

Received: July 14, 1990; accepted: October 19, 1990

SYNTHESIS OF ASYMMETRIC POLYFLUORO-DIACETYLENE MONOMERS

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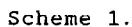
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SUMMARY

Asymmetric diacetylene monomers with polyfluoro-aromatic rings for nonlinear optics were prepared by the cross coupling of 1-bromo-acetylenes with polyfluoro-aromatic acetylenes which were prepared by nucleophilic substitution on penta-fluorophenyltrimethylsilylacetylene.

INTRODUCTION

Solid-state polymerization of diacetylenes is known to give peculiar single crystals of conjugated polymers as shown in Scheme 1 [1,2] and has caught considerable attention on their nonlinear optical properties [3-5]. It is well known that polydiacetylenes with methylene groups next to the conjugated main chain almost have the same values of THG (third harmonic generation), approximately 10^{-10} esu [6,7]. To achieve large THG, previously we reported an efficient method for synthesis of symmetric fluoro-diacetylenes [8] and we found that these polydiacetylenes have larger THG than that of polydiacetylenes

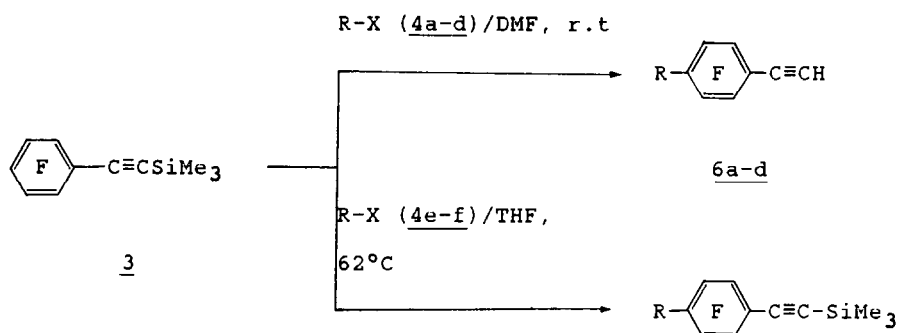


Fluoro-diacetylenes were derived from the fluoro-aromatic terminal acetylenes. Previously we have reported that the Pd-catalyzed coupling of pentafluoriodobenzene (1) with terminal acetylenes gave fluoro-aromatic acetylenes in good yield [11] and chosen the trimethylsilyl group (as in 2) as a protecting group because it can be quantitatively removed by treatment with dilute alkali to give fluoro-aromatic terminal acetylenes [12] (Scheme 2).



We found that the nucleophilic substitution on pentafluorophenyl-trimethylsilylacetylene (3) is very easy and gives only

para-substituted products [12]. Nucleophiles, ArOK (4a-d), reacted with (3) in DMF at room temperature to yield p-aryloxy-tetrafluorophenylacetylenes (6a-d) in good yield as shown in Scheme 3, but p-Cl-C₆H₄-OK reacted with (3) to give insoluble polymer (this result is now under study). ArMgBr (4e-f) as nucleophiles reacted with (3) in THF under reflux to give (p-aryl-tetrafluorophenyl)trimethylsilylacetylenes (5e-f) which yield p-aryl-tetrafluorophenylacetylenes (6e-f) after the removal of trimethylsilyl group with aqueous dilute sodium hydroxide. Some examples are shown in Table 1.



a-d; X = K

a; R = PhO

b; R = 4-MeC₆H₄O

c; R = 4-BrC₆H₄O

d; R = 3,5-diMeC₆H₃O

e-f; X = MgBr

e; R = Ph

f; R = 4-MeOC₆H₄

Scheme 3.

TABLE 1

Preparation of p-substituted-tetrafluorophenylacetylenes 6

<u>4</u>	Nucleophile	solvent/ temp./time ^a (°C) (h)	Product <u>5</u> Hydrolysis			Product <u>6</u>	
			No	Yield ^b	time ^c	No	yield ^b
			(%)		(h)	(%)	
<u>4a</u>		DMF/r.t./1.5h	-	-	-	<u>6a</u>	97
<u>4b</u>		DMF/r.t./1.5h	-	-	-	<u>6b</u>	93
<u>4c</u>		DMF/THF (1:1)/ 0-r.t./3.5h	-	-	-	<u>6c</u>	75
<u>4d</u>		DMF/r.t./2.5h	-	-	-	<u>6d</u>	75
<u>4e</u>		THF/62/11h	<u>5e</u>	92	3h	<u>6e</u>	89
<u>4f</u>		THF/62/10h	<u>5f</u>	85	4h	<u>6f</u>	82

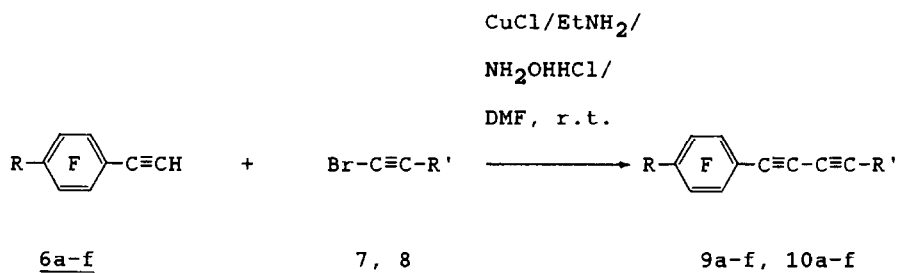
^a Nucleophilic substitution on (3) with (4c) in DMF at r.t. mainly gave polymer, the reaction was carried out in THF/DMF (1/1) at 0-r.t. to mainly give p-(4-bromo-phenoxy)-tetrafluorophenylacetylene (6c).

^b Isolated yields.

^c All reactions were carried out in MeOH at r.t..

Our attention was focused on the synthesis of asymmetric fluoro-diacetylenes by the Chodkiewicz-Cadiot coupling reaction [13] of p-substituted-tetrafluorophenylacetylenes (6a-f) and 1-bromo-acetylenes (7) and (8) (Scheme 4).

We found that fluoro-diacetylenes with aryloxy groups have reactivities in solid-state polymerization. (9b), (9c), (9d) and (10c) turned violet, red and blue upon exposure to day light to give insoluble black polydiacetylenes due to partial solid-state photopolymerization of these monomer crystals (Table 2).



9; R'=HOCH₂; 10; R'=Ph

6a; R=PhO

7; R'=HOCH₂

a; R=PhO

6b; R=4-MeC₆H₄O

8; R'=Ph

b; R=4-MeC₆H₄O

6c; R=4-BrC₆H₄O

c; R=4-BrC₆H₄O

6d; R=3,5-diMeC₆H₃O

d; R=3,5-diMeC₆H₃O

6e; R=Ph

e; R=Ph

6f; R=4-MeOC₆H₄

f; R=4-MeOC₆H₄

Scheme 4.

TABLE 2

Preparation and solid-state reactivities of Asymmetric Fluoro-Diacetylenes 9 and 10

Fluoro-diacetylenes <u>9</u> , <u>10</u>	Yield ^a (%)	Solid-state reactivities ^b photopolymerization
<u>9a</u>	87	-
<u>9b</u>	75	++
<u>9c</u>	80	++
<u>9d</u>	79	+
<u>9e</u>	85	-
<u>9f</u>	73	-
<u>10a</u>	88	-
<u>10b</u>	91	-
<u>10c</u>	86	+++
<u>10d</u>	74	-
<u>10e</u>	90	-
<u>10f</u>	77	-

^a Isolated yields.

^b "-": Unreactivities of the solid-state polymerization; "+": Colorless crystal turned yellow upon exposure to day light; "++": Colorless monomer crystals turned deep red and violet upon exposure to day light; "+++": Colorless crystal turned deep blue upon exposure to day light.

EXPERIMENTAL

M.p.s are uncorrected. M.p.s were measured with a micro melting point apparatus. IR spectra were determined with a Shimadzu IR-440 spectrometer. ^1H -NMR spectra were run on a FX-90Q (90 MHz) spectrometer using CDCl_3 as solvent. ^{19}F -NMR spectra were recorded on a Varian EM 360 L (60 MHz) spectrometer (high field is positive). MS spectra were measured with a Finnigan-4021 spectrometer.

p-Phenoxy-tetrafluorophenylacetylenes (6a): A Typical Procedure: To a solution of pentafluorophenyl-trimethylsilylacetylene (3; 2.0 g, 7.6 mmol) in DMF (15 ml) was added potassium phenoxide (4a; 2 g, 15 mmol). The reaction mixture was stirred at room temperature for 1.5 h and then the mixture was diluted with water. The product was extracted with ether (2x15 ml) and purified by chromatography on silica gel using petroleum ether (bp 60–90°C)/ethyl acetate (5/1) as an eluent to afford a white solid. Recrystallization from methanol-water gave white crystals of (6a): m.p. 73–74°C. IR (KBr): 3300, 1640, 1595, 1490, 1460 cm^{-1} ; ^1H -NMR (CDCl_3/TMS): δ = 3.34 (s, 1 H, $\text{C}\equiv\text{C-H}$), 6.68–7.18 (m, 5 H, H_{arom}); ^{19}F -NMR ($\text{CDCl}_3/\text{CF}_3\text{COOH}$): δ = 59.00 (m, 2 F, F_{arom}), 76.78 (m, 2 F, F_{arom}) ppm; MS: m/z 266 (M^+ , 100%), 77 (53%); Analysis, Found: C 63.44%, H 2.28%, F 28.77%; Calc. for $\text{C}_{14}\text{H}_6\text{F}_4\text{O}$: C 63.16%, H 2.26%, F 28.57%.

p-(4-Methyl-phenoxy)-tetrafluorophenylacetylene (6b): m.p. 81–82°C. IR (KBr): 3289, 1640, 1600, 1500, 1433 cm^{-1} ; ^1H -NMR (CDCl_3/TMS): δ = 2.20 (s, 3 H, CH_3), 3.40 (s, 1 H, $\text{C}\equiv\text{C-H}$),

6.75 (d, 2 H, H_{arom} , $J = 7.2$ Hz), 6.97 (d, 2 H, H_{arom} , $J = 7.2$ Hz) ppm; ^{19}F -NMR ($\text{CDCl}_3/\text{CF}_3\text{COOH}$): $\delta = 59.45$ (m, 2 F, F_{arom}), 76.78 (m, 2 F, F_{arom}) ppm; MS: m/z 280 (M^+ , 100%), 91 (33%); Analysis, Found: C 64.45%, H 3.03%, F 27.21%; Calc. for $\text{C}_{15}\text{H}_8\text{F}_4\text{O}$: C 64.29%, H 2.86%, F 27.14%.

p-(4-Bromo-phenoxy)-tetrafluorophenylacetylene (6c): m.p. 104-105°C. IR (KBr): 3300, 1500, 1480, 1438 cm^{-1} ; ^1H -NMR (CDCl_3/TMS): $\delta = 3.61$ (s, 1 H, $\text{C}\equiv\text{C-H}$), 6.83 (d, 2 H, H_{arom} , $J = 8.3$ Hz), 7.42 (d, 2 H, H_{arom} , $J = 8.3$ Hz); ^{19}F -NMR ($\text{CDCl}_3/\text{CF}_3\text{COOH}$): $\delta = 60.00$ (m, 2 F, F_{arom}), 77.98 (m, 2 F, F_{arom}) ppm; MS: m/z 346 ($M+1$, 67%), 344 ($M-1$, 69%), 237 (100%), 157 (40%), 155 (46%); Analysis, Found: C 48.78%, H 1.20%, F 22.25%; Calc. for $\text{C}_{14}\text{H}_5\text{BrF}_4\text{O}$: C 48.70%, H 1.45%, F 22.03%.

p-(3,5-Dimethyl-phenoxy)-tetrafluorophenylacetylene (6d): m.p. 70-71°C. IR (KBr): 3297, 2840, 2100, 1620, 1596, 1500, 1432 cm^{-1} ; ^1H -NMR (CDCl_3/TMS): $\delta = 2.34$ (s, 6 H, $2\times\text{CH}_3$), 3.63 (s, 1H, $\text{C}\equiv\text{C-H}$), 6.62 (s, 2 H, H_{arom}), 6.80 (s, 1 H, H_{arom}) ppm; ^{19}F -NMR ($\text{CDCl}_3/\text{CF}_3\text{COOH}$): $\delta = 60.05$ (m, 2F, F_{arom}), 77.56 (m, 2 F, F_{arom}) ppm; MS: m/z 295 ($M+1$, 100%), 294 (M^+ , 27%), 105 (43%); Analysis, Found: C 65.57%, H 3.68%, F 25.96%; Calc. for $\text{C}_{16}\text{H}_{10}\text{F}_4\text{O}$: C 65.31%, H 3.40%, F 25.85%.

Fluoro-aromatic acetylenes, (5e), (5f), (6e) and (6f), were prepared by the method reported previously [12].

p-Phenyl-tetrafluorophenyl-trimethylsilylacetylene (5e): m.p. 93-94°C. IR (KBr): 2920, 2115, 1480, 1475, 1440 cm^{-1} ; ^1H -NMR

(CDCl₃/TMS): δ = 0.02 (s, 9 H, Si(CH₃)₃), 7.08 (s, 5 H, H_{arom}) ppm; ¹⁹F-NMR (CDCl₃/CF₃COOH): δ = 59.50 (m, 2 F, F_{arom}), 67.20 (m, 2 F, F_{arom}) ppm; MS: m/z 322 (M⁺, 61%), 307 (100%); Analysis, Found: C 63.18%, H 4.25%, F 23.71%; Calc. for C₁₇H₁₄F₄Si: C 63.35%, H 4.35%, F 23.60%.

p-(4-Methoxy-phenyl)-tetrafluorophenyl-trimethylsilylacetylene (5f): m.p. 118-119°C. IR (KBr): 2934, 2170, 1614, 1520, 1480, 1420 cm⁻¹; ¹H-NMR (CDCl₃/TMS): δ = 0.03 (s, 9H, Si(CH₃)₃), 3.56 (s, 3 H, OCH₃), 6.64 (d, 2 H, H_{arom}, J = 7.2 Hz), 7.04 (d, 2 H, H_{arom}, J = 7.2 Hz) ppm; ¹⁹F-NMR (CDCl₃/CF₃COOH): δ = 58.30 (m, 2 F, F_{arom}), 66.82 (m, 2 F, F_{arom}) ppm; MS: m/z 352 (M⁺, 100%), 337 (77%); Analysis, Found: C 61.35%, H 4.28%, F 21.51%; Calc. for C₁₈H₁₆F₄OSi: C 61.36%, H 4.55%, F 21.59%.

p-Phenyl-tetrafluorophenylacetylene (6e): m.p. 76-77°C. IR (KBr): 3300, 2100, 1483, 1475, 1400 cm⁻¹; ¹H-NMR (CDCl₃/TMS): δ = 3.23 (s, 1H, C≡C-H), 7.20 (s, 5H, H_{arom}) ppm; ¹⁹F-NMR (CDCl₃/CF₃COOH): δ = 59.30 (m, 2 F, F_{arom}), 66.32 (m, 2 F, F_{arom}) ppm; MS: m/z 250 (M⁺, 100); Analysis, Found: C 66.92%, H 2.15%, F 30.17%; Calc. for C₁₄H₆F₄: C 67.20%, H 2.40%, F 30.40%.

p-(4-Methoxy-phenyl)-tetrafluorophenylacetylene (6f): m.p. 140-141°C. IR (KBr): 3300, 2151, 1600, 1504, 1497 cm⁻¹; ¹H-NMR (CDCl₃/TMS): δ = 3.25 (s, 1H, C≡C-H), 3.65 (s, 3 H, OCH₃), 6.55 (d, 2 H, H_{arom}, J=7.4 Hz), 7.16 (d, 2 H, H_{arom}, J=7.4 Hz) ppm; ¹⁹F-NMR (CDCl₃/CF₃COOH): δ = 58.80 (m, 2F, F_{arom}), 66.92 (m, 2F, F_{arom}) ppm; MS: 280 (M⁺, 100%); Analysis, Found: C 64.50%, H 3.04%, F 27.33%; Calc. for C₁₅H₈F₄O: C 64.29%, H 2.86%, F 27.14%.

Preparation of asymmetric fluoro-diacetylenes 9 and 10 [13]5-(p-Phenoxy-tetrafluorophenyl)-penta-2,4-diyn-1-ol (9a):

A Typical Procedure: p-Phenoxy-tetrafluorophenylacetylene (6a; 100 mg, 0.38mmol) was dissolved in DMF (2 ml). Then, hydroxylamine hydrochloride (10 mg) and cuprous chloride (10 mg) in 70 percent ethylamine (0.5 ml) were added. A yellow solution was formed. 1-Bromo-propargyl alcohol (7; 100 mg, 0.74 mmol) dissolved in DMF (2 ml) was added with stirring over a period of about 10 min. When the reaction mixture started to turn blue, a small amount of hydroxylamine hydrochloride was added. The temperature of the reaction was maintained at 25-35°C. After 35 min. the mixture was acidified with dilute sulfuric acid and extracted with ether. The ether was removed under reduced pressure. The crude product was purified by chromatography on silica gel using petroleum ether (bp 60-90°C)/ethyl acetate (5:1) as an eluent to afford a white solid. Recrystallization from methanol-water gave white crystal of (9a); m.p. 126-127°C. IR (KBr): 3400, 1600, 1495, 1455, 1230, 1200, 1170, 1100, 1030, 998, 945, 766, 697 cm⁻¹; ¹H-NMR (CDCl₃/TMS): δ = 1.79 (s, 1 H, OH), 4.57 (s, 2 H, OCH₂), 7.00-7.60 (m, 5 H, H_{arom}) ppm; ¹⁹F-NMR (CDCl₃/CF₃COOH): δ = 59.00 (m, 2 F, F_{arom}), 77.23 (m, 2F, F_{alFOM}) ppm; MS: m/z 320 (M⁺, 82%), 77 (100%); Analysis, Found: C 63.57%, H 2.31%, F 23.67%; Calc. for C₁₇H₈F₄O₂: C 63.75%, H 2.50%, F 23.75%.

The following compounds were prepared similarly.

5-[p-(4-Methyl-phenoxy)-tetrafluorophenyl]-penta-2,4-diyn-1-ol (9b): m.p. 115-116°C. IR (KBr): 3400, 1500, 1449, 1230,

1200, 1175, 1100, 1020, 996, 944, 823 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3/TMS): δ = 1.70 (s, 1H, OH), 2.33 (s, 3H, CH_3), 4.43 (s, 2H, OCH_2), 6.83 (d, 2 H, H_{arom} , J = 7.8 Hz), 7.13 (d, 2 H, H_{arom} , J = 7.8 Hz) ppm; $^{19}\text{F-NMR}$ ($\text{CDCl}_3/\text{CF}_3\text{COOH}$): δ = 58.72 (m, 2 F, F_{arom}), 76.83 (m, 2 F, F_{arom}) ppm; MS: m/z 334 (M^+ , 100%), 91 (40%); Analysis, Found: C 64.61%, H 2.87%, F 22.81%; Calc. for $\text{C}_{18}\text{H}_{10}\text{F}_4\text{O}_2$: C 64.67%, H 2.99%, F 22.75%.

5-[p-(4-Bromo-phenoxy)-tetrafluorophenyl]-penta-2,4-diyn-1-ol (9c): m.p. 136-137°C. IR (KBr): 3335, 1497, 1480, 1443, 1230, 1200, 1165, 1024, 1010, 995, 942, 830 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3/TMS): δ = 1.80 (t, 1 H, OH, J = 6.1 Hz), 4.47 (d, 2 H, OCH_2 , J = 6.1 Hz), 6.90 (d, 2 H, H_{arom} , J = 9.7 Hz), 7.50 (d, 2H, H_{arom} , J = 9.7 Hz) ppm; $^{19}\text{F-NMR}$ ($\text{CDCl}_3/\text{CF}_3\text{COOH}$): δ = 59.12 (m, 2 F, F_{arom}), 77.22 (m, 2 F, F_{arom}) ppm; MS: m/z 400 ($\text{M}+1$, 100%), 398 ($\text{M}-1$, 87%), 157 (25%), 155 (27%); Analysis, Found: C 50.89%, H 1.49%, Br 20.20%, F 19.47%; Calc. for $\text{C}_{17}\text{H}_7\text{BrF}_4\text{O}_2$: C 51.13%, H 1.75%, Br 20.05%, F 19.05%.

5-[p-(3,5-Dimethyl-phenoxy)-tetrafluorophenyl]-penta-2,4-diyn-1-ol (9d): m.p. 103-104°C. IR (KBr): 3335, 1600, 1497, 1450, 1343, 1295, 1242, 1143, 1100, 1023, 997, 850, 700, 680 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3/TMS): δ = 1.64 (s, 1 H, OH), 2.35 (s, 6 H, $2 \times \text{CH}_3$), 4.48 (s, 2 H, OCH_2), 6.60 (s, 2H, H_{arom}), 6.80 (s, 1H, H_{arom}) ppm; $^{19}\text{F-NMR}$ ($\text{CDCl}_3/\text{CF}_3\text{COOH}$): δ = 59.50 (m, 2 F, F_{arom}), 77.50 (m, 2 F, F_{arom}) ppm; MS: m/z 348 (M^+ , 100%), 105 (13%); Analysis, Found: C 65.18%, H 3.20%, F 21.69%; Calc. for $\text{C}_{19}\text{H}_{12}\text{F}_4\text{O}_2$: C 65.52%, H 3.45%, F 21.84%.

5-(p-Phenyl-tetrafluorophenyl)-penta-2,4-diyn-1-ol (9e): m.p., 136-137°C. IR (KBr): 3335, 2202, 1484, 1440, 1404, 1360, 1323, 1125, 980, 917, 850, 792, 750, 728, 693, 648 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3/TMS): δ = 2.00 (s, 1 H, OH), 4.33 (s, 2 H, OCH_2), 7.38 (s, 5 H, H_{arom}) ppm; $^{19}\text{F-NMR}$ ($\text{CDCl}_3/\text{CF}_3\text{COOH}$): δ = 59.20 (m, 2 F, F_{arom}), 66.60 (m, 2 F, F_{arom}) ppm; MS: m/z 304 (M^+ , 100%), 287 (13%); Analysis, Found: C 66.99%, H 2.43%, F 25.11%; Calc. for $\text{C}_{17}\text{H}_8\text{F}_4\text{O}$: C 67.11%, 2.63%, F 25.00%.

5-[p-(4-Methoxy-phenyl)-tetrafluorophenyl]-penta-2,4-diyn-1-ol (9f): m.p. 132-133°C. IR (KBr): 3335, 1610, 1483, 1420, 1398, 1337, 1300, 1260, 1240, 1182, 1160, 1040, 980, 860, 840, 780, 600, 534 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3/TMS): δ = 1.78 (s, 1 H, OH), 3.85 (s, 3 H, OCH_3), 4.85 (s, 2 H, OCH_2), 7.03 (d, 2 H, H_{arom} , $J=8.0\text{Hz}$), 7.43 (d, 2H, H_{arom} , $J = 8.0 \text{ Hz}$) ppm; $^{19}\text{F-NMR}$ ($\text{CDCl}_3/\text{CF}_3\text{COOH}$): δ = 60.00 (m, 2 F, F_{arom}), 67.34 (m, 2 F, F_{arom}) ppm; MS: m/z 334 (M^+ , 100%), 317 (14%); Analysis, Found: C 64.56%, H 3.04%, F 22.75%; Calc. for $\text{C}_{18}\text{H}_{10}\text{F}_4\text{O}_2$: C 64.67%, H 2.99%, F 22.75%.

1-(p-Phenoxy-tetrafluorophenyl)-4-phenyl-butadiyne (10a): m.p. 145-146°C. IR (KBr): 2200, 1600, 1485, 1442, 1206, 1168, 1023, 990, 880, 760, 745, 690 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3/TMS): δ = 6.97-7.70 (m, H_{arom}) ppm; $^{19}\text{F-NMR}$ ($\text{CDCl}_3/\text{CF}_3\text{COOH}$): δ = 59.00 (m, 2 F, F_{arom}), 77.45 (m, 2 F, F_{arom}) ppm; MS: m/z 366 (M^+ , 100%), 289 (28%); 77 (38%); Analysis, Found: C 72.34%, H 2.49%, F 20.87%; Calc. for $\text{C}_{22}\text{H}_{10}\text{F}_4\text{O}$: C 72.13%, H 2.73%, F 20.77%.

1-[p-(4-Methyl-phenoxy)-tetrafluorophenyl]-4-phenyl-butadi-
yne (10b): m.p. 137-138°C. IR (KBr): 2200, 1600, 1500, 1484, 1443, 1200, 1170, 1020, 990, 879, 820, 760, 690 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3/TMS): δ = 2.35 (s, 3 H, CH_3), 6.80-7.68 (m, H_{arom}) ppm; $^{19}\text{F-NMR}$ ($\text{CDCl}_3/\text{CF}_3\text{COOH}$): δ = 59.33 (m, 2 F, F_{arom}), 77.34 (m, 2 F, F_{arom}) ppm; MS: m/z 380 (M^+ , 100), 289 (12%), 91 (25%); Analysis, Found: C 72.85%, H 2.93%, F 20.67%; Calc. for $\text{C}_{23}\text{H}_{12}\text{F}_4\text{O}$: C 72.63%, H 3.16%, F 20.00%.

1-[p-(4-Bromo-phenoxy)-tetrafluorophenyl]-4-phenyl-butadiyne (10c): m.p. 148-149°C. IR (KBr): 2203, 1500, 1484, 1445, 1214, 1170, 1020, 995, 880, 763, 690 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3/TMS): δ = 6.80-7.60 (m, H_{arom}) ppm; $^{19}\text{F-NMR}$ ($\text{CDCl}_3/\text{CF}_3\text{COOH}$): δ = 59.00 (m, 2 F, F_{arom}), 77.50 (m, 2 F, F_{arom}) ppm; MS: m/z 446 ($\text{M}+1$, 86%), 445 (M^+ , 24%), 444 ($\text{M}-1$, 100%), 289 (39%); Analysis, Found: C 59.12%, H 1.97%, F 16.88%; Calc. for $\text{C}_{22}\text{H}_9\text{BrF}_4\text{O}$: C 59.32%, H 2.02%, F 17.08%.

1-[p-(3,5-Dimethyl-phenoxy)-tetrafluorophenyl]-4-phenyl-butadiyne (10d): m.p. 136-137°C. IR (KBr): 2200, 1620, 1590, 1485, 1440, 1287, 1160, 1120, 1063, 1000, 930, 870, 840, 760, 690 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3/TMS): δ = 2.35 (s, 6 H, $2\times\text{CH}_3$), 6.63 (s, 2 H, H_{arom}), 6.80 (s, 1 H, H_{arom}), 7.40-7.68 (m, 5 H, H_{arom}) ppm; $^{19}\text{F-NMR}$ ($\text{CDCl}_3/\text{CF}_3\text{COOH}$): δ = 59.33 (m, 2 F, F_{arom}), 77.64 (m, 2 F, F_{arom}) ppm; MS: m/z 395 ($\text{M}+1$, 39%), 394 (M^+ , 100%), 289 (10%), 105 (10%), 77 (21%); Analysis, Found: C 72.89%, H 3.45%, F 19.54%; Calc. for $\text{C}_{24}\text{H}_{14}\text{F}_4\text{O}$: C 73.10%, H 3.55%, F 19.29%.

1-(p-Phenyl-tetrafluorophenyl)-4-phenyl-butadiyne (10e): m.p. 125-126°C. IR (KBr): 2200, 1483, 1440, 1410, 980, 835, 756, 727, 698, 683, 644 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3/TMS): δ = 7.20-7.56 (m, H_{arom}) ppm; $^{19}\text{F-NMR}$ ($\text{CDCl}_3/\text{CF}_3\text{COOH}$): δ = 59.33 (m, 2 F, F_{arom}) 66.87 (m, 2 F, F_{arom}); MS: m/z 350 (M^+ , 100%); Analysis, Found: C 75.27%, H 2.59%, F 21.52%; Calc. for $\text{C}_{22}\text{H}_{10}\text{F}_4$: C 75.43%, H 2.86%, F 21.71%.

1-[p-(4-Methoxy-phenyl)-tetrafluorophenyl]-4-phenyl-butadiyne (10f): m.p. 129-130°C. IR (KBr): 2203, 1618, 1480, 1448, 1420, 1304, 1260, 1185, 1040, 980, 970, 840, 770, 700, 600, 530 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3/TMS): δ = 3.87 (s, 3 H, OCH_3), 7.00-7.67 (m, 9 H, H_{arom}) ppm; $^{19}\text{F-NMR}$ ($\text{CDCl}_3/\text{CF}_3\text{COOH}$): δ = 60.00 (m, 2 F, F_{arom}), 67.50 (m, 2 F, F_{arom}) ppm; MS: m/z 381 (M^+ , 37%), 380 (M^+ , 100%); Analysis, Found: C 72.74%, H 3.43%, F 19.20%; Calc. for $\text{C}_{23}\text{H}_{12}\text{F}_4\text{O}$: C 72.63%, H 3.16%, F 20.00%.

ACKNOWLEDGEMENT

The authors would like to thank Prof. C. Hu of Shanghai Institute of Organic Chemistry for useful discussions during this work.

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