Synthesis of *N*-(2-hydroxyphenyl)-1,8-naphthalimide and its derivatization at the hydroxy group

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The reaction of 1,8-naphthalic anhydride with 2-aminophenol afforded *N*-(2-hydroxyphenyl)-1,8-naphthalimide, which was then derivatized at the hydroxy group.

Key words: *N*-(2-hydroxyphenyl)-1,8-naphthalimide, alkylation, phenols, [2+3]-cycloaddition, 1,2,3-triazoles, polynaphthalimides.

N-Aryl-1,8-naphthalimides may be of interest as compounds modeling the structure of the repeating units of the corresponding polynaphthalimides (PNI) based on 1,4,5,8-napthalenetetracarboxylic acid dianhydride and aromatic diamines. The data obtained in investigations of the synthesis of model functional naphthalimides and their chemical modifications are useful for the estimation of the optimal conditions for the polycondensation followed by polymer-analogous reactions of the target PNI. These polymers are characterized by high oxidative and thermal stability and good film formation and, in the presence of ionogenic groups, show promise as membranes in low-temperature fuel cells.[1] Studies of the three-dimensional structures of model naphthalimide molecules provide information on the three-dimensional structures of the repeating units in PNI. In addition, *N*-aryl-1,8-naphthalimides have fluorescence properties and can emit radiation in the UV region due to which they are of interest as fluorescent dyes.[2]

In the present study, we investigated the possibility of derivatization of *N*-(2-hydroxyphenyl)-1,8-naphthalimide (**1**) with sulfo- and carboxy-substituted alkyl and aryl moieties. Earlier, compound **1** (see Ref. 3) and some its analogs[2] have been synthesized by heating the starting anhydride and the corresponding primary amine in pyridine in the presence of zinc acetate and 4 Å molecular sieves. Evidently, the above-described method is unsuitable for the synthesis of PNI because the latter are insoluble in pyridine. In addition, the fact that the final products were isolated from the reaction mixture by chromatography indicates that side reactions occur.

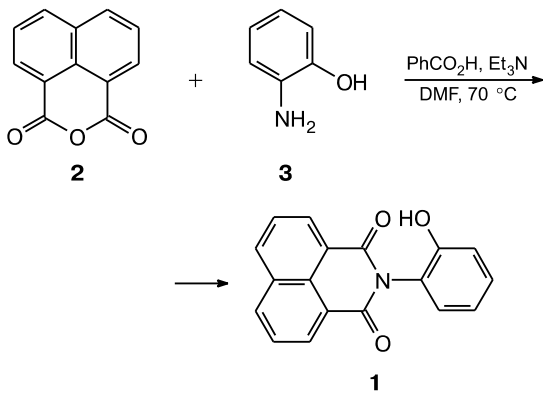
Certain naphthalimides and PNI can be easily prepared by performing the reactions in phenols in the presence of a carboxylic acid and an organic base as the catalysts.[4] However, a serious drawback of this method is that it requires the use of toxic and aggressive phenols as solvents.

The synthesis of PNI can be performed in dipolar aprotic solvents, but, as a rule, PNI are insoluble in these solvents. However, earlier it has been found that the presence of certain substituents, in particular, the hydroxy group (that is present in the starting amine as well) in PNI can substantially improve the solubility of the polymers, and in this case the synthesis can be carried out in dipolar aprotic solvents.[4]

Hence, we chose *N*-(2-hydroxyphenyl)-1,8-naphthalimide (**1**) as the model compound for PNI with hydroxy groups, the conditions of its synthesis being similar to the conditions of the polymer synthesis (dipolar aprotic solvents, heating, and the catalysis by a carboxylic acid—organic base system, in the absence of which high-molecular-weight PNI cannot be synthesized).[1,4]

In the present study, we found that imide **1** can be synthesized in quantitative yield by the reaction of 1,8-naphthalenedicarboxylic acid anhydride (**2**) with 2-aminophenol (**3**) in DMF upon heating (60—120 °C) in the presence of benzoic acid and triethylamine as the catalysts (Scheme 1).

Scheme 1



2 **3** **1**

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 501—509, March, 2011.

The alkylation of the hydroxy group in compound **1** was also performed in DMF. Initially, the phenoxide was generated with the use of the deprotonating agent (NaH, K_2CO_3, or Bu^tOK) and then an alkylating agent was added. The alkylation was most efficient when phenoxide was generated with the use of sodium hydride.

1,3-Propane sultone and sodium 3-bromopropanesulfonate were chosen for the introduction of the alkylsulfo group (Scheme 2).

The modification occurred in high yield when these reagents were taken in a slight excess, no advantages of a particular reagent being observed.

The introduction of functional arenes into molecule **1** was performed in two steps (Scheme 3). Initially, compound **1** was alkylated with propargyl bromide. Then the [2+3]-cycloaddition at the triple bond of propargyl ether **5** (Huisgen reaction) was performed in the presence of CuI.[5] The structure of product **5** was completely confirmed by ^{1}H NMR and Fourier-transform infrared spectroscopy, elemental analysis, and X-ray diffraction (Fig. 1).

Aryl azides **6—8** used in the cycloaddition were synthesized in quantitative yields from the corresponding anilines by the diazotization followed by the treatment of the diazonium salt with sodium azide. Then azides **6—8** (after recrystallization or immediately in the reaction mixture) were mixed with a solution of propargyl derivative **5** in DMSO and the catalysts (see Scheme 3).

The 1,3-dipolar addition of alkyne **5** to azides **6—8** readily occurs upon heating to 80 °C and the addition of D,L-proline (in the absence of the latter, the reaction does not proceed). It should be noted that triethylamine does not facilitate this reaction.

The azido group gives an intense absorption band in the IR spectra in the region of 2000—2400 cm^{-1},[6] due to which (in combination with ^{1}H NMR spectroscopy) azide transformations can be easily monitored. In the case of azides, which were synthesized in the present study, the azide group is manifested at 2100—2120 cm^{-1}.

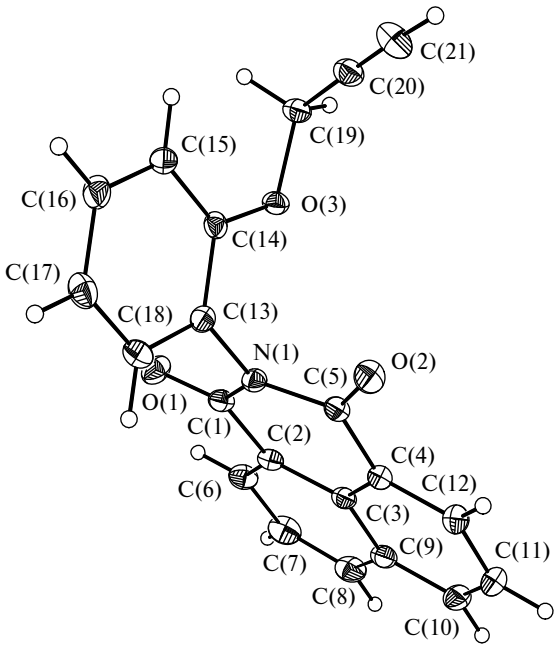


Fig. 1. Molecular structure of compound **5**.

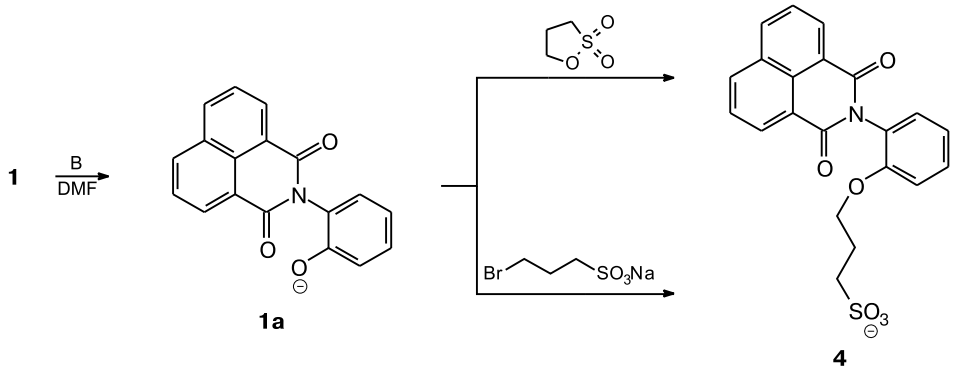
On passing to polymer-analogous reactions, IR monitoring becomes a convenient tool since the sampling requires a short time. The reactions with propargyl bromide and then with the certain azide are accomapnied by substantial changes in the arrangement and the shape of bands in the IR spectra in the range of 3700—1500 cm^{-1}.

The structure of phosphonate **9** was confirmed by X-ray diffraction (Fig. 2).

Carboxy groups of enhanced acidity were introduced into model naphthalimide **1** with the use of ethyl bromodifluoroacetate (Scheme 4).

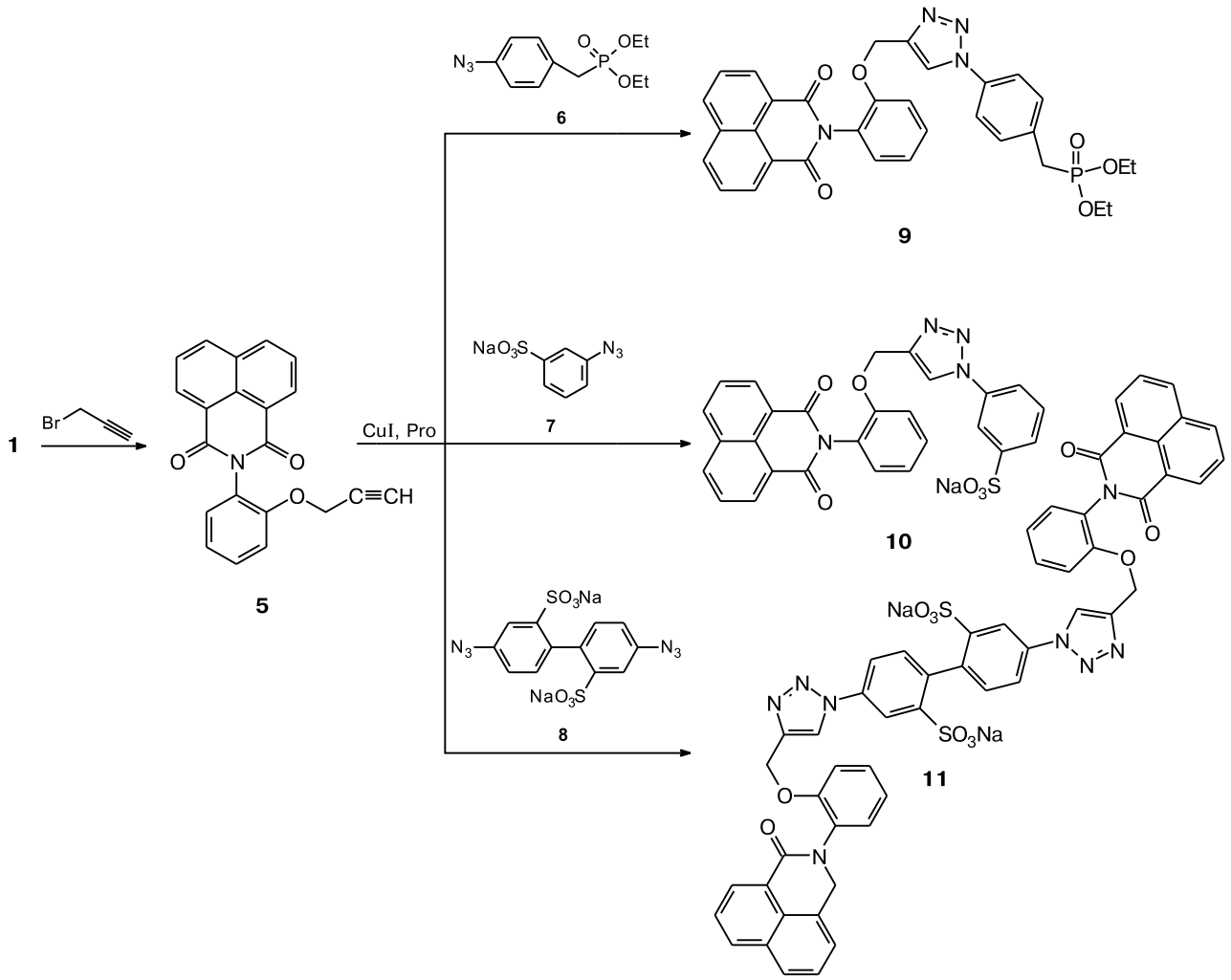
It appeared that the reaction of compound **1** with ethyl bromodifluoroacetate reaction was not completed. The ^{19}F NMR data indicate that the alkylating agent is consumed in side reactions. It remains unclear why the reac-

Scheme 2



B is a base.

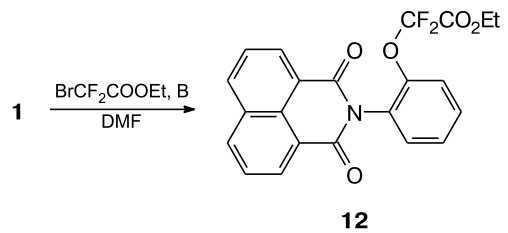
Scheme 3



tion of phenoxide **1a** with ethyl bromodifluoroacetate occurred only during the first day in spite of the presence of **1a** in the reaction mixture for several days and the addition of an excess of the base for the more complete deprotonation of the hydroxy group.

To optimize the procedure for the synthesis, the ratio of the reagents and the reaction temperature were varied. We found that the temperature has only a slight effect on the outcome of the reaction in the range of 2—80 °C although the heating results in an increase in the fraction of by-products. The additional purification of ethyl bromodifluoroacetate by distillation does not raise the yield. A change in the ratio of the reacting components showed that the addition of an excess of ethyl bromodifluoroacetate results in a substantial increase in the yield of the target product (from 25 to 70% in the case of 2 and 4 equiv. of the reagent, respectively).

Scheme 4



Due to a substantial difference in the positions of the signals for the fluorine atoms of the starting ethyl bromodifluoroacetate and product **12** (δ –62.19 and –75.53, respectively, in DMSO-d_6), the course of the reaction can be roughly monitored by ^{19}F NMR spectroscopy. However, ^{19}F NMR spectroscopy provides only the qualitative monitoring of the reaction because the starting compound **1** does not contain fluorine atoms and the ratio of the integrated intensities of the signals not always corresponds to the actual conversion of **1**.

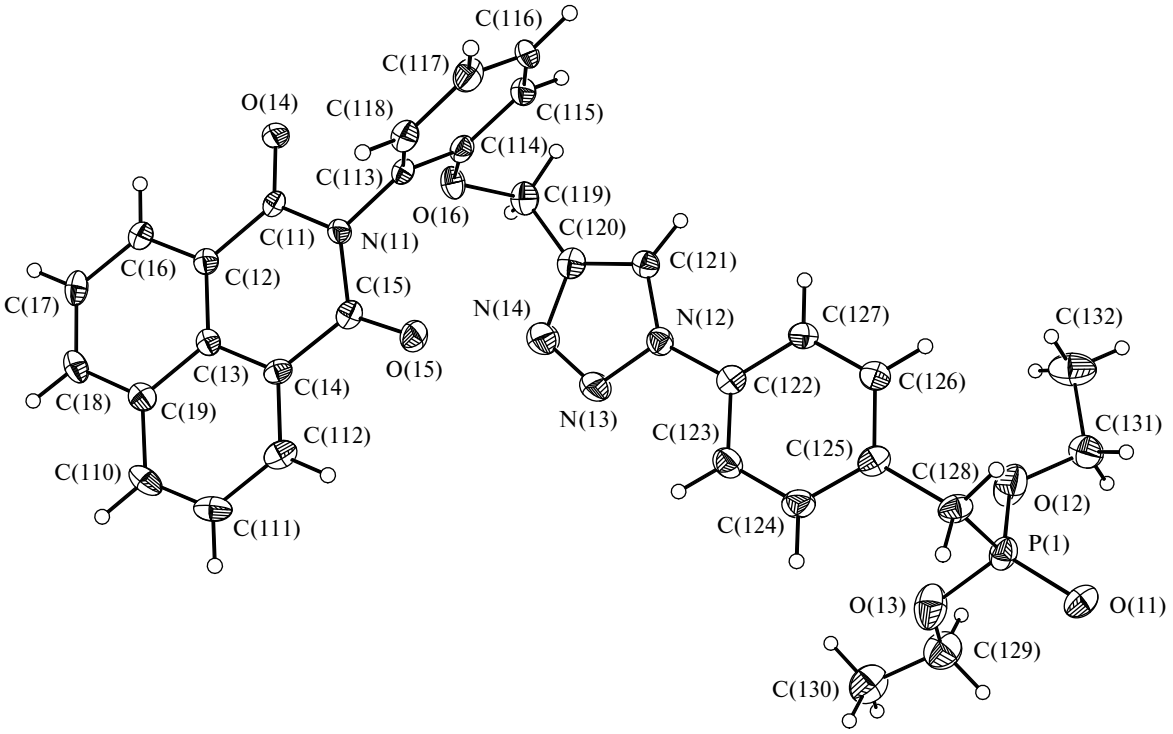


Fig. 2. Molecular structure of compound **9**. One of two crystallographically independent molecules is shown.

Based on the X-ray diffraction study of substitution products **5**, **9**, and **12**, certain conclusions were made about the spatial arrangement of the *N*-aryl-1,8-naphthalimides molecules containing *ortho* substituents in the phenyl ring and about their crystal packing.

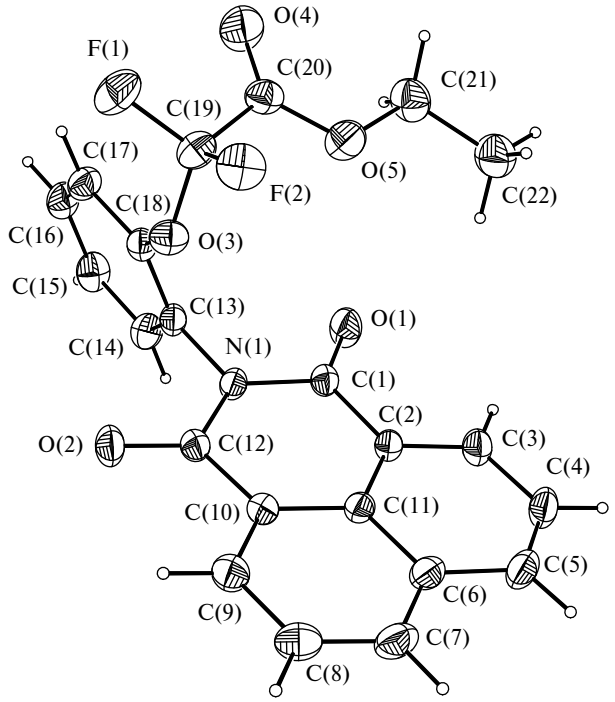


Fig. 3. Molecular structure of compound **12**.

In all molecules, the *N*-aryl-1,8-naphthalimide moieties have similar structures (Figs 1—3). Thus, the tricyclic system is planar, and the phenyl ring is twisted about the C—N bond by 108.9 (**5**), 95.3° (**9**), 103.2, and 102.3° (in two independent molecules of **12**). The C—N bond length is 1.438(2), 1.440(1), 1.441(3), and 1.450(3) Å in **5**, **9**, and two independent molecules of **12**, respectively. This is consistent with the data published in the literature.[7] The deviation of the oxygen atom bound to the phenyl ring is small (0.01—0.09 Å). The average C(Ph)—O bond length is 1.365 Å.

An increase in the degree of branching of the O-substituent (**12** > **5** > **9**) has an effect only on the angle of rotation of the phenyl ring with respect to the tricyclic system. The bond lengths and bond angles in all these molecules have standard values.

The molecular packing in the crystal structures of **5**, **9**, and **12** is determined by π—π stacking interactions between the aromatic rings and is complicated with an increase in the number of aromatic rings in the molecule (**5**, **9** → **12**). In the structure of **5**, two molecules are linked together by the π—π stacking interaction only between the tricyclic moieties (the distance between the planes $d = 3.35$ Å) to form intermolecular dimers (Fig. 4).

In the structure of **12**, the π—π stacking interaction is also observed between the tricyclic moieties, re-

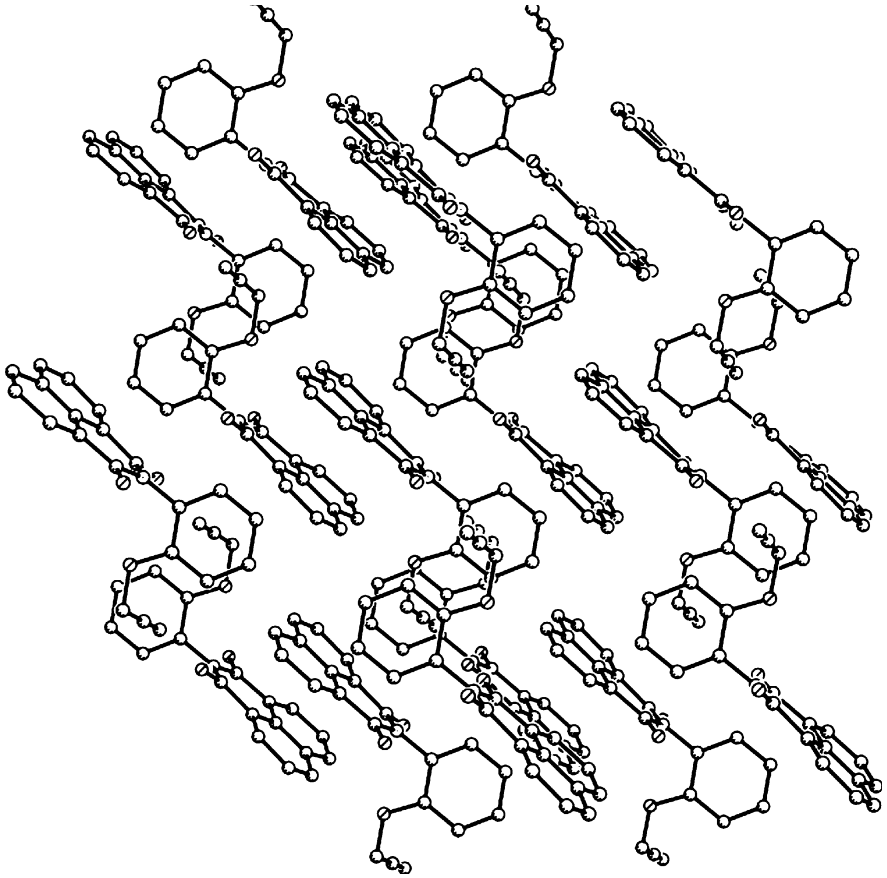


Fig. 4. Crystal packing of compound **5**.

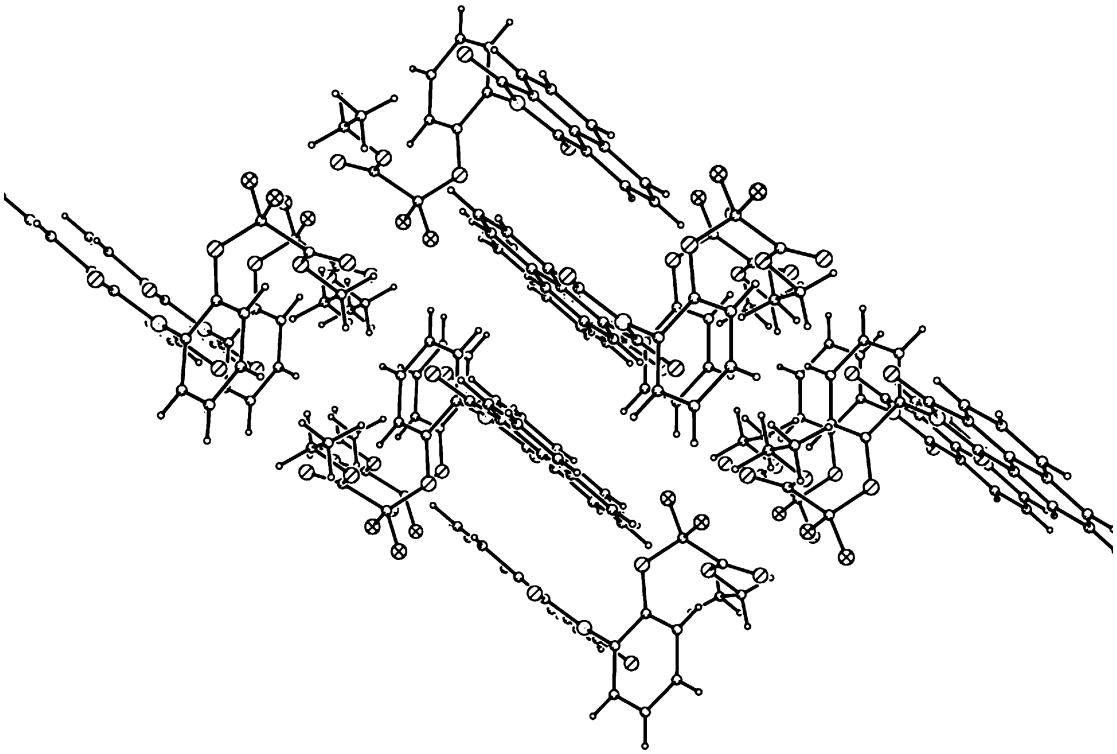


Fig. 5. Crystal packing of compound **12**.

sulting in stacks of the molecules (Fig. 5) running along the *a* axis (the distances between the planes d = 3.40 and 3.57 Å).

In molecule **9**, the phenyltriazole moiety is orthogonal to the *N*-phenyl ring but is parallel to the tricyclic moiety (the dihedral angle between the planes is 4.0°). As a result, there are π—π stacking interactions between all aromatic moieties (the interplanar distances are 3.4—3.5 Å). The crystal structure is composed of there are double layers (parallel to the *ab* plane and separated by the $O{=}P(OEt)_2$ substituents) (Fig. 6).

To sum up, we studied the conditions of the alkylation of the hydroxy group in compound **1**. Based on the results of the study, the corresponding polymer-analogous reactions of poly(2-hydroxyphenyl)naphthalimides can be similarly investigated.

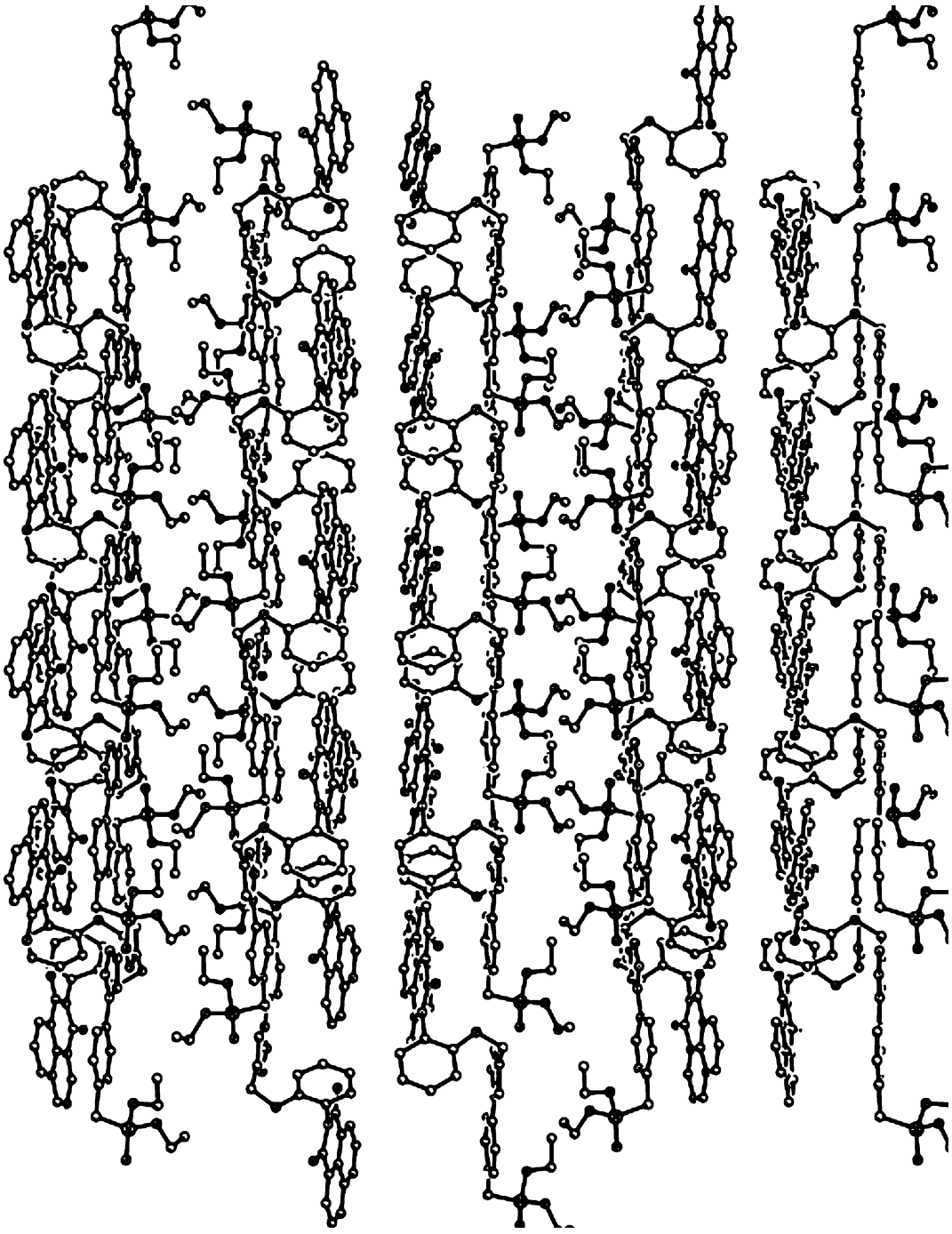


Fig. 6. Crystal packing of compound **9**.

Experimental

The melting points were determined on a Boetius hot-stage apparatus and are uncorrected. The ^{1}H, ^{31}P, and ^{19}F NMR spectra were recorded on Bruker AMX-400 (400.13 MHz), Bruker Avance-400 (161.98 MHz), and Bruker AV-300 (282.40 MHz) instruments in DMSO-d_6. The chemical shifts δ were calculated based on the residual signals for protons of the deuterated solvent as the internal standard (^{1}H) and 85% H_3PO_4 (^{31}P) and $CFCl_3$ (^{19}F) as the external standards. The assignments in the NMR spectra are the authors' opinion.

The IR absorption spectra of samples were recorded on a Magma-IR 750 Nicolet Fourier-transform infrared spectrometer in the 4000—400 cm^{-1} region.

The course of the reactions was monitored and the purity of the reaction products was checked by TLC on Silufol UV-254 plates using ethanol—toluene (3 : 1, v/v) (*A*) and ethyl acetate—toluene (1 : 5, v/v) (*B*) mixtures as the eluents.

***N*-(2-Hydroxyphenyl)-1,8-naphthalimide (1).** Dimethylformamide (6 mL) and triethylamine (0.455 g, 4.5 mmol) were added to a mixture of 1,8-naphthalenedicarboxylic acid anhydride **2** (1.784 g, 9 mmol), *o*-aminophenol **3** (1.03 g, 9.5 mmol), and benzoic acid (0.549 g, 4.5 mmol). The synthesis was carried out with stirring at 70 °C for 12 h. In the course of the reaction, the reactants first dissolved and then the product precipitated. The course of the reaction was monitored by TLC (system *B*, R_f = 0.7). The precipitate that formed was filtered off, washed with acetone, and dried *in vacuo* at 140 °C. The yield was 2.4 g (90%), m.p. 328—331 °C. ^{1}H NMR (400 MHz), δ: 6.94 (t, 1 H, *o*-C_6H_4, $^{3}J_{H-H}$ = 7.6 Hz); 7.00 (d, 1 H, *o*-C_6H_4, $^{3}J_{H-H}$ = = 8.2 Hz); 7.25 (d, 1 H, $^{3}J_{H-H}$ = 7.8 Hz); 7.30 (d, 1 H, *o*-C_6H_4, $^{3}J_{H-H}$ = 7.7 Hz); 7.90 (t, 2 H, H(3)C, H(6)C, $^{3}J_{H-H}$ = 7.7 Hz); 8.50 (d, 4 H, H(2)C, H(4)C, H(5)C, H(7)C, $^{3}J_{H-H}$ = 7.2 Hz); 9.69 (br.s, 1 H, HO). IR (KBr), ν/cm^{-1}: 3301 (OH); 1703, 1650 (C=O). Found (%): C, 74.77; H, 3.79; N, 4.84. $C_{18}H_{11}NO_3$. Calculated (%): C, 74.73; H, 3.83; N, 4.84.

Sodium or potassium salt of *N*-[2-(3-sulfopropoxy)phenyl]-1,8-naphthalimide (4). Potassium carbonate (0.173 g, 1.25 mmol) or potassium *tert*-butoxide (0.123 g, 1.1 mmol) was added to a solution of compound **1** (0.289 g, 1 mmol) in DMF (2 mL). After 30 min, propane sultone (0.134 g, 1.1 mmol) was added. The reaction was carried out at ~20 °C for 8 h. The course of the reaction was monitored by TLC (system *A*, R_f = 0.4). After completion of the reaction, the mixture was diluted with water. The precipitate that formed upon cooling was filtered off, dried, and recrystallized from water. The yield was 0.35 g (78%) and 0.31 g (69%) in the reactions with the use of potassium carbonate and potassium *tert*-butoxide, respectively.

The synthesis with the use of sodium hydride (0.042 g, 1.05 mmol) as the base in THF was carried out in a similar way at 50 °C. The yield was 0.239 g (60%), m.p. > 300 °C (decomp.). ^{1}H NMR (400 MHz), δ: 1.70—1.85 (m, 2 H, $CH_2C\underline{H}_2CH_2$); 2.22—2.40 (m, 2 H, CH_2SO_3); 3.98—4.13 (m, 2 H, OCH_2); 7.07 (t, 1 H, *o*-C_6H_4, $^{3}J_{H-H}$ = 6.9 Hz); 7.20 (d, 1 H, *o*-C_6H_4, $^{3}J_{H-H}$ = 7.9 Hz); 7.35 (d, 1 H, *o*-C_6H_4, $^{3}J_{H-H}$ = 6.9 Hz); 7.44 (t, 1 H, *o*-C_6H_4, $^{3}J_{H-H}$ = 6.8 Hz); 7.92 (t, 2 H, C(3)H, C(6)H, $^{3}J_{H-H}$ = 7.4 Hz); 8.53 (d, 4 H, C(2)H, C(4)H, C(5)H, C(7)H, $^{3}J_{H-H}$ = 7.0 Hz). Found (%): C, 56.16; H, 3.56; N, 3.15; S, 7.18. $C_{21}H_{16}KNO_6S$. Calculated (%): C, 56.11; H, 3.59; N, 3.12; S, 7.13.

***N*-(2-Propargyloxyphenyl)-1,8-naphthalimide (5).** Potassium *tert*-butoxide (0.123g, 1.1 mmol) was added to a solution of compound **1** (0.289 g, 1 mmol) in DMF (2 mL), and then propargyl bromide (0.131 g, 1.1 mmol) was added dropwise. The synthesis was carried out at ~20 °C for 8 h (TLC monitoring). Then water was added to the mixture. The precipitate that formed was filtered off, washed with water until neutral pH, dried, recrystallized from an ethanol—acetone mixture, and dried *in vacuo* at 60 °C. The yield was 0.32 g (75%), m.p. 173—176 °C. ^{1}H NMR (400 MHz), δ: 3.52 (t, 1 H, CCH, $^{3}J_{H-H}$ = 4.1 Hz); 4.78 (d, 2 H, OCH_2, $^{4}J_{H-H}$ = 4.1 Hz); 7.15 (t, 1 H, *o*-C_6H_4, $^{3}J_{H-H}$ = 7.6 Hz); 7.30 (d, 1 H, *o*-C_6H_4, $^{3}J_{H-H}$ = 7.6 Hz); 7.40 (d, 1 H, *o*-C_6H_4, $^{3}J_{H-H}$ = 7.5 Hz); 7.3 (t, 1 H, *o*-C_6H_4, $^{3}J_{H-H}$ = 7.3 Hz); 7.92 (t, 2 H, C(3)H, C(6)H, $^{3}J_{H-H}$ = 7.4 Hz); 8.52 (d, 2 H, C(4)H, CH(5), $^{3}J_{H-H}$ = 7.6 Hz); 8.53 (d, 2 H, C(2)H, C(7)H, $^{3}J_{H-H}$ = = 8.3 Hz). IR (KBr), ν/cm^{-1}: 3235 (C≡CH); 1710, 1668 (C=O); 1237 ($ArOCH_2$). Found (%): C, 77.00; H, 3.99; N, 4.33. $C_{21}H_{13}NO_3$. Calculated (%): C, 77.05; H, 4.00; N, 4.28.

Diethyl 4-azidobenzylphosphonate (6). Diethyl 4-aminobenzylphosphonate (Acros Organics) was subjected to diazotization according to the procedure described[8] for toluidine. Then an equivalent amount of a 30% aqueous sodium azide solution was added to the aqueous solution of the diazonium salt cooled to 0 °C in such a way as to maintain the temperature below 5 °C. The mother liquor over the oil that formed was removed by decantation. The oil was dried *in vacuo* over P_2O_5. The reaction occurred quantitatively. ^{1}H NMR (400 MHz), δ: 1.17 (t, 6 H, Me, $^{3}J_{H-H}$ = 7.1 Hz); 3.23 (d, 2 H, CH_2P, $^{2}J_{H-P}$ = 21.5 Hz); 3.95 (dq, 4 H, $MeC\underline{H}_2$, $^{3}J_{H-H}$ = $^{3}J_{H-P}$ =7.3 Hz); 7.04—7.12 (m, 2 H, C_6H_4); 7.28—7.36 (m, 2 H, C_6H_4). ^{31}P NMR, δ: 26.47 (s, CH_2P). Found (%): C, 49.02; H, 6.01; N, 15.65; P, 11.52. $C_{11}H_{16}N_3O_3P$. Calculated (%): C, 49.07; H, 5.99; N, 15.61; P, 11.50.

Sodium 3-azidobenzenesulfonate (7). The diazonium salt was synthesized from methanilic acid according to the procedure described earlier[8] for sulfanilic acid. Then an equivalent amount of a 30% aqueous sodium azide solution was added to the aqueous solution of the diazonium salt cooled to 5 °C in such a way as to maintain the temperature below 12 °C. The precipitate of the azide that formed was filtered off and dried. The reaction occurred quantitatively. ^{1}H NMR (400 MHz), δ: 7.04—7.09 (m, 1 H, C(4)H); 7.27—7.31 (m, 1 H, C(2)H); 7.38 (t, 1 H, C(5)H, $^{3}J_{H-H}$ = 7.6 Hz); 7.42 (d, 1 H, C(6)H, $^{3}J_{H-H}$ = 7.6 Hz). IR (KBr), ν/cm^{-1}: 2107 (N_3); 1213, 1175, 1047 (SO_3^-). Found (%): C, 32.55; H, 1.80; N, 19.03; S, 14.47. $C_6H_4N_3NaO_3S$. Calculated (%): C, 32.58; H, 1.82; N, 19.00; Na, 10.39; S, 14.50.

Sodium 4,4′-diazidodiphenyl-2,2′-disulfonate (8). The diazonium salt was synthesized from 4,4′-diaminodiphenyl-2,2′-disulfonic acid according to a known procedure.[8] Then an equivalent amount of a 30% aqueous sodium azide solution was added to the aqueous solution of the diazonium salt cooled to 10 °C in such a way as to maintain the temperature below 20 °C. The reaction occurred quantitatively. The reaction mixture was concentrated to dryness, and the residue was recrystallized from an isopropanol—water mixture. ^{1}H NMR (400 MHz), δ: 6.93—7.00 (m, 2 H, C(5)H, C(5′)H); 7.31—7.38 (m, 2 H, C(6)H, C(6′)H); 7.56 (s, 2 H, C(3)H, C(3′)H). IR (KBr), ν/cm^{-1}: 2116 (N_3); 1233, 1205, 1043, 1032 (SO_3^-). Found (%): C, 32.70; H, 1.38; N, 19.00; S, 14.54. $C_{12}H_6N_6Na_2O_6S_2$. Calculated (%): C, 32.73; H, 1.37; N, 19.09; S, 14.56.

Diethyl 4-[5-(2-naphthalimidophenoxymethyl)-1*H*-1,2,3-triazol-1-yl]benzylphosphonate (9). An ethanolic solution of azide **6** (0.23 g, 1 mmol), copper(I) iodide (0.01 g), sodium ascorbate (0.01 g), and D,L-proline (0.01 g) were added to a suspension of compound **5** (0.271 g, 0.829 mmol) in a 1 : 1 ethanol—water mixture (4 mL). The reaction was carried out at 80 °C (TLC monitoring). After completion of the reaction, the precipitate that formed was filtered off, dried, and recrystallized from acetone. The yield was 70%, m.p. > 300 °C (decomp.). ^{1}H NMR (300 MHz), δ: 1.19 (t, 6 H, Me, $^3J_{H-H}$ = 7.0 Hz); 3.33 (d, 2 H, CH_2P, $^2J_{H-P}$ = 21.8 Hz); 3.95 (dq, 4 H, $MeC\underline{H}_2$, $^3J_{H-H}$ = = $^3J_{H-P}$ = 7.3 Hz); 5.26 (s, 2 H, CH_2O); 7.10—7.20 (m, 1 H, C_6H_4); 7.35—7.52 (m, 5 H, C_6H_4); 7.63 (d, 2 H, C_6H_4, $^3J_{H-H}$ = = 8.2 Hz); 7.87 (t, 2 H, C(3)H, C(6)H, $^3J_{H-H}$ = 7.7 Hz); 8.49 (d, 4 H, C(2)H, C(4)H, C(5)H, C(7)H, $^3J_{H-H}$ = 7.8 Hz); 8.52 (s, 1 H, HC het.). ^{31}P NMR, δ: 26.13 (s, CH_2P). Found (%): C, 63.88; H, 4.66; N, 9.63; P, 5.29. $C_{31}H_{27}N_4O_6P$. Calculated (%): C, 63.91; H, 4.67; N, 9.62; P, 5.32.

Sodium 3-[5-(2-naphthalimidophenoxymethyl)-1*H*-1,2,3-triazol-1-yl]benzenesulfonate (10). 3-Azidobenzenesulfonic acid **7** (0.223 g, 1 mmol) was added to a solution of compound **5** (0.3 g, 0.917 mmol) in DMSO (3 mL). Then copper(I) iodide (0.01 g), sodium ascorbate (0.01 g), and D,L-proline (0.01 g) were added as the catalytic system. The reaction was carried out at 80 °C (TLC monitoring). After completion of the reaction, the precipitate that formed was filtered off, dried, and recrystallized from an acetone—water mixture. The yield was 0.4 g (80%), m.p. > 300 °C (decomp.). ^{1}H NMR (400 MHz), δ: 5.27 (s, 2 H, CH_2); 7.11—7.19 (m, 1 H, C_6H_4); 7.39 (d, 1 H, C_6H_4, ^3J = 7.6 Hz); 7.47—7.57 (m, 3 H, C_6H_4); 7.62 (d, 1 H, C_6H_4, ^3J = 7.9 Hz); 7.70 (d, 1 H, C_6H_4, ^3J =7.5 Hz); 7.90 (t, 2 H, C(3)H, C(6)H, ^3J = 7.7 Hz); 7.99 (s, 1 H, *m*-C_6H_4); 8.50 (d, 2 H, C(4)H, C(5)H, ^3J = 8.2 Hz); 8.52 (d, 2 H, C(2)H, C(7)H, ^3J = 7.2 Hz); 8.57 (s, 1 H, HC het.). Found (%): C, 59.09; H, 3.13; N, 10.20; S, 5.82. $C_{27}H_{17}N_4NaO_6S$. Calculated (%): C, 59.12; H, 3.12; N, 10.21; S, 5.85.

Disodium 4,4′-bis[5-(2-naphthalimidophenoxymethyl)-1*H*-1,2,3-triazol-1-yl]diphenyl-2,2′-disulfonate (11). An equivalent amount of an aqueous solution of azide **8** was added to a solution of compound **5** (0.33 g, 1 mmol) in DMSO (3 mL). Then copper(I) iodide (0.01 g), sodium ascorbate (0.01 g), and D,L-proline (0.01 g) were added as the catalytic system. The reaction was carried out at 80 °C (TLC monitoring). After completion of the reaction, the precipitate that formed was filtered off, dried, and recrystallized from an acetone—water mixture (1 : 1). The yield was 0.55 g (75%), m.p. > 300 °C (decomp.). ^{1}H NMR (400 MHz), δ: 5.29 (m, 4 H, CH_2); 7.11—7.19 (m, 2 H, *o*-C_6H_4); 7.40 (d, 2 H, *o*-C_6H_4, $^3J_{H-H}$ = 7.9 Hz); 7.46 (d, 2 H, H(6)C, $^3J_{H-H}$ = 7.8 Hz); 7.48—7.55 (m, 4 H, *o*-C_6H_4); 7.62 (d, 2 H, C(5)H, $^3J_{H-H}$ = 8.0 Hz); 7.87—7.98 (m, 4 H, $C_{10}H_6$); 8.28

Table 1. Crystallographic characteristics and refinement statistics for compounds **5**, **9**, and **12**

Compound	**5**	**9**	**12**
Molecular formula	$C_{21}H_{13}NO_3$	$C_{32}H_{29}N_4O_6$	$C_{22}H_{15}F_2NO_5$
Molecular weight	327.32	596.56	411.35
Space group	*P*-1	$Pna2_1$	*P*-1
T/K	100	100	295
a/Å	8.4541(7)	17.123(1)	8.4013(5)
b/Å	8.8692(8)	9.4125(6)	9.3718(6)
c/Å	11.0406(6)	35.270(2)	11.9756(7)
α/deg	102.354(2)	90.0	78.657(1)
β/deg	104.074(2)	90.0	84.324(1)
γ/deg	93.840(2)	90.0	89.963(1)
V/Å^3	778.18(11)	5684.4(6)	919.78(10)
Z	2	8	2
d_{calc}/g cm^{-3}	1.397	1.394	1.485
Crystal color, habit	Colorless plate	Colorless plate	Colorless plate
Crystal dimensions/mm	0.65×0.45×0.30	0.55×0.40×0.25	0.45×0.30×0.20
Diffractometer	«Bruker Apex II CCD»	«Bruker Apex II CCD»	«Bruker Apex II CCD»
μ/cm^{-1}	0.94	1.51	1.19
Scan mode		ϕ/ω	
$2\theta_{max}$/deg	56.0	54.0	60.0
Total number of reflections	6798	56927	11964
Number of independent reflections (R_{int})	3727 (0.0169)	12298 (0.0541)	5311 (0.0203)
R_1 (based on *F* for reflections with $I > 2\sigma(I)$) (number of reflections)	0.0381 (3190)	0.0452 (10752)	0.0438 (3427)
wR_2 (based on F^2 for all reflections)	0.1081	0.1045	0.0973
Number of refined parameters	226	775	272
Residual electron density/e·Å^{-3}, ρ_{max}/ρ_{min}	0.338/−0.239	0.825/−0.445	0.208/−0.205
GOOF	1.017	1.015	1.018
F(000)	340	2496	424

(s, 2 H, C(3)H); 8.47—8.54 (m, 8 H, $C_{10}H_6$); 8.55 (s, 2 H, HC het.). Found (%): C, 59.20; H, 2.97; N, 10.26; S, 5.80. $C_{54}H_{32}N_8Na_2O_{12}S_2$. Calculated (%): C, 59.23; H, 2.95; N, 10.23; S, 5.86.

***N*-[2-(1,1-Difluoro-2-ethoxy-2-oxoethoxy)phenyl]-1,8-naphthalimide (12).** Potassium *tert*-butoxide (0.123 g, 1.1 mmol) was added to a solution of compound **1** (0.289 g, 1 mmol) in DMF (2 mL). After a while, ethyl bromodifluoroacetate (0.406 g, 2 mmol) was added dropwise. The reaction mixture turned brown and a substance began to precipitate. According to the TLC data, two products formed. The reaction was carried out at 50 °C for 3 days. According to the TLC data, the reaction was not brought to completion. The reaction mixture was poured into cold water. The precipitate that formed was filtered off and recrystallized. According to the TLC and ^{1}H NMR data, the precipitate consisted of product **12** and the starting compound **1** in a ratio of 2 : 1.

The reaction in the presence of potassium carbonate (0.18 g, 1.3 mmol) was carried out in a similar way at 50 °C. After the addition of water, a white precipitate formed. The precipitate was filtered off. Then an ethanol—acetone mixture was added to the precipitate, and the residue that remained undissolved was filtered off. According to the TLC data, this residue is the starting imide **1**. The precipitate that formed from the solvent mixture was filtered off and dried. According to the ^{1}H NMR data, the precipitate consisted of product **12** and the starting compound **1** in a ratio of 1 : 2. IR of the mixture, ν/cm^{-1}: 3305 (OH); 1706, 1669 (C=O); 1240—1100 (CF_2, $ArOCH_2$).

The reaction with the use of 4 equiv. of ethyl bromodifluoroacetate afforded 0.33 g of the precipitate. According to the ^{1}H NMR data, the precipitate consisted of product **12** and the starting compound **1** in a ratio of 4 : 1.

Product **12** was separated from an admixture of the starting compound by recrystallization from an acetone—water mixture. The yield was 0.16 g (50%), m.p. >300 °C (decomp.). ^{1}H NMR (400 MHz), δ: 0.50 (t, 3 H, Me, $^3J_{H-H}$ = 7.1 Hz); 3.86 (dq, 2 H, CH_2, $^3J_{H-H}$ = 7.1 Hz); 7.49—7.57 (m, 2 H, *o*-C_6H_4); 7.58—7.67 (m, 2 H, *o*-C_6H_4); 7.94 (t, 2 H, C(3)H, C(6)H, $^3J_{H-H}$ = 7.8 Hz); 8.55 (d, 2 H, C(4)H, C(5)H, $^3J_{H-H}$ = 7.2 Hz); 8.53 (d, 2 H, C(2)H, C(7)H, $^3J_{H-H}$ = 8.3 Hz). ^{19}F NMR, δ: −75.53 (s, CF_3). Found (%): C, 64.20; H, 3.66; F, 9.27; N, 3.39. $C_{22}H_{15}F_2NO_5$. Calculated (%): C, 64.24; H, 3.68; F, 9.24; N, 3.41.

X-ray diffraction study. Single crystals of the compounds were obtained by crystallization from acetone (**5** and **9**) or an ethyl acetate—ethanol mixture (**12**). The X-ray data collection and structure refinement statistics are given in Table 1. Absorption corrections were not applied. The structures solved by direct methods. All nonhydrogen atoms were located in difference electron density maps and refined based on F^2_{hkl} with anisotropic displacement parameters. All hydrogen atoms were positioned geometrically and refined using the riding model with $U(H) = nU(C)$, where $U(C)$ are the equivalent thermal parameters of the carbon atoms to which the corresponding H atoms are bonded, n = 1.5 for CH groups and 1.2 for CH_2 and CH_3 groups.

All calculations were carried out with the use of the SHELXTL PLUS 5 program package.[9]

The atomic coordinates, bond lengths, bond angles, and thermal parameters were deposited with the Cambridge Crystallographic Data Centre (CCDC 770667-9) and can be obtained, free of charge, on application to (www.ccdc.cam.uk/conts/retrieving.html; CCDC, 12 Union Road, Cambridge CB2 1EZ; fax: +44 1223 335 033; or deposit@ccdc.cam.ac.uk).

We thank E. I. Goryunov for help in the interpretation of the NMR spectra.

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Received May 25, 2010;
in revised form February 25, 2011