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UV induced hydrophosphination of dimethyl 2-vinylcyclopropane-1,1-dicarboxylate towards phosphine chalcogenides†

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Dimethyl 2-vinylcyclopropane-1,1-dicarboxylate underwent a hydrophosphination reaction with either a primary or secondary phosphine under photolytic conditions. Notably, a free radical initiator was not required. The resulting tertiary phosphines were derivatized using S_8 to afford moisture and air stable yellow or colorless oils in a 27%–73% isolated yield. A series of control reactions were performed, and we propose that this UV induced hydrophosphination reaction proceeds through a radical mechanism.

Introduction

Phosphorus containing compounds are ubiquitous in our everyday lives and have found applications in pharmaceuticals, antimicrobial agents, pesticides, flame retardants, high tech plastics and more. Phosphorus chemistry has had a profound impact on industries relying on phosphine ligands and metal catalysis for production of high value chemical products.[1] Phosphine chalcogenides in particular have been shown to have applications as a transfer agent, anion-selective electrodes, metal sequestration, as fluorescent materials for metal ions of environmental concern, as anchor units for single molecule junctions, in polymer chemistry and as ligands for coordination chemistry, catalysis and asymmetric synthesis.[2] For these reasons, there is considerable interest in developing new and efficient synthetic routes towards organophosphines. While there are a multitude of ways to synthesize these compounds, one common method is the hydrophosphination reaction of alkenes, where a P–H bond is formally added to an unsaturated compound to form a P–C and C–H bond. There are a variety of ways to perform hydrophosphination reactions, including the use of acid, base, metal catalysts, or free-radical initiator.[3] Hydrophosphination reactions using free radical initiator are one of the most efficient methods to mediate C–P bond formation. These reactions can be conducted using either heat or light and typically are atom economic with little to no byproduct formation.

There have been recent reports of P–H bond addition reactions progressing without an initiator or catalyst. In these reports, secondary phosphines, their respective chalcogenides or phosphine–boranes were successfully added to either a series of unactivated olefins, alkynes, aldehydes, ketones, isocyanate and isothiocyanate (Scheme 1).[4] These transformations highlight how simple and straightforward it is to create regioselective anti-*Markovnikov* organophosphine products. There are no reports of a definitive mechanism for some of these P–H bond additions. Gusarova and coworkers proposed a concerted mechanism involving a four or six membered cyclic transition state.[4f,5] Alonso *et al.* postulated an ionic pathway involving two molecules of phosphine participating in a transition state.[4d,e] Ultimately, it is still unclear as to whether these catalyst or initiator free hydrophosphination reactions proceed through either route.

Herein, we report a light induced and initiator free hydrophosphination of dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (**3**) with primary and secondary aryl and alkyl phosphines. The newly formed tertiary phosphines were subsequently sulfurized to form air and moisture stable phosphine sulfides. We probed the reaction mechanism through a series of control reactions. The phosphine chalcogenides produced in this study can potentially be used as ligands for metal coordination chemistry.[2]

Results and discussion

Our study commenced with the treatment of **3** with secondary phosphine (**1a** or **1b**) in the presence of azobisisobutylnitrile (AIBN) under thermal (75 °C) or photolytic conditions (λ_{max} = 360 nm). After further experiments, it was discovered that a free radical initiator was not required. The optimized reaction

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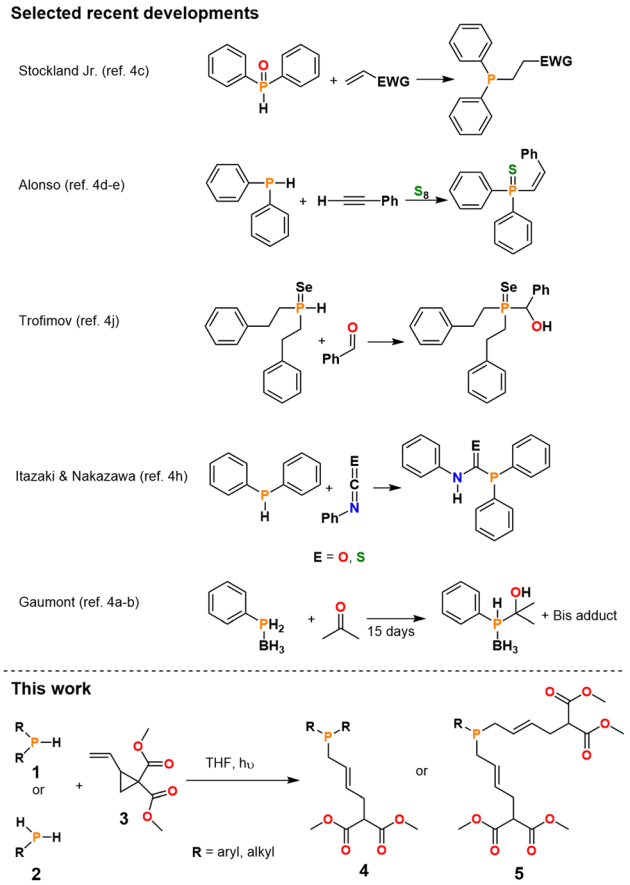
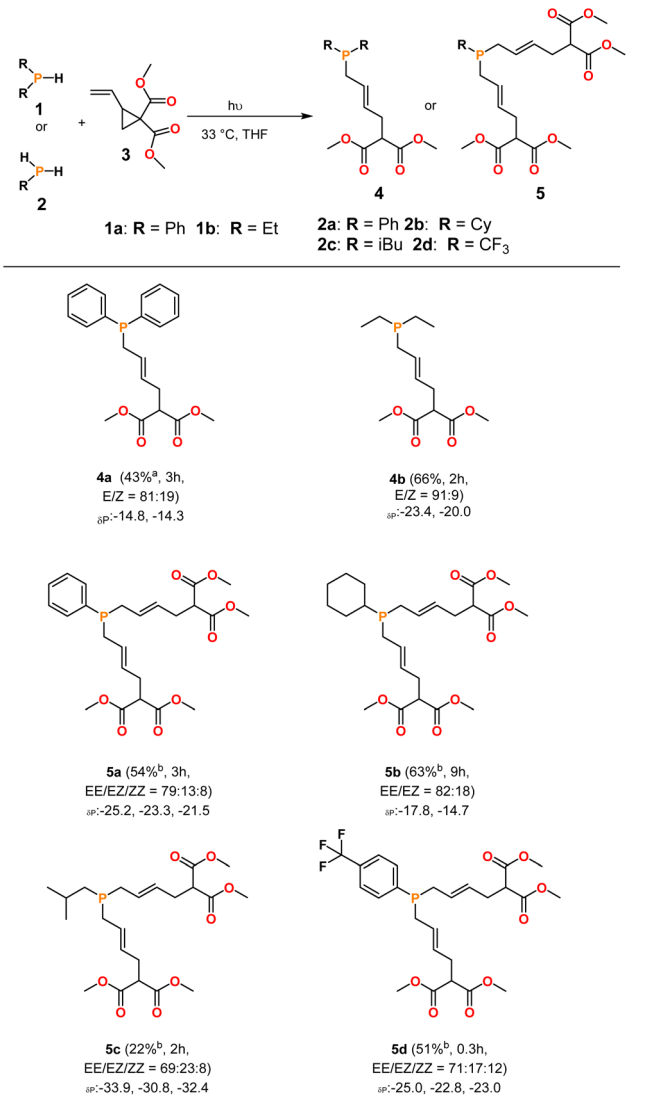


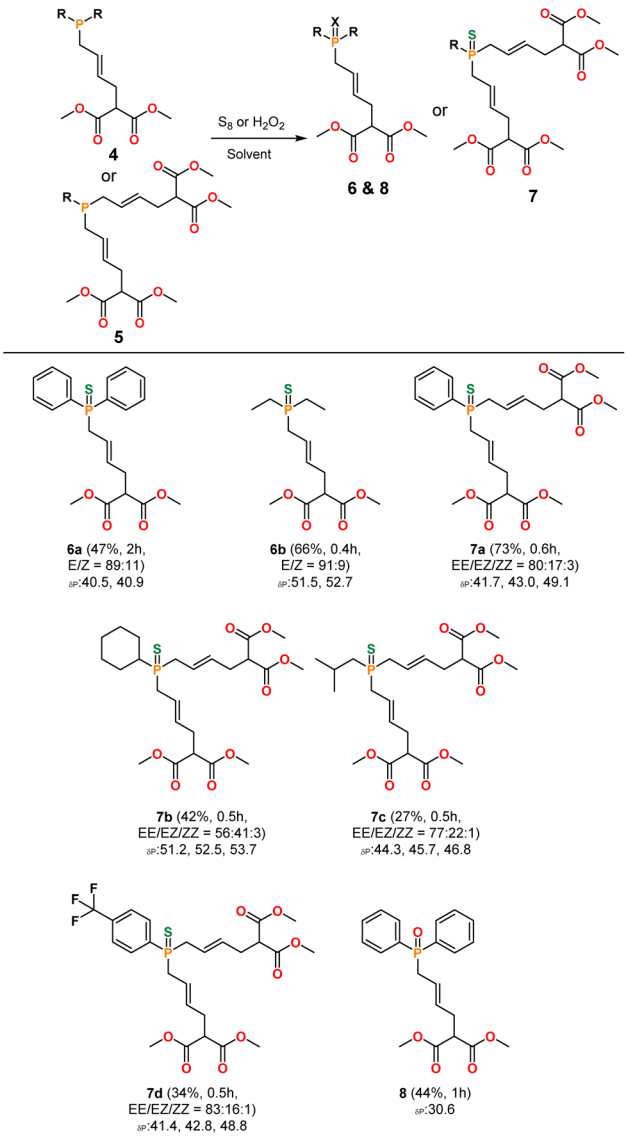
Scheme 1 Initiator free hydrophosphination reactions.



Scheme 2 The substrate scope of primary and secondary phosphines in the hydrophosphination of **3**. Only the *E* isomer of compound **4** is shown in the scheme. The *EE* isomer of compound **5** is shown. Compound **4a**, **5a**, **5b**, **5c** and **5d** were not isolated. [a] NMR conversion was obtained using a 60 μL 0.22 M PPh_3 standard and $^{31}P\{^1H\}$ NMR integration for compound **4a**. [b] NMR conversion were obtained using a 60 μL 0.21 M ferrocene standard and ^1H NMR integration.

conditions required 1 : 1.5 stoichiometric equivalents of **3** and secondary phosphine in THF under photolytic conditions (Table S1†). The reaction mixture was charged into a quartz NMR tube and irradiated with UV light. UV irradiation was created by a 400 W mercury lamp, and all reactions were performed in duplicates. Two signals were observed in the $^{31}P\{^1H\}$ NMR spectra of compounds **4**. The NMR conversion and yield obtained were 43% and 66% for compound **4a** and **4b** respectively (Scheme 2). Compound **4a** was not isolated in its pure form, so the NMR conversion was obtained *via* $^{31}P\{^1H\}$ NMR spectroscopy while using a 60 μL 0.22 M triphenylphosphine (PPh_3) internal standard (Fig. S1†). Furthermore, we characterized the phosphines as much as possible. The signals present in the NMR spectrum of compounds **4** confirmed the formation of tertiary phosphines. The signals also suggested the presence of *E* and *Z* isomers. The more intense signal was assigned to the *E* isomer.[6]

Cyclopropane **3** was then treated with a series of primary phosphines (**2**). The optimized reaction conditions (Table S2†) required 1 : 2.55 stoichiometric equivalents of primary phosphine to cyclopropane in THF (Scheme 2). The reaction mixture was irradiated with UV light to fully convert primary phosphine to tertiary phosphine. Three signals were observed in the $^{31}P\{^1H\}$ NMR spectra of compounds **5a**, **5c**, and **5d** suggesting the formation of three isomers. However, compound **5b**, spectrum only contained 2 signals. The isomers formed were perhaps *EE*, *ZZ* and *EZ*. The most prominent signal in the $^{31}P\{^1H\}$ NMR spectrum was assigned to the *EE* isomer, the second more intense signal corresponded to the *EZ* isomer, and finally the least intense signal was assigned to the *ZZ* isomer. Compounds **5** were not isolated in their pure form, and as a result, the NMR conversion were obtained through ^1H NMR integration in the presence of a 60 μL 0.21 M ferrocene internal standard (Fig. S2†) and were characterized as much as was viable. The NMR conversion ranged from 22%–63%. The lowest NMR conversion were obtained with monoisobutyl phosphine perhaps due to the decomposition of

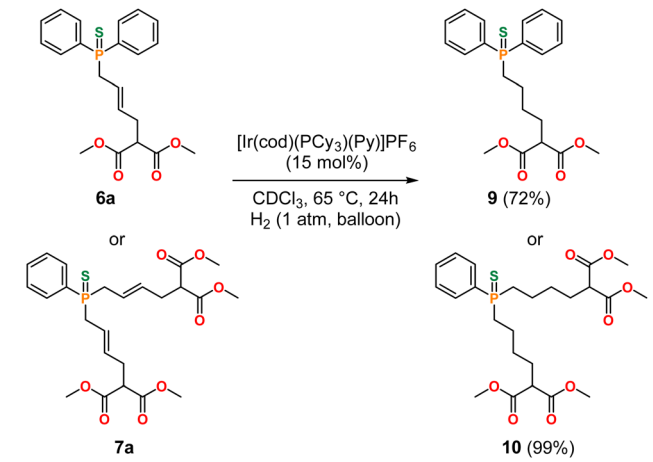


Scheme 3 Crude material were used for the sulfurization and oxidation reactions. The sulfurization or oxidation of phosphines yield is 100% relative to the amount of P(III) species in the material. The products were isolated using flash column chromatography. Compound **8** could also be isolated using recrystallization. Only the *E* and *EE* isomers are shown in the scheme.

cyclopropane during P–H bond addition. A 0.250 mg scale reaction was performed to synthesize compound **4b**. A 91% yield was obtained after irradiating the reaction mixture for 5 h.

Compounds **4** and **5** were sulfurized forming compounds **6** and **7** (Scheme 3). The compounds were isolated *via* flash chromatography as either yellow or colorless air and moisture stable oils. The yields ranged from 27%–73%. Compound **4a** was oxidized using H_2O_2, and compound **8** was obtained as a white solid *via* column chromatography or recrystallization. Single crystals suitable for X-ray diffraction were grown from benzene and cyclohexane (Fig. 1). The $^{31}P\{^1H\}$ NMR spectra of compounds **6**, **7**, and **8** were similar to compound **3** and **4**, however the signals were shifted downfield. Compound **8** only had one phosphorus signal, perhaps due to the signals of the *E* and *Z* isomers overlapping.

To confirm the formation of isomers, compounds **6a** and **7a** were hydrogenated using Crabtree's catalyst ($[Ir(cod)(PCy_3)(Py)]PF_6$) (Scheme 4).[6] The reactions were monitored *via* $^{31}P\{^1H\}$ NMR spectroscopy and products **9** and **10** were isolated



Scheme 4 Hydrogenation of compounds **6a** and **7a** with Crabtree's catalyst. Reaction conditions: **6a** or **7a** (0.1 mmol), Crabtree's catalyst (15 mol%) and $CDCl_3$ (20 mL). Products were isolated using flash chromatography. Only the *E* and *EE* isomers are shown in the scheme.

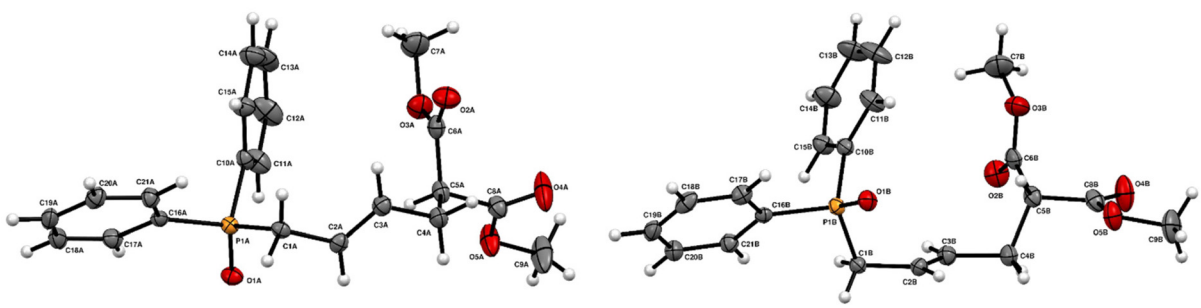


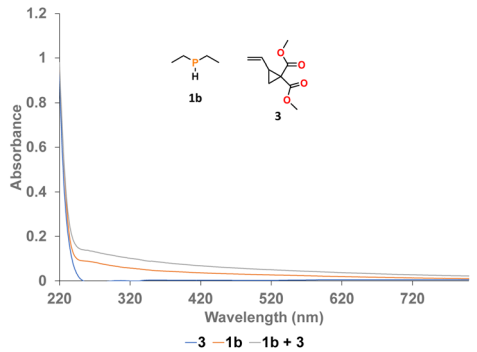
Fig. 1 ORTEP representation of unit cell molecule A and B of **8**. Thermal ellipsoids drawn at 50% probability level.

upon full conversion of **6a** and **7a**. Upon hydrogenation, the signals for the geometrical isomers in the $^{31}P\{^{1}H\}$ NMR spectra converged (δ_P = 42.5 (**9**) and 46.4 (**10**)). Compounds **9** and **10** were isolated in 72% and quantitative yields, respectively.

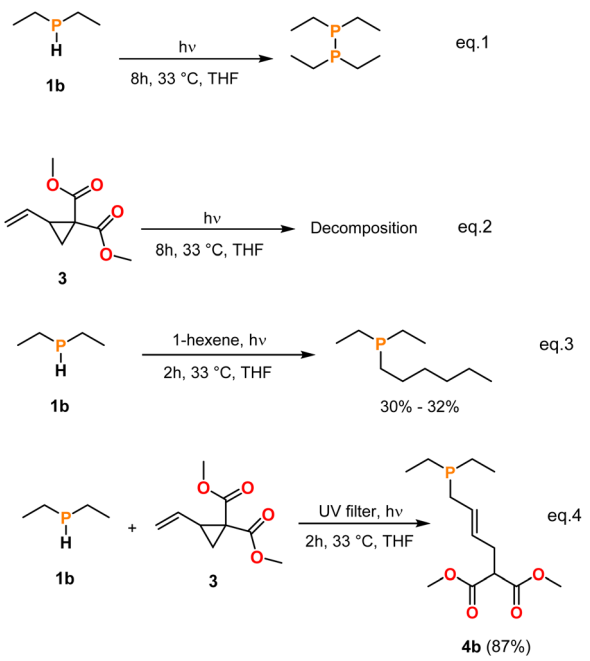
A series of control reactions were performed to probe the mechanism of the P–H bond addition of cyclopropane **3** (Scheme 5, Table S3†). It was determined that light was required to perform P–H bond addition without a free radical initiator. Hydrophosphination did not proceed under dark conditions. In another control experiment **1b** was irradiated with UV light, $^{31}P\{^{1}H\}$ NMR spectroscopy showed the formation of tetraethyldiphosphine (eqn (1), Fig. S3†). This suggested that a phosphinyl radical was formed during the reaction. Compound **3** was irradiated with UV light and underwent decomposition; possibly *via* polymerization (eqn (2)). To determine which one of **1b** and **3** were the chromophore, **1b** was irradiated in the presence of 1-hexene to form diethylhexylphosphine (eqn (3)). The results indicated that another olefin can be used as a substrate for P–H bond addition in our system. Cyclopropane **3** was treated with **1b** in the presence of 1 stoichiometric equivalent of a variety of typical radical traps. There was no formation of product when (2,2,6-tetramethylpiperdin-1-yl)oxyl (TEMPO) and 1,1-diphenylethylene (DPE) were used as radical scavengers. This implies that P–H bond addition proceeds through a radical mechanism. In another experiment, a reaction vessel charged with **1b** and **3** was submerged in UV filter solutions (1.77 M aqueous solution of $NiSO_4{\cdot}H_2O$ and 0.29 M aqueous solution of $CoSO_4{\cdot}H_2O$ and 1.16×10^{-4} M of 1,4 diphenyl butadiene in diethyl ether). Compound **4b** was obtained with an 87% yield (eqn (4)). Although, the yields were higher, the reaction setup using UV filter solutions was inconvenient. As a result, the yields of the other substrates were not optimized using solution filters. The UV solution filters allowed a 15% transmission in the range of 245–270 nm (λ_{max} = 256 nm).[7] The higher yields obtained indicated that UVC light (200 nm–290 nm) was the UV radiation needed to facilitate P–H bond addition. A monochromatic light source with a wavelength of 256 nm may also be the ideal light source to facilitate hydrophosphination reactions in our system.

To supplement our data, we also performed UV-vis spectroscopy on the reagents in the same stoichiometric ratio we used to replicate reaction conditions (Scheme 6). The UV-vis revealed that these compounds did not absorb light in the visible region, thus corroborating the results indicating that UVC light is needed to facilitate P–H bond addition.

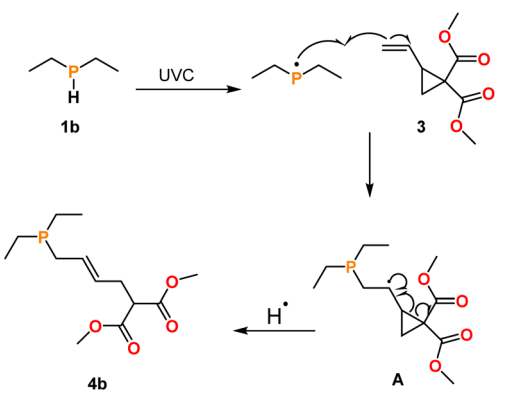
The mechanistic insights provided from the control reactions and previous reports allow us to propose a mechanism (Scheme 7).[8] Upon irradiation of UVC light, a phosphinyl radical was formed *via* photolysis of **1b**. The phosphinyl radical will undergo radical addition to **3** and form a phosphine-cyclopropyl radical adduct (**A**). Intermediate **A** then ring opens and undergoes hydrogen atom transfer (HAT) to form **4b**.



Scheme 6 UV-vis spectrum of compound **1** and **3**.



Scheme 5 Selected control reactions.



Scheme 7 Proposed mechanism.

Conclusions

In summary, we developed a UV light promoted hydrophosphination reaction of **3** with primary and secondary phosphine without the need for a free radical initiator. Upon irradiation, **3** reacted with a range of alkyl and aryl phosphine substrates. The compounds were subsequently sulfurized to obtain moisture and air stable phosphine sulfides. Despite the reaction not requiring an initiator, it still proceeded through a radical pathway. Some uncertainties on where the radical originated from to trigger the reaction remain and further investigation is underway. Future work includes exploring coordination chemistry and catalysis with phosphine sulfides.

Experimental

General considerations

All reactions were carried out under inert atmosphere either in a nitrogen filled MBraun Labmaster 130 glovebox or using Schlenk glassware and methods unless otherwise stated. Solvents were obtained from Caledon and dried using an mBraun Solvent Purification System (SPS). Dried solvents were collected under vacuum in a flame dried Strauss flask and stored over 4 Å molecular sieves. THF was dried and distilled from sodium/benzophenone and collected under N_2. Deuterated solvents were dried over CaH_2 and distilled under nitrogen atmosphere and stored in the glovebox over 4 Å molecular sieves. Unless otherwise stated, all commercially available compounds were used as provided without further purification. Dimethyl 2-vinylcyclopropane-1,1-dicarboxylate was prepared based on the published literature.[9] 4-Trifluoromethylphenylphosphine was synthesized based a modified version of a literature preparation.[10,11] Hydrogenation of phosphine sulfides (**6a** & **7a**) were performed based on published literature.[6] Thin layer chromatography (TLC) was performed on Silicycle, aluminium backed TLC, silica, 200 μm, F254. Visualization on TLC was achieved using UV light, iodine and basic $KMnO_4$. Column chromatography was undertaken on silica gel purchased from Silicycle Chemical Division Inc. (230–400 mesh). NMR spectra were recorded on a BRUKER 400™, BRUKER 600™ and INOVA 400™ (^{1}H 400 MHz, $^{31}P\{^1H\}$ 161.82 MHz, $^{13}C\{^1H\}$100 MHz, $^{19}F\{^1H\}$ 376 MHz). Proton chemical shifts were quoted in parts per million (ppm) and referenced to tetramethylsilane (TMS).[12] The chemical shifts for $^{31}P\{^1H\}$ were referenced using an external standard 85% H_3PO_4; $\delta_P = 0$. Chemical shifts for $^{13}C\{^1H\}$ were reported in ppm and referenced to tetramethylsilane. Chemical shifts for $^{19}F\{^1H\}$ were reported in ppm and referenced to trifluoroacetic acid. The following abbreviations were used to describe peak multiplicities when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, n = nontet, dd = doublet of doublet, td = triplet of doublet, ddd = doublet of doublet of doublets, m = multiplet. Coupling constants (*J*), were reported in hertz (Hz). Fourier Transform Infrared (FTIR) spectroscopy was conducted using a Bruker Alpha II compact FT-IR spectrometer. Frequencies were given in reciprocal centimetres (cm^{-1}) in absorbance mode. Solution UV-vis absorption spectra were recorded using a Cary 5000 UV-vis-NIR spectrophotometer scanning from 200 nm to 800 nm. Unless otherwise stated photoinitiation was performed in a quartz glassware using a UV-box from Ace Glass Incorporated (Vineland, NJ, USA) equipped with a 400 W Mercury Bulb with an energy density of UVA (320–400 nm, 9999 mJ cm^{-2}), UVB (290–320 nm, 9462 mJ cm^{-2}), UVC (200–290 nm, 2016 mJ cm^{-2}), and UVV (395–445 nm, 6066 mJ cm^{-2}). This was determined by using a PP2-H-U Power Puck II purchased from EIT Instrument Markets (Sterling, VA, USA). Melting points were determined using a Gallenkamp melting point apparatus. High resolution mass spectra (HRMS) were obtained on a Thermo Scientific DFS mass spectrometer using electrospray ionization (ESI-MS). Relaxation delay (d_1) studies were performed on **4a** to confirm an appropriate relaxation delay was established to accurately integrate $^{31}P\{^1H\}$ NMR spectra. The NMR experiments were performed on compound **4a** using a INOVA 400™: array size – 10, first value (relaxation delay) – 1 s, increment – 2.0 s, last value – 19, total time of the experiment – 1 hour, 5 minutes, 7 seconds. Pulse angle – 45°, acquisition time – 0.844 seconds, steady state – –4. $^{31}P\{^1H\}$ NMR spectra of all $10d_1$ studies experiments were recorded in $CDCl_3$. **4a** was normalized to 1.00 while **1a** was integrated during each experiment. The results indicated that changing the relaxation delay did not affect the integrations.

Detailed procedures for the synthesis of phosphine, phosphine sulfides, phosphine oxide & hydrogenations

General procedure for the synthesis of tertiary phosphine (4–5). Secondary phosphine (**2**, 1.5 equiv.), or primary phosphine (**1**, 1 equiv.) were treated with either 2.55 equiv. or 1 equiv. of dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (**3**), respectively in THF (0.3 M). The reagents were charged into a quartz NMR tube and the reaction mixture was continuously irradiated with UV light for 0.6 h–9 h. Once **1**, or **3** was consumed, the reaction mixture was transferred into a vial and concentrated *in vacuo*, where a colourless oil was obtained. If polymer was detected, THF (5 mL) was added, and the mixture was transferred to a centrifuge tube. The supernatant was separated from the polymer, and the volatiles were removed *in vacuo*, a colourless or yellow oil was obtained.

(*E*)-2-(4-(Diphenylphosphaneyl)but-2-en-1-yl) malonate & dimethyl (*Z*)-2-(4-(diphenylphosphaneyl)but-2-en-1-yl) malonate (4a). Reagents used: diphenylphosphine (**1a**, 0.07 g, 71 μL, 0.4071 mmol, 1.5 equiv.), **3** (0.05 g, 0.2714 mmol, 1 equiv.); THF: 0.9 mL; UV irradiation: 3 h. Isolated materials contained a mixture of **1a**, **4a** and small amounts of **3**. $^{31}P\{^1H\}$ NMR conversion was determined by integration of the NMR spectrum in the presence of 0.22 M PPh_3 internal standard: **4a** (43%), **1a** (6%), unknown impurity (13%). ^{1}H NMR ($CDCl_3$): 7.36 (m, 22H), 5.55 (m, 2H), 5.35 (m, 1H), 3.67 (s, 6H), 3.29 (t, $^3J_{H-H}$ = 8 Hz, 1H), 2.79 (m, 2H), 2.60 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ_C = 169.4, 134.4, 134.1, 133.0, 128.7, 128.5, 128.3, 52.6, 51.9, 32.4, 32.0. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_P = –14.8, –14.3.

HRMS (ESI-MS) (*m*/*z*): $^{13}C_{21}{}^{1}H_{23}{}^{23}Na^{16}O_4{}^{31}P$: calculated 393.1232 ([$M^+$]); found 393.1361.

Dimethyl (*E*)-2-(4-(diethylphosphaneyl)but-2-en-1-yl) malonate & dimethyl (*Z*)-2-(4-(diethylphosphaneyl)but-2-en-1-yl) malonate (4b). Reagents used: diethylphosphine (**1b**, 0.04 g, 47 μL, 0.4072 mmol, 1.5 equiv.), and **3** (0.05 g, 0.2714 mmol, 1 equiv.); THF: 0.9 mL; UV irradiation: 2 h. Yield: 0.04 g (66%). ^{1}H NMR (C_6D_6): 5.38 (m, 1H), 5.22 (m, 1H), 3.27 (t, $^3J_{H–H}$ = 4 Hz, 1H), 3.22 (s, 5H), 2.58 (td, $^3J_{H–H}$ = 8 Hz, $^3J_{H–H}$ = 4 Hz, 2H), 1.90 (dd, $^3J_{H–H}$ = 8 Hz, $^3J_{H–H}$ = 4 Hz, 2H), 1.11 (q, $^3J_{H–H}$ = 8 Hz, 4H), 0.89 (t, $^3J_{H–H}$ = 8 Hz, 3H), 0.85 (t, $^3J_{H–H}$ = 8 Hz, 3H). ^{13}C{^{1}H} NMR (C_6D_6) δ_C = 169.2, 128.9, 127.4, 52.4, 51.9, 32.4, 29.8 ($^2J_{C–P}$ = 10 Hz), 18.4, 8 ($^2J_{C–P}$ = 20 Hz), 9.9 ($^3J_{C–P}$ = 10 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ_P = −23.4, −20.0. IR: 2955, 1732, 1435, 1338, 1270, 1231, 1194, 1152, 1026, 968, 760, 672, 482. HRMS (ESI-MS) (*m*/*z*): $^{13}C_{21}{}^{1}H_{23}{}^{16}O_5{}^{31}P$: calculated 274.1334 ([$M^+$]); found 274.1341.

Scaled up procedure for the synthesis of 4b. Reagents used: diethylphosphine (**1b**, 0.18 g, 234 μL, 2.0359 mmol, 1.5 equiv.), and **3** (0.25 g, 1.357 mmol, 1 equiv.); THF: 4.5 mL; UV irradiation: 5 h. Yield: 0.34 g (91%).

Tetramethyl 2,2′-((2*E*,2′*E*)-(phenylphosphanediyl)bis(but-2-ene-4,1-diyl))dimalonate & tetramethyl 2,2′-((2*Z*,2′*Z*)-(phenylphosphanediyl)bis(but-2-ene-4,1-diyl))dimalonate & tetramethyl 2,2′-((2*Z*,2′*E*)-(phenylphosphanediyl)bis(but-2-ene-4,1-diyl))dimalonate (5a). Reagents used: phenylphosphine (**2a**, 0.05 g, 50 μL, 0.4541 mmol, 1 equiv.), **3** (0.21 g, 1.158 mmol, 2.55 equiv.); THF: 1.5 mL; UV irradiation: 2 h. Isolated materials contained a mixture of **3**, polymeric containment and **5a**. NMR conversion (^{1}H NMR integration): 0.12 g (54%). ^{1}H NMR ($CDCl_3$): 7.26 (m, 5H), 5.33 (m, 2H), 5.22 (m, 2H), 3.60 (s, 8H), 3.24 (t, $^3J_{H–H}$ = 8 Hz, 2H), 2.45 (td, $^3J_{H–H}$ = 8 Hz, $^3J_{H–H}$ = 4 Hz, 4H), 2.31 (m, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ_C = 169.4, 137.2, 133.3, 133.2 ($^2J_{C–P}$ = 20 Hz), 132.2 ($^2J_{C–P}$ = 20 Hz), 128.8, 128.4, 52.6, 52.0, 32.0, 30.4 ($^2J_{C–P}$ = 10 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P = −25.2, −23.3, −21.5. HRMS (ESI-MS) (*m*/*z*): $^{13}C_{24}{}^{1}H_{32}{}^{16}O_8{}^{31}P$: calculated 479.1790 ([$M^+$]); found 479.1835.

Tetramethyl 2,2′-((2*E*,2′*E*)-(cyclohexylphosphanediyl)bis(but-2-ene-4,1-diyl))dimalonate & tetramethyl 2,2′-((2*Z*,2′*Z*)-(cyclohexylphosphanediyl)bis(but-2-ene-4,1-diyl))dimalonate & tetramethyl 2,2′-((2*Z*,2′*E*)-(cyclohexylphosphanediyl)bis(but-2-ene-4,1-diyl))dimalonate (5b). Reagents used: monocyclohexylphosphine (**2b**, 0.05 g, 0.4305 mmol, 1 equiv.), **3** (0.20 g, 1.098 mmol, 2.55 equiv.); THF: 1.43 mL; UV irradiation: 9 h. Isolated materials contained a mixture of **3**, polymeric contaminant and **5b**. NMR conversion (^{1}H NMR integration): 0.11 g (54%). ^{1}H NMR ($CDCl_3$): 5.50 (m, 2H), 5.38 (m, 2H), 3.73 (s, 11H), 3.42 (t, $^3J_{H–H}$ = 8 Hz, 2H), 2.14 (d, $^3J_{H–H}$ = 4 Hz 4H), 1.75–1.68 (m, 5H), 1.25–1.11 (m, 5H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P = −17.8, −14.7. ^{13}C{^{1}H} NMR ($CDCl_3$): δ_C = 169.4, 128.9, 127.3, 52.6, 52.1, 32.1, 29.3, 29.2, 26.9, 26.5, 26.3. HRMS (ESI-MS) (*m*/*z*): $^{13}C_{24}{}^{1}H_{38}{}^{16}O_8{}^{31}P$: calculated 484.2226 ([$M^+$]); found 485.2304.

Tetramethyl 2,2′-((2*E*,2′*E*)-(isobutylphosphanediyl)bis(but-2-ene-4,1-diyl))dimalonate & tetramethyl 2,2′-((2*Z*,2′*Z*)-(isobutylphosphanediyl)bis(but-2-ene-4,1-diyl))dimalonate & tetramethyl 2,2′-((2*Z*,2′*E*)-(isobutylphosphanediyl)bis(but-2-ene-4,1-diyl))dimalonate (5c). Reagents used: monoisobutylphosphine (**2c**, 0.05 g, 70 μL, 0.5549 mmol, 1 equiv.), **3** (0.26 g, 1.414 mmol, 2.55 equiv.); THF: 1.8 mL; UV irradiation: 2 h. Isolated materials contained a mixture of **3**, polymeric contaminant and **5c**. NMR conversion (^{1}H NMR integration): 0.05 g (22%). ^{1}H NMR (C_6D_6): 5.52–5.45 (m, 2H), 5.43–5.33 (m, 2H), 3.73 (s, 15H), 3.42 (t, $^3J_{H–H}$ = 8 Hz, 2H), 2.61 (m, 4H), 2.09 (m, 3H), 1.65 (non, 1H), 1.24 (d, $^3J_{H–H}$ = 8 Hz, 2H), 0.97 (d, $^3J_{H–H}$ = 8 Hz, 6H). ^{13}C{^{1}H} NMR (C_6D_6): δ_C = 169.2, 128.9, 52.4, 52.0, 35.9 ($^1J_{C–P}$ = 20 Hz), 32.4, 30.1 ($^1J_{C–P}$ = 10 Hz), 26.7 ($^2J_{C–P}$ = 20 Hz), 24.4 ($^3J_{C–P}$ = 10 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ_P = −33.9, −32.4, −30.7. $^{13}C_{22}{}^{1}H_{35}{}^{23}Na^{16}O_8{}^{31}P$: calculated 481.1962 ([M + Na]$^+$); found 481.1953.

Tetramethyl 2,2′-((2*E*,2′*E*)-((4-(trifluoromethyl)phenyl)phosphanediyl)bis(but-2-ene-4,1-diyl))dimalonate & tetramethyl 2,2′-((2*Z*,2′*Z*)-((4-(trifluoromethyl)phenyl)phosphanediyl)bis(but-2-ene-4,1-diyl))dimalonate & tetramethyl 2,2′-((2*Z*,2′*E*)-((4-(trifluoromethyl)phenyl)phosphanediyl)bis(but-2-ene-4,1-diyl))dimalonate (5d). Reagent used: 4-trifluoromethylphenylphosphine (**5d**, 0.05 g, 0.2809 mmol, 1 equiv.), **3** (0.13 g, 0.7162 mmol, 2.55 equiv.); THF: 0.94 mL; UV irradiation: 0.6 h. Isolated materials contained a mixture of **3**, polymeric contaminant and **5d**. A yellow oil and polymer mixture was obtained NMR conversion (^{1}H NMR integration): 0.08 g (51%). ^{1}H NMR ($CDCl_3$): 7.59–7.50 (m, 2H), 5.45–5.31 (m, 3H), 3.70 (s, 12H), 3.42 (t, 1H), 2.56 (m, 4H), 2.45 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ_C = 169.3, 133.5, 133.2, 132.4, 128.7, 127.5, 125.0, 52.6, 51.9, 32.0, 29.9. ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P = −25.0, −23.0, −22.8. ^{19}F{^{1}H} NMR ($CDCl_3$): $\delta_{F\ =}$ −62.8, 62.9. HRMS (ESI-MS) (*m*/*z*): $^{13}C_{25}{}^{1}H_{30}{}^{19}F_3{}^{23}Na^{16}O_8{}^{31}P$: calculated 569.1523 ([M + Na]$^+$); found 569.1534.

General procedure for the sulfurization of tertiary phosphine (6–7). Tertiary phosphine, elemental sulfur, and toluene were charged to a 20 mL Scintillation vial. The reaction mixture was stirred for 0.4 h–2 h at room temperature. Any unreacted sulfur was filtered from the reaction mixture *via* vacuum filtration, the filtrate was concentrated *in vacuo* and an oil was obtained. The crude products were purified *via* flash column chromatography (EtOAc/hexanes) to yield an oil.

Dimethyl (*E*)-2-(4-(diphenylphosphorothioyl)but-2-en-1-yl) malonate & dimethyl (*Z*)-2-(4-(diphenylphosphorothioyl)but-2-en-1-yl) malonate (6a). Reagent used: crude compound (contains **1a**) **4a** (0.50 g, 1.360 mmol, 1 equiv.) and S_8 (0.35 g, 1.360 mmol, 1 equiv.); toluene: 5 mL. The reaction mixture was left to stir for 2 h. The crude yellow oil was purified by flash column chromatography (EtOAc/hexanes, 30% : 70%, R_f = 0.40, visualized with UV light) to yield a pale-yellow oil. Yield: 0.25 g (47%). ^{1}H NMR ($CDCl_3$): 7.78 (m, 5H), 7.47 (m, 7H), 5.58 (m, 1H), 5.46 (m, 1H), 3.68 (s, 6H), 3.29 (t, $^3J_{H–H}$ = 8 Hz, 1H), 3.23 (dd, $^3J_{H–H}$ = 16 Hz, $^3J_{H–H}$ = 8 Hz, 2H), 2.55 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ_C = 169.2, 133.0, 132.5 ($^1J_{C–P}$ = 20 Hz), 132.2, 131.7, 131.5 ($^3J_{C–P}$ = 10 Hz), 128.7 ($^4J_{C–P}$ = 12 Hz), 122.4 ($^3J_{C–P}$ = 10 Hz), 52.7, 51.6, 38.1 ($^2J_{C–P}$ = 50 Hz), 31.9. ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P = 40.9, 40.5. IR: 3053 (C–H (aromatic) str., w), 2951 (C–H (aromatic) str., w), 1750 (C═O str., s), 1481, 1435,

1400, 1336, 1309, 1270, 1232, 1193, 1153, 1101, 1046, 1026, 998, 968, 833, 795, 744, 706, 692, 621, 610, 511, 484. HRMS (ESI-MS) (*m*/*z*): $^{13}C_{21}{}^{1}H_{23}{}^{16}O_4{}^{31}P{}^{16}S$: calculated 402.1054 ($[M]^+$); found 402.1062.

Dimethyl (*E*)-2-(4-(diethylphosphorothioyl)but-2-en-1-yl)malonate & dimethyl (*Z*)-2-(4-(diethylphosphorothioyl)but-2-en-1-yl)malonate (6b). Reagent used: compound **4b** (0.07 g, 0.271 mmol, 1 equiv.), and S_8 (0.01 g, 0.051 mmol, 1/8 equiv.); toluene: 2 mL. The reaction mixture was left to stir for 0.4 h. The crude colourless oil was purified by flash column chromatography (EtOAc/hexanes, 30% : 70%, R_f = 0.26, visualized with basic $KMnO_4$) to yield a yellow oil. Yield: 0.04 g (66%). ^{1}H NMR ($CDCl_3$): 5.57 (m, 2H), 3.73 (s, 6H), 3.44 (t, $^3J_{H-H}$ = 8 Hz, 1H), 2.65 (m, 3H), 2.60 (m, 1H), 1.79 (m, 5H), 1.18 (m, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ_C = 169.2, 131.5, 123.4, 52.8, 51.5, 35.2 ($^2J_{C-P}$ = 50 Hz), 31.9, 22.9 ($^2J_{C-P}$ = 60 Hz), 6.4 ($^3J_{C-P}$ = 10 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P = 52.7, 51.5. IR: 2960 (C–H str., w), 1732 (C═O str., s), 1435, 1408, 1339, 1259, 1232, 1192, 1143, 1087, 1014, 795, 769, 677, 562. HRMS (ESI-MS) (*m*/*z*): $^{13}C_{13}{}^{1}H_{22}{}^{16}O_4{}^{31}P{}^{16}S$: calculated 305.0976 ($[M - H]^+$); found 305.0982.

Tetramethyl 2,2′-((2*E*,2′*E*)-2-(phenylphosphorothioyl)bis(but-2-ene-4,1-diyl)) dimalonate & tetramethyl 2,2′-((2*Z*,2′*Z*)-2-(phenylphosphorothioyl)bis(but-2-ene-4,1-diyl)) dimalonate & tetramethyl 2,2′-((2*Z*,2′*E*)-2-(phenylphosphorothioyl)bis(but-2-ene-4,1-diyl)) dimalonate (7a). Reagent used: crude **5a** (0.22 g, 0.4702 mmol, 1 equiv.), and S_8 (0.13 g, 0.5220 mmol, 1.1 equiv.); toluene: 2 mL. The reaction mixture was left to stir for 0.6 h. The crude product was purified by flash column chromatography (EtOAc/hexanes, 30% : 70%, R_f = 0.14, visualized with $KMnO_4$) to yield a colourless oil. Yield: 0.18 g (73%). ^{1}H NMR ($CDCl_3$): 7.80 (m, 2H), 7.50 (m, 3H), 5.51 (m, 4H), 3.71 (s, 12H), 3.37 (t, $^3J_{H-H}$ = 8 Hz, 2H), 2.87 (dd, $^3J_{H-P}$ = 16 Hz, $^3J_{H-H}$ = 8 Hz, 4H), 2.59 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ_C = 169.2, 132.2 ($^3J_{C-P}$ = 20 Hz), 132.1, 131.8, 131.4, 131.3, 128.7 ($^3J_{C-P}$ = 10 Hz), 52.8, 51.6, 37.1 ($^2J_{C-P}$ = 50 Hz), 31.9. ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P = 49.1, 43.0, 41.7. IR: 2952 (C–H str., w), 1729 (C═O str., s), 1434, 1402, 1269, 1232, 1193, 1150, 1105, 1021, 970, 842, 747, 694, 599, 485. HRMS (ESI-MS) (*m*/*z*): $^{13}C_{21}{}^{1}H_{23}{}^{16}O_5{}^{31}P$: calculated 510.1477 ($[M]^+$); found 510.1480.

Tetramethyl 2,2′-((2*E*,2′*E*)-(cyclohexylphosphorothioyl)bis(but-2-ene-4,1-diyl))dimalonate & tetramethyl 2,2′-((2*Z*,2′*Z*)-(cyclohexylphosphorothioyl))bis(but-2-ene-4,1-diyl)dimalonate & tetramethyl 2,2′-((2*Z*,2′*E*)-(cyclohexylphosphorothioyl))bis(but-2-ene-4,1-diyl)dimalonate (7b). Reagent used: crude **5b** (0.21 g, 0.4305 mmol, 1 equiv.) and S_8 (0.13 g, 0.5220 mmol, 1.2 equiv.); toluene: 5 mL. The reaction mixture was left to stir for 0.5 h. The crude colourless oil was purified by gradient flash column chromatography (EtOAc/hexanes, 10%:90% (fraction 1–14), 30% : 70% (fraction 15–32) R_f = 0.10, visualized with $KMnO_4$) to yield a colourless oil. Yield: 0.09 g (42%). ^{1}H NMR ($CDCl_3$) = 5.58 (m, 4H), 3.74 (s, 12H), 3.47 (t, $^3J_{H-H}$ = 8 Hz, 5H), 2.66 (dd, $^3J_{H-H}$ = 12 Hz, $^3J_{H-H}$ = 8 Hz, 4H), 2.60 (m, 4H), 1.82 (m, 9H), 1.44 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ_C = 169.3, 131.5, 123.3, 52.8, 51.6, 37.2, ($^2J_{C-P}$ = 25 Hz) 33.0 ($^1J_{C-P}$ = 50 Hz), 26.4, 26.2, 25.8, 25.4. ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P = 53.7, 52.5, 51.3. IR: 2949, 2853, 1730 (C═O str., s), 1732, 1405, 1269, 1232, 1194, 1151, 1041, 1021, 972, 855, 832, 696, 602. HRMS (ESI-MS) (*m*/*z*): $^{13}C_{24}{}^{1}H_{36}{}^{16}O_8{}^{31}P{}^{16}S$: calculated 515.1868 ($[M - H]^+$); found 515.1873.

Tetramethyl 2,2′-((2*E*,2′*E*)-(isobutylphosphorothioyl)bis(but-2-ene-4,1-diyl))dimalonate & tetramethyl 2,2′-((2*Z*,2′*Z*)-(isobutylphosphorothioyl)bis(but-2-ene-4,1-diyl))dimalonate & tetramethyl 2,2′-((2*Z*,2′*E*)-(isobutylphosphorothioyl)bis(but-2-ene-4,1-diyl))dimalonate (7c). Reagent used: crude **5c** (0.23 g, 0.4994 mmol, 1 equiv.) and S_8 (0.14 g, 0.5458 mmol, 1.1 equiv.); toluene: 5 mL. The reaction mixture was left to stir for 0.5 h. The crude product was purified by flash column chromatography (EtOAc/hexanes, 30% : 70%, R_f = 0.24, visualized with $KMnO_4$) to yield a colourless oil. Yield 0.07 g, (27%). ^{1}H NMR ($CDCl_3$): 5.57 (m, 4H), 3.74 (s, 12H), 3.46 (t, $^3J_{H-H}$ = 8 Hz, 2H), 2.67 (m, 4H), 2.60 (dd, $^3J_{H-H}$ = 12 Hz, $^3J_{H-H}$ = 4 Hz, 4H), 2.22 (non, $^3J_{H-H}$ = 12 Hz, $^3J_{H-H}$ = 8 Hz, 1H), 1.65 (dd, $^3J_{H-H}$ = 12 Hz, $^2J_{H-H}$ = 8 Hz, 2H), 1.06 (d, $^3J_{H-H}$ = 8 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ_C = 169.2, 132.0, 123.3, 52.8, 51.6, 37.0 ($^2J_{C-P}$ = 40 Hz), 36.6 ($^2J_{C-P}$ = 50 Hz), 32.0, 24.6, 23.9. ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P = 46.8, 45.7, 44.3. IR: 2954 (C–H str., w), 1730 (C═O str., s), 1732 (C═O str., s), 1434, 1404, 1340, 1232, 1195, 1152, 1044, 972, 842, 696, 592, 484. HRMS (ESI-MS) (*m*/*z*): $^{13}C_{22}{}^{1}H_{36}{}^{16}O_8{}^{31}P{}^{16}S$: calculated 491.1868 ($[M + H]^+$); found 491.1863.

Tetramethyl 2,2′-((2*E*,2′*E*)-((4-(trifluoromethyl)phenyl)phosphorothioyl)bis(but-2-ene-4,1-diyl))dimalonate & tetramethyl 2,2′-((2*Z*,2′*Z*)-((4-(trifluoromethyl)phenyl) phosphorothioyl)bis(but-2-ene-4,1-diyl))dimalonate & tetramethyl 2,2′-((2*Z*,2′*E*)-((4-(trifluoromethyl)phenyl) phosphorothioyl)bis(but-2-ene-4,1-diyl))dimalonate (7d). Reagent used: crude **5d** (0.19 g, 0.3489 mmol, 1 equiv.) and S_8 (0.02 g, 0.5458 mmol, 1.6 equiv.); toluene: 2 mL. The reaction mixture was left to stir for 2 h. The crude product was purified by flash column chromatography (EtOAc/hexanes, 30% : 70%, R_f = 0.21, visualized with UV light) to yield a colourless oil. Yield: 0.05 g (34%). ^{1}H NMR ($CDCl_3$): 7.97 (d, $^3J_{H-H}$ = 8 Hz, 2H), 7.75 (d, $^3J_{H-H}$ = 8 Hz, 2H), 5.53–5.50 (m, 4H), 3.72 (t, 12H), 3.38 (t, $^3J_{H-H}$ = 8 Hz, 2H), 2.88 (td, $^3J_{H-H}$ = 16 Hz, $^3J_{H-H}$ = 8 Hz, 3H), 2.61 (dd, $^3J_{H-H}$ = 8 Hz, $^3J_{H-H}$ = 4 Hz, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ_C = 169.2, 132.8, 132.7, 125.5, 122.1, 52.8, 51.4, 36.9, 31.9. ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P = 47.3, 42.8, 41.4. ^{19}F{^{1}H} NMR ($CDCl_3$): δ_F = −63.1. IR: 2954 (C–H (aromatic) str., w), 1730 (C═O str., s), 1435 (P–C, s), 1397, 1323, 1128, 1061, 1016, 971, 834, 702, 600, 504. HRMS (ESI-MS) (*m*/*z*): $^{13}C_{25}{}^{1}H_{30}{}^{19}F_3{}^{11}Na\ {}^{16}O_8{}^{31}P{}^{16}S$: calculated 601.1243 ($[M + Na]^+$); found 601.1252.

General procedure for the oxidation of tertiary phosphine (8). Compound **1a** (0.05 g, 47 μL, 0.2714 mmol, 1 equiv.), **3** (0.05 g, 0.2714 mmol, 1 equiv.) were charged to a quartz NMR tube. The reaction mixture was irradiated with UV light for 2–3 h with and progress of the reaction was monitored *via* ^{31}P{^{1}H} spectroscopy. Once cyclopropane **3** was consumed, the reaction was concentrated *in vacuo* and a colourless oil was obtained. The oil was cooled in an ice bath, dissolved in MeCN (5 mL) and 30% H_2O_2 solution (1 mL, 9.800 mmol, 36 equiv.) was added dropwise to the solution at 0 °C. Upon adding H_2O_2, the yellow solution changed into a colourless solution

and the reaction mixture was left to stir for 1 h. The mixture was then extracted with DCM (3 × 20 mL), after which the organic layer was washed once with brine (50 mL). Afterwards, the organic layer was suspended and dried over $MgSO_4$. Evaporation of the volatiles yielded a colourless oil, and the crude product was recrystallized using minimal amount of EtOAc or flash column chromatography (EtOAc/MeOH, 95% : 5%, R_f = 0.39, visualized with UV light or $KMnO_4$), a white powdered solid was isolated.

Dimethyl (*E*)-2-(4-(diphenylphosphoryl)but-2-en-1-yl) malonate (8). Yield: 0.05 g (44%). M.p: 112.8 °C. ^{1}H NMR ($CDCl_3$): 7.71–7.66 (m, 4H), 7.52–7.44 (m, 7H), 5.57–5.42 (m, 2H), 3.68 (s, 6H), 3.27 (t, $^3J_{H-H}$ = 8 Hz, 1H), 3.05 (dd, $^3J_{H-H}$ = 16 Hz, $^3J_{H-H}$ = 8 Hz, 2H), 2.53 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ_C = 169.2, 133.0, 132.2, 132.1, 131.2 (d, $^3J_{C-P}$ = 9 Hz), 128.7 (d, $^1J_{C-P}$ = 20 Hz), 122.1, 52.7, 51.6, 35.0 (d, $^1J_{C-P}$ = 70 Hz), 32.0. P{^{1}H} NMR ($CDCl_3$): δ_P = 30.6. IR: 2952 (C–H (aromatic) str., w), 2849 (C–H (aromatic) str., w), 1750 (C=O str., s), 1732 (C=O str., s), 1590, 1486, 1436 (P–C, s), 1318, 1277, 1232, 1176, 1152 (P=O, str., s), 118, 1070, 1052, 998, 968, 914, 844, 737, 717, 696, 614, 556, 520, 504, 430. HRMS (ESI-MS) (*m*/*z*): $^{13}C_{21}{}^1H_{22}{}^{16}O_5{}^{31}P$: calculated 385.1205 ([M − H$^+$]$^-$); found 385.1209. XRD quality crystals were grown using benzene and cyclohexane as solvent.

General procedure for hydrogenation (9 & 10). 0.05 M stock solution of compound **6a** or **7a** in $CDCl_3$, Crabtree's catalyst (15 mol%) and $CDCl_3$ (20 mL) were charged to a two neck Schlenk flask. The flask was evacuated and refilled with H_2 (1 atm, balloon) three times.[4] The reaction mixture was heated to reflux at 60 °C and monitored *via* ^{31}P{^{1}H} and ^{1}H NMR spectroscopy. The mixture was then filtered through a pad of Celite. The filtrate was evaporated *in vacuo* and purified by flash column chromatography yielding an oil.

Dimethyl 2-(4-(diphenylphosphorothioyl)butyl)malonate (9). Reagents used: compound **6a** (0.05 g, 0.1317 mmol, 1 equiv.), Crabtree's catalyst (0.02 g, 0.0199 mmol, 15 mol%). Reflux time: 23 h. Chromatography: EtOAc/hexanes, 35% : 65%, R_f = 0.37, visualized with UV light. A dark yellow oil was obtained. Yield: 0.05 g (99%). ^{1}H NMR ($CDCl_3$): 7.81 (m, 4H), 7.47 (m, 6H), 3.71 (s, 6H), 3.31 (t, $^3J_{H-H}$ = 4 Hz, 1H), 2.43 (m, 2H), 1.88 (m, 2H), 1.66 (m, 4H), 1.44 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ_C = 169.8, 132.9 ($^1J_{C-P}$ = 80 Hz), 131.6, 131.2 ($^4J_{C-P}$ = 10 Hz), 128.8 ($^3J_{C-P}$ = 20 Hz), 52.7, 51.5, 32.4 ($^1J_{C-P}$ = 60 Hz), 28.4, 28.3, 22.0. ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P = 42.5. IR: 3053 (C–H (aromatic) str., w), 2949 (C–H (aromatic) str., w), 1730 (C=O str., s), 1481, 1435 (P–C (aromatic) str., m), 1341, 1290, 1262, 1241, 1197, 1154, 1101, 998, 848, 784, 692, 622, 610, 513, 487, 457. HRMS (ESI-MS) (*m*/*z*): $^{13}C_{21}{}^1H_{24}{}^{16}O_4{}^{31}P{}^{16}S$: calculated 403.1133 ([M − H]$^+$); found 403.1151.

Tetramethyl 2,2′-((phenylphosphorothioyl)bis(butane-4,1-diyl))dimalonate (10). Reagents used: compound **7a** (0.05 g, 0.0979 mmol, 1 equiv.), Crabtree's catalyst (0.01 g, 0.0149 mmol, 15 mol%). Reflux time: 21 h. Chromatography: EtOAc/hexanes, 50% : 50%, R_f = 0.40, visualized with iodine. A yellow oil was obtained. Yield: 0.04 g (72%). ^{1}H NMR ($CDCl_3$): 7.83 (m, 2H), 7.50 (m, 3H), 3.71 (s, 12H), 3.29 (t, $^3J_{H-H}$ = 4 Hz, 2H), 2.06 (m, 4H), 1.85 (m, 4H), 1.70 (m, 5H), 1.36 (m, 7H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ_C = 169.8, 131.7, 131.0 ($^2J_{C-P}$ = 10 Hz), 130.9 ($^1J_{C-P}$ = 70 Hz), 128.9 ($^3J_{C-P}$ = 10 Hz), 52.7, 51.5, 33.1 ($^2J_{C-P}$ = 50 Hz), 28.4, 28.3 ($^1J_{C-P}$ = 10 Hz), 22.0. ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P = 46.4. IR: 2952 (C–H (aromatic) str., w), 2863 (C–H (aromatic) str., w), 1730 (C=O str., s), 1434, 1289, 1241, 1198, 1153, 1103, 1008, 795, 745, 695, 560. HRMS (ESI-MS) (*m*/*z*): $^{13}C_{24}{}^1H_{34}{}^{16}O_8{}^{31}P{}^{32}S$: calculated 513.1712 ([M − H]$^+$); found 513.1719.

General procedure for the hydrophosphination of 1-hexene with diethylphosphine. Diethylphosphine (**1b**, 0.08 g, 75 μL, 0.8911 mmol, 1.5 equiv.), 1-hexene (0.05 g, 74 μL 0.5941 mmol, 1 equiv.) and 0.9 mL of THF were charged to quartz NMR tube. The reaction mixture was irritated with UV light, for 2 h. The progress of the reaction was monitored *via* ^{31}P{^{1}H} spectroscopy. The volatiles were removed *in vacuo*, and a colourless oil was obtained.

Diethylhexylphosphine. Yield: 0.03 g (32%). ^{1}H NMR ($CDCl_3$): 1.35 (m, 10H), 1.28 (m, 4H), 1.06 (t, $^3J_{H-H}$ = 8 Hz, 3H), 1.02 (t, $^3J_{H-H}$ = 3 Hz, 3H), 0.88 (t, $^3J_{H-H}$ = 8 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ_C = 31.8, 31.4 ($^1J_{C-P}$ = 10 Hz), 26.4 ($^2J_{C-P}$ = 10 Hz), 26.0 ($^3J_{C-P}$ = 10 Hz), 22.7, 19.0 ($^2J_{C-P}$ = 10 Hz), 14.2, 9.8 ($^2J_{C-P}$ = 10 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ_P = −22.7.

Author contributions

This project was conceived by MAK & PJR. All experiments were performed by JAA, and the manuscript was written by JAA with contributions from MAK & PJR. All authors approved the final version of the manuscript.

Conflicts of interest

The are no conflicts to declare.

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