

Supporting Information

Direct Electrochemical difluorination and azo-fluorination of *gem*-difluorostyrenes

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Table of Contents

| | |
|---|----|
| 1. Materials and Methods: | 2 |
| 2. Information for reaction set up: | 3 |
| 2.1. Small scale reaction: | 3 |
| 2.2. Large scale reaction: | 4 |
| 3. General Procedure for compound Synthesis: | 4 |
| 3.1. Procedure for the synthesis of 3a : | 4 |
| 3.2. Procedure for the synthesis of 5n/5n' : | 5 |
| 3.3. Procedure for the synthesis of 5b : | 5 |
| 3.4. Procedure for the synthesis of 7 : | 6 |
| 3.5. Procedure for the synthesis of 8 : | 6 |
| 3.6. Procedure for the synthesis of 9 : | 7 |
| 3.7. Procedure for the synthesis of 10 : | 7 |
| 3.8 Procedure for Gram Scale Synthesis: | 8 |
| 4. Optimization of the reaction: | 8 |
| 4.1 Optimization table of diflorination reaction. | 8 |
| 4.2 Optimization table of fluoroazotion reaction. | 9 |
| 5. Mechanistic studies: | 9 |
| 5.1 Cyclic voltametry studies: | 9 |
| 5.2 Radical trapping experiment: | 10 |
| 5.3 Test of normal styrene derivative | 11 |
| 6. Characterization of Products: | 12 |
| 7. NMR Spectrum: | 26 |

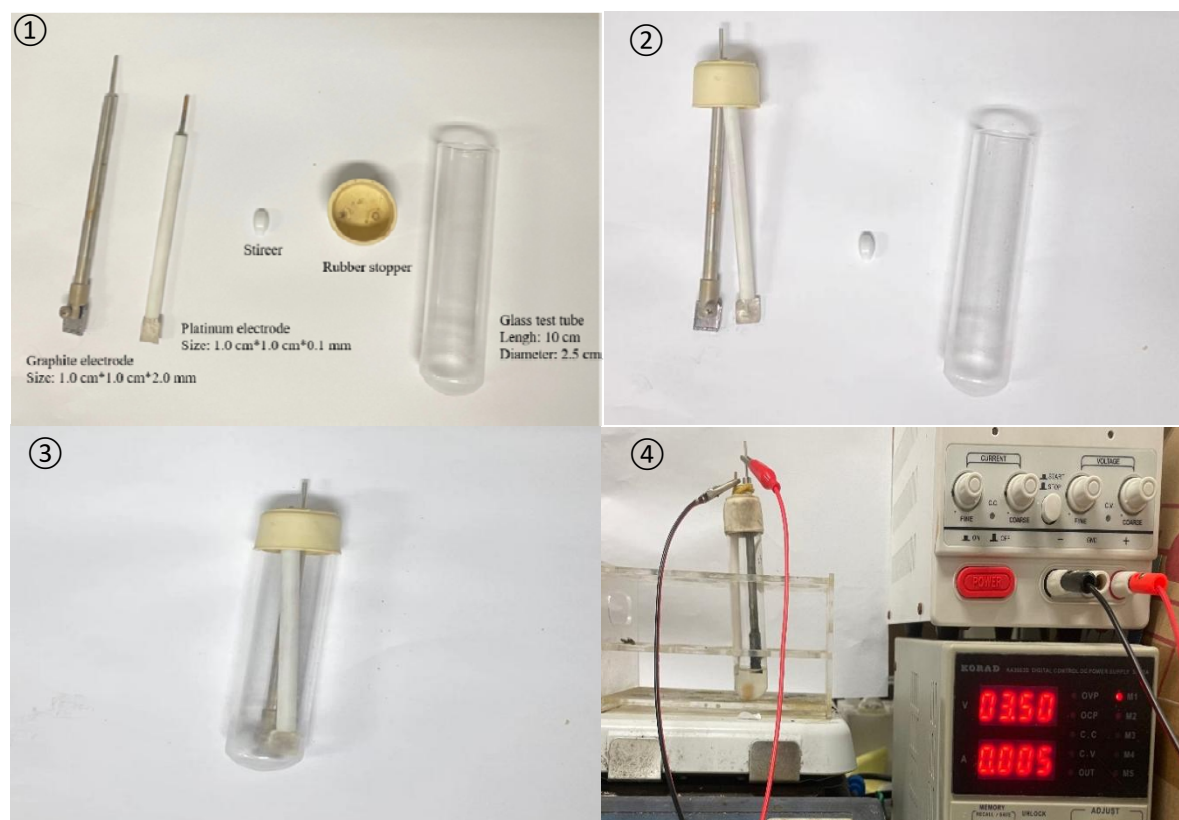
1. Materials and Methods:

All commercially available reagents were used without further purification. Analytical grade solvents were bought from Energy Chemical Co., LTD and used without processed. The reactions were carried out under constant cell potential (otherwise noted), an ambient atmosphere, magnetically stirred, and monitored by thin layer chromatography (TLC), visualized by fluorescence quenching under UV light. Flash chromatography was performed on silica gel (200-300 mesh). Cyclic voltammograms were recorded on a CHI 660E potentiostat. The UV spectrum was recorder on a UV-visible absorption instrument (Model: FLA4000, Version: VER 6.0). The instrument for electrolysis is dual display potentiostat (DJS-292B) (made in China). Platinum plate electrodes (10 mm×10 mm×0.1 mm or 30 mm×30 mm×0.1 mm, purity, 99.99%). Graphite electrodes are bought from Jilong Carbon company. All deuterated solvents were purchased from Meryer (Shanghai) chemical technology

Co., LTD. NMR spectra were recorded on a Bruker Ascend 300 spectrometer operating at 300 MHz for ^1H acquisitions, 75 MHz for ^{13}C acquisitions and 282 MHz for ^{19}F acquisitions. Chemical shifts were referenced to the residual proton solvent peaks (^1H : CDCl_3 , δ 7.26; $(\text{CD}_3)_2\text{SO}$, δ 2.50; CD_3OD , δ 3.31; CD_3CN , δ 1.94), solvent ^{13}C signals (CDCl_3 , δ 77.16; $(\text{CD}_3)_2\text{SO}$, δ 39.52; CD_3OD , δ 49.00), dissolved or external neat PhCF_3 (^{19}F , δ -63.3 relative to CFC_3). Signals are listed in ppm, and multiplicity identified as s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants in Hz; integration. High-resolution mass spectra were obtained using Agilent LC-UV-TOFmass spectrometer. Yields refer to purified and spectroscopically pure compounds.

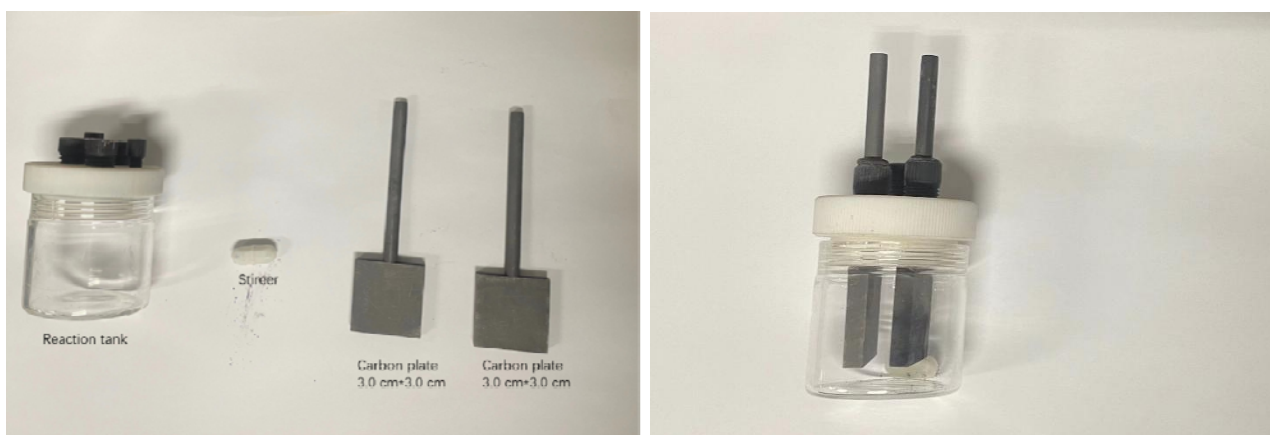
2. Information for reaction set up:

2.1. Small scale reaction:



The detail process for home-made electrolysis equipment (follow the steps 1 to 4): 1) Prepare the materials in picture 1 according to the specific information displayed. 2) push the electrode to pass through the rubber stopper and set the distance between the two electrodes in 1.2 cm as shown in picture 2. The graphite anode was bought from Jinglong special carbon company and the purity of platinum sheet is 99.99%. 3) using the rubber stopper to cap on the glass test tube as in picture 3. 4) the reaction set-up was shown in picture 4.

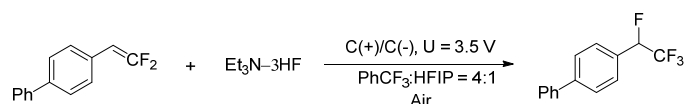
2.2. Large scale reaction:



The large scale reaction setup was using the commercially available equipment bought in Stony-lab (stonyLab.com). The size of carbon electrode is 3.0 cm * 3.0 cm * 0.2 cm. The carbon electrodes can be directly insert into the cell.

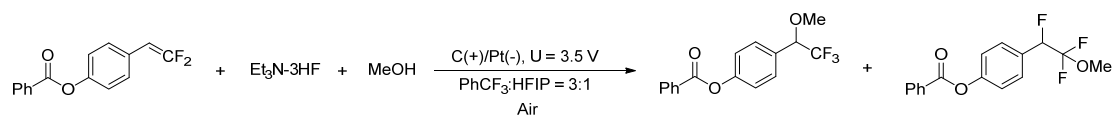
3. General Procedure for compound Synthesis:

3.1. Procedure for the synthesis of 3a:



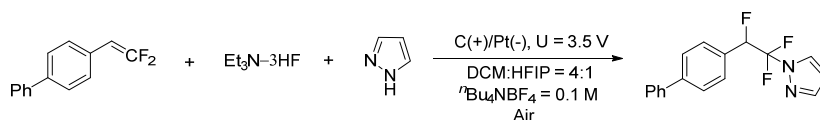
A solution of **1a** (0.5 mmol, 108 mg, 1.0 eq.), Et₃N-3HF (1.0 mL), PhCF₃ (4.0 mL), HFIP (1.0 mL) was stirred at rt under air in an oven-dried undivided test tube which was equipped with graphite carbon plate (1.0 cm×1.0 cm×2.0 mm) as the anode and the cathode. The reaction mixture was stirred and electrolyzed at a constant cell potential of 3.5 V under room temperature and stopped until complete consumption of **1a** (monitored by TLC), around 3 h. The electricity was firstly disconnected and the electrode was removed from the test tube before rinsing twice with dichloromethane. The reaction mixture was poured into the separatory funnel and distilled water was added (10 mL). The mixture was extracted three times with dichloromethane (20 mL). The combined organic layers was dried with anhydrous sodium sulfate, filtered, concentrated, and purified with column chromatography on silica gel or preparative thin layer chromatography (elution: petroleum ether).

3.2. Procedure for the synthesis of 5n/5n' :



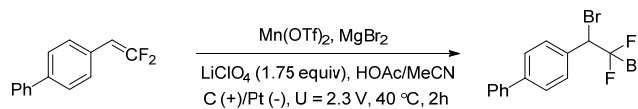
A solution of **1a** (0.5 mmol, 108 mg, 1.0 eq.), Et₃N-3HF (1.0 mL), MeOH (1.0 mL), PhCF₃ (3.0 mL), HFIP (1.0 mL) was stirred at rt under air in an oven-dried undivided test tube which was equipped with graphite carbon plate (1.0 cm×1.0 cm×2.0 mm) as the anode and platinum plate electrode (1.0 cm×1.0 cm×0.1 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant cell potential of 3.5 V under room temperature and stopped until complete consumption of **1a** (monitored by TLC), around 4 h. The electricity was firstly disconnected and the electrode was removed from the test tube before rinsing twice with dichloromethane. The reaction mixture was poured into the separatory funnel and distilled water was added (10 mL). The mixture was extracted three times with dichloromethane (20 mL). The combined organic layers was dried with anhydrous sodium sulfate, filtered, concentrated, and purified with column chromatography on silica gel or preparative thin layer chromatography (elution: petroleum ether).

3.3. Procedure for the synthesis of 5b :



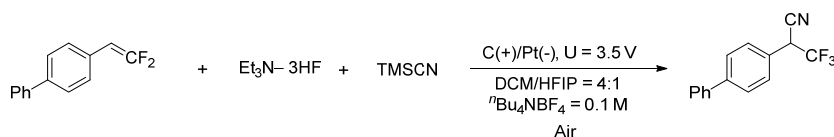
A solution of **1a** (0.5 mmol, 108 mg, 1.0 eq.), Et₃N-3HF (1 mmol, 161 mg, 2.0 eq.), Pyrazole (1.0 mmol, 136 mg, 2.0 eq.), ⁿBu₄NBF₄ (0.1 M), DCM (4.0 mL), HFIP (1.0 mL) was stirred at rt under air in an oven-dried undivided test tube which was equipped with graphite carbon plate (1.0 cm×1.0 cm×2.0 mm) as the anode and platinum plate electrode (1.0 cm×1.0 cm×0.1 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant cell potential of 3.5 V under room temperature and stopped until complete consumption of **1a** (monitored by TLC), around 5 h. The electricity was firstly disconnected and the electrode was removed from the test tube before rinsing twice with dichloromethane. The reaction mixture was poured into the separatory funnel and distilled water was added (10 mL). The mixture was extracted three times with dichloromethane (20 mL). The combined organic layers was dried with anhydrous sodium sulfate, filtered, concentrated, and purified with column chromatography on silica gel or preparative thin layer chromatography (elution: petroleum ether/ethyl acetate).

3.4. Procedure for the synthesis of 7:



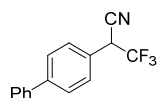
To an oven-dried glass test tube (20.0 mL) equipped with a magnetic stirbar was added MgBr₂ (184.0 mg, 1.0 mmol, 2.0 equiv.) and Mn(OTf)₂ (5.1 mg, 0.025 mmol, 5 mol%). The glass test tube were fitted with carbon plate (1.0 cm×1.0 cm×2.0 mm) as the anode and platinum plate electrode (1.0 cm×1.0 cm×0.1 mm) as the cathode, respectively, maintaining a distance of 1.2 cm between the closest point of the two electrodes. The cell was sealed and flushed with nitrogen gas for 5 minutes, followed by addition via syringe of electrolyte solution (0.1 M LiClO₄ in MeCN, 5 mL), **1a** (108.0 mg, 0.5 mmol, 1 equiv), and acetic acid (1.0 mL). The reaction mixture was then purged with nitrogen gas for another 5 minutes. A nitrogen-filled balloon was adapted through a septum to sustain a nitrogen atmosphere. Electrolysis was initiated at a constant current of 80 mA at 40 °C (oil bath temperature). The reaction was allowed to proceed for 5 h. The whole reaction mixture was then extracted with dichloromethane, the organic layer was dried over Na₂SO₄, added to silica gel and spin-dried, transferred to a short silica gel column (7-10 cm long, about 50 g) and purified with petroleum ether, then Concentration in vacuo gave pure product (119.0 mg, 69% yield).

3.5. Procedure for the synthesis of 8:



A solution of **1a** (0.5 mmol, 108 mg, 1.0 eq.), Et₃N-3HF (1 mmol, 161 mg, 2.0 eq.), TMSCN (1 mmol, 99 mg, 2.0 eq.), DCM (4.0 mL), HFIP (1.0 mL) was stirred at rt under air in an oven-dried undivided test tube which was equipped with graphite carbon plate (1.0 cm×1.0 cm×2.0 mm) as the anode and platinum plate electrode (1.0 cm×1.0 cm×0.1 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant cell potential of 3.5 V under room temperature and stopped until complete consumption of **1a** (monitored by TLC), around 4 h. The electricity was firstly disconnected and the electrode was removed from the test tube before rinsing twice with dichloromethane. The reaction mixture was poured into the separatory funnel and distilled water was added (10 mL). The mixture was extracted three times with dichloromethane (20 mL). The combined organic layers was used to run GC-MS. The flowing GC-MS result was obtained.

2-([1,1'-biphenyl]-4-yl)-3,3,3-trifluoropropanenitrile (**8**)



Mass Spectrometry: GCMS (EI-TOF) (m/z): calcd for C₁₅H₁₀F₃N, 261.1, found, 262.1.

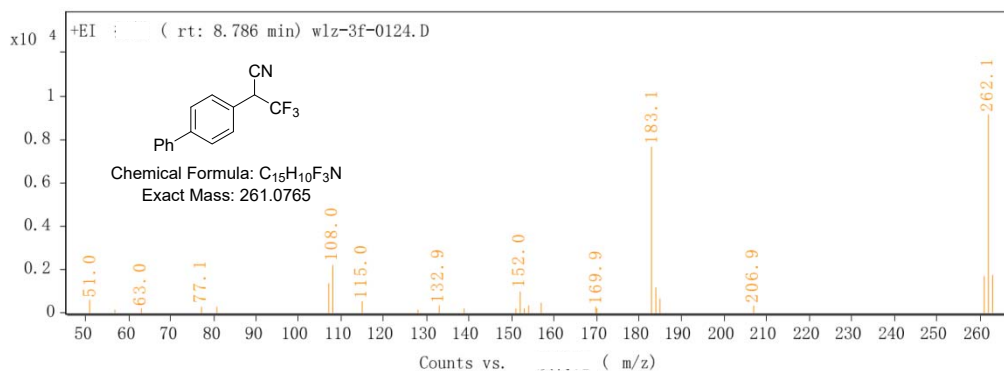
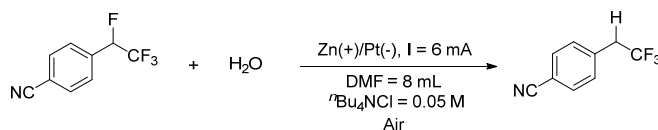


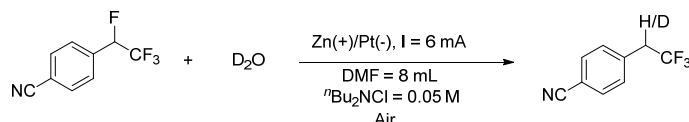
Figure S1 GC-MS information of generation of **8**

3.6. Procedure for the synthesis of **9**:



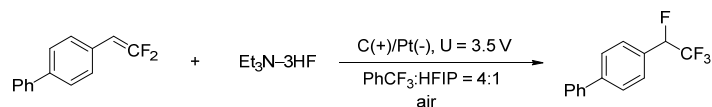
Reaction conditions: undivided cell, Zn plate anode (2 cm×1 cm×0.1 cm), graphite rod cathode (1.0 cm×1.0 cm×2.0 mm), constant current (I = 6 mA), 1 (0.8 mmol), 2 (1.0 μL), electrolyte, dry DMF (8 mL), air, 26 °C, 15 h. Separation and purification by HPLC (Beijing chuangxintongheng Model: P-3122605571); Column: Manf. No. K63935, cosmosil packed column; solvent system: Methanol : H₂O = 40% : 60% to 100% :0 for 20 min.

3.7. Procedure for the synthesis of **10**:



Reaction conditions: undivided cell, Zn plate anode (2 cm×1 cm×0.1 cm), graphite rod cathode (1.0 cm×1.0 cm×2.0 mm), constant current (I = 6 mA), 1 (0.8 mmol), D₂O (1.0 μL), electrolyte, dry DMF (8 mL), air, 26 °C, 15 h. Separation and purification by HPLC (Beijing chuangxintongheng Model: P-3122605571); Column: Manf. No. K63935, cosmosil packed column; solvent system: Methanol : H₂O = 40% : 60% to 100% :0 for 20 min. We got a mixture of **9** and **10**. DMF may also work as proton source.

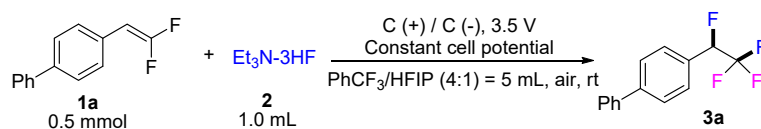
3.8 Procedure for Gram Scale Synthesis:



To an oven-dried reaction tank (50.0 mL) equipped with a magnetic stirbar was added **1a** (10 mmol, 2.16 g, 1.0 eq.), Et₃N-3HF (10.0 mL), PhCF₃ (40 mL) and HFIP (10 mL), The glass test tube were fitted with carbon plate (3.0 cm×3.0 cm) as the anode and carbon plate (2.5 cm×2.5 cm) as the cathode, respectively, maintaining a distance of 4.0 cm between the closest point of the two electrodes. Electrolysis was initiated at a constant voltage of 3.5 V at room temperature. The reaction was allowed to proceed for 6 h. After 3h, the anode was replaced for another carbon plate. The whole reaction mixture was then extracted with dichloromethane, the organic layer was dried over Na₂SO₄, added to silica gel and spin-dried, transferred to a silica gel column and purified with petroleum ether, then Concentration in vacuo gave pure white solid **3a** (1.19 g, 47% yield).

4. Optimization of the reaction:

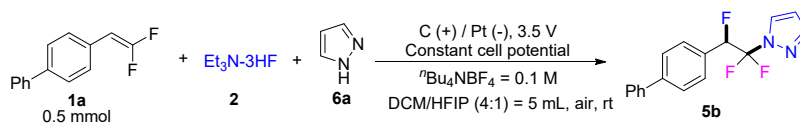
4.1 Optimization table of difluorination reaction.



| Entry | Variation from standard conditions | Yield (3a) |
|-------|---|---------------------|
| 1 | none | 65% |
| 2 | Py-HF instead of Et ₃ N-HF | 53% |
| 3 | Et ₃ N-HF (0.8 mL) | 58% |
| 4 | Et ₃ N-HF (1.2 mL) | 64% |
| 5 | 0.5 mmol <i>n</i> Bu ₄ NPF ₆ as electrolyte | 55% |
| 6 | Pt as cathode | 61% |
| 7 | Pt as both anode and cathode | trace |
| 8 | glassy carbon as both anode and cathode | 55% |
| 9 | glassy carbon as anode | 55% |
| 10 | RVC as anode | 57% |
| 11 | PhCF ₃ as the solvent | 58% |
| 12 | HFIP as the solvent | 18% |
| 13 | under N ₂ | 67% |
| 14 | no electricity | 0% |

Reaction condition: Graphite plate as cathode and anode (1.0 cm * 1.0 cm * 2.0 mm), constant cell potential, **1a** (1.0 equiv, 0.5 mmol), **2a** (1.0 mL), PhCF₃/HFIP (4 mL:1 mL), room temperature, Air, 3 h.

4.2 Optimization table of fluoroazotiation reaction.

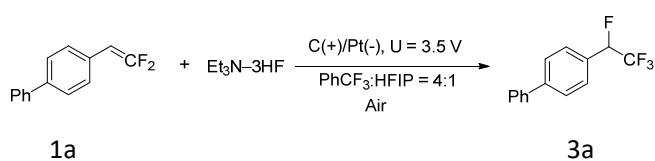


| Entry | Variation from standard conditions | Yield (5b) ^[b] |
|-------|---|---------------------------|
| 1 | none | 40% |
| 2 | Electrolyzer | trace |
| 3 | 2:4 = 2:1 | 33% |
| 4 | 2:4 = 4:1 | 11% |
| 5 | 0.5 mmol <i>n</i> Bu ₄ NPF ₆ as electrolyte | 25% |
| 6 | graphite as both anode and cathode | 28% |
| 7 | Pt as both anode and cathode | trace |
| 8 | MeCN:DCM = 1:4 | 27% |
| 9 | MeCN:DCM = 2:3 | 23% |
| 10 | MeCN:AcOH = 10:1 | 15% |
| 11 | PhCF ₃ :HFIP = 4:1 | 40% |
| 12 | DCM:HFIP = 3:1 | 35% |
| 13 | PhCl ₂ as the solvent | trace |
| 14 | PhNO ₂ as the solvent | trace |
| 15 | under N ₂ | 32% |
| 16 | no electricity | 0% |

Reaction condition: a platinum plate as cathode (1.0 cm * 1.0 cm * 0.1 mm) and a graphite plate as anode (1.0 cm * 1.0 cm * 2.0 mm), constant cell potential, **1a** (1.0 equiv, 0.5 mmol), **2a** (2.0 equiv, 1.0 mmol), **6a** (2.0 equiv, 1.0 mmol), *n*Bu₄NBF₄ (0.1 M), DCM/HFIP (4 mL:1 mL), room temperature, Air, 5 h.

5. Mechanistic studies:

5.1 Cyclic voltametry studies:



Cyclic voltammograms were recorded on a CHI 660E potentiostat. The cyclic voltammograms of compounds **1a**, Et₃N-3HF, and **3a** were recorded in an electrolyte of *n*Bu₄NBF₄ (0.1 M) in HFIP/PhCF₃ (1:4) using a graphite working electrode (diameter, 2 mm), a Pt wire auxiliary electrode and a SCE reference electrode. The scan rate is 100 mV/s.

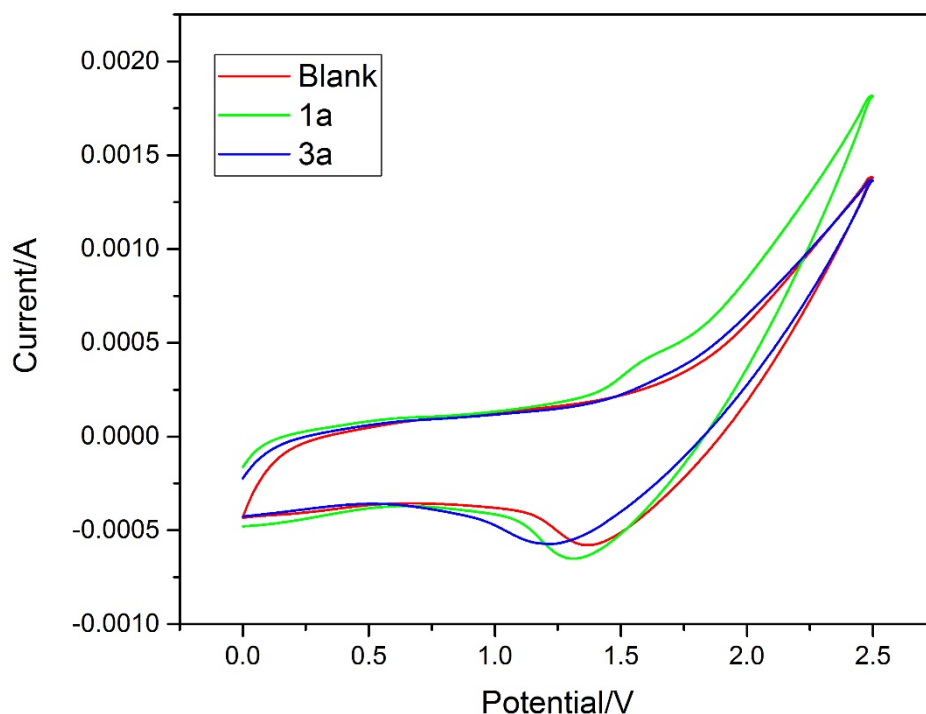
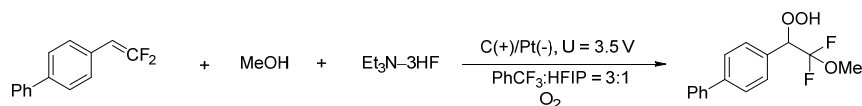


Figure S2 Cyclic voltammetry studies of the reaction components

5.2 Radical trapping experiment:



A solution of **1a** (0.5 mmol, 108 mg, 1.0 eq.), Et₃N-3HF (1 mL), MeOH (1.0 mL), HFIP (1 mL), PhCF₃ (3 mL) was stirred at rt under O₂ in an oven-dried undivided test tube which was equipped with carbon plate (1.0 cm×1.0 cm×2.0 mm) as the anode and platinum plate electrodes (1.0 cm×1.0 cm×0.1 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a controlled cell potential of 3.5 V under room temperature and stopped until complete consumption of **1a** (monitored by TLC). The reaction mixture was taken a little bit to run GC-MS and the results were listed below. Compound **13** was detected.

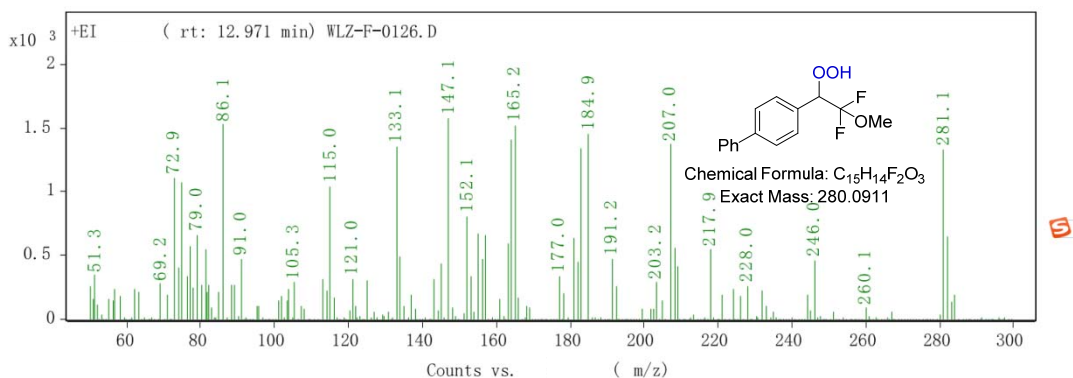


Figure S3 GC-MS information of radical trapping experiment

5.3 Test of normal styrene derivative:

we tried to use 4-vinylbiphenyl as substrate for the electrochemical fluorination reaction. Unfortunately, 4-vinylbiphenyl was totally consumed, but no product could be able to isolated in the resulting messy mixture. The cyclic voltammograms of 4-vinylbiphenyl was also recorded on a CHI 660E potentiostat. The cyclic voltammograms of compound 4-vinylbiphenyl was recorded in an electrolyte of $\text{Et}_3\text{N}\cdot 3\text{HF}$ in HFIP/ PhCF_3 (1:4) using a graphite working electrode (diameter, 2 mm), a Pt wire auxiliary electrode and a SCE reference electrode. The scan rate is 100 mV/s. It can be seen that 4-vinylbiphenyl was easy to oxidize in the current electrochemical condition, while no fluorination reaction could happen.

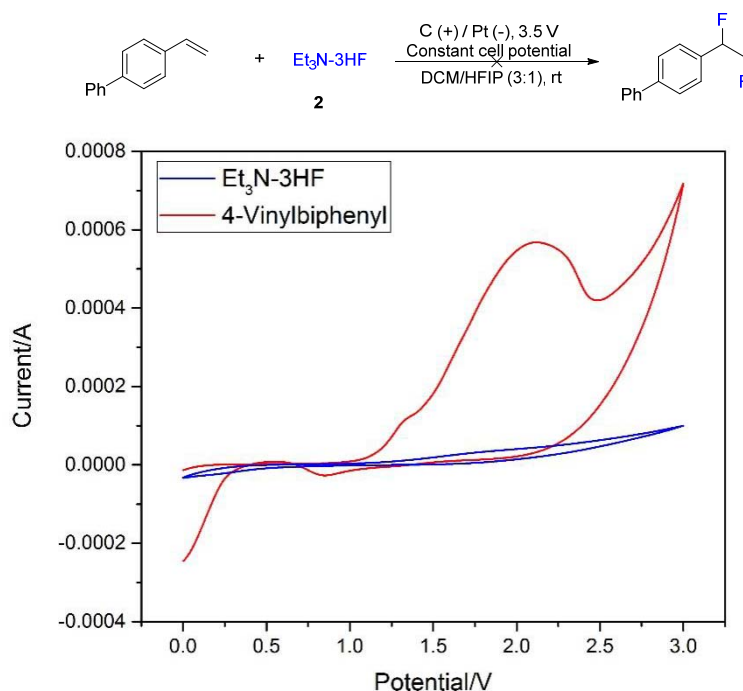
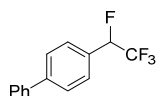


Figure S4 Cyclic voltammetry studies of the styrene derivative

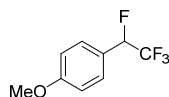
6. Characterization of Products:

4-(1,2,2,2-Tetrafluoroethyl)-1,1'-biphenyl (3a)



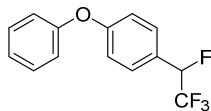
White solid (76 mg, 65 % yield, electrolysis time: 3.2 h, $R_f = 0.67$ (petroleum ether); M.P. 36.5-38.3 °C; NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 7.67 (d, $J = 7.9$ Hz, 2H), 7.62–7.59 (m, 2H), 7.54 (d, $J = 8.2$ Hz, 2H), 7.50–7.45 (m, 2H), 7.42–7.36 (m, 1H), 5.75–5.54 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, δ): 143.6 (d, $J = 1.9$ Hz, 1C), 140.2, 129.1, 128.1, 127.8 (d, $J = 6.6$ Hz, 1C), 127.6, 127.4, 120.6 (qd, $J = 28.9, 279.6$ Hz, 1C), 89.0 (qd, $J = 35.5, 185.25$ Hz, 1C). ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -78.6 (d, $J = 7.2$ Hz, 3F), -194.1 (dd, $J = 3.5, 7.0$ Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $\text{C}_{14}\text{H}_{11}\text{F}_4^+$ ($[\text{M} + \text{H}]^+$), 255.0791, found, 255.0790.

1-Methoxy-4-(1,2,2,2-tetrafluoroethyl)benzene (3b)



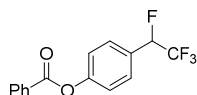
Colorless oil (75 mg, 61 % yield, electrolysis time: 3.6 h, $R_f = 0.72$ (petroleum ether); NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 7.39 (d, $J = 8.5$ Hz, 2H), 6.96 (d, $J = 8.6$ Hz, 2H), 5.63–5.42 (m, 1H), 3.84 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, δ): 161.4, 129.1 (d, $J = 5.8$ Hz, 1C), 122.6, 122.5 (qd, $J = 20.3, 321.9$ Hz, 1C), 114.3, 89.0 (qd, $J = 36.4, 219.0$ Hz, 1C), 55.5. ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -78.9 (d, $J = 13.6$ Hz, 3F), -190.1 (dd, $J = 13.3, 26.8$ Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $\text{C}_9\text{H}_9\text{F}_4\text{O}^+$ ($[\text{M} + \text{H}]^+$), 209.0584, found, 209.0575.

1-Phenoxy-4-(1,2,2,2-tetrafluoroethyl)benzene (3c)



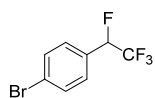
White solid (79 mg, 68 % yield, electrolysis time: 3.4 h, $R_f = 0.67$ (petroleum ether); M.P. 39.5-40.8 °C; NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 7.45–7.37 (m, 4H), 7.19 (t, $J = 7.3$ Hz, 1H), 7.09–7.05 (m, 4H), 5.67–5.47 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, δ): 159.7 (d, $J = 1.8$ Hz, 2C), 156.2, 130.1, 129.1 (d, $J = 6.2$ Hz, 1C), 124.3, 119.9, 118.4, 117.8 (qd, $J = 30.2, 235.7$ Hz, 1C), 89.2 (qd, $J = 34.9, 185.3$ Hz, 1C). ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -78.8 (d, $J = 13.3$ Hz, 3F), -191.9 (dd, $J = 13.1, 26.3$ Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $\text{C}_{14}\text{H}_{11}\text{F}_4\text{O}^+$ ($[\text{M} + \text{H}]^+$), 271.0741, found, 271.0728.

4-(1,2,2,2-Tetrafluoroethyl)phenyl benzoate (3d)

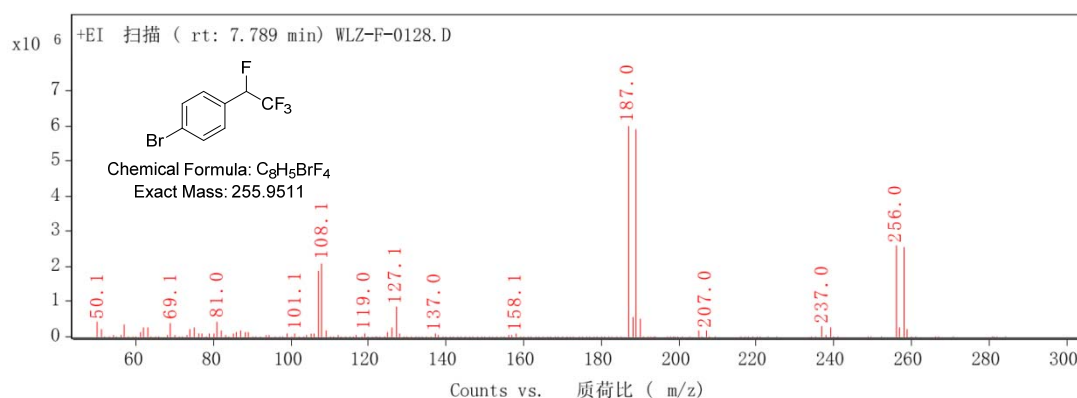


Colorless oil (81 mg, 71 % yield, electrolysis time: 3.9 h, $R_f = 0.32$ (petroleum ether)); NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 8.00 (d, $J = 7.1$ Hz, 2H), 7.38 (t, $J = 7.1$ Hz, 1H), 7.53 (t, $J = 8.0$ Hz, 4H), 7.33 (d, $J = 8.5$ Hz, 2H), 5.74–5.53 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, δ): 165.0, 152.7, 134.0, 130.4, 129.3, 128.8 (d, $J = 4.4$ Hz, 1C), 128.7, 127.9 (d, $J = 20.4$ Hz, 1C), 122.4, 120.6 (qd, $J = 17.4$, 279.9 Hz, 1C), 87.1 (qd, $J = 34.8$, 228.8 Hz, 1C). ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -78.6 (d, $J = 13.0$ Hz, 3F), -193.8 (dd, $J = 13.1$, 25.9 Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $\text{C}_{15}\text{H}_{11}\text{F}_4\text{O}_2^+$ ($[\text{M} + \text{H}]^+$), 299.0690, found, 299.0693.

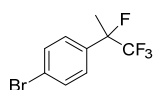
1-Bromo-4-(1,2,2,2-tetrafluoroethyl)benzene (3e)



Colorless oil (64 mg, 55 % yield, electrolysis time: 3.6 h, $R_f = 0.47$ (petroleum ether)); NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 7.60 (d, $J = 8.2$ Hz, 2H), 7.33 (d, $J = 8.2$ Hz, 2H), 5.56 (dq, $J = 44.0$, 6.0 Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, δ): 132.2, 129.3 (d, $J = 20.0$ Hz, 1C), 128.8 (d, $J = 6.5$ Hz, 1C), 125.1 (d, $J = 2.0$ Hz, 1C), 122.1 (qd, $J = 279.8$, 28.8 Hz, 1C), 88.5 (dq, $J = 186.2$, 35.0 Hz, 1C). ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -78.9 (d, $J = 12.6$ Hz, 3F), -195.1 (dd, $J = 12.2$, 25.7 Hz, 1F). Mass Spectrometry: GCMS (EI-TOF) (m/z): calcd for $\text{C}_8\text{H}_5\text{BrF}_4$, 256.0, found, 256.0.

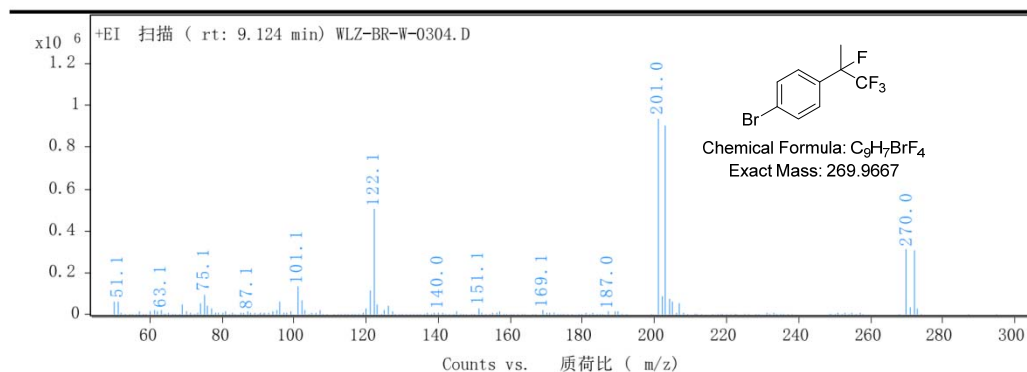


1-Bromo-4-(1,1,1,2-tetrafluoropropan-2-yl)benzene (3f)

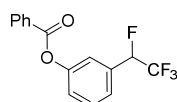


Colorless oil (76 mg, 65 % yield, electrolysis time: 3.8 h, $R_f = 0.72$ (petroleum ether)); NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 7.56 (d, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 8.4$ Hz, 2H), 1.88 (dq, $J = 23.0$, 1.0 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, δ): 134.7 (d, $J = 21.8$ Hz, 1C), 131.9

(d, $J = 1.0$ Hz, 1C), 127.5 (d, $J = 9.2$ Hz, 1C), 124.0 (d, $J = 1.4$ Hz, 1C), 123.0 (qd, $J = 282.4, 30.4$ Hz, 1C), 88.5 (dq, $J = 184.0, 32.0$ Hz, 1C), 20.9 (d, $J = 22.8$ Hz, 1C). ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -81.5 (d, $J = 6.9$ Hz, 3F), -163.6 (dd, $J = 7.0, 13.9$ Hz, 1F). Mass Spectrometry: GCMS (EI-TOF) (m/z): calcd for $\text{C}_9\text{H}_7\text{BrF}_4$, 270.0, found, 270.0.

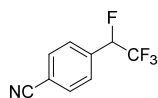


3-(1,2,2,2-Tetrafluoroethyl)phenyl benzoate (3g)



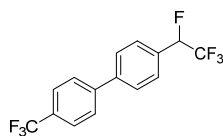
Colorless oil (69 mg, 75 % yield, electrolysis time: 3.6 h, $R_f = 0.30$ (petroleum ether)); NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 8.22 (d, $J = 7.2$ Hz, 2H), 7.66 (t, $J = 7.4$ Hz, 1H), 7.53 (t, $J = 7.8$ Hz, 3H), 7.38 (s, 3H), 5.75–5.54 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, δ): 165.0, 151.3, 134.0, 132.0 (d, $J = 19.9$ Hz, 1C), 130.2 (d, $J = 24.2$ Hz, 1C), 129.1 (d, $J = 36.6$ Hz, 1C), 124.7 (d, $J = 6.6$ Hz, 1C), 124.1, 120.7 (d, $J = 7.3$ Hz, 1C), 119.3 (qd, $J = 37.3, 252.1$ Hz, 1C), 88.5 (dd, $J = 34.9, 186.8$ Hz, 1C). ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -78.6 (d, $J = 12.2$ Hz, 3F), -195.3 (dd, $J = 12.9, 25.7$ Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $\text{C}_{15}\text{H}_{11}\text{F}_4\text{O}_2^+$ ($[\text{M} + \text{H}]^+$), 299.0690, found, 299.0676.

4-(1,2,2,2-Tetrafluoroethyl)benzonitrile (3h)



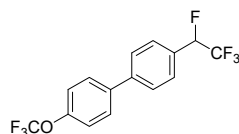
Colorless oil (38 mg, 31 % yield, electrolysis time: 3.2 h, $R_f = 0.58$ (petroleum ether)); ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 7.76 (d, $J = 8.0$ Hz, 2H), 7.59 (d, $J = 8.1$ Hz, 2H), 5.77–5.57 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, δ): 139.9 (d, $J = 35.0$ Hz, 1C), 135.2 (d, $J = 22.3$ Hz, 1C), 132.7, 127.9 (d, $J = 7.4$ Hz, 1C), 117.9 (qd, $J = 17.5, 234.7$ Hz, 1C), 88.3 (qd, $J = 35.9, 191.3$ Hz, 1C). ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -78.5 (d, $J = 12.5$ Hz, 3F), -197.6 (dd, $J = 12.7, 25.4$ Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): $\text{C}_9\text{H}_6\text{F}_4\text{N}^+$ ($[\text{M} + \text{H}]^+$), 204.0431, found, 204.0422.

4-(1,2,2,2-Tetrafluoroethyl)-4'-(trifluoromethyl)-1,1'-biphenyl (3i)



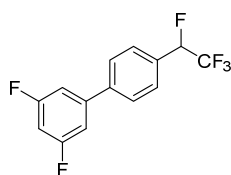
White solid (58 mg, 58 % yield, electrolysis time: 3.2 h, $R_f = 0.68$ (petroleum ether); M.P. 41.2-43.5 °C; NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 7.75–7.70 (m, 5H), 7.66 (s, 1H), 7.58 (d, $J = 8.2$ Hz, 2H), 5.77–5.56 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, δ): 143.8, 142.1, 130.4, 130.1 (d, $J = 12.9$ Hz, 1C), 128.0 (d, $J = 6.4$ Hz, 2C), 127.8 (d, $J = 6.0$ Hz, 2C), 126.1–126.0 (m, 1C), 122.5 (qd, $J = 28.7$, 232.6 Hz, 1C), 87.9 (qd, $J = 35.6$, 185.3 Hz, 1C). ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -62.5 (s, 3F), -78.7 (d, $J = 13.2$ Hz, 3F), -194.8 (dd, $J = 12.7$, 25.8 Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $\text{C}_{15}\text{H}_{10}\text{F}_7$ ($[\text{M} + \text{H}]^+$), 323.0665, found, 323.0673.

4-(2,2-Difluorovinyl)-4'-(trifluoromethoxy)-1,1'-biphenyl (3j)



White solid (56 mg, 50 % yield, electrolysis time: 3.3 h, $R_f = 0.67$ (petroleum ether); M.P. 42.8-45.8 °C; NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 7.61 (t, $J = 7.9$ Hz, 4H), 7.54 (d, $J = 8.2$ Hz, 2H), 7.31 (d, $J = 8.2$ Hz, 2H), 5.78–5.54 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, δ): 149.3, 142.2, 138.9, 129.7 (d, $J = 19.4$ Hz, 1C), 128.8, 128.3 (d, $J = 6.7$ Hz, 1C), 127.9 (d, $J = 6.6$ Hz, 1C), 127.5 (d, $J = 14.5$ Hz, 1C), 121.5, 122.4 (qd, $J = 18.5$, 257.1 Hz, 1C), 88.9 (qd, $J = 34.9$, 185.3 Hz, 1C). ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -57.8 (s, 3F), -78.7 (d, $J = 13.2$ Hz, 3F), -194.5 (dd, $J = 13.2$, 26.2 Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $\text{C}_{15}\text{H}_{10}\text{F}_7\text{O}^+$ ($[\text{M} + \text{H}]^+$), 339.0614, found, 339.0638.

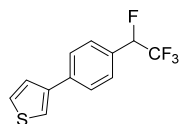
3,5-Difluoro-4'-(1,2,2,2-tetrafluoroethyl)-1,1'-biphenyl (3k)



Colorless oil (58 mg, 50 % yield, electrolysis time: 3.7 h, $R_f = 0.68$ (petroleum ether); NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 7.61–7.53 (m, 4H), 7.46–7.38 (m, 1H), 7.02–6.90 (m, 2H), 5.75–5.69 (m, 0.5H), 5.60–5.54 (m, 0.5H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, δ): 163.1 (dd, $J = 11.8$, 214.7 Hz, 1C), 159.7 (dd, $J = 11.7$, 215.6 Hz, 1C), 137.4, 131.7–131.5 (m, 1C), 129.8 (d, $J = 19.7$ Hz, 1C), 129.4 (d, $J = 2.9$ Hz, 1C), 127.6 (d, $J = 6.5$ Hz, 1C), 124.5–124.4 (m, 1C), 120.5 (qd, $J = 29.0$, 279.9 Hz, 1C), 112.0 (dd, $J = 21.1$, 3.8 Hz, 1C), 104.7 (t, $J = 26.3$ Hz, 1C), 88.9 (qd, $J = 34.9$, 180.0 Hz, 1C). ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -78.6 (d, $J = 12.7$ Hz,

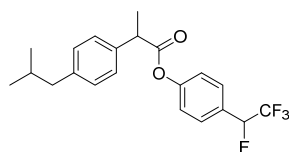
3F), -110.3 (d, $J = 7.9$ Hz, 1F), -113.4 (d, $J = 7.47$ Hz, 1F), -194.7 (dd, $J = 13.1, 26.3$ Hz, 1F). Mass Spectrometry:HRMS (ESI-TOF) (m/z): calcd for $C_{14}H_9F_6^+$ ($[M + H]^+$), 291.0603, found, 291.0614.

3-(4-(1,2,2,2-Tetrafluoroethyl)phenyl)thiophene (3l)



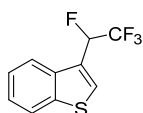
Colorless oil (41 mg, 35 % yield, electrolysis time: 3.5 h, $R_f = 0.65$ (petroleum ether); NMR Spectroscopy: 1H NMR (300 MHz, $CDCl_3$, 25 °C, δ): 7.67 (d, $J = 8.2$ Hz, 2H), 7.49 (d, $J = 8.7$ Hz, 3H), 7.43–7.37 (m, 2H), 5.71–5.51 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, δ): 141.4, 138.1, 129.2 (d, $J = 82.4, 147.2$ Hz, 1C), 127.9 (d, $J = 6.5$ Hz, 1C), 126.8 (d, $J = 2.8$ Hz, 1C), 126.3, 121.5, 120.7 (qd, $J = 33.1, 263.8$ Hz, 1C), 89.0 (qd, $J = 30.0, 187.5$ Hz, 1C). ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C, δ): -78.7 (d, $J = 12.9$ Hz, 1F), -194.1 (dd, $J = 12.5, 26.0$ Hz, 1F). Mass Spectrometry:HRMS (ESI-TOF) (m/z): calcd for $C_{12}H_9F_4S^+$ ($[M + H]^+$), 261.0356, found, 261.0347.

4-(1,2,2,2-tetrafluoroethyl)phenyl 2-(4-isobutylphenyl)propanoate (3m)



White solid (61 mg, 55 % yield, electrolysis time: 3.7 h, $R_f = 0.35$ (petroleum ether/ethyl acetate = 20 : 1 (v/v)); M.P. 48.5-50.2 °C; NMR Spectroscopy: 1H NMR (300 MHz, $CDCl_3$, 25 °C, δ): 7.45 (d, $J = 8.4$ Hz, 2H), 7.33 (d, $J = 8.0$ Hz, 2H), 7.18 (d, $J = 8.1$ Hz, 2H), 7.12 (d, $J = 8.3$ Hz, 2H), 5.69–5.48 (m, 1H), 3.98 (dd, $J = 7.1, 14.2$ Hz, 1H), 2.51 (d, $J = 7.2$ Hz, 2H), 1.97–1.83 (m, 1H), 1.64 (d, $J = 7.1$ Hz, 3H), 0.94 (d, $J = 6.6$ Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, δ): 173.0, 152.7, 141.1, 137.1, 129.7, 128.5 (d, $J = 6.5$ Hz, 1C), 127.7 (d, $J = 20.2$ Hz, 1C), 127.4, 124.2 (d, $J = 30.3$ Hz, 1C), 122.0, 123.7 (qd, $J = 30.3, 281.2$ Hz, 1C), 87.7 (qd, $J = 37.5, 172.5$ Hz, 1C), 45.3 (d, $J = 17.7$ Hz, 1C), 30.3, 22.5, 18.5. ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C, δ): -78.8 (d, $J = 13.0$ Hz, 3F), -193.7– -193.9 (m, 1F). Mass Spectrometry:HRMS (ESI-TOF) (m/z): calcd for $C_{21}H_{23}F_4O_2^+$ ($[M + H]^+$), 383.1629, found, 383.1618.

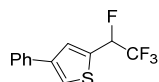
3-(1,2,2,2-tetrafluoroethyl)benzo[b]thiophene (3n)



Colorless oil (54 mg, 45 % yield, electrolysis time: 3.6 h, $R_f = 0.67$ (petroleum ether); NMR Spectroscopy: 1H NMR (300 MHz, $CDCl_3$, 25 °C, δ): 7.92–7.84 (m, 2H), 7.74 (d, $J = 1.7$ Hz, 1H), 7.48–7.39 (m, 2H), 6.07 (dd, $J = 6.0, 12.1$ Hz, 0.5H), 5.92 (dd, $J = 6.1, 12.1$ Hz, 0.5H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, δ): 140.4, 136.8, 128.8 (d, J

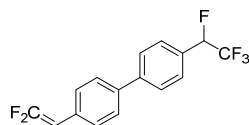
= 8.1 Hz, 1C), 125.4 (d, $J = 13.2$ Hz, 1C), 125.1 (d, $J = 9.7$ Hz, 1C), 123.1, 122.2, 120.3 (qd, $J = 34.5, 273.7$ Hz, 1C), 85.3 (qd, $J = 35.7, 187.5$ Hz, 1C). ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -77.6 (s, 3F), -192.3 (s, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $\text{C}_{10}\text{H}_7\text{F}_4\text{S}^+$ ($[\text{M} + \text{H}]^+$), 235.0199, found, 235.0172.

4-Phenyl-2-(1,2,2,2-tetrafluoroethyl)thiophene (3o)



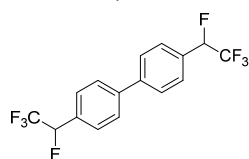
Colorless oil (36 mg, 30 % yield, electrolysis time: 3.7 h, $R_f = 0.66$ (petroleum ether); NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 7.58 (d, $J = 7.1$ Hz, 4H), 7.43 (t, $J = 7.1$ Hz, 2H), 7.34 (t, $J = 7.2$ Hz, 1H), 5.95–5.89 (m, 0.5H), 5.80–5.75 (m, 0.5H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, δ): 142.7, 135.0, 131.8 (d, $J = 21.7$ Hz, 1C), 129.3 (d, $J = 5.3$ Hz, 1C), 129.1, 127.9, 126.5, 123.6 (d, $J = 2.9$ Hz, 1C), 120.1 (qd, $J = 30.0, 307.8$ Hz, 1C), 85.3 (qd, $J = 72.9, 180.8$ Hz, 0.5C). ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -78.4 (d, $J = 14.2$ Hz, 3F), -178.4 (dd, $J = 72.9, 36.4$ Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $\text{C}_{12}\text{H}_9\text{F}_4\text{S}^+$ ($[\text{M} + \text{H}]^+$), 261.0356, found, 261.0356.

4-(2,2-Difluorovinyl)-4'-(1,2,2,2-tetrafluoroethyl)-1,1'-biphenyl (3p)



White solid (74 mg, 65 % yield, electrolysis time: 3.5 h, $R_f = 0.64$ (petroleum ether); M.P. 36.3–37.1 °C; NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 7.67 (d, $J = 8.1$ Hz, 2H), 7.60 (s, 1H), 7.56 (d, $J = 6.0$ Hz, 2H), 7.52 (s, 1H), 7.43 (d, $J = 8.3$ Hz, 2H), 5.74–5.68 (m, 0.5H), 5.60–5.54 (m, 0.5H), 5.37 (d, $J = 3.7$ Hz, 0.5H), 5.29 (d, $J = 3.7$ Hz, 0.5H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, δ): 142.8, 138.7, 130.2 (d, $J = 6.8$ Hz, 1C), 129.5, 129.2, 128.3–128.2 (m, 1C), 127.9 (d, $J = 6.4$ Hz, 1C), 127.6, 127.4, 120.5 (qd, $J = 30.5, 281.0$ Hz, 1C), 88.7 (qd, $J = 13.6, 150.0$ Hz, 1C). ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -78.7 (d, $J = 13.2$ Hz, 2F), -81.4 (d, $J = 29.5$ Hz, 1F), -83.3 (d, $J = 29.3$ Hz, 1F), 194.3 (dd, $J = 13.1, 26.1$ Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $\text{C}_{16}\text{H}_{11}\text{F}_6^+$ ($[\text{M} + \text{H}]^+$), 317.0759, found, 317.0740.

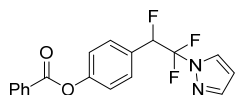
4,4'-Bis(1,2,2,2-tetrafluoroethyl)-1,1'-biphenyl (3q)



White solid (87 mg, 68 % yield, electrolysis time: 3.6 h, $R_f = 0.68$ (petroleum ether); M.P. 35.2–36.5 °C; NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 7.67 (d, $J = 8.1$ Hz, 4H), 7.56 (d, $J = 8.2$ Hz, 4H), 5.76–5.70 (m, 1H), 5.61–5.55 (m, 1H).

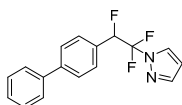
^{13}C NMR (75 MHz, CDCl_3 , 25 °C, δ): 142.4, 130.0 (d, $J = 19.6$ Hz, 2C), 128.0 (d, $J = 6.5$ Hz, 2C), 127.7, 120.5 (qd, $J = 29.1$, 308.1 Hz, 2C), 88.9 (qd, $J = 34.7$, 187.5 Hz, 2C). ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -78.7 (d, $J = 12.9$ Hz, 6F), -194.5– -194.7 (m, 2F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $\text{C}_{16}\text{H}_{11}\text{F}_8^+$ ($[\text{M} + \text{H}]^+$), 355.0728, found, 355.0703.

4-(1,2,2-Trifluoro-2-(1H-pyrazol-1-yl)ethyl)phenyl benzoate (5a)



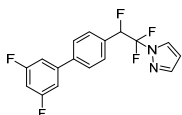
White solid (610mg, 45 % yield, electrolysis time: 5.8 h, $R_f = 0.48$ (petroleum ether/ethyl acetate = 20 : 1 (v/v)); M.P. 102.5-105.8 °C; NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 8.05 (d, $J = 7.4$ Hz, 2H), 7.59 (d, $J = 12.4$ Hz, 1H), 7.51 (t, $J = 7.3$ Hz, 1H), 7.37 (t, $J = 7.8$ Hz, 2H), 7.31 (d, $J = 8.5$ Hz, 2H), 7.12 (d, $J = 2.7$ Hz, 1H), 7.09 (s, 2H), 6.32–6.11 (m, 2H). ^{13}C NMR (75MHz, CDCl_3 , 25°C, δ): 165.0, 152.3, 142.8, 133.9, 130.3, 129.4, 128.8 (d, $J = 6.9$ Hz, 1C), 128.5 (d, $J = 2.0$ Hz, 1C), 128.4, 122.0, 119.9 (t, $J = 305.2$ Hz, 1C), 107.8, 89.7 (qd, $J = 27.5$, 187.5 Hz, 1C). ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -92.5 (dd, $J = 13.08$, 207.8 Hz, 1F), -96.8 (dd, $J = 17.8$, 207.8 Hz, 1F), -193.1 (dd, $J = 14.0$, 17.2 Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $\text{C}_{18}\text{H}_{14}\text{F}_3\text{N}_2\text{O}_2^+$ ($[\text{M} + \text{H}]^+$), 347.1002, found, 347.1000.

1-(2-([1,1'-Biphenyl]-4-yl)-1,1,2-trifluoroethyl)-1H-pyrazole (5b)



White solid (56 mg, 40 % yield, electrolysis time: 5.3 h, $R_f = 0.42$ (petroleum ether/ethyl acetate = 20 : 1 (v/v)); M.P. 114.5-115.7 °C; NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 7.76 (s, 1H), 7.73 (d, $J = 2.1$ Hz, 1H), 7.61 (t, $J = 2.8$ Hz, 1H), 6.47 (t, $J = 7.4$ Hz, 4H), 7.46 (t, $J = 7.1$ Hz, 4H), 7.38 (t, $J = 7.1$ Hz, 1H), 6.50–6.28 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, δ): 143.0 (d, $J = 1.7$ Hz, 1C), 142.8, 140.3, 130.1, 129.8, 129.0, 128.4, 127.9 (d, $J = 4.6$ Hz, 2C), 127.3, 120.1 (t, $J = 202.9$ Hz, 1C), 107.7, 90.0 (qd, $J = 35.5$, 172.5 Hz, 1C). ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -91.8 (dd, $J = 207.9$, 13.7 Hz, 1F), -97.2 (dd, $J = 208.0$, 17.9 Hz, 1F), -193.2 (dd, $J = 13.7$, 18.2 Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $\text{C}_{17}\text{H}_{14}\text{F}_3\text{N}_2^+$ ($[\text{M} + \text{H}]^+$), 303.1104, found, 303.1112.

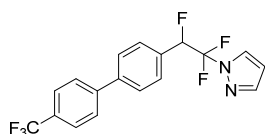
1-(2-(3',5'-Difluoro-[1,1'-biphenyl]-4-yl)-1,1,2-trifluoroethyl)-1H-pyrazole (5c)



White solid (40 mg, 30 % yield, electrolysis time: 5.6 h, $R_f = 0.41$ (petroleum ether/ethyl acetate = 20 : 1 (v/v)); M.P. 108.5-112.7 °C; NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 7.77–7.73 (m, 2H), 7.56 (d, $J = 8.2$ Hz, 2H), 7.48 (d, $J = 8.3$ Hz, 2H), 7.11–7.08 (m, 2H), 6.85–6.77 (m, 1H), 6.50–6.29 (m, 2H). ^{13}C NMR (75

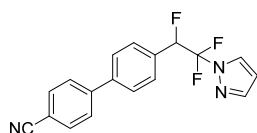
MHz, CDCl₃, 25 °C, δ): 165.1 (d, *J* = 12.9 Hz, 1C), 161.8 (d, *J* = 13.02 Hz, 1C), 143.6 (t, *J* = 9.56 Hz, 1C), 142.8, 140.6, 131.3 (d, *J* = 22.0 Hz, 1C), 128.4, 128.2 (d, *J* = 6.7 Hz, 1C), 127.2, 120.3 (t, *J* = 254.5 Hz, 1C), 110.2 (m, 1C), 107.8, 103.2 (d, *J* = 25.2 Hz, 1C), 90.5 (qd, *J* = 35.7, 187.5 Hz, 1C). ¹⁹F NMR (282 MHz, CDCl₃, 25 °C, δ): -91.8 (dd, *J* = 208.1, 13.6 Hz, 1F), -96.9 (dd, *J* = 208.1, 18.0 Hz, 1F), -100.3 (s, 2F), -193.9 (dd, *J* = 13.4, 17.6 Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C₁₇H₁₂F₅N₂⁺ ([M + H]⁺), 339.0915, found, 339.0917.

1-(1,1,2-Trifluoro-2-(4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)ethyl)-1H-pyrazole (5d)



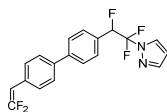
White solid (46 mg, 35 % yield, electrolysis time: 5.4 h, *R_f* = 0.45 (petroleum ether/ethyl acetate = 20 : 1 (v/v))); M.P. 103.5-106.9 °C; NMR Spectroscopy: ¹H NMR (300 MHz, CDCl₃, 25 °C, δ): 7.76 (d, *J* = 9.0 Hz, 2H), 7.70 (s, 4H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 6.50–6.29 (m, 2H). ¹³C NMR (75 MHz, CDCl₃, 25 °C, δ): 143.9, 142.8, 141.6, 131.1 (d, *J* = 20.1 Hz, 1C), 129.9 (t, *J* = 33.3 Hz, 1C), 128.4, 128.2 (d, *J* = 6.7 Hz, 1C), 127.7, 127.5, 126.0 (dd, *J* = 3.7, 7.4 Hz, 1C), 119.0 (t, *J* = 265.7 Hz, 1C), 107.9, 89.7 (qd, *J* = 23.4, 180.0 Hz, 1C). ¹⁹F NMR (282 MHz, CDCl₃, 25 °C, δ): -62.5 (s, 3F), -91.6 (dd, *J* = 13.5, 208.4 Hz, 1F), -97.1 (dd, *J* = 17.9, 208.3 Hz, 1F), -193.7 (dd, *J* = 13.7, 17.7 Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C₁₈H₁₃F₆N₂⁺ ([M + H]⁺), 371.0977, found, 371.0968.

4'-(1,1,2-Trifluoro-2-(1H-pyrazol-1-yl)ethyl)-[1,1'-biphenyl]-4-carbonitrile (5e)



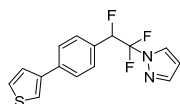
White solid (61 mg, 45% yield, electrolysis time: 5.3 h, *R_f* = 0.47 (petroleum ether/ethyl acetate = 20 : 1 (v/v))); M.P. 119.5-204.7 °C; NMR Spectroscopy: ¹H NMR (300 MHz, CDCl₃, 25 °C, δ): 7.76–7.72 (m, 4H), 7.67 (d, *J* = 5.5 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.3 Hz, 2H), 6.50–6.29 (m, 2H). ¹³C NMR (75 MHz, CDCl₃, 25 °C, δ): 144.8, 142.8, 140.9, 132.8, 131.6 (d, *J* = 20.0 Hz, 1C), 128.3 (t, *J* = 7.7 Hz, 1C), 127.9, 127.4, 118.9, 111.7, 107.9, 89.8 (qd, *J* = 23.9, 180.0 Hz, 1C). ¹⁹F NMR (282 MHz, CDCl₃, 25 °C, δ): -91.5 (dd, *J* = 13.4, 208.3 Hz, 1F), -97.0 (dd, *J* = 17.9, 208.5 Hz, 1F), -193.9 (dd, *J* = 13.7, 17.9 Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for C₁₈H₁₃F₃N₃⁺ ([M + H]⁺), 328.1056, found, 328.1039.

1-(2-(4'-(2,2-Difluorovinyl)-[1,1'-biphenyl]-4-yl)-1,1,2-trifluoroethyl)-1H-pyrazole (5f)



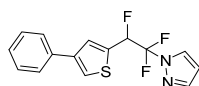
White solid (59 mg, 45 % yield, electrolysis time: 5.5 h, $R_f = 0.41$ (petroleum ether/ethyl acetate = 20 : 1 (v/v)); M.P. 112.5-115.7 °C; NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 7.75 (d, $J = 11.4$ Hz, 2H), 7.64–7.60 (m, 4H), 7.55 (d, $J = 8.1$ Hz, 2H), 7.49 (d, $J = 8.0$ Hz, 2H), 7.50–6.28 (m, 2H), 5.73–5.56 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, δ): 142.8, 142.5 (d, $J = 1.5$ Hz, 1C), 141.8 (d, $J = 1.0$ Hz, 1C), 130.9 (d, $J = 1.6$ Hz, 1C), 130.6 (d, $J = 1.6$ Hz, 1C), 130.5, 129.9 (d, $J = 1.6$ Hz, 1C), 129.7, 128.4, 128.1 (d, $J = 6.7$ Hz, 1C), 127.9 (d, $J = 6.7$ Hz, 1C), 127.5 (d, $J = 17.6$ Hz, 1C), 120.0 (t, $J = 267.3$ Hz, 1C), 107.8, 91.6–86.9 (m, 1C). ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -78.6 (s, 2F), -91.7 (dd, $J = 208.2, 13.54$ Hz, 1F), -97.2 (dd, $J = 208.2, 18.0$ Hz, 1F), -193.5 – -194.5 (m, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $\text{C}_{19}\text{H}_{14}\text{F}_5\text{N}_2^+$ ($[\text{M} + \text{H}]^+$), 365.1072, found, 365.1057.

1-(1,1,2-Trifluoro-2-(4-(thiophen-3-yl)phenyl)ethyl)-1H-pyrazole (5g)



White solid (39 mg, 28 % yield, electrolysis time: 5.7 h, $R_f = 0.48$ (petroleum ether/ethyl acetate = 20 : 1 (v/v)); M.P. 108.5-110.7 °C; NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 7.76 (d, $J = 1.1$ Hz, 1H), 7.71 (d, $J = 2.0$ Hz, 2H), 7.61 (d, $J = 8.0$ Hz, 2H), 7.50–7.48 (m, 1H), 7.42–7.39 (m, 4H), 6.44–6.23 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, δ): 142.8, 141.5, 137.6, 129.6, 128.4, 128.0 (d, $J = 6.7$ Hz, 1C), 126.7, 126.6, 126.3, 121.3, 118.3 (t, $J = 210.5$ Hz, 1C), 107.8, 90.8 (qd, $J = 33.5, 112.5$ Hz, 1C). ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -92.3 (dd, $J = 207.7, 13.8$ Hz, 1F), -96.9 (dd, $J = 207.9, 18.2$ Hz, 1F), -193.3 (dd, $J = 13.6, 17.9$ Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $\text{C}_{15}\text{H}_{12}\text{F}_3\text{N}_2\text{S}^+$ ($[\text{M} + \text{H}]^+$), 309.0668, found, 309.0662.

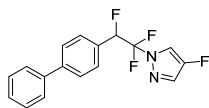
1-(1,1,2-Trifluoro-2-(4-phenylthiophen-2-yl)ethyl)-1H-pyrazole (5h)



Colorless oil (25 mg, 18% yield, electrolysis time: 5.3 h, $R_f = 0.44$ (petroleum ether/ethyl acetate = 20 : 1 (v/v)); M.P. 102.5-105.2 °C; NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 7.78 (d, $J = 15.1$ Hz, 2H), 7.53 (d, $J = 7.0$ Hz, 3H), 7.45–7.37 (m, 3H), 7.30 (t, $J = 7.1$ Hz, 1H), 6.69 (t, $J = 8.6$ Hz, 0.5H), 6.54 (t, $J = 10.7$ Hz, 0.5H), 6.41 (s, 1H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, δ): 142.9, 142.3, 135.2, 129.1, 128.9 (d, $J = 5.4$ Hz, 1C), 128.4, 127.7, 126.5, 123.2 (d, $J = 2.2$ Hz, 1C), 128.0, 120.1 (t, $J = 272.4$ Hz, 1C), 86.7 (qd, $J = 38.6, 225.0$ Hz, 1C). ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -92.1 (dd, $J = 36.9, 65.7$ Hz, 1F), -95.8 (dd, $J = 18.7, 206.3$ Hz, 1F),

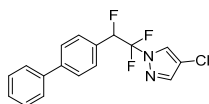
-179.5 (dd, $J = 15.4, 18.4$ Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{15}H_{12}F_3N_2S^+$ ($[M + H]^+$), 309.0668, found, 309.0659.

1-(2-([1,1'-Biphenyl]-4-yl)-1,1,2-trifluoroethyl)-4-fluoro-1H-pyrazole (5i)



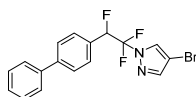
White solid (70 mg, 47% yield, electrolysis time: 5.5 h, $R_f = 0.45$ (petroleum ether/ethyl acetate = 20 : 1 (v/v))); M.P. 116.5-118.9 °C; NMR Spectroscopy: 1H NMR (300 MHz, $CDCl_3$, 25 °C, δ): 7.62 (t, $J = 8.6$ Hz, 6H), 7.47 (t, $J = 8.3$ Hz, 4H), 7.39 (t, $J = 7.1$ Hz, 1H), 6.45–6.23 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, δ): 150.3 (d, $J = 249.7$ Hz, 1C), 141.75 (d, $J = 222.0$ Hz, 1C), 131.0 (d, $J = 15.0$ Hz, 1C), 129.8, 129.5, 129.0, 128.0 (d, $J = 5.6$ Hz, 2C), 127.4 (d, $J = 5.6$ Hz, 2C), 121.2 (t, $J = 277.8$ Hz, 1C), 114.3 (d, $J = 28.3$ Hz, 2C), 89.7 (qd, $J = 35.5, 165.0$ Hz, 1C). ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C, δ): -91.1 (dd, $J = 208.1, 13.5$ Hz, 1F), -98.3 (dd, $J = 208.1, 18.0$ Hz, 1F), -174.1 (s, 1F), -193.1 (dd, $J = 15.6, 18.0$ Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{17}H_{12}F_4N_2Na^+$ ($[M + Na]^+$), 343.0829, found, 343.0829.

1-(2-([1,1'-Biphenyl]-4-yl)-1,1,2-trifluoroethyl)-4-chloro-1H-pyrazole (5j)



White solid (79 mg, 51% yield, electrolysis time: 5.4 h, $R_f = 0.45$ (petroleum ether/ethyl acetate = 20 : 1 (v/v))); M.P. 117.2-119.8 °C; NMR Spectroscopy: 1H NMR (300 MHz, $CDCl_3$, 25 °C, δ): 7.74 (s, 1H), 7.69 (d, $J = 0.7$ Hz, 1H), 7.62 (t, $J = 8.3$ Hz, 4H), 7.46 (t, $J = 7.3$ Hz, 4H), 7.38 (t, $J = 7.1$ Hz, 1H), 6.42–6.21 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, δ): 143.3 (d, $J = 1.7$ Hz, 1C), 141.4, 140.3, 129.6, 129.4, 129.0, 128.0 (t, $J = 3.2$ Hz, 1C), 127.4 (d, $J = 6.9$ Hz, 2C), 126.3, 121.4 (t, $J = 163.7$ Hz, 1C), 113.1, 89.2 (qd, $J = 36.9, 232.5$ Hz, 1C). ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C, δ): -90.7 (dd, $J = 208.6, 17.7$ Hz, 1F), -98.4 (dd, $J = 208.6, 17.7$ Hz, 1F), -193.1 (dd, $J = 13.9, 18.0$ Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{17}H_{13}ClF_3N_2^+$ ($[M + H]^+$), 337.0714, found, 337.0708.

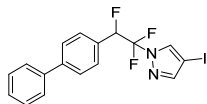
1-(2-([1,1'-Biphenyl]-4-yl)-1,1,2-trifluoroethyl)-4-bromo-1H-pyrazole (5k)



White solid (84 mg, 48 % yield, electrolysis time: 5.6 h, $R_f = 0.43$ (petroleum ether/ethyl acetate = 20 : 1 (v/v))); M.P. 120.5-123.9 °C; NMR Spectroscopy: 1H NMR (300 MHz, $CDCl_3$, 25 °C, δ): 7.78 (s, 1H), 7.72 (d, $J = 0.7$ Hz, 1H), 7.61 (t, $J = 8.4$ Hz, 4H), 7.46 (t, $J = 7.2$ Hz, 4H), 7.38 (t, $J = 7.1$ Hz, 1H), 6.42–6.21 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, δ): 143.4, 143.3 (d, $J = 1.6$ Hz, 1C), 140.3, 129.6, 129.4, 129.0, 128.5, 128.0 (t, $J = 2.8$ Hz, 1C), 127.4 (d, $J = 6.8$ Hz, 2C), 116.7 (t, $J = 288.1$ Hz, 1C), 96.4, 89.5 (qd, $J = 35.3, 202.5$ Hz, 1C). ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C, δ):

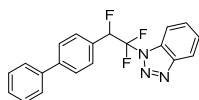
-90.6 (dd, $J = 208.8, 13.7$ Hz, 1F), -98.5 (dd, $J = 208.6, 17.6$ Hz, 1F), -193.1 (dd, $J = 13.4, 17.5$ Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{17}H_{13}BrF_3N_2^+$ ($[M + H]^+$), 381.0209, found, 381.0221.

1-(2-([1,1'-Biphenyl]-4-yl)-1,1,2-trifluoroethyl)-4-iodo-1H-pyrazole (5l)



White solid (62 mg, 20% yield, electrolysis time: 5.2 h, $R_f = 0.45$ (petroleum ether/ethyl acetate = 20 : 1 (v/v))); M.P. 122.5-124.6 °C; NMR Spectroscopy: 1H NMR (300 MHz, $CDCl_3$, 25 °C, δ): 7.81 (s, 1H), 7.76 (s, 1H), 7.61 (t, $J = 8.3$ Hz, 4H), 7.46 (t, $J = 7.1$ Hz, 4H), 7.38 (t, $J = 7.0$ Hz, 1H), 6.42–6.21(m,1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, δ): 147.6, 143.3, 140.3, 132.8, 129.7, 129.4, 129.0, 128.0 (t, $J = 2.9$ Hz, 1C), 127.4 (d, $J = 6.2$ Hz, 2C), 120.0 (t, $J = 294.4$ Hz, 1C), 89.8 (qd, $J = 27.3, 187.5$ Hz, 1C). ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C, δ): -90.4 (dd, $J = 208.8, 13.7$ Hz, 1F), -98.3 (dd, $J = 208.8, 17.7$ Hz, 1F), -193.1 (dd, $J = 13.5, 17.5$ Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{17}H_{13}F_3IN_2^+$ ($[M + H]^+$), 429.0070, found, 429.0062.

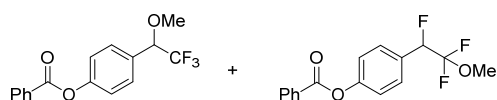
1-(2-([1,1'-Biphenyl]-4-yl)-1,1,2-trifluoroethyl)-1H-benzo[d][1,2,3]triazole (5m)



White solid (69 mg, 30 % yield, electrolysis time: 5.3 h, $R_f = 0.45$ (petroleum ether/ethyl acetate = 20 : 1 (v/v))); M.P. 123.2-125.4 °C; NMR Spectroscopy: 1H NMR (300 MHz, $CDCl_3$, 25 °C, δ): 8.12 (t, $J = 8.0$ Hz, 1H), 7.66 (t, $J = 8.0$ Hz, 4H), 7.58 (t, $J = 8.0$ Hz, 6H), 7.44 (d, $J = 7.0$ Hz, 2H), 7.36 (d, $J = 6.7$ Hz, 1H), 6.75–6.54 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, δ):145.9, 143.5, 140.2, 133.1 (d, $J = 184.6$ Hz, 1C), 129.6, 129.0, 128.4 (d, $J = 6.5$ Hz, 1C), 128.0, 127.4 (d, $J = 11.2$ Hz, 1C), 125.5, 120.6, 118.2 (t, $J = 194.8$ Hz, 1C), 111.6–111.4 (m, 1C), 90.6 (qd, $J = 32.7, 187.5$ Hz, 1C). ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C, δ): -87.6 (t, $J = 13.3, 0.5F$), -88.4 (t, $J = 13.3$ Hz, 0.5F), -96.1 (t, $J = 16.8$ Hz, 0.5F), -96.9 (t, $J = 17.6$ Hz, 0.5F), -191.2 (dd, $J = 14.1, 30.4$ Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $C_{20}H_{15}F_3N_3^+$ ($[M + H]^+$), 354.1213, found, 354.1210

4-(2,2,2-trifluoro-1-methoxyethyl)phenyl benzoate (5n)

4-(1,2,2-trifluoro-2-methoxyethyl)phenyl benzoate (5n')

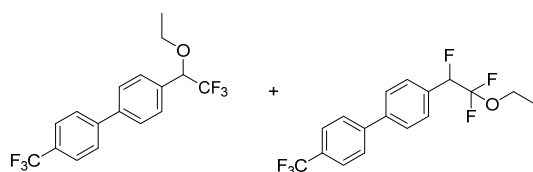


Colorless oil (79 mg, 55 % yield, electrolysis time: 4.3 h, $R_f = 0.45$ (petroleum ether/ethyl acetate = 50 : 1 (v/v))); NMR Spectroscopy: 1H NMR (300 MHz, $CDCl_3$, 25 °C, δ): 8.13 (d, $J = 7.7$ Hz, 4H), 7.56 (t, $J = 7.2$ Hz, 2H), 7.43 (t, $J = 7.4$ Hz, 8H), 7.20 (t, $J = 4.9$ Hz, 4H), 5.51–5.32 (m, 1H), 4.49–4.42 (m, 1H), 3.51 (s, 1H), 3.36 (s,

1H). ¹³C NMR (75 MHz, CDCl₃, 25 °C, δ): 165.1, 152.0, 133.9, 130.3, 129.5 (d, *J* = 7.4 Hz, 1C), 128.8 (d, *J* = 6.7 Hz, 1C), 122.1, 121.8, 91.3 (dd, *J* = 37.2, 72.2 Hz, 0.5C), 88.7 (dd, *J* = 35.0, 67.8 Hz, 0.5C), 81.1 (dd, *J* = 32.9, 63.9 Hz, 0.5C), 119.3 (t, *J* = 252.1 Hz, 1C), 88.5 (qd, *J* = 34.9, 195.0 Hz, 1C), 58.4, 50.7 (d, *J* = 7.2 Hz, 1C). ¹⁹F NMR (282 MHz, CDCl₃, 25 °C, δ): -76.7 (s, 3F), -87.1 (dd, *J* = 12.7, 141.4 Hz, 1F), -89.2 (dd, *J* = 14.4, 141.4 Hz, 1F), -192.0 (t, *J* = 13.5 Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (*m/z*): calcd for C₁₆H₁₄F₃O₃⁺ ([M + H]⁺), 311.0890, found, 311.0872.

4-(1-Ethoxy-2,2,2-trifluoroethyl)-4'-(trifluoromethyl)-1,1'-biphenyl (5o)

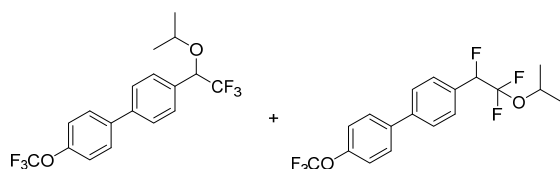
4-(2-Ethoxy-1,2,2-trifluoroethyl)-4'-(trifluoromethyl)-1,1'-biphenyl (5o')



Colorless oil (64 mg, 52 % yield, electrolysis time: 4.2 h, *R_f* = 0.45 (petroleum ether/ethyl acetate = 50 : 1 (v/v))); NMR Spectroscopy: ¹H NMR (300 MHz, CDCl₃, 25 °C, δ): 7.73 (s, 8H), 7.66 (d, *J* = 8.2 Hz, 4H), 7.60 (t, *J* = 1.5 Hz, 4H), 5.64–5.45 (m, 1H), 4.73–4.67 (m, 1H), 4.02 (dd, *J* = 7.2, 14.3 Hz, 2H), 3.66 (dd, *J* = 7.1, 14.0 Hz, 2H), 1.33 (d, *J* = 2.6 Hz, 1H), 1.30 (t, *J* = 2.9 Hz, 4H), 1.28 (s, 1H). ¹³C NMR (75 MHz, CDCl₃, 25 °C, δ): 144.1, 141.0, 133.0 (t, *J* = 43.5 Hz, 1C), 130.0 (d, *J* = 29.9 Hz, 1C), 128.9, 128.2 (d, *J* = 45.7 Hz, 1C), 127.6 (d, *J* = 3.1 Hz, 1C), 127.3, 125.9 (dd, *J* = 4.5, 8.2 Hz, 1C), 122.6 (t, *J* = 269.8 Hz, 1C), 119.3 (t, *J* = 252.1 Hz, 1C), 90.4 (qd, *J* = 30.1, 247.5 Hz, 1C), 79.5 (d, *J* = 30.9 Hz, 1C), 66.6, 60.1 (t, *J* = 6.4 Hz, 1C), 15.1 (d, *J* = 19.4 Hz, 1C). ¹⁹F NMR (282 MHz, CDCl₃, 25 °C, δ): -62.5 (s, 3F), -76.6 (s, 3F), -84.4 (dd, *J* = 13.3, 143.0 Hz, 1F), -85.8 (t, *J* = 14.2, 144.2 Hz, 1F), -192.7 (t, *J* = 13.7 Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (*m/z*): calcd for C₁₇H₁₅F₆O⁺ ([M + H]⁺), 349.1022, found, 349.1028.

4-(2,2,2-Trifluoro-1-isopropoxyethyl)-4'-(trifluoromethoxy)-1,1'-biphenyl (5p)

4-(2,2-Difluoro-2-isopropoxy-1-methoxyethyl)-4'-(trifluoromethoxy)-1,1'-biphenyl (5p')

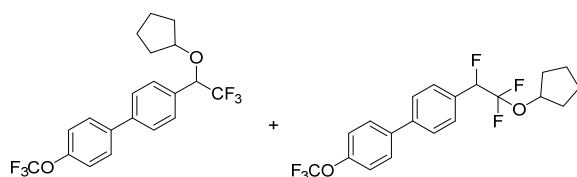


Colorless oil (57 mg, 45 % yield, electrolysis time: 4.5 h, *R_f* = 0.45 (petroleum ether/ethyl acetate = 50 : 1 (v/v))); NMR Spectroscopy: ¹H NMR (300 MHz, CDCl₃, 25 °C, δ): 7.62 (d, *J* = 2.9 Hz, 2H), 7.59 (d, *J* = 2.7 Hz, 3H), 7.55 (t, *J* = 6.5 Hz, 6H), 7.30 (d, *J* = 8.5 Hz, 4H), 5.57–5.38 (m, 1H), 4.77–4.51 (m, 2H), 3.81–3.68 (m, 1H), 1.27 (t, *J* = 3.2 Hz, 5H), 1.25 (s, 3H), 1.23 (s, 1H), 1.18 (d, *J* = 6.2 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃, 25 °C, δ): 149.1, 141.0 (d, *J* = 7.6 Hz, 1C), 139.4, 133.6, 132.4 (d, *J*

= 22.0 Hz, 1C), 128.8, 128.7, 128.1 (d, $J = 7.0$ Hz, 1C), 127.3, 127.0, 121.4, 119.0 (t, $J = 256.0$ Hz, 1C), 91.0 (qd, $J = 27.5, 187.5$ Hz, 1C), 72.3, 69.4 (t, $J = 5.1$ Hz, 1C), 23.4 (d, $J = 2.5$ Hz, 1C), 23.0, 21.4. ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -57.8 (d, $J = 2.4$ Hz, 3F), -76.8 (s, 3F), -82.0 (dd, $J = 13.6, 144.6$ Hz, 1F), -83.3 (dd, $J = 14.1, 144.2$ Hz, 1F), -192.1 (t, $J = 14.1$ Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $\text{C}_{18}\text{H}_{17}\text{F}_6\text{O}_2^+$ ($[\text{M} + \text{H}]^+$), 379.1127, found, 379.1115.

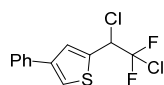
4-(1-(Cyclopentyloxy)-2,2,2-trifluoroethyl)-4'-(trifluoromethoxy)-1,1'-biphenyl (5q)

4-(2-(Cyclopentyloxy)-2,2-difluoro-1-methoxyethyl)-4'-(trifluoromethoxy)-1,1'-biphenyl (5q')



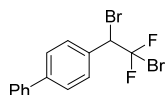
Colorless oil (46 mg, 33 % yield, electrolysis time: 4.6 h, $R_f = 0.45$ (petroleum ether/ethyl acetate = 50 : 1 (v/v))); NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 7.63 (d, $J = 2.3$ Hz, 2H), 7.60 (d, $J = 2.2$ Hz, 3H), 7.54 (t, $J = 9.7$ Hz, 7H), 7.30 (d, $J = 8.3$ Hz, 4H), 5.57–5.38 (m, 1H), 4.82–4.66 (m, 2H), 4.07 (d, $J = 3.0$ Hz, 1H), 1.80–1.69 (m, 5H), 1.25 (s, 12H), 1.59–1.54 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, δ): 149.1, 141.0 (d, $J = 9.0$ Hz, 1C), 139.4 (d, $J = 3.8$ Hz, 1C), 133.4, 132.4 (d, $J = 20.1$ Hz, 1C), 128.9, 128.7, 128.1 (d, $J = 6.9$ Hz, 1C), 127.3, 127.0, 121.4, 119.0 (t, $J = 255.5$ Hz, 1C), 90.9 (qd, $J = 37.5, 180.0$ Hz, 1C), 81.8, 33.5, 33.0, 31.9, 23.5 (d, $J = 4.9$ Hz, 1C). ^{19}F NMR (282MHz, CDCl_3 , 25 °C, δ): -57.8 (s, 3F), -76.8 (s, 3F), -81.6 (dd, $J = 13.8, 144.6$ Hz, 1F), -83.3 (dd, $J = 14.4, 144.2$ Hz, 1F), -192.4 (t, $J = 14.0$ Hz, 1F). Mass Spectrometry:HRMS (ESI-TOF) (m/z): calcd for $\text{C}_{20}\text{H}_{19}\text{F}_6\text{O}_2^+$ ($[\text{M} + \text{H}]^+$), 405.1284, found, 405.1264.

2-(1,2-Dichloro-2,2-difluoroethyl)-4-phenylthiophene (6)



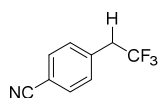
Colorless oil (92 mg, 70 % yield, electrolysis time: 5.3 h, $R_f = 0.60$ (petroleum ether)); NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25° C, δ): 7.57 (d, $J = 1.6$ Hz, 1H), 7.54 (s, 1H), 7.48 (s, 1H), 7.45 (s, 1H), 7.43 (s, 1H), 7.38 (t, $J = 7.1$ Hz, 1H), 7.22 (s, 1H), 5.45–5.40 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3 , 25°C, δ): 138.3, 133.4, 131.8, 131.1, 128.7, 128.1, 128.6, 128.3, 126.5, 122.6, 60.4 (t, $J = 30.7$ Hz, 1C). ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -58.7 (d, $J = 163.0$ Hz, 1F), -60.9 (d, $J = 163.0$ Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $\text{C}_{12}\text{H}_9\text{Cl}_2\text{F}_2\text{S}^+$ ($[\text{M} + \text{H}]^+$), 292.9765, found, 292.9771.

4-(1,2-Dibromo-2,2-difluoroethyl)-1,1'-biphenyl (7)



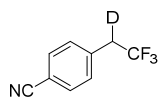
Colorless oil (119 mg, 69 % yield, electrolysis time: 5.2 h, $R_f = 0.62$ (petroleum ether); NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 7.64–7.57 (m, 6H), 7.47 (t, $J = 7.0$ Hz, 2H), 7.39 (t, $J = 7.1$ Hz, 1H), 5.43–5.35 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, δ): 143.0, 140.1, 133.3, 130.1, 129.1, 128.1, 127.6, 127.3, 115.6 (t, $J = 309.2$ Hz, 1C), 55.1 (t, $J = 25.0$ Hz, 1C). ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -45.7 (d, $J = 156.7$ Hz, 1F), -54.8 (d, $J = 157.0$ Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $\text{C}_{14}\text{H}_{11}\text{Br}_2\text{F}_2^+$ ($[\text{M} + \text{H}]^+$), 374.9190, found, 374.9169.

4-(2,2,2-Trifluoroethyl)benzonitrile (9)



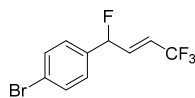
Colorless oil (93 mg, 83 % yield, electrolysis time: 3.1 h, $R_f = 0.45$ (petroleum ether); NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 7.67 (d, $J = 8.0$ Hz, 2H), 7.43 (d, $J = 8.0$ Hz, 2H), 3.49–3.39 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, δ): 135.3, 132.5, 131.0, 118.3, 112.3, 40.3 (dd, $J = 30.5, 60.7$ Hz, 1C). ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -65.5 (s, 3F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $\text{C}_9\text{H}_7\text{F}_3\text{N}^+$ ($[\text{M} + \text{H}]^+$), 186.0525, found, 186.0522.

4-(2,2,2-Trifluoroethyl-1-*d*)benzonitrile (10)



Colorless oil (36 mg, 32 % yield, H/D = 7:3, electrolysis time: 3.1 h, $R_f = 0.45$ (petroleum ether); NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 7.67 (d, $J = 8.1$ Hz, 2H), 7.43 (d, $J = 8.0$ Hz, 2H), 3.50–3.39 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, δ): 135.3 (d, $J = 2.8$ Hz, 1C), 132.5, 131.0, 127.0 (t, $J = 188.7$ Hz, 1C), 118.3, 112.4, 40.2 (dd, $J = 29.9, 60.0$ Hz, 1C). ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -65.5 (s, 3F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $\text{C}_9\text{H}_6\text{DF}_3\text{N}^+$ ($[\text{M} + \text{H}]^+$), 187.0588, found, 187.0585.

(*E*)-1-Bromo-4-(1,4,4,4-tetrafluorobut-2-en-1-yl)benzene (12)



Colorless oil (52 mg, 45 % yield, electrolysis time: 4.2 h, $R_f = 0.35$ (petroleum ether); NMR Spectroscopy: ^1H NMR (300 MHz, CDCl_3 , 25 °C, δ): 7.56 (d, $J = 8.0$ Hz, 2H), 7.22 (d, $J = 7.3$ Hz, 2H), 6.58–6.45 (m, 1H), 6.10–5.87 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C, δ): 137.1 (dd, $J = 6.3, 12.6$ Hz, 0.5C), 136.8 (dd, $J = 6.4, 12.6$ Hz, 0.5C), 135.4 (d, $J = 20.2$ Hz, 1C), 132.3, 128.4 (d, $J = 5.6$ Hz, 1C), 123.8 (d, $J = 3.1$

Hz, 1C), 120.5–118.9 (m, 1C), 91.6, 89.3. ^{19}F NMR (282 MHz, CDCl_3 , 25 °C, δ): -64.5 (s, 3F), -174.3 (d, $J = 1.3$ Hz, 1F). Mass Spectrometry: HRMS (ESI-TOF) (m/z): calcd for $\text{C}_{10}\text{H}_8\text{BrF}_4^+$ ($[\text{M} + \text{H}]^+$), 282.9740, found, 282.9728.

7. NMR Spectrum:

