

Supporting Information

***O*-Acetyl Substituted Phenol Ester Synthesis via Direct Oxidative Esterification Utilizing Ethers as An Acylating Source with Cu₂(dhtp) Metal-Organic Framework as A Recyclable Catalyst**

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Materials and instrumentation

All reagents and starting materials were obtained commercially from Sigma-Aldrich and Merck, and were used as received without any further purification unless otherwise noted. Nitrogen physisorption measurements were conducted using a Micromeritics 2020 volumetric adsorption analyzer system. Samples were pretreated by heating under vacuum at 150 °C for 3 h. A Netzsch Thermoanalyzer STA 409 was used for thermogravimetric analysis (TGA) with a heating rate of 10 °C/min under a nitrogen atmosphere. X-ray powder diffraction (XRD) patterns were recorded using a Cu K α radiation source on a D8 Advance Bruker powder diffractometer. Scanning electron microscopy studies were conducted on a S4800 Scanning Electron Microscope (SEM). Transmission electron microscopy studies were performed using a JEOL JEM 1400 Transmission Electron Microscope (TEM) at 80 kV. The Cu₂(dhtp) sample was dispersed on holey carbon grids for TEM observation. Elemental analysis with atomic absorption spectrophotometry (AAS) was performed on an AA-6800 Shimadzu. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet 6700 instrument, with samples being dispersed on potassium bromide pellets.

Gas chromatographic (GC) analyses were performed using a Shimadzu GC 2010-Plus equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μ m). The temperature program for GC analysis held samples at 120 °C for 0.5 min; heated them from 120 to 130 °C at 40 °C/min; held them at 130 °C for 1 min; heated them from 130 to 280 °C at 40 °C/min; and finally held them at 280 °C for 1.5 min.. Inlet and detector temperatures were set constant at 280 °C. The GC yield was calculated using

diphenyl ether as the internal standard. GC-MS analyses were analyzed on a Shimadzu GCMS-QP2010Ultra with a ZB-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μ m). The temperature program for GC-MS analysis held samples at 50 °C for 2 min; heated samples from 50 to 280°C at 10 °C/min and held them at 280 °C for 10 min. Inlet temperature was set constant at 280 °C. MS spectra were compared with the spectra gathered in the NIST library. The ^1H NMR and ^{13}C NMR were recorded on Bruker AV 500 spectrometers using residual solvent peak as a reference.

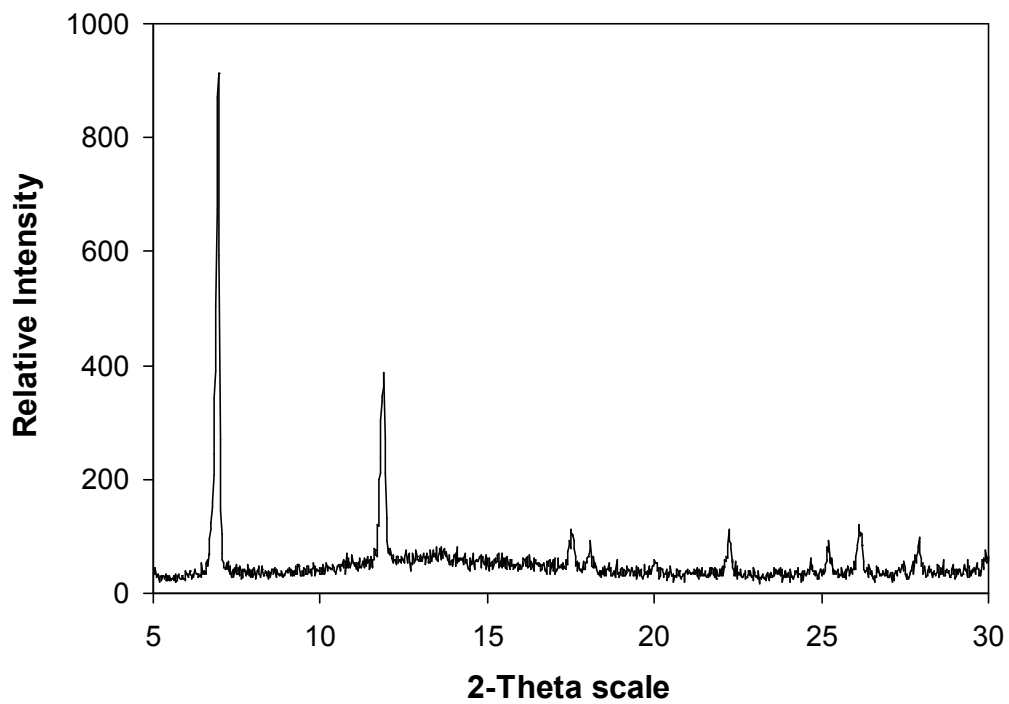


Fig. S1. X-ray powder diffractograms of the $\text{Cu}_2(\text{dhtp})$.

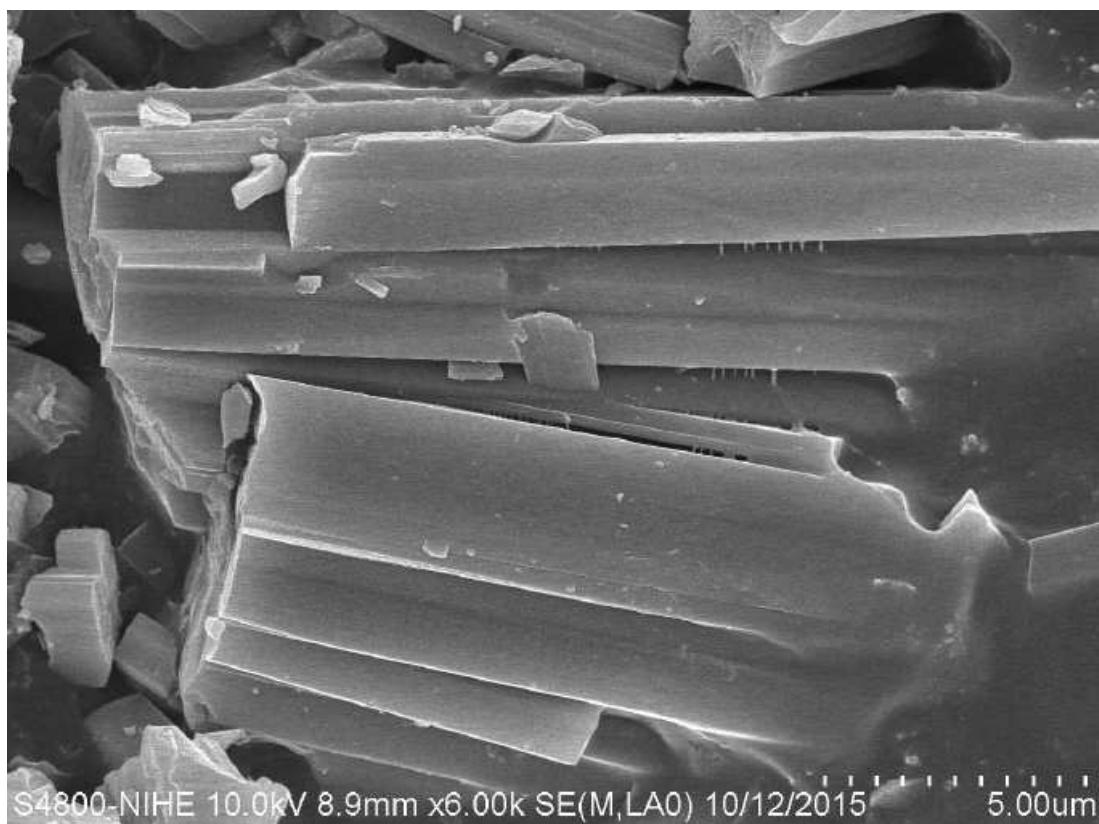


Fig. S2. SEM micrograph of the Cu₂(dhtp).

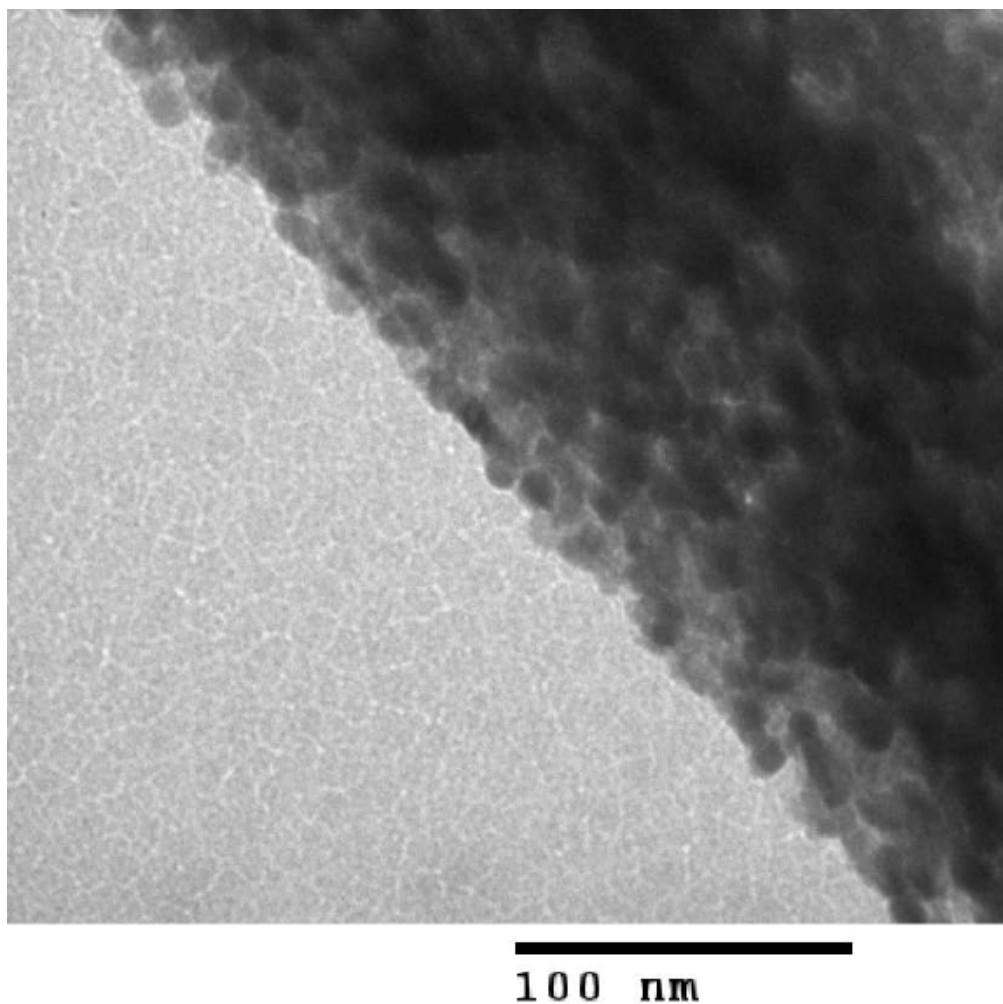


Fig. S3. TEM micrograph of the $\text{Cu}_2(\text{dhtp})$.

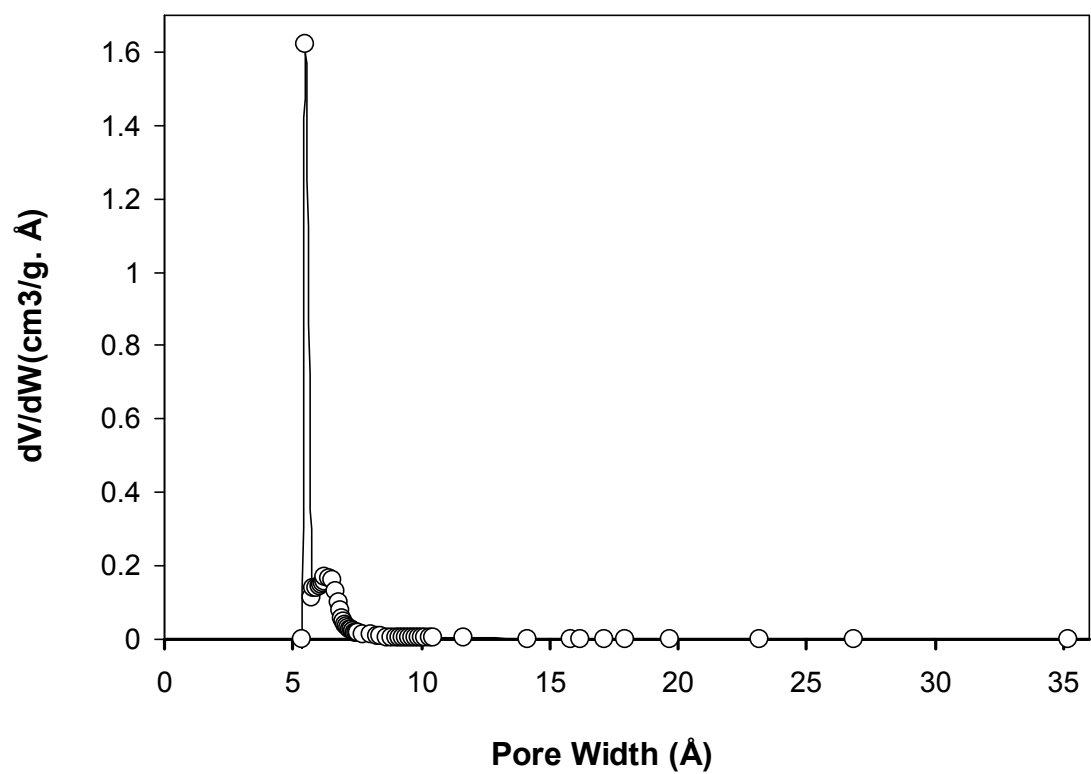


Fig. S4. Pore size distribution of the Cu₂(dhtp).

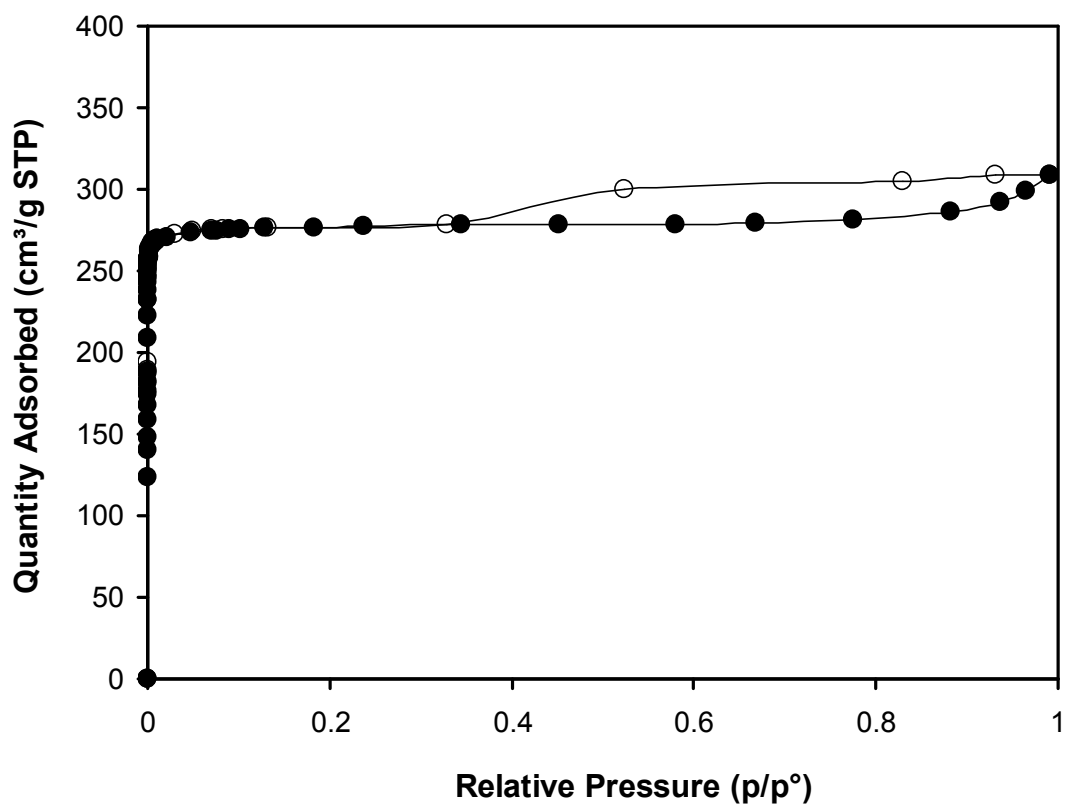


Fig. S5. Nitrogen adsorption/desorption isotherm of the Cu₂(dhtp). Adsorption data are shown as closed circles and desorption data as open circles.

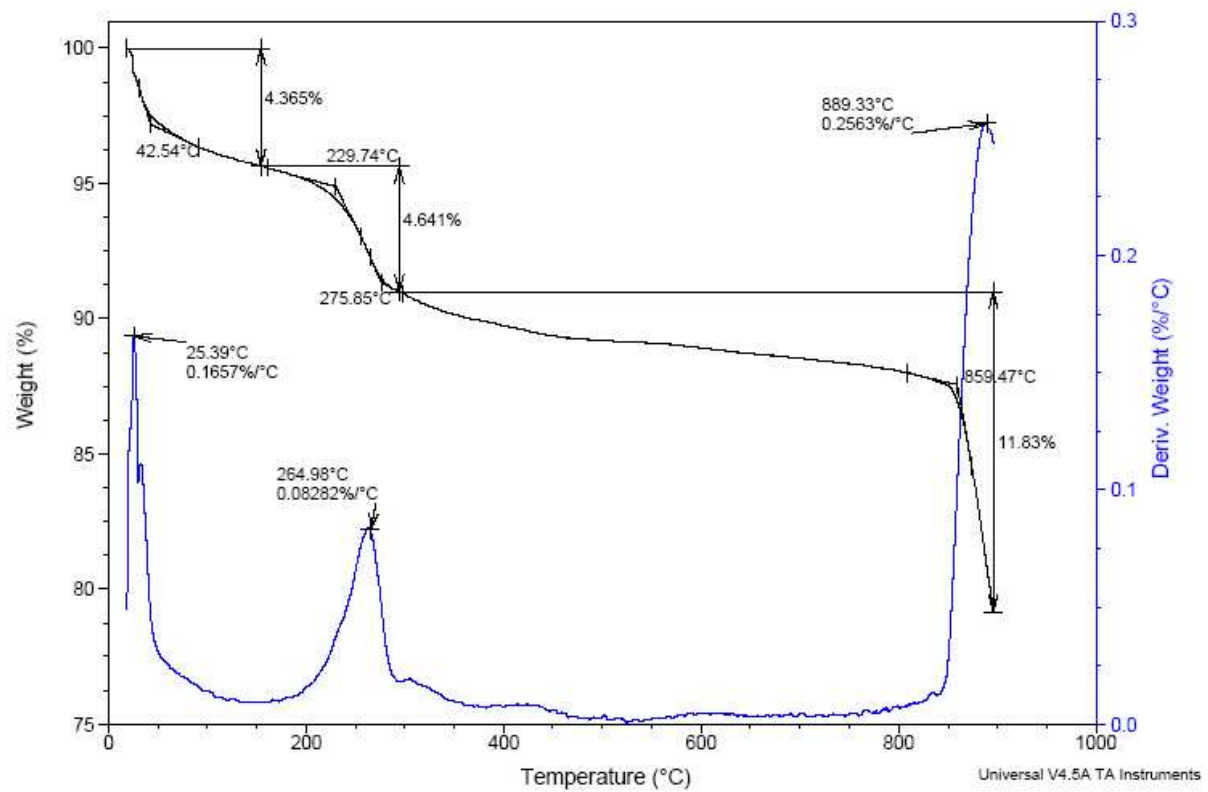


Fig. S6. TGA analysis of the $\text{Cu}_2(\text{dhtp})$.

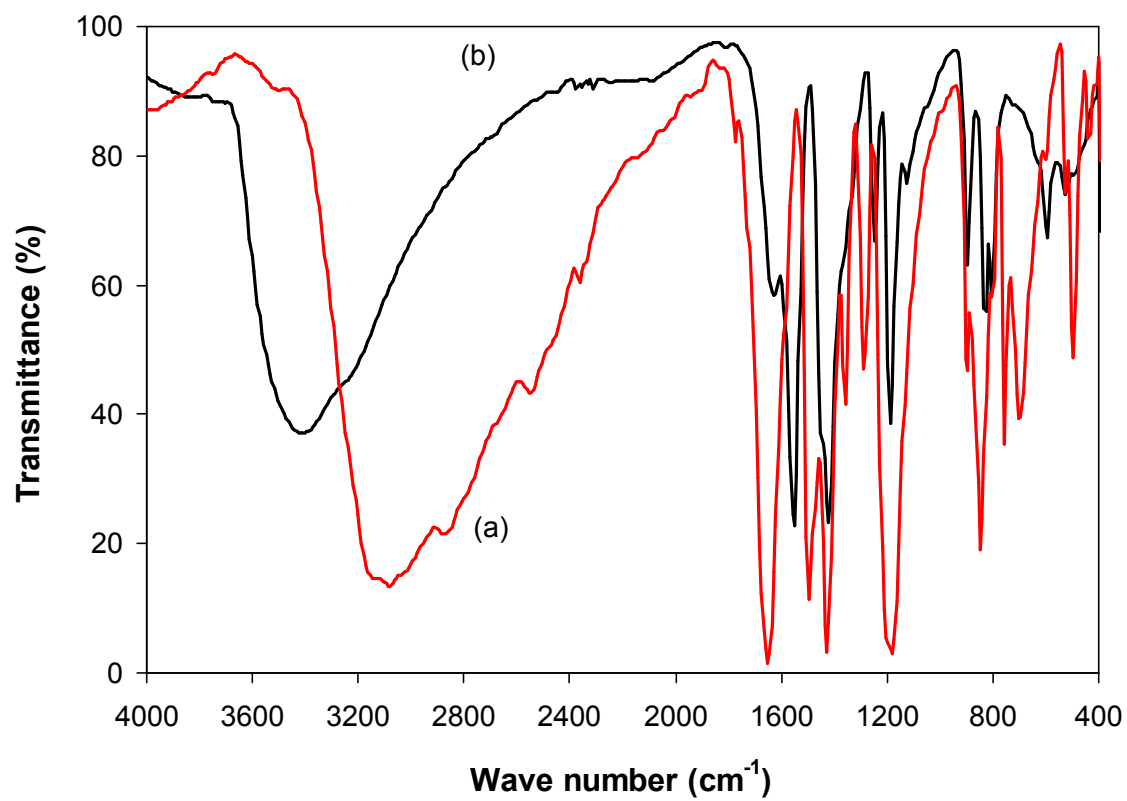


Fig. S7. FT-IR spectra of terephthalic acid (a), and the $\text{Cu}_2(\text{dhtp})$ (b).

Characterization Data for Products

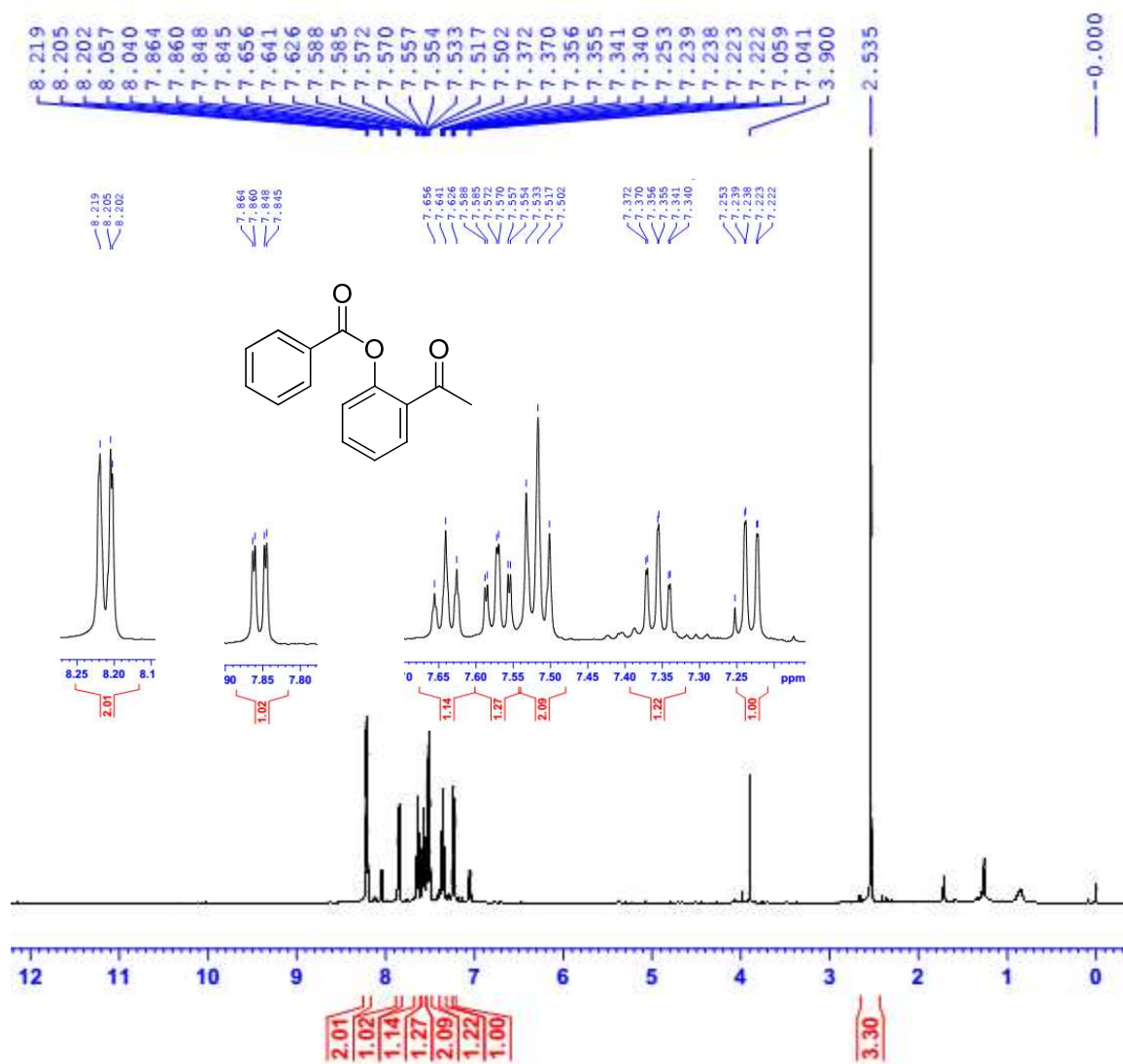


Fig. S8. ¹H NMR spectra of 2-Acetylphenyl Benzoate

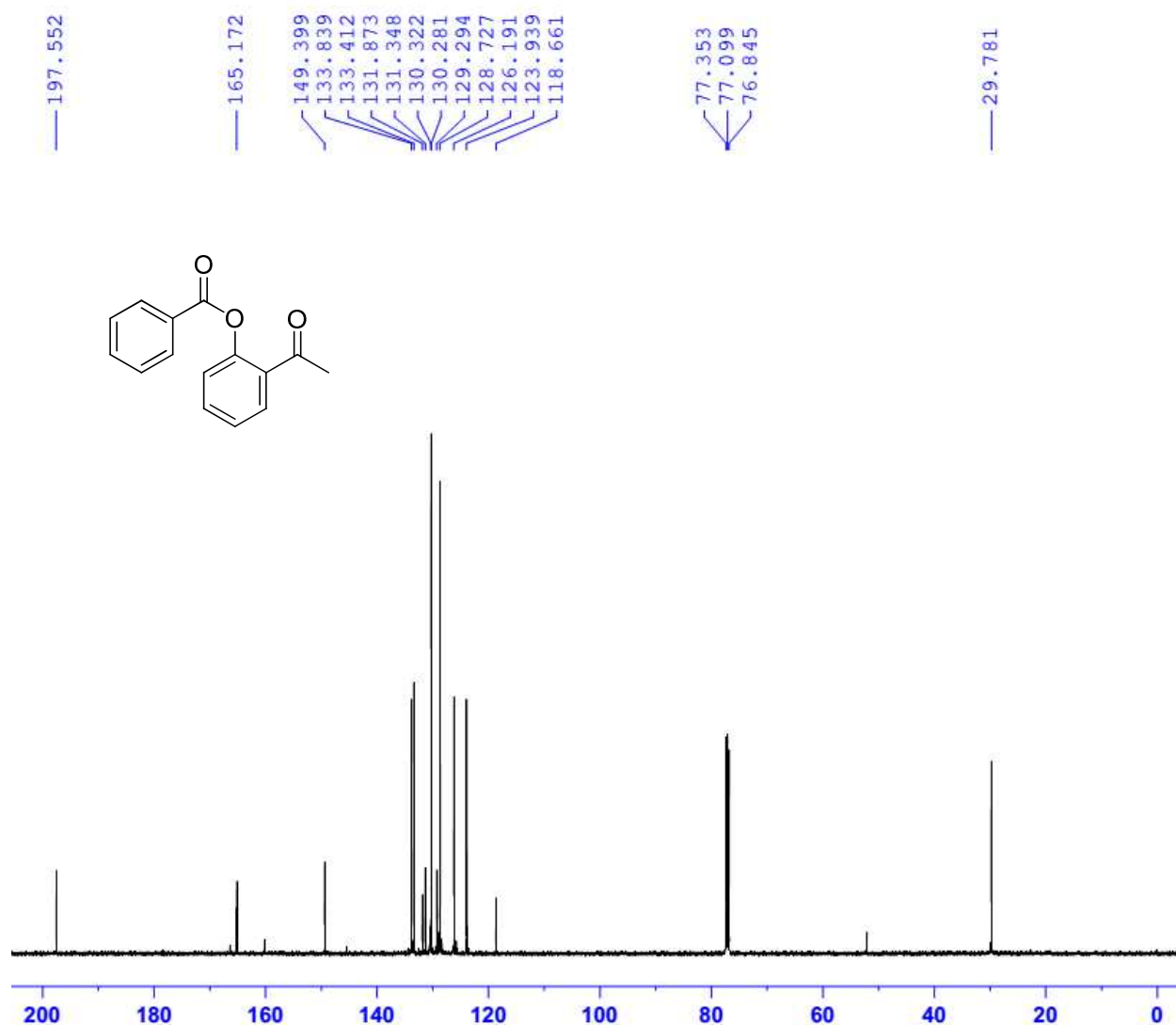


Fig. S9. ¹³C NMR spectra of 2-Acetylphenyl Benzoate

➤ 2-Acetylphenyl Benzoate

Prepared as shown in the general experimental procedure and purified on silica gel (hexane/ethyl acetate = 10:1), yellow liquid, 70% yield. ¹H NMR (500 MHz, CDCl₃, ppm): δ = 8.21 (d, *J* = 7.75 Hz, 2H), δ = 7.85 (dd, *J* = 7.75 Hz, *J* = 1.5 Hz, 1H), δ = 7.65 (t, *J* = 7.5 Hz, 1H), δ = 7.58 (dt, *J* = 7.75 Hz, *J* = 1.5 Hz, 1H), δ = 7.53 (t, *J* = 7.5 Hz, 2H), δ = 7.35 (dt, *J* = 8 Hz, *J* = 0.5 Hz, 1H), δ = 7.25 (dd, *J* = 8 Hz, *J* = 0.5 Hz, 1H), δ = 2.53 (s, CH₃). ¹³C NMR (125 MHz, CDCl₃,

ppm): δ = 197.6; 165.2; 149.4; 133.8; 133.4; 131.8; 131.3; 130.4; 130.3; 129.3; 128.7; 126.2; 123.9; 118.7; 29.8

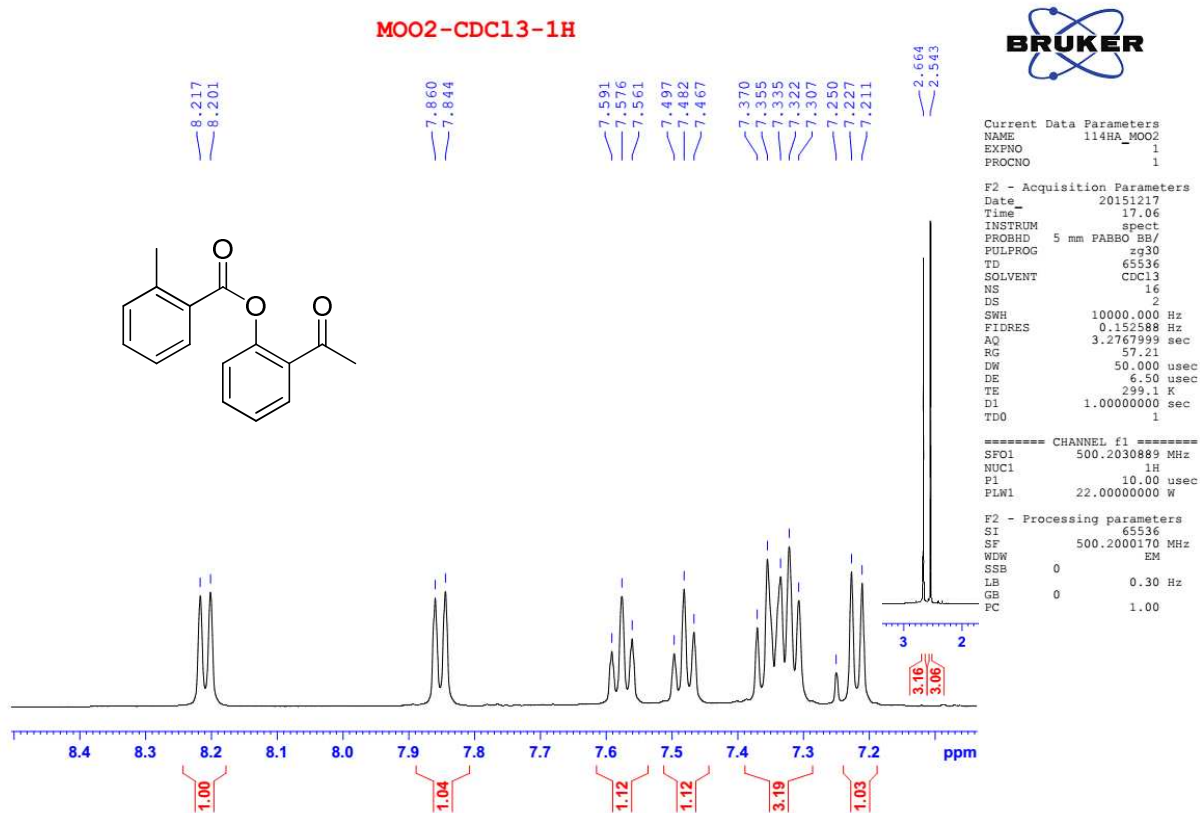


Fig. S10. ^1H NMR spectra of 2-Acetylphenyl 2-Methylbenzoate

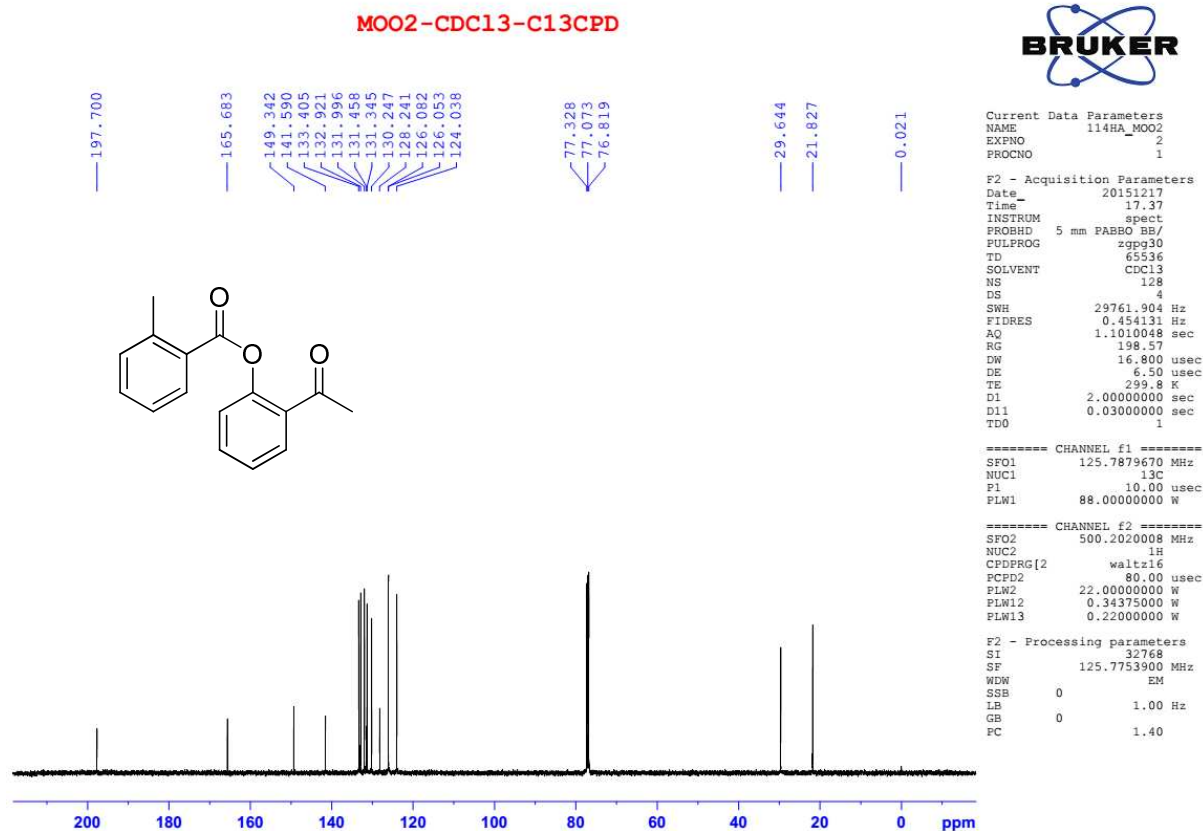


Fig. S11. ¹³C NMR spectra of 2-Acetylphenyl 2-Methylbenzoate

➤ 2-Acetylphenyl 2-Methylbenzoate

Prepared as shown in the general experimental procedure and purified on silica gel (hexane/ethyl acetate = 8:1), yellow liquid, 68% yield. ¹H NMR (500 MHz, CDCl₃, ppm): δ = 8.21 (d, *J* = 8 Hz, 1H), δ = 7.85 (d, *J* = 8 Hz, 1H), δ = 7.58 (t, *J* = 7.5 Hz, 1H), δ = 7.48 (t, *J* = 7.5 Hz, 1H), δ = 7.37 ÷ 7.31 (m, 3H), δ = 7.22 (d, *J* = 8 Hz, 1H), δ = 2.66 (s, CH₃), δ = 2.54 (s, CH₃). ¹³C NMR (125 MHz, CDCl₃, ppm): δ = 197.7; 165.7; 149.3; 141.6; 133.4; 132.9; 132; 131.4; 131.3; 130; 128.2; 126.1; 126; 124; 29.6; 21.8

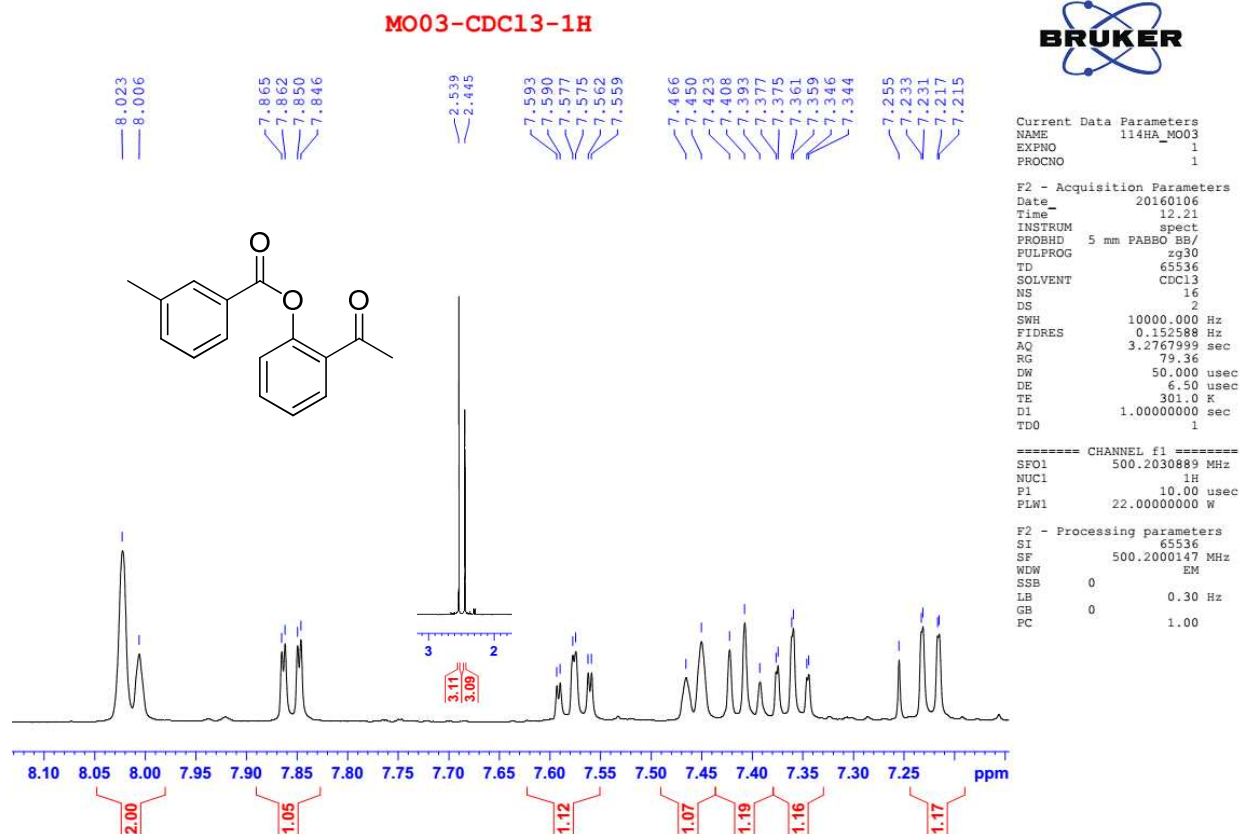


Fig. S12. ^1H NMR spectra of 2-Acetylphenyl 3-Methylbenzoate

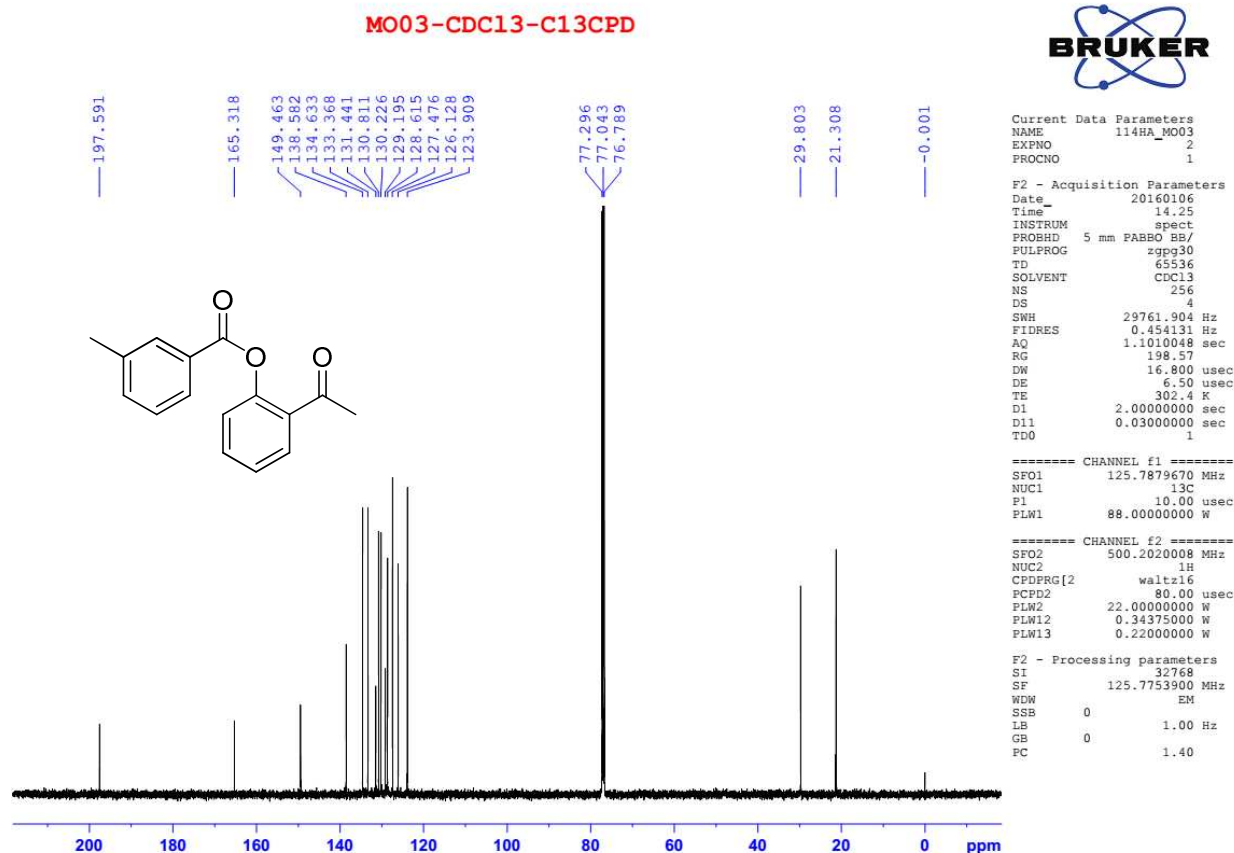


Fig. S13. ^{13}C NMR spectra of 2-Acetylphenyl 3-Methylbenzoate

➤ 2-Acetylphenyl 3-Methylbenzoate

Prepared as shown in the general experimental procedure and purified on silica gel (hexane/ethyl acetate = 6:1), yellow liquid, 70% yield. ^1H NMR (500 MHz, CDCl_3 , ppm): δ = 8.01 (d, J = 8.5 Hz, 2H), δ = 7.86 (dd, J = 7.5 Hz, J = 1.5 Hz, 1H), δ = 7.58 (dt, J = 7.5 Hz, J = 1.5 Hz, 1H), δ = 7.46 (d, J = 8 Hz, 1H), δ = 7.41 (t, J = 7.5 Hz, 1H), δ = 7.36 (dt, J = 8 Hz, J = 1 Hz, 1H), δ = 7.22 (dd, J = 8 Hz, J = 1 Hz, 1H), δ = 2.54 (s, CH_3), δ = 2.44 (s, CH_3). ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ = 197.6; 165.3; 149.5; 138.6; 134.6; 133.4; 131.4; 130.8; 130.2; 129.2; 128.6; 127.5; 126.1; 123.9; 29.8; 21.3

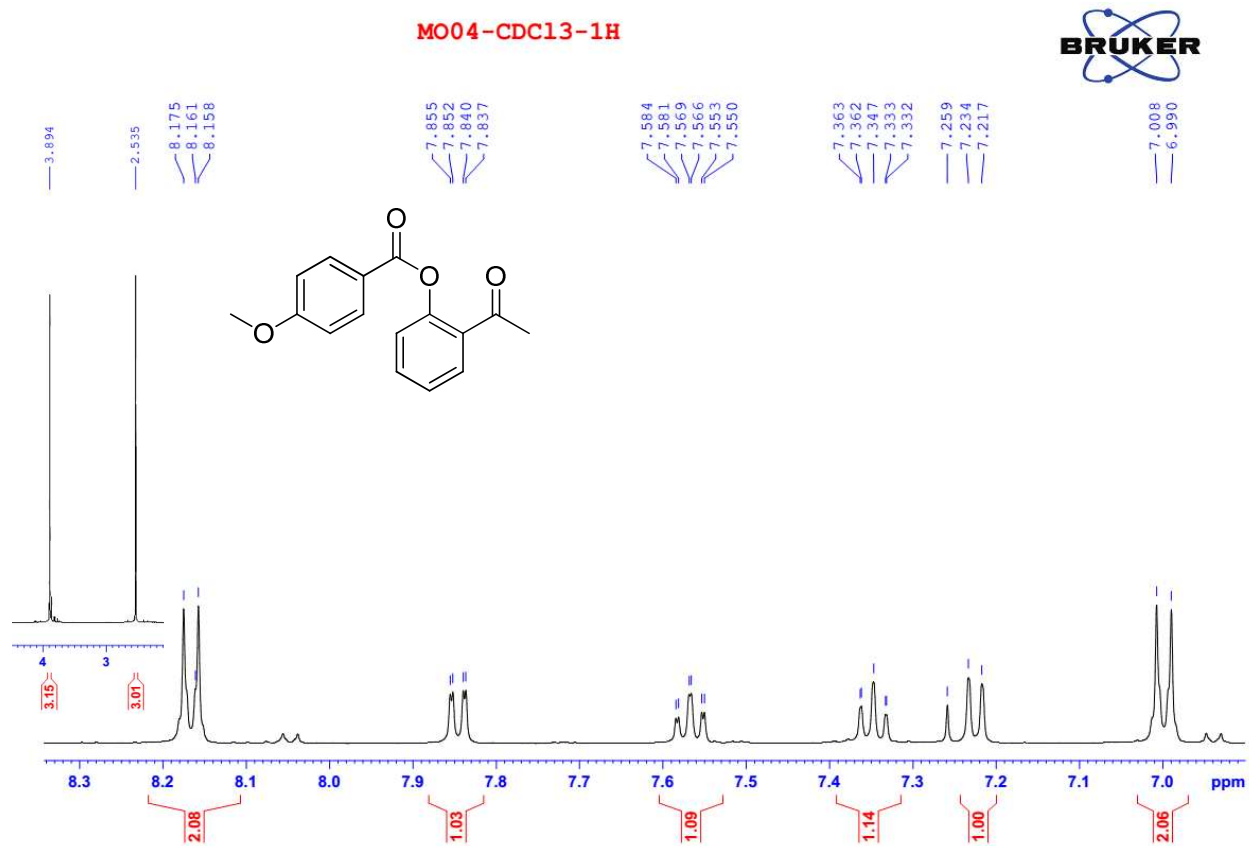


Fig. S14. ^1H NMR spectra of 2-Acetylphenyl 4-Methoxybenzoate

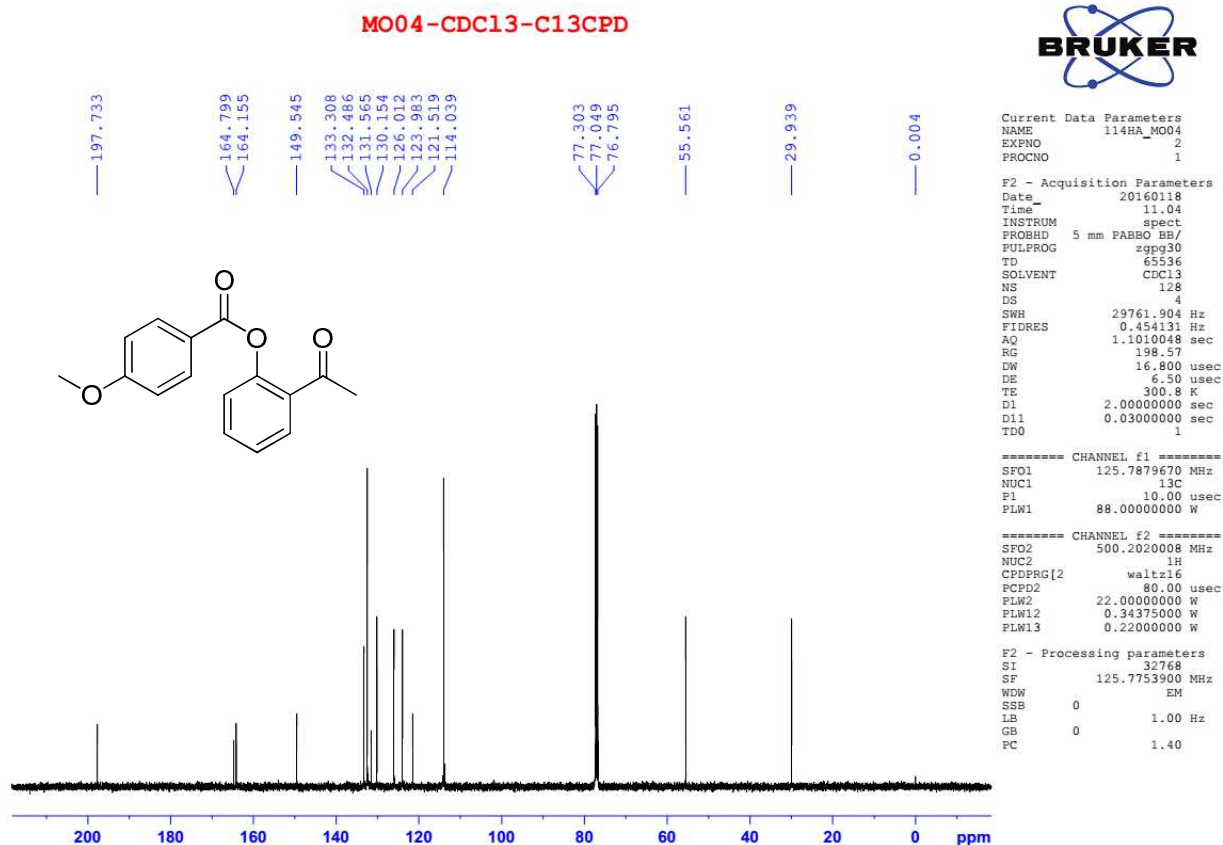


Fig. S15. ^{13}C NMR spectra of 2-Acetylphenyl 4-Methoxybenzoate

➤ 2-Acetylphenyl 4-Methoxybenzoate

Prepared as shown in the general experimental procedure and purified on silica gel (hexane/ethyl acetate = 2:1), yellow liquid, 65% yield. ^1H NMR (500 MHz, CDCl_3 , ppm): δ = 8.17 (d, J = 8.5 Hz, 2H), δ = 7.85 (dd, J = 7.5 Hz, J = 1.5 Hz, 1H), δ = 7.57 (dt, J = 7.5 Hz, J = 1.5 Hz, 1H), δ = 7.35 (t, J = 7.5 Hz, 1H), δ = 7.23 (d, J = 8.5 Hz, 1H), δ = 7.00 (d, J = 7.5 Hz, 2H), δ = 3.89 (s, CH_3), δ = 2.53 (s, CH_3). ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ = 197.7; 164.8; 164.1; 149.5; 133.3; 132.5; 131.6; 130.1; 126; 124; 121.5; 114; 55.6; 29.9

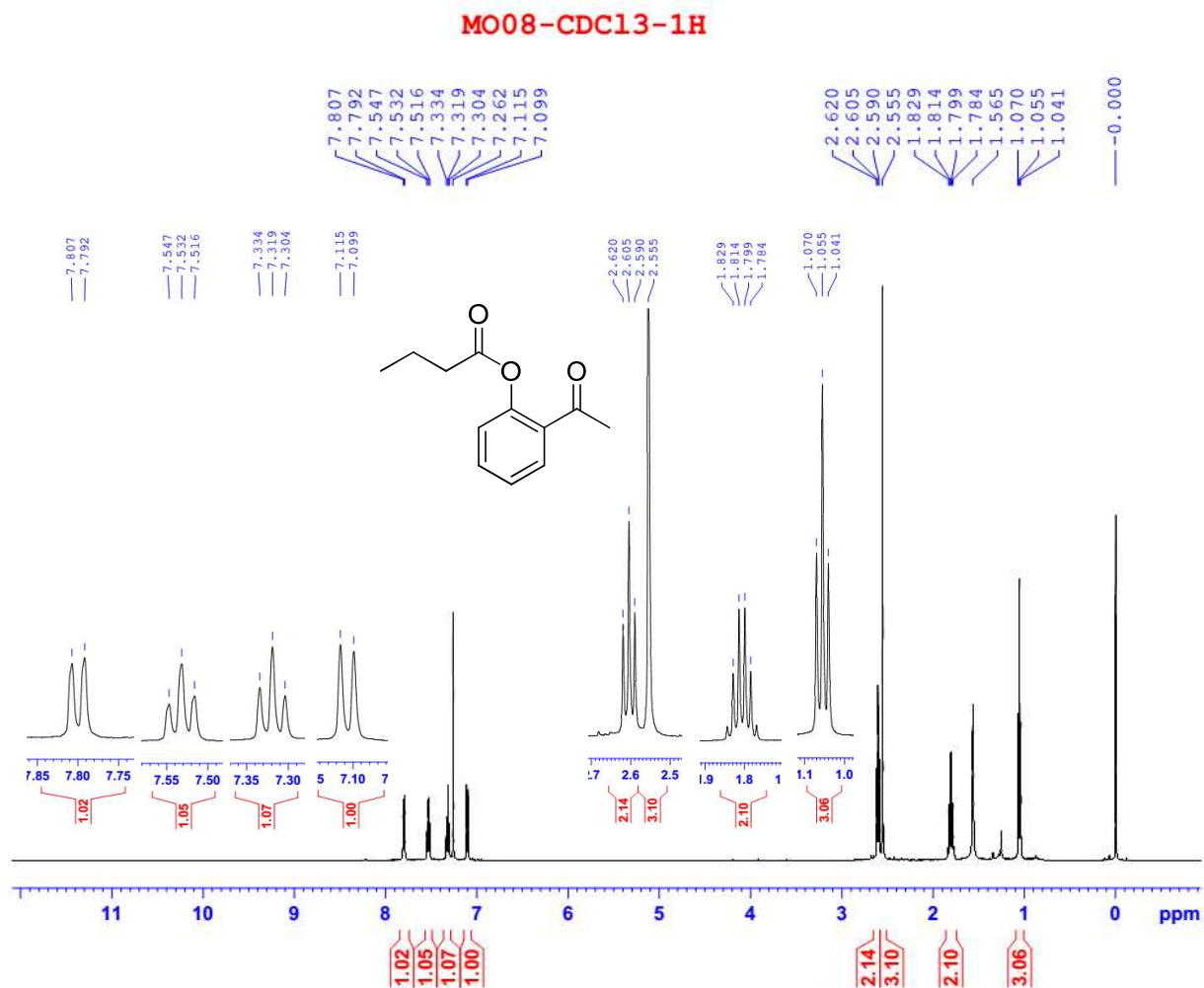


Fig. S16. ^1H NMR spectra of 2-Acetylphenyl Butyrate

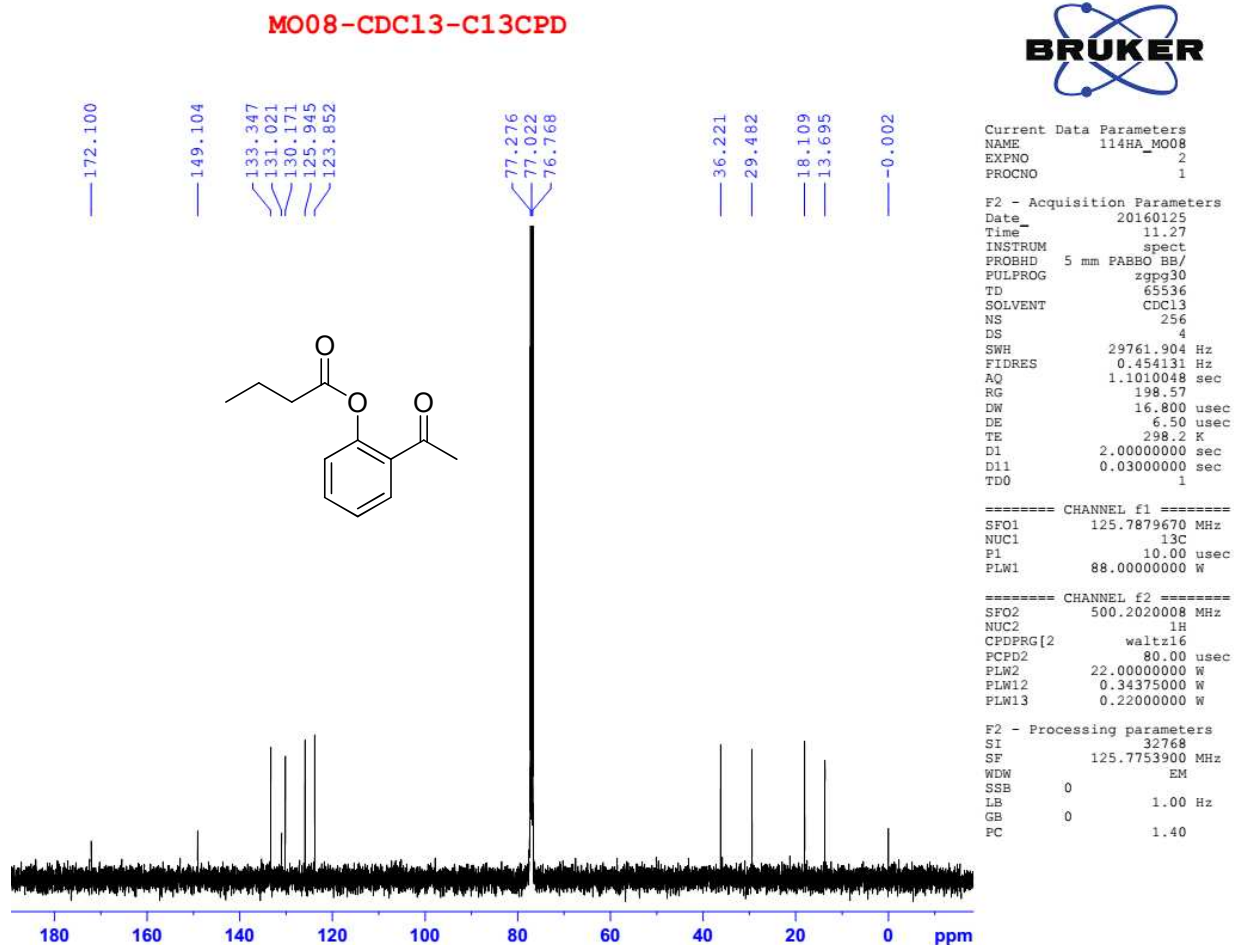


Fig. S17. ^{13}C NMR spectra of 2-Acetylphenyl Butyrate

➤ 2-Acetylphenyl Butyrate

Prepared as shown in the general experimental procedure and purified on silica gel (hexane/ethyl acetate = 6:1), yellow liquid, 52% yield. ^1H NMR (500 MHz, CDCl_3 , ppm): δ = 7.80 (d, J = 7.5 Hz, 1H), δ = 7.53 (t, J = 7.5 Hz, 1H), δ = 7.32 (t, J = 7.5 Hz, 1H), δ = 7.11 (d, J = 8 Hz, 1H), δ = 2.61 (t, J = 7.5 Hz, CH_2), δ = 2.55 (s, CH_3), δ = 1.81 (m, 2H), δ = 1.05 (t, J = 7.5, CH_3). ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ = 172.1; 149.1; 133.3; 131; 130.2; 125.9; 123.8; 36.2; 29.5; 18.1; 13.7

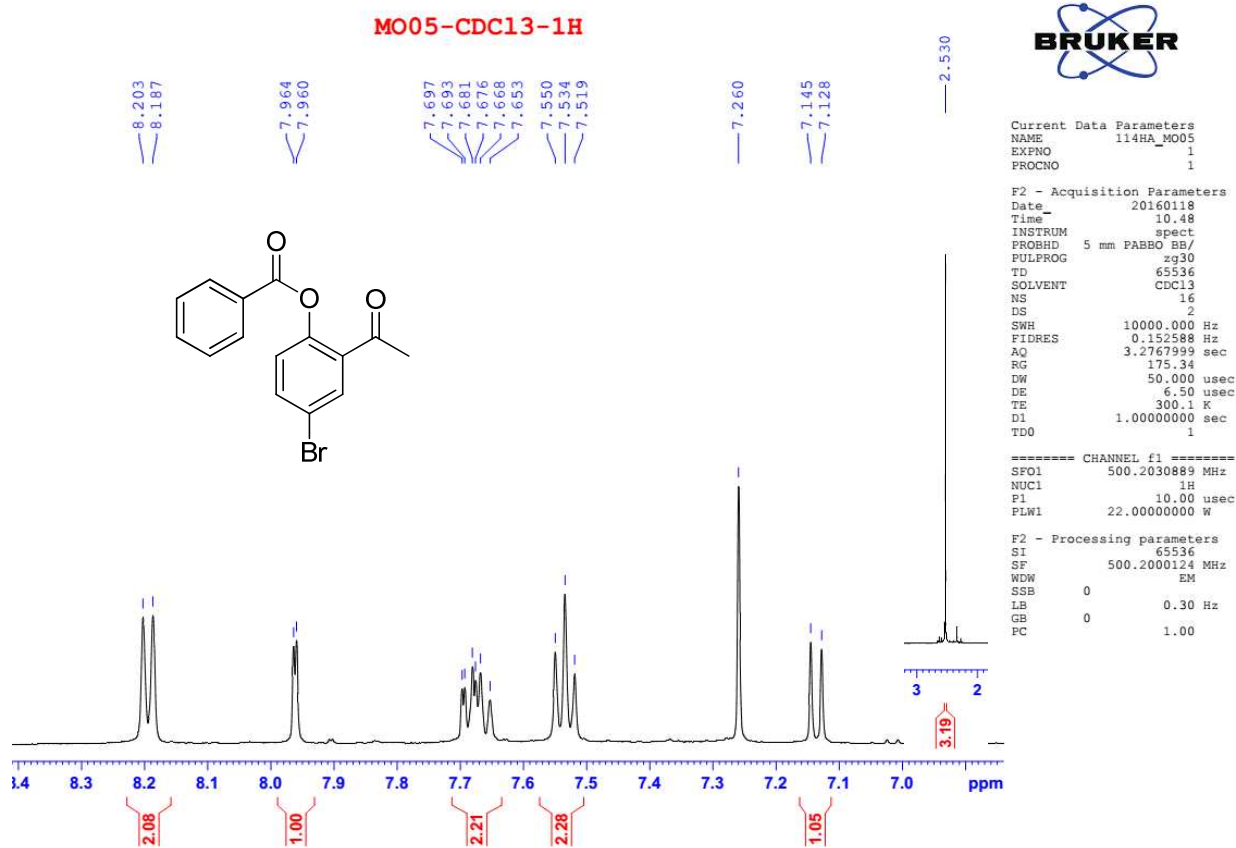


Fig. S18. ^1H NMR spectra of 2-Acetyl-5-bromophenyl Benzoate

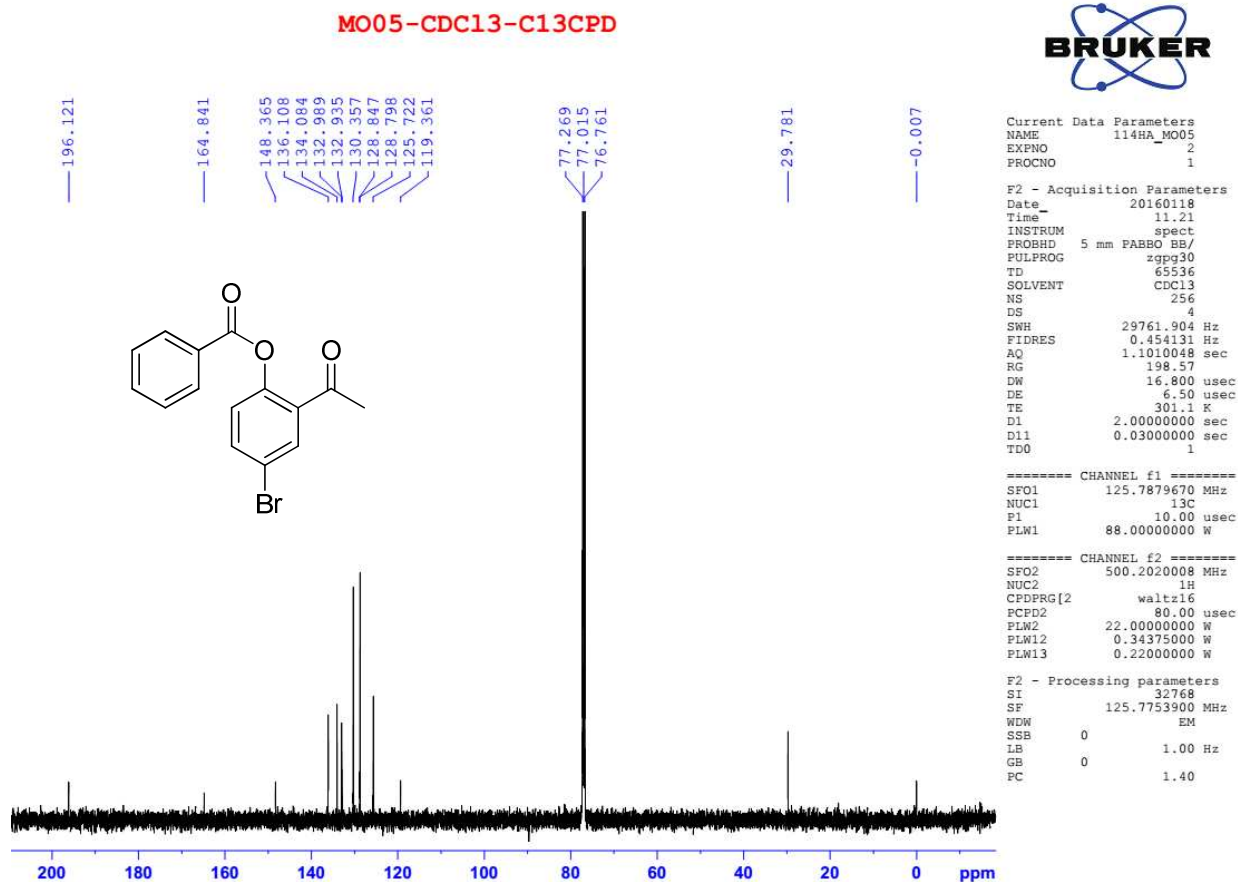


Fig. S19. ^{13}C NMR spectra of 2-Acetyl-5-bromophenyl Benzoate

➤ 2-Acetyl-5-bromophenyl Benzoate

Prepared as shown in the general experimental procedure and purified on silica gel (hexane/ethyl acetate = 6:1), yellow liquid, 60% yield. ^1H NMR (500 MHz, CDCl_3 , ppm): δ = 8.2 (d, J = 8 Hz, 2H), δ = 7.93 (d, J = 2 Hz, 1H), δ = 7.70 ÷ 7.65 (m, 2H), δ = 7.53 (t, J = 8 Hz, 2H), δ = 7.14 (d, J = 8.5 Hz, 1H), δ = 2.53 (s, CH_3). ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ = 196.1; 164.8; 148.4; 136.1; 134; 133; 132.9; 130.3; 128.8; 128.7; 125.7; 119.4; 29.8

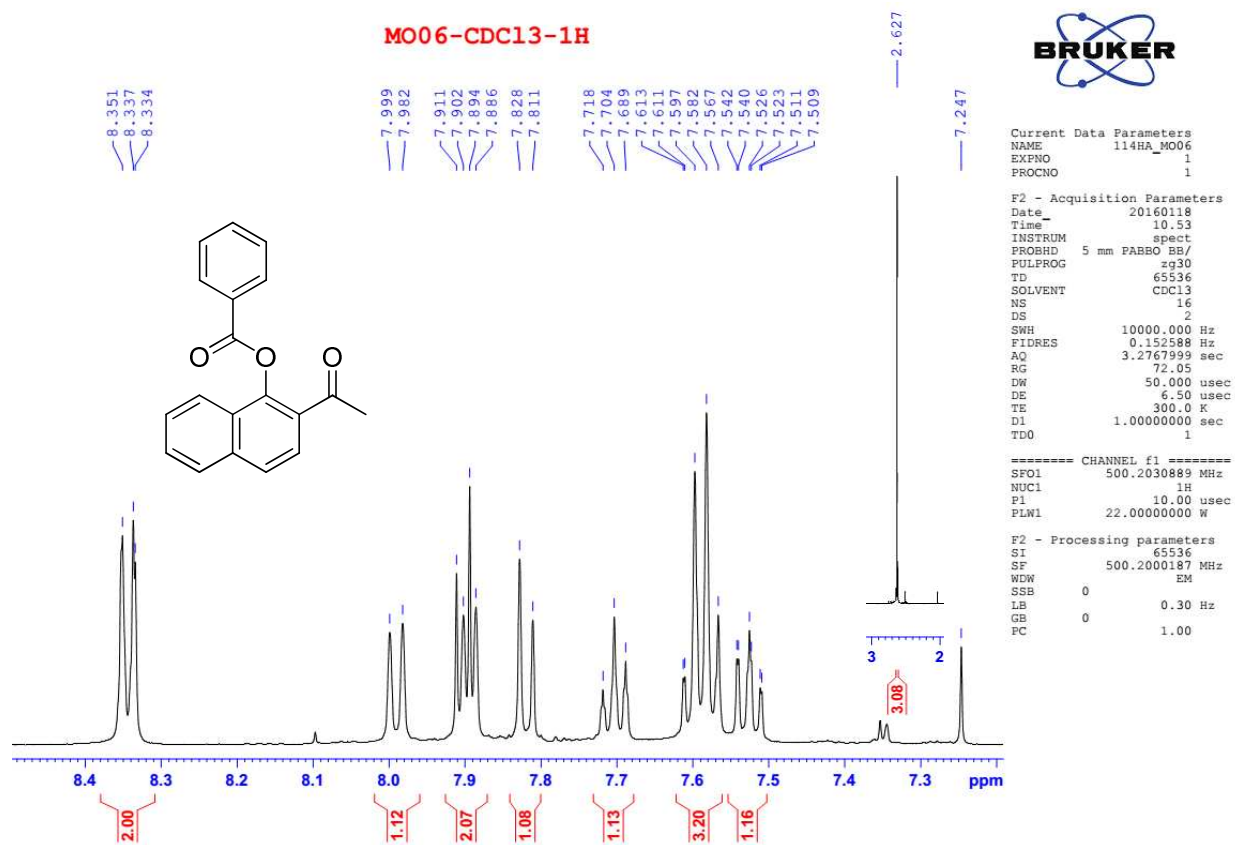


Fig. S20. ^1H NMR spectra of 2-Acetylnaphthyl Benzoate

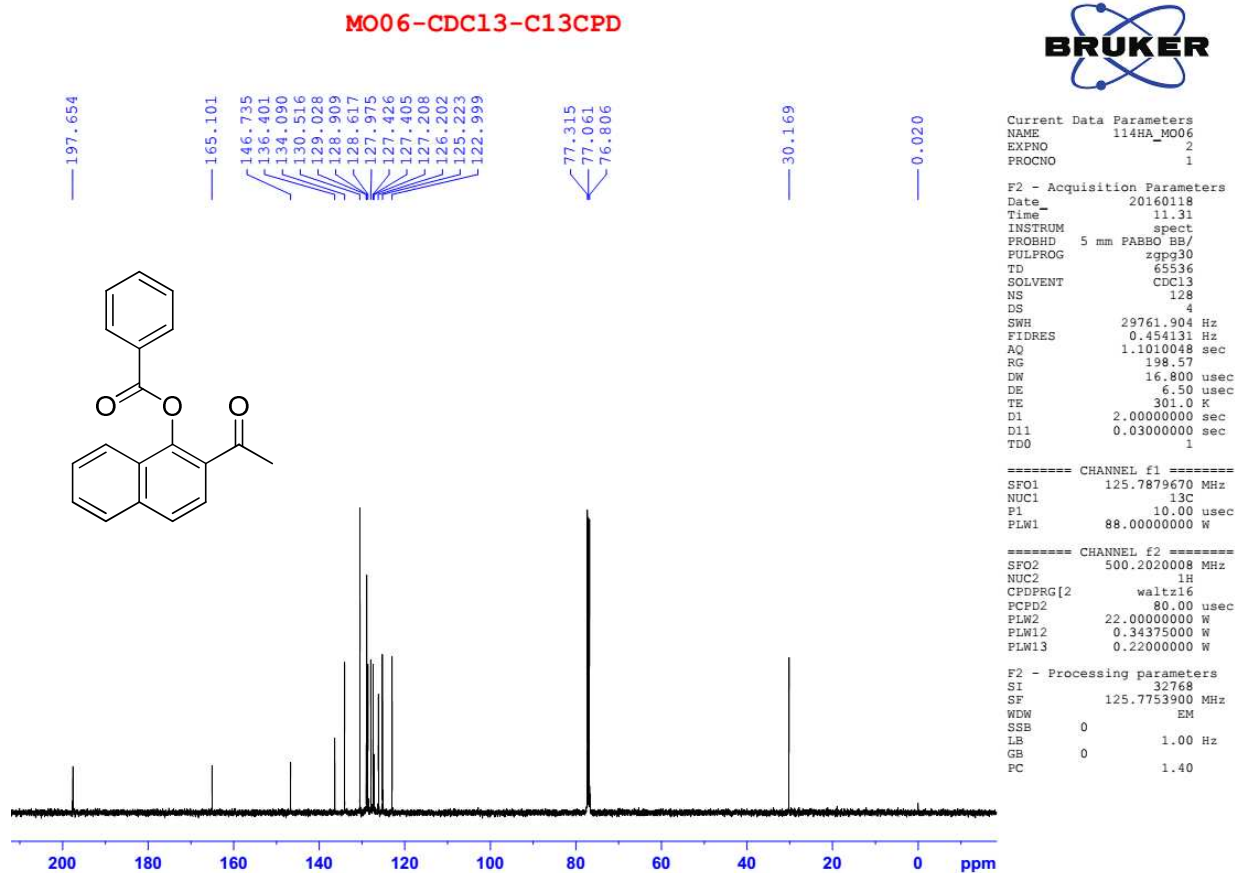


Fig. S21. ¹³C NMR spectra of 2-Acetylnaphthyl Benzoate

➤ 2-Acetylnaphthyl Benzoate

Prepared as shown in the general experimental procedure and purified on silica gel (hexane/ethyl acetate = 6:1), yellow liquid, 50% yield. ¹H NMR (500 MHz, CDCl₃, ppm): δ = 8.34 (d, *J* = 8.5 Hz, 2H), δ = 7.99 (d, *J* = 8.5 Hz, 1H), δ = 7.90 (q, *J* = 4 Hz, 2H), δ = 7.82 (d, *J* = 8.5 Hz, 1H), δ = 7.70 (t, *J* = 7.5 Hz, 1H), δ = 7.61 ÷ 7.57 (m, 3H), δ = 7.52 (t, *J* = 7.5 Hz, 1H), δ = 2.63 (s, CH₃). ¹³C NMR (125 MHz, CDCl₃, ppm): δ = 197.6; 165.1; 146.7; 136.4; 134.1; 130.5; 129; 128.9; 128.6; 128; 127.5; 127.4; 127.2; 126.2; 125.2; 123; 30.2

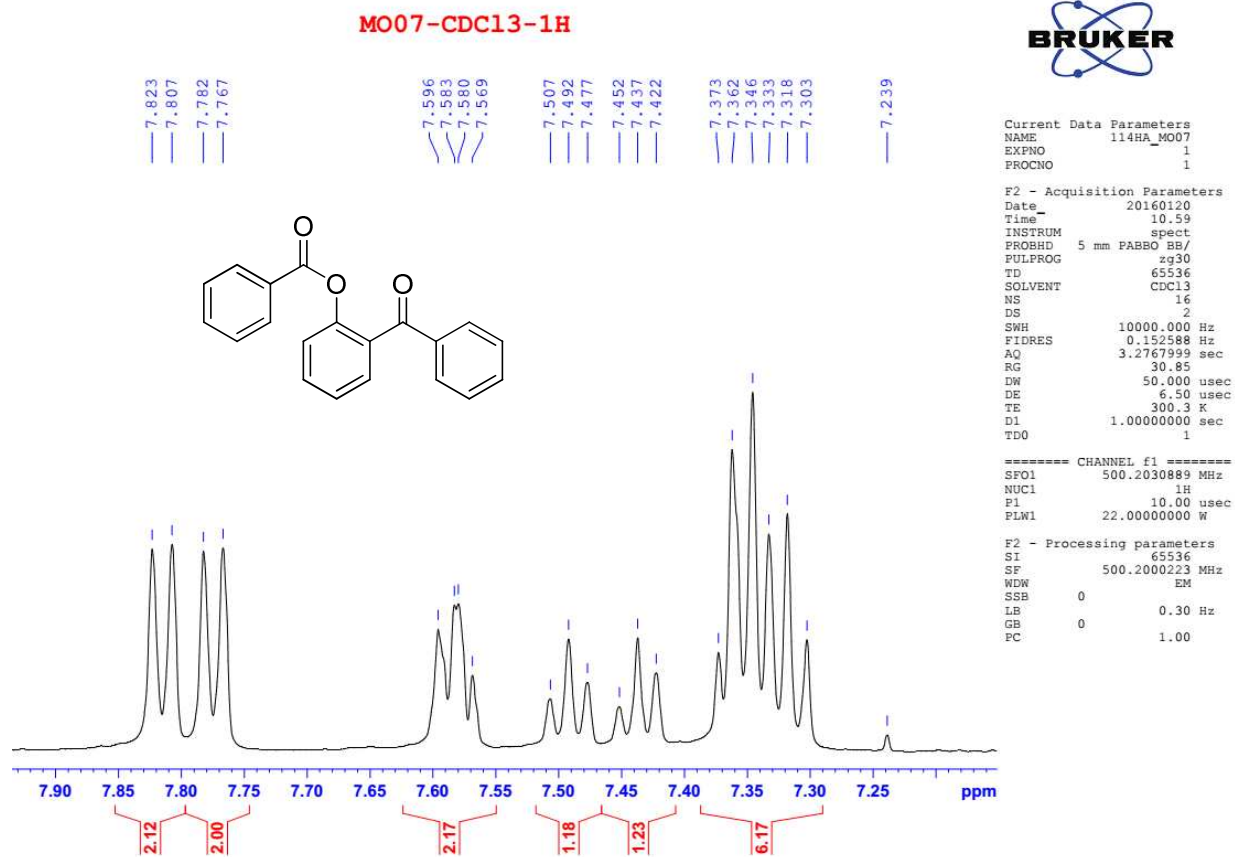


Fig. S22. ^1H NMR spectra of 2-Benzoylphenyl Benzoate

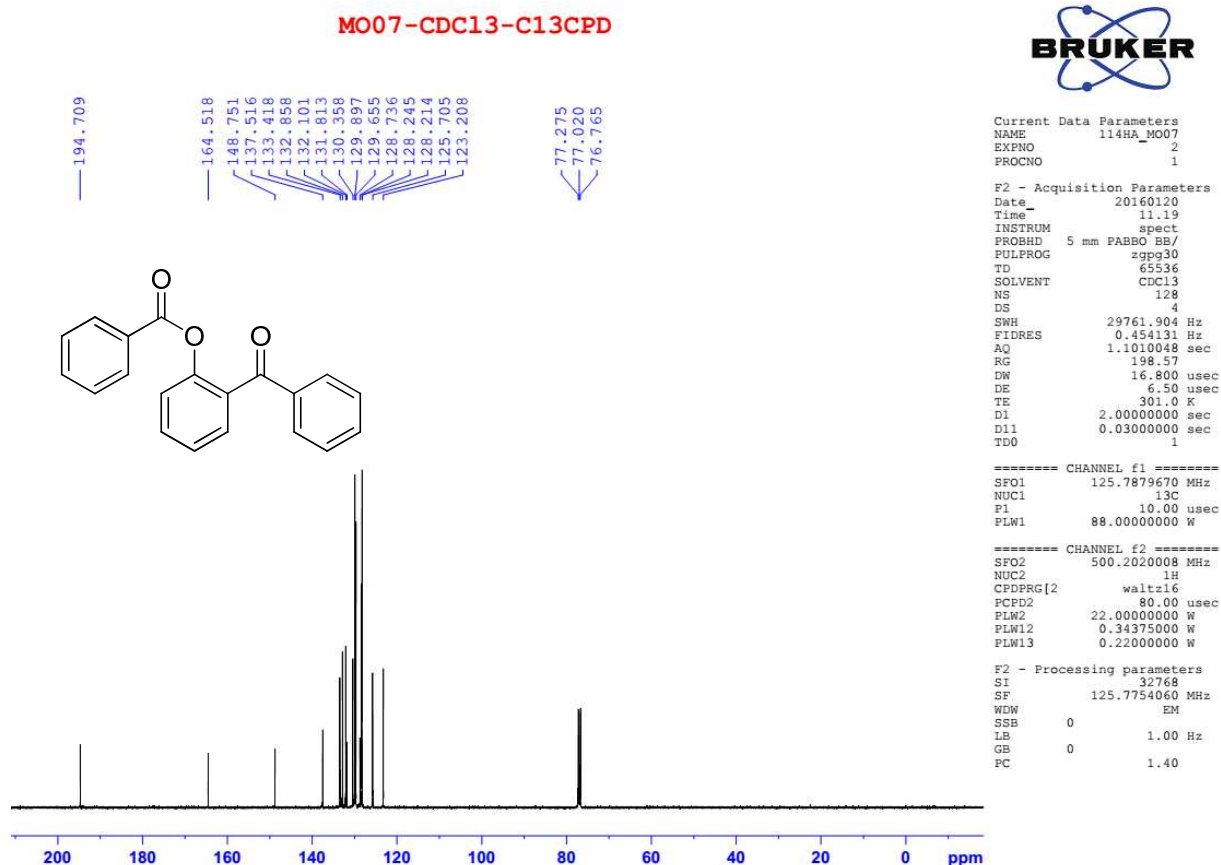


Fig. S23. ¹³C NMR spectra of 2-Benzoylphenyl Benzoate

➤ 2-Benzoylphenyl Benzoate

Prepared as shown in the general experimental procedure and purified on silica gel (hexane/ethyl acetate = 8:1), yellow liquid, 55% yield. ¹H NMR (500 MHz, CDCl₃, ppm): δ = 7.82 (d, *J* = 8 Hz, 2H), δ = 7.77 (d, *J* = 7.5 Hz, 2H), δ = 7.58 (t, *J* = 7 Hz, 2H), δ = 7.49 (t, *J* = 7.5 Hz, 1H), δ = 7.44 (t, *J* = 7.5 Hz, 1H), δ = 7.37 ÷ 7.30 (m, 6H). ¹³C NMR (125 MHz, CDCl₃, ppm): δ = 194.7; 164.5; 148.7; 137.5; 133.4; 132.8; 132.1; 131.8; 130.3; 129.9; 129.6; 128.7; 128.2; 128.1; 125.7; 123.2