Supporting Information

A Direct Oxidative Esterification of Aldehydes with Alcohols Mediated by Photochemical C-H Bromination

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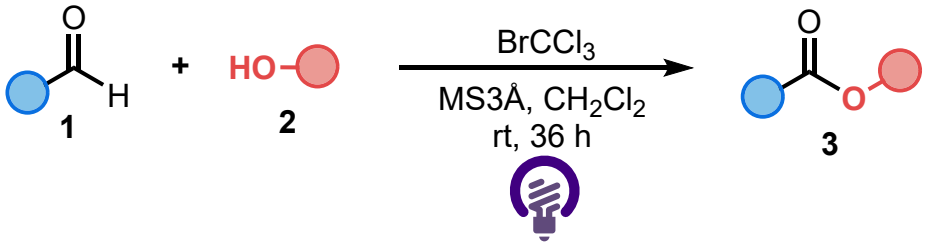
1. General information

Reagents were used as received from commercial suppliers unless otherwise indicated. Heating reactions were conducted by using an oil bath. Analytical thin layer chromatography (TLC) was performed with aluminum TLC plates (Merck TLC silica gel 60F254). Column chromatography was performed with Kanto Chemical silica gel 60N (40-100 mesh, spherical, neutral). IR spectra were recorded on IRSpirit-T. ^{1}H and ^{13}C NMR spectra were recorded on a Varian NMR System PS600 or a Varian 400MR ASW. Chemical shifts in the NMR spectra are reported in ppm with reference to the internal residual solvents (^{1}H NMR, $CDCl_3$ 7.26 ppm, DMSO 2.50 ppm; ^{13}C NMR, $CDCl_3$ 77.0 ppm). The following abbreviations are used to designate the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High-resolution mass spectra were recorded on Bruker micrOTOF II (ESI–TOF–MS). All melting points are reported in degree Celsius (°C) (uncorrected) and were measured on a YAZAWA (BY-2) micro melting point. Photochemical reaction was carried out with a photoreactor (EvoluChem™ PhotoRedOx Box) and LED (HCK1012-01-013, 380 nm, 18 W and HCK1012-01-011, 365 nm, 18W).

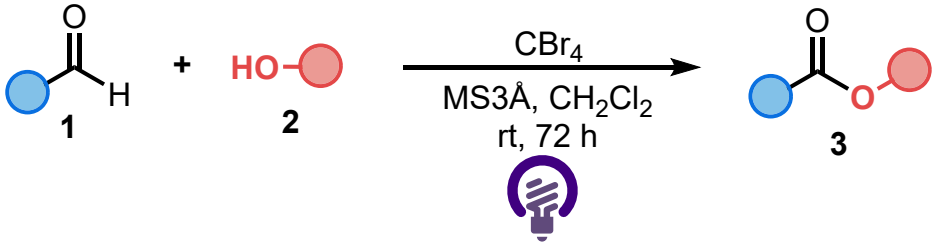
2. Experimental section

General procedure for the photochemical esterification (Method A)



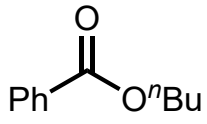
Aldehyde **1** (0.2 mmol), alcohol **2** (0.26 mmol), bromotrichloromethane (60.0 µL, 0.6 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL) were added into a 4 mL borosilicate vial. After bubbling with argon for 5 min, the resulting solution was stirred at room temperature under light irradiation (λ_{ex} = 380 nm) for 36 h. The reaction mixture was diluted with CH_2Cl_2 and washed with H_2O. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography to give the ester **3**.

General procedure for the photochemical esterification (Method B)



Aldehyde **1** (0.2 mmol), alcohol **2** (0.26 mmol), tetrabromomethane (199.0 mg, 0.6 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL) were added into a 4 mL borosilicate vial. After bubbling with argon for 5 min, the resulting solution was stirred at room temperature under light irradiation (λ_{ex} = 365 nm) for 72 h. The reaction mixture was diluted with CH_2Cl_2 and washed with H_2O. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography to give the ester **3**.

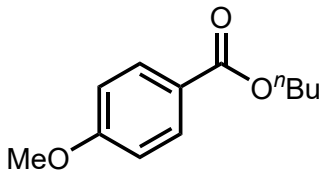
Butyl benzoate (3a, Method A)[1]



The reaction was carried out with benzaldehyde **1a** (20.4 μL, 0.2 mmol), 1-butanol **2a** (24.0 μL, 0.26 mmol), bromotrichloromethane (60.0 μL, 0.6 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by flash chromatography (hexane/EtOAc = 100:1) to give the product **3a** (30.5 mg, 86%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.4, 1.2 Hz, 2H), 7.55 (tt, J = 7.5, 1.5 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 4.33 (t, J = 6.6 Hz, 2H), 1.78-1.73 (m, 2H), 1.52-1.45 (m, 2H), 0.98 (t, J = 7.5 Hz, 3H).

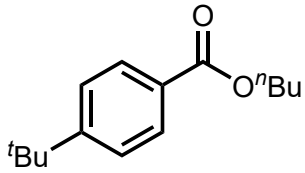
Butyl 4-methoxybenzoate (3b, Method A)[1]



The reaction was carried out with *p*-methoxy benzaldehyde **1b** (24.3 μL, 0.2 mmol), 1-butanol **2a** (24.0 μL, 0.26 mmol), bromotrichloromethane (60.0 μL, 0.6 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by flash chromatography (hexane/EtOAc = 70:1 to 20:1) to give the product **3b** (36.1 mg, 87%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, J = 9.0 Hz, 2H), 6.91 (d, J = 9.0 Hz, 2H), 4.29 (t, J = 6.6 Hz, 2H), 3.86 (s, 3H), 1.76-1.71 (m, 2H), 1.50-1.44 (m, 2H), 0.97 (t, J = 7.5 Hz, 3H).

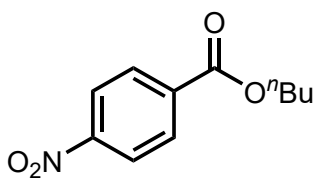
Butyl 4-(*tert*-butyl)benzoate (3c, Method A)[2]



The reaction was carried out with 4-(*tert*-butyl)benzaldehyde **1c** (33.4 μL, 0.2 mmol), 1-butanol **2a** (24.0 μL, 0.26 mmol), bromotrichloromethane (60.0 μL, 0.6 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by PTLC (hexane/EtOAc = 10:1) to give the product **3c** (34.4 mg, 73%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.8 Hz, 2H), 7.45 (d J = 8.8 Hz, 2H), 4.31 (t, J = 6.6 Hz, 2H), 1.78-1.71 (m, 2H), 1.52-1.42 (m, 2H), 1.34 (s, 9H), 0.98 (t, J = 7.4 Hz, 3H).

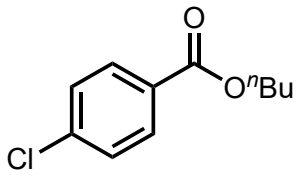
Butyl 4-nitrobenzoate (3d, Method B)[1]



The reaction was carried out with *p*-nitro benzaldehyde **1d** (30.2 mg, 0.2 mmol), 1-butanol **2a** (24.0 μL, 0.26 mmol), tetrabromomethane (199.0 mg, 0.6 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by PTLC

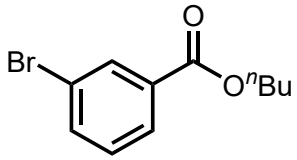
(hexane/EtOAc = 10:1) to give the product **3d** (36.4 mg, 82%) as a colorless oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 (d, J = 8.4 Hz, 2H), 8.21 (d, J = 9.0 Hz, 2H), 4.38 (t, J = 6.9 Hz, 2H), 1.81-1.76 (m, 2H), 1.52-1.46 (m, 2H), 1.00 (t, J = 7.5 Hz, 3H).

Butyl 4-chlorobenzoate (3e, Method A)[3]



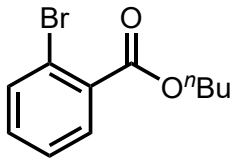
The reaction was carried out with 4-chlorobenzaldehyde **1e** (28.1 mg, 0.2 mmol), 1-butanol **2a** (24.0 μL, 0.26 mmol), bromotrichloromethane (60.0 μL, 0.6 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by PTLC (preparative thin-layer chromatography) (hexane/EtOAc = 10:1) to give the product **3e** (20.8 mg, 49%) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.8 Hz, 2H), 7.41 (d, J = 8.8 Hz, 2H), 4.32 (t, J = 6.6 Hz, 2H), 1.78-1.71 (m, 2H), 1.52-1.42 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H).

Butyl 3-bromobenzoate (3f, Method A)[3]



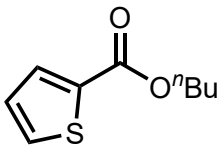
The reaction was carried out with 3-bromobenzaldehyde **1f** (23.4 μL, 0.2 mmol), 1-butanol **2a** (24.0 μL, 0.26 mmol), bromotrichloromethane (60.0 μL, 0.6 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by flash chromatography (hexane/EtOAc = 100:1 to 50:1) to give the product **3f** (29.7 mg, 58%) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (t, J = 1.6 Hz, 1H), 7.97 (dt, J = 7.6, 1.4 Hz, 1H), 7.68 (ddd, J = 8.0, 2.0, 1.2 Hz, 1H), 7.32 (t, J = 7.8 Hz, 1H), 4.33 (t, J = 6.8 Hz, 2H), 1.81-1.72 (m, 2H), 1.52-1.43 (m, 2H), 0.98 (t, J = 7.6 Hz, 3H).

Butyl 2-bromobenzoate (3g, Method A)[4]



The reaction was carried out with 2-bromobenzaldehyde **1g** (23.1 μL, 0.2 mmol), 1-butanol **2a** (24.0 μL, 0.26 mmol), bromotrichloromethane (60.0 μL, 0.6 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by flash chromatography (hexane/EtOAc = 100:1 to 50:1) to give the product **3g** (31.2 mg, 61%) as a colorless oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (dd, J = 7.8, 1.8 Hz, 1H), 7.66 (dd, J = 7.2, 1.2 Hz, 1H), 7.36 (td, J = 7.8, 1.2 Hz, 1H), 7.32 (td, J = 7.8, 1.8 Hz, 1H), 4.35 (t, J = 6.6 Hz, 2H), 1.78-1.74 (m, 2H), 1.52-1.46 (m, 2H), 0.98 (t, J = 7.5 Hz, 3H).

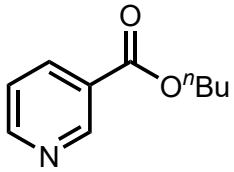
Butyl thiophene-2-carboxylate (3h, Method A)[5]



The reaction was carried out with 2-thiophenecarboxaldehyde **1h** (18,2 μL, 0.2 mmol), 1-butanol **2a** (24.0 μL, 0.26 mmol), bromotrichloromethane (60.0 μL, 0.6 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by flash chromatography (hexane/EtOAc = 100:1) to give the product **3h** (11.6 mg, 31%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (dd, J = 3.6, 1.8 Hz, 1H), 7.54 (dd, J = 4.8, 1.2 Hz, 1H), 7.10 (dd, J = 5.4, 3.6 Hz, 1H), 4.30 (t, J = 6.6 Hz, 2H), 1.76-1.71 (m, 2H), 1.49-1.43 (m, 2H), 0.98 (t, J =7.2 Hz, 3H).

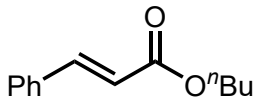
Butyl nicotinate (3i, Method A)[1]



The reaction was carried out with 3-pyridinecarboxaldehyde **1i** (18.8 μL, 0.2 mmol), 1-butanol **2a** (24.0 μL, 0.26 mmol), bromotrichloromethane (60.0 μL, 0.6 mmol), $NaHCO_3$ (118.0 mg, 1.4 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by flash chromatography (hexane/EtOAc = 10:1 to 7:1) to give the product **3i** (25.1 mg, 70%) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.22 (d, J = 1.8 Hz, 1H), 8.77 (dd, J = 5.4, 1.8 Hz, 1H), 8.30 (dt, J = 7.8, 1.8 Hz, 1H), 7.40 (ddd, J = 7.8, 4.8, 0.6 Hz, 1H), 4.36 (t, J = 6.9 Hz, 2H), 1.79-1.74 (m, 2H), 1.51-1.45 (m, 2H), 0.98 (t, J = 7.5 Hz, 3H).

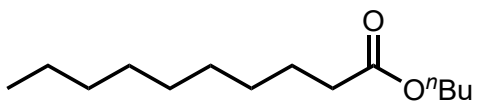
Butyl cinnamate (3j Method B)[6]



The reaction was carried out with cinnamaldehyde **1j** (25.2mg, 0.2 mmol), 1-butanol **2a** (24.0 μL, 0.26 mmol), tetrabromomethane (199.0 mg, 0.6 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by flash chromatography (hexane/EtOAc = 100:1) to give the product **3j** (28.5 mg, 70%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, J = 15.6 Hz, 1H), 7.54-7.52 (m, 2H), 7.40-7.37 (m, 3H), 6.44 (d, J =15.6 Hz, 1H), 4.21 (t, J = 6.9 Hz, 2H), 1.72-1.67 (m, 2H), 1.46-1.41 (m, 2H), 0.97 (t, J = 7.5 Hz, 3H).

Butyl decanoate (3k, Method A)[7]

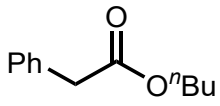


The reaction was carried out with decanal **1k** (37.7 μL, 0.2 mmol), 1-butanol **2a** (24.0 μL, 0.26 mmol), bromotrichloromethane (60.0 μL, 0.6 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by flash chromatography (hexane/EtOAc = 100:1) to give the product **3k** (44.0 mg, 96%) as a

colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.06 (t, J = 6.9 Hz, 2H), 2.28 (t, J = 7.5 Hz, 2H), 1.66-1.57 (m, 4H), 1.42-1.34 (m, 2H), 1.31-1.25 (m, 12H), 0.93 (t, J = 7.5 Hz, 3H), 0.87 (t, J = 7.2 Hz, 3H).

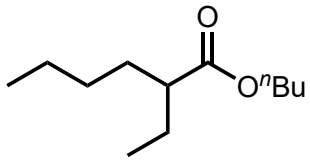
Butyl 2-phenylacetate (3l, Method B)[1]



The reaction was carried out with phenylacetaldehyde **1l** (22.9 mg, 0.2 mmol), 1-butanol **2a** (24.0 μL, 0.26 mmol), tetrabromomethane (199.0 mg, 0.6 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by flash chromatography (hexane/EtOAc = 100:1) to give the product **3l** (20.7 mg, 54%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34-7.31 (m, 2H), 7.29-7.24 (m, 3H), 4.09 (t, J = 6.6 Hz, 2H), 3.61 (s, 2H), 1.62-1.57 (m, 2H), 1.37-1.31 (m, 2H), 0.91 (t, J = 7.5 Hz, 3H).

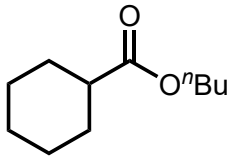
Butyl 2-ethylhexanoate (3m, Method A)[1]



The reaction was carried out with 2-ethylhexanal **1m** (31.3 μL, 0.2 mmol), 1-butanol **2a** (24.0 μL, 0.26 mmol), bromotrichloromethane (60.0 μL, 0.6 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by flash chromatography (hexane/EtOAc = 100:1) to give the product **3m** (32.0 mg, 80%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.08 (t, J = 6.6 Hz, 2H), 2.27-2.23 (m, 1H), 1.64-1.57 (m, 5H), 1.54-1.21 (m, 7H), 0.94 (t, J = 7.8 Hz, 3H), 0.90-0.87 (m, 6H).

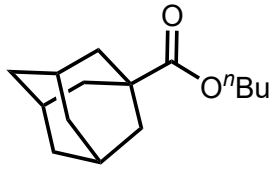
Butyl cyclohexanecarboxylate (3n, Method A)[1]



The reaction was carried out with aldehyde **1n** (37.7 μL, 0.2 mmol), 1-butanol **2a** (24.0 μL, 0.26 mmol), bromotrichloromethane (60.0 μL, 0.6 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by flash chromatography (hexane/EtOAc = 100:1) to give the product **3n** (30.4 mg, 82%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.05 (t, J = 6.6 Hz, 2H), 2.28 (tt, J = 11.4, 3.6 Hz, 1H), 1.90-1.88 (m, 2H), 1.76-1.73 (m, 2H), 1.64-1.57 (m, 3H), 1.46 -1.34 (m, 4H), 1.31-1.18 (m, 3H), 0.93 (t, J = 7.2 Hz, 3H).

Butyl adamantane-1-carboxylate (3o, Method A)[1]

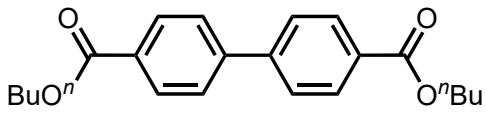


The reaction was carried out with aldehyde **1o**[2] (37.7 μL, 0.2

mmol), 1-butanol **2a** (24.0 μL, 0.26 mmol), bromotrichloromethane (60.0 μL, 0.6 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by flash chromatography (hexane/EtOAc = 100:1) to give the product **3o** (45.7 mg, 97%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.04 (t, J = 6.6 Hz, 2H), 2.02-2.00 (m, 3H), 1.88 (d, J = 3.0 Hz, 6H), 1.74-1.68 (m, 6H), 1.62-1.57 (m, 2H), 1.41-1.35 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H).

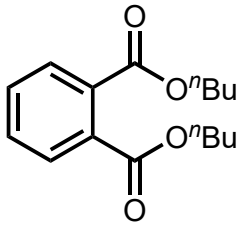
Dibutyl [1,1'-biphenyl]-4,4'-dicarboxylate (3p, Method B)[8]



The reaction was carried out with 4,4'-biphenyldicarboxaldehyde **1p** (26.9 mg, 0.2 mmol), 1-butanol **2a** (110 μL, 1.2 mmol), tetrabromomethane (398.9 mg, 1.2 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by PTLC (hexane/EtOAc = 10:1) to give the product **3p** (45.4 mg, 63%) as awhite solide.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, J = 8.4 Hz, 4H), 7.69 (d, J = 8.4 Hz, 4H), 4.36 (t, J = 6.6 Hz, 4H), 1.82-1.76 (m, 4H), 1.53-1.47 (m, 4H), 1.00 (t, J = 7.5 Hz, 6H).

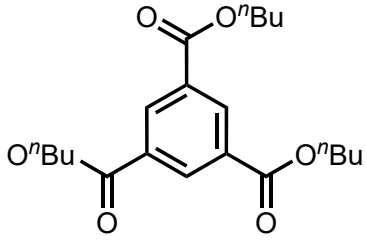
Dibutyl phthalate (3q, Method B)[9]



The reaction was carried out with *o*-phthalaldehyde **1q** (26.9 mg, 0.2 mmol), 1-butanol **2a** (110 μL, 1.2 mmol), tetrabromomethane (398.9 mg, 1.2 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by PTLC (hexane/EtOAc = 10:1) to give the product **3q** (24.4 mg, 42%) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73-7.70 (m, 2H), 7.54-7.51 (m, 2H), 4.35 (t, J = 6.6 Hz, 2H), 1.74-1.69 (m, 4H), 1.47-1.41 (m, 4H), 0.96 (t, J = 7.2 Hz, 3H).

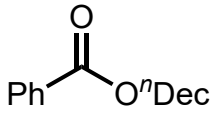
Tributyl benzene-1,3,5-tricarboxylate (3r, Method B)[10]



The reaction was carried out with benzene-1,3,5-tricarbaldehyde **1r** (32.4 mg, 0.2 mmol), 1-butanol **2a** (164 μL, 1.8 mmol), tetrabromomethane (599.5 mg, 1.8 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by PTLC (hexane/EtOAc = 10:1) to give the product **3r** (35.4 mg, 54 %) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.84 (s, 3H), 4.38 (t, J = 6.6 Hz, 2H), 1.81-1.76 (m, 6H), 1.54-1.46 (m, 6H), 0.99 (t, J = 7.5 Hz, 9H).

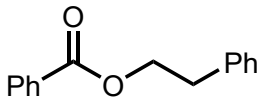
Decyl benzoate (3s, Method A)[1]



The reaction was carried out with benzaldehyde **1a** (20.4 μL, 0.2 mmol), 1-decanol **2s** (49.6 μL, 0.26 mmol), bromotrichloromethane (60.0 μL, 0.6 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by flash chromatography (hexane/EtOAc = 100:1) to give the product **3s** (54.2 mg, 98%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.4, 1.2 Hz, 2H), 7.55 (tt, J = 7.5, 1.5 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 4.32 (t, J = 6.6 Hz, 2H), 1.79-1.74 (m, 2H), 1.47-1.42 (m, 2H), 1.38-1.27 (m, 12H), 0.88 (t, J = 6.9 Hz, 3H).

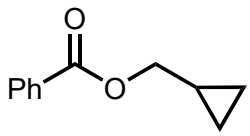
Phenethyl benzoate (3t, Method A)[11]



The reaction was carried out with benzaldehyde **1a** (20.4 μL, 0.2 mmol), 2-phenylethanol **2t** (30.6 μL, 0.26 mmol), bromotrichloromethane (60.0 μL, 0.6 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by flash chromatography (hexane/EtOAc = 300:1 to 100:1) to give the product **3t** (32.4 mg, 72%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.4, 1.2 Hz, 2H), 7.55 (tt, J = 7.5, 1.5 Hz, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.35-7.29 (m, 4H), 7.25-7.24 (m, 1H), 4.54 (t, J = 7.2 Hz, 2H), 3.09 (t, J = 7.2 Hz, 2H).

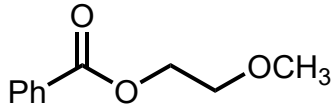
Cyclopropylmethyl benzoate (3u, Method A)[12]



The reaction was carried out with benzaldehyde **1a** (20.4 μL, 0.2 mmol), alcohol **2u** (20.6 μL, 0.26 mmol), bromotrichloromethane (60.0 μL, 0.6 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by PTLC (hexane/EtOAc = 10:1) to give the product **3u** (7.3 mg, 21%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, J = 7.2 Hz, 2H), 7.58 (tt, J = 7.5, 1,2 Hz, 2H), 7.47 (t, J = 7.8 Hz, 2H), 4.36 (d, J = 7.2 Hz, 2H), 1.32-1.25 (m, 2H), 0.67-0.63 (m, 2H),0.41-0.38 (m, 2H).

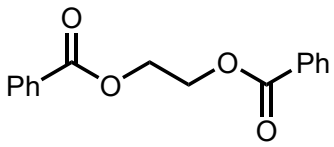
2-Methoxyethyl benzoate (3v, Method A)[13]



The reaction was carried out with benzaldehyde **1a** (20.4 μL, 0.2 mmol), alcohol **2v** (20.6 μL, 0.26 mmol), bromotrichloromethane (60.0 μL, 0.6 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by PTLC (hexane/EtOAc = 10:1) to give the product **3v** (12.9 mg, 36%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (m, J = 7.2 Hz, 2H), 7.56 (tt, J = 7.5, 1.5 Hz, 1H), 7.44 (t, J = 8.1 Hz, 2H), 4.49-4.47 (m, 2H), 3.76-3.73 (m, 1H), 3.44 (s, 3H).

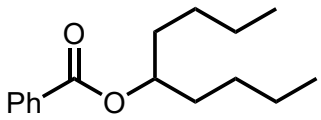
Ethane-1,2-diyl dibenzoate (3w, Method A)[14]



The reaction was carried out with benzaldehyde **1a** (20.4 μL, 0.2 mmol), ethane-1,2-diol **2w** (29 μL, 0.52 mmol), bromotrichloromethane (60.0 μL, 0.6 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by PTLC (hexane/EtOAc = 10:1) to give the product **3w** (13.0 mg, 24%) as a color less oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (dd, J = 7.8, 1.8 Hz, 4H), 7.55 (t, J = 6.9 Hz, 1H), 7.43 (t, J = 7.8 Hz, 4H), 4.66 (s, 4H).

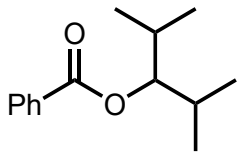
Nonan-5-yl benzoate (3x, Method A)[15]



The reaction was carried out with benzaldehyde **1a** (20.4 μL, 0.2 mmol), 5-nonaol **2x** (45.2 μL, 0.26 mmol), bromotrichloromethane (60.0 μL, 0.6 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by flash chromatography (hexane/EtOAc = 100:1) to give the product **3x** (41.9 mg, 84%) as a color less oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.4, 1.2 Hz, 2H), 7.55 (tt, J = 7.5, 1.2 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 5.15-5.11 (m, 1H), 1.71-1.61 (m, 4H), 1.39-1.29 (m, 8H), 0.90-0.88 (m, 6H).

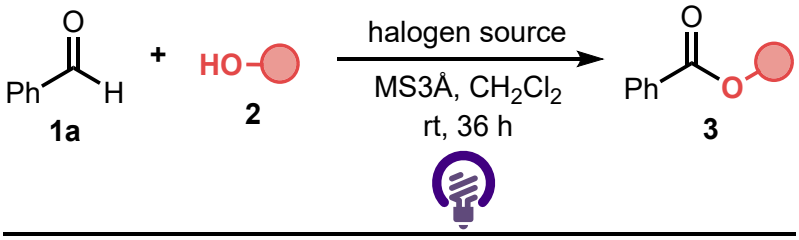
2,4-Dimethylpentan-3-yl benzoate (3y, Method A)[16]

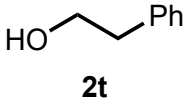
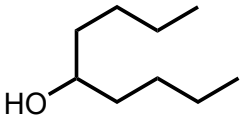


The reaction was carried out with benzaldehyde **1a** (20.4 μL, 0.2 mmol), 2,4-dimethyl-3-pentanol **2y** (36.4 μL, 0.26 mmol), bromotrichloromethane (60.0 μL, 0.6 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL). The residue was purified by flash chromatography (hexane/EtOAc = 100:1) to give the product **3y** (30.1 mg, 68%) as a colorless oil.

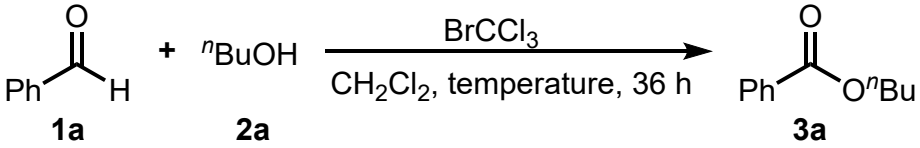
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (dd, J = 8.4, 1.2 Hz, 2H), 7.56 (tt, J = 7.5, 1.2 Hz, 1H), 7.45 (t, J = 7.8 Hz, 2H), 4.85 (t, J = 6.0 Hz, 1H), 2.08-2.00 (m, 2H), 0.96-0.94 (m,12H).

Photochemical esterification with halogen sources



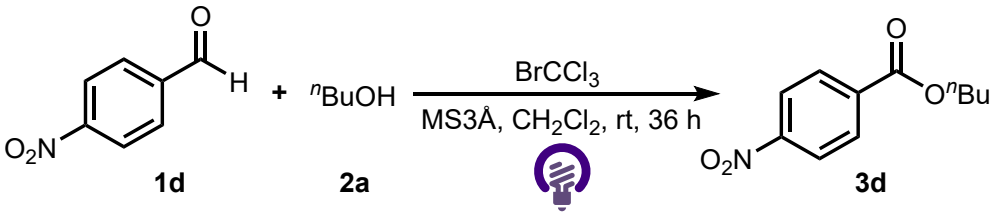
alcohol	halogen source	yield (%)
 2t	$BrCCl_3$	72
	NBS	0
 2x	$BrCCl_3$	82
	NBS	0

Esterification under thermal condition



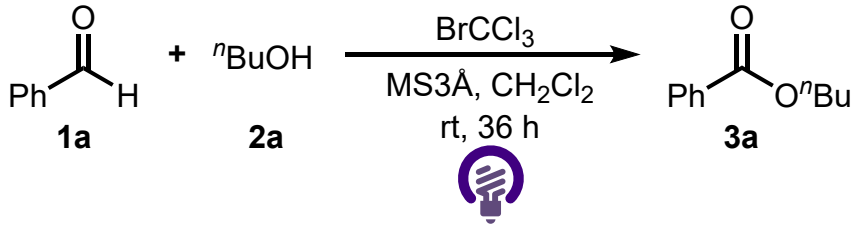
entry	condition	yield (%)
1	380 nm irradiation, rt	86
2	reflux without light irradiation	11

Examination of the photochemical esterification of 4-nitrobenzaldehyde



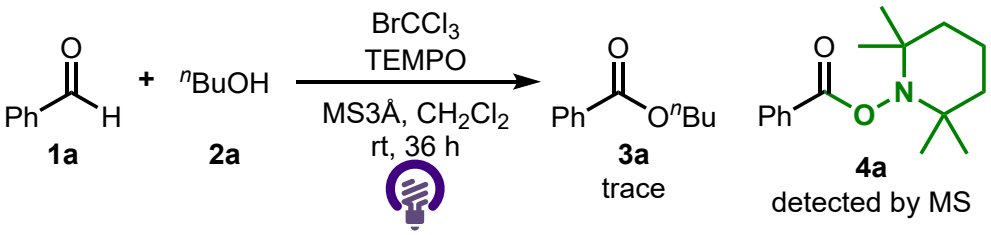
entry	halogen source	light	yield (%)
1	$BrCCl_3$	380 nm LED	23
2	CBr_4	380 nm LED	41
3	CBr_4	365 nm LED	**82**

Photochemical esterification under gram-scale condition

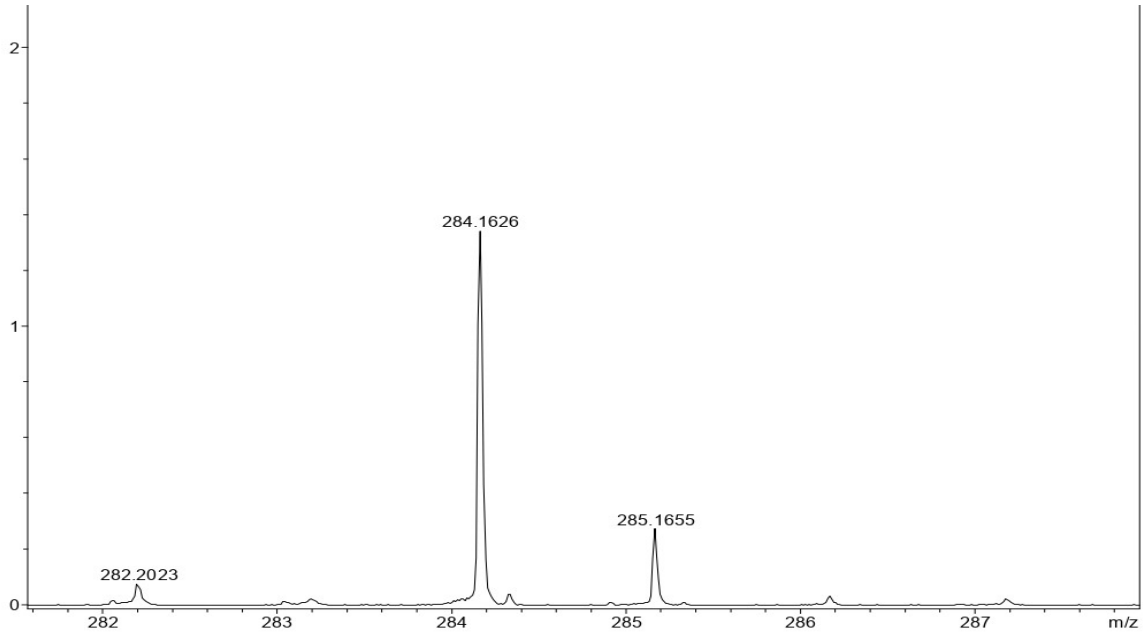


Aldehyde **1a** (1.01 mL, 10 mmol), 1-butanol **2a** (1.1 mL, 12 mmol), bromotrichloromethane (2.94 mL, 3.0 mmol), MS3Å (500 mg), and CH_2Cl_2 (100 mL) were added into a 100 mL 2 neck flask. After bubbling with argon for 5 min, the resulting solution was stirred at room temperature under light irradiation (λ_{ex} = 380 nm × 2) for 36 h. The reaction mixture was diluted with CH_2Cl_2 and washed with H_2O. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (hexane/EtOAc = 50:1) to give the product **3a** (1.15g, 65%) as a colorless oil.

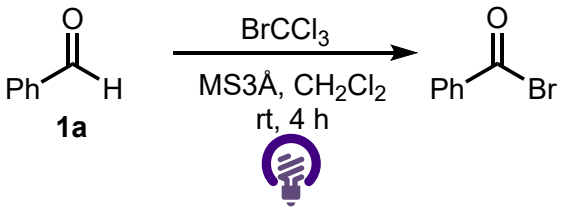
Mechanistic study of the photochemical esterification



Benzaldehyde **1a** (20.4 μL, 0.2 mmol), 1-butanol **2a** (24.0 μL, 0.26 mmol), bromotrichloromethane (60.0 μL, 0.6 mmol), MS3Å (50 mg), TEMPO (93.8 mg, 0.6 mmol) and CH_2Cl_2 (2.0 mL) were added into a 4 mL borosilicate vial. After bubbling with argon for 5 min, the resulting solution was stirred at room temperature under light irradiation (λ_{max} = 380 nm) for 36 h. The reaction mixture was diluted with CH_2Cl_2 and washed with H_2O. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The compound **4a** was detected by HRMS (ESI TOF) analysis (calcd for $C_{16}H_{23}NO_2Na$ $[M + Na]^+$ 284.1626, found 284.1626). Then, the residue was purified by flash chromatography (hexane/EtOAc = 100:1) to give the trace amount of product **3a**.

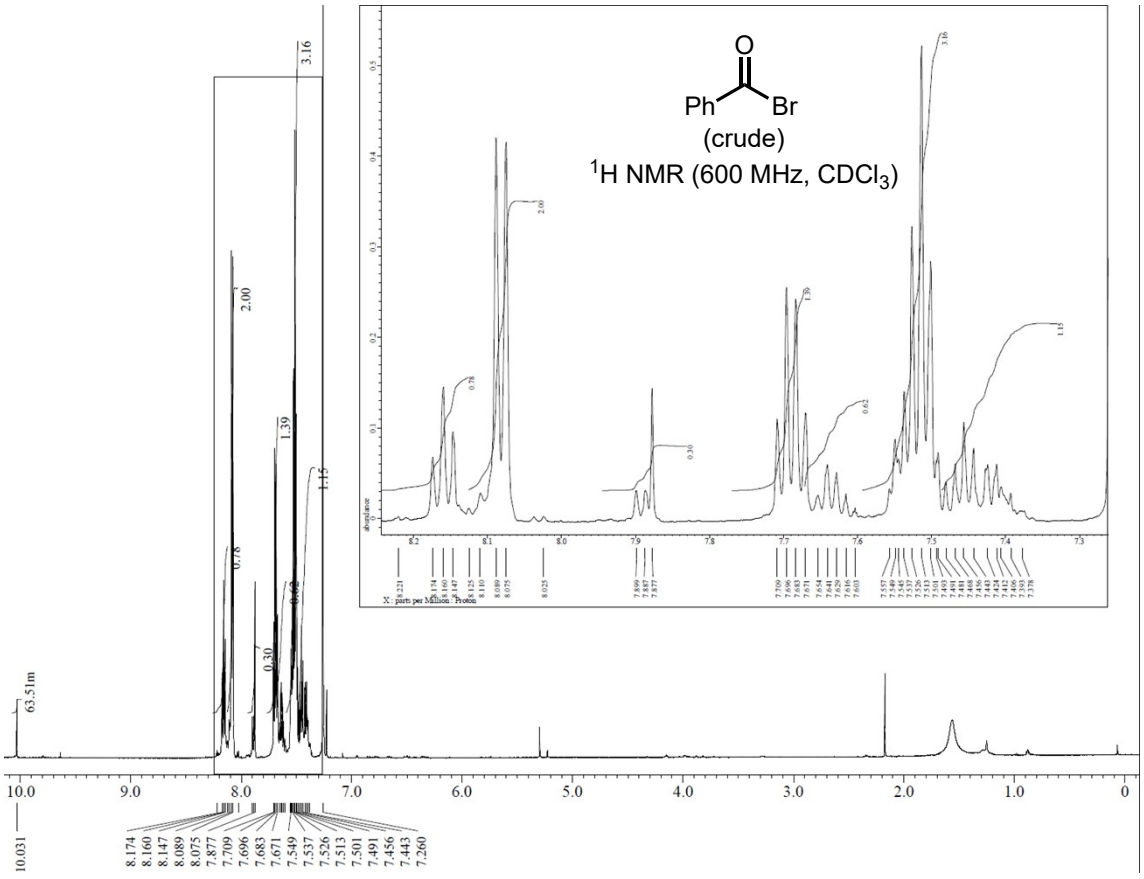


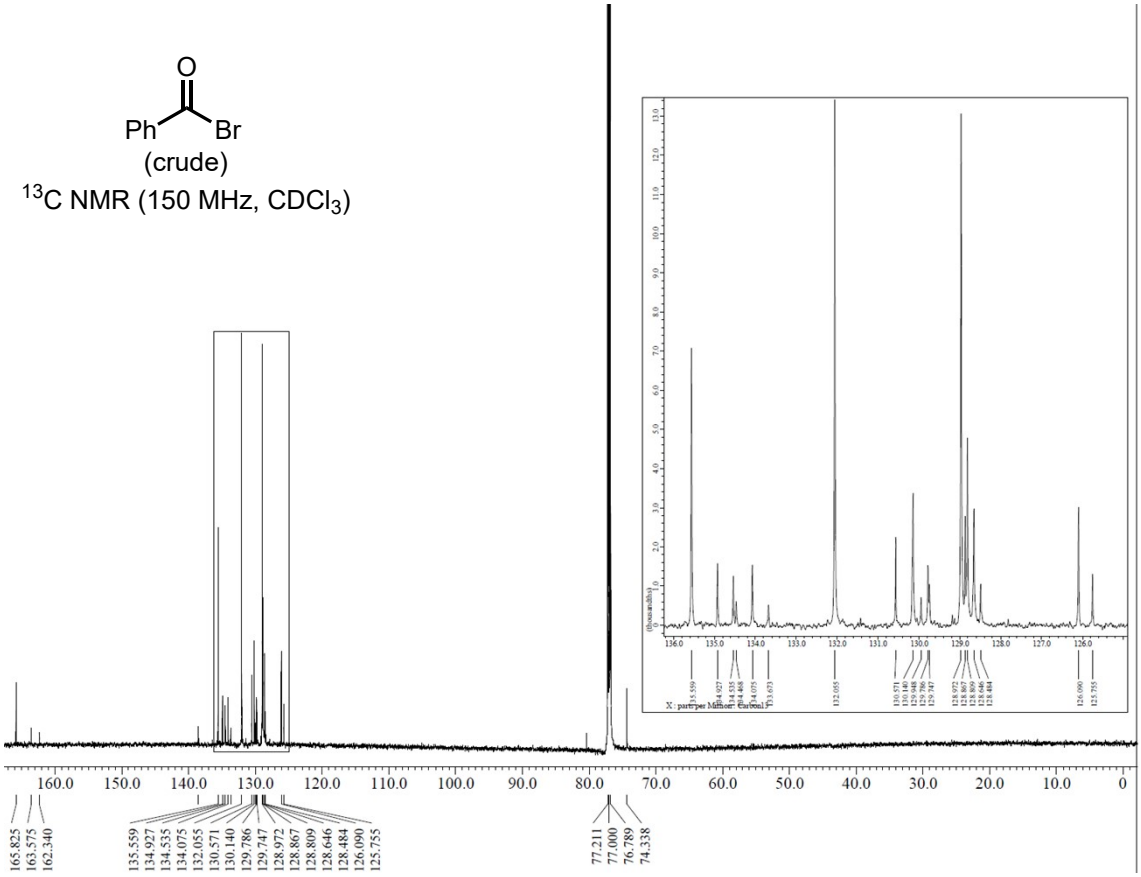
Examination of the generation of acyl bromide



Benzaldehyde **1a** (20.4 μL, 0.2 mmol), bromotrichloromethane (60.0 μL, 0.6 mmol), MS3Å (50 mg), and CH_2Cl_2 (2.0 mL) were added into a 4 mL borosilicate vial. After bubbling with argon for 5 min, the resulting solution was stirred at room temperature under light irradiation (λ_{ex} = 380 nm) for 4 h. The reaction mixture was concentrated under reduced pressure to give the crude product. The ^1H and ^{13}C NMR peak of benzoyl bromide were confirmed by comparison with the previous literature.[17]

Benzoyl bromide; ^1H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, J = 8.4 Hz, 2H), 7.71-7.67 (m, 1H), 7.56-7.49 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.8, 135.6, 135.0, 132.1, 129.0.




O
Ph
Br
(crude)
13C NMR (150 MHz, CDCl3)
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
165.825
163.575
162.340
135.559
134.927
134.535
134.075
132.055
130.571
130.140
129.786
129.747
128.972
128.867
128.809
128.646
128.484
126.090
125.755
77.211
77.000
76.789
74.338

3. Reference

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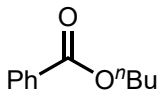
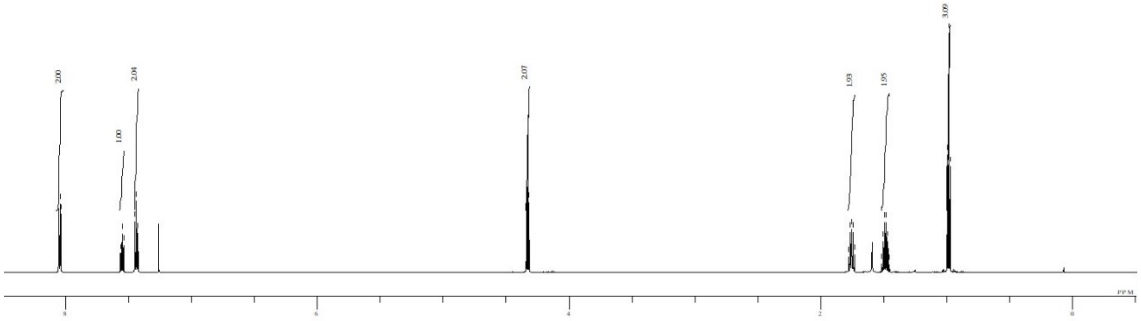
17. Kanga, S.; La, M. T.; Kim, H.-K. *Tetrahedron Lett.* 2018, **59**, 3541–3546.

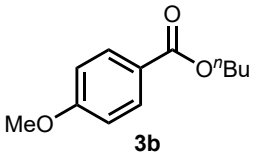
4. ^{1}H and ^{13}C NMR spectra data



3a

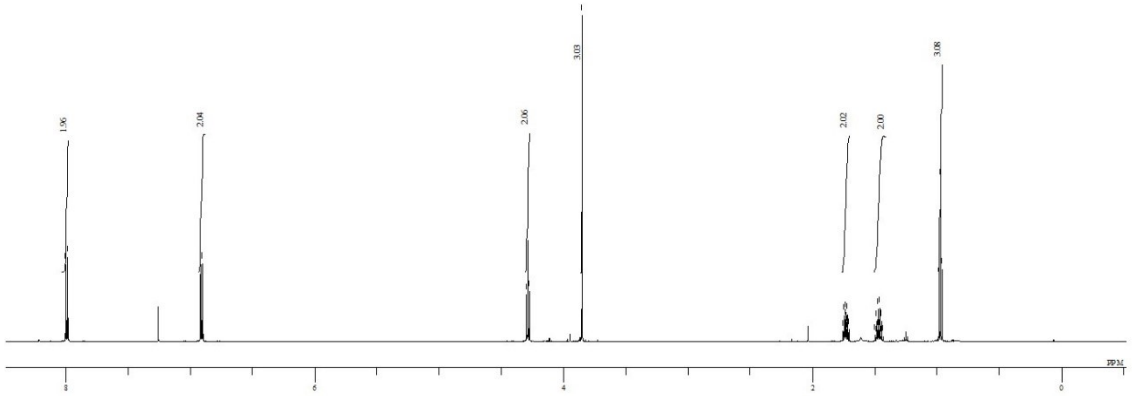
^{1}H NMR (600 MHz, $CDCl_3$)

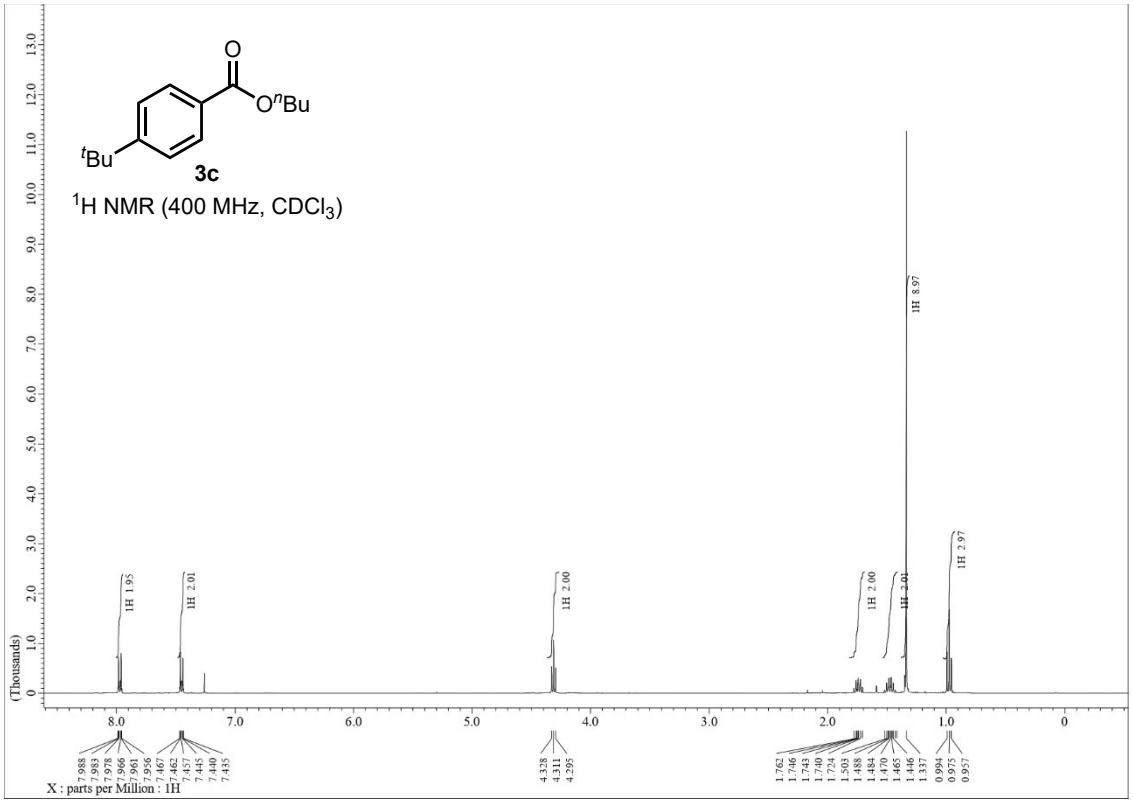


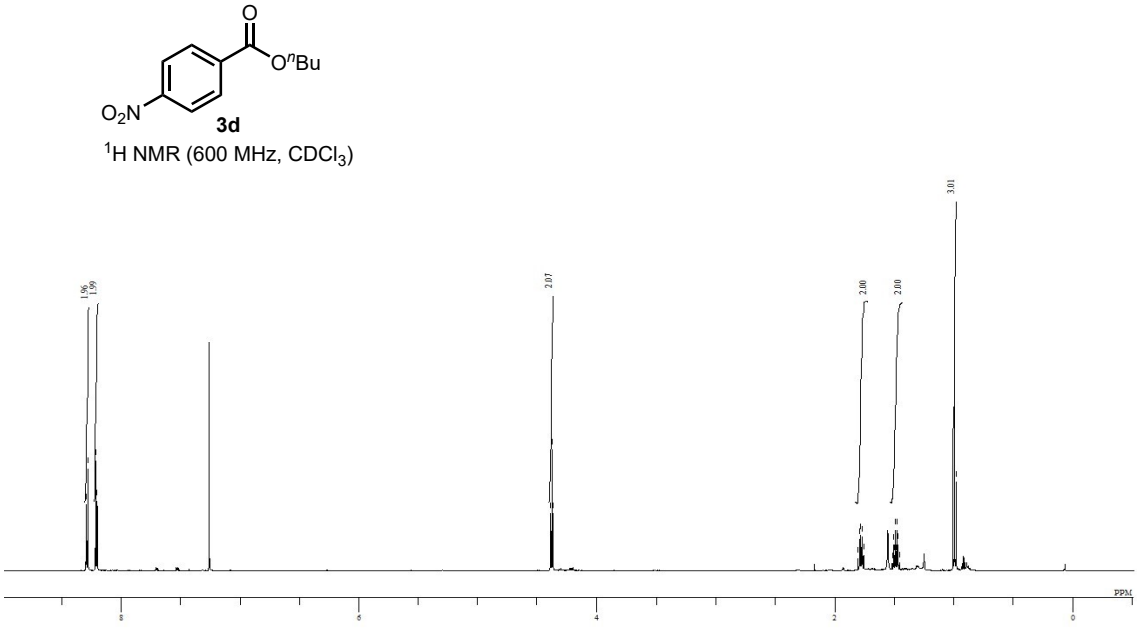


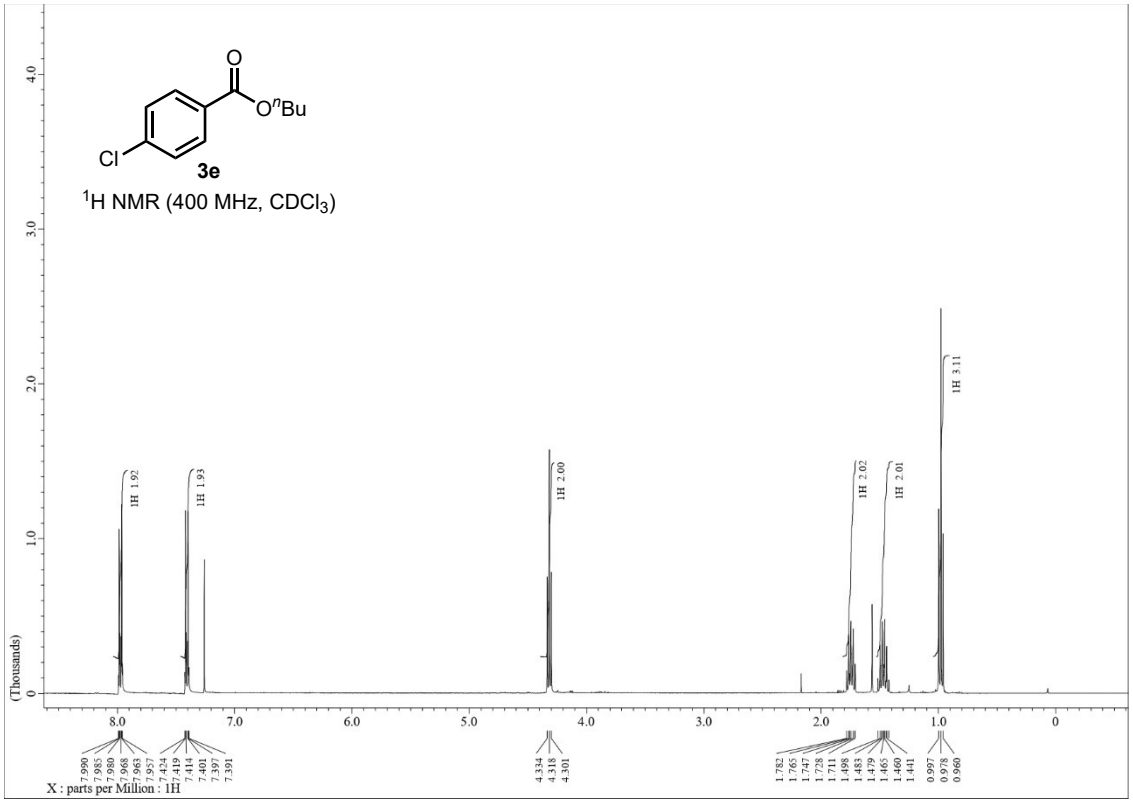
3b

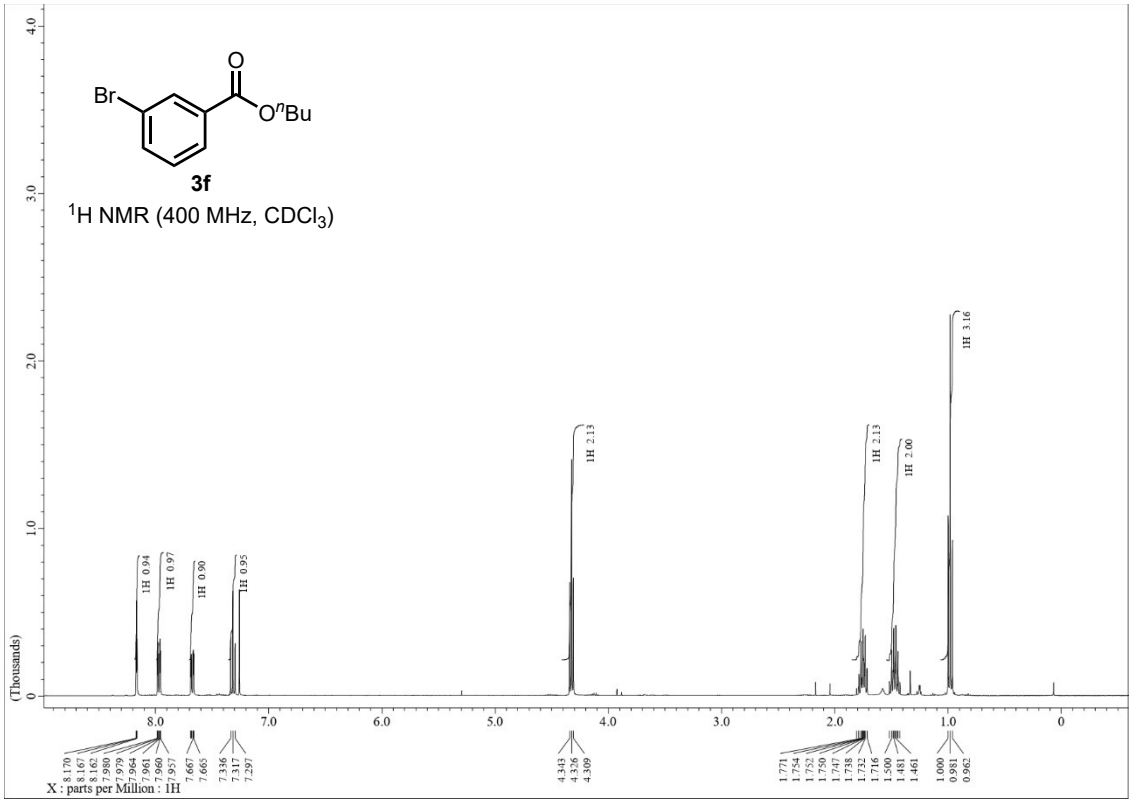
^{1}H NMR (600 MHz, $CDCl_3$)

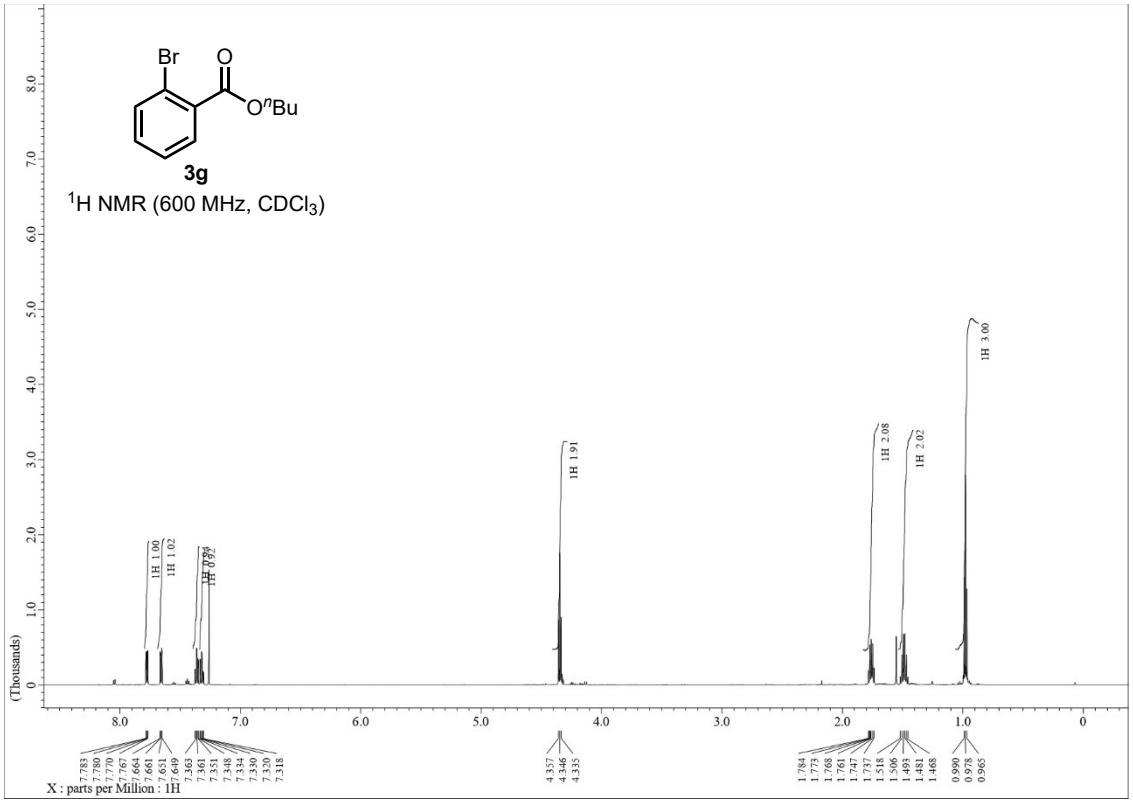


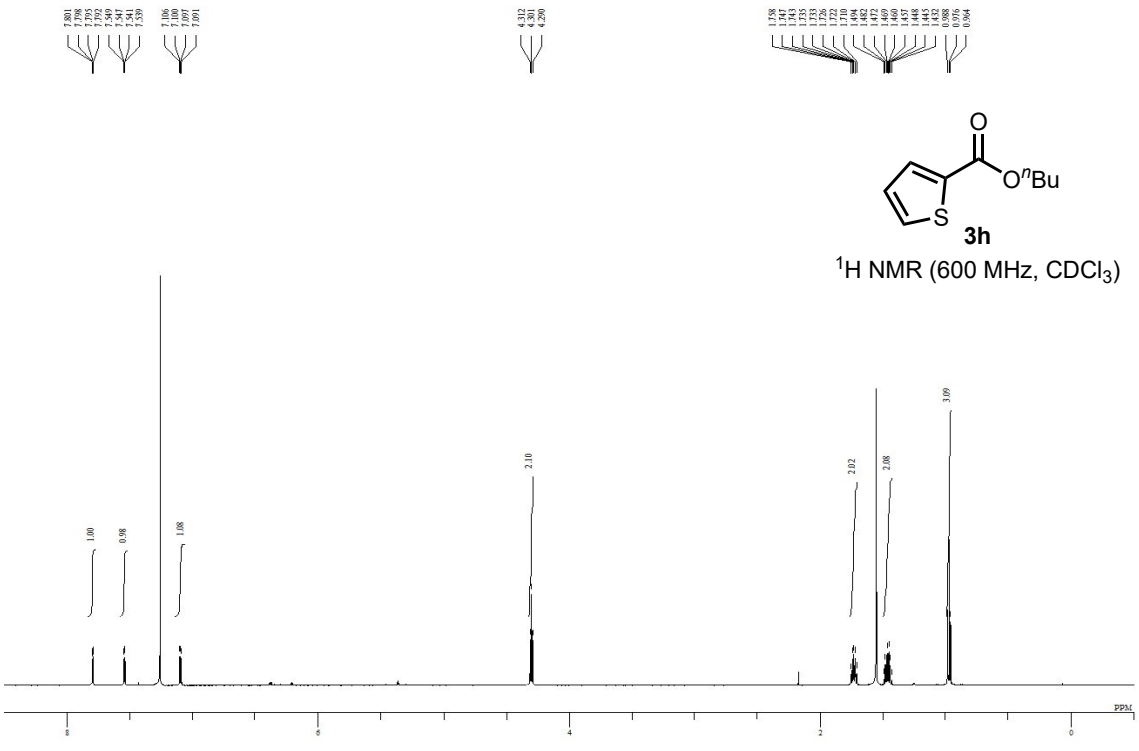

O
O^{n}Bu
^{t}Bu
3c
^{1}H NMR (400 MHz, CDCl$_3$)
1H 1.95
1H 2.01
1H 2.00
1H 2.00
1H 2.01
1H 8.97
1H 2.97
(Thousands)
X : parts per Million : 1H

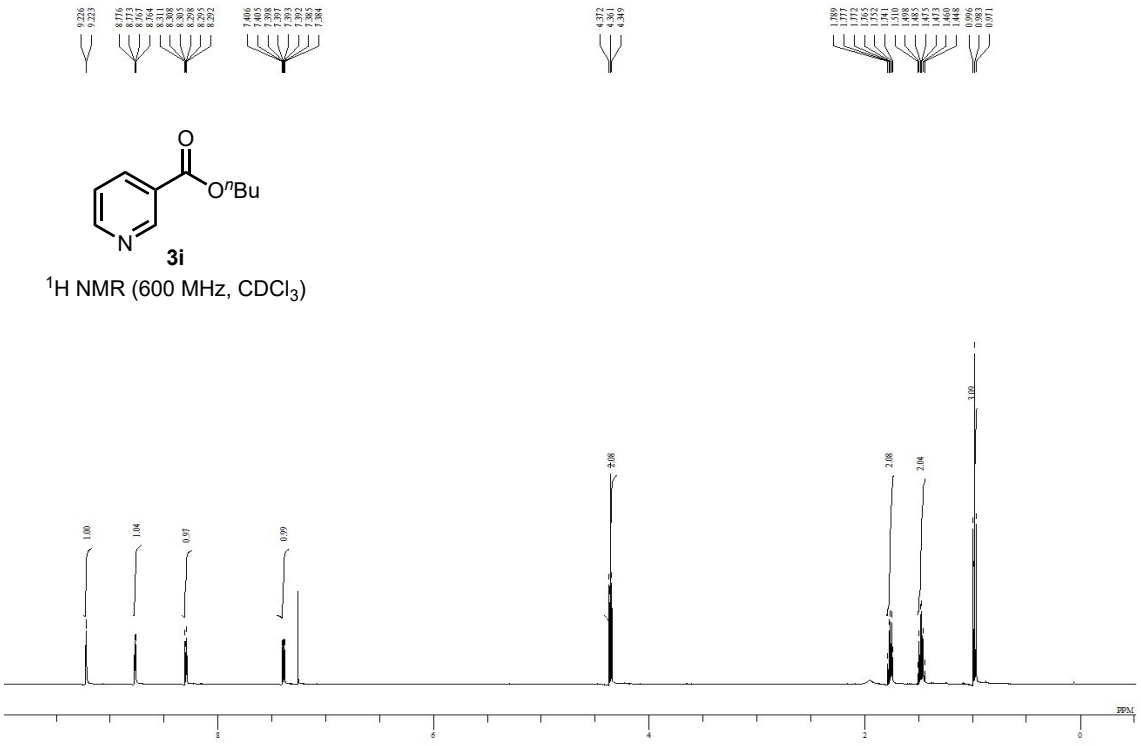

O
O^{n}Bu
O$_2$N
3d
^{1}H NMR (600 MHz, CDCl$_3$)
1.96
1.99
2.07
2.00
2.00
3.01
PPM


O
O^{n}Bu
Cl
3e
^{1}H NMR (400 MHz, CDCl$_3$)
(Thousands)
X : parts per Million : 1H


O
Br
O^{n}Bu
3f
^{1}H NMR (400 MHz, CDCl$_3$)
(Thousands)
X : parts per Million : 1H

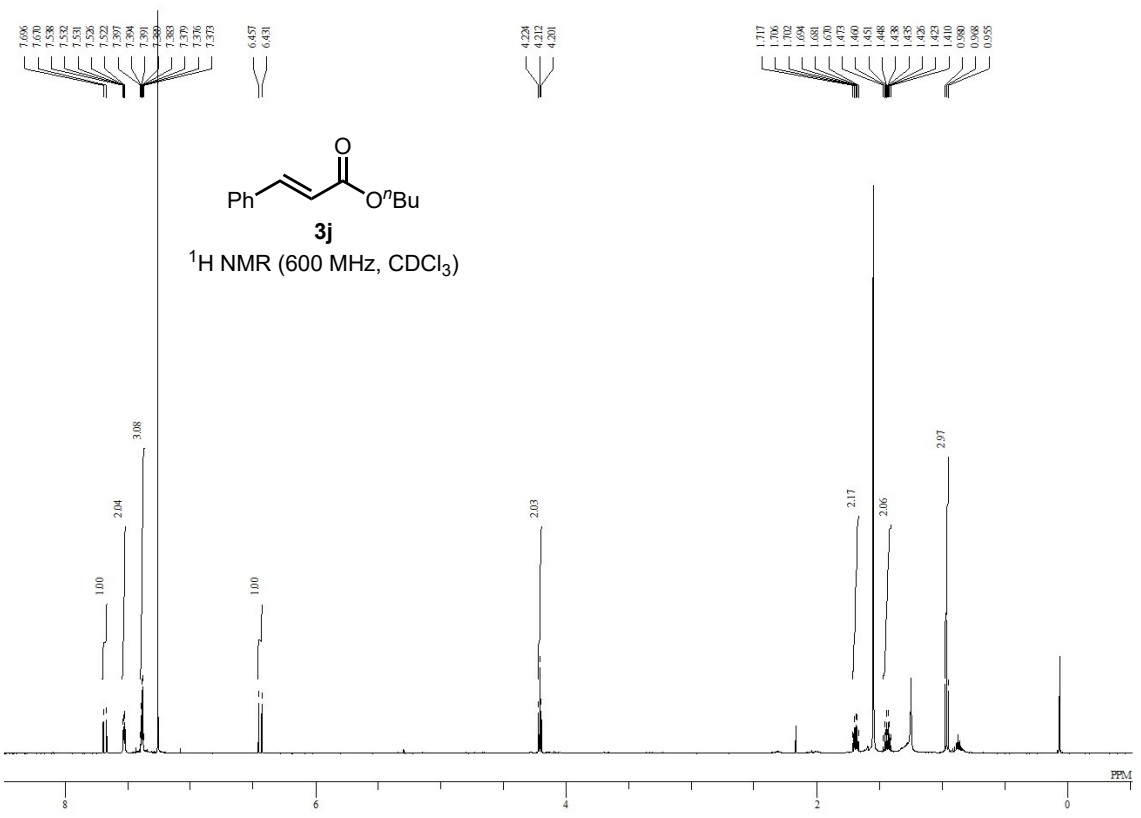

Br
O
O^{n}Bu
3g
^{1}H NMR (600 MHz, CDCl$_3$)
(Thousands)
X : parts per Million : 1H


O
O^{n}Bu
S
3h
^{1}H NMR (600 MHz, CDCl$_3$)
PPM



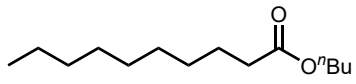
3i

^{1}H NMR (600 MHz, $CDCl_3$)



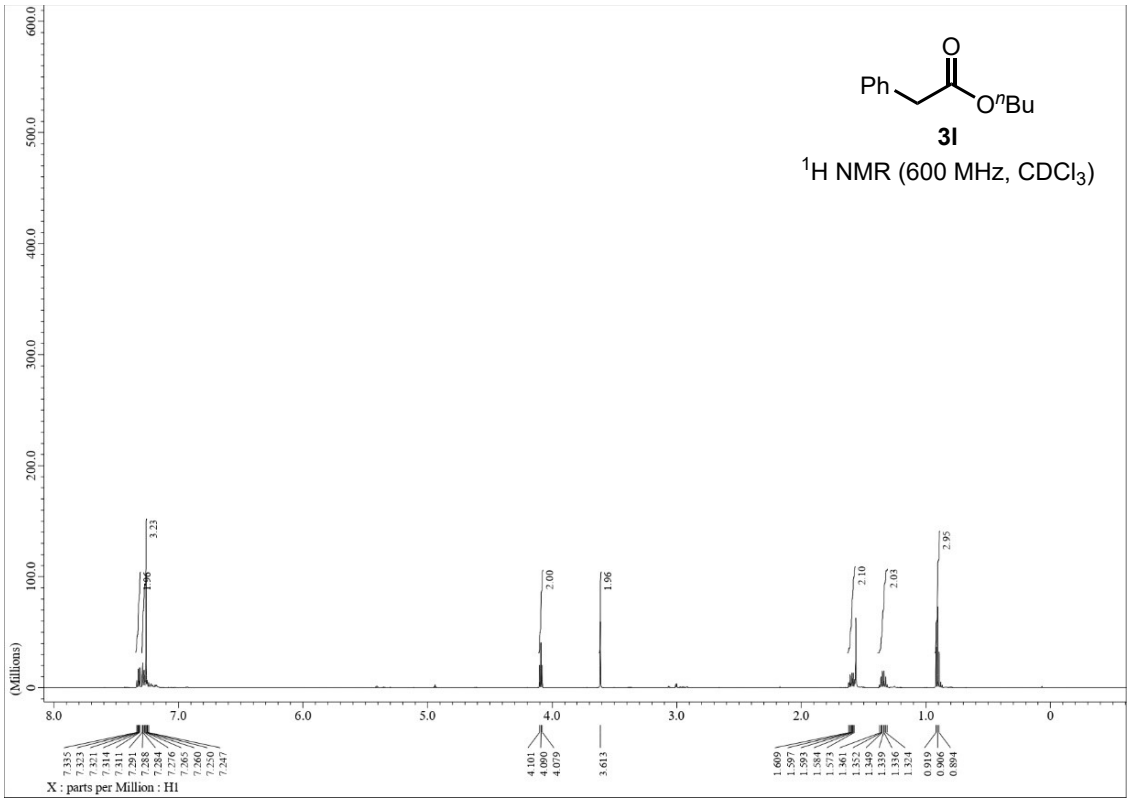
3j

^{1}H NMR (600 MHz, $CDCl_3$)



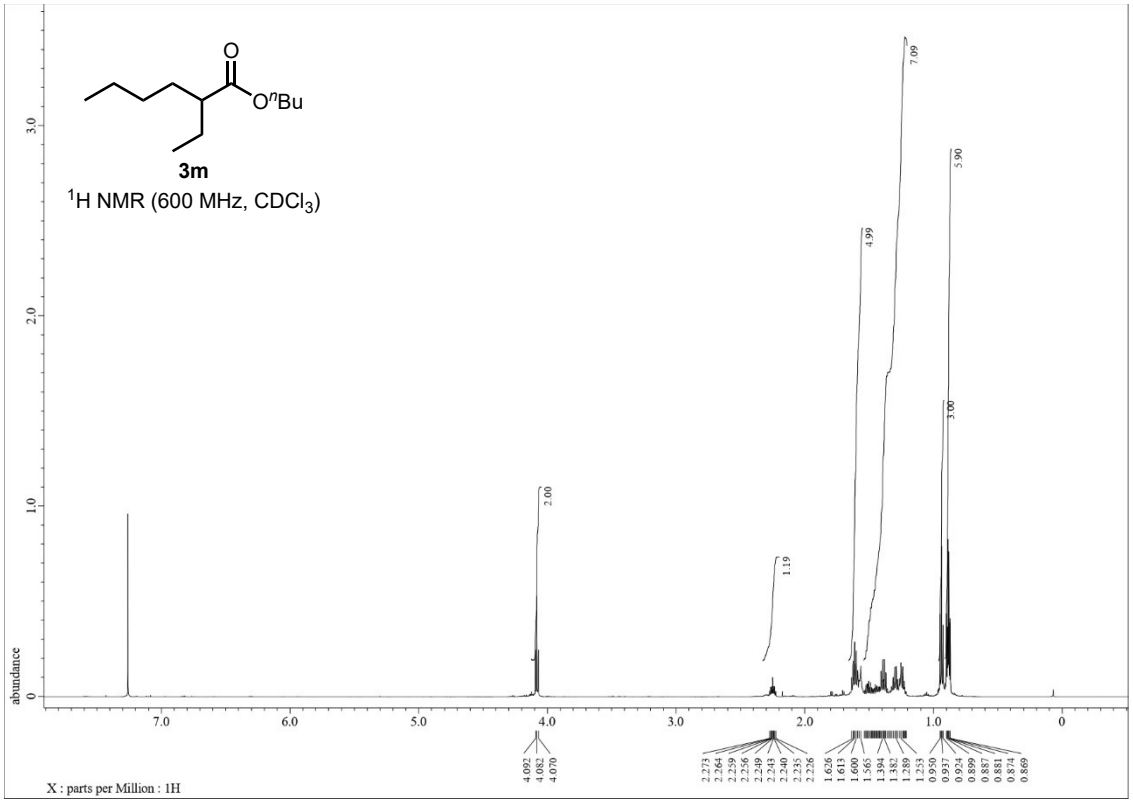
3k

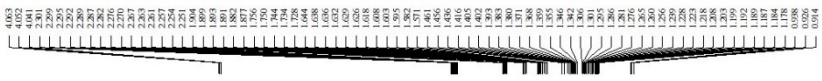
^{1}H NMR (600 MHz, $CDCl_3$)

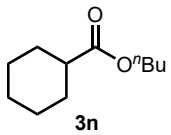


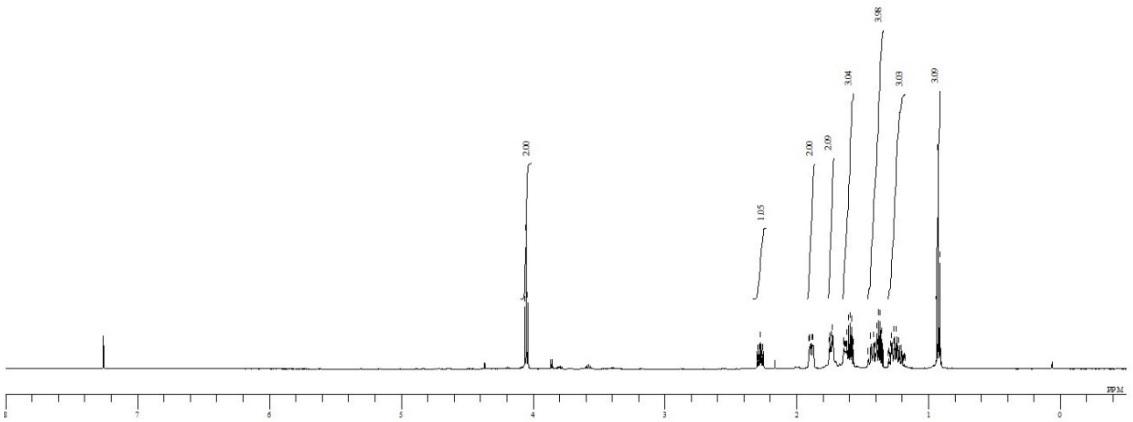
3l

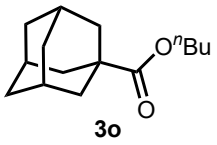
^{1}H NMR (600 MHz, $CDCl_3$)


O
O^{n}Bu
3m
^{1}H NMR (600 MHz, CDCl$_3$)
abundance
X : parts per Million : 1H



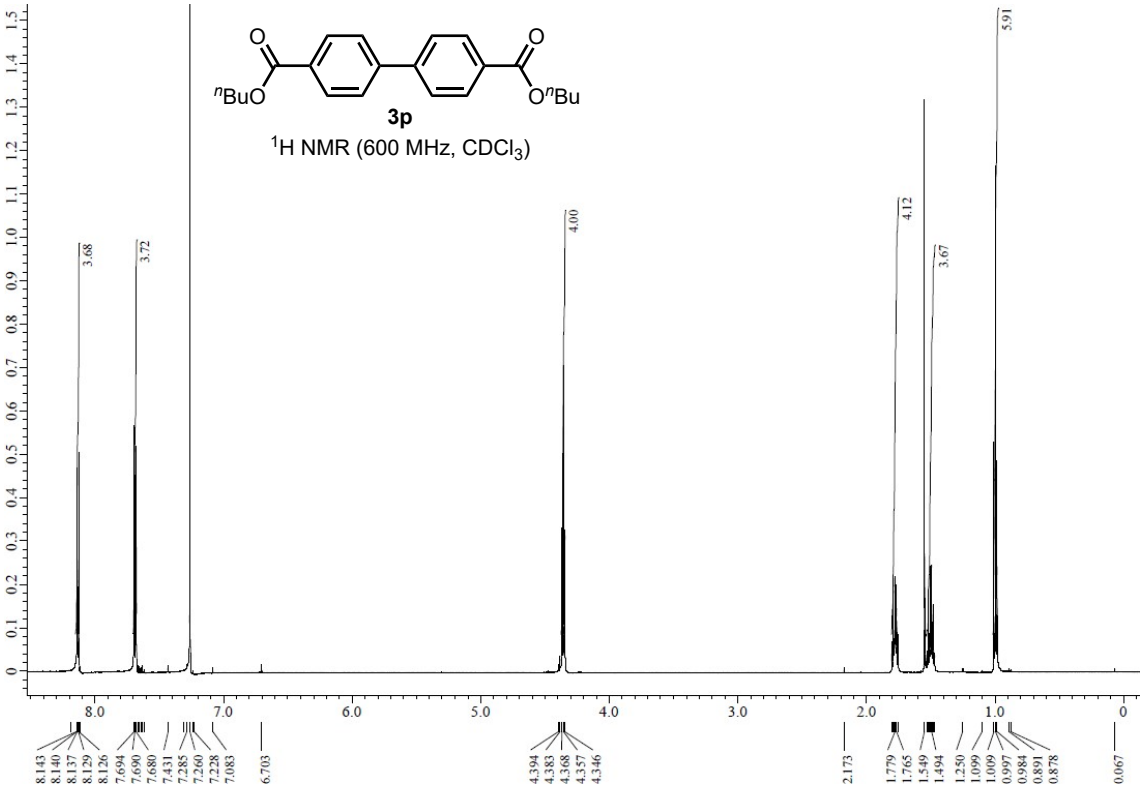

O
O^{n}Bu
3n
^{1}H NMR (600 MHz, CDCl$_3$)





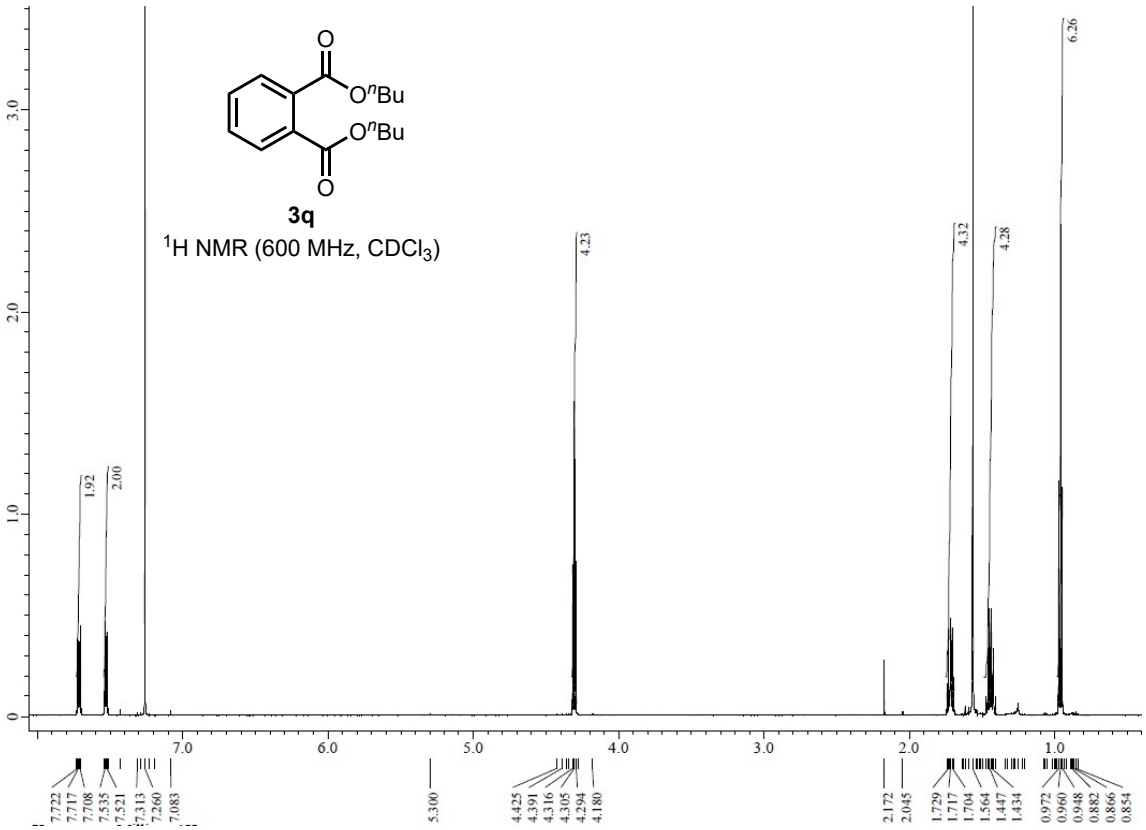
3o

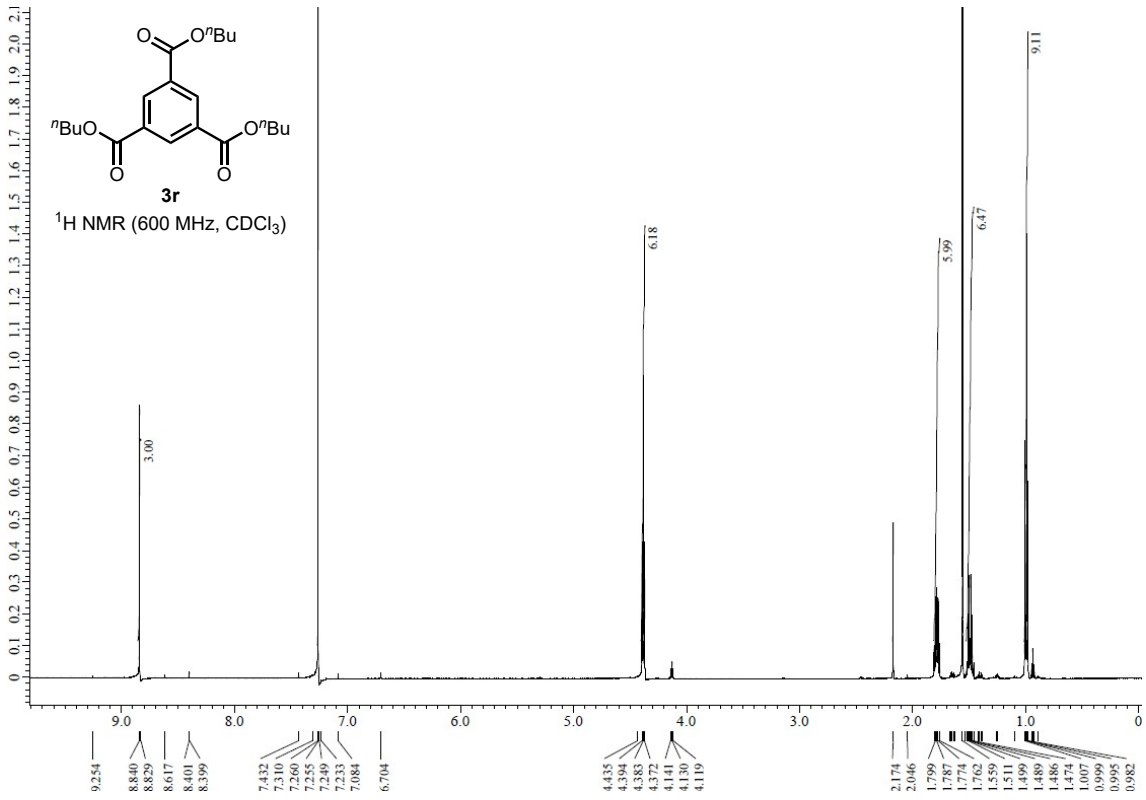
^{1}H NMR (600 MHz, $CDCl_3$)

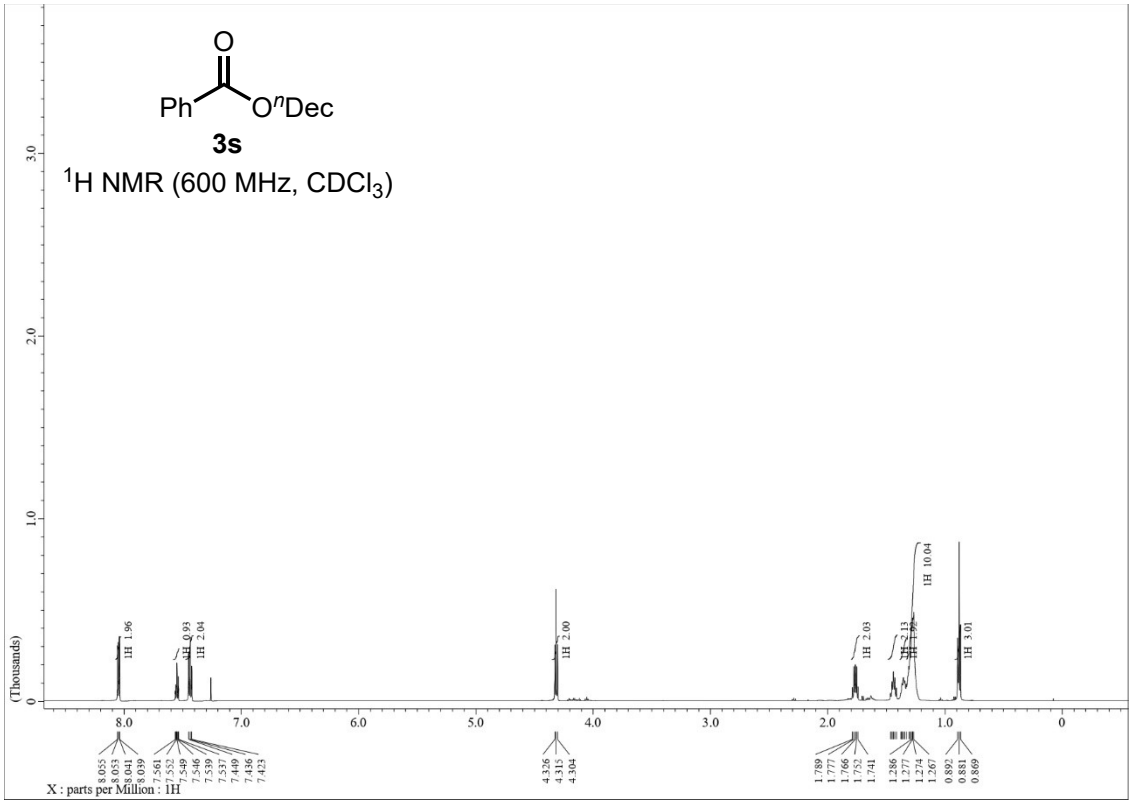


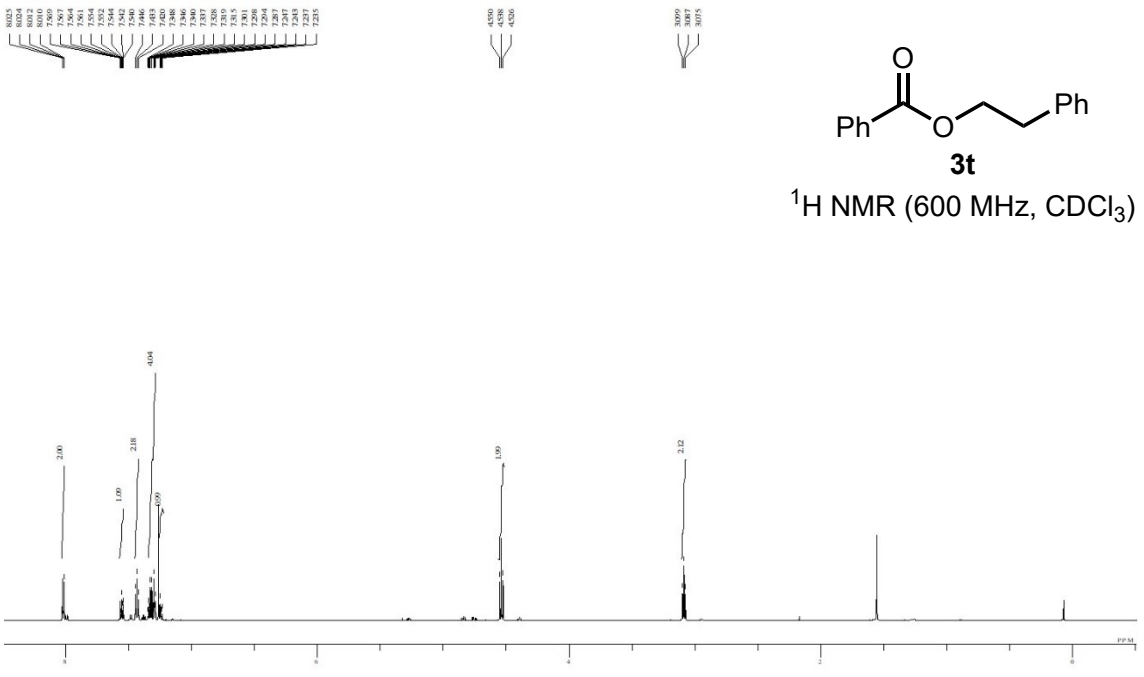
3p

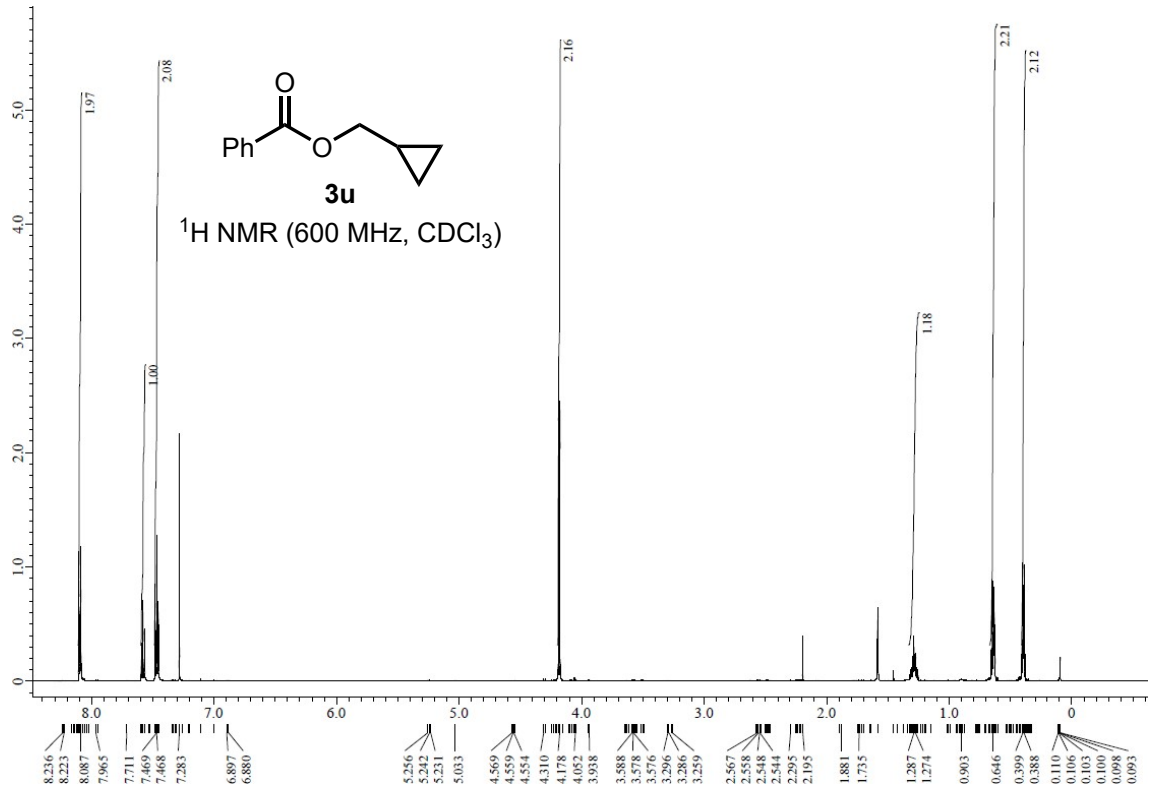
^{1}H NMR (600 MHz, $CDCl_3$)

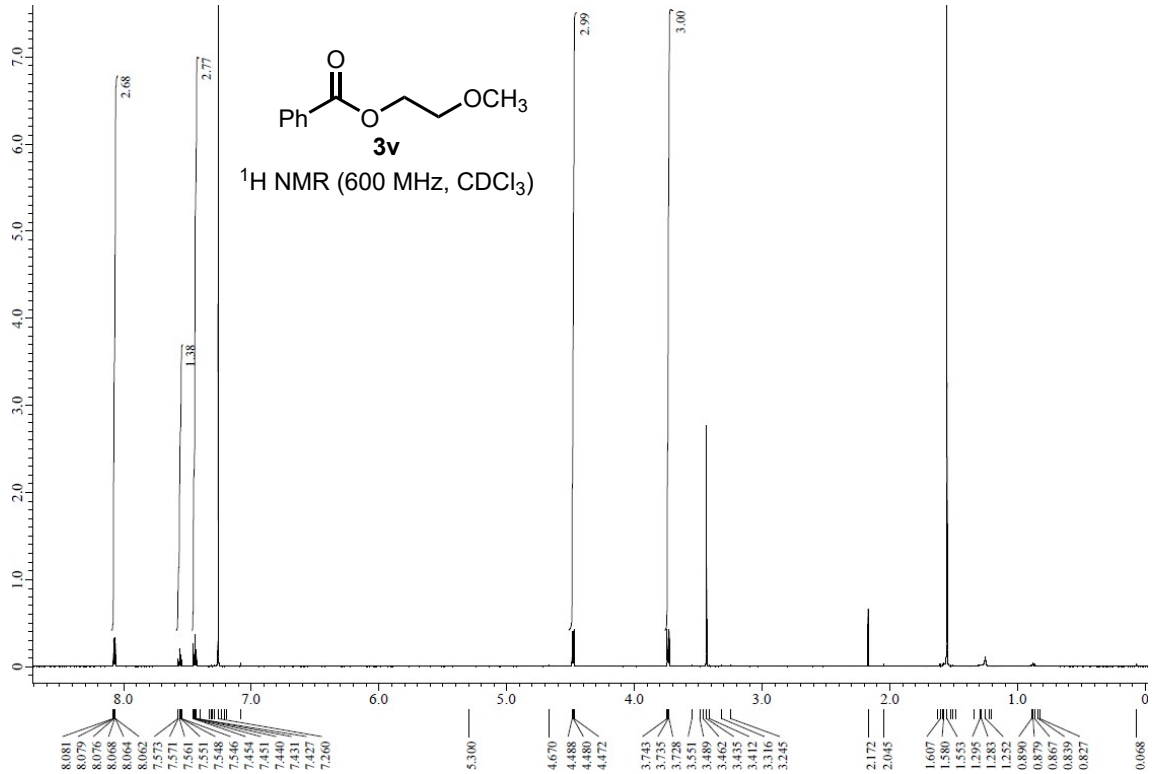

O
O^{n}Bu
O^{n}Bu
O
3q
^{1}H NMR (600 MHz, CDCl$_3$)
6.26
4.32
4.28
4.23
2.00
1.92

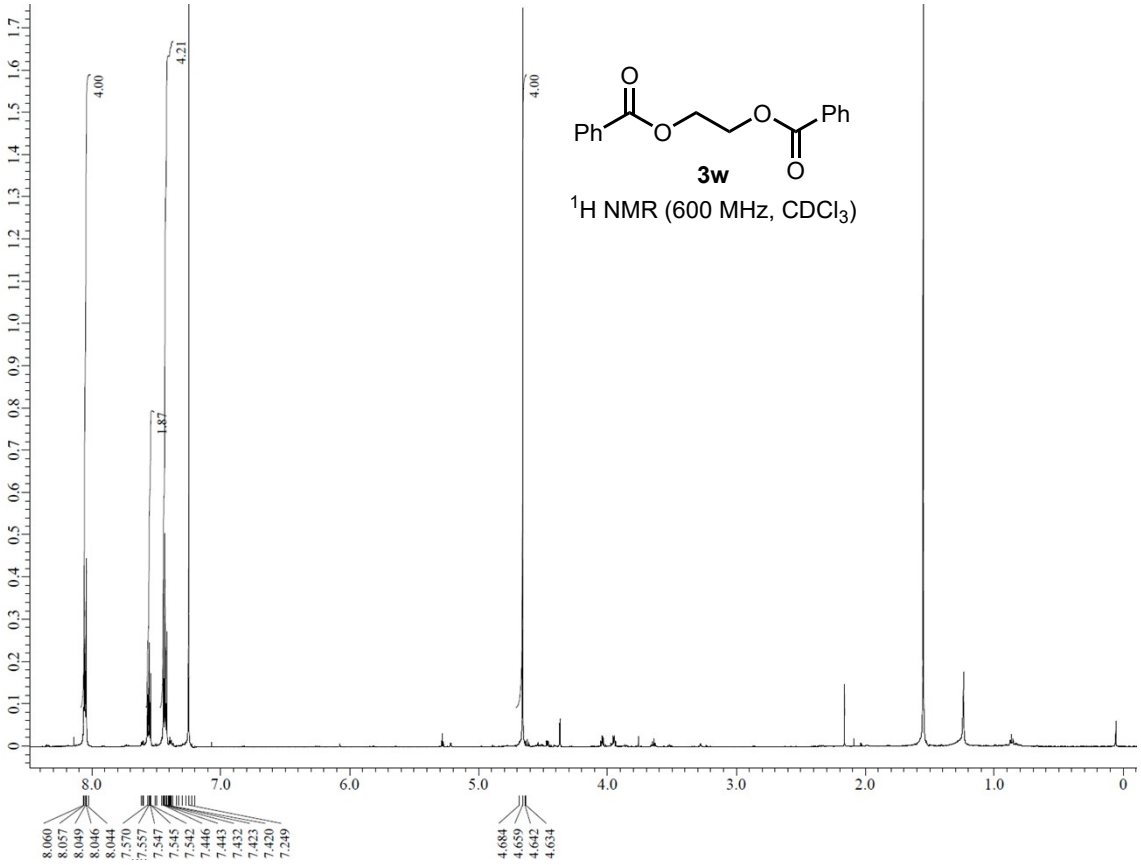

O
O^{n}Bu
^{n}BuO
O
O^{n}Bu
O
3r
^{1}H NMR (600 MHz, CDCl$_3$)
9.11
6.47
5.99
6.18
3.00


O
Ph
O^{n}Dec
3s
^{1}H NMR (600 MHz, CDCl$_3$)
(Thousands)
X : parts per Million : 1H


O
Ph
O
Ph
3t
^{1}H NMR (600 MHz, CDCl$_3$)

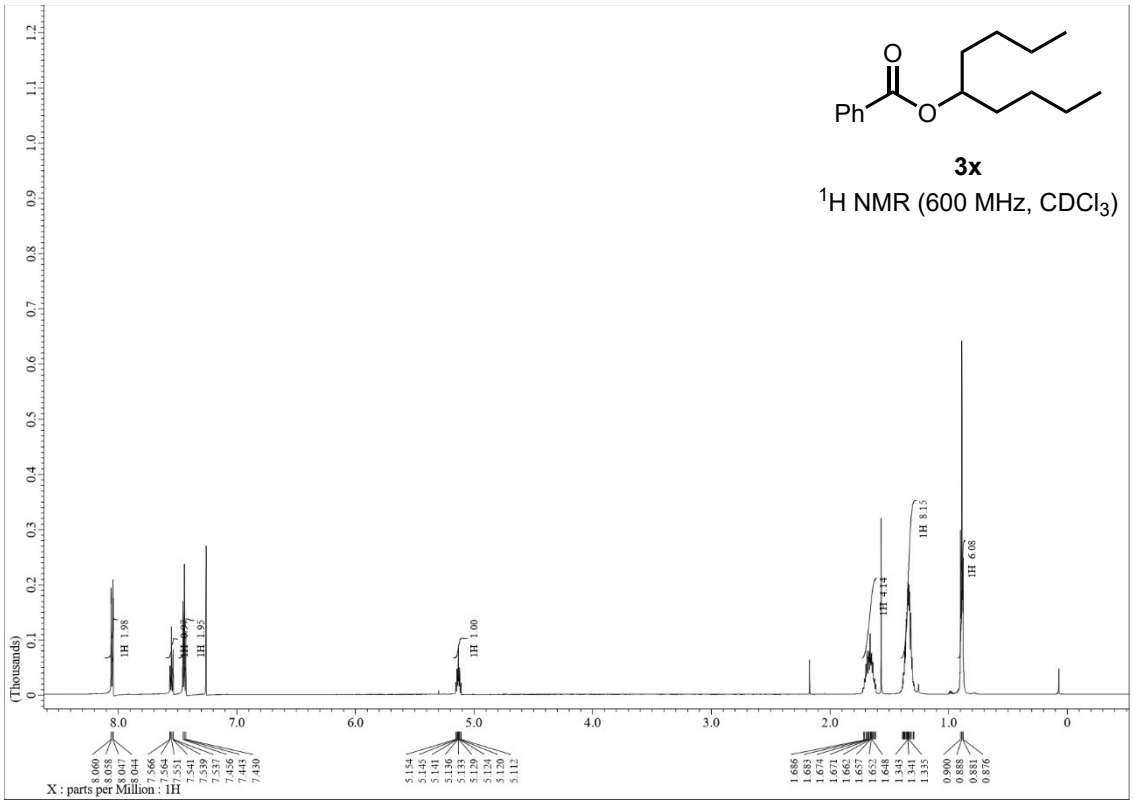

Ph
O
O
3u
1H NMR (600 MHz, CDCl3)


Ph
O
O
OCH3
3v
1H NMR (600 MHz, CDCl3)



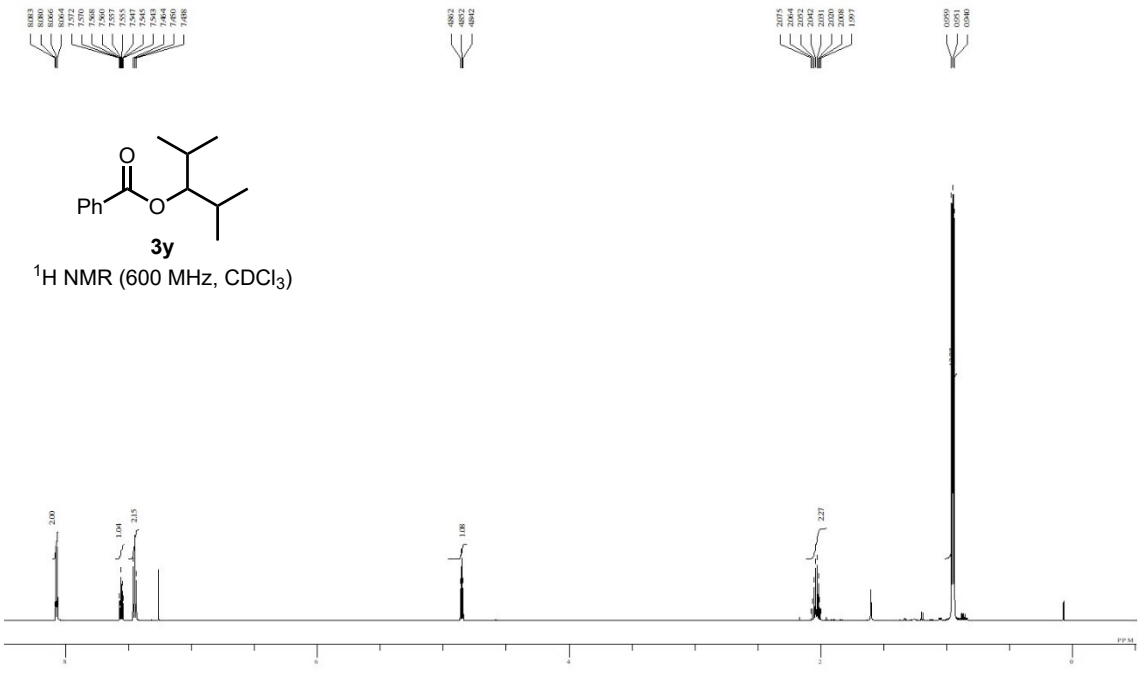
3w

^{1}H NMR (600 MHz, $CDCl_3$)



3x

^{1}H NMR (600 MHz, $CDCl_3$)



3y

^{1}H NMR (600 MHz, $CDCl_3$)