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PAPER

Synthesis of spirocyclic thiazolidinediones using ring-closing metathesis and one-pot sequential ring-closing/cross metathesis†

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A novel synthetic route to spirocyclic thiazolidinediones is reported by utilizing ring-closing metathesis (RCM). A selective cross metathesis (CM) of *N*-allyl azaspiro derivatives with different olefins has been demonstrated to prepare substituted azaspiro-[4.4]nonenediones. The X-ray crystal structure of a spirocyclic thiazolidinedione dimer is described, which has been prepared in two steps from thiazolidinedione using a one-pot sequential ring-closing and self metathesis. Cross metathesis proceeds smoothly with both electron rich and poor olefins. The symmetrical bis-thiazolidinedione spirocyclic system can be used as CM coupling partner with olefins. One-pot sequential RCM-CM has been developed for the synthesis of substituted spirocyclic compounds. The methodology allows a quick access to thia-azaspiro-[4.4]nonene and -[4.5]decene-dione ring systems from readily available starting materials which are not otherwise accessible.

Introduction

Olefin metathesis has emerged as a powerful tool for the construction of carbon–carbon double bonds.[1,2] It has been extensively used in the areas of small molecule, natural product and polymer synthesis.[1] The commercial availability of well-defined catalysts (Fig. 1) and their tolerance to a variety of functional groups significantly widened the scope of olefin metathesis.[1,2]

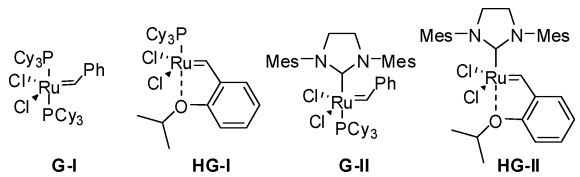

Fig. 1 Metathesis catalysts.

There are numerous applications of ring-closing metathesis (RCM) to the syntheses of heterocyclic compounds.[2,3] Thiazolidinediones and spirocyclic thiazolidines are potential chemotherapeutic agents with antidiabetic, antipsychotic, sedative and anaesthetic activities.[4,5] Despite their synthetic/medicinal utility, to the best of our knowledge only a few syntheses of 5-spirocyclic thiazolidiones have been described in the literature[5] and only a few compounds are reported.[6] Most of the applications of thiazolidinediones are described in patents.[6]

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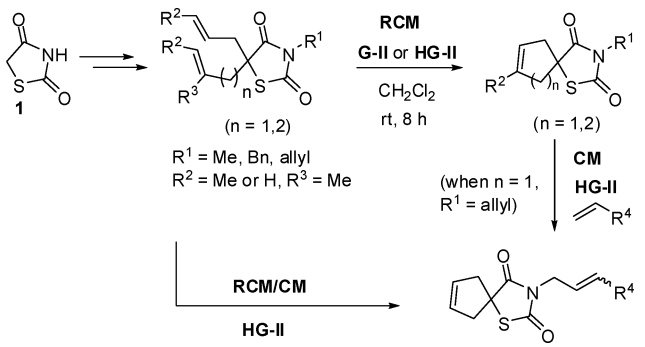
Herein we report the RCM,[7] cross metathesis (CM) and a selective one-pot sequential RCM/CM on thiazolidinedione-containing substrates for the rapid construction of novel thia-azaspirocyclic ring systems (Scheme 1).

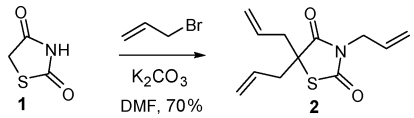


Scheme 1 RCM route to spirocyclic thiazolidinediones and selective cross metathesis (CM) and one-pot sequential RCM/CM to substituted thiazolidinediones.

Results and discussion

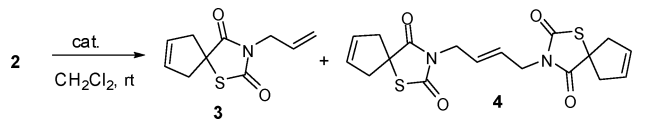
In ongoing research aimed at diversity oriented synthesis[8] of functionalized thiazole derivatives,[9,10] we found that treatment of thiazolidinedione **1** with allyl bromide in the presence of K_2CO_3 in DMF afforded the triallyl derivative **2** in 70% yield (Scheme 2). Initially, we examined the ability of Grubbs[1] (**G-I** and **G-II**) and Hoveyda-Grubbs[1] (**HG-I** and **HG-II**) ruthenium alkylidenes (Fig. 1) to catalyze a selective RCM of **2** (Table 1).

As shown in Table 1, the best results were found using 2 mol% of **G-II** or **HG-II** in CH_2Cl_2 at rt to give spirocyclopentenyl



Scheme 2 Preparation of triallyl thiazolidinedione **2**.

Table 1 Optimization of RCM of **2**



Entry	Cat. (mol%), time	Conv. (%)[a]	Ratio[a] of **3** : **4**	Yield (%)[b] **3**, **4**
1	**G-I** (5), 12 h	89	97 : 3	65[c], —
2	**HG-I** (5), 12 h	55	83 : 17	39[d], —
3	**G-II** (5), 12 h	>99	74 : 26	71, 17
4	**G-II** (5), 18 h[e]	>99	60 : 40	54, 32
5	**G-II** (2), 8 h	>99	87 : 13	85, 5
6	**HG-II** (2), 8 h	>99	85 : 15	83, 9
7	**HG-II** (5), 12 h	>99	60 : 40	54, 35
8	**HG-II** (5), 18 h[e]	>99	10 : 90	5, 87

[a] Percent conversions and $E:Z$ ratios were determined by ^{1}H NMR analysis of crude reaction mixture. [b] Isolated yields after chromatography. [c] 13% of starting material **2** left. [d] 41% of **2** left. [e] 40 °C.

thiazolidine **3** in high isolated yield (entries 5 and 6). Incomplete conversion and low yields of isolated product **3** were observed using 5 mol% of **G-I** or **HG-I**. Further optimization showed that increasing the catalyst loading of **G-II** and **HG-II** to 5 mol% enhanced the yield of **4** (Table 1, entries 7 and 8) derived from homodimerization of the RCM product **3**. Dimer **4** was obtained as the sole product by using **HG-II** giving longer reaction times at 40 °C. The structure of dimer **4** was confirmed by single crystal X-ray analysis (Fig. 2, ESI†).[11] The packing diagram of dimer **4** shows a body centered cubic arrangement in the unit cell (Fig. 2B).

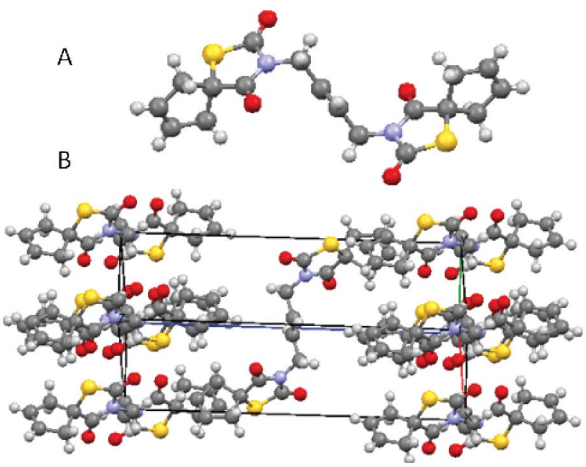
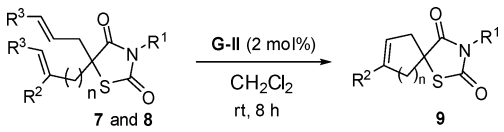


Fig. 2 (A) X-Ray crystal structure and (B) the packing diagram of dimer **4**.

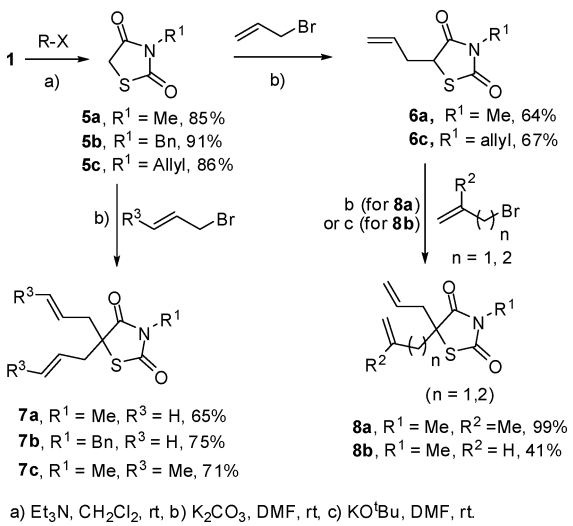
Next we examined the RCM of other thiazolidinedione substrates **7** and **8** (Scheme 3, Table 2). Substrates **7** and **8** were prepared from **1** by base mediated selective alkylation with alkyl halides *via* **5** and **6** (Scheme 3). *N*-Alkylation of **1** was selectively carried out using Et_3N to give the corresponding

Table 2 RCM of thiazolidinedione derivative **7** and **8**



Entry	Substrate	Product	Yield (%)[a]
1	**7a**	**9a**	95
2	**7b**	**9b**	98
3	**7c**	**9a**[b]	80
4	**8a**	**9c**	99
5	**8b**	**9d**	81

[a] Isolated yield after chromatography. [b] 5 mol% of **G-II**, 24 h.

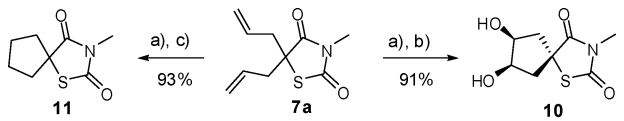


Scheme 3 Preparation of thiazolidinediones **7** and **8**.

thiazolidinediones **5** in high yield.[12] Alkylation at C5 of **5** and **6** was done using either K_2CO_3 or KO^{t}Bu depending on the alkenyl halide (Scheme 3).

RCM of compounds **7** and **8** using 2 mol% of **G-II** in CH_2Cl_2 proceeded smoothly to give the corresponding spirocyclic compounds **9** (Table 2). The yields for the RCM step ranged from 80 to 99%. Longer reaction time (24 h) and 5 mol% of **G-II** were required for RCM of **7c** to give compound **9a** in 80% yield (entry 3). Spirocyclic compound **9c** was prepared in near quantitative yield (entry 4). Spirocyclohexenyl derivative **9d** was efficiently prepared by RCM of **8b** in 81% isolated yield (Table 2, entry 5).

Compound **9a** was further functionalized to give the corresponding diol **10**. The diol **10** was prepared using a one-pot two-step process involving RCM of **7a** and dihydroxylation[13] of **9a** in 91% overall yield. A two step (RCM/hydrogenation)[10c,14] one pot procedure was also developed to prepare **11**, a known compound[5,15] in 93% overall yield (Scheme 4).

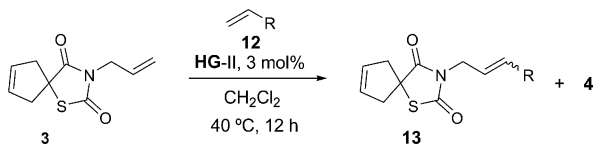


a) **G-II**, CH_2Cl_2, rt, 8 h; b) OsO_4, NMO, ^tBuOH (cat.), acetone-water (5:1); c) Hydrogenation Reactor, MeOH, 1 h.

Scheme 4 One pot RCM/dihydroxylation and RCM/hydrogenation.

We turned next to examine the feasibility of selective cross metathesis of *N*-allyl azaspiro substrate **3** with different alkenes (Table 3). Unlike RCM and ring-opening metathesis polymerization (ROMP), cross metathesis (CM),[16] is largely unexplored. Spirocyclic compound **3** possessing a cyclic double bond can also undergo ring-opening cross metathesis (ROCM).[17] The terminal double bond of substrate **3** was found to selectively cross with both electron-poor and electron-rich olefins **12** to give *E*-selective thiazolidinedione derivatives **13** as the major product. The reactions were carried out using 3 mol% of **HG-II** in CH_2Cl_2 at 40 °C.

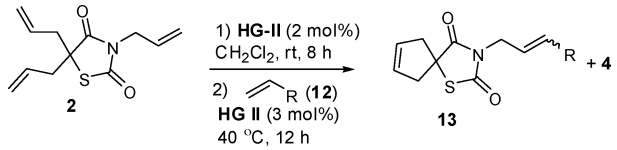
Table 3 Cross metathesis of thia-azaspirocyclic compound **3**



Entry	Olefin **12**	Ratio[a] **13**:**4**	Ratio **13** (*E*/*Z*)[a]	Yield (%)[b] **13**
1	**12a**	92:8	83:17	**13a**, 78
2	**12b**	100:0	85:15	**13b**, 67
3	**12c**	100:0	96:4	**13c**, 58
4	**12d**	84:16	>99	**13d**, 53
5	**12e**	90:10	—[c]	**13e**, 60[d]

Conditions: 5 equiv. of **12** in entry 1, 3 equiv. in entry 2 and 5, 1.5 equiv. in entries 3 and 4.[a] Determined by ^1H NMR analysis of crude reaction mixture. [b] Isolated yields after chromatography. [c] Not detected. [d] *E* only.

Table 4 One-pot RCM and CM



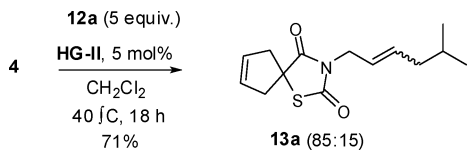
Entry	Olefin **12**	Ratio[a] **13**:**4**	Ratio **13** (E/Z)[a]	Yield (%)[b] **13**
1	**12a**	80:20	87:13	**13a**, 71
2	**12d**	67:43	>99	**13d**, 47

Conditions: 5 equiv. of **12a** and 1.5 equiv of **12d**.[a] Determined by ^1H NMR analysis of crude reaction mixture. [b] Isolated yields after chromatography.

CM of **3** with 5 equiv. of 4-methylpent-1-ene **12a** afforded **13a** in 78% (*E*/*Z*, 87:13) yield. Treatment of **3** with other olefins **12b–12e** afforded **13b–13e** in moderate isolated yields (53–67%, entries 2–5).

Based on these successful results of selective CM with a variety of olefins we have demonstrated one-pot sequential RCM–CM promoted by **HG-II** catalyst (Table 4) for the synthesis of substituted spirocyclic compounds **13**. One-pot processes are of considerable current interest because several chemical reactions can be performed in only one operation avoiding the handling and isolation of intermediates.[18,19] Substrate **2** was first treated with 2 mol% **HG-II** in CH_2Cl_2 and after completion of the RCM step; olefin **12a** or **12d** was added. Spirocyclic derivatives **13a** and **13d** were obtained in improved yield (Table 4) compared to the two-step procedure (66% and 45% overall yield for **13a** and **13d**).

In some cases (Tables 3 and 4) formation of self dimerization product **4** was observed. Following these observations, dimer **4** was used as coupling partner with **12a** (Scheme 5) in the presence of 5 mol% **HG-II** in CH_2Cl_2 (40 °C) to furnish **13a** in 71% isolated yield (*E*/*Z*, 85:15). Use of symmetric disubstituted olefin **4** containing heteroatoms N, S and O as CM coupling partner can find applications in the synthesis of polymers with novel properties.[20]



Scheme 5 Cross metathesis using dimer **4**.

Conclusion

In summary we have developed a general solution for the synthesis of thia-azaspiro-[4.4]nonene and [4.5]decene-dione ring systems from readily available starting materials which are not otherwise accessible. This new RCM, CM and one-pot metathesis platform will expand the scope and utility of novel spirocyclic thiazolidinediones in materials, medicines and biology.

Experimental section

General methods

All experiments were carried out under an inert atomosphere of argon in flame-dried flasks. Solvents were dried using standard procedures reported in D. D. Perrin, W. L. F. Armarego, Purification of Laboratory Chemicals, Pergamon Press, Oxford, 3rd edn, 1988. All starting materials were obtained from commercial suppliers and used as received. Products were purified by flash chromatography on silica gel (100–200 mesh, Merck). Unless otherwise stated, yields refer to analytical pure samples. Melting points were measured with BÜCHI Melting Point B-545 and are uncorrected. NMR spectra were recorded in $CDCl_3$ unless otherwise stated. ^{1}H NMR spectra were recorded at 500 MHz using Brüker ADVANCE 500 MHz and JEOL 400 MHz instruments at 278 K. Signals are quoted as δ values in ppm using residual protonated solvent signals as internal standard ($CDCl_3$: δ 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, br = broad, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on either a JEOL-400 (100 MHz), or a Brüker ADVANCE 500 MHz (125 MHz) with complete proton decoupling. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane with the solvent as the internal reference ($CDCl_3$: δ 77.23 ppm). Infrared (FTIR) spectra were recorded on a Perkin Elmer spectrophotometer with the KBr disk and KBr plate techniques for solid and liquid samples, ν_{max} cm^{-1}. HRMS analyses were performed with Q-TOF YA263 high resolution (Water Corporation) instruments by +ve mode electrospray ionization. Hydrogenation was carried out with H-Cube Hydrogenation Reactor (THALESNANO nanotechnology). Single crystal X-ray analysis of dimer **4** was recorded on a Brucker high resolution X-ray diffractometer instrument.

Preparation of 3,5,5-triallylthiazolidine-2,4-dione (2). To a suspension of 2,4-thiazolidinedione 1 (500 mg, 4.27 mmol, 1 equiv.) and K_2CO_3 (2.95 g, 21.35 mmol, 5 equiv.) in dry DMF (10 mL) was added allyl bromide (1.8 mL, 21.35 mmol, 5 equiv.). The resulting mixture was stirred at rt for 18 h. The reaction was stopped by adding water and then the mixture was extracted with EtOAc (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue was then purified by column chromatography on silica gel with EtOAc–hexane (5 : 95) to give compound **2** (707 mg, 70%) as colorless oil; ^{1}H NMR (500 MHz): 5.76–5.66 (3H, m), 5.22–5.15 (6H, m), 4.13 (2H, dt, J = 5.9, 1.3 Hz), 2.73–2.69 (2H, m), 2.63–2.58 (2H, m); ^{13}C NMR (125 MHz): 175.9, 170.1, 130.7, 130.2, 121.3, 118.6, 62.9, 43.6, 42.5; IR (neat): 3417, 3083, 2983, 2917, 2352, 1748, 1732, 1694, 1682, 1434, 1378 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{16}NO_2S$ $[M+H]^+$: 238.0893; Found 238.0965.

Preparation of thiazolidinediones 5

General procedure. MeI or BnBr or allyl bromide (3 equiv.) was added to a solution of 2,4-thiazolidinedione **1** (1 equiv.) and Et_3N (3 equiv.) in CH_2Cl_2 (0.7 M) at 0 °C and stirred for 7 h while warming to ambient temperature. The reaction mixture was quenched with water and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was then purified by column chromatography on silica gel with EtOAc–hexane (10/90 to 20/80) to provide compounds **5**.

3-Methylthiazolidine-2,4-dione (5a). Yield: 85%; obtained as a colorless liquid, solidifies upon storage in refrigerator; ^{1}H NMR (400 MHz): 3.13 (2H, s), 2.07 (3H, s); ^{13}C NMR (100 MHz): 171.7, 171.4, 33.7, 27.9; IR (KBr): 3398, 2990, 2948, 2637, 2371, 1744, 1674, 1425, 1400 cm^{-1}; HRMS (ESI) calcd for $C_4H_9N_2O_2S$ $[M+NH_4]^+$: 149.0385; Found 149.0263

3-Benzylthiazolidine-2,4-dione (5b). Yield: 91%; colorless solid; m.p. 61.8 °C;^{1}H NMR (400 MHz): 7.45–7.41 (2H, m), 7.37–7.31 (3H, m), 4.15 (2H, s), 3.12 (2H, s); ^{13}C NMR (100 MHz): 171.6, 171.1, 135.0, 128.9, 128.7, 128.3, 45.3, 33.7; IR (KBr): 3210, 3082, 2950, 2325, 2126, 1421, 1255 cm^{-1}; HRMS (ESI) calcd for $C_{10}H_{10}NO_2S$ $[M+H]^+$: 208.0424; Found 208.0762.

3-Allylthiazolidine-2,4-dione (5c). Yield: 86%; colorless oil; ^{1}H NMR (500 MHz): 5.82–5.73 (1H, m), 5.28–5.19 (2H, m), 4.19 (2H, dt, J = 6.0, 1.2 Hz), 3.95 (2H, s); ^{13}C NMR (125 MHz): 171.1, 170.8, 129.9, 118.8, 43.7, 33.6. IR (neat): 3420, 3086, 2989, 2942, 1752, 1683, 1429, 1378, 1332 cm^{-1}; HRMS (ESI) calcd for $C_6H_8NO_2S$ $[M+H]^+$: 158.0267; Found 158.1054.

Preparation of C5-allyl thiazolidinediones 6

General procedure. To a suspension of 2,4-thiazolidinedione 5 (1 equiv.) and K_2CO_3 (1 equiv.) in dry DMF (0.5 M) was added allyl bromide (0.7 equiv.). The resulting mixture was stirred at rt for 8 h. The reaction was stopped by adding water and then the mixture was extracted with EtOAc (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue was then purified by column chromatography on silica gel with EtOAc–hexane (5/95 to 10/90) to give compounds **6**.

5-Allyl-3-methylthiazolidine-2,4-dione (6a). Yield: 64%; colorless oil; ^{1}H NMR (400 MHz): 5.45–5.32 (1H, m), 4.69 (1H, d, J = 7.6 Hz), 4.65 (1H, s), 3.52 (1H, dd, J = 11.3, 5.0 Hz), 2.04 (3H, s), 1.90–1.83 (1H, m), 1.47–1.38 (1H, m); ^{13}C NMR (125 MHz): 173.9, 171.0, 131.9, 119.6, 49.0, 36.5, 27.6; IR: (neat) 3813, 3417, 2921, 2352, 2328, 1682, 1416, 1367 cm^{-1}; HRMS (ESI) calcd for $C_7H_{10}NO_2S$ $[M+H]^+$: 172.0424; Found 172.0497.

3,5-Diallylthiazolidine-2,4-dione (6c). Yield: 67%; colorless oil; ^{1}H NMR (500 MHz): 5.80–5.72 (2H, m), 5.24–5.17 (4H, m), 4.27 (1H, dd, J = 8.7, 4.0 Hz), 4.19–4.16 (2H, m), 2.94–2.90 (1H, m), 2.64–2.58 (1H, m); ^{13}C NMR (125 MHz): 173.5, 170.7, 131.8, 130.0, 119.9, 118.8, 49.1, 43.7, 36.6; IR (neat): 3418, 3084, 2930, 1754, 1694, 1428, 1379, 1330, 1264 cm^{-1}; HRMS (ESI) calcd. for $C_9H_{12}NO_2S$ $[M+H]^+$: 198.0580; Found 198.0670.

Preparation of thiazolidinediones 7a–b

General procedure. To a suspension of 2,4-thiazolidinedione **5a** or **5b** (1 equiv.) and K_2CO_3 (5 equiv.) in dry DMF (0.5 M) was added allyl bromide (5 equiv.). The resulting mixture was stirred at rt for 18 h. The reaction was stopped by adding water and then the mixture was extracted with EtOAc (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue

was then purified by column chromatography on silica gel with EtOAc–hexane (5/95 to 15/85) to give compound **7a** or **7b** as colorless oils.

5,5-Diallyl-3-methylthiazolidine-2,4-dione (7a). Yield: 65%; colorless oil; ^{1}H NMR (500 MHz): 5.76–5.68 (2H, m), 5.21–5.17 (4H, m), 3.04 (3H, s), 2.73–2.69 (2H, m), 2.64–2.60 (2H, m); ^{13}C NMR (125 MHz): 176.3, 170.5, 130.7, 121.0, 63.1, 42.3, 27.5; IR (neat): 3898, 3813, 3418, 3081, 2917, 2353, 2337, 1679, 1372 cm^{-1}; HRMS (ESI) calcd for $C_{10}H_{14}NO_2S$ [M+H]$^+$: 212.0737; Found 212.0738.

5,5-Diallyl-3-benzylthiazolidine-2,4-dione (7b). Yield: 75%; colorless oil; ^{1}H NMR (500 MHz): 7.40–7.39 (2H, m), 7.37–7.32 (3H, m), 5.74–5.66 (2H, m), 5.21 (1H, dd, J = 2.8, 1.3 Hz), 5.17 (1H, dd, J = 2.8, 1.3 Hz), 5.14–5.13 (1H, m), 5.12–5.11 (1H, m), 4.77 (2H, s), 2.78–2.74 (2H, m), 2.68–2.64 (2H, m); ^{13}C NMR (125 MHz): 176.2, 170.4, 135.2, 130.5, 128.6, 128.4, 127.9, 121.2, 62.8, 45.1, 42.5; IR (neat): 3410, 2918, 2353, 1682, 1383, 1336 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{18}NO_2S$ [M+H]$^+$: 288.1050; Found 288.0931.

5,5-Di-(*E*)-but-2-enyl)-3-methylthiazolidine-2,4-dione (7c). To a suspension of 2,4-thiazolidinedione **5a** (200 mg, 1.52 mmol, 1 equiv.) and K_2CO_3 (1.05 g, 7.6 mmol, 5 equiv.) in dry DMF (5 mL) was added (*E*)-1-bromobut-2-ene (0.62 mL, 6.08 mmol, 4 equiv.). The resulting mixture was stirred at rt for 18 h. The reaction was stopped by adding water and then the mixture was extracted with EtOAc (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue was then purified by column chromatography on silica gel with EtOAc–hexane (5 : 95) to give compound **7c** (257.7 mg, 71%) as colorless oil; ^{1}H NMR (400 MHz): 5.24–5.13 (2H, m), 4.90–4.80 (2H, m), 1.99 (3H, s), 1.49–1.42 (2H, m), 1.38–1.31 (2H, m), 0.26 (3H, s), 0.24 (3H, s); ^{13}C NMR (125 MHz): 177.0, 171.2, 132.0, 64.4, 41.4, 27.5, 18.0; IR (neat): 3898, 3813, 3417, 3081, 2917, 2352, 2336, 1679 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{18}NO_2S$ [M+H]$^+$: 240.1050; Found 240.1295.

Preparation of thiazolidinediones 8a–b

5-Allyl-3-methyl-5-(2-methylallyl)thiazolidine-2,4-dione (8a). To a suspension of 2,4-thiazolidinedione **10a** (100 mg, 0.58 mmol, 1 equiv.) and K_2CO_3 (240.46 mg, 1.74 mmol, 3 equiv.) in dry DMF (5 mL) was added 3-bromo-2-methylprop-1-ene (0.17 mL, 1.74 mmol, 3 equiv.). The resulting mixture was stirred at rt for 8 h. The reaction was stopped by adding water and then the mixture was extracted with EtOAc (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue was then purified by column chromatography on silica gel with EtOAc-hexane (5 : 95) to give compound **8a** (128.7 mg, 99%) as colorless oil; ^{1}H NMR (500 MHz): 5.75–5.66 (1H, m), 5.20–5.18 (1H, m), 5.16 (1H, m), 4.93–4.92 (1H, m), 4.80 (1H, s_{br}), 3.04 (3H, s), 2.82–2.79 (1H, m), 2.72–2.67 (1H, m), 2.60–2.55 (2H, m), 1.73 (3H, s); ^{13}C NMR (125 MHz): 176.9, 170.9, 139.4, 130.8, 121.2, 117.0, 62.9, 45.4, 43.2, 27.6, 24.2; IR (neat): 3417, 3288, 3082, 2917, 2353, 2337, 1372, 1280 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{16}NO_2S$ [M+H]$^+$: 226.0893; Found 226.0860.

3,5-Diallyl-5-(but-3-enyl)thiazolidine-2,4-dione (8b). To a suspension of 2,4-thiazolidinedione **6c** (200 mg, 1.01 mmol, 1 equiv.) and KO^{t}Bu (136.01 mg, 1.21 mmol, 1.2 equiv.) in dry DMF (5 mL) was added 4-bromobut-1-ene (0.12 mL, 1.21 mmol, 1.2 equiv.). The resulting mixture was stirred at rt for 12 h. The reaction was stopped by adding water and then the mixture was extracted with EtOAc (3 × 20 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue was then purified by column chromatography on silica gel with EtOAc–hexane (5 : 95) to give compound **8b** (103 mg, 41%) as colorless oil; ^{1}H NMR (400 MHz): 5.75–5.72 (3H, m), 5.30–5.18 (4H, m), 5.10–4.97 (2H, m), 4.21–4.15 (2H, m), 2.97–2.78 (1H, m), 2.74–2.68 (1H, m), 2.66–2.59 (1H, m), 2.24–2.26 (1H, m), 2.18–2.10 (1H, m), 2.00–1.92 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$): 175.3, 169.2, 135.2, 129.6, 129.1, 120.3, 117.8, 114.9, 62.0, 42.6, 42.3, 36.3, 27.9. IR (neat): 3698, 3613, 3417, 3089, 2717, 2352, 1752, 1689, 1426, 1371 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{18}NO_2S$ [M+H]$^+$: 252.1050; Found 252.1024.

Preparation of ring-closing metathesis products 3 and 9

General procedure. To a stirring solution of **2**, **7** or **8** (1 equiv.) in CH_2Cl_2 (0.05 M) was added **G-II** (2 mol%) and stirred for 8 h at room temperature. The reaction mixture was then concentrated and purified on silica gel (EtOAc–hexane, 10 : 90 to 20 : 80) to yield products **3** and **9**.

3-Allyl-1-thia-3-azaspiro[4.4]non-7-ene-2,4-dione (3). Yield: 85%; colorless oil; ^{1}H NMR (500 MHz): 5.86–5.77 (1H, m), 5.75 (2H, s), 5.25–5.24 (2H, m), 4.24 (2H, dt, J = 5.8, 1.3 Hz), 3.35–3.30 (2H, m), 2.92–2.89 (2H, m); ^{13}C NMR (125 MHz): 177.7, 170.8, 130.2, 128.0, 118.6, 61.7, 47.9, 43.9. IR (neat): 3417, 2925, 2849, 2353, 1689, 1372, 1219 cm^{-1}; HRMS (ESI) calcd for $C_{10}H_{12}NO_2S$ [M+H]$^+$: 210.0580; Found 210.0521.

3-Methyl-1-thia-3-azaspiro[4.4]non-7-ene-2,4-dione (9a). Yield: 95%; colorless oil; ^{1}H-NMR (500 MHz): 5.75 (2H, s), 3.37–3.30 (2H, m), 3.14 (3H, s), 2.92–2.89 (2H, m); ^{13}C-NMR (100 MHz): 178.2, 171.4, 128.1, 61.0, 47.9, 28.9; IR (neat): 3417, 3070, 2947, 2845, 1747, 1682, 1428, 1367, 1279 cm^{-1}; HRMS (ESI) calcd for $C_8H_{10}NO_2S$ [M+H]$^+$: 184.0424; Found 184.0507.

3-Benzyl-1-thia-3-azaspiro[4.4]non-7-ene-2,4-dione (9b). Yield: 98%; colorless oil; ^{1}H NMR (400 MHz): 7.39–7.37 (2H, m), 7.35–7.28 (3H, m), 5.74 (2H, s), 4.79 (2H, s), 3.33–3.28 (2H, m), 2.92–2.87 (2H, m), ^{13}C NMR: (100 MHz): 177.9, 171.0, 135.3, 128.7, 128.6, 128.1, 128.0, 61.6, 47.9, 47.3; IR (neat): 3414, 3066, 3034, 2933, 2844, 1748, 1497, 1456, 1429, 1381, 1335, 1305 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{14}NO_2S$ [M+H]$^+$, 260.0737; Found 260.0779.

3,7-Dimethyl-1-thia-3-azaspiro[4.4]non-7-ene-2,4-dione (9c). Yield: 99%; colorless oil; ^{1}H NMR (500 MHz): 5.33–5.11 (1H, m), 3.33–3.24 (2H, m), 3.13 (3H, s), 2.86–2.82 (1H, m), 2.74–2.70 (1H, m), 1.78 (3H, s); ^{13}C NMR (100 MHz): 178.1, 171.5, 137.9, 121.5, 62.4, 51.3, 47.9, 28.0, 16.0; IR (neat): 3614, 3170, 2945, 2744, 1645, 1582, 1427, 1360, 1271, 1204; HRMS (ESI) calcd for $C_9H_{12}NO_2S$ [M+H]$^+$: 198.0580; Found 198.0504.

3-Allyl-1-thia-3-azaspiro[4.5]dec-7-ene-2,4-dione (9d). Yield: 81%, colorless oil; ^{1}H NMR (500 MHz): 5.85–5.77 (2H, m), 5.75–5.72 (1H, m), 5.25–5.20 (2H, m), 4.22 (2H, dt, J = 5.8, 1.1 Hz),

3.00–2.96 (1H, m), 2.39–2.25 (4H, m), 1.95–1.93 (1H, m); ^{13}C NMR (125 MHz): 177.4, 170.9, 130.3, 126.6, 123.5, 118.5, 58.5, 43.5, 35.9, 32.0, 22.7. IR (neat): 3415, 2924, 2363, 1689, 1376, 1260 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{14}NO_2S$ [M+H]$^+$: 224.0737; Found 224.0828.

Synthesis of diol 10. To a stirred solution of **7a** (50 mg, 0.24 mmol, 1 equiv.) in CH_2Cl_2 (3 mL) was added **G-II** (4.0 mg, 2 mol%) at rt. After completion of starting material **7a** (8 h, TLC monitoring), the CH_2Cl_2 was concentrated and the crude product was directly used for OsO_4 dihydroxylation. The crude product was dissolved in acetone–water (5 : 1) and *N*-methylmorpholine *N*-oxide (NMO, 30.9 mg, 0.26 mmol, 1.1 equiv., 60 wt% in water) and osmium tetraoxide (3.0 mg, 0.012 mmol, 0.05 equiv., 2.5 wt% in *tert*-butanol) were added. The reaction mixture was stirred for 2 h at room temperature under argon and, upon completion (TLC), was quenched with saturated sodium bisulfite, diluted with water, and extracted with ethyl acetate. The combined EtOAc portions were dried (Na_2SO_4), filtered, and concentrated. The residue was purified by filtration through a short silica gel column to afford the diol **10** (47.4 mg, 91%) as colorless solid (m.p. 117.6 °C).

7,8-Dihydroxy-3-methyl-1-thia-3-azaspiro[4.4]nonane-2,4-dione (10). ^{1}H NMR (400 MHz): 3.67–3.64 (2H, m), 2.07 (3H, s), 1.56 (1H, d, *J* = 7.6 Hz), 1.51(1H, d, *J* = 6.8 Hz), 1.08 (1H, d, *J* = 5.1 Hz), 1.03 (1H, d, *J* = 4.7 Hz); ^{13}C-NMR (125 MHz): 178.9, 171.8, 73.7, 58.1, 45.4, 28.0; IR (neat): 3436, 2930, 2361, 1736, 1676, 1428, 1373, 1279 cm^{-1}; HRMS (ESI) calcd for $C_8H_{12}NO_4S$ [M+H]$^+$: 218.0479; Found, 218.0538.

Synthesis of spirocyclopentyl thiazolidinedione 11. To a stirred solution of **7a** (30 mg, 0.14 mmol, 1 equiv.) in CH_2Cl_2 (3 mL) was added **G-II** (2.4 mg, 2 mol%). The reaction mixture was stirred at rt for 8 h. The CH_2Cl_2 was then concentrated and MeOH (5 mL) was added. The reaction was kept in a H-Cube Hydrogenation Reactor for 1 h. The mixture was concentrated and purified by flash chromatography to yield (24.2 mg, 93%) of **11** as a colorless oil, which solidifies on cooling (upon storage in refrigerator).

3-Methyl-1-thia-3-azaspiro[4.4]nonane-2,4-dione 11. ^{1}H NMR (400 MHz): 2.10 (3H, s), 1.28–1.18 (2H, s), 0.90–0.82 (2H, s), 0.72–0.61 (2H, s), 0.51–0.40 (2H, s); ^{13}C NMR (125 MHz): 178.5, 171.2, 63.6, 41.0, 28.0, 25.4; IR (neat): 3411, 2926, 2354, 1682, 1428, 1367, 1277 cm^{-1}; HRMS (ESI) calcd for $C_8H_{12}NO_2S$ [M+H]$^+$: 186.0580; Found 186.0640.

Preparation of cross metathesis products 13

General procedure. To a solution of **3** (1 equiv.) and olefin 13 (1.5–5 equiv.) in CH_2Cl_2 (0.05 M) was added **HG-II** (3 mol%) and stirred at 40 °C for 12 h. The reaction mixture was concentrated and purified on silica gel (EtOAc–hexane, 5/95 to 20/80) to yield products **13**.

(*E*)-3-(5-Methylhex-2-enyl)-1-thia-3-azaspiro[4.4]non-7-ene-2,4-dione (13a). Yield: 78%; colorless oil; ^{1}H NMR (500 MHz): 5.78–5.65 (1H, m), 5.74 (2H, s), 5.46–5.37 (1H, m), 4.17 (2H, d, *J* = 7.9 Hz), 3.29–3.24 (2H, m), 2.91–2.87 (2H, m), 1.90 (2H, t, *J* = 8.7 Hz), 1.66–1.58 (1H, m), 0.86 (3H, s), 0.84 (3H, s); ^{13}C NMR (100 MHz): 177.7, 170.8, 135.2, 128.0, 122.9, 61.6, 47.9, 43.5, 41.4, 28.4, 22.2; IR (neat): 3400, 2956, 1683, 1428, 1379, 1335 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{20}NO_2S$ [M+H]$^+$, 266.1206; Found 266.1316.

(*E*)-3-(5-Bromopent-2-enyl)-1-thia-3-azaspiro[4.4]non-7-ene-2,4-dione (13b). Yield: 67%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): 5.80–5.66 (1H, m), 5.75 (2H, s), 5.60–5.56 (m, 1H), 4.20 (2H, d, *J* = 7.6 Hz), 3.37–3.30 (4H, m), 2.92–2.89 (2H, m), 2.59 (2H, q, *J* = 8.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 177.6, 170.8, 132.3, 128.1, 125.1, 61.7, 47.9, 43.1, 35.3, 31.6; IR (neat): 3415, 2920, 2847, 2359, 2081, 1654, 1380, 1330 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{14}BrNO_2SNa$ [M+Na]$^+$: 337.9829; Found 337.9828.

(*E*)-3-(4-(4-Methoxyphenyl)but-2-enyl)-1-thia-3-azaspiro[4.4]-non-7-ene-2,4-dione (13c). Yield: 58%; colorless oil; ^{1}H NMR (500 MHz): 7.07–7.05 (2H, m), 6.84–6.82 (2H, m), 5.90–5.84 (1H, m), 5.74 (2H, s), 5.54–5.47 (1H, m), 4.21 (2H, dd, *J* = 6.3, 1.0 Hz), 3.79 (3H, s), 3.33–3.29 (4H, m), 2.92–2.88 (2H, m); ^{13}C NMR (100 MHz): 177.7, 170.9, 158.1, 134.9, 131.5, 129.4, 128.0, 123.1, 113.8, 61.6, 55.2, 47.8, 43.4, 37.52; IR (neat): 3392, 2925, 2360, 1677, 1507, 1378 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{19}NO_3SNa$ [M+Na]$^+$: 352.0986; Found 352.0953.

3-Cinnamyl-1-thia-3-azaspiro[4.4]non-7-ene-2,4-dione (13d). Yield: 53%; colorless oil; ^{1}H NMR (400 MHz): 7.37–7.32 (2H, m), 7.30–7.29 (2H, m), 7.28–7.25 (1H, m), 6.69 (1H, d, *J* = 16.0 Hz), 6.20–6.15 (1H, m), 5.78 (2H, s), 4.39 (2H, dd, *J* = 5.5, 1.4 Hz), 3.35–3.30 (2H, m), 2.93–2.88 (2H, m); ^{13}C NMR (500 MHz): 177.7, 170.9, 136.0, 135.0, 128.6, 128.1, 128.0, 126.6, 121.3, 61.7, 47.9, 43.7; IR (neat): 3404, 2924, 2855, 2356, 1751, 1679, 1424, 1379, 1330 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{16}NO_2S$ [M+H]$^+$: 286.0893; Found 286.1051.

(*E*)-Methyl 4-(2,4-dioxo-1-thia-3-azaspiro[4.4]non-7-en-3-yl)but-2-enoate (13e). Yield: 60%; colorless oil; ^{1}H NMR (400 MHz): 6.84–6.75 (1H, m), 5.91–5.84 (1H, m), 5.74 (2H, s), 4.36 (2H, dd, *J* = 6.9, 2.0 Hz), 3.71 (3H, s), 3.34–3.30 (2H, m), 2.95–2.89 (2H, m); ^{13}C NMR (125 MHz): 177.3, 170.4, 165.8, 139.5, 128.0, 123.5, 61.8, 51.7, 47.9, 41.9; IR (neat): 3420, 2952, 2371, 1724, 1681, 1435, 1380, 1350, 1279 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{13}NO_4SNa$ [M+Na]$^+$: 290.0465; Found 290.0463.

General procedure for one-pot sequential metathesis of 2. To a solution of **2** (1 equiv.) in CH_2Cl_2 (0.05 M) was added **HG-II** (2 mol%). The mixture was stirred for 8 h at room temp. Then olefins **12a** and **12d** (3 to 5 equiv.) and **HG-II** (3 mol%) were added and stirred at 40 °C for 12 h. The reaction mixture was concentrated and purified on silica gel (EtOAc–hexane, 5/95 to 20/80) to yield products **13a** and **13d**.

Preparation of dimer 4. To a stirred solution of **2** (20 mg, 0.08 mmol, 1 equiv.) in CH_2Cl_2 (2 mL) was added **HG-II** (2.5 mg, 0.004 mmol, 5 mol%). The reaction mixture was heated at 40 °C for 18 h. The solvent was then removed under reduced pressure, and the residue purified by flash column chromatography on silica gel (EtOAc–hexane, 20/80) to give **4** (27 mg, 87%) as colorless crystal (EtOAc/hexane); m.p.148.4 °C. ^{1}H NMR (500 MHz): 5.75 (4H, s), 5.74–5.73 (2H, m), 4.21–4.20(4H, m), 3.32–3.29 (4H, m), 2.92–2.89 (4H, m); ^{13}C NMR (125 MHz): 177.5, 170.7, 128.0, 127.3, 61.6, 47.9, 42.6; IR (neat): 3397, 2945, 2362, 1750, 1673, 1432, 1389, 1356, 1322, 1244 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{19}N_2O_4S_2$ [M+H]$^+$: 391.0778; Found 391.0721; HRMS (ESI) calcd for $C_{18}H_{18}N_2O_4S_2Na$ [M+Na]$^+$: 413.0608; Found 413.0472.

Cross metathesis of 4 with olefin 12a. To a stirred solution of 4 (20 mg, 0.05 mmol, 1 equiv) and olefin **12a** (32 μL, 0.25 mmol, 5 equiv.) in CH_2Cl_2 (2 mL) was added **HG-II** (3.1 mg, 0.005 mmol, 10 mol%). The reaction mixture was heated at 40 °C for 18 h. The solvent was then removed under reduced pressure, and the residue purified by flash column chromatography on silica gel (EtOAc–hexane, 1/99 to 5/95) to give **13a** (9.2 mg, 71%) as a mixture of *E*/*Z* in a ratio of 85 : 15.

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