

Supporting Information for
**Enzyme-like chemoselective *O*-acylation of aminoalcohols
catalyzed by a Zinc cluster**

Takashi Ohshima,* Takanori Iwasaki, Yusuke Maegawa, Asako Yoshiyama, and
Kazushi Mashima*

*To whom the correspondence should be addressed.

E-mail: ohshima@chem.es.osaka-u.ac.jp, mashimna@chem.es.osaka-u.ac.jp

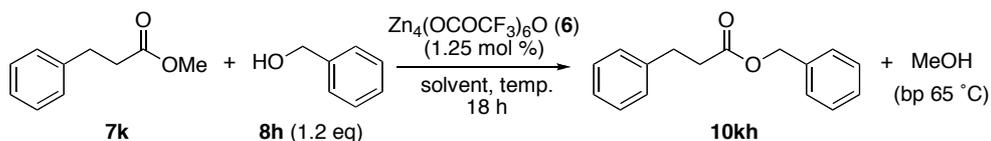
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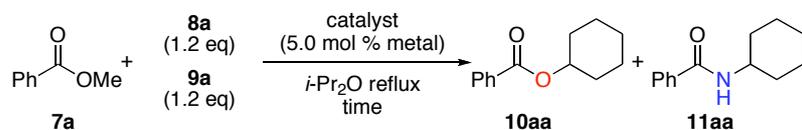
Materials and Methods

References

Optimization of Reaction Conditions



Because transesterification is an equilibrium reaction, without the use of large excess amounts of either esters or alcohols, the reaction should be performed at a temperature higher than 65 °C (boiling point of MeOH) to remove the resulting MeOH. The reaction conducted under toluene-refluxed conditions (111 °C) afforded the product in 95% yield. At a lower temperature (80 °C), however, the product was obtained in only 48% yield. Thus, to screen for the best solvent system, we examined solvent effects at temperatures of 80 °C or lower, and found that diisopropyl ether-refluxed conditions produced the best results. This solvent forms a roughly 1:1 azeotrope with methanol, which boils ca. 10 °C lower than pure diisopropyl ether (b.p. = 68 °C) at atmospheric pressure,^{SI-1} making it easy to remove MeOH from the reaction mixture.

Table S1. Effects of Catalyst on the Chemoselective Acylation of Alcohol

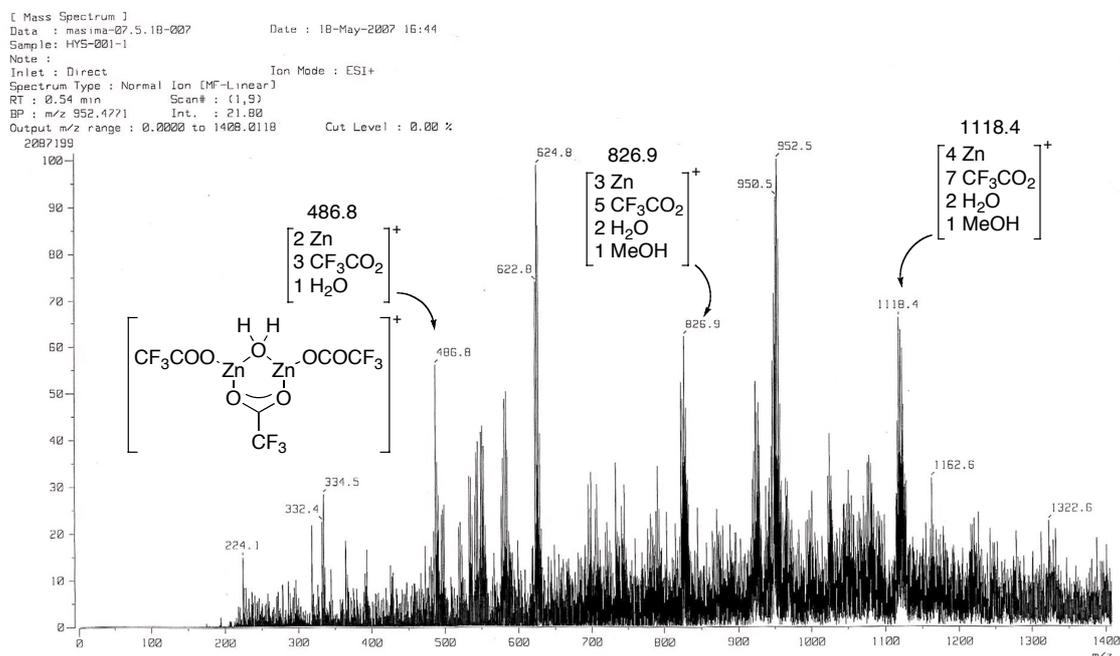
entry	catalyst	time (h)	ester 10aa (%) ^a	amide 11aa (%) ^a
1	Zn(OAc) ₂ (5 mol %)	18	7	<1
2	Zn ₄ (OAc) ₆ O (1.25 mol % = 5 mol % Zn)	18	82	1
3	Zn(OCOCF ₃) ₂ (5 mol %)	6	43	<1
4	Zn ₄ (OCOCF ₃) ₆ O (6) (1.25 mol % = 5 mol % Zn)	6	75	1
5	Zn ₄ (OCOCF ₃) ₆ O (6) (1.25 mol % = 5 mol % Zn)	18	96	1
6	Al(O- <i>i</i> -Pr) ₃ (10 mol %)	18	12	46

^a Yield was determined by GC analysis using DM-5 column.

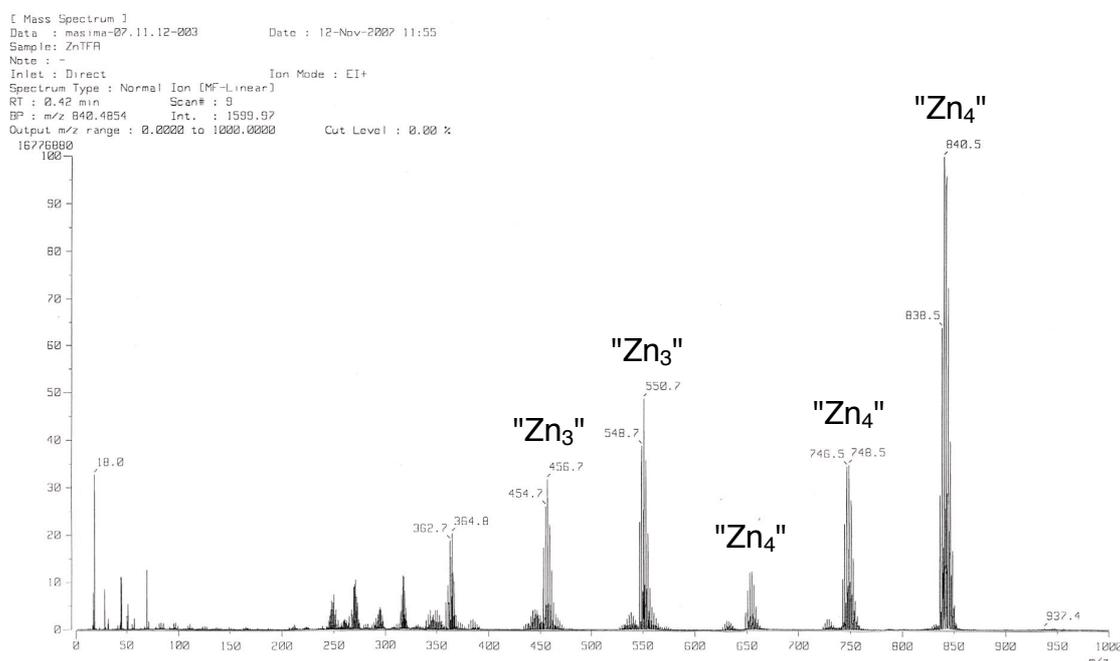
Although so-called monomeric Zn complex Zn(OCOCF₃)₂ showed moderate reactivity (entry 3, 6 h, 43% yield), when the Zn cluster **6** was used as a catalyst for this chemoselective acylation reaction, alcohol **8a** was selectively acylated to afford ester **10aa** (entry 4, 6 h, 75% yield; entry 5, 18 h 96% yield), along with only 1% of amide **11aa**. Based on Mass spectroscopy analysis (*vide infra*), we found that Zn(OCOCF₃)₂ does not exist as a *monomer* but rather as an *oligomeric mixture*. Because Zn(OCOCF₃)₂ affords a catalytically active oligomeric species, similar to the derivatives of Zn₄(OCOCF₃)₆O, the catalytic activity of Zn(OCOCF₃)₂ and Zn₄(OCOCF₃)₆O depends on how easy it is to generate cluster species bearing the Zn–O–Zn bimetallic active sites. *The advantage of the tetranuclear cluster is obvious*, however, when Zn(OAc)₂ (entry 1, 18 h, 7% yield) and Zn₄(OAc)₆O (entry 2, 18 h, 82% yield) are compared.

Figure S1. Mass analysis of $\text{Zn}(\text{OCOCF}_3)_2$ and $\text{Zn}_4(\text{OCOCF}_3)_6\text{O}$.

ESI-Mass of $\text{Zn}(\text{OCOCF}_3)_2$ in MeOH



EI-Mass of $\text{Zn}(\text{OCOCF}_3)_2$



We found that so-called monomeric $\text{Zn}(\text{OCOCF}_3)_2$ does not exist as a *monomer* but rather as an *oligomeric mixture* based on ESI-Mass spectroscopy analysis (Figure S1). Major peaks can be assigned to the tetranuclear Zn complex $[\text{Zn}_4(\text{OCOCF}_3)_7(\text{H}_2\text{O})_2(\text{MeOH})]^+$ ($m/z = 1119$), trinuclear Zn complex

$[\text{Zn}_3(\text{OCOCF}_3)_5(\text{H}_2\text{O})_2(\text{MeOH})]^+$ ($m/z = 827$), and dinuclear Zn complex $[\text{Zn}_2(\text{OCOCF}_3)_3(\text{H}_2\text{O})]^+$ ($m/z = 487$). Other major peaks ($m/z = 625$ and 953) can also be assigned to the dinuclear and trinuclear Zn complexes, respectively, based on the mass spectroscopy pattern. It was thus confirmed that under the present reaction conditions, so-called monomeric Zn complex $\text{Zn}(\text{OCOCF}_3)_2$ became an oligomer whose Zn–O–Zn bimetallic active site is almost the same as that of the tetranuclear Zn complex. Therefore, we selected the tetranuclear trifluoroacetate complex as the catalyst. EI-Mass spectroscopy analysis also suggested the existence of trinuclear Zn complexes and tetranuclear Zn complexes based on mass spectroscopy pattern.

ESI-Mass of $\text{Zn}_4(\text{OCOCF}_3)_6\text{O}$ (6) in MeOH

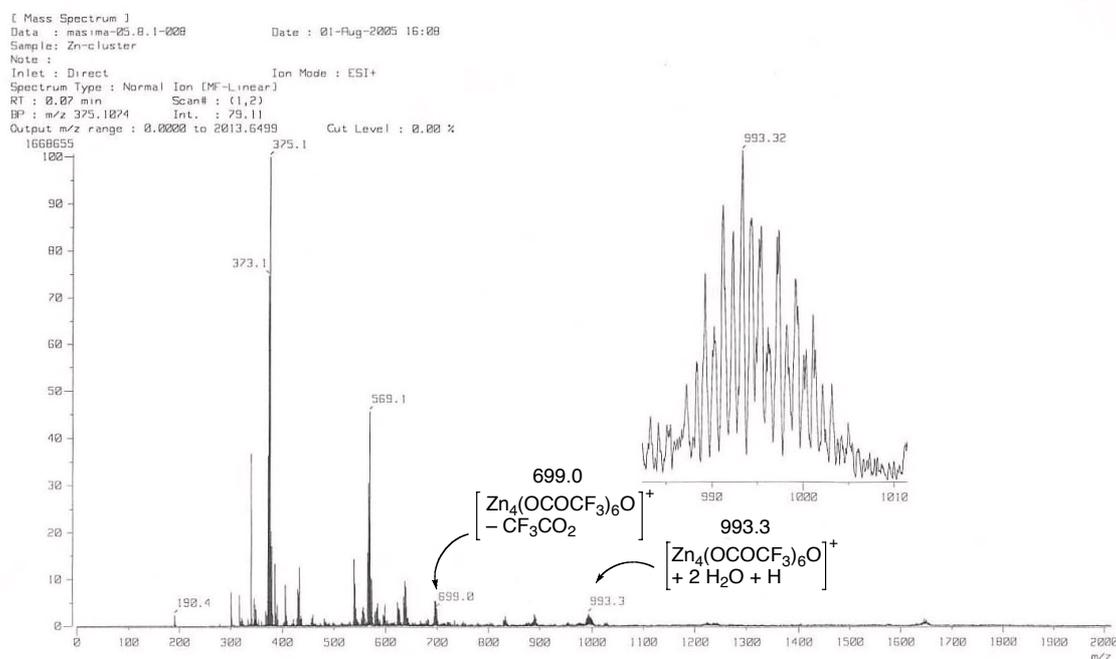
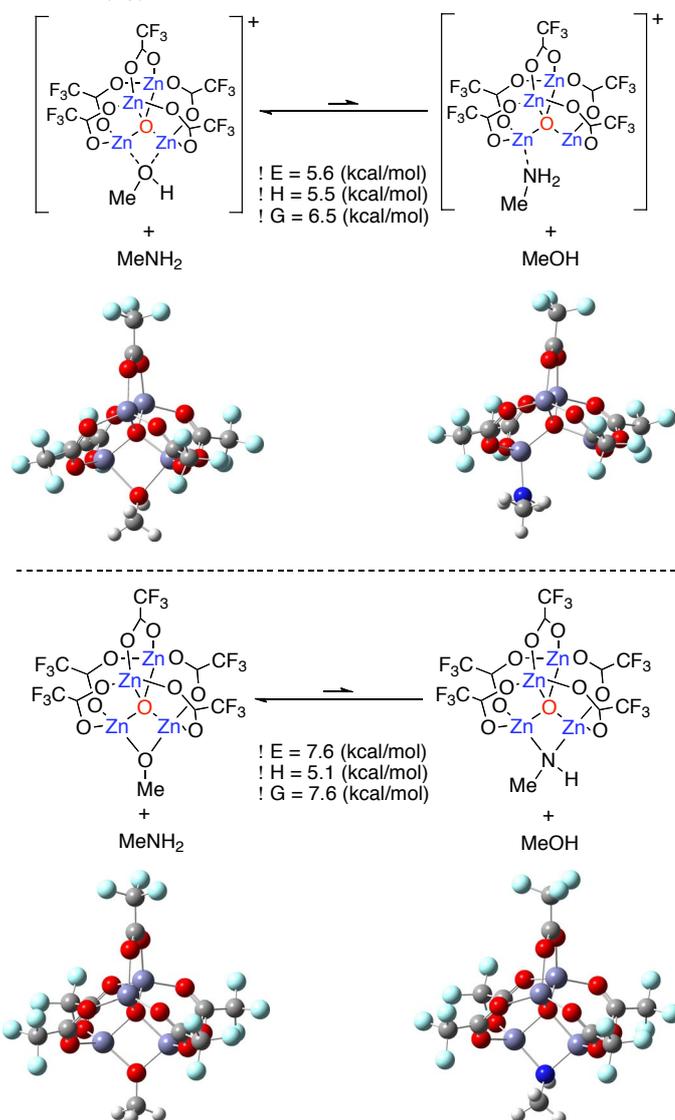


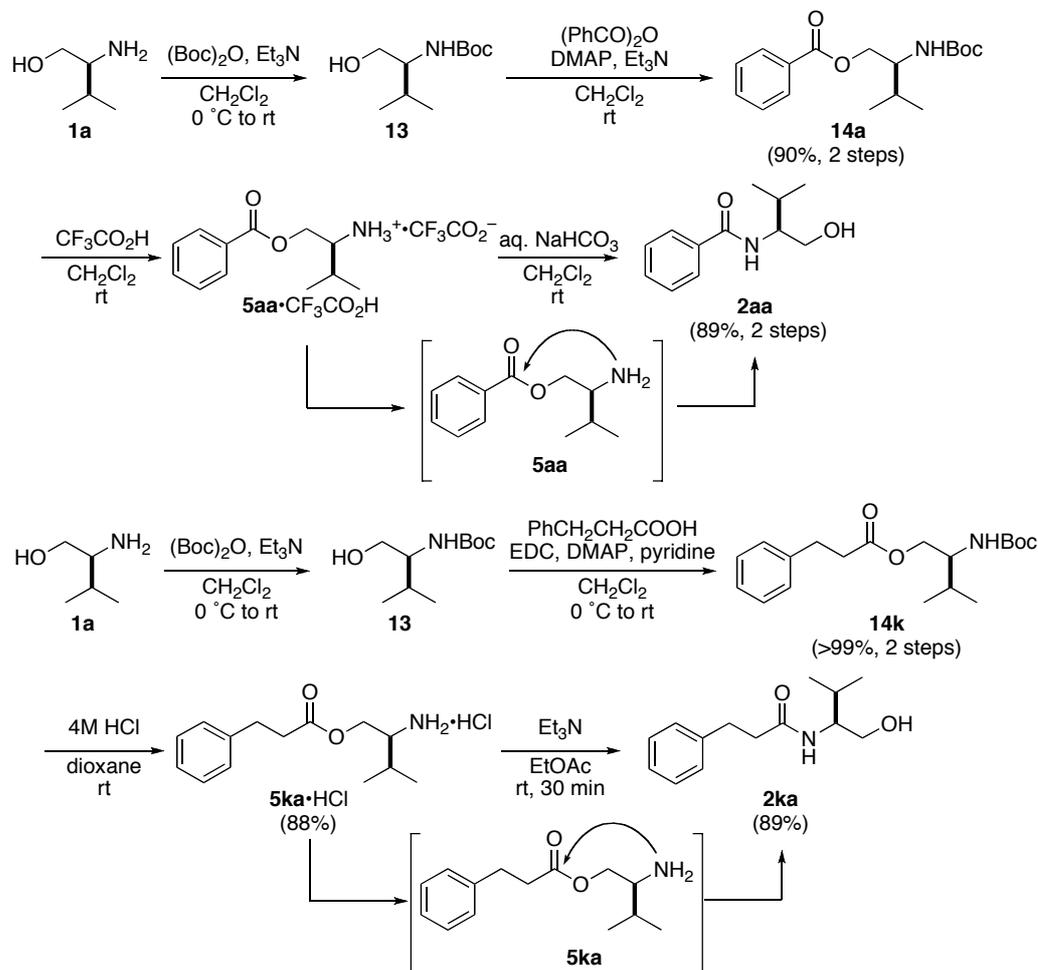
Figure S2. DFT calculations of Zn complexes.

B3LYP/6-31G(d,p)



To evaluate the relative stability of the alkoxide and amide complexes, we performed DFT calculations. All of the geometries of the Zn complexes, MeOH, and MeNH₂ were fully optimized with Gaussian 03 at the B3LYP/6-31G(d,p) level followed by frequency calculations to determine the nature of the stationary points. The reported energies include zero-point energy corrections at the level of the geometry optimization. These calculations indicated that the Zn alkoxide complex is thermodynamically more stable than the Zn amide complex (7.6 kcal/mol) and that the MeOH adduct is more stable than the MeNH₂ adduct (5.6 kcal/mol), suggesting a highly oxophilic, rather than azaphilic, property of the trifluoroacetate bridged μ -oxo tetranuclear Zn clusters.

Scheme S1. *N*→*O* Acyl Transfer Reaction of β -Aminoalcohol



The trifluoroacetic acid salt of aminoester **5aa** was synthesized through *N*-protection (**1a**→**13**), *O*-acylation (**13**→**14a**), and *N*-deprotection (**14a**→**5aa**·CF₃CO₂H). After treatment with aqueous NaHCO₃ to provide free **5aa**, a complete *O*→*N* acyl transfer reaction (**5aa**→**2aa**) proceeded to give hydroxyamide **2aa** in 89% yield (2 steps). Complete *O*→*N* acyl transfer reaction of **5ka** also proceeded to give hydroxyamide **2ka**.

Although we proposed that the Zn cluster-catalyzed oxazoline formation would proceed through transamidation,¹⁰ the results shown in this manuscript suggest that it proceeds through transesterification and the following complete *O*→*N* acyl transfer reaction. Under the conditions for transesterification (*i*-Pr₂O reflux), oxazoline formation did not proceed at all (Table 2, entry 1).

Experimental

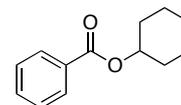
General: Nuclear magnetic resonance (^1H NMR, ^{13}C NMR, and ^{19}F NMR) spectra were measured on a Varian MERCURY300-C/H spectrometer operating at 300 MHz (^1H NMR), 75 MHz (^{13}C NMR), and 282 MHz (^{19}F NMR), in 5 mm NMR tubes. All ^1H NMR chemical shifts were reported in ppm relative to internal references of TMS at δ 0.00. All ^{13}C NMR chemical shifts were reported in ppm relative to carbon resonance in chloroform- d_7 at δ 77.00, THF- d_8 at δ 25.20. The ^{19}F NMR chemical shifts were reported in ppm relative to external references of α,α,α -trifluorotoluene at δ -63.9. Low and high resolution mass spectra were recorded by JEOL JMS-700. IR spectra were recorded on Jasco FT/IR-230 spectrometer and Jasco FT/IR-410 spectrometer. Elemental analyses were conducted by Perkin-Elmer 2400II. Melting points were measured using Yanaco micro melting point apparatus. GC analyses were recorded on a Shimadzu GC-14A gas chromatograph with J&W Scientific DB-5 column. All catalytic reactions were carried out by the standard Schlenk techniques under an argon atmosphere. Diisopropyl ether and toluene were distilled from benzophenone ketyl.

Preparation of tetranuclear zinc cluster **6.**¹⁰ Under an inert atmosphere of argon, zinc trifluoroacetate hydrate (845 mg, 2.73 mmol as a monohydrate) was heated at 120 °C for 4 h under reduced pressure (≤ 0.02 mmHg) to remove water. The resulting dry powder was then heated at 360 °C on sand bath, and the μ -oxo-tetranuclear zinc cluster **6** was sublimed from the reaction mixture. The zinc cluster was collected and stored under an inert atmosphere of argon (545 mg, 84%); white solid; IR (nujol NaCl, ν/cm^{-1}) 2923, 1701, 1202, 856, 796, 730; ^{13}C NMR (75 MHz, THF- d_8 , 35 °C) δ 116.97 (q, $J_{\text{C-F}} = 288$ Hz, CF_3COO), 163.81 (q, $J_{\text{C-F}} = 38$ Hz, CF_3COO); ^{19}F NMR (282 MHz, THF- d_8 , 35 °C) δ -78.88 (s); MS (ESI) m/z (relative intensity) 933 ($[\text{M}+2\text{H}_2\text{O}+\text{H}^+]$, 3); Anal. calcd for $\text{C}_{12}\text{F}_{18}\text{O}_{13}\text{Zn}_4$: C15.08%; found C 15.52%.

General procedure for the chemoselective acylation of alcohol in the presence of the same equivalent of amine. The Zn cluster **6** (0.015 mmol, 0.05 mmol Zn), ester (1.0 mmol), alcohol (1.2 mmol), and amine (1.2 mmol) in diisopropyl ether (1.7 mL) were refluxed for periodic time under an argon atmosphere (Ar gas purge, 15~20 mL/min). The resulting mixture was concentrated *in vacuo* and purified by silica gel column chromatography. Yield of ester and amide were determined by GC analysis or

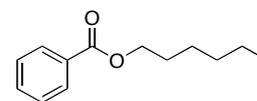
isolation by silica gel column chromatography.

Cyclohexyl benzoate (10aa)



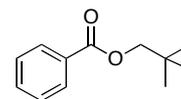
Purified by flush column chromatography (silica gel, Hexane/EtOAc = 40/1); colorless oil; IR (neat NaCl, ν/cm^{-1}) 2938, 1714, 1451, 1316, 1113, 1026, 910, 713; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.2–2.0 (m, 10H, *cyclohexyl*), 5.0–5.1 (m, 1H, *OCH*), 7.4–7.6 (m, 3H, *Ph*), 8.0–8.1 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 23.80, 25.64, 31.76, 72.94, 127.99, 129.26, 130.85, 132.34, 165.55; MS (EI) m/z (relative intensity) 204 ($[\text{M}^+]$, 1), 105 (100), 77 (35); HRMS (EI) m/z calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_2$ 204.1150 found 204.1159.

Hexyl benzoate (10ab)



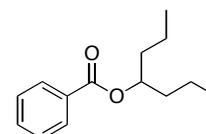
Purified by flush column chromatography (silica gel, Hexane/EtOAc = 20/1); colorless oil; IR (neat NaCl, ν/cm^{-1}) 2931, 2859, 1720, 1603, 1452, 1314, 1274, 1176, 1112, 1070, 1027, 711; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 0.90 (s, $J = 6.9$ Hz, 3H, CH_2CH_3), 1.3–1.5 (m, 6H, *methylene*), 1.77 (tt, $J = 6.9, 6.6$ Hz, 2H, OCH_2CH_2), 4.32 (t, $J = 6.6$ Hz, 2H, OCH_2CH_2), 7.4–8.1 (m, 5H, *Ph*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 13.93, 22.51, 25.70, 28.70, 31.45, 65.10, 128.28, 129.51, 130.63, 132.71, 166.64; MS (EI) m/z (relative intensity) 206 ($[\text{M}^+]$, 4), 123 (100), 105 (96); HRMS (EI) m/z calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_2$ 206.1307 found 206.1288.

2,2-Dimethylpropyl benzoate (10ac)



Purified by flush column chromatography (silica gel, Hexane/EtOAc = 40/1); colorless oil; IR (neat NaCl, ν/cm^{-1}) 2959, 1723, 1478, 1452, 1370, 1314, 1278, 1115, 1070, 1027, 975, 711; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.04 (s, 9H, $\text{C}(\text{CH}_3)_3$), 4.01 (s, 2H, OCH_2), 7.4–7.6 (m, 3H, *Ph*), 8.0–8.1 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 26.73, 31.73, 74.16, 128.10, 129.28, 130.40, 132.52, 166.17; MS (EI) m/z (relative intensity) 192 ($[\text{M}^+]$, 1), 137 (8), 123 (8), 105 (100), 77 (23); HRMS (EI) m/z calcd. for $\text{C}_{12}\text{H}_{16}\text{O}_2$ 192.1150 found 192.1164.

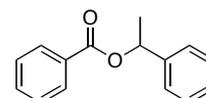
4-Heptyl benzoate (10ad)



Purified by flush column chromatography (silica gel, Hexane/EtOAc = 40/1); colorless

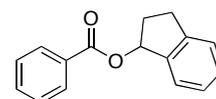
oil; IR (neat NaCl, ν/cm^{-1}) 2959, 2873, 1716, 1451, 1274, 1109, 1069, 1026, 935, 711; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 0.93 (t, $J = 7.2$ Hz, 6H, CH_3), 1.3–1.8 (m, 8H, *methylene*), 5.17 (tt, $J = 7.2, 5.1$ Hz, 1H, OCH), 7.2–7.5 (m, 3H, *Ph*), 8.0–8.1 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 14.17, 18.79, 36.59, 74.52, 128.02, 129.28, 130.71, 132.35, 165.94; MS (EI) m/z (relative intensity) 220 ($[\text{M}^+]$, 2), 177 (7), 105 (100), 77 (75); HRMS (EI) m/z calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_2$ 220.1463 found 220.1474.

α -Methylbenzyl benzoate (10ae)



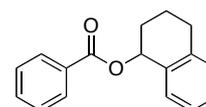
Purified by flush column chromatography (silica gel, Hexane/EtOAc = 40/1); colorless oil; IR (neat NaCl, ν/cm^{-1}) 2981, 1718, 1495, 1451, 1315, 1271, 1110, 1068, 1027, 761, 713; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.65 (d, $J = 6.6$ Hz, 3H, CH_3), 6.13 (q, $J = 6.6$ Hz, 1H, OCH), 7.2–7.5 (m, 8H, *Ph*), 8.0–8.1 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 22.44, 72.78, 125.75, 127.57, 128.02, 128.24, 129.32, 130.32, 132.53, 141.48, 165.29; MS (EI) m/z (relative intensity) 226 ($[\text{M}^+]$, 5), 105 (100), 77 (22); HRMS (EI) m/z calcd. for $\text{C}_{15}\text{H}_{14}\text{O}_2$ 226.0994 found 226.0985.

1-Indanyl benzoate (10af)



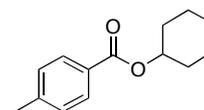
Purified by flush column chromatography (silica gel, Hexane/EtOAc = 20/1); white solid; mp 39–40°C; IR (film NaCl, ν/cm^{-1}) 2944, 2852, 1714, 1602, 1480, 1451, 1349, 1315, 1269, 1176, 1111, 1069, 1026, 934, 895, 756, 712; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 2.23 (dddd, $J = 15.9, 8.4, 8.4, 3.6$ Hz, 1H, 2-*indane*), 2.62 (dddd, $J = 15.9, 7.2, 6.0, 5.4$ Hz, 1H, 2-*indane*), 2.91 (ddd, $J = 16.2, 8.4, 5.4$ Hz, 1H, 3-*indane*), 3.17 (ddd, $J = 16.2, 8.4, 6.0$ Hz, 1H, 3-*indane*), 6.45 (dd, $J = 7.2, 3.6$ Hz, 1H, 1-*indane*), 7.2–7.5 (m, 7H, *Ar*), 8.0–8.1 (m, 2H, *Ar*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 30.26, 32.46, 78.91, 124.79, 125.64, 126.71, 128.24, 128.91, 129.65, 130.56, 132.80, 141.13, 144.35, 166.52; MS (EI) m/z (relative intensity) 238 ($[\text{M}^+]$, 1), 193 (1), 133 (8), 116 (100), 105 (33), 77 (15); HRMS (EI) m/z calcd. for $\text{C}_{16}\text{H}_{14}\text{O}_2$ 238.0994 found 238.0972.

1,2,3,4-Tetrahydro-1-naphthyl benzoate (10ag)



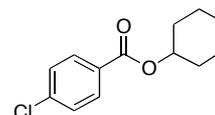
Purified by flush column chromatography (silica gel, Hexane/EtOAc = 20/1); colorless oil; IR (neat NaCl, ν/cm^{-1}) 2942, 1714, 1602, 1493, 1451, 1268, 1112, 1061, 1026, 908, 734; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.8–2.1 (m, 4H, 2,3-*tetrahydronaphthyl*), 2.79 (ddd, $J = 16.8, 8.1, 6.0$ Hz, 1H, 4-*tetrahydronaphthyl*),

2.92 (ddd, $J = 16.8, 5.7, 5.1$ Hz, 1H, 4-tetrahydronaphthyl), 6.25 (dd, $J = 4.5, 4.5$ Hz, 1H, 1-tetrahydronaphthyl), 7.2–7.6 (m, 7H, Ar), 8.0–8.1 (m, 2H, Ar); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 19.09, 29.05, 29.27, 70.67, 126.08, 128.05, 128.27, 129.04, 129.50, 129.70, 130.76, 132.80, 134.72, 137.99, 166.22; MS (EI) m/z (relative intensity) 252 ($[\text{M}^+]$, 3), 130 (100), 105 (40), 84 (36); HRMS (EI) m/z calcd. for $\text{C}_{17}\text{H}_{16}\text{O}_2$ 252.1150 found 252.1166.



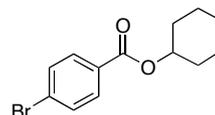
Cyclohexyl 4-methylbenzoate (10ba)

Purified by flush column chromatography (silica gel, Hexane/EtOAc = 40/1 to 4/1); colorless oil; IR (film NaCl, ν/cm^{-1}) 2936, 2859, 1714, 1613, 1451, 1318, 1277, 1177, 1108, 1038, 1018, 943, 922, 841, 754; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.3–1.6 (m, 6H, cyclohexyl), 1.8–2.0 (m, 4H, cyclohexyl), 2.39 (s, 3H, methyl), 5.01 (tt, $J = 8.7, 3.9$ Hz, 1H, OCH), 7.21 (d, $J = 8.1$ Hz, 2H, Ar), 7.93 (d, $J = 8.1$ Hz, 2H, Ar); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 21.50, 23.61, 25.47, 31.62, 72.69, 128.34, 128.89, 129.50, 143.13, 165.97; MS (EI) m/z (relative intensity) 218 ($[\text{M}^+]$, 1), 137 (100), 119 (98), 91 (35); HRMS (EI) m/z calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_2$ 218.1307 found 218.1294.



Cyclohexyl 4-chlorobenzoate (10ca)

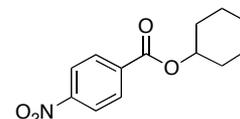
Purified by flush column chromatography (silica gel, Hexane/EtOAc = 40/1 to 4/1); white solid; mp 37 °C; IR (neat NaCl, ν/cm^{-1}) 2938, 2860, 1715, 1594, 1488, 1450, 1400, 1276, 1172, 1116, 1014, 849, 761; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.3–1.7 (m, 6H, cyclohexyl), 1.8–2.0 (m, 4H, cyclohexyl), 5.02 (tt, $J = 9.0, 3.6$ Hz, 1H, OCH), 7.39 (d, $J = 8.7$ Hz, 2H, Ar), 7.97 (d, $J = 8.7$ Hz, 2H, Ar); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 23.61, 25.41, 31.58, 73.36, 128.54, 129.50, 130.89, 139.05, 165.05; MS (EI) m/z (relative intensity) 238 ($[\text{M}^+]$, 1), 203 (2), 157 (69), 139 (100), 111 (32), 82 (61); HRMS (EI) m/z calcd. for $\text{C}_{13}\text{H}_{15}\text{O}_2\text{Cl}$ 238.0761 found 238.0747.



Cyclohexyl 4-bromobenzoate (10da)

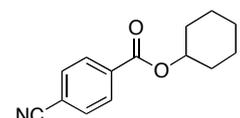
Purified by flush column chromatography (silica gel, Hexane/EtOAc = 40/1 to 4/1); white solid; mp 44 °C; IR (neat NaCl, ν/cm^{-1}) 2937, 2859, 1715, 1591, 1484, 1450, 1397, 1274, 1114, 1011, 847, 757; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.2–1.6 (m, 6H, cyclohexyl), 1.8–2.0 (m, 4H, cyclohexyl), 5.02 (tt, $J = 8.7, 3.9$ Hz, 1H, OCH), 7.56 (d, $J = 8.7$ Hz, 2H, Ar), 7.90 (d, $J = 8.7$ Hz, 2H, Ar); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ

23.62, 25.42, 31.58, 73.41, 127.68, 129.96, 131.05, 131.56, 165.18; MS (EI) m/z (relative intensity) 284 ($[M(^{81}\text{Br})^+]$, 67), 282 ($[M(^{79}\text{Br})^+]$, 69), 185 (87), 183 (90), 157 (37), 155 (36), 82 (100); HRMS (EI) m/z calcd. for $\text{C}_{13}\text{H}_{15}\text{O}_2^{79}\text{Br}$ 282.0255 found 282.0249, calcd. for $\text{C}_{13}\text{H}_{15}\text{O}_2^{81}\text{Br}$ 284.0236 found 284.0247.



Cyclohexyl 4-nitrobenzoate (10ea)

Purified by flush column chromatography (silica gel, Hexane/EtOAc = 40/1 to 4/1); pale yellow solid; mp 51-52 °C; IR (neat NaCl, ν/cm^{-1}) 2939, 2861, 1721, 1608, 1529, 1349, 1280, 1116, 1013, 874, 835, 720; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.3–1.7 (m, 6H, *cyclohexyl*), 1.8–2.0 (m, 4H, *cyclohexyl*), 5.07 (tt, $J = 9.0, 3.9$ Hz, 1H, OCH), 8.20 (d, $J = 9.0$ Hz, 2H, Ar), 8.28 (d, $J = 9.0$ Hz, 2H, Ar); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 23.60, 25.33, 31.52, 74.35, 123.40, 130.58, 136.40, 150.44, 164.01; MS (FAB) m/z (relative intensity) 250 ($[M+H^+]$, 12), 150 (15), 147 (25).

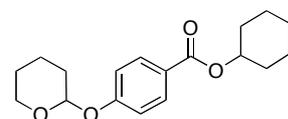


Cyclohexyl 4-cyanobenzoate (10fa)

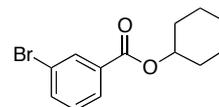
Purified by flush column chromatography (silica gel, Hexane/EtOAc = 40/1 to 4/1); white solid; mp 61-62 °C; IR (neat NaCl, ν/cm^{-1}) 2939, 2860, 2231, 1720, 1451, 1406, 1280, 1108, 1013, 915, 862, 768, 734, 692; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.3–1.7 (m, 6H, *cyclohexyl*), 1.8–2.0 (m, 4H, *cyclohexyl*), 5.05 (tt, $J = 8.7, 3.9$ Hz, 1H, OCH), 7.73 (d, $J = 8.4$ Hz, 2H, Ar), 8.14 (d, $J = 8.4$ Hz, 2H, Ar); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 23.54, 25.29, 31.47, 74.11, 116.10, 117.94, 129.97, 132.05, 134.81, 164.22; MS (EI) m/z (relative intensity) 229 ($[M^+]$, 1), 148 (32), 130 (100), 102 (43), 82 (91); HRMS (EI) m/z calcd. for $\text{C}_{14}\text{H}_{15}\text{N O}_2$ 229.1103 found 229.1120.

Cyclohexyl 4-(tetrahydropyran-2-yloxy)benzoate (10ga)

Purified by flush column chromatography (silica gel, Hexane/EtOAc = 40/1 to 4/1); white solid; mp 60-61 °C; IR (neat NaCl, ν/cm^{-1}) 2939, 2859, 2252, 1712, 1606, 1508, 1453, 1244, 1202, 1169, 1113, 1038, 959, 919, 771, 733; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.3–2.0 (m, 16H, *cyclohexyl*, *THP*), 3.6–3.9 (m, 2H, 3-*THP*), 5.00 (tt, $J = 8.7, 3.6$ Hz, 1H, OCH), 5.49 (t, $J = 3.0$ Hz, 1H, 2-*THP*), 7.06 (d, $J = 9.0$ Hz, 2H, Ar), 7.98 (d, $J = 9.0$ Hz, 2H, Ar); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 18.52, 23.64, 25.07, 25.51, 30.13, 31.67, 61.96, 72.57, 96.10, 115.81, 124.22, 131.33, 160.69, 165.70; MS (FAB) m/z (relative intensity) 350 ($[M+H^+]$, 7), 223 (13), 121 (57),



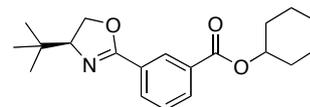
85 (100).



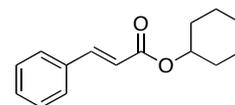
Cyclohexyl 3-bromobenzoate (10ha)

Purified by flush column chromatography (silica gel, Hexane/EtOAc = 40/1 to 4/1); colorless oil; IR (neat NaCl, ν/cm^{-1}) 2937, 2859, 1720, 1570, 1450, 1422, 1254, 1122, 1013, 943, 920, 747, 718; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.3–2.0 (m, 10H, *cyclohexyl*), 5.02 (tt, $J = 9.0, 3.9$ Hz, 1H, OCH), 7.29 (t, $J = 7.8$ Hz, 1H, Ar), 7.65 (dt, $J = 7.8, 1.5$ Hz, 1H, Ar), 7.96 (dt, $J = 7.8, 1.5$ Hz, 1H, Ar), 8.16 (t, $J = 1.5$ Hz, 1H, Ar); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 23.60, 25.36, 31.53, 73.58, 122.31, 128.04, 129.74, 132.43, 132.95, 135.49, 164.48; MS (EI) m/z (relative intensity) 284 ($[\text{M}^{(81)\text{Br}}]^+$, 3), 282 ($[\text{M}^{(79)\text{Br}}]^+$, 3), 185 (75), 183 (76), 157 (26), 155 (25), 82 (100); HRMS (EI) m/z calcd. for $\text{C}_{13}\text{H}_{15}\text{O}_2^{79}\text{Br}$ 282.0255 found 282.0254, calcd. for $\text{C}_{13}\text{H}_{15}\text{O}_2^{81}\text{Br}$ 284.0236 found 284.0209.

(S)-4-tert-Butyl-2-(3-cyclohexyloxycarbonylphenyl)oxazoline (10ia)



Purified by flush column chromatography (silica gel, Hexane/EtOAc = 20/1 to 2/1); colorless oil; IR (neat NaCl, ν/cm^{-1}) 2940, 2863, 1719, 1655, 1478, 1450, 1359, 1275, 1239, 1119, 1074, 1014, 973, 914, 733; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 0.96 (s, 9H, tBu), 1.0–2.0 (m, 10H, *cyclohexyl*), 4.06 (dd, $J = 9.3, 7.2$ Hz, 1H, 5-oxazoline), 4.25 (dd, $J = 8.4, 7.2$ Hz, 1H, 4-oxazoline), 4.37 (dd, $J = 9.3, 8.4$ Hz, 1H, 5-oxazoline), 5.04 (tt, $J = 9.0, 3.9$ Hz, 1H, OCH), 7.47 (t, $J = 7.5$ Hz, 1H, 5-Ar), 8.1–8.2 (m, 2H, 4,6-Ar), 8.57 (t, $J = 1.5$ Hz, 1H, 2-Ar), 8.16 (t, $J = 1.5$ Hz, 1H, Ar); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 23.76, 25.44, 25.85, 31.66, 34.01, 68.87, 73.48, 76.34, 128.26, 128.40, 129.19, 131.32, 132.05, 132.35, 162.49, 165.35; MS (EI) m/z (relative intensity) 329 ($[\text{M}^+]$, 1), 272 (100), 191 (46); HRMS (EI) m/z calcd. for $\text{C}_{20}\text{H}_{27}\text{NO}_3$ 329.1991 found 329.1972; $[\alpha]_{589}^{25} -54.0$ (c 1.0, CHCl_3).

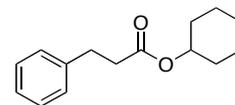


Cyclohexyl 3-phenylpropenoate (10ja)

Purified by flush column chromatography (silica gel, Hexane/EtOAc = 40/1 to 4/1); colorless oil; IR (neat NaCl, ν/cm^{-1}) 2937, 2859, 1711, 1638, 1450, 1307, 1281, 1174, 1039, 1017, 980, 919, 768, 733; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.3–1.9 (m, 10H, *cyclohexyl*), 4.89 (tt, $J = 9.0, 3.9$ Hz, 1H, OCH), 6.41 (d, $J = 15.9$ Hz, 1H, $\text{CH}=\text{CH}$),

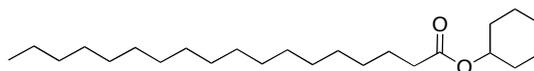
7.3–7.4 (m, 3H, *Ph*), 7.5 (m, 2H, *Ph*), 7.66 (d, $J = 15.9$ Hz, 1H, CH=CH); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 23.64, 25.31, 31.59, 72.51, 118.81, 127.83, 128.66, 129.91, 134.47, 144.03, 166.16; MS (EI) m/z (relative intensity) 230 ($[\text{M}^+]$, 7), 149 (64), 131 (100), 103 (32); HRMS (EI) m/z calcd. for $\text{C}_{15}\text{H}_{18}\text{O}_2$ 230.1307 found 230.1321.

Cyclohexyl 3-phenylpropionate (10ka)



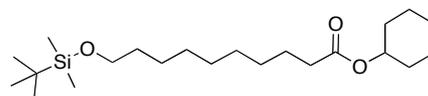
Purified by flush column chromatography (silica gel, Hexane/EtOAc = 40/1); colorless oil; IR (film NaCl, ν/cm^{-1}) 2937, 2859, 1731, 1453, 1291, 1255, 1179, 1042, 1015, 750, 699; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.2–1.8 (m, 10H, *cyclohexyl*), 2.59 (t, $J = 7.8$ Hz, 2H, PhCH_2CH_2), 2.94 (t, $J = 7.8$ Hz, 2H, PhCH_2CH_2), 4.7–4.8 (m, 1H, OCH), 7.1–7.3 (m, 5H, *phenyl*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 23.77, 25.46, 31.14, 31.66, 36.27, 72.57, 126.02, 128.15, 128.28, 140.50, 172.06; MS (EI) m/z (relative intensity) 232 ($[\text{M}^+]$, 10), 150 (100), 104 (83); HRMS (EI) m/z calcd. for $\text{C}_{15}\text{H}_{20}\text{O}_2$ 232.1463 found 232.1455.

Cyclohexyl octadecanoate (10la)



Purified by flush column chromatography (silica gel, Hexane/EtOAc = 40/1); white solid; mp 40–41 °C; IR (film NaCl, ν/cm^{-1}) 2918, 2851, 1733, 1464, 1174, 1019, 719; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 0.88 (t, $J = 6.9$ Hz, 3H, CH_3), 1.1–1.9 (m, 42H, *methylene, cyclohexyl*), 2.26 (t, $J = 7.5$ Hz, 2H, CH_2 COO), 4.76 (tt, $J = 9.0, 3.9$ Hz, 1H, OCH); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 14.06, 22.67, 13.75, 25.13, 24.45, 29.13, 29.26, 29.34, 29.47, 29.59, 29.69, 31.69, 31.92, 34.80, 72.24, 173.30; MS (FAB) m/z (relative intensity) 367 ($[\text{M}^+]$, 3), 285 (100), 257 (10), 154 (12), 137 (13); HRMS (FAB) m/z calcd. for $\text{C}_{24}\text{H}_{47}\text{O}_2$ 367.3576 found 367.3606.

Cyclohexyl 10-*tert*-butyldimethylsiloxydecanoate (10ma)

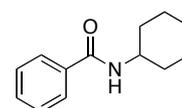


Purified by flush column chromatography (silica gel, Hexane/EtOAc = 40/1 to 2/1); colorless oil; IR (film NaCl, ν/cm^{-1}) 2932, 2857, 1733, 1464, 1361, 1255, 1183, 1099, 1040, 1018, 836, 776, 735; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 0.03 (s, 6H, CH_3), 0.88 (s, 9H, *t-Bu*), 1.2–1.9 (m, 24H, *cyclohexyl, methylene*), 2.25 (t, $J = 7.5$ Hz, 2H, CH_2COO), 3.58 (t, $J = 6.6$ Hz, 2H, SiOCH_2), 4.75 (tt, $J = 9.3, 4.2$ Hz, 1H, OCH); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ –5.30, 18.33, 23.73, 25.09, 25.44, 25.76, 25.95, 29.09,

29.19, 29.34, 29.41, 31.66, 32.86, 34.76, 63.26, 72.22, 173.25; MS (FAB) m/z (relative intensity) 385 ($[M+H]^+$, 5), 281 (14), 221 (21), 147 (36), 73 (100).

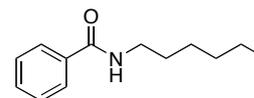
For the purpose of GC analysis, authentic samples of amide **11** were prepared by acylation reactions of the corresponding amines **9** with acid chloride or acid anhydride.

N-Cyclohexylbenzamide (11aa)



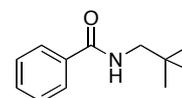
Purified by extraction; white solid; mp 154-156 °C; IR (film NaCl, ν/cm^{-1}) 3314, 2930, 2852, 1627, 1538, 1331, 1240, 694; 1H NMR (300 MHz, $CDCl_3$, 35 °C) δ 1.2–2.0 (m, 10H, *cyclohexyl*), 3.9–4.0 (m, 1H, *NHCH*), 6.05 (bs, 1H, *NH*), 7.3–7.5 (m, 3H, *Ph*), 7.7–7.8 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, $CDCl_3$, 35 °C) δ 25.05, 25.67, 33.23, 48.73, 126.61, 128.12, 130.82, 134.82, 134.87, 166.22; MS (EI) m/z (relative intensity) 203 ($[M^+]$, 47), 122 (75), 105 (100), 77 (40); HRMS (EI) m/z calcd. for $C_{13}H_{17}NO$ 203.1310 found 203.1287.

N-Hexylbenzamide (11ab)

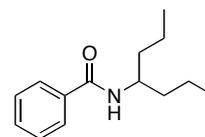


Purified by flush column chromatography (silica gel, Hexane/EtOAc = 2/1); white solid; mp. 42-44 °C; IR (film NaCl, ν/cm^{-1}) 3318, 2929, 2858, 1642, 1578, 1541, 1491, 1310, 695; 1H NMR (300 MHz, $CDCl_3$, 35 °C) δ 0.89 (s, $J = 6.9$ Hz, 3H, CH_2CH_3), 1.2–1.4 (m, 6H, *methylene*), 1.61 (tt, $J = 7.8, 7.2$ Hz, 2H, $NHCH_2CH_2$), 3.44 (dt, $J = 7.2, 5.4$ Hz, 2H, $NHCH_2CH_2$), 6.23 (bs, 1H, *NH*), 7.4–7.8 (m, 5H, *Ph*); ^{13}C NMR (75 MHz, $CDCl_3$, 35 °C) δ 13.93, 22.51, 26.63, 29.63, 31.47, 40.10, 126.81, 128.47, 131.20, 134.95, 167.48; MS (EI) m/z (relative intensity) 205 ($[M^+]$, 13), 162 (10), 134 (20), 105 (100); HRMS (EI) m/z calcd. for $C_{13}H_{19}NO$ 205.1467 found 205.1478.

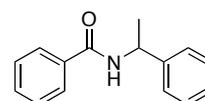
N-2,2-Dimethylpropylbenzamide (11ac)



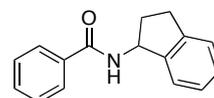
Purified by extraction; white solid; mp 113-114 °C; IR (neat NaCl, ν/cm^{-1}) 3375, 2964, 1639, 1541, 1492, 1309, 1290, 1208, 1075, 1030, 943, 898, 802, 750, 716, 695; 1H NMR (300 MHz, $CDCl_3$, 35 °C) δ 0.99 (s, 9H, $C(CH_3)_3$), 3.28 (d, $J = 6.6$ Hz, 2H, $NHCH_2$), 6.14 (bs, 1H, *NH*), 7.4–7.5 (m, 3H, *Ph*), 7.7–7.8 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, $CDCl_3$, 35 °C) δ 14.26, 19.39, 37.81, 49.44, 126.58, 128.31, 130.96, 135.00, 166.72; MS (EI) m/z (relative intensity) 191 ($[M^+]$, 18), 134 (42), 105 (100), 77 (31); HRMS (EI) m/z calcd. for $C_{12}H_{17}NO$ 191.1310 found 191.1291.

N-4-Heptylbenzamide (11ad)

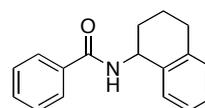
Purified by extraction; white solid; mp 110-111 °C; IR (film NaCl, ν/cm^{-1}) 3311, 2956, 2871, 1633, 1535, 1318, 1161, 695; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 0.94 (t, $J = 7.2$ Hz, 6H, CH_3), 1.3–1.6 (m, 8H, *methylene*), 4.1–4.2 (m, 1H, *NHCH*), 5.75 (d, $J = 8.7$ Hz, 1H, *NH*), 7.4–7.5 (m, 3H, *Ph*), 7.7–7.8 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 14.26, 19.39, 37.81, 49.44, 126.58, 128.31, 130.96, 135.00, 166.71; MS (EI) m/z (relative intensity) 219 ($[\text{M}^+]$, 5), 176 (41), 105 (100), 77 (23); HRMS (EI) m/z calcd. for $\text{C}_{14}\text{H}_{21}\text{NO}$ 219.1623 found 219.1631.

rac-N- α -Methylbenzylbenzamide (11ae)

Purified by recrystallization from toluene; white solid; mp 122-124 °C; IR (film NaCl, ν/cm^{-1}) 3300, 1634, 1535, 1490, 1276, 697; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.61 (d, $J = 6.9$ Hz, 3H, CH_3), 5.34 (qd, $J = 6.9, 6.9$ Hz, 1H, *NHCH*), 6.29 (bs, 1H, *NH*), 7.3–7.5 (m, 8H, *Ph*), 7.7–7.8 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 22.26, 49.68, 126.40, 127.08, 127.59, 128.68, 128.88, 131.55, 134.81, 143.28, 166.57; MS (EI) m/z (relative intensity) 225 ($[\text{M}^+]$, 57), 210 (10), 105 (100), 77 (37); HRMS (EI) m/z calcd. for $\text{C}_{15}\text{H}_{15}\text{NO}$ 225.1154 found 225.1146.

N-Benzoyl-1-aminoindane (11af)

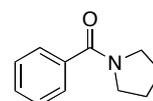
Purified by flush column chromatography (silica gel, Hexane/EtOAc = 4/1); white solid; mp 145 °C; IR (film NaCl, ν/cm^{-1}) 3298, 3065, 2943, 2848, 1633, 1539, 1490, 1350, 1308, 1158, 1076, 766, 745, 695; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.93 (dddd, $J = 16.2, 7.8, 7.8, 7.8$ Hz, 1H, *2-indane*), 2.70 (dddd, $J = 16.2, 7.8, 7.8, 4.5$ Hz, 1H, *2-indane*), 2.91 (ddd, $J = 16.2, 7.8, 7.8$ Hz, 1H, *3-indane*), 3.04 (ddd, $J = 16.2, 7.8, 4.5$ Hz, 1H, *3-indane*), 5.69 (ddd, $J = 7.8, 7.8, 6.6$ Hz, 1H, *1-indane*), 6.34 (d, $J = 6.6$ Hz, 1H, *NH*), 7.2–7.5 (m, 7H, *Ar*), 7.8 (m, 2H, *Ar*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 30.32, 34.19, 55.20, 124.12, 124.89, 126.86, 126.94, 128.09, 128.57, 131.47, 134.60, 143.19, 143.56, 167.19; MS (EI) m/z (relative intensity) 237 ($[\text{M}^+]$, 37), 116 (100), 105 (67), 77 (46); HRMS (EI) m/z calcd. for $\text{C}_{16}\text{H}_{15}\text{NO}$ 237.1154 found 237.1173.

N-Benzoyl-1,2,3,4-tetrahydro-1-naphthylamine (11ag)

Purified by flush column chromatography (silica gel, Hexane/EtOAc

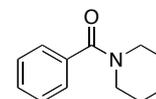
= 8/1); white solid; mp 128-130 °C; IR (film NaCl, ν/cm^{-1}) 3305, 3060, 2935, 1633, 1539, 1488, 1317, 1270, 1080, 739, 695; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.8–2.2 (m, 4H, 2,3-tetrahydronaphthyl), 2.7–2.9 (m, 2H, 4-tetrahydronaphthyl), 2.79 (ddd, $J = 16.8, 8.1, 6.0$ Hz, 1H, 4-tetrahydronaphthyl), 5.3–5.4 (m, 1H, 1-tetrahydronaphthyl), 6.40 (bs, 1H, NH), 7.1–7.5 (m, 7H, Ar), 7.7–7.8 (m, 2H, Ar); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 20.08, 29.25, 30.19, 47.95, 126.31, 126.92, 127.31, 128.49, 128.68, 129.19, 131.36, 134.70, 136.69, 137.65, 166.65; MS (EI) m/z (relative intensity) 251 ($[\text{M}^+]$, 24), 130 (100), 105 (38), 77 (25); HRMS (EI) m/z calcd. for $\text{C}_{17}\text{H}_{17}\text{NO}$ 251.1310 found 251.1320.

***N*-Benzoylpyrrolidine (11ah)**



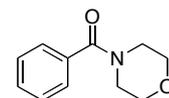
Purified by extraction; colorless oil; IR (neat NaCl, ν/cm^{-1}) 3060, 2973, 2877, 1624, 1576, 1424, 1340, 1229, 1204, 1179, 1076, 1027, 923, 792, 722; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.8–1.9 (m, 4H, 3,4-pyrrolidine), 3.40, 3.64 (bs, 4H, 2,5-pyrrolidine), 7.4–7.5 (m, 5H, Ph); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 24.28, 26.21, 45.96, 49.38, 126.91, 128.05, 129.55, 137.20, 169.51; MS (EI) m/z (relative intensity) 175 ($[\text{M}^+]$, 60), 174 (27), 146 (17), 105 (100), 77 (47); HRMS (EI) m/z calcd. for $\text{C}_{11}\text{H}_{13}\text{NO}$ 175.0997 found 175.0985.

***N*-Benzoylpiperidine (11ai)**



Purified by flush column chromatography (silica gel, Hexane/EtOAc = 4/1 to 2/1); white solid; mp 47-48 °C; IR (film NaCl, ν/cm^{-1}) 2937, 2855, 1633, 1444, 1277, 1111, 1028, 1004, 788, 732, 708; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.3–1.8 (m, 6H, 3,4,5-piperidine), 3.4–3.7 (bd, 4H, 2,6-piperidine), 7.3 (bs, 5H, Ph); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 24.58, 26.08, 42.97, 48.66, 126.77, 128.34, 129.27, 136.59, 170.27; MS (EI) m/z (relative intensity) 189 ($[\text{M}^+]$, 37), 188 (100), 105 (73), 77 (33); HRMS (EI) m/z calcd. for $\text{C}_{12}\text{H}_{15}\text{NO}$ 189.1154 found 189.1149.

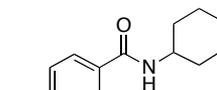
***N*-Benzoylmorpholine (11aj)**



Purified by flush column chromatography (silica gel, Hexane/EtOAc = 2/1 to 1/1); white solid; mp 72-74 °C; IR (film NaCl, ν/cm^{-1}) 2984, 2913, 2859, 1626, 1427, 1272, 1254, 1113, 1020, 841, 738, 714; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 3.69 (bs, 8H, morpholine), 7.41 (bs, 5H, Ph); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 66.83, 127.02,

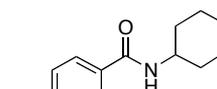
128.47, 129.78, 135.35, 170.36; MS (EI) m/z (relative intensity) 191 ($[M^+]$, 22), 190 (38), 105 (100), 84 (57), 77 (39); HRMS (EI) m/z calcd. for $C_{11}H_{13}NO_2$ 191.0946 found 191.0938.

***N*-Cyclohexyl-4-chlorobenzamide (11ca)**



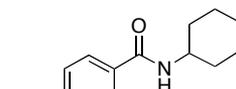
Purified by flush column chromatography (silica gel, Hexane/EtOAc = 40/1 to 4/1); white solid; mp 192-193 °C; IR (film NaCl, ν/cm^{-1}) 3293, 2933, 2855, 1632, 1541, 1450, 1152, 1092, 895, 842, 720, 681; 1H NMR (300 MHz, $CDCl_3$, 35 °C) δ 1.1–1.8 (m, 8H, *cyclohexyl*), 2.0–2.1 (m, 2H, *cyclohexyl*), 3.96 (ttd, $J = 10.8, 7.8, 3.9$ Hz, 1H, NHCH), 5.92 (bs, 1H, NH), 7.39 (d, $J = 8.4$ Hz, 2H, Ar), 7.68 (d, $J = 8.4$ Hz, 2H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 35 °C) δ 24.88, 25.56, 33.21, 48.85, 128.28, 128.73, 133.54, 137.45, 165.53; MS (EI) m/z (relative intensity) 237 ($[M^+]$, 32), 156 (74), 139 (100), 111 (31); HRMS (EI) m/z calcd. for $C_{13}H_{16}NOCl$ 237.0920 found 237.0917.

***N*-Cyclohexyl-4-bromobenzamide (11da)**



Purified by flush column chromatography (silica gel, Hexane/EtOAc = 40/1 to 4/1); white solid; mp 201-205 °C; IR (film NaCl, ν/cm^{-1}) 3288, 2929, 2853, 1632, 1541, 840, 719; 1H NMR (300 MHz, $CDCl_3$, 35 °C) δ 1.1–1.8 (m, 8H, *cyclohexyl*), 2.0–2.1 (m, 2H, *cyclohexyl*), 3.96 (ttd, $J = 10.8, 7.8, 3.9$ Hz, 1H, NHCH), 5.91 (bs, 1H, NH), 7.55 (d, $J = 8.4$ Hz, 2H, Ar), 7.62 (d, $J = 8.4$ Hz, 2H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 35 °C) δ 24.87, 25.55, 33.19, 48.86, 125.83, 128.47, 131.72, 134.00, 165.63; MS (EI) m/z (relative intensity) 283 ($[M(^{81}Br)^+]$, 16), 281 ($[M(^{79}Br)^+]$, 17), 240 (100), 238 (72); HRMS (EI) m/z calcd. for $C_{13}H_{16}NO^{79}Br$ 281.0415 found 281.0428, calcd. for $C_{13}H_{16}NO^{81}Br$ 283.0396 found 283.0391.

***N*-Cyclohexyl-4-nitrobenzamide (11ea)**

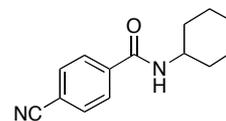


Purified by flush column chromatography (silica gel, Hexane/EtOAc = 40/1 to 4/1); white solid; mp 209-210 °C; IR (film NaCl, ν/cm^{-1}) 3316, 2936, 1633, 1600, 1543, 1519, 1455, 1348, 868, 841, 729, 690; 1H NMR (300 MHz, $CDCl_3$, 35 °C) δ 1.2–1.8 (m, 8H, *cyclohexyl*), 2.0–2.1 (m, 2H, *cyclohexyl*), 3.99 (ttd, $J = 10.5, 8.1, 3.9$ Hz, 1H, NHCH), 6.03 (bs, 1H, NH), 7.90 (d, $J = 9.0$ Hz, 2H, Ar), 8.27 (d, $J = 9.0$ Hz, 2H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, 35 °C) δ 24.85, 25.48, 33.11, 49.25,

123.76, 128.03, 140.73, 149.54, 164.58; MS (EI) m/z (relative intensity) 248 ($[M^+]$, 23), 205 (12), 167 (100), 150 (71); HRMS (EI) m/z calcd. for $C_{13}H_{16}N_2O_3$ 248.1161 found 248.1164.

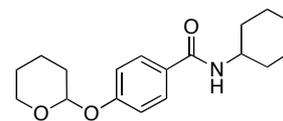
***N*-Cyclohexyl-4-cyanobenzamide (11fa)**

Purified by flush column chromatography (silica gel, Hexane/EtOAc = 40/1 to 4/1); white solid; mp 179-182 °C; IR (film NaCl, ν/cm^{-1}) 3289, 2941, 2857, 1632, 1541, 854; 1H NMR (300 MHz, $CDCl_3$, 35 °C) δ 1.2–1.8 (m, 8H, *cyclohexyl*), 2.0–2.1 (m, 2H, *cyclohexyl*), 3.98 (ttd, $J = 10.8, 7.8, 3.6$ Hz, 1H, NHCH), 5.96 (bs, 1H, NH), 7.72 (d, $J = 8.4$ Hz, 2H, Ar), 7.84 (d, $J = 8.4$ Hz, 2H, Ar); MS (EI) m/z (relative intensity) 228 ($[M^+]$, 29), 185 (12), 147 (100), 130 (95); HRMS (EI) m/z calcd. for $C_{14}H_{16}N_2O$ 228.1263 found 228.1243.



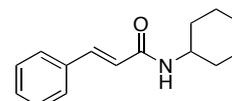
***N*-Cyclohexyl-4-(tetrahydropyran-2-yloxy)benzamide (11ga)**

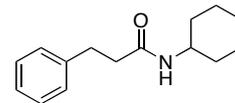
Purified by flush column chromatography (silica gel, Hexane/EtOAc = 40/1 to 4/1); white solid; mp 162-165 °C; IR (film NaCl, ν/cm^{-1}) 3327, 2933, 1629, 1541, 1505, 1239, 1112, 1038, 966, 921, 768; 1H NMR (300 MHz, $CDCl_3$, 35 °C) δ 1.1–2.1 (m, 16H, *cyclohexyl*, *THP*), 3.6 (m, 1H, 3-*THP*), 3.8–3.9 (m, 1H, 3-*THP*), 3.96 (ttd, $J = 10.8, 7.8, 3.9$ Hz, 1H, NHCH), 5.47 (t, $J = 3.0$ Hz, 1H, 2-*THP*), 5.83 (bs, 1H, NH), 7.06 (d, $J = 8.7$ Hz, 2H, Ar), 7.69 (d, $J = 8.7$ Hz, 2H, Ar); MS (FAB) m/z (relative intensity) 304 ($[M+H^+]$, 23), 220 (33), 207 (21), 147 (76); HRMS (EI) m/z calcd. for $C_{18}H_{26}NO_3$ 304.1913 found 304.1899.



***N*-Cyclohexyl-3-phenylpropenamide (11ja)**

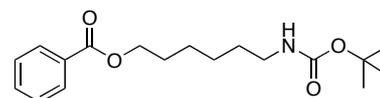
Purified by flush column chromatography (silica gel, Hexane/EtOAc = 40/1 to 4/1); white solid; mp 181-184 °C; IR (film NaCl, ν/cm^{-1}) 3278, 2928, 2853, 1653, 1617, 1556, 1447, 1344, 1220, 979, 726; 1H NMR (300 MHz, $CDCl_3$, 35 °C) δ 1.1–1.8 (m, 10H, *cyclohexyl*), 3.92 (ttd, $J = 10.5, 8.1, 3.9$ Hz, 1H, NHCH), 5.45 (bs, 1H, NH), 6.35 (d, $J = 15.6$ Hz, 1H, CH=CH), 7.3–7.5 (m, 5H, Ph), 7.60 (d, $J = 15.6$ Hz, 1H, CH=CH); MS (EI) m/z (relative intensity) 229 ($[M^+]$, 46), 118 (12), 148 (36), 131 (100), 103 (42); HRMS (EI) m/z calcd. for $C_{15}H_{19}NO$ 229.1467 found 229.1482.



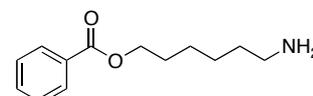
N-Cyclohexyl-3-Phenylpropionamide (11ka)

Purified by recrystallization (EtOAc/Hexane); white solid; mp 113-114 °C; IR (film NaCl, ν/cm^{-1}) 3304, 2936, 2851, 1635, 1543, 1450, 1246, 1220, 1152, 1102, 977, 891, 744, 701; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 0.9–1.9 (m, 10H, *cyclohexyl*), 2.43 (t, $J = 7.5$ Hz, 2H, PhCH_2CH_2), 2.95 (t, $J = 7.5$ Hz, 2H, PhCH_2CH_2), 3.72 (m, 1H, *NCH*), 5.11 (bs, 1H, *NH*), 7.4–8.1 (m, 5H, *phenyl*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 24.78, 25.52, 31.88, 33.11, 38.77, 48.04, 126.18, 128.38, 128.47, 140.97, 170.99; MS (EI) m/z (relative intensity) 231 ($[\text{M}^+]$, 100), 150 (76), 133 (31), 105 (77).

General procedure for the chemoselective acylation of aminoalcohol. The Zn cluster **6** (0.015 mmol, 0.05 mmol Zn), ester (3.0 mmol), and aminoalcohol (3.6 mmol) in diisopropyl ether (5.0 mL) were refluxed for periodic time under an argon atmosphere. The resulting mixture was concentrated *in vacuo*, and then treated with $(\text{Boc})_2\text{O}$ /triethylamine/ CH_2Cl_2 to protect the remaining amino group as a Boc carbonate. After the Boc protection, resulting mixture was purified by silica gel column chromatography.

6-(tert-Butoxycarbonylamino)hexyl**benzoate****(Boc-5ab)**

Purified by flush column chromatography (silica gel, Hexane/EtOAc = 10/1 to 4/1); colorless oil; IR (film NaCl, ν/cm^{-1}) 3383, 2934, 2861, 1718, 1520, 1365, 1315, 1276, 1174, 1027; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.44 (s, 9H, *Boc*), 1.2–1.6 (m, 6H, *methylene*), 1.78 (tt, $J = 6.6, 6.6$ Hz, 2H, *methylene*), 3.12 (td, $J = 6.6, 6.6$ Hz, 2H, NHCH_2), 4.32 (t, $J = 6.6$ Hz, 2H, OCH_2), 4.52 (bs, 1H, *NH*), 7.4–7.6 (m, 3H, *Ph*), 8.0–8.1 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 25.74, 26.44, 28.40, 28.67, 30.01, 40.48, 64.86, 128.29, 129.51, 130.51, 132.76, 155.99, 165.71; MS (EI) m/z (relative intensity) 321 ($[\text{M}^+]$, 1), 248 (7), 220 (24), 105 (64), 57 (100); HRMS (EI) m/z calcd. for $\text{C}_{18}\text{H}_{27}\text{NO}_4$ 321.1940 found 321.1983.

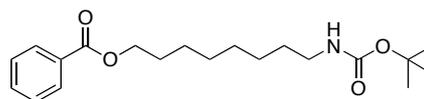
6-Aminohexyl benzoate (5ab)

Purified by extraction; pale yellow oil; IR (neat NaCl, ν/cm^{-1}) 2980, 1717, 1632, 1416, 1274, 1158; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ

1.4–1.5 (m, 4H, *methylene*), 1.59 (tt, $J = 7.5, 6.9$ Hz, 2H, *methylene*), 1.77 (tt, $J = 7.5, 6.9$ Hz, 2H, *methylene*), 2.81 (t, $J = 7.5$ Hz, 2H, NHCH_2), 3.90 (bs, 2H, NH_2), 4.30 (t, $J = 6.6$ Hz, 2H, OCH_2), 7.4–7.6 (m, 3H, *Ph*), 8.0–8.1 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 25.66, 26.31, 28.56, 31.06, 41.09, 64.82, 128.30, 129.49, 130.43, 132.80, 166.67; MS (EI) m/z (relative intensity) 221 ($[\text{M}^+]$, 5), 220 (5), 123 (63), 100 (100), 84 (80); HRMS (EI) m/z calcd. for $\text{C}_{13}\text{H}_{19}\text{NO}_2$ 221.1416 found 221.1445.

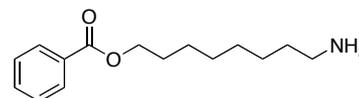
**8-(*tert*-Butoxycarbonylamino)octyl
(Boc-5ac)**

benzoate



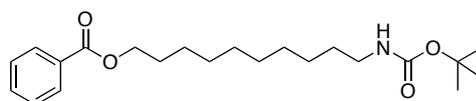
Purified by flush column chromatography (silica gel, Hexane/EtOAc = 10/1 to 2/1); colorless oil; IR (neat NaCl, ν/cm^{-1}) 3383, 2930, 1718, 1520, 1453, 1365, 1275, 1174, 1113, 1070, 1027, 713; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.3–1.5 (m, 10H, *methylene*), 1.44 (s, 9H, *Boc*), 1.79 (tt, $J = 7.2, 6.6$ Hz, 2H, OCH_2CH_2), 3.09 (td, $J = 6.6, 6.6$ Hz, 2H, NHCH_2), 4.31 (t, $J = 6.6$ Hz, 2H, OCH_2), 4.55 (bs, 1H, *NH*), 7.4–7.6 (m, 3H, *Ph*), 8.0–8.1 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 25.90, 26.64, 28.37, 28.64, 29.10, 29.99, 40.57, 64.97, 128.24, 129.46, 130.53, 132.69, 155.95, 166.58; MS (FAB) m/z (relative intensity) 350 ($[\text{M}+\text{H}^+]$, 6), 294 (14), 250 (100), 105 (33); HRMS (FAB) m/z calcd. for $\text{C}_{20}\text{H}_{32}\text{NO}_4$ 350.2331 found 350.2307.

8-Aminooctyl benzoate (5ac)



Purified by extraction; pale yellow solid; mp 60–62 °C; IR (film NaCl, ν/cm^{-1}) 3297, 2928, 2855, 1714, 1653, 1602, 1583, 1454, 1315, 1274, 1176, 1115, 1070, 1027, 713; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.3–1.5 (m, 10H, *methylene*), 1.76 (tt, $J = 6.9, 6.9$ Hz, 2H, OCH_2CH_2), 2.10 (bs, 2H, NH_2), 2.68 (t, $J = 6.9$ Hz, 2H, NH_2CH_2), 4.31 (t, $J = 6.9$ Hz, 2H, OCH_2), 7.4–7.6 (m, 3H, *Ph*), 8.0–8.1 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 25.83, 26.70, 28.63, 29.14, 29.24, 33.30, 41.90, 64.97, 128.21, 129.44, 130.50, 132.67, 166.56; MS (EI) m/z (relative intensity) 249 ($[\text{M}^+]$, 6), 248 (16), 144 (22), 105 (90), 77 (55); HRMS (EI) m/z calcd. for $\text{C}_{15}\text{H}_{23}\text{NO}_2$ 249.1729 found 249.1706.

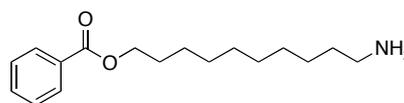
**10-(*tert*-Butoxycarbonylamino)decanyl
benzoate (Boc-5ad)**



Purified by flush column chromatography (silica gel, Hexane/EtOAc = 10/1 to 2/1);

white solid; mp 44-45 °C; IR (film NaCl, ν/cm^{-1}) 3383, 2928, 2856, 1715, 1519, 1454, 1391, 1365, 1275, 1175, 1114, 1070, 1027, 713; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.2–1.5 (m, 14H, *methylene*), 1.44 (s, 9H, *Boc*), 1.76 (tt, $J = 6.6$, 6.6 Hz, 2H, OCH_2CH_2), 3.09 (td, $J = 6.6$, 6.6 Hz, 2H, NHCH_2), 4.31 (t, $J = 6.6$ Hz, 2H, OCH_2), 4.52 (bs, 1H, *NH*), 7.3–7.6 (m, 3H, *Ph*), 8.0–8.1 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 25.97, 26.73, 28.40, 28.69, 29.18, 29.19, 29.36, 29.39, 30.05, 40.65, 65.03, 128.25, 129.49, 130.57, 132.70, 155.95, 166.61; MS (FAB) m/z (relative intensity) 378 ($[\text{M}+\text{H}^+]$, 2), 322 (8), 278 (100), 105 (33); HRMS (FAB) m/z calcd. for $\text{C}_{22}\text{H}_{36}\text{NO}_4$ 378.2644 found 378.2669.

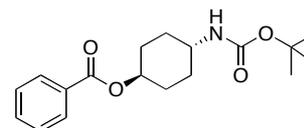
10-Aminodecanyl benzoate (5ad)



Purified by extraction; pale yellow solid; mp 68-70

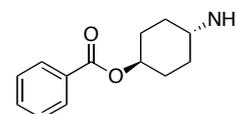
°C; IR (film NaCl, ν/cm^{-1}) 3357, 2923, 2853, 1715, 1557, 1453, 1315, 1276, 1176, 1115, 1070, 1027, 711; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.3–1.5 (m, 16H, *methylene*, NH_2), 1.76 (tt, $J = 6.6$, 6.6 Hz, 2H, OCH_2CH_2), 2.67 (t, $J = 6.6$ Hz, 2H, NH_2CH_2), 4.31 (t, $J = 6.6$ Hz, 2H, OCH_2), 7.4–7.5 (m, 3H, *Ph*), 8.0–8.1 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 25.95, 26.79, 28.66, 29.16, 29.37, 29.43, 33.65, 42.11, 65.00, 128.21, 129.44, 130.54, 132.66, 166.55; MS (EI) m/z (relative intensity) 277 ($[\text{M}^+]$, 8), 276 (13), 172 (15), 156 (76), 105 (77), 77 (44); HRMS (EI) m/z calcd. for $\text{C}_{17}\text{H}_{27}\text{NO}_2$ 277.2042 found 277.2036.

***trans*-4-(*tert*-Butoxycarbonylamino)cyclohexyl benzoate (Boc-5ae)**



Purified by flush column chromatography (silica gel, Hexane/EtOAc = 10/1 to 4/1); white solid; mp 139-141 °C; IR (film NaCl, ν/cm^{-1}) 3381, 2943, 2865, 1715, 1519, 1452, 1366, 1319, 1277, 1114, 1047, 1028, 713; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.2–1.7 (m, 4H, *cyclohexyl*), 1.45 (s, 9H, *Boc*), 2.0–2.1 (m, 4H, *cyclohexyl*), 3.5 (m, 1H, NHCH), 4.44 (bs, 1H, *NH*), 4.94 (tt, $J = 10.5$, 3.9 Hz, 1H, OCH), 7.4–7.6 (m, 3H, *Ph*), 8.0–8.1 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 27.79, 28.41, 30.01, 30.79, 48.61, 72.44, 128.28, 129.54, 130.66, 132.80, 155.24, 166.02.

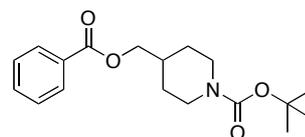
***trans*-4-Aminocyclohexyl benzoate (5ae)**



Purified by extraction, pale yellow solid; mp 89-93 °C; IR (film

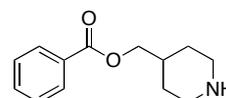
NaCl, ν/cm^{-1}) 3358, 2941, 2862, 1714, 1451, 1318, 1278, 1117, 1070, 1025, 937, 712; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.29 (dddd, $J = 12.9, 12.9, 10.5, 3.6$ Hz, 2H, *ax-cyclohexyl*), 1.38 (bs, 2H, NH_2), 1.56 (dddd, $J = 12.9, 12.9, 10.5, 3.9$ Hz, 2H, *ax-cyclohexyl*), 1.9–2.0 (m, 2H, *eq-cyclohexyl*), 2.1–2.2 (m, 2H, *eq-cyclohexyl*), 2.78 (tt, $J = 10.5, 3.9$ Hz, 1H, NCH), 4.94 (tt, $J = 10.5, 3.9$ Hz, 1H, OCH), 7.4–7.6 (m, 3H, *Ph*), 8.0–8.1 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 30.08, 34.11, 49.44, 73.02, 128.18, 129.44, 130.76, 132.65, 165.97; MS (EI) m/z (relative intensity) 219 ($[\text{M}^+]$, 2), 114 (10), 97 (100); HRMS (EI) m/z calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}_2$ 219.1259 found 219.1286.

***N*-tert-Butoxycarbonylpiperidine-4-ylmethyl benzoate
(Boc-5af)**



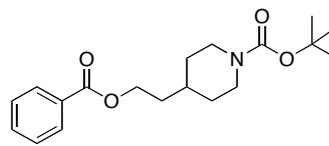
Purified by flush column chromatography (silica gel, Hexane/EtOAc = 10/1 to 1/1); white solid; mp 54–55 °C; IR (film NaCl, ν/cm^{-1}) 2940, 1695, 1602, 1416, 1365, 1272, 1176, 1070, 1207, 1003, 864, 769, 713; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.29 (ddd, $J = 24.9, 11.7, 4.5$ Hz, 2H, *piperidine*), 1.46 (s, 9H, *Boc*), 1.77 (m, 2H, *piperidine*), 1.9–2.0 (m, 1H, *piperidine*), 2.74 (ddd, $J = 12.6, 12.6, 2.4$ Hz, 2H, *piperidine*), 4.1–4.2 (m, 2H, *piperidine*), 4.19 (d, $J = 6.6$ Hz, 2H, OCH_2), 7.4–7.6 (m, 3H, *Ph*), 8.0–8.1 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 27.74, 28.40, 28.76, 35.78, 43.50, 68.77, 79.38, 128.33, 129.50, 130.24, 132.91, 154.79, 166.42; MS (FAB) m/z (relative intensity) 320 ($[\text{M}+\text{H}^+]$, 8), 264 (100), 246 (35), 204 (52), 142 (87), 105 (60); HRMS (FAB) m/z calcd. for $\text{C}_{18}\text{H}_{26}\text{NO}_4$ 320.1862 found 320.1830.

Piperidine-4-ylmethyl benzoate (5af)



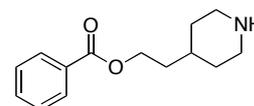
Purified by extraction; yellow oil; IR (neat NaCl, ν/cm^{-1}) 3329, 2941, 2852, 1717, 1602, 1450, 1315, 1276, 1114, 1070, 1026, 986, 755, 713; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.33 (ddd, $J = 12.6, 12.0, 4.2$ Hz, 2H, *piperidine*), 1.80 (d, $J = 12.6$ Hz, 2H, *piperidine*), 1.9–2.0 (m, 1H, *piperidine*), 2.43 (bs, 1H, NH), 2.65 (ddd, $J = 12.0, 12.0, 2.4$ Hz, 2H, *piperidine*), 3.13 (d, $J = 12.0$ Hz, 2H, *piperidine*), 4.18 (d, $J = 6.6$ Hz, 2H, OCH_2), 7.4–7.6 (m, 3H, *Ph*), 8.0–8.1 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 29.82, 35.88, 45.99, 69.33, 128.29, 129.50, 130.34, 132.82, 166.51; MS (FAB) m/z (relative intensity) 220 ($[\text{M}+\text{H}^+]$, 100), 147 (28), 105 (65); HRMS (FAB) m/z calcd. for $\text{C}_{13}\text{H}_{18}\text{NO}_2$ 220.1338 found 220.1330.

***N*-tert-Butoxycarbonylpiperidine-4-ylethyl benzoate
(Boc-5ag)**



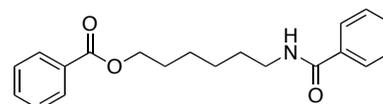
Purified by flush column chromatography (silica gel, Hexane/EtOAc = 10/1 to 1/1); colorless oil; IR (neat NaCl, ν/cm^{-1}) 2976, 2930, 2851, 1692, 1602, 1584, 1424, 1365, 1315, 1278, 1070, 1026, 966, 918, 733, 713; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.19 (ddd, $J = 24.0, 12.9, 4.2$ Hz, 2H, *piperidine*), 1.46 (s, 9H, *Boc*), 1.5–1.7 (m, 1H, *piperidine*), 1.7–1.8 (m, 2H, *piperidine*), 1.73 (td, $J = 6.6, 6.6$ Hz, 2H, OCH_2CH_2), 2.71 (ddd, $J = 15.3, 15.3, 2.4$ Hz, 2H, *piperidine*), 4.09 (d, $J = 12.3$ Hz, 2H, *piperidine*), 4.38 (t, $J = 6.6$ Hz, 2H, OCH_2), 7.4–7.6 (m, 3H, *Ph*), 8.0–8.1 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 28.42, 32.00, 33.22, 35.25, 43.89, 62.67, 79.23, 128.31, 129.48, 130.35, 132.84, 154.80, 166.52; MS (FAB) m/z (relative intensity) 334 ($[\text{M}+\text{H}^+]$, 4), 278 (16), 234 (100), 232 (38), 105 (36); HRMS (FAB) m/z calcd. for $\text{C}_{19}\text{H}_{28}\text{NO}_4$ 334.2018 found 334.2016.

Piperidine-4-ylethyl benzoate (5ag)



Purified by extraction; yellow oil; IR (neat NaCl, ν/cm^{-1}) 3329, 2923, 2847, 1717, 1602, 1451, 1315, 1277, 1176, 1116, 1070, 1026, 973, 755, 713; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.22 (ddd, $J = 24.0, 12.0, 3.9$ Hz, 2H, *piperidine*), 1.5–1.7 (m, 1H, *piperidine*), 1.73 (td, $J = 6.6, 6.6$ Hz, 2H, OCH_2CH_2), 1.7–1.8 (m, 2H, *piperidine*), 2.62 (ddd, $J = 12.0, 12.0, 2.4$ Hz, 2H, *piperidine*), 2.5 (bs, 1H, *NH*), 3.10 (d, $J = 12.0$ Hz, 2H, *piperidine*), 4.37 (t, $J = 6.6$ Hz, 2H, OCH_2), 7.4–7.6 (m, 3H, *Ph*), 8.0–8.1 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 33.04, 33.26, 35.76, 46.32, 32.69, 128.28, 129.46, 130.41, 132.77, 166.55; MS (FAB) m/z (relative intensity) 234 ($[\text{M}+\text{H}^+]$, 100), 207 (12), 147 (41), 105 (39); HRMS (FAB) m/z calcd. for $\text{C}_{14}\text{H}_{20}\text{NO}_2$ 234.1494 found 234.1479.

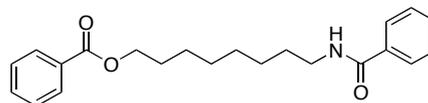
6-(Benzolyamino)hexyl benzoate (12ab)



Purified by flush column chromatography (silica gel, Hexane/EtOAc to EtOAc/MeOH = 95/5); white solid; mp 79–81 °C; IR (film NaCl, ν/cm^{-1}) 3327, 2935, 1716, 1643, 1540, 1490, 1276, 1114, 712; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.4–1.8 (m, 8H, *methylene*), 3.47 (dt, $J = 6.6, 6.6$ Hz, 2H, NHCH_2), 4.33 (t, $J = 6.6$ Hz, 2H, OCH_2), 6.19 (bs, 1H, *NH*), 7.3–7.6 (m, 6H, *Ph*), 7.7–7.8 (m, 2H,

Ph), 8.0–8.1 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 25.73, 26.59, 28.68, 29.63, 39.92, 64.81, 126.82, 128.32, 128.52, 129.52, 130.49, 131.28, 132.81, 134.87, 166.67, 167.49; MS (EI) m/z (relative intensity) 325 ($[\text{M}^+]$, 1), 220 (5), 203 (7), 105 (53); HRMS (EI) m/z calcd. for $\text{C}_{20}\text{H}_{23}\text{NO}_3$ 325.1678 found 325.1685.

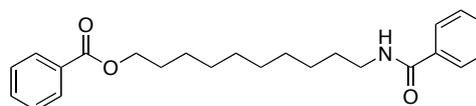
8-(Benzoylamino)octyl benzoate (12ac)



Purified by flush column chromatography (silica gel,

Hexane/EtOAc = 10/1 to 2/1); white solid; mp 55–57 °C; IR (film NaCl, ν/cm^{-1}) 3333, 2930, 2856, 1716, 1643, 1540, 1490, 1452, 1314, 1276, 1176, 1114, 1070, 1027, 712; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.4–1.8 (m, 12H, *methylene*), 3.44 (td, $J = 6.9$, 6.9 Hz, 2H, NHCH_2), 4.31 (t, $J = 6.6$ Hz, 2H, OCH_2), 6.20 (bs, 1H, *NH*), 7.4–7.6 (m, 6H, *Ph*), 7.7–7.8 (m, 2H, *Ph*), 8.0–8.1 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 25.93, 26.87, 28.66, 29.11, 29.14, 29.63, 40.03, 65.00, 126.81, 128.29, 128.49, 129.50, 130.54, 131.23, 132.75, 134.91, 166.65, 167.47; MS (EI) m/z (relative intensity) 353 ($[\text{M}^+]$, 5), 248 (16), 232 (16), 134 (25), 105 (100), 77 (47); HRMS (EI) m/z calcd. for $\text{C}_{22}\text{H}_{27}\text{NO}_3$ 353.1991 found 353.1991.

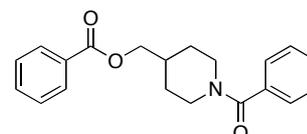
10-(Benzoylamino)decanyl benzoate (12ad)



Purified by flush column chromatography (silica

gel, Hexane/EtOAc = 10/1 to 2/1); white solid; mp 66–67 °C; IR (film NaCl, ν/cm^{-1}) 3348, 2921, 2851, 1713, 1633, 1604, 1578, 1538, 1476, 1450, 1340, 1284, 1130, 1072, 1026, 709, 690; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.3–1.7 (m, 14H, *methylene*), 1.76 (tt, $J = 6.6$, 6.6 Hz, 2H, OCH_2CH_2), 3.44 (td, $J = 6.6$, 6.6 Hz, 2H, NHCH_2), 4.31 (t, $J = 6.6$ Hz, 2H, OCH_2), 6.16 (bs, 1H, *NH*), 7.3–7.6 (m, 6H, *Ph*), 7.7–7.8 (m, 2H, *Ph*), 8.0–8.1 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 25.98, 26.95, 28.70, 29.18, 29.24, 29.38, 29.67, 40.09, 65.07, 126.81, 128.29, 128.50, 129.51, 130.59, 131.23, 132.75, 134.95, 166.67, 167.46; MS (EI) m/z (relative intensity) 381 ($[\text{M}^+]$, 3), 276 (12), 260 (7), 162 (20), 135 (100), 84 (93); HRMS (EI) m/z calcd. for $\text{C}_{24}\text{H}_{31}\text{NO}_3$ 381.2304 found 381.2264.

***N*-Benzoylpiperidine-4-ylmethyl benzoate (12af)**

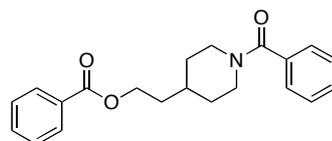


Purified by flush column chromatography (silica gel,

Hexane/EtOAc = 10/1 to 1/1); white solid; mp 86–88 °C; IR (film NaCl, ν/cm^{-1}) 2941,

1717, 1633, 1448, 1274, 1109, 976, 711; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.42 (bs, 2H, *piperidine*), 1.85 (bs, 2H, *piperidine*), 2.94 (bs, 2H, *piperidine*), 2.0–2.2 (m, 1H, *piperidine*), 3.95 (bs, 1H, *piperidine*), 4.23 (d, $J = 6.6$ Hz, 2H, OCH_2), 4.80 (bs, 1H, *piperidine*), 7.4–7.6 (m, 8H, *Ph*), 8.0–8.1 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 27.75, 29.21, 35.96, 68.50, 126.82, 128.40, 128.42, 129.52, 130.12, 133.01, 136.22, 166.42, 170.40; MS (FAB) m/z (relative intensity) 324 ($[\text{M}+\text{H}^+]$, 31), 264 (8), 105 (100), 77 (22); HRMS (FAB) m/z calcd. for $\text{C}_{20}\text{H}_{22}\text{NO}_3$ 324.1600 found 324.1603.

***N*-Benzoylpiperidine-4-ylethyl benzoate (12ag)**



Purified by flush column chromatography (silica gel, Hexane/EtOAc = 10/1 to 1/1); colorless oil; IR (film NaCl, ν/cm^{-1}) 2929, 2857, 1715, 1633, 1447, 1315, 1277, 1110, 1071, 966, 711; ^1H NMR (300 MHz, CDCl_3 , 35 °C) δ 1.26 (bs, 2H, *piperidine*), 1.7–1.9 (bs, 4H, *piperidine*, OCH_2CH_2), 2.88 (bs, 2H, *piperidine*), 3.77 (m, 1H, *piperidine*), 4.39 (d, $J = 6.0$ Hz, 2H, OCH_2), 4.73 (bs, 1H, *piperidine*), 7.3–7.6 (m, 8H, *Ph*), 8.0–8.1 (m, 2H, *Ph*); ^{13}C NMR (75 MHz, CDCl_3 , 35 °C) δ 32.53, 33.47, 35.20, 62.59, 126.84, 128.39, 128.40, 129.45, 129.52, 130.31, 132.95, 136.38, 166.55, 170.32; MS (FAB) m/z (relative intensity) 338 ($[\text{M}+\text{H}^+]$, 65), 232 (6), 105 (100), 77 (22); HRMS (FAB) m/z calcd. for $\text{C}_{21}\text{H}_{24}\text{NO}_3$ 338.1756 found 338.1726.

References

SI-1 Gmehling, J.; Menke, J.; Krafczyk, J.; Fischer, K. *Azeotropic Data*; Wiley-VCH: Weinheim, 2004.