165. Efficient Synthesis of 1,2-Bis(2,2′-bipyridinyl)ethane and 1,2-Bis(1,10-phenanthrolinyl)ethane Ligands by Oxidative Coupling of the Corresponding Monomeric Methylene Carbanions

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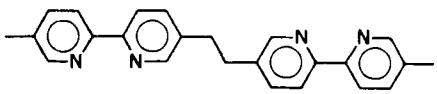
Several dimeric 1,2-bis(2,2′-bipyridinyl)ethane (**1**, **2**, **6**, **7**, and **9**) and 1,2-bis(1,10-phenanthrolinyl)ethane (**3**, **4**, and **5**) ligands have been synthesized in high yield by oxidative coupling of the corresponding monomeric methylene carbanions using as oxidating agents Br_2, I_2, and 1,2-dibromoethane. The structure of the compounds obtained from three tetramethyl-2,2′-bipyridines and one tetramethyl-1,10-phenanthroline have been assigned on the basis of their ^{1}H-NMR spectra. The electronic absorption and emission properties of these new ligands are reported. They display intense fluorescence spectra.

Polypyridine ligands display a variety of interesting complexation properties and have been extensively used in the synthesis of photosensitive and electroactive complexes [1]. Studies on polynuclear metal complexes are limited [2] [3], although they play an important role in redox catalysis [4]. The synthesis and complexation properties of two 4,4′-dimethyl-2,2′-bipyridine units linked with two [3a] [5] and three CH_2 [5] groups have been described. Recently, oligobipyridine ligands have been shown to form double stranded helicates in the presence of Cu(I) cations [6].

During our work on the monofunctionalization of 2,2′-bipyridine subunits [7], we found that reaction of the monocarbanion of 5,5′-dimethyl-2,2′-bipyridine with Br_2 gave, in high yield, 1,2-bis(5′-methyl-2,2′-bipyridin-5-yl)ethane (**1**). We wish to describe here the application of this method to the coupling of methylated pyridine, 2,2′-bipyridines (bpy), and 1,10-phenanthrolines (phen).

Synthesis. – All the isomeric anions were prepared with 1 equiv. of lithium diisopropyl amide (LDA) in THF at −80°. The use of *t*-BuOK or $NaNH_2$ under the same conditions does not generate the anion, while BuLi itself leads to a complicated mixture of products. The Me groups in the 6,6′- and 4,4′-positions in a tetramethyl-2,2′-bipyridine and the 2,9- and 4,7-positions in a tetramethyl-1,10-phenanthroline are much more reactive than Me substituents in the 5,5′(bpy)- and 3,8(phen)-positions, in accordance with the stability of the corresponding carbanion. When two stable carbanions can be formed (*e.g.* in the 4- and 6-positions of 2,2′-bipyridine), a mixture of three products (detected by the presence of three CH_2 signals in the ^{13}C-NMR spectrum in a 1:1:1 ratio) is obtained (see **9**). The formation of this three-compound mixture is consistent with a radical mechanism, *via* an intermediate formed by electron transfer from the carbanion to the oxidant. Total decoloration of the carbanion solution was observed only after the addition of 1 equiv. of



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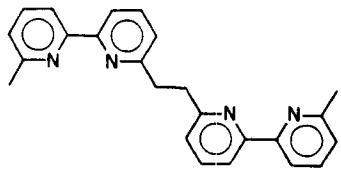

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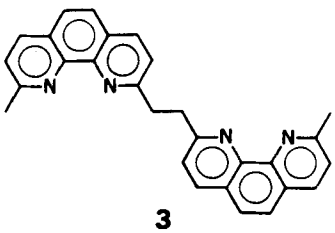

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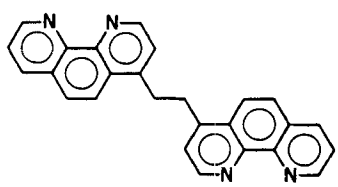

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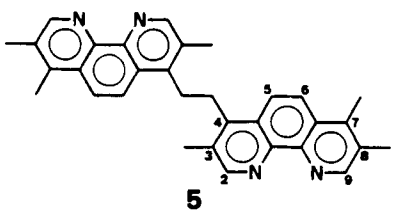

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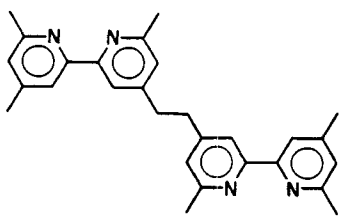

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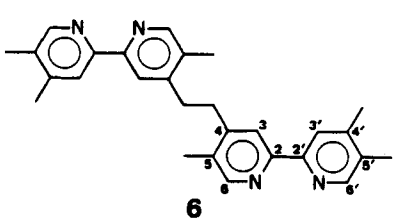

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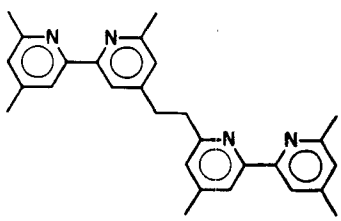

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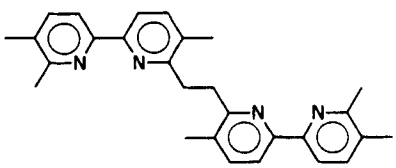

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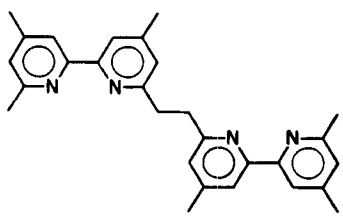

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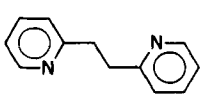

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the oxidant. The best results for the coupling reaction were obtained using Br_2 and 1,2-dibromoethane (see the *Table*). The latter reagent has been used earlier for the same purpose [3a].

Structure of the Ligands. – Coupling of a 2,2′-bipyridine or a 1,10-phenanthroline substituted by four Me groups may lead to several possible isomers. The unsymmetrical products coupled in the positions 4 and 5, or 5 and 6 in the 2,2′-bipyridine, and in the positions 3 and 4 in the 1,10-phenanthroline could be excluded on the basis of the NMR spectra. The exact coupling positions have been assigned by nuclear *Overhauser* enhancement (NOE) experiments. In the case of ligand **5**, the possibility that the compound was 1,2-bis(4,7,8-trimethyl-1,10-phenanthroline-3-yl)ethane was ruled out by the observation of strong NOE between the CH_2 protons, Me–C(3) and H–C(5) or H–C(6), as well as betweeen Me–C(3) and H–C(2). In the case of ligand **6**, the observation of strong NOE between the CH_2 protons, Me–C(5) and H–C(3), as well as between Me–C(5′) and H–C(6′) ruled out the isomeric structure 1,2-bis(4,4′,5′-trimethyl-2,2′-bipyridine-5-

Table. *Yields and Spectroscopic Properties of the Products Obtained by Reaction of the Monomethylene Carbanion with Oxidants Br_2, I_2, or 1,2-Dibromoethane*

Carbanion precursor	Isolated yield [%]					
	Ligand	Br_2	I_2	1,2-Dibromoethane	λ_{obs}; $10^{-3} \cdot \varepsilon$[a]) [nm] [$M^{-1} \cdot cm^{-1}$]	λ_{em} [nm][b])
5,5′-Dimethyl-2,2′-bipyridine	**1**	56	43	75	244; 49.5 250; 51.2 289; 73.7 299 (sh)	359
6,6′-Dimethyl-2,2′-bipyridine	**2**	68	–	70	236; 35.9 243; 33.3 288, 60.4	369
2,9-Dimethyl-1,10-phenanthroline	**3**	54	–	66	230; 89.9 268; 54.3 276 (sh)	367
4-Methyl-1,10-phenanthroline	**4**	40	33	–	231; 99.7 263, 88.2	375
3,4,7,8-Tetramethyl-1,10-phenanthroline	**5**	57	–	67	240; 107.4 268; 110.0	370
4,4′,5,5′-Tetramethyl-2,2′-bipyridine	**6**	86	77	–	246; 52.5 253; 52.7 285; 68.9 292 (sh)	370
5,5′,6,6′-Tetramethyl-2,2′-bipyridine	**7**	82	–	80	243; 68.2 250; 42.1 292; 42.3 302 (sh)	355, 390
2-Methylpyridine	**8**	68	–	77	254; 11.5 260; 12.9 266; 9.4	–

[a]) MeCN soln. at r.t.

[b]) Broad intense emission from 320 to 470 nm measured in MeCN, except for **5**, **6**, and **7** ($CHCl_3$). Excitation wavelength: 270 nm.

yl)ethane. In the case of ligand **7**, the structure 1,2-bis(5′,6,6′-trimethyl-2,2′-bipyridine-5-yl)ethane was ruled out by the observation of strong NOE between the CH_2 protons and Me–C(5), between Me–C(5′), Me–C(6′), and H–C(4′), as well as between Me–C(5), the CH_2 protons, and H–C(4).

Properties of the Ligands. – All of the new ligands, with the exception of **8**, display an intense fluorescence in the 320–470-nm region when excited in their π-π^* absorption band *(Table)*. This property contrasts with the absence of emission from the corresponding starting 2,2′-bipyridine or 1,10-phenanthroline compounds when excited under the same conditions. Presumably, the radiation is emitted by an excited complex species formed by interaction of one electronically excited part of the molecule with the second part of the same molecule in the ground state [8]. This process seems to be favored by the linking of two 2,2′-bipyridines or 1,10-phenanthrolines. Most of these new ligands readily formed dimeric Fe(II), Cu(I), Re(I), and Ru(II) complexes [9]. Work is in progress in order to synthesize mixed dinuclear complexes and to study their photophysical and electron-transfer properties.

Experimental Part

General. THF was distilled over benzophenone/Na. $(i\text{-Pr})_2NH$ was dried over KOH. BuLi was titrated before use, and concentrations were typically 1.4 to 1.7N. 5,5′-Dimethyl-2,2′-bipyridine [10], 6,6′-dimethyl-2,2′-bipyridine [11], 4,4′,6,6′-tetramethyl-2,2′-bipyridine [12] (m.p. 144–145°; ^{1}H-NMR (CD_2Cl_2): 8.04 (*s*, H–C(3), H–C(3′)); 6.99 (*s*, H–C(5), H–C(5′)); 2.54 (*s*, 2 Me); 2.34 (*s*, 2 Me)), and 4,4′,5,5′-tetramethyl-2,2′-bipyridine [12] (m.p. 250°, ^{1}H-NMR (CD_2Cl_2): 8.32 (*s*, H–C(6), H–C(6′)); 8.15 (*s*, H–C(3), H–C(3′)); 2.34 (*s*, 2 Me); 2.28 (*s*, 2 Me)) were prepared according to literature procedures. For 5,5′,6,6′-tetramethyl-2,2′-bipyridine the same procedure as in [12] was used, but the compound was purified by chromatography (SiO_2, 100% CH_2Cl_2 to 5% CH_3OH/CH_2Cl_2 gradient elution), m.p. 190°; ^{1}H-NMR (CD_2Cl_2): 8.12 (*d*, J = 7.8, H–C(3), H–C(3′)); 7.50 (*d*, J = 7.8, H–C(4), H–C(4′)); 2.53 (*s*, 2 Me); 2.31 (*s*, 2 Me). 2,9-Dimethyl-1,10-phenanthroline, 4-methyl-1,10-phenanthroline, 3,4,7,8-tetramethyl-1,10-phenanthroline, and α-picoline are commercially available. All products were purified by recrystallization (or distillation for α-picoline) and dried prior to use.

General Procedure. One equiv. of starting material (1-g scale) was dissolved in THF (100 ml degassed under Ar) to a 250-ml round bottom flask. One equiv. of LDA was added dropwise *via* a cannula at –80°. The final deep colors for the monocarbanion were as follows: red (for precursor of **1**); blue (**2**); orange-red (**3**); green (**4**); green (**5**); red (**6**); blue (**7**); green (**8**); orange (**9**). After stirring at –80° for 4 h under Ar, a degassed THF soln. (20 ml) containing 1 equiv. of the oxidant (Br_2, I_2, or 1,2-dibromoethane) was added dropwise. In most cases, the total addition of the oxidant resulted in disappearance of the color. After warming to *ca.* 0°, the mixture was quenched with H_2O (10 ml). The org. solvent was evaporated and the aq. phase extracted; CH_2Cl_2 (2 × 50 ml); dried ($MgSO_4$), and the solvent removed under vacuum. The coupling product was either purified by recrystallization or by chromatography (see below). The yields are listed in the *Table*.

1,2-Bis(5′-methyl-2,2′-bipyridin-5-yl)ethane (**1**). 5,5′-Dimethyl-2,2′-bipyridine (1 g, 5.4 mmol) afforded, after recrystallization of the crude product in CH_2Cl_2/hexane, compound **1** (0.55 g (56%) using Br_2 as an oxidant, 0.43 g (43%) with I_2, 0.75 g (75%) with $BrCH_2CH_2Br$) as white crystals. M.p. 214–216°. ^{1}H-NMR (CD_2Cl_2): 8.44 (*m*, 4 H, H–C(6,6′)); 8.28 (*m*, 4 H, H–C(3,3′)); 7.61 (*m*, 4 H, H–C(4,4′)); 3.02 (*s*, 2 CH_2); 2.37 (*s*, 2 Me). ^{13}C-NMR ($CDCl_3$, TMS): 154.55; 153.57; 149.59; 149.25; 137.43; 136.92; 135.84; 133.19; 120.48; 120.42; 34.34 (CH_2); 18.34 (CH_3). EI-MS: 366 (70, M^+), 183 (100, $M^+/2$). Anal. calc. for $C_{24}H_{22}N_4$: C 78.66, H 6.05, N 15.29; found: C 78.52, H 5.89, N 15.11.

1,2-Bis(6′-methyl-2,2′-bipyridin-6-yl)ethane (**2**). 6,6′-Dimethyl-2,2′-bipyridine (1 g, 5.4 mmol) afforded, on recrystallization of the crude product from hexane, compound **2** (0.67 g (68%) using Br_2, 0.7 g (70%) with $BrCH_2CH_2Br$) as white crystals. M.p. 131–133°. ^{1}H-NMR (CD_2Cl_2): 8.24 (*m*, 4 H, H–C(3,3′)); 7.68 (*t*, J = 7.8, 4 H, H–C(4,4′)); 7.17 (*m*, 4 H, H–C(5,5′)); 3.38 (*s*, 2 CH_2); 2.59 (*s*, 2 Me). ^{13}C-NMR ($CDCl_3$, TMS): 160.65; 157.76; 156.04; 155.87; 136.96; 123,03; 122.82; 118.42; 118.24; 37.74 (CH_2); 24.68 (CH_3). EI-MS: 366 (60, M^+), 197 (100). Anal. calc. for $C_{24}H_{22}N_4$: C 78.60, H 6.05; N 15.28; found: C 78.55, H 6.11, N 15.06.

1,2-Bis(9-methyl-1,10-phenanthrolin-2-yl)ethane (**3**). 2,9-Dimethyl-1,10-phenanthroline (3 g, 14.4 mmol) gave after reaction a yellowish solid which was purified by chromatography (SiO_2, 100% CH_2Cl_2 to 5% CH_3OH/CH_2Cl_2 gradient elution) to give **3** (1.6 g (54%) with Br_2, 1.95 g (66%) with $BrCH_2CH_2Br$) as a white solid. M.p. > 260°. ^{1}H-NMR (CD_2Cl_2): 8.19 (*d*, *J* = 5.0, 2 H, H–C(4) or H–C(7)), 8.15 (*d*, *J* = 4.9, 2 H, H–C(4) or H–C(7)); 7.73 (*s*, 4 H, H–C(5), H–C(6)); 7.70 (*d*, *J* = 8.3, 2 H, H–C(3) or H–C(8)); 7.52 (*d*, *J* = 8.2, 2 H, H–C(3) or H–C(8)); 3.76 (*s*, 2 CH_2); 2.91 (*s*, 2 Me). ^{13}C-NMR ($CDCl_3$, TMS): 162.14; 159.35; 136.57; 136.29; 127.32; 126.89; 125.63; 125.56; 123.48; 122.95; 39.24 (CH_2); 25.93 (CH_3). EI-MS: 414 (90, M^+), 221 (100). Anal. calc. for $C_{28}H_{22}N_4$: C 81.13, H 5.35, N 13.52; found: C 81.07, H 5.20, N 13.42.

1,2-Bis(1,10-phenanthrolin-4-yl)ethane (**4**). 4-Methyl-1,10-phenanthroline (1 g, 5.2 mmol) gave after reaction a dark residue which was chromatographed (Al_2O_3 neutral, 1% CH_3OH/CH_2Cl_2 to 5% CH_3OH/CH_2Cl_2 gradient elution) to give **4** (0.4 g (40%) with Br_2 0.33 g (33%) with I_2) as a pale yellow solid. M.p. 180–183° (dec.). ^{1}H-NMR (CD_2Cl_2): 9.13 (*dd*, *J* = 4.3, ^2J = 1.7, 2 H, H–C(9)); 8.98 (*d*, *J* = 4.5, 2 H, H–C(2)); 8.29 (*dd*, ^1J = 8.1, ^2J = 1.7, 2 H, H–C(7)); 7.67 (*AB*, *J* = 4.3, 2 H, H–C(5) or H–C(6)); 7.63 (*AB*, *J* = 4.3, 2 H, H–C(5) or H–C(6)); 7.65 (*dd*, ^1J = 8.1, ^2J = 4.3, 2 H, H–C(8)); 7.40 (*d*, *J* = 4.6, 2 H, H–C(3)); 1.67 (*s*, 2 CH_2). ^{13}C-NMR ($CDCl_3$, TMS): 150.58; 150.01; 146.39; 135.91; 128.18; 127.31; 126.65; 123.18; 121.57; 32.89 (CH_2). EI-MS: 386 (85, M^+), 193 (100, $M^+/2$). Anal. calc. for $C_{26}H_{18}N_4$: C 80.81, H 4.69, N 14.50; found: C 80.57, H 4.37, N 14.12.

1,2-Bis(3,7,8-trimethyl-1,10-phenanthrolin-4-yl)ethane (**5**). 3,4,7,8-Tetramethyl-1,10-phenanthroline (1 g, 4.2 mmol) gave, after recrystallization of the crude product in CH_2Cl_2/hexane 1:1, compound **5** (10.57 g, (57%) using Br_2, 0.67 g (67%) with $BrCH_2CH_2Br$) as white crystals. M.p. > 260°. ^{1}H-NMR (CD_2Cl_2): 8.86 (*s*, 2 H, H–C(9)); 8.83 (*s*, 2 H, H–C(2)); 8.04 (*s*, 4 H, H–C(5), H–C(6)); 3.54 (*s*, 2 CH_2); 2.68 (*s*, 6 H, CH_3–C(7)); 2.53 (*s*, 6 H, CH_3–C(8)); 2.38 (*s*, 6 H, CH_3–C(3)); proton relaxation times in s: T_1 3.32 (H–C(9)); 2.16 (H–C(2)); 0.78 (H–C(5), H–C(6)); 0.34 (CH_2); 0.98 (CH_3–C(7)); 0.74 (CH_3–C(8)); 0.71 (CH_3–C(3)). ^{13}C-NMR (CD_2Cl_2): 152.01; 151.62; 143.82; 141.46; 131.12; 130.52; 125.80; 126.42; 122.63; 121.41; 28.23 (CH_2); 17.31 (CH_3); 16.95 (CH_3); 14.34 (CH_3). EI-MS: 470 (80, M^+), 236 (100, $[M + H]^+/2$). Anal. calc. for $C_{32}H_{30}N_4$: C 81.67, H 6.43, N 11.91; found: C 81.73, H 6.68, N 11.94.

1,2-Bis(4′,5′,5-trimethyl-2,2′-bipyridin-4-yl)ethane (**6**). 4,4′,5,5′-Tetramethyl-2,2′-bipyridine (1 g, 4.7 mmol) gave, after recrystallization of the crude product from CH_2Cl_2/hexane 1:1, compound **6** (0.85 g (86%) using Br_2 0.76 g (77%) with I_2) as white crystals. M.p. > 260°. ^{1}H-NMR (CD_2Cl_2): 8.38 (*s*, 2 H, H–C(6)); 8.34 (*s*, 2 H, H–C(6′)); 8.26 (*s*, 2 H, H–C(3)); 8.17 (*s*, 2 H, H–C(3′)); 3.01 (*s*, 2 CH_2); 2.355 (*s*, 6 H, CH_3–C(4′), or CH_3–C(5)); 2.349 (*s*, 6 H, CH_3–C(4′) or CH_3–C(5)); 2.29 (*s*, 6 H, CH_3–C(5′)); proton relaxation time in s: T_1 3.01 (H–C(6)); 3.39 (H–C(6′)); 2.36 (H–C(3)); 3.59 (H–C(3′)); 0.67 (CH_2); 1.06 (CH_2); 1.06 (CH_3–C(4′) or CH_3–C(5)); 1.3 (CH_3–C(5′)). ^{13}C-NMR ($CDCl_3$, TMS): 154.78; 154.08; 150.22; 149.48; 149.19; 146.75; 132.24; 131.38; 121.58; 120.37; 32.67 (CH_2); 19.32 (CH_3); 16.34 (CH_3); 16.08 (CH_3). EI-MS: 422 (85, M^+), 211 (100, $M^+/2$). Anal. calc. for $C_{28}H_{30}N_4$: C 79.58, H 7.16, N 13.26; found: C 79.51, H 7.19, N 13.21.

1,2-Bis(5,5′,6′-trimethyl-2,2′-bipyridin-6-yl)ethane (**7**). 5,5′,6,6′-Tetramethyl-2,2′-bipyridine (0.5 g, 2.36 mmol) gave, after purification by chromatography (Al_2O_3 neutral, 2% CH_3OH/CH_2Cl_2), compound **7** (0.41 g (82%) using Br_2, 0.40 g (80%) with $BrCH_2CH_2Br$). M.p. 200–201°. ^{1}H-NMR (CD_2Cl_2): 8.14 (*d*, *J* = 7.9, 2 H, H–C(3)); 8.12 (*d*, *J* = 7.9, 2 H, H–C(3)); 7.52 (*d*, *J* = 7.9, 2 H, H–C(4)); 7.50 (*d*, *J* = 7.9, 2 H, H–C(4)); 3.36 (*s*, 2 CH_2); 2.54 (*s*, 6 H, CH_3–C(6′)); 2.35 (*s*, 6 H, CH_3–C(5)); 2.31 (*s*, 6 H, CH_3–C(5′)); proton relaxation time in s: T_1 3.74 (H–C(3)); 4.24 (H–C(3′)); 2.48 (H–C(4)); 3.32 (H–C(4′)); 0.94 (CH_2); 1.41 (CH_3–C(6)); 1.12 (CH_3–C(5)); 1.31 (CH_3–C(5′)). ^{13}C-NMR ($CDCl_3$): 159.03; 156.14; 153.39; 138.03; 137.77; 130.88; 130.74; 118.32; 117.89; 33.64 (CH_2); 22.83 (CH_3); 19.05 (CH_3); 18.62 (CH_3). EI-MS: 422 (100, M^+), 225 (60). Anal. calc. for $C_{28}H_{30}N_4$: C 79.58, H 7.16, N 13.26; found: C 78.04, H 6.65, N 15.03.

1,2-Bis(2,2′-pyridin-2-yl)ethane **8**. α-Picoline (1 g, 10.7 mmol) afforded, after recrystallization of the crude product in Et_2O, compound **9** (0.67 g (68%) using Br_2, 0.77 (78%) with $BrCH_2CH_2Br$) as white solid. M.p. 49–50°. ^{1}H-NMR ($CDCl_3$): 8.54 (*m*, 2 H, H–C(6)); 7.54 (*m*, 2 H, H–C(4)); 7.12 (*m*, 4 H, H–C(3), H–C(5)); 3.23 (*s*, 2 CH_2). ^{13}C-NMR ($CDCl_3$): 159.59 (CC); 147.70 (CH); 134.54 (CH); 121.32 (CH); 119.53 (CH); 36.60 (CH_2). EI-MS: 184 (65, M^+), 106 (100). Anal. calc. for $C_{12}H_{12}N_2$: C 78.23, H 6.56, N 15.21; found: C 78.04, H 6.65, N 15.03.

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