Supplementary Material (ESI) for Green Chemistry

Supporting Information

Metal- and Solvent-free Conditions for Acylation Reaction Catalyzed by Carbon Tetrabromide (CBr_4)

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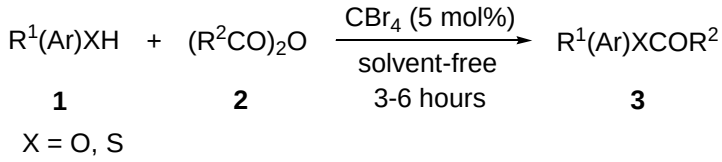
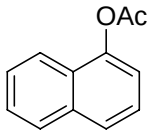
General Procedure for CBr_4 catalyzed acylation reaction:



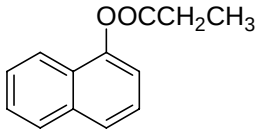
A mixture of substrate **1** (0.5 mmol), acid anhydride **2** (0.55 mmol, 1.1 equiv.), and CBr_4 (5 mol%) under solvent-free condition was stirred at 60 °C under air atmosphere. After completion of the reaction as indicated by TLC, the reaction mixture was diluted with H_2O (2 mL) and extracted with Et_2O (2 × 3 mL). The organic phase was washed successively with 2% aqueous NaOH (3 mL) and saturated brine (3 mL). After dried with Na_2SO_4 and concentrated under reduced pressure, the crude product was separated and purified by flash chromatography column (silica gel) to afford the corresponding product (in some cases, the crude product was of sufficient purity and could be used for spectra analysis directly without further purification.). (All the products are known compounds. The characterizations of these compounds are identical with the literature reports.)



3aa

naphthalen-1-yl acetate

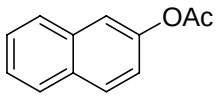
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 2.44 (s, 3H), 7.27-7.52 (m, 4H), 7.72-7.87 (m, 3H).



3ab

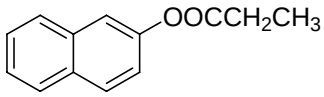
naphthalen-1-yl propionate

^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 1.32 (t, *J* = 7.58 Hz, 3H), 2.71-2.75 (m, 2H), 7.24-7.49 (m, 4H), 7.69-7.84 (m, 3H).



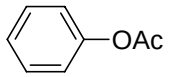
3ba

naphthalen-2-yl acetate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 2.36 (s, 3H), 7.25-7.48 (m, 3H), 7.56 (s, 1H), 7.84-7.87 (m, 3H).



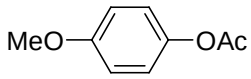
3bb

naphthalen-2-yl propionate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 1.27 (t, *J* = 7.58 Hz, 3H), 2.60-2.64 (m, 2H), 7.22-7.45 (m, 3H), 7.55-7.84 (m, 4H).



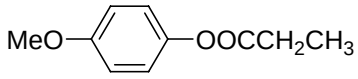
3ca

phenyl acetate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 2.29 (s, 3H), 7.07-7.37 (m, 5H).



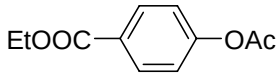
3da

4-methoxyphenyl acetate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 2.28 (s, 3H), 3.79 (s, 3H), 6.87 (d, *J* = 8.80 Hz, 2H), 6.99 (d, *J* = 8.80 Hz, 2H).



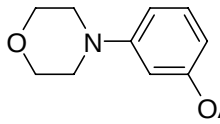
3db

4-methoxyphenyl propionate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 1.23 (t, *J* = 7.56 Hz, 3H), 2.54-2.57 (m, 2H), 3.80 (s, 3H), 6.87 (d, *J* = 8.80 Hz, 2H), 6.98 (d, *J* = 8.80 Hz, 2H).



3ea

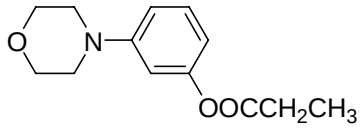
ethyl 4-acetoxybenzoate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 1.36 (t, *J*= 7.32 Hz, 3H), 2.31 (s, 3H), 4.34-4.38 (m, 2H), 7.15 (d, *J* = 8.80 Hz, 2H), 8.06 (d, *J* = 8.80 Hz, 2H).



3fa

3-morpholinophenyl acetate

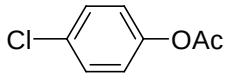
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 2.23 (s, 3H), 3.09 (t, *J* = 4.80 Hz, 4H), 3.78 (t, *J* = 4.58 Hz, 4H), 6.55 (d, *J* = 6.88 Hz, 2H), 6.71 (d, *J* = 7.36 Hz, 1H), 7.19 (t, *J* = 8.24 Hz, 1H).



3fb

3-morpholinophenyl propionate

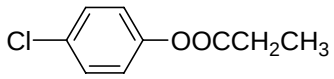
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 1.20 (t, *J* = 7.56 Hz, 3H), 2.51-2.56 (m, 2H), 3.08-3.10 (m, 4H), 3.78-3.79 (m, 4H), 6.56 (d, *J* = 8.28 Hz, 2H), 6.70 (d, *J* = 7.76 Hz, 1H), 7.19 (d, *J* = 8.02 Hz, 1H).



3ga

4-chlorophenyl acetate

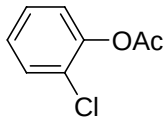
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 2.27 (s, 3H), 7.01 (d, *J* = 8.72 Hz, 2H), 7.32 (d, *J* = 8.72 Hz, 2H).



3gb

4-chlorophenyl propionate

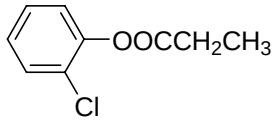
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 1.21 (t, *J* = 7.56 Hz, 3H), 2.53-2.56 (m, 2H), 6.87 (d, *J* = 8.72 Hz, 2H), 7.30 (d, *J* = 8.24 Hz, 2H).



3ha

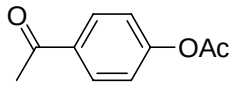
2-chlorophenyl acetate

^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 2.33 (s, 3H), 7.12-7.18 (m, 2H), 7.24 (d, *J* = 7.80 Hz, 1H), 7.42 (d, *J* = 7.80 Hz, 1H).



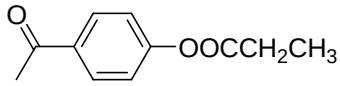
3hb

2-chlorophenyl propionate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 1.28 (t, *J* = 7.56 Hz, 3H), 2.62-2.66 (m, 2H), 7.12-7.27 (m, 3H), 7.42 (d, *J* = 7.80 Hz, 1H).



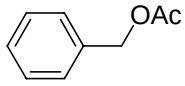
3ia

4-acetylphenyl acetate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 2.18 (s, 3H), 2.45 (s, 3H), 7.05 (d, *J* = 8.68 Hz, 2H), 6.99 (d, *J* = 8.68 Hz, 2H).



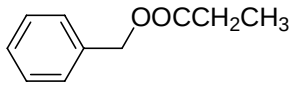
3ib

4-acetylphenyl propionate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 1.15 (t, *J* = 7.56 Hz, 3H), 2.45-2.50 (m, 5H), 7.06 (d, *J* = 9.16 Hz, 2H), 7.84 (d, *J* = 8.72 Hz, 2H).



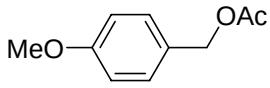
3ja

benzyl acetate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 2.09 (s, 3H), 5.10 (s, 2H), 7.33-7.36 (m, 5H).



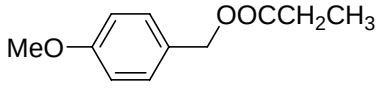
3jb

benzyl propionate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 1.14 (t, *J* = 7.58 Hz, 3H), 2.36-2.38 (m, 2H), 5.11 (s, 2H), 7.34-7.36 (m, 5H).



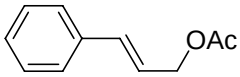
3ka

4-methoxybenzyl acetate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 2.06 (s, 3H), 3.79 (s, 3H), 5.03 (s, 2H), 6.87 (d, *J* = 8.80 Hz, 2H), 7.28 (d, *J* = 8.76 Hz, 2H).



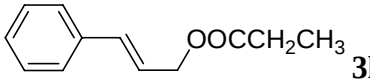
3kb

4-methoxybenzyl propionate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 1.12 (t, *J* = 7.62 Hz, 3H), 2.32-2.36 (m, 2H), 3.80 (s, 3H), 5.05 (s, 2H), 6.87 (d, *J* = 8.60 Hz, 2H), 7.28 (d, *J* = 8.60 Hz, 2H).



3la

cinnamyl acetate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 2.10 (s, 3H), 4.72 (d, *J* = 6.32 Hz, 2H), 6.26-6.32 (m, 1H), 6.63 (d, *J* = 15.64 Hz, 1H), 7.30-7.40 (m, 5H).



3lb

Cinnamyl propionate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 1.15 (t, *J* = 7.85 Hz, 3H), 2.34-2.38 (m, 2H), 4.73 (d, *J* = 6.36 Hz, 2H), 6.26-6.30 (m, 1H), 6.62 (d, *J* = 15.64 Hz, 1H), 7.27-7.39 (m, 5H).

$AcO(CH_2)_9OAc$ **3ma**

^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 1.18 (s, 10H), 1.44-1.49 (m, 4H), 1.90 (s, 6H), 3.89 (t, *J* = 6.88 Hz, 4H).

$CH_3CH_2COO(CH_2)_9OOCCH_2CH_3$ **3mb**

^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 1.01 (t, *J* = 7.56 Hz, 6H), 1.21 (s, 10H), 1.48-1.53 (m, 4H), 2.18-2.24 (m, 4H), 3.94 (t, *J* = 6.88 Hz, 4H).

$AcO(CH_2)_6OAc$ **3na**

^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 1.38-1.41 (m, 4H), 1.62-1.66 (m, 4H), 2.05 (s, 6H), 4.04 (t, *J* = 6.84 Hz, 4H).

$CH_3CH_2COO(CH_2)_6OOCCH_2CH_3$ **3nb**

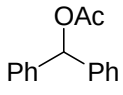
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 1.12 (t, *J* = 7.58 Hz, 6H), 1.39-1.40 (m, 4H), 1.64-1.65 (m, 4H), 2.32-2.35 (m, 4H), 4.06 (t, J = 6.60 Hz, 4H).

$CH_3(CH_2)_6OAc$ **3oa**

Heptyl acetate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 0.87 (t, *J* = 6.64 Hz, 3H), 1.29-1.36 (m, 8H), 1.59-1.64 (m, 2H), 2.04 (s, 3H), 4.04 (t, *J*= 6.88 Hz, 2H).

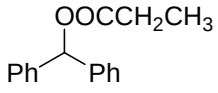
$CH_3(CH_2)_6OOCCH_2CH_3$ **3ob**

Heptyl propionate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 0.82 (t, *J* = 6.64 Hz, 3H), 1.08 (t, *J* = 7.56 Hz, 3H), 1.24-1.28 (m, 8H), 1.54-1.59 (m, 2H), 2.25-2.30 (m, 2H), 4.00 (t, *J* = 6.64 Hz, 2H).



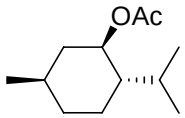
3pa

benzhydryl acetate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 2.20 (s, 3H), 6.98 (s, 1H), 7.33-7.44 (m, 10H).



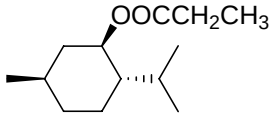
3pb

Benzhydryl propionate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 1.13 (t, *J* = 7.56 Hz, 3H), 2.39-2.45 (m, 2H), 6.90 (s, 1H), 7.23-7.35 (m, 10H).



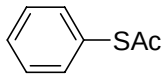
3qa

(*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl acetate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 0.66 (d, *J*= 7.32 Hz, 3H), 0.75-1.01 (m, 9H), 1.23-1.29 (m, 1H), 1.36-1.40 (m, 1H), 1.55-1.59 (m, 2H), 1.75-1.79 (m, 1H), 1.88-1.94 (m, 4H), 4.56-4.58 (m, 1H).



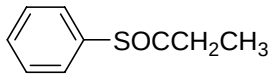
3qb

(*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl propionate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 0.71 (d, *J* = 6.88 Hz, 3H), 0.78-0.94 (m, 8H), 0.99-1.12 (m, 4H), 1.27-1.45 (m, 2H), 1.58-1.63 (m, 2H), 1.78-1.82 (m, 1H), 1.90-1.94 (m, 1H), 2.21-2.26 (m, 2H), 4.59-4.65 (m, 1H).



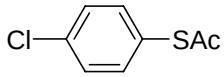
3sa

S-phenyl ethanethioate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 2.39 (s, 3H), 7.38-7.39 (m, 5H).



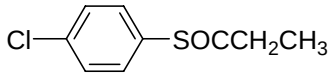
3sb

S-phenyl propanethioate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 1.20 (t, *J* = 7.62 Hz, 3H), 2.64-2.68 (m, 2H), 7.39-7.40 (m, 5H).



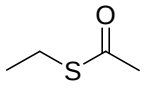
3ta

S-4-chlorophenyl ethanethioate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 2.41 (s, 3H), 7.31-7.36 (m, 4H).



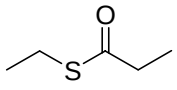
3tb

S-4-chlorophenyl propanethioate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 1.20 (t, *J* = 7.56 Hz, 3H), 2.65-2.69 (m, 2H), 7.32-7.36 (m, 4H).



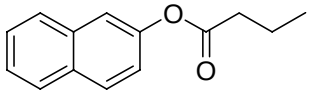
3ua

S-ethyl ethanethioate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 1.18 (t, *J* = 7.10 Hz, 3H), 1.98 (s, 3H), 4.03-3.09 (m, 2H).



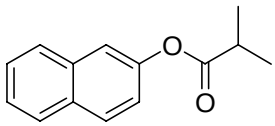
3ub

S-ethyl propanethioate
^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 1.11 (t, *J* = 7.56 Hz, 3H), 1.18 (t, *J* = 7.34 Hz, 3H), 1.98 (s, 3H), 2.49-2.55 (m, 2H), 2.80-2.86 (m, 2H).



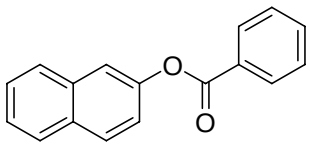
3bc

^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 1.11 (t, *J* = 7.34 Hz, 3H), 1.82-1.91 (m, 2H), 2.62 (t, *J* = 7.32 Hz, 2H), 7.25 (d, *J* = 8.68 Hz, 1H), 7.45-7.53 (m, 2H), 7.59 (s, 1H), 7.81-7.88 (m, 3H).



3bd

^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 1.38 (d, *J* = 6.88 Hz, 6H), 2.85-2.92 (m, 1H), 7.22 (d, *J* = 8.72 Hz, 1H), 7.45-7.52 (m, 2H), 7.57 (s, 1H), 7.80-7.87 (m, 3H).



3be

^{1}H NMR (400M Hz, $CDCl_3$): δ (ppm) 7.36 (dd, *J* = 8.72, 2.28 Hz, 1H), 7.48-7.56 (m, 4H), 7.64-7.71 (m, 2H), 7.83-7.92 (m, 3H), 8.26-8.28 (m, 2H).