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Selective conversion of primary amides to esters promoted by $KHSO_4$

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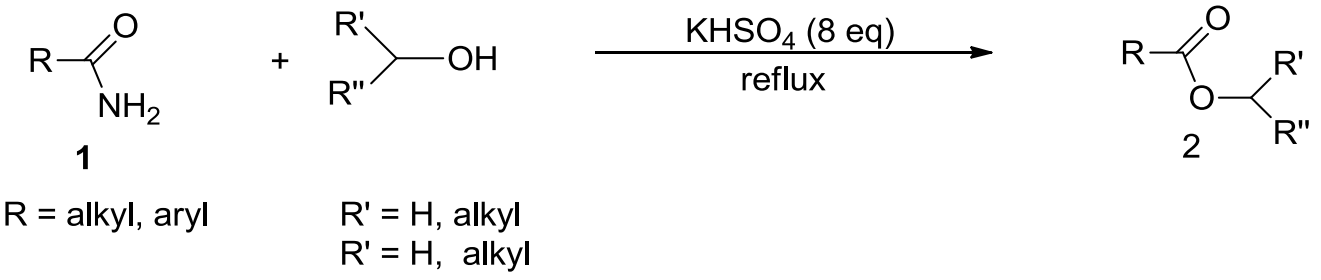
Abstract

Primary amides, either aliphatic or aromatic, are easily converted to the corresponding esters via reflux in lower primary alcohols in the presence of $KHSO_4$. Secondary amides lead to complicated mixtures under analogous conditions, whereas tertiary amides were inert. Use of isopropyl alcohol resulted in the formation of product at slower rate and lower yield along with side products, whereas, use of tertiary alcohols did not give successful conversion and allyl and benzyl alcohol provided complex mixtures.

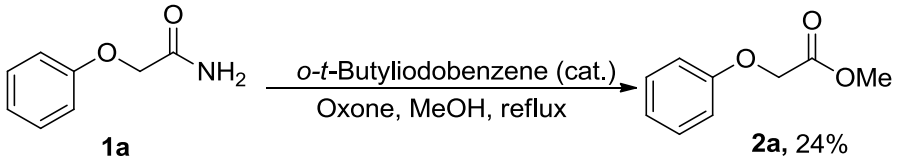


Keywords: Amide, ester, alcoholysis, $KHSO_4$, selective conversion

Introduction

Carboxylic acids and their derivatives, such as amides and esters, play important roles in nature as well as in artificial chemicals. The interconversion of these derivatives is a frequently encountered transformation by chemists. Not surprisingly, the conversion of carboxylic acids or esters to amides proceeds usually much easier than the reverse process, due to the high stability of the amide functionality, which has been well utilized by nature to build the back bone of protein structures. The hydrolysis of amides to carboxylic acids usually requires strongly acidic or basic conditions,[1,2] enzymatic,[3] or metal catalysis,[4] except in special cases where N-C=O conjugation is prevented because of constraint[5] or where the nitrogen is a part of a heterocyclic structure such as imidazole.[6] Similarly, strongly acidic conditions are usually required to effect the alcoholysis of amides to esters. Examples include the use of HCl gas,[7,8] BF_3 gas,[9] $SOCl_2$,[10] Me_3SiCl,[11] nitrite/Me_3SiCl,[12] or $TsOH.H_2O$[13] for such transformations. Additionally, $TiCl_4$, in combination with one equiv of aqueous HCl, was found to catalyze conversion of amides to esters.[14] More recently, $Zn(OTf)_2$ has been reported to catalyze the esterification of a special type of amides, β-hydroxyethylamides.[15] Acidic Amberlyst resins[16] have been reported as milder reagents to convert amides and hydrazides to esters, which required up to 168 h of heating to achieve good yields in some instances. Truly mild reaction and selective conversion has been only achieved with enzymatic method.[17] Thus, milder, economical, selective, and convenient methods to covert amides to esters are still in need.

Previously, it has been reported that carboxamides go through Hofmann rearrangement in the presence of Oxone® and catalytic amount of *o*-*t*-butyliodobenzene in refluxing methanol.[18] Interestingly, when 2-phenoxyacetamide (**1a**) was treated under such conditions, methyl 2-phenoxyacetate (**2a**) was also obtained in 24% yield as a side product (Scheme 1). Further experiments showed that this was a not a specific reaction that only occurred with **1a**. It also occurred with other aliphatic amides, but not with aromatic amides under analogous reaction conditions. We decided to explore the scope and limit of the reaction and wish to report the results of this study herein.



Scheme 1. Treatment of **1a** with Oxone/*o*-*t*-butyliodobenzene (cat.) in MeOH.

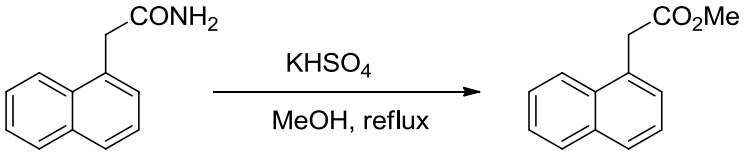
Results and Discussion

It was at first questioned how this reaction proceeded and the role of each reagent. Tests showed that *o*-*t*-butyliodobenzene was not needed for the esterification. Furthermore, replacing Oxone with $KHSO_4$ led to the formation of the product in higher yield. Thus, it was concluded that this was an acid promoted alcoholysis of the amides, which became the focus of the study. Optimization of the reaction was carried out with 2-(naphthalen-1-yl)acetamide (**1b**) and 4, 6, 8, and 10 equivalents of $KHSO_4$ in refluxing methanol (Table 1). The reaction was complete in 12 h when 8 equiv of $KHSO_4$ were used. Higher excess of $KHSO_4$ did not increase the yield, nor shorten the reaction time. Microwave irradiation at 90 ^oC did not seem to accelerate the reaction much. Remarkably, with $KHSO_4$, the methyl ester was the only product and the pure product can be obtained

by trituration of the semi-solid residue with a suitable organic solvent after removal of methanol in vacuo, whereas with Oxone, a few side products, although in tiny quantities, were also produced, which necessitates a column chromatography purification process to obtain the pure product.

Subsequently, the reaction of various amides with methanol was explored under optimized conditions (Table 2). Generally, the reaction went faster with aliphatic amides (Table 2, entries 1 - 4), and slower with aromatic amides (Table 2, entries 5 - 14). It should also be noted that the reaction was very sluggish with secondary amides, and did not proceed at all with the tertiary amide tested. Additionally, no reaction was observed when sulfonamide or benzonitrile was used instead of carboxamides.

Table 1. Optimization of reaction conditions with **1b** and $KHSO_4$ in refluxing methanol



1b **2b**

Entry	Equiv of $KHSO_4$	Reaction time (h)	Isolated yield (%)
1	4	24	71
2	6	17	100
3	8	12	100
4	10	12	91
5[a]	8	5	33

[a]Microwave reactor was used for this reaction at 90 ^{o}C.

Table 2. Conversion of amides to methyl esters with methanol/$KHSO_4$ at 65 ^{o}C

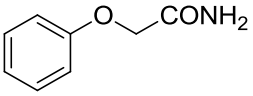
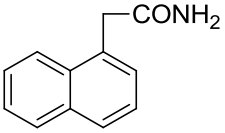
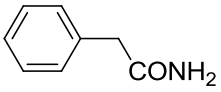
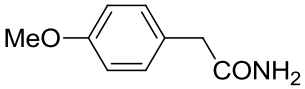
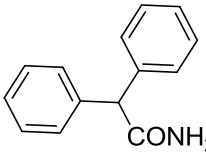
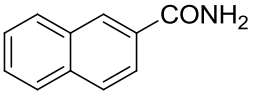
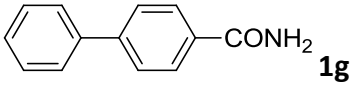
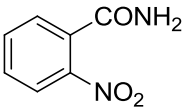
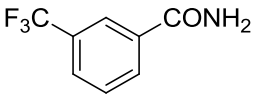
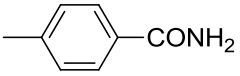
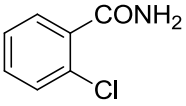
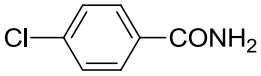
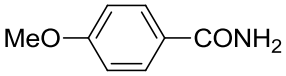
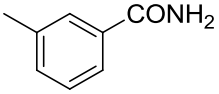
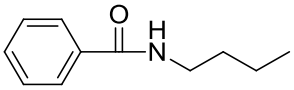
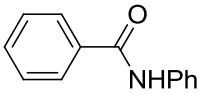
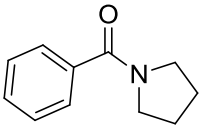
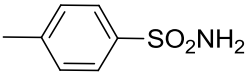
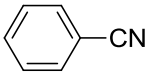
Entry	Amide	Structure	Reaction time (h)	Yield (%)
1	**1a**		14	86
2	**1b**		12	100
3	**1c**		14	93
4	**1d**		16	93
5	**1e**		48	88
6	**1f**		24	86

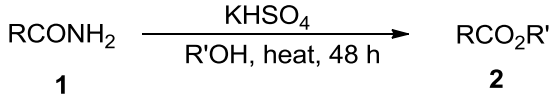
Table 2. Continued

Entry	**Amide**	Structure	Reaction time (h)	Yield (%)
7	**1g**	 **1g**	60	78
8			60	86
9	**1i**		36	90
10	**1j**		48	91
11	**1k**		72	89
12	**1l**		60	92
13	**1m**		72	90
14	**1n**		48	83
15	**1o**		48	Trace
16	**1p**		48	Trace
17	**1q**		48	0
18	**1r**		16	0
19	**1s**		24	0

It was then tested whether this method works with other alcohols with **1f** (Table 3). The method provided the corresponding esters in high yields for primary alcohols, and a moderate yield with isopropyl alcohol in 48 h. No product was observed with *t*-butyl alcohol, while allyl alcohol and benzyl alcohol provided complex mixture. A possible explanation for this was due to water formation from these alcohols, via either intramolecular or intermolecular dehydration (*vide infra*), in the presence of $KHSO_4$. Surprisingly, ethylene glycol also produced only a trace of ester. Unlike other primary alcohols, however, ethylene glycol (15 mL) dissolved all $KHSO_4$ (1.1 g) when heated to 85 ^{o}C, which prompted us that the reaction occurred at the surface of the solid $KHSO_4$, not in solution. Indeed, adding water to the reaction system significantly slowed down the reaction (entry 12, table 3 vs. entry 1, table 3). It should be noted that **1f** did not dissolve well in MeOH/H_2O (2:1). To exclude the possibility that low solubility of **1f** in MeOH/H_2O caused the low yield, we also tested **1n** with MeOH/H_2O (2:1), where all **1n** dissolved in the mixed solvent. Again, lower conversion rate was observed.

When treated with water, **1n** was hydrolyzed to the corresponding carboxylic acid only in 34% in 48 h. Similar treatment of **1a**, an aliphatic amide with good water solubility, produced the carboxylic acid in 100% yield in 48 h, confirming our observation that aliphatic amides reacted faster than aromatic amides (Table 2). These observations support the explanation that water formation from alcohols was a possible cause for the lower yield or no product formation when dehydration of alcohols is significant.

Table 3. Alcoholysis (hydrolysis) of selected amides in the presence of solid $KHSO_4$



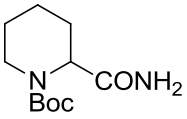
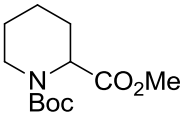
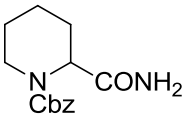
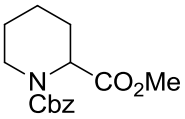
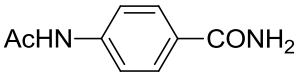
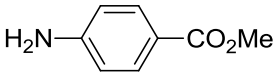
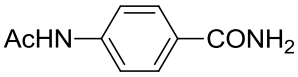
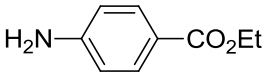
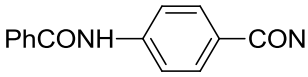
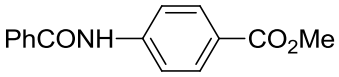
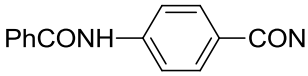
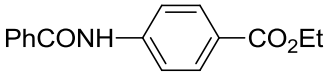
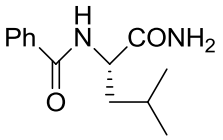
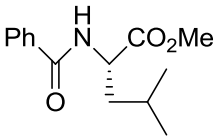
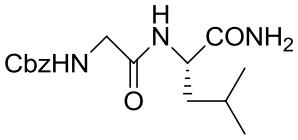
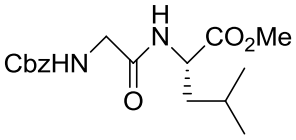
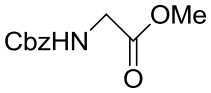
Entry	Amide	Solvent	Temp.(^oC)	Product **2**	Yield (%)
1	**1f**	Methanol	65	**2f**, R'=Me	**86**
2		Ethanol	78	**2fa**, R'=Et	**92**
3		2-Chloroethanol	127	**2fb**, R'=2-ClEt	**83**
4		Isopropyl alcohol	83	**2fc,** R'=*i*-Pr	**34**
5		*t*-Butyl alcohol	82	0	0
6		Allyl alcohol	97		Complex mixture
7		Benzyl alcohol	85	Complex mixture	
8		*n*-Propanol	97	**2fd** R'=1-Pr	**77**
9		*n*-Butanol	118	**2fe** R'=1-Bu	**75**
10		Ethylene glycol[a]	85	trace	
11		Ethylene glycol-acetonitrile (1:5)	85	trace	
12		Methanol-Water (2:1)	65	**2f** 15[a]	**41**[b]
13	**1n**	Methanol-Water (2:1)	65	**2n**	**60**[b]
14		Water[b]	100	**2n**	**0**[b]
15	**1a**	Water[b]	100	**2a**	**0**[b]

[a]All $KHSO_4$ was dissolved during the reaction. [b]The corresponding carboxylic acids, 2-naphthoic acid, *m*-toluic acid, and phenoxyacetic acid, were obtained in 15%, 25%, 34%, and 100% respectively.

$KHSO_4$ is easily available, inexpensive, safe, and non-toxic reagent and has been known to catalyze organic reactions, such as acetal formation, Michael addition, heterocycle formation.[20] Goswami et al.[21] also reported that $KHSO_4$-SiO_2-MeOH deprotects efficiently esters to alcohols, presumably through trans-esterification reaction. HSO_4^- has a *p*Ka of 1.99[19] and is considered as a medium-strength acid. Thus, this is a milder method to convert amides, particularly primary amides, to esters of primary alcohols, comparing to reported methods.[7-14,16] We tested this method on some compounds with two or more amide (carbamate) functionalities (Table 4) to study the selectivity of this method. Boc and acetyl protection groups were removed under the reaction condition (entries 1, 3, 4, table 4), while most of Cbz and benzoyl protection groups remained (entries 2, 5 - 8, table 4). It is interesting to note that this method showed good selectivity towards primary amides, which is understandable since the reaction probably occurred at the surface of the solid $KHSO_4$ and primary amides are more accessible due to less steric hindrance. We also tested our reaction

on chiral amides. The *ee* value of **3g** (Entry 7, Table 4) was determined via optical rotation to be 86%, indicating a 7% racemization during the esterification process.

Table 4. Selectivity of solid $KHSO_4$ promoted amide alcoholysis in refluxing alcohol

Entry	Amide	Alcohol	Time (h)	Product code	Product structure	Yield (%)
1		MeOH	48	**3a**		25[a]
2		MeOH	48	**3b**		0
3		MeOH	48	**3c**		35[b]
4		EOH	48	**3d**		93
5		MeOH	48	**3e**		39
6		EtOH	48	**3f**		55[c]
7		MeOH	25	**3g**		72
8		MeOH	24	**3h**		43
				3ha		18

[a]The Boc protection group was lost during the reaction and the product was recovered by treating the crude residue with K_2CO_3/Boc_2O in methanol. [b]Yield after recrystallization from 1:1 hexanes/ethyl acetate. [c]29% starting amide was recovered.

Conclusions

It has been demonstrated that primary amides, either aliphatic or aromatic, when treated with a primary alcohol in the presence of solid $KHSO_4$, are converted very easily the corresponding esters via rather simple workup. This method also selectively converts primary amides into the corresponding esters in the presence of secondary amides. Solid $KHSO_4$ promotes the reaction faster than dissolved $KHSO_4$. The observed selectivity

is possibly due to steric hindrance.. Only slight racemization was observed when an optically active amide was converted to the methyl ester.

Experimental Section

Typical alcoholysis procedure. A mixture of the amide (**1**, 1 mmol), alcohol (15 mL), and pulverized potassium bisulfate (1.1 g, 8 mmol) was refluxed for the specified time. The alcohol was removed in vacuo and the residue was triturated with hexanes (or other appropriate solvent such as DCM or ethyl acetate to dissolve the product). Removal of hexanes in vacuo provided the following pure products.

2a.[22] ^{1}H NMR: δ 3.81 (s, 3 H), 4.64 (s, 2 H), 6.91 (m, 2 H), 7.00 (m, 1 H), 7.30 (m, 2 H).

2b.[10] ^{1}H NMR: δ 3.64 (s, 2 H), 3.70 (s, 3 H), 7.30 (m, 5 H).

2c.[23] ^{1}H NMR: δ 3.68 (s, 3 H), 4.09 (s, 2 H), 7.42 (m, 2 H), 7.51 (m, 2 H), 7.80 (dd, *J* 2.0, 7.6 Hz, 1 H), 7.87 (dd, *J* 1.6, 8.0Hz, 1 H), 7.99 (d, *J* 8.4 Hz, 1 H).

2d.[23] ^{1}H NMR: δ 3.57 (s, 2 H), 3.69 (s, 3 H), 3.79 (s, 3 H), 6.86 (d, *J* 8.8 Hz, 2 H), 7.20 (d, *J* 8.4 Hz, 2 H).

2e.[25] ^{1}H NMR: δ 3.74 (s, 3 H), 5.03 (s, 1 H), 7.24-7.34 (m, 10 H).

2f.[25] ^{1}H NMR: δ 3.99 (s, 3 H), 7.57 (m, 2 H), 7.88 (d, *J* 8.8 Hz, 2 H), 7.95 (d, *J* 7.6 Hz, 1 H), 8.06 (dd, *J* 1.6, 8.8 Hz, 1 H), 8.62 (s, 1 H).

2g.[26] ^{1}H NMR: δ 3.94 (s, 3 H), 7.40 (m, 1 H), 7.47 (m, 2 H), 7.63 (m, 2 H), 7.67 (d, *J* 8.4 Hz, 2 H), 8.11 (d, *J* 8.4 Hz, 2 H).

2h.[27] ^{1}H NMR: δ 3.93 (s, 3 H), 7.31 (m, 1 H), 7.63 (ddd, *J* 2.0, 7.6 Hz, 1 H), 7.68 (ddd, *J* 1.6, 7.6 Hz, 1 H), 7.75 (dd, *J* 2.0, 7.6 Hz, 1 H), 7.92 (dd, *J* 1.6, 7.6 Hz, 1 H).

2i.[24] ^{1}H NMR: δ 3.96 (s, 3 H), 7.59 (m, *J* 1 H), 7.82 (m, 1 H), 8.23 (m, 1 H), 8.31 (m, 1 H).

2j.[10] ^{1}H NMR: δ 2.41 (s, 3 H), 3.90 (s, 3 H), 7.23 (d, *J* 8.4 Hz, 2 H), 7.93 (d, *J* 8.4 Hz, 2 H).

2k.[28] ^{1}H NMR: δ 3.94 (s, 3 H), 7.31 (m, 1 H), 7.43 (m, 2 H), 7.82 (dd, *J* 1.6, 8.0 Hz, 1 H).

2l.[10] ^{1}H NMR: δ 3.91 (s, 3 H), 7.41 (d, *J* 8.8 Hz, 2 H), 7.97 (d, 2 H).

2m.[25] ^{1}H NMR: δ 3.86 (s, 3 H), 3.88 (s, 3 H), 6.91 (d, *J* 9.2 Hz, 2 H), 7.99 (d, 2 H).

2n.[10] ^{1}H NMR: δ 2.4 (s, 3 H), 3.91 (s, 3 H), 7.32 (dd, *J* 7.6 Hz, 1 H), 7.36 (m, 1 H), 7.84 (m, 1 H), 7.86 (m, 1 H).

2fa.[29] ^{1}H NMR: δ 1.45 (t, *J* 7.2 Hz, 3 H), 4.45 (q, *J* 7.2 Hz, 2 H), 7.57 (m, 2 H), 7.88 (d, *J* 8.4 Hz, 2 H), 7.96 (d, *J* 8 Hz, 1 H), 8.07 (dd, *J* 2.0, 8.8 Hz, 1 H), 8.61 (s, 1 H).

2fb. White solid, mp: 27-29 ^{o}C. ^{1}H NMR: δ 3.87 (m, 2 H), 4.64 (m, 2H), 7.58 (m, 2 H), 7.89 (m, 2 H), 7.97 (d, *J* 8.0 Hz, 1 H), 8.08 (dd, *J* 1.6, 8.8 Hz, 1 H), 8.64(s, 1 H); ^{13}C: δ 41.7, 64.6, 125.2, 126.7, 126.8, 127.8, 128.3, 128.4, 129.4, 131.4, 132.4, 135.7, 166.4; HRMS (EI) calcd. for $C_{13}H_{11}ClO_2$: 234.0448; found: 234.0445.

2fc. ^{1}H NMR: δ 1.43 (d, *J* 6.0 Hz, 6 H), 5.33 (hept, *J* 6.0 Hz, 2 H), 7.56 (m, 2 H), 7.87 (d, *J* 8.4 Hz, 2 H), 7.96 (d, *J* 8 Hz, 1 H), 8.07 (dd, *J* 2.0, 8.4 Hz, 1 H), 8.60 (s, 1 H); ^{13}C: δ 22.0, 68.5, 125.3, 126.6, 127.7, 128.0, 128.10, 128.12, 129.3, 130.9, 132.5, 135.4, 166.3.

2fd.[30] ^{1}H NMR: δ 1.08 (t, *J* 7.2 Hz, 3 H), 1.85 (m, 2 H), 4.35 (t, *J* 6.8 Hz, 2 H), 7.57 (m, 2 H), 7.88 (d, *J* 8.4 Hz, 2 H), 7.96 (d, *J* 8 Hz, 1 H), 8.07 (dd, *J* 2.0, 8.8 Hz, 1 H), 8.62 (s, 1 H).

2fe.[31] ^{1}H NMR: δ 1.01 (t, *J* 7.2 Hz, 3 H), 1.53 (m, 2 H), 1.81 (m, 2 H), 4.40 (t, *J* 6.4 Hz, 2 H), 7.57 (m, 2 H), 7.88 (d, *J* 8.4 Hz, 2 H), 7.96 (d, *J* 8 Hz, 1 H), 8.07 (dd, *J* 1.6, 8.8 Hz, 1 H), 8.61 (s, 1 H).

Phenoxyacetic acid.[32] ^{1}H NMR: δ 4.70 (s, 2 H), 6.93(dd, *J* 0.8, 8.4 Hz, 2 H), 7.03(dd, *J* 7.6 Hz, 1 H), 7.32(dd, *J* 7.6, 8.4 Hz, 2 H), 8.89 (br s, 1 H).

2-Naphthoic acid.[33] ^{1}H NMR (DMSO-d_6): δ 7.61 (m, 2 H), 7.97 (m, 3 H), 8.10 (d, *J* 8.0 Hz, 1 H), 8.59 (s, 1 H), 13.06 (br s, 1 H).

***m*-Toluic acid.**[34] ^{1}H NMR (DMSO-d_6): δ 2.34 (s, 3 H), 7.35 (dd, *J* 7.6 Hz, 1 H), 7.41 (d, *J* 7.6 Hz, 1H), 7.72 (d, *J* 7.2 Hz), 1 H), 7.75 (s, 1 H), 12.86 (s, 1 H); 13C: 21.3, 126.9, 128.9, 130.2, 131.1, 133.9, 138.3, 167.8.
3a.[35] ^{1}H NMR: δ 1.23 (m, 1 H), 1.44 (m, 9 H), 1.65 (m, 4 H), 2.19 (m, 1 H), 2.93 (m, 1 H), 3.71 (s, 3 H), 3.96 (m, 1 H), 4.89 (m, 1 H).
3c.[36] ^{1}H NMR: δ 3.85 (s, 3 H), 4.03 (br. s, 2 H), 6.64 (d, *J* 8.4 Hz, 2 H), 7.85 (d, *J* 8.4 Hz, 2 H); ^{13}C: δ 51.6, 113.8, 119.7, 131.6, 150.8, 167.2
3d.[37] ^{1}H NMR: δ 1.36 (t, 3 H), 4.09 (br. s, 2 H), 4.31 (q, *J* 7.2 Hz, 2 H), 6.64 (d, *J* 8.4 Hz, 2 H), 7.85 (d, *J* 8.4 Hz, 2 H).
3e.[38] ^{1}H NMR: δ 8.066 (d, *J*= 8.4 Hz, 2H), 7.96 (bs, 1 H), 7.88 (d, *J* 8.4 Hz, 2 H), 7.74 (d, *J* 8.4 Hz, 2 H), 7.61-7.56 (m, 1 H), 7.53-7.49 (m, 2 H),), 3.92 (s, 3 H)
^{13}C NMR: δ 52.1, 119.2, 125.8, 127.1, 128.9, 130.9, 132.2, 134.5, 142.1, 165.8, 166.6
3f.[39] ^{1}H NMR: δ 1.31 (t, *J* 7.2 Hz, 3 H), 4.28 (q, *J* 7.2 Hz, 2 H), 7.54 (m, 2 H), 7.59 (m, 1 H), 7.94 (m, 6 H), 10.55 (s, 1 H); 13C (DMSO): 14.7, 60.9, 120.0, 125.0, 128.2, 128.9, 130.5, 132.3, 135.0, 144.1, 165.8, 166.4.
3g.[40] ^{1}H NMR: δ 7.78 (d, *J*= 8.4 Hz, 2 H), 7.51-7.47 (m, 1 H), 7.44-7.39 (m, 2 H), 6.54 (d, *J* 7.6 Hz, 1 H), 4.90-4.85 (m, 1 H), 3.77 (s, 3 H), 1.80-1.63 (m, 2 H), 0.97(t, *J*= 6.8 Hz, 6 H); ^{13}C NMR: δ 22.0, 22.8, 24.9, 51.2, 52.4, 127.1, 128.6, 131.7, 133.9, 167.2, 173.8. *ee*, 85.6%.
3h.[41] ^{1}H NMR δ 0.89 (d, *J* 5.6, 6 H), 1.61-1.48 (m, 3 H), 3.66 (s,3H), 3.89 (m, 2 H), 4.62-4.56 (m, 1 H), 5.08 (s, 2 H), 5.90 (bs, 1 H), 6.97 (bs, 1 H), 7.26-7.31 (m,5 H); ^{13}C NMR (100 MHz, CDCl3) δ 21.8, 22.75, 24.76, 25.0, 41.2, 44.3, 50.7, 52.3, 67.1, 128.1, 128.3, 128.5, 136.2, 156.7, 169.3,173.4
3ha.[25] ^{1}H NMR: δ 7.32-7.30 (m, 5 H), 5.31 (bs, 1 H), 5.13 (s, 2 H), 3.98 (d, *J* 5.6 Hz, 2 H), 3.8 (s, 3 H). ^{13}C: δ 42.6, 52.3, 67.1, 128.1, 128.2, 128.5, 136.2, 156.3, 170.5.

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References

1. O'Connor, C. *Quarterly Rev. Chem. Soc*. **1970**, *24,* 553-564. https://doi.org/10.1039/qr9702400553
2. Cox, R.A. *Can. J. Chem*. **2005**, *83*, 1391-1399. https://doi.org/10.1139/v05-142
3. Sharma, M.; Sharma, N.N.; Bhalla, T.C. *Rev. Environ. Sci. Biotechnol.* **2009**, *8*, 343–366. https://doi.org/10.1007/s11157-009-9175-x
4. Hegg, E.L.; Burstyn, J.N. *Coord. Chem. Rev*. **1998**, *173*, 133-165. https://doi.org/10.1016/S0010-8545(98)00157-X
5. Szostak, M.; Aube, J. *Chem. Rev*. **2013**, *113*, 5701-5765. https://doi.org/10.1021/cr4000144
6. Fife, T.H. *Acc. Chem. Res*. *1993*, **26**, 326-331. https://doi.org/10.1021/ar00030a005
7. H. A. Taylor, T. W. Davis, *J. Phys. Chem.* **1928**, *32*, 1467–1480. https://doi.org/10.1021/j150292a003

8. E. Emmet Reid, *Am. Chem. J.* **1909**, *41*, 483–510.
9. Sowa, F. J., Toole, S. G. *J. Am. Chem. Soc*. **1937**, *58*, 1971 - 1973.
10. Li, L.-C., Ren, J., Liao, T.-G., Jiang, J.-X., Zhu, H.-J. *Eur. J. Org. Chem.* **2007**, 1026–1030. https://doi.org/10.1002/ejoc.200600853
11. Xue, C.; Luo, F.-T. *J. Chinese Chem. Soc.*, **2004**, *51*, 359-362 https://doi.org/10.1002/jccs.200400055
12. Lee. J. G., Seo, Y. S. *Bull. Korean Chem. Soc.* **1995**, *16*, 377-379.
13. Taber, D.F.; Rahimizadeh, M. *J. Org. Chem.* **1992**, *57*, 4037-4038. https://doi.org/10.1021/jo00040a061
14. Fisher, L,. Caroons, J. M., Satbler, R., Lundberg, R., Zaidi, S., Sorensen, C. M., Sparacino, M. L., Muchowski, J. M. *Can. J. Chem*. **1994**, *72*, 142-145. https://doi.org/10.1139/v94-022
15. Kita, Y.; Nishii, Y.; Higuchi, T.; Mashima, K. *Angew. Chem. Int. Ed.* **2012**, *51*, 5723–5726. https://doi.org/10.1002/anie.201201789
16. Greenlee, W. J., Thorsett, E. D. *J. Org. Chem*. **1981**, *46*, 5351-5353. https://doi.org/10.1021/jo00339a019
17. Meos, H., Haga, M., Tõugu, V. *Tetra. Lett*. **1995**, *36*, 2343-2346. https://doi.org/10.1016/0040-4039(95)00251-7
18. Sattenapally, N.; Potturi, H.K.; Sharma, J.; Hou, Y. Abstracts of Papers, 245th ACS National Meeting & Exposition, New Orleans, LA, United States, April 7-11, 2013 ORGN-367.
19. Smith, M.B.; March, J. Advanced Organic Chemistry. Reactions, Mechanisms, and Structure. Wiley 6th Ed. Wiley-Interscience; CRC: Boca Raton, Fl.,1993; pp 57-67.
20. Baghernejad, B. *Eur. J. Chem*. **2012**, *3*, 125-128. https://doi.org/10.5155/eurjchem.3.1.125-128.182
21. Goswami, A.; Das, R.N.; Borthakur, N. *Ind. J. Chem*. **2007**, *46B*, 1893-1895.
22. AIST: Integrated Spectral Database System of Organic Compounds. (Data were obtained from the National Institute of Advanced Industrial Science and Technology (Japan))
23. Huddar, S.N.; Deshmukh, S.S.; Akamanchi, K.G. *ARKIVOC* **2011**, 67-71.
24. Xu, J.; Luo, D.-F.; Xiao, B.; Liu, Z.-J.; Gong, T.-J.; Liu, L. *Chem. Commun*. **2011**, *47*, 4300-4302. https://doi.org/10.1039/c1cc10359h
25. Heller, S.T.; Sarpong, R. *Org. Lett*. **2010**, *12,* 4572-4575. https://doi.org/10.1021/ol1018882
26. Ackermann, L.; Christian J. Gschrei, C.J.; Althammer, A.; Riederer, M. *Chem. Commun*. **2006**, 1419-1421.
27. Wu, X.-F.; Darcel, C. *Eur. J. Org. Chem*. **2009**, 1144-1147. https://doi.org/10.1002/ejoc.200801176
28. Kaganovsky, L.; Gelman, D.; Rueck-Braun, K. *J. Organomet. Chem*. **2010**, *695*, 260-266. https://doi.org/10.1016/j.jorganchem.2009.10.001
29. Zhao, Y.; Jin, L.; Li, P.; Lei, A. *J. Am. Chem. Soc*. **2008**, *130*, 9429-9433. https://doi.org/10.1021/ja801116s
30. Gowrisankar, S.; Neumann, H.; Beller, M. *Angew. Chem. Int. Ed*. **2011**, *50*, 5139-5143. https://doi.org/10.1002/anie.201008035
31. Maki, B.E.; Chan, A.; Phillips, E.M.; Scheidt, K.A. *Org. Lett*. **2007**, *9*, 371-374. https://doi.org/10.1021/ol062940f

32. Jimenez, F.; Cruz, M.d.C.; Zuniga, C.; Martinez, M.A.; Chamorro, G.; Diaz, F.; Tamariz, J. *Med. Chem. Res*. **2010**, *19*, 33-57.
33. Bonvin, Y.; Callens, E.; Larrosa, I.; Henderson, D.A.; Oldham, J.; Burton, A.J.; Barrett, A.G.M. *Org. Lett*. **2005**, *7*, 4549-4552. https://doi.org/10.1021/ol051765k
34. Kobayashi, K.; Kondo, Y. *Org. Lett*. **2009**, *11*, 2035-2037. https://doi.org/10.1021/ol900528h
35. Soicke, A.; Reuter, C.; Winter, M.; Neudoerfl, J.-M.; Schloerer, N.; Kuehne, R.; Schmalz, H.-G. *Eur. J. Org. Chem*. **2014**, 6467-6480. https://doi.org/10.1002/ejoc.201402737
36. Yang, H.; Li, Y.; Jiang, M.; Wang, J.; Fu, H. *Chem. Eur. J.* **2011**, *17*, 5652-5660. https://doi.org/10.1002/chem.201003711
37. Banik, B.K.; Banik, I.; Becker, F.F. *Org. Syn.* **2005***, 81*, 188-194. https://doi.org/10.15227/orgsyn.081.0188
38. Yamane, M.; Ren, W. J. *J. Org. Chem.*, **2010**, *75*, 8410–8415. https://doi.org/10.1021/jo101611g
39. Miura, T.; Takahashi, Y.; Murakami, M. *Chem. Commun*. **2007**, 3577-3579. https://doi.org/10.1039/b709203b
40. Karnik, Anil V.; Kamath, Suchitra S. *J. Org. Chem.* **2007**, *72*, 7435–7438. https://doi.org/10.1021/jo070962p
41. Whitteck, J.T.; Ni, W.; Griffin, B.M.; Eliot, A.C.; Thomas, P.M.; Kelleher, N.L.; Metcalf, W.W.; van der Donk, W.A. *Angew. Chem., Int. Ed*. **2007**, *46*, 9089-9092. https://doi.org/10.1002/anie.200703810

