General Method for the Preparation of Functionalized Fluorinated Phenyl Alkynes

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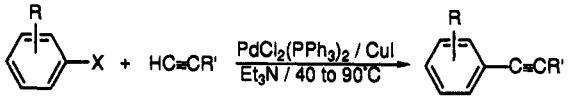
In the presence of cuprous iodide, the palladium-catalyzed coupling reaction of 4-substituted tetrafluorophenyl iodides 1 with terminal alkynes proceeds readily in diisopropylamine or triethylamine to afford the corresponding fluorinated phenylalkynes in excellent yields under mild conditions. A variety of substituents on F-benzenes such as methoxy, dimethylamino, hydro, acyl, piperidino, and morpholino do not interfere with the coupling reaction. The reaction works well with 1-alkynes containing functional groups, including alkyl, alkenyl, phenyl, vinyl ether, alkoxy, phenoxy, hydroxy, amino, trimethylsilyl, and cyano, to give the corresponding (fluorophenyl)alkynes. With dialkynes, 2 equiv of the fluorinated phenyl iodide give bis(fluorophenyl)dialkynes in good yields. When 1,4-dibromotetrafluorobenzene reacts with an excess of alkyne in diisopropylamine, the bis-alkynylated tetrafluorobenzenes are obtained in good yields. However, in triethylamine the reaction gives a mixture of mono- and bis-alkynylated products. This method provides a practical approach to fluorinated phenyl functionalized alkynes.

Introduction

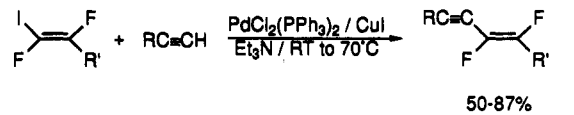
In recent years, there has been considerable interest in the synthesis of fluorinated aryl alkynes, since they have been demonstrated as important substances in organic synthesis and material science.[1,2] However, few convenient and practical approaches to the fluorinated aryl alkynes have been described. Existing routes to such compounds involve a halogenation–dehydrohalogenation sequence with fluorine-containing aryl ketones[3] and attack of an acetylide on fluorinated aromatic rings.[4,5] However, halogenation–dehydrohalogenation requires multistep reactions and the overall yield is low. Although in some cases, nucleophilic attack of acetylides on fluorinated arenes gives the corresponding products in good yields, no alkynylated products are obtained when polyfluoroarenes containing electron-donating groups react with lithium acetylides. On the other hand, upon reaction of hexafluorobenzene or pentafluorobenzenes bearing electron-withdrawing groups with acetylide, a mixture of monoalkynylated and bis-alkynylated fluorobenzenes is obtained.[4,5] In addition, not only does the orientation of substitution depend upon the aromatic substituent, but harsh reaction conditions preclude the utilization of many functionalities.

In contrast to fluorinated aryl alkynes, non-fluorinated aryl alkynes have been prepared *via* direct reaction of aryl and substituted aryl halides with cuprous acetylides in pyridine[6-8] or with terminal alkynes catalyzed by palladium at elevated temperatures.[9,10] However, in the presence of cuprous iodide, the palladium-catalyzed reaction proceeds under mild conditions and gives the aryl alkynes in excellent yields.[11] This methodology has been widely utilized in the preparation of a variety of functionalized aryl alkynes[12-15] and biologically active compounds.[16-18]



34-97%

Recently, we reported[19] that in the presence of cuprous iodide the palladium-catalyzed reaction of fluorinated vinyl iodides with terminal alkynes and triethylamine gave the corresponding fluorinated enynes in good yields.



50-87%

R' : F, CF_3, Ph, $(^iPrO)_2P(O)$

A key step in this coupling reaction is the oxidative addition of the fluorinated vinyl iodide to a palladium(0) complex to generate a fluorinated vinyl palladium(II) species. Although the fluorinated aryl halides are well known to oxidatively add to palladium(0) to provide fluorinated aryl palladium complexes,[20,21] very little work

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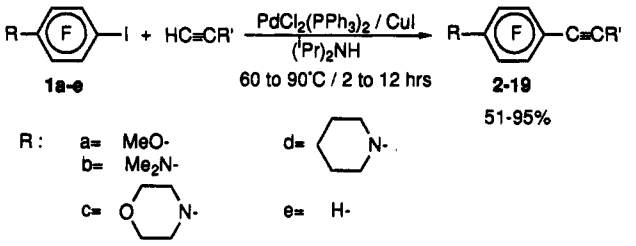
has been reported using these palladium complexes in organic synthesis.[22] Recent work suggested that the fluorinated aryl palladium complex could be used in coupling reactions with alkenes.[22] While this work was in progress, a similar approach has also been recently reported.[23,24] In a preliminary communication[25] we briefly described the facile coupling reaction of fluorinated phenyl iodides with terminal alkynes catalyzed by palladium in the presence of cuprous iodide to produce the fluorinated phenyl alkynes in excellent yields under mild conditions. We now wish to present in detail the results of the synthesis of a variety of fluorinated functionalized alkynes.

Results and Discussion

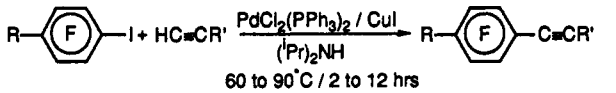
Several para-substituted tetrafluorophenyl iodides were prepared *via* treatment of pentafluorophenyl iodide or bromide with the corresponding nucleophiles according to literature procedures.[26] The para-substituted tetrafluorophenyl iodides **1** react with terminal alkynes in the presence of a catalytic amount of bis(triphenylphosphine)-palladium dichloride and cuprous iodide in diisopropylamine to afford the corresponding fluorinated aryl alkynes in good yields. The reaction is general for alkyl- or trimethylsilyl-substituted alkynes, and other substituents such as methoxy, *N,N*-dimethylamino, piperidino, and morpholino do not interfere with the coupling reaction. For example, upon reaction of 4-methoxytetrafluorophenyl iodide (**1a**) with 1-octyne and diisopropylamine in the presence of $PdCl_2(PPh_3)_2$ at 80 °C for 3 h, **2c** was isolated in 95% yield. Reaction of (trimethylsilyl)acetylene with **1a** and **1b** gives the 4-methoxy-substituted **2e** and 1-[4-(dimethylamino)-2,3,5,6-tetrafluorophenyl]-2-(trimethylsilyl)ethyne (**3b**) in 72 and 87% yields, respectively, under the same conditions.



The conjugated alkynes are also efficient substrates and more active than the alkyl-substituted alkynes under the coupling conditions. The reactions of phenylacetylene and 1-ethynylcyclohexene with **1** can be conducted under milder conditions. For example, when phenylacetylene is treated with **1b** at 60 °C for 2 h, the corresponding alkyne **7b** was obtained in 90% yield. The results are summarized in Table I.

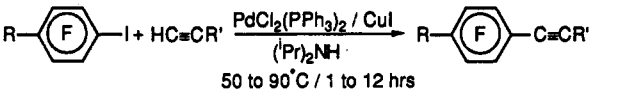
Ether groups can be tolerated in the coupling reaction. As illustrated in Table II, with 4-substituted tetrafluorophenyl iodide in triethylamine, propargyl ether gives the coupling products in good yields. Although alkynylation of non-fluorinated aryl halides catalyzed by palladium in aqueous medium has been recently published,[27] there are no reports describing the palladium-catalyzed reaction with fluorinated substrates in protic solvents. We

Table I. Coupling Reaction of Para-Substituted Iodotetrafluorobenzenes with Alkyl-, Trimethylsilyl-, Phenyl-, and 1-Cyclohexenyl-Substituted Alkynes



entry	product	R	R′	% yield
1	**2a**	MeO	$CH_2(CH_2)_2CH_3$	81
2	**2b**		$CH_2(CH_2)_3CH_3$	79
3	**2c**		$CH_2(CH_2)_4CH_3$	95
4	**2d**		$CH_2(CH_2)_5CH_3$	89
5	**2e**		$SiMe_3$	72
6	**3a**	Me_2N	$CH_2(CH_2)_3CH_3$	83
7	**3b**		$SiMe_3$	87
8	**4**		$CH_2(CH_2)_2CH_3$	89
9	**5**		$CH_2(CH_2)_2CH_3$	77
10	**6**	MeO	C_6H_5	74
11	**7a**	Me_2N	c-C_6H_9	61
12	**7b**		C_6H_5	90
13	**8**		C_6H_5	78
14	**9**		C_6H_5	87

Table II. Coupling Reaction of Para Substituted Iodotetrafluorobenzenes with Ether-, Hydroxyl-, Cyano-, Amino- Substituted Alkynes



entry	product	R	R′	% yield
15	**10a**	MeO	$CH_2OC_6H_5$	80
16	**10b**		CH_2OCH_3	84
17	**10c**		*Z*-CH=CHOCH$_3$	80
18	**11**	Me_2N	*Z*-CH=CHOCH$_3$	68
19	**12**		CH_2OCH_3	73
20	**13a**		CH_2OCH_3	73
21	**13b**		*Z*-CH=CHOCH$_3$	66
22	**14**	H	*Z*-CH=CHOCH$_3$	51
23	**15a**	MeO	CH_2OH	74
24	**15b**		$C(CH_3)_2OH$	84
25	**15c**		c-$C_6H_{10}OH$	77
26	**15d**		$CH(OH)CH_3$	80
27	**15e**		$(CH_2)_3C{\equiv}N$	96
28	**16a**	Me_2N	$CH(OH)CH_3$	67
29	**16b**		$C(CH_3)_2OH$	70
30	**16c**		c-C_5H_8OH	70
31	**16d**		c-$C_6H_{10}NH_2$	91
32	**16e**		$C(CH_3)_2NH_2$	84
33	**17a**		CH_2OH	93
34	**17b**		$C(CH_3)_2NH_2$	87
35	**18a**		CH_2OH	85
36	**18b**		$C(CH_3)_2NH_2$	89
37	**19**	H	$C(CH_3)_2OH$	69

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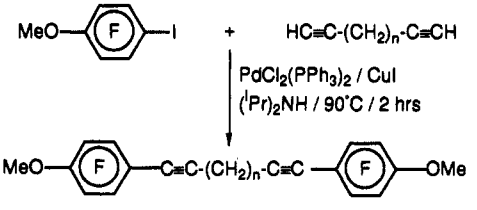
found that the palladium-catalyzed reaction of **1** with alkynes proceeds readily in aqueous solution. As shown in Table II (entries 17, 18, 21, 22) when *cis*-1-methoxy-1-buten-3-yne, commercially available as a solution containing 40% methanol and 10% water, was used as a substrate the corresponding fluorinated aryl-substituted enyne ethers could be isolated in good yields. Although small amounts of byproducts were detected by ^{19}F NMR analysis of the reaction mixture, they were neither isolated nor identified. The configuration of the *cis*-vinyl hydrogens of alkyne is preserved throughout the reaction, as characterized by ^{1}H NMR and determined by the 6.6-Hz coupling.

The success achieved in the palladium-catalyzed coupling reaction of **1** with terminal alkynes in protic solvents prompted us to investigate the reaction of **1** with terminal alkynes containing protic functionalities. The coupling reaction with functionalized alkynes would provide a wide variety of fluorinated aryl alkynes, which would be invaluable in fluorocarbon chemistry since the preparation of fluorinated aryl functionalized alkynes was unsuccessful with previous methods.[3-5]

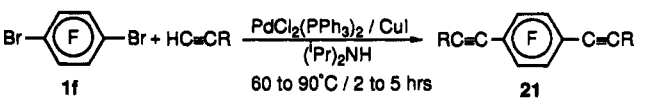
In the presence of cuprous iodide, the reaction of **1** with propargyl alcohols and amines can be accomplished when catalyzed by palladium in diisopropylamine at 60–90 °C. Primary, secondary, and tertiary hydroxy and amino groups are preserved in the products. The yields are good to excellent and the products are readily isolated by chromatography (Table II). Reaction of 5-hexynenitrile with **1a** also gives the coupling product **15e** in 96% yield under the same conditions.

Terminal dialkynes provide bis-fluorinated phenyl-substituted dialkynes when treated with 2 equiv of **1**. For example, when **1a** reacts with 1,6-heptadiyne in triethylamine at 90 °C for 2 h, in the presence of 5 mol % palladium and 1 mol % cuprous iodide as a catalyst system, 1,7-bis(4-methoxytetrafluorophenyl)heptadiyne **20a** is isolated in 80% yield. Similarly, with the longer chain dialkynes the fluorinated aryl dialkynes are isolated in 75–82% yields.



20a:	n= 3	80%
20b:	n= 4	75%
20c:	n= 6	82%

Fluorinated phenyl bromides also undergo the coupling with terminal akynes with palladium and cuprous iodide catalysis. The reaction of 1,4-dibromotetrafluorobenzene (**1f**) with 2 equiv of 1-hexyne or 1-heptyne in diisopropylamine at 80 °C gives bis(hexynyl)- and bis(heptynyl)-tetrafluorobenzenes **21** in 74 and 80% yields, respectively. However, in triethylamine the reaction is not clean. For example, upon treatment of 1,4-dibromotetrafluorobenzene with 2.5 equiv of 1-heptyne in triethylamine at 80 °C over 10 h, a mixture of bis-heptynyltetrafluorobenzene, 4-heptynyltetrafluorophenyl bromide, and 1,4-dibromotetrafluorobenzene (**1f**) is observed by ^{19}F NMR. Even when a large excess of 1-heptyne was used and the reaction



1f **21**

21a:	R= n-C_4H_9	74%
21b:	R= n-C_5H_{11}	80%

mixture is heated at 80–90 °C for a prolonged period of time, the yield of bis(heptynyl)tetrafluorobenzene **21b** was not improved, and some 1,4-dibromotetrafluorobenzene remained in the reaction mixture.

Thus, para-substitution of the perfluorophenyl iodides with electron-donating functional groups, such as methoxy, hydro, *N*,*N*-dimethylamino, piperidino, and morpholino, does not impede the reaction. It was of interest to explore the effect of electron-withdrawing substituents at the para position of the pentafluoroaryl halides in the reaction with terminal alkynes under similar conditions. The acyl group was introduced to the para position of bromotetrafluorobenzene *via* the coupling reaction between the 4-bromotetrafluorophenylcopper reagent[28] with an acyl chloride.

Treatment of 1,4-dibromotetrafluorobenzene with excess acid-washed cadmium in DMF at room temperature overnight produces the 4-bromotetrafluorophenylcadmium reagent, which subsequently undergoes a quantitative metathesis reaction with cuprous bromide at room temperature. The copper reagent couples with propionyl chloride at room temperature in 30 min to afford an 80% isolated yield of ethyl 4-bromotetrafluorophenyl ketone (**1g**). In the presence of a catalytic amount of $PdCl_2(PPh_3)_2$ and CuI, ethyl 4-bromotetrafluorophenyl ketone undergoes coupling with 1-hexyne and phenylacetylene in diisopropylamine solvent at 60 °C for 3 h to give ethyl 4-(1-hexynyl-2,3,5,6-tetrafluorophenyl) ketone (**22a**) and ethyl 4-(phenylethynyl)-2,3,5,6-tetrafluorophenyl) ketone (**22b**) in 75 and 81% yields, respectively (Scheme I).

The coupling reaction appears to involve Pd(0) catalysis, generated by the reduction of palladium(II) by attack of the acetylide anion on the organopalladium halide to form (triphenylphosphine)dialkynylpalladium, followed by reductive elimination of the disubstituted acetylene to form bis(triphenylphosphine)palladium(0). In fact, a small amount of 1,4-diphenylbutadiyne was isolated in the reaction of para-substituted-tetrafluorophenyl iodides with phenylacetylene (in the entries 10–14). The resulting palladium(0) enters the catalytic cycle (Scheme II) by oxidative addition of the para-substituted-tetrafluorophenyl iodide, followed by alkynylation to generate palladium(II) species. Finally, reductive elimination gave coupled product and regenerated Pd(0) catalyst.

In conclusion, we have presented a general method for the preparation of para-substituted tetrafluorophenyl alkynes *via* the palladium-cuprous iodide catalyzed coupling reaction of fluorinated aryl halides with terminal alkynes. The reaction works well with 4-hydro-, 4-methoxy-, 4-(*N*,*N*-dimethylamino)-, 4-piperidino-, and 4-morpholinotetrafluorophenyl iodide, and 4-acyltetrafluorophenyl bromide. With 2 equiv of alkynes, 1,4-dibromotetrafluorobenzene gives the corresponding dialkynylated products. When α,ω-dialkynes are used as substrates, the α,ω-bis(fluorophenyl)-substituted dialkynes are obtained. A variety of functionalities in the

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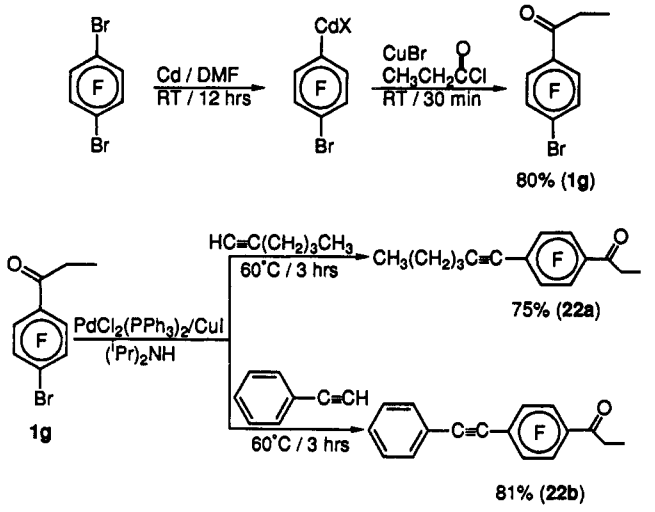
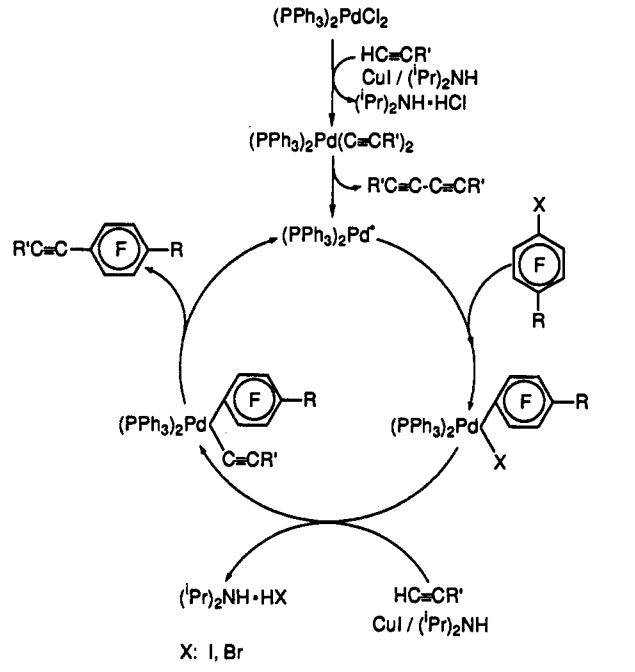
Scheme I



Scheme II



alkynes are tolerated under the reaction conditions. The ready availability of the catalysts and alkyne precursors, the ease of preparation of substituted fluorinated aryl halides, the simplicity of the experimental procedure, and the high yields obtained make this approach a useful route to fluorinated aryl alkynes.

Experimental Section

Materials. 4-Hydrotetrafluorophenyl iodide, 4-methoxytetrafluorophenyl iodide, 4-morpholinotetrafluorophenyl iodide, 4-piperidinotetrafluorophenyl iodide, and 4-(*N,N*-dimethylamino)tetrafluorophenyl iodide were prepared according to literature methods.[25] All 1-alkynes, α,ω-alkynes, palladium dichloride, cuprous iodide, diisopropylamine, and 1,4-dibromotetrafluorobenzene were purchased from Aldrich Chemical Co.

All reactions were monitored by ^{19}F NMR analysis of the reaction mixtures on a JEOL FX90Q spectrometer. The ^{1}H, ^{19}F, and ^{13}C NMR spectra of final products were obtained on a Bruker AC-300 spectrometer ($CDCl_3$, $CFCl_3$, or TMS internal references). FT-IR spectra were recorded on a Mattson Cygnus 100 spectrometer as CCl_4 solutions in a 0.1-cm path length cell. Low-resolution mass spectra were obtained on a TRIO-1 GC-MS and high-resolution mass spectra on VG ANALYTICAL 11-250J at 70 eV. GLPC analysis were recorded on a Hewlett-Packard 5890A gas chromatograph with an OV-101 column and thermal conductivity detector. Melting points were obtained on a Thomas Hoover capillary melting point apparatus in open-ended capillaries and are uncorrected.

Preparation of 1-(4-Methoxy-2,3,5,6-tetrafluorophenyl)-1-nonyne (2d). In a typical experimental procedure, a 50-mL, two-necked, round-bottomed flask equipped with a septum, a Teflon-coated magnetic stir-bar, and a water condenser topped with a nitrogen inlet was charged with 1.5 g (5.0 mmol) of 4-methoxy-1-iodotetrafluorobenzene, 0.9 g (7.2 mmol) of 1-nonyne, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^{i}Pr)_2NH$. The solution was stirred at 70 °C under a nitrogen atmosphere. After complete consumption of starting material (determined by ^{19}F NMR analysis of the reaction mixture) the mixture was cooled to room temperature and gravity filtered, and the solid was washed with 20 mL of CH_2Cl_2. The filtrate was concentrated by rotary evaporation to give a crude product, which was purified through a flash chromatography column packed with silica gel, and eluted with hexane to yield 1.4 g (89%) of **2d**: GLPC purity 96.8%, of 1-(4-methoxytetrafluorophenyl)-1-nonyne: ^{19}F NMR ($CFCl_3$, $CDCl_3$) −159.2 (m, 2F), −139.6 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 0.9 (t, $^{3}J_{H-H}$ = 6.8 Hz, 3H), 1.3 (m, 6H), 1.4 (m, 2H), 1.6 (m, 2H), 2.5 (t, $^{3}J_{H-H}$ = 6.9 Hz, 2H), 4.1 (t, $^{5}J_{H-F}$ = 1.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, TMS) 148.0 (dm, J_{C-F} = 250.2 Hz), 141.2 (dm, J_{C-F} = 246.5 Hz), 138.5 (tt, $^{2}J_{C-F}$ = 12.2, $^{3}J_{C-F}$ = 3.7 Hz), 102.9 (t, $^{4}J_{C-F}$ = 3.6 Hz), 99.0 (t, $^{2}J_{C-F}$ = 18.1 Hz), 65.6 (t, $^{3}J_{C-F}$ = 3.8 Hz), 62.2 (t, $^{4}J_{C-F}$ = 3.7 Hz), 32.3 (s), 29.2 (s), 28.7 (s), 23.0 (s), 20.0 (s), 14.2 (s); FTIR (CCl_4, cm^{-1}) 2932.4 (m), 2859.8 (w), 2244.8 (w, C≡C), 1646.7 (w), 1492.4 (s), 1428.9 (m), 1202.6 (w), 1076.6 (m), 991.4 (m); GC-MS (*m/z*) 302 (M^+, 25.9), 259 (17.4), 245 (82.5), 219 (86.4), 193 (100.0), 81 (18.2), 55 (32.3), 43 (58.1).

Preparation of 1-(4-Methoxy-2,3,5,6-tetrafluorophenyl)-1-hexyne (2a). Similarly, **2a** was prepared from 1.5 g (5 mmol) of 4-methoxy-1-iodotetrafluorobenzene, 0.6 g (7.2 mmol) of 1-hexyne, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^{i}Pr)_2NH$. Usual workup gave 1.1 g (81%) of **2a**: GLPC purity 94.9%; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −159.2 (m, 2F), −139.7 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 0.9 (t, $^{3}J_{H-H}$ = 7.3 Hz, 3H), 1.5 (m, 2H), 1.6 (m, 2H), 2.5 (t, $^{3}J_{H-H}$ = 6.8 Hz, 2H), 4.1 (t, $^{5}J_{H-F}$ = 1.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, TMS) 147.8 (dm, J_{C-F} = 254.1 Hz), 141.1 (dm, J_{C-F} = 246.7 Hz), 138.4 (tt, $^{2}J_{C-F}$ = 12.0, $^{3}J_{C-F}$ = 3.2 Hz), 102.8 (t, $^{4}J_{C-F}$ = 3.5 Hz), 98.8 (t, $^{2}J_{C-F}$ = 18.3 Hz), 65.6 (t, $^{3}J_{C-F}$ = 3.8 Hz), 62.3 (t, $^{4}J_{C-F}$ = 3.7 Hz), 30.6 (s), 22.2 (s), 19.6 (s), 13.7 (s); FTIR (CCl_4, cm^{-1}) 2963.0 (s), 2960.3 (s), 2875.3 (m), 2837.9 (w), 2246.9 (w, C≡C), 1646.4 (w), 1506.9 (s), 1487.9 (s), 1430.0 (s), 1202.7 (m), 1166.0 (w), 1076.3 (s), 1045.4 (m), 996.3 (s), 986.4 (s); GC-MS (*m/z*) 260 (M^+, 43.6), 245 (100.0), 217 (95.5), 202 (38.1), 169 (19.2), 43 (63.6), 41 (49.2).

Preparation of 1-(4-Methoxy-2,3,5,6-tetrafluorophenyl)-1-heptyne (2b). Similarly, **2b** was prepared from 1.5 g (5 mmol) of 4-methoxy-1-iodotetrafluorobenzene, 0.7 g (7.2 mmol) of 1-heptyne, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^{i}Pr)_2NH$. Usual workup gave 1.1 g (79%) of **2b**; GLPC purity 97.0%; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −159.2 (m, 2F), −139.6 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 0.9 (t, $^{3}J_{H-H}$ = 7.1 Hz, 3H), 1.4 (m, 4H), 1.6 (m, 2H), 2.5 (t, $^{3}J_{H-H}$ = 7.0 Hz, 2H), 4.1 (s, 3H); ^{13}C NMR ($CDCl_3$, TMS) 147.9 (dm, J_{C-F} = 255.0 Hz), 141.1 (dm, J_{C-F} = 246.6 Hz), 138.5 (tt, $^{2}J_{C-F}$ = 12.3, $^{3}J_{C-F}$ = 3.8 Hz), 102.9 (t, $^{4}J_{C-F}$ = 3.7 Hz), 98.9 (t, $^{2}J_{C-F}$ = 18.3 Hz), 65.6 (t, $^{3}J_{C-F}$ = 4.1 Hz), 62.2 (t, $^{4}J_{C-F}$ = 3.9 Hz), 31.3 (s), 28.3 (s), 22.5 (s), 20.0 (s), 14.1 (s); FTIR (CCl_4, cm^{-1}) 2959.4 (s), 2936.4 (s), 2862.6 (m), 2247.1 (w, C≡C), 1646.6 (w), 1487.9 (s), 1430.6 (s), 1202.7 (m), 1165.8 (w), 1059.4 (s), 986.8 (s); GC-MS (*m/z*) 274 (M^+, 33.7), 245 (100.0), 231 (17.3), 219 (84.4), 217 (97.4), 202 (48.1), 193 (63.6), 174 (32.8), 81 (44.8), 55 (23.4), 41 (80.2).

Preparation of 1-(4-Methoxy-2,3,5,6-tetrafluorophenyl)-1-octyne (2c). Similarly, **2c** was prepared from 1.5 g (5 mmol) of 4-methoxy-1-iodotetrafluorobenzene, 0.8 g (7.2 mmol) of 1-octyne, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^{i}Pr)_2NH$. Usual workup gave 1.4 g (95%) of **2c**: GLPC purity 92.0%; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −159.2 (m, 2F), −139.6 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 0.9 (t, $^{3}J_{H-H}$ = 6.8 Hz, 3H), 1.3 (m, 4H), 1.5 (m, 2H), 1.6 (m, 2H), 2.5 (t, $^{3}J_{H-H}$ = 6.9 Hz, 2H), 4.1 (t, $^{5}J_{H-F}$ = 1.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, TMS)

148.0 (dm, J_{C-F} = 250.9 Hz), 141.2 (dm, J_{C-F} = 246.8 Hz), 138.6 (tt, $^2J_{C-F}$ = 12.0 , $^3J_{C-F}$ = 3.3 Hz), 102.8 (t, $^4J_{C-F}$ = 3.4 Hz), 99.0 (t, $^2J_{C-F}$ = 18.0 Hz), 65.7 (m), 62.2 (t, $^4J_{C-F}$ = 4.0 Hz), 31.7 (s), 28.7 (s), 22.9 (s), 20.0 (s), 14.1 (s); FTIR (CCl_4, cm^{-1}) 2934.1 (s), 2860.5 (m), 2245.5 (w, C≡C), 1646.3 (w), 1492.2 (s), 1428.2 (s), 1202.7 (m), 1165.7 (w), 1076.1 (s), 996.2 (s); GC-MS (*m/z*) 288 (M^+, 28.9), 259 (20.4), 245 (84.3), 217 (79.2), 202 (41.5), 193 (100.0), 169 (23.0), 43 (88.7), 41 (77.4).

Preparation of 1-(4-Methoxy-2,3,5,6-tetrafluorophenyl)-2-(trimethylsilyl) ethyne (2e). Similarly, **2e** was prepared from 1.5 g (5 mmol) of 4-methoxy-1-iodotetrafluorobenzene, 0.7 g (7.1 mmol) of (trimethylsilyl)acetylene, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.0 g (72%) of **2e**: mp 40 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −158.8 (m, 2F), −138.2 (m, 2F); ^1H NMR ($CDCl_3$, TMS) 0.3 (s, 9H), 4.1 (t, $^5J_{H-F}$ = 1.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, TMS) 148.2 (dm, J_{C-F} = 252.8 Hz), 141.1 (dm, J_{C-F} = 247.5 Hz), 139.4 (m), 107.9 (t, $^4J_{C-F}$ = 3.8 Hz), 98.6 (t, $^2J_{C-F}$ = 18.2 Hz), 88.9 (t, $^3J_{C-F}$ = 3.8 Hz), 62.5 (t, $^4J_{C-F}$ = 3.4 Hz), 0.3 (s); FTIR (CCl_4, cm^{-1}) 2960.9 (w), 2900.9 (w), 2838.1 (w), 2170.7 (w, C≡C), 1646.2 (w), 1504.3 (s), 1427.7 (m), 1252.2 (m), 1145.1 (w), 1034.4 (s), 1021.8 (s), 990.3 (s), 922.7 (m); GC-MS (*m/z*) 276 (M^+, 5.2), 261 (42.1), 207 (7.4), 171 (31.3), 85 (31.0), 71 (74.0), 69 (57.5), 57 (100.0).

Preparation of 1-[4-(*N,N*-Dimethylamino)-2,3,5,6-tetrafluorophenyl]-1-heptyne (3a). Similarly, **3a** was prepared from 1.6 g (5 mmol) of 4-(*N,N*-dimethylamino)-1-iodotetrafluorobenzene, 0.7 g (7.2 mmol) of 1-heptyne, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.2 g (83%) of **3a**: GLPC purity 100.0%; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −153.0 (m, 2F), −140.6 (m, 2F); ^1H NMR ($CDCl_3$, TMS) 0.9 (t, $^3J_{H-H}$ = 7.1 Hz, 3H), 1.4 (m, 4H), 1.6 (m, 2H), 2.5 (t, $^3J_{H-H}$ = 7.1 Hz, 2H), 3.0 (t, ^5J = 2.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, TMS) 148.1 (dm, J_{C-F} = 247.9 Hz), 141.9 (dm, J_{C-F} = 242.9 Hz), 131.4 (tt, $^2J_{C-F}$ = 10.9, $^3J_{C-F}$ = 4.8 Hz), 101.7 (t, $^4J_{C-F}$ = 3.6 Hz), 96.6 (t, $^2J_{C-F}$ = 18.2 Hz), 66.3 (t, $^3J_{C-F}$ = 4.1 Hz), 43.2 (t, $^4J_{C-F}$ = 4.6 Hz), 31.3 (s), 28.5 (s), 22.5 (s), 20.0 (s), 14.1 (s); FTIR (CCl_4, cm^{-1}) 2935.0 (m), 2861.6 (w), 2812.2 (w), 2237.9 (w, C≡C), 1645.0 (w), 1514.0 (m), 1486.8 (s), 1432.6 (m), 1272.7 (w), 1219.8 (w), 1047.5 (w), 979.4 (m); GC-MS (*m/z*) 287 (M^+, 57.6), 258 (42.3), 244 (26.8), 230 (100.0), 214 (52.2), 206 (36.4), 193 (20.8), 186 (17.6); HRMS calcd for $C_{15}H_{17}F_4N$ 287.1297, obsd 287.1315.

Preparation of 1-[4-(*N,N*-Dimethylamino)-2,3,5,6-tetrafluorophenyl]-2-(trimethylsilyl)ethyne (3b). Similarly, **3b** was prepared from 1.6 g (5 mmol) of 4-(*N,N*-dimethylamino)-1-iodotetrafluorobenzene, 0.7 g (7.1 mmol) of (trimethylsilyl)-acetylene, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.3 g (87%) of **3b**: mp 44–45 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −153.0 (m, 2F), −139.4 (m, 2F); ^1H NMR ($CDCl_3$, TMS) 0.3 (s, 9H), 3.0 (t, $^5J_{H-F}$ = 2.3 Hz, 6H); ^{13}C NMR ($CDCl_3$, TMS) 148.4 (dm, J_{C-F} = 249.4 Hz), 141.7 (dm, J_{C-F} = 244.3 Hz), 132.6 (tt, $^2J_{C-F}$ = 9.8, $^3J_{C-F}$ = 4.6 Hz), 106.4 (t, $^4J_{C-F}$ = 3.4 Hz), 95.5 (t, $^2J_{C-F}$ = 18.1 Hz), 89.8 (t, $^3J_{C-F}$ = 3.6 Hz), 43.4 (t, $^4J_{C-F}$ = 4.8 Hz), 1.2 (s); FTIR (CCl_4, cm^{-1}) 2960.7 (w), 2899.0 (w), 2853.4 (w), 2813.4 (w), 2362.5 (w, C≡C), 2166.7 (w), 2068.8 (w), 1644.0 (w), 1516.9 (m), 1488.6 (s), 1431.1 (m), 1251.6 (m), 997.1 (m); GC-MS (*m/z*) 289 (M^+, 31.8), 274 (11.6), 171 (19.9), 149 (43.2), 97 (32.4), 83 (40.3), 71 (59.7), 69 (66.8), 57 (100.0).

Preparation of 1-(4-Morpholino-2,3,5,6-tetrafluorophenyl)-1-hexyne (4). Similarly, **4** was prepared from 1.8 g (5 mmol) of 4-morpholino-1-iodotetrafluorobenzene, 0.6 g (7.2 mmol) of 1-hexyne, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.4 g (89%) of **4**: GLPC purity 94.4%; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −152.4 (m, 2F), −139.9 (m, 2F); ^1H NMR ($CDCl_3$, TMS) 0.9 (t, $^3J_{H-H}$ = 7.3 Hz, 3H), 1.5 (m, 2H), 1.6 (m, 2H), 2.5 (t, $^3J_{H-H}$ = 6.8 Hz, 2H), 3.3 (m, 4H), 3.8 (m, 4H); ^{13}C NMR ($CDCl_3$, TMS) 147.8 (dm, J_{C-F} = 252.7 Hz), 142.1 (dm J_{C-F} = 245.3 Hz), 129.7 (tt, $^2J_{C-F}$ = 10.9, $^3J_{C-F}$ = 4.6 Hz), 102.3 (t, $^4J_{C-F}$ = 3.3 Hz), 98.1 (t, $^2J_{C-F}$ = 18.2 Hz), 67.4 (s), 65.9 (t, $^3J_{C-F}$ = 4.1 Hz), 51.3 (t, $^4J_{C-F}$ = 3.5 Hz), 30.5 (s), 22.0 (s), 19.6 (s), 13.6 (s); FTIR (CCl_4, cm^{-1}) 2963.1 (m), 2934.6 (w), 2859.7 (m), 2239.4 (w, C≡C), 1645.2 (w), 1487.0 (s), 1450.0 (m), 1375.3 (w), 1258.5 (w), 1189.7 (w), 1119.8 (m), 984.2 (m); GC-MS (*m/z*) 316 (M^+ + 1, 18.1), 315 (M^+, 100.0), 314 (13.3), 300 (7.0), 286 (2.5), 272 (18.8), 257 (32.5), 242 (78.7), 228 (14.7), 214 (48.6), 201 (17.1), 200 (19.9), 186 (20.8), 151 (2.9), 121 (2.0), 67 (3.6), 57 (15.9).

Preparation of 1-(4-Piperidino-2,3,5,6-tetrafluorophenyl)-1-hexyne (5). Similarly, **5** was prepared from 1.8 g (5 mmol) of 4-piperidino-1-iodotetrafluorobenzene, 0.6 g (7.2 mmol) of 1-hexyne, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.2 g (77%) of **5**: GLPC purity 97.0%; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −140.2 (m, 2F), −152.5 (m, 2F); ^1H NMR ($CDCl_3$, TMS) 0.9 (t, $^3J_{H-H}$ = 7.0 Hz, 3H), 1.5 (m, 4H), 1.6 (m, 6H), 2.5 (t, $^3J_{H-H}$ = 7.0 Hz, 2H), 3.2 (s, 4H); ^{13}C NMR ($CDCl_3$, TMS) 147.9 (dm, J_{C-F} = 248.6 Hz), 142.2 (dm, J_{C-F} = 238.1 Hz), 131.4 (tm, $^2J_{C-F}$ = 11.7 Hz), 101.6 (t, $^4J_{C-F}$ = 3.1 Hz), 97.0 (t, $^2J_{C-F}$ = 18.4 Hz), 66.3 (m), 52.5 ($^4J_{C-F}$ = 3.3 Hz), 30.8 (s), 26.8 (s), 24.4 (s), 22.2 (s), 19.7 (s), 13.7 (s); FTIR (CCl_4, cm^{-1}) 2938.7 (m), 2859.8 (w), 2239.4 (w, C≡C), 1644.0 (w), 1485.2 (s), 1451.7 (w), 1382.8 (w), 1228.1 (w), 1082.7 (w), 980.7 (m); GC-MS (*m/z*) 313 (M^+, 67.0), 312 (M^+ − 1, 100.0), 298 (8.3), 284 (4.3), 270 (24.3), 256 (6.8), 214 (23.0), 186 (12.8).

Preparation of 1-(4-Methoxy-2,3,5,6-tetrafluorophenyl)-2-phenylethyne (6). Similarly, **6** was prepared from 1.5 g (5 mmol) of 4-methoxy-1-iodotetrafluorobenzene, 0.7 g (7.0 mmol) of phenylacetylene, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.0 g (74%) of **6**: mp 70–73 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −158.7 (m, 2F), −138.5 (m, 2F); ^1H NMR ($CDCl_3$, TMS) 4.1 (s, 3H), 7.3 (m, 3H), 7.5 (m, 2H); ^{13}C NMR ($CDCl_3$, TMS) 147.4 (dm, J_{C-F} = 255.2 Hz), 140.9 (dm, J_{C-F} = 246.5 Hz), 138.9 (tt, $^2J_{C-F}$ = 11.5, $^3J_{C-F}$ = 3.6 Hz), 131.9 (s), 129.4 (s), 128.5 (s), 122.1 (s), 100.4 (t, $^4J_{C-F}$ = 3.5 Hz), 98.1 (t, $^2J_{C-F}$ = 18.1 Hz), 74.1 (t, $^3J_{C-F}$ = 3.9 Hz), 62.2 (t, $^4J_{C-F}$ = 3.8 Hz); FTIR (CCl_4, cm^{-1}) 3059.7 (w), 3021.0 (w), 2948.5 (w), 2838.9 (w), 2222.3 (w, C≡C), 1645.7 (w), 1599.2 (w), 1508.9 (s), 1493.9 (s), 1429.8 (s), 1194.1 (w), 1127.3 (s), 1008.9 (s), 921.1 (w); GC-MS (*m/z*) 281 (M^+ + 1, 15.3), 280 (M^+, 100.0), 279 (74.0), 253 (8.6), 237 (42.1), 217 (13.2), 203 (22.5), 201 (11.9), 187 (9.8), 167 (2.2), 115 (8.6), 105 (4.0), 93 (5.7), 63 (2.1), 51 (2.5).

Preparation of 1-[4-(*N,N*-Dimethylamino)-2,3,5,6-tetrafluorophenyl]-2-(1-cyclohexenyl)ethyne (7a). Similarly, **7a** was prepared from 1.6 g (5 mmol) of 4-(*N,N*-dimethylamino)-1-iodotetrafluorobenzene, 0.8 g (7.5 mmol) of 1-cyclohexenylacetylene, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 0.9 g (61%) of **7a**: mp 50–51 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −153.0 (m, 2F), −140.0 (m, 2F); ^1H NMR ($CDCl_3$, TMS) 1.6 (m, 4H), 2.1 (m, 2H), 2.2 (m, 2H), 3.0 (t, $^5J_{H-F}$ = 2.2 Hz, 6H), 6.2 (m, 1H); ^{13}C NMR ($CDCl_3$, TMS) 147.5 (dm, J_{C-F} = 249.1 Hz), 141.7 (dm, J_{C-F} = 244.0 Hz), 136.9 (s), 131.6 (tt, $^2J_{C-F}$ = 11.0, $^3J_{C-F}$ = 4.6 Hz), 120.6 (s), 101.6 (t, $^4J_{C-F}$ = 3.0 Hz), 96.2 (t, $^2J_{C-F}$ = 18.2 Hz), 72.3 (t, $^3J_{C-F}$ = 4.2 Hz), 43.2 (t, $^4J_{C-F}$ = 3.9 Hz), 29.1 (s), 26.0 (s), 22.5 (s), 21.7 (s); FTIR (CCl_4, cm^{-1}) 2938.8 (m), 2860.9 (w), 2812.3 (w), 2211.1 (w, C≡C), 1643.4 (w), 1515.2 (m), 1487.7 (s), 1432.6 (m), 1220.0 (w), 1083.7 (w), 979.1 (m); GC-MS (*m/z*) 297 (M^+, 34.2), 269 (27.5), 223 (25.2), 205 (29.6), 161 (24.6), 149 (100.0), 110 (31.3), 95 (43.9).

Preparation of 1-[4-(*N,N*-Dimethylamino)-2,3,5,6-tetrafluorophenyl]-2-phenylethyne (7b). Similarly, **7b** was prepared from 1.6 g (5 mmol) of 4-(*N,N*-dimethylamino)-1-iodotetrafluorobenzene, 0.7 g (7.0 mmol) of phenylacetylene, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.3 g (90%) of **7b**: mp 84–85 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −152.8 (m, 2F), −139.6 (m, 2F); ^1H NMR ($CDCl_3$, TMS) 2.9 (t, $^5J_{H-H}$ = 2.3 Hz, 6H), 7.3 (m, 3H), 7.5 (m, 2H); ^{13}C NMR ($CDCl_3$, TMS) 147.6 (dm, J_{C-F} = 249.4 Hz), 141.4 (dm J_{C-F} = 243.2 Hz), 131.9 (tm, $^2J_{C-F}$ = 10.2 Hz), 131.7 (s), 129.0 (s), 128.4 (s), 122.5 (s), 99.4 (t, $^4J_{C-F}$ = 3.0 Hz), 95.3 (t, $^2J_{C-F}$ = 18.2 Hz), 75.0 (t, $^3J_{C-F}$ = 4.1 Hz), 43.1 (t, $^4J_{C-F}$ = 4.7 Hz); FTIR (CCl_4, cm^{-1}) 3065.6 (w), 2941.8 (w), 2895.3 (w), 2813.2 (w), 2224.0 (w, C≡C), 1643.2 (w), 1598.6 (w), 1517.0 (m), 1487.5 (s), 1431.6 (s), 1218.7 (w), 1089.8 (m), 985.3 (m); GC-MS (*m/z*) 293 (M^+, 45.2), 283 (12.2), 207 (18.6), 171 (55.8), 97 (51.0), 83 (69.2), 71 (100.0).

Preparation of 1-(4-Morpholino-2,3,5,6-tetrafluorophenyl)-2-phenylethyne (8). Similarly, **8** was prepared from 1.8 g (5 mmol) of 4-morpholino-1-iodotetrafluorobenzene, 0.7 g (7.0 mmol) of phenylacetylene, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.3 g (78%) of **8**: mp 120–121 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −152.2 (m, 2F), −138.8 (m, 2F); ^1H NMR ($CDCl_3$, TMS) 3.3 (m,

4H), 3.8 (m, 4H), 7.3 (m, 3H), 7.5 (m, 2H); ^{13}C NMR ($CDCl_3$, TMS) 147.5 (dm, J_{C-F} = 251.7 Hz), 141.9 (dm, J_{C-F} = 246.6 Hz), 131.8 (s), 130.4 (t, $^2J_{C-F}$ = 11.9 Hz), 129.2 (s), 128.5 (s), 122.2 (s), 100.0 (t, $^4J_{C-F}$ = 3.4 Hz), 97.2 (t, $^2J_{C-F}$ = 18.2 Hz), 67.3 (s), 51.2 (t, $^4J_{C-F}$ = 3.6 Hz); FTIR (CCl_4, cm^{-1}) 2966.6 (w), 2894.2 (w), 2858.4 (w), 2224.7 (w, C≡C), 1700.2 (w), 1506.6 (m), 1487.8 (s), 1443.9 (m), 1375.2 (w), 1258.5 (w), 1153.9 (w), 1120.3 (m), 983.6 (m); GC-MS (*m/z*) 335 (M^+, 49.6), 277 (91.6), 263 (13.3), 249 (9.8), 149 (12.8), 138 (47.5), 111 (28.1), 97 (43.0), 83 (44.2), 69 (63.6), 57 (100.0).

Preparation of 1-(4-Piperidino-2,3,5,6-tetrafluorophenyl)-2-phenylethyne (9). Similarly, **9** was prepared from 1.8 g (5 mmol) of 4-piperidino-1-iodotetrafluorobenzene, 0.7 g (7.0 mmol) of phenylacetylene, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.4 g (87%) of **9**: mp 70–72 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −152.4 (m, 2F), −139.5 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 1.6 (m, 6H), 3.2 (m, 4H), 7.3 (m, 3H), 7.5 (m, 2H); ^{13}C NMR ($CDCl_3$, TMS) 147.7 (dm, J_{C-F} = 245.5 Hz), 141.9 (dm, J_{C-F} = 240.0 Hz), 131.8 (s), 129.2 (m), 129.0 (s), 128.4 (s), 122.5 (s), 99.5 (t, $^4J_{C-F}$ = 3.3 Hz), 95.9 (t, $^2J_{C-F}$ = 19.1 Hz), 75.1 (m), 52.3 (t, $^4J_{C-F}$ = 3.5 Hz), 26.5 (s), 24.1 (s); FTIR (CCl_4, cm^{-1}) 2939.9 (s), 2853.4 (m), 2223.5 (w, C≡C), 1642.8 (m), 1598.1 (w), 1484.2 (s), 1443.6 (s), 1382.9 (m), 1227.9 (m), 1113.4 (m), 980.7 (m), GC-MS (*m/z*) 334 (M^+ + 1, 32.4), 333 (M^+, 4.3), 332 (M^+ − 1, 18.9), 256 (62.5), 249 (48.4), 229 (68.7), 201 (74.2), 154 (57.8), 132 (77.3), 114 (74.2), 83 (20.3), 76 (64.1), 57 (100.0).

Preparation of 1-(4-Methoxy-2,3,5,6-tetrafluorophenyl)-3-phenoxy-1-propyne (10a). Similarly, **10a** was prepared from 1.5 g (5 mmol) of 4-methoxy-1-iodotetrafluorobenzene, 0.9 g (7.0 mmol) of phenyl propargyl ether, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.2 g (80%) of **10a**: mp 82–84 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −158.5 (m, 2F), −138.0 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 4.1 (t, $^5J_{H-F}$ = 1.7 Hz, 3H), 4.9 (s, 2H), 7.0 (m, 3H), 7.3 (m, 2H); ^{13}C NMR ($CDCl_3$, TMS) 157.7 (s), 147.8 (dm, J_{C-F} = 252.8 Hz), 141.0 (dm, J_{C-F} = 246.4 Hz), 139.5 (tt, $^2J_{C-F}$ = 12.1, $^3J_{C-F}$ = 3.4 Hz), 129.6 (s), 121.8 (s), 115.1 (s), 96.6 (t, $^2J_{C-F}$ = 18.5 Hz), 95.5 (t, $^4J_{C-F}$ = 3.6 Hz), 72.3 (t, $^3J_{C-F}$ = 4.0 Hz), 62.2 (t, $^4J_{C-F}$ = 3.8 Hz), 56.5 (s); FTIR (CCl_4, cm^{-1}) 3043.9 (w), 2947.9 (w), 2839.1 (w), 1646.4 (w), 1599.5 (m), 1589.6 (m), 1498.5 (s), 1429.7 (m), 1370.8 (w), 1213.6 (m), 1074.7 (s), 994.2 (s); GC-MS (*m/z*) 310 (M^+, 5.4), 217 (63.0), 202 (12.8), 167 (6.6), 149 (22.8), 123 (11.8), 111 (16.8), 97 (25.7), 83 (32.8), 71 (55.1), 57 (100.0).

Preparation of 1-(4-Methoxy-2,3,5,6-tetrafluorophenyl)-3-methoxy-1-propyne (10b). Similarly, **10b** was prepared from 1.5 g (5 mmol) of 4-methoxy-1-iodotetrafluorobenzene, 0.5 g (7.0 mmol) of methyl propargyl ether, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.0 g (84%) of **10b**: GLPC purity 98.8%; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −158.6 (m, 2F), −138.7 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 3.5 (s, 3H), 4.1 (t, $^5J_{H-F}$ = 1.5 Hz, 3H), 4.4 (s, 2H); ^{13}C NMR ($CDCl_3$, TMS) 147.4 (dm, J_{C-F} = 251.8 Hz), 140.5 (dm, J_{C-F} = 247.5 Hz), 139.0 (m), 96.7 (t, $^2J_{C-F}$ = 18.2 Hz), 96.5 (t, $^4J_{C-F}$ = 2.8 Hz), 70.7 (t, $^3J_{C-F}$ = 3.4 Hz), 61.8 (t, $^4J_{C-F}$ = 3.9 Hz), 59.8 (s), 57.2 (s); FTIR (CCl_4, cm^{-1}) 2996.5 (w), 2941.4 (w), 2823.7 (w), 1647.1 (w), 1507.8 (s), 1429.4 (m), 1354.1 (m), 1188.3 (w), 1108.0 (m), 1068.0 (m); GC-MS (*m/z*) 248 (M^+, 62.2), 233 (8.7), 217 (100.0), 202 (51.3), 174 (43.9), 161 (10.6), 143 (23.3), 124 (21.8), 117 (12.2), 105 (25.3), 93 (12.8); HRMS Calcd for $C_{11}H_8F_4O_2$ 248.0460, obsd 248.0468.

Preparation of (*Z*)-1-methoxy-4-(4-methoxy-2,3,5,6-tetrafluorophenyl)-1-buten-3-yne (10c). Similarly, **10c** was prepared from 1.5 g (5 mmol) of 4-methoxy-1-iodotetrafluorobenzene, 0.6 g (7.3 mmol) of *cis*-1-methoxy-1-buten-3-yne, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.0 g (80%) of **10c**: GLPC purity 98.0%; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −159.1 (m, 2F), −139.0 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 3.8 (s, 3H), 4.1 (t, $^5J_{H-F}$ = 1.4 Hz, 3H), 4.8 (d, $^3J_{H-H}$ = 6.5 Hz, 1H), 6.4 (d, $^3J_{H-H}$ = 6.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, TMS) 158.3 (s), 147.2 (dm, J_{C-F} = 250.2 Hz), 141.0 (dm, J_{C-F} = 246.4 Hz), 138.4 (tt, $^2J_{C-F}$ = 12.4, $^3J_{C-F}$ = 3.7 Hz), 98.9 (t, $^2J_{C-F}$ = 18.2 Hz), 95.9 (t, $^4J_{C-F}$ = 3.4 Hz), 84.3 (s), 77.1 (t, $^3J_{C-F}$ = 4.1 Hz), 62.3 (t, $^4J_{C-F}$ = 3.6 Hz), 61.0 (s); FTIR (CCl_4, cm^{-1}) 3013.3 (w), 2938.2 (w), 2854.7 (w), 2209.2 (w, C≡C), 1804.4 (w), 1625.3 (m), 1494.8 (s), 1429.7 (m), 1387.1 (w), 1271.5 (m), 1116.6 (s), 1055.9 (m), 991.4 (s); GC-MS (*m/z*) 260 (M^+, 21.4), 245 (9.0), 217 (16.5), 202 (7.0), 185 (5.7), 171 (22.5), 152 (8.5), 135 (10.1), 123 (11.4), 97 (14.4), 83 (29.8), 69 (43.6), 57 (100.0).

Preparation of (*Z*)-1-Methoxy-4-[4-(*N*,*N*-dimethylamino)-2,3,5,6-tetrafluorophenyl]-1-buten-3-yne (11). Similarly, **11** was prepared from 1.6 g (5 mmol) of 4-(*N*,*N*-dimethylamino)-1-iodotetrafluorobenzene, 0.6 g (7.3 mmol) of *cis*-1-methoxy-1-buten-3-yne, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 0.9 g (68%) of **11**: GLPC purity 100.0%; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −153.1 (m, 2F), −140.1 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 3.0 (t, $^5J_{H-F}$ = 2.3 Hz, 6H), 3.8 (s, 3H), 4.8 (d, $^3J_{H-H}$ = 6.6 Hz, 1H), 6.4 (d, $^3J_{H-H}$ = 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, TMS) 157.7 (s), 147.4 (dm, J_{C-F} = 249.2 Hz), 141.6 (dm, J_{C-F} = 243.0 Hz), 131.5 (tt, $^2J_{C-F}$ = 13.3, $^3J_{C-F}$ = 4.8 Hz), 96.3 (t, $^2J_{C-F}$ = 17.9 Hz), 94.7 (t, $^4J_{C-F}$ = 3.6 Hz), 84.6 (s), 77.9 (t, $^3J_{C-F}$ = 4.3 Hz), 60.9 (s), 43.2 (t, $^4J_{C-F}$ = 4.3 Hz); FTIR (CCl_4, cm^{-1}) 2937.4 (w), 2897.3 (w), 2853.3 (w), 2207.8 (w, C≡C), 1734.6 (w), 1641.8 (m), 1514.4 (m), 1489.5 (s), 1431.5 (m), 1268.5 (m), 1221.0 (w), 1109.6 (s), 1049.6 (s), 982.0 (s); GC-MS (*m/z*) 273 (M^+, 20.5), 207 (14.6), 171 (86.1), 112 (23.5), 95 (24.5), 85 (32.6), 70 (59.6), 55 (64.2), 43 (100.0).

Preparation of 1-(4-Morpholino-2,3,5,6-tetrafluorophenyl)-3-methoxy-1-propyne (12). Similarly, **12** was prepared from 1.8 g (5 mmol) of 4-morpholino-1-iodotetrafluorobenzene, 0.5 g (7.0 mmol) of methyl propargyl ether, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.1 g (73%) of **12**: mp 64–65 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −152.1 (m, 2F), −138.8 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 3.3 (m, 4H), 3.5 (s, 3H), 3.8 (m, 4H), 4.4 (s, 2H); ^{13}C NMR ($CDCl_3$, TMS) 147.9 (dm, J_{C-F} = 252.8 Hz), 141.8 (dm, J_{C-F} = 245.3 Hz), 130.9 (tm, $^2J_{C-F}$ = 10.9 Hz), 96.4 (t, $^4J_{C-F}$ = 3.2 Hz), 96.2 (t, $^2J_{C-F}$ = 18.2 Hz), 71.8 (t, $^3J_{C-F}$ = 4.1 Hz), 67.4 (s), 60.4 (s), 57.7 (s), 51.3 (t, $^4J_{C-F}$ = 3.6 Hz); FTIR (CCl_4, cm^{-1}) 2966.7 (m), 2894.2 (m), 2858.6 (m), 2236.5 (w, C≡C), 1644.6 (m), 1504.3 (s), 1479.7 (s), 1374.9 (m), 1353.7 (m), 1187.7 (m), 1118.2 (m), 1103.7 (m), 1005.1 (m), 986.5 (m); GC-MS (*m/z*) 303 (M^+, 100.0), 272 (37.9), 228 (14.8), 214 (60.2), 200 (19.3), 186 (33.6), 177 (33.1), 167 (14.8), 149 (5.5), 136 (6.2), 123 (5.9), 107 (9.7).

Preparation of 1-(4-Piperidino-2,3,5,6-tetrafluorophenyl)-3-methoxy-1-propyne (13a). Similarly, **13a** was prepared from 1.8 g (5 mmol) of 4-piperidino-1-iodotetrafluorobenzene, 0.5 g (7.0 mmol) of methyl propargyl ether, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.1 g (73%) of **13a**: GLPC purity 100.0%; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −152.2 (m, 2F), −139.5 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 1.7 (m, 6H), 3.2 (m, 4H), 3.4 (s, 3H), 4.4 (s, 2H); ^{13}C NMR ($CDCl_3$, TMS) 147.9 (dm, J_{C-F} = 246.8 Hz), 141.9 (dm, J_{C-F} = 240.2 Hz), 132.4 (tm, $^2J_{C-F}$ = 10.8 Hz), 95.6 (t, $^2J_{C-F}$ = 3.3 Hz), 95.1 (m), 72.3 (m), 60.4 (s), 57.7 (s), 52.3 (t, $^4J_{C-F}$ = 3.6 Hz), 26.6 (s), 24.2 (s); FTIR (CCl_4, cm^{-1}) 2940.6 (m), 2852.8 (m), 2236.3 (w, C≡C), 1643.6 (m), 1478.6 (m), 1338.7 (m), 1102.7 (s), 1072.4 (m); GC-MS (*m/z*) 301 (M^+, 100.0), 270 (63.4), 232 (13.1), 214 (40.3), 186 (36.2), 167 (12.8), 136 (6.9), 123 (7.3), 105 (5.5), 69 (9.1), 55 (20.3).

Preparation of (*Z*)-1-methoxy-4-(4-piperidino-2,3,5,6-tetrafluorophenyl)-1-buten-3-yne (13b). Similarly, **13b** was prepared from 1.8 g (5 mmol) of 4-piperidino-1-iodotetrafluorobenzene, 0.6 g (7.3 mmol) of *cis*-1-methoxy-1-buten-3-yne, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.0 g (66%) of **13b**: GLPC purity 100.0%; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −152.5 (m, 2F), −140.0 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 1.6 (m, 6H), 3.2 (m, 4H), 3.8 (s, 3H), 4.7 (d, $^3J_{H-H}$ = 6.5 Hz, 1H), 6.4 (d, $^3J_{H-H}$ = 6.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, TMS) 157.6 (s), 147.4 (dm, J_{C-F} = 248.9 Hz), 142.0 (dm, J_{C-F} = 240.4 Hz), 131.4 (tm, $^2J_{C-F}$ = 11.0 Hz), 97.2 (t, $^2J_{C-F}$ = 18.3 Hz), 94.9 (t, $^4J_{C-F}$ = 3.4 Hz), 84.7 (s), 77.9 (t, $^3J_{C-F}$ = 4.2 Hz), 60.8 (s), 52.4 (t, $^4J_{C-F}$ = 3.5 Hz), 26.7 (s), 24.2 (s); FTIR (CCl_4, cm^{-1}) 2935.2 (s), 2853.6 (m), 2206.3 (w, C≡C), 1647.6 (s), 1523.2 (s), 1443.2 (s), 1385.0 (s), 1272.8 (s), 1139.1 (s), 983.7 (s); GC-MS (*m/z*) 313 (M^+, 100.0), 312 (58.4), 270 (13.6), 214 (37.0), 186 (17.0), 167 (5.1), 136 (3.7).

Preparation of (*Z*)-1-Methoxy-4-(2,3,5,6-tetrafluorophenyl)-1-buten-3-yne (14). Similarly, **14** was prepared from 1.4 g (5 mmol) of 4-hydro-1-iodotetrafluorobenzene, 0.6 g (7.3 mmol) of *cis*-1-methoxy-1-buten-3-yne, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$.

Usual workup gave 0.6 g (51%) of 14: ^{19}F NMR ($CFCl_3$, $CDCl_3$) −140.0 (m, 2F), −138.0 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 3.9 (s, 3H), 4.8 (d, $^3J_{H-H}$ = 6.5 Hz, 1H), 6.5 (d, $^3J_{H-H}$ = 6.5 Hz, 1H), 7.0 (m, 1H); ^{13}C NMR ($CDCl_3$, TMS) 159.1 (m), 146.8 (dm, J_{C-F} = 251.1 Hz), 146.2 (dm, J_{C-F} = 247.8 Hz), 106.4 (tt, $^2J_{C-F}$ = 18.2, $^3J_{C-F}$ = 4.6 Hz), 105.6 (t, $^2J_{C-F}$ = 23.1 Hz), 97.8 (t, $^4J_{C-F}$ = 3.6 Hz), 84.2 (s), 77.6 (t, $^3J_{C-F}$ = 4.4 Hz), 61.1 (s); FTIR (CCl_4, cm^{-1}) 3080.5 (w), 2937.8 (w), 2861.2 (w), 2205.1 (w, C≡C), 1734.3 (w), 1675.1 (w), 1623.7 (m), 1502.4 (s), 1382.0 (w), 1270.7 (m), 1177.0 (m), 1137.3 (m), 1104.2 (m), 936.3 (s); GC-MS (*m/z*) 230 (M$^+$, 9.2), 149 (9.7), 134 (5.8), 119 (14.3), 105 (5.5), 99 (8.1), 91 (8.4), 74 (10.0), 59 (14.6), 44 (17.4).

Preparation of 3-(4-Methoxy-2,3,5,6-tetrafluorophenyl)-2-propyn-1-ol (15a). Similarly, **15a** was prepared from 1.5 g (5 mmol) of 4-methoxy-1-iodotetrafluorobenzene, 0.4 g (7.1 mmol) of propargyl alcohol, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 0.9 g (74%) of **15a**: mp 75–77 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −158.6 (m, 2F), −138.6 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 2.8 (s, 1H), 4.1 (t, $^5J_{H-F}$ = 1.5 Hz, 3H), 4.6 (s, 2H); ^{13}C NMR ($CDCl_3$, TMS) 147.7 (dm, J_{C-F} = 251.5 Hz), 140.8 (dm, J_{C-F} = 243.0 Hz), 139.2 (m), 98.7 (t, $^4J_{C-F}$ = 3.5 Hz), 97.2 (t, $^2J_{C-F}$ = 18.2 Hz), 70.5 (t, $^3J_{C-F}$ = 3.8 Hz), 62.2 (t, $^4J_{C-F}$ = 3.7 Hz), 51.5 (s); FTIR (CCl_4, cm^{-1}) 3618.8 (m), 3470.0 (br), 3016.2 (w), 2946.2 (m), 2868.8 (w), 2838.7 (w), 2440.0 (w), 2020.0 (w), 1646.2 (m), 1505.4 (s), 1495.6 (s), 1429.4 (s), 1377.3 (m), 1203.0 (m), 1072.7 (s), 993.4 (s); GC-MS (*m/z*) 234 (M$^+$, 12.4), 217 (6.5), 203 (11.3), 185 (8.5), 171 (12.1), 163 (14.2), 149 (13.7), 137 (11.1), 123 (17.5), 111 (23.0), 97 (34.2), 83 (40.5), 69 (61.2), 57 (100.0).

Preparation of 4-(4-Methoxy-2,3,5,6-tetrafluorophenyl)-2-methyl-3-butyn-2-ol (15b). Similarly, **15b** was prepared from 1.5 g (5 mmol) of 4-methoxy-1-iodotetrafluorobenzene, 0.6 g (7.1 mmol) of 2-methyl-3-butyn-2-ol, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.1 g (84%) of **15b**: mp 74–75 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −158.8 (m, 2F), −138.7 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 1.6 (s, 6H), 3.1 (s, 1H), 4.1 (m, 3H); ^{13}C NMR ($CDCl_3$, TMS) 147.6 (dm, J_{C-F} = 251.4 Hz), 140.9 (dm, J_{C-F} = 247.1 Hz), 138.0 (m), 105.5 (t, $^4J_{C-F}$ = 3.6 Hz), 97.6 (m), 67.2 (m), 65.9 (s), 62.2 (t, $^4J_{C-F}$ = 3.9 Hz), 31.2 (s); FTIR (CCl_4, cm^{-1}) 3608.7 (m), 3483.5 (br), 2987.1 (m), 2941.1 (w), 2838.9 (w), 2231.7 (w, C≡C), 1646.2 (w), 1503.3 (s), 1491.8 (s), 1364.7 (m), 1326.9 (m), 1196.3 (s), 1170.0 (s), 1143.1 (s), 1044.1 (s), 1033.8 (s), 990.3 (s); GC-MS (*m/z*) 262 (M$^+$, 12.7), 247 (27.1), 207 (15.6), 163 (14.3), 149 (24.3), 135 (22.6), 109 (20.4), 95 (31.4), 81 (42.3), 69 (68.0), 55 (100.0).

Preparation of 1-[(4-Methoxy-2,3,5,6-tetrafluorophenyl)ethynyl]-1-cyclohexanol (15c). Similarly, **15c** was prepared from 1.5 g (5 mmol) of 4-methoxy-1-iodotetrafluorobenzene, 0.9 g (7.2 mmol) of 1-ethynyl-1-cyclohexanol, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.2 g (77%) of **15c**: mp 75–76 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −158.8 (m, 2F), −138.6 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 1.3 (m, 1H), 1.5–1.8 (m, 8H), 2.0–2.2 (m, 2H), 4.1 (t, $^5J_{H-F}$ = 1.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, TMS) 147.5 (dm, J_{C-F} = 251.7 Hz), 140.8 (dm, J_{C-F} = 246.7 Hz), 139.0 (m), 104.5 (t, $^4J_{C-F}$ = 3.6 Hz), 97.6 (t, $^2J_{C-F}$ = 18.4 Hz), 69.5 (t, $^3J_{C-F}$ = 4.7 Hz), 62.3 (t, $^4J_{C-F}$ = 3.5 Hz), 39.8 (s), 39.7 (s), 25.2 (s), 23.3 (s); FTIR (CCl_4, cm^{-1}) 3606.3 (w), 2939.3 (m), 2857.4 (w), 1646.2 (w), 1504.3 (s), 1492.0 (s), 1429.7 (m), 1142.9 (w), 1052.8 (m), 991.7 (m); GC-MS (*m/z*) 302 (M$^+$, 26.4), 287 (41.1), 271 (50.0), 259 (100.0), 246 (46.5), 231 (57.9), 217 (19.3), 206 (35.6), 149 (95.5), 125 (18.8), 104 (16.2), 74 (9.2), 60 (13.1).

Preparation of 4-(4-Methoxy-2,3,5,6-tetrafluorophenyl)-3-butyn-2-ol (15d). Similarly, **15d** was prepared from 1.5 g (5 mmol) of 4-methoxy-1-iodotetrafluorobenzene, 0.5 g (7.1 mmol) of D,L-3-butyne-2-ol, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.0 g (80%) of **15d**: GLPC purity 100.0%; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −158.7 (m, 2F), −138.7 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 1.6 (d, $^3J_{H-H}$ = 6.6 Hz, 3H), 3.4 (s, 1H), 4.1 (t, $^5J_{H-F}$ = 1.5 Hz, 3H), 4.8 (q, $^3J_{H-H}$ = 6.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, TMS) 147.6 (dm, J_{C-F} = 251.6 Hz), 140.8 (dm, J_{C-F} = 247.5 Hz), 139.2 (m), 102.5 (t, $^4J_{C-F}$ = 3.2 Hz), 97.3 (t, $^2J_{C-F}$ = 18.2 Hz), 68.8 (t, $^3J_{C-F}$ = 3.5 Hz), 62.2 (t, $^4J_{C-F}$ = 3.6 Hz), 58.9 (s), 24.0 (s); FTIR (CCl_4, cm^{-1}) 3616.0 (m), 3400.0 (br), 2989.1 (m), 2944.5 (m), 2887.6 (w), 2839.0 (w), 1645.1 (m), 1505.3 (s), 1490.3 (s), 1429.4 (s), 1376.6 (m), 1253.3 (m), 1108.7 (s), 1003.2 (s), 992.8 (s); GC-MS (*m/z*) 248 (M$^+$, 36.7), 233 (100.0), 218 (22.1), 217 (27.6), 205 (31.2), 149 (5.2), 69 (5.9).

Preparation of 1-(4-Methoxy-2,3,5,6-tetrafluorophenyl)-5-cyano-1-pentyne (15e). Similarly, **15e** was prepared from 1.5 g (5 mmol) of 4-methoxy-1-iodotetrafluorobenzene, 0.7 g (7.1 mmol) of 5-cyano-1-pentyne, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.3 g (96%) of **15e**: GLPC purity 97.0%; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −158.7 (m, 2F), −139.4 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 2.0 (t, J = 7.0 Hz, 2H), 2.6 (t, J = 7.2 Hz, 2H), 2.7 (t, J = 6.8 Hz, 2H), 4.1 (t, $^5J_{H-F}$ = 1.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, TMS) 147.8 (dm, J_{C-F} = 250.3 Hz), 141.0 (dm, J_{C-F} = 243.0 Hz), 138.9 (m), 119.3 (s), 99.6 (t, $^4J_{C-F}$ = 3.6 Hz), 97.9 (t, $^2J_{C-F}$ = 18.2 Hz), 67.3 (t, $^3J_{C-F}$ = 3.8 Hz), 62.4 (t, $^4J_{C-F}$ = 3.8 Hz), 24.6 (s), 19.0 (s), 16.2 (s); FTIR (CCl_4, cm^{-1}) 2945.5 (m), 2839.3 (w), 2250.9 (w, C≡C), 1646.9 (w), 1492.6 (s), 1454.9 (m), 1430.0 (s), 1348.3 (w), 1309.5 (w), 1203.3 (m), 1165.5 (w), 1078.3 (s), 991.2 (s); GC-MS (*m/z*) 271 (M$^+$, 68.9), 256 (9.8), 230 (38.9), 217 (100.0), 202 (30.4), 187 (13.0), 174 (16.9), 161 (13.7), 143 (6.9), 123 (13.2), 105 (11.9).

Preparation of 4-[4-(*N*,*N*-Dimethylamino)-2,3,5,6-tetrafluorophenyl]-3-butyn-2-ol (16a). Similarly, **16a** was prepared from 1.5 g (5 mmol) of 4-(*N*,*N*-dimethylamino)-1-iodotetrafluorobenzene, 0.5 g (7.1 mmol) of D,L-3-butyne-2-ol, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 0.9 g (67%) of **16a**: mp 74–75 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −152.8 (m, 2F), −139.7 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 1.6 (d, $^3J_{H-H}$ = 6.6 Hz, 3H), 3.0 (t, $^5J_{H-F}$ = 2.2 Hz, 6H), 3.2 (s, 1H), 4.8 (q, $^3J_{H-H}$ = 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, TMS) 147.6 (dm, J_{C-F} = 249.6 Hz), 141.2 (dm, J_{C-F} = 243.9 Hz), 132.0 (t, $^2J_{C-F}$ = 10.4 Hz), 101.3 (m), 94.4 (t, $^2J_{C-F}$ = 18.5 Hz), 69.5 (t, $^3J_{C-F}$ = 3.5 Hz), 58.9 (s), 43.0 (t, $^4J_{C-F}$ = 4.2 Hz), 24.1 (s); FTIR (CCl_4, cm^{-1}) 3616.0 (w), 2989.2 (w), 2935.6 (w), 2813.6 (w), 2236.1 (w, C≡C), 1642.8 (m), 1517.4 (m), 1488.4 (s), 1432.3 (m), 1093.3 (m), 981.3 (s); GC-MS (*m/z*) 261 (M$^+$, 90.2), 246 (100.0), 217 (43.6), 216 (21.3), 149 (14.5), 122 (5.5), 97 (5.5), 85 (25.8), 71 (51.0).

Preparation of 4-[4-(*N*,*N*-Dimethylamino)-2,3,5,6-tetrafluorophenyl]-2-methyl-3-butyn-2-ol (16b). Similarly, **16b** was prepared from 1.6 g (5 mmol) of 4-(*N*,*N*-dimethylamino)-1-iodotetrafluorobenzene, 0.6 g (7.1 mmol) of 2-methyl-3-butyn-2-ol, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.0 g (70%) of **16b**: mp 77–78 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −152.8 (m, 2F), −139.8 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 1.6 (s, 6H), 3.0 (t, $^5J_{H-F}$ = 2.3 Hz, 6H), 3.1 (s, 1H); ^{13}C NMR ($CDCl_3$, TMS) 147.7 (dm, J_{C-F} = 250.2 Hz), 141.5 (dm, J_{C-F} = 244.2 Hz), 132.6 (tt, $^2J_{C-F}$ = 11.0, $^3J_{C-F}$ = 4.8 Hz), 104.5 (t, $^4J_{C-F}$ = 3.6 Hz), 94.9 (t, $^2J_{C-F}$ = 19.3 Hz), 67.9 (t, $^3J_{C-F}$ = 4.3 Hz), 65.9 (s), 43.1 (t, $^4J_{C-F}$ = 4.3 Hz), 31.2 (s); FTIR (CCl_4, cm^{-1}) 3609.3 (w), 2986.6 (w), 2937.5 (w), 2813.3 (w), 1643.1 (w), 1517.0 (m), 1486.6 (s), 1432.4 (m), 1216.8 (w), 1016.2 (m) 980.3 (m); GC-MS (*m/z*) 275 (M$^+$, 7.7), 259 (8.6), 207 (16.3), 171 (21.3), 149 (29.7), 83 (66.3), 71 (100.0).

Preparation of 1-[[4-(*N*,*N*-Dimethylamino)-2,3,5,6-tetrafluorophenyl]ethynyl]-1-cyclopentanol (16c). Similarly, **16c** was prepared from 1.6 g (5 mmol) of 4-(*N*,*N*-dimethylamino)-1-iodotetrafluorobenzene, 0.8 g (7.2 mmol) of 1-ethynyl-1-cyclopentanol, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.1 g (70%) of **16c**: mp 65–67 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −152.8 (m, 2F), −139.8 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 1.8–1.9 (m, 4H), 2.1 (m, 2H), 2.2 (s, 1H), 3.0 (t, $^5J_{H-F}$ = 2.3 Hz, 6H); ^{13}C NMR ($CDCl_3$, TMS) 147.7 (dm, J_{C-F} = 250.0 Hz), 141.5 (dm, J_{C-F} = 243.3 Hz), 131.9 (tt, $^2J_{C-F}$ = 10.9, $^3J_{C-F}$ = 3.8 Hz), 103.8 (m), 95.2 (t, $^2J_{C-F}$ = 18.3 Hz), 75.1 (s), 68.8 (t, $^3J_{C-F}$ = 3.4 Hz), 43.2 (t, $^4J_{C-F}$ = 4.2 Hz), 42.5 (s), 23.7 (s); FTIR (CCl_4, cm^{-1}) 3607.5 (w), 2954.4 (w), 2876.8 (w), 2813.2 (w), 1642.5 (w), 1515.6 (m), 1486.8 (s), 1432.6 (m), 1212.0 (w), 1063.9 (w), 980.5 (m); GC-MS (*m/z*) 301 (M$^+$, 5.6), 256 (48.8), 192 (31.1), 160 (54.76), 128 (79.2), 96 (29.0), 84 (11.0), 64 (100.0).

Preparation of 1-[[4-(*N*,*N*-Dimethylamino)-2,3,5,6-tetrafluorophenyl]ethynyl]-1-cyclohexylamine (16d). Similarly, **16d** was prepared from 1.6 g (5 mmol) of 4-(*N*,*N*-dimethylamino)-1-iodotetrafluorobenzene, 0.9 g (7.3 mmol) of 1-ethynylcyclohexylamine, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.4 g (91%) of **16d**: mp 47–48 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$)

−152.9 (m, 2F), −140.0 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 1.2–1.4 (m, 8H), 1.9 (m, 4H), 3.0 (t, $^5J_{H-F}$ = 2.1 Hz, 6H); ^{13}C NMR ($CDCl_3$, TMS) 147.7 (dm, J_{C-F} = 249.8 Hz), 141.7 (dm, J_{C-F} = 244.5 Hz), 131.5 (tt, $^2J_{C-F}$ = 10.6, $^3J_{C-F}$ = 4.5 Hz), 106.7 (t, $^4J_{C-F}$ = 3.8 Hz), 95.8 (t, $^2J_{C-F}$ = 17.8 Hz), 68.6 (t, $^3J_{C-F}$ = 4.5 Hz), 43.2 (t, $^4J_{C-F}$ = 4.5 Hz), 50.7 (s), 40.4 (s), 25.4 (s), 23.5 (s); FTIR (CCl_4, cm^{-1}) 2936.6 (m), 2855.1 (w), 2812.7 (w), 2225.5 (w, C≡C), 1643.1 (w), 1516.5 (m), 1487.2 (s), 1432.6 (m), 1258.9 (w), 1219.6 (w), 979.5 (s); GC-MS (*m/z*) 314 (M$^+$, 18.8), 271 (100.0), 216 ((13.3), 149 (9.4), 97 (13.4), 83 (16.7), 69 (23.7).

Preparation of 4-[4-(*N,N*-Dimethylamino)-2,3,5,6-tetrafluorophenyl]-2-amino-2-methyl-3-butyne (16e). Similarly, **16e** was prepared from 1.6 g (5 mmol) of 4-(*N,N*-dimethylamino)-1-iodotetrafluorobenzene, 0.6 g (7.2 mmol) of 1,1-dimethylpropargylamine, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.1 g (84%) of **16e**: mp 44–45 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −152.9 (m, 2F), −140.2 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 1.5 (s, 6H), 1.8 (s, 2H), 3.0 (t, $^5J_{H-F}$ = 2.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, TMS) 147.6 (dm, J_{C-F} = 249.0 Hz), 141.6 (dm, J_{C-F} = 244.2 Hz), 131.5 (tt, $^2J_{C-F}$ = 10.9, $^3J_{C-F}$ = 4.6 Hz), 107.9 (t, $^4J_{C-F}$ = 3.6 Hz), 95.6 (t, $^2J_{C-F}$ = 18.1 Hz), 65.8 (t, $^3J_{C-F}$ = 4.1 Hz), 43.2 (t, $^4J_{C-F}$ = 4.4 Hz), 46.1 (s), 31.5 (s); FTIR (CCl_4, cm^{-1}) 2960.6 (w), 2899.0 (w), 2813.6 (w), 2166.8 (w, C≡C), 2068.9 (w), 1643.9 (w), 1513.1 (m), 1485.8 (s), 1431.3 (m), 1251.7 (w), 979.8 (m), 842.7 (s); GC-MS (*m/z*) 275 (M$^+$ + 1, 39.6), 244 (49.4), 229 (74.7), 224 (50.2), 182 (29.4), 170 (41.2), 157 (100.0), 145 (45.7), 133 (42.0), 118 (21.1).

Preparation of 3-(4-Morpholino-2,3,5,6-tetrafluorophenyl)-2-propyn-1-ol (17a). Similarly, **17a** was prepared from 1.8 g (5 mmol) of 4-morpholino-1-iodotetrafluorobenzene, 0.4 g (7.1 mmol) of propargyl alcohol, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.3 g (93%) of **17a**: mp 125–127 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −152.1 (m, 2F), −138.9 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 2.3 (t, $^3J_{H-H}$ = 6.3 Hz, 1H), 3.3 (m, 4H), 3.8 (m, 4H), 4.5 (d, $^3J_{H-H}$ = 6.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, TMS) 147.8 (dm, J_{C-F} = 251.2 Hz), 141.8 (dm, J_{C-F} = 244.3 Hz), 130.8 (tt, $^2J_{C-F}$ = 10.9, $^3J_{C-F}$ = 4.8 Hz), 98.4 (m), 96.4 (t, $^2J_{C-F}$ = 15.7 Hz), 71.1 (t, $^3J_{C-F}$ = 4.1 Hz), 67.3 (s), 51.5 (s), 51.2 (t, $^4J_{C-F}$ = 3.7 Hz); FTIR (CCl_4, cm^{-1}) 3619.1 (w), 2966.5 (w), 2938.1 (w), 2917.5 (w), 2910.8 (w), 2859.2 (w), 1645.0 (w), 1489.1 (s), 1458.0 (w), 1449.7 (w), 1375.2 (w), 1261.1 (w), 1120.1 (m), 1086.4 (m), 1027.8 (m), 1003.2 (m), 985.3 (s); GC-MS (*m/z*) 289 (M$^+$, 89.9), 272 (5.7), 259 (4.1), 231 (33.9), 203 (81.0), 185 (17.2), 174 (15.0), 155 (12.6), 123 (17.5), 105 (21.8), 97 (22.5), 83 (31.0), 71 (50.9), 57 (100.0); HRMS calcd for $C_{13}H_{11}F_4O_2N$ 289.0726, obsd 289.0723.

Preparation of 4-(4-Morpholino-2,3,5,6-tetrafluorophenyl)-2-amino-2-methyl-3-butyne (17b). Similarly, **17b** was prepared from 1.8 g (5 mmol) of 4-morpholino-1-iodotetrafluorobenzene, 0.6 g (7.2 mmol) of 1,1-dimethylpropargylamine, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.4 g (87%) of **17b**: mp 94–96 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −152.3 (m, 2F), −139.6 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 1.5 (s, 6H), 1.8 (s, 2H), 3.3 (m, 4H), 3.8 (m, 4H); ^{13}C NMR ($CDCl_3$, TMS) 147.5 (dm, J_{C-F} = 251.4 Hz), 141.9 (dm, J_{C-F} = 244.1 Hz), 130.0 (tt, $^2J_{C-F}$ = 10.9, $^3J_{C-F}$ = 4.5 Hz), 108.5 (t, $^4J_{C-F}$ = 3.5 Hz), 97.4 (t, $^2J_{C-F}$ = 18.2 Hz), 65.6 (t, $^3J_{C-F}$ = 3.8 Hz), 51.3 (t, $^4J_{C-F}$ = 3.6 Hz), 67.3 (s), 46.1 (s), 31.4 (s); FTIR (CCl_4, cm^{-1}) 2973.7 (m), 2911.7 (w), 2894.4 (w), 2858.8 (m), 2229.0 (w, C≡C), 1644.8 (w), 1487.4 (s), 1449.5 (m), 1375.5 (m), 1257.5 (m), 1161.9 (s), 1120.1 (s), 1000.6 (s), 986.2 (s); GC-MS (*m/z*) 316 (M$^+$, 7.1), 301 (56.6), 259 (4.5), 243 (7.0), 238 (8.0), 201 (10.8), 171 (9.5), 149 (9.7), 121 (27.8), 111 (18.0), 97 (26.7), 83 (37.4), 71 (55.3), 57 (100.0); HRMS calcd for $C_{15}H_{16}F_4ON_2$ 316.1199, obsd 316.1216.

Preparation of 3-(4-Piperidino-2,3,5,6-tetrafluorophenyl)-2-propyn-1-ol (18a). Similarly, **18a** was prepared from 1.8 g (5 mmol) of 4-piperidino-1-iodotetrafluorobenzene, 0.4 g (7.1 mmol) of propargyl alcohol, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.2 g (85%) of **18a**: mp 40–42 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −152.2 (m, 2F), −139.6 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 1.6 (m, 6H), 2.5 (s, 1H), 3.2 (m, 4H), 4.5 (s, 2H); ^{13}C NMR ($CDCl_3$, TMS) 148.0 (dm, J_{C-F} = 246.9 Hz), 141.9 (dm, J_{C-F} = 237.5 Hz), 132.3 (tm, $^2J_{C-F}$ = 11.0 Hz), 97.7 (t, $^4J_{C-F}$ = 3.3 Hz), 94.9 (t, $^2J_{C-F}$ = 18.4 Hz), 71.4 (t, $^3J_{C-F}$ = 3.5 Hz), 52.3 (t, $^4J_{C-F}$ = 3.5 Hz), 51.6 (s), 26.5 (s), 24.1 (s); FTIR (CCl_4, cm^{-1}) 3618.7 (w), 3463.8 (br), 2939.2 (s), 2854.9 (m), 2237.9 (w, C≡C), 1643.6 (m), 1481.2 (s), 1381.9 (m), 1228.2 (w), 1080.6 (s), 994.3 (s); GC-MS (*m/z*) 287 (M$^+$, 91.6), 286 (100.0), 270 (8.5), 203 (24.7), 186 (11.8), 155 (8.3), 123 (7.8), 105 (6.9).

Preparation of 4-(4-Piperidino-2,3,5,6-tetrafluorophenyl)-2-amino-2-methyl-3-butyne (18b). Similarly, **18b** was prepared from 1.8 g (5 mmol) of 4-piperidino-1-iodotetrafluorobenzene, 0.6 g (7.2 mmol) of 1,1-dimethylpropargylamine, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.4 g (89%) of **18b**: mp 90–91 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −152.5 (m, 2F), −140.2 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 1.5 (s, 6H), 1.6–1.7 (m, 6H), 1.8 (s, 2H), 3.2 (m, 4H); ^{13}C NMR (acetone-d_6, TMS) 148.1 (dm, J_{C-F} = 247.8 Hz), 142.7 (dm, J_{C-F} = 243.0 Hz), 132.2 (tm, $^2J_{C-F}$ =11.1 Hz), 109.9 (t, $^4J_{C-F}$ = 2.9 Hz), 96.8 (t, $^2J_{C-F}$ =, 18.4 Hz), 65.5 (t, $^3J_{C-F}$ = 3.6 Hz), 52.9 (m), 46.6 (s), 31.9 (s), 27.2 (s), 24.7 (s); FTIR (CCl_4, cm^{-1}) 2975.9 (w), 2939.9 (m), 2853.6 (w), 2227.4 (w, C≡C), 1642.9 (w), 1487.0 (s), 1443.2 (m), 1381.9 (w), 1178.5 (m), 1119.7 (m), 981.6 (s); GC-MS (*m/z*) 314 (M$^+$, 3.4), 299 (15.9), 283 (4.3),171 (32.8), 157 (7.6), 129 (10.0), 112 (18.1), 97 (23.6), 83 (36.5), 71 (57.0).

Preparation of 4-(2,3,5,6-Tetrafluorophenyl)-2-methyl-3-butyn-2-ol (19). Similar, **19** was prepared from 1.4 g (5 mmol) of 4-hydrido-1-iodotetrafluorobenzene, 0.4 g (7.1 mmol) of 2-methyl-3-butyn-2-ol, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 0.8 g (69%) of **19**: mp 65–66 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −139.6 (m, 2F), −137.4 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 1.7 (s, 6H), 3.1 (s, 1H), 7.0 (m, 1H); ^{13}C NMR ($CDCl_3$, TMS) 146.9 (dm, J_{C-F} = 252.4 Hz), 145.9 (dm, J_{C-F} = 247.7 Hz), 107.1 (t, $^4J_{C-F}$ = 3.9 Hz), 106.3 (t, $^2J_{C-F}$ = 22.8 Hz), 105.0 (tm, $^2J_{C-F}$ = 4.5 Hz), 67.6 (t, $^3J_{C-F}$ = 4.3 Hz), 66.0 (s), 31.1 (s); FTIR (CCl_4, cm^{-1}) 3607.7 (m), 3478.2 (br), 3079.6 (w), 2987.4 (m), 2934.7 (w), 2236.6 (w, C≡C), 1642.9 (w), 1604.8 (m), 1502.4 (s), 1325.6 (m), 1213.6 (m), 1177.5 (s), 1055.0 (m), 940.5 (s); GC-MS (*m/z*) 232 (M$^+$, 4.2), 217 (82.0), 201 (9.4), 187 (5.9), 174 (100.0), 149 (3.2), 129 (3.9), 124 (27.2), 105 (19.6).

Preparation of 1,7-Bis(4-methoxy-2,3,5,6-tetrafluorophenyl)-1,6-heptadiyne (20a). Similarly, **20a** was prepared from 3.7 g (12 mmol) of 4-methoxy-1-iodotetrafluorobenzene, 0.5 g (5.0 mmol) of 1,6-heptadiyne, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.8 g (80%) of **20a**: mp 59–61 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −159.0 (m, 2F), −139.4 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 2.0 (quintet, $^3J_{H-H}$ = 7.0 Hz, 2H), 2.7 (t, $^3J_{H-H}$ = 7.0 Hz, 4H), 4.1 (t, $^5J_{H-F}$ = 1.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, TMS) 147.9 (dm, J_{C-F} = 253.9 Hz), 141.1 (dm, J_{C-F} = 246.7 Hz), 138.7 (tt, $^2J_{C-F}$ = 12.2, $^3J_{C-F}$ = 3.7 Hz), 101.1 (t, $^4J_{C-F}$ = 3.7 Hz), 98.4 (t, $^2J_{C-F}$ = 17.8 Hz), 66.5 (t, $^3J_{C-F}$ = 3.8 Hz), 62.3 (t, $^4J_{C-F}$ = 3.7 Hz), 27.4 (s), 19.1 (s); FTIR (CCl_4, cm^{-1}) 2945.5 (w), 2837.9 (w), 2247.9 (w, C≡C), 1646.5 (w), 1492.9 (s), 1428.8 (m), 1203.0 (m), 1166.7 (w), 1075.4 (s), 993.1 (s); GC-MS (*m/z*) 448 (M$^+$, 60.7), 433 (17.4), 417 (8.6), 398 (11.1), 385 (15.8), 367 (13.1), 355 (9.4), 323 (11.8), 269 (10.1), 244 (20.1), 229 (39.2), 217 (100.0), 202 (91.1), 174 (64.5), 169 (56.3), 161 (39.5), 123 (30.1), 105 (35.4), 81 (23.7).

Preparation of 1,8-Bis(4-methoxy-2,3,5,6-tetrafluorophenyl)-1,7-octadiyne (20b). Similarly, **20b** was prepared from 3.7 g (12 mmol) of 4-methoxy-1-iodotetrafluorobenzene, 0.5 g (5.0 mmol) of 1,7-octadiyne, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.7 g (75%) of **20b**: mp 98–99 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −159.0 (m, 2F), −139.4 (m, 2F); ^{1}H NMR ($CDCl_3$, TMS) 1.8 (m, 4H), 2.6 (m, 4H), 4.1 (t, $^5J_{H-F}$ = 1.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, TMS) 147.8 (dm, J_{C-F} = 251.1 Hz), 141.0 (dm, J_{C-F} = 246.5 Hz), 138.5 (tt, $^2J_{C-F}$ = 12.1, $^3J_{C-F}$ = 3.4 Hz), 101.9 (t, $^4J_{C-F}$ = 3.6 Hz), 98.6 (t, $^2J_{C-F}$ = 18.4 Hz), 66.1 (t, $^3J_{C-F}$ = 4.0 Hz), 62.3 (t, $^4J_{C-F}$ = 3.6 Hz), 27.4 (s), 19.4 (s); FTIR (CCl_4, cm^{-1}) 3013.2 (w), 2947.7 (w), 2866.8 (w), 2837.9 (w), 2248.4 (w, C≡C), 1646.4 (w), 1494.1 (s), 1429.0 (m), 1202.9 (w), 1076.3 (m), 991.3 (m); GC-MS (*m/z*) 462 (M$^+$, 29.7), 447 (21.5), 434 (33.2), 421 (36.3), 403 (13.7), 283 (9.6), 269 (17.4), 230 (16.5), 217 (100.0), 202 (89.1), 193 (78.5), 174 (56.6), 169 (41.8), 151 (30.1) 123 (18.6), 99 (15.1), 85 (26.6), 71 (39.1).

Preparation of 1,10-Bis(4-methoxy-2,3,5,6-tetrafluorophenyl)-1,9-decadiyne (20c). Similarly, **20c** was prepared from 3.7 g (12 mmol) of 4-methoxy-1-iodotetrafluorobenzene, 0.7 g (5.0 mmol) of 1,9-decadiyne, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03

g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 2.0 g (82%) of **20c**: mp 78–79 °C; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −159.1 (m, 2F), −139.6 (m, 2F); ^1H NMR ($CDCl_3$, TMS) 1.6 (m, 4H), 1.7 (m, 4H), 2.5 (t, $^3J_{H-H}$ = 6.7 Hz, 4H), 4.1 (s, 6H); ^{13}C NMR ($CDCl_3$, TMS) 147.9 (dm, J_{C-F} = 252.7 Hz), 141.1 (dm, J_{C-F} = 246.6 Hz), 138.6 (tt, $^2J_{C-F}$ = 12.2, $^3J_{C-F}$ = 3.6 Hz), 102.7 (t, $^4J_{C-F}$ = 3.7 Hz), 98.8 (t, $^2J_{C-F}$ = 18.5 Hz), 65.7 (t, $^3J_{C-F}$ = 3.8 Hz), 62.3 (t, $^4J_{C-F}$ = 3.7 Hz), 28.5 (s), 28.4 (s), 19.9 (s); FTIR (CCl_4, cm^{-1}) 2942.1 (m), 2862.2 (w), 2247.2 (w, C≡C), 1646.4 (w), 1492.8 (s), 1428.8 (m), 1202.8 (w), 1166.0 (w), 1077.8 (m), 991.3 (s); GC-MS (*m/z*) 462 (28.3), 449 (25.7), 407 (19.7), 382 (26.3), 297 (17.3), 283 (26.5), 269 (52.5), 245 (29.0), 230 (73.7), 217 (100.0), 193 (89.8), 169 (61.3), 151 (35.9), 105 (40.9), 91 (24.6), 81 (35.4), 71 (42.3).

Preparation of 1,4-Bis(hexynyl)tetrafluorobenzene (21a). Similarly, **21a** was prepared from 1.5 g (5 mmol) of 1,4-dibromotetrafluorobenzene, 1.1 g (13.5 mmol) of 1-hexyne, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.1 g (74%) of **21a**: ^{19}F NMR ($CFCl_3$, $CDCl_3$) −139.2 (s); ^1H NMR ($CDCl_3$, TMS) 0.9 (t, J = 6.4 Hz, 6H), 1.6 (m, 8H), 2.5 (t, J = 6.4 Hz, 4H); FTIR (CCl_4, cm^{-1}) 2961 (m), 2935 (m), 2875 (w), 2232 (w, C≡C), 1483 (s), 1315 (w), 981 (m); GC-MS (*m/z*) 310 (M^+, 29.1), 295 (46.6), 267 (12.8), 239 (16.7), 224 (20.7), 219 (14.2), 211 (30.7), 201 (11.3), 187 (18.2), 80 (10.4), 67 (15.2), 43 (68.1), 41 (100.0).

Preparation of 1,4-Bis(heptynyl)tetrafluorobenzene (21b). Similarly, **21b** was prepared from 1.53 g (5 mmol) of 1,4-dibromotetrafluorobenzene, 1.2 g (12.5 mmol) of 1-heptyne, 0.18 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.03 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 1.3 g (80%) of **21b**: ^{19}F NMR ($CFCl_3$, $CDCl_3$) −139.1 (s); ^1H NMR ($CDCl_3$, TMS) 0.9 (t, J = 5.9 Hz, 6H), 1.5 (m, 12H), 2.5 (t, J = 6.6 Hz, 4H); FTIR (CCl_4, cm^{-1}) 2959 (m), 2933 (m), 2862(w), 2231 (w, C≡C), 1480 (s), 1316 (w), 981 (m); GC-MS (*m/z*) 338 (M^+, 6.4), 309 (14.8), 283 (7.0), 281 (2.8), 267 (2.1), 253 (2.3), 239 (5.5), 224 (9.1), 211 (11.9), 187 (6.0), 175 (1.9), 81 (23.5), 55 (33.3), 41 (100.0).

Preparation of Ethyl (4-Bromotetrafluorophenyl) ketone (1g). A dry 100-mL, two-necked round-bottomed flask equipped with septum, a Teflon-coated stir-bar, and a nitrogen inlet was charged with 3.1 g (10 mmol) of 1,4-dibromo-2,3,5,6-tetrafluorobenzene, 1.7 g (15 mmol) of acid-washed cadmium, and 50 mL of dry DMF. The solution was stirred under a nitrogen atmosphere at room temperature overnight. After complete consumption of the starting material (determined by ^{19}F NMR analysis of the reaction mixture), the reaction mixture was filtered through a medium-fritted Schlenk-funnel under N_2 pressure into a 100-mL flask which contained 2.0 g (14 mmol) of CuBr and a Teflon-coated stir bar under a nitrogen atmosphere. The reaction mixture was stirred for 5 min after which 1.4 g (15 mmol) of propionyl chloride was added dropwise into the reaction mixture *via* syringe. After the addition was completed, the reaction mixture was stirred for 30 min triturated with 100 mL Et_2O, and washed with (4 × 100 mL) water. The ether layer was concentrated by rotary evaporation, purified by chromatography column packed with silica gel, and eluted with hexane/CH_2Cl_2 (9.5/0.5) to yield 2.3 g (80%) of **1g**: GLPC purity 100.0%; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −131.8 (m, 2F), −141.2 (m, 2F); ^1H NMR ($CDCl_3$, TMS) 2.9 (q, $^3J_{H-H}$ = 7.2 Hz, 2H), 1.2 (t, $^3J_{H-H}$ = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, TMS) 194.7 (s), 144.9 (dm, J_{C-F} = 247.8 Hz), 143.5 (dm, J_{C-F} = 254.4 Hz), 119.3 (t, $^2J_{C-F}$ = 19.1 Hz), 102.4 (t, $^2J_{C-F}$ = 22.2 Hz), 38.2 (s), 7.2 (s); GC-MS (*m/z*) 286 (M^+, 25.1), 284 (22.4), 257 (100.0), 255 (100.0), 229 (74.5), 227 (72.5), 179 (11.7), 177 (11.9), 176 (44.7), 149 (14.2), 148 (100.0), 129 (24.6), 117 (36.5), 99 (18.9), 98 (85.1), 79 (49.4), 74 (14.5), 57 (82.3).

Preparation of Ethyl 1-Hexynyl-2,3,5,6-tetrafluorophenyl Ketone (22a). Similarly, **22a** was prepared from 0.6 g (2 mmol) of ethyl 4-bromotetrafluorophenyl ketone, 0.33 g (4 mmol) of 1-hexyne, 0.07 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.01 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 0.4 g (75%) of **22a**: GLPC purity 95.0%; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −136.9 (m, 2F), −143.5 (m, 2F); ^1H NMR ($CDCl_3$, TMS) 2.9 (q, $^3J_{H-H}$ = 7.2 Hz, 2H), 2.5 (t, $^3J_{H-H}$ = 6.9 Hz, 2H), 1.6 (m, 2H), 1.5 (m, 2H), 1.2 (t, $^3J_{H-H}$ = 7.2 Hz, 3H), 0.9 (t, $^3J_{H-H}$ = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, TMS) 195.4 (s), 147.5 (dm, J_{C-F} = 256.2 Hz), 143.8 (dm, J_{C-F} = 251.4 Hz), 119.3 (t, $^2J_{C-F}$ = 18.5 Hz), 107.7 (tm, $^2J_{C-F}$ = 18.3 Hz), 106.7 (t, $^4J_{C-F}$ = 3.5 Hz), 65.8 (t, $^3J_{C-F}$ = 3.0 Hz), 38.6 (s), 30.6 (s), 22.3 (s), 19.8 (s), 13.7 (s), 7.7 (s); FTIR (CCl_4, cm^{-1}) 2938.7 (w), 2238.9 (w, C≡C), 1720.3 (m, C=O), 1646.6 (w), 1477.1 (s), 1308.3 (w), 1169.7 (w), 976.1 (m); GC-MS (*m/z*) 286 (M^+, 6.2), 271 (10.2), 257 (100.0), 243 (2.5), 229 (2.6), 215 (10.1), 214 (13.0), 201 (36.0), 186 (22.3), 177 (12.2), 167 (8.6), 151 (4.9), 136 (4.1), 123 (5.1), 99 (5.1), 86 (1.7), 75 (3.7), 67 (7.3), 57 (37.0).

Preparation of Ethyl 4-(Phenylethynyl)-2,3,5,6-tetrafluoropheny Ketone (22b). Similarly, **22b** was prepared from 0.6 g (2 mmol) of ethyl 4-bromotetrafluorophenyl ketone, 0.4 g (4 mmol) of phenylacetylene, 0.07 g (5.0 mol %) of $PdCl_2(PPh_3)_2$, 0.01 g (3.0 mol %) of CuI, and 20 mL of $(^iPr)_2NH$. Usual workup gave 0.5 g (81%) of **22b**: GLPC purity 95.0%; ^{19}F NMR ($CFCl_3$, $CDCl_3$) −135.9 (m, 2F), −143.0 (m, 2F); ^1H NMR ($CDCl_3$, TMS) 7.6 (m, 2H), 7.4 (m, 3H), 2.9 (q, $^3J_{H-H}$ = 7.2 Hz, 2H), 1.2 (t, $^3J_{H-H}$ = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, TMS) 195.1 (s), 146.6 (dm, J_{C-F} = 254.5 Hz), 143.4 (dm, J_{C-F} = 251.8 Hz), 131.9 (s), 129.8 (s), 128.5 (s), 121.3 (s), 119.4 (t, $^2J_{C-F}$ = 18.7 Hz), 106.8 (tm, $^2J_{C-F}$ = 17.9 Hz), 103.5 (t, $^4J_{C-F}$ = 3.5 Hz), 73.8 (t, $^3J_{C-F}$ = 4.1 Hz), 38.3 (s), 7.4 (s); FTIR (CCl_4, cm^{-1}) 2983.9 (w), 2942.8 (w), 2224.3 (w, C≡C), 1719.4 (m, C=O), 1645.4 (w), 1482.2 (s), 1348.9 (w), 1322.4 (w), 1125.9 (w); GC-MS (*m/z*) 306 (M^+, 31.7), 277 (100.0), 249 (18.7), 230 (9.0), 204 (3.0), 199 (12.9), 179 (2.8), 149 (2.1), 139 (5.7).

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Supplementary Material Available: Copies of ^{13}C NMR spectra for compounds (47 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information.