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3,5-Bis(pentafluorosulfanyl)phenylboronic acid: A new organocatalyst for Conia-ene carbocyclization of 1,3-dicarbonyl compounds having terminal alkynes

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ABSTRACT

3,5-Bis(pentafluorosulfanyl)phenylboronic acid **1** was introduced as an efficient organocatalyst for Conia-ene carbocyclization of 1,3-dicarbonyl compounds having terminal alkynes. A variety of 2-alkynic 1,3-dicarbonyl compounds were smoothly converted to ene-carbocyclization products in moderate to excellent yields. Compared with the reported catalyst, 3-nitro phenylboronic acid, catalyst **1** is slightly better in a non-polar solvent such as toluene and Solkane® 365mfc (1,1,1,3,3-pentafluorobutane). These results indicate that the SF_5 function can be a lipophilic and sterically demanding alternative to the NO_2 group in catalyst design.

1. Introduction

Much attention has been focused on the design of high-quality catalysts, including organocatalysts and organometallic catalysts, for chemical reactions to synthesize complex molecules [1,2]. Electronic tuning is recognized as one of the most important tools in catalyst design; in particular, electronegativity and steric effects are important aspects of the intuitive approach that helps chemists to understand the nature of catalysts. Among various approaches available, fluorine substitution on molecules is highly attractive for this purpose. It is a gross understatement to say that introduction of fluorine into organic molecules often leads to significant changes in their physical, chemical and even biological properties, in spite of its less steric effect. The specific physical and chemical properties of fluorine within fluorine-containing compounds, especially its strong electronegativity, lipophilicity and reaction ability, dramatically differ from those of other halogens and lead to changes in the interaction between the molecule and components of the surrounding environment [3]. Fluorine-substitution is a fundamental strategy for developing novel advanced materials, pharmaceuticals and agrochemicals. Functional groups such as trifluoromethyl (CF_3) [4], triflyl (SO_2CF_3) [5], trifluoromethylsulfenyl (SCF_3) [6], and trifluoromethoxy (OCF_3) [7] groups have also been actively studied next to the simple fluorine-substitution. On the other hand, the utility of the pentafluorosulfanyl (SF_5) group is rather undeveloped. The function of SF_5 as an electron-withdrawing group is one of the strongest, as strong as the nitro (NO_2) group. The SF_5 function is sterically demanding, chemically and thermally stable [8]. Outstanding lipophilic properties are often observed when the SF_5 function is incorporated into molecules, which is a fundamental difference from the NO_2 group. These unique properties of SF_5 compounds will show remarkable influences on physical properties other than those observed with fluorine or trifluoromethyl groups. Although the introduction of the SF_5 group into organic molecules is a challenge [8b,9], a series of aromatic compounds with an SF_5 function are going to be readily available thanks to the efforts by Umemoto and UBE America Inc. [8d,10]. Their significant developments in the preparation of SF_5-containing aromatic compounds led to the proposal of many potential applications in pharmaceuticals [11], agrochemicals [12] and advanced materials [13]. These facts directed us to use SF_5 in catalyst design. However, to the best of our knowledge, no reports on the application of these SF_5-containing organic compounds in catalysis had been reported. As a part of our ongoing research program toward the development of novel synthetic methodologies in fluorine-related chemistry, we disclose herein the first performance of an SF_5 compound, 3,5-bis(pentafluorosulfanyl)-phenyl boronic acid (**1**), in catalysis for Conia-ene carbocyclization of 1,3-dicarbonyl compounds to provide the desired cyclopentene derivatives in high yields (Scheme 1).

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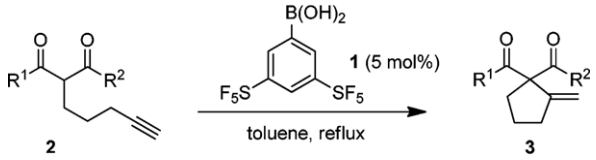
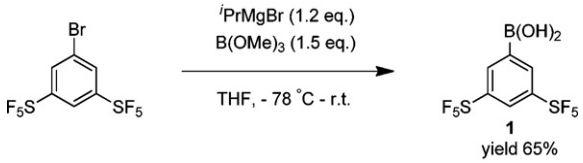


Scheme 1. 3,5-Bis(pentafluorosulfanyl)phenyl boronic acid **1** effectively catalyzes the *Conia-ene* carbocyclization of 1,3-dicarbonyl compounds having terminal alkynes.



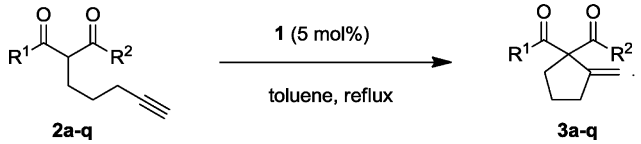
Scheme 2. Synthesis of 3,5-bis(pentafluorosulfanyl)phenyl boronic acid **1**.

2. Results and discussion

The carbocyclization of 1,3-dicarbonyl compounds represented by the Conia-ene reaction is one of the most common methodologies for the formation of five-membered rings which allows cyclopentanes to bear a methylene substituent adjacent to the newly formed quaternary carbon center [14]. The reaction can be conducted under thermal conditions, a strong mineral acid, base or metal ion catalysis [15]. Recently, Dixon et al. reported that arylboronic acids catalyze the Conia-ene reaction and that acids bearing strong electron-withdrawing groups on the aromatics afford better reactivity, 3-nitrobenzeneboronic acid ($pKa_1 = 6.93$) being the most efficient [15f,16]. However, we experienced poor solubility of 3-nitrobenzeneboronic acid into some organic solvents such as Solkane®365mfc, which is an environmentally benign solvent [17]. We then were interested in using 3,5-bis(pentafluorosulfanyl)phenyl boronic acid (**1**) as an alternative catalyst to 3-nitrobenzeneboronic acid due to its similar acidity ($pKa_1 = 5.76$) [16] and outstanding solubility in organic solvents. Based on our calculations, the solubility of 3-nitro phenylboronic acid (log *P*: 0.98) in an organic solvent is much lower than 3,5-bis(pentafluorosulfanyl)phenylboronic acid (log *P*: 3.6) [18]. Target compound **1** was easily synthesized from commercially available 1,3-bis(pentafluorosulfanyl)-5-bromobenzene and trimethyl borate (Scheme 2).

With catalyst **1** in hand, we examined its performance in Conia-ene carbocyclization using a variety of 1,3-dicarbonyl compounds **2** (Table 1). Without addition of catalyst, only 19% yield of **3a** was obtained after 24 h (entry 1). In contrast to this, with 5 mol% of catalyst **1** in the same condition, substrates **2a–f** bearing electron-donating groups, or not, afforded excellent yields of **3a–f**; even the *o*-substituted aromatic substrate gave 91% yield of **3c** within 48 h (entries 2–7). On the other hand, for electron-deficient substrates **2g–i**, the yields of **3g–i** somewhat decreased as the electron-withdrawing effect was enhanced (entries 8–10). This result shows that the electron-withdrawing group is not favored under these conditions. Sterically hindered naphthyl keto-ester **2j** also afforded desired product **3j** in 86% yield (entry 11). Furthermore, aliphatic esters **2k–m** also proved to be good substrates and reacted smoothly. The comparable yields of methyl, ethyl and isopropyl substrates indicated that the steric effect of the keto moiety minimally influenced the yield of the reaction (entries 12–14). In contrast to the keto moiety, the ester moiety had a significant effect on the reaction. For benzyl ester **2n**, **3n** was obtained in 96% after 16 h, but a complex mixture was observed for *tert*-butyl ester **2o** even after 3 days of stirring (entries 15 and 16). 1,3-Diketones **2p–q** could also be efficiently converted to the desired products **3p–q**. In the catalysis of **1**, a yield of 75% and 95% was obtained for methyl and phenyl ketone, respectively (entries 17 and 18).

Table 1
Compound **1** catalyzed Conia-ene carbocyclization of acetylenic dicarbonyl compounds **2**.[a]



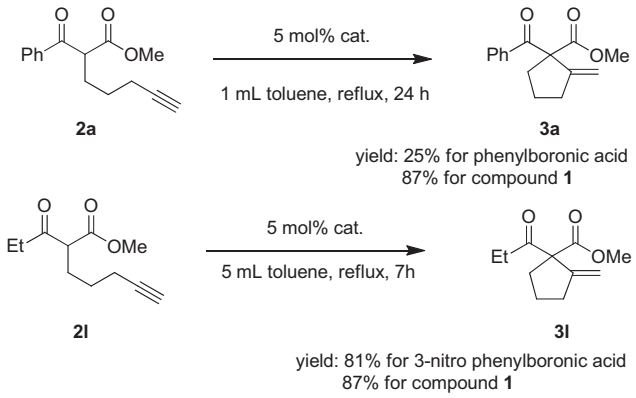
Entry	2	R^1	R^2	Time (h)	Yield (%)[b]
1[c]	**2a**	–Ph	–OMe	24	19
2	**2a**	–Ph	–OMe	24	87
3	**2b**	–Ph	–OEt	40	70
4	**2c**	-*o*-Me–Ph	–OMe	48	91
5	**2d**	-*m*-Me–Ph	–OMe	21	91
6	**2e**	-*p*-Me–Ph	–OMe	58	71
7	**2f**	-*p*-OMePh	–OMe	24	91
8	**2g**	-*p*-Br–Ph	–OMe	65	86
9	**2h**	-*p*-Cl–Ph	–OMe	72	75
10	**2i**	-*p*-F–Ph	–OMe	48	42
11	**2j**	naphthalene-2-yl	–OMe	45	86
12	**2k**	–Me	–OMe	3	86
13	**2l**	–Et	–OMe	6	78
14	**2m**	-*i*-Pr	–OMe	14	78
15	**2n**	–Me	–OBn	16	96
16	**2o**	–Me	–O^{t}Bu	72	n.d.
17	**2p**	–Ph	–Me	40	75
18	**2q**	–Ph	–Ph	19	95

[a] Reaction condition: 0.2 mmol S.M., 1.0 mL dry toluene, reflux.
[b] Isolated yield.
[c] Without addition of catalyst.

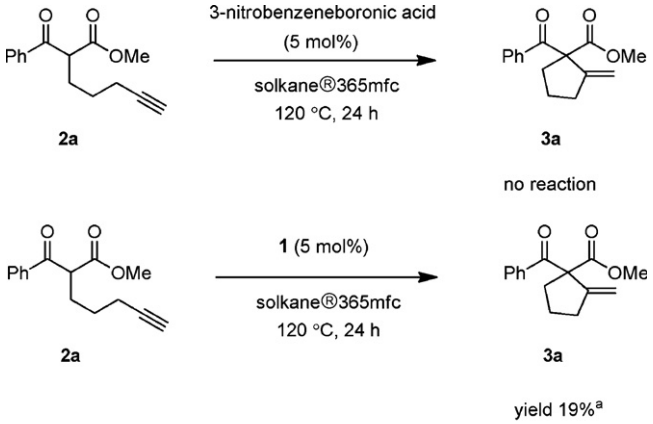
The reactivity between catalyst **1** and conventional phenylboronic acid and Dixon's catalyst, 3-nitro benzeneboronic acid, was next investigated. While the efficiency of catalysis of **1** was much higher than that of unactivated benzeneboronic acid (87% *vs* 25%), similar reactivity was observed for catalyst **1** and 3-nitro benzeneboronic acid (87% *vs* 81%) (Scheme 3).

We finally examined the Conia-ene carbocyclization in Solkane®365mfc. As shown in Table 2, a yield of 19% was obtained with catalyst **1** after 24 h, but there was no reaction when 3-nitro phenylboronic acid was used (Scheme 4). Although the conversion was low when catalyst **1** was used, its efficiency was higher than 3-nitro phenylboronic acid in Solkane®365mfc.

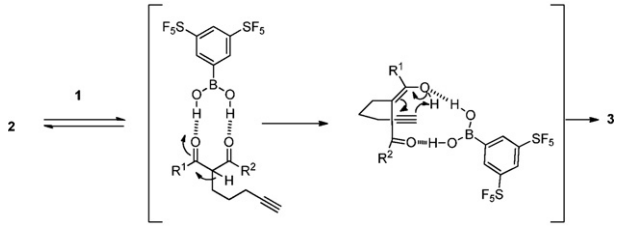
The possible mechanism is proposed to be similar to Dixon's [15f]. First, 1,3-dicarbonyl starting material is promoted to be enolized by the catalysis of **1**. Then a subsequent concerted ene reaction of this enol form would afford the product (Scheme 5).



Scheme 3. Comparison of efficiency of catalyst **1** and other boronic acids.



Scheme 4. Comparison of efficiency of **1** and 3-nitro phenylboronic acid in Solkane®365mfc.



Scheme 5. Proposed mechanistic pathway.

3. Conclusion

In summary, an aromatic pentafluorosulfanyl compound was applied as an organocatalyst for the first time in the Conia-ene carbocyclization of 1,3-dicarbonyl compounds. Compared with 3-nitro phenylboronic acid, catalyst **1** was slightly more efficient in a non-polar solvent. These results indicate that the SF_5 function can be used as a lipophilic and sterically demanding alternative to the NO_2 group in catalyst design. Further use of **1** for asymmetric Conia-ene carbocyclization of 1,3-dicarbonyl compounds is under investigation [19].

4. Experimental

All reactions were performed in oven-dried glassware under a positive pressure of nitrogen. Solvents were transferred *via* syringe and were introduced into the reaction vessels through a rubber septum. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica-gel (60-F254). The TLC plates were visualized with UV light and 7% phosphomolybdic acid or $KMnO_4$ in water/heat. Column chromatography was carried out on a column packed with silica-gel 60N spherical neutral size 63–210 μm. The ^1H NMR (300 MHz), ^{19}F NMR (282 MHz) and ^{13}C NMR (150.9 MHz) spectra for solution in $CDCl_3$ were recorded on a Buruker-600, a Varian Gemini-300. Chemical shifts (δ) are expressed in ppm downfield from internal TMS, $CHCl_3$, CD_3CN and d_4-MeOH. Mass spectra were recorded on a SHIMADZU GCMS-QP5050A or SHIMAZU LCMS-2010EV (ESI-MS). The CCl_3F was used as internal standard for ^{19}F NMR. Infrared spectra were recorded on a JASCO FT/IR-200 spectrometer. Anhydrous toluene was distilled over CaH_2.

4.1. Synthesis of 3,5-bis(pentafluorosulfanyl)phenyl boronic acid **1**

To a solution of 1,3-bis(pentafluorosulfanyl)-5-bromobenzene (1.23 g, 3.0 mmol) in THF (4 mL) at −78 °C under nitrogen was added a solution of *i*-PrMgBr in Et_2O (5.1 mL, 3.6 mmol) dropwise. The reaction mixture was then allowed to warm to 0 °C and stirred for 30 min. The subsequent mixture was then added to a solution of $B(OMe)_3$ (0.5 mL, 4.5 mmol) in THF (6 mL) at −78 °C dropwise. Warmed it to room temperature and stirred overnight. The mixture was acidified with aqueous 10% HCl and extracted with ethyl acetate (3× 30 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and filtered before being concentrated under reduced pressure. The crude product was purified through flash chromatography on silica gel (hexane/ethyl acetate = 8/2) to obtain a white solid (728 mg, yield 65%). ^1H NMR (CD_3CN, 300 MHz) δ 6.54 (s, 2H, $B(OH)_2$), 8.31 (m, 1H, Ar–H), 8.38 (s, 2H, Ar–H); ^{13}C NMR (CD_3OD, 150.9 MHz) δ 125.0 (2C, Ar–C), 134.2 (overlapping signal, 2C, Ar–C1 and Ar–C4), 153.3 (t, J_{C-F} = 18.1 Hz, 2C, Ar–C); ^{19}F NMR (CD_3CN, 282 MHz) δ −63.57 (dd, J = 148.3, 12.4 Hz, 4F), −83.14 (m, 1F); IR (KBr, cm^{-1}) 3433, 1604, 1456, 1431, 1360, 1139, 1025, 836, 727; m.p.: >250 °C; GC–MS (EI, m/z) 374 $[M]^+$, 330 $[(M+H)\text{-}B(OH)_2]^+$, HRMS (EI) calcd. for $C_6H_4F_{10}S_2$ $[(M+H)\text{-}B(OH)_2]^+$: 329.9595, found: 329.9614.

4.2. General procedure of the Conia-ene carbocyclization of 1,3-dicarbonyl compounds with alkynes

To a mixture of 1,3-dicarbonyl compounds (**2a**–**q**) and 3,5-bis(pentafluorosulfanyl)phenyl boronic acid (**1**), dry toluene was added. The resulting solution was reflux at 120 °C until complete consumption of the starting materials which was indicated by TLC. The solvent was then removed under reduced pressure and the obtained crude product was purified by flash column chromatography on silica gel to give the corresponding products (**3a**–**q**).

1-Benzoyl-2-methylenecyclopentanecarboxylic acid methyl ester (**3a**). Yield = 87%, white solid. ^1H NMR was in agreement with the literature [14c]. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.64–1.81 (m, 1H, $CCH_2CH_2(\alpha)$), 1.84–1.90 (m, 1H, $CCH_2CH_2(\beta)$), 2.15–2.24 (m, 1H, $CH_2CH_2(\alpha)C{=}$), 2.50–2.54 (m, 2H, $COCCH_2$), 2.80–2.89 (m, 1H, $CH_2CH_2(\beta)C{=}$), 3.66 (s, 3H, OCH_3), 5.19 (s, 1H, $=CH_2(\alpha)$), 5.36 (s, 1H, $=CH_2(\beta)$), 7.40–7.45 (m, 2H, Ar–H), 7.50–7.56 (m, 1H, Ar–H), 7.82–7.85 (m, 2H, Ar–H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 24.5 (CCH_2CH_2), 34.4 ($COCCH_2$), 36.9 ($CH_2C{=}$), 52.9 ($COOCH_3$), 67.6 (COCCO), 112.1 ($C{=}CH_2$), 128.6 (2C, Ar–C), 128.9 (2C, Ar–C), 132.9 (Ar–C), 135.4 (Ar–C), 149.1 ($C{=}CH_2$), 172.5 ($COOCH_3$), 195.3 ($C{=}O$); IR (KBr, cm^{-1}) 3016, 2975, 2951, 1729, 1681, 1595, 1488, 1453, 1320, 1250, 1159, 1079, 991; m.p.: 82–83 °C; MS (ESI, m/z) 267 $[M+Na]^+$.

1-Benzoyl-2-methylenecyclopentanecarboxylic acid ethyl ester (**3b**). Yield = 70%, colorless oil. ^1H NMR was in agreement with the literature [14b]. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.06 (t, J = 7.2 Hz, 3H, OCH_2CH_3), 1.64–1.79 (m, 1H, $CCH_2CH_2(\alpha)$), 1.81–1.91 (m, 1H, $CCH_2CH_2(\beta)$), 2.14–2.23 (m, 1H, $CH_2CH_2(\alpha)C{=}$), 2.49–2.54 (m, 2H, $COCCH_2$), 2.81–2.90 (m, 1H, $CH_2CH_2(\beta)C{=}$), 4.07–4.19 (m, 2H, $COOCH_2$), 5.22 (s, 1H, $=CH_2(\alpha)$), 5.36 (m, 1H, $=CH_2(\beta)$), 7.42 (t, J = 7.5 Hz, 2H, Ar–H), 7.50–7.55 (m, 1H, Ar–H), 7.83 (d, J = 7.2 Hz, 2H, Ar–H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 13.8 (OCH_2CH_3), 24.4 (CCH_2CH_2), 34.5 ($COCCH_2$), 36.9 ($CH_2C{=}$), 61.7 ($COOCH_2$), 67.5 (COCCO), 111.9 ($C{=}CH_2$), 128.5 (2C, Ar–C), 128.9 (2C, Ar–C), 132.8 (Ar–C), 135.5 (Ar–C), 149.5 ($C{=}CH_2$), 171.9 ($COOCH_2$), 195.5 ($C{=}O$); IR ν_{max} (film)/cm^{-1} 2977, 2960, 1733, 1686, 1597, 1580, 1447, 1389,1267, 1021, 887; MS (ESI, m/z) 281 $[M+Na]^+$.

1-(2-methylbenzoyl)-2-methylenecyclopentanecarboxylic acid methyl ester (**3c**). Yield = 91%, slightly yellow solid. ^1H NMR was in agreement with the literature [15f]. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.64–1.81 (m, 2H, CCH_2CH_2), 2.20 (dt, J = 13.2, 7.2 Hz, 1H,

$CH_2CH_2(\alpha)C=$), 2.40 (s, 3H, Ar–CH_3), 2.43–2.52 (m, 2H, COCCH_2), 2.66 (dt, J = 12.9, 6.0 Hz, 1H, $CH_2CH_2(\beta)C=$), 3.64 (s, 3H, OCH_3), 5.24 (t, J = 1.8 Hz, 1H, $=CH_2(\alpha)$), 5.35 (t, J = 1.8 Hz, 1H, $=CH_2(\beta)$), 7.16 (t, J = 7.5 Hz, 1H, Ar–H), 7.25–7.34 (m, 3H, Ar–H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 20.9 (Ar–CH_3), 24.3 (CCH_2CH_2), 34.4 ($COCCH_2$), 37.0 ($CH_2C=$), 52.8 ($COOCH_3$), 69.9 (COCCO), 112.7 ($C=CH_2$), 125.2 (Ar–C), 126.5 (Ar–C), 130.5 (Ar–C), 131.8 (Ar–C), 137.6 (Ar–C), 137.9 (Ar–C), 149.3 ($C=CH_2$), 172.1 ($COOCH_3$), 201.3 ($C=O$); IR (KBr, cm^{-1}) 2976, 2948, 1731, 1677, 1648, 1599, 1455, 1247, 1074, 908; m.p.: 53–54 °C; MS (ESI, m/z) 281 $[M+Na]^+$.

1-(3-Methylbenzoyl)-2-methylenecyclopentanecarboxylic acid methyl ester (**3d**). Yield = 91%, white solid. ^{1}H NMR was in agreement with the literature [15f]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.63–1.74 (m, 1H, $CCH_2CH_2(\alpha)$), 1.76–1.92 (m, 1H, $CCH_2CH_2(\beta)$), 2.18 (dt, J = 13.2, 6.9 Hz, 1H, $CH_2CH_2(\alpha)C=$), 2.41 (s, 3H, Ar–CH_3), 2.48–2.53 (m, 2H, COCCH_2), 2.83 (dt, J = 13.2, 6.9 Hz, 1H, $CH_2CH_2(\beta)C=$), 3.66 (s, 3H, OCH_3), 5.18 (s, 1H, $=CH_2(\alpha)$), 5.35 (s, 1H, $=CH_2(\beta)$), 7.29–7.35 (m, 2H, Ar–H), 7.58 (d, J = 7.5 Hz, 1H, Ar–H), 7.68 (s, 1H, Ar–H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 21.5 (Ar–CH_3), 24.4 (CCH_2CH_2), 34.4 ($COCCH_2$), 36.9 ($CH_2C=$), 52.8 ($COOCH_3$), 67.6 (COCCO), 112.0 ($C=CH_2$), 125.9 (Ar–C), 128.3 (Ar–C), 129.5 (Ar–C), 133.6 (Ar–C), 135.3 (Ar–C), 138.5 (Ar–C), 149.5 ($C=CH_2$), 172.5 ($COOCH_3$), 195.4 ($C=O$); IR (KBr, cm^{-1}) 2972, 2951, 1730, 1683, 1648, 1599, 1453, 1274, 1150, 905; m.p.: 41–43 °C; MS (ESI, m/z) 281 $[M+Na]^+$.

1-(4-Methylbenzoyl)-2-methylenecyclopentanecarboxylic acid methyl ester (**3e**). Yield = 71%, slightly yellow solid. ^{1}H NMR was in agreement with the literature [14c]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.63–1.76 (m, 1H, $CCH_2CH_2(\alpha)$), 1.78–1.92 (m, 1H, $CCH_2CH_2(\beta)$), 2.18 (dt, J = 13.2, 7.2 Hz, 1H, $CH_2CH_2(\alpha)C=$), 2.40 (s, 3H, Ar–CH_3), 2.48–2.53 (m, 2H, COCCH_2), 2.83 (dt, J = 13.2, 6.6 Hz, 1H, $CH_2CH_2(\beta)C=$), 3.66 (s, 3H, OCH_3), 5.18 (s, 1H, $=CH_2(\alpha)$), 5.35 (s, 1H, $=CH_2(\beta)$), 7.22 (d, J = 7.8 Hz, 2H, Ar–H), 7.74 (d, J = 8.1 Hz, 2H, Ar–H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 21.7 (Ar–CH_3), 24.4 (CCH_2CH_2), 34.4 ($COCCH_2$), 37.0 ($CH_2C=$), 52.8 ($COOCH_3$), 67.5 (COCCO), 111.9 ($C=CH_2$), 129.1 (2C, Ar–C), 129.3 (2C, Ar–C), 132.6 (Ar–C), 143.7 (Ar–C), 149.5 ($C=CH_2$), 172.6 ($COOCH_3$), 194.8 ($C=O$); IR (KBr, cm^{-1}) 2950, 1730, 1680, 1605, 1571, 1430, 1250, 1159, 995; m.p.: 42–44 °C; MS (ESI, m/z) 281 $[M+Na]^+$.

1-(4-Methoxybenzoyl)-2-methylenecyclopentanecarboxylic acid methyl ester (**3f**). Yield = 91%, colorless oil. ^{1}H NMR was in agreement with the literature [15f]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.66–1.80 (m, 1H, $CCH_2CH_2(\alpha)$), 1.82–1.89 (m, 1H, $CCH_2CH_2(\beta)$), 2.18 (dt, J = 13.2, 7.5 Hz, 1H, $CH_2CH_2(\alpha)C=$), 2.47–2.53 (m, 2H, COCCH_2), 2.83 (dt, J = 13.2, 6.6 Hz, 1H, $CH_2CH_2(\beta)C=$), 3.67 (s, 3H, $COOCH_3$), 3.86 (s, 3H, Ar–OCH_3), 5.18 (t, J = 2.4 Hz, 1H, $=CH_2(\alpha)$), 5.35 (t, J = 2.1 Hz, 1H, $=CH_2(\beta)$), 6.90 (d, J = 9.0 Hz, 2H, Ar–H), 7.82 (d, J = 9.0 Hz, 2H, Ar–H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 24.4 (CCH_2CH_2), 34.4 ($COCCH_2$), 37.0 ($CH_2C=$), 52.8 ($COOCH_3$), 55.5 (Ar–OCH_3), 67.4 (COCCO), 111.9 ($C=CH_2$), 113.8 (2C, Ar–C), 127.9 (Ar–C), 131.3 (2C, Ar–C), 149.6 ($C=CH_2$), 163.2 (Ar–C), 172.7 ($COOCH_3$), 193.8 ($C=O$); IR ν_{max} (film)/cm^{-1} 2953, 1733, 1680, 1601, 1575, 1457, 1252, 1158, 1027, 844; MS (ESI, m/z) 297 $[M+Na]^+$.

1-(4-Bromobenzoyl)-2-methylenecyclopentanecarboxylic acid methyl ester (**3g**). Yield = 86%, white solid. ^{1}H NMR was in agreement with the literature [15f]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.66–1.79 (m, 1H, $CCH_2CH_2(\alpha)$), 1.82–1.91 (m, 1H, $CCH_2CH_2(\beta)$), 2.15 (dt, J = 13.2, 6.9 Hz, 1H, $CH_2CH_2(\alpha)C=$), 2.51 (t, J = 7.2 Hz, 2H, COCCH_2), 2.82 (dt, J = 13.2, 6.6 Hz, 1H, $CH_2CH_2(\beta)C=$), 3.67 (s, 3H, OCH_3), 5.18 (s, 1H, $=CH_2(\alpha)$), 5.36 (s, 1H, $=CH_2(\beta)$), 7.57 (d, J = 8.4 Hz, 2H, Ar–H), 7.70 (d, J = 8.7 Hz, 2H, Ar–H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 24.4 (CCH_2CH_2), 34.3 ($COCCH_2$), 36.8 ($CH_2C=$), 52.9 ($COOCH_3$), 67.5 (COCCO), 112.3C=CH_2), 128.1 (Ar–C), 130.4 (2C, Ar–C), 131.9 (2C, Ar–C), 134.1 (Ar–C), 149.2 ($C=CH_2$), 172.2 ($COOCH_3$), 194.3 ($C=O$); IR (KBr, cm^{-1}) 2972, 2953, 1730, 1690, 1645, 1584, 1452, 1267, 1081, 991; m.p.: 54–56 °C (lit. [15f] 75–77 °C); MS (ESI, m/z) 345 $[M+Na]^+$.

1-(4-Chlorobenzoyl)-2-methylenecyclopentanecarboxylic acid methyl ester (**3h**). Yield = 75%, white semi-solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.65–1.79 (m, 1H, $CCH_2CH_2(\alpha)$), 1.82–1.91 (m, 1H, $CCH_2CH_2(\beta)$), 2.15 (dt, J = 13.2, 6.9 Hz, 1H, $CH_2CH_2(\alpha)C=$), 2.48–2.53 (m, 2H, COCCH_2), 2.85 (dt, J = 13.2, 6.6 Hz, 1H, $CH_2CH_2(\beta)C=$), 3.67 (s, 3H, OCH_3), 5.18 (s, 1H, $=CH_2(\alpha)$), 5.36 (s, 1H, $=CH_2(\beta)$), 7.40 (d, J = 9.0 Hz, 2H, Ar–H), 7.78 (d, J = 8.4 Hz, 2H, Ar–H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 24.4 (CCH_2CH_2), 34.3 ($COCCH_2$), 36.8 ($CH_2C=$), 52.9 ($COOCH_3$), 67.8 (COCCO), 112.2 ($C=CH_2$), 128.9 (2C, Ar–C), 130.3 (2C, Ar–C), 133.6 (Ar–C), 139.3 (Ar–C), 149.2 ($C=CH_2$), 172.3 ($COOCH_3$), 194.1 ($C=O$); IR (KBr, cm^{-1}) 2953, 1736, 1687, 1572, 1487, 1247, 1158, 884; MS (ESI, m/z) 301 $[M+Na]^+$, HRMS (ESI) calcd. for $C_{15}H_{15}ClNaO_3$ $[M+Na]^+$: 301.0607, found: 301.0607.

1-(4-Fluorobenzoyl)-2-methylenecyclopentanecarboxylic acid methyl ester (**3i**). Yield = 42%, colorless oil. ^{1}H NMR was in agreement with the literature [14c]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.67–1.78 (m, 1H, $CCH_2CH_2(\alpha)$), 1.79–1.93 (m, 1H, $CCH_2CH_2(\beta)$), 2.12–2.19 (m, 1H, $CH_2CH_2(\alpha)C=$), 2.51 (t, J = 7.5 Hz, 2H, COCCH_2), 2.81 (dt, J = 13.2, 6.9 Hz, 1H, $CH_2CH_2(\beta)C=$), 3.67 (s, 3H, OCH_3), 5.18 (s, 1H, $=CH_2(\alpha)$), 5.36 (s, 1H, $=CH_2(\beta)$), 7.10 (t, J = 8.7 Hz, 2H, Ar–H), 7.87 (dd, J = 8.9, 5.7 Hz, 2H, Ar–H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 24.5 (CCH_2CH_2), 34.4 ($COCCH_2$), 36.9 ($CH_2C=$), 52.9 ($COOCH_3$), 67.5 (COCCO), 112.2 ($C=CH_2$), 115.8 (d, J_{C-F} = 21.0 Hz, 2C, Ar–C), 131.5 (Ar–C), 131.6 (d, J_{C-F} = 9.0 Hz, 2C, Ar–C), 149.3 ($C=CH_2$), 165.5 (d, J_{C-F} = 253.5 Hz, Ar–C), 172.4 ($COOCH_3$), 193.8 ($C=O$); IR ν_{max} (film)/cm^{-1} 2954, 2877, 1738, 1682, 1651, 1598, 1506, 1240, 1157, 1083, 850; MS (ESI, m/z) 285 $[M+Na]^+$.

1-(2-Naphthoyl)-2-methylenecyclopentanecarboxylic acid methyl ester (**3j**). Yield = 86%, white solid. ^{1}H NMR was in agreement with the literature [14c]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.61–1.79 (m, 1H, $CCH_2CH_2(\alpha)$), 1.84–1.94 (m, 1H, $CCH_2CH_2(\beta)$), 2.29 (m, 1H, $CH_2CH_2(\alpha)C=$), 2.56 (t, J = 6.6 Hz, 2H, COCCH_2), 2.94 (dt, J = 19.8, 6.6 Hz, 1H, $CH_2CH_2(\beta)C=$), 3.66 (s, 3H, OCH_3), 5.23 (s, 1H, $=CH_2(\alpha)$), 5.39 (s, 1H, $=CH_2(\beta)$), 7.51–7.62 (m, 2H, Ar–H), 7.84–7.95 (m, 4H, Ar–H), 8.35 (s, 1H, Ar–H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 24.5 (CCH_2CH_2), 34.5 ($COCCH_2$), 37.2 ($CH_2C=$), 52.9 ($COOCH_3$), 67.8 (COCCO), 112.2 ($C=CH_2$), 124.8 (Ar–C), 126.9 (Ar–C), 127.8 (Ar–C), 128.4 (Ar–C), 128.7 (Ar–C), 129.8 (Ar–C), 130.5 (Ar–C), 132.6 (Ar–C), 132.7 (Ar–C), 135.4 (Ar–C), 149.6 ($C=CH_2$), 172.7 ($COOCH_3$), 195.3 ($C=O$); IR (KBr, cm^{-1}) 2980, 2953, 1731, 1676, 1454, 1281, 1125, 997; m.p.: 97–98 °C; MS (ESI, m/z) 317 $[M+Na]^+$.

1-Acetyl-2-methylenecyclopentanecarboxylic acid methyl ester (**3k**). Yield = 86%, colorless oil. ^{1}H NMR was in agreement with the literature [14b]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.65–1.80 (m, 2H, CCH_2CH_2), 2.15–2.24 (m, 4H, partly overlapping signal, CH_3CO and $CH_2CH_2(\alpha)C=$), 2.36–2.48 (m, 3H, partly overlapping signal, $COCCH_2$ and $CH_2CH_2(\beta)C=$), 3.75 (s, 3H, OCH_3), 5.23 (t, J = 1.8 Hz, 1H, $=CH_2$), 5.30 (t, J = 1.8 Hz, 1H, $=CH_2$); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 24.2 (CCH_2CH_2), 26.7 (CH_3CO), 34.0 ($COCCH_2$), 35.1 ($CH_2C=$), 52.8 ($COOCH_3$), 70.5 (COCCO), 112.3 ($C=CH_2$), 148.8 ($C=CH_2$), 171.8 ($COOCH_3$), 203.7 ($C=O$); IR ν_{max} (film)/cm^{-1} 2955, 1742, 1716, 1648, 1434, 1310, 1263, 1065, 833; MS (ESI, m/z) 205 $[M+Na]^+$.

2-Methylene-1-propionylcyclopentanecarboxylic acid methyl ester (**3l**). Yield = 78%, colorless oil. ^{1}H NMR was in agreement with the literature [15f]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.07 (t, J = 7.5 Hz, 3H, CH_2CH_3), 1.66–1.79 (m, 2H, CCH_2CH_2), 2.15–2.24 (m,1H, $CH_2CH_2(\alpha)C=$), 2.36–2.56 (m, 4H, partly overlapping signal, CH_2CH_3 and $COCCH_2$), 2.58–2.67 (m, 1H, $CH_2CH_2(\beta)C=$), 3.74 (s, 3H, OCH_3), 5.21 (s, 1H, $=CH_2(\alpha)$), 5.29 (s, 1H, $=CH_2(\beta)$); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 8.6 (CH_2CH_3), 24.2 (CCH_2CH_2), 32.3 (CH_2CH_3), 34.0 ($COCCH_2$), 35.2 ($CH_2C=$), 52.7 ($COOCH_3$), 70.3 (COCCO), 112.2

(C=CH_2), 148.8 (*C*=CH_2), 171.9 (*C*OOCH$_3$), 206.7 (*C*=O); IR ν_{max} (film)/cm^{-1} 2954, 2879, 1742, 1715, 1648, 1456, 1376, 1265, 1192, 1075, 1007, 897; MS (ESI, *m*/*z*) 219 [M+Na]$^+$.

1-Isobutyryl-2-methylenecyclopentanecarboxylic acid methyl ester (**3m**). Yield = 78%, colorless oil. ^{1}H NMR was in agreement with the literature [15f]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.07 (d, J = 6.6 Hz, 3H, CH(C*H*$_3$)$_2$(α)), 1.10 (d, J = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$(β)), 1.65–1.78 (m, 2H, CCH$_2$C*H*$_2$), 2.22–2.31 (m, 1H, CH$_2$C*H*$_2$(α)C=), 2.35–2.48 (m, 3H, partly overlapping signal, COCC*H*$_2$ and CH$_2$C*H*$_2$(β)C=), 2.98 (m, 1H, C*H*(CH$_3$)$_2$), 3.75 (s, 3H, OC*H*$_3$), 5.24 (s, 1H, =C*H*$_2$(α)), 5.30 (s, 1H, =C*H*$_2$(β)); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 20.7 (1C, CH(*C*H$_3$)$_2$(α)), 20.8 (1C, CH(*C*H$_3$)$_2$(β)), 24.1 (CCH$_2$*C*H$_2$), 33.9 (COC*C*H$_2$), 34.7 (*C*H$_2$C=), 37.5 (*C*H(CH$_3$)$_2$), 52.6 (COO*C*H$_3$), 71.0 (*C*OCCO), 112.5 (C=*C*H$_2$), 148.4 (*C*=CH$_2$), 171.8 (*C*OOCH$_3$), 210.3 (*C*=O); IR ν_{max} (film)/cm^{-1} 2970, 2875, 1744, 1715, 1647, 1458, 1380, 1264, 1191, 964, 899; MS (ESI, *m*/*z*) 233 [M+Na]$^+$.

1-Acetyl-2-methylenecyclopentanecarboxylic acid benzyl ester (**3n**). Yield = 96%, colorless oil. ^{1}H NMR was in agreement with the literature [15f]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.67–1.79 (m, 2H, CCH$_2$C*H*$_2$), 2.17 (s, 3H, C*H*$_3$CO), 2.18–2.24 (m, 1H, CH$_2$C*H*$_2$(α)C=), 2.38–2.47 (m, 3H, partly overlapping signal, COCC*H*$_2$ and CH$_2$C*H*$_2$(β)C=), 5.18 (s, 2H, OC*H*$_2$Ph), 5.21 (t, J = 2.1 Hz, 1H, =C*H*$_2$(α)), 5.28 (t, J = 1.8 Hz, 1H, =C*H*$_2$(β)), 7.28–7.39 (m, 5H, Ar–H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 24.2 (CCH$_2$*C*H$_2$), 26.7 (*C*H$_3$CO), 34.1 (COC*C*H$_2$), 35.1 (*C*H$_2$C=), 67.3 (*C*OCCO), 70.5 (OC*H*$_2$Ph), 112.4 (C=*C*H$_2$), 128.3 (Ar–C), 128.4 (2C, Ar–C), 128.6 (2C, Ar–C), 135.5 (Ar–C), 148.6 (*C*=CH$_2$), 171.1 (*C*OOCH$_3$), 203.4 (*C*=O); IR ν_{max} (film)/cm^{-1} 3033, 2958, 2878, 1738, 1648, 1498, 1455, 1434, 1230, 1140, 1083, 992; MS (ESI, *m*/*z*) 281 [M+Na]$^+$.

1-(1-Benzoyl-2-methylenecyclopentyl)ethanone (**3p**). Yield = 75%, slightly yellow solid. ^{1}H NMR was in agreement with the literature [15f]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.70–1.86 (m, 2H, CCH$_2$C*H*$_2$), 2.17–2.28 (m, 4H, partly overlapping signal, COC*H*$_3$ and CH$_2$C*H*$_2$(α)C=), 2.44–2.58 (m, 2H, COCC*H*$_2$), 2.74 (dt, J = 13.5, 6.6 Hz, 1H, CH$_2$C*H*$_2$(β)C=), 5.12 (t, J = 2.1 Hz, 1H, =C*H*$_2$(α)), 5.41 (t, J = 2.1 Hz, 1H, =C*H*$_2$(β)), 7.42 (m, 2H, Ar–H), 7.50–7.55 (m, 1H, Ar–H), 7.76–7.79 (m, 2H, Ar–H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 24.3 (CCH$_2$*C*H$_2$), 27.3 (*C*OCH$_3$), 34.4 (COC*C*H$_2$), 35.9 (*C*H$_2$C=), 75.5 (*C*OCCO), 113.3 (C=*C*H$_2$), 128.5 (2C, Ar–C), 129.4 (2C, Ar–C), 132.9 (Ar–C), 135.5 (Ar–C), 149.1 (*C*=CH$_2$), 198.1 (Ph*C*OC), 204.6 (*C*OCH$_3$); IR (KBr, cm^{-1}) 2964, 1693, 1595, 1579, 1447, 1239, 1132, 903; m.p.: 40–41 °C; MS (ESI, *m*/*z*) 251 [M+Na]$^+$.

(2-Methylenecyclopentane-1,1-diyl)bis(phenylmethanone) (**3q**). Yield = 95%, slightly yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.80–1.85 (m, 2H, CCH$_2$C*H*$_2$), 2.61–2.69 (m, 4H, partly overlapping signal, COC*H*$_2$ and CH$_2$C*H*$_2$C=), 4.96 (d, J = 2.1 Hz, 1H, =C*H*$_2$(α)), 5.39 (d, J = 2.1 Hz, 1H, =C*H*$_2$(β)), 7.31–7.36 (m, 4H, Ar–H), 7.41–7.47 (m, 2H, Ar–H), 7.79–7.82 (m, 4H, Ar–H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ 23.6 (CCH$_2$*C*H$_2$), 34.9 (COC*C*H$_2$), 37.7 (*C*H$_2$C=), 73.6 (*C*OCCO), 113.4 (C=*C*H$_2$), 128.5 (4C, Ar–C), 129.6 (4C, Ar–C), 132.8 (2C, Ar–C), 136.0 (2C, Ar–C), 150.4 (*C*=CH$_2$), 198.2 (2C, Ph*C*OC); IR (KBr, cm^{-1}) 2957, 1679, 1646, 1578, 1447, 1235, 1183, 889; m.p.: 86–88 °C; MS (ESI, *m*/*z*) 313 [M+Na]$^+$, HRMS (ESI) calcd. for $C_{20}H_{18}NaO_2$ [M+Na]$^+$: 313.1204, found: 313.1216.

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