Thallium(III) Chloride: A Mild and Efficient Catalyst for Acylation of Alcohols, Phenols and Thiols, and for Geminal Diacylation of Aldehydes under Solvent-Free Conditions

Santosh T. Kadam, Sung Soo Kim*

Department of Chemistry, Inha University, Incheon 402-751, Korea
Fax +82(32)8675604; E-mail: sungsoo@inha.ac.kr

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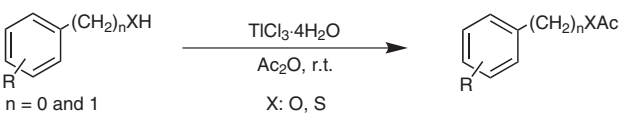
Abstract: Thallium(III) chloride is a simple and efficient catalyst for acylation of alcohols, phenols and thiols. It is also very effective for geminal diacylation of aldehydes. The acylation reaction using acetic anhydride proceeds in excellent yield in the presence of catalytic amounts of thallium(III) chloride (1 mol%) at room temperature within relatively short reaction times (<20 min). Structurally diverse alcohols, phenols, thiols and aldehydes undergo acylation under solvent-free conditions.

Key words: acylation, gem-diacylation, thallium chloride, alcohols, thiols, aldehydes

Functional group protection lies at the heart of multifunctional synthesis of target molecules, and protection of alcohol, phenol and thiol moieties represent one of the most ubiquitous steps in chemistry.[1] These functional groups frequently require transformation due to their prevalence in drugs and pharmaceuticals. Protection of the functionalities are commonly achieved through acylation with acetic anhydride;[2] the acyl group is easily introduced, is stable under acidic conditions and is easily removed by mild alkaline hydrolysis. The poor nucleophilic properties of the hydroxyl group can be improved through activation to an anhydride and various activators have been employed for this purpose. Such activators include nucleophilic DMAP,[3a] *n*-Bu_3P,[3b] and other catalytic systems such as $CoCl_2$,[3c] $ZnCl_2$,[3d] $ZrCl_4$,[3e] $InCl_3$,[3f] nitrobenzeneboronic acid,[3g] and iodine.[3h] Recently, many triflates and perchlorates have also been reported, such as: $Sc(OTf)_3$,[4a] $In(OTf)_3$,[4b] $Cu(OTf)_2$,[4c] $Al(OTf)_3$,[4d] $Ce(OTf)_3$,[4e] $Gd(OTf)_3$,[4f] $LiClO_4$,[5a] $CuClO_4$,[5b] and $MgClO_4$.[5c] Other catalysts such as montmorillonite,[6a] $La(NO_3)_3$,[6b] yttria-zirconia,[6c] trichloroisocyanuric acid,[6d] Nafion-H,[6e] and N-heterocyclic carbenes,[6f] have also been used for the acylation of alcohols.

The use of thallium in organic chemistry began in 1970 and it is still being developed.[7] Thallium salts can promote a number of reactions such as oxidative and non-oxidative cyclizations, and aromatic thallation reactions.[8] The three most commonly used thallium salts are thallium acetate, thallium nitrate and thallium trifluoroacetate (TTFA). Thallium nitrate has been used as a catalyst for oxidative rearrangement of aryl and alkyl ketones to esters,[9] ring-contraction of alkylcyclohexanones,[10] synthesis of polyalkylated indole with a ring-contraction reaction,[11] rearrangement of homoallylic alcohol,[12] ring opening of cyclopropanes,[13] and electrophilic cyclization reactions.[14] TTFA has also been reported to promote disulfide bond formation.[15]

In a continuation of our work on acylations,[16] we wish to report herein the acylation of alcohols, phenols and thiols with acetic anhydride using catalytic amounts of thallium(III) chloride at room temperature under solvent-free conditions (Scheme 1, Table 1). All reactions proceeded in excellent yields within quite short reaction times. For the generalization of this catalyst, a large-scale (10.0 mmol) acylation of alcohol was also carried out and found to proceed rapidly in excellent yield. Various benzylic alcohols having electron-donating and electron-withdrawing substituents underwent acylation with very high yields (entries 1–8). Benzylic alcohols containing halogen substituents underwent acylation smoothly with excellent yield (entries 4–6), which indicates that electronic effects of the halogen atom do not influence the reaction. The method also tolerates alcohols with double bonds, such as cinnamyl alcohol and also secondary alcohols (entries 10 and 11). This catalytic system is also applicable to heterocyclic alcohols such as thiophen-2-ylmethanol and pyridin-2-ylmethanol, which give the corresponding acetates in quite high yield, though these require 'relatively longer' reaction times (20 min; entries 12 and 13). This catalyst is also able to convert primary and secondary aliphatic alcohols and neopentyl alcohol into the corresponding acetates in good yields (entries 14–16). Interestingly, phenols also underwent the acylation in the presence of thallium(III) chloride (entries 17–21). The *para*- and *meta*-methoxy-substituted phenols have no effect on the reactivity (entries 20 and 21). Strongly deactivating nitro and cyano groups afforded the corresponding acetates within two and six minutes, respectively. Here again, there were no obvious substituent effects in operation. It was observed that this method was also applicable



Scheme 1

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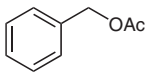
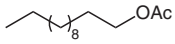
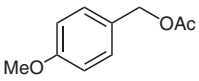
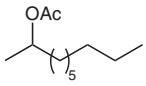
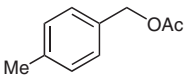
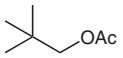
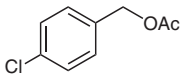
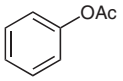
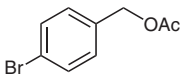
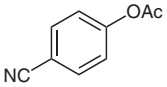
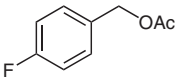
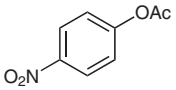
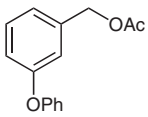
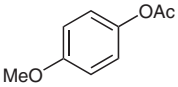
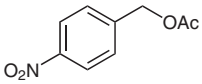
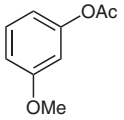
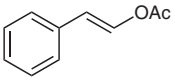
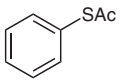
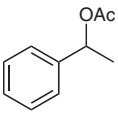
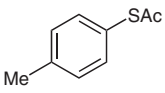
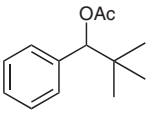
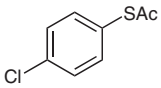
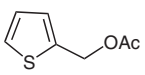
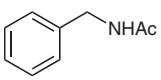
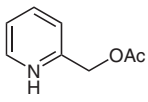
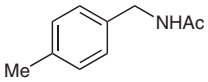
to thiols (entries 22–24). Thiols having electron-donating and electron-withdrawing substituents underwent acylation with high yield in 'relatively long' reaction times (14–20 min). Unfortunately, thallium(III) chloride was unable to catalyze the acylation of amines (entries 25 and 26). When benzoic anhydride was used as an acylating agent with benzyl alcohol, only 20% product was obtained after an overnight reaction. We examined thallium nitrate as a catalyst under the same reaction conditions for the acylation of benzyl alcohol, and found that this catalyst also gave the product, however, the yield was quite low (58%) and the reaction required longer reaction times (6 h). Hence thallium(III) chloride is superior to thallium nitrate in terms of both reaction time and yield.

Table 1 Catalytic Acylation of Alcohols, Phenols and Thiols with Acetic Anhydride Catalyzed by $TlCl_3 \cdot 4H_2O$[a]

Entry	Product	Time (min)	Yield (%)[b]	Entry	Product	Time (min)	Yield (%)[b]
1		4 6[c]	99 97[c]	14		7	95
2		6	96	15		15	97
3		8	95	16		30	90[d]
4		6	96	17		2	99
5		3	99	18		2	97
6		4	99	19		6	99
7		3	99	20		6	91
8		7	99	21		5	94
9		4	98	22		14	90
10		6	99	23		20	87
11		65	72	24		16	92
12		20	87	25		–	–
13		20	99	26		–	–

[a] Reagents and conditions: Alcohol (1 mmol), Ac_2O (2 mmol), $TlCl_3 \cdot 4H_2O$ (1 mol%), r.t. All products were characterized by ^1H and ^{13}C NMR spectroscopy and compared with literature data.[16,24]
[b] Isolated yield.
[c] Large-scale reaction employing 10.0 mmol of benzyl alcohol.
[d] Conversion determined by ^1H NMR spectroscopy.

These results clearly indicate that low catalyst loading (1.0 mol%) and short reaction times (mostly <10 min) under solvent-free conditions are ideal for the present acylations. $La(NO_3)_3$[6b] needs 10 mol% of the catalyst with 10–20 minutes reaction time. Nitroboronic acid[3g] requires 2.5 mol% of the catalyst with 3–10 equivalents of acylating agent and reaction times of 7–12 hours. $Cu(OTf)_2$[4c] requires 2.5 mol% catalyst and 2.0 equivalents of reagent with 1–12 hours reaction time in dichloromethane.

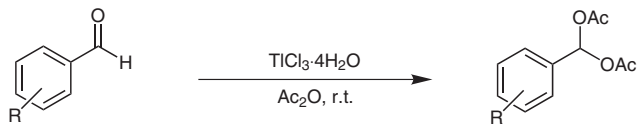
Next we turned our attention to the possibility of geminal diacylation of aldehydes. The formation of geminal-diacylated aldehydes is an important organic transformation because such compounds serve as building blocks for asymmetric allylic alkylation.[17] The diacyl functionality has also been used as protecting groups for aldehydes in addition to acetal, oxathioacetals and thioacetals.[18] Several methods have been reported for the preparation of *gem*-diacylated aldehydes with acetic anhydride. Some examples of the reagents and catalysts that have been developed for this purpose include: $InCl_3$,[19a] $LiBF_4$,[19b] CAN,[19c] I_2,[19d] $FeCl_3$,[19e] $HClO_4$–SiO_2,[19f] tetrabutylammonium tribromide (TBATB),[19g] acetonyltriphenylphosphonium bromide (ATPB),[19h] Wells–Dawson acid,[19i] and some metal triflates, such as: $Cu(OTf)_2$,[20a] $Bi(OTf)_3$,[20b] and $Sc(OTf)_3$.[20c] Other new reactions are also known that employ heterogeneous catalysts such as naflon-H,[21a] montmorillonite,[21b] graphite,[21c] amberlyst [21d] and PVC-$FeCl_3$.[21e]

Although these methods are quite efficient, many have some drawbacks such as harsh reaction conditions, requirement of excess amounts of acetic anhydride (1–8 equiv), expensive graphite and moisture sensitive catalysts, or require the use of organic solvents and long reaction times. Therefore an alternative method, which is simple, mild, efficient and solvent-free, would be desirable.

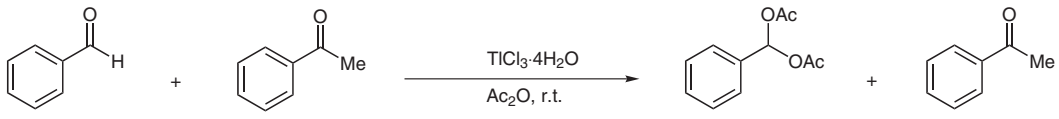
Diacylation of aldehydes with acetic anhydride proceeds in excellent yield under the same reaction conditions describe for the acylation of alcohols (Scheme 2, Table 2). Various types of aromatic and aliphatic aldehydes were used for the reactions. Electron-donating groups on the ring (entries 2–4) produced diacylal products with high yield, as did cinnamaldehyde, which gave the corresponding product in 98% yield (entry 6). Increasing the side-chain length had little influence on the reaction (entry 7). *p*-Chlorobenzaldehyde yielded the corresponding diacyl within 10 minutes (95%), while *o*-chlorobenzaldehyde required 18 minutes (98%) and *m*-chlorobenzaldehyde required 15 min for 91% yield (entries 8, 9 and 10). This again indicates that there were no conspicuous substituent or steric effects of the chlorine atom on diacylation. Since electron-withdrawing groups (*m*-F, *p*-NO_2 and *p*-CN; entries 12, 13 and 14) also gave the corresponding diacyls with excellent yields, electronic effects thus exerted no serious influence on the reactions. Similarly *m*-phenoxybenzaldehyde (entry 15) also rapidly gave 98% yield of the diacylated product (6 min).

Long-chain aliphatic and cyclic aliphatic aldehydes reacted to give the product with 'relatively' low yields (entries 16–19; 78–90%). Since this catalytic system did not produce any acylal from ketones under the same conditions (acetophenone, for example, gave no acylal even after increasing the catalyst loading up to 5 mol% after 18 h; entry 20), the possibility of chemoselective protection of an aldehyde in the presence of a ketone was investigated. As shown in Scheme 3, when a 1:1 mixture of benzaldehyde and acetophenone was allowed to react with acetic anhydride for 18 hours, NMR analysis of the product showed it to consist of a 1:1 mixture of benzaldehyde diacetyl acetal and acetophenone, indicating that the ketone was unreactive under these reaction conditions. The generality and excellence of this thallium(III) chloride methodology can be easily demonstrated by comparing the data with literature results. LiOTf[22] requires 20 mol% of the catalyst and 5–8 equivalents of acylating reagent with 15 hours reaction time at 60 °C, whereas NBS[23] needs 10 mol% of the catalyst for conversion of aldehydes with 8 hours reaction time. $Cu(OTf)_2$[20a] demands 2.5 mol% of the catalyst with 4 hours reaction time in dichloromethane as solvent. ATPB[19h] requires reflux conditions for *gem*-diacylation in 5–14 hours reaction time. In contrast, thallium(III) chloride needs only 1 mol% catalyst at room temperature with relatively short reaction times of 10–20 minutes under solvent-free conditions.

In conclusion, we have found that thallium(III) chloride is a highly efficient catalyst for the acylation of alcohols, phenols and thiols under solvent-free conditions at room temperature, giving acylation products with excellent yields in short reaction times. Thallium(III) chloride is also an efficient catalyst for the *gem*-diacylation of aldehydes, with a range of aliphatic and aromatic aldehydes undergoing diacylation under solvent-free conditions. The notable advantage of this method is that it is air-stable and simple, uses a commercially available catalyst and gives very high yields in short reaction times. This catalytic system is also suitable for large-scale acylation, which may be utilized for industrial applications.

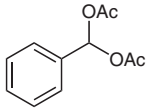
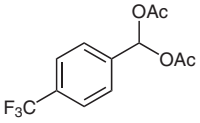
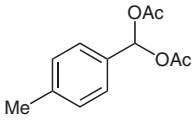
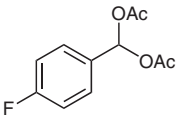
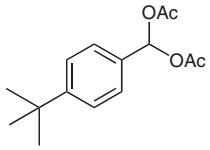
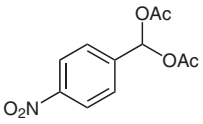
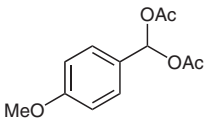
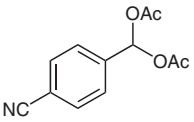
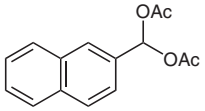
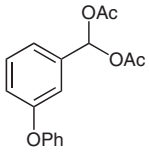
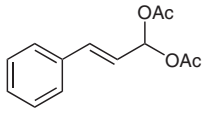
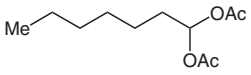
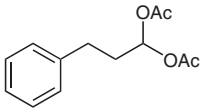
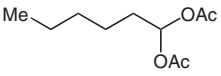
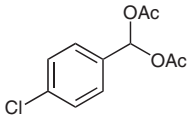
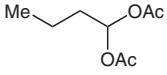
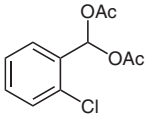
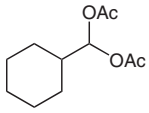
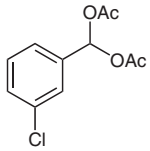
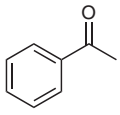


Scheme 2



Scheme 3

Table 2 Diacylation of Aldehydes with Acetic Anhydride Catalyzed by $TlCl_3 \cdot 4H_2O$[a]

Entry	Product	Time (min)	Yield (%)[b]	Entry	Product	Time (min)	Yield (%)[b]
1		6 10[c]	99 97[c]	11		12	94
2		16	80	12		0	95
3		15	80	13		16[d]	89
4		20	94	14		12	93
5		20	98	15		6	98
6		15	96	16		6	78
7		8	91	17		8	90
8		10	95	18		12	86
9		18	98	19		12	82
10		15	91	20		18h[d]	–

[a] Reagents and conditions: Aldehyde (1 mmol), Ac_2O (2 mmol), $TlCl_3 \cdot 4H_2O$ (1 mol%), r.t. All products were characterized by ^1H and ^{13}C NMR spectroscopy and compared with literature data.[19g,25]
[b] Isolated yield.
[c] Large-scale reaction employed 10.0 mmol of benzaldehyde.
[d] 5 mol% of catalyst.

In all cases the ^1H NMR (200 MHz) spectra were recorded in $CDCl_3$ on a Varian Gemini 200 instrument. Chemical shifts (δ) are reported in ppm with TMS as internal standard. ^{13}C NMR data were collected on a Varian Gemini 400 instrument (100 MHz). Some compounds were also identified by HRMS (EI) on Jeol DMX 303 and GCMS (EI, 70eV) mass spectrometers. Data were collected using a 1200L Single Quadrupole GC/MS system with 3800GC/Varian.

Acylation of Alcohols, Phenols and Thiols; General Procedure

Thallium(III) chloride (3.1 mg, 1.0 mol%) was added to a mixture of alcohol (phenol or thiol; 1 mmol) and Ac_2O (2.0 mmol). The reaction mixture was stirred at r.t. for the appropriate time (see Table 1). Upon completion (reaction monitored by TLC), the reaction mixture was diluted with aq $NaHCO_3$ (10 mL) and extracted with EtOAc (3 × 20 mL). Concentration of the combined organic

layer under vacuum gave a crude mass, which was purified by column chromatography with silica gel.

gem-Diacylation of Aldehydes; General Procedure

Thallium(III) chloride (3.1 mg, 1.0 mol%) was added to a mixture of aldehyde (1 mmol) and Ac_2O (2.0 mmol). The reaction mixture was stirred at r.t. for the appropriate time (see Table 1). Upon completion (reaction monitored by TLC), the reaction mixture was diluted with aq $NaHCO_3$ (10 mL) and extracted with EtOAc (3 × 20 mL). Concentration of the combined organic layer under vacuum gave a crude mass, which was purified by column chromatography with silica gel.

Benzyl Acetate (Table 1, entry 1)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.00 (s, 3 H), 5.01 (s, 2 H), 7.32–7.37 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.94, 66.19, 128.04, 128.06, 128.14, 128.36, 135.76, 170.58.

HRMS (EI+): *m*/*z* [M + H]$^+$ calcd for $C_9H_{10}O_2$: 150.0684; found: 150.0680.

GCMS (EI, 70 eV): *m*/*z* (%) = 149.90 (100) [M$^+$].

4-Methoxybenzyl Acetate (Table 1, entry 2)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.42 (s, 3 H), 4.15(s, 3 H), 5.39 (s, 2 H), 7.22–7.26 (m, 2 H), 7.60–7.67 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.78, 55.96, 65.54, 114.23, 127.21, 127.78, 128.12, 159.39, 170.32.

4-Methylbenzyl Acetate (Table 1, entry 3)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.10 (s, 3 H), 2.37 (s, 3 H), 5.09 (s, 2 H), 7.20–7.26 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.87, 21.45, 65.96, 128.11, 128.89, 132.70, 137.66, 170.40.

HRMS (EI+): *m*/*z* [M + H] calcd for $C_{10}H_{12}O$: 164.0837; found: 164.0837.

4-Chlorobenzyl Acetate (Table 1, entry 4)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.07 (s, 3 H), 5.02 (s, 2 H), 7.42–7.58 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.92, 65.35, 128.56, 129.45, 133.93, 134.30, 170.48.

3-Phenoxybenzyl Acetate (Table 1, entry 7)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.30 (s, 3 H), 5.26 (s, 2 H), 7.22–7.32, (m, 5 H), 7.51–7.55 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.55, 65.36, 117.94, 118.65, 122.32, 129.41, 129.49, 137.68, 156.51, 157.08, 170.04.

4-Nitrobenzyl Acetate (Table 1, entry 8)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.34 (s, 3 H), 5.24 (s, 2 H), 7.28–7.30 (m, 2 H), 8.23–8.28 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.98, 109.25, 118.01, 122.24, 132.59, 152.65, 169.29.

(*E*)-2-Phenylethenyl Acetate (Table 1, entry 9)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.98 (s, 3 H), 4.60 (d, *J* = 6.2 Hz, 1 H), 6.20–6.22 (m, 1 H), 6.54 (d, *J* = 15.9 Hz, 1 H), 7.17–7.30 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.95, 123.00, 126.432, 127.88, 128.42, 133.99, 136.01, 170.55.

Pyridin-2-ylmethyl Acetate (Table 1, entry 13)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.13 (s, 3 H), 5.19 (s, 2 H), 7.20 (d, *J* = 1.6 Hz 1 H), 7.31 (d, *J* = 1.7 Hz, 1 H), 7.17 (d, *J* = 1.6 Hz, 1 H), 8.56 (d, *J* = 4.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.95, 64.97, 123.00, 126.432, 127.88, 128.42, 133.99, 136.01, 170.55.

Phenyl Acetate (Table 1, entry 17)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.49 (s, 3 H), 7.21–7.28 (m, 2 H), 7.51–7.56 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.95, 122.77, 129.23, 130.93, 148.92, 168.88.

4-Cyanophenyl Acetate (Table 1, entry 18)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.33 (s, 3 H), 7.21–7.28 (m, 2 H), 7.66–7.77 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.98, 109.12, 118.42, 122.53, 133.39, 153.63, 170.18.

HRMS (EI+): *m*/*z* [M + H]$^+$ calcd for $C_9H_7NO_2$: 161.0477; found: 161.0487.

3-Methoxyphenyl Acetate (Table 1, entry 21)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.25 (s, 3 H), 3.76 (s, 3 H), 6.65–6.79 (m, 3 H), 7.22–7.28 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.86, 55.13, 107.39, 111.31, 113.50, 129.50, 151.35, 160.15, 169.96.

***S*-Phenyl Ethanethioate (Table 1, entry 22)**

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.42 (s, 3 H), 7.32–7.34 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.13, 127.90, 129.14, 129.37, 134.39, 193.95.

HRMS (EI+): *m*/*z* [M + H] calcd for C_8H_8OS: 152.0296; found: 152.0284.

***S*-*p*-Tolyl Ethanethioate (Table 1, entry 23)**

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.37 (s, 3 H), 2.40 (s, 3 H), 7.21–7.25 (m, 2 H), 7.29–7.31 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.98, 30.01, 124.40, 128.47, 129.97, 134.36, 137.36, 139.64, 194.51.

***S*-4-Chlorophenyl Ethanethioate (Table 1, entry 24)**

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.42 (s, 3 H), 7.28–7.30 (m, 2 H), 7.31–7.36 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.16, 126.32, 129.43, 125.63, 135.82, 193.37.

Phenylmethanediyl Diacetate (Table 2, entry 1)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.14 (s, 6 H), 7.41 (s, 3 H), 7.54 (s, 2 H), 7.61 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.63, 89.53, 126.50, 128.43, 129.57, 135.35, 168.57.

HRMS (EI+): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{12}O_4$: 208.0736; found: 208.0739.

4-Tolylmethanediyl Diacetate (Table 2, entry 2)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.16 (s, 6 H), 2.41 (s, 3 H), 7.24 (d, *J* = 16 Hz, 2 H), 7.42 (d, *J* = 16 Hz, 2 H), 7.65 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.21, 21.72, 89.72, 126.54, 129.19, 132.57, 139.71, 168.70.

HRMS (EI+): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{14}O_4$: 222.0892; found: 222.0893.

Naphthalen-2-ylmethanediyl Diacetate (Table 2, entry 5)
^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.15 (s, 6 H), 7.48–7.53 (m 3 H), 7.75 (s, 1 H), 7.89–7.90 (m, 3 H), 8.28 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.81, 89.54, 124.05, 124.87, 125.95, 125.99, 126.68, 128.69, 130.21, 130.53, 130.77, 133.88, 168.67.

HRMS (EI+): *m/z* $[M + H]^+$ calcd for $C_{15}H_{14}O_4$: 258.0892; found: 258.0895.

(1*E*)-1-Phenylprop-1-ene-3,3-diyl Diacetate (Table 2, entry 6)
^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.08 (s, 6 H), 6.18 (d, *J* = 15.9 Hz, 1 H), 6.83 (d, *J* = 15.9 Hz 1 H), 7.27–7.39 (m, 5 H), 7.45 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.86, 89.70, 121.67, 126.99, 128.64, 128.80, 135.58, 168.65.

(4-Chlorophenyl)methanediyl Diacetate (Table 2, entry 8)
^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.11 (s, 6 H), 7.38 (d, *J* = 8 Hz, 2 H), 7.44 (d, *J* = 8 Hz, 2 H), 7.31 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.71, 88.91, 128.08, 128.75, 133.95, 135.61, 168.57.

(4-Nitrophenyl)methanediyl Diacetate (Table 2, entry 13)
^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.15 (s, 6 H), 7.26 (d, *J* = 8 Hz, 2 H), 7.34 (s, 1 H), 8.25 (d, *J* = 8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.70, 88.31, 123.81, 127.84, 141.88, 148.61, 168.51.

HRMS (EI+): *m/z* $[M + H]^+$ calcd for $C_{11}H_{11}NO_6$: 253.0586; found: 253.0586.

(3-Phenoxyphenyl)methanediyl Diacetate (Table 2, entry 15)
^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.20 (s, 6 H), 7.05 (d, *J* = 4 Hz, 2 H), 7.14–7.20 (m, 3 H), 7.33 (t, *J* = 8 Hz, 1 H), 7.38–7.41 (m, 3 H), 7.62 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.72, 89.09, 116.81, 119.04, 119.60, 121.24, 123.59, 129.77, 129.91, 137.29, 156.56, 157.49, 168.60.

Heptane-1,1-diyl Diacetate (Table 2, entry 16)
^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.2 Hz, 3 H), 1.31–1.41 (m, 8 H), 1.85 (m, 2 H), 2.21 (s, 6 H), 6.29 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.92, 22.43, 23.27, 28.96, 31.61, 31.97, 90.53, 170.57.

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