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Rh(I)-catalyzed CO gas-free carbonylative cyclization of organic halides with tethered nucleophiles using aldehydes as a substitute for carbon monoxide

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Abstract

The CO gas-free carbonylative cyclization of organic halides, with tethered nitrogen, oxygen, and carbon nucleophiles, with aldehydes as a substitute for carbon monoxide can be achieved in the presence of a catalytic amount of a rhodium complex. The reaction involves the decarbonylation of the aldehyde by the rhodium catalyst, and the successive carbonylation of an organic halide utilizing the rhodium carbonyl that is formed in situ. Aldehydes having electron-withdrawing groups showed a higher ability to donate the carbonyl moiety.

Keywords: CO gas-free carbonylation; Aldehyde; Carbonylative cyclization; Rhodium catalyst

1. Introduction

Transition metal-catalyzed carbonylative coupling reactions of organic halides and pseudohalides with various nucleophiles is a powerful tool for the synthesis of a wide variety of carboxylic acids and their derivatives (Scheme 1a) [1]. Intramolecular variants, in which the substrates contain both an organic halide unit and a nucleophilic counterpart, also have been in widespread use for a long time (Scheme 1b) [2–4], due to their versatility for use in the synthesis of cyclic carbonyl compounds [5]. Recent notable progress in these synthetic methods represents the successful elimination of the need for the direct use of carbon monoxide, achieved by utilizing various organic and inorganic carbonyls as a substitute for carbon monoxide [6,7]. Thus, carbonylation has become more useful due to its experimental simplicity and ease of use.

During the course of our attempts to develop a strategy for catalytic CO gas-free carbonylations using aldehydes as a substitute for carbon monoxide [8], we also reported, in a preliminary communication, that this method is applicable to the intramolecular aminocarbonylation of aryl halides in which nitrogen-containing nucleophiles are tethered [8b]. The methodology involves synergism achieved by using two catalytic processes, i.e., the decarbonylation of aldehydes by a transition-metal catalyst and the successive carbonylation of organic substrates by carbonyl transfer from the metal carbonyl that is formed. Here the carbonylative cyclization reaction of organic halides using aldehydes as a substitute for carbon monoxide has been examined further with particular emphasis on versatility of nucleophile counterparts tethered to the organic halides.

2. Results and discussion

2.1. Carbonylative cyclization of organic halides tethering heteroatom-nucleophiles with aldehydes [9]

The reaction of *N*-Ts-2-bromobenzylamine (**1a**) (0.25 mmol) with pentafluorobenzaldehyde (0.50 mmol) and K_2CO_3 (0.50 mmol) in xylene (2 mL) at 130 °C in the presence of $[RhCl(cod)]_2$ (0.00625 mmol) and dppp [10]

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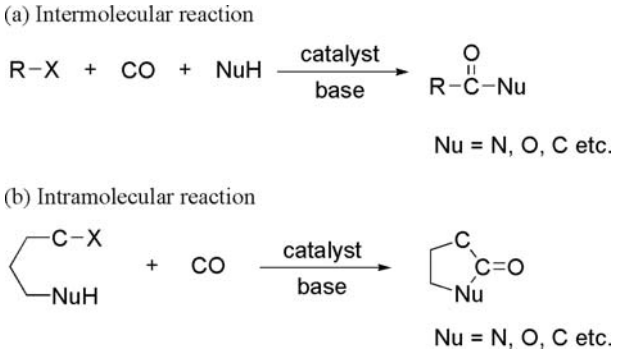
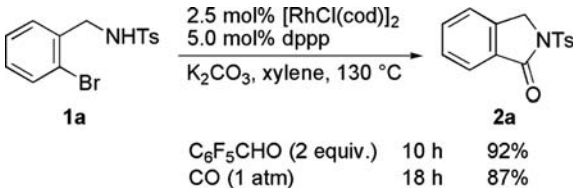


Scheme 1. Carbonylative coupling of organic halides with nucleophiles.

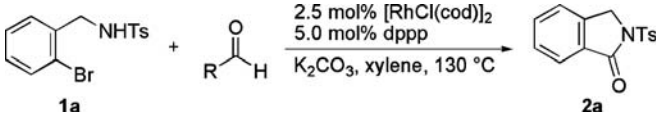
(0.0125 mmol) afforded the benzolactam **2a** in 92% yield (Eq. (1)). When the reaction of **1a** was carried out under the same conditions using 1 atm of carbon monoxide instead of C_6F_5CHO, **2a** was obtained in 87% yield, although a longer reaction time (18 h) was required for the complete consumption of **1a**. These results show that the presence of excess carbon monoxide appears to inhibit the catalysis.



(1)

The ability to donate a carbonyl was investigated using other aldehydes (Table 1). Among them, the reaction of *trans*-cinnamaldehyde (5 equiv) and paraformaldehyde (10 equiv) resulted in the formation of **2a** in 93% and 69% yields, respectively (entries 1 and 2), while *p*-trifluoromethylbenzaldehyde (2 equiv) and 2-naphthaldehyde (5 equiv) afforded a lower yield of **2a** (entries 3 and 4). In the case of benzaldehyde, *p*-anisaldehyde, and decanal, **2a** was produced in only trace amounts (entries 5–7).

Table 1
Rh(I)-catalyzed carbonylative cyclization of bromobenzene **1a**[a]



Entry	R	Time (h)	Yield[b] (%)
1	(*E*)-PhCH=CH_2 (5 equiv)	4	93
2	H (10 equiv)[c]	8	69
3	*p*-$CF_3C_6H_4$ (2 equiv)	9	14
4	2-Naphthyl (5 equiv)	24	14
5	Ph (2 equiv)	17	Trace
6	*p*-$MeOC_6H_4$ (2 equiv)	10	Trace
7	$CH_3(CH_2)_8$ (2 equiv)	9	Trace

[a] Conditions: **1a** (0.25 mmol), aldehyde, $[RhCl(cod)]_2$ (0.00625 mmol), dppp (0.0125 mmol, K_2CO_3 (0.5 mmol, and xylene (2 mL) at 130 °C under N_2 flow.
[b] Isolated yields.
[c] Paraformaldehyde was used.

Some other rhodium complexes, such as RhCl(CO)-$(PPh_3)_2$ (86%), $[RhCl(cod)]_2$/dppe [10] (51%), and $[RhCl(cod)]_2$/dppb [10] (32%), also showed catalytic activity. A high temperature is not essential for the reaction to proceed; **2a** was obtained in 59% yield at 110 °C in a 19 h reaction.

The results of carbonylative cyclization reactions of various bromobenzenes are summarized in Table 2. When the substituent on the nitrogen atom was changed to Boc [10], the corresponding benzolactam **2b** was obtained in 53% yield along with 15% of the unreacted substrate (entry 1), while no lactams were obtained from the reaction of substrates having other substituents, such as H, Ac, Bn, and *p*-$MeOC_6H_4$. Replacing the Br atom in **1a** with a Cl also resulted in the formation of **2a** in high yields both with pentafluorobenzaldehyde and *trans*-cinnamaldehyde as the source of the carbonyl (entries 2 and 3). The carbonylation reaction described here can also be applied to the syntheses of six- and seven-membered benzolactams. Under similar conditions, the reactions of *N*-Ts-2-(2-bromophenyl)ethylamine (**3**) with pentafluorobenzaldehyde and *trans*-cinnamaldehyde gave the six-membered benzolactam **4** in 84% and 93% yields, respectively (entries 4 and 5). In the case of *N*-Ts-3-(2-bromophenyl)propylamine (**5**), pentafluorobenzaldehyde served as a more efficient source of carbonyl than *trans*-cinnamaldehyde, in contrast to the above reactions; the reaction of **5** with pentafluorobenzaldehyde for 48 h afforded 66% of the seven-membered benzolactam **6** along with 16% of recovered **5**, while, with cinnamaldehyde, 17% of **6** was obtained and 77% of **5** was recovered (entries 6 and 7). For the bromobenzene **7**, in which a β-aminoalcohol connects the nucleophilic portion with an aryl bromide, the corresponding benzolactam **8** was produced (entries 8 and 9). Interestingly, the reactions of alkyl halides with a tethered nitrogen nucleophile **9a** and **9b** reacted, leading to the formation of γ-butyrolactam **10** (entries 10 and 11) [11].

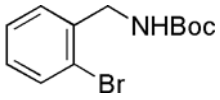
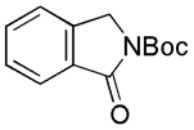
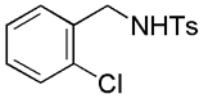
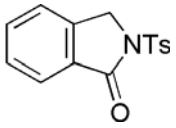
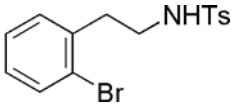
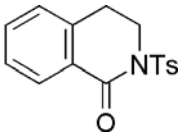
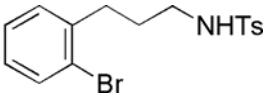
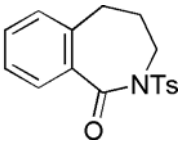
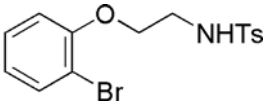
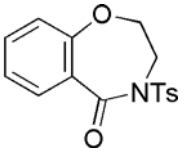
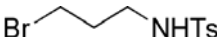
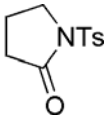
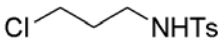
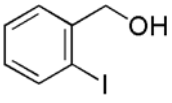
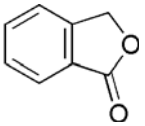
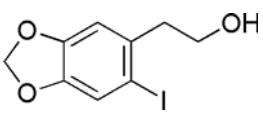
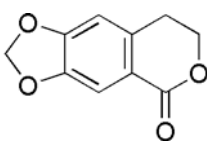
Moreover, the exchange of the nucleophilic moiety from NHTs to OH led to the formation of the corresponding lactones. *o*-Iodobenzyl alcohol (**11**) was converted to phthalide (**12**) in good yields under similar conditions (entry 12). This same reaction sequences also afford six- and seven-membered benzolactones **14** and **15** in 51% and 57% yields, respectively (entries 13 and 14).

2.2. Carbonylative cyclization of organic halides with tethered carbon-nucleophiles with aldehydes

The present protocol was applicable to the carbonylative cyclization of aryl halides with tethered carbon nucleophiles such as active methyne carbons, as well as heteroatoms.

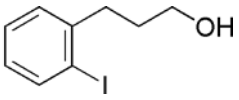
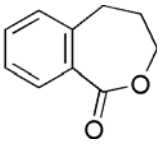
Using the identical catalyst systems, the treatment of *o*-iodobenzylmalonate **17** with pentafluorobenzaldehyde in the presence of 0.55 equiv of K_2CO_3 gave 1-indanone **18** in 75% yield (Table 2, entry 1). This represents the first demonstration of the use of the CO gas-free method in

Table 2
Rh(I)-catalyzed carbonylative cyclization of organic halides with tethered nitrogen- and oxygen-nucleophiles[a]

Entry	Substrate	Aldehyde[b]	Time (h)	Yield[c] (%)	Product
1	**1b** 	A	48	53(15)	**2b** 
2	**1c** 	A	24	82	**2a** 
3		B	8	91	
4	**3** 	A	25	84	**4** 
5		B	20	93	
6	**5** 	A	48	66(16)	**6** 
7		B	48	17(77)	
8	**7** 	A	48	33	**8** 
9		B	48	38	
10[d]	**9a** 	A	18	85	**10** 
11[e]	**9b** 	A	24	69	
12[f]	**11** 	A	24	65	**12** 
13[f]	**13** 	A	24	51	**14** 

(*continued on next page*)

Table 2 (*continued*)

Entry	Substrate	Aldehyde[b]	Time (h)	Yield[c] (%)	Product
14[f]	**15** 	A	24	57	**16** 

[a] Conditions: organic halide (0.25 mmol), aldehyde (1.25 mmol), [RhC1(cod)]$_2$ (0.00625 mmol), dppp (0.0125 mmol) K_2CO_3 (0.5 mmol) and xylene (2 mL) at 130 °C under N_2 flow.
[b] Aldehyde A: C_6F_5CHO; B,(*E*)-PhCH=CH_2CHO.
[c] Isolated yields. Values in parentheses represent the yields of the recovered substrate.
[d] Dppb (10 mol%) was used as a ligand.
[e] BINAP (20 mol%) was used as a ligand.
[f] 0.275 mmol of K_2CO_3 was used.

the carbonylative cyclization of organic halides with tethered carbon-nucleophiles.

The ability of aldehydes to donate their carbonyl was also investigated. All of the aldehydes examined, regardless of whether they were aromatic or aliphatic aldehydes, served as a carbonyl source. For aromatic aldehydes, the electronic property of the attached substituents was responsible for the catalysis. Aldehydes with electron-withdrawing groups (entries 1 and 2) donated a carbonyl moiety more efficiently than those with electron-donating group (entry 5). An α,β-unsaturated aldehyde, such as *trans*-cinnamaldehyde, was also reactive (entry 6). The reaction was tolerant to the use of aliphatic aldehydes (entries 7 and 8) and paraformaldehyde, an equivalent to formaldehyde (entry 9).

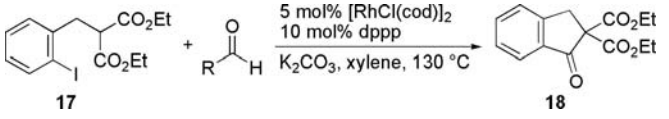
When the reaction of **17** was carried out under the same conditions using 1 atm of carbon monoxide instead of C_6F_5CHO, it was complete in a shorter time, although the yield was lower (56%).

With C_6F_5CHO, (*E*)-PhCH=CH_2CHO, and *p*-$CF_3C_6H_4CHO$, which led to smooth transformation (Table 3), the reaction of various substrates with a tethered carbon-nucleophile were examined and the results are summarized in Table 4. Although some optimization of the reaction conditions was required, the carbonylation system readily led to the synthesis of cyclic ketones. The introduction of two methoxy group on the aromatic ring had no effect on the reaction, resulting in the formation of 1-indanone **20** (entries 1–3). Cyanoacetic acid ester **21** was tolerated, leading to the corresponding 1-indanone **22** (entries 4–6). For substrate **23**, which contains a phenylsulfonylacetate unit, the ester group was lost during the carbonylation reaction prior to workup (entries 7–9). Unfortunately, no carbonylated product was obtained for the reaction of *o*-iodobenzylacetoacetate **25** (entries 10–12). The reaction was tolerant with respect to the synthesis of six- and seven-membered ketones, **28** and **30** (entries 13–18). In addition to iodobenzenes, the reaction of an alkenyl iodide **31** containing a malonate unit proceeded to give 2-cyclopentenone **32** although in low yields (entries 19–21). The efficiency of the reaction of each substrate was not dependent on the aldehyde used, C_6F_5CHO, (*E*)-PhCH=CH_2CHO, and *p*-$CF_3C_6H_4CHO$.

2.3. Ability of aldehydes to donate the carbonyl

A possible mechanism for the present carbonylative cyclization catalysis is outlined in Scheme 2. This mechanism involves (a) the formation of the rhodium carbonyl **C** via the oxidative addition of the aldehyde to the rhodium metal (**A**), followed by the migration of R from the carbonyl to the rhodium metal center (**B**), and the reductive elimination of R–H, (b) the oxidative addition of the aryl halide to rhodium(I) to give arylrhodium(III) halide **D**, (c) the transfer of the carbonyl ligand from the rhodium carbonyl **C** to the arylrhodium **D** (formation of the new rhodium carbonyl species **E**), (d) the insertion of the received CO into the rhodium–carbon bond of **E** to give

Table 3
Rh(I)-catalyzed carbonylative cyclization of iodobenzene **17**[a]

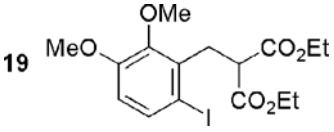
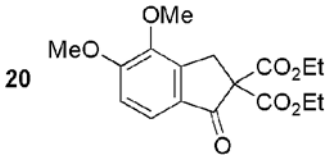
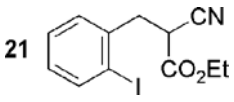
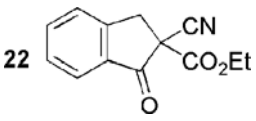
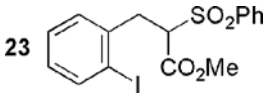
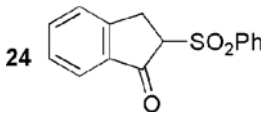
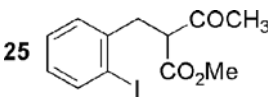
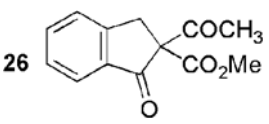
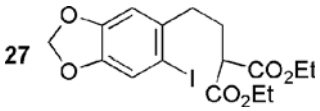
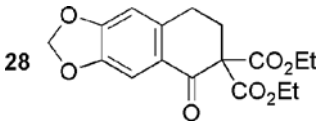
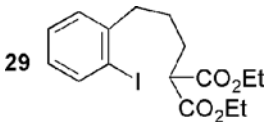
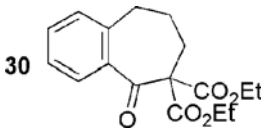
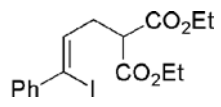
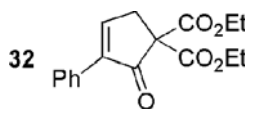


17 **18**

Entry	R	Time	Yield[b]
1	C_6F_5	36	75
2	*p*-$CF_3C_6H_4$	36	73
3	Ph	42	50(35)
4	2-Naphthyl	36	33
5	*p*-$MeOC_6H_4$	24	40
6	(*E*)-PhCH=CH_2	20	82
7	$PhCH_2CH_2$	20	53
8	$CH_3(CH_2)_8$	20	37
9	H[c]	42	37(21)

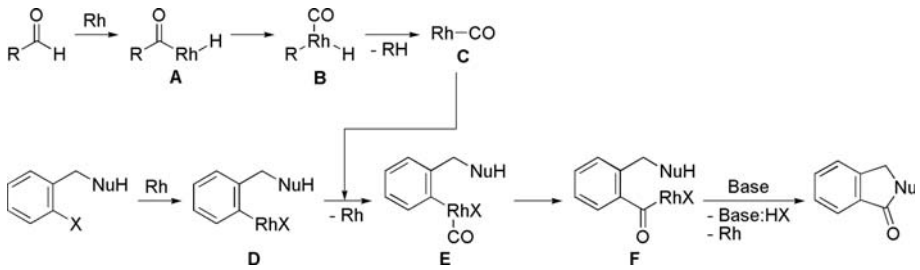
[a] Conditions: **17** (0.25 mmol), aldehyde (1.25 mmol), [RhC1(cod)]$_2$ (0.0125 mmol), dppp (0.025 mmol), K_2CO_3 (0.138 mmol), and xylene (2 mL) at 130 °C under N_2 flow.
[b] Isolated yields. Values in parentheses represent the yields of recovered **17**.
[c] 10 equiv of paraformaldehyde was used.

Table 4
Rh(I)-catalyzed carbonylative cyclization of organic iodides tethering carbon-nucleophiles[a]

Entry	Substrate	Aldehyde[b]	Time	Yield[c]	Product
1		A	36	71	
2		B	24	82	
3		C	24	68	
4[d]		A	24	51	
5[d]		B	24	58	
6[d]		C	24	48	
7		A	48	22	
8		B	48	25	
9		C	48	18	
10[d]		A	48	0	
11[d]		B	48	0	
12[d]		C	48	0	
13		A	36	70	
14		B	24	75	
15		C	24	67	
16[d]		A	48	50	
17[d]		B	48	57	
18[d]		C	48	55	
19		A	24	12	
20		B	24	28	
21		C	24	17	

[a] Conditions: organic iodide (0.25 mmol), aldehyde (1.25 mmol), $[RhCl(cod)]_2$ (0.0125 mmol), dppp (0.025 mmol), K_2CO_3 (0.138 mmol), and xylene (2 mL) at 130 °C under N_2 flow.
[b] Aldehyde A: C_6F_5CHO; B, (*E*)-PhCH=CH_2CHO; C, *p*-$CF_3C_6H_4CHO$.
[c] Isolated yields.
[d] The reactions were carried out at 145 °C.

acylrhodium(III) complex **F**, and (e) the reductive cleavage of the acyl–rhodium bond to produce the carbonylated product and regeneration the rhodium(I) complex. Consistent with the tendency observed in the CO gas-free Pauson–Khand-type reaction of enynes with aldehydes [8a], the use of aldehydes having electron-withdrawing groups, such as



Scheme 2. A possible reaction pathway for CO gas-free carbonylative cyclization of organic halides with aldehydes.

C_6F_5CHO, (*E*)-PhCH=CH_2CHO, and *p*-$CF_3C_6H_4CHO$, led to the efficient formation of the carbonylated products. Considering that the smooth decarbonylation is essential for effective catalysis, the results can be rationalized as follows: in reactions using C_6F_5CHO, (*E*)-PhCH=CH_2CHO, and *p*-$CF_3C_6H_4CHO$, migration of the R from the carbonyl to the Rh center (**A** → **B**) would readily occur due to thermodynamic stability of **B**, which stems from the strength of Rh–carbon bond ($R = C_6F_5$, (*E*)-Ph–CH=CH, and *p*-$CF_3C_6H_4$) [12,13]. Consequently, optimal carbonylation catalysis would result.

3. Conclusion

The catalytic CO gas-free carbonylative cyclization of organic halides with a tethered nucleophile with aldehydes as a substitute for carbon monoxide, is described. The carbonylation reaction consists of the decarbonylation of the aldehyde by the rhodium complex and the successive carbonylation of the organic halide utilizing the rhodium carbonyl that is formed in situ. The system tolerates not only heteroatoms, such as nitrogen and oxygen, but active methyne carbons as a nucleophilic counterpart. The reaction proceeds smoothly when electron-poor aldehydes are used, which leads to the efficient decarbonylation that is essential for the overall carbonylation catalysis. This carbonylation system, which uses a combination of the rhodium catalyst and aldehydes, has a wider scope of applications than other CO gas-free carbonylations reported to date.

4. Experimental

4.1. General information

^1H NMR and ^{13}C NMR were recorded on a JEOL JNM-ECP500 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (Hz), integration, and interpretation. Infrared spectra (IR) were obtained on a JASCO FT/IR-420 spectrometer; absorption peaks are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained on a SHIMADZU GCMS-QP 5000 instrument with ionization voltages of 70 eV. High resolution mass spectra (HRMS) were obtained on a JEOL JMS-700. Analytical GC was carried out on a HITACHI G-3900 gas chromatography, equipped with a flame ionization detector. Column chromatography was performed on SiO_2 (MERCK Silica gel 60). Xylene was distilled from $LiAlH_4$ and stored over molecular sieves 4 Å. $[RhCl(cod)]_2$ was prepared using the method reported [14].

4.2. Typical procedure

In a 5 mL two-necked flask equipped reflux condenser were placed $[RhCl(cod)]_2$, dppp and xylene (0.5 mL), and the mixture was stirred at room temperature for 15 min to turn out to a light yellow suspension. After an aldehyde, a substrate and xylene (1.5 mL) were added, the mixture was degassed, charged with N_2, and stirred at 130 °C under N_2 flow until the substrate was consumed. The reaction was pursued by monitoring with GC or TLC. After the reaction mixture was filtrated and the filtrate was concentrated in vacuo, the residue was purified by column chromatography on silica gel.

4.3. Characterization data of the carbonylated products

4.3.1. 2,3-Dihydro-2-[(4-methylphenyl)sulfonyl]-1H-isoindol-1-one (2)

White solid; mp 216–218 °C; R_f 0.29 (hexane/AcOEt = 2/1); ^1H NMR ($CDCl_3$) δ 2.42 (s, 3H), 4.91 (s, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.47 (t, $J = 8.0$ Hz, 1H), 7.49 (d, $J = 8.0$ Hz, 1H), 7.64 (t, $J = 8.0$ Hz, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 8.03 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.62, 49.80, 123.30, 124.98, 128.09, 128.77, 129.71, 130.16, 133.82, 135.35, 140.97, 145.19, 166.06; IR (KBr) 2932 w, 1924 w, 1783 w, 1724 s, 1655 w, 1594 m, 1543 w, 1509 w, 1491 w, 1469 m, 1450 s, 1398 w, 1363 s, 1341 m, 1311 m, 1289 s, 1220 m, 1174 s, 1130 s, 1119 m, 1089 s, 1019 m, 891 m, 817 m, 751 m, 730 s, 702 m, 681 s, 664 s; MS, *m/z* (relative intensity, %); 224 (17), 223 ($M^+ - SO_2$, 100), 222 (79), 195 (21), 194 (20), 132 (22), 111 (10), 104 (10), 92 (13), 91 (54), 89 (15), 77 (37), 76 (14), 65 (45), 63 (13), 51 (24), 50 (13). Exact mass-FAB calcd for $C_{15}H_{14}NO_3S$ ($M^+ + H$) 288.0694; found 288.0693.

*4.3.2. 2,3-Dihydro-1-oxo-1H-isoindolecarboxylic acid 1,1-dimethyl ester (**2b**)*

White solid; mp 119–120 °C; R_f 0.17 (hexane/AcOEt = 4/1); ^{1}H NMR ($CDCl_3$) δ 1.61 (s, 9H), 4.77 (s, 2H), 7.47–7.49 (m, 2H), 7.64 (dt, $J = 8.0$ Hz, $J = 1.0$ Hz 1H), 7.91 (d, $J = 7.5$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 28.12, 49.11, 83.12, 123.01, 124.99, 128.48, 131.46, 133.49, 140.64, 150.42, 166.62; IR (KBr) 2983 m, 2939 m, 2928 m, 2877 w, 2855 w, 2363 w, 2010 w, 1966 w, 1890 w, 1781 s, 1715 m, 1701 m, 1612 w, 1598 w, 1524 w, 1508 w, 1471 m, 1455 s, 1391 m, 1362 s, 1331 s, 1230 s, 1275 s, 1254 s, 1221 m, 1170 s, 1150 s, 1103 m, 1087 m, 1032 w, 1012 w, 947 s, 917 w, 880 w, 854 m, 843 m, 806 w, 768 s, 746 s, 680 w; MS, *m*/*z* (relative intensity, %); 134 (11), 133 (100), 132 (39), 105 (42), 104 (65), 78 (15), 77 (43), 76 (14), 56 (19), 52 (10), 51 (26), 50 (21). Exact mass-FAB calcd for $C_{13}H_{15}NO_3Na$ ($M^+ + Na$) 256.0950; found 256.0943.

*4.3.3. 3,4-Dihydro-2-[(4-methylphenyl)sulfonyl]-1(2H)-isoquinolinone (**4**)*

White solid; mp 132–133 °C; R_f 0.24 (hexane/AcOEt = 2/1); ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 3H), 3.13 (t, $J = 6.0$ Hz, 2H), 4.23 (t, $J = 6.0$ Hz, 2H), 7.22 (d, $J = 8.0$ Hz, 1H), 7.31 (t, $J = 8.0$ Hz, 1H), 7.33 (d, $J = 8.0$ Hz, 2H), 7.47 (t, $J = 8.0$ Hz, 1H), 7.98 (d, $J = 8.5$ Hz, 2H), 7.99 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.61, 28.89, 44.68, 127.33, 127.39, 128.14, 128.52, 129.12, 129.38, 133.45, 136.10, 139.21, 144.70, 163.39; IR (KBr) 2945 m, 2921 m, 1924 w, 1686 s, 1599 s, 1493 m, 1471 s, 1458 s, 1426 s, 1386 s, 1352 s, 1308 s, 1244 s, 1210 m, 1189 s, 1164 s, 1115 s, 1089 s, 1065 s, 1035 s, 979 s, 923 m, 834 s, 814 s, 769 s, 743 s, 704 s, 684 s, 658 s, 632 s; MS, *m*/*z* (relative intensity, %); 238 (11), 237 (65), 236 (46), 237 ($M^+ - SO_2$, 65),119 (10), 118 (100), 91 (38), 90 (39), 89 (22), 77 (10), 65 (28). Exact mass-FAB calcd for $C_{16}H_{16}NO_3S$ ($M^+ + H$) 302.0851; found 302.0850.

*4.3.4. 2,3,4,5-Tetrahydro-2-[(4-methylphenyl)sulfonyl]-1H-2-benzazepin-1-one (**6**)*

White solid; mp 117–118 °C; R_f 0.28 (hexane/ether = 1/1); ^{1}H NMR ($CDCl_3$) δ 2.17 (quint, $J = 6.5$ Hz, 2H), 2.43 (s, 3H), 2.84 (t, $J = 6.5$ Hz, 2H), 3.82 (t, $J = 6.5$ Hz, 2H), 7.15 (d, $J = 7.5$ Hz, 1H), 7.28 (t, $J = 7.5$ Hz, 1H), 7.42 (t, $J = 7.5$ Hz, 1H), 7.60 (t, $J = 7.5$ Hz, 1H), 8.01 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.55, 29.19, 29.61, 44.77, 127.11, 128.64, 128.82, 129.32, 129.38, 132.57, 133.88, 136.04, 137.93, 144.67, 170.12; IR (KBr) 2950 m, 2928 w, 1692 s, 1599 m, 1495 w, 1451 m, 1355 s, 1329 m, 1310 s, 1259 s, 1223 w, 1189 m, 1168 s, 1108 m, 1085 s, 1056 m, 1036 m, 1002 s, 879 w, 848 w, 805 m, 788 m, 764 m, 742 s, 705 s, 688 s, 656 m; MS, *m*/*z* (relative intensity, %); 316 ($M^+ + H$, 0.14), 252 (10), 251 (52), 145 (11), 144 (100), 120 (15), 117 (24), 116 (34), 104 (14), 103 (12), 91 (38), 89 (10), 78 (13), 77 (19), 65 (25), 51 (10). Exact mass-FAB calcd for $C_{17}H_{18}NO_3S$ ($M^+ + H$) 316.1007; found 316.1000.

*4.3.5. 3,4-Dihydro-2-[(4-methylphenyl)sulfonyl]-1,4-benzoxazepin-5(2H)-one (**8**)*

Colorless oil; R_f 0.29 (hexane/AcOEt=3/1); ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3H), 4.15 (t, $J = 5.5$ Hz, 2H), 4.46 (t, $J = 5.5$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 1H), 7.16 (t, $J = 7.0$ Hz, 1H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.66 (dd, $J = 7.5$ Hz, $J = 2.0$ Hz, 1H), 7.99 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.69, 43.75, 73.14, 114.38, 122.22, 124.49, 127.05, 128.78, 129.53, 131.11, 134.68, 145.07, 154.11, 167.50; IR (neat) 1690 s; MS, *m*/*z* (relative intensity, %); 253 ($M^+ - SO_2$, 84), 252 (24), 146 (51), 134 (10), 133 (11), 120 (18), 119 (100), 105 (45), 92 (10), 91 (44), 77 (17), 76 (13), 65 (33), 51 (10). Exact mass-FAB calcd for $C_{16}H_{16}NO_4S$ ($M^+ + H$) 318.0801, found 318.0804.

*4.3.6. 1-[(4-Methylphenyl)sulfonyl]-2-pyrrolidinone (**10**)*

White solid; mp 113–114 °C; R_f 0.11 (hexane/AcOEt = 2/1); ^{1}H NMR ($CDCl_3$) δ 2.08 (quint $J = 8.0$ Hz, 2H), 2.43 (t, $J = 8.5$ Hz, 2H), 2.44 (s, 3H), 3.99 (t $J = 7.5$ Hz, 2H), 7.34 (d, $J = 8.5$ Hz, 2H), 7.93 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.11, 21.62, 32.16, 47.20, 127.99, 129.61, 135.05, 145.12, 173.31; IR (KBr) 2997, w, 2916 w, 2915 w, 1925 w, 1729 s, 1685 w, 1653 w, 1596 m, 1490 w, 1459 b w, 1420 w, 1397 w, 1354 s, 1299 m, 1239 w, 1216 m, 1200 m, 1185 m, 1171 s, 1119 s, 1089 w, 1070 w, 1023 w, 962 m, 887 w, 839 w, 815 m, 755 w, 715 m, 665 s, 602 m; MS, *m*/*z* (relative intensity, %); 240 ($M^+ + H$, 0.06), 175 (52), 174 (14), 155 (10), 120 (91), 92 (10), 91 (100), 65 (39), 56 (10). Exact mass-FAB calcd for $C_{11}H_{13}NO_3SNa$ ($M^+ + Na$) 262.0514, found 262.0521.

*4.3.7. Phthalide (**12**)*

White solid; mp 69–70 °C; R_f 0.17 (hexane/AcOEt = 5/1); ^{1}H NMR ($CDCl_3$) δ 5.34 (s, 2H), 7.51 (d, $J = 7.5$ Hz, 1H), 7.55 (t, $J = 7.5$ Hz, 1H), 7.70 (t, $J = 8.0$ Hz, 1H), 7.94 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 69 64, 122.07, 125.75, 125.81, 129.04, 134.00, 146.50, 171.10; IR (KBr) 2943 w, 2924 w, 2863 w, 2110 w, 1992 w, 1957 w, 1810 w, 1750 s, 1714 m, 1616 w, 1595 w, 1542 w, 1467 m, 1439 m, 1369 m, 1318 w, 1287 m, 1219 m, 1198 w, 1111 w, 1092 w, 1053 s, 1018 m, 1002 m, 879 w, 848 w, 799 w, 742 s, 700 w, 680 w; MS, *m*/*z* (relative intensity, %); 134 (M^+, 36), 133 (12), 105 (100), 77 (49), 76 (13), 51 (21), 50 (18). Exact mass-EI calcd for C_8H_6O 134.0368, found 134.0363.

*4.3.8. 7,8-Dihydro-5H-1,3-dioxo[4,5-g][2]benzopyran-5-one (**14**)*

White solid; mp 130–131 °C; R_f 0.14 (hexane/AcOEt = 2/1); ^{1}H NMR ($CDCl_3$) δ 2.96 (t, $J = 6.5$ Hz, 2H), 4.49 (t, $J = 6.5$ Hz, 2H), 6.04 (s, 2H), 6.68 (s, 1H), 7.50 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 27.95, 67.08, 101.87, 106.93, 109.59, 118.90, 135.91, 147.33, 152.19, 164.69; IR (KBr) 2920 w, 1738 w, 1698 s, 1620 w, 1558 w, 1498 s, 1483 m, 1449 m, 1411 m, 1396 m, 1341 m, 1256 s, 1231 m, 1194 w, 1119 m, 1082 m, 1057 m, 1032 s, 987 w, 956 w,

937 m, 903 w, 882 w, 823 w, 778 w, 749 w, 729 w, 712 w, 685 w, 607 w; MS, *m/z* (relative intensity, %); 192 (M^+, 100), 162 (38), 134 (84), 104 (18), 81 (19), 77 (10), 76 (24), 63 (10), 53 (12), 51 (14), 50 (24). Exact mass-EI calcd for $C_{10}H_8O_4$ 192.0422, found 192.0418.

4.3.9. 4,5-Dihydro-2-benzoxepin-1(3H)-one (**16**)

White solid; mp 53–54 °C; R_f 0.34 (hexane/AcOEt = 2/1); ^{1}H NMR ($CDCl_3$) δ 2.13 (quint $J = 7.0$ Hz, 2H), 2.91 (t, $J = 7.0$ Hz, 2H), 4.16 (t $J = 6.5$ Hz, 2H), 7.23 (d, $J = 7.5$ Hz, 1H), 7.37 (t, $J = 7.5$ Hz, 1H), 7.49 (t, $J = 7.0$ Hz, 1H), 7.72 (d, $J = 7.5$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 27.67, 29.35, 66.48, 127.30, 128.58, 130.13, 131.54, 132.59, 137.46, 172.40; IR (KBr) 2980 m, 2957 w, 2932 w, 2897 w, 2869 w, 1969 w, 1869 w, 1713 s, 1604 w, 1542 w, 1508 w, 1465 m, 1450 m, 1381 m, 1352 n, 1318 m, 1297 m, 1276 s, 1252 s, 1220 m, 1198 m, 1168 w, 1110 s, 1094 s, 1058 s, 1034 w, 1006 m, 972 m, 947 m, 894 w, 875 w, 831 w, 799 m, 776 s, 752 w, 724 m, 707 m, 644 w; MS, *m/z* (relative intensity, %); 162 (M^+, 80), 134 (13), 133 (12), 132 (62), 131 (100), 105 (21), 104 (89), 103 (29), 92 (12), 91 (14), 89 (15), 78 (35), 77 (38), 76 (12), 63 (16), 57 (12), 51 (33), 50 (17). Exact mass-EI calcd for $C_{10}H_{10}O_2$ 162.0681, found 162.0687.

4.3.10. 1,3-Dihydro-1-oxo-2H-indene-2,2-dicarboxylic acid diethyl ester (**18**)

Colorless oil; R_f 0.23 (hexane/AcOEt = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.29 (t, $J = 7.5$ Hz, 6H), 3.82 (s, 2H), 4.27 (q, $J = 7.5$ Hz, 2H), 4.28 (q, $J = 7.5$ Hz, 2H), 7.42 (t, $J = 7.5$ Hz, 1H), 7.50 (d, $J = 8.0$ Hz, 1H), 7.64 (t, $J = 7.5$ Hz, 1H), 7.81 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.99, 36.17, 62.56, 67.26, 125.30, 126.25, 128.09, 134.33, 135.70, 151.89, 166.90, 194.53; IR (neat) 2983 s, 2939 m, 2906 m, 2874 w, 2361 w, 2105 w, 1951 w, 1820 w, 1757 s, 1739 s, 1729 s, 1606 s, 1590 s, 1465 s, 1444 s, 1391 m, 1366 s, 1327 m, 1258 s, 1212 s, 1181 s, 1093 s, 1063 s, 1010 s, 959 w, 912 s, 859 s, 843 m, 827 w, 782 m, 766 s, 694 m, 669 m, 640 m; MS, *m/z* (relative intensity, %); 276 (M^+, 10), 231 (10), 203 (38), 159 (21), 158 (25), 157 (100), 130 (14), 102 (11). Exact mass-EI calcd for $C_{15}H_{16}O_5$ 276.0997, found 276.0996.

4.3.11. 4,5-Dimethoxy-1,3-dihydro-1-oxo-2H-indene-2,2-dicarboxylic acid diethyl ester (**20**)

White solid; mp 70–71 °C; R_f 0.09 (hexane/AcOEt = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.29 (t, $J = 6.5$ Hz, 6H), 3.76 (s, 2H), 3.94 (s, 3H), 3.96 (s, 3H), 4.27 (dq, $J = 6.5$ Hz, $J = 6.5$ Hz, 4H), 7.00 (d, $J = 8.5$ Hz, 1H), 7.58 (d, $J = 8.5$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.81, 32.83, 56.20, 60.35, 62.33, 67.27, 112.98, 121.82, 127.97, 144.44, 144.94, 158.32, 166.89, 192.58; IR (KBr) 2979 m, 2950 w, 2905 w, 2843 w, 1757 s, 1718 s, 1603 m, 1498 m, 1471 m, 1457 m, 1423 w, 1390 w, 1367 w, 1340 w, 1281 s, 1255 s, 1224 s, 1186 m, 1162 m, 1108 w, 1079 s, 1065 s, 1042 m, 1009 m, 967 m, 918 m, 873 w, 855 w, 838 w, 817 w, 760 w, 740 w, 687 w, 654 w, 629 w; MS, *m/z* (relative intensity, %); 336 (M^+, 13), 263 (21), 218 (20), 217 (100). Exact mass-EI calcd for $C_{17}H_{20}O_7$ 336.1209, found 336.1211.

4.3.12. 2-Cyano-2,3-dihydro-1-oxo-1H-indene-2-carboxylic acid ethyl ester (**22**)

White solid; mp 51–52 °C; R_f 0.11 (hexane/AcOEt = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.35 (t, $J = 7.0$ Hz, 3H), 3.70 (d, $J = 17.5$ Hz, 1H), 3.95 (d, $J = 17.5$ Hz, 1H), 4.33 (q, $J = 7.0$ Hz, 2H), 7.50 (t, $J = 7.5$ Hz, 1H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.74 (t, $J = 7.5$ Hz, 1H), 7.86 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.91, 37.54, 54.31, 54.21, 115.82, 126.31, 126.49, 128.96, 132.12, 136.95, 151.54, 164.06, 190.71; IR (KBr) 2992 w, 2939 w, 2872 w, 2250 w, 1744 s, 1732 s, 1607 m, 1600 m, 1587 m, 1465 m, 1421 m, 1389 w, 1366 w, 1304 w, 1280 m, 1240 s, 1203 s, 1154 m, 1139 w, 1116 w, 1061 w, 1015 w, 983 m, 963 w, 903 m, 859 m, 798 w, 789 w, 757 m, 705 w, 689 w, 643 w, 607 w; MS, *m/z* (relative intensity, %); 229 (M^+, 16), 184 (14), 158 (12), 157 (94), 156 (100), 155 (11), 146 (11), 130 (26), 129 (18), 128 (28), 127 (11), 102 (19), 101, (26), 77 (20), 76 (17), 75 (13), 51 (17), 50 (14). Exact mass-FAB calcd for $C_{13}H_{12}NO_3$ 230.0818 ($M^+ + H$), found 230.0822.

4.3.13. 2,3-Dihydro-2-(phenylsulfonyl)-1H-inden-1-one (**24**)

White solid; mp 59–60 °C; R_f 0.14 (hexane/AcOEt = 5/1); ^{1}H NMR ($CDCl_3$) δ 3.55 (q, $J = 8.5$ Hz, 1H), 3.82 (dd, $J = 18.5$ Hz, $J = 3.0$ Hz, 1H), 4.29 (dd, $J = 8.5$ Hz, $J = 3.5$ Hz, 1H), 7.39 (t, $J = 7.5$ Hz, 1H), 7.50 (d, $J = 7.5$ Hz, 1H), 7.57 (t, $J = 7.5$ Hz, 2H), 7.63 (t $J = 7.5$ Hz, 1H), 7.68 (t, $J = 7.5$ Hz, 1H), 7.72 (d, $J = 8.0$ Hz, 1H), 7.93 (d, $J = 7.5$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 28.05, 68.61, 124.85, 126.39, 128.21, 129.06, 129.27, 134.23, 135.73, 135.93, 137.47, 151.81, 194.44; IR (KBr) 2957 m, 2363 w, 1968 w, 1705 s, 1604 m, 1588 w, 1474 w, 1465 w, 1446 m, 1431 w, 1332 m, 1315 s, 1305 s, 1281 s, 1246 w, 1216 m, 1199 w, 1174 w, 1145 s, 1100 w, 1083 m, 1024 m, 1003 m, 969 w, 942 w, 926 w, 840 w, 808 w, 771 m, 760 m, 752 s, 730 m, 689 m, 637 w; MS, *m/z* (relative intensity, %); 272 (M^+, 0.55), 208 (14), 132 (11), 131 (100), 130 (37), 103 (19), 102 (13), 77 (41), 51 (17). Exact mass-EI calcd for $C_{15}H_{13}O_3S$ ($M^+ + H$) 273.0585, found 273.0591.

4.3.14. 7,8-Dihydro-5-oxo-naphtho[2,3-d]-1,3-dioxole-6,6(5H)-dicarboxylic acid diethyl ester (**28**)

White solid; mp 130–131 °C; R_f 0.09 (hexane/AcOEt = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.27 (t, $J = 9.0$ Hz, 6H), 2.71 (t, $J = 7.5$ Hz, 2H), 2.88 (t, $J = 7.5$ Hz, 2H), 4.27 (q, $J = 9.0$ Hz, 4H), 6.01 (s, 2H), 6.62 (s, 1H), 7.47 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.93, 26.09, 30.09, 62.18, 66.34, 101.79, 106.87, 107.77, 125.93, 139.63, 147.22, 152.62, 167.69, 188.55; IR (KBr) 2982 s, 2939 s, 2906 s, 2780 w, 2648 w, 2360 w, 2258 w, 2089 w, 1747 s, 1731 s, 1680 s, 1616 s, 1505 s, 1483 s, 1441 s, 1390 s, 1367 s, 1350 s, 1329 s, 1250 s, 1204 s, 1178 s, 1095 s, 1079 s, 1039 s, 935 s, 919 s, 885 m, 858 s, 826 m, 758 m, 741 m, 707 m, 667 w, 634 m; MS, *m/z* (relative intensity, %); 334 (M^+, 42), 289 (12), 262 (16), 261 (100), 260 (10), 233 (16),

217 (21), 216 (16), 215 (82), 214 (27), 189 (49), 188 (45), 187 (22), 162 (23), 159 (17), 134 (60), 104 (13), 102 (12), 77 (11), 76 (19). Exact mass-EI calcd for $C_{17}H_{18}O_7$ 334.1053, found 334.1052.

4.3.15. 5,7,8,9-Tetrahydro-5-oxo-6H-benzocycloheptene-6,6-dicarboxylic acid diethylester (**30**)

White solid; mp 53–54 °C; R_f 0.11 (hexane/AcOEt = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.24 (t, $J = 6.5$ Hz, 6H), 1.98 (quint, $J = 6.0$ Hz, 2H) 2.47 (t, $J = 6.0$ Hz, 2H), 2.83 (t, $J = 6.0$ Hz, 2H), 4.24 (q, $J = 7.0$ Hz, 4H), 7.14 (d, $J = 7.5$ Hz, 1H), 7.31 (t, $J = 8.0$ Hz, 1H), 7.41 (t, $J = 7.5$ Hz, 1H), 7.66 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.80, 23.17, 30.07, 33.19, 60.07, 126.67, 129.28, 130.30, 132.23, 138.40, 138.82167.73, 198.79; IR (KBr) 2981 s, 2960 s, 2940 s, 2907 m, 2871 m, 1747 s, 1731 s, 1681 s, 1598 s, 1463 s, 1448 s, 1390 m, 1366 m, 1351 m, 1324 m, 1294 s, 1247 s, 1220 s, 1207 s, 1165 s, 1127 w, 1097 m, 1085 m, 1037 m, 1016 s, 981 w, 956 m, 903 m, 859 m, 820 m, 778 m, 622 m; MS, *m*/*z* (relative intensity, %); 304 (M^+, 30), 276 (47), 249 (26), 258 (24), 241 (19), 230 (18), 213 (30), 212 (76), 203 (24), 202 (89), 201 (24), 186 (29), 185 (63), 184 (37), 175 (13), 173 (19), 159 (11), 158 (19), 157 (35), 156 (20), 145 (19), 144 (36), 143 (12), 132 (48), 131 (92), 130 (27), 129 (100), 128 (50), 127 (39), 118 (12),117 (13), 116 (12), 115 (30), 105 (12), 104 (77), 103 (38), 102 (13), 99 (13), 91 (42), 90 (22), 89 (17), 78 (28), 77 (33), 65 (11), 55 (18), 51 (14). Exact mass-FAB calcd for $C_{17}H_{20}O_5Na$ ($M^+ + Na$) 327.1209, found 327.1180.

4.3.16. 2-Oxo-3-phenyl-3-cyclopentene-1,1-dicarboxylic acid diethyl ester (**32**)

White solid; mp 142–143 °C; R_f 0.06 (hexane/AcOEt = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.30 (t, $J = 7.0$ Hz, 6H), 3.37 (d, $J = 3.0$ Hz, 2H), 4.28 (dq, $J = 7.0$ Hz, $J = 1.0$ Hz, 2H), 7.34–7.41 (m, 3H), 7.70 (dd, $J = 7.5$ Hz, $J = 1.5$ Hz, 2H), 7.86 (t, $J = 3.0$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.94, 36.08, 62.55, 66.07, 127.16, 128.49, 128.89, 130.54, 140.88, 156.47, 166.64, 195.24; IR (KBr) 2989 w, 2942 w, 2905 w, 2358 w, 1756 s, 1722 s, 1706 s, 1448 w, 1426 w, 1386 w, 1365 w, 1326 w, 1304 w, 1255 s, 1177 m, 1161 w, 1113 w, 1093 w, 1058 w, 1034 m, 990 w, 870 m, 854 w, 813 w, 764 m, 750 w, 739 w, 691 m; MS, *m*/*z* (relative intensity, %); 302 (M^+, 47), 257 (15), 256 (22), 229 (20), 228 (100), 200 (10), 185 (15), 184 (39), 183 (62), 156 (33), 155 (19), 144 (11), 128 (31), 127 (21), 115 (22), 105 (16), 102 (21), 77 (13), 53 (13). Exact mass-EI calcd for $C_{17}H_{18}O_5$ 302.1154, found 302.1149.

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[10] Abbreviation: dppp = 1,3-bis(diphenylphosphino)propane, dppe = 1,2-bis(diphenylphosphino)ethane, dppb = 1,4-bis(diphenylphosphino)butane, Boc = *tert*-butoxycarbonyl.

[11] 4% of *N*-Ts-azetidine also was obtained in the reaction of *N*-Ts-3-bromopropylamine (**9a**). The reaction of the isolated azetidine with aldehydes (C_6F_5CHO and (*E*)-PhCH=CH_2CHO) under the catalysis gave no carbonylated product. Therefore, the carbonylation of **9a** is found to proceed not through the azetidine intermediate.

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