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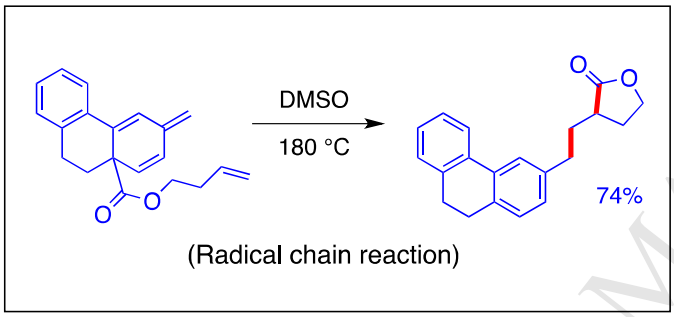
Graphical abstract



Methoxycarbonyl Migration in 3-Methylene-1,4-cyclohexadienes. An Extension of the von Auwers Rearrangement.

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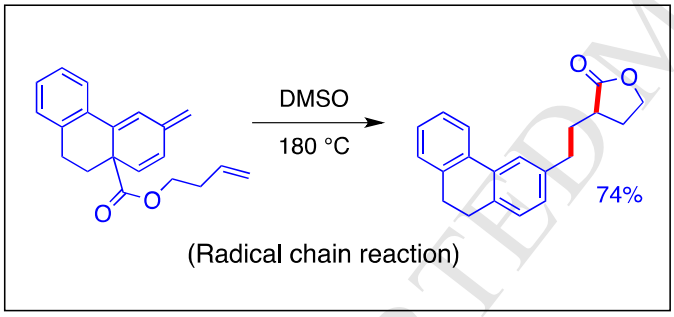
† This article is dedicated to Prof. Neil Garg, recipient of the 2015 Tetrahedron Young Investigator award

Abstract: Upon heating, 3-methylene-1,4-cyclohexadienes possessing an alkoxycarbonyl substituent in position 6 undergo rearrangement and concomitant aromatization to give the corresponding arylacetates. This transformation represents a modification of the von Auwers rearrangement and proceeds by a radical chain mechanism. The intermediate alkoxycarbonyl radical can be intercepted allowing further useful synthetic variations.



Keywords: von Auwers rearrangement; radical chain; aromatics.

1 Introduction

In connection with an industrial project, we required a concise synthesis of aromatic structures related to compounds **1**-**3**. These belong to a family of potent antagonists of specific receptors of human thromboxane A2, a ~~most~~ powerful inducer of platelet aggregation, bronchoconstriction and vasoconstriction. Ramatroban, for example, has found

clinical use against allergic rhinitis and asthma.[1] Our task was to devise an original route to Terutroban and analogs thereof.

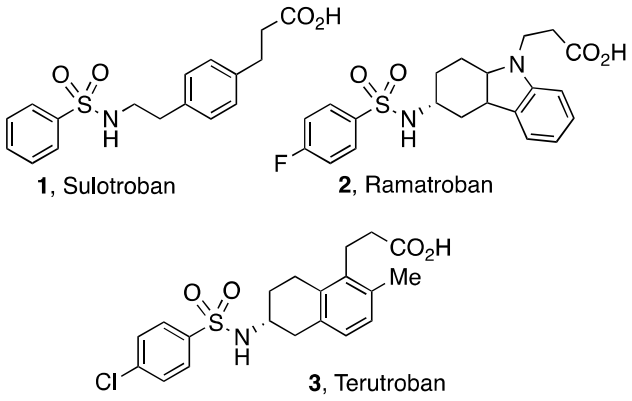
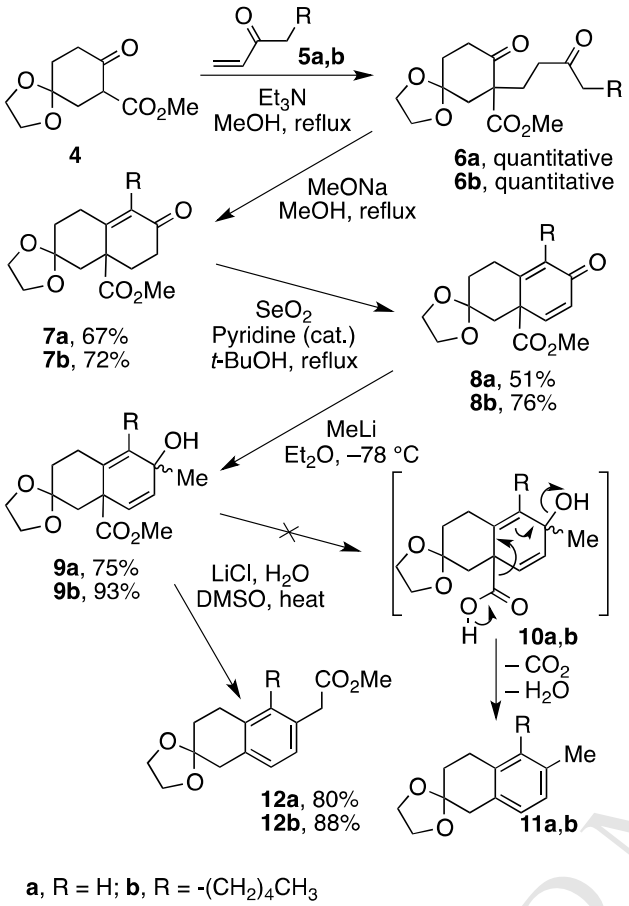


Figure 1. Examples of antagonists of thromboxane A2 receptors.

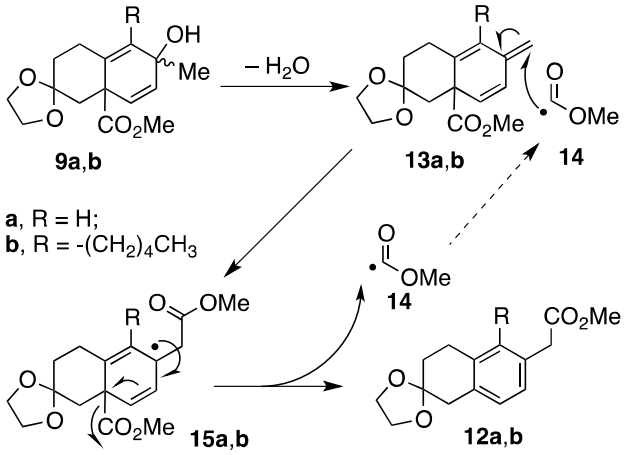
One promising route to the Terutroban family, outlined in Scheme 1, relied on a classical Robinson annelation between ketoester **4** and enones **5a**,**b**. The Michael addition leading to the corresponding adducts **6a**,**b** could be induced with triethylamine in methanol and proceeded smoothly and quantitatively. The ring-closing aldol and crotonization were accomplished with sodium methylate. The resulting cyclohexenones **7a**,**b** were next dehydrogenated by oxidation with selenium dioxide into the corresponding cyclohexadienones **8a**,**b** followed by addition of methylithium to give dienols **9a**,**b** in acceptable, non-optimized overall yield. The subsequent key step in the sequence called for a Krapcho-type cleavage of the methyl ester[2] and concomitant decarboxylation and aromatisation by elimination of a water molecule (**9a**,**b** → **10a**,**b** → **11a**,**b**). Heating **9a** or **9b** with lithium chloride in DMSO resulted in a clean transformation; however, the product, isolated in good yield in either case, was neither **11a** nor **11b**. The spectroscopic data indicated the structures to be **12a** and **12b**, respectively. An nmr experiment in deuterated DMSO indicated that lithium chloride is not necessary and that elimination of water starts taking place at around 75 °C, but the rearrangement only starts at temperatures higher than 110 °C.



Scheme 1. An unexpected von Auwers rearrangement.

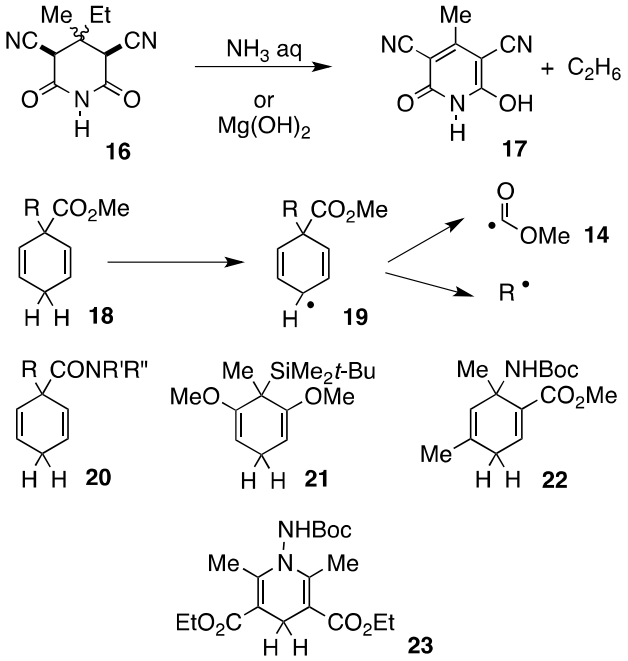
2 Results and Discussion

The most plausible mechanistic pathway for this transformation is displayed in Scheme 2 and involves a radical chain process that sets in after a dehydration step leading to triene intermediates **13a**,**b**. Thermolysis leads to the formation of a small amount of methoxycarbonyl radicals **14** which initiate the addition-fragmentation chain reaction.



Scheme 2. A radical chain mechanism.

Cleavage of a carbon-carbon bond in 1,4-cyclohexadienyl and related radicals is well precedented, even if the process has not received the attention it deserves from synthetic organic chemists. As early as 1897, Guareschi described the reaction that bears his name, whereby exposure of cyclic imide **16** to ammonia or magnesium hydroxide causes its gradual conversion into **17** with release of ethane gas (Scheme 3).[3] This transformation is believed to proceed via fragmentation of intermediate hydropyridinyl radical (c.f. all carbon analog **19**) to furnish an ethyl radical (an not the less stable methyl radical). Later, it was found that addition of radicals to aromatic rings is a reversible process, even for unstabilized radicals such as methyl or even aryl radicals.[4] This ready reversibility, due to the important energy gain when aromaticity is restored, is indeed the key element that allows benzene and other aromatic solvents to be used as media for many radical reactions. The reversible addition of radicals to aromatic solvents can nevertheless cause a considerable slowing down of the overall radical process.[5] More recently, Studer and Walton have exploited the aromatisation to generate carbon, nitrogen and silicon centered radicals from the appropriate 1,4-dihydrobenzene precursors (Scheme 3).[6]

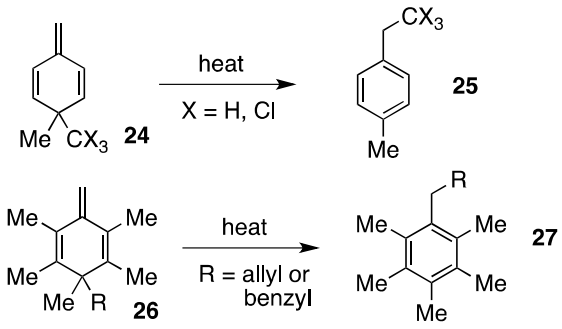


Scheme 3. Fragmentations of cyclohexadienyl and related radicals.

Thus, hydrogen atom abstraction from cyclohexadienes **18** generates radical **19**, which undergoes fragmentation to produce methoxycarbonyl radical **14**.[7] Precursors **18** are readily obtained through the Birch reduction but the competing generation of radical R• diminishes somewhat the synthetic utility of this approach. Walton and collaborators extended this strategy to the formation of carbamoyl radicals by starting with the amide analogs **20**.[8] Studer expanded this concept to organosilicon derivative **21**, a reagent allowing the convenient generation of silyl radicals which can then be engaged in various reactions typical of these species.[9] In yet another variation, Studer proposed derivatives **22** and **23** as sources of nitrogen centered radicals.[10] The latter, hydrazide based reagents are easily accessible and therefore particularly attractive.

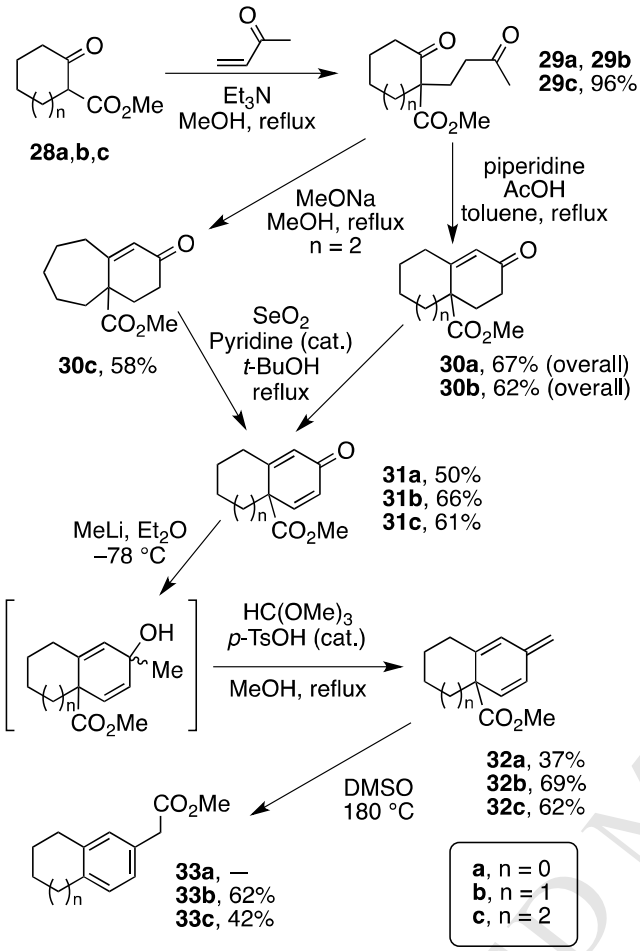
A closer analogy to our work is the rearrangement discovered by von Auwers at the turn of the 20th century. It concerns the isomerization of cylohexadienes **24** into aromatic derivatives **25**.[11] This transformation was initially thought to proceed by an ionic mechanism but, some 50 years later, evidence adduced first by Bird and Cookson and subsequently by a few other groups pointed firmly to a radical chain mechanism analogous to the one displayed in Scheme 2.[12] The rearrangement was also extended to allylic and benzylic groups by Miller and Lai in 1972 (Scheme 4, **26** → **27**),[12d] but, as far as we know, no isomerizations involving

alkoxycarbonyl groups have been described.



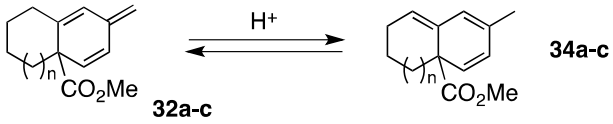
Scheme 4. Early examples of the von Auwers rearrangement.

We accidentally stumbled into this variation of the von Auwers rearrangement and, while it was ancillary to the initial purpose of accessing analogs of Terutroban **3**, we were curious to explore, even briefly, its scope and synthetic potential. We therefore prepared a series of similar substrates and examined their behavior. Five-, six-, and seven-membered ring ketoesters **28a-c** were thus subjected to the Robinson annelation sequence to give bicyclic enones **30a-c** (Scheme 5). In the case of the five- and six-membered Michael adducts **29a** and **29b**, heating with catalytic amounts of piperidine and acetic acid in refluxing toluene proved effective for the ring-closure, whereas the seven-membered ring congener **29c** required heating with sodium methylate in methanol. Dehydrogenation with selenium dioxide, addition of methyl lithium and dehydration gave a moderate overall yield of the corresponding key precursors **32a-c** for the von Auwers rearrangement. Disappointingly, heating **32a** in DMSO led mostly to decomposition, in contrast to **32b** and **32c** which furnished a reasonable yield of the rearranged products **33b** and **33c** respectively (Scheme 5).



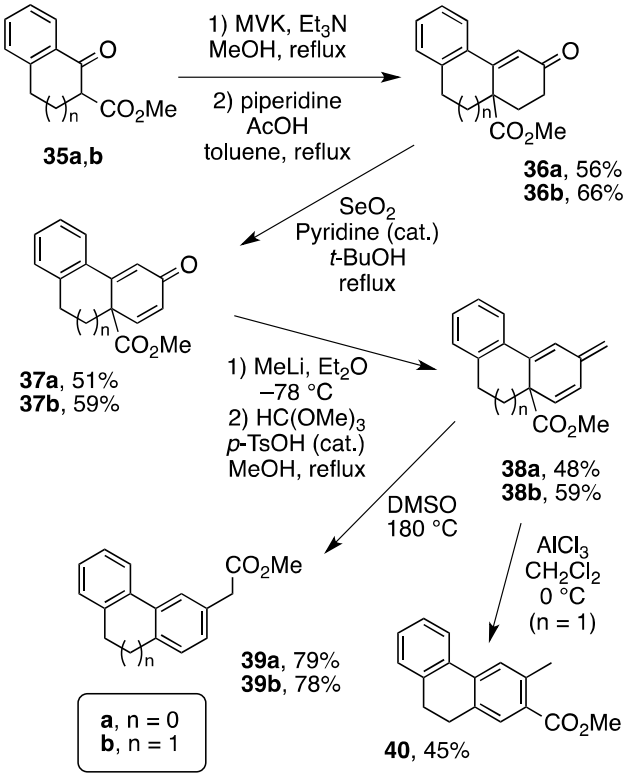
Scheme 5. Further examples of methoxycarbonyl migration.

The conditions for rearrangement could perhaps have been rendered milder by inducing the chain reaction at a lower temperature with the help of added radical initiators. This was not done in this case but it is certainly feasible (c.f. reaction in Scheme 9 below). We also noticed a complication arising from the propensity of compounds **32a-c**, and especially **32a**, to isomerize into compounds **34a-c** (Scheme 6). This occurred even upon standing in deuterated chloroform which had been filtered through a pad of alumina. Traces of acid and/or metallic salts could catalyze this process. Halogenated solvents are known to contain sometimes trace amounts of copper and iron salts. Isomers **34a-c** cannot obviously undergo the desired rearrangement.



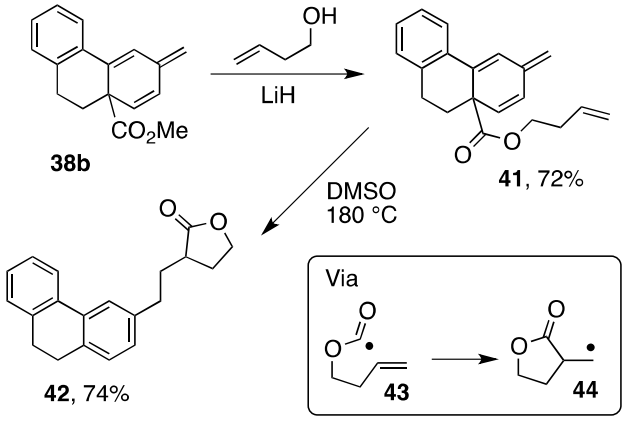
Scheme 6. Acid induced alkene shift.

With these considerations in mind, we next studied the rearrangement of substrates **38a** and **38b**, which cannot undergo the above isomerization. They were prepared by an identical sequence starting from aromatic ketoesters **35a** and **35b** (Scheme 7). We were pleased to find that heating compounds **38a** and **38b** in DMSO triggered the desired transformation leading to aromatized products **39a** and **39b** respectively in high yield. We made an interesting observation when we attempted to convert the ester group in **38b** into an amide and thus extend the von Auwers rearrangement to the amide series. All our attempts at accomplishing this transformation using a number of primary and secondary amines under typical aminolysis conditions failed, in all likelihood because of the congested environment of the tertiary ester group. In a last desperate essay, we tried to activate the ester with anhydrous aluminum trichloride in cold dichloromethane according to a procedure recommended by Wenkert and Liu.[13] A clean reaction ensued to give rearranged product **40** in nearly quantitative yield (Scheme 7). This reaction was complete in a few seconds and occurred in the presence or absence of the amine partner. The mechanism is presumably cationic, of the Friedel-Crafts type, but whether it is an intra- or inter-molecular process will have to be determined by further experimentation. Its generality also needs to be ascertained as, from a synthetic standpoint, it could serve as a convenient route to aromatic structures with unusual substitution patterns.



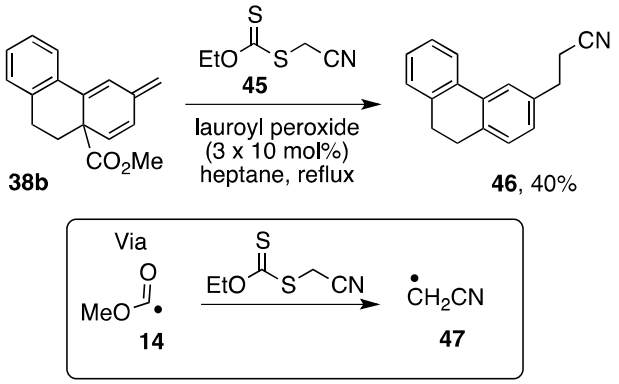
Scheme 7. Examples starting with aromatic ketoesters.

Transesterification proved easier to accomplish and, by exposing compound **38b** to 3-buten-1-ol in the presence of lithium hydride, we could convert the methyl ester into butenyl ester **41** in good yield (Scheme 8). Heating this substance in DMSO gave rise to lactone **42**, also in good yield. In this case, the alkoxycarbonyl radical intermediate **43** can cyclise into primary radical **44**,[14] which then undergoes addition on the more reactive exocyclic alkene in substrate **41**. This transformation illustrates some of the synthetic potential of the present rearrangement and further confirms the radical nature of the process.



Scheme 8. Example of lactone formation.

Finally, we performed the rearrangement in the presence of xanthate **45** as a radical relay (Scheme 9). The underlying assumption is that the methoxycarbonyl radical intermediate **14** will react with the radicophilic xanthate **45** to generate the more stable cyanomethyl radical **47**, and this in turn will react with substrate **38b** to give nitrile **46**. The reaction of cyanomethyl radical **47** with its xanthate precursor **45** is reversible and degenerate, and does not compete with the desired transformation.[15] In the event, heating a solution of compound **38b** and xanthate **45** in refluxing heptane in the presence of 3 x 10 mol% of lauroyl peroxide led to a 1:0.3 mixture of the desired product **46** and the "normal" von Auwers rearrangement product **39b**. These could not be separated easily by chromatography and the mixture was thus treated with methanolic potassium hydroxide at room temperature; this caused selective saponification of the latter and allowed clean separation from the former. In this manner, nitrile **46** was obtained in a modest but unoptimized 40% yield. The generality and scope of this variation remain to be determined by further experimentation but this promising preliminary result is very encouraging.



Scheme 9. Another variation on the von Auwers rearrangement.

3 Conclusion

In summary, we have described a synthetically useful variation on the venerable, but little known von Auwers rearrangement. Our results are preliminary and require a more systematic optimization of the experimental conditions and a better delineation of the substrate scope. There are also numerous conceivable modifications and extensions that have to be tested. Nevertheless, this study opens the way for interesting and unusual approaches to aromatic derivatives and it is hoped that it will encourage synthetic chemists to revisit this chemistry and explore its potential.

4 Experimental

4.1 General Experimental Methods

Purification procedures were in accordance with the instructions in D. D. Perrin and W. L. F. Armarego, "Purification of Laboratory Chemicals", Fourth Edition, The Bath Press, Bath, 2002. All reactions were carried out under dry, oxygen free nitrogen. Flash chromatography was performed on silica gel (SDS, 60 Å C. C. 40-63 mm) as the stationary phase. Thin Layer Chromatography (TLC) was performed on alumina plates pre-coated with silica gel (Merck silica gel, 60 F254), which were visualized by the quenching of UV fluorescence when applicable (λmax = 254 nm and/or 366 nm) and/or by staining with vanillin or anisadehyde in acidic ethanol followed by heating. Infrared spectra were recorded as solutions in CH_2Cl_2 using NaCl cells, on a Perkin-Elmer FT 2000. Absorption maxima (nmax) are reported in wavenumbers (cm^{-1}) and only selected peaks are reported. Magnetic resonance spectra were recorded at room temperature on a Bruker Avance DPX 400 instrument. Proton magnetic

resonance spectra (^{1}H NMR) were recorded at 400 MHz and coupling constants (J) are reported to ± 0.5 Hz. The following abbreviations were utilized to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintuplet, hex = hexuplet, hept = heptuplet, oct = octuplet and m = multiplet. Carbon magnetic resonance spectra (^{13}C NMR) were recorded in the same instrument at 100.6 MHz. Chemical shifts (δH, δC) are quoted in parts per million (ppm) and are referenced to TMS (0 ppm). Low-resolution mass spectra (m/z) were recorded by chemical ionization (CI/NH_3) on a Hewlett-Packard HP 5989B and only report molecular species ([M+H]+, [M+NH_4]+) and other major fragments. High-resolution mass spectra were recorded by positive electron impact ionization (EI+) at 70 e.V. on a JEOL JMS-GCmate II mass spectrometer. The quoted masses are accurate to ± 5 ppm. The names of the molecules that appear in the following pages were generated using either Beilstein AutoNom 2000 (CAS) or ChemBioDraw Ultra 11.0. Ketoesters **4**, **28a,b,c**, and **35a,b** were prepared by literature procedures.[16]

4.2 General procedures

4.2.1 General procedure for the preparation of methyl β-ketoesters

A solution of freshly distilled dimethyl carbonate (12 eq.) and ketone (1 eq.) in anhydrous THF (0.5 mL/mmol of ketone) was added to a suspension of NaH (60%wt, 1.4 eq., previously washed with *n*-pentane under nitrogen) in anhydrous THF (1 mL/mmol of ketone). The mixture was refluxed until starting ketone was totally consumed (about 3 h) then cooled to 0 °C and acetic acid (1.6 mL of a 10% aqueous solution per mmol of ketone) was added. The organic layer was separated and the aqueous phase further extracted with Et_2O. The combined organic layers were washed with saturated sodium hydrogen carbonate solution and brine, dried over magnesium sulfate, filtrated and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to yield the desired β-ketoester.

4.2.2 General procedure for the Michael addition and Robinson annulation

The vinyl ketone (2 eq.) was added to a solution of β-ketoester (1 eq.) in methanol (2 mL/mmol of β-ketoester). Triethylamine (0.3 eq.) was then added and the mixture was refluxed until the starting β-ketoester was totally consumed (1 to 3 h). The mixture was concentrated under reduced pressure and the resulting oil was purified by flash column chromatography on silica gel to yield the desired diketone.

Sodium methylate was prepared by dissolving sodium (2.5 eq.) in methanol (7 mL/mmol of diketone), and this solution was added to the diketone (1 eq.). The mixture was refluxed until the diketone was totally consumed (about 2 h). The solvent was removed under reduced pressure, Et_2O and water were then added, the organic layer was separated and the aqueous phase extracted

with Et_2O. The combined organic layers were washed with brine, dried over magnesium sulfate, filtrated and concentrated under reduced pressure to yield the desired enone.

4.2.3 General procedure for oxidation using selenium dioxide

A solution of the enone (1 eq.), selenium dioxide (2.4 eq.), and pyridine (1 drop/mmol of enone) in *t*-butanol (20 mL/mmol of enone) was stirred at reflux until the enone was totally consumed (24 to 48 h). The mixture was filtered over silica gel (elution with ethyl acetate), and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to yield the desired dienone.

4.3 Experimental Procedures and Spectroscopic Data

4.3.1 Methyl 8-Oxo-7-(3-oxo-butyl)-1,4-dioxa-spiro[4.5]decane-7-carboxylate (6a)

Following the general procedure for Michael addition, the reaction was carried out using ketoester **4** (3.63 g, 16.9 mmol) and methyl vinyl ketone (2.75 mL, 33.9 mmol) as Michael acceptor. Flash column chromatography (ethyl acetate-petroleum ether: 90-10 to 75-25) gave **6a** (4.81 g, quant.) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 4.06-3.91 (m, 4H), 3.73 (s, 3H), 3.09-2.97 (m, 1H), 2.72 (ddd, 1H, J = 4.8, 10.6, 16.0 Hz), 2.58 (d, 1H, J = 13.0 Hz), 2.47 (td, 1H, J = 4.2, 14.4 Hz), 2.23 (ddd, 1H, J = 5.1, 10.9, 16.2 Hz), 2.12 (s, 3H), 2.06-1.95 (m, 3H), 1.85-1.73 (m, 1H), 1.76 (d, 1H, J = 13.8 Hz). ^{13}C NMR (100 MHz; $CDCl_3$): δ_C 207.5, 207.1, 172.7, 106.5, 64.9, 64.3, 57.2, 52.3, 42.5, 38.9, 37.7, 35.3, 29.9, 28.9. IR (CCl_4): ν_{max} (cm^{-1}) 2954, 1751, 1732, 1164. HRMS (EI, m/z): calculated (found) for $C_{14}H_{20}O_6$, 284.1260 (284.1258).

4.3.2 Methyl 8-oxo-7-(3-oxo-octyl)-1,4-dioxa-spiro[4.5]decane-7-carboxylate (6b)

Following general procedure for Michael addition, the reaction was carried out using ketoester **4** (1.70 g, 7.94 mmol) and 2-octen-3-one (2.0 g, 15.9 mmol) as Michael acceptor. Flash column chromatography (ethyl acetate-petroleum ether: 90-10 to 75-25) gave **6b** (2.70 g, quant.) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 4.03-3.85 (m, 4H), 3.68 (s, 3H), 3.05-2.91 (m, 1H), 2.62 (ddd, 1H, J = 4.9, 10.9, 17.4 Hz), 2.53 (d, 1H, J = 13.9 Hz), 2.41 (td, 1H, J = 3.9, 14.5 Hz), 2.32 (t, 2H, J = 7.3 Hz), 2.15 (m, 1H), 2.04-1.91 (m, 3H), 1.80-1.71(m, 1H), 1.72 (d, 1H, J = 13.9 Hz), 1.50 (q, 2H, J = 7.4 Hz), 1.31-1.14 (m, 4H), 0.83 (t, 3H, J = 7.0 Hz). ^{13}C NMR (100 MHz; $CDCl_3$): δ_C 209.8, 206.9, 172.6, 106.4, 64.8, 64.2, 57.2, 52.2, 42.7, 42.4, 37.8, 37.6, 35.2, 31.3, 28.8, 23.4, 22.3, 13.8. IR (CCl_4): ν_{max} (cm^{-1}) 2958, 1751, 1728, 1160. HRMS (EI, m/z) calculated (found) for $C_{18}H_{28}O_6$, 340.1886 (340.1886).

4.3.3 Methyl 6'-Oxo-4',6',7',8'-tetrahydro-3'H-spiro[[1,3]dioxolane-2,2'-naphthalene]-8'a-carboxylate (7a)

Following general procedure for Robinson annulation, the reaction was carried out starting with diketone **6a** (4.32 g, 15.2 mmol) and gave crude **7a** (2.71 g, 67%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.97 (s, 1H), 4.05-3.83 (m, 4H), 3.73 (s, 3H), 2.96-2.84 (m, 1H), 2.61 (dd, 1H, J = 2.7, 13.7 Hz), 2.52-2.44 (m, 1H), 2.38-2.28 (m, 2H), 2.25-2.14 (m,1H), 1.97-1.72 (m, 3H), 1.51 (d, 1H, J = 13.7 Hz). ^{13}C NMR (100 MHz; $CDCl_3$): δ_C 198.3, 173.9, 160.3, 127.2,

107.0, 64.7, 64.3, 52.6, 48.4, 43.9, 35.8, 34.8, 34.4, 31.6. IR (CCl_4): ν_{max} (cm^{-1}) 2953, 1736, 1684, 1223. HRMS (EI, m/z) calculated (found) for $C_{14}H_{18}O_5$, 266.1154 (266.1161).

4.3.4 Methyl 5'-butyl-6'-oxo-4',6',7',8'-tetrahydro-3'H-spiro[[1,3]dioxolane-2,2'-naphthalene]-8'a-carboxylate (7b)

Following the general procedure for the Robinson annulation, the reaction was carried out starting with diketone **6b** (2.00 g, 5.88 mmol) and gave crude **7b** (1.36 g, 72%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 4.06-3.85 (m, 4H), 3.71 (s, 3H), 2.94-2.85 (m, 1H), 2.70-2.63 (m, 1H), 2.58 (dd, J = 3.0, 13.7 Hz, 1H), 2.48-2.30 (m, 3H, CH 10), 2.29-2.14 (m, 2H), 1.94-1.82 (m, 2H, CH-5), 1.77-1.68 (m, 1H), 1.54 (d, 1H, J = 13.7 Hz), 1.38-1.24 (m, 4H), 0.90 (t, 3H, J = 6.2 Hz). ^{13}C NMR (100 MHz; $CDCl_3$): δ_C 197.5, 174.6, 153.0, 136.8, 106.9, 64.6, 64.2, 52.4, 49.1, 44.5, 35.3, 34.8, 34.7, 31.4, 26.9, 25.1, 22.7, 14.0. IR (CCl_4): ν_{max} (cm^{-1}) 2958, 1742, 1675, 1220. HRMS (EI, m/z) calculated (found) for $C_{18}H_{26}O_5$, 322.1780 (322.1782).

4.3.5 Methyl 6'-oxo-4',6'-dihydro-3'H-spiro[[1,3]dioxolane-2,2'-naphthalene]-8'a-carboxylate (8a)

Following the general procedure for oxidation with selenium dioxide, the reaction was carried out starting with enone **7a** (2.71 g, 10.2 mmol). Purification by flash column chromatography (petroleum ether-ethyl acetate: 80-20) gave dienone **8a** (1.36 g, 51%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.74 (d, 1H, J = 9.8 Hz), 6.30-6.24 (m, 2H, CH-2), 4.08-3.90 (m, 4H), 3.73 (s, 3H), 3.02 (tdd, 1H, J = 1.5, 5.3, 14.1 Hz), 2.77 (dd, 1H, J = 3.0, 13.4 Hz), 2.53 (ddd, 1H, J = 2.2, 4.8, 14.0 Hz), 1.93 (ddt, 1H, J = 2.6, 5.3, 12.7 Hz), 1.75 (td, 1H, J = 4.9, 14.1 Hz), 1.52 (d, 1H, J = 13.4 Hz). ^{13}C NMR (100 MHz; $CDCl_3$): δ_C 185.7, 170.1, 158.7, 147.7, 129.4, 127.0, 107.2, 64.9, 64.3, 53.1, 52.0, 42.3, 35.8, 31.6. IR (CCl_4): ν_{max} (cm^{-1}) 2954, 2887, 1737, 1671. HRMS (EI, m/z) calculated (found) for $C_{14}H_{16}O_5$, 264.0998 (264.099).

4.3.6 Methyl 5'-butyl-6'-oxo-4',6'-dihydro-3'H-spiro[[1,3]dioxolane-2,2'-naphthalene]-8'a-carboxylate (8b)

Following the general procedure for oxidation with selenium dioxide, the reaction was carried out starting with enone **7b** (530 g, 1.64 mmol). Purification by flash column chromatography (petroleum ether-ethyl acetate: 80-20) gave dienone **8b** (400 mg, 76%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.67 (d, 1H, J = 9.8 Hz), 6.28 (d, 1H, J = 9.8 Hz), 4.09-3.92 (m, 4H), 3.71 (s, 3H), 3.02 (ddd, 1H, J = 2.8, 4.5, 14.3 Hz), 2.75 (td, 1H, J = 4.8, 14.7 Hz), 2.75 (d, 1H, J = 13.4 Hz), 2.57-2.41 (m, 2H), 1.97-1.89 (m, 1H), 1.66 (ddd, 1H, J = 4.7, 12.9, 14.3 Hz), 1.51 (d, 1H, J = 13.4 Hz), 1.41-1.28 (m, 4H), 0.91 (t, 3H, J = 7.0 Hz). ^{13}C NMR (100 MHz; $CDCl_3$): δ_C 185.0, 170.7, 151.9, 146.7, 136.9, 129.2, 107.3, 64.8, 64.2, 52.9, 52.0, 42.5, 35.7, 31.6, 22.7, 26.7, 24.7, 14.0. IR (CCl_4): ν_{max} (cm^{-1}) 2963, 2872, 1728, 1674. HRMS (EI, m/z) calculated (found) for $C_{18}H_{24}O_5$, 320.1624 (320.1624).

4.3.7 Methyl 6'-hydroxy-6'-methyl-4',6'-dihydro-3'H-spiro[[1,3]dioxolane-2,2'-naphthalene]-8'a-carboxylate (9a)

To a solution of dienone **8a** (833 mg, 3.2 mmol) in Et_2O (12.5 mL) maintained at -78°C was slowly added ethereal methyllithium (1.2 M, 2.65 mL, 3.2 mmol). The mixture was stirred at –

78°C for 1 h then poured onto a saturated ammonium chloride solution, and the layers were separated. The aqueous layer was extracted with Et_2O and the combined organic layers were washed with brine, dried over magnesium sulfate, filtered and concentrated under reduced pressure. Purification by flash column chromatography (petroleum ether-ethyl acetate: 80-20) gave carbinol **9a** (662 mg, 75%) as colorless oil, consisting of an inseparable mixture of two diastereoisomers (dr = 85:15) which was used directly in the next step. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.26 (s, 1H), 6.73 (d, 1H, J = 8.2 Hz), 6.59 (d, 1H, J = 8.2 Hz), 4.03-3.99 (m, 4H), 2.94-2.89 (m, 4H), 2.59 (t, 2H, J = 7.3 Hz), 1.94 (t, 2H, J = 6.9 Hz), 1.51-1.35 (m, 4H), 0.93 (t, 3H, J = 7.0 Hz). ^{13}C NMR (100 MHz; $CDCl_3$; major diastereoisomer): δ_C 173.0, 136.5, 133.2, 128.9, 128.6, 107.8, 65.6, 64.5, 64.0, 52.3, 48.5, 42.6, 36.4, 30.8, 28.8.

4.3.8 Methyl 5'-butyl-6'-hydroxy-6'-methyl-4',6'-dihydro-3'H-spiro[[1,3]dioxolane-2,2'-naphthalene]-8'a-carboxylate (9b) and olefin (13b)

To a solution of dienone **8b** (259 mg, 0.81 mmol) in Et_2O (3.5 mL) maintained at -78°C was slowly added ethereal methyllithium (1.2 M, 675 µL, 0.81 mmol). The mixture was stirred at -78°C for 1 h then poured onto a saturated ammonium chloride solution, and the layers were separated. The aqueous layer was extracted with Et_2O and the combined organic layers were washed with brine, dried over magnesium sulfate, filtered and concentrated under reduced pressure. Purification by flash column chromatography (petroleum ether-ethyl acetate: 80-20) gave **9b** (253 mg, 93%) as colorless oil, consisting of an inseparable mixture of 2 diastereoisomers, which rapidly evolved into a mixture with olefin **13b**. This carbinol was therefore used quickly in the next step. NMR data for olefin **13b** : ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.21 (d, 1H, J = 9.6 Hz), 5.56 (d, 1H, J = 9.6 Hz), 5.11 (s, 1H), 4.89 (s, 1H), 4.02-3.86 (m, 4H), 3.67 (s, 3H), 2.88-2.80 (m, 1H,), 2.67-2.55 (m, 1H), 2.58-2.47 (m, 1H), 2.44-2.37 (m, 1H), 1.86-1.78 (m, 1H), 1.67-1.57 (m, 1H), 1.52 (d, 1H, J = 13.3 Hz), 1.43-1.32 (m, 4H), 0.93 (t, 3H, J = 7.0 Hz). ^{13}C NMR (100 MHz; $CDCl_3$): δ_C 173.2, 137.9, 134.1, 131.0, 129.5, 129.4, 111.7, 107.7, 64.5, 64.0, 52.2, 51.3, 43.6, 36.2, 31.4, 22.9, 27.1, 25.7, 14.1.

4.3.9 Methyl (3',4'-dihydro-1'H-spiro[[1,3]dioxolane-2,2'-naphthalen]-6'-yl)-acetate (12a)

A solution of the diasteriomeric mixture of carbinols **9a** (36 mg, 0.13 mmol) in DMSO-d_6 (0.4 mL) was heated at 180°C for 1 h. The mixture was cooled to room temperature, and without concentration, purification by flash column chromatography (petroleum ether-ethyl acetate: 90-10) gave rearranged product **12a** (27 mg, 80%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.06-6.98 (m, 3H), 4.05-4.00 (m, 4H), 3.67 (s, 3H), 3.55 (s, 2H), 3.00-2.94 (m, 4H), 1.95 (t, 2H). ^{13}C NMR (100 MHz; $CDCl_3$): δ_C 172.2, 135.5, 133.3, 131.6, 129.5, 129.3, 126.8, 108.2, 64.5, 52.0, 40.8, 38.8, 31.7, 27.9. IR (CCl_4): ν_{max} (cm^{-1}) 2953, 2881, 1742, 1262. HRMS (EI, m/z) calculated (found) for $C_{15}H_{18}O_4$, 262.1205 (262.1202).

4.3.10 Methyl (5'-butyl-3',4'-dihydro-1'H-spiro[[1,3]dioxolane-2,2'-naphthalen]-6'-yl)-acetate (12b)

A solution of **9b** (55 mg, 0.16 mmol), lithium chloride (14 mg, 0.32 mmol) and a drop of water in DMSO (0.3 mL) was heated at 180°C for 3 h. The mixture was cooled to room temperature, diluted with Et_2O, washed with water, and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered and

concentrated under reduced pressure. Purification by flash column chromatography (petroleum ether-ethyl acetate: 90-10) gave **12b** (46 mg, 88%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.02 (d, 1H, J = 7.8 Hz), 6.87 (d, 1H, J = 7.8 Hz), 4.03 (s, 4H), 3.67 (s, 3H), 3.62 (s, 2H), 3.00-2.92 (m, 4H, CH2-4), 2.64-2.57 (m, 2H), 1.98 (t, 2H, J = 6.7 Hz), 1.49-1.36 (m, 4H), 0.96 (t, 3H, J = 6.9 Hz). ^{13}C NMR (100 MHz; $CDCl_3$): δ_C 172.5, 139.4, 134.0, 133.7, 130.1, 128.5, 127.2, 107.9 (C-6), 64.5, 52.0, 39.4, 38.7, 31.9, 31.6, 23.3, 29.0, 25.4, 13.9. IR (CCl_4): ν_{max} (cm^{-1}) 2955, 2875, 1740, 1262. HRMS (EI, m/z) calculated (found) for $C_{19}H_{26}O_4$, 318.1831(318.1831).

4.3.11 Methyl 7-oxo-1,2,3,4,4a,7-hexahydronaphthalene-4a-carboxylate (31b)

A solution of compound **30b** (600 mg, 2.88 mmol, 1.0 eq.), prepared from keto-ester **28b** according to the general procedure above, SeO_2 (768 mg, 6.92 mmol, 2.4 eq.) and pyridine (3 drops) in *t*BuOH (58 mL) was refluxed for 33 h. The mixture was then cooled to room temperature and filtrated on silica gel with AcOEt as solvent. The crude was evaporated under reduced pressure and the residue was purified by column chromatography (petroleum ether/AcOEt: from 85/15 to 75/25) to give dienone **31b** as a yellow solid (394 mg, 1.91 mmol, 66 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.73 (d, 1H, J = 9.9 Hz), 6.29 (dd, 1H, J_1 = 1.4 Hz, J_2 = 9.9 Hz), 6.21 (tapp, 1H, J = 1.6 Hz), 3.71 (s, 3H), 2.67 (ddd, 1H, J_1 = 2.6 Hz, J_2 = 4.9 Hz, J_3 = 13.1 Hz), 2.54 – 2.48 (m, 1H), 2.36 (dddd, 1H, J_1 = 1.4 Hz, J_2 = 4.9 Hz, J_3 = 13.4 Hz, J_4 = 13.5 Hz), 2.01 – 1.94 (m, 1H), 1.83 – 1.75 (m, 1H), 1.55 (ddt, 1H, J_1 = 3.6 Hz, J_2 = 13.5 Hz, J_3 = 13.6 Hz), 1.37 (ddt, 1H, J_1 = 4.0 Hz, J_2 = 13.0 Hz, J_3 = 13.1 Hz), 1.35 (dt, 1H, J_1 = 3.9 Hz, J_2 = 13.3 Hz). ^{13}C NMR (100 MHz; $CDCl_3$): δ_C 186.19, 170.39, 161.18, 147.96, 129.55, 125.97, 53.62, 53.08, 37.42, 34.57, 27.56, 22.84. IR (CCl_4): ν_{max} (cm^{-1}) 2944, 1739, 1669, 1541, 1222. HRMS (EI+) calculated (found) for $C_{12}H_{14}O_3$: 206.0943 (206.0941).

4.3.12 Methyl 2-oxo-4a,5,6,7,8,9-hexahydro-2*H*-benzo[7]annulene-4a-carboxylate (31c)

A solution of compound **30c** (600 mg, 2.70mmol, 1.0 eq.) prepared from ketoester **28c** according to the general procedure above, SeO_2 (720 mg, 6.49 mmol, 2.4 eq.) and pyridine (3 drops) in *t*BuOH (54 mL) was refluxed for 33 h. The mixture was then cooled to room temperature and filtrated over silica gel with AcOEt as solvent. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography (petroleum ether/AcOEt: 80/20) to give dienone **31c** as a yellow oil (363 mg, 1.65 mmol, 61 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.76 (d, 1H, J = 9.8 Hz), 6.32 (d, 1H, J = 9.8 Hz), 6.27 (bs, 1H), 3.67 (s, 3H), 2.58 (ddd, 1H, J_1 = 2.7 Hz, J_2 = 5.2 Hz, J_3 = 12.8 Hz), 2.39 – 2.29 (m, 2H), 2.06 (dd, 1H, J_1 = 8.8 Hz, J_2 = 14.6 Hz), 2.00 – 1.94 (m, 1H), 1.77 – 1.65 (m, 2H), 1.48 – 1.33 (m, 2H), 1.14 – 1.03 (m, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ_C 186.17, 170.97, 163.55, 149.70, 129.99, 129.40, 55.77, 53.17, 35.64, 34.32, 30.46, 29.70, 23.14. IR (CCl_4): ν_{max} (cm^{-1}) 2931, 2858, 1736, 1669, 1223. HRMS (EI+) calculated (found) for $C_{13}H_{16}O_3$: 220.1099 (220.1104).

4.3.13 Methyl 3-oxo-9,9a-dihydro-3*H*-fluorene-9a-carboxylate (37a)

A solution of compound **36a** (980 mg, 4.05 mmol, 1.0 eq.) prepared from ketoester **35a** by the general, SeO_2 (1.08 g, 9.72 mmol, 2.4 eq.) and pyridine (4 drops) in *t*BuOH (81 mL) was refluxed for 28 h. The mixture was then cooled to room temperature and filtrated over silica gel with AcOEt as solvent. The filtrate was evaporated under reduced pressure and the residue was

purified by column chromatography (petroleum ether/AcOEt: 80/20) to give enone **37a** as a yellow solid (491 mg, 2.05 mmol, 51 %). ^{1}H NMR (400 MHz, CDCl3): δ_H 7.59 (d, 1H, J = 7.5 Hz), 7.39 – 7.36 (m, 2H), 7.35 – 7.30 (m, 1H), 7.05 (d, 1H, J = 9.7 Hz), 6.58 (d, 1H, J = 1.4 Hz), 6.41 (dd, 1H, J_1 = 1.4 Hz, J_2 = 9.7 Hz), 3.86 (d, 1H, J = 15.1 Hz), 3.58 (s, 3H), 3.06 (d, 1H, J = 15.1 Hz). ^{13}C NMR (100 MHz; $CDCl_3$): δ_C 186.66, 170.15, 162.26, 145.21, 143.00, 137.23, 132.10, 131.24, 127.88, 125.69, 122.44, 120.75, 59.78, 53.80, 39.47. IR (CCl_4): ν_{max} (cm^{-1}) 3028, 2954, 2842, 1737, 1665, 1606, 1230, 1214. HRMS (EI+) calculated (found) for $C_{15}H_{12}O_3$ 240.0786 (240.0792).

4.3.14 Methyl 6-oxo-6,8a,9,10-tetrahydrophenanthrene-8a-carboxylate (37b)

A solution of enone **36b** (12.8 g, 50.0 mmol, 1.0 eq.) prepared from ketoester **35b** by the general procedure, SeO_2 (13.3 g, 120 mmol, 2.4 eq.) and pyridine (50 drops) in *t*BuOH (1.0 L) was refluxed for 28 h. The mixture was then cooled to room temperature and filtrated over silica gel with AcOEt as solvent. The crude was evaporated under reduced pressure and the residue was purified by column chromatography (petroleum ether/AcOEt: 80/20) to give dienone **37b** as a yellow solid (7.5 g, 29.5 mmol, 59 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.66 (dd, 1H, J_1 = 0.8 Hz, J_2 = 7.8 Hz), 7.33 (dt, 1H, J_1 = 1.3 Hz, J_2 = 7.4 Hz), 7.29 – 7.25 (m, 1H), 7.17 (d, 1H, J = 7.6 Hz), 6.88 (d, 1H, J = 9.8 Hz), 6.68 (d, 1H, J = 1.6 Hz), 6.42 (dd, 1H, J_1 = 1.6 Hz, J_2 = 9.8 Hz), 3.57 (s, 3H), 3.14 (ddd, 1H, J_1 = 6.0 Hz, J_2 = 12.3 Hz, J_3 = 18.1 Hz), 2.99 (dd, 1H, J_1 = 6.0 Hz, J_2 = 17.7 Hz), 2.77 (ddd, 1H, J_1 = 1.3 Hz, J_2 = 5.9 Hz, J_3 = 13.2 Hz), 1.92 (ddd, 1H, J_1 = 6.3 Hz, J_2 = 12.4 Hz, J_3 = 13.1 Hz). ^{13}C NMR (100 MHz; $CDCl_3$): δ_C 186.25, 169.85, 154.74, 147.19, 136.13, 132.93, 130.37, 130.24, 129.19, 126.93, 125.41, 123.68, 53.21, 51.31, 32.40, 26.14. IR (CCl_4): ν_{max} (cm^{-1}) 3023, 2955, 2933, 2849, 1736, 1665, 1228. HRMS (EI+) calculated (found) for $C_{16}H_{14}O_3$ 254.0943 (254.0945).

4.3.15 Methyl 7-methylene-1,2,3,4,4a,7-hexahydronaphthalene-4a-carboxylate (32b)

To a solution of compound **31b** (370 mg, 1.8 mmol, 1.0 eq.) in diethyl ether (7.2 mL) at - 78 °C under a nitrogen atmosphere was added MeLi (1.8 mmol, 1.0 eq.) drop-wise. After 1 h at -78°C, NH_4Cl (aq. sat.) was added to the reaction mixture and then water. The water layer was extracted three times with diethyl ether. The combined organic layers were washed with NaCl (aq. sat.), dried over magnesium sulfate and concentrated under reduced pressure. The crude was then dissolved in MeOH (10 mL). $HC(OMe)_3$ (1.2 mL) and *p*-TSA (1 crystal) were added to the reaction mixture which was then refluxed for 20 min. Water was added and the water layer was extracted three times with diethyl ether. The combined organic layers were washed with NaCl (aq. sat.), dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography (pentane/diethyl ether: 90/10) to give olefin **32b** as a colorless oil (253 mg, 1.24 mmol, 69 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.23 (d, 1H, J = 9.6 Hz), 6.12 (s, 1H), 5.62 (d, 1H, J = 9.6 Hz), 4.86 (s, 1H), 4.82 (s, 1H), 3.70 (s, 3H), 2.44 – 2.38 (m, 1H); 2.33 – 2.17 (m, 2H), 1.85 – 1.76 (m, 1H), 1.74 – 1.67 (m, 1H), 1.51 – 1.30 (m, 3H). ^{13}C NMR (100 MHz; $CDCl_3$): δ_C 173.18, 141.38, 137.76, 131.39, 127.83, 122.84, 111.99, 52.45, 52.25, 37.76, 34.05, 27.77, 23.63. IR (CCl_4): ν_{max} (cm^{-1}) 2937, 2860, 1732, 1217. HRMS (EI+) calculated (found) for $C_{13}H_{16}O_2$: 204.1150 (204.1157).

4.3.16 Methyl 2-methylene-4a,5,6,7,8,9-hexahydro-2*H*-benzo[7]annulene-4a-carboxylate (32c)

To a solution of compound **32c** (350 mg, 1.6 mmol, 1.0 eq.) in diethyl ether (6.4 mL) at - 78 °C under a nitrogen atmosphere was added MeLi (1.6 mmol, 1.0 eq.) drop-wise. After 1 h at -78°C, NH_4Cl (aq. sat.) was added to the reaction mixture and then water. The water layer was extracted three times with diethyl ether. The combined organic layers were washed with NaCl (aq. sat.), dried over magnesium sulfate and concentrated under reduced pressure. The crude was then dissolved in MeOH (10 mL). $HC(OMe)_3$ (1.0 mL) and *p*-TSA (1 crystal) were added to the reaction mixture which was then refluxed for 20 min. Water was added and the water layer was extracted three times with diethyl ether. The combined organic layers were washed with NaCl (aq. sat.), dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography (pentane/diethyl ether: 90/10) to give alkene **32c** as a yellow oil (216 mg, 0.99 mmol, 62 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.30 (d, 1H, J = 9.6 Hz), 6.21 (s, 1H), 5.66 (d, 1H, J = 9.6 Hz), 4.88 (s, 1H), 4.86 (s, 1H), 3.66 (s, 3H), 2.44 – 2.38 (m, 1H), 2.19 – 2.10 (m, 2H), 1.96 – 1.83 (m, 2H), 1.77 – 1.68 (m, 1H), 1.67 – 1.58 (m, 1H), 1.38 – 1.18 (m, 3H). ^{13}C NMR (100 MHz; $CDCl_3$): δ_C 174.06, 143.21, 137.95, 132.97, 128.44, 126.63, 112.07, 54.03, 52.44, 38.25, 33.82, 31.14, 30.25, 23.31. IR (CCl_4): ν_{max} (cm^{-1}) 2929, 2856, 1732, 1223. HRMS (EI+) calculated (found) for $C_{14}H_{18}O_2$: 218.1307 (218.1310).

4.3.17 Methyl 2-(5,6,7,8-tetrahydronaphthalen-2-yl)acetate (33b)

A solution of compound **32b** (102 mg, 0.50 mmol) in DMSO (1.25 mL) was heated at 180 °C for 40 min. Then water was added to the reaction mixture. The water layer was extracted three times with diethyl ether. The combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. The residue was then purified by column chromatography (pentane/diethyl ether: 95/5) to give rearranged product **33b** as a colorless oil (63 mg, 0.31 mmol, 62 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.06 – 6.99 (m, 3H), 3.71 (s, 3H), 3.58 (s, 2H), 2.79 – 2.74 (m, 4H), 1.84 – 1.77 (m, 4H). ^{13}C NMR (100 MHz; $CDCl_3$): δ_C 172.17, 137.18, 135.83, 130.75, 129.71, 129.19, 129.13, 51.83, 40.67, 29.17, 28.91, 23.03, 22.98. IR (CCl_4): ν_{max} (cm^{-1}) 2933, 1743, 1436, 1259. HRMS (EI+) calculated (found) for $C_{13}H_{16}O_2$: 204.1150 (204.1158).

4.3.18 Methyl 2-(6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-2-yl)acetate (33c)

A solution of compound **32c** (102 mg, 0.47 mmol) in DMSO (1.25 mL) was heated at 180 °C for 40 min. Then water was added to the reaction mixture. The water layer was extracted three times with diethyl ether. The combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. The residue was then purified by column chromatography (pentane/diethyl ether: 95/5) to give the rearranged product **33c** as a colorless oil (43 mg, 0.19 mmol, 42 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.06 (d, 1H, J = 7.5 Hz), 7.02 (bs, 1H), 7.00 (dd, 1H, J_1 = 1.7 Hz, J_2 = 7.5 Hz), 3.70 (s, 3H), 3.57 (s, 2H), 2.79 – 2.75 (m, 4H), 1.87 – 1.79 (m, 2H), 1.67 – 1.60 (m, 4H). ^{13}C NMR (100 MHz; $CDCl_3$): δ_C 172.29, 143.68, 142.28, 131.32, 129.88, 129.24, 129.55, 51.95, 40.73, 36.63, 36.29, 32.69, 28.24, 28.21. IR (CCl_4): ν_{max} (cm^{-1}) 2925, 2852, 1742, 1439, 1264, 1153, 1019. HRMS (EI+) calculated (found) for $C_{14}H_{18}O_2$: 218.1307 (218.1310).

4.3.19 Methyl 3-methylene-9,9a-dihydro-3*H*-fluorene-9a-carboxylate (38a)

To a solution of compound **37a** (480 mg, 2.0 mmol, 1.0 eq.) in THF (20 mL) at -78 °C under a nitrogen atmosphere was added MeLi (2.0 mmol, 1.0 eq.) drop-wise. After 1 h at - 78°C, NH4Cl (aq. sat.) was added to the reaction mixture and then water. The water layer was extracted three times with diethyl ether. The combined organic layers were washed with NaCl (aq. sat.), dried over magnesium sulfate and concentrated under reduced pressure. The crude was then dissolved in MeOH (10 mL). $HC(OMe)_3$ (1 mL) and *p*-TSA (1 crystal) were added to the reaction mixture which was then refluxed for 20 min. Water was added and the water layer was extracted three times with diethyl ether. The combined organic layers were washed with NaCl (aq. sat.), dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography (pentane/diethyl ether: 90/10) to give alkene **38a** as a yellow solid (230 mg, 0.97 mmol, 48 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.54 – 7.50 (m, 1H), 7.28 – 7.22 (m, 3H), 6.75 (s, 1H), 6.41 (s, 1H), 6.41 (d, 1H, J = 9.4 Hz), 6.09 (d, 1H, J = 9.5 Hz), 5.21 (s, 1H), 5.03 (s, 1H), 3.71 (d, 1H, J = 15.3 Hz), 3.57 (s, 3H), 2.97 (d, 1H, J = 15.3 Hz). ^{13}C NMR (100 MHz; $CDCl_3$): δ_C 173.41, 143.62, 142.22, 139.10, 138.60, 130.26, 128.67, 128.08, 127.19, 125.28, 120.84, 119.79, 115.99, 57.91, 52.90, 40.74. IR (CCl_4): ν_{max} (cm^{-1}) 3027, 2953, 1732, 1435. HRMS (EI+) calculated (found) for $C_{16}H_{14}O_2$: 238.0994 (238.0985).

4.3.20 Methyl 6-methylene-6,8a,9,10-tetrahydrophenanthrene-8a-carboxylate (38b)

To a solution of compound **37b** (550 mg, 2.16 mmol, 1.0 eq.) in THF (22 mL) at -78 °C under a nitrogen atmosphere was added MeLi (2.16 mmol, 1.0 eq.) drop-wise. After 1 h at - 78°C, NH_4Cl (aq. sat.) was added to the reaction mixture and then water. The water layer was extracted three times with diethyl ether. The combined organic layers were washed with NaCl (aq. sat.), dried over magnesium sulfate and concentrated under reduced pressure. The crude was then dissolved in MeOH (10 mL). $HC(OMe)_3$ (1 mL) and *p*-TSA (1 crystal) were added to the reaction mixture which was then refluxed for 20 min. Water was added and the water layer was extracted three times with diethyl ether. The combined organic layers were washed with NaCl (aq. sat.), dried over magnesium sulfate and concentrated under reduced pressure. The crude was purified by column chromatography (pentane/diethyl ether: 90/10) to give alkene **38b** as a yellow solid (320 mg, 1.27 mmol, 59 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.67 – 7.63 (m, 1H), 7.22 – 7.16 (m, 1H), 7.09 – 7.05 (m, 1H), 6.75 (s, 1H), 6.35 (d, 1H, J = 9.6 Hz), 5.82 (d, 1H, J = 9.6 Hz), 5.10 (s, 1H), 5.03 (s, 1H), 3.56 (s, 3H), 3.02 (ddd, 1H, J_1 = 6.1 Hz, J_2 = 12.7 Hz, J_3 = 17.6 Hz), 2.87 (dd, 1H, J_1 = 5.8 Hz, J_2 = 17.5 Hz), 2.53 (ddd, 1H, J_1 = 0.9 Hz, J_2 = 5.8 Hz, J_3 = 13.1 Hz), 1.91 (ddd, 1H, J_1 = 6.2 Hz, J_2 = 12.8 Hz, J_3 = 12.9 Hz). ^{13}C NMR (100 MHz; $CDCl_3$): δ_C 172.76, 137.96, 136.74, 135.32, 134.78, 131.01, 129.08, 128.18, 127.70, 126.23, 124.39, 122.57, 114.45, 123.68, 52.53, 50.06, 33.45, 26.74. IR (CCl_4): ν_{max} (cm^{-1}) 3023, 2952, 1732, 1687, 1435, 1216. HRMS (EI+) calculated (found) for $C_{17}H_{16}O_2$: 252.1150 (252.1154).

4.3.21 Methyl 2-(9*H*-fluoren-3-yl)acetate (39a)

A solution of compound **38a** (100 mg, 0.43 mmol) in DMSO (2.0 mL) was heated at 180 °C for 1 h. Then water was added to the reaction mixture. The water layer was extracted three times with diethyl ether. The combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. The residue was then purified by column chromatography

(pentane/DCM: from 85/15 to 70/30) to give rearranged product **39a** as a white solid (79 mg, 0.34 mmol, 79 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.78 (d, 1H, J = 7.5 Hz), 7.71 (bs, 1H), 7.54 (bd, 1H, J = 7.4 Hz), 7.50 (d, 1H, J = 7.7 Hz), 7.38 (t, 1H, J = 7.4 Hz), 7.30 (dt, H, J_1 = 1.1 Hz, J_2 = 7.4 Hz), 7.22 (dd, 1H, J_1 = 1.3 Hz, J_2= 7.7 Hz), 3.88 (s, 2H), 3.74 (s, 2H), 3.72 (s, 3H). ^{13}C NMR (100 MHz; $CDCl_3$): δ_C 172.25, 143.51, 142.20, 142.11, 141.35, 132.51, 127.74, 126.81, 126.71, 125.08, 125.00, 120.73, 119.94, 52.09, 41.32, 36.64. IR (CCl_4): ν_{max} (cm^{-1}) 3073, 3051, 3020, 2952, 2900, 1734, 1453, 1435, 1255, 1155, 1018. HRMS (EI+) calculated (found) for $C_{16}H_{14}O_2$: 238.0994 (238.0993).

4.3.22 Methyl 2-(9,10-dihydrophenanthren-3-yl)acetate (39b)

A solution of compound **38b** (180 mg, 0.71 mmol) in DMSO (2.4 mL) was heated at 180 °C for 1 h. Then water was added to the reaction mixture. The water layer was extracted three times with diethyl ether. The combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. The residue was then purified by column chromatography (pentane/DCM: from 85/15 to 70/30) to give the rearranged product **39b** as a white solid (140 mg, 0.55 mmol, 78 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.76 (d, 1H, J = 7.7 Hz, C5**H**); 7.67 (bs, 1H), 7.33 – 7.29 (m, 1H), 7.25 – 7.22 (m, 2H), 7.20 (d, 1H, J = 7.7 Hz), 7.15 (bd, 1H, J = 7.7 Hz), 3.72 (s, 3H), 3.68 (s, 2H), 2.86 (bs, 4H). ^{13}C NMR (100 MHz; $CDCl_3$): δ_C 172.16, 137.39, 136.23, 134.72, 134.17, 132.48, 128.34, 128.15, 128.10, 127.47, 126.90, 124.61, 123.72, 52.07, 41.15, 29.01, 28.67. IR (CCl_4): ν_{max} (cm^{-1}) 3022, 2952, 1897, 2839, 1743, 1614, 1435, 1258, 1157, 1017. HRMS (EI+) calculated (found) for $C_{17}H_{16}O_2$: 252.1150 (252.1146).

4.3.23 Methyl 3-methyl-9,10-dihydrophenanthrene-2-carboxylate (40)

A solution of compound **48b** (159 mg, 0.63 mmol, 1.0 eq.) in CH_2Cl_2 (3 mL) was added dropwise to a suspension of anhydrous $AlCl_3$ (168 mg, 1.26 mmol, 2.0 eq.) in CH_2Cl_2 (3 mL) at 25 °C. After 10 min, the reaction mixture was poured onto ice water, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layers were washed with brine, dried over magnesium sulfate, filtered and concentrated. Purification by flash colum chromatography (petroleum ether-diethyl ether: 90-10) gave **40** (71 mg, 45%) as an orange oil.^{1}H NMR (400 MHz, $CDCl_3$) : δ_H 7.68 (d, J = 7.4 Hz, 2H), 7.58 (d, J = 1.0 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.24 – 7.18 (m, 2H), 3.89 (s, 3H), 3.26 – 3.11 (m, 2H), 2.84 – 2.70 (m, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, CDCl3): δ 168.7, 137.7, 136.0, 135.9, 134.2, 129.8, 129.8, 128.5, 127.9, 127.8, 127.0, 124.1, 52.1, 28.8, 25.5, 21.3. IR (neat): ν_{max} (cm^{-1}) 2948, 1722 1435 1325 1248, 1195. HRMS (EI+) calculated (found) for $C_{17}H_{16}O_2$: 252.1150 (252.1147).

4.3.24 But-3-enyl 6-methylene-6,8a,9,10-tetrahydrophenanthrene-8a-carboxylate (41)

A solution of LiH (16 mg, 2.0 mmol, 1.0 eq.) in but-3-en-1-ol (2.0 mL) was heated at 40 °C for 5 min. Compound **38b** (504 mg, 2.0 mmol, 1.0 eq.) was added and the reaction mixture was refluxed in a Dean-Stark apparatus for 4.5 h. Then water and NH4Cl (aq. sat.) were added to the reaction mixture. The water layer was extracted two times with AcOEt. The combined organic layers were washed with NaCl (aq. sat.), dried over magnesium sulfate and concentrated under reduced pressure. The residue was then purified by column chromatography (petroleum ether/AcOEt: from 100/0 to 96/4) to give ester **41** as a colorless oil (420 mg, 1.44 mmol, 72 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.66 – 7.61 (m, 1H), 7.21 – 7.14 (m, 2H), 7.08 – 7.04 (m, 1H),

6.74 (s, 1H), 6.34 (d, 1H, J = 9.6 Hz), 5.83 (d, 1H, J = 9.6 Hz), 5.55 – 5.45 (m, 1H), 5.09 (s, 1H), 5.02 (s, 1H), 4.94 – 4.88 (m, 2H), 4.08 (dt, 1H, J_1 = 6.6 Hz, J_2 = 10.8), 3.95 (dt, 1H, J_1 = 6.5 Hz, J_2 = 10.8), 3.01 (ddd, 1H, J_1 = 6.0 Hz, J_2 = 12.6 Hz, J_3 = 18.3 Hz), 2.86 (dd, 1H, J_1 = 5.9 Hz, J_2 = 17.5), 2.52 (dd, 1H, J_1 = 5.3 Hz, J_2 = 13.0 Hz), 2.19 – 2.13 (m, 2H), 1.90 (ddd, 1H, J_1 = 6.2 Hz, J_2 = 12.6 Hz, J_3 = 12.8 Hz). ^{13}C NMR (100 MHz; $CDCl_3$): δ_C 172.20, 138.02, 136.81, 135.25, 134.96, 133.61, 131.06, 129.00, 128.11, 127.61, 126.17, 124.38, 122.40, 117.03, 114.23, 64.20, 50.09, 33.48, 32.84, 26.69. IR (CCl_4): ν_{max} (cm^{-1}) 3074, 2932, 1728, 1687, 1230, 1188. HRMS (EI+) calculated (found) for $C_{20}H_{20}O_2$: 292.1463 (292.1463).

4.3.25 3-(2-(9,10-dihydrophenanthren-3-yl)ethyl)dihydrofuran-2(3H)-one (42)

A solution of ester **41** (140 mg, 0.48 mmol) in DMSO (1.5 mL) was heated at 170 °C for 20 min. Then water was added to the reaction mixture. The water layer was extracted three times with diethyl ether. The combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. The residue was then purified by column chromatography (pentane/AcOEt: from 98/2 to 0/100) to give lactone **42** as a yellowish oil (103 mg, 0.35 mmol, 74 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.76 (d, 1H, J = 7.7 Hz), 7.60 (d, 1H, J = 1.7 Hz), 7.34 – 7.28 (m, 1H), 7.25 – 7.22 (m, 2H), 7.17 (d, 1H, J = 7.6 Hz), 7.08 (dd, 1H, J_1 = 1.6 Hz, J_2 = 7.6 Hz), 4.36 (ddd, 1H, J_1 = 2.7 Hz, J_2 = 8.5 Hz, J_3 = 9.0 Hz), 4.18 (ddd, 1H, J_1 = 6.6 Hz, J_2 = 9.1 Hz, J_3 = 9.7 Hz), 2.90 – 2.73 (m, 2H), 2.86 (bs, 4H), 2.59 – 2.50 (m, 1H), 2.41 (dddd, 1H, J_1 = 2.7 Hz, J_2 = 6.7 Hz, J_3 = 9.3 Hz, J_4 = 12.5 Hz), 2.30 (dddd, 1H, J_1 = 5.2 Hz, J_2 = 7.1 Hz, J_3 = 9.0 Hz, J_4 = 14.1 Hz), 1.99 (dddd, 1H, J_1 = 8.4 Hz, J_2 = 9.7 Hz, J_3 = 10.0 Hz, J_4 = 12.4 Hz), 1.81 (dddd, 1H, J_1 = 6.0 Hz, J_2 = 8.8 Hz, J_3 = 8.8 Hz, J_4 = 14.8 Hz). ^{13}C NMR (100 MHz; $CDCl_3$): δ_C 179.32, 139.24, 137.42, 135.29, 134.53, 134.31, 128.24, 128.12, 127.38 (2 carbons), 126.88, 123.73, 123.58, 66.41, 38.37, 33.22, 32.05, 29.09, 28.81, 28.60. IR (CCl_4): ν_{max} (cm^{-1}) 3016, 2938, 2838, 1781, 1492, 1450, 1372, 1145, 1031. HRMS (EI+) calculated (found) for $C_{20}H_{20}O_2$: 292.1463 (292.1469).

4.3.26 3-(9,10-dihydrophenanthren-3-yl)propanenitrile (46)

To a solution of compound **38b** (2.0 mmol, 1.0 eq.) and *S*-cyanomethyl-*O*-ethyl xanthate **45** (5.0 mmol, 2.5 eq.) in refluxing heptane (20 mL) under a nitrogen atmosphere was added 10 mol% of DLP every 90 min until completion of the reaction. This took 30 mol% of DLP in total. The solvent was evaporated under reduced pressure and then KOH (1M, 2 mL) and MeOH (1 mL) were added to the residue. After 1 h at 40 °C, the reaction mixture was extracted three times with diethyl ether. The combined organic layers were washed with NaCl (aq. sat.), dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/AcOEt: from 98/2 to 95/5) to give nitrile **46** as a colorless oil (17 mg, 0.81 mmol, 40 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.75 (d, 1H, J = 7.7 Hz), 7.61 (d, 1H, J = 1.4 Hz), 7.34 – 28 (m, 1H), 7.25 -7.23 (m, 2H), 7.21 (d, 1H, J = 7.6 Hz), 7.10 (dd, 1H, J_1 = 1.7 Hz, J_2 = 7.6 Hz), 3.01 (t, 2H, J = 7.4 Hz), 2.86 (bs, 4H), 2.66 (t, 2H, J = 7.4 Hz).^{13}C NMR (100 MHz; $CDCl_3$): δ_C 137.43, 136.63, 136.38, 134.98, 134.05, 128.59, 128.17, 127.61, 127.11, 126.99, 123.64, 123.59, 119.20, 31.5, 28.98, 28.65, 19.53. IR (CCl_4): ν_{max} (cm^{-1}) 3019, 2936, 2898, 2249, 1730, 1261. HRMS (EI+) calculated (found) for $C_{17}H_{15}N$: 233.1204 (233.1202).

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