Synthesis of Sufactant Tetracyanoanthraquinodimethanes for Conducting Langmuir–Blodgett Films

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The synthesis of surfactant 11,11,12,12-tetracyanoanthraquinodimethanes (TCNAQ) (**2a**–**h**) with different hydrophilic groups such as amino, sulfonyl and carbonyl at the head of long-chain substituents is described. Highly homogeneous conducting Langmuir–Blodgett (LB) films with stable conductivities of 1–5 S cm^{-1} are obtained when using binary mixtures of surfactant TCNAQ (**2c**,**d**,**f**) as acceptors and surfactant tetrathiafulvalenes as donors.

Conducting Langmuir–Blodgett films with high quality of film morphology, possessing reproducible and stable properties, are interesting in view of the development of molecular electronics. For the creation of charge–transfer complexes with the purpose of obtaining conducting LB films, surfactant tetracyanoquinodimethanes (TCNQs) with long-chain alkylic substituents are used as acceptors. The conductivity of such films obtained from mixtures of surfactant TCNQ molecules and surfactant tetrathiafulvalenes as donors is *ca.* 1 S cm^{-1}.[1] Molecules of TCNQ show poor hydrophilic properties and heterogeneous monolayers are formed for this reason owing to a high crystallization tendency and bad spreading. Therefore, LB films of surfactant TCNQ molecules are deposited unsatisfactorily on solid substrates.[2] The synthesis of new surfactant acceptors for the creaction of conducting LB films with excellent morphology, high values of conductivity and stable properties is a very worthwhile goal.

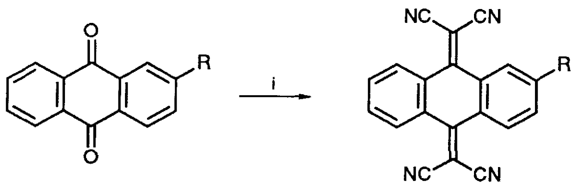
TCNQ was found to be an electron acceptor with an electron affinity of 2.7–2.8 eV.[3] The electron affinity of TCNAQ is lower than that of TCNQ, but the stability of TCNAQ is greater. The introduction of hydrophilic groups such as amino, sulfonyl or carbonyl into the head of a long-chain substituent can improve molecular spreading on water subphases. In addition, the presence of an electron-withdrawing group such as sulfonyl or carbonyl at the head of a long-chain substituent increases the electron affinity of the molecule.

In this work the synthesis of surfactant acceptors with different hydrophilic groups such as amino, sulfonyl or carbonyl at the head of a long-chain substituent linked to a TCNAQ fragment is reported. The investigation of the surfactant properties of compounds **2a**–**h** as a function of hydrophilic groups (amino, sulfonyl or carbonyl) at the head of the hydrocarbon chain is presented. The possibility of a highly-conducting LB film resulting from the mixture of surfactant TCNAQ molecules (**2c**, **d**, **f**) and surfactant tetrathiafulvalenes is shown.

Results

Surfactant 11,11,12,12-tetracyanoanthraquinodimethanes (**2a**–**h**) were synthesized by Knovenagel condensation of surfactant anthraquinodimethanes (**1a**–**h**) with malononitrile. By a modification of a well-known procedure[4] and optimization of reaction conditions an excellent, high-yielding synthesis of compounds **2a**–**h** was achieved.

All compounds are characterized by their ^{1}H NMR and IR-spectra as well as by microanalytical data (Tables 1 and 2). For an investigation of the surfactant properties of acceptors **2a**–**h**, solutions of these compounds (0.3 mg cm^{-3}) were prepared in hexane–chloroform (2:1). The deposition of multilayers was carried out by the Langmuir–Blodgett technique. Pure distilled water was used as a subphase. The ratio of donor and acceptor molecules in the mixture used varied from 2:0.5 to 0.5:2. Because the formation of conducting films of charge–transfer complexes is very complicated and delicate we controlled the following two parameters: the film conductivity and the presence of a separate phase for the donor or acceptor surplus in the electron diffraction patterns of the films obtained. The empirically-chosen optimum ratio of 1.5:1 was used by us due to the higher value of the film conductivity on the one hand, and the absence of precipitation of the second phase in electron diffraction patterns of the films on the other hand. The surface pressure was maintained at 20–22 mN m^{-1} and the speed of substrate dipping was 0.5–1.0 cm min^{-1}. Conducting LB films were deposited on sapphire substrates with a system of chromium electrodes.



1a-h **2a-h**

R

a $NHCO_{15}H_{31}$
b $NHCOC_{19}H_{39}$
c $CONHC_{18}H_{37}$
d $SO_2NHC_{18}H_{37}$

R

e $SO_2OC_{17}H_{35}$
f $CO_2C_{17}H_{35}$
g $CO_2C_{12}H_{25}$
h $CO_2C_8H_{17}$

Scheme 1 *Reagents and conditions:* i, $CH_2(CN)_2$, $TiCl_4$, pyridine/$C_2H_4Cl_2$, reflux 5 min

The conductance of the LB films consisting of 4–20 monolayers deposited on hydrophobic sapphire substrates with chromium electrodes was measured by a two-probe technique. The distribution of current in the normal direction was estimated due to the fact that we studied multilayers with different thicknesses. The resistance of the film-electrode junction was calculated approximately by using data obtained from different samples with the distance between the electrodes varying from 0.02–1 mm. Taking these data into account we calculated the values of conductivity, only attributing them to conducting areas because in this case it is possible to compare the properties of LB films with different thicknesses of monolayers (as well as the properties of the films) with those of normal conducting materials. The thickness of the conducting area was estimated using the model we constructed in agreement with the data on molecule length and on area per molecule.

Table 1 ^{1}H NMR spectroscopic data for compounds **1a–h** and **2a–h**

	δ (ppm)						
Compound	1-H	3-H	4-H	5,8-H	6,7-H	2-R	*J*/Hz
1a^a	8.46 (d)	8.09 (dd)	8.16 (d)	8.16–8.22 (m)	7.90–7.94 (m)	10.54 (1 H, s, NH), 2.39 (2 H, t,), 1.62 (2 H, m), 1.20 (24 H, m), 0.83 (3 H, m)	$J_{1,3}$ = 1.93 $J_{3,4}$ = 8.77
1b^a	8.44 (d)	8.07 (dd)	8.15 (d)	8.17–8.21 (m)	7.86–7.91 (m)	10.28 (1 H, s, NH), 2.38 (2 H, t), 1.64 (2 H, m), 1.22 (32 H, m), 0.84 (3 H, m)	$J_{1,3}$ = 2.19 $J_{3,4}$ = 8.41
1c^{a,c}	8.63	8.3	8.3	8.20–8.30 (m)	7.80–7.90 (m)	3.32 (2 H, m), 1.59 (2 H, m), 1.27 (18 H, s), 0.84 (3 H, m)	
1d^b	8.77 (d)	8.26 (dd)	8.48 (d)	8.30–8.40 (m)	7.80–7.90 (m)	4.52 (1 H, s, NH), 3.04 (2 H, m), 1.92 (2 H, m), 1.49 (2 H, m), 1.25 (30 H, m), 0.88 (3 H, m)	$J_{1,3}$ = 1.71 $J_{3,4}$ = 8.30
1e^a	8.44 (d)	8.09 (dd)	8.21 (d)	8.20–8.30 (m)	7.80–7.90 (m)	4.26 (2 H, t), 1.67 (2 H, *m*), 1.25 (32 H, m), 0.85 (3 H, m)	$J_{1,3}$ = 1.83 $J_{3,4}$ = 8.40
1f^a	8.69 (d)	8.40 (dd)	8.32 (d)	8.22–8.26 (m)	7.92–7.97 (m)	4.37 (2 H, m), 1.77 (2 H, m), 1.25 (28 H, m), 0.84 (3 H, m)	$J_{1,3}$ = 1.47 $J_{3,4}$ = 8.40
1g^b	8.94 (d)	8.44 (dd)	8.38 (d)	8.30–8.40 (m)	7.80–7.90 (m)	4.40 (2 H, t), 1.83 (2 H, m), 1.26 (18 H, m), 0.87 (3 H, m)	$J_{1,3}$ = 1.71 $J_{3,4}$ = 8.06
1h^b	8.94 (d)	8.44 (dd)	8.38 (d)	8.30–8.40 (m)	7.80–7.90 (m)	4.40 (2 H, t), 1.83 (2 H, m), 1.31 (10 H, m), 0.89 (3 H, m)	$J_{1,3}$ = 1.71 $J_{3,4}$ = 8.06
2a^a	8.66 (d)	7.92 (dd)	8.21 (d)	8.20–8.28 (m)	7.81–7.86 (m)	10.64 (1 H, s, NH), 2.40 (2 H, m), 1.60 (2 H, m), 1.22 (24 H, m), 0.85 (3 H, m)	$J_{1,3}$ = 1.46 $J_{3,4}$ = 8.41
2b^a	8.61 (d)	7.92 (dd)	8.18 (d)	8.21–8.27 (m)	7.77–7.82 (m)	10.37 (1 H, s, NH), 2.38 (2 H, t), 1.62 (2 H, t), 1.24 (32 H, m), 0.85 (3 H, m)	$J_{1,3}$ = 1.83 $J_{3,4}$ = 8.77
2c^a	8.69 (d)	8.21 (dd)	8.34 (d)	8.20–8.30 (m)	7.70–7.80 (m)	8.78 (1 H, s, NH), 3.32 (2 H, m), 1.59 (2 H, m), 1.22 (32 H, m), 0.84 (3 H, m)	$J_{1,3}$ = 1.47 $J_{3,4}$ = 8.04
2d^b	8.68 (d)	8.20 (dd)	8.37 (d)	8.25–8.30 (m)	7.77–7.82 (m)	4.69 (1 H, s, NH), 3.10 (2 H, t), 1.24 (32 H, m), 0.88 (3 H, m)	$J_{1,3}$ = 1.83 $J_{3,4}$ = 8.41
2e^a	8.51 (d)	7.99 (dd)	8.20 (d)	8.20–8.30 (m)	7.80–7.90 (m)	4.25 (2 H, t), 1.67 (2 H, t), 1.25 (28 H, m), 0.86 (3 H, m)	$J_{1,3}$ = 1.46 $J_{3,4}$ = 8.40
2f^a	8.80	8.38	8.38	8.20–8.30 (m)	7.80–7.90 (m)	4.35 (2 H, m), 1.73 (2 H, m), 1.25 (28 H, s), 0.84 (3 H, m)	
2g^b	8.90	8.3	8.37	8.20–8.30 (m)	7.70–7.80 (m)	4.39 (2 H, m), 1.80 (2 H, s), 1.27 (18 H, s), 0.88 (3 H, m)	
2h^b	8.90 (d)	8.39 (dd)	8.32 (d)	8.20–8.30 (m)	7.70–7.80 (m)	4.40 (2 H, m), 1.80 (2 H, m), 1.31 (10 H, m), 0.89 (3 H, m)	$J_{1,3}$ = 1.0 $J_{3,4}$ = 8.80

^{a} In [$^2H_6$]DMSO. ^{b} In $CDCl_3$. ^{c} NH exchanges with ND.

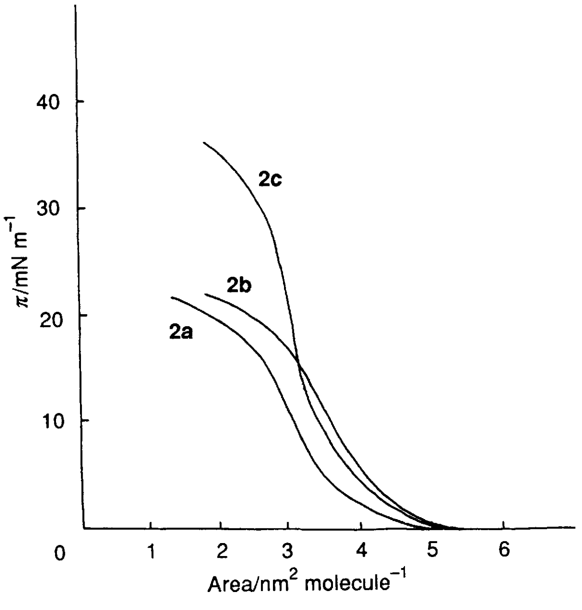


Fig. 1 Surface pressure (π) *vs.* surface area isotherms for **2a–c**

To investigate the influence of a hydrophilic amino group at the head of a long-chain substituent on the surfactant properties of an acceptor, 2-(pentadecylcarbonylamino)anthraquinone (**1a**) and 2-(nonadecylcarbonylamino)anthraquinone (**1b**) were synthesized from commercial 2-aminoanthraquinone and then converted into **2a**, **b**. Surface pressure–area isotherms for **2a**, **b** are presented in Fig. 1. It is obvious that **2a**, **b** possess poor surfactant properties. Low collapse pressures pointed out the impossibility of depositing satisfactory LB films onto the substrate. The character of the surface pressure–area isotherm of **2b** shows that an increase in hydrocarbon chain length leads to no noticeable improvement in surfactant properties. At a deposition pressure of *ca.* 10 mN m^{-1} the films were obtained by the Langmuir–Schaefer technique, but the quality of these films was very poor owing to the instability of the monolayer at low pressure. We supposed that the hydrophilic and electron-donating amino group linked to the TCNAQ fragment is conjugated to the latter owing to a redistribution of electron density. Therefore, we decided to synthesise the acceptor with an amino group separated from the TCNAQ fragment by some other group.

Compound **2c** differs from **2a**, **b** by arrangement order of the amino and carbonyl groups. The collapse pressure for the monolayer of surfactant compound **2c** (Fig. 1) is considerably higher than that for **2a**, **b** and is *ca.* 30 mN m^{-1}. The deposition of multilayers by the Langmuir–Blodgett technique resulted in LB films with homogeneous thickness and good morphology. The films were checked by visual observation, which resulted in a film possessing homogeneous interference colour, and optical (× 300) and transmission electron microscopy which show the absence of bulk crystals inserted into the LB film obtained in this way.

To investigate the influence of the sulfonyl group at the head of a long-chain substituent on surfactant properties, some derivatives of anthraquinone were synthesized from anthraquinone-2-sulphonic acid chloride and then transformed into **2d**, **e**. The nature of the surface pressure–area isotherm of compound **2d** (Fig. 2) corresponds to the viscous aggregation of surfactant molecules at the air–water interface, but this does not prevent the deposition of LB films by an LB technique. Deposition of the monolayer onto the solid substrates was carried out at a constant surface pressure of 22 mN m^{-1}, the area

Table 2 Yields and analytical and spectroscopic data for compounds **1a–h** and **2a–h**

Compound	Molecular formula[a]	Yield (%)	M.p./°C (decomp.)	ν_{max}/cm^{-1} [b]
1a	$C_{30}H_{39}NO_3$ 461.5	90	186–187	3355 (NH), 1720, 1675 (C=O)
1b	$C_{34}H_{47}NO_3$ 517.5	92	187–188	3350 (NH), 1720, 1675 (C=O)
1c	$C_{33}H_{45}NO_3$ 503.5	95	154–155	3365 (NH), 1680, 1655 (C=O)
1d	$C_{32}H_{45}NO_4S$ 549.5	86	148–149	3300 (NH), 1680 (C=O), 1570 (S=O)
1e	$C_{31}H_{42}NO_5S$ 536.5	84	115–116	1680 (C=O), 1570 (S=O)
1f	$C_{32}H_{42}O_4$ 504.5	96	98–99	1735, 1680 (C=O)
1g	$C_{27}H_{32}O_4$ 434.4	96	96–97	1735, 1680 (C=O)
1h	$C_{23}H_{24}O_4$ 378.4	98	86–87	1735, 1680 (C=O)
2a	$C_{36}H_{39}N_5O$ 557.6	97	195–196	3310 (NH), 2240 (C≡N)
2b	$C_{40}H_{47}N_5O$ 613.7	96	208–209	3260 (NH), 2232 (C≡N), 1680 (C=O)
2c	$C_{39}H_{45}N_5O$ 599.7	98	116–117	3300 (NH), 2230 (C≡N), 1650 (C=O)
2d	$C_{38}H_{45}N_5O_2S$ 645.7	98	224–225	3300 (NH), 2230 (C≡N), 1580 (S=O)
2e	$C_{37}H_{42}N_4O_3S$ 632.7	96	304–305	2235 (C≡N), 1575 (S=O)
2f	$C_{38}H_{42}N_4O_2$ 600.6	97	102–103	2237 (C≡N), 1730 (C=O)
2g	$C_{33}H_{32}N_4O_2$ 530.5	98	118–119	2237 (C≡N), 1735 (C=O)
2h	$C_{29}H_{24}N_4O_2$ 474.5	98	126–127	2237 (C≡N), 1735 (C=O)

[a] All compounds gave satisfactory elemental analyses. [b] Nujol.

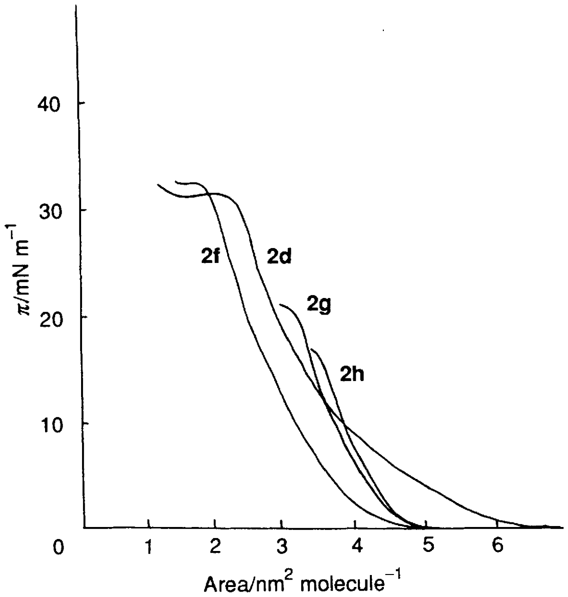


Fig. 2 Surface pressure (π) *vs.* surface area isotherms for **2d**, **f**, **h**, **h**

per molecule in the monolayer being equal to 3.7 nm^2. All LB films obtained are of highly homogeneous thickness. Because only a single monolayer is transferred to the substrate during one act of deposition, the transfer ratio is 1 in this case and was determined as the reduction in area of the floating film per deposition cycle compared with the substrate-coated area.

The introduction of a sulfonyloxy fragment instead of a sulfonylamino group in compound **2e** resulted in lower solubility of this compound. We could not obtain monolayers of surfactant compound **2e** because of its low solubility in hexane–chloroform mixtures.

For an investigation of the influence of a carbonyl group at the head of a long-chain substituent on the surfactant properties of the acceptor we synthesized compound **1f** from anthraquinone-2-carboxylic acid chloride which was then transformed into **2f**.

It appeared that surfactant compound **2f** formed LB films of excellent quality. The apparently high spreading tendency of **2f** may be connected with the presence of an oxycarbonyl group at the head of a long-chain substituent, which increases the hydrophilic properties of the compound. LB films of high quality and uniform morphology were obtained at a deposition pressure of 20 mN m^{-1}; the area per molecule is *ca.* 3.7 nm^2.

To investigate the dependence of surfactant properties on the length of the hydrophobic tail, compounds **2g**, **h** were synthesized in analogy to **2f**. The surface pressure–area isotherms of compounds **2g**, **h** (Fig. 2) show that a decrease in the length of the hydrocarbon chain from $C_{17}H_{35}$ to $C_{12}H_{25}$ leads to lower collapse pressures and makes the deposition of LB-films of satisfactory quality impossible.

Compounds **2c**, **d**, **f** with good surfactant properties may be used as acceptors for obtaining conducting LB films in mixtures with surfactant tetrathiafulvalenes as donors. Our investigations show that the LB films of acceptors **2c**, **d**, **f** do not have their own conductivity as well as surfactant TCNQ. Investigations on the conducting properties of acceptors **2c**, **d**, **f** in mixtures with hexadecylbis(ethylenedithio)tetrathiafulvalene and hexadecylethylenedithiopropylenedithiotetrathiafulvalene were carried out according to the literature method.[5] It was shown that compound **2c** in a mixture with tetrathiafulvalene derivatives gives LB films of homogeneous morphology and conductivity of *ca.* 0.1–0.5 S cm^{-1} which are stable for at least 3 months. Compounds **2d**, **f** in the mixture with tetrathiafulvalene derivatives yielded LB films of excellent quality having a stable conductivity of 1–5 S cm^{-1}. The fact that the conductivity of LB films formed from a mixture of acceptors **2d**, **f** with tetrathiafulvalene derivatives is about ten times higher than that of LB films obtained from a mixture of acceptor **2c** with tetrathiafulvalene derivatives can perhaps be explained by the fact that the electron affinity of acceptors **2d**, **f** is higher than that of **2c**.

The results of our study show that the presence of carbonyl or sulfonyl groups at the head of a long-chain substituent leads to an improvement in the spreading ability of surfactant compounds on a water surface. Homogeneous LB films with good morphology are formed as a result. Conducting LB films with a conductivity of *ca.* 1–5 S cm^{-1} were formed from mixtures of molecules **2d**, **f** as acceptors and tetrathiafulvalene derivatives as donors.*

Experimental

All starting reagents were purchased from Merck or Aldrich Chemical Co. Compounds used in the preparation of LB films were purified by HPLG chromatography (Waters 600E, Millipore). NMR spectra were recorded on a Bruker WP-200-SY spectrometer at 200 MHz with tetramethylsilane as internal standard. IR spectra were determined on a UR-20 spectrometer.

The chlorides of hexanoic acid, eicosoic acid and anthraquinone-2-carboxylic acid were prepared according to a literature procedure.[6] The chlorides of anthraquinone-2-sulfonic acid were also prepared according to a literature procedure.[7]

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* Our results on the investigation of other physical properties of LB films described were presented at the Vth International Conference on Langmuir–Blodgett Films, Paris, France, 1991.

Preparation of Anthraquinones **1a**–**h**.—2-(*Pentadecylcarbonylamino*)*anthraquinone* **1a**. A solution of 2-aminoanthraquinone (10.0 mol) and hexadecanoic acid chloride (10.1 mmol) in a mixture of dimethylformamide (2 cm^3) and chlorobenzene (50 cm^3) was refluxed for 1.5 h. The solution was cooled to room temperature and the resulting precipitate was filtered and washed with toluene. Recrystallization from methanol resulted in **1a**.

2-(*Nanodecylcarbonylamino*)*anthraquinone* **1b** was prepared as for **1a**.

2-(*Octadecylaminocarbonyl*)*anthraquinone* **1c**. Anthraquinone-2-carboxylic acid chloride (10.0 mmol) and octadecylamine (10.0 mmol) were refluxed for 3 h in chloroform. The resulting solution was cooled to room temperature and evaporated under reduced pressure. Recrystallization from methanol yielded **1c**.

2-(*Octadecylaminosulfonyl*)*anthraquinone* **1d**. To a mixture of anthraquinone-2-sulfonic acid chloride (10.0 mmol) and octadecylamine (10.0 mmol) in chloroform (100 cm^3) was added pyridine (0.8 cm^3) and the mixture was refluxed for 4 h. The solution was cooled to room temperature and evaporated under reduced pressure. Recrystallization from methanol resulted in **1d**.

2-(*Heptadecyloxysulfonyl*)*anthraquinone* **1e**. To a solution of anthraquinone-2-sulphonic acid chloride (5.0 mmol) and heptadecan-1-ol (5.0 mmol) in dimethylformamide (15 cm^3) was added pyridine (0.3 cm^3) and the mixture was stirred at 50–60 °C for 2 h. The solution was cooled to room temperature and poured into water (100 cm^3). The resulting precipitate was filtered, washed with water and dried. Recrystallization from methanol yielded **1e**.

2-(*Heptadecyloxycarbonyl*)*anthraquinone* **1f**. Anthraquinone-2-carboxylic acid chloride (10.0 mmol) and heptadecan-1-ol (10.0 mmol) in CCl_4 (50 cm^3) were refluxed for 0.5 h. The solution was cooled to room temperature and evaporated under reduced pressure. Recrystallization from methanol yielded **1f**.

2-(*Dodecyloxycarbonyl*)*anthraquinone* **1g** *and* 2-(*octyloxycarbonyl*)*anthraquinone* **1h**. These were prepared as for **1f**.

Surfactant 11,11,12,12-*Tetracyanoanthraquinodimethanes* **2a**–**h**. *General Procedure*.—To a solution of **1a**–**h** (1 mmol) and malononitrile (5 mmol) in dry dichloroethane (50 cm^3) was added $TiCl_4$ (2 cm^3) at 0 °C and pyridine (4 cm^3) was added dropwise over 20 min. The ice-bath was removed and the mixture was refluxed for 5 min. The mixture was then cooled to room temperature and the solvent was evaporated under reduced pressure. The residue was treated with 15% aqueous HCl solution with vigorous stirring until the residue had dissolved. The resulting solution was extracted with chloroform, and the chloroform extracts were washed with water several times, dried and evaporated under reduced pressure. Recrystallization from methanol yielded **2a**–**h**.

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