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A Novel Metal-free Reductive Esterification of *N*-Tosylhydrazones with Carboxylic Acids

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A novel method for the synthesis of esters via reductive coupling of *N*-tosylhydrazones with carboxylic acids under metal-free conditions has been developed. Various functional groups were found to be tolerable under the reaction conditions to afford low to good yields.

Keywords metal-free, *N*-tosylhydrazones, esterification, carboxylic acids

Introduction

Since the discovery of *N*-tosylhydrazone in the mid-20th century, it has been a versatile synthetic intermediate for almost 60 years.[1] Most leading scientists shed light on metal catalyzed cross-coupling reactions of *N*-tosylhydrazone with aryl halides,[2] aryl sulfonates,[3] alkynes,[4] azoles,[5] and in the cascade carbonylation,[6] which have shown generality of this reagent to build useful functionalities for synthetic compounds. However, in the course of this research, the metal-free reactions with regard to tosylhydrazones were limited to certain reactions, to the best of our knowledge, only four reports on the use of tosylhydrazones with pinacolborane,[7] arylboronic acids,[8] alcohols,[9] and thiols[10] were documented (Scheme 1). Inspired from the mechanism proposed by Valdés,[8,9] we hypothesized that carboxylic acids could be a decent nucleophile to attack the diazo intermediate under the standard conditions. Thus, herein, we will describe this metal-free reductive coupling as a novel and straightforward approach to synthesize esters.

Results and Discussion

To test our hypothesis, 3-phenoxybenzoic acid (**1c**) and 1-(1-(4-methoxy phenyl) ethylidene)-2-tosylhydrazine (**2c**) were refluxed in 1,4-dioxane with the presence of 4 equiv. K_2CO_3. With the same substrate molar ratio, the reaction underwent sluggishly. However, excess tosylhydrazones improved the yield dramatically. As for optimized conditions, 2 equiv. of tosylhydrazones increased the isolated yield up to 86% (Scheme 2).

To further explore the generality of this novel reductive esterification reaction, we screened the substrate scopes from aromatic to aliphatic carboxylic acids under the optimized conditions. As shown in Table 1, all of the screened carboxylic acids were proven to be reliable substrates affording the corresponding esters with low to good yields. Aromatic carboxylic acids bearing electron-donating groups (2,6-dimethyl, *m*-phenoxy, *o*-methoxy) exhibited better yields than those with electron-withdrawing groups (*o*-I, *p*-NO_2, *p*-formyl), for an instance, *para*-substituted nitro group impaired the yield to 30% (Entry 6). Using DMF as solvent occasionally enhanced the reaction yields (Entries 5—8). It is worth mentioning that the formyl-group does survive in this reductive esterification conditions, albeit with only low yield as 36% in DMF (Entry 7). Aliphatic carboxylic acids afforded medium yields to corresponding esters, and even for high steric trimethylacetic acid, the reaction took place smoothly to give 60% yield (Entry 9).

Further extension of scopes for *N*-tosylhydrazones was also investigated. As depicted in Table 2, the *N*-tosylhydrazones applied can be conjugated with aromatic rings bearing electron-rich and electron-deficient substituents giving medium to good yields (Entries 1—8). Apparently, electron-deficient substituents (Entries 2, 4, 6) enervated the carbene intermediates which led to lower yields as compared with substrates with electron-rich groups. Delightfully, tosylhydrazones with aliphatic skeletons were also proven to be good substrates for this novel reductive esterification reaction (Entries 9, 10). Furthermore, the tosylhydrazones prepared from aromatic or aliphatic aldehydes were

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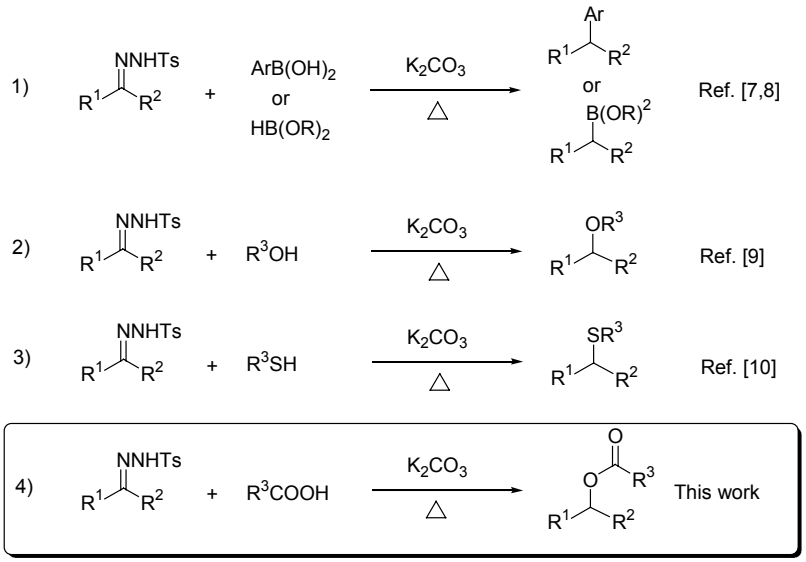
Scheme 1 Metal-free reductive coupling reactions of *N*-tosylhydrazones



Scheme 2 The optimization of reaction conditions

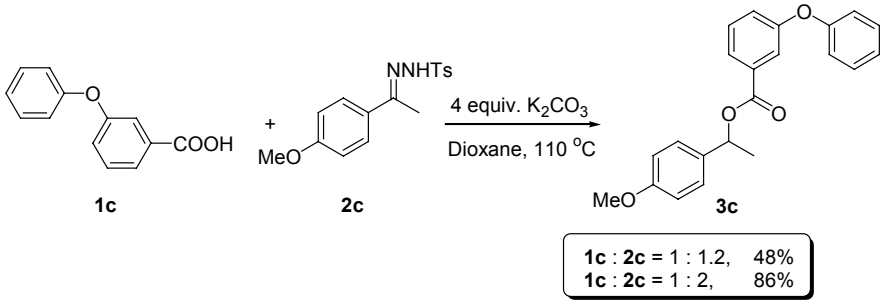
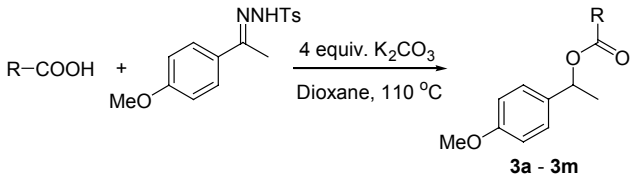


Table 1 The scope of carboxylic acids[a]



Entry	R	Product	Yield[b,c]/%
1	Ph	**3a**	40 (71)
2	2,6-Dimethyl-C_6H_3	**3b**	66
3	*m*-PhO-C_6H_4	**3c**	86
4	*o*-MeO-C_6H_4	**3d**	59
5	*o*-I-C_6H_4	**3e**	40 (48)
6	*p*-NO_2-C_6H_4	**3f**	30 (49)
7	*p*-Formyl-C_6H_4	**3g**	Trace (36)
8	*trans*-PhCH=CH_2	**3h**	25 (53)
9	—*t*-Bu	**3i**	60
10	—*i*-Bu	**3j**	51
11	Diphenyacetic acid	**3k**	70

[a] 0.5 mmol carboxylic acid, 1 mmol *N*-tosylhydrazone and 2 mmol K_2CO_3, 18 h; [b] Isolated yield; [c] DMF as solvent in parentheses.

tolerant with the reaction conditions to form the corresponding esters in moderate to high yields (Entries 11—14).

Experimental

For a typical reaction, 0.5 mmol carboxylic acid, 1 mmol *N*-tosylhydrazone and 2 mmol K_2CO_3 were charged into 25 mL oven-dried flask, and backfilled with nitrogen three times. 5 mL fresh-distilled 1,4-dioxane or DMF was then injected into the flask, followed by heating up to 110 ℃ for 18 h. The reaction was monitored by TLC until starting materials consumed, then removed all of the volatiles for further purification on silica chromatography.

1-(4-Methoxyphenyl) ethyl benzoate (3a) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09 (d, J=6.8 Hz, 2H), 7.57 (t, J=7.2 Hz, 1H), 7.46 (t, J=7.6 Hz, 2H), 7.42 (d, J=8.4 Hz, 2H), 6.93 (d, J=8.8 Hz, 2H), 6.13 (q, J=6.4 Hz, 1H), 3.83 (s, 3H), 1.69 (d, J=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.9, 159.3, 133.9, 132.8, 130.7, 129.6, 128.3, 127.6, 113.9, 72.6, 55.3, 22.2; HRMS (ESI) calcd for $C_{16}H_{16}O_3Na$ [M + Na]$^+$ 279.0997, found 279.1001.

1-(4-Methoxyphenyl)ethyl 2,6-dimethylbenzoate

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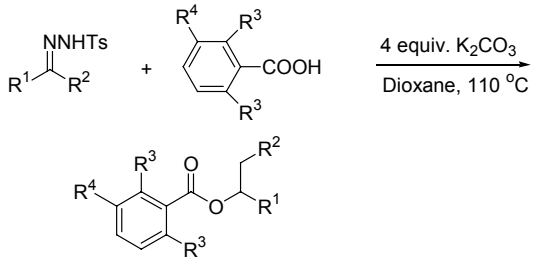
Table 2 The scope of *N*-tosylhydrazones[a]



4a - 4n

Entry	R^3=H, R^4=Ph—O—		Product	Yield[b,c]/%
	R^1	R^2		
1	Ph	CH_3	**4a**	56
2	*o*-BrC_6H_4	CH_3	**4b**	42
3	*p*-$MeOC_6H_4$	CH_3	**4c (3c)**	86
4	*p*-$CF_3C_6H_4$	CH_3	**4d**	27
5	*p*-ClC_6H_4	CH_3	**4e**	71
6	*m*-$NO_2C_6H_4$	CH_3	**4f**	40
7	Ph	CH_2CH_3	**4g**	66
8	*p*-$CH_3C_6H_4$	CH_3	**4h**	60
9	Cyclohexane		**4i**	38 (58)
10	C_3H_7	CH_3	**4j**	66
	R^3=CH_3, R^4=H			
11	H	Ph	**4k**	85
12	H	*p*-OCH_3-C_6H_4	**4l**	89
13	H	*p*-F-C_6H_4	**4m**	55
14	H	$CH(CH_3)_2$	**4n**	56

[a] 0.5 mmol carboxylic acid, 1 mmol *N*-tosylhydrazone and 2 mol K_2CO_3, 18 h; [b] Isolated yield; [c] DMF as solvent in parentheses.

(3b) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 (d, J=8.4 Hz, 2H), 7.19 (t, J=6.8 Hz, 1H), 7.03 (d, J=7.6 Hz, 2H), 6.92 (d, J=8.4 Hz, 2H), 6.16 (q, J=6.4 Hz, 1H), 3.84 (s, 3H), 2.26 (s, 6H), 1.68 (d, J=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.3, 159.4, 134.7, 134.2, 133.3, 129.1, 128.0, 127.5, 113.8, 72.8, 55.3, 21.8, 19.5; HRMS (ESI) calcd for $C_{18}H_{20}O_3Na$ [M + Na]$^+$ 307.1305 , found 307.1304.

1-(4-Methoxyphenyl)ethyl 3-phenoxybenzoate (3c) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (s, 1H), 7.73 (t, J=7.0 Hz, 1H), 7.36—7.44 (m, 5H), 7.21 (dd, J=2.4, 8.4 Hz, 1H), 7.17 (t, J=7.2 Hz, 1H), 7.04 (d, J=7.6 Hz, 2H), 6.92 (d, J=8.8 Hz, 2H), 6.11 (q, J=6.4 Hz, 1H), 3.83 (s, 3H), 1.67 (d, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.3, 159.3, 157.4, 156.7, 133.7, 132.5, 129.9, 129.7, 127.6, 124.4, 123.7, 123.2, 119.8, 119.1, 113.9, 73.0, 55.3, 22.2; HRMS (ESI) calcd for $C_{22}H_{20}O_4Na$ [M+Na]$^+$ 371.1254; found 371.1254.

1-(4-Methoxyphenyl)ethyl 2-methoxybenzoate (3d) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (dd, J=1.6, 8.0 Hz, 1H), 7.46—7.50 (m, 1H), 7.43 (d, J=8.4 Hz, 2H), 6.97—7.01 (m, 2H), 6.92 (d, J=8.8 Hz, 2H), 6.13 (q, J=6.4 Hz, 1H), 3.92 (s, 3H), 3.83 (s, 3H), 1.67 (d, J=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.4, 159.3, 159.2, 134.1, 133.4, 131.6, 127.6, 120.5, 120.1, 113.8, 112.1, 72.4, 56.0, 55.3, 22.2; HRMS (ESI) calcd for $C_{17}H_{18}O_4Na$ [M+Na]$^+$ 309.1097, found 309.1094.

1-(4-Methoxyphenyl)ethyl 2-iodobenzoate (3e) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (d, J=8.0 Hz, 1H), 7.80 (dd, J=1.6, 7.6 Hz, 1H), 7.39—7.45 (m, 3H), 7.15 (t, J=7.6 Hz, 1H), 6.93 (d, J=8.4 Hz, 2H), 6.15 (q, J=6.4 Hz, 1H), 3.84 (s, 3H), 1.72 (d, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.9, 159.4, 141.3, 135.5, 133.2, 132.5, 130.9, 127.9, 127.8, 113.9, 94.0, 73.8, 55.3, 22.0; HRMS (ESI) calcd for $C_{16}H_{15}IO_3Na$ [M+Na]$^+$ 404.9958, found 404.9965.

1-(4-Methoxyphenyl)ethyl 4-nitrobenzoate (3f) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (d, J=8.8 Hz, 2H), 8.24 (d, J=8.8 Hz, 2H), 7.42 (d, J=8.8 Hz, 2H), 6.94 (d, J=8.4 Hz, 2H), 6.15 (q, J=6.4 Hz, 1H), 3.84 (s, 3H), 1.72 (d, J=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.0, 159.6, 150.5, 136.0, 133.0, 130.7, 127.7, 123.5, 114.0, 74.0, 55.3, 21.9; HRMS (ESI) calcd for $C_{16}H_{15}NO_5Na$ [M + Na]$^+$ 324.0842, found 324.0836.

1-(4-methoxyphenyl) ethyl 4-formylbenzoate (3g) ^{1}H NMR(400 MHz, $CDCl_3$) δ: 10.12 (s, 1H), 8.24 (d, J=8.0 Hz, 2H), 7.97 (d, J=8.0 Hz, 2H), 7.43 (d, J=8.4 Hz, 2H), 6.94 (d, J=8.8 Hz, 2H), 6.15 (q, J=6.4 Hz, 1H), 3.84 (s, 3H), 1.71 (d, J=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.7, 164.8, 159.5, 139.1, 135.6, 133.3, 130.2, 129.5, 127.7, 114.0, 73.5, 55.3, 22.0; HRMS (ESI) calcd for $C_{17}H_{16}O_4Na$ [M + Na]$^+$ 307.0946, found 307.0950.

(*E*)-1-(4-Methoxyphenyl) ethyl cinnamate (3h) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (d, J=16.0 Hz, 1H), 7.53—7.56 (m, 2H), 7.38—7.41 (m, 5H), 6.93 (d, J=8.4 Hz, 2H), 6.48 (d, J=16 Hz, 1H), 6.02 (q, J=6.4 Hz, 1H), 3.84 (s, 3H), 1.64 (d, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.3, 159.3, 144.7, 134.5, 133.8, 130.2, 128.9, 128.1, 127.6, 118.5, 113.9, 72.1, 55.3, 22.0; HRMS (ESI) calcd for $C_{18}H_{18}O_3Na$ [M+Na]$^+$ 305.1148, found 305.1151.

1-(4-Methoxyphenyl) ethyl pivalate (3i) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.20 (d, J=8.8 Hz, 2H), 6.80 (d, J=8.8 Hz, 2H), 5.73 (q, J=6.4 Hz, 1H), 3.73 (s, 3H), 1.42 (d, J=6.8 Hz, 3H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.7, 159.1, 134.3, 127.2, 113.8, 71.6, 55.2, 38.7, 27.1, 22.2. HRMS (ESI) calcd for $C_{18}H_{18}O_3Na$ [M+Na]$^+$ 259.1310, found 259.1307.

1-(4-Methoxyphenyl)ethyl 3-methylbutanoate (3j) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32 (d, J=8.4 Hz, 2H), 6.90 (d, J=8.4 Hz, 2H), 5.89 (q, J=6.4 Hz, 1H), 3.83 (s, 3H), 2.21 (d, J=7.2 Hz, 2H), 2.05—2.17 (m, 1H), 1.54 (d, J=6.8 Hz, 3H), 0.95 (d, J=6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.5, 159.2, 133.9, 127.6, 113.8, 71.7, 55.3, 43.8, 25.8, 22.4, 22.3, 22.0; HRMS (ESI) calcd for $C_{14}H_{20}O_3Na$ [M + Na]$^+$ 259.1310, found 259.1312.

1-(4-Methoxyphenyl) ethyl 2,2-diphenylacetate (3k) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.22—7.35 (m,

12H), 6.87 (d, J=8.8 Hz, 2H), 5.96 (q, J=6.4 Hz, 1H), 5.07 (s, 1H), 3.83 (s, 3H), 1.55 (d, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.7, 159.3, 138.8, 138.6, 133.4, 128.7, 128.6, 128.5, 127.6, 127.2, 127.1, 113.7, 72.9, 57.2, 55.3, 21.9; HRMS (ESI) calcd for $C_{23}H_{22}O_3Na$ $[M+Na]^+$ 369.1461, found 369.1458.

1-Phenylethyl 3-phenoxybenzoate (4a) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, J=7.6 Hz, 1H), 7.71 (s, 1H), 7.34—7.43 (m, 7H), 7.29 (t, J=7.2 Hz, 1H), 7.18 (dd, J=2.4, 8.0 Hz, 1H), 7.13 (t, J=7.2 Hz, 1H), 7.01 (d, J=8.4 Hz, 2H), 6.10 (q, J=6.4 Hz, 1H), 1.65 (d, J=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.2, 157.4, 156.7, 141.6, 132.4, 129.9, 129.7, 128.6, 128.0, 126.1, 124.4, 123.8, 123.2, 119.8, 119.1, 73.2, 22.4; HRMS (ESI) calcd for $C_{21}H_{18}O_3Na$ $[M+Na]^+$ 341.1148, found 341.1147.

1-(2-Bromophenyl)ethyl 3-phenoxybenzoate (4b) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, J=7.6 Hz, 1H), 7.76 (s, 1H), 7.59 (d, J=8.0 Hz, 1H), 7.54 (d, J=7.6 Hz, 1H), 7.45 (t, J=8.0 Hz, 1H), 7.40 (t, J=7.6 Hz, 2H), 7.35 (t, J=7.6 Hz, 1H), 7.25 (dd, J=2.0, 8.4 Hz, 1H), 7.18 (t, J=7.2 Hz, 2H), 7.07 (d, J=8.0 Hz, 2H), 6.42 (q, J=6.4 Hz, 1H), 1.68 (d, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.9, 157.6, 156.6, 141.2, 133.0, 132.0, 130.0, 129.8, 129.2, 127.9, 126.8, 124.3, 123.9, 123.2, 121.8, 119.6, 119.2, 72.4, 21.3; HRMS (ESI) calcd for $C_{21}H_{17}BrO_3Na$ $[M+Na]^+$ 419.0253, found 419.0255.

1-(4-Methoxyphenyl)ethyl 3-phenoxybenzoate (4c) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (d, J=7.6 Hz, 1H), 7.73 (t, J=7.0 Hz, 1H), 7.36—7.44 (m, 5H), 7.20 (dd, J=1.6, 8.4 Hz, 1H), 7.15 (t, J=7.2 Hz, 1H), 7.03 (d, J=7.6 Hz, 2H), 6.91 (d, J=8.8 Hz, 2H), 6.08 (q, J=6.4 Hz, 1H), 3.83 (s, 3H), 1.67 (d, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.3, 159.3, 157.4, 156.7, 133.7, 132.5, 129.9, 129.7, 127.6, 124.4, 123.7, 123.2, 119.8, 119.1, 113.9, 73.0, 55.3, 22.2; HRMS (ESI) calcd for $C_{22}H_{20}O_4Na$ $[M+Na]^+$ 371.1254, found 371.1254.

1-(4-(Trifluoromethyl)phenyl)ethyl-3-phenoxybenzoate (4d) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, J=7.6 Hz, 1H), 7.73 (s, 1H), 7.65 (d, J=8.4 Hz, 2H), 7.55 (d, J=8.4 Hz, 2H), 7.44 (t, J=8.0 Hz, 1H), 7.39 (t, J=7.6 Hz, 2H), 7.24 (dd, J=2.0, 8.0 Hz, 1H), 7.18 (t, J=7.2 Hz, 1H), 7.05 (d, J=7.6 Hz, 2H),6.15 (q, J=6.4 Hz, 1H), 1.69 (d, J=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ: 165.1, 157.6, 156.6, 145.6, 131.9, 130.1 (t, $^2J_{C-F}$=32.3 Hz), 129.9, 126.2, 125.6 (t, $^3J_{C-F}$=3.7 Hz), 124.3, 124.0 (t, $^1J_{C-F}$=270.5 Hz), 123.8, 123.4, 120.0, 119.1, 72.4, 22.4; HRMS (ESI) calcd for $C_{22}H_{17}F_3O_3Na$ $[M+Na]^+$ 409.1022, found 409.1020.

1-(4-Chlorophenyl) ethyl 3-phenoxybenzoate (4e) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, J=7.6 Hz, 1H), 7.69 (s, 1H), 7.31—7.42 (m, 7H), 7.19 (dd, J=2.0, 8.0 Hz, 1H), 7.14 (t, J=7.2 Hz, 1H), 7.01 (d, J=8.0 Hz, 2H), 6.06 (q, J=6.4 Hz, 1H), 1.63 (d, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.2, 157.5, 156.6, 140.2, 133.7, 132.1, 129.9, 129.8, 128.8, 127.5, 124.3, 123.8, 123.3, 119.7, 119.1, 72.5, 22.3; HRMS (ESI) calcd for $C_{21}H_{17}ClO_3Na$ $[M+Na]^+$ 375.0758, found 375.0761.

1-(3-Nitrophenyl) ethyl 3-phenoxybenzoate (4f) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.31 (s, 1H), 8.20 (d, J=8.4 Hz, 1H), 7.84 (d, J=7.6 Hz, 1H), 7.77 (d, J=7.6 Hz, 1H), 7.73 (s, 1H), 7.57 (t, J=8.0 Hz, 1H), 7.45 (t, J=7.6 Hz, 1H), 7.39 (t, J=7.6 Hz, 2H), 7.25 (dd, J=2.0, 8.4 Hz, 1H), 7.18 (t, J=7.2 Hz, 1H), 7.05 (d, J=8.0 Hz, 2H), 6.19 (q, J=6.4 Hz, 1H), 1.73 (d, J=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.1, 157.6, 156.6, 143.8, 132.2, 131.6, 130.0, 129.9, 129.7, 124.3, 123.9, 123.5, 123.0, 121.0, 119.7, 119.2, 72.0, 22.3; HRMS (ESI) calcd for $C_{21}H_{17}NO_5Na$ $[M+Na]^+$ 386.0999, found 386.0995.

1-Phenylpropyl 3-phenoxybenzoate (4g) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (d, J=7.6 Hz, 1H), 7.64 (s, 1H), 7.18—7.34 (m, 8H), 7.11 (dd, J=2.4, 8.0 Hz, 1H), 7.06 (t, J=7.2 Hz, 1H), 6.94 (d, J=8.0 Hz, 2H), 5.81 (t, J=6.8 Hz, 1H), 1.82—2.02 (m, 2H), 0.87 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.3, 157.5, 156.7, 140.5, 132.4, 129.9, 129.7, 128.4, 127.9, 126.5, 124.3, 123.8, 123.1, 119.7, 119.1, 78.2, 29.5, 10.0; HRMS (ESI) calcd for $C_{22}H_{20}O_3Na$ $[M+Na]^+$ 355.1305, found 355.1304.

1-*p*-Tolylethyl 3-phenoxybenzoate (4h) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, J=7.6 Hz, 1H), 7.74 (s, 1H), 7.34—7.44 (m, 5H), 7.15—7.23 (m, 4H), 7.04 (d, J=8.0 Hz, 2H), 6.11 (q, J=6.4 Hz, 1H), 2.38 (s, 3H), 1.67 (d, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.3, 157.4, 156.7, 138.7, 137.7, 132.4, 129.9, 129.7, 129.2, 126.1, 124.4, 123.7, 123.2, 119.8, 119.1, 73.2, 22.3, 21.2; HRMS (ESI) calcd for $C_{22}H_{20}O_3Na$ $[M+Na]^+$ 355.1305, found 355.1301.

Cyclohexyl 3-phenoxybenzoate (4i) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (d, J=7.6 Hz, 1H), 7.72 (s, 1H), 7.36—7.44 (m, 3H), 7.20 (dd, J=2.4, 8.0 Hz, 1H), 7.16 (t, J=7.2 Hz, 1H), 7.04 (d, J=7.6 Hz, 2H), 5.01—5.07 (m, 1H), 1.93—1.98 (m, 2H), 1.78—1.82 (m, 2H), 1.56—1.62 (m, 2H), 1.35—1.51 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.4, 157.3, 156.8, 132.9, 129.9, 129.6, 124.3, 123.6, 123.0, 119.8, 119.0, 73.3, 31.6, 25.4, 23.6; HRMS (ESI) calcd for $C_{19}H_{20}O_3Na$ $[M+Na]^+$ 319.1305, found 319.1308.

Pentan-2-yl 3-phenoxybenzoate (4j) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, J=7.6 Hz, 1H), 7.68 (s, 1H), 7.33—7.41 (m, 3H), 7.17 (dd, J=2.4, 8.4 Hz, 1H), 7.13 (t, J=7.2 Hz, 1H), 7.01 (d, J=7.6 Hz, 2H), 5.11—5.19 (m, 1H), 1.67—1.76 (m, 1H), 1.52—1.61 (m, 1H), 1.36—1.46 (m, 2H), 1.32 (d, J=6.4 Hz, 2H), 0.93 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.6, 157.3, 156.8, 132.8, 129.9, 129.6, 124.3, 123.7, 123.0, 119.8, 119.0, 71.8, 38.2, 20.0, 18.7, 14.0; HRMS (ESI) calcd for $C_{18}H_{20}O_3Na$ $[M+Na]^+$ 307.1305, found 307.1308).

Benzyl 2,6-dimethylbenzoate (4k) ^{1}H NMR ($CDCl_3$) δ: 7.35 (d, J=6.8 Hz, 2H), 7.24—7.30 (m, 3H), 7.08 (t, J=7.6 Hz, 1H), 6.92 (d, J=7.6 Hz, 2H), 5.27 (s, 2H), 2.19 (s, 6H); ^{13}C NMR ($CDCl_3$) δ: 169.8, 135.6,

135.0, 133.7, 129.4, 128.7, 128.6, 128.4, 127.6, 66.9, 19.7; HRMS (ESI) calcd for $C_{16}H_{17}O_2$ $[M+H]^+$ 241.1223, found 241.1226.

4-Methoxybenzyl 2,6-dimethylbenzoate (4l) ^{1}H NMR ($CDCl_3$) δ: 7.38 (d, J=8.4 Hz, 2H), 7.15 (t, J=7.6 Hz, 1H), 6.99 (d, J=7.6 Hz, 2H), 6.89 (d, J=8.4 Hz, 2H), 5.30 (s, 2H), 3.80 (s, 3H), 2.25 (s, 6H); ^{13}C NMR ($CDCl_3$) δ: 169.9, 159.8, 134.9, 133.8, 130.6, 129.3, 127.8, 127.5, 113.9, 66.6, 55.3, 19.7; HRMS (ESI) calcd for $C_{17}H_{19}O_3$ $[M+H]^+$ 271.1329, found 271.1323.

4-Fluorobenzyl 2,6-dimethylbenzoate (4m) ^{1}H NMR ($CDCl_3$) δ: 7.32—7.36 (m, 2H), 7.08 (t, J=7.6 Hz, 1H), 6.97 (t, J=8.4 Hz, 2H), 6.92 (d, J=7.6 Hz, 2H), 5.23 (s, 2H), 2.17 (s, 6H); ^{13}C NMR ($CDCl_3$) δ: 169.7, 162.8 (d, $^1J_{CF}$=245.7 Hz), 135.0, 133.6, 131.6 (d, $^4J_{CF}$=3.1 Hz), 130.8 (d, $^3J_{CF}$=8.1 Hz), 130.7, 129.4, 127.6, 115.5 (d, $^2J_{CF}$=21.3 Hz), 66.1, 19.7; HRMS (ESI) calcd for $C_{16}H_{15}O_2FNa$ $[M+Na]^+$ 281.0948, found 281.0948.

Isobutyl 2,6-dimethylbenzoate (4n) ^{1}H NMR ($CDCl_3$) δ: 7.22 (t, J=7.6 Hz, 1H), 7.07 (d, J=7.6 Hz, 2H), 4.15 (d, J=6.4 Hz, 2H), 2.36 (s, 6H), 2.04—2.14 (m, 1H), 1.04 (d, J=6.4 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ: 170.2, 134.8, 134.3, 129.2, 127.5, 71.3, 27.8, 19.7, 19.3; HRMS (ESI) calcd for $C_{13}H_{19}O_2$ $[M+H]^+$ 207.1380, found 207.1378.

Conclusions

In conclusion, we have developed a novel method for reductive coupling of *N*-tosylhydrazones with carboxylic acids under metal-free conditions to access esters. Various functional groups were found to be tolerable under the reaction conditions to afford the corresponding esters with low to good yields.

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