Abstract: Cationic electrocyclization of α-benzoyldiphenylmethanols in the presence of superacid provides fluorenes, phenanthrols and benzofurans in good to moderate yields. A single substitution leads to regioselective cationic electrocyclizations.

Key words: carbocations, electrocyclizations, regioselectivity, superacid, diphenylmethyl cations

Diphenylmethyl cations 1 and related diarylmethyl cations substituted with electron-withdrawing groups constitute a typical class of destabilized cations, i.e. carbocations bearing electron-withdrawing groups directly attached to the carbenium ion center. The prototype diphenylmethyl cations 1 (Scheme 1) bearing electron-withdrawing substituents (RC=O) have been generated in the presence of acids, or by flash-laser photolysis, and characterized as discrete stable ions. The cations 1 undergo three modes of electrocyclization reactions (see Scheme 2): (1) cyclization to form benzofurans 3, (2) cyclization to give fluorenes 4, and (3) cyclization to give phenanthrols 5. The first isolation of the relevant carbocation, the di-p-anisyl(4-methoxybenzoyl)methyl cation (1a), as a stable crystalline antimony pentafluoride salt, was reported by Takeuchi et al., who showed that heating the salt 1a in a neutral solvent (1,2-dichloroethane, 50°C, 8 h), gave the benzofuran 3a in 94% yield (Scheme 3). In contrast to this heteroatom cyclization process, the acetyl, acid, ester and amide analogs underwent electrocyclic coupling of the two aromatic rings, leading to fluorene derivatives. Thus, α-acetyldiphenylmethanol (2b) gave 9-acetyfluorene (4b), whereas α-methoxycarbonyldiphenylmethanol (2c) gave 9-methoxycarbonylfluorene (4c) (Scheme 1). The chemical behavior of the monocations 1, generated under neutral and strongly acidic conditions were also reported from this laboratory, and were divergent from those described. α-Benzoyldiphenylmethanol (2d, R1 = R2 = H, Scheme 2), a precursor of the unsubstituted cation 1d (Scheme 4), reacted in trifluoromethanesulfonic acid (TFSA) at −48°C to afford the fluorene 4d, along with the phenanthrene derivative 9-phenylphenanthr-10-ol (5d) (Scheme 2). No benzofurans 3 were obtained in TFSA. This superacid-catalyzed fluorene cyclization of 2d was also reported by Olah and Wu in the same acid, although the yields were a little divergent. The same authors also reported the formation of 9-phenanthrol (79% yield) by TFSA-catalyzed cyclization of benzoin. The monocations 1c and 1d could be generated as stable entities at −50°C by the reaction of the α-chloro ketones 6c and 6d with silver salts (Scheme 4). However, no fluorene, phenanthrol or benzofuran was formed under these neutral conditions. When the stable cation was added to TFSA at −48°C, fluorene and the phenanthrol were produced (Scheme 2). This led to the proposals that the fluorenes 4 and phenanthrols 5 do not arise directly from the monocation 1, and that the real intermediate is the dication 7 (Scheme 1), formed by protonation of the α-carbonyl group by TFSA. The involvement of the dicationic intermediate 7 was supported by kinetic studies of the acidity-dependent reactions, and by theoretical evaluation of energetics.

In this context, α-benzoyldiphenylmethanols 2d−k can produce fluorene, phenanthrol and benzofuran by acid-
catalyzed electrocyclization through cationic intermediates (Scheme 2). The former two cyclizations represent an acid-catalyzed electrocyclization wherein two aromatic rings participate, and the latter cyclization represents a heteroatom cyclization, all these being of synthetic interest. There has been no systematic study of the ring-closing regiochemistry of cationic electrocyclization wherein several modes of cyclization are possible. Herein we deal with the substituent effects on the modes of the relevant electrocyclization reactions in order to reveal the synthetic potential of cationic electrocyclizations in which benzene rings participate.

The α-benzoyldiphenylmethanols 2d–k (except 2g, see experimental) can be readily prepared through the addition of Grignard reagents to O-trimethylsilylated cyanohydrins 9 of substituted benzophenones 8, followed by acidic hydrolysis of the intermediate imines (Scheme 5).

The acid-catalyzed cyclizations of α-benzoyldiphenylmethanols 2d–k were studied, and yields and reaction conditions are summarized in the Table. In the case of the parent α-benzoyldiphenylmethanol (2d), superacid-catalyzed cyclization favored the formation of the fluorene 4d (76%) over that of 9-phenylphenanthrol 5d (9%). Therefore the ratio of the yields of fluorene/phenanthrol (ratio 4d:5d in the Table) was 8.4. This can be understood in terms of feasibility of formation of 5-membered ring over 6-membered ring. A single substituent on the benzene ring can significantly modify the cyclization preference (Table). Methyl substitution at one of the benzene rings of the diphenylmethanol moiety as in 2e affords a mixture of fluorene 4e and phenanthrol 5e, the former being favored.
over the latter. The ratio of the yields of fluorene/phenanthrol (6.3) decreased as compared with that of 2d (8.4). Thus, the methyl substituent changed the modes of the cyclizations to some extent.

On the other hand, pentafluoro substitution as in 2g can lead to exclusive formation of the phenanthrol derivative 5'g. This is a reasonable outcome because the fluorene cyclization was inhibited due to the perfluoro substitution. However, substitution of a single fluorine atom on the benzene ring as in 2f can change the cyclization preference: 2f favored the formation of phenanthrol (5'f, 45% yield) over fluorene (4f, 35% yield) (ratio 4/5 = 0.78).

Generally in the case of the phenanthrene cyclizations, two regio-isomers are possible, 5 and 5' (Scheme 2). In the cases of 2f and 2g, a single isomer of the phenanthrols 5'f and 5'g, respectively, was predominantly formed while the methyl analog 2e favored the phenanthrol structure 5e. In the case of trifluoromethyl group as the R1 substituent, the TFSA-catalyzed cyclization of 2h at –45°C for 30 minutes gave the phenanthrol 5'h exclusively in 44% yield. No isomer of the phenanthrol 5h or fluorene 4h was formed. When the acid catalyst is trifluoroacetic acid (TFA), a much weaker acid than TFSA, no cyclized product was formed from 2h (Table). Instead, α-benzoylphenyl(p-trifluoromethylphenyl)methyl trifluoroacetate was obtained in 27% yield, together with the recovery (47%) of the starting alcohol 2h. The former product can be formed by nucleophilic attack of trifluoroacetate anion to the corresponding carbocation 1 (see Scheme 1). This result is consistent with the previous proposals that the fluorenes 4 and phenanthrols 5 do not arise from the monocations 1, and that the cyclizations require superacid catalysis. 8,9

Substitution of a methoxy group at the R1 position also has a significant effect on the cyclizations. The substrate 2i exclusively affords the benzofuran derivative 3i (Scheme 2). A single substitution of a methoxy group is sufficient to activate the benzofuran cyclization (cf. 1a in Scheme 3). In the case of the benzofuran cyclization, two regioisomers are also possible. In this case a single isomer, 3i rather than 3'i, was predominantly formed. The benzofuran cyclization of 2i can also be catalyzed by

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Table

<table>
<thead>
<tr>
<th>Substrate</th>
<th>R1</th>
<th>R2</th>
<th>Acid</th>
<th>Temp. (°C)a</th>
<th>Time (h)</th>
<th>Yieldb</th>
<th>Ratio</th>
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a ± 2°C.
b Isolated yields.
c Ratio of the yields of fluorene (4)/phenanthrol (5).
d Reference 8a.
e α-Benzoylphenyl(p-trifluoromethylphenyl)methyl trifluoroacetate (27%) and recovery (47%).
between cyclized isomers (i.e. benzofurans).

**Table**

Substitution of the benzene ring of the benzyl moiety, i.e. influence of substituent \( \text{R}_2 \), was also studied. The methyl group at the \( \text{R}_2 \) position as in \( 2j \) produced fluorene \( 4j \) (69% yield) and phenanthrol \( 5j \) (5% yield). The ratio of the yields of fluorene/phenanthrol (4.9) decreased as compared with that in the case of \( 2d \) (8.4), suggesting encouragement of the phenanthrene cyclization by the \( \text{CH}_3 \) group. On the other hand, fluorene substitution at the \( \text{R}_2 \) position in \( 2k \) suppressed the formation of phenanthrol, and the fluorene \( 4k \) was exclusively formed (83%) (Table).

In summary, cationic electrocyclizations of the \( \alpha \)-benzoyldiphenylmethanols in the presence of superacid provide fluorenes, phenanthrols and benzofurans in good to moderate yields. Although substituent effects on the cationic electrocyclization reactions have been poorly studied, the present work reveals a trend that relatively electron-rich benzene rings preferentially participate in the relevant cationic electrocyclizations. This tendency is crucial for the observed selectivities between fluorene/phenanthrol cyclizations (except in the case of \( 2e \)), and between cyclized isomers (i.e. benzofurans \( 3i \) and \( 3i' \), and phenanthrols \( 5 \) and \( 5' \)). The present substitution effects therefore provide regioselective cationic electrocyclizations with synthetic potential.

The melting points were measured with a Yanaco Micro Melting Point Apparatus (MP-500D) and are uncorrected. \( ^{1} \text{H} \) NMR (400 MHz) spectra were recorded on a JEOL Caliber-GX400 NMR spectrometer with TMS as an internal reference in \( \text{CDCl}_3 \) as the solvent, unless otherwise specified. Chemical shifts are shown in ppm. Coupling constants are given in Hertz. HRMS (EI+) spectra were recorded, the present work reveals a trend that relatively electron-rich benzene rings preferentially participate in the relevant cationic electrocyclizations. This tendency is crucial for the observed selectivities between fluorene/phenanthrol cyclizations (except in the case of \( 2e \)), and between cyclized isomers (i.e. benzofurans \( 3i \) and \( 3i' \), and phenanthrols \( 5 \) and \( 5' \)). The present substitution effects therefore provide regioselective cationic electrocyclizations with synthetic potential.

**Table**

- **Phenanthrene 4e**: Colorless needles; mp 118.0–119.6°C (recrystallized from \( \text{CH}_2 \text{Cl}_2 – \text{hexane} \)).
- **Fluorene 4e**: Colorless solid.
- **Acid-Catalyzed Reaction of \( \alpha \)-Benzoylphenyl(p-tolyl)methanol (2e)**
- ** Phenanthrene 4e**: Colorless needles; mp 118.0–119.6°C (recrystallized from \( \text{CH}_2 \text{Cl}_2 – \text{hexane} \)).
- **Fluorene 4e**: Colorless solid.
- **Acid-Catalyzed Reaction of \( \alpha \)-Benzoylphenyl(p-tolyl)methanol (2e)**
- ** Phenanthrene 4e**: Colorless needles; mp 118.0–119.6°C (recrystallized from \( \text{CH}_2 \text{Cl}_2 – \text{hexane} \)).
- **Fluorene 4e**: Colorless solid.
was added a solution of 9f (2.706 g, 9.7 mmol) in anhyd Et2O (4 mL) over 20 min. The mixture was stirred at r.t. for 6 h and added to an aqueous solution of 10% H2SO4 (200 mL) and stirred at r.t. for 18 h. The mixture was extracted with CHCl3, and the organic layer was washed with brine and dried (Na2SO4). The residue, obtained after evaporation of the solvent, was dissolved in EtOH (35 mL), and the resultant solution was treated with 3 N aq HCl (3 mL) at 50°C for 5 h. The solution was evaporated to give a residue which was flash-chromatographed (EtOAc–hexane, 1:99) to give 2f (1.791 g, 60%) as colorless needles; mp 78.4–79.4°C (recrystallized from CH2Cl2–hexane).

HRMS (EI+): m/z = 273 (M+ − COPh).


Acid-Catalyzed Reaction of α-Benzoyl(4-fluorophenyl)phenylmethanol (2f)
To pre-cooled TFSA (27.8 mL, 500 equiv) at −48°C (in a dry ice-MeCN bath) was added a solution of 2f (200 mg, 0.65 mmol) over 10 min. After stirring at −48°C for 2.5 h, the mixture was poured into ice-water (200 mL), extracted with CHCl3, and the organic layer was washed with brine and dried (Na2SO4). The solvent was evaporated to give a residue which was flash-chromatographed (CHCl3–hexane, 3:7) to give phenanthrol 5'f (85 mg, 45%) as a pink solid and fluorene 4f (65 mg, 34%) as colorless solid.

Phenanthrol 5’T
Colorless solid; mp 149.1–150.0°C (recrystallized from hexane).

HRMS (EI+): m/z = 360 (M+).

MS (EI+): m/z = 201 (M+ − COPh).

Anal. Calcd for C20H13FO: C, 83.03; H, 4.96.

Acid-Catalyzed Reaction of α-Benzoyl(pentafluorophenyl)phenylmethanol (2g)
To pre-cooled TFSA (23.4 mL, 500 equiv) at −48°C (in a dry ice-McCN bath) was added 2g (200 mg, 0.53 mmol) over 5 min. After stirring at −48°C for 1 h, the mixture was poured into ice-water (400 mL), extracted with CHCl3, the CHCl3 layer washed with brine and dried (Na2SO4). The solvent was evaporated to give a residue which was flash-chromatographed (CHCl3–hexane, 5:7) to give phenanthrol 5'g (67 mg, 41%) as a solid.

Phenanthrol 5’g
Off-white powder; mp 140.0–144.2°C (recrystallized from hexane–CHCl3).

HRMS (EI+): m/z = 360.0554. Found: 360.0573.

α-Trimethylsilylcyanoaldimin of 4-Trifluoromethylbenzophenone (9b)
To a solution of 8h (3.00 g, 12 mmol) and a catalytic amount of ZnI2 (191 mg, 0.66 mmol) in CH2Cl2 (40 mL) was added TMSCN (2.38 g, 2 equiv) at 0°C over 30 min. The mixture was stirred at 40°C for 24 h. The residue, obtained after evaporation of the solvent, was diluted with CHCl3, and the organic layer was washed with brine and dried (Na2SO4). The solvent was evaporated to give 9h in quantitative yield as a yellow oil.

HRMS (EI+): m/z = 349 (M+).

α-Benzoylphenyl(4-trifluoromethylphenyl)methanol (2h)
To the Grignard reagent prepared from bromobenzene (4.706 g, 3 equiv) and Mg turnings (801 mg, 3.3 equiv) in anhyd Et2O (14 mL) was added a solution of 9h (3.491 g, 10 mmol) in anhyd Et2O (4 mL) over 30 min. The mixture was stirred at r.t. for 4 h. The mixture was added to an aqueous solution of 10% aq H2SO4 (200 mL), and stirred at r.t. for 11 h. The mixture was extracted with CHCl3, and the resultant solution was treated with 3 N aq HCl (8 mL) at 40°C for 3 h. The solvent was evaporated to give a residue, which was diluted with CHCl3. The organic layer was washed with brine and dried (Na2SO4). The residue, obtained after evaporation of the solvent, was flash-chromatographed (EtOAc–hexane, 1:9) to give 2h (3.0824 g, 86%) as a yellow oil which solidified; colorless solid; mp 64.9–69.0°C (recrystallized from hexane).

HRMS (EI+): m/z = 273 (M+ − COPh).


Acid-Catalyzed Reaction of α-Benzoyl(pentafluorophenyl)phenylmethanol (2g)
To pre-cooled TFSA (23.4 mL, 500 equiv) at −48°C (in a dry ice-McCN bath) was added 2g (200 mg, 0.53 mmol) over 10 min. After stirring at −48°C for 30 min, the mixture was poured into ice-water
(300 mL), extracted with CHCl₃, and the organic layer was washed with brine and dried (Na₂SO₄). The solvent was evaporated to give a residue, which was flash chromatographed (CHCl₃–hexane, 3:7) to give phenanthrol 5h (83.3 mg, 44%) as a solid.

**Phenanthrol 5h**
Pale yellow powder; mp 170.0–171.1°C (recrystallized from hexane).

1H NMR (CDCl₃): δ = 7.714 (2 H, dd, J = 8.43, 1.28 Hz), 7.448–7.228 (10 H, m), 6.865 (2 H, dd, J = 6.78, 2.20 Hz), 4.985 (1 H, s), 3.804 (3 H, s).

MS (EI⁺): m/z = 253 (M⁺ – COPh).

**TFSA-Catalyzed Reaction of α-Benzoyl(4-methoxyphenyl)phenylmethanol (2i)**
To pre-cooled TFSA (27.6 mL, 500 equiv) at –48°C (in a dry ice-MeCN bath) was added a solution of 2i (200 mg, 0.63 mmol) in CH₂Cl₂ (3 mL) over 10 min. After stirring at 24°C even for 10 h, the reaction was very slow. After gentle heating at 40°C for 22 h, the mixture was poured into ice-water. It was extracted with CHCl₃, and the organic layer was washed with brine and dried (Na₂SO₄). The organic solvent was evaporated to give a residue which was flash chromatographed (CHCl₃–hexane, 1:4 to 2:3) to give benzo furan 3i (88 mg, 46%) as a colorless solid.

**Benzo furan 3i**
Colorless powder; mp 126.0–126.9°C (recrystallized from hexane).

1H NMR (CDCl₃): δ = 7.619 (2 H, dd, J = 6.72, 1.65 Hz), 7.513–7.239 (9 H, m), 7.099 (1 H, d, J = 2.20 Hz), 6.876 (1 H, dd, J = 8.62, 2.20 Hz), 3.890 (3 H, s).

MS (EI⁺): m/z = 300 (M⁺).

**O-Trimesilislycyanohydrid of 4-Methoxybenzone (9j)**
To a solution containing 8j (2.00 g, 9.4 mmol) and a catalytic amount of ZnI₂ (150 mg, 0.47 mmol) in anhyd CH₂Cl₂ (31 mL) was added TMSCN (3.73 g, 4 equiv) at 0°C over 15 min. The mixture was stirred at 40°C for 12 h. The residue, obtained after evaporation of the solvent, was diluted with CHCl₃. The organic layer was washed with brine, dried (Na₂SO₄) and the solvent was evaporated to give 9j (2.790 g, 95%) as a yellow oil.

1H NMR (CDCl₃): δ = 7.483 (2 H, dd, J = 8.06, 2.10, 1.65 Hz), 7.391 (2 H, dd, J = 8.98, 2.20 Hz), 7.355–7.329 (3 H, m), 6.866 (2 H, dd, J = 8.17, 2.20 Hz), 0.129 (9 H, s).

MS (EI⁺): m/z = 311 (M⁺).

**α-Benzoyl(4-methoxyphenyl)phenylmethanol (2j)**
To the Grignard reagent prepared from bromobenzene (4.22 g, 3 equiv) and Mg turnings (718 mg, 3.3 equiv) in anhyd Et₂O (7 mL) was added a solution of 9j (2.79 g, 9.4 mmol) in anhyd Et₂O (4 mL) over 30 min. The mixture was stirred at r.t. for 4 h and added to 10% aq H₂SO₄ (200 mL) and stirred at r.t. for 18 h. The mixture was extracted with CHCl₃, and the organic layer was washed with brine, and dried (Na₂SO₄). The residue obtained after evaporation of the solvent was dissolved in EtOH (35 mL), and the resultant solution was treated with 3 N aq HCl (5 mL) at 50°C for 12 h. The solvent was evaporated to give a residue, which was diluted with CHCl₃, and the organic layer was washed with brine, and dried (Na₂SO₄). The residue, obtained after evaporation of the solvent, was flash chromatographed (EtOAc–hexane, 1:9) to give 2j (550 mg, 19%) as a yellow oil.
was flash-chromatographed (EtOAc–hexane, 1:19) to give 2j (2.5146 g, 75%) as a yellow oil which solidified; colorless solid; mp 64.5–65.5°C (recrystallized from hexane).

1H NMR (CDCl3): δ = 7.635 (2 H, d, J = 8.06 Hz), 7.424–7.324 (10 H, m), 7.079 (2 H, d, J = 7.88 Hz), 5.188 (1 H, s), 3.799 (3 H, s).

MS (EI+): m/z = 183 (M+ – COPhCH3).


Acid-Catalyzed Reaction of α-(4-Methylbenzoyl)diphenylmethanol (2j)

To pre-cooled TFSA (58.5 mL, 500 equiv) at –48°C (in a dry ice–methanol (2j) bath) was added 2j (400 mg, 1.33 mmol) over 5 min. After stirring at –48°C for 1 h, the mixture was poured into ice-water (300 mL) and extracted with CHCl3. The organic layer was washed with brine and dried (Na2SO4). The solvent was evaporated to give a residue which was flash-chromatographed (CHCl3–hexane, 1:4 to 1:1) to give phenanthrol 5j (51.6 mg, 14%) as a colorless oil (solidified) and fluorene 4j (260.5 mg, 69%) as a yellow solid.

Fluorene 4j

Colorless needles; mp 126.9–128.5°C (recrystallized from hexane).

HRMS (EI+): m/z = 288 (M+).


1H NMR (CDCl3): δ = 7.860 (2 H, d, J = 7.68 Hz), 7.667 (2 H, dd, J = 9.62, 6.78 Hz), 7.476–7.283 (6 H, m), 6.979 (2 H, t, J = 8.61 Hz), 5.509 (1 H, s).

MS (EI+): m/z = 284 (M+).

Fluorene 4k

Colorless needles; mp 126.0–126.7°C (recrystallized from hexane).

1H NMR (CDCl3): δ = 7.860 (2 H, d, J = 7.68 Hz), 7.667 (2 H, dd, J = 9.62, 6.78 Hz), 7.476–7.283 (6 H, m), 6.979 (2 H, t, J = 8.61 Hz), 5.509 (1 H, s).

MS (EI+): m/z = 284 (M+).

Fluorene 4k

Colorless needles; mp 126.0–126.7°C (recrystallized from hexane).

1H NMR (CDCl3): δ = 7.860 (2 H, d, J = 7.68 Hz), 7.667 (2 H, dd, J = 9.62, 6.78 Hz), 7.476–7.283 (6 H, m), 6.979 (2 H, t, J = 8.61 Hz), 5.509 (1 H, s).

MS (EI+): m/z = 284 (M+).

Fluorene 4k

Colorless needles; mp 126.0–126.7°C (recrystallized from hexane).

1H NMR (CDCl3): δ = 7.860 (2 H, d, J = 7.68 Hz), 7.667 (2 H, dd, J = 9.62, 6.78 Hz), 7.476–7.283 (6 H, m), 6.979 (2 H, t, J = 8.61 Hz), 5.509 (1 H, s).

MS (EI+): m/z = 284 (M+).

Fluorene 4k

Colorless needles; mp 126.0–126.7°C (recrystallized from hexane).

1H NMR (CDCl3): δ = 7.860 (2 H, d, J = 7.68 Hz), 7.667 (2 H, dd, J = 9.62, 6.78 Hz), 7.476–7.283 (6 H, m), 6.979 (2 H, t, J = 8.61 Hz), 5.509 (1 H, s).

Fluorene 4k

Colorless needles; mp 126.0–126.7°C (recrystallized from hexane).

1H NMR (CDCl3): δ = 7.860 (2 H, d, J = 7.68 Hz), 7.667 (2 H, dd, J = 9.62, 6.78 Hz), 7.476–7.283 (6 H, m), 6.979 (2 H, t, J = 8.61 Hz), 5.509 (1 H, s).

Fluorene 4k

Colorless needles; mp 126.0–126.7°C (recrystallized from hexane).

1H NMR (CDCl3): δ = 7.860 (2 H, d, J = 7.68 Hz), 7.667 (2 H, dd, J = 9.62, 6.78 Hz), 7.476–7.283 (6 H, m), 6.979 (2 H, t, J = 8.61 Hz), 5.509 (1 H, s).

Fluorene 4k

Colorless needles; mp 126.0–126.7°C (recrystallized from hexane).

1H NMR (CDCl3): δ = 7.860 (2 H, d, J = 7.68 Hz), 7.667 (2 H, dd, J = 9.62, 6.78 Hz), 7.476–7.283 (6 H, m), 6.979 (2 H, t, J = 8.61 Hz), 5.509 (1 H, s).

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References


(5) Photochemical cyclizations of methoxy-substituted benzoin esters (e.g., 4'-methoxybenzoin acetate) to give benzofurans (2-phenyl-6-methoxybenzofuran) was reported by Sheehan, J. C.; Wilson, R. M.; Oxford, A. W. J. Am. Chem. Soc. 1971, 93, 7222.

(6) It was reported that phenanthrolyldiphenylmethanol (2h, R = CH3) and α-benzoyldiphenylmethane 2d, R = R = H) cyclized in H2SO4–CHCl3 by an electrocyclization mechanism between the benzene ring and the carbonyl group, resulting in the formation of the corresponding benzo[2]furans. Although the formation of the fluorene derivative 4d from 2d also has been reported under similar conditions. 32


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