Synthesis of Unsymmetrical N-Heterocyclic Carbene–Nitrogen–Phosphine Chelated Ruthenium (II) Complexes and their Reactivity in Acceptorless Dehydrogenative Coupling of Alcohols to Esters

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1. Crystal data for complex 2

CCDC No. of complex 2 is 1904695.

Table S1. Crystallographic data for complex 2.

| Property                              | Value                                      |
|---------------------------------------|--------------------------------------------|
| Empirical formula                    | C_{45}H_{44}Cl_{3}N_{3}O_{2}P_{2}Ru        |
| Formula weight                        | 928.19                                     |
| Temperature/K                         | 293.15                                     |
| Crystal system                        | triclinic                                  |
| Space group                           | P-1                                        |
| a/Å                                   | 9.6104(4)                                  |
| b/Å                                   | 15.2013(7)                                 |
| c/Å                                   | 19.2006(8)                                 |
| α/°                                   | 79.193(4)                                  |
| β/°                                   | 76.374(4)                                  |
| γ/°                                   | 74.033(4)                                  |
| Volume/Å³                             | 2598.2(2)                                  |
| Z                                      | 2                                          |
| ρ calc/g/cm³                          | 1.186                                      |
| Absorption coefficient/mm⁻¹           | 0.551                                      |
| F(000)                                | 952.0                                      |
| Crystal size/mm³                      | 0.35 × 0.25 × 0.2                         |
| Radiation                             | Mo Kα (λ = 0.71073)                        |
| 2Θ range for data collection/°       | 5.764 to 52.74                             |
| Index ranges                          | -12≤h≤11, -18≤k≤18, -23≤l≤23               |
| Reflections collected                 | 21191                                      |
| Independent reflections               | 10549 [R_{int}=0.0308, R_{sigma}= 0.0557]  |
| Data/restraints/parameters            | 10549/0/513                                |
| Goodness-of-fit on F²                 | 1.098                                      |
| Final R indexes [I>2σ(I)]             | R₁=0.0749, wR₂ = 0.2127                    |
| Final R indexes [all data]            | R₁=0.0873, wR₂ = 0.2267                    |
| Largest diff. peak/hole/ e Å⁻³        | 0.95/-1.78                                 |
|          | Bond Angles |                  |                  |
|----------|-------------|------------------|------------------|
|          | P1 Ru1 P2   | 161.32(5)        | C43 C38 C39      |
|          | N3 Ru1 P1   | 83.33(11)        | C19 C14 P1       |
|          | N3 Ru1 P2   | 92.72(11)        | C15 C14 P1       |
|          | N3 Ru1 C1   | 84.36(18)        | C15 C14 C19      |
|          | C1 Ru1 P1   | 97.69(13)        | C37 C32 P2       |
|          | C1 Ru1 P2   | 100.09(13)       | C33 C32 P2       |
|          | C44 Ru1 P1  | 91.24(18)        | C33 C32 C37      |
|          | C44 Ru1 P2  | 91.73(18)        | C24 C25 C20      |
|          | C44 Ru1 N3  | 174.1(2)         | C11 C12 C13      |
|          | C20 P1 Ru1  | 114.65(17)       | C9 C8 C13        |
|          | C20 P1 C13  | 105.5(3)         | C9 C8 C7         |
|          | C20 P1 C14  | 104.8(2)         | N3 C6 C5         |
|          | C13 P1 Ru1  | 107.50(17)       | N3 C7 C8         |
|          | C14 P1 Ru1  | 121.11(18)       | C26 C31 C30      |
|          | C14 P1 C13  | 101.6(2)         | C20 C21 C22      |
|          | C26 P2 Ru1  | 111.51(18)       | C28 C27 C26      |
|          | C26 P2 C32  | 103.3(3)         | C14 C19 C18      |
|          | C38 P2 Ru1  | 114.14(19)       | C36 C37 C32      |
|          | C38 P2 C26  | 102.7(3)         | N2 C5 C6         |
|          | C38 P2 C32  | 101.2(3)         | C34 C33 C32      |
|          | C32 P2 Ru1  | 121.71(19)       | C14 C15 C16      |
|          | C6 N3 Ru1   | 116.5(3)         | C38 C39 C40      |
|          | C7 N3 Ru1   | 129.5(4)         | C23 C22 C21      |
|          | C7 N3 C6    | 113.6(5)         | C2 C3 N2         |
|          | C1 N2 C5    | 127.9(5)         | C17 C18 C19      |
|          | C3 N2 C1    | 110.7(5)         | C25 C24 C23      |
|          | C3 N2 C5    | 121.4(5)         | C12 C11 C10      |
|          | N2 C1 Ru1   | 127.3(4)         | C18 C17 C16      |
|          | N1 C1 Ru1   | 130.0(4)         | C33 C34 C35      |
|          | N1 C1 N2    | 102.6(4)         | C38 C43 C42      |
|          | O1 C44 Ru1  | 175.2(5)         | C37 C36 C35      |
|          | C1 N1 C4    | 126.4(5)         | C11 C10 C9       |
|          | C1 N1 C2    | 112.1(5)         | C41 C40 C39      |
|          | C2 N1 C4    | 121.5(5)         | C17 C16 C15      |
|          | C25 C20 P1  | 117.0(4)         | C10 C9 C8        |
|          | C21 C20 P1  | 123.3(5)         | C3 C2 N1         |
|          | C21 C20 C25 | 119.2(6)         | C22 C23 C24      |

Table S2. Bond Angles for Complex 2.
| C31 C26 P2 | 117.8(5) | C34 C35 C36 | 117.8(7) |
|------------|---------|-------------|---------|
| C31 C26 C27| 119.9(6)| C40 C41 C42| 119.6(9) |
| C27 C26 P2 | 122.2(5)| C27 C28 C29| 119.7(7) |
| C12 C13 P1 | 122.2(4)| C29 C30 C31| 119.3(7) |
| C12 C13 C8 | 117.7(5)| C30 C29 C28| 120.5(7) |
| C8 C13 P1  | 120.0(4)| C41 C42 C43| 120.7(10)|
| C39 C38 P2 | 118.2(6)| C13 C45 C12 | 112.9(8) |
| C43 C38 P2 | 122.5(6)|             |         |
Table S3. Bond Lengths for Complex 2.

|         |                  |                  |
|---------|------------------|------------------|
| Ru1 P1  | 2.3147(13)       | C14 C15 1.386(9) |
| Ru1 P2  | 2.3791(13)       | C32 C37 1.403(9) |
| Ru1 N3  | 2.178(4)         | C32 C33 1.396(9) |
| Ru1 C1  | 2.179(5)         | C25 C24 1.374(9) |
| Ru1 C44 | 1.834(6)         | C12 C11 1.371(9) |
| P1 C20  | 1.823(6)         | C8 C7 1.463(8)   |
| P1 C13  | 1.837(5)         | C8 C9 1.407(8)   |
| P1 C14  | 1.831(5)         | C6 C5 1.519(8)   |
| P2 C26  | 1.852(6)         | C31 C30 1.410(9) |
| P2 C38  | 1.827(6)         | C21 C22 1.394(10)|
| P2 C32  | 1.853(6)         | C27 C28 1.370(9) |
| Cl2 C45 | 1.78(3)          | C19 C18 1.396(10)|
| O1 C44  | 1.161(7)         | C37 C36 1.361(10)|
| Cl3 C45 | 1.64(3)          | C33 C34 1.357(11)|
| N3 C6   | 1.471(7)         | C15 C16 1.411(9) |
| N3 C7   | 1.269(7)         | C39 C40 1.427(13)|
| N2 C1   | 1.372(7)         | C22 C23 1.375(12)|
| N2 C5   | 1.446(7)         | C3 C2 1.307(10)  |
| N2 C3   | 1.367(8)         | C18 C17 1.316(12)|
| C1 N1   | 1.348(7)         | C24 C23 1.395(12)|
| N1 C4   | 1.470(8)         | C11 C10 1.372(11)|
| N1 C2   | 1.384(8)         | C17 C16 1.367(12)|
| C20 C25 | 1.413(8)         | C34 C35 1.371(13)|
| C20 C21 | 1.373(9)         | C43 C42 1.432(12)|
| C26 C31 | 1.367(9)         | C36 C35 1.384(12)|
| C26 C27 | 1.393(9)         | C10 C9 1.386(10)|
| C13 C12 | 1.400(8)         | C40 C41 1.344(18)|
| C13 C8  | 1.408(8)         | C41 C42 1.342(17)|
| C38 C39 | 1.376(10)        | C28 C29 1.389(12)|
| C38 C43 | 1.373(10)        | C30 C29 1.372(12)|
| C14 C19 | 1.391(8)         |                  |
2. NMR spectra of complexes

Figure S1. $^1$H NMR spectrum of complex 1 (400.1 MHz, CD$_2$Cl$_2$).

Figure S2. $^{31}$P NMR spectrum of complex 1 (162.0 MHz, CD$_2$Cl$_2$).
Figure S3. $^1$H NMR spectrum of complex 2 (400.1 MHz, CD$_2$Cl$_2$).

Figure S4. $^{13}$C NMR spectrum of complex 2 (100.6 MHz, CD$_2$Cl$_2$).
Figure S5. $^{31}$P NMR spectrum of complex 2 (162.0 MHz, CD$_2$Cl$_2$).
3. Optimization of ADC reaction conditions

Table S4. Effect of bases on ADC reaction of alcohol $^a$.

| entry | base     | temp (°C) | conv (%) | yield of aldehyde (%) | yield of ester (%) |
|-------|----------|-----------|----------|-----------------------|--------------------|
| 1     | KOH      | 110       | 26       | 8                     | 17                 |
| 2     | NaOH     | 110       | 50       | 6                     | 44                 |
| 3     | CsOH     | 110       | 51       | 18                    | 33                 |
| 4     | KOtBu    | 110       | 40       | 7                     | 33                 |
| 3     | NaOtBu   | 110       | 54       | 7                     | 47                 |
| 6     | LiOtBu   | 110       | 47       | 4                     | 43                 |
| 7     | NaH      | 110       | 65       | 5                     | 60                 |
| 8     | Cs2CO3   | 110       | 79       | 2                     | 77                 |
| 9     | EtONa    | 110       | 75       | 27                    | 48                 |

$^a$Reaction Condition: benzyl alcohol (1.0 mmol, 104 µL), complex 1 (0.01 mmol, 8.3 mg), base (0.3 mmol), toluene (2 ml) and reflux under N$_2$ for 24 h. All conversions and yields were determined by GC.
**Table S5.** Effect of bases and base loadings on ADC reaction of alcohol.

![Chemical structure](image)

| entry | base     | quantity of base (mmol) | conv (%) | yield of aldehyde (%) | yield of ester (%) |
|-------|----------|-------------------------|----------|-----------------------|-------------------|
| 1     | Cs$_2$CO$_3$ | 0                       | 2        | 2                     | NR                |
| 2     | Cs$_2$CO$_3$ | 0.01                    | 31       | 7                     | 24                |
| 3     | Cs$_2$CO$_3$ | 0.03                    | 67       | 3                     | 64                |
| 4     | Cs$_2$CO$_3$ | 0.1                     | 72       | 2                     | 70                |
| 5     | Cs$_2$CO$_3$ | 0.3                     | 79       | 2                     | 77                |
| 6     | Cs$_2$CO$_3$ | 0.5                     | 94       | 6                     | 88                |
| 7     | Cs$_2$CO$_3$ | 0.7                     | >99      | 20                    | 80                |
| 8     | Cs$_2$CO$_3$ | 0.3                     | 94       | 6                     | 88                |
| 9     | NaH        | 0.3                     | >99      | 16                    | 84                |
| 10    | NaO$^t$Bu  | 0.3                     | >99      | 13                    | 87                |

*Reaction Condition: benzyl alcohol (1.0 mmol, 104 µL), complex 1 (0.01 mmol, 8.3 mg), toluene (2 ml) and reflux under N$_2$ for 24 h. All conversions and yields were determined by GC.*
Table S6. Effect of reaction temperature and reaction time on ADC of alcohol $^a$.

![Chemical Reaction Diagram]

| entry | temp (°C) | time (h) | conv (%) | yield of aldehyde (%) | yield of ester (%) |
|-------|-----------|----------|----------|-----------------------|--------------------|
| 1     | 80        | 24       | 65       | 16                    | 49                 |
| 2     | 90        | 24       | 73       | 14                    | 59                 |
| 3     | 100       | 24       | 77       | 11                    | 66                 |
| 4     | 120       | 24       | 79       | 14                    | 65                 |
| 5     | 110       | 24       | 94       | 6                     | 88                 |
| 6     | 110       | 26       | 99       | 2                     | 97                 |
| 7     | 110       | 30       | >99      | 3                     | 97                 |

$^a$Reaction Condition: benzyl alcohol (1.0 mmol, 104 µL), complex 1 (0.01 mmol, 8.3 mg), $\text{Cs}_2\text{CO}_3$ (0.5 mmol, 163 mg), toluene (2 ml), under $\text{N}_2$. All conversions and yields were determined by GC.
Table S7. Effect of catalyst loading on ADC of alcohol.  

![Chemical structure](image)

| entry | cat. (mol %) | conv (%) | yield of aldehyde (%) | yield of ester (%) |
|-------|--------------|----------|-----------------------|-------------------|
| 1     | RuHCl(CO)(PPh₃)₃ | 13       | 7                     | 6                 |
| 2     | 1 (0)        | 4        | 4                     | NR                |
| 3     | 1(0.05)      | 17       | 2                     | 15                |
| 4     | 1(0.1)       | 42       | 5                     | 37                |
| 5     | 1(0.2)       | 50       | 4                     | 46                |
| 6     | 1(0.5)       | 65       | 2                     | 63                |
| 7     | 1(1)         | >99      | 3                     | 97                |
| 8     | 2(1)         | 97       | 3                     | 94                |

反应条件：苯甲醇 (1.0 mmol, 104 µL), Cs₂CO₃ (0.5 mmol, 163 mg), 甲苯 (2 ml), 于 N₂ 氛围下回流 26 h。所有转化率及产率均通过 GC 确定。

aReaction Condition: benzyl alcohol (1.0 mmol, 104 µL), Cs₂CO₃ (0.5 mmol, 163 mg), toluene (2 ml), reflux under N₂ for 26 h. All conversions and yields were determined by GC.
4. Mechanistic study

4.1 Reaction profiles NMR spectra in-situ

Condition (from bottom to top):
1) Benzyl alcohol (0.5 mmol, 52 µL), complex 1 (0.03 mmol, 25 mg), Cs₂CO₃ (0.5 mmol, 163 mg), 1 ml Toluene-d₈, 110°C, under N₂, 1 min.
2) Benzyl alcohol (0.5 mmol, 52 µL), complex 1 (0.03 mmol, 25 mg), Cs₂CO₃ (0.5 mmol, 163 mg), 1 ml Toluene-d₈, 110°C, under N₂, 10 min.
3) Benzyl alcohol (0.5 mmol, 52 µL), complex 1 (0.03 mmol, 25 mg), Cs₂CO₃ (0.5 mmol, 163 mg), 1 ml Toluene-d₈, 110°C, under N₂, 30 min.
4) Benzyl alcohol (0.5 mmol, 52 µL), complex 1 (0.03 mmol, 25 mg), Cs₂CO₃ (0.5 mmol, 163 mg), 1 ml Toluene-d₈, 110°C, under N₂, 1.0 h.
5) Benzyl alcohol (0.5 mmol, 52 µL), complex 1 (0.03 mmol, 25 mg), Cs₂CO₃ (0.5 mmol, 163 mg), 1 ml Toluene-d₈, 110°C, under N₂, 2.0 h.
4.2 NMR spectra of reaction mixture.

Figure S6. $^1$H NMR spectra of ADC reaction mixture for (a) 1 min, (b) 10 min, (c) 0.5 h, (d) 1.0 h, (e) 2.0 h (400.1 MHz, Toluene-$d^8$).
Figure S7. $^1$H NMR spectra (Chemical shift is negative) of ADC reaction mixture for (a) 1 min, (b) 10 min, (c) 0.5 h, (d) 1.0 h, (e) 2.0 h (400.1 MHz, Toluene-$d_8$).

Figure S8. $^{31}$P NMR spectra of ADC reaction mixture for (a) 1 min, (b) 10 min, (c) 0.5 h, (d) 1.0 h, (e) 2.0 h (162.0 MHz, Toluene-$d_8$).
4.3 HR-MS results of reaction mixture.

Chemical Formula: C_{33}H_{33}N_{3}O_{2}PRu^+  
Exact Mass: 636.1348  
Molecular Weight: 635.6772  
Found: 636.1283

![HR-MS result of reaction mixture.](image)

**Figure S9.** HR-MS result of reaction mixture.

Chemical Formula: C_{26}H_{27}N_{3}OPRu^+  
Exact Mass: 530.0930  
Molecular Weight: 529.5553  
Found: 530.0772  
ESI^+

![HR-MS result of reaction mixture.](image)

**Figure S10.** HR-MS result of reaction mixture.
4.4 Control experiments about Tishchenko coupling of benzaldehyde to benzyl Benzoate.

Scheme S1. Cs$_2$CO$_3$ catalyzed Tishchenko coupling of benzaldehyde to benzyl Benzoate.

A Schlenk tube was loaded with Cs$_2$CO$_3$ (0.5 mmol, 163 mg), anhydrous and anaerobic toluene (2 mL), and benzyl aldehyde (1.0 mmol, 101 µL). The mixture was heated to 110 °C and stirred for 26 h. At the end of reaction, the mixture was cooled to room temperature and diluted with 2 mL dichloromethane and filtered with Celite. The filtrate was evaporated to remove organic solvents. Dibromomethane (0.5 mmol, 35 µL) was added to the reaction mixture as internal standard. An aliquot of mixture was taken out, and subjected to NMR analysis with CDCl$_3$ as solvent. Yield of benzyl benzoate: 0%. The same reaction was repeated in the presence of complex 1. NMR yield of benzyl benzoate: 47%.

Scheme S2. Cs$_2$CO$_3$ catalyzed Tishchenko coupling of benzaldehyde to benzyl Benzoate in the presence of benzyl alcohol.

In glovebox, a Schlenk tube was loaded with Cs$_2$CO$_3$ (0.5 mmol, 163 mg), anhydrous and anaerobic toluene (2 mL), and benzyl alcohol (1.0 mmol, 104 µL), benzyl aldehyde (1.0 mmol, 101 µL). The mixture was heated to 110 °C and stirred for 1 h, 2 h, 4 h, 8 h, 12 h, 26 h, respectively. After the reaction, the mixture was cooled to room temperature and diluted with 2 mL dichloromethane and filtered with Celite. After evaporated to remove organic solvents, dibromomethane (1.0 mmol, 70 µL) was added to the reaction mixture as internal standard. An aliquot of mixture was taken out, and subjected to NMR analysis with CDCl$_3$ as solvent. NMR yields of benzyl benzoate were illustrated in Table S8.

Scheme S3. Complex 1/Cs$_2$CO$_3$ catalyzed Tishchenko coupling of benzaldehyde to benzyl Benzoate in the presence of benzyl alcohol.

In glovebox, a Schlenk tube was loaded with Cs$_2$CO$_3$ (0.5 mmol, 163 mg), complex 1 (1% mol, 8.3 mg), anhydrous and anaerobic toluene (2 mL), and benzyl alcohol (1.0 mmol, 104 µL), benzyl aldehyde (1.0 mmol, 101 µL). The mixture was heated to
110 °C and stirred for 1 h, 2 h, 4 h, 8 h, 12 h, 26 h, respectively. After the reaction, the mixture was cooled to room temperature and diluted with 2 mL dichloromethane and filtered with Celite. After evaporated to remove organic solvents, dibromomethane (1.0 mmol, 70 µL) was added to the reaction mixture as internal standard. An aliquot of mixture was taken out, and subjected to NMR analysis with CDCl₃ as solvent. NMR yields of benzyl benzoate were illustrated in Table S9.
Table S8. Cs$_2$CO$_3$ Catalyzed Tishchenko Coupling of Benzaldehyde to Benzyl Benzoate in the Presence of Benzyl Alcohol$^a$.

| entry | base   | time (h) | residual alcohol (%) | yield of ester (%) |
|-------|--------|----------|----------------------|--------------------|
| 1     | Cs$_2$CO$_3$ | 1        | 98                   | 7                  |
| 2     | Cs$_2$CO$_3$ | 2        | 97                   | 12                 |
| 3     | Cs$_2$CO$_3$ | 4        | 98                   | 22                 |
| 4     | Cs$_2$CO$_3$ | 8        | 98                   | 29                 |
| 5     | Cs$_2$CO$_3$ | 12       | 96                   | 36                 |
| 6     | Cs$_2$CO$_3$ | 26       | 98                   | 42                 |

$^a$Reaction Condition: benzyl aldehyde (1.0 mmol, 101 µL), benzyl alcohol (1.0 mmol, 104 µL), Cs$_2$CO$_3$ (0.5 mmol, 163 mg), toluene (2 ml). Yield determined by $^1$H NMR using dibromomethane as an internal standard.
Table S9. Complex 1/Cs$_2$CO$_3$ Catalyzed Dehydrogenative Coupling of Benzyl Alcohol in the Presence of Benzaldehyde $^a$.

| entry | cat. (mol %) | base    | time (h) | residual alcohol (%) | yield of ester (%) |
|-------|--------------|---------|----------|----------------------|-------------------|
| 1     | 1(1)         | Cs$_2$CO$_3$ | 1        | 84                   | 49                |
| 2     | 1(1)         | Cs$_2$CO$_3$ | 2        | 74                   | 51                |
| 3     | 1(1)         | Cs$_2$CO$_3$ | 4        | 70                   | 58                |
| 4     | 1(1)         | Cs$_2$CO$_3$ | 8        | 66                   | 67                |
| 5     | 1(1)         | Cs$_2$CO$_3$ | 12       | 34                   | 74                |
| 6     | 1(1)         | Cs$_2$CO$_3$ | 26       | 13                   | 90                |

$^a$Reaction Condition: benzyl aldehyde (1.0 mmol, 101 µL), benzyl alcohol (1.0 mmol, 104 µL), Cs$_2$CO$_3$ (0.5 mmol, 163 mg), complex 1 (1% mol, 8.3 mg), toluene (2 ml). Yield determined by $^1$H NMR using dibromomethane as an internal standard.
Figure S11. Reaction Rate of Benzyl Alcohol with Benzaldehyde in the Presence of Catalyst 1 and in the Absence of Catalyst 1.
5. NMR spectra of substrates

5.1 Characterization Data of esters

**benzyl benzoate (3a).** $^1$H NMR (CDCl$_3$, 400.1 MHz) $\delta$ 8.01 (m, 2H), 7.49 (m, 1H), 7.3-7.4 (m, 7H), 5.30 (s, 2H). $^{13}$C NMR (CDCl$_3$, 100.6 MHz) $\delta$ 166.47, 136.25, 133.14, 130.28, 129.83, 128.73, 128.51, 128.36, 128.30, 66.77.

**4-methoxybenzyl 4-methoxybenzoate (3b).** $^1$H NMR (CDCl$_3$, 400.1 MHz) $\delta$ 8.02 (d, $J = 8.9$ Hz, 2H), 7.39 (d, $J = 8.7$ Hz, 2H), 6.92 (d, $J = 5.7$ Hz, 2H), 6.90 (d, $J = 5.9$ Hz, 2H), 5.28 (s, 2H), 3.84 (s, 3H), 3.81 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100.6 MHz) $\delta$ 165.21, 162.31, 158.52, 130.64, 128.95, 127.35, 121.60, 112.88, 112.52, 65.18, 54.34, 54.21.

**4-methylbenzyl 4-methylbenzoate (3c).** $^1$H NMR (CDCl$_3$, 400.1 MHz) $\delta$ 7.87 (d, $J = 7.9$ Hz, 2H), 7.25 (d, $J = 7.1$ Hz, 2H), 7.14–7.08 (m, 4H), 5.22 (s, 2H), 2.30 (s, 3H), 2.27 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100.6 MHz) $\delta$ 165.52, 142.59, 136.97, 132.15, 128.69, 128.21, 128.01, 127.27, 126.44, 65.44, 20.62, 20.18.

**4-(trifluoromethyl)benzyl 4-(trifluoromethyl)benzoate (3d).** $^1$H NMR (CDCl$_3$, 400.1 MHz) $\delta$ 8.12 (d, $J = 8.1$ Hz, 2H), 7.65 (d, $J = 8.2$ Hz, 2H), 7.59 (d, $J = 8.1$ Hz, 2H), 7.49 (d, $J = 8.0$ Hz, 2H), 5.37 (s, 2H). $^{13}$C NMR (CDCl$_3$, 100.6 MHz) $\delta$ 164.03, 138.53, 133.75 (q, $J = 32.7$ Hz), 131.94, 129.64 (q, $J = 32.6$ Hz), 129.11, 127.26, 124.66 (q, $J = 3.8$ Hz), 124.51 (q, $J = 3.7$ Hz), 122.95 (d, $J = 272.2$ Hz), 122.55 (d, $J = 272.7$ Hz), 65.22.

**4-chlorobenzyl 4-chlorobenzoate (3e).** $^1$H NMR (CDCl$_3$, 400.1 MHz) $\delta$ 7.99 (d, $J = 8.6$ Hz, 2H), 7.42 (d, $J = 8.6$ Hz, 2H), 7.37 (m, 4H), 5.31 (s, 2H). $^{13}$C NMR (CDCl$_3$, 100.6 MHz) $\delta$ 165.48, 139.68, 134.33, 134.30, 131.10, 129.69, 128.87, 128.81, 128.37, 66.14.

**4-fluorobenzyl 4-fluorobenzoate (3f).** $^1$H NMR (CDCl$_3$, 400.1 MHz) $\delta$ 8.1 (m, 2H), 7.4 (m, 2H), 7.1 (m, 4H), 5.3 (s, 2H). $^{13}$C NMR (CDCl$_3$, 100.6 MHz) $\delta$ 164.82 (d, $J = 254.2$ Hz), 164.36, 161.68 (d, $J = 247.0$ Hz), 131.21 (d, $J = 9.3$ Hz), 130.72 (d, $J = 3.2$ Hz), 129.23 (d, $J = 8.3$ Hz), 125.23 (d, $J = 3.0$ Hz), 114.64, 114.42, 65.09.

**3-chlorobenzyl 3-chlorobenzoate (3g).** $^1$H NMR (CDCl$_3$, 400.1 MHz) $\delta$ 7.98 (t, $J = 1.8$ Hz, 1H), 7.89 (m, 1H), 7.48 (m, 1H), 7.39 – 7.30 (m, 2H), 7.26 (t, $J = 1.3$ Hz, 2H), 7.20 (s, 1H), 5.27 (s, 2H). $^{13}$C NMR (CDCl$_3$, 100.6 MHz) $\delta$ 164.05, 136.59, 133.59, 133.52, 132.22, 130.53, 128.95, 128.76, 128.75, 127.57, 127.27, 126.84, 125.27, 65.15.

**3-fluorobenzyl 3-fluorobenzoate (3h).** $^1$H NMR (CDCl$_3$, 400.1 MHz) $\delta$ 7.90 – 7.84 (m, 1H), 7.75 (m, 1H), 7.43 (td, $J = 8.0$, 5.6 Hz, 1H), 7.40 – 7.33 (m, 1H), 7.31 – 7.24 (m, 1H), 7.21 (d, $J = 7.6$ Hz, 1H), 7.15 (d, $J = 9.4$ Hz, 1H), 7.05 (td, $J = 8.4$, 2.1 Hz, 1H), 5.36 (s, 2H). $^{13}$C NMR (CDCl$_3$, 100.6 MHz) $\delta$ 164.10 (d, $J = 3.1$ Hz), 161.86 (d, $J = 246.6$ Hz), 161.53 (d, $J = 247.3$ Hz), 137.15 (d, $J = 7.4$ Hz), 130.99 (d, $J = 7.5$ Hz), 129.21 (d, $J = 8.2$ Hz), 129.07 (d, $J = 7.8$ Hz), 124.43 (d, $J = 3.1$ Hz), 122.54 (d, $J = 3.0$ Hz), 119.24 (d, $J = 21.3$ Hz), 115.57 (d, $J = 23.1$ Hz), 114.25 (d, $J = 21.1$ Hz), 113.93 (d, $J = 22.0$ Hz), 65.11 (d, $J = 1.9$ Hz).

**2-methylbenzyl 2-methylbenzoate (3i).** $^1$H NMR (CDCl$_3$, 400.1 MHz) $\delta$ 7.85 (d, $J =
8.0 Hz, 1H), 7.40 – 7.26 (m, 2H), 7.14 (m, 5H), 5.26 (s, 2H), 2.52 (s, 3H), 2.33 (s, 3H). 13C NMR (CDCl3, 100.6 MHz) δ 166.28, 139.38, 135.95, 133.02, 131.02, 130.69, 129.63, 129.35, 128.37, 128.23, 127.46, 125.01, 124.68, 63.88, 20.77, 17.98.

2-chlorobenzyl 2-chlorobenzoate (3j). 1H NMR (CDCl3, 400.1 MHz) δ 8.02 (m, 1H), 7.52 – 7.47 (m, 1H), 7.40 – 7.32 (m, 4H), 7.21 (m, 2H), 5.40 (s, 2H). 13C NMR (CDCl3, 100.6 MHz) δ 165.17, 135.01, 132.71, 132.09, 131.98, 128.89, 128.76, 128.70, 128.65, 128.57, 128.47, 127.38, 125.86, 63.00.

3-phenylpropyl 3-phenylpropanoate (3m). 1H NMR (CDCl3, 400.1 MHz) δ 7.30 (m, 4H), 7.26 – 7.14 (m, 6H), 4.11 (t, J = 6.5 Hz, 2H), 2.98 (t, J = 7.8 Hz, 2H), 2.70 – 2.55 (m, 4H), 2.03 – 1.88 (m, 2H). 13C NMR (CDCl3, 100.6 MHz) δ 171.91, 140.15, 139.48, 127.47, 127.39, 127.36, 127.25, 125.23, 124.96, 62.78, 34.83, 31.10, 29.94, 29.13.

pyridin-3-ylmethyl nicotinate (3o). 1H NMR (CDCl3, 400.1 MHz) δ 9.08 (d, 1H, J = 4.0 Hz), 8.78 (d, 1H, J = 8.0 Hz), 8.67 (s, 1H), 8.52 (d, 1H, J = 4.0 Hz), 8.28 (m, 1H), 7.54 (m, 2H), 7.40 (m, 1H), 5.38 (s, 2H). 13C NMR (CDCl3, 100.6 MHz) δ 163.91, 152.72, 149.93, 148.46, 148.32, 136.15, 135.58, 130.39, 124.58, 122.74, 122.37, 63.46.

furan-3-ylmethyl furan-3-carboxylate (3p). 1H NMR (CDCl3, 400.1 MHz) δ 7.94 (m, 1H), 7.45 (m, 1H), 7.37 – 7.28 (m, 2H), 6.67 (m, 1H), 6.40 (m, 1H), 5.08 (s, 2H). 13C NMR (CDCl3, 100.6 MHz) δ 161.97, 146.86, 142.74, 142.41, 140.67, 119.38, 118.20, 109.63, 108.80, 56.71.

thiophen-3-ylmethyl thiophene-3-carboxylate (3q). 1H NMR (CDCl3, 400.1 MHz) δ 8.05 (m, 1H), 7.47 (m, 1H), 7.31 – 7.20 (m, 3H), 7.08 (m, 1H), 5.25 (s, 2H). 13C NMR (CDCl3, 100.6 MHz) δ 161.50, 135.83, 132.45, 131.93, 126.93, 126.61, 125.22, 125.02, 123.33, 60.47.

thiophen-2-ylmethyl thiophene-2-carboxylate (3r). 1H NMR (CDCl3, 400.1 MHz) δ 7.82 (m, 1H), 7.56 (m, 1H), 7.34 (m, 1H), 7.17 (d, J = 3.3 Hz, 1H), 7.09 (m, 1H), 7.01 (m, 1H), 5.48 (s, 2H). 13C NMR (CDCl3, 100.6 MHz) δ 160.9, 136.7, 132.8, 132.4, 131.7, 127.4, 126.8, 126.0, 125.8, 60.0.

acetophenone (3s). 1H NMR (DMSO-d6, 400.1 MHz) δ 8.01 – 7.87 (m, 2H), 7.67 – 7.61 (m, 1H), 7.53 (m, 2H), 2.58 (s, 3H). 13C NMR (CDCl3, 100.6 MHz) δ 197.21, 136.07, 132.10, 127.28, 25.57.

2-methoxybenzyl 4-methoxybenzoate (4ba). 1H NMR (CDCl3, 400.1 MHz) δ 8.05 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 7.4 Hz, 1H), 7.32 (t, J = 7.3 Hz, 1H), 6.97 (t, J = 7.5 Hz, 1H), 6.92 (d, J = 8.7 Hz, 3H), 5.40 (s, 2H), 3.86 (s, 3H), 3.85 (s, 3H). 13C NMR (CDCl3, 100.6 MHz) δ 165.27, 162.28, 156.42, 130.69, 128.31, 128.25, 123.64, 121.80, 119.38, 112.53, 109.40, 60.83, 54.41, 54.38.

4-(trifluoromethyl)benzyl 4-methoxybenzoate (4bb). 1H NMR (CDCl3, 400.1 MHz) δ 8.04 (d, J = 8.8 Hz, 2H), 7.65 (d, J = 8.1 Hz, 2H), 7.56 (d, J = 7.9 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 5.39 (s, 2H), 3.87 (s, 3H). 13C NMR (CDCl3, 100.6 MHz) δ 165.99, 163.63, 140.34, 131.80, 130.59 – 129.93 (m), 128.09 – 127.97 (m), 125.55 (q, J = 3.8 Hz), 124.06 (q, J = 271.9 Hz), 122.09, 113.74, 65.43, 55.47.

4-methoxybenzyl 4-(trifluoromethyl)benzoate (4bb’). 1H NMR (CDCl3, 400.1 MHz) δ 8.16 (d, J = 8.1 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.7 Hz, 2H), 6.93 (d, J
= 8.7 Hz, 2H), 5.33 (s, 2H), 3.82 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100.6 MHz) δ 165.32, 159.82, 134.43 (q, $J = 32.5$ Hz), 133.47, 130.29 – 130.27 (m), 130.08, 127.64, 125.39 (q, $J = 3.8$ Hz), 123.63 (q, $J = 272.8$ Hz), 114.04, 67.16, 55.32.

2-chlorobenzyl 4-methoxybenzoate (4bc). $^1$H NMR (CDCl$_3$, 400.1 MHz) δ 8.02 (d, $J = 8.9$ Hz, 2H), 7.51 – 7.44 (m, 1H), 7.40 – 7.35 (m, 1H), 7.26 – 7.21 (m, 2H), 6.89 (d, $J = 9.0$ Hz, 2H), 5.41 (s, 2H), 3.82 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100.6 MHz) δ 165.99, 163.53, 134.00, 131.82, 131.76, 129.72, 129.60, 129.44, 126.91, 122.32, 113.70, 63.79, 55.47.

2-methylpentyl 4-methoxybenzoate (4bd). $^1$H NMR (CDCl$_3$, 400.1 MHz) δ 7.99 (d, $J = 8.9$ Hz, 2H), 6.91 (d, $J = 8.9$ Hz, 2H), 4.22 – 4.01 (m, 2H), 3.83 (s, 3H), 1.97 – 1.82 (m, 1H), 1.48 – 1.29 (m, 4H), 1.00 (d, $J = 6.8$ Hz, 3H), 0.91 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (CDCl$_3$, 100.6 MHz) δ 165.46, 162.22, 130.51, 121.98, 112.55, 68.59, 54.40, 34.72, 31.46, 18.99, 16.00, 13.27.

2-ethylbutyl 4-methoxybenzoate (4be). $^1$H NMR (CDCl$_3$, 400.1 MHz) δ 7.92 (d, $J = 8.9$ Hz, 2H), 6.84 (d, $J = 8.8$ Hz, 2H), 4.15 (d, $J = 5.8$ Hz, 2H), 3.78 (s, 3H), 1.58 (m, 1H), 1.44 – 1.30 (m, 4H), 1.00 (d, $J = 6.8$ Hz, 3H), 0.87 (t, $J = 7.5$ Hz, 6H). $^{13}$C NMR (CDCl$_3$, 100.6 MHz) δ 166.54, 163.25, 131.53, 123.02, 113.58, 66.66, 55.42, 40.55, 23.54, 11.15.

Neopentyl 4-methoxybenzoate (4bf). $^1$H NMR (CDCl$_3$, 400.1 MHz) δ 8.01 (d, $J = 9.0$ Hz, 2H), 6.92 (d, $J = 9.0$ Hz, 2H), 3.98 (s, 2H), 3.86 (s, 3H), 1.03 (s, 9H). $^{13}$C NMR (CDCl$_3$, 100.6 MHz) δ 165.38, 162.24, 130.49, 121.95, 112.56, 72.91, 54.39, 30.59, 25.58.

Isopentyl 4-methoxybenzoate (4bg). $^1$H NMR (CDCl$_3$, 400.1 MHz) δ 7.99 (d, $J = 8.9$ Hz, 2H), 6.91 (d, $J = 8.9$ Hz, 2H), 4.32 (t, $J = 6.8$ Hz, 2H), 3.83 (s, 3H), 1.79 (m, 1H), 1.65 (q, $J = 6.8$ Hz, 2H), 0.98 (s, 3H), 0.96 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100.6 MHz) δ 165.45, 162.22, 130.51, 121.95, 112.53, 62.32, 54.39, 36.46, 24.21, 21.51.

Methyl 4-methoxybenzoate (4bh). $^1$H NMR (CDCl$_3$, 400.1 MHz) δ 7.99 (d, $J = 8.8$ Hz, 2H), 6.91 (d, $J = 8.8$ Hz, 2H), 3.88 (s, 3H), 3.85 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100.6 MHz) δ 165.83, 162.28, 130.55, 121.57, 112.56, 54.38, 50.83.

2-ethylbutyl 4-(trifluoromethyl)benzoate (4bj). $^1$H NMR (CDCl$_3$, 400.1 MHz) δ 8.15 (d, $J = 8.1$ Hz, 2H), 7.71 (d, $J = 8.2$ Hz, 2H), 4.29 (d, $J = 5.7$ Hz, 2H), 1.81 – 1.59 (m, 1H), 1.46 (m, 4H), 0.96 (t, $J = 7.5$ Hz, 6H). $^{13}$C NMR (CDCl$_3$, 100.6 MHz) δ 165.51, 134.32 (q, $J = 32.5$ Hz), 129.93 – 129.91 (m), 129.04, 125.40 (q, $J = 3.8$ Hz), 123.65 (q, $J = 272.7$ Hz), 67.54, 40.44, 23.48, 11.11.

cyclohexyl 4-methoxybenzoate (4bk). $^1$H NMR (CDCl$_3$, 400.1 MHz) δ 8.00 (d, $J = 8.9$ Hz, 2H), 6.91 (d, $J = 8.9$ Hz, 2H), 5.00 (m, 1H), 3.85 (s, 3H), 2.01 – 1.85 (m, 2H), 1.79 (m, 2H), 1.57 (m, 3H), 1.49 – 1.29 (m, 3H). $^{13}$C NMR (CDCl$_3$, 100.6 MHz) δ 164.75, 162.13, 130.49, 122.44, 112.46, 71.63, 54.39, 30.67, 24.49, 22.67.
5.2 NMR spectra of self-esters

![NMR spectra](image)

**Figure S12.** $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of benzyl benzoate (3a).

![NMR spectra](image)

**Figure S13.** $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of benzyl benzoate (3a).
**Figure S14.** $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of 4-methoxybenzyl 4-methoxybenzoate (3b).

**Figure S15.** $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of 4-methoxybenzyl 4-methoxybenzoate (3b).
Figure S16. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of 4-methylbenzyl 4-methylbenzoate (3c).

Figure S17. $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of 4-methylbenzyl 4-methylbenzoate (3c).
Figure S18. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of 4-(trifluoromethyl) benzyl 4-(trifluoromethyl) benzoate (3d).

Figure S19. $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of 4-(trifluoromethyl) benzyl 4-(trifluoromethyl) benzoate (3d).
Figure S20. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of 4-chlorobenzyl 4-chlorobenzoate (3e).

Figure S21. $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of 4-chlorobenzyl 4-chlorobenzoate (3e).
Figure S22. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of 4-fluorobenzyl 4-fluorobenzoate (3f).

Figure S23. $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of 4-fluorobenzyl 4-fluorobenzoate (3f).
Figure S24. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of 3-chlorobenzyl 3-chlorobenzoate (3g).

Figure S25. $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of 3-chlorobenzyl 3-chlorobenzoate (3g).
Figure S26. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of 3-fluorobenzyl 3-fluorobenzoate (3h).

Figure S27. $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of 3-fluorobenzyl 3-fluorobenzoate (3h).
Figure S28. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of 2-methylbenzyl 2-methylbenzoate (3i).

Figure S29. $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of 2-methylbenzyl 2-methylbenzoate (3i).
Figure S30. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of 2-chlorobenzyl 2-chlorobenzoate (3j).

Figure S31. $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of 2-chlorobenzyl 2-chlorobenzoate (3j).
Figure S32. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of 3-phenylpropyl 3-phenylpropanoate (3m).

Figure S33. $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of 3-phenylpropyl 3-phenylpropanoate (3m).
Figure S34. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of pyridin-3-ylmethyl nicotinate (3o).

Figure S35. $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of pyridin-3-ylmethyl nicotinate (3o).
Figure S36. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of furan-3-ylmethyl furan-3-carboxylate (3p).

Figure S37. $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of furan-3-ylmethyl furan-3-carboxylate (3p).
Figure S38. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of thiophen-3-ylmethyl thiophene-3-carboxylate (3q).

Figure S39. $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of thiophen-3-ylmethyl thiophene-3-carboxylate (3q).
Figure S40. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of thiophen-2-ylmethyl thiophene-2-carboxylate (3r).

Figure S41. $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of thiophen-2-ylmethyl thiophene-2-carboxylate (3r).
**Figure S42.** $^1$H NMR spectrum of (400.1 MHz, DMSO-$d_6$) of acetophenone (3x).

**Figure S43.** $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of acetophenone (3x).
5.3 NMR spectra of cross-esters

Figure S44. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of 2-methoxybenzyl 4-methoxybenzoate (4ba).

Figure S45. $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of 2-methoxybenzyl 4-methoxybenzoate (4ba).
Figure S46. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of 4-(trifluoromethyl)benzyl 4-methoxybenzoate (4bb).

Figure S47. $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of 4-(trifluoromethyl)benzyl 4-methoxybenzoate (4bb).
Figure S48. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of 4-methoxybenzyl 4-(trifluoromethyl) benzoate (4bb').

Figure S49. $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of 4-methoxybenzyl 4-(trifluoromethyl) benzoate (4bb').
**Figure S50.** $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of 2-chlorobenzyl 4-methoxybenzoate (4bc).

**Figure S51.** $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of 2-chlorobenzyl 4-methoxybenzoate (4bc).
Figure S52. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of 2-methylpentyl 4-methoxybenzoate (4bd).

Figure S53. $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of 2-methylpentyl 4-methoxybenzoate (4bd).
**Figure S54.** $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of 2-ethylbutyl 4-methoxybenzoate (**4be**).

**Figure S55.** $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of 2-ethylbutyl 4-methoxybenzoate (**4be**).
Figure S56. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of neopentyl 4-methoxybenzoate (4bf).

Figure S57. $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of neopentyl 4-methoxybenzoate (4bf).
Figure S58. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of isopentyl 4-methoxybenzoate (4bg).

Figure S59. $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of isopentyl 4-methoxybenzoate (4bg).
Figure S60. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of methyl 4-methoxybenzoate (4bh).

Figure S61. $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of methyl 4-methoxybenzoate (4bh).
Figure S62. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of 2-ethylbutyl 4-(trifluoromethyl) benzoate (4bj).

Figure S63. $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of 2-ethylbutyl 4-(trifluoromethyl) benzoate (4bj).
Figure S64. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of cyclohexyl 4-methoxybenzoate (4bk).

Figure S65. $^{13}$C NMR spectrum of (100.6 MHz, CDCl$_3$) of cyclohexyl 4-methoxybenzoate (4bk).
5.4 Typical $^1$H NMR (CDCl$_3$, 400.1 MHz) spectra obtained for the substrate scope

Figure S66. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of naphthalen-2-ylmethyl 2-naphthoate (3n).

Figure S67. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of hexyl hexanoate (3s).
Figure S68. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of octyl octanoate (3t).

Figure S69. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of dodecyl dodecanoate (4u).
Figure S70. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of 2-methylpentyl 2-methylpentanoate (3v).

Figure S71. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of 2-methylpentyl 2-methylpentanoate (4w).
Figure S72. $^1$H NMR spectrum of (400.1 MHz, CDCl$_3$) of 2-ethylbutyl benzoate (4bi).