

C–C Coupling | Hot Paper |

Palladium-Catalyzed Oxidative Cross-Coupling of α -Cyanoketene Dithioacetals with OlefinsXiaoge Yang,^[a] Zhuqing Liu,^[a] Chenglin Sun,^[a] Jiping Chen,^[a] and Zhengkun Yu^{*[a, b]}

Abstract: Efficient palladium-catalyzed cross-coupling reactions of the internal olefins α -cyanoketene dithioacetals with a variety of olefins were achieved in dioxane/HOAc/DMSO (9:3:1 v/v/v) under air atmosphere or by means of AgOAc as the terminal oxidant. Electron-deficient terminal olefins reacted to form the linear diene derivatives with air as the oxidant. Styrenes underwent the cross-coupling to give both

the linear and branched dienes when using AgOAc as the oxidant. Unactivated cyclic and linear internal olefin substrates both reacted in the presence of a catalytic amount of benzoquinone in air to produce skipped dienes. The typical products were structurally confirmed by X-ray crystallography.

Introduction

Cross-coupling of two C–H bonds catalyzed by transition metals under oxidative conditions (cross-dehydrogenative coupling, CDC)^[1] constitutes a straightforward route to maximize atom economy in the construction of carbon–carbon bonds, since this method can avoid prefunctionalization of one cross-coupling partner to a (pseudo)halide and the other to an organometallic nucleophile.^[2] Functionalized dienes are important building blocks in organic synthesis.^[3] Vinylogous compounds are usually accessed through Wittig reactions from carbonyl compounds^[4] or transition metal-catalyzed cross-coupling such as Heck,^[5] and Suzuki^[6] reactions. Under transition metal catalysis, C–H olefination of directing group-bearing arenes^[7] and electron-rich heterocyclic compounds^[8] as well as some activated cyclic olefins^[9] has recently been well investigated, but direct cross-coupling between two open-chain olefins has been paid less attention due to the difficulty in direct activation of an olefinic C–H bond.^[10] In principle, transition metal-catalyzed CDC reactions of two different olefins can be utilized as a direct method to synthesize conjugate diene derivatives. In 2004, Ishii and co-workers reported oxidative cross-coupling of acrylates with vinyl carboxylates by a 20 mol% Pd(OAc)₂/HPMoV/O₂ system.^[10] Later, Loh and co-workers documented palladium-catalyzed oxidative C–H olefination of acrylates,^[11a–c] and vinyl ketones^[11d] with simple

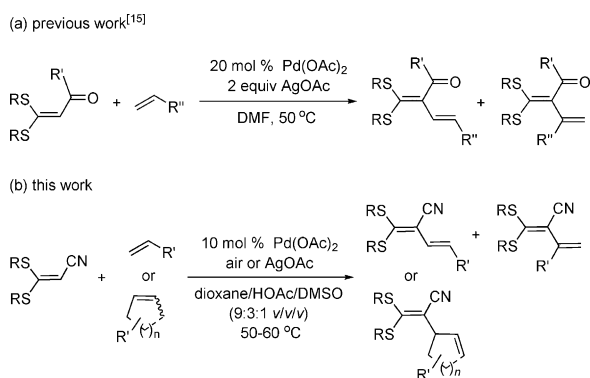
olefins, and ruthenium-catalyzed oxidative stereo- and chemo-selective cross-coupling between two electron-deficient acrylates.^[11e] Liu and co-workers realized palladium-catalyzed oxidative vinylic C–H olefination with allylic esters.^[12] To improve the olefination efficiency of vinylogous C–H bonds with olefins, the groups of Loh and Glorius both introduced a directing group to one of the olefin substrates to enable selective oxidative cross-coupling between two terminal olefins, achieving C–H olefination of enamides,^[13a, 14a] acrylamides,^[13b] and carbonyl-bearing olefins^[14b] with different olefin partners. However, in most of the above-mentioned cases, the oxidative cross-coupling occurred between two terminal olefins, suggesting that olefination of internal vinylogous C–H bonds is very challenging. In addition, cross-couplings between two olefins usually require high catalyst loadings, and stoichiometric copper- or silver-based oxidants, which offsets the benefits of using less functionalized substrates to access diene derivatives to some extent. In this area, greener and more efficient catalytic systems effective for C–H olefination of internal olefins are strongly desired.

To realize the direct C–H olefination of an internal olefin with an open-chain terminal olefin as the coupling partner, low reactivity of the internal olefinic C–H bond should be overcome. In 2010, we developed a strategy to activate an internal olefinic C–H bond by introducing a structural element, that is, 1,2-dithiane functionality, at the terminal position of an olefin, and an electron-withdrawing carbonyl at the other end of the carbon–carbon double bond to polarize the olefin molecule.^[15] In this case, direct olefination of the internal olefins α -oxoketene dithioacetals^[16] with terminal olefins such as acrylates and styrenes was efficiently performed by using Pd(OAc)₂ (20 mol%) as the catalyst, and AgOAc (2 equiv) as the terminal oxidant under air atmosphere (Scheme 1 a). During our ongoing investigation of α -oxoketene dithioacetals, we became interested in the C–H activation of α -cyanoketene dithioacetals because a cyano group exhibits stronger electron-withdrawing

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Scheme 1. Olefination of α -EWG ketene dithioacetals with olefins.

ability and less steric hindrance than an acetyl or aroyl moiety, which can render the internal olefin molecule more polarized. In addition, cyano is a versatile coordinating moiety to transition metals^[17a,b] and may be transformed to different functionalities in organic synthesis.^[17c,d] Herein, we report the direct cross-coupling of α -cyanoketene dithioacetals with terminal olefins, generating 1,3- or 1,4-diene derivatives under mild conditions (Scheme 1 b).

Results and Discussion

Initially, the cross-coupling reaction of α -cyanoketene dithioacetal **1a** with *tert*-butyl acrylate (**2a**) was explored to screen the reaction conditions (Table 1). Under the same conditions

employed in our previous work (Scheme 1a),^[15] the reaction was carried out over a period of 5 h to afford the corresponding CDC product, that is, 1,3-diene **3a**, isolated in 74% yield, and the homocoupling product **4** (14%) obtained as a byproduct (Table 1, entry 1). Lowering the catalyst loading to 10 mol% slowed down the reaction and a satisfactory yield was only reached over a period of 30 h (Table 1, entry 2). Dioxane, HOAc, DMSO, or a mixture of dioxane and HOAc (3:1 v/v) as the solvent diminished the reaction efficiency (Table 1, entries 3–6), whereas an acidic mixture of dioxane, HOAc, and DMSO (9:3:1 v/v/v)^[8a] as the medium promoted the reaction to completion within 3 h, furnishing **3a** in 95% yield (isolated product) without occurrence of the homocoupling of **1a** (Table 1, entry 8; see the Supporting Information for details). Among the metal salt oxidants screened, both AgOAc and Ag₂CO₃ worked efficiently (Table 1, entries 8–11). To our delight, O₂ and air could effectively act as the sole oxidants for the desired reaction to generate **3a** (Table 1, entries 12–16), giving yields comparable to those obtained by using AgOAc as the terminal oxidant within 7 h. The ability of molecular dioxygen to effect the facile oxidation of Pd⁰ species in the catalytic cycle is ascribed to the presence of DMSO in the reaction medium, which acts as a ligand with both hard (*O*-) and soft (*S*-) donor atoms and facilitates the redox cycling between palladium(II) and palladium(0) in the reaction.^[18] Thus, the reaction conditions were optimized as those for Table 1, entry 15: Pd(OAc)₂ (10 mol%) as the catalyst, dioxane/HOAc/DMSO (9:3:1 v/v/v) as the solvent, air (balloon), *T* = 50 °C, and *t* = 7 h.

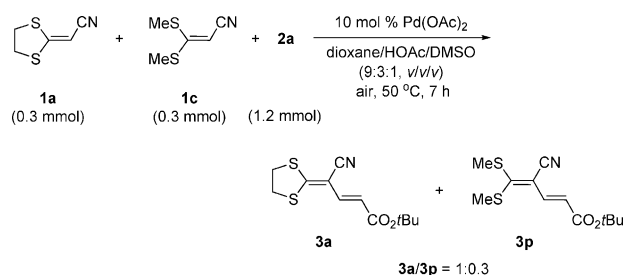
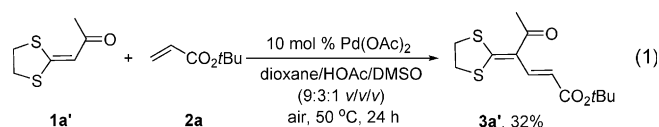
Under the optimal conditions, the scope of electron-deficient terminal olefins was explored (Table 2). The CDC reactions of **1a** with alkyl and phenyl acrylates proceeded efficiently to form the target products **3a–e** in 87–99% yields by varying the reaction time (7–18 h). However, *N,N*-dimethylacrylamide, acrylonitrile, α,β -unsaturated ketones (enones), and vinyl phenyl sulfone exhibited lower reactivity than the acrylate partners, reacting with **1a** to provide **3f–k** in 52–67% yields. Unexpectedly, the reaction of **1a** with cyclohex-2-enone gave both the target product **3j** (60%) and the conjugate addition product **3j'** (18%). Expanding the dithiane moiety to S(CH₂)₃S significantly lessened the reactivity of the corresponding α -cyanoketene dithioacetal **1b**, and its reactions with the acrylate and acrylamide partners only afforded **3l–o** in 52–65% yields. The acyclic α -cyanoketene dithioacetals **1c** (R = Me) and **1d** (R = Et) underwent reactions with *tert*-butyl acrylate (**2a**) to produce the target products **3p** and **3q** in poor yields (12–29%), demonstrating a remarkable steric/electronic effect from the dithiane functionality. The molecular structures of functionalized dienes **3** were further confirmed by X-ray crystallographic structural determination of **3e** (Figure 1 and the Supporting Information). In the solid state, the single crystal structure of **3e** adopts an (*E*)-configuration for the dienyl moiety, and NMR spectroscopy also reveals an (*E*)-CH=CH functionality in compounds **3**.

For comparison, α -oxoketene dithioacetal **1a'** was treated with **2a** under the same conditions to form the target product **3a'** (32% GC yield), demonstrating an obvious electronic effect from the α -electron-withdrawing group in the ketene dithioacetal substrate [Eq. (1)].

Table 1. Screening of conditions for the reaction of α -cyanoketene dithioacetal **1a** with *tert*-butyl acrylate **2a**.^[a]

Entry	Oxidant	Solvent	<i>T</i> [h]	Conversion ^[b] of 1a [%]
1 ^[c]	AgOAc	DMF	5	98 (74) ^[d]
2 ^[e]	AgOAc	DMF	30	95 (71)
3	AgOAc	dioxane	3	6
4	AgOAc	HOAc	3	39
5	AgOAc	DMSO	3	98 (59) ^[f]
6	AgOAc	dioxane/HOAc (3:1 v/v)	3	48
7	AgOAc	HOAc/DMSO (3:1 v/v)	3	97
8	AgOAc	dioxane/HOAc/DMSO ^[g]	3	98 (95)
9	Cu(OAc) ₂	dioxane/HOAc/DMSO ^[g]	3	83
10	Ag ₂ CO ₃	dioxane/HOAc/DMSO ^[g]	3	98
11	K ₂ S ₂ O ₈	dioxane/HOAc/DMSO ^[g]	3	51
12	O ₂ ^[h]	dioxane/HOAc/DMSO ^[g]	3	86
13	O ₂ ^[h]	dioxane/HOAc/DMSO ^[g]	7	98 (94)
14	air ^[i]	dioxane/HOAc/DMSO ^[g]	3	86
15	air ^[i]	dioxane/HOAc/DMSO ^[g]	7	98 (94)
16 ^[j]	air ^[i]	dioxane/HOAc/DMSO ^[g]	7	57

[a] Conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), Pd(OAc)₂ (10 mol%), oxidant (0.75 mmol), solvent (2 mL), 50 °C, air; [b] determined by GC analysis; yields of isolated product given in parentheses; [c] Pd(OAc)₂ (20 mol%), AgOAc (2 equiv), 50 °C; [d] **4** was also isolated in 14% yield; [e] Pd(OAc)₂ (10 mol%), AgOAc (2 equiv), 50 °C; [f] **4** was also isolated in 39% yield; [g] dioxane/HOAc/DMSO (9:3:1 v/v/v); [h] O₂ balloon; [i] air balloon; [j] 5 mol% Pd(OAc)₂ was used.



Scheme 2. Competition reactions.

Table 3. Direct olefination of α -cyanoketene dithioacetal **1a** with styrenes **5**.^[a]

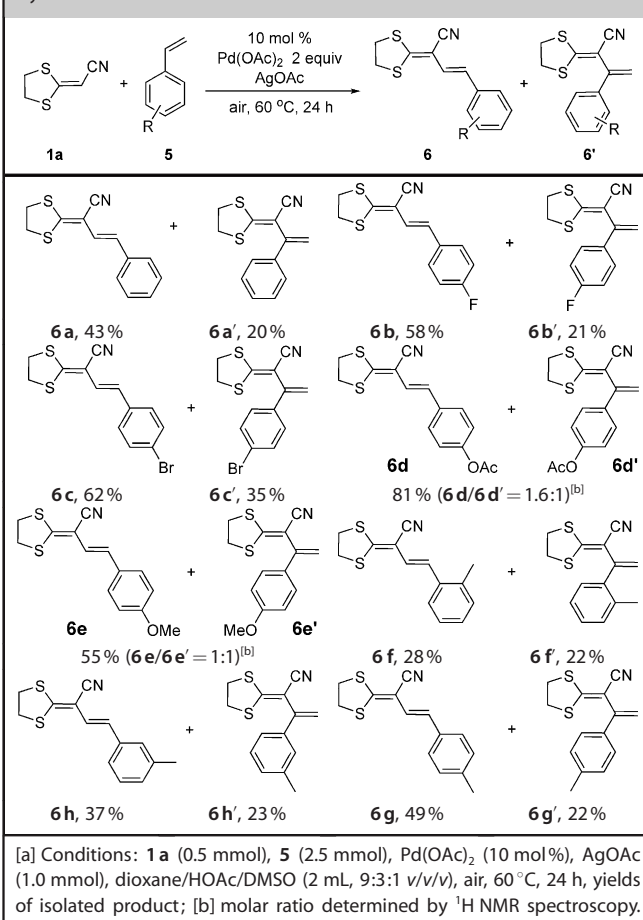


Table 2. Substrate scope for the reaction of **1** with **2**.^[a]

[a] Conditions: **1** (0.5 mmol), **2** (1.0 mmol), Pd(OAc)₂ (10 mol%), dioxane/HOAc/DMSO (2 mL, 9:3:1 v/v/v), air, 50 °C, yields of isolated product.

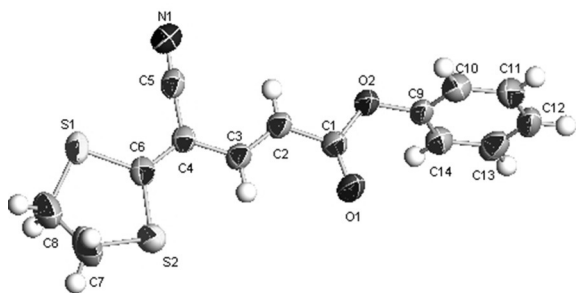


Figure 1. Molecular structure of **3e** with thermal ellipsoids set at 50% level of probability.

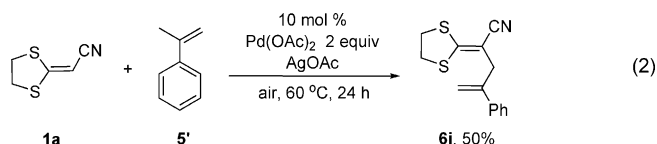
To elucidate the steric/electronic effect from the thioalkyl moiety in **1**, the competition reactions between **1a** and **1c** with **2a** were conducted under the optimal conditions for the synthesis of **3a** (Scheme 2). ¹H NMR spectroscopy indicated the formation of a 1:0.3 molar ratio mixture of **3a** and **3p**. This result suggests that a rigid backbone benefits the internal C–H activation of **1a**.

Next, styrenes were investigated as coupling partners for **1a** (Table 3). Under the conditions given in Table 2, these reactions were rather sluggish, and 2 equivalents of AgOAc as the termi-

nal oxidant, 5 equivalents of styrenes, and a higher temperature (60 °C) were required to drive the reactions to completion. The cross-coupling reactions of **1a** with unactivated styrene, 4-fluoro- and 4-bromostyrenes afforded two separable 1,3-diene products, that is, (*E*)-**6a–c** (43–62%) and their terminal isomers **6a'–c'** (20–35%). In the cases where 4-acetoxy- or 4-methoxystyrenes were used as coupling partners, inseparable pairs of 1,3-diene isomers, that is, **6d/6d'** (81%, 1.6:1), and **6e/6e'** (55%, 1:1), respectively, were obtained. The steric and electronic effects of the substituent on the aryl backbone of the styrene substrates had various impact on the reaction efficiency. *Ortho*-methyl obviously lessened the styrene reactivity to give

6f (28%) and **6f'** (22%), whereas *meta*- and *para*-methyl groups did not show this negative impact. Besides the steric hindrance from *ortho*-methyl, the electronic effect may also play a role, because a *para*-methyl group is more electron-donating than an *ortho*-methyl group, by comparing the standard Hammett constants for a methyl group at the *para* and *ortho* positions of an aryl moiety (respectively equal to -0.17 and -0.12),^[19a,b] so *para*-methyl should facilitate the electrophilic attack of a Pd^{II} species upon the olefinic carbon-carbon double bond of styrene to a greater degree than *ortho*-methyl.^[19c] In comparison to the cross-coupling of styrenes with α -oxoketene dithioacetals in our previous report,^[15] in which the molar ratio of the (*E*) to terminal olefins was about 4:1–7:1, the present system exhibited a much lower regioselectivity.

Unexpectedly, the reaction of **1a** with α -methylstyrene **5'** led to the allylation product **6i** [50%; Eq. (2)], which is presumably attributed to β -H elimination of the in situ-generated organopalladium intermediate selectively occurring on the less bulky methyl group.^[20] It should be noted that addition of ligands (20 mol%) such as 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine, 1,10-phenanthroline, PPh₃, PCy₃, 1,2-bis(diphenylphosphino)ethane (dppe), or 1,3-bis(diphenylphosphino)propane (dppp) to the catalyst system did not improve the reaction efficiency (see the Supporting Information for details).



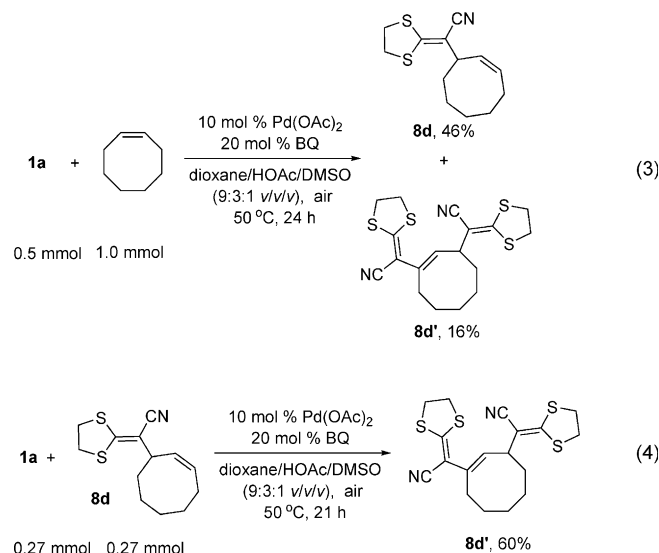
Next, cross coupling reactions of **1a** with unactivated cyclic olefins and open-chain linear internal olefins, *trans*- and *cis*-4-octenes, were performed under air atmosphere (Table 4). In a fashion similar to the synthesis of the allylation product **6i** from the reaction of **1a** with α -methylstyrene **5'** [Eq. (2)], the *pseudo*-allylation products, that is, skipped 1,4-dienes **8a** (61%), **8b** (57%), **8c** (60%), and **8d** (43%), were obtained from cyclopentene, cyclohexene, cycloheptene, and cyclooctene, respectively. Both *trans*- and *cis*-4-octenes exhibited lower reactivities to form the target products **8e** (34–37%), revealing isomerization of the internal C=C bond during the reaction. To enhance the reaction efficiency, variation of the reaction conditions by elevating the reaction temperature, increasing the loading of the cyclic or linear olefins, and/or using 2 equivalents of AgOAc as the terminal oxidant, had no positive impact. To our surprise, 20 mol% of benzoquinone (BQ)^[21] was found to remarkably improve the reaction efficiency for cyclopentene, cyclohexene, and *trans*- and *cis*-4-octenes, rendering the formation of **8a** (72%), **8b** (73%), and **8e** (80–84%) in much higher yields. α -Cyanoketene dithioacetals **1b–d** also underwent the same type of reactions to afford the target products **8f–i** in much lower yields (34–59%). These results suggest that BQ may efficiently promote oxidation of the palladium(0) species to the palladium(II) catalyst in the catalytic cycle under the acidic reaction conditions. It is noteworthy that **1a** reacted with cyclooctene in the presence of 20 mol% of BQ to give **8d** in 46% yield with **8d'** (16%) formed as the

Table 4. Reactions of α -cyanoketene dithioacetals **1** with unactivated olefins **7**.^[a]

8a	8b	8c	8d
61% (72%) ^[b]	57% (73%) ^[b]	60% (61%) ^[b]	43% (46%) ^[b]
8e	8e	8f	8g
37% (84%) ^[b]	34% (80%) ^[b]	(59%) ^[b]	(49%) ^[c]
from <i>trans</i> -4-octene	from <i>cis</i> -4-octene		
8h , (34%) ^[c]			8i , (38%) ^[c,d]

[a] Conditions: **1** (0.5 mmol), **7** (1.0 mmol), Pd(OAc)₂ (10 mol%), dioxane/HOAc/DMSO (2 mL, 9:3:1 v/v/v), air, 50 °C, 24 h, yields of isolated product based on **1**; [b] BQ (20 mol%); [c] BQ (2 equiv); [d] cyclopentene (1.5 mmol), 60 °C. BQ = *p*-benzoquinone.

minor product [Eq. (3)]. Under the same conditions, **8d** was treated with **1a** in 1:1 molar ratio to produce **8d'** in 60% yield [isolated product; Eq. (4)]. Compound **8d'** was structurally characterized by the X-ray crystallographic single crystal analysis (Figure 2 and the Supporting Information).



A plausible mechanism is proposed for the formation of 1,3-dienes **3**, **6**, and **6'** in Scheme 3. The reaction is initiated by the electrophilic attack of Pd(OAc)₂ at the internal olefinic C–H bond of α -cyanoketene dithioacetal **1**, releasing HOAc and

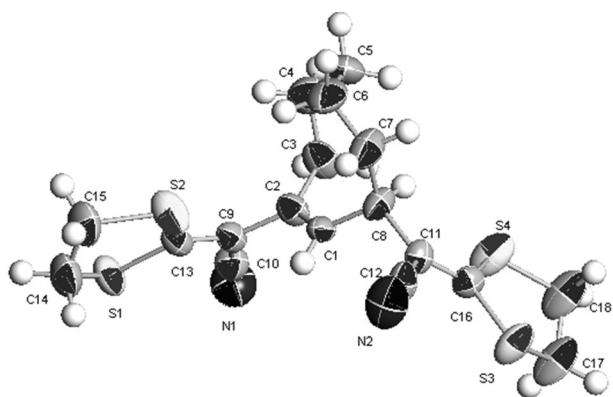
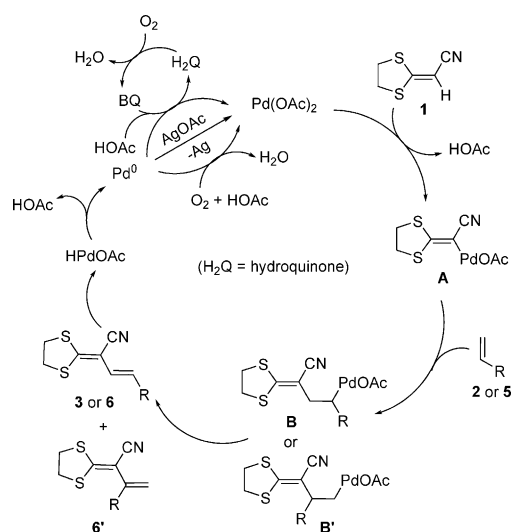
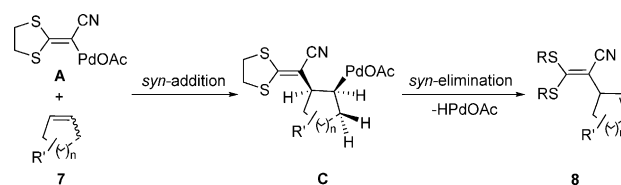


Figure 2. Molecular structure of **8d'** with thermal ellipsoids set at 50% level of probability.



Scheme 3. Proposed mechanism.

forming organopalladium species **A**. Subsequent insertion of the olefinic C=C bond to **A** yields intermediates **B/B'** from which 1,3-dienes **3**, **6**, and **6'** can be produced by β -H elimination. In the case of using acrylates as the coupling partners, regioselectively formed intermediate **B** undergoes reductive elimination to afford the target product of type **3**. When a styrene is used as the substrate, insertion of its olefinic C=C bond to the Pd–C bond of species **A** is not very regioselective,^[19c,22] leading to two kinds of 1,3-diene isomers, that is, **6** and **6'**. The in situ-generated HPdOAc species is further reduced to a Pd⁰ species, which is then oxidized with air and/or AgOAc and BQ to regenerate the Pd^{II} catalyst under the stated conditions, finishing the catalytic cycle. In the case of using an unactivated cyclic or linear internal olefin, the C=C bond is inserted at the Pd–C bond of species **A** to form intermediate **C** through *syn* addition, from which *syn* elimination occurs to yield skipped diene **8** (Scheme 4).^[23] Palladium-catalyzed direct cross-coupling reactions between indenes and electron-deficient olefins gave the desired 1,3-diene products in the presence of Pd(OAc)₂ (10 mol%), Cu(OAc)₂ (1 equiv), and O₂ (1 atm), in HOAc at 60 °C.^[24]



Scheme 4. Formation of the skipped diene products.

Conclusions

In summary, palladium-catalyzed direct olefination of the internal olefins α -cyanoketene dithioacetals with various activated and unactivated olefins was successfully developed through C–H bond activation with air or AgOAc as the terminal oxidant under mild conditions. The present protocol has demonstrated rare examples of internal olefinic C–H functionalization and provides a concise route to access highly functionalized 1,3-dienes and skipped 1,4-dienes under transition metal catalysis.

Experimental Section

General considerations

¹H and ¹³C NMR spectra were recorded on a Bruker DRX-400 spectrometer and all chemical shift values refer to $\delta_{\text{TMS}} = 0.00$ ppm or CDCl₃ (δ (¹H), 7.26 ppm; δ (¹³C), 77.16 ppm) or [D₆]DMSO (δ (¹H), 2.50 ppm; δ (¹³C), 39.52 ppm). The HRMS (ESI) analysis was achieved on a Waters GC-TOF CA156 mass spectrometer. All the melting points were uncorrected. Analytical TLC plates, Sigma-Aldrich silica gel 60F₂₀₀ were viewed by UV light (254 nm). Chromatographic purifications were performed on SDZF silica gel 160. All chemical reagents were purchased from commercial sources and used as received unless otherwise indicated.

General procedure for the olefination of α -cyanoketene dithioacetals **1** with olefins **2**

Under air atmosphere, a mixture of **1** (0.5 mmol), **2** (1.0 mmol), Pd(OAc)₂ (10 mol%), and dioxane/HOAc/DMSO (2 mL, 9:3:1 v/v/v) was stirred at 50 °C and monitored by TLC analysis on silica gel. When the starting material **1** had been completely consumed, water (20 mL) was added. The solution was filtered, and the filter cake was washed with EtOAc (3 \times 10 mL). The organic phases were separated and combined, dried over anhydrous MgSO₄, and filtered. All volatiles were removed by evaporation under reduced pressure. The resulting residue was purified by column chromatography on silica gel with petroleum ether (60–90 °C)/EtOAc (3:1 v/v) as the eluent.

(E)-tert-Butyl 4-cyano-4-(1,3-dithiolan-2-ylidene)but-2-enoate (3a): 127 mg, 94% yield, yellow solid; m.p. 123–125 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.22$ and 5.94 (d each, $J = 15.1$ Hz, 1:1H, CH=CH), 3.61 (s, 4H, 2 \times CH₂S), 1.46 ppm (s, 9H, *t*Bu); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): $\delta = 170.2$ (Cq, S–C=C), 165.8 (Cq, O=C–O), 136.9 and 119.7 (CH=CH), 115.7 (Cq, CN), 96.0 (Cq, S–C=C), 80.8 (Cq, O–C(CH₃)₃), 39.7 and 38.8 (SCH₂CH₂S), 28.1 ppm (C(CH₃)₃); HRMS (ESI) calcd for C₁₂H₁₅NO₂S₂ [M]⁺: 269.0544; found: 269.0553.

2,3-Di(1,3-dithiolan-2-ylidene)succinonitrile (4): 10 mg, 14% yield; yellow crystalline solid; m.p. 238–240 °C; ¹H NMR (400 MHz, [D₆]DMSO, 25 °C, TMS): $\delta = 3.75$ ppm (s); ¹³C NMR (100 MHz,

[D₆]DMSO, 25 °C, TMS): δ = 172.9 (Cq, S=C), 116.4 (Cq, CN), 88.0 (Cq, S=C), 40.9 ppm (SCH₂CH₂S); HRMS (ESI) calcd for C₁₀H₈N₂S₄ [M]⁺: 283.9570; found: 283.9568.

(E)-Butyl 4-cyano-4-(1,3-dithiolan-2-ylidene)but-2-enoate (3b): 133 mg, 99% yield; yellow solid; m.p. 123–125 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.31 and 6.01 (d each, J = 15.1 Hz, 1:1 H, CH=CH), 4.13 (t, J = 6.7 Hz, 2H, OCH₂), 3.63 (m, 4H, 2×CH₂S), 1.62 and 1.37 (m each, 2:2H, CH₂CH₂CH₃), 0.91 ppm (t, J = 7.4 Hz, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 171.0 (Cq, S=C), 166.6 (Cq, O=C-O), 137.8 and 117.8 (CH=CH), 115.6 (Cq, CN), 95.9 (Cq, S=C), 64.5 (OCH₂), 39.7 and 38.8 (SCH₂CH₂S), 30.7 and 19.2 (CH₂CH₂CH₃), 13.7 ppm (CH₃); HRMS (ESI) calcd for C₁₂H₁₃NO₂S₂ [M]⁺: 269.0544; found: 269.0550.

(E)-Ethyl 4-cyano-4-(1,3-dithiolan-2-ylidene)but-2-enoate (3c): 105 mg, 87% yield; yellow solid; m.p. 87–89 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.31 and 6.00 (d each, J = 15.1 Hz, 1:1 H, CH=CH), 4.18 (q, 2H, OCH₂CH₃), 3.63 (m, 4H, 2×CH₂S), 1.27 ppm (t, J = 7.1 Hz, 3H, OCH₂CH₃); ¹³C (100 MHz, CDCl₃, 25 °C, TMS): δ = 171.0 (Cq, S=C), 166.5 (Cq, O=C-O), 137.8 and 117.8 (CH=CH), 115.6 (Cq, CN), 95.9 (Cq, S=C), 60.6 (OCH₂), 39.7 and 38.8 (SCH₂CH₂S), 14.3 ppm (CH₂CH₃); HRMS (ESI) calcd for C₁₀H₁₁NO₂S₂ [M]⁺: 241.0231; found: 241.0239.

(E)-Benzyl 4-cyano-4-(1,3-dithiolan-2-ylidene)but-2-enoate (3d): 146 mg, 96% yield; yellow solid; m.p. 133–134 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.40–7.30 (m, 6H, C₆H₅ and CH), 6.09 (d, J = 15.1 Hz, 1H, CH), 5.20 (s, 2H, CH₂Ph), 3.59 ppm (s, 4H, 2×CH₂S); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 171.7 (Cq, S=C), 166.3 (Cq, O=C-O), 138.4 and 117.2 (CH=CH), 136.0 (Cq, C₆H₅), 128.6, 128.3, and 128.2 (C₆H₅), 115.6 (Cq, CN), 95.9 (Cq, S=C), 66.4 (CH₂Ph), 39.8 and 38.9 ppm (SCH₂CH₂S); HRMS (ESI) calcd for C₁₅H₁₃NO₂S₂ [M]⁺: 303.0388; found: 303.0395.

(E)-Phenyl 4-cyano-4-(1,3-dithiolan-2-ylidene)but-2-enoate (3e): 137 mg, 95% yield; yellow solid; m.p. 143–145 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.53 and 6.24 (d each, J = 15.1 Hz, 1:1 H, CH=CH), 7.40 (t, J = 7.8 Hz), 7.24 (t, J = 7.4 Hz), and 7.14 (d, J = 7.7 Hz) (2:1:2H, Ph), 3.64 ppm (s, 4H, 2×CH₂S); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 172.7 (Cq, S=C), 165.0 (Cq, O=C-O), 150.8 (Cq, C₆H₅), 139.6 and 125.9 (CH=CH), 129.5, 121.6, and 116.5 (aromatic CH), 115.6 (Cq, CN), 95.9 (Cq, S=C), 39.8 and 38.9 ppm (SCH₂CH₂S); HRMS (ESI) calcd for C₁₄H₁₁NO₂S₂: 289.0231; found: 289.0242.

(E)-4-Cyano-4-(1,3-dithiolan-2-ylidene)-N,N-dimethylbut-2-enamide (3f): 80 mg, 67% yield; yellow solid; m.p. 190–192 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.30 and 6.43 (dd each, J = 14.6, 1.4 Hz, 1:1 H, CH=CH), 3.59 (s, 4H, 2×CH₂S), 3.07 and 2.98 ppm (s each, 3:3H, 2×NCH₃); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 169.1 (Cq, S=C), 165.8 (Cq, O=C-O), 136.0 and 117.1 (CH=CH), 116.2 (Cq, CN), 96.4 (Cq, S=C), 39.6 and 38.7 (SCH₂CH₂S), 37.4 and 35.9 ppm (NCH₃); HRMS (ESI) calcd for C₁₀H₁₂N₂OS₂ [M]⁺: 240.0391; found: 240.0394.

(E)-4-(1,3-Dithiolan-2-ylidene)pent-2-enedinitrile (3g): 53 mg, 55% yield; yellow solid; m.p. 194–196 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.06 and 5.48 (d each, J = 15.7 Hz, 1:1 H, CH=CH), 3.68 (m, 4H, 2×CH₂S); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS) δ = 172.8 (Cq, S=C), 142.9 and 95.0 (CH=CH), 117.8 and 114.7 (Cq, CN), 95.5 (Cq, S=C), 39.9 and 39.0 ppm (SCH₂CH₂S); HRMS (ESI) calcd for C₈H₆N₂S₂ [M]⁺: 193.9972; found: 193.9979.

(E)-2-(1,3-Dithiolan-2-ylidene)-5-oxohept-3-enenitrile (3h): 59 mg, 52% yield; yellow solid; m.p. 123–125 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.26 and 6.38 (d each, J = 15.0 Hz, 1:1 H, CH=CH), 3.65 (s, 4H, 2×CH₂S), 2.58 (q, J = 7.3 Hz, 2H, CH₂CH₃), 1.12 ppm (t, J = 7.3 Hz, 3H, CH₂CH₃); ¹³C NMR (100 MHz,

CDCl₃, 25 °C, TMS): δ = 199.8 (Cq, C=O), 171.3 (Cq, S=C), 135.1 and 124.5 (CH=CH), 115.6 (Cq, CN), 96.5 (S=C), 39.6 and 38.8 (SCH₂CH₂S), 35.7 (CH₂CH₃), 8.1 ppm (CH₂CH₃); HRMS (ESI) calcd for C₁₀H₁₁NO₂S₂ [M]⁺: 225.0282; found: 225.0292.

(E)-2-(1,3-Dithiolan-2-ylidene)-5-oxo-phenylpent-3-enenitrile (3i): 82 mg, 60% yield; yellow solid; m.p. 158–160 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.98 (d, J = 8.0 Hz, 2H, aromatic CH), 7.58–7.52 (m, 2H, aromatic CH and CH), 7.47 (t, J = 7.6 Hz, 2H, aromatic CH), 7.15 (d, J = 14.7 Hz, 1H, CH), 3.65 ppm (s, 4H, 2×CH₂S); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 189.1 (Cq, C=O), 172.8 (Cq, S=C), 137.8 and 120.8 (CH=CH), 133.1, 128.7, and 128.4 (aromatic CH, Ph), 115.9 (Cq, CN), 96.8 (Cq, S=C), 39.8 and 38.9 ppm (SCH₂CH₂S); HRMS (ESI) calcd for C₁₄H₁₁NO₂S₂ [M]⁺: 273.0282; found: 273.0285.

2-(1,3-Dithiolan-2-ylidene)-2-(3-oxocyclohexyl-1-enyl)acetonitrile (3j): 71 mg, 60% yield; yellow solid; m.p. 126–128 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 6.27 (s, 1H, CH=C), 3.66 and 3.57 (m each, 4H, 2×CH₂S), 2.65 (t, J = 5.6 Hz), 2.42 (t, J = 6.2 Hz), and 2.07 ppm (m) (2:2:2H, CH₂CH₂CH₂); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 198.6 (Cq, C=O), 169.0 (Cq, S=C), 153.6 (Cq, C=CH), 126.7 (C=CH), 117.1 (Cq, CN), 98.2 (S=C), 37.4 and 37.0 (SCH₂CH₂S), 40.9, 29.1, and 22.4 ppm (CH₂ each); HRMS (ESI) calcd for C₁₁H₁₁NO₂S₂ [M]⁺: 237.0282; found: 237.0291.

(E)-2-(1,3-Dithiolan-2-ylidene)-4-(phenylsulfonyl)but-3-enenitrile (3k): 93 mg, 60% yield; yellow solid; m.p. 151–153 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.88 (d, J = 7.5 Hz), 7.62 (t, J = 7.4 Hz), and 7.54 (t, J = 7.8 Hz) (2:1:2H, Ph), 7.35 and 6.46 (d each, J = 14.6 Hz, 1:1 H, CH=CH), 3.70–3.65 ppm (m, 4H, 2×CH₂S); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 174.4 (Cq, S=C), 140.6 (Cq, Ph), 135.6 and 126.3 (CH=CH), 133.5, 129.4, and 127.6 (aromatic CH, Ph), 115.2 (Cq, CN), 93.9 (Cq, S=C), 40.0 and 39.0 ppm (SCH₂CH₂S); HRMS (ESI) calcd for C₁₃H₁₁NO₂S₃ [M]⁺: 308.9952; found: 308.9954.

(E)-tert-Butyl 4-cyano-4-(1,3-dithian-2-ylidene)but-2-enoate (3l): 92 mg, 65% yield; yellow solid; m.p. 108–110 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.54 and 6.04 (d each, J = 15.3 Hz, 1:1 H, CH=CH), 3.09 and 3.04 (t each, J = 6.9 Hz, 2:2H, SCH₂CH₂CH₂S), 2.26 (p, J = 6.9 Hz, 2H, SCH₂CH₂CH₂S), 1.45 ppm (s, 9H, tBu); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 166.1 (Cq, S=C), 165.9 (Cq, O=C-O), 134.4 and 121.0 (CH=CH), 114.9 (Cq, CN), 104.3 (Cq, S=C), 80.7 (Cq, O-C(CH₃)₃), 29.45 and 29.39 (SCH₂CH₂CH₂S), 28.1 (C(CH₃)₃), 23.4 ppm (SCH₂CH₂CH₂S); HRMS (ESI) calcd for C₁₃H₁₇NO₂S₂ [M]⁺: 283.0701; found: 283.0707.

(E)-Butyl 4-cyano-4-(1,3-dithian-2-ylidene)but-2-enoate (3m): 74 mg, 52% yield; yellow solid; m.p. 107–109 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.62 and 6.09 (d each, J = 15.3 Hz, 1:1 H, CH=CH), 4.12 (t, J = 6.6 Hz, 2H, OCH₂CH₂CH₂CH₃), 3.10 and 3.05 (t each, J = 6.9 Hz, 2:2H, SCH₂CH₂CH₂S), 2.27 (p, J = 6.9 Hz, 2H, SCH₂CH₂CH₂S), 1.65–1.58 (m, 2H, OCH₂CH₂CH₂CH₃), 1.41–1.32 (m, 2H, OCH₂CH₂CH₂CH₃), 0.90 ppm (t, J = 7.4 Hz, 3H, OCH₂CH₂CH₂CH₃); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 167.3 (Cq, S=C), 166.8 (Cq, O=C-O), 135.3 and 118.8 (CH=CH), 114.8 (Cq, CN), 104.1 (Cq, S=C), 64.5 (OCH₂C₃H₇), 30.7 (OCH₂CH₂CH₂CH₃), 29.52 and 29.47 (SCH₂CH₂CH₂S), 23.4 (SCH₂CH₂CH₂S), 19.1 (OCH₂CH₂CH₂CH₃), 13.7 ppm (OCH₂CH₂CH₂CH₃); HRMS (ESI) calcd for C₁₃H₁₇NO₂S₂ [M-OBu]⁺ = 225.9996; found: 226.0004.

(E)-Benzyl 4-cyano-4-(1,3-dithian-2-ylidene)but-2-enoate (3n): 84 mg, 53% yield; yellow solid; m.p. 64–66 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.71 and 6.18 (d, J = 15.3 Hz, 1:1 H, CH=CH), 7.37–7.30 (m, 5H, C₆H₅), 5.20 (s, 2H, CH₂Ph), 3.09 and 3.03 (t each, J = 6.8 Hz, 2:2H, SCH₂CH₂CH₂S), 2.25 ppm (p, J = 6.8 Hz, 2H, SCH₂CH₂CH₂S); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 168.1 (Cq,

S=C=C), 166.5 (Cq, O=C-O), 136.01 (Cq, C₆H₅), 135.97 and 118.3 (CH=CH), 128.6, 128.3, and 128.2 (aromatic CH), 114.8 (Cq, CN), 104.0 (Cq, S=C=C), 66.4 (CH₂Ph), 29.6 and 29.5 (SCH₂CH₂CH₂S), 23.4 ppm (SCH₂CH₂CH₂S); HRMS (ESI) calcd for C₁₆H₁₅NO₂S₂, [M-OBn]⁺ = 210.0047; found: 210.0056.

(E)-4-Cyano-4-(1,3-dithian-2-ylidene)-N,N-dimethylbut-2-enamide (3 o): 74 mg, 58% yield; yellow solid; m.p. 163–165 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.58 and 6.50 (d each, J = 14.7 Hz, 1:1 H, CH=CH), 3.07–2.96 (m, 10H, 2×NCH₃ and SCH₂CH₂CH₂S), 2.22 ppm (p, J = 6.9 Hz, 2H, SCH₂CH₂CH₂S); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 166.0 (Cq, S=C=C), 165.2 (Cq, CON(CH₃)₂), 133.5, and 118.2 (CH=CH), 115.4 (Cq, CN), 104.6 (Cq, S=C=C), 37.4 and 35.9 (2×NCH₃), 29.4 and 29.3 (SCH₂CH₂CH₂S), 23.4 ppm (SCH₂CH₂CH₂S); HRMS (ESI) calcd for C₁₁H₁₄N₂O₂S₂ [M]⁺: 254.0548; found: 254.0553.

(E)-tert-Butyl 4-cyano-5,5-bis(methylthio)penta-2,4-dienoate (3 p): 39 mg, 29% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS) δ = 7.77 and 6.23 (d each, J = 15.5 Hz, 1:1 H, CH=CH), 2.60 and 2.50 (s each, 3:3 H, 2×CH₃), 1.50 (s, 9H, tBu); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS) δ = 165.7 (Cq, O=C-O), 164.5 (Cq, S=C=C), 136.1 and 123.9 (CH=CH), 115.2 (Cq, CN), 110.9 (Cq, S=C=C), 81.0 (Cq, O-C(CH₃)₃), 28.1 (C(CH₃)₃), 18.7 and 18.5 (SCH₃); HRMS (ESI) calcd for C₁₂H₁₇NO₂S₂ [M]⁺: 271.0701; found: 271.0707.

(E)-tert-Butyl 4-cyano-5,5-bis(ethylthio)penta-2,4-dienoate (3 q): 18 mg, 12% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.82 and 6.25 (d each, J = 15.5 Hz, 1:1 H, CH=CH), 3.07 and 2.99 (q each, J = 7.4 Hz, 2:2 H, 2×SCH₂CH₃), 1.50 (s, 3×3 H, tBu), 1.34 and 1.29 ppm (t each, J = 7.5 Hz, 3:3 H, 2×SCH₂CH₃); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 165.7 (Cq, O=C-O), 161.6 (Cq, S=C=C), 136.2 and 124.1 (CH=CH), 115.3 (Cq, CN), 113.5 (Cq, S=C=C), 81.0 (Cq, O-C(CH₃)₃), 30.4 and 30.3 (2×SCH₂CH₃), 28.1 (C(CH₃)₃), 15.0 and 14.8 ppm (2×SCH₂CH₃); HRMS (ESI) calcd for C₁₄H₂₁NO₂S₂: [M-OrBu]⁺ = 226.0360, Found: 226.0375.

General procedure for the olefination of α-cyanoketene dithioacetal 1a with styrenes 5

Under air atmosphere, a mixture of **1a** (0.5 mmol), **5** (2.5 mmol), Pd(OAc)₂ (10 mol%), AgOAc (1.0 mmol), and dioxane/HOAc/DMSO (2 mL, 9:3:1 v/v/v) was stirred at 60 °C for 24 h. Water (20 mL) was then added, the solution was filtered, and the filter cake was washed with EtOAc (3×10 mL). The organic phases were separated and combined, dried over anhydrous MgSO₄, filtered, and all volatiles were removed by evaporation under reduced pressure. The resultant residue was purified by column chromatography on silica gel with petroleum ether (60–90 °C)/CH₂Cl₂ (5:1 v/v) as the eluent.

(E)-2-(1,3-Dithiolan-2-ylidene)-4-phenylbut-3-enitrile (6a): 53 mg, 43% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.42 (d, J = 7.4 Hz), 7.34 (t, J = 7.5 Hz), and 7.26 (t, J = 7.5 Hz) (2:2:1 H, Ph), 6.78 and 6.69 (d each, J = 15.6 Hz, 1:1 H, CH=CH), 3.63–3.57 ppm (m, 4H, SCH₂CH₂S); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 159.9 (Cq, S=C=C), 136.4 (Cq, C₆H₅), 129.7 and 123.1 (CH=CH), 128.8, 128.1, and 126.6 (Ph), 116.6 (Cq, CN), 98.3 (Cq, S=C=C), 39.4 and 38.4 ppm (SCH₂CH₂S); HRMS (ESI) calcd for C₁₃H₁₁NS₂ [M]⁺: 245.0333; found: 245.0340.

2-(1,3-Dithiolan-2-ylidene)-3-phenylbut-3-enitrile (6a'): 25 mg, 20% yield; yellow solid; m.p. 89–91 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.38–7.34 (m, 5H, Ph), 5.64 and 5.51 (s each, 1:1 H, CH₂=C), 3.53 and 3.44 ppm (m each, 2:2 H, SCH₂CH₂S); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 164.7 (Cq, S=C=C), 143.8 (Cq, C=CH₂), 137.5 (Cq, C₆H₅), 128.6, 128.5, and 127.5 (Ph), 118.36 (CH₂=C), 118.38 (Cq, CN), 97.8 (S=C=C), 39.9 and 38.1 ppm (SCH₂CH₂S); HRMS (ESI) calcd for C₁₃H₁₁NS₂ [M]⁺: 245.0333; found: 245.0341.

(E)-2-(1,3-Dithiolan-2-ylidene)-4-(4-fluorophenyl)but-3-enitrile (6b): 76 mg, 58% yield; yellow solid; m.p. 147–149 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.38 (t, J = 6.2 Hz), and 7.02 (t, J = 8.1 Hz) (2:2 H, C₆H₄), 6.71 and 6.59 (d each, J = 15.6 Hz, 1:1 H, CH=CH), 3.59 ppm (s, 4H, SCH₂CH₂S); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 162.6 (d, J = 246.7 Hz, Cq, C-F), 160.2 (Cq, S=C=C), 132.6 (d, J = 3.3 Hz, Cq, p-C of C₆H₄F), 128.5 (CH=CH-Ar), 122.9 (d, J = 2.2 Hz, CH=CH-Ar), 128.2 (d, J = 8.0 Hz, CH, m-C of C₆H₄F), 115.8 (d, J = 21.6 Hz, CH, o-C of C₆H₄F), 116.5 (Cq, CN), 98.3 (Cq, S=C=C), 39.4 and 38.4 ppm (SCH₂CH₂S); HRMS (ESI) calcd for C₁₃H₁₀FNS₂ [M]⁺: 263.0239; found: 263.0239.

2-(1,3-Dithiolan-2-ylidene)-3-(4-fluorophenyl)but-3-enitrile (6b'): 28 mg, 21% yield; yellow solid; m.p. 57–59 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.34 (t, J = 6.3 Hz) and 7.04 (t, J = 8.3 Hz) (2:2 H, C₆H₄), 5.59 and 5.48 (s each, 1:1 H, C=CH₂), 3.53 and 3.45 ppm (m each, 2:2 H, SCH₂CH₂S); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 165.2 (Cq, S=C=C), 163.0 (d, J = 246.7 Hz, Cq, C-F), 142.8 (Cq, C=CH₂), 133.7 (d, J = 3.3 Hz, Cq, p-C of C₆H₄F), 129.3 (d, J = 8.2 Hz, CH, m-C of C₆H₄F), 115.5 (d, J = 21.6 Hz, CH, o-C of C₆H₄F), 118.3 (C=CH₂), 115.4 (Cq, CN), 97.5 (Cq, S=C=C), 39.9 and 38.2 ppm (SCH₂CH₂S); HRMS (ESI) calcd for C₁₃H₁₀FNS₂ [M]⁺: 263.0239; found: 263.0246.

(E)-2-(1,3-Dithiolan-2-ylidene)-4-(4-bromophenyl)but-3-enitrile (6c): 101 mg, 62% yield; yellow solid; m.p. 181–183 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.44 and 7.27 (d each, J = 8.5 Hz, 2:2 H, C₆H₄), 6.67 (s, 2H, CH=CH), 3.60 ppm (m, 4H, SCH₂CH₂S); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 160.8 (Cq, S=C=C), 135.3 and 121.8 (Cq, C₆H₄), 131.9 and 128.0 (C₆H₄), 128.3 and 123.7 (CH=CH), 116.4 (Cq, CN), 98.2 (Cq, S=C=C), 39.4 and 38.4 ppm (SCH₂CH₂S); HRMS (ESI) calcd for C₁₃H₁₀BrNS₂ [M]⁺: 322.9438; found: 322.9445.

2-(1,3-Dithiolan-2-ylidene)-3-(4-bromophenyl)but-3-enitrile (6c'): 57 mg, 35% yield; yellow solid; m.p. 95–97 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.48 and 7.23 (d each, J = 8.4 Hz, 2:2 H, C₆H₄), 5.63 and 5.51 (s each, 1:1 H, C=CH₂), 3.54 and 3.46 ppm (m each, 2:2 H, SCH₂CH₂S); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 165.3 (Cq, S=C=C), 142.8 (Cq, C=CH₂), 136.5 and 122.9 (Cq, C₆H₄), 131.7 and 129.1 (C₆H₄), 118.9 (C=CH₂), 118.2 (Cq, CN), 97.2 (Cq, S=C=C), 40.0 and 38.2 ppm (SCH₂CH₂S); HRMS (ESI) calcd for C₁₃H₁₀BrNS₂ [M]⁺: 322.9438; found: 322.9445.

(E)-4-(3-Cyano-3-(1,3-dithiolan-2-ylidene)prop-enyl)phenyl acetate (6d) and 4-(3-cyano-3-(1,3-dithiolan-2-ylidene)prop-1-en-2-yl)phenyl acetate (6d'): 6d/6d' = 1.6:1. 123 mg, 81% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): for **6d δ = 7.40 and 7.05 (d each, J = 8.6 Hz, 2:2 H, C₆H₄), 6.72 and 6.62 (d each, J = 15.6 Hz, 1:1 H, CH=CH), 3.58–3.55 (m, 4H, SCH₂CH₂S), 2.28 ppm (s, 3H, OCOCH₃); for **6d'** δ = 7.37 and 7.08 (d each, J = 8.7 Hz, 2:2 H, C₆H₄), 5.62 and 5.48 (s, C=CH₂), 3.51 and 3.43 (m, 4H, SCH₂CH₂S), 2.28 ppm (s, 3H, OCOCH₃); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): for **6d** δ = 169.3 (Cq, S=C=C), 160.4 (Cq, OCOCH₃), 150.4 and 134.2 (Cq each, C₆H₄), 128.6 and 123.3 (CH=CH), 127.5 and 121.9 (C₆H₄), 116.4 (Cq, CN), 98.3 (Cq, S=C=C), 39.4 and 38.4 (SCH₂CH₂S), 21.12 ppm (OCOCH₃); for **6d'** δ = 169.2 (Cq, S=C=C), 165.2 (Cq, OCOCH₃), 151.0 and 135.1 (Cq each, C₆H₄), 142.9 (Cq, C=CH₂), 118.6 (C=CH₂), 128.5 and 121.7 (C₆H₄), 118.3 (Cq, CN), 97.4 (Cq, S=C=C), 39.9 and 38.2 (SCH₂CH₂S), 21.14 ppm (OCOCH₃); HRMS (ESI) calcd for C₁₅H₁₃NO₂S₂ [M]⁺: 303.0388; found: 303.0385.**

(E)-2-(1,3-Dithiolan-2-ylidene)-4-(4-methoxyphenyl)but-3-enitrile (6e) and 2-(1,3-dithiolan-2-ylidene)-3-(4-bromophenyl)but-3-enitrile (6e'): 6e/6e' = 1:1. 76 mg, 55% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): for **6e δ = 7.35 (d, J = 8.5 Hz) and 6.87 (m) (2:2 H, C₆H₄), 6.70 and 6.54 (d each, J = 15.6 Hz, 1:1 H, CH=CH), 3.80 (s, 3H, OCH₃), 3.54 ppm (m, 4H, SCH₂CH₂S); for **6e'****

$\delta = 7.29$ (d, $J = 8.6$ Hz) and 6.87 (m) (2:2H, C₆H₄), 5.55 and 5.39 (s each, 1:1H, C=CH₂), 3.80 (s, 3H, OCH₃), 3.49 and 3.42 ppm (m each, 2:2H, 2 × CH₂S); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): for **6e** $\delta = 160.1$ (Cq, S=C=C), 159.7 and 129.1 (Cq, C₆H₄), 129.3 and 121.2 (CH=CH), 127.9 and 114.3 (C₆H₄), 116.7 (Cq, CN), 98.6 (Cq, S=C=C), 55.38 (OCH₃), 39.4 and 38.4 ppm (SCH₂CH₂S); for **6e'** $\delta = 164.7$ (Cq, S=C=C), 158.6 and 129.9 (Cq, C₆H₄), 143.3 (Cq, C=CH₂), 128.7 and 114.0 (C₆H₄), 116.7 (C=CH₂), 118.6 (Cq, CN), 97.9 (Cq, S=C=C), 55.36 (OCH₃), 39.9 and 38.1 ppm (SCH₂CH₂S); HRMS (ESI) calcd for C₁₄H₁₃NOS₂ [M]⁺: 275.0439; found: 275.0446.

(E)-2-(1,3-Dithiolan-2-ylidene)-4-o-tolylbut-3-enenitrile (6f): 36 mg, 28% yield; yellow solid; m.p. 98–100 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.46$ and 7.18 – 7.16 (m each, 1:3H, C₆H₄), 6.99 and 6.60 (d each, $J = 15.5$ Hz, 1:1H, CH=CH), 3.60 (m, 4H, SCH₂CH₂S), 2.39 ppm (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): $\delta = 159.8$ (Cq, S=C=C), 136.2, and 135.4 (Cq, C₆H₄), 130.6, and 128.0 (CH=CH), 127.7, 126.2, 125.3, and 124.3 (C₆H₄), 116.5 (Cq, CN), 98.9 (Cq, S=C=C), 39.3 and 38.3 (SCH₂CH₂S), 19.8 ppm (CH₃); HRMS (ESI) calcd for C₁₄H₁₃NS₂ [M]⁺: 259.0489; found: 259.0495.

2-(1,3-Dithiolan-2-ylidene)-3-o-tolylbut-3-enenitrile (6f'): 29 mg, 22% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.27$ and 7.20 – 7.14 (m each, 1:3H, C₆H₄), 5.71 and 5.23 (s each, 1:1H, C=CH₂), 3.40–3.33 (m, 4H, SCH₂CH₂S), 2.22 ppm (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): $\delta = 161.9$ (Cq, S=C=C), 143.4 (Cq, C=CH₂), 138.0 and 137.0 (Cq, C₆H₄), 130.4, 130.0, 128.6, and 125.9 (aromatic CH), 118.3 (C=CH₂), 118.2 (Cq, CN), 99.1 (Cq, S=C=C), 41.0 and 37.0 (SCH₂CH₂S), 19.8 ppm (CH₃); HRMS (ESI) calcd for C₁₄H₁₃NS₂ [M]⁺: 259.0489; found: 259.0494.

(E)-2-(1,3-Dithiolan-2-ylidene)-4-m-tolylbut-3-enenitrile (6g): 64 mg, 49% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.23$ and 7.08 (m each, 3:1H, C₆H₄), 6.71 (q, $J = 15.6$ Hz, 2H, CH=CH), 3.58 (m, 4H, SCH₂CH₂S), 2.36 ppm (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): $\delta = 160.1$ (Cq, S=C=C), 138.4 and 136.3 (Cq, C₆H₄), 129.8 and 123.8 (CH=CH), 129.0, 128.7, 127.4, and 123.0 (C₆H₄), 116.6 (Cq, CN), 98.5 (Cq, S=C=C), 39.4 and 38.4 (SCH₂CH₂S), 21.5 ppm (CH₃); HRMS (ESI) calcd for C₁₄H₁₃NS₂ [M]⁺: 259.0489; found: 259.0497.

2-(1,3-Dithiolan-2-ylidene)-3-m-tolylbut-3-enenitrile (6g'): 29 mg, 22% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.25$ and 7.17 (m each, 1:3H, C₆H₄), 5.63 and 5.48 (s each, 1:1H, C=CH₂), 3.52 and 3.44 (m each, 2:2H, SCH₂CH₂S), 2.37 ppm (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): $\delta = 164.6$ (Cq, S=C=C), 143.9 (Cq, C=CH₂), 138.2 and 137.5 (Cq, C₆H₄), 129.5, 128.4, 128.1, and 124.6 (C₆H₄), 118.5 (Cq, CN), 118.2 (C=CH₂), 97.9 (Cq, S=C=C), 39.9 and 38.1 (SCH₂CH₂S), 21.5 ppm (CH₃); HRMS (ESI) calcd for C₁₄H₁₃NS₂ [M]⁺: 259.0489; found: 259.0497.

(E)-2-(1,3-Dithiolan-2-ylidene)-4-p-tolylbut-3-enenitrile (6h): 48 mg, 37% yield; yellow solid; m.p. 117–119 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.32$ and 7.14 (d each, $J = 8.0$ Hz, 2:2H, C₆H₄), 6.75 and 6.64 (d each, $J = 15.6$ Hz, 1:1H, CH=CH), 3.62–3.56 (m, 4H, SCH₂CH₂S), 2.35 ppm (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): $\delta = 159.0$ (Cq, S=C=C), 138.1 and 133.6 (Cq, C₆H₄), 129.9 and 122.2 (CH=CH), 129.5 and 126.6 (aromatic CH), 116.5 (Cq, CN), 98.8 (Cq, S=C=C), 39.3 and 38.3 (SCH₂CH₂S), 21.3 ppm (CH₃); HRMS (ESI) calcd for C₁₄H₁₃NS₂ [M]⁺: 259.0489; found: 259.0500.

2-(1,3-Dithiolan-2-ylidene)-3-p-tolylbut-3-enenitrile (6h'): 30 mg, 23% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.26$ and 7.16 (d each, $J = 8.0$ Hz, 2:2H, C₆H₄), 5.61 and 5.45 (s each, 1:1H, C=CH₂), 3.52 and 3.44 (m each, 2:2H, SCH₂CH₂S), 2.36 ppm (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): $\delta = 164.3$ (Cq, S=C=C), 143.7 (Cq, C=CH₂), 138.6 and 134.6 (Cq, C₆H₄), 129.2 and

127.3 (C₆H₄), 118.4 (Cq, CN), 117.6 (C=CH₂), 98.1 (Cq, S=C=C), 39.9 and 38.0 (SCH₂CH₂S), 21.2 ppm (CH₃); HRMS (ESI) calcd for C₁₄H₁₃NS₂ [M]⁺: 259.0489; found: 259.0499.

2-(1,3-Dithiolan-2-ylidene)-4-phenylbut-3-enenitrile (6i): 65 mg, 50% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): $\delta = 7.42$ and 7.33 (m each, 2:3H, C₆H₅), 5.46, and 5.21 (s each, 1:1H, C=CH₂), 3.53 (s, 4H, SCH₂CH₂S), 3.45 ppm (s, 2H, CH₂); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): $\delta = 161.8$ (Cq, S=C=C), 142.8 (Cq, C=CH₂), 140.0 (Cq, C₆H₅), 128.4, 127.9, and 126.1 (C₆H₅), 118.7 (Cq, CN), 114.9 (C=CH₂), 94.9 (Cq, S=C=C), 40.1 and 38.5 (SCH₂CH₂S), 39.4 ppm (CH₂); HRMS (ESI) calcd for C₁₄H₁₃NS₂ [M]⁺: 259.0489; found: 259.0498.

General procedure for the reactions of α -cyanoketene dithioacetals **1** with unactivated olefins **7**

Under air atmosphere, a mixture of **1** (0.5 mmol), **7** (1.0 mmol), Pd(OAc)₂ (10 mol %), *p*-BQ (20 mol %), and dioxane/HOAc/DMSO (2 mL, 9:3:1 v/v/v) was stirred at 50 °C for 24 h. Water (20 mL) was then added. The solution was filtered and the filter cake was washed with EtOAc (3 × 10 mL). The organic phases were separated and combined, dried over anhydrous MgSO₄, filtered, and all volatiles were removed by evaporation under reduced pressure. The resultant residue was purified by column chromatography on silica gel with petroleum ether (60–90 °C)/EtOAc (10:1 v/v) as the eluent.

2-(Cyclopent-2-enyl)-2-(1,3-dithiolan-2-ylidene)acetoneitrile (8a): 75 mg, 72% yield; white solid; m.p. 83–85 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): $\delta = 5.91$ and 5.59 (m each, 1:1H, CH=CH), 3.57 (m, 1H), 3.50 (m, 4H, SCH₂CH₂S), 2.50 (m, 1H), 2.28 (m, 2H, CH₂), 1.79 ppm (m, 1H); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): $\delta = 158.9$ (Cq, S=C=C), 133.9 and 130.3 (CH=CH), 118.1 (Cq, CN), 101.4 (S=C=C), 50.6 (CH), 39.3 and 38.2 (SCH₂CH₂S), 32.2 and 29.3 ppm (CH₂); HRMS (ESI) calcd for C₁₀H₁₁NS₂ [M]⁺: 209.0333; found: 209.0340.

2-(Cyclohex-2-enyl)-2-(1,3-dithiolan-2-ylidene)acetoneitrile (8b): 82 mg, 73% yield; white solid; m.p. 76–78 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): $\delta = 5.87$ – 5.84 (m) and 5.51 (d, $J = 10.0$ Hz) (1:1H, CH=CH), 3.54–3.47 (m, 4H, 2 × CH₂S), 3.07 (m, 1H, CH), 2.01 (m, 2H, CH₂), 1.92–1.80 (m, 2H, CH₂), 1.65–1.54 ppm (m, 2H, CH₂); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): $\delta = 159.6$ (Cq, S=C=C), 130.3 and 126.6 (CH=CH), 118.3 (Cq, CN), 101.6 (S=C=C), 41.5 (CH), 39.3 and 38.2 (SCH₂CH₂S), 27.7, 24.5, and 21.2 ppm (CH₂); HRMS (ESI) calcd for C₁₁H₁₃NS₂ [M]⁺: 223.0489; found: 223.0496.

2-(Cyclohept-2-enyl)-2-(1,3-dithiolan-2-ylidene)acetoneitrile (8c): 72 mg, 61% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): $\delta = 5.87$ (m) and 5.61 (d, $J = 11.1$ Hz) (1:1H, CH=CH), 3.50 (m, 4H, SCH₂CH₂S), 3.19 (d, $J = 8.9$ Hz, 1H, CH), 2.24 (m, 1H), 2.11 (m, 1H), 2.00 (m, 1H), 1.68 (m, 4H), 1.38 ppm (m, 1H); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): $\delta = 158.7$ (Cq, S=C=C), 133.5 and 132.8 (CH=CH), 118.3 (Cq, CN), 102.7 (S=C=C), 45.9 (CH), 39.2 and 38.2 (SCH₂CH₂S), 32.9, 30.1, 28.7, and 26.6 ppm (CH₂ each); HRMS (ESI) calcd for C₁₂H₁₅NS₂ [M]⁺: 237.0646; found: 237.0653.

2-(Cyclooct-2-enyl)-2-(1,3-dithiolan-2-ylidene)acetoneitrile (8d): 58 mg, 46% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): $\delta = 5.78$ – 5.71 and 5.41 – 5.36 (m each, 1:1H, CH=CH), 3.49 (m, 4H, SCH₂CH₂S), 3.39 (m, 1H, CH), 2.14 (m, 2H, CH₂), 1.65 (m, 5H), 1.48 (m, 1H), 1.32 ppm (m, 2H); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): $\delta = 159.7$ (Cq, S=C=C), 130.9 and 129.1 (CH=CH), 118.0 (Cq, CN), 101.1 (S=C=C), 39.1 and 38.2 (SCH₂CH₂S), 41.5 (CH), 34.7, 29.5, 26.9, 26.7, and 25.2 ppm (CH₂ each); HRMS (ESI) calcd for C₁₃H₁₇NS₂ [M]⁺: 251.0802; found: 251.0806.

(E)-2,2'-(Cyclooctene-1,3-diyl)bis(2-(1,3-dithiolan-2-ylidene)acetoneitrile) (8d'): 16 mg, 16% yield; white solid; m.p. = 141–143 °C;

^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 5.67 (d, J = 9.0 Hz, 1H, C=CH), 3.55–3.49 (m, 8H, $2 \times \text{SCH}_2\text{CH}_2\text{S}$), 3.43–3.37 (m, 1H, allyl CH), 2.50–2.40 (m, 2H, CH_2), 1.84–1.74 (m, 4H, $2 \times \text{CH}_2$), 1.71–1.62 (m, 2H, CH_2), 1.52–1.39 ppm (m, 2H, CH_2); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C, TMS): δ = 162.0 and 160.7 (Cq each, $2 \times \text{S}-\text{C}=\text{C}$), 137.2 (Cq, C=CH), 130.8 (C=CH), 118.1 and 117.8 (Cq each, $2 \times \text{CN}$), 100.1 and 99.9 (Cq each, $2 \times \text{S}-\text{C}=\text{C}$), 42.9 (allyl CH), 39.3, 39.2, 38.3, and 37.8 ($2 \times \text{SCH}_2\text{CH}_2\text{S}$), 35.1, 30.3, 29.3, 26.6, and 25.4 ppm ($5 \times \text{CH}_2$); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{S}_4$ [M] $^+$: 392.0509; found: 392.0515.

2-(1,3-Dithiolan-2-ylidene)-3-propylhept-4-enenitrile (8e): 106 mg, 84% yield; yellow oil; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 5.56–5.49 (m), and 5.27 (dd, J = 15.2, 7.7 Hz) (1:1H, CH=CH), 3.47 (s, 4H, $\text{SCH}_2\text{CH}_2\text{S}$), 2.88 (q, J = 7.4 Hz, 1H), 2.00–1.97, 1.54–1.46, and 1.31–1.25 (m each, 2:2:2H, $3 \times \text{CH}_2$), 0.94 (t, J = 7.4 Hz, 3H, CH_3), 0.87 ppm (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C, TMS): δ = 159.3 (Cq, S=C), 133.6 and 127.9 (CH=CH), 117.8 (Cq, CN), 100.7 (S=C), 47.7 (CH), 39.1 and 38.1 ($\text{SCH}_2\text{CH}_2\text{S}$), 36.2, 25.5, and 20.3 (CH_2 each), 13.9, and 13.6 ppm (CH_3 each); HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{19}\text{NS}_2$ [M] $^+$: 253.0959; found: 253.0962.

2-(Cyclopent-2-enyl)-2-(1,3-dithian-2-ylidene)acetonitrile (8f): 66 mg, 59% yield; yellow oil; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 5.92 and 5.54 (m each, 1:1H, CH=CH), 3.88 (m, 1H, CH), 3.01 (m, 4H, $2 \times \text{SCH}_2$), 2.54–2.47 (m, 1H), 2.35–2.27 (m, 1H), 2.24–2.15 (m, 3H, $\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}$ and CH), 1.81–1.74 ppm (m, 1H); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C, TMS): δ = 153.0 (Cq, S=C), 134.0 and 130.2 (CH=CH), 117.0 (Cq, CN), 111.1 (Cq, S=C), 46.7 (CH), 32.3 and 29.3 (CH_2 each), 28.9 ($2 \times \text{SCH}_2$), 23.3 ppm ($\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}$); HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{13}\text{NS}_2$ [M] $^+$: 223.0489; found: 223.0500.

2-(1,3-Dithian-2-ylidene)-3-propylhept-4-enenitrile (8g): 66 mg, 49% yield; yellow oil; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 5.54 (dt, J = 15.3, 6.3 Hz, 1H, CH=CH), 5.30 (dd, J = 15.3, 7.8 Hz, 1H, CH=CH), 3.28 (q, J = 7.6 Hz, 1H, CH), 3.00 (m, 4H, $2 \times \text{SCH}_2$), 2.18 (p, J = 6.8 Hz, 2H, $\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}$), 2.01 (p, 2H, CH_2), 1.52 (m, 2H, CH_2), 1.28 (m, 2H, CH_2), 0.96 and 0.89 ppm (t each, J = 7.4 Hz, 3:3H, $2 \times \text{CH}_3$); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C, TMS): δ = 153.2 (Cq, S=C), 133.8 and 128.0 (CH=CH), 116.8 (Cq, CN), 110.8 (Cq, S=C), 43.5 (CH), 36.0, 25.5, and 20.3 (CH_2 each), 28.9 and 28.8 ($2 \times \text{SCH}_2$), 23.4 ($\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}$), 13.9 and 13.6 ppm ($2 \times \text{CH}_3$); HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{21}\text{NS}_2$ [M] $^+$: 267.1115; found: 267.1126.

2-(Cyclopent-2-enyl)-3,3-bis(methylthio)acrylonitrile (8h): 36 mg, 34% yield; yellow oil; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 5.96 and 5.55 (m, 1:1H, CH=CH), 4.16 (m, 1H, CH), 2.59–2.52 (m, 1H, CH_2), 2.43 (s, 6H, $2 \times \text{SCH}_3$), 2.39–2.30 (m, 1H, CH), 2.27–2.19 (m, 1H, CH), 1.86–1.77 ppm (m, 1H, CH); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C, TMS): δ = 153.0 (Cq, S=C), 134.4 and 130.1 (CH=CH), 121.1 (Cq, S=C), 117.0 (Cq, CN), 48.6 (CH), 32.3 and 29.6 ($2 \times \text{CH}_2$), 18.2 and 17.2 ppm ($2 \times \text{SCH}_3$); HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{13}\text{NS}_2$ [M] $^+$: 211.0489; found: 211.0495.

2-(Cyclopent-2-enyl)-3,3-bis(ethylthio)acrylonitrile (8i): 45 mg, 38% yield; yellow oil; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 5.97–5.94 and 5.56–5.53 (m each, 1:1H, CH=CH), 4.26–4.21 (m, 1H, CH), 2.94–2.85 (m, 4H, $2 \times \text{SCH}_2\text{CH}_3$), 2.59–2.52 (m, 1H, CH_2), 2.38–2.30 (m, 1H, CH_2), 2.27–2.19 (m, 1H, CH_2), 1.86–1.77 (m, 1H, CH_2), 1.28 and 1.25 ppm (t each, J = 6.1 Hz, 3:3H, $2 \times \text{SCH}_2\text{CH}_3$); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C, TMS): δ = 150.0 (Cq, S=C), 134.3 and 130.2 (CH=CH), 124.2 (Cq, S=C), 117.2 (Cq, CN), 48.6 (CH), 32.4 and 29.6 ($2 \times \text{CH}_2$), 29.3 and 28.6 ($2 \times \text{SCH}_2$), 15.3 and 14.6 ppm ($2 \times \text{SCH}_2\text{CH}_3$); HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{17}\text{NS}_2$ [M] $^+$: 239.0802; found: 239.0812.

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