



Strategic utilization of catalytic metathesis and photo-thermal metathesis in caged polycyclic frames

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ABSTRACT

Highly functionalized cage compounds have been prepared via cross-metathesis (CM) using Grubbs modified *N*-tolyl catalyst **7**. A strategic utilization of photo-thermal metathesis and catalytic metathesis sequence for the synthesis of functionalized caged molecules has been demonstrated.

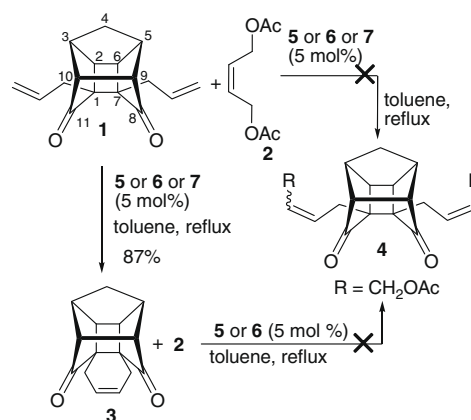
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1. Introduction

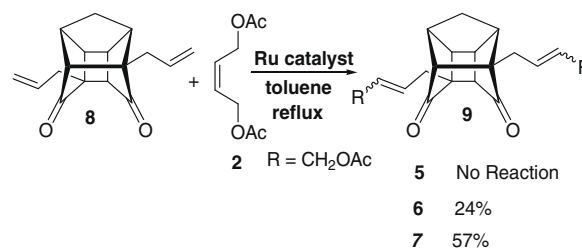
Caged polycyclic compounds have found several applications in diverse areas of organic chemistry.¹ Recently, they have served as useful synthons for the synthesis of both natural and non-natural products.² Some of these polycyclic compounds are highly symmetrical in nature,³ and possess inherent ring strain. Due to the lack of conformational mobility, their molecular architecture has generated considerable attention. Caged systems play an important role in medicinal chemistry and also they are useful building blocks for high energy materials.⁴

Olefin metathesis⁵ has emerged as a powerful tool in organic synthesis and it has opened up a new set of organic transformations such as ring-closing metathesis (RCM), enyne metathesis (EM), cross-metathesis⁶ (CM) and ring-opening cross-metathesis (ROCM) suitable for C–C bond formation. In view of varied applications of highly functionalized caged systems^{1–4}, we have extended the utility of CM towards the synthesis of intricate caged polycycles. The two allyl moieties present in dione **1** appear to be useful handle for the incorporation of new functional groups

in caged molecular frame. In this regard, caged dione **1** has been subjected to CM with olefin **2** in the presence of metathesis catalysts such as Grubbs second generation catalyst **5**,⁷ and Grubbs-Hoveyda catalyst **6**⁸ (Fig. 1) under a variety of reaction conditions. In all these experiments, RCM product **3** has been generated



Scheme 1. Non participation of ally groups of in CM.



Scheme 2. Both allyl groups participating in CM.

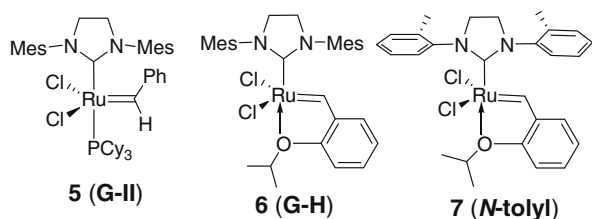
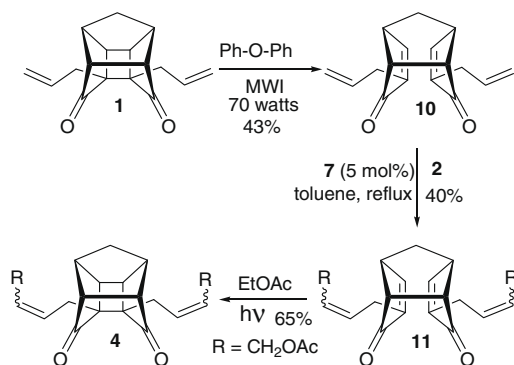
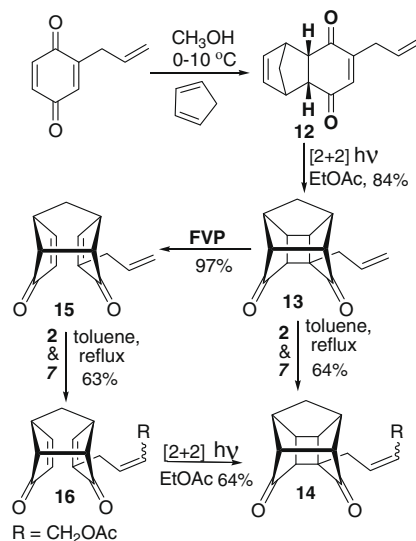


Figure 1. Various ruthenium catalysts used in metathesis.

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Scheme 3. The strategic combination of photo-thermal metathesis, CM and [2+2] photocycloaddition generating caged polycyclic compounds.



Scheme 4. Synthesis of functionalized caged compounds.

Table 1
CM of various polycyclic compounds with 1,4-di-acetoxy-2-butene using catalyst 7

| S.No. | Substrate | CM product (yield %) |
|-------|-----------|----------------------|
| 1 | | |
| 2 | | |
| 3 | | |
| 4 | | |
| 5 | | |
| 6 | | |

^aAll the cross-metathesis reactions have been performed using 5–7 mol % of catalyst 7 under toluene reflux conditions.

^bThe references mentioned with substrates indicate the procedures for their preparation.

^cThe CM products have been isolated as *E/Z* isomeric mixtures. However, in the olefinic region of ¹H NMR spectrum there is no spread out of the signals and therefore it is not possible to find out the ratio of *cis/trans* isomers.

instead of the desired CM product **4**. Grubbs and co-workers have recognized that NHC modified catalyst such as **7**⁹, where mesityl groups in Hoveyda catalyst has been replaced by tolyl moiety, show better efficiency in CM process involving sterically congested olefins. However, efforts to realize the CM with caged system **1** with the olefin **2** in the presence of the catalyst precursor **7** were futile. Also, our attempts to obtain **4** via ROCM of compound **3** with *cis*-1,4-diacetoxy-2-butene **2** proved to be unsuccessful (Scheme 1).

The molecular model of pentacyclic system **1** suggests that the presence of C₁–C₇ bond may be forcing the two allyl groups in close proximity thereby facilitating the formation of RCM product **3**. Also, we have observed that, the ‘proximity’ between the olefinic groups in a given substrate plays a crucial role in determining the outcome of the RCM reaction.¹⁰ A series of CM experiments were performed with caged compound **8**, where the two allyl groups are apart (compared to those in **1**) from each other. These experiments revealed that the corresponding CM product with the olefin **2** can be obtained using catalyst **6** or **7**. When the dione **8** has been treated with the olefin **2** in the presence of the catalyst **6**, the CM product **9** was obtained in 24% yield. The catalyst **7** was found to be more efficient in this transformation and gave 57% yield of the desired CM product **9**. However, catalyst **5** was not effective to promote the CM between dione **8** and the olefin **2** (Scheme 2). These results reinforced the assumption that the distance between the two interacting olefinic moieties determines the selectivity between RCM and CM.

At this point, we envisioned that moving the two allyl groups in caged system, apart from each other may be a useful alternative and ‘uncaged’ *cis,syn,cis* tricyclic compound¹¹ such as **10** may undergo CM with the olefin **2**.

‘Photo-thermal Metathesis’¹² is a valuable tool to assemble various natural products containing triquinane molecular frames. It appeared that the tactical utilization of photo-thermal metathesis and CM towards the construction of functionalized caged molecular entities is a viable proposition. The photo-thermal metathesis of compound **1** in diphenyl ether under microwave irradiation (MWI) conditions gave a linear *cis,syn,cis* tricyclic compound **10** in 43% yield where the two allyl groups are located away from each other. The CM of compound **10** with 1,4-diacetoxy-2-butene **2** in the presence of the modified (*N*-tolyl) Grubbs catalyst **7** gave the product **11** in a 40% yield. In the next step, the desired CM product **4** has been realized in an indirect route via a [2+2] photocycloaddition of compound **11** in good yield (Scheme 3).

To expand the scope of the methodology, we prepared the mono-allyl caged compound **13** by the [2+2] photocycloaddition of a known Diels–Alder¹³ adduct **12**.¹⁴ The CM of caged dione **13** with 1,4-diacetoxy-2-butene **2** by using modified (*N*-tolyl) Grubbs catalyst **7** in toluene under reflux conditions gave the CM product **14** in 64% yield. To generate a wide range of substrates for CM strategy, the caged system **13** has been subjected to flash vacuum pyrolysis (FVP) conditions at 560–580 °C to give the mono-allyl triquinane derivative **15** in 97% yield which underwent CM with the olefin **2** in the presence of **7** to afford compound **16** in 63% yield. The structure of a triquinane derivative **16** has been established on the basis of NMR data. Further, *cis-syn-cis* nature of the tricyclic compound has been further confirmed by the [2+2] photocycloaddition of **16** to generate caged system **14** (Scheme 4).

We prepared substrates **17** and **19** according to literature procedures^{15,16} and subjected to CM with alkene **2**. The CM products **18** and **20** were characterized by ¹H NMR and mass spectroscopic data. Various functionalized caged compounds prepared via CM reaction are included in Table 1. Initial studies have indicated that 1,4-di-acetoxy-2-butene is the best coupling partner in the cross-metathesis with these caged systems. We plan to elaborate this methodology with other coupling partners.

2. Conclusions

A variety of functionalized caged compounds have been prepared using CM strategy. The strategic combination of photo-thermal metathesis and CM has been demonstrated to deliver the intricate caged polycycles. Compounds generated here may serve as useful building blocks for further functionalization of caged polycyclic systems.

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General procedure for cross-metathesis: The catalyst **7** was added to a solution of diketone **10** (50 mg, 0.23 mmol) in dry and degassed (by bubbling nitrogen) toluene. The reaction mixture was slightly warmed and 1, 4-di-acetoxy-2-butene **2** (66 mg 0.45 mmol) was added. The reaction mixture was refluxed under N₂ for 12 h. At the conclusion of the reaction (TLC monitoring) the

reaction mixture was cooled to rt and the solvent was removed under reduced pressure to obtain the crude compound which was purified by column chromatography (ethyl acetate/petroleum ether) to deliver the CM product **11** in 40% yield.

Spectroscopic data for new compounds: (**4**) ^1H NMR (400 MHz, CDCl_3): δ 1.92–2.24 (m, 12H), 2.46–2.51 (m, 2H), 2.75–2.87 (m, 2H), 2.90 (s, 2H), 4.45–4.47 (m, 4H), 5.51–5.64 (m, 4H). ^{13}C NMR (100.5 MHz CDCl_3): δ 21.1, 24.1, 28.7, 29.8, 41.4, 41.5, 41.7, 43.7, 53.9, 55.4, 55.5, 60.3, 64.8, 126.8, 128.2, 128.5, 129.4, 170.9, 212.7. IR (Neat) ν_{max} : 1027, 1736, 2927 cm^{-1} . HRMS (Q-ToF): m/z calcd for $\text{C}_{23}\text{H}_{27}\text{O}_6$ [$\text{M}+\text{H}$] $^+$: 399.1808 found 399.1825.

Compound **9**: ^1H NMR (400 MHz, CDCl_3): δ 1.82–1.86 (m, 2H), 2.06 (s, 3H), 2.06 (s, 3H), 2.17–2.43 (m, 6H), 2.51 (d, 1H, $J = 6.4$ Hz), 2.67 (d, 1H, $J = 5.5$ Hz), 2.83–2.91 (m, 1H), 3.07 (dt, 1H, $J = 11.2, 6$ Hz), 4.50–4.52 (m, 4H), 5.60–5.78 (m, 4H). ^{13}C NMR (100.5 MHz CDCl_3): δ 21.1, 28.8, 32.1, 34.0, 35.3, 39.7, 41.9, 44.0, 47.2, 47.3, 47.4, 47.6, 47.7, 51.4, 60.1, 60.2, 60.3, 60.3, 61.6, 64.7, 126.4, 126.9, 128.0, 128.2, 129.7, 129.8, 130.5, 170.9, 170.9, 212.1, 213.3. IR (Neat) ν_{max} : 1024, 1712, 3054 cm^{-1} . Mass [$\text{M}-\text{COCH}_3$] 355.1642 was observed.

Compound **10**: ^1H NMR (400 MHz, CDCl_3): δ 1.85 (dt, 1H, $J = 14.4, 1.6$ Hz), 2.21 (dt, 1H, $J = 14.4, 10$ Hz), 2.60–2.82 (m, 4H), 3.28–3.42 (m, 4H), 5.02–5.06 (m, 4H), 5.07–5.78 (m, 2H), 7.020–7.026 (m, 2H). ^{13}C NMR (100.5 MHz CDCl_3): δ 29.1, 31.6, 47.9, 48.1, 53.8, 116.7, 134.2, 143.8, 159.6, 206.5. IR (Neat) ν_{max} : 1220, 1459, 2940 cm^{-1} . HRMS (Q-ToF): m/z calcd for $\text{C}_{17}\text{H}_{19}\text{O}_2$ [$\text{M}+\text{H}$] $^+$: 255.1385 found 255.1387.

Compound **11**: ^1H NMR (400 MHz, CDCl_3): δ 1.81–1.86 (m, 1H), 2.01 (s, 6H), 2.20–2.26 (m, 1H), 2.72–2.82 (m, 4H), 3.28–3.39 (m, 2H), 3.40–3.42 (m, 2H), 4.51 (dd, $J = 6.1$ Hz, 4H), 5.55–5.77 (m, 4H), 7.00–7.01 (m, 2H). ^{13}C NMR (100.5 MHz CDCl_3): δ 21.0, 27.8, 31.8, 48.2, 53.7, 64.7, 126.3, 129.9, 131.1, 143.4, 159.6, 170.8, 206.4. IR (Neat) ν_{max} : 1026, 1717, 1665 cm^{-1} . HRMS (Q-ToF): m/z calcd for $\text{C}_{23}\text{H}_{26}\text{O}_6$ [$\text{M}+\text{Na}$] $^+$: 421.1627 found 421.1646.

Compound **13**: ^1H NMR (400 MHz, CDCl_3): δ 1.79–2.30 (m, 3H), 2.35–2.86 (m, 8H), 4.98 (d1/2ABq, 1H, $J = 10, 4.8, 1.6$ Hz), 5.05 (d1/2ABq, 1H, $J = 17, 8, 1.4$ Hz), 5.72–5.83 (m, 1H). ^{13}C NMR (100.5 MHz CDCl_3): δ 33.7, 36.6, 40.9, 42.3, 43.7, 44.3, 47.9, 51.5, 54.8, 55.0, 118.6, 132.7, 212.3. IR (Neat) ν_{max} : 1031, 1655, 2945 cm^{-1} . HRMS (Q-ToF): m/z calcd for $\text{C}_{14}\text{H}_{15}\text{O}_2$ [$\text{M}+\text{H}$] $^+$: 215.1072 found 215.1063.

Compound **14**: ^1H NMR (400 MHz, CDCl_3): δ 1.90–1.93 (m, 1H), 2.01–2.08 (m, 4H), 2.27–2.48 (m, 3H), 2.68–2.77 (m, 2H), 2.84–2.93 (m, 3H), 3.08–3.13 (m, 1H), 4.50–4.52 (m, 2H), 5.66–5.70 (m, 2H). ^{13}C NMR (100.5 MHz CDCl_3): δ 21.0, 27.7, 32.3, 36.7, 41.0, 42.4, 42.6, 43.8, 44.4, 48.1, 48.2, 51.6, 54.9, 55.1, 60.2, 64.7, 127.0, 128.3, 128.8, 129.7, 170.8, 212.0, 212.1. IR (Neat) ν_{max} : 1031, 1663, 2947 cm^{-1} . HRMS (Q-ToF): m/z calcd for $\text{C}_{17}\text{H}_{19}\text{O}_4$ [$\text{M}+\text{H}$] $^+$: 287.1283 found 287.1277.

Compound **15**: ^1H NMR (400 MHz, CDCl_3): δ 1.89 (dt, 1H, $J = 14, 2$ Hz), 2.27 (dt, 1H, $J = 14, 10$ Hz), 2.60–2.86 (m, 2H), 3.21–3.29 (m, 2H), 3.40–3.55 (m, 2H), 5.01–5.06 (m, 2H), 5.67–5.77 (m, 1H), 5.88 (dd, 1H, $J = 5.6, 2.4$ Hz), 7.033–7.038 (m, 1H), 7.47 (dd, 1H, $J = 5.6, 2.4$ Hz). ^{13}C NMR (100.5 MHz CDCl_3): δ 29.1, 31.8, 48.2, 50.3, 53.1, 53.7, 116.7, 133.2, 133.9, 143.8, 159.0, 166.3, 206.4, 207.5. IR (Neat) ν_{max} : 1640, 1718, 2935 cm^{-1} . HRMS (Q-ToF): m/z calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2\text{Na}$ [$\text{M}+\text{Na}$] $^+$: 237.0891; found 237.0898.

Compound **16**: ^1H NMR (400 MHz, CDCl_3): δ 1.88 (dt, 2H, $J = 14, 2$ Hz), 2.01 (s, 3H), 2.22–2.30 (m, 1H), 2.76–2.85 (m, 2H), 3.20–3.28 (m, 2H), 3.40–3.54 (m, 2H), 4.51 (d, 1H, $J = 6.1$ Hz), 5.54–5.68 (m, 2H), 5.88 (dd, 1H, $J = 5.8, 2.4$ Hz), 7.00–7.08 (m, 1H), 7.45 (dd, 1H, $J = 5.2, 2.4$ Hz). ^{13}C NMR (100.5 MHz CDCl_3): δ 21.0, 23.2, 27.6, 31.8, 48.3, 50.4, 53.2, 53.7, 53.8, 60.1, 64.7, 125.7, 126.3, 129.6, 130.9, 133.2, 143.4, 159.1, 159.3, 166.5, 166.6, 170.8, 206.4, 207.6. IR (Neat) ν_{max} : 1025, 1629, 1715 cm^{-1} . HRMS (Q-ToF): m/z calcd for $\text{C}_{17}\text{H}_{18}\text{O}_4$ [$\text{M}+\text{Na}$] $^+$: 309.1103; found 309.1117.

Compound **18**: ^1H NMR (400 MHz, CDCl_3): δ 1.83–1.90 (m, 1H), 2.06–2.21 (m, 10H), 2.23–2.46 (m, 4H), 2.51 (d, 1H, $J = 6.4$ Hz), 2.68 (d, 1H, $J = 5.1$ Hz), 2.83–2.92 (m, 2H), 3.04–3.12 (m, 1H), 4.50–4.68 (m, 4H), 5.55–5.78 (m, 4H). ^{13}C NMR (100.5 MHz CDCl_3): δ 21.0, 29.7, 34.5, 34.7, 43.8, 44.0, 45.5, 45.6, 49.3, 49.5, 58.9, 60.0, 64.7, 125.9, 126.8, 131.8, 132.4, 170.8, 218.7. IR (Neat) ν_{max} : 1026, 1735, 2962 cm^{-1} . HRMS (Q-ToF): m/z calcd for $\text{C}_{23}\text{H}_{28}\text{O}_6\text{Na}$ [$\text{M}+\text{Na}$] $^+$: 423.1784; found 423.1782.

Compound **20**: ^1H NMR (300 MHz, CDCl_3): δ 1.84–1.94 (m, 1H), 2.05–2.08 (m, 5H), 2.21–2.28 (m, 3H), 2.32–2.46 (m, 2H), 2.66–2.78 (m, 3H), 2.82–2.90 (m, 2H), 4.46–4.66 (m, 2H), 5.55–5.75 (m, 2H). ^{13}C NMR (100.5 MHz CDCl_3): δ 21.0, 29.7, 34.5, 34.8, 39.3, 40.7, 40.8, 43.2, 43.5, 45.5, 45.6, 48.0, 48.9, 49.1, 58.5, 59.0, 60.0, 64.7, 125.9, 126.7, 131.9, 132.5, 170.8, 217.7, 218.6. IR (Neat) ν_{max} : 1017, 1752, 2966 cm^{-1} . Mass [$\text{M}-\text{OCH}_3$] 257.0024 was observed.