Generation and Intermolecular Additions of Pyridylmethyl Radicals

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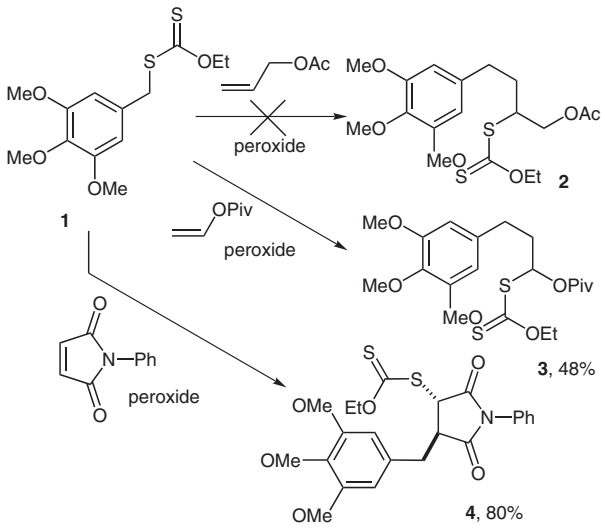
This paper is dedicated with respect to the memory of Professor Albert I. Meyers.

Abstract: 2-, 3-, or 4-Pyridylmethyl radicals can be made to add to nonactivated alkenes to give a variety of otherwise inaccessible pyridine derivatives. Bicyclic structures can be obtained by combining the radical addition with ionic ring-closure steps.

Key words: radical additions, heterocycles, pyridines, alkenes, cyclization

We have developed over the past few years a powerful radical process based on the chemistry of xanthates and related derivatives.[1] This technology provides one of the most general solutions to the problem of the intermolecular creation of C–C bonds starting with nonactivated alkenes. The success of this approach hinges on providing the intermediate radicals with a relatively long lifetime under concentrated conditions, thereby enabling bimolecular additions even to poorly reactive radical traps.[1]



Scheme 1

In contrast to various radicals we have so far examined, benzyl radicals proved too unreactive towards simple alkenes. For instance, reaction of *S*-3,4,5-trimethoxybenzyl xanthate **1** with allyl acetate did not lead to the expected adduct **2** in any significant yield under the usual conditions (Scheme 1).[2] Some activation of the alkene appeared necessary in this case. Thus, a moderate, but useful, yield of adduct **3** was observed with the more reactive vinyl pivalate, whereas addition to the strongly electrophilic *N*-methylmaleimide proceeded with high efficiency to give *trans*-addition product **4** in 80% yield.

We hoped, nevertheless, to expand the scope and utility of the xanthate transfer process by switching to the pyridine series. By increasing the electrophilic character of the radical, it appeared possible to enhance the rate of addition and overcome the kinetic barrier. If successful, a new route to valuable pyridine derivatives would become available. Pyridine motifs are ubiquitous in biologically active substances and in ligands for transition metals in organometallic chemistry.[3,4]

To test this approach, we prepared xanthate **5** by the reaction of potassium *O*-ethyl xanthate with commercially available 2-chloro-5-(chloromethyl)pyridine (Scheme 2). The inclusion of the chlorine group in position 2 serves two purposes. On the one hand, it sterically and electronically diminishes the nucleophilicity of the pyridine nitrogen and, thus, eliminates the formation of potential inhibitors by slow ionic decomposition of the xanthate group.[5] On the other, the presence of the chlorine at this particular position provides a very useful handle for further modifications through direct or transition-metal-catalyzed substitutions.[3,4]

In the event, we were gratified to find that addition of lauroyl peroxide (DLP) to a concentrated solution of **5** and allyl acetate in refluxing 1,2-dichloroethane led to the formation of the expected adduct **7** in 49% yield (or 61% based on recovered starting materials), through the addition of the intermediate radical **6**.

Addition to various other alkenes was accomplished in the same manner, as shown by the examples pictured in Scheme 2. In some of the reactions, 1,2-dichloroethane was replaced by methyl ethyl ketone or ethyl acetate. In fact, the process tolerates a broad variety of solvents. The desired transformation appeared to be fairly general, and the yields, albeit somewhat variable, were reasonable (yields in parentheses are based on recovered starting material throughout the article). The main side product was 1,2-bis(6-chloro-3-pyridyl)ethane, arising from the symmetrical coupling of two 6-chloro-3-pyridylmethyl radicals. Even though pyridylmethyl radicals proved more reactive than their benzyl counterpart, this reactivity remains comparatively modest. Their concentration thus builds up in the medium to a point where unwanted radical

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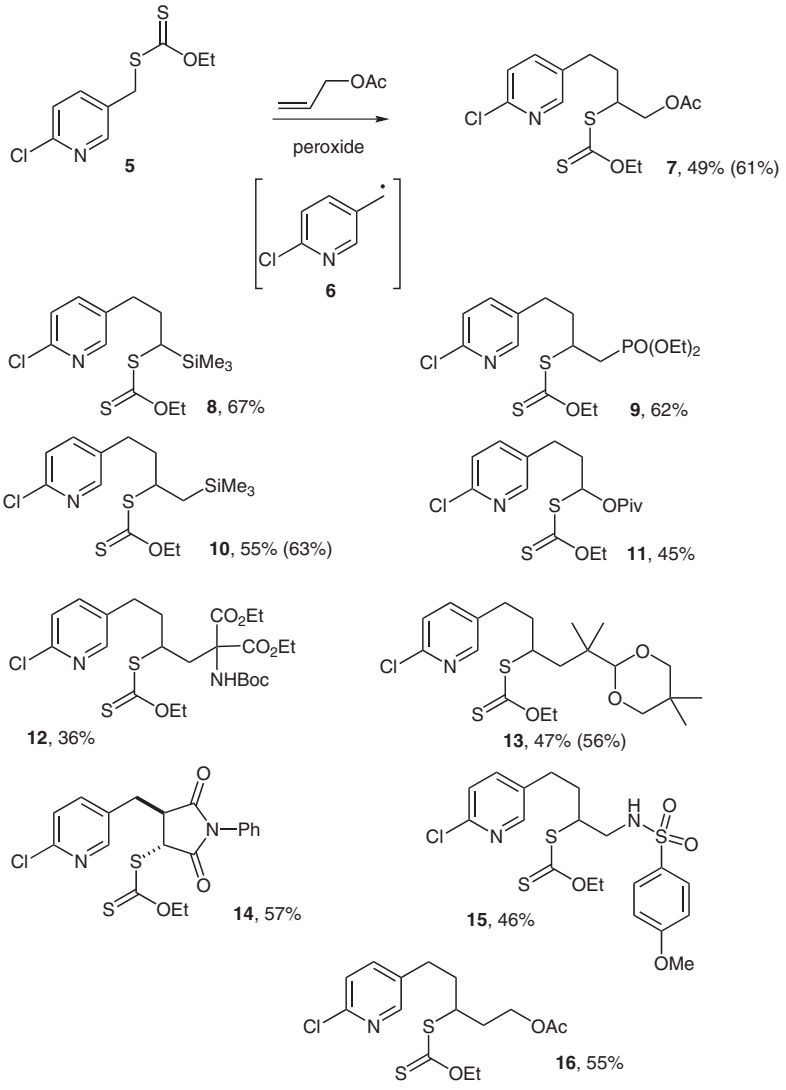
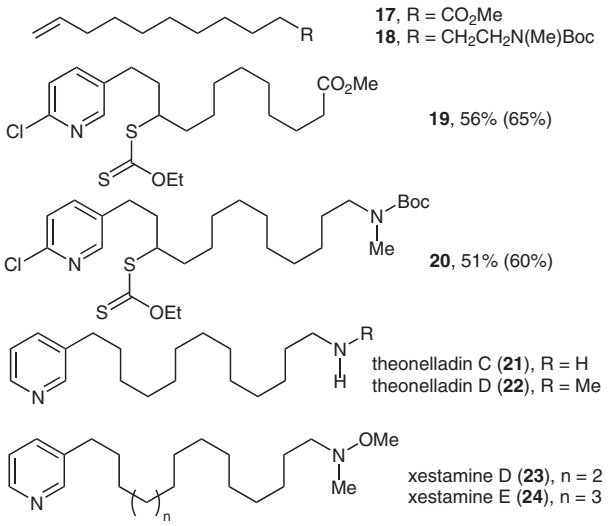


Scheme 2



Scheme 3

couplings become competitive.[6] It is worth stressing, finally, that many functional groups are compatible with the reaction conditions and that the process allows the expedient modification of the side chain of the pyridine ring. Access to most of the structures in Scheme 2 would have been tedious at best with conventional approaches.

The successful addition to the long-chain methyl undec-10-enoate (**17**) and homologous carbamate **18**, displayed in Scheme 3, opens the possibility of a simple access to a number of pyridine alkaloids[7] such as the antileukemic theonalledins C (**21**) and D (**22**),[7a–7d] or the antimicrobial xestamines D (**23**) and E (**24**).[7e,f]

Radical **6** derived from xanthate **5** is in the *meta* position with respect to the nitrogen atom and therefore only experiences indirectly its electronegativity. It was therefore important to explore and compare the behavior of the *ortho* and *para* isomeric xanthates **25** and **26**. These were prepared from the corresponding chloropicolines by a Wohl–Ziegler bromination with *N*-bromosuccinimide[7] and displacement of the bromine with potassium *O*-ethyl

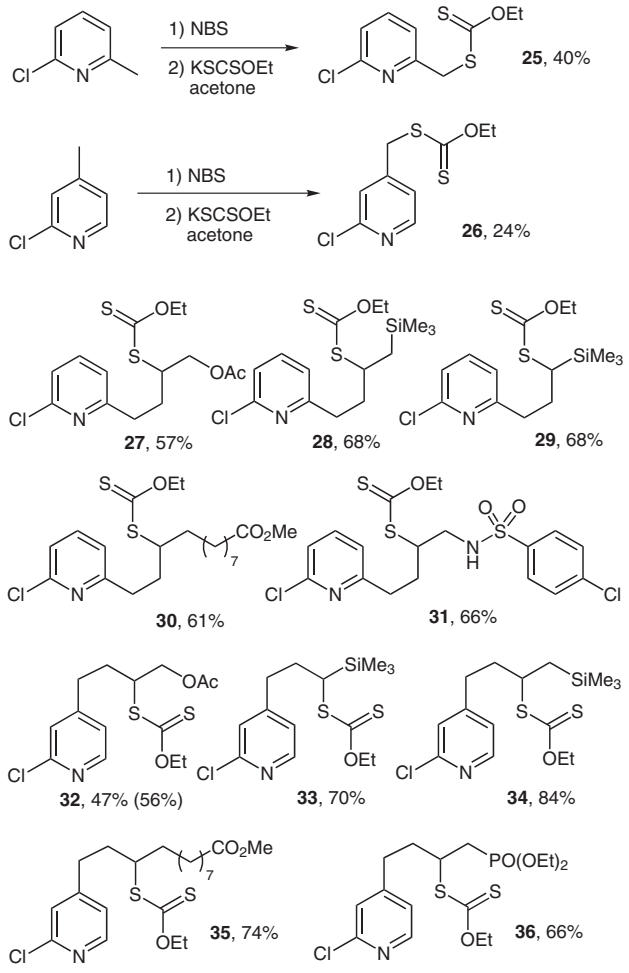
xanthate (Scheme 4). The modest overall yield is due to the somewhat inefficient bromination step.

Addition to allyl acetate, allyltrimethylsilane, trimethyl(vinyl)silane, and methyl undec-10-enoate gave adducts **27**–**30** from xanthate **25** and the corresponding adduct **32**–**35** from xanthate **26**. Two further successful additions of xanthate **25** to *N*-allyl-4-chlorobenzenesulfonamide and of xanthate **26** to diethyl allylphosphonate were performed to give the respectively compounds **31** and **36** in an identical yield of 66%.

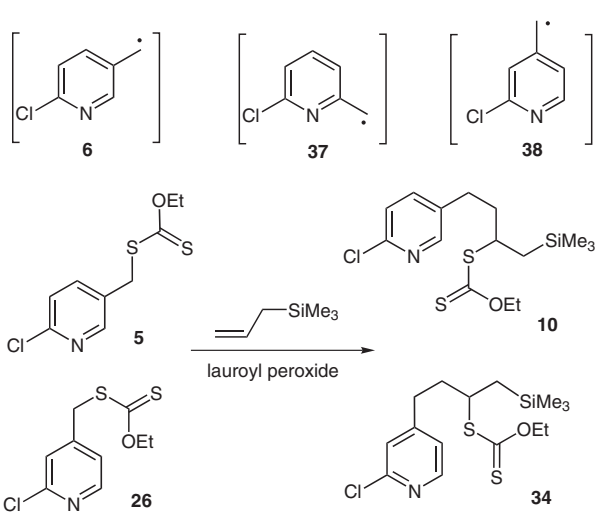
Even though a similar broad compatibility with the alkene partner was observed, the yields in most cases were noticeably higher than for additions of xanthate **5**. This is presumably due to the increased electrophilic character of the corresponding *ortho* and *para* radicals **37** and **38** because of better delocalization towards the more electronegative nitrogen atom of the pyridine ring, as compared with the isomeric *meta* radical **6** (Scheme 5).

The enhanced reactivity of xanthate **26** over xanthate **5** was ascertained by a competition experiment towards allyltrimethylsilane. Examination of the crude mixture in the early stages of the reaction by NMR spectroscopy indicated a 3:1 preference in favor of adduct **34** over **10** (Scheme 5).

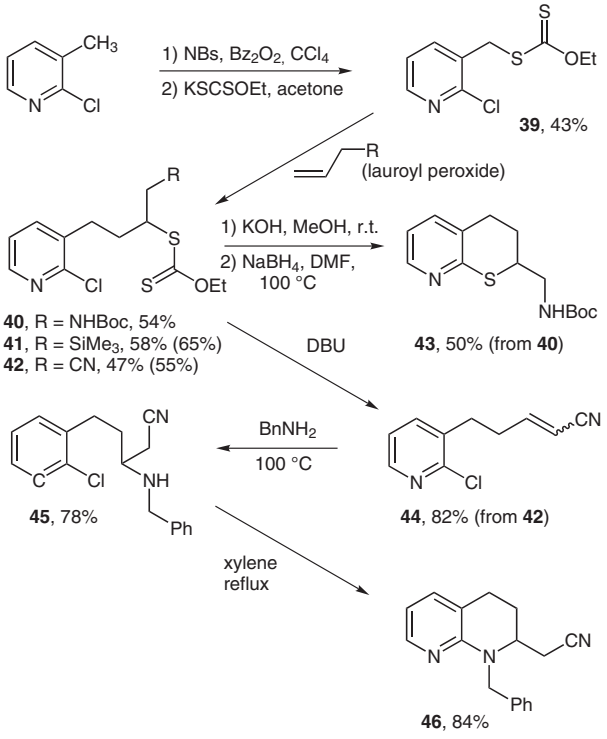
The synthetic utility of the chlorine atom on the pyridine ring can be gauged by the sequences displayed in Scheme 6. The radical addition products (e.g., **40**–**42**) derived from the 2-chloro-substituted xanthate **39** may be easily transformed into interesting bicyclic pyridine structures by intramolecular substitution of the chlorine atom. Thus, saponification of the xanthate in adduct **40** with sodium hydroxide and heating the resulting thiol in *N*,*N*-dimethylformamide in the presence of sodium borohydride gave rise to the rare 2*H*-thiopyrano[2,3-*b*]pyridine structure **43** in 50% overall yield.[8] The role of the borohydride is to reverse any aerial oxidation of the thiol into the disulfide, which is difficult to avoid on a small scale. Alternatively, the xanthate group in the addition product **42**



Scheme 4

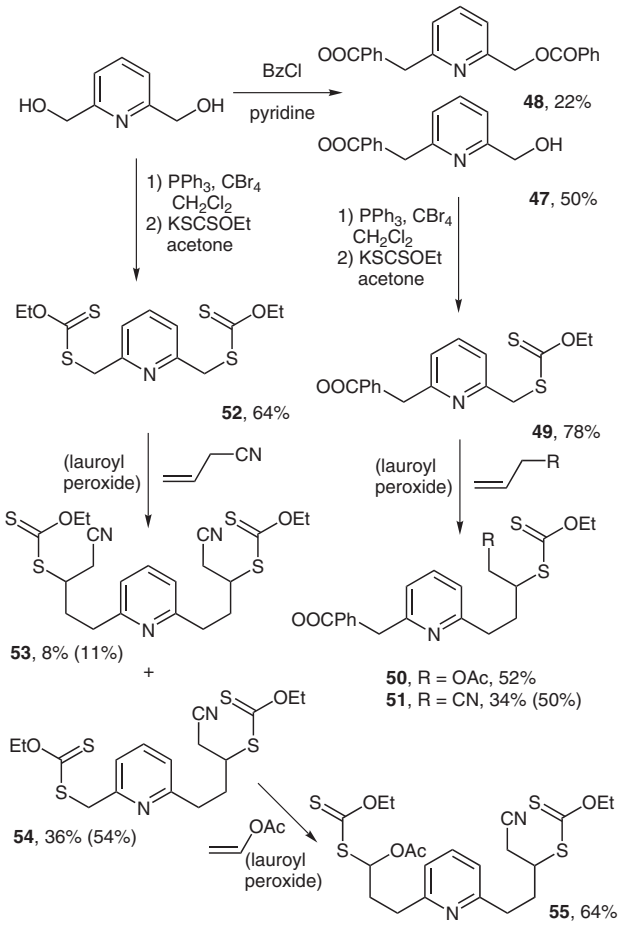


Scheme 5



Scheme 6

to allyl cyanide could be easily eliminated with base, since it is located in the β-position with respect to the nitrile group. In turn, the unsaturated nitrile **44** thus produced can undergo Michael addition with benzylamine to furnish adduct **45**, which is then converted into tetrahydroazaquinoline **46** in good overall yield by heating in refluxing xylene. Tetrahydroazaquinolines represent a class of valuable compounds for medicinal chemistry[9,10] and a library of such structures could in principle be built by simply replacing the benzylamine with various other primary amines.



Scheme 7

Finally, it is important to stress that the main requirement for a successful xanthate transfer addition is to block the nefarious nucleophilic activity of the pyridine nucleus. The chlorine atom, even though highly useful, may be replaced by various other functional groups that are able to shield the pyridine nitrogen. Some possibilities are collected in Scheme 7.

For example, reaction of 2,6-pyridinedimethanol with one equivalent of benzoyl chloride gave monobenzoate **47** in addition to lesser amounts of dibenzoate **48**. Conversion of the free alcohol into the corresponding bromide then into xanthate **49** using standard conditions proceeded smoothly. The radical addition to allyl acetate and cyanide gave respectively the expected adducts **50** and **51** in synthetically useful yields. Also interesting is the behavior of bis-xanthate **52** derived from the same starting diol. Reasonable selectivity in the radical monoaddition could be accomplished leading to **54**, with only minor amounts of symmetrical adduct **53** being formed. The former substance underwent a second radical addition to vinyl acetate to furnish unsymmetrical addition product **55** in 64% yield as a 1:1 mixture of diastereomers. Only the xanthate in the 'benzylic' position in **54** participates actively in the radical chain process since it much easier to cleave than the other, purely aliphatic xanthate. By altering the alkene partners, it should be possible to access numerous unsymmetrically substituted pyridines.

In summary, we have described a simple and direct, yet effective and versatile, route to various pyridine derivatives. The process is convergent, atom-economical, and compatible with a variety of useful functional groups. It complements our earlier and different route to pyridine structures[5a] and, more generally, highlights the broad utility of radical-based approaches, which have been largely neglected in this area of heterocyclic chemistry.

Solvents were used as received. Merck Geduran SI 60 Å silica gel (35–70 μm) was used for column chromatography. IR spectra were recorded on a Perkin-Elmer 1420 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded using 400 MHz ARX 400 Bruker spectrometers; spectra are referenced to the residual proton resonances of the solvents. Petroleum ether = PE.

Xanthate Adducts; General Procedure

A soln of xanthate (1 mmol) and the desired alkene (4 mmol) in DCE, MEK, PhCl, or EtOAc (1 mL) was refluxed for 10 min under N_2. DLP (5 mol%) or dicumyl peroxide was then added to the refluxing soln, followed by additional portions (5 mol%) every 1.5 h until the starting xanthate was completely consumed. The mixture was then cooled to r.t., concentrated under reduced pressure, and purified by flash chromatography (silica gel).

***S*-6-Chloro-3-pyridylmethyl *O*-Ethyl Dithiocarbonate (5)**

To a soln of the commercially available 2-chloro-5-(chloromethyl)pyridine (1 g, 6.17 mmol) in acetone (12 mL) was added under N_2 and portionwise potassium *O*-ethyl xanthate (1.09 g, 1.1 equiv). After addition of H_2O, evaporation of the acetone, and extraction with Et_2O, the combined organic layers were dried ($MgSO_4$), filtered, and evaporated under reduced pressure to give the pure **5** (94% yield) as pale yellow crystals; mp 60–61 °C (EtOAc–PE).

IR (Nujol): 1582, 1561 (C=N), 1229, 1053 cm^{-1} (C–O, CS).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 2.3 Hz, 1 H, CH_{Ar}), 7.67 (dd, *J* = 2.3 Hz, *J* = 8.2 Hz, 1 H, CH_{Ar}), 7.29 (d, *J* = 8.2 Hz, 1 H, CH_{Ar}), 4.65 (q, *J* = 7.2 Hz, 2 H, OCH_2CH_3), 4.33 (s, 2 H, CH_2S), 1.43 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.7 (C=S), 150.5 (C_{Ar}), 149.9 (CH_{Ar}), 139.3 (CH_{Ar}), 131.4 (C_{Ar}), 124.2 (CH_{Ar}), 70.6 (OCH_2CH_3), 36.5 (CH_2S), 13.8 (OCH_2CH_3).

MS (CI, NH_3): *m*/*z* = 248, 250 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_9H_{10}ClNOS_2$: 246.9892; found: 246.9888.

S-1-(Acetoxymethyl)-3-(6-chloro-3-pyridyl)propyl O-Ethyl Dithiocarbonate (7)

Following the general procedure using xanthate (0.8 mmol, 1 equiv) and allyl acetate (4 equiv) in DCE (0.8 mL). After the addition of DLP (2 × 5 mol%), further allyl acetate (4 equiv) and DLP (2 × 5 mol%) were added. Column chromatography (silica gel, toluene–Et_2O, 95:5) furnished **7** (49% yield, 61% based on recovered starting material) as a pale yellow oil.

IR (CCl_4): 1748 (OCOMe), 1584, 1560 (C=N), 1224, 1054 cm^{-1} (C–O, CS).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 2.4 Hz, 1 H, CH_{Ar}), 7.48 (dd, *J* = 2.5 Hz, *J* = 8.1 Hz, 1 H, CH_{Ar}), 7.26 (d, *J* = 8.5 Hz, 1 H, CH_{Ar}), 4.65 (q, *J* = 7.1 Hz, 2 H, OCH_2CH_3), 4.31 (dd, *J* = 5.0 Hz, *J* = 11.4 Hz, 1 H, CH_2OCO), 4.26 (dd, *J* = 6.0 Hz, *J* = 11.4 Hz, 1 H, CH_2OCO), 3.95 (m, 1 H, CHS), 2.84 (m, 1 H, CH_2Ar), 2.73 (m, 1 H, CH_2Ar), 2.07 (ms, 4 H, CH_3CO, CH_2CHS), 1.94 (m, 1 H, CH_2CHS), 1.42 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.6 (C=S), 170.6 ($OCOCH_3$), 149.6 (CH_{Ar}), 149.4 (C_{Ar}), 138.9 (CH_{Ar}), 135.1 (C_{Ar}), 124.1 (CH_{Ar}), 70.5 (OCH_2CH_3), 65.4 (CH_2OAc), 48.8 (CHS), 32.1, 29.4 (2 CH_2), 20.8 ($COCH_3$), 13.8 (OCH_2CH_3).

MS (CI, NH_3): *m*/*z* = 348, 350 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{14}H_{18}ClNO_3S_2$: 347.0417; found: 347.0417.

S-3-(6-Chloro-3-pyridyl)-1-(trimethylsilyl)propyl O-Ethyl Dithiocarbonate (8)

Following the general procedure using xanthate **5** (100 mg, 0.40 mmol) and trimethyl(vinyl)silane (243 mg, 2.42 mmol, 6 equiv) in MEK (0.4 mL) and requiring DLP (40 mol%) to go to completion. Further trimethyl(vinyl)silane (121 mg, 1.21 mmol, 3 equiv) was added to the mixture after 6 h. Flash chromatography (silica gel, PE–EtOAc, 95:5) afforded **8** (94 mg, 67%) as crystals; mp 48–49 °C.

IR (CCl_4): 2956, 1561, 1458, 1382, 1218, 1109, 1051 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 2.4 Hz, 1 H, CH_{Ar}), 7.40 (dd, J_1 = 2.4 Hz, J_2 = 8.0 Hz, 1 H, CH_{Ar}), 7.15 (d, *J* = 8.4 Hz, 1 H, CH_{Ar}), 4.59 (q, *J* = 7.2 Hz, 2 H, OCH_2CH_3), 3.13 (dd, J_1 = 4.0 Hz, J_2 = 10.0 Hz, 1 H, SiCHS), 2.79–2.72 (m, 1 H, CH_2Ar), 2.66–2.59 (m, 1 H, CH_2Ar), 2.05–1.96 (m, 1 H, CH_2CHS), 1.77–1.67 (m, 1 H, CH_2CHS), 1.35 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 0.05 [s, 9 H, $Si(CH_3)_3$].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 215.7 (C=S), 149.3 (CH_{Ar}), 148.8 (C), 138.6 (CH_{Ar}), 135.8 (C), 123.6 (CH_{Ar}), 70.2 (OCH_2CH_3), 36.2 (SiCHS), 32.4 (CH_2CHS), 30.6 (CH_2Ar), 13.6 (OCH_2CH_3), –2.7 $[Si(CH_3)_3]$.

MS (CI, NH_3): *m*/*z* = 348 $[M + H]^+$ (100%);

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{14}H_{22}ClNOS_2Si$: 347.060

1; found: 347.0588.

S-3-(6-Chloro-3-pyridyl)-1-[(diethoxyphosphoryl)methyl]propyl O-Ethyl Dithiocarbonate (9)

Following the general procedure using xanthate (0.8 mmol, 1 equiv) and diethyl allylphosphonate (4 equiv) in DCE (0.2 mL) and DLP (32.5 mol%). Column chromatography (silica gel, gradient toluene–EtOAc, 10:0 to 6:4) furnished **9** (62% yield) as a yellow oil.

IR (CCl_4): 1583, 1560 (C=N), 1221, 1050 cm^{-1} (C–O, CS).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 2.4 Hz, 1 H, CH_{Ar}), 7.52 (dd, *J* = 2.5 Hz, *J* = 8.2 Hz, 1 H, CH_{Ar}), 7.25 (d, *J* = 8.1 Hz, 1 H, CH_{Ar}), 4.65 (q, *J* = 7.1 Hz, 2 H, OCH_2CH_3), 4.09 (m, 4 H, 2 CH_3CH_2OP), 3.97 (m, 1 H, CHS), 2.84 (ddd, *J* = 4.9 Hz, *J* = 9.8 Hz, *J* = 14.4 Hz, 1 H, CH_2Ar), 2.71 (ddd, *J* = 7.1 Hz, *J* = 9.5 Hz, *J* = 14.1 Hz, 1 H, CH_2Ar), 2.40 (m, 2 H, CH_2CH_2Ar, CH_2P), 2.16 (ddd, *J* = 9.9 Hz, *J* = 15.4 Hz, *J* = 16.9 Hz, 1 H, CH_2P), 2.03 (m, 1 H, CH_2CH_2Ar), 1.42 (t, *J* = 7.1 Hz, 3 H, 2 OCH_2CH_3), 1.31 (td, *J* = 7.1 Hz, 6 H, 2 CH_3CH_2OP).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.5 (C=S), 149.6 (CH_{Ar}), 149.2 (C_{Ar}), 138.9 (CH_{Ar}), 135.2 (C_{Ar}), 123.9 (CH_{Ar}), 70.1 (OCH_2CH_3), 61.9 (t, *J* = 6.7 Hz, 2 CH_3CH_2OP), 44.8 (CHS), 34.4 (d, *J* = 3.1 Hz, CH_2CHS), 31.5 (d, *J* = 136.2 Hz, CH_2P), 29.2 (CH_2Ar), 16.4 (d, *J* = 6.1 Hz, 2 CH_3CH_2OP), 13.7 (OCH_2CH_3).

MS (CI, NH_3): *m*/*z* = 426, 428 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{25}ClNO_4PS_2$: 425.0651; found: 425.0657.

S-3-(6-Chloro-3-pyridyl)-1-[(trimethylsilyl)methyl]propyl O-Ethyl Dithiocarbonate (10)

Following the general procedure using xanthate **5** (100 mg, 0.40 mmol) and allyltrimethylsilane (185 mg, 1.61 mmol, 4 equiv) in MEK (0.4 mL) and requiring DLP (40 mol%) to go to completion. Further allyltrimethylsilane (93 mg, 0.80 mmol, 2 equiv) was as added to the mixture after 6 h. Flash chromatography (silica gel, PE–Et_2O, 25:2) afforded **10** (80 mg, 55%) as a light yellow oil, together with recovered starting xanthate (13 mg). The yield based on recovered starting xanthate was 63%.

IR (CCl_4): 2953, 1584, 1561, 1458, 1383, 1250, 1215, 1110, 1054 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 2.8 Hz, 1 H, CH_{Ar}), 7.44 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 1 H, CH_{Ar}), 7.21 (d, *J* = 8.4 Hz, 1 H, CH_{Ar}), 4.62 (q, *J* = 7.2 Hz, 2 H, OCH_2CH_3), 3.88–3.81 (m, 1 H, CHS), 2.74–2.68 (m, 2 H, CH_2Ar), 1.99–1.92 (m, 2 H, CH_2CHS), 1.39 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.13 (dd, J_1 = 7.2 Hz, J_2 = 14.8 Hz, 1 H, CH_2Si), 1.04 (dd, J_1 = 8.0 Hz, J_2 = 15.2 Hz, 1 H, CH_2Si), 0.03 [s, 9 H, $Si(CH_3)_3$].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 214.0 (C=S), 149.4 (CH_{Ar}), 149.1 (C), 138.7 (CH_{Ar}), 135.6 (C), 123.8 (CH_{Ar}), 69.6 (OCH_2CH_3), 47.9 (CHS), 38.4 (CH_2CHS), 29.3 (CH_2Ar), 22.9 (CH_2Si), 13.7 (OCH_2CH_3), –0.8 $[Si(CH_3)_3]$.

MS (CI, NH_3): *m*/*z* = 362 $[M + H]^+$ (100%).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{24}ClNOS_2Si$: 361.0757; found: 361.0758.

S-3-(6-Chloro-3-pyridyl)-1-(2,2-dimethylpropanoyl)propyl O-Ethyl Dithiocarbonate (11)

Following the general procedure using xanthate (1 mmol, 1 equiv) and vinyl pivalate (2 equiv) in DCE (1 mL). After the addition of DLP (2 × 5 mol%), further alkene (2 equiv) and DLP (2 × 5 mol%) were added. Column chromatography (silica gel, gradient toluene–EtOAc, 10:0 to 98:2) afforded **11** (45% yield) as a colorless oil.

IR (CCl_4): 1739 (OCO), 1228, 1052 cm^{-1} (C–O, CS).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 2.0 Hz, 1 H, CH_{Ar}), 7.49 (dd, *J* = 2.6 Hz, *J* = 8.2 Hz, 1 H, CH_{Ar}), 7.26 (d, *J* = 8.1 Hz, 1 H, CH_{Ar}), 6.61 (t, *J* = 6.5 Hz, 1 H, CHS), 4.63 (m, 2 H, OCH_2CH_3), 2.74 (t, *J* = 7.9 Hz, 2 H, CH_2), 2.24 (m, 2 H, CH_2), 1.40 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.20 [s, 9 H, $C(CH_3)_3$].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.9 (C=S), 176.8 (C=O), 149.6 (CH_{Ar}), 138.8 (CH_{Ar}), 124.1 (CH_{Ar}), 80.1 (CHS), 70.3 (OCH_2CH_3), 38.9 [$C(O)Me_3$], 35.4, 28.2 (2 CH_2), 27.0 [$C(CH_3)_3$], 13.7 (OCH_2CH_3).

MS (CI, NH_3): *m*/*z* = 376, 378 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M - SCSOCH_2CH_3]^+$ calcd for $C_{13}H_{17}ClNO_2$: 254.0948; found: 254.0952.

_S_-1-{2-[(_tert_-Butoxycarbonyl)amino]-2,2-bis(ethoxycarbonyl)ethyl}-3-(6-chloro-3-pyridyl)propyl _O_-Ethyl Dithiocarbonate (12)

Following the general procedure using xanthate (0.8 mmol, 1 equiv) and alkene (4 equiv) in PhCl (0.2 mL) and DLP (27.5 mol%) in an oil bath at 100 °C. Column chromatography (gradient PE–EtOAc, 10:0 to 8:2) gave **12** (36% yield) as a colorless oil.

IR (CCl_4): 3419 (NH), 1741, 1720 (C=O), 1217, 1052 cm^{-1} (C–O, CS).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, J = 2.3 Hz, 1 H, CH_{Ar}), 7.46 (dd, J = 2.5 Hz, J = 8.2 Hz, 1 H, CH_{Ar}), 7.23 (d, J = 8.1 Hz, 1 H,, CH_{Ar}), 6.04 (s, 1 H, NH), 4.63 (qd, J = 7.1 Hz, 2 H, OCH_2CH_3), 4.28 (m, 2 H, $CO_2CH_2CH_3$), 4.18 (m, 2 H, $CO_2CH_2CH_3$), 3.71 (m, 1 H, CHS), 2.91 (dd, J = 2.7 Hz, J = 15.5 Hz, 1 H, CH_2), 2.69 (m, 3 H, CH_2, CH_2), 1.99 (m, 2 H, CH_2), 1.43 [s + t, 12 H, $OC(CH_3)_3$, OCH_2CH_3], 1.27 (t, J = 7.1 Hz, 3 H, $CO_2CH_2CH_3$), 1.24 (t, J = 7.1 Hz, 3 H, $CO_2CH_2CH_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.9 (C=S), 167.8 ($OCOCMe_3$), 154.1 (CONH), 149.7 (CH_{Ar}), 149.3 (C_{Ar}), 138.8 (CH_{Ar}), 135.5 (C_{Ar}), 124.0 (CH_{Ar}), 80.7 (CMe_3), 70.1 (OCH_2CH_3), 65.3 (C_q), 63.2, 62.6 (2 $CO_2CH_2CH_3$), 45.4 (CHS), 37.8, 36.1, 29.4 (3 CH_2), 28.3 [$C(CH_3)_3$], 14.1, 13.9 (2 $CO_2CH_2CH_3$), 13.8 (OCH_2CH_3).

MS (CI, NH_3): m/z = 563, 565 $[M + H]^+$.

HRMS (EI): m/z $[M]^+$ calcd for $C_{24}H_{35}ClN_2O_7S_2$: 562.1574; found: 562.1572.

_S_-1-[2-(6-Chloro-3-pyridyl)ethyl]-3-(5,5-dimethyl-1,3-dioxan-2-yl)-3-methylbutyl _O_-Ethyl Dithiocarbonate (13)

Following the general procedure using xanthate (0.8 mmol, 1 equiv) and alkene (4 equiv) in PhCl (0.2 mL) and DLP (35 mol%) in an oil bath at 100 °C. Column chromatography (silica gel, gradient PE–Et_2O, 10:0 to 9:1) furnished **13** (47% yield, 56% based on recovered starting material) as a solid. Recrystallization (PE) afforded white crystals; mp 65–66 °C.

IR (CCl_4): 1214, 1054 (C–O, CS), 1110 cm^{-1} (C–O–C).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.21 (d, J = 2.1 Hz, 1 H, CH_{Ar}), 7.47 (dd, J = 2.5 Hz, J = 8.2 Hz, 1 H, CH_{Ar}), 7.22 (d, J = 8.1 Hz, 1 H, CH_{Ar}), 4.63 (q, J = 7.1 Hz, 2 H, OCH_2CH_3), 4.08 [s, 1 H, $CH(CH_2O)_2$], 3.86 (m, 1 H, CHS), 3.57 (d, J = 10.9 Hz, 2 H, CH_2O), 3.35 (d, J = 10.8 Hz, 2 H, CH_2O), 2.71 (m, 2 H, CH_2Ar), 1.97 (dd, J = 7.2 Hz, J = 15.4 Hz, 2 H, CH_2CH_2Ar), 1.75 (d, J = 5.6 Hz, 2 H, CH_2CHS), 1.40 (t, J = 7.1 Hz, 3 H, OCH_2CH_3), 1.13 (s, 3 H, CH_3), 0.98 (s, 3 H, CH_3), 0.97 (s, 3 H, CH_3), 0.69 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 214.4 (C=S), 149.6 (CH_{Ar}), 149.1 (C_{Ar}), 138.9 (CH_{Ar}), 136.0 (C_{Ar}), 123.9 (CH_{Ar}), 106.6 (CH), 77.34, 77.27 (2 CH_2O), 69.8 (OCH_2CH_3), 46.6 (CHS), 40.6, 39.2 (2 CH_2), 38.2, 30.2 (OC_qMe_2, C_qMe_2), 29.4 (CH_2), 23.0, 22.9, 22.5, 21.8 (4 CH_3), 13.9 (OCH_2CH_3).

MS (CI, NH_3): m/z = 446, 448 $[M + H]^+$.

HRMS (EI): m/z $[M]^+$ calcd for $C_{21}H_{32}ClNO_3S_2$: 445.1512; found: 445.1509.

_S_-4-[(6-Chloro-3-pyridyl)methyl]-2,5-dioxo-1-phenylpyrrolidin-3-yl _O_-Ethyl Dithiocarbonate (14)

Following the general procedure using _N_-phenylmaleimide (0.58 mmol, 1 equiv) and xanthate (2 equiv) in PhCl (0.5 mL) and DLP (5 mol%) in an oil bath at 100 °C. The addition product crystallized from the mixture and the obtained crystals were triturated (Et_2O–MeOH) to yield the pure **14** (57% yield) as pink crystals; mp 164–165 °C.

IR (Nujol): 1782, 1711 (C=O), 1235, 1042 cm^{-1} (C–O, CS).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.34 (d, J = 2.2 Hz, 1 H, CH_{Ar}), 7.61 (dd, J = 2.5 Hz, J = 8.2 Hz, 1 H, CH_{Ar}), 7.49 (t, J = 7.4 Hz, 2 H, CH_{Ar}), 7.42 (t, J = 7.4 Hz, 1 H, CH_{Ar}), 7.32 (d, J = 8.2 Hz, 1 H, CH_{Ar}), 7.26 (d, J = 7.2 Hz, 2 H, CH_{Ar}), 4.66 (m, 2 H, OCH_2CH_3), 4.22 (d, J = 6.8 Hz, 1 H, CHS), 3.67 (dd, J = 6.1 Hz, J = 12.7 Hz, 1 H, $CHCH_2$), 3.32 (apparent d, J = 5.9 Hz, 2 H, CH_2CH), 1.43 (t, J = 7.1 Hz, 3 H, OCH_2CH_3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 210.6 (C=S), 175.1 (C=O), 172 (C=O), 150.3 (CH_{Ar}), 148.6 (C_{Ar}), 140.4 (CH_{Ar}), 132.8, 132.1 (2 C_{Ar}), 128.9, 128.4, 126.6, 123.7 (6 CH_{Ar}), 71.0 (OCH_2CH_3), 50.0, 49.9 (CHS, CH), 30.9 (CH_2Ar), 13.3 (OCH_2CH_3).

HRMS (EI): m/z $[M – SCSOEt]^+$ calcd for $C_{16}H_{12}ClN_2O_2S$: 299.0587; found: 299.0586.

_S_-3-(6-Chloro-3-pyridyl)-1-[(4-methoxyphenylsulfonylamino)methyl]propyl _O_-Ethyl Dithiocarbonate (15)

Following the general procedure as the solvent using xanthate (0.8 mmol, 1 equiv) and alkene (4 equiv) in PhCl (0.2 mL) and DLP (4 × 5 mol%) in an oil bath at 100 °C. Column chromatography (gradient PE–EtOAc, 10:0 to 8:2) gave **15** (46% yield) as a colorless oil.

IR (CCl_4): 3270 (NH), 1593 (C=C, C=N), 1333, 1155 (NSO_2), 1222, 1053 cm^{-1} (C–O, CS).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, J = 2.5 Hz, 1 H, CH_{Ar}), 7.77 (d, J = 9.0 Hz, 2 H, CH_{Ar}), 7.47 (dd, J = 2.5 Hz, J = 8.2 Hz, 1 H, CH_{Ar}), 7.25 (d, J = 8.2 Hz, 1 H, CH_{Ar}), 6.97 (d, J = 8.9 Hz, 2 H, CH_{Ar}), 4.86 (br t, J = 5.8 Hz, 1 H, NH), 4.61 (qd, 2 H, OCH_2CH_3), 3.87 (m, 1 H, CHS), 3.73 (s, 3 H, OCH_3), 3.24 (m, 2 H, CH_2N), 2.79 (m, 1 H, CH_2CHS), 2.69 (m, 1 H, CH_2CHS), 2.07 (m, 1 H, CH_2CH_2CHS), 1.90 (m, 1 H, CH_2CH_2CHS), 1.41 (t, J = 7.1 Hz, 3 H, OCH_2CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.5 (C=S), 163.0 (C_{Ar}), 149.6 (CH_{Ar}), 149.3 (C_{Ar}), 139.0 (CH_{Ar}), 135.1, 131.4 (2 C_q), 129.2 (CH_{Ar}), 124.1 (CH_{Ar}), 114.4 (CH_{Ar}), 70.6 (OCH_2CH_3), 55.7 (OCH_3), 49.9 (CHS), 46.2 (CH_2N), 32.01, 29.3 (2 CH_2), 13.8 (OCH_2CH_3).

MS (CI, NH_3): m/z = 475, 477 $[M + H]^+$.

HRMS (EI): m/z $[M – SCSOCH_2CH_3]^+$ calcd for $C_{16}H_{18}ClN_2O_3S$: 353.0727; found: 353.0724.

_S_-1-(2-Acetoxyethyl)-3-(6-chloro-3-pyridyl)propyl _O_-Ethyl Dithiocarbonate (16)

Following the general procedure using xanthate (0.8 mmol, 1 equiv) and alkene (4 equiv) in heptane (0.2 mL) and dicumyl peroxide (2 × 25 mol%) as the initiator. Column chromatography (silica gel, gradient PE–EtOAc, 95:5 to 8:2) afforded **16** (55% yield) as a colorless oil.

IR (CCl_4): 1743 (OCOMe), 1583, 1560 (C=N), 1226, 1053 cm^{-1} (C–O, CS).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.19 (s, 1 H, CH_{Ar}), 7.46 (dd, J = 1.8 Hz, J = 8.2 Hz, 1 H, CH_{Ar}), 7.23 (dd, J = 1.1 Hz, J = 8.2 Hz, 1 H), 4.61 (qd, J = 7.1 Hz, 2 H, OCH_2CH_3), 4.16 (m, 2 H, CH_2OAc), 3.82 (m, 1 H, CHS), 2.74 (m, 2 H, CH_2), 2.01 (m, 7 H, 2 CH_2, $COCH_3$), 1.39 (t, J = 7.1 Hz, 3 H, OCH_2CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.4 (C=S), 170.9 ($OCOCH_3$), 149.6 (CH_{Ar}), 149.3 (C_{Ar}), 138.8 (CH_{Ar}), 135.4 (C_{Ar}), 124.0 (CH_{Ar}), 70.2 (OCH_2CH_3), 61.6 (CH_2OAc), 47.5 (CHS), 35.7, 33.3, 29.4 (3 CH_2), 20.9 ($COCH_3$), 13.8 (OCH_2CH_3).

HRMS (EI): m/z $[M]^+$ calcd for $C_{15}H_{20}ClNO_3S_2$: 361.0573; found: 361.0568.

***N*-(_tert_-Butoxycarbonyl)-*N*-methyldodec-11-enamine (18)**

To a stirred soln of dodec-11-enal (1.45 g, 7.96 mmol) in MeOH (26.0 mL) was added 10% $MeNH_2$ in MeOH (3.7 mL, 11.9 mmol) and the mixture was stirred at r.t. for 1 h. The mixture was treated

with $NaBH_4$ (435 mg, 11.7 mmol) and stirred for an additional 1 h. The MeOH was evaporated under reduced pressure and the residue was taken up in CH_2Cl_2 and H_2O. The organic layer was separated, dried (anhyd $MgSO_4$), filtered, and evaporated under reduced pressure. The crude *N*-methyldodec-11-enamine (1.3 g) was used in the next step without further purification.

To a stirred soln of *N*-methyldodec-11-enamine (1.3 g, 6.63 mmol) in CH_2Cl_2 (40 mL) at 0 °C under N_2, was added dropwise Boc_2O (1.4 g, 6.63 mmol), and the soln was stirred at r.t. for 24 h. CH_2Cl_2 and H_2O were added and the organic layer was separated, dried (anhyd $MgSO_4$), filtered, and evaporated under reduced pressure. The residue was purified by flash chromatography (silica gel, PE–EtOAc, 95:5) to yield **18** (1.62 g, 68%, two steps) as a light yellow oil.

IR: 2974, 2927, 2856, 1695, 1459, 1394, 1307, 1164 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 5.78–5.68 (m, 1 H, CH_2=C*H*), 4.94–4.84 (m, 2 H, CH=CH_2), 3.12 (t, *J* = 6.0 Hz, 2 H, CH_2N), 2.76 (s, 3 H, NCH_3), 1.99–1.94 (m, 2 H, CH_2=CHCH_2), 1.46–1.17 (m, 16 H), 1.39 [s, 9 H, $C(CH_3)_3$].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.6 (C=O), 138.9 (CH_2=*C*H), 114.0 (*C*H_2=CH), 78.8 (C), 48.6 (CH_2N), 33.8 (NCH_3), 33.7 (CH_2), 29.4 (2 CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.0 (CH_2), 28.8 (CH_2), 28.3 [$COC(CH_3)_3$], 27.7 (CH_2), 26.5 (CH_2).

MS (CI, NH_3): *m*/*z* = 298 $[M + H]^+$ (10%).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{35}NO_2$: 297.2668; found: 297.2673.

Methyl 12-(6-Chloro-3-pyridyl)-10-(ethoxythiocarbonylsulfanyl)dodecanoate (19)

Following the general procedure using xanthate (2.01 mmol, 1 equiv) and methyl undec-10-enoate (4 equiv) in DCE (0.2 mL) and DLP (32.5 mol%). Column chromatography (silica gel, PE–EtOAc, 95:5) furnished **19** (56% yield, 65% based on recovered starting material) as a yellow oil.

IR (CCl_4): 1740 (CO_2Me), 1583, 1561 (C=N), 1216, 1054 cm^{-1} (C–O, CS).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 2.4 Hz, 1 H, CH_{Ar}), 7.48 (dd, *J* = 2.4 Hz, *J* = 8.2 Hz, 1 H, CH_{Ar}), 7.25 (d, *J* = 8.2 Hz, 1 H, CH_{Ar}), 4.65 (q, *J* = 7.1 Hz, 2 H, OCH_2CH_3), 3.74 (m, 1 H, CHS), 3.67 (s, 3 H, OCH_3), 2.74 (m, 2 H, CH_2), 2.30 (t, 2 H, CH_2), 1.96 (m, 2 H, CH_2), 1.65 (m, 4 H, 2 CH_2), 1.42 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.28 (m, 10 H, 5 CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 214.4 (C=S), 174.3 (C=O), 149.6 (CH_{Ar}), 149.2 (C_{Ar}), 138.9 (CH_{Ar}), 135.8 (C_{Ar}), 124.0 (CH_{Ar}), 69.9 (OCH_2CH_3), 51.5, 50.8 (CHS, OCH_3), 35.8, 34.3, 34.1, 29.6, 29.4, 29.3, 29.2, 29.1, 26.8, 24.9 (CH_2), 13.9 (OCH_2CH_3).

MS (CI, NH_3): *m*/*z* = 446, 448 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{21}H_{32}ClNO_3S_2$: 445.1512; found: 445.1510.

***S*-11-[(*tert*-Butoxycarbonyl)(methyl)amino]-1-[2-(6-chloro-3-pyridyl)ethyl]undecyl *O*-Ethyl Dithiocarbonate (20)**

Following the general procedure using xanthate **5** (70 mg, 0.28 mmol) and **18** (334 mg, 1.13 mmol, 4 equiv) in MEK (0.3 mL) and requiring DLP (35 mol%) to go to completion. Flash chromatography (silica gel, PE–Et_2O, 6:1) afforded **20** (86 mg, 51%) as a yellow oil, together with recovered starting xanthate (12 mg). The yield based on recovered starting xanthate was 60%.

IR: 2929, 2856, 1695, 1459, 1392, 1216, 1163, 1110, 1054 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 2.0 Hz, 1 H, CH_{Ar}), 7.44 (dd, J_1 = 2.4 Hz, J_2 = 8.0 Hz, 1 H, CH_{Ar}), 7.21 (d, *J* = 8.0 Hz, 1 H, CH_{Ar}), 4.60 (q, *J* = 7.2 Hz, 2 H, OCH_2CH_3), 3.73–3.66 (m, 1 H, CHS), 3.14 (t, *J* = 6.8 Hz, 2 H, NCH_2), 2.79 (s, 3 H, NCH_3), 2.74–2.67 (m, 2 H, CH_2Ar), 2.00–1.85 (m, 2 H, CH_2CHS), 1.69–1.62 (m, 2 H, CH_2CHS), 1.47–1.18 (m, 16 H), 1.41 [s, 9 H, $C(CH_3)_3$], 1.38 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 214.2 (C=S), 155.7 (C=O), 149.4 (CH_{Ar}), 149.1 (C), 138.7 (CH_{Ar}), 135.6 (C), 123.8 (CH_{Ar}), 78.9 (C), 69.8 (OCH_2CH_3), 50.6 (CHS), 48.7 (CH_2N), 35.6 (*C*H_2CHS), 34.1 (*C*H_2CHS), 33.9 (NCH_3), 29.6, 29.5, 29.4 (7 CH_2), 28.5 [$COC(CH_3)_3$], 26.8 (CH_2), 26.7 (CH_2), 13.8 (OCH_2CH_3).

MS (CI, NH_3): *m*/*z* = 545 $[M + H]^+$ (100%).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{27}H_{45}ClN_2O_3S_2$: 544.2560; found: 544.2559.

***S*-(6-Chloro-2-pyridyl)methyl *O*-Ethyl Dithiocarbonate (25)**

2-Chloro-6-methylpyridine (710 mg, 5.56 mmol), NBS (990 mg, 5.56 mmol), and Bz_2O_2 (130 mg) in CCl_4 (17 mL) were refluxed for 3 h under N_2. The succinimide was removed by filtration and to the filtrate was added CH_2Cl_2. The organic layer was washed with 5% aq NaOH and H_2O, dried (anhyd $MgSO_4$), filtered, and evaporated under reduced pressure. The residue was purified by flash chromatography (silica gel, PE–Et_2O, 25:2) to yield 2-(bromomethyl)-6-chloropyridine (648 mg, 56%) as an inseparable mixture with the starting compound (52 mg); this sample was used in the next step without further purification.

To a soln of 2-(bromomethyl)-6-chloropyridine (648 mg, 3.14 mmol) in acetone (10 mL) was added portionwise potassium *O*-ethyl xanthate (553 mg, 2.46 mmol) at 0 °C under N_2. The mixture was stirred at r.t. until complete consumption of the starting material. Acetone was evaporated under reduced pressure and the residue was taken up in CH_2Cl_2, washed with sat. aq NH_4Cl and H_2O, dried (anhyd $MgSO_4$), filtered, and evaporated under reduced pressure. The residue was purified by flash chromatography (silica gel, PE–Et_2O, 25:2) to yield **25** (560 mg, 72%) as a yellow oil.

IR: 2987, 1577, 1562, 1434, 1220, 1137, 1113, 1054 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.56 (t, *J* = 8.0 Hz, 1 H, CH_{Ar}), 7.31 (d, *J* = 7.6 Hz, 1 H, CH_{Ar}), 7.16 (d, *J* = 8.0 Hz, 1 H, CH_{Ar}), 4.58 (q, *J* = 7.2 Hz, 2 H, OCH_2CH_3), 4.41 (s, 2 H, CH_2S), 1.34 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.9 (C=S), 157.0 (C), 150.6 (C), 139.1 (CH_{Ar}), 122.8 (CH_{Ar}), 121.5 (CH_{Ar}), 70.2 (OCH_2CH_3), 41.0 (*C*H_2Ar), 13.6 (OCH_2CH_3).

MS (CI, NH_3): *m*/*z* = 248 $[M + H]^+$ (100%).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_9H_{10}ClNOS_2$: 246.9892; found: 246.9900.

***S*-2-Chloro-4-pyridyl)methyl *O*-Ethyl Dithiocarbonate (26)**

2-Chloro-4-methylpyridine (1.0 g, 7.83 mmol), NBS (1.4 g, 7.83 mmol), and Bz_2O_2 (180 mg) in CCl_4 (23 mL) were refluxed for 3 h under N_2. The succinimide was removed by filtration and CH_2Cl_2 was added to the filtrate. The organic layer was washed with 5% aq NaOH and H_2O, dried (anhyd $MgSO_4$), filtered, and evaporated under reduced pressure. The residue was purified by flash chromatography (silica gel, PE–EtOAc, 25:2) to yield 4-(bromomethyl)-2-chloropyridine (480 mg, 29%) as a yellow oil.

To a soln of 4-(bromomethyl)-2-chloropyridine (430 mg, 2.08 mmol) in acetone (10 mL) was added portionwise potassium *O*-ethyl xanthate (366 mg, 2.28 mmol) at 0 °C under N_2. The mixture was stirred at r.t. until complete consumption of the starting material. Acetone was evaporated under reduced pressure and the residue was taken up in CH_2Cl_2, washed with sat. aq NH_4Cl and H_2O, dried (anhyd $MgSO_4$), filtered, and evaporated under reduced pressure. The residue was purified by flash chromatography (silica gel, PE–Et_2O, 25:2) to yield **26** (450 mg, 84%) as a yellow oil.

IR: 2987, 1588, 1380, 1229, 1113, 1052 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 5.2 Hz, 1 H, CH_{Ar}), 7.26 (s, 1 H, CH_{Ar}), 7.15 (dd, J_1 = 1.2 Hz, J_2 = 5.2 Hz, 1 H, CH_{Ar}), 4.56 (q, *J* = 7.2 Hz, 2 H, OCH_2CH_3), 4.24 (s, 2 H, CH_2S), 1.33 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 211.9 (C=S), 151.40 (C), 149.4 (CH_{Ar}), 148.7 (C), 124.0 (CH_{Ar}), 122.4 (CH_{Ar}), 70.5 (OCH_2CH_3), 38.0 (CH_2S), 13.5 (OCH_2CH_3).

MS (CI, NH_3): *m*/*z* = 248 $[M + H]^+$ (100%).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_9H_{10}ClNOS_2$: 246.9892; found: 246.9885.

_S_-1-(Acetoxymethyl)-3-(6-chloro-2-pyridyl)propyl _O_-Ethyl Dithiocarbonate (27)

Following the general procedure using xanthate **25** (100 mg, 0.40 mmol) and allyl acetate (162 mg, 1.61 mmol, 4 equiv) in MEK (0.4 mL) and requiring DLP (20 mol%) to go to completion. Flash chromatography (silica gel, PE–EtOAc, 9:1) afforded **27** (80 mg, 57%) as a light yellow oil.

IR: 2956, 1582, 1558, 1437, 1216, 1111, 1050 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.53 (t, *J* = 7.6 Hz, 1 H, CH_{Ar}), 7.14 (d, *J* = 8.0 Hz, 1 H, CH_{Ar}), 7.05 (d, *J* = 7.6 Hz, 1 H, CH_{Ar}), 4.61 (dq, J_1 = 2.0 Hz, J_2 = 7.2 Hz, 2 H, OCH_2CH_3), 4.30–4.21 (m, 2 H, CH_2OAc), 3.99–3.93 (m, 1 H, CHS), 2.99–2.92 (m, 1 H, CH_2Ar), 2.89–2.82 (m, 1 H, CH_2Ar), 2.29–2.20 (m, 1 H, CH_2CHS), 2.06–1.96 (m, 1 H, CH_2CHS), 2.04 (s, 3 H, $OCCH_3$), 1.38 (dt, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 3 H, OCH_2CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.8 (C=S), 170.5 (C=O), 161.5 (C), 150.8 (C), 138.9 (CH_{Ar}), 121.8 (CH_{Ar}), 121.4 (CH_{Ar}), 70.1 (OCH_2CH_3), 65.4 (CH_2OAc), 48.8 (CHS), 34.8 (CH_2Ar), 30.2 (CH_2CHS), 20.7 ($OCCH_3$), 13.6 (OCH_2CH_3).

MS (CI, NH_3): *m*/*z* = 348 $[M + H]^+$ (100%).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{14}H_{18}ClNO_3S_2$: 347.0417; found: 347.0416.

_S_-3-(6-Chloro-2-pyridyl)-1-[(trimethylsilyl)methyl]propyl _O_-Ethyl Dithiocarbonate (28)

Following the general procedure using xanthate **25** (100 mg, 0.40 mmol) and allyltrimethylsilane (185 mg, 1.61 mmol, 4 equiv) in MEK (0.4 mL) and requiring DLP (20 mol%) to go to completion. Further allyltrimethylsilane (93 mg, 0.80 mmol, 2 equiv) were added to the mixture after 4.5 h. Flash chromatography (silica gel, PE–Et_2O, 25:2) afforded **28** (100 mg, 68%) as a light yellow oil.

IR: 2955, 1582, 1558, 1438, 1214, 1111, 1054 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.52 (t, *J* = 8.0 Hz, 1 H, CH_{Ar}), 7.12 (d, *J* = 8.0 Hz, 1 H, CH_{Ar}), 7.04 (d, *J* = 7.6 Hz, 1 H, CH_{Ar}), 4.60 (dq, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 2 H, OCH_2CH_3), 3.87–3.80 (m, 1 H, CHS), 2.90–2.85 (m, 2 H, CH_2Ar), 2.23–2.14 (m, 1 H, CH_2CHS), 2.06–1.97 (m, 1 H, CH_2CHS), 1.38 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.12 (dd, J_1 = 7.2 Hz, J_2 = 14.8 Hz, 1 H, CH_2Si), 1.06 (dd, J_1 = 8.0 Hz, J_2 = 14.8 Hz, 1 H, CH_2Si), 0.03 [s, 9 H, $Si(CH_3)_3$].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 214.2 (C=S), 162.2 (C), 150.7 (C), 138.8 (CH_{Ar}), 121.6 (CH_{Ar}), 121.4 (CH_{Ar}), 69.4 (OCH_2CH_3), 48.0 (CHS), 36.5 (CH_2CHS), 34.9 (CH_2Ar), 23.2 (CH_2Si), 13.7 (OCH_2CH_3), –0.8 [$Si(CH_3)_3$].

MS (CI, NH_3): *m*/*z* = 362 $(M + H]^+$ (100%).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{24}ClNOS_2Si$: 361.0757; found: 361.0741.

_S_-3-(6-Chloro-2-pyridyl)-1-(trimethylsilyl)propyl _O_-Ethyl Dithiocarbonate (29)

Following the general procedure using xanthate **25** (100 mg, 0.40 mmol) and trimethyl(vinyl)silane (245 mg, 2.42 mmol, 6 equiv) in MEK (0.4 mL) and requiring DLP (25 mol%) to go to completion. Flash chromatography (silica gel, PE–Et_2O, 25:1) afforded **29** (95 mg, 68%) as a light yellow oil.

IR: 2956, 1582, 1558, 1437, 1216, 1111, 1050 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.52 (t, *J* = 7.6 Hz, 1 H, CH_{Ar}), 7.12 (d, *J* = 7.6 Hz, 1 H, CH_{Ar}), 7.04 (d, *J* = 7.6 Hz, 1 H, CH_{Ar}), 4.63 (q, *J* = 7.2 Hz, 2 H, OCH_2CH_3), 3.20 (dd, J_1 = 3.6 Hz, J_2 = 10.4 Hz, 1 H, SiCHS), 3.01–2.93 (m, 1 H, CH_2Ar), 2.84 (ddd, J_1 = 6.0 Hz, J_2 = 10.4 Hz, J_3 = 16.4 Hz, 1 H, CH_2Ar), 2.29–2.21 (m, 1 H, CH_2CHS), 1.89–1.79 (m, 1 H, CH_2CHS), 1.40 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 0.10 [s, 9 H, $Si(CH_3)_3$].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 216.2 (C=S), 162.6 (C), 150.7 (C), 138.8 (CH_{Ar}), 121.5 (CH_{Ar}), 121.3 (CH_{Ar}), 70.2 (OCH_2CH_3), 36.7 (CHS), 36.4 (CH_2Ar), 30.7 (CH_2CHS), 13.8 (OCH_2CH_3), –2.6 [$Si(CH_3)_3$].

MS (CI, NH_3): *m*/*z* = 348 $[M + H]^+$ (100%).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{14}H_{22}ClNOS_2Si$: 347.0601; found: 347.0602.

Methyl 12-(6-Chloro-2-pyridyl)-10-(ethoxythiocarbonylsulfanyl)dodecanoate (30)

Following the general procedure using xanthate **25** (100 mg, 0.40 mmol) and methyl undec-10-enoate (320 mg, 1.61 mmol, 4 equiv) in DCE (0.4 mL) and requiring DLP (20 mol%) to go to completion. Flash chromatography (silica gel, PE–Et_2O, 25:2) afforded **30** (110 mg, 61%) as a light yellow oil.

IR: 2930, 2856, 1741, 1582, 1559, 1438, 1214, 1111, 1055 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.51 (t, *J* = 7.6 Hz, 1 H, CH_{Ar}), 7.11 (d, *J* = 7.6 Hz, 1 H, CH_{Ar}), 7.03 (d, *J* = 7.2 Hz, 1 H, CH_{Ar}), 4.59 (q, *J* = 7.2 Hz, 2 H, OCH_2CH_3), 3.75–3.70 (m, 1 H, CHS), 3.62 (s, 3 H, OCH_3), 2.92–2.79 (m, 2 H, CH_2Ar), 2.25 (t, *J* = 7.6 Hz, 2 H, $OCCH_2$), 2.17–2.08 (m, 1 H, CH_2CHS), 2.02–1.93 (m, 1 H, CH_2CHS), 1.69–1.61 (m, 2 H, $CHSCH_2$), 1.59–1.53 (m, 2 H), 1.40–1.34 (m, 2 H), 1.36 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.23 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 214.4 (C=S), 174.1 (C=O), 162.2 (C), 150.6 (C), 138.8 (CH_{Ar}), 121.5 (CH_{Ar}), 121.2 (CH_{Ar}), 69.6 (OCH_2CH_3), 51.3 (OCH_3), 50.8 (CHS), 35.0 (CH_2Ar), 34.1 ($CHSCH_2$), 33.9 ($OCCH_2$), 33.8 (CH_2CHS), 29.2 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 28.9 (CH_2), 26.6 (CH_2), 24.8 (CH_2), 13.7 (OCH_2CH_3).

MS (CI, NH_3): *m*/*z* = 446 $[M + H]^+$ (100%).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{21}H_{32}ClNO_3S_2$: 445.1512; found: 445.1505.

_S_-1-[(4-Chlorophenylsulfonylamino)methyl]-3-(6-chloro-2-pyridyl)propyl _O_-Ethyl Dithiocarbonate (31)

Following the general procedure using xanthate **25** (100 mg, 0.40 mmol) and *N*-allyl-4-chlorobenzenesulfonamide (372 mg, 1.61 mmol, 4 equiv) in DCE (0.4 mL) and requiring DLP (20 mol%) to go to completion. Flash chromatography (silica gel, PE–EtOAc, 8:2) afforded **31** (128 mg, 66%) as a light yellow oil.

IR: 2956, 1582, 1558, 1437, 1216, 1111, 1050 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.8 Hz, 2 H, CH_{Ar}), 7.53 (t, *J* = 8.0 Hz, 1 H, CH_{Ar}), 7.44 (d, *J* = 8.8 Hz, 2 H, CH_{Ar}), 7.13 (d, *J* = 8.0 Hz, 1 H, CH_{Ar}), 7.03 (d, *J* = 7.6 Hz, 1 H, CH_{Ar}), 5.62 (t, *J* = 6.4 Hz, 1 H, NH), 4.56 (q, *J* = 7.2 Hz, 2 H, OCH_2CH_3), 3.79 (ddd, J_1 = 6.0 Hz, J_2 = 8.8 Hz, J_3 = 14.8 Hz, 1 H, CHS), 3.27 (t, *J* = 6.0 Hz, 2 H, CH_2N), 2.93–2.86 (m, 1 H, CH_2Ar), 2.84–2.77 (m,

1 H, CH_2Ar), 2.22–2.14 (m, 1 H, CH_2CHS), 2.02–1.92 (m, 1 H, CH_2CHS), 1.36 (t, J = 7.2 Hz, 3 H, OCH$_2$CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.5 (C=S), 161.3 (C), 150.7 (C), 139.1 (CH_{Ar}), 139.0 (C), 138.4 (C), 129.3 (2 CH_{Ar}), 128.4 (2 CH_{Ar}), 121.9 (CH_{Ar}), 121.5 (CH_{Ar}), 70.3 (OCH$_2$CH$_3$), 49.9 (CHS), 46.0 (CH$_2$N), 34.3 (CH$_2$Ar), 30.2 (CH$_2$CHS), 13.6 (OCH$_2$$CH_3$).

MS (CI, NH_3): m/z = 479 $[M + H]^+$ (100%).

HRMS (EI): m/z $[M]^+$ calcd for $C_{18}H_{20}Cl_2N_2O_3S_3$: 478.0013; found: 477.9991.

S-1-(Acetoxymethyl)-3-(2-chloro-4-pyridyl)propyl *O*-Ethyl Dithiocarbonate (32)

Following the general procedure using xanthate **26** (100 mg, 0.40 mmol) and allyl acetate (162 mg, 1.61 mmol, 4 equiv) in MEK (0.4 mL) and requiring DLP (15 mol%) to go to completion. Flash chromatography (silica gel, PE–EtOAc, 9:1) afforded **32** (66 mg, 47%) as a light yellow oil, together with recovered starting xanthate (24 mg). The yield based on recovered starting xanthate was 56%.

IR: 2940, 1749, 1590, 1384, 1225, 1112, 1054 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (d, J = 5.2 Hz, 1 H, CH_{Ar}), 7.15 (br s, 1 H, CH_{Ar}), 7.03 (dd, J_1 = 1.2 Hz, J_2 = 4.8 Hz, 1 H, CH_{Ar}), 4.63 (q, J = 7.2 Hz, 2 H, OCH_2CH$_3$), 4.30 (dd, J_1 = 4.8 Hz, J_2 = 11.6 Hz, 1 H, CH$_2$OAc), 4.23 (dd, J_1 = 6.4 Hz, J_2 = 11.6 Hz, 1 H, CH$_2$OAc), 3.95–3.91 (m, 1 H, CHS), 2.86–2.79 (m, 1 H, CH_2Ar), 2.76–2.68 (m, 1 H, CH_2Ar), 2.12–2.03 (m, 1 H, CH_2CHS), 2.06 (s, 3 H, O=CCH$_3$), 2.01–1.88 (m, 1 H, CH_2CHS), 1.40 (t, J = 7.2 Hz, 3 H, OCH$_2$CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.4 (C=S), 170.5 (C=O), 153.1 (C), 151.7 (C), 149.6 (CH_{Ar}), 124.1 (CH_{Ar}), 122.5 (CH_{Ar}), 70.4 (OCH$_2$CH$_3$), 65.2 (CH$_2$OAc), 48.7 (CHS), 32.0 (CH$_2$Ar), 31.1 (CH$_2$CHS), 20.7 (Ac), 13.7 (OCH$_2$$CH_3$).

MS (CI, NH_3): m/z = 348 $[M + H]^+$ (100%).

HRMS (EI): m/z $[M]^+$ calcd for $C_{14}H_{18}ClNO_3S_2$: 347.0417; found: 347.0419.

S-3-(2-Chloro-4-pyridyl)-1-(trimethylsilyl)propyl *O*-Ethyl Dithiocarbonate (33)

Following the general procedure using xanthate **26** (100 mg, 0.40 mmol) and trimethyl(vinyl)silane (245 mg, 2.42 mmol, 6 equiv) in MEK (0.4 mL) and requiring DLP (20 mol%) to go to completion. Flash chromatography (silica gel, PE–Et$_2$O, 25:3) afforded **33** (98 mg, 70%) as a light yellow oil.

IR: 2956, 1589, 1548, 1385, 1219, 1111, 1050 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (d, J = 4.8 Hz, 1 H, CH_{Ar}), 7.12 (br s, 1 H, CH_{Ar}), 7.00 (dd, J_1 = 1.6 Hz, J_2 = 4.8 Hz, 1 H, CH_{Ar}), 4.63 (dq, J_1 = 1.2 Hz, J_2 = 7.2 Hz, 2 H, OCH_2CH$_3$), 3.17 (dd, J_1 = 4.0 Hz, J_2 = 10.0 Hz, 1 H, SiCHS), 2.84–2.76 (m, 1 H, CH_2Ar), 2.66 (ddd, J_1 = 6.0 Hz, J_2 = 11.2 Hz, J_3 = 16.8 Hz, 1 H, CH_2Ar), 2.11–2.02 (m, 1 H, CH_2CHS), 1.81–1.71 (m, 1 H, CH_2CHS), 1.40 (t, J = 7.2 Hz, 3 H, OCH$_2$CH_3), 0.10 [s, 9 H, Si(CH$_3$)$_3$].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 215.9 (C=S), 154.2 (C), 151.5 (C), 149.4 (CH_{Ar}), 124.1 (CH_{Ar}), 122.6 (CH_{Ar}), 70.4 (OCH$_2$CH$_3$), 36.5 (CHS), 33.5 (CH$_2$Ar), 31.7 (CH$_2$CHS), 13.8 (OCH$_2$$CH_3$), –2.6 [Si(CH$_3$)$_3$].

MS (CI, NH_3): m/z = 348 $[M + H]^+$ (100%).

HRMS (EI): m/z $[M]^+$ calcd for $C_{14}H_{22}ClNOS_2Si$: 347.0601; found: 347.0604.

S-3-(2-Chloro-4-pyridyl)-1-[(trimethylsilyl)methyl]propyl *O*-Ethyl Dithiocarbonate (34)

Following the general procedure using xanthate **26** (100 mg, 0.40 mmol) and allyltrimethylsilane (185 mg, 1.61 mmol, 4 equiv) in MEK (0.4 mL) and requiring DLP (15 mol%) to go to completion. Flash chromatography (silica gel, PE–Et$_2$O, 25:3) afforded **34** (131 mg, 84%) as a light yellow oil.

IR: 2954, 1590, 1385, 1216, 1112, 1053 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, J = 5.2 Hz, 1 H, CH_{Ar}), 7.11 (s, 1 H, CH_{Ar}), 7.00 (dd, J_1 = 1.2 Hz, J_2 = 5.2 Hz, 1 H, CH_{Ar}), 4.61 (dq, J_1 = 1.2 Hz, J_2 = 7.2 Hz, 2 H, OCH_2CH$_3$), 3.85–3.81 (m, 1 H, CHS), 2.73–2.68 (m, 2 H, CH_2Ar), 2.00–1.93 (m, 2 H, CH_2CHS), 1.38 (t, J = 7.2 Hz, 3 H, OCH$_2$CH_3), 1.10 (dd, J_1 = 7.6 Hz, J_2 = 15.2 Hz, 1 H, CH$_2$Si), 1.02 (dd, J_1 = 8.0 Hz, J_2 = 15.2 Hz, 1 H, CH$_2$Si), 0.03 [s, 9 H, Si(CH$_3$)$_3$].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.8 (C=S), 153.8 (C), 151.5 (C), 149.4 (CH_{Ar}), 124.0 (CH_{Ar}), 122.6 (CH_{Ar}), 69.6 (OCH$_2$CH$_3$), 47.8 (CHS), 37.5 (CH$_2$CHS), 31.9 (CH$_2$Ar), 22.8 (CH$_2$Si), 13.7 (OCH$_2$$CH_3$), –0.8 [Si(CH$_3$)$_3$].

MS (CI, NH_3): m/z = 362 $[M + H]^+$ (100%).

HRMS (EI): m/z $[M]^+$ calcd for $C_{15}H_{24}ClNOS_2Si$: 361.0757; found: 361.0745.

Methyl 12-(2-Chloro-4-pyridyl)-10-(ethoxythiocarbonylsulfanyl)dodecanoate (35)

Following the general procedure using xanthate **26** (100 mg, 0.40 mmol) and methyl undec-10-enoate (320 mg, 1.61 mmol, 4 equiv) in DCE (0.4 mL) and requiring DLP (20 mol%) to go to completion. Flash chromatography (silica gel, PE–EtOAc, 9:1) afforded **35** (134 mg, 74%) as a light yellow oil.

IR: 2931, 2857, 1741, 1590, 1548, 1461, 1384, 1216, 1113, 1054 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, J = 5.2 Hz, 1 H, CH_{Ar}), 7.10 (s, 1 H, CH_{Ar}), 6.99 (dd, J_1 = 1.2 Hz, J_2 = 5.2 Hz, 1 H, CH_{Ar}), 4.58 (q, J = 7.2 Hz, 2 H, OCH_2CH$_3$), 3.71–3.64 (m, 1 H, CHS), 3.59 (s, 3 H, OCH$_3$), 2.74–2.62 (m, 2 H, CH_2Ar), 2.23 (t, J = 7.2 Hz, 2 H, O=CCH$_2$), 1.98–1.87 (m, 2 H, CH_2CHS), 1.66–1.60 (m, 2 H, CH_2CHS), 1.59–1.51 (m, 2 H), 1.37–1.33 (m, 2 H), 1.35 (t, J = 7.2 Hz, 3 H, OCH$_2$CH_3), 1.22 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 214.0 (C=S), 174.0 (C=O), 153.8 (C), 151.4 (C), 149.3 (CH_{Ar}), 124.0 (CH_{Ar}), 122.5 (CH_{Ar}), 69.7 (OCH$_2$CH$_3$), 51.2 (OCH$_3$), 50.5 (CHS), 34.6 (CH$_2$CHS), 34.0 (CH$_2$CHS), 33.8 (O=CCH$_2$), 32.0 (CH$_2$Ar), 29.1 (CH$_2$), 29.0 (CH$_2$), 28.9 (CH$_2$), 28.8 (CH$_2$), 26.5 (CH$_2$), 24.7 (CH$_2$), 13.6 (OCH$_2$$CH_3$).

MS (CI, NH_3): m/z = 446 $[M + H]^+$ (100%).

HRMS (EI): m/z $[M]^+$ calcd for $C_{21}H_{32}ClNO_3S_2$: 445.1512; found: 445.1498.

S-3-(2-Chloro-4-pyridyl)-1-[(diethoxyphosphoryl)methyl]propyl *O*-Ethyl Dithiocarbonate (36)

Following the general procedure using xanthate **26** (100 mg, 0.40 mmol) and allyl diethylphosphonate (287 mg, 1.61 mmol, 4 equiv) in DCE (0.4 mL) and requiring DLP (20 mol%) to go to completion. Evaporation of the excess of alkene followed by flash chromatography (silica gel, EtOAc–toluene, 3:2) afforded **36** (112 mg, 66%) as a light yellow oil.

IR: 2984, 1590, 1584, 1388, 1222, 1111, 1051 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, J = 5.2 Hz, 1 H, CH_{Ar}), 7.13 (s, 1 H), 7.02 (dd, J_1 = 1.2 Hz, J_2 = 5.2 Hz, 1 H, CH_{Ar}), 4.59 (q, J = 7.2 Hz, 2 H, OCH_2CH$_3$), 4.08–4.00 (m, 4 H, 2 CH$_2$OP), 3.95–3.85 (m, 1 H, CHS), 2.79 (ddd, J_1 = 4.8 Hz, J_2 = 9.6 Hz, J_3 = 14.4 Hz, 1 H, CH_2Ar), 2.66 (ddd, J_1 = 7.2 Hz, J_2 = 9.2 Hz, J_3 = 14.0 Hz, 1 H, CH_2Ar), 2.41–2.29 (m, 2 H, CH$_2$P, CH_2CHS), 2.15–2.05 (m, 1 H, CH$_2$P), 2.03–1.93 (m, 1 H, CH_2CHS), 1.36 (t, J = 7.2 Hz, 3 H, OCH$_2$CH_3), 1.25 (t, J = 7.2 Hz, 6 H, 2 CH_3CH$_2$OP).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.2 (C=S), 153.2 (C), 151.5 (C), 149.4 (CH_{Ar}), 124.1 (CH_{Ar}), 122.6 (CH_{Ar}), 70.0 (OCH_2CH_3), 61.8 (t, *J* = 6.3 Hz, CH_2OP), 44.7 (CHS), 33.4 (d, *J* = 3.0 Hz, CH_2CHS), 31.7 (CH_2Ar), 31.5 (d, *J* = 135.5 Hz, CH_2P), 16.3 (d, *J* = 6.0 Hz, 2 CH_3CH_2OP), 13.6 (OCH_2CH_3).

MS (CI, NH_3): *m*/*z* = 426 $[M + H]^+$ (100%).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{25}ClNO_4PS_2$: 425.0651; found: 425.0642.

S-(2-Chloro-3-pyridyl)methyl *O*-Ethyl Dithiocarbonate (39)

2-Chloro-3-methylpyridine (1.0 g, 7.83 mmol), NBS (1.4 g, 7.83 mmol), and Bz_2O_2 (180 mg) in CCl_4 (23 mL) were refluxed for 3 h under N_2. The succinimide was removed by filtration and to the filtrate was added CH_2Cl_2. The organic layer was washed with 5% aq NaOH and H_2O, dried (anhyd $MgSO_4$), filtered, and evaporated under reduced pressure. The residue was purified by flash chromatography (silica gel, PE–Et_2O, 25:3) to yield 3-(bromomethyl)-2-chloropyridine (800 mg, 49%) as a yellow oil.

To a soln of 3-(bromomethyl)-2-chloropyridine (800 mg, 3.87 mmol) in acetone (11 mL) was added portionwise potassium *O*-ethyl xanthate (681 mg, 4.26 mmol) at 0 °C under N_2. The mixture was stirred at r.t. until complete consumption of the starting material. Acetone was evaporated under reduced pressure and the residue was taken up in CH_2Cl_2, washed with sat. aq NH_4Cl and H_2O, dried (anhyd $MgSO_4$), filtered, and evaporated under reduced pressure. The residue was purified by flash chromatography (silica gel, PE–Et_2O, 6:1) to yield **39** (850 mg, 88%) as a yellow oil.

IR: 2987, 1561, 1409, 1220, 1112, 1051 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (dd, J_1 = 2.0 Hz, J_2 = 4.8 Hz, 1 H, CH_{Ar}), 7.81 (dd, J_1 = 2.0 Hz, J_2 = 7.6 Hz, 1 H, CH_{Ar}), 7.17 (dd, J_1 = 4.4 Hz, J_2 = 7.2 Hz, 1 H, CH_{Ar}), 4.60 (q, *J* = 7.2 Hz, 2 H, OCH_2CH_3), 4.41 (s, 2 H, CH_2S), 1.36 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.8 (C=S), 152.0 (C), 148.4 (CH_{Ar}), 139.2 (CH_{Ar}), 130.9 (C), 122.4 (CH_{Ar}), 70.4 (OCH_2CH_3), 37.1 (CH_2S), 13.6 (OCH_2CH_3).

MS (CI, NH_3): *m*/*z* = 248 $[M + H]^+$ (100%).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_9H_{10}ClNOS_2$: 246.9892; found: 246.9888.

S-1-[(*tert*-Butoxycarbonylamino)methyl]-3-(2-chloro-3-pyridyl)propyl *O*-Ethyl Dithiocarbonate (40)

Following the general procedure using xanthate **39** (200 mg, 0.81 mmol) and *N*-(*tert*-butoxycarbonyl)allylamine (507 mg, 3.23 mmol, 4 equiv) in DCE (0.8 mL) and requiring DLP (35 mol%) to go to completion. Flash chromatography (silica gel, PE–EtOAc, 8:2) afforded **40** (176 mg, 54%) as a yellow oil.

IR: 3455, 2978, 2931, 1720, 1503, 1410, 1222, 1168, 1111, 1055 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (dd, J_1 = 1.6 Hz, J_2 = 4.8 Hz, 1 H, CH_{Ar}), 7.53 (d, *J* = 7.2 Hz, 1 H, CH_{Ar}), 7.12 (dd, J_1 = 4.8 Hz, J_2 = 7.6 Hz, 1 H, CH_{Ar}), 4.95–4.93 (m, 1 H, NH), 4.60 (q, *J* = 7.2 Hz, 2 H, OCH_2CH_3), 3.82–3.76 (m, 1 H, CHS), 3.55–3.49 (m, 1 H, NCH_2), 3.40–3.33 (m, 1 H, NCH_2), 2.94–2.79 (m, 2 H, CH_2Ar), 2.07–1.99 (m, 1 H, CH_2CHS), 1.92–1.83 (m, 1 H, CH_2CHS), 1.38 [s, 9 H, $C(CH_3)_3$], 1.37 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.0 (C=S), 155.8 (C=O), 151.0 (C), 147.4 (CH_{Ar}), 139.0 (CH_{Ar}), 135.1 (C), 122.5 (CH_{Ar}), 79.4 (C), 70.1 (OCH_2CH_3), 51.2 (CHS), 43.3 (CH_2N), 30.6 (CH_2CHS), 30.5 (CH_2Ar), 28.2 (3 CH_3), 13.6 (OCH_2CH_3).

MS (CI, NH_3): *m*/*z* (%) = 405 $[M + H]^+$ (80), 349 $[M + NH_4 - t\text{-Bu}]^+$ (100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{25}ClN_2O_3S_2$: 404.0995; found: 404.1007.

S-3-(2-Chloro-3-pyridyl)-1-[(trimethylsilyl)methyl]propyl *O*-Ethyl Dithiocarbonate (41)

Following the general procedure using xanthate **39** (200 mg, 0.81 mmol) and allyltrimethylsilane (369 mg, 3.23 mmol, 4 equiv) in DCE (0.8 mL), and requiring DLP (40 mol%) to go to completion. Flash chromatography (silica gel, PE–Et_2O, 25:3) afforded **41** (171 mg, 58%) as a yellow oil, together with recovered starting xanthate (21 mg). The yield based on recovered starting xanthate was 65%.

IR: 2954, 2901, 1560, 1447, 1409, 1250, 1214, 1112, 1055 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (dd, J_1 = 2.0 Hz, J_2 = 4.8 Hz, 1 H, CH_{Ar}), 7.51 (d, J_1 = 2.0 Hz, J_2 = 7.6 Hz, 1 H, CH_{Ar}), 7.14 (dd, J_1 = 4.8 Hz, J_2 = 7.2 Hz, 1 H, CH_{Ar}), 4.61 (q, *J* = 7.2 Hz, 2 H, OCH_2CH_3), 3.83 (ddd, J_1 = 4.8 Hz, J_2 = 8.0 Hz, J_3 = 14.8 Hz, 1 H, CHS), 2.88–2.78 (m, 2 H, CH_2Ar), 2.09–2.00 (m, 1 H, CH_2CHS), 1.96–1.87 (m, 1 H, CH_2CHS), 1.39 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.15 (dd, J_1 = 6.8 Hz, J_2 = 14.8 Hz, 1 H, CH_2Si), 1.06 (dd, J_1 = 8.0 Hz, J_2 = 14.8 Hz, 1 H, CH_2Si), 0.03 [s, 9 H, $Si(CH_3)_3$].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 214.1 (C=S), 151.1 (C), 147.3 (CH_{Ar}), 138.9 (CH_{Ar}), 135.5 (C), 122.5 (CH_{Ar}), 69.5 (OCH_2CH_3), 48.1 (CHS), 36.1 (CH_2CHS), 30.5 (CH_2Ar), 23.0 (CH_2Si), 13.7 (OCH_2CH_3), –0.8 [$Si(CH_3)_3$].

MS (CI, NH_3): *m*/*z* = 362 $[M + H]^+$ (100%);

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{24}ClNOS_2Si$: 361.0757; found: 361.0754.

S-3-(2-Chloro-3-pyridyl)-1-(cyanomethyl)propyl *O*-Ethyl Dithiocarbonate (42)

Following the general procedure using xanthate **39** (200 mg, 0.81 mmol) and allyl cyanide (216 mg, 3.23 mmol, 4 equiv) in DCE (0.8 mL) and requiring DLP (45 mol%) to go to completion. Flash chromatography (silica gel, PE–EtOAc, 8:2) afforded **42** (120 mg, 47%) as a yellow oil, together with recovered starting xanthate (30 mg). The yield based on recovered starting xanthate was 55%.

IR: 2985, 2928, 1561, 1411, 1226, 1112, 1054 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (dd, J_1 = 2.0 Hz, J_2 = 4.8 Hz, 1 H, CH_{Ar}), 7.53 (d, J_1 = 2.0 Hz, J_2 = 7.6 Hz, 1 H, CH_{Ar}), 7.16 (dd, J_1 = 4.8 Hz, J_2 = 7.6 Hz, 1 H, CH_{Ar}), 4.63 (q, *J* = 7.2 Hz, 2 H, OCH_2CH_3), 3.89–3.82 (m, 1 H, CHS), 2.99–2.92 (m, 1 H, CH_2Ar), 2.91–2.89 (m, 2 H, $NCCH_2$), 2.81 (ddd, J_1 = 6.0 Hz, J_2 = 9.6 Hz, J_3 = 16.0 Hz, 1 H, CH_2Ar), 2.22–2.13 (m, 1 H, CH_2CHS), 2.08 (ddd, J_1 = 5.2 Hz, J_2 = 10.0 Hz, J_3 = 19.6 Hz, 1 H, CH_2CHS), 1.40 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 211.7 (C=S), 151.0 (C), 147.8 (CH_{Ar}), 138.8 (CH_{Ar}), 134.1 (C), 122.7 (CH_{Ar}), 116.8 (CN), 70.5 (OCH_2CH_3), 45.8 (CHS), 31.5 (CH_2CHS), 30.4 (CH_2Ar), 23.8 (CH_2CN), 13.6 (OCH_2CH_3).

MS (CI, NH_3): *m*/*z* = 315 $[M + H]^+$ (100%).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{15}ClN_2OS_2$: 314.0314; found: 314.0314.

2-[(*tert*-Butoxycarbonylamino)methyl]-3,4-dihydro-2*H*-thiopyrano[2,3-*b*]pyridine (43)

To a soln of xanthate **40** (110 mg, 0.27 mmol) in MeOH (1.5 mL) was added KOH (61 mg, 1.10 mmol) at r.t. under N_2. The mixture was stirred at r.t. for 1 h and MeOH was evaporated under reduced pressure. The residue was dissolved in DMF (1.2 mL), $NaBH_4$ (10 mg, 0.27 mmol) was added and the mixture was stirred at 100 °C for 1 h under N_2. CH_2Cl_2 and H_2O were added and the organic layer was separated, washed with H_2O, dried (anhyd $MgSO_4$), filtered, and evaporated under reduced pressure. The residue was purified by

flash chromatography (silica gel, PE–EtOAc, 7:3) to yield **43** (38 mg, 50%) as a white powder; mp 131–132 °C.

IR: 3458, 2975, 2928, 1720, 1502, 1407, 1367, 1248, 1168, 1087 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.24 (dd, J_1 = 1.2 Hz, J_2 = 4.4 Hz, 1 H, CH_{Ar}), 7.26 (d, J = 6.8 Hz, 1 H, CH_{Ar}), 6.90 (dd, J_1 = 4.8 Hz, J_2 = 7.6 Hz, 1 H, CH_{Ar}), 5.00–4.98 (m, 1 H, NH), 3.62–3.58 (m, 1 H, CHS), 3.53–3.46 (m, 1 H, NCH_2), 3.35–3.28 (m, 1 H, NCH_2), 2.91–2.85 (m, 1 H, CH_2Ar), 2.83–2.76 (m, 1 H, CH_2Ar), 2.24–2.18 (m, 1 H, CH_2CHS), 1.84 (ddd, J_1 = 4.0 Hz, J_2 = 9.2 Hz, J_3 = 18.0 Hz, 1 H, CH_2CHS), 1.43 [s, 9 H, $C(CH_3)_3$].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.2 (C), 155.9 (C=O), 147.7 (CH_{Ar}), 136.6 (CH_{Ar}), 129.9 (C), 119.2 (CH_{Ar}), 79.6 (C), 45.1 (CH_2N), 43.1 (CHS), 28.3 (3 CH_3), 27.8 (CH_2Ar), 25.8 (CH_2CHS).

MS (CI, NH_3): m/z = 281 $[M + H]^+$ (100%).

HRMS (EI): m/z $[M]^+$ calcd for $C_{14}H_{20}N_2O_2S$: 280.1246; found: 280.1256.

3-(Benzylamino)-5-(2-chloro-3-pyridyl)pentanenitrile (45)

To a stirred soln of xanthate **42** (0.15 g, 0.477 mmol) in $CDCl_3$ (5 mL) was added DBU (0.214 mL, 1.43 mmol) at r.t. The mixture was stirred at r.t. for 5 h and then diluted with CH_2Cl_2, washed with sat. $NaHCO_3$ and H_2O. The organic layer was dried (anhyd $MgSO_4$), filtered, and evaporated under reduced pressure. The residue was purified by flash chromatography (silica gel, PE–EtOAc, 6:4) to yield **44** (75 mg, 82%) as a mixture of *Z*/*E* isomers in a ratio 1:1. A soln of the latter (0.185 g, 0.96 mmol) and $BnNH_2$ (1.05 mL, 10 equiv) was heated at 100 °C until consumption of the starting material. After evaporation of the excess of $BnNH_2$ under a N_2 flow, the residue was purified by flash chromatography (silica gel, PE–EtOAc, 6:4) to yield **45** (224 mg, 78%) as a yellow oil.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.30 (dd, J = 1.9 Hz, J = 4.7 Hz, 1 H, CH_{Ar}), 7.53 (dd, J = 1.9 Hz, J = 7.5 Hz, 1 H, CH_{Ar}), 7.36 (m, 5 H, CH_{Ar}), 7.20 (dd, J = 4.8 Hz, J = 7.5 Hz, 1 H, CH_{Ar}), 3.96 (d, J = 13.1 Hz, 1 H, NCH_2Ph), 3.81 (d, J = 13.1 Hz, 1 H, NCH_2Ph), 2.97 (m, 2 H, CH, CH_2Ar), 2.82 (m, 1 H, CH_2Ar), 2.69 (dd, J = 5.7 Hz, J = 16.8 Hz, 1 H, CH_2CN), 2.56 (dd, J = 4.7 Hz, J = 16.8 Hz, 1 H, CH_2CN), 1.94 (m, 2 H, CH_2), 1.51 (br s, 1 H, NH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.0 (C_q), 147.5 (CH_{Ar}), 139.4 (C_q), 138.8, 128.5, 128.0, 127.3, 122.6 (CH_{Ar}), 117.6 (CN), 52.7 (CH), 50.6 (CH_2Ph), 33.8, 29.4, 22.8 (3 CH_2).

MS (CI, NH_3): m/z = 300 $[M + H]^+$.

(1-Benzyl-1,2,3,4-tetrahydro-1,8-naphthyridin-2-yl)acetonitrile (46)

A soln of **45** (0.224 g, 0.75 mmol) in xylene (1 mL) was refluxed for 6 h under N_2. After evaporation of the solvent under an N_2 flow, the residue was purified by flash chromatography (silica gel, PE–EtOAc, 7:3) to yield **46** (165 mg, 84%) as a yellow oil.

IR (CCl_4): 2249 (CN), 1593, 1570 cm^{-1} (C=N).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, J = 3.5 Hz, 1 H, CH_{Ar}), 7.33 (m, 6 H, CH_{Ar}), 6.64 (dd, J = 4.9 Hz, J = 7.2 Hz, 1 H, CH_{Ar}), 5.56 (d, J = 15.8 Hz, 1 H, NCH_2Ph), 4.53 (d, J = 15.8 Hz, 1 H, NCH_2Ph), 3.91 (m, 1 H, CH), 2.88 (m, 2 H, CH_2Ar), 2.64 (dd, J = 4.8 Hz, J = 16.8 Hz, 1 H, CH_2CN), 2.47 (dd, J = 9.4 Hz, J = 16.9 Hz, 1 H, CH_2CN), 2.20 (m, 1 H, CHCH_2), 1.97 (m, 1 H, CHCH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.9 (C_{Ar}), 146.4 (CH_{Ar}), 138.7 (C_{Ar}), 136.4 (CH_{Ar}), 128.7 (2 CH_{Ar}), 127.4 (2 CH_{Ar}), 127.2 (CH_{Ar}), 117.6, 115.4 (C_q, CN), 113.1 (CH_{Ar}), 52.2 (CH), 49.5 (NCH_2Ph), 29.9, 22.7, 20.6 (3 CH_2).

MS (CI, NH_3): m/z = 264 $[M + H]^+$.

HRMS (EI): m/z $[M]^+$ calcd for $C_{17}H_{17}N_3$: 263.1422; found: 263.1419.

6-(Benzoyloxy)pyridine-2-methanol (47)

To a soln of 2,6-pyridinedimethanol (1 g, 7.19 mmol) in anhyd pyridine (1 mL) was added BzCl (0.84 mL, 7.19 mmol) at 0 °C. After extraction with CH_2Cl_2, washing with sat. $NaHCO_3$ and H_2O, the residue was column chromatographed (silica gel) to afford monobenzoate **47** (50% yield) as a white solid, which was used without further purification, and dibenzoate **48** (22% yield).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.12 (dd, J = 1.2 Hz, J = 8.4 Hz, 2 H, CH_{Ar}), 7.72 (t, J = 7.7 Hz, 1 H, CH_{Ar}), 7.60 (t, J = 7.4 Hz, 1 H, CH_{Ar}), 7.47 (t, J = 7.7 Hz, 2 H, CH_{Ar}), 7.36 (d, J = 7.7 Hz, 1 H, CH_{Ar}), 7.20 (d, J = 7.7 Hz, 1 H, CH_{Ar}), 5.49 (s, 2 H, CH_2OCOAr), 4.78 (s, 2 H, CH_2OH), 3.87 (s, 1 H, OH).

***S*-{6-[(Benzoyloxy)methyl]-2-pyridyl}methyl *O*-Ethyl Dithiocarbonate (49)**

To a mixture of monobenzoate **47** (0.8 g, 3.28 mmol) and PPh_3 (1.1 equiv, 0.95g), dissolved in anhyd CH_2Cl_2 (15 mL), was added at 0 °C, under N_2 and portionwise, CBr_4 (1.31 g, 1.2 equiv). The mixture was then filtered through a column (silica gel, gradient PE–EtOAc) to afford the bromo derivative (95% yield) as a white solid.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.12 (dd, J = 1.0 Hz, J = 8.1 Hz, 2 H, CH_{Ar}), 7.73 (t, J = 7.8 Hz, 1 H, CH_{Ar}), 7.59 (t, J = 7.4 Hz, 1 H, CH_{Ar}), 7.47 (t, J = 7.7 Hz, 2 H, CH_{Ar}), 7.40 (d, J = 7.7 Hz, 1 H, CH_{Ar}), 7.37 (d, J = 7.8 Hz, 1 H, CH_{Ar}), 5.48 (s, 2 H, CH_2OCOAr), 4.56 (s, 2 H, CH_2Br).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.2 (C=O), 156.7, 156.1 (C_{Ar}), 137.9, 133.3 (CH_{Ar}), 129.9 (CH_{Ar}, C_{Ar}), 128.5 (CH_{Ar}), 122.7, 120.8 (CH_{Ar}), 67.0 (CH_2OCOAr), 33.7 (CH_2Br).

MS (CI, NH_3): m/z = 306, 308 $[M + H]^+$.

To a soln of the bromide derivative (1 g, 3.26 mmol) in acetone (7.5 mL) was added under N_2 and portionwise potassium *O*-ethyl xanthate (0.661 g, 1.1 equiv). After addition of H_2O, evaporation of acetone and extraction with CH_2Cl_2, the organic layers were dried ($MgSO_4$), filtered, and evaporated under reduced pressure to give a residue, which was purified by column chromatography (silica gel, gradient PE–EtOAc, 9:1 to 8:2) to give pure **49** (82% yield). Recrystallization (Et_2O–PE) afforded off-white crystals; mp 40–41 °C (PE–Et_2O).

IR (CCl_4): 1727 (OCOAr), 1588 (C=N), 1219, 1055 cm^{-1} (C–O, CS).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, J = 8.4 Hz, 2 H, CH_{Ar}), 7.67 (t, J = 7.8 Hz, 1 H, CH_{Ar}), 7.59 (t, J = 7.4 Hz, 1 H, CH_{Ar}), 7.47 (t, J = 7.6 Hz, 2 H, CH_{Ar}), 7.37 (d, J = 7.8 Hz, 1 H, CH_{Ar}), 7.34 (d, J = 7.7 Hz, 1 H, CH_{Ar}), 5.47 (s, 2 H, CH_2OCOAr), 4.64 (qd, J = 7.1 Hz, 2 H, OC$H_2$$CH_3$), 4.53 (s, 2 H, CH_2S), 1.40 (td, J = 7.1 Hz, 3 H, OCH_2CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.8 (C=S), 166.2 (C=O), 156.04, 156.03 (2 C_{Ar}), 137.5, 133.3 (2 CH_{Ar}), 129.9 (C_qAr, 2 CH_{Ar}), 129.8 (2 CH_{Ar}), 122.4, 120.2 (2 CH_{Ar}), 70.3 (OCH_2CH_3), 67.1 (CH_2OCOAr), 41.9 (CH_2S), 13.8 (OCH_2CH_3).

MS (CI, NH_3): m/z = 348 $[M + H]^+$.

***S*-1-(Acetoxymethyl)-3-{6-[(benzoyloxy)methyl]-2-pyridyl}propyl *O*-Ethyl Dithiocarbonate (50)**

Following the general procedure using xanthate (0.5 mmol, 1 equiv) and allyl acetate (4 equiv) in DCE (0.5 mL). After the addition of DLP (2 × 5 mol%), further alkene (2 equiv) and DLP (5 mol%) were added. Column chromatography (silica gel, gradient PE–EtOAc, 10:0 to 8:2) afforded **50** (52% yield) as a colorless oil.

IR (CCl_4): 1731 (C=O), 1588 (C=N), 1225, 1055 cm^{-1} (C–O, CS).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 7.3 Hz, 2 H, CH_{Ar}), 7.66 (t, *J* = 7.7 Hz, 1 H, CH_{Ar}), 7.61 (t, *J* = 7.1 Hz, 1 H, CH_{Ar}), 7.49 (t, *J* = 7.8 Hz, 2 H, CH_{Ar}), 7.31 (d, *J* = 7.7 Hz, 1 H, CH_{Ar}), 7.13 (d, *J* = 7.7 Hz, 1 H, CH_{Ar}), 5.49 (s, 2 H, CH_2OCOAr), 4.66 (q, *J* = 7.1 Hz, 2 H, OCH_2CH_3), 4.36 (dd, *J* = 5.1 Hz, *J* = 11.5 Hz, 1 H), 4.31 (dd, *J* = 5.9 Hz, *J* = 11.5 Hz, 1 H, CH_2OAc), 4.06 (m, 1 H, CHS), 3.06 (m, 1 H, CH_2Ar), 2.96 (m, 1 H, CH_2Ar), 2.31 (m, 1 H, CHCHS), 2.09 H, (s + m, 4 H, CHCHS, CH_3CO), 1.43 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.1 (C=S), 170.7 ($OCOCH_3$), 166.2 (OCOAr), 160.3, 155.6 (2 C_qAr), 137.3, 133.2 (2 CH_{Ar}), 129.9 (C_qAr), 129.8, 128.5 (4 CH_{Ar}), 122.1, 119.1 (2 CH_{Ar}), 70.2 (OCH_2CH_3), 67.2 (CH_2OCOAr), 65.6 (CH_2OCOCH_3), 49.0 (CHS), 35.2 (CH_2Ar), 30.5 (CH_2CHS), 20.8 (CH_3CO), 13.8 (OCH_2CH_3).

MS (CI, NH_3): *m*/*z* = 448 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{22}H_{25}NO_5S_2$: 447.1174; found: 447.1173.

S-3-{6-[(Benzoyloxy)methyl]-2-pyridyl}-1-(cyanomethyl)propyl *O*-Ethyl Dithiocarbonate (51)

Following the general procedure using xanthate (0.5 mmol, 1 equiv) and allyl cyanide (3 equiv) in MEK (0.5 mL). After the addition of DLP (3 × 5 mol%), further alkene (3 equiv) and DLP (3 × 5 mol%) were added. Column chromatography (silica gel, PE–EtOAc, 10:0 to 7:3) afforded **51** (34% yield, 50% based on recovered starting material) as a colorless oil.

IR (CCl_4): 2250 (CN), 1726 (COAr), 1589 (C=N), 1223, 1054 cm^{-1} (C–O, CS).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (dd, *J* = 1.3 Hz, *J* = 8.3 Hz, 2 H, CH_{Ar}), 7.64 (t, *J* = 7.7 Hz, 1 H, CH_{Ar}), 7.59 (br t, *J* = 7.4 Hz, 1 H, CH_{Ar}), 7.47 (t, *J* = 7.7 Hz, 2 H, CH_{Ar}), 7.29 (d, *J* = 7.7 Hz, 1 H, CH_{Ar}), 7.11 (d, *J* = 7.7 Hz, 1 H, CH_{Ar}), 5.46 (s, 2 H, CH_2OCOAr), 4.64 (q, *J* = 7.1 Hz, 2 H, OCH_2CH), 3.95 (m, 1 H, CHS), 2.97 (m + t, 4 H, CH_2Ar, CH_2CN), 2.36 (m, 1 H, CH_2CHS), 2.21 (m, 1 H, CH_2CHS), 1.42 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.3 (C=S), 166.2 (OCOAr), 159.5, 155.7 (2 C_{Ar}), 137.3, 133.2 (2 CH_{Ar}), 129.9 (C_{Ar}), 129.8, 128.5 (4 CH_{Ar}), 122.1, 119.3 (2 CH_{Ar}), 117.1 (CN), 70.4 (OCH_2CH_3), 67.2 (CH_2OCOAr), 45.9 (CHS), 34.8, 31.8 (CH_2Ar, CH_2CN), 23.9 (CH_2CHS), 13.8 (OCH_2CH_3).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{21}H_{22}N_2O_3S_2$: 414.1072; found: 414.1068.

O,*O*′-Diethyl *S*,*S*′-(Pyridine-2,6-diyldimethanediyl) Bis(dithiocarbonate) (52)

To a mixture of 2,6-pyridinedimethanol (0.25 g, 1.79 mmol) and PPh_3 (1.13 g, 2.4 equiv) in anhyd CH_2Cl_2 (15 mL) was added at 0 °C, under N_2 and portionwise, CBr_4 (1.43 g, 2.4 equiv). The mixture was then filtered through a column (silica gel, gradient PE–EtOAc) to afford the known 2,6-bis(bromomethyl)pyridine (70% yield) as a white solid.

To a soln of 2,6-bis(bromomethyl)pyridine (1.26 mmol) in acetone (2.5 mL) was added under N_2 and portionwise potassium *O*-ethyl xanthate (0.44 g, 2.2 equiv). The mixture was stirred at r.t. until consumption of the starting material. H_2O was then added and the acetone evaporated to give the pure **52** (91% yield) as a pale yellow oil.

IR (CCl_4): 1574 (C=N), 1217, 1054 cm^{-1} (C–O, CS).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (t, *J* = 7.8 Hz, 1 H, CH_{Ar}), 7.31 (d, *J* = 7.7 Hz, 2 H, 2 CH_{Ar}), 4.65 (qd, *J* = 7.1 Hz, 4 H, 2 OCH_2CH_3), 4.50 (s, 4 H, 2 CH_2S), 1.41 (td, *J* = 7.1 Hz, 6 H, 2 OCH_2CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.7 (C=S), 156.0 (C_{Ar}), 137.3 (CH_{Ar}), 121.8 (CH_{Ar}), 70.3 (OCH_2CH_3), 41.9 (CH_2S), 13.8 (OCH_2CH_3).

MS (CI, NH_3): *m*/*z* = 348 $[M + H]^+$.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{17}NO_2S_2$: 347.0142; found: 347.0144.

S-1-(Cyanomethyl)-3-{6-[(ethoxythiocarbonylsulfanyl)methyl]-2-pyridyl}propyl *O*-Ethyl Dithiocarbonate (54) and Diaddition Product 53

Following the general procedure using xanthate (0.57 mmol, 1 equiv) and allyl cyanide (6 equiv) in EtOAc (0.3 mL). After the addition of DLP (3 × 5 mol%), further alkene (6 equiv) and DLP (3 × 5 mol%) were added. Chromatography (gradient PE–Et_2O, 10:0 to 8:2) furnished the monoaddition product **54** (36% yield, 54% based on recovered starting material) as a colorless oil and the diaddition product **53** (8% yield, 11% based on recovered starting material) as an oil.

Monoaddition Product 54

IR (CCl_4): 2251 (CN), 1584 (C=N), 1220, 1051 cm^{-1} (C–O, CS).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (t, *J* = 7.7 Hz, 1 H, CH_{Ar}), 7.25 (d, *J* = 7.7 Hz, 1 H, CH_{Ar}), 7.04 (d, *J* = 7.7 Hz, 1 H), 4.64 (m, 4 H, 2 OCH_2CH_3), 4.49 (s, 2 H, CH_2S), 3.94 (m, 1 H, CHS), 2.95 (m, 4 H, CH_2CN, CH_2Ar), 2.33 (m, 1 H, CH_2CHS), 2.19 (m, 1 H, CH_2CHS), 1.41 (2 td, *J* = 7.1 Hz, 6 H, 2 OCH_2CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.8, 212.2 (2 C=S), 159.6, 155.6 (2 C_{Ar}), 137.2 (CH_{Ar}), 121.6, 120.9 (2 CH_{Ar}), 117.2 (CN), 70.4, 70.2 (OCH_2CH_3), 45.8 (CHS), 42.0 (CH_2S), 34.7, 31.7 (CH_2Ar, CH_2CN), 23.9 (CH_2CHS), 13.8, 13.7 (OCH_2CH_3).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{22}N_2O_2S_4$: 414.0564; found: 414.0567

Diaddition Product 53

IR (CCl_4): 2249 (C≡N), 1583 (C=N), 1220, 1052 cm^{-1} (C–O, CS).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (t, *J* = 7.7 Hz, 1 H, CH_{Ar}), 6.99 (d, *J* = 7.7 Hz, 2 H, 2 CH_{Ar}), 4.65 (q, *J* = 7.1 Hz, 4 H, 2 OCH_2CH_3), 3.95 (m, 2 H, CHS), 2.96 (m, 8 H, 4 CH_2), 2.36 (m, 2 H, 2 CH_2CHS), 2.20 (m, 2 H, 2 CH_2CHS), 1.43 (t, *J* = 7.1 Hz, 6 H, 2 OCH_2CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.6, 212.5 (C=S), 159.5 (2 C_{Ar}), 137.2 (2 CH_{Ar}), 120.9 (2 CH_{Ar}), 117.3 (2 C≡N), 70.1 (2 OCH_2CH_3), 46.1, 46.0 (2 CHS), 35.0, 34.9 (2 CH_2), 31.8 (2 CH_2), 23.9 (2 CH_2), 13.9 (2 OCH_2CH_3).

HRMS (EI): *m*/*z* $[M - CSOCH_2CH_3]^+$ calcd for $C_{18}H_{22}N_3OS_3$: 392.0925; found: 392.0926.

5-{6-[2-Acetoxy-2-(ethoxythiocarbonylsulfanyl)propyl]-2-pyridyl}-2-(ethoxythiocarbonylsulfanyl)pentanenitrile (55)

Following the general procedure as the solvent using xanthate **54** (0.17 mmol, 1 equiv), vinyl acetate (6 equiv) in EtOAc (0.1 mL) and DLP (2 × 5 mol%). Chromatography (gradient PE–EtOAc, 10:0 to 8:2) furnished the addition product **55** (64% yield) as a yellow oil as a mixture of 2 diastereomers.

IR (CCl_4): 2250 (C≡N), 1583 (C=N), 1223, 1054 cm^{-1} (C–O, CS).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (t, *J* = 7.7 Hz, 1 H, CH_{Ar}), 6.98 (dd, *J* = 4.0 Hz, *J* = 7.6 Hz, 2 H, CH_{Ar}), 6.70 (2 t, overlapping, *J* = 6.6 Hz, *J* = 8.7 Hz, 1 H, CHS), 4.62 (m, 4 H, 2 OCH_2CH_3), 3.93 (m, 1 H, CHS), 2.92 (m, 6 H, 3 CH_2), 2.37 (m, 3 H, CH_2, CH_2), 2.18 (m, 1 H, CH_2), 2.07 (s, 1.5 H, CH_3CO), 2.06 (s, 1.5 H, CH_3CO), 1.42, 1.39 (2 t, overlapping, *J* = 7.1 Hz, 6 H, 2 OCH_2CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.5, 210.4 (C=S), 169.43, 169.42 (C=O), 159.6, 159.37, 159.36 (2 C_{Ar}), 137.0 (CH_{Ar}), 120.7,

120.6 (CH_{Ar}), 117.3 (CN), 80.51, 80.49 (CHS), 70.5, 70.2 (OCH_2CH_3), 46.0, 45.9 (CHS), 34.95, 34.93, 33.9, 33.7, 31.84, 31.81 (5 CH_2), 23.90, 23.89 (CH_3CO), 13.8, 13.7 (OCH_2CH_3).

MS (CI, NH_3): m/z = 501 $[M + H]^+$.

HRMS (EI): m/z $[M]^+$ calcd for $C_{21}H_{28}N_2O_4S_4$: 500.09321; found: 500.09310.

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