

Palladium(II)-Catalyzed Michael-Type Hydroarylation of Nitroalkenes Using Aryltins and Sodium Tetraarylborates

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A variety of aryltin compounds and sodium tetraarylborates can be employed for Michael-type hydroarylation reactions of nitroalkenes to afford β-arylnitroalkanes in moderate to good yields in the presence of either LiCl, $MgCl_2$, or $CaCl_2$ and a catalytic amount of palladium(II) salt (0.05 molar amount) in acetic acid. Results show that 50–70% of aryl groups out of all in these aryl compounds can be transferred to the products in this hydroarylation. The addition of a catalytic amount (0.05–0.10 molar amount) of a Lewis acid chloride, $BiCl_3$ or $SbCl_3$, much improves the product yield in some cases.

A variety of organoheteroatom compounds such as organoborons,[1] organotins,[2] and organoantimonys[3] have been known to react with α,β-unsaturated ketones and aldehydes in the presence of a catalytic amount of Pd(II) salt to give the corresponding Michael-type hydroarylation compounds, β-aryl-substituted saturated ketones and aldehydes, respectively. Although there are several reports of transition metal [Rh(I),[4a] Cu(II)[4b]]-catalyzed Michael-type hydroarylation or hydroalkylation of nitroalkenes using organoborons and organozincs, examples that use a palladium salt as catalyst are quite rare.[4c] We have now examined carefully Pd(II)-catalyzed hydroarylation of nitroalkenes using several arylheteroatom compounds in acetic acid (AcOH) by taking the atom economy[5] of aryl groups into account and have found that aryl groups of aryltins and sodium tetraarylborates could be transferred quite effectively to the products, β-arylnitroalkanes. The addition of the salt of a Group 15 element, such as $BiCl_3$, $SbCl_3$, Bi_2O_3 etc., in a catalytic amount much improved the product yield in this catalytic system in some cases. Details of the results of this Michael-type hydroarylation are reported here.[6]

Results and Discussion

Palladium(II)-Catalyzed Hydrophenylation of Nitroalkenes Using Tetraphenyltin. At first, the catalytic system used so far for the hydroarylation reaction of α,β-unsaturated ketones and aldehydes with aryltin compounds was examined for use with nitroalkenes.[2] Thus, β-nitrostyrene (2-nitro-1-phenylethene, **1a**, 2 mmol) was treated with Ph_4Sn (**2m**, 0.5 mmol, 0.25 molar amount to **1a**) in the presence of $PdCl_2$ (0.02 mmol, 0.01 molar amount to **1a**) and LiCl (4 mmol, 2 molar amounts to **1a**) in AcOH (20 mL) at 25 °C for 20 h. As a result, biphenyl (**4m**) was mainly obtained together with a Michael-type hydroarylated product, 2-nitro-1,1-diphenylethane (**3am**) (Scheme 1; Table 1, Entry 1). Unfortunately, the yield of **4m** much increased at a higher temperature (50 °C) without any improvement of the yield of **3am** (Table 1, Entries 1–4), unlike the case of the reaction using α,β-unsaturated ketones and aldehydes.[2] A larger amount of $PdCl_2$ (0.1 mmol, 0.05 molar amount to **1a**) was needed for producing **3am** as a major product, where more than two phenyl groups of **2m** could be transferred to the hydroarylated product (Table 1, Entry 5). The presence of LiCl was necessary for this catalytic system to afford the hydroarylated product efficiently (Table 1, Entries 5 and 6). Instead of LiCl, the chlorides $CaCl_2$ and $MgCl_2$ were also effective as an additive (Table 1, Entries 7 and 8). The complex $[PdCl_2(PhCN)_2]$ was as effective as $PdCl_2$ as a catalyst (Table 1, Entry 9), while $[PdCl_2(PPh_3)_2]$, rhodium salts such as $RhCl_3 \cdot 3H_2O$, $[RhCl(CO)_2]_2$, and $[Rh_3O(OAc)_6(H_2O)_3]OAc$, and copper salts such as $CuCl_2$, $Cu(NO_3)_2 \cdot 3H_2O$, CuCl, and CuI were revealed to be ineffective for this hydroarylation.

A similar treatment of other nitroalkenes bearing a substituent on the phenyl ring of **1a**, such as *p*-$CH_3C_6H_4CH{=}CHNO_2$ (**1b**), *p*-$CH_3OC_6H_4CH{=}CHNO_2$ (**1c**), *p*-$ClC_6H_4CH{=}CHNO_2$ (**1d**), *p*-$BrC_6H_4CH{=}CHNO_2$ (**1e**), *m*-$NO_2C_6H_4CH{=}CHNO_2$ (**1f**), and *o*-$NO_2C_6H_4CH{=}CHNO_2$ (**1g**), afforded the corresponding hydroarylated products (**3bm**, **3cm**, **3dm**, **3em**, **3fm**, and **3gm**, respectively) in moderate to good yields (Scheme 1; Table 2, Entries 2–7), where no appreciable substituent effects were observed. From nitroalkenes having an alkyl group in place of an aryl group such as *n*-$C_7H_{15}CH{=}CHNO_2$ (**1h**) and *c*-$C_6H_{11}CH{=}CHNO_2$ (**1i**), the selectivity for the expected nitroalkane products became higher, sacrificing the formation of biphenyl (Table 2, Entries 8 and 9). The hydroarylation of β-substituted-α-nitroalkenes, which bear a bulky alkyl substituent or heteroaryl group at the β-carbon such as 3,3-dimethyl-1-nitro-1-butene [**1j**, $(CH_3)_3CCH{=}CHNO_2$], 2-(2-nitroethenyl)thiophene (**1k**, 2-$C_4H_3SCH{=}CHNO_2$), and 2-(2-nitroethenyl)furan (**1l**, 2-$C_4H_3OCH{=}CHNO_2$), did not proceed well, biphenyl being the main product (Table 2, Entries 10–12). No hydroarylation occurred for α,β-disubstituted-α-nitroalkenes such as **5** and **6**, both having a substituent on the same carbon atom where a nitro group is present, probably due to the steric hindrance at

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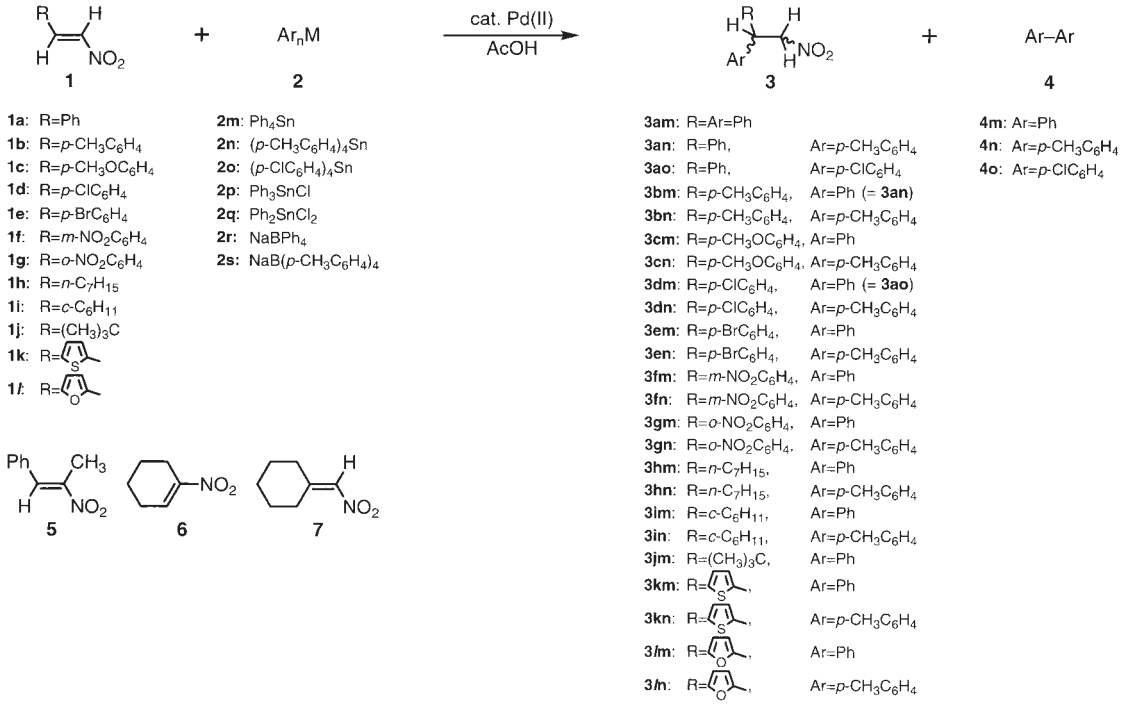


Scheme 1. Hydroarylation of nitroalkenes

Table 1. Pd(II)-Catalyzed Hydrophenylation of β-Nitrostyrene (**1a**) Using Ph_4Sn (**2m**)[a]

Entry	Pd catalyst/mmol		Additive/mmol		Isolated yield/%[b]	
					3am	**4m**
1	$PdCl_2$	0.02	LiCl	4	14	23
2[c]	$PdCl_2$	0.02	LiCl	4	12	45
3	$PdCl_2$	0.04	LiCl	4	30	32
4[d]	$PdCl_2$	0.04	LiCl	4	12	48
5	$PdCl_2$	0.1	LiCl	4	52	39
6	$PdCl_2$	0.1	—		5	15
7	$PdCl_2$	0.1	$CaCl_2$	2	46	31
8	$PdCl_2$	0.1	$MgCl_2$	2	45	33
9	$[PdCl_2(PhCN)_2]$	0.1	LiCl	4	52	31

a) Reaction conditions: **1a** (2 mmol) and **2m** (0.5 mmol) in AcOH (20 mL) at 25 °C for 20 h. b) Based on **2m**: 2 mmol of **3am** and 1 mmol of biphenyl (**4m**) correspond to 100% yield, respectively. c) At 50 °C for 5 h. d) At 50 °C for 2 h.

the arylpalladation step (see "Plausible Reaction Scheme"). The application of this reaction to **7**, which could be regarded as a β,β-disubstituted-α-nitroalkene, resulted in the major formation of biphenyl (**4m**) together with a small amount of a complex mixture which contained little of the corresponding expected hydroarylated product.

It is worth noting that this type of catalytic reaction could not be applied to such Michael-type acceptors as α,β-unsaturated esters and nitriles.

Palladium(II)-Catalyzed Hydroarylation of β-Nitrostyrene Using Other Arylating Reagents. The hydroarylation of **1a** with some tetraaryltins was next investigated using the above catalytic system. Thus, **1a** (2 mmol) was treated with Ar_4Sn (0.5 mmol) in the presence of $PdCl_2$ (0.1 mmol) and LiCl (4 mmol) in AcOH (20 mL) at 25 °C for 20 h. As a result, the hydroarylation with $(p\text{-}CH_3C_6H_4)_4Sn$ (**2n**) was revealed to be more efficient than that with Ph_4Sn (**2m**), affording a larger amount of the Michael-type hydroarylated product (**3an** = **3bm**) together with a smaller amount of biaryl (**4n**) (Table 3, Entry 2). On the contrary, biaryl **4o** was obtained as the main product in the case of $(p\text{-}ClC_6H_4)_4Sn$ (**2o**) (Table 3, Entry 3). Arylating reagents other than tetraaryltins were also investigated: these include Ph_3SnCl (**2p**), Ph_2SnCl_2 (**2q**), Ph_4Ge, Ph_3Sb, $Ph_3Sb(OAc)_2$, Ph_3Bi, $Ph_3Bi(OAc)_2$, $PhB(OH)_2$, $NaBPh_4$ (**2r**), and $NaB(p\text{-}CH_3C_6H_4)_4$ (**2s**). Thus, one molar amount of **1a** was treated with one molar amount of arylating reagent as aryl group(s) (i.e.; a quarter molar amount of Ph_4Ge, one third molar amount of **2p**, Ph_3Sb, $Ph_3Sb(OAc)_2$, Ph_3Bi, $Ph_3Bi(OAc)_2$, **2r**, and **2s**, a half molar amount of **2q**, and one molar amount of $PhB(OH)_2$, respectively) in the presence of $PdCl_2$ (0.05 molar amount) and LiCl (2 molar amounts) in AcOH at 25 °C for 20 h. Among these reagents, **2q** and **2r** mainly afforded the Michael-type hydroarylated product **3am** together with a small amount of biphenyl (**4m**), phenyl groups

Table 2. Pd(II)-Catalyzed Hydrophenylation of Nitroalkenes (**1**) Using Ph_4Sn (**2m**)[a]

Entry	1	Isolated yield/%[b]	
		3	4m
1[c]	**1a**	**3am**, 52	39
2	**1b**	**3bm**, 59	31
3	**1c**	**3cm**, 50	33
4	**1d**	**3dm**, 50	43
5	**1e**	**3em**, 53	35
6	**1f**	**3fm**, 37	36
7	**1g**	**3gm**, 50	47
8	**1h**	**3hm**, 68	13
9	**1i**	**3im**, 54	9
10	**1j**	**3jm**, 6	75
11	**1k**	**3km**, 24	51
12	**1l**	**3lm**, 3	27

a) Reaction conditions: **1** (1 mmol), **2m** (0.25 mmol), $PdCl_2$ (0.05 mmol), and LiCl (2 mmol) in AcOH (10 mL) at 25 °C for 20 h. b) Based on **2m**: 1 mmol of **3** and 0.5 mmol of biphenyl (**4m**) correspond to 100% yield, respectively. c) Double scale reaction.

Table 3. Pd(II)-Catalyzed Hydrophenylation of β-Nitrostyrene (**1a**) Using Various Arylating Reagents (**2**)[a]

Entry	2/mmol	Isolated yield/%[b]	
		3	4
1	**2m** 0.5	**3am**, 52	**4m**, 39
2	**2n** 0.5	**3an**, 67	**4n**, 19
3	**2o** 0.5	**3ao**, 13	**4o**, 71
4	**2p** 0.67	**3am**, 39	**4m**, 44
5	**2q** 1.0	**3am**, 70	**4m**, 19
6	**2r** 0.67	**3am**, 59	**4m**, 12
7[c]	**2s** 0.33	**3an**, 19	**4n**, 3

a) Reaction conditions: **1a** (2 mmol), $PdCl_2$ (0.1 mmol), and LiCl (4 mmol) in AcOH (20 mL) at 25 °C for 20 h. b) Based on **2**; 2 mmol as Ar group: 2 mmol of **3** and 1 mmol of biaryl (**4**) correspond to 100% yield, respectively. c) Half scale reaction.

being transferred more efficiently to **1a** than those of **2m** (Table 3, Entries 5 and 6). In the case of Ph_3Bi and $Ph_3Bi(OAc)_2$, **4m** was formed almost exclusively. During the treatment of **2q** in the presence of $PdCl_2$ and LiCl, the reaction mixture turned from orange solution to yellow turbid solution, where the complexation might occur. Unexpectedly, both **2p** and **2s** were not so active as an arylating reagent in this catalytic system (Table 3, Entries 4 and 7). The reagent $Ph_3Sb(OAc)_2$ scarcely reacted with **1a**. In this catalytic system, the reagent $PhB(OH)_2$ was quite inactive, unlike the catalytic system reported by Hayashi and co-workers.[7]

Arylating reagents such as **2n**, **2q**, and **2r** were next treated with several other nitroalkenes in this catalytic system. The typical results are listed in Table 4. The hydroarylation of β-nitrostyrene derivatives (**1b–1f**) using these reagents proceeded as effectively as that of **1a**, but no substituent effect was clearly revealed (Table 4, Entries 1, 2, 7, 8, 12, and 13). The hydroarylation was also applicable to nitroalkenes **1h** and **1i** (Table 4, Entries 3, 4, 9, 10, and 14), where little biaryl formation occurs. Nitroalkenes **1k** and **1l** could also be used (Table 4, Entries 5, 6, 11, and 15), but no reaction occurred with nitroalkenes **5** and **6**.

Table 4. Pd(II)-Catalyzed Hydrophenylation of Nitroalkenes (**1**) Using Various Arylating Reagents (**2**)[a]

Entry	2/mmol	1	Isolated yield/%[b]	
			3	4
1	**2n** 0.25	**1b**	**3bn**, 63	**4n**, 24
2	**2n** 0.25	**1e**	**3en**, 67	**4n**, 20
3	**2n** 0.25	**1h**	**3hn**, 43	**4n**, 3
4	**2n** 0.25	**1i**	**3in**, 42	**4n**, 3
5	**2n** 0.25	**1k**	**3kn**, 35	**4n**, 37
6	**2n** 0.25	**1l**	**3ln**, 22	**4n**, 50
7	**2q** 0.5	**1b**	**3bm**, 66	**4m**, 18
8	**2q** 0.5	**1f**	**3fm**, 37	**4m**, 16
9	**2q** 0.5	**1h**	**3hm**, 72	**4m**, 3
10	**2q** 0.5	**1i**	**3im**, 66	**4m**, 9
11	**2q** 0.5	**1k**	**3km**, 45	**4m**, 33
12	**2r** 0.33	**1c**	**3cm**, 61	**4m**, 12
13	**2r** 0.33	**1d**	**3dm**, 62	**4m**, 20
14	**2r** 0.33	**1h**	**3hm**, 49	**4m**, 10
15	**2r** 0.33	**1k**	**3km**, 52	**4m**, 16

a) Reaction conditions: **1** (1 mmol), $PdCl_2$ (0.05 mmol), and LiCl (2 mmol) in AcOH (10 mL) at 25 °C for 20 h. b) Based on **2**; 1 mmol as Ar group: 1 mmol of **3** and 0.5 mmol of biaryl (**4**) correspond to 100% yield, respectively.

It has been well known[1c] that **2r** partly decomposes in AcOH as shown in Eq. 1 to produce triphenylborane and benzene, indicating that one of the four phenyl groups is wasted. Therefore, the hydroarylation was also carried out in other solvents such as

$$\underset{\mathbf{2r}}{NaBPh_4} + AcOH \rightarrow Ph_3B + PhH + AcONa \quad (1)$$

tetrahydrofuran (THF) and ethanol (EtOH), hoping to utilize all phenyl groups. However, little of the expected product **3am** was obtained in these solvents even when several basic inorganic salts such as NaOAc, Li_2CO_3, $LiOH\cdot H_2O$, and LiOAc were added in order to make transmetallation of phenyl groups more efficient.[5e]

The Effect of Added Lewis Acid. Since it has been found that the presence of antimony(III) chloride ($SbCl_3$) was effective for the Michael-type hydroarylation of α,β-unsaturated carbonyl compounds using sodium tetraarylborates and arylboronic acids in AcOH,[1b,c] the effect of Lewis acid upon the reaction between **1a** and Ph_4Sn (**2m**) was next examined. The treatment of **1a** (1 mmol) with **2m** (0.25 mmol, 0.25 molar amount to **1a**) in the presence of $PdCl_2$ (0.05 mmol, 0.05 molar amount to **1a**), LiCl (2 mmol, 2 molar amounts to **1a**), and $SbCl_3$ (0.1 mmol, 0.1 molar amount to **1a**) in AcOH (10 mL) at 25 °C for 20 h afforded **3am** in a quite high yield together with a diminishing amount of biphenyl (**4m**), where more than three out of four phenyl groups of **1a** were transferred to the hydroarylated product (Table 5, Entry 1). This catalytic hydroarylation reaction was then carried out in the presence of a Lewis acid other than $SbCl_3$, such as SbOCl, Sb_2O_3, $BiCl_3$, Bi_2O_3, $Bi(NO_3)_3\cdot 5H_2O$, $Bi(OTf)_3$, $BF_3\cdot OEt_2$, $AlCl_3$, or $InCl_3$.

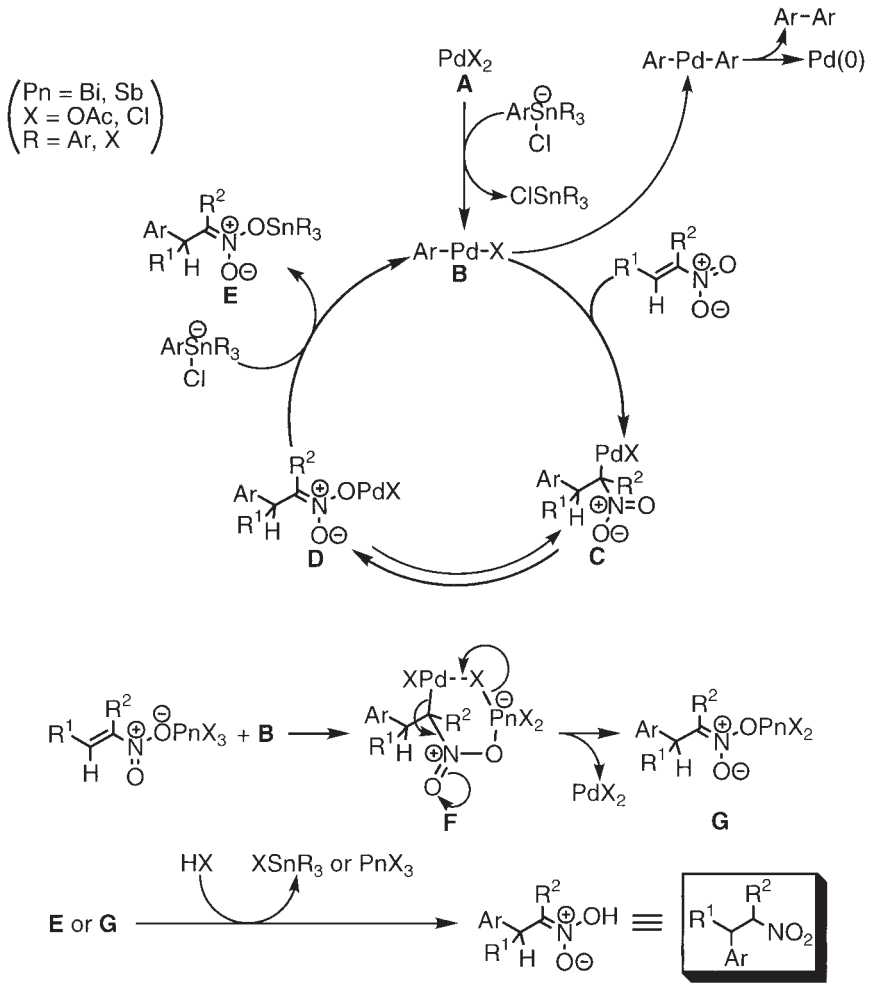
Table 5. The Effect of Lewis Acid Added in the Pd-Catalyzed Reaction between β-Nitrostyrene (**1a**) and Ph_4Sn (**2m**)[a)]

Entry	Lewis Acid/mmol		Isolated yield/%[b)]	
			3am	**4m**
1	$SbCl_3$	0.1	78	10
2	SbOCl	0.1	77	15
3	Sb_2O_3	0.05	84	10
4	$BiCl_3$	0.1	83	16
5[c)]	$BiCl_3$	0.1	75	8
6	$BiCl_3$	0.05	74	14
7[c)]	$BiCl_3$	0.05	71	14
8	Bi_2O_3	0.05	85	15
9	$Bi(NO_3)_3 \cdot 5H_2O$	0.1	81	9
10	$Bi(OTf)_3$	0.1	74	15
11	—		52	39

a) Reaction conditions: **1a** (1 mmol), **2m** (0.25 mmol), $PdCl_2$ (0.05 mmol), and LiCl (2 mmol) in AcOH (10 mL) at 25 °C for 20 h. b) Based on **2m**; 1 mmol of **3am** and 0.5 mmol of biphenyl (**4m**) correspond to 100% yield, respectively. c) For 5 h.

Eventually, it was revealed that the salts of a Group 15 element such as Sb_2O_3, $BiCl_3$, Bi_2O_3, and $Bi(NO_3)_3 \cdot 5H_2O$ were slightly more effective than $SbCl_3$ (Table 5, Entries 3, 4, 8, and 9).[8] However, the salts SbOCl and $Bi(OTf)_3$ were slightly less effective than them (Table 5, Entries 2 and 10). Here, it is worth noting that bismuth salt showed a remarkable activity, since the salt was not effective in similar hydroarylations of α,β-unsaturated aldehydes and ketones. The effect of Bi(Ⅲ) salt as a Lewis acid catalyst in many organic transformations is of current interest[9] and the present result should be another example of such effect. The reaction proceeded even using a reduced amount (0.05 molar amount to **1a**) of $BiCl_3$ and in a shortened reaction time (5 h), though the yield of products slightly lowered (Table 5, Entries 5–7). On the other hand, the salts of a Group 13 element such as $BF_3 \cdot OEt_2$, $AlCl_3$, and $InCl_3$ did not show any positive effects in this reaction.

By considering these results, we mainly carried out further investigations in the presence of $BiCl_3$ for 20 h. Thus, a similar treatment of other nitroalkenes such as **1b**, **1c**, **1d**, **1e**, **1f**, **1h**, and **1i** in the presence of $BiCl_3$ afforded the corresponding hydroarylated products (**3bm**, **3cm**, **3dm**, **3em**, **3fm**, **3hm**, and **3im**, respectively) in higher yields together with biphenyl (**4m**), where slightly fewer than four phenyl groups of **2m** could be transferred to the products (Table 6, Entries 1, 3–7, 9, and 10) as observed in the reaction with **1a**. The presence of $BiCl_3$ in the hydroarylation of **1g**, **1j**, **1k**, and **1l** using **2m** did not give any appreciable positive effect (Table 6, Entries 8,



Scheme 2. Plausible reaction pathway

Table 6. Hydrophenylation of Nitroalkenes Using Ar_4Sn (**2**) in the Presence of $BiCl_3$[a)]

Entry	1	2	Isolated yield/%[b)]	
			3	4
1	**1a**	**2m**	**3am**, 83 (52)	**4m**, 16 (39)
2	**1a**	**2n**	**3an**, 76 (67)	**4n**, 17 (19)
3	**1b**	**2m**	**3bm**, 82 (59)	**4m**, 10 (31)
4	**1c**	**2m**	**3cm**, 81 (50)	**4m**, 15 (33)
5	**1d**	**2m**	**3dm**, 88 (50)	**4m**, 6 (43)
6	**1e**	**2m**	**3em**, 85 (53)	**4m**, 13 (35)
7	**1f**	**2m**	**3fm**, 77 (37)	**4m**, 16 (36)
8	**1g**	**2m**	**3gm**, 55 (50)	**4m**, 28 (47)
9	**1h**	**2m**	**3hm**, 78 (68)	**4m**, 3 (13)
10	**1i**	**2m**	**3im**, 80 (54)	**4m**, 1 (9)
11	**1j**	**2m**	**3jm**, 5 (6)	**4m**, 70 (75)
12	**1k**	**2m**	**3km**, 25 (24)	**4m**, 39 (51)
13	**1l**	**2m**	**3lm**, 7 (3)	**4m**, 21 (27)

a) Reaction conditions: **1** (1 mmol), **2** (0.25 mmol), $PdCl_2$ (0.05 mmol), LiCl (2 mmol), and $BiCl_3$ (0.1 mmol) in AcOH (10 mL) at 25 °C for 20 h. b) Based on **2**: 1 mmol of **3** and 0.5 mmol of biaryl (**4**) correspond to 100% yield, respectively. The yields obtained in the absence of $BiCl_3$ are shown in parentheses.

11–13), showing that the addition of $BiCl_3$ does not always make the hydroarylation more efficient. No hydroarylation occurred to **5** or **6** even in the presence of $BiCl_3$ or $SbCl_3$. In the case of **7**, a complex mixture was obtained whether $BiCl_3$ is present or not.

Plausible Reaction Scheme. Although the details are not yet known, Scheme 2 is proposed for this catalytic Michael-type addition reaction using organotin compounds as an example. The transmetallation of Sn(IV) moiety of aryltin(IV) compounds by Pd(II) (**A**) occurs to give an Ar–Pd(II)–X (X = OAc or Cl) species (**B**), which adds to nitroalkenes to afford an alkylpalladium(II) species (**C**).[10] The Pd(II) species **C** might be in equilibrium with a palladium(II) nitronate (**D**) to which the other organotin(IV) compound attacks to afford a tin(IV) nitronate (**E**), regenerating the Ar–Pd(II)–X species. The species **E** is hydrolyzed (solvolyzed) to lead to the hydroarylated product. A similar reaction scheme has already been proposed in the reaction between the corresponding Rh enolate and arylboron compounds.[11] The role of metal chloride (mainly LiCl) is to make a Pd(II) salt soluble and also to make the transmetallation step more facile by coordination to aryltin(IV) compounds.[12] In the presence of the salt of a Group 15 element, such as $BiCl_3$, $SbCl_3$, and Bi_2O_3 [abbreviated as PnX_3: it is assumed that Bi_2O_3 turns to $Bi(OAc)_3$ or Bi(O)OAc in AcOH], the salt may coordinate to the oxygen atom of the nitro group of nitroalkenes. Then the carbopalladation occurs to give the species **F**, from which a Pd(II) species is eliminated to give a Group 15 nitronate (**G**). In the cases of **1j**, **5**, **6**, and **7**, the substituent at the carbon atom where a nitro and/or alkyl group attaches might prevent the attack of the species **B** to the alkenic part, although the exact reason is not yet known. For the formation of biaryl, the second transmetallation of Sn(IV) moiety of aryltin(IV) compounds by the species **B** occurs to give Ar–Pd(II)–Ar species, followed by the reductive elimination.

Experimental

General. Melting points were determined on a Yanaco MP-J3 micro melting point apparatus and are uncorrected. The ^1H and ^{13}C NMR spectra were recorded with JEOL JNM-AL300 spectrometer for solutions in $CDCl_3$ with Me_4Si as an internal standard. Chemical shifts are reported in δ ppm units downfield from Me_4Si. High resolution mass spectra (FAB HRMS) were obtained with a JEOL JMX-SX 102A spectrometer. The isolation of a pure product was carried out by column chromatography on SiO_2 (Merck 60, 230–400 mesh, Merck KGaA.).

Materials. Solvents except AcOH and EtOH were freshly distilled under N_2 prior to use; tetrahydrofuran (THF) was distilled from sodium diphenylketyl; C_6H_6 and CH_2Cl_2 were distilled from calcium hydride. Nitroalkenes such as **1b**, **1c**, **1d**, **1e**, **1f**, **1h**, **1i**, **1j**, and **7** were prepared from the corresponding carbonyl compounds and nitromethane in the presence of NaOH, KOH, or NaOMe in MeOH according to the literature procedure,[13] typical physical data being shown below. Other nitroalkenes such as **1a**, **1g**, **1k**, **1l**, **5**, and **6** are commercial products. The palladium complexes such as $[PdCl_2(PhCN)_2]$[14a] and $[PdCl_2(PPh_3)_2]$[14b] were prepared by the literature methods. The compound $[Rh_3O(OAc)_6(H_2O)_3]OAc$ was prepared by the literature method from $RhCl_3 \cdot 3H_2O$ and AgOAc in aqueous AcOH.[14c] Lithium acetate was prepared from $LiOH \cdot H_2O$ and acetic anhydride under reflux, followed by evaporation of unreacted acetic anhydride. Commercially available chlorides such as $MgCl_2$, $SbCl_3$, and $BiCl_3$ were dehydrated by thionyl chloride and dried under vacuum prior to use. Arylating reagents such as **2m**, **2p**, **2q**, **2r**, **2s**, Ph_4Ge, Ph_3Sb, and $PhB(OH)_2$ are commercial products. Tetraaryltins such as **2n** and **2o** were prepared from the corresponding Grignard reagents and $SnCl_4$ (as C_6H_6 solution) in THF, followed by recrystallization.[2,15] Triphenylbismuthine (Ph_3Bi) was prepared from phenylmagnesium bromide and $BiCl_3$, followed by recrystallization from petroleum ether.[16] Bismuth triflate [$Bi(OTf)_3$] was prepared from trifluoromethanesulfonic acid and Ph_3Bi,[17] and used without further purification. The compounds such as $Ph_3Sb(OAc)_2$[18] and $Ph_3Bi(OAc)_2$[16] were prepared by the literature methods, using CH_2Cl_2 as solvent.

***p*-Methyl-β-nitrostyrene (1b):** Recrystallized from hexane–toluene, mp 101–102 °C (lit. 102 °C,[19] 103–103.5 °C[20]); ^1H NMR ($CDCl_3$, 300 MHz) δ 2.41 (s, 3H), 7.24–7.27 (d, J = 8.0 Hz, 2H), 7.43–7.46 (d, J = 8.0 Hz, 2H), 7.54–7.59 (d, J = 13.6 Hz, 1H), 7.96–8.02 (d, J = 13.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.66, 127.27, 129.18, 130.13, 136.29, 139.17, 143.09.

***p*-Methoxy-β-nitrostyrene (1c):** Recrystallized from hexane–benzene, mp 85.5–87.5 °C (lit. 90 °C,[21] 86 °C,[22] 86–87 °C,[23,24]); ^1H NMR ($CDCl_3$, 300 MHz) δ 3.87 (s, 3H), 6.94–6.98 (d, J = 8.6 Hz, 2H), 7.49–7.55 (d, J = 8.6 Hz, 2H and d, J = 13.7 Hz, 1H), 7.95–8.01 (d, J = 13.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.52, 114.91, 122.54, 131.15, 135.03, 139.01, 162.93.

***p*-Chloro-β-nitrostyrene (1d):** Recrystallized from toluene, mp 111–113 °C (lit. 111–112 °C,[25] 112–112.5 °C,[23] 113–114 °C[26,27]); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.41–7.51 (m, 4H), 7.53–7.59 (d, J = 13.8 Hz, 1H), 7.94–7.99 (d, J = 13.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 128.51, 129.76, 130.24, 137.40, 137.66, 138.31.

***p*-Bromo-β-nitrostyrene (1e):** Recrystallized from toluene, mp 151–153 °C (lit. 150.5–151 °C,[27] 156–158 °C[28]); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.39–7.44 (d, J = 8.6 Hz, 2H), 7.55–7.63 (d, J = 13.7 Hz, 1H and d, J = 8.6 Hz, 2H), 7.92–7.97 (d, J =

13.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 126.77, 128.93, 130.37, 132.73, 137.45, 137.75.

***m*,*β*-Dinitrostyrene (1f):** Recrystallized from ethyl acetate, mp 124.5–126 °C (lit. 124.5–125.5 °C[23]); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.64–7.71 (t, $J = 8.0$ Hz, 1H and d, $J = 13.8$ Hz, 1H), 7.85–7.89 (d, $J = 8.0$ Hz, 1H), 8.03–8.08 (d, $J = 13.8$ Hz, 1H), 8.34–8.38 (d, $J = 8.0$ Hz, 1H), 8.42 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 123.47, 126.21, 130.61, 131.82, 134.41, 136.22, 139.28, 148.83.

1-Nitro-1-nonene (1h): Obtained as pale yellow oil, bp 150 °C (bath temp., 5 mmHg, 1 mmHg = 133.322 Pa) (lit. 91–95 °C/0.2–0.3 mmHg[29]); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.86–0.92 (t, $J = 6.7$ Hz, 3H), 1.20–1.44 (m 8H), 1.46–1.55 (quartet-d, $J = 7.3$, 1.5 Hz, 2H), 2.23–2.31 (quartet, $J = 7.3$ Hz, 2H), 6.95–7.01 (dt, $J = 13.4$, 1.5 Hz, 1H), 7.23–7.33 (dt, $J = 13.4$, 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.95, 22.51, 27.65, 28.37, 28.84, 28.98, 31.57, 139.47, 142.78.

(2-Nitroethenyl)cyclohexane (1i): Obtained as pale yellow oil, bp 115–120 °C (bath temp., 6 mmHg) (lit. 100 °C/0.4 mmHg[30]); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.14–1.41 (m, 5H), 1.69–1.84 (m 5H), 2.21–2.32 (m, 1H), 6.91–6.96 (dd, $J = 13.5$, 0.9 Hz, 2H), 7.18–7.29 (dd, $J = 13.5$, 7.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.20, 25.37, 31.16, 37.27, 138.02, 147.03.

3,3-Dimethyl-1-nitro-1-butene (1j): Obtained as pale yellow oil, bp 70 °C (bath temp., 7 mmHg) (lit. 40 °C/2 mmHg[31]); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.17 (s, 9H), 6.88–6.93 (d, $J = 13.6$ Hz, 1H), 7.24–7.30 (d, $J = 13.6$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.21, 32.47, 137.01, 151.76.

(Nitromethylene)cyclohexane (7): Obtained as yellow oil, bp 100–130 °C (bath temp., 6 mmHg) (lit. 50–52 °C/0.2 mmHg,[32] 83 °C/3 mmHg[33]); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.61–1.78 (m, 6H), 2.19–2.24 (t, $J = 6.0$ Hz, 2H), 2.83–2.88 (t, $J = 6.0$ Hz, 2H), 6.92 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.59, 27.14, 28.05, 28.72, 34.18, 132.08, 155.65.

Tetra(*p*-tolyl)tin (2n): Recrystallized from benzene–ethyl acetate, mp 242–242.5 °C (lit. 238 °C[15c]); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.35 (s, 12H), 7.18–7.21 (d, $J = 7.8$ Hz, 8H), 7.45–7.49 (d, $J = 7.8$ Hz, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.48, 129.38, 134.42, 137.15, 138.76.

Tetrakis(*p*-chlorophenyl)tin (2o): Recrystallized from benzene–petroleum ether, mp 198–201 °C (lit. 199 °C[15c]); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.36–7.58 (m, 16H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 129.19, 134.62, 136.26, 138.09.

General Procedure for Palladium(II)-Catalyzed Michael-Type Addition Using Aryltin Compounds (for Example, Table 1, Entry 5). A mixture of $PdCl_2$ (0.018 g, 0.10 mmol), LiCl (0.170 g, 4.01 mmol), and AcOH (5 mL) was stirred to give a homogeneous red solution. To this solution, β-nitrostyrene (**1a**, 0.298 g, 2.00 mmol), tetraphenyltin (**2m**, 0.214 g, 0.501 mmol), and AcOH (15 mL) were added and the resulting mixture was stirred at 25 °C. After stirring for 20 h, the mixture was poured into brine (150 mL) and extracted with diethyl ether or ethyl acetate (30 mL × 5). The organic layer was washed with dilute HCl (ca. 3 mol·dm^{-3}, 30 mL × 3), water (30 mL × 2), and saturated $NaHCO_3$ solution (usually 50 mL × 2) and then dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the brownish yellow residue was subjected to column chromatography to give biphenyl (**4m**, 0.061 g, 0.392 mmol, 39.1% yield) and 2-nitro-1,1-diphenylethane (**3am**, 0.239 g, 1.05 mmol, 52.4% yield).

General Procedure for Palladium(II)-Catalyzed Michael-Type Addition Using Aryltin Compounds in the Presence of Sb_2O_3 or Bi_2O_3 (for Example, Table 5, Entry 8). A mixture of $PdCl_2$ (0.009 g, 0.05 mmol), LiCl (0.085 g, 2.0 mmol), Bi_2O_3 (0.023 g, 0.049 mmol), and AcOH (1 mL) was stirred to give a homogeneous red solution. To this solution, **1a** (0.149 g, 0.999 mmol), **2m** (0.107 g, 0.250 mmol), and AcOH (9 mL) were added. After stirring for 20 h, the mixture was similarly treated as described above to afford **4m** (0.0118 g, 0.0765 mmol, 15.3% yield) and **3am** (0.193 g, 0.848 mmol, 84.8% yield).

General Procedure for Palladium(II)-Catalyzed Michael-Type Addition Using Aryltin Compounds in the Presence of Some Other Additive (for Example, Table 5, Entry 4). To a homogeneous red solution which consisted of $PdCl_2$ (0.009 g, 0.05 mmol), LiCl (0.085 g, 2.0 mmol), and AcOH (1 mL), **1a** (0.149 g, 0.999 mmol), **2m** (0.107 g, 0.250 mmol), $BiCl_3$ (0.032 g, 0.101 mmol), and AcOH (9 mL) were added successively and the resulting mixture was stirred for 20 h. The mixture was then treated as above to afford **4m** (0.0122 g, 0.0791 mmol, 15.8% yield) and **3am** (0.188 g, 0.829 mmol, 82.9% yield).

The physical data of the produced hydroarylated compounds are shown below in which **3em**, **3en**, **3fm**, **3gm**, **3hm**, **3hn**, **3im**, **3in**, **3jm**, **3km**, **3kn**, **3lm**, and **3ln** are new compounds.

2-Nitro-1,1-diphenylethane (3am): Obtained as pale yellow oil (lit. mp 68–70 °C,[34] 69–70 °C[35]); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.81–4.91 (m, 3H), 7.16–7.28 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 48.88, 79.16, 127.53, 127.60, 128.96, 139.15.

2-Nitro-1-phenyl-1-(*p*-tolyl)ethane (3an = 3bm): Obtained as pale yellow oil (lit. mp 47–48 °C[35]); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.27 (s, 3H), 4.79–4.91 (m, 3H), 7.08–7.10 (m, 4H), 7.14–7.29 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.94, 48.57, 79.22, 127.43, 127.48, 127.57, 128.93, 129.64, 136.23, 137.20, 139.47.

1-(4-Chlorophenyl)-2-nitro-1-phenylethane (3ao = 3dm): Obtained as pale yellow oil (lit. mp 67–68 °C[35]); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.82–4.86 (m, 3H), 7.07–7.30 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 48.01, 78.58, 127.32, 127.51, 128.84, 128.88, 133.10, 137.65, 138.57.

2-Nitro-1,1-di(*p*-tolyl)ethane (3bn): Obtained as pale yellow oil (lit. bp 162 °C/0.4 mmHg[35]); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.22 (s, 6H), 4.74–4.83 (m, 3H), 7.03–7.06 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.78, 48.10, 79.15, 127.31, 129.47, 136.38, 136.93.

1-(*p*-Methoxyphenyl)-2-nitro-1-phenylethane (3cm): Obtained as yellow oil (lit. bp 166–168 °C/0.4 mmHg[35]); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.68 (s, 3H), 4.63–5.10 (m, 3H), 6.79–6.82 (d, $J = 7.7$ Hz, 2H), 7.09–7.12 (d, $J = 7.7$ Hz, 2H), 7.16–7.29 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 48.04, 54.99, 79.17, 114.18, 127.26, 127.38, 128.55, 128.77, 131.09, 139.46, 158.72.

1-(*p*-Bromophenyl)-2-nitro-1-phenylethane (3em): Obtained as pale yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.76–4.87 (m, 3H), 7.03–7.06 (d, $J = 7.9$ Hz, 2H), 7.13–7.31 (m, 5H), 7.34–7.38 (d, $J = 7.9$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 48.06, 78.51, 121.27, 127.32, 127.53, 128.89, 129.18, 131.84, 138.13, 138.45. Found: C, 55.04; H, 4.11; N, 4.38%. Calcd for $C_{14}H_{12}BrNO_2$: C, 54.92; H, 3.95; N, 4.58%.

1-(*p*-Bromophenyl)-2-nitro-1-(*p*-tolyl)ethane (3en): Obtained as pale yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.22 (s, 3H), 4.57–4.82 (m, 3H), 7.00–7.05 (m, 6H), 7.32–7.35 (d, $J = 7.3$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.81, 47.82, 78.67, 121.23, 127.25, 129.18, 129.62, 131.86, 135.51, 137.28, 138.45. Found: C, 56.15; H, 4.42; N, 4.14%. Calcd for $C_{15}H_{14}BrNO_2$: C, 56.27; H, 4.41; N, 4.37%.

2-Nitro-1-(*m*-nitrophenyl)-1-phenylethane (3fm): Obtained as pale yellow viscous oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.03–5.12 (m, 3H), 7.23–7.32 (m, 5H), 7.38–7.44 (t, $J = 7.8$ Hz, 1H), 7.58–7.62 (d, $J = 7.5$ Hz, 1H), 8.00–8.04 (d, $J = 7.7$ Hz, 1H), 8.14 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 48.45, 78.39, 122.60, 127.66, 128.08, 129.32, 130.09, 134.05, 138.01, 138.14, 141.58, 148.47. HRMS (FAB) found: 273.0880. Calcd for $C_{14}H_{13}N_2O_4$ ($M + H^+$): 273.0875.

2-Nitro-1-(*o*-nitrophenyl)-1-phenylethane (3gm): Obtained as pale yellow viscous oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.94–5.11 (dd + dd, $J = 7.9$, 13.6 Hz, 2H), 5.58–5.65 (t, $J = 8.0$ Hz, 1H), 7.20–7.32 (m, 5H), 7.34–7.43 (m, 2H), 7.50–7.56 (t, $J = 7.6$ Hz, 1H), 7.81–7.85 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 42.83, 77.76, 125.10, 127.64, 127.80, 128.45, 128.96, 129.00, 133.16, 133.32, 137.24, 149.29. HRMS (FAB) found: 273.0873. Calcd for $C_{14}H_{13}N_2O_4$ ($M + H^+$): 273.0875.

1-Nitro-2-phenylnonane (3hm): Obtained as pale yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.82–0.88 (t, $J = 6.7$ Hz, 3H), 1.00–1.45 (m, 10H), 1.63–1.71 (quartet, $J = 7.1$ Hz, 2H), 3.38–3.49 (quintet, $J = 7.6$ Hz, 1H), 4.48–4.60 (dd + dd, $J = 12.1$, 7.5 Hz, 2H), 7.16–7.36 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.00, 22.54, 26.84, 28.96, 29.22, 31.68, 32.97, 44.34, 80.98, 127.47, 128.85, 139.54, 142.79. Found: C, 71.99; H, 9.58; N, 5.43%. Calcd for $C_{15}H_{23}NO_2$: C, 72.25; H, 9.30; N, 5.62%.

1-Nitro-2-*p*-tolylnonane (3hn): Obtained as yellow oil, bp 195 °C/1 mmHg (bath temp); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.82–0.88 (t, $J = 6.8$ Hz, 3H), 1.05–1.40 (m, 10H), 1.61–1.69 (quartet, $J = 7.2$ Hz, 2H), 2.32 (s, 3H), 3.34–3.45 (quintet, $J = 7.6$ Hz, 1H), 4.45–4.58 (dd + dd, $J = 16.2$, 7.7 Hz, 2H), 7.04–7.08 (d, $J = 8.1$ Hz, 2H), 7.12–7.15 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.01, 21.02, 22.56, 26.87, 28.98, 29.26, 31.70, 32.99, 44.00, 81.15, 127.33, 129.54, 136.46, 137.11. Found: C, 73.20; H, 9.76; N, 5.03%. Calcd for $C_{16}H_{25}NO_2$: C, 72.96; H, 9.57; N, 5.32%.

(2-Nitro-1-phenylethyl)cyclohexane (3im): Obtained as pale yellow solid (from column chromatography), white crystal (recrystallized from hexane), mp 65–66.5 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.79–1.28 (m, 5H), 1.44–1.67 (m, 4H), 1.74–1.83 (m, 2H), 3.22–3.31 (ddd, $J = 12.3$, 9.9, 5.7 Hz, 1H), 4.57–4.66 (dd, $J = 12.3$, 9.9 Hz, 1H), 4.75–4.82 (dd, $J = 12.3$, 5.7 Hz, 1H), 7.11–7.15 (d, $J = 8.1$ Hz, 2H), 7.23–7.34 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.02, 26.03, 26.08, 30.50, 30.91, 40.83, 50.18, 78.79, 127.29, 128.09, 128.49, 138.75. Found: C, 72.12; H, 8.06; N, 5.94%. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00%.

(2-Nitro-1-*p*-tolylethyl)cyclohexane (3in): Obtained as pale yellow viscous oil, bp 180 °C/1 mmHg (bath temp); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.82–1.28 (m, 5H), 1.44–1.67 (m, 4H), 1.72–1.81 (m, 2H), 2.31 (s, 3H), 3.17–3.26 (ddd, $J = 12.1$, 10.1, 5.8 Hz, 1H), 4.54–4.63 (dd, $J = 12.1$, 10.1 Hz, 1H), 4.72–4.79 (dd, $J = 12.1$, 5.8 Hz, 1H), 6.99–7.03 (d, $J = 8.0$ Hz, 2H), 7.08–7.12 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.88, 25.97, 25.99, 26.03, 30.39, 30.84, 40.75, 49.76, 78.80, 127.88, 129.10, 135.58, 136.73. Found: C, 72.92; H, 8.43; N, 5.48%. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66%.

3,3-Dimethyl-1-nitro-2-phenylbutane (3jm):[36] Obtained as pale yellow solid (from column chromatography), white crystal (recrystallized from benzene–petroleum ether), mp 70–71 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.95 (s, 9H), 3.32–3.38 (dd, $J = 5.3$, 10.6 Hz, 1H), 4.75–4.89 (dd + dd, $J = 5.3$, 13.8 Hz and 10.6, 13.8 Hz, 2H), 7.16–7.19 (d, $J = 7.3$ Hz, 2H), 7.24–7.31 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.02, 33.68, 54.34, 77.21, 127.42, 128.13, 129.07, 137.58. Found: C, 69.38; H, 8.17; N, 6.78%. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76%.

2-(2-Nitro-1-phenylethyl)thiophene (3km): Obtained as pale yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.80–4.95 (m, 2H), 5.05–5.11 (t, $J = 7.9$ Hz, 1H), 6.85–6.90 (m, 2H), 7.12–7.15 (d, $J = 5.0$ Hz, 1H), 7.20–7.44 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 44.46, 79.61, 124.94, 125.02, 126.86, 127.38, 127.87, 128.91, 138.63, 142.26. Found: C, 61.67; H, 4.74; N, 5.89%. Calcd for $C_{12}H_{11}NO_2S$: C, 61.78; H, 4.75; N, 6.00%.

2-[2-Nitro-1-(*p*-tolyl)ethyl]thiophene (3kn): Obtained as pale yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.31 (s, 3H), 4.83–4.98 (dd + dd, $J = 7.5$, 12.6 Hz, 2H), 5.04–5.10 (t, $J = 7.9$ Hz, 1H), 6.86–6.93 (m, 2H), 7.11–7.29 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.99, 44.29, 79.90, 124.91, 125.04, 126.92, 127.33, 129.70, 135.71, 137.77, 142.67. Found: C, 63.21; H, 5.32; N, 5.46%. Calcd for $C_{13}H_{13}NO_2S$: C, 63.13; H, 5.30; N, 5.66%.

2-(2-Nitro-1-phenylethyl)furan (3lm): Obtained as pale yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.76–4.82 (dd, $J = 6.9$, 11.7 Hz, 1H), 4.89–4.94 (t, $J = 7.3$ Hz, 1H), 4.97–5.04 (dd, $J = 7.6$, 11.7 Hz, 1H), 6.10–6.12 (d, $J = 3.0$ Hz, 1H), 6.29–6.32 (dd, $J = 1.8$, 2.9 Hz, 1H), 7.23–7.36 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 43.49, 78.01, 107.40, 110.42, 127.83, 128.07, 129.03, 136.87, 142.52, 151.98. Found: C, 66.21; H, 5.10; N, 6.15%. Calcd for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45%.

2-[2-Nitro-1-(*p*-tolyl)ethyl]furan (3ln): Obtained as pale yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.31 (s, 3H), 4.72–4.79 (dd, $J = 7.4$, 11.1 Hz, 1H), 4.84–4.90 (t, $J = 7.4$ Hz, 1H), 4.94–5.01 (dd, $J = 7.4$, 11.1 Hz, 1H), 6.08–6.10 (d, $J = 1.8$ Hz, 1H), 6.27–6.30 (t, $J = 1.8$ Hz, 1H), 7.11–7.17 (m, 4H), 7.33–7.35 (d, $J = 1.8$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.99, 43.11, 78.06, 107.21, 110.35, 127.65, 129.64, 133.79, 137.80, 142.41, 152.20. Found: C, 67.24; H, 5.77; N, 5.57%. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06%.

The following three new compounds and a known **3dn**,[35] which appeared in Scheme 1, but not in the Tables, were isolated. Their physical data are also shown here.

1-(*p*-Methoxyphenyl)-2-nitro-1-(*p*-tolyl)ethane (3cn): Obtained as yellow oil; 55% isolated yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.29 (s, 3H), 3.72 (s, 3H), 4.80–4.90 (m, 3H), 6.82–6.85 (d, $J = 8.1$ Hz, 2H), 7.08–7.16 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.87, 47.83, 55.08, 79.39, 114.24, 127.36, 127.60, 129.56, 131.46, 136.59, 137.02, 158.77. Found: C, 70.78; H, 6.16; N, 4.88%. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16%.

1-(*p*-Chlorophenyl)-2-nitro-1-(*p*-tolyl)ethane (3dn): Obtained as pale yellow oil (lit. bp 174 °C/0.5 mmHg[35]); 63% isolated yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.26 (s, 3H), 4.79–4.88 (m, 3H), 7.07–7.14 (m, 6H), 7.21–7.24 (d, $J = 7.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.76, 47.75, 78.76, 127.22, 128.82, 128.89, 129.60, 133.07, 135.59, 137.28, 137.92.

2-Nitro-1-(*m*-nitrophenyl)-1-(*p*-tolyl)ethane (3fn): Obtained as pale yellow viscous oil; 62% isolated yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.31 (s, 3H), 4.94–5.10 (m, 3H), 7.10–7.13 (d, $J = 8.2$ Hz, 2H), 7.14–7.18 (d, $J = 8.2$ Hz, 2H), 7.46–7.52 (t, $J = 7.8$ Hz, 1H), 7.61–7.65 (d, $J = 9.2$ Hz, 1H), 8.07–8.13 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.90, 48.10, 78.54, 122.50, 127.33, 129.96, 133.76, 134.72, 137.96, 141.62, 148.48. Found: C, 63.00; H, 4.96; N, 9.76%. Calcd for $C_{15}H_{14}N_2O_4$: C, 62.93; H, 4.93; N, 9.79%.

2-Nitro-1-(*o*-nitrophenyl)-1-(*p*-tolyl)ethane (3gn): Obtained as pale yellow viscous oil; 52% isolated yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.28 (s, 3H), 4.92–5.11 (dd + dd, J = 8.0, 13.8 Hz, 2H), 5.55–5.62 (t, J = 8.0 Hz, 1H), 7.08–7.14 (m, 4H), 7.36–7.43 (m, 2H), 7.52–7.59 (t, J = 7.7 Hz, 1H), 7.83–7.87 (d, J = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.98, 42.73, 78.01, 125.27, 127.67, 128.52, 129.10, 129.82, 133.24, 133.75, 134.34, 137.82, 149.49. Found: C, 62.51; H, 4.93; N, 9.71%. Calcd for $C_{15}H_{14}N_2O_4$: C, 62.93; H, 4.93; N, 9.79%.

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