Palladium-Catalyzed Monoarylation of Nitroalkanes

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A general protocol for the Pd-catalyzed-arylation of nitroalkanes is described. Substituted aryl bromides as well as aryl chlorides can be coupled efficiently with a variety of nitroalkanes under mild conditions to selectively yield the monoarylated products. This method tolerates a number of functional groups including ketones, esters, and olefins. Notably, the arylation of nitroalkanes can be effected chemoselectively over ketone and ester arylation.

Introduction

Several procedures for the Pd-catalyzed α-arylation of ketones with a variety of aryl bromides, chlorides, and triflates have recently been reported.[1] These methods have also been extended to other carbonyl substrates including esters and amides.[2] Additionally, we have reported that catalysts based on 2-di-*tert*-butylphosphino-2′-methylbiphenyl (**1**) and $Pd(OAc)_2$ were particularly efficient in the arylation of malonate esters, 1,3-diketones, and in isolated cases, nitroalkanes.[1e] Herein, we report in full the protocol for the arylation of nitroalkanes.[3] This method allows for the selective monoarylation of nitroalkanes under mild conditions that tolerate several functional groups including ethers, esters, ketones, and olefins. Additionally, the arylation of nitroalkanes can be performed chemoselectively in the presence of enolizable esters and ketones.[4]

Results and Discussion

Our initial studies were performed using bromobenzene or 4-chlorotoluene and nitroethane as coupling partners. After screening a variety of reaction conditions, we found that Cs_2CO_3 was effective as base, although K_3PO_4 was sometimes suitable. Stronger bases such as metal alkoxides were not as effective. It was readily apparent that catalysts based on di-*tert*-butyl-substituted phosphine ligands yielded significant amounts of products while the dicyclohexyl- or diphenyl-substituted ligands did not promote nitroalkane arylation at all. Of the biaryl ligands screened, **1** proved most effective, although commercially available 2-di-*tert*-butylphosphinobiphenyl generally gave satisfactory yields.[5] In addition, we found that catalysts based on Pd_2dba_3 were more active than catalysts based on $Pd(OAc)_2$; presumably the in situ reduction of the Pd(II) is inefficient under the reaction conditions.

As shown in Table 1, a variety of aryl bromides and aryl chlorides can be efficiently coupled with nitroalkanes. Electron-withdrawing aryl bromides react cleanly to furnish the desired nitroalkanes in good yield. For example, 4-bromomethylbenzoate reacts with nitroethane to furnished the desired product in 85% yield (entry 6). Electronically neutral aryl bromides are also good substrates for the reaction; 4-*tert*-butylbromobenzene is efficiently coupled with nitroethane and nitropropane to give the arylated products in 95 and 81% yields, respectively (entries 3, 11). Although the reaction is more practical when performed at elevated temperatures (45−60 °C), the arylation also proceeds at room temperature, albeit very slowly (entry 11). Aryl bromide substrates with electron-donating groups (e.g., OMe) in the *ortho* or *para* position of the aryl bromide are transformed in high yield as well (entries 5, 12). Additionally, aryl chlorides can be used with this catalyst system; electron-withdrawing substituents on the aryl chloride allow for an efficient transformation (entries 10, 14, 16). In addition, the reaction of *m*-chloroanisole with nitropropane afforded the desired nitroalkane in 68% isolated yield (entry 13). Double arylation of the nitroalkane was not observed in any of the examples studied. In fact, subjecting phenyl nitromethane to the arylation protocol resulted in no reaction. Reactions with nitromethane yielded the desired arylated compounds; however, yields were low and multiple products were observed.

The arylation of carbonyl-derived enolates has been demonstrated to be an efficient process.[1,2] Moreover, the Heck arylation of terminal alkenes is has proven to be one of the most powerful transformations in modern organic synthesis.[6] We queried whether coupling partners containing enolizable ketones and esters, as well as terminal olefins, would be suitable in the nitroalkane arylation reaction. In the cases studied, we found that the desired arylation α to the nitro group was observed; no ketone arylation products were detected (Table 2,

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(1) (a) Palucki, M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 11108. (b) Hamann, B. C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 12382. (c) Ahman, J.; Wolfe, J. P.; Troutman, M. V.; Palucki, M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 1918. (d) Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 1473. (e) Fox, J. M.; Huang, X. H.; Chieffi, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2000**, *122*, 1360 and references therein.

(2) (a) Shaughnessy, K. H.; Hamann, B. C.; Hartwig, J. F. *J. Org. Chem.* **1998**, *63*, 6546. (b) Moradi, W. A.; Buchwald, S. L *J. Am. Chem. Soc.* **2001**, *123*, 7996. (c) Lee, S.; Beare, N. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 8410.

(3) The Pd-catalyzed intramolecular α-arylation of nitroalkanes has been reported: Muratake, H.; Nakai, H. *Tetrahedron Lett.* **1999**, *40*, 2355−2358.

(4) For other methods for the α-arylation of nitroalkanes, see: (a) Aleksandrowicz, P.; Piotrowska, H.; Sas, W. *Tetrahedron* **1982**, *38*, 1321−1327. (b) Kozyrod, R. P.; Pinhey, J. T. *Tetrahedron Lett.* **1981**, *22*, 783−784. (c) Kornblum, N.; Taylor, H. J. *J. Org. Chem.* **1963**, *28*, 1424−1425. (d) Park, K. P.; Clapp, L. B. *J. Org. Chem.* **1964**, *29*, 2108−2109.

(5) For the synthesis of these ligands, see: Tomori, H.; Fox, J. M.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 5334−5341.

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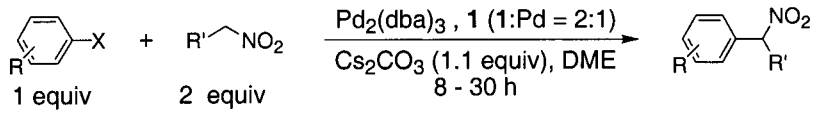
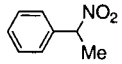
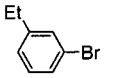
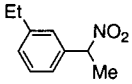
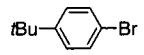
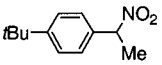
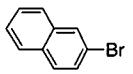
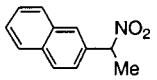
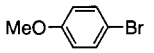
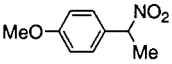
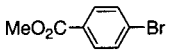
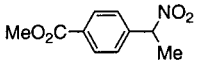
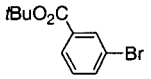
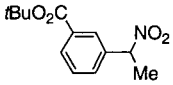
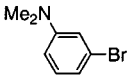
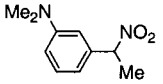
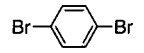
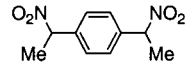
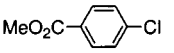
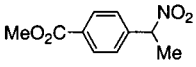
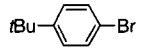
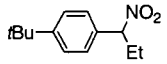
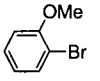
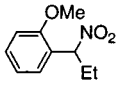
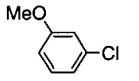
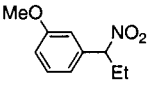
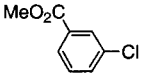
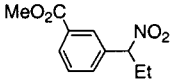
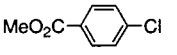
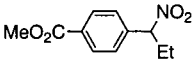
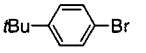
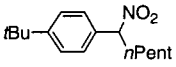
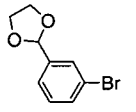
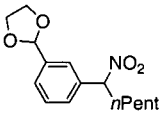
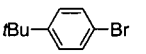
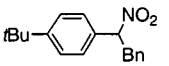
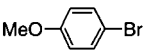
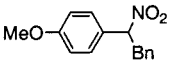
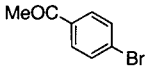
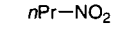
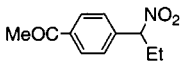
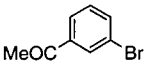
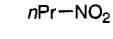
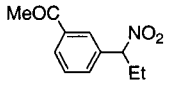
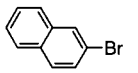
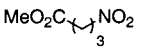
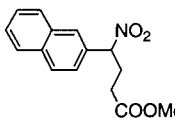
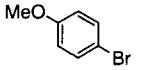
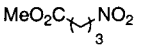
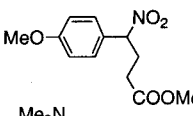
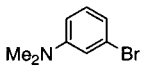
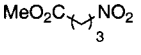
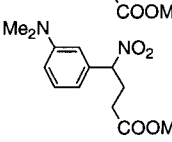
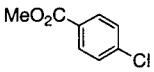
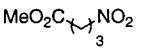
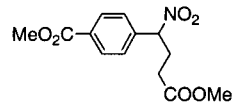
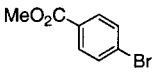
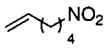
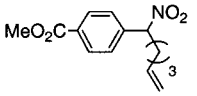
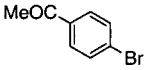
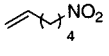
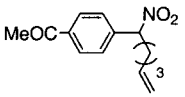
Table 1. Pd-Catalyzed α-Arylation of Nitroalkanes



Entry	Halide	Nitroalkane	Product	T [°C]	Mol% Pd	% Yield[a]
1		Et–NO_2		50	3	90
2		Et–NO_2		50	3	95
3		Et–NO_2		50	1.5	95
4		Et–NO_2		50	3	96
5		Et–NO_2		50	3	94
6		Et–NO_2		50	2	85
7		Et–NO_2		50	3	82
8		Et–NO_2		50	1.5	98
9[b]		Et–NO_2		50	10	62
10		Et–NO_2		50	3	71
11		*n*Pr–NO_2		rt[c]	2	81
12		*n*Pr–NO_2		50	10	95
13		*n*Pr–NO_2		55	1.5	68
14		*n*Pr–NO_2		55	1.5	65
15		*n*Pr–NO_2		60	2	86
16[d]		*n*Hex–NO_2		50	2	92
17		*n*Hex–NO_2		55	5	85
18[d]		Bn–NO_2		50	5	65
19[d]		Bn–NO_2		50	5	62

[a] Isolated yields are an average of two runs. All compounds >95% pure as determined by ^{1}H NMR, GC, or combustion analysis. [b] 4 equiv of nitroalkane and 2.2 equiv of base were used. [c] Reaction performed for 96 h. [d] 1 equiv of nitroalkane and 1.1 equiv of base was used.

Table 2. Chemoselective Pd-Catalyzed α-Arylation of Nitroalkanes

Entry	Halide	Nitroalkane	Product	T [°C] / t [h]	Mol% Pd	% Yield[a]
1				45/35	3	80
2				45/33	3	63
3				50/22	5	78
4				50/22	5	72
5				50/24	5	75
6				50/24	5	67
7				50/18	2	67
8[b]				rt/60	3	64

[a] Isolated yields are an average of two runs. All compounds >95% pure as determined by ^{1}H NMR, GC, or combustion analysis. 1 equiv of nitroalkane and 1.1 equiv of base were used. [b] 1.5 equiv of nitroalkane and 1.1 equiv of base were used.

entries 1−3). This chemoselective arylation could also be effected with an activated aryl chloride (entry 4). It should be noted that di-*tert*-butylphosphino-derived ligands such as **1** are not efficient supporting ligands for ketone arylation.[1e] Olefins were also tolerated under the reaction conditions; no Heck-type addition across the olefin was observed, and the desired nitroalkanes were isolated in moderate yield (entries 5, 6).

Conclusions

In summary, we have developed a general protocol for the Pd-catalyzed monoarylation of nitroalkanes. Using a catalyst based on **1** and Pd_2dba_3, this transformation may be carried out under mild conditions. The nitroalkane can be chemoselectively arylated in the presence of enolizable ketone and ester groups, and an olefin-substituted nitroalkane was also tolerated under the reaction conditions.

Experimental Section

General. Reactions were carried out in a dried resealable Schlenck tube purchased from Kontes. Flash chromatography was performed on Silicycle ultrapure silica gel (230−400 mesh). Elemental analyses were performed by Atlantic Microlabs, Inc, Norcross GA. Dimethoxyethane and dodecane (used as internal standard) were purchased in small SureSeal bottles from Aldrich Chemical Co. and used as received. Tris(dibenzylideneacetone)dipalladium was purchased from Strem Chemical, Inc. Sodium *tert*-butoxide (NaO*t*-Bu), nitroethane, 1-nitropropane, 1-nitrohexane, and 6-nitro-1-hexene were purchased from Aldrich Chemical Co. K_3PO_4 was purchased from Fluka. Cs_2CO_3 was purchased from Chemetall. Moisture sensitive bases were stored under nitrogen in a Vacuum Atmospheres glovebox, and small samples were taken out, stored in a desiccator on the bench, and replaced every 2 weeks. All materials were weighed in the air. 2-Di-*tert*-butylphosphino-2′-methylbiphenyl (**1**),[5] 2-phenylnitroethane,[7] 4-nitrobutyric acid methyl ester,[8] and *tert*-butyl-3-bromobenzoate[9] were synthesized as described the literature. IR spectra were obtained by placing neat samples directly on the DiComp probe of an ASI REACTIR in situ IR instrument. Yields in tables refer to isolated yields (average of two runs) of compounds estimated to be ≥95% pure as determined by ^{1}H NMR, GC, and combustion analysis. Melting points were taken with a MEL-TEMP apparatus. Compounds that are described more than once in the same table were completely characterized once. Other samples of these compounds were characterized by comparing their ^{1}H and ^{13}C NMR spectra to those of the fully characterized product, and their purity was confirmed by GC analysis. Compounds previously described in the literature were characterized only by ^{1}H and ^{13}C NMR.

General Reaction Procedure for the Arylation of Nitroalkanes. Method A. A dried resealable Schlenk tube

(6) For reviews on the Heck arylation, see: (a) Brase, S.; deMeijere, A. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: New York, 1998; pp 99−166. (b) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009−3066.

(7) Gilbert, K. E.; Borden, W. Y. *J. Org. Chem.* **1979**, *44*, 659.
(8) Chasar, D. W. *Synthesis* **1982**, 841.
(9) Taylor, E. C.; Ray, P. S. *J. Org. Chem.* **1988**, *53*, 35.

containing a stir bar was charged with 1.0 mmol of the aryl bromide or aryl chloride, the appropriate amount of $Pd_2(dba)_3$ and 2-(di-*tert*-butylphosphinyl)-2′-methylbiphenyl (**1**) as indicated, and 1.2 equiv of Cs_2CO_3. The reaction vessel was capped with a rubber septum, evacuated, and backfilled with argon three times, and dimethoxyethane (5 mL) and 1.0−2.0 equiv of the appropriate nitroalkane were added via syringe under argon. After the mixture was stirred vigorously for 1 min at room temperature, the Schlenk tube was sealed and placed in a preheated oil bath at the given temperature for the time indicated. After the reaction was complete, as judged by either GC or TLC analysis, the reaction mixture was allowed to cool to ambient temperature. The unpurified mixture was quenched with a solution of sat. aqueous NH_4Cl (2 mL, two times), the aqueous phase was extracted with ether (2 mL), and the combined organic phases were washed with brine. The solvent was then removed, and the remaining oil was purified by flash column chromatography.

Method B. A dried resealable Schlenk tube containing a stir bar was charged with the appropriate amount of $Pd_2(dba)_3$ and 2-(di-*tert*-butylphosphinyl)-2′-methylbiphenyl (**1**) as indicated and 1.2 equiv of Cs_2CO_3. The reaction vessel was capped with a rubber septum, evacuated, and backfilled with argon three times, and 1.0 mmol of the aryl bromide or aryl chloride, dimethoxyethane (5 mL), and 1.0−2.0 equiv of the appropriate nitroalkane were added sequentially via syringe under argon. The mixture was stirred vigorously for 1 min at room temperature, the Schlenk tube was sealed and placed in a preheated oil bath at the given temperature for the time indicated. After the reaction was complete, as judged by either GC or TLC analysis, the reaction mixture was allowed to cool to ambient temperature. The unpurified mixture was quenched with a solution of sat. aqueous NH_4Cl (2 mL, two times), the aqueous phase was extracted with ether (2 mL), and the combined organic phases were washed with brine. Then the solvent was removed, and the remaining oil was purified by flash column chromatography.

(1-Nitroethyl)benzene (Table 1, entry 1). The reaction was carried out according to general procedure, method B. Flash column chromatography (diethyl ether:hexanes 1:20) yielded the known compound[10,11] as a volatile (removal of solvent by a stream of air) colorless oil (0.136 g, 0.90 mmol, 90%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.48−7.40 (m, 5H), 5.62 (q, 1H, J = 6.9 Hz), 1.89 (d, 3H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 135.7, 129.9, 129.1, 127.5, 86.3, 19.5 ppm.

3-(1-Nitroethyl)ethylbenzene (Table 1, entry 2). The reaction was carried out according to general procedure, method B. Flash column chromatography (diethyl ether: hexanes 1:20) yielded a colorless oil (0.170 g, 0.95 mmol, 95%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.36−7.20 (m, 4H), 5.60 (q, 1H, J = 7.2 Hz), 2.67 (q, 2H, J = 7.6 Hz), 1.89 (d, 3H, J = 7.2 Hz), 1.25 (t, 3H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 145.4, 135.8, 129.5, 129.2, 127.1, 124.8, 86.5, 28.9, 19.7, 15.6, ppm; IR (neat, cm^{-1}) ν: 2968, 2935, 2875, 1549, 1453, 1385, 1360, 1165, 1065, 893, 853, 807, 712, 699. Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31. Found: C, 66.85; H, 7.43.

4-*tert*-Butyl-(1-nitroethyl)benzene (Table 1, entry 3). The reaction was carried out according to general procedure, method B. Flash column chromatography (diethyl ether: hexanes 1:20) yielded the known compound[11] as a colorless oil (0.197 g, 0.95 mmol, 95%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.41 (m, 4H), 5.61 (q, 1H, J = 7.2 Hz), 1.89 (d, 3H, J = 7.2 Hz), 1.32 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 153.2, 132.8, 127.4, 126.2, 86.2, 34.9, 31.5, 19.6 ppm.

2-(1-Nitroethyl)naphthalene (Table 1, entry 4). The reaction was carried out according to general procedure, method A. Vigorous stirring is important due to the reaction heterogeneity. Additionally, 10 mL of DME were used. Flash column chromatography (diethyl ether:hexanes 1:10) yielded a crystalline solid; mp 51 °C (0.193 g, 0.96 mmol, 96%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.94−7.84 (m, 4H), 7.60−7.53 (m, 3H), 5.80 (m, 1H), 2.01 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 133.9, 133.2, 133.0, 129.2, 128.5, 127.9, 127.5, 127.3, 127.0, 124.3, 86.5, 19.7 ppm; IR (neat, cm^{-1}) ν: 3060, 2977, 2869, 1549, 1385, 1355, 1281, 1115, 824, 785, 745, 697. Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51. Found: C, 71.73; H, 5.46.

4-(1-Nitroethyl)methoxybenzene (Table 1, entry 5). The reaction was carried out according to general procedure, method B. Flash column chromatography (diethyl ether: hexanes 1:20) yielded the known compound[11] as an oil (0.170 g, 0.94 mmol, 94%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.41 (m, 2H), 6.92 (m, 2H), 5.58 (q, 1H, J = 6.9 Hz), 3.82 (s, 3H), 1.88 (d, 3H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 160.8, 129.1, 127.8, 114.4, 85.9, 55.5, 19.5 ppm.

4-(1-Nitroethyl)benzoic Acid Methyl Ester (Table 1, entry 6 and entry 10). The reaction was carried out according to general procedure, method A. Flash column chromatography (toluene 100%) yielded the known compound[11] as a pale yellow oil which solidified to a crystalline solid; mp 49 °C (0.178 g, 0.85 mmol, 85%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.08 (m, 2H), 7.54 (m, 2H), 5.67 (q, 1H, J = 6.9 Hz), 3.94 (s, 3H), 1.93 (d, 3H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 166.5, 140.1, 131.6, 130.5, 127.7, 85.9, 52.6, 19.7 ppm.

3-(1-Nitroethyl)benzoic Acid *tert*-Butyl Ester (Table 1, entry 7). The reaction was carried out according to general procedure, method B. Flash column chromatography (diethyl ether:hexanes 1:8) yielded a colorless oil (0.206 g, 0.82 mmol, 82%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.07−8.02 (m, 2H), 7.64 (m, 1H), 7.48 (m, 1H), 5.66 (q, 1H, J = 6.9 Hz), 1.93 (d, 3H, J = 6.9 Hz), 1.61 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 165.1, 135.8, 133.1, 131.4, 131.0, 129.2, 128.8, 85.9, 81.9, 28.4, 19.6 ppm; IR (neat, cm^{-1}) ν: 2979, 2935, 1711, 1551, 1385, 1368, 1297, 1256, 1160, 1115, 849, 753, 731,689; Anal. Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82. Found: C, 62.22; H, 6.97.

3-(1-Nitroethyl)dimethylaminobenzene (Table 1, entry 8). The reaction was carried out according to general procedure, Method B. Flash column chromatography (diethyl ether: hexanes 1:20 to 1:10) yielded a yellow oil (0.190 g, 0.98 mmol, 98%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.29−7.23 (m, 1H), 6.80−6.72 (m, 3H), 5.57 (q, 1H, J = 6.9 Hz), 2.98 (s, 6H), 1.89 (d, 3H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 150.9, 136.7, 129.8, 115.0, 113.6, 111.0, 86.9, 40.6, 19.7 ppm; IR (neat, cm^{-1}) ν: 2989, 2894, 2809, 1603, 1546, 1503, 1441, 1383, 1358, 1231, 1063, 994, 961, 851, 756, 702, 691. Anal. Calcd for $C_{10}H_{14}N_2O_2$: C, 61.84; H, 7.27. Found: C, 61.94; H, 7.33.

1,4-Bis(1-nitroethyl)benzene (Table 1, entry 9). The reaction was carried out according to general procedure, method A (but on a 0.5 mmol scale). 4-Dibromobenzene was purified by column chromatography (SiO_2, 100% hexanes) prior to use. Flash column chromatography (diethyl ether:hexanes 1:4 to 1:2) yielded a crystalline solid (presumably as a mixture of isomers); mp 63 °C (0.069 g, 0.31 mmol, 62%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.52 (s, 4H), 5.64 (q, 2H, J = 6.6 Hz), 1.91 (d, 6H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 137.2, 128.3, 85.8, 19.6 ppm; IR (neat, cm^{-1}) ν: 2995, 2944, 2900, 1683, 1546, 1385, 1356, 1295, 1063, 1000, 864, 847, 697. Anal. Calcd for $C_{10}H_{12}N_2O_4$: C, 53.57; H, 5.39. Found: C, 53.82; H, 5.48.

4-*tert*-Butyl-(1-nitropropyl)benzene (Table 1, entry 11). The reaction was carried out according to general procedure, method B. Flash column chromatography (diethyl ether: hexanes 1:50) yielded a colorless oil (0.179 g, 0.81 mmol, 81%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.42 (m, 4H), 5.37 (dd, 1H, J = 9.0 Hz, 6.3 Hz), 2.52 (m, 1H), 2.11 (m, 1H), 1.33 (s, 9H), 1.00 (t, 3H, 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 153.1, 131.7, 127.6, 126.1, 93.0, 34.9, 31.4, 27.4, 10.9 ppm; IR (neat, cm^{-1}) ν: 2966, 2906, 2873, 1549, 1461, 1364, 1270, 1108, 1019, 805, 672. Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.56; H, 8.65. Found: C, 70.64; H, 8.78.

2-Methoxy-(1-nitropropyl)benzene (Table 1, entry 12). The reaction was carried out according to general procedure, method B. Flash column chromatography (diethyl ether: hexanes 1:10) yielded a colorless oil (0.185 g, 0.95 mmol, 95%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.45 (m, 1H), 7.37 (m, 1H), 7.02 (m, 1H), 6.93 (m, 1H), 5.91 (dd, 1H, J = 8.4 Hz, 6.6 Hz), 3.86 (s, 3H), 2.48 (m, 1H), 2.11 (m, 1H), 1.02 (d, 3H, J = 7.2 Hz);

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(11) Baruah, A.; Kalita, B.; Barua, N. C. *Synlett* **2000**, 1064.

^{13}C NMR ($CDCl_3$, 75 MHz) δ: 157.2, 130.9, 127.7, 123.2, 121.0, 111.0, 85.8, 55.8, 26.7, 11.0 ppm; IR (neat, cm^{-1}) ν: 2975, 2941, 2883, 2842, 1603, 1547, 1493, 1465, 1368, 1248, 1027, 812, 753. Anal. Calcd for $C_{10}H_{13}NO_3$: C, 61.53; H, 6.71. Found: C, 61.76; H, 6.76.

3-Methoxy-(1-nitropropyl)benzene (Table 1, entry 13). The reaction was carried out according to general procedure, method B. Flash column chromatography (diethyl ether: hexanes 1:8) yielded a colorless oil (0.133 g, 0.68 mmol, 68%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.31 (t, 1H, J = 8.1 Hz), 7.05−6.91 (m, 3H), 5.33 (m, 1H), 3.82 (s, 3H), 2.49 (m, 1H), 2.10 (m, 1H), 0.98 (t, 3H, 7.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 160.1, 136.0, 130.2, 120.2, 115.3, 113.5, 93.1, 55.5, 27.5, 10.8 ppm; IR (neat, cm^{-1}) ν: 2975, 2941, 2840, 1602, 1547, 1492, 1457, 1368, 1264, 1162, 1046, 787, 689. Anal. Calcd for $C_{10}H_{13}NO_3$: C, 61.53; H, 6.71. Found: C, 61.55; H, 6.81.

3-Methoxycarbonyl-(1-nitropropyl)benzene (Table 1, entry 14). The reaction was carried out according to general procedure, method B. Flash column chromatography (diethyl ether:hexanes 1:8 to 1:5) yielded a pale yellow oil (0.145 g, 0.65 mmol, 65%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.14 (s, 1H), 8.09 (d, 1H, J = 7.5 Hz), 7.68 (d, 1H, J = 7.8 Hz) 7.50 (t, 1H, J = 7.8 Hz), 5.43 (dd, 1H, J = 8.4 Hz, 6.3 Hz), 3.94 (s, 3H), 2.53 (m, 1H), 2.16 (m, 1H), 1.00 (t, 3H, 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 166.5, 135.0, 132.3, 131.2, 131.1, 129.4, 129.2, 92.7, 52.6, 27.5, 10.8 ppm; IR (neat, cm^{-1}) ν: 2977, 2954, 2883, 1721, 1549, 1434, 1368, 1285, 1200, 1109, 735, 691. Anal. Calcd for $C_{11}H_{13}NO_4$: C, 59.19; H, 5.87. Found: C, 59.40; H, 5.86.

4-Methoxycarbonyl-(1-nitropropyl)benzene (Table 1, entry 15). The reaction was carried out according to general procedure, method A. Flash column chromatography (diethyl ether:hexanes 1:8) yielded a colorless oil (0.191 g, 0.86 mmol, 86%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.08 (d, 2H, J = 8.7), 7.55 (d, 2H, J = 8.4 Hz), 5.42 (dd, 1H, J = 9.0 Hz, 6.3 Hz), 3.93 (s, 3H), 2.53 (m, 1H), 2.15 (m, 1H), 1.00 (t, 3H, 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 166.5, 139.1, 131.7, 130.4, 128.0, 92.7, 52.6, 27.6, 10.8 ppm; IR (neat, cm^{-1}) ν: 2977, 2956, 2885, 1721, 1549, 1436, 1368, 1279, 1185, 1113, 1021, 731. Anal. Calcd for $C_{11}H_{13}NO_4$: C, 59.19; H, 5.87. Found: C, 59.48; H, 5.95.

4-*tert*-Butyl-(1-nitrohexyl)benzene (Table 1, entry 16). The reaction was carried out according to general procedure, method B. Flash column chromatography (diethyl ether: hexanes 1:100, the column was twice as long as for the other separations, toluene:hexane 1:3 can be better if starting material is left) yielded a colorless oil (0.242 g, 0.92 mmol, 92%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.41 (s, 4H), 5.44 (dd, 1H, J = 9.0 Hz, 6.3 Hz), 2.49 (m, 1H), 2.05 (m, 1H), 1.32 (s, 15H), 0.89 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 153.1, 131.9, 127.6, 126.1, 91.6, 34.9, 34.0, 31.4, 31.3, 26.0, 22.5, 14.1 ppm; IR (neat, cm^{-1}) ν: 2960, 2933, 2871, 1551, 1465, 1364, 1270, 1109, 828, 774. Anal. Calcd for $C_{16}H_{25}NO_2$: C, 72.97; H, 9.57. Found: C, 72.97; H, 9.59.

2-[3-(1-nitrohexyl)phenyl]-[1,3]dioxolane (Table 1, entry 17). The reaction was carried out according to general procedure, method B. Flash column chromatography (diethyl ether:hexanes 1:8) yielded a yellow oil (0.237 g, 0.85 mmol, 85%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.60−7.40 (m, 4H), 5.82 (s, 1H), 5.47 (dd, 1H, J = 9.0 Hz, 6.3 Hz), 4.17−4.03 (m, 4H), 2.50 (m, 1H), 2.05 (m, 1H), 1.33 (s, 6H), 0.88 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 139.0, 135.0, 129.3, 128.6, 128.2, 126.1, 103.3, 91.6, 65.6, 34.2, 31.3, 25.9, 22.5, 14.1 ppm; IR (neat, cm^{-1}) ν: 2958, 2931, 1549, 1364, 1165, 1079, 969, 700. Anal. Calcd for $C_{15}H_{21}NO_4$: C, 64.50; H, 7.58. Found: C, 64.59; H, 7.70.

1-(4-*tert*-Butyl-phenyl)-2-phenylnitroethane (Table 1, entry 18). The reaction was carried out according to general procedure, method B. Flash column chromatography (diethyl ether:hexanes 1:10; no starting material should be left prior to purification) yielded a pale yellow oil (0.184 g, 0.65 mmol, 65%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.49−7.18 (m, 9H), 5.70 (dd, 1H, J = 5.1 Hz, 9.9 Hz), 3.81 (dd, 1H, J = 9.9 Hz, 14.5 Hz), 3.31 (dd, 1H, J = 5.1 Hz, 14.5 Hz), 1.33 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 153.4, 135.9, 131.5, 129.1, 129.0, 127.6, 127.6, 126.2, 92.7, 40.2, 34.9, 31.4 ppm; IR (neat, cm^{-1}) ν: 3033, 2964, 2906, 2869, 1551, 1364, 1270, 1111, 1019, 855, 745, 699. Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.30; H, 7.47. Found: C, 76.16; H, 7.44.

1-(4-Methoxy-phenyl)-2-phenylnitroethane (Table 1, entry 19). The reaction was carried out according to general procedure, method B. Flash column chromatography (diethyl ether:hexanes 1:20) yielded a crystalline solid; mp 79 °C (0.129 g, 0.50 mmol, 50%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.45 (m, 2H), 7.30−7.15 (m, 5H), 6.93−6.90 (m, 2H), 5.66 (dd, 1H, J = 6.0 Hz, 9.3 Hz), 3.82 (s, 3H), 3.77 (dd, 1H, J = 9.3 Hz, 14.4 Hz), 3.33 (dd, 1H, J = 6.0 Hz, 14.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 160.9, 135.7, 129.4, 129.1, 129.0, 127.5, 126.5, 114.5, 92.3, 55.5, 40.2 ppm; IR (neat, cm^{-1}) ν: 3012, 2904, 2834, 1609, 1546, 1513, 1455, 1366, 1254, 1177, 1028, 836, 735, 699. Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88. Found: C, 70.11; H, 5.80.

4-Acetyl-(1-nitropropyl)benzene (Table 2, entry 1). The reaction was carried out according to general procedure, method A. Flash column chromatography (diethyl ether: hexanes 1:5) yielded a pale yellow oil which solidifies upon standing; mp 39 °C (0.166 g, 0.80 mmol, 80%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.98 (d, 2H, J = 6.8 Hz), 7.56 (d, 2H, J = 6.8 Hz), 5.42 (dd, 1H, J = 8.7 Hz, 6.6 Hz), 2.61 (s, 3H), 2.51 (m, 1H), 2.12 (m, 1H), 0.99 (t, 3H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 197.5, 139.1, 138.2, 129.1, 128.2, 92.6, 27.6, 26.9, 10.7 ppm; IR (neat, cm^{-1}) ν: 2977, 2941, 2883, 1684, 1609, 1547, 1416, 1360, 1266, 959, 805. Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32. Found: C, 64.03; H, 6.40.

3-Acetyl-(1-nitropropyl)benzene (Table 2, entry 2). The reaction was carried out according to general procedure, method B. Flash column chromatography (diethyl ether: hexanes 1:5) yielded a pale yellow oil (0.131 g, 0.63 mmol, 63%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.05 (s, 1H), 8.00 (d, 1H, J = 7.8 Hz) 7.71 (d, 1H, J = 7.8 Hz), 7.53 (t, 1H, J = 7.8 Hz), 5.44 (dd, 1H, J = 8.7 Hz, 6.3 Hz), 2.63 (s, 3H), 2.55 (m, 1H), 2.14 (m, 1H), 1.00 (t, 3H, 6.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 197.5, 137.9, 135.2, 132.3, 129.9, 129.6, 127.8, 92.7, 27.6, 26.9, 10.8 ppm; IR (neat, cm^{-1}) ν: 2977, 2941, 2883, 1686, 1547, 1360, 1272, 1189, 1084, 799, 764, 691; Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32. Found: C, 64.10; H, 6.38.

4-(Naphthalene-2-yl)-4-nitrobutyric Acid Methyl Ester (Table 2, entry 3). The reaction was carried out according to general procedure, method A. Flash column chromatography (diethyl ether:hexanes 1:3) yielded a viscous oil which solidified upon storage; mp 37 °C (0.218 g, 0.80 mmol, 80%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.95−7.85 (m, 4H), 7.60−7.52 (m, 3H), 5.78 (m, 1H), 3.70 (s, 3H), 2.97−2.82 (m, 1H), 2.62−2.50 (m, 1H), 2.41 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 172.5, 134.0, 133.1, 131.3, 129.4, 128.5, 128.2, 127.9, 127.4, 127.1, 124.2, 90.3, 52.2, 30.2, 29.0 ppm; IR (neat, cm^{-1}) ν: 3058, 2954, 1735, 1549, 1511, 1437, 1360, 1200, 1177, 1129, 909, 861, 818, 749, 731. Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53. Found: C, 65.98; H, 5.59.

4-(4-Methoxy-phenyl)-4-nitrobutyric Acid Methyl Ester (Table 2, entry 4). The reaction was carried out according to general procedure, method B. Flash column chromatography (diethyl ether:hexanes 1:3) yielded a yellow oil (0.179 g, 0.79 mmol, 71%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.39 (m, 2H), 6.92 (m, 2H), 5.54 (m, 1H), 3.82 (s, 3H), 3.69 (s, 3H), 2.82−2.70 (m, 1H), 2.50−2.32 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 172.5, 161.0, 129.3, 126.1, 114.6, 89.7, 55.5, 52.1, 30.3, 28.9 ppm; IR (neat, cm^{-1}) ν: 2956, 2842, 1737, 1611, 1549, 1515, 1439, 1360, 1308, 1254, 1179, 1117, 1030, 913, 834, 733. Anal. Calcd for $C_{12}H_{15}NO_5$: C, 56.91; H, 5.97. Found: C, 56.94; H, 5.90.

4-(3-Dimethylamino-phenyl)-4-nitrobutyric Acid Methyl Ester (Table 2, entry 5). The reaction was carried out according to general procedure, method B. Flash column chromatography (diethyl ether:hexanes 1:3) yielded a yellow oil (0.192 g, 0.72 mmol, 72%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.24 (m, 1H), 6.77−6.70 (m, 3H), 5.51 (dd, 1H, J = 6.5 Hz, 8.6 Hz), 3.68 (s, 3H), 2.95 (s, 6H), 2.80−2.69 (m, 1H), 2.50−2.32 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 172.6, 151.0, 135.0, 129.9, 115.2, 113.8, 111.2, 90.7, 52.1, 40.6, 30.3, 29.0 ppm; IR (neat, cm^{-1}) ν: 2954, 2894, 2811, 1737, 1603, 1547, 1503, 1439,

1360, 1233, 1200, 1171, 1063, 996, 849, 764. Anal. Calcd for $C_{13}H_{18}N_2O_4$: C, 58.63; H, 6.81. Found: C, 58.93; H, 6.80.

4-(4-Methoxycarbonylphenyl)-4-nitrobutyric Acid Methyl Ester (Table 2, entry 6). The reaction was carried out according to general procedure, method A. Flash column chromatography (diethyl ether:hexanes 1:3) yielded a pale yellow oil (0.187 g, 0.67 mmol, 67%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.06 (d, 2H, J = 8.3 Hz), 7.52 (d, 2H, J = 8.3 Hz), 5.65 (m, 1H), 3.91 (s, 3H), 3.67 (s, 3H), 2.85−2.70 (m, 1H), 2.50−2.32 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 172.3, 166.3, 138.5, 131.8, 130.5, 127.9, 89.6, 52.6, 52.2, 30.0, 29.0 ppm; IR (neat, cm^{-1}) ν: 3002, 2956, 2448, 1725, 1613, 1551, 1437, 1360, 1279, 1185, 1111, 1021, 731. Anal. Calcd for $C_{13}H_{15}NO_6$: C, 55.51; H, 5.38. Found: C, 55.47; H, 5.53.

6-(4-Methoxycarbonylphenyl)-6-nitro-1-hexene (Table 2, entry 7). The reaction was carried out according to general procedure, method A. Flash column chromatography (diethyl ether:hexanes 1:15) yielded a colorless oil (0.176 g, 0.67 mmol, 67%, some mixed fractions had to be purified by prep. TLC otherwise the yield is slightly lower). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.08 (d, 2H, J = 8.4 Hz), 7.55 (d, 2H, J = 8.1 Hz), 5.75 (m, 1H), 5.50 (dd, 1H, J = 8.7 Hz, 6.3 Hz), 5.07−4.99 (m, 2H), 3.94 (s, 3H), 2.50 (m, 1H), 2.12 (m, 3H), 1.42 (m 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 166.5, 139.1, 137.4, 131.7, 130.5, 128.0, 116.0, 91.1, 52.6, 33.5, 33.1, 25.3 ppm; IR (neat, cm^{-1}) ν: 2954, 1723, 1551, 1436, 1279, 1185, 1111, 917, 731; Anal. Calcd for $C_{14}H_{17}NO_4$: C, 63.86; H, 6.51. Found: C, 63.65; H, 6.53.

6-(4-Acetylphenyl)-6-nitro-1-hexene (Table 2, entry 8). The reaction was carried out according to general procedure, method B. Flash column chromatography (diethyl ether: hexanes 1:5) yielded a pale yellow oil (0.158 g, 0.64 mmol, 64%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.97 (d, 2H, J = 8.1 Hz), 7.55 (d, 2H, J = 8.4 Hz), 5.70 (m, 1H), 5.50 (dd, 1H, J = 8.4 Hz, 6.3 Hz), 5.06−4.97 (m, 2H), 2.60 (s, 3H), 2.50 (m, 1H), 2.11 (m, 3H), 1.40 (m 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 197.5, 139.2, 138.3, 137.3, 129.1, 128.2, 116.0, 91.0, 33.5, 33.0, 26.9, 25.3 ppm; IR (neat, cm^{-1}) ν: 2933, 1686, 1609, 1549, 1360, 1266, 917, 834, 778. Anal. Calcd for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93. Found: C, 68.16; H, 6.97.

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