Magnesium-Promoted One-Pot Double C-Acylation and Cycloaddition of Anthracene and Double C-Acylation of Benzyl Acrylates

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Abstract: Treatment of anthracene or benzyl acrylate with magnesium turnings for Grignard reaction in the presence of various acid chlorides in *N*,*N*-dimethylformamide at room temperature brought about one-pot reductive double C-acylation or tandem intermolecular cycloaddition to give the corresponding C-diacylated products in satisfactory yields.

Key words: magnesium, anthracene, double acylation, cycloaddition, benzyl acrylate

Introduction of an acyl group to the carbon–carbon double bond of activated olefins may be one of the most attractive, important and useful techniques for carbon–carbon bond formation.[1] We have already reported electrochemical[2] or Mg-promoted[3] C-acylation of α,β-unsaturated carbonyl compounds to afford the corresponding C-acylated 1,4-dicarbonyl compounds in the stereo- and regioselective manners. Furthermore, monoacylation of stilbenes had also been demonstrated by our group.[4] However, in these reactions, the corresponding double C-acylated products were not detected in the product mixtures, but only the C-monoacylated products were exclusively obtained.

On the other hand, we have recently developed electroreductive one-pot vicinal double C-acylation of styrenes and methacryl esters with acid anhydrides or *N*-acylimidazole derivatives.[5]

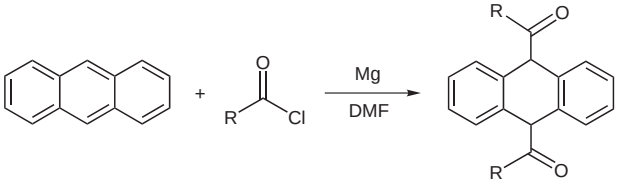
In this study, we wish to present the first Mg-promoted one-pot double C-acylation and unique tandem intermolecular cycloaddition of anthracene (**1**) and benzyl acrylate (**6**) with a variety of acid chlorides **2** to give the corresponding novel 9,10-diacyl-9,10-dihydroanthracenes **3** and 1,4-diketones **7**, respectively, as the predominant products in good yields (Scheme 1).

Scheme 1 Mg-promoted one-pot double C-acylation of anthracene

Optimization of the reaction conditions for the present Mg-promoted one-pot double C-acylation of anthracene with acid chlorides has been accomplished by changing the solvent, the equivalent of acylating agent and magnesium on the basis of anthracene (**1**) to find that the desired double C-acylation products were obtained most efficiently by using 10 equivalents of acid chloride and 10 equivalents of Mg turnings for Grignard reaction in anhydrous *N*,*N*-dimethylformamide (DMF) at 15–20 °C under a nitrogen atmosphere.

Under the optimized conditions, the reaction proceeded with a variety of acid chlorides (**2a**–**d**) very smoothly in DMF at room temperature to give the mixtures of the corresponding two stereoisomers, 9,10-diacylated 9,10-dihydroanthracenes (**3Aa**–**d**, and **3Ba**–**d**), in moderate to good yields, as shown in Table 1.[6,7]

Table 1 Double C-Acylation of Anthracene in the Presence of Various Acid Chlorides[a]



Entry	R	Product (%)[b]	Isomeric ratio
1	Me (**2a**)	73 (**3a**)	68 (**3Aa**):32(**3Ba**)
2	Et (**2b**)	78 (**3b**)	78 (**3Ab**):22 (**3Bb**)
3	*n*-Pr (**2c**)	88 (**3c**)	82 (**3Ac**):18 (**3Bc**)
4	*i*-Pr (**2d**)	59 (**3d**)	>99 (**3Ad**):<1 (**3Bd**)

[a] Reaction conditions: anthracene (5 mmol), acid chloride (10 equiv), Mg (10 equiv), DMF (40 mL), 15–25 °C, 15 h reaction time, under N_2 atmosphere.
[b] GC yield.

The stereoisomeric ratios became larger with the increase in bulkiness of the alkyl groups of acid chlorides **2a**–**d**. It may be quite interesting that these two stereoisomers may be characterized as the *cis*-*exo*- and *cis*-*endo*-isomers by their same chemical shifts in 9- and 10-protons of each isomer of 9,10-diacylated anthracene, in which these *cis*-*exo*- and *cis*-*endo*-isomers were found to appear as one singlet at δ = 5.10–5.23 ppm for the major stereoisomers

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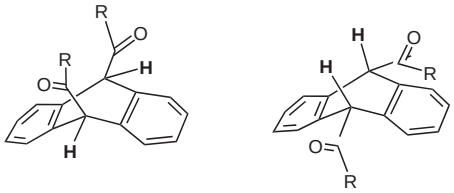
3Aa–d and at δ = 4.87–4.89 ppm for the minor isomers **3Ba–d**, respectively, as shown in Scheme 2. The *cis-exo*-isomers **3Aa–d** are presumably more stable than the *cis-endo*-isomers **3Ba–d** because of steric hindrance between two acyl groups and two benzene rings. The low-field shift in the chemical shift of the *exo*-isomers **3Aa–d** may be attributed to a diamagnetic anisotropy effect induced by the ring current of their two phenyl rings.



	cis-exo-isomer (3Aa–d)	*cis-endo*-isomer (3Ba–d)
δ value:	5.10–5.23 ppm	4.87–4.89 ppm

Scheme 2 Chemical shift of H-9 and H-10 (one singlet) in ^{1}H NMR

Similarly, employment of more sterically bulky acid chlorides such as ethyl succinyl chloride (**2e**) and 4-chlorobutyryl chloride (**2f**) as the acylating agents in the present reaction brought about formation of only the corresponding *exo*-stereoisomers, 9,10-di(3-carboethoxy propionyl)-9,10-dihydroanthracene (**3Ae**: 60% yield) and 9,10-di(4-chlorobutyryl)-9,10-anthracene (**3Af**: 67% yield), respectively, as shown in Scheme 3.

The present Mg-promoted carbon–carbon bond formation was successfully applied to novel cycloaddition of anthracene with α,ω-dicarboxylic acid dichlorides **4a**,**b** such as succinyl and glycolyl dichlorides to give the corresponding dibenzobicyclic compounds **5a**,**b**, as shown in Scheme 4. The optimum results of these Mg-promoted cycloaddition were obtained to give the corresponding adducts **5a**,**b** as almost single products in 63% and 34% yields when each five equivalents of Mg turnings for Grignard reaction and acid dichloride based on anthracene were used in diluted solution (35 mM) of DMF at room temperature under nitrogen atmosphere.

The absolute structure of the product **5a** formed from cycloaddition of anthracene with succinyl dichloride was confirmed by X-ray analysis of the single crystal, as shown Figure 1, and the bridgehead methine protons of **5a** were found to appear at δ = 5.14 ppm as the singlet in its ^{1}H NMR spectrum, which shows good consistence with the chemical shift of the 9,10-bridgehead protons of *exo*-stereoisomers **3Aa–f**, the major products among 9,10-diacylated products of anthracene (**1**), as mentioned before.

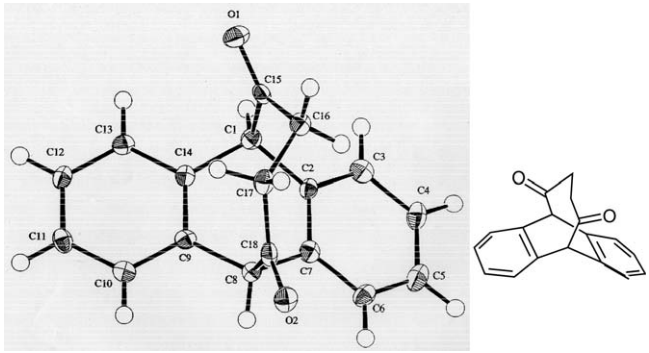
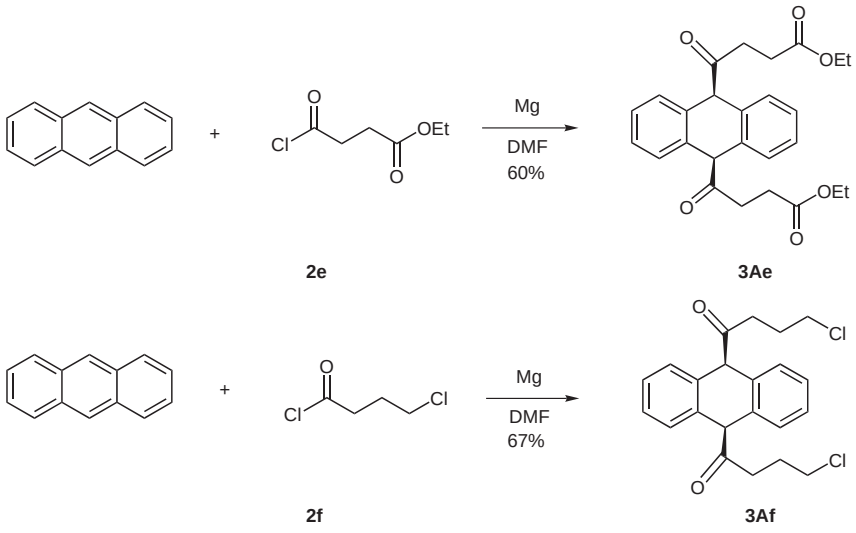


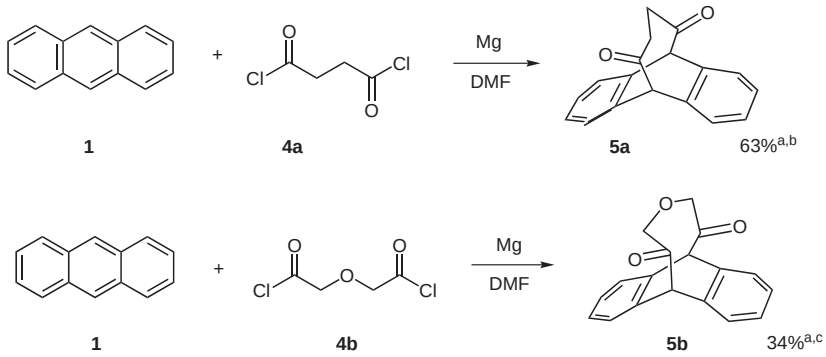
Figure 1 X-ray crystal structure of **5a**

Furthermore, similar one-pot double C-acylation was also observed in Mg-promoted reduction of benzyl acrylate (**6**) with acid chlorides in DMF. Thus, treatment of benzyl acrylate with Mg turnings at room temperature (15–25 °C) in the presence of various acid chlorides in DMF brought about one-pot vicinal double C-acylation to give the corresponding diketoesters **7a–d** in moderate to good yields, accompanying formation of monoacylated products **8a–d** in small amounts as by-products (Table 2).

In order to obtain some information for reaction mechanism of the present one-pot Mg-promoted double C-acylation, reduction potential of starting substrates, an-

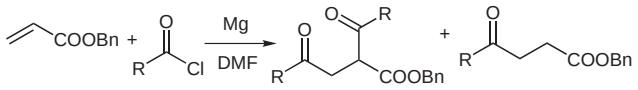


Scheme 3 Double C-acylation of anthracene in the presence of ethyl succinyl chloride or 4-chlorobutyryl chloride



Scheme 4 Cycloaddition of anthracene in the presence of various acid dichlorides. *Reaction conditions*: substrate (5 mmol), acid chloride (5 equiv), Mg (5 equiv), 15–25 °C, reaction time 15 h, under N_2 atmosphere; [a] GC yield; [b] DMF (100 mL); [c] TMSCl (0.5 equiv), DMF (140 mL).

Table 2 Double C-Acylation of Benzyl Acrylates in the Presence of Various Acid Chlorides[a]



6 2 7 8

Entry	R	GC yield (%)	
		7	**8**
1	Et (**2b**)	76 (**7a**)	24 (**8a**)
2	*n*-Pr (**2c**)	61 (**7b**)	8 (**8b**)
3	*i*-Pr (**2d**)	43 (**7c**)	14 (**8c**)
4	*i*-Bu (**2g**)	44 (**7d**)	8 (**8d**)

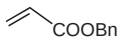
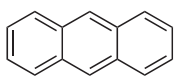
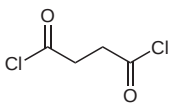
[a] Reaction conditions: substrate (10 mmol), acid chloride (7 equiv), Mg (6 equiv), DMF (60 mL), 15–25 °C, 16 h reaction time, under N_2 atmosphere.

thracene and benzyl acrylate, and acid chlorides were analyzed by cyclic voltammetry, as shown in Table 3.

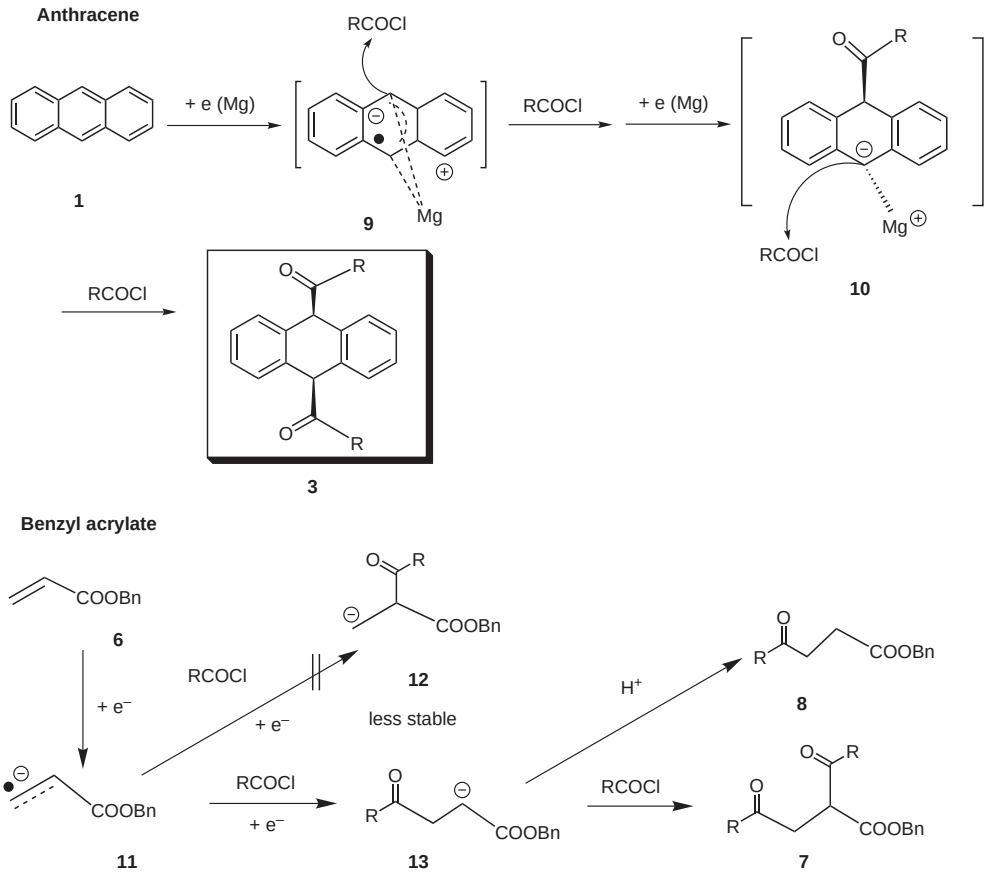
No reduction wave of acid chloride was observed in the range of 0 V to –3.00 V. On the other hand, clear reduction wave of anthracene and benzyl acrylate was obtained at –1.77 V and –2.20 V, respectively, which may be accessible by Mg-promoted reduction. The following reaction scheme may be proposed as one of the most plausible reaction mechanisms for the present one-pot double C-acylation of anthracene with acid chlorides, although the detailed mechanism has not been clear as yet. The first electron transfer from Mg metal to anthracene (**1**) may generate the corresponding anion radicals **9** which may be delocalized predominantly at the 9- and the 10-positions and the Mg cation may coordinate at these positions. Subsequently, the first electrophilic attack of an acylating agent takes place at either of the 9- and 10-positions of anthracene (**1**) from the opposite side of Mg cation, followed by the fast second electron transfer, giving more stable benzylic anions **10**, which may still coordinate with Mg cation. The second electrophilic attack of another acylating agent to benzylic anion from the opposite side of Mg cation may give a stereoisomeric mixture of the *cis-exo*- and/or the *cis-endo*-9,10-diacylated 9,10-dihydroanthracenes **3a**–**f**, in which the *cis-exo*-isomer may be sterically more favorable as a major component, as shown in Scheme 5.

In the case of benzyl acrylate (**6**), similarly the first electron transfer from Mg metal to the benzyl acrylate may generate the corresponding anion radical **11**, which may be subjected to the first electrophilic attack of acid chloride to the β-carbon of the activated olefin to give more stable α-ester anion **13** rather than the less stable terminal methylene anion **12** after the fast second electron transfer preferentially rather than less stable methylene anions **12**. Subsequently, the second electrophilic acylation and protonation took place toward benzylic anions **13** to give vicinal double C-acylation products **7**.

Table 3 Reduction Potentials of Active Olefines and Acid Chlorides[a]

Substrate	Reduction potential (V vs. Ag/AgCl)	Substrate	Reduction potential (V vs. Ag/AgCl)
	–2.20		No wave (0 to –3.00)
	–1.77		No wave (0 to –3.00)

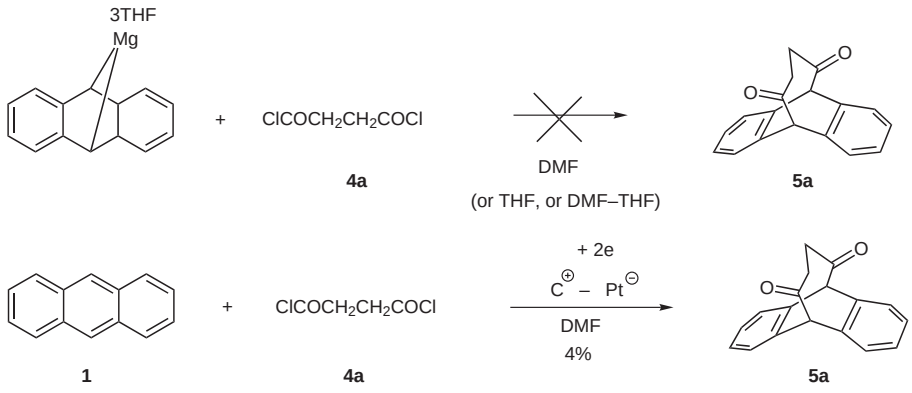
[a] Working electrode: Pt, counter electrode: Pt, reference electrode: Ag/AgCl, solvent: DMF (15 mL), supporting electrolyte: 1% *n*-Bu_4NClO_4, scan rate: 200 mV/s.



Scheme 5 Proposed reaction mechanism of double C-acylation by anthracene and benzyl acrylate

According to the hitherto known reaction by Mg–anthracene·3THF complex,[8] it might be postulated that this reaction might proceed through Mg–anthracene complex.[9] However, many attempts from reactions of commercially available Mg–anthracene·3THF[10] complex with propionyl or succinyl chloride in various solvent systems such as only DMF, only THF, and a 1:1 mixture of DMF and THF at various temperatures from 60 °C to 15 °C under the conditions similar to those of the present Mg-promoted reaction have never given any of the corresponding diacylated products, but just a mixture of 9,10-dihydroanthracene and anthracene.[11] Furthermore, the cycloaddition product **5a** was obtained yet in low yield (4%)[12] from electroreduction of anthracene in DMF containing succinyl chloride using a Pt-plate as the cathode and a carbon-rod as the anode, and Et_4NOTs as supporting electrolyte (Scheme 6). These experimental facts may clearly indicate that the present reaction may take place through an electron-transfer mechanism from Mg metal, and Mg–anthracene complex may not be involved or may not play any important role.

In conclusion, novel one-pot double C-acylation and cycloaddition of anthracene or benzyl acrylate by electron transfer from easily available Mg metal was successfully achieved to obtain the useful 9,10-diacyl-9,10-dihydro-



Scheme 6

anthracene derivatives or related bicyclic compounds. The reaction is characterized by a simple procedure, satisfactory yield, mild conditions, a unique reaction type, environmental preference and much usefulness of the products.

Acknowledgment

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(6) **Typical Procedure for Mg-Promoted One-Pot Double Acylation of Anthracene**

In a 50-mL three-necked flask of nitrogen atmosphere were introduced 30 mL of anhyd DMF as solvent, anthracene (5 mmol) as starting material and magnesium metal (10 equiv). Acid chloride (10 equiv) dissolved in 10 mL of DMF was slowly added at 0–5 °C over 20 min. The reaction mixture was stirred at 20–25 °C for 15 h. After reaction, the mixture was poured into sat. $NaHCO_3$ solution. Organic materials were extracted with three 100-mL portions of EtOAc. The organic layer was washed with sat. NaCl solution and dried over anhyd $MgSO_4$. After removal of $MgSO_4$ by filtration and evaporation of the solvent, the isolation by column chromatography gave diacylated compounds in satisfactory yields.

(7) All the products obtained in this study were characterized by spectroscopic methods (^{1}H NMR, ^{13}C NMR, IR, mass spectra) and elemental analysis, or by comparison of spectroscopic and chromatographic behaviors with those of authentic samples.

9,10-Diacetyl-9,10-dihydroanthracene (3a)

Diastereomeric ratio = 68:32. Mp 151–152 °C (major isomer), 137 °C (minor isomer). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major isomer) = 1.71 (s, 6 H), 5.11 (s, 2 H), 7.27–7.35 (m, 8 H) ppm; δ (minor isomer) = 2.19 (s, 6 H), 4.89 (s, 2 H), 7.32–7.41 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ (major isomer) = 25.50, 58.75, 128.32, 128.68, 130.84, 205.95 ppm; δ (minor isomer) = 28.28, 60.83, 127.47, 129.24, 134.00, 204.74 ppm. IR (KBr): 3070, 3020, 3010, 2960, 2920, 1700, 1490 cm^{-1}. MS (EI): *m/z* = 264 [M$^+$]. Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.93; H, 6.23.

9,10-Dipropionyl-9,10-dihydroanthracene (3b).

Diastereomeric ratio = 78:22. Mp 134–135 °C (major isomer), 106–108 °C (minor isomer). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major isomer) = 0.82 (t, *J* = 7.2 Hz, 6 H), 1.99 (q, *J* = 7.2 Hz, 4 H), 5.16 (s, 2 H), 7.27–7.35 (m, 8 H) ppm; δ (minor isomer) = 0.95 (t, *J* = 7.0 Hz, 6 H), 2.54 (q, *J* = 7.0 Hz, 4 H), 4.88 (s, 2 H), 7.29–7.35 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ (major isomer) = 8.32, 31.18, 58.36, 128.09, 128.63, 131.23, 209.11 ppm; δ (minor isomer) = 7.78, 33.95, 60.00, 127.23, 129.18, 134.17, 207.25 ppm. IR (KBr): 3030, 2980, 2940, 2890, 1700, 1480 cm^{-1}. MS (EI): *m/z* = 292 [M$^+$]. Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 82.23; H, 7.03.

9,10-Di(*n*-butyryl)-9,10-dihydroanthracene (3c).

Diastereomeric ratio = 82:18. Mp 113–114 °C (major isomer), 91–93 °C (minor isomer). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major isomer) = 0.60 (t, *J* = 7.3 Hz, 6 H), 1.35 (sext, *J* = 7.3 Hz, 4 H), 1.92 (t, *J* = 7.3 Hz, 4 H), 5.14 (s, 2 H), 7.27–7.36 (m, 8 H) ppm; δ (minor isomer) = 0.82 (t, *J* = 7.4 Hz, 6 H), 1.50 (sext, *J* = 7.4 Hz, 4 H), 2.48 (t, *J* = 7.4 Hz, 4 H), 4.87 (s, 2 H), 7.30–7.39 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ (major isomer) = 13.47, 17.35, 39.68, 58.53, 128.09, 128.73, 131.01, 208.26 ppm; δ (minor isomer) = 13.65, 17.14, 42.37, 60.30, 127.28, 129.22, 134.03, 206.59 ppm. IR (KBr): 3030, 2960, 2930, 2870, 1710, 1480 cm^{-1}. MS (EI): *m/z* = 320 [M$^+$]. Anal. Calcd for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55. Found: C, 82.20; H, 7.57.

9,10-Di(isobutyryl)-9,10-dihydroanthracene (3d).

Mp 131–133 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.69 (d, *J* = 6.8 Hz, 12 H), 2.39 (sept, *J* = 6.8 Hz, 2 H), 5.23 (s, 2 H), 7.26–7.36 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.70, 37.22, 58.36, 127.88, 129.17, 130.86, 212.44 ppm. IR (KBr): 3060, 3020, 2970, 2930, 2870, 1710, 1490 cm^{-1}. MS (EI): *m/z* = 320 [M$^+$]. Anal. Calcd for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55. Found: C, 82.39; H, 7.53.

Diethyl 2,3,5,6-Dibenzocyclohexane-1,4-bis(1′,1″-dioxa)dibutanoate (3e).

Mp 110–111 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (t, *J* = 7.2 Hz, 6 H), 2.32–2.39 (m, 8 H), 4.04 (q, *J* = 7.2 Hz, 4 H), 5.20 (s, 2 H), 7.29–7.37 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.14, 28.10, 32.74, 57.74, 60.50, 128.30, 128.70, 130.95, 172.16, 206.59 ppm. IR (KBr): 2980, 2920, 1730, 1710, 1490 cm^{-1}. LCMS (APCI): *m/z* = 437 [M + H]. Anal. Calcd for $C_{26}H_{28}O_6$: C, 71.54; H, 6.47. Found: C, 71.33; H, 6.44.

9,10-Di(4-chlorobutyryl)-9,10-dihydroanthracene (3f).

Mp 116 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.80 (quin, *J* = 6.8 Hz, 4 H), 2.13 (t, *J* = 6.8 Hz, 4 H), 3.28 (t, *J* = 6.8 Hz, 4 H), 5.18 (s, 2 H), 7.28–7.38 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.77, 34.60, 43.91, 58.27, 128.39, 128.70, 130.74, 207.02 ppm. IR (KBr): 3070, 3020, 2960, 2950, 2930, 2900, 1700, 1490 cm^{-1}. LCMS (APCI): *m/z* = 390 [M + H]. Anal. Calcd for $C_{22}H_{22}Cl_2O_2$: C, 67.87; H, 5.70. Found: C, 67.78, H, 5.71.

7,8,9,10-Dibenzobicyclo[4.2.2]deca-2,5-dione (5a).

Mp 145–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.22 (s, 4 H), 5.14 (s, 2 H), 7.33–7.45 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.64, 62.82, 128.16, 128.54, 132.72, 206.48 ppm. IR (KBr): 3060, 3030, 3020, 2950, 2910, 1690, 1470 cm^{-1}. MS (EI): *m/z* = 262 [M$^+$]. Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.03; H, 5.65.

8,9,10,11-Dibenzobicyclo[5.2.2]4-oxaundeca-2,5-dione (5b).

Mp 175–176 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.93 (s, 4 H), 5.19 (s, 2 H), 7.34–7.43 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 60.48, 79.70, 128.32, 128.42, 131.29, 204.78 ppm. IR (KBr): 3060, 3050, 2950, 2920, 1710, 1480

cm^{-1}. MS (EI): *m/z* = 278 [M$^+$]. Anal. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.95; H, 5.20.

Benzyl 2-(1-Oxopropyl)-4-oxohexanoate (7a).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02 (t, *J* = 7.3 Hz, 3 H), 1.03 (t, *J* = 7.3 Hz, 3 H), 2.46 (q, *J* = 7.3 Hz, 2 H), 2.59–2.74 (m, 2 H), 2.93 (dd, *J* = 5.6, 18.3 Hz, 1 H), 3.15 (dd, *J* = 8.4, 18.3 Hz, 1 H), 4.07 (dd, *J* = 5.6, 8.4 Hz, 1 H), 5.12 (d, *J* = 12.5 Hz, 1 H), 5.16 (d, *J* = 12.5 Hz, 1 H), 7.30–7.38 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.56, 7.63, 35.63, 36.24, 40.38, 52.73, 67.25, 128.04, 128.34, 128.48, 134.98, 168.65, 204.73, 208, 25 ppm. IR (neat): 3034, 2979, 2940, 2882, 1743, 1715, 1655, 1608, 1498, 1457, 1377 cm^{-1}. MS (EI): *m/z* = 276 [M$^+$]. Anal. Calcd for $C_{28}H_{28}N_8O_{10}$ [di-(2,4-dinitrophenylhydrazone)]: C, 52.83; H, 4.43; N, 17.60. Found: C, 52.78; H, 4.69; N, 17.31.

Benzyl 2-(1-Oxobutyl)-4-oxoheptanoate (7b).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 7.4 Hz, 3 H), 0.89 (t, *J* = 7.4 Hz, 3 H), 1.57 (sext, *J* = 7.4 Hz, 4 H), 2.41 (t, *J* = 7.4 Hz, 2 H), 2.54–2.67 (m, 2 H), 2.91 (dd, *J* = 5.8, 18.3 Hz, 1 H), 3.12 (dd, *J* = 8.3, 18.3 Hz, 1 H), 4.06 (dd, *J* = 5.8, 8.3 Hz, 1 H), 5.12 (d, *J* = 12.2 Hz, 1 H), 5.16 (d, *J* = 12.2 Hz, 1 H), 7.30–7.37 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.42, 13.61, 16.80, 17.18, 40.65, 44.38, 44.68, 53.03, 67.23, 128.14, 128.34, 128.46, 135.01, 168.63, 203.97, 207.76 ppm. IR (neat): 3036, 2966, 2936, 2877, 1742, 1713, 1648, 1609, 1498, 1456, 1407, 1377cm^{-1}. MS (EI): *m/z* = 304 [M$^+$]. Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95. Found: C, 71.15; H, 8.11.

Benzyl 2-(2-Methyl-1-oxopropyl)-5-methyl-4-oxohexanoate (7c).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (d, *J* = 6.8 Hz, 3 H), 1.09 (d, *J* = 7.1 Hz, 3 H), 1.10 (d, *J* = 7.1 Hz, 3 H), 1.13 (d, *J* = 7.1 Hz, 3 H), 2.63 (sept, *J* = 6.8 Hz, 1 H), 2.83–2.98 (m, 2 H), 3.15 (dd, *J* = 8.2, 18.3 Hz, 1 H), 4.24 (dd, *J* = 5.6, 8.2 Hz, 1 H), 5.12 (d, *J* = 12.2 Hz, 1 H), 5.16 (d, *J* = 12.2 Hz, 1 H), 7.26–7.38 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.76, 18.12, 18.17, 18.66, 38.62, 40.68, 40.79, 51.39, 67.29, 128.17, 128.35, 128.48, 135.03, 168.89, 207.90, 211.25 ppm. IR (neat): 3035, 2972, 2935, 2875, 1743, 1713, 1648, 1609, 1498, 1456, 1384 cm^{-1}. MS (EI): *m/z* = 304 [M$^+$]. Anal. Calcd for $C_{30}H_{32}N_8O_{10}$ [di(2,4-dinitrophenylhydrazone)]: C, 54.21; H, 4.85; N,16.86. Found: C, 53.94; H, 5.05; N, 16.68.

Benzyl 2-(3-Methyl-1-oxobutyl)-6-methyl-4-oxoheptanoate (7d).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.81 (d, *J* = 6.6 Hz, 3 H), 0.87 (d, *J* = 6.6 Hz, 3 H), 0.89 (d, *J* = 6.6 Hz, 3 H), 0.91 (d, *J* = 6.6 Hz, 3 H), 2.07–2.17 (m, 2 H), 2.31 (d, *J* = 7.1 Hz, 2 H), 2.48 (d, *J* = 6.8 Hz, 2 H), 2.88 (dd, *J* = 5.8, 18.4 Hz, 1 H), 3.10 (dd, *J* = 8.3, 18.4 Hz, 1 H), 4.03 (dd, *J* = 5.8, 8.3 Hz, 1 H), 5.12 (d, *J* = 12.1 Hz, 1 H), 5.17 (d, *J* = 12.1 Hz, 1 H), 7.26–7.38 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.18, 22.46, 22.50, 22.52, 23.92, 24.72, 41.16, 51.45, 51.61, 53.35, 67.29, 128.29, 128.41, 128.50, 134.99, 168.62, 203.49, 207.56 ppm. IR (neat): 3034, 2959, 2935, 2872, 1743, 1715, 1649, 1610, 1499, 1457, 1368 cm^{-1}. MS (EI): *m/z* = 332 [M$^+$]. Anal. Calcd for $C_{32}H_{36}N_8O_{10}$ [di(2,4-dinitrophenylhydrazone)]: C, 55.49; H, 5.24; N,16.18. Found: C, 55.51; H, 5.14; N, 16.18.

Benzyl 4-Oxohexanoate (8a).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (t, *J* = 7.3 Hz, 3 H), 2.47 (q, *J* = 7.3 Hz, 2 H), 2.65 (t, *J* = 6.2 Hz, 2 H), 2.73 (t, *J* = 6.2 Hz, 2 H), 5.14 (s, 2 H), 7.34–7.35 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.70, 27.97, 35.85, 36.52, 66.42, 128.14, 128.18, 128.50, 135.80, 172.65, 209.33 ppm. IR (neat): 3034, 2977, 2939, 2882, 1735, 1719, 1648, 1608, 1498, 1379 cm^{-1}. MS (EI): *m/z* = 220 [M$^+$]. Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.63; H, 7.09.

Benzyl 4-Oxoheptanoate (8b).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.4 Hz, 3 H), 1.61 (sext, *J* = 7.4 Hz, 2 H), 2.42 (t, *J* = 7.4 Hz, 2 H), 2.64 (t, *J* = 6.3 Hz, 2 H), 2.72 (t, *J* = 6.3 Hz, 2 H), 5.14 (s, 2 H), 7.30–7.38 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.63, 17.19, 27.90, 36.93, 44.61, 66.39, 128.12, 128.16, 128.48, 135.80, 172.60, 208.86 ppm. IR (neat): 3034, 2962, 2939, 1735, 1715, 1648, 1608, 1498 1456, 1383 cm^{-1}. MS (EI): *m/z* = 234 [M$^+$]. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 72.01, H, 8.01.

Benzyl 5-Methyl-4-oxohexanoate (8c).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11 (d, *J* = 6.8 Hz, 6 H), 2.59–2.65 (m, 3 H), 2.78 (t, *J* = 6.5 Hz, 2 H), 5.11 (s, 2 H), 7.31–7.36 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.15, 27.94, 34.65, 40.72, 66.36, 128.13 (× 2), 128.47, 135.82, 172.65, 212.52 ppm. IR (neat): 3034, 2971, 2934, 2876, 1735, 1712, 1608, 1498, 1456, 1384 cm^{-1}. MS (EI): *m/z* = 234 [M$^+$]. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.84, H, 7.95.

Benzyl 6-Methyl-4oxoheptanoate (8d).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (d, *J* = 6.7 Hz, 6 H), 2.10–2.20 (m, 1 H), 2.32 (d, *J* = 6.7 Hz, 2 H), 2.63 (t, *J* = 6.2 Hz, 2 H), 2.71 (t, *J* = 6.2 Hz, 2 H), 5.11 (s, 2 H), 7.33–7.35 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.50, 24.62, 27.87, 37.51, 51.69, 66.39, 128.14, 128.17, 128.50, 135.82, 172.61, 208.57 ppm. IR (neat): 3034, 2972, 2957, 2935, 2872, 1735, 1718, 1606, 1497, 1466, 1385 cm^{-1}. MS (EI): *m/z* = 248 [M$^+$]. Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.56; H, 8.29.

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(10) Mg–anthracene·3THF complex can be available from Sigma-Aldrich Co. Ltd.

(11) Treatment of anthracene(**1**) with isobutyryl chloride and succinyl dichloride in the presence of 5 equiv of THF (based on **1**) in DMF under the similar conditions as mentioned above, gave the corresponding adducts **2d** and **5a** in 56–59% and 61–63% yields, respectively.

(12) **Typical Procedure for Electroreductive Double C-Acylation of Anthracene Derivatives.**
Into a 100-mL beaker-type undivided cell equipped with platinum plates [20 × 30 × 0.5 mm, Nacalai Tesque (Kyoto, Japan), 99%] as the cathode and a carbon bar as the anode were introduced 60 mL of anhyd DMF as a solvent, *n*-Et_4NOTs (15 mmol) as a supporting electrolyte, acid dichloride (25 mmol) and anthracene (5 mmol). The electrolysis was carried out under constant current conditions (current density: 7 mA/cm^2) at –5 °C to 5 °C with magnetic stirring until 8 F/mol of electricity was passed. After the reaction, the reaction mixture was poured into sat. $NaHCO_3$ solution when acid dichloride was used as the acylating agent. Organic materials were extracted with three 100 mL portions of Et_2O. The combined ethereal solution was washed with sat. NaCl solution and dried over anhyd $MgSO_4$. After removal of $MgSO_4$ by filtration and evaporation of the solvent, the isolation by column chromatography gave diacylated compounds in low yields (4%).