Synthesis, Absorption Spectra, and Photostability of Triarylmethane Dye Ethynylogues Containing Trifluoromethyl Group(s)

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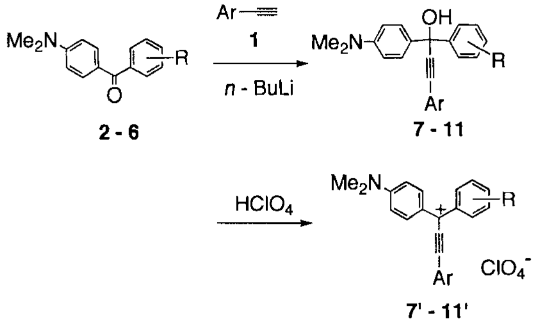
Triarylmethane dye ethynylogues **7'–11'** containing trifluoromethyl group(s) are synthesized in moderate to good yields by treating 1,1,3-triaryl-2-propyn-1-ols, prepared from diaryl ketones and lithium arylacetylides bearing trifluoromethyl group(s), with perchloric acid. The first absorption bands of a series of triarylmethane dye ethynylogues containing trifluoromethyl group(s) **11'** are observed around 700 nm. The photostability of the triarylmethane dyes is also examined.

Introduction of fluorine and a per(or poly)fluoroalkyl group into a molecule allows a modification of the properties of the obtained compound over a rather wide range[1]. Dyes bearing a trifluoromethyl group such as CI Acid Red 266[2] and coumarins[3] have been reported to show higher stability towards UV irradiation. Triphenylmethane dyes are important in dye chemistry from the viewpoint of the structure. Recently, new triphenylmethane dye ethynylogues, having absorption bands near the infrared region, have been synthesized[4]. Photofading of Malachite Green (MG, CI Basic Green 4) has been reported to give the triarylmethanol derivative of MG, 4-(dimethylamino)benzophenone, and 4-(dimethylamino)phenol[5]. Similarly, Crystal Violet (CV, CI Basic Violet 3) has been found to give leuco and demethylated derivatives of CV, Michler's ketone, and 4-(dimethylamino)phenol[6]. The active species formed in the photofading of triphenylmethane dyes under oxidative conditions have been proposed to be singlet oxygen species generated by selfsensitization of the substrate in the presence of oxygen[6]. Therefore, introduction of electron-withdrawing and bulky trifluoromethyl group(s) into triarylmethane dye ethynylogues may suppress the electrophilic oxidation reaction. In our continuing study of the synthesis and properties of fluorine-containing dyes[7], the synthesis and absorption spectra of new triarylmethane dye ethynylogues containing trifluoromethyl group(s) and their photostability are described in this report.

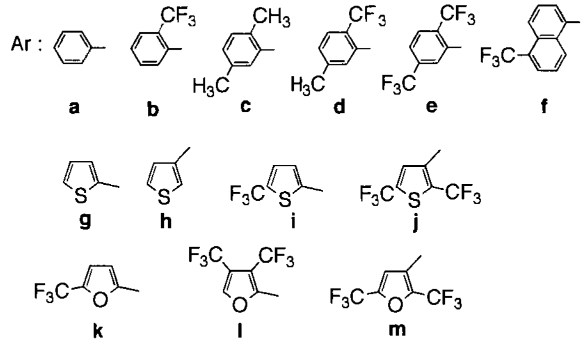
Results and Discussion

The synthesis of triarylmethane dye ethynylogues containing trifluoromethyl group(s) is shown in Scheme 1. Arylacetylenes **1** containing trifluoromethyl group(s) are synthesized as described in refs.[8–15]. Lithium arylacetylides, prepared from arylacetylenes and *n*-butyllithium, are allowed to react with ketones **2–6** to give the corresponding propyn-1-ols (hydrols) **7–11**, which are treated with perchloric acid to give triarylmethane dye ethynylogues **7'–11'**.

Scheme 1



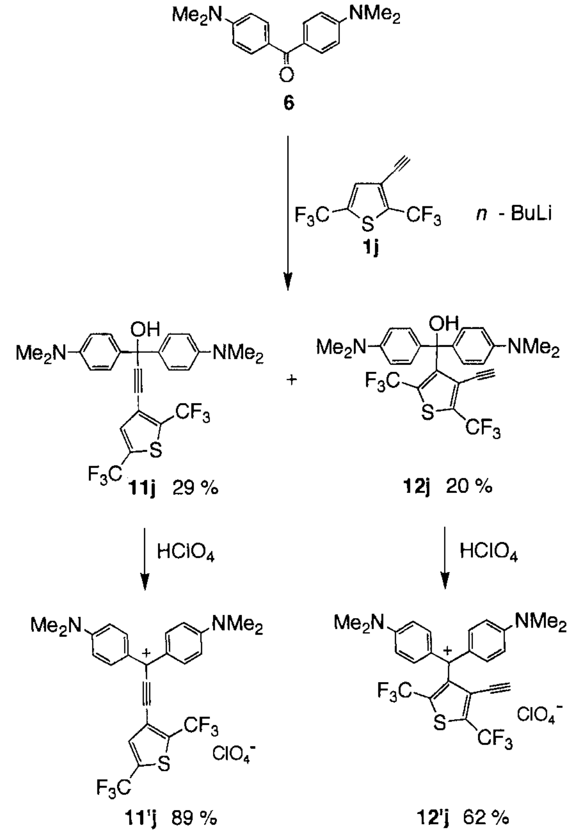
	2,7	3,8	4,9	5,10	6,11
R	H	2-CF_3	3-CF_3	4-CF_3	4-NMe_2



3-Ethynyl-2,5-bis(trifluoromethyl)thiophene (**1j**) reacts with ketone **6** in the presence of *n*-butyllithium to afford both the 2-propyn-1-ol **11j** and triarylmethanol **12j**

(Scheme 2). The hydrols **11j** and **12j** are converted into the corresponding triarylmethane dyes **11'j** and **12'j**.

Scheme 2



In the reaction of 2-ethynyl-3,4-bis(trifluoromethyl)furan (**1l**) with ketones **2** and **6**, both the corresponding propyn-1-ols **7l** and **11l** and triarylmethanols **12l** and **13l** are also obtained and subsequently converted into the corresponding dyes **7'l**, **12'l**, and **13'l** with perchloric acid (Scheme 3).

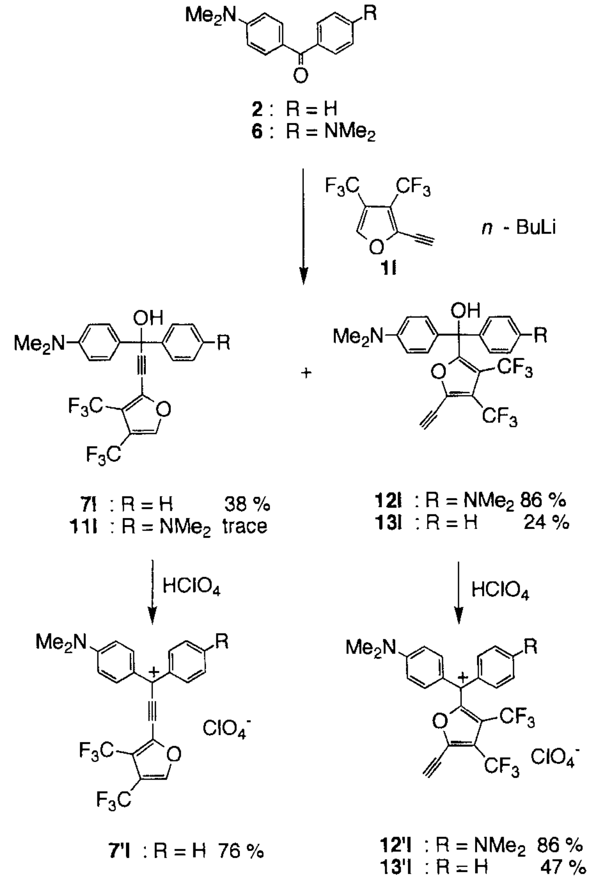
These results suggest that the hydrogen atoms on the thienyl and furyl rings bearing two electron-withdrawing trifluoromethyl groups in a molecule are as acidic as that of the acetylenic one to form the corresponding lithio intermediates.

The absorption bands of triarylmethane dye ethynylogues **7'**–**11'** are compiled in Table 1. These dyes have first and second absorption bands in the visible region. Both the absorption bands of a series of triarylmethane dye ethynylogues **7'** are hypsochromic compared with those of **11'**. For example, the first absorption bands of **7'a** and **11'a** are observed at 514 and 688 nm and the second ones at 278 and 492 nm, respectively (runs 1, 13).

The first absorption bands of a series of dyes **7'** are more bathochromic in the order of aryl, 2-thienyl > 3-thienyl > phenyl (runs 1, 6, 7). Introduction of trifluoromethyl group(s) into the phenyl moieties give rise to hypsochromic shifts (runs 1–4). The second absorption bands of this series of dyes **7'** except **7'f** are observed around 280 nm (runs 1–9).

In a series of dyes **11'**, the first absorption band of 2-thienyl derivative **11'g** is slightly bathochromic compared with those of phenyl and 3-thienyl derivatives **11'a** and **11'h** (runs 13, 19, 20). Introduction of electron-withdrawing trifluoromethyl group(s) into each aryl moiety causes bathochromic shifts (runs 13–17, 19, 21, 22). The second absorption bands of dyes **11'** are more bathochromic in the order of aryl, 2-thienyl > 3-thienyl > phenyl (runs 13, 19, 20). Introduction of trifluoromethyl group(s) into the phenyl and thienyl moieties also causes a hypsochromic shift (runs 13–17, 20–22). No remarkable difference in the first and second absorption bands between thienyl and furyl derivatives are observed (runs 21, 23).

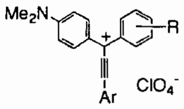
Scheme 3

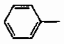
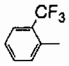
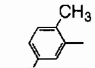
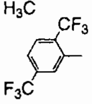
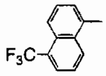
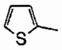
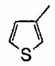
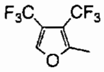
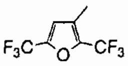
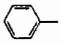
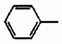
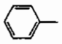
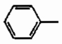
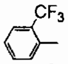
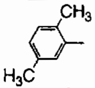
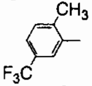
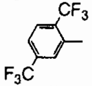
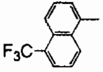
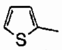
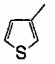
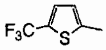
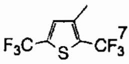
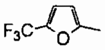


The absorption bands of triarylmethane dyes **12'**–**14'** are listed in Table 2. The first absorption band of **12'j** is more hypsochromic than that of the corresponding ethynylogue **11'j** (run 1, run 23 in Table 1), due to the non-planarity of three aryl moieties. Those of trifluoromethyl-substituted thienyl and furyl derivatives **12'j** and **12'l** are more bathochromic than the corresponding phenyl derivative **14'a** (runs 1, 2, 4).

Stabilities of various kinds of triarylmethane dyes upon UV irradiation are shown in Figures 1–4. The photostability of triphenylmethane dyes decreases in the order of **14'a** > **15'** > **11'** > **16'** (Figure 1). Dye **16'** has been found to be remarkably unstable. In a series of Malachite Green (MG, CI Basic Green 4), introduction of trifluoromethyl group into the *o*-, *m*-, and *p*-positions improves the photostability (Figure 2). This result may be attributed to the

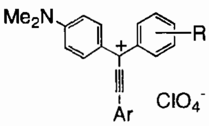
Table 1. Absorption spectra of triarylmethane dye ethynylogues

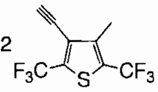
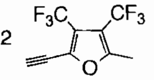
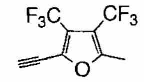
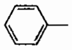


Run	Compd	R	Ar	λ_{max} /nm (ε)
1	**7a**	H		514 (40600), 278 (10400)
2	**7b**	H		496 (42300), 275 (12400)
3	**7c**	H		532 (40900), 283 (10400)
4	**7e**	H		487 (35200), 270 (10400)
5	**7f**	H		535 (36900), 317 (9600)
6	**7g**	H		548 (44600), 284 (10900)
7	**7h**	H		529 (41400), 278 (9600)
8	**7l**	H		491 (31400), 279 (10000)
9	**7m**	H		478 (35000), 278 (8400)
10	**8a**	2-CF_3		493 (36800), 279 (10400)
11	**9a**	3-CF_3		506 (32600), 279 (9400)
12	**10a**	4-CF_3		504 (29800), 278 (8800)
13	**11a**	4-NMe_2		688 (87000), 492 (32000)
14	**11b**	4-NMe_2		704 (101000), 488 (35400)
15	**11c**	4-NMe_2		688 (94300), 509 (36900)
16	**11d**	4-NMe_2		703 (100300), 490 (36200)
17	**11e**	4-NMe_2		715 (103000), 485 (33000)
18	**11f**	4-NMe_2		701 (78600), 518 (32900)
19	**11g**	4-NMe_2		694 (108000), 522 (47600)
20	**11h**	4-NMe_2		687 (108200), 502 (40000)
21	**11i**	4-NMe_2		710 (69800), 504 (27800)
22	**11j**	4-NMe_2		715 (103800), 486 (33500)
23	**11k**	4-NMe_2		713 (79300), 500 (31100)

[a] Isolated yield. – [b] Measured in CH_2Cl_2.

Table 2. Absorption spectra of triarylmethane dyes



Run	Compd	R	Ar	λ_{max} /nm (ε) [a]
1	**12'j**	4-NMe2		659 (105000), 420 (9100)
2	**12'l**	4-NMe2		686 (106000), 451 (15000)
3	**13'l**	H		472 (26400), 275 (10600)
4	**14'a**	4-NMe2		623 (116000), 432 (19200)

[a] Measured in CH_2Cl_2.

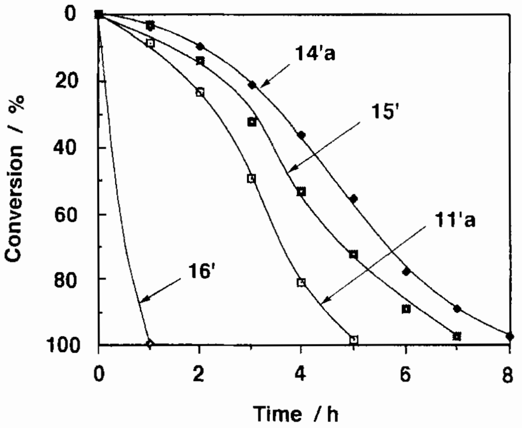


Figure 1. Photostability of triphenylmethane dyes

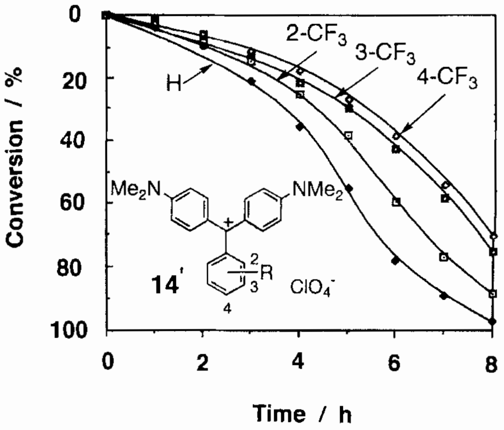


Figure 2. Photostability of triphenylmethane dyes containing trifluoromethyl group(s)

higher oxidation potentials of the trifluoromethyl derivatives compared with those of the unsubstituted compounds, resulting in a suppression of the photochemical oxidation reaction. In the case of triphenylmethane dye ethynologues, the stability is also improved by the introduction of trifluoromethyl group(s) (Figure 3), whereas in the case of thienyl-triarylmethane ethynylogues, no remarkable effect of substituted trifluoromethyl group(s) is observed (Figure 4).

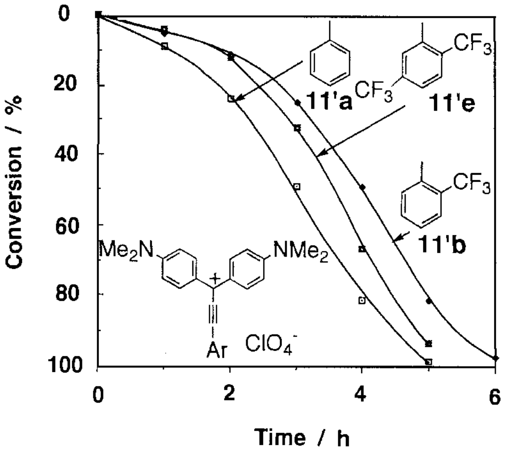


Figure 3. Photostability of triphenylmethane dye ethynylogues containing trifluoromethyl group(s)

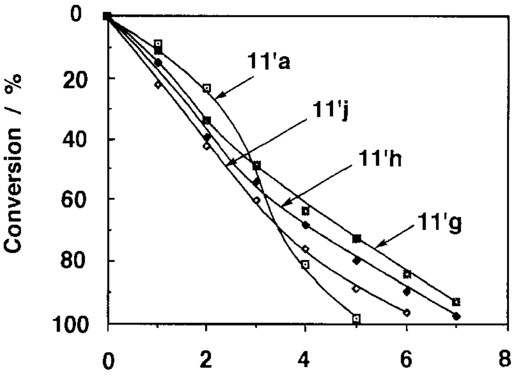


Figure 4. Photostability of triarylmethane dye ethynylogoues

Experimental

Melting points: Yanagimoto micro melting point apparatus. – ^{1}H NMR: Jeol JNM-270GX. – MS: Shimadzu QP-1000. – UV: Shimadzu UV-160A.

Materials: Phenylacetylene (**1a**), 4-(dimethylamino)benzophenone (**2**), and 4,4'-bis(dimethylamino)benzophenone (**6**) were purchased from Tokyo Kasei Kogyo Co., Ltd. [2-(Trifluoromethyl)phenyl]acetylene (**1b**)[8], (2,5-dimethylphenyl)acetylene (**1c**)[9], [5-methyl-2-(trifluoromethyl)phenyl]acetylene (**1d**)[9], [2,5-bis(trifluoromethyl)phenyl]acetylene (**1e**)[8], [5-(trifluoromethyl)-1-naphthyl]acetylene (**1f**)[10], 2-ethynylthiophene (**1g**)[11], 3-ethynylthiophene (**1h**)[12], 2-ethynyl-5-(trifluoromethyl)thiophene (**1i**)[13], 3-ethynyl-2,5-bis(trifluoromethyl)thiophene (**1j**)[13], 2-ethynyl-5-(trifluoromethyl)furan (**1k**)[13], 2-ethynyl-3,4-bis(trifluoromethyl)furan (**1l**)[14], 3-ethynyl-2,5-bis(trifluoromethyl)furan (**1m**)[15], 4-(dimethylamino)-4'-(trifluoromethyl)benzophenone (**5**)[16], 1,1-Bis[4-(dimethylamino)phenyl]-3-phenyl-2-propyn-1-ol (**11a**)[4a] were synthesized as described in the literature.

Synthesis of 4-(Dimethylamino)benzophenones: To a dry ether solution (85 ml) of a (trifluoromethyl)benzoyl chloride (12.5 g, 0.06 mol), was added anhydrous aluminium chloride (63.6 g, 0.238 mol) in small portions at 0°C. To the mixture was then added *N,N*-dimethylaniline (21.8 g, 0.179 mol). After refluxing for 30 min the mixture was poured into a 20% aqueous solution (300 ml) of sodium hydroxide. After removal of the excess dimethylaniline by steam distillation, the resulting precipitate was filtered, dried, and recrystallized from ethanol. The physical and spectral data are listed below.

4-(Dimethylamino)-2'-(trifluoromethyl)benzophenone (**3**): Yield 4.9 g (28%), m.p. 119–121°C. – ^{1}H NMR (CDCl$_3$): δ = 3.07 (s, 6H), 6.63 (d, J = 8.8 Hz, 2H), 7.37 (d, J = 6.7 Hz, 1H), 7.57 (t, J = 6.7 Hz, 1H), 7.58 (t, J = 6.7 Hz, 1H), 7.68 (d, J = 8.8 Hz, 2H), 7.75 (d, J = 6.7 Hz, 1H). – MS (EI, 70 eV), *m/z* (%): 293 (65) [M$^+$], 148 (100). – $C_{16}H_{14}F_3NO$ (293.3): calcd. C 65.52, H 4.81, N 4.78; found C 65.67, H 4.80, N 4.66.

4-(Dimethylamino)-3'-(trifluoromethyl)benzophenone (**4**): Yield 5.6 g (32%), m.p. 84–86°C. – ^{1}H NMR (CDCl$_3$): δ = 3.10 (s, 6H), 6.69 (d, J = 8.8 Hz, 2H), 7.59 (t, J = 7.6 Hz, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.77 (d, J = 8.8 Hz, 2H), 7.90 (d, J = 7.6 Hz, 1H), 7.98 (s, 1H). – MS (EI, 70 eV), *m/z* (%): 293 (40) [M$^+$], 148 (100). – $C_{16}H_{14}F_3NO$ (293.3): calcd. C 65.52, H 4.81, N 4.78; found C 65.80, H 4.84, N 4.71.

Synthesis of 1,1,3-Triaryl-2-propyn-1-ols. General Procedure: To a dry ethereal solution (50 ml) of the arylacetylene **1** (20 mmol) and *n*-butyllithium (20 mmol) was added the ketone (10 mmol). The mixture was stirred for 16 h at 0°C under nitrogen. After the reaction was complete, the mixture was poured into water (100 ml). The ethereal layer was separated and dried with sodium sulfate. After evaporation of the solvent the product was separated by column chromatography (SiO$_2$, AcOEt/C_6H_{14}, 1:2). The physical and spectral data are given below.

1-[4-(Dimethylamino)phenyl]-1,3-diphenyl-2-propyn-1-ol (**7a**): Yield 301 mg (46%), m.p. 151–153°C. – ^{1}H NMR (CDCl$_3$): δ = 2.76 (s, 1H), 2.94 (s, 6H), 6.69 (d, J = 9.0 Hz, 2H), 7.29–7.37 (m, 6H), 7.49–7.52 (m, 4H), 7.66–7.69 (m, 2H). – MS (EI, 70 eV), *m/z* (%): 327 (100) [M$^+$], 310 (49), 250 (47). – $C_{23}H_{21}NO$ (327.4): calcd. C 84.37, H 6.47, N 4.28; found C 84.69, H 6.50, N 4.51.

1-[4-(Dimethylamino)phenyl]-1-phenyl-3-[2-(trifluoromethyl)phenyl]-2-propyn-1-ol (**7b**): Yield 616 mg (78%), m.p. 100–101°C. – ^{1}H NMR (CDCl$_3$): δ = 2.92 (s, 7H, overlapping 6H and 1H), 6.68 (d, J = 8.9 Hz, 2H), 7.24–7.45 (m, 6H), 7.49 (d, J = 8.9 Hz, 2H), 7.61–7.68 (m, 3H). – MS (EI, 70 eV), *m/z* (%): 395 (100) [M$^+$], 378 (35). – $C_{24}H_{20}F_3NO$ (395.4): calcd. C 72.90, H 5.10, N 3.54; found C 72.73, H 5.09, N 3.52.

1-[4-(Dimethylamino)phenyl]-3-(2,5-dimethylphenyl)-1-phenyl-2-propyn-1-ol (**7c**): Yield 405 mg (57%), m.p. 129–130°C. – ^{1}H NMR (CDCl$_3$): δ = 2.28 (s, 3H), 2.41 (s, 3H), 2.79 (s, 1H), 2.93 (s, 6H), 6.68 (d, J = 9.0 Hz, 2H), 7.03 (d, J = 7.9 Hz, 1H), 7.08 (d, J = 7.9 Hz, 1H), 7.29 (s, 1H), 7.27–7.37 (m, 3H), 7.51 (d, J = 9.0 Hz, 2H), 7.67–7.70 (m, 2H). – MS (EI, 70 eV), *m/z* (%): 355 (100) [M$^+$], 338 (25), 121 (44). – $C_{25}H_{25}NO$ (355.5): calcd. C 84.47, H 7.09, N 3.94; found C 84.18, H 7.38, N 3.54.

3-[2,5-Bis(trifluoromethyl)phenyl]-1-[4-(dimethylamino)phenyl]-1-phenyl-2-propyn-1-ol (**7e**): Yield 824 mg (89%), oil. – ^{1}H NMR (CDCl$_3$): δ = 2.94 (s, 7H, overlapping 6H and 1H), 6.69 (d, J = 9.0 Hz, 2H), 7.25–7.39 (m, 3H), 7.45–7.48 (m, 2 H), 7.63–7.88 (m, 5 H). – MS (EI, 70 eV), *m/z* (%): 463 (100) [M$^+$], 446 (41).

1-[4-(Dimethylamino)phenyl]-1-phenyl-3-[5-(trifluoromethyl)-1-naphthyl]-2-propyn-1-ol (**7f**): Yield 499 mg (56%), m.p. 124–125°C. – ^{1}H NMR (CDCl$_3$): δ = 2.95 (s, 6 H), 2.96 (s, 1 H), 6.71 (d, J = 8.8 Hz, 2 H), 7.27–7.41 (m, 3 H), 7.56 (d, J = 8.8 Hz, 2 H), 7.52–7.60 (m, 2 H), 7.73–7.76 (m, 2 H), 7.82 (d, J = 7.8 Hz, 1 H), 7.89 (d, J = 7.8 Hz, 1 H), 8.17 (d, J = 7.8 Hz, 1 H), 8.54 (d, J = 7.8 Hz, 1 H). – MS (EI, 70 eV), *m/z* (%): 445 (100) [M$^+$], 428 (31). – $C_{28}H_{22}F_3NO$ (445.5): calcd. C 75.49, H 4.98, N 3.15; found C 75.18, H 4.89, N 3.20.

1-[4-(Dimethylamino)phenyl]-1-phenyl-3-(2-thienyl)-2-propyn-1-ol (**7g**): Yield 360 mg (54%), m.p. 144–145°C. – ^{1}H NMR (CDCl$_3$): δ = 2.82 (s, 1 H), 2.93 (s, 6 H), 6.68 (d, J = 9.2 Hz, 2 H), 6.97 (dd, J = 4.9/4.3 Hz, 1 H), 7.25–7.36 (m, 5 H), 7.46 (d, J = 9.2 Hz, 2 H), 7.63–7.66 (m, 2 H). – MS (EI, 70 eV), *m/z* (%): 333 (94) [M$^+$], 316 (32), 121 (100). – $C_{21}H_{19}NOS$ (333.5): calcd. C 75.64, H 5.74, N 4.20; found C 76.23, H 6.05, N 4.14.

1-[4-(Dimethylamino)phenyl]-1-phenyl-3-(3-thienyl)-2-propyn-1-ol (**7h**): Yield 474 mg (71%), m.p. 166–167°C. – ^{1}H NMR (CDCl$_3$): δ = 2.76 (s, 1 H), 2.93 (s, 6 H), 6.69 (d, J = 8.8 Hz, 2 H), 7.16 (d, J = 4.9 Hz, 1 H), 7.25–7.36 (m, 4 H), 7.46–7.50 (m, 1 H), 7.48 (d, J = 8.8 Hz, 2 H), 7.64–7.67 (m, 2 H). – MS (EI, 70 eV), *m/z* (%): 333 (100) [M$^+$], 316 (51), 121 (87). – $C_{21}H_{19}NOS$ (333.5): calcd. C 75.64, H 5.74, N 4.20; found C 76.27, H 6.10, N 4.16.

3-[3,4-Bis(trifluoromethyl)-2-furyl]-1-[4-(dimethylamino)phenyl]-1-phenyl-2-propyn-1-ol (**7l**): Yield 344 mg (38%), m.p. 115–117°C. – ^{1}H NMR (CDCl$_3$): δ = 2.84 (s, 1 H), 2.94 (s, 6 H), 6.68 (d, J = 8.8 Hz, 2 H), 7.29–7.38 (m, 3 H), 7.40 (d, J = 8.8 Hz, 2 H), 7.57–7.60 (m, 2 H), 7.74 (s, 1 H). – MS (EI, 70 eV), *m/z* (%): 453 (74) [M$^+$], 436 (26), 105 (100). – $C_{23}H_{17}F_6NO_2$ (453.4): calcd. C 60.93, H 3.78, N 3.09; found C 60.68, H 3.57, N 3.02.

3-[2,5-Bis(trifluoromethyl)-3-furyl]-1-[4-(dimethylamino)phenyl]-1-phenyl-2-propyn-1-ol (**7m**): Yield 299 mg (33%), oil. – ^{1}H NMR (CDCl$_3$): δ = 2.78 (s, 1 H), 2.94 (s, 6 H), 6.67 (d, J = 9.0 Hz, 2 H), 6.93 (s, 1 H), 7.28–7.37 (m, 3 H), 7.40 (d, J = 9.0 Hz, 2 H), 7.57–7.60 (m, 2 H). – MS (EI, 70 eV), *m/z* (%): 453 (81) [M$^+$], 436 (39), 120 (100).

1-[4-(Dimethylamino)phenyl]-3-phenyl-1-[2-(trifluoromethyl)phenyl]-2-propyn-1-ol (**8a**): Yield 142 mg (18%), oil. – ^{1}H NMR (CDCl$_3$): δ = 2.90 (s, 1 H), 2.95 (s, 6 H), 6.67 (d, J = 8.8 Hz, 2 H), 7.29–7.59 (m, 7 H), 7.37 (d, J = 8.8 Hz, 2 H), 7.76 (d, J = 7.6 Hz, 1 H), 8.07 (d, J = 7.6 Hz, 1 H). – MS (EI, 70 eV), *m/z* (%): 395 (100) [M$^+$], 378 (23), 294 (52).

1-[4-(Dimethylamino)phenyl]-3-phenyl-1-[3-(trifluoromethyl)phenyl]-2-propyn-1-ol (**9a**): Yield 498 mg (63%), oil. – ^{1}H NMR (CDCl$_3$): δ = 2.85 (s, 1 H), 2.95 (s, 6 H), 6.69 (d, J = 8.8 Hz, 2 H), 7.31–7.38 (m, 3 H), 7.42 (d, J = 7.9 Hz, 1 H), 7.49 (d, J = 8.8 Hz, 2 H), 7.49–7.54 (m, 3 H), 7.81 (d, J = 7.9 Hz, 1 H), 8.01 (s, 1 H). – MS (EI, 70 eV), *m/z* (%): 395 (99) [M$^+$], 378 (32), 294 (92), 148 (100).

1-[4-(Dimethylamino)phenyl]-3-phenyl-1-[4-(trifluoromethyl)phenyl]-2-propyn-1-ol (**10a**): Yield 150 mg (19%), m.p. 122–124°C. – ^{1}H NMR (CDCl$_3$): δ = 2.83 (s, 1 H), 2.95 (s, 6 H), 6.69 (d, J = 8.5 Hz, 2 H), 7.33–7.35 (m, 3 H), 7.49 (d, J = 8.5 Hz, 2 H), 7.48–7.53 (m, 2 H), 7.59 (d, J = 8.5 Hz, 2 H), 7.79 (d, J = 8.5 Hz, 2 H). – MS (EI, 70 eV), *m/z* (%): 395 (100) [M$^+$], 378 (43), 294 (44), 148 (53). – $C_{24}H_{20}F_3NO$ (395.4): calcd. C 72.90, H 5.10, N 3.54; found C 73.18, H 5.22, N 3.40.

1,1-Bis[4-(dimethylamino)phenyl]-3-phenyl-2-propyn-1-ol (**11a**): Yield 533 mg (72%), m.p. 161–162°C (ref.[4a] 163–164°C).

1,1-Bis[4-(dimethylamino)phenyl]-3-[2-(trifluoromethyl)phenyl]-2-propyn-1-ol (**11b**): Yield 684 mg (78%), m.p. 127–128°C. – ^{1}H NMR (CDCl$_3$): δ = 2.83 (s, 1 H), 2.92 (s, 12 H), 6.69 (d, J = 9.0 Hz, 4 H), 7.37 (t, J = 8.2 Hz, 1 H), 7.43 (t, J = 8.2 Hz, 1 H), 7.49 (d, J = 9.0 Hz, 4 H), 7.61 (d, J = 8.2 Hz, 1 H), 7.65 (d, J = 8.2 Hz, 1 H). – MS (EI, 70 eV), *m/z* (%): 438 (100) [M$^+$], 421 (56), 148 (85). – $C_{26}H_{25}F_3N_2O$ (438.5): calcd. C 71.21, H 5.75, N 6.39; found C 71.08, H 5.79, N 6.31.

1,1-Bis[4-(dimethylamino)phenyl]-3-(2,5-dimethylphenyl)-2-propyn-1-ol (**11c**): Yield 430 mg (54%), m.p. 169–170°C. – ^{1}H NMR (CDCl$_3$): δ = 2.27 (s, 3 H), 2.42 (s, 3 H), 2.72 (s, 1 H), 2.93 (s, 12 H), 6.69 (d, J = 8.9 Hz, 4 H), 7.02 (d, J = 7.8 Hz, 1 H), 7.08 (d, J = 7.8 Hz, 1 H), 7.29 (s, 1 H), 7.52 (d, J = 8.9 Hz, 4 H). – MS (EI, 70 eV), *m/z* (%): 398 (80) [M$^+$], 381 (100), 148 (51), 121 (44). – $C_{27}H_{30}N_2O$ (398.6): calcd. C 81.37, H 7.59, N 7.03; found C 80.98, H 7.78, N 6.61.

1,1-Bis[4-(dimethylamino)phenyl]-3-[5-methyl-2-(trifluoromethyl)phenyl]-2-propyn-1-ol (**11d**): Yield 706 mg (78%), m.p. 163–164°C. – ^{1}H NMR (CDCl$_3$): δ = 2.35 (s, 3 H), 2.71 (s, 1 H), 2.93 (s, 12 H), 6.69 (d, J = 8.7 Hz, 4 H), 7.18 (d, J = 8.4 Hz, 1 H), 7.44–7.54 (m, 2 H), 7.49 (d, J = 8.7 Hz, 4 H). – MS (EI, 70 eV), *m/z* (%): 452 (100) [M$^+$], 435 (54), 148 (30). – $C_{27}H_{27}F_3N_2O$ (452.5): calcd. C 71.66, H 6.01, N 6.19; found C 71.46, H 6.17, N 5.92.

3-[2,5-Bis(trifluoromethyl)phenyl]-1,1-bis[4-(dimethylamino)phenyl]-2-propyn-1-ol (**11e**): Yield 770 mg (76%), m.p. 144–145°C. – ^{1}H NMR (CDCl$_3$): δ = 2.84 (s, 1 H), 2.93 (s, 12 H), 6.69 (d, J = 9.0 Hz, 4 H), 7.47 (d, J = 9.0 Hz, 4 H), 7.63 (d, J = 8.2 Hz, 1 H), 7.78 (d, J = 8.2 Hz, 1 H), 7.87 (s, 1 H). – MS (EI, 70 eV), *m/z* (%): 506 (100) [M$^+$], 489 (55), 148 (35). – $C_{27}H_{24}F_6N_2O$ (506.5): calcd. C 64.02, H 4.78, N 5.53; found C 63.53, H 4.75, N 5.50.

1,1-Bis[4-(dimethylamino)phenyl]-3-[5-(trifluoromethyl)-1-naphthyl]-2-propyn-1-ol (**11f**): Yield 557 mg (57%), m.p. 106–107°C. – ^{1}H NMR (CDCl$_3$): δ = 2.80 (s, 1 H), 2.95 (s, 12 H), 6.73 (d, J = 8.9 Hz, 4 H), 7.55–7.58 (m, 2 H), 7.57 (d, J = 8.9 Hz, 4 H), 7.82 (d, J = 7.5 Hz, 1 H), 7.89 (d, J = 7.5 Hz, 1 H), 8.17 (d, J = 7.5 Hz, 1 H), 8.58 (d, J = 7.5 Hz, 1 H). – MS (EI, 70 eV), *m/z* (%): 488 (99) [M$^+$], 471 (51), 148 (100), 121 (35). – $C_{30}H_{27}F_3N_2O$ (488.6): calcd. C 73.75, H 5.57, N 5.74; found C 73.32, H 5.63, N 5.18.

1,1-Bis[4-(dimethylamino)phenyl]-3-(2-thienyl)-2-propyn-1-ol (**11g**): Yield 565 mg (75%), m.p. 174–175°C. – ^{1}H NMR (CDCl$_3$): δ = 2.70 (s, 1 H), 2.94 (s, 12 H), 6.69 (d, J = 8.5 Hz, 4 H), 6.97 (dd, J = 5.5/3.7 Hz, 1 H), 7.24 (d, J = 3.7 Hz, 1 H), 7.25 (d, J = 5.5 Hz, 1 H), 7.47 (d, J = 8.5 Hz, 4 H). – MS (EI, 70 eV), *m/z* (%): 376 (65) [M$^+$], 359 (50), 148 (100). – $C_{23}H_{24}N_2OS$ (376.5): calcd. C 73.37, H 6.43, N 7.44; found C 73.81, H 6.74, N 7.43.

1,1-Bis[4-(dimethylamino)phenyl]-3-(3-thienyl)-2-propyn-1-ol (**11h**): Yield 233 mg (31%), m.p. 180–181°C. – ^{1}H NMR (CDCl$_3$): δ = 2.68 (s, 1 H), 2.93 (s, 12 H), 6.69 (d, J = 8.5 Hz, 4 H), 7.15 (d, J = 4.7 Hz, 1 H), 7.25 (dd, J = 4.7/3.7 Hz, 1 H), 7.48 (d, J = 8.5 Hz, 4 H), 7.48 (d, J = 3.7 Hz, 1 H). – MS (EI, 70 eV), *m/z* (%): 376 (77) [M$^+$], 359 (78), 148 (100). – $C_{23}H_{24}N_2OS$ (376.5): calcd. C 73.37, H 6.43, N 7.44; found C 72.84, H 6.34, N 7.57.

3-[2,5-Bis(trifluoromethyl)-3-thienyl]-1,1-bis[4-(dimethylamino)phenyl]-2-propyn-1-ol (**11j**): Yield 297 mg (29%), m.p. 112–113°C. – ^{1}H NMR (CDCl$_3$): δ = 2.70 (s, 1 H), 2.94 (s, 12 H), 6.69 (d, J = 8.9 Hz, 4 H), 7.43 (d, J = 8.9 Hz, 4 H), 7.47 (s, 1 H). – MS (EI, 70 eV), *m/z* (%): 512 (100) [M$^+$], 495 (81). –

$C_{25}H_{22}F_6N_2OS$ (512.5): calcd. C 58.58, H 4.33, N 5.47; found C 58.44, H 4.38, N 5.24.

Bis[4-(dimethylamino)phenyl][4-ethenyl-2,5-bis(trifluoromethyl)-3-thienyl]methanol (**12j**): Yield 205 mg (20%), oil. – ^{1}H NMR ($CDCl_3$): δ = 2.82 (s, 1H), 2.95 (s, 12H), 3.05 (s, 1H), 6.65 (d, *J* = 9.2 Hz, 4H), 7.19 (d, *J* = 9.2 Hz, 4H). – MS (EI, 70 eV), *m/z* (%): 512 (100) [M$^+$], 495 (30), 148 (37), 121 (66).

Bis[4-(dimethylamino)phenyl][5-ethynyl-3,4-bis(trifluoromethyl)-2-furyl]methanol (**12l**): Yield 854 mg (86%), m.p. 186–187°C. – ^{1}H NMR ($CDCl_3$): δ = 2.86 (s, 1H), 2.95 (s, 12H), 3.51 (s, 1H), 6.66 (d, *J* = 9.0 Hz, 4H), 7.10 (d, *J* = 9.0 Hz, 4H). – MS (EI, 70 eV), *m/z* (%): 496 (69) [M$^+$], 479 (83), 148 (100). – $C_{25}H_{22}F_6N_2O_2$ (496.5): calcd. C 60.48, H 4.47, N 5.64; found C 61.08, H 4.43, N 6.80.

[4-(Dimethylamino)phenyl][5-ethynyl-3,4-bis(trifluoromethyl)-2-furyl]phenylmethanol (**13l**): Yield 218 mg (24%), m.p. 142–143°C. – ^{1}H NMR ($CDCl_3$): δ = 2.86 (s, 7H, overlapping 6H and 1H), 3.53 (s, 1H), 6.66 (d, *J* = 9.2 Hz, 2H), 7.04 (d, *J* = 9.2 Hz, 2H), 7.29–7.34 (m, 5H). – MS (EI, 70 eV), *m/z* (%): 453 (96) [M$^+$], 436 (46), 148 (40), 105 (100). – $C_{23}H_{17}F_6NO_2$ (453.4): calcd. C 60.93, H 3.78, N 3.09; found C 61.00, H 3.63, N 2.80.

Synthesis of Triarylmethane Dye Ethynylogues Containing Trifluoromethyl Group(s) **7'–13'**. *General Procedure:* To a benzene solution (100 ml) of 1,1,3-triaryl-2-propyn-1-ol **7–13** (2.0 mmol) was added 60% aqueous perchloric acid (2.0 mmol) at room temp. The mixture was stirred at room temp. for 24 h. After the reaction was complete, the precipitate was filtered, dried and recrystallized from acetone/hexane. The physical and spectral data are listed below.

7'a: Yield 794 mg (97%), m.p. 167–168°C (dec.). – MS (FAB, Xe), *m/z*: 310 [M$^+$ – ClO_4]. – **7'b**: Yield 907 mg (95%), m.p. 181–184°C (dec.). – MS (FAB, Xe), *m/z*: 378 [M$^+$ – ClO_4]. – **7'c**: Yield 665 mg (76%), m.p. 171–185°C (dec). – MS (FAB, Xe), *m/z*: 338 [M$^+$ – ClO_4]. – **7'e**: Yield 829 mg (76%), m.p. 115–125°C (dec). – MS (FAB, Xe), *m/z*: 446 [M$^+$ – ClO_4]. – **7'f**: Yield 749 mg (71%), m.p. 163–170°C (dec). – MS (FAB, Xe), *m/z*: 428 [M$^+$ – ClO_4]. – **7'g**: Yield 781 mg (96%), m.p. 184–187°C (dec). – MS (FAB, Xe), *m/z*: 316 [M$^+$ – ClO_4]. – **7'h**: Yield 798 mg (96%), m.p. 173–175°C (dec). – MS (FAB, Xe), *m/z*: 316 [M$^+$ – ClO_4]. – **7'l**: Yield 814 mg (76%), m.p. 90–94°C (dec). – MS (FAB, Xe), *m/z*: 436 [M$^+$ – ClO_4]. – **7'm**: Yield 600 mg (56%), m.p. 163–165°C (dec). – MS (FAB, Xe), *m/z*: 436 [M$^+$ – ClO_4]. – **8'a**: Yield 449 mg (47%), m.p. 126–128°C (dec). – MS (FAB, Xe), *m/z*: 378 [M$^+$ – ClO_4]. – **9'a**: Yield 468 mg (49%), m.p. 149–151°C (dec). – MS (FAB, Xe), *m/z*: 378 [M$^+$ – ClO_4]. – **10'a**: Yield 267 mg (28%), m.p. 175–177°C (dec). – MS (FAB, Xe), *m/z*: 378 [M$^+$ – ClO_4]. – **11'a**: Yield 679 mg (75%), m.p. 212–215°C (dec) [ref.[4a] 189°C (dec)]. – **11'b**: Yield 864 mg (83%), m.p. 225–230°C (dec). – MS (FAB, Xe), *m/z*: 421 [M$^+$ – ClO_4]. – **11'c**: Yield 855 mg (89%), m.p. 210–215°C (dec). – MS (FAB, Xe), *m/z*: 381 [M$^+$ – ClO_4]. – **11'd**: Yield 855 mg (80%), m.p. 253–255°C (dec). – MS (FAB, Xe), *m/z*: 435 [M$^+$ – ClO_4]. – **11'e**: Yield 895 mg (76%), m.p. 254–258°C (dec). – MS (FAB, Xe), *m/z*: 489 [M$^+$ – ClO_4]. – **11'f**: Yield 1095 mg (68%), m.p. >300°C. – MS (FAB, Xe), *m/z*: 471 [M$^+$ – ClO_4]. – **11'g**: Yield 880 mg (96%), m.p. >300°C. – MS (FAB, Xe), *m/z*: 359 [M$^+$ – ClO_4]. – **11'h**: Yield 853 mg (93%), m.p. >300°C. – MS (FAB, Xe), *m/z*: 359 [M$^+$ – ClO_4]. – **11'i**: Yield 663 mg (63%), m.p. 146–148°C (dec). – ^{1}H NMR ($CDCl_3$): δ = 3.40 (s, 12H), 7.04 (d, *J* = 9.5 Hz, 4H), 7.48 (d, *J* = 4.2 Hz, 1H), 7.56 (d, *J* = 4.2 Hz, 1H), 7.90 (d, *J* = 9.5 Hz, 4H). – MS (FAB, Xe), *m/z*: 427 [M$^+$ – ClO_4]. – **11'j**: Yield 1058 mg (89%), m.p. 215–217°C (dec). – MS (FAB, Xe), *m/z*: 495 [M$^+$ – ClO_4]. – **11'k**: Yield 817 mg (80%), m.p. 218–225°C (dec). – ^{1}H NMR ($CDCl_3$): δ = 3.38 (s, 12H), 7.02 (d, *J* = 8.7 Hz, 4H), 7.09 (br s, 1H), 7.28 (br s, 1H), 7.88 (d, *J* = 8.7 Hz, 4H). – MS (FAB, Xe), *m/z*: 411 [M$^+$ – ClO_4]. – **12'j**: Yield 737 mg (62%), m.p. 254–257°C (dec). – MS (FAB, Xe), *m/z*: 495 [M$^+$ – ClO_4]. – **12'l**: Yield 995 mg (86%), m.p. 125–135°C (dec). – MS (FAB, Xe), *m/z*: 479 [M$^+$ – ClO_4]. – **13'l**: Yield 503 mg (47%), m.p. 218–225°C (dec). – MS (FAB, Xe), *m/z*: 436 [M$^+$ – ClO_4].

Stability Measurement of Triarylmethane Dyes Under UV Irradiation: A dichloromethane solution (20 ml) of dyes ($1.25 \cdot 10^{-2}$ mmol dm^{-3}) in borosilicate glass was irradiated under the influence of atmospheric oxygen with a 200-W high-pressure mercury lamp by using a merry-go-round apparatus at room temp. The stability (conversion) was calculated on the basis of the changes of the absorbance at the absorption maximum of the solution by irradiation. The conversion is defined according to eq. (1),

$$\text{Conversion (\%)} = [(A_0 - A_t)/A_0] \cdot 100 \qquad (1)$$

where A_0 and A_t are the absorbance of the solution at 0 and *t* hours, respectively.

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[1] [1a] W. A. Sheppard, C. M. Sharts, *Organic Fluorine Chemistry*, W. A. Benjamin Inc., New York, **1969**. – [1b] R. D. Chambers, *Fluorine in Organic Chemistry*, John Wiley & Sons, NewYork, **1973**.

[2] N. Ishikawa, *Dyes Chem.* **1983**, *28*, 152–159.

[3] M. Matsui, K. Shibata, H. Muramatsu, H. Sawada, M. Nakayama, *Chem. Ber.* **1992**, *125*, 467–471.

[4] [4a] S. Akiyama, K. Yoshida, M. Hayashida, K. Nakashima, S. Nakatsuji, M. Iyoda, *Chem. Lett.* **1981**, 311–314. – [4b] S. Akiyama, K. Nakashima, S. Nakatsuji, M. Hamada, Y. Izaki, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 947–948. – [4c] S. Nakatsuji, N. Okamoto, K. Nakashima, S. Akiyama, *Chem. Lett.* **1986**, 329–332. – [4d] S. Akiyama, S. Nakatsuji, K. Nakashima, M. Watanabe, *J. Chem. Soc., Chem. Commun.* **1987**, 710–711. – [4e] S. Akiyama, S. Nakatsuji, K. Nakashima, S. Yamasaki, *Dyes Pig.* **1988**, *9*, 459–466. – [4f] S. Akiyama, S. Nakatsuji, K. Nakashima, M. Watanabe, H. Nakazumi, *J. Chem. Soc., Perkin Trans. 1*, **1988**, 3155–3161.

[5] J. J. Porter, S. B. Spears Jr., *Textile Chemist Colorist*, **1970**, *2*, 191–195.

[6] N. Kuramoto, T. Kitao, *Dyes Pig.* **1982**, *3*, 49–58.

[7] [7a] M. Matsui, S. Kawamura, K. Shibata, H. Muramatsu, M. Mitani, H. Sawada, M. Nakayama, *J. Fluorine Chem.* **1992**, *57*, 209–217. – [7b] M. Matsui, B. Joglekar, Y. Ishigure, K. Shibata, H. Muramatsu, Y. Murata, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1790–1794.

[8] K. Kodaira, K. Okuhara, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1625–1631.

[9] M. Nishida, K. Hosokawa, T. Ueda, T. Aoki, H. Muramatsu, *J. Fluorine Chem.* **1989**, *43*, 35–51.

[10] T. Okano, K. Ito, K. Kodaira, K. Hosokawa, M. Nishida, T. Ueda, H. Muramatsu, *J. Fluorine Chem.* **1988**, *38*, 139–152.

[11] K. Okuhara, *J. Org. Chem.* **1976**, *41*, 1487–1494.

[12] S. Tanaka, K. Okuhara, K. Kaeriyama, *Makromol. Chem.* **1986**, *187*, 2793–2800.

[13] M. Nishida, S. Fujii, T. Aoki, Y. Hayakawa, H. Muramatsu, T. Morita, *J. Fluorine Chem.* **1990**, *46*, 445–459.

[14] T. Okano, T. Ueda, K. Ito, K. Kodaira, K. Hosokawa, H. Muramatsu, *J. Fluorine Chem.* **1986**, *31*, 451–459.

[15] Y. Hayakawa, M. Nishida, A. Okumura, M. Matsui, H. Muramatsu, *Polymer Bull.* **1992**, *28*, 293–299.

[16] J. R. DoAmaral, E. J. Blanz Jr., F. A. French, *J. Med. Chem.* **1969**, *12*, 21–25.

[17] J. M. Eisenhart, A. B. Ellis, *J. Org. Chem.* **1985**, *50*, 4108–4113.

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