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One-pot three components synthesis of *O*-acetylcyanohydrins with TMSCN, acetic anhydride and carbonyl compounds under solvent-free condition

Santosh T. Kadam, Sung Soo Kim *

Department of Chemistry, Inha University, Incheon 402-751, South Korea

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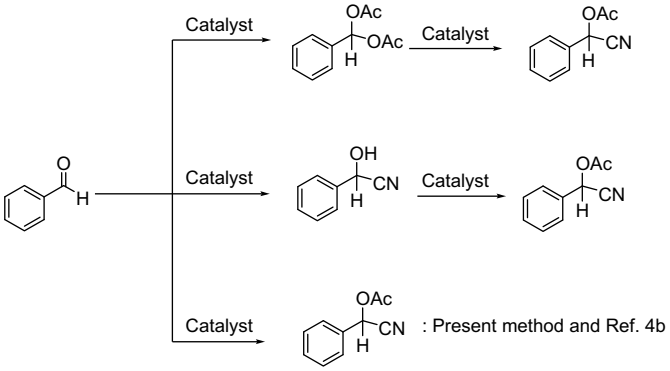
ABSTRACT

One-pot three components synthesis of *O*-acetylcyanohydrins has been developed in the presence of $B(C_6F_5)_3$ as the catalyst. Variety of aldehydes or ketones reacts with TMSCN and acetic anhydride (Ac_2O) under the influence of 1 mol % of $B(C_6F_5)_3$ to give good to excellent yield of the products without solvent at rt.

1. Introduction

Cyanohydrins have shown the broad interest in recent years because of their synthetic utility when transferring their functionality into the bioactive and natural products. Cyanohydrins can be readily converted into functionalized compounds such as α-hydroxy acid, α-hydroxy alehyde, α-amino alcohol and 1,2-diol.[1] Cyanohydrin silyl ethers are prepared by the reaction of TMSCN (trimethylsilylcyanide) with aldehydes or ketones under the influence of the catalyst. Cyanohydrins and their silyl ethers show serious drawback of the instability due to the reversibility of the cyanohydrin formation unless an excess of cyanide source is used. Several procedure affording *O*-silylated,[2] *O*-phosphorylated,[3] *O*-acetylated[4] and *O*-formylated[5] cyanohydrin products from the aldehydes or ketones have been established. *O*-Acetyl cyanohydrin is a stable intermediate that undergoes further transformation without loss of enantiomeric purity,[6]and shows potential insecticide activity.[7]

Acetylcyanohydrins have been prepared via several methods (Scheme 1). Sydnes et al. have prepared the acetylcyanohydrins from the aldehydes through acylals in two step reaction in presence of titanium (IV) chloride.[4a] Grieng et al. reported the hydroxynitrile lyase catalyzed synthesis of acetylcyanohydrins in two step reactions.[4c] $Sc(OTf)_3$ has been employed for the one-pot esterification of trimethylsilyl ether using acid anhydride or acid chloride.[8] Iron (III)chloride was used as the catalyst for the preparation of acetylcyanohydrin by reaction of aldehyde with TMSCN and acetic anhydride.[4b] Some of the catalytic method required two step reaction path at −78 °C and use of equimolar amount of the catalyst.[4a] Other catalytic method demanded excess amount of metal cyanide and acylating agent (4 equiv) with long reaction time.[9] The lack of facile and single step synthetic methodology under mild reaction condition has prompted us to develop an efficient one-pot procedure for the synthesis of acetylcyanohydrins under solvent-free condition.



Scheme 1. Comparison of the methods for the synthesis of *O*-acetylcyanohydrins.

* Corresponding author. Fax: +82 32 867 5604.
E-mail address: sungsoo@inha.ac.kr (S.S. Kim).

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With increasing environmental concern, the need for solvent-free and environmentally benign method have become of significant importance. According to the principle of green chemistry, synthetic method should be designed to minimize the energy input by running the reaction at ambient temperature and reduce the reaction steps to avoid the unnecessary use of solvent.[10] In this regard the development of one-pot reaction under solvent-free condition at rt is desirable.

$B(C_6F_5)_3$, **1** is a air-stable, water-tolerant, and thermally stable Lewis acid.[11] **1** shows comparable acid strength to BF_3 but induces no problem associated with reactive B–F bond. **1** functions typical carbonyl-activating capacity in aldol and Diels–Alder type reactions.[11] Recently, this catalyst has found wide applications such as hydrosilation of alcohols,[12] carbonyl groups,[13] and imines,[14] Ferrier azaglycosylation with sulfonamides and carbamate,[15] reduction of carbonyl group to methylene,[16] and direct cyanation of alcohol[17] (Fig. 1).

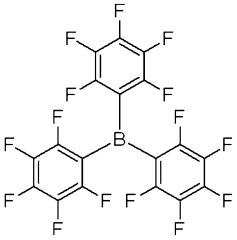


Fig. 1. Tris (pentafluorophenyl) borane, **1**.

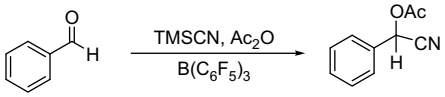
2. Results and discussions

In light of the success in developing several catalytic systems for the synthesis of chiral,[18] achiral cyanosilyl ethers,[19] and acetylation of alcohols,[20] we extend our studies to the *O*-acetylcyanohydrin synthesis. We wish to herein report a simple one-pot method for the synthesis *O*-acetyl cyanohydrins at rt. This could be the first example of borane-catalyzed synthesis of *O*-acetylcyanohydrins under solvent-free condition.

The study involving **1**-catalyzed reaction of benzaldehyde with TMSCN and acetic anhydride is shown in Table 1. Use of 5 mol % of **1** in CH_2Cl_2 is able to produce the acetylcyanohydrin at rt with poor yield (33%) within 7 h reaction time. Among the solvent tested for the reaction, $CHCl_3$ shows the highest yield of 48% (entry 4), while THF gave no acetylcyanohydrin under same reaction condition (entry 3). It is very interesting mention that the highest yield (92%) in 3 h reaction time is observed when benzaldehyde reacts with TMSCN and acetic anhydride in the presence of 1 mol % of **1** without using solvent (entry 9).

The synthesis of various acetylcyanohydrins from carbonyl compounds under the reaction conditions of entry 9, Table 1 is shown in Table 2. The unsubstituted benzaldehyde produces the 92% yield of desired product (entry 1). When bezoyl chloride is

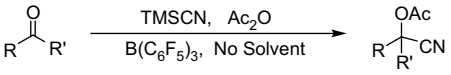
Table 1
One-pot three components synthesis of *O*-acetylcyanohydrins catalyzed by $B(C_6F_5)_3$ under various conditions[a]



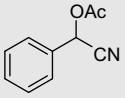
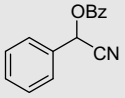
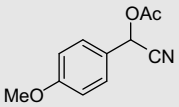
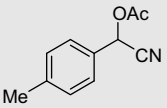
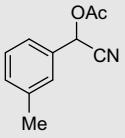
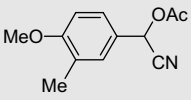
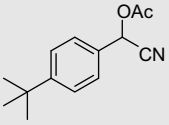
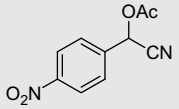
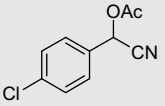
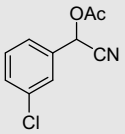
Entry	Catalyst (mol %)	Solvent	Time (h)	Yield[b] (%)
1	5	CH_2Cl_2	7	33
2	5	CH_3CN	7	21
3	5	THF	7	0
4	5	$CHCl_3$	7	48
5	5	CH_3NO_2	7	15
6	5	Toluene	7	28
7	5	No solvent	3	90
8	3	No solvent	3	90
9	1	No solvent	3	92
10	0.5	No solvent	3	76

[a] Reagent and conditions: Aldehyde (1 mmol), TMSCN (1.2 mmol), Ac_2O (2 mmol) at rt.
[b] Isolated yield.

Table 2
Synthesis of *O*-acetylcyanohydrins with TMSCN, acetic anhydride and aldehydes or ketones catalyzed by $B(C_6F_5)_3$[a]

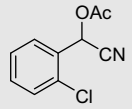
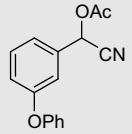
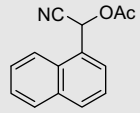
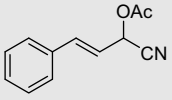
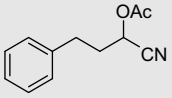
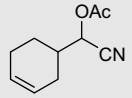
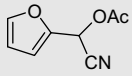
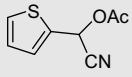
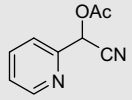
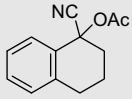
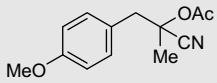
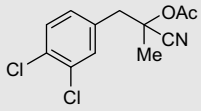
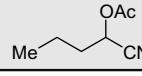


R: Aromatic or Aliphatic
R': H and Me

Entry	Product	Time (h)/Yield[b] (%)
1		3/92
2		5/88[c]
3		3/85
4		3/94
5		3/90
6		3/98
7		3/89
8		8/71
9		3/95
10		3/91

(*continued on next page*)

Table 2 (*continued*)

Entry	Product	Time (h)/Yield[b] (%)
11		8/75
12		3/96
13		3/95
14		3/90
15		4/90
16		6/73
17		3/71
18		3/95
19		3/91
20		6/90
21		6/98
22		6/97
23		6/95
24[d]		NR

[a] Reagent and conditions: Aldehydes/Ketones (1 mmol), TMSCN (1.2 mmol), $B(C_6F_5)_3$ (1 mol%) and Ac_2O (2 mmol) were employed at rt.
[b] Isolated yield.
[c] Benzoyl chloride was used instead of Ac_2O.
[d] The aldehyde without benzene ring gives no reaction.

used for the cyanobenzoylation of benzaldehyde, it gives 88% of the product within 5 h reaction time (entry 2). Relative to acetic anhydride, benzoyl chloride shows longer reaction time with lower yield. The electron-releasing substituents at the *para* position of benzaldehyde (MeO, Me, *tert*-Butyl) exhibit quite high yield of corresponding acetylcyanohydrin within 3 h reaction time (entries 3–7). The benzaldehyde having two electron-donating substituents (*p*-MeO and *m*-Me) yields the desired product with excellent yield (98%) (entry 6). The strongly electron-withdrawing *p*-nitrobenzaldehyde undergoes smooth reaction with moderate yield in relatively longer reaction time (8 h, 71%) (entry 8). This could be the electronic effect of nitro group which exerts the critical role for the reaction. The reactivity of halogen substituted benzaldehydes for acetylcyanation is tested. The *o*-, *m*-, and *p*-chlorobenzaldehydes allow reaction with TMSCN and acetic anhydride (entries 9–11). Relative to *p*- and *m*-chlorobenzaldehydes, *o*-chlorobenzaldehyde requires the longer reaction time and lower yield (8 h, 75%). This indicates that the steric hindrance of chlorine atom may play the important role in the reaction. The moderate electron-releasing *m*-phenoxy benzaldehyde produces the excellent yield (96%) (entry 12). The unsubstituted napthaldehyde undergoes the smooth reaction with considerably high yield (entry 13). Furthermore, the cinnamaldehyde and hydrocinnamaldehyde offer the corresponding acetylcyanohydrin in good yield (entries 14 and 15). Hydrocinnamaldehyde needs longer reaction time (4 h) relative to cinnamaldehyde (3 h) in spite of the same yield obtained. It should be mention that 3-cyclohexane-1-carboxaldehyde with enolizable hydrogen is able to produce the desired product with moderate yield within longer reaction time (entry 16). Acid sensitive 2-furaldehyde undergoes smooth reaction with lower yield of 71% (entry 17). Similarly other heterocyclic 2-thiophenaldehyde and 2-pyridinecarboxaldehyde produce corresponding acetylcyanohydrin with considerably good yield (entries 18 and 19). The same catalytic method is equally applicable for the synthesis of acetylcyanohydrin from ketones (entries 20–23). Cyclohexanone and α-tetralone undergo smooth acetylcynation in 6 h reaction time with excellent yield (90 and 98%) (entries 20 and 21). Phenylacetone having strong electron-donating substituent (*p*-MeO) on benzene ring yields the product with surprisingly good yield (entry 22). Similarly phenylacetone with electron-withdrawing chlorine substituent on *para* and *meta* position produces the corresponding acetylcyanohydrin with good yield (entry 23). Relative to aldehyde, ketone takes about twice longer reaction time for the reaction (6 h). This may be due to the steric and electronic effects of the ketone for the nucleophilic addition. The lowest catalyst loading at rt under the solvent-free condition is the advantage of present catalytic system over other literature methods (Table 3).

Table 3
$B(C_6F_5)_3$ catalyzed synthesis of *O*-acetylcyanohydrins in comparison with other literatures

Entry	Catalyst	Mol%	Solvent	Temp (°C)	Reference
1	$B(C_6F_5)_3$	1.0	No solvent	rt	Present method
2	$TiCl_4$	1.1 equiv	CH_2Cl_2	−78	4a
3	$FeCl_3$	5.0	CH_3NO_2	0 to rt	4b
4	$Sc(OTf)_3$	1.0	CH_3CN	rt	8

3. Summary

A very simple and convenient method for the synthesis of *O*-acetylcyanohydrins through one-pot three components coupling reaction is described. Aldehydes or ketones, TMSCN and acetic anhydride are coupled using **1** as the catalyst without help of the solvent. The major advantage of the method is the lowest catalyst quantity under solvent-free condition. Aldehydes and ketones result in similar yield of products but ketones require relatively longer reaction time than aldehydes. The non-metallic and solvent-free condition becomes 'environmentally friendly'.

4. Experimental section

4.1. General

In all cases the ^{1}H NMR (200 MHz) spectra were recorded with Varian Gemini 2000 spectrometer. Chemical shifts are reported in ppm in $CDCl_3$ with tetramethylsilane as an internal standard. ^{13}C NMR data were collected on a Varian Gemini 2000 spectrometer (100 MHz). GC–MS were recorded with 1200L Single Quadrupole GC/MS System with 3800GC/Varian.

4.2. General procedure for the synthesis of *O*-acetylcyanohydrin

To a mixture of aldehyde (1 mmol) and TMSCN (1.2 mmol), $B(C_6F_5)_3$ (1 mol %) and Ac_2O (2 mmol) were added at rt. The completion of the reaction was monitored with TLC. After the completion of reaction, the reaction mixture was filtered and concentrated. The viscous mass was subjected to silica gel flash column chromatography to obtain the pure compound.

^{1}H and ^{13}C NMR data for known products are given below which is same with literature values.[4a,c,e,8] HRMS values for new products are given (entries 6, 7, 21–23).

4.2.1. Cyano(phenyl)methyl acetate (entry 1)

^{1}H NMR ($CDCl_3$, 200 MHz): 2.16 (s, 3H), 6.40 (s, 1H), 7.43–7.51 (m, 5H). ^{13}C NMR ($CDCl_3$, 400 MHz): 20.46, 62.86, 116.20, 127.88, 129.27, 130.42, 131.68, 168.96.

4.2.2. Cyano(phenyl)methyl benzoate (entry 2)

^{1}H NMR ($CDCl_3$, 200 MHz): 6.66 (s, 1H), 7.40–7.66 (m, 5H), 8.17–8.03 (m, 5H). ^{13}C NMR ($CDCl_3$, 400 MHz): 63.3, 116.2, 127.9, 128.1, 128.7, 128.9, 129.3, 130.1, 130.4, 130.5, 131.8, 134.1, 134.6, 164.6. HRMS-EI+: *m*/*z* Calcd for $C_{15}H_{11}NO_2$: 237.0790; found: 237.0787.

4.2.3. Cyano(4-methoxyphenyl)methyl acetate (entry 3)

^{1}H NMR ($CDCl_3$, 200 MHz): 2.12 (s, 3H), 3.81 (s, 3H), 6.34 (s, 1H), 7.92 (d, *J*=6 Hz, 2H), 7.45 (d, *J*=8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz): 20.46, 55.41, 62.62, 114.56, 116.47, 123.86, 129.66, 161.13, 169.07.

4.2.4. Cyano(p-tolyl)methyl acetate (entry 4)

^{1}H NMR ($CDCl_3$, 200 MHz): 2.15 (s, 3H), 2.38 (s, 3H), 6.36 (s, 1H), 7.25 (d, *J*=8 Hz, 2H), 7.36 (d, *J*=8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz): 20.4, 21.2, 62.7, 116.3, 127.9, 128.9, 129.9, 140.6, 169.0.

4.2.5. Cyano(m-tolyl)methyl acetate (entry 5)

^{1}H NMR ($CDCl_3$, 200 MHz): 2.15 (s, 3H), 2.32 (s, 3H), 6.37 (s, 1H), 7.34–7.25 (m, 4H). ^{13}C NMR ($CDCl_3$, 400 MHz): 20.4, 21.3, 62.9, 116.2, 124.9, 128.4, 129.1, 131.1, 131.6, 139.2, 168.9.

4.2.6. Cyano(4-methoxy-3-methylphenyl)methyl acetate (entry 6)

^{1}H NMR ($CDCl_3$, 200 MHz): 2.13 (s, 3H), 2.23 (s, 3H), 3.84 (s, 3H), 6.31 (s, 1H), 6.84 (d, *J*=8.4 Hz, 1H), 7.32 (d, *J*=10 Hz, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz): 16.1, 20.4, 55.4, 62.7, 110.0, 116.5, 123.3, 127.1, 127.7, 130.2, 159.2, 169.0. HRMS-EI+: *m*/*z* Calcd for $C_{12}H_{13}NO_3$: 219.0895; found: 219.0893.

4.2.7. (4-tert-Butylphenyl)(cyano)methyl acetate (entry 7)

^{1}H NMR ($CDCl_3$, 200 MHz): 1.33 (s, 9H), 2.15 (s, 3H), 6.39 (s, 1H), 6.94 (d, *J*=8 Hz, 2H), 7.42 (d, *J*=8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz): 20.5, 31.1, 34.8, 62.7, 116.2, 126.7, 127.7, 128.7, 153.2, 169.0. HRMS-EI+: *m*/*z* Calcd for $C_{14}H_{17}NO$: 231.1259; found: 231.1257.

4.2.8. Cyano(4-nitrophenyl)methyl acetate (entry 8)

^{1}H NMR ($CDCl_3$, 200 MHz): 2.15 (s, 3H), 6.50 (s, 1H), 7.74 (d, *J*=11 Hz, 2H), 8.30 (d, *J*=11 Hz, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz): 20.3, 61.7, 115.1, 123.8, 124.4, 128.8, 138.1, 168.6.

4.2.9. (4-Chlorophenyl)(cyano)methyl acetate (entry 9)

^{1}H NMR ($CDCl_3$, 200 MHz): 2.16 (s, 3H), 6.37 (s, 1H), 7.74 (d, *J*=8 Hz, 2H), 8.42 (d, *J*=8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz): 20.4, 61.1, 115.8, 122.2, 129.5, 130.2, 136.6, 168.6.

4.2.10. (3-Chlorophenyl)(cyano)methyl acetate (entry 10)

^{1}H NMR ($CDCl_3$, 200 MHz): 2.16 (s, 3H), 6.38 (s, 1H), 7.44–7.39 (m, 3H), 7.51 (s, 1H). ^{13}C NMR ($CDCl_3$, 400 MHz): 20.3, 62.0, 115.7, 125.9, 127.8, 130.5, 130.5, 133.6 135.0, 168.8.

4.2.11. 2-Chlorophenyl(cyano)methyl acetate (entry 11)

^{1}H NMR ($CDCl_3$, 200 MHz): 2.19 (s, 3H), 6.71 (s, 1H), 7.45–7.36 (m, 3H), 7.75–7.70 (m, 1H). ^{13}C NMR ($CDCl_3$, 400 MHz): 20.2, 60.2, 115.3, 127.6, 129.4, 130.2, 131.75, 133.4, 168.6.

4.2.12. Cyano(3-phenoxyphenyl)methyl acetate (entry 12)

^{1}H NMR ($CDCl_3$, 200 MHz): 2.14 (s, 3H), 6.34 (s, 1H), 7.05–7.01 (m, 3H), 7.16–7.13 (m, 2H), 7.40–7.34 (m, 4H). ^{13}C NMR ($CDCl_3$, 400 MHz): 20.4, 62.5, 116.0, 117.7, 119.4, 120.11, 122.2, 124.1, 130.0, 130.7, 133.6, 156.2, 158.1, 168.9. HRMS-EI+: *m*/*z* Calcd for $C_{16}H_{13}NO_3$: 267.0895; found: 267.0899.

4.2.13. Cyano(naphthalen-1-yl)methyl acetate (entry 13)

^{1}H NMR ($CDCl_3$, 200 MHz): 2.16 (s, 3H), 7.04 (s, 1H), 7.65–7.48 (m, 4H), 7.82 (d, *J*=7.6 Hz, 1H), 7.93 (q, *J*=8 Hz, 2H), 8.01 (d, *J*=8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 400 MHz): 20.4, 61.3, 116.2, 122.6, 125.1, 126.6, 127.0, 127.6, 127.7, 129.2, 130.0, 131.5, 133.9, 169.1.

4.2.14. (E)-1-Cyano-3-phenylallyl acetate (entry 14)

^{1}H NMR ($CDCl_3$, 200 MHz): 2.16 (s, 3H), 6.03 (d, *J*=7.2 Hz, 1H), 6.20 (dd, *J*=16.4, 7.2 Hz, 1H), 6.98 (d, *J*=16 Hz, 1H), 7.42–7.33 (m, 5H). ^{13}C NMR ($CDCl_3$, 400 MHz): 20.4, 61.5, 118.4, 127.2, 128.8, 129.4, 134.4, 137.7, 168.9.

4.2.15. 1-Cyano-3-phenylpropyl acetate (entry 15)

^{1}H NMR ($CDCl_3$, 200 MHz): 2.10 (s, 3H), 2.20 (q, *J*=13 Hz, 2H), 2.81 (t, *J*=8.6 Hz, 2H), 5.25 (t, *J*=6.8 Hz, 1H), 7.32–7.16 (m, 5H). ^{13}C NMR ($CDCl_3$, 400 MHz): 20.3, 30.7, 33.7, 60.5, 116.8, 126.7, 128.3, 128.8, 139.1, 168.1.

4.2.16. Cyano(cyclohex-3-enyl)methyl acetate (entry 16)

^{1}H NMR ($CDCl_3$, 200 MHz): 1.51–1.48 (m, 2H), 2.05–1.93 (m, 4H), 2.15 (s, 3H), 2.20–2.16 (m, 2H), 5.25 (d, *J*=8 Hz, 1H), 5.73–5.64 (m, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz): 20.3, 23.9, 24.2, 26.6, 36.3, 64.9, 116.3, 124.3, 127.1, 170.9.

4.2.17. Cyano(furan-2-yl)methyl acetate (entry 17)

^{1}H NMR ($CDCl_3$, 200 MHz): 2.21 (s, 3H), 6.48 (s, 1H), 6.83 (d, *J*=4 Hz, 1H), 7.18 (d, *J*=3.6 Hz, 1H), 7.25 (d, *J*=2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 400 MHz): 20.2, 70.2, 113.4, 114.1, 142.2, 154.3, 169.6.

4.2.18. Cyano(thiophen-2-yl)methyl acetate (entry 18)

^{1}H NMR ($CDCl_3$, 200 MHz): 2.12 (s, 3H), 6.60 (s, 1H), 7.01 (t, *J*=9 Hz, 1H), 7.35 (d, *J*=6 Hz, 1H), 7.42 (d, *J*=8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 400 MHz): 20.3, 58.1, 115.6, 127.2, 129.0, 129.6, 133.4, 168.8. HRMS-EI+: *m*/*z* Calcd for $C_8H_7NO_2S$: 181.0197; found: 191.0198.

4.2.19. Cyano(pyridin-2-yl)methyl acetate (entry 19)

^{1}H NMR ($CDCl_3$, 200 MHz): 2.21 (s, 3H), 6.44 (s, 1H), 7.34 (t, *J*=13.6 Hz, 1H), 7.50 (d, *J*=8.8 Hz, 1H), 7.78 (t, *J*=8.6 Hz, 1H), 8.62 (d,

J=7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 400 MHz): 20.3, 63.8, 115.5, 121.9, 124.8, 137.6, 150.0, 150.8, 168.7.

4.2.20. 1-Cyanocyclohexyl acetate (entry 20)

^{1}H NMR ($CDCl_3$, 200 MHz): 1.21–1.29 (m, 2H), 1.51–1.80 (m, 6H), 2.01 (s, 3H), 2.21–2.18 (m, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz): 21.0, 21.9, 24.4, 34.9, 72.5, 118.4, 168.7.

4.2.21. 1-Cyano-1,2,3,4-tetrahydronaphthalen-1-yl acetate (entry 21)

^{1}H NMR ($CDCl_3$, 200 MHz): 1.07–1.95 (m, 2H), 2.10 (s, 3H), 2.56–2.53 (m, 2H), 2.86–2.85 (m, 2H), 1.51–1.80 (m, 6H), 2.01 (s, 3H), 2.21–2.18 (m, 2H), 7.15 (d, J=8.4 Hz, 1H), 7.32–7.25 (m, 2H), 7.71 (d, J=8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 400 MHz): 180.3, 21.3, 28.3, 33.0, 71.8, 118.3, 126.8, 128.9, 129.5, 129.9, 131.4, 137.0, 168.8. HRMS-EI+: m/z Calcd for $C_{13}H_{13}NO_2$: 215.0946; found: 215.0945.

4.2.22. 2-Cyano-1-(4-methoxyphenyl)propan-2-yl acetate (entry 22)

^{1}H NMR ($CDCl_3$, 200 MHz): 1.67 (s, 3H), 2.08 (s, 3H), 3.18 (dd, J=12, 10 Hz, 2H), 3.79 (s, 3H), 6.86 (d, J=8 Hz, 2H), 7.20 (d, J=8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz): 21.0, 21.9, 24.4, 34.9, 72.5, 118.4, 168.7. HRMS-EI+: m/z Calcd for $C_{13}H_{15}NO_3Si$: 233.1052; found: 233.1050.

4.2.23. 2-Cyano-1-(3,4-dichlorophenyl)propan-2-yl acetate (entry 23)

^{1}H NMR ($CDCl_3$, 200 MHz): 1.74 (s, 3H), 2.10 (s, 3H), 3.20 (dd, J=13, 7 Hz, 2H), 7.18 (d, J=8 Hz, 1H), 7.40 (s, 1H), 7.44 (d, J=8.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 400 MHz) 21.0, 24.2, 43.9, 71.2, 118.0, 130.0, 130.4, 132.1, 132.4, 133.3, 168.9. HRMS-EI+: m/z Calcd for $C_{13}H_{11}Cl_2NO_2$: 271.0167; found: 271.0172.

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