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A convergent, modular access to complex amines

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This paper is dedicated with respect and admiration to Professor Steven V. Ley, recipient of the 2009 Tetrahedron Prize

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ABSTRACT

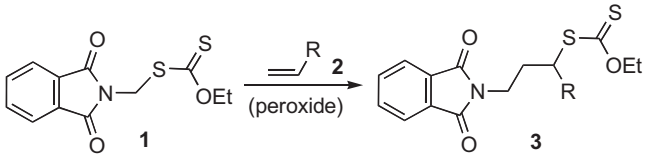
Various xanthates can be added to *N*-vinyl phthalimide with little formation of oligomers, if the xanthate is used in excess and the medium slightly diluted. The adduct xanthates thus obtained can in turn undergo radical additions to numerous olefins, providing a convergent and modular access to densely functionalized amines.

1. Introduction

The amino group occupies a central position in organic chemistry, and the synthesis of numerous natural products, such as amino-acids or alkaloids, or medicinal compounds, the vast majority of which contain one or more nitrogen atoms, hinges heavily on the ability to access functionalized amine intermediates or end products. As a consequence, the development of new flexible routes to amines remains a very worthwhile endeavor. We now report what we believe is an exceedingly powerful extension of an earlier approach, allowing the expedient assembly of highly functional internal primary amines conveniently protected as their phthalimido derivatives.

Recently, we described a versatile, practical radical aminomethylation of alkenes based on the degenerative xanthate transfer reaction,[1] namely the addition of xanthate **1** to alkene **2** to give adduct **3**, as summarized by the first equation in Scheme 1.[2] We later expanded this strategy to the arylaminomethylation of alkenes and to the synthesis of usefully functionalized amines starting from aminoacids.[3]

At the origin of our work in this area was a puzzling and frustrating observation: in contrast to additions to vinyl acetate or *N*-vinyl pyrrolidone, the corresponding radical additions of xanthates **4** to



Scheme 1.

N-vinyl phthalimide **5** furnished mostly oligomers **7** and only a small yield of the desired adducts **6** (Scheme 2; PhthN=phthalimido throughout). All three alkenes readily polymerize,[4] yet no difficulties were encountered in controlling the addition with the first two. In only one case, namely addition of AIBN derived xanthate ($Me_2C(CN)SCSOEt$, **4a**)[5] could we secure a good yield of mono-adduct under the usual conditions. Since xanthate additions to *N*-vinyl phthalimide **5** would constitute a simple, convergent, and flexible route to a vast number of variously functionalized, phthalimido protected primary amines **6**, we decided to re-examine this addition.

The difference in the behavior of *N*-vinyl phthalimide **5**, as compared to that of vinyl acetate and *N*-vinyl pyrrolidone, was attributed to the existence of resonance structures **8a** and **8b**, which impart a certain degree of allylic character to the adduct radical **8**.[6] Such conjugation is expected to be much less significant in the case of an acetate or a pyrrolidone group. The deleterious consequence of this stabilization in the present context can be understood by examining the fragmentation tendency of key intermediate **9** in Scheme 2. The formation of desired addition

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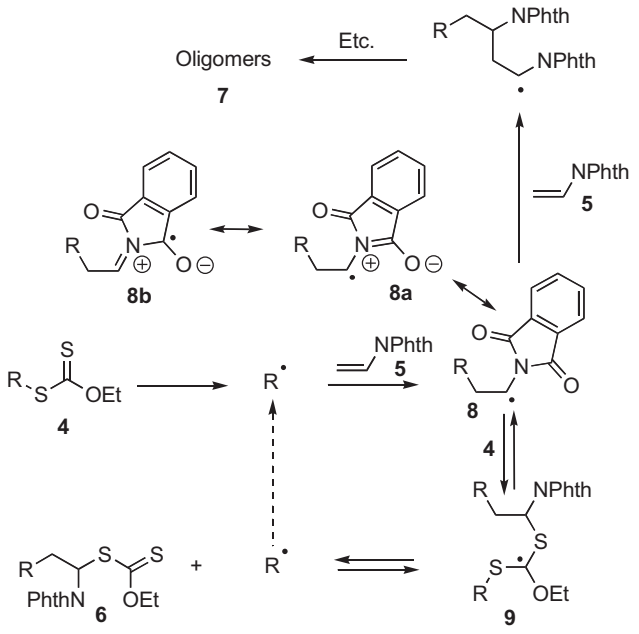


Scheme 2.

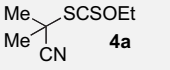
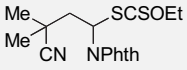
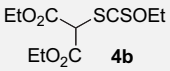
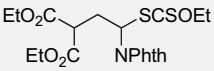
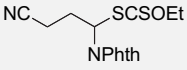
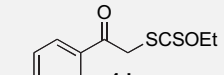
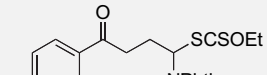
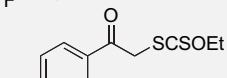
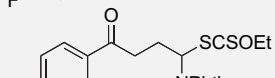
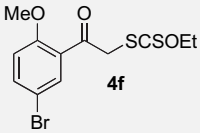
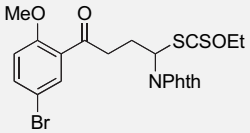
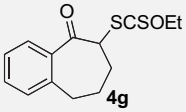
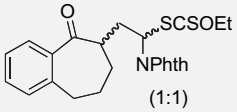
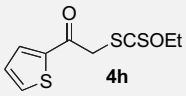
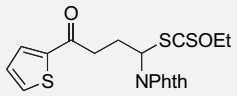
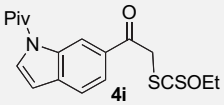
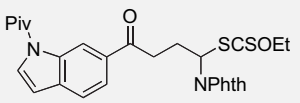
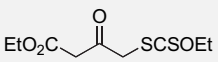
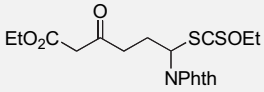
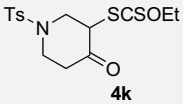
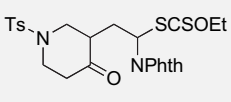
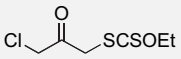
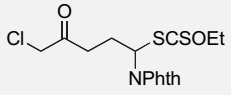
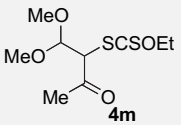
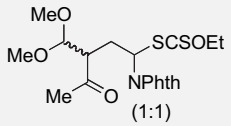
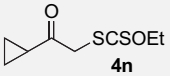
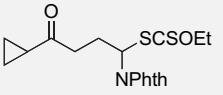
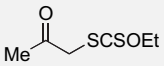
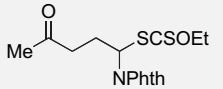
product **6** is favored when the collapse of this intermediate leads preferentially to radical R• and not back to adduct radical **8**. Unfortunately, the enhanced stabilization of **8** provided by the phthalimido group promotes the unwanted back fragmentation. This causes a build up in the concentration of **8** and encourages the formation of oligomer **7** by further additions to *N*-vinyl phthalimide **5**. In the case of AIBN derived xanthate **4a**, the corresponding radical ($Me_2C{\cdot}(CN)$) is sufficiently more stable than adduct radical **8** to shift the equilibrium in the right direction and allow clean obtention of mono-adduct **6a** (**6**, R=($Me_2C(CN)$–)).

While decisive, the extra stabilization provided by the phthalimido group is nevertheless expected to be small in absolute energy terms. It appeared therefore possible to curtail the unwanted oligomerization by a modification of the experimental parameters.

The additions of xanthates are normally conducted under a high concentration of 1–4 M and the olefinic partner is normally used in 1.5 to 3-fold and sometimes up to 5-fold excess, depending on its reactivity and volatility. If, instead, xanthate **4** is used in excess, the equilibrium should shift to increase the concentration of tertiary radical **9** at the expense of adduct radical **8**. This lowering of the concentration of **8** would automatically cause a decrease in the rate of oligomer formation. The rate of the bimolecular oligomerisation pathway may be further diminished by diluting the reaction medium. Thus, instead of using the usual two-fold excess of olefin, a two-fold excess of the xanthate and a 0.5 M concentration were employed instead.

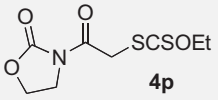
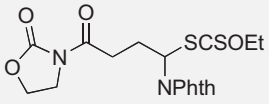
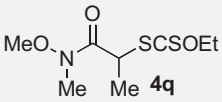
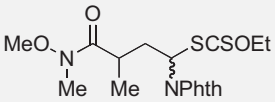
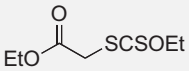
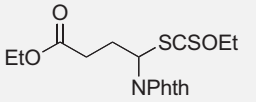
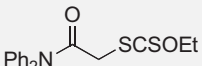
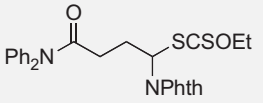
We were gratified to find that these modified conditions worked quite nicely for xanthates derived from for diethyl malonate, acetonitrile, and functionalized ketones (Table 1, **6a**–**m**). The yield remained modest or poor with simpler xanthates **4n** and **4o** derived from cyclopropyl methyl ketone and from acetone, respectively. In these two cases, the efficiency was significantly improved to 72% and 82%, respectively, by increasing further the excess of xanthate to four-fold and further decreasing the dilution to 0.25 M. The same observation was made for *N*-acetyl oxazolidone derived xanthate **4p**. For the *N*,*O*-dimethyl acetylhydroxamic acid xanthate **4q**, a three-fold excess and a 0.33 M concentration were sufficient to secure a good yield (76%) of the desired adduct **6q**. With acetate or acetanilide xanthates, **4r** and **4s**, which otherwise add efficiently to ordinary terminal alkenes (e.g., allyl acetate), the extensive formation of oligomers could not be avoided unfortunately.

Table 1

Xanthate **4**	Radical adduct **6**	Yield[a] (%)
 **4a**		**6a**, 74
 **4b**		**6b**, 95
 **4c**		**6c**, 73
 **4d**		**6d**, 69
 **4e**		**6e**, 79
 **4f**		**6f**, 50
 **4g**	 (1:1)	**6g**, 87
 **4h**		**6h**, 64
 **4i**		**6i**, 72
 **4j**		**6j**, 62
 **4k**		**6k**, 86
 **4l**		**6l**, 72
 **4m**	 (1:1)	**6m**, 73
 **4n**		**6m**, 23 57[b]
 **4o**		**6o**, 22 72[b]

(*continued on next page*)

Table 1 (*continued*)

Xanthate **4**	Radical adduct **6**	Yield[a] (%)
 **4p**		**6p**, 45 82[b]
 **4q**		**6q**, 76[c]
 **4r**		**6r**, —[d]
 **4s**		**6s**, —[d]

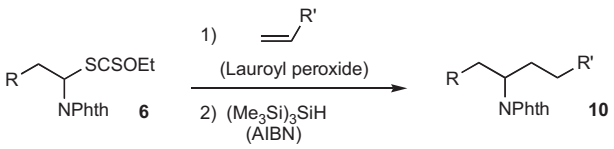
[a] Except for **6a**, yields refer to reactions with 2 equiv of xanthate **4** with *N*-vinyl phthalimide **5** in refluxing ethyl acetate at 0.5 M concentration.
[b] Yield using 4 equiv of xanthate **4** at 0.25 M concentration.
[c] Yield using 3 equiv of xanthate **4** at 0.33 M concentration.
[d] Extensive oligomer formation.

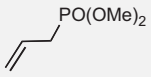
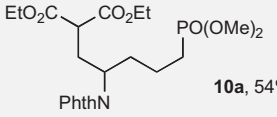
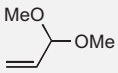
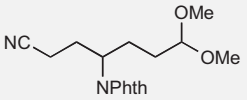
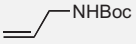
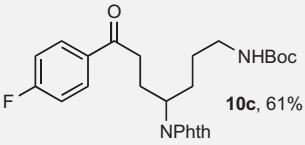
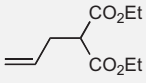
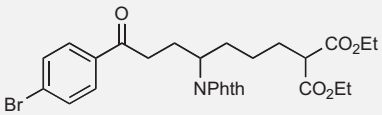
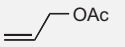
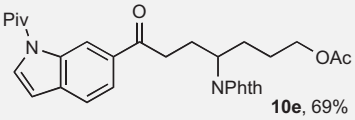
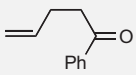
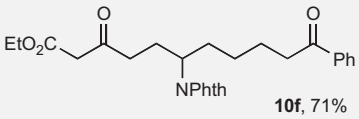
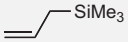
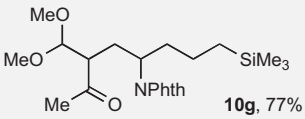
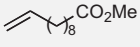
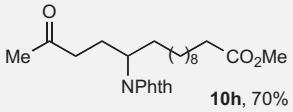
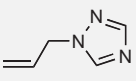
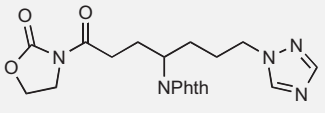
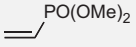
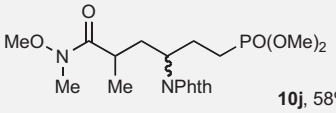
Notwithstanding these, ultimately rather minor limitations, the access to xanthate adducts **6** to *N*-vinyl phthalimide opens up vast opportunities for the synthesis of complex, highly functionalized amines. The stabilizing effect of the phthalimide group, initially the cause of the difficulties we faced, now becomes a tremendous asset because its presence will facilitate considerably the addition of xanthates **6** to various other olefins. Thus, to the functional groups contributed by the first xanthate **4**, additional functionality can be brought in by the olefinic partner, resulting in a modular, convergent approach to primary amines protected as their phthalimido derivatives. A selection of such structures is compiled in Table 2, where a number of adducts to *N*-vinyl phthalimide were made to react with various olefins. To simplify the structural determination and description, the xanthate group in the adduct was reduced off using tris(trimethylsilyl)silane (TTMSS).[7] The overall yield for the two steps was good in most cases, and the tolerance for functional groups quite broad and in line with our earlier studies.

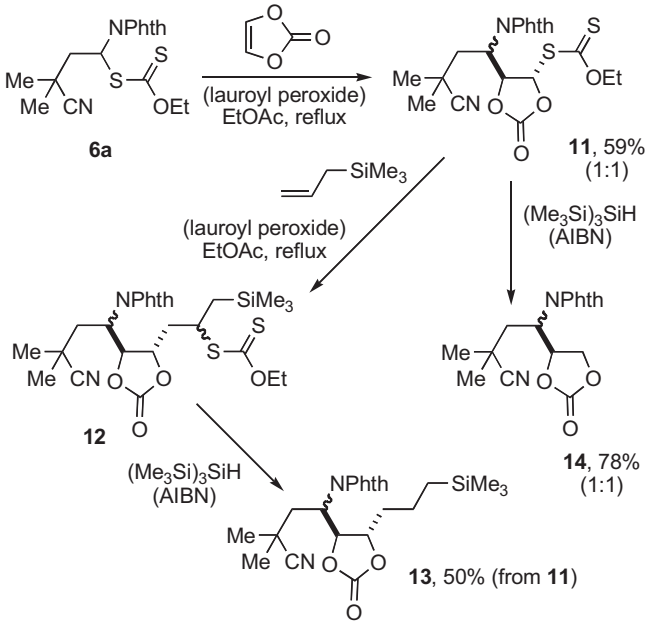
The synthesis of any of the protected amines pictured in Table 2 using traditional methods would be very tedious at best. The complexity of the structures accessible by the present, unique modular approach may be further underscored by the sequence displayed in Scheme 3. By starting with xanthate **6a**, made by addition of xanthate **4a** to *N*-vinyl phthalimide **5**, it is possible to perform a second radical addition to vinylidene carbonate then a third addition to allyl trimethylsilane to give finally **12**. Thus, one xanthate and three different olefins could be stitched together using the same radical process. To simplify characterisation, the xanthate group was reduced off to give **13** in 50% overall yield from **11**. The latter was also cleanly reduced into **14**. Except in the addition to vinylidene carbonate, which not unexpectedly, takes place in a trans fashion, the relative stereochemistry cannot otherwise be controlled. This lack of diastereoselectivity is inherent to the free radical nature of the intermediates and not to the method itself.

The xanthate group in the first adduct can also be used to construct cyclic derivatives through an intramolecular radical addition. While further treatment of compound **6d** with stoichiometric amounts of lauroyl peroxide furnished only a small and

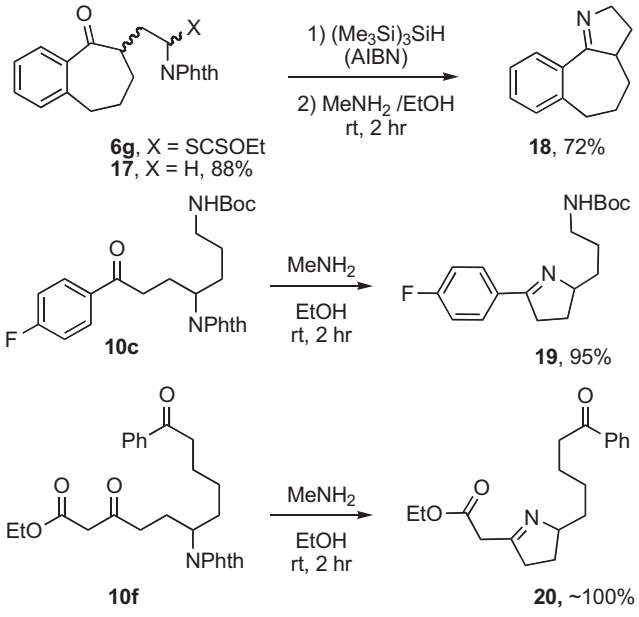
Table 2



Xanthate **6**	Alkene	Radical adduct **6**
6b		 **10a**, 54%
6c		 **10b**, 84%
6d		 **10c**, 61%
6e		 **10d**, 50%
6i		 **10e**, 69%
6j		 **10f**, 71%
6m		 **10g**, 77%
6o		 **10h**, 70%
6p		 **10i**, 73%
6q		 **10j**, 58%

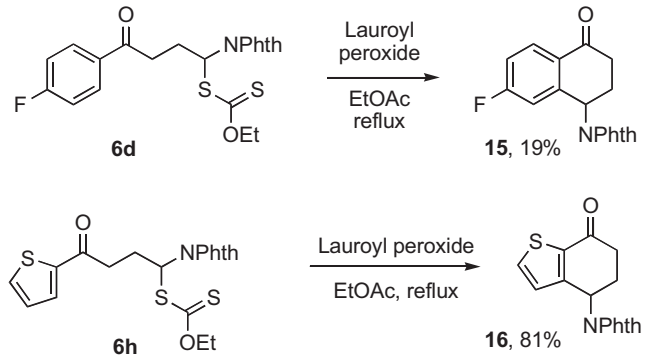


Scheme 3.



Scheme 5.

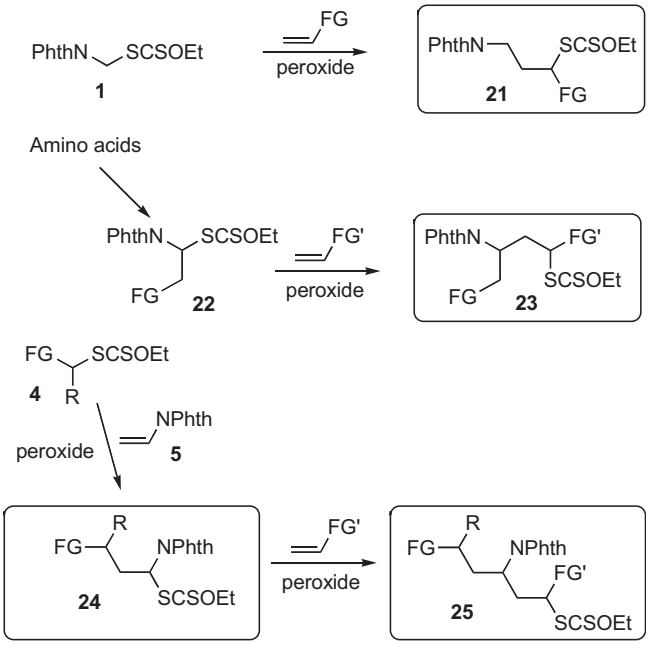
disappointing 19% yield of tetralone **15** (Scheme 4), the corresponding reaction with thiophene adduct **6h** gave a high yield (81%) of ketone **16**. The steric hindrance caused by the large phthalimido group appears to be of lesser consequence in the latter transformation, in addition to the fact that the temporary disruption of the aromaticity during the cyclization onto the thiophene ring is energetically less costly.



Scheme 4.

By exploiting the presence in the adducts of various functional groups, such as ketones, esters, nitriles, masked aldehydes (as in **6m**) etc., it is possible to construct nitrogen containing heterocycles by combining the radical process with classical ionic ring-closures. For example, reductive removal of the xanthate in **6g** gave **17** in 88% yield and release of the amine group resulted in spontaneous ring closure to give pyrrolenine **18** (72%), whereas deprotection of adducts **10c** and **10f** furnished, respectively, pyrrolenines **19** and **20** in essentially quantitative yield (Scheme 5). The other amino group in the **19** remained safely protected as the Boc derivative.

In conclusion, we now have in hand a unified, flexible, and convergent strategy for assembling primary aliphatic amines consisting of three main routes summarised in Scheme 6. All hinge on the hitherto unappreciated stabilising effect of the phthalimido group (or imides more generally). Whereas addition of the parent xanthate **1** or aminoacid derived xanthates **22** to functional group (FG or FG′) containing alkenes furnishes terminal or internal amine derivatives **21** and **23**, respectively, the present addition of a xanthate **4** to *N*-vinyl phthalimide **5** is more powerful as it provides access to both terminal and internal amines (**24** and **25**, and reduction products thereof). In all cases, a very broad variety of densely functionalized amines can be rapidly assembled.



Scheme 6.

2. Experimental

2.1. General conditions

Anhydrous dichloromethane was obtained by distillation from calcium hydride under nitrogen. Anhydrous THF and diethyl ether were obtained by distillation from sodium benzophenone ketyl

under nitrogen. Other solvents were used as supplied by commercial sources. Petroleum ether refers to the fraction of light petroleum ether, boiling between 40–60 °C. Purification procedures were in accordance with the instructions in D.D. Perrin and W.L.F. Armarego, *Purification of Laboratory Chemicals*, 4th ed.; The Bath, Bath, 2002. All reactions were carried out under dry, oxygen free nitrogen. Flash chromatography was performed on silica gel (SDS, 60 Å C. C. 40–63 μm) as the stationary phase. Thin Layer Chromatography (TLC) was performed on aluminum plates pre-coated with silica gel (Merck silica gel, 60 F_{254}), which were visualized by the quenching of UV fluorescence when applicable (λ_{max}=254 nm and/or 366 nm) and/or by staining with anisaldehyde or vanillin in acidic ethanol followed by heating. When compounds could not be visualized with anisaldehyde or vanillin, a solution of phosphomolybdic acid in ethanol or a potassium permanganate aqueous solution was used. Infrared spectra were recorded as solutions in $CDCl_3$ using CaF_2 cells, on a Perkin–Elmer FT 1600 or FT 2000. Absorption maxima (ν_{max}) are reported in wave numbers (cm^{-1}) and only selected peaks are reported. Magnetic resonance spectra were recorded at ambient temperature on either a Bruker AMX 400, or a Bruker Avance DPX 400 instruments. Proton magnetic resonance spectra (^1H NMR) were recorded at 400 MHz and coupling constants (J) are reported to ±0.5 Hz. The following abbreviations were utilized to describe peak patterns when appropriate: br=broad, s=singlet, d=doublet, t=triplet, q=quartet and m=multiplet. Carbon magnetic resonance spectra (^{13}C NMR) were recorded at 100 MHz. Chemical shifts (δ_H, δ_C) are quoted in parts per million (ppm) and are referenced to the residual solvent peak ($CDCl_3$: δ_H=7.26 and δ_C=77.0). High-resolution mass spectra were recorded by positive electron impact ionization (EI^+) at 70 eV on a JEOL JMS-GCmate II mass spectrometer. The quoted masses are accurate to ±5 ppm. DLP corresponds to di-lauroyl peroxide (often sold under lauroyl peroxide or laurox).

2.2. General procedure for the addition xanthate 4a–s to *N*-vinyl phthalimide 5

A magnetically stirred solution of *N*-vinyl phthalimide **5** (1 equiv) and xanthate (2 equiv to 4 equiv) in 1,2-dichloroethane (2 mL/mmol to 4 mL/mmol of **5**) was heated at reflux for 15 min. DLP (2–5 mol %) was then added and additional DLP (5 mol %) was added every 60 min until total consumption of **5**. The mixture was then cooled to room temperature and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel to yield the desired compounds **6**.

*2.2.1. S-3-Cyano-1-(1,3-dioxoisoindolin-2-yl)-3-methylbutyl O-ethyl carbonodithioate (**6a**).* The reaction was run with xanthate **4a** (1.5 mmol) and *N*-vinyl-phthalimide (1 mmol) in 1,2-dichloroethane (0.5 mL). The reaction was completed after addition of 15 mol % of DLP. After evaporation of the solvent, the residue was purified by chromatography on silica gel using a gradient (petroleum ether/ethyl acetate: 95/5) and the addition product was isolated as a pale yellow oil in 74% yield. ^1H NMR (400 MHz, $CDCl_3$): 7.87 (m, 2H), 7.74 (m, 2H), 6.53 (dd, 1H, J=3.4, 12.2 Hz), 4.66 (q, 2H, J=7.1 Hz), 3.08 (dd, 1H, J=12.2, 14.5 Hz), 2.00 (dd, 1H, J=3.4, 14.6 Hz), 1.54 (s, 3H), 1.40 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 210.8, 167.2, 134.6, 131.6, 123.9, 123.6, 70.7, 54.5, 42.7, 30.5 (Cq, CMe_2), 28.7, 24.9, 13.8. IR ($CDCl_3$): ν_{max} 2235, 1781, 1724, 1371, 1224, 1051. HRMS (EI^+): m/z calculated for $C_{14}H_{13}N_2O_2$ [M–SC(S)OEt]=241.0977, found: 241.0976.

*2.2.2. Diethyl 2-[2-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-2-ethoxythiocarbonylsulfanyl-ethyl]-malonate (**6b**).* Following the general procedure, the reaction was carried out with a solution of xanthate **4b** (527 mg, 2.32 mmol) and *N*-vinyl phthalimide (200 mg, 1.16 mmol) in 1,2-dichloroethane (2 mL) and needed 7 mol % of DLP to go to completion. Flash chromatography on silica gel (ethyl acetate/petroleum ether, 0:10 to 3:7 v/v) afforded **6b** (500 mg, 95%) as a pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$): 7.86 (dd, 2H, J=3.0, 5.5 Hz), 7.75 (dd, 2H, J=3.1, 5.4 Hz), 6.37 (dd, 1H, J=6.8, 9.3 Hz), 4.62 (q, 2H, J=7.1 Hz), 4.21 (dq, 2H, J=1.8, 7.1 Hz), 4.08 (ddt, 2H, J=3.6, 7.1, J=10.8 Hz), 3.43 (t, 1H, J=7.3 Hz), 2.84 (m, 2H), 1.40 (t, 3H, J=7.1 Hz), 1.27 (t, 3H, J=7.2 Hz), 1.20 (t, 3H, J=7.1 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): 210.20, 168.06, 167.95, 166.56, 134.49, 131.59, 123.70, 70.64, 62.02, 61.92, 55.71, 49.57, 32.24, 14.04, 13.97, 13.72. IR ($CDCl_3$): ν_{max} 2927, 2855, 1784, 1754, 1726, 1469, 1377, 1227, 1111, 1048. HRMS (EI^+): m/z calculated for $C_{20}H_{23}O_7NS_2$ M=453.0916, found: 453.0919, calculated for $C_{17}H_{18}O_6N$ [M–SC(S)OEt]=332.1134, found: 332.1127.

*2.2.3. S-[3-Cyano-1-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-propyl]-O-ethyl dithiocarbonate (**6c**).* Following the general procedure, the reaction was carried out with a solution of xanthate **4c** (356 mg, 2.32 mmol) and *N*-vinyl phthalimide (200 mg, 1.16 mmol) in 1,2-dichloroethane (2 mL) and needed 2 mol % of DLP to go to completion. Flash chromatography on silica gel (ethyl acetate/petroleum ether, 0:10 to 3:7 v/v) afforded **6c** (283 mg, 73%) as a pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$): 7.89 (dd, 2H, J=3.1, 5.5 Hz), 7.77 (dd, 2H, J=3.0, 5.5 Hz), 6.38 (m, 1H), 4.66 (q, 2H, J=7.1 Hz), 2.66 (m, 1H), 2.54 (m, 3H), 1.43 (t, 3H, J=7.1 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): 210.04, 166.76, 134.72, 131.46, 123.91, 118.01, 70.99, 55.44, 29.43, 15.06, 13.75. IR ($CDCl_3$): ν_{max} 2927, 2855, 1783, 1727, 1470, 1377, 1333, 1228, 1111, 1051. HRMS (EI^+): m/z calculated for $C_{15}H_{14}O_3N_2S_2$ M=334.0446, found: 334.0447, calculated for $C_{12}H_9O_2N_2$ [M–SC(S)OEt]=213.0664, found: 213.0662.

*2.2.4. S-[1-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-4-(4-fluorophenyl)-4-oxo-butyl]-O-ethyl dithiocarbonate (**6d**).* Following the general procedure, the reaction was carried out with a solution of xanthate **4d** (597 mg, 2.32 mmol) and *N*-vinyl phthalimide (200 mg, 1.16 mmol) in 1,2-dichloroethane (2 mL) and needed 15 mol % of DLP to go to completion. Flash chromatography on silica gel (ethyl acetate/petroleum ether, 0:10 to 3:7 v/v) afforded xanthate **6d** (342 mg, 69%) as a pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$): 7.92 (dd, 2H, J=5.4, 8.9 Hz), 7.85 (dd, 2H, J=3.0, 5.5 Hz), 7.74 (dd, 2H, J=3.1, 5.5 Hz), 7.09 (t, 2H, J=8.6 Hz), 6.38 (t, 1H, J=7.9 Hz), 4.60 (dq, 2H, J=2.5, 7.1 Hz), 3.10 (m, 2H), 2.65 (ddd, 2H, J=2.7, 7.5, 14.6 Hz), 1.38 (t, 3H, J=7.1 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): 211.04, 196.24, 166.80, 165.83 (d, J=257.3 Hz), 134.44, 132.99, 131.62, 130.72 (d, J=9.3 Hz), 123.69, 115.75 (d, J=21.8 Hz), 70.61, 57.49, 35.28, 30.94, 28.10, 23.73. IR ($CDCl_3$): ν_{max} 2985, 2938, 1780, 1718, 1687, 1599, 1380, 1232, 1111, 1048. HRMS (EI^+): m/z calculated for $C_{18}H_{13}O_3NF$ [M–SC(S)OEt]=310.0879, found: 310.0878.

*2.2.5. S-[4-(4-Bromo-phenyl)-1-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-4-oxo-butyl]-O-ethyl dithiocarbonate (**6e**).* Following the general procedure, the reaction was carried out with a solution of xanthate **4e** (737 mg, 2.32 mmol) and *N*-vinyl phthalimide (200 mg, 1.16 mmol) in 1,2-dichloroethane (2 mL) and needed 15 mol % of DLP to go to completion. Flash chromatography on silica gel (ethyl acetate/petroleum ether, 0:10 to 3:7 v/v) afforded xanthate **6e** (450 mg, 79%) as a pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$): 7.83 (dd, 2H, J=3.0, 5.5 Hz), 7.73 (dd, 2H, J=4.2, 7.5 Hz), 7.73 (d, 2H, J=8.6 Hz), 7.53 (d, 2H, J=8.6 Hz), 6.36 (t, 1H, J=7.9 Hz), 4.59 (dq, 2H, J=2.6, 7.1 Hz), 3.09 (dt, 2H, J=5.3, 6.9 Hz), 2.63 (ddd, 2H, J=3.4, 7.4, J=14.6 Hz), 1.36 (t, 3H, J=7.1 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): 210.99, 196.82, 166.77, 134.46, 131.95, 131.59, 129.58, 123.69, 70.61, 57.43, 35.31, 28.03, 13.75. IR ($CDCl_3$): ν_{max} 2985, 2962, 2902, 1780,

1723, 1688, 1587, 1470, 1380, 1365, 1333, 1229, 1111, 1048. HRMS (EI^+): *m/z* calculated for $C_{21}H_{18}O_4NS_2Br$ M=490.9861, found: 490.9866, calculated for $C_{18}H_{13}O_3NBr$[M−SC(S)OEt]=370.0079, found: 370.0087.

*2.2.6. S-[4-(5-Bromo-2-methoxy-phenyl)-1-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-4-oxo-butyl]-O-ethyl dithiocarbonate (**6f**).* Following the general procedure, the reaction was carried out with a solution of xanthate **4f** (806 mg, 2.32 mmol) and *N*-vinyl phthalimide (200 mg, 1.16 mmol) in 1,2-dichloroethane (2 mL) and needed 15 mol % of DLP to go to completion. Flash chromatography on silica gel (ethyl acetate/petroleum ether, 0:10 to 3:7 v/v) afforded xanthate **6f** (300 mg, 50%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.85 (dd, 2H, *J*=3.2, 5.2 Hz), 7.74 (dd, 2H, *J*=3.0, 5.5 Hz), 7.70 (d, 1H, *J*=1.5 Hz), 7.50 (dd, 1H, *J*=1.6, 8.8 Hz), 6.81 (d, 1H, *J*=8.9 Hz), 6.35 (t, 1H, *J*=8.0 Hz), 4.61 (q, 2H, *J*=7.1 Hz), 3.82 (s, 3H), 3.10 (m, 2H), 2.58 (m, 2H), 1.38 (t, 1H, *J*=7.1 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): 211.18, 198.51, 166.76, 157.69, 136.20, 134.43, 133.05, 131.62, 129.00, 123.64, 113.55, 70.54, 57.48, 55.86, 40.69, 28.20, 13.77. IR ($CDCl_3$): ν_{max} 2927, 2855, 1782, 1724, 1685, 1481, 1378, 1269, 1225, 1112, 1049. HRMS (EI^+): *m/z* calculated for $C_{22}H_{20}O_5NS_2Br$ M=520.9966, found: 520.9964, calculated for $C_{19}H_{15}O_4NBr$[M−SC(S)OEt]=400.0184, found: 400.0184.

*2.2.7. S-[1-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-2-(5-oxo-6,7,8,9-tetrahydro-5H-benzocyclohepten-6-yl)-ethyl]-O-ethyl dithiocarbonate (**6g**).* Following the general procedure, the reaction was carried out with a solution of xanthate **4g** (615 mg, 2.32 mmol) and *N*-vinyl phthalimide (200 mg, 1.16 mmol) in 1,2-dichloroethane (2 mL) and needed 15 mol % of DLP to go to completion. Flash chromatography on silica gel (ethyl acetate/petroleum ether, 0:10 to 3:7 v/v) afforded xanthate **6g** (440 mg, 87%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): *Diastereoisomer 1*: 7.84 (dd, 2H, *J*=3.1, 5.4 Hz), 7.80 (dd, 2H, *J*=3.1, 5.4 Hz), 7.62 (dd, 1H, *J*=1.2, 7.6 Hz), 7.42 (dd, 1H, *J*=0.9, 7.6 Hz), 7.26 (m, 1H), 7.17 (m, 1H), 6.36 (m, 1H), 4.55 (m, 2H), 2.90 (m, 2H), 2.34 (m, 1H), 2.08 (m, 2H), 1.68 (m, 2H), 1.40 (t, 3H, *J*=7.1 Hz). *Diastereoisomer 2*: 7.74 (dd, 2H, *J*=3.0, 5.5 Hz), 7.70 (dd, 2H, *J*=3.0, 5.5 Hz), 7.42 (dd, 1H, *J*=0.9, 7.6 Hz), 7.33 (dt, 1H, *J*=1.1, 7.4 Hz), 7.17 (m, 2H), 6.36 (m, 1H), 4.61 (q, 2H, *J*=7.2 Hz), 2.90 (m, 4H), 2.34 (m, 1H), 2.08 (m, 2H), 1.68 (m, 2H), 1.35 (t, 3H, *J*=7.1 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): *Diastereoisomer 1*: 211.20, 204.68, 166.71, 141.57, 139.27, 134.33, 131.72, 131.42, 130.03, 128.60, 126.24, 123.66, 70.44, 56.64, 47.06, 34.86, 33.70, 30.56, 25.46, 13.75. *Diastereoisomer 2*: 210.78, 205.25, 166.67, 142.50, 139.71, 134.33, 131.63, 131.29, 129.78, 128.73, 126.46, 123.61, 70.48, 55.85, 47.44, 34.57, 33.88, 30.88, 25.68, 13.72. IR ($CDCl_3$): ν_{max} 2930, 2857, 1779, 1720, 1682, 1470, 1380, 1364, 1230, 1112, 1047. HRMS (EI^+): *m/z* calculated for $C_{24}H_{23}O_4NS_2$ M=453.1069, found: 453.1088, calculated for $C_{21}H_{18}O_3N$ [M−SC(S)OEt]=332.1287, found: 332.1284.

*2.2.8. S-[1-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-4-oxo-4-thiophen-2-yl-butyl]-O-ethyl dithiocarbonate (**6h**).* Following the general procedure, the reaction was carried out with a solution of xanthate **4h** (569 mg, 2.32 mmol) and *N*-vinyl phthalimide (200 mg, 1.16 mmol) in 1,2-dichloroethane (2 mL) and needed 45 mol % of DLP to go to completion. Flash chromatography on silica gel (ethyl acetate/petroleum ether, 0:10 to 3:7 v/v) afforded xanthate **6h** (200 mg, 64%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.86 (dd, 2H, *J*=3.1, 5.4 Hz), 7.76 (dd, 2H, *J*=3.0, 5.5 Hz), 7.68 (dd, 1H, *J*=0.9, 3.8 Hz), 7.62 (dd, 1H, *J*=0.9, 4.9 Hz), 7.11 (dd, 1H, *J*=3.9, 4.8 Hz), 6.39 (t, 1H, *J*=7.9 Hz), 4.62 (m, 2H), 3.09 (dt, 2H, *J*=2.3, 7.2 Hz), 2.67 (m, 2H), 1.40 (t, 3H, *J*=7.1 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): 210.86, 190.73, 166.75, 143.66, 134.47, 133.97, 132.20, 131.54, 128.19, 123.67, 70.62, 57.29, 36.01, 28.25, 13.74. IR ($CDCl_3$): ν_{max} 2928, 2856, 1780, 1720, 1666, 1470, 1380, 1356, 1236, 1111, 1047. HRMS (EI^+): *m/z* calculated for $C_{19}H_{17}O_4NS_3$ M=419.0320, found: 419.0323, calculated for $C_{16}H_{12}O_3NS$ [M−SC(S)OEt]=298.0538, found: 298.0546.

*2.2.9. S-[4-[1-(2,2-Dimethyl-propionyl)-1H-indol-6-yl]-1-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-4-oxo-butyl]-O-ethyl dithiocarbonate (**6i**).* Following the general procedure, the reaction was carried out with a solution of xanthate **4i** (807 mg, 2.32 mmol) and *N*-vinyl phthalimide (200 mg, 1.16 mmol) in 1,2-dichloroethane (2 mL) and needed 15 mol % of DLP to go to completion. Flash chromatography on silica gel (ethyl acetate/petroleum ether, 0:10 to 3:7 v/v) afforded xanthate **6i** (450 mg, 72%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 9.12 (d, 1H, *J*=0.6 Hz), 7.93 (d, 1H, *J*=3.8 Hz), 7.92 (m, 1H), 7.89 (dd, 2H, *J*=3.1, 5.5 Hz), 7.77 (dd, 2H, *J*=3.0, 5.5 Hz), 7.61 (d, 1H, *J*=8.2 Hz), 6.69 (d, 1H, *J*=3.8 Hz), 6.40 (t, *J*=7.89 Hz, 1H), 4.66 (m, 2H), 3.29 (t, 2H, *J*=7.2 Hz), 2.73 (q, 2H, *J*=7.1 Hz), 1.57 (s, 9H), 1.44 (t, 3H, *J*=7.1 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): 210.94, 197.88, 177.08, 166.80, 136.33, 134.31, 133.28, 131.71, 128.86, 123.66, 123.33, 120.54, 118.03, 108.09, 70.53, 57.32, 41.41, 35.30, 28.69, 13.76. IR ($CDCl_3$): ν_{max} 2959, 2933, 1774, 1742, 1713, 1686, 1427, 1371, 1307, 1239, 1190, 1079, 1045. HRMS (EI^+): *m/z* calculated for $C_{28}H_{28}O_5N_2S_2$ M=536.1440, found: 536.1442, calculated for $C_{25}H_{23}O_4N_2$[M−SC(S)OEt]=415.1658, found: 415.1664.

*2.2.10. Ethyl 6-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-6-ethoxythiocarbonylsulfanyl-3-oxo-hexanoate (**6j**).* Following the general procedure, the reaction was carried out with a solution of xanthate **4j** (870 mg, 3.47 mmol) and *N*-vinyl phthalimide (300 mg, 1.73 mmol) in 1,2-dichloroethane (4 mL) and needed 10 mol % of DLP to go to completion. Flash chromatography on silica gel (ethyl acetate/petroleum ether, 0:10 to 3:7 v/v) afforded xanthate **6j** (456 mg, 62%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.83 (m, 2H), 7.72 (m, 2H), 6.25 (t, 1H, *J*=7.9 Hz), 4.59 (q, 2H, *J*=7.1 Hz), 4.11 (q, 2H, *J*=7.1 Hz), 3.38 (s, 2H), 2.69 (m, 2H), 2.47 (dd, 2H, *J*=7.2, 14.7 Hz), 1.37 (t, 3H, *J*=7.1 Hz), 1,20 (t, 3H, *J*=7.1 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): 210.86, 200.51, 166.83, 166.73, 134.45, 131.59, 123.65, 70.57, 61.43, 57.093, 49.23, 39.58, 27.35, 14.06, 13.70. IR ($CDCl_3$): ν_{max} 2983, 2959, 2928, 2855, 1782, 1724, 1469, 1378, 1227, 1112, 1049. HRMS (EI^+): *m/z* calculated for $C_{19}H_{21}O_6NS_2$ M=423.0810, found: 423.0784, calculated for $C_{16}H_{16}O_5N$ [M−SC(S)OEt]=302.1028, found: 302.1039.

*2.2.11. S-{1-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-2-[4-oxo-1-(toluene-4-sulfonyl)-piperidin-3-yl]-ethyl}-O-ethyl dithiocarbonate (**6k**).* Following the general procedure, the reaction was carried out with a solution of xanthate **4k** (860 mg, 2.32 mmol) and *N*-vinyl phthalimide (200 mg, 1.16 mmol) in 1,2-dichloroethane (2 mL) and needed 15 mol % of DLP to go to completion. Flash chromatography on silica gel (ethyl acetate/petroleum ether, 0:10 to 3:7 v/v) afforded xanthate **6k** (540 mg, 86%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): *Diastereoisomer 1*: 7.87 (dd, 2H, *J*=2.5, 5.4 Hz), 7.77 (dd, 2H, *J*=3.2, 5.7 Hz), 7.69 (d, 2H, *J*=8.2 Hz), 7.33 (d, 2H, *J*=8.4 Hz), 6.34 (t, 1H, *J*=7.7 Hz), 4.65 (q, 2H, *J*=7.0 Hz), 4.05 (ddd, 1H, *J*=2.2, 5.1 Hz, *J*=11.7 Hz), 3.94 (m, 1H), 2.86 (dt, 1H, *J*=3.8, 11.6 Hz), 2.64 (m, 4H), 2.43 (s, 3H), 2.11 (m, 2H), 1.41 (t, 3H, *J*=7.1 Hz). *Diastereoisomer 2*: 7.87 (dd, 2H, *J*=2.7, 5.5 Hz), 7.75 (dd, 2H, *J*=3.2, 5.7 Hz), 7.61 (d, 2H, *J*=8.2 Hz), 7.30 (d, 2H, *J*=8.4 Hz), 6.38 (dd, 1H, *J*=6.1, 9.7 Hz), 4.63 (q, 2H, *J*=7.0 Hz,), 3.94 (m, 2H), 2.64 (m, 5H), 2.42 (s, 3H), 2.11 (m, 2H), 1.42 (t, 3H, *J*=7.0 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): *Diastereoisomer 1*: 206.02, 166.86, 144.18, 134.45, 131.66, 129.00, 127.56, 123.75, 70.74, 56.10, 51.05, 47.02, 46.69, 40.48, 31.21, 21.57, 13.73. *Diastereoisomer 2*: 205.69, 166.70, 144.22, 134.53, 131.61, 129.00, 127.48, 123.79, 70.74, 50.93, 55.52, 46.60, 46.58, 40.41, 30.62, 21.57, 13.73. IR ($CDCl_3$): ν_{max} 2982, 2926, 2854, 1781, 1723, 1599, 1470, 1367, 1226, 1170, 1112, 1048. HRMS (EI^+): *m/z* calculated for $C_{25}H_{26}O_6N_2S_3$ M=546.0953, found:

546.0929, calculated for $C_{22}H_{21}O_5N_2S$[M−SC(S)OEt]=425.1171, found: 425.1162.

*2.2.12. S-[5-Chloro-1-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-4-oxo-pentyl]-O-ethyl dithiocarbonate (**6l**).* Following the general procedure, the reaction was carried out with a solution of xanthate **4l** (491 mg, 2.32 mmol) and *N*-vinyl phthalimide (200 mg, 1.16 mmol) in 1,2-dichloroethane (2 mL) and needed 15 mol % of DLP to go to completion. Flash chromatography on silica gel (ethyl acetate/petroleum ether, 0:10 to 3:7 v/v) afforded xanthate **6l** (320 mg, 72%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.84 (dd, 2H, *J*=3.1, 5.3 Hz), 7.74 (dd, 2H, *J*=3.1, 5.4 Hz), 6.26 (t, 1H, *J*=7.8 Hz), 4.60 (q, 2H, *J*=7.1 Hz), 4.05 (s, 2H), 2.75 (m, 2H), 2.51 (q, 2H, *J*=7.1 Hz), 1.38 (t, 3H, *J*=7.1 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): 210.85, 200.72, 166.79, 134.53, 131.54, 123.73, 70.69, 57.08, 48.00, 36.43, 27.46, 13.74. IR ($CDCl_3$): ν_{max} 2984, 2959, 2928, 2956, 1782, 1721, 1470, 1379, 1226, 1112, 1050. HRMS (EI^+): *m*/*z* calculated for $C_{16}H_{16}O_4NS_2Cl$ M=385.0209, found: 385.0216, calculated for $C_{15}H_{14}O_3NCl$ [M−SC(S)OEt]=264.0427, found: 264.0422.

*2.2.13. S-[3-Dimethoxymethyl-4-oxo-1-(1-oxo-1,3-dihydro-isoindol-2-yl)-pentyl]-O-ethyl dithiocarbonate (**6m**).* Following the general procedure, the reaction was carried out with a solution of xanthate **4m** (583 mg, 2.32 mmol) and *N*-vinyl phthalimide (200 mg, 1.16 mmol) in 1,2-dichloroethane (2 mL) and needed 7 mol % of DLP to go to completion. Flash chromatography on silica gel (ethyl acetate/petroleum ether, 0:10 to 3:7 v/v) afforded xanthate **6m** (342 mg, 73%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): *Diastereoisomer 1*: 7.86 (dd, 2H, *J*=3.0, 5.5 Hz), 7.75 (dd, 2H, *J*=3.1, 5.5 Hz), 6.24 (t, 1H, *J*=7.9 Hz), 4.62 (q, 2H, *J*=7.2 Hz), 4.31 (d, 1H, *J*=7.4 Hz), 3.29 (s, 3H), 3.27 (s, 3H), 3.07 (ddd, 1H, *J*=3.9, 7.2, 10.7 Hz), 2.67 (m, 1H), 2.52 (m, 1H), 2.12 (s, 3H), 1.39 (t, *J*=7.1 Hz, 3H). *Diastereoisomer 2*: 7.84 (dd, 2H, *J*=3.0, 5.4 Hz), 7.73 (dd, 2H, *J*=3.1, 5.5 Hz), 6.16 (dd, 1H, *J*=6.0, 10.3 Hz), 4.60 (q, 2H, *J*=7.2 Hz), 4.34 (d, 1H, *J*=7.1 Hz), 3.36 (s, 3H), 3.32 (s, 3H), 2.85 (m, 1, H), 2.52 (m, 1H), 2.40 (ddd, *J*=14.37, 7.41, 3.93 Hz, 1H), 2.24 (s, 3H), 1.42 (t, *J*=7.2 Hz, 3H), 1.38 (t, *J*=7.1 Hz, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): *Diastereoisomer 1*: 210.91, 166.83, 134.52, 131.55, 123.72, 105.47, 70.54, 56.69, 55.80, 53.51, 52.57, 31.36, 13.74. *Diastereoisomer 2*: 210.33, 166.67, 134.45, 131.55, 123.67, 105.17, 70.64, 56.07, 55.70, 53.18, 53.12, 31.15, 13.71. IR ($CDCl_3$): ν_{max} 2928, 2855, 1779, 1720, 1380, 1231, 1111, 1048. HRMS (EI^+): *m*/*z* calculated for $C_{19}H_{23}O_6NS_2$ M=425.0967, found: 425.0946, calculated for $C_{13}H_{11}O_3N$ [M−SC(S)OEt/CH$(OMe)_2$]=229.0739, found: 229.0743.

*2.2.14. S-[4-Cyclopropyl-1-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-4-oxo-butyl]-O-ethyl dithiocarbamate (**6n**). Method a*: Following the general procedure, the reaction was carried out with a solution of xanthate **4n** (472 mg, 2.32 mmol) and *N*-vinyl phthalimide (200 mg, 1.16 mmol) in 1,2-dichloroethane (2 mL) and needed 7 mol % of DLP to go to completion. Flash chromatography on silica gel (ethyl acetate/petroleum ether, 0:10 to 3:7 v/v) afforded xanthate **6n** (100 mg, 23%) as a pale yellow oil. *Method b*: Following the general procedure, the reaction was carried out with a solution of **4n** (944 mg, 4.64 mmol) and *N*-vinyl phthalimide (200 mg, 1.16 mmol) in 1,2-dichloroethane (4 mL) and needed 15 mol % of DLP to go to completion. Flash chromatography on silica gel (ethyl acetate/petroleum ether, 0:10 to 3:7 v/v) afforded **6n** (250 mg, 57%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.86 (dd, 2H, *J*=3.1, 5.4 Hz), 7.74 (dd, 2H, *J*=3.0, 5.5 Hz), 6.28 (dd, 1H, *J*=7.3, 8.6 Hz), 4.62 (q, 2H, *J*=7.1 Hz), 2.72 (m, 2H), 2.51 (m, 2H), 1.86 (m, 1H), 1.39 (t, 3H, *J*=7.2 Hz), 0.96 (m, 2H), 0.83 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 211.10, 208.41, 166.80, 134.42, 131.64, 123.67, 70.54, 57.40, 40.16, 27.66, 20.54, 13.77, 11.09, 10.99. IR ($CDCl_3$): ν_{max} 2957, 2927, 2855, 1782, 1724, 1469, 1379, 1361, 1224, 1112, 1051. HRMS (EI^+): *m*/*z* calculated for $C_{18}H_{19}O_4NS_2$ M=377.0756, found: 377.0738, calculated for $C_{15}H_{14}O_3N$ [M−SC(S)OEt]=256.0974, found: 256.0982.

*2.2.15. S-[1-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-4-oxo-pentyl]-O-ethyl dithiocarbonate (**6o**). Method a*: Following the general procedure, the reaction was carried out with a solution of xanthate **4o** (412 mg, 2.32 mmol) and *N*-vinyl phthalimide (200 mg, 1.16 mmol) in 1,2-dichloroethane (2 mL) and needed 7 mol % of DLP to go to completion. Flash chromatography on silica gel (ethyl acetate/petroleum ether, 0:10 to 3:7 v/v) afforded xanthate **6o** (90 mg, 22%) as a pale yellow oil. *Method b*: Following the general procedure, the reaction was carried out with a solution of xanthate **4o** (824 mg, 4.64 mmol) and *N*-vinyl phthalimide (200 mg, 1.16 mmol) in 1,2-dichloroethane (4 mL) and needed 15 mol % of DLP to go to completion. Flash chromatography on silica gel (ethyl acetate/petroleum ether, 0:10 to 3:7 v/v) afforded xanthate **6o** (290 mg, 72%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.86 (dd, 2H, *J*=3.1, 5.4 Hz), 7.75 (dd, 2H, *J*=3.0, 5.5 Hz), 6.26 (t, 1H, *J*=7.8 Hz), 4.62 (q, 2H, *J*=7.1 Hz), 2.61 (m, 2H), 2.47 (m, 2H), 2.12 (s, 3H), 1.39 (t, 3H, *J*=7.1 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): 211.06, 166.82, 134.45, 131.60, 123.70, 70.59, 57.32, 40.22, 29.96, 27.49, 13.76. IR ($CDCl_3$): ν_{max} 2927, 2855, 1781, 1724, 1469, 1378, 1356, 1225, 1111, 1047. HRMS (EI^+): *m*/*z* calculated for $C_{16}H_{17}O_4NS_2$ M=351.0599, found: 351.0596, calculated for $C_{13}H_{12}O_3N$ [M−SC(S)OEt]=230.0817, found: 230.0819.

*2.2.16. S-[1-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-4-oxo-4-(2-oxo-oxazolidin-3-yl)-butyl]-O-ethyl dithiocarbonate (**6p**). Method a*: Following the general procedure, the reaction was carried out with a solution of **4p** (576 mg, 2.32 mmol) and *N*-vinyl phthalimide (200 mg, 1.16 mmol) in 1,2-dichloroethane (2 mL) and needed 10 mol % of DLP to go to completion. Flash chromatography on silica gel (ethyl acetate/petroleum ether, 0:10 to 4:6 v/v) afforded xanthate **6p** (220 mg, 45%) as a pale yellow oil. *Method b*: Following the general procedure, the reaction was carried out with a solution of xanthate **4p** (1.152 mg, 4.64 mmol) and *N*-vinyl phthalimide (200 mg, 1.16 mmol) in 1,2-dichloroethane (4 mL) and needed 15 mol % of DLP to go to completion. Flash chromatography on silica gel (ethyl acetate/petroleum ether, 0:10 to 4:6 v/v) afforded xanthate **6p** (400 mg, 82%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.82 (dd, 2H, *J*=3.1, 5.4 Hz), 7.71 (dd, 2H, *J*=3.0, 5.5 Hz), 6.29 (t, 1H, *J*=7.9 Hz), 4.58 (q, 2H, *J*=7.1 Hz), 4.38 (ddd, 2H, *J*=2.9, 7.4 Hz, *J*=8.6 Hz), 3.97 (m, 2H), 3.01 (m, 2H), 2.54 (q, 2H, *J*=7.2 Hz), 1.36 (t, 3H, *J*=7.1 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): 210.83, 171.46, 166.84, 153.52, 134.47, 131.57, 123.65, 70.60, 62.30, 56.84, 42.56, 31.85, 28.02, 21.08, 13.74. IR ($CDCl_3$): ν_{max} 2988, 2926, 1782, 1720, 1387, 1364, 1229, 1112, 1046. HRMS (EI^+): *m*/*z* calculated for $C_{18}H_{18}O_6N_2S_2$ M=422.0606, found: 422.0604, calculated for $C_{15}H_{13}O_5N_2$ [M−SC(S)OEt]=301.0824, found: 301.0819.

*2.2.17. S-[1-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-3-(methoxymethyl-carbamoyl)-butyl]-O-ethyl dithiocarbonate (**6q**).* Following the general procedure, the reaction was carried out with a solution of xanthate **4q** (515 mg, 2.32 mmol) and *N*-vinyl phthalimide (200 mg, 1.16 mmol) in 1,2-dichloroethane (3 mL) and needed 15 mol % of DLP to go to completion. Flash chromatography on silica gel (ethyl acetate/petroleum ether, 0:10 to 4:6 v/v) afforded xanthate **6q** (350 mg, 76%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): *Diastereoisomer 1*: 7.84 (dd, 2H, *J*=2.9, 5.6 Hz), 7.73 (dd, 2H, *J*=3.1, 5.4 Hz), 6.30 (dd, 1H, *J*=6.2, 9.5 Hz), 4.61 (q, 2H, *J*=7.1 Hz), 3.55 (s, 3H), 2.97 (s, 3H), 2.91 (m, 1H), 2.74 (m, 1H), 2.13 (td, 1H, *J*=6.1, 13.8 Hz), 1.39 (t, 3H, *J*=6.8 Hz), 1.18 (d, 3H, *J*=7.0 Hz). *Diastereoisomer 2*: 7.84 (dd, 2H, *J*=2.9, 5.6 Hz), 7.73 (dd, 2H, *J*=3.1, 5.4 Hz), 6.23 (dd, 1H, *J*=6.5, 9.9 Hz), 4.59 (q, 2H, *J*=7.1 Hz), 3.14 (s, 3H), 3.50 (s, 3H), 2.91 (m, 1H), 2.52 (m, 1H), 2.34 (m, 1H), 1.37 (m, 3H), 1.16 (d, 3H, *J*=6.9 Hz). ^{13}C NMR

(100.6 MHz, $CDCl_3$): *Diastereoisomer 1*: 211.02, 166.66, 134.35, 131.68, 123.52, 70.43, 61.26, 60.43, 56.34, 36.67, 33.71, 17.33, 13.75. *Diastereoisomer 2*: 210.42, 166.75, 134.35, 131.68, 123.50, 70.43, 61.37, 60.43, 55.45, 36.10, 33.71, 17.62, 13.72. IR ($CDCl_3$): ν_{max} 2976, 2938, 2856, 1780, 1720, 1655, 1469, 1380, 1355, 1230, 1112, 1046. HRMS (EI^+): *m/z* calculated for $C_{18}H_{18}O_6N_2S_2$ M=422.0606, found: 422.0604, calculated for $C_{15}H_{13}O_5N_2$ [M−SC(S)OEt]= 301.0824, found: 301.0819.

2.3. General procedure for radical addition of xanthates 6 to olefins

A magnetically stirred solution of xanthate **6** (1 equiv) and olefin (2 equiv) in 1,2-dichloroethane or ethyl acetate (1 mL/mmol of **6**) was heated at reflux for 15 min. DLP (5 mol %) was then added and additional DLP (5 mol %) was added every 60 min until total consumption of **6**. The mixture was then cooled to room temperature and the solvent was evaporated under reduced pressure. AIBN was added to a soltution of the crude product of the previous addition with tris(trimethylsilyl)silane (TTMSS, 1.5 equiv) and a 1:1 mixture of toluene and cyclohexane under a nitrogen atmosphere. The reaction mixture was then heated to reflux for one hour. The mixture was then cooled to room temperature and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel to yield the desired products **10**.

*2.3.1. Diethyl 2-[5-(dimethoxy-phosphoryl)-2-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-pentyl]-malonate (**10a**).* Following the general procedure, the reaction was carried out with a solution of xanthate **6b** (400 mg, 0.88 mmol) and dimethyl allylphosphonate (184 μL, 1.76 mmol) in 1,2-dichloroethane (1.9 mL) and needed 25 mol % of DLP to go to completion. The reduction was carried out on the crude product with TTMSS (407 μL, 1.32 mmol), AIBN (30 mg, 0.18 mmol) in toluene and cyclohexane (1.8 mL). Flash chromatography on silica gel (ethyl acetate/petroleum ether, 8:2 to 10:0 v/v) afforded **10a** (230 mg, 54%) as a pale colorless oil. ^1H NMR (400 MHz, $CDCl_3$): 7.83 (dd, 2H, *J*=3.1, 5.4 Hz), 7.73 (dd, 2H, *J*=3.0, 5.5 Hz), 4.21 (m, 3H), 4.01 (m, 2H), 3.69 (d, 3H, *J*=3.0 Hz), 3.67 (d, 3H, *J*=3.0 Hz), 3.24 (dd, 1H, *J*=5.7, 9.3 Hz), 2.71 (ddd, 1H, *J*=5.7, 11.1, 14.4 Hz), 2.35 (m, 1H), 2.22 (m, 1H), 1.76 (m, 3H), 1.54 (m, 2H), 1.24 (t, 3H, *J*=7.1 Hz), 1.16 (t, 3H, *J*=7.1 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): 166.72, 168.60, 168.32, 134.14, 131.70, 123.34, 61.79, 61.65, 52.32 (d, *J*=6.7 Hz), 49.53, 49.29, 33.20 (d, *J*=16.5 Hz), 31.16, 24.83, 23.44, 19.46 (d, *J*=4.9 Hz), 14.01, 14.94. HRMS (EI^+): *m/z* calculated for $C_{22}H_{30}O_9NP$ M=483.1658, found: 483.1674, calculated for $C_{15}H_{19}O_5NP[M-CH(CO_2Et)_2]$= 324.1001, found: 324.0986.

*2.3.2. 4-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-7,7-dimethoxy-heptanenitrile (**10b**).* Following the general procedure, the reaction was carried out with a solution of xanthate **6c** (250 mg, 0.75 mmol) and acrolein dimethylacetal (265 μL, 2.24 mmol) in 1,2-dichloroethane (1.8 mL) and needed 15 mol % of DLP to go to completion. The reduction was carried out on the crude product with TTMSS (234 μL, 1.47 mmol), AIBN (25 mg, 0.15 mmol) in toluene and cyclohexane (1.5 mL). Flash chromatography on silica gel (ethyl acetate/petroleum ether, 0:10 to 3:7 v/v) afforded **10b** (200 mg, 84%) as a pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$): 7.81 (dd, 2H, *J*=3.0, 5.2 Hz), 7.71 (dd, 2H, *J*=3.1, 5.2 Hz), 4.31 (t, 1H, *J*=5.5 Hz), 4.26 (m, 1H), 3.25 (s, 3H), 3.22 (s, 3H), 2.50 (m, 1H), 2.32 (dd, 2H, *J*=5.3, 7.2 Hz), 2.16 (dtd, 1H, *J*=5.3, 10.4, 15.5 Hz), 2.05 (td, 1H, *J*=7.1, 13.8 Hz), 1.78 (ddd, 1H, *J*=5.4, 10.7, *J*=19.3 Hz), 1.52 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 168.51, 134.31, 134.28, 131.55, 123.47, 118.78, 103.78, 53.22, 52.76, 50.84, 29.41, 28.18, 27.15, 14.84. IR ($CDCl_3$): ν_{max} 2935, 2835, 1774, 1712, 1469, 1395, 1373, 1362, 1129, 1050. HRMS (EI^+): *m/z* calculated for $C_{17}H_{20}O_4N_2$ M=316.1423, found: 316.1420, calculated for $C_{16}H_{17}O_3N_2$ [M−OMe]=285.1239, found: 285.1232.

*2.3.3. tert-Butyl [4-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-7-(4-fluoro-phenyl)-7-oxo-heptyl]-carbamate (**10c**).* Following the general procedure, the reaction was carried out with a solution of xanthate **6d** (300 mg, 0.70 mmol) and *N*-allyl-*tert*-butyl carbamate (210 mg, 1.40 mmol) in 1,2-dichloroethane (1.4 mL) and needed 20 mol % of DLP to go to completion. The reduction was carried out on the crude product with TTMSS (323 μL, 1.05 mmol), AIBN (23 mg, 0.14 mmol) in toluene and cyclohexane (1 mL). Flash chromatography on silica gel (ethyl acetate/petroleum ether, 10:0 to 3:7 v/v) afforded **10c** (200 mg, 61%) as a pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$): 7.83 (dd, 2H, *J*=5.4, 8.7 Hz), 7.76 (dd, 2H, *J*=3.1, 5.4 Hz), 7.67 (dd, 2H, *J*=3.0, 5.4 Hz), 7.01 (t, 2H, *J*=8.6 Hz), 4.63 (s, 1H), 4.27 (m, 1H), 3.07 (s, 2H), 2.88 (m, 2H), 2.48 (m, 1H), 2.14 (m, 2H), 1.78 (ddd, 1H, *J*=5.4, 10.6, 19.5 Hz), 1.36 (m, 2H), 1.36 (s, 9H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 197.30, 168.64, 165.71 (d, *J*=254.7 Hz), 155.94 (br s), 134.07, 133.15 (d, *J*=3.0 Hz), 131.70, 130.65 (d, *J*=9.3 Hz), 123.29, 115.63 (d, *J*=21.9 Hz), 79.16 (br s), 51.56, 40.08 (br s), 35.40, 29.72, 28.42, 27.32, 26.96. IR ($CDCl_3$): ν_{max} 2981, 2933, 1773, 1710, 1508, 1393, 1368, 1239, 1157. HRMS (EI^+): *m/z* calculated for $C_{26}H_{29}O_5N_2F$ M=468.2060, found: 468.2055, calculated for $C_{21}H_{20}O_3N_2F[M-C(O)O^tBu]$=367.1458, found: 367.1450.

*2.3.4. Diethyl 2-[7-(4-Bromo-phenyl)-4-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-7-oxo-heptyl]-malonate (**10d**).* Following the general procedure, the reaction was carried out with a solution of xanthate **6e** (350 mg, 0.71 mmol) and allyl ethylmalonate (285 μL, 1.42 mmol) in 1,2-dichloroethane (1.4 mL) and needed 20 mol % of DLP to go to completion. The reduction was carried out on the crude product with TTMSS (323 μL, 1.06 mmol), AIBN (23 mg, 0.14 mmol) in toluene and cyclohexane (1 mL). Flash chromatography on silica gel (ethyl acetate/petroleum ether, 10:0 to 3:7 v/v) afforded **10d** (203 mg, 50%) as a pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$): 7.80 (dd, 2H, *J*=3.0, 5.5 Hz), 7.71 (dd, 2H, *J*=3.1, 5.4 Hz), 7.69 (d, 2H, *J*=8.8 Hz), 7.52 (d, 2H, *J*=8.6 Hz), 4.27 (ddd, 1H, *J*=4.8, 9.9, 15.1 Hz), 4.16 (m, 1H), 4.13 (q, 4H, *J*=7.0 Hz), 3.25 (t, 1H, *J*=7.5 Hz), 2.89 (m, 2H), 2.50 (m, 1H), 2.18 (m, 2H), 1.88 (m, 4H), 1.21 (t, 3H, *J*=7.1 Hz), 1.19 (t, 3H, *J*=7.1 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): 197.87, 169.24, 168.61, 135.43, 134.06, 131.87, 131.70, 129.55, 128.22, 123.28, 61.35, 51.82, 51.51, 35.45, 32.10, 28.33, 26.89, 24.44, 14.06. IR ($CDCl_3$): ν_{max} 2984, 2963, 2939, 2870, 1772, 1720, 1709, 1587, 1469, 1395, 1178, 1071, 1011. HRMS (EI^+): *m/z* calculated for $C_{28}H_{30}O_7NBr$ M=571.1206, found: 571.1206, calculated for $C_{21}H_{20}O_3N_2F$ [M−OEt]=526.0865, found: 526.0850.

*2.3.5. Acetic acid 7-[1-(2,2-dimethyl-propionyl)-1H-indol-6-yl]-4-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-7-oxo-heptyl ester (**10e**).* Following the general procedure, the reaction was carried out with a solution of xanthate **6i** (200 mg, 0.37 mmol) and allyl acetate (162 μL, 1.49 mmol) in 1,2-dichloroethane (600 μL) and needed 20 mol % of DLP to go to completion. The reduction was carried out on the crude product with TTMSS (171 μL, 0.56 mmol), AIBN (12 mg, 0.07 mmol) in toluene and cyclohexane (1 mL). Flash chromatography on silica gel (ethyl acetate/petroleum ether, 10:0 to 3:7 v/v) afforded **10e** (132 mg, 69%) as a pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$): 9.03 (s, 1H), 7.86 (d, 1H, *J*=3.8 Hz), 7.82 (dd, 1H, *J*=1.5, 8.2 Hz), 7.79 (dd, 2H, *J*=3.0, 5.5 Hz), 7.69 (dd, 2H, *J*=3.0, 5.4 Hz), 7.54 (d, 1H, *J*=8.2 Hz), 6.62 (d, 1H, *J*=3.9 Hz), 4.35 (tt, 1H, *J*=4.9, 10.0 Hz), 4.05 (t, 2H, *J*=6.5 Hz), 3.05 (m, 2H), 2.54 (tdd, 1H, *J*=6.7, 10.1, 13.6 Hz), 2.24 (m, 2H), 2.01 (s, 3H), 1.90 (m, 1H), 1.64 (m, 2H), 1.50 (s, 9H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 198.98, 177.03, 171.10, 168.65, 136.32, 133.94, 133.87, 133.14, 131.81, 128.72, 123.29, 120.48, 118.01, 108.06, 63.95, 51.56, 41.38, 35.38, 29.02, 28.68, 27.17, 25.90, 20.98. IR ($CDCl_3$): ν_{max} 2959, 2933, 1774, 1742, 1713, 1686, 1427, 1371,

1307, 1239, 1190, 1079, 1045. HRMS (EI^+): *m/z* calculated for $C_{30}H_{32}O_6N_2$ M=516.2260, found: 516.2275.

*2.3.6. Ethyl 6-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-3,11-dioxo-11-phenyl-undecanoate (**10f**).* Following the general procedure, the reaction was carried out with a solution of xanthate **6j** (400 mg, 0.94 mmol) and 1-phenyl-pent-4-en-1-one (454 mg, 2.83 mmol) in 1,2-dichloroethane (1 mL) and needed 20 mol % of DLP to go to completion. The reduction was carried out on the crude product with TTMSS (435 μL, 1.41 mmol), AIBN (28 mg, 0.18 mmol) in toluene and cyclohexane (2 mL). Flash chromatography on silica gel (ethyl acetate/petroleum ether, 10:0 to 3:7 v/v) afforded **10f** (300 mg, 71%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.89 (d, 2H, *J*=7.2 Hz), 7.81 (dd, 2H, *J*=3.0, 5.3 Hz), 7.71 (dd, 2H, *J*=3.0, 5.3 Hz), 7.52 (t, 1H, *J*=7.3 Hz), 7.42 (dd, 2H, *J*=7.3 Hz), 4.13 (m, 1H), 4.12 (m, 2H), 3.36 (s, 2H), 2.90 (t, 2H, *J*=7.2 Hz), 2.50 (m, 2H), 2.33 (m, 1H), 2.25–1.95 (m, 2H), 1.72 (m, 3H), 1.27 (m, 2H), 1.14 (m, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 201.66, 199.90, 168.63, 166.99, 136.90, 134.07, 134.03, 132.91, 131.66, 128.54, 127.98, 123.23, 61.31, 51.34, 49.27, 39.86, 38.27, 32.18, 26.28, 28.11, 23.75, 14.05. IR ($CDCl_3$): ν_{max} 2934, 2862, 1772, 1709, 1686, 1469, 1372, 1332, 1248, 1181, 1115, 1028. HRMS (EI^+): *m/z* calculated for $C_{27}H_{29}O_6N$ M=463.1995, found: 463.1997, calculated for $C_{25}H_{24}O_5N$ [M−OEt]=418.1654, found: 418.1656.

*2.3.7. 2-[3-Dimethoxymethyl-4-oxo-1-(3-trimethylsilanylpropyl)-pentyl]-isoindole-1,3-dione (**10g**).* Following the general procedure, the reaction was carried out with a solution of xanthate **6m** (300 mg, 0.74 mmol) and allyl trimethylsilane (234 μL, 1.47 mmol) in 1,2-dichloroethane (1.5 mL) and needed 15 mol % of DLP to go to completion. The reduction was carried out on the crude product with TTMSS (342 μL, 1.11 mmol), AIBN (24 mg, 0.15 mmol) in toluene and cyclohexane (2 mL). Flash chromatography on silica gel (ethyl acetate/petroleum ether, 10:0 to 3:7 v/v) afforded **10g** (240 mg, 77%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): *Diastereoisomer 1*: 7.80 (dd, 2H, *J*=3.1, 5.5 Hz), 7.70 (dd, 2H, *J*=3.1, 5.4 Hz), 4.23 (d, 1H, *J*=7.7 Hz), 4.20 (m, 1H), 3.23 (s, 3H), 3.18 (s, 3H), 2.76 (ddd, 1H, *J*=2.7, 7.8 Hz, *J*=10.9 Hz), 2.34 (ddd, 1H, *J*=2.8, 11.9, 14.4 Hz), 2.14 (s, 3H), 2.05 (m, 1H), 1.90 (td, 1H, *J*=4.5, 14.5 Hz), 1.64 (m, 1H), 1.16 (m, 2H), 0.42 (m, 2H), −0.15 (s, 9H). *Diastereoisomer 2*: 7.77 (dd, 2H, *J*=3.5, 5.9 Hz), 7.67 (dd, 2H, *J*=3.0, 5.5 Hz), 4.30 (d, 1H, *J*=7.5 Hz), 4.03 (m, 1H), 3.31 (s, 3H), 3.27 (s, 3H), 2.83 (m, 1H), 2.47 (m, 1H), 2.05 (m, 2H), 1.97 (s, 3H), 1.64 (m, 1H), 1.16 (m, 2H), 0.42 (m, 2H), −0.15 (s, 9H). ^{13}C NMR (100.6 MHz, $CDCl_3$): *Diastereoisomer 1*: 211.46, 170.42, 135.84, 133.43, 125.00, 107.32, 57.60, 55.60, 53.99, 52.23, 38.27, 34.23, 32.39, 22.53, 17.79, 0.00. *Diastereoisomer 2*: 210.29, 170.34, 135.76, 133.43, 124.91, 107.32, 57.17, 55.11, 53.99, 51.25, 37.91, 32.06, 25.19, 22.53, 17.79, 0.00. IR ($CDCl_3$): ν_{max} 2955, 2837, 1772, 1709, 1393, 1373, 1360, 1248, 1118, 1070. HRMS (EI^+): *m/z* calculated for $C_{22}H_{33}O_5NSi$ M=419.2128, found: 419.2134, calculated for $C_{21}H_{30}O_5NSi$[M−Me]=404.1893, found: 404.1875.

*2.3.8. Methyl 12-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-15-oxo-hexadecanoate (**10h**).* Following the general procedure, the reaction was carried out with a solution of xanthate **6o** (100 mg, 0.31 mmol) and methyl 10-undecenoate (140 μL, 0.62 mmol) in 1,2-dichloroethane (600 μL) and needed 10 mol % of DLP to go to completion. The reduction was carried out on the crude product with TTMSS (143 μL, 0.47 mmol), AIBN (10 mg, 0.06 mmol) in toluene and cyclohexane (1 mL). Flash chromatography on silica gel (ethyl acetate/petroleum ether, 10:0 to 3:7 v/v) afforded **10h** (93 mg, 70%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.81 (dd, 2H, *J*=3.0, 5.4 Hz), 7.70 (dd, 2H, *J*=3.1, 5.3 Hz), 4.15 (m, 1H), 3.63 (s, 1H), 2.38 (m, 1H), 2.27 (m, 3H), 2.02 (s, 3H), 1.70 (s, 1H), 1.56 (m, 3H), 1.22 (m, 16H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 174.37, 168.75, 134.01, 131.76, 123.23, 51.79, 51.47, 40.60, 34.14, 32.37, 29.99, 29.45, 29.41, 29.37, 29.22, 29.20, 29.15, 26.60, 26.41, 24.98. IR ($CDCl_3$): ν_{max} 2930, 2857, 1771, 1709, 1468, 1438, 1396, 1372, 1200, 1172, 1088. HRMS (EI^+): *m/z* calculated for $C_{24}H_{33}O_5N$ M=415.2359, found: 415.2355, calculated for $C_{22}H_{30}O_4N$[M−COMe]=372.2175, found: 372.2177.

*2.3.9. 2-[4-Oxo-4-(2-oxo-oxazolidin-3-yl)-1-(3-1,2,4-triazol-1-yl-propyl)-butyl]-isoindole-1,3-dione (**10i**).* Following the general procedure, the reaction was carried out with a solution of xanthate **6p** (141 mg, 0.33 mmol) and allyl triazole (73 mg, 0.67 mmol) in 1,2-dichloroethane (600 μL) and needed 10 mol % of DLP to go to completion. The reduction was carried out on the crude product with TTMSS (153 μL, 0.50 mmol), AIBN (11 mg, 0.07 mmol) in toluene and cyclohexane (1 mL). Flash chromatography on silica gel (ethyl acetate/petroleum ether, 10:0 to 3:7 v/v) afforded **10i** (99 mg, 73%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 8.04 (s, 1H), 7.89 (s, 1H), 7.81 (dd, 2H, *J*=3.0, 5.4 Hz), 7.72 (dd, 2H, *J*=3.1, 5.4 Hz), 4.38 (m, 2H), 4.29 (m, 1H), 4.17 (t, 2H, *J*=7.0 Hz), 3.98 (m, 2H), 2.96 (ddd, 1H, *J*=6.8, 8.4, 16.8 Hz), 2.80 (td, 1H, *J*=6.1, 17.5 Hz), 2.40 (m, 1H), 2.15 (m, 2H), 1.85 (m, 2H), 1.74 (m, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 172.30, 168.70, 152.10, 143.04, 134.22, 131.60, 123.38, 62.15, 48.83, 42.52, 31.62, 29.07, 26.85, 26.81. IR ($CDCl_3$): ν_{max} 2254, 1781, 1709, 1389, 1373, 1334, 1275, 1224, 1112, 1088. HRMS (EI^+): *m/z* calculated for $C_{20}H_{21}O_5N_5$ M=411.1543, found: 411.1550, calculated for $C_{17}H_{17}O_3N_4$ [M-C(O)OC_2H_4N]=325.1301, found: 325.1303.

*2.3.10. [3-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-5-(methoxy-methyl-carbamoyl)-hexyl]-phosphonic acid dimethyl ester (**10j**).* Following the general procedure, the reaction was carried out with a solution of xanthate **6q** (300 mg, 0.76 mmol) and dimethyl vinylphosphonate (206 mg, 1.51 mmol) in 1,2-dichloroethane (1 mL) and needed 25 mol % of DLP to go to completion. The reduction was carried out on the crude product with TTMSS (340 μL, 1.10 mmol), AIBN (24 mg, 0.14 mmol) in toluene and cyclohexane (1.4 mL). Flash chromatography on silica gel (ethyl acetate/petroleum ether, 10:0 to 3:7 v/v) afforded **10j** (180 mg, 58%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): *Diastereoisomer 1*: 7.76 (m, 2H), 7.67 (dd, 2H, *J*=3.3, 5.3 Hz), 4.06 (m, 1H), 3.64 (m, 6H), 3.34 (s, 3H), 3.07 (s, 3H), 2.72 (m, 1H), 2.34 (m, 1H), 2.22 (m, 1H), 2.06 (m, 1H), 1.95 (m, 1H), 1.63 (m, 2H), 1.04 (d, 3H, *J*=6.9 Hz). *Diastereoisomer 1*: 7.76 (m, 2H), 7.68 (dd, 2H, *J*=3.3, 5.2 Hz), 4.21 (ddd, 1H, *J*=4.6, 10.1, 15.0 Hz), 3.64 (m, 6H), 3.42 (s, 3H), 2.87 (s, 3H), 2.72 (m, 1H), 2.52 (ddd, 1H, *J*=6.5, 10.7, 14.1 Hz), 2.22 (m, 2H), 1.95 (m, 1H), 1.63 (m, 2H), 1.07 (d, 3H, *J*=6.8 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): *Diastereoisomer 1*: 169.05, 134.62, 132.26, 123.69, 61.77, 52.96 (br s), 51.42, 51.29, 36.07, 32.87, 26.48, 26.23, 23.32, 21.90, 17.66. *Diastereoisomer 1*: 168.91, 134.66, 132.26, 123.72, 61.66, 52.96 (br s), 51.23, 51.10, 36.21, 33.59, 26.44, 26.19, 23.32, 21.90, 18.94. IR ($CDCl_3$): ν_{max} 2955, 2940, 2853, 1773, 1744, 1709, 1651, 1469, 1392, 1373, 1250, 1182, 1063, 103. HRMS (EI^+): *m/z* calculated for $C_{18}H_{25}O_7N_2P$ [MH^+-CH_3]=412.1399, found: 412.1410, calculated for $C_{16}H_{19}O_6N_2P$[$MH^+-2CH_3-CH_2O$]=366.0981, found: 366.0961.

*2.3.11. S-{5-[3-Cyano-1-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-3,3-dimethyl-propyl]-2-oxo-[1,3]dioxolan-4-yl}-O-ethyl dithiocarbonate (**11**).* The reaction was run with xanthate **6a** (0.29 mmol) and vinylidene carbonate (1.16 mmol) in ethyl acetate (0.3 mL). The reaction was completed after addition of 30 mol % of DLP. After evaporation of the solvent, the residue was purified by chromatography on silica gel using a gradient (petroleum ether/ethyl acetate: 7/3) and the addition product was isolated as a glass in 59% yield and as a mixture of diastereoisomers in a 1:1 ratio. ^{1}H NMR (400 MHz, $CDCl_3$): 7.92 (m, 2H), 7.80 (m, 2H), 6.40, 6.30 (two d, 1H, *J*=5.5, 6.0 Hz), 5.31, 5.26 (two dd, 1H, *J*=6.0, 9.9, 5.5, 8.5 Hz), 4.78 (m, 2H), 4.52 (m, 1H), 2.95, 2.90 (two dd, 1H, *J*=11.9 Hz, *J*=14.7 Hz, *J*=11.6 Hz, *J*=14.8 Hz), 1.96, 1.60 (two dd, 1H, *J*=2.5, 14.8 Hz, *J*=2.1, 14.8 Hz), 1.52, 1.35 (two t, 3H, *J*=7.1 Hz), 1.50, 1.48, 1.45, 1.43 (4s, 6H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 206.6, 205.8, 168.2 (br s), 151.8, 151.6, 134.8, 134.7, 131.3 (br s), 124.0 (br s), 123.7, 123.4, 85.5, 85.3, 78.8,

77.1, 71.8, 71.4, 49.85, 49.84, 37.8, 36.5, 30.0, 29.5, 28.9, 28.4, 25.5, 25.0, 13.7, 13.4. IR ($CDCl_3$): ν_{max} 2237, 1839, 1778, 1721, 1375, 1244, 1049. HRMS (EI^+): *m/z* calculated for $C_{20}H_{20}N_2O_6S_2$: 448.0763, found: 448.0769, calculated for $C_{17}H_{15}N_2O_5$ [M−$SCSOCH_2CH_3$]: 327.0981, found: 327.0984.

*2.3.12. S-(2-{5-[2-Cyano-1-(1,3-dioxo-indan-2-yl)-2,2-dimethyl-ethyl]-2-oxo-[1,3]dioxolan-4-yl}-1-(trimethylsilanylmethyl)-ethyl)-O-ethyl dithiocarbonate (**12**).* The reaction was run with xanthate **11** (0.145 mmol) and allyl trimethylsilane (4 equiv, 0.58 mmol) in ethyl acetate (0.5 mL). The reaction was complete after addition of 20 mol % of DLP. After evaporation of the solvent, the residue was purified by chromatography on silica gel using a gradient (petroleum ether/ethyl acetate:8/2) and the addition product **12** was isolated as a colorless oil in 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 7.87 (m, 2H), 7.76 (m, 2H), 4.88 (m, 1H), 4.76–4.45 (m, 3H), 4.38, 4.22, 3.96, 3.76 (4 m, 1H), 2.80 (m, 1H), 2.29–1.76 (5 m, 3H), 1.45–0.8 (m, 12H), 0.10, 0.09, −0.018 (3s, 9H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 213.1, 212.9, 212.3, 168.3 168.2 (br s), 153.1, 153.0, 152.9, 152.8, 134.8, 134.7, 134.6, 131.5, 131.4, 124.1, 123.4, 123.9, 123.8, 79.6, 79.4, 78.8, 78.74, 78.71, 78.5, 77.7, 77.2, 70.3, 70.2, 69.9, 69.7, 50.1, 50.07, 49.97, 49.91, 45.5, 45.0, 44.9, 44.6, 44.2, 43.9, 41.6, 41.0, 38.4, 38.1, 36.57, 36.3, 29.9, 29.7, 29.46, 29.43, 29.0, 28.7, 28.4, 25.5, 25.4, 24.9, 23.6, 23.5, 21.6, 21.3, 13.9, 13.8, 13.79, 13.71, −0.63, −0.72, −0.79. IR ($CDCl_3$): ν_{max} 2237, 1839, 1778, 1721, 1375, 1244, 1049. HRMS (EI^+): *m/z* calculated for $C_{23}H_{29}N_2O_5Si$ [M−$SCSOCH_2CH_3$]: 441.1846, found: 441.1844.

*2.3.13. 4-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-4-{5-[3-(ethyl-dimethyl-silanyl)-propyl]-2-oxo-[1,3]dioxolan-4-yl}-2,2-dimethyl-butyronitrile (**13**).* The reaction was run with xanthate **11** (1.27 mmol) and allyl trimethylsilane (3 equiv, 0.6 mL) in ethyl acetate (1.27 mL). The reaction was completed after addition of 10 mol % of DLP. After evaporation of the solvent, the residue was taken up in a 1:1 mixture of toluene/cyclohexane (10 mL) and tris(trimethylsilyl)silane (1.5 equiv, 0.6 mL) and AIBN (0.25 mmol, 41 mg) was added. The resulting mixture was refluxed under nitrogen until consumption of the starting xanthate. After evaporation of the solvent, the residue was purified by chromatography on silica gel using a gradient (petroleum ether/ethyl acetate:8/2) and the reduced product **13** was isolated in 50% yield over two steps and as about 1:1 mixture of two diastereoisomers. A pure fraction of each diastereoisomer was isolated and characterized. Less polar diastereioisomer: ^{1}H NMR (400 MHz, $CDCl_3$): 7.86 (dd, 2H, *J*=3.0, 5.4 Hz), 7.74 (dd, 2H, *J*=3.0, 5.4 Hz), 4.76 (dd, 1H, *J*=4.9, 8.2 Hz), 4.61 (m, 1H), 4.52 (m, 1H), 2.83 (dd, 1H, *J*=11.7, 14.5 Hz), 1.81 (m, 1H), 1.72 (m, 1H), 1.51 (m, 2H), 1.46 (dd, 1H, *J*=1.9, 14.6 Hz), 1.42 (s, 3H), 1.38 (s, 3H), 0.53 (m, 2H), −0.02 (s, 9H). ^{13}C NMR (100.6 MHz, $CDCl_3$): ^{13}C NMR (100 MHz, $CDCl_3$) 168.3 (br s), 153.4, 134.6, 131.4, 123.8 (br s), 123.5 (br s), 79.7, 79.1, 49.6, 38.6, 36.2, 29.9, 29.7, 28.3, 25.4, 19.2, 16.2, −1.7. More polar diastereoisomer: 7.86 (m, 2H), 7.77 (dd, 2H, *J*=5.81, 3.33 Hz), 4.87 (dd, 1H, *J*=5.05 Hz), 4.53 (dt, 1H, *J*=10.99, 2.27 Hz), 4.30 (dt, 1H, *J*=5.81, 7.68 Hz), 2.85 (dd, 1H, *J*=14.65, 12.13 Hz), 1.91 (dd, 1H, *J*=14.65, 2.27 Hz), 1.69 (m, 1H), 1.41 (s, 3H), 1.40 (s, 3H), 1.25 (m, 1H), 0.86 (m, 1H), 0.33 (m, 1H), 0.19 (m, 1H), 0.12 (m, 1H), 0.00 (s, 9H). More polar diastereoisomer: 170.41 (br s), 155.42, 136.84, 133.18 (br s), 125.84 (br s), 81.59, 80.33, 51.94, 40.16, 39.77, 31.40, 30.97, 26.86, 20.66, 18.06, 0.00. IR ($CDCl_3$): ν_{max} 2955, 1806(br), 1717, 1384, 1367, 1185. HRMS (EI^+): *m/z* calculated for $C_{23}H_{30}N_2O_5Si$ 442.1924, found: 442.1920.

*2.3.14. 4-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-2,2-dimethyl-4-(2-oxo-[1,3]dioxolan-4-yl)-butyronitrile (**14**).* A solution of xanthate **11** (0.21 mmol) in a 1:1 mixture of toluene/cyclohexane (2 mL) were added tris(trimethylsilyl)silane (0.42 mmol, 0.133 mL) and AIBN (0.042 mmol, 7 mg). The resulting mixture was refluxed under nitrogen until consumption of the starting xanthate. After evaporation of the solvent, the residue was purified by chromatography on silica gel using a gradient (petroleum ether/ethyl acetate:1/1) and the reduced product **14** was isolated as an oil in 78% yield and as about 1:1 mixture of two diastereoisomers. ^{1}H NMR (400 MHz, $CDCl_3$) 7.87 (dd, 2H, *J*=2.9, 5.1 Hz), 7.76 (m, 2H), 5.32 (m, 0.45H), 5.23 (q, 0.5H, *J*=7.7 Hz), 4.69 (m, 0.5H), 4.60 (m, 1H), 4.46 (t, 0.45H, *J*=8.4 Hz), 4.37 (m, 0.5H), 4.14 (dd, 0.45H, *J*=6.6, 8.9 Hz), 2.82 (q, 1H, *J*=12.6 Hz), 1.94 (dd, 1H, *J*=2.3, 14.8 Hz), 1.47, 1.43 (overlapping dd+s, 3.5H, *J*=2.1 Hz), 1.40 (s, 1.5H), 1.39 (s, 1.5H). ^{13}C NMR (100 MHz, $CDCl_3$) 168.3 (br s), 153.9, 153.7, 134.9, 134.7, 131.4, 131.2, 123.9 (br s), 123.6, 75.2, 74.4, 67.2, 67.0, 49.9, 49.4, 38.2, 36.2, 29.9; 29.4, 28.9, 28.3, 25.4, 24.8. MS (CI, NH_3) 329 $(MH)^+$, 346 $(MH+NH_3)^+$. HRMS (EI^+): *m/z* calculated for $C_{17}H_{16}N_2O_5$ 328.10592, found: 328.10590.

*2.3.15. 2-(7-Fluoro-4-oxo-1,2,3,4-tetrahydro-naphthalen-1-yl)-isoindole-1,3-dione (**15**).* A magnetically stirred solution of xanthate **6d** (450 mg, 1.04 mmol) in 1,2-dichloroethane (10 mL) was refluxed for 15 min. DLP (20 mol %) was then added and additional DLP (20 mol %) was added every 60 min until total consumption of **6d**. The mixture was then cooled to room temperature and the solvent was evaporated under reduced pressure. Flash chromatography on silica gel (ethyl acetate/petroleum ether, 8:2 to 6:4 v/v) afforded **15** (61 mg, 19%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.16 (dd, 1H, *J*=8.6, 6.0 Hz), 7.91 (dd, 2H, *J*=5.1, 3.0 Hz), 7.8 (dd, 2H, *J*=5.2, 3.0 Hz), 7.07 (dt, 1H, *J*=8.6, 2.3 Hz), 6.73 (dd, 1H, *J*=9.2, 1.2 Hz), 5.71 (dd, 1H, *J*=10.9, 4.2 Hz), 2.96–2.91 (m, 2H), 2.74 (ddd, 1H, *J*=17.2, 13.8, 4.6 Hz), 2.30 (ddd, 1H, *J*=13.3, 9.1, 4.5 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): 194.6, 167.6, 166.2 (d, *J*=254.7 Hz), 144.4 (d, *J*=8.3 Hz), 134.5, 131.7, 131.1 (d, *J*=9.7 Hz), 129.0 (d, *J*=2.5 Hz), 123.8, 115.6 (d, *J*=21.8 Hz), 112.2 (d, *J*=22.9 Hz), 48.7, 37.5, 27.6. IR (CCl_4): ν_{max} 2927, 2854, 1779, 1720, 1695, 1383, 1368, 1264.

*2.3.16. 2-(7-Oxo-4,5,6,7-tetrahydro-benzo[b]thiophen-4-yl)-isoindole-1,3-dione (**16**).* A magnetically stirred solution of xanthate **6i** (120 mg, 0.29 mmol) in 1,2-dichloroethane (3 mL) was refluxed for 15 min. DLP (20 mol %) was then added and additional DLP (20 mol %) was added every 60 min until total consumption of **6i**. The mixture was then cooled to room temperature and the solvent was evaporated under reduced pressure. Flash chromatography on silica gel (ethyl acetate/petroleum ether, 8:2 to 6:4 v/v) afforded **16** (70 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): 7.86 (dd, 2H, *J*=3.1, 5.4 Hz), 7.76 (dd, 2H, *J*=3.0, 5.5 Hz), 7.59 (d, 1H, *J*=5.0 Hz), 6.78 (d, 1H, *J*=5.0 Hz), 5.66 (dd, 1H, *J*=5.0, 10.9 Hz), 2.93 (m, 1H), 2.73 (m, 1H), 2.31 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 190.46, 171.19, 167.56, 149.45, 137.17, 134.52, 134.46, 131.71, 125.94, 123.66, 47.30, 37.56, 29.14. IR ($CDCl_3$): ν_{max} 2961, 2929, 1779, 1716, 1665, 1425, 1383, 1363, 1329, 1292, 1110. HRMS (EI^+): *m/z* calculated for $C_{16}H_{11}NO_3S$: 297.0460, found: 297.0464.

*2.3.17. 2-[2-(5-Oxo-6,7,8,9-tetrahydro-5H-benzocyclohepten-6-yl)-ethyl]-isoindole-1,3-dione (**17**).* The reduction was carried out on **6h** (400 mg, 0.91 mmol) with TTMSS (421 μL, 1.37 mmol), AIBN (30 mg, 0.18 mmol) in toluene and cyclohexane (1.8 mL). Flash chromatography on silica gel (ethyl acetate/petroleum ether, 10:0 to 3:7 v/v) afforded the desired intermediate **17** (256 mg, 88%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.81 (dd, 2H, *J*=3.0, 5.4 Hz), 7.69 (dd, 2H, *J*=3.0, 5.4 Hz), 7.60 (dd, 1H, *J*=0.8, 7.6 Hz), 7.36 (dt, 1H, *J*=1.2, 7.4 Hz), 7.24 (m, 1H), 7.19 (d, 1H, *J*=7.5 Hz), 3.75 (m, 2H), 2.95 (m, 3H), 2.36 (qd, 1H, *J*=7.2, 14.2 Hz), 2.10 (m, 2H), 1.82 (dt, 1H, *J*=6.4, 12.8 Hz), 1.64 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$):205.96, 168.35, 133.89, 131.29, 129.90, 128.62, 126.35, 123.25, 47.35, 36.15, 33.81, 30.57, 30.05, 25.58. IR ($CDCl_3$): ν_{max} 2941, 2867, 1773, 1712, 1682, 1441, 1397, 1360, 1078. HRMS (EI^+): *m/z* calculated for $C_{21}H_{19}NO_3$: 333.1365, found: 333.1366.

*2.3.18. 2,3,3a,4,5,6-Hexahydrobenzo[6,7]cyclohepta[1,2-b]pyrrole (**18**).* A solution of **17** (200 mg, 0.63 mmol) and methylamine (33%

in ethanol, 1.5 mL) in ethanol (1.5 mL) was stirred at room temperature for 12 h. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 8:2 to 2:8 v/v) afforded **18** (90 mg, 72%) contaminated by 12% of *N*-methylphthalimide as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.74 (dd, 1H, *J*=1.1, 7.5 Hz), 7.26 (dt, 1H, *J*=1.4, 7.3 Hz), 7.21 (dt, 1H, *J*=1.1, 7.4 Hz), 7.12 (d, 1H, *J*=7.3 Hz), 3.99 (m, 1H), 3.84 (m, 1H), 2.97 (ddd, 2H, *J*=3.1, 9.4, 13.1 Hz), 2.73 (ddd, 1H, *J*=2.9, 7.7 Hz, *J*=14.8 Hz), 2.25 (dtd, 1H, *J*=5.9, 8.6, 14.4 Hz), 2.00 (m, 1H), 1.85 (m, 2H), 1.64 (tdd, 1H, *J*=5.2, 5.9, 10.3 Hz), 1.56 (ddd, 1H, *J*=3.0, 5.7 Hz, *J*=13.0 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$):179.43, 141.18, 135.58, 133.90, 129.88, 129.75, 128.84, 126.37, 123.20, 58.80, 48.98, 35.23, 32.17, 32.07, 26.22. IR ($CDCl_3$): ν_{max} 2933, 2864, 1710, 1450, 1353, 1224. HRMS (EI^+): *m*/*z* calculated for $C_{13}H_{14}N$ M−H^+=184.1126, found: 184.1121.

*2.3.19. tert-Butyl {3-[5-(4-fluoro-phenyl)-3,4-dihydro-2H-pyrrol-2-yl]-propyl}-carbamate (**19**).* A solution of **10c** (85 mg, 0.18 mmol) and methylamine (33% in ethanol, 400 μL) in ethanol (400 μL) was stirred at room temperature for 5 h. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 10:0 to 7:3 v/v) afforded **19** (55 mg, 95%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.83 (dd, 2H, *J*=5.5, 8.7 Hz), 7.08 (t, 2H, *J*=8.7 Hz), 5.07 (br s, 1H), 4.15 (m, 1H), 3.19 (m, 2H), 3.00 (m, 1H), 2.85 (m, 1H), 2.22 (m, 1H), 1.70 (m, 3H), 1.59 (m, 2H), 1.44 (s, 9H). ^{13}C NMR (100.6 MHz, $CDCl_3$): 171.03, 164.20 (d, *J*=250.5 Hz), 156.12, 130.92 (d, *J*=2.3 Hz), 129.76 (d, *J*=8.5 Hz), 115.43 (d, *J*=21.7 Hz), 78.97 (br s), 72.99, 40.82, 35.11, 34.16, 28.99, 28.52, 27.37. IR ($CDCl_3$): ν_{max} 2931, 2868, 1706, 1602, 1510, 1367, 1235, 1168, 1157. HRMS (EI^+): *m*/*z* calculated for $C_{18}H_{25}O_2N_2F$ M=320.1900, found: 320.1907.

*2.3.20. Ethyl [5-(5-oxo-5-phenyl-pentyl)-pyrrolidin-(2Z)-ylidene]-acetate (**20**).* A solution of **10f** (300 mg, 0.65 mmol) and methylamine (33% in ethanol, 1.4 mL) in ethanol (1.4 mL) was stirred at room temperature for 5 h. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 10:2 to 7:3 v/v) afforded **20** (200 mg, 100%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 8.02 (s, 1H), 7.95 (d, 2H, *J*=7.6 Hz), 7.56 (t, 1H, *J*=7.3 Hz), 7.46 (t, 2H, *J*=7.6 Hz), 4.48 (s, 1H), 4.10 (q, 2H, *J*=7.1 Hz), 3.76 (m, 1H), 2.99 (t, 2H, *J*=7.3 Hz), 2.58 (m, 2H), 2.10 (m, 1H), 1.77 (m, 2H), 1.51 (m, 5H), 1.25 (t, 3H, *J*=7.1 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): 200.03, 170.83, 165.92, 137.02, 133.02, 128.64, 128.06, 59.56, 58.45, 38.36, 36.21, 31.87, 28.37, 26.18, 24.15, 14.77. IR ($CDCl_3$): ν_{max} 2980, 2935, 2862, 1682, 1652, 1592, 1449, 1295, 1241, 1151, 1049. HRMS (EI^+): *m*/*z* calculated for $C_{19}H_{25}O_3N$ M=315.1834, found: 315.1835.

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