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Titanium superoxide – a stable recyclable heterogeneous catalyst for oxidative esterification of aldehydes with alkylarenes or alcohols using TBHP as an oxidant†

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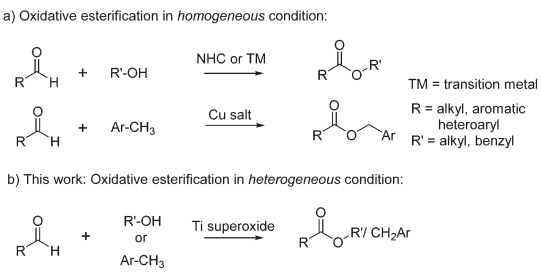
Titanium superoxide efficiently catalysed the oxidative esterification of aldehydes with alkylarenes or alcohols, under truly heterogeneous conditions, to afford the corresponding benzyl and alkyl esters in excellent yields. Mechanistic studies have established that this "one pot" direct oxidative esterification process proceeds through a radical pathway, proven by a FTIR spectral study of a titanium superoxide–aldehyde complex as well as spin trapping experiments with TEMPO. The intramolecular version of this protocol has been successfully demonstrated in the concise synthesis of 3-butylphthalide, an anti-convulsant drug.

Introduction

Carboxylic esters are not only among the most important and abundant functional groups in nature but also serve effectively as versatile 'building blocks' in the synthesis of fine chemicals, natural products, polymeric materials, *etc*. In particular, benzyl esters are useful functional groups found in medicinal and natural products and are widely used as protecting groups for a range of functionalities including carboxyl groups.[1] The traditional esterification processes involve a two-step procedure of stoichiometric activation of a carboxylic acid as an anhydride, acyl halide or activated ester followed by subsequent nucleophilic substitution with alcohols,[2] while benzyl esters are commonly prepared by way of nucleophilic displacement of a carboxylate ion on benzyl bromide.[3] Quite recently, the oxidative esterification of aldehydes with alcohols or alkyl aromatics in the presence of oxidants and catalysts has emerged as an alternative to traditional protocols since such raw materials are abundantly available in industry (Scheme 1).[4]

Despite the fact that alkyl aromatics are less utilized in oxidative esterification due to the low reactivity of sp^3 C–H bonds, a new method of esterification *via* C–H activation of alkyl aromatics with carboxylic acids has been developed and a variety of transition metals (Pd, Cu, Rh and Pt) have shown excellent catalytic activity in this C–H bond activating esterification.[5]



Scheme 1 Some of the approaches to oxidative esterification.

Further, a metal-free methodology for the synthesis of benzylic esters has been developed *via* oxidative C–O bond formation at the sp^3 benzylic carbon of various alkylbenzenes with carboxylic acids.[6] However, these approaches suffer from narrow substrate scope, use of stoichiometric amounts of toxic and hazardous heavy metal oxidants,[7] dry reaction conditions, longer reaction time, poor yields as well as low reaction efficiency. The development of a single-step oxidative esterification of aldehydes under truly heterogeneous catalytic conditions that minimize hazardous wastes is highly desirable from both economic and environmental points of view.

Sometime ago, we have reported a novel method for the preparation of a stable titanium superoxide catalyst from readily and cheaply available titanium tetraalkoxides and 50% H_2O_2.[8] Subsequently, its catalytic activities toward the oxidation of N–H bonds of aromatic and aliphatic 1° amines as well as O–H bonds of phenols[9a] and *anti*-Markovnikov aminobromination of olefins[9b] have been reported. To the best of

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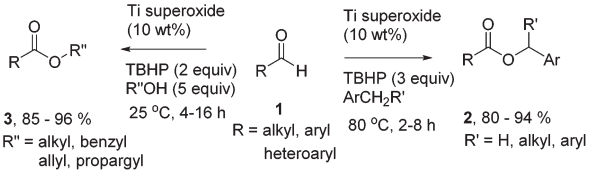


Scheme 2 Ti superoxide catalysed esterification of aldehydes with alkyl arenes or alcohols.

our knowledge, metal catalyzed direct esterification of aldehydes with un-activated alkylbenzenes under heterogeneous conditions has not explored. In this communication, we wish to report Ti-superoxide catalyzed for the direct conversion of aldehydes into carboxylic esters *via* direct C–H activation of alkylarenes or using alcohols (Scheme 2).

Results and discussion

Initially, as a model substrate, 4-nitrobenzaldehyde was oxidatively esterified with MeOH (1 equiv.), in the presence of TBHP (3 equiv.) and Ti superoxide (20 wt%) in excess toluene as a solvent at 80 °C to obtain a mixture of the corresponding benzyl and methyl esters (**2a** & **3a**) in a ratio 2 : 1 with 96% conversion (Table 1). When the reaction was conducted using 1 equiv. of TBHP, in the absence of MeOH, and using toluene as a solvent, benzyl ester **2a** indeed was obtained in 40% yield. However, when the TBHP concentration was increased to 3 equiv., a reasonably high yield of **2a** (75%) was realized; while use of 70% TBHP under the same reaction conditions gave only low yield of **2a** (25%). Unexpectedly, with 30% H_2O_2 and stirring the mixture at 25 °C, the reaction proceeded to give 4-nitrobenzoic acid in 90% yield. Further, a considerable improvement in the yield of **2a** (89%) was achieved when the Ti superoxide concentration was reduced to 10 wt% with TBHP (3 equiv.) (entry 6), possibly due to less decomposition of TBHP on a Ti superoxide matrix. A remarkable reactivity pattern was achieved when MeOH was used as the coupling partner with 2 equiv. of TBHP, and carrying out the reaction at 25 °C to afford the corresponding methyl 4-nitrobenzoate **3a** in 90% yield. The drastic condition (80 °C) required in the case of toluene as a reactant to undergo oxidation may be due to the higher bond dissociation energy of the benzylic C–H bond. However, no reaction took place with other catalysts such as titanium silicalite-I, $Ti(O^iPr)_4$ or TiO_2 [TBHP (3 equiv.), toluene, 80 °C or 25 °C].

Table 1 Oxidative esterification of 4-nitrobenzaldehyde with toluene or MeOH: optimization studies[a]

No.	Reactants	Catalyst (wt%)	Oxidants (equiv.)	t (°C)	**2a** or **3a**[b] (%)
1	MeOH + $PhCH_3$ [c]	Ti superoxide (20)	TBHP[d] (3)	80	92[e]
2	$PhCH_3$	Ti superoxide (20)	TBHP (1)	80	40
3	$PhCH_3$	Ti superoxide (20)	TBHP (3)	80	75
4	$PhCH_3$	Ti superoxide (20)	70% TBHP (3)	80	25
5	$PhCH_3$	Ti superoxide (20)	30% H_2O_2 (3)	25	—[f]
6	$PhCH_3$	Ti superoxide (10)	TBHP (3)	80	89
7	MeOH	Ti superoxide (10)	TBHP (2)	25	90

[a] 4-Nitrobenzaldehyde (5 mmol), toluene or methanol (25 mmol), 5 h. [b] Isolated yields of benzyl or methyl ester after chromatographic purification. [c] MeOH (5 mmol) and $PhCH_3$ were used as solvents. [d] TBHP refers to *tert*-butyl hydroperoxide (5–6 M solution in decane). [e] A mixture of **2a** and **3a** was formed in a 2 : 1 ratio. [f] 90% yield of 4-nitrobenzoic acid was isolated.

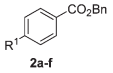
We then applied the optimized procedure of Ti superoxide catalyzed esterification to a variety of aldehydes having both electron-donating and -withdrawing groups to determine the scope of the esterification process, and the results are presented in Table 2. As can be seen, several aldehydes (aromatic, aliphatic, heteroaromatic, α,β-unsaturated aldehydes, *etc.*) with electron-rich (OMe, SMe) and -deficient (CN, NO_2, halo) groups underwent esterification both with toluene and methanol and produced the corresponding benzyl and methyl esters respectively in excellent yields (70–94%). The present protocol is also found successful in diesterifying *o*- and *p*-phthalaldehyes in a single step to provide the respective diesters (**2l**, **2m**, **3l**) in 86–92% yields. Interestingly, this protocol is quite successful on a large scale production of dioctyl phthalate (**3r**), a plasticizer in the polymer industry,[9c] with excellent yields (96%) in the 100 g scale (see the ESI†).

In order to further extend the scope of the esterification process, other aromatic hydrocarbons such as 4-OMe-toluene (**4a**), ethyl benzene (**4b**), xylenes (**4d–e**), and mesitylene (**4f**) were investigated under the reaction conditions with nitrobenzaldehydes as the substrate (Table 3). In all cases studied, excellent yields of benzylic esters (**4a–f**) were indeed obtained in 70–92% yields. Additionally, a variety of simple alcohols (primary, secondary, even tertiary), unsaturated alcohols (allylic, propargylic) and optically active [(*S*)-borneol, (−)-menthol] alcohols can be successfully employed to afford the corresponding esters [(**5a–g**) and **2a**] in high yields (52–82%) (Table 4). The enantiomeric purity of **5g** was determined to be 99.7% based on comparison of its specific rotation with the reported value $[\alpha]_D^{25}$ −83.5 (*c* 2, $CHCl_3$) {lit.[10b] $[\alpha]_D^{25}$ −83.7 (*c* 1.5, $CHCl_3$)}, thereby confirming that optical integrity was retained in the product.

Mechanistic studies

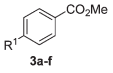
To gain some insight into the mechanism of the reaction, the following experiments were performed (Scheme 3): (i) a competitive esterification experiment involving benzoic acid and 4-nitrobenzaldehyde (**1a**) with toluene under the reaction conditions produced the corresponding 4-nitrobenzyl benzoate (**2a**) in 88% yield. This rules out the *in situ* formation of benzoic acid during the reaction course; (ii) addition of BHT (2,6-di-*tert*-butyl-4-methylphenol) as a radical scavenger resulted in decrease of yield (trace amount) of ester products. (iii) Further, when TEMPO (1 equiv.) was treated with **1a** in the absence of either toluene or MeOH, under the reaction conditions, the corresponding TEMPO-ester adduct **6** was isolated

Table 2 Ti superoxide catalysed esterification of aldehydes with toluene or MeOH: substrate scopes[a,b]



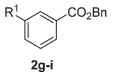
2a-f

2b, R^1 = OMe, 88%, 8 h
2c, R^1 = SMe, 79%, 8 h
2d, R^1 = H, 88%, 5 h
2e, R^1 = F, 92%, 3 h
2f, R^1 = CN, 96%, 4 h
2g, R^1 = NO_2, 86%,4 h
2h, R^1 = Br, 94%,6 h
2i, R^1 = Cl, 86%, 5 h

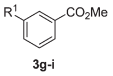


3a-f

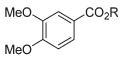
3b, R^1 = OMe, 82%,10 h
3c, R^1 = SMe, 82%,10 h
3d, R^1 = Cl, 90%, 5 h
3e, R^1 = CF_3 ,88%, 5 h
3f, R^1 = CN, 92%, 8 h
3g, R^1 = NO_2, 86%, 5 h
3h, R^1 = Br, 88%, 8 h
3i, R^1 = Cl, 90%, 6 h

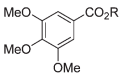


2g-i



3g-i



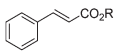


2j, R = Bn, 90%, 6 h
3j, R = Me, 86%, 12 h

2k, R = Bn, 92%, 8 h
3k, R = Me, 84%, 12 h

2l, R = Bn, 92%, 5 h

2m, R = Bn, 90%, 6 h
3l, R = Me, 86%, 8 h

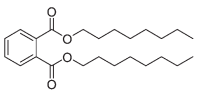


2n, R = Bn, 80%, 6 h
3m, R = Me, 76%, 12 h

2o, R = Bn, 88%, 4 h
3n, R = Me, 70%, 8 h

2p, R = Bn, 86%, 5 h
3o, R = Me, 72%, 8 h

2q, R = Bn, 92%, 5 h



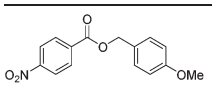
2r, R = Bn, 92% 5 h
3p, R = Me, 88% 10 h

2s, R = Bn, 90%, 6 h
3q, R = Me, 86%, 12 h

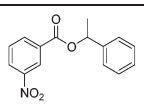
3r, 96% 6 h; 100 g scale

[a] Reaction conditions: for benzyl esters: aldehyde (1 mmol), Ti superoxide (10 wt%), TBHP (3 mmol), toluene (5 mmol), 80 °C; for methyl esters: aldehyde (1 mmol), Ti superoxide (10 wt%), TBHP (2 mmol), methanol (5 mmol), 25 °C. [b] Isolated yield of esters after column chromatographic purification.

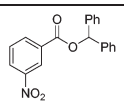
Table 3 Ti superoxide catalyzed esterification of nitroaldehydes with alkyl arenes[a,b]



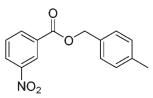
4a 70%, 8 h



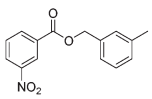
4b, 88%, 6 h



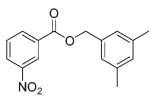
4c, 88%, 6 h



4d, 90%, 4 h



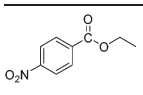
4e, 88, 4 h



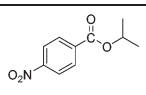
4f, 92%, 3 h

[a] Reaction conditions: nitrobenzaldehydes (1 mmol), Ti superoxide (10 wt%), TBHP (3 mmol), alkylarenes (1 mmol), CH_3CN, 80 °C. [b] Isolated yields of benzyl ester after chromatographic purification.

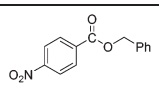
Table 4 Ti superoxide catalyzed esterification of aldehydes with a variety of alcohols[a,b]



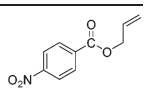
5a, 80%, 8 h



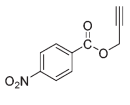
5b, 78%, 10 h



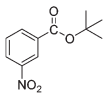
2a, 72%, 10 h



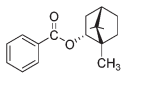
5c, 82%, 9 h



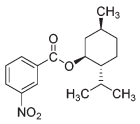
5d, 80%, 10 h



5e, 52%, 10 h



5f, 80%, 6 h

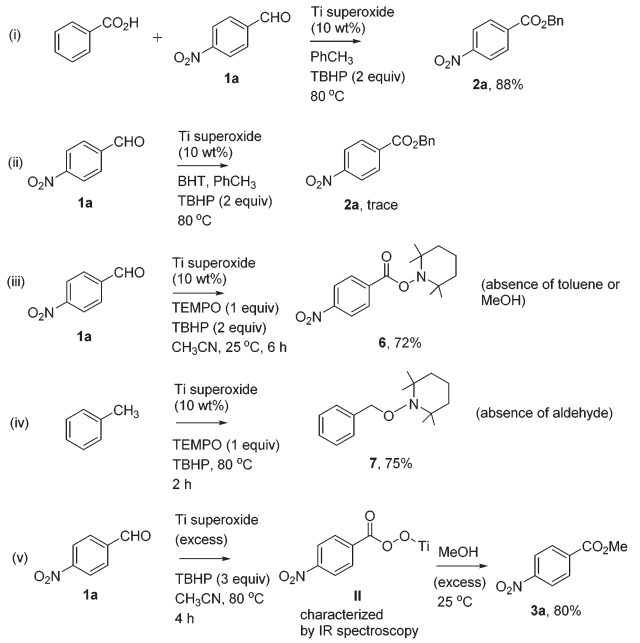


5g, 81%, 6 h

[a] Reaction conditions: aldehydes (1 mmol), Ti superoxide (10 wt%), TBHP (2 mmol), alcohols (5 mmol), CH_3CN, 25 °C. [b] Isolated yield of esters after column chromatographic purification.

in 72% yield. This result indicates the involvement of a benzoyl radical in the catalytic cycle; (iv) it was further evidenced that the reaction between toluene and TEMPO (1 equiv.), under oxidative esterification, in the absence of aldehyde, producing benzyl oxyaminated product **7** in 75% yield; (v) in the absence of either toluene or methanol, **1a** under the same protocol with excess Ti superoxide gave the solid intermediate **II**, which was characterized by the FTIR spectrum (a strong carbonyl absorption frequency at 1742 cm^{-1}) (Fig. 1); compound **II** on further reaction with MeOH gave methyl ester **3a** in 80% yield; this study confirms the formation of species **C** in the catalytic cycle; (vi) when ethyl benzene was subjected to oxidation with TBHP (1 equiv.) and Ti superoxide (10 wt%) in the absence of aldehyde gave 1-phenylethan-1-ol (60% yield); (vii) when the aforementioned reaction was carried out in the presence of light without a catalyst, no reaction took place. This rules out the role of light in the reaction.

Based on the above observation, a possible catalytic cycle is proposed in Scheme 4. Thermal decomposition of TBHP in



Scheme 3 Control experiments demonstrating the radical pathway.

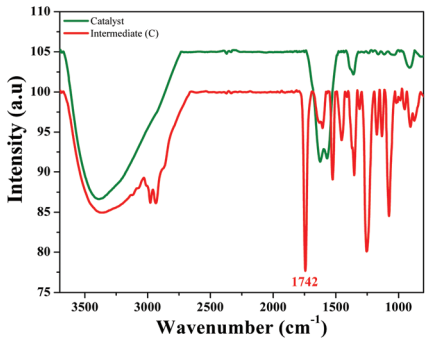
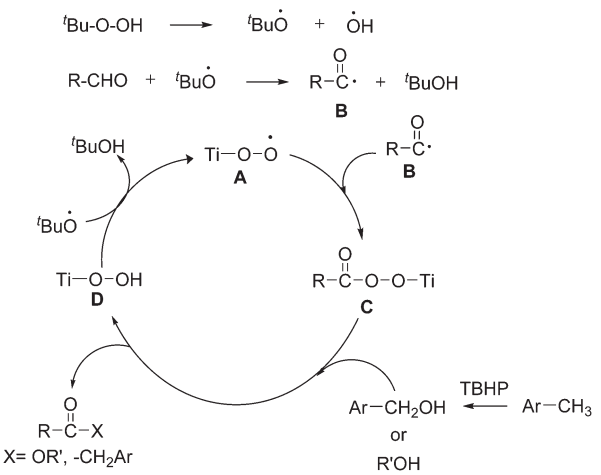


Fig. 1 FTIR spectra of Ti superoxide and peroxo intermediate (**C**).



Scheme 4 Catalytic cycle for oxidative esterification of aldehydes.

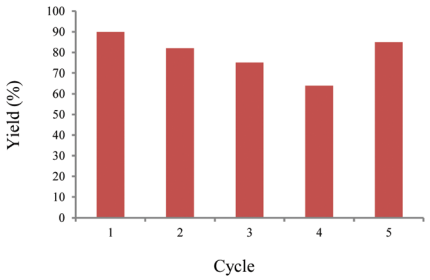
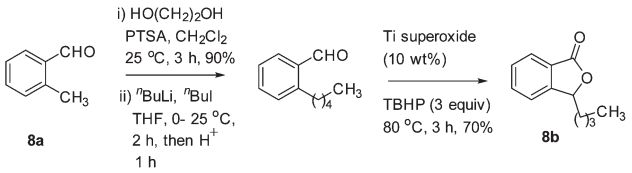


Fig. 2 Reusability study of the catalyst in the case of 4-nitrobenzaldehyde with methanol.



Scheme 5 Synthesis of anti-convulsant drug 3-butylphthalide.

the presence of aldehyde generates acyl radical **B**, which subsequently couples with a titanium superoxide radical ion to form a Ti peroxo species **C**. Nucleophilic attack of alcohol onto **C** produces an ester with the liberation of hydroxyl species **D**. Finally, 1 mole of TBHP is utilized to oxidize **D** to regenerate catalyst **A** ready for the next catalytic cycle.

The catalyst can be recovered readily by simple filtration and was reused successfully for 5 cycles in the oxidative esterification of **1a** with methanol. The results are shown in Fig. 2, wherein, a slight decrease in catalytic efficiency could be observed after the 4th cycle. However, by the addition of one more equivalent of TBHP after the 4th cycle reaction mixture, its activity was restored to the original level (yield of ester: 80%). The catalyst was found to be quite active and did not deteriorate as proven by the reusability study, powder XRD of the used catalyst and AAS analysis of the reaction sample for Ti leaching.

Finally, its intramolecular version is demonstrated in the short synthesis of 3-butylphthalide,[11] an anti-convulsant agent used in the treatment of stroke. Thus, *o*-pentylbenzaldehyde, readily obtained from *o*-tolualdehyde (**8a**), was subjected to intramolecular oxidative esterification under the present protocol to afford **8b** in 70% yield (Scheme 5).

Conclusion

In summary, we have demonstrated, for the first time, a new, practical, and truly heterogeneous catalytic procedure for the oxidative esterification of aldehydes with alkylarenes that leads to the production of a variety of esters in excellent yields. Also, we have successfully achieved its application to the sterically

challenged and natural alcohols using the present protocol. The reaction is convenient to be carried out under environmentally benign and mild conditions, displaying a wide range of substrate scope tolerating a variety of functional groups as demonstrated in the synthesis of 3-butyl phthalide. Further work to expand this catalytic process to an asymmetric intramolecular version is under investigation.

Experimental section

General

Solvents were purified and dried by standard procedures before use; petroleum ether of boiling range 60–80 °C was used. Melting points were uncorrected and recorded on a Buchi B-542 instrument. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer unless mentioned otherwise. Infrared spectra were recorded on a Shimadzu FTIR-8400 spectrometer and absorption is expressed in cm^{-1}. ESI-MS were recorded on a Thermo Finnigan LCQ Advantage spectrometer in the ESI mode with a spray voltage of 4.8 kV. All chemicals were purchased from Sigma-Aldrich and used without further purification. Purification was done using column chromatography (230–400 mesh). In the ^{13}C NMR spectrum, the C-peak at 96.1 corresponds to CCl_4, as we have used the $CDCl_3$: CCl_4 (7 : 3) solvent for the NMR study. Optical rotations were measured using the sodium D line on a JASCO-181 digital polarimeter.

General experimental procedure for the preparation of benzyl esters (2a–s)

In an oven dried round bottom flask containing 4-nitrobenzaldehyde **1a** (1 g, 6.61 mmol) and titanium superoxide as catalyst (0.1 g, 10 wt%) in dry toluene (3.0 g, 33.05 mmol) was added TBHP in decane (5–6 M) (3.6 mL, 19.83 mmol) in a dropwise manner under a nitrogen atmosphere. Then the flask was fitted with a condenser and the mixture was heated at 80 °C for 3 h. After the complete disappearance of aldehyde (judged by TLC; using DNP solution), the flask was cooled to 25 °C, and the mixture filtered through a sintered funnel using CH_2Cl_2 as an eluent. Then the organic layer was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by column chromatography over silica (230–400 mesh) using petroleum ether/ethyl acetate (19 : 1 v/v) as an eluent to give benzyl 4-nitrobenzoate (**2a**).

Preparation of the titanium superoxide catalyst[8a]

To a stirred solution of 50% aq. H_2O_2 (5.98 g, 0.175 mmol) was added titanium tetraisopropoxide ($Ti(O^iPr)_4$ (5.0 g, 0.0175 mmol) in anhydrous methanol (50 mL) over 40 min under a nitrogen atmosphere with continuous stirring at 25 °C for 2 h. The yellow-colored solid formed was filtered on a sintered funnel, washed thoroughly with anhydrous methanol, and dried under reduced pressure (3 mm Hg) at 25 °C for 1 h to give titanium superoxide 98% yield.

Benzyl 4-nitrobenzoate (2a). Yield: 90%; 1.53 g; colorless gum; IR ($CHCl_3$, cm^{-1}): ν_{max} 2910, 2828, 1717, 1605, 1523, 1330, 1262, 1128; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.09–8.40 (m, 4H), 7.28–7.52 (m, 5H), 5.40 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.4, 150.7, 135.5, 135.3, 130.8, 128.8, 128.5, 123.5, 67.6; HRMS (ESI): calc. for $[(C_{14}H_{12}NO_4)H]$ (M + H) 258.0766, found 258.0760.

Benzyl 4-methoxybenzoate (2b). Yield: 88%; 1.56 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 3021, 2937, 1711, 1520, 1125; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.02 (d, J = 9.0 Hz, 2H), 7.19–7.49 (m, 5H), 6.90 (d, J = 9.1 Hz, 2H), 5.33 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.0, 163.4, 136.3, 131.8, 128.6, 128.1, 122.6, 113.6, 66.4, 55.3; HRMS (ESI): calc. for $[(C_{14}H_{15}O_3)H]$ (M + H) 243.1021, found 243.1025.

Benzyl 4-(methylthio)benzoate (2c). Yield: 79%; 1.3 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 3027, 2953, 2923, 1712, 1307, 1269, 1254, 1162; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.08 (dd, J = 8.3, 1.4 Hz, 2H), 7.54 (d, J = 7.3 Hz, 1H), 7.33–7.48 (m, 7H), 5.36 (s, 2H), 1.26 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.2, 144.4, 136.0, 132.9, 130.1, 129.7, 128.5, 128.3, 128.2, 128.1, 127.8, 66.6, 29.7; HRMS (ESI): calc. for $[(C_{15}H_{14}O_2S)H]$ (M + H) 259.0793, found 259.0795.

Benzyl benzoate (2d). Yield: 72%; 1.44 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 3021, 2957, 1721, 1600, 1525; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.09 (d, J = 7.1 Hz, 2H), 7.52–7.63 (m, 1H), 7.31–7.51 (m, 7H), 5.38 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.2, 136.1, 133.0, 129.8, 128.6, 128.4, 128.2, 66.7; HRMS (ESI): calc. for $[(C_{14}H_{12}O_2)H]$ (M + H) 213.0916, found 213.0919.

Benzyl 4-fluorobenzoate (2e). Yield: 92%; 1.7 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 3030, 2812, 1725, 1610, 1525, 1101; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.98–8.16 (m, 2H), 7.33–7.46 (m, 5H), 7.02–7.17 (m, 1H), 5.34 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 167.1, 166.2, 165.3, 164.5, 136.1, 135.9, 132.9, 132.3, 132.2, 130.2, 129.7, 128.6, 128.6, 128.3, 128.2, 128.2, 126.4, 126.4, 115.6, 115.4, 66.8; HRMS (ESI): calc. for $[(C_{14}H_{11}FO_2)H]$ (M + H) 231.0821, found 231.0825.

Benzyl 4-cyanobenzoate (2f). Yield: 96%; 1.7 g; colorless gum; IR ($CHCl_3$, cm^{-1}): ν_{max} 3011, 2982, 2115, 1717, 1610, 1501; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.16 (d, J = 8.7 Hz, 2H) 7.73 (d, J = 8.7 Hz, 2H), 7.33–7.49 (m, 5H), 5.39 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.6, 135.3, 133.9, 132.1, 130.2, 128.7, 128.6, 128.4, 117.7, 116.6, 67.5; HRMS (ESI): calc. for $[(C_{15}H_{11}NO_2)H]$ (M + H) 238.0868, found 238.0860.

Benzyl 3-nitrobenzoate (2g). Yield: 86%; 1.4 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 2975, 1718, 1512, 1421, 1115, 708; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.88 (s, 1H), 8.30–8.48 (m, 2H), 7.65 (t, J = 8.0 Hz, 1H), 7.43–7.48 (m, 2H), 7.33–7.43 (m, 3H), 5.41 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 163.9, 148.0, 135.1, 135.0, 131.6, 129.4, 128.5, 128.4, 128.2, 127.2, 124.3, 67.3; HRMS (ESI): calc. for $[(C_{14}H_{11}NO_4)H]$ (M + H) 258.0766, found 258.0770.

Benzyl 3-bromobenzoate (2h). Yield: 94%; 1.4 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 3100, 2980, 1720, 1421, 1125; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.98–8.21 (m, 2H), 7.55–775 (m, 1H), 7.38–7.48 (m, 6H), 5.36 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$):

δ 165.0, 135.9, 133.0, 132.6, 129.9, 128.6, 128.1, 122.4, 67.1; HRMS (ESI): calc. for $[(C_{14}H_{11}BrO_2)H]$ (M + H) 291.0021, found 291.0021.

Benzyl 3-chlorobenzoate (2i). Yield: 86%; 1.5 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 3105, 2920, 2810, 1715, 1580, 1417; ^1H NMR (200 MHz, $CDCl_3$): δ 7.96–8.15 (m, 2H), 7.49–7.62 (m, 1H), 7.34–7.45 (m, 5H), 5.36 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.3, 136.1, 133.0, 130.2, 129.8, 128.7, 128.6, 128.4, 128.2, 128.2, 127.9, 66.7; HRMS (ESI): calc. for $[(C_{14}H_{11}ClO_2)H]$ (M + H) 247.0526, found 247.0522.

Benzyl 3,4-dimethoxybenzoate (2j). Yield: 90%; 1.47 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 2981, 2910, 1711, 1575, 1135, 763; ^1H NMR (200 MHz, $CDCl_3$): δ 7.70 (dd, J = 8.5, 2.1 Hz, 1H), 7.56 (d, J = 2.3 Hz, 1H), 7.29–7.49 (m, 5H), 6.86 (d, J = 8.2 Hz, 1H), 5.34 (s, 2H), 3.93 (s, 3H), 3.92 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.9, 152.9, 142.2, 136.0, 128.5, 128.2, 128.1, 125.0, 106.9, 106.7, 66.7, 60.8, 56.1; HRMS (ESI): calc. for $[(C_{16}H_{16}O_4)H]$ (M + H) 273.1127, found 273.1132.

Benzyl 3,4,5-trimethoxybenzoate (2k). Yield: 92%; 1.41 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 3050, 2911, 1710, 1616, 1400; ^1H NMR (200 MHz, $CDCl_3$): δ 7.21–7.49 (m, 7H), 5.35 (s, 2H), 3.81–3.96 (m, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.9, 152.9, 148.4, 136.1, 130.0, 128.4, 128.2, 127.9, 123.5, 122.4, 111.9, 110.0, 66.3, 55.7; HRMS (ESI): calc. for $[(C_{17}H_{18}O_5)H]$ (M + H) 303.1232, found 303.1232.

1,2-Dibenzyl phthalate (2l). Yield: 92%; 2.37 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 2971, 1811, 1720, 1541, 1410; ^1H NMR (200 MHz, $CDCl_3$): δ 7.67–7.79 (m, 2H), 7.47–7.58 (m, 2H), 7.27–7.37 (m, 10H), 5.20 (s, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 167.1, 135.5, 132.0, 131.0, 129.0, 128.5, 128.4, 128.3, 67.3; HRMS (ESI): calc. for $[(C_{22}H_{18}O_4)H]$ (M + H) 347.1283, found 347.1285.

1,4-Dibenzyl phthate (2m). Yield: 90%; 2.32 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 3071, 2911, 1720, 1611, 1580, 1051; ^1H NMR (200 MHz, $CDCl_3$): δ 8.07–8.14 (m, 4H), 7.33–7.46 (m, 10H), 5.37 (s, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.5, 135.7, 134.0, 129.7, 128.7, 128.5, 128.3, 67.1; HRMS (ESI): calc. for $[(C_{22}H_{18}O_4)H]$ (M + H) 347.1283, found 347.1283.

Benzyl cinnamate (2n). Yield: 80%; 1.4 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 3027, 2983, 2923, 1712, 1617, 1307, 1278, 1162, 805, 767; ^1H NMR (200 MHz, $CDCl_3$): δ 7.72 (d, J = 16.0 Hz, 1H), 7.28–7.54 (m, 11H), 6.47 (d, J = 16.0 Hz, 1H), 5.24 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.6, 145.2, 136.1, 134.4, 130.4, 128.9, 128.6, 128.4, 128.2, 118.0, 66.3; HRMS (ESI): calc. for $[(C_{16}H_{14}O_2)H]$ (M + H) 239.1072, found 239.1075.

Benzyl acrylate (2o). Yield: 88%; 2.54 g; colorless liduid; IR ($CHCl_3$, cm^{-1}): ν_{max} 2931, 2848, 1720, 1621, 1580, 1515, 1421; ^1H NMR (200 MHz, $CDCl_3$): δ 7.35–7.44 (m, 6H), 6.48 (dd, J = 17.2, 1.7 Hz, 1H), 6.18 (dd, J = 17.3, 10.2 Hz, 1H), 5.87 (dd, J = 10.2, 1.6 Hz, 1H), 5.21 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.7, 135.8, 130.9, 128.5, 128.3, 128.2, 66.2; HRMS (ESI): calc. for $[(C_{10}H_{10}O_2)H]$ (M + H) 163.0759, found 163.0760.

Benzyl (*E*)-but-2-enoate (2p). Yield: 88%; 2.21 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 3010, 2971, 2882, 1725, 1652, 1568, 1312; ^1H NMR (200 MHz, $CDCl_3$): δ 7.34 (s, 5H), 6.89–7.13 (m, 1H), 5.80–5.98 (m, 1H), 5.16 (s, 2H), 1.89 (dd, J = 6.88, 1.7 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.1, 145.0, 136.3, 128.6, 128.2, 128.2, 122.7, 66.0, 18.1; HRMS (ESI): calc. for $[(C_{11}H_{12}O_2)H]$ (M + H) 177.0916, found 177.0910.

Benzyl propionate (2q). Yield: 90%; 2.51 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 2958, 2934, 2839, 1713, 1606, 1511, 1462, 1373, 1258, 1167, 1098, 1029, 847, 769, 741, 721; ^1H NMR (200 MHz, $CDCl_3$): δ 7.32–7.36 (m, 6H), 5.11 (s, 2H), 2.37 (q, J = 7.3 Hz, 2H), 1.16 (t, J = 7. 6 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.2, 136.1, 133.0, 129.8, 128.5, 128.4, 128.2, 66.7, 27.6, 9.2; HRMS (ESI): calc. for $[(C_{10}H_{12}O_2)H]$ (M + H) 165.0916, found 165.0917.

Benzyl thiophene-3-carboxylate (2r). Yield: 92%; 1.79 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 3027, 2923, 1712, 1524, 1417, 1374, 1356, 1273,1258, 1094; ^1H NMR (200 MHz, $CDCl_3$): δ 7.77–7.95 (m, 1H), 7.50–7.65 (m, 1H), 7.32–7.48 (m, 5H), 7.06–7.18 (m, 1H), 5.34 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 161.9, 135.9, 134.0, 133.8, 133.6, 132.4, 128.6, 128.3, 128.2, 127.9, 127.7, 66.7; HRMS (ESI): calc. for $[(C_{12}H_{10}O_2S)H]$ (M + H) 219.0480, found 219.0490.

Benzyl nicotinate (2s). Yield: 90%; 1.79 g; colorless gum; IR ($CHCl_3$, cm^{-1}): ν_{max} 3102, 2987, 2897, 1720, 1624, 1528, 1325, 1014; ^1H NMR (200 MHz, $CDCl_3$): δ 9.26 (s, 1H), 8.77 (d, J = 3.5 Hz, 1H), 8.31 (dt, J = 8.0, 2.0 Hz, 1H), 7.25–7.50 (m, 6H), 5.39 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.9, 153.4, 151.0137.1, 135.5, 128.7, 128.5, 128.3, 126.0, 123.2, 67.1; HRMS (ESI): calc. for $[(C_{13}H_{11}NO_2)H]$ (M + H) 214.0868, found 214.0873.

General experimental procedure for the preparation of methyl esters (3a–q)

In an oven dried round bottom flask containing 4-nitrobenzaldehyde **1a** (1 g, 6.61 mmol) and titanium superoxide as catalyst (0.1 g, 10 wt%) in dry MeOH (1.32 mL, 33.05 mmol) was added TBHP in decane (5–6 M) (2.4 mL, 13.22 mmol) in a dropwise manner under a nitrogen atmosphere. Then the flask was stirred at 25 °C for 6 h. After the complete disappearance of aldehyde (judged by TLC; using DNP solution), the reaction mixture was filtered through a sintered funnel using CH_2Cl_2 as an eluent. Then the organic layer was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by column chromatography over silica (230–400 mesh) using petroleum ether/ethyl acetate (19 : 1 v/v) as an eluent to give methyl 4-nitrobenzoate (**3a**).

Methyl 4-nitrobenzoate (3a). Yield: 88%; 1.0 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 2810, 1718, 1620, 1524, 1105; ^1H NMR (200 MHz, $CDCl_3$): δ 8.24 (m, 4H), 3.97 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.9, 150.3, 135.3, 130.5, 123.3, 52.6; HRMS (ESI): calc. for $[(C_8H_7NO_4)H]$ (M + H) 182.0453, found 182.0455.

Methyl-4-methoxybenzoate (3b). Yield: 82%; 1.0 g; colorless solid; mp.: 49–51 °C (lit.[4k] mp. 49 °C); IR ($CHCl_3$, cm^{-1}): ν_{max} 3050, 2980, 2910, 1716, 1615, 1548, 1258; ^1H NMR (200 MHz, $CDCl_3$): δ 7.98 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.5, 163.2,

131.5, 122.6, 113.5, 55.2, 51.7; HRMS (ESI): calc. for $[(C_9H_{10}O_3)H]$ (M + H) 167.0708, found 167.0710.

Methyl 4-(methylthio)benzoate (3c). Yield: 82%; 0.98 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 2920, 1718, 1658, 1541, 1325, 1258; ^1H NMR (200 MHz, $CDCl_3$): δ 7.86–8.02 (m, 2H), 7.16–7.33 (m, 2H), 3.90 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.5, 145.2, 129.5, 125.9, 124.5, 51.7, 14.4; HRMS (ESI): calc. for $[(C_9H_{10}SO_2)H]$ (M + H) 183.0480, found 183.0485.

Methyl-4-chlorobenzoate (3d). Yield: 90%; 1.09 g; colorless gum; IR ($CHCl_3$, cm^{-1}): ν_{max} 2952, 2937, 1725, 1613, 1548, 1256; ^1H NMR (200 MHz, $CDCl_3$): δ 7.97 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.9, 139.3, 130.9, 128.6, 52.1; HRMS (ESI): calc. for $[(C_8H_7ClO_2)H]$ (M + H) 171.0213, found 171.0215.

Methyl 4-(trifluoromethyl)benzoate (3e). Yield: 88%; 1.03 g; colorless gum; IR ($CHCl_3$, cm^{-1}): ν_{max} 2972, 1725, 1657, 1585, 1158; ^1H NMR (200 MHz, $CDCl_3$): δ 8.14 (m, J = 8.2 Hz, 2H), 7.70 (m, J = 8.2 Hz, 2H), 3.95 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.5, 135.7, 135.4, 134.7, 134.1, 133.3, 132.5, 129.9, 128.0, 126.2, 125.4, 125.3, 125.2, 125.1, 120.8, 52.3; HRMS (ESI): calc. for $[(C_9H_7F_3O_2)H]$ (M + H) 205.0476, found 205.0475.

Methyl-4-cyanobenzoate (3f). Yield: 90%; 1.13 g; colorless gum; IR ($CHCl_3$, cm^{-1}): ν_{max} 2974, 2225, 1725, 1658, 1425, 1121; ^1H NMR (200 MHz, $CDCl_3$): δ 8.14 (d, J = 8.5 Hz, 2H), 7.75 (d, J = 8.6 Hz, 2H), 3.96 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.1, 133.9, 132.1, 130.1, 117.7, 116.5, 52.6; HRMS (ESI): calc. for $[(C_9H_7NO_2)H]$ (M + H) 162.0555, found 162.0559.

Methyl 3-nitrobenzoate (3g). Yield: 86%; 1.03 g; colorless solid; mp. 78–80 °C (lit.[4k] mp. 78 °C); IR ($CHCl_3$, cm^{-1}): 2857, 1722, 1620, 1587, 1232; ^1H NMR (200 MHz, $CDCl_3$): δ 8.81–8.87 (m, 1H), 8.34–8.44 (m, 2H), 7.61–7.69 (m, 1H), 3.99 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.6, 148.2, 135.1, 131.8, 129.5, 127.2, 124.4, 52.6; HRMS (ESI): calc. For $[(C_8H_7NO_4)H]$ (M + H) 182.0453, found 182.0455.

Methyl 3-bromobenzoate (3h). Yield: 88%; 1.02 g; colorless gum; IR ($CHCl_3$, cm^{-1}): ν_{max} 2910, 1722, 1590, 1257, 1187; ^1H NMR (200 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.95 (d, J = 9.2 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.27–7.36 (m, 1H), 3.92 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.4, 135.7, 132.6, 132.0, 129.8, 128.1, 122.4, 52.2; HRMS (ESI): calc. for $[(C_8H_7BrO_2)H]$ (M + H) 214.9708, found 214.9708.

Methyl 3-chlorobenzoate (3i). Yield: 90%; 1.09 g; colorless gum; IR ($CHCl_3$, cm^{-1}): ν_{max} 2910, 1728, 1535, 1283, 1125; ^1H NMR (200 MHz, $CDCl_3$): δ 8.00 (t, J = 1.8 Hz, 1H), 7.90 (dt, J = 7.7, 1.3 Hz, 1H), 7.47–7.56 (m, 1H), 7.38 (d, J = 7.7 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.5, 134.5, 132.8, 131.8, 129.5, 127.6, 52.2; HRMS (ESI): calc. for $[(C_8H_7ClO_2)H]$ (M + H) 171.0213, found 171.0215.

Methyl-3,4-dimethoxybenzoate (3j). Yield: 86%; 1.0 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 3110, 2911, 1715, 1625, 1368, 1152; ^1H NMR (200 MHz, $CDCl_3$): δ 7.66 (dd, J = 8.5, 1.9 Hz, 1H), 7.53 (d, J = 1.8 Hz, 1H), 6.87 (d, J = 8.3 Hz, 1H), 3.93 (s, 6H) 3.89 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.6, 152.9, 148.6, 123.4, 111.9, 110.2, 55.8, 51.8; HRMS (ESI): calc. for $[(C_{10}H_{12}O_4)H]$ (M + H) 197.0814, found 197.0815.

Methyl-3,4,5-trimethoxybenzoate (3k). Yield: 84%; 0.96 g; colorless solid; mp. 82–85 °C (lit.[4k] mp. 82 °C); IR ($CHCl_3$, cm^{-1}): ν_{max} 2991, 1720, 1547, 1180; ^1H NMR (200 MHz, $CDCl_3$): δ 7.28 (s, 2H), 3.89–3.93 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.4, 152.9, 142.1, 125.0, 106.8, 60.7, 56.1, 52.1; HRMS (ESI): calc. for $[(C_{11}H_{14}O_5)H]$ (M + H) 227.0919, found 227.0920.

Dimethyl terephthalate (3l). Yield: 88%; 1.27 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 3012, 2987, 1725, 1645, 1058; ^1H NMR (200 MHz, $CDCl_3$): δ 7.77 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 3.74 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.8, 144.7, 132.7, 128.0, 56.0; HRMS (ESI): calc. for $[(C_{10}H_{10}O_4)H]$ (M + H) 195.0657, found 195.0650.

Methyl cinnamate (3m). Yield: 76%; 0.93 g; colorless gum; IR ($CHCl_3$, cm^{-1}): ν_{max} ^1H NMR (200 MHz, $CDCl_3$): δ 7.71 (d, J = 16.0 Hz, 1H), 7.48–7.59 (m, 2H), 7.35–7.44 (m, 3H), 6.46 (d, J = 16.0 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 167.3, 144.8, 134.3, 130.2, 128.8, 128.0, 117.7, 51.6; HRMS (ESI): calc. for $[(C_{10}H_{10}O_2)H]$ (M + H) 163.0759, found 163.0760.

Methyl acrylate (3n). Yield: 70%; 1.07 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 1720, 1621, 1569, 1428, 1104; ^1H NMR (200 MHz, $CDCl_3$): δ 6.40 (dd, J = 17.2, 1.7 Hz, 1H), 6.11 (dd, J = 17.2, 10.3 Hz, 1H), 5.81 (dd, J = 10.3, 1.7 Hz, 1H), 3.75 (s, 3H),; ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.2, 130.3, 127.9, 51.2; HRMS (ESI): calc. for $[(C_4H_6O_2)H]$ (M + H) 87.0446, found 87.0445.

Methyl (*E*)-but-2-enoate (3o). Yield: 72%; 1.02 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 1725, 1652, 1590, 1442, 1236; ^1H NMR (200 MHz, $CDCl_3$): δ 6.98 (dd, J = 15.6, 6.9 Hz, 1H), 5.85 (dd, J = 15.5, 1.6 Hz, 1H), 3.72 (s, 3H), 1.88 (dd, J = 6.9, 1.7 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.3, 144.1, 121.9, 50.7, 17.3; HRMS (ESI): calc. for $[(C_5H_8O_2)H]$ (M + H) 101.0603, found 101.0609.

Methyl thiophene-2-carboxylate (3p). Yield: 88%; 1.11 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 2912, 1725, 1645, 1560, 1512, 1464, 1237; ^1H NMR (200 MHz, $CDCl_3$): δ 7.81 (d, J = 3.0 Hz, 1H), 7.56 (d, J = 4.6 Hz, 1H), 7.11 (t, J = 4.3 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 162.5, 133.4, 133.3, 132.2, 127.6, 77.6, 76.4, 52.0; HRMS (ESI): calc. for $[(C_6H_6SO_2)$-H] (M + H) 143.0167, found 143.0169.

Methyl nicotinate (3q). Yield: 86%; 1.10 g; colorless gum; IR ($CHCl_3$, cm^{-1}): ν_{max} 3011, 2987, 1718, 1625, 1485, 1201, 1101, 748; ^1H NMR (200 MHz, $CDCl_3$): δ 9.22 (m, 1H), 8.77 (m, 1H), 7.39 (m, 1H), 8.29 (m, 1H), 3.95 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.6, 153.3, 150.7, 136.9, 125.8, 123.1, 52.2; HRMS (ESI): calc. for $[(C_7H_7NO_2)H]$ (M + H) 138.0555, found 138.0559.

Dioctyl phthalate (3r). To a well-stirred solution of phthaldialdehyde (**1r**) (100 g, 0.745 mol) in dry CH_3CN (1000 mL), 1-octanol (194.18 g, 1.491 mol) and titanium superoxide (10 g) were added. Then TBHP in decane (5–6 M) (542.56 mL, 2.98 mol) was added dropwise to the reaction mixture and kept stirring at 25 °C for 6 h. After the reaction (checked by TLC), the reaction mixture was filtered off through a sintered

funnel. Then the organic layer was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by column chromatography over silica (230–400 mesh) using petroleum ether/ethyl acetate (19 : 1 v/v) as an eluent to give the desired dioctyl phthalate (**3r**). Yield: 96%; 279.53 g; IR ($CHCl_3$, cm^{-1}): ν_{max} 3112, 1720, 1621, 1580, 1460, 1150, 1012, 845; ^1H NMR (200 MHz, $CDCl_3$): δ 7.46–7.60 (m, 2H), 4.28 (t, J = 6.7 Hz, 4H), 1.62–1.90 (m, 5H), 1.22–1.44 (m, 22H), 0.85–0.93 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 167.4, 132.4, 130.7, 128.8, 65.7, 31.8, 29.2, 29.2, 28.6, 26.0, 22.6, 14.1; HRMS (ESI): calc. for $[(C_{24}H_{38}O_4)H]$ (M + H) 391.2848, found 391.2840.

General experimental procedure for the preparation of esters (4a–f), (5a–h) and 2a

In an oven dried round bottom flask containing benzaldehydes (1 equiv.), alcohols or alkylbenzenes (1 equiv.) and titanium superoxide as catalyst (0.1 g, 10 wt%) in dry CH_3CN (10 mL) was added TBHP in decane (2 or 3 equiv.) in a dropwise manner. Then the flask was stirred at 25 °C or heated at 80 °C. After the complete disappearance of aldehyde (judged by TLC), the reaction mixture was filtered through a sintered funnel using CH_2Cl_2 as an eluent. Then the organic layer was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by column chromatography over silica (230–400 mesh) using petroleum ether/ethyl acetate (19 : 1 v/v) as an eluent to give the corresponding esters.

4-Nitrophenyl 4-methoxybenzoate (4a). Yield: 70%; 1.47 g; colorless gum; IR ($CHCl_3$, cm^{-1}): ν_{max} 3105, 2985, 1714, 1637, 1549, 1275, 812; ^1H NMR (200 MHz, $CDCl_3$): δ 8.25 (d, J = 8.7 Hz, 2H), 8.03 (d, J = 8.8 Hz, 2H), 7.59 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 5.42 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 163.8, 156.0, 148.4, 143.6, 136.6, 131.9, 128.3, 123.9, 113.8, 64.9, 55.4; HRMS (ESI): calc. for $[(C_{15}H_{13}NO_5)H]$ (M + H) 288.0872, found 288.0875.

1-Phenylethyl 3-nitrobenzoate (4b). Yield: 88%; 1.57 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 3015, 2985, 2910, 1718, 1642, 1587, 1235, 1148; ^1H NMR (200 MHz, $CDCl_3$): δ 8.88 (t, J = 1.8 Hz, 1H), 8.33–8.47 (m, 2H), 7.64 (t, J = 8.0 Hz, 1H), 7.28–7.51 (m, 5H), 6.16 (q, J = 6.6 Hz, 1H), 1.72 (d, J = 6.7 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 163.5, 148.3, 140.9, 135.2, 132.3, 129.5, 128.7, 128.2, 127.3, 126.1, 124.5, 74.1, 22.2; HRMS (ESI): calc. for $[(C_{15}H_{13}NO_4)H]$ (M + H) 272.0923, found 272.0926.

Benzhydryl 3-nitrobenzoate (4c). Yield: 88%; 1.94 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 3120, 3050, 1717, 1630, 1545, 1289, 1110; ^1H NMR (200 MHz, $CDCl_3$): δ 8.82–9.02 (m, 1H), 8.31–8.48 (m, 2H), 7.62 (t, J = 7.9 Hz, 1H), 7.39–7.44 (m, 4H), 7.32–7.38 (m, 4H), 7.26–7.32 (m, 2H), 7.14 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 163.3, 148.4, 139.5, 135.3, 132.1, 129.6, 128.7, 128.3, 127.5, 127.2, 124.7, 78.4; HRMS (ESI): calc. for $[(C_{20}H_{15}NO_4)H]$ (M + H) 334.1079, found 334.1082.

4-Methylbenzyl 3-nitrobenzoate (4d). Yield: 90%; 1.61 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 3012, 2950, 1718, 1655, 1584, 1431, 1165; ^1H NMR (200 MHz, $CDCl_3$): δ 8.86 (t, J = 1.8 Hz, 1H), 8.29–8.48 (m, 2H), 7.63 (t, J = 8.0 Hz, 1H), 7.29–7.45 (m, 2H), 7.14–7.26 (m, 2H), 5.36 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.2, 148.3, 138.5, 135.3, 132.3, 132.1, 129.4, 128.7, 127.4, 124.7, 67.6, 21.3; HRMS (ESI): calc. for $[(C_{15}H_{13}NO_4)H]$ (M + H) 272.0923, found 272.0920.

3-Methylbenzyl 3-nitrobenzoate (4e). Yield: 88%; 1.57 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 3050, 2965, 1718, 1650, 1580, 1480, 1257, 1106; ^1H NMR (200 MHz, $CDCl_3$): δ 8.85 (t, J = 1.9 Hz, 1H), 8.37 (dt, J = 8.0, 2.0 Hz, 2H), 7.62 (t, J = 8.0 Hz, 1H), 7.19–7.33 (m, 3H), 7.08–7.18 (m, 1H), 5.35 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.1, 148.3, 138.3, 135.2, 135.1, 131.9, 129.5, 129.3, 129.2, 128.6, 127.3, 125.6, 124.6, 67.6, 21.4; HRMS (ESI): calc. for $[(C_{15}H_{13}NO_4)H]$ (M + H) 272.0923, found 272.0925.

3,5-Dimethylbenzyl 3-nitrobenzoate (4f). Yield: 92%; 1.73 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 3140, 2980, 1720, 1620, 1580, 1465, 1290, 1108; ^1H NMR (200 MHz, $CDCl_3$): δ 8.88 (t, J = 1.8 Hz, 1H), 8.33–8.56 (m, 2H), 7.65 (t, J = 8.0 Hz, 1H), 6.92–7.15 (m, 3H), 5.34 (s, 2H), 2.36 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.1, 148.3, 138.2, 135.2, 135.0, 132.0, 130.2, 129.4, 127.3, 126.4, 124.6, 67.6, 21.2; HRMS (ESI): calc. for $[(C_{16}H_{15}NO_4)H]$ (M + H) 286.1079, found 286.1075.

Ethyl 4-nitrobenzoate (5a). Yield: 80%; 1.03 g; colorless solid; mp. 97–99 °C (lit.[4k] mp. 97–98 °C); IR ($CHCl_3$, cm^{-1}): ν_{max} 3102, 3010, 2950, 1724, 1620, 1580, 1456, 1140, 1011; ^1H NMR (200 MHz, $CDCl_3$): δ 8.30 (d, J = 8.9 Hz, 2H), 8.21 (d, J = 8.9 Hz, 2H), 4.43 (q, J = 7.3, 14.6 Hz, 2H), 1.44 (t, J = 7.4 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.4, 150.5, 135.8, 130.6, 123.5, 61.9, 14.2; HRMS (ESI): calc. for $[(C_9H_9NO_4)H]$ (M + H) 196.0610, found 196.0615.

Isopropyl-4-nitrobenzoate (5b). Yield: 78%; 1.07 g; colorless solid, mp.: 105–108 °C (lit.[4k] mp. 105–106 °C); IR ($CHCl_3$, cm^{-1}): ν_{max} 3112, 2980, 1713, 1620, 1509, 1480, 1253, 1120; ^1H NMR (200 MHz, $CDCl_3$): δ 8.27 (d, J = 8.5 Hz, 2H), 8.19 (d, J = 8.5 Hz, 2H), 5.24–5.33 (m, 1H), 1.40 (d, J = 6.1 Hz, 7H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.1, 150.3, 136.2, 130.5, 123.4, 69.6, 21.8; HRMS (ESI): calc. for $[(C_{10}H_{11}NO_4)H]$ (M + H) 210.0766, found 210.0761.

Allyl-4-nitrobenzoate (5c). Yield: 82%; 1.12 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 3115, 2980,1720, 1620, 1580, 1470, 1320, 1153; ^1H NMR (200 MHz, $CDCl_3$): δ 8.17–8.34 (m, 4H), 5.93–6.14 (m, 1H), 5.28–5.50 (m, 2H), 4.86 (d, J = 5.8 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.1, 150.6, 135.5, 131.6, 130.7, 123.5, 119.0, 66.3; HRMS (ESI): calc. for $[(C_{10}H_9NO_4)H]$ (M + H) 208.0610, found 208.0615.

Prop-2-yn-1-yl 4-nitrobenzoate (5d). Yield: 80%; 1.08 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 2990, 2975, 1716, 1620, 1580, 1410, 1260, 1150, 949, 748; ^1H NMR (200 MHz, $CDCl_3$): δ 8.19–8.36 (m, 4H), 4.97 (d, J = 2.5 Hz, 2H), 2.54 (t, J = 2.5 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 163.8, 150.8, 134.7, 130.9, 123.6, 75.8, 53.2; HRMS (ESI): calc. for $[(C_{10}H_7NO_4)H]$ (M + H) 206.0453, found 206.0459.

***tert*-Butyl 3-nitrobenzoate (5e).** Yield: 52%; 0.76 g; colorless oil; IR ($CHCl_3$, cm^{-1}): ν_{max} 2996, 1725, 1610, 1520, 1490, 1260, 1152, 1050; ^1H NMR (200 MHz, $CDCl_3$): δ 1.65 (s, 9H), 7.51–7.74 (m, 1H), 8.25–8.53 (m, 2H), 8.79 (s, 1H); ^{13}C NMR

(50 MHz, $CDCl_3$): δ 163.2, 148.22, 135.0, 133.7, 129.2, 126.8, 124.3, 82.3, 28.1; HRMS (ESI): calc. for $[(C_{11}H_{13}NO_4)H]$ (M + H) 224.0923, found 224.0929.

(1*R*,2*S*,4*R*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl benzoate (5f). Yield: 80%; 1.60 g; pale yellow gum; $[\alpha]_D^{25}$ −44.8 (*c* 2.5, $CHCl_3$) {lit.[10a] $[\alpha]_D^{30}$ −45 (*c* 1.0, $CHCl_3$)}; IR ($CHCl_3$, cm^{-1}): ν_{max} 2980, 1720, 1630, 1528, 1470, 1125, 1080, 945; ^1H NMR (200 MHz, $CDCl_3$): δ 7.92–8.13 (m, 2H) , 7.36–7.61 (m, 3H), 5.01–5.19 (m, 1H), 2.32–2.62 (m, 1H), 1.98–2.23 (m, 1H), 1.65–1.96 (m, 3H), 1.05–1.59 (m, 5H), 0.92 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.6, 132.7, 130.9, 129.5, 128.3, 80.4, 49.1, 47.9, 45.0, 37.0, 28.2, 27.4, 19.8, 19.0, 13.7; HRMS (ESI): calc. for $[(C_{17}H_{22}O_2)H]$ (M + H) 259.1698, found 259.1690.

(1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl 3-nitrobenzoate (5g). Yield: 81%; 1.63 g; colorless gum; $[\alpha]_D^{25}$ −83.5 (*c* 2, $CHCl_3$) {lit.[10b] $[\alpha]_D^{25}$ −83.7 (*c* 1.5, $CHCl_3$)}; IR ($CHCl_3$, cm^{-1}): ν_{max} 3110, 2950, 1725, 1580, 1425, 1350, 1230, 1050, 948; ^1H NMR (200 MHz, $CDCl_3$): δ 8.84 (s, 1H), 8.32–8.47 (m, 3H), 7.65 (t, *J* = 8.0 Hz, 1H), 4.99 (td, *J* = 10.8, 4.5 Hz, 1H), 1.86–2.21 (m, 1H), 1.69–1.86 (m, 2H), 1.53–1.67 (m, 2H), 1.22–1.34 (m, 1H), 1.01–1.20 (m, 3H), 0.94 (dd, *J* = 6.7, 3.4 Hz, 8H), 0.80 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 163.9, 148.4, 135.3, 132.6, 129.5, 127.2, 124.6, 76.1, 47.2, 40.9, 34.3, 31.5, 26.6, 23.6, 22.1, 20.8, 16.5; HRMS (ESI): calc. for $[(C_{17}H_{23}NO_4)H]$ (M + H) 306.1705, found 306.1710.

2,2,6,6-Tetramethylpiperidin-1-yl-3-nitrobenzoate (6). To a stirred solution of 4-nitrobenzaldehyde (0.5 g, 3.3 mmol), 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) (0.51 g, 3.3 mmol) and titanium superoxide (0.1 g, 10 wt%) in dry CH_3CN (10 mL), TBHP (5–6 M solution in decane) (1.2 mL, 6.6 mmol) was added dropwise *via* a syringe and kept stirring at 25 °C for 6 h. After the reaction (checked by TLC), the reaction mixture was filtered through a sintered funnel using CH_2Cl_2 as an eluent. Then the organic layer was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by column chromatography over silica (230–400 mesh) using petroleum ether/ethyl acetate (4 : 1 v/v) as an eluent to give **6**. Yield: 72%; 1.45 g; colorless gum; IR ($CHCl_3$, cm^{-1}): ν_{max} 2985, 1725, 1620, 1590, 1435, 1156, 1085, 835; ^1H NMR (200 MHz, $CDCl_3$): δ 8.29 (m, 1H), 8.09 (m, 1H), 7.40–7.65 (m, 2H), 1.70–1.87 (m, 3H), 1.62 (m, 2H), 1.41–1.53 (m, 1H), 1.29 (s, 6H), 1.13 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.3, 132.8, 130.6, 129.5, 128.4, 123.6, 60.4, 39.0, 31.9, 20.8, 17.0; HRMS (ESI): calc. for $[(C_{16}H_{22}N_2O_4)H]$ (M + H) 307.1652, found 307.1648.

(((2,2,6,6-Tetramethylcyclohexyl)oxy)methyl)benzene (7). To a well-stirred solution of 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) (1 g, 6.41 mmol) in dry toluene (10 mL), Ti superoxide (0.1 g, 10 wt%) and TBHP (5–6 M in decane) (2.3 mL, 12.82 mmol) were added in a dropwise manner and heated at 80 °C for 2 h. After that, the reaction mixture was filtered through a sintered funnel using CH_2Cl_2 as an eluent. Then the organic layer was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, and evaporated in *vacuo*. The crude product was purified by column chromatography over silica (230–400 mesh) using petroleum ether/ethyl acetate (19 : 1 v/v) as an eluent to give **7**. Yield: 75%; 2.03 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 3011, 2980, 2851, 1621, 1590, 1365, 1150, 890, 748; ^1H NMR (200 MHz, $CDCl_3$): δ 7.29–7.43 (m, 5H), 4.84 (s, 2H), 1.43–1.65 (m, 6H), 1.27 (s, 6H), 1.16 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 138.3, 128.2, 127.4, 127.3, 78.7, 60.0, 39.7, 33.1, 20.3, 17.1; HRMS (ESI): calc. for $[(C_{16}H_{25}O)H]$ (M + H) 248.2009, found 248.2020.

Synthesis of 3-butylphthalide (8b). To a stirred solution of *ortho*-tolualdehyde **8a** (1 g, 8.32 mmol) in CH_2Cl_2 (25 mL), ethylene glycol (0.516 g, 8.32 mmol) and PTSA (0.316 g, 1.66 mmol) were added and kept stirring at 25 °C for 3 h. After the reaction was complete (judged by TLC), the organic layer was extracted with CH_2Cl_2, washed with aqueous saturated $NaHCO_3$ solution, dried over dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by column chromatography over silica (230–400 mesh) using petroleum ether/ethyl acetate (9 : 1 v/v) as an eluent to furnish 2-(*o*-tolyl)-1,3-dioxolane **8a′** in 90% yield.

Then to a stirred solution of **8a′** (1 g, 6.09 mmol) in dry THF (30 mL), ^{n}BuLi in hexane (1.6 M) (4.5 mL, 7.3 mmol) was added *via* a syringe in a dropwise manner at 0 °C and kept stirring for 30 min at the same temperature. Then ^{n}BuI (1.12 g, 6.09 mmol) in dry THF (5 mL) was slowly added to the reaction mixture at 0 °C and left for stirring at 25 °C for 2 h. After the reaction was complete (checked by TLC), it was quenched with 2 N HCl (10 mL) and kept stirring for another 1 h. Then the organic layer was extracted with ether, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. After that, the crude product without further purification and characterization, was subjected to intra-molecular oxidative esterification using TBHP in decane (5–6 M) (3.3 mL, 18.27 mmol) and titanium superoxide (0.1 g, 10 wt%) and it was heated at 80 °C for 3 h. After the reaction was complete (checked by TLC), it was filtered through a sintered funnel using CH_2Cl_2 as an eluent. Then the organic layer was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by column chromatography over silica (230–400 mesh) using petroleum ether/ethyl acetate (9 : 1 v/v) as an eluent to give 3-butylphthalide **8b** in 70% yield.

2-(*o*-Tolyl)-1,3-dioxolane (8a′). Yield: 90%; 1.23 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 3112, 2920, 1645, 1580, 1360, 1050, 845, 755; ^1H NMR (200 MHz, $CDCl_3$): δ 7.46–7.60 (m, 1H), 7.15–7.29 (m, 3H), 5.97 (s, 1H), 4.10–4.20 (m, 2H), 3.98–4.09 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 136.5, 135.3, 133.5, 130.5, 128.8, 125.7, 125.6, 102.0, 65.1, 18.7; HRMS (ESI): calc. for $[(C_{10}H_{12}O_2)H]$ (M + H) 165.0916, found 165.0912.

3-Butylphthalide (8b). Yield: 70%; 0.81 g; colorless liquid; IR ($CHCl_3$, cm^{-1}): ν_{max} 3112, 2920, 1735, 1612, 1520, 1186, 1070; ^1H NMR (200 MHz, $CDCl_3$): δ 7.88 (d, *J* = 7.5 Hz, 1H), 7.61–7.74 (m, 1H), 7.40–7.58 (m, 2H), 5.47 (dd, *J* = 7.6, 4.1 Hz, 1H), 1.94–2.16 (m, 1H), 1.65–1.87 (m, 1H), 1.23–1.58 (m, 4H), 0.81–0.99 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.1, 150.0, 133.7, 128.8, 126.113.8, 125.5, 121.6, 81.1, 34.4, 26.8, 22.3; HRMS (ESI): calc. for $[(C_{12}H14O_2)H]$ (M + H) 191.1072, found 191.1076.

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Notes and references

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