Electronic Supplementary Information for

Discovery of lanthanide metal oxide catalyst for transesterification reaction by fluorescence-based high-throughput screening method and application to biodiesel production

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1. General information

All chemical reagents were purchased from commercial sources (Sigma-Aldrich, Alfa Aesar, Tokyo Chemical Industry, Duksan Pure Chemicals, Daejung Chemicals & Metals, and Samchun Pure Chemical) and used as received without further purification. Nuclear magnetic resonance (NMR) spectra were obtained using a JEOL 400 MHz NMR spectrometer (JEOL, Tokyo, Japan). The high-resolution mass spectrum was recorded on an Agilent 6200 quadrupole time-of-flight mass spectrometer (Agilent Technologies, Santa Clara, CA, USA). Fluorescence spectra were obtained using an Agilent Cary Eclipse fluorescence spectrophotometer (Agilent Technologies).

2. Synthesis and characterization of pyrene excimer probe, Bis(4-(1-pyrenyl)butyl) maleate (BPBM)

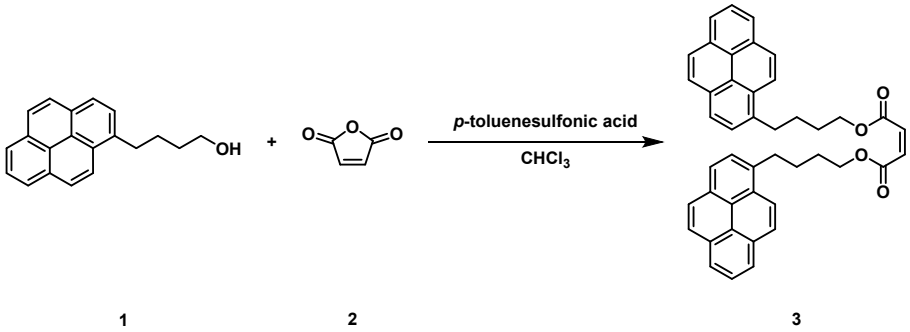

Figure S1. Synthesis of pyrene excimer fluorescent probe, bis(4-(1-pyrenyl)butyl) maleate (**BPBM**).

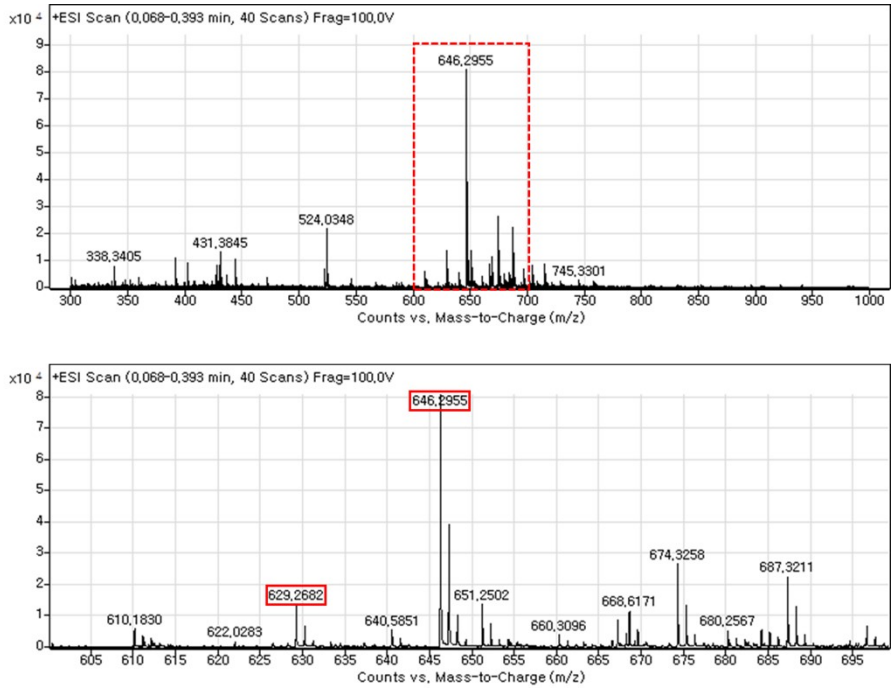

Figure S2. HRMS of bis(4-(1-pyrenyl)butyl) maleate (**BPBM**)

3. Characterization of selected metal oxide catalyst

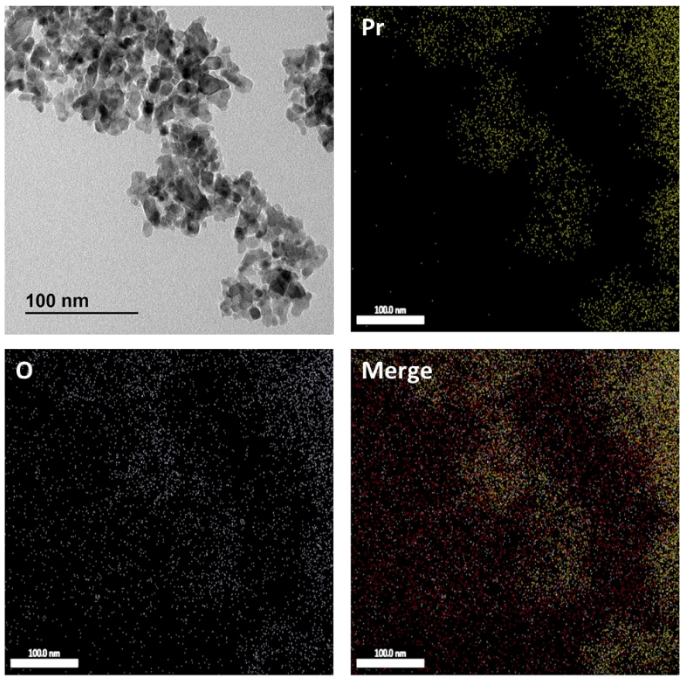

Figure S3. STEM and elemental mapping images of PrO_2 catalyst. Yellow and white dots represent praseodymium and oxygen, respectively. Red dots represent carbon and are observed due to the carbon grid.

4. Substrate scope (characterization of ester products)

Benzyl benzoate (3aa)

Dichloromethane as an eluent. Colorless oil (323.9 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–8.10 (m, 2H), 7.54–7.59 (m, 1H), 7.32–7.47 (m, 7H), 5.37 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.58, 136.17, 133.17, 130.25, 129.83, 128.73, 128.51, 128.37, 128.30, 66.83.

4-Bromobenzyl benzoate (3ab)

Dichloromethane as an eluent. Colorless oil (432.4 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05–8.08 (m, 2H), 7.55–7.59 (m, 1H), 7.50–7.53 (m, 2H), 7.42–7.47 (m, 2H), 7.31–7.34 (m, 2H), 5.31 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.45, 135.19, 133.32, 131.89, 129.99, 129.82, 128.57, 122.42, 66.03.

4-Methoxybenzyl benzoate (3ac)

Ethyl acetate/hexane (1/20, v/v) as an eluent. White solid (155.1 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05–8.08 (m, 2H), 7.53–7.57 (m, 1H), 7.38–7.45 (m, 4H), 6.90–6.94 (m, 2H), 5.30 (s, 2H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.66, 159.77, 133.08, 130.38, 130.21, 129.80, 128.46, 128.29, 114.10, 66.68, 55.43.

4-Nitrobenzyl benzoate (3ad)

Dichloromethane/hexane (1/1, v/v) as an eluent. Yellow solid (371.9 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–8.26 (m, 2H), 8.08–8.11 (m, 2H), 7.58–7.62 (m, 3H), 7.45–7.49 (m, 2H), 5.46 (s, 2H).

Hexyl benzoate (3ae)

Dichloromethane as an eluent. Colorless oil (300.2 mg, 91%)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03–8.06 (m, 2H), 7.53–7.58 (m, 1H), 7.42–7.46 (m, 2H), 4.32 (t, J = 6.7 Hz, 2H), 1.73–1.80 (m, 2H), 1.57 (s, 2H), 1.41–1.49 (m, 2H), 1.32–1.38 (m, 4H), 0.89–0.92 (m, 3H).

Cyclohexyl benzoate (3af)

Dichloromethane as an eluent. Colorless oil (321.0 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–8.07 (m, 2H), 7.52–7.57 (m, 1H), 7.41–7.46 (m, 2H), 5.00–5.07 (m, 1H), 1.92–1.98 (m, 2H), 1.75–1.83 (m, 2H), 1.30–1.64 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.14, 132.80, 131.16, 129.66, 128.40, 73.16, 31.78, 25.62, 23.80.

Hexadecyl benzoate (3ag)

Dichloromethane as an eluent. White solid (506.4 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03–8.07 (m, 2H), 7.50–7.56 (m, 1H), 7.39–7.44 (m, 2H), 4.32 (t, *J* = 6.7 Hz, 2H), 1.72–1.81 (m, 2H), 1.26–1.47 (m, 26H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.65, 132.79, 130.65, 129.61, 128.34, 65.17, 32.04, 29.81, 29.78, 29.70, 29.65, 29.48, 29.40, 28.84, 26.15, 22.79, 14.19

1-Phenylethyl benzoate (3ah)

Ethyl acetate/hexane (1/50, v/v) as an eluent. Pale yellow oil (175.5 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–8.10 (m, 2H), 7.54–7.58 (m, 1H), 7.42–7.46 (m, 4H), 7.35–7.39 (m, 2H), 7.28–7.32 (m, 1H), 6.14 (q, *J* = 6.6 Hz, 1H), 1.68 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.94, 141.92, 133.05, 130.66, 129.77, 128.68, 128.46, 128.02, 126.18, 73.05, 22.55.

Benzyl 4-bromobenzoate (3ba)

Dichloromethane as an eluent. Colorless oil (441.7 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.96 (m, 2H), 7.56–7.60 (m, 2H), 7.34–7.47 (m, 5H), 5.37 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.74, 135.86, 131.80, 131.31, 129.12, 128.73, 128.46, 128.33, 128.25, 67.03.

Benzyl 4-nitrobenzoate (3ca)

Ethyl acetate/hexane (1/100, v/v) as an eluent. White solid (369.5 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21–8.28 (m, 4H), 7.34–7.47 (m, 5H), 5.40 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.63, 150.68, 135.59, 135.34, 130.92, 128.84, 128.75, 128.54, 123.65, 67.74

Benzyl 4-aminobenzoate (3da)

Dichloromethane as an eluent. Brown solid (75.8 mg, 21%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.91 (m, 2H), 7.30–7.45 (m, 5H), 6.62–6.65 (m, 2H), 5.47–5.25 (2H), 4.06 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.59, 151.05, 136.72, 131.91, 128.65, 128.17, 128.15, 119.80, 113.92, 66.21.

5. Yield calculation of biodiesel production with soybean oil by ^{1}H NMR

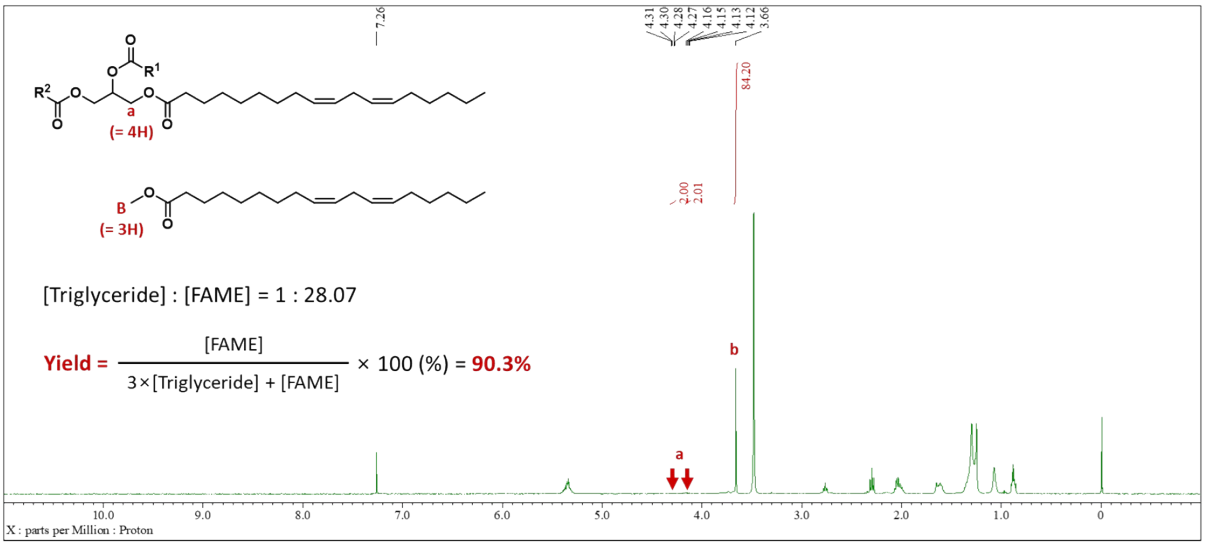

Figure S4. NMR spectrum of the aliquot after solvothermal reaction of soybean oil and yield calculation.

6. NMR spectra

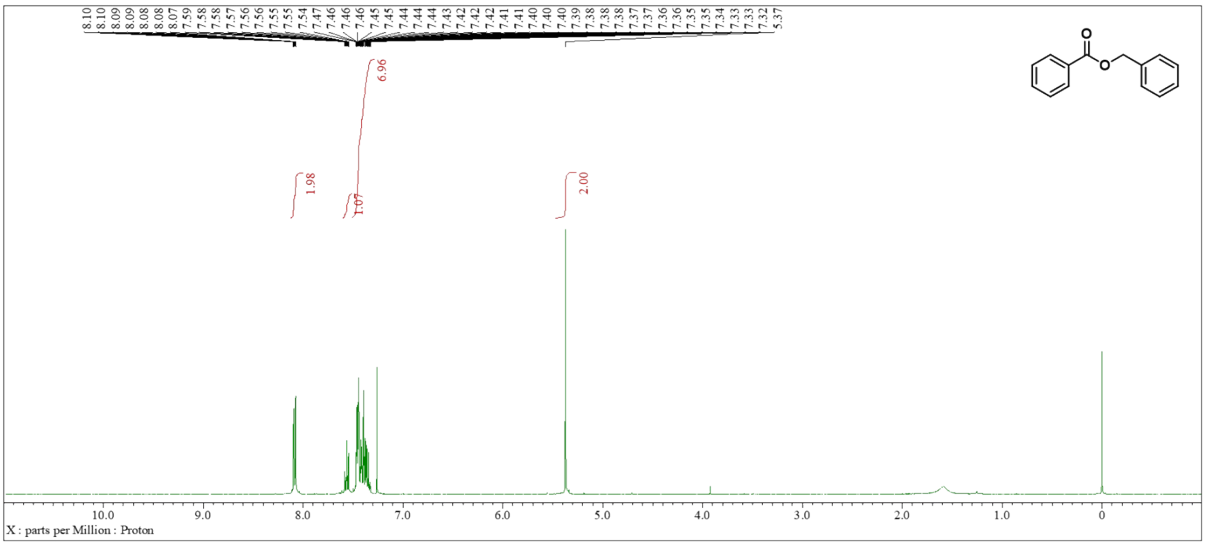

Figure S5. ^{1}H NMR of benzyl benzoate (**3aa**)

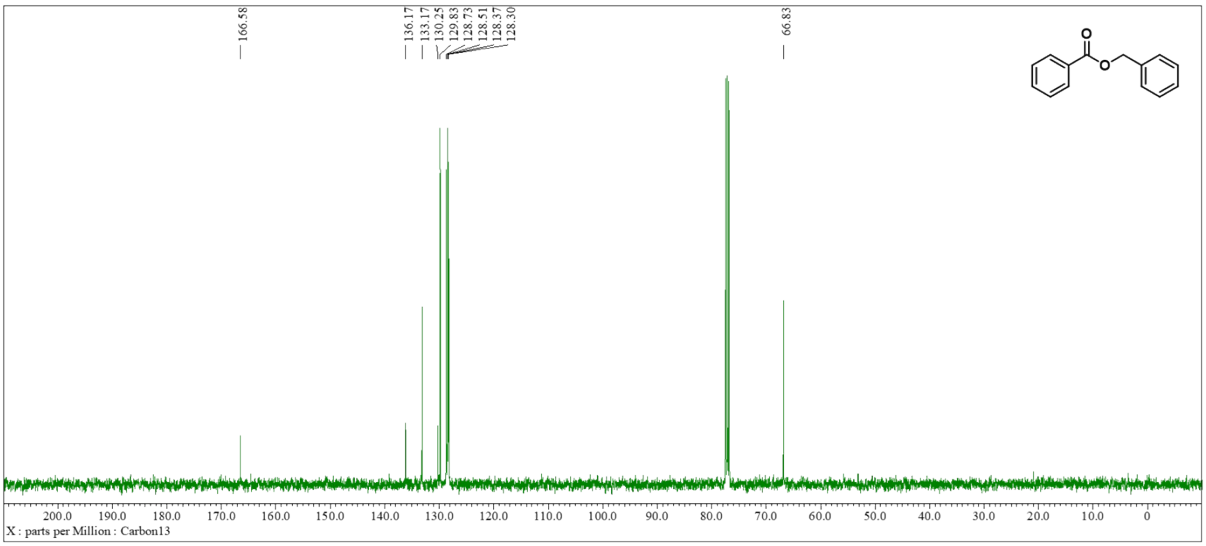

Figure S6. ^{13}C NMR of benzyl benzoate (**3aa**)

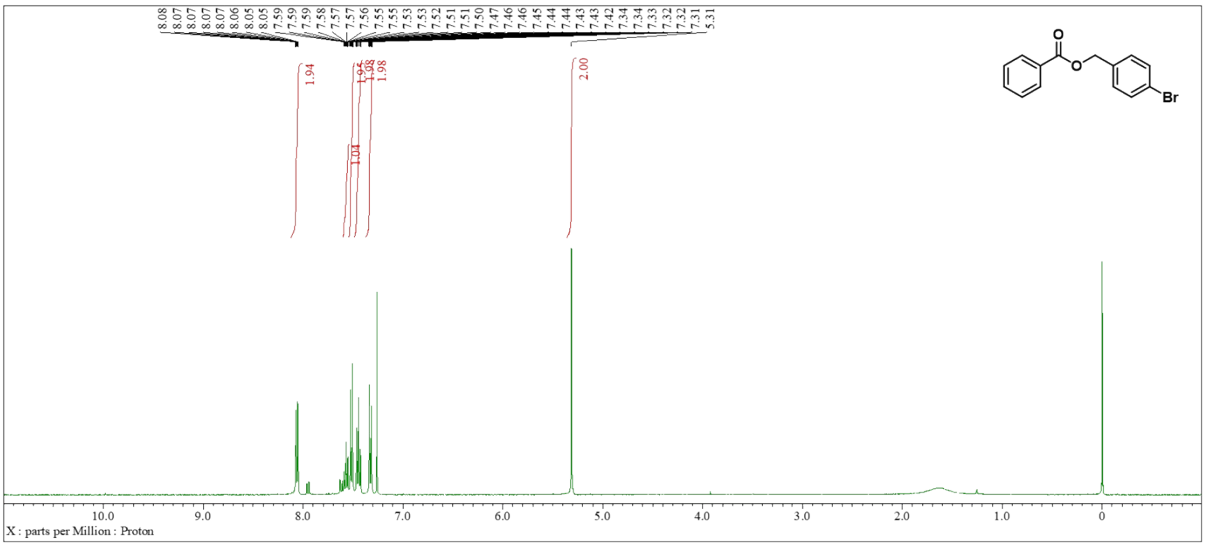

Figure S7. ^{1}H NMR of 4-bromobenzyl benzoate (**3ab**)

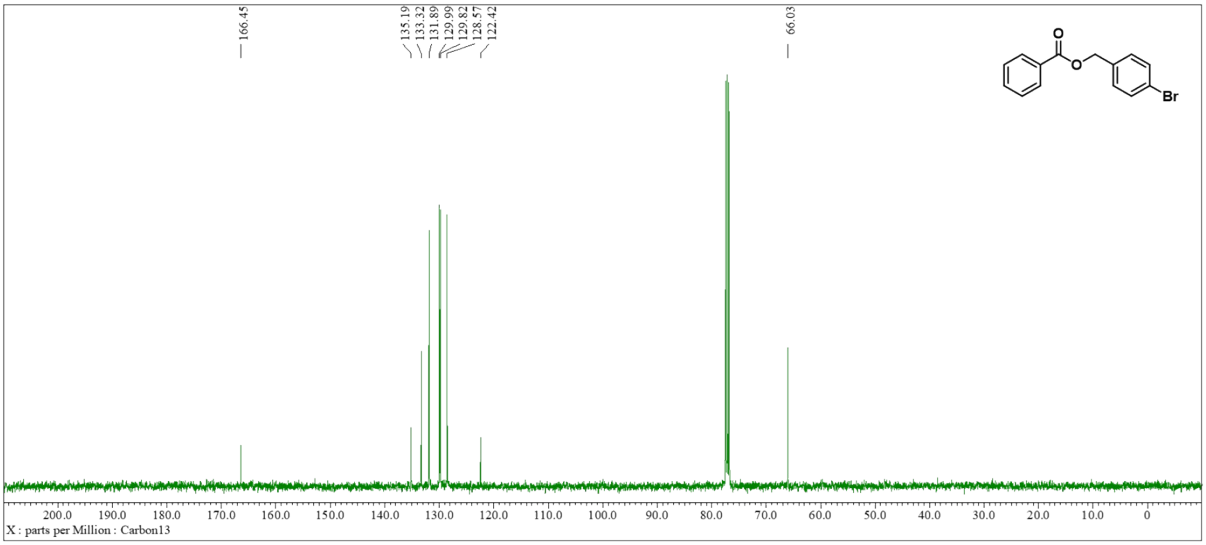

Figure S8. ^{13}C NMR of 4-bromobenzyl benzoate (**3ab**)

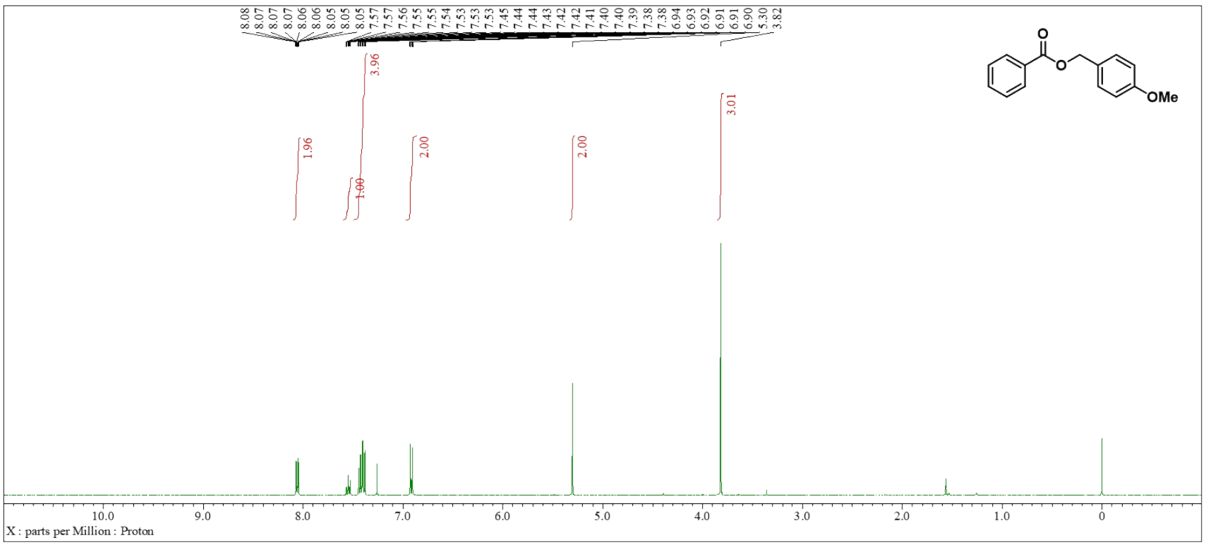

Figure S9. ^{1}H NMR of 4-methoxybenzyl benzoate (**3ac**)

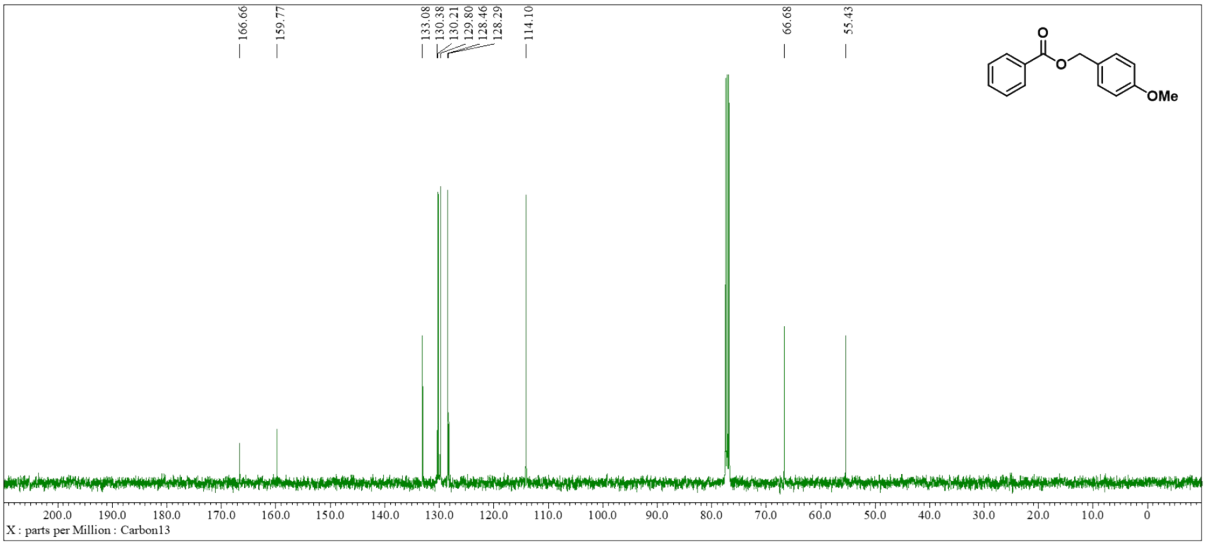

Figure S10. ^{13}C NMR of 4-methoxybenzyl benzoate (**3ac**)

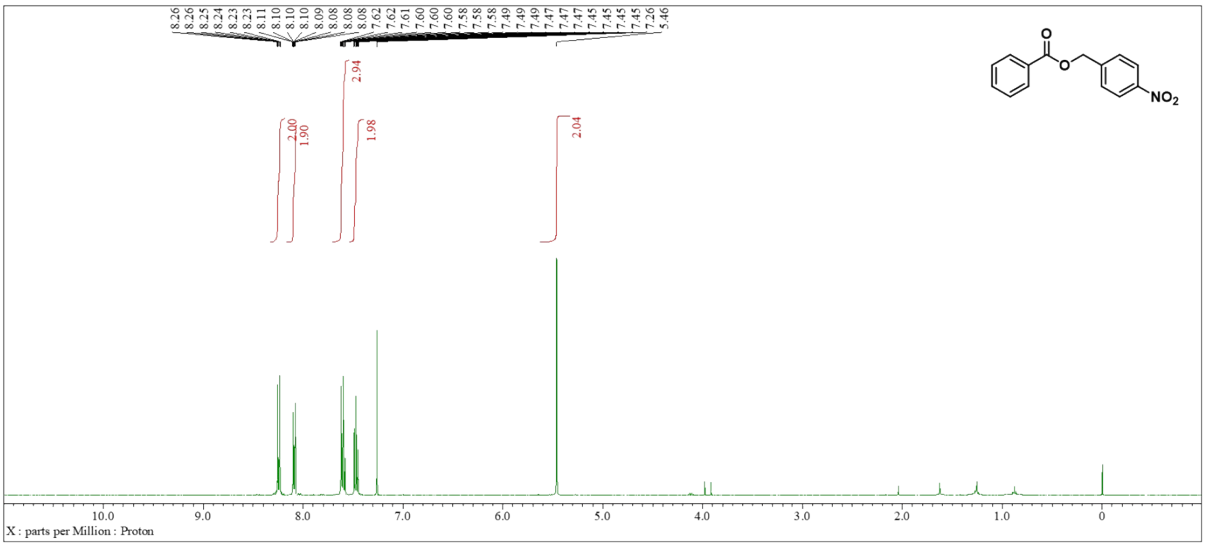

Figure S11. ^{1}H NMR of 4-nitrobenzyl benzoate (**3ad**)

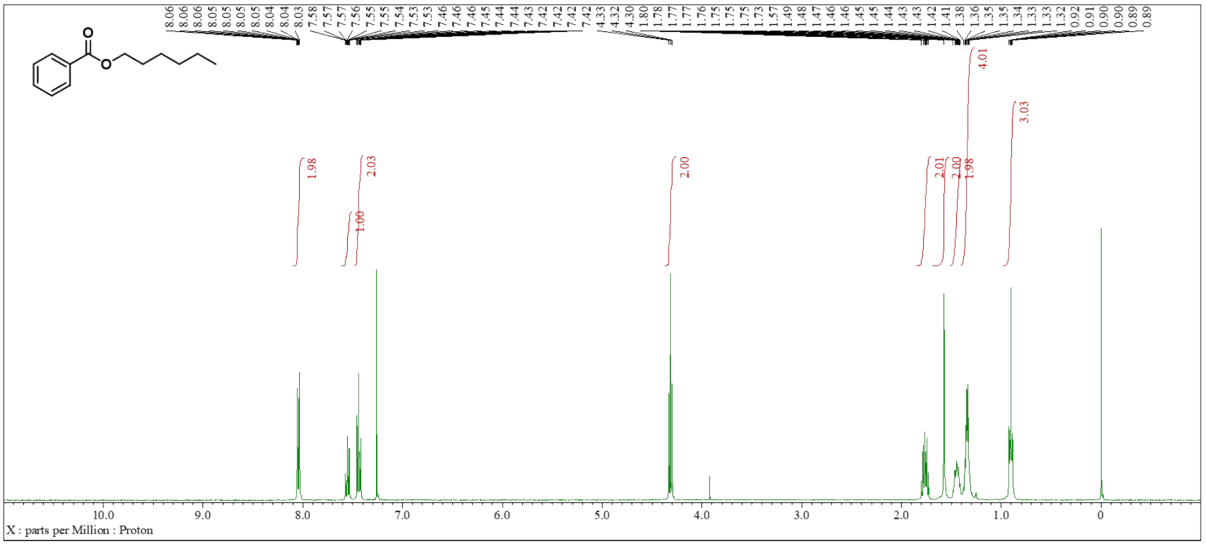

Figure S12. ^{1}H NMR of hexyl benzoate (**3ae**)

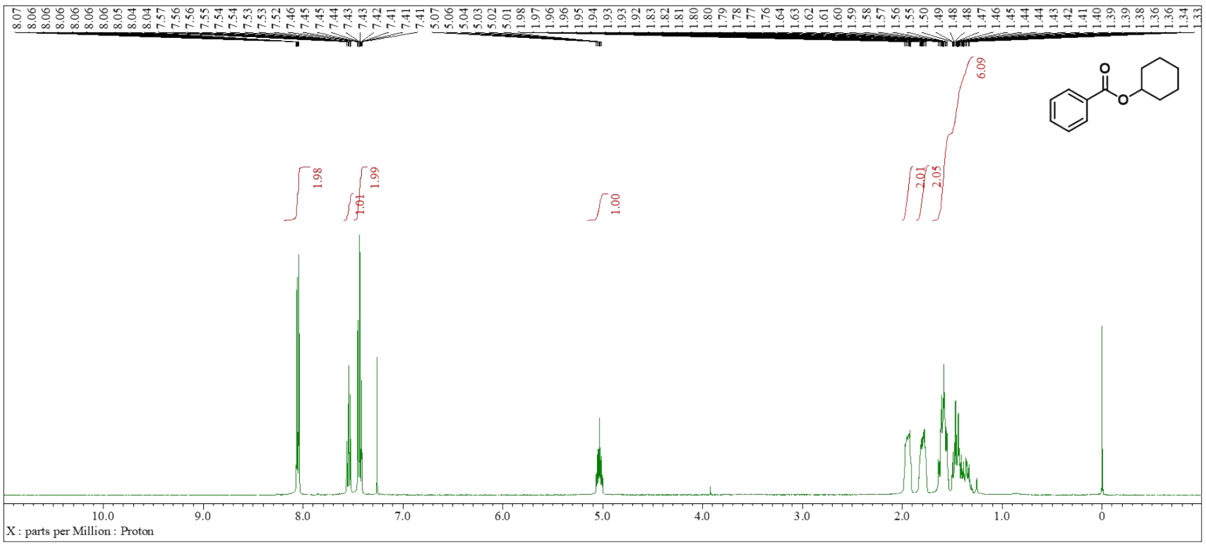

Figure S13. ^{1}H NMR of cyclohexyl benzoate (**3af**)

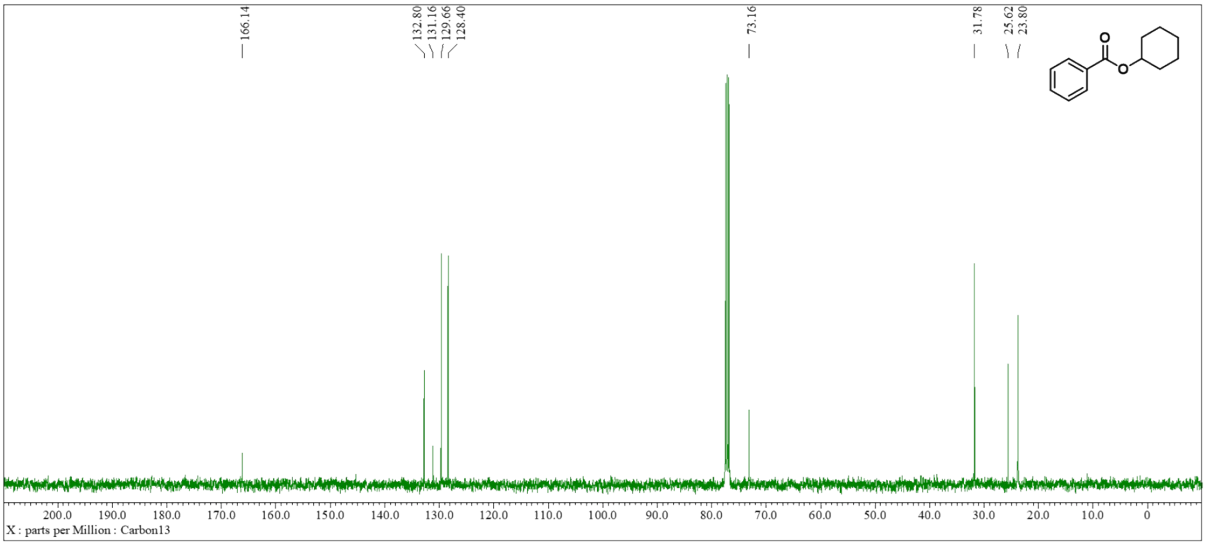

Figure S14. ^{13}C NMR of cyclohexyl benzoate (**3af**)

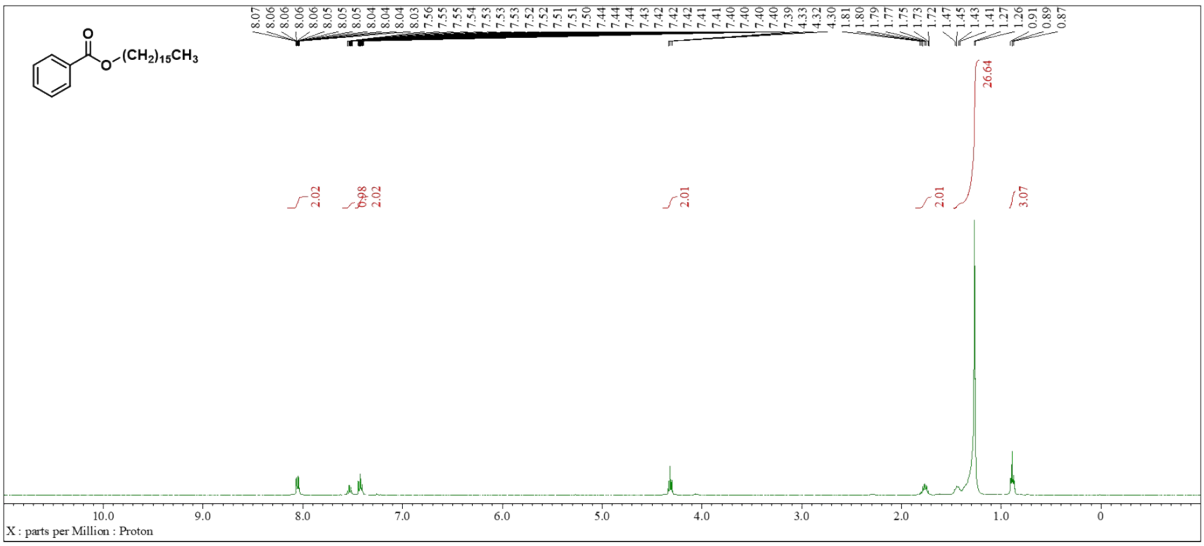

Figure S15. ^{1}H NMR of hexadecyl benzoate (**3ag**)

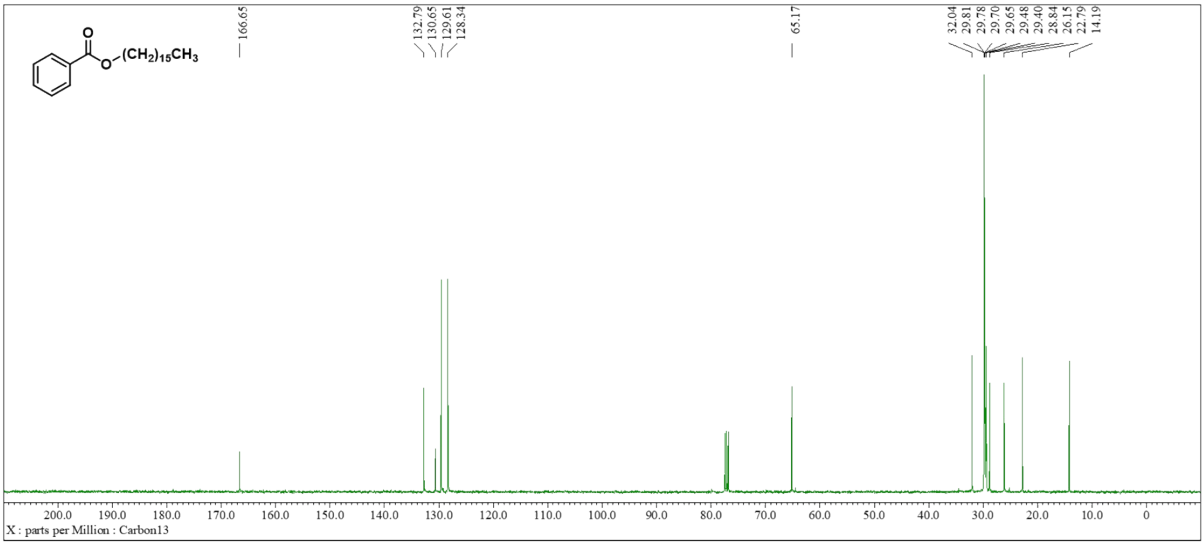

Figure S16. ^{13}C NMR of hexadecyl benzoate (**3ag**)

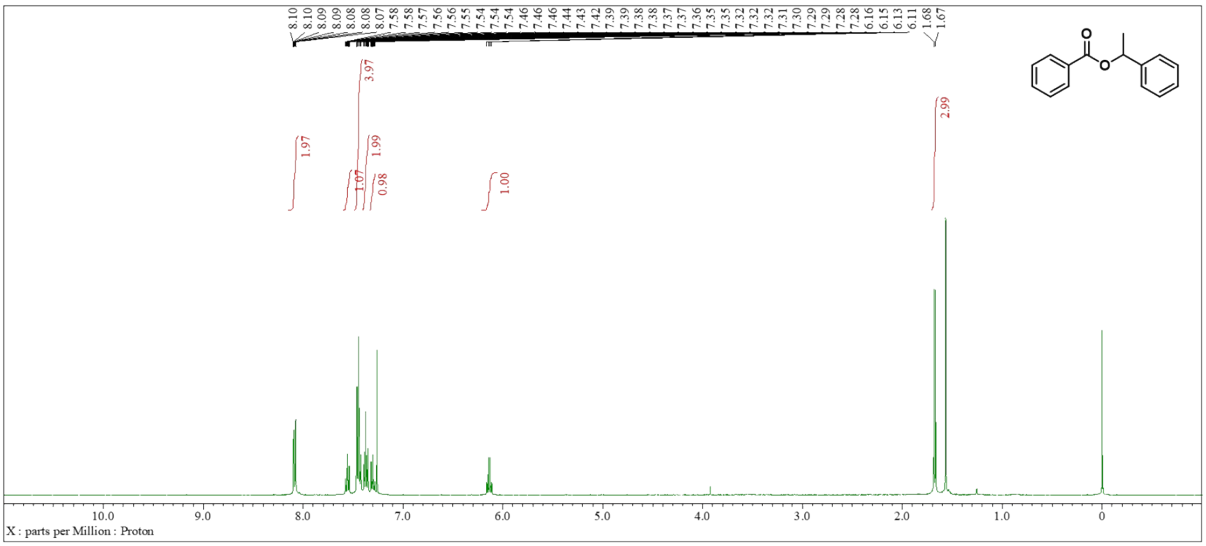

Figure S17. ^{1}H NMR of 1-phenylethyl benzoate (**3ah**)

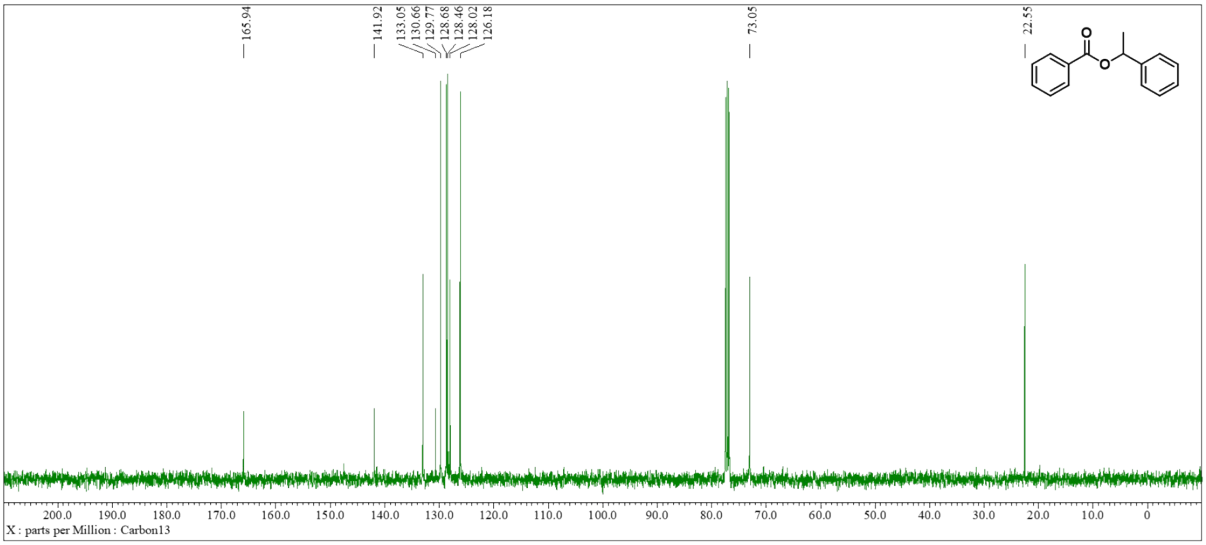

Figure S18. ^{13}C NMR of 1-phenylethyl benzoate (**3ah**)

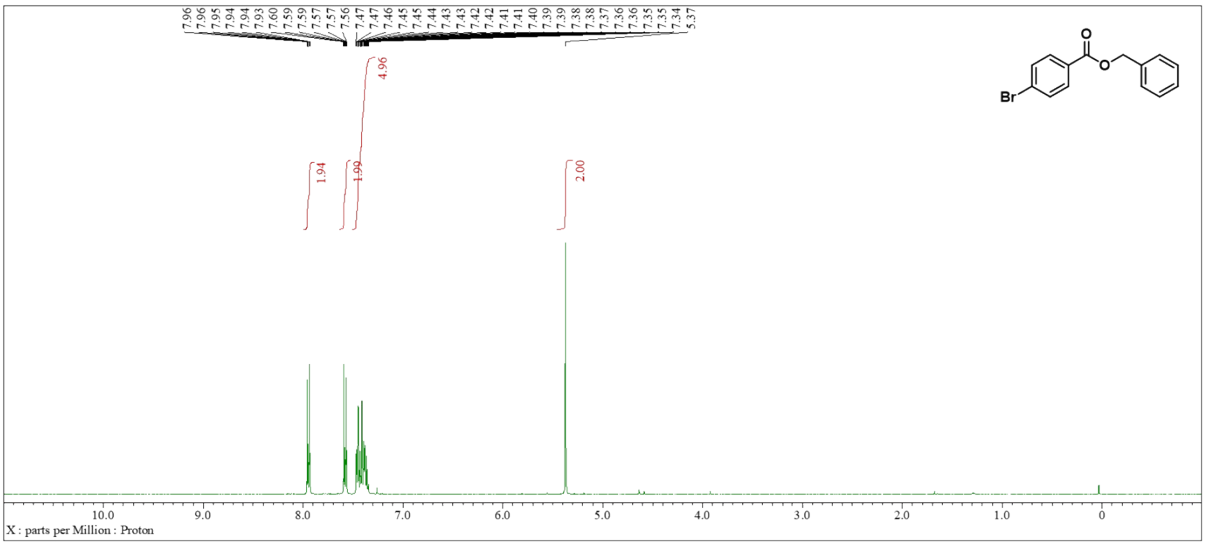

Figure S19. ^{1}H NMR of benzyl 4-bromobenzoate (**3ba**)

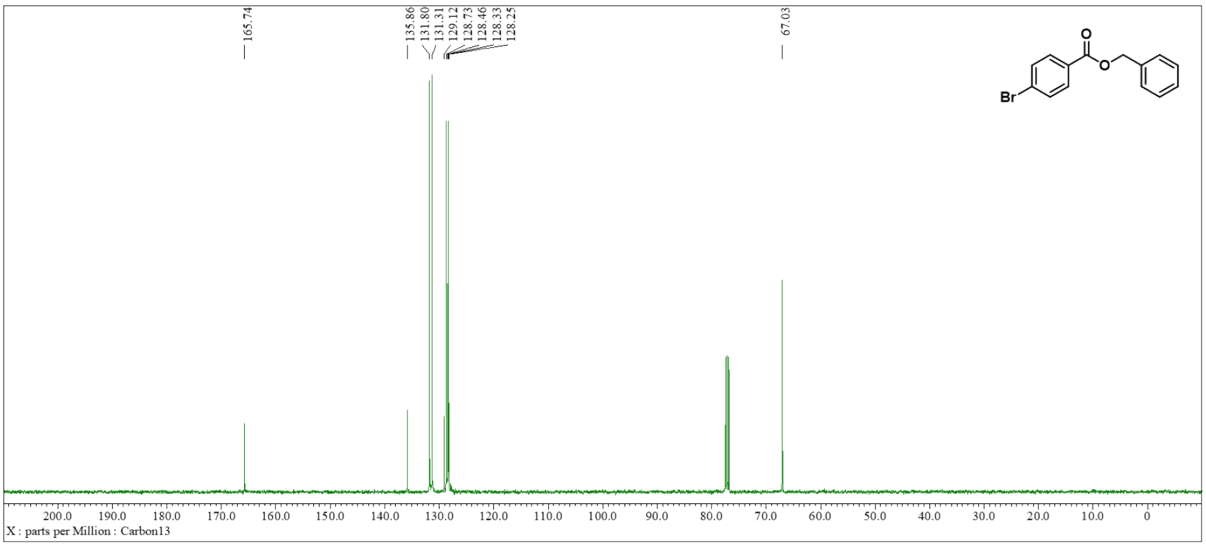

Figure S20. ^{13}C NMR of benzyl 4-bromobenzoate (**3ba**)

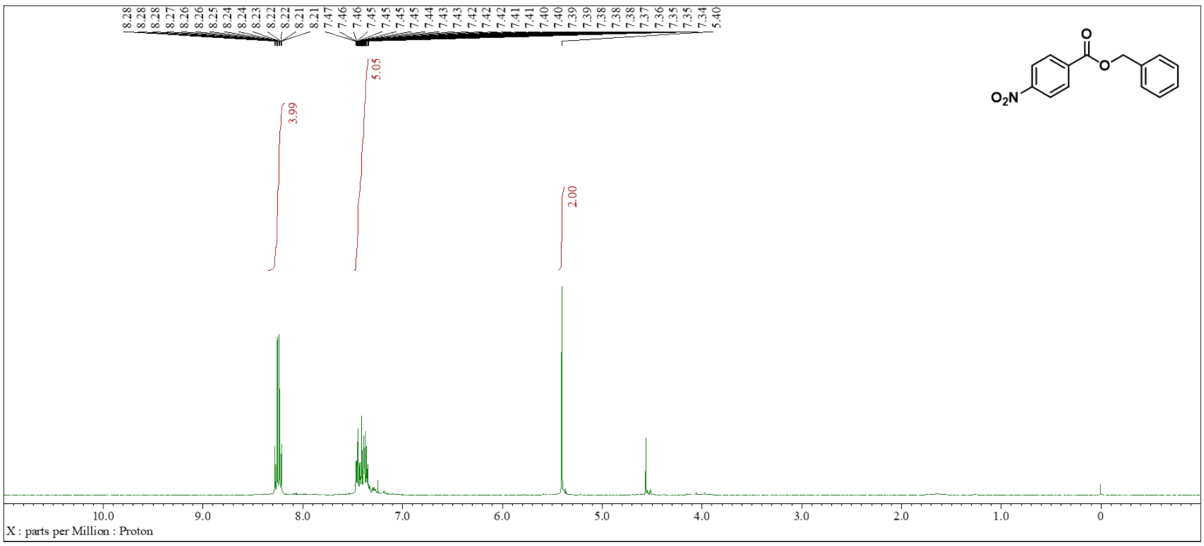

Figure S21. ^{1}H NMR of benzyl 4-nitrobenzoate (**3ca**)

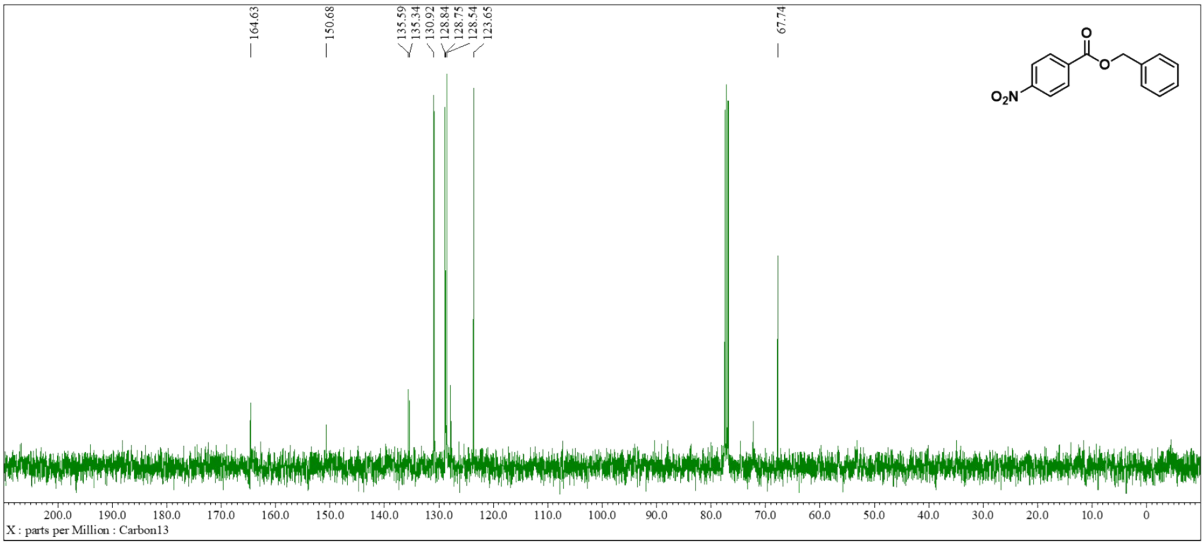

Figure S22. ^{13}C NMR of benzyl 4-nitrobenzoate (**3ca**)

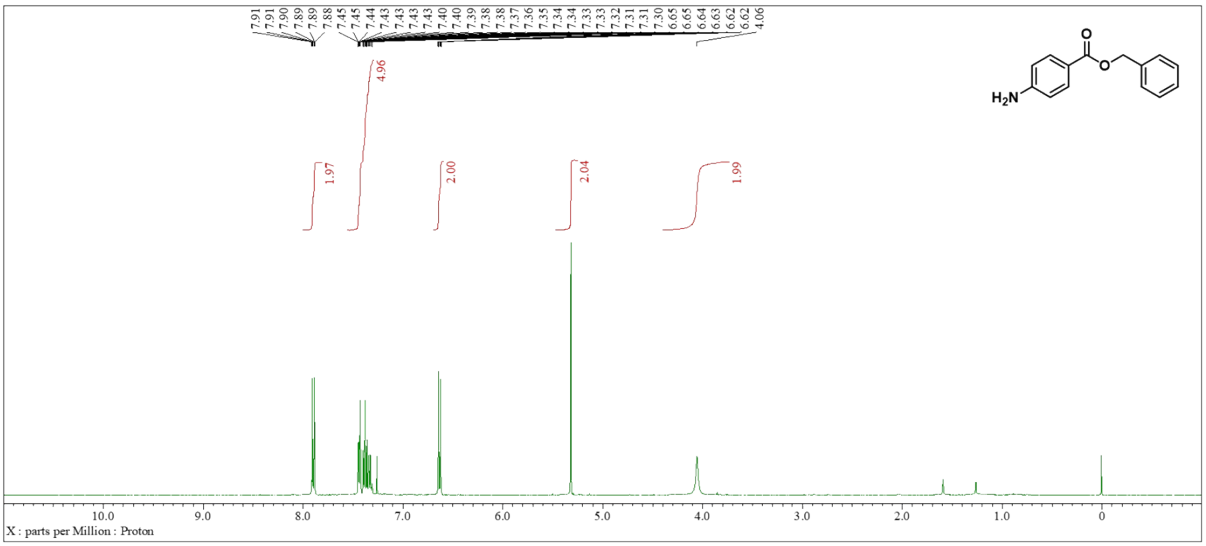

Figure S23. ^{1}H NMR of benzyl 4-aminobenzoate (**3da**)

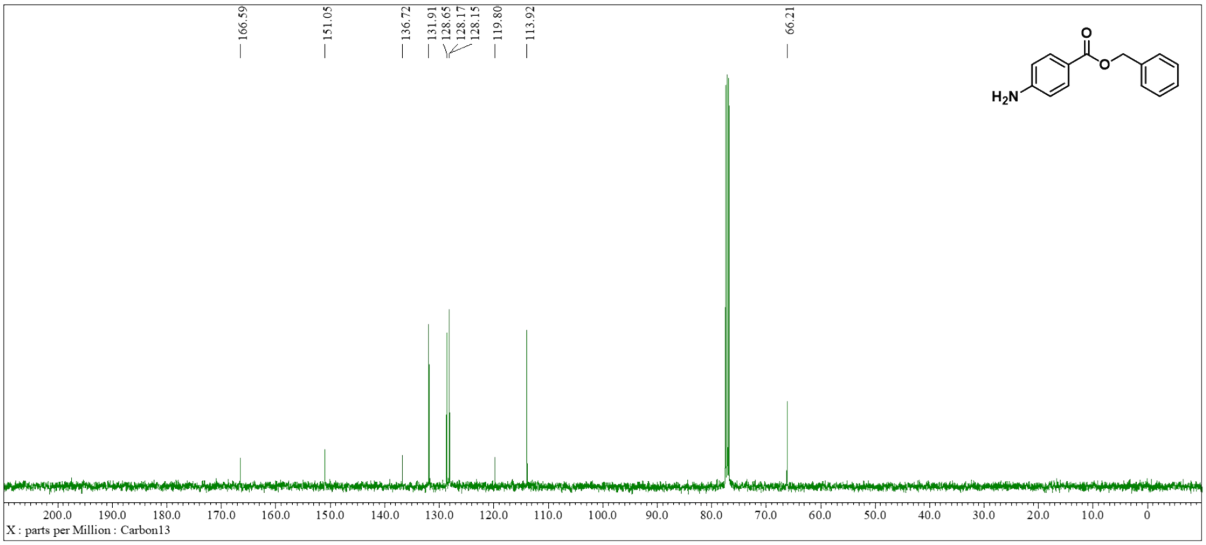

Figure S24. ^{13}C NMR of benzyl 4-aminobenzoate (**3da**)