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An organophosphorus-mediated cross-Rauhut–Currier/Wittig domino reaction for the efficient synthesis of trisubstituted cyclopentenes†

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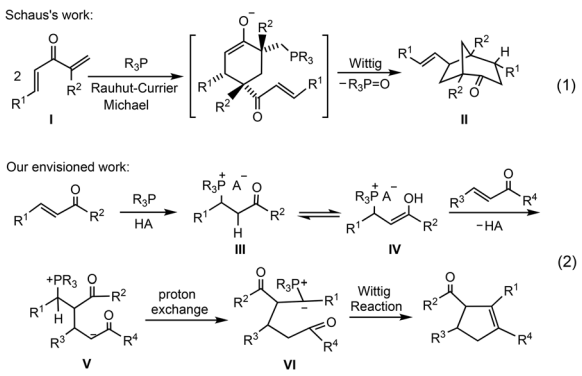
An efficient organophosphorus-mediated cross-Rauhut–Currier/Wittig domino reaction of vinyl ketones with chalcones has been developed for the synthesis of trisubstituted cyclopentenes. The new synthetic method has the advantages of mild reaction conditions, high efficiency, environmental friendliness and satisfactory yields.

Introduction

As a graceful strategy for the efficient formation of a carbon–carbon bond, the Rauhut–Currier reaction, which creates a new carbon–carbon bond between the α-position of an activated alkene and the β-position of a second activated alkene, has drawn much attention.[1] The domino reaction can form two or more chemical bonds in a single reaction with the advantages of step-efficiency and environmental friendliness. Because a Rauhut–Currier intermediate contains both nucleophilic and electrophilic atoms, the Rauhut–Currier reaction can be readily incorporated into a domino process.[2] After the twentieth century, many domino reactions initiated by Rauhut–Currier reactions have been developed for the formation of multiple carbon–carbon bonds in a single reaction, such as cross-Rauhut–Currier/Michael,[3] cross-Rauhut–Currier/aldol,[4] cross-Rauhut–Currier/Michael/S_N2,[5] cross-Rauhut–Currier/aldol/allylic S_N,[6] and Rauhut–Currier/Michael/Wittig[7] domino reactions.

Moreover, the Wittig reaction is one of the most important processes for the formation of carbon–carbon double bonds. Nevertheless, only one report discloses a domino reaction combining the Rauhut–Currier reaction with the Wittig reaction. In 2006, Schaus *et al.* developed a Rauhut–Currier/Michael/Wittig domino reaction of 1,4-dien-3-ones **I** to give bicyclo[3.2.1]octenones **II** (Scheme 1, eqn (1)).[7] However, the Rauhut–Currier reaction in this domino reaction is limited to homodimerization of α,β-unsaturated ketones. In our previous work on the MBH-type of reaction of α,β-unsaturated ketones with allylic acetates, we found that the addition of a proton acid could decrease homodimers of the α,β-unsaturated ketones.[8] Thus, we envisioned that an α,β-unsaturated ketone could undergo a nucleophilic addition with a tertiary phosphine (PR_3), followed by a protonation to form keto intermediate **III** (Scheme 1, eqn (2)). Keto intermediate **III** could change into enol intermediate **IV** by a keto–enol tautomerism. The enol in **IV** may nucleophilically attack the β-carbon of another α,β-unsaturated ketone to generate zwitterion intermediate **V**. Through intramolecular proton exchange, **V** could change into phosphonium ylide **VI**. Successively, the intramolecular Wittig reaction of ylide **VI** may lead to multisubstituted cyclopentene. Multisubstituted cyclopentenes as important intermediates have been widely applied in organic synthesis.[9]



Scheme 1 Domino reactions combining the Rauhut–Currier reaction with the Wittig reaction.

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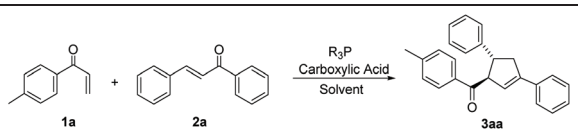
Results and discussion

Initially, vinyl ketone **1a** and chalcone **2a** were chosen as model substrates to explore and optimize their cross-Rauhut–Currier/Wittig domino reaction. When the reaction was performed at 100 °C using $(n\text{-Bu})_3$P (100 mol%) as a Lewis base catalyst and PivOH as a proton acid in dioxane under a nitrogen atmosphere, we were pleased to find that the expected trisubstituted cyclopentene **3aa** was obtained in 56% yield (entry 1, Table 1). Then, other tertiary phosphines were screened, but none of them led to better yields for **3aa** (compare entries 2–5 with entry 1, Table 1). Other carboxylic acids besides PivOH were examined in the domino reaction, and HOAc proved to be the most efficient among them (entries 6–8, Table 1; also see the ESI†). Increasing or decreasing the amount of HOAc led to lower yields of **3aa** (compare entries 9 and 10 with entry 7, Table 1). Switching the solvent from dioxane to toluene, dimethyl ether or acetonitrile gave lower or no yield of **3aa** (compare entries 11–13 with entry 7, Table 1). No matter whether the temperature was increased or decreased, lower yields of **3aa** were obtained. It's noteworthy that in the absence of HOAc, only a dimer by the homo-Rauhut–Currier reaction of **1a** and a cycloaddition product by the homo-Rauhut–Currier/Wittig domino reaction of **1a** were obtained; no desired product **3aa** was isolated (entry 16; also see the ESI†). The experimental result suggests again that the proton acid could avoid generating a large amount of enolic anion adducts of vinyl ketone **1a** with $(n\text{-Bu})_3$P, which could react readily with another vinyl ketone **1a** to give its homo-dimer.[8] Thus, it can be concluded that the optimized reaction should be performed at 100 °C in the presence of $(n\text{-Bu})_3$P (100 mol%) and HOAc (2.0 equiv.) in 1,4-dioxane under nitrogen.

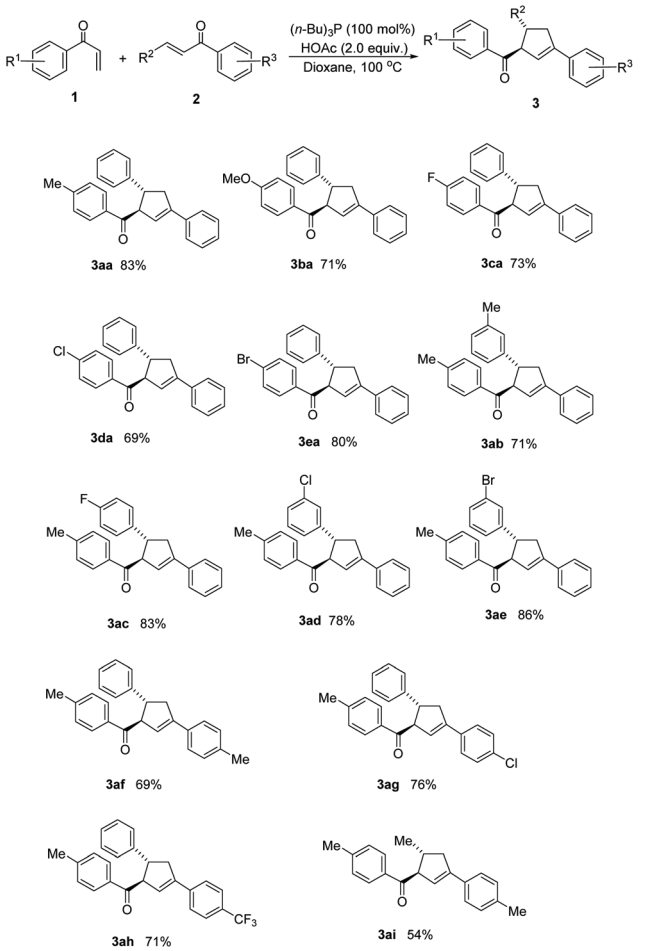
Under the optimized conditions, we found that various aryl vinyl ketones **1a–e**, which carried either electron-donating or electron-withdrawing groups on the benzene ring (in **1a–e**), were able to undergo the cross-Rauhut–Currier/Wittig domino reaction smoothly with chalcone **2a** to give the desired trisubstituted cyclopentenes **3aa–ea** in satisfactory yields (Scheme 2). The structure of trisubstituted cyclopentene **3da** was further determined by single-crystal X-ray diffraction besides ^{1}H NMR and ^{13}C NMR spectroscopy and HRMS (Fig. 1).[10] However, when 4-nitrophenyl vinyl ketone was employed, no expected cycloaddition product was obtained. Then, various chalcones **2b–h** were examined in the cross-Rauhut–Currier/Wittig domino reaction. The experimental results demonstrated that chalcones **2b–h** bearing either electron-donating or electron-withdrawing groups on the phenyl rings were also able to undergo the domino reaction expediently with vinyl ketone **1a**, affording the desired trisubstituted cyclopentenes **3ab–ah** in

Table 1 Optimization of the cross-Rauhut–Currier/Wittig domino reaction of vinyl ketone **1a** with chalcone **2a** [a]



Entry	R_3P	Carboxylic acid	Solvent	Yield[b] (%)
1	$(n\text{-Bu})_3$P	PivOH	Dioxane	56
2	Me_3P	PivOH	Dioxane	29
3	$(t\text{-Bu})_3$P	PivOH	Dioxane	0
4	Cy_3P	PivOH	Dioxane	Trace
5	Ph_3P	PivOH	Dioxane	Trace
6	$(n\text{-Bu})_3$P	BzOH	Dioxane	40
7	$(n\text{-Bu})_3$P	HOAc	Dioxane	83
8	$(n\text{-Bu})_3$P	p-NO_2BzOH	Dioxane	0
9[c]	$(n\text{-Bu})_3$P	HOAc	Dioxane	61
10[d]	$(n\text{-Bu})_3$P	HOAc	Dioxane	50
11	$(n\text{-Bu})_3$P	HOAc	Toluene	76
12	$(n\text{-Bu})_3$P	HOAc	DME	0
13	$(n\text{-Bu})_3$P	HOAc	CH_3CN	0
14[e]	$(n\text{-Bu})_3$P	HOAc	Dioxane	47
15[f]	$(n\text{-Bu})_3$P	HOAc	Dioxane	66
16	$(n\text{-Bu})_3$P	—	Dioxane	0

[a] The mixture of **1a** (0.1 mmol), **2a** (0.2 mmol), phosphine (100 mol%), and acid (2.0 equiv.) was stirred in solvent (2 mL) at 100 °C for 48 h under N_2 (1 atm). [b] Isolated yield. [c] 1.0 equiv. HOAc. [d] 3.0 equiv. HOAc. [e] 90 °C. [f] 110 °C.



Scheme 2 The cross-Rauhut–Currier/Wittig domino reaction of vinyl ketones **1** with α,β-unsaturated ketones **2**.

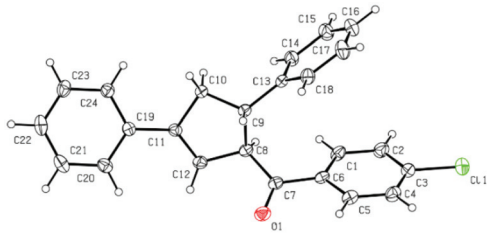


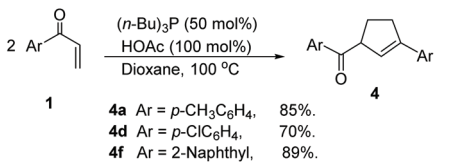
Fig. 1 X-ray structure of trisubstituted cyclopentene **3da**.

yields of 69–86%. The domino reaction tolerated a range of functional groups on the benzene ring in chalcones **2b–h**, such as fluoro, chloro, bromo, trifluoromethyl, and methyl groups. Moreover, when β-methyl-α,β-unsaturated ketone **2i** was employed in the domino reaction with vinyl ketone **1a**, the desired product **3ai** was also obtained, albeit in a lower yield. The domino reaction has excellent diastereoselectivity to give *trans*-cyclopentenes **3**, and no corresponding *cis*-stereoisomer was obtained.

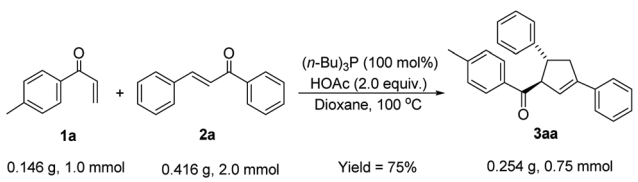
In the absence of chalcone **2**, vinyl ketone **1a** underwent a homo-Rauhut–Currier/Wittig domino reaction to give the cycloaddition product **4a** in an 85% yield under the optimized conditions (Scheme 3). The naphthyl group instead of the benzene group in aryl vinyl ketone **1f** also led to the dimer of **4f** in a good yield.

From the perspective of the mechanism for the cross-Rauhut–Currier/Wittig domino reaction, we successfully utilized the organophosphorus properties that the neutral phosphorus can serve as a nucleophile and the cationic phosphorus can stabilize an α-carbanion to perform the cross-Rauhut–Currier reaction and the successive Wittig reaction, respectively.

In order to demonstrate the practicality of this methodology, we performed the cross-Rauhut–Currier/Wittig domino reaction at a larger scale (Scheme 4). When vinyl ketone **1a** (1.0 mmol) and chalcone **2a** (2.0 mmol) were employed under the optimized conditions, the reaction proceeded smoothly as well, affording the desired product **3aa** (0.75 mmol) in 75% yield.



Scheme 3 The homo-Rauhut–Currier/Wittig domino reaction of vinyl ketones **1**.



Scheme 4 The upscaling reaction.

Conclusions

In conclusion, we have developed a new cross-Rauhut–Currier/Wittig domino reaction of vinyl ketones **1** with chalcones **2** mediated by $(n\text{-Bu})_3$P (100 mol%) in the presence of HOAc, affording the desired trisubstituted cyclopentenes **3**. The cross-Rauhut–Currier/Wittig domino reaction is compatible with various functional groups to afford a range of trisubstituted cyclopentenes in moderate to good yields. Organophosphorus in different phases of the domino reaction may not only serve as a nucleophile but also stabilize an α-carbanion to perform the cross-Rauhut–Currier reaction and the successive Wittig reaction, respectively. The new synthetic method for trisubstituted cyclopentenes also has the advantages of mild reaction conditions, high efficiency and environmental friendliness, which make it possible to apply the method in organic synthesis and the synthesis of related natural products.

Experimental

General procedure and characterization data

The general procedure for the cross-Rauhut–Currier/Wittig domino reaction of vinyl ketone **1** with α,β-unsaturated ketone **2** is as follows.

To a solution of vinyl ketone **1** (0.1 mmol), α,β-unsaturated ketone **2** (0.2 mmol), and HOAc (0.2 mmol) in dioxane (2.0 mL) was added $(n\text{-Bu})_3$P (20.2 mg, 0.1 mmol, 100 mol%). The reaction mixture was stirred at 100 °C for 48 h under nitrogen. Then, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; ethyl acetate/petroleum ether = 1/100 as the eluent) to give the desired trisubstituted cyclopentene **3**.

(3,5-Diphenylcyclopent-2-en-1-yl)(4-tolyl)methanone (3aa). White solid (28.1 mg, 83% yield); mp: 127–128 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.85 (d, J = 8.0 Hz, 2H, Ar), 7.47–7.44 (m, 2H, Ar), 7.34–7.19 (m, 10H, Ar), 6.17 (q, J = 2.1 Hz, 1H, CHC*H*=C), 4.72–4.69 (m, 1H, C*H*CH=C), 4.23–4.18 (m, 1H, C*H*CH_2), 3.45–3.39 (m, 1H, CHC*H*H), 3.04–2.97 (m, 1H, CHCH*H*), 2.40 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 198.7, 146.2, 144.2, 144.0, 135.5, 133.9, 129.3, 128.9, 128.7, 128.4, 127.8, 127.3, 126.5, 126.0, 123.1, 63.3, 44.9, 41.9, 21.7; HR-MS (EI-TOF) (M^+) calculated for $C_{25}H_{22}O$ 338.1671, found 338.1672.

(3,5-Diphenylcyclopent-2-en-1-yl)(4-methoxyphenyl)methanone (3ba). White solid (25.1 mg, 71% yield); mp: 175–176 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.95–7.91 (m, 2H, Ar), 7.47–7.45 (m, 2H, Ar), 7.34–7.20 (m, 8H, Ar), 6.92–6.89 (m, 2H, Ar), 6.17 (q, J = 2.0 Hz, 1H, CHC*H*=C), 4.71–4.67 (m, 1H, C*H*CH=C), 4.19 (dt, J = 8.8, 6.0 Hz, 1H, C*H*CH_2), 3.86 (s, 3H, OCH_3), 3.43 (ddt, J = 16.4, 9.2, 2.2 Hz, 1H, CHC*H*H), 3.01 (ddt,

J = 16.0, 5.6, 2.0 Hz, 1H, CHCH*H*); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 197.7, 163.6, 146.2, 144.2, 135.5, 131.0, 129.4, 128.7, 128.4, 127.8, 127.3, 126.5, 126.0, 123.2, 113.8, 63.1, 55.5, 45.1, 41.9; HR-MS (EI-TOF) (M^+) calculated for $C_{25}H_{22}O_2$ 354.1620, found 354.1614.

(3,5-Diphenylcyclopent-2-en-1-yl)(4-fluorophenyl)methanone (3ca). White solid (25.0 mg, 73% yield); mp: 114–115 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.97–7.94 (m, 2H, Ar), 7.48–7.46 (m, 2H, Ar), 7.35–7.20 (m, 8H, Ar), 7.13–7.07 (m, 2H, Ar), 6.16 (q, J = 2.0 Hz, 1H, CHC*H*=C), 4.70–4.67 (m, 1H, C*H*CH=C), 4.18–4.13 (m, 1H, C*H*CH$_2$), 3.47–3.39 (m, 1H, CHC*H*H), 3.05–2.99 (m, 1H, CHCH*H*); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 197.7, 165.8 (d, J = 253.6 Hz), 145.9, 144.6, 135.3, 132.8 (d, J = 3.1 Hz), 131.3 (d, J = 9.2 Hz), 128.7, 128.4, 127.9, 127.2, 126.6, 126.0, 122.4, 115.7 (d, J = 21.8 Hz), 63.3, 45.2, 41.9; HR-MS (EI-TOF) (M^+) calculated for $C_{24}H_{19}FO$ 342.1420, found 342.1423.

(4-Chlorophenyl)(3,5-diphenylcyclopent-2-en-1-yl)methanone (3da). White solid (24.7 mg, 69% yield); mp: 121–122 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.88–7.85 (m, 2H, Ar), 7.48–7.21 (m, 12H, Ar), 6.14 (q, J = 2.1 Hz, 1H, CHC*H*=C), 4.69–4.66 (m, 1H, C*H*CH=C), 4.14 (dt, J = 9.2, 5.6 Hz, 1H, C*H*CH$_2$), 3.43 (ddt, J = 16.0, 9.2, 2.2 Hz, 1H, CHC*H*H), 3.02 (ddt, J = 16.0, 5.6, 2.4 Hz, 1H, CHCH*H*); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 198.1, 145.8, 144.7, 139.6, 135.3, 134.7, 130.1, 128.9, 128.8, 128.5, 128.0, 127.2, 126.7, 126.0, 122.3, 63.4, 45.1, 41.9; HR-MS (EI-TOF) (M^+) calculated for $C_{24}H_{19}ClO$ 358.1124, found 358.1121.

(4-Bromophenyl)(3,5-diphenylcyclopent-2-en-1-yl)methanone (3ea). White solid (32.2 mg, 80% yield); mp: 131–132 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.80–7.77 (m, 2H, Ar), 7.59–7.56 (m, 2H, Ar), 7.47–7.45 (m, 2H, Ar), 7.33–7.22 (m, 8H, Ar), 6.14 (q, J = 2.1 Hz, 1H, CHC*H*=C), 4.68–4.65 (m, 1H, C*H*CH=C), 4.14 (dt, J = 9.2, 5.6 Hz, 1H, C*H*CH$_2$), 3.43 (ddt, J = 15.6, 8.8, 2.2 Hz, 1H, CHC*H*H), 3.02 (ddt, J = 16.4, 5.6, 2.0 Hz, 1H, CHCH*H*); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 198.3, 145.8, 144.7, 135.3, 135.1, 131.9, 130.2, 128.8, 128.5, 128.4, 128.0, 127.2, 126.7, 126.0, 122.2, 63.4, 45.1, 41.9; HR-MS (EI-TOF) (M^+) calculated for $C_{24}H_{19}BrO$ 402.0619, found 402.0618.

(3-Phenyl-5-(3-tolyl)cyclopent-2-en-1-yl)(4-tolyl)methanone (3ab). White solid (25.0 mg, 71% yield); mp: 103–104 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.86 (d, J = 8.4 Hz, 2H, Ar), 7.47–7.45 (m, 2H, Ar), 7.34–7.02 (m, 9H, Ar), 6.17 (q, J = 2.1 Hz, 1H, CHC*H*=C), 4.71–4.69 (m, 1H, C*H*CH=C), 4.17 (dt, J = 9.2, 5.6 Hz, 1H, C*H*CH$_2$), 3.41 (ddt, J = 16.4, 9.2, 2.2 Hz, 1H, CHC*H*H), 3.00 (ddt, J = 16.4, 5.6, 2.0 Hz, 1H, CHCH*H*), 2.41 (s, 3H, *p*-C*H*$_3$), 2.32 (s, 3H, *m*-C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 198.8, 146.1, 144.2, 143.9, 138.3, 135.5, 133.9, 129.3, 128.9, 128.6, 128.4, 128.0, 127.8, 127.2, 126.0, 124.2, 123.1, 63.4, 44.7, 41.9, 21.6, 21.5; HR-MS (EI-TOF) (M^+) calculated for $C_{26}H_{24}O$ 352.1827, found 352.1827.

(5-(4-Fluorophenyl)-3-phenylcyclopent-2-en-1-yl)(4-tolyl)methanone (3ac). White solid (29.5 mg, 83% yield); mp: 151–152 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.85 (d, J = 8.0 Hz, 2H, Ar), 7.46–7.44 (m, 2H, Ar), 7.33–7.23 (m, 7H, Ar), 6.97 (t, J = 8.8 Hz, 2H, Ar), 6.16 (q, J = 2.0 Hz, 1H, CHC*H*=C), 4.67–4.63 (m, 1H, C*H*CH=C), 4.22–4.17 (m, 1H, C*H*CH$_2$), 3.45–3.37 (m, 1H, CHC*H*H), 2.99–2.92 (m, 1H, CHCH*H*), 2.40 (s, 3H, C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 198.5, 161.6 (d, J = 242.8 Hz), 144.2, 144.1, 141.7 (d, J = 3.0 Hz), 135.4, 133.9, 129.4, 128.8, 128.7 (d, J = 7.9 Hz), 128.4, 127.9, 125.9, 122.9, 115.4 (d, J = 21.0 Hz), 63.4, 44.1, 41.9, 21.7; HR-MS (EI-TOF) (M^+) calculated for $C_{25}H_{21}FO$ 356.1576, found 356.1578.

(5-(3-Chlorophenyl)-3-phenylcyclopent-2-en-1-yl)(4-tolyl)methanone (3ad). White solid (29.0 mg, 78% yield); mp: 105–106 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.87 (d, J = 8.0 Hz, 2H, Ar), 7.46–7.44 (m, 2H, Ar), 7.34–7.19 (m, 9H, Ar), 6.17 (q, J = 2.0 Hz, 1H, CHC*H*=C), 4.69–4.66 (m, 1H, C*H*CH=C), 4.22 (dt, J = 8.8, 6.0 Hz, 1H, C*H*CH$_2$), 3.42 (ddt, J = 16.0, 8.8, 2.2 Hz, 1H, CHC*H*H), 2.97 (ddt, J = 16.4, 6.0, 2.2 Hz, 1H, CHCH*H*), 2.42 (s, 3H, C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 198.2, 148.2, 144.2, 144.1, 135.2, 134.4, 133.8, 129.9, 129.4, 128.8, 128.4, 127.9, 127.3, 126.7, 126.0, 125.6, 122.8, 63.1, 44.3, 41.7, 21.7; HR-MS (EI-TOF) (M^+) calculated for $C_{25}H_{21}ClO$ 372.1281, found 372.1282.

(5-(3-Bromophenyl)-3-phenylcyclopent-2-en-1-yl)(4-tolyl)methanone (3ae). White solid (35.9 mg, 86% yield); mp: 121–122 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.86 (d, J = 8.0 Hz, 2H, Ar), 7.48–7.43 (m, 3H, Ar), 7.36–7.24 (m, 7H, Ar), 7.15 (t, J = 7.8 Hz, 1H, Ar), 6.16 (q, J = 2.0 Hz, 1H, CHC*H*=C), 4.68–4.65 (m, 1H, C*H*CH=C), 4.20 (dt, J = 9.2, 5.6 Hz, 1H, C*H*CH$_2$), 3.42 (ddt, J = 16.4, 9.2, 2.2 Hz, 1H, CHC*H*H), 2.96 (ddt, J = 16.0, 5.8, 2.0 Hz, 1H, CHCH*H*), 2.41 (s, 3H, C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 198.1, 148.5, 144.2, 144.0, 135.2, 133.7, 130.3, 129.6, 129.4, 128.9, 128.4, 128.0, 126.1, 126.0, 122.8, 122.7, 63.2, 44.2, 41.7, 21.7; HR-MS (EI-TOF) (M^+) calculated for $C_{25}H_{21}BrO$ 416.0776, found 416.0777.

(5-Phenyl-3-(4-tolyl)cyclopent-2-en-1-yl)(4-tolyl)methanone (3af). White solid (24.3 mg, 69% yield); mp: 111–112 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.85 (d, J = 8.0 Hz, 2H, Ar), 7.36–7.21 (m, 9H, Ar), 7.12 (d, J = 8.0 Hz, 2H, Ar), 6.11–6.10 (m, 1H, CHC*H*=C), 4.69–4.68 (m, 1H, C*H*CH=C), 4.22–4.17 (m, 1H, C*H*CH$_2$), 3.43–3.37 (m, 1H, CHC*H*H), 3.01–2.96 (m, 1H, CHCH*H*), 2.40 (s, 3H, COArC*H*$_3$), 2.33 (s, 3H, C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 198.8, 146.3, 144.1, 143.9, 137.7, 134.0, 132.7, 129.3, 129.1, 128.9, 128.7, 127.2, 126.4, 125.9, 122.0, 63.3, 44.8, 41.9, 21.6, 21.2; HR-MS (EI-TOF) (M^+) calculated for $C_{26}H_{24}O$ 352.1827, found 352.1831.

(3-(4-Chlorophenyl)-5-phenylcyclopent-2-en-1-yl)(4-tolyl)methanone (3ag). White solid (28.3 mg, 76% yield); mp: 147–148 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.83 (d, J = 8.4 Hz, 2H, Ar), 7.38–7.22 (m, 11H, Ar), 6.16 (q, J = 2.0 Hz, 1H, CHC*H*=C), 4.72–4.70 (m, 1H, C*H*CH=C), 4.18 (dt, J = 8.8, 6.0 Hz, 1H, C*H*CH$_2$), 3.38 (ddt, J = 16.0, 9.2, 2.2 Hz, 1H, CHC*H*H), 2.97 (ddt, J = 16.4, 6.0, 2.0 Hz, 1H, CHCH*H*), 2.40 (s, 3H, C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 198.6, 145.9, 144.1, 143.1, 133.9, 133.8, 133.5, 129.4, 128.9, 128.7, 128.6, 127.2, 127.1, 126.6, 123.7, 63.2, 45.0, 41.9, 21.7; HR-MS (EI-TOF) (M^+) calculated for $C_{25}H_{21}ClO$ 372.1281, found 372.1279.

(5-Phenyl-3-(4-(trifluoromethyl)phenyl)cyclopent-2-en-1-yl)-(4-tolyl)methanone (3ah). White solid (28.8 mg, 71% yield);

mp: 73–74 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.84 (d, J = 8.0 Hz, 2H, Ar), 7.59–7.53 (m, 4H, Ar), 7.32–7.23 (m, 7H, Ar), 6.29 (q, J = 2.0 Hz, 1H, CHC*H*=C), 4.76–4.74 (m, 1H, C*H*CH=C), 4.19 (dt, J = 9.2, 5.6 Hz, 1H, C*H*CH_2), 3.43 (ddt, J = 16.4, 9.2, 2.2 Hz, 1H, CHC*H*H), 3.01 (ddt, J = 16.4, 6.0, 2.0 Hz, 1H, CHCH*H*), 2.41 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 198.5, 145.7, 144.2, 143.1, 138.8, 133.7, 129.4, 128.9, 128.8, 127.2, 126.6, 126.2, 125.7, 125.4 (q, J = 3.8 Hz), 63.2, 45.0, 41.8, 21.7; HR-MS (EI-TOF) (M^+) calculated for $C_{26}H_{21}F_3O$ 406.1544, found 406.1551.

(5-Methyl-3-(4-tolyl)cyclopent-2-en-1-yl)(4-tolyl)methanone (3ai). White solid (15.7 mg, 54% yield); mp: 78–79 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.94 (d, J = 8.0 Hz, 2H, Ar), 7.31–7.28 (m, 4H, Ar), 7.10 (d, J = 8.0 Hz, 2H, Ar), 6.01 (d, J = 2.0 Hz, 1H, CHC*H*=C), 4.21–4.19 (m, 1H, C*H*CH=C), 3.13–2.98 (m, 2H, CH_3CHCH_2), 2.43–2.38 (m, 4H, CH_3C*H*CH_2 and COArCH_3), 2.32 (s, 3H, ArCH_3), 1.22 (d, J = 6.8 Hz, 3H, CH_3CHCH_2); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 199.8, 144.1, 143.7, 137.3, 134.4, 133.2, 129.3, 129.0, 128.7, 125.7, 122.4, 62.2, 41.3, 34.8, 21.7, 21.2, 21.1; HR-MS (EI-TOF) (M^+) calculated for $C_{21}H_{22}O$ 290.1671, found 290.1668.

4-Tolyl(3-(4-tolyl)cyclopent-2-en-1-yl)methanone (4a). White solid (23.5 mg, 85% yield); mp: 162–163 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.94 (d, J = 8.4 Hz, 2H, Ar), 7.34–7.28 (m, 4H, Ar), 7.10 (d, J = 8.0 Hz, 2H, Ar), 6.12 (q, J = 2.0 Hz, 1H, CHC*H*=C), 4.66–4.61 (m, 1H, C*H*CH=C), 2.95–2.76 (m, 2H, $CHCH_2CH_2$), 2.53–2.43 (m, 4H, CHC*H*HCH_2 and COArCH_3), 2.38–2.30 (m, 4H, CHCH*H*CH_2 and CH_3); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 200.0, 145.0, 143.7, 137.3, 134.1, 133.1, 129.3, 129.0, 128.7, 125.8, 122.9, 54.4, 33.1, 26.4, 21.7, 21.2; HR-MS (EI-TOF) (M^+) calculated for $C_{20}H_{20}O$ 276.1514, found 276.1514.

(4-Chlorophenyl)(3-(4-chlorophenyl)cyclopent-2-en-1-yl)-methanone (4d). Yellow solid (22.2 mg, 70% yield); mp: 97–98 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.97 (d, J = 8.4 Hz, 2H, Ar), 7.47 (d, J = 8.8 Hz, 2H, Ar), 7.36 (d, J = 8.0 Hz, 2H, Ar), 7.27 (d, J = 8.4 Hz, 2H, Ar), 6.13 (q, J = 2.0 Hz, 1H, CHC*H*=C), 4.63–4.59 (m, 1H, C*H*CH=C), 2.92–2.77 (m, 2H, $CHCH_2CH_2$), 2.51–2.33 (m, 2H, $CHCH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 198.9, 144.5, 139.6, 134.8, 134.1, 133.4, 130.0, 129.1, 128.5, 127.2, 123.9, 54.4, 33.0, 26.5; HR-MS (EI-TOF) (M^+) calculated for $C_{18}H_{14}Cl_2O$ 316.0422, found 316.0423.

Naphthalen-2-yl(3-(naphthalen-2-yl)cyclopent-2-en-1-yl)-methanone (4f). White solid (31.0 mg, 89% yield); mp: 152–153 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.60 (s, 1H, Ar), 8.12 (dd, J = 8.6, 1.8 Hz, 1H, Ar), 8.01 (d, J = 8.0 Hz, 1H, Ar), 7.95–7.89 (m, 2H, Ar), 7.82–7.73 (m, 4H, Ar), 7.67–7.56 (m, 3H, Ar), 7.47–7.41 (m, 2H, Ar), 6.39 (q, J = 2.0 Hz, 1H, CHC*H*=C), 4.92–4.87 (m, 1H, C*H*CH=C), 3.13–2.96 (m, 2H, $CHCH_2CH_2$), 2.66–2.44 (m, 2H, $CHCH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 200.2, 145.3, 135.6, 134.0, 133.4, 133.2, 132.9, 132.6, 130.2, 129.6, 128.6, 128.5, 128.2, 127.8, 127.7, 127.6, 126.8, 126.2, 125.9, 124.8, 124.6, 124.5, 124.2, 54.7, 33.1, 26.6; HR-MS (EI-TOF) (M^+) calculated for $C_{26}H_{20}O$ 348.1514, found 348.1514.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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10 CCDC 2022239† contains the supplementary crystallographic data for **3da**.