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PCl_3-mediated transesterification and aminolysis of *tert*-butyl esters via acid chloride formation

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Abstract

A PCl_3-mediated conversion of *tert*-butyl esters into esters and amides in one-pot under air is developed. This novel protocol is highlighted by the synthesis of skeletons of bioactive molecules and gram-scale reactions. Mechanistic studies revealed that this transformation involves the formation of an acid chloride in situ, which is followed by reactions with alcohols or amines to afford the desired products.

Keywords

acid chlorides, amides, esters, phosphorus trichloride, *tert*-butyl esters

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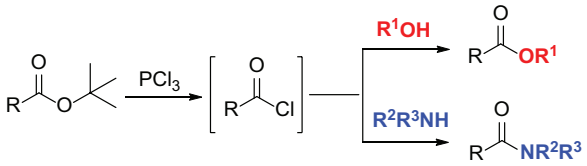

R, R^1, R^2, R^3 = Aryl, Alkyl, Alkenyl, H, etc.

Introduction

Ester and amide functionalities are ubiquitous in pharmaceuticals, natural products, agriculture, functional materials, and synthetic organic chemistry.[1–7] Traditional methods for the preparation of esters and amides involve the reactions of carboxylic acids with alcohols or amines.[5,6] However, these methods suffer from dry reaction conditions and the generation of toxic wastes. In recent years, the transesterification and aminolysis of esters have represented alternative routes for the synthesis of various esters and amides.[8–11] However, transesterification and aminolysis of esters usually require the use of transition-metal catalysts such as Pd,[12,13] Co,[14] Ru,[15,16] and Au,[17] excess of bases,[18,19] metal alkoxides,[10,20] carbenes,[21–23] and so on,[24–28] which are limited by high costs, low availability, and harsh reaction conditions. Moreover, there are only a few examples involving the transesterification and aminolysis of esters using the same system. Thus, the development of an efficient, low-cost, and environmentally friendly methodology for the synthesis of esters and amides is in high demand.

Phosphorus trichloride (PCl_3) is a cheap and readily available industrial chemical. Recently, we became intrigued by the fact that PCl_3 may serve as a green chlorinating reagent due to one molecule of PCl_3 having three chlorine atoms. The need for esters and amides in our ongoing research encouraged us to investigate methods for their synthesis. To the best of our knowledge, there has been no report on the reaction of PCl_3 with esters that provides the corresponding acid chlorides for further reactions, albeit there are a few examples of the conversion of *tert*-butyl esters into acid chlorides having been reported, some of them using a large excess of chlorinating reagents.[29] Herein, we report an efficient PCl_3-mediated transesterification and aminolysis of esters, providing the corresponding esters and amides in good-to-high yields (Scheme 1). Notably, when a large-scale reaction was conducted, only 2/3 equiv. of PCl_3 was required.

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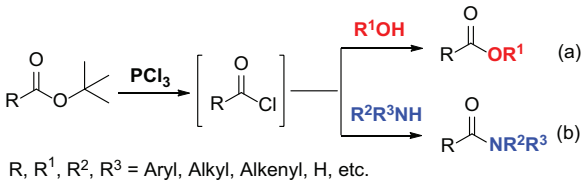
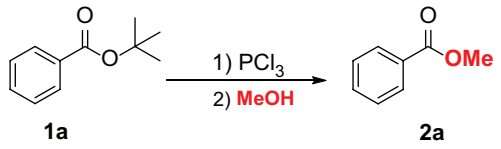


Scheme 1. PCl_3-mediated transesterification and aminolysis of *tert*-butyl esters.

Table 1. Optimization of the reaction conditions.[a]



Entry	Conditions	Yield (%)[b]
1	sealed tube, N_2	83
2	**sealed tube, air**	**92**
3	sealed tube, air	44[c]
4	sealed tube, air	92[d]
5	sealed tube, 60 °C, air	87
6	sealed tube, 2/3 equiv. of PCl_3, air	78

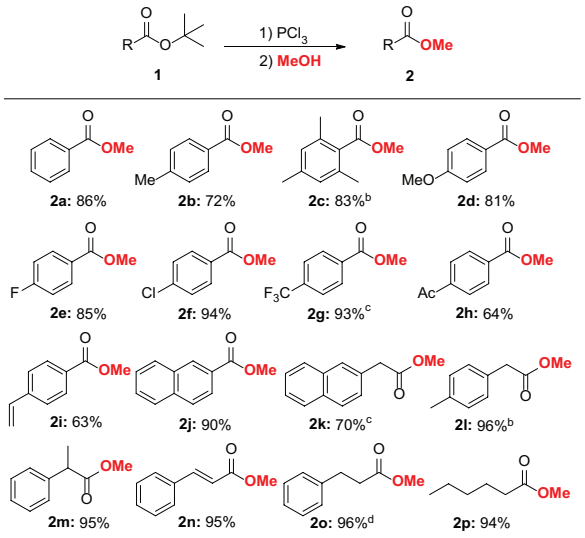
[a]Conditions: (1) **1a** (0.3 mmol), PCl_3 (0.3 mmol), and CH_3CN (0.6 mL) were stirred at 80 °C for 3 h under air and (2) MeOH (5.0 equiv.) was added and the mixture was stirred at 80 °C for 2 h.
[b]GC yield based on **1a** using dodecane as an internal standard.
[c]MeOH (3.0 equiv.) was used.
[d]MeOH (6.0 equiv.) was used.
The bold in Table 1 means the optimal reaction condition.

Results and discussion

We initiated our research on the transesterification of *tert*-butyl benzoate. As demonstrated in Table 1, *tert*-butyl benzoate (**1a**) and PCl_3 (1.0 equiv.) were stirred in CH_3CN at 80 °C for 3 h, then MeOH (5.0 equiv.) was added under N_2 to afford methyl benzoate (**2a**) in 83% yield (entry 1). Similarly, when the reaction was conducted in air, the product was generated in 92% yield (entry 2). Further reducing or increasing the amount of MeOH did not improve the reaction efficiency (entries 3 and 4). An 87% yield of the product was generated when the reaction temperature was lowered to 60 °C (entry 5). To our delight, when 2/3 equiv. of PCl_3 was used, a 78% yield of methyl benzoate was obtained (entry 6). We also examined the reactivity of methyl, isopropyl, and phenyl benzoate in this reaction. However, no product was detected by gas chromatography–mass spectrometry (GC-MS).

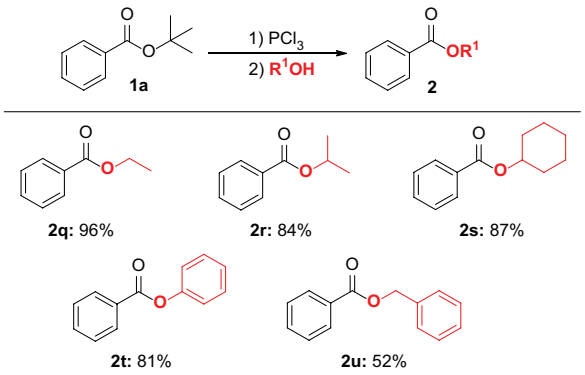
Next, the generality of this transesterification was explored. We were pleased to find that the reaction of various *tert*-butyl esters with MeOH proceeded efficiently in one-pot to give the corresponding products in good to excellent yields. As shown in Table 2, both electron-rich and electron-deficient substrates provided the corresponding aryl esters (**2a–h**) under the optimized reaction conditions in good to excellent yields. A vinyl group at the *para* position was tolerated well (**2i**) and *tert*-butyl 2-naphthoate underwent this reaction smoothly to give **2j** in 90% yield.

Table 2. Substrate scope with various *tert*-butyl esters.[a]



[a]Conditions: (1) **1** (1.3 mmol), PCl_3 (1.3 mmol), and CH_3CN (2.0 mL) were stirred in a sealed 25-mL Schlenk tube at 80 °C for 3 h under air and (2) MeOH (5.0 equiv.) was added and the mixture was stirred at 80 °C for 2 h. Yield of isolated products are given.
[b]Step (1) was performed at 60 °C for 6 h and step (2) was performed at 60 °C for 2 h.
[c]Steps (1) and (2) were performed at 100 °C for 3 and 2 h, respectively.
[d]Steps (1) and (2) were performed at 60 °C for 3 and 2 h, respectively.

Table 3. Substrate scope with different alcohols.[a]



[a]Conditions: (1) **1a** (1.3 mmol), PCl_3 (1.3 mmol), and CH_3CN (2.0 mL) were stirred in a sealed tube at 80 °C for 3 h under air and (2) R^1OH (6.0 equiv.) was added and the mixture was stirred at 80 °C for 11 h. Yield of isolated products are given.

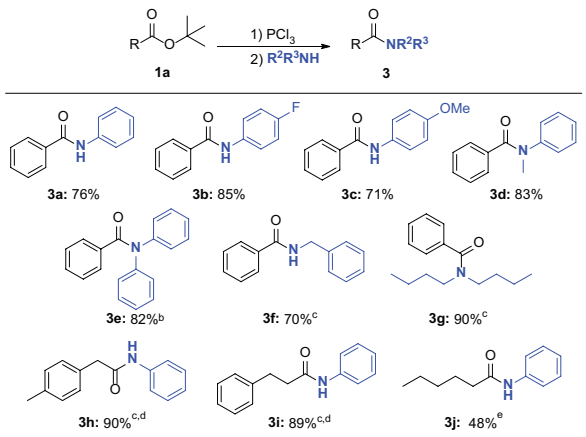
Moreover, benzyl esters such as *tert*-butyl 2-(naphthalen-2-yl)acetate, *tert*-butyl 2-(*p*-tolyl)acetate, and *tert*-butyl 2-phenylpropanoate were also found to be suitable substrates (**2k–m**). The alkenyl ester *tert*-butyl cinnamate reacted readily to afford methyl cinnamate (**2n**) in 95% yield. It should be noted that alkyl esters, such as *tert*-butyl 3-phenylpropanoate and *tert*-butyl hexanoate, exhibited good reactivity, furnishing the expected products **2o** and **2p** in 96% and 94% yield, respectively.

We next explored the reaction of *tert*-butyl benzoate with different alcohols under similar conditions (Table 3). Gratifyingly, by prolonging the reaction time to 11 h, ethanol and isopropanol were amenable to this transesterification and the expected products **2q** and **2r** were obtained in

good to excellent yields. Notably, when sterically hindered alcohols, such as cyclohexanol and phenol, were subjected to the reaction, 87% and 81% yields of the products **2s** and **2t** were achieved, respectively. Benzyl alcohol provided the corresponding product **2u** in a modest yield.

We subsequently investigated if this PCl_3-mediated system could be applicable for the aminolysis of *tert*-butyl esters (Table 4). For primary amines, such as aniline, 4-fluoroaniline, and 4-methoxyaniline, moderate-to-good yields of the amidated products **3a–c** were obtained.

Table 4. PCl_3-mediated aminolysis of *tert*-butyl esters.[a]



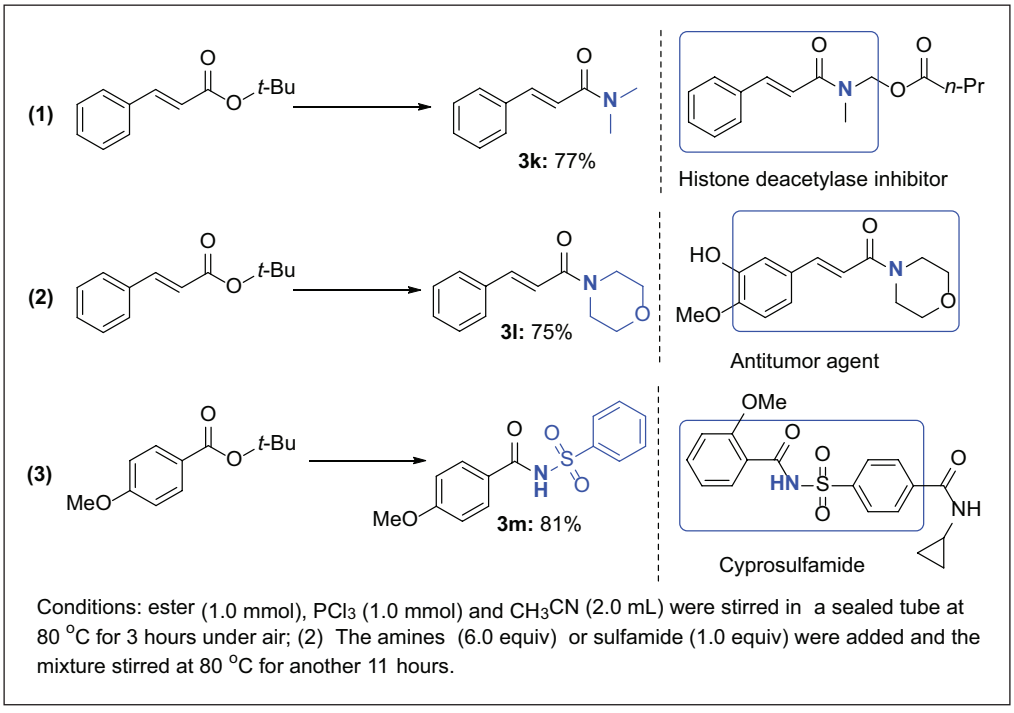
[a]Conditions: (1) **1a** (1.3 mmol), PCl_3 (1.3 mmol), and CH_3CN (2.0 mL) were stirred in a sealed tube at 80 °C for 3 h under air and (2) R^2R^3NH (1.0 equiv.) was added and the mixture stirred at 80 °C for 2 h. Isolated yields.
[b]Step (2) was performed at 100 °C for 2 h.
[c]Amine (3.0 equiv.) was used.
[d]Steps (1) and (2) were performed at 60 °C for 6 and 2 h, respectively.
[e]Step (2) was performed at 80 °C for 0.5 h.

Moreover, secondary amines, such as *N*-methylaniline and diphenylamine, were also successfully employed to give the amide products **3d** and **3e** in 83% and 82% yields, respectively. To our delight, this aminolysis reaction could also be extended to aliphatic amines and aliphatic *tert*-butyl esters giving products **3f–j**.

Reactions to synthesize valuable skeletons of bioactive molecules were conducted to demonstrate the potential synthetic utility of this aminolysis reaction (Scheme 2). Thus, dimethylamine and morpholine were subjected to this reaction to afford the corresponding skeletons of bioactive molecules[30–32] in 77% and 75% yields, respectively (equations (1) and (2)). Interestingly, benzenesulfonamide could also be converted into the product **3m**, which is the scaffold of the biologically active compound cyprosulfamide (equation (3)).[33]

The value of this PCl_3-mediated system lies further on the scalability of the reaction. As depicted in Scheme 3, gram-scale reactions were conducted on 10-mmol scale with a reduced quantity of PCl_3 usage (2/3 equiv.) and the desired products, such as methyl benzoate and *N,N*-dibutylbenzamide, were obtained in 81% and 90% yields, respectively. As one molecule of PCl_3 has three chlorine atoms which can be utilized in the reaction, this may account for the lower PCl_3 loading.[34]

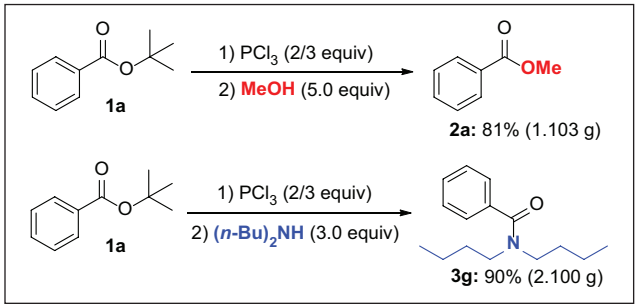
A series of control experiments have been carried out to probe the mechanism (Scheme 4). A 93% yield of benzoyl chloride was generated when **1a** and PCl_3 were stirred in CH_3CN at 80 °C for 3 h under air (equation (4)). This result indicated that acid chlorides are the key intermediates which react with alcohols and amines to afford the products. To study the formation of acid chlorides from esters, 1.5 equiv. of HCl instead of PCl_3 were subjected to the reaction and a 90% yield of benzoic acid and 8% of **2a** were



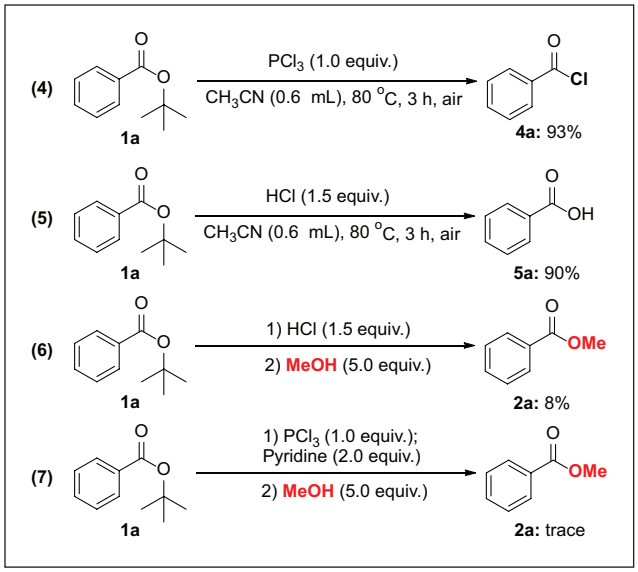
Scheme 2. The synthesis of skeletons of bioactive molecules.

obtained, respectively (equations (5) and (6)). The reaction was suppressed in the presence of 2.0 equiv. of pyridine (equation (7)). We attribute the trace yield of **2a** to the neutralization of HCl which was easily formed by the reaction of PCl_3 with water in air or in the solvent. These results indicate that HCl generated in situ plays an important role in the reaction. As we reported previously, benzoic acids can react with PCl_3 or the P-Cl reagent to afford acid chlorides.[34] Thus, there are two roles played by PCl_3 in this reaction: formation of HCl in situ and the chloride reagent.

Based on the above results and our previous reports,[29,34] a possible mechanism has been proposed. As shown in Scheme 5, we considered two processes for this reaction. The first involves hydrolysis of ester **1** to give the corresponding acid **5** with the aid of HCl. Subsequent reaction of acid **5** with $(OH)_nPCl_{3-n}$ ($n = 0, 1, 2$), then forms the corresponding acyl chlorides **4**. The second is the complexation of **1** with **6** followed by the elimination of a *tert*-butyl cation to afford chlorides **7**. The resulting intermediate **7** then reacts with HCl to afford **4**. The reaction of **4** with the alcohol or amine provides the product **2** or **3**, respectively.



Scheme 3. Scale-up reactions.



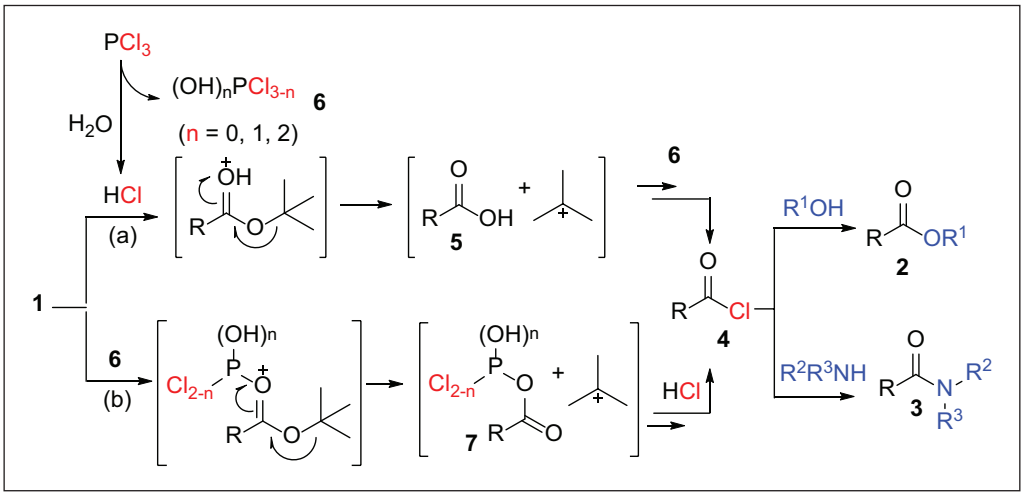
Scheme 4. Control experiments.

Conclusion

In summary, using cheap and readily available PCl_3, an efficient transesterification and aminolysis of *tert*-butyl esters has successfully been demonstrated. Mechanistic studies revealed that the reaction proceeds via an acid chloride. This new method provides an efficient and simple protocol to synthesize a wide range of esters and amides from *tert*-butyl esters. Furthermore, this approach has been applied to the synthesis of the frameworks of bioactive molecules and is easily scaled up even when 2/3 equiv. of PCl_3 are used.

Experimental

Unless otherwise noted, all reactions were carried out in sealed oven-dried Schlenk tubes under air. Reagents and solvents were obtained from commercial suppliers and used without purification. Flash column chromatography was performed using 200–300 mesh silica gel. Visualization on thin-layer chromatography (TLC) was achieved by the use of UV light (254 nm). A FULI GC-9790II equipped with a flame ionization detector (FID) detector was used to analysis the reaction mixture. ^1H nuclear magnetic resonance (NMR) and ^{13}C NMR spectra were recorded on a



Scheme 5. Possible mechanisms.

Bruker AV-II 500-MHz NMR spectrometer (^{1}H: 500 MHz, ^{13}C: 125.76 MHz) in $CDCl_3$ or DMSO-d_6. The coupling constants *J* are given in Hz. Chemical shifts for ^{1}H NMR are referred to internal Me_4Si (0 ppm). GC-MS was recorded on a Shimadzu GCMS-QP2010 plus equipped with an electron ionization (EI) ion source. Substrates **1c**,[35] **1d**,[36] **1f**,[37] **1g**,[38] **1h–m**,[39] **1n**,[37] **1o**,[39] and **1p**[36] were synthesized according to the known methods.

Typical procedure for the preparation of the target molecules: Under air, *tert*-butyl ester **1** (1.3 or 0.3 mmol), PCl_3 (1.0 equiv.), and CH_3CN (0.6 mL) were added to a 25-mL sealed Schlenk tube equipped with a magnetic stir bar. The mixture was stirred at 80 °C for 3 h. Next, the corresponding alcohol (5.0 equiv.) or amine (1.0 or 3.0 equiv.) was added to the reaction and the mixture was stirred at the indicated temperature for the indicated amount of time. The mixture was then quenched with aqueous $NaHCO_3$ solution and extracted with EtOAc (×3). The combined organic layer was dried over $MgSO_4$ and filtered. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel to give the analytically pure product **2** or **3**.

Methyl benzoate (**2a**):[40] Colorless oil; yield: 86% (152.1 mg). Petroleum ether/EtOAc = 10/1. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07–8.05 (m, 2H), 7.59–7.56 (m, 1H), 7.47–7.44 (m, 2H), 3.93 (s, 3H). ^{13}C NMR (125.76 MHz $CDCl_3$): δ 167.2, 133.0, 130.1, 129.6, 128.4, 52.2. GC-MS (EI, 70 eV): *m*/*z* = 136 (M^+).

Methyl 4-methylbenzoate **(2b)**:[40] Colorless oil; yield: 72% (140.5 mg). Eluent: petroleum ether/EtOAc = 10/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 3.80 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 167.2, 143.6, 129.6, 129.1, 127.4, 51.9, 21.6. GC-MS (EI, 70 eV): *m*/*z* = 150 (M^+).

Methyl 2,4,6-trimethylbenzoate (**2c**):[41] Colorless oil; yield: 83% (192.1 mg). Eluent: petroleum ether/EtOAc = 10/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 6.66 (s, 2H), 3.70 (s, 3H), 2.11 (s, 6H), 2.09 (s, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 170.6, 139.3, 135.2, 130.9, 128.4, 51.7, 21.1, 19.8. GC-MS (EI, 70 eV): *m*/*z* = 178 (M^+).

Methyl 4-methoxybenzoate (**2d**):[40] White solid; yield: 81% (174.8 mg). Eluent: petroleum ether/EtOAc = 10/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 7.93–7.90 (m, 2H), 6.86–6.83 (m, 2H), 3.81 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 166.9, 163.3, 131.6, 122.6, 113.6, 55.4, 51.9. GC-MS (EI, 70 eV): *m*/*z* = 166 (M^+).

Methyl 4-fluorobenzoate (**2e**):[42] Colorless oil; yield: 85% (170.2 mg). Eluent: petroleum ether/EtOAc = 10/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 8.02–8.00 (m, 2H), 7.08–7.04 (m, 2H), 3.87 (s, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 165.5, 165.2 (d, $J_{C\text{-}F}$ = 252.2 Hz), 131.6 (d, $J_{C\text{-}F}$ = 9.3 Hz), 125.9 (d, $J_{C\text{-}F}$ = 2.6 Hz), 114.9 (d, $J_{C\text{-}F}$ = 21.9 Hz), 51.6. GC-MS (EI, 70 eV): *m*/*z* = 154 (M^+).

Methyl 4-chlorobenzoate (**2f**):[40] White solid; yield: 94% (207.7 mg). Eluent: petroleum ether/EtOAc = 10/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 165.8, 138.9, 130.5, 128.2, 128.1, 51.8. GC-MS (EI, 70 eV): *m*/*z* = 170 (M^+).

Methyl 4-(trifluoromethyl)benzoate (**2g**):[40] Light yellow oil; yield: 93% (246.6 mg). Eluent: petroleum ether/EtOAc = 10/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 165.4, 133.9 (q, $J_{C\text{-}F}$ = 32.7 Hz), 132.9, 129.5, 124.9 (q, $J_{C\text{-}F}$ = 3.1 Hz), 123.1 (q, $J_{C\text{-}F}$ = 272.8 Hz), 52.0. GC-MS (EI, 70 eV): *m*/*z* = 204 (M^+).

Methyl 4-acetylbenzoate (**2h**):[43] White solid; yield: 64% (148.1 mg). Eluent: petroleum ether/EtOAc = 10/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 8.06 (d, *J* = 8.5 Hz, 2H), 7.94 (d, *J* = 8.5 Hz, 2H), 3.88 (s, 3H), 2.58 (s, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 197.1, 165.8, 139.7, 133.4, 129.4, 127.7, 52.0, 26.4. GC-MS (EI, 70 eV): *m*/*z* = 178 (M^+).

Methyl 4-vinylbenzoate (**2i**):[44] White solid; yield: 63% (132.7 mg). Eluent: petroleum ether/EtOAc = 10/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 6.70–6.64 (m, 1H), 5.79 (d, *J* = 17.5 Hz, 1H), 5.30 (d, *J* = 11.0 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 166.4, 141.4, 135.5, 129.4, 128.8, 125.6, 116.0, 51.6. GC-MS (EI, 70 eV): *m*/*z* = 162 (M^+).

Methyl 2-naphthoate (**2j**):[40] Light yellow solid; yield: 90% (217.6 mg). Eluent: petroleum ether/EtOAc = 10/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 8.54 (s, 1H), 7.89 (dd, *J* = 1.5 Hz, 8.5 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.54–7.46 (m, 2H), 3.91 (s, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 167.3, 135.5, 132.5, 131.1, 129.4, 128.3, 128.2, 127.8, 127.4, 126.7, 125.2, 52.3. GC-MS (EI, 70 eV): *m*/*z* = 186 (M^+).

Methyl 2-(naphthalen-2-yl)acetate (**2k**):[45] White solid; yield: 70% (182.0 mg). Eluent: petroleum ether/EtOAc = 10/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 7.74–7.01 (m, 3H), 7.65 (s, 1H), 7.41–7.32 (m, 3H), 3.71 (s, 2H), 3.62 (s, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 172.1, 133.5, 132.5, 131.5, 128.3, 128.0, 127.7, 127.7, 127.4, 126.2, 125.9, 52.2, 41.4. GC-MS (EI, 70 eV): *m*/*z* = 200 (M^+).

Methyl 2-(p-tolyl)acetate (**2l**):[46] Colorless oil; yield: 96% (204.7 mg). Eluent: petroleum ether/EtOAc = 10/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 7.07–7.02 (m, 4H), 3.57 (s, 3H), 3.48 (s, 2H), 2.22 (s, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 171.8, 136.3, 130.5, 128.9, 128.7, 51.6, 40.3, 20.6. GC-MS (EI, 70 eV): *m*/*z* = 164 (M^+).

Methyl 2-phenylpropanoate (**2m**):[47] Light yellow oil; yield: 95% (202.5 mg). Eluent: petroleum ether/EtOAc = 10/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 7.39–7.34 (m, 4H), 7.31–7.28 (m, 1H), 3.78 (q, *J* = 7.0 Hz, 1H), 3.69 (s, 3H), 1.55 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 174.5, 140.1, 128.2, 127.0, 126.7, 51.6, 45.0, 18.2. GC-MS (EI, 70 eV): *m*/*z* = 164 (M^+).

Methyl cinnamate (**2n**):[42] Light yellow solid; yield: 95% (200.1 mg). Eluent: petroleum ether/EtOAc = 10/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 7.63 (d, *J* = 16.0 Hz, 1H), 7.47–7.45 (m, 2H), 7.33–7.30 (m, 3H), 6.38 (d, *J* = 16.0 Hz, 1H), 3.74 (s, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 167.5, 144.9, 134.4, 130.3, 128.9, 128.1, 117.8, 51.7. GC-MS (EI, 70 eV): *m*/*z* = 162 (M^+).

Methyl 3-phenylpropanoate (**2o**):[48] Light yellow oil; yield: 96% (204.7 mg). Eluent: petroleum ether/EtOAc = 10/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 7.19–7.16 (m, 2H), 7.11–7.08 (m, 3H), 3.55 (s, 3H), 2.85 (t, *J* = 7.5 Hz,

2H), 2.52 (t, J=8.0 Hz, 2H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 172.9, 140.2, 128.1, 127.8, 125.8, 51.2, 35.3, 30.5. GC-MS (EI, 70 eV): m/z=164 (M^+).

Methyl hexanoate (**2p**):[40] Colorless oil; yield: 94% (158.9 mg). Eluent: petroleum ether. ^{1}H NMR (500 MHz $CDCl_3$): δ 3.60 (s, 3H), 2.23 (t, J=7.5 Hz, 2H), 1.59–1.53 (m, 2H), 1.27–1.22 (m, 4H), 0.83 (t, J=7.0 Hz, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 174.3, 51.4, 34.1, 31.3, 24.6, 22.3, 13.9. GC-MS (EI, 70 eV): m/z=130 (M^+).

Ethyl benzoate (**2q**):[47] Light yellow oil, yield 96% (187.2 mg). Eluent: petroleum ether/EtOAc=10/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 7.99–7.97 (m, 2H), 7.50–7.46 (m, 1H), 7.38–7.35 (m, 2H), 4.31 (q, J=7.5 Hz, 2H), 1.33 (t, J=7.0 Hz, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 166.7, 132.8, 130.5, 129.5, 128.3, 61.0, 14.4. GC-MS (EI, 70 eV): m/z=150 (M^+).

Isopropyl benzoate (**2r**):[47] Light yellow oil; yield: 84% (179.1 mg). Eluent: petroleum ether/EtOAc=10/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 7.94–7.95 (m, 2H), 7.47–7.44 (m, 1H), 7.36–7.33 (m, 2H), 5.21–5.14 (m, 1H), 1.29 (d, J=6.5 Hz, 6H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 166.1, 132.7, 130.9, 129.5, 128.3, 68.4, 22.0. GC-MS (EI, 70 eV): m/z=164 (M^+).

Cyclohexyl benzoate (**2s**):[49] Light yellow oil; yield: 87% (230.7 mg). Eluent: petroleum ether/EtOAc=10/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 7.98–7.96 (m, 2H), 7.46–7.43 (m, 1H), 7.35–7.32 (m, 2H), 4.97–4.92 (m, 1H), 1.87–1.84 (m, 2H), 1.71–1.69 (m, 2H), 1.52–1.47 (m, 3H), 1.40–1.24 (m, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 166.0, 132.7, 131.0, 126.5, 128.3, 73.0, 31.7, 25.5, 23.7. GC-MS (EI, 70 eV): m/z=204 (M^+).

Phenyl benzoate (**2t**):[47] White solid; yield: 81% (208.5 mg). Eluent: petroleum ether/EtOAc=10/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 8.15–8.13 (m, 2H), 7.58–7.55 (m, 1H), 7.46–7.42 (m, 2H), 7.38–7.34 (m, 2H), 7.22–7.17 (m, 1H), 7.15–7.13 (m, 2H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 165.2, 151.0, 133.6, 130.2, 129.6, 129.5, 128.6, 125.9, 121.8. GC-MS (EI, 70 eV): m/z=198 (M^+).

Benzyl benzoate (**2u**):[40] Colorless oil; yield: 52% (143.3 mg). Eluent: petroleum ether/EtOAc=10/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 8.17–8.15 (m, 2H), 7.62–7.59 (m, 1H), 7.53–7.44 (m, 6H), 7.42–7.39 (m, 1H), 5.44 (s, 2H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 166.5, 136.1, 133.1, 130.2, 129.8, 128.7, 128.5, 128.3, 128.3, 66.8. GC-MS (EI, 70 eV): m/z=212 (M^+).

N-phenylbenzamide (**3a**):[50] White solid; yield: 76% (194.6 mg). Eluent: petroleum ether/EtOAc=5/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 7.81–7.78 (m, 3H), 7.58–7.57 (m, 2H), 7.50–7.47 (m, 1H), 7.44–7.41 (m, 2H), 7.31 (t, J=8.0 Hz, 2H), 7.09 (t, J=7.5 Hz, 1H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 165.8, 137.9, 135.0, 131.9, 129.1, 128.8, 127.0, 124.6, 120.2. GC-MS (EI, 70 eV): m/z=197 (M^+).

N-(4-Fluorophenyl)benzamide (**3b**):[51] White solid; yield: 85% (237.6 mg). Eluent: petroleum ether/EtOAc=5/1. ^{1}H NMR (500 MHz DMSO-d_6) δ 10.30 (s, 1H), 7.97–7.94 (m, 2H), 7.82–7.78 (m, 2H), 7.61–7.57 (m, 1H), 7.55–7.51 (m, 2H), 7.22–7.17 (m, 2H). ^{13}C NMR (125.76 MHz, DMSO-d_6) δ 165.9, 158.8 (d, $J_{C\text{-}F}$= 240.2 Hz) 136.0 (d, $J_{C\text{-}F}$=2.5 Hz), 135.3, 132.1, 128.9, 128.1, 122.7, 115.6 (d, $J_{C\text{-}F}$=22.6 Hz). GC-MS (EI, 70 eV): m/z=215 (M^+).

(4-Methoxyphenyl)benzamide (**3c**):[50] Light yellow solid; yield: 71% (209.5 mg). Eluent: petroleum ether/EtOAc=5/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 7.79 (d, J=7.5 Hz, 2H), 7.73 (brs, 1H), 7.48–7.45 (m, 3H), 7.42–7.39 (m, 2H), 6.85–6.82 (m, 2H), 3.74 (s, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 165.7, 156.7, 135.0, 131.7, 131.0, 128.8, 127.0, 122.1, 114.3, 55.5. GC-MS (EI, 70 eV): m/z=227 (M^+).

N-Methyl-N-phenylbenzamide (**3d**):[50] Light yellow oil; yield: 83% (227.7 mg). Eluent: petroleum ether/EtOAc=5/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 7.22–7.21 (m, 2H), 7.17–7.13 (m, 3H), 7.09–7.04 (m, 3H), 6.95 (d, J=7.5 Hz, 2H), 3.42 (s, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 170.7, 144.9, 135.9, 129.6, 129.2, 128.7, 127.7, 126.9, 126.5, 38.4. GC-MS (EI, 70 eV): m/z=211 (M^+).

N,N-Diphenylbenzamide (**3e**):[50] White solid; yield: 82% (291.1 mg). Eluent: petroleum ether/EtOAc=5/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 7.39–7.38 (m, 2H), 7.23–7.20 (m, 5H), 7.16–7.08 (m, 8H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 170.8, 143.9, 136.1, 130.2, 129.2, 129.1, 127.9, 127.5, 126.4. GC-MS (EI, 70 eV): m/z=273 (M^+).

Benzylbenzamide (**3f**):[50] White solid, yield 70% (192.0 mg). Eluent: petroleum ether/EtOAc=5/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 7.73–7.71 (m, 2H), 7.45–7.42 (m, 1H), 7.38–7.34 (m, 2H), 7.29–7.21 (m, 5H), 6.36 (brs, 1H), 4.58 (d, J=5.5 Hz, 2H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 167.4, 138.2, 134.4, 131.6, 128.8, 128.6, 128.0, 127.7, 127.0, 44.2. GC-MS (EI, 70 eV): m/z=211 (M^+).

N,N-Dibutylbenzamide (**3g**):[52] Light yellow oil; yield: 90% (272.6 mg). Eluent: petroleum ether/EtOAc=5/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 7.30–7.25 (m, 5H), 3.41–3.10 (m, 4H), 1.57–1.32 (m, 6H), 1.04–0.70 (m, 8H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 171.6, 137.4, 129.0, 128.3, 126.4, 48.7, 44.4, 30.8, 29.6, 20.3, 19.7, 13.9, 13.6. GC-MS (EI, 70 eV): m/z=233 (M^+).

N-Phenyl-2-(p-tolyl)acetamide (**3h**):[53] White solid; yield: 90% (263.3 mg). Eluent: petroleum ether/EtOAc=5/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 7.34–7.33 (m, 2H), 7.20–7.17 (m, 3H), 7.14–7.10 (m, 4H), 7.01–6.98 (m, 1H), 3.61 (s, 2H), 2.29 (s, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 169.51, 137.68, 137.43, 131.33, 129.95, 129.46, 128.93, 124.44, 119.87, 44.41, 21.15. GC-MS (EI, 70 eV): m/z=225 (M^+).

N,3-Diphenylpropanamide (**3i**):[53] White solid; yield: 89% (260.3 mg). Eluent: petroleum ether/EtOAc=5/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 7.75–7.70 (m, 1H), 7.35–7.33 (m, 2H), 7.17–7.06 (m, 7H), 6.98–6.95 (m, 1H), 2.90 (t, J=8.0 Hz, 2H), 2.52 (t, J=8.0 Hz, 2H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 171.02, 140.66, 137.89, 128.96, 128.65, 128.41, 126.38, 124.39, 120.30, 39.25, 31.64. GC-MS (EI, 70 eV): m/z=225 (M^+).

N-Phenylhexanamide (**3j**):[54] White solid; yield: 48% (119.2 mg). Eluent: petroleum ether/EtOAc=5/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 7.53–7.51 (m, 2H), 7.38 (brs, 1H), 7.30 (t, J=8.0 Hz, 2H), 7.11–7.08 (m, 1H), 2.35 (t, J=7.5 Hz, 2H), 1.75–1.69 (m, 2H), 1.38–1.33 (m, 4H), 0.90 (t, J=7.0 Hz, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 171.61,

138.00, 128.98, 124.18, 119.84, 37.80, 31.44, 25.37, 22.45, 13.96. GC-MS (EI, 70 eV): m/z = 191 (M^+).

N,N-Dimethylcinnamamide (**3k**):[55] White solid; yield: 77% (134.8 mg). Eluent: petroleum ether/EtOAc = 5/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 7.69 (d, J = 15.5 Hz, 1H), 7.56–7.54 (m, 2H), 7.41–7.34 (m, 3H), 6.91 (d, J = 15.5 Hz, 1H), 3.18–3.09 (m, 6H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 166.7, 142.4, 135.3, 129.6, 128.8, 127.8, 117.4, 37.5, 36.0. GC-MS (EI, 70 eV): m/z = 175 (M^+).

(E)-1-Morpholino-3-phenylprop-2-en-1-one (**3l**):[56] White solid; yield: 75% (162.8 mg). Eluent: petroleum ether/EtOAc = 5/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 7.63 (d, J = 15.5 Hz, 1H), 7.47–7.45 (m, 2H), 7.33–7.28 (m, 3H), 6.78 (d, J = 15.5 Hz, 1H), 3.66–3.62 (m, 8H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 165.6, 143.3, 135.1, 129.8, 128.9, 127.8, 116.5, 66.9, 46.2, 42.5. GC-MS (EI, 70 eV): m/z = 217 (M^+).

4-Methoxy-N-(phenylsulfonyl)benzamide (**3m**):[57] White solid; yield: 81% (235.7 mg). Eluent: petroleum ether/EtOAc = 5/1. ^{1}H NMR (500 MHz $CDCl_3$): δ 9.47 (brs, 1H), 8.10–8.08 (m, 2H), 7.75–7.32 (m, 2H), 7.59–7.56 (m, 1H), 7.50–7.46 (m, 2H), 6.81–6.80 (m, 2H), 3.74 (s, 3H). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 164.0, 163.8, 138.6, 134.0, 130.2, 129.0, 128.6, 123.1, 114.2, 55.6. GC-MS (EI, 70 eV): m/z = 291 (M^+).

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Supplemental material

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