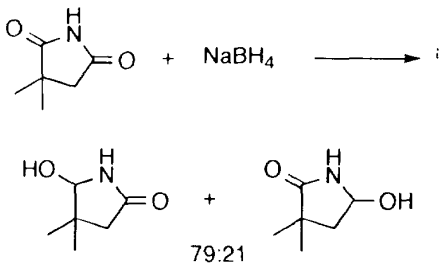


a monoalkylation process followed by a protolysis of the second allylsilane moiety (23% yield).

The stereochemistry of compounds **4** and **8**-**11** is deduced from presence of differents signals for vinyl groups in ^{13}C and ^{1}H NMR spectra.

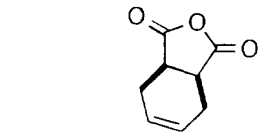


The high regioselectivity results from the addition to the less hindered carbonyl group. However, Speckamp has shown that the borohydride reduction of *gem*-disubstituted succinimides takes place preferentially at the seemingly more hindered carbonyl adjacent to the *gem* substituents. This remarkable regioselectivity was attributed to the reactant following a trajectory that is above, but not perpendicular to, the plane of the ring [18].



Comparison with our results suggests that addition of diallylsilane **1** to 2,2-dimethylsuccinic anhydride in the presence of $TiCl_4$ is dependent on several combined factors.

Substitution in the α- and β-position of succinic anhydride modifies the stereochemistry of the reaction. For instance, compound **13** led to the expected lactones **14** and **15** (inseparable mixture in 2:3 ratio, 35% yield) along with the unexpected lactone **16** (21% yield) in which the two vinyl groups are both on the same side of the spirolactone as the oxygen atom.



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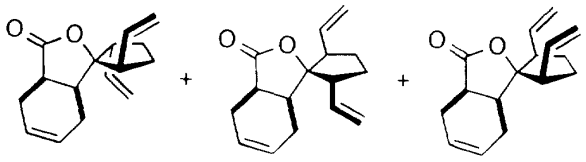
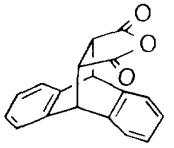
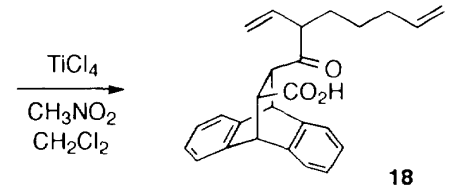


14 **15** **16**

The reaction of **1** with the Diels-Alder adduct **17** did not lead to the expected diallyllactone. Effectively, the presence of a very hindered face dramatically reduces the reactivity of this anhydride. Ketoacid **18**, which arises from a monoalkylation process followed by a protolysis, was the only compound isolated in 11% yield from the reaction mixture. In contrast, reaction of **17** with allyltrimethylsilane led to the dialkylated lactone **19** in a fair yield 54%.

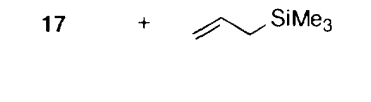


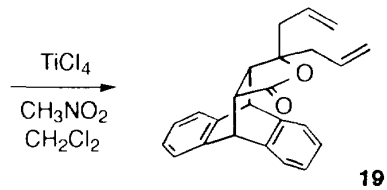
17



18

Many desirable natural products contain γ-lactone moieties. These act as, for example, natural flavor components, pheromones [19] or lignans [20]. On the other hand, over the past decades, the problem of the five-membered ring construction has appeared in various guises due to its presence in numerous natural product series. Addition of BISTRO to cyclic anhydrides represents a solution for both of these challenges.





19

Experimental section

General

All reactions were run under argon in oven-dried glassware. TLC was performed on silica gel 60 F_{254}. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions at 200 and 50 MHz respectively. Carbon-proton couplings were determined using DEPT sequence experiments [21]. Diastereoselectivity was determined by GC or ^1H NMR analyses prior to any purification. CH_2Cl_2 was distilled over P_2O_5. BISTRO was prepared according to a previously described procedure [10].

Representative procedure for the addition of allylsilanes to anhydrides

A three-necked flask equipped with a thermometer, septum cap, magnetic stirring bar, and argon outlet was charged with anhydrous CH_2Cl_2 (15 mL) and anhydrous nitromethane (2.2 mL, 40 mmol). The solution was cooled to $-60°C$, $TiCl_4$ was added (2.3 mL, 20 mmol) and then anhydride (10 mmol) in CH_2Cl_2 (2 mL). After 15 min of stirring at $-70°C$, the solution was cooled to $-90°C$ and BISTRO (2.79 g, 11 mmol) or allyltrimethylsilane (2.39 mL, 21 mmol) in CH_2Cl_2 (3 mL) was added over 10 min. The resulting solution was warmed to $-60°C$ and stirred for 15 h. The reaction was quenched by addition of aqueous saturated NH_4Cl solution (20 mL) and extracted with CH_2Cl_2 (3×15 mL). The extracts were washed until neutrality, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by chromatography on silica gel, eluted with a gradient of pentane/ether.

• *(dl)-6,9-Divinyl-1-oxaspiro[4.4]nonan-2-one* **4**

Using the procedure described above, reaction of 1.0 g of succinic anhydride and BISTRO gave 1.50 g (78% yield) of **4** after purification.

4 IR 1 774, 1 638, 1 234 cm^{-1}.

^1H NMR ($CDCl_3$) δ 5.85 (2H, m), 5.05 (4H, m), 2.75 (1H, dd, J = 7.6, 4.1 Hz), 2.48 (1H, m), 2.48 (2H, m), 2.22-1.66 (6H, m).

^{13}C NMR ($CDCl_3$) δ 176.4 (s), 138.2 (d), 135.9 (d), 118.3 (t), 116.9 (t), 97.1 (s), 53.4 (d), 53.1 (d), 29.1 (t), 28.9 (t), 28.8 (t), 26.7 (t).

• *4-Methylhepta-1,6-dien-4-ol* **5**

Using the procedure described above, reaction of 0.945 mL of acetic anhydride and allyltrimethylsilane gave 0.74 g (59% yield) of **5** after purification [17].

5 IR 3 409, 1 644, 1 157 cm^{-1}.

^1H NMR ($CDCl_3$) δ 5.93-5.72 (2H, m), 5.12-5.02 (4H, m), 2.19 (4H, d, J = 7.4 Hz), 1.13 (3H, s).

^{13}C NMR ($CDCl_3$) δ 133.9 (d)(2C), 118.7 (t)(2C), 77.1 (s), 46.19 (t)(2C), 26.7 (q).

• *5,5-Diprop-2-enyldihydrofuran-2(3H)-one* **6**

Using the procedure described above, reaction of 1.0 g of succinic anhydride and allyltrimethylsilane gave 1.08 g (68% yield) of **6** after purification.

6 IR 1 772, 1 191 cm^{-1}.

^1H NMR ($CDCl_3$) δ 5.66 (2H, ddt, J = 18.4, 8.9, 7.3 Hz), 5.08-4.99 (4H, m), 2.42 (2H, t, J = 8.55 Hz), 2.34-2.26 (4H, m), 1.95 (2H, t, J = 8.55 Hz).

^{13}C NMR ($CDCl_3$) δ 176.3 (s), 131.4 (d)(2C), 119.5 (t)(2C), 86.7 (s), 43.1 (t)(2C), 28.8 (t), 28.6 (t).

• *7-Chloro-9-[(trimethylsilyl)methyl]-1-oxaspiro-[4.5] decan-2-one* **7**

Using the procedure described above, but without nitromethane, reaction of 1.0 g of succinic anhydride and allyltrimethylsilane gave 0.93 g (56% yield) of **6** and 0.30 g (11% yield) of **7** after purification.

7 M p 63°C.

IR (film) 1 780, 1 549, 764 cm^{-1}

^1H NMR ($CDCl_3$) δ 4.40 (1H, m), 2.54 (2H, t, J = 8.35 Hz), 2.37 (1H, m), 2.25 (1H, m), 2.09 (1H, m), 1.97 (2H, t, J = 8.35 Hz), 1.92 (1H, m), 1.89 (1H, m), 1.43 (1H, m), 1.19 (1H, m), 0.49 (2H, m), 0.01 (9H, s).

^{13}C NMR ($CDCl_3$) δ 176.3 (s), 84.7 (s), 54.9 (d), 46.7 (t), 42.7 (t), 42.5 (t), 35.1 (t), 28.0 (t), 24.6 (d), 24.1 (t), −0.49 (q).

• *(dl)-6,9-Divinyl-1-oxaspiro[4.4]non-3-en-2-one* **8**

Using the procedure described above, reaction of 0.98 g of maleic anhydride and BISTRO gave 0.254 g (26% yield) of **8** after purification.

8 IR (film) 1 756, 1 639, 921 cm^{-1}

^1H NMR ($CDCl_3$) δ 7.21 (1H, d, J = 5.63 Hz), 6.04 (1H, d, J = 5.63 Hz), 5.63 (2H, m), 5.05 (4H, m), 2.83 (1H, m), 2.75 (1H, m), 2.22-1.66 (4H, m).

^{13}C NMR ($CDCl_3$) δ 171.7 (s), 156.8 (d), 137.1 (d), 133.5 (d), 121.3 (d), 118.0 (t), 116.4 (t), 98.9 (s), 53.1 (d), 50.0 (d), 29.7 (t), 29.0 (t).

Anal calc for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found : C, 75.47; H, 7.56.

• *(dl)-3-Methylene-6,9-divinyl-1-oxaspiro[4.4]nonan-2-one* **9**

Using the procedure described above, reaction of 1.12 g of itaconic anhydride and BISTRO gave 0.145 g (13% yield) of **9** after purification.

9 IR 1 762, 1 639, 1 267 cm^{-1}.

^1H NMR ($CDCl_3$) δ 6.13 (1H, t, J = 2.75 Hz), 5.69 (2H, m), 5.52 (1H, m), 5.09 (4H, m), 2.97 (1H, 1/2AB, t, J = 17.5, 2.75 Hz), 2.63 (1H, 1/2AB, t, J = 17.5, 2.75 Hz), 2.8-2.57 (2H, m), 2.22-1.66 (4H, m).

^{13}C NMR ($CDCl_3$) δ 171.7 (s), 138.1 (d), 135.3 (s), 135.1 (d), 121.4 (t), 118.0 (t), 116.4 (t), 93.7 (s), 53.3 (d), 53.0 (d), 32.5 (t), 28.4 (t), 28.3 (t).

Anal calc for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found : C, 76.58; H, 8.15.

• *(dl)-3,3-Dimethyl-6,9-divinyl-1-oxaspiro[4.4]nonan-2-one* **10**, *(dl)-4,4-dimethyl-6,9-divinyl-1-oxaspiro-[4.4] nonan-2-one* **11** *and 2,2-dimethyl-4-oxo-5-vinyldec-9-enoic acid* **12**

Using the procedure described above, reaction of 1.28 g of 2,2-dimethylsuccinic anhydride and BISTRO gave 0.614 g (48% yield) of **10**, 0.025 g (2%) of **11** and 0.510 g (23% yield) of **12** after purification.

10 IR 1 766, 1 238 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$) δ 5.62-5.37 (2H, m), 5.04-4.87 (4H, m), 2.63 (1H, td, J = 8.6, 2.5 Hz), 2.21 (1H, q, J = 9.0 Hz), 2.07 (1H, 1/2 AB, J = 13.6 Hz), 1.76 (1H, 1/2 AB, J = 13.6 Hz), 1.90-1.25 (4H, m), 1.12 (3H, s), 1.07 (3H, s).

^{13}C NMR ($CDCl_3$) δ 181.0 (s), 138.4 (d), 135.5 (d), 118.0 (t), 116.3 (t), 92.9 (s), 53.2 (d), 52.2 (d), 39.5 (s), 38.5 (t), 28.3 (t), 27.7 (t), 26.0 (q), 25.4 (q).

Anal calc for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found : C, 76.28; H, 9.26.

11 IR 1 769, 1 212 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$) δ 5.81 (1H, dt, J = 17.04, 9.82 Hz), 5.76 (1H, dt, J = 17.2, 9.57 Hz), 5.22-4.98 (4H, m), 2.95 (1H, q, J = 9.57 Hz), 2.85 (1H, dd, J = 9.4, 7.5 Hz), 2.72 (1H, 1/2 AB d, J = 17.1, 0.87 Hz), 2.05 (1H, 1/2 AB, J = 17.1 Hz), 2.10-1.40 (4H, m), 1.19 (3H), 1.16 (3H).

^{13}C NMR ($CDCl_3$) δ 176.2 (s), 138.3 (d), 137.0 (d), 117.7 (t), 116.5 (t), 95.1 (s), 51.8 (d), 47.9 (d), 46.2 (t), 40.5 (s), 29.1 (t), 28.5 (t), 25.4 (q), 21.7 (q).

12 IR (neat) 3 500-2 500, 1 787, 1 226, 1 018, 913 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$) δ 5.82-5.48 (2H, m), 5.10-4.86 (4H, m), 2.97 (1H, m), 2.78-2.71 (2H, m), 1.96 (2H, m), 2.00-1.20 (4H, m), 1.17 (3H, s), 1.15 (3H, s).

^{13}C NMR ($CDCl_3$) δ 208.5 (s), 184.0 (s), 138.2 (d), 136.0 (d), 118.1 (t), 114.7 (t), 57.4 (d), 50.7 (t), 39.6 (s), 34.4 (t), 30.0 (t), 26.1 (t), 25.4 (q), 25.1 (q).

• *(2S*,5S*,3'aR*,7'aS*)-2,5-Divinyl-3'a,4',7',7'a-tetrahydrospiro[cyclopentane-1,1'-isobenzofuran]-3(1H)-one* **14** *and (2R*,5R*,3'aR*,7'aS*)-2,5-divinyl-3'a,4',7',7'a-tetrahydrospiro[cyclopentane-1,1'-isobenzofuran]-3(1H)-one* **15** *and (2S*,5R*,3'aR*,7'aS*)-2,5-dimethyl-3'a,4',7',7'a-tetrahydrospiro[cyclopentane-1.1'-isobenzofuran]-3(1H)-one* **16**

Using the procedure described above, reaction of 1.52 g of *cis*-1,2,3,6-tetrahydrophtalic anhydride and BISTRO gave 0.53 g (35% yield) of **14** and **15**, and 0.319 g (21% yield) of **16** after purification.

14 and **15**. IR 1 769, 1 216, 1 173, 921, 674 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$) δ 5.89-5.52 (2H, m), 5.16-4.80 (4H, m), 2.81 (1H, dt, J = 6.7, 3.0 Hz), 2.64 (2H, m), 2.20 (1H, dt, J = 7.3, 3.0 Hz), 2.12 (4H, m), 2.04-1.50 (5H, m).

^{13}C NMR ($CDCl_3$) δ 178.9 and 178.3 (s), 137.8 and 137.4 (d), 137.2 and 136.0 (d), 127.1 and 125.8 (d), 125.3 and 124.8 (d), 117.6 and 116.5 (t), 115.6 and 115.4 (t), 95.9 and 95.8 (s), 56.0 and 54.2 (d), 49.3 and 48.2 (d), 39.6 and 38.5 (t), 37.6 and 37.1 (t), 30.8 and 30.7 (d), 28.8 and 28.5 (d), 22.75 and 22.7 (t), 22.2 and 21.7 (t).

Anal calc for $C_{16}H_{20}0_2$: C, 76.65; H, 8.25. Found : C, 76.57; H, 8.30.

16 IR 1 767, 1 265, 738 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$) δ 5.92-5.72 (2H, m), 5.65 (2H, t, J = 2.5 Hz), 5.21-5.02 (4H, m), 3.31 (1H, tm, J = 9.0 Hz), 2.87 (1H, t, J = 7.7 Hz), 2.74 (1H, q, J = 9.3 Hz), 2.49-2.13 (4H, m), 2.07-1.87 (2H, m), 1.75-1.23 (3H, m).

^{13}C NMR ($CDCl_3$) δ 164.3 (s), 129.3 (d), 128.8 (d), 118.2 (d), 118.1 (d), 111.6 (t), 111.4 (t), 95.3 (s), 55.5 (d), 54,6 (d), 44.3 (t), 43.2 (t), 36.4 (d), 34.9 (d), 30.6 (t), 30.0 (t).

• *12-(2-Vinylheptanoyl)-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic acid* **18**

Using the procedure described above, reaction of 2.76 g of adduct **17** and BISTRO gave 0.409 g (11% yield) of **18** after purification.

18 IR 3 420, 1 745, 1 641, 1 050 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$) δ 7.39-7.07 (8H, m), 5.90-5.55 (2H, m), 5.28-5.03 (4H, m), 4.67 (1H, d, J = 4.10 Hz), 4.48 (1H, d, J = 2.25 Hz), 3.37 (1H, dd, J = 9.61, 4.10 Hz), 2.78-2.52 (3H, m), 2.28 (2H, d, J = 7.18 Hz).

^{13}C NMR ($CDCl_3$) δ 175.4 (s), 144.1 (s), 141.8 (s), 141.4 (s), 139.7 (s), 132.5 (d), 131.0 (d), 126.63 (d), 126.56 (d), 126.4 (d), 126.3 (d), 125.9 (d), 125.4 (d), 124.4 (d), 123.3 (d), 121.0 (t), 119.3 (t), 87.3 (s), 49.1 (t), 48.8 (t), 45.4 (d), 45.1 (d), 38.1 (d).

• *14,14-Diallyl-9,10,14,15-tetrahydro-9,10[3',4'] furanoanthracen-12(11H)-one* **19**

Using the procedure described above, reaction of 2.76 g of adduct **17** and allyltrimethylsilane gave 1.85 g (54% yield) of **19** after purification.

19 IR 1 755, 1 208, 929, 744 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$) δ 7.36-7.26 (4H, m), 7.19-7.07 (4H, m), 5.90-5.54 (2H, m), 5.28-5.03 (4H, m), 4.67 (1H, d, J = 4.10 Hz), 4.48 (1H, d, J = 2.25 Hz), 3.37 (1H, dd, J = 9.63, 4.10 Hz), 2.78-2.52 (2H, m), 2.64 (1H, dd, J = 9.63, 2.25 Hz), 2.28 (2H, d, J = 7.18 Hz).

^{13}C NMR ($CDCl_3$) δ 175.4 (s), 144.1 (s), 141.8 (s), 141.4 (s), 139.7 (s), 132.5 (d), 131.0 (d), 126.6 (d), 126.5 (d), 126.4 (d), 126.3 (d), 125.9 (d), 125.4 (d), 124.4 (d), 123.3 (d), 120.9 (t), 119.3 (t), 87.3 (q), 49.1 (t), 48.8 (t), 45.4 (d), 45.2 (d), 45.1 (d), 38.1 (d).

Anal calc for $C_{24}H_{22}O_2$: C, 84.18; H, 6.24. Found : C, 84.27; H, 6.18.

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