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SYNTHESIS OF 1,4-DICARBONYL COMPOUNDS AND 4-KETO PIMELATES BY PALLADIUM-CATALYZED CARBONYLATION OF SILOXYCYCLOPROPANES

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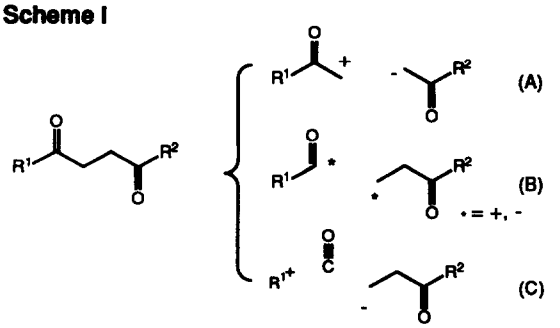
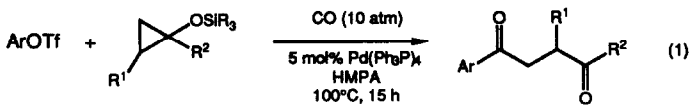
Abstract: *Palladium-catalyzed reaction of a siloxycyclopropane with an aryl triflate under carbon monoxide pressure (10-20 atm) in HMPA and that with carbon monoxide in chloroform provides new synthetic routes to 1,4-dicarbonyl compounds and 4-keto pimelates, respectively. The reaction of a siloxycyclopropane with a vinyl triflate, on the other hand, gives an acyloxycyclopropane instead.*

Syntheses of cyclic and acyclic compounds often rely on the elaboration of polycarbonyl compounds, among which 1,3- and 1,4-disposition of carbonyl functionality have proven particularly useful. While Claisen-type condensation has provided an important method for the preparation of 1,3-dicarbonyl compounds, the classical synthesis of 1,4-dicarbonyl compounds and their higher homologues relying on disconnection A in Scheme I is not particularly versatile.[1] Hence, disconnection B which involves either acyl anion[2] or homoenolate anion[3,4] have been explored as a useful alternative synthetic approach. Of the latter disconnection, metal-catalyzed coupling reactions of metal homoenolates (3-metallo carbonyl compounds)[5] with acid chlorides are especially straightforward. The disconnection C shown in Scheme I represents an entirely new, third strategy that relies on coupling of three-components, a metal homoenolate, carbonyl monoxide, and an aryl-cation synthon.[6] Practically, the reaction involves a palladium-catalyzed coupling of an aryl trifluoromethanesulfonate (triflate),[7] carbon monoxide, and a siloxycyclopropane 1 (eq 1), and is complementary to dissection B in that the synthesis basically starts from phenol derivatives instead of benzoic acid or benzaldehyde derivatives required in the second approach.

Scheme I

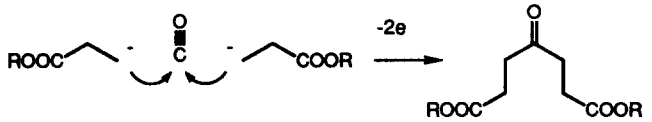




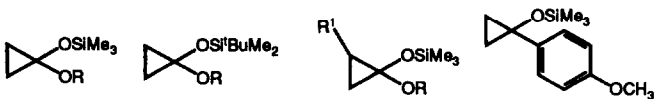
Tf = SO_2CF_3 **1**: R^1 = H, alkyl, R^2 = alkyl, aryl, alkoxy

In a similar context, we also found a synthetic route to 4-keto pimelates that involves three component-coupling involving two molecules of a siloxycyclopropane and carbon monoxide (Scheme II).[8] We report, in this article, details of the new syntheses of 1,4-dicarbonyl and 1,4,7-tricarbonyl compounds from siloxycyclopropanes and carbon monoxide.

Scheme II



Synthesis of 4-Keto Pimelates via Carbonylative Dimerization of Siloxycyclopropanes.[8] Before starting the studies on the palladium-catalyzed carbonylation reactions, we felt it necessary to investigate the basic behavior of siloxycyclopropanes toward carbon monoxide, and during this investigations we developed a new synthesis of 4-keto pimelates through oxidative coupling of two molecules of propionate homoenolates and one molecule of carbon monoxide (Scheme II). This route to keto pimelates differs from the existing ones, both mechanistically and strategically, and is expected to prove synthetically useful. Owing to their polyfunctional nature, 4-keto pimelates have served as useful intermediates for organic synthesis, i.e., for the preparation of 1,4-cyclohexanedione derivatives.[9]



2a: R = Et
b: R = ^{i}Pr
c: R = ^{n}Hex

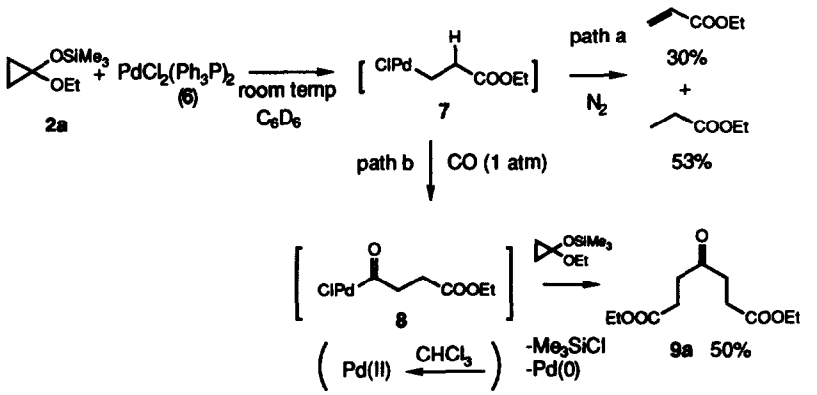
3a: R = Et
b: R = ^{i}Pr

4a: R = Me, R^1 = Me
b: R = Et, R^1 = Me
c: R = Et, R^1 = ^{n}Hex

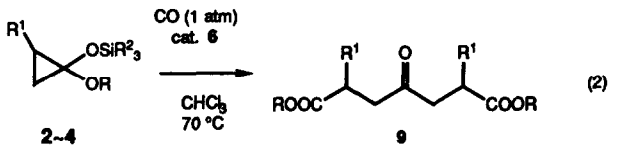
5

When 1-ethoxy-1-(trimethylsiloxy)cyclopropane (**2a**)[10] was treated with 0.5 equiv of $PdCl_2(Ph_3P)_2$ (**6**) in C_6D_6 under nitrogen, one obtains a mixture of ethyl acrylate (30%) and propionate (53%) (Scheme III, path a). The formation of 3-palladiopropionate intermediate **7** was strongly suggested. With the view to study CO insertion reaction of **7**, we repeated the reaction under 1 atm CO atmosphere, and were pleasantly surprised not only to find our aim fulfilled but to detect the formation of an unusual three-component coupling product, 4-keto pimelate **9a**. The reaction was rather slow, giving **9a** in 27% and 50% (based on Pd) after 16 and 60 h, respectively. In this carbonylative dimerization, the carbonyl carbon originated from carbon monoxide has been oxidized with $PdCl_2$, which precipitated as a palladium mirror.

Scheme III



Mechanistically, this reaction may consist of three stages (Scheme III): The first stage, the formation of **7**, is in common with the acrylate-forming reaction. In the second stage (path b), **7** undergoes CO insertion to produce an acylpalladium species **8**, which, in the third stage, acts as an acylating agent[4] for another molecule of **2a** to give the keto pimelate **9a**.



(2)

9a: R = Et, R^1 = H

Catalytic reaction always being more desirable than stoichiometric one in synthetic chemistry, studies to make this keto pimelate synthesis catalytic with respect to palladium was immediately started. We soon found that the use of chloroform as a solvent realizes an efficient catalytic cycle. Thus, when **2a** was heated in chloroform in the presence of 5 mol% of **6** at 60°C for 15 h, the desired keto pimelate was formed in 36% yield. Chloroform is considered to act as a reoxidant[11] of the Pd(0) species produced together with **9a** (cf. Scheme III). A wide variety of palladium/phosphine catalysts worked with essentially equal efficiency (Table I) except for a

bidentate phosphine ligand which gave none of the desired product. Use of higher CO (10 atm) pressure effected little improvement of the yield. Willkinson's catalyst proved to be ineffective (entry 8). In all cases examined, the reaction was very clean giving **9**, a small amount of ethyl propionate, and the starting cyclopropane. Low conversion was found to be due to deactivation of the catalyst, and higher conversion was achieved simply by adding the catalyst in a few portions with intervals of half a day, and the yield ranging from 60 to 80% were reproducibly obtained by using net 5-7 mol% of $PdCl_2(Ph_3P)_2$. The results of the keto pimelate synthesis (eq 2) are summarized in Table II (entries 1-4). We have not been able to find conditions to effect the coupling of ketone homoenolate precursor **5**, though such reaction would generate a versatile synthesis of 1,4,7-triketones.

Table I. Effects of the Catalysts in the Synthesis of Keto Pimelate **9a**.[a]

entry	catalyst	CO(atm)	temp(°C)	% yield[b]
1	$PdCl_2(Ph_3P)_2$	1	60	36
2	$PdCl_2(PhCN)_2 + 2\ Ph_3P$	1	60	48
3	$PdCl_2(PhCN)_2$ + dppe	1	60	0
4	$Pd(Ph_3P)_4$	1	60	35
5	$PdCl_2(PhCN)_2 + 2\ (MeO)_3P$	1	60	38
6	$PdCl_2(PhCN)_2 + 2\ (PhO)_3P$	1	60	30
7	$PdCl_2(Ph_3P)_2$	10	100	30
8	$RhCl(Ph_3P)_3$	1	60	0

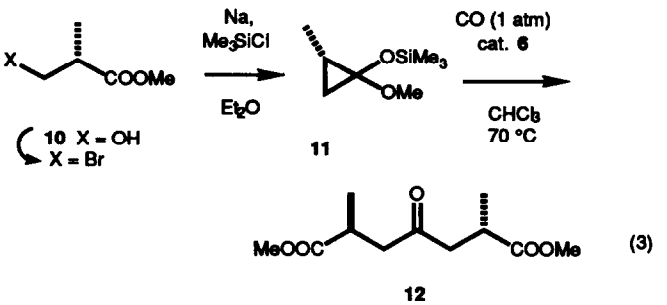
[a]The reaction was performed in $CHCl_3$ in the presence of 5 mol % of the catalyst for 15 hours. [b]Yield determined by GC.

Table II. Synthesis of 4-Keto Pimelates[a]

entry	cyclopropane	product (**9**)	% yield[b]
1	**2a**	R = Et, R^1 = H (**9a**)	65
2	**3a**	R = Et, R^1 = H (**9a**)	59
3	**2b**	R = ^{i}Pr, R^1 = H	79
4	**2c**	R = ^{n}Hex, R^1 = H	63
5	**4a**	R = Me, R^1 = Me	60
6	**4b**	R = Et, R^1 = Me	60[c]
7	**4c**	R = Et, R^1 = ^{n}Hex	69[c]

[a]The reaction was performed in $CHCl_3$ in the presence of net 5 mol % of $PdCl_2(PPh_3)_2$ added in a few portions at 60 °C under CO atmosphere. [b]Isolated yield. [c]A 1:1 diastereomeric mixture. The structural assignment rests on the analogy to that of the chiral pimelate (eq 3).

Symmetrical 2,6-disubstituted keto pimelates have become readily available by the present reaction. The carbonylative coupling of 2-methyl-substituted cyclopropane **4a** afforded 2,6-dimethyl-4-keto pimelate as an exclusive product due to cleavage of the less hindered C_1-C_3 bond in 60% yield (Table II, entries 5 and 6). Starting from a racemic starting material, we obtained the product as a 1:1 diastereomeric mixture. We have previously reported[12] the synthesis of a homochiral 2-methylcyclopropane **11** from commercially available methyl β-hydroxyisobutyrate (**10**), and its conversion to a corresponding zinc homoenolate of homochiral methyl 2-methylpropionate. When **11** was subjected to the present reaction conditions, there formed the expected keto pimelate as a single diastereomer **12** as analyzed by capillary GC, indicating that the coupling reaction has taken place without affecting the C_2-chiral center of the starting material. In view of the mechanistic similarity between this reaction and the 4-keto ester synthesis described below, we expect that **11** would serve also for the synthesis of homochiral 2-methyl-4-oxobutyrate.



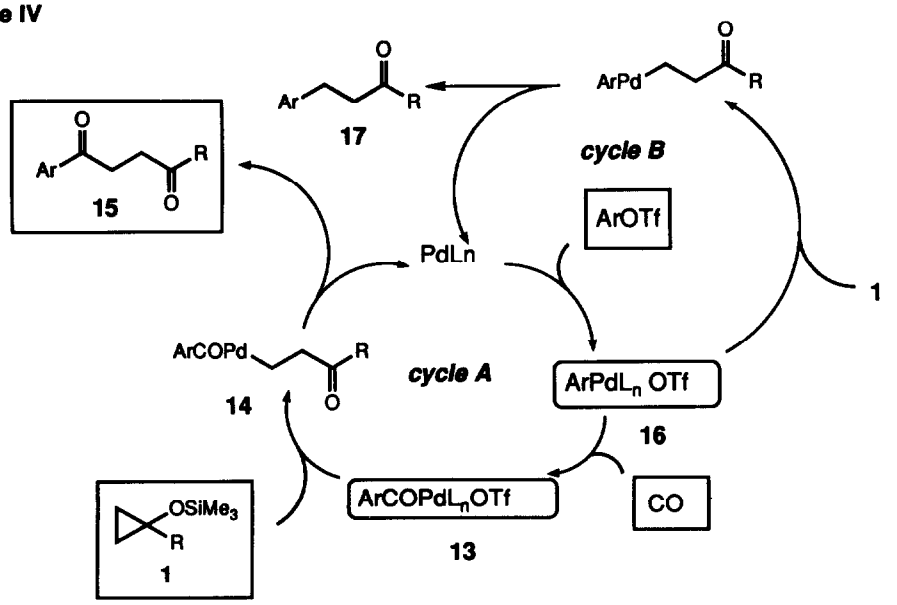
Carbonylative Arylation of Siloxycyclopropanes: Synthesis of 1,4-Keto Esters and 1,4-Diketones.[7] Having established the reaction of siloxycyclopropanes with carbon monoxide itself, we then proceeded to study its coupling with an aryl-cation synthon by a strategy fashioned after disconnection C in Scheme I. On the basis of our prior knowledge of the related palladium-catalyzed reaction of siloxycyclopropanes[4,12] as well as the one gained in the studies above, we could envision several problems from a mechanistic scheme summarized in Scheme IV.

The crucial catalytic cycle of the reaction (cycle A) may be the same as the one reported recently,[4] which involves the interaction between the acylpalladium complex **13** and the electron-rich cyclopropane **1**. The reaction then proceeds via **14** to give the final product **15**. By the use of CO pressure, the formation of the arylated product **17** through cycle B[13] involving the reaction of **1** with the palladium complex **16** has been effectively suppressed. The metal-mediated cleavage of cyclopropanes being basically an electrophilic process,[4b,14] **1** reacts

preferentially with the more electrophilic acyl complex **13** than with the aryl complex **16** if the CO atmosphere maintains a significantly high concentration of **13** in the reaction mixture.

Since the keto pimelate formation described above needs initial ring opening of the siloxycyclopropane with $PdCl_2 \cdot L_n$, this reaction will not interfere with cycle A, if the reaction is once started with Pd(0) and the following catalytic cycle proceeds as indicated. In fact, we only saw this reaction when the three-component coupling was attempted in $CHCl_3$.

Scheme IV



Brief studies of the reaction conditions modeled after those we reported previously established the optimum conditions of the three-component coupling. We mainly focused on the reaction of **2a** with p-trifluoromethanesulfonyloxyacetophenone (eq 4). There was found a clear solvent effect on the product yield (Table III). HMPA which has often proven uniquely effective in the related reactions was found much superior than other common dipolar aprotic solvents, e.g., N,N'-dimethylpropylene urea (DMPU) or DMSO. $CHCl_3$ which is the solvent of choice in the related palladium-catalyzed reaction of **2** with acid chloride turned out to be a very poor solvent, and not unexpectedly tended to give 4-keto pimelates via a pathway described above. Since the arylation[13] and carbonylation compete each other in the present reaction (vide supra), effective concentration of CO in solution is important. Thus, although CO pressure of 10 atm was sufficient to completely suppress the arylation under our standard conditions using magnetic stirring bar on a scale where <<1 mL of solvent was used, 20 atm was necessary on a larger scale wherein stirring inevitably became less efficient.

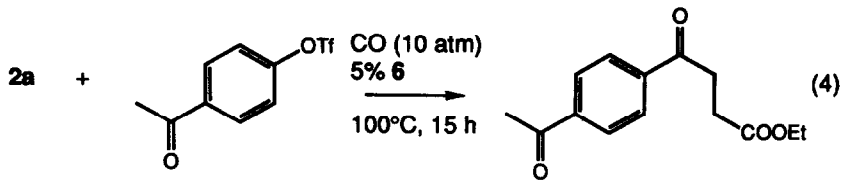
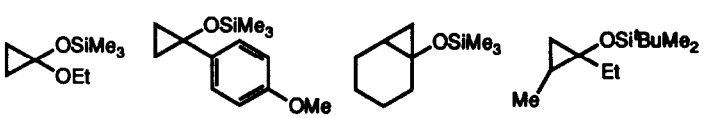


Table III. Solvent Effects on the Carbonylative Arylation (eq 4).

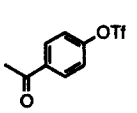
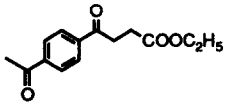
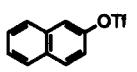
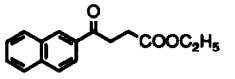
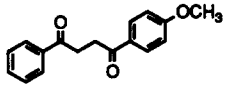
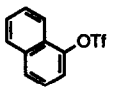
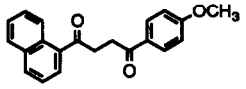
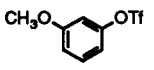
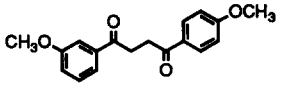
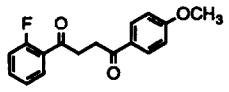
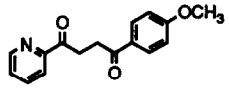
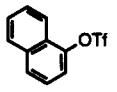
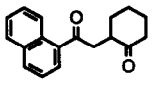
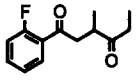
solvent	1,4-keto ester (% yield)	ArOTf (recovery) (%)
HMPA	87	~0
DMPU	12	88
DMSO	0	84
$CHCl_3$	0	100

The standard reaction conditions are the following : a mixture of a siloxycyclopropane (3-4 mmol), an aryl triflate (2 mmol), and 3-5 mol% of $Pd(Ph_3P)_4$ in a few ml of hexamethylphosphoric triamide (HMPA) is heated at 100 °C with stirring for half a day under 10-20 atm CO atmosphere in an autoclave to obtain a 1,4-dicarbonyl compound after chromatographic purification (eq 1). The reaction of bromobenzene gave only 20% of the 1,4-keto ester under the optimum condition, presumably owing to the lower electrophilicity of the incipient benzoylpalladium bromide complex. Siloxycyclopropanes that serve as precursors of ester- (**2a**)[10] and ketone-homoenolates (**5**, **18**, and **19**)[5a] have been successfully employed in the present reaction. The cleavage of the cyclopropane ring took place exclusively at the C-C bond connected to the siloxy group in **18** and **19**.The same regioselectivity has also been found in the related reactions.[3,4,13] Several representative aryl triflates bearing electron-withdrawing and donating substituents have been coupled with the siloxycyclopropanes (Table IV) to obtain 1,4-dicarbonyl compounds including an interesting tricarbonyl compound (entry 1). The reaction may also be useful for the functionalization of heteroaromatic triflates (entry 7).

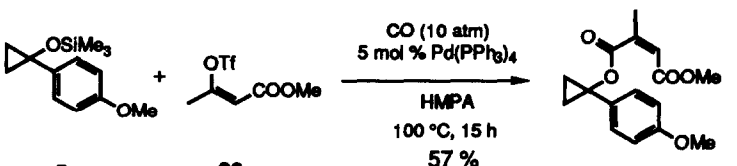


2a **5** **18** **19**

Table IV. Synthesis of 1,4-Dicarbonyl Compounds

entry	cyclopropane	triflate	product	yield [%]
1	**2a**			87
2	**2a**			52
3	**5**			55
4	**5**			73
5	**5**			61
6	**5**			43
7	**5**			27
8	**18**			59
9	**19**			39

Among a few kinds of side products which were *a priori* expected to form, we noted only a single one, a carbonyl compound formed by desilylation/ring-opening of the starting siloxycyclopropane. We have previously noted that C- and O-acylation reactions compete in the palladium-catalyzed acylation of zinc homoenolate.[15] Although there was found no sign of the O-acylation in the carbonylative *arylation*, the O-acylation reaction emerged as an exclusive reaction pathway in the reaction of a vinyl triflate (eq 5). Thus, the carbonylative reaction of a *Z*-vinyl triflate **20** gave an unsaturated ester **21** as a single isomer, probably, proceeding with retention of the olefin geometry. A related O-acylation reaction has also been observed in the palladium-catalyzed acylation of zinc homoenolate of alkyl propionates.[3a]



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In summary, the catalytic reactions described above provide conceptually novel synthetic approaches to 1,4-dicarbonyl and 1,4,7-tricarbonyl compounds, and acyloxycyclopropanes. Now, these reactions together with other approaches using stoichiometric metal homoenolates have established that the homoenolate chemistry provides useful methods for the synthesis of 1,4-dicarbonyl and related compounds.

Experimental Section

General. All reactions dealing with palladium compounds, except otherwise noted, were carried out under nitrogen. Palladium catalysts were weighed quickly in air and transferred to a reaction vessel, which was filled with nitrogen by several evacuation/flush cycles. Routine chromatography was carried out as described by Still[16] using hexane/AcOEt as eluent.

^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were measured for a $CDCl_3$ solution of a sample on a JEOL FX-200 instrument. Where noted, a 60 MHz ^{1}H NMR machine (Hitachi R24B) was also used. ^{1}H NMR spectra are reported in parts per million from internal tetramethylsilane, and ^{13}C NMR spectra from $CDCl_3$ (77.0 ppm). IR spectra were recorded on a Hitachi 260-10 instrument or a JASCO IR-800; absorptions were reported in cm^{-1}. Gas chromatographic (GC) analysis was performed on a Shimadzu 4BM, 8A, or 14A machine equipped with a glass capillary columns (0.25 mm I.D. x 25 m) coated with OV-1, OV-17, or HR-1.

Material. Ethereal solvents were distilled from sodium benzophenone ketyl immediately before use. CH_2Cl_2, $CHCl_3$, and $CDCl_3$ were distilled successively from P_2O_5 and K_2CO_3 under nitrogen. HMPA, DMPU, and DMSO was distilled in vacuo from calcium hydride and stored over molecular sieves. Siloxycyclopropanes were prepared as previously described.[5a,10]

Stoichiometric Synthesis of Diethyl 4-Keto Pimelate. A mixture of dichloro[bis-(triphenylphosphine)]palladium (**6**) (35 mg, 0.05 mmol), **2a** (18.6 μL, 0.10 mmol) in 0.5 mL of C_6D_6 was heated at 80 °C under 1 atm CO atmosphere, and the progress of the reaction was monitored by ^{1}H NMR. The yield of the title keto pimelate was <4%, 27% and 50%, after 3, 16, and 60 h, respectively. After chromatographic purification, 5.9 mg (50%) of the product was isolated: ^{1}H NMR 1.26 (t, J = 7.6 H, 6 H), 2.60 (m, 4 H), 2.77 (m, 4 H), 4.14 (1, J = 7.6 Hz, 4 H). Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.39; H, 7.88. Found: C, 57.29; H, 7.86.

Catalytic Synthesis of Diisopropyl 4-Keto Pimelate. A mixture of **6** (35 mg, 0.05 mmol) and **2b** (377 mg, 2.00 mmol) in 4 mL of $CHCl_3$ was heated at 60°C under 1 atm of CO atmosphere. After 16 h, additional 35 mg of **6** in 2.5 mL of $CHCl_3$ was added and heating was continued for 32 h. Solvent was removed and the residue was purified on silica gel (hexane/AcOEt) to give 201 mg of the title compound (79%): IR (neat) 2980, 1735, 1375, 1110; ^1H NMR (CCl_4, 60 MHz) 1.20 (d, J = 6.0 H, 12 H), 2.53 (m, 8 H), 4.90 (qq, J = 6.0 6.0 Hz, 2 H). Anal. Calcd for $C_{13}H_{22}O_5$: C, 60.45; H, 8.58. Found: C, 60.47; H, 8.56.

Spectral Properties of 4-Ketopimelates: Dihexyl 4-Keto Pimelate. IR (neat) 2925, 1740, 1720; ^1H NMR (60 MHz, CCl_4) 0.90 (m, 6 H, CH_3), 0.9-1.8 (m, 16 H, CH_2), 2.5 (m, 8H, $COCH_2$), 3.97 (m, 4 H, CH_2COO). Anal. Calcd for $C_{19}H_{34}O_5$: C, 66.64; H, 10.01. Found: C, 66.82; H, 10.06.

Diethyl 2,6-Dimethyl-4-pimelate. A dl and meso mixture: IR (neat) 2985, 1735, 1385, 1030; ^1H NMR (200 MHz, $CDCl_3$) 1.16 (d, J = 6.7 Hz, 6 H, C*H*$_3$CH), 1.23 (t, J = 7.0 Hz, 6 H, CH_2CH_3), 2.46 (m, 2 H), 2.8-3.0 (m, 4 H), 4.10 (two overlapping pairs of q, J = 7.0 Hz, 4 H, COOC*H*H). Anal. Calcd for $C_{13}H_{22}O_5$: C, 60.45; H, 8.58. Found: C, 60.29; H, 8.39.

Diethyl 2,6-Dihexyl-4-ketopimelate. A dl and meso mixture: IR (neat) 2925, 1735, 1120; ^1H NMR (60 MHz, CCl_4) 0.83 (m, 6 H, CH_3), 0.8-1.19 (m, 20 H, CH_2), 1.2 (t, J = 7.0 Hz, 6 H, $COOCH_2CH_3$), 1.9-2.9 (m, 6 H, $COCH_2CHCOO$), 4.0 (q, J = 7.0 Hz, 4 H, $COOCH_2$). Anal. Calcd for $C_{23}H_{42}O_5$: C, 69.31; H, 10.62. Found: C, 69.50; H, 10.72.

Dimethyl (2*S*, 6*S*)-2,6-Dimethyl-4-pimelate. ^1H NMR (200 MHz, $CDCl_3$) 1.12 (d, J = 7 Hz, 6 H, $CHCH_3$), 2.48 (m, 2 H) 2.8-3.1 (m, 4 H), 3.71 (s, 6 H, $COOCH_3$); ^{13}C NMR (50 MHz, $CDCl_3$) 17.1 ($CHCH_3$), 34.6 (*C*H), 46.0 ($COCH_2$), 51.9 ($COOCH_3$), 176.1 (CO), 206.7 (C=O). The position of the 2,6-methyl groups was determined by long-range selective proton decoupling method.

Catalytic Synthesis of 1,4-Diketones. 1-(4-Methoxyphenyl)-4-(1-naphthyl)butane-1,4-dione. To an autoclave was placed a mixture of 1-trimethylsiloxy-1-(4-methoxyphenyl)cyclopropane (45.2 μL, 0.2 mmol), 1-naphthyl trifluoromethanesulfonate (39 μL, 0.2 mmol), $Pd(Ph_3P)_4$ (11.6 mg, 0.01 mmol), and HMPA (0.5 mL) under carbon monoxide pressure (10 kg/cm^{-1}), and the mixture was stirred with a magnetic stirring bar at 90°C for 40 h. The reaction mixture was diluted with ether (3 mL), and washed five times with 0.5 mL each of water. The aqueous layer was extracted with 1 mL of ether. The combined organic layer was washed with sat. brine (0.5 mL x 2), and dried over $MgSO_4$. Purification of a crude oily product on silica gel (20% EtOAc in hexane) gave 46.3 mg (73%) of the title compound as pale yellow crystals: IR (neat) 3020, 1670, 1600; ^1H NMR (200 MHz, $CDCl_3$) 3.51 (s, 4 H, CH_2), 3.89 (s, 3 H, OCH_3), 6.97 (distorted d, J = 8.6 Hz, 2 H, aromatic H), 7.54 (m, 3 H, aromatic H), 7.8-8.1 (m,

5 H, aromatic H), 8.63 (distorted d, J = 8.6 Hz, 2 H, aromatic H). Anal. Calcd for $C_{21}H_{18}O_3$: C, 79.23; H, 5.70. Found: C, 79.25; H, 5.86.

Spectral Properties of 4-Ketoesters and 1,4-Diketones. 1-(4-Methoxyphenyl)-4-phenylbutane-1,4-dione, 2-(2-naphthyl-2-oxoethyl)cyclohexanone were identical with authentic samples.

Ethyl 4-(4-acetylphenyl)-4-oxobutanoate. Mp 75-76°C; IR (neat) 1725, 1685, 1265; ^1H NMR (200 MHz, $CDCl_3$) 1.26 (t, J = 9.1 Hz, 3H), 2.64 (s, 3H), 2.77 (t, J = 6.7 Hz, 2H), 3.33 (t, J = 6.7 Hz, 2 H), 4.14 (q, J = 9.1 Hz, 2H), 8.03 (m, 4 H). Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.61; H, 6.42.

Ethyl 4-(2-naphthyl)-4-oxobutanoate. The title keto ester formed as a 81:19 mixture with the 4-ketopimelate **9a**. ^1H HMR (200 MHz, $CDCl_3$) 1.27 (t, J = 6.8 Hz, 3 H), 2.83 (t, J = 6.7 Hz, 2H), 3.44 (t, J = 6.7 Hz, 2H), 4.19 (q, J = 6.8 Hz, 2H), 7.4-7.7 (m, 3H), 7.8-8.0 (m, 4H).

1-(3-Methoxyphenyl)-4-(4-methoxyphenyl)butane-1,4-dione. IR (neat) 2910, 1675, 1600, 1265, 1245, 1170; ^1H NMR (60 MHz, CCl_4) 3.33 (s, 4 H, CH_2), 3.78 (br s, 6 H, OCH_3), 6.7-7.0 (distorted d, J = 9 Hz, 2 H, aromatic H), 6.9-7.7 (m, 4 H, aromatic H), 7.8-8.1 (distorted d, J = 9 Hz, 2 H, aromatic H). Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.37; H, 6.10.

1-(2-Fluorophenyl)-4-(4-methoxyphenyl)butane-1,4-dione. ^1H NMR (200 MHz, $CDCl_3$) 3.42 (m, 4 H, CH_2), 3.88 (s, 3 H, OCH_3), 6.94 (m, 2 H, aromatic H), 7.1-7.3 (m, 2 H, aromatic H), 7.53 (m, 1 H, aromatic H), 7.91 (dd, J = 1.9, 7.6 Hz, 1 H, aromatic H), 8.02 (m, 2 H, aromatic H). Anal. Calcd for $C_{17}H_{15}O_3F$: C, 71.32; H, 5.28. Found: C, 71.35; H, 5.29.

1-(2-Pyridyl)-4-(4-Methoxyphenyl)butane-1,4-dione. ^1H NMR (200 MHz, $CDCl_3$) 3.43 (t, J = 6.7 Hz, 2 H, CH_2), 3.81 (t, J = 6.7 Hz, 2 H, CH_2), 2.89 (s, 3 H, OCH_3), 7.0 (distorted d, J = 8.6 Hz, 2 H, aromatic H), 7.53 (ddd, J = 1.5, 4.8, 7.6 Hz, 1 H, aromatic H), 7.90 (dt, J = 2.3, 7.6 Hz, 1 H, aromatic H), 8.18 (distorted d, J = 8.6 Hz, 2 H, aromatic H), 8.22 (dt, J = 7.6, 1.5 Hz, 1 H, aromatic H), 8.77 (ddd, J = 1.5, 2.3, 4.8 Hz, 1 H, aromatic H).

1-(2-Fluorophenyl)-3-methylhexane-1,4-dione. ^1H NMR (200 MHz, $CDCl_3$) 1.10 (d, J = 7.1 Hz, 3 H, C*H*CH_3), 1.16 (t, J = 7.3 Hz, 3 H, CHC*H*$_3$), 2.67 (q, J = 7.3 Hz, 2 H, COC*H*$_2$$CH_3$), 2.97 (dt, J = 18, 3.8 Hz, 1 H, ArCOC*H*), 3.21 (m, 1 H, CH), 3.54 (ddd, J = 3.8, 9.5, 18 Hz, 1 H, ArCOC*H*), 7.05-7.26 (m, 2 H, aromatic H), 7.5 (m, 1 H, aromatic H), 7.83 (dt, J = 1.9, 7.6 Hz, 1 H, aromatic H). Anal. Calcd for $C_{13}H_{15}O_2F$: C, 70.25; H, 6.80. Found: C, 70.22; H, 6.84.

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