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The Heck-type arylation of allylic alcohols with arenediazonium salts

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Abstract

The Heck coupling of ArN_2BF_4 with secondary allylic alcohols, carried out in methanol using $Pd(dba)_2$ as catalyst without extra ligands and base, leads to the corresponding β-arylated carbonyl compounds. Such conditions afford arylated acetals from primary allylic alcohols.
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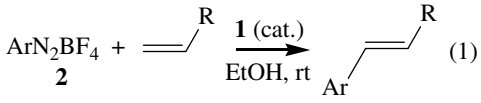
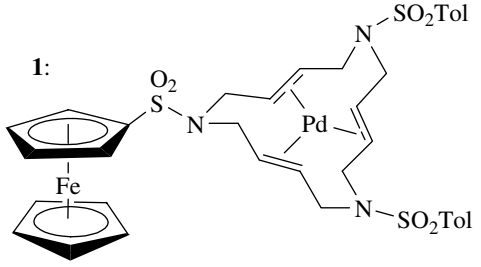
1. Introduction

Some of us have recently reported the arylation of styrene and α, β-unsaturated esters with arenediazonium tetrafluoroborates using a palladium(0) complex of a 15-membered macrocyclic triolefin (**1**) as the catalyst (Eq. (1)) [1]. Such phosphine-free palladium(0) complexes are air- and moisture-stable and recoverable catalysts for a variety of reactions [2]. Our interest in the arylation of allylic alcohols [3] urged us to use **1** as the catalyst with ArN_2BF_4 (**2**) as arylating agents since we expected the recovery of the catalyst [1]. Furthermore, the reaction of **2** with carbon–carbon double bonds can occur at ambient or moderate temperature in the absence of a base [1,4][1] while the reaction of aryl halides with allylic alcohols requires basic conditions and usually the heating of the mixture [3,6].





(1)

2. Results and discussion

Preliminary experiments carried out in ethanol using 5% of **1**, a 1:1 mixture of PhN_2BF_4 (**2a**) and 3-methylbut-3-en-2-ol (***3a***) at room temperature led to both 1-phenyl-2-methylbutan-3-one (***4aa***) and 1-phenyl-2-methylbut-1-en-3-ol (***5aa***) with low yields (Eq. (2),

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[1] Some Heck reactions with arenediazonium tetrafluoroborates have been carried in the presence of a base [5].

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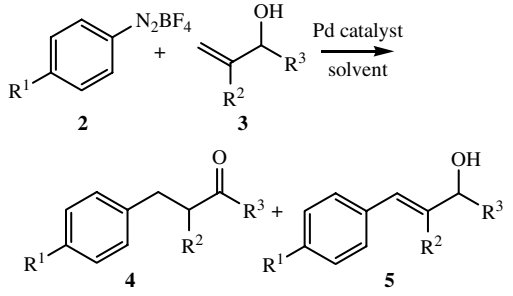
Table 1
Arylation of 3-methylbut-3-en-2-ol with ArN_2BF_4 using **1** (0.05 equiv.) as the catalyst

Run	**2**	**2**:**3*a*** ratio	Solvent	*t* (°C)	Time	Products, yield %
1	**2a**	1:1	EtOH	rt	4.25 h	**4a*a***, 21; **5a*a***, 11
2	**2a**	1:1	MeOH	rt	3.5 h	**4a*a***, 31; **5a*a***, 10
3	**2a**	1:1	MeOH	45	40 min	**4a*a***, 46; **5a*a***, <3
4	**2b**	1:1	MeOH	45	40 min	**4b*a***, 51
5	**2a**	1.5:1	MeOH	45	1 h	**4a*a***, 51
6	**2b**	1.5:1	MeOH	45	1 h	**4b*a***, 72
7	**2c**	1.5:1	MeOH	45	1 h	**4c*a***, 60
8	**2d**	1.5:1	MeOH	45	1 h	**4d*a***, 47

Table 1, run 1). No reaction was observed in THF while, in methanol, the yield increased, especially when the reaction was performed at 45 °C (runs 2 and 3). The use of *p*-tolylN_2 BF_4 (**2b**) in MeOH at 45 °C led selectively to ketone **4b*a*** (run 4). Further experiments carried out in MeOH at 45 °C, using an excess of $R^1C_6H_4N_2BF_4$ (R^1 = H, *p*-Me, *p*-*t*-Bu, *p*-F) towards the allylic alcohol, afforded the corresponding ketones with yields up to 72% (runs 5–8). Unfortunately, **1** was decomplexed in the course of these experiments, the macrocyclic ligand being almost quantitatively recovered.



a: R^1 = H; **b**: R^1 = Me; **c**: R^1 = *t*-Bu; **d**: R^1 = F; **e**: R^1 = NO_2; **f**: R^1 = MeO
a: R^2 = R^3 = Me; ***b***: R^2 = Me, R^3 = CH_2CHMe_2; ***c***: R^2 = Me, R^3 = H; ***d***: R^2 = R^3 = H

(2)

The instability of **1** in the course of the above reactions and, consequently, its un-recyclability, urge us to envisage the use of more common Pd catalysts. Actually, a careful study of the literature reveals three reports relating the Pd-catalysed arylation of allylic alcohols with diazonium salts [7–9]. In 1977 and 1981, a Japanese team disclosed the room temperature reaction of primary allylic alcohols, **3*c*** and **3*d***, with $R^1C_6H_4N_2Cl$ (**6a**: R^1 = H; **6b**: *p*-Me; **6e**: *p*-NO_2 ; **6f**: *p*-MeO) in aqueous acetonitrile using a base, NaOAc, and a Pd^0 catalyst (**6**:**3** ratio = 1:2); the reaction of **3*c*** was performed only with **6a** yielding 64% of **4a*c*** and 3% of 2-phenyl-2-methylpropionaldehyde, while no more than 41% yield of mixtures of cinnamaldehyde and the α- and β-arylated aldehydes was obtained from the reaction of **3*d*** with **6a** or **6b**, this yield dropping to 20% and virtually 0% with **6f** and **6e**, respectively [7,8]. In 2001, an article in the Chinese literature reported yields up to 63% for the arylation of alcohols **3*a***, **3*c*** and **3*d***, with **2** (**2**:**3** ratio = 1:1.5) at 60 °C in EtOH using $Pd(OAc)_2$ as the catalyst [9].

In our hands however, the coupling of **2b** with **3*a*** using the Chinese procedure provided **4b*a*** in no more than 13% yield instead of the reported 58%; a similar result was obtained using MeOH as the solvent, or using an excess of **2b** and increasing the amount of the catalyst from 2% to 5%. The use of other Pd^{II} catalysts, $PdCl_2$ and $PdCl_2(MeCN)_2$, in MeOH at 50 °C for 2 h yielded 35–39% of **4b*a***. Therefore, we tested various Pd^0 catalysts. Pd/C was inefficient, and no more than 38% yield was attained with $Pd(PPh_3)_4$ or with palladium nanoparticles prepared as previously described [10]. In contrast, the yields were improved to 60–69% with $Pd(dba)_2$ as the catalyst (Table 2, runs 1 and 2). Consequently, the use of this catalyst was retained to perform other arylations.

Under $Pd(dba)_2$-catalyzed conditions, the arylation of the secondary alcohols with various arenediazonium tetrafluoroborates led to the expected ketones with fair to high yields (runs 3–7 and 9–14), except with the arylating agent bearing a *p*-methoxy substituent (Entry 8). The negative effect of the *p*-methoxy substituent has already been reported by Matsuda et al. [7], but, in contrast to this team, we obtained a fair yield instead of trace with the *p*-nitro substituted arylating agent (run 7).

The arylation of primary alcohol **3*c*** with **2a**, **2e** and **2f** occured at the unsubstituted olefinic carbon and provided acetals **7**, while the arylation of **3d** led to acetals **7** and **8** (Eq. (3) and Table 3). From these primary alcohols, we never isolated the arylated aldehydes. That contrasts with the results of Cai et al., who reported exclusively the formation of arylated aldehydes from primary allylic alcohols and arenediazonium tetrafluoroborates using EtOH as the solvent [9].

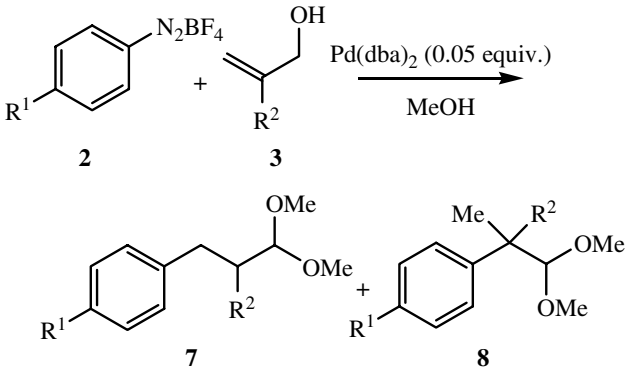
Table 2
Arylation of secondary allylic alcohols with ArN_2BF_4 (1.5 equiv.) in MeOH using $Pd(dba)_2$ (0.05 equiv.) as the catalyst

Run	**2**	**3**	*t* (°C)	Time	Product, yield %
1	**2b**	**3*a***	rt	15 h	**4b*a***, 60
2	**2b**	**3*a***	50	2 h	**4b*a***, 69
3	**2a**	**3*a***	rt	24 h	**4a*a***, 33
4	**2a**	**3*a***	50	2 h	**4a*a***, 43
5	**2c**	**3*a***	rt	23 h	**4c*a***, 63
6	**2d**	**3*a***	rt	24 h	**4d*a***, 49
7	**2e**	**3*a***	rt	25 h	**4e*a***, 52
8	**2f**	**3*a***	rt	29 h	**4f*a***, <15
9	**2a**	**3*b***	rt	6.5 h	**4a*b***, 59
10	**2b**	**3*b***	rt	7.5 h	**4b*b***, 65
11	**2c**	**3*b***	rt	7.5 h	**4c*b***, 72
12	**2c**	**3*b***	50	2.5 h	**4c*b***, 83
13	**2d**	**3*b***	rt	7.5 h	**4d*b***, 65
14	**2d**	**3*b***	50	2.5 h	**4d*b***, 75

Table 3
Arylation of primary allylic alcohols with ArN_2BF_4 (1.5 equiv.) in MeOH using Pd(dba)2 (0.05 equiv.) as the catalyst

Run	2	3	t (°C)	Time	Products, yield %
1	**2a**	**3*c***	rt	10 h	**7a*c***, 61
2	**2a**	**3*c***	50	2 h	**7a*c***, 67
3	**2e**	**3*c***	rt	9 h	**7e*c***, 79
4	**2e**	**3*c***	50	2 h	**7e*c***, 83
5	**2f**	**3*c***	rt	9 h	**7f*c***, 53
6	**2f**	**3*c***	50	2 h	**7f*c***, 60
7	**2a**	**3*d***	rt	9 h	**7a*d*** + **8a*d***, 32 (87/13)[a]
8	**2a**	**3*d***	50	2 h	**7a*d*** + **8a*d***, 40 (84/16)[a]
9	**2e**	**3*d***	rt	9 h	**7e*d***, 73;**8e*d*,12**
10	**2e**	**3*d***	50	2 h	**7e*d***,76; **8e*d***,13
11	**2f**	**3*d***	rt	9 h	**7f*d*** + **8f*d***,34 (62/38)[a]
12	**2f**	**3*d***	50	2 h	**7f*d*** + **8f*d***,40 (62/38)[a]

[a] An inseparable mixture of **7** and **8** was obtained, the ratio was calculated via ^{1}H NMR integration.



a: R^1 = H; **e**: R^1 = NO_2; **f**: R^1 = MeO
c: R^2 = Me; ***d***: R^2 = H

(3)

3. Conclusion

The arylation of allylic alcohols with arenediazonium tetrafluoroborates can be carried out in MeOH using $Pd(dba)_2$ as the catalyst. The expected ketones are obtained from secondary alcohols while the primary alcohols led to protected aldehydes.

4. Experimental

General: Arenediazonium tetrafluoroborates were prepared from commercial aromatic amines according to published methods [11]. 3-Methylbut-3-en-2-ol [12], 2,5-dimethylhex-1-en-3-ol [13] and $Pd(dba)_2$ [14] were prepared according to reported procedures. ^{1}H and ^{13}C NMR (250 and 62.5 MHz or 200 and 50 MHz) spectra were obtained on Bruker AC spectrometers using TMS as internal standard and $CDCl_3$ as solvent.

Reaction of arenediazonium salts with allylic alcohols, general procedure: A solution of the allylic alcohol (0.70 mmol) in methanol (2 mL) was added to a magnetically stirred mixture of the arenediazonium salt (1.05 mmol) and $Pd(dba)_2$ (0.035 mmol) in methanol (20 mL). The reaction mixture was stirred under the conditions depicted in Tables. After addition of saturated $NaHCO_3$ aqueous solution (20 mL), the resulting mixture was extracted with dichloromethane (2×15 mL). The combined organic fractions were washed with water, dried over anhydrous sodium sulfate, and evaporated. The products were purified by flash chromatography.

The NMR data of **4a*a*** [15], **4c*a*** [16], **4f*a*** [17], **7a*c*** [18], **7a*d*** [19], **8a*d*** [20], **7f*d*** [21], **8f*d*** [22] were in agreement with literature.

4.1. 3-Methyl-4-(p-tolyl)butan-2-one (*4ba*)

Colorless oil. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.09 (d, J = 6.8 Hz, 3H), 2.10 (s, 3H), 2.31 (s, 3H), 2.52 (dd, J = 12.4 and 6.5 Hz, 1H), 2.81 (sext, J = 6.5 Hz, 1H), 2.96 (dd, J = 12.4 and 6.5 Hz, 1H), 7.20 (d, J = 6.8 Hz, 2H), 7.6 (d, J = 6.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 16.2, 21.0, 28.8, 38.5, 48.9, 128.8, 129.1, 135.7, 136.5, 212.3. IR (neat) ν (cm^{-1}): 2926, 1713. Anal. Calc. for $C_{12}H_{16}O$ (176.0): C, 81.80; H, 9.10. Found: C, 81.96; H, 9.12%.

4.2. 4-(p-Fluorophenyl)-3-methylbutan-2-one (*4da*)

Colorless oil. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.09 (d, J = 6.9 Hz, 3H), 2.09 (s, 3H), 2.54 (dd, J = 13.4 and 7.3 Hz, 1H), 2.80 (sext, J = 7.0 Hz, 1H), 2.97 (dd, J = 13.4 and 6.9 Hz, 1H), 6.91–7.02 (m, 2H), 7.06–7.19 (m, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 16.7, 29.3, 38.4, 49.3, 115.6 (d, $^2J_{CF}$ = 21 Hz), 130.7 (d, $^3J_{CF}$ = 7.7 Hz), 135.7 (d, $^4J_{CF}$ = 3.2 Hz), 161.9 (d, $^1J_{CF}$ = 242.6 Hz), 212.4. IR (neat) ν (cm^{-1}): 2971, 2933, 1713, 1510, 1222. MS (EI) m/z (%): 180 (M^+, 39), 165 (44), 137 (21), 109 (100), 83 (23), 43 (89). Anal. Calc. for $C_{11}H_{13}FO$ (180.2): C, 73.31; H, 7.27. Found: C, 72.96; H, 7.62%.

4.3. 3-Methyl-4-(p-nitrophenyl)butan-2-one (*4ea*)

Pale yellow solid. M.p. 64 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.14 (d, J = 7.0 Hz, 3H), 2.13 (s, 3H), 2.66 (dd, J = 13.4 and 7.0 Hz, 1H), 2.87 (sext, J = 7.0 Hz, 1H), 3.12 (dd, J = 13.4 and 7.0 Hz, 1H), 7.32 (d, J = 8.5 Hz, 2H), 8.15 (d, J = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 17.4, 29.6, 39.0, 49.1, 124.5, 130.6, 147.4, 148.5, 211.9. IR (neat) ν (cm^{-1}): 2971, 2930, 1703, 1602, 1508, 1345. MS (EI) m/z (%): 207 (M^+, 2), 192 (3), 165 (5), 136 (11), 115 (70), 89 (100), 78 (82). Anal. Calc. for $C_{11}H_{13}NO_3$ (207.2): C,

63.76; H, 6.32; N, 6.76. Found: C, 63.86; H, 6.37; N, 6.71%.

4.4. 2,5-Dimethyl-1-phenylhexan-3-one (**4ab**)

Colorless oil. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.75 (d, J = 6.5, 3H), 0.76 (d, J = 6.5, 3H), 0.98 (d, J = 6.9 Hz, 3H), 1.89–2.27 (3H), 2.45 (dd, J = 13.2 and 7.3 Hz, 1H), 2.74 (sext, J = 6.9 Hz, 1H), 2.90 (dd, J = 13.2 and 7.0 Hz, 1H), 7.02–7.24 (m, 5H). ^{13}C NMR ($CDCl_3$, 63.5 MHz): δ 15.0, 21.1, 21.2, 22.7, 37.5, 46.9, 49.6, 124.7, 126.9, 127.6, 138.4, 212.5. IR (neat) ν (cm^{-1}): 2957, 2930, 1711, 1454, 1366. MS (CI) m/z (%): 222 ($[M + NH_4]^+$, 100), 205 ($[M + H]^+$, 91), 91 (38). Anal. Calc. for $C_{14}H_{20}O$ (204.3): C, 82.30; H, 9.87. Found: C, 82.14; H, 10.36%.

4.5. 2,5-Dimethyl-1-(p-tolyl)hexan-3-one (**4bb**)

Colorless oil. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.84 (d, J = 6.4 Hz, 6H), 1.05 (d, J = 6.8 Hz, 3H), 2.00–2.38 (3H), 2.31 (s, 3H), 2.49 (dd, J = 13.3 and 7.4 Hz, 1H), 2.77 (sext, J = 7.0 Hz, 1H), 2.93 (dd, J = 13.3 and 6.9 Hz, 1H), 7.03 (d, J = 8.2 Hz, 2H), 7.08 (d, J = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 16.7, 21.4, 23.0, 23.1, 24.5, 38.9, 48.8, 51.4, 129.3, 129.5, 136.0, 137.1, 214.4. IR (neat) ν (cm^{-1}): 2957, 2930, 1712. MS (EI) m/z (%): 218 (M^+, 61), 161 (64), 133 (70), 117 (36), 105 (100), 85 (92), 57 (84). Anal. Calc. for $C_{15}H_{22}O$ (218.3): C, 82.52; H, 10.16. Found: C, 82.65; H, 10.67%.

4.6. 1-(p-tert-Butylphenyl)-2,5-dimethylhexan-3-one (**4cb**)

Colorless oil. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.82 (d, J = 6.5, 6H), 1.06 (d, J = 6.8 Hz, 3H), 1.30 (s, 9H), 1.98–2.34 (3H), 2.51 (dd, J = 13.2 and 7.3 Hz, 1H), 2.79 (sext, J = 6.9 Hz, 1H), 2.93 (dd, J = 13.1 and 6.9 Hz, 1H), 7.07 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 16.8, 22.9, 23.0, 24.5, 31.8, 34.8, 38.9, 48.7, 51.4, 125.7, 129.1, 137.2, 149.4, 214.5. IR (neat) ν (cm^{-1}): 2960, 1712. MS (EI) m/z (%): 260 (M^+, 6), 245 (14), 147 (36), 117 (31), 85 (48), 57 (100). Anal. Calc. for $C_{18}H_{28}O$ (260.4): C, 83.02; H, 10.84. Found: C, 83.29; H, 11.04%.

4.7. 1-(p-Fluorophenyl)-2,5-dimethylhexan-3-one (**4db**)

Colorless oil. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.83 (d, J = 6.6, 6H), 1.06 (d, J = 6.8 Hz, 3H), 1.99–2.35 (m, 3H), 2.51 (dd, J = 13.3 and 7.0 Hz, 1H), 2.77 (sext, J = 7.0 Hz, 1H), 2.95 (dd, J = 13.3 and 7.3 Hz, 1H), 6.90–7.00 (m, 2H), 7.05–7.13 (m, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 16.9, 22.9, 23.0, 24.5, 38.5, 48.9, 51.5, 115.5 (d, $^2J_{CF}$ = 21 Hz), 130.8 (d, $^3J_{CF}$ = 7.8 Hz), 136.0 (d, $^4J_{CF}$ = 3.2 Hz), 161.9 (d, $^1J_{CF}$ = 242.1 Hz), 214.1. IR (neat) ν (cm^{-1}): 2959, 2872, 1711, 1510. MS (CI) m/z (%): 240 ($[M + NH_4]^+$, 100), 223 ($[M + H]^+$, 59), 109 (82), 85 (78). Anal. Calc. for $C_{14}H_{19}$ FO (222.3): C, 75.64; H, 8.61. Found: C, 75.90; H, 8.69%.

4.8. 1-(3,3-Dimethoxy-2-methyl-1-propyl)-4-nitrobenzene (**7ec**)

Pale yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.85 (d, J = 6.8, 3H), 1.98–2.15 (m, 1H), 2.46 (dd, J = 13.4 and 9.6 Hz, 1H), 3.01 (dd, J = 13.4 and 4.5 Hz, 1H), 3.38 (s, 3H), 3.40 (s, 3H), 4.06 (d, J = 5.8 Hz, 1H), 7.32 (d, J = 8.6 Hz, 2H), 8.14 (d, J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.6, 38.4, 38.5, 54.7, 55.3, 108.6, 124.0, 130.5, 146.9, 149.5. IR (neat) ν (cm^{-1}): 2916, 2845, 1601, 1519, 1346. MS (EI) m/z (%): 208 ($[M - OCH_3]^+$, 30), 192 (20), 136 (19), 115 (29), 89 (49), 75 (100). Anal. Calc. for $C_{12}H_{17}NO_4$ (239.3): C, 60.24; H, 7.16; N, 5.85. Found: C, 60.39; H, 7.38; N, 5.77%.

4.9. 1-(3,3-Dimethoxy-2-methylpropyl)-4-methoxybenzene (**7fc**)

Colorless oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.84 (d, J = 6.8, 3H), 1.98–2.10 (m, 1H), 2.29 (dd, J = 13.4 and 9.2 Hz, 1H), 2.83 (dd, J = 13.4 and 4.6 Hz, 1H), 3.37 (s, 3H), 3.38 (s, 3H), 3.80 (s, 3H), 4.05 (d, J = 6.0 Hz, 1H), 6.82 (d, J = 8.6 Hz, 2H), 7.08 (d, J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.3, 37.6, 38.3, 54.5, 54.7, 55.6, 108.7, 114.0, 130.5, 133.0, 158.2. IR (neat) ν (cm^{-1}): 2933, 2829, 1611, 1512, 1247. MS (EI) m/z (%): 224 ($[M]^+$, 20), 192 (90), 177 (78), 161 (70), 121 (100), 91 (46), 75 (98). Anal. Calc. for $C_{13}H_{20}O_3$ (224.3): C, 69.61; H, 8.99. Found: C, 69.52; H, 9.33%.

4.10. 1-(3,3-Dimethoxy-1-propyl)-4-nitrobenzene (**7ed**)

Pale yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.85–2.00 (m, 2H), 2.79 (t, J = 8.0 Hz, 2H), 3.34 (s, 6H), 4.36 (t, J = 5.6 Hz, 1H), 7.35 (d, J = 8.7 Hz, 2H), 8.15 (d, J = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 31.1, 34.0, 53.4, 103.9, 124.1, 129.6, 147.0, 150.0. IR (neat) ν (cm^{-1}): 2919, 1601, 1519, 1345. MS (EI) m/z (%): 194 ($[M - OCH_3]^+$, 37), 162 (30), 136 (43), 89 (42), 75 (100). Anal. Calc. for $C_{11}H_{15}$ NO_4 (225.2): C, 58.66; H, 6.71; N, 6.22. Found: C, 58.75; H, 6.48; N, 5.87%.

4.11. 1-(1,1-Dimethoxy-2-propyl)-4-nitrobenzene (**8ed**)

Pale yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.31 (d, J = 6.6 Hz, 3H), 3.00–3.22 (m, 1H), 3.28 (s, 3H), 3.39 (s, 3H), 4.36 (d, J = 6.2 Hz, 1H), 7.40 (d, J = 8.0 Hz, 2H), 8.15 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 17.1, 43.7, 54.9, 55.7, 108.7,

124.0, 129.6, 147.3, 151.3. IR (neat) ν (cm^{-1}): 2924, 1600, 1518, 1344. MS (EI) *m/z* (%): 194 ($[M - OCH_3]^+$, 48), 115 (22), 103 (26), 75 (100).

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