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Unexpected formation of 4,4-dimethyl-1,2-disubstituted-dicarbonyl cyclopentanes from ketone enolate anions and 1,3-diiodo-2,2-dimethylpropane†

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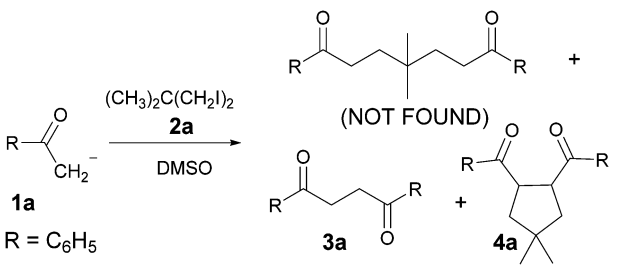
Cyclic 1,4-dicarbonyl compounds can be easily obtained by mixing a solution of aryl methyl or alkyl methyl ketone enolate anions with 1,3-diiodo-2,2-dimethylpropane in DMSO. This represents the first example of dimerization of ketone enolate anions using a simple diiodoalkane as a reagent followed by subsequent double alkylation with bis-iodide yielding a cyclopentane adduct. This methodology allows the use of a simple potassium *tert*-butoxide as a base at room temperature for the formation of three C–C bonds resulting in a relatively complex five-membered ring diketone structure under transition-metal-free conditions.

Introduction

1,4-Dicarbonyl compounds are useful synthons for the synthesis of a number of heterocyclic systems; for instance, the condensation of 1,4-dicarbonyl compounds with primary amines constitutes a particularly useful method for the generation of pyrroles. This reaction, known as the Paal–Knorr reaction (cyclocondensation of 1,4-dicarbonyl compounds), is applicable to a wide variety of γ-dicarbonyl compounds and primary amines.[1] 2,5-Disubstituted furans are straightforwardly obtained in very good yields by treatment of the 1,4-dicarbonyl compounds with Lawesson's reagent.[2] These substituted furans, thiophenes, pyrroles and pyrrolidines[3] represent important five-membered heterocycles that are found in natural products, in addition to being pharmaceutically important substrates.[4] Even though the classical Paal–Knorr condensation is well known, the synthesis of the starting γ-dicarbonyl materials is still a challenge. Although many synthetic procedures are available for their formation, most of the current methods often require harsh conditions, stoichiometric amounts of transition metals such as Cu(II) or Fe(II) for the oxidative dimerization of ketone enolate anions, and long reaction time.[5] Alternatively, Rh(I) or Ru(II) catalysed addition of arylboronic acids or terminal alkynes to α,β-unsaturated ketones is reported, giving 1,4-diketones.[6] Another interesting approach is the reported aerobic oxidative synthesis of 1,2-dioxane derivatives and their fragmentation into 1,4-dicarbonyl compounds by Ce(IV)[7] and more recently the use of photoredox catalysis demonstrated its applicability in the preparation of such diketo compounds through reduction of β-ketosulfones by photo-generated Ru(I).[8]

α-Haloketones are also used for this purpose, however strong reducing agents such as Zn(0), In(I), tetramethylethylenediamine or catalysis by Co(I) or Zn(II) are necessary.[9]

The formation of carbon–carbon bonds is central to organic synthesis. Even though numerous effective methods have been published, the direct C–C bond-formation reaction between two sp^3 C–H bonds is still under study.[10] Photoinduced as well as thermal nucleophilic substitution reactions between an acetophenone enolate anion (**1a**) and neopentyl iodide have been reported in dimethyl sulfoxide (DMSO).[11] When we explored the reaction between **1a** and 1,3-diiodo-2,2-dimethylpropane (**2a**), instead of the 1,7-dicarbonyl compound, the unexpected umpolung dimerization of anion **1a**, compound **3a**, was observed, together with 1,2-disubstituted cyclopentane **4a** (eqn (1)).



(1)

Even though the dimerization of ketone/ester enolate anions has been severely investigated,[12] herein, we report a novel reaction

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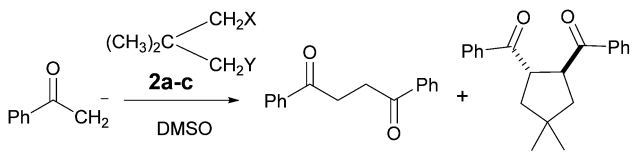
where the straightforward formation of valuable 1,2-dicarbonyl cyclopentane compounds can be achieved starting from simple materials in a "one-pot" procedure. This methodology represents an outstanding carbon–carbon bond-forming reaction between the sp^3 C–H bonds of two methyl groups. It is important to mention that similar compounds could be prepared by electro-oxidative cyclization of 1,6-dienes in DMSO.[13] The present methodology represents a simple alternative for the synthesis of five-membered ring diketones. In addition, we also advance a reaction mechanism based on non-kinetic evidence.

Results and discussion

We start exploring the reaction between *in situ* generated anion **1a**, which was formed by acid–base deprotonation of acetophenone with *tert*-BuOK, and 1,3-diiodo-2,2-dimethylpropane (**2a**). After 1 hour of reaction, substrate **2a** is completely consumed and two reaction products are formed, diphenacyl (**3a**) and 4,4-dimethyl-1,2-dibenzoylcyclopentane (**4a**) in 42 and 25% yield respectively (Table 1, entry 1, eqn (2)). The former is rationalized as a dimer form of anion **1a** and the latter as a product derived from a secondary process where deprotonated **3a** reacts with diiodide **2a**. The spectroscopic data of **4a** are consistent with a *trans* relative conformation of both benzoyl groups. The relative stereochemistry was assigned based on the specific comparison to previously published similar compounds.[13]

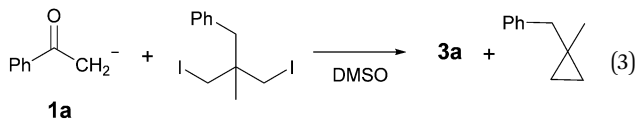


2a: X = Y = I; **2b**: X= Y = Br; **2c**: X= I, Y = Cl

(2)

The yield of cyclic product **4a** depends on the nucleophile/diiodide ratio, at a fixed concentration of substrate **2a**. A good yield of **4a** can be achieved with a **1 : 2** ratio of 10 (Table 1, entry 1). Upon decreasing the ketone enolate anion concentration, the yield of **4a** decreases at a point where the reaction becomes selective to dimer **3a** at equal concentrations of anion **1a** and alkyl iodide **2a** (Table 1, entries 2–4).

The correlation between the ratio and yields suggests that cyclization is slower than dimerization. It is also reported in the literature that the dianion of 1,4-diketone **3a** can be obtained in THF using LDA as a base; under this condition the intermediate could be trapped by electrophiles like benzyl bromide and trimethylsilyl chloride.[14] When 1,3-diiodopropane is used as a substrate, the alkyl halide is completely consumed and no reaction products are obtained (Table 1, entry 5). Probably fast β-elimination competes efficiently yielding a very volatile propene as a product; whereas, in neopentyl-like substrates, elimination reaction is not possible due to the absence of β hydrogen atoms. Finally, 1,3-dibromo-2,2-dimethylpropane (**2b**) and 1-iodo-3-chloro-2,2-dimethylpropane (**2c**) are not reactive, in both cases neither dimer **3a** nor the cyclopentane **4a** is formed. This indicates that the presence of both iodine atoms is essential for the reaction to occur (Table 1, entries 6 and 7). In the reaction of 2-benzyl-2-methyl-1,3-diiodopropane (Table 1, entry 8, eqn (3)) 1-benzyl-1-methylcyclopropane was obtained, indicating that volatile 1,1-dimethylcyclopropane is formed in the reaction of **2a**. This observation can account for the low mass balance found considering **2a** as the limiting reagent in these reactions. Finally, although a relatively large **1 : 2** ratio is necessary for the moderate formation of cyclopentane derivative **4**, this methodology possesses advantages such as the use of a simple potassium *tert*-butoxide as a base at room temperature in a "one pot" procedure, for the formation of three C–C bonds, resulting in a five-membered ring diketone structure.



(3)

Table 1 Reaction between an acetophenone enolate anion (**1a**) and 1,3-dihalo-2,2-dimethylpropane (**2**) in DMSO[a]

Entry	Substrate	Ratio **1 : 2**	Product yield[b] (%) **3a**	**4a**
1	**2a**, X = Y = I	10 : 1	42	25
2	**2a**	5 : 1	34	19
3	**2a**	2.5 : 1	34	3
4	**2a**	1 : 1	13	—
5	1,3-Diiodopropane	10 : 1	—	—
6	**2b**, X = Y = Br	10 : 1	nr[c]	
7	**2c**, X = I, Y = Cl	10 : 1	nr[c]	
8	2-Benzyl-2-methyl-1,3-diiodopropane	5 : 1	13[d]	—

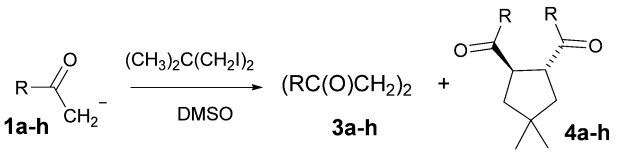
[a] [**2**] = 0.05 M, stirred at room temperature under a nitrogen atmosphere for 1 h. Reactions were quenched with NH_4NO_3. [b] Determined by GC using the internal standard method, error <5%. [c] nr, no reaction. [d] Together with 80% of 1-benzyl-1-methylcyclopropane.

Scope of the reaction

The observed reactivity of the acetophenone enolate anion toward 1,3-diiodo-2,2-dimethylpropane encouraged us to further explore the potential of ketone enolate anions in the synthesis of 1,4-dicarbonyl compounds. No significant difference in the **3a**/**4a** product yield ratio was found when using 5 or 10 molar excess of anion **1a** toward diiodide **2a** (Table 1, entries 1 and 2). For this reason we select the former conditions to explore the scope of the reaction. Quite a few examples of the use of different ketones are included, the criteria for the selection of ketones were the inclusion of electron-donating and electron-withdrawing groups in the phenyl moiety and the use of aliphatic ketones in order to range amply the pK_a values of the methyl ketones employed (up to 6 pK_a units). The results for these reactions are outlined in Table 2.

From Table 2, it is possible to conclude that this methodology is appropriate for substrates bearing electron-donating and electron-withdrawing groups. However, a remarkable reduction in reactivity is observed in 4-methoxy, H, 4-chloro, 4-methyl, 4-cyano acetophenones to the unreactive 4-nitro derivative, giving 48, 34, 29, 28, and 12% yields and no reaction respectively

Table 2 Scope of the reaction in the formation of 1,4-dicarbonyl compounds from aryl and alkyl methyl ketones with 1,3-diiodo-2,2-dimethylpropane in DMSO[a]



Entry	Ketone enolate anion[b] (pK_a)	Product yield[c] (%) 3	3
1	**1a**, R = C_6H_5 (24.7)	**3a**, 19%	**4a**, 34%
2	**1b**, R = 4-$CH_3OC_6H_4$ (25.7)	Not found	**4b**, 48%
3	**1c**, R = 4-$CH_3C_6H_4$ (25.2)	**3c**, 14.3%	**4c**, 28%
4	**1d**, R = 4-ClC_6H_4 (23.8)	**3d**, 12.1%	**4d**, 29%
5	**1e**, R = 4-CNC_6H_4 (22.0)	Not found	**4e**, 12%
6	**1f**, R = 4-$NO_2C_6H_4$ (<22)	nr[d]	nr[d]
7	**1g**, R = 2-$C_{10}H_7$ (23)	Not found	**4g**, 50%
8	**1h**, R = 1-adamantyl (27.7)[e]	**3h**, 5%	**4h**, 30%

[a] [**1**] = 0.25 M, [**2a**] = 0.05 M stirred at room temperature under a nitrogen atmosphere for 1 h. Reactions were quenched with NH_4NO_3. [b] From ref. 14 and 15. [c] Determined by GC using the internal standard method, error <5%. [d] nr, no reaction. [e] pK_a of pinacolone (3,3-dimethyl-2-butanone).

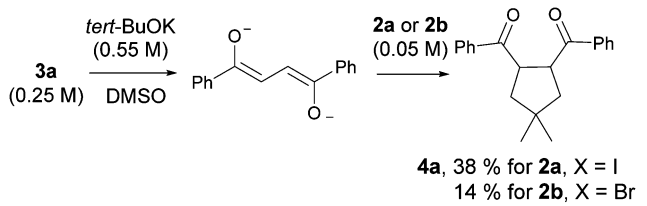
(Table 2, entries 1–6). 2-Acethylnaphthalene with a relatively low pK_a value (pK_a = 23) is also considered, this anion shows a good performance giving 4,4-dimethyl-1,2-di(2-naphthoyl)cyclopentane (**4g**) in 50% yield (Table 2, entry 7). These reactions are not only exclusive of aryl methyl ketones, but the aliphatic 1-adamantyl methyl ketone is also reactive giving the cyclic 1,4-dicarbonyl derivative **4h** in 30% yield (Table 2, entry 8).

Overall, a qualitative trend is found for the reactivity where ketones with pK_a higher than 22 are reactive, indicating that the strength of the ketone anion enolate as a base is important to trigger the reaction (iodine abstraction step, see mechanistic discussion below). However, a quantitative relationship between reactivity and thermodynamic pK_a values could not be found probably due to the fact that the follow-up reaction to the dimerization reaction like deprotonation of dimers and nucleophilic substitution toward substrate 2 may also play an important role in the overall reactivity.

Proposed mechanism

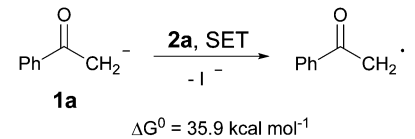
In order to prove the sequence of reactions indicated in Scheme 1, isolated dimer **3a** was deprotonated with 2 equivalents of potassium *tert*-butoxide. Then diiodide **2a** or dibromide **2b** was added, and in both reactions product **4a** was obtained in 38 and 14% yield respectively (Scheme 1). These results agree with the mediation of a ketone enolate dianion. Moreover, the reactivity observed is in agreement with the expected reactivity order in a S_N reaction, where alkyl iodide is more reactive than alkyl bromide.

Formation of a dimer: due to their low oxidation potential, ketone enolate anions are likely to undergo single-electron transfer (SET) oxidation using different reagents, namely $CuCl_2$, $FeCl_3$, and I_2.[12] Under our experimental conditions, diiodide **2a** may act as an electron acceptor triggering a chain dimerization reaction that eventually ends in dimer **3a** (eqn (4)–(6)). However, reaction

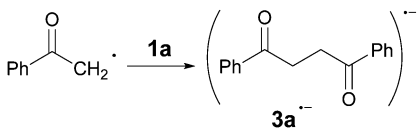


Scheme 1 Cyclic 1,4-diketone formation.

indicated in eqn (4) is very unlikely based on thermodynamic grounds, the Gibbs free energy for the single-electron transfer reaction from anion **1a** to 1,3-diido-2,2-dimethylpropane is extremely endergonic to be feasible, ΔG^0 = 35.9 kcal mol^{-1}, estimated from the electrochemical properties found in the literature, $E^{ox}_{PhCOCH_2^-} = 0.143$ and $E^{red}_{2a} = -1.70$ both *vs.* NHE.[16,17]



(4)



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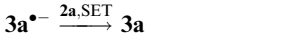
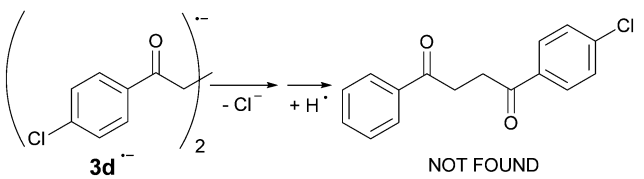


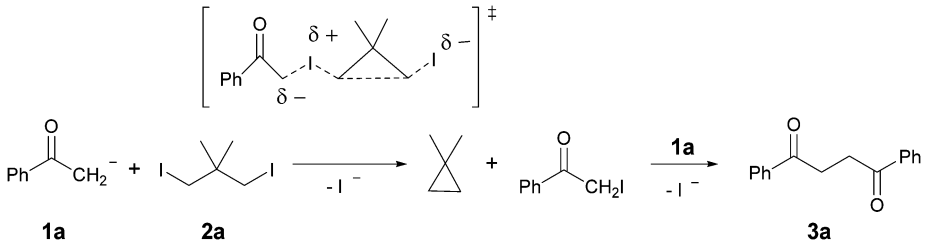
(6)

By reinforcing the absence of SET reaction, no dechlorination products were formed in the reaction of the 4-chloroacetophenone enolate anion (**1d**) with **2a** (Table 2, entry 4). If the radical anion of **3d** is formed, fragmentation to give an aryl radical and chloride anions would end in a mixture of **3d** and **3a** together with 1-(4-chlorophenyl)-4-phenylbutane-1,4-dione and a mixture of **4d** and **4a** (eqn (7)).[18]



(7)

Alternatively, a more likely mechanism for the formation of dimer **3** by consecutive reactions is presented in Scheme 2 as follows: first, iodine atom abstraction of **2a** by anion **1a**, C–I bond formation may be achieved with C–C bond formation and C–I bond fragmentation to give phenacyl iodide and 1,1-dimethylcyclopropane, possibly in a concerted process. The presence of both iodine atoms is essential since no reaction occurred with bromo derivative **2b** and iodo, chloro derivative **2c**. The formation of 1,1-dimethylcyclopropane was evidenced by using a substrate with a higher molecular weight (eqn (3) and Table 1, entry 8). Reaction between phenacyl iodide and anion **1a** ultimately renders dimer **3**. The last reaction was previously described in the NaI mediated phenacyl bromide reduction by rongalite.[19]



Scheme 2 Mechanism proposed for the formation of dimer **3**.

The moderate yield found for product **4** in these reactions can be explained by the fact that two equivalents of the limiting reagent **2a** are necessary, one for the formation of diphenacyl (**3**) and another for the formation of a cyclopentane derivative.

Conclusions

The results described herein highlight the development of a new approach for the preparation of five-membered ring 1,4-dicarbonyl compounds by straightforwardly mixing acid–base generated ketone enolate anions **1a–e**, **g–h** and diiodide **2a** in DMSO at room temperature. Using this very simple methodology, three new C–C bonds are formed and also a number of examples are included using different aryl/alkyl methyl ketones. Their compatibility with both electron-donating and electron-withdrawing groups has also been demonstrated. Furthermore, the strength of the ketone enolate anion seems to play an important role in the reaction mechanism since we have observed that methyl ketones with pK_a less than 22 are not able to give dimer **3**.

Experimental section

Materials and methods

General. ^{1}H NMR (400.16 MHz) and ^{13}C NMR (100.62 MHz) were conducted on a high resolution spectrometer 400 MHz in $CDCl_3$ as a solvent. Coupling constants are given in Hz and chemical shifts are reported in ppm. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, dd = double doublet, m = multiplet) and coupling constants (J). Gas chromatographic (GC) analyses were performed on an instrument using a flame ionization detector equipped with a VF-5ms column (30 m × 0.25 mm × 0.25 μm). Gas chromatographic-mass spectrometer analyses were carried out on a GC-MS equipped with a quadrupole detector and a VF-5ms column (30 m × 0.25 mm × 0.25 μm). High resolution mass spectra were recorded using a MS/MS instrument in pure products. These data were obtained by EI or ESI mode ionization and TOF detection. Melting points were measured using an electrical instrument and uncorrected. GC quantification was performed by the internal standard method.

Chemicals. *tert*-BuOK, acetophenone, 4-methoxyacetophenone, 4-methylacetophenone, 4-chloroacetophenone, 4-cyanoacetophenone, 4-nitroacetophenone, 2-acethylnaphthalene and 1-adamanthylmethylketone were all high-purity commercial samples used without further purification. DMSO was distilled under vacuum and stored over molecular sieves (4 Å). Anions **1a–h** were generated *in situ* by acid–base deprotonation using potassium *tert*-butoxide. 1,3-Dihalo-2,2-dimethylpropane **2** was synthesized by reaction of the corresponding tosylate with KI, KBr or LiCl in DMF as previously reported.[17] 1,3-Diiodo-2-methyl-2-benzylpropane was synthesized following a procedure found in the literature.[20]

All the reaction products were isolated by radial chromatography from the reaction mixture and characterized by ^{1}H and ^{13}C NMR and mass spectrometry. 1-Benzyl-1-methylcyclopropane and all the ketone dimers of anions **1a–e** and **g–h** are well known and exhibited physical properties identical to those reported in the literature.[20–24]

Representative experimental procedure. These reactions were carried out in a 10 mL three-necked Schlenk tube, equipped with a nitrogen gas inlet and a magnetic stirrer. The tube was dried under vacuum, filled with nitrogen and then filled with dried DMSO (10 mL). *tert*-BuOK (154.4 mg, 1.37 mmol), a ketone precursor of anions **1a–h** (1.25 mmol), and diiodide **2a** (162 mg, 0.5 mmol) were added to the degassed solvent under nitrogen. After 1 h, the reaction was quenched by the addition of ammonium nitrate in excess and 10 mL of water, and the mixture was extracted with methylene chloride (3 × 20 mL). The organic extract was washed twice with water and dried over anhydrous $MgSO_4$, and the products were quantified by GC using the internal standard method, or isolated by radial chromatography from the crude product reaction mixture.

4,4-Dimethyl-1,2-dibenzoylcyclopentane (4a). The compound was purified by radial thin-layer chromatography eluting with petroleum ether/diethyl ether (90 : 10 → 50 : 50) and isolated as oil. δ_H (400.16 MHz; $CDCl_3$; Me_4Si): 1.10 (s, 6H, 2Me), 1.82 (dd, 2H, CH_{2b}, $J_{1,1'}$ 8.8, $J_{1,2}$ 12.8), 2.22 (dd, 2H, CH_{2a}, $J_{1',1}$ 8.8, $J_{1',2}$ 12.8), 4.61–4.64 (m, 2H, 2CH); 7.43–7.46 (m, 4H, Ph); 7.52–7.54 (m, 2H, Ph); 7.99–8.01 (m, 4H, Ph). δ_C (100.04 MHz, $CDCl_3$; Me_4Si): 29.0, 40.6, 46.3, 48.3, 128.6, 128.7, 133.0, 136.6, 201.8. m/z (EI): 306 (M^+, 2%); 201 (100); 105 (97); 77 (33). HRMS (EI) for $C_{21}H_{22}O_2$ $[M + H]^+$ calculated: 307.1698; found: 307.1691.

4,4-Dimethyl-1,2-di(4-methoxybenzoyl)cyclopentane (4b). The compound was purified by radial thin-layer chromatography eluting with petroleum ether/diethyl ether (90 : 10 → 50 : 50) and isolated as a white solid, mp: 106–107 °C. δ_H (400.16 MHz; $CDCl_3$; Me_4Si): 1.10 (s, 6H, 2Me), 1.71 (dd, 2H, CH_{2b}, $J_{1,1'}$ 8.7, $J_{1,2}$ 12.7), 2.07 (dd, 2H, CH_{2a}, $J_{1',1}$ 8.7, $J_{1',2}$ 12.7), 4.54–4.57 (m, 2H, 2CH), 3.85 (s, 6H, 2OMe), 6.92 (d, 4H, Ar, J_o 8.9), 7.98 (d, 4H, Ar, J_o 8.9). δ_C (100.04 MHz, $CDCl_3$; Me_4Si): 29.1, 40.5, 46.5, 48.1,

55.4, 113.7, 129.7, 131.0, 163.4, 200.4. *m/z* (EI): 366 (M^+, 2%), 231 (71); 135 (100); 107 (8); 92 (8); 77 (13). HRMS (EI) for $C_{23}H_{26}O_4$ $[M + H]^+$ calculated: 367.1909; found: 367.1909.

4,4-Dimethyl-1,2-di(4-methylbenzoyl)cyclopentane (4c). The compound was purified by radial thin-layer chromatography eluting with petroleum ether/diethyl ether (90 : 10 → 50 : 50) and isolated as oil. δ_H (400.16 MHz; $CDCl_3$; Me_4Si): 1.09 (s, 6H, 2Me), 1.71 (dd, 2H, CH_{2b}, $J_{1,1'}$ 8.0, $J_{1,2}$ 16.0), 2.08 (dd, 2H, CH_{2a}, $J_{1',1}$ 8.0, $J_{1',2}$ 16.0), 4.54–4.63 (m, 2H, 2CH), 7.25 (dd, 4H, Ar, J_m 4.0, J_o 8.0), 7.90 (dd, 4H, Ar, J_m 4.0, J_o 8.0). δ_C (100.04 MHz, $CDCl_3$; Me_4Si): 21.8, 29.2, 40.7, 46.5, 48.3, 129.0, 129.4, 134.3, 143.9, 201.6. *m/z* (EI): 334 (M^+, 2%), 215 (91); 119 (100); 91 (30); 65(6). HRMS (ESI) for $C_{23}H_{26}O_2$ $[M + Na]^+$ calculated: 357.1830; found: 357.1838.

4,4-Dimethyl-1,2-di(4-chlorobenzoyl)cyclopentane (4d). The compound was purified by radial thin-layer chromatography eluting with petroleum ether/diethyl ether (90 : 10 → 50 : 50) and isolated as a white solid, mp: 141–142 °C. δ_H (400.16 MHz; $CDCl_3$; Me_4Si): 1.10 (s, 6H, 2Me), 1.70 (dd, 2H, CH_{2b}, $J_{1,1'}$ 8.0, $J_{1,2}$ 12.0), 2.08 (dd, 2H, CH_{2a}, $J_{1',1}$ 8.0, $J_{1',2}$ 12.0), 4.48–4.58 (m, 2H, 2CH), 7.42 (d, 4H, Ar, J_o 12.0), 7.92 (d, 4H, Ar, J_0 12.0). δ_C (100.04 MHz, $CDCl_3$; Me_4Si): 29.2, 40.9, 46.3, 48.4, 129.1, 130.2, 135.0, 139.8, 200.6. *m/z* (EI): 374 (M^+, 1%); 235 (90); 139 (100); 111 (26); 75 (6). HRMS (ESI) for $C_{21}H_{20}Cl_2O_2$ $[M + Na]^+$ calculated: 397.0733; found: 397.0732.

4,4-Dimethyl-1,2-di(4-cyanobenzoyl)cyclopentane (4e). The compound was purified by radial thin-layer chromatography eluting with petroleum ether/diethyl ether (90 : 10 → 50 : 50) and isolated as a white solid. δ_H (400.16 MHz; $CDCl_3$; Me_4Si): 1.26 (s, 6H, 2Me), 1.74 (dd, 2H, CH_{2b}, $J_{1,1'}$ 8.4, $J_{1,2}$ 12.8), 2.13 (dd, 2H, CH_{2a}, $J_{1',1}$ 8.4, $J_{1',2}$ 12.8), 4.60–4.68 (m, 2H, 2CH), 7.48 (d, 4H, Ar, J_o 7.6), 8.01 (d, 2H, Ar, J_o 7.6). δ_C (100.04 MHz, $CDCl_3$; Me_4Si): 29.0, 40.6, 46.3, 48.3, 128.5, 128.7, 133.0, 136.7, 201.8. *m/z* (EI): 356 (M^+, 2%), 226 (71); 130 (100); 102 (8). HRMS (EI) for $C_{23}H_{20}N_2O_2$ $[M + H]^+$ calculated: 357.1603; found: 357.1609.

4,4-Dimethyl-1,2-di(2-naphthoyl)cyclopentane (4g). The compound was purified by radial thin-layer chromatography eluting with petroleum ether/diethyl ether (90 : 10 → 50 : 50) and isolated as a white solid, mp: 109–110 °C. δ_H (400.16 MHz; $CDCl_3$; Me_4Si): 1.2 (s, 6H, 2Me), 1.82 (dd, 2H, CH_{2b}, $J_{1,1'}$ 8.8, $J_{1,2}$ 12.8), 2.22 (dd, 2H, CH_{2a}, $J_{1',1}$ 8.8, $J_{1',2}$ 12.8), 4.82–4.87 (m, 2H, 2CH), 7.50–7.60 (m, 4H, Naph), 7.80–7.90 (m, 4H, Naph), 7.98 (d, 2H, Naph, J_o 8.0), 8.05 (dd, 2H, Naph, J_m 1.6, J_o 8.8), 8.60 (s, 2H, Naph). δ_C (100.04 MHz, $CDCl_3$; Me_4Si): 29.1, 40.8, 46.5, 48.5, 124.4, 126.7, 127.7, 128.4, 128.4 129.7, 130.7, 132.6, 134.0, 135.6, 201.9. *m/z* (EI): 406 (M^+, 9%); 252 (15); 251 (72); 156 (9); 155 (100); 127 (58). HRMS (EI) for $C_{29}H_{26}O_2$ $[M + H]^+$ calculated: 407.2011; found: 407.2014.

4,4-Dimethyl-1,2-di(1-adamantylmethanone)cyclopentane (4h). The compound was purified by radial thin-layer chromatography eluting with petroleum ether/diethyl ether (90 : 10 → 50 : 50) and isolated as a white solid, mp: 191.5–192.5 °C. δ_H (400.16 MHz; $CDCl_3$; Me_4Si): 1.07 (s, 6H, 2Me), 1.63–1.79 (m, 34H, 2Ada), 3.88 (m, 2H, 2CH). δ_C (100.04 MHz, $CDCl_3$; Me_4Si): 27.8, 29.7, 36.5, 37.6, 40.6, 46.9, 46.9, 47.9, 217.5OO. *m/z* (EI): 422 (M^+, 3%); 287 (12); 259 (79); 135 (100); 93 (12); 79 (12). HRMS (EI) for $C_{29}H_{42}O_2$ $[M + H]^+$ calculated: 423.3263; found: 423.3262.

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