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Supporting Information

A Novel Aromatic Carbocation-based Coupling Reagent for Esterification and Amidation Reactions

Thanh V. Nguyen* and Demelza J. M. Lyons

Department of Chemistry, Curtin University, Perth, WA 6102, Australia E-mail: <u>thanhvinh.nguyen@curtin.edu.au</u>

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General Methods

Reactions, unless otherwise stated, were conducted under a positive pressure of dry nitrogen in oven-dried glassware. Tetrahydrofuran (THF), benzene, toluene and diethyl ether were dried over sodium wire and distilled from sodium benzophenone ketyl. Dichloromethane was dried by distillation from calcium hydride. Triethylamine and diisopropylethylamine were dried over 4Å molecular sieves. Magnesium sulfate was dried at 140 °C for 12 h prior to use. Commercially available reagents were used as purchased unless otherwise noted. Analytical thin layer chromatography was performed using silica gel plates pre-coated with silica gel 60 F_{254} (0.2 mm). Flash chromatography employed 230-400 mesh silica gel. Solvents used for chromatography are quoted as volume/volume ratios.

¹H NMR spectra were recorded at 298 K unless otherwise stated using Bruker Avance III 400 MHz spectrometers. Data is expressed in parts per million (ppm) downfield shift from tetramethylsilane with residual solvent as an internal reference (δ 7.26 ppm for chloroform) and is reported as position (δ in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (*J* in Hz) and integration (number of protons).

¹³C NMR spectra were recorded at 298 K unless otherwise stated using Bruker Avance III 100 MHz spectrometers with complete proton decoupling. Data is expressed in parts per million (ppm) downfield shift relative to the internal reference (δ 77.2 ppm for the central peak of deuterated chloroform) and is reported as position (δ in ppm).

Optimization of esterification reaction between phenylacetic acid and phenyl ethanol

Entry	Solvent	Equiv of 1	Base	Time	Yield
1	CH ₃ CN	1.5	Et ₃ N (4 equiv)	60 min	59%
2	EtOAc	1.5	Et ₃ N (4 equiv)	60 min	43%
3	Benzene	1.5	Et ₃ N (4 equiv)	60 min	48%
4	THF	1.5	Et ₃ N (4 equiv)	60 min	34%
5	Acetone	1.5	Et ₃ N (4 equiv)	60 min	24%
6	Toluene	1.5	Et ₃ N (4 equiv)	60 min	57%
7	DCE	1.5	Et ₃ N (4 equiv)	60 min	84%
8	CH ₃ Cl	1.5	Et ₃ N (4 equiv)	60 min	88%
9	CH ₃ Cl	1.1	Et ₃ N (4 equiv)	60 min	85%
10	CH ₂ Cl ₂	1.5	Et ₃ N (4 equiv)	60 min	92%
11	CH_2Cl_2	1.1	Et ₃ N (4 equiv)	60 min	90%
12	CH ₂ Cl ₂	1.1	Et ₃ N (4 equiv)	30 min	91%
13	CH ₂ Cl ₂	1.1	Et ₃ N (3 equiv)	30 min	90%
14	CH ₂ Cl ₂	1.1	DBU (3 equiv)	30 min	58%
15	CH ₂ Cl ₂	1.1	DIPEA (3 equiv)	30 min	89%

General procedure for tropylium chloride mediated esterification reactions (Table 1)

$$O \xrightarrow{\text{OH}} R^1 \xrightarrow{\text{(i) TropCl}_2 (1, 1.05 \text{ equiv}), \text{ Et}_3 \text{N} (3.0 \text{ equiv})}_{\text{(ii) R}^2 \text{OH} (1.1 \text{ equiv})} \xrightarrow{\text{O}}_{\text{R}^1} R^2 \xrightarrow{\text{O}}_{\text{R}^2} R^2$$

To a solution of tropylium chloride 1 (170 mg, 1.05 mmol), prepared according to the reported procedure,¹ in dry dichloromethane (3 mL) was slowly added a mixture of the carboxylic acid (1.0 mmol) and triethylamine (3.0 mmol) in dichloromethane solution (2 mL) and the reaction mixture was stirred at rt for the indicated time. The alcohol (1.1 mmol) was added and the reaction mixture was stirred at rt for 2-16 h until the starting materials were totally consumed as checked by TLC. The reaction mixture was concentrated under reduced pressure and then purified by column chromatography (SiO₂, hexanes:EtOAc 9:1 \rightarrow 7:3) to obtain the ester product.

General procedure for tropylium chloride mediated amidation reactions (Table 2)

$$\begin{array}{c} O \\ & (i) \operatorname{TropCl}_{2}(1, 1.05 \text{ equiv}), \operatorname{Et}_{3} N \text{ (3 equiv)} \\ \hline \\ R^{1} \\ & (ii) \operatorname{R}^{3} \operatorname{R}^{4} N H \text{ (1.1 equiv)} \\ & \operatorname{CH}_{2} \operatorname{Cl}_{2}, \operatorname{rt} \end{array} \xrightarrow{} \begin{array}{c} R^{3} \\ O \\ R^{1} \\ \end{array}$$

To a solution of tropylium chloride 1 (170 mg, 1.05 mmol), prepared according to the reported procedure, in dry dichloromethane (3 mL) was slowly added a mixture of the carboxylic acid (1.0 mmol) and triethylamine (3.0 mmol) in dichloromethane solution (2 mL) and the reaction mixture was stirred at rt for the indicated time. The amine (1.1 mmol) was added and the reaction mixture was stirred at rt for 1-8 h until the starting materials were totally consumed as checked by TLC. The reaction mixture was concentrated under reduced pressure and then purified by column chromatography (SiO₂, hexanes:EtOAc 8:2 \rightarrow 6:4) to obtain the amide product.

¹ Nguyen, T. V.; Bekensir, A. Org. Lett. 2014, 16, 1720.

General procedure for catalytic coupling reactions of carboxylic acids (Table 3)

$$\begin{array}{c} O \\ H \\ R^{1} \\ (1.1 \text{ equiv}) \end{array} \xrightarrow{\text{tropone (10 mol%), Et_3N (3 equiv)}} \\ \begin{array}{c} O \\ R^{1} \\ (COCl)_2 (1.2 equiv over 12 h) \\ CH_2Cl_2, rt \end{array} \xrightarrow{\text{COCC}} \\ \begin{array}{c} O \\ R^{1} \\ X = O, NR' \end{array}$$

A solution of oxalyl chloride (152 mg, 1.2 mmol) in dichloromethane (8 mL) was added via syringe pump over 12 h to a stirring solution of the carboxylic acid (1.0 mmol), the alcohol or the amine substrate (1.1 mmol), triethylamine (3.0 mmol) and tropone (10 mol%) in dichloromethane (5 mL) at rt. DMAP (10 mol%) was also added to the reaction mixture before the addition of oxalyl chloride for the indicated reactions. After the addition was completed, the reaction mixture was stirred at rt for another 2 h. The reaction mixture was then concentrated under reduced pressure and purified by column chromatography (SiO₂, hexanes:EtOAc 9:1 \rightarrow 6:4) to obtain the ester or amide product.



¹³C NMR studies for mechanistic investigation (Figure S1)

Figure 1. 13C NMR studies of reaction profiles (pertinent sections, 100 MHz, 25 °C, CDCl₃)

The presence of acid anhydrides in the reaction mixtures was demystified by a study monitoring the transformation of benzoic acid by ¹³C NMR spectroscopy (Figure S1) under different reaction conditions. We observed the reactions of: **(B)** benzoic acid with the slow addition of 1.2 equiv oxalyl chloride over 12 h in the presence of 0.1 equiv of tropone and 3.0 equiv of Et₃N; **(C)** benzoic acid with a stoichiometric amount (1.05 equiv) of pre-formed tropylium chloride (1) and 3.0 equiv of Et₃N after 45 minutes; **(D)** quenching of **(C)** after 60 minutes with *n*-butylamine (1.1 equiv). These were cross-referenced against ¹³C NMR spectra of pure samples of **(A)** benzoyl chloride, **(E)** *n*-butylbenzamide, **(F)** tropylium chloride (1) and **(G)** tropone. Evidences from this study suggested that while a stoichiometric amount of tropylium chloride converted the acid to its acid chloride, predominantly converted the acid to its anhydride instead.

Characterization data of products

Ethyl phenylacetate² (Table 1, entry 1): Prepared according to the general procedure from phenylacetic acid to yield a colorless oil (147 mg, 0.89 mmol, 89% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.40-7.25 (m, 5H), 4.17 (q, J = 8.0 Hz, 2H), 3.63 (s, 2H), 1.27 (t, J = 8.0 Hz, 3H ppm. ¹³C NMR (100 MHz, CDCl₃) δ 170.3, 138.4, 128.7, 127.8, 127.4, 126.8, 43.7, 23.1 ppm.

(2-Phenyl)ethyl phenylacetate³ (Table 1, entry 2): Prepared according to the general procedure from phenylacetic acid to yield a colorless oil (216 mg, 0.90 mmol, 90% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.39-7.25 (m, 8H), 7.21 (d, J = 8.0 Hz, 2H), 4.37 (t, J = 8.0 Hz, 2H), 3.65 (s, 2H), 2.97 (t, J = 8.0 Hz, 2H) ppm. 13 C NMR (100 MHz, CDCl₃) δ 171.6, 138.9, 134.1, 129.4, 129.0, 128.7, 128.6, 127.2, 126.6, 65.4, 41.5, 35.2 ppm.

4-Methoxybenzyl phenylacetate⁴ (Table 1, entry 3): Prepared according to the general procedure from phenylacetic acid to yield a colorless oil (238 mg, 0.93 mmol, 93% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.26-7.16 (m, 7H), 6.79 (d, J = 8.0 Hz, 2H), 4.99 (s, 2H), 3.72 (s, 3H), 3.55 (s, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 171.7, 159.8, 134.1, 130.2, 129.5, 128.7, 128.2, 127.3, 114.1, 66.6, 55.4, 41.5 ppm.

² Ke, J.; He, C.; Liu, H.; Xu, H.; Lei, A. *Chem. Commun.* **2013**, *49*, 6767. ³ Sølvhøj, A.; Madsen, R. *Organometallics.* **2011**, *30*, 6044.

⁴ Roof, A.: van Woerden, H.: Cerfontain, H. *Tetrahedron* **1976**, *32*, 2967.

Ethyl benzoate⁵ (Table 1, entry 4): Prepared according to the general procedure from benzoic acid to yield a colorless oil (90 mg, 0.60 mmol, 60% yield).



¹H NMR (400 MHz, CDCl₃) δ 8.07-8.03 (m, 2H), 7.56-7.51 (m, 1H), 7.45-7.40 (m, 2H), 4.38 (q, J = 8.0 Hz, 2H), 1.39 (t, J = 8.0 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 166.7, 132.9, 130.7, 129.6, 128.4, 61.0, 14.4 ppm.

Phenyl benzoate⁶ (Table 1, entry 5): Prepared according to the general procedure from benzoic acid to yield a white solid (137 mg, 0.69 mmol, 69% yield).



¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, J = 8.0 Hz, 2H), 7.55 (t, J = 8.0 Hz, 1H), 7.41 (m, 2H), 7.32 (m, 2H), 7.16 (m, 1H), 7.13 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 165.3, 151.2, 133.7, 130.3, 129.8, 129.7, 128.7, 126.0, 121.9 ppm.

n-Octyl benzoate⁷ (Table 1, entry 6): Prepared according to the general procedure from benzoic acid to yield a white solid (155 mg, 0.66 mmol, 66% yield).



¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, J = 8.0 Hz, 2H), 7.58-7.53 (m, 1H), 7.49-7.42 (m, 2H), 4.32 (t, J = 9.0 Hz, 2H), 1.77 (m, 2H), 1.50-1.20 (m, 10H), 0.89 (t, J = 8.0 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 166.9, 132.9, 130.8, 129.7, 128.5, 65.3, 32.0, 29.4 (two coincident resonances), 28.9, 26.2, 22.8, 14.3 ppm.

⁵ Jagadeesh, R. V.; Junge, H.; Pohl, M.-M.; Radnik, J.; Brueckner, A.; Beller, M. J. Am. Chem. Soc. 2013, 135, 10776.

⁶ Ang, W.; Lo, L.; Lam, Y. Tetrahedron. 2014, 70, 8545.

⁷ Sattenapally, N.; Wang, W.; Liu, H.; Gao, Y. Tetrahedron Lett. 2013, 54, 6665.

Benzyl butyrate⁸ (Table 1, entry 7): Prepared according to the general procedure from nbutyric acid to yield a colorless oil (146 mg, 0.82 mmol, 82% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.45-7.25 (m, 5H), 5.12 (s, 2H), 2.34 (td, J = 8.0 Hz, 4.0 Hz, 2H), 1.75-1.60 (m, 2H), 0.98 (dt, J = 8.0 Hz, 4.0 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 173.5, 136.3, 128.6, 128.4, 128.3, 66.1, 36.3, 18.5, 13.7 ppm.

Phenyl butyrate⁹ (Table 1, entry 8): Prepared according to the general procedure from *n*butyric acid to yield a colorless oil (144 mg, 0.88 mmol, 88% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.41-7.39 (m, 2H), 7.28-7.24 (m, 1H), 7.14-7.11 (m, 2H), 2.57 (t, J = 8.0 Hz, 2H), 1.84 (m, 2H), 1.09 (t, J = 8.0 Hz, 2H) ppm.¹³C NMR (100 MHz, CDCl₃) δ 172.2, 150.9, 129.5, 125.8, 121.7, 36.4, 18.6, 13.8 ppm.

4-Methoxyphenyl butyrate¹⁰ (Table 1, entry 9): Prepared according to the general procedure from *n*-butyric acid to yield a colorless oil (179 mg, 0.92 mmol, 92% yield).



¹H NMR (400 MHz, CDCl₃) δ 6.97 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 8.0 Hz, 2H), 3.79 (s, 3H), 2.52 (t, J = 8.0 Hz, 2H), 1.78 (m, 2H), 1.04 (t, J = 8.0 Hz, 3H) ppm. 13 C NMR (100 MHz, CDCl₃) δ 172.6, 157.3, 144.4, 122.5, 114.6, 55.7, 36.3, 18.6, 13.8 ppm.

4-Cyanophenyl butyrate¹⁰ (Table 1, entry 10): Prepared according to the general procedure from *n*-butyric acid to yield a colorless oil (151 mg, 0.80 mmol, 80% yield).



⁸ Hu, B.; Li, Y.; Li, Z.; Meng, X. Org. Biomol. Chem. **2013**, 11, 4138. ⁹ Somers, N.; Kazlauskas, R. Tetrahedron **2004**, 15, 2991.

¹⁰ Suzuki, H.: Padmanabhan, S.: Ogawa, T. *Chem. Lett.* **1989**, *6*, 1017.

¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, J = 12.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 2.54 (t, J = 8.0 Hz, 2H), 1.76 (m, 2H), 1.01 (t, J = 8.0 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 171.2, 154.1, 133.6, 122.8, 118.3, 109.6, 36.1, 18.3, 13.6 ppm.

Methyl octanoate¹¹ (**Table 1, entry 11**): Prepared according to the general procedure from *n*-octanoic acid to yield a colorless oil (138 mg, 0.87 mmol, 87% yield).



¹H NMR (400 MHz, CDCl₃) δ 3.65 (s, 3H), 2.28 (t, J = 8.0 Hz, 2H), 1.60 (m, 2H), 1.32-1.20 (m, 8H), 0.86 (t, J = 8.0 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 174.5, 51.6, 34.3, 31.8, 29.3, 29.1, 25.1, 22.7, 14.2 ppm.

Methyl decanoate¹² (Table 1, entry 12): Prepared according to the general procedure from *n*-decanoic acid to yield a colorless oil (158 mg, 0.85 mmol, 85% yield).



¹H NMR (400 MHz, CDCl₃) δ 3.64 (s, 3H), 2.28 (t, J = 8.0 Hz, 2H), 1.60 (m, 2H), 1.33-1.22 (m, 12H), 0.86 (t, J = 8.0 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 174.5, 51.6, 34.3, 32.0, 29.6, 29.4 (two coincident resonances), 29.3, 25.1, 22.8, 14.2 ppm.

Methyl dodecanoate¹¹ (Table 1, entry 13): Prepared according to the general procedure from *n*-dodecanoic acid to yield a colorless oil (174 mg, 0.81 mmol, 81% yield).



¹H NMR (400 MHz, CDCl₃) δ 3.64 (s, 3H), 2.28 (t, J = 8.0 Hz, 2H), 1.60 (m, 2H), 1.35-1.18 (m, 16H), 0.86 (t, J = 8.0 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 174.5, 51.5, 34.3, 32.1, 29.8, 29.6, 29.5, 29.4, 29.3, 25.1, 22.8, 14.2 ppm.

¹¹ Rajbongshi, K.; Sarma, M.; Phukan, P. *Tetrahedron Lett.* **2014**, *55*, 5358.

¹² Dawar, P.; Raju, M.; Ramakrishna, R. Synth. Commun. 2014, 44, 836.

Methyl tetradecanoate¹³ (Table 1, entry 14): Prepared according to the general procedure from *n*-tetradecanoic acid to yield a colorless oil (194 mg, 0.80 mmol, 80% yield).



¹H NMR (400 MHz, CDCl₃) δ 3.64 (s, 3H), 2.28 (t, J = 8.0 Hz, 2H), 1.60 (m, 2H), 1.35-1.18 (m, 20H), 0.86 (t, J = 8.0 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 174.4, 51.5, 34.3, 32.1, 29.8 (two coincident resonances), 29.7, 29.6, 29.5, 29.4, 29.3, 25.1, 22.8, 14.2 ppm.

Methyl hexadecanoate¹⁴ (Table 1, entry 15): Prepared according to the general procedure from *n*-hexadecanoic acid to yield a white solid (233 mg, 0.86 mmol, 86% yield).



¹H NMR (400 MHz, CDCl₃) δ 3.66 (s, 3H), 2.29 (t, J = 8.0 Hz, 2H), 1.60 (m, 2H), 1.35-1.18 (m, 24H), 0.87 (t, J = 8.0 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 174.5, 51.6, 34.3, 32.1, 29.9 (three coincident resonances), 29.8 (three coincident resonances), 29.6, 29.5, 29.4, 29.3, 25.2, 22.9, 14.3 ppm.

Methyl octadecanoate¹⁵ (Table 1, entry 16): Prepared according to the general procedure from *n*-octadecanoic acid to yield a white solid (245 mg, 0.82 mmol, 82% yield).



¹H NMR (400 MHz, CDCl₃) δ 3.66 (s, 3H), 2.29 (t, J = 8.0 Hz, 2H), 1.60 (m, 2H), 1.40-1.15 (m, 28H), 0.88 (t, J = 8.0 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 174.5, 51.6, 34.3, 32.1, 29.9 (three coincident resonances), 29.8 (two coincident resonances), 29.6 (two coincident resonances), 29.5, 29.4, 25.2, 22.9, 14.3 ppm.

 ¹³ Si, C.; Lei, X.; Xiaonan, L.; Meiming, L. Synthesis. 2014, 46, 263.
¹⁴ Rajabi, F.; Arancon, R.; Luque, R. Cat. Commun. 2014, 59, 101.

¹⁵ Rajabi, F.: Luque, R. *RSC Adv.* **2014**, *4*, 5152.

N,N-Diethyl dodecanamide¹⁶ (Table 2, entry 1): Prepared according to the general procedure from *n*-dodecanoic acid to yield a white solid (189 mg, 0.74 mmol, 74% yield).



¹H NMR (400 MHz, CDCl₃) δ 3.28 (q, J = 4.0 Hz, 2H), 3.21 (q, J = 4.0 Hz, 2H), 2.19 (t, J = 8.0 Hz, 2H), 1.54 (m, 2H), 1.30-1.10 (m, 16H), 1.06 (t, J = 8.0 Hz, 3H), 1.01 (t, J = 8.0 Hz, 3H), 0.78 (t, J = 8.0 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 172.4, 42.0, 40.1, 33.2, 32.0, 29.7 (two coincident resonances), 29.6 (three coincident resonances), 29.4, 25.6, 22.7, 14.5, 14.1, 13.2 ppm.

1-(piperidin-1-yl)hexadecan-1-one¹⁶ (Table 2, entry 2): Prepared according to the general procedure from *n*-hexadecanoic acid to yield a white solid (233 mg, 0.72 mmol, 72% yield).



¹H NMR (400 MHz, CDCl₃) δ 3.46 (bs, 4H), 2.31 (t, J = 8.0 Hz, 2H), 1.70-1.45 (m, 8H), 1.40-1.15 (m, 24H), 0.87 (t, J = 8.0 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 171.8, 33.6, 32.1, 29.9, 29.8 (three coincident resonances), 29.7 (two coincident resonances), 29.6, 29.5, 26.1 (broad), 25.7, 24.8, 22.9, 14.3 ppm.

1-(benzoyl)piperidine¹⁷ (**Table 2, entry 3**): Prepared according to the general procedure from benzoic acid to yield a white solid (129 mg, 0.68 mmol, 68% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.34 (bs, 5H), 3.61 (bs, 2H), 3.33 (bs, 2H), 1.90-1.20 (m, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 170.3, 136.5, 129.4, 128.4, 126.8, 48.5 (broad), 43.0 (broad), 26.1 (broad), 24.6 ppm.

¹⁶ Pathak, U.; Bhattacharyya, S.; Pandey, L.; Mathur, S.; Jaim, R. RSC Adv. 2014, 4, 3900.

¹⁷ Vrijdag, J.; Delgado, F.; Alonso, N.; De Borggraeve, W.; Perez-Macias, N.; Alcazar, J. *Chem. Commun.* **2014**, *50*, 15094.

N,N-Diethylbenzamide¹⁸ (Table 2, entry 4): Prepared according to the general procedure from benzoic acid to yield a white solid (126 mg, 0.71 mmol, 71% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.37-7.32 (m, 5H), 3.52 (bs, 2H), 3.23 (bs, 2H), 1.21 (bs, 3H), 1.10 (bs, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 171.4, 137.4, 129.2, 128.5, 126.4, 43.4 (broad), 39.4 (broad), 14.3 (broad), 13.0 (broad) ppm.

N,N-Diíopropylbenzamide¹⁹ (Table 2, entry 5): Prepared according to the general procedure from benzoic acid to yield a white solid (125 mg, 0.61 mmol, 61% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.37-7.28 (m, 5H), 3.66 (bs, 2H), 1.46 (bs, 6H), 1.25 (bs, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 171.2, 138.9, 128.8, 128.6, 125.7, 51.0 (broad), 46.1 (broad), 20.9 (broad) ppm.

N-Benzylbenzamide²⁰ (Table 2, entry 6): Prepared according to the general procedure from benzoic acid to yield a white solid (133 mg, 0.63 mmol, 63% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.79 (m, 2H), 7.55-7.25 (m, 8H), 6.61 (bs, 1H), 4.63 (d, J = 4.0 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 167.5, 138.4, 134.6, 131.7, 128.9, 128.7, 128.0, 127.7, 127.1, 44.3 ppm.

¹⁸ Han, Q.; Xiong, X.; Li, S. Cat. Commun. **2014**, 58, 85.

¹⁹ Mei, H.; Hu, J.; Xiao, S.; Lei, Y.; Li, G. *App. Cat.* **2014**, *475*, 40.

²⁰ Pineda, A.; Gomez, L.; Balu, A. M.; Sebastian, V.; Ojeda, M.; Arruebo, M.; Romero, A. A.; Santamaria, J.; Luque, R. *Green Chem.* **2013**, *15*, 2043.

N-Benzyl 4-methoxybenzamide²¹ (Table 2, entry 7): Prepared according to the general procedure from 4-methoxybenzoic acid to yield a white solid (157 mg, 0.65 mmol, 65% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, J = 8.0 Hz, 2H), 7.26-7.20 (m, 5H), 6.82 (d, J = 8.0 Hz, 2H), 6.70 (t, J = 6.0 Hz, 1H), 4.53 (d, J = 8.0 Hz, 2H), 3.76 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 167.1, 162.3, 138.6, 129.0, 128.8, 127.9, 127.5, 126.8, 113.8, 55.5, 44.1 ppm.

N-Benzyl phenylacetamide²² (Table 2, entry 8): Prepared according to the general procedure from phenylacetic acid to yield a white solid (191 mg, 0.85 mmol, 85% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.40-7.25 (m, 10H), 4.50 (d, J = 8.0 Hz, 2H), 4.29 (s, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 160.0, 137.0, 132.8, 130.0, 129.0, 128.8, 128.0 (two coincident resonances), 127.4, 43.7, 43.4 ppm.

N-Benzylacetamide²³ (Table 2, entry 9): Prepared according to the general procedure from acetic acid to yield a white solid (128 mg, 0.86 mmol, 86% yield).

H_3C^{-} CONHBn

¹H NMR (400 MHz, CDCl₃) δ 7.45-7.25 (m, 5H), 6.52 (bs, 1H), 4.36 (d, J = 4.0 Hz, 2H), 1.96 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 171.1, 136.1, 128.7 (two coincident resonances), 128.4, 66.5, 21.1 ppm.

N-Benzylbutyramide²⁴ (Table 2, entry 10): Prepared according to the general procedure from butyric acid to yield a white solid (140 mg, 0.79 mmol, 79% yield).

CONHBn

²¹ Ghosh, S. C.; Ngiam, J. S. Y.; Seayad, A. M.' Dang, T. T.' Johannes, C. W.; Chen, A. *Tetrahedron Lett.* **2013**, *54*, 4922.

²² Gernigon, N.; Zheng, H.; Hall, D. G. *Tetrahedron Lett.* **2013**, *54*, 4475.

²³ Rao, S. N.; Mohan, D. C.; Adimurthy, S. *Org. Lett.* **2013**, *15*, 1496.

²⁴ Davulcu, S.; Allen, C. L.; Milne, K.; Williams, J. M. J. Chem. Cat. Chem. 2013, 5, 435.

¹H NMR (400 MHz, CDCl₃) δ 7.40-7.25 (m, 5H), 6.59 (bs, 1H), 4.38 (d, J = 8.0 Hz, 2H), 2.19-2.15 (m, 2H), 1.71-1.63 (m, 2H), 0.94 (t, J = 8H, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) & 173.2, 138.6, 128.6, 127.6, 127.3, 43.4, 38.5, 19.2, 13.8 ppm.

Dodecanamide²⁵ (Table 2, entry 11): Prepared according to the general procedure from ndodecanoic acid to yield a white solid (134 mg, 0.67 mmol, 67% yield).



¹H NMR (400 MHz, CDCl₃) δ 5.56 (bs, 2H), 2.23 (t, J = 8.0 Hz, 2H), 1.64 (m, 2H), 1.40-1.15 (m, 16H), 0.88 (t, J = 8.0 Hz, 3H) ppm. 13 C NMR (100 MHz, CDCl₃) δ 172.4, 36.0, 32.1, 29.8, 29.7, 29.5, 29.4, 25.7, 22.9, 14.3 ppm.

4-Methoxybenzamide²⁶ (Table 2, entry 12): Prepared according to the general procedure from 4-methoxybenzoic acid to yield a white solid (94 mg, 0.62 mmol, 62% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, J = 8.0 Hz, 2H), 6.94 (d, J = 8.0 Hz, 2H), 5.81 (bs, 2H), 3.86 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 169.3, 163.0, 129.6, 125.3, 114.1, 55.6 ppm.

Boc-L-Ala-L-Phe-OMe²⁷ (Table 2, entry 13): Prepared according to the general procedure from Boc-L-Ala-OH to yield an off-white solid (252 mg, 0.72 mmol, 72% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.30-7.20 (m, 3H), 7.10 (d, J = 8.0 Hz, 2H), 6.56 (d, J = 8.0 Hz, 1H), 4.98 (m, 1H), 4.85 (m, 1H), 4.14 (bs, 1H), 3.70 (s, 3H), 3.20-3.05 (m, 2H), 1.43 (s, 9H), 1.26 (d, J = 8.0 Hz, 3H) ppm. 13 C NMR (100 MHz, CDCl₃) δ 172.5, 171.9, 155.5, 135.9, 129.4, 128.7, 127.3, 80.3, 53.3, 52.5, 50.2, 38.1, 28.5, 18.4 ppm.

 ²⁵ Ma, X.; He, Y.; Lu, M. Synth. Commun. 2013, 44, 474.
²⁶ Patil, U. B.; Singh, A. S.; Nagarkar, J. M. RSC Adv. 2014, 4, 1102.

²⁷ Ray, S.: Das, A. K.: Baneriee, A. Chem. Comm. **2006**, 2816.

Boc-*L***-Phe-***L***-Ala-OMe**²⁸ (**Table 2, entry 14**): Prepared according to the general procedure from Boc-*L***-Phe-OH to yield an off-white solid (263 mg, 0.75 mmol, 75% yield).**



¹H NMR (400 MHz, CDCl₃) δ 7.35-7.15 (m, 5H), 6.24 (d, J = 8.0 Hz, 1H), 5.04 (m, 1H), 4.52 (m, 1H), 4.35 (bs, 1H), 3.71 (s, 3H), 3.15-3.00 (m, 2H), 1.41 (s, 9H), 1.35 (d, J = 8.0 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 172.8, 170.9, 155.4, 136.5, 129.4, 128.7, 127.0, 80.3, 55.6, 52.5, 48.2, 38.4, 28.5, 18.4 ppm.

Boc-*L***-Val-***L***-Phe-OMe**²⁹ (**Table 2, entry 15**): Prepared according to the general procedure from Boc-*L***-Val-OH to yield an off-white solid (292 mg, 0.77 mmol, 77% yield).**



¹H NMR (400 MHz, CDCl₃) δ 7.30-7.20 (m, 3H), 7.11 (d, J = 8.0 Hz, 2H), 6.36 (bs, 1H), 5.07 (bs, 1H), 4.86 (m, 1H), 3.89 (bs, 1H), 3.71 (s, 3H), 3.20-3.00 (m, 2H), 2.09–1.99 (m, 1H), 1.44 (s, 9H), 0.95-0.80 (m, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 172.0, 171.6, 155.9, 136.0, 129.4, 128.8, 127.4, 80.1, 60.0, 53.3, 52.5, 38.2, 31.0, 28.5, 19.3, 17.9 ppm.

(2-Phenyl)ethyl dodecanoate³⁰ (Table 3, product 2): Prepared according to the general procedure from *n*-dodecanoic acid to yield a colorless oil (260 mg, 0.90 mmol, 90% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.32-7.16 (m, 5H), 4.27 (t, J = 8.0 Hz, 2H), 2.92 (t, J = 8.0 Hz, 2H), 2.26 (t, J = 8.0 Hz, 2H), 1.58 (m, 2H), 1.35-1.15 (m, 16H), 0.88 (t, J = 8.0 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 173.9, 138.0, 129.0, 128.6, 126.6, 64.8, 34.5, 32.1, 29.8, 29.6, 29.5, 29.4, 29.3, 25.1, 22.8, 14.2 ppm.

²⁸ Chen, H.; Xu, X.; Liu, L.; Tang, G.; Zhao, Y. RSC Adv. **2013**, *3*, 16247.

²⁹ Wu, W.; Zhang, Z.; Liebeskind, L. S. J. Am. Chem. Soc. 2011, 133, 14256.

³⁰ Zeng, R.; Sheng, H.; Zheng, Y.; Feng, Y.; Chen, Z.; Wang, J.; Chen, M.; Zhu, M.; Guo, Q. *J. Org. Chem.* **2014**, *79*, 9246.

Cylohexyl dodecanoate³¹ (**Table 3, product 4**): Prepared according to the general procedure from *n*-dodecanoic acid to yield a colorless oil (223 mg, 0.79 mmol, 79% yield).



¹H NMR (400 MHz, CDCl₃) δ 4.74 (m, 1H), 2.25 (t, J = 8.0 Hz, 2H), 1.81 (m, 2H), 1.68 (m, 2H), 1.61 (m, 2H), 1.45-1.15 (m, 22H), 0.86 (t, J = 8.0 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 173.5, 72.4, 34.9, 32.1, 31.8, 29.8, 29.6, 29.5, 29.4, 29.3, 25.6, 25.3, 23.9, 22.8, 14.3 ppm.

Isooctyl dodecanoate³² (Table 3, product 5): Prepared according to the general procedure from *n*-dodecanoic acid to yield a colorless oil (244 mg, 0.78 mmol, 78% yield).



¹H NMR (400 MHz, CDCl₃) δ 4.88 (m, 1H), 2.24 (t, J = 8.0 Hz, 2H), 1.65-1.40 (m, 4H), 1.45-1.20 (m, 24H), 1.18 (d, J = 4.0 Hz, 3H), 0.86 (t, J = 8.0 Hz, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 173.7, 70.9, 36.2, 34.9, 32.1, 31.9, 29.8, 29.7, 29.5 (two coincident resonances), 29.3 (two coincident resonances), 25.6, 25.3, 22.8, 22.7, 20.2, 14.2 (two coincident resonances) ppm.

Methyl 1-undecenoate³³ (**Table 3, product 7**): Prepared according to the general procedure from 1-decenoic acid to yield a colorless oil (153 mg, 0.77 mmol, 77% yield).



¹H NMR (400 MHz, CDCl₃) δ 5.81 (m, 1H), 5.01-4.92 (m, 2H), 3.67 (s, 3H), 2.30 (t, J = 8.0 Hz, 2H), 2.04 (m, 2H), 1.62 (m, 2H), 1.50-1.20 (m, 10H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 174.5, 139.3, 114.3, 51.6, 34.3, 33.9, 29.4, 29.3 (two coincident resonances), 29.2, 29.0, 25.1 ppm.

³³ Gersch, M.; Gut, F.; Korotkov, V.; Lehmann, J.; Böttcher, T.; Rusch, M.; Hedberg, C.; Waldmann, H.; Klebe, G.; Sieber, S. Angew. Chem. Int. Ed. **2013**, *52*, 3009.

³¹ Zhan, S.; Tao, X.; Cai, L.; Liu, X.; Liu T. Green Chem. **2014**, *16*, 4649.

³² Sukenik, C.; Bergman. J. Am. Chem. Soc. **1976**, 98, 6613.

Methyl oleate³⁴ (Table 3, product 8): Prepared according to the general procedure from oleic acid to yield a colorless oil (240 mg, 0.81 mmol, 81% yield).



¹H NMR (400 MHz, CDCl₃) δ 5.34 (m, 2H), 3.66 (s, 3H), 2.29 (t, J = 8.0 Hz, 2H), 2.00 (m, 4H), 1.61 (m, 2H), 1.40-1.20 (m, 20H), 0.87 (t, J = 8.0 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 174.5, 130.2, 130.0, 51.6, 34.3, 32.1, 30.0, 29.9, 29.7, 29.5, 29.3 (three coincident resonances), 27.4, 27.3, 25.1, 22.9, 14.3 ppm.

10-Decanolide³⁵ (**Table 3, product 9**): Prepared according to the general procedure from 10hydroxy decanoic acid to yield a colorless oil (121 mg, 0.71 mmol, 71% yield).



¹H NMR (400 MHz, CDCl₃) δ 4.09 (t, J = 8.0 Hz, 2H), 2.47 (t, J = 8.0 Hz, 2H), 1.75-1.67 (m, 4H), 1.45-1.25 (m, 10H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 174.1, 64.4, 34.7, 29.3, 29.1, 28.9 (two coincident resonances), 28.4, 26.0, 24.7 ppm.

16-Hexadecanolide³⁶ (**Table 3, product 10**): Prepared according to the general procedure from 10-hydroxy decanoic acid to yield a colorless oil (186 mg, 0.73 mmol, 73% yield).



¹H NMR (400 MHz, CDCl₃) δ 4.12 (t, J = 8.0 Hz, 2H), 2.32 (t, J = 8.0 Hz, 2H), 1.72-1.57 (m, 4H), 1.45-1.20 (m, 22H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 174.1, 64.4, 34.7, 29.7, 28.7, 28.2, 27.9 (two coincident resonances), 27.7 (two coincident resonances), 27.1, 27.0, 26.9, 26.8, 25.6, 25.1 ppm.

³⁴ Characterization data matched authentic sample from Sigma-Aldrich.

³⁵ Morales-Serna., J. A.; Sanchez, E.; Velazquez, R.; Bernal, J.; Garcia-Rios, E.; Gavino, R.; Negron-Silva, G.; Cardenas, J. Org. Biomol. Chem. **2010**, *8*, 4940.

³⁶ Ishihara, K.; Kubota, M.; Kurihara, H.; Yamamoto, H. J. Org. Chem. 1996, 61, 4560.

2-Benzofuranone³⁷ (Table 3, product 11): Prepared according to the general procedure from 10-hydroxy decanoic acid to yield a yellow oil (123 mg, 0.92 mmol, 92% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.35-7.10 (m, 4H), 3.75 (s, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 174.2, 154.9, 129.0, 124.8, 124.2, 123.2, 110.9, 33.1 ppm.

4-Methoxyphenyl cinnamate³⁸ (Table 3, product 13): Prepared according to the general procedure from cinnamic acid to yield a white solid (181 mg, 0.71 mmol, 71% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 16.0 Hz, 1H), 7.60-7.57 (m, 2H), 7.45-7.40 (m, 3H), 7.10 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 6.63 (d, J = 16.0 Hz, 2H), 3.82 (s, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 165.9, 157.4, 146.6, 144.5, 134.4, 130.8, 129.2, 128.4, 122.5, 117.6, 114.7, 55.8 ppm.

N-Butylbenzamide³⁹ (Table 3, product 15): Prepared according to the general procedure from benzoic acid to yield a white solid (69 mg, 0.39 mmol, 39% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.75 (m, 2H), 7.46 (m, 1H), 7.41 (m, 2H), 6.18 (bs, 1H), 3.45 (q, J = 4.0 Hz, 2H), 1.60 (m, 2H), 1.40 (m, 2H), 0.96 (t, J = 8.0 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 167.7, 135.0, 131.5, 128.7, 127.0, 40.0, 31.9, 20.3, 14.0 ppm.

 ³⁷ Rit, R.; Yadav, M.; Sahoo, A. *Org. Lett.* 2014, *16*, 968.
³⁸ Ruiz, D.; Romanelli, G.; Vázquez, P.; Aution, J. *App. Cat.* 2010, *374*, 110.

³⁹ Wang, N.; Zou, X.; Ma, J.; Li, F. Chem. Commun. 2014, 50, 8303.

N,N-Diisopropyl 4-phenylbutyramide⁴⁰ (**Table 3, product 18**): Prepared according to the general procedure from 4-phenylbutyric acid to yield a white solid (205 mg, 0.83 mmol, 83% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.35-7.15 (m, 5H), 3.87 (m, 1H), 3.48 (bs, 1H), 2.68 (t, J = 8.0 Hz, 2H), 2.28 (t, J = 8.0 Hz, 2H), 1.95 (m, 2H), 1.38 (d, J = 4.0 Hz, 6H), 1.65 (d, J = 8.0 Hz, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 172.0, 142.1, 128.7, 128.5, 126.0, 48.5, 45.9, 35.5, 34.4, 27.1, 21.1, 20.9 ppm.

N,N-Dicyclohexyl 4-phenylbutyramide⁴⁰ (**Table 3, product 19**): Prepared according to the general procedure from 4-phenylbutyric acid to yield a white solid (252 mg, 0.77 mmol, 77% yield).



¹H NMR (400 MHz, CDCl₃) δ 7.30-7.15 (m, 5H), 3.32 (bs, 1H), 2.67 (t, J = 8.0 Hz, 2H), 2.46 (bs, 1H), 2.28 (t, J = 8.0 Hz, 2H), 1.95 (m, 2H), 1.77 (m, 4H), 1.63 (m, 4H), 1.46 (m, 4H), 1.30-1.10 (m, 8H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 172.3, 142.4, 128.6, 128.5, 126.1, 48.5, 45.9, 35.6, 34.4, 29.6, 29.5, 26.1, 22.9, 21.0, 20.9 ppm.

⁴⁰ Al-Jallo, H.; Hussain, A.; Mansoor, H.; Sameh, A.; Al-Saidi, S. J. Chem. Eng. Data 1984, 29, 479.

NMR spectra







400 MHz, ¹H NMR, CDCI₃



































Table 3, product 9





Table 3, product 11







