SHORT PAPER

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Synthesis of 4-aryl-butylamine fluorescent probes†

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A short synthesis of the fluorescent probes 4-(9-anthracenyl)butyl amine (three steps), 4-(9-phenanthrenyl)butyl amine (three steps) and 4-(1-pyrenyl)butyl amine (two steps) without chromatographic purification is described.

Keywords: 4-aryl-butylamine flourescent probes

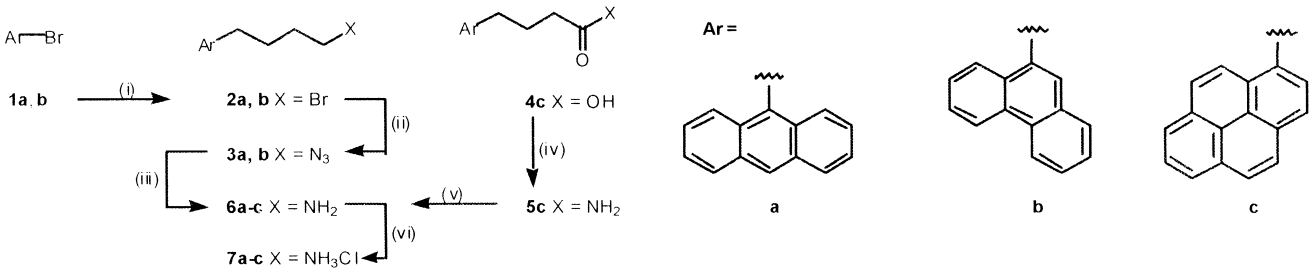
The use of fluorescent compounds as probes is of great importance in different fields because of their ability to provide information about the systems at the molecular level.[1–3] Many applications of fluorescence can be found in the literature, for example in the areas of chromatography,[4] combinatorial chemistry,[5] molecular biology and medicine,[6] as chemosensors,[7] and in material science.[8] Fluorescent compounds that can be covalently attached to the species to be studied, usually referred to as fluorescent labels, are particularly valuable because they can be used to obtain structural information about the samples. For example, if a block copolymer is labelled with appropriate fluorescent compounds at the junction between the blocks, one can determine the width of the interface between the core and corona in block copolymer micelles.[9] In the same way, one can characterise the compatibility of two polymers in a blend by labelling the blend components,[10] the interdiffusion in a polymer latex film leading to a mechanically rigid film,[11] the effects of polymer extrusion in a die wall,[12] *etc*.

Probes based on the aromatic hydrocarbons pyrene[13,14] anthracene[15] and phenanthrene[16] have been widely used because of their useful photophysic properties. Also, they are excellent in the study hydrophobic samples, and are chemically robust and resilient to photobleaching. The self quenching of pyrene leads to the formation of an excited dimer species (excimer) that emits light at a different wavelength form the isolated pyrene molecule.[17] Excimer formation has been used to study the dynamics and kinetics of different systems.[18] On the other hand, phenanthrene and anthracene form an efficient energy donor–acceptor pair. Phenanthrene transfers electronic energy to anthracene through a dipole–dipole coupling mechanism,[19] with a Förster radius of about 2.5 nm. This means that the phenanthrene fluorescence is altered whenever anthracene is within a distance of *ca* 0–7.5 nm. If different parts or components of a given sample are selectively labelled with these dyes, it is possible to obtain their spatial distribution over the sample volume.[9,10]

Although many fluorescent probes are commercially available,[2] the use of covalently attached probes requires that the dyes possess specific reactive groups that are attached in a particular way to the fluorescent moiety. For example, in some cases it is of crucial importance that the fluorescent probe is attached by a long enough alkyl chain in order that the fluorescent phenomena become less disturbed by electronic interaction with the species to which the dye is to be attached. Usually, such probes have to be tailor-made to meet the required specifications.

In the present work, we start from readily available commercial compounds containing the pyrene, phenanthrene and anthracene units, and envisage a simple methodology for the preparation of 4-aryl-butylamines as fluorescent probes containing an amine linker group and a butyl group spacer.

The 4-arylbutyl bromide **2a** was prepared in 47% yield by lithium–bromide exchange of 9-bromoanthracene **1a** followed by reaction with an excess of 1,4-dibromobutane using standard conditions.[16] This bromide was then converted into the corresponding azide **3a** in quantitative yield using a recently reported method (NaN_3 in DMSO)[20] followed by reduction under standard H_2/Pd/C conditions to give the amine **6a** which was then



Scheme 1

Reagents and conditions: i, Et_2O, *n*-BuLi (1.5 equiv), 0°C to r.t. then 1,4-dibromobutane (4.0 mol equiv), reflux, 2 h; **2a** (47 %), **2b** (48 %). ii, DMSO, NaN_3 (1.1 equiv), r.t., 19–23 h; quant. iii, EtOH, Pd/C (10 %), r.t., 72 h; quant. iv, CH_2Cl_2, $(COCl)_2$ (1.05 equiv), DMF (cat.), reflux, 1.5 h then NH_3 (excess), r.t., 80 %. v, THF, $BH_3.Me_2S$ (2.5 mol equiv), slow distillation, 1.5 h, 97 %. vi, Et_2O, HCl (excess), r.t.

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converted to the corresponding ammonium chloride **7a**. The above methodology was also applied to the preparation of the 4-(9-phenanthrenyl)butyl amine hydrochloride **7b** starting from 9-bromophenanthrene **1b**. This simple and short method (four steps) allowed the preparation of **7a** and **7b** with an overall yield of 35 and 41% respectively and without the need of chromatographic purification. The 4-(1-pyrenyl)butyl amine **6c** has been prepared in the literature from the corresponding alcohol by a three steps procedure in 53% overall yield.[13] By an alternative method we also prepared the amine **6c** by conversion of 1-pyrenebutyric acid **4c** into the corresponding amide **5c** followed by reduction with borane-dimethyl sulfide.[21] This simple overall 3 steps procedure allowed the preparation of the 4-(1-pyrenyl)butyl amine hydrochloride **7c** in 69% overall yield and also without chromatographic purification.

In summary, we have described convenient, simple and short procedures for the preparation of the fluorescent probes **7a–c** in moderate overall yields.

Experimental

All glassware was oven dried and cooled in a desiccator prior to use. Tetrahydrofuran (THF) and diethyl ether were pre-dried over sodium wire and distilled from sodium/benzophenone under dinitrogen. Dichloromethane was distilled from calcium hydride powder under dinitrogen. ^{1}H and ^{13}C NMR spectra were recorded on a Brüker AMX 400 spectrometer. Infrared spectra (IR) were recorded on a Mattson FT-IR Satellite 3000 spectrometer as thinly dispersed films (from dichloromethane) or as suspensions in Nujol. Thin layer chromatography (TLC) was carried out using MN Alugram® SIL G/ UV$_{254}$ (Art. 818133). The plates were visualised using ultraviolet light (254 nm). Melting points (uncorrected) were determined on a Electrothermal Mod. IA 6304 capillary melting point apparatus. Microanalyses were carried out at the Laboratório de Análises do Instituto Superior Técnico in Lisbon.

4-(9-anthracenyl)butyl bromide **2a**: To a stirred solution of 9-bromoanthracene **1a** (3.084 g, 11.99 mmol) in anhydrous diethyl ether (20 ml) under argon at 0°C was added dropwise (4 min) *n*-butyllithium (7.5 ml, 2.4 M in hexanes, 1.5 equiv) and the mixtune was stirred at r.t. for 75 min. 1,4-Dibromobutane (5.8 ml, 4.0 mol equiv) was added at once and the mixture refluxed for 2 h., then cooled to room temperature and partioned between dichloromethane (70 ml) and water (70 ml). The aqueous phase was extracted with dichloromethane (2 × 70 ml), the combined organic phase was dried with $MgSO_4$ and the solvent removed under reduced pressure to give a yellow liquid residue. *n*-Hexane (80 ml) was added and a slow formation of solid **2a** (1.772 g, 47%) was observed to give a slightly yellow powder; R_f = 0.38 (*n*-hexane), m.p. 113–114.5°C, m.p. 115–116°C (EtOH, white needles); IR (film) ν = 3079, 3052, 2948, 2924, 2888, 2868, 1622, 1445, 1352, 1224, 885, 732 cm^{-1}; δ_H (400 MHz; $CDCl_3$) 1.96–2.03 (m, 2H, $ArCH_2(CH_2)_2CH_2Br$), 2.10–2.19 (m, 2H, $ArCH_2(CH_2)_2CH_2Br$), 3.50 (t, 2H, *J* = 6.8 Hz, $ArCH_2$), 3.64 (t, 2H, *J* = 8.0 Hz, CH_2Br), 7.47–7.57 (m, 4H, Ar), 8.03 (d, 2H, *J* = 8.0 Hz, Ar), 8.27 (d, 2H, *J* = 8.8 Hz, Ar), 8.37 (s, 1H, Ar); δ_C (100 MHz; $CDCl_3$) 26.90, 29.60, 32.98, 33.46, 124.17, 124.79, 125.55, 125.84, 129.23, 129.50, 131.56, 134.13; Anal. calcd. for $C_{18}H_{17}Br$: C 69.02%; H 5.47%. Found: C 69.05%; H 5.50%.

4-(9-anthracenyl)butyl azide **3a**: 2a (1.546 g, 4.93 mmol) was added to a stirred solution of sodium azide (0.356 g, 1.1 equiv) in dimethyl sulfoxide (11 ml) at room temperature (water bath, 20°C). After 19 h, water (22 ml) was added (exothermic) and the precipitate was filtered to give **3a** (1.352, quant) as a yellow powder, R_f = 0.22 (*n*-hexane: dichloromethane 9.5:0.5); m.p. 78.5–79°C (*n*-hexane, white small needles, complete decomposition when attempted the dissolution of **3a** in refluxing ethyl acetate); IR (film) ν = 3081, 3053, 2941, 2862, 2094 (N_3), 1623, 1445, 1349, 1263, 884, 839, 731 cm–1; δ_H (400 MHz; $CDCl_3$) 1.82–1.96 (m, 4H, $ArCH_2(CH_2)_2CH_2N_3$), 3.35 (t, 2H, *J* = 6.4 Hz, CH_2N_3), 3.65 (t, 2H, *J* = 8.4 Hz, $ArCH_2$), 7.47–7.60 (m, 4H, Ar), 8.03 (d, 2H, *J* = 8.0 Hz, Ar), 6.26 (d, 2H, *J* = 8.8 Hz, Ar), 8.36 (s, 1H, Ar); δ_C (100 MHz; $CDCl_3$) 27.26, 28.25, 29.20, 51.30, 124.12, 124.77, 125.54, 125.82, 129.22, 129.48, 131.55, 134.15; Anal. calcd. for: $C_{18}H_{17}N_3$: C 78.52%; H 6.22%; N 15.3%. Found: C 78.49%; H 6.28%; N 15.1%.

4-(9-anthracenyl)butyl amine **6a**: A mixture of **3a** (1.186 g, 4.31 mmol) and Pd/C (10%, 0.0436 g) in absolute ethanol (80 ml) under dihydrogen (balloon) was stirred liquorously for 2.5 days at room temperature. The mixture was filtered, the filtrate washed with dichloromethane (20 ml), concentrated *in vacuo* to give **6a** (1.068 g, 99%) as a brown viscous liquid; IR (film) ν = 3368 (NH), 3299 (NH), 3081, 3052, 2928, 2857, 1623, 1469, 1445, 1350, 1158, 1012, 883, 840, 789, 732, 634, 602 cm^{-1}; δ_H (400 MHz; $CDCl_3$) 1.52 (br, 2H, NH_2), 1.69 (br, 4H, $ArCH_2(CH_2)_2CH_2NH_2$), 2.57 (br, 2H, CH_2NH_2), 3.48 (br, 2H, $ArCH_2$), 7.40–7.48 (m, 4H, Ar), 7.88 (d, 2H, *J* = 7.6 Hz, Ar), 8.18 (s, 1H, Ar), 8.21 (d, 2H, *J* = 8.8 Hz, Ar); δ_C (100 MHz; $CDCl_3$) 25.72, 27.89, 33.13, 41.22, 123.68, 124.09, 124.76, 124.99, 128.56, 128.86, 130.92, 134.24. To the above residue dissolved in anhydrous dichloromethane (20 ml) was bubbled HCl in excess. The solvent was evaporated, diethyl ether was added (30 ml, formation of solid) and the solid filtered to give 4-(9-anthracenyl)butyl amine hydrochloride **7a** (0.927 g, 75%) as a slightly yellow powder, m.p. 120°C (dec), 204–208°C; IR (nujol) ν = 3395 (NH), 2724, 1621, 1519, 1158, 1021, 883, 741, 728 cm^{-1}; δ_H (400 MHz; CD_3OD) 1.90 (br, 4H, $ArCH_2(CH_2)_2CH_2NH_2HCl$), 2.96 (br, 2H, CH_2NH_2HCl), 3.71 (br, 2H, $ArCH_2$), 7.48 (t, 2H, *J* = 7.2 Hz, Ar), 7.55 (td, 2H, *J* = 8.8, 1.2 Hz, Ar), 8.03 (d, 2H, *J* = 8.0 Hz, Ar), 8.33 (d, 2H, *J* = 8.8 Hz, Ar), 8.38 (s, 1H, Ar); δ_C (100 MHz; CD_3OD) 27.90, 28.81, 29.23, 40.79, 125.26, 125.90, 126.74, 126.96, 130.29, 130.92, 133.09, 134.94; *m/z* (FAB) 250 (MH^+), 233, 191; HRMS calcd. for $C_{18}H_{20}N$: 250.15957, found: 250.15876.

4-(9-phenanthrenyl)butyl bromide **2b**: Prepared as described for **2a** using 9-bromophenanthrene **1b** (2.508 g, 9.75 mmol). The crude product as a white solid was crystallised from ethyl acetate:methanol to give **2b** (1.468 g, 48%) as white cubes; R_f = 0.19 (*n*-hexane), m.p. 113.5–114°C, lit.[22] m.p. 114.5–116.5°C; IR (film) ν = 3076, 3047, 2946, 2917, 2857, 1627, 1598, 1434, 1247, 1196, 913, 748, 739, 723, cm^{-1}; δ_H (400 MHz; $CDCl_3$) 1.86–1.99 (m, 4H, $ArCH_2(CH_2)_2CH_2Br$), 3.06 (t, 2H, *J* = 7.2 Hz, $ArCH_2$), 3.39 (t, 2H, *J* = 6.8 Hz, CH_2Br), 7.48–7.60 (m, 5H, Ar), 7.75 (dd, 1H, *J* = 8.4, 1.2 Hz, Ar), 8.00 (dd, 1H, *J* = 6.0, 2.4 Hz, Ar), 8.58 (d, 1H, *J* = 7.6 Hz, Ar), 8.66 (dd, 1H, *J* = 7.2, 2.0 Hz, Ar); δ_C (100 MHz; $CDCl_3$) 28.57, 32.49, 32.69, 33.60, 122.44, 123.27, 124.28, 126.04, 126.19, 126.56, 126.63, 128.04, 129.69, 130.74, 131.08, 131.79, 135.86; Anal. calcd. for $C_{18}H_{17}Br$: C 69.02%; H 5.47%. Found: C 70.67%; H 5.87%

4-(9-phenanthrenyl)butyl azide **3b**: Prepared as described for **3a** using **2b** (1.312 g, 4.19 mmol); reaction time 23 h. **3a** (1.145 g, quant) was obtained as a yellow powder, R_f = 0.22 (*n*-hexane: dichloromethane 9.5:0.5), Rf = 0.60 (*n*-hexane: ethyl acetate 9.5:0.5); m.p. 77.5–78°C (EtOH, white small needles); IR (film) ν = 3076, 2942, 2861, 2096 (N_3), 1626, 1599, 1494, 1464, 1448, 1356, 1268, 885, 741 cm^{-1}; δ_H (400 MHz; $CDCl_3$) 1.62^{-1}.69 (m, 2H, $ArCH_2(CH_2)_2CH_2N_3$), 1.76–1.83 (m, 2H, $ArCH_2(CH_2)_2CH_2N_3$), 3.03 (t, 2H, *J* = 7.6 Hz, CH_2), 3.22 (t, 2H, *J* = 6.8 Hz, CH_2), 7.47–7.58 (m, 5H, Ar), 7.72 (dd, 1H, *J* = 6.8, 2.0 Hz, Ar), 7.97 (dd, 1H, *J* = 6.8, 2.4 Hz, Ar), 8.55 (d, 1H, *J* = 7.6 Hz, Ar), 8.63 (dd, 1H, *J* = 7.2, 2.0 Hz, Ar); δ_C (100 MHz; $CDCl_3$) 27.16, 28.90, 32.86, 51.36, 122.43, 123.28, 124.24, 126.04, 126.18, 126.56, 126.64, 128.04, 129.68, 130.74, 131.07, 131.79, 135.87; Anal. calcd. for $C_{18}H_{17}N_3$: C 78.52%; H 6.22%; N 15.26%. Found: C 78.50%; H 6.20%; N 15.01%.

4-(9-phenanthrenyl)butyl amine **6b**: Prepared as described for **6a** using **3b** (0.912 g, 3.31 mmol). The amine **6b** (0.820 g, 99%) was obtained as a slightly yellow powder, m.p. 215–218°C (dec); IR (nujol) ν = 3419 (NH), 2724, 2689, 1601, 1252, 1150, 1040, 1002, 945, 907, cm^{-1}; δ_H (400 MHz; $(CD_3)_2SO$) 1.68–1.87 (m, 4H, $ArCH_2(CH_2)_2CH_2NH_2$), 2.87 (dd, 2H, *J* = 7.2, 6.8 Hz, CH_2), 3.07 (dd, 2H, *J* = 8.0, 7.2 Hz, CH_2), 7.55–7.68 (m, 5H, Ar), 7.85 (dd, 1H, *J* = 6.8, 1.2 Hz, Ar), 8.10 (dd, 1H, *J* = 8.0, 3.6 Hz, Ar), 8.68 (d, 1H, *J* = 7.6 Hz, Ar), 8.77 (dd, 1H, *J* = 9.2, 3.6 Hz, Ar); δ_C (100 MHz; $(CD_3)_2SO$) 27.59, 27.99, 33.08, 40.04, 123.53, 124.35, 125.44, 127.02, 127.46, 127.67, 128.00, 129.07, 130.23, 131.29, 131.71, 132.51, 136.97; To the amine **6b** (0.316 g, 1.27 mmol) in methanol (20 ml) was bubbled HCl in excess. The solvent was evaporated, and the solid residue was crystallised from dichloromethane (20 ml) to give 4-(9-phenanthrenyl)butyl amine hydrochloride **7b** (0.309 g, 85%) as a white powder, m.p. 230(dec)–252°C (methanol: Et_2O); IR (nujol) ν = 3444, 2727, 1602, 1253, 1210, 1156, 1000, 946, 906, 790, 732 cm^{-1}; δ_H (400 MHz; $(CD_3)_2SO$) 1.72–1.80 (m, 4H, $ArCH_2(CH_2)_2CH_2NH_2HCl$), 2.82 (t, 2H, *J* = 7.2 Hz, CH_2), 3.12 (t, 2H, *J* = 6.8 Hz, CH_2), 7.60–7.71 (m, 5H, Ar), 7.91 (dd, 1H, *J* = 6.4, 2.0 Hz, Ar), 8.15 (t, 1H, *J* = 4.4 Hz, Ar), 8.78 (d, 1H, *J* = 8.0, Ar), 8.86 (dd, 1H, *J* = 5.2, 1.2 Hz, Ar); δ_C (100 MHz; $(CD_3)_2SO$) 26.81, 27.20, 32.24, 38.79, 122.87, 123.65, 124.64, 126.12, 126.45, 126.66, 127.05, 128.15, 129.30, 130.36, 130.80, 131.55, 136.10; *m/z* (FAB) 250 (MH^+), 233, 191, 176, 154; HRMS calcd. for $C_{18}H_{20}N$: 250.15958, found:250.15868.

4-(1-pyrenyl)butyric amide **5c**: To a stirred solution of 1-pyrenebutyric acid **4c** (4.279 g, 14.84 mmol) and anhydrous dimethylformamide

(cat. amount) in anhydrous dichloromethane (100 ml) under argon at r.t. was added dropwise oxalyl chloride (1.36 ml, 1.05 equiv). After 30 min (gas liberation after 2 min) the suspension was refluxed for 1.5 h. The yellow solution was cooled to room temperature and bubbled with NH_3 in excess (instantaneous formation of precipitate). The reaction mixture was partioned between water (300 ml) and ethyl acetate (500 ml). The aqueous phase was extracted with ethyl acetate (2×400 ml), the combined organic phase was dried with $MgSO_4$, the solvent removed under reduced pressure and the solid product was crystallised from ethyl acetate (400 ml): *n*-hexane (100 ml) to give **5c** (2.875 g, 67%) as slightly yellow small needles; m.p. 180–181°C, m.p. 181.5–182°C (after three crystallisations); $R_f = 0.72$ (ethyl acetate: ethanol 9.5: 0.5). The mother fraction was crystallised from ethyl acetate: *n*-hexane to give more **5c** (0.553 g, 13.0%); m.p. 180–182°C; IR (nujol) $\nu = 3400$ (NH), 3200 (NH), 1650 (C = O), 1615, 1304, 1179, 837, 721 cm^{-1}; δ_H (400 MHz; $CDCl_3$) 2.20–2.27 (m, 2H, $ArCH_2CH_2$), 2.34 (t, 2H, $J = 6.9$ Hz, CH_2CONH_2), 3.43 (t, 2H, $J = 7.5$ Hz, $ArCH_2$), 5.35 (br, 2H, $CONH_2$), 7.87 (d, 1H, $J = 7.8$ Hz, Ar), 7.80 (t, 1H, $J = 7.6$ Hz, Ar), 8.03 (s, 2H, Ar), 8.11 (d, 2H, $J = 9.0$ Hz, Ar), 8.17 (dd, 2H, $J = 7.6$, 2.4 Hz, Ar), 8.31 (d, 1H, $J = 9.2$ Hz, Ar); δ_C (100 MHz; $(CD_3)_2SO$) 27.54, 32.46, 34.92, 123.86, 124.53, 124.62, 125.13, 125.27, 126.46, 126.84, 127.56, 127.81, 127.85, 128.54, 129.67, 130.81, 131.27, 137.00, 174.61; Anal. calcd. for $C_{20}H_{17}NO$: C 83.60%; H 5.96%; N 4.87%. Found: C 83.83%; H 6.00%; N 5.00%.

4-(1-pyrenyl)butyl amine ***6c****:* To stirred reflux solution of **5c** (3.154 g, 11.0 mmol) in anhydrous tetrahydrofuran (17 ml) under argon was added dropwise (30 min) $BH_3.Me_2S$ (2.7 ml, 2.5 mol equiv, gas liberation) and the mixture was distilled slowly Me_2S / tetrahydrofuran (8 ml) for 1.5 h. The reaction mixture was cooled to r.t., then methanol (4.5 ml, 3 mol equiv) was added dropwise (vigorous gas liberation) and the reaction mixture was poured into an aqueous HCl solution (3M, 100 ml, pH < 4, formation of precipitate). The mixture was cooled (ice/water bath), basified with aqueous NaOH solution (pH > 9), extracted with diethyl ether (3×100 ml). The combined organic phase was dried with $MgSO_4$ and the solvent removed under reduced pressure to give **6c** (2.916 g, 97%) as a yellow viscous liquid; identical spectral data to those previously reported.[13] To the amine dissolved in anhydrous diethyl ether (50 ml), was bubbled HCl in excess (formation of precipitate) and the mixture was filtered to give 4-(1-pyrenyl)butyl amine hydrochloride **7c** (2.942 g, 89%) as brown cubes; m.p. 232(dec)–259°C; IR (nujol) $\nu = 3381$ (NH), 3171, 2725, 1602, 1156, 958, 841, 722 cm^{-1}; δ_H (400 MHz; $(CD_3)_2SO$) 1.69–1.76 (m, 2H, $ArCH_2(CH_2)_2$), 1.79–1.86 (m, 2H, $ArCH_2(CH_2)_2$), 2.82 (t, 2H, $J = 7.3$ Hz, CH_2NH_2HCl), 3.33 (t, 2H, $J = 7.5$ Hz, $ArCH_2$), 7.94 (d, 1H, $J = 7.8$ Hz, Ar), 8.04 (t, 1H, $J = 7.6$ Hz, Ar), 8.11 (dd, 2H, $J = 10.6$, 9.0 Hz, Ar), 8.20 (dd, 2H, $J = 9.2$, 7.2 Hz, Ar), 8.25 (dd, 2H, $J = 7.4$, 5.2 Hz, Ar), 8.33 (d, 1H, $J = 9.3$ Hz, Ar); δ_C (100 MHz; $(CD_3)_2SO$) 27.23, 28.42, 32.23, 38.81, 123.85, 124.51, 124.60, 125.14, 125.27, 126.50, 126.89, 127.60, 127.82, 128.47, 129.68, 130.79, 131.27, 136.81; Anal. calcd. for $C_{20}H_{20}NCl$: C 77.53%; H 6.51%; N 4.52%. Found: C 77.70%; H 6.55%; N 4.53%.

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