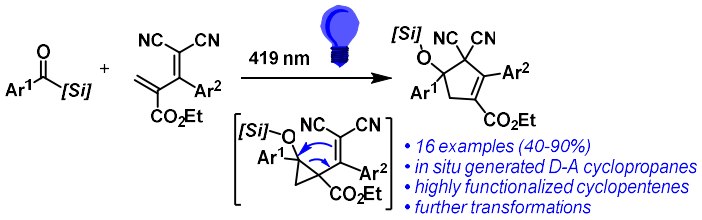
Functionalized cyclopentenes via formal [4+1] cycloaddition of photogenerated-siloxycarbenes from acyl silanes

João R. Vale[a,b], Rafael F. Gomes[a], Carlos A. M. Afonso[a]* and Nuno R. Candeias[b,c]*

a) iMed.ULisboa, Faculty of Pharmacy, Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisbon, Portugal; b) Faculty of Engineering and Natural Sciences, Tampere University, Korkeakoulunkatu 8, 33101 Tampere, Finland; c) LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

Supporting Information Placeholder



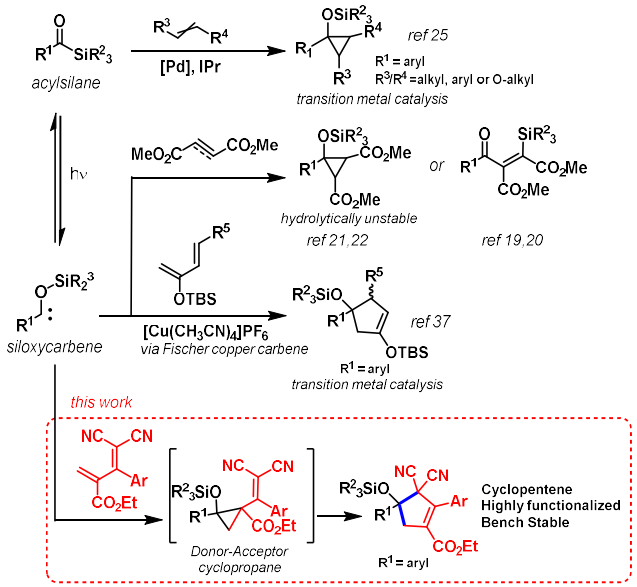
ABSTRACT: This work describes the first formal cycloaddition reaction of photogenerated-nucleophilic carbenes derived from acylsilanes with electrophilic dienes. The resulting transient donor-acceptor cyclopropane rearranges to its stable and highly functionalized cyclopentene isomer in an unprecedented metal-free process. The cyclopropanation-vinyl cyclopropane rearrangement sequence was corroborated by computational calculations. The cyclopropane formation corresponds to the higher energetic barrier but the vinylcyclopropane-cyclopentene rearrangement proceeds through different mechanisms, although of comparable energies, depending on the stereochemistry of the cyclopropane.

INTRODUCTION

Acylsilanes have recently attracted considerable attention in the field of organic synthesis mainly due to their ability to generate nucleophilic carbenes.[1–3] The metal-free UV/visible irradiation of acylsilanes presents an atom-efficient way to deliver siloxycarbenes upon reversible 1,2-Brook rearrangement. Despite their clean production, these carbenes have seen limited applications due to their low reactivity and fast reversibility to the acylsilane precursor that can also undergo homolytic cleavage.[4] The siloxycarbenes generated by irradiation of acylsilanes can undergo a plethora of X-H insertions, such as O-H,[5] N-H,[6] S-H,[4] Si-H[7,8] and B-H.[9] Although limited to its intramolecular version, C-H insertion of siloxycarbenes has been explored in the preparation of benzofurans,[10] while thermolytic methods proved synthetically non-useful.[11,12] B-C insertion was also observed with organoboronic esters allowing an elegant photochemical transition metal-free cross-coupling.[13] The repertoire of reactions by siloxycarbenes also encompasses the nucleophilic addition to aldehydes,[14,15] trifluoromethyl ketones,[16] and carbon dioxide.[17]

Cyclopropanation, a classical carbene reaction,[18] is elusive due to the nucleophilic nature of the siloxycarbene. Activated alkynes have been shown to undergo slow inter- and intramolecular cyclopropenation following ring collapse to give β-silylated enones (Scheme 1).[19,20] Concerning olefins, only the highly electron-withdrawing dialkyl fumarate and maleate have been reported to undergo cyclopropanation,[21,22] yielding cyclopropyl silyl ethers that are prone to ring-opening through hydrolysis, and are therefore not synthetically useful for cyclopropane synthesis. The intramolecular cyclopropanation seems unattainable as the acylsilane carbonyl reacts preferably in a [2+2]-photocycloaddition reaction.[23,24] All in all, formal cyclopropanation of olefins with acylsilane-derived carbenes remains poorly explored due to the required presence of electron-withdrawing groups in the olefin which renders instability to resulting silyl ether cyclopropanes. Recently, further advances on the topic rely heavily on transition metal catalysis. Cyclopropanation of non-activated olefins using acylsilanes was achieved through palladium catalysis, via a Fischer-type carbene complex without the involvement of a photogenerated siloxycarbene (Scheme 1, top).[25]

Scheme 1. Cycloaddition reactions of siloxycarbenes



The formation of cyclopentenes through the intermediacy of siloxycarbene was recently achieved via the umpolung strategy (Scheme 1).[26] The photogenerated carbene complexes with copper to form an electrophilic Fischer-type carbene that reacts with highly electron-rich dienes in (4+1) cycloaddition, thus circumventing the electronic mismatch between the traditional nucleophilic siloxycarbene and electron-rich dienes. Such finding led us to hypothesize that a metal-free strategy using acylsilanes to synthesize cyclopentenes could be achieved by

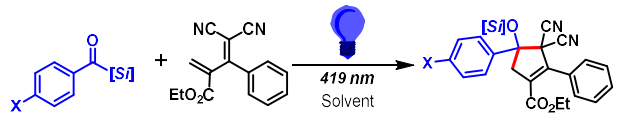
tuning the electronic nature of the diene. We envisioned that the reaction of an acylsilane-derived carbene with an electron-withdrawing diene would lead to a donor-acceptor (D – A) cyclopropane[27–30] that would be a prone candidate for vinyl cyclopropane rearrangement[31–33] ultimately forming a stable cyclopentene. Notwithstanding the reactivity of D-A cyclopropanes, the vinylcyclopropane-cyclopentene rearrangement usually requires the presence of Lewis acids of variable strength[34–37] depending on the electronic nature of the cyclopropane substituents.

Dicyano-2-methylenebut-3-enoates have been previously used as electron-withdrawing dienes for the inverse-electron-demand Diels–Alder reactions,[38] and its terminal olefin was observed to undergo cyclopropanation with diazo compounds.[39] Hence, this highly electrophilic diene was considered a suitable candidate for the trapping of siloxycarbenes derived from benzoyl silanes.

Results and Discussion

The studies were initiated using *p*-toluoyltrimethylsilane **1a** as carbene precursor and diene **2a** in slight excess. Prolonged irradiation at 419 nm of a hexane/DCM solution gladly resulted in the domino production of cyclopentene **3** in a 20% yield (Table 1, entry 1), despite the absence of any Lewis acid catalyst. Additional measures taken to remove any traces of moisture, i. e. using dry solvents and molecular sieves, proved futile and *p*-tolualdehyde was the main side product.

Table 1. Optimization of the cyclopropanation/vinyl cyclopropane rearrangement sequence.



2a 3

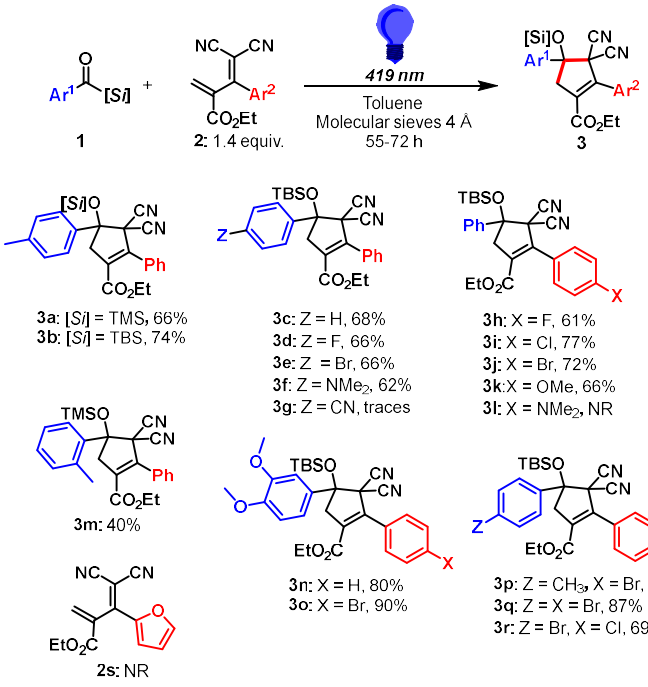
1a: [Si] = TMS, X = Me
1b: [Si] = TBS, X = Me
1o: [Si] = TBDPS, X = H

Entry[a]	Solvent	Time (h)	**1** / [**1**] (mM)	Diene **2a** (eq.)	**3** Yield (%)
1	DCM/Hex	12	**1a** / 20	1.2	20
2	Toluene	12	**1a** / 20	1.2	30
3	Toluene	55	**1a** / 20	2.8	65
4	Toluene	55	**1a** / 40	2.8	trace
5	Toluene	23	**1a** / 10	2.8	70
6	Toluene	23	**1a** / 10	1.4	66
7	Toluene	55	**1b** / 10	1.4	70
8	Toluene	55	**1b** / 20	1.4	74
9	Toluene	48	**1o** / 10	1.4	0

[a] General procedure: Acylsilane **1** (0.1 mmol), diene and molecular sieves 4 Å (200 mg/mL of solvent) are dissolved in solvent in a sealed Pasteur pipette. Solution purged with argon for 15 minutes and irradiated at 419 nm until reaction progress halts.

Notably, no cyclopropane intermediate was isolated nor detected in the crude reaction mixture, indicating that the vinyl cyclopropane rearrangement is a highly favored process not requiring high temperatures or catalyst. The use of dry toluene as solvent and the addition of molecular sieves now suppressed the aldehyde formation and the increase of the diene to 2.8 equivalents led to cyclopentene **3** yield increase to 70% (Table 1, entry 5). The amount of diene could be reduced by 1.4 equivalents without significantly compromising the yield (Table 1, entry 6). As small amounts of diallylated product **4** (Scheme 4) were detected in every experiment with **1a**, and suspecting on the lability of the TMS-group, the benzoyl silane was decorated with a bulkier TBS. Despite the longer reaction times required to reach full conversion, the desilylated product was not detected and **3b** was obtained in a slightly improved 74% yield (Table 1, entry 7). The cyclopentene structure was confirmed through x-ray diffraction analysis of product **3b** (see Supporting Information). Irradiation of even bulkier benzoyl *t*-butyldiphenylsilane **1o** (Table 1, entry 9) led to no conversion and full recovery of starting material. With the optimal reaction conditions cleared, we investigated the scope of the reaction by changing the aryl groups of the benzoylsilane and the diene (Scheme 2). Para substitution within the aromatic ring of the benzoylsilane was well tolerated, allowing electron-donating (**3f** and **3n**) and slightly electron-withdrawing substituents (**3d**, **3e**, **3q**, and **3r**). Meta- (**3n** and **3o**) and orto-(**3m**) substitution was also tolerated. Only the highly electron-withdrawing nitrile was unreactive towards the formation of cyclopentene **3g**, presumably due to the lower nucleophilicity of the generated carbene. Substitution on the aromatic ring of the diene was more challenging. Moderate electron-withdrawing groups such as halogens were compatible (**3h-3j, 3p-r**) as well as electron-donating groups such as methoxy (**3k**). However, highly electron-donating groups such as dimethylamine (**2l**) led to no reactivity, a result of its higher LUMO-energy. Furan derivative **2s** was surprisingly unreactive. Nitro and nitrile derivatives would likely present suitable reactivity, as highly electron-withdrawing dienes, but their synthesis proved impossible with the used protocol.[38]

Scheme 2. Scope of the cyclopropanation/vinyl cyclopropane rearrangement sequence.



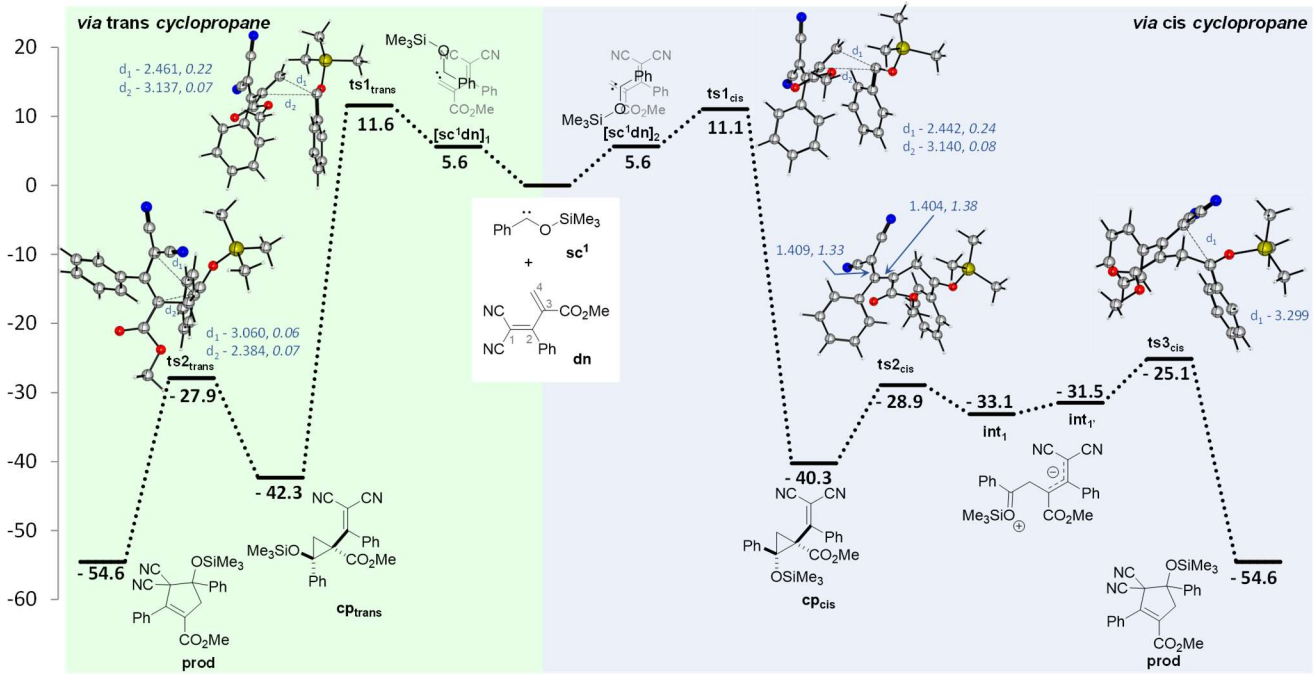
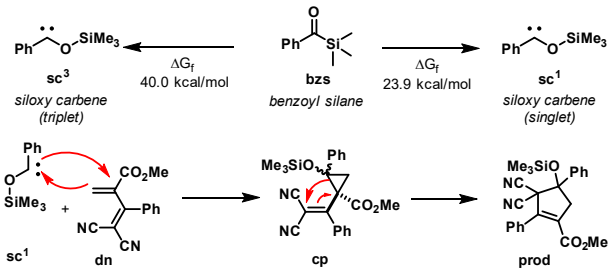


Figure 1: Free energy profile (M06-2X/6-311++G**//M06-2X/6-31+G**) and mechanistic representation for cyclopropanation-rearrangement to cyclopentene of separated model substrates siloxycarbene sc^1 and diene dn. The minimum and the transition states were optimized, and the energy values (kcal/mol) refer to the optimized sc^1 and dn and include the thermal correction to Gibbs Free energy in toluene. Bond lengths (in Å) and Wiberg index (italics) of relevant bonds are presented.

Scheme 3. Thermodynamics of benzoyl silane-derived siloxycarbene formation and working mechanism investigated by DFT



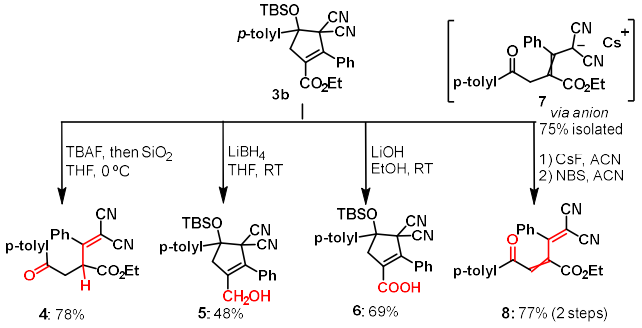
While the ring-enlargement of cyclopropanes has been studied computationally for several systems,[40–42] similar studies for the expansion of vinylcyclopropanes containing an electron-deficient alkene remain elusive. Hence, mechanistic insights were obtained through computational calculations using density functional theory[43] (DFT) studies at the M06-2X/6-311++G (d, p)//M06-2X/6-31+G(d, p) level of theory (Figure 1). The energies' comparison of the two siloxycarbenes attainable from benzoylsilane shows large stability of the singlet species **sc^1** over the triplet one **sc^3** (Scheme 3, top). The 16.1 kcal/mol difference is well in agreement with the recent studies presented by Priebbenow.[44] The computational study proceeded considering the formation of cyclopropane derivatives **cp**, for which the two possible diastereomers were investigated (Scheme 3, bottom). Alternatively, the addition of carbene **sc1** to the terminal carbon of the diene was also considered. Despite the identification of a transition state for the C-C bond formation (with subsequent charge delocalization to the methylenemalononitrile unit), following the intrinsic reaction coordinates invariably resulted in the formation of cyclopropane derivatives. This clearly demonstrates the preference for a route that encompasses cyclopropane as an intermediate.

The interaction of the siloxycarbene with the diene is slightly unfavorable by 5.6 kcal/mol in comparison to the initial pair of reactants. In both cases, **$[sc^1dn]_1$** and **$[sc^1dn]_2$**, a π-π attractive interaction between the phenyl substituents (3.4 - 4.4 Å) of both species seems to hold the two reactants together. Despite the overlap of the phenyl substituents in both pairs, the location of the silyl group relative to the methylenemalononitrile differs, with **$[sc^1dn]_1$** keeping the units close to each other, in contrast with **$[sc^1dn]_2$** in which one is kept apart from another. Generally, regardless of the relative geometry of the substituents of the cyclopropane derivatives, the formation of the three-membered rings accounts for the most energy-demanding step of the whole process. The formation of the two diastereomeric cyclopropane derivatives requires the transposition of energy barriers of 11.6 or 11.1 kcal/mol for the respective formation of the trans (**cp_{trans}**) or cis (**cp_{cis}**) diastereomer. The cyclopropanation transition states are very similar in nature and energies; the forming C-C bonds of the siloxycarbene carbon with C4 are shorter (2.44 – 2.46 Å) than the ones forming with C3 (3.14 Å), but still incipient as also confirmed by the weak Wiberg indices (WI = 0.1 – 0.2). The two diastereomeric cyclopropane derivatives differ in energy by 2.0 kcal/mol with a slight preference towards the trans diastereomer, where the repulsion between the phenyl and methylene malononitrile substituents is diminished. The steric constraints imposed by the cyclopropane substituents are also noticeable in the C-C bond lengths, as the C-C bond between the quaternary carbons is the most distended of the cyclopropane ring (1.55 Å in **cp_{trans}** and 1.57 Å in **cp_{cis}**). The cyclopropane rearrangement to the cyclopentene differs slightly depending on the relative positions of the substituents in the cyclopropane. The **$ts2_{trans}$** transition state was calculated for the

ring enlargement of **cp**$_{trans}$, being 14.4 kcal/mol less stable than its immediate precursor. Also, in this case, the C-C bonds involved are incipient (2.38 – 3.06 Å) and weak (0.1 Wiberg index). The formation of the cyclopentane **prod** from the siloxycarbene is highly favored as determined by its ΔG_f of -54.6 kcal/mol. Despite numerous attempts to calculate a similar synchronous transition state for the ring enlargement from **cp**$_{cis}$, such a process seems more likely to proceed through charged intermediate **int**$_1$ and **int**$_{1'}$ due to the steric clash of the bulky phenyl and methylene malononitrile substituents in the cis positions. Hence, the charged intermediate **int**$_1$ is reached by cleavage of the elongated C-C bond between the quaternary carbons of **cp**$_{cis}$ (1.57 Å in **cp**$_{cis}$ and 2.39 Å in **ts2**$_{cis}$), as the C-OSi bond becomes stronger (d = 1.38 Å; WI = 0.95 in **cp**$_{cis}$ and d = 1.28 Å; WI = 1.29 in **ts2**$_{cis}$). A change in conformation in **int**$_1$ by rotation of the C-C bond between C3 and C4 gives rise to **int**$_{1'}$, which undergoes C-C bond formation through a 6.4 kcal/mol energy barrier. The determined transition state **ts3**$_{cis}$ is again an early transition one as the forming C-C bond is still very incipient with 3.30 Å length. When considering the energies involved in both pathways, i.e. through each diastereomer of the cyclopropane, they likely compete with each other and a preference for one of the diastereomeric cyclopropanes is improbable.

After the development of the protocol for the cycloaddition of photogenerated carbene with dicyano-2-methylenebut-3-enoates, we set out to investigate further transformations to the resulting cyclopentene molecules (Scheme 4). TBAF promoted desilylation of **3b**, followed by purification via silica column chromatography delivered the ring-opened product **4** in good yield via acid-promoted retro-aldol. The ester moiety was selectively reduced to the primary alcohol **5** via $LiBH_4$ reduction and hydrolyzed to the carboxylic acid **6** with LiOH. Attempts at palladium-catalyzed hydrogenation of the olefin or its oxidation (*m*-CPBA or H_2O_2) invariably led to the recovery of the starting material, demonstrating remarkable stability of the carbon-carbon double bond. Efforts to reduce the nitrile (with DIBAL, $LiAlH_4$, or BH_3) or hydrolysis under acidic or basic conditions led in all cases to an unidentifiable mixture of compounds. Desilylation in anhydrous conditions using CsF yielded **7** (1:0.2 *trans*/*cis* ratio), a room temperature stable allylic anion, that could be quenched with equimolar NBS to yield novel diene **8** (as an interconvertible 1:0.2 *cis*/*trans* mixture).

Scheme 4. Chemical transformations of the siloxycyclopentene core.



Conclusion

In summary, we expanded the scope of acylsilane-derived carbenes reactivity towards the preparation of new highly functionalized cyclopentene scaffolds, which can be modified without disruption of the cyclic core. To the best of our knowledge, this work presents the first entry on the cycloaddition of photogenerated siloxycarbenes with dienes without the use of transition metal catalysis, paving the way for the use of easily prepared acylsilanes toward the metal-free synthesis of other cyclopentanes. While sensitive to stereochemical constraints, the metal-free cyclopropane ring expansion to cyclopentene proceeds with similar energy requirements for both diastereomeric cyclopropanes as demonstrated by DFT calculations.

Experimental Section

General information: NMR spectra were recorded in a Bruker Fourier 300 (Bruker, Massachusetts, USA), a Bruker Avance III (300 MHz) or a Bruker Fourier 400 (Bruker, Massachusetts, USA) using $CDCl_3$, D_2O or $(CD_3)_2SO$ as deuterated solvents. All coupling constants are expressed in Hz and chemical shifts (δ) in ppm. Multiplicities are given as: s (singlet), d (doublet), dd (double doublet), dt (double triplet), t (triplet), td (triple triplet), tt (triple triplet), q (quartet), quint (quintuplet) and m (multiplet). Irradiation experiments were performed in a home-made Rayonet inspired reactor with 16 lamps (419 nm). High Resolution Mass spectra were recorded in a Thermo Scientific Q Exactive hybrid quadrupole-Orbitrap mass spectrometer (Thermo Scientific Q Exactive Plus). Reaction mixtures were analyzed by thin layer chromatography using Merck silica gel 60F254 aluminium plates and visualized by UV light or stained with potassium permanganate or phosphomolybdic acid stain. Column chromatography was performed with silica gel Geduran® Si 60 (0.040-0.063 mm) purchased from Merck. All solvents were distilled before use. Dry THF and DCM were obtained from INERT pure solv micro apparatus. Toluene was dried by standing in freshly activated 4Å molecular sieves (20% m/v). Acetonitrile was dried by refluxing with CaH. All reagents used were purchased from Fluorochem, Alfa Aesar, TCI or Sigma-Aldrich. X-ray crystallographic analysis of 3b was conducted using Bruker D8 Venture diffractometer equipped with a Photon 100 CMOS detector and an Oxford Cryostem Cooler, using graphite monochromated Mo-Kα radiation (λ= 0.71073 Å). Dienes **2** were synthesized according to a reported procedure[38] and used immediately after purification. Dithianes **8** were prepared according to a reported procedure.[45,46]

*Ethyl 4,4-dicyano-3-(4-(dimethylamino)phenyl)-2-methylenebut-3-enoate (**2l**):* Following the reported procedure, [38] **2l** was obtained in 12% yield (53 mg) as a red oil. Column eluent hexane/DCM (20:80) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 2H), 6.84 (s, 1H), 6.70 – 6.64 (m, 2H), 6.03 (s, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.10 (s, 6H), 1.20 (t, J = 7.1 Hz, 3H). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ 167.8, 163.8, 153.7, 138.7, 133.9, 132.0, 120.6, 115.3, 114.7, 111.4, 62.1, 40.1, 14.1. HRMS *m/z*: $[M+H]^+$ calculated for $C_{17}H_{18}N_3O_2^+$ 296.13935, found 296.13834.

*General procedure for preparation of silyl dithianes **9a-f**, **9n**, adapted from a reported procedure*[47]: Dithiane **8** (9.5 mmol) was dissolved in 40 mL of dry THF, in a dried, argon-filled round-bottom flask. The solution was cooled to -78 °C and *n*BuLi (2.5M solution in hexanes, 1.2 equiv., 11.4 mmol) was added dropwise. The solution was stirred at -78 °C for ten minutes after which *tert*-butyldimethylsilyl chloride (11.4 mmol, 1.2 equiv.) was added dropwise at this temperature. The solution was stirred at -78 °C for an additional ten minutes and then left warming to RT for a minimum of one hour. The reaction was quenched with 40 mL of a saturated aqueous NH_4Cl solution. The layers were separated, and the organic phase was collected. The aqueous phase was extracted with MTBE (2 × 40

mL) and the organic phases combined, dried over $MgSO_4$ and filtered. After vacuum evaporation of the solvent, the crude was purified via silica column chromatography (eluent hexane/EtOAc mixture) to yield silyldithiane **9**.

*Trimethyl(2-(p-tolyl)-1,3-dithian-2-yl)silane (**9a**)*[48]: following the general procedure, **9a** was obtained in 89% yield (2.38 g) as a colorless oil. Trimethylsilyl chloride was used instead of TBSCl. Column eluent 100% hexane. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.79 – 7.74 (m, 2H), 7.17 (d, J = 8.0 Hz, 2H), 2.83 – 2.74 (m, 2H), 2.45 – 2.38 (m, 2H), 2.35 (s, 3H), 2.09 – 1.83 (m, 2H), 0.06 (s, 9H).

*Tert-butyldimethyl(2-(p-tolyl)-1,3-dithian-2-yl)silane (**9b**):* following the general procedure, **9b** was obtained in 89% yield (2.017 g) as a colorless oil. Column eluent 100% hexane. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.83 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 2.83 – 2.73 (m, 2H), 2.41 – 2.35 (m, 2H), 2.35 (s, 3H), 2.08 – 1.80 (m, 2H), 0.82 (s, 9H), 0.13 (s, 6H). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ 137.6, 135.0, 130.2, 129.2, 48.6, 28.0, 25.3, 25.3, 21.0, 19.9, -6.8. **HRMS m/z:** $[M+H]^+$ calculated for $C_{17}H_{29}S_2Si^+$ 325.1474, found 325.1470.

*Tert-butyldimethyl(2-phenyl-1,3-dithian-2-yl)silane (**9c**)*[49]: following the general procedure, **9c** was obtained in 82% yield (508 mg) as a colorless oil. Column eluent 100% hexane. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.99 – 7.96 (m, 2H), 7.40 – 7.33 (m, 2H), 7.20 – 7.15 (m, 1H), 2.83 – 2.73 (m, 2H), 2.43 – 2.36 (m, 2H), 2.10 – 1.82 (m, 2H), 0.81 (s, 9H), 0.15 (s, 6H). **HRMS m/z:** $[M+H]^+$ calculated for $C_{16}H_{27}S_2Si^+$ .311.1318, found 311.1313.

*Tert-butyl(2-(4-fluorophenyl)-1,3-dithian-2-yl)dimethylsilane (**9d**)*[50]: following the general procedure, **9d** was obtained in 73% yield (483 mg) as a colorless oil. Column eluent 100% hexane. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.96 – 7.89 (m, 2H), 7.09 – 7.02 (m, 2H), 2.80 – 2.70 (m, 2H), 2.40 (dt, J = 14.3, 3.9 Hz, 2H), 2.09 – 1.83 (m, 2H), 0.83 (s, 9H), 0.13 (s, 6H).

*(2-(4-Bromophenyl)-1,3-dithian-2-yl)(tert-butyl)dimethylsilane (**9e**):* following the general procedure, **9e** was obtained in 69% yield (536 mg) as a colorless oil. A freshly prepared solution of LDA was used as base. Column eluent 100% hexane. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.87 – 7.83 (m, 2H), 7.50 – 7.45 (m, 2H), 2.78 – 2.68 (m, 2H), 2.43 – 2.36 (m, 2H), 2.08 – 1.83 (m, 2H), 0.84 (s, 9H), 0.12 (s, 6H). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ 140.5, 132.2, 131.5, 119.6, 48.4, 28.1, 25.3, 25.2, 20.0, -6.9. **HRMS m/z:** $[M+H]^+$ calculated for $C_{16}H_{26}BrS_2Si^+$ 389.0423, found 389.0417.

*4-(2-(Tert-butyldimethylsilyl)-1,3-dithian-2-yl)-N,N-dimethylaniline (**9f**):* following the general procedure, **9f** was obtained in 94% yield (667 mg) as a white amorphous solid. Column eluent hexane/EtOAc (99:1) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.79 – 7.74 (m, 2H), 6.76 – 6.71 (m, 2H), 2.97 (s, 6H), 2.82 (td, J = 14.1, 2.8 Hz, 2H), 2.36 (dt, J = 14.3, 3.9 Hz, 2H), 2.07 – 1.80 (m, 2H), 0.84 (s, 9H), 0.11 (s, 6H). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ 148.3, 131.1, 128.0, 112.5, 48.4, 40.7, 28.1, 25.5, 25.2, 19.8, -6.8. **HRMS m/z:** $[M+H]^+$ calculated for $C_{18}H_{32}NS_2Si^+$ 354.1740, found 354.1731.

*Tert-butyl(2-(3,4-dimethoxyphenyl)-1,3-dithian-2-yl)dimethylsilane (**9n**):* following the general procedure, **9f** was obtained in 89% yield (270 mg) as a white amorphous solid. Column eluent hexane/EtOAc (94:6) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.57 (d, J = 2.4 Hz, 1H), 7.50 (dd, J = 8.5, 2.4 Hz, 1H), 6.87 (d, J = 8.5 Hz, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 2.81 (td, J = 14.0, 2.8 Hz, 2H), 2.40 (dt, J = 14.2, 3.7 Hz, 2H), 2.08 – 1.84 (m, 2H), 0.82 (s, 9H), 0.14 (s, 6H). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ 148.8, 146.9, 133.2, 122.7, 113.8, 110.9, 56.1, 56.0, 48.5, 28.0, 25.4, 25.3, 19.9, -6.7. **HRMS m/z:** $[M+H]^+$ calculated for $C_{18}H_{31}O_2S_2Si^+$ 371.1529, found 371.1524.

*General procedure for preparation of acylsilanes **1a-f**, **1n**, adapted from reported procedure*[51]: Dithiane **9** (3.5 mmol) was dissolved in 17 mL of acetonitrile (sonication and gentle heating were usually required). Then, 5 mL of a saturated aqueous $NaHCO_3$ solution was added and the mixture cooled to 0°C. Then, I_2 (35 mmol, 10 equiv.) was added slowly in portions. After addition, the reaction was left at room temperature for 1 hour. 20 mL of water was added followed by continued addition of NaS_2O_3. The mixture was vigorously stirred until the dark brown color of iodine faded to give a bright yellow solution. Then, the aqueous phase was extracted with MTBE (3 × 20 mL), and the organic phases combined, dried over $MgSO_4$ and filtered. After vacuum evaporation of the solvent the crude was purified via silica column chromatography (eluent hexane/EtOAc mixture) to yield benzoylsilane **1**.

*p-Tolyl(trimethylsilyl)methanone (**1a**)*[52]: following the general procedure, **1a** was obtained in 99% yield (677 mg) as a yellow oil. Column eluent hexane/DCM (6:4). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.59 (d, J = 8.2 Hz, 2H), 7.13 – 7.10 (m, 2H), 2.25 (s, 3H), 0.21 (s, 9H).

*(Tert-butyldimethylsilyl)(p-tolyl)methanone (**1b**)*[53]: following the general procedure, **1b** was obtained in 77% yield (1.117 g), as a yellow amorphous solid. Column eluent hexane/DCM (8:2). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.62 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 7.9 Hz, 2H), 2.30 (s, 3H), 0.86 (s, 9H), 0.26 (s, 6H). **HRMS m/z:** $[M+H]^+$ calculated for $C_{14}H_{23}OSi^+$ 235.1513, found 235.1512.

*(Tert-butyldimethylsilyl)(phenyl)methanone (**1c**)*[49]: following the general procedure, **1c** was obtained in 91% yield (303 mg) as a yellow oil. Column eluent hexane/DCM (8:2). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.71 – 7.68 (m, 2H), 7.47 – 7.33 (m, 3H), 0.86 (s, 9H), 0.27 (s, 6H). **HRMS m/z:** $[M+H]^+$ calculated for $C_{13}H_{21}OSi^+$ 221.1356, found 221.1354.

*(Tert-butyldimethylsilyl)(4-fluorophenyl)methanone (**1d**)*[50]: following the general procedure, **1d** was obtained in 87% yield (291 mg) as a yellow oil. Column eluent hexane/EtOAc (98:2). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 2H), 7.07 – 6.99 (m, 2H), 0.85 (s, 9H), 0.27 (s, 3H).

*(4-Bromophenyl)(tert-butyldimethylsilyl)methanone (**1e**):* following the general procedure, **1e** was obtained in 87% yield (350 mg) as a yellow oil. Column eluent hexane/EtOAc (98:2). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.58 – 7.48 (m, 4H), 0.85 (s, 9H), 0.26 (s, 6H). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ 234.7, 141.4, 132.0, 129.2, 127.8, 26.8, 17.1, -4.6. **HRMS *m/z*:** $[M+H]^+$ calculated for $C_{13}H_{20}BrOSi^+$ 299.0461, found 299.0460.

*(Tert-butyldimethylsilyl)(4-(dimethylamino)phenyl)methanone (**1f**):* following the general procedure, **1f** was obtained in 40% yield (194 mg) as a yellow amorphous sold. Column eluent hexane/EtOAc (85:15). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 2H), 6.59 – 6.54 (m, 2H), 2.95 (s, 6H), 0.86 (s, 9H), 0.25 (s, 6H). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ 230.5, 153.2, 132.4, 130.3, 110.7, 40.2, 27.0, 17.0, -4.2. **HRMS *m/z*:** $[M+H]^+$ calculated for $C_{15}H_{26}NOSi^+$ 264.1778, found 264.1773.

*4-((Trimethylsilyl)carbonyl)benzonitrile (**1g**):* dithiane **8g** (443 mg, 2 mmol) was dissolved in 9 mL of dry THF, in a dried, argon-filled round-bottom flask. The solution was cooled to -78 °C and *n*BuLi (0.96 mL of 2.5M solution in hexanes, 1.2 equiv., 2.4 mmol) was added dropwise. The solution was stirred at -78 °C for ten minutes after which trimethylsilyl chloride (303 μL, 2.4 mmol, 1.2 equiv.) was added dropwise at this temperature.

The solution was stirred at -78 °C for an additional ten minutes and then left warming to RT for a minimum of one hour. The reaction was quenched with 10 mL of a saturated aqueous NH_4Cl solution. The layers were separated, and the organic phase collected. The aqueous phase was extracted with MTBE (2 × 10 mL) and the organic phases combined, dried over $MgSO_4$ and filtered. The crude containing **9g** was redissolved in 12 mL of acetonitrile. Then, 4 mL of saturated aqueous $NaHCO_3$ solution was added and the mixture cooled to 0°C. Then, I_2 (5.08 g, 20 mmol, 10 equiv.) was added slowly in portions. After addition, the reaction was left at room temperature for 1 hour. Water was added (20 mL) followed by NaS_2O_3, and the mixture vigorously stirred until the dark brown color of iodine faded to give a bright yellow solution. Then, the aqueous phase was extracted with MTBE (3 × 20 mL), and the organic phases combined, dried over $MgSO_4$ and filtered. After vacuum evaporation of the solvent the crude was purified via silica column chromatography eluent hexane/EtOAc (96:4) to yield acylsilane **1g** in 54% yield (220 mg, 1.08 mmol) as a bright yellow oil, as previously reported.[51] **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.89 – 7.86 (m, 2H), 7.79 – 7.76 (m, 2H), 0.38 (s, 9H).

*o-Tolyl(trimethylsilyl)methanone (**1m**):* The benzotriazole hemiaminal ether (535 mg, 2 mmol) was dissolved in dry THF (9 mL), in a dried, argon-filled round-bottom flask. The solution was cooled to -78 °C and *n*BuLi (0.96 mL of 2.5M solution in hexanes, 1.2 equiv., 2.4 mmol) was added dropwise. The solution was stirred at -78 °C for ten minutes after which trimethylsilyl chloride (303 µL, 2.4 mmol, 1.2 equiv.) was added dropwise at this temperature. The solution was stirred at -78 °C for an additional ten minutes and then left warming to RT for a minimum of one hour. The reaction was quenched with 10 mL of a 1 M HCl solution. The layers were separated, and the organic phase collected. The aqueous phase was extracted with MTBE (2 × 10 mL) and the organic phases combined, dried over $MgSO_4$ and filtered. The crude oil was redissolved in 10 mL of acetone and $FeCl_3 \cdot 6H_2O$ added. After 1 hour, the acetone was evaporated, and the crude oil dissolved in 10 mL of hexane and filtered. The liquid was evaporated under reduced pressure and the crude purified via silica column chromatography eluent hexane 100% to give **1m** in 95% yield (364 mg, 1.9 mmol) as a bright yellow oil, with similar spectral characterization as previously reported.[52] **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.58 (dd, J = 7.2, 1.8 Hz, 1H), 7.37 – 7.22 (m, 3H), 2.42 (s, 3H), 0.32 (s, 9H).

*(Tert-butyldimethylsilyl)(3,4-dimethoxyphenyl)methanone (**1n**):* following the general procedure, **1n** was obtained in 90% yield (176 mg) as a yellow amorphous solid. Column eluent hexane/EtOAc (92:8). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.52 (dd, J = 8.3, 1.9 Hz, 1H), 7.36 (d, J = 1.9 Hz, 1H), 6.91 (d, J = 8.3 Hz, 1H), 3.94 (s, 3H), 3.91 (s, 3H), 0.96 (s, 9H), 0.36 (s, 6H). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ 232.5, 153.1, 149.3, 136.7, 124.6, 110.0, 108.0, 56.2, 55.9, 26.9, 17.0, -4.3. **HRMS m/z:** $[M+H]^+$ calculated for $C_{15}H_{25}O_3Si^+$ 281.1567, found 281.1561.

*General procedure for the synthesis of cyclopentenes **3**:* acylsilane **1** (0.1 mmol) and diene **2** (0.14 mmol, 1.4 equiv.) were dissolved in 0.5 mL of dry toluene in a sealed Pasteur pipette. 100 mg of molecular sieves 4 Å were added and the solution was purged with argon for 15 minutes and irradiated at 419 nm from a minimum of 24 to maximum 72 h. Reaction progress was monitored by TLC and stopped upon full consumption of acylsilane **1**. Toluene was evaporated under reduced pressure and the crude purified via silica column chromatography (eluent hexane/EtOAc) to give cyclopentenes **3**.

*Ethyl 3,3-dicyano-2-phenyl-4-(p-tolyl)-4-((trimethylsilyl)oxy)cyclopent-1-ene-1-carboxylate (**3a**):* following the general procedure, **3a** was obtained in 66% yield (29.5 mg) as an off-white amorphous solid. 23 h reaction. Column eluent hexane/EtOAc (95:5). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.58 (d, J = 8.3 Hz, 2H), 7.45 – 7.38 (m, 5H), 7.27 (d, J = 8.0 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.88 (d, J = 17.1 Hz, 1H), 3.36 (d, J = 17.1 Hz, 1H), 2.40 (s, 3H), 1.07 (t, J = 7.1 Hz, 3H), 0.07 (s, 9H). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ 163.6, 143.7, 140.0, 135.2, 134.5, 131.7, 129.9, 129.6, 128.5, 128.2, 126.6, 112.4, 112.1, 89.0, 61.5, 60.6, 43.4, 21.3, 13.8, 1.3. **HRMS m/z:** $[M+H]^+$ calculated for $C_{26}H_{29}N_2O_3Si^+$ 445.1942, found 445.1942.

*Ethyl 4-((tert-butyldimethylsilyl)oxy)-3,3-dicyano-2-phenyl-4-(p-tolyl)cyclopent-1-ene-1-carboxylate (**3b**):* following the general procedure, **3b** was obtained in 74% yield (36.2 mg) as an off-white amorphous solid. 55 h reaction. Column eluent hexane/EtOAc (94:6). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.61 (d, J = 8.3 Hz, 2H), 7.46 – 7.36 (m, 5H), 7.27 (d, J = 7.9 Hz, 2H), 4.12 (qd, J = 7.1, 2.0 Hz, 2H), 3.90 (d, J = 17.1 Hz, 1H), 3.36 (d, J = 17.0 Hz, 1H), 1.07 (t, J = 7.1 Hz, 3H), 0.93 (s, 9H), 0.00 (s, 3H), -0.22 (s, 3H). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ 163.5, 144.1, 140.2, 135.0, 134.5, 131.7, 129.9, 129.7, 128.6, 128.2, 126.9, 112.4, 112.3, 89.0, 61.5, 60.1, 43.1, 25.7, 21.4, 18.5, 13.9, -3.3, -3.5. **HRMS m/z:** $[M+H]^+$ calculated for $C_{29}H_{35}N_2O_3Si^+$ 487.2411, found 487.2412.

*Ethyl 4-((tert-butyldimethylsilyl)oxy)-3,3-dicyano-2,4-diphenylcyclopent-1-ene-1-carboxylate (**3c**):* following the general procedure, **3c** was obtained in 68% yield (32.1 mg) as an off-white amorphous solid. 55 h reaction. Column eluent hexane/EtOAc (94:6). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.76 – 7.73 (m, 2H), 7.49 – 7.38 (m, 8H), 4.13 (qd, J = 7.1, 1.9 Hz, 2H), 3.94 (d, J = 17.0 Hz, 2H), 3.40 (d, J = 17.0 Hz, 1H), 1.08 (t, J = 7.1 Hz, 3H), 0.94 (s, 9H), 0.02 (s, 3H), -0.22 (s, 3H). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ 163.4, 144.0, 138.0, 134.4, 131.6, 130.2, 129.9, 129.0, 128.6, 128.2, 126.9, 112.3, 112.2, 89.0, 61.5, 60.0, 43.0, 25.7, 18.5, 13.8, -3.3, -3.6. **HRMS m/z:** $[M+H]^+$ calculated for $C_{28}H_{33}N_2O_3Si^+$ 473.2255, found 473.2255.

*Ethyl 4-((tert-butyldimethylsilyl)oxy)-3,3-dicyano-4-(4-fluorophenyl)-2-phenylcyclopent-1-ene-1-carboxylate (**3d**):* following the general procedure, **3d** was obtained in 66% yield (32.6 mg) as an off-white amorphous solid. 72 h reaction. Column eluent hexane/EtOAc (93:7). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 2H), 7.46 – 7.37 (m, 5H), 7.21 – 7.14 (m, 2H), 4.12 (qd, J = 7.1, 1.8 Hz, 2H), 3.89 (d, J = 17.1 Hz, 1H), 3.39 (d, J = 17.0 Hz, 1H), 1.07 (t, *J* = 7.1 Hz, 3H), 0.94 (s, 9H), 0.04 (s, 3H), -0.21 (s, 3H). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ 165.3, 163.3, 162.0, 144.0, 134.2, 134.1, 134.1, 131.5, 130.0, 129.1, 128.9, 128.6, 128.2, 116.2, 116.0, 112.1, 112.1, 88.5, 61.5, 60.1, 43.1, 25.7, 18.5, 13.8, -3.2, -3.5. **^{19}F{1H} NMR** (376 MHz, $CDCl_3$) δ -110.6. **HRMS m/z:** $[M]^+$ calculated for $C_{28}H_{31}FN_2O_3Si^+$ 490.2082, found 490.2082.

*Ethyl 4-(4-bromophenyl)-4-((tert-butyldimethylsilyl)oxy)-3,3-dicyano-2-phenylcyclopent-1-ene-1-carboxylate (**3e**):* following the general procedure, **3e** was obtained in 66% yield (36.5 mg) as an off-white amorphous solid. 55 h reaction. Column eluent hexane/EtOAc (90:10). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.62 (s, 4H), 7.46 – 7.37 (m, 5H), 4.12 (qd, J = 7.1, 1.9 Hz, 2H), 3.87 (d, J = 17.1 Hz, 1H), 3.38 (d, J = 17.0 Hz, 1H), 1.07 (t, J = 7.1 Hz, 3H), 0.94 (s, 9H), 0.05 (s, 3H), -0.19 (s, 3H). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ 163.3, 143.9, 137.1, 134.2, 132.3, 131.4, 130.0, 128.6, 128.6, 128.2, 124.6, 112.0, 112.0, 88.5, 61.6, 60.0, 42.8, 25.7, 18.5, 13.8, -3.2, -3.5. **HRMS m/z:**

$[M+H]^+$ calculated for $C_{28}H_{32}BrN_2O_3Si^+$ 551.1360, found 551.1361.

*Ethyl 4-((tert-butyldimethylsilyl)oxy)-3,3-dicyano-4-(4-(dimethylamino)phenyl)-2-phenylcyclopent-1-ene-1-carboxylate (**3f**):* following the general procedure, **3f** was obtained in 62% yield (32 mg) as an off-white amorphous solid. 48 h reaction. Column eluent hexane/DCM (65:35). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.55 (d, J = 8.9 Hz, 2H), 7.45 – 7.37 (m, 5H), 6.73 (d, J = 9.0 Hz, 2H), 4.11 (qd, J = 7.1, 2.1 Hz, 2H), 3.87 (d, J = 17.0 Hz, 1H), 3.33 (d, J = 17.0 Hz, 1H), 3.01 (s, 6H), 1.07 (t, J = 7.1 Hz, 3H), 0.93 (s, 9H), -0.00 (s, 3H), -0.17 (s, 3H). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ 163.7, 151.2, 144.2, 134.5, 131.9, 129.7, 128.5, 128.2, 128.0, 124.8, 112.7, 112.5, 111.8, 89.3, 61.3, 60.3, 43.3, 40.2, 25.7, 18.5, 13.8, -3.3, -3.5. **HRMS m/z:** $[M+H]^+$ calculated for $C_{30}H_{38}N_3O_3Si^+$ 516.26770, found 516.2670.

*Ethyl 4-((tert-butyldimethylsilyl)oxy)-3,3-dicyano-2-(4-fluorophenyl)-4-phenylcyclopent-1-ene-1-carboxylate (**3h**):* following the general procedure, **3h** was obtained in 61% yield (30.2 mg) as an off-white amorphous solid. 55 h reaction. Column eluent hexane/EtOAc (93:7). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 2H), 7.49 – 7.47 (m, 3H), 7.42 – 7.38 (m, 2H), 7.19 – 7.11 (m, 2H), 4.15 (qd, J = 7.1, 2.4 Hz, 2H), 3.92 (d, J = 17.1 Hz, 1H), 3.39 (d, J = 17.0 Hz, 1H), 1.12 (t, J = 7.1 Hz, 3H), 0.93 (s, 9H), 0.00 (s, 3H), -0.23 (s, 3H). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ 165.3, 163.2, 162.0, 143.1, 137.8, 134.9, 130.5, 130.3, 130.3, 129.1, 127.6, 127.5, 126.9, 116.0, 115.7, 112.3, 112.1, 89.0, 61.6, 60.0, 43.0, 25.7, 18.5, 13.9, -3.3, -3.6. **^{19}F{1H} NMR** (376 MHz, $CDCl_3$) δ -110.3 **HRMS m/z:** $[M]^+$ calculated for $C_{28}H_{31}FN_2O_3Si^+$ 490.2082, found 490.2082.

*Ethyl 4-((tert-butyldimethylsilyl)oxy)-2-(4-chlorophenyl)-3,3-dicyano-4-phenylcyclopent-1-ene-1-carboxylate (**3i**):* following the general procedure, **3i** was obtained in 77% yield (39.1 mg) as an off-white amorphous solid. 55 h reaction. Column eluent hexane/EtOAc (92:8). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.74 – 7.71 (m, 2H), 7.50 – 7.42 (m, 5H), 7.36 – 7.33 (m, 2H), 4.15 (qd, J = 7.1, 2.3 Hz, 2H), 3.92 (d, J = 17.2 Hz, 1H), 3.39 (d, J = 17.1 Hz, 1H), 1.13 (t, J = 7.1 Hz, 3H), 0.93 (s, 9H), 0.00 (s, 3H), -0.23 (s, 3H). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ 163.1, 142.9, 137.8, 136.2, 135.1, 130.3, 130.0, 129.7, 129.1, 129.0, 126.9, 112.2, 112.0, 89.0, 61.7, 59.8, 43.0, 25.7, 18.5, 13.9, -3.3, -3.6. **HRMS m/z:** $[M+H]^+$ calculated for $C_{28}H_{32}ClN_2O_3Si^+$ 507.1865, found 507.1825.

*Ethyl 2-(4-bromophenyl)-4-((tert-butyldimethylsilyl)oxy)-3,3-dicyano-4-phenylcyclopent-1-ene-1-carboxylate (**3j**):* following the general procedure, **3j** was obtained in 72% yield (40.0 mg) as an off-white amorphous solid. 55 h reaction. Column eluent hexane/DCM (60:40). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.62 (s, 4H), 7.46 – 7.44 (m, 3H), 7.41 – 7.36 (m, 2H), 4.12 (qd, J = 7.1, 1.9 Hz, 2H), 3.87 (d, J = 17.1 Hz, 1H), 3.38 (d, J = 17.0 Hz, 1H), 1.07 (t, J = 7.1 Hz, 3H), 0.94 (s, 9H), 0.05 (s, 3H), -0.19 (s, 3H). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ 163.3, 143.9, 137.1, 134.2, 132.3, 131.4, 130.0, 128.6, 128.6, 128.2, 124.6, 112.0, 112.0, 88.5, 61.6, 60.0, 42.8, 25.7, 18.5, 13.8, -3.2, -3.5. **HRMS m/z:** $[M]^+$ calculated for $C_{28}H_{31}BrN_2O_3Si^+$ 550.1282, found 550.1284.

*Ethyl 4-((tert-butyldimethylsilyl)oxy)-3,3-dicyano-2-(4-methoxyphenyl)-4-phenylcyclopent-1-ene-1-carboxylate (**3k**):* following the general procedure, **3k** was obtained in 66% yield (33.2 mg) as an off-white amorphous solid. 72 h reaction. Column eluent hexane/EtOAc (90:10). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.76 – 7.72 (m, 2H), 7.50 – 7.45 (m, 3H), 7.40 – 7.35 (m, 2H), 6.99 – 6.94 (m, 2H), 4.16 (qd, J = 7.1, 2.0 Hz, 2H), 3.91 (d, J = 17.0 Hz, 1H), 3.84 (s, 3H), 3.37 (d, J = 17.0 Hz, 1H), 0.92 (s, 9H), 0.01 (s, 3H), -0.23 (s, 3H). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ 163.6, 160.9, 144.1, 138.0, 133.1, 130.1, 129.9, 129.0, 127.0, 123.7, 114.0, 112.6, 112.4, 88.9, 61.4, 59.9, 55.4, 43.1, 25.7, 18.5, 14.0, -3.3, -3.6. **HRMS m/z:** $[M+H]^+$ calculated for $C_{29}H_{35}N_2O_4Si^+$ 503.2361, found 503.2357.

*Ethyl 3,3-dicyano-2-phenyl-4-(o-tolyl)-4-((trimethylsilyl)oxy)cyclopent-1-ene-1-carboxylate (**3m**):* following the general procedure, **3m** was obtained in 40% yield (17.7 mg) as an off-white amorphous solid. 72 h reaction. Column eluent hexane/EtOAc (93:7). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.50 – 7.22 (m, 9H), 4.15 – 4.08 (m, 2H), 3.94 (d, J = 17.0 Hz, 1H), 3.50 (d, J = 17.0 Hz, 1H), 2.70 (s, 3H), 1.04 (t, J = 7.1 Hz, 3H), 0.10 (s, 9H). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ 163.5, 142.9, 138.9, 136.4, 135.2, 133.8, 131.6, 129.8, 129.7, 128.5, 128.3, 128.0, 126.2, 112.7, 112.3, 91.1, 61.6, 60.0, 46.2, 24.3, 13.8, 1.4. **HRMS m/z:** $[M+H]^+$ calculated for $C_{26}H_{29}N_2O_3Si^+$ 445.1942, found 445.1942.

*Ethyl 4-((tert-butyldimethylsilyl)oxy)-3,3-dicyano-4-(3,4-dimethoxyphenyl)-2-phenylcyclopent-1-ene-1-carboxylate (**3n**):* following the general procedure, **3n** was obtained in 80% yield (42.5 mg), off-white amorphous solid. 48 h reaction. Column eluent hexane/EtOAc (92:8). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 6H), 7.19 (dd, J = 8.4, 2.3 Hz, 1H), 6.90 (d, J = 8.4 Hz, 1H), 4.19 – 4.04 (m, 2H), 3.93 (s, 3H), 3.92 (s, 3H), 3.90 (d, J = 17.0 Hz, 1H), 3.34 (d, J = 17.0 Hz, 1H), 1.06 (t, J = 7.1 Hz, 3H), 0.95 (s, 9H), 0.03 (s, 3H), -0.18 (s, 3H). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ 163.5, 150.3, 149.2, 144.1, 134.3, 131.7, 130.3, 129.9, 128.6, 128.1, 119.3, 112.4, 112.3, 110.5, 110.0, 89.0, 61.4, 60.3, 56.0, 55.9, 42.9, 25.7, 18.5, 13.8, -3.3, -3.5. **HRMS m/z:** $[M+H]^+$ calculated for $C_{30}H_{37}N_2O_5Si^+$ 533.2466, found 533.2463.

*Ethyl 2-(4-bromophenyl)-4-((tert-butyldimethylsilyl)oxy)-3,3-dicyano-4-(3,4-dimethoxyphenyl)cyclopent-1-ene-1-carboxylate (**3o**):* following the general procedure, **3o** was obtained in 90% yield (54.8 mg), off-white amorphous solid. 48 h reaction. Column eluent hexane/EtOAc (85:15). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 2.3 Hz, 1H), 7.28 (d, J = 8.3 Hz, 2H), 7.17 (dd, J = 8.4, 2.3 Hz, 1H), 6.92 (d, J = 8.4 Hz, 1H), 4.20 – 4.12 (m, 2H), 3.94 (s, 6H), 3.90 (d, J = 17.2 Hz, 1H), 3.35 (d, J = 17.1 Hz, 1H), 1.14 (t, J = 7.1 Hz, 3H), 0.95 (s, 9H), 0.04 (s, 3H), -0.16 (s, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 163.1, 150.3, 149.2, 142.9, 135.0, 131.9, 130.5, 130.0, 129.8, 124.4, 119.2, 112.2, 112.1, 110.5, 109.8, 89.1, 61.6, 60.0, 56.0, 55.9, 42.8, 25.6, 18.4, 13.9, -3.4, -3.6. **HRMS m/z:** $[M+H]^+$ calculated for $C_{30}H_{36}BrN_2O_5Si^+$ 611.1571, found 611.1583.

*Ethyl 2-(4-bromophenyl)-4-((tert-butyldimethylsilyl)oxy)-3,3-dicyano-4-(p-tolyl)cyclopent-1-ene-1-carboxylate (**3p**):* following the general procedure, **3p** was obtained in 69% yield (39.0 mg), yellow amorphous solid. 48 h reaction. Column eluent hexane/EtOAc (85:15). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.0 Hz, 4H), 7.25 (d, J = 8.1 Hz, 4H), 4.18 – 4.07 (m, 2H), 3.87 (d, J = 17.1 Hz, 1H), 3.33 (d, J = 17.1 Hz, 1H), 2.38 (s, 3H), 1.10 (t, J = 7.1 Hz, 3H), 0.90 (s, 9H), -0.03 (s, 3H), -0.24 (s, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 163.1, 142.9, 140.3, 135.1, 134.8, 131.9, 130.5, 129.9, 129.7, 126.8, 124.4, 112.2, 112.1, 89.0, 61.6, 59.8, 43.1, 25.7, 21.4, 18.4, 13.9, -3.3, -3.6. **HRMS m/z:** $[M+H]^+$ calculated for $C_{29}H_{34}BrN_2O_3Si^+$ 565.1517, found 565.1526.

*Ethyl 2,4-bis(4-bromophenyl)-4-((tert-butyldimethylsilyl)oxy)-3,3-dicyanocyclopent-1-ene-1-carboxylate (**3q**)*: following the general procedure, **3q** was obtained in 87% yield (52.4 mg),

white amorphous solid. 72 h reaction. Column eluent hexane/DCM (68:32). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 6H), 7.25 (d, J = 8.3 Hz, 2H), 4.20 – 4.08 (m, 2H), 3.85 (d, J = 17.1 Hz, 1H), 3.35 (d, J = 17.1 Hz, 1H), 1.11 (t, J = 7.1 Hz, 3H), 0.91 (s, 9H), 0.02 (s, 3H), -0.21 (s, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 162.9, 142.7, 136.9, 134.9, 132.3, 131.9, 130.2, 129.8, 128.5, 124.7, 124.6, 111.8 (2), 88.5, 61.8, 59.7, 42.8, 25.6, 18.4, 13.9, -3.2, -3.5. **HRMS m/z:** $[M+H]^+$ calculated for $C_{28}H_{31}Br_2N_2O_3Si^+$ 631.0445, found 631.0461.

*Ethyl 4-(4-bromophenyl)-4-((tert-butyldimethylsilyl)oxy)-2-(4-chlorophenyl)-3,3-dicyanocyclopent-1-ene-1-carboxylate **(3r)***: following the general procedure, **3r** was obtained in 69% yield (40.6 mg), pale oil. 72 h reaction. Column eluent hexane/DCM (70:30). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 4H), 7.44 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 4.18 – 4.09 (m, 2H), 3.87 (d, J = 17.1 Hz, 1H), 3.37 (d, J = 17.1 Hz, 1H), 1.13 (t, J = 7.1 Hz, 3H), 0.93 (s, 9H), 0.03 (s, 3H), -0.20 (s, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 163.0, 142.8, 136.9, 136.3, 134.9, 132.3, 129.7, 129.6, 129.0, 128.5, 124.8, 111.9 (2), 88.5, 61.8, 59.8, 42.8, 25.6, 18.4, 13.9, -3.2, -3.5. **HRMS m/z:** $[M+H]^+$ calculated for $C_{28}H_{31}BrClN_2O_3Si^+$ 585.0970, found 585.0979.

*Ethyl 4,4-dicyano-2-(2-oxo-2-(p-tolyl)ethyl)-3-phenylbut-3-enoate **(4)**:* cyclopentene **3b** (10 mg, 20 µmol) was dissolved in THF (1 mL) in a round-bottom flask. The solution was cooled to 0°C and TBAF·H_2O (7.1 mg, 23 µmol, 1.1 equiv.) was added. After 10 min at 0°C the solution was warmed to room temperature. Ketone **4** was purified by silica column flash chromatography with dry loading, using hexane/EtOAc (80:20) as eluent to give **4** as an amorphous off-white solid in 78% yield (5.8 mg, 16 µmol). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.72 (d, J = 8.2 Hz, 2H), 7.51 – 7.39 (m, 3H), 7.27 – 7.20 (m, 4H), 4.83 (dd, J = 8.3, 5.5 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 3.74 (dd, J = 18.4, 5.5 Hz, 1H), 3.17 (dd, J = 18.4, 8.4 Hz, 1H), 2.39 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ 195.4, 175.2, 168.6, 145.0, 133.6, 133.3, 131.8, 129.6, 129.4, 128.3, 127.6, 112.4, 112.1, 90.0, 63.0, 47.9, 38.7, 21.8, 14.2. **HRMS m/z:** $[M+H]^+$ calculated for $C_{23}H_{21}N_2O_3^+$ 373.1547, found 373.1544.

*5-((Tert-butyldimethylsilyl)oxy)-3-(hydroxymethyl)-2-phenyl-5-(p-tolyl)cyclopent-2-ene-1,1-dicarbonitrile **(5)**:* cyclopentene **3b** (20 mg, 41 µmol) was dissolved in dry THF (2 mL) in a round-bottom flask and the resulting Solution cooled to 0°C. $LiBH_4$ (3 mg, 135 µmol, 3.3 equiv.) was added and the reaction warmed to room temperature. After 3 h, water (9.7 µL, 540 µmol, 13.2 equiv.) was added and the solution left stirring for 5 minutes. Then, the solvent was evaporated and the crude purified by silica flash column chromatography, using hexane/EtOAc as eluent (80:20) to give alcohol **5** in 48% yield (8.8 mg, 20 µmol). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.61 (d, J = 8.3 Hz, 2H), 7.47 – 7.41 (m, 3H), 7.34 – 7.32 (m, 2H), 7.25 (d, J = 6.7 Hz, 2H), 4.44 – 4.33 (m, 2H), 3.76 (d, J = 17.0 Hz, 1H), 3.21 (d, J = 17.0 Hz, 1H), 2.39 (s, 3H), 0.92 (s, 9H), 0.01 (s, 3H), -0.23 (s, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 144.1, 139.9, 135.9, 132.0, 131.5, 129.6, 129.4, 129.1, 128.6, 127.1, 113.6, 113.6, 89.2, 59.7, 58.7, 43.6, 25.8, 21.4, 18.5, -2.9, -3.4. **HRMS m/z:** $[M+H]^+$ calculated for $C_{27}H_{33}N_2O_2Si^+$ 445.2306, found 445.2304.

*4-((Tert-butyldimethylsilyl)oxy)-3,3-dicyano-2-phenyl-4-(p-tolyl)cyclopent-1-ene-1-carboxylic acid **(6)**:* cyclopentenone **3b** (6 mg, 12 µmol) was dissolved in EtOH (1 mL). LiOH (20 µL of 1 M aqueous solution, 20 µmol, 2 equiv.) was added and the solution stirred for 5 h at room temperature. Then, the solvent was evaporated and the crude purified by silica flash column chromatography, using hexane/EtOAc/AcOH (60:40:0.1) as eluent to give carboxylic acid **6** in 69% yield (3.8 mg, 8.3 µmol) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.3 Hz, 2H), 7.47 – 7.39 (m, 5H), 7.27 (d, J = 6.6 Hz, 2H), 3.90 (d, J = 17.1 Hz, 1H), 3.36 (d, J = 17.0 Hz, 1H), 2.40 (s, 3H), 0.92 (s, 9H), -0.00 (s, 3H), -0.23 (s, 3H). **^{13}C{1H} NMR** (100 MHz, $CDCl_3$) δ 167.3, 146.3, 140.3, 134.8, 133.4, 131.3, 130.2, 129.8, 128.8, 128.2, 126.9, 112.2, 112.1, 88.9, 60.3, 43.2, 25.7, 21.4, 18.5, -3.2, -3.5. **HRMS m/z:** $[M+H]^+$ calculated for $C_{27}H_{31}N_2O_3Si^+$ 459.2098, found 459.2091.

*Cesium 1,1-dicyano-3-(ethoxycarbonyl)-5-oxo-2-phenyl-5-(p-tolyl)pent-2-en-1-ide **(7)**:* cyclopentene **3b** (10 mg, 20 µmol) was dissolved in dry ACN (1 mL) in an oven-dried round-bottom flask, under argon atmosphere. CsF (94 mg, 620 µmol, 30 equiv.) was added and the solution left stirring for 3 hours. The solvent was evaporated, and the crude mixture was redissolved in acetone. The solid CsF excess was filtered off through celite and the filtrate evaporated to give salt **7** as a bright yellow oil in 75% yield (7.6 mg, 15 µmol) as a 1:0.2 mixture of *E/Z* isomers. **7** can be converted to **4** simply via passing through silica plug. **7a** (major): **^{1}H NMR** (400 MHz, $(CD_3)_2CO$) δ 7.94 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 7.21 (s, 5H), 4.39 (s, 2H), 3.52 (q, J = 7.1 Hz, 2H), 2.39 (s, 3H), 0.59 (t, J = 7.1 Hz, 3H). **^{13}C{1H} NMR** (100 MHz, $(CD_3)_2CO$) δ 199.6, 169.8, 158.2, 144.9, 143.2, 136.8, 130.2, 129.7, 129.0, 127.9, 127.8, 125.2, 102.0, 58.7, 43.1, 40.2, 21.6, 14.1. **7b** (minor): **^{1}H NMR** (400 MHz, $(CD_3)_2CO$) δ 7.70 (d, J = 8.2 Hz, 2H), 7.29 – 7.20 (m, 7H) 4.06 (q, J = 7.1 Hz, 2H), 3.60 (s, 2H), 2.33 (s, 3H), 1.12 (t, J = 7.1 Hz, 3H). **HRMS m/z:** $[M+2H]^+$ calculated for $C_{23}H_{21}N_2O_3Si^+$ 373.1547, found 373.1544.

*Ethyl 2-(2,2-dicyano-1-phenylvinyl)-4-oxo-4-(p-tolyl)but-2-enoate **(8)**:* Cyclopentene **3b** (20 mg, 40 µmol) was dissolved in dry ACN (2 mL) in an oven-dried round-bottom flask, under argon atmosphere. CsF (180 mg, 1.2 mmol, 30 equiv.) was added and the solution left stirring for 3 hours. Excess CsF was filtered through celite and NBS (7.1 mg, 40 µmol, 1 equiv.) was added to the filtrate solution. The bright yellow colour of the intermediate **7** quickly fades. The solvent was quickly evaporated. Analysis of the ^{1}H NMR crude at this stage reveals a *E/Z* ratio of 0.45:1. The crude was purified by silica flash column chromatography, using hexane/EtOAc as eluent (80:20) to give diene **8** in 77% yield (11.4 mg, 31 µmol) in a *E/Z* ratio of 1:0.2 in thermodynamic equilibrium (S-Figure 2). **8a** (major): **^{1}H NMR** (400 MHz, $(CD_3)_2CO$) δ 8.41 (s, 1H), 7.96 (d, J = 8.2 Hz, 2H), 7.78 – 7.76 (m, 2H), 7.69 – 7.53 (m, 3H), 7.40 (d, J = 8.2 Hz, 2H), 4.31 (q, J = 7.1 Hz, 2H), 2.43 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H). **^{13}C{1H} NMR** (100 MHz, $(CD_3)_2CO$) δ 189.1, 172.2, 163.4, 146.7, 139.8, 138.7, 134.4, 134.2, 133.6, 130.6, 130.2, 129.9, 129.8, 113.5, 113.4, 85.4, 63.6, 21.7, 14.1. **8b** (minor): **^{1}H NMR** (400 MHz, $(CD_3)_2CO$) δ 7.99 – 7.39 (m, 10H), 3.96 (q, J = 7.1 Hz, 2H), 2.43 (s, 3H), 0.89 (t, *J* = 7.1 Hz, 3H). **HRMS m/z:** $[M+H]^+$ calculated for $C_{23}H_{19}N_2O_3$ 371.1390, found 371.1384. Note: Prolonged heating of the reaction crude at 40°C also delivers the same relative *E/Z* ratio of isomers, further confirming thermodynamic equilibrium. Identification of isomers was conducted via analysis of the ethyl ester β-hydrogen which shows characteristic lower field shift from *trans* to *cis* conformation (relative to ester), from 7.79 to 8.41 ppm.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Full accounts on computational calculations, X-ray crystallographic analysis for **3b**, and ^{1}H and ^{13}C NMR copies of spectra for all novel compounds (PDF).

Corresponding Authors

Nuno R. Candeias – Faculty of Engineering and Natural Sciences, Tampere University, 33101 Tampere, Finland; LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal; Email: ncandeias@ua.pt; orcid.org/0000-0003-2414-9064;
Carlos A. M. Afonso - iMed.ULisboa, Faculty of Pharmacy, Universidade De Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisboa, Portugal; Email: carlosafonso@ff.ulisboa.pt; orcid.org/ 0000-0002-7284-5948

Authors

João R. Vale - Faculty of Engineering and Natural Sciences, Tampere University, 33101 Tampere, Finland; iMed.ULisboa, Faculty of Pharmacy, Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisboa, Portugal; orcid.org/ 0000-0003-0411-9618
Rafael F. Gomes – iMed.Ulisboa, Faculty of Pharmacy, Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisboa, Portugal; orcid.org/ 0000-0002-2598-8540

Author Contributions

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