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Free-radical functionalisation of vinylcyclopropanes

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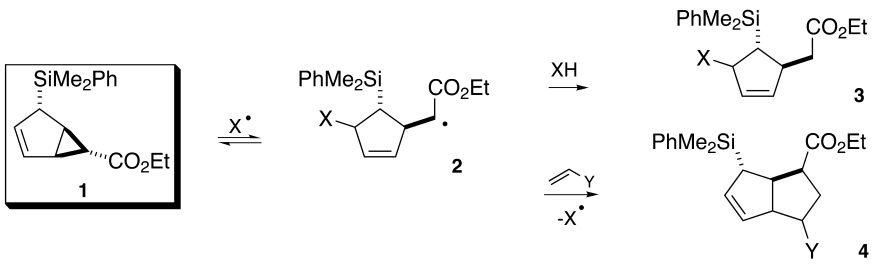
Abstract—Free-radical mediated cyclopropane ring opening of 2-silylbicyclo[3.1.0]hexane **1** has been carried out leading to the corresponding trisubstituted cyclopentenes **5** and **6** in good yield with complete 1,2-stereocontrol. [3+2]-Annulation has also been performed by trapping the resulting radical with electron-rich and electron-poor olefins, leading to the corresponding polycyclic compounds. Further studies on the functionalisation of dihydropyridines and pyrroles using this methodology is also described.

During the course of our studies directed towards the stereocontrolled elaboration of silylcyclopentadienes and cyclohexadienes, we have developed a useful entry towards cyclopropanes such as **1** through monocyclopropanation of silylcyclopentadienes (Scheme 1).[1] An enantioselective route has recently been developed in our laboratories which further enhances the value of such synthons as intermediates for organic synthesis.[2] While the usefulness of such substrates has been demonstrated with the stereocontrolled synthesis of carba-sugars as well as carba-C-disaccharides,[1] we envisioned that the vinylcyclopropane moiety present in **1** should also provide a useful platform for radical transformations through cyclopropane ring opening. Pionnering work by Feldman,[3] Oshima[4] and Jung[5] have shed light on this transformation which enables the rapid elaboration of vinylcyclopropanes into diverse structural motifs such as 1,3-diols, 1,3-disubstituted cyclopentanes and polycyclic systems. Moreover, the presence of a homoallyl- or an allylsilyl moiety in the resulting products **3** and **4** should also allow for further transformations. We report here our results on the free-radical functionalisation of vinylcyclopropane such as **1**. An extension of the methodology to the functionalisation of heterocyclic vinylcyclopropane analogues has also been carried out.

Cyclopropane ring opening induced by free radicals is usually a very fast process ($k \sim 10^8 - 10^9\ s^{-1}$), eventually generating a new radical which can then add onto a range of radical acceptors.[6] It was thus anticipated that addition of a radical species (i.e. X=RS˙) onto the vinyl moiety of **1** would induce the cyclopropane ring opening and produce a stabilized cyclopentenylmethyl radical such as **2**. This could then be reduced to form the highly functionalised addition product **3** (Scheme 1). Radical **2** could also add onto the double bond of a radical acceptor to form a new radical which upon 5-*exo*-trig cyclisation and elimination of X would provide bicyclic compounds such as **4**. Overall, the latter transformation can be considered as a [3+2]-annulation, which would be catalytic in X.



Scheme 1.

Keywords: radicals; cyclopropanes; silicon and compounds; selenium and compounds; annulation; allylsilanes.
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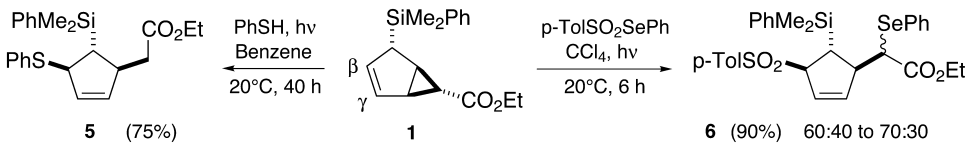
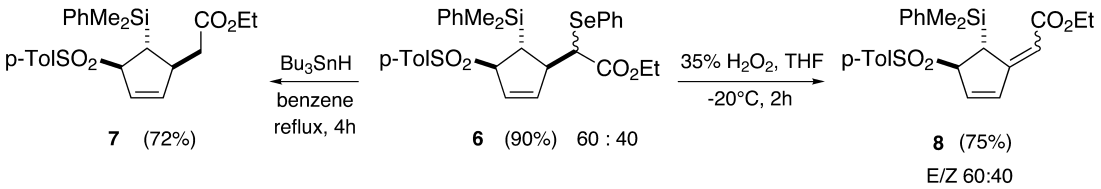


Scheme 2.

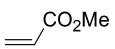
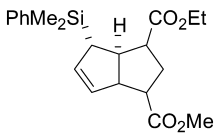
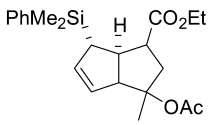
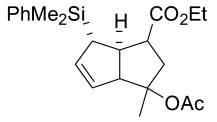
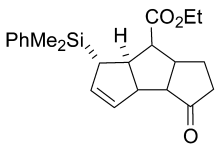
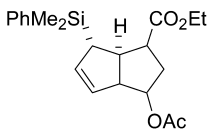


Scheme 3.

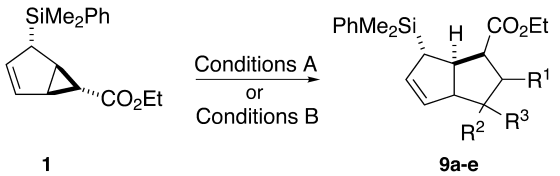
Our preliminary investigations focused on the radical-induced ring opening of **1** using PhSH under irradiation in benzene (Scheme 2).[7] We were pleased to find that addition of the thiophenoxy radical onto the allylsilane moiety occurred readily to provide cyclopentene **5** in good yield. The addition of the thiophenoxy group was completely diastereoselective occuring *anti* relative to the sterically hindered silicon group.[8] Similarly, addition of *p*-$TolSO_2$-SePh onto **1** led to the cyclopropane fragmentation which was followed by the transfer of the phenylselenyl group α to the ester function.[9] The cyclopentene **6** was thus obtained in 90% yield as a mixture (from 60:40 to 70:30) of diastereomers (Scheme 2). When the reaction was carried out with $PhSO_2I$, a clean desilylation of **1** occurred instead of the cyclopropane-ring opening.

Cyclopentenes **5** and **6** are valuable synthons for organic synthesis, having several useful functional groups that can

Table 1. Radical annulation of cyclopropane **1** (Scheme 4)

Entry	Olefin	Product	Conditions	Time	*T* (°C)	Stereoisomers ratio[a]	Yield (%)[b]
1			**A**	2 d	20	74:23:3	35
2		**9a**	**B**	16 h	20	60:40	58
3			**A**	2 d	20	62:27:10	59
4		**9b**	**B**	16 h	20	60:40	72
5			**A**	6 d	20	45:45:10	32
6		**9c**	**B**	16 h	20	46:44:10	60
7			**A**	6 d	40	33:29:22:16	36
8		**9d**	**B**	16 h	20	33:33:22:12	51
9			**B**	16 h	20	44:40:16	63
		9e					

[a] Estimated from the ^1H NMR and GC analysis of the crude reaction mixture after removal of the excess of olefin.
[b] Purified yield including all stereoisomers.



1 9a-e

Scheme 4. *Conditions* **A**: $R^1CH{=}CR^2R^3$ (10 equiv.), PhSSPh (0.3 equiv.) Benzene, sunlamp (300 W). *Conditions* **B**: (1) *p*-$TolSO_2SePh$, CCl_4, sunlamp (300 W); (2) $R^1CH{=}CR^3R^3$ (10 equiv.), $(Bu_3Sn)_2$ (1.2 equiv.) Benzene, sunlamp (300 W).

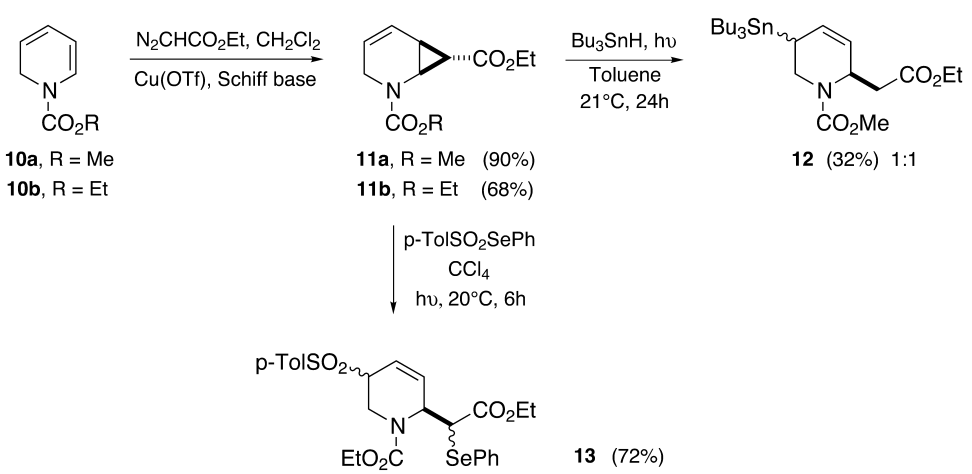
be elaborated further. Reduction of the selenyl group in **6** with Bu_3SnH led to the corresponding sulfone **7**, whose stereochemistry was determined using ^1H NMR (Scheme 3). As above with PhSH, it was concluded that the addition of the sulfonyl group had occurred *anti* relative to the silicon group with complete 1,2-stereocontrol.[8] In parallel, elimination of the selenyl group in **6** through stereospecific *syn*-elimination of the selenoxide led to a 40:60 *Z*/*E* mixture[10] of the unsaturated esters **8**, thus confirming that only the stereochemistry of the stereogenic centre α to the ester function was not controlled during the radical process (Scheme 3).

The regioselectivity of these free-radical reactions is noteworthy. In both cases, the thiophenoxy and the sulfonyl radicals attack the carbon centre β to the bulky silicon group, suggesting that these additions might be reversible.[11] The formation of a more stable radical α to the ester function after cyclopropane ring opening probably provides the necessary driving force to the process.[12]

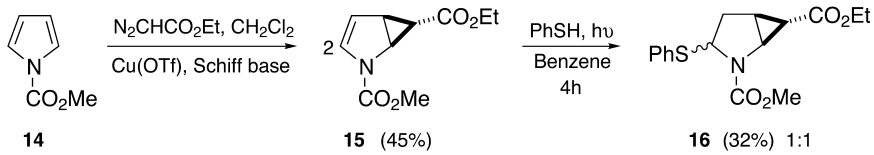
Having established the reactivity of vinylcyclopropanes **1** towards sulfur centered radicals, we then studied the ability of the radical **2** to add to electron-rich and electron-poor olefins.[5] The reactions were performed starting from **1**, using a substoichiometric amount of PhSSPh (30 mol%) and an excess of the olefin in benzene under irradiation. The results are summarised in Table 1 (conditions **A**, Scheme 4). Annulation products **9a**–**d** were obtained in moderate yields and as a mixture of stereoisomers, independently of the nature of the radical acceptors. The different isomers could not be separated through chromatography and therefore their relative configurations were not determined. Nevertheless, the ratio could be estimated through ^1H NMR and confirmed through GC analysis. It is noteworthy that the reaction worked equally well with electron-poor and electron-rich olefins. The silicon group, although on a remote stereogenic centre, was able to partially control the selectivity, since in some cases a stereoisomer was clearly predominant over the others (entries 1 and 3).[5,13]

In order to improve the yield of this annulation, we then considered a two steps approach, starting again from **1**, but proceeding through the cyclopentene intermediate **6** (conditions **B**, Scheme 4). Phenylselenoacetates are excellent precursors for ambiphilic radicals and were shown to add efficiently to carbon–carbon multiple bonds.[14] In our case, cleavage of the C–Se bond in **6** under irradiation should generate a radical such as **2** (X=*p*-$TolSO_2$) which could then add onto olefins followed, as above, by a 5-*exo*-trig cyclisation and β-fragmentation with elimination of the *p*-toluenesulfonyl radical. Reaction of the sulfonyl radical with hexabutylditin will then complete the chain process.[15] Such a route was studied with the same olefins as above and the results summarized in Table 1 (conditions **B**, Scheme 4). Annulation products **9a**–**e** were obtained in significantly better yields and with shorter reaction time, but again as a mixture of diastereomers. Surprisingly, the stereoisomers ratio differed when changing from conditions **A** to conditions **B**.[5] This may be due to the decomposition which is likely to occur in conditions **A** where long reaction times are required. Nevertheless, although the stereocontrol is low, this annulation is rather efficient since bi- and tricyclic systems are constructed, in good overall yield, in only three or fours steps starting from cyclopentadiene.

The strategy was then extended to heterocycles such as piperidines and pyrroles containing a vinylcyclopropane moiety. Such precursors are easily available through cyclopropanation of the corresponding heterocycle.[16] For instance, cyclopropanation of 1,2-dihydropyridine **10a**[17] gave the cyclopropane **11a** in excellent yield as a single diastereomer (two rotamers) (Scheme 5). Interestingly, the electron-rich double bond was cyclopropanated selectively. Addition of PhSH in the same conditions as above unfortunately did not afford the expected dihydropiperidine.



Scheme 5.



Scheme 6.

A similar result was obtained upon addition of $(TMS)_3SiH$ under photochemical conditions or Et_3B-O_2 initiation. We eventually found that addition of Bu_3SnH onto the double bond initiated the ring fragmentation which was followed by the reduction of the radical to form the 2,5-disubstituted dihydropiperidine **12** as a 1:1 mixture of diastereomers, albeit in modest yield. When *p*-$TolSO_2SePh$ was used, the fragmentation product **13** was isolated, again as a mixture of diastereomers, in a more satisfying 72% yield.[18] Although the mixture partially crystallized upon standing in pentane, the occurrence of rotamers prevented the unambiguous determination of the relative configuration of the major crystalline isomer. This strategy, however, provides an easy access to highly functionalised unsaturated piperidines in only three steps starting from pyridine.

In parallel, the methodology was applied to the pyrrole series. Cyclopropane **15**[16b] was obtained from **14**[19] in a reasonable yield (corrected yield: 75%) and as a single diastereomer (stereochemistry as shown), in good agreement with recent reports by Reiser et al.[20] To our surprise, treatment of the pyrrole analogue **15** as above (PhSH, UV lamp), led to the addition of PhSH without cyclopropane ring fragmentation, albeit in modest yield. ^1H NMR as well as $^1H-^{13}C$ correlation experiments on the resulting product **16** unambiguously showed that the PhS group is located in α position relative to the N-carbomethoxy group (δ=5.26 and 5.49 ppm) (Scheme 6). **16** was obtained as a 1:1 mixture of both diastereomers indicating that addition of PhSH has occurred without diastereofacial selectivity. The origin of the absence of fragmentation in the pyrrole series as compared to the pyridine series is presently unclear. An ionic process, involving reaction of the enaminic moiety of **15** with acidic thiophenol cannot be ruled out. This would provide an iminium intermediate which could react further with thiophenol to give **16** as a mixture of diastereoisomers. Surprisingly, attempts to open the cyclopropane ring of **15** using *p*-$TolSO_2SePh$ were unsuccessful, leading to low yield (<30%) of a product which structure was consistent with that of a pyrrole such as **15** having a *p*-$TolSO_2$ group at C-2.

As a summary, we reported here on a rapid elaboration of original vinylcyclopropane systems under free-radical conditions providing the polyfunctionalized cyclopentanes, in a limited number of steps starting from the corresponding dienes. This methodology efficiently complements the functionalisation of synthons such as **1** through ionic processes.[1] In parallel, we demonstrated using a similar approach that building up of 2,5-disubstituted-3,4-dihydropiperidines could be easily performed in three steps starting from pyridine. Further studies are now under way to explore the rapid and stereoselective functionalisation of such synthons en route to various types of pyrrolizidine alkaloids.

1. Experimental

1.1. General

^1H NMR and ^{13}C NMR were recorded on a Bruker AC-200 FT (^1H: 200 MHz, ^{13}C: 50 MHz), Bruker AC-250 FT (^1H: 250 MHz, ^{13}C: 63 MHz) using $CDCl_3$ as an internal reference unless otherwise stated. The chemical shifts (δ) and coupling constants (J) are expressed in ppm and Hz, respectively. IR spectra were recorded on a Perkin–Elmer Paragon 1000 FT-IR spectrophotometer. Low resolution and high-resolution mass spectra were recorded on Micromass autospec-Q mass spectrometer (EI with ionisation potential of 70 eV, LSIMS with ionisation potential of 35 keV, matrix: 3-nitrobenzyl alcohol). Elemental analyses were performed by the Service Central d'Analyse, Vernaison, CNRS, France. Gas chromatography was performed on a Hewlett–Packard 4890 apparatus equipped with a capillary column SPB™-1 [poly(dimethylsiloxane)]. Melting points were recorded on electrothermal digital melting point apparatus and are uncorrected. SD silica gel 60 AC.C (70–200 μm) was used for column chromatography. All anhydrous and inert atmosphere reactions were performed with oven dried glass apparatus under nitrogen atmosphere. Toluene and benzene were distilled from sodium and benzophenone. CH_2Cl_2 was distilled from CaH_2.

1.1.1. Ethyl [(1*S,4*R**,5*R**)-5-(dimethylphenylsilyl)-4-(phenylthio)cyclopent-2-en-1-yl]acetate (5).** To a solution of vinylcyclopropane **1** (504 mg, 1.76 mmol) in degassed toluene (10 mL) was added at room temperature PhSH (0.2 mL, 1.94 mmol). The temperature was maintained to 20°C during irradiation with a sunlamp (300 W) for 40 h. Then, the solvent was removed and the yellow crude mixture purified by gel chromatography (Petroleum ether/EtOAc, 95/5), affording **5** as a colourless oil (521 mg, 75%). IR (Film, KBr) ν_{max} (cm^{-1}) 3069, 2979, 2962, 1733 (C=O), 1606, 1583, 1479, 1251 (Si–C), 833, 736, 700; ^1H NMR δ 7.51–7.22 (10H, m, aromatic *H*), 5.77 (2H, s, 2×vinylic *H*), 4.10–4.01 (3H, m, C*H*SPh, $CO_2CH_2CH_3$), 3.05–3.01 (1H, m, $CHCH_2CO_2Et$), 2.19–2.16 (2H, m, CH_2CO_2Et), 1.39 (1H, t, J=3.5 Hz, C*H*Si), 1.24 (3H, t, J=7.1 Hz, $CO_2CH_2CH_3$), 0.28 (3H, s, $SiCH_3$), 0.24 (3H, s, $SiCH_3$); ^{13}CNMR δ 172.1, 136.9, 136.5, 135.1, 133.9, 133.1, 132.3, 129.2, 128.8, 127.8, 127.3, 60.2, 55.8, 43.9, 41.7, 35.7, 14.2, −4.8, −5.1; MS (CI, NH_3) *m*/*z* (%) 397 ($[M]^+$, 0.5), 351 (1), 287 (22), 244 (5), 181 (6), 135 (100), 107 (24), 79 (42). Anal. calcd for $C_{23}H_{28}O_2SSi$: C 69.65, H 7.12, S 8.08, Si 7.08; found: C 69.72, H 7.20, S 7.98, Si 7.01.

1.1.2. Ethyl [(1*S,4*R**,5*R**)-5-(dimethylphenylsilyl)-4-[(4-methylphenyl)sulfonyl]cyclopent-2-en-1-yl](phenylselenyl)acetate (6).** A solution of vinylcyclopropane **1** (573 mg, 2.0 mmol) and *p*-$TolSO_2SePh$ (311 mg,

1.0 mmol) in degassed CCl_4 (3.0 mL) was irradiated for 6 h using a sunlamp (300 W) in a cooling bath in order to maintain the temperature to 20°C. The solution was then concentrated in vacuo and the resulting yellow oil was purified by gel chromatography (Petroleum ether/EtOAc 90/10 to 70/30) to give **6** as a yellow solid and as a 6/4 mixture of diastereomers (515 mg, 90%). Mp 96°C. IR (Film, KBr) ν_{max} (cm^{-1}) 3070, 3050, 2977, 2928, 2871, 2254, 1702 (C=O), 1624, 1597, 1428, 1380, 1253 (Si–C), 1210, 1145, 1085. *Minor*. ^{1}H NMR δ 7.60–7.07 (14H, m, aromatic *H*), 6.35–6.25 (1H, m, vinylic *H*), 5.59–5.55 (1H, m, vinylic *H*), 4.12–3.74 (4H, m), 3.20–3.05 (1H, m), 2.35 (3H, s, ArCH_3), 1.57–1.55 (1H, m), 1.16 (3H, t, *J*=7.1 Hz, $CO_2CH_2CH_3$), 0.12 (3H, s, SiCH_3), 0.11 (3H, s, SiCH_3); ^{13}C NMR δ 172.3, 142.1, 135.0, 134.7, 133.8, 129.0, 128.9, 127.8, 124.8, 74.6, 60.5, 48.9, 48.7, 29.9, 21.1, 14.2, −4.7, −5.6; *Major*: ^{1}H NMR δ 7.60–7.07 (14H, m, aromatic *H*), 6.00–5.95 (1H, m, vinylic *H*), 5.70–5.66 (1H, m, vinylic *H*), 4.12–3.74 (4H, m), 3.20–3.05 (1H, m), 2.35 (3H, s, ArCH_3), 2.16–2.14 (1H, m), 1.01 (3H, t, *J*=7.3 Hz, $CO_2CH_2CH_3$), 0.19 (3H, s, SiCH_3), 0.16 (3H, s, SiCH_3); ^{13}CNMR δ 173.2, 144.5, 141.3, 134.5, 134.1, 129.8, 129.5, 129.2, 128.9, 128.1, 128.0, 125.3, 74.3, 60.8, 49.7, 48.8, 28.6, 21.7, 13.9, −4.9, −5.5; MS (LSIMS) *m/z* (%) 621 ([M+Na]$^+$); HRMS [M+Na] calcd for $C_{30}H_{34}O_4NaSSiSe$: 621.101000; found: 621.100733.

1.1.3. Ethyl [(1*S,4*R**,5*R**)-5-(dimethylphenylsilyl)-4-[(4-methylphenyl)sulfonyl]cyclopent-2-en-1-yl] acetate (7).** A solution of cyclopentene **6** (120 mg, 0.20 mmol), Bu_3SnH (0.11 mL, 0.40 mmol) and AIBN (10 mg, 0.06 mmol) in benzene (4 mL) was refluxed for 4 h. A second portion of AIBN (10 mg, 0.06 mmol) was then added and the reflux was maintained for 3 h. The reaction mixture was then concentrated in vacuo to afford a crude oil, which was purified by gel chromatography (Petroleum ether/EtOAc 90/10 to 80/20). This gave **7** as a colourless oil (54 mg, 72%). IR (Film, KBr) ν_{max} (cm^{-1}) 3069, 3049, 2254, 1732 (C=O), 1597, 1428, 1372, 1312, 1253 (Si–C), 1143, 1087, 1015; ^{1}H NMR δ 7.68 (2H, d, *J*=6.6 Hz, aromatic *H*), 7.42–7.30 (7H, m, aromatic *H*), 6.13–6.10 (1H, m, vinylic *H*), 5.62–5.58 (1H, m, vinylic *H*), 4.07 (2H, q, *J*=7.1 Hz, $CO_2CH_2CH_3$), 4.08 (1H, br s, C*H*SO_2), 3.12–3.06 (1H, m, C*H*CH_2CO_2Et), 2.47 (3H, s, ArCH_3), 2.27 (2H, d, *J*=7.6 Hz, CH_2CO_2Et), 1.75–1.73 (1H, m, C*H*Si), 1.20 (3H, t, *J*=7.1 Hz, $CO_2CH_2CH_3$), 0.25 (3H, s, SiCH_3), 0.24 (3H, s, SiCH_3); ^{13}C NMR δ 172.7, 144.9, 142.8, 136.2, 135.2, 133.9, 129.7, 129.4, 129.2, 127.9, 123.9, 74.7, 60.3, 44.3, 41.0, 29.0, 21.7, 14.2, −5.4, −5.6.

1.1.4. Ethyl[(4*R,5*R**)-5-(dimethylphenylsilyl)-4-[(4-methylphenyl)sulfonyl]cyclopent-2-en-1-ylidene] acetate (8).** To a solution of cyclopentene **6** (150 mg, 0.25 mmol) in THF (1.5 mL) was added at −20°C a 35% solution of H_2O_2 in water (0.4 mL). The reaction mixture was stirred 2 h at −20°C then diluted with CCl_4 (5 mL) and washed with water (3×2 mL). The organic layer was decanted and the aqueous layer extracted with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and the solvent evaporated in vacuo to afford a colourless oil (129 mg) which was purified by gel chromatography (Petroleum ether/EtOAc 80/20). This gave **8** as a 6/4 *E*/*Z* mixture (82 mg, 75%). IR (Film, KBr) ν_{max} (cm^{-1}) 3070, 2977, 2360, 2254, 1723 (C=O), 1597, 1477, 1438, 1428, 1314, 1290, 1254 (Si–C), 1087, 912, 732; *Z isomer*: ^{1}H NMR δ 7.55 (2H, d, *J*=8.6 Hz, aromatic *H*), 7.39–7.13 (7H, m, aromatic *H*), 6.36 (1H, dd, *J*=5.5, 1.2 Hz, vinylic *H*), 6.23 (1H, dd, *J*=5.5, 3.0 Hz, vinylic *H*), 5.46 (1H, d, *J*=1.4 Hz, C*H*CO_2Et), 4.14–3.99 (3H, m, C*H*SO_2, $CO_2CH_2CH_3$), 3.97 (1H, s, C*H*Si), 2.37 (3H, s, ArCH_3), 1.23 (3H, t, *J*=7.1 Hz, $CO_2CH_2CH_3$), 0.19 (3H, s, SiCH_3), 0.14 (3H, s, SiCH_3); *E isomer*: ^{1}H NMR δ 7.55 (2H, d, *J*=8.6 Hz, aromatic *H*), 7.39–7.13 (8H, m, aromatic *H*, vinylic *H*), 6.19–6.15 (1H, m, vinylic *H*), 5.15 (1H, s, C*H*CO_2Et), 4.14–3.99 (3H, m, C*H*SO_2, CO_2CH_2-CH_3), 2.86 (1H, s, C*H*Si), 2.38 (3H, s, ArCH_3), 1.21 (3H, t, *J*=7.1 Hz, $CO_2CH_2CH_3$), 0.25 (3H, s, SiCH_3), 0.23 (3H, s, SiCH_3).

General protocol for the annulation of vinylcyclopropane **1** (*Method A*). A solution of vinylcyclopropane **1** (143 mg, 0.50 mmol), olefin (5 mmol) and PhSSPh (31 mg, 0.14 mmol) in degassed benzene (1.5 mL) was irradiated using a UV lamp (300W). The temperature was maintained as indicated in Table 1. The progression of the reaction was monitored using GC or TLC. When the reaction was complete, the solvent was removed under vacuum and the residue purified by chromatography (Petroleum ether/EtOAc 97/3 to 80/20).

General protocol for the annulation of cyclopentene **6** (*Method B*). A solution of cyclopentene **6** (100 mg, 0.176 mmol), olefin (1.76 mmol) and $(Bu_3Sn)_2$ (80 μL, 0.21 mmol) in degassed benzene (5 mL) was irradiated for 16 h using a UV lamp (300 W) in a cooling bath, in order to maintain the temperature at 20°C. The progression of the reaction was monitored using GC or TLC. When the reaction was complete, the solvent was removed under vacuum and the residue purified by gel chromatography (Petroleum ether/ethyl acetate 97/3 to 80/20).

1.1.5. 1-Ethyl 3-methyl 6-(dimethylphenylsilyl)-1,2,3,3a,6,6a-hexahydropentalene-1,3-dicarboxylate (9a). Following procedure **A**, **9a** was obtained after two days as a 74/23/3 mixture of diastereomers (65 mg, 35%). Following procedure **B**, **9a** was obtained as a 60/40 mixture of diastereomers (38 mg, 58%). GC: 200°C, 5°C/min up to 300°C, t_R 9.5, 10.0, 10.7 min; *Major isomer*. IR (CCl_4) ν_{max} (cm^{-1}) 3051, 2952, 1734 (C=O), 1551, 1435, 1375, 1250 (Si–C), 1180, 784, 761; ^{1}H NMR δ 7.50–7.45 (2H, m, aromatic H), 7.37–7.30 (3H, m, aromatic *H*), 5.59 (1H, dt, *J*=5.5, 2.2 Hz, vinylic C*H*), 5.34 (1H, dt, *J*=5.5, 2.2 Hz, vinylic C*H*), 4.17 (1H, dq, *J*=10.8, 7.1 Hz, $CO_2CH_2CH_3$), 3.91 (1H, dq, *J*=10.8, 7.1 Hz, $CO_2CH_2CH_3$), 3.66 (3H, s, CO_2CH_3), 3.43–3.35 (1H, m), 3.11–3.05 (2H, m), 2.77–2.72 (1H, m), 2.02–1.98 (3H, m), 1.21 (3H, t, *J*=7.1 Hz, $CO_2CH_2CH_3$), 0.26 (3H, s, SiCH_3), 0.23 (3H, s, SiCH_3); ^{13}C NMR δ 176.5, 174.1, 137.6, 133.9, 133.1, 129.0, 128.7, 127.7, 60.2, 58.1, 55.1, 48.9, 46.7, 44.2, 37.8, 30.3, 14.2, −4.4, −5.4; MS (EI) *m/z* (%) 373 ([M+1]$^+$), 372 ([M]$^+$), 135 (100); HRMS [M] calcd for $C_{21}H_{28}O_4Si$: 372.175688; found: 372.175570.

1.1.6. Ethyl-3-ethoxy-6-(dimethylphenylsilyl)-1,2,3,3a,6,6a-hexahydropentalene-1-carboxylate (9b). Following procedure **A**, **9b** was obtained after 2 days as a 62/27/10 mixture of diastereomers (105 mg, 59%). Following

procedure **B**, **9b** was obtained as a 60/40 mixture of diastereomers (46 mg, 72%). GC: 160°C, 5°C/min up to 210°C, then 10 min, 5°C/min up to 300°C, t_R 14.8, 15.0, 15.2 min; *Major isomer*. IR (Film, KBr) ν_{max} (cm^{-1}) 3047, 2974, 1731 (C═O), 1481, 1443, 1373, 1342, 1250 (Si–C), 1180, 1113; ^1H NMR δ 7.50–7.45 (2H, m, aromatic *H*), 7.36–7.30 (3H, m, aromatic *H*), 5.57 (1H, dt, *J*=5.7, 2.0 Hz, vinylic C*H*), 5.31 (1H, dt, *J*=5.7, 2.0 Hz, vinylicC*H*), 4.19 (1H, dq, *J*=10.8, 7.1 Hz, $CO_2CH_2CH_3$), 3.89 (1H, dq, *J*=10.8, 7.1 Hz, $CO_2CH_2CH_3$), 3.70–3.30 (4H, m), 2.10–1.50 (3H, m), 1.40–1.10 (8H, m), 0.26 (3H, s, $SiCH_3$), 0.23 (3H, s, $SiCH_3$); ^{13}C NMR δ 174.5, 137.7, 134.0, 133.8, 129.0, 127.7, 127.2, 83.7, 63.6, 60.2, 58.6, 47.7, 42.8, 37.7, 31.7, 15.5, 14.2, −4.3, −5.5; MS (EI) *m/z* (%) 359 ($[M+1]^+$), 358 ($[M]^+$), 135 (100); HRMS [M] calcd for $C_{21}H_{30}O_3Si$: 358.196424; found: 358.197480.

1.1.7. Ethyl-3-(acetyloxy)-3-methyl-6-(dimethylphenylsilyl)-1,2,3,3a,6,6a-hexahydropentalene-1-carboxylate (9c). Following procedure **A**, **9c** was obtained after 6 days as a 45/45/10 mixture of diastereomers (60 mg, 32%). Following procedure **B**, **9c** was obtained as a 46/44/10 mixture of diastereomers (44 mg, 60%). GC: 200°C, 5°C/min up to 230°C, then 10 min, 5°C/min up to 300°C, t_R 9.9, 10.7, 11.2 min.

Data for the inseparable mixture of three diastereomers. IR (Film, KBr) ν_{max} (cm^{-1}) 3072, 2955, 1733 (C═O), 1551, 1368, 1250 (Si–C), 1014, 784, 761; ^1H NMR δ 7.60–7.25 (5H, m, aromatic *H*), 5.65–5.55 (1.02H, m, vinylic *H*), 5.55–5.49 (0.44H, m, vinylic *H*), 5.45–5.39 (0.10H, m, vinylic *H*), 5.35–5.28 (0.44H, m, vinylic *H*), 4.27–3.85 (2H, m, $CO_2CH_2CH_3$), 3.32–2.90 (2H, m), 2.50–1.10 (13H, m), 0.32–0.12 (6H, m, $SiCH_3$); ^{13}C NMR δ 175.3, 174.6, 173.7, 173.2, 170.6, 170.4, 146.1, 137.5, 134.6, 134.2, 133.9, 133.85, 133.8, 132.5, 132.3, 129.15, 129.1, 127.7, 127.6, 126.7, 126.5, 126.4, 125.7, 91.6, 90.1, 89.2, 62.7, 61.2, 60.6, 60.5, 60.4, 60.1, 40.9, 38.6, 38.0, 28.8, 28.4, 26.8, 25.3, 24.3, 23.9, 22.7, 22.6, 22.5, 22.3, 22.1, 21.6, 21.5, 20.8, 20.1, 17.5, 14.2, 13.6, −4.4, −4.6, −4.7, −4.9, −5.1, −5.4; MS (EI) *m/z* (%) 387 ($[M+1]^+$), 386 ($[M]^+$), 371 (6), 342 (1), 135 (100); HRMS [M] calcd for $C_{22}H_{30}O_4Si$: 386.191338; found: 386.190490.

1.1.8. Ethyl 6-(dimethylphenylsilyl)-3-oxo-2,3,3a,3b,6,6a,7,7a-octahydro-1*H*-cyclopenta[a]pentalene-7-carboxylate (9d). Following procedure **A**, **9d** was obtained after 6 days as a 33/29/22/16 mixture of diastereomers (66 mg, 36%). Following procedure **B**, **9d** was obtained as a 33/33/22/12 mixture of diastereomers (33 mg, 51%). GC: 220°C, 5°C/min up to 250°C, then 10 min, 5°C/min up to 300°C, t_R 9.3, 9.5, 9.9, 10.9 min.

Data for the inseparable mixture of four diastereomers. IR (Film, KBr) ν_{max} (cm^{-1}) 3051, 2952, 1734 (C═O), 1551, 1435, 1375, 1250 (Si–C), 1180, 784, 761; ^1H NMR δ 7.65–7.20 (5H, m, aromatic *H*), 5.63–5.34 (2H, m, vinylic *H*), 4.40–3.76 (2H, m, $CO_2CH_2CH_3$), 3.48–3.39 (1H, m), 3.22–2.66 (3H, m), 2.60–2.40 (1H, m), 2.37–1.68 (4H, m), 1.40–1.10 (3H, m, $CO_2CH_2CH_3$), 0.90–0.77 (1H, m), 0.48–0.10 (6H, m, $SiCH_3$); ^{13}C NMR δ 220.4, 137.5, 134.0, 133.9, 133.8, 132.0, 131.0, 130.7, 130.6, 129.8, 129.2, 127.8, 127.7, 127.6, 65.9, 60.7, 60.6, 60.4, 60.2, 57.2, 56.9, 55.5, 54.1, 54.0, 53.6, 52.9, 51.3, 46.0, 45.2, 44.4, 42.7, 41.2, 41.0, 39.6, 37.5, 36.9, −4.6, −4.8, −5.1, −5.4; MS (EI) *m/z* (%) 369 ($[M+1]^+$), 368 ($[M]^+$), 135 (100); HRMS [M] calcd for $C_{22}H_{28}O_3Si$: 368.180773; found: 368.180970.

1.1.9. Ethyl-3-(acetyloxy)-6-(dimethylphenylsilyl)-1,2,3,3a,6,6a-hexahydropentalene-1-carboxylate (9e). Following procedure **B**, **9e** was obtained as a 44/40/16 mixture of diastereomers (ratio determined using 1H NMR) (41 mg, 63%).

Data for the inseparable mixture of three diastereomers. IR (Film, KBr) ν_{max} (cm^{-1}) 3048, 2956, 1732 (C═O), 1427, 1375, 1245 (Si–C), 1181, 1034, 821, 733, 701; ^1H NMR δ 7.93–7.16 (5H, m, aromatic *H*), 6.07–5.91 (0.96H, m, vinylic *H*), 5.80–5.70 (0.38H, m, vinylic *H*), 5.68–5.58 (0.14H, m, vinylic *H*), 5.38–5.28 (0.38H, m, vinylic *H*), 5.26–5.12 (0.14H, m, vinylic *H*), 4.68–4.18 (2H, m, $CO_2CH_2CH_3$), 3.75–3.20 (2H, m), 2.65–1.90 (5H, m), 1.80–1.45 (6H, m), 0.70–0.52 (6H, m, $SiCH_3$); ^{13}C NMR δ 173.6, 134.6, 134.0, 133.9, 133.8, 132.2, 129.2, 128.2, 127.8, 126.2, 79.7, 79.2, 60.5, 58.9, 58.0, 51.1, 50.8, 48.1, 46.9, 43.0, 41.9, 37.9, 34.9, 32.6, 27.9, 26.9, 21.5, 21.3, 17.6, 14.3, 13.7, −4.3, −4.7, −5.4; MS (EI) *m/z* (%) 373 ($[M+1]^+$), 372 ($[M]^+$), 135 (59); HRMS [M] calcd for $C_{21}H_{28}O_4Si$: 372.175688; found: 372.175690.

1.1.10. 7-Ethyl 2-methyl 2-azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylate (11a). A solution of copper(I) trifluoromethanesulfonate–benzene complex (38 mg, 0.15 mmol) and a Schiff base (*N*,*N*′-bis[(1*E*)-phenylmethylene]ethane-1,2-diamine, 57 mg, 0.24 mmol) in dry CH_2Cl_2 (15 mL) was stirred for 1 h at room temperature under a nitrogen atmosphere. Methyl pyridine-1(2*H*)-carboxylate **10a**[17a] (0.7 g, 5 mmol) in dry CH_2Cl_2 (2 mL) was added to the green mixture and stirred for 10 min. Ethyl diazoacetate (0.65 mL, 6 mmol) was then added slowly over a period of 16 h using a syringe pump. The solvent was removed under reduced pressure and the remaining brown oil was purified by column chromatography through florisil (Petroleum ether/EtOAc 80/20) affording the expected cyclopropane **11a** as a colourless oil (1 g, 90%). IR (Film, KBr) ν_{max} (cm^{-1}) 2983, 2907, 2872, 1715 (C═O), 1446, 1368, 1305, 1183, 1039, 1006, 848, 773, 688; ^1H NMR (signal doubling due to rotamers) δ 6.03–6.01 (1H, m, vinylic *H*), 5.76–5.68 (1H, m, vinylic *H*), 4.23–4.04 (4H, m, $CO_2CH_2CH_3$, NCH_2), 3.75 (3H, s, CO_2CH_3), 3.73–3.56 (1H, m, NC*H*), 2.20–2.08 (m, 1H, C*H*–CH═CH), 1.68–1.59 (1H, m, C*H*CO_2Et), 1.27–1.25 (3H, m, $CO_2CH_2CH_3$); ^{13}C NMR δ 172.0, 155.0, 124.6, 121.7, 60.4, 52.8, 40.1, 36.0, 34.3, 21.1, 13.9; MS (CI, NH_3) *m/z* (%) 226 ($[M+1]^+$, 100), 192 (10), 180 (20), 166 (12), 152 (20), 120 (6), 106 (13), 94 (22), 80 (42); HRMS [M+Na] calcd for $C_{11}H_{15}NO_4$: 248.0893234; found: 248.09005.

1.1.11. 2-Azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylic-7-ethyl ester-2-ethyl ester (11b). Following the general procedure reported above for **11a**, **11b** was obtained as a colourless oil (68%). IR (Film, KBr) ν_{max} 3048–2871, 1713 (C═O), 1657, 926, 773, 687 cm^{-1}; ^1H NMR δ 6.06–5.94 (m, 1H, vinylic *H*), 5.80–5.60 (m, 1H, vinylic *H*), 4.27–4.02 (m, 4H, 2×$CO_2CH_2CH_3$), 4.01–3.45 (m, 3H, CH_2N, C*H*N), 2.17–2.05 (m, 1H, C*H*–CH═CH), 1.64–1.50 (m,

1H, C*H*CO_2Et), 1.25 (t, *J*=7.1 Hz, 6H, 2×$CO_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$) δ 170.6, 156.5, 125.1, 122.00, 61.6, 61.5, 40.0, 36.3, 34.6, 21.4, 14.5, 14.2; MS (EI) *m/z* (%): 239 (23) $[M]^+$, 210 (33), 194 (28), 166 (100), 138 (77), 120 (85), 94 (79); HRMS [M] calcd for $C_{12}H_{17}NO_4$: 239.115758; found: 239.115868.

1.1.12. Methyl 6-(2-ethoxy-2-oxoethyl)-3-(tributylstannyl)-3,6-dihydropyridine-1(2*H*)-carboxylate (12). To a solution of cyclopropane **11a** (380 mg, 1.8 mmol) in degassed toluene (25 mL) was added at room temperature, Bu_3SnH (0.2 mL, 1.94 mmol) and AIBN (40 mg, 0.24 mmol). The mixture was maintained to 21°C and irradiated with a sunlamp (300 W) for 24 h. Then, the solvent was removed and the yellow crude oil was purified by gel chromatography (Petroleum ether/EtOAc 90/10) affording 12 as a 1/1 mixture of diastereomers (289 mg, 32%). *First eluting isomer* (88 mg). IR (Film, KBr) ν_{max} (cm^{-1}) 2956, 1705 (C=O), 1636, 1446, 1408, 1356, 1253, 1158, 1028, 959, 767, 746, 664; ^{1}HNMR (Toluene d_8, 100°C) δ 6.15–6.11 (1H, m, vinylic *H*), 5.62 (1H, ddd, *J*=1.3, 3.6 Hz, 10.0 Hz, vinylic *H*), 5.05–5.04 (1H, m, NC*H*), 4.47 (1H, d, *J*=13.6 Hz, NCH_2), 4.17 (2H, q, *J*=7.1 Hz, $CO_2CH_2CH_3$), 3.74 (3H, s, CO_2CH_3), 3.45 (1H, dd, *J*=3.6, 13.6 Hz, NCH_2), 2.75 (1H, dd, *J*=5.8, 14.2 Hz, CH_2CO_2Et), 2.62 (1H, dd, *J*=7.8, 14.2 Hz, CH_2CO_2Et), 2.14–2.11 (1H, m, C*H*Sn), 1.79–1.72 (6H, m, 3×CH_2), 1.60–1.50 (6H, m, 3×CH_2), 1.24 (3H, t, *J*=7.1 Hz, $CO_2CH_2CH_3$), 1.22–1.08 (15H, m, 3×CH_2, 3×CH_3); ^{13}C NMR (Toluene d_8, 100°C) δ 170.9, 155.0, 132.1, 119.5, 60.4, 52.4, 49.6, 40.2, 29.0, 27.3, 13.6, 8.3; MS (CI, NH_3) *m/z* (%) 516 ($[M]^+$, 3), 460 (21), 430 (13), 321 (13), 291 (33), 264 (43), 234 (67), 209 (47), 179 (71), 138 (100), 94 (69); HRMS [M+Na] calcd for $C_{23}H_{43}NO_4Sn$: 540.2106234; found: 540.212695. *Second eluting isomer* (201 mg). IR (Film, KBr) ν_{max} (cm^{-1}) 2956, 2927, 2872, 1737 (C=O), 1705 (C=O), 1463, 1410, 1372, 1296, 1239, 1157, 1114, 1078, 1035, 911, 865, 767, 730, 663; ^{1}H NMR (Toluene d_8, 100°C) δ 6.06 (1H, d, *J*=10.0 Hz, vinylic C*H*), 5.77 (1H, ddd, *J*=2.8, 4.4, 10.0 Hz, vinylic *H*), 5.18 (1H, m, NC*H*), 4.55 (1H, dd, *J*=6.2, 13.6 Hz, NCH_2), 4.17 (2H, q, *J*=7.1 Hz, $CO_2CH_2CH_3$), 3.73 (3H, s, CO_2CH_3), 3.34 (1H, dd, *J*=11.5, 13.6 Hz, NCH_2), 2.77 (1H, dd, *J*=6.5, 14.2 Hz, CH_2CO_2Et), 2.64 (1H, dd, *J*=7.6, 14.2 Hz, CH_2CO_2Et), 2.50–2.46 (1H, m, C*H*Sn), 1.77–1.65 (6H, m 3×CH_2), 1.56–1.47 (6H, m, 3×CH_2), 1.24 (3H, t, *J*=7.1 Hz, $CO_2CH_2CH_3$), 1.14–1.07 (15H, m, 3×CH_2, 3×CH_3); ^{13}CNMR (Toluene d_8, 100°C) δ 172.1, 170.6, 130.7, 123.5, 60.4, 52.3, 49.0, 40.2, 28.9, 27.2, 13.5, 8.3; MS (CI, NH_3) *m/z* (%) 517 ($[M+1]^+$, 4), 460 (43), 430 (10), 321 (8), 291 (24), 264 (29), 233 (41), 209 (32), 179 (43), 138 (100), 94 (64); HRMS [M+Na] calcd for $C_{23}H_{43}NO_4Sn$: 540.2106234; found: 540.213162.

1.1.13. 3-Benzenesulfonyl-6-(Ethoxycarbonylphenylselanylmethyl)-3,6-dihydro-2*H*-pyridine-1-carboxylic ethyl ester (13). A solution of **11b** (0.22 g, 0.93 mmol) and *p*-$TolSO_2SePh$ (0.161 g, 0.466 mmol) in degassed CCl_4 (3.0 mL) was irradiated for 6 h using a sunlamp (300 W) in a cooling bath in order to maintain the temperature to 20°C. The solution was then concentrated in vacuo and the resulting yellow oil was purified by gel chromatography (Petroleum ether/EtOAc 9/1) to give **13** as a colourless oil and as an inseparable mixture of diastereomers (184 mg, 72%).

Data for the crystalline isomer. Mp 105–106°C. IR (Film, KBr) ν_{max} 2981, 1704 (C=O), 1597, 1301, 1148, 1134, 743 cm^{-1}; ^{1}H NMR δ 7.67 (d, *J*=8 Hz, 2H, aromatic *H*), 7.56 (d, *J*=8 Hz, 2H, aromatic *H*), 7.41–7.23 (m, 5H, aromatic *H*), 6.19–5.92 (m, 2H, vinylic *H*), 5.01–5.81 (m, 1H), 4.45–4.32 (m, 1H), 4.25–3.83 (m, 5H), 3.50–3.28 (m, 1H), 2.89–2.71 (m, 1H), 2.45 (s, 3H, CH_3Ar), 1.30–1.09 (m, 6H, 2×CH_3CH_2O). ^{13}C NMR ($CDCl_3$) δ 170.5, 155.0, 145.4, 135.8, 131.6, 129.9, 129.2, 128.8, 128.1, 120.4, 62.2, 61.4, 59.4, 52.2, 47.8, 36.9, 21.7, 14.5, 13.9. MS (LSIMS) *m/z* (%): 574 (31) $[M+Na]^+$, 552 (15), 550 (9)$[M]^+$, 394 (8), 308 (100). HRMS [M+Na] $C_{25}H_{29}NO_6SSe$: calcd. 574.077850; found: 574.077354.

1.1.14. 6-Ethyl 2-methyl 2-azabicyclo[3.1.0]hex-3-ene-2,6-dicarboxylate (15). A solution of copper(I) trifluoromethanesulfonate–benzene complex (61 mg, 0.24 mmol) and a Schiff base (*N*,*N*′-bis[(1*E*)-phenylmethylene]ethane-1,2-diamine, 90 mg, 0.38 mmol) in dry CH_2Cl_2 (20 mL) was stirred for 1 h at room temperature under a nitrogen atmosphere. Methyl 1*H*-pyrrole-1-carboxylate **14**[19] (1 g, 8 mmol) in dry CH_2Cl_2 (2 mL) was then added to the green mixture and stirred for 10 min. Ethyl diazoacetate (1 mL, 9.6 mmol) was then added slowly over a period of 24 h using a syringe pump. The solvent was removed under reduced pressure and the remaining brown oil was purified by gel chromatography (Petroleum ether/EtOAc 90/10) affording the expected cyclopropane **15** as a colourless oil (751 mg, 45%; corrected yield: 75%). IR (Film, KBr) ν_{max} (cm^{-1}) 3115, 2983, 2959, 1712 (C=O), 1588, 1450, 1401, 1175, 1015, 835, 762; ^{1}H NMR (signal doubling due to rotamers) ^{1}H NMR (signal doubling due to rotamers) δ 6.60 (1H, s, vinylic *H*), 6.47 (1H, s, vinylic *H*), 5.41 (2H, d, *J*=10.3 Hz, vinylic *H*), 4.44 (1H, d, *J*=4.7 Hz, C*H*N), 4.31 (1H, d, *J*=4.7 Hz, C*H*N), 4.13–4.11 (4H, m, $CO_2CH_2CH_3$), 3.80 (6H, s, CO_2CH_3), 2.75 (2H, br s, CH), 1.29–1.25 (6H, m, $CO_2CH_2CH_3$), 0.98 (2H, d, *J*=9.5 Hz, C*H*); ^{13}C NMR δ 172.7, 152.6, 129.8, 128.9, 110.9, 110.7, 60.7, 53.1, 44.1, 43.8, 31.9, 30.7, 23.1, 23.0, 14.2; MS (CI, NH_3) *m/z* (%) 212 ($[M+1]^+$, 10), 211 ($[M]^+$, 8), 182 (13), 165 (43), 152 (1), 138 (100), 122 (7), 106 (17), 94 (50), 79 (10). Anal. calcd for $C_{10}H_{13}NO_4$: C 56.87, H 6.20, N 6.63; found: C 56.72, H 6.14, N 6.68.

1.1.15. 6-Ethyl 2-methyl 3-(phenylthio)-2-azabicyclo-[3.1.0]hexane-2,6-dicarboxylate (16). To a solution of vinylcyclopropane **15** (109 mg, 0.51 mmol) in degassed toluene (10 mL) was added at room temperature PhSH (0.05 mL, 0.51 mmol). The mixture was irradiated with a sunlamp (300 W) for 4 h, then the solvent was removed under vacuum. The yellow crude oil was purified by gel chromatography (Petroleum ether/EtOAc 90/10) affording 16 as a colourless oil and as an inseparable 1/1 mixture of diastereomers (52 mg, 32%). IR (Film, KBr) ν_{max} (cm^{-1}) 3059, 2982, 2955, 2871, 1717 (C=O), 1583, 1447, 1378, 1321, 1270, 1162, 1124, 1028, 971, 852, 749, 694; ^{1}H NMR (Toluene d_8, 100°C) δ 7.62–7.46 (4H, m aromatic *H*), 7.24–7.16 (6H, m, aromatic *H*), 5.49 (1H, d, *J*=8.3 Hz, C*H*SPh), 5.26 (1H, dd, *J*=2.3, 7.4 Hz, C*H*SPh), 4.27 (1H, d, *J*=6.6 Hz, C*H*N), 4.15–4.02 (4H, m, 2×$CO_2CH_2CH_3$),

3.83 (1H, dd, J=1.5, 6.8 Hz, C*H*N), 3.53 (3H, s, CO_2CH_3), 3.48 (3H, s, CO_2CH_3), 2.78 (1H, dd, J=1.7, 3.8 Hz, C*H*), 2.40–2.20 (4H, m, 2×CH_2), 2.11–2.05 (2H, m, 2×C*H*CO_2-Et), 1.50 (1H, dd, J=1.5, 3.4 Hz, C*H*), 1.20–1.13 (6H, m, 2×$CO_2CH_2CH_3$); ^{13}C NMR (Toluene d_8, 100°C) δ 137.1, 134.8, 128.6–124.4, 70.3, 66.4, 59.9, 51.8, 44.8, 36.5, 35.4, 34.1, 23.4, 13.7; MS (FAB) *m/z* (%) 321 ([M]$^+$, 0.3), 212 (100), 186 (10), 166 (65), 154 (45), 138 (88), 108 (32), 94 (50), 80 (38), 59 (40); HRMS [M+Na] calcd for $C_{16}H_{19}NO_4S$: 344.0927; found: 344.0927.

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