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A Facile Synthetic Route to New Fluorinated Building-Blocks of 1-Fluoroalkynes and 1-Fluorodiynes†

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A facile and direct fluorination process of alkynes and diynes was developed. In the presence of *n*-butyllithium, the reaction of a series of terminal alkynes and diynes with the electrophilic fluorinating reagent (NFSI) proceeded to afford various 1-fluoroalkynes and 1-fluoro-1,3-diynes in moderate to high yields.

Keywords electrophilic fluorination, terminal alkyne, terminal 1,3-diyne, 1-fluoroacetylene

Introduction

The application of organofluorine compounds has received extensive attention in the area of pharmaceutical industry, agrochemical and material science due to their unique chemical, physical and biological properties.[1] Construction of new fluorinated building-blocks applicable to the synthesis of organofluorine compounds is of considerable importance and still in great demand.[2] Fluorinated alkynes are potentially intriguing building blocks due to the unique behavior of acetylene, especially in transition metal-catalyzed processes.[3] Among all the useful methods for synthesis of 1-fluoroacetylenes,[4] curiously, the direct fluorination process remains underdeveloped. While there are many effective reaction systems for the efficient synthesis of 1-haloacetylenes,[5] no known protocols exist for which the analogous transformation can be performed with alkynes.

Since the emergence of electrophilic fluorinating agents, there are an increasing number of reports on their applications in the construction of various fluorinated molecules, including fluoroalkanes, fluoroalkenes, fluoroarenes, α-fluorocarbonyl compounds and analogues.[6] However, electrophilic fluorination transformation of alkynes has been ignored. Development of new organic transformations for the construction of fluorinated building-blocks has been our interest and research objective.[7] As part of our ongoing studies, herein we present a facile and direct fluorination reaction of alkynes with electrophilic fluorinating reagents in the presence of *n*-butyllithium. This rapid approach would provide a wide range of fluorinated alkynes and dikynes.

Results and Discussion

We envisioned that acidic alkynes could be transformed into the corresponding acetylide anion in the treatment with suitable base, subsequently tripped by electrophilic fluorinating reagents to furnish the fluoroalkynes. To test this hypothesis, we conducted a fluorination reaction of phenylacetylene **1a** in the presence of sodium hydroxide and *N*-fluorobenzenesulfonimide (NFSI) as electrophilic fluorinating reagent in tetrahydrofuran (THF) at room temperature (Table 1, Entry 1). The ^{19}F NMR analysis of the crude reaction mixture revealed that only a trace amount of fluorinated product **2a** was detected. The use of sodium hydride and diethylzinc gave the similar results (Entries 2 and 3). When *n*-butyllithium was used as base, the fluorinated product **2a** was obtained in 21% yield (Entry 4). Further examination on the temperature in the same test reaction revealed that the yield can be significantly improved from 38% (Entry 5) to 63% (Entry 6). Other electrophilic fluorinating reagents such as Selectfluor and *N*-fluoropyridinium triflate (NFPY-OTf) displayed lower reactivity in this transformation reaction (Entries 7 and 8). A substantial change of the solvent to toluene and ether led to a marginal lower yield (Entries 9 and 10). It was noteworthy that the fluorinated product **2a** is stable at room temperature for three months, and no change was detected by the ^{19}F NMR spectrum.

To determine the scope of this protocol, a series of aromatic-substituted acetylenes were employed as substrates under the optimized reaction conditions. Not only electron-donating but also electron-withdrawing substituents on the aromatic ring of acetylenes were

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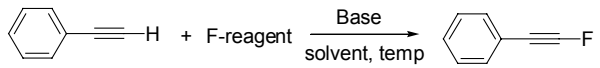
† Dedicated to Professor Weiyuan Huang on the occasion of his 90th birthday.

Table 1 Screening of base and fluorinating reagents in the synthesis of fluorinated phenylacetylene



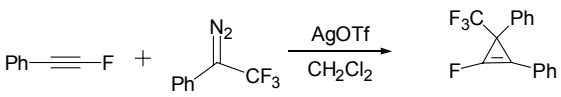
1a **2a**

Entry[a]	Base	Fluorinating reagent	Temp./℃	Yield[b]/%
1	NaOH	NFSI	25	—
2	NaH	NFSI	25	—
3	Et_2Zn	NFSI	25	—
4	*n*-BuLi	NFSI	25	21
5	*n*-BuLi	NFSI	−40 to 25	38
6	*n*-BuLi	NFSI	−78 to 25	63
7	*n*-BuLi	Selectfluor	−78 to 25	10
8	*n*-BuLi	NFPY-OTf	−78 to 25	8
9[c]	*n*-BuLi	NFSI	−78 to 25	52
10[d]	*n*-BuLi	NFSI	−78 to 25	60

[a] The reaction employed a molar ratio of **1a**∶base∶fluorinating reagent = 1∶1.1∶1.2 (equiv.). [b] Yield of isolated product. [c] Toluene was used. [d] Ether was used.

tolerated to this reaction, giving the fluorinated products in 48%—80% yield (Table 2). It appears that the positions of the substituents on the aromatic ring of alkynes have a very limited effect on the reactivity. For example, 2-, 3- and 4-methoxyl-substituted 1-aromaticacetylenes gave the corresponding products in the yields of 57%, 48% and 58%, respectively (Table 2, Entries 3—5). Additionally, 1-ethynylnaphthalene is also a viable substrate, affording the desired product in 80% yield. Interestingly, when 1-fluorophenylacetylene was treated with (1-diazo-2,2,2-trifluoroethyl)benzene, the novel fluorinated cyclopropene **3** was obtained in 95% yield (Scheme 1).[8]

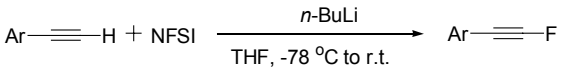
Scheme 1 Synthetic transformation of 1-fluoroacetylene



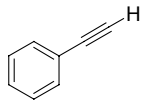
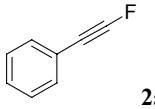
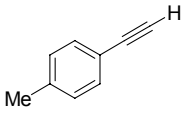
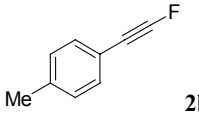
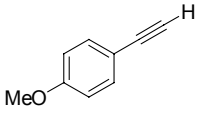
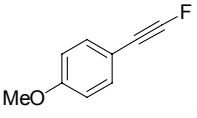
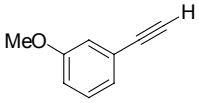
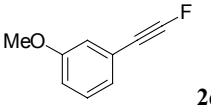
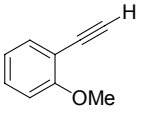
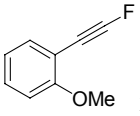
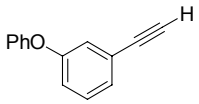
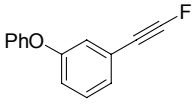
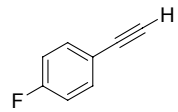
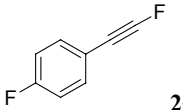
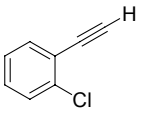
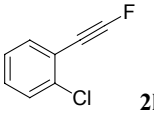
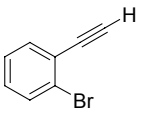
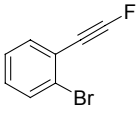
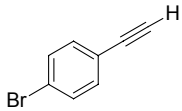
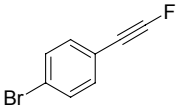
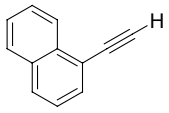
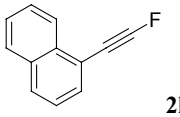
2a **3**, 95% yield

In spite of the structural similarities between an alkyne and 1,3-diyne, the unique juxtaposition of two acetylene units in a 1,3-diyne could beget unusual properties, both from a chemical as well as biological point of view.[3c,9] However, such substrates are unexplored in the electrophilic fluorination reactions. In order to extend our novel protocol to the synthesis of fluorinated diynes, a series of terminal 1,3-diynes **4** were tested (Table 3). The reaction of terminal 1,3-diynes **4** with NFSI proceeded smoothly in presence of *n*-BuLi to afford the 1-fluoro-1,3-diynes **5** in good to high yields (63%—90%) (Entries 1—8). Notably, when a cyclohexenyl-substituted diyne was employed, the fluorinated product **5i** was also obtained in 85% yield (Entry 9).

Table 2 Synthesis of 1-fluoroalkynes[a]



1 **2**

Entry	Alkyne **1**	Product **2**	Yield[b]/%
1		 **2a**	63
2		 **2b**	48
3		 **2c**	58
4		 **2d**	48
5		 **2e**	57
6		 **2f**	65
7		 **2g**	73
8		 **2h**	76
9		 **2i**	68
10		 **2j**	53
11		 **2k**	80

[a] The reaction employed a molar ratio of **1**∶base∶fluorinating reagent = 1∶1.1∶1.2 (equiv.). [b] Yield of isolated product.

Conclusions

In conclusion, we have developed a convenient and rapid procedure for the synthesis of fluorinated alkynes by using NFSI as electrophilic fluorinating reagent. This protocol is compatible with a large variety of

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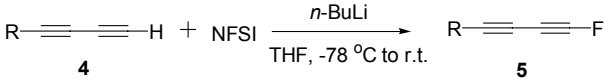
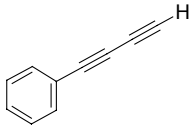
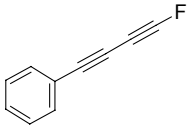
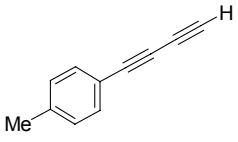
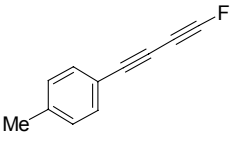
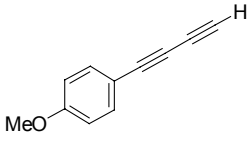
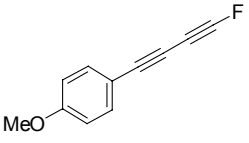
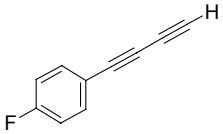
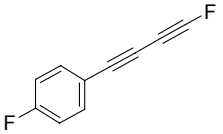
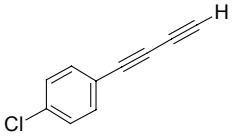
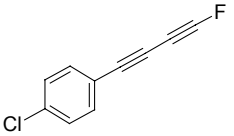
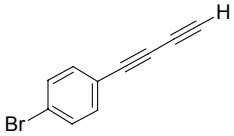
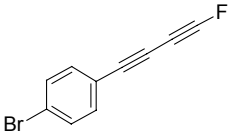
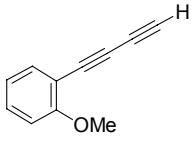
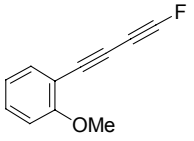
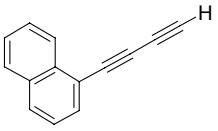
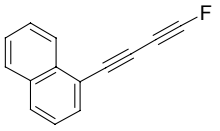
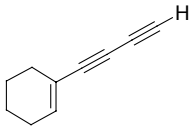
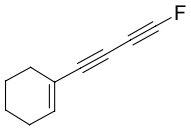
Table 3 Synthesis of 1-fluoro-1,3-diynes[a]



4 **5**

Entry[a]	Alkyne **1**	Product **2**	Yield[b]/%
1	 **4a**	 **5a**	65
2	 **4b**	 **5b**	63
3	 **4c**	 **5c**	88
4	 **4d**	 **5d**	78
5	 **4e**	 **5e**	57
6	 **4f**	 **5f**	73
7	 **4g**	 **5g**	82
8	 **4h**	 **5h**	90
9	 **4i**	 **5i**	85

[a] The reaction employed a molar ratio of **4**: base: fluorinating reagent＝1∶1.1∶1.2 (equiv.). [b] Yield of isolated product.

terminal alkynes, furnishing the fluorinated alkynes in 48%—80% yields. In the following transformation of fluorinated alkyne synthesized, a highly functionalized fluorocyclopropene has been successfully prepared in excellent yield (95%). Furthermore, by extending this protocol to terminal 1,3-diynes, the direct fluorination reactions proceeded well to afford the novel fluorinated diynes in good to high yields. Further synthetic applica-

tion of these fluorinated alkynes and diynes are ongoing in our laboratory and will be reported in due course.

Experimental

Tetrahydrofuran (THF), toluene, and ether were distilled from sodium/benzophenone prior to use. All purchased reagents were used without further purification. Analytical thin layer chromatography was performed on 0.20 mm Qingdao Haiyang silica gel plates. Silica gel (200—300 mesh) (from Qingdao Haiyang Chem. Company, Ltd.) was used for flash chromatography. *n*-Butyllithium (2.4 mol/L solution in toluene) was purchased from ACROS Organics. Standard reagents and solvents were purified according to known procedures.

^{1}H, ^{13}C and ^{19}F NMR were recorded on Bruker AV 400 MHz at 400 MHz (^{1}H), 100 MHz (^{13}C), as well as 376 MHz (^{19}F). Chemical shifts were reported relative to the solvent resonance as the internal standard ($CDCl_3$ and $CFCl_3$). MS spectra were recorded on a VG-7070E or HP 5988A spectrometer using the ESI method.

General procedure for the synthesis of 1-fluoroacetylene 2

A solution of phenylacetylene (0.20 mmol, 20.4 mg) in THF (5.0 mL) was added dropwise with *n*-BuLi (2.40 mol/L, 92 μL, 0.22 mmol, 1.1 equiv.) over 5 min at −78 ℃ under Ar atmosphere. The resulting suspension was stirred at this temperature for 30 min, and a solution of NFSI (98%, 0.24 mmol, 77.1 mg, 1.2 equiv.) in THF (3.0 mL) was added. After stirring at this temperature for 1 h, the cooling bath was removed and the reaction was allowed to slowly warm to room temperature and stirred for 18 h. The reaction was quenched with saturated ammonium chloride solution and the organic layers were separated. The aqueous layer was washed twice with diethyl ether and the combined organic layer was washed with brine, dried over $MgSO_4$, filtered, then concentrated *in vacuo*. The residue was purified on silica using hexane as solvent system to afford the fluorinated product **2a** (15.1 mg, 63% yield).

1-Fluoro-2-phenylacetylene (2a) White solid; m.p. 75—77 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (dd, J=7.8, 1.6 Hz, 2H), 7.43—7.33 (m, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −100.81 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 132.53, 129.24, 128.47, 121.84, 81.61, 73.99; IR (KBr) v: 2924, 2850, 2150, 1592, 1485, 1439, 1264, 1024, 915, 755, 686, 525 cm^{-1}; MS (70 eV) *m/z* (%): 79.0 (100), 101.1 ([M−F]$^+$, 62).

1-Fluoro-2-(4-methylphenyl)acetylene (2b) Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (d, J=8.1 Hz, 2H), 7.17 (d, J=7.9 Hz, 2H), 2.39 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −101.80 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.50, 132.41, 129.23, 118.81, 81.56, 73.47, 21.55; IR (KBr) v: 2921, 2853, 2348, 1729, 1432, 1297, 1189, 1081, 995, 813, 737, 688, 656, 528 cm^{-1}; MS (70 eV) *m/z* (%): 87 (100), 102.1 (82), 134.0 ([M]$^+$, 20).

1-Fluoro-2-(4-methoxyphenyl)acetylene (2c) Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (d, J=8.8 Hz, 2H), 6.87 (d, J=8.7 Hz, 2H), 3.84 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −134.34 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.04, 130.72, 129.27, 114.19, 81.25, 72.99, 55.32; IR (KBr) v: 2931, 2843, 2137, 1599, 1505, 1248, 1165, 1021, 915, 832, 687, 596, 531 cm^{-1}; MS (70 eV) *m/z* (%): 101.7 (100), 189.5 ([M+K]$^+$, 5).

1-Fluoro-2-(3-methoxyphenyl)acetylene (2d) Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, J=7.2 Hz, 2H), 7.54—7.65 (m, 2H), 4.06 (s, 3H); ^{19}F NMR (376 MHz, CDCl3) δ: −103.50 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 129.40, 124.65, 124.37, 117.03, 116.73, 115.31, 84.30, 83.58, 55.22; IR (film) v: 2921, 2853, 2348, 1729, 1432, 1297, 1189, 1081, 995, 813, 688, 656, 528 cm^{-1}; MS (70 eV) *m/z* (%): 101.7 (100), 189.5 ([M+K]$^+$, 10).

1-Fluoro-2-(2-methoxyphenyl)acetylene (2e) Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24—7.26 (m, 1H), 7.06 (d, J=1.2 Hz, 1H), 7.02 (d, J=1.2 Hz, 1H), 6.88—6.95 (m, 1H), 3.84 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −103.42 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.14, 130.32, 128.79, 120.44, 11.32, 110.72, 81.38, 80.24, 55.66; IR (film) v: 2919, 2855, 2196, 1726, 1589, 1489, 1462, 1245, 1162, 1025, 940, 786, 752, 591 cm^{-1}; MS (70 eV) *m/z* (%): 101.7 (100), 189.3 ([M+K]$^+$, 7).

1-Fluoro-2-(3-phenoxyphenyl)acetylene (2f) Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40—7.34 (m, 2H), 7.32—7.25 (m, 2H), 7.20—7.11 (m, 2H), 7.10—6.99 (m, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −103.48 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 129.91, 129.75, 126.98, 123.94, 123.75, 123.57, 122.01, 119.54, 119.42, 119.26, 83.05, 77.68; IR (film) v: 2919, 2850, 2196, 1585, 1392, 1265, 1154, 969, 797, 771, 637, 605, 564 cm^{-1}; MS (70 eV) *m/z* (%): 101.9 (15), 110.9 (100), 156.8 (52), 212.0 ([M]$^+$, 5).

1-Fluoro-2-(4-fluorophenyl)acetylene (2g) Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.15—7.09 (m, 2H), 7.02—6.98 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −101.17 (s), −108.46 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.59, 134.50, 116.03, 115.81, 80.43, 73.54; IR (film) v: 2924, 2853, 2195, 1679, 1593, 1488, 1220, 1091, 1016, 824, 755, 620, 513 cm^{-1}; MS (70 eV) *m/z* (%): 109.2 (16), 110.7 (100), 138.3 ([M]$^+$, 6).

1-Fluoro-2-(2-chlorophenyl)acetylene (2h) Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (d, J=7.6 Hz, 1H), 7.44 (d, J=8.0 Hz, 1H), 7.33 (t, J=7.1 Hz, 1H), 7.28—7.24 (t, J=7.2, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −107.42 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.99, 134.39, 130.29, 129.47, 126.57, 121.83, 79.42, 78.39; IR (film) v: 2926, 2856, 2197, 1696, 1489, 1377, 1093, 962, 836, 730, 520 cm^{-1}; MS (70 eV) *m/z* (%): 102.1 (73), 113.0 (100), 155.0 ([M+H]$^+$, 10).

1-Fluoro-2-(2-bromophenyl)acetylene (2i) Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50—7.40 (m, 2H), 7.38−7.28 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −120.10 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 129.02,

128.84, 128.55, 127.74, 126.03, 125.80, 82.00, 74.40; IR (film) *v*: 2926, 2856, 2196, 1600, 1493, 1377, 1248, 1086, 1031, 834, 755, 699, 516 cm^{-1}; MS (70 eV) *m/z* (%): 113.0 (16), 296.1 (2[M−H]$^-$, 100).

1-Fluoro-2-(4-bromophenyl)acetylene (2j) Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.37 (dd, J=7.5 Hz, 3.6 Hz, 2H), 7.06 (t, J=8.0 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −108.49 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 132.51, 128.46, 116.02, 115.80, 80.43, 73.74; IR (film) *v*: 2920, 2851, 1967, 1668, 1638, 1459, 1400, 1235, 969, 752, 524 cm^{-1}; MS (70 eV) *m/z* (%): 113.0 (20), 296.1 (2[M−H]$^-$, 100).

1-Fluoro-2-(1-naphthyl)acetylene (2k) Yellow solid; m.p. 175—177 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.46 (d, J=8.3 Hz, 1H), 7.94 (d, J=8.0 Hz, 1H), 7.86 (d, J=7.6 Hz, 1H), 7.81 (d, J=7.1 Hz, 1H), 7.68—7.51 (m, 2H), 7.50—7.46 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −103.37 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 133.61, 132.18, 131.32, 129.36, 128.39, 127.04, 126.57, 126.14, 125.17, 119.88, 81.17, 78.92; IR (KBr) *v*: 2919, 2850, 2197, 1585, 1456, 1392, 1154, 1012, 969, 797, 757, 637, 576 cm^{-1}; MS (70 eV) *m/z* (%): 112.7 (100), 156.8 (50), 170.2 ([M]$^+$, 8).

Procedure for Ag(I)-catalyzed cyclopropenation of 1-fluoro-2-phenyl alkyne with (1-diazo-2,2,2-trifluoroethyl)benzene

A mixture of 1-fluoro-2-phenylacetylene (0.4 mmol, 48.0 mg, 2.0 equiv.) and AgOTf catalyst (98%, 0.02 mmol, 1.0 mg, 0.1 equiv.) was weighed in a 25-mL one-necked round bottom flask covered with aluminum foil to exclude light. The mixture was dissolved in dichloromethane (2 mL) and stirred at room temperature under an atmosphere of argon. (1-Diazo-2,2,2-trifluoroethyl)benzene (0.2 mmol, 37.3 mg, 1.0 equiv.) in dichloromethane (8.0 mL) was then added to the former solution via syringe pump for 1 h. Then, the mixture was stirred for additional 1 h and concentrated *in vacuo*. The residue was purified on silica using hexane as solvent system to afford the desired product **3** as yellow oil (52.9 mg, 95% yield).

1,3-Diphenyl-2-fluoro-3-trifluoromethylcyclopropene (3) Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.79—7.73 (m, 1H), 7.66—7.55 (m, 2H), 7.54—7.45 (m, 3H), 7.44—7.41 (m, 1H), 7.41—7.30 (m, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −64.11 (s), −67.15 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 132.091, 130.56, 130.07, 129.56, 129.09, 128.65 (q, $^1J_{F\text{-}C}$=249 Hz), 128.51, 128.02, 127.67, 122.01, 103.34, 76.89 (q, $^2J_{F\text{-}C}$=32.5 Hz); IR (film) *v*: 2921, 2851, 2202, 1490, 1445, 1298, 1253, 1164, 1132, 1028, 924, 757, 689, 591, 525 cm^{-1}; MS (70 eV) *m/z* (%): 227.9 (100), 233.9 (80), 318.3 ([M+K+H]$^+$, 45).

General procedure for the synthesis of 1-fluoro-1,3-diynes 5

To a solution of 1, 3-diyne (0.20 mmol, 20.4 mg, 1.0 equiv.) in THF (5.0 mL) was added dropwise *n*-BuLi (2.40 mol/L, 92 μL, 0.22 mmol, 1.1 equiv.) over 5 min at −78 ℃ under Ar atmosphere. The resulting suspension was stirred at this temperature for 30 min, and a solution of NFSI (98%, 0.24 mmol, 77.1 mg, 1.2 equiv.) in THF (3.0 mL) was added. After stirring at this temperature for 1 h, the cooling bath was removed and the reaction was allowed to slowly warm to room temperature and stirred for 18 h. The reaction was quenched with saturated ammonium chloride solution and the layers were separated. The aqueous layer was washed twice with diethyl ether and the combined organic layer was washed with brine, dried over $MgSO_4$, filtered then concentrated *in vacuo*. The residue was purified on silica using hexane as solvent system to afford the fluorinated product **5a** (18.7 mg, 65% yield).

1-(4-Fluorobuta-1,3-diynyl)benzene (5a) White solid; m.p. 110—112 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.60—7.51 (m, 2H), 7.45—7.32 (m, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −62.75 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 133.31, 130.12, 128.65, 120.54, 77.96, 74.63, 67.42, 63.92; IR (KBr) *v*: 2917, 2849, 2199, 1600, 1486, 1442, 1280, 1177, 998, 906, 747, 678, 523 cm^{-1}; MS (70 eV) *m/z* (%): 84.6 (46), 101.8 (100), 144.0 ([M]$^+$, 9).

1-(4-Fluorobuta-1,3-diynyl)-4-methylbenzene (5b) White solid; m.p. 143—145 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.45 (d, J=8.0 Hz, 2H), 7.16 (d, J=7.9 Hz, 2H), 2.39 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −128.79 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.59, 133.15, 129.36, 117.43, 78.02, 73.99, 67.06, 63.75, 21.71; IR (KBr) *v*: 2919, 2851, 2195, 1679, 1599, 1359, 1182, 937, 883, 755, 689, 590, 522 cm^{-1}; MS (70 eV) *m/z* (%): 112.9 (38), 157.1 (100), 158.8 ([M]$^+$, 11).

1-(4-Fluorobuta-1,3-diynyl)-4-methoxybenzene (5c) Yellow solid; m.p. 187—189 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.50 (d, J=8.8 Hz, 2H), 6.87 (d, J=8.7 Hz, 2H), 3.85 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −103.49; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.95, 134.29, 114.40, 112.45, 77.99, 73.60, 67.06, 63.89, 29.68; IR (KBr) *v*: 2918, 2849, 2199, 1664, 1507, 1463, 1252, 1174, 1026, 822, 730, 527 cm^{-1}; MS (70 eV) *m/z* (%): 84.9 (32), 102.0 (100), 174.0 ([M]$^+$, 5).

1-(4-Fluorobuta-1,3-diynyl)-4-fluorobenzene (5d) Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.55 (dd, J=8.0, 4.0 Hz, 2H), 7.06 (dd, J=8.0, 4.0 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −74.68 (s), −106.65 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.42, 135.33, 116.24, 116.01, 75.25, 74.23, 67.14, 63.54; IR (film) *v*: 2923, 2851, 2195, 1679, 1489, 1260, 1091, 1014, 801, 755, 704, 524 cm^{-1}; MS (70 eV) *m/z* (%): 110.7 (100), 160.7 ([M−H]$^-$, 9).

1-(4-Fluorobuta-1,3-diynyl)-4-chlorobenzene (5e) Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.55 (dd, J=8.1, 4.0 Hz, 2H), 7.06 (dd, J=8.0, 4.0 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −106.63 (s); ^{13}C NMR (100 MHz, DMSO) δ: 134.11, 131.82, 124.11, 119.97, 74.61, 74.20, 71.93, 67.93; IR (film) *v*: 2921, 2851, 2202, 1669, 1588, 1488, 1398, 1261, 1089, 1013, 823, 760, 521 cm^{-1}; MS (70 eV) *m/z* (%): 110.6 (100), 178.0

([M]$^+$, 5).

1-(4-Fluorobuta-1,3-diynyl)-4-bromobenzene (5f) Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (dd, J=8.0, 3.6 Hz, 2H), 7.40—7.36 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −108.65 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.90, 134.82, 116.03, 115.81, 74.28, 73.31, 71.33, 67.99; IR (film) v: 2919, 2851, 2198, 1598, 1505, 1376, 1261, 1029, 996, 813, 748, 723, 521 cm^{-1}; MS (70 eV) *m/z* (%): 110.7 (100), 222.2 ([M]$^+$, 7).

1-(4-Fluorobuta-1,3-diynyl)-2-methoxybenzene (5g) Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.7—7.50 (m, 2H), 7.42 (d, J=7.2 Hz, 1H), 7.28 (t, J=7.3 Hz, 1H), 3.88 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −103.57 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.04, 133.69, 129.23, 127.79, 120.64, 110.80, 78.12, 74.71, 67.94, 64.18, 30.77; IR (film) v: 2962, 2925, 2198, 1726, 1592, 1450, 1358, 1271, 1183, 1021, 938, 883, 737, 687, 591 cm^{-1}; MS (70 eV) *m/z* (%): 84.6 (30), 102.1 (100), 174.2 ([M]$^+$, 8).

1-(4-Fluorobuta-1,3-diynyl)naphthalene (5h) Yellow solid; m.p. 175—177 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.34 (d, J=8.0 Hz, 1H), 7.90 (dd, J=8.2, 4.0 Hz, 2H), 7.84 (d, J=7.1 Hz, 1H), 7.65 (dd, J=8.2, 3.9 Hz, 1H), 7.58 (t, J=7.4 Hz, 1H), 7.46 (t, J=7.7 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −101.87 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.30, 133.32, 133.06, 130.63, 128.67, 127.61, 126.92, 125.92, 125.21, 118.20, 79.05, 76.57, 68.44, 64.40; IR (KBr) v: 2924, 2850, 2196, 1600, 1457, 1397, 1264, 1031, 824, 755, 699, 514 cm^{-1}; MS (70 eV) *m/z* (%): 84.9 (77), 101.9 (100), 130.0 (54), 194.0 ([M]$^+$, 10).

1-(4-Fluorobuta-1,3-diynyl)cyclohex-1-ene (5i) Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.41 (d, J=1.6 Hz, 1H), 2.15—2.05 (m, 4H), 1.69—1.58 (m, 2H), 1.41—1.28 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −82.00 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.68, 118.78, 79.59, 72.20, 66.53, 63.55, 28.29, 26.11, 21.96, 21.14; IR (film) v: 2925, 2853, 2191, 1615, 1457, 1264, 918, 741, 706, 518 cm^{-1}; MS (70 eV) *m/z* (%): 85.0 (29), 101.9 (100), 130.0 (30), 166.9 ([M+NH_4]$^+$, 24).

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