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Rhodium-Catalyzed Amination of Aromatic Olefins [1]

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Summary. The oxidative amination of styrene with secondary amines in the presence of cationic rhodium catalysts yields regiospecifically the corresponding *anti-Markovnikov* enamines. Styrene as the hydrogen acceptor gave concomitantly ethylbenzene. In the presence of 1,5-cyclooctadiene (*cod*) preferential reduction to cyclooctene takes place. The addition of *cod* reduces the rate of the reaction, but also the amount of ethylbenzene produced. Here, for the first time the ratio of enamine: ethylbenzene is > 1, which is favourable in case of more expensive styrene derivatives. A screening of various ligands for oxidative amination reveals that hemilabile 2-(ω-phosphino-*n*-alkyl)-pyridines are superior ligands for this reaction compared to simple alkyl and aryl phosphines.

Keywords. Amination; Enamines; Homogeneous catalysis; Rhodium; Transition metal.

Introduction

Amines and their derivatives are of fundamental importance for organic chemistry as natural products, pharmacological agents, fine chemicals, and dyes [2]. In general, the synthesis of amine derivatives involves classical organic chemistry such as nucleophilic substitution or nitration of aromatics and subsequent reduction. Apart from reductive amination of carbonyl compounds, the atom-efficient synthesis of amines is rare. Hence, there is considerable interest in the development of new efficient catalytic routes for the construction of carbon-nitrogen bonds. In this respect, the catalytic amination of olefins is a particularly convenient method for the synthesis of amine derivatives [3]. Amination of olefins can take place either as hydroamination to give alkylamines or as oxidative amination to yield enamines or imines [4]. Recently, we discovered the first intermolecular oxidative amination of aromatic olefins providing enamines in *anti-Markovnikov* regiochemistry (Scheme 1) [5].

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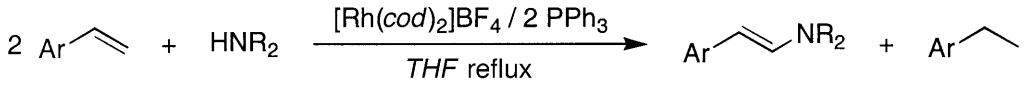


Ar = aryl; *R* = aryl, alkyl

Scheme 1

Results and Discussion

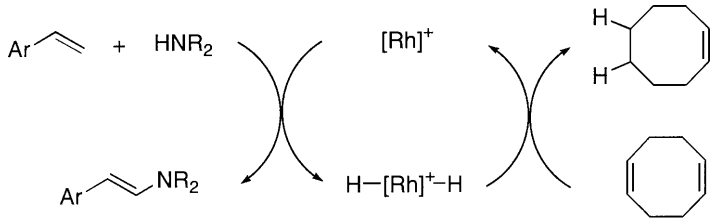
By means of cationic rhodium catalysts, the oxidative amination of styrene was achieved using secondary amines such as piperidine or morpholine in refluxing *THF*. Concurrently, a second molecule of styrene is reduced to give ethylbenzene. In general, the reaction tolerates various substituents at the aromatic core of the olefin [6] as well as on the amine. In order to get satisfactory yields of enamines, an excess of styrene (4–10 equivalents referred to the amine) has to be applied. Due to the price and availability of substituted styrenes we were interested whether oxidants other than styrene might be used for this reaction. Therefore, we tested several oxidants for the reaction of styrene with piperidine, diethylamine, and morpholine. The results are summarized in Table 1.

Applying previously optimized conditions (2.5 mol% $[Rh(cod)_2]BF_4$/2 PPh_3, *THF*, reflux, 20 h) [7], enamine yields of 40–74% were obtained. In the presence of 0.5 equivalents of N-methylmorpholine-N-oxide (*NMO*) or benzoquinone no reaction occured at all. We assume that the cationic rhodium(I) catalyst is oxidized to an inactive rhodium(III) species. Furthermore, N-oxides can act as anionic ligands [8] which destroy the catalytic activity of cationic catalysts. Next, we tested olefins (in addition to styrene) to regenerate the active catalyst due to their hydrogen acceptor capability. It is obvious that only olefins can be applied which are not aminated by the rhodium catalyst under the given conditions. Here, we used different amounts of cyclohexene, 1,3-cyclohexadiene, and 1,5-cyclooctadiene

Table 1. Amination of styrene in the presence of various oxidants[a]

Amine	Oxidant (mol%)	Enamine (%)	Ethylbenzene (%)	Enamine / Ethylbenzene
Piperidine	–	55	57	1
Piperidine	Cyclohexene (40)	17	18	1
Piperidine	1,3-Cyclohexadiene (100)	< 0.1	< 0.1	–
Diethylamine	–	40	54	0.8
Diethylamine	Cyclohexene (40)	23	24	1
Morpholine	–	74	84	0.9
Morpholine	*cod* (25)	27	6	4.5

[a] Molar ratio of styrene:amine = 4:1, 2.5 mol% $[Rh(cod)_2]BF_4$/2 PPh_3 relative to the amine, 20 h, reflux in *THF*; the yield refers to the amine and was determined by GC with hexadecane as internal standard



Scheme 2

(*cod*). In general, we observed a decreasing enamine yield with increasing olefin concentration. However, by adding 0.25 equivalents of 1,5-cyclooctadiene the ratio of enamine:ethylbenzene is above unity for the first time. This demonstrates that reduction of styrene is suppressed at the expense of hydrogenation of *cod* as the product, cyclooctene (*coe*), is detected in the reaction mixture (Scheme 2). The complete reduction of *cod* to cyclooctane takes place only to a very small extent (< 2%).

In order to study this effect more thoroughly, the reaction of styrene with morpholine was performed in the presence of different concentrations of *cod*; the results are shown in Fig. 1.

In the presence of 0.1 equivalent of *cod* (refers to the amine) a reduced yield of ethylbenzene (51% *vs*. 84%) was observed, whereas the enamine yield (74%) was nearly constant compared to the reaction without addition of *cod*. Addition of more *cod* led to decreased enamine yields, but an increase of the enamine:ethylbenzene ratio was observed, *e.g*. the addition of 0.5 equivalents of *cod* gave an enamine:ethylbenzene ratio of 7.5 (ethylbenzene < 2%).

The decrease of the yield of enamine with increasing concentration of *cod* is explained by the favourable coordination of *cod* to the central metal, thus blocking coordination sides needed for styrene to react with the amine [9]. Nevertheless, synthetically useful yields of enamine can be achieved even in the presence of 0.25 equivalents *cod* if the reaction time is prolonged to 65 h. Here, the yield of enamine again is 74%. Interestingly, the addition of *cod* seems to have a stabilizing effect on

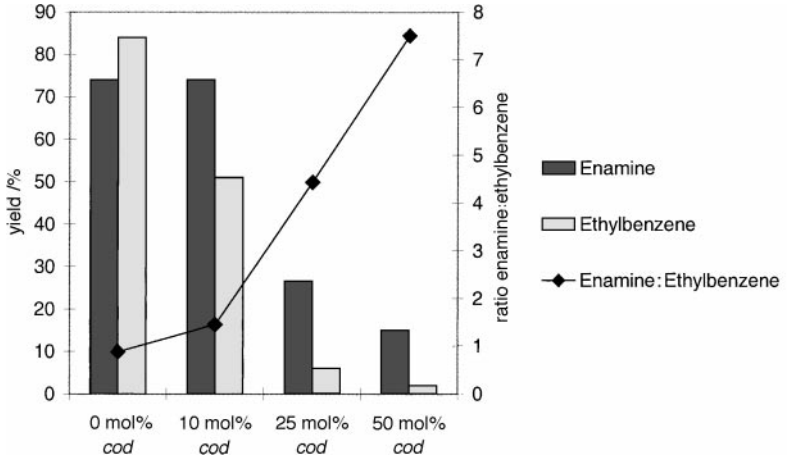
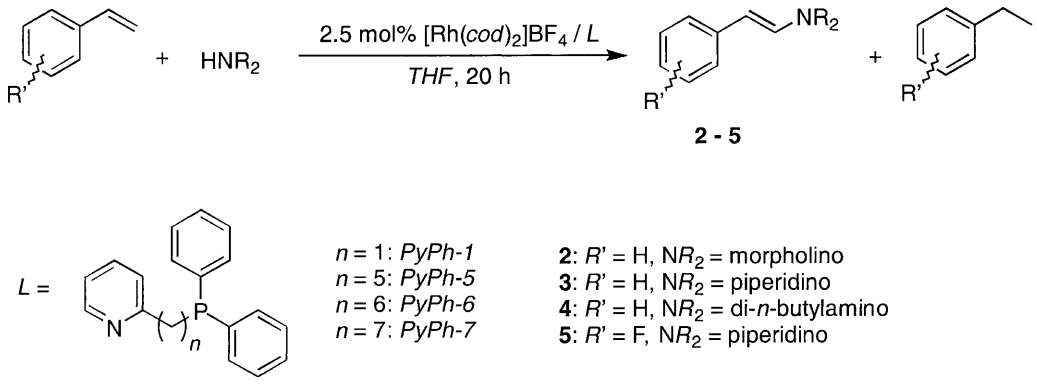


Fig. 1. Oxidative amination of styrene with morpholine in the presence of *cod*



Scheme 3

the active catalyst, since without *cod* catalyst deactivation is observed after approximately 20 h.

It is noteworthy that in case of amination of styrene with morpholine we also observed the formation of 2-phenylethyl-morpholine. The amount of this hydroamination product is not affected by the presence of *cod*. This gives additional support for a parallel *anti-Markovnikov* hydroamination pathway [7], since hydrogenation of 2-phenylethenyl-morpholine is unlikely in the presence of *cod*.

In addition to the search for alternative oxidation reagents, we were interested in improving the catalyst system. So far, $[Rh(cod)_2]BF_4$/2 PPh_3 was assumed to be the most efficient catalyst system for the oxidative amination of olefins. Previously we have shown that variation of the triphenylphosphine ligand (substitution with electron withdrawing groups (*e.g.* F, CF_3) or electron donating groups (*e.g.* OCH_3, CH_3) lowers the enamine yield [7]. Phosphines with large *Tolman* angles (*e.g.* P(*o*-tolyl)$_3$) inhibit the reaction at all. Trialkylphosphines, *e.g.* tricyclohexylphosphine, trimethylphosphine, or tri-*n*-butyl-phosphine give lower yields of N-2-phenylethenyl-morpholine compared to PPh_3. Chelating phosphines like 1,2-*bis*-diphenylphosphino-ethane (*dppe*), but also 1,1′-bisphenylferrocenylphosphine again inhibit the activity of the catalyst. Hence, the tolerance of the catalyst for the added ligand is very small. It seems that a subtle balance between stabilization of the central metal and creation of free coordination sites on the rhodium center is a prerequisite for successful catalysis. We assume that phosphines with an additional hemilabile coordination site might fulfill these requirements. Hence, we tested a series of P,N-ligands of the general formula 2-pyridine-$(CH_2)_n$-PPh_2 ($n = 1$, 5–7; Scheme 3) [10].

Table 2 shows the obtained results for the amination of styrene with morpholine, piperidine, and di-*n*-butylamine. Applying standard conditions (styrene:amine ratio = 4:1, 2.5 mol% $[Rh(cod)_2]BF_4$/2 PPh_3, *THF*, 20 h, 100°C, pressure tube), enamine yields of 74, 55, and 48% were obtained. Next, the P,N-ligands were tested with Rh:P ratios of 1:1 and 1:2. In the presence of 2-diphenylphosphinomethyl-pyridine (*PyPh-1*) and 2-(5-diphenylphosphinopentyl)-pyridine (*PyPh-5*), very small yields of enamines (0–10%) were observed. However, applying 5 mol% of 2-(6-diphenylphosphinohexyl)-pyridine (*PyPh-6*) or 2-(7-diphenylphosphinoheptyl)-pyridine (*PyPh-7*) as the ligand, improved results compared to PPh_3 were

Table 2. Influence of hemilabile P,N-ligands [10] on the oxidative amination[a] of aromatic olefins in comparison of PPh_3

	Ligand								
	PPh_3	*PyPh-1*		*PyPh-5*		*PyPh-6*		*PyPh-7*	
	Rh:*L* 1:2	Rh:*L* 1:1	Rh:*L* 1:2	Rh:*L* 1:1	Rh:*L* 1:2	Rh:*L* 1:1	Rh:*L* 1:2	Rh:*L* 1:1	Rh:*L* 1:2
Enamine	(%)[b]	(%)[b]		(%)[b]		(%)[b]		(%)[b]	
2	74	6	1	4	4	46	74	64	76
3	55	10	< 1	5	5	31	72	51	72
4	48	1	< 1	–	–	14	42	21	52
5	18	–	–	–	–	–	–	–	30

[a] Reaction conditions: molar ratio of styrene:amine = 4:1, 2.5 mol% $[Rh(cod)_2]BF_4$/*L* or 2*L* relative to the amine, *THF*, 20 h at 100°C in a pressure tube, [b] the yield refers to the amine (Experimental) and was determined by GC with hexadecane as internal standard

obtained. Similarly, the reaction of 4-fluorostyrene with piperidine proceeds significantly better in the presence of *PyPh-7* (30 *vs.* 18%).

In conclusion, we report two improvements of the rhodium-catalyzed oxidative amination of aromatic olefins. Our studies demonstrate that 1,5-cyclooctadiene acts as an improved hydrogen acceptor compared to styrenes, thus reducing the amount of ethylbenzene. This result is important for the oxidative amination of more expensive substituted styrenes. In addition, for the first time ligands are described which give superior results compared to the standard system ($[Rh(cod)_2]BF_4$/2 PPh_3). We expect this finding to be of value for oxidative aminations of other substrates, too.

Experimental

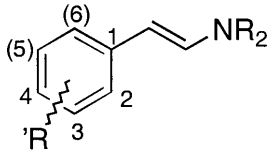
All operations were carried out in an inert atmosphere (Ar). *THF* was freshly distilled from sodium tetraethylaluminate under Ar prior to use. Amines, olefins, and oxidants were purchased from Aldrich or Fluka. Amines were distilled from CaH_2. Olefins were dried over 4 Å molecular sieves before use. $[Rh(cod)_2]BF_4$ [11] and ω-2-pyridyl-*n*-alkylphosphines [10] were prepared according to literature procedures.

Physical measurements

^1H and ^{13}C NMR spectra were recorded on a Bruker AM 360 spectrometer at 25°C. Mass spectroscopic analysis was performed on a Finnigan MAT 311A. GCs for analysis of catalytic reactions were recorded with a HP 6890 gas chromatograph using a HP-1 capillary column. GC/MS-studies were conducted on a HP 5890 with 70 eV electron impact ionization (detector: HP 5970 B).

General procedure for the amination of styrenes with amines in the presence of cod or oxidants

45 mg (0.11 mmol) $[Rh(cod)_2]BF_4$ and 58 mg (0.22 mmol) PPh_3 were suspended in 10 cm^3 *THF*. Subsequently, 4.40 mmol of the amine, 17.6 mmol of styrene, and the corresponding amount of *cod*



Scheme 4

(see Fig. 1) or oxidant (see Table 1) were added at room temperature. The mixture was heated to reflux for 20 h. The yields were determined by gas chromatography using hexadecane as internal standard.

General procedure for the amination of styrenes

[Rh(*cod*)$_2$]BF_4 (0.11 mmol) and the phosphine (0.11 or 0.22 mmol) were suspended in 10 cm^3 *THF*. Subsequently, the amine (4.40 mmol) and styrene (17.60 mmol) were added at room temperature. The mixture was heated in a pressure tube for 20 h at 100°C. The yields were determined by GC with hexadecane as the internal standard. In the case of 4-fluorostyrene, the reaction mixture was hydrogenated to the corresponding alkylamine (24 h, 1 bar H_2, 0.5 g 5% Pd/C). After hydrogenation the catalyst was separated by filtration, the solvent was removed *in vacuo* and the residue was taken up in CH_2Cl_2 (20 cm^3). After extraction with 5% HCl (3 × 20 cm^3), the combined aqueous phases were carefully brought to $pH = 9$ (NaOH) and then extrated with CH_2Cl_2 (3 × 20 cm^3). The combined organic phases were dried over $MgSO_4$. The solvent was removed *in vacuo* and the product was purified by column chromatography and dried in high vacuum. The yields were determined by GC and refer to the amine.

(E)-N-(2-Phenylethenyl)-diethylamine (**1**; $C_{12}H_{17}N$)

According to the general procedure, 0.45 cm^3 diethylamine (4.4 mmol), 2.0 cm^3 styrene (17.6 mmol), 45 mg [Rh(*cod*)$_2$]BF_4 (0.11 mmol), and 58 mg PPh_3 (0.22 mmol) were refluxed in 10 cm^3 *THF* for 20 h. The title compound was isolated by distillation.

GC-yield: 40%; ^{1}H NMR (360 MHz, δ, $CDCl_3$): 7.22–7.18 (m, 4H, H-2, H-3), 7.00–6.96 (m, 1H, H-4), 6.76 (d, ^3J(H,H) = 14.1 Hz, 1H, CH–N), 5.28 (d, ^3J(H,H) = 14.1 Hz, 1H, Ph–CH), 3.19 (q, ^3J(H,H) = 7.2 Hz, 4H, N–CH_2), 1.17 (t, ^3J(H,H) = 7.2 Hz, 6H, N–CH_2–CH_3) ppm; ^{13}C NMR (91 MHz, δ, $CDCl_3$): 140.2 (C-1), 138.3 (N–CH), 128.2 (C-3), 123.0 (C-2), 122.3 (C-4), 95.1 (Ph–CH), 46.7 (N–CH_2), 13.8 (CH_3) ppm; MS (EI, 70 eV): $m/z = 175$ [M^+], 160 [M^+-CH_3], 146 [M^+-C_2H_5], 130 [C_6H_5–$C_2H_2NCH^+$], 117 [M^+-CH_2–N–$(CH_3)_2$], 103 [C_6H_5–CH=CH^+].

(E)-N-(2-Phenylethenyl)-morpholine (**2**; $C_{12}H_{15}NO$)

According to the general procedure, 0.38 cm^3 morpholine (4.4 mmol), 2.0 cm^3 styrene (17.6 mmol), 45 mg [Rh(*cod*)$_2$]BF_4 (0.11 mmol), and 58 mg PPh_3 (0.22 mmol) were reacted in 10 cm^3 *THF* for 20 h at 100°C. The title compound was isolated by distillation (148°C, 0.1 mbar).

GC-yield: 74%; ^{1}H NMR (360 MHz, δ, $CDCl_3$): 7.27 (m, 2H, H-2), 7.24 (m, 2H, H-3), 7.10 (m, 1H, H-4), 6.53 (d, ^3J(H,H) = 14.0 Hz, 1H, CH–N), 5.36 (d, ^3J(H,H) = 14.0 Hz, 1H, Ph–CH), 3.68 (t, ^3J(H,H) = 4.8 Hz, 4H, O–CH_2), 2.95 (t, ^3J(H,H) = 4.8 Hz, 4H, N–CH_2) ppm; ^{13}C NMR (91 MHz, δ, $CDCl_3$): 139.8 (N–CH), 138.6 (C-1), 128.5 (C-2), 124.4 (C-4), 124.2 (C-3), 101.5 (Ph–C), 66.5 (O–C), 49.1 (N–CH_2) ppm; MS (EI, 70 eV): $m/z = 189$ [M^+], 158 [M^+-CH_3O], 130 [C_6H_5–$C_2H_2NCH^+$], 104 [C_6H_5–$C_2H_3^+$], 91 [C_6H_5–CH_2^+], 77 [$C_6H_5^+$].

(E)-N-(2-Phenylethenyl)-piperidine (**3**; $C_{13}H_{17}N$)

According to the general procedure, 0.44 cm^3 piperidine (4.4 mmol), 2.0 cm^3 styrene (17.6 mmol), 45 mg $[Rh(cod)_2]BF_4$ (0.11 mmol), and 58 mg PPh_3 (0.22 mmol) were reacted in 10 cm^3 *THF* for 20 h at 100°C. The title compound was isolated by distillation.

GC-yield: 55%; ^{1}H NMR (360 MHz, δ, $CDCl_3$): 7.22–7.19 (m, 4H, H-2, H-3), 7.02–6.99 (m, 1H, H-4), 6.67 (d, ^3J(H,H) = 14.2 Hz, 1H, CH–N), 5.37 (d, ^3J(H,H) = 14.2 Hz, 1H, Ph–CH), 3.03 (t, ^3J(H,H) = 4.8 Hz, 4H, N–CH_2), 1.66–1.57 (m, 6H, N–CH_2–CH_2–CH_2) ppm; ^{13}C NMR (91 MHz, δ, $CDCl_3$): 140.3 (N–CH), 139.5 (C-1), 128.4 (C-3), 123.8 (C-2), 123.6 (C-4), 99.4 (Ph–CH), 49.7 (N–CH_2), 25.3 (N–CH_2–CH_2), 24.3 (N–CH_2–CH_2–CH_2) ppm; MS (EI, 70 eV): m/z = 187 [M^+], 130 [C_6H_5–$C_2H_2NCH^+$], 104 [C_6H_5–$C_2H_3^+$].

(E)-N-(2-Phenylethenyl)-di-n-butylamine (**4**; $C_{16}H_{25}N$)

According to the general procedure, 0.74 cm^3 di-*n*-butylamine (4.4 mmol), 2.0 cm^3 styrene (17.6 mmol), 45 mg $[Rh(cod)_2]BF_4$ (0.11 mmol), and 58 mg PPh_3 (0.22 mmol) were reacted in 10 cm^3 *THF* for 20 h at 100°C. The title compound was isolated by distillation.

GC-yield: 48%; ^{1}H NMR (360 MHz, δ, $CDCl_3$): 7.22–7.19 (m, 4H, H-2, H-3), 7.02–6.99 (m, 1H, H-4), 6.81 (d, ^3J(H,H) = 14.1 Hz, 1H, CH–N), 5.16 (d, ^3J(H,H) = 14.1 Hz, 1H, Ph–CH), 3.12 (t, ^3J(H,H) = 7.2 Hz, 4H, N–CH_2), 1.59 (quin, ^3J(H,H) = 7.2 Hz, 4H, N–CH_2–CH_2), 1.39 (sext, ^3J(H,H) = 7.3 Hz, 4H, N–CH_2–CH_2–CH_2), 1.00 (t, ^3J(H,H) = 7.3 Hz, 6H, CH_3) ppm; ^{13}C NMR (91 MHz, δ, $CDCl_3$): 140.4 (C-1), 138.5 (N–CH), 128.5 (C-3), 123.1 (C-2), 122.6 (C-4), 95.4 (Ph–CH), 51.5 (N–CH_2), 30.1 (N–CH_2–CH_2), 20.3 (N–CH_2–CH_2–CH_2), 14.0 (CH_3) ppm; MS (EI, 70 eV): m/z = 231 [M^+], 188 [M^+-C_3H_7], 146 [M^+-C_6H_{14}], 130 [C_6H_5–$C_2H_2NCH^+$], 103 [C_6H_5–CH=CH^+], 84 [CH=N–$(CH_2)_3$–CH_3^+].

(E)-N-(2-(4-Fluorophenyl)-ethenyl)-piperidine (**5**; $C_{13}H_{16}FN$)

According to the general procedure, 0.44 cm^3 piperidine (4.4 mmol), 2.1 cm^3 4-fluorostyrene (17.6 mmol), 45 mg $[Rh(cod)_2]BF_4$ (0.11 mmol), and 58 mg PPh_3 (0.22 mmol) were reacted in 10 cm^3 *THF* for 20 h at 100°C. MS (EI, 70 eV): m/z = 205 [M^+], 162 [M^+-C_3H_7], 148 [M^+-C_3H_7N], 135 [M^+-C_4H_8N], 122 [F–C_6H_4–$C_2H_3^+$]. The isolation was performed by hydrogenation according to the general procedure, and the product **6** was purified by column chromatography (*n*-hexane:ethyl acetate:NEt_3 = 1:1:0.01). GC-yield: 18%.

N-(2-(4-Fluorophenyl)-ethyl)-piperidine (**6**; $C_{13}H_{18}FN$)

^{1}H NMR (360 MHz, δ, $CDCl_3$): 7.22–7.11 (m, 2H, H-3), 6.94 (t, ^3J(H,H) = 8.6 Hz, 2H, H-2), 2.83–2.75 (m, 2H, Ph–CH_2), 2.55–2.44 (m, 6H, N–CH_2–CH_2–Ph, N–CH_2), 1.61 (quin, ^3J(H,H) = 5.4 Hz, 4H, N–CH_2–CH_2), 1.47 (m, 2H, N–CH_2–CH_2–CH_2) ppm; ^{13}C NMR (91 MHz, δ, $CDCl_3$): 161.3 (d, ^1J(C,F) = 243.2 Hz, C-4), 136.1 (C-1), 129.9 (d, ^3J(C,F) = 7.8 Hz, C-2), 114.9 (d, ^2J(C,F) = 65.4 Hz, C-3), 61.3 (N–CH_2), 54.5 (N–CH_2–CH_2–CH_2), 32.7 (Ph–CH_2), 25.9 (N–CH_2–CH_2–CH_2), 24.3 (N–CH_2–CH_2–CH_2) ppm; MS (EI, 70 eV): m/z = 207 [M^+], 109 [F–C_6H_4–CH_2^+], 98 [C_4H_8N–CH_2^+].

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