

Electronic Supporting Information

Esterification of Glycerol and Solketal by Oxidative NHC-Catalysis under Heterogeneous Batch and Flow Conditions

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Screening of reaction conditions with soluble triazolium pre-catalysts A-C (Table 1).

Entries 1-3. A stirred mixture of glycerol **1** (11 mg, 0.12 mmol), 1-naphtaldehyde **2a** (16 μ L, 0.12 mmol), oxidant **6** (49 mg, 0.12 mmol), durene (16 mg, 0.12 mmol) and the stated pre-catalyst (0.012 mmol) in anhydrous THF (1.0 mL) was degassed under vacuum and saturated with argon (by an Ar-filled balloon) three times. Then, DBU was added (3.6 μ L, 0.024 mmol), and the reaction was stirred at room temperature for the stated time. Yield and selectivity were evaluated by ¹HNMR analysis of the reaction mixture (durene as internal standard).

Entries 4-6. A stirred mixture of glycerol **1** (11 mg, 0.12 mmol), 1-naphtaldehyde **2a** (16 μ L, 0.12 mmol), oxidant **6** (49 mg, 0.12 mmol), durene (16 mg, 0.12 mmol) and pre-catalyst **C** (4.4 mg, 0.012 mmol) in anhydrous THF (1.0 mL) was degassed under vacuum and saturated with argon (by an Ar-filled balloon) three times. Then, the stated base was added (0.024 mmol), and the reaction was stirred at room temperature for 1 h. Yield and selectivity were evaluated by ¹HNMR analysis of the reaction mixture (durene as internal standard).

Entry 7. A stirred mixture of glycerol **1** (11 mg, 0.12 mmol), 1-naphtaldehyde **2a** (16 μ L, 0.12 mmol), oxidant **6** (49 mg, 0.12 mmol), durene (16 mg, 0.12 mmol) and pre-catalyst **C** (1.2 mg, 0.003 mmol) in anhydrous THF (1.0 mL) was degassed under vacuum and saturated with argon (by an Ar-filled balloon) three times. Then, NEt₃ was added (20 μ L of a 0.15 M solution in THF, 0.003 mmol), and the reaction was stirred at room temperature for 1 h. Yield and selectivity were evaluated by ¹HNMR analysis of the reaction mixture (durene as internal standard).

Entries 8-9. A stirred mixture of glycerol **1** (stated amount), 1-naphtaldehyde **2a** (16 μ L, 0.12 mmol), oxidant **6** (49 mg, 0.12 mmol), durene (16. mg, 0.12 mmol) and pre-catalyst **C** (1.2 mg, 0.003 mmol) in anhydrous THF (1.0 mL) was degassed under vacuum and saturated with argon (by an Ar-filled balloon) three times. Then, NEt₃ was added (20 μ L of a 0.15 M ₃ solution in THF, 0.003 mmol), and the reaction was stirred at room temperature for 1 h. Yield and selectivity were evaluated by ¹HNMR analysis of the reaction mixture (durene as internal standard).

Entry 10. A stirred mixture of glycerol **1** (11 mg, 0.12 mmol), 1-naphtaldehyde **2a** (16 μ L, 0.12 mmol), TEMPO (28 mg, 0.18 mmol), durene (16. mg, 0.12 mmol) and pre-catalyst **C** (1.2 mg, 0.003 mmol) in anhydrous THF (1.0 mL) was degassed under vacuum and saturated with argon (by an Ar-filled balloon) three times. Then, NEt₃ was added (20 μ L of a 0.15 M solution in THF, 0.003 mmol), and the reaction was stirred at room temperature for 4 h. Yield and selectivity were evaluated by ¹HNMR analysis of the reaction mixture (durene as internal standard).

Entry 11. A stirred mixture of glycerol **1** (11 mg, 0.12 mmol), 1-naphtaldehyde **2a** (16 μ L, 0.12 mmol), MnO₂ (52 mg, 0.6 mmol), durene (16 mg, 0.12 mmol) and pre-catalyst **C** (1.2 mg, 0.003 mmol) in anhydrous THF (1.0 mL) was degassed under vacuum and saturated with argon (by an Ar-filled balloon) three times. Then, NEt₃ was added (8.4 μ L, 0.06 mmol), and the reaction was stirred at room temperature for 24 h. Yield and selectivity were evaluated by ¹HNMR analysis of the reaction mixture (durene as internal standard).

Entry 12. A stirred mixture of glycerol **1** (11 mg, 0.12 mmol), 1-naphtaldehyde **2a** (16 μ L, 0.12 mmol), durene (16 mg, 0.12 mmol) and pre-catalyst **C** (1.2 mg, 0.003 mmol) in anhydrous THF (1.0 mL) was stirred under O₂ atmosphere (by an O₂-filled balloon). Then, NEt₃ was added (40 μ L of a 0.15 M solution in THF, 0.006 mmol), and the reaction was stirred at room temperature for 24 h. Yield and selectivity were evaluated by ¹HNMR analysis of the reaction mixture (durene as internal standard).

Entries 13-14. A stirred mixture of glycerol **1** (stated amount), 1-naphtaldehyde **2a** (16 μ L, 0.12 mmol), **7** (5 mg, 0.024 mmol), **8** (3.4 mg, 0.006 mmol), durene (16 mg, 0.12 mmol) and pre-catalyst **C** (1.2 mg, 0.003 mmol) in anhydrous THF (1.0 mL) was stirred under an air atmosphere (by a compressed air-filled balloon). Then, NEt₃ was added (8.3 μ L, 0.06 mmol), and the reaction was stirred at room temperature for 24 h. Yield and selectivity were evaluated by ¹HNMR analysis of the reaction mixture (durene as internal standard).

Entry 15. A stirred mixture of glycerol **1** (11 mg, 0.12 mmol), 1-naphtaldehyde **2a** (16 μ L, 0.12 mmol), **7** (5 mg, 0.024 mmol), **8** (3.4 mg, 0.006 mmol), durene (16 mg, 0.12 mmol) and pre-catalyst **C** (1.2 mg, 0.003 mmol) in anhydrous THF (1.0 mL) was stirred under an air atmosphere (by a compressed air-filled balloon). Then, NEt₃ was added (8.3 μ L, 0.06 mmol), and the reaction was stirred at 50 °C for 24 h. Yield and selectivity were evaluated by ¹HNMR analysis of the reaction mixture (durene as internal standard).

Screening of reaction conditions with supported triazolium pre-catalysts D-F (Table 2).

Entries 1-2. A stirred mixture of glycerol **1** (33 mg, 0.36 mmol), 1-naphtaldehyde **2a** (16 μ L, 0.12 mmol), **7** (5 mg, 0.024 mmol), **8** (3.4 mg, 0.006 mmol), durene (16 mg, 0.12 mmol), and pre-catalyst **D** (17 mg, 0.012 mmol, loading = 0.71 mmol g⁻¹) in anhydrous THF (1.0 mL) was stirred under an air atmosphere (by a compressed air-filled balloon). Then, the stated base was added (0.06 mmol),

and the reaction was stirred at room temperature for 24 h. Yield and selectivity were evaluated by ¹HNMR analysis of the reaction mixture (durene as internal standard).

Entries 3-4. A stirred mixture of glycerol **1** (33 mg, 0.36 mmol), 1-naphtaldehyde **2a** (16 μL, 0.12 mmol), **7** (5 mg, 0.024 mmol), **8** (3.4 mg, 0.006 mmol), durene (16 mg, 0.12 mmol), and pre-catalyst **D** (17 mg, 0.012 mmol, loading = 0.71 mmol g⁻¹) in the stated solvent (1.0 mL) was stirred under an air atmosphere (by a compressed air-filled balloon). Then, DBU was added (9 μL, 0.06 mmol), and the reaction was stirred at room temperature for 24 h. Yield and selectivity were evaluated by ¹HNMR analysis of the reaction mixture (durene as internal standard).

Entry 5. A stirred mixture of glycerol **1** (33 mg, 0.36 mmol), 1-naphtaldehyde **2a** (16 μL, 0.12 mmol), **7** (5 mg, 0.024 mmol), **8** (3.4 mg, 0.006 mmol), durene (16 mg, 0.12 mmol), and pre-catalyst **E** (18 mg, 0.012 mmol, loading = 0.66 mmol g⁻¹) in anhydrous THF (1.0 mL) was stirred under an air atmosphere (by a compressed air-filled balloon). Then, DBU was added (9 μL, 0.06 mmol), and the reaction was stirred at room temperature for 24 h. Yield and selectivity were evaluated by ¹HNMR analysis of the reaction mixture (durene as internal standard).

Entry 6. A stirred mixture of glycerol **1** (33 mg, 0.36 mmol), 1-naphtaldehyde **2a** (16 μL, 0.12 mmol), **7** (5 mg, 0.024 mmol), **8** (3.4 mg, 0.006 mmol), durene (16 mg, 0.12 mmol), and pre-catalyst **F** (20 mg, 0.012 mmol, loading = 0.59 mmol g⁻¹) in anhydrous THF (1.0 mL) was stirred under an air atmosphere (by a compressed air-filled balloon). Then, DBU was added (9 μL, 0.06 mmol), and the reaction was stirred at room temperature for 24 h. Yield and selectivity were evaluated by ¹HNMR analysis of the reaction mixture (durene as internal standard).

Entries 7-11. A stirred mixture of glycerol **1** (33 mg, 0.36 mmol), 1-naphtaldehyde **2a** (16 μL, 0.12 mmol), **7** (5 mg, 0.024 mmol), **8** (3.4 mg, 0.006 mmol), durene (16 mg, 0.12 mmol), and pre-catalyst **F** (20 mg, 0.012 mmol, loading = 0.59 mmol g⁻¹) in the stated solvent (1.0 mL) was stirred under an air atmosphere (by a compressed air-filled balloon). Then, DBU was added (9 μL, 0.06 mmol), and the reaction was stirred at room temperature for 24 h. Yield and selectivity were evaluated by ¹HNMR analysis of the reaction mixture (durene as internal standard). For *entry 11*, the deep eutectic mixture (Choline Cl:Glycerol) was prepared as follows: a vigorous stirred solution of glycerol (630 mg, 6.84 mmol) and Choline Cl (478 mg, 3.42 mmol) was heated at 80 °C for 2 h under an argon atmosphere. After this period, the mixture was cooled to room temperature and used as the reaction solvent.

Entries 12-13. A stirred mixture of glycerol **1** (22 mg, 0.24 mmol), 1-naphtaldehyde **2a** (16 μL, 0.12 mmol), **7** (5 mg, 0.024 mmol), **8** (3.4 mg, 0.006 mmol), durene (16 mg, 0.12 mmol), and pre-catalyst **F** (20 mg, 0.012 mmol, loading = 0.59 mmol g⁻¹) in Me-THF (1.0 mL) was stirred under an air

atmosphere (by a compressed air-filled balloon). Then, DBU was added (9 μL , 0.06 mmol), and the reaction was stirred at the stated temperature for 24 h. Yield and selectivity were evaluated by ^1H NMR analysis of the reaction mixture (durene as internal standard).

Entry 14. A stirred mixture of glycerol **1** (33 mg, 0.36 mmol), 1-naphtaldehyde **2a** (16 μL , 0.12 mmol), **7** (5 mg, 0.024 mmol), **8** (3.4 mg, 0.006 mmol), durene (16 mg, 0.12 mmol), and pre-catalyst **F** (20 mg, 0.012 mmol, loading = 0.59 mmol g^{-1}) in Me-THF (1.0 mL) was stirred under an air atmosphere (by a compressed air-filled balloon). Then, DBU was added (9. μL , 0.06 mmol), and the reaction was stirred at room temperature for 8 h (40% conversion as established by ^1H NMR analysis). Then, catalyst **F** was removed by filtration and the filtrate was stirred at room temperature for additional 16 h.

Entry 15. A stirred mixture of glycerol **1** (33 mg, 0.36 mmol), 1-naphtaldehyde **2a** (16 μL , 0.12 mmol), oxidant **6** (49 mg, 0.12 mmol), durene (16 mg, 0.12 mmol) and pre-catalyst **F** (20 mg, 0.012 mmol, loading = 0.59 mmol g^{-1}) in Me-THF (1.0 mL) was degassed under vacuum and saturated with argon (by an Ar-filled balloon) three times. Then, DBU was added (3.6 μL , 0.024 mmol), and the reaction was stirred at room temperature for 24 h. Yield and selectivity were evaluated by ^1H NMR analysis of the reaction mixture (durene as internal standard).

Entries 16-17. A stirred mixture of glycerol **1** (33 mg, 0.36 mmol), 1-naphtaldehyde **2a** (16 μL , 0.12 mmol), **7** (5 mg, 0.024 mmol), **8** (3.4 mg, 0.006 mmol), durene (16 mg, 0.12 mmol), and pre-catalyst **F** (20 mg, 0.012 mmol, loading = 0.59 mmol g^{-1}) in Me-THF (1.0 mL) was stirred under an air atmosphere (by a compressed air-filled balloon). Then, DBU was added (9 μL , 0.06 mmol), and the reaction was stirred at room temperature for 24 h. After this period, catalyst was recycled by simple filtration and washing of the resin with ethyl acetate. Yield and selectivity were evaluated by ^1H NMR analysis of the reaction mixture (durene as internal standard).

Entries 18-19. A stirred mixture of glycerol **1** (33 mg, 0.36 mmol), 1-naphtaldehyde **2a** (16 μL , 0.12 mmol), oxidant **6** (49 mg, 0.12 mmol), durene (16 mg, 0.12 mmol), and pre-catalyst **F** (20 mg, 0.012 mmol, loading = 0.59 mmol g^{-1}) in Me-THF (1.0 mL) was degassed under vacuum and saturated with argon (by an Ar-filled balloon) three times. Then, DBU was added (3.6 μL , 0.024 mmol), and the reaction was stirred at room temperature for 24 h. After this period, catalyst was recycled by simple filtration and washing of the resin with ethyl acetate. Yield and selectivity were evaluated by ^1H NMR analysis of the reaction mixture (durene as internal standard).

Characterization data of monoesters **3a-i** and **17a-i** and diester **4a**.

2,3-Dihydroxypropyl 1-naphthoate (3a). Column chromatography with 1:1 cyclohexane-EtOAc afforded **3a** (27 mg, 90%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ = 8.88 (d, *J* = 7.4 Hz, 1H, Ar), 8.19 (dd, *J* = 7.4, 1.3 Hz, 1H, Ar), 8.03 (d, *J* = 8.3 Hz, 1H, Ar), 7.88 (dd, *J* = 8.3, 1.3 Hz, 1H, Ar), 7.64-7.58 (m, 1H, Ar), 7.57-7.42 (m, 2H, Ar), 4.58-4.42 (m, 2H, CH₂₍₁₎), 4.20-4.05 (m, 1H, CH₂₍₂₎), 3.77 (m, 2H, CH₂₍₃₎), 2.93 (d, *J* = 5.0 Hz, 1H, OH₍₂₎), 2.47 (t, *J* = 5.7 Hz, 1H, OH₍₃₎); ¹³C NMR (101 MHz, CDCl₃) δ = 167.8, 133.8 (2 C), 131.3, 130.5, 128.6, 128.0, 126.3 (2 C), 125.6, 124.4, 70.4, 65.8, 63.5. HRMS (ESI/Q-TOF) calcd for C₁₄H₁₅O₄ ([M + H]⁺) 247.0965, found: 247.1003.

2-Hydroxypropane-1,3-diyl bis(1-naphthoate)(4a). Column chromatography with 3:1 cyclohexane-EtOAc afforded **4a** (30 mg, 59%; entry 12, Table 1) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ = 8.92 (d, *J* = 7.6 Hz, 2H, Ar), 8.23 (dd, *J* = 7.6, 1.3 Hz, 2H, Ar), 8.04 (d, *J* = 8.3 Hz, 2H, Ar), 7.88 (dd, *J* = 8.3, 1.3 Hz, 2H, Ar), 7.61 (m, 3H, Ar), 7.55-7.34 (m, 3H, Ar), 4.77-4.55 (m, 4H, CH₂₍₁₎+CH₂₍₃₎), 4.56-4.45 (m, 1H, CH₂₍₂₎), 2.79 (d, *J* = 5.2 Hz, 1H, OH₍₂₎); ¹³C NMR (101 MHz, CDCl₃) δ = 167.5 (2 C), 133.8 (4 C), 131.3 (2 C), 130.5 (2 C), 128.6 (2 C), 128.0 (2 C), 126.3 (4 C), 125.6 (2 C), 124.5 (2 C), 68.7, 66.0 (2 C). HRMS (ESI/Q-TOF) calcd for C₂₅H₂₁O₅ ([M + H]⁺) 401.1384, found: 401.1358.

2,3-Dihydroxypropyl 4-bromobenzoate (3b). Column chromatography with 3:1 cyclohexane-EtOAc afforded **3b** (41 mg, 60%) as a pale yellow oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.90 (d, *J* = 8.9 Hz, 2H, Ar), 7.59 (d, *J* = 8.9 Hz, 2H, Ar), 4.56-4.28 (m, 2H, CH₂₍₁₎), 4.07 (m, 1H, CH₂₍₂₎), 3.70 (m, 2H, CH₂₍₃₎), 2.65 (d, *J* = 4.6 Hz, 1H, OH₍₂₎), 2.17 (t, *J* = 5.7 Hz, 1H, OH₍₃₎); ¹³C NMR (101 MHz, CDCl₃) δ = 166.3, 131.9 (2 C), 131.3 (2 C), 128.6, 128.5, 70.3, 66.0, 63.4. HRMS (ESI/Q-TOF) calcd for C₁₀H₁₂BrO₄ ([M + H]⁺) 274.9913, found: 274.9961.

2,3-Dihydroxypropyl cinnamate (3c). Column chromatography with gradient from 1:2 cyclohexane-EtOAc to 10:1 EtOAc:MeOH afforded **3c** (46 mg, 83%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.74 (d, *J* = 16.1 Hz, 1H, CH₍₃₎), 7.58-7.49 (m, 2H, Ar), 7.46-7.31 (m, 3H, Ar), 6.49 (d, *J* = 16.1 Hz, 1H, CH₍₂₎), 4.40-4.25 (m, 2H, CH₍₁₎), 4.07-3.97 (m, 1H, CH₍₂₎), 3.80-3.62 (m, 2H, CH₂₍₃₎), 2.62 (bs, 1H, OH₍₂₎), 2.16 (bs, 1H, OH₍₃₎); ¹³C NMR (101 MHz, CDCl₃) δ = 167.4, 150.0, 134.1, 130.6, 128.9 (2 C), 128.2 (2 C), 117.1, 70.3, 65.4, 63.3. HRMS (ESI/Q-TOF) calcd for C₁₂H₁₅O₄ ([M + H]⁺) 223.0965, found: 223.0916.

2,3-Dihydroxypropyl decanoate (3d). Column chromatography with gradient from 1:1 cyclohexane-EtOAc to EtOAc afforded **3d** (35 mg, 57%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ = 4.27-4.08 (m, 2H, CH₂₍₁₎), 3.98-3.86 (m, 1H, CH₍₂₎), 3.76-3.51 (m, 2H, CH₂₍₃₎), 2.58 (bs, 1H, OH₍₂₎), 2.35

(t, $J = 7.5$ Hz, 2H, CH₂₍₂₎), 2.16 (bs, 1H, OH₍₃₎), 1.72-1.53 (m, 2H, CH₂₍₃₎), 1.35-1.17 (m, 12H, CH₂), 0.87 (t, $J = 6.7$ Hz, 3H, CH₃₍₁₀₎); ¹³C NMR (101 MHz, CDCl₃) $\delta = 174.5, 70.3, 65.3, 63.4, 34.2, 31.9, 29.5, 29.3$ (2 C), 29.2, 25.0, 22.7, 14.2. HRMS (ESI/Q-TOF) calcd for C₁₃H₂₇O₄ ([M + H]⁺) 247.1904, found: 247.1926.

2,3-Dihydroxypropyl palmitate (3e). Column chromatography with gradient from 1:1 cyclohexane-EtOAc to EtOAc afforded **3e** (52 mg, 63%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) $\delta = 4.25-4.10$ (m, 2H, CH₂₍₁₎), 4.00-3.89 (m, 1H, CH₍₂₎), 3.74-3.55 (m, 2H, CH₂₍₃₎), 2.56 (bs, 1H, OH₍₂₎), 2.35 (t, $J = 7.5$ Hz, 2H, CH₂₍₂₎), 2.13 (bs, 1H, OH₍₃₎), 1.69-1.55 (m, 2H, CH₂₍₃₎), 1.38-1.17 (m, 24H, CH₂), 0.87 (t, $J = 6.6$ Hz, 3H, CH₃₍₁₆₎); ¹³C NMR (101 MHz, CDCl₃) $\delta = 174.5, 70.3, 65.2, 63.4, 34.2, 32.0, 29.8-29.5$ (5 C), 29.7, 29.5, 29.4, 29.3, 29.2, 25.0, 22.8, 14.2. HRMS (ESI/Q-TOF) calcd for C₁₉H₃₉O₄ ([M + H]⁺) 331.2843, found: 331.2802.

2,3-Dihydroxypropyl 3,7-dimethyloct-6-enoate (3f). Column chromatography with 2:1 dichloromethane-EtOAc afforded **3f** (37 mg, 61%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) $\delta = 5.08$ (t, $J = 7.1$ Hz, 1H, CH₍₆₎), 4.26-4.09 (m, 2H, CH₂₍₁₎), 3.99-3.88 (m, 1H, CH₍₂₎), 3.76-3.53 (m, 2H, CH₂₍₃₎), 2.56 (bs, 1H, OH₍₂₎), 2.44-2.31 (m, 1H, CH₂₍₂₎), 2.25-2.07 (m, 2H, CH₂₍₂₎+OH₍₃₎), 1.98 (m, 3H, CH₂₍₅₎+CH₍₃₎), 1.68 (s, 3H, CH₃₍₇₎), 1.60 (s, 3H, CH₃₍₇₎), 1.44-1.13 (m, 2H, CH₂₍₄₎), 0.97 (d, $J = 6.8$, 3H, CH₃₍₃₎); ¹³C NMR (101 MHz, CDCl₃) $\delta = 173.7, 124.1, 70.3, 65.1, 63.3, 41.6, 36.7, 30.9, 30.0, 25.7, 25.3, 19.6, 17.6$. HRMS (ESI/Q-TOF) calcd for C₁₃H₂₅O₄ ([M + H]⁺) 245.1747, found: 245.1711.

2,3-Dihydroxypropyl 4-hydroxy-3-methoxybenzoate (3g). Column chromatography with gradient from 1:2 cyclohexane-EtOAc to 20:1 EtOAc:MeOH afforded **3g** (38 mg, 63%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) $\delta = 7.65$ (dd, $J = 8.3, 1.9$ Hz, 1H, Ar), 7.54 (d, $J = 1.9$ Hz, 1H, Ar), 6.95 (d, $J = 8.3$ Hz, 1H, Ar), 6.10 (bs, 1H, OH_{Ar}), 4.53-4.31 (m, 2H, CH₂₍₁₎), 4.13-4.01 (m, 1H, CH₍₂₎), 3.95 (s, 3H, OCH₃), 3.78-3.59 (m, 2H, CH₂₍₃₎), 2.62 (bs, 1H, OH₍₂₎), 2.22 (bs, 1H, OH₍₃₎); ¹³C NMR (101 MHz, CDCl₃) $\delta = 166.9, 150.4, 146.2, 124.4, 121.5, 114.1, 111.8, 70.4, 65.6, 63.3, 56.1$. HRMS (ESI/Q-TOF) calcd for C₁₁H₁₅O₆ ([M + H]⁺) 243.0863, found: 243.0891.

2,3-Dihydroxypropyl furan-2-carboxylate (3h). Column chromatography with 1:5 cyclohexane-EtOAc afforded **3h** (42 mg, 91%) as a pale yellow oil. ¹H NMR (300 MHz, CDCl₃) $\delta = 7.60$ (dd, $J = 1.7, 0.7$ Hz, 1H, Ar), 7.23 (dd, $J = 3.5, 0.7$ Hz, 1H, Ar), 6.53 (dd, $J = 3.5, 1.7$ Hz, 1H, Ar), 4.48-4.32 (m, 2H, CH₂₍₁₎), 4.11-3.99 (m, 1H, CH₍₂₎), 3.83-3.63 (m, 2H, CH₂₍₃₎), 2.74 (d, $J = 3.5$ Hz, 1H, OH₍₂₎), 2.25 (bs, 1H, OH₍₃₎); ¹³C NMR (101 MHz, CDCl₃) $\delta = 159.0, 146.8, 144.1, 118.9, 112.1, 70.2, 65.8, 63.3$. HRMS (ESI/Q-TOF) calcd for C₈H₁₁O₅ ([M + H]⁺) 187.0601, found: 187.0615.

(5-((2,3-Dihydroxypropoxy)carbonyl)furan-2-yl)methyl 5-(hydroxymethyl)furan-2-carboxylate (**3i**). Column chromatography with gradient from EtOAc to 20:1 EtOAc:MeOH afforded **3i** (81 mg, 95%) as a pale yellow oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.23-7.08 (m, 2H, Ar), 6.67-6.52 (m, 1H, Ar), 6.52-6.38 (m, 1H, Ar), 5.31 (m, 2H, CH₂(OCO)), 4.68 (m, 2H, CH₂(OH)), 4.57-4.31 (m, 2H, CH₂(₁)), 4.14-3.99 (m, 1H, CH₂(₂)), 3.80-3.60 (m, 2H, CH₂(₃)), 2.62 (bs, 1H, OH(₂)), 2.17 (bs, 2H, OH(₃)+OH_{furan}); ¹³C NMR (101 MHz, CDCl₃) δ = 158.8, 158.6, 158.0, 153.4, 144.3, 143.3, 119.8, 119.4, 112.9, 109.6, 70.1, 65.9, 63.3, 57.9, 57.5. HRMS (ESI/Q-TOF) calcd for C₁₅H₁₇O₉ ([M + H]⁺) 341.0867, found: 341.0814.

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl 1-naphthoate (**17a**). Column chromatography with 10:1 cyclohexane-EtOAc afforded **17a** (66 mg, 92%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ = 8.92 (d, *J* = 7.4 Hz, 1H, Ar), 8.23 (dd, *J* = 7.4, 1.3 Hz, 1H, Ar), 8.04 (d, *J* = 8.3 Hz, 1H, Ar), 7.89 (dd, *J* = 8.3, 1.3 Hz, 1H, Ar), 7.66-7.58 (m, 1H, Ar), 7.58-7.46 (m, 2H, Ar), 4.58-4.40 (m, 3H, CH₄+CH₂(OCO)), 4.19 (dd, *J* = 8.5, 6.1 Hz, 1H, CH₂(₅)), 3.93 (dd, *J* = 8.5, 5.6 Hz, 1H, CH₂(₅)), 1.48 (s, 3H, CH₃(₂)), 1.41 (s, 3H, CH₃(₂)); ¹³C NMR (101 MHz, CDCl₃) δ = 167.5, 134.2, 134.0, 131.7, 130.8, 128.9, 128.2, 127.0, 126.6, 126.1, 124.8, 110.2, 74.1, 66.8, 65.4, 27.1, 25.7. HRMS (ESI/Q-TOF) calcd for C₁₇H₁₈NaO₄ ([M + Na]⁺) 309.1097, found: 309.1126.

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl 4-bromobenzoate (**17b**). Column chromatography with 8:1 cyclohexane-EtOAc afforded **17b** (56 mg, 71%) as a pale yellow oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.91 (d, *J* = 8.9 Hz, 2H, Ar), 7.58 (d, *J* = 8.9 Hz, 2H, Ar), 4.50-4.41 (m, 1H, CH₄), 4.41-4.28 (m, 2H, CH₂(OCO)), 4.14 (dd, *J* = 8.5, 6.1 Hz, 1H, CH₂(₅)), 3.86 (dd, *J* = 8.5, 5.6 Hz, 1H, CH₂(₅)), 1.45 (s, 3H, CH₃(₂)), 1.38 (s, 3H, CH₃(₂)); ¹³C NMR (101 MHz, CDCl₃) δ = 165.6, 131.7 (2 C), 131.2 (2 C), 128.6, 128.3, 109.9, 73.6, 66.3, 65.3, 26.7, 25.3. HRMS (ESI/Q-TOF) calcd for C₁₃H₁₅BrNaO₄ ([M + Na]⁺) 337.0046, found: 337.0011.

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl cinnamate (**17c**). Column chromatography with 6:1 cyclohexane-EtOAc afforded **17c** (36 mg, 55%) as a pale yellow oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.73 (d, *J* = 16.1 Hz, 1H, CH₃), 7.57-7.47 (m, 2H, Ar), 7.44-7.35 (m, 3H, Ar), 6.48 (d, *J* = 16.1 Hz, 1H, CH₂), 4.46-4.36 (m, 1H, CH₄), 4.36-4.17 (m, 2H, CH₂(OCO)), 4.13 (dd, *J* = 8.5, 6.1 Hz, 1H, CH₂(₅)), 3.81 (dd, *J* = 8.5, 5.6 Hz, 1H, CH₂(₅)), 1.47 (s, 3H, CH₃(₂)), 1.39 (s, 3H, CH₃(₂)); ¹³C NMR (101 MHz, CDCl₃) δ = 166.7, 145.5, 134.2, 130.4, 128.9 (2 C), 128.1 (2 C), 117.4, 109.9, 73.7, 66.4, 64.9, 26.7, 25.4. HRMS (ESI/Q-TOF) calcd for C₁₅H₁₈NaO₄ ([M + Na]⁺) 285.1097, found: 285.1146.

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl decanoate (**17d**). Column chromatography with 9:1 cyclohexane-EtOAc afforded **17d** (49 mg, 68%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ = 4.36-4.26 (m, 1H, CH₄), 4.20-4.10 (m, 2H, CH₂(OCO)), 4.07 (dd, *J* = 8.5, 6.1 Hz, 1H, CH₂(₅)), 3.73

(dd, $J = 8.5, 5.6$ Hz, 1H, CH₂₍₅₎), 2.34 (t, $J = 7.6$ Hz, 2H, CH₂₍₂₎), 1.67-1.58 (m, 2H, CH₂₍₃₎), 1.43 (s, 3H, CH₃₍₂₎), 1.37 (s, 3H, CH₃₍₂₎), 1.34-1.19 (m, 12H, CH₂), 0.87 (t, $J = 6.7$ Hz, 3H, CH₃₍₁₀₎); ¹³C NMR (101 MHz, CDCl₃) $\delta = 173.7, 109.8, 73.6, 66.3, 64.5, 34.1, 31.8, 29.4, 29.2$ (2 C), 29.1, 26.7, 25.4, 24.9, 22.7, 14.1. HRMS (ESI/Q-TOF) calcd for C₁₆H₃₀NaO₄ ([M + Na]⁺) 309.2036, found: 309.2076.

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl palmitate (**17e**). Column chromatography with 10:1 cyclohexane-EtOAc afforded **17e** (48 mg, 52%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) $\delta = 4.37-4.26$ (m, 1H, CH₄), 4.20-4.10 (m, 2H, CH_{2(OCO)}), 4.08 (dd, $J = 8.5, 6.1$ Hz, 1H, CH₂₍₅₎), 3.74 (dd, $J = 8.5, 5.6$ Hz, 1H, CH₂₍₅₎), 2.34 (t, $J = 7.6$ Hz, 2H, CH₂₍₂₎), 1.68-1.58 (m, 2H, CH₂₍₃₎), 1.43 (s, 3H, CH₃₍₂₎), 1.37 (s, 3H, CH₃₍₂₎), 1.34-1.18 (m, 24H, CH₂), 0.87 (t, $J = 6.7$ Hz, 3H, CH₃₍₁₆₎); ¹³C NMR (101 MHz, CDCl₃) $\delta = 173.7, 109.9, 73.7, 66.4, 64.6, 34.2, 32.0, 31.0, 29.7-29.5$ (5 C), 29.5, 29.4, 29.3, 29.2, 26.8, 25.5, 25.0, 22.8, 14.2. HRMS (ESI/Q-TOF) calcd for C₂₂H₄₂NaO₄ ([M + Na]⁺) 393.2975, found: 393.2949.

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl 3,7-dimethyloct-6-enoate (**17f**). Column chromatography with 10:1 cyclohexane-EtOAc afforded **17f** (65 mg, 91%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) $\delta = 5.08$ (t, $J = 7.7, 6.2$ Hz, 1H, CH₆), 4.38-4.25 (m, 1H, CH₄), 4.22-4.10 (m, 2H, CH_{2(OCO)}), 4.07 (dd, $J = 8.5, 6.1$ Hz, 1H, CH₂₍₅₎), 3.73 (dd, $J = 8.5, 5.6$ Hz, 1H, CH₂₍₅₎), 2.36 (dd, $J = 15.3, 5.9$ Hz, 1H, CH₂₍₂₎), 2.16 (dd, $J = 15.3, 7.9$ Hz, 1H, CH₂₍₂₎), 2.08-1.88 (m, 3H, CH_{2(5)+CH(3)}), 1.67 (s, 3H, CH₃₍₇₎), 1.59 (s, 3H, CH₃₍₇₎), 1.42 (s, 3H, CH₃₍₂₎), 1.37 (s, 3H, CH₃₍₂₎), 1.31-1.14 (m, 2H, CH₂₍₄₎), 0.94 (d, $J = 6.8$ Hz, 3H, CH₃₍₃₎); ¹³C NMR (101 MHz, CDCl₃) $\delta = 173.0, 131.6, 124.2, 109.8, 73.6, 66.4, 64.4, 41.5, 36.7, 29.9, 26.9, 26.7, 25.7, 25.4, 19.6, 17.6$. HRMS (ESI/Q-TOF) calcd for C₁₆H₂₈NaO₄ ([M + Na]⁺) 307.1880, found: 307.1845.

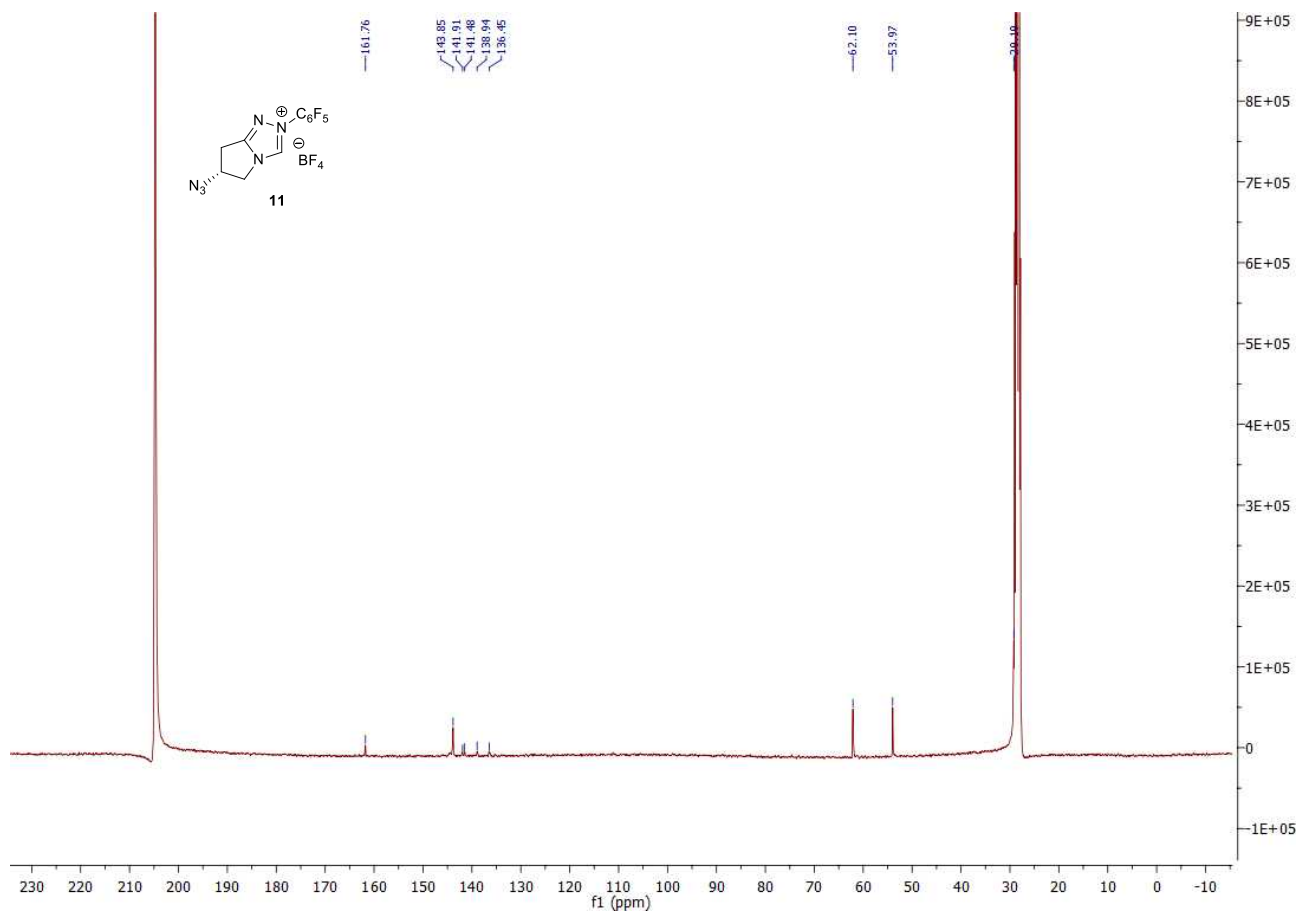
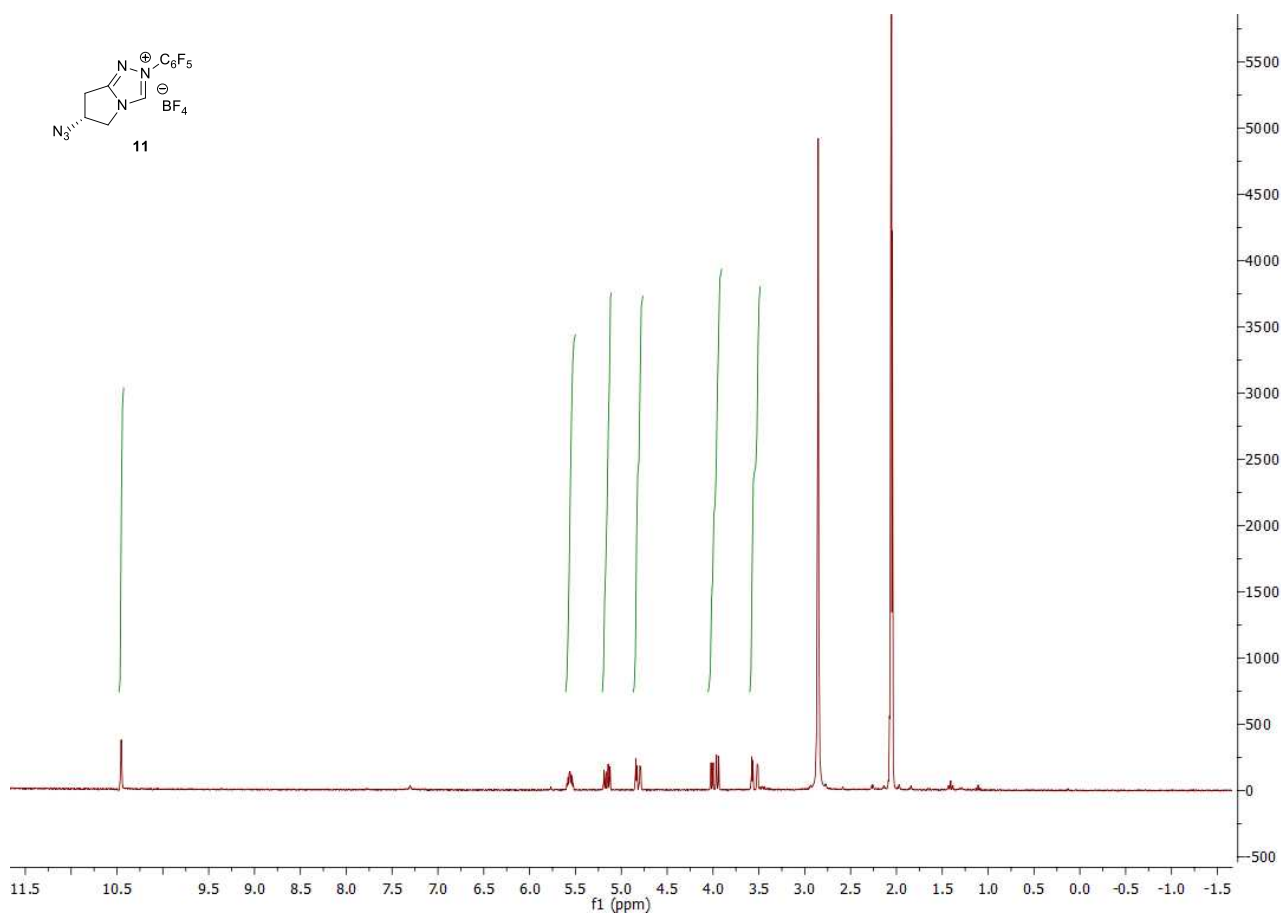
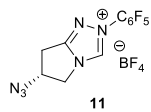
(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl 4-hydroxy-3-methoxybenzoate (**17g**). Column chromatography with 2:1 diethyl ether-cyclohexane afforded **17g** (56 mg, 80%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) $\delta = 7.66$ (dd, $J = 8.3, 1.9$ Hz, 1H, Ar), 7.56 (d, $J = 1.9$ Hz, 1H, Ar), 6.94 (d, $J = 8.3$ Hz, 1H, Ar), 6.05 (bs, 1H, OH_{Ar}), 4.50-4.39 (m, 1H CH₄), 4.38-4.32 (m, 2H, CH_{2(OCO)}), 4.14 (dd, $J = 8.5, 6.1$ Hz, 1H, CH₂₍₅₎), 3.94 (s, 3H, OCH₃), 3.87 (dd, $J = 8.5, 5.6$ Hz, 1H, CH₂₍₅₎), 1.46 (s, 3H, CH₃₍₂₎), 1.39 (s, 3H, CH₃₍₂₎); ¹³C NMR (101 MHz, CDCl₃) $\delta = 166.2, 150.2, 146.1, 124.4, 121.81, 114.1, 111.8, 109.8, 73.7, 66.4, 64.9, 56.1, 26.7, 25.4$. HRMS (ESI/Q-TOF) calcd for C₁₄H₁₈NaO₆ ([M + Na]⁺) 305.0996, found: 305.1014.

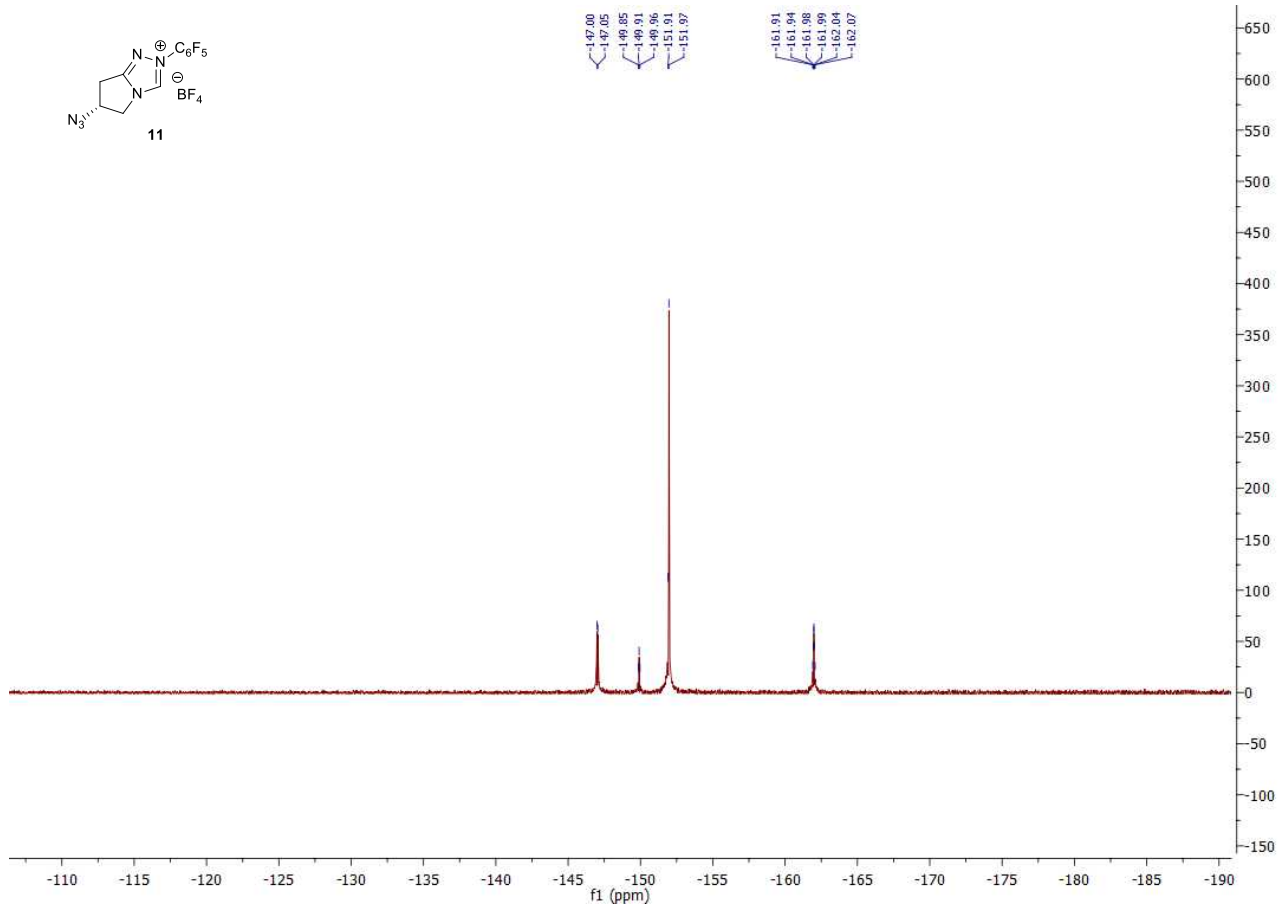
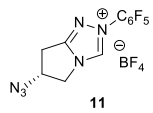
(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl furan-2-carboxylate (**17h**). Column chromatography with dichloromethane afforded **17h** (50 mg, 89%) as a pale yellow oil. ¹H NMR (300 MHz, CDCl₃) $\delta = 7.59$ (dd, $J = 1.7, 0.7$ Hz, 1H, Ar), 7.22 (dd, $J = 3.5, 0.7$ Hz, 1H, Ar), 6.51 (dd, $J = 3.5, 1.7$ Hz, 1H, Ar), 4.48-4.38 (m, 1H, CH₄), 4.38-4.30 (m, 2H, CH_{2(OCO)}), 4.13 (dd, $J = 8.5, 6.1$ Hz, 1H, CH₂₍₅₎),

3.84 (dd, $J = 8.5, 5.6$ Hz, 1H, CH₂₍₅₎), 1.45 (s, 3H, CH₃₍₂₎), 1.38 (s, 3H, CH₃₍₂₎); ¹³C NMR (101 MHz, CDCl₃) $\delta = 158.4, 146.6, 144.2, 118.4, 111.9, 109.9, 73.5, 66.3, 64.9, 26.7, 25.4$. HRMS (ESI/Q-TOF) calcd for C₁₁H₁₄NaO₅ ([M + Na]⁺) 249.0733, found: 249.0760.

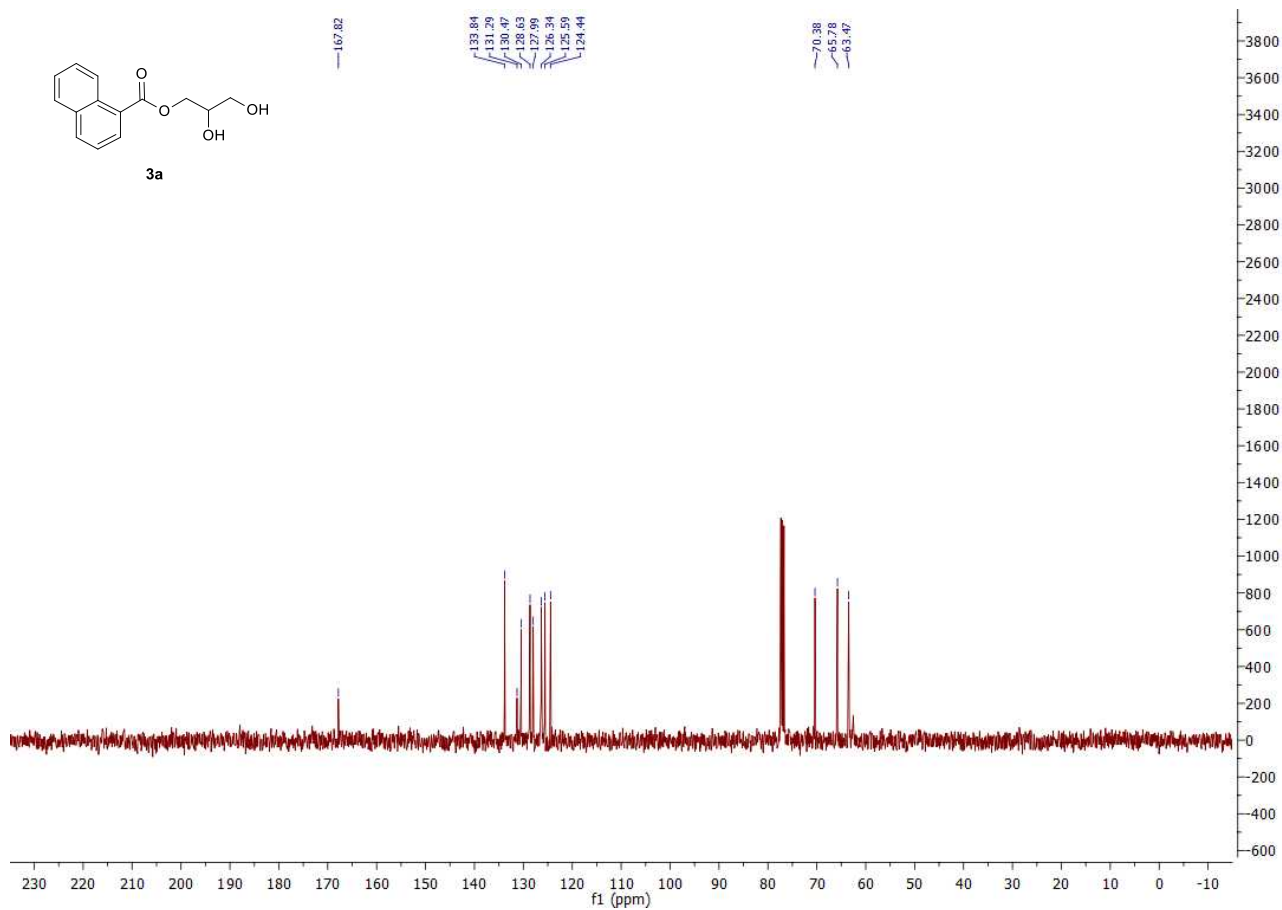
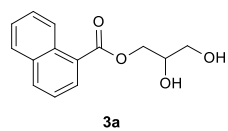
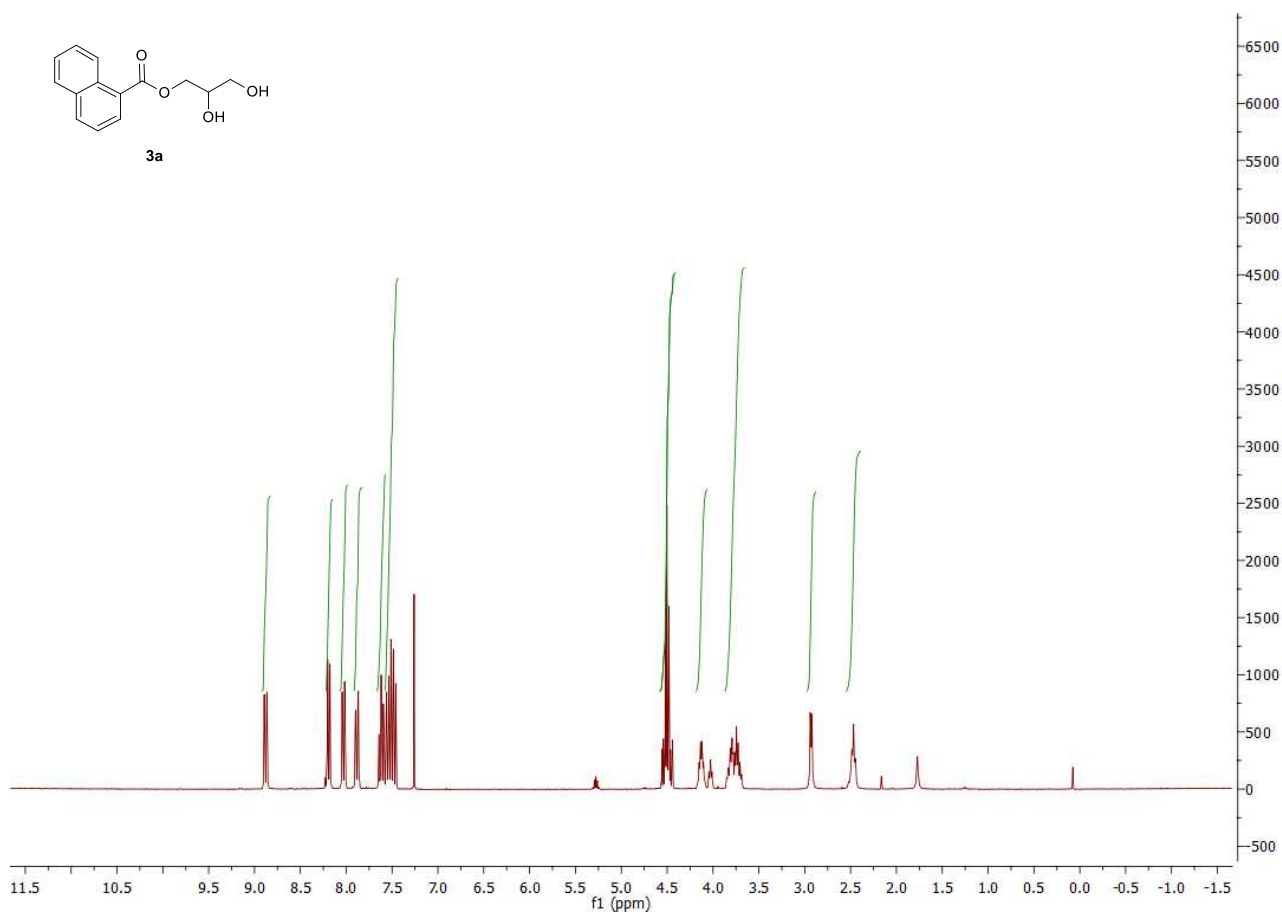
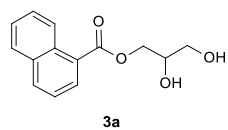
(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl 5-(hydroxymethyl)furan-2-carboxylate (17i). Column chromatography with 4:1 dichloromethane-EtOAc afforded **17i** (51 mg, 79%) as a pale yellow oil. ¹H NMR (300 MHz, CDCl₃) $\delta = 7.17$ (d, $J = 3.5$ Hz, 1H, Ar), 6.42 (d, $J = 3.5$ Hz, 1H, Ar), 4.68 (d, $J = 6.4$ Hz, 2H, CH₂₍₅₎), 4.47-4.37 (m, 1H CH₄), 4.37-4.31 (m, 2H, CH_{2(OCO)}), 4.13 (dd, $J = 8.5, 6.1$ Hz, 1H, CH₂₍₅₎), 3.84 (dd, $J = 8.5, 5.6$ Hz, 1H, CH₂₍₅₎), 1.99 (t, $J = 6.4$ Hz, 1H, OH), 1.45 (s, 3H, CH₃₍₂₎), 1.38 (s, 3H, CH₃₍₂₎); ¹³C NMR (101 MHz, CDCl₃) $\delta = 158.9, 158.7, 144.1, 119.6, 110.3, 109.8, 73.9, 66.7, 65.3, 58.0, 27.0, 25.7$. HRMS (ESI/Q-TOF) calcd for C₁₂H₁₆NaO₆ ([M + Na]⁺) 279.0839, found: 279.0800.

^1H (300 MHz) ^{13}C (101 MHz) and ^{19}F (376 MHz) spectra (acetone- d_6) of **11**

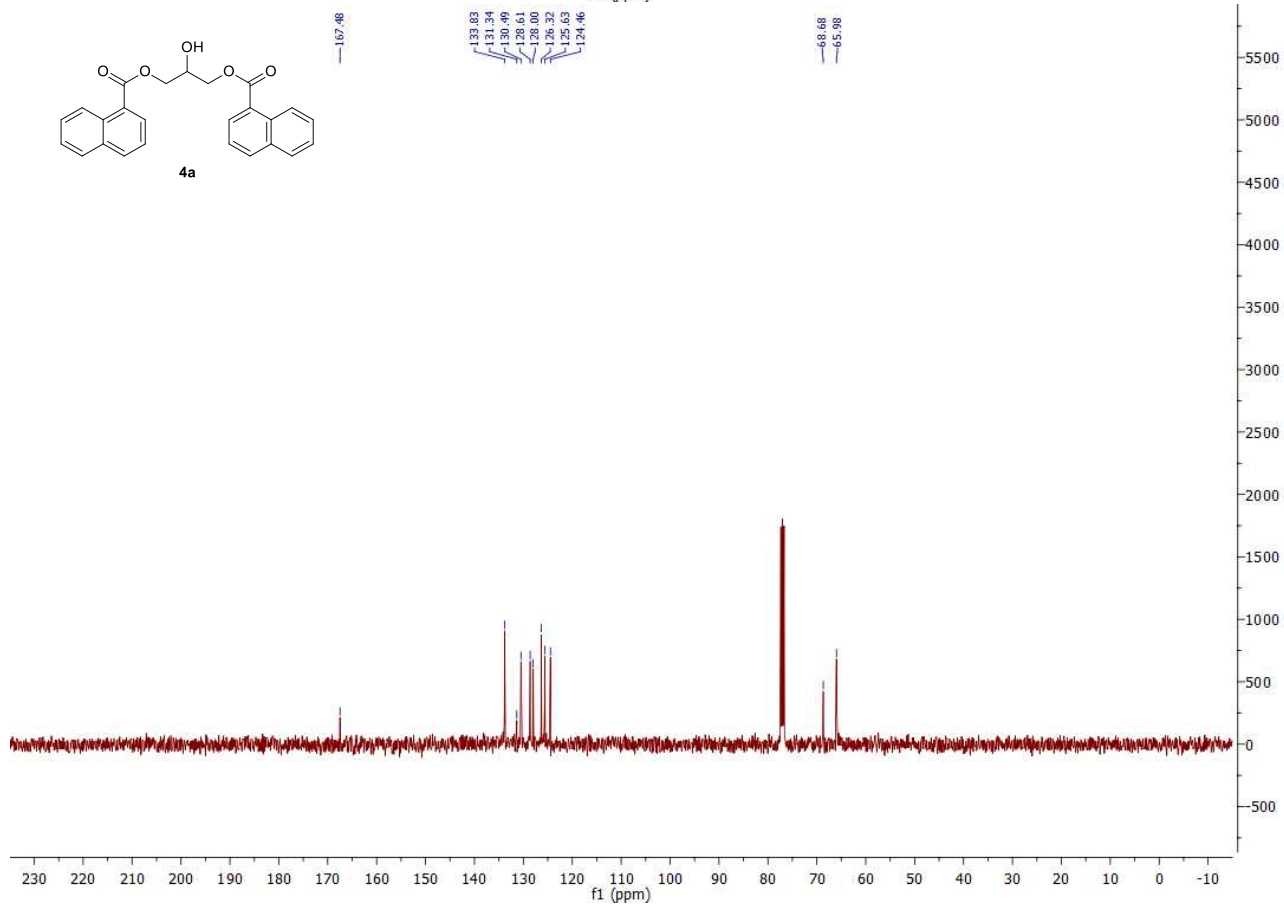
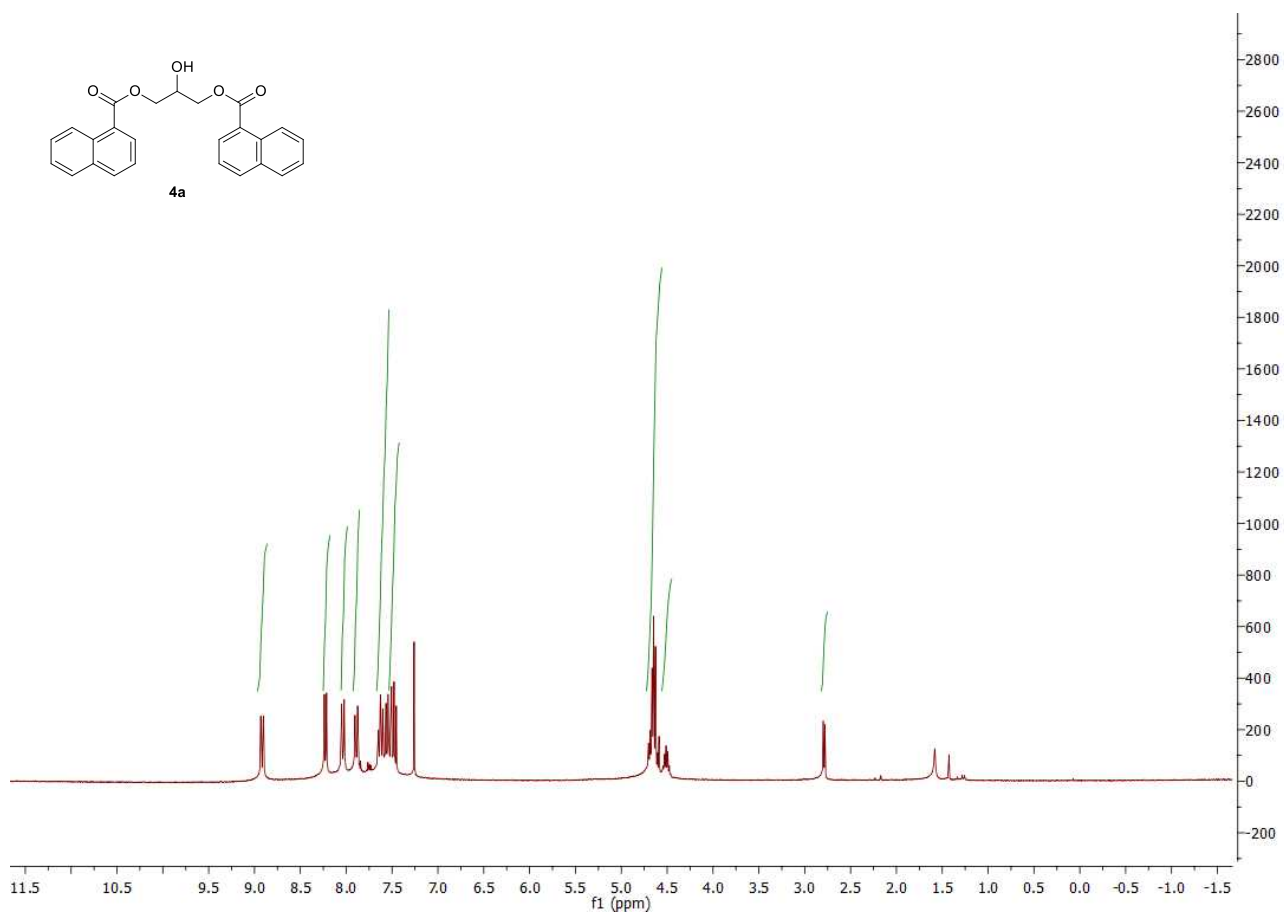




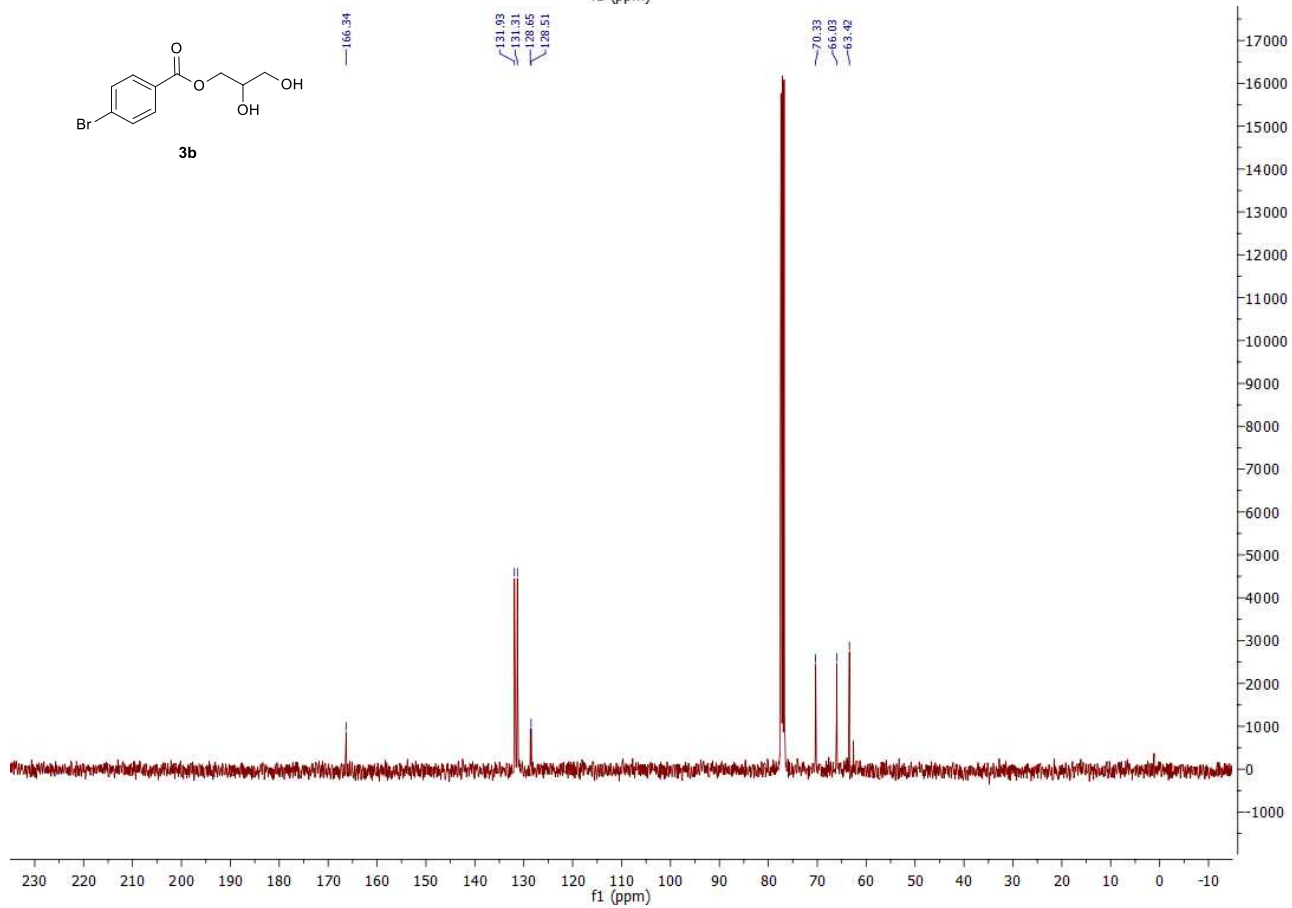
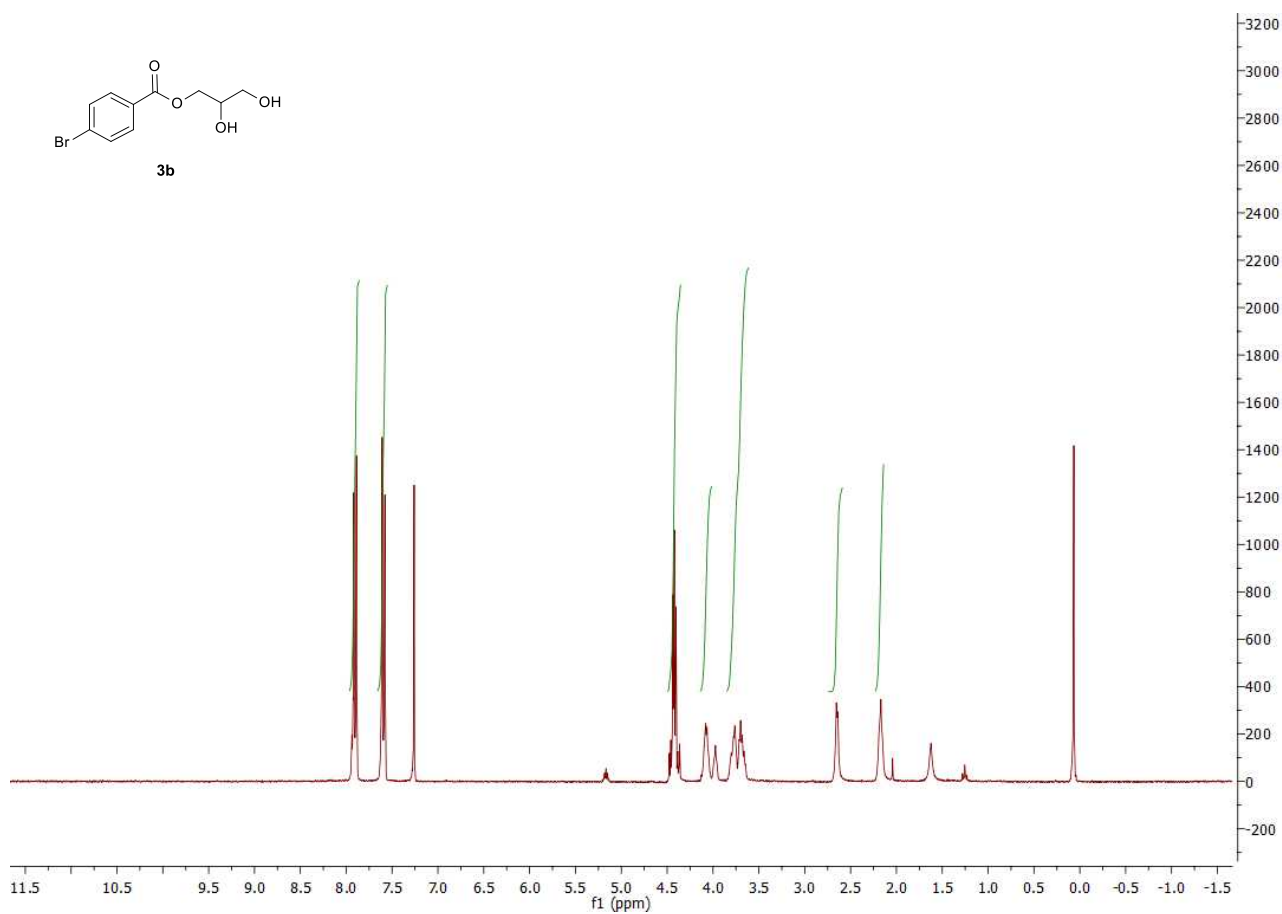
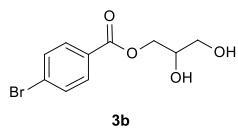
^1H (300 MHz) and ^{13}C (101 MHz) spectra (CDCl_3) of 3a



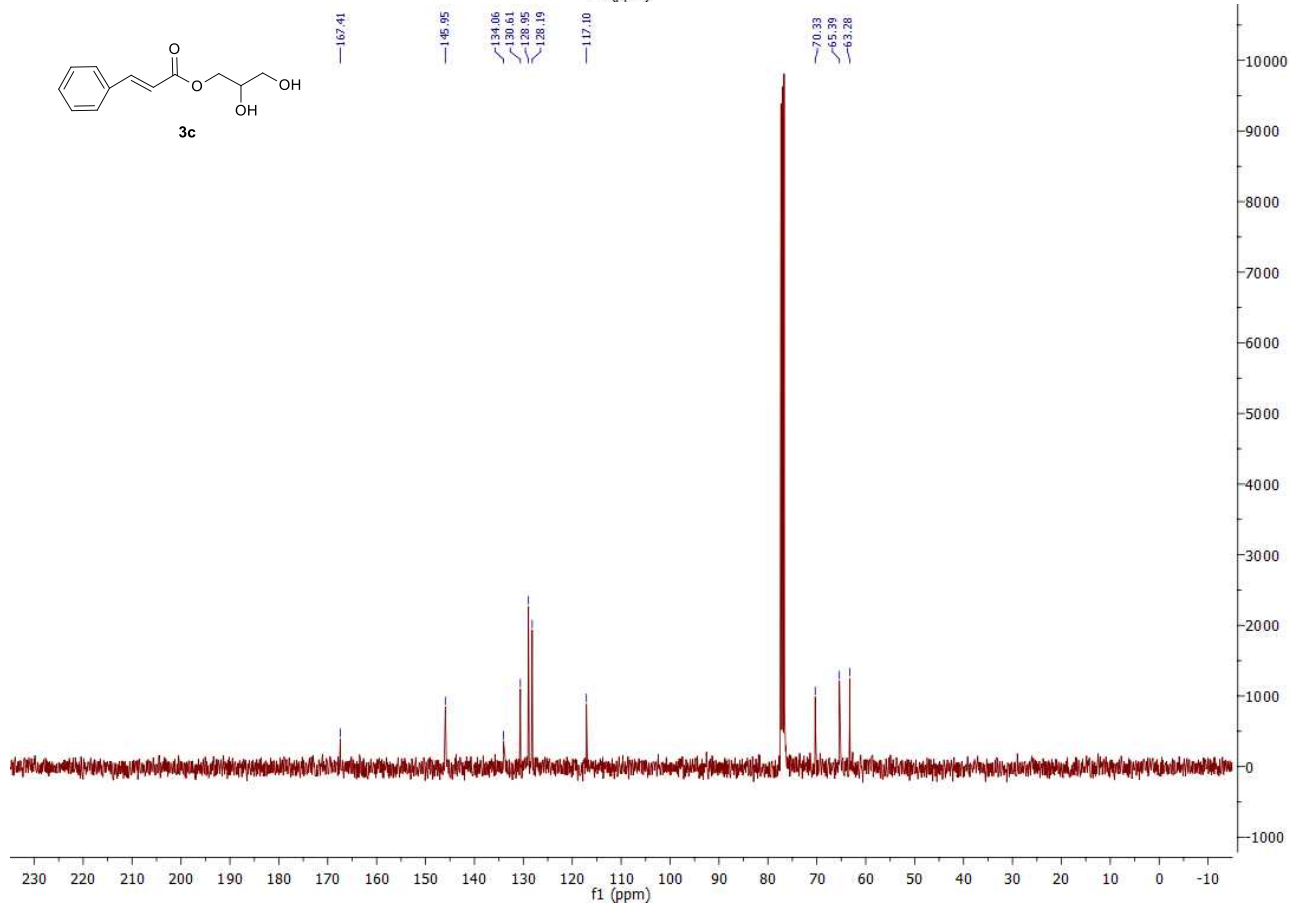
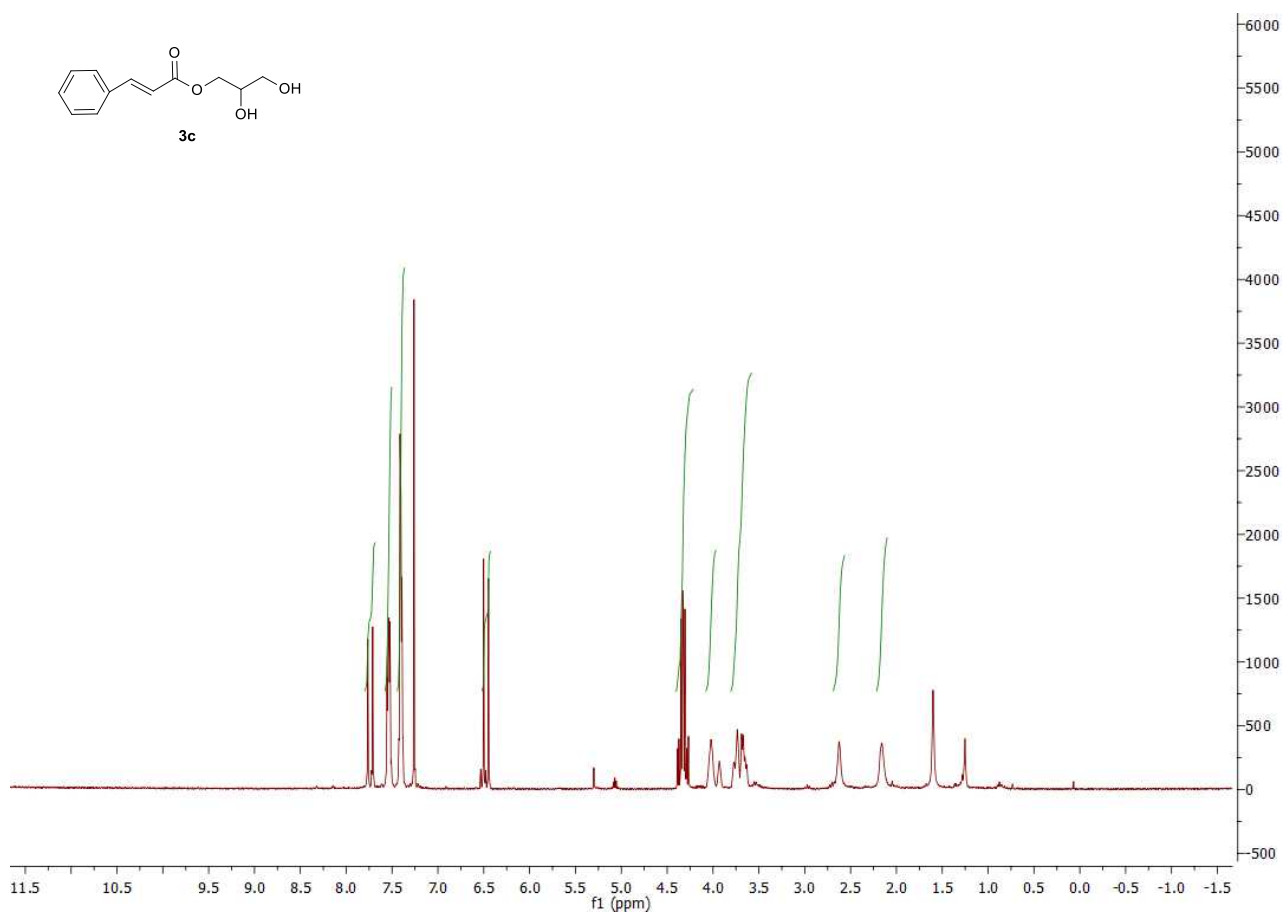
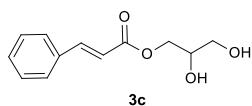
^1H (300 MHz) and ^{13}C (101 MHz) spectra (CDCl_3) of 4a



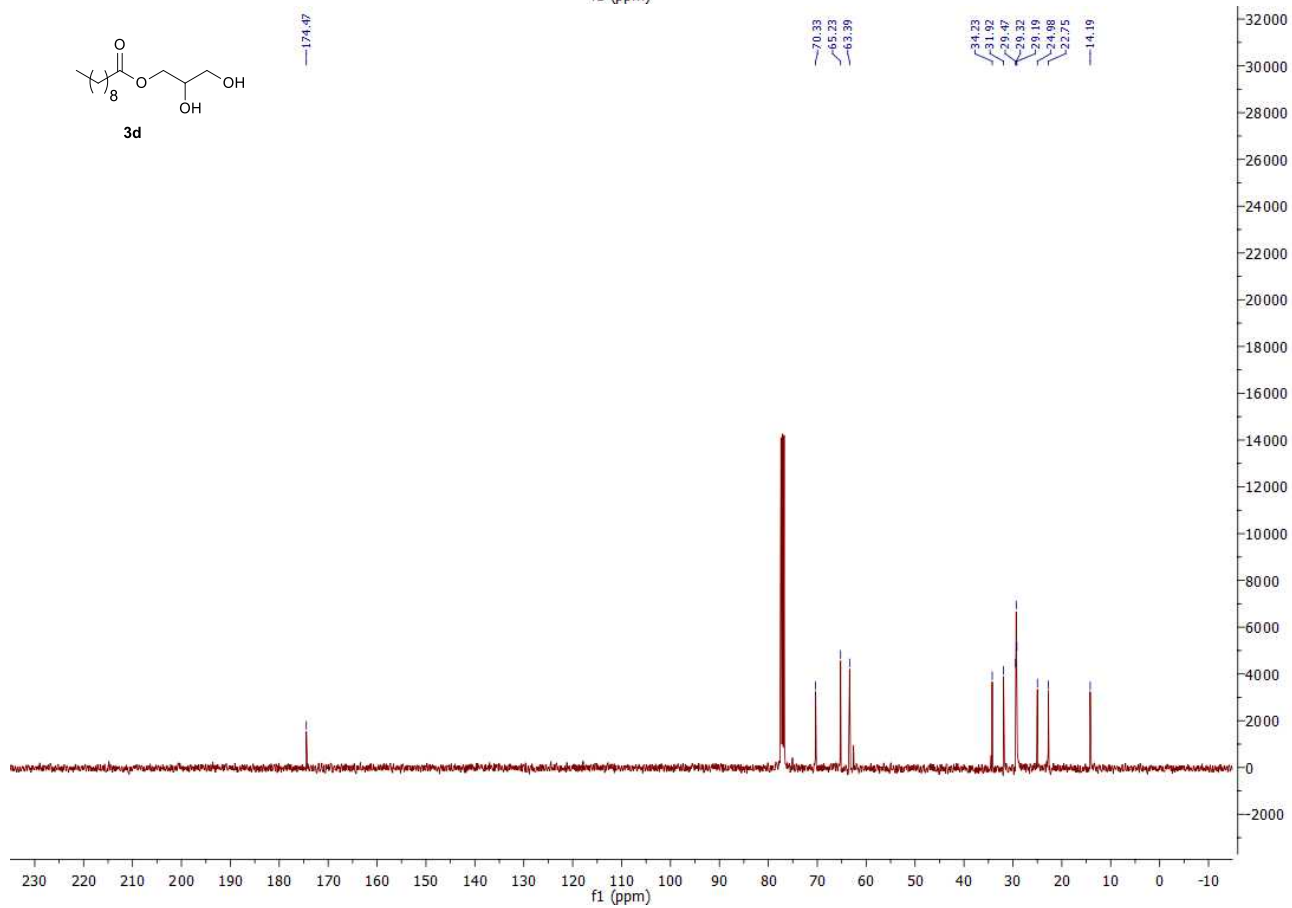
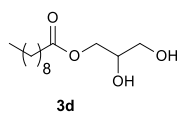
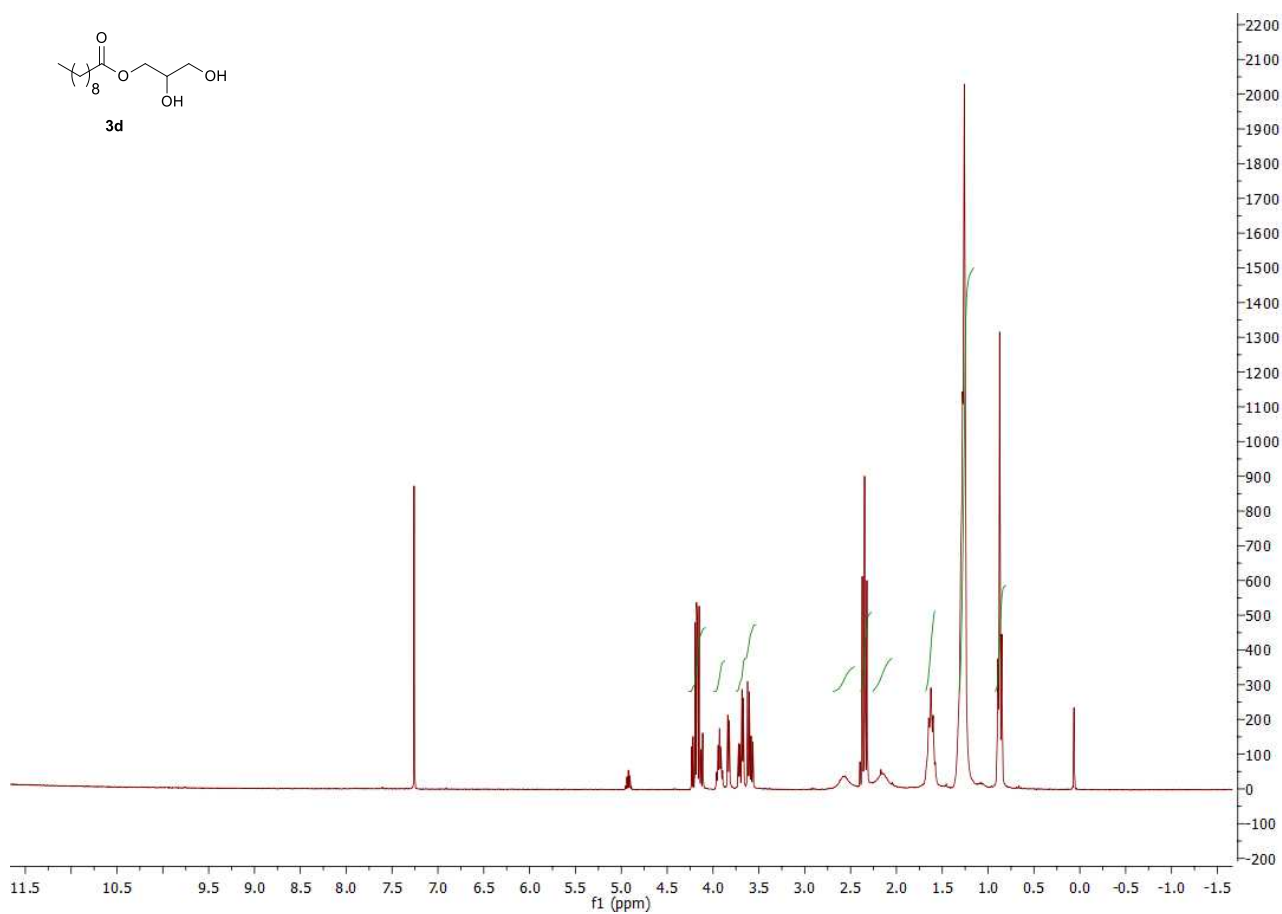
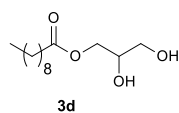
^1H (300 MHz) and ^{13}C (101 MHz) spectra (CDCl_3) of **3b**



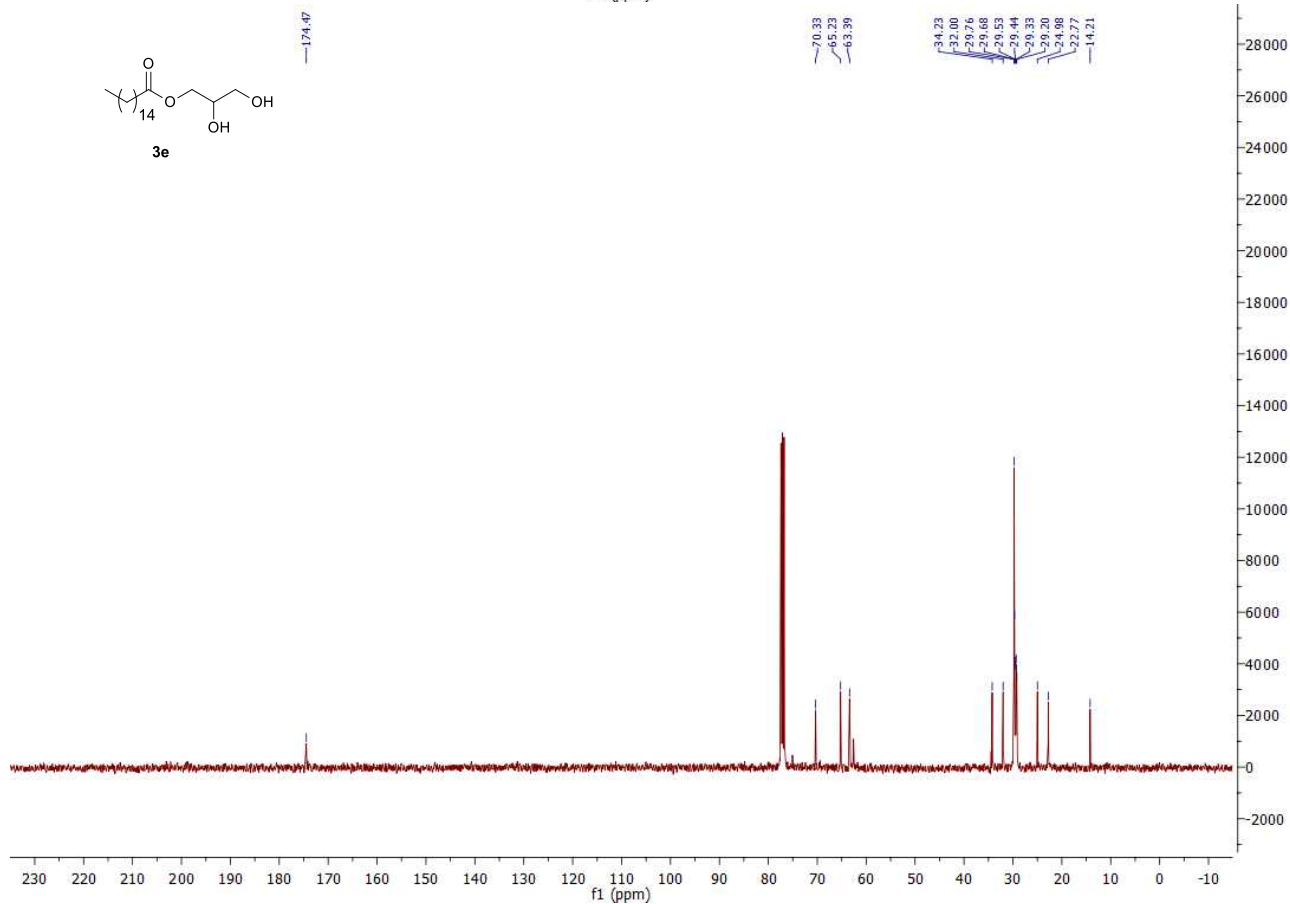
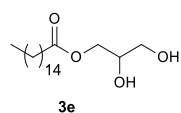
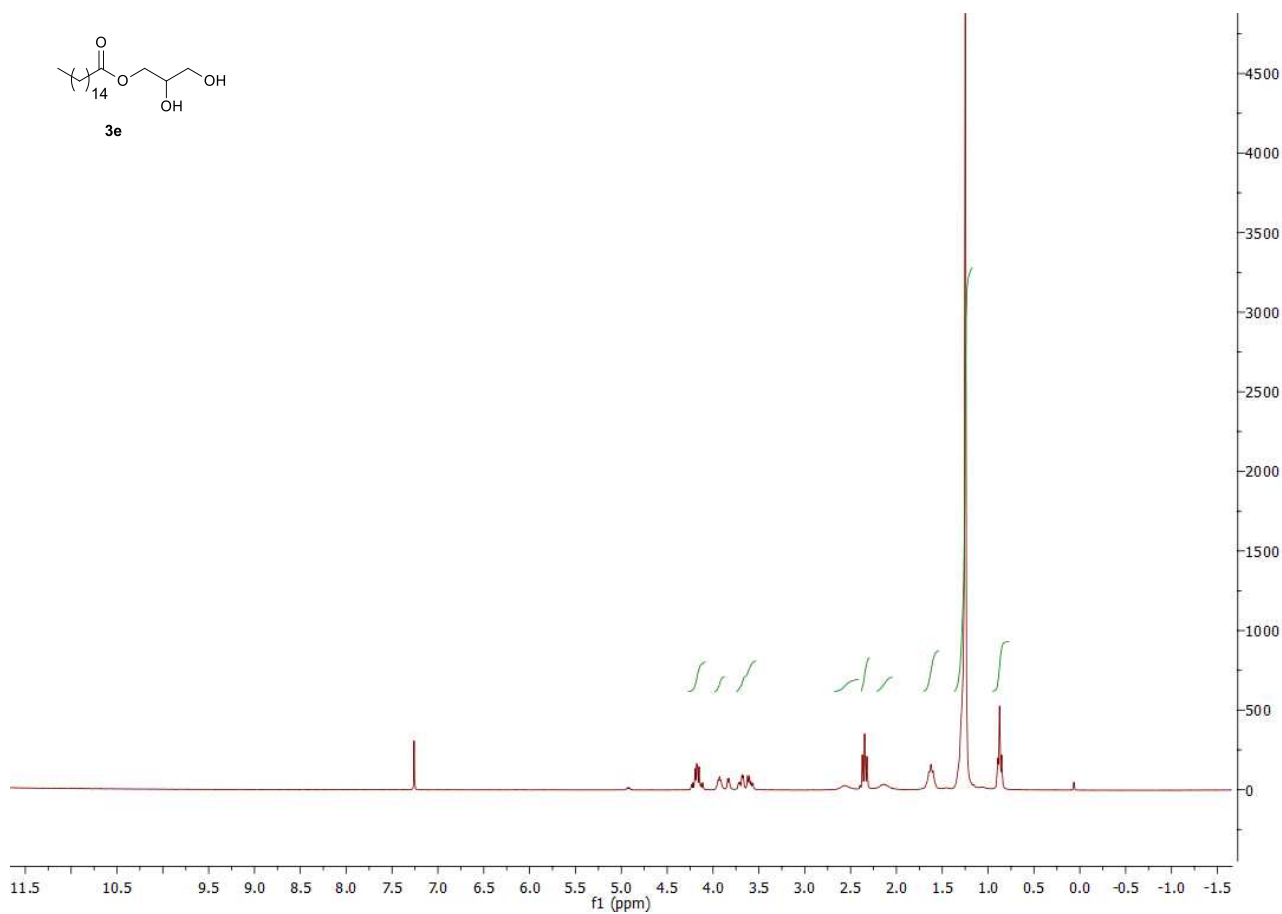
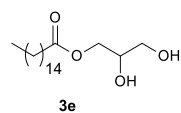
^1H (300 MHz) and ^{13}C (101 MHz) spectra (CDCl_3) of **3c**



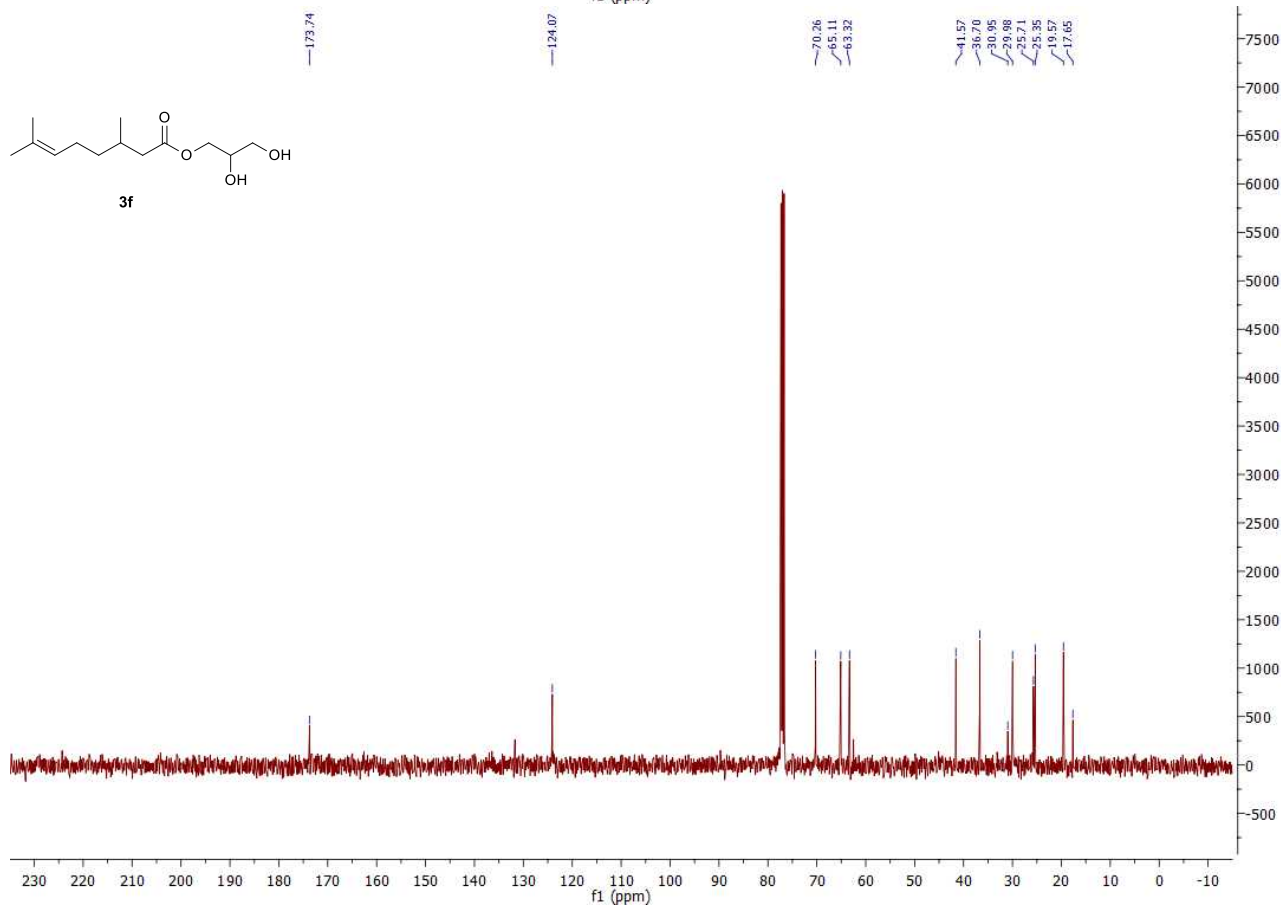
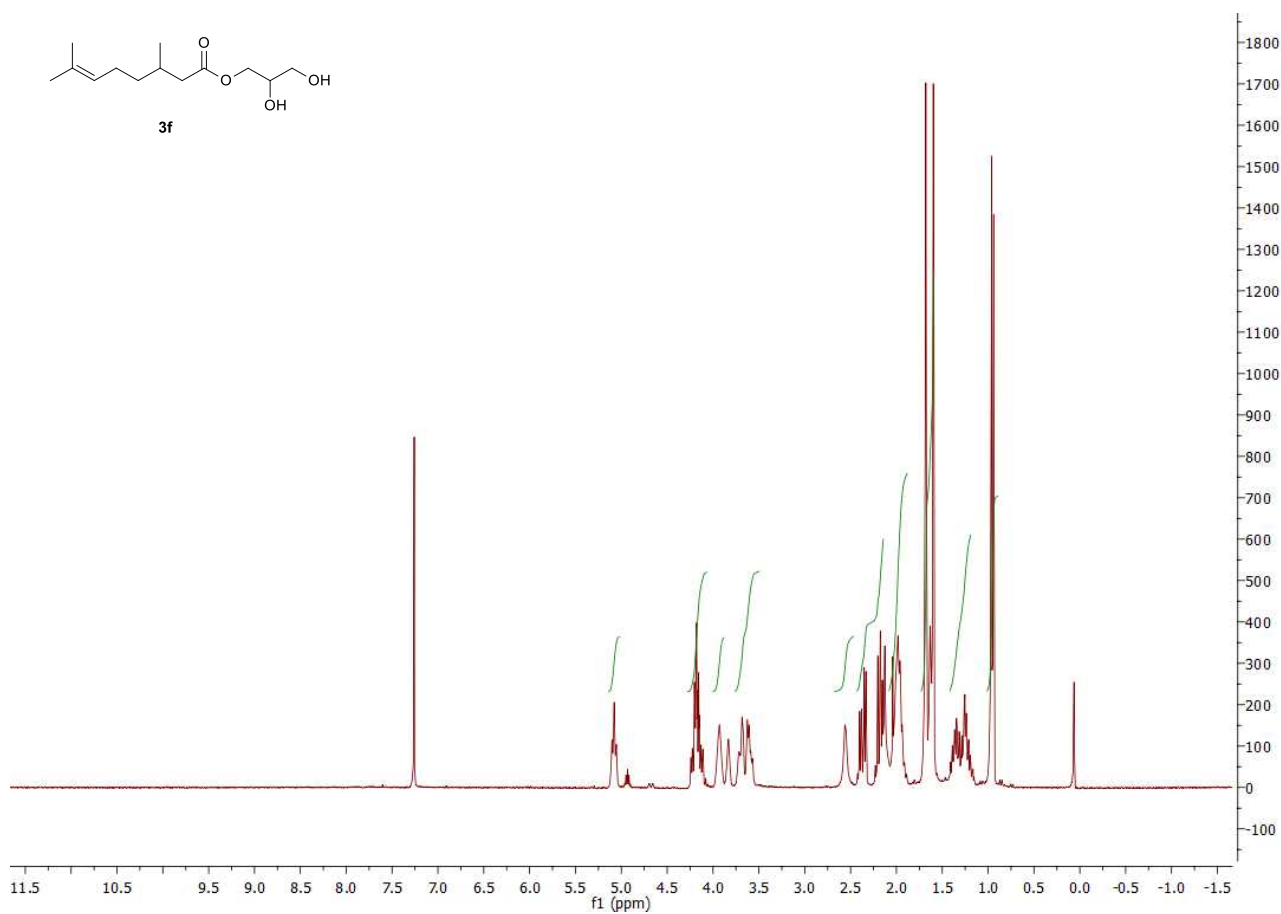
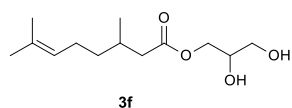
^1H (300 MHz) and ^{13}C (101 MHz) spectra (CDCl_3) of **3d**



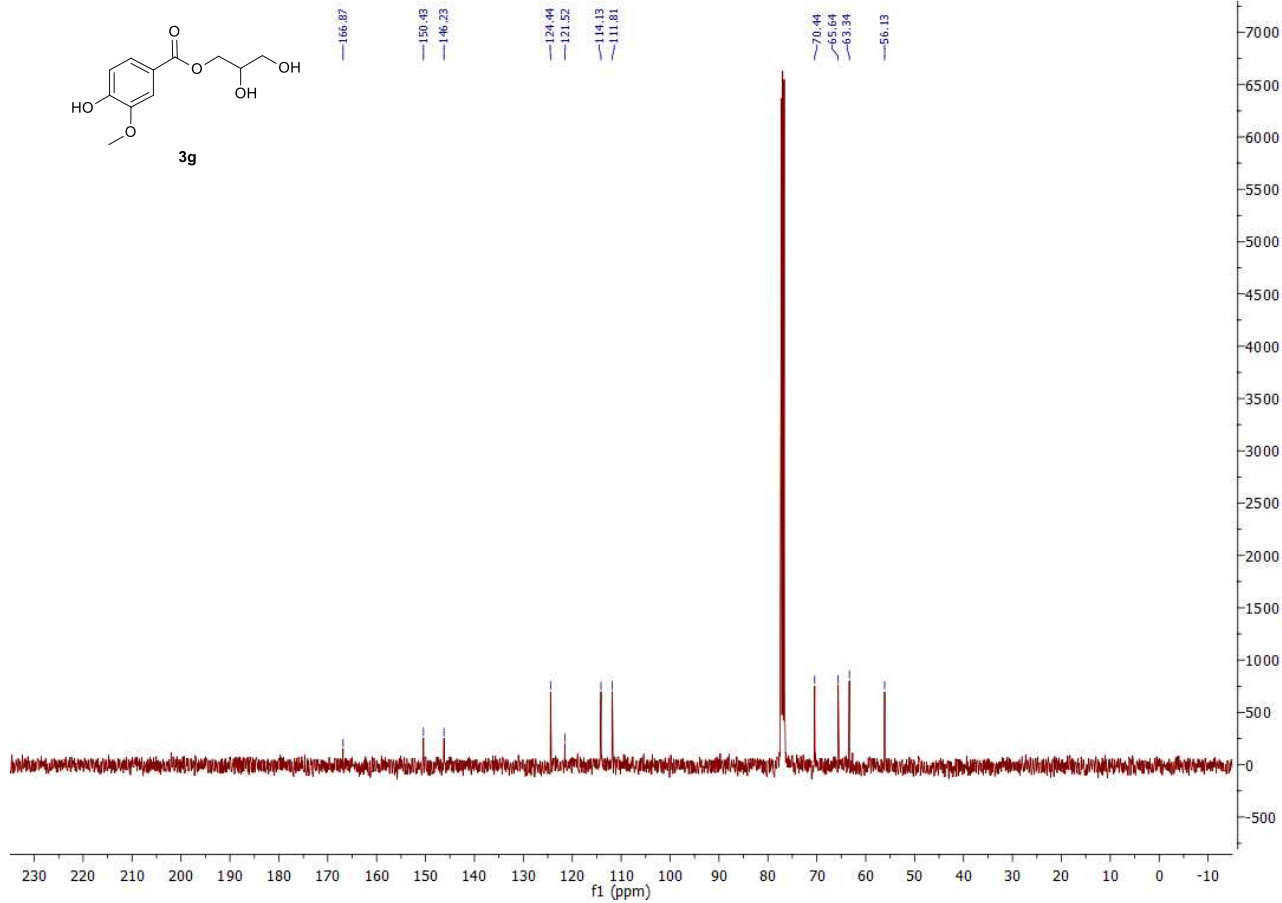
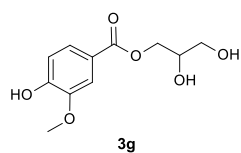
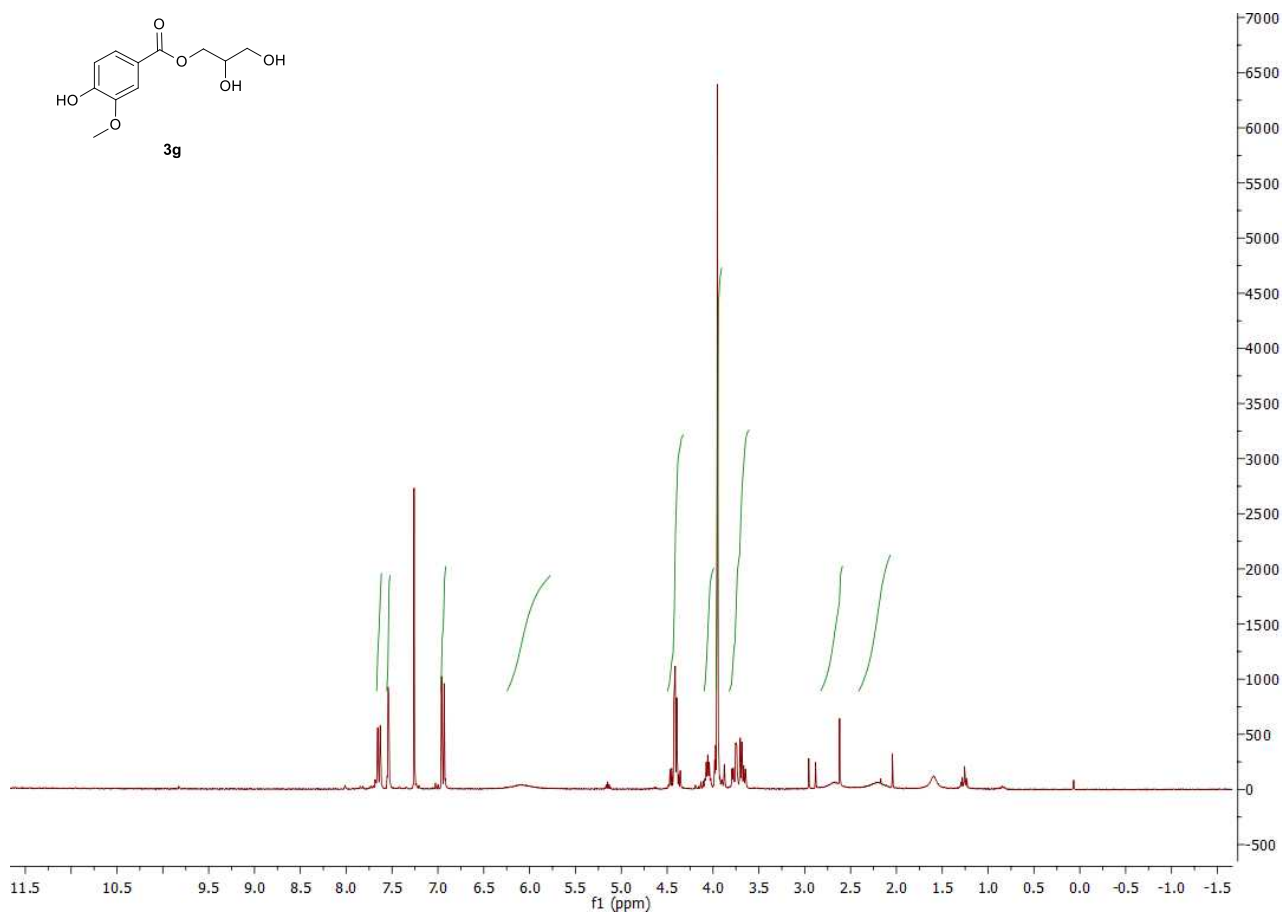
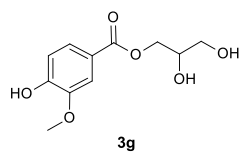
^1H (300 MHz) and ^{13}C (101 MHz) spectra (CDCl_3) of **3e**



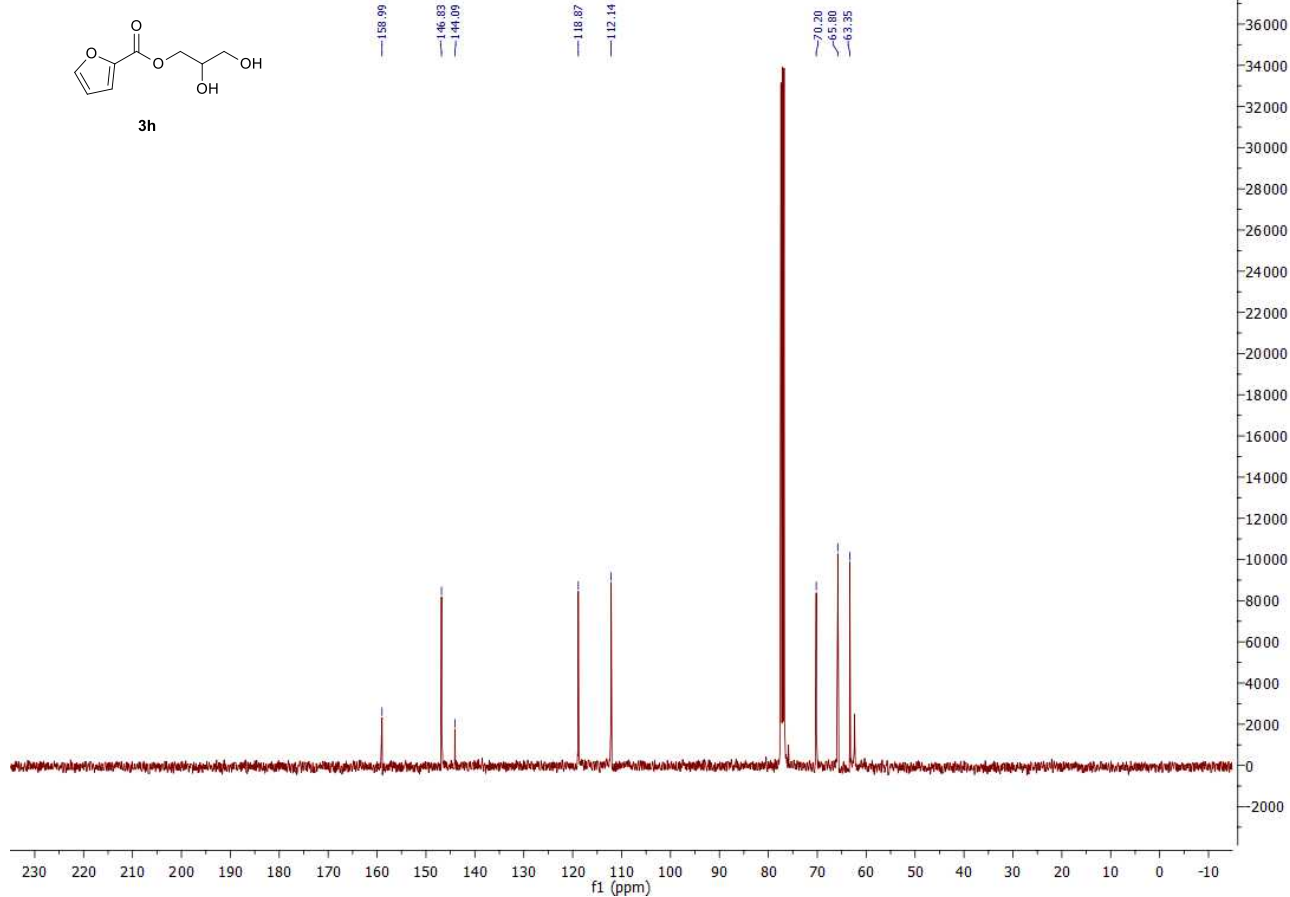
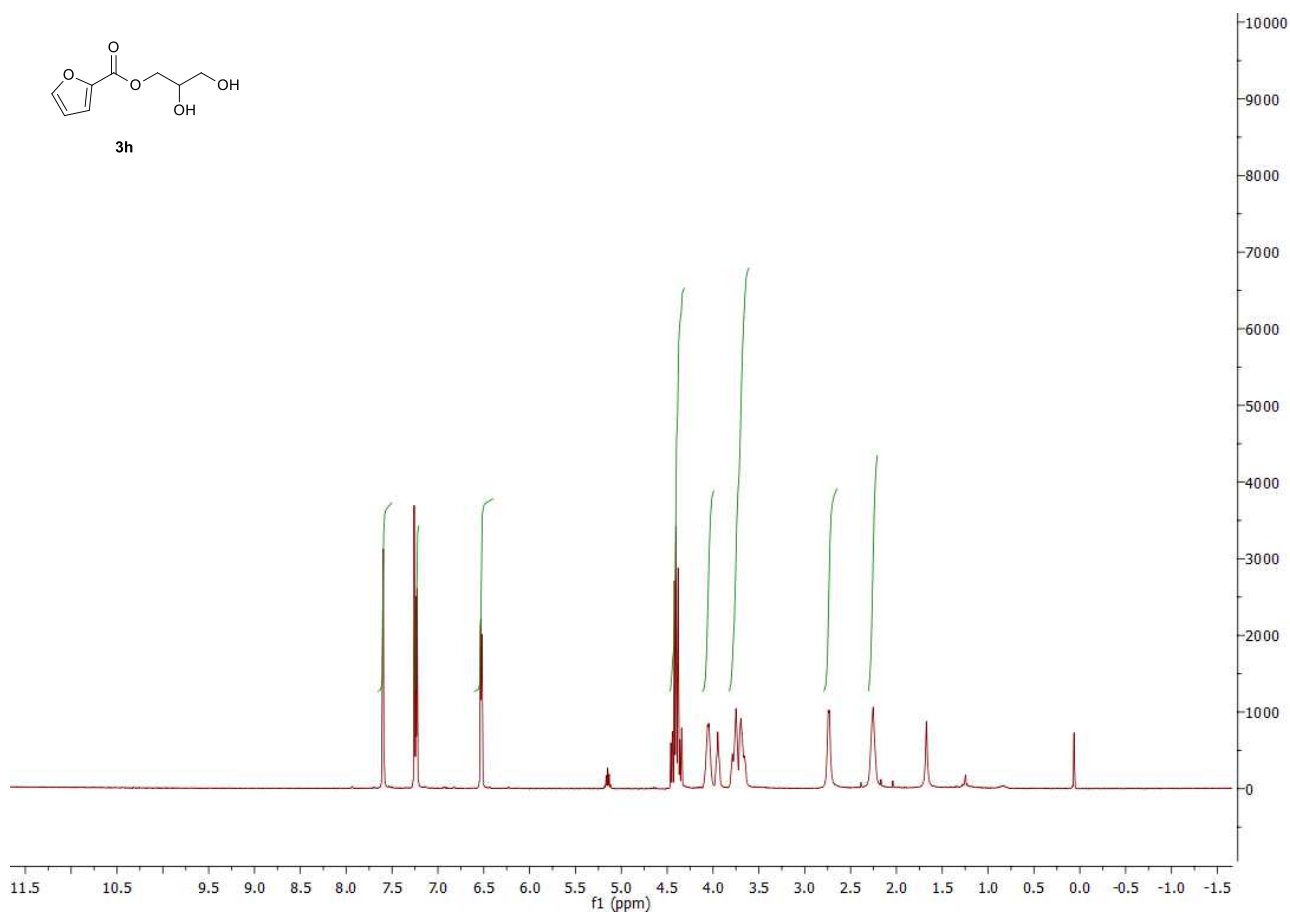
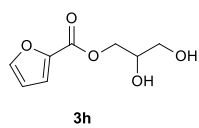
^1H (300 MHz) and ^{13}C (101 MHz) spectra (CDCl_3) of **3f**



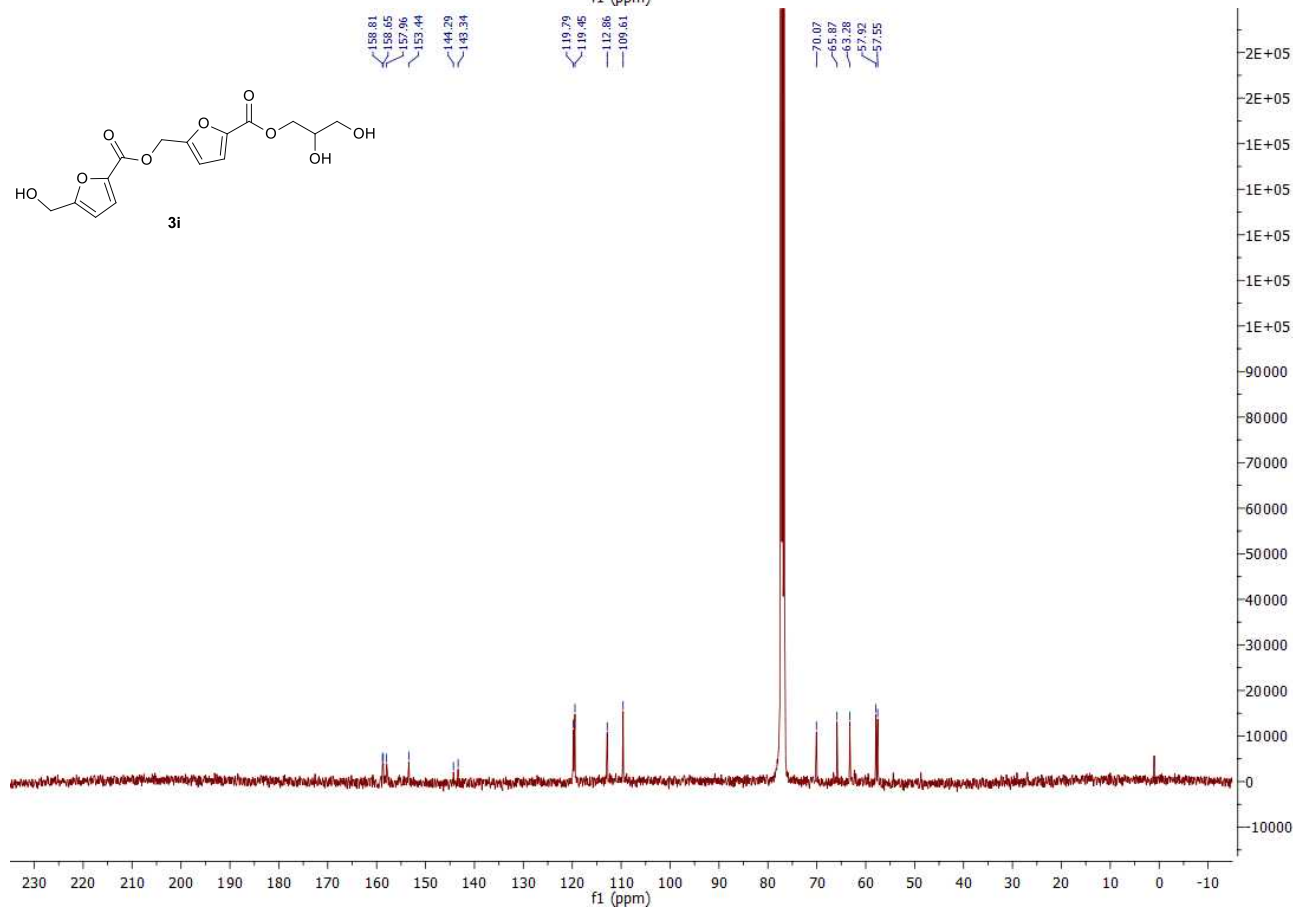
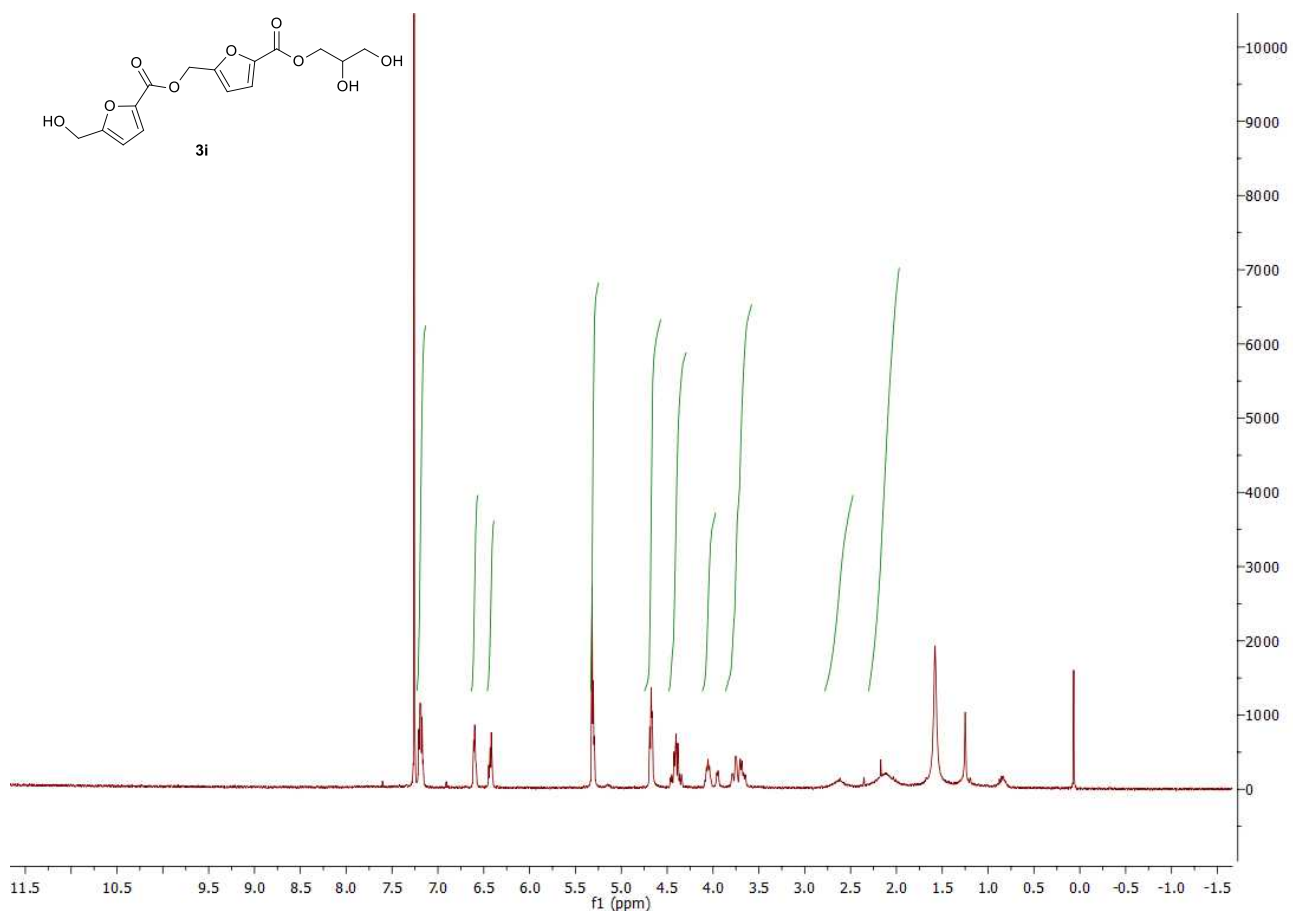
^1H (300 MHz) and ^{13}C (101 MHz) spectra (CDCl_3) of 3g



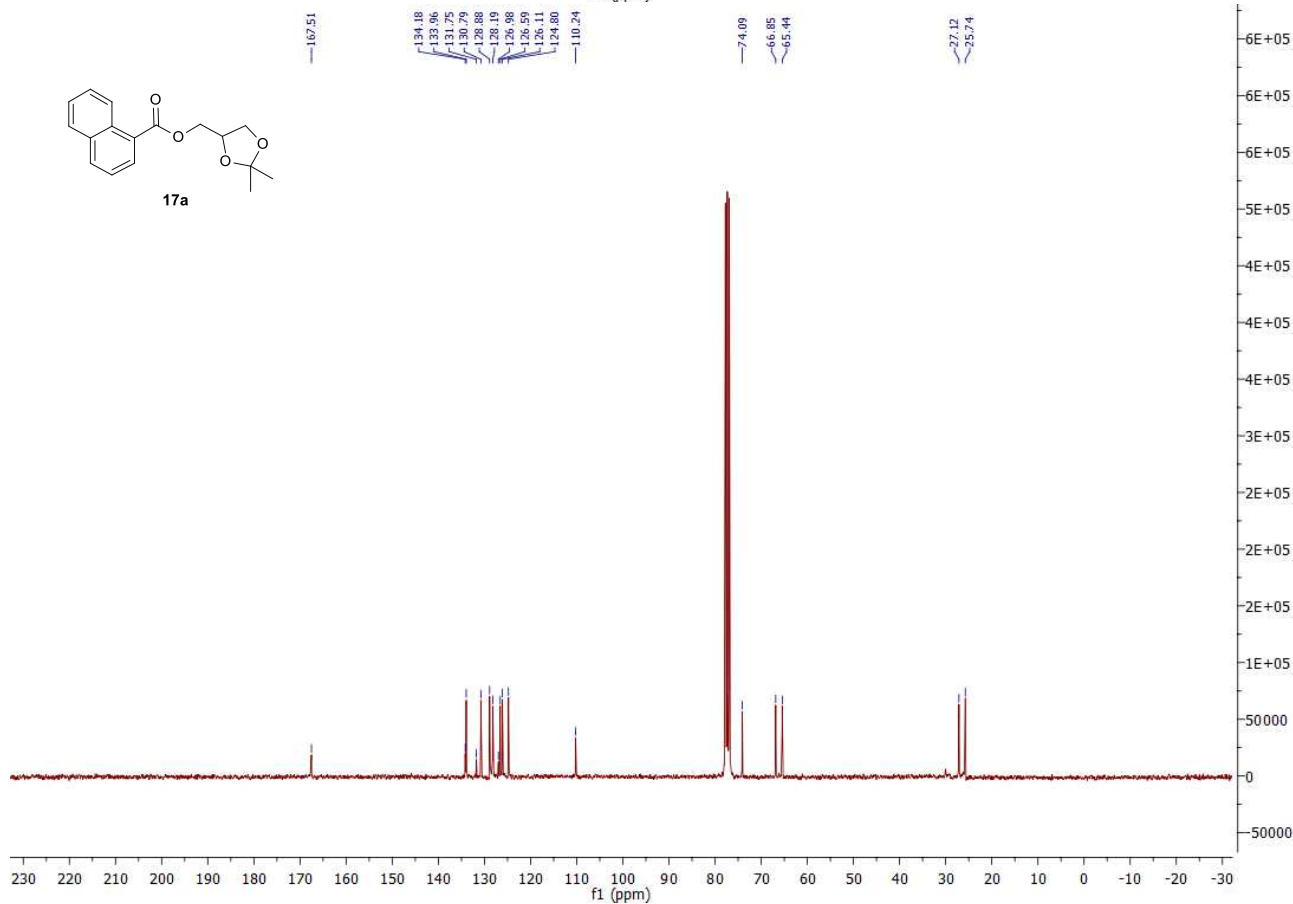
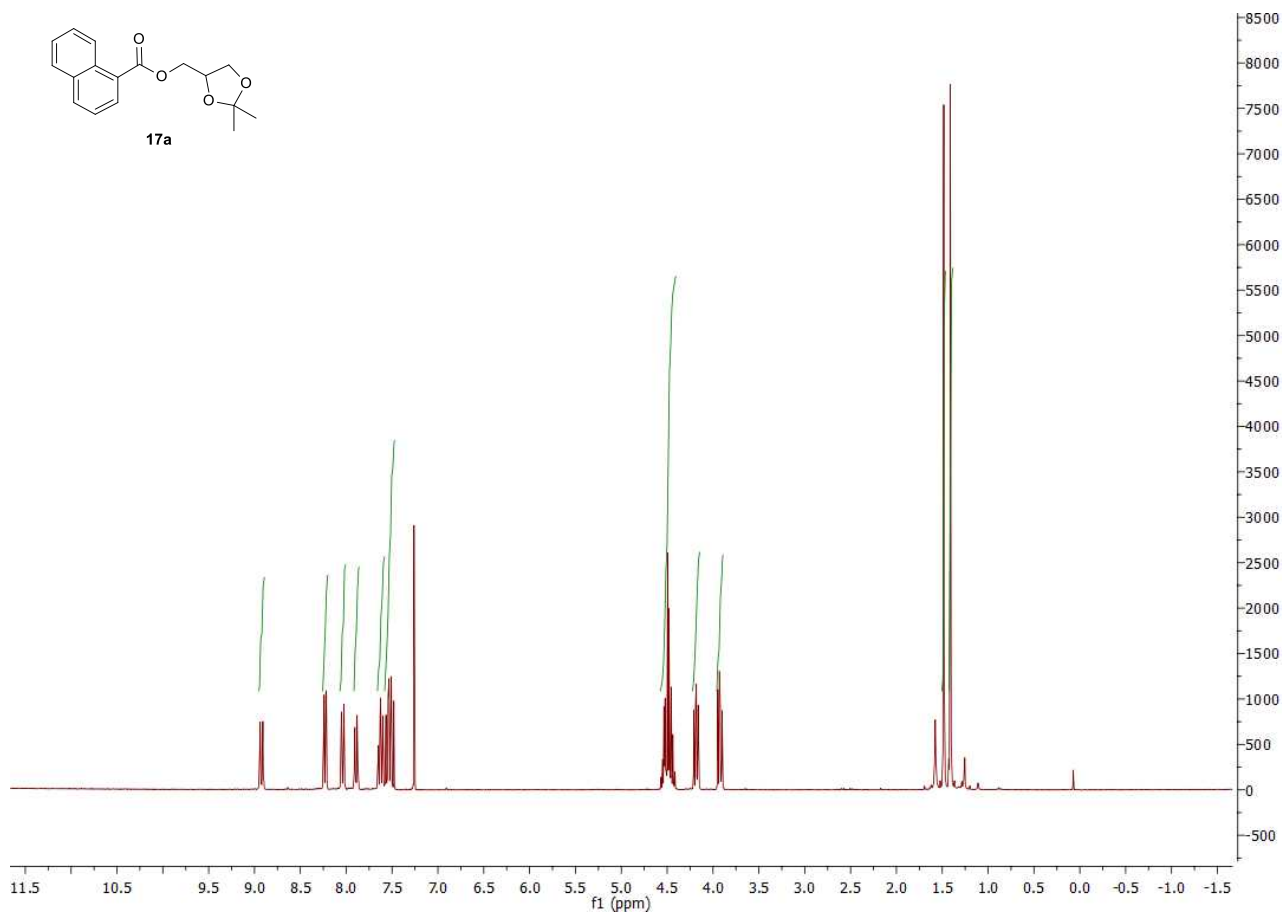
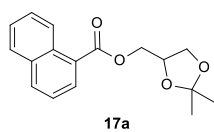
^1H (300 MHz) and ^{13}C (101 MHz) spectra (CDCl_3) of **3h**



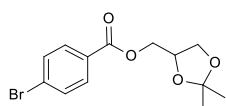
^1H (300 MHz) and ^{13}C (101 MHz) spectra (CDCl_3) of **3i**



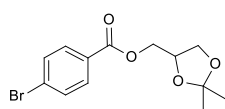
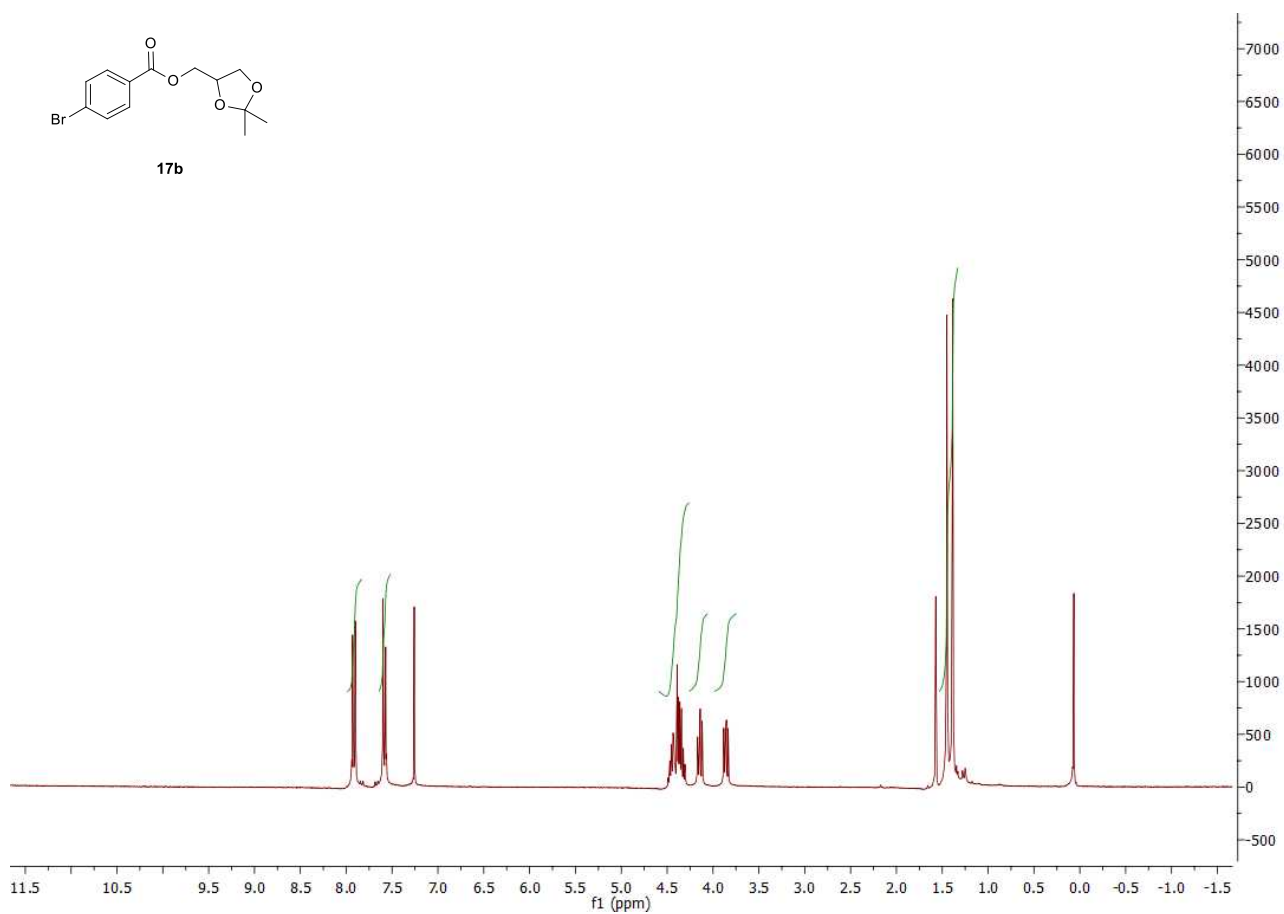
^1H (300 MHz) and ^{13}C (101 MHz) spectra (CDCl_3) of 17a



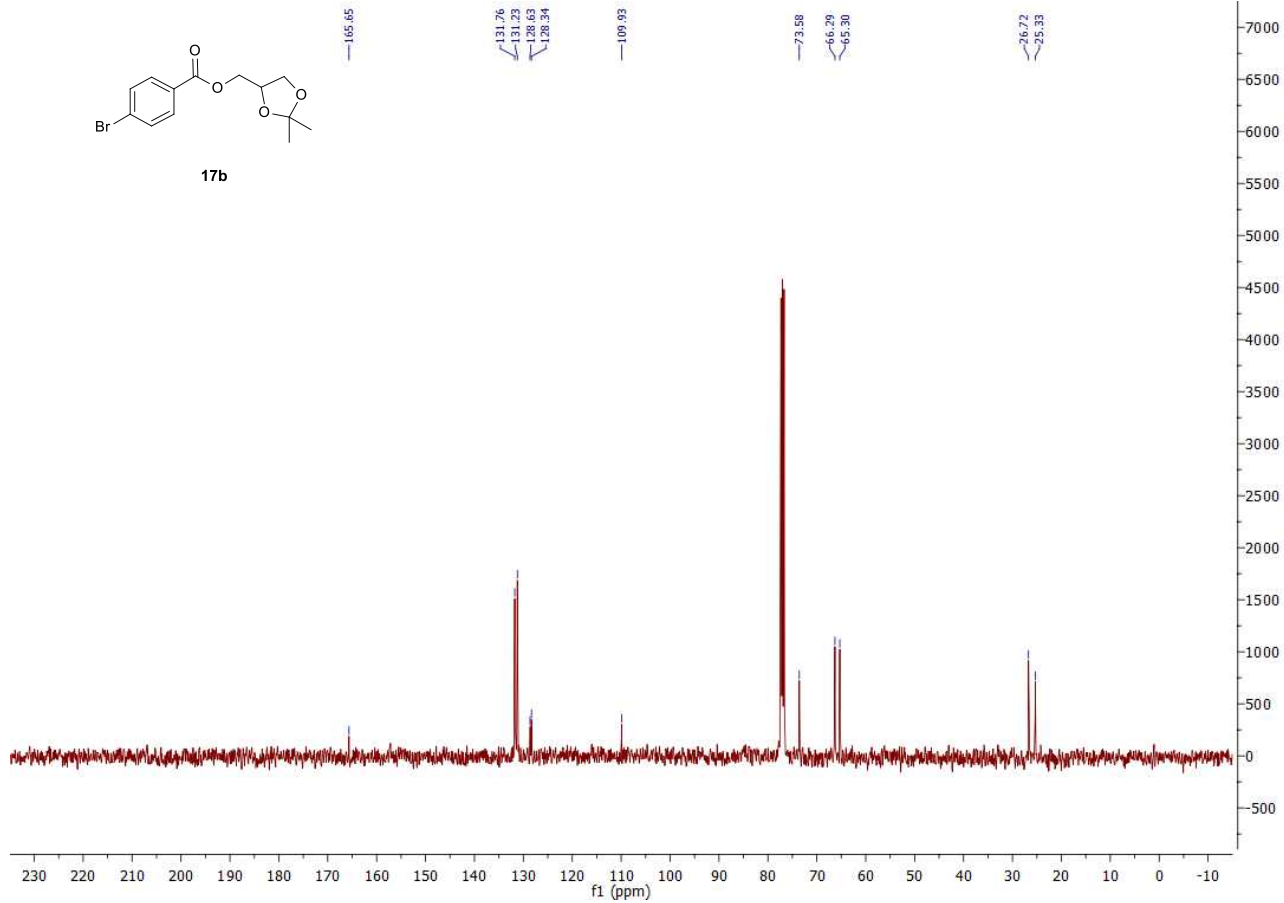
^1H (300 MHz) and ^{13}C (101 MHz) spectra (CDCl_3) of 17b



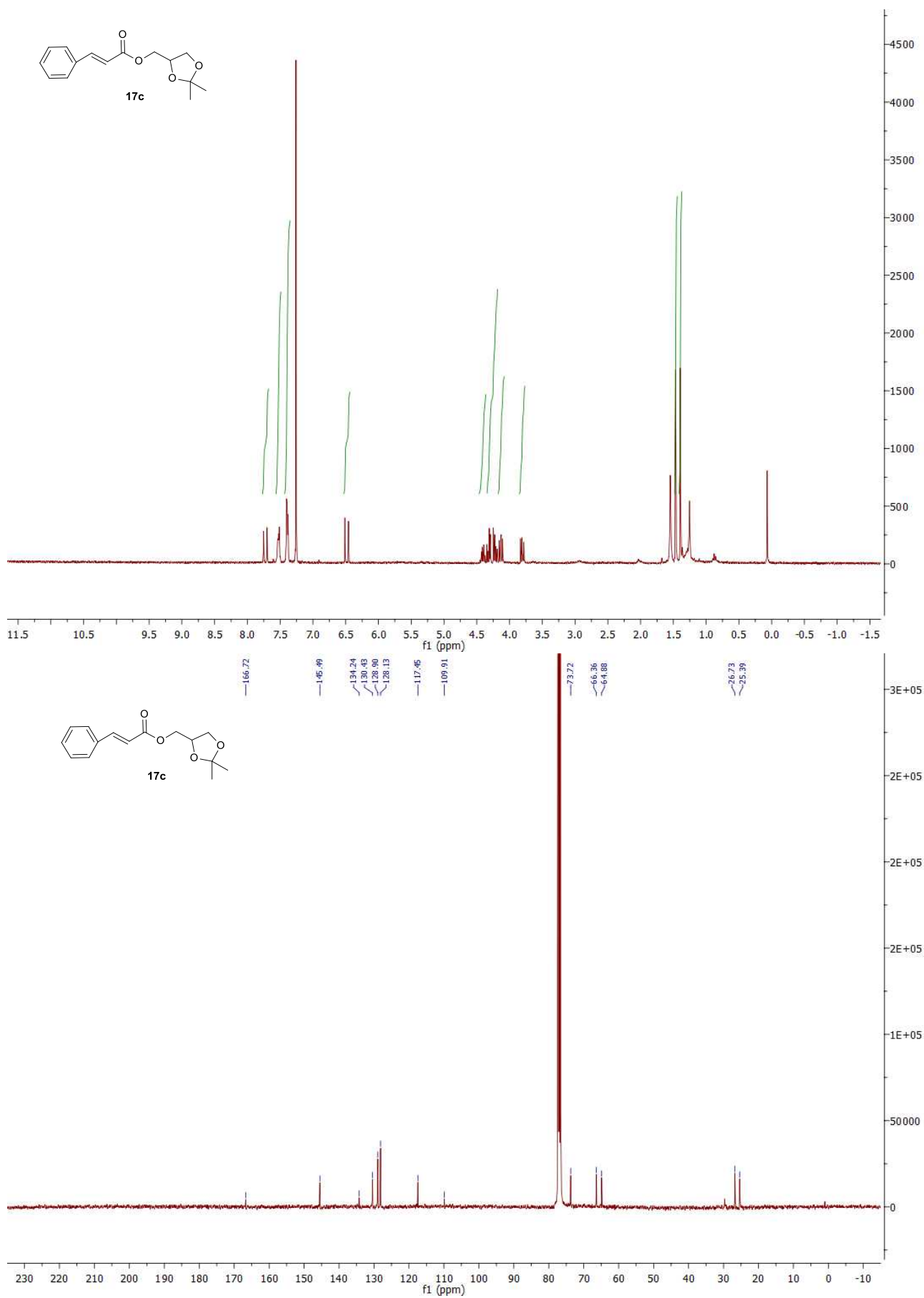
17b



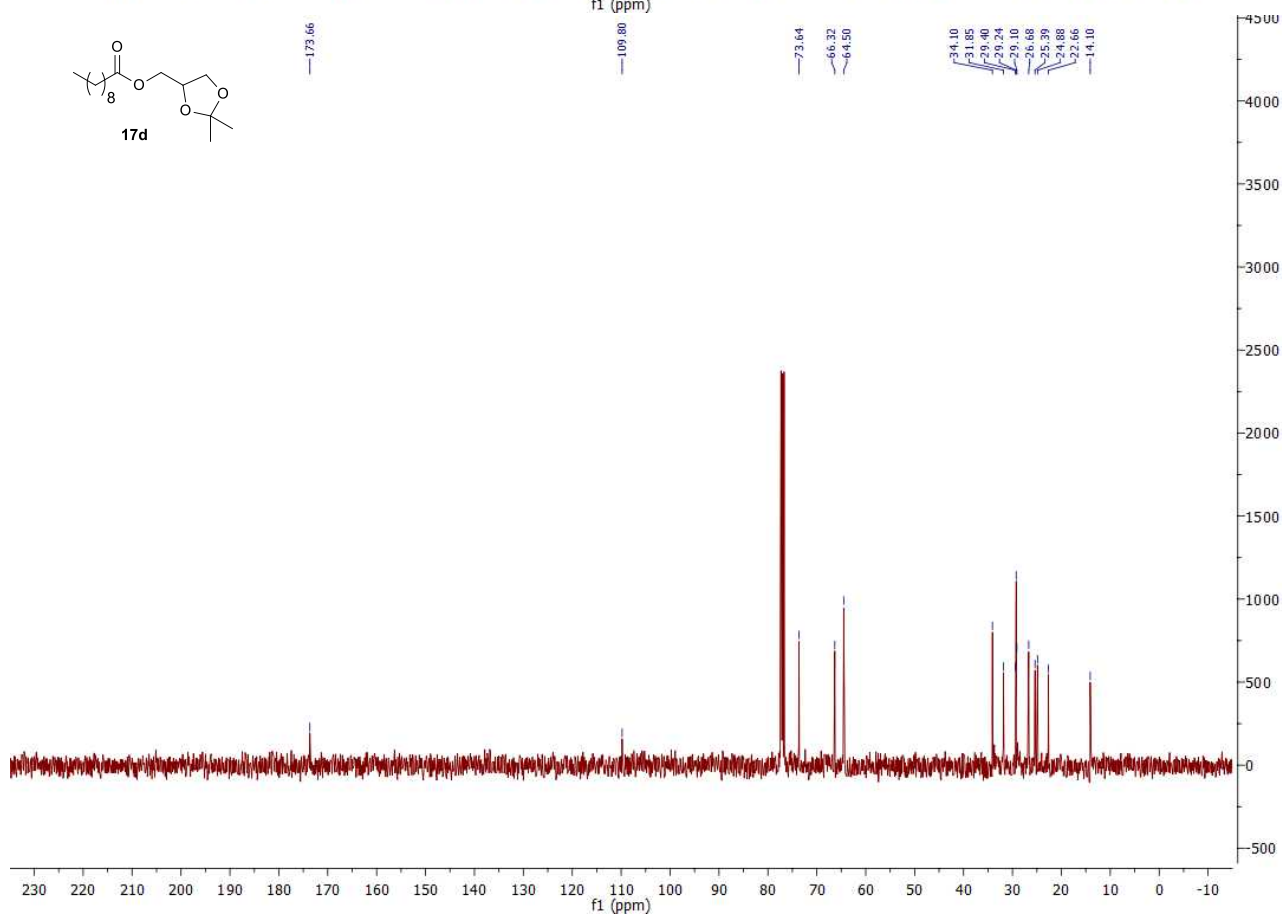
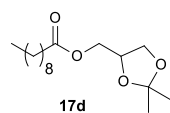
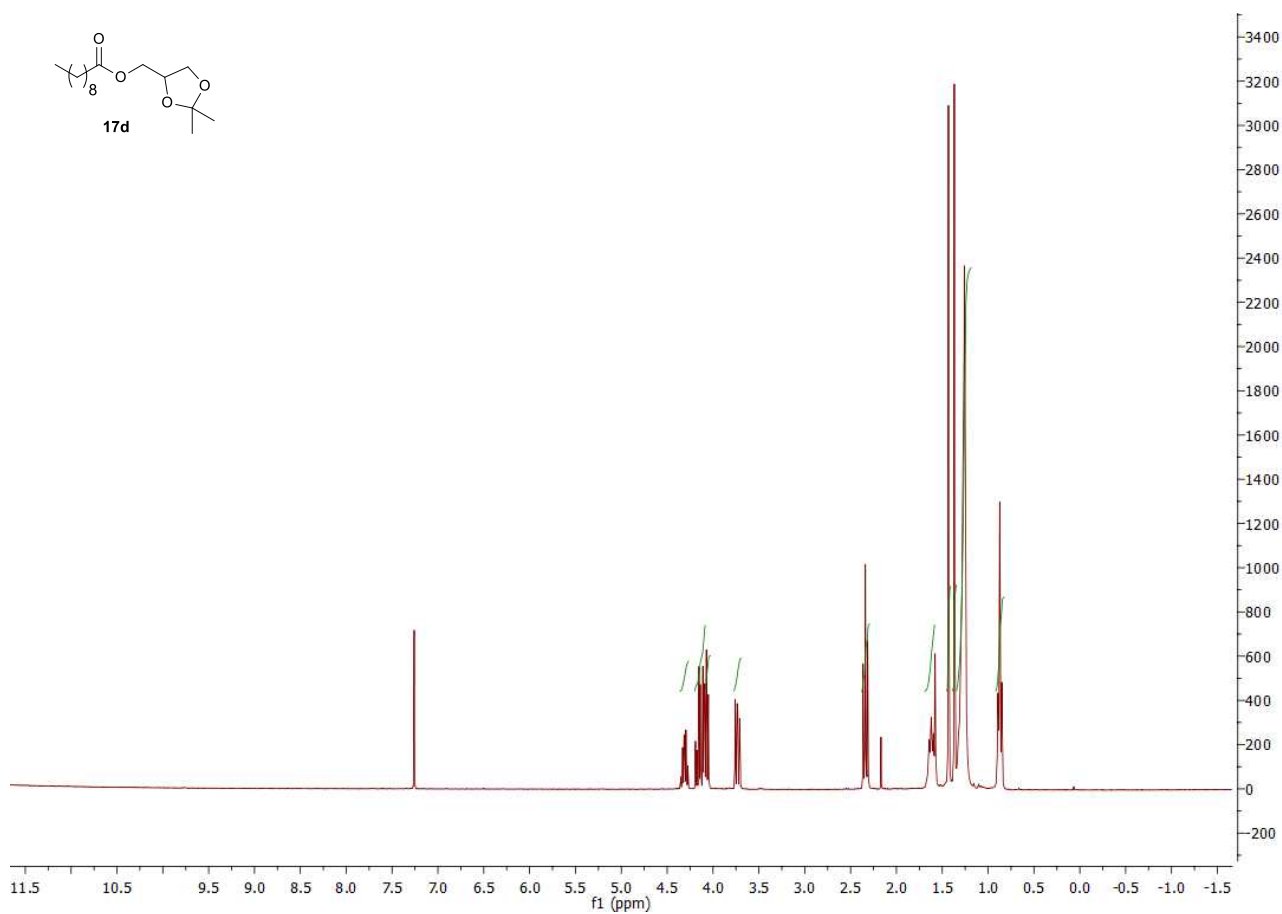
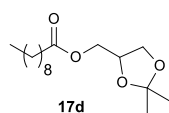
17b



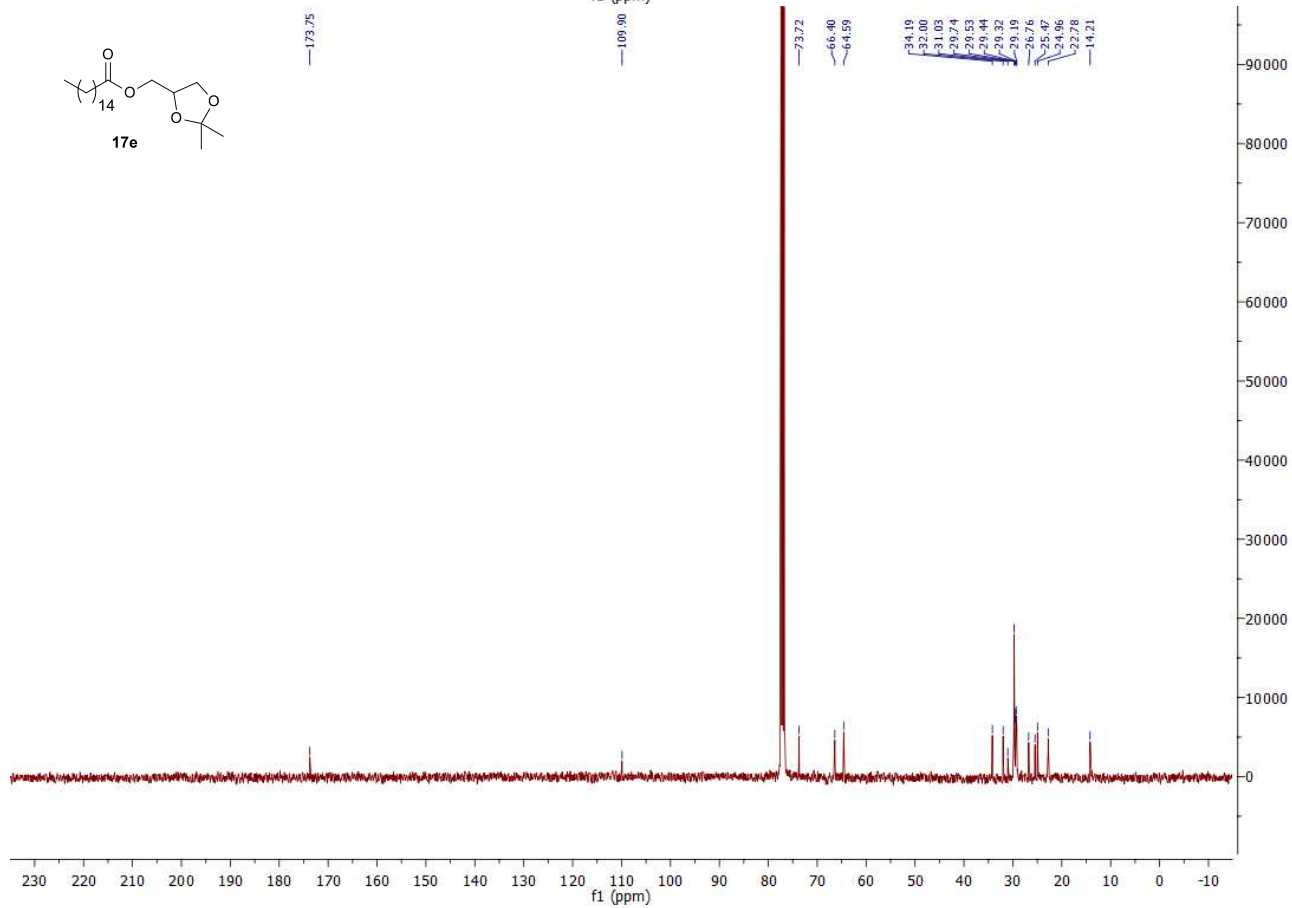
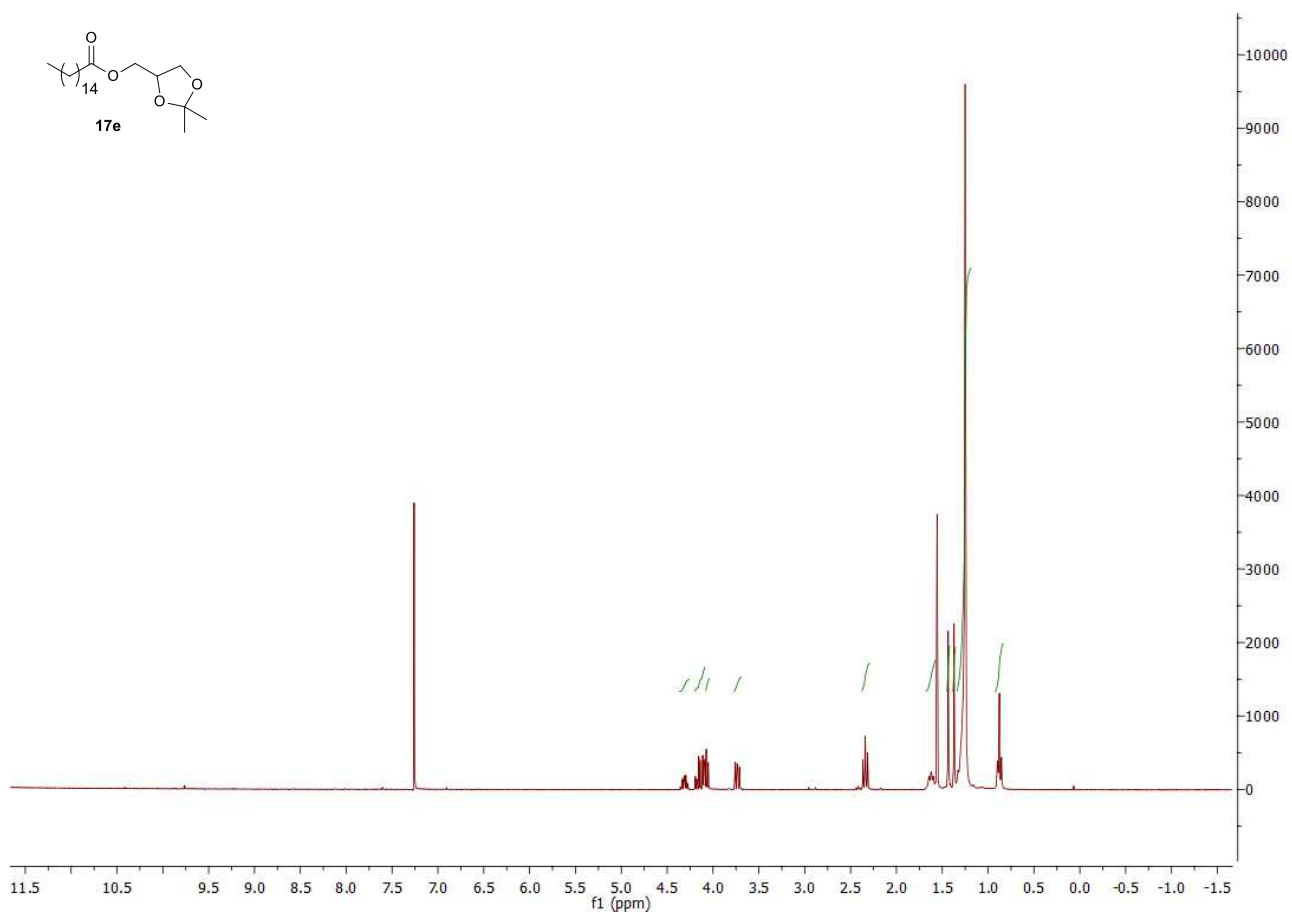
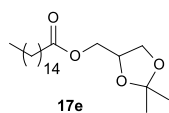
^1H (300 MHz) and ^{13}C (101 MHz) spectra (CDCl_3) of 17c



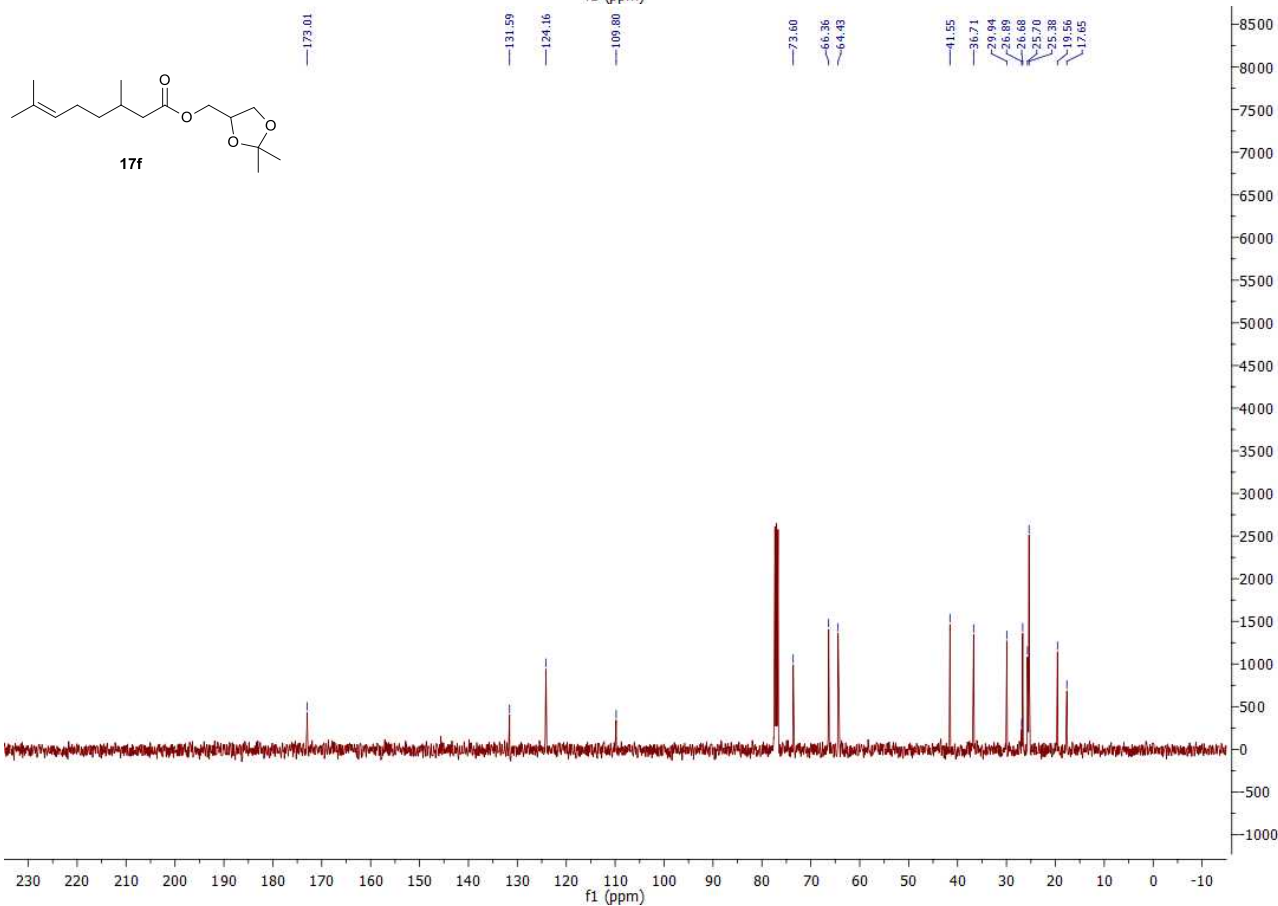
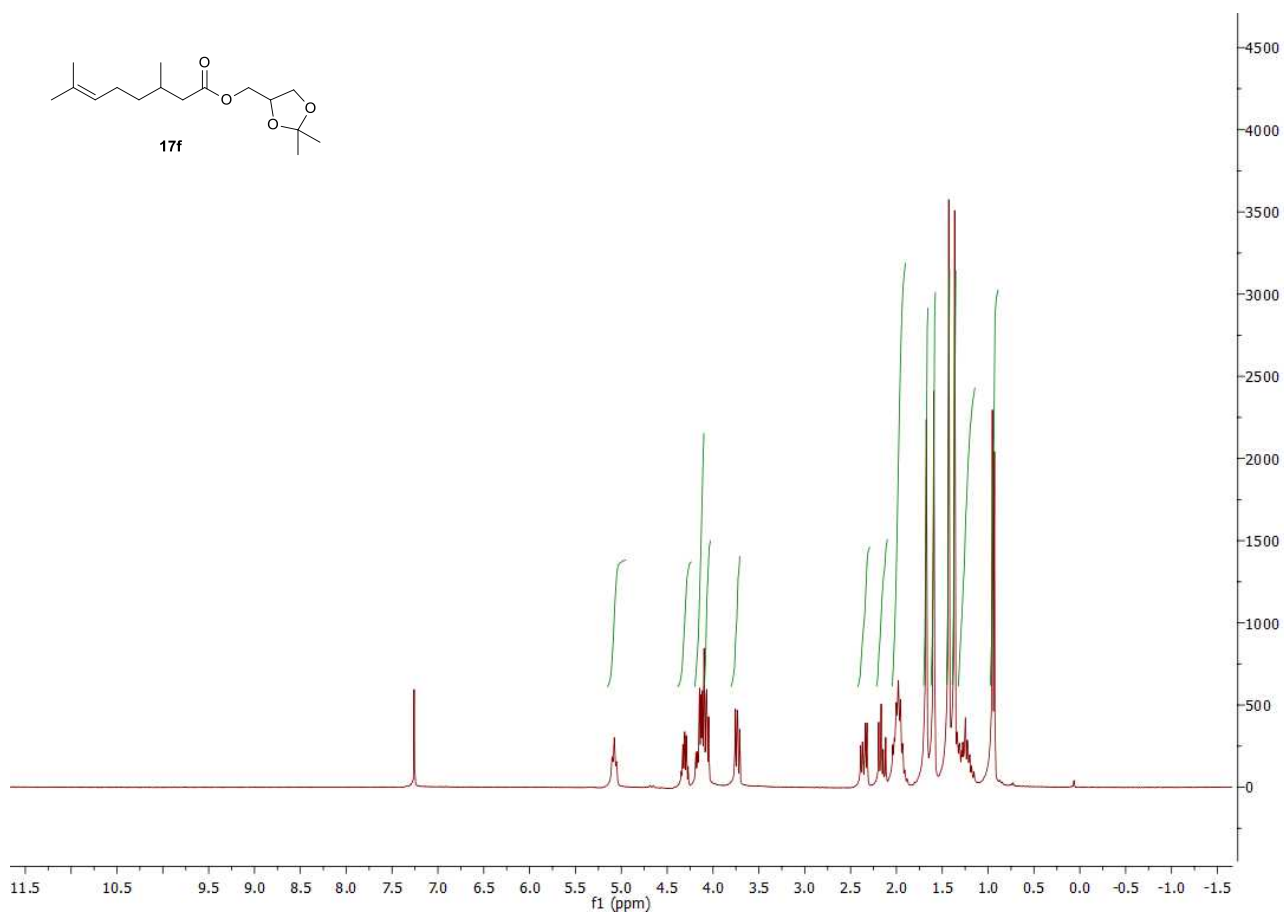
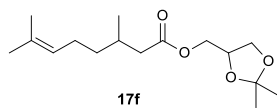
^1H (300 MHz) and ^{13}C (101 MHz) spectra (CDCl_3) of 17d



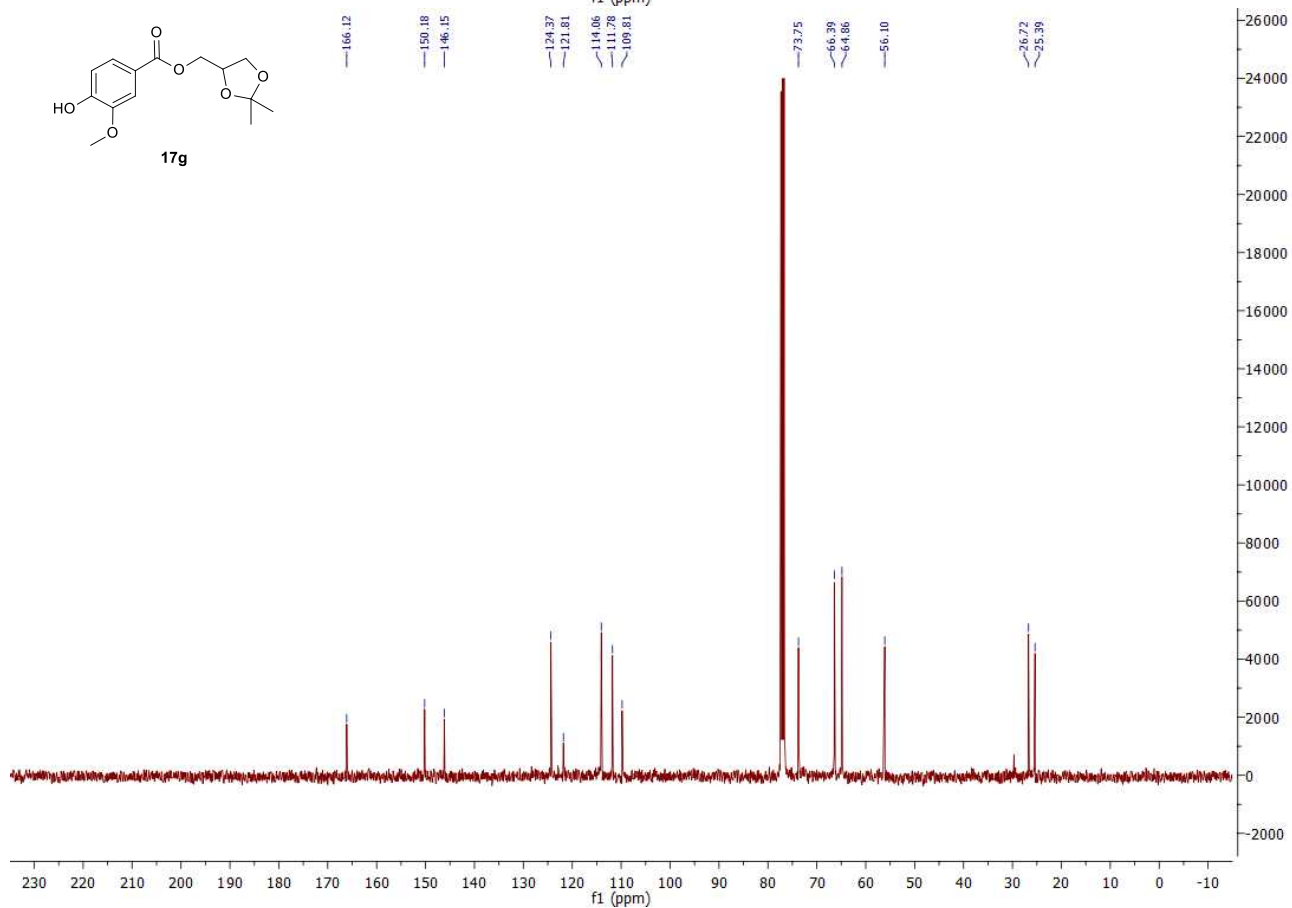
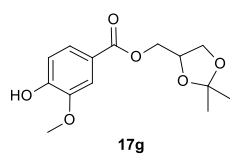
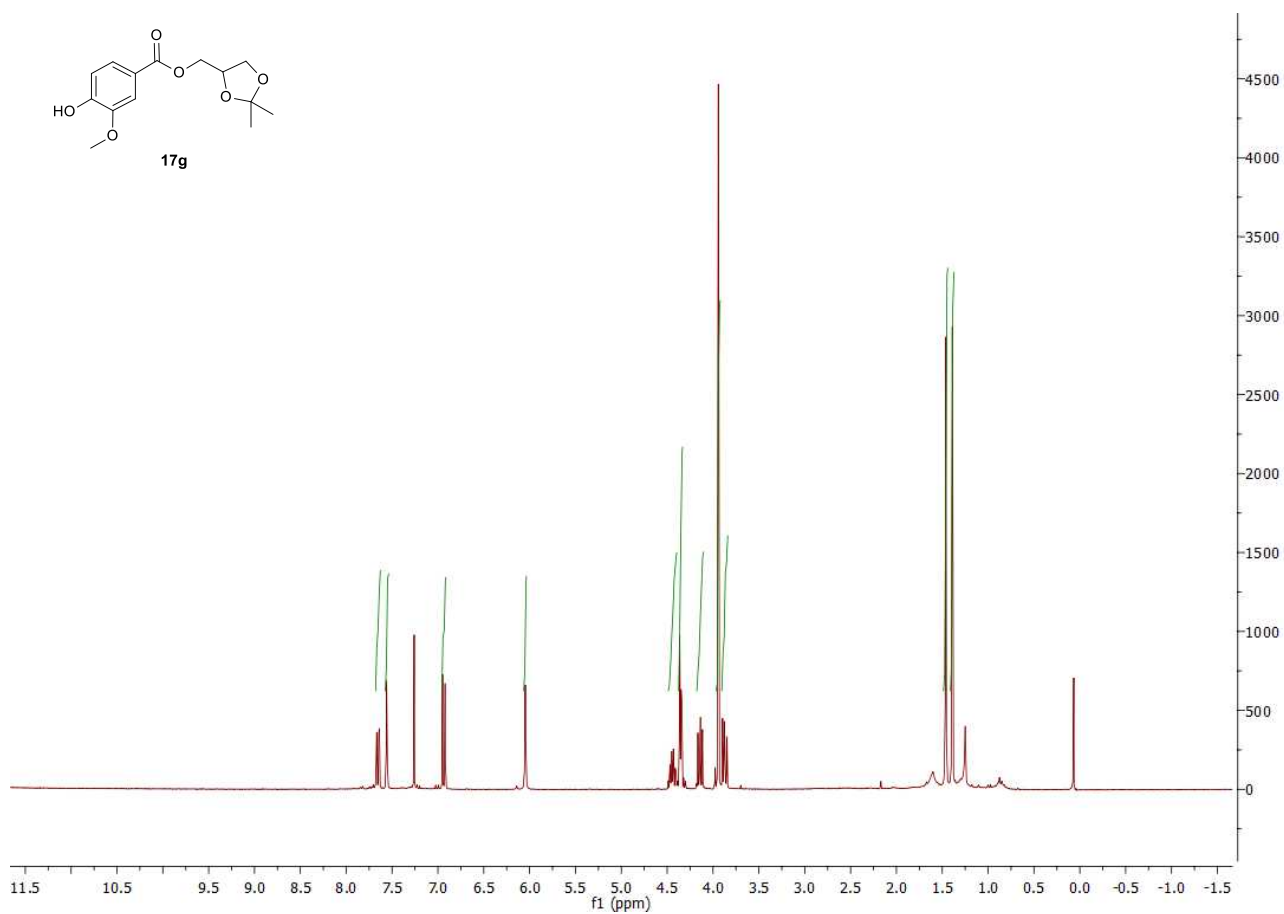
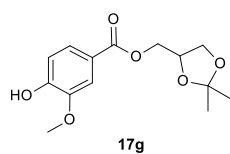
^1H (300 MHz) and ^{13}C (101 MHz) spectra (CDCl_3) of 17e



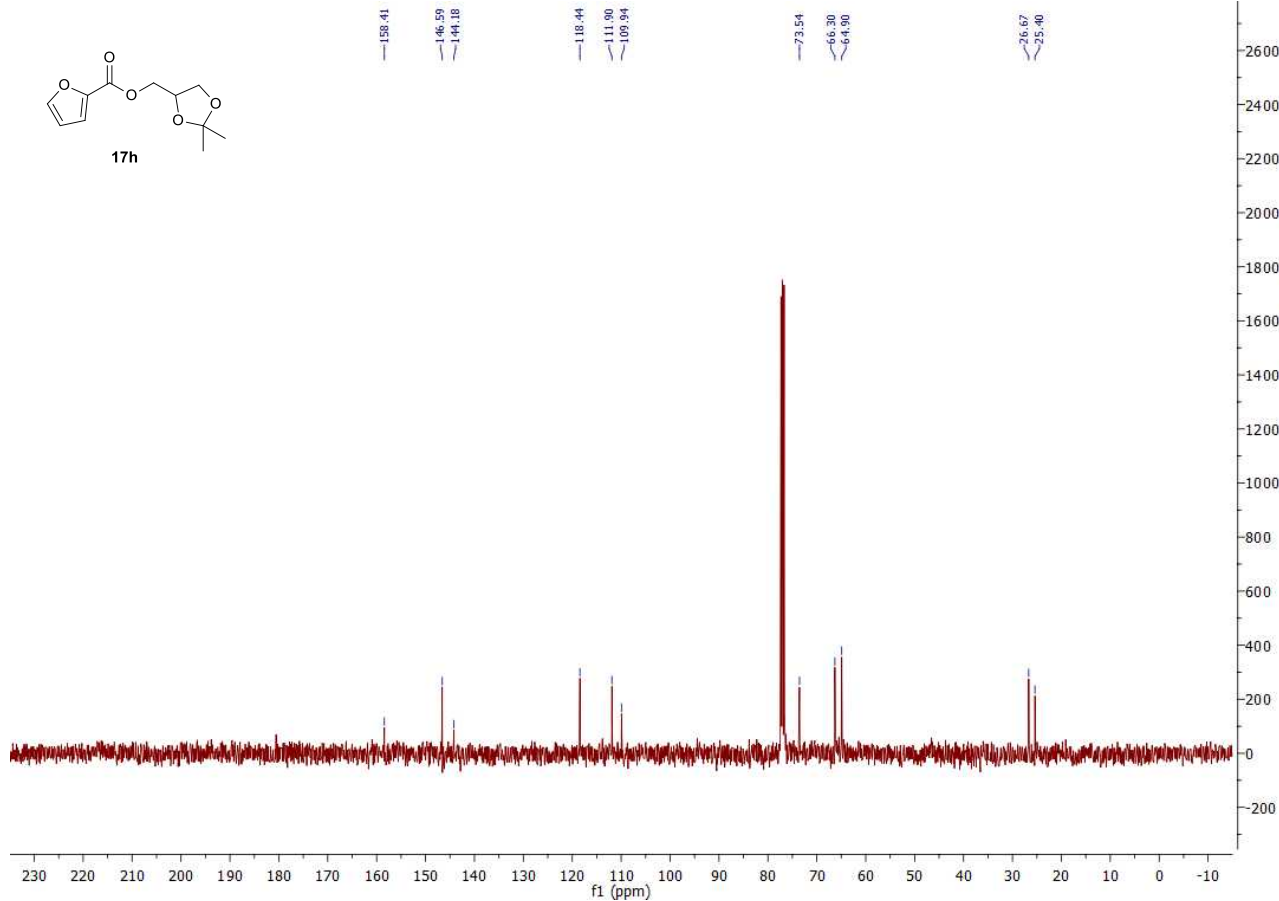
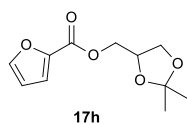
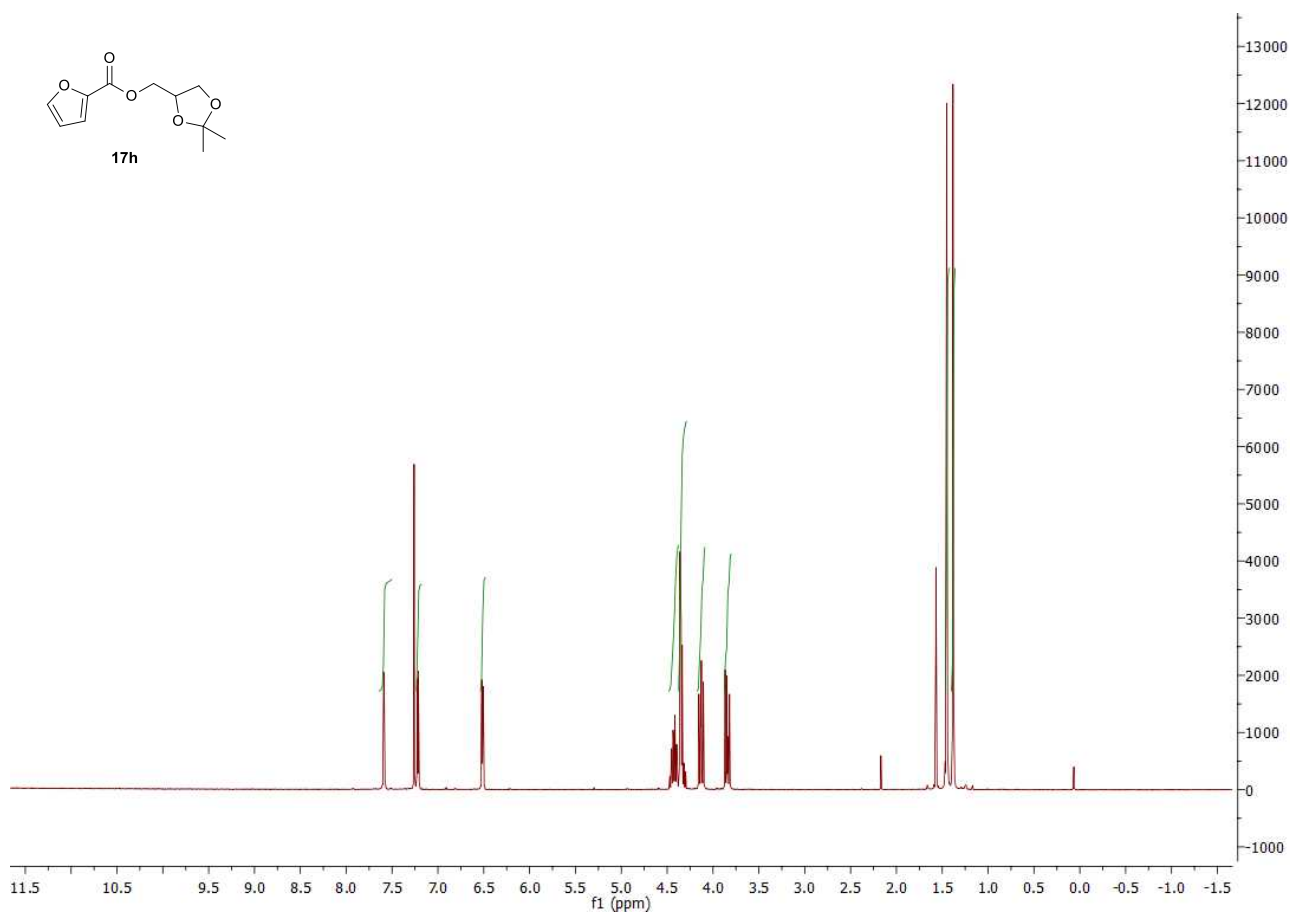
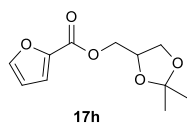
^1H (300 MHz) and ^{13}C (101 MHz) spectra (CDCl_3) of 17f



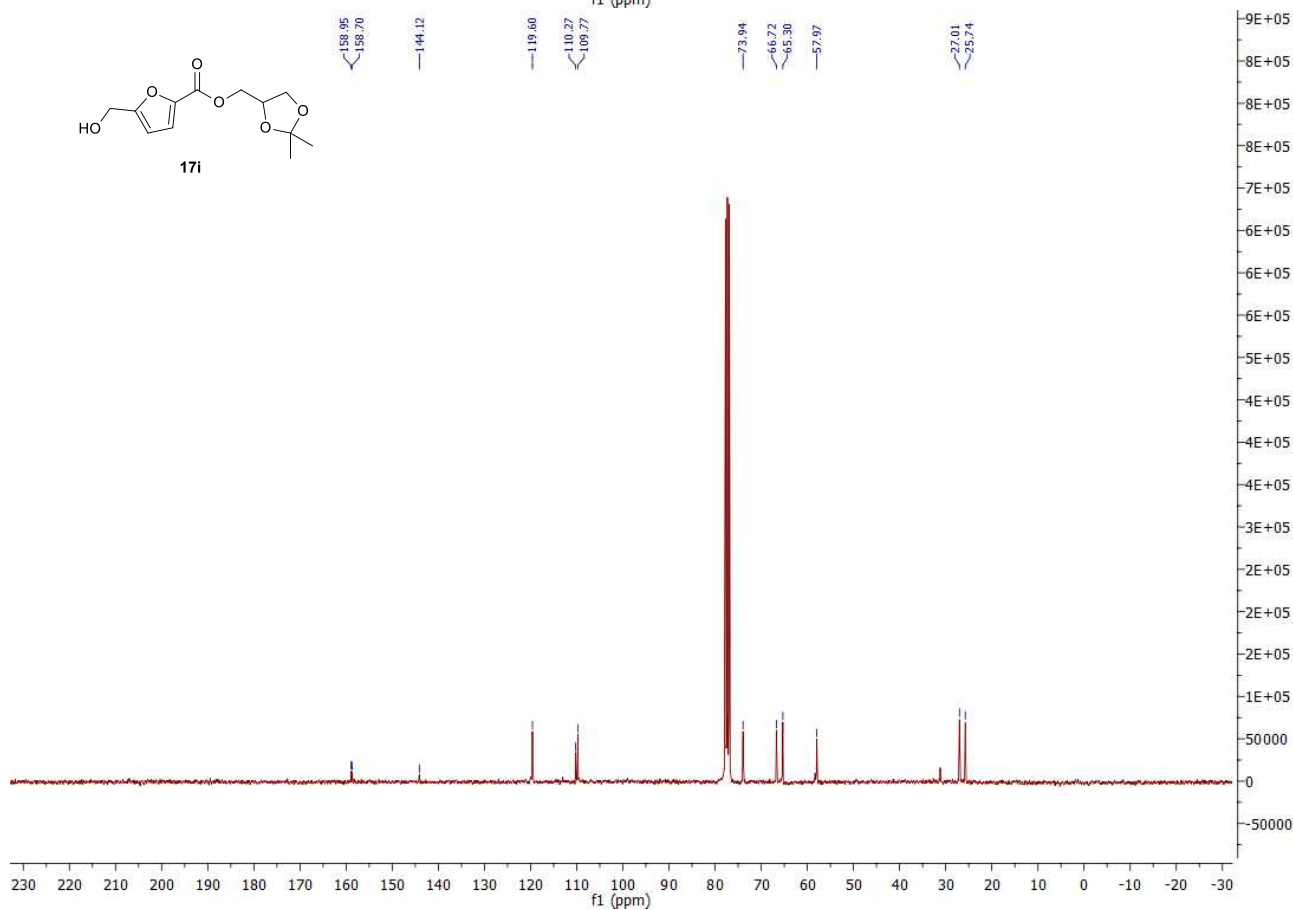
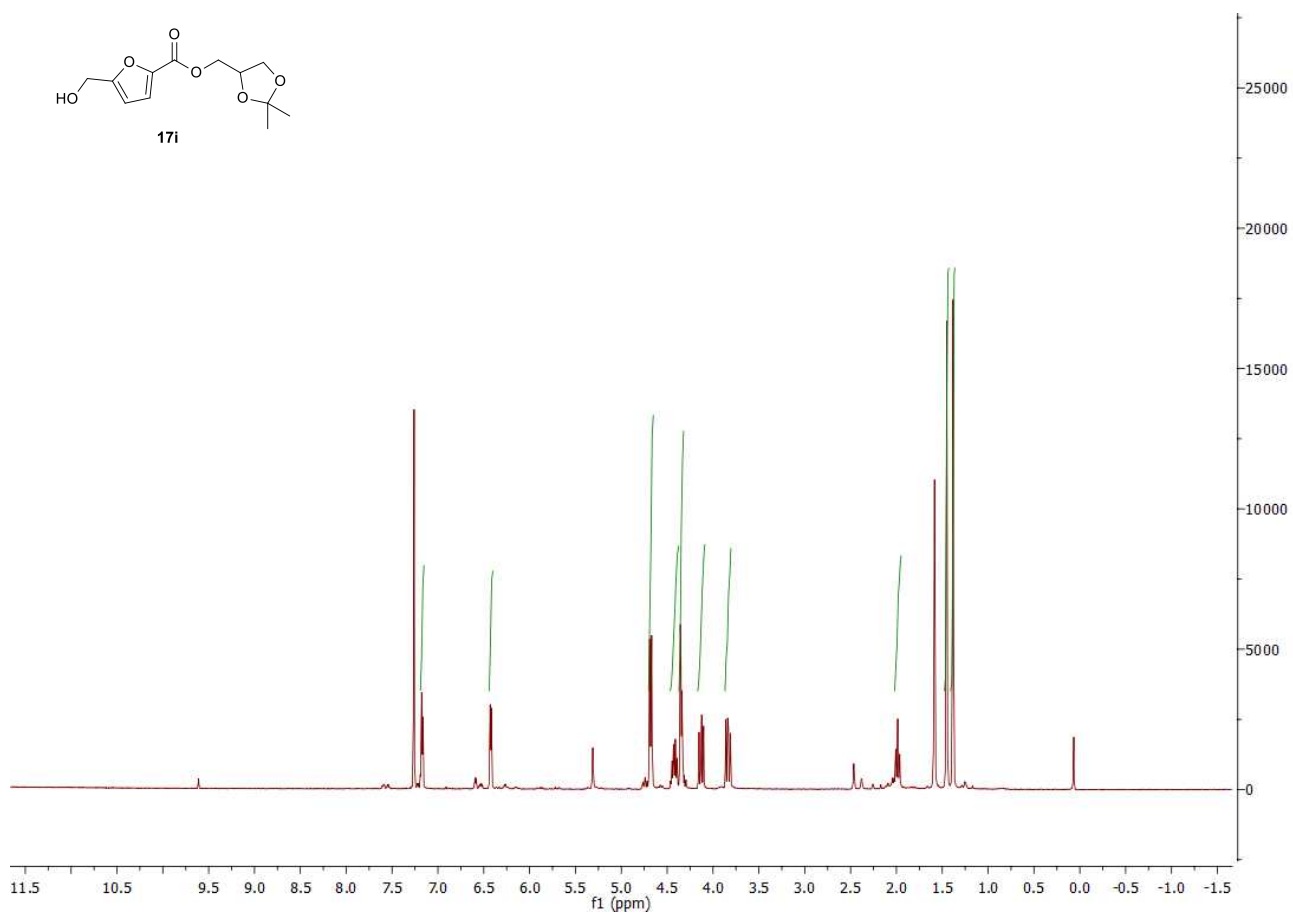
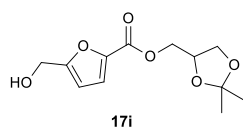
^1H (300 MHz) and ^{13}C (101 MHz) spectra (CDCl_3) of 17g



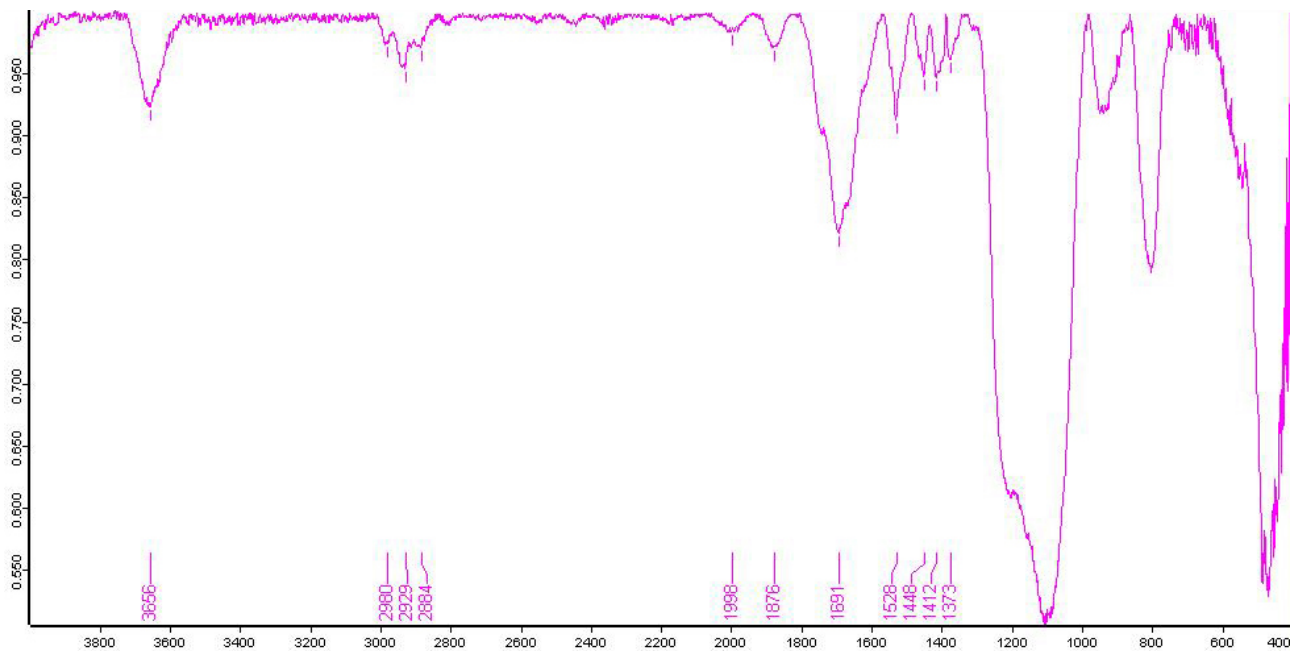
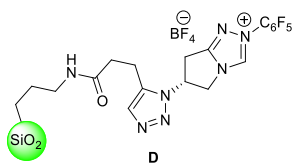
^1H (300 MHz) and ^{13}C (101 MHz) spectra (CDCl_3) of 17h



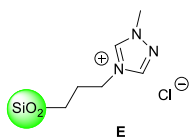
^1H (300 MHz) and ^{13}C (101 MHz) spectra (CDCl_3) of 17i



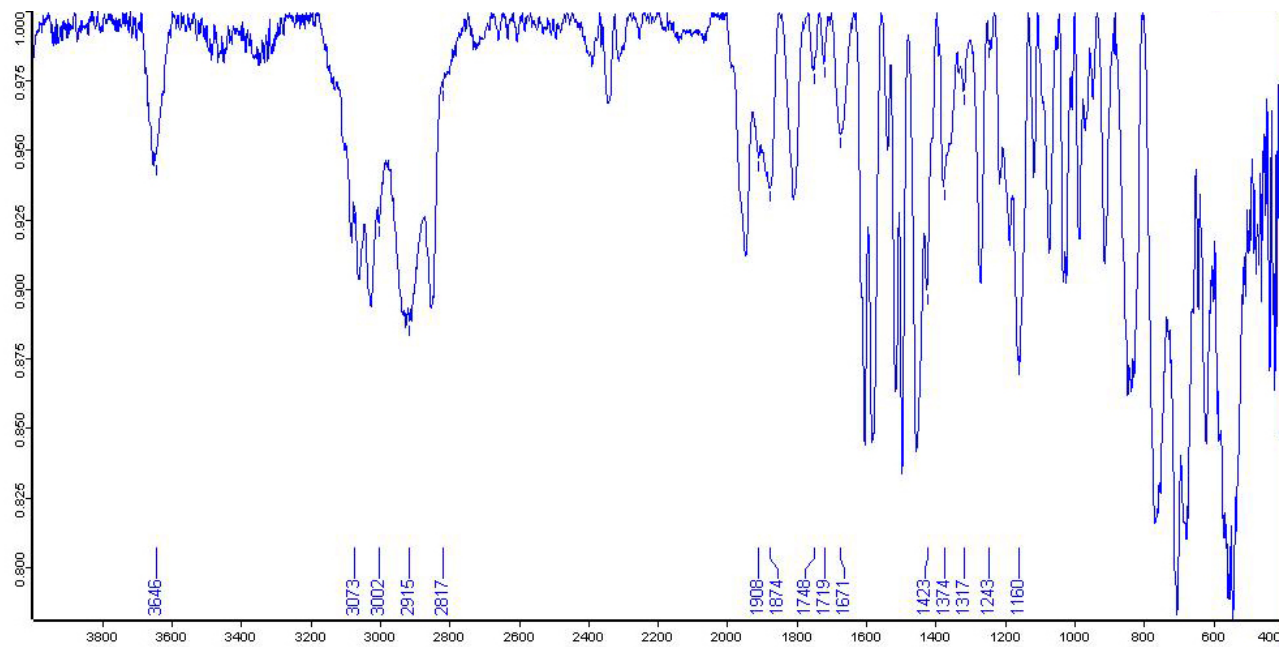
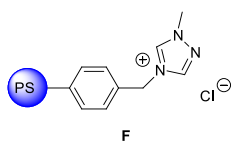
FT-IR spectra of pre-catalyst D



FT-IR spectra of pre-catalyst E

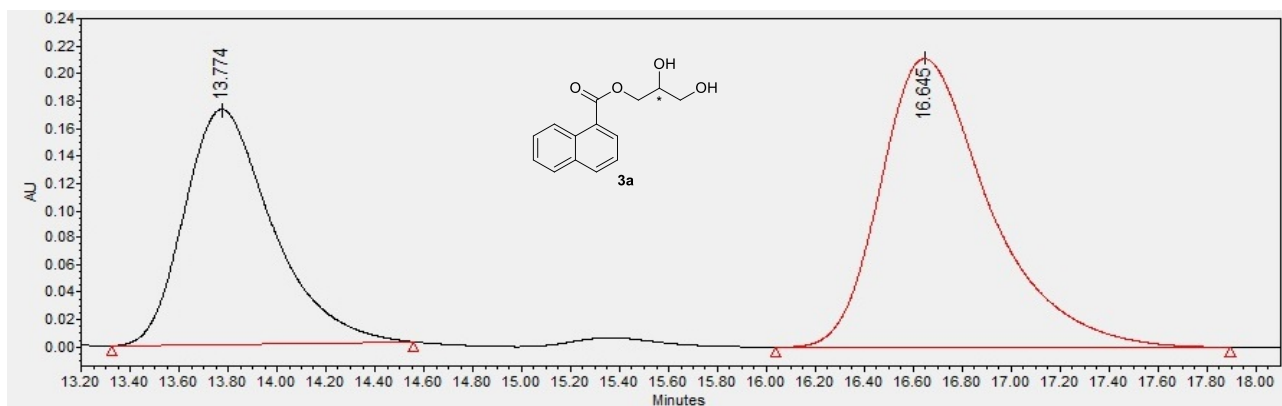


FT-IR spectra of pre-catalyst F

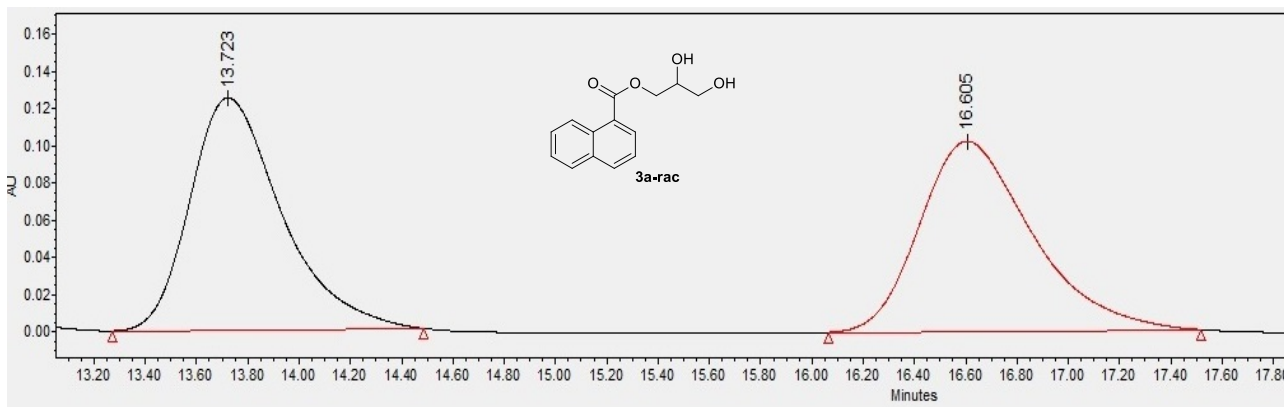


HPLC chromatograms of **3a** (Table 2, entry 2)

Enantiomeric excess (ee) of **3a** was evaluated by HPLC: 21% ee (Lux Cellulose 1 column, *n*-hexane/*i*-propanol = 85/15, flow rate 1.0 mL/min, $\lambda = 240$ nm); $t_r = 13.77$ and 16.65 min.



	Retention Time (min)	Area ($\mu\text{V}\cdot\text{sec}$)	Name	% Area	Height (μV)
1	13.774	4290198		39.59	172181
2	16.645	6545906		60.41	211157



	Name	Retention Time (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)
1		13.723	3097920	49.90	124714
2		16.605	3110433	50.10	102148